SUPPORTING INFORMATION

Push-Pull D-π-Ru-π-A chromophores: synthesis, electrochemical, photophysical and second order nonlinear optical properties

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General Methods

All reactions were conducted under a dry nitrogen atmosphere using Schlenk techniques, but workups were carried out in air. The starting materials were purchased from Sigma-Aldrich, TCI or Alfa-Aesar and were used as received. The solvents were used as received except tetrahydrofuran that was distilled under a dry nitrogen atmosphere over sodium and benzophenone. The extra dry chloroform stabilized on amylene (50-150 ppm) used for photophysical measurement was purchased from Acros Organics. Compounds **9**,[1] **10,**[2] chloro-bis(1,2-bis(diphenylphosphino)ethane)ruthenium triflate[3] and 4-[(*E*)-2-(4-ethynylphenyl)ethenyl]-pyrimidine[4] were obtained according to reported procedures. NMR spectra were acquired at room temperature on a Bruker AC-300 spectrometer (^{1}H at 300 MHz, ^{13}C at 75 MHz, ^{31}P at 121 MHz) and referenced as follows: ^{1}H NMR, residual $CHCl_3$ (δ = 7.26 ppm); $^{13}C\{^{1}H\}$ NMR, internal $CDCl_3$ (δ = 77.16 ppm); $^{31}P\{^{1}H\}$ NMR, external H_3PO_4 (δ = 0.00 ppm). The chemical shifts δ are reported in parts per million relative to TMS (^{1}H, 0.0 ppm) and $CDCl_3$ (^{13}C, 77.16 ppm). The coupling constant *J* is given in Hz. In the ^{1}H NMR spectra, the following abbreviations are used to describe the peak pattern: s (singlet), d (doublet), dd (doublet of doublet), t (triplet), and m (multiplet). Acidic impurities in $CDCl_3$ were removed by treatment with anhydrous K_2CO_3 and $CDCl_3$ was stored under 4Å molecular sieves. IR spectra were recorded on a Perkin-Elmer spectrum 100 spectrometer with an ATR sampling accessory. UV-visible spectra were recorded on a Perkin-Elmer Lambda 25 spectrometer using standard 10 mm quartz cells. High resolution mass analyses were performed at the “Centre Régional de Mesures Physiques de l'Ouest” (CRMPO, University of Rennes 1, France) using a Bruker MicroTOFQ II apparatus. Column chromatographies were performed using silica gel Acros SI 60 (60–200 mesh ASTM). Thin-layer chromatography (TLC) was carried out on EMD Silica Gel 60 F_{254} (Merck) or EMD aluminum oxide 150 F_{254} (neutral) plates that were visualized with 365 nm UV light.

Cyclic voltammetry experimental details

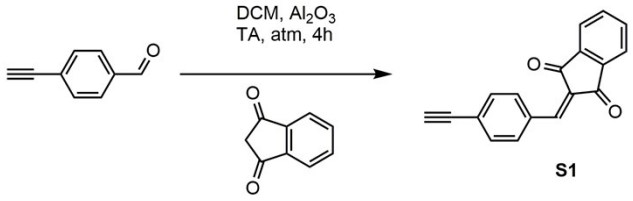
The electrochemical studies were performed in a glovebox (Jacomex) (O_2 < 1 ppm, H_2O < 1 ppm) with a home-made 3-electrode cell (WE: Pt, RE: Ag wire, CE: Pt). Ferrocene standard was added at the end of each experiment. The redox potential of the Fc^+/Fc couple in CH_2Cl_2/NBu_4PF_6 was measured experimentally with reference to the standard calomel electrode (SCE): $E^0(Fc^+/Fc)$ = 0.47 V *vs*. SCE, and recalibrated vs. NHE assuming that E^0(SCE) = 0.24 V *vs*. NHE. The potential of the cell was controlled by an AUTOLAB PGSTAT 100 (Metrohm) potentiostat monitored by the NOVA© software (Metrohm). Dichloromethane was freshly distilled from CaH_2 and kept under Ar in the glovebox. The supporting salt NBu_4PF_6 was synthesized from NBu_4OH (Fluka) and HPF_6 (Aldrich). It was then purified, dried under vacuum for 48 hours at 100 °C, and then kept under N_2 in the glovebox. Thin layer room UV-Vis spectro-electrochemistry was performed with a specific home-designed cell in a reflectance mode (WE: Pt diameter 3mm, RE: Pt wire, CE: Pt wire) with an optical path of 0.2 mm. The UV-Vis optic fiber probe used was purchased from Ocean Optics. Time-resolved UV-Vis detection was performed with QEPro spectrometer (Ocean optics).

Computational details

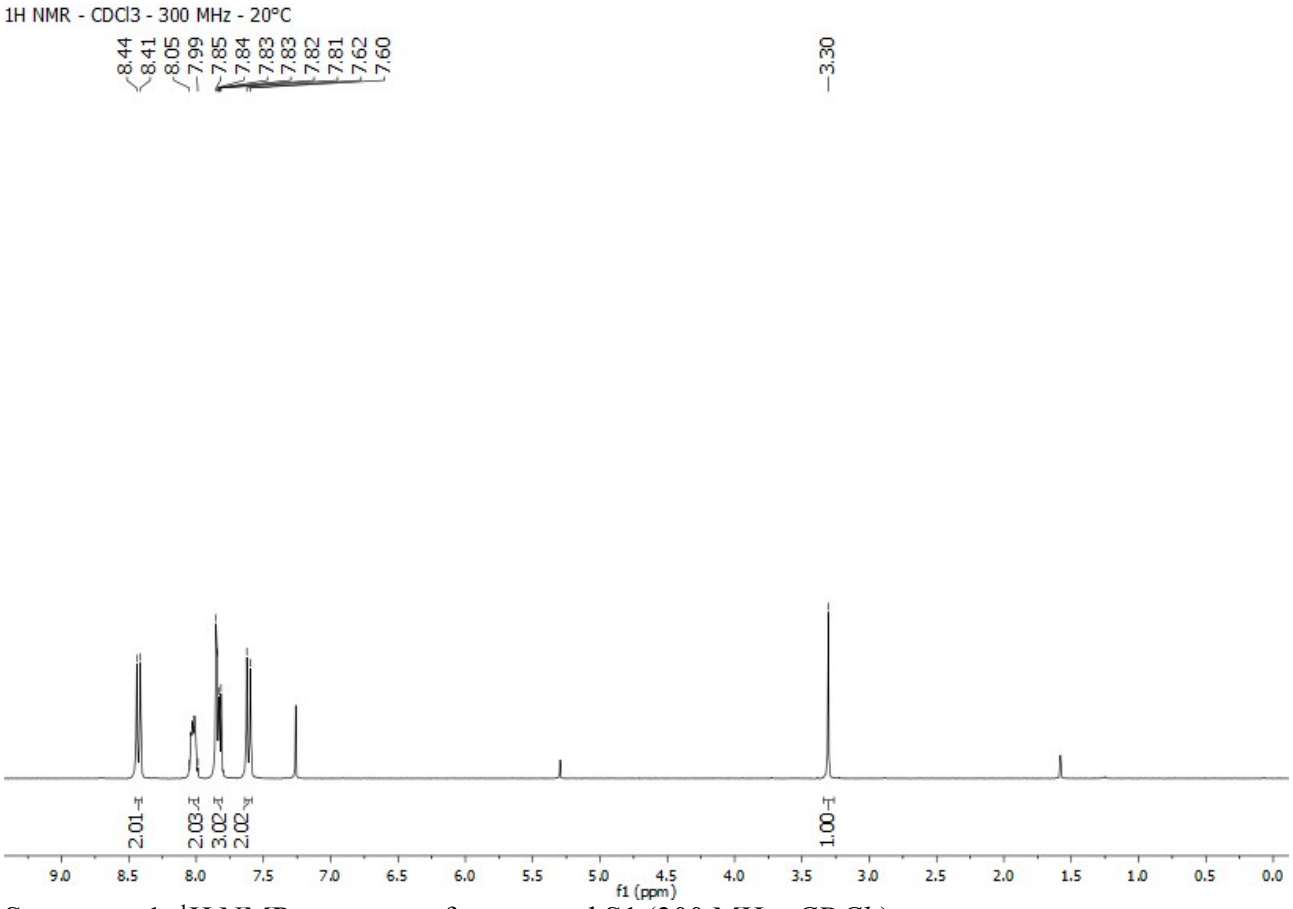
Geometry optimizations were carried out using the Gaussian 09 package,[5] employing the PBE0 functional,[6–8] together with the D3 version of Grimme's empirical dispersion (Becke-Johnson damping)[9] and using the standard double-ξ LANL2DZ basis set[10–13] augmented with Ahlrichs polarization functions.[14] Solvent (chloroform) effects have been taken into account using the PCM model.[15,16] All stationary points were fully characterized via analytical frequency calculations as true minima (no imaginary values). The geometries obtained from DFT calculations were used to perform natural atomic orbital analysis with the NBO 5.0 program.[17] The composition of the molecular orbitals was calculated using the AOMix program.[18] The ionization energies and electron affinities have been calculated considering the energies of the optimized neutral and ionic structures (solvent corrections performed). The UV-visible transitions were calculated by means of TDDFT calculations[19] on the optimized geometries with the CAM-B3LYP functional[20] which is more

appropriate than PBE0 for computing charge-transfer excitation energies. Only singlet-singlet transitions have been taken into account. Only the transitions with non-negligible oscillator strengths are discussed in the paper. Charge transfers associated with the major transitions of lowest energy have been illustrated by plots of the differences between the densities of the involved ground- and excited states and quantified by associated charge transfer values and distances as defined by Adamo and coworkers.[21–23]

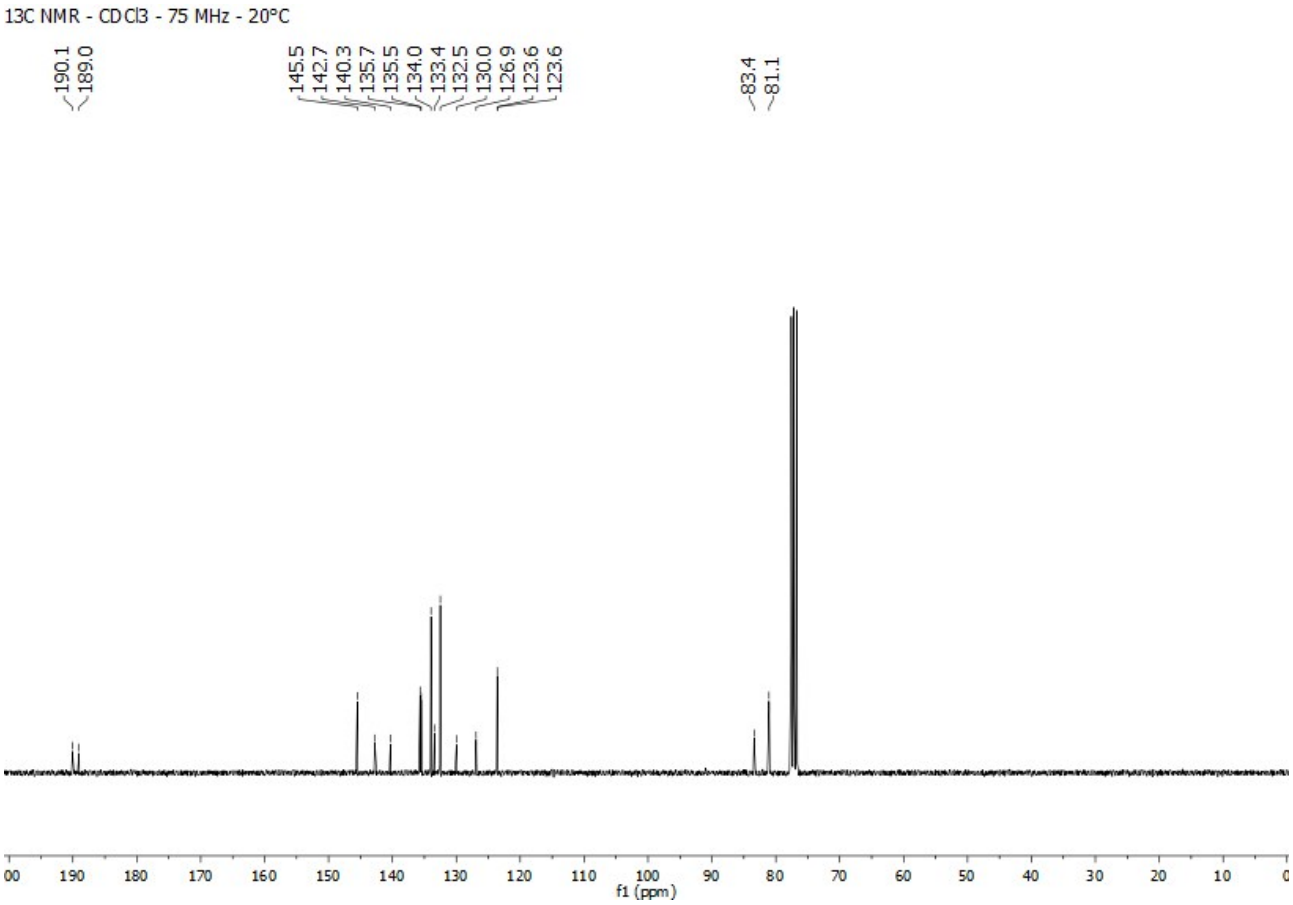
Synthesis of precursor S1



In a round-bottom flask of 250 mL, 4-ethynylbenzaldehyde (500 mg, 3.84 mmol, 1 eq), indane-1,3-dione (675 mg, 4.62 mmol, 1.2 eq) and alumina oxide (Al_2O_3) (2.0 g, 19.6 mmol, 5.1 eq) were introduced into circa 70 mL of dichloromethane. The mixture was stirred for 4h at room temperature and then filtered over filter paper. The solvent was removed under *vacuum* and the solid obtained was washed twice with ethanol and filtered over fritted funnel. The residue was purified by column chromatography on silica gel (petroleum ether/dichloromethane, 25:75) to give a brown solid in 66% yield (650 mg, 2.51 mmol). MP: 180°C; NMR (δ (ppm), $CDCl_3$): ^{1}H (300 MHz): 8.43 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 8.05 – 7.99 (m, 2H), 7.86 – 7.81 (m, 3H), 7.61 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 3.30 (s, 1H); $^{13}C\{^1H\}$ (75 MHz): 190.1, 189.0, 145.5, 142.7, 140.3, 135.7, 135.5, 134.0, 133.4, 132.5, 130.0, 126.9, 123.6, 123.6, 83.4, 81.1; IR (ATR, cm^{-1}): 3383, 3281, 3097, 3063, 1722, 1684, 1579, 1364, 1344, 1203, 1177, 1153, 1076, 989, 841, 732; HRMS (ESI): m/z, calculated for $[M+Na]^+$ ($C_{18}H_{10}O_2Na$): 281.0573, found: 281.0573

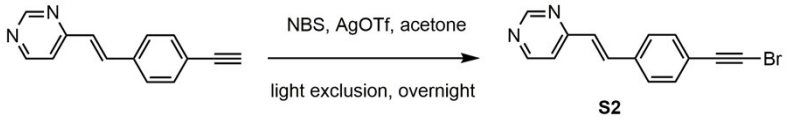


Spectrum 1: ^{1}H NMR spectrum of compound **S1** (300 MHz, $CDCl_3$)



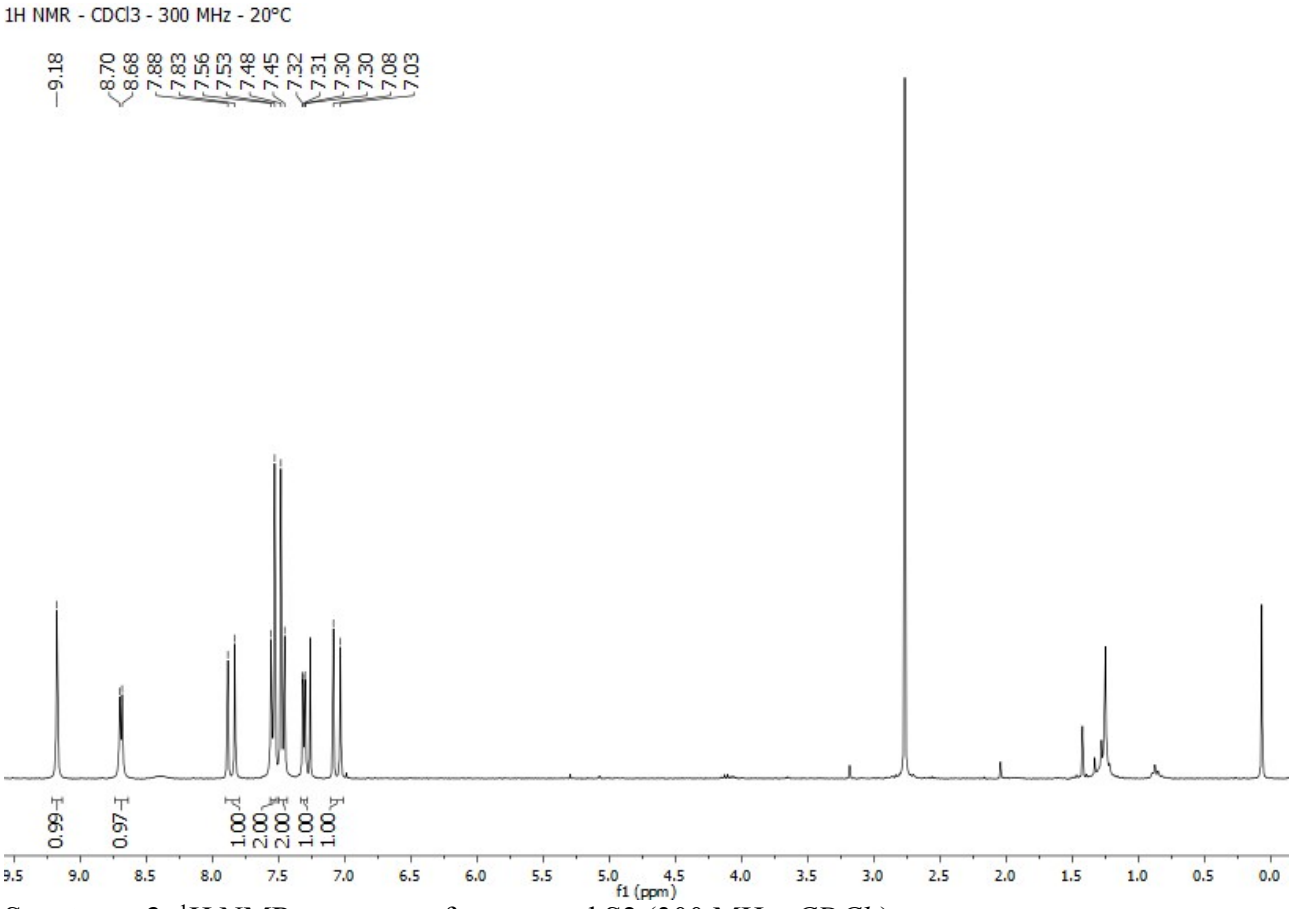
Spectrum 2: ^{13}C NMR spectrum of compound **S1** (75 MHz, $CDCl_3$)

Synthesis of precursor S2

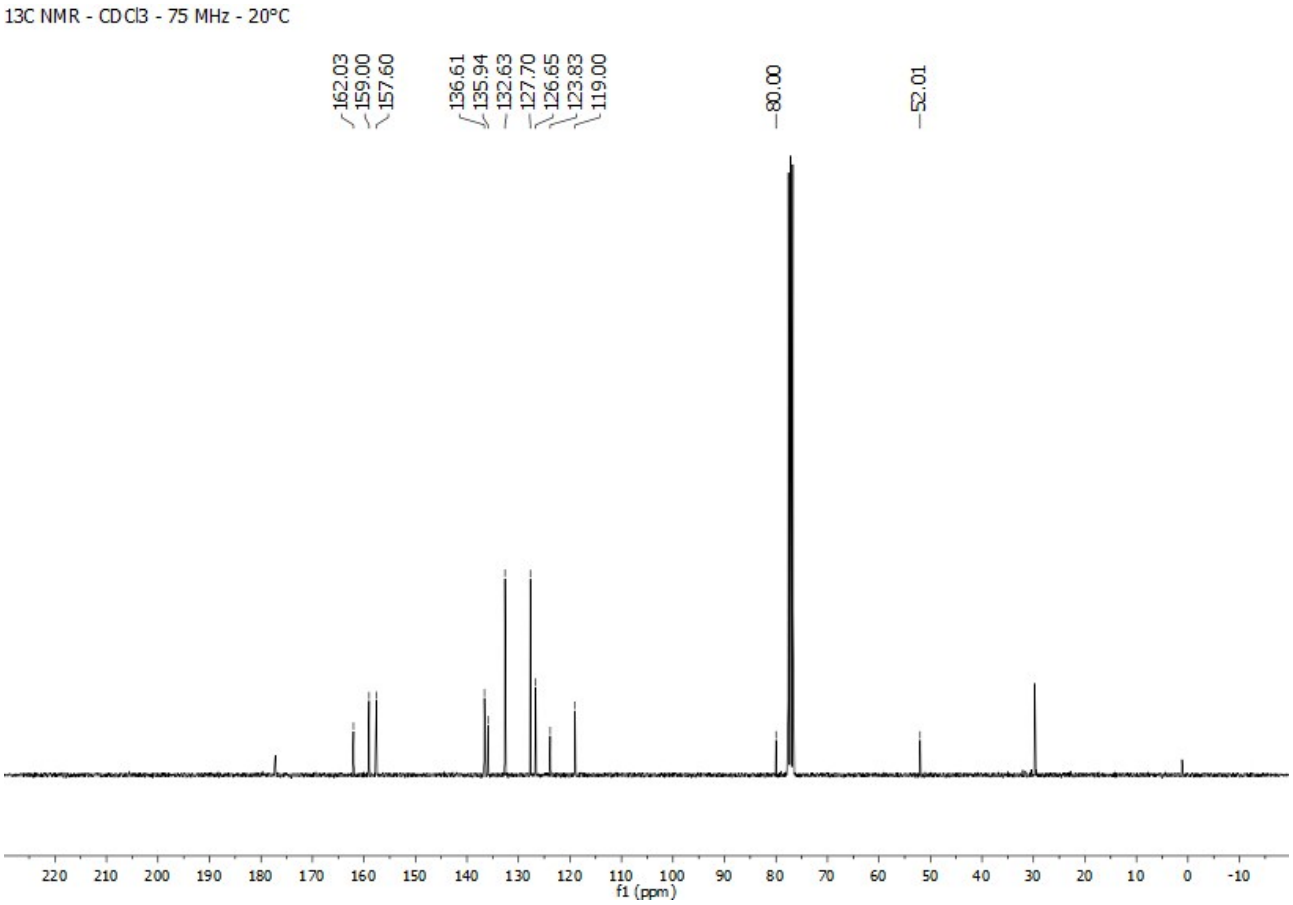


S2

In a round-bottom flask of 100 mL protected from light, 4-[(*E*)-2-(4-ethynylphenyl)ethenyl]-pyrimidine[4] (202 mg, 979 µmol, 1 eq) was dissolved in 30 mL of acetone. *N*-bromosuccinimide (242 mg, 1.36 mmol, 1.4 eq) and silver triflate (44 mg, 171 µmol, 0.2 eq) were introduced and the mixture was stirred at room temperature for 2h. The reaction was quenched with water, the phases were separated and the aqueous phase was extracted with 3×40 mL of dichloromethane. The organic phases were combined and the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel (ethyl acetate) and the product was obtained as a beige solid in 69 % yield (195 mg, 684 µmol). T_{dec}: 180°C; NMR (δ (ppm), $CDCl_3$): ^1H (300 MHz): 9.18 (s, 1H), 8.69 (d, $^3J_{HH}$ = 5.3 Hz, 1H), 7.86 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 7.54 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.47 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.31 (dd, J_{HH} = 5.3, 1.4 Hz, 1H), 7.06 (d, $^3J_{HH}$ = 16.0 Hz, 1H); $^{13}C\{^1H\}$ (75 MHz): 162.0, 159.0, 157.6, 136.6, 135.9, 132.6, 127.7, 126.7, 123.8, 119.0, 80.0, 52.0; IR (ATR, cm^{-1}): 3034, 2188, 1771, 1708, 1634, 1574, 1384, 1176, 1164, 970, 837, 815; HRMS (ESI): m/z, calculated for $[M+H]^+$ ($C_{14}H_{10}N_2{}^{79}Br$): 285.0022, found: 285.0021

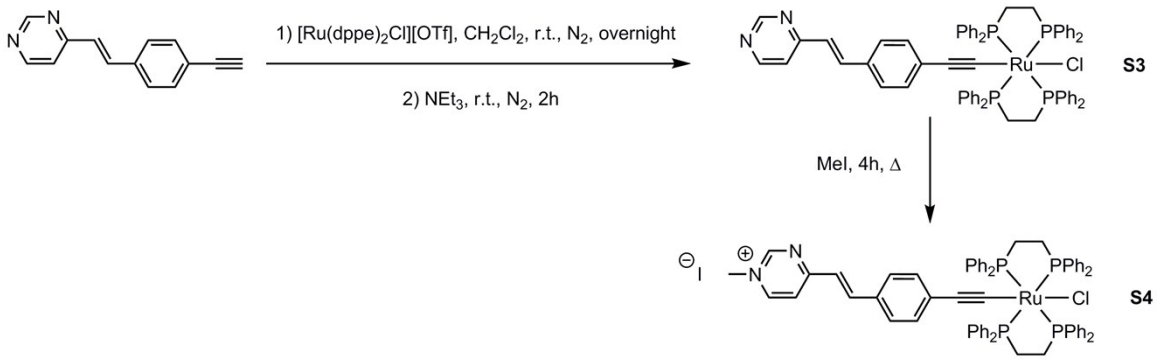


Spectrum 3: ^{1}H NMR spectrum of compound **S2** (300 MHz, $CDCl_3$)

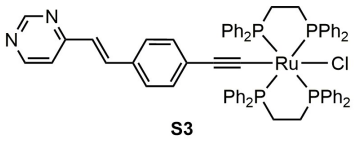


Spectrum 4: ^{13}C NMR spectrum of compound **S2** (75 MHz, $CDCl_3$)

