Supplementary Material

Synthesis and photophysics of platinum capped phenylene ethynylene oligomers

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1. Materials and Instruments

All solvents and chemicals used for synthesis of the platinum acetylide oligomers were reagent grade and used without purification unless noted. Silica gel (Silicycle Inc., 230-400 mesh, 40-63 microns, 60 Å) was used for all flash chromatography. All silyl-acetylene starting materials were purchased from GFS Chemical; potassium tetrachloroplatinate and palladium-bis(triphenylphosphyl) dichloride were purchased from Strem Chemicals; all other chemicals were purchased from Sigma-Aldrich. NMR spectra were recorded using Varian 300 MHz or Bruker 500 MHz spectrometers using deuterated chloroform ($CDCl_3$) as the solvent and tetramethylsilane (TMS) as the internal reference. The synthesis of compounds **1**,[2] **2**,[3] **5**,[4] **6-11**,[5] **14-20**,[5] and **24-26**,[5] have been previously described in the literature.

Steady-state absorption spectra were recorded on a Varian Cary 100 dual-beam spectrophotometer. Corrected steady-state emission measurements were conducted on a PTI fluorescence spectrometer. Samples were degassed by argon purging for 30 min and concentrations were adjusted to produce "optically dilute" solutions (i.e., A_{max}< 0.20) in THF. Quantum yields were calculated using $Ru(byp)_3Cl_2$ as a known reference.[6]

Time-resolved emission measurements were carried out on a home-built apparatus consisting of a Continuum Surelite series Nd:YAG laser as the excitation source (λ = 355 nm, 10 ns fwhm, < 1mJ/pulse) and detection measured with a Princeton Instruments PI-MAX intensified CCD camera detector coupled to an Acton SpectraPro 150 spectrograph. The camera delay was set to 150 ns, and the gate set to 10 μs. The spectrum was recorded as an average of 500 images. The signal was relatively low, therefore the slit to the CCD was opened up (> 50 microns) until emission was detected. Samples were degassed in THF for 45 minutes with argon in a longneck fluorescence cell.

Transient absorption measurements were conducted on a home-built apparatus,[7] which used a Nd: YAG laser for excitation and a PI-Max intensified CCD camera coupled with a spectrograph as a detector. Sample concentrations were adjusted so that $A_{355\ nm} \approx 0.8$. Triplet lifetimes were calculated using TA decay data via single exponential global fitting parameters in the SpecFit analysis software.

Fluorescence lifetimes were obtained using the time correlated single photon counting technique (TCSPC) with a PicoQuant FluoTime 100 Compact Fluorescence Lifetime Spectrophotometer. Excitation was achieved using a UV pulsed diode laser (λ_{max} 375 nm, P <10

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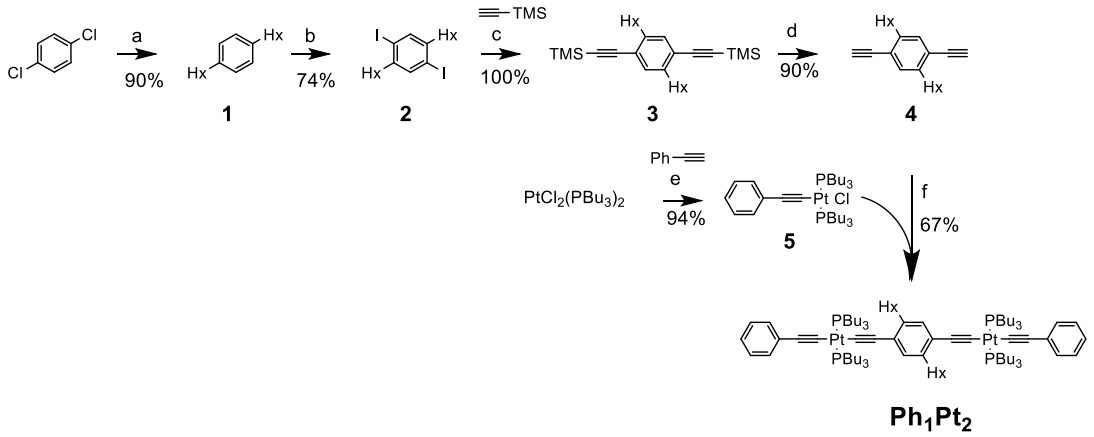
mW). The laser was pulsed using an external BK Precision 4011A 5 MHz function generator. Decays were obtained using biexponential fitting parameters within the PicoQuant PicoHarp software.

The triplet molar extinction coefficients were determined using relative actinometry with benzophenone as the actinometer. Benzophenone has a known molar absorption coefficient of ε(525 nm) = 7870 ± 1200 M^{-1} cm^{-1} and a triplet quantum yield of ΦT = 1.0.REF Sample solutions were prepared in benzene with matched optical densities of 0.60 at 355 nm. In the incident pulse fluence range used (I = 0-500 μJ/cm^2) in this determination, the transient absorption, ΔA, varied linearly with I for each sample with exception to the **Ph_9Pt_2** compound.

2. Synthesis



a) n-HxMgBr, $NiCl_2$dppp, dry ether, 0->35°C, 20h; b) I_2/$NaIO_4$, H_2SO_4, AcOH/Ac_2O; c) $Pd(PPh_3)_2Cl_2$/CuI, THF/iPr_2NH, 70°C,12h; d) TBAF, THF, rt, dark, 2h;e) Et_2NH, THF, 50°C, 12h; f) CuI, THF/Et_2NH, rt, 1.5h.

Scheme S-1. Synthesis of the **Ph_1Pt_2** oligomer.

cis-Bis(tributylphosphine)dichloroplatinum(II),[1] **1**,[2] **2**,[3] **5**, [4] were prepared by literature methods.

2.1.1. Synthesis of 1,4-di-n-hexylbenzene (1) is a known compound and was prepared by the literature method.[2] Yield 90%. B.p.(100 mtorr) 90°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 6H), 1.3 (m, 4H), 1.6 (m, 12H), 2.6 (t, 4H), 7.1 (s, 4H).

2.1.2. Synthesis of 1,4-di-n-hexyl-2,5-diiodobenzene (2) is known and was prepared by literature procedure.[3] Sodium periodate (6.0 g, 28 mmol, 40% excess) and diiodine (21.3 g, 84 mmol, 40% excess) were stirred into a mixture of glacial acetic acid (100 mL) and acetic anhydride (50 mL) at 5°C. Concentrated sulfuric acid (26.6 mL, 500 mmol) was added slowly to the stirring suspension. 1,4-Dihexylbenzene (17.3 g, 70 mmol) was added to this solution and stirring was

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continued for 4 h at room temperature. The reaction mixture was then poured into an ice-water mixture containing previously dissolved Na_2SO_3 (fume hood). Over about 15 minutes, all precipitate was formed and filtered, washing with cold ethanol. Recrystallization of the product from ethanol resulted in 26 g of pure white, needle-like crystals. Yield 74%. M.p. 47°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 6H), 1.35 (m, 12H), 1.55 (m, 4H), 2.6 (t, 4H), 7.6 (s, 2H).

2.1.3. Synthesis of 2,5-Bis-trimethylsilanylethynyl-1,4-dihexylbenzene (3). To a round bottom-flask was added 2,5-diiodo-1,4-dihexylbenzene (3.0g, 6.02 mmol), isopropanol (20 mL) and THF (30 mL). The mixture was stirred and degassed with argon for 20 min, then $Pd(PPh_3)Cl_2$ (0.211 g, 0.301 mmol) and CuI (57 mg, 0.301 mmol) were added quickly. The flask was degassed for an additional 5 min, and then TMS-acetylene (2.13 mL, 15.1 mmol) was added via syringe. The solution was heated to 70°C and reacted for 12 h under argon gas. The solvents were evaporated, then the crude oil was diluted with ether, washed with water and brine, then dried over $NaSO_{4(s)}$. The filtered solute was dried and run through a short silica plug using 90:10 petroleum ether: CH_2Cl_2 as eluent. The product was collected and the solvent evaporated to give 2.7g of yellow oil. Yield 100%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.22 (t, 18H), 0.88 (m, 6H), 1.31 (m, 12H), 1.60 (m, 4H), 2.68 (t, 4H), 7.22 (s, 2H). ^{13}C NMR ($CDCl_3$) δ 0.2, 14.4, 22.9, 29.5, 30.9, 32.0, 34.4, 99.0, 104.2, 122.8, 132.7, 142.8. The product was used as is toward further reaction.

2.1.4. Synthesis of 2,5-Diethynyl-1,4-dihexylbenzene (4). Methanol (15 mL), THF (10 mL), and 2,5-bis-trimethylsilanylethynyl-1,4-dihexylbenzene (1.0 g, 2.29 mmol) were degassed with argon for 30 min, then powdered KOH (0.77 g, 13.7 mmol) was added. The reaction was stirred in a dark flask for 2 h at room temperature until a crude aliquot confirmed the reaction was complete via NMR. The reaction was then quenched with water, diluted with ether, and the organic layer dried over $NaSO_{4(s)}$. After filtration, the solute was evaporated to afford the crude product as 0.62 g of pure yellow oil. Yield 93%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.85 (t, 6H), 1.25 (m, 12H), 1.55 (m, 4H), 2.63 (t, 4H), 3.26 (s, 2H), 7.27 (s, 2H). This crude product was used as is toward further synthesis.

2.1.5. Synthesis of trans-Bis(tributylphosphine)chloro(2-phenylethynyl)-platinum(II) (5) is a known compound and was prepared by literature methods.[4] Yield 94%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, 18H), 1.35-1.65 (m, 24H), 2.0 (m, 12H), 7.1-7.3 (m, 5H); ^{31}P NMR ($CDCl_3$) δ 7.94 (J_{Pt-P} = 2373.81 Hz).

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2.1.6. Synthesis of Ph_1Pt_2. The crude 2,5-diethynyl-1,4-dihexylbenzene (0.26 g, 0.89 mmol), trans-bis(tributylphosphine)chloro(2-phenylethynyl)-platinum(II) (1.5 g, 2.04 mmol), diethylamine (18 mL) and THF (12 mL) were mixed and degassed with argon for 30 min, followed by the addition of CuI (5 mg, 26.5 μmol). The solution was allowed to react for 1.5 h and then quenched with water. The organics were extracted with CH_2Cl_2 and dried over $NaSO_{4(s)}$. After filtration and evaporation of solvent, the crude yellow oil was loaded onto a column (silica, flash) loaded with 2:1 hexanes/CH_2Cl_2. Fraction 2 (R_f~0.3) was a dark yellow band that exhibited yellow phosphorescence under long wave UV light under argon stream. The solvent was evaporated, and this fraction was collected as 1.0 g of solid yellow product. Yield 67%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85 (t, 42H), 1.25-155 (m, 64H), 2.63 (t, 24H), 3.26 (s, 4H), 7.30 (m, 2H), 7.25 (t, 5H), 7.10 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.44, 139.44, 131.40, 131.40, 130.81, 130.81, 129.23, 129.23, 127.89, 127.79, 127.79, 124.79, 124.79, 124.66, 124.66, 110.94, 110.82, 110.70, 108.80, 108.12, 34.24, 32.09, 30.60, 29.62, 26.40, 26.09, 24.45, 24.40, 24.35, 23.98, 23.85, 23.71, 22.77, 21.97, 14.17, 13.87. ^{31}P NMR ($CDCl_3$) δ 4.44 (J_{Pt-P} = 2367.08 Hz). Mass Spec. (APCI-HR) Calc'd for $C_{86}H_{146}P_4Pt_2$ [M^++H] 1694.9765; Found [M^++H] 1694.9741.

