

SUPPORTING INFORMATION

Incorporation of a platinum center in the pi-conjugated core of push-pull chromophores for NLO.

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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 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. Compounds **S2**,^[1] **S3**,^[2] **12**,^[3] **S8**,^[4] **16**^[5] and **17**^[5] were obtained according to reported procedures. NMR spectra were acquired at room temperature on a Bruker AC-300 spectrometer (¹H at 300 MHz, ¹³C at 75 MHz, ³¹P at 121 MHz) and referenced as follows: ¹H NMR, residual CHCl₃ (δ = 7.26 ppm); ¹³C{¹H} NMR, internal CDCl₃ (δ = 77.16 ppm); ³¹P{¹H} NMR, external H₃PO₄ (δ = 0.00 ppm). The chemical shifts δ are reported in parts per million relative to TMS (¹H, 0.0 ppm) and CDCl₃ (¹³C, 77.16 ppm). The coupling constant *J* is given in Hz. In the ¹H 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 CDCl₃ were removed by treatment with anhydrous K₂CO₃. 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) 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 F₂₅₄ (Merck) or EMD aluminum oxide 150 F₂₅₄ (neutral) plates that were visualized with 365 nm UV light.

Cyclic voltammetry experimental details

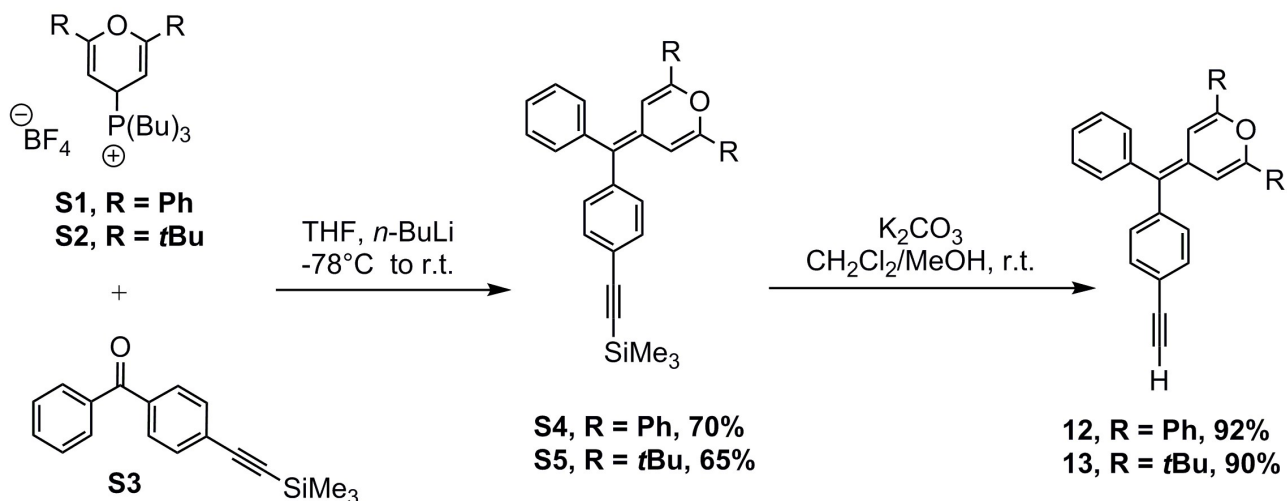
The electrochemical studies were performed in a glovebox (Jacomex) (O₂ < 1 ppm, H₂O < 1 ppm) with a home-made 3-electrode cell (WE: Pt, RE: Ag wire, CE: Pt). Ferrocene standard was added at the end of each experiment. The redox potential of the Fc⁺/Fc couple in CH₂Cl₂/NBu₄PF₆ was

measured experimentally with reference to the standard calomel electrode (SCE): $E_0(\text{Fc}^+/\text{Fc}) = 0.47$ V vs. SCE, and recalibrated vs. NHE assuming that $E_0(\text{SCE}) = 0.24$ 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.

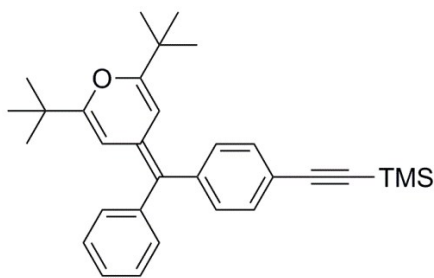
Computational details

Geometry optimizations were carried out using the Gaussian 09 package,^[6] employing the PBE0 functional,^[7] together with the D3 version of Grimme's empirical dispersion (Becke-Johnson damping)^[8] and using the standard double- ξ LANL2DZ basis set^[9] augmented with Ahlrichs polarization functions.^[10] Solvent (chloroform) effects have been taken into account using the PCM model.^[11] 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.^[12] The composition of the molecular orbitals was calculated using the AOMix program.^[13] The ionization energies and electron affinities discussed above 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^[14] on the optimized geometries with the CAM-B3LYP functional^[15] 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.^[16] The MO diagrams of Figures B and C correspond to CAM-B3LYP calculations.

Synthesis of precursors 12 and 13

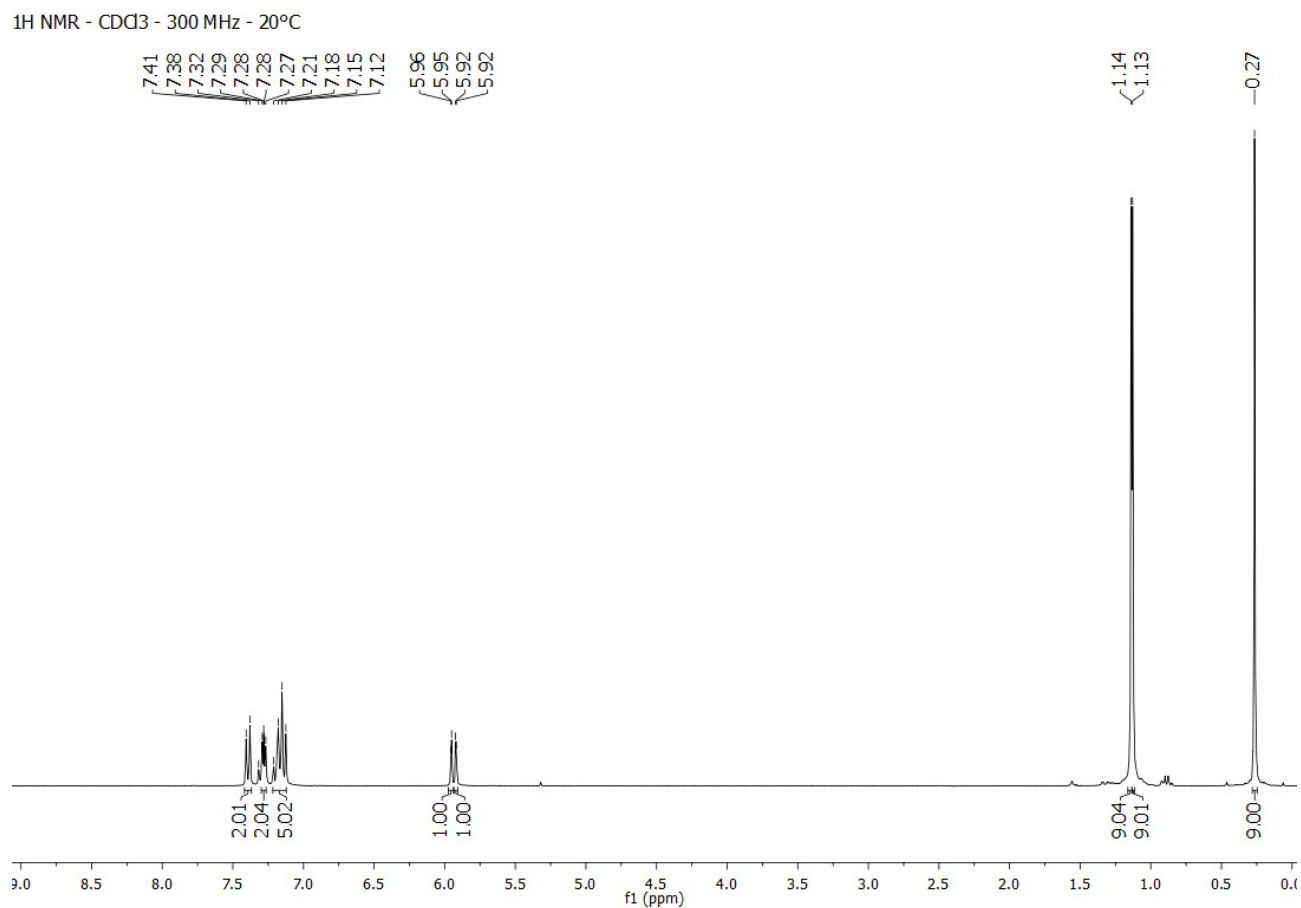


Compound S5:

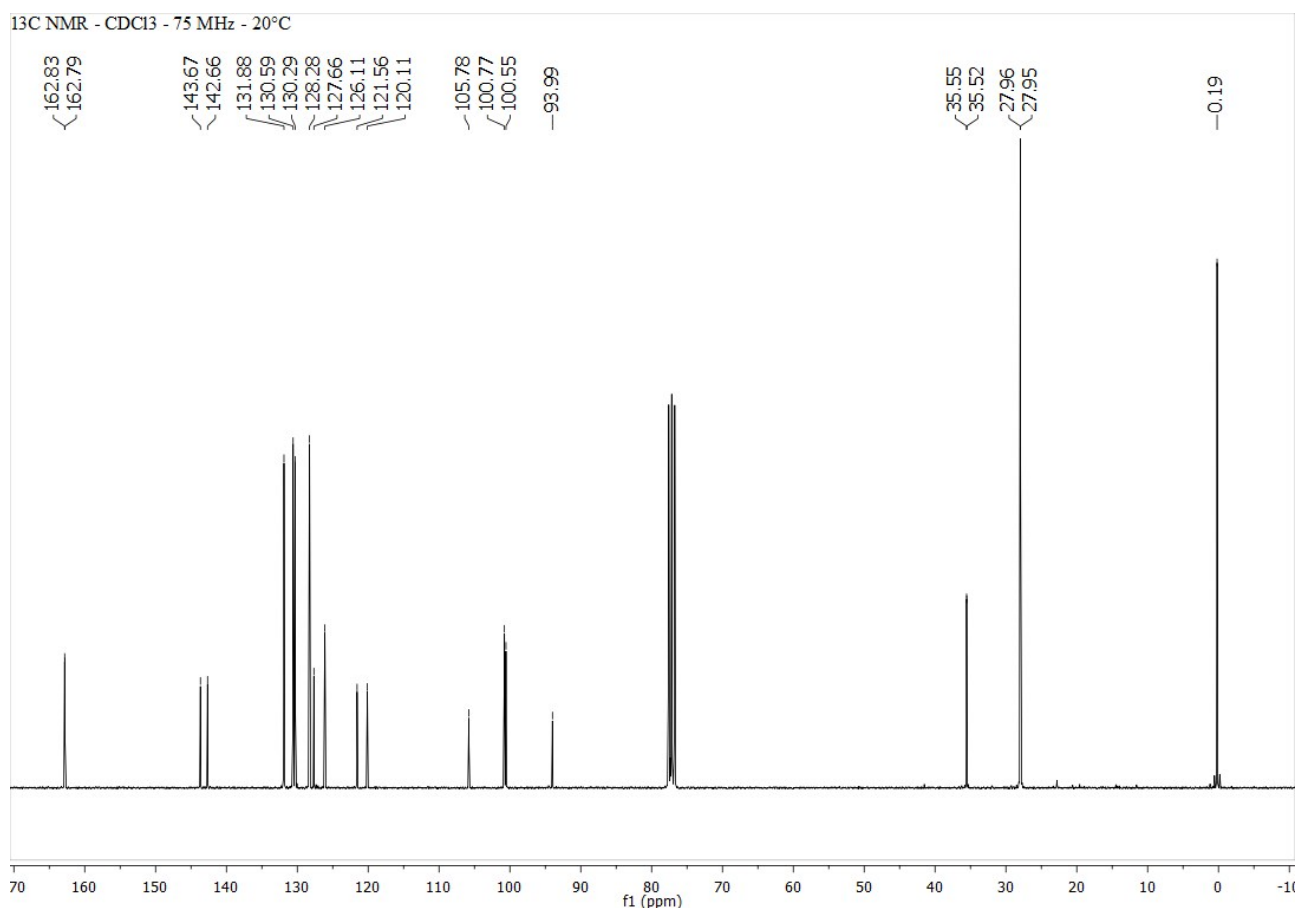


A Schlenk flask was charged with tributyl(2,6-di-*tert*-butyl-4*H*-pyran-4-yl)phosphonium tetrafluoroborate (**S2**) (600 mg, 1.24 mmol), 30 mL of anhydrous THF and *n*-BuLi 2.5 M in hexanes (0.5 mL, 1.24 mmol) at -78°C under argon protection. The solution was stirred at -78°C for 15 min and 4-(2-trimethylsilylethynyl)benzophenone (**S3**) (346 mg, 1.24 mmol) dissolved in dry THF (10 mL) was added dropwise. The solution was stirred at -78°C under argon for 30 min and then moved to room temperature and stirred overnight. After completion of the reaction, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/dichloromethane, 5:1) to give a yellow solid. Yield: 367 mg, 65%. mp: $204\text{--}206^\circ\text{C}$; NMR (δ (ppm), CDCl_3): ^1H (300 MHz): 7.39 (d, $^3J_{\text{HH}} = 8.0$ Hz, 2H), 7.32 – 7.25 (m, 2H), 7.22 –

7.11 (m, 5H), 5.95 (d, $^4J_{\text{HH}} = 2.0$ Hz, 1H), 5.92 (d, $^4J_{\text{HH}} = 1.9$ Hz, 1H), 1.14 (s, 9H), 1.13 (s, 9H), 0.27 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ (75 MHz): 162.8, 162.8, 143.7, 142.7, 131.9, 130.6, 130.3, 128.3, 127.7, 126.1, 121.6, 120.1, 105.8, 100.8, 100.6, 94.0, 35.5, 35.5, 28.0, 27.9, 0.2; HRMS (ESI): m/z , calculated for M^+ ($\text{C}_{31}\text{H}_{38}\text{OSi}$): 454.2686, found: 454.2688.

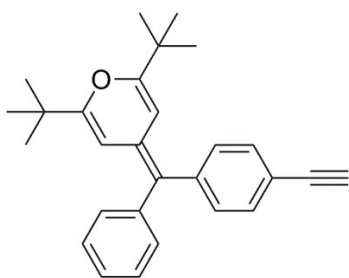


Spectrum 1: ^1H NMR spectrum of compound **S5** (300 MHz, CDCl_3)



Spectrum 2: ¹³C NMR spectrum of compound **S5** (75 MHz, CDCl₃)

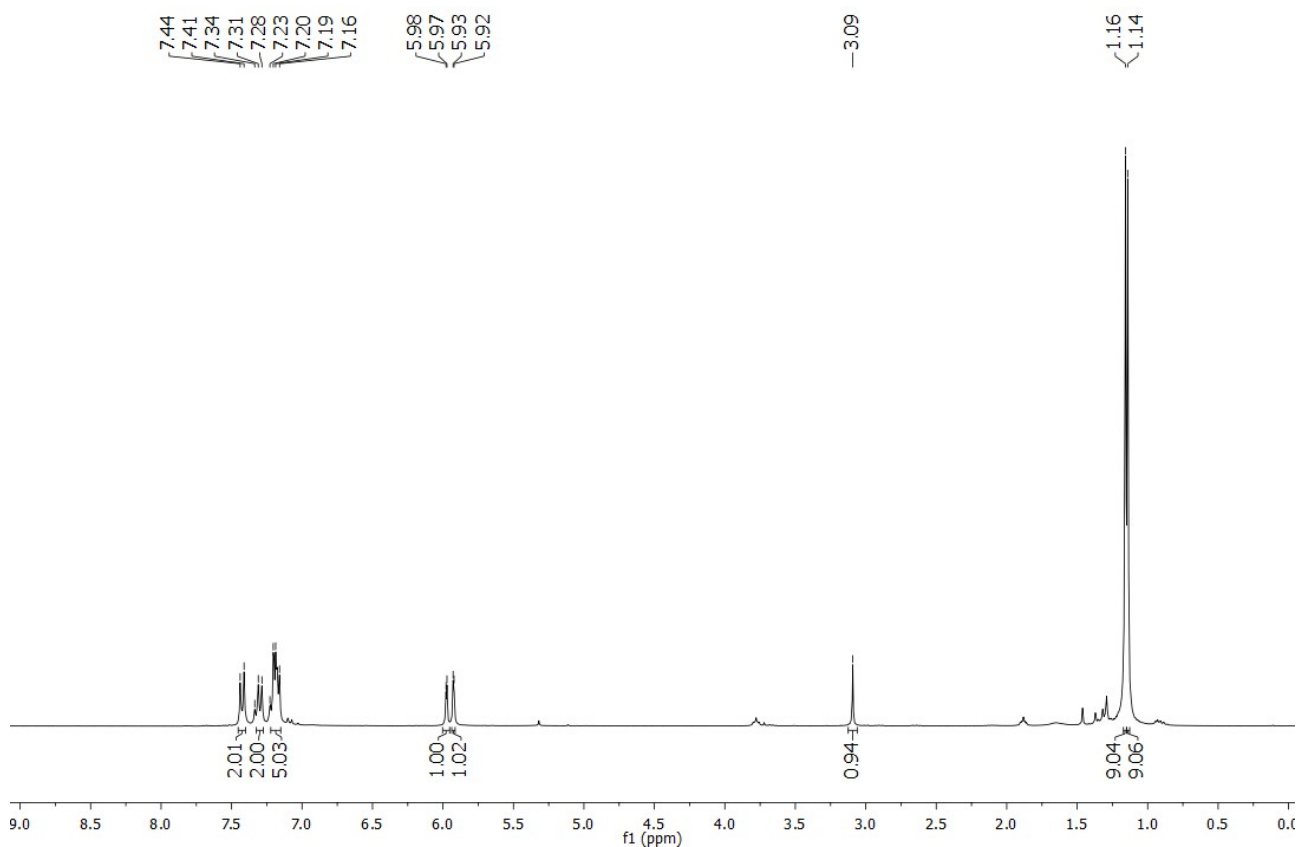
Compound 13



K₂CO₃ (275 mg, 2.0 mmol) was added to a methanol (10 mL) and dichloromethane (20 mL) solution of compound (**S5**) (465 mg, 1.0 mmol), and the reaction mixture was stirred at room temperature overnight. The suspension was then diluted with a mixture of water and dichloromethane (1:1, 30 mL) and the organic layer was extracted with dichloromethane (3 × 30 mL). The combined organic extracts were dried over MgSO₄, filtered, and evaporated. The residue

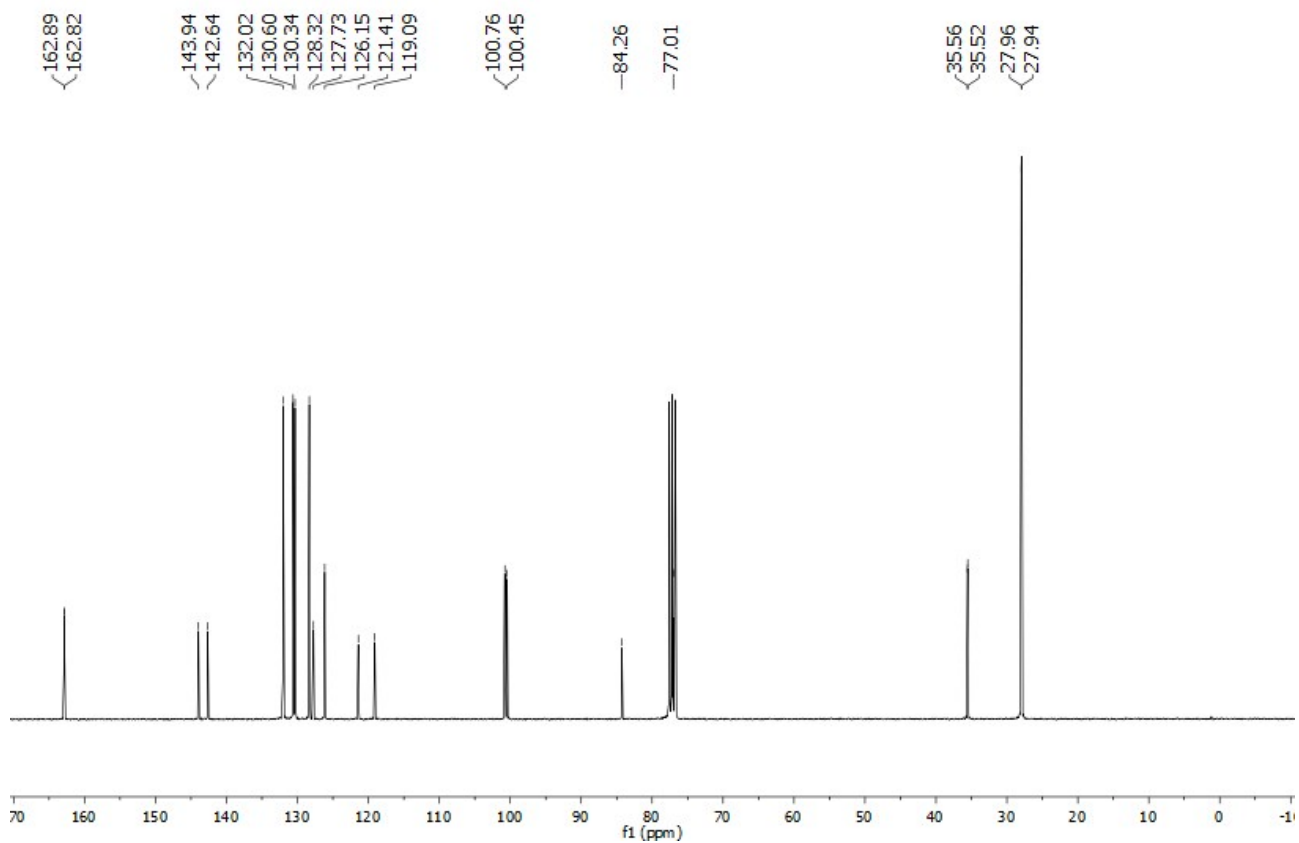
was purified by column chromatography on silica gel (hexane/dichloromethane, 5:1) to give a beige solid. Yield: 352 mg, 92%. mp: 200-202°C; NMR (δ (ppm), CDCl_3): ^1H (300 MHz): 7.43 (d, $^3J_{\text{HH}} = 8.2$ Hz, 2H), 7.35 – 7.27 (m, 2H), 7.26 – 7.13 (m, 5H), 5.97 (d, $^4J_{\text{HH}} = 2.0$ Hz, 1H), 5.92 (d, $^4J_{\text{HH}} = 2.0$ Hz, 1H), 3.09 (s, 1H), 1.16 (s, 9H), 1.14 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$: 162.9, 162.8, 143.9, 142.6, 132.0, 130.6, 130.3, 128.3, 127.7, 126.1, 121.4, 119.1, 100.8, 100.4, 84.3, 77.0, 35.6, 35.5, 28.0, 27.9; HRMS (ESI): m/z , calculated for $\text{M}^{+\bullet}$ ($\text{C}_{28}\text{H}_{30}\text{O}$): 382.2291, found: 382.2293

^1H NMR - CDCl_3 - 300 MHz - 20°C



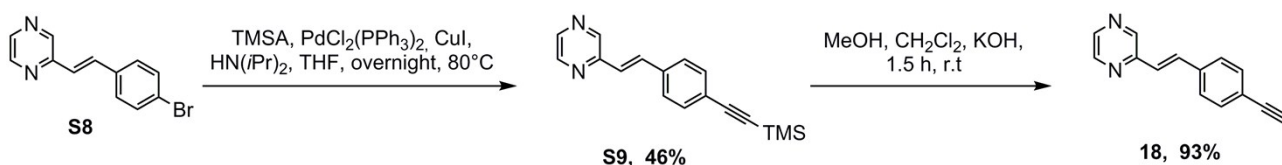
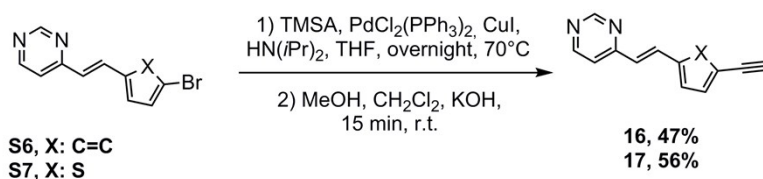
Spectrum 3: ^1H NMR spectrum of compound **13** (300 MHz, CDCl_3)

^{13}C NMR - CDCl_3 - 75 MHz - 20°C

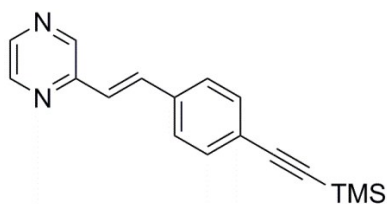


Spectrum 4: ^{13}C NMR spectrum of compound **13** (75 MHz, CDCl_3)

