**Electronic and steric effects of Platinum(II) di-yne and poly-yne substituents on the photo-switching behaviour of stilbene: Experimental and theoretical insights**

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# Supporting Information

# Tables

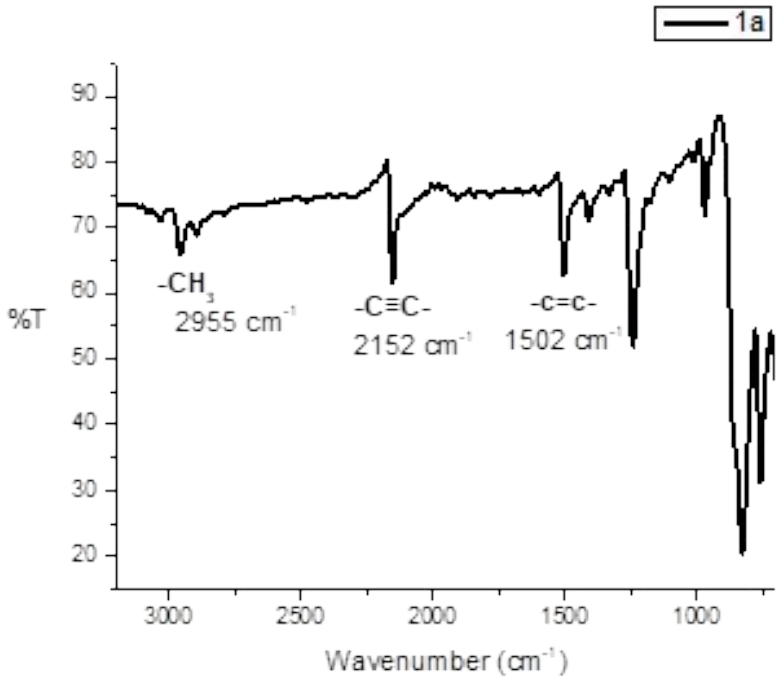



**Figure S1**. FTIR spectrum of **1a**.

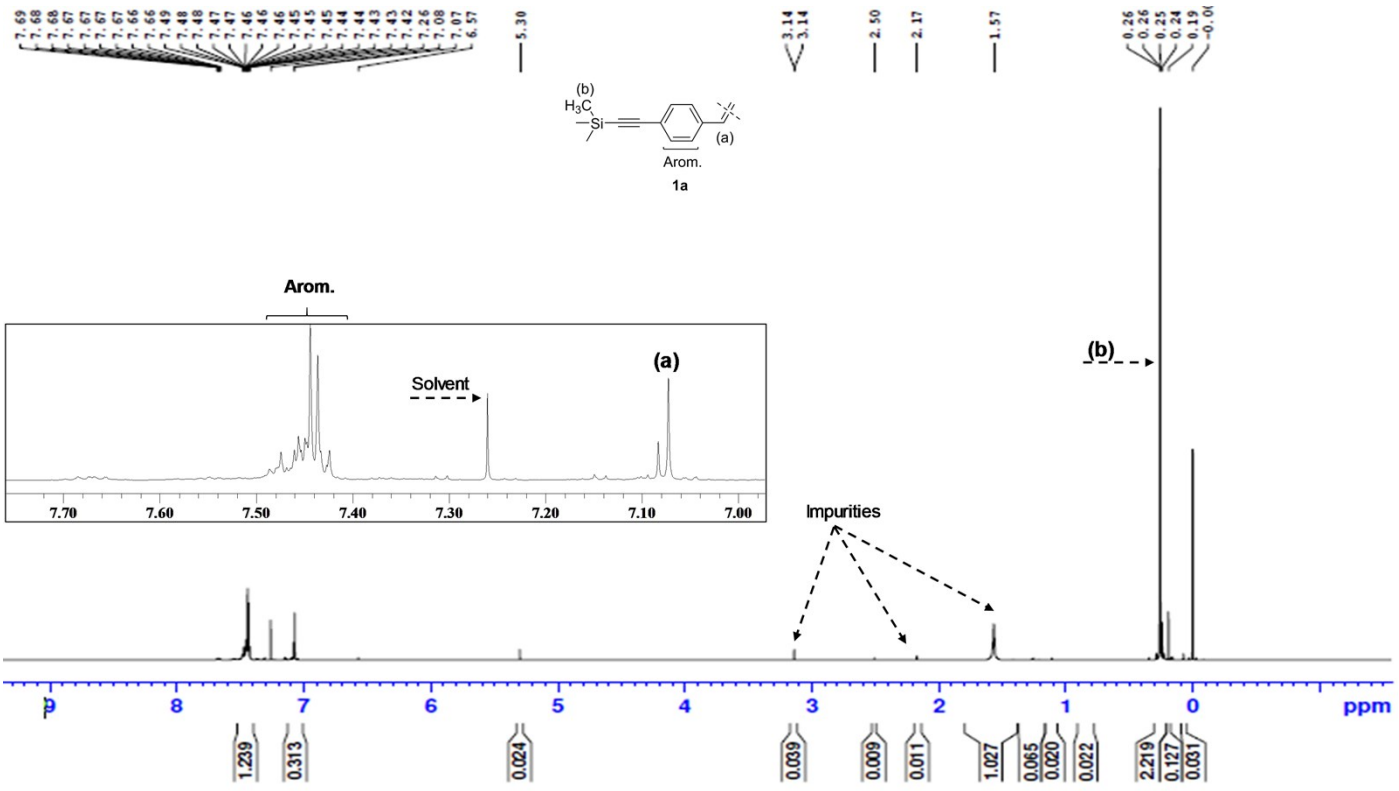