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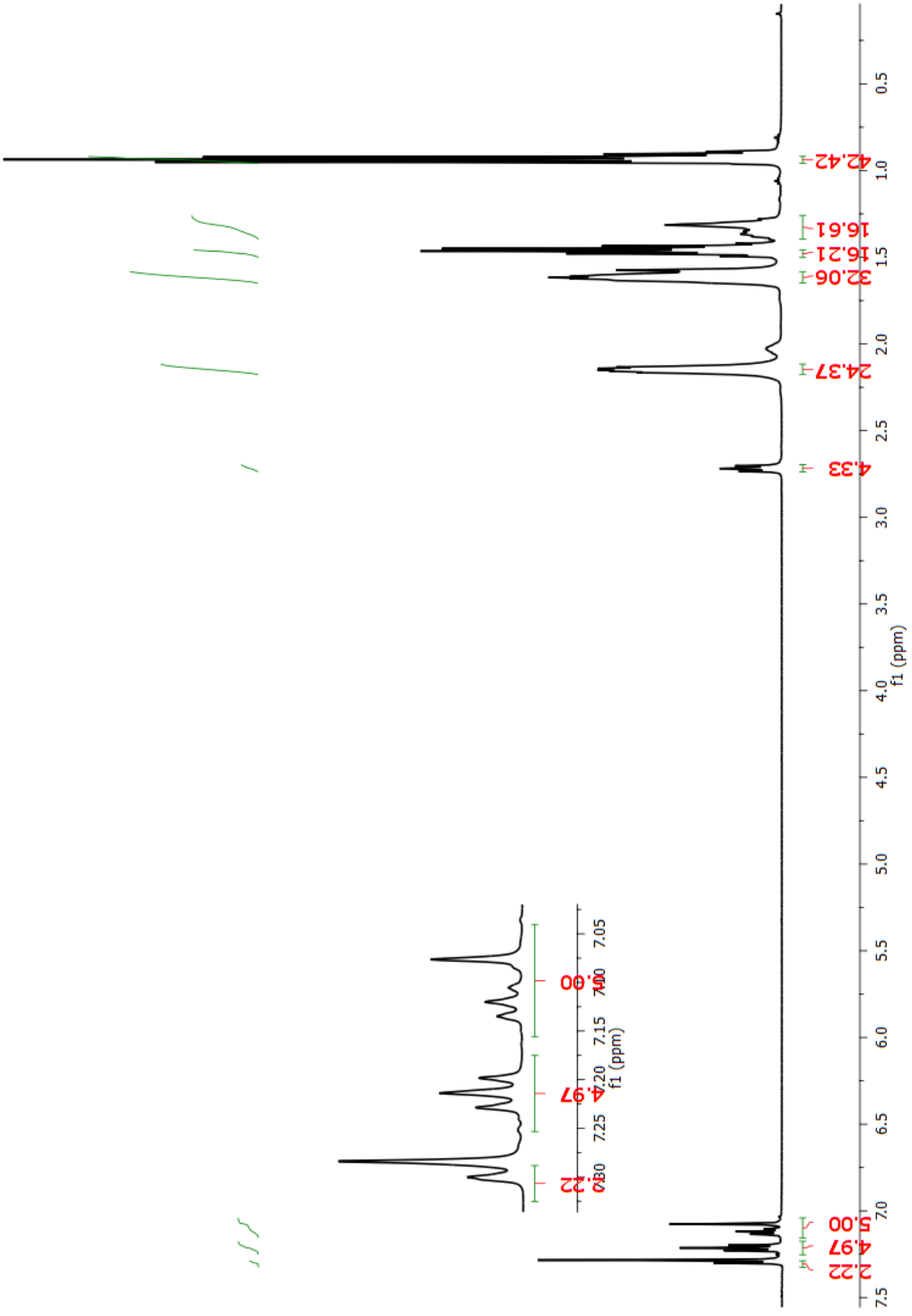

Figure S-1. ^{1}H NMR spectra of ***Ph$_1$Pt$_2$***.

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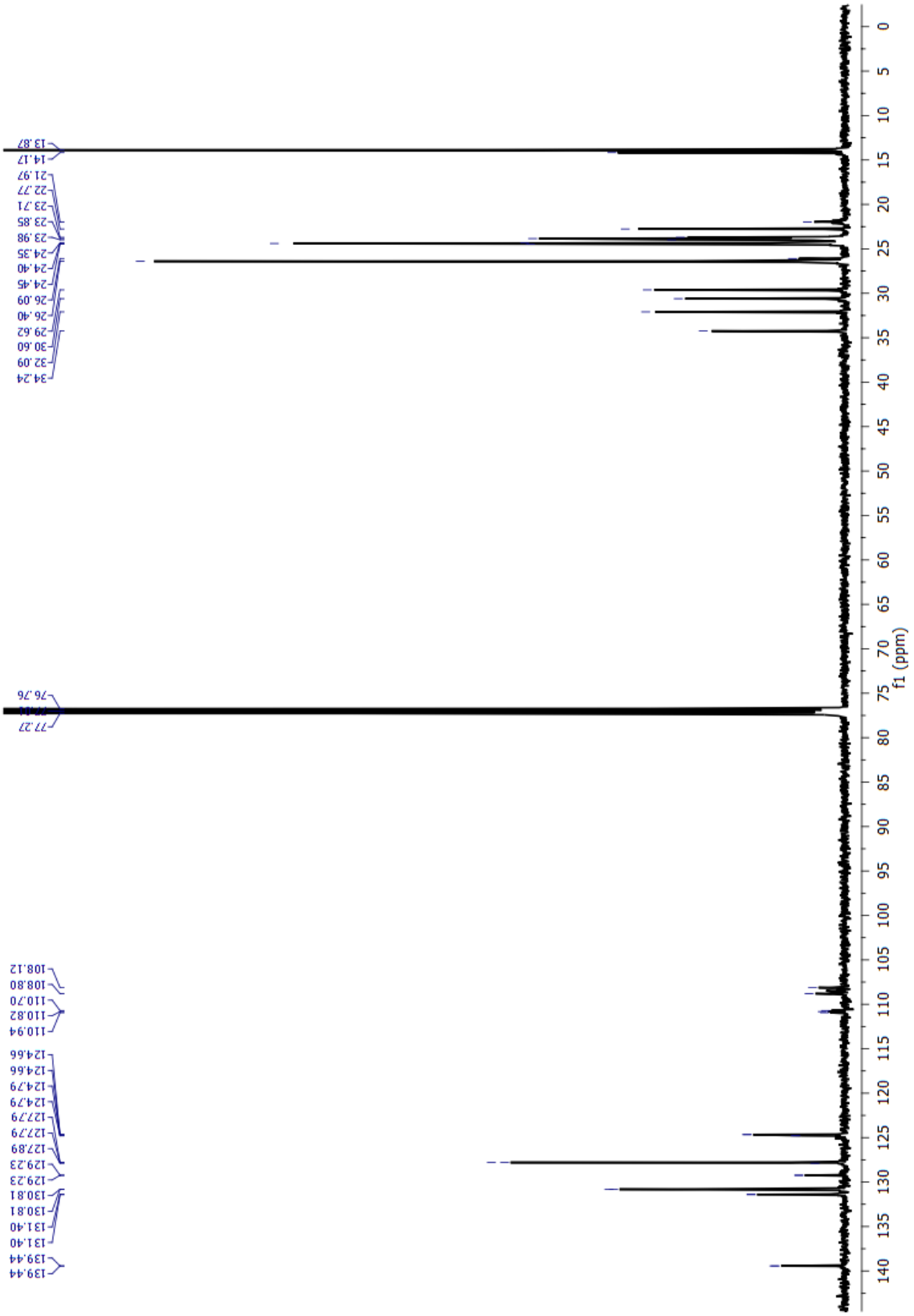

Figure S-2. ^{13}C NMR spectra of ***Ph$_1$Pt$_2$***.

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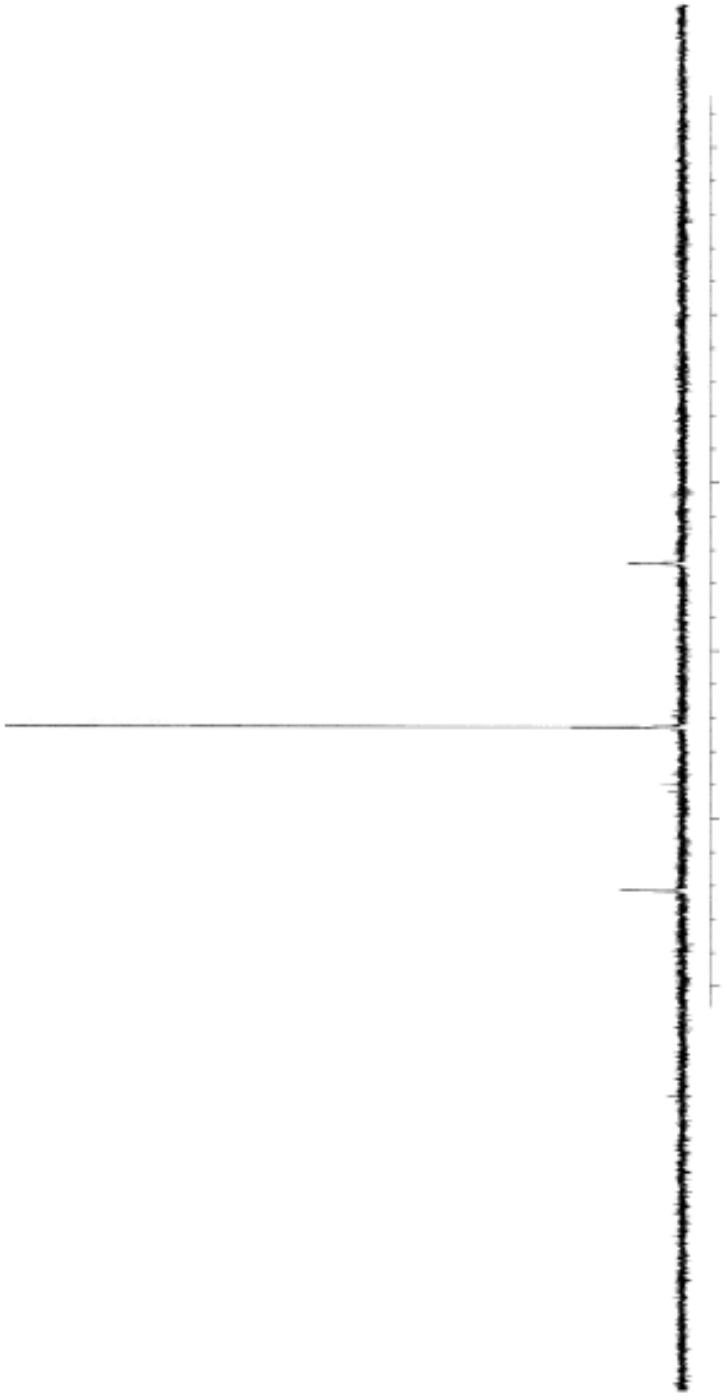

Figure S-3. ^{31}P NMR of **Ph$_1$Pt$_2$.**

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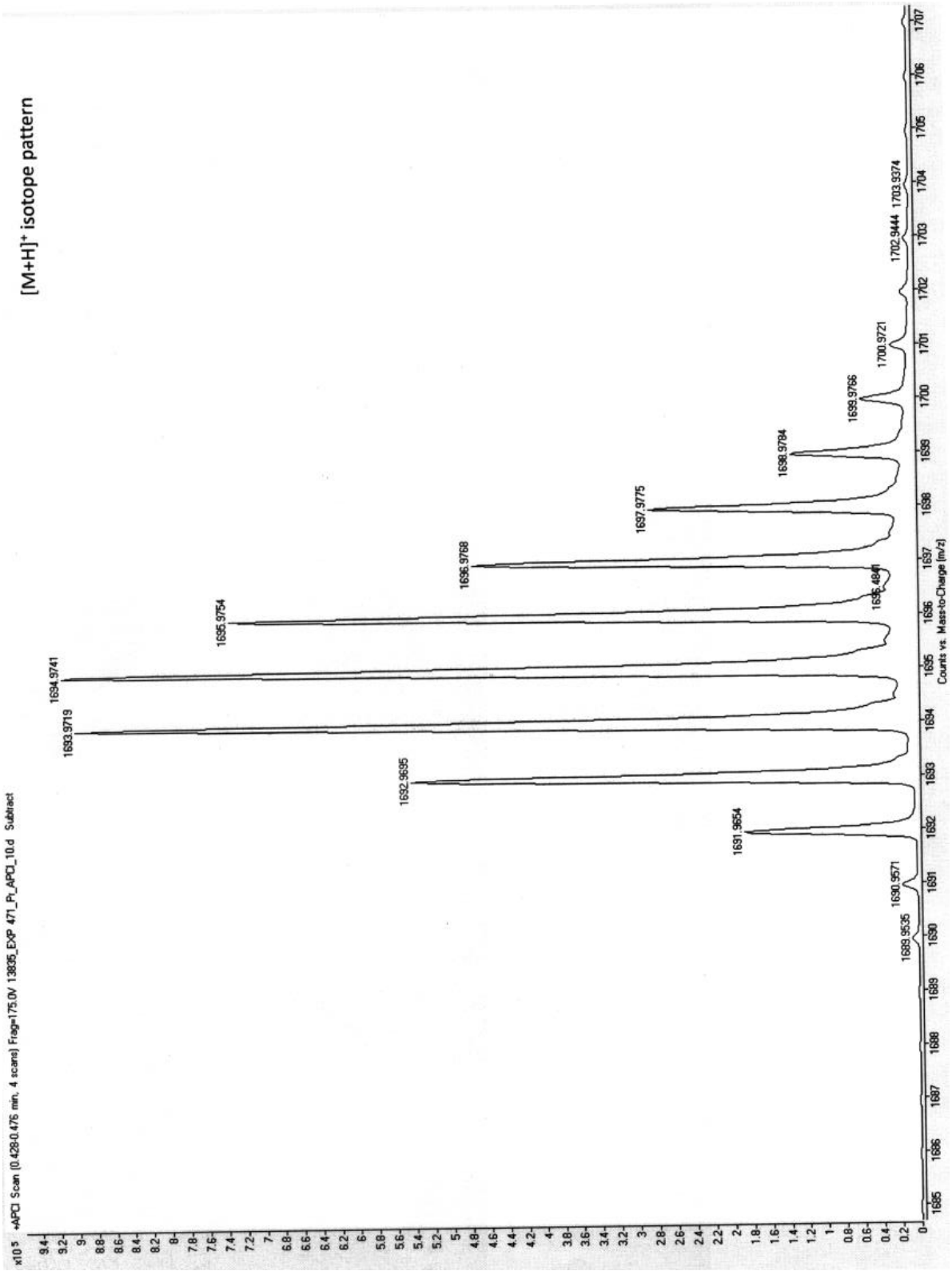