Synthesis of precursors 16-18

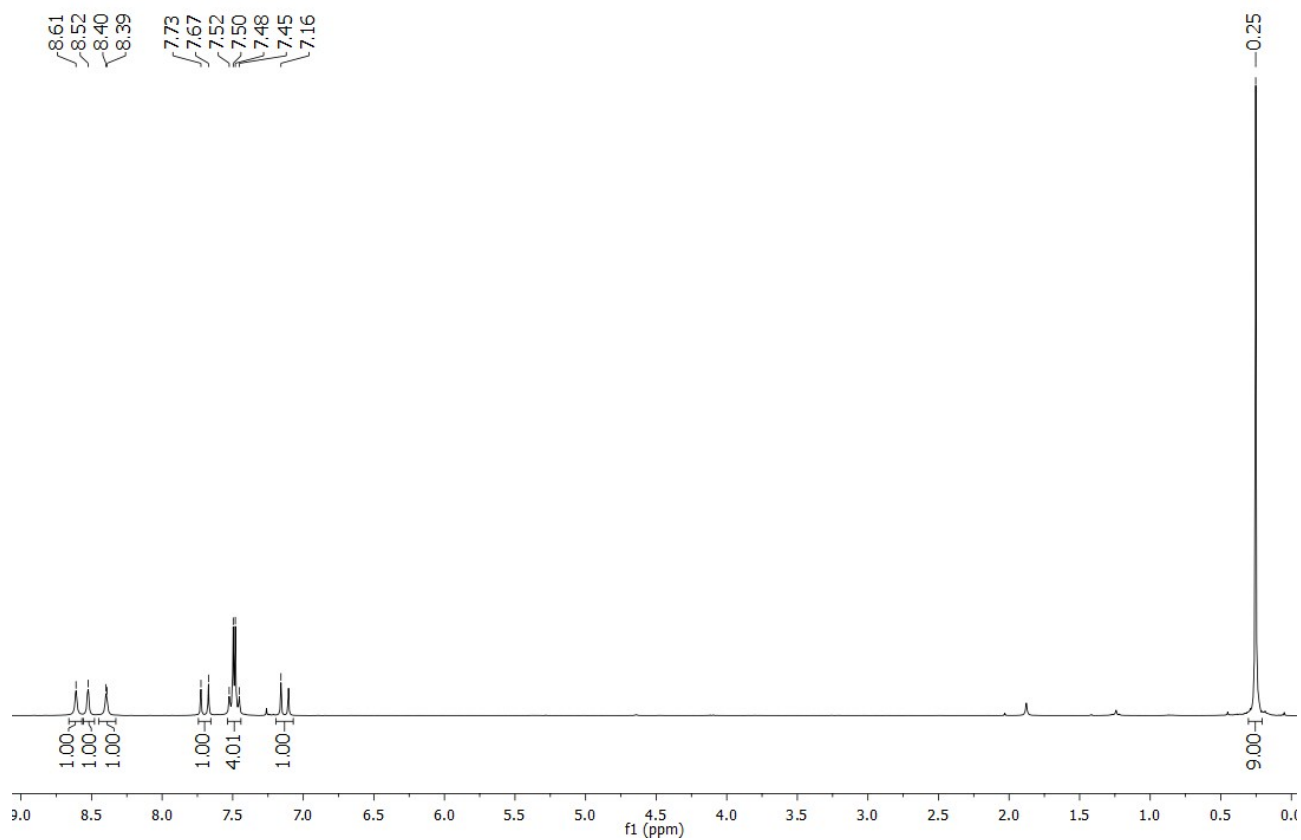


Compound S9

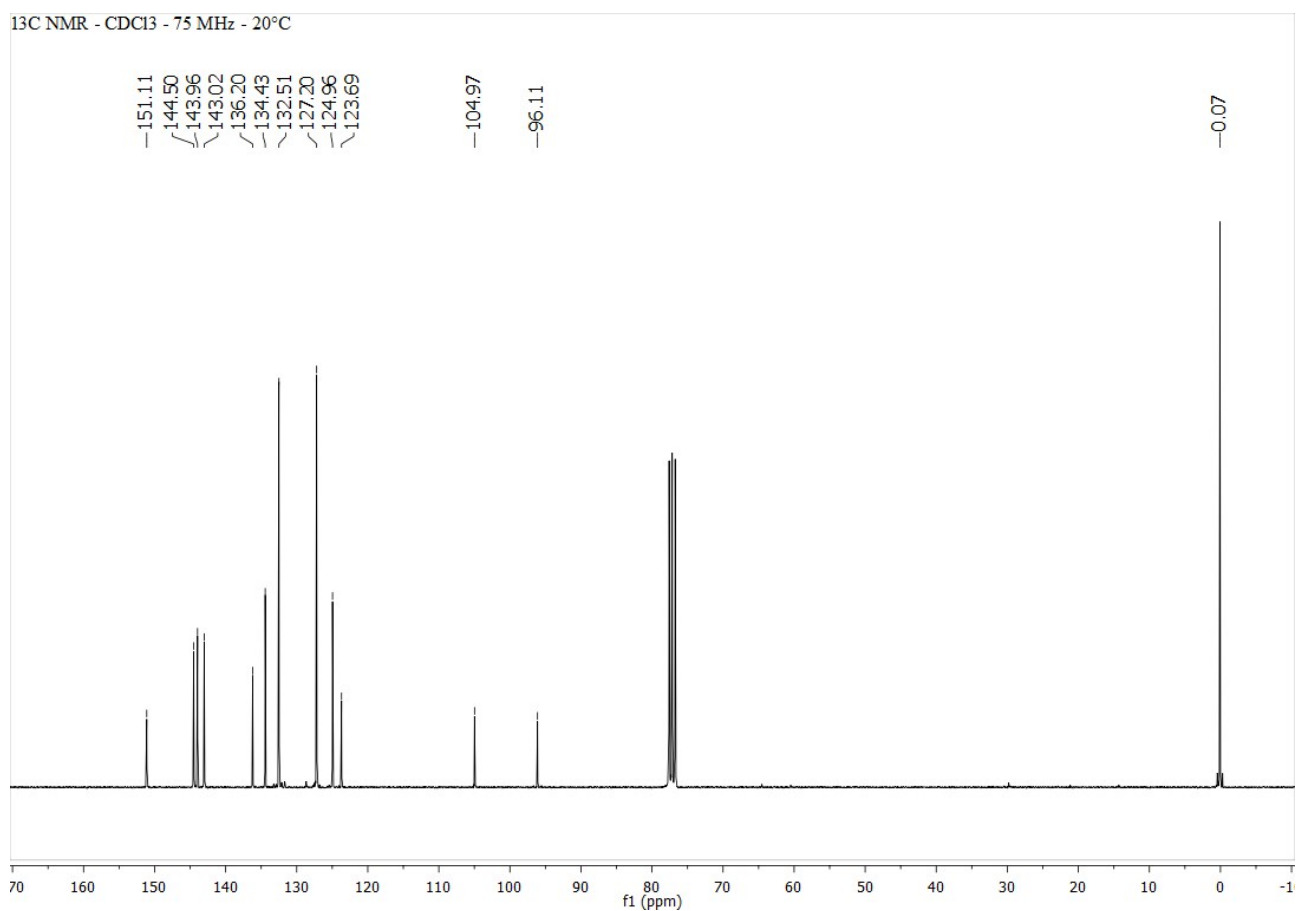


A suspension of **S8** (1.19 g, 4.6 mmol), Pd(PPh₃)₂Cl₂ (320 mg, 0.46 mmol), and CuI (43 mg, 0.23 mmol) in diisopropylamine (5 mL) and THF (15 mL) was degassed three times in a pressure tube. The trimethylsilylacetylene (4.21g, 46 mmol) was then added. The mixture was heated at 80°C overnight. The suspension was then diluted with a mixture of water and dichloromethane (1:1, 30 mL) and the organic layer was extracted with dichloromethane (3 × 30 mL). The combined organic extracts were dried over MgSO₄, filtered, and evaporated. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, 1:2) to give a slightly beige solid. Yield: 590 mg, 46%. Mp: 144-146°C. NMR (δ (ppm), CDCl₃): ¹H (300 MHz): 8.61 (s, 1H), 8.52 (s, 1H), 8.39 (d, ³J_{HH} = 2.4 Hz, 1H), 7.70 (d, ³J_{HH} = 16.1 Hz, 1H), 7.54 – 7.44 (m, 4H), 7.13 (d, ³J_{HH} = 16.1 Hz, 1H), 0.25 (s, 9H); ¹³C{¹H} (75 MHz): 151.1, 144.5, 144.0, 143.0, 136.2, 134.4, 132.5, 127.2, 125.0, 123.7, 105.0, 96.1, 0.1; IR (ATR, cm⁻¹): 3034, 2959, 2155, 1247, 1138, 831, 755; HRMS (ESI): m/z, calculated for [M+Na]⁺ (C₁₇H₁₈N₂NaSi): 301.1137, found: 301.1134

^1H NMR - CDCl_3 - 300 MHz - 20°C

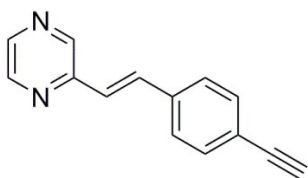


Spectrum 5: ^1H NMR spectrum of compound **S9** (300 MHz, CDCl_3)



Spectrum 6: ¹³C NMR spectrum of compound **S9** (75 MHz, CDCl₃)

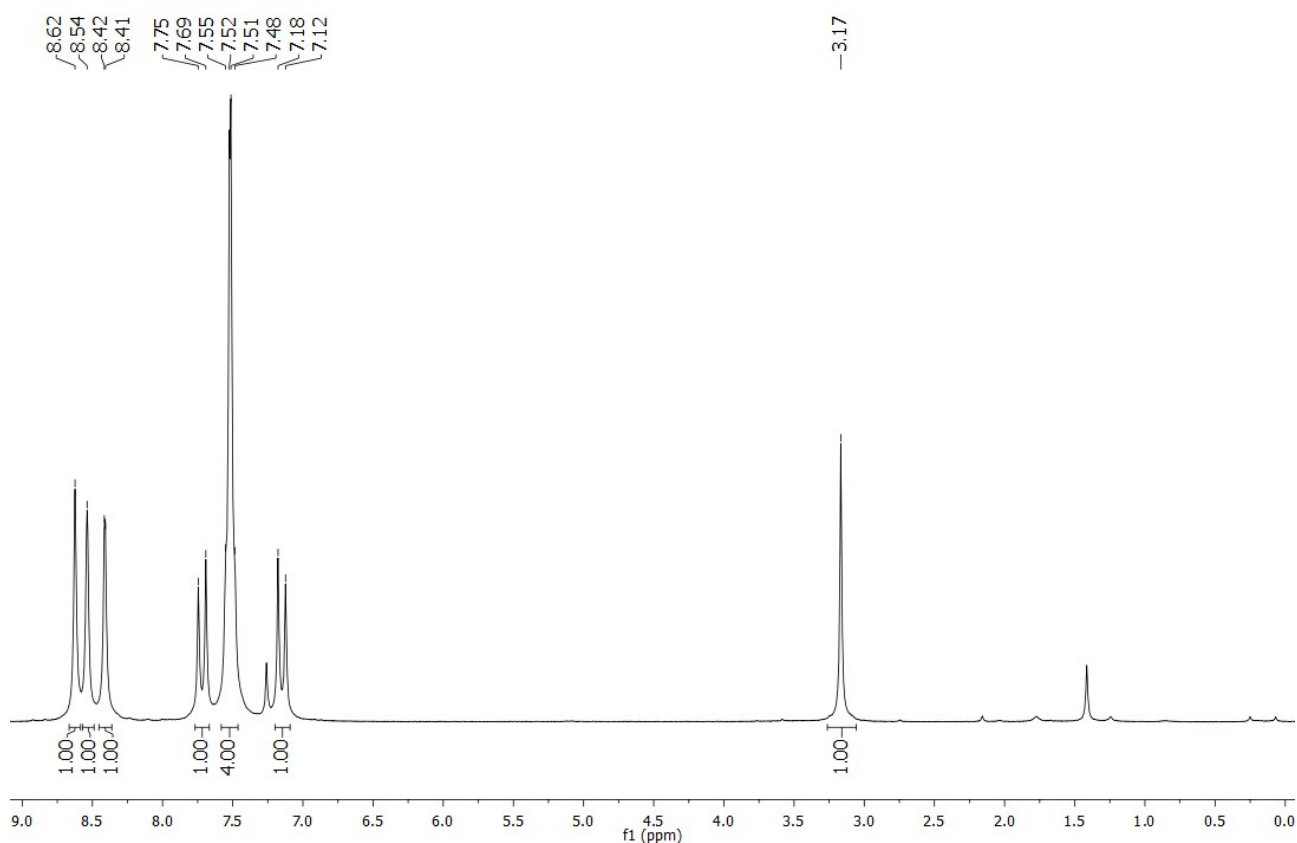
Compound 18



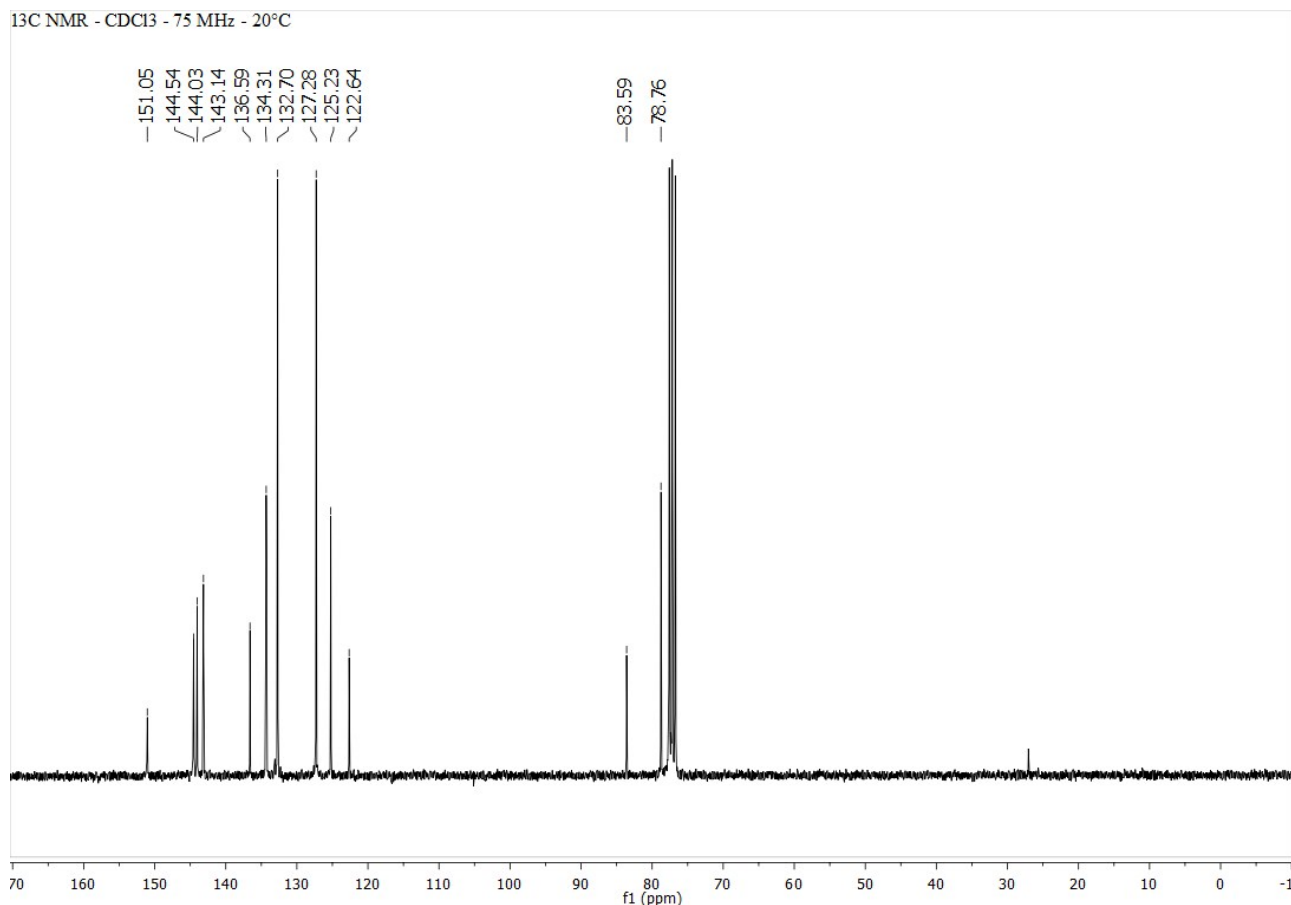
A suspension of **S9** (640 mg, 2.3 mmol) in a solution of potassium hydroxide in methanol (1 M, 30 mL) was quickly stirred at room temperature for 30 min. The solution was then neutralized with 1 M aqueous HCl and the precipitate was slowly filtered, washed with water (2 × 100 mL) and dried. The crude product was crystallized from dichloromethane/cyclohexane to afford **12** as a brown

powder. Yield: 440 mg, 93%. mp: 130-132°C. NMR (δ (ppm), CDCl_3): ^1H (300 MHz): 8.62 (s, 1H), 8.54 (s, 1H), 8.41 (d, $^3J_{\text{HH}} = 2.5$ Hz, 1H), 7.72 (d, $^3J_{\text{HH}} = 16.1$ Hz, 1H), 7.60 – 7.40 (m, 4H), 7.15 (d, $^3J_{\text{HH}} = 16.0$ Hz, 1H), 3.17 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ (75 MHz): 151.0, 144.5, 144.0, 143.1, 136.6, 134.3, 132.7, 127.3, 125.2, 122.6, 83.6, 78.8; IR (ATR, cm^{-1}): 3174, 2095, 1915, 1635, 1411, 1400, 1136, 838, 812; HRMS (ESI): m/z , calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{14}\text{H}_{11}\text{N}_2$): 207.0922, found: 207.0920

^1H NMR - CDCl_3 - 300 MHz - 20°C

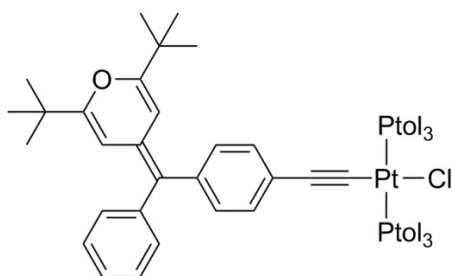


Spectrum 7: ^1H NMR spectrum of compound **18** (300 MHz, CDCl_3)



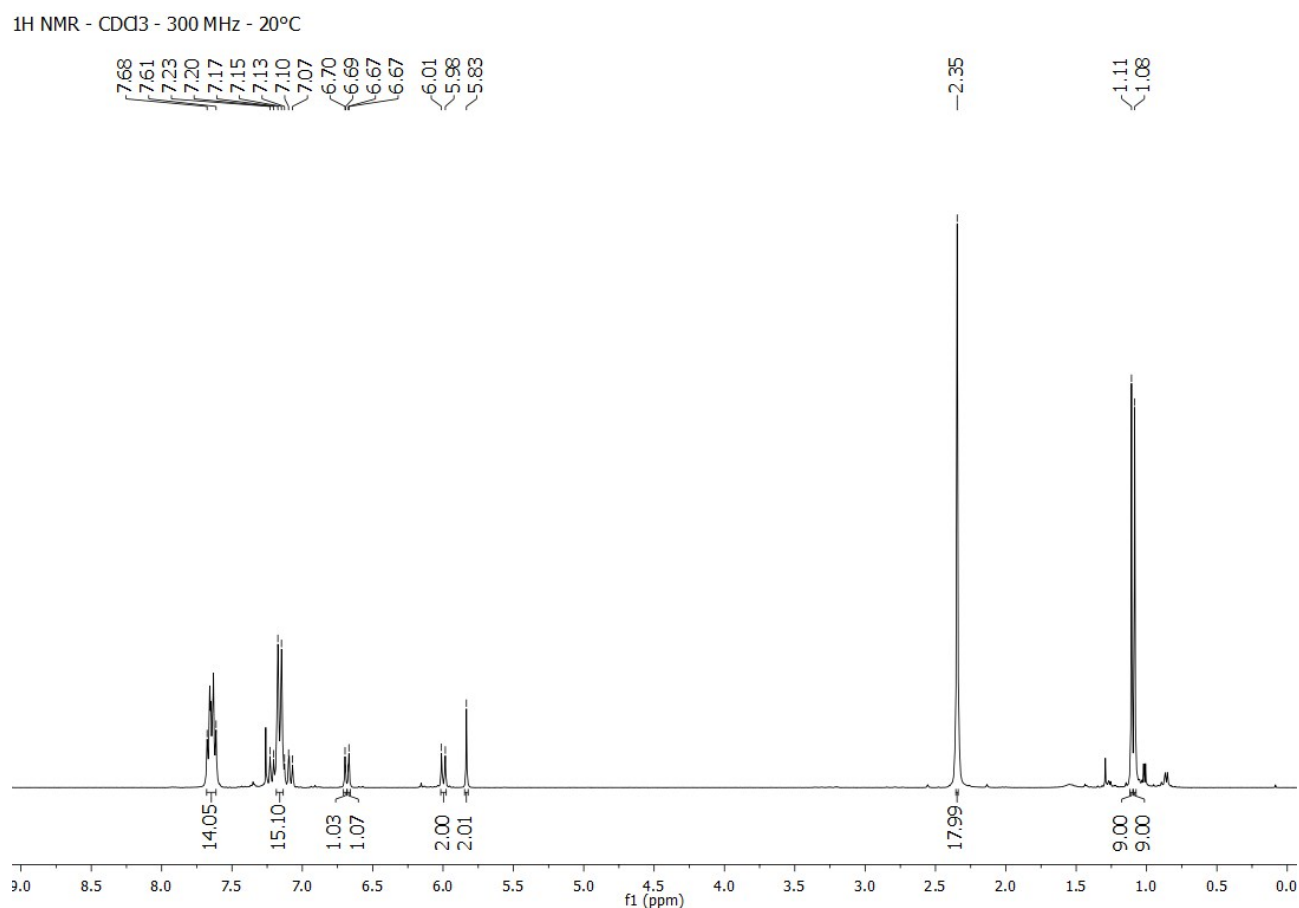
Spectrum 8: ¹³C NMR spectrum of compound **18** (75 MHz, CDCl₃)

Compound 15

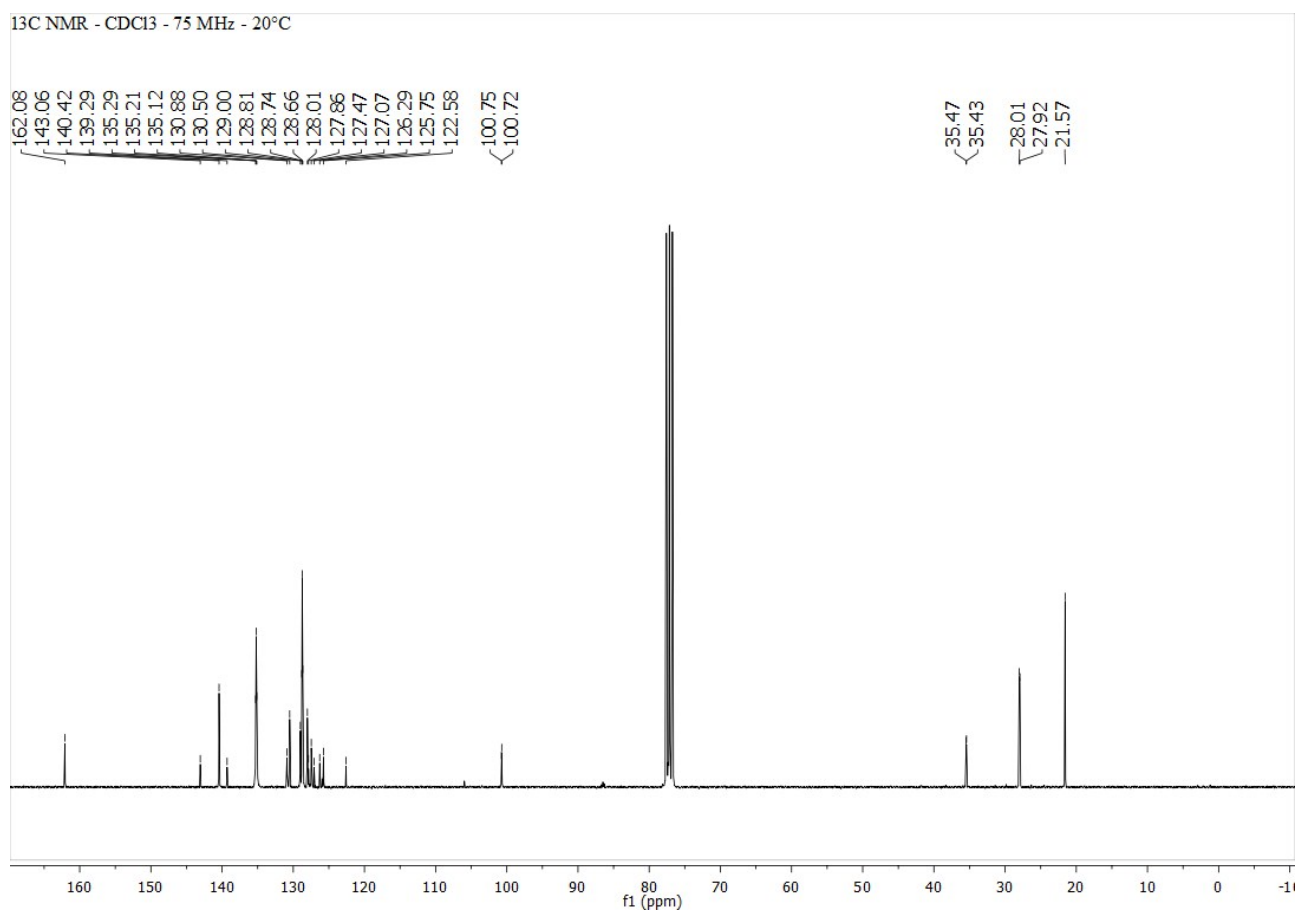


A Schlenk flask, charged with **13** (283 mg, 0.74 mmol), *cis*-dichlorobis(*para*-tolylphosphine)platinum (704 mg, 0.805 mmol), and cuprous iodide (10 mg), was degassed and back-filled with argon three times. Then diethylamine (25 mL) and dried THF (50 mL) were introduced into the reaction flask by syringe. The reaction mixture was stirred under argon protection at 60°C overnight. The solvent was then removed under reduced pressure. The residue

was purified by column chromatography on silica gel (dichloromethane/petroleum ether, from 1:2 to 2:1) to give **15** as a pale yellow solid. Yield: 546 mg, 60%. MP: 160-162°C; NMR (δ (ppm), CDCl_3): ^1H (300 MHz): 7.70 – 7.59 (m, 14H), 7.24 – 7.06 (m, 15H), 6.69 (d, $^4J_{\text{HH}} = 1.5$ Hz, 1H), 6.67 (d, $^4J_{\text{HH}} = 1.4$ Hz, 1H), 6.00 (d, $^3J_{\text{HH}} = 8.3$ Hz, 2H), 5.83 (s, 2H), 2.35 (s, 18H), 1.11 (s, 9H), 1.08 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ (75 MHz): 162.1, 143.1, 140.4, 139.3, 135.3, 135.2, 135.1, 130.9, 130.5, 129.0, 128.8, 128.7, 128.7, 128.0, 127.9, 127.5, 127.1, 126.3, 125.7, 122.6, 100.8, 100.7, 35.5, 35.4, 28.0, 27.9, 21.6; ^{31}P (121 MHz): 19.68 (s, $^1J_{\text{PtP}} = 2635$ Hz) ^[17]; HRMS (ESI): m/z , calculated for M^+ ($\text{C}_{70}\text{H}_{71}\text{O}^{35}\text{ClP}_2^{195}\text{Pt}$): 1219.4311, found: 1219.4320