Syntheses of complexes S3 and S4

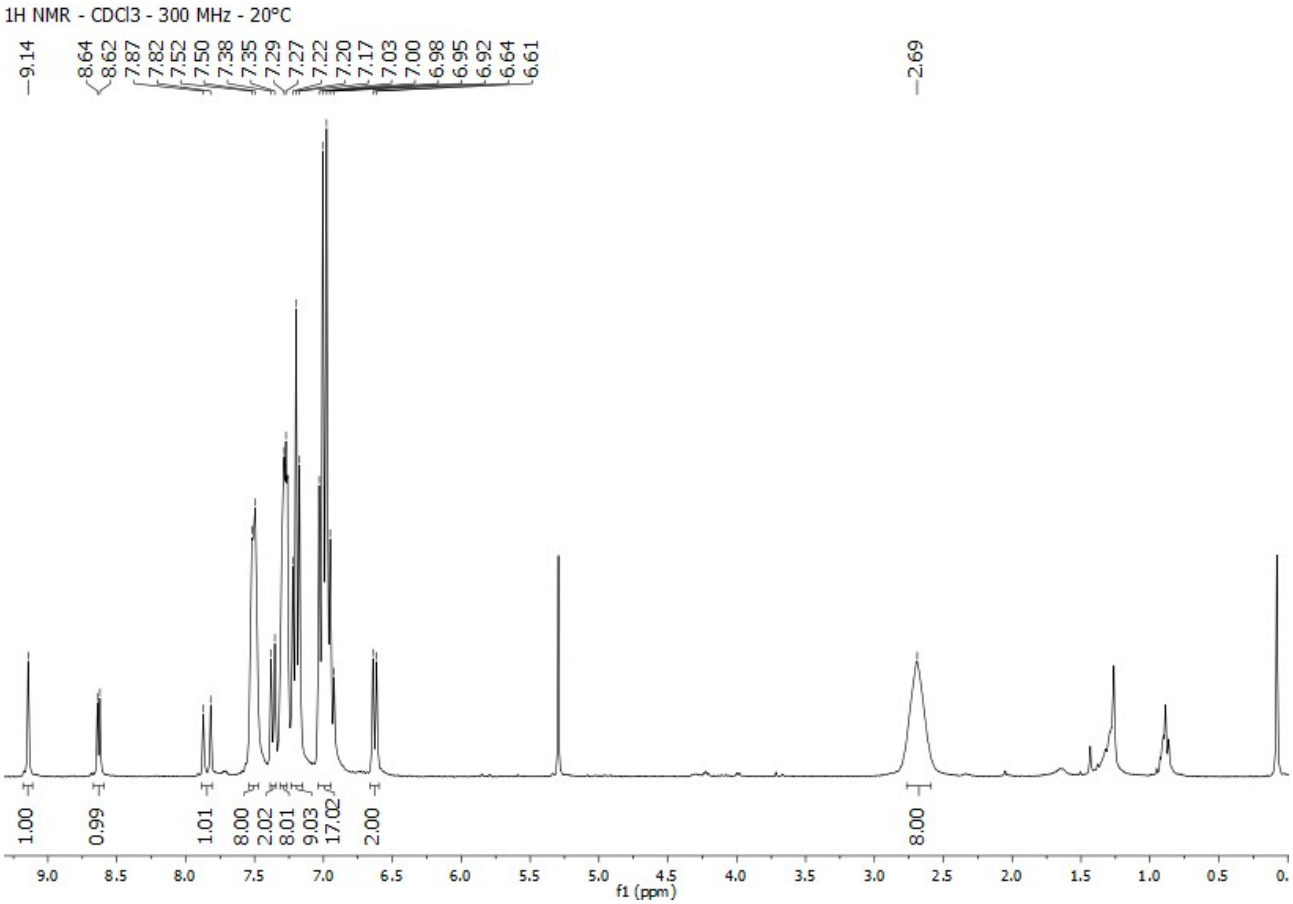


Compound S3

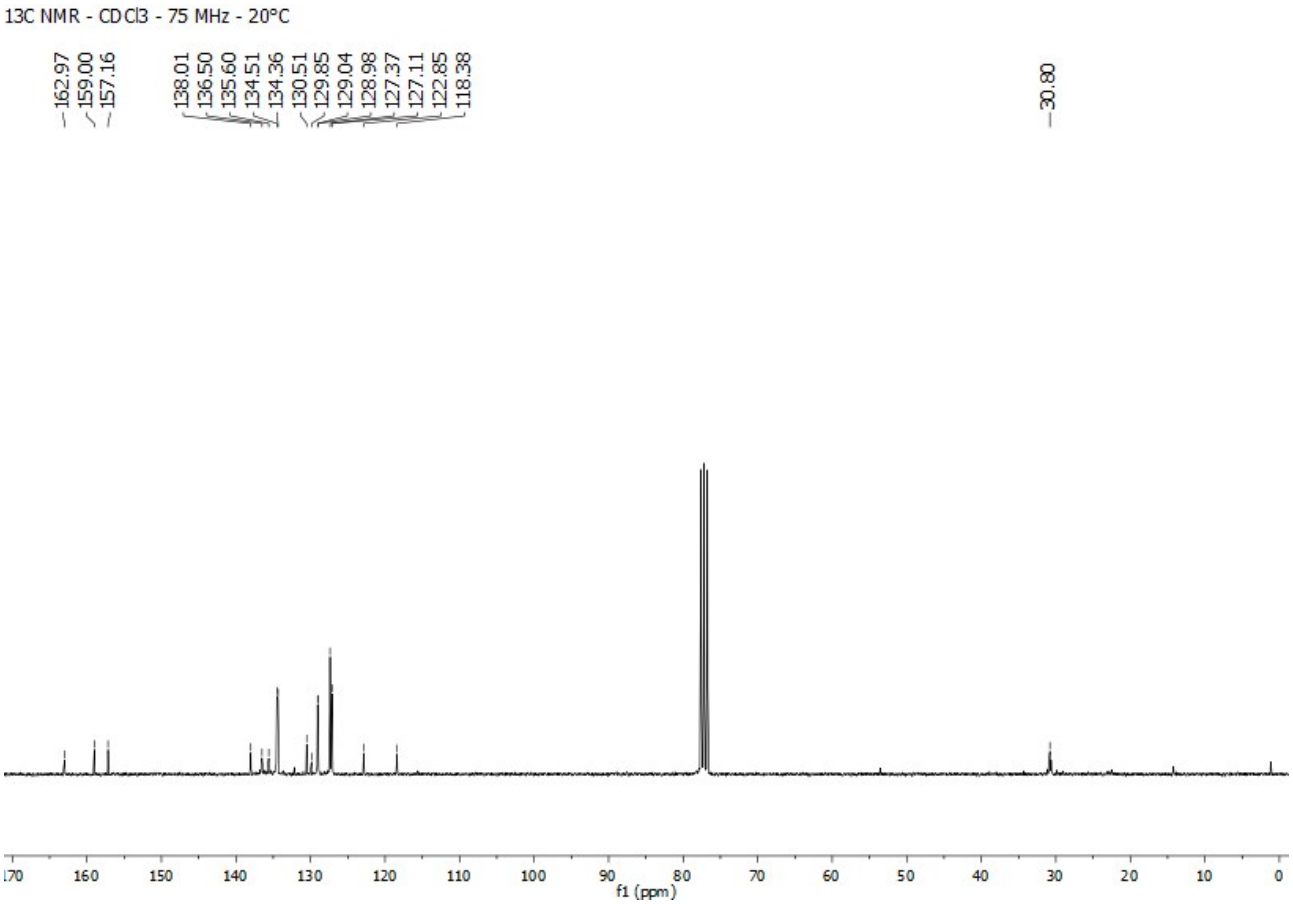


S3

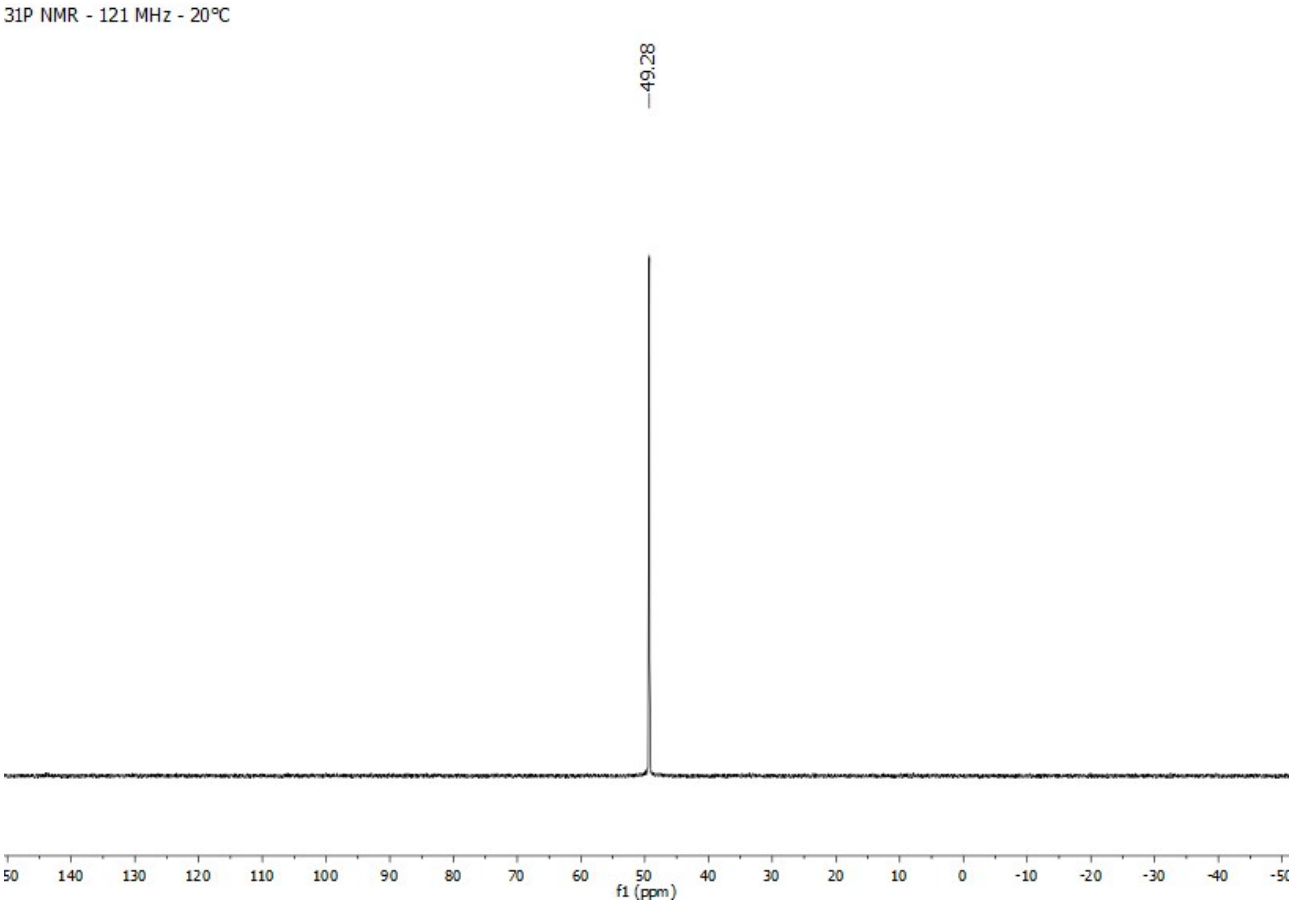
A Schlenk flask, charged with 4-[(*E*)-2-(4-ethynylphenyl)ethenyl]-pyrimidine[4] (133 mg, 645 µmol, 1 eq) and chloro-bis(1,2-bis(diphenylphosphino)ethane)ruthenium triflate[3] (700 mg, 647 µmol, 1 eq) were degassed and back-filled with nitrogen several times. Then dry dichloromethane (20 mL) was introduced into the reaction flask. The reaction mixture was stirred under nitrogen protection at room temperature for 4h. Triethylamine (0.4 mL, 290 mg, 2.87 mmol, 4.4 eq) was then added and the mixture was stirred at room temperature for 1h. The solvent was then removed under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate) to give compound **9** as a dark orange powder in 42% yield (308 mg, 271 mmol); T_{dec}: 150°C; NMR (δ (ppm), $CDCl_3$): ^1H (300 MHz): 9.14 (s, 1H), 8.63 (d, $^3J_{HH}$ = 5.3 Hz, 1H), 7.85 (d, $^3J_{HH}$ = 15.9 Hz, 1H), 7.55 – 7.46 (m, 8H), 7.37 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.33 – 7.26 (m, 8H), 7.24 – 7.16 (m, 9H), 7.05 – 6.90 (m, 17H), 6.63 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 2.69 (s, 8H); $^{13}C\{^1H\}$ (75 MHz): 163.0, 159.0, 157.2, 138.0, 136.5, 135.6, 134.5, 134.4, 130.5, 129.9, 129.0, 129.0, 127.4, 127.1, 122.8, 118.4, 30.8; ^{31}P (121 MHz): 49.28; IR (ATR, cm^{-1}): 3050, 2919, 2048, 1568, 1432, 1171, 1094, 836, 811, 741, 692; HRMS (ESI): m/z, calculated for $M^{+\bullet}$ ($C_{66}H_{57}N_2{}^{35}ClP_4{}^{102}Ru$): 1138.2199, found: 1138.2197



Spectrum 5: ^{1}H NMR spectrum of compound **S3** (300 MHz, $CDCl_3$)

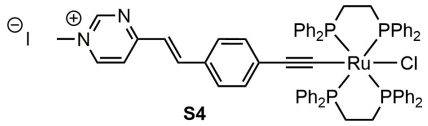


Spectrum 6: ^{13}C NMR spectrum of compound **S3** (75 MHz, $CDCl_3$)



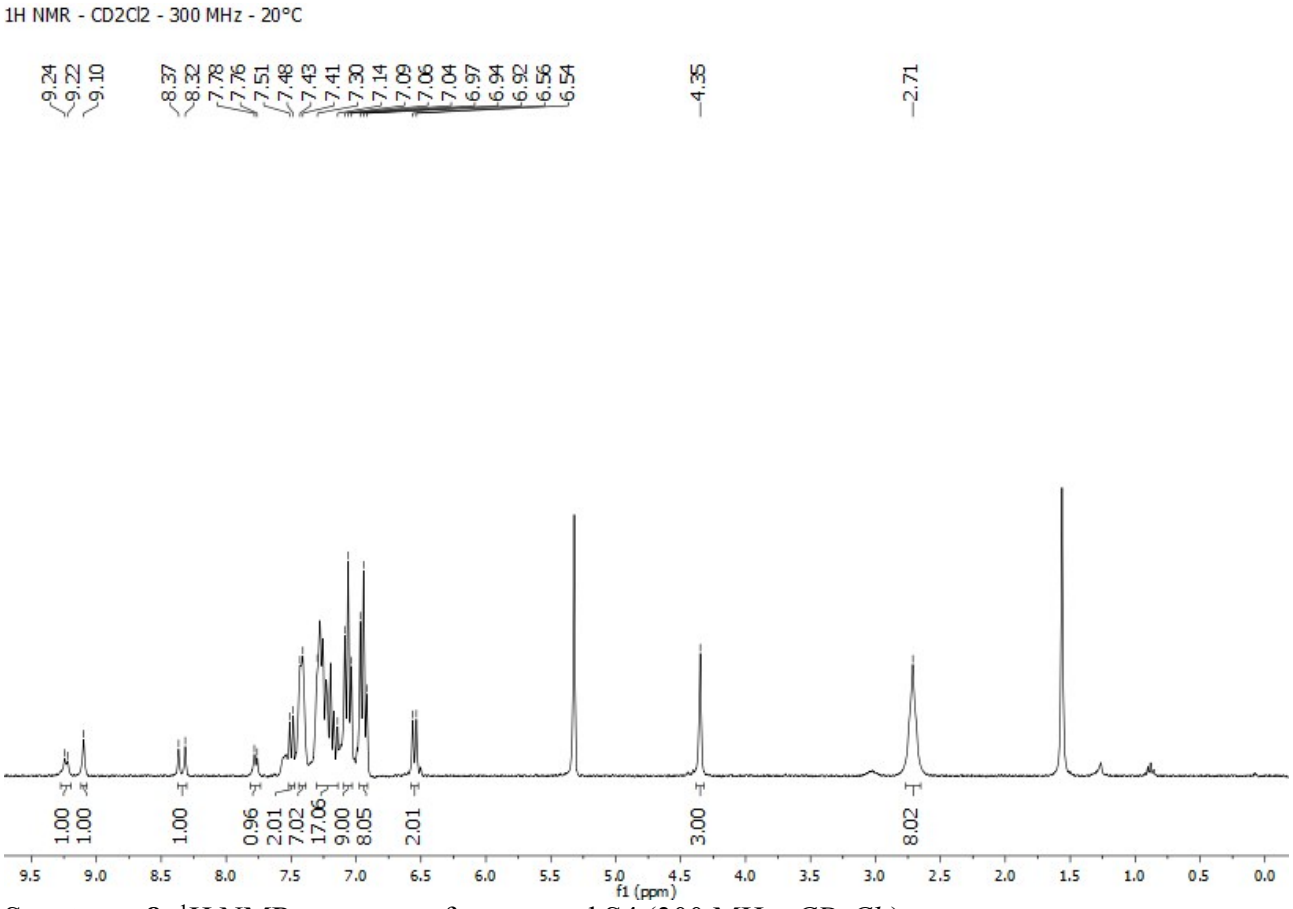
Spectrum 7: ^{31}P NMR spectrum of compound **S3** (121 MHz, *CDCl₃*)

Compound S4

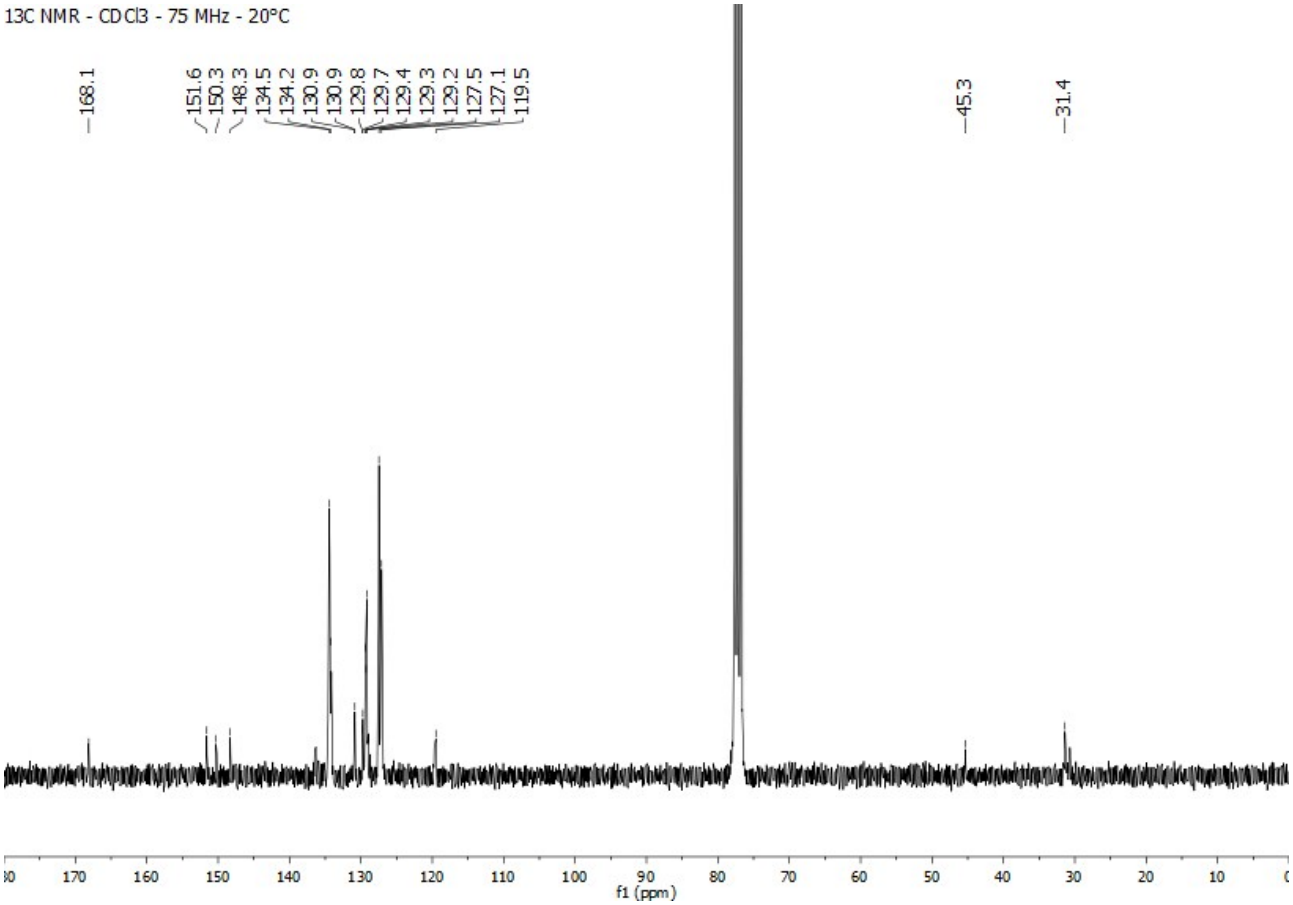


S4

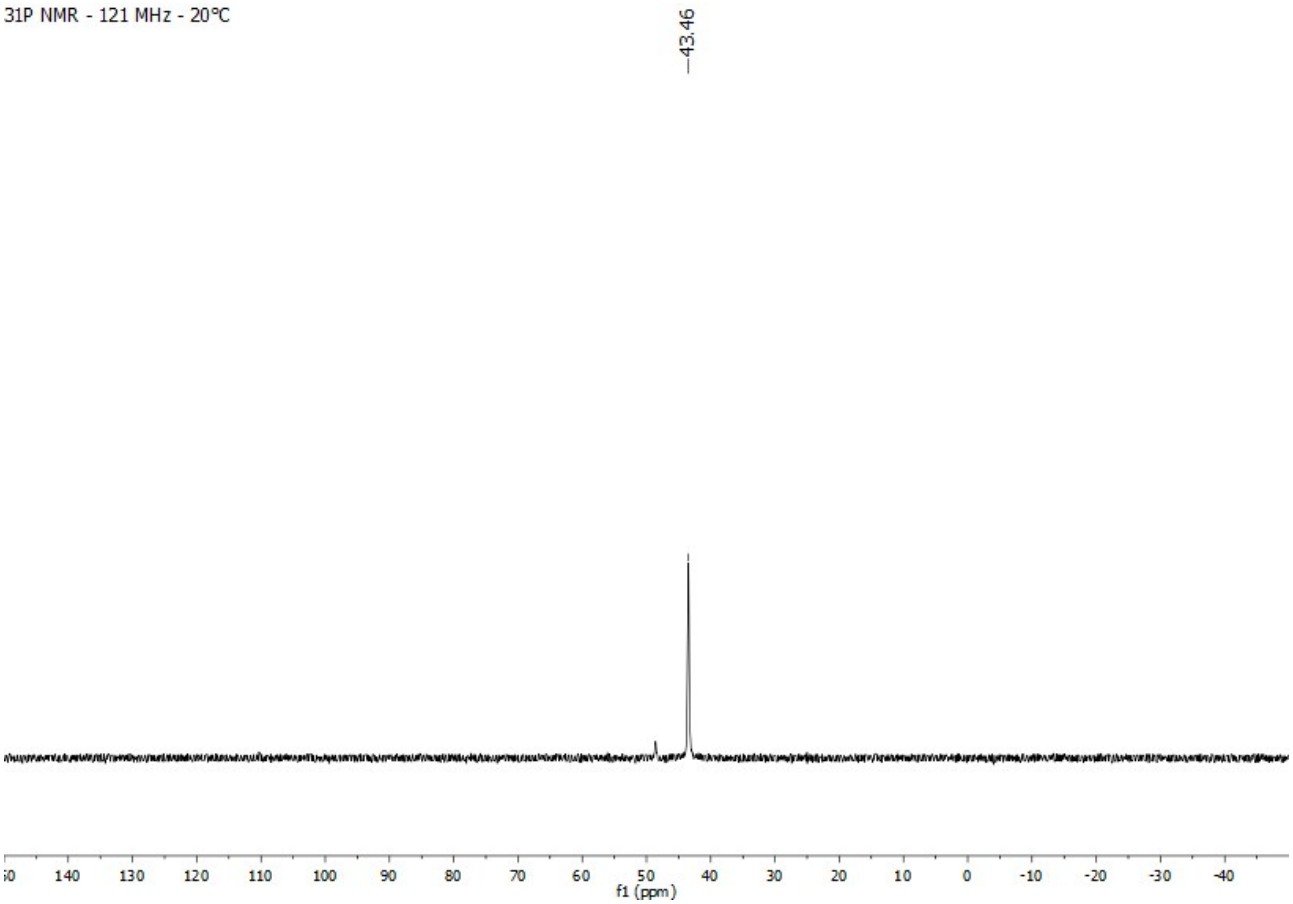
A mixture of compound **S3** (70 mg, 61 µmol) and methyl iodide (5 mL) was refluxed for 4h. The methyl iodide was evaporated under vacuum. The residue was washed with *n*-pentane. The compound was obtained as a dark blue powder in 95% yield (75 mg, 58 µmol). T_{dec}: 180°C; NMR (δ (ppm), CD_2Cl_2): ^1H (300 MHz): 9.23 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 9.10 (s, 1H), 8.34 (d, $^3J_{HH}$ = 15.3 Hz, 1H), 7.77 (d, $^3J_{HH}$ = 6.6 Hz, 1H), 7.50 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.45 – 7.38 (m, 7H), 7.32 – 7.14 (m, 17H), 7.10 – 7.03 (m, 9H), 6.98 – 6.91 (m, 8H), 6.55 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 4.35 (s, 3H), 2.71 (s, 8H); $^{13}C\{^1H\}$ (75 MHz): 152.4, 150.3, 149.0, 135.1, 135.0, 134.8, 134.4, 131.3, 130.2, 129.8, 129.6, 127.9, 127.7, 127.5, 119.9, 119.6, 45.2, 30.3; ^{31}P (121 MHz): 43.46; IR (ATR, cm^{-1}): 3410, 3047, 2923, 2037, 1558, 1431, 1159, 740, 690; HRMS (ESI): m/z, calculated for C^+ ($C_{67}H_{60}N_2{}^{35}ClP_4{}^{102}Ru$): 1153.2433, found: 1153.2447



Spectrum 8: ^{1}H NMR spectrum of compound **S4** (300 MHz, CD_2Cl_2)

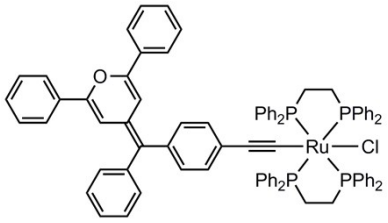


Spectrum 9: ^{13}C NMR spectrum of compound **S4** (75 MHz, CD_2Cl_2)

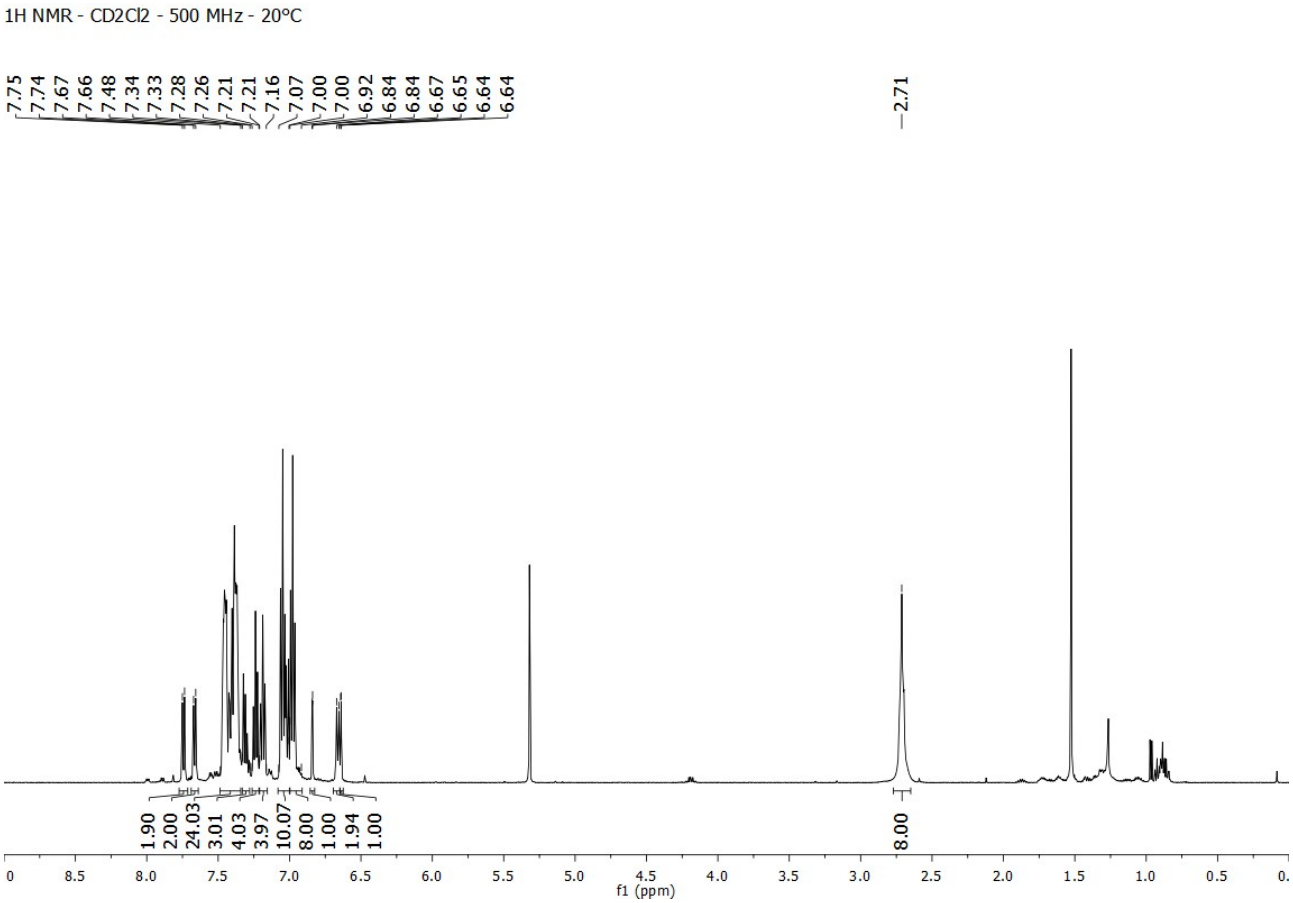


Spectrum 10: ^{31}P NMR spectrum of compound **S4** (121 MHz, CD_2Cl_2)