Figure S-4. APCI-HRMS, $[M+H]^+$ isotope pattern of **Ph_1Pt_2.**

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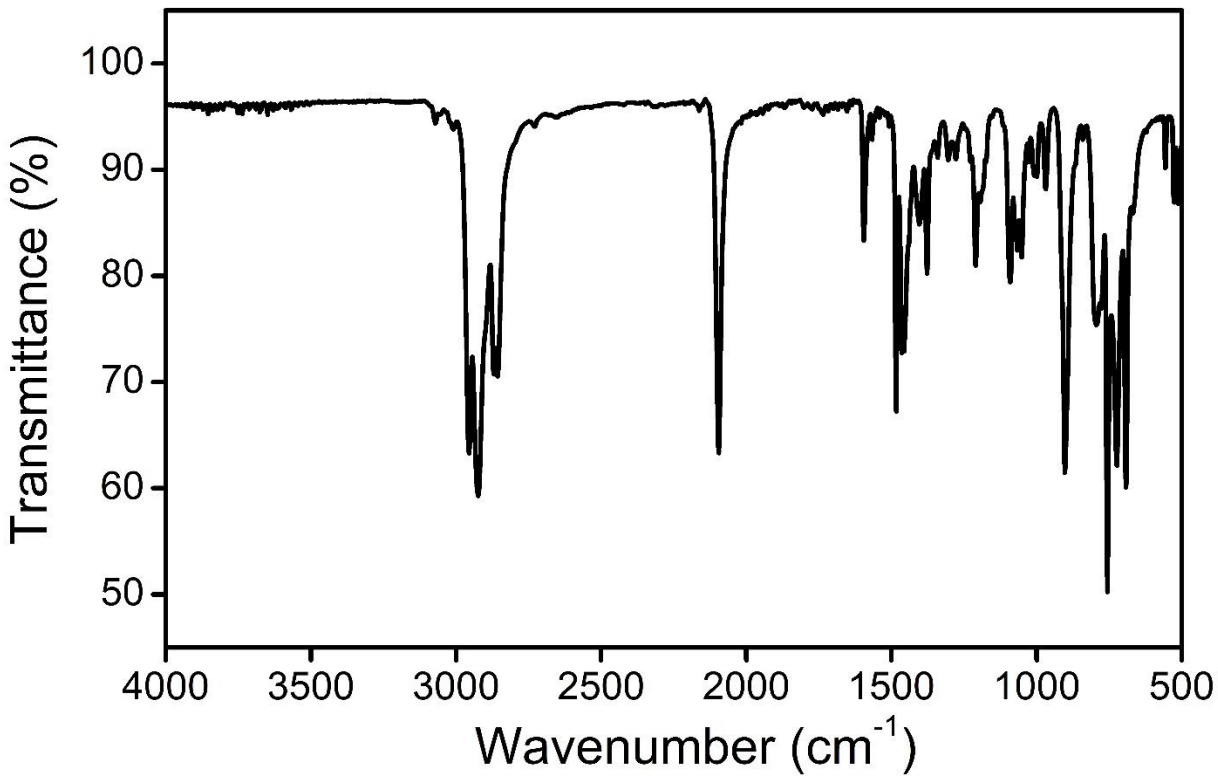
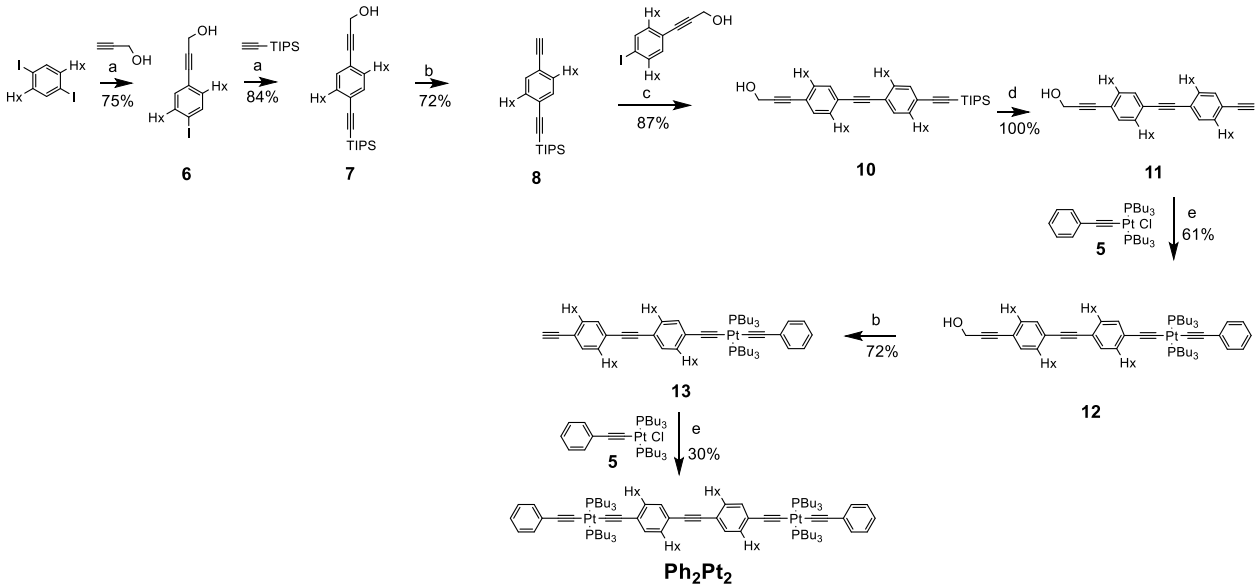


Figure S-5. IR spectrum of **Ph_1Pt_2.**



a) $Pd(PPh_3)_2Cl_2$/CuI, THF/piperidine, 50°C, 12h; b) MnO_2/KOH, ether, rt, dark, 12h; c)$Pd(PPh_3)_2Cl_2$/CuI, THF/piperidine, rt, 12h; d) TBAF, THF, rt, 2h; e) CuI, $NHEt_2$/THF, rt, 4h.

Scheme S-2. Synthesis of the **Ph_2Pt_2** oligomer.

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Compounds **6-11**,[5] were prepared by literature methods.

2.2.1. Synthesis of 3-(2,5-Dihexyl-4-iodo-phenyl)-prop-2-yn-1-ol (6) is a known compound and was prepared by the literature method[5] to afford a brown/tan solid. Yield 75%. M.p. 37.5-38.0°C (Lit. 38.4-38.6°C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (m, 6H), 1.22-1.42 (m, 12H), 1.47-1.65 (m, 5H), 2.61 (d, 2H), 2.63 (d, 2H), 4.50 (d, 2H), 7.21 (s, 1H), 7.63 (s, 1H).

2.2.2. Synthesis of 3-{2,5-Dihexyl-4-[(triisopropylsilanyl)-ethynyl]-phenyl}-prop-2-yn-1-ol (7) is known and was prepared by the literature method[5] to produce a yellow-orange oil. Yield 84%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (m, 6H), 1.15 (s, 21H) 1.22-1.42 (m, 12H), 1.58-1.65 (m, 4H), 2.69 (d, 2H), 2.73 (d, 2H), 4.50 (d, 2H), 7.22 (s, 1H), 7.26 (s, 1H).

2.2.3. Synthesis of (4-Ethynyl-2,5-dihexyl-phenylethynyl)-triisopropyl-silane (8) is a known compound and was prepared according to literature method[5] to afford an orange oil. Yield 72%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.85-0.95 (m, 6H), 1.17 (s, 21H) 1.22-1.42 (m, 12H), 1.59-1.66 (m, 4H), 2.75 (m, 4H), 3.29 (s, 1H), 7.30 (s, 1H), 7.31 (s, 1H).

2.2.4. Synthesis of 3-(4-{2,5-Dihexyl-4-[(triisopropylsilanyl)-ethynyl]-phenylethynyl}-2,5-dihexyl-phenyl)-prop-2-yn-1-ol (10) is a known compound prepared from literature method[5] to afford the product as a yellow oil. Yield 87%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82-0.95 (m, 12H), 1.15 (s, 21H) 1.21-1.45 (m, 24H), 1.55 (s, 1H), 1.58-1.72 (m, 8H), 2.66-2.80 (m, 8H), 4.51 (d, 2H), 7.25 (s, 1H), 7.26 (s, 1H), 7.27 (s, 1H), 7.28 (s, 1H).

2.2.5. Synthesis of 3-[4-(4-Ethynyl-2,5-dihexyl-phenylethynyl)-2,5-dihexyl-phenyl]-prop-2-yn-1-ol (11). To a round bottom flask with a stir bar was added compound **10** (1.3 g, 1.73 mmol) and THF (20 mL). The mixture was degassed for 30 min with argon followed by the addition of TBAF, 1 M in THF (3.47 mL, 3.47 mmol) via a syringe. The solution was allowed to react at room temperature for 2 h before it was quenched with water. The organic solution was extracted with ether and dried over magnesium sulfate. After filtration of the drying agent and evaporation of solvent, 1.3 g of yellow/brown oil was collected as the crude product. Yield (crude) 100%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81-0.92 (m, 12H), 1.15 (s, 21H) 1.20-1.42 (m, 24H), 1.55-1.71 (m, 8H), 2.67-2.80 (m, 8H), 3.29 (s, 1H), 4.51 (s, 2H), 7.26-7.27 (m, 2H), 7.30-7.31 (m, 2H). The product was used without further purification toward the next step of the synthesis.

2.2.6. Synthesis of compound $Ph_2OH_1Pt_1$ (12). To a round bottom flask with a stir bar was added compound **11** (181 mg, 0.252 mmol), compound **5** (0.40 g, 0.509 mmol), THF (10 mL) and diethylamine (8 mL). The mixture was degassed with argon for 30 min, followed by the addition

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of CuI (1.7 mg, 9.1 μmol). The solution reacted for 4 h at room temperature, followed by evaporation of the solvent once TLC confirmed the complete disappearance of the free acetylene starting material. The crude product was diluted with CH_2Cl_2, washed with water and brine, and dried over $NaSO_{4(s)}$. The crude material was concentrated into an oil and loaded onto a column (silica, flash) prepped with 3:1 hexanes/CH_2Cl_2. The third fraction was eluted as a yellow band, exhibiting orange phosphorescence on TLC with long-wave UV light under argon flow. Evaporation of the solvent afforded 200 mg of yellow oil product used as is toward further synthesis. Yield 61%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.84-0.96 (t, 30H), 1.25-1.72 (m, 57H), 2.09-2.17 (m, 12H), 2.69-2.82 (m, 8H), 4.54 (d, $^3J_{(H,H)}$ = 6Hz, 2H), 7.08-7.31 (m, 9H). ^{31}P NMR ($CDCl_3$) δ 4.45 (J_{Pt-P} = 2360.45 Hz).

2.2.7. Synthesis of compound $Ph_2(CCH)_1Pt_1$ (13). $Ph_2OH_1Pt_1$ (12) (200 mg, 0.155 mmol) and ether (20 mL) were stirred and degassed 30 min under argon flow in a dark flask, followed by a total of 5 sequential additions (at 1-hour intervals) of MnO_2 (0.336g, 3.87 mmol) and powdered KOH (87 mg, 1.55 mmol). The reaction was allowed to go to completion at room temperature overnight, then it was filtered through a silica plug and rinsed with diethyl ether, to collect the crude deprotected product. The solvent of the filtrate was evaporated to afford 140 mg of crude product as a yellow oil. Yield (crude) 72%. The crude product was used as is toward the next step of the synthesis without further purification.