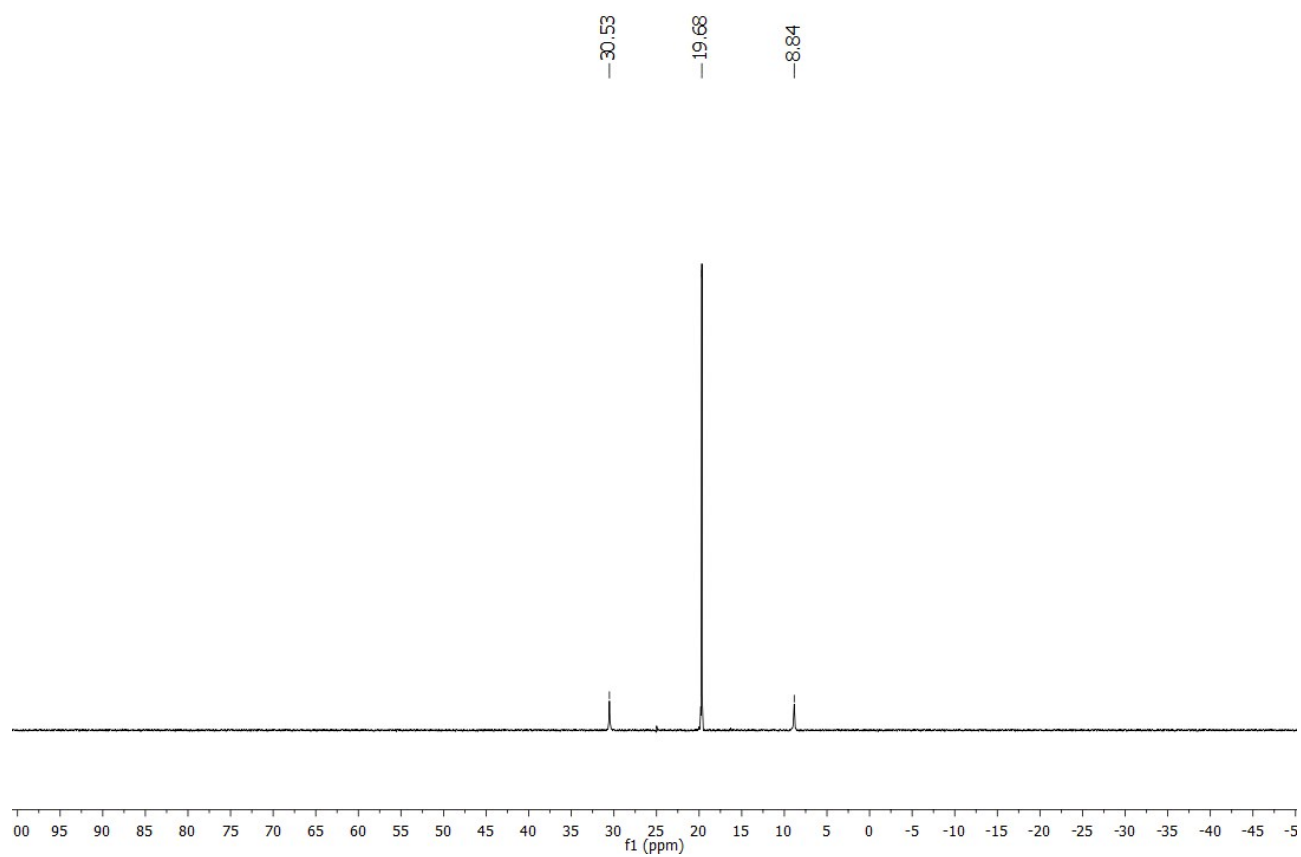


Spectrum 9: ^1H NMR spectrum of compound **15** (300 MHz, CDCl_3)



Spectrum 10: ^{13}C NMR spectrum of compound **15** (75 MHz, CDCl_3)

^{31}P NMR - CDCl_3 - 121 MHz - 20°C



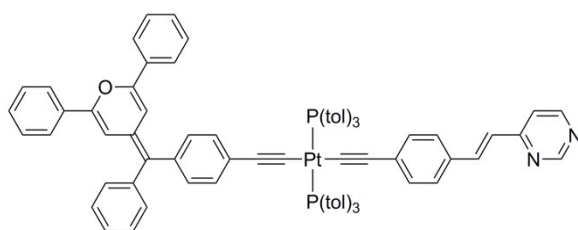
Spectrum 11: ^{31}P NMR spectrum of compound **15** (121 MHz, CDCl_3)

Synthesis of complexes 1-4

General procedure for the synthesis of Compounds 1-4

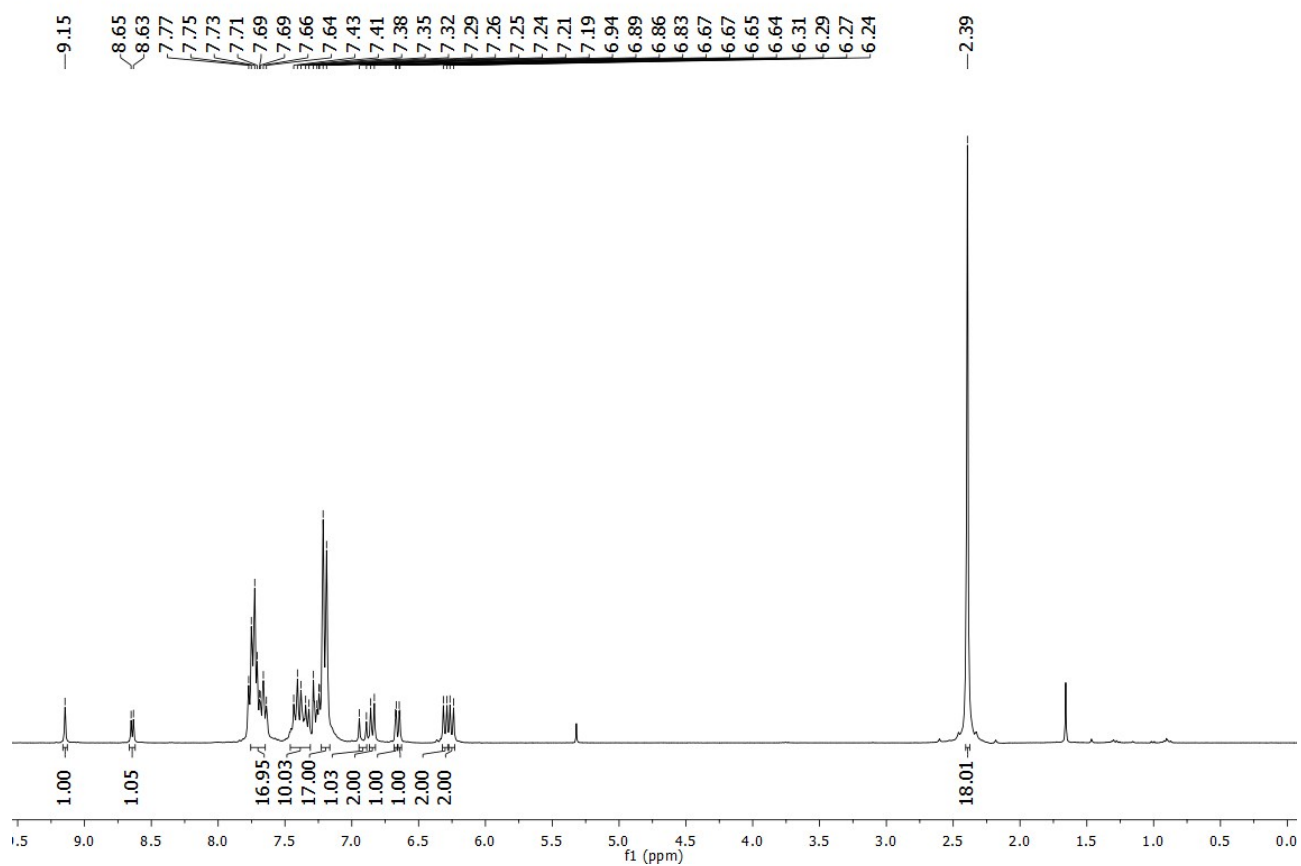
A 100 mL Schlenk flask, charged with the corresponding chloro complex (0.16 mmol), the corresponding bromodiazine derivative (0.16 mmol), and cuprous iodide (3.0 mg, 10 mol %), was degassed and back-filled with nitrogen three times. Then diethylamine (20 mL) and dried THF (20 mL) were introduced into the reaction flask. The reaction mixture was stirred under nitrogen atmosphere at room temperature overnight. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, 1:1).

Compound 1



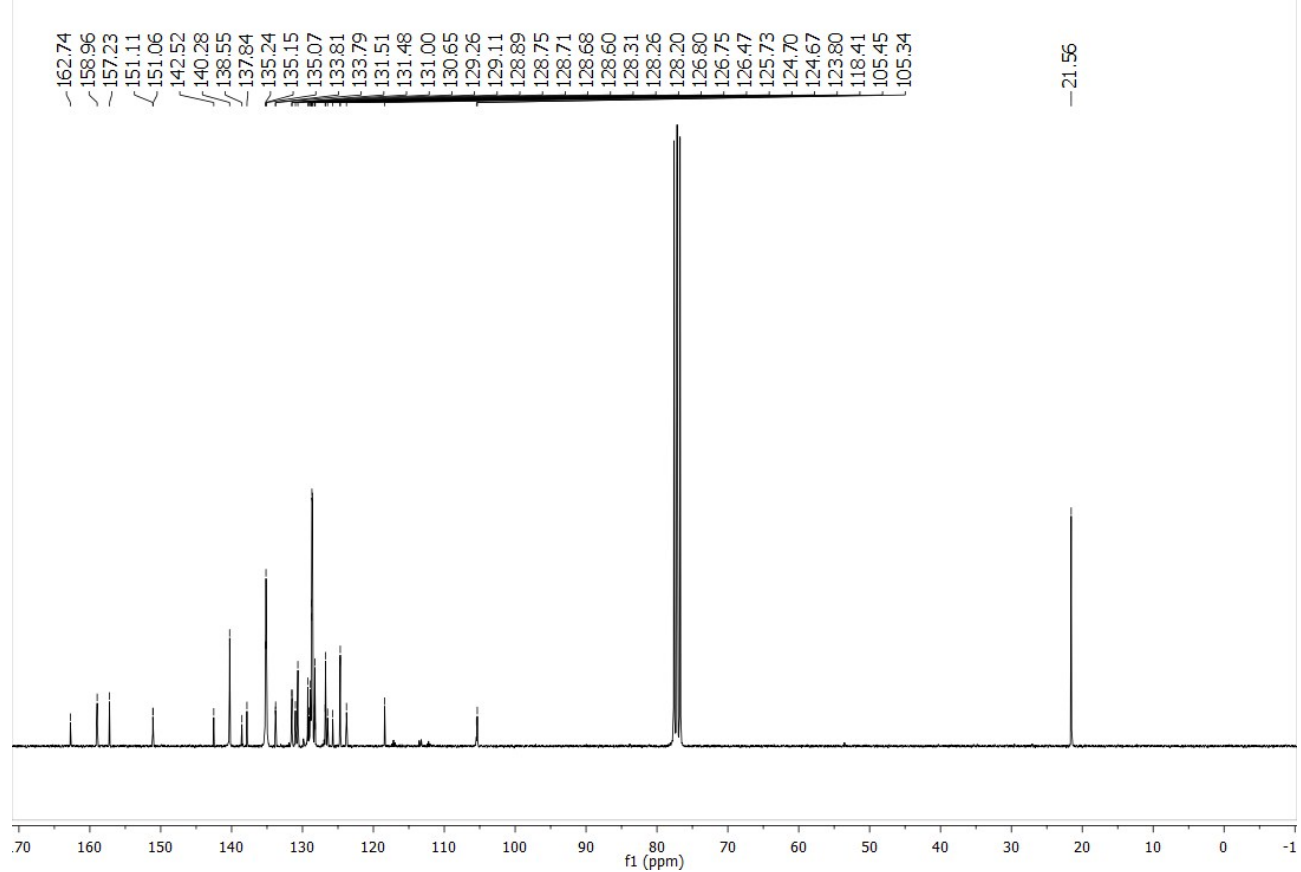
The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, from 6:4 to 4:6) to give a yellow powder. Yield: 134 mg, 59%. mp: 184°C (dec.); NMR (δ (ppm), CDCl₃): ¹H (300 MHz): 9.15 (s, 1H), 8.64 (d, ³J_{HH} = 5.3 Hz, 1H), 7.77 – 7.64 (m, 17H), 7.43 – 7.32 (m, 10H), 7.24 – 7.18 (m, 17H), 6.92 (d, ³J_{HH} = 16 Hz, 1H), 6.84 (d, ³J_{HH} = 8.1 Hz, 2H), 6.67 (d, ⁴J_{HH} = 1.6 Hz, 1H), 6.64 (d, ⁴J_{HH} = 1.7 Hz, 1H), 6.30 (d, ³J_{HH} = 8.2 Hz, 2H), 6.25 (d, ³J_{HH} = 8.1 Hz, 2H), 2.39 (s, 18H); ¹³C{¹H} (75 MHz): 162.7, 159.0, 157.2, 151.1, 151.1, 142.5, 140.3, 138.5, 137.8, 135.2, 135.2, 135.1, 133.8, 133.8, 131.5, 131.5, 131.0, 130.7, 129.3, 129.1, 128.9, 128.7, 128.7, 128.7, 128.6, 128.3, 128.3, 128.2, 126.8, 126.7, 126.5, 125.7, 124.7, 124.7, 123.8, 118.4, 105.5, 105.3, 21.6 [¹⁸]; ³¹P (121 MHz): 16.72 (s, ¹J_{PtP} = 2609 Hz) [¹⁷]; IR (ATR, cm⁻¹): 3022, 2922, 2098, 1569, 1098, 839, 803, 761, 695; HRMS (ESI): m/z, calculated for M⁺ (C₈₈H₇₂N₂OP₂¹⁹⁵Pt): 1429.4762, found: 1429.4751.

^1H NMR - CDCl_3 - 300 MHz - 20°C



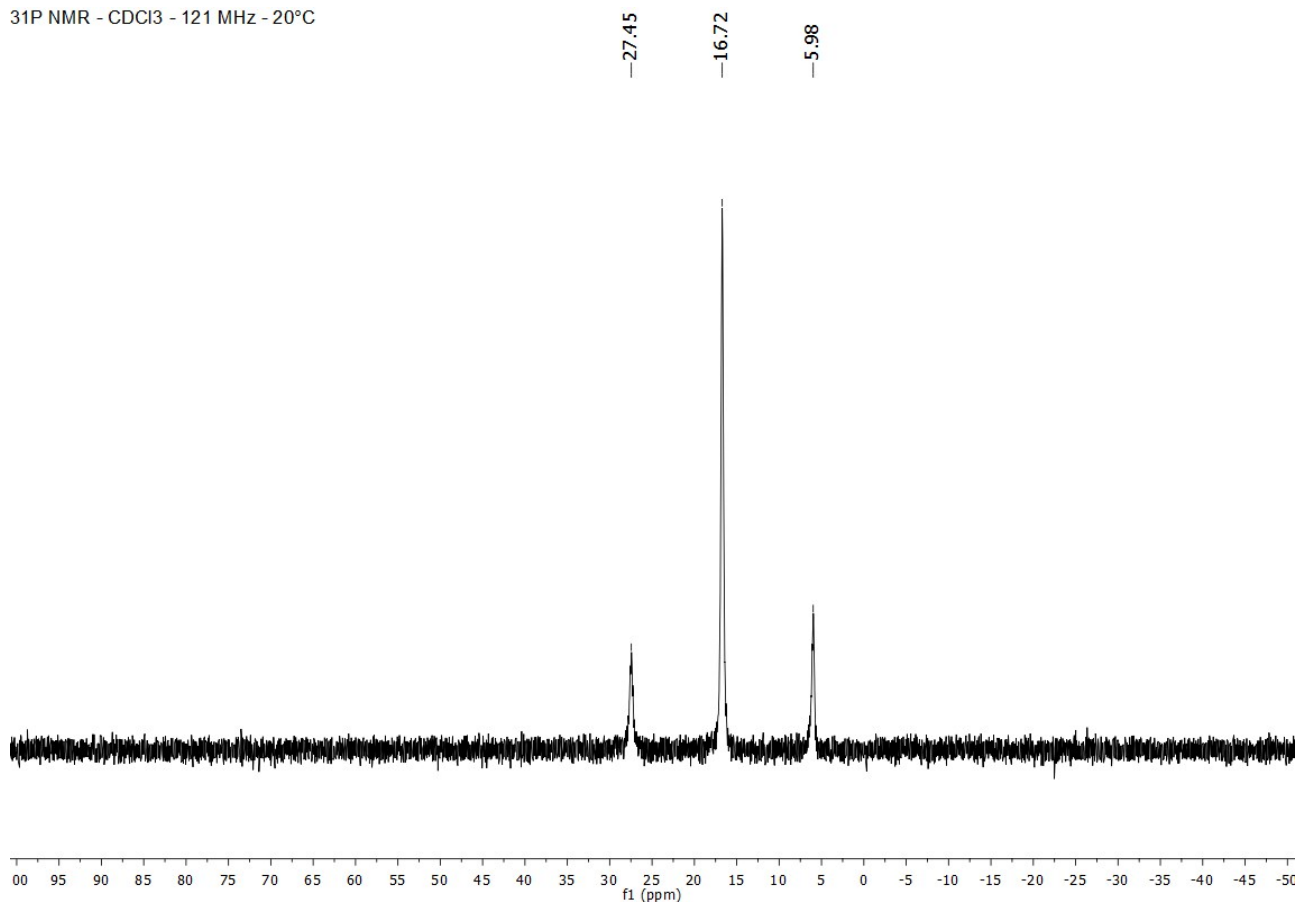
Spectrum 12: ^1H NMR spectrum of compound **1** (300 MHz, CDCl_3)

^{13}C NMR - CDCl_3 - 75 MHz - 20°C



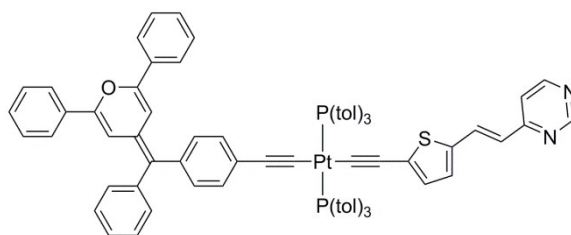
Spectrum 13: ^{13}C NMR spectrum of compound **1** (75 MHz, CDCl_3)

^{31}P NMR - CDCl_3 - 121 MHz - 20°C



Spectrum 14: ^{31}P NMR spectrum of compound **1** (121 MHz, CDCl_3)

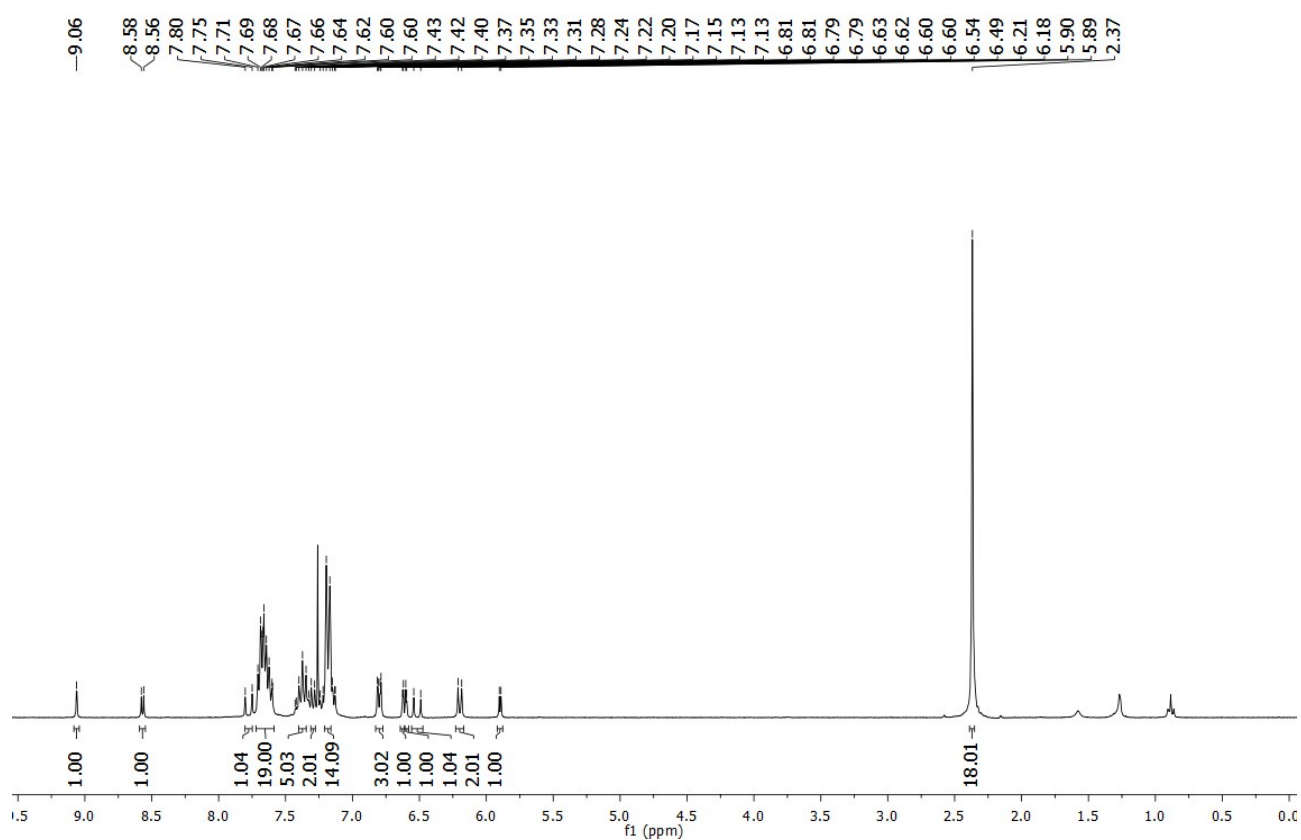
Compound 2



The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, from 1:1 to 0:1) to give an orange powder. Yield: 495 mg, 86%. mp: 135°C (dec.); NMR (δ (ppm), CDCl_3): ^1H (300 MHz): 9.06 (s, 1H), 8.57 (d, $^3J_{\text{HH}} = 5.3$ Hz, 1H), 7.78 (d, $^3J_{\text{HH}} = 15.5$ Hz, 1H), 7.72 – 7.59 (m, 19H), 7.43 – 7.33 (m, 5H), 7.30 (d, $^3J_{\text{HH}} = 7.5$ Hz, 2H), 7.24 – 7.13 (m, 14H), 6.81–6.79 (m, 3H), 6.62 (d, $^4J_{\text{HH}} = 1.9$ Hz, 1H), 6.60 (d, $^4J_{\text{HH}} = 1.9$ Hz, 1H), 6.52 (d, $^3J_{\text{HH}} = 15.5$ Hz, 1H), 6.20 (d, $^3J_{\text{HH}} = 8.2$ Hz, 2H), 5.90 (d, $^3J_{\text{HH}} = 3.8$ Hz, 1H), 2.37 (s, 18H); $^{13}\text{C}\{^1\text{H}\}$ (75 MHz): 162.5, 158.9, 157.1, 151.1, 151.1, 142.5, 140.4, 138.7, 137.4, 135.2, 135.1, 135.0, 133.8, 132.9,

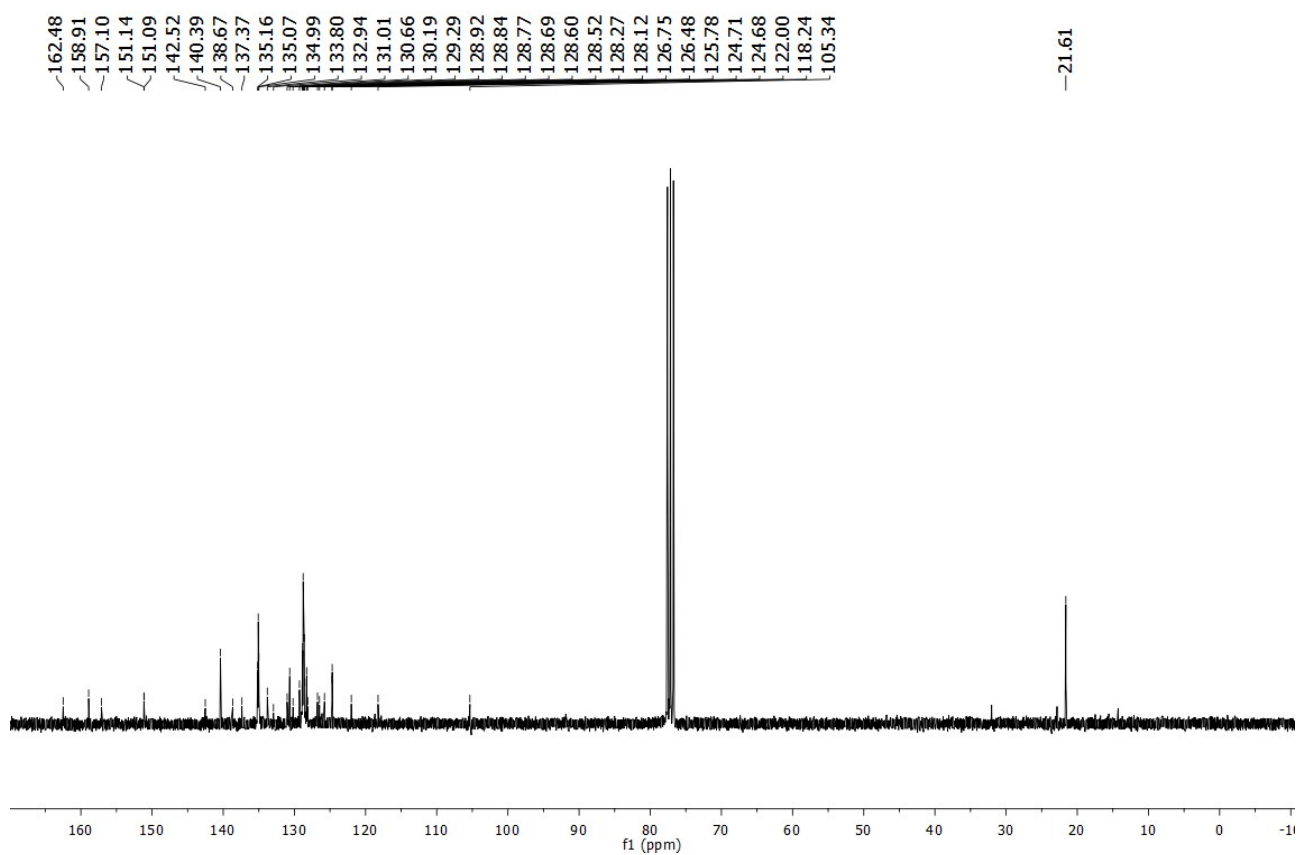
131.0, 130.7, 130.2, 129.3, 128.9, 128.8, 128.8, 128.7, 128.6, 128.5, 128.3, 128.1, 126.8, 126.5, 125.8, 124.7, 124.7, 122.0, 118.2, 105.3, 21.6 ^[18]; ³¹P (121 MHz): 16.46 (s, ¹J_{PtP} = 2593 Hz) ^[17]; IR (ATR, cm⁻¹): 3024, 2920, 2094, 1652, 1575, 1498, 1099, 805, 762, 697; HRMS (ESI): m/z, calculated for M⁺ (C₈₆H₇₀N₂OP₂S¹⁹⁵Pt): 1435.4326, found: 1435.4294.