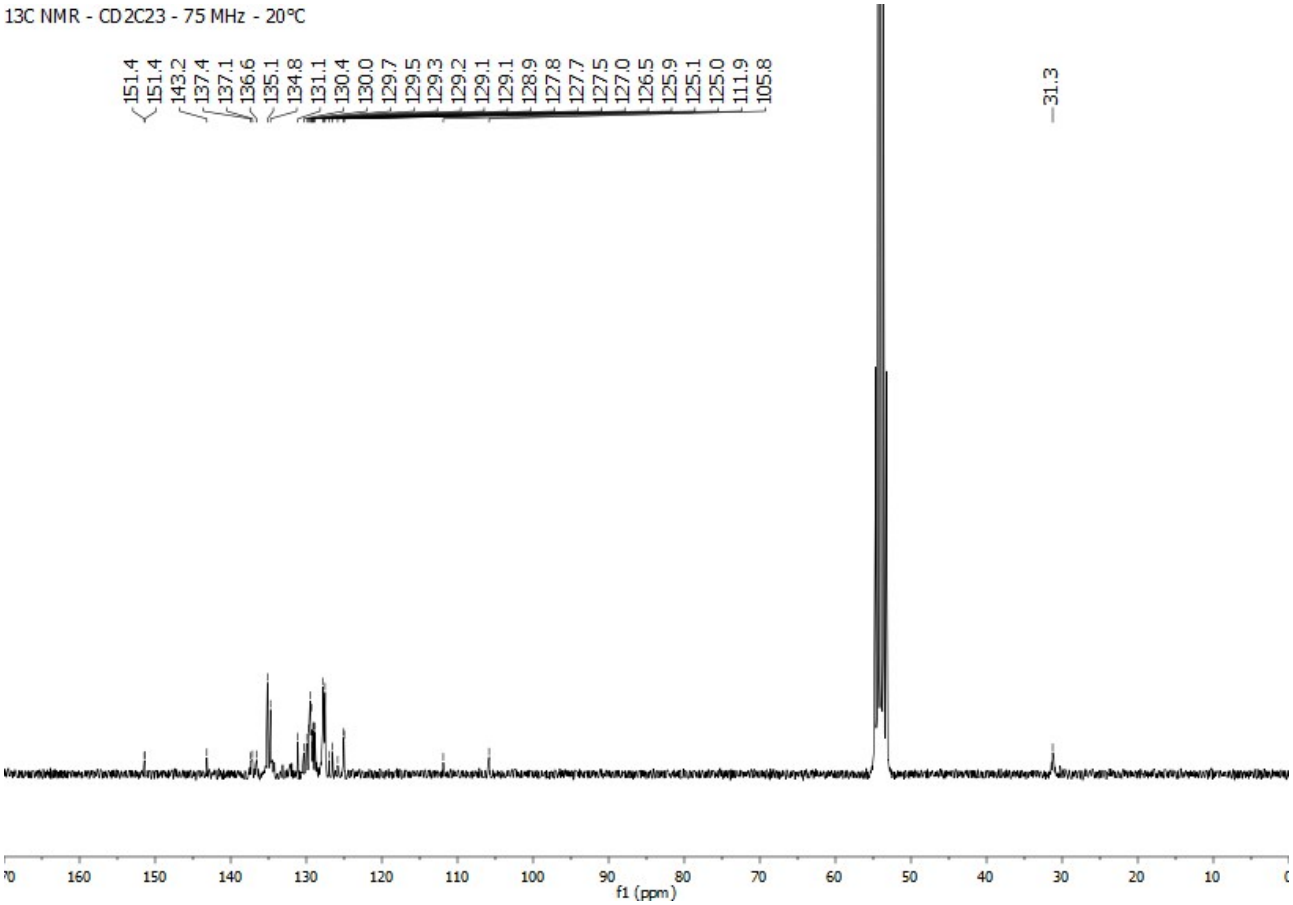
Synthesis of S5



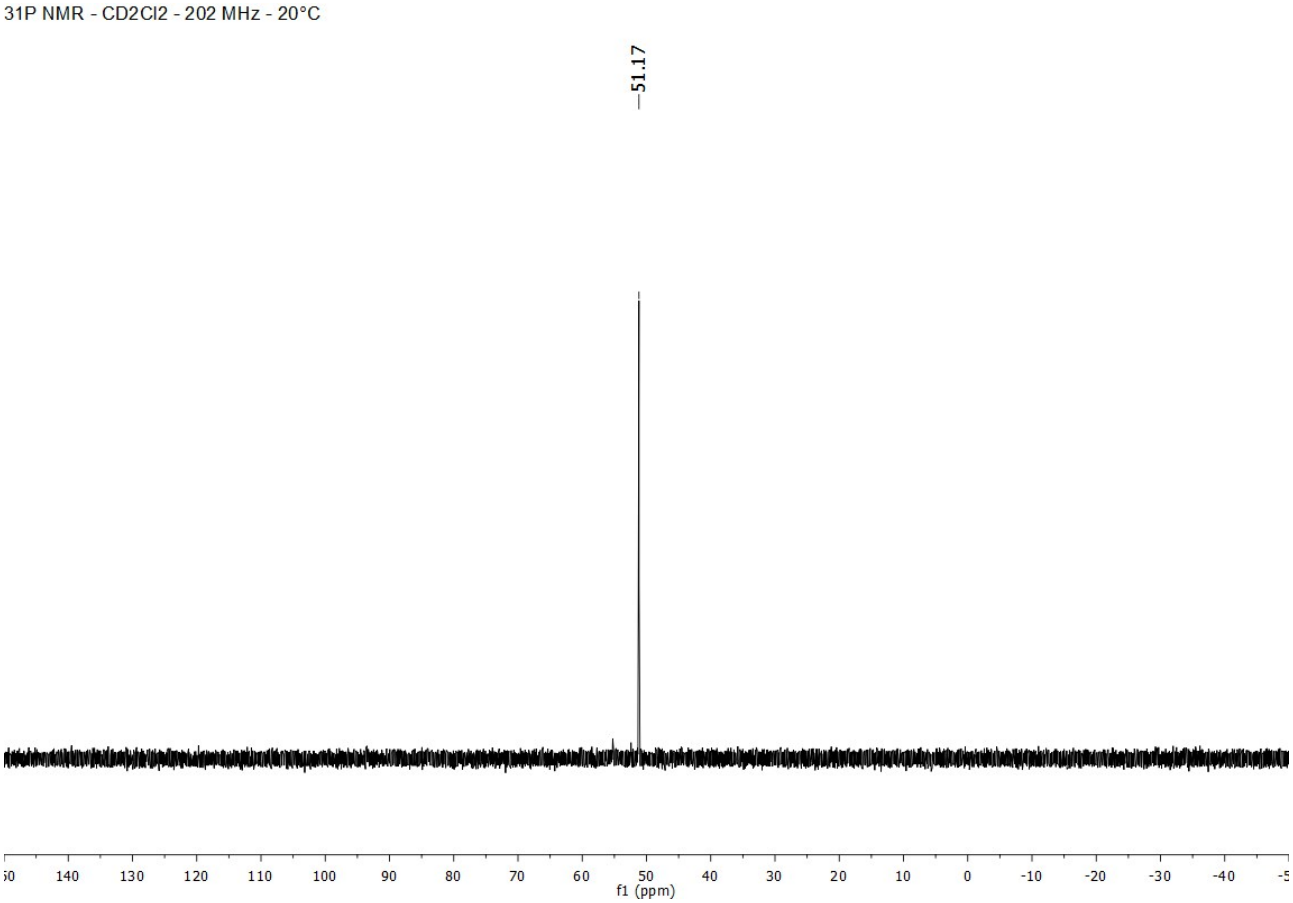
A Schlenk flask, charged with 4-((4-ethynylphenyl)(phenyl)methylene)-2,6-di-phenyl-4*H*-pyran (**9**)[1] (156 mg, 370 µmol, 1 eq) and chloro-bis(1,2-bis(diphenylphosphino)ethane)ruthenium triflate[3] (400 mg, 370 µmol, 1 eq), was degassed and back-filled with nitrogen several times. Then dry dichloromethane (20 mL) was introduced into the reaction flask. The reaction mixture was stirred under nitrogen protection at room temperature overnight. Triethylamine (0,25 mL, 182 mg, 1.8 mmol, 5 eq) was then added and the mixture was stirred at room temperature for 1h. The solvent was then removed under reduced pressure. The residue was purified by column chromatography on silica gel (dichloromethane/ethyl acetate, 1:1), recrystallized in CH_2Cl_2/*n*-hexane and the compound **S5** was obtained as a yellow compound in 35% yield (175 mg, 129 µmol). T_{dec}: 174°C; NMR (δ (ppm), CD_2Cl_2): ^{1}H (500 MHz): 7.74 (d, $^3J_{HH}$ = 7.6 Hz, 2H), 7.66 (d, $^3J_{HH}$ = 7.4 Hz, 2H), 7.49 – 7.34 (m, 24H), 7.33 – 7.28 (m, 3H), 7.26 – 7.21 (m, 4H), 7.21 – 7.16 (m, 4H), 7.08 – 7.00 (m, 10H), 7.00 – 6.91 (m, 8H), 6.84 (d, $^4J_{HH}$ = 1.9 Hz, 1H), 6.66 (d, J = 8.1 Hz, 2H), 6.64 (d, $^4J_{HH}$ = 1.9 Hz, 1H), 2.71 (s, 8H); ^{13}C{^{1}H} (75 MHz): 151.4, 151.4, 143.2, 137.4, 137.1, 136.6, 135.1, 134.8, 131.1, 130.4, 130.0, 129.7, 129.5, 129.3, 129.2, 129.1, 129.1, 128.9, 127.8, 127.7, 127.5, 127.0, 126.5, 125.9, 125.1, 125.0, 111.9, 105.8, 31.3; ^{31}P (202 MHz): 51.17; IR (ATR, cm^{-1}): 3051, 2923, 2070, 1652, 1585, 1486, 1433, 1276, 1095, 765, 743, 691; HRMS (ESI): m/z, calculated for $M^{+\bullet}$ ($C_{84}H_{69}O^{35}ClP_4{}^{102}Ru$): 1354.3026, found: 1354.3040



Spectrum 11: ^{1}H NMR spectrum of compound **S5** (500 MHz, CD_2Cl_2)



Spectrum 12: ^{13}C NMR spectrum of compound **S5** (75 MHz, CD_2Cl_2)



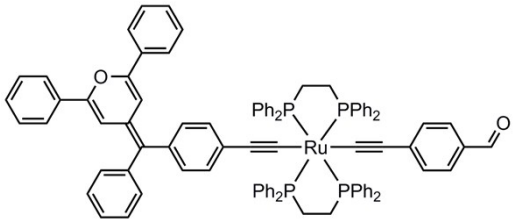
Spectrum 13: ^{31}P NMR spectrum of compound **S5** (202 MHz, CD_2Cl_2)

Syntheses of compounds 1 to 6

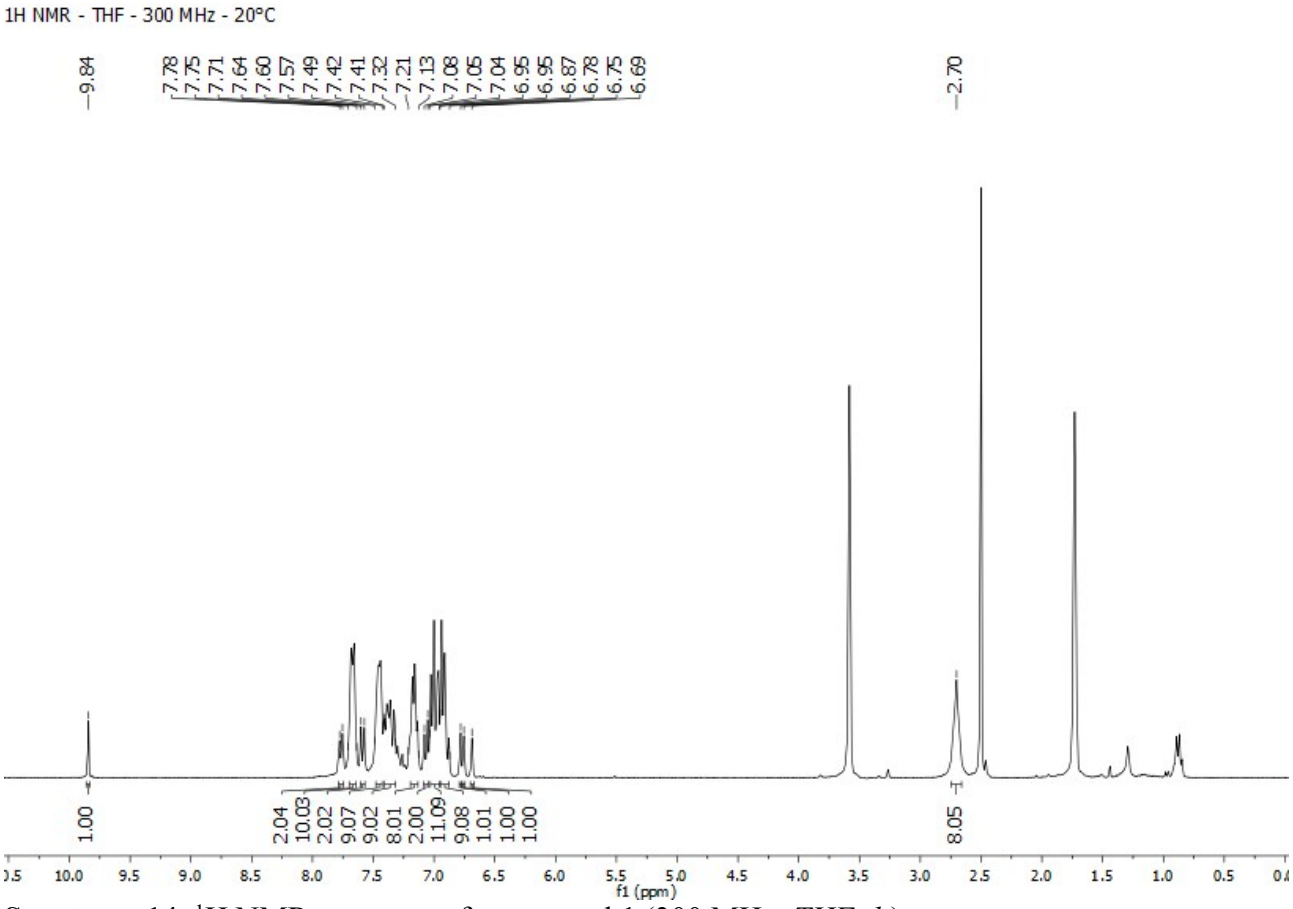
Example of procedure for the synthesis of compound **6**

A Schlenk flask, charged with 4-((4-ethynylphenyl)(phenyl)methylene)-2,6-di-*tert*-butyl-4*H*-pyran (**10**)[2] (156 mg, 406 µmol, 1.1 eq) and chloro-bis(1,2-bis(diphenylphosphino)ethane)ruthenium triflate[3] (400 mg, 370 µmol, 1 eq), was degassed and back-filled with nitrogen several times. Then dry dichloromethane (20 mL) was introduced into the reaction flask. The reaction mixture was stirred under nitrogen protection at room temperature for 4h. Triethylamine (0.5 mL, 363 mg, 3.6 mmol, 10 eq) was then added and the mixture was stirred at room temperature for 1h. 4-[(*E*)-2-(4-ethynylphenyl)ethenyl]-pyrimidine[4] (76 mg, 370 µmol, 1 eq) and silver triflate (142 mg, 554 µmol, 1.5 eq) were introduced into the Schlenk flask and the reaction mixture was stirred under nitrogen protection at room temperature overnight. The solvent was then removed under reduced pressure. The residue was purified by column chromatography on silica gel (dichloromethane/ethyl acetate, 1:1).

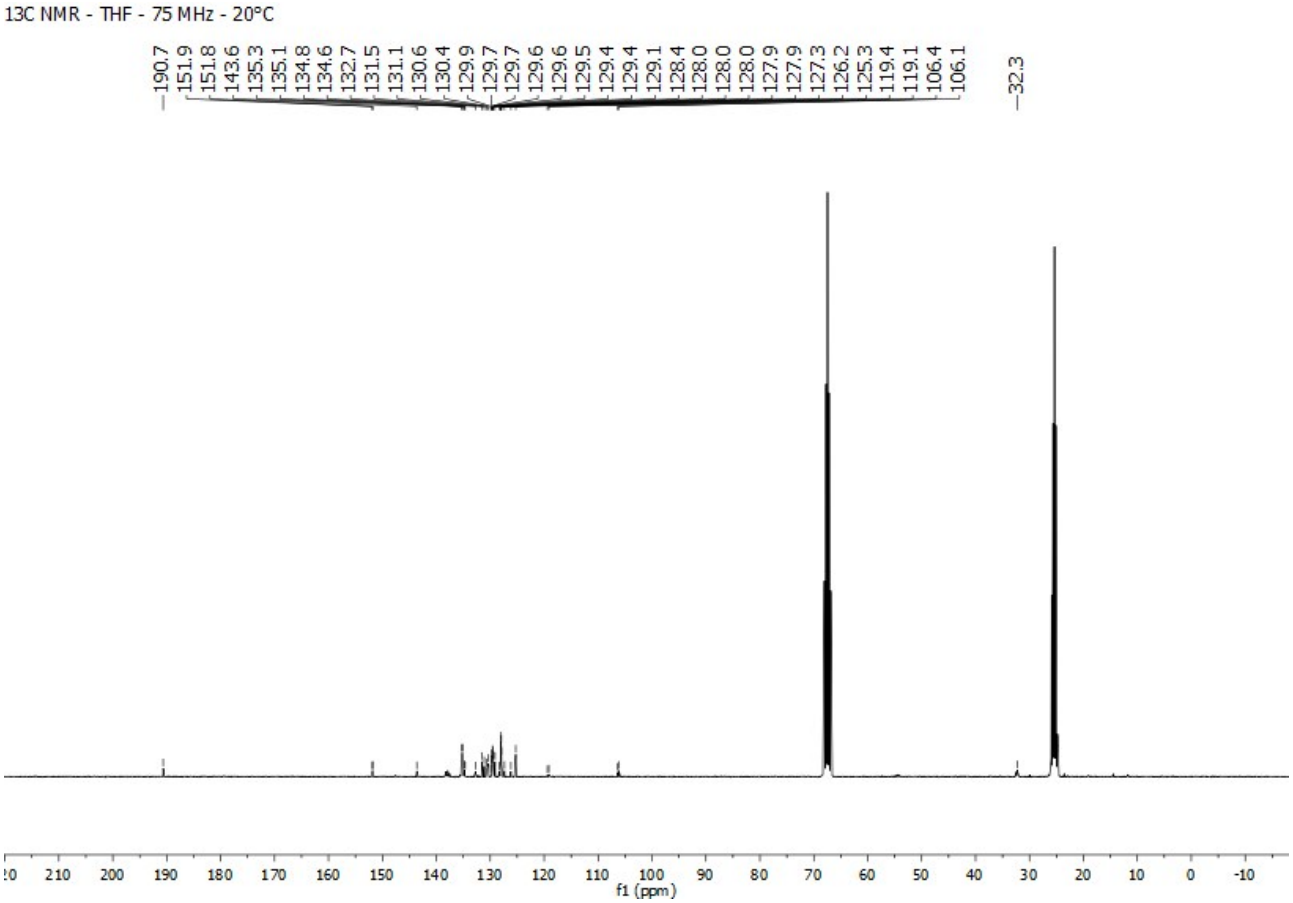
Compound 1



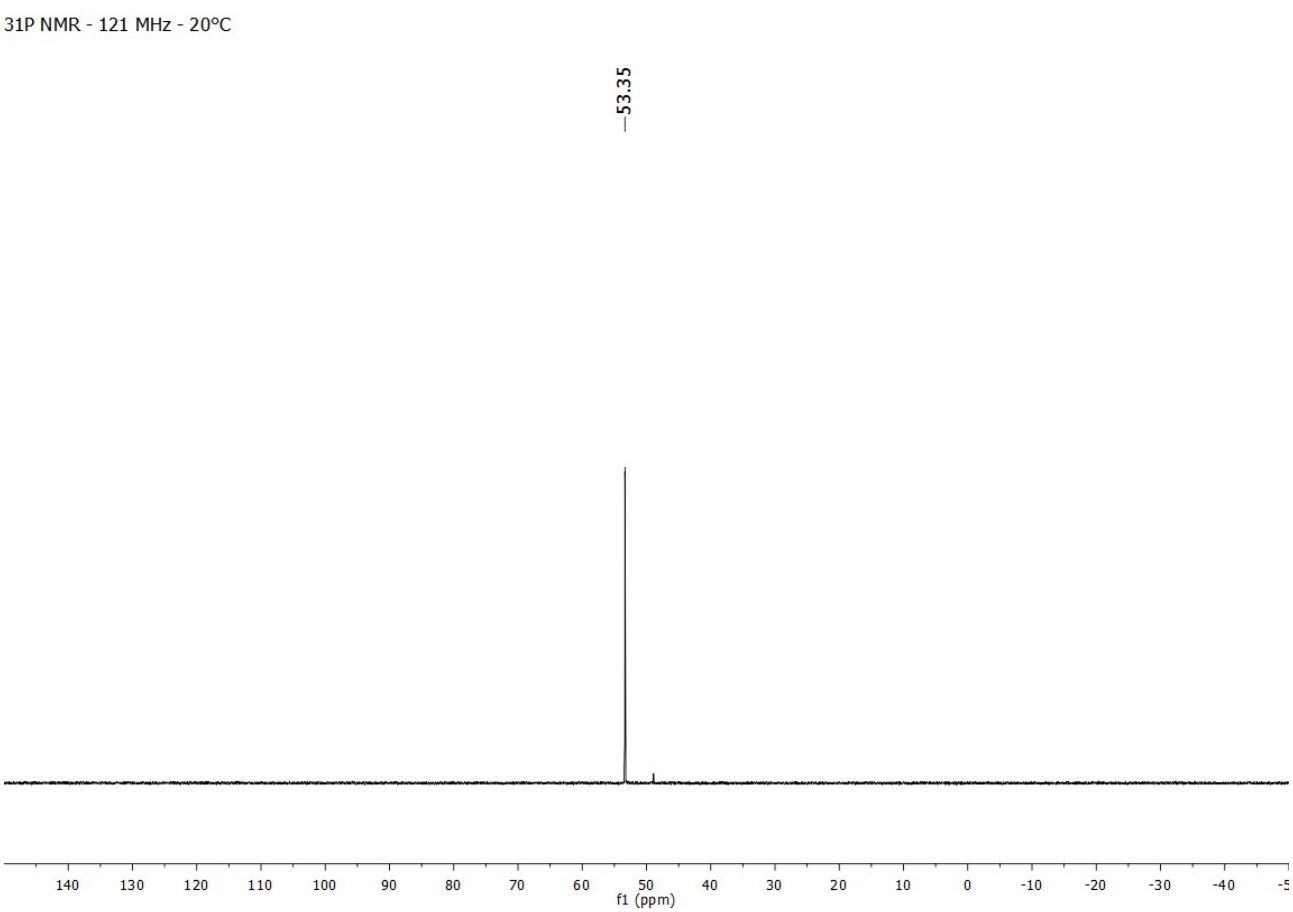
Yellow solid. Yield: 364 mg, 68%. T_{dec}: 160°C; NMR (δ (ppm), THF-d_8): ^{1}H (300 MHz): 9.84 (s, 1H), 7.76 (d, $^3J_{HH}$ = 7.2 Hz, 2H), 7.71 – 7.63 (m, 10H), 7.59 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.49 – 7.42 (m, 9H), 7.41 – 7.32 (m, 9H), 7.21 – 7.12 (m, 8H), 7.07 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.04 – 6.95 (m, 11H), 6.95 – 6.87 (m, 9H), 6.78 (s, 1H), 6.75 (s, 1H), 6.69 (s, 1H), 2.70 (s, 8H); ^{13}C{^{1}H} (75 MHz): 190.7, 151.9, 151.8, 143.6, 135.3, 135.1, 134.8, 134.6, 132.7, 131.5, 131.1, 130.6, 130.4, 129.9, 129.7, 129.7, 129.6, 129.6, 129.5, 129.4, 129.4, 129.1, 128.4, 128.0, 128.0, 128.0, 127.9, 127.9, 127.3, 126.2, 125.3, 119.4, 119.1, 106.4, 106.1, 32.3; ^{31}P (121 MHz): 53.35; IR (ATR, cm^{-1}): 3054, 2921, 2729, 2168, 2041, 1681, 1647, 1583, 1212, 1156, 1096, 741, 691; HRMS (ESI): m/z, calculated for $M^{+\bullet}$ ($C_{93}H_{74}O_2P_4{}^{102}Ru$): 1448.3677, found: 1448.3687



Spectrum 14: ^{1}H NMR spectrum of compound **1** (300 MHz, *THF-d_8*)

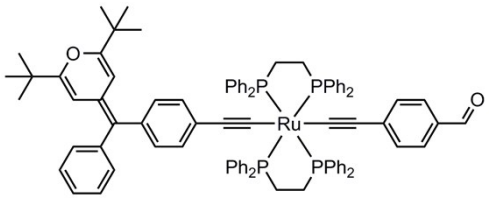


Spectrum 15: ^{13}C NMR spectrum of compound **1** (75 MHz, *THF-d_8*)