2.2.8. Synthesis of compound Ph_2Pt_2. $Ph_2(CCH)_1Pt_1$ (13) (140 mg, 0.111 mmol), compound **5** (204 mg, 0.277 mmol), diethylamine (10 mL) and THF (10 mL) were stirred and degassed with argon for 30 min, followed by the addition of CuI (0.5 mg). The solution was allowed to react at room temperature for 4 h, and then the solvent was evaporated. The crude product mixture was diluted with CH_2Cl_2, washed with water and brine and then dried over $NaSO_{4(s)}$. After filtration and evaporation of solvent, the crude oil was loaded onto a column (silica, flash) prepped and eluted with 1:1 hexanes/CH_2Cl_2. The first fraction eluted was a yellow band whose spot-on TLC (long wave UV/argon stream) exhibited orange phosphorescence. The solvent was evaporated to afford 70 mg of yellow solid product. Yield 30%. Elemental Analysis for $C_{106}H_{174}P_4Pt_2$: Calculated C 64.87%, H 8.94%; Found C 64.43%, H 8.67%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.83-0.96 (m, 48H), 1.22-1.72 (m, 80H), 1.95-2.28 (m, 24H), 2.68-2.80 (m, 8H), 7.07-7.31 (m, 14H). ^{31}P NMR ($CDCl_3$) δ 4.51 (J_{Pt-P} = 2359.16 Hz).

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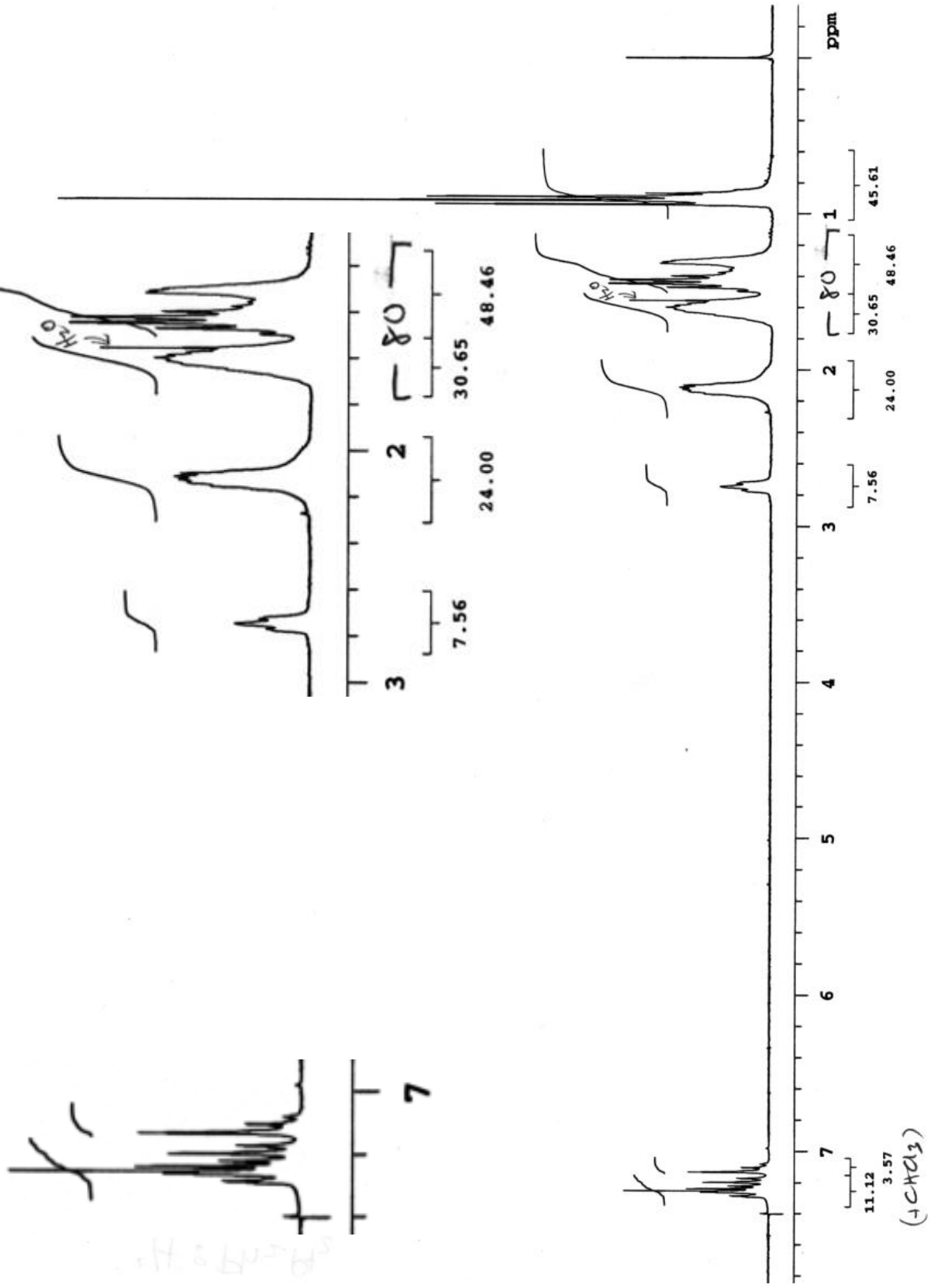

Figure S-6. ^{1}H NMR of **Ph_2Pt_2**.

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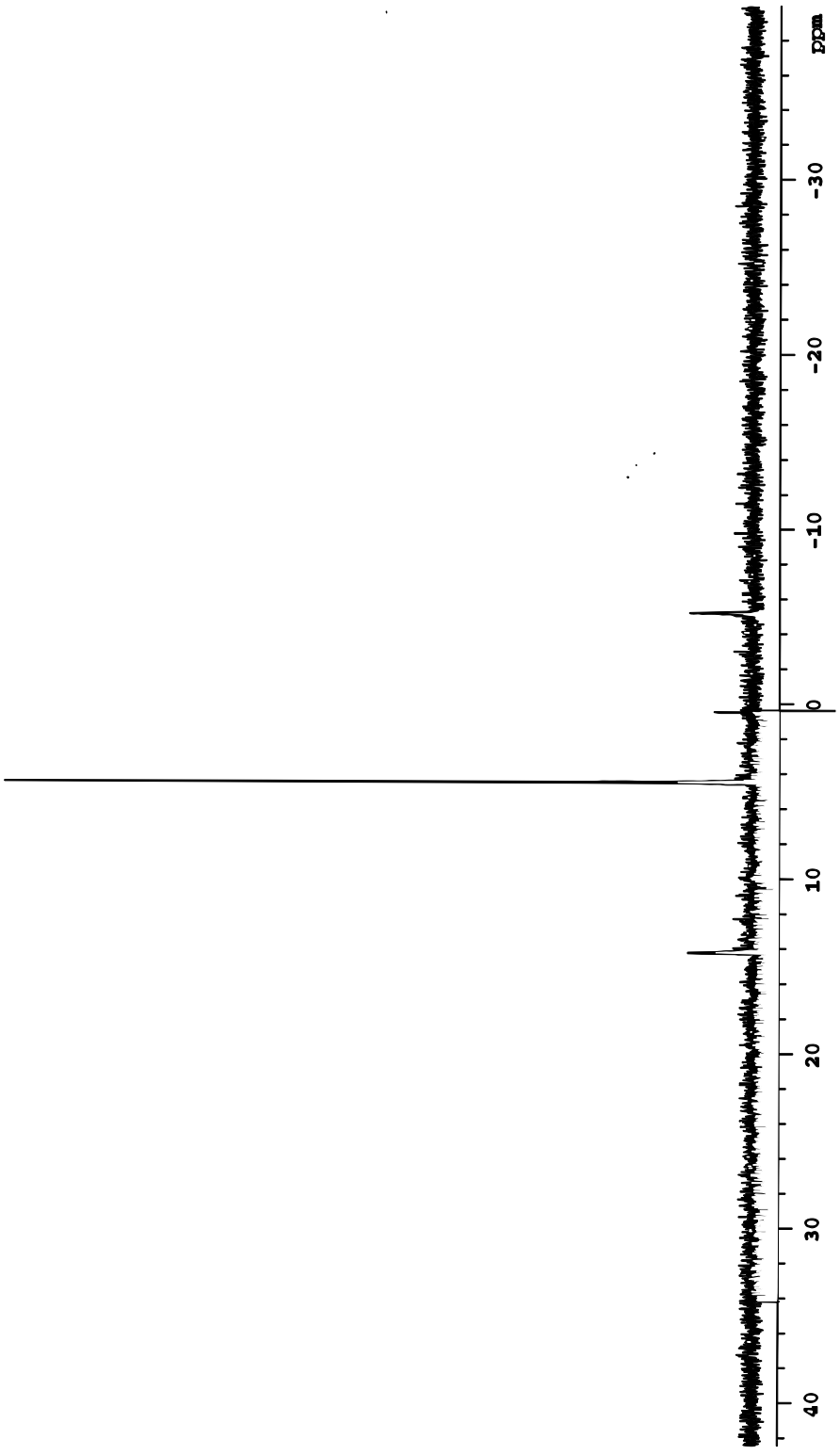

Figure S-7. ^{31}P NMR of **Ph_2Pt_2**.

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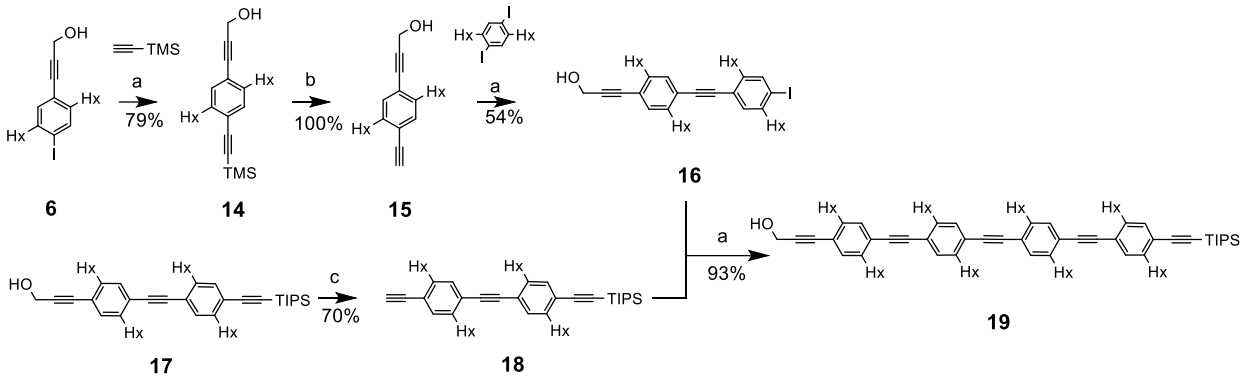

a) $Pd(PPh_3)_2Cl_2$/CuI, THF/piperidine, rt, 12h; b) KOH, MeOH/THF, rt, dark, 2h; c) MnO_2/KOH, ether, rt, dark, 12h.

Scheme S-3. Synthesis of orthogonally protected intermediate compound **19**.

Compounds **14-19**,[5] were prepared by literature methods.

2.3.1. Synthesis of 3-(2,5-Dihexyl-4-trimethylsilanylethynyl-phenyl)-prop-2-yn-1-ol (14) is a known compound prepared by literature procedure[5] to afford a brown oil product. Yield 79%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.19 (s, 9H), 0.74-0.86 (m, 6H), 1.15-1.32 (m, 12H), 1.43-1.58 (m, 4H), 2.10 (br s, 1H), 2.54-2.62 (m, 4H), 4.43 (s, 2H), 7.13 (s, 1H), 7.17 (s, 1H).

2.3.2. Synthesis of 3-(4-Ethynyl-2,5-dihexyl-phenyl)-prop-2-yn-1-ol (15) is known and was prepared by literature method[5] to produce the product as a red/brown oil. Yield 100%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82-0.92 (m, 6H), 1.18-1.40 (m, 12H), 1.51-1.65 (m, 4H), 2.10 (br s, 1H), 2.62-2.74 (m, 4H), 3.26 (s, 1H), 4.51 (s, 2H), 7.23 (s, 1H), 7.27 (s, 1H).