¹H NMR - CDCl₃ - 300 MHz - 20°C

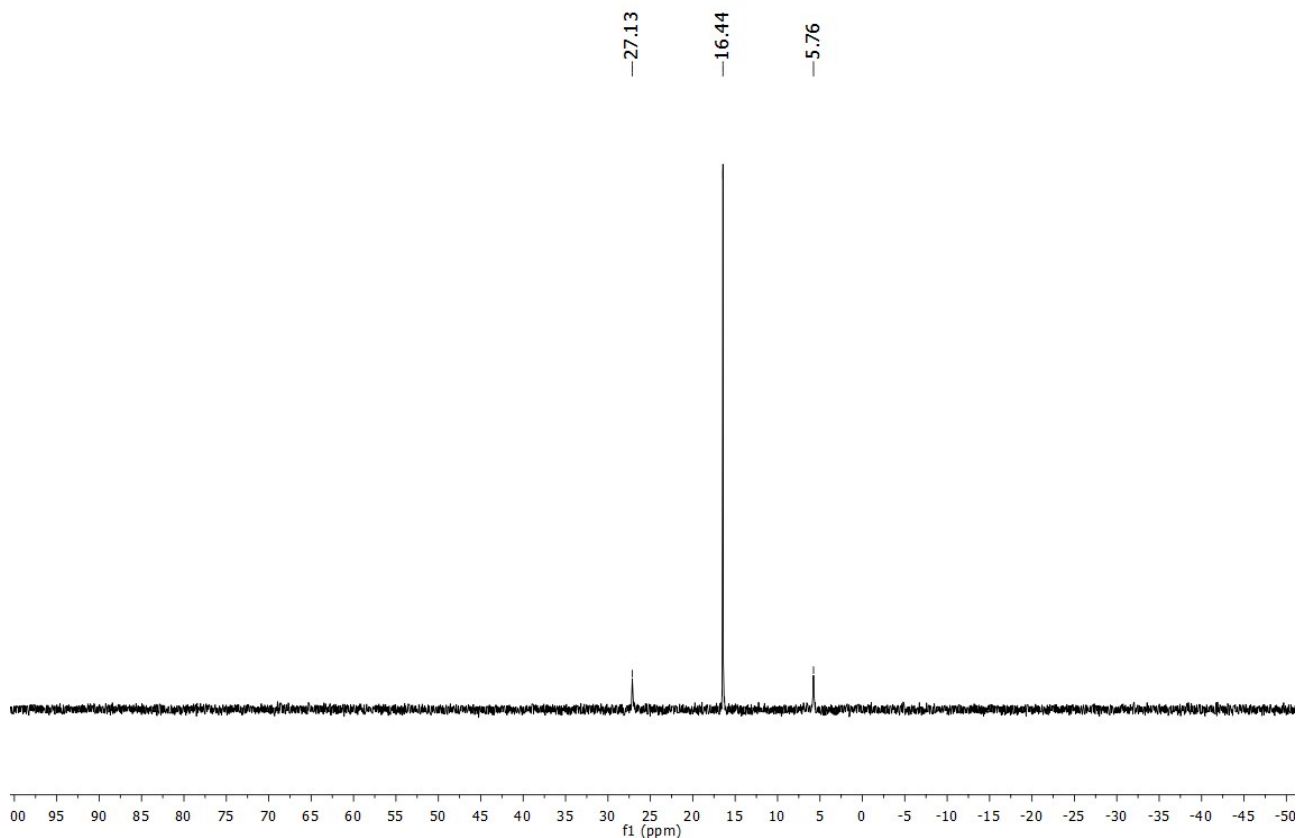


Spectrum 15: ¹H NMR spectrum of compound **2** (300 MHz, CDCl₃)

^{13}C NMR - CDCl_3 - 75 MHz - 20°C

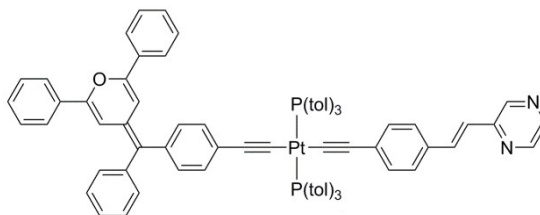


Spectrum 16: ^{13}C NMR spectrum of compound **2** (75 MHz, CDCl_3)



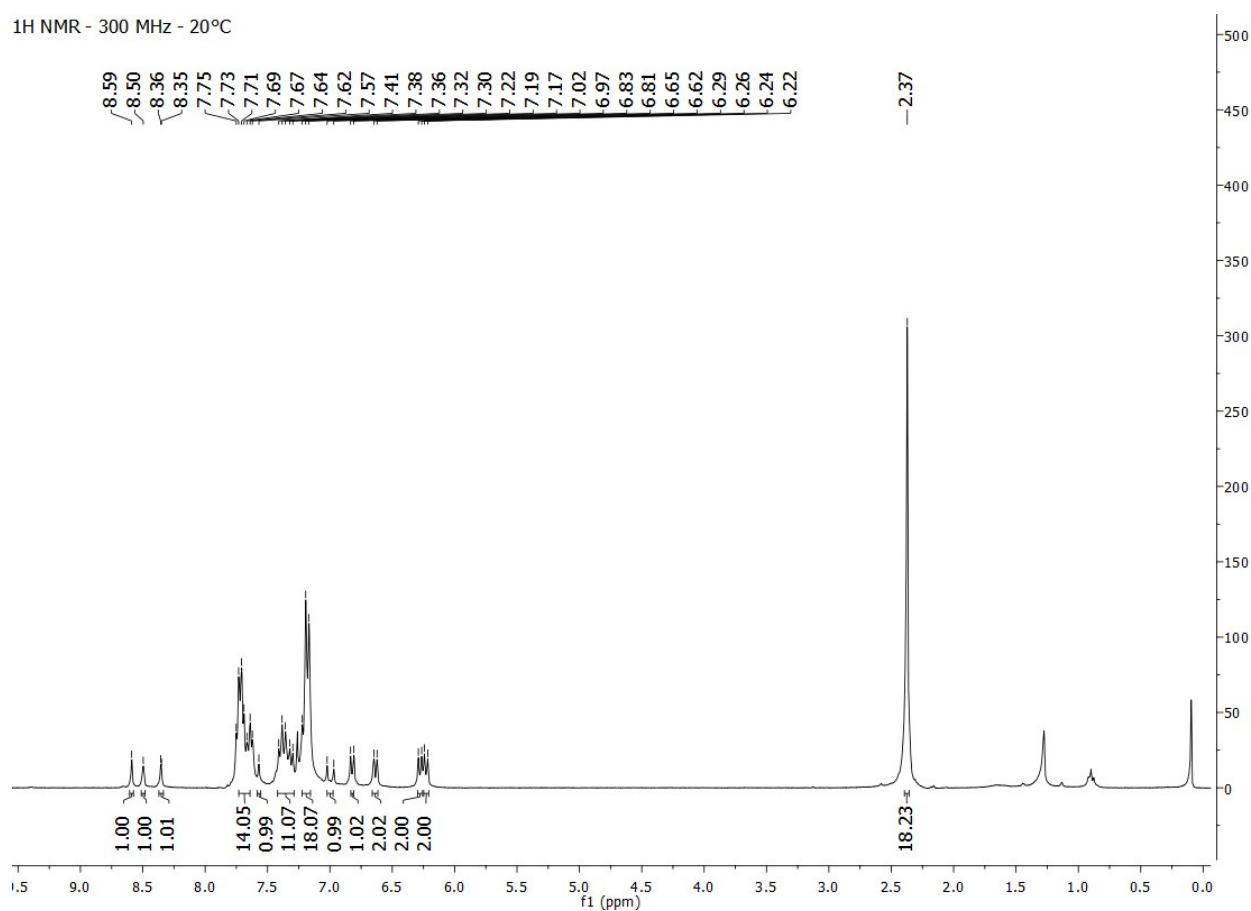
Spectrum 17: ³¹P NMR spectrum of compound **2** (121 MHz, CDCl₃)

Compound 3



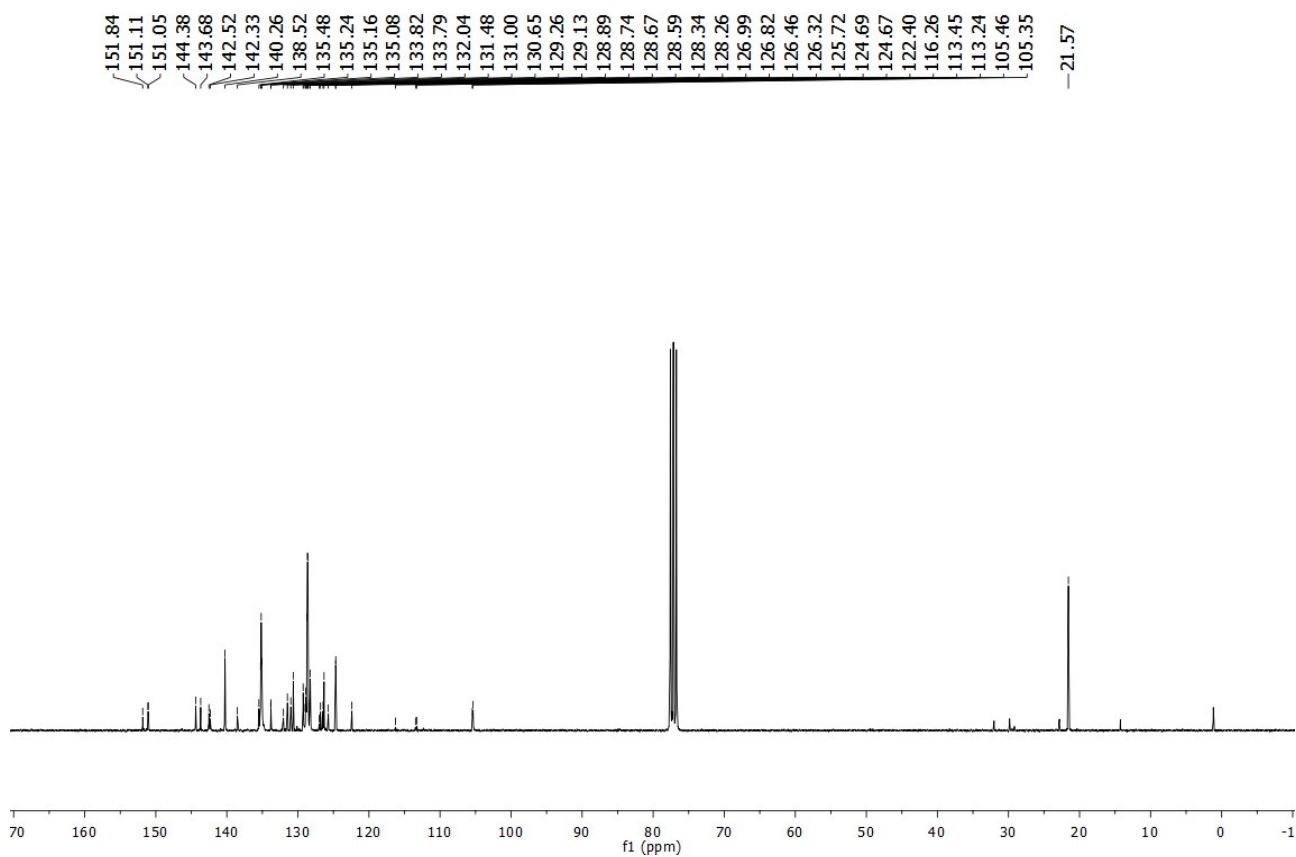
The crude product was purified by column chromatography on silica gel (hexane/dichloromethane, from 1:1 to 0:1) to give a yellow powder. Yield: 220 mg, 65%. mp: 170°C (dec.); NMR (δ (ppm), CDCl₃): ¹H (300 MHz): 8.59 (s, 1H), 8.50 (s, 1H), 8.35 (d, ³J_{HH} = 1.9 Hz, 1H), 7.76 – 7.60 (m, 14H), 7.57 (s, 1H), 7.42 – 7.28 (m, 11H), 7.25 – 7.14 (m, 18H), 7.00 (d, ³J_{HH} = 16.0 Hz, 1H), 6.82 (d, ³J_{HH} = 7.8 Hz, 1H), 6.63 (d, ³J_{HH} = 7.6 Hz, 2H), 6.28 (d, ³J_{HH} = 8.0 Hz, 2H), 6.23 (d, ³J_{HH} = 7.9

Hz, 2H), 2.37 (s, 18H); $^{13}\text{C}\{^1\text{H}\}$ (75 MHz): 151.8, 151.1, 151.1, 144.4, 143.7, 142.5, 142.3, 140.3, 138.5, 135.5, 135.2, 135.2, 135.1, 133.8, 133.8, 132.0, 131.5, 131.0, 130.7, 129.3, 129.1, 128.9, 128.7, 128.7, 128.6, 128.3, 128.3, 127.0, 126.8, 126.5, 126.3, 125.7, 124.7, 124.7, 122.4, 116.3, 113.4, 113.2, 105.5, 105.3, 21.6; ^{31}P (121 MHz): 16.84 (s, $^1J_{\text{PtP}} = 2617$ Hz) ^[17]; IR (ATR, cm^{-1}): 2920, 2097, 1659, 1596, 1498, 1396, 1097, 836, 802, 762, 687; HRMS (ESI): m/z , calculated for M^+ ($\text{C}_{88}\text{H}_{72}\text{N}_2\text{OP}_2^{195}\text{Pt}$): 1429.47623, found: 1429.4765.

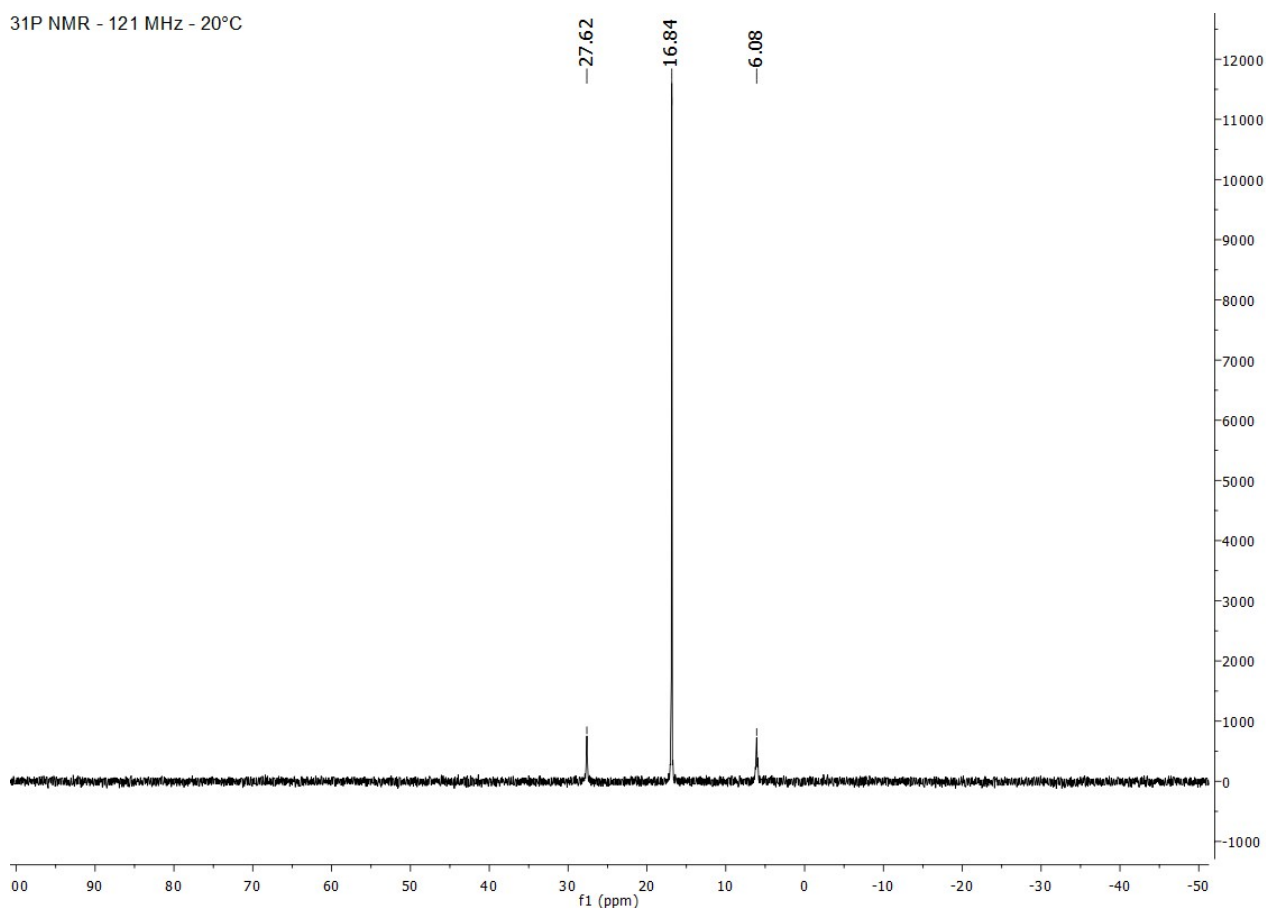


Spectrum 18: ^1H NMR spectrum of compound **3** (300 MHz, CDCl_3)

^{13}C NMR - CDCl_3 - 75 MHz - 20°C

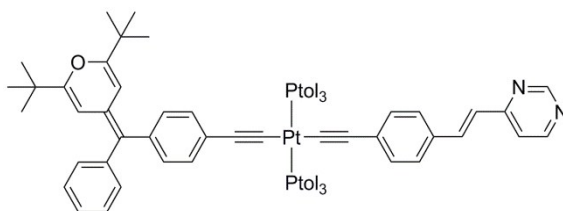


Spectrum 19: ^{13}C NMR spectrum of compound **3** (75 MHz, CDCl_3)



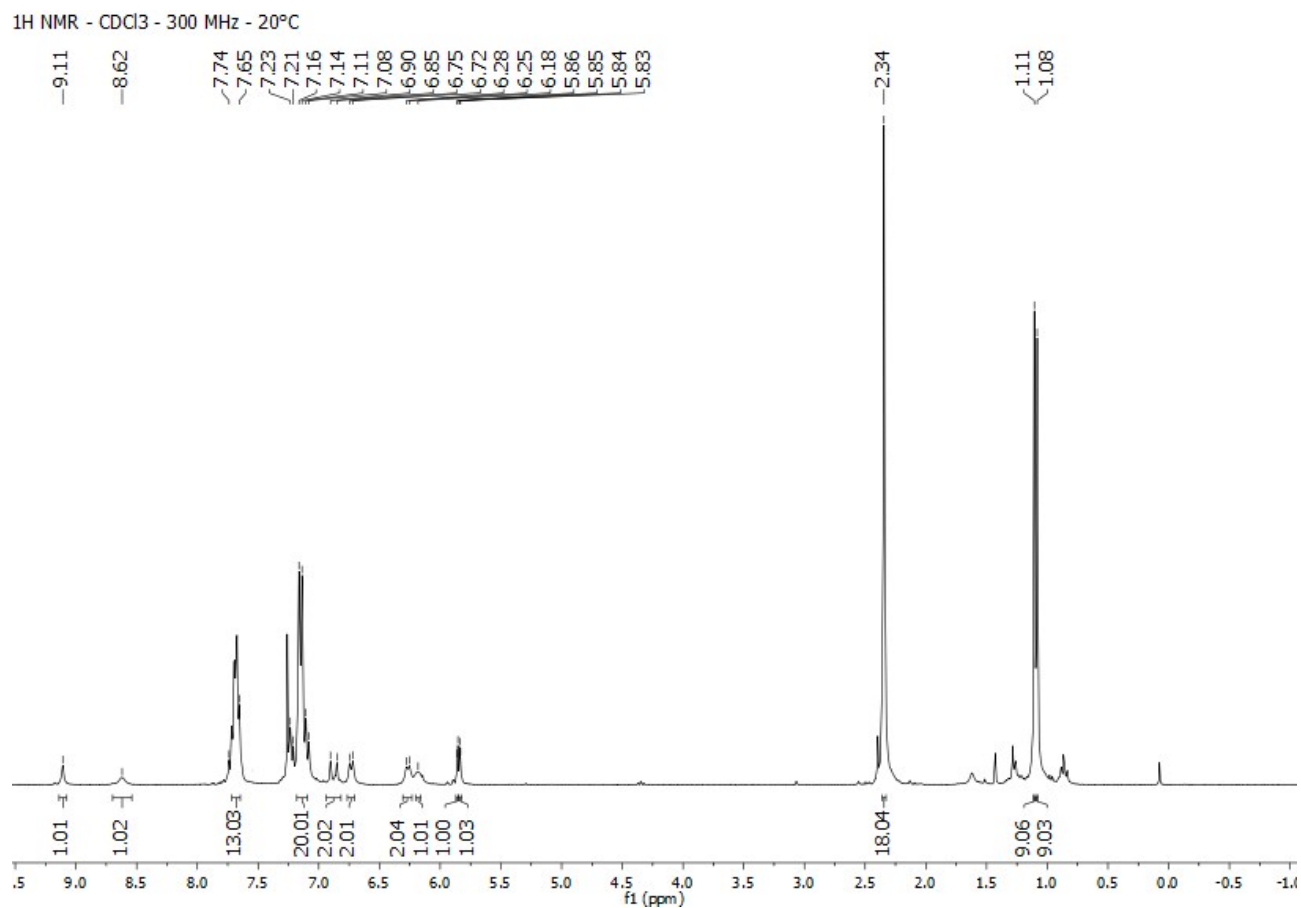
Spectrum 20: ^{31}P NMR spectrum of compound **3** (121 MHz, CDCl_3)