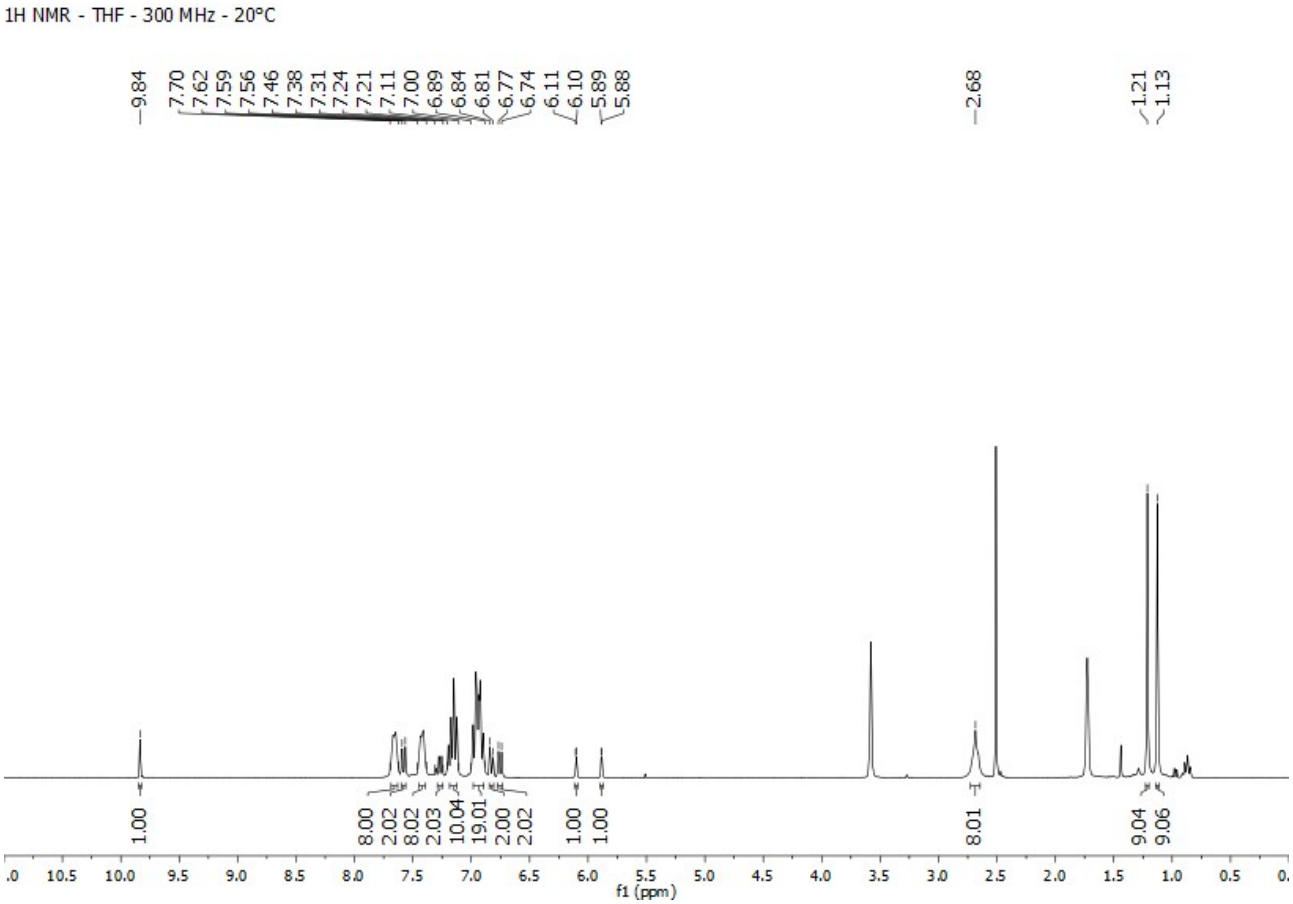


Spectrum 16: ^{31}P NMR spectrum of compound **1** (121 MHz, *THF-d_8*)

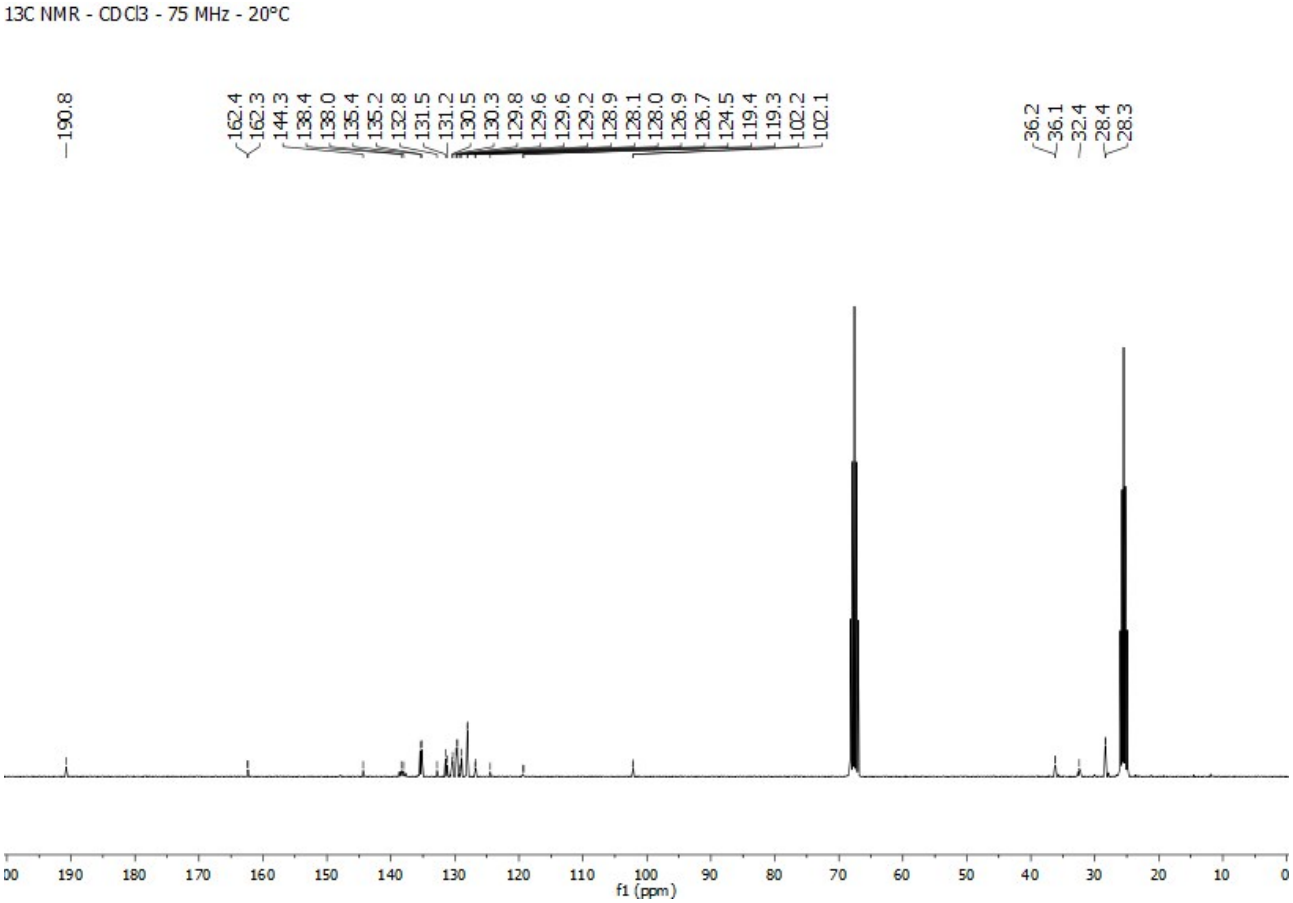
Compound 2



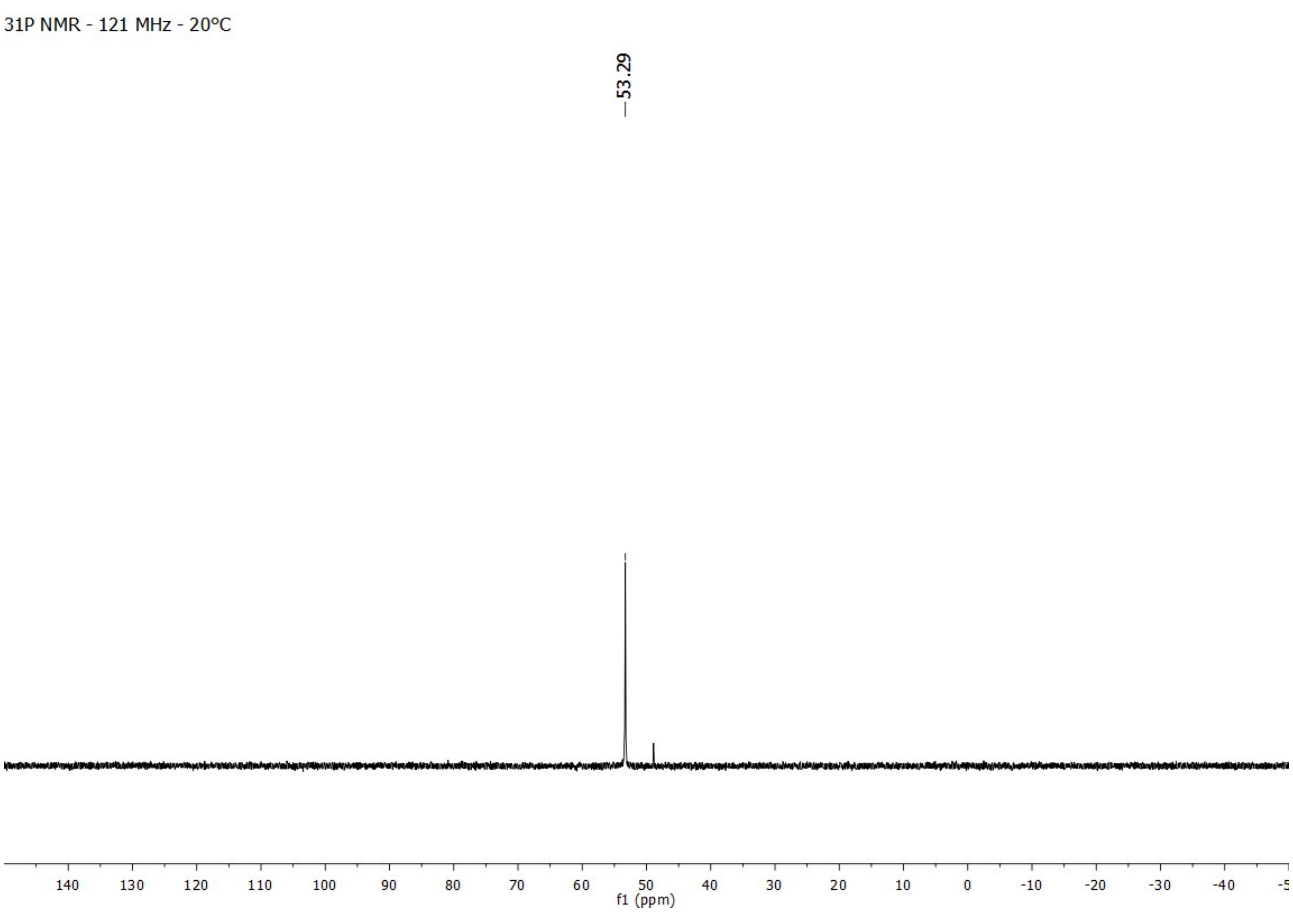
Yellow solid. Yield: 380 mg, 73%. T_{dec}: 130°C; NMR (δ (ppm), THF-d_8): ^{1}H (300 MHz): 9.84 (s, 1H), 7.70 – 7.62 (m, 8H), 7.58 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 7.46 – 7.38 (m, 8H), 7.31 – 7.24 (m, 2H), 7.21 – 7.10 (m, 10H), 7.01 – 6.88 (m, 19H), 6.83 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 6.75 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 6.10 (d, $^{4}J_{HH}$ = 1.9 Hz, 1H), 5.88 (d, $^{4}J_{HH}$ = 1.9 Hz, 1H), 2.68 (s, 8H), 1.21 (s, 9H), 1.13 (s, 9H); ^{13}C{^{1}H} (75 MHz): 190.8, 162.4, 162.3, 144.3, 138.4, 138.0, 135.4, 135.2, 132.8, 131.5, 131.2, 130.5, 130.3, 129.8, 129.6, 129.6, 129.2, 128.9, 128.1, 128.0, 126.9, 126.7, 124.5, 119.4, 119.3, 102.2, 102.1, 36.2, 36.1, 32.4, 28.4, 28.3; ^{31}P (121 MHz): 53.29; IR (ATR, cm^{-1}): 3053, 2962, 2926, 2041, 1683, 1653, 1583, 1433, 1211, 1156, 1095, 741, 691; HRMS (ESI): m/z, calculated for $M^{+\bullet}$ ($C_{89}H_{82}O_2P_4{}^{102}Ru$): 1408.4303, found: 1408.4325



Spectrum 17: ^{1}H NMR spectrum of compound **2** (300 MHz, *THF-d_8*)

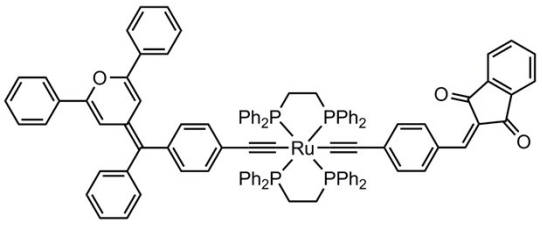


Spectrum 18: ^{13}C NMR spectrum of compound **2** (75 MHz, *THF-d_8*)

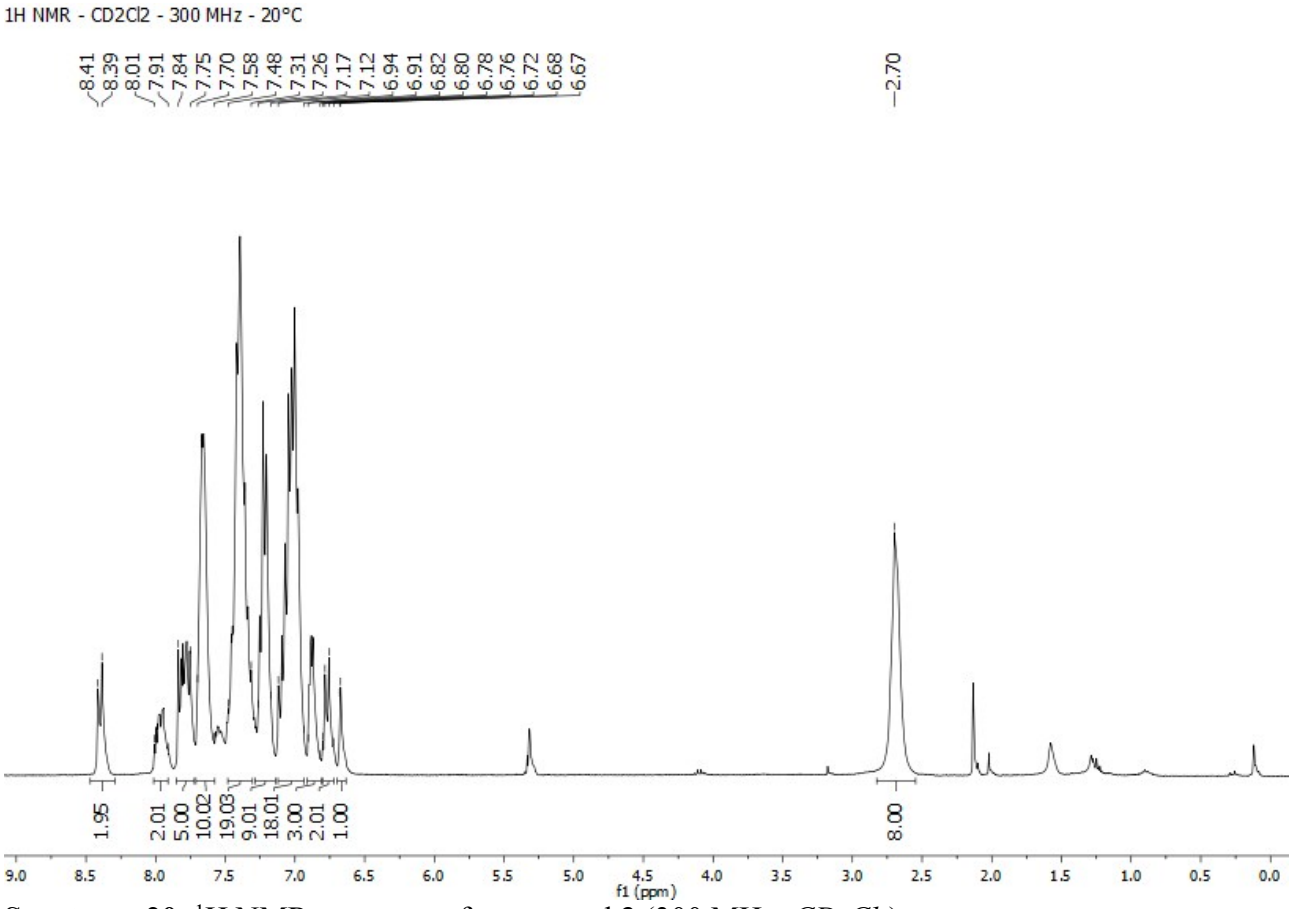


Spectrum 19: ^{31}P NMR spectrum of compound **2** (121 MHz, *THF-d_8*)

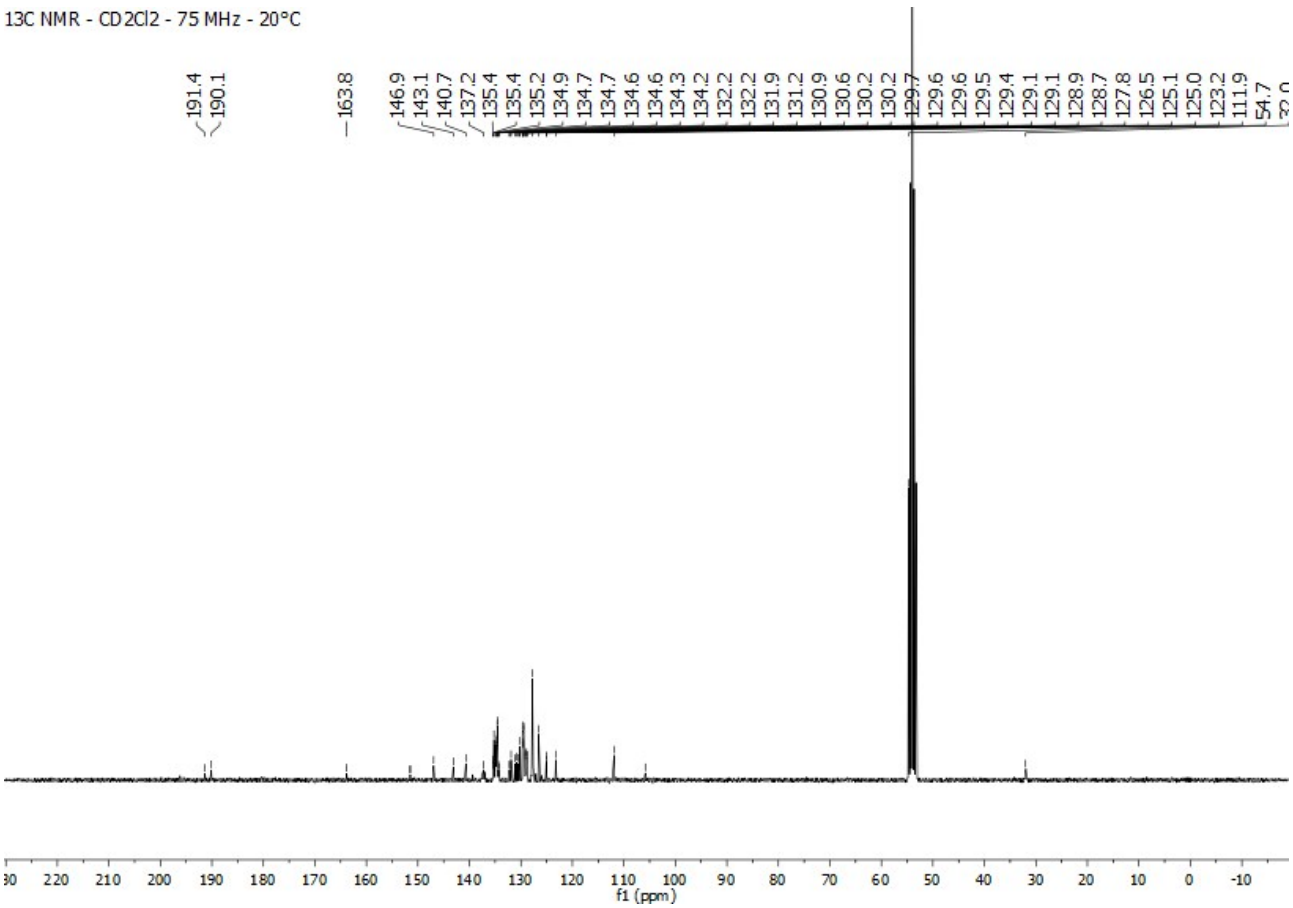
Compound 3



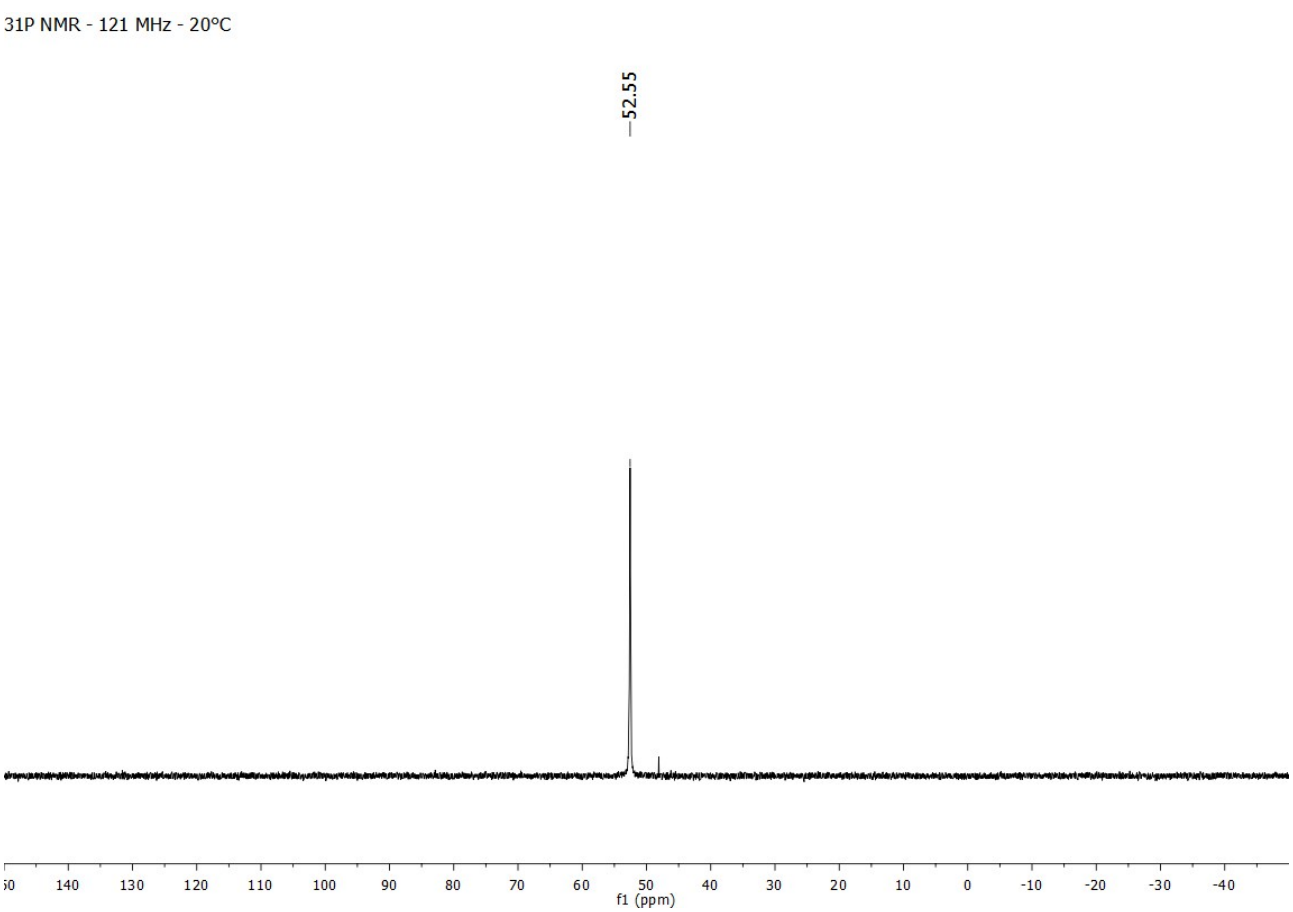
Black solid. Yield: 379 mg, 65%. T_{dec}: 180°C; NMR (δ (ppm), CD_2Cl_2): ^{1}H (300 MHz): 8.40 (d, $^3J_{HH}$ = 8.5 Hz, 1H), 8.01 – 7.90 (m, 2H), 7.85 – 7.72 (m, 5H), 7.71 – 7.58 (m, 10H), 7.48 – 7.30 (m, 19H), 7.29 – 7.14 (m, 9H), 7.12 – 6.93 (m, 18H), 6.91 – 6.82 (m, 3H), 6.80 – 6.72 (m, 2H), 6.68 (d, $^4J_{HH}$ = 1.9 Hz, 1H), 2.70 (s, 8H); ^{13}C{^{1}H} (75 MHz): 191.4, 190.1, 163.8, 151.5, 151.5, 146.9, 143.1, 140.7, 137.2, 135.4, 135.4, 135.2, 134.9, 134.7, 134.7, 134.6, 134.6, 134.3, 134.2, 132.2, 132.2, 131.9, 131.2, 130.9, 130.6, 130.2, 130.2, 129.7, 129.6, 129.6, 129.5, 129.4, 129.1, 129.1, 128.9, 128.7, 127.8, 126.5, 125.1, 125.0, 123.2, 111.9, 105.8, 54.7, 32.0; ^{31}P (121 MHz): 52.55; IR (ATR, cm^{-1}): 3050, 2025, 1676, 1542, 1516, 1493, 1205, 1172, 1152, 1077, 990, 836, 734, 691; HRMS (ESI): m/z, calculated for $M^{+\bullet}$ ($C_{102}H_{78}O_3P_4{}^{102}Ru$): 1576.3940, found: 1576.3950



Spectrum 20: ^{1}H NMR spectrum of compound **3** (300 MHz, CD_2Cl_2)

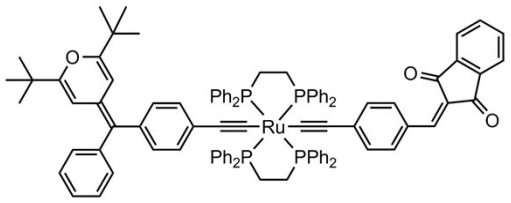


Spectrum 21: ^{13}C NMR spectrum of compound **3** (75 MHz, CD_2Cl_2)