**Figure S2**. $^{1}$H-NMR spectrum of **1a**.

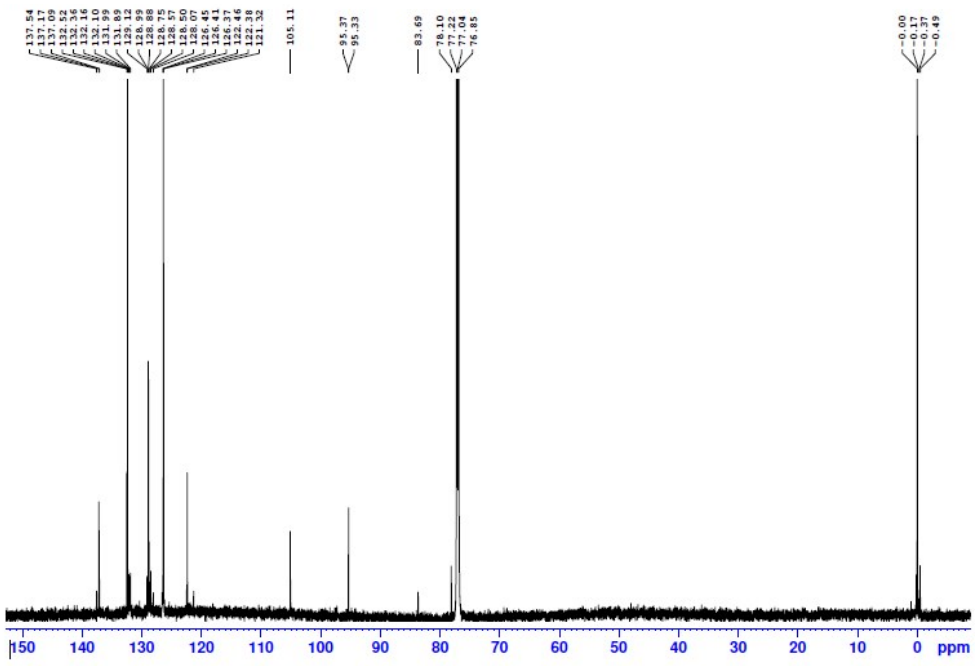



**Figure S3**. $^{13}$C-NMR spectrum of **1a**.

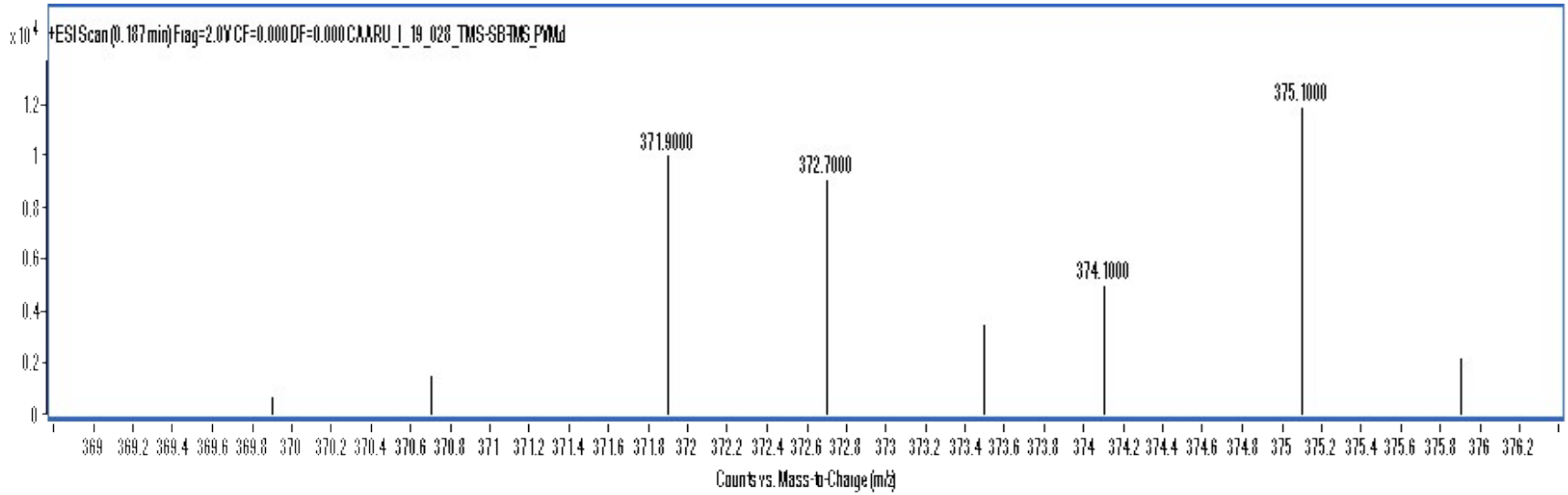