Compound 4



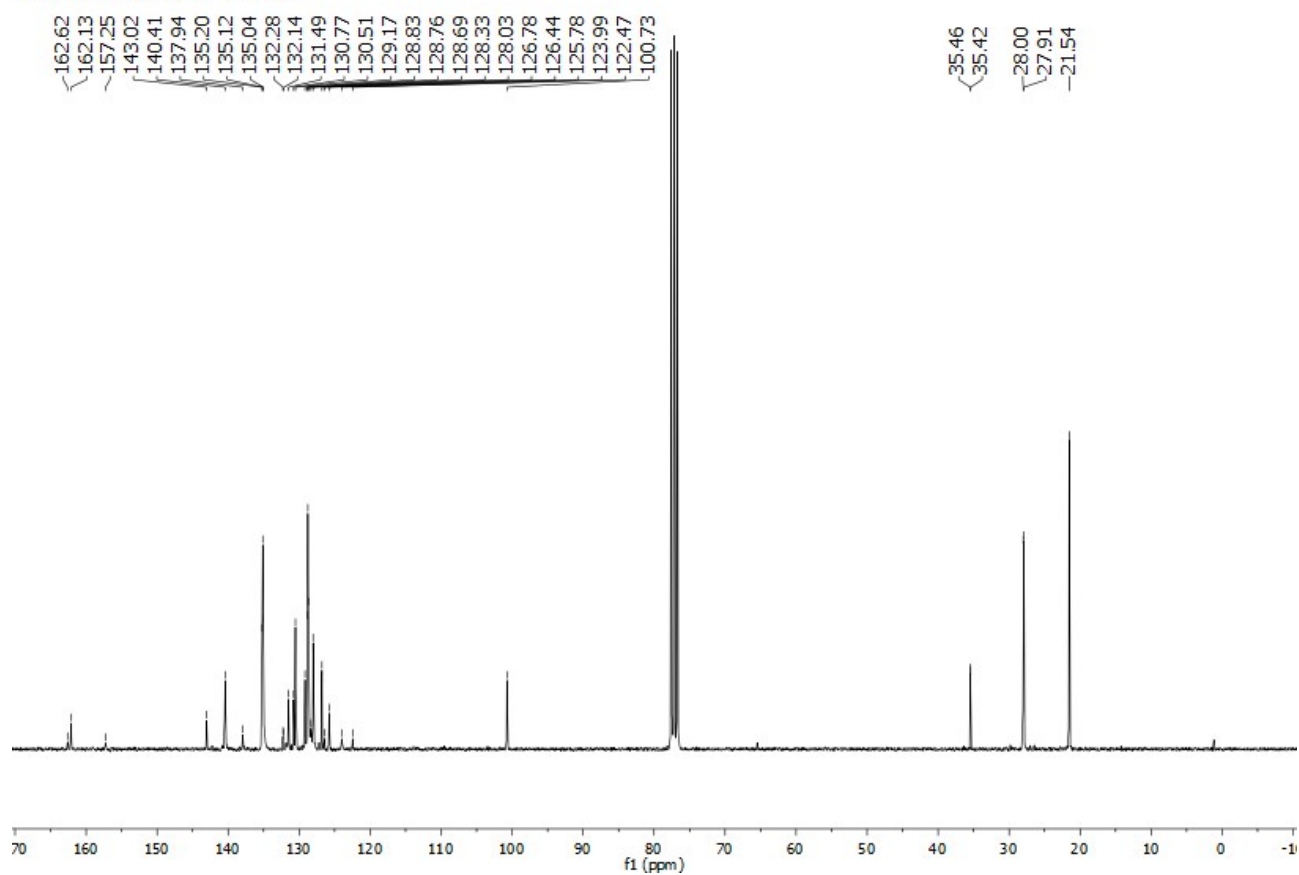
Column chromatography on dried silica gel (petroleum ether/ethyl acetate, from 1:1 to 0:1) to give a bright yellow powder. Yield: 145 mg, 64%. mp: 120°C (dec.); NMR (δ (ppm), CDCl_3): ^1H (300 MHz): 9.11 (s, 1H), 8.62 (s, 1H), 7.77 – 7.60 (m, 13H), 7.25 – 7.04 (m, 20H), 6.88 (d, $^3J_{\text{HH}} = 15.9$ Hz, 2H), 6.73 (d, $^3J_{\text{HH}} = 8.0$ Hz, 2H), 6.27 (d, $^3J_{\text{HH}} = 7.6$ Hz, 2H), 6.18 (s, 1H), 5.86 (d, $^4J_{\text{HH}} = 1.8$ Hz, 1H), 5.84 (d, $^4J_{\text{HH}} = 1.8$ Hz, 1H), 2.34 (s, 18H), 1.11 (s, 9H), 1.08 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ (75 MHz): 162.6, 162.1, 157.3, 143.0, 140.4, 137.9, 135.2, 135.1, 135.0, 132.3, 132.1, 131.5, 130.8, 130.5, 129.2, 128.8, 128.8, 128.7, 128.3, 128.0, 126.8, 126.4, 125.8, 124.0, 122.5, 100.7, 35.5, 35.4, 28.0,

27.9, 21.5^[18] ; ³¹P (121 MHz): 16.47 (s, ¹J_{PtP} = 2615 Hz) ^[17]; IR (ATR, cm⁻¹): 3022, 2958, 2866, 2103, 1672, 1571, 1100, 802, 706; HRMS (ESI): m/z, calculated for M⁺ (C₈₄H₈₀N₂OP₂¹⁹⁵Pt): 1389.5388, found: 1389.5387.



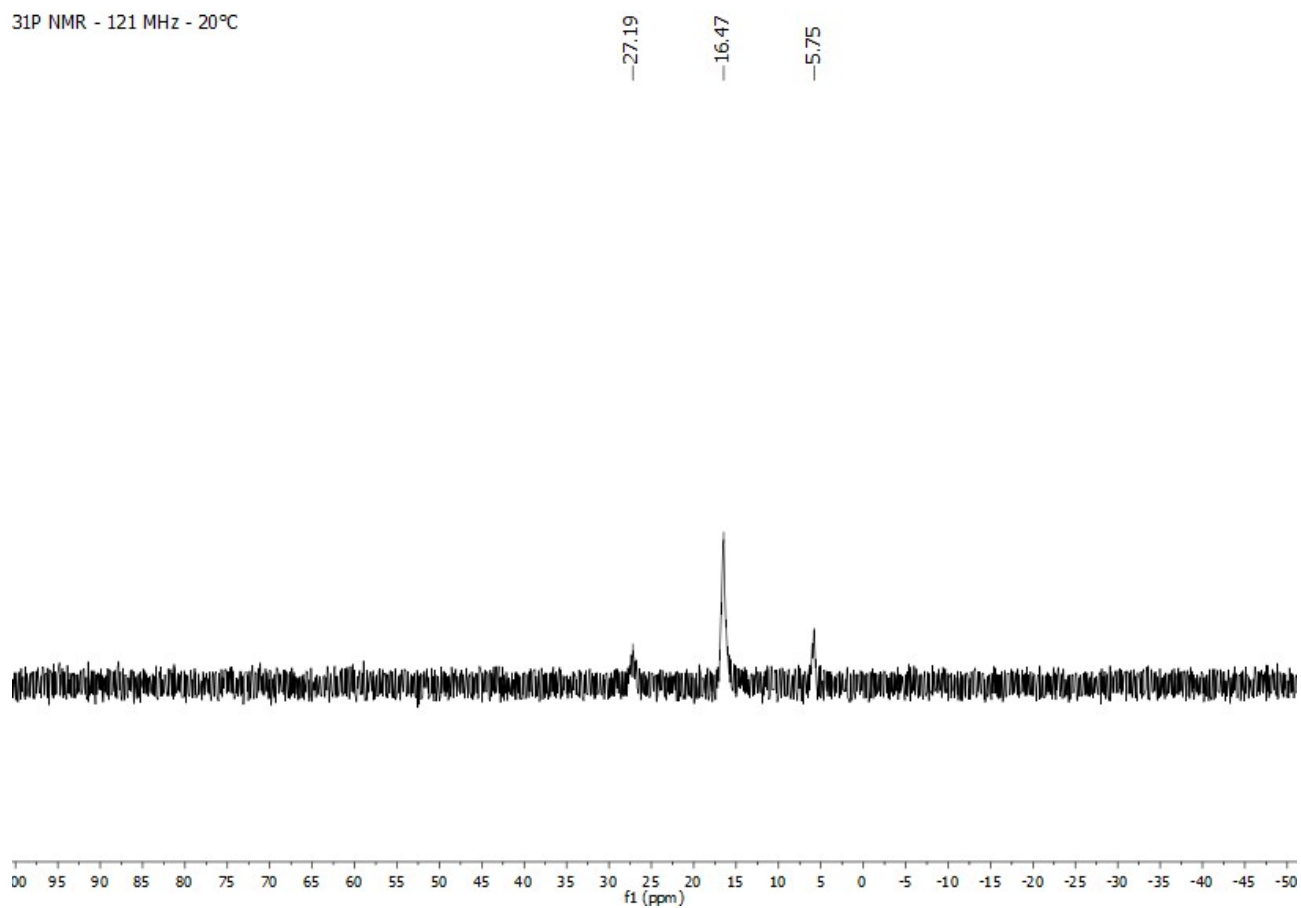
Spectrum 21: ¹H NMR spectrum of compound **4** (300 MHz, CDCl₃)

^{13}C NMR - CDCl_3 - 75 MHz - 20°C



Spectrum 22: ^{13}C NMR spectrum of compound **4** (75 MHz, CDCl_3)

^{31}P NMR - 121 MHz - 20°C



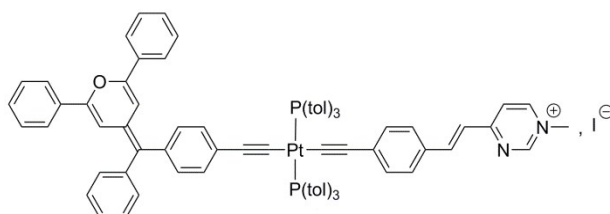
Spectrum 23: ^{31}P NMR spectrum of compound **4** (121 MHz, CDCl_3)

Synthesis of complexes 5-7

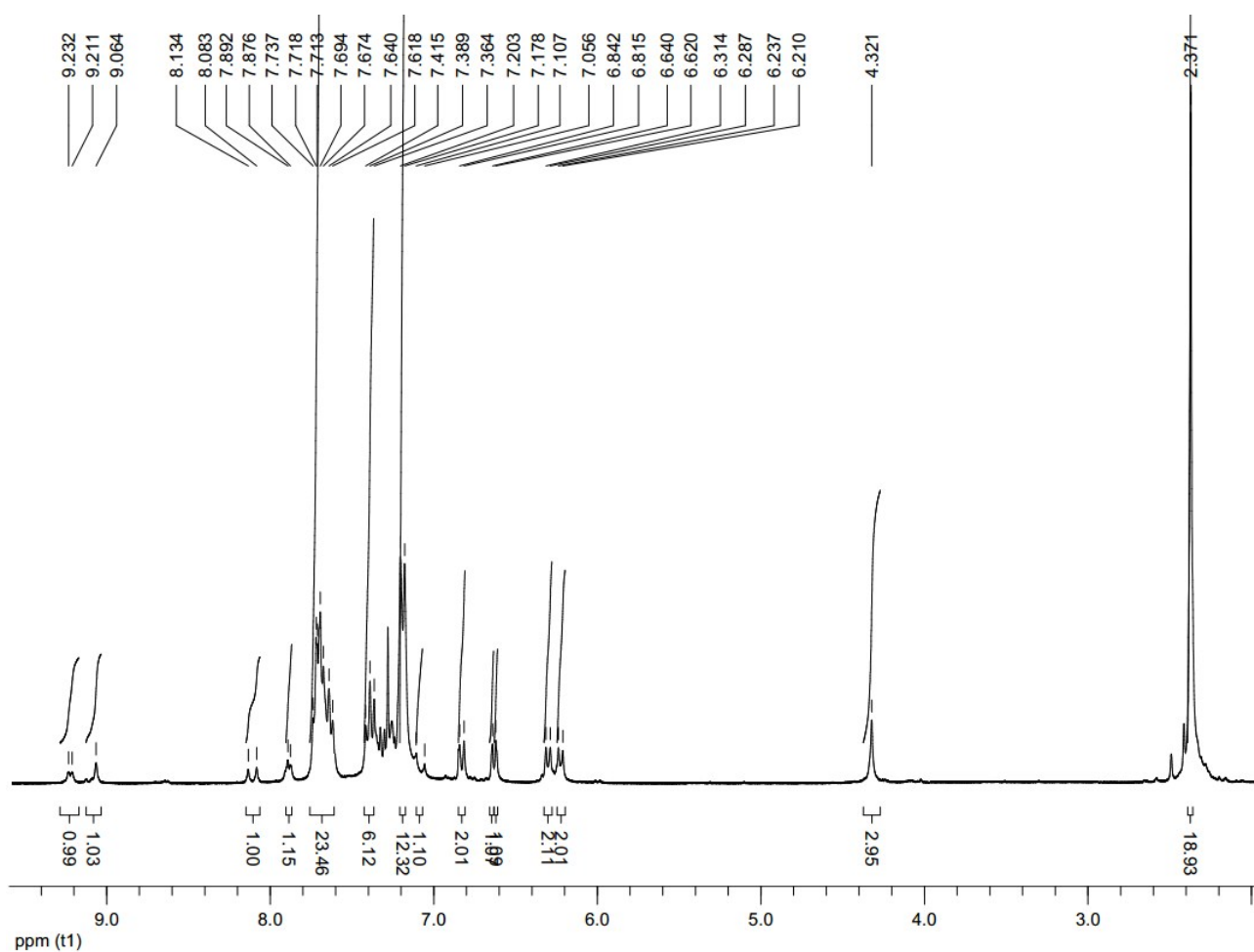
General procedure for the synthesis of Compounds 5-7

A mixture of pyrimidine derivative (0.05 mmol) and methyl iodide (5 mL) was stirred for 4h. The methyl iodide was evaporated under vacuum.

Compound 5

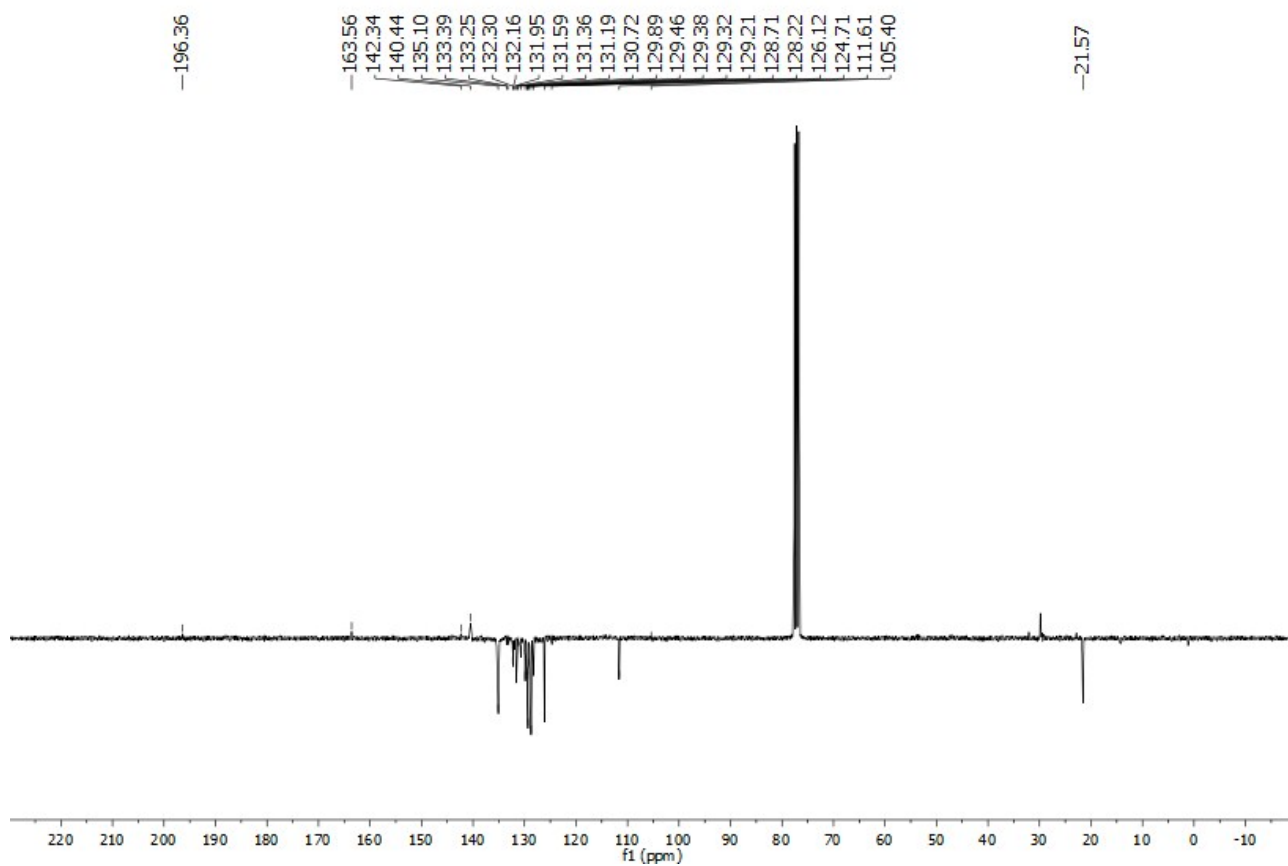


The compound was precipitated from dichloromethane/*n*-hexane to give **6** a dark red powder. Yield: 75 mg, 95%. mp: 130°C (dec.); NMR (δ (ppm), CDCl₃): ¹H (300 MHz): 9.20 (d, ³*J*_{HH} = 6.9 Hz, 1H), 9.04 (s, 1H), 8.09 (d, ³*J*_{HH} = 15.3 Hz, 1H), 7.87 (d, ³*J*_{HH} = 6.9 Hz, 1H), 7.73 – 7.51 (m, 24H), 7.45 – 7.27 (m, 6H), 7.25 – 7.11 (m, 13H), 7.06 (d, ³*J*_{HH} = 15.5 Hz, 1H), 6.81 (d, ³*J*_{HH} = 8.2 Hz, 2H), 6.62 (s, 1H), 6.60 (s, 1H), 6.28 (d, ³*J*_{HH} = 8.1 Hz, 2H), 6.20 (d, ³*J*_{HH} = 8.1 Hz, 2H), 4.30 (s, 3H), 2.35 (s, 18H); ¹³C{H} (75 MHz): 196.4, 163.6, 142.3, 140.4, 135.1, 133.4, 133.2, 132.3, 132.2, 132.0, 131.6, 131.4, 131.2, 130.7, 129.9, 129.5, 129.4, 129.3, 129.2, 128.7, 128.2, 126.1, 124.7, 111.6, 105.4, 47.0, 21.6 ^[18]; ³¹P (121 MHz): 16.78 (s, ¹*J*_{PtP} = 2596 Hz) ^[17]; IR (ATR, cm⁻¹): 3021, 2962, 2098, 1652, 1578, 1169, 1096, 1018, 799; HRMS (ESI): *m/z*, calculated for M⁺ (C₈₉H₇₅N₂OP₂¹⁹⁵Pt): 1444.4997, found: 1444.5014

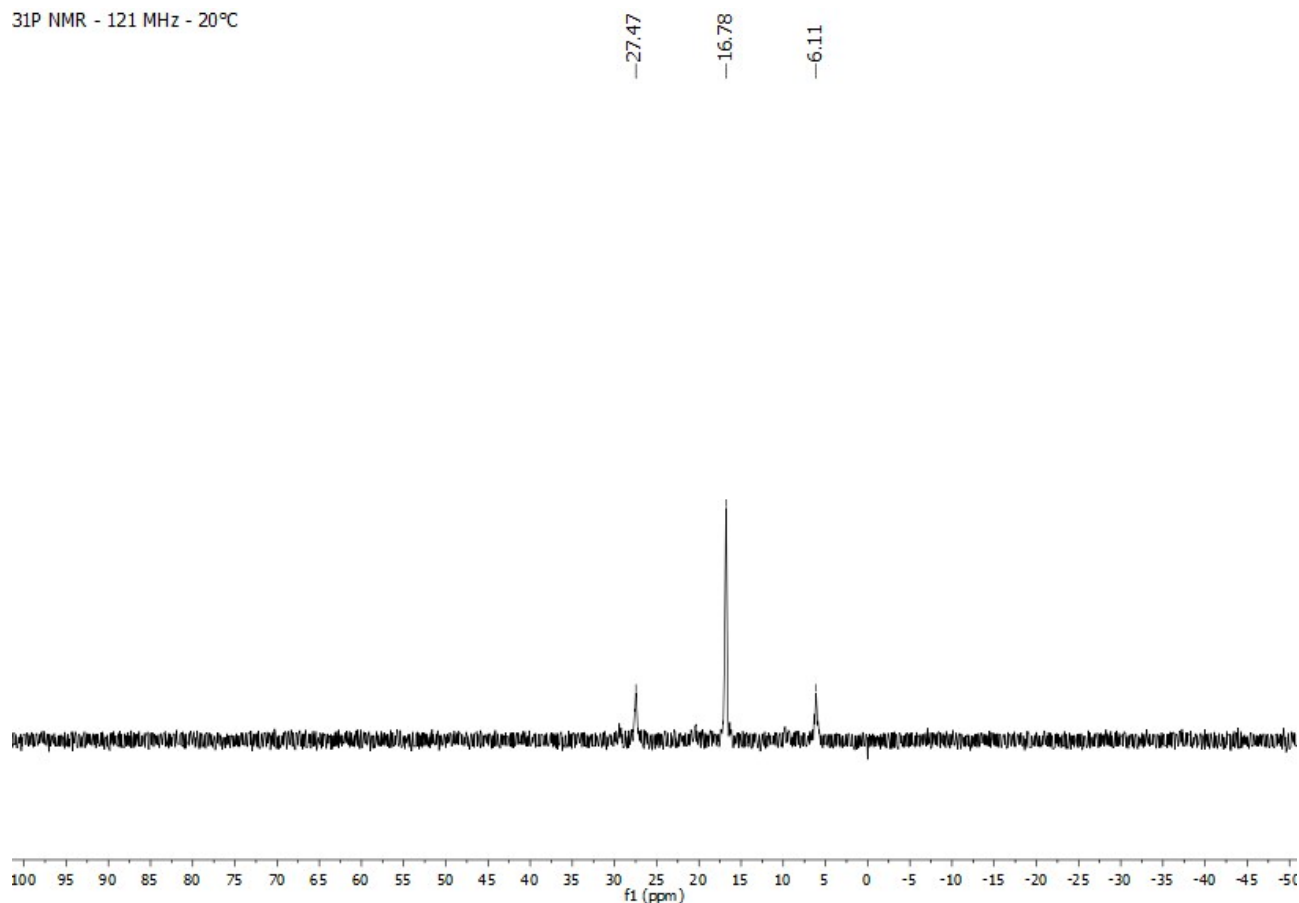


Spectrum 24: ^1H NMR spectrum of compound **5** (300 MHz, CDCl_3)

^{13}C NMR - CDCl_3 - 75 MHz - 20°C

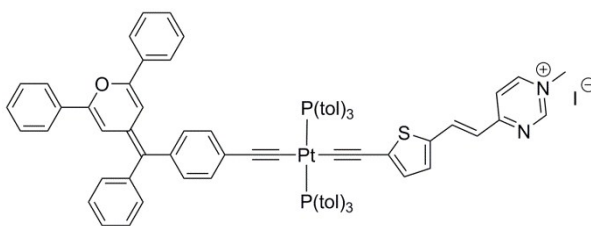


Spectrum 25: ^{13}C NMR spectrum of compound **5** (75 MHz, CDCl_3)



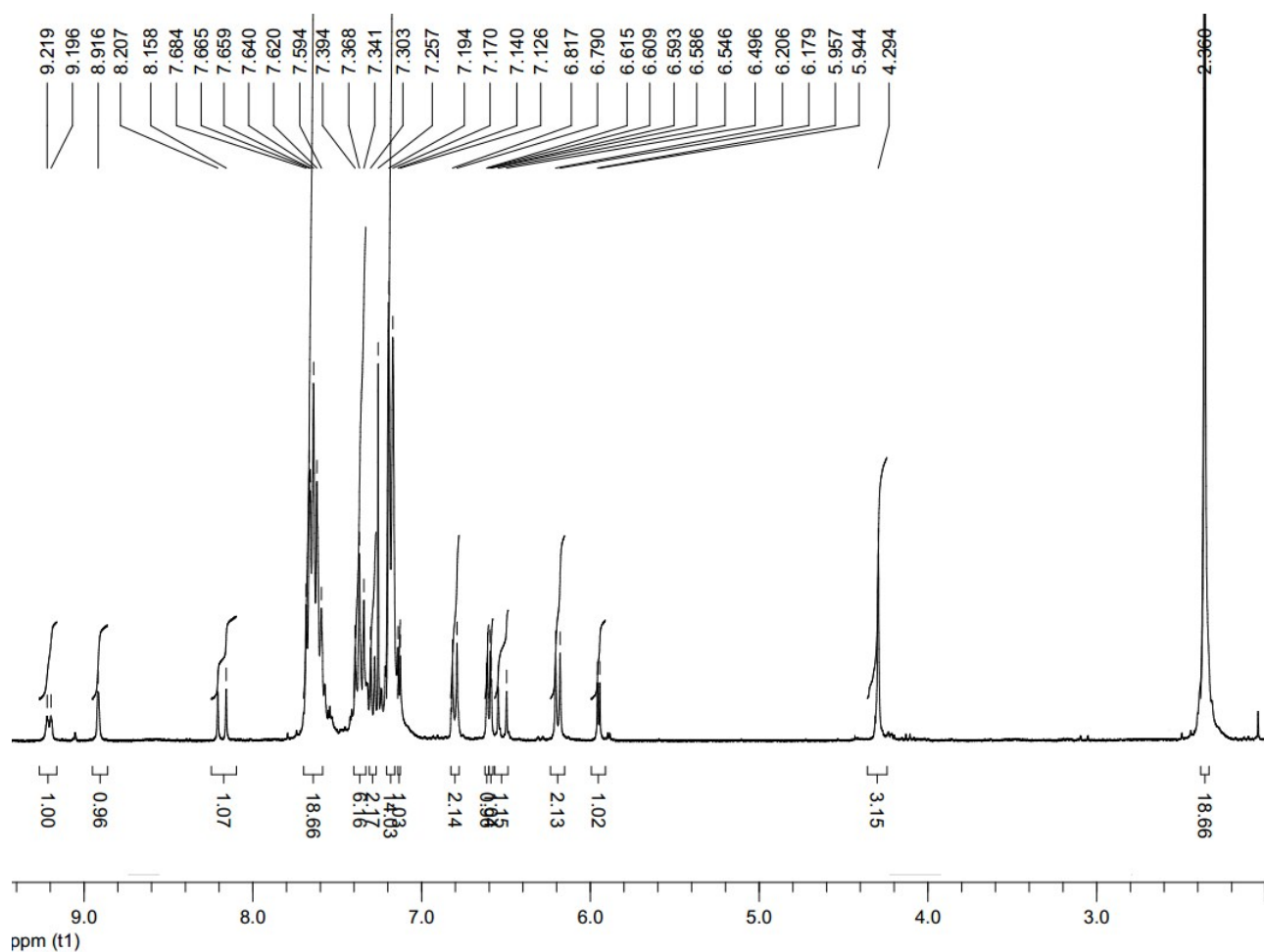
Spectrum 26: ^{31}P NMR spectrum of compound **5** (121 MHz, CDCl_3)