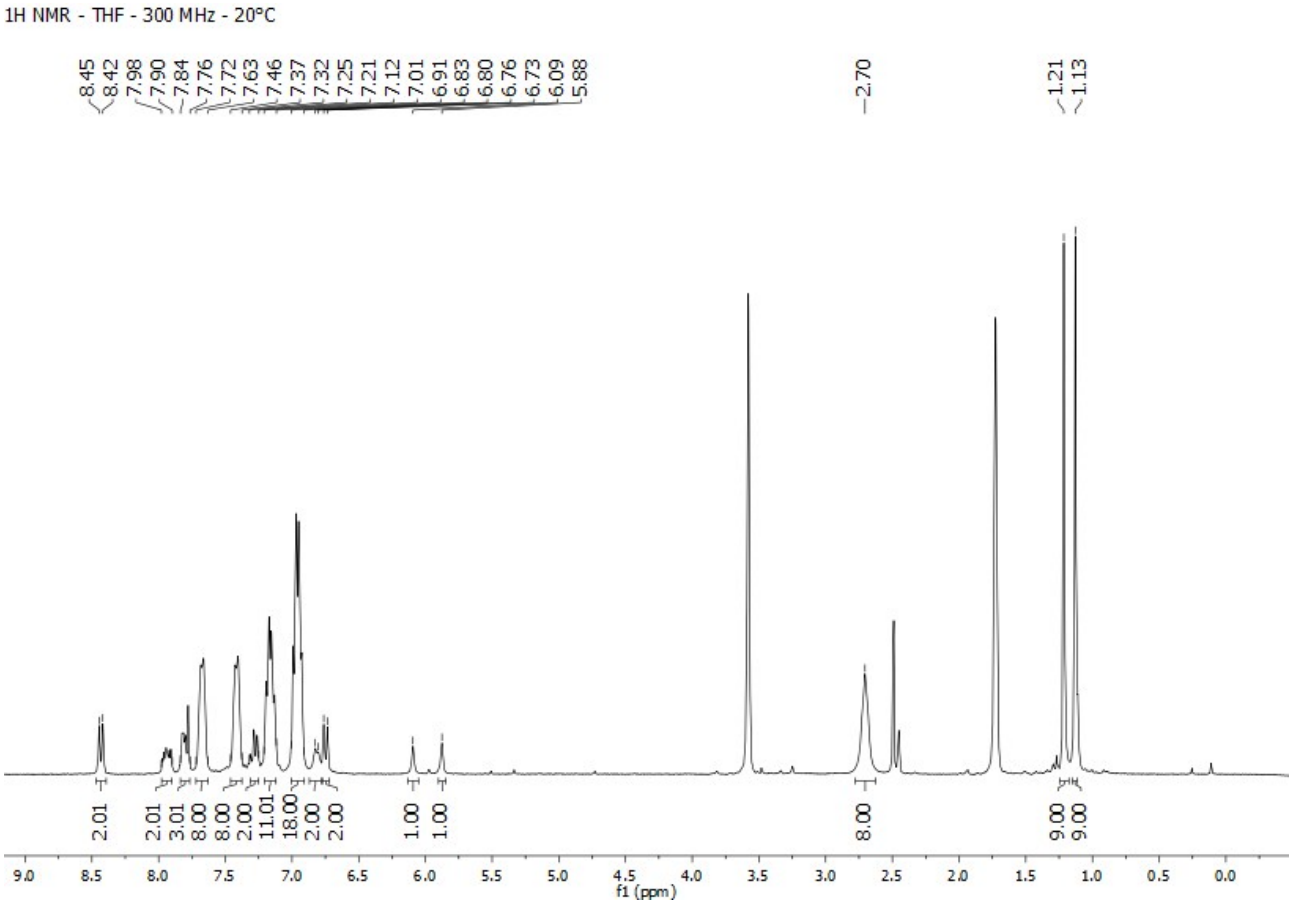


Spectrum 22: ^{31}P NMR spectrum of compound **3** (121 MHz, CD_2Cl_2)

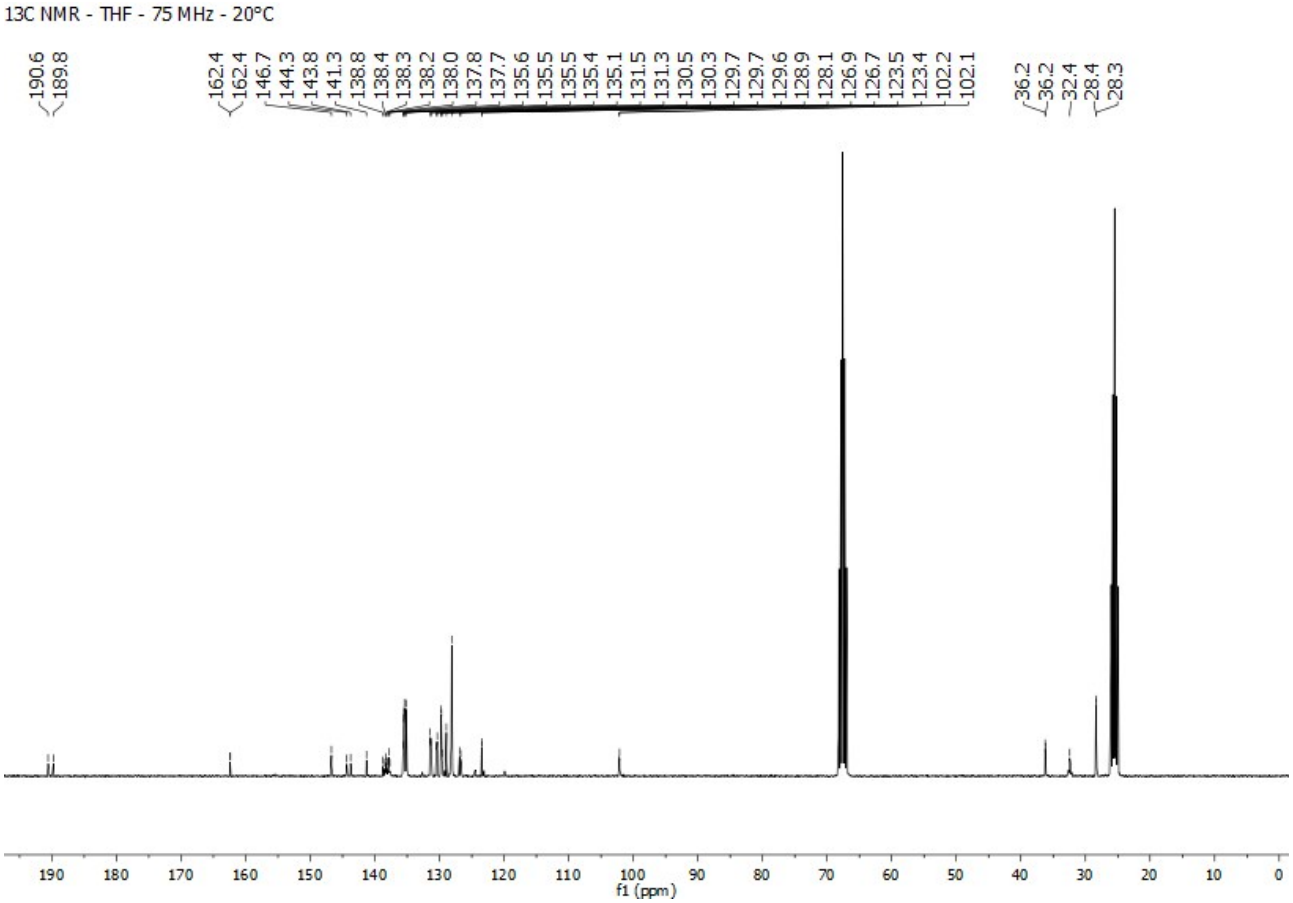
Compound 4



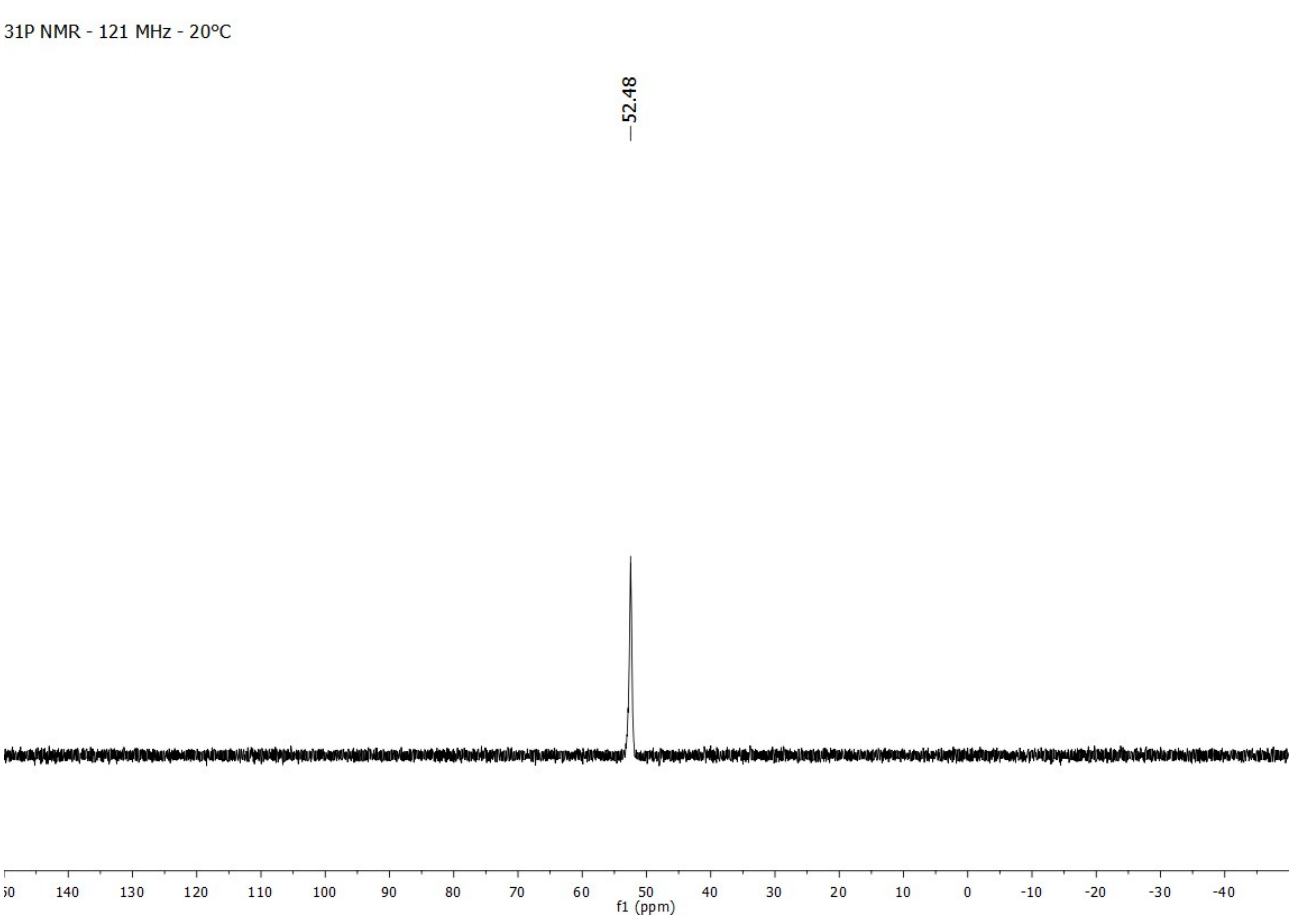
Black solid. Yield: 341 mg, 70%. T_{dec}: 145°C; NMR (δ (ppm), THF-d_8): ^{1}H (300 MHz): 8.43 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.98 – 7.90 (m, 2H), 7.84 – 7.76 (m, 3H), 7.72 – 7.63 (m, 8H), 7.46 – 7.37 (m, 8H), 7.32 – 7.24 (m, 2H), 7.21 – 7.11 (m, 11H), 7.01 – 6.91 (m, 18H), 6.81 (d, $^3J_{HH}$ = 7.1 Hz, 2H), 6.75 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 6.09 (s, 1H), 5.88 (s, 1H), 2.70 (s, 8H), 1.21 (s, 9H), 1.13 (s, 9H); ^{13}C{^{1}H} (75 MHz): 190.6, 189.8, 162.4, 162.4, 146.7, 144.3, 143.8, 141.3, 138.8, 138.4, 138.3, 138.2, 138.0, 137.8, 137.7, 135.6, 135.5, 135.5, 135.4, 135.1, 131.5, 131.3, 130.5, 130.3, 129.7, 129.7, 129.6, 128.9, 128.1, 126.9, 126.7, 123.5, 123.4, 102.2, 102.1, 36.2, 36.2, 32.4, 28.4, 28.3[24]; ^{31}P (121 MHz): 52.48; IR (ATR, cm^{-1}): 3050, 2964, 2029, 1675, 1544, 1520, 1495, 1206, 1172, 1152, 991, 737, 691; HRMS (ESI): m/z, calculated for $M^{+\bullet}$ ($C_{98}H_{86}O_3P_4{}^{102}Ru$): 1536.4566, found: 1536.4577



Spectrum 23: ^{1}H NMR spectrum of compound **4** (300 MHz, *THF-d_8*)

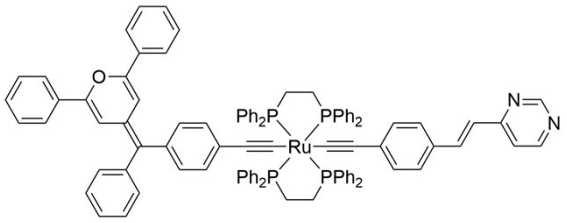


Spectrum 24: ^{13}C NMR spectrum of compound **4** (75 MHz, *THF-d_8*)

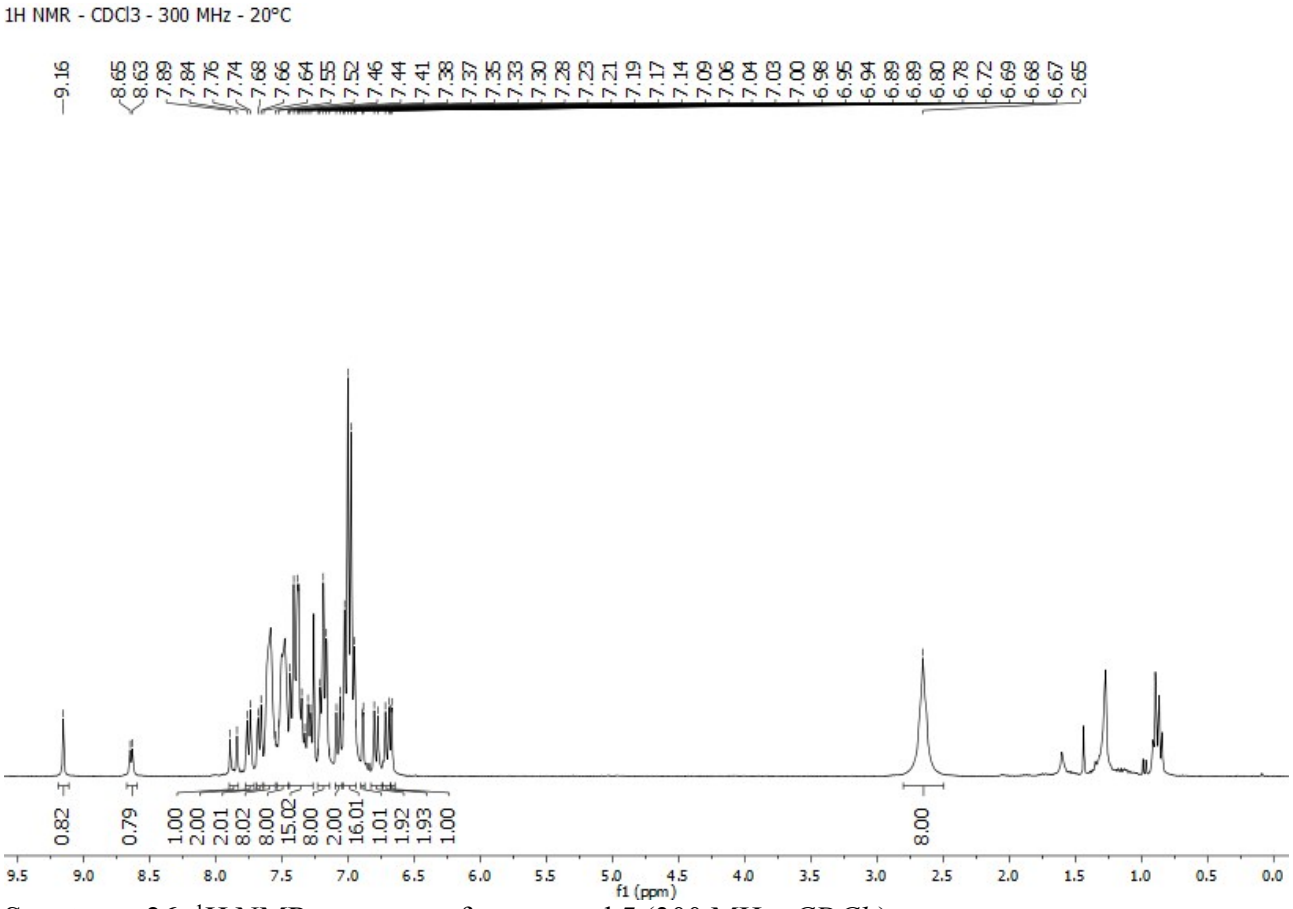


Spectrum 25: ^{31}P NMR spectrum of compound **4** (121 MHz, *THF-d_8*)

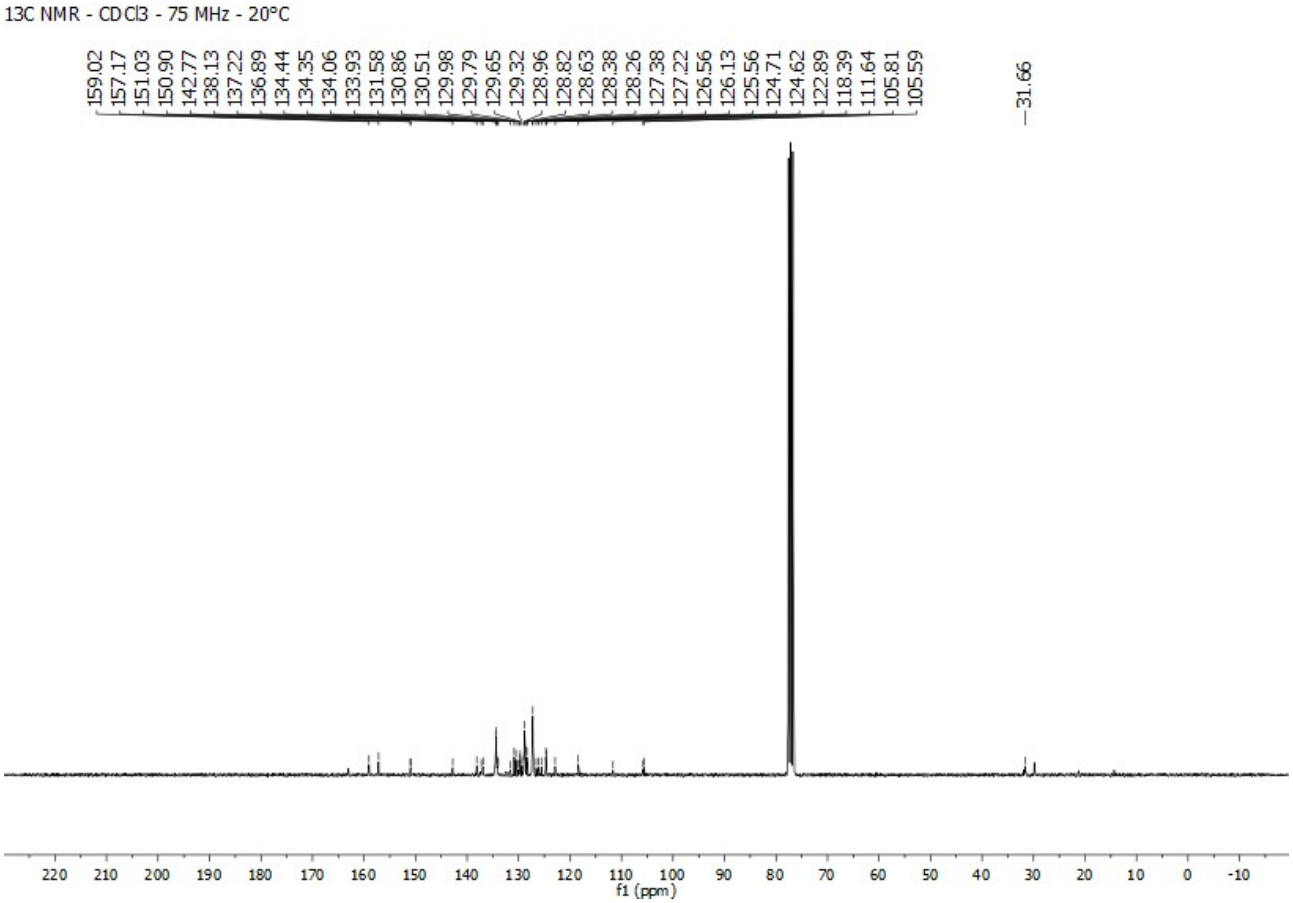
Compound 5



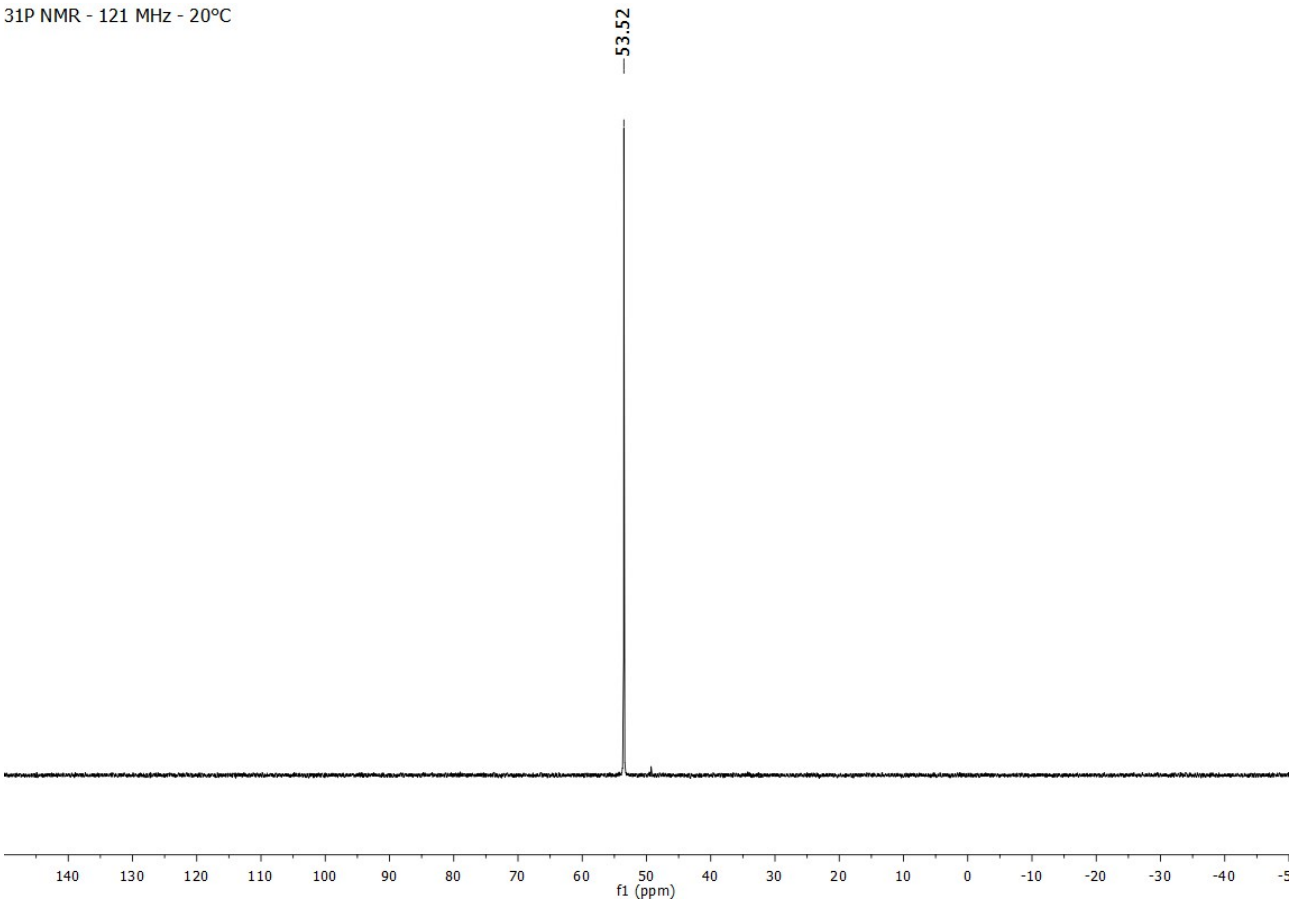
Dark orange solid. Yield: 310 mg, 55%. T_{dec}: 140°C; NMR (δ (ppm), $CDCl_3$): ^{1}H (300 MHz): 9.16 (s, 1H), 8.64 (d, $^3J_{HH}$ = 5.2 Hz, 1H), 7.87 (d, $^3J_{HH}$ = 15.9 Hz, 1H), 7.75 (d, $^3J_{HH}$ = 7.0 Hz, 2H), 7.67 (d, $^3J_{HH}$ = 6.8 Hz, 2H), 7.64 – 7.55 (m, 8H), 7.52 – 7.45 (m, 8H), 7.45 – 7.27 (m, 15H), 7.23 – 7.14 (m, 8H), 7.08 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 7.04 – 6.94 (m, 16H), 6.89 (d, $^4J_{HH}$ = 1.9 Hz, 1H), 6.79 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 6.71 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 6.67 (d, $^4J_{HH}$ = 1.9 Hz, 1H), 2.65 (s, 8H); ^{13}C{^{1}H} (75 MHz): 159.0, 157.2, 151.0, 150.9, 142.8, 138.1, 137.2, 136.9, 134.4, 134.4, 134.1, 133.9, 131.6, 130.9, 130.5, 130.0, 129.8, 129.6, 129.3, 129.0, 128.8, 128.6, 128.4, 128.3, 127.4, 127.2, 126.6, 126.1, 125.6, 124.7, 124.6, 122.9, 118.4, 111.6, 105.8, 105.6, 31.7[24]; ^{31}P (121 MHz): 53.52; IR (ATR, cm^{-1}): 3049, 2914, 2046, 1568, 1432, 1171, 1092, 836, 742, 691; HRMS (ESI): m/z, calculated for $M^{+\bullet}$ ($C_{98}H_{78}N_2OP_4{}^{102}Ru$): 1524.4103, found: 1524.4119



Spectrum 26: ^{1}H NMR spectrum of compound **5** (300 MHz, $CDCl_3$)

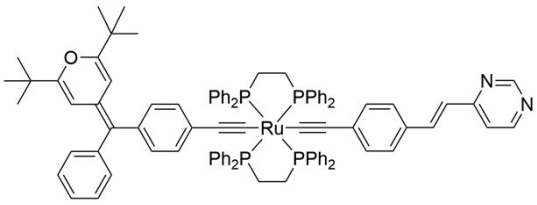


Spectrum 27: ^{13}C NMR spectrum of compound **5** (75 MHz, $CDCl_3$)