2.3.3. Synthesis of 3-[4-(2,5-Dihexyl-4-iodo-phenylethynyl)-2,5-dihexyl-phenyl]-prop-2-yn-1-ol (16) is known and was prepared by literature method[5] to afford the product as a yellow solid. Yield 54%. M.p. 58.2-59.0°C (Lit. 62°C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82-1.00 (m, 12H), 1.20-1.51 (m, 24H), 1.51-1.77 (m, 8H), 1.84 (t, 1H), 2.63-2.85 (m, 8H), 4.53 (d, 2H), 7.29-7.34 (3 s, 3H), 7.70 (s, 1H).

2.3.4. Synthesis of $Ph_2TIPS_1(CCH)_1$ (18) is a known compound and was prepared according to literature method[5] to afford the product as a brown/red oil. Yield 70%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82-0.95 (m, 12H), 1.15 (s, 21H) 1.22-1.48 (m, 24H), 1.56-1.73 (m, 8H), 2.68-2.8 (m, 8H), 3.37 (s, 1H), 7.32-7.34 (4 s, 4H).

2.3.5. Synthesis of $Ph_4TIPS_1OH_1$ (19) is a known compound prepared similarly to literature methods,[5] only $Pd_2(dba)_3$/CuI/PPh_3 (0.045/0.08/0.15 equiv. vs. starting material, where 1.0 equiv = 1.12 mmol) was used rather than the $Pd(PPh_3)_2Cl_2$/CuI catalyst system, minimizing the amount of acetylene dimer formation drastically. Yield 96%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81-0.98 (m,

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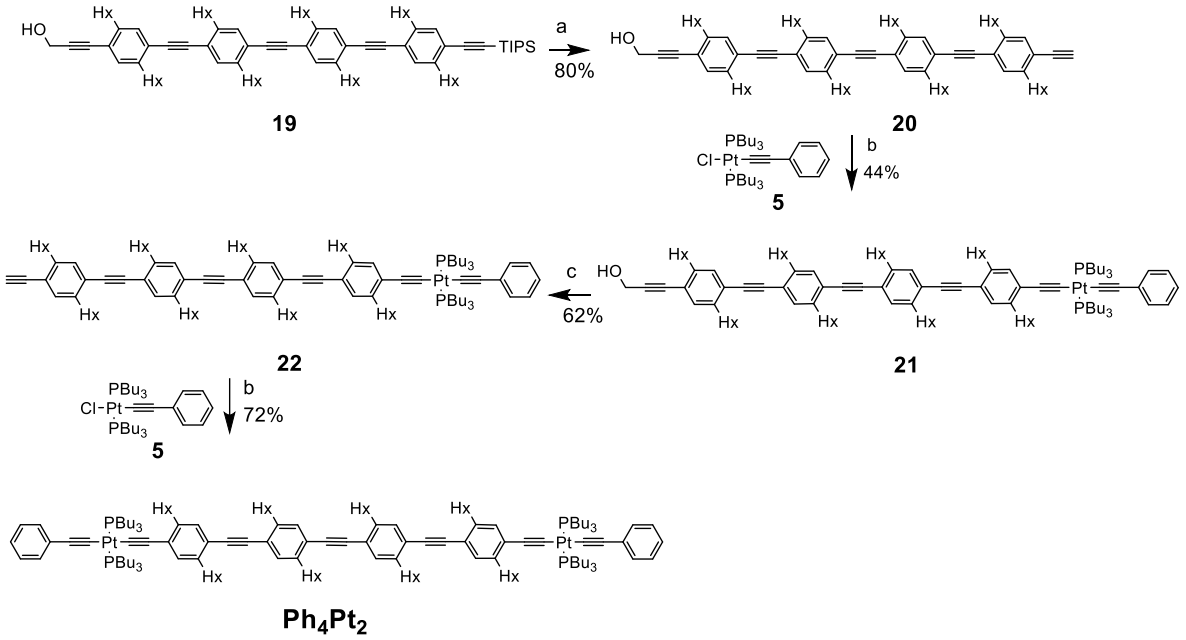
24H), 1.16 (s, 21H), 1.35-1.52 (m, 48H), 1.54-1.79 (m, 16H), 2.71-2.88 (m, 16H), 4.52 (s, 2H), 7.31-33 (2 s, 2H), 7.35-7.36 (2 s, 2H), 7.39-7.40 (2 s, 4H).



a) TBAF, THF, rt, 2h; b) CuI, THF/$NHEt_2$, rt, 4h; c)MnO_2/KOH, ether, rt, dark, 4h.

Scheme S-4. Synthesis of the **Ph_4Pt_2** oligomer.

Compound **20**,[5] were prepared by literature method.

2.4.1. Synthesis of $Ph_4OH_1(CCH)_1$ (20) is known and was prepared according to literature method[5], however, the product was purified by column chromatography (silica, flash) prepped, and eluted with 1:1 petroleum ether/CH_2Cl_2. The product was collected in the first fraction as a yellow solid. Yield 80%. Mp 89-91°C (Lit. 91°C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82-0.98 (m, 24H), 1.24-1.48 (m, 48H), 1.59-1.76 (m, 16H), 2.71-2.87 (m, 16H), 3.30 (s, 1H) 4.54 (d, 2H), 7.29 (s, 1H), 7.34 (m, 3H), 7.37-7.39 (m, 4H).

2.4.2. Synthesis of $Ph_4OH_1Pt_1$ (21). To a round bottom-flask were added compound $Ph_4OH_1(CCH)_1$ (20) (0.10 g, 0.089 mmol), compound **5** (78 mg, 0.106 mmol), THF (7 mL) and diethylamine (10 mL). The solution was degassed under argon flow for 30 min, followed by the addition of CuI (0.5 mg). The solution was allowed to react at room temperature for 1.5 h until TLC revealed the completion of the reaction. The solution was quenched with water and the organic solvent was extracted with CH_2Cl_2 and dried ($NaSO_4$). Filtration of the drying agent and

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evaporation of the solvent gave a crude yellow/orange oil that was loaded onto a column (silica, flash) prepped with 2:1 petroleum ether/CH_2Cl_2, then switched to 1:1 after elution of fraction 2. The first two fractions that eluted (R_r ~ 0.8 and 0.5) were biproducts. The third fraction eluted was a yellow band (R_f ~ 0.3); the solvent was evaporated to yield 70 mg of yellow oil that slowly became a solid. Yield 44%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82-1.00 (m, 42H), 1.21-1.81 (m, 88H), 2.02 -2.22 (m, 12H), 2.69-2.88 (m, 16H), 4.56 (s, 2H), 7.09-7.40 (m, 13H). ^{31}P NMR ($CDCl_3$) δ 4.57 (J_{Pt-P} = 2361.37 Hz). Mass Spec. (APCI-HR) Calc'd for $C_{115}H_{174}OP_2Pt$ $[M+Cl]^+$ 1864.2392; Found $[M+Cl]^+$ 1864.2392.

2.4.3. Synthesis of $Ph_4(CCH)_1Pt_1$ (22). The starting material compound $Ph_4OH_1Pt_1$ (21) (0.18 g, 0.098 mmol) and ether (15 mL) were stirred and degassed with argon for 30 min in a dark flask. Hourly portions (3 total) of MnO_2 (0.214 g, 2.46 mmol) and powdered KOH (55 mg, 0.984 mmol) were then added until the reaction was complete. TLC monitoring showed reaction completion after 4 h. The reaction was filtered through a small plug of silica, washing with ether, then the concentrated filtrate was separated on a column (silica, flash) prepped with 3:1 petroleum ether/CH_2Cl_2. Fraction 1 was a small byproduct of the deprotection, and fraction 2 (eluted as a light-yellow band, TLC showing green fluorescence and red phosphorescence under long wave UV light/argon flow) was collected as 110 mg of yellow oil product. Yield 62%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82-0.96 (m, 42H), 1.24-1.51 (m, 60H), 1.52-1.77 (m, 28H), 2.04 -2.20 (m, 12H), 2.71-2.88 (m, 16H), 3.31 (s, 1H) 4.56 (s, 2H), 7.08-7.39 (m, 13H). ^{31}P NMR ($CDCl_3$) δ 4.53 (J_{Pt-P} = 2360.98 Hz). The product was used as is toward further synthesis.

2.4.4. Synthesis of Ph_4Pt_2. Di-ethylamine (10 mL), compound $Ph_4(CCH)_1Pt_1$ (22) (110 mg, 0.0611 mmol) and compound **5** (104 mg, 0.141 mmol) were stirred and degassed with argon for 30 min, followed by the addition of CuI (<1 mg, about 0.04 equiv.). The reaction was allowed to stir at room temperature for 2 h, then quenched with water when TLC revealed that the reaction was complete. The organics were extracted with CH_2Cl_2 and dried ($NaSO_4$); after filtration of the drying agent and evaporation of solvent, the crude oil was loaded onto a column (silica, flash) prepped and eluted with 2:1 hexanes/CH_2Cl_2. The first fraction eluted as a yellow band (R_f ~ 0.25), and TLC revealed the spot as being fluorescent blue/green and phosphorescent red (with argon flow). Collection of the fraction afforded 110 mg of yellow solid product. Yield 72%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82-0.97 (m, 60H), 1.22-1.76 (m, 112H), 2.10-2.25 (m, 24H), 2.71-2.87 (m, 16H), 7.09-7.24 (m, 8H), 7.26-7.31 (m, 6H), 7.33-7.37 (m, 4H). ^{31}P NMR ($CDCl_3$) δ 4.54 (J_{Pt-P} =

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2363.43 Hz). Mass Spec. (APCI-HR) Calc'd for $C_{146}H_{230}P_4Pt_2$ [M^++H] 2499.6346; Found [M^++H] 2499.6371.

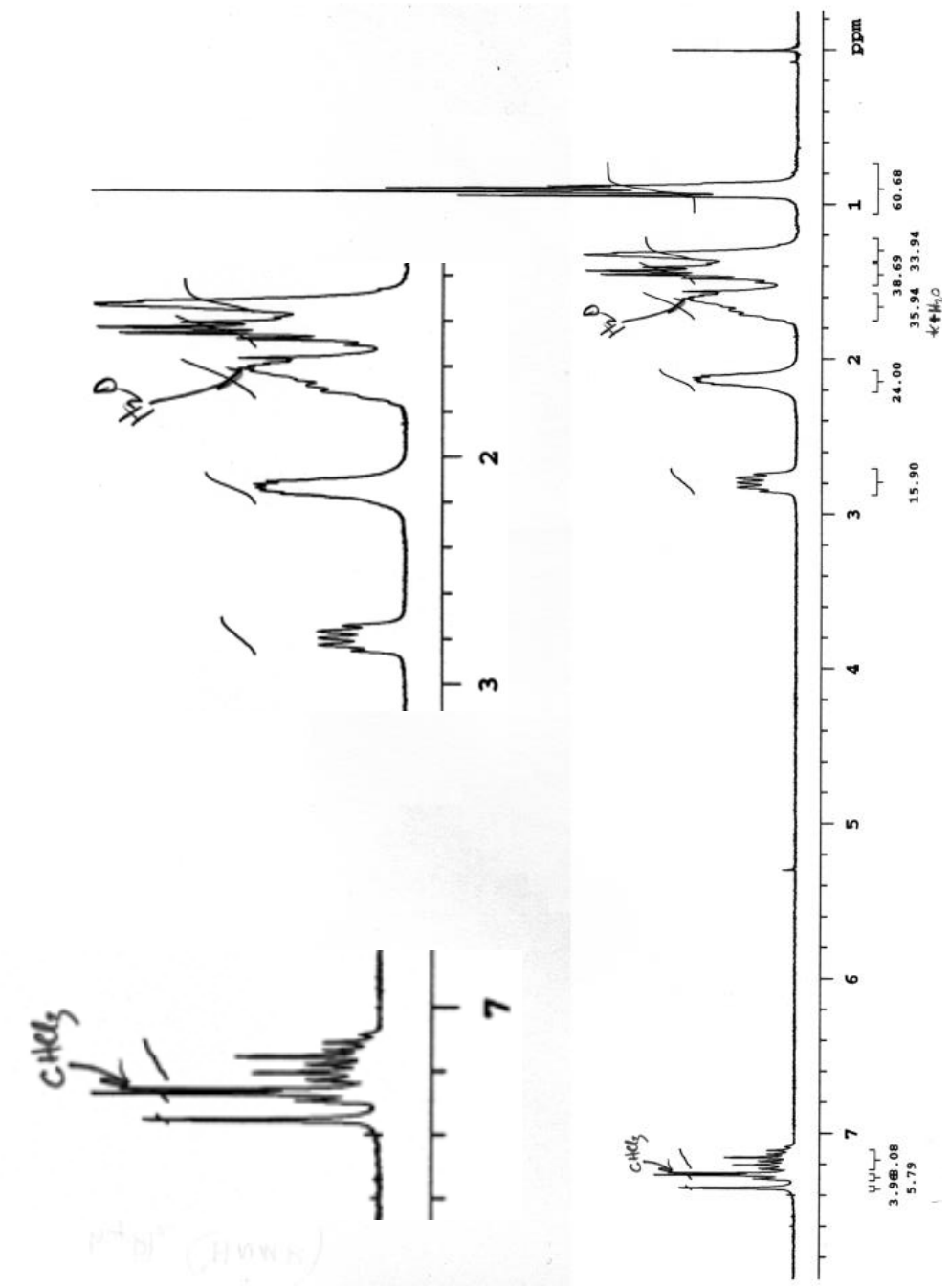

Figure S-8. ^{1}H NMR of **Ph_4Pt_2**.