Compound 6



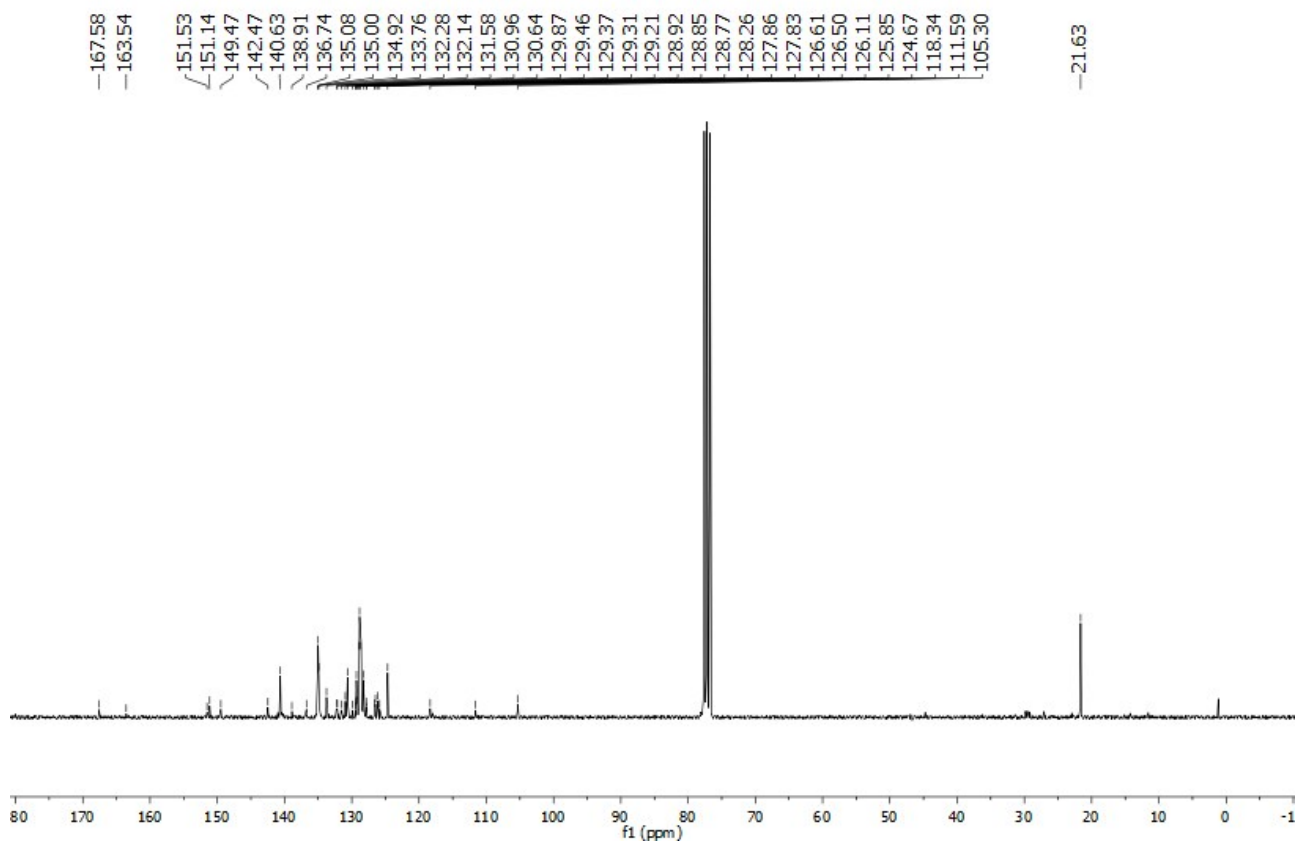
The compound was precipitated from dichloromethane/*n*-heptane to give **6** a dark purple powder. Yield: 73 mg, 91%. mp: 120°C (dec); NMR (δ (ppm), CDCl_3): ^1H (300 MHz): δ = 9.21 (d, $^3J_{\text{HH}}$ = 6.8 Hz, 1H), 8.92 (s, 1H), 8.19 (d, $^3J_{\text{HH}}$ = 14.8 Hz, 1H), 7.70 – 7.58 (m, 18H), 7.41 – 7.33 (m, 6H), 7.29 (d, $^3J_{\text{HH}}$ = 7.5 Hz, 2H), 7.22 – 7.15 (m, 14H), 7.14 (d, $^3J_{\text{HH}}$ = 4.2 Hz, 1H), 6.81 (d, $^3J_{\text{HH}}$ = 8.3 Hz, 2H), 6.61 (d, $^4J_{\text{HH}}$ = 1.9 Hz, 1H), 6.59 (d, $^4J_{\text{HH}}$ = 1.9 Hz, 1H), 6.52 (d, $^3J_{\text{HH}}$ = 14.8 Hz, 1H), 6.20 (d, $^3J_{\text{HH}}$ = 8.2 Hz, 2H), 5.95 (d, $^3J_{\text{HH}}$ = 4.0 Hz, 1H), 4.30 (s, 3H), 2.36 (s, 18H); ^{13}C { ^1H } (75 MHz): δ = 167.6, 163.5, 151.2, 151.1, 149.5, 142.5, 140.8, 140.6, 140.2, 138.9, 136.7, 135.1, 135.0, 134.9,

133.8, 132.3, 132.1, 131.6, 131.0, 130.6, 129.9, 129.5, 129.4, 129.3, 129.2, 128.9, 128.8, 128.8, 128.6, 128.3, 128.3, 127.9, 126.6, 126.5, 126.1, 125.9, 124.7, 118.3, 111.6, 105.3, 105.1, 44.7, 21.6 [18]; ^{31}P (121 MHz): 16,45 (s, $^1J_{\text{PtP}} = 2575$ Hz) [17]; IR (ATR, cm^{-1}): 3021, 2920, 2083, 1651, 1575, 1407, 1275, 1189, 801; HRMS (ESI): m/z , calculated for M^+ ($\text{C}_{87}\text{H}_{73}\text{N}_2\text{OP}_2\text{S}^{195}\text{Pt}$): 1450.4561, found: 1450.4567

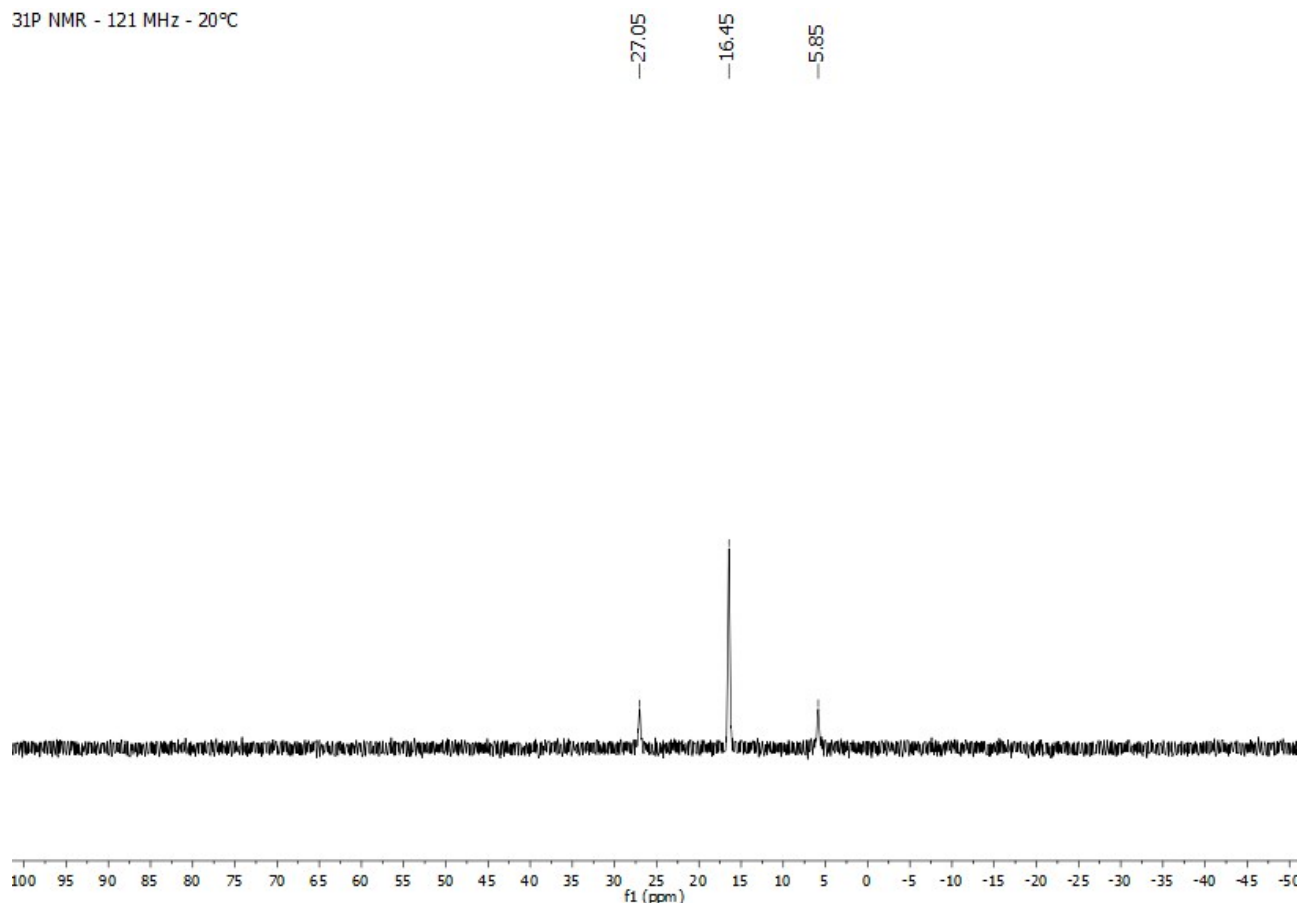


Spectrum 27: ^1H NMR spectrum of compound **6** (300 MHz, CDCl_3)

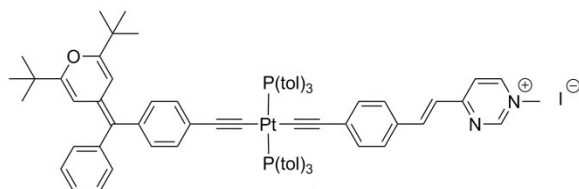
^{13}C NMR - CDCl_3 - 75 MHz - 20°C



Spectrum 28: ^{13}C NMR spectrum of compound **6** (75 MHz, CDCl_3)



Spectrum 29: ^{31}P NMR spectrum of compound **6** (121 MHz, CDCl_3)

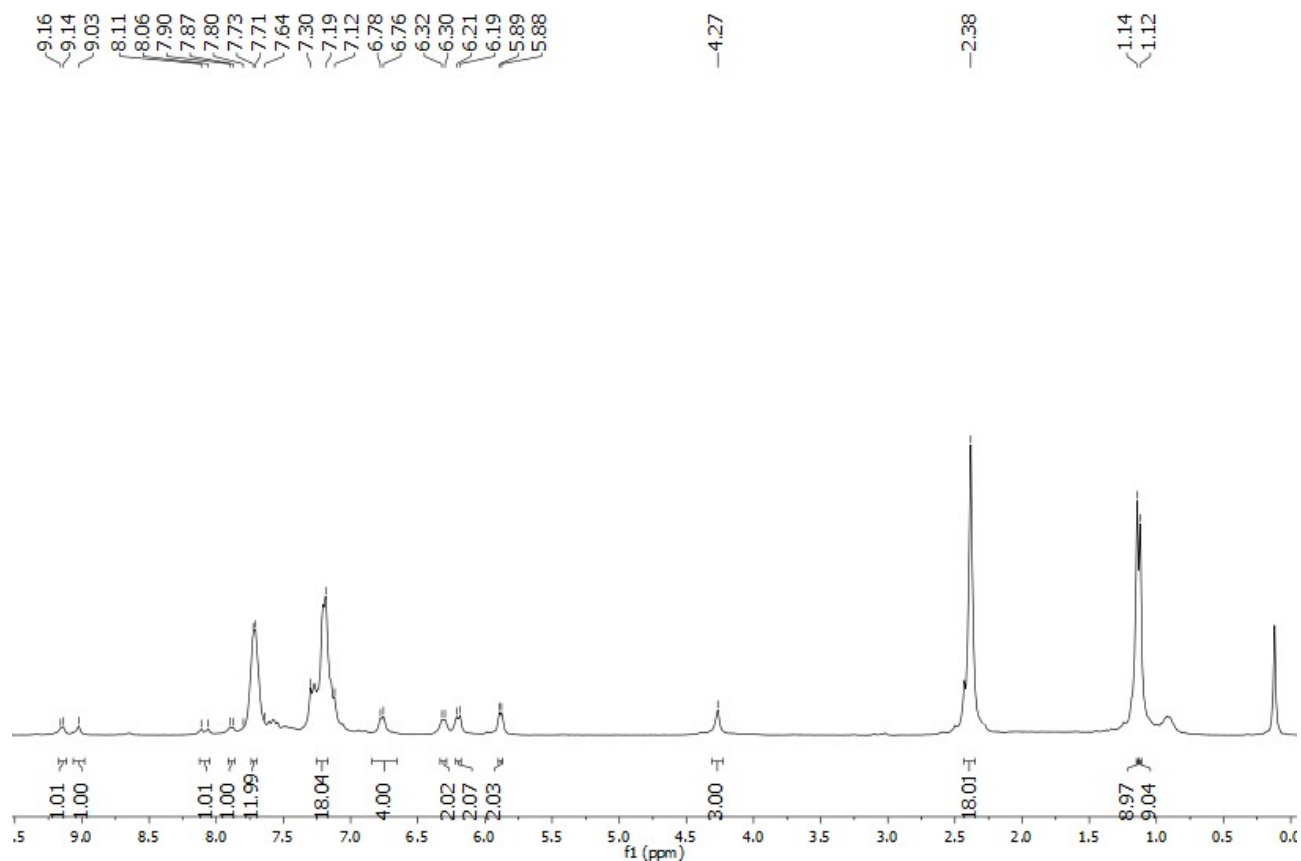


Compound 7

The compound was precipitated from dichloromethane/*n*-hexane to give **7** a dark red powder. Yield: 67 mg, 96%. mp: 135°C (dec) NMR (δ (ppm), CDCl_3): ^1H (300 MHz): 9.15 (d, $^3J_{\text{HH}} = 6.4$ Hz, 1H), 9.03 (s, 1H), 8.09 (d, $^3J_{\text{HH}} = 15.5$ Hz, 1H), 7.89 (d, $^3J_{\text{HH}} = 7.5$ Hz, 1H), 7.81 – 7.63 (m, 12H), 7.33 – 7.09 (m, 18H), 6.77 (d, $^3J_{\text{HH}} = 6.8$ Hz, 4H), 6.31 (d, $^3J_{\text{HH}} = 7.1$ Hz, 2H), 6.20 (d, $^3J_{\text{HH}} = 7.7$ Hz, 2H), 5.89 (s, 1H), 5.88 (s, 1H), 4.27 (s, 3H), 2.38 (s, 18H), 1.14 (s, 9H), 1.12 (s, 9H); ^{13}C NMR (75 MHz): 168.2, 162.1, 151.8, 150.5, 147.6, 143.0, 140.5, 140.3, 140.1, 135.1, 135.0, 134.9, 132.2, 132.1, 131.6, 130.7, 130.5, 129.3, 129.1, 128.8, 128.7, 128.6, 128.4, 128.0, 126.3, 125.7, 122.5, 120.9, 119.6, 114.2, 109.5, 100.7, 45.1, 35.4, 35.4, 27.9, 27.9, 21.6; ^{31}P NMR (121

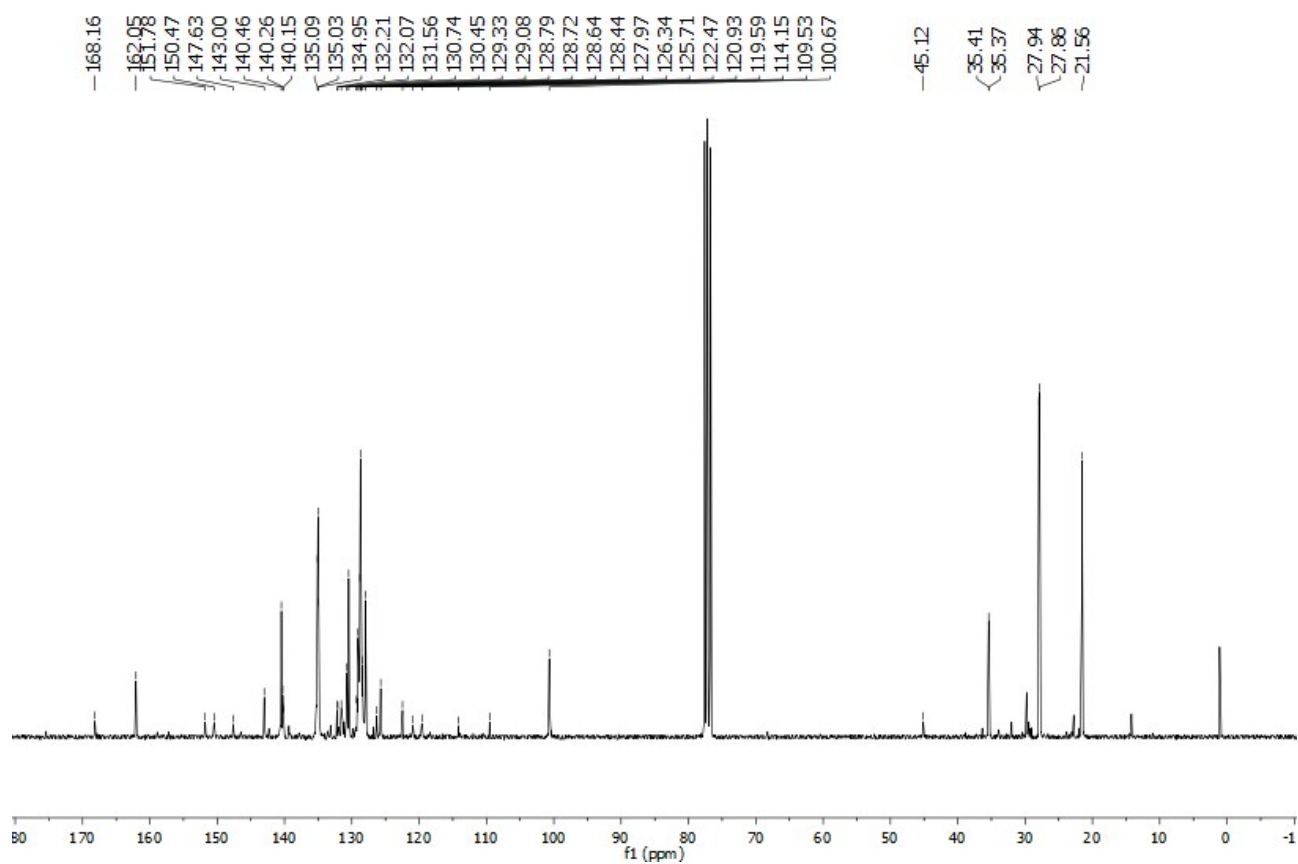
MHz): 16.69 (s, $^1J_{\text{PtP}} = 2602$ Hz) $^{[17]}$; IR (ATR, cm^{-1}): 3021, 2961, 2921, 2867, 2099, 1579, 1471, 1170, 1099, 802; HRMS (ESI): m/z , calculated for M^{++} ($\text{C}_{85}\text{H}_{83}\text{N}_2\text{OP}_2^{195}\text{Pt}$): 1404.5623, found: 1404.5580

^1H NMR - CDCl_3 - 300 MHz - 20°C



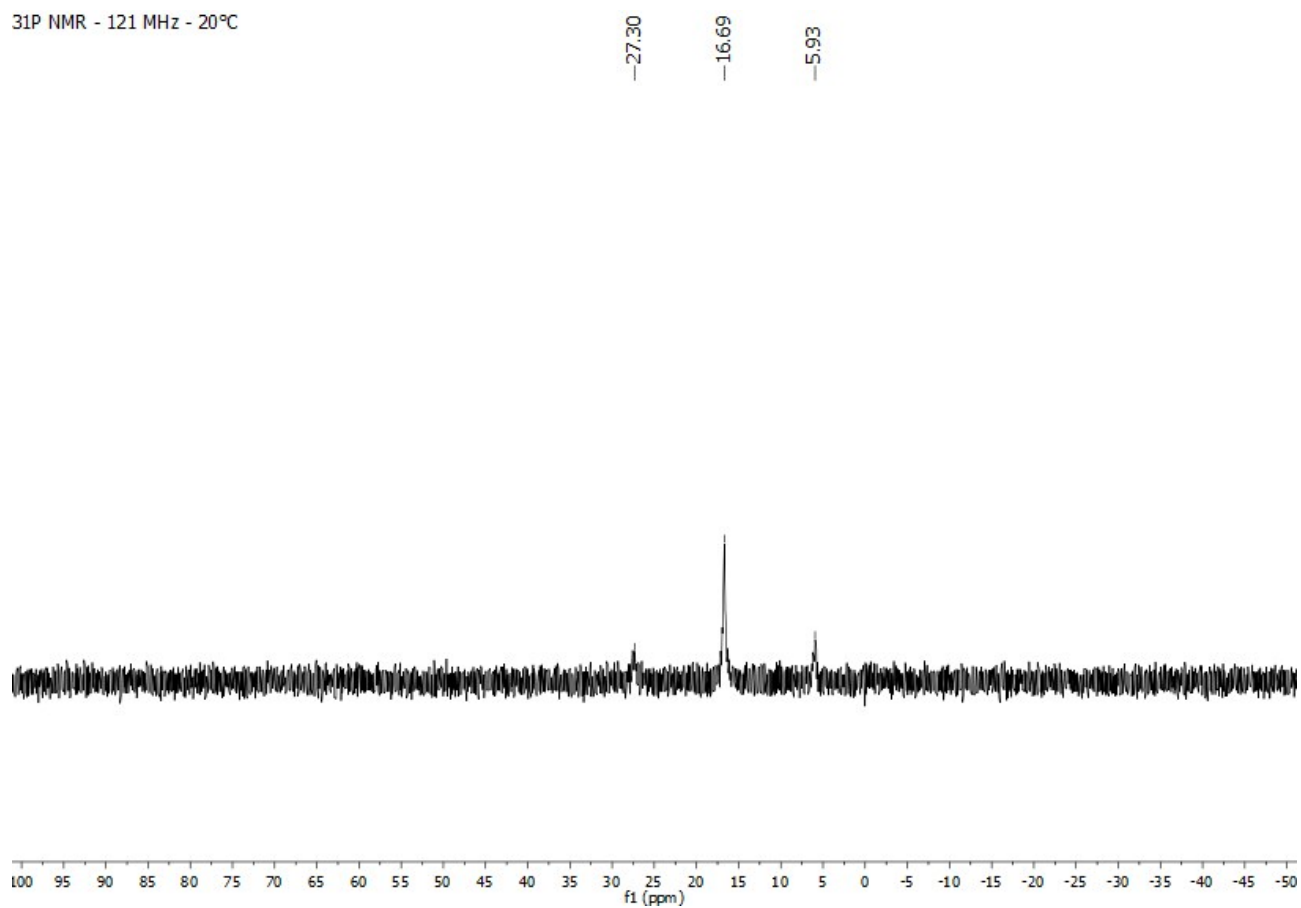
Spectrum 30: ^1H NMR spectrum of compound 7 (300 MHz, CDCl_3)

^{13}C NMR - CDCl_3 - 75 MHz - 20°C



Spectrum 31: ^{13}C NMR spectrum of compound **7** (75 MHz, CDCl_3)

^{31}P NMR - 121 MHz - 20°C



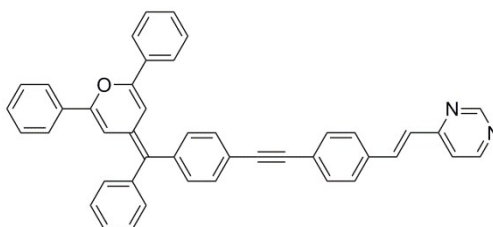
Spectrum 32: ^{31}P NMR spectrum of compound **7** (121 MHz, CDCl_3)

Synthesis of compounds 8 and 9

General procedure for the synthesis of compounds 8 and 9

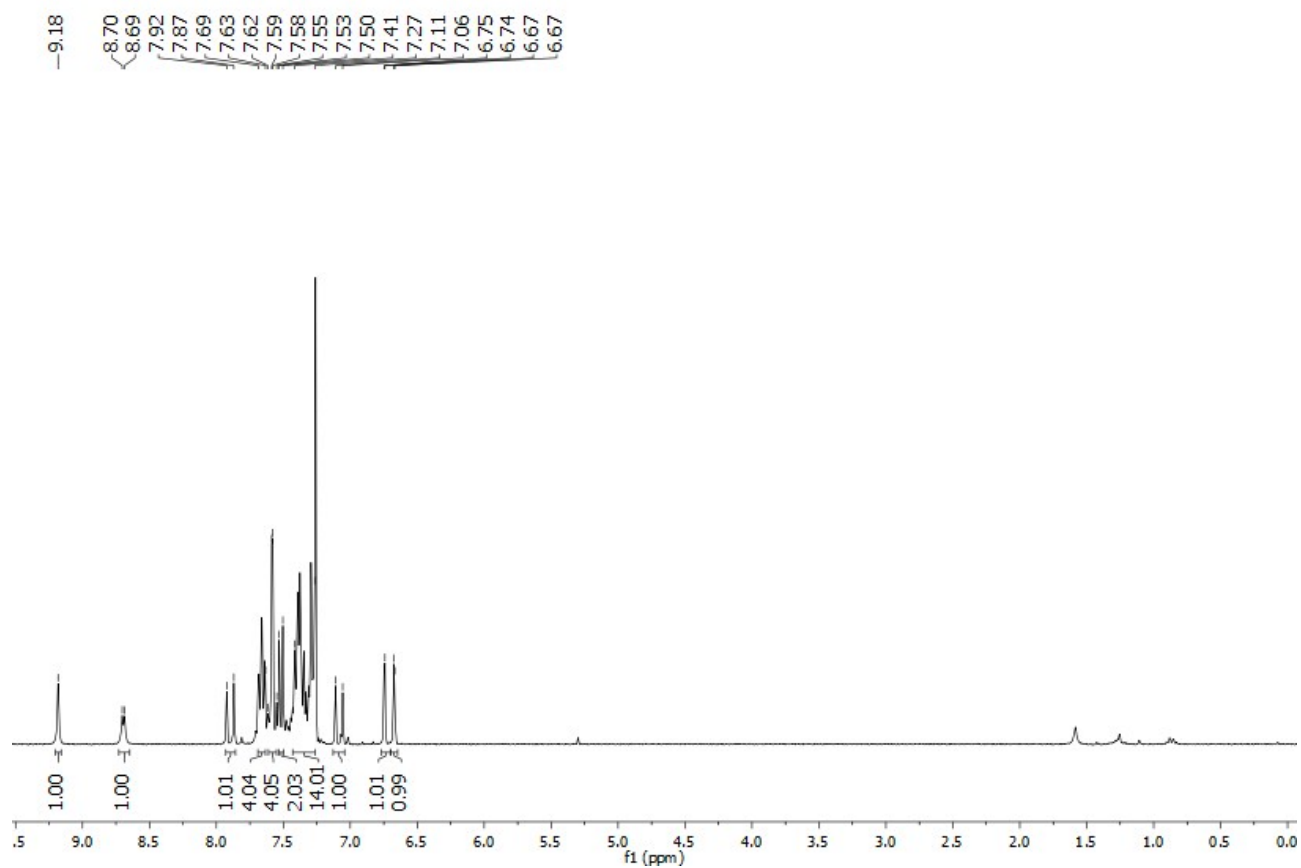
In a Schlenk tube, pyranilidene derivative **12** (418 mg, 1.0 mmol, 1.3 eq), bromodiazine derivative (0.75 mmol, 1 eq), copper iodide (70 mg, 0.35 mmol, 0.5 eq) and PdCl₂(PPh₃)₂ (160 mg, 0.22 mmol, 0.3 eq) were dried under vacuum for 30 minutes. 25 mL of anhydrous THF and 20 mL of diisopropylamine were added and degassed. The mixture was stirred at 60°C overnight under nitrogen atmosphere. The solvent was then removed. The crude material was purified by column chromatography (petroleum ether/ethyl acetate, 1:1 to 0:1). The compound was precipitated from CH₂Cl₂/*n*-heptane and obtained as a powder.