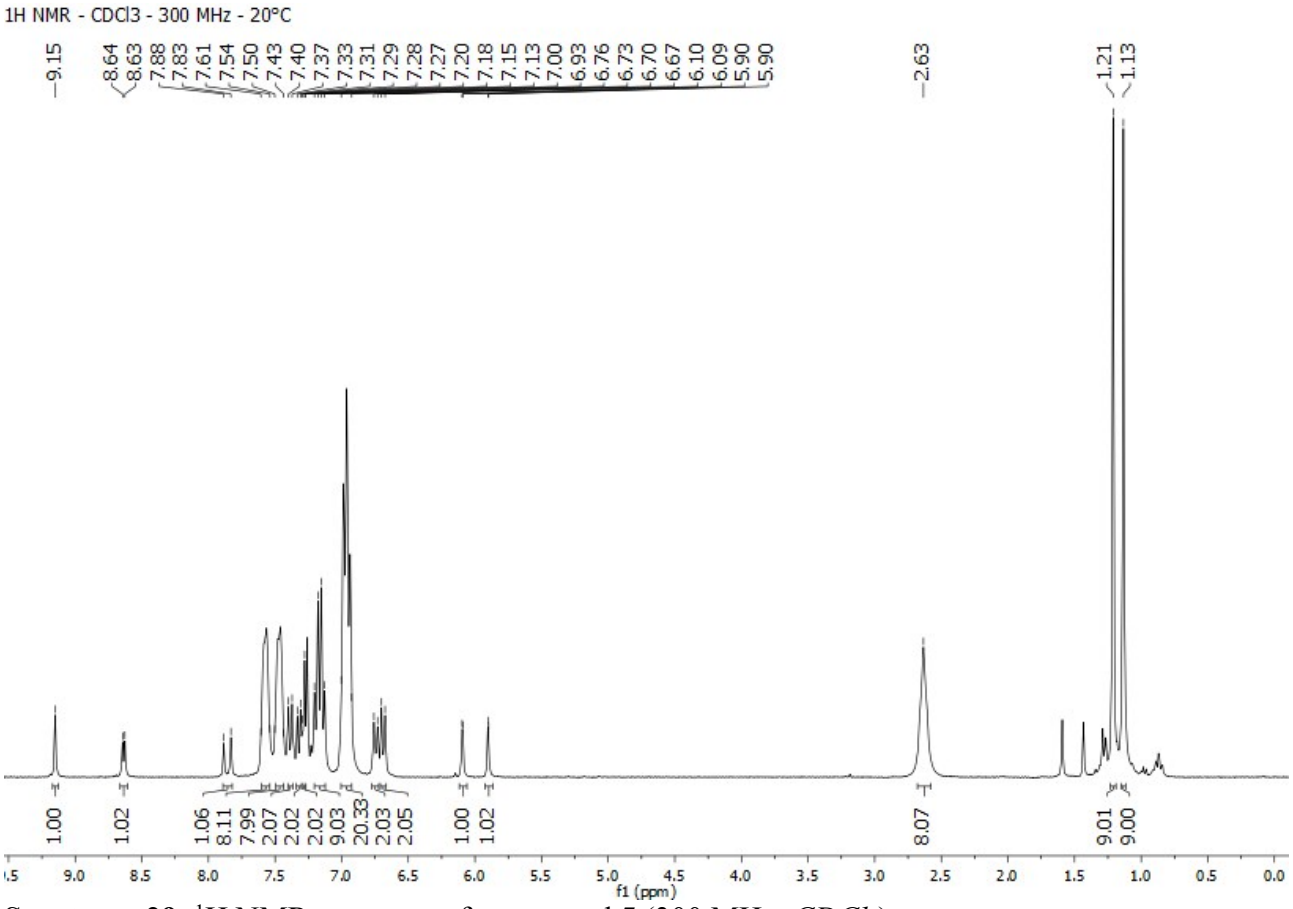


Spectrum 28: ^{31}P NMR spectrum of compound **5** (121 MHz, *$CDCl_3$*)

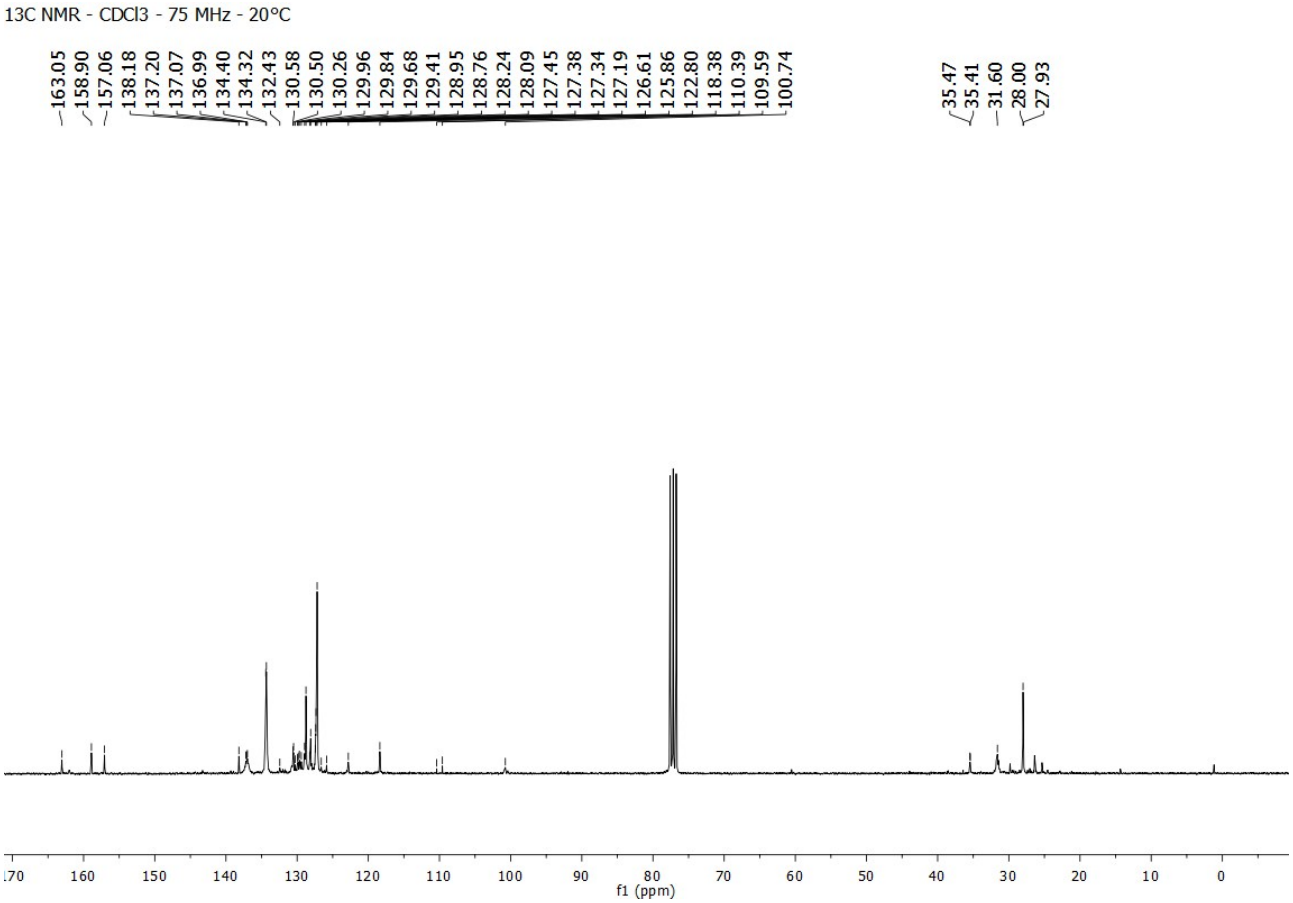
Compound 6



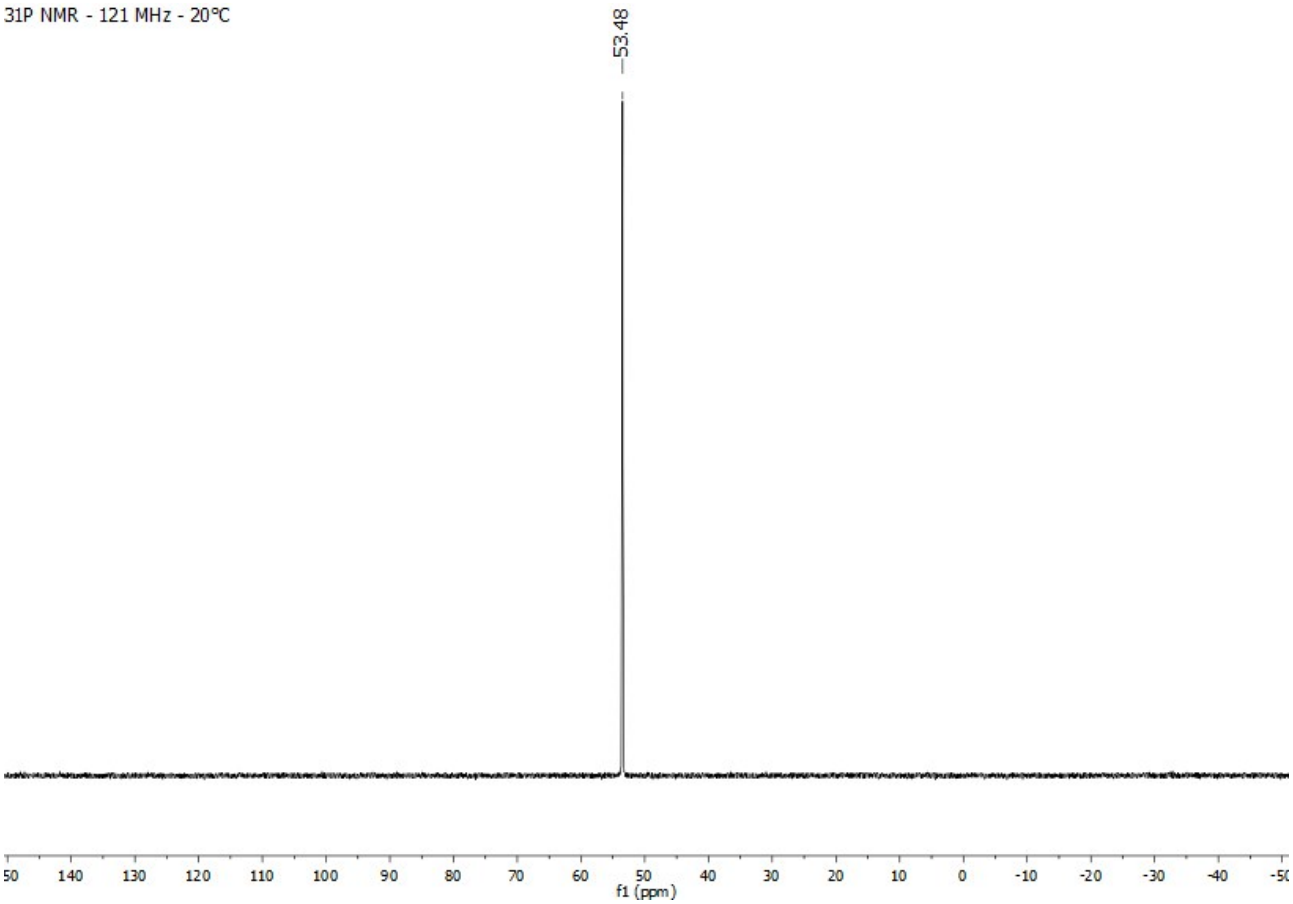
Dark orange solid. Yield: 329 mg, 60%. T_{dec}: 210°C; NMR (δ (ppm), $CDCl_3$): ^{1}H (300 MHz): 9.15 (s, 1H), 8.64 (d, $^{3}J_{HH}$ = 5.3 Hz, 1H), 7.86 (d, $^{3}J_{HH}$ = 16.0 Hz, 1H), 7.61 – 7.53 (m, 8H), 7.50 – 7.43 (m, 8H), 7.39 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 7.32 (d, $^{3}J_{HH}$ = 7.3 Hz, 2H), 7.30 – 7.27 (m, 2H), 7.22 – 7.12 (m, 9H), 7.01 – 6.92 (m, 20H), 6.74 (d, $^{3}J_{HH}$ = 8.1 Hz, 2H), 6.69 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 6.09 (d, $^{4}J_{HH}$ = 1.6 Hz, 1H), 5.90 (d, 4JHH = 1.7 Hz, 1H), 2.63 (s, 8H), 1.21 (s, 9H), 1.13 (s, 9H); $^{13}C\{^{1}H\}$ (75 MHz): 163.0, 158.9, 157.1, 138.2, 137.2, 137.1, 137.0, 134.4, 134.3, 132.4, 130.6, 130.5, 130.3, 130.0, 129.8, 129.7, 129.4, 129.0, 128.8, 128.2, 128.1, 127.4, 127.4, 127.3, 127.2, 126.6, 125.9, 122.8, 118.4, 110.4, 109.6, 100.7, 35.5, 35.4, 31.6, 28.0, 27.9; ^{31}P (121 MHz): 53.48; IR (ATR, cm^{-1}): 3051, 2960, 2924, 2045, 1653, 1629, 1589, 1569, 1433, 1171, 1095, 834, 741, 692; HRMS (ESI): m/z, calculated for $M^{+\bullet}$ ($C_{94}H_{86}N_2OP_4{}^{102}Ru$): 1484.4729, found: 1484.4745



Spectrum 29: ^{1}H NMR spectrum of compound **5** (300 MHz, $CDCl_3$)



Spectrum 30: ^{13}C NMR spectrum of compound **5** (75 MHz, $CDCl_3$)

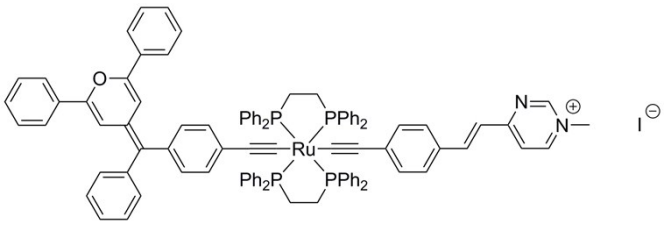


Spectrum 31: ^{31}P NMR spectrum of compound **5** (121 MHz, $CDCl_3$)

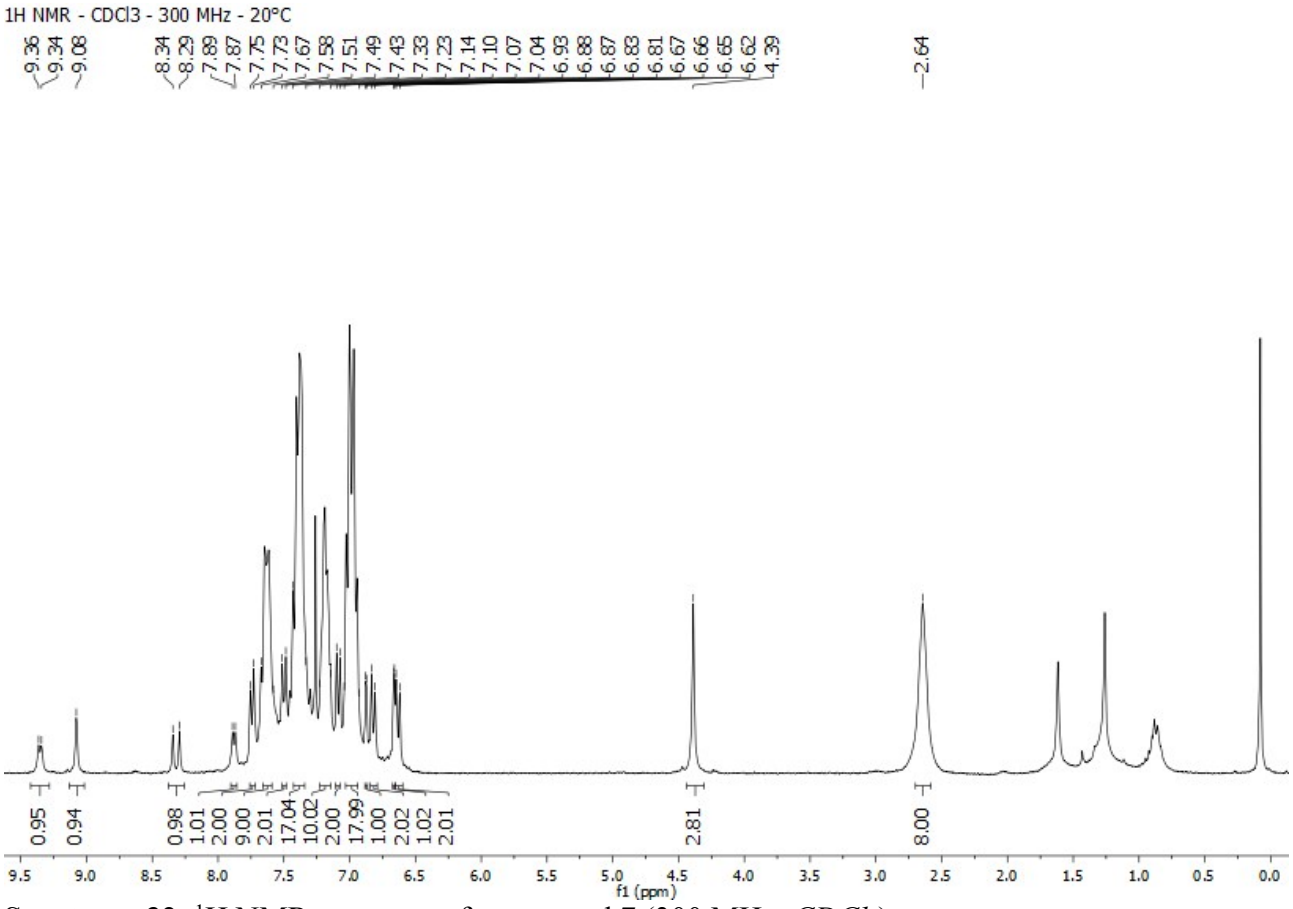
Syntheses of 7 and 8

General procedure. A mixture of pyrimidine complex derivative (0.1 mmol) and methyl iodide (5 mL) was refluxed for 20h. The methyl iodide was evaporated under vacuum. The compound was analysed without further purification.

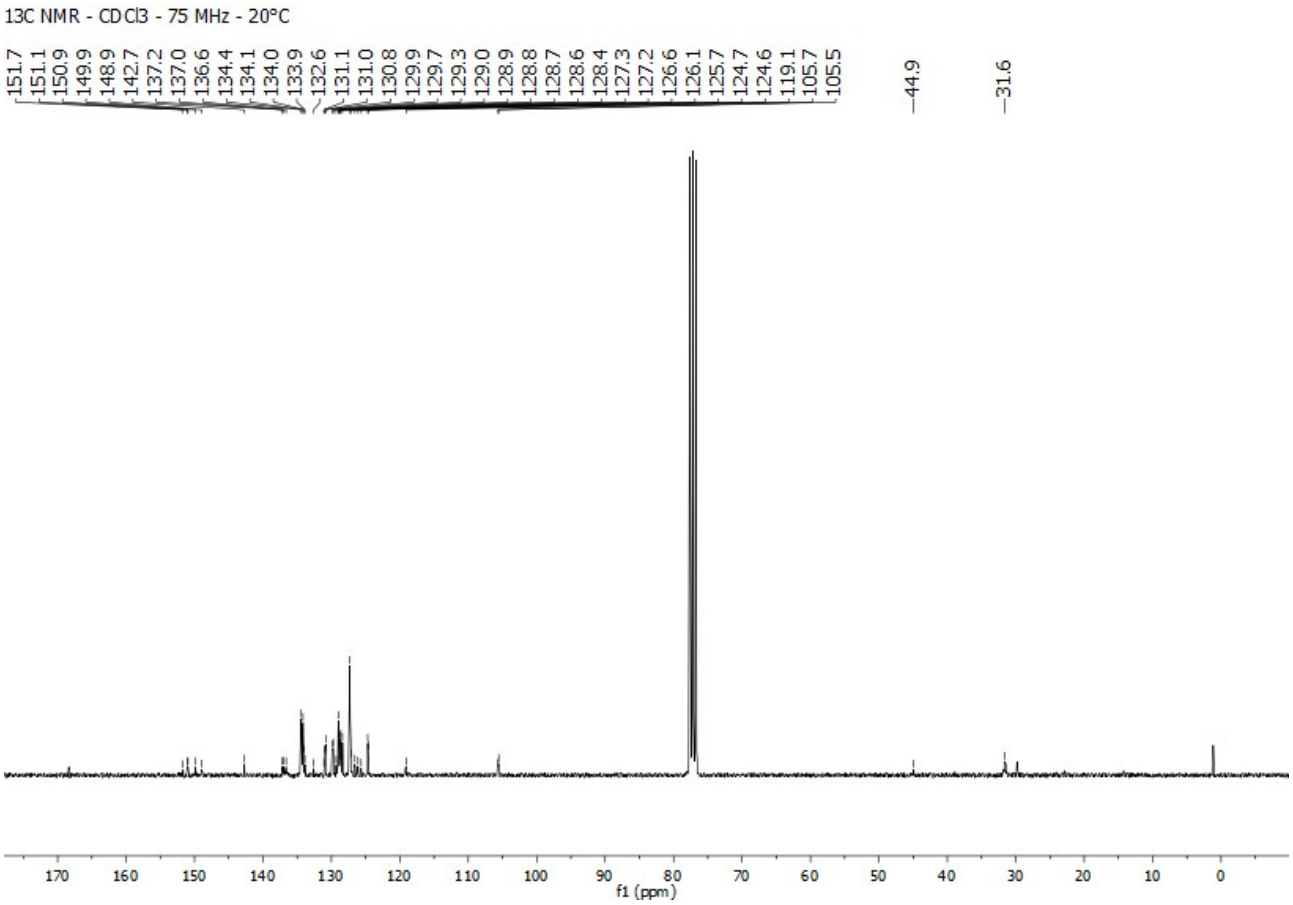
Compound 7



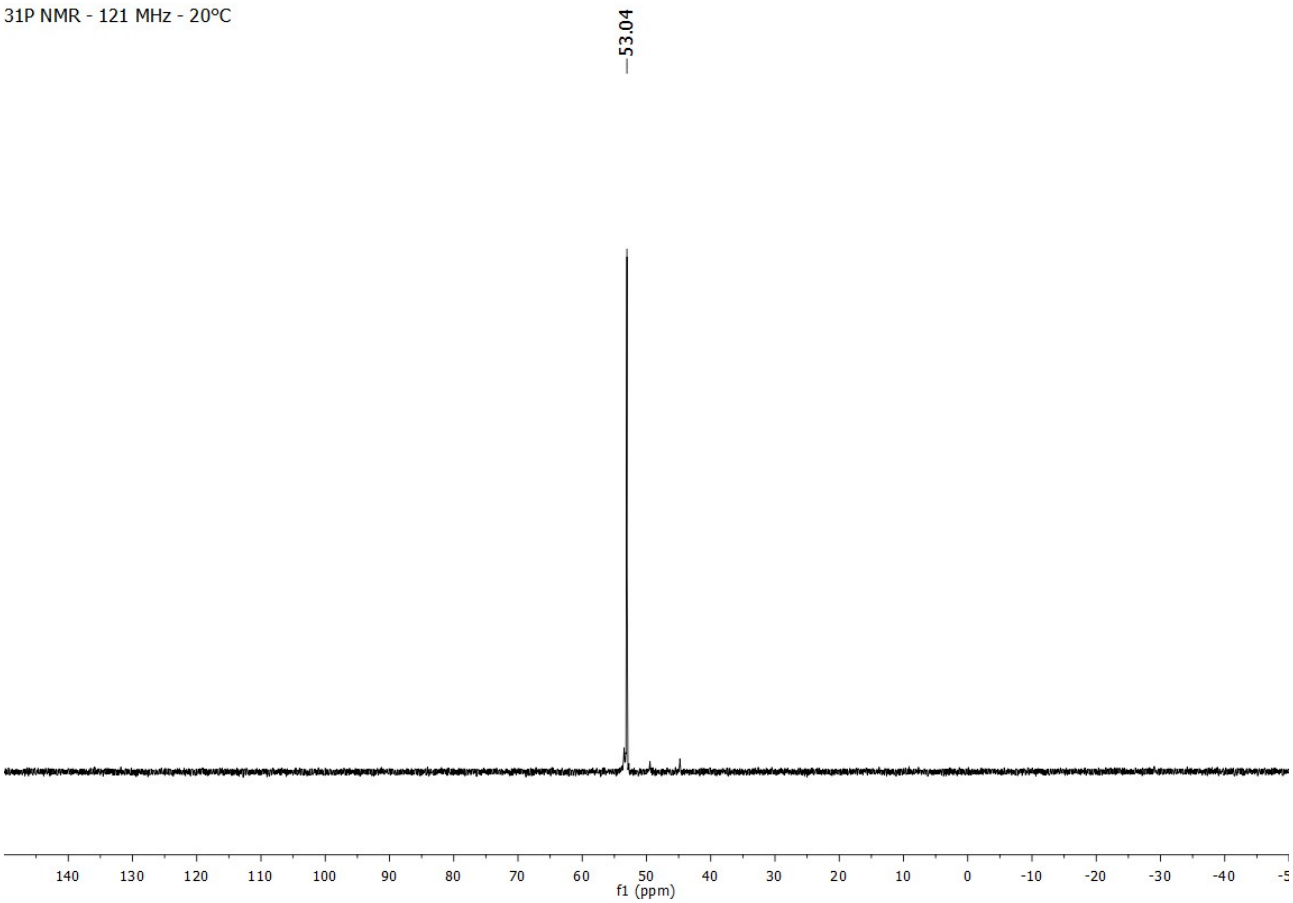
Dark red solid. Yield: 104 mg, 95%. T_{dec}: 200°C; NMR (δ (ppm), $CDCl_3$): ^1H (300 MHz): 9.35 (d, $^3J_{HH}$ = 6.8 Hz, 1H), 9.08 (s, 1H), 8.32 (d, $^3J_{HH}$ = 15.3 Hz, 1H), 7.88 (d, $^3J_{HH}$ = 6.7 Hz, 1H), 7.74 (d, $^3J_{HH}$ = 7.0 Hz, 2H), 7.68 – 7.58 (m, 9H), 7.50 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.43 – 7.33 (m, 17H), 7.23 – 7.13 (m, 10H), 7.09 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 7.04 – 6.92 (m, 18H), 6.88 (d, $^4J_{HH}$ = 1.6 Hz, 1H), 6.82 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 6.66 (d, $^4J_{HH}$ = 1.8 Hz, 1H), 6.63 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 4.39 (s, 3H), 2.64 (s, 8H); $^{13}C\{^1H\}$ (75 MHz): 151.7, 151.1, 150.9, 149.9, 148.9, 142.7, 137.2, 137.0, 136.6, 134.4, 134.1, 134.0, 133.9, 132.6, 131.1, 131.0, 130.8, 129.9, 129.7, 129.3, 129.0, 128.9, 128.8, 128.7, 128.6, 128.4, 127.3, 127.2, 126.6, 126.1, 125.7, 124.7, 124.6, 119.1, 105.7, 105.5, 44.9, 31.6[24]; ^{31}P (121 MHz): 53.04; IR (ATR, cm^{-1}): 3050, 2921, 2035, 1560, 1465, 1432, 1194, 1162, 1093, 1067, 1027, 741, 691; HRMS (ESI): m/z, calculated for M^+ ($C_{99}H_{81}N_2OP_4{}^{102}Ru$): 1539.4337, found: 1539.4354



Spectrum 32: ^{1}H NMR spectrum of compound **7** (300 MHz, $CDCl_3$)

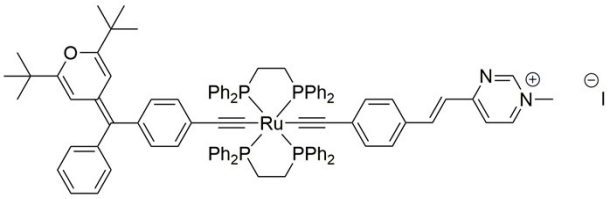


Spectrum 33 ^{13}C NMR spectrum of compound **7** (75 MHz, $CDCl_3$)