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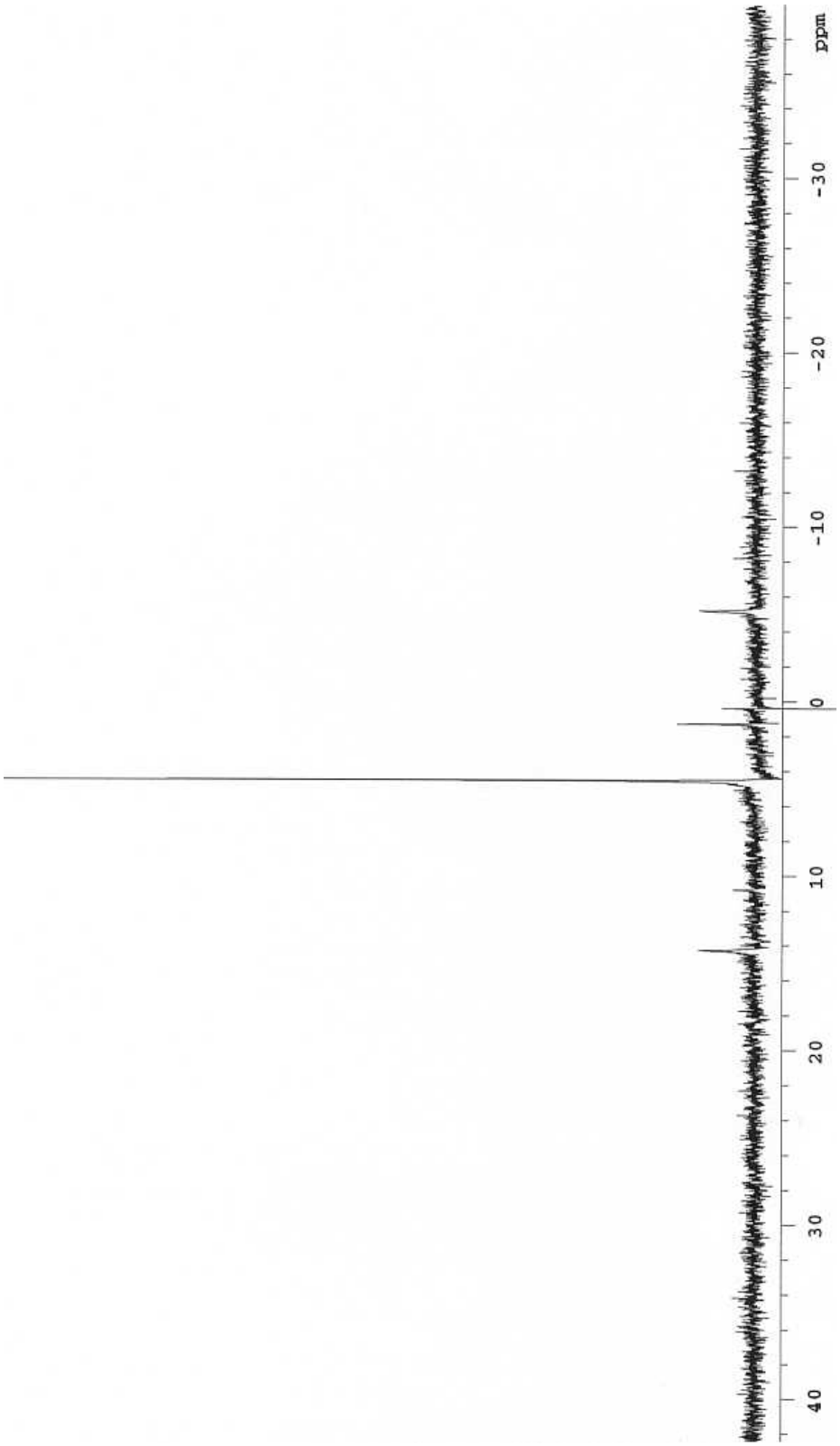

Figure S-9. ^{31}P NMR of **Ph_4Pt_2**.

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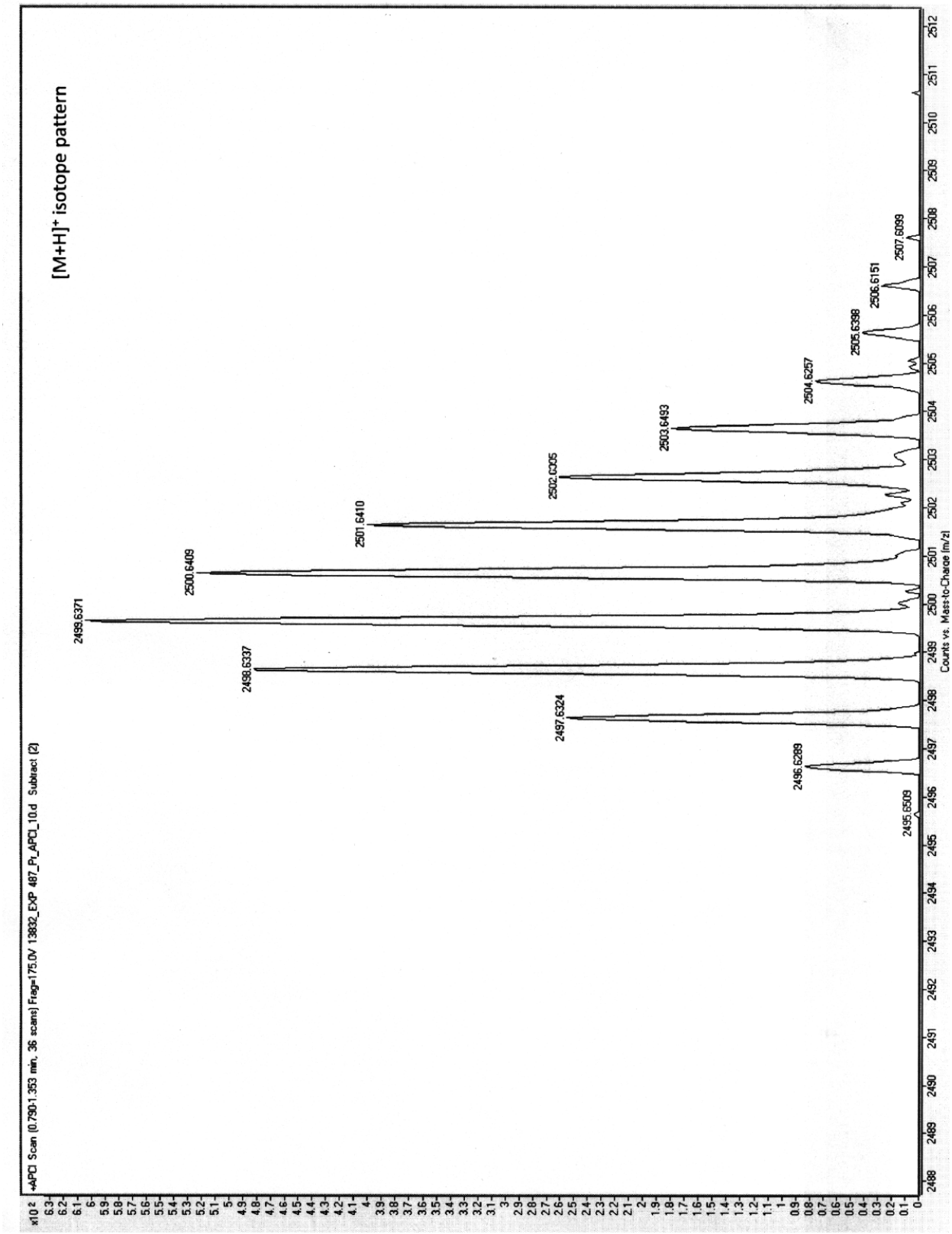

Figure S-10. APCI-HRMS, $[M+H]^+$ isotope pattern of **Ph_4Pt_2.**

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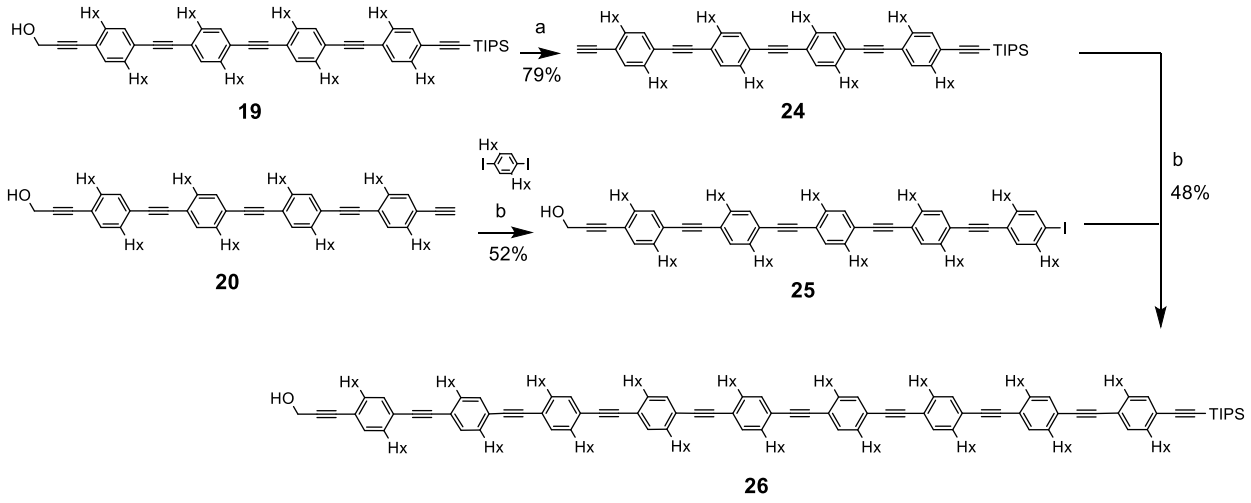

a) MnO_2/KOH, ether, rt, dark, 12h; b) $Pd_2(dba)_3$/CuI/PPh3, THF/piperidine, rt, 12h.

Scheme S-5. Synthesis of intermediate compound **26**.

Compounds **24-26**,[5] were prepared by literature methods.

2.5.1. Synthesis of $Ph_4TIPS_1(CCH)_1$ (24) is a known compound prepared by literature method[5] to afford the product as a yellow solid. Yield 79%. M.p. 79°C (Lit 79°C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82-0.95 (m, 24H), 1.16 (s, 21H) 1.26-1.50 (m, 48H), 1.59-1.79 (m, 16H), 2.72-2.87 (m, 16H), 3.31 (s, 1H), 7.31-7.4 (m, 8H).

2.5.2. Synthesis of $Ph_5I_1OH_1$ (25) is a known compound prepared by literature method[5] to afford a yellow solid. Yield 52%. M.p. 120°C (Lit. 121°C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81-0.99 (m, 30H), 1.25-1.51 (m, 60H), 1.56-1.81 (m, 20H), 2.64-2.90 (m, 20H), 4.58 (s, 2H), 7.31 (s, 1H), 7.34 (s, 1H), 7.36 (s, 1H), 7.40 (br s, 6H), 7.72 (s, 1H).

2.5.3. Synthesis of $Ph_9TIPS_1OH_1$ (26) is a known compound prepared by literature method[5] to yield the product as a bright yellow solid. Yield 48%. M.p. 184.5-186.0°C (Lit. 187°C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81-0.98 (m, 54H), 1.16 (s, 21H), 1.26-1.79 (m, 144H), 2.71-2.89 (m, 36H), 4.52 (s, 2H), 7.31-33 (2 s, 2H), 7.35-7.36 (2 s, 2H), 7.37-7.45 (m, 14H).