**Figure S4**. ESI-MS spectrum of **1a**.

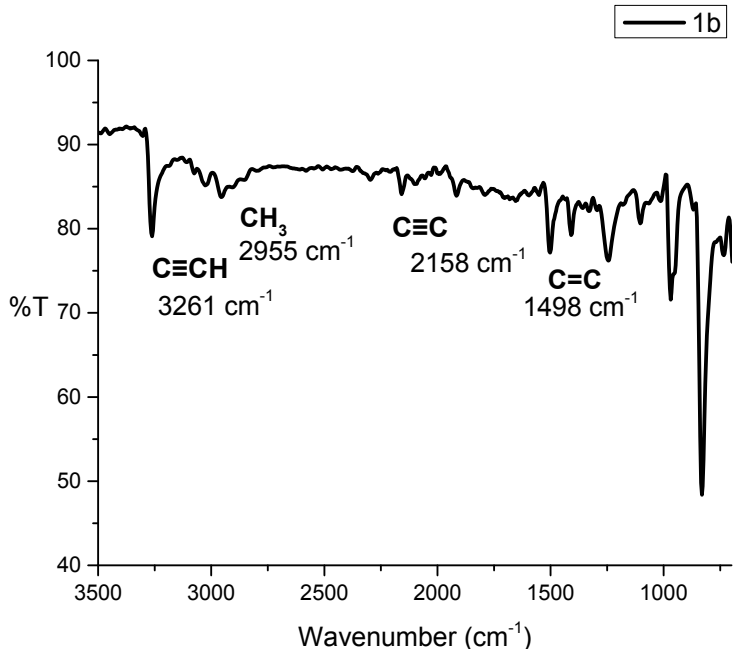



**Figure S5**. FTIR spectrum of **1b**.

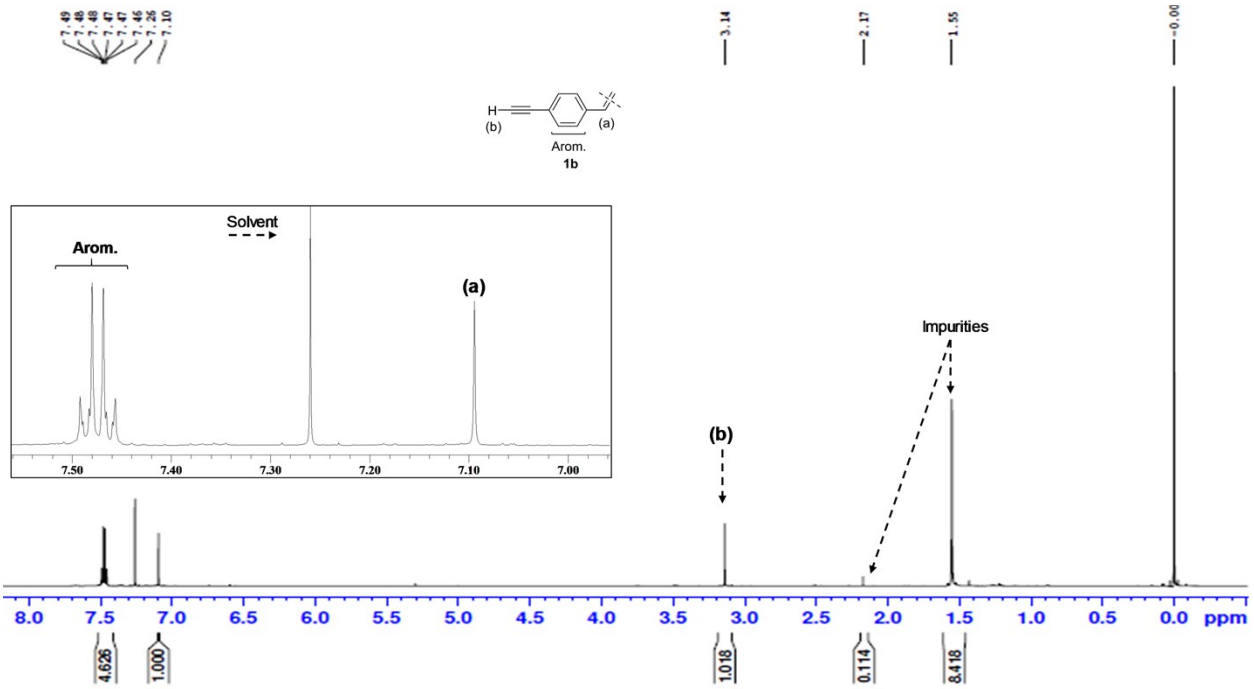