Compound 8



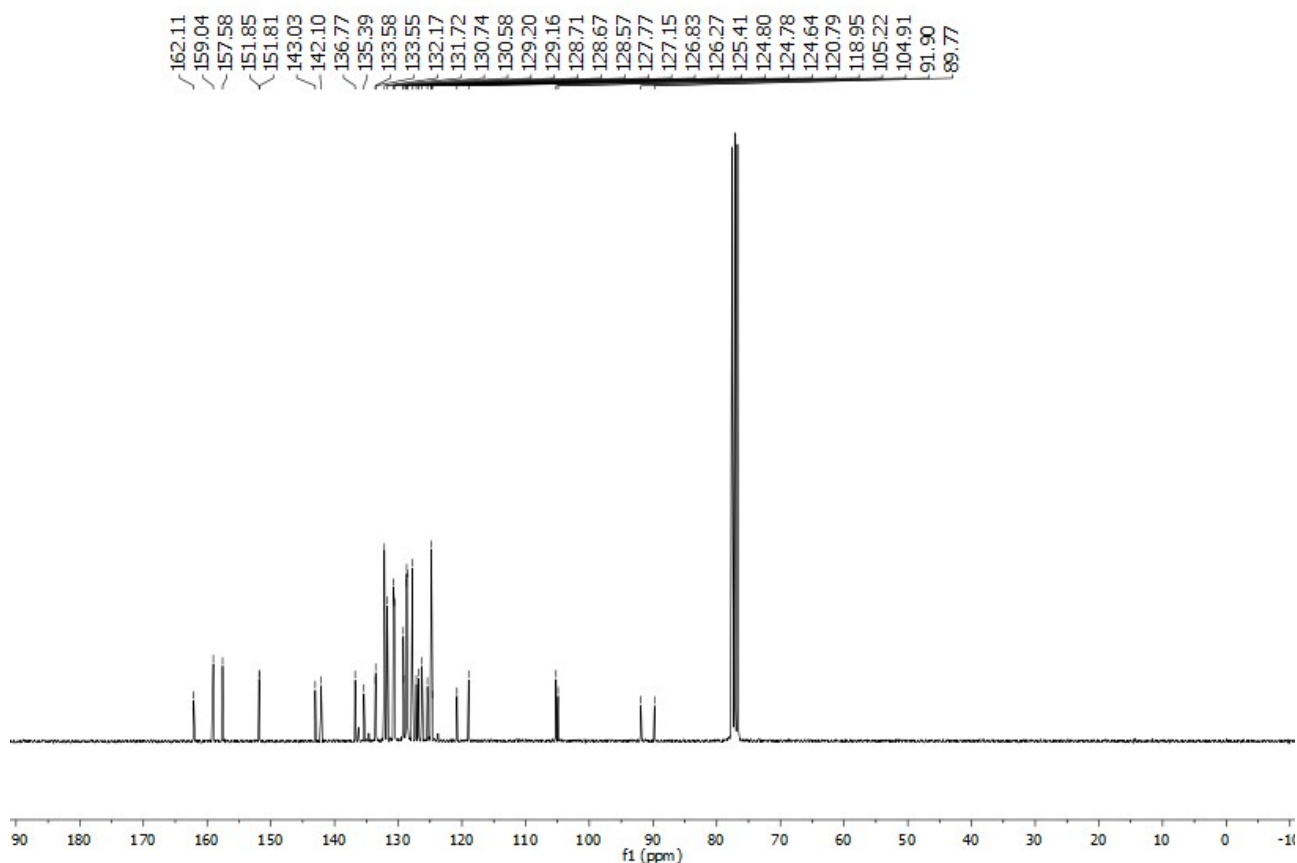
Aspect: orange powder. Yield: 157 mg, 34%. mp = 180°C (dec.); NMR (δ (ppm), CDCl₃): ¹H (300 MHz): 9.18 (s, 1H), 8.69 (d, ³J_{HH} = 5.1 Hz, 1H), 7.90 (d, ³J_{HH} = 16.0 Hz, 1H), 7.70 – 7.63 (m, 4H), 7.63 – 7.54 (m, 4H), 7.52 (d, ³J_{HH} = 8.2 Hz, 2H), 7.45 – 7.27 (m, 14H), 7.08 (d, ³J_{HH} = 16.0 Hz, 1H), 6.74 (d, ⁴J_{HH} = 2.0 Hz, 1H), 6.67 (d, ⁴J_{HH} = 2.0 Hz, 1H); ¹³C{¹H} (75 MHz): 162.1, 159.0, 157.6, 151.8, 151.8, 143.0, 142.1, 136.8, 135.4, 133.6, 133.6, 132.2, 131.7, 130.7, 130.6, 129.2, 129.2, 128.7, 128.7, 128.6, 127.8, 127.2, 126.8, 126.3, 125.4, 124.8, 124.8, 124.6, 120.8, 118.9, 105.2, 104.9, 91.9, 89.8; IR (ATR, cm⁻¹): 3027, 2207, 1662, 1571, 1385, 1064, 834, 691; HRMS (ESI): m/z, calculated for M⁺ (C₄₄H₃₀N₂O): 602.2353, found: 602.2358.

¹H NMR - CDCl₃ - 300 MHz - 20°C



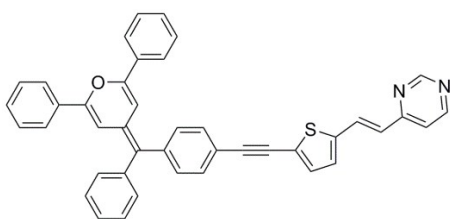
Spectrum 33: ¹H NMR spectrum of compound **8** (300 MHz, CDCl₃)

¹³C NMR - CDCl₃ - 75 MHz - 20°C



Spectrum 34: ¹³C NMR spectrum of compound **8** (75 MHz, CDCl₃)

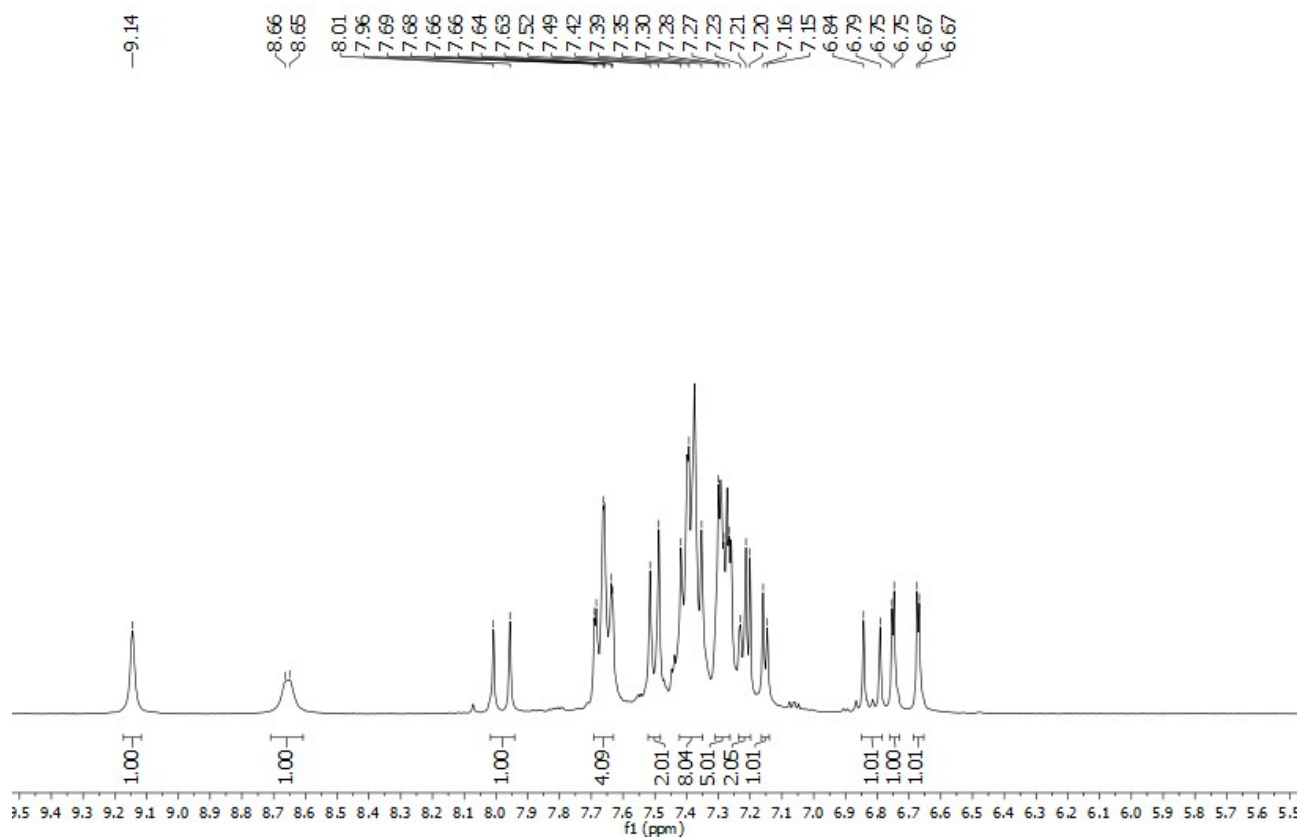
Compound 9



Aspect: red powder. Yield: 120 mg, 26%. mp= 180°C (dec.); NMR (δ (ppm), CDCl₃): ¹H (300 MHz): 9.14 (s, 1H), 8.66 (d, ³J_{HH} = 4.1 Hz, 1H), 7.98 (d, ³J_{HH} = 15.6 Hz, 1H), 7.73 – 7.60 (m, 4H), 7.52 – 7.46 (m, 2H), 7.45 – 7.32 (m, 8H), 7.33 – 7.23 (m, 5H), 7.24 – 7.19 (m, 2H), 7.15 (d, ³J_{HH} = 3.8 Hz, 1H), 6.82 (d, ³J_{HH} = 15.6 Hz, 1H), 6.75 (d, ⁴J_{HH} = 2.0 Hz, 1H), 6.67 (d, ⁴J_{HH} = 2.0 Hz, 1H); ¹³C{¹H} (75 MHz): 161.7, 158.9, 157.5, 151.9, 151.9, 143.3, 142.3, 142.0, 133.5, 133.5, 132.8, 131.5, 130.7, 130.6, 130.0, 129.8, 129.2, 129.2, 128.7, 128.7, 128.6, 127.3, 126.9, 125.3, 125.3,

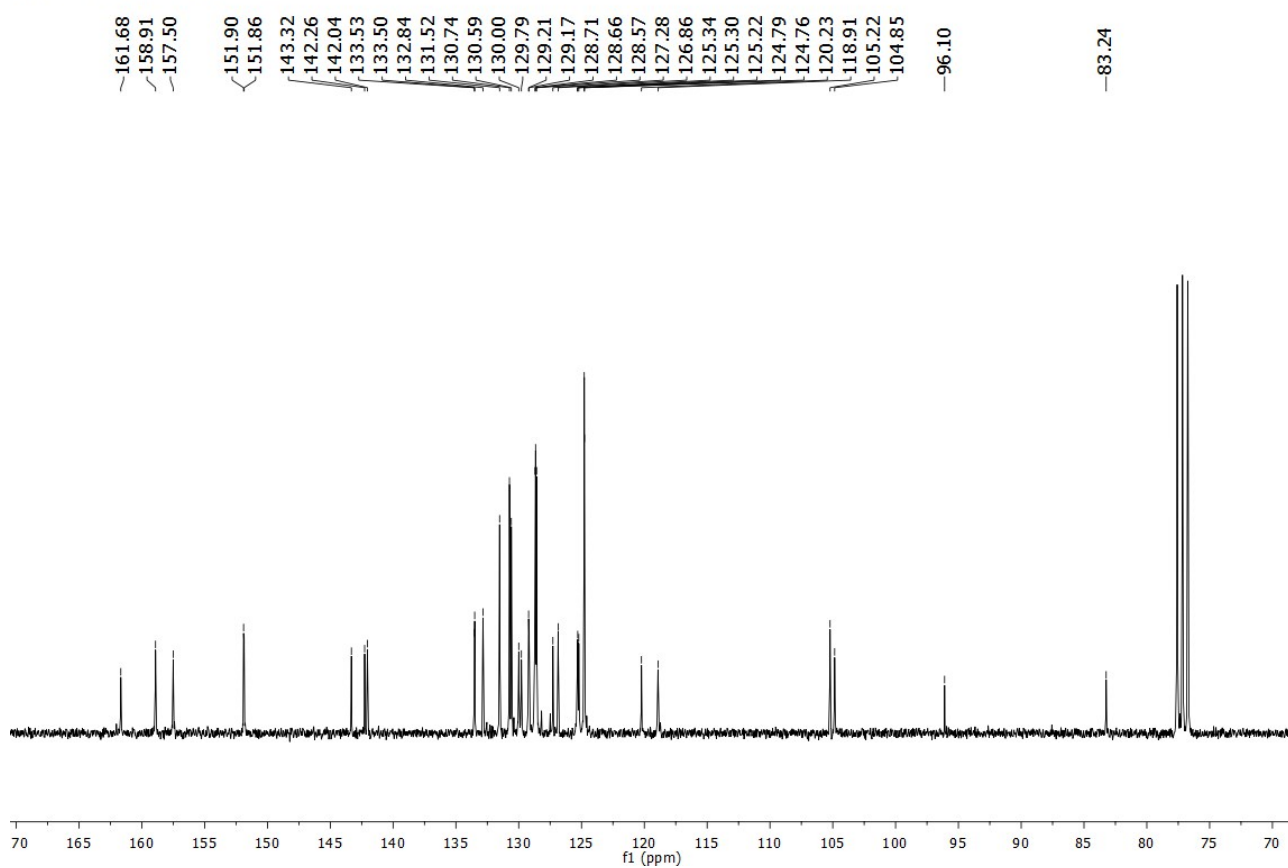
125.2, 124.8, 124.8, 120.2, 118.9, 105.2, 104.8, 96.1, 83.2; IR (ATR, cm^{-1}): 3027, 2196, 1572, 1385, 1166, 953, 841, 763, 693; IR (ATR, cm^{-1}): 3028, 2196, 1653, 1622, 1572, 1384, 1287, 1166, 1075, 953, 841, 763, 693; HRMS (ESI): m/z , calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{42}\text{H}_{29}\text{N}_2\text{OS}$): 609.1996, found: 609.1996.

^1H NMR - CDCl_3 - 300 MHz - 20°C



Spectrum 35: ^1H NMR spectrum of compound **9** (300 MHz, CDCl_3)

^{13}C NMR - CDCl_3 - 75 MHz - 20°C



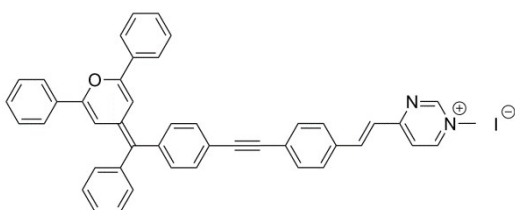
Spectrum 36: ^{13}C NMR spectrum of compound **9** (75 MHz, CDCl_3)

Synthesis of compounds 10 and 11

General procedure for the synthesis of compounds 10 and 11

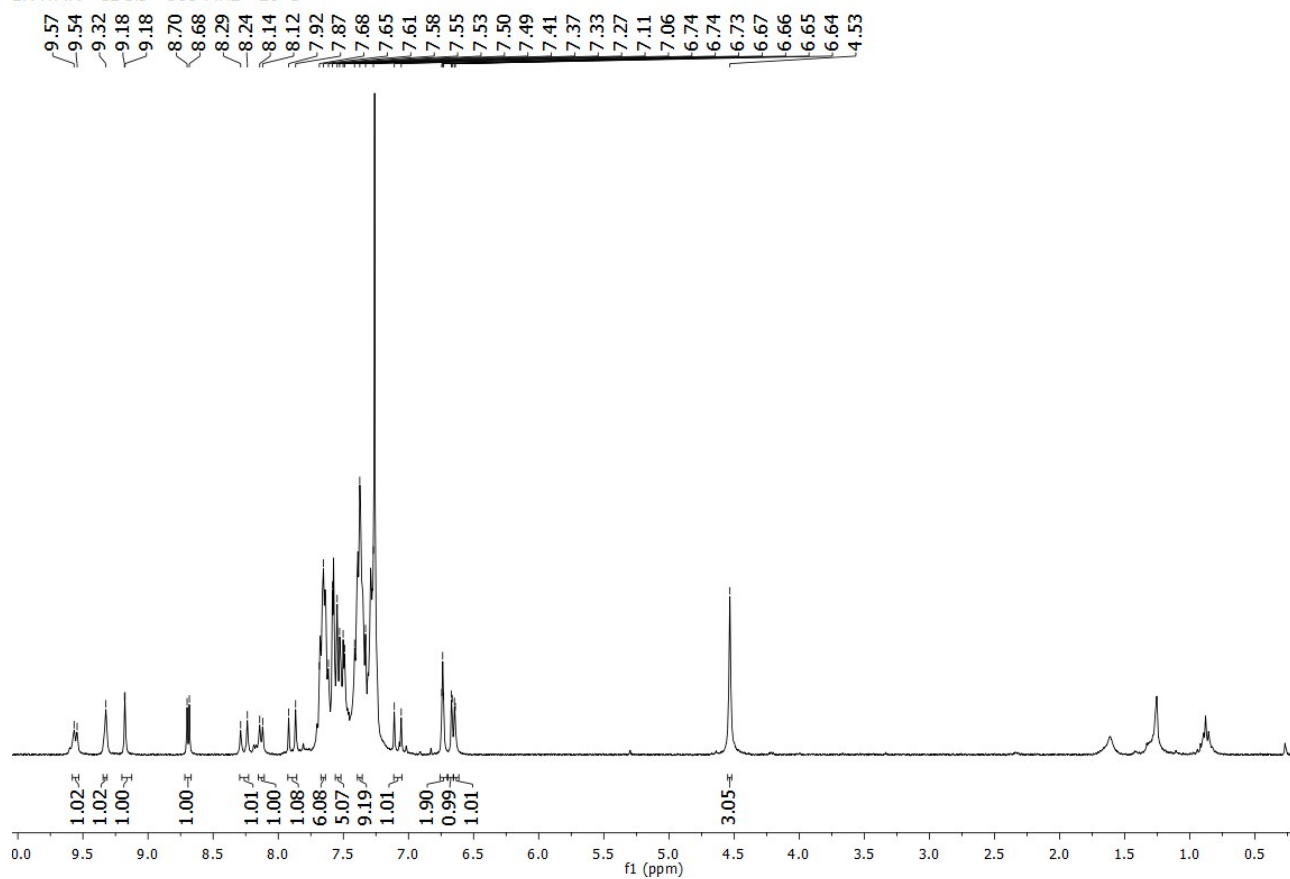
A mixture of pyrimidine derivative (0.05 mmol) and methyl iodide (5 mL) was refluxed for 4h. The methyl iodide was evaporated under vacuum. The product was then precipitated from dichloromethane/hexane.

Compound 10



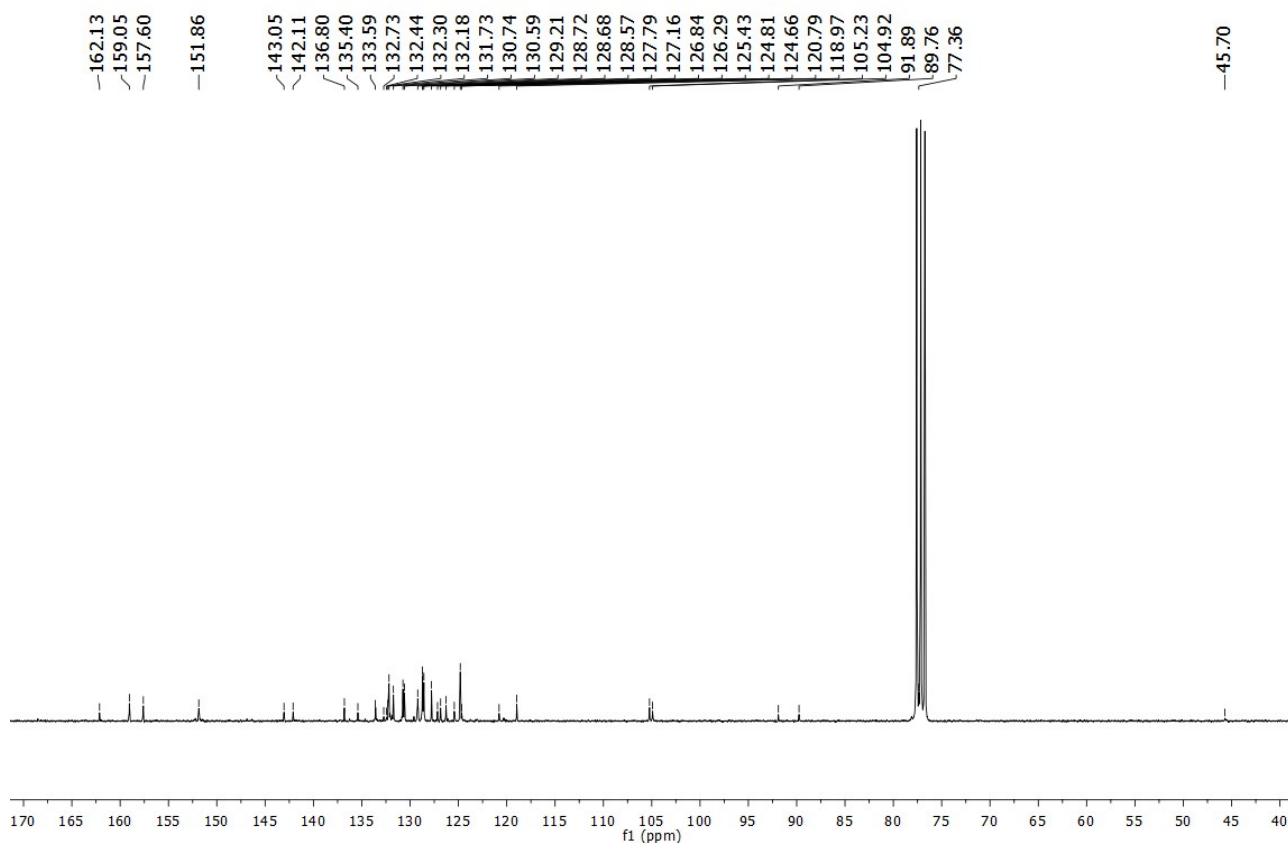
Aspect: dark powder. Yield: 115 mg, 93%. mp = 230°C (dec.). NMR (δ (ppm), CDCl_3): ^1H (300 MHz): 9.56 (d, $^3J_{\text{HH}} = 7.0$ Hz, 1H), 9.32 (s, 1H), 9.18 (d, $^3J_{\text{HH}} = 1.3$ Hz, 1H), 8.69 (d, $^3J_{\text{HH}} = 5.2$ Hz, 1H), 8.26 (d, $^3J_{\text{HH}} = 15.4$ Hz, 1H), 8.13 (d, $^3J_{\text{HH}} = 6.9$ Hz, 1H), 7.89 (d, $^3J_{\text{HH}} = 16.0$ Hz, 1H), 7.70 – 7.60 (m, 6H), 7.60 – 7.48 (m, 5H), 7.42 – 7.32 (m, 9H), 7.08 (d, $^3J_{\text{HH}} = 16.0$ Hz, 1H), 6.74 (m, 2H), 6.67 (d, $^4J_{\text{HH}} = 2.0$ Hz, 1H), 6.64 (d, $^4J_{\text{HH}} = 2.0$ Hz, 1H), 4.53 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ (75 MHz): 162.1, 159.0, 157.6, 151.9, 143.0, 142.1, 136.8, 135.4, 133.6, 132.7, 132.4, 132.3, 132.2, 131.7, 130.7, 130.6, 129.2, 128.7, 128.7, 128.6, 127.8, 127.2, 126.8, 126.3, 125.4, 124.8, 124.7, 120.8, 119.0, 105.2, 104.9, 91.9, 89.8, 77.4, 45.7; IR (ATR, cm^{-1}): 3027, 2209, 1654, 1610, 1590, 1575, 1475, 1385, 1179, 840, 764, 694; HRMS: m/z, calculated for $\text{M}^{+\bullet}$ ($\text{C}_{45}\text{H}_{33}\text{N}_2\text{O}$): 617.2587, found: 617.2591.