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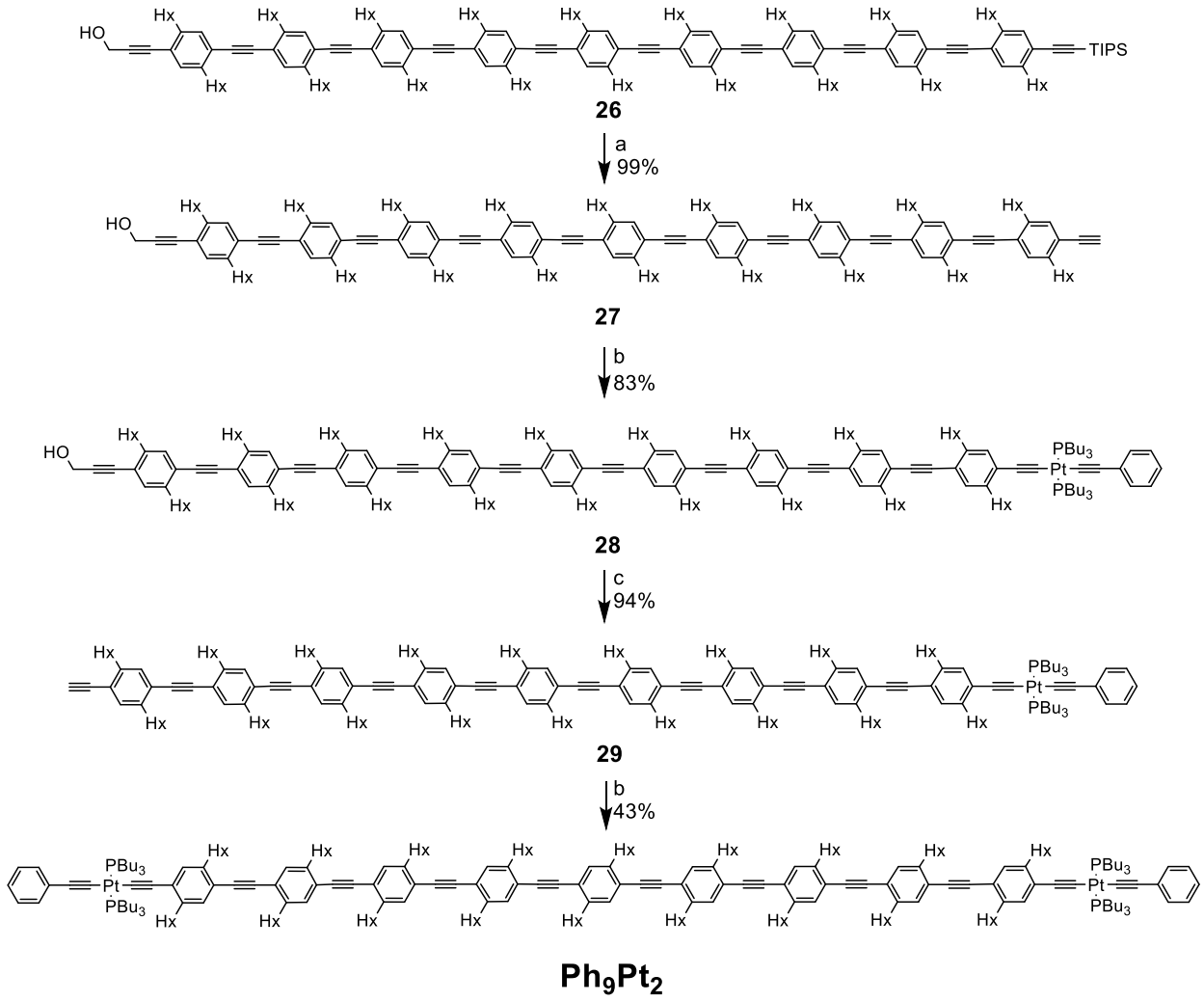

a) TBAF, THF, 2h, dark, rt; b) CuI, $NHEt_2$/THF, rt, 3h; c) MnO_2/KOH, ether, dark, rt.

Scheme S-6. Synthesis of the **Ph_9Pt_2** oligomer.

2.6.1. Synthesis of $Ph_9OH_1(CCH)_1$ (27). Deprotection of $Ph_9TIPS_1OH_1$ (26) (170 mg, 0.065 mmol) was accomplished by degassing this starting material in THF (15 mL) for 30 min with argon, followed by the addition of 1 M TBAF in THF (0.176 mL, 0.176 mmol) via syringe. The reaction was allowed to stir in a dark flask for 2 h until complete, and then quenched with water. The organic portion was extracted with CH_2Cl_2, dried over $NaSO_{4(s)}$, followed by filtration of the drying agent and evaporation of the solvent to afford a crude oil. This crude mixture was loaded onto a column (silica, flash) prepped and eluted with 1:1 petroleum ether/CH_2Cl_2. The product was eluted as a bright yellow band on the column (R_f 0.5), exhibiting bright yellow fluorescence on TLC. The collected fractions were evaporated to give the product as 160 mg of a bright yellow

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solid. Yield 99%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82-0.97 (m, 54H), 1.25-1.51 (m, 108H), 1.59-1.80 (m 36H), 2.69-2.90 (m, 36H), 3.30 (s, 1H), 4.53 (d, $^{3}J_{(H,H)}$ = 6Hz, 2H), 7.28-7.39 (m, 18H). The material was used as is toward further synthesis.

2.6.2. Synthesis of $Ph_9OH_1Pt_1$ (28). To a round bottom flask equipped with stir bar was added $Ph_9OH_1(CCH)_1$ (27) (0.150 g, 0.061 mmol), compound **5** (0.120 g, 0.164 mmol), THF (10 mL) and diethylamine (9 mL). The solution was stirred and degassed under argon flow for 30 min, followed by the addition of CuI (0.4 mg, 2.20 μmol). The reaction was stirred at room temperature for 3 h until TLC confirmed that all of the limiting reagent was consumed, and the reaction was quenched with water. The organic portions were extracted with CH_2Cl_2, washed with saturated $NH_4Cl_{(aq)}$ and brine, and then dried over $NaSO_{4(s)}$. The solvent was evaporated after filtration of the drying agent to give a bright yellow crude solid that was loaded onto a column (silica, flash) prepped with 3:1 petroleum ether/CH_2Cl_2. Fractions 1 and 2 were eluted as either starting materials or side products. The solvent was increased gradually to 2:1 petroleum ether/CH_2Cl_2 and the third fraction (bright yellow band, fluorescent yellow on column) was collected as the product, 160 mg of a bright yellow solid (no phosphorescence was apparent by TLC under $N_{2(g)}$ flow). Yield 83%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82-1.00 (m, 72H), 1.22-1.82 (m, 180H), 2.00-2.22 (m, 12H), 2.66-3.02 (m, 36H), 4.56 (s, 2H), 7.09-7.42 (m, 23H). ^{31}P NMR ($CDCl_3$) δ 4.55 (J_{Pt-P} = 2357.93 Hz). The compound was used as is toward further synthesis.

2.6.3. Synthesis of $Ph_9(CCH)_1Pt_1$ (29). A mixture of $Ph_9OH_1Pt_1$ (25) (160 mg, 50.4 μmol) and ether (20 mL) was stirred and degassed under argon flow for 30 min in a dark flask, followed by five hourly addition of portions of MnO_2 (107 mg, 1.23 mmol) and powdered KOH (28 mg, 0.49 mmol) until the reaction was complete. After 5 h, the reaction was almost finished and it was left to run to completion overnight; the solution was filtered through a silica gel plug, washed with CH_2Cl_2, and the filtrate was collected and evaporated. The crude oil was loaded onto a column (silica, flash) prepped with 2:1 petroleum ether/CH_2Cl_2. The first fraction was a small amount of byproduct (fluorescent blue on column). The second fraction to elute was fluorescent yellow on the column. This large fraction was collected and the solvent evaporated to afford 150 mg of yellow oil as product. Yield 94%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.72-0.98 (m, 72H), 1.20-1.82 (m, 168H), 2.02-2.24 (m, 12H), 2.66-2.94 (m, 36H), 3.31 (s, 1H), 7.08-7.42 (m, 23H). ^{31}P NMR ($CDCl_3$) δ 4.54 (J_{Pt-P} = 2362.20 Hz). The compound was used as is for further reaction.

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2.6.4. Synthesis of Ph_9Pt_2. A round bottom flask was charged with $Ph_9(CCH)_1Pt_1$ (26) (150 mg, 47.7 μmol), compound **5** (105 mg, 0.143 mmol), THF (10 mL) and diethylamine (15 mL). The solution was degassed for 45 min under argon flow, followed by the addition of a catalytic amount of CuI (0.4 mg, 1.91 μmol). The reaction was stirred at room temperature for 4 h then quenched with water. The organics were extracted with CH_2Cl_2, washed with $NH_4Cl_{(aq)}$ and brine, then dried over $NaSO_{4(s)}$. The drying agent was removed and the solvent evaporated to afford a crude yellow oil. The crude oil was loaded onto a column (silica, flash) prepped with 4:1 petroleum ether/CH_2Cl_2. The first few fractions to elute were organic byproducts and the excess starting material. The third fraction was eluted as a yellow band (fluorescent yellow on the column). This fraction was collected and the solvent evaporated to yield 80 mg of pure yellow (slowly forming) solid product. (*About 20 mg of product was also collected with the fourth fraction, containing acetylene starting material byproduct.) Yield 43%. Elemental Analysis for $C_{247}H_{370}P_4Pt_2$: Calculated C 76.89%, H 9.78%; Found C 76.81%, H 10.10%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.80-0.97 (m, 90H), 1.22-1.79 (m, 192H), 2.04-2.21 (m, 24H), 2.64-2.91 (m, 36H), 7.09-7.24 (m, 9H), 7.26-7.32 (m, 5H), 7.34-7.40 (m, 14H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.93, 141.84, 141.68, 141.25, 140.23, 132.44, 132.36, 132.25, 132.00, 131.84, 130.80, 127.84, 123.44, 122.91, 122.80, 122.68, 122.19, 118.64, 94.17, 93.27, 93.09, 92.79, 91.52, 34.23, 32.04, 31.90, 31.85, 30.81, 30.73, 30.49, 29.71, 29.54, 29.38, 29.32, 26.40, 24.46, 24.41, 24.35, 24.04, 23.91, 23.77, 22.77, 22.68, 14.12, 13.86. ^{31}P NMR ($CDCl_3$) δ 4.56 ($J_{Pt\text{-}P}$ = 2357.85 Hz).

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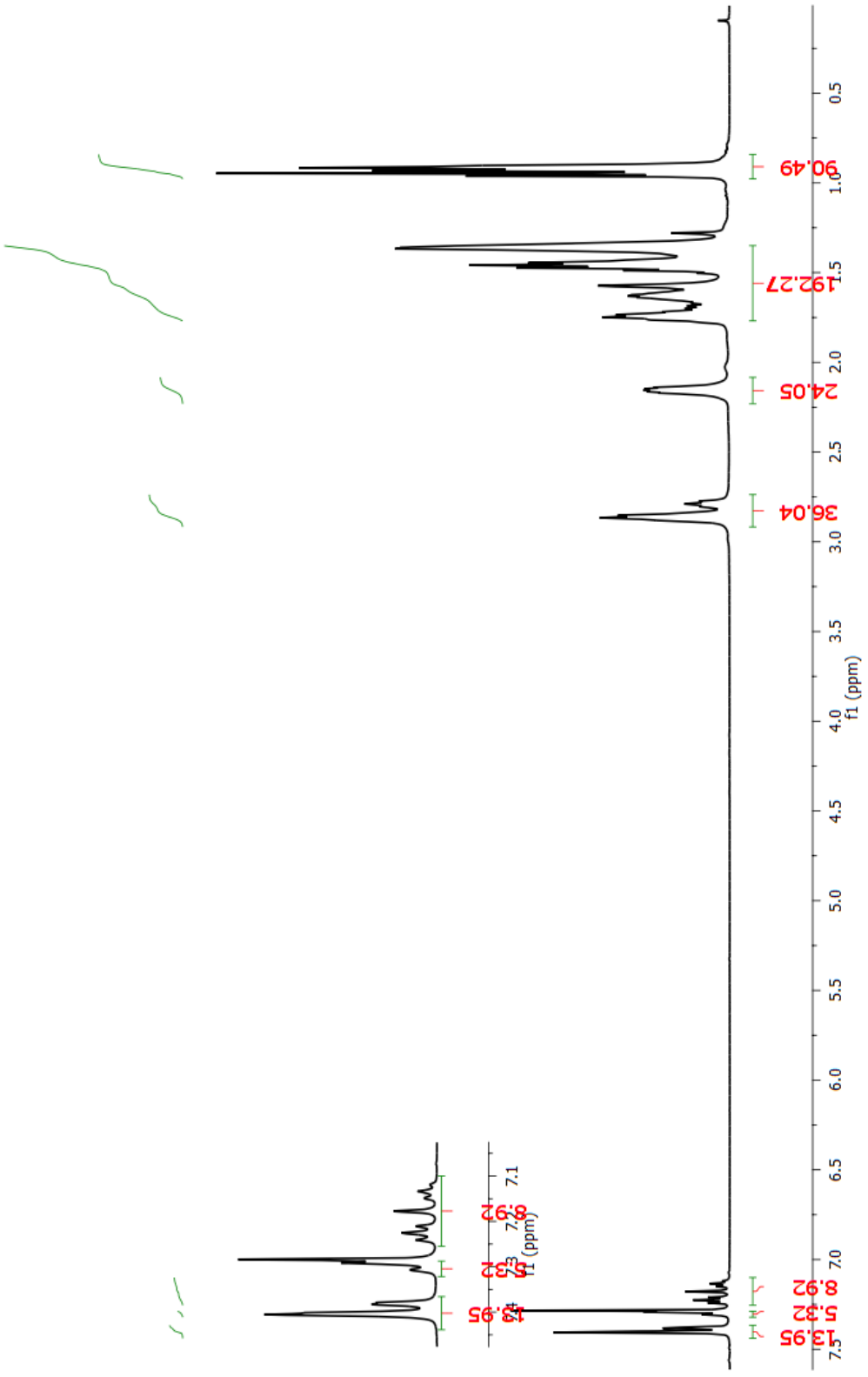

Figure S-11. ^{1}H NMR of **Ph$_9$Pt$_2$**.