**Figure S6**. $^{1}$H-NMR spectrum of **1b**.

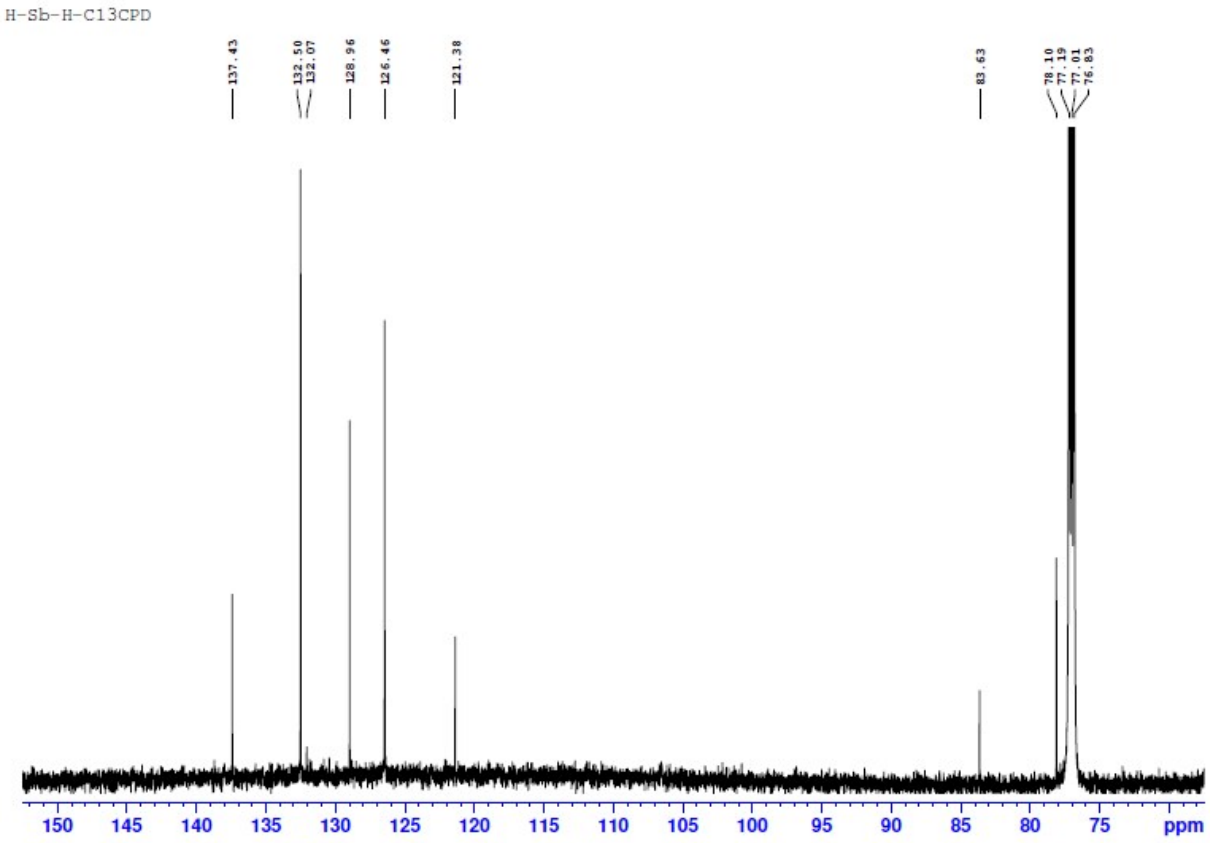



**Figure S7**. $^{13}$C-NMR spectrum of **1b**.

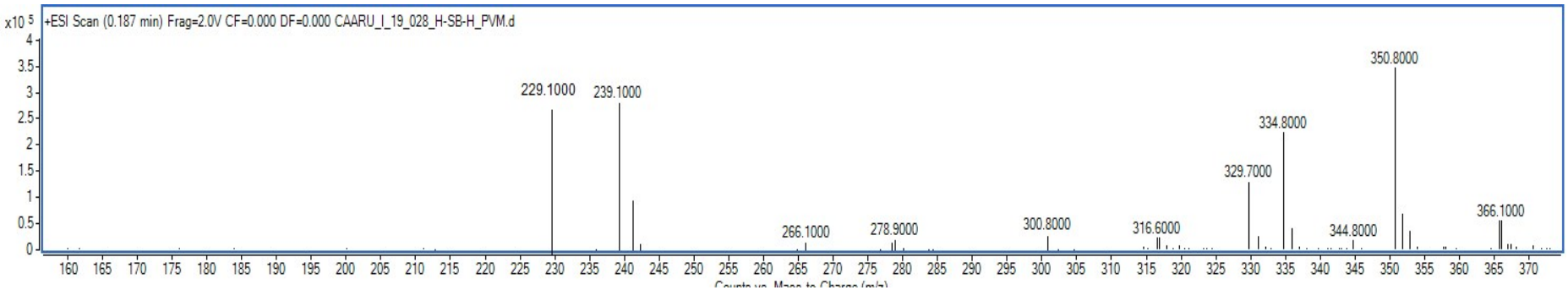



**Figure S8**. ESI-MS spectrum of **1b**.