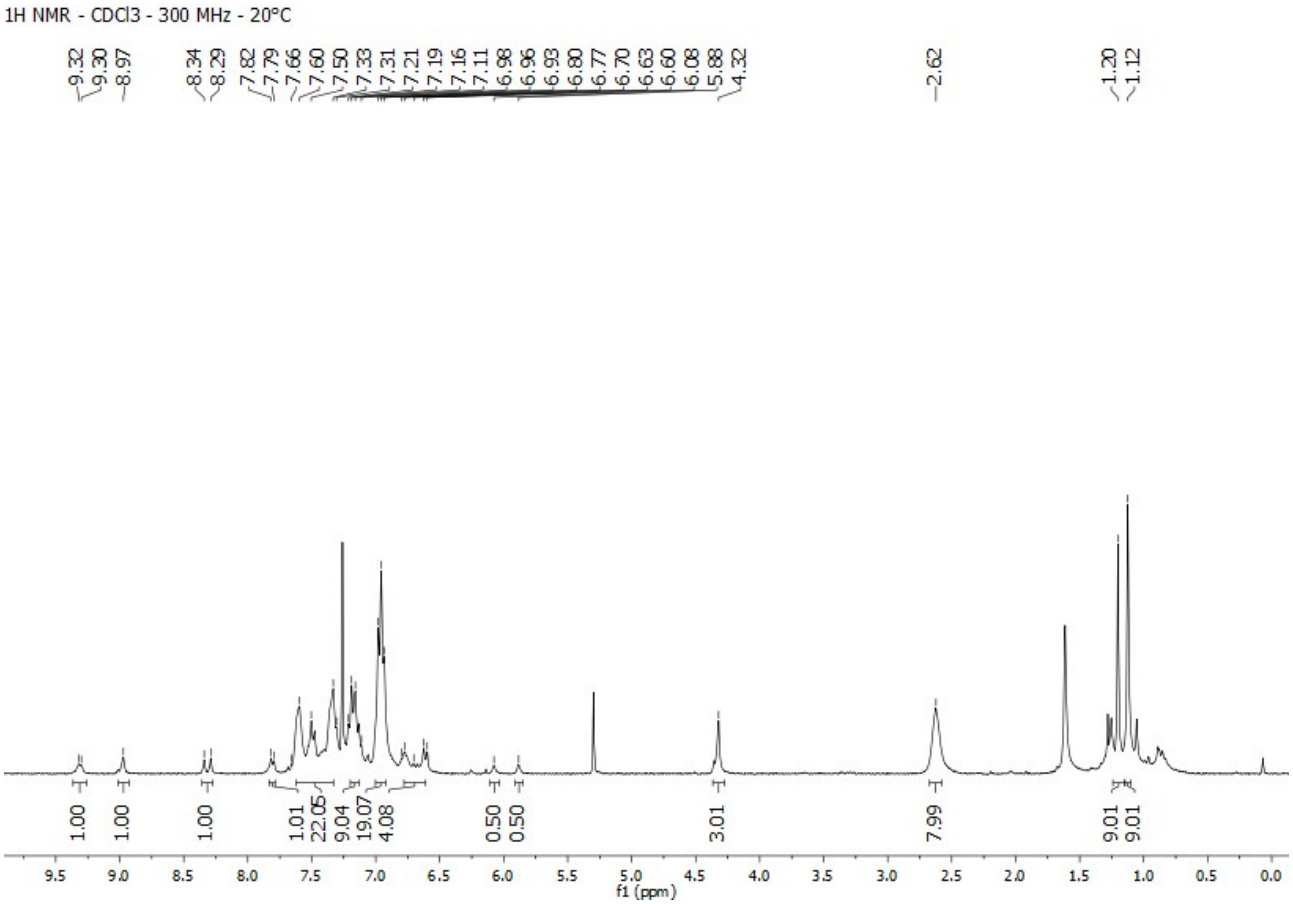


Spectrum 34: ^{31}P NMR spectrum of compound **7** (121 MHz, *$CDCl_3$*)

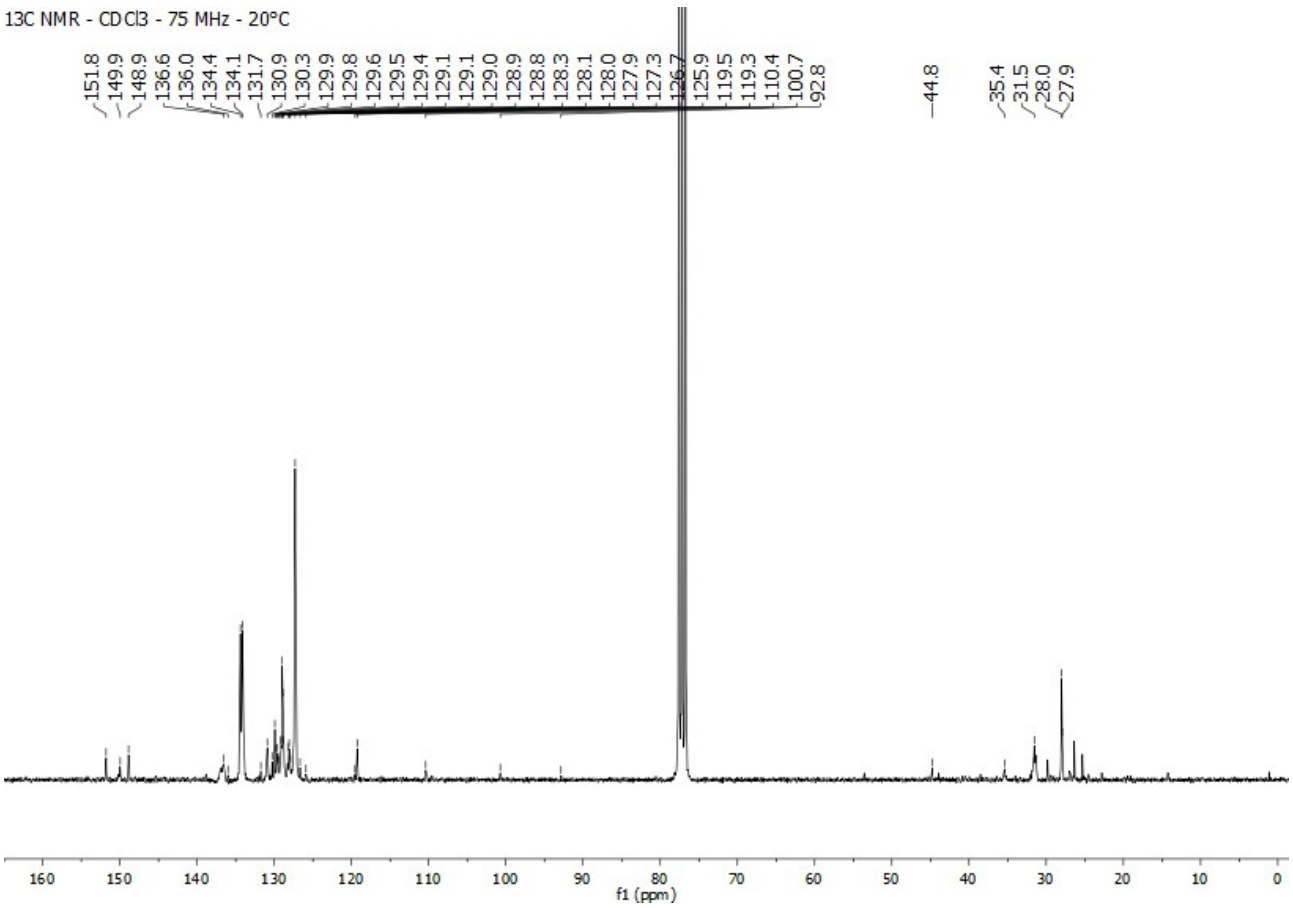
Compound 8



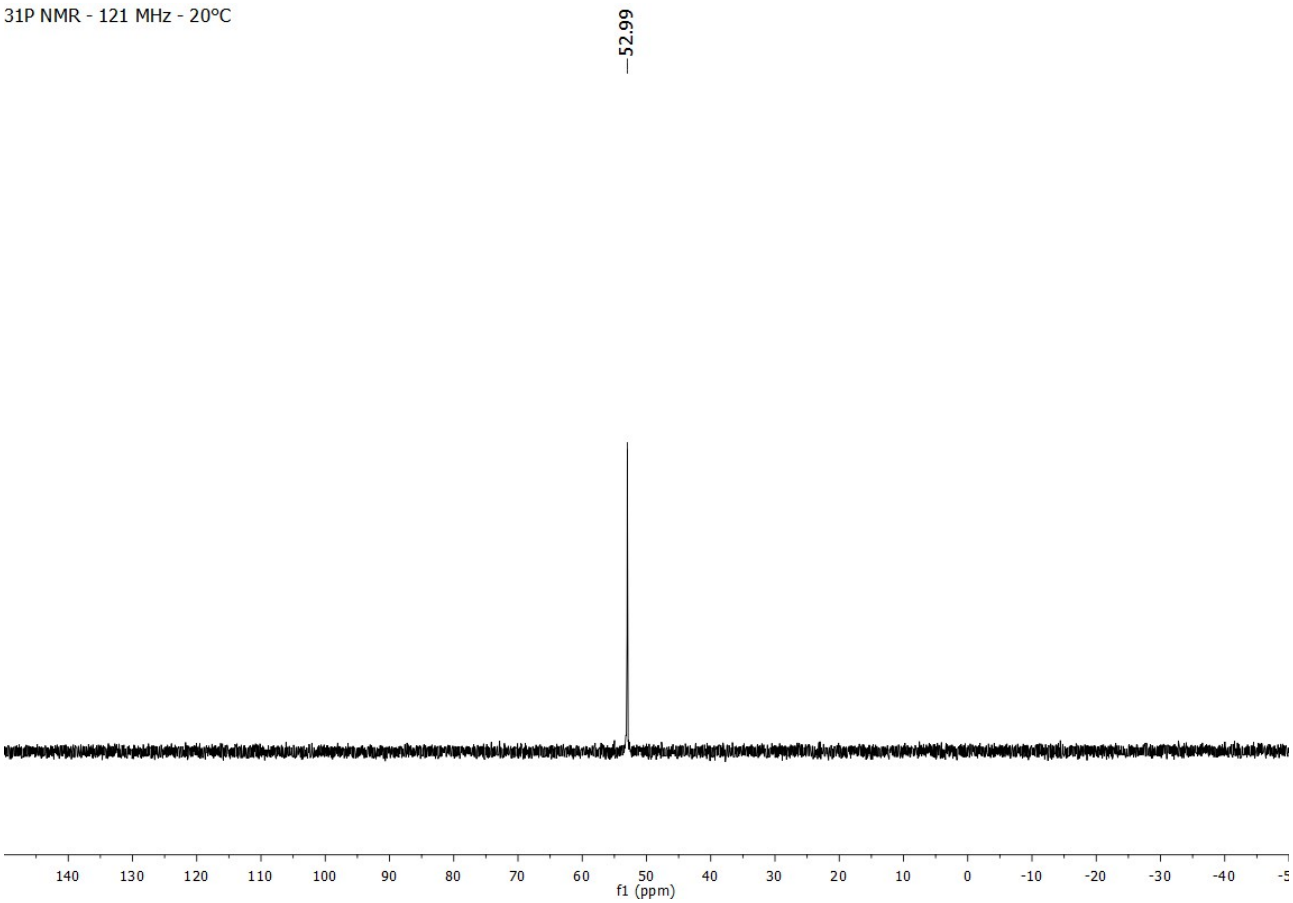
Dark red solid. Yield: 105 mg, 96%. T_{dec}: 260°C; NMR (δ (ppm), $CDCl_3$): ^1H (300 MHz): 9.31 (d, $^3J_{HH}$ = 6.2 Hz, 1H), 8.97 (s, 1H), 8.31 (d, $^3J_{HH}$ = 15.3 Hz, 1H), 7.81 (d, $^3J_{HH}$ = 7.1 Hz, 1H), 7.67 – 7.28 (m, 22H), 7.23 – 7.10 (m, 9H), 7.01 – 6.90 (m, 19H), 6.81 – 6.58 (m, 4H), 6.08 (s, 1H), 5.88 (s,1H), 4.32 (s, 3H), 2.62 (s, 8H), 1.20 (s, 9H), 1.12 (s, 9H); $^{13}C\{^1H\}$ (75 MHz): 151.8, 149.9, 148.9, 136.6, 136.0, 134.4, 134.1, 131.7, 130.9, 130.3, 129.9, 129.8, 129.6, 129.5, 129.4, 129.1, 129.1, 129.0, 128.9, 128.8, 128.3, 128.1, 128.0, 127.9, 127.3, 126.7, 125.9, 119.5, 119.3, 110.4, 100.7, 92.8, 44.8, 35.4, 31.5, 28.0, 27.9[24]; ^{31}P (121 MHz): 52.99; IR (ATR, cm^{-1}): 3050, 2962, 2036, 1608, 1562, 1465, 1432, 1195, 1162, 1095, 838, 741, 691; HRMS (ESI): m/z, calculated for M^+ ($C_{95}H_{89}N_2OP_4{}^{102}Ru$): 1499.4963, found: 1499.4977



Spectrum 35: ^{1}H NMR spectrum of compound **8** (300 MHz, $CDCl_3$)



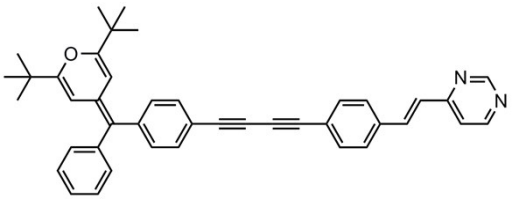
Spectrum 36: ^{13}C NMR spectrum of compound **8** (75 MHz, $CDCl_3$)



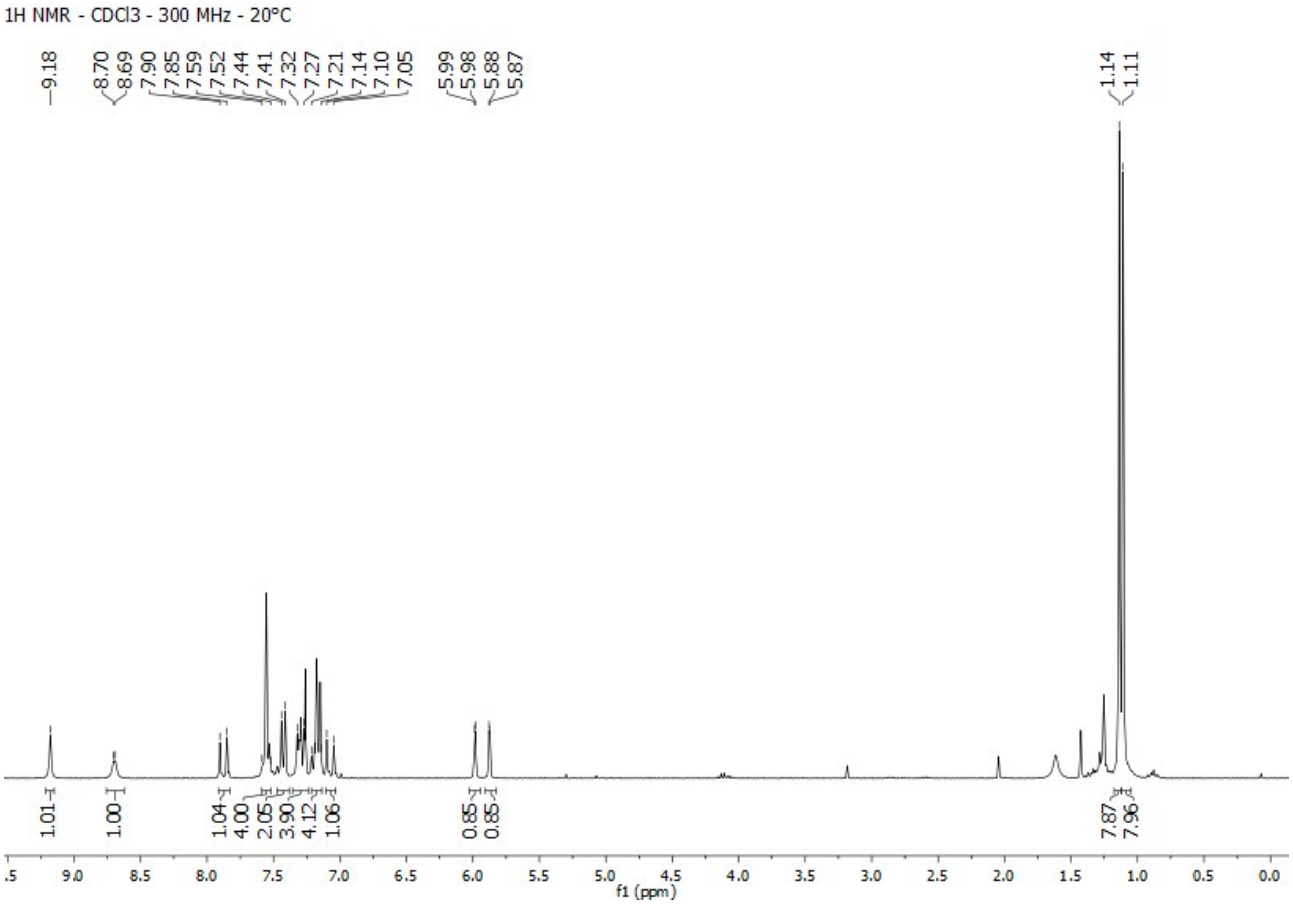
Spectrum 37: ^{31}P NMR spectrum of compound **8** (121 MHz, $CDCl_3$)

Syntheses of complexes 12 and 13

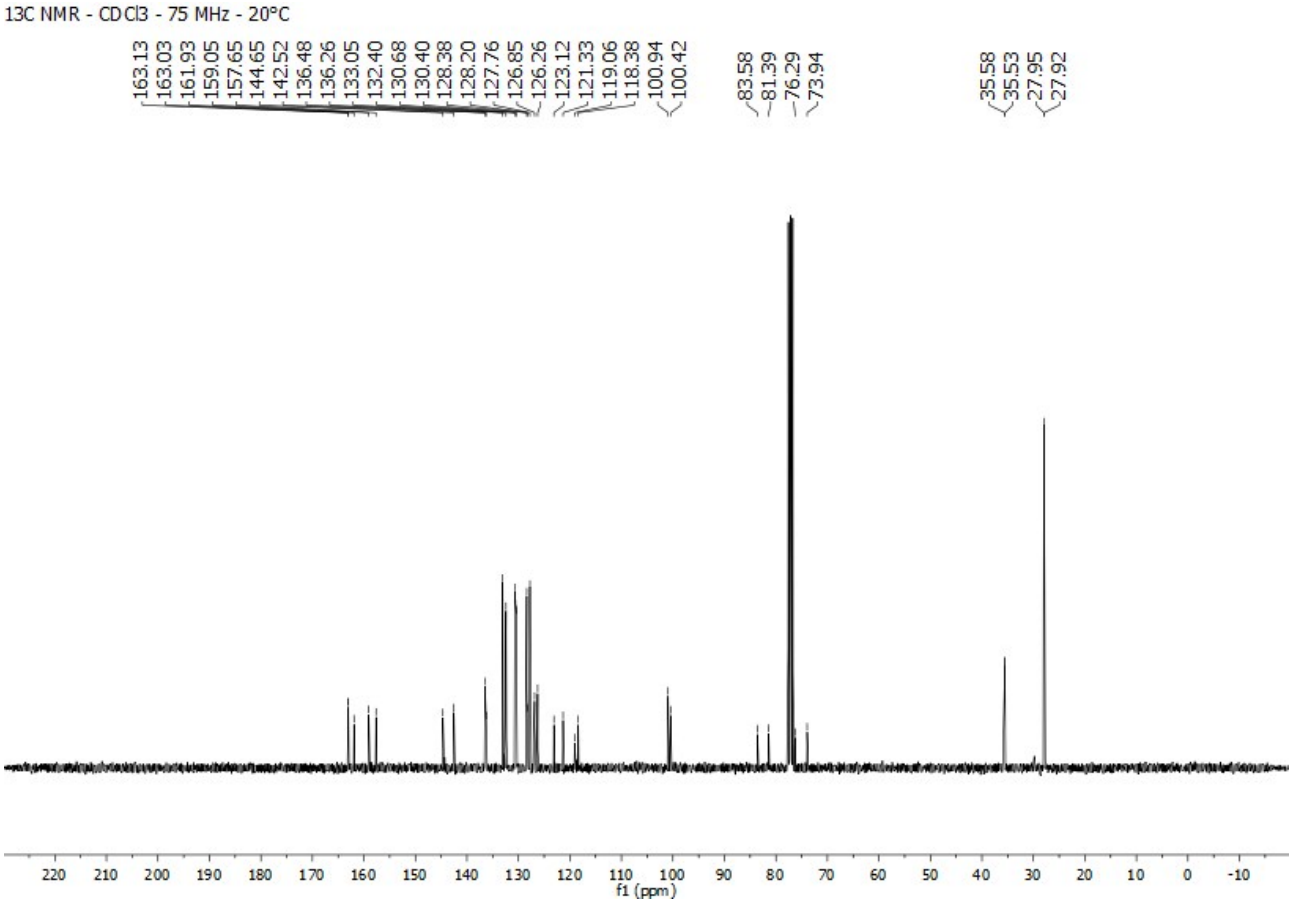
Compound 12



A Schlenk flask, charged with 4-((4-ethynylphenyl)(phenyl)methylene)-2,6-di-*tert*-butyl-4*H*-pyran (**10**)[2] (145 mg, 379 µmol, 1.1 eq), copper iodide CuI (20 mg, 105 µmol, 0.3 eq) and 4-[(*E*)-2-(4-bromoethynylphenyl)ethenyl]-pyrimidine[4] (108 mg, 379 µmol, 1 eq) were degassed and back-filled with nitrogen several times. Then dry dichloromethane (10 mL) and triethylamine NEt_3 (0.1 mL, 73 mg, 714 µmol, 1.9 eq) were introduced into the reaction flask. The reaction mixture was stirred under nitrogen protection at room temperature overnight. The reaction was quenched with water (50 mL) and the aqueous phase was extracted with dichloromethane (2×50 mL). The organic phases were combined and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate) to give compound **12** as a yellow powder in 31% yield (69 mg, 118 µmol). T_{dec}: 135°C; NMR (δ (ppm), $CDCl_3$): ^{1}H (300 MHz): 9.18 (s, 1H), 8.70 (d, $^3J_{HH}$ = 4.4 Hz, 1H), 7.88 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 7.59 – 7.52 (m, 4H), 7.43 (m, 2H), 7.34 – 7.24 (m, 4H), 7.23 – 7.13 (m, 4H), 7.07 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 5.98 (d, $^4J_{HH}$ = 1.9 Hz, 1H), 5.88 (d, $^4J_{HH}$ = 1.9 Hz, 1H), 1.14 (s, 9H), 1.11 (s, 9H); ^{13}C{^{1}H} (75 MHz): 163.1, 163.0, 161.9, 159.0, 157.7, 144.7, 142.5, 136.5, 136.3, 133.0, 132.4, 130.7, 130.4, 128.4, 128.2, 127.8, 126.9, 126.3, 123.1, 121.3, 119.1, 118.4, 100.9, 100.4, 83.6, 81.4, 76.3, 73.9, 35.6, 35.5, 28.0, 27.9; IR (ATR, cm^{-1}): 2968, 2211, 1673, 1571, 1462, 1387, 1105, 980, 927, 839, 823, 697; HRMS (ESI): m/z, calculated for $[M+H]^+$ ($C_{42}H_{39}N_2O$): 587.3057, found: 587.3060

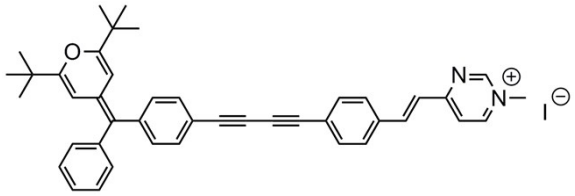


Spectrum 38 [1]H NMR spectrum of compound **12** (300 MHz, *$CDCl_3$*)

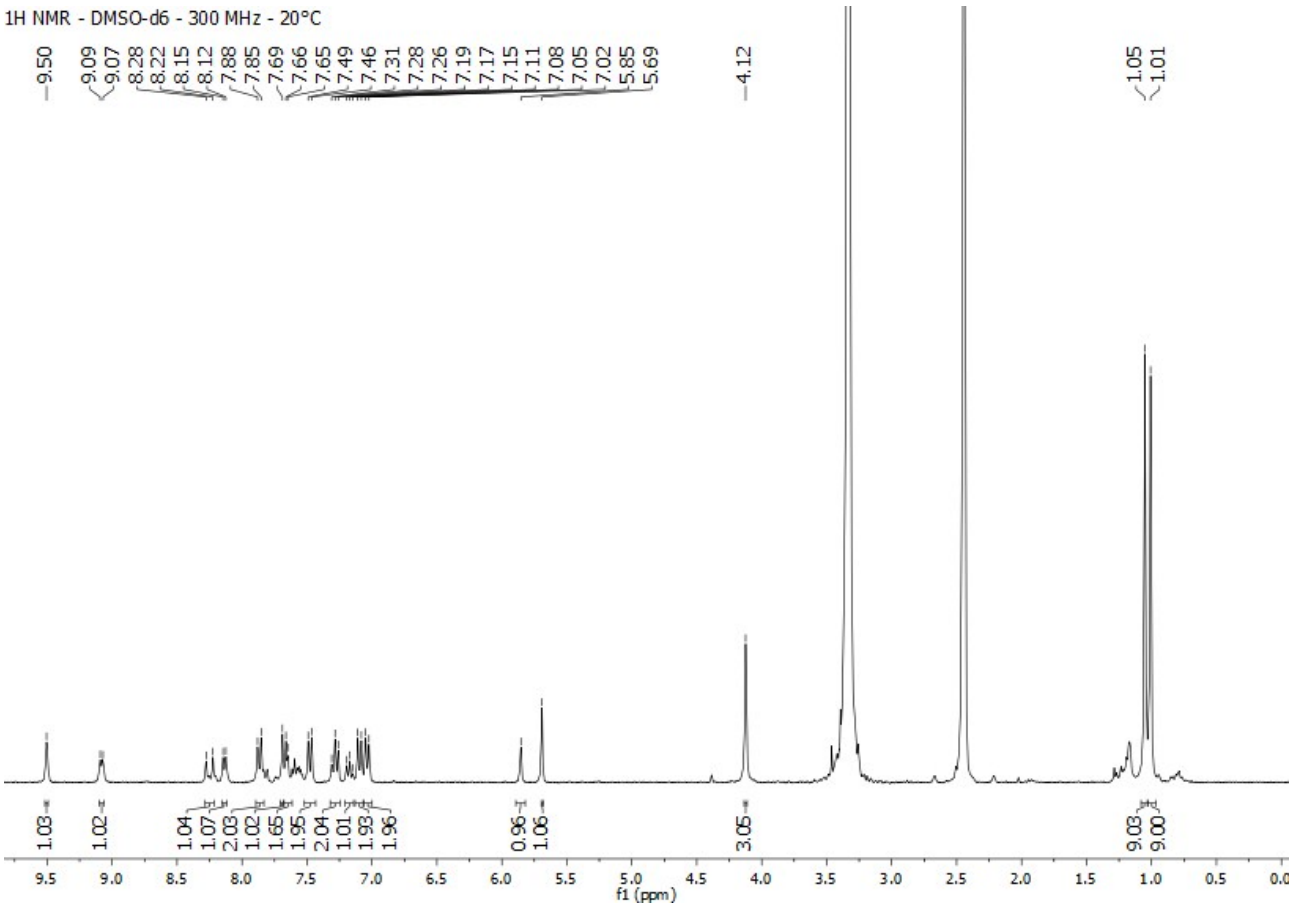


Spectrum 39: [13]C NMR spectrum of compound **12** (75 MHz, *$CDCl_3$*)