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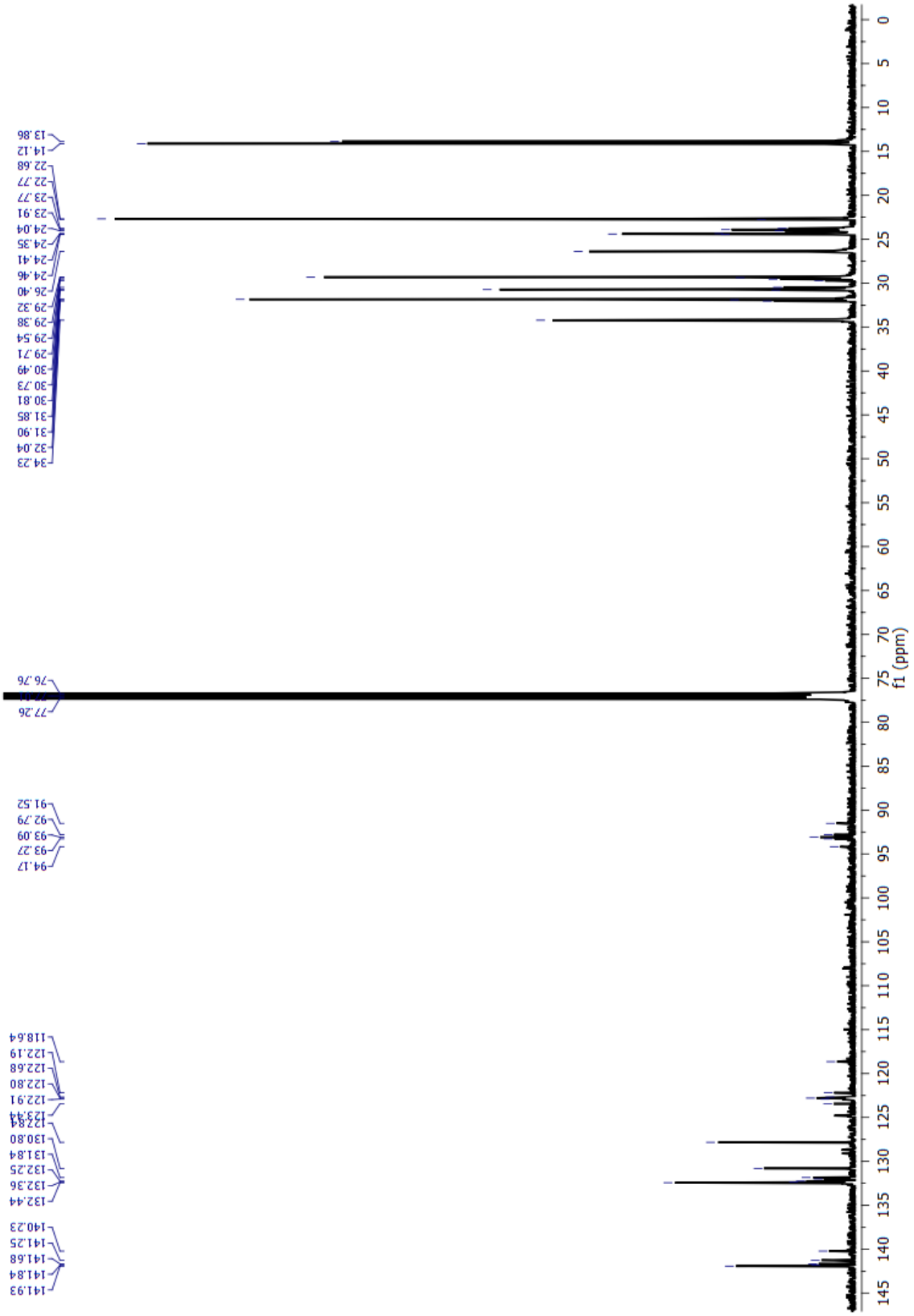

Figure S-12. ^{13}C NMR of **Ph$_9$Pt$_2$**.

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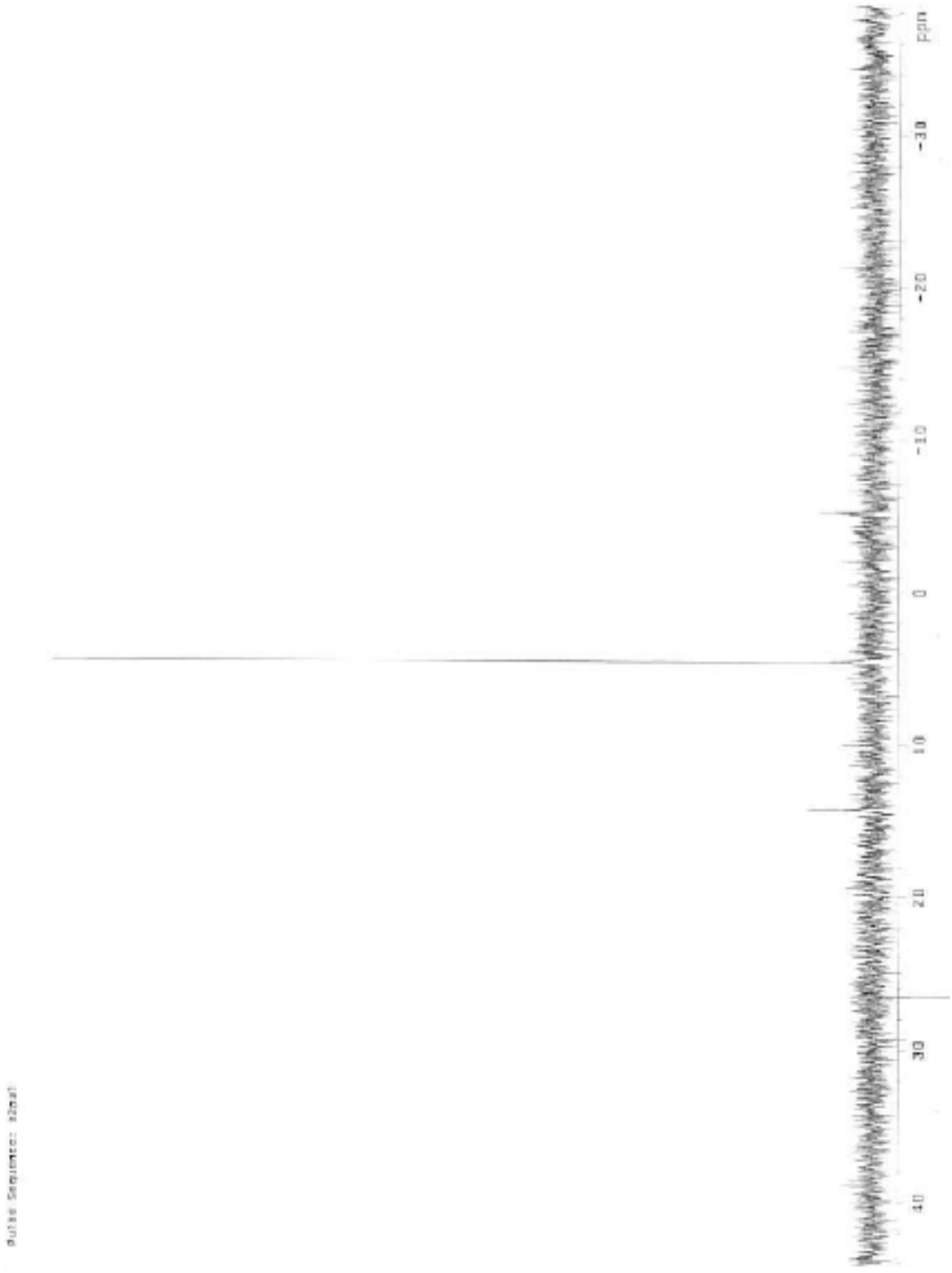

Figure S-13. ^{31}P NMR of **Ph$_9$Pt$_2$**.

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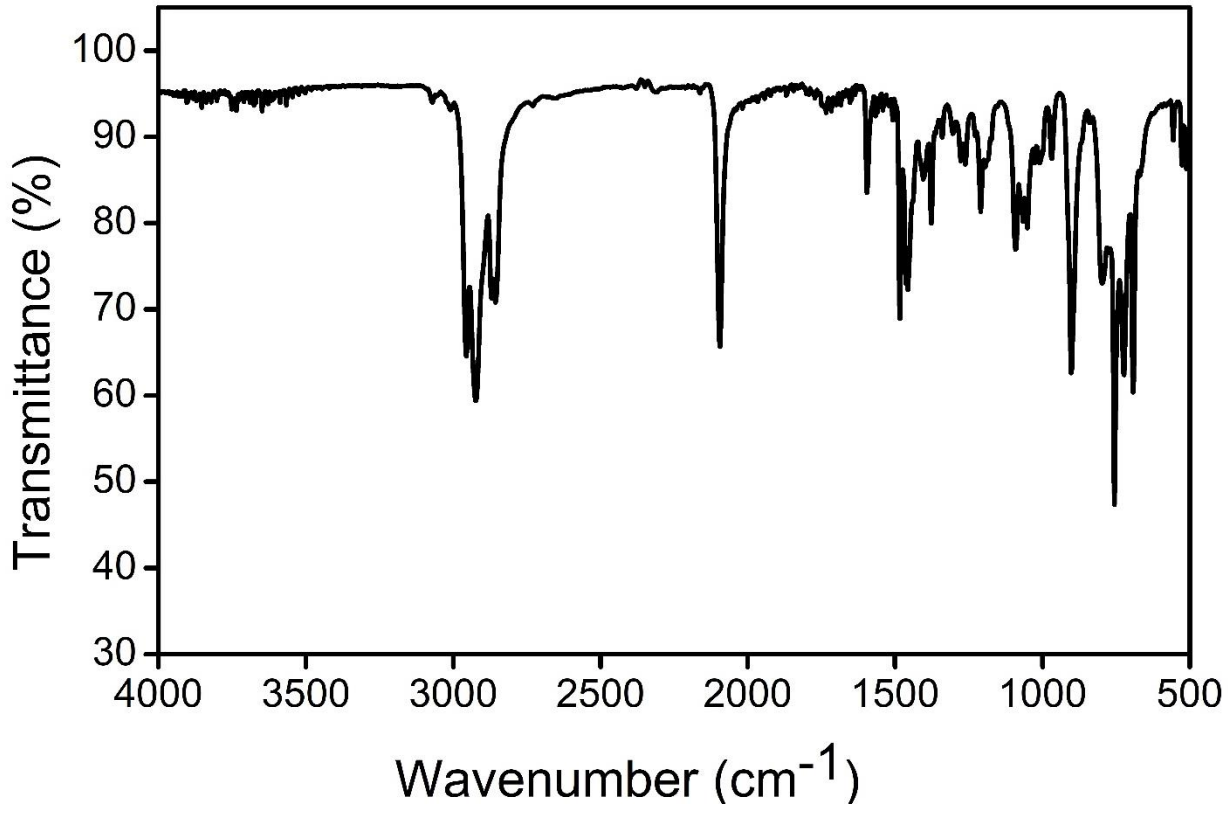

Figure S-14. IR spectrum of **Ph_9Pt_2**.

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