¹H NMR - CDCl₃ - 300 MHz - 20°C



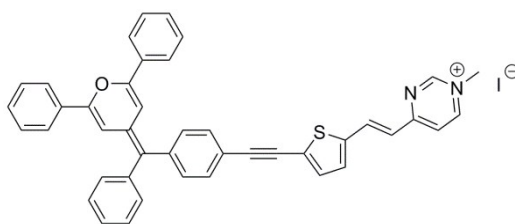
Spectrum 37: ¹H NMR spectrum of compound **10** (300 MHz, CDCl₃)

^{13}C NMR - CDCl_3 - 75 MHz - 20°C



Spectrum 38: ^{13}C NMR spectrum of compound **10** (75 MHz, CDCl_3)

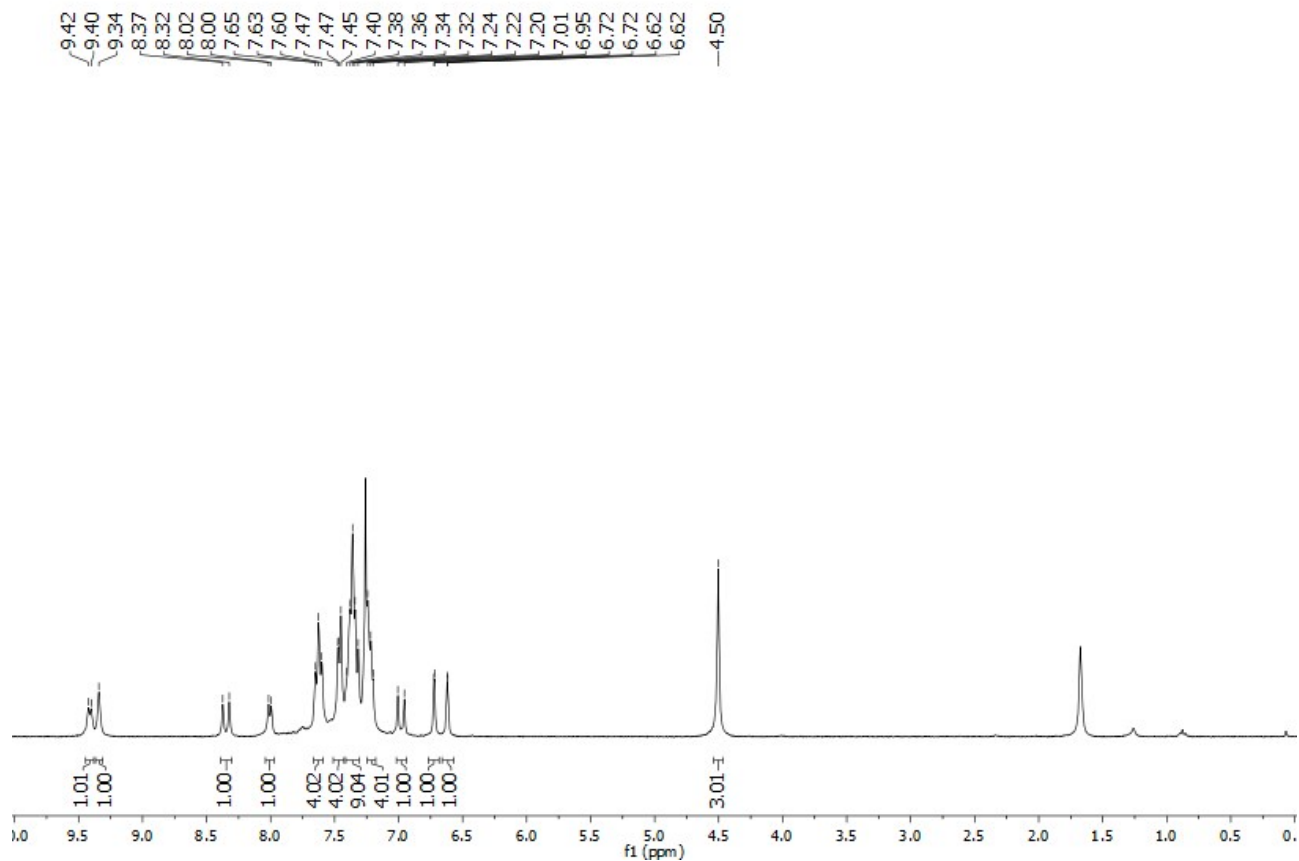
Compound 11



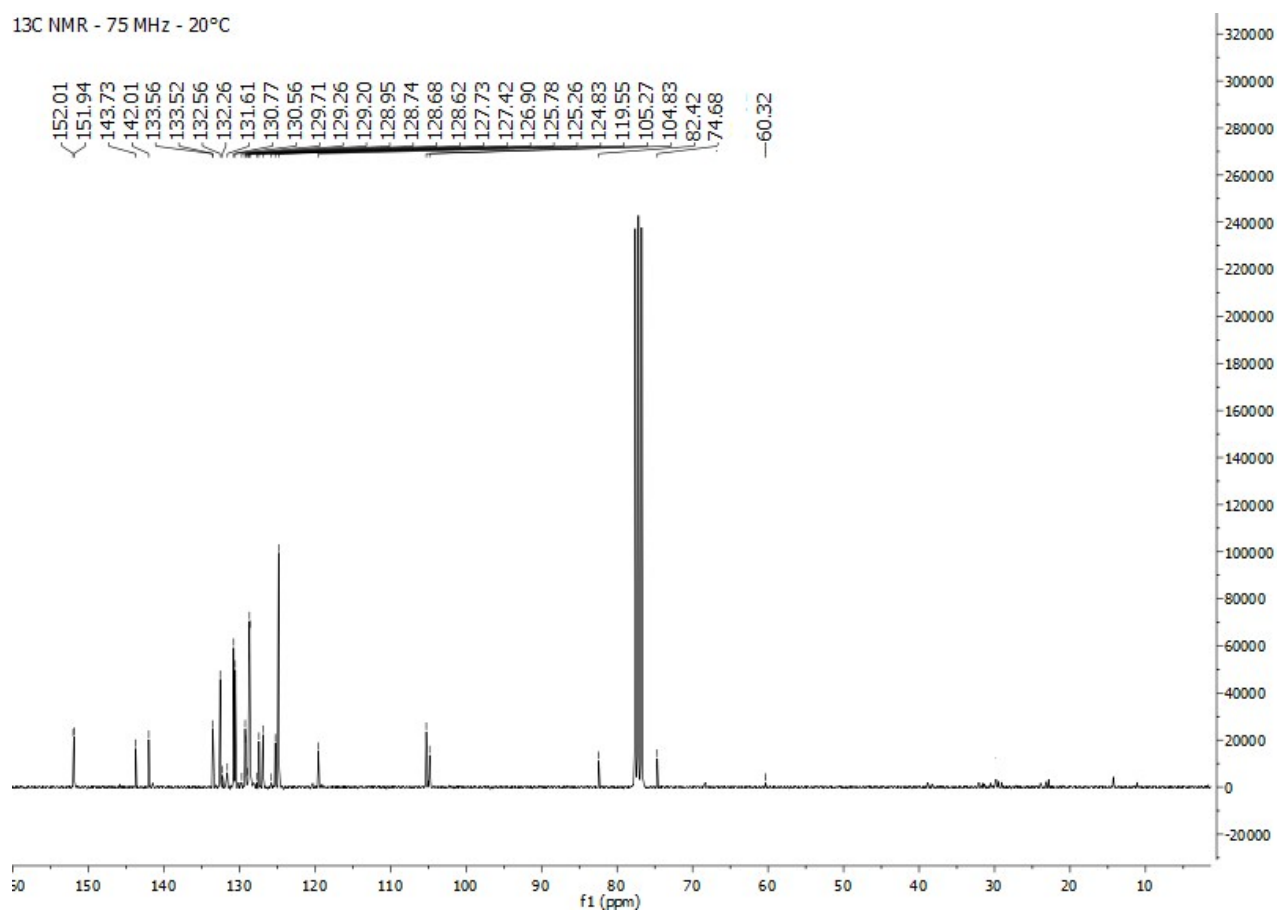
Aspect: dark powder. Yield: 115 mg, 96%. mp= 230°C (dec.). NMR (δ (ppm), CDCl_3): ^1H (300 MHz): 9.41 (d, $^3J_{\text{HH}} = 6.5$ Hz, 1H), 9.34 (s, 1H), 8.35 (d, $^4J_{\text{HH}} = 15.4$ Hz, 1H), 8.01 (d, $^3J_{\text{HH}} = 6.1$ Hz, 1H), 7.66 – 7.59 (m, 4H), 7.49 – 7.43 (m, 4H), 7.41 – 7.33 (m, 9H), 7.25 – 7.19 (m, 4H), 6.98 (d, $^4J_{\text{HH}} = 15.2$ Hz, 1H), 6.72 (d, $^4J_{\text{HH}} = 1.5$ Hz, 1H), 6.62 (d, $^4J_{\text{HH}} = 1.5$ Hz, 1H), 4.50 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ (75 MHz): 152.0, 151.9, 143.7, 142.0, 133.6, 133.5, 132.6, 132.3, 131.6, 130.8, 130.6, 129.7, 129.3, 129.2, 128.9, 128.7, 128.7, 128.6, 127.7, 127.4, 126.9, 125.8, 125.3, 124.8, 119.6, 105.3, 104.8, 82.4, 74.7, 60.3 $^{[3]}$; IR (ATR, cm^{-1}): 3060, 2924, 2854, 1659, 1595, 1448, 1260, 1233,

1022, 760, 695; HRMS (ESI): m/z , calculated for M^{+} ($C_{43}H_{31}N_2OS$): 623.2152, found: 623.2151.

1H NMR - $CDCl_3$ - 300 MHz - 20°C



Spectrum 39: 1H NMR spectrum of compound **11** (300 MHz, $CDCl_3$)



Spectrum 40: ^{13}C NMR spectrum of compound **11** (75 MHz, CDCl_3)

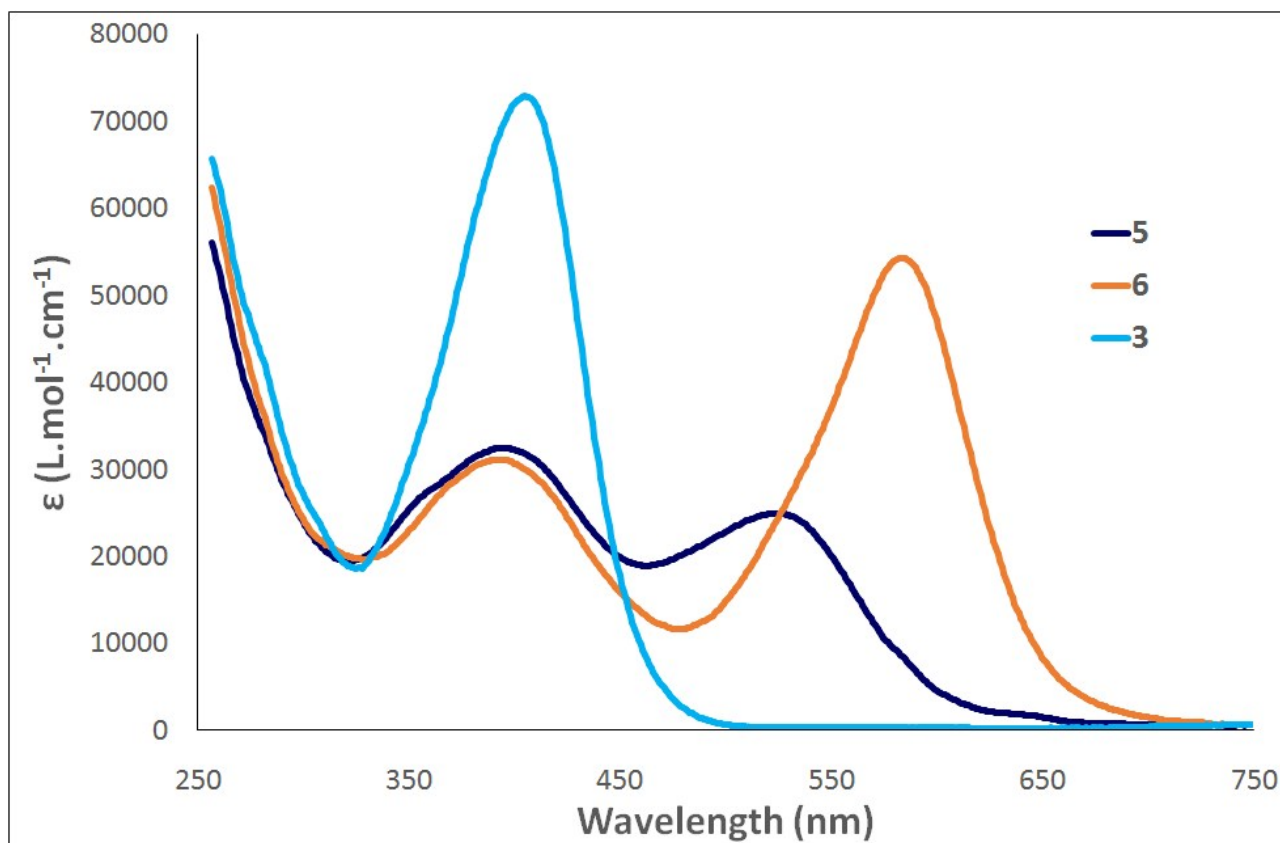


Figure S1: UV-Vis spectra of compounds **3**, **5** and **6** in CHCl_3 .

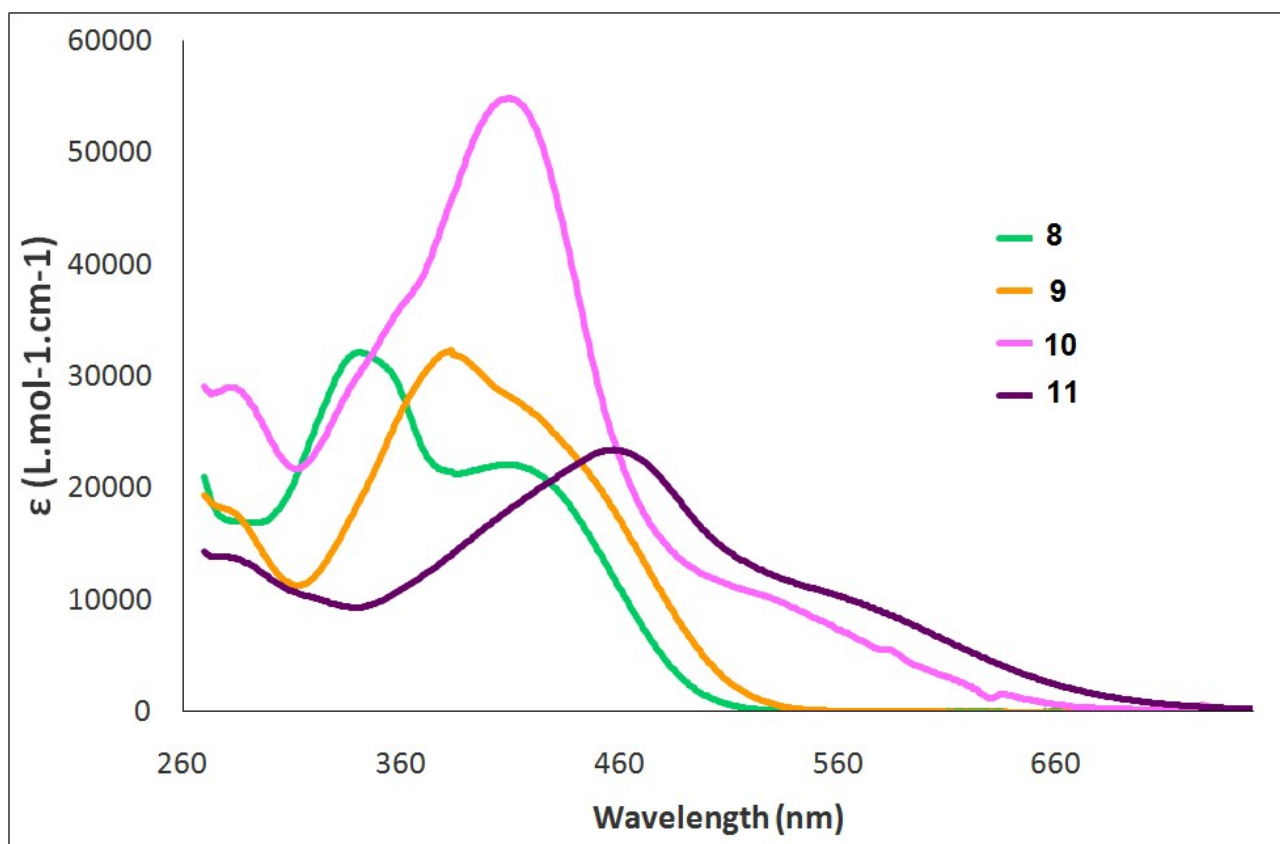


Figure S2: UV-Vis spectra of compounds **8-11** in CHCl_3 .

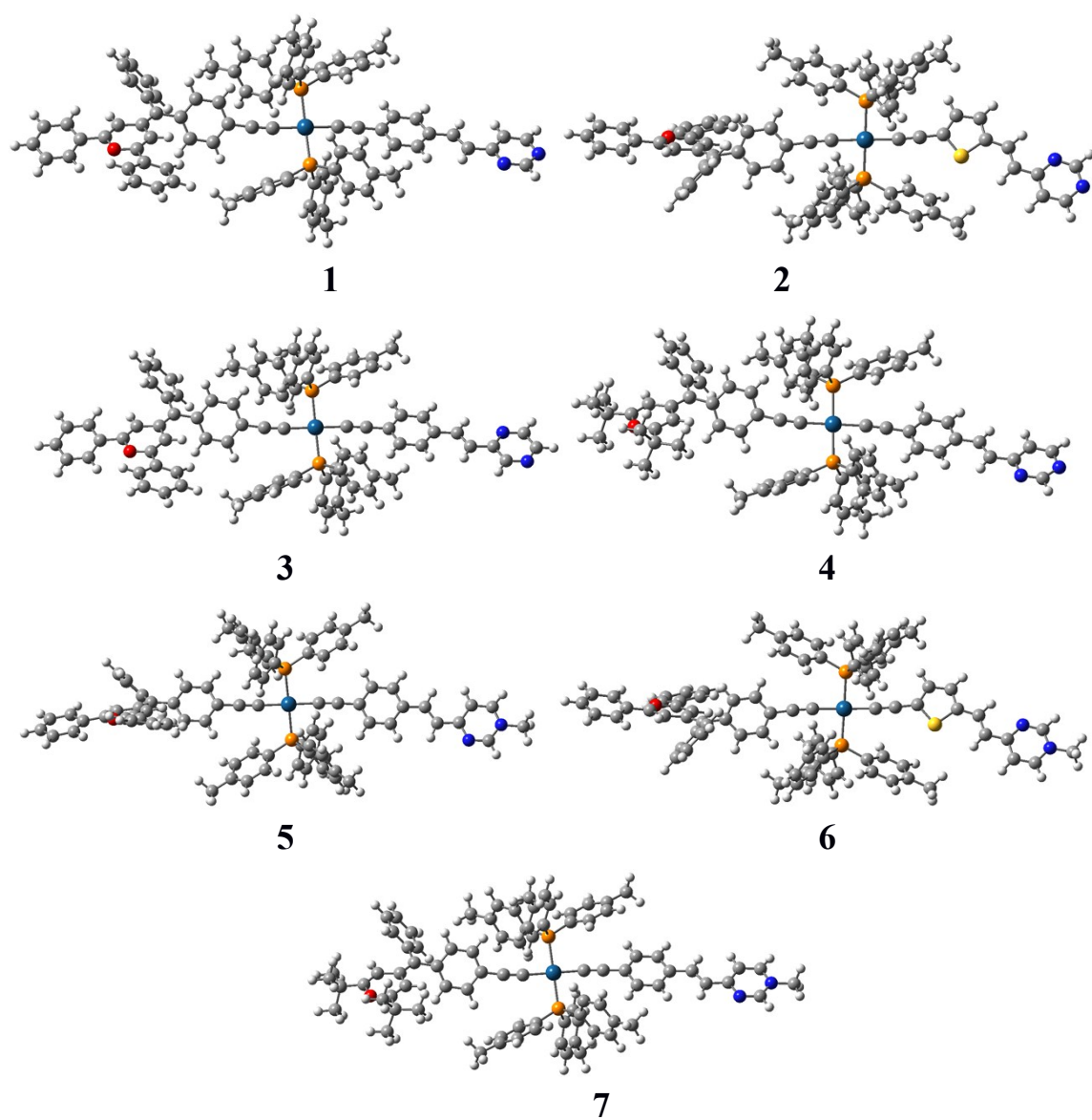


Figure S3: DFT-optimized molecular structures of complexes 1-7.

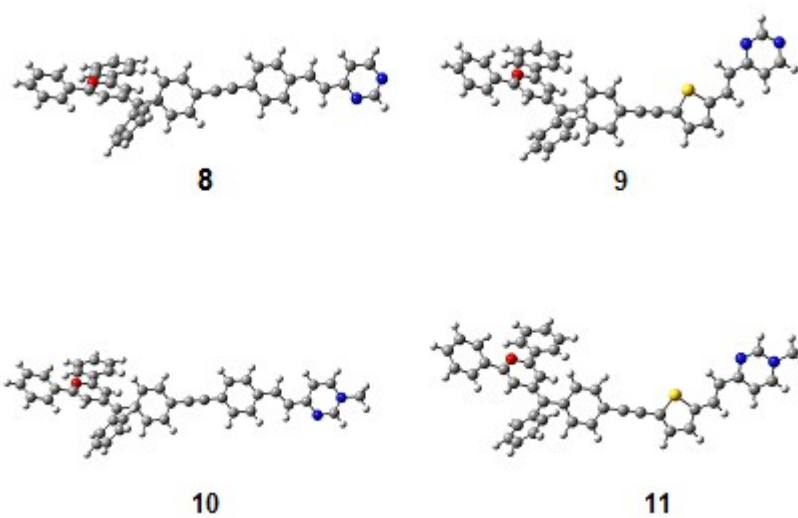


Figure S4: DFT-optimized molecular structures of compounds **8-11**.

Table S1. TDDFT-computed UV-vis data for compounds **8-11**. Experimental λ_{max} values are also reported for comparison. Computed oscillator strengths (o.s.) are given in parentheses.

Compound	λ_{max} [nm] (exp. values, see Table 1)	λ_{max} [nm] (simulated spectra, see Figure C)	λ_{calc} [nm] and o.s. [u.a.] (major computed transitions)	Major contributions
8	341 408	357 431	356 (0.82) 430 (2.04)	H $\rightarrow$ L+1 H $\rightarrow$ L
9	383	376	375 (0.86) 451 (1.90)	H-1 $\rightarrow$ L and H $\rightarrow$ L+1 H $\rightarrow$ L
10	409 540	402 543	403 (1.18) 543 (1.65)	H-1 $\rightarrow$ L H $\rightarrow$ L
11	457 579	413 588	401 (0.74) 431(0.66) 588 (1.68)	H $\rightarrow$ L+1 H-1 $\rightarrow$ L H $\rightarrow$ L

Table S2. Computed energetic data for the investigated compounds.

	1	2	3	4	5	6	7	8	9	10	11
HOMO-LUMO gap (eV)	2.78	2.75	2.85	2.69	1.42	1.54	1.33	2.70	2.60	1.53	1.57
Ionisation energy (eV)	4.72	4.72	4.71	4.65	4.91	4.92	4.83				
Electronic affinity (eV)	-2.56	-2.30	-2.16	-2.55	-3.77	-3.70	-3.76				

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- [17] This coupling represents a satellite (d, $^{195}\text{Pt} = 33.8\%$), and is not reflected in the peak multiplicity given.
- [18] All the atoms of carbon were not observed.