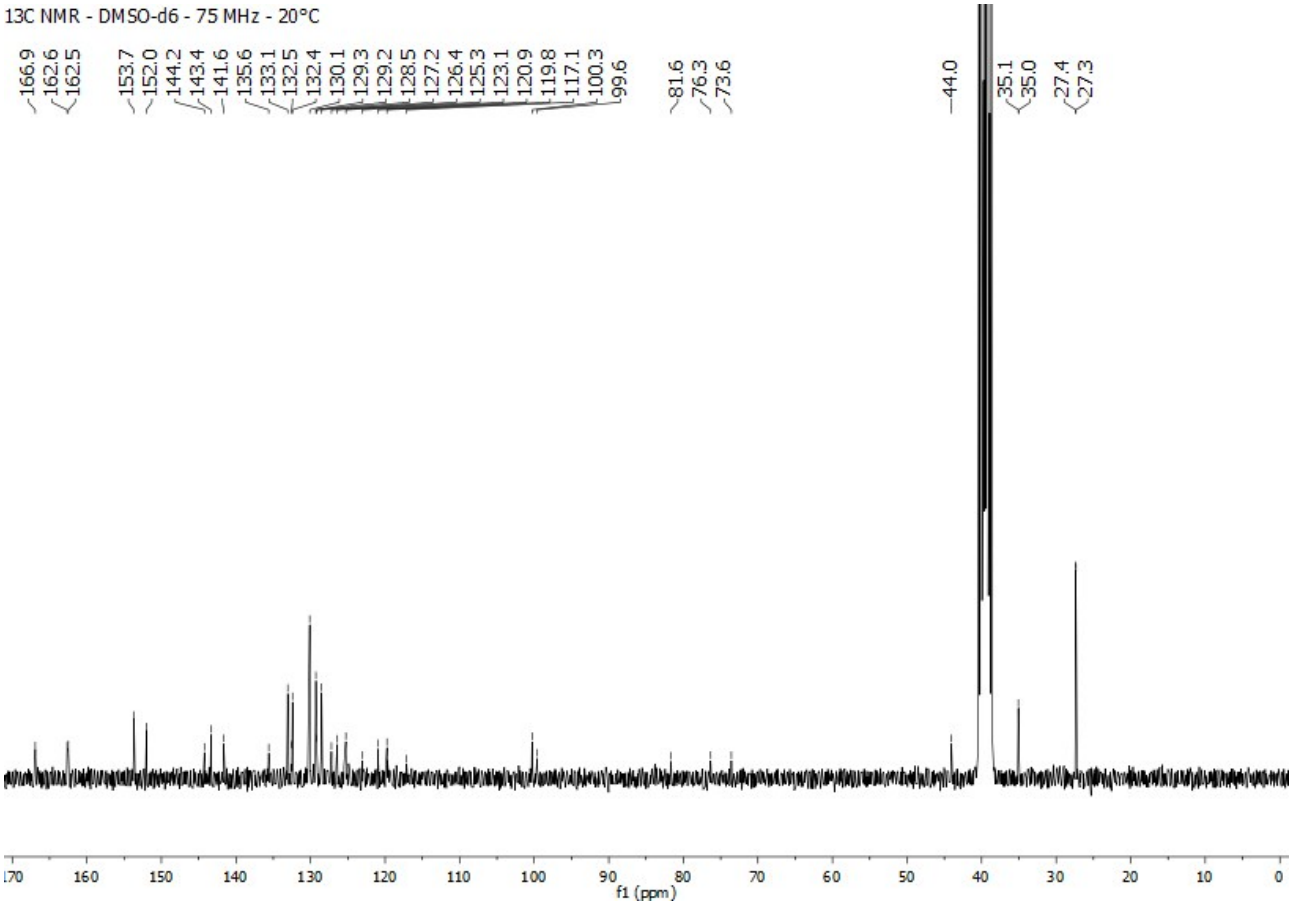
Compound 13



A mixture of compound **12** (40 mg, 68 µmol) and methyl iodide (5 mL) was refluxed for 22h. The methyl iodide was evaporated under vacuum. The compound **13** obtained as a red solid in 90% yield (45 mg, 62 µmol) was analysed without further purification. T_{dec}: 155°C; NMR (δ (ppm), DMSO-d_6): ^{1}H (300 MHz): 9.50 (s, 1H), 9.08 (d, $^3J_{HH}$ = 7.0 Hz, 1H), 8.25 (d, $^3J_{HH}$ = 15.8 Hz, 1H), 8.14 (d, $^3J_{HH}$ = 6.7 Hz, 1H), 7.87 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.69 (s, 1H), 7.66 (d, $^3J_{HH}$ = 3.9 Hz, 2H), 7.48 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 7.28 (t, J = 7.6 Hz, 2H), 7.17 (t, J = 6.9 Hz, 1H), 7.10 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.04 (d, $^3J_{HH}$ = 7.7 Hz, 2H), 5.86 (s, 1H), 5.69 (s, 1H), 4.12 (s, 3H), 1.05 (s, 9H), 1.01 (s, 9H); ^{13}C{^{1}H} (75 MHz): 166.9, 162.6, 162.5, 153.7, 152.0, 144.2, 143.4, 141.6, 135.6, 133.1, 132.5, 132.4, 130.1, 129.3, 129.2, 128.5, 127.2, 126.4, 125.3, 123.1, 120.9, 119.8, 117.1, 100.3, 99.6, 81.6, 76.3, 73.6, 44.0, 35.1, 35.0, 27.4, 27.3[25]; IR (ATR, cm^{-1}): 3407, 2963, 2927, 2869, 2205, 1669, 1610, 1590, 1477, 1177, 1105, 927, 840, 825, 701; HRMS (ESI): m/z, calculated for C^+ ($C_{43}H_{41}N_2O$): 601.3213, found: 601.3220



Spectrum 40: ^{1}H NMR spectrum of compound **13** (300 MHz, *DMSO-d_6*)



Spectrum 41: ^{13}C NMR spectrum of compound **13** (75 MHz, *DMSO-d_6*) [25]

Spectroelectrochemistry data

Compound 8

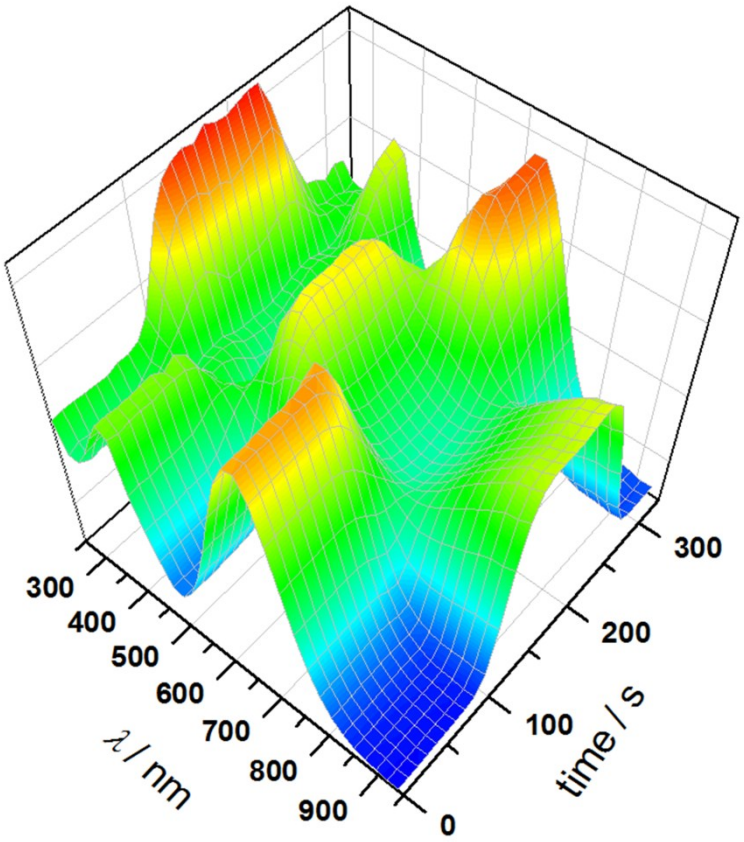


Figure S1. UV-Vis monitoring of the oxidation of compound **8** (ca. 1 mM) in CH_2Cl_2/NBu_4PF_6 0.1 M by cyclic potential sweeping under thin-layer conditions (optical path: 200 μm).

Compound 12

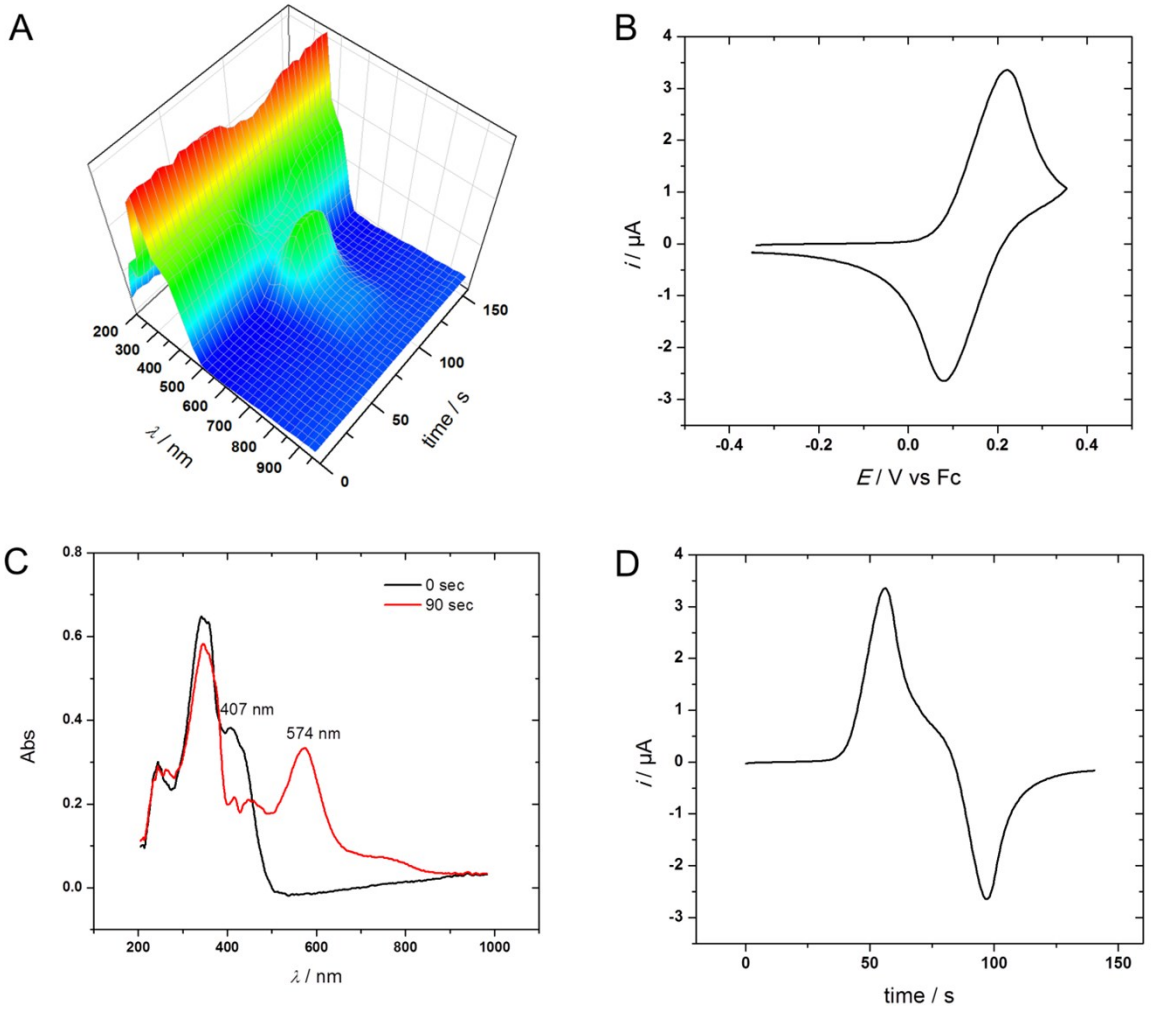


Figure S2. A) UV-Vis monitoring of the oxidation of compound **12** (ca. 1 mM) in CH_2Cl_2/NBu_4PF_6 0.1 M by cyclic potential sweeping under thin-layer conditions (optical path: 200 µm); B) Resulting current variation vs potential (CV) obtained upon oxidation; C) Selected UV-Vis spectra obtained during the monitoring; D) Resulting current variation vs time.

Compound 13

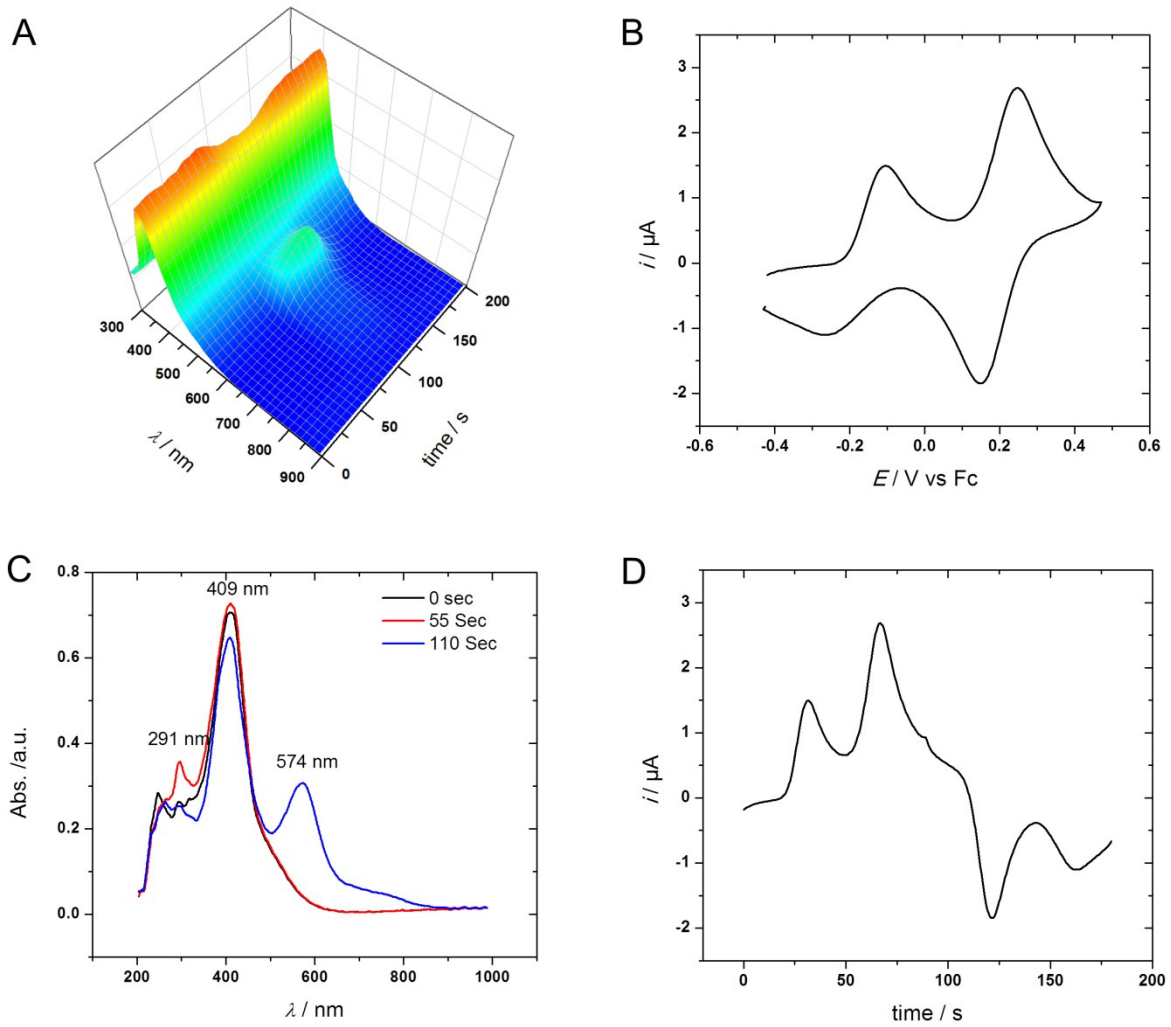


Figure S3. A) UV-Vis monitoring of the oxidation of compound **13** (ca. 1 mM) in CH_2Cl_2/NBu_4PF_6 0.1 M by cyclic potential sweeping under thin-layer conditions (optical path: 200 µm); B) Resulting current variation vs potential (CV) obtained upon oxidation; C) Selected UV-Vis spectra obtained during the monitoring; D) Resulting current variation vs time.

Compound S4

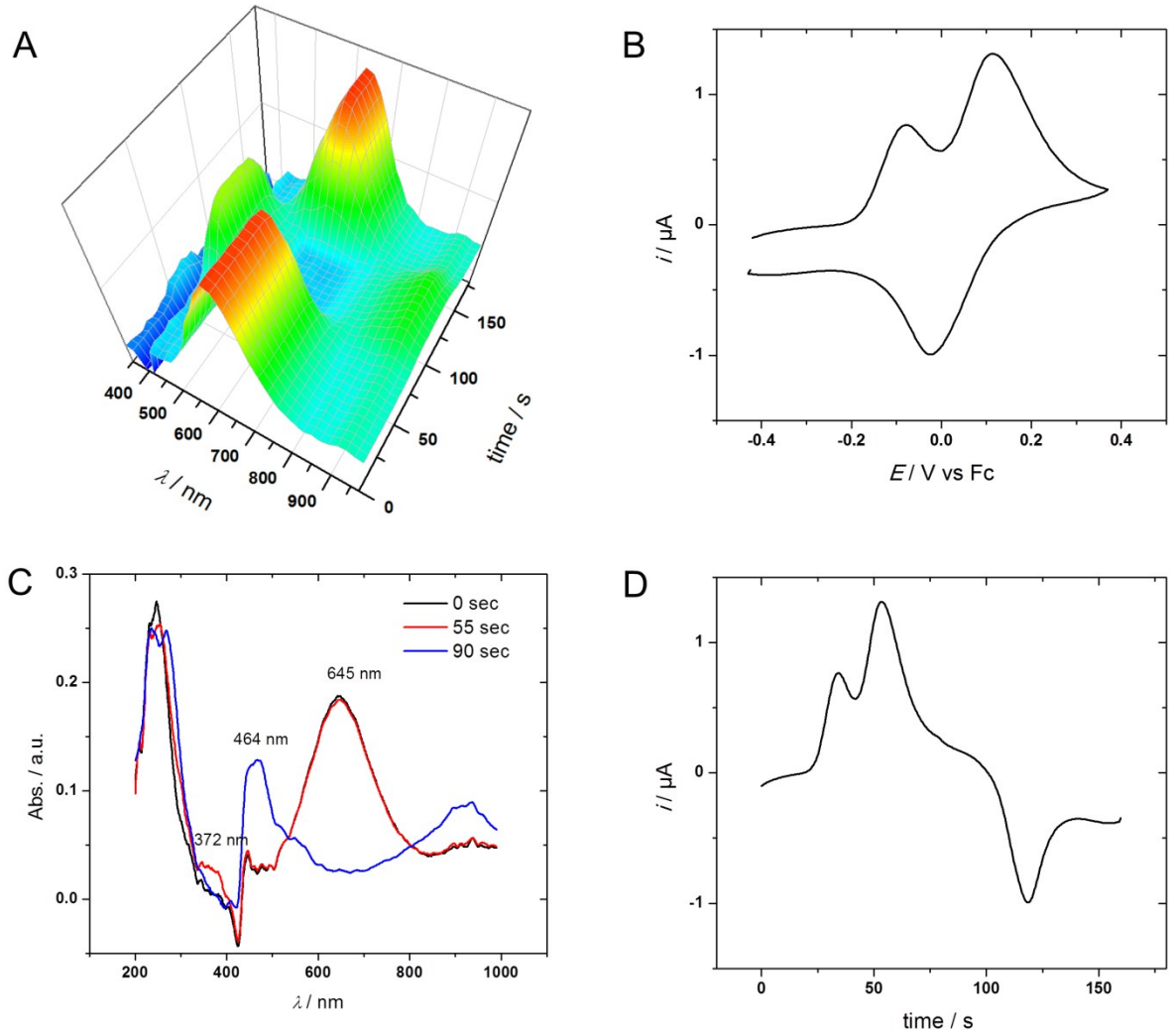


Figure S4. A) UV-Vis monitoring of the oxidation of compound **S4** (ca. 1 mM) in CH_2Cl_2/NBu_4PF_6 0.1 M by cyclic potential sweeping under thin-layer conditions (optical path: 200 µm); B) Resulting current variation vs potential (CV) obtained upon oxidation; C) Selected UV-Vis spectra obtained during the monitoring; D) Resulting current variation vs time.

DFT/TD-DFT complementary results

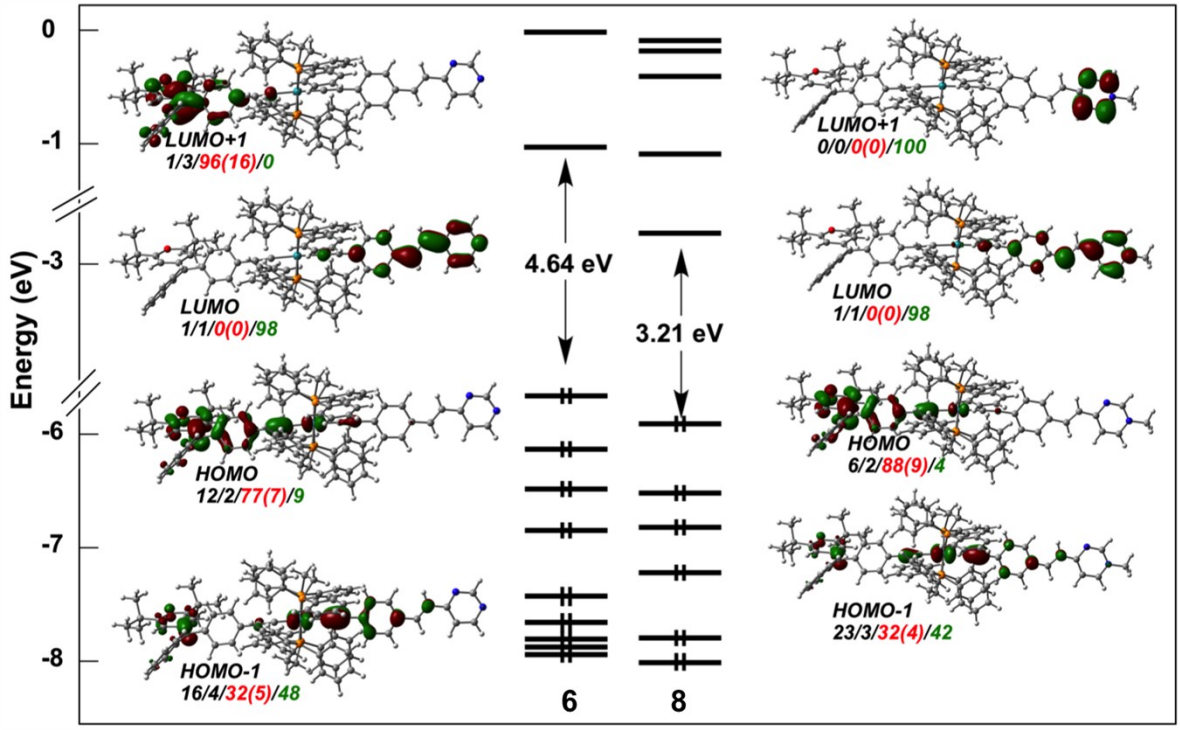


Figure S5: Kohn-Sham orbital diagrams of **6** and **8**. The numbers correspond to the following fragment contributions to the orbital localizations (%): *Ru/phosphines/pyranylidene branch/diazine branch*.

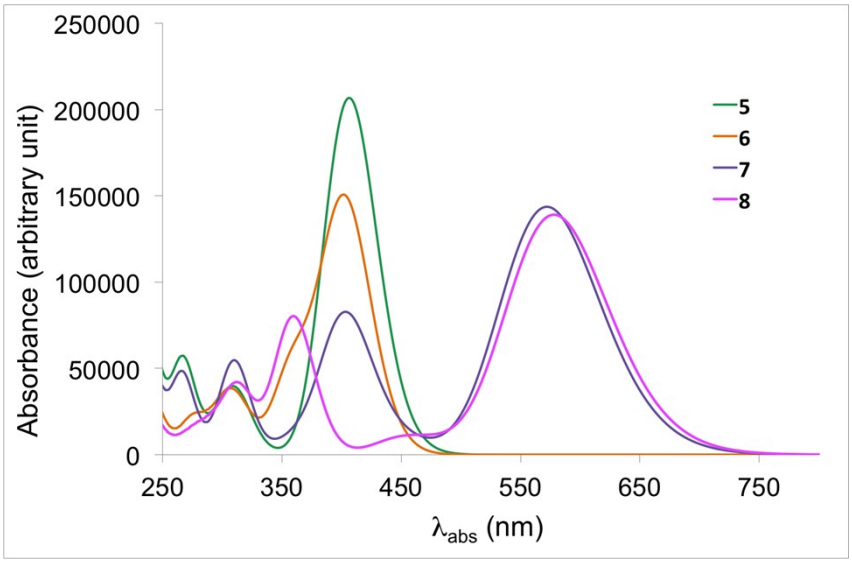


Figure S6: TD-DFT-simulated UV-vis spectra of complexes **5-8** (see Computational details).

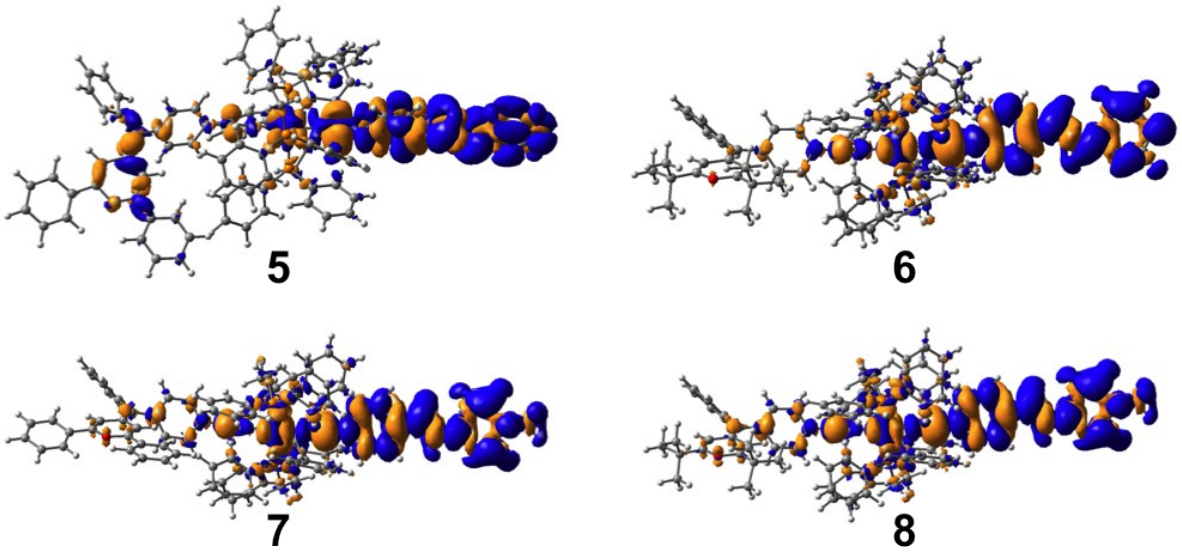


Figure S7: Density difference plots[21-23] associated with the transitions of lowest energy computed for complexes **5-8**. The blue and yellow colors indicate an increase and decrease of density upon excitation, respectively (see Computational details).

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24 All the atoms of carbon were not observed.

25 The solubility in DSMO-*d6* was bad, that is why the resolution was low. The solubility in other deuterated solvents was non-existent ($CDCl_3$, CD_2Cl_2) or not tried.