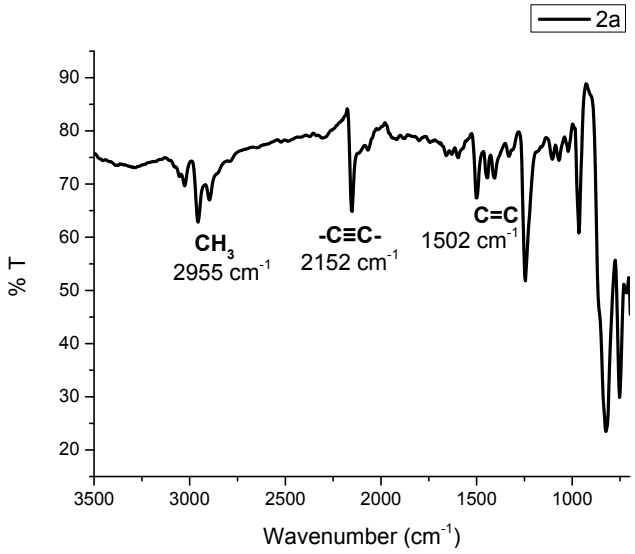



**Figure S9**. FTIR spectrum of **2a.**

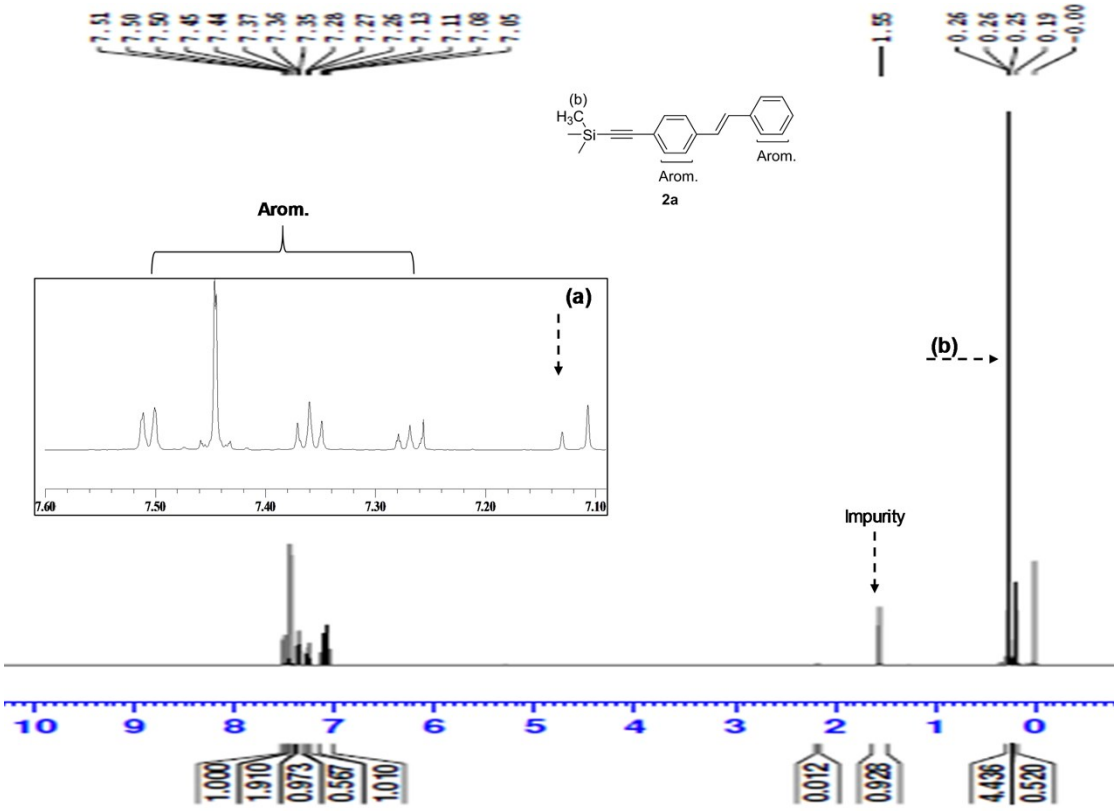



**Figure S10**. $^{1}$H-NMR spectrum of **2a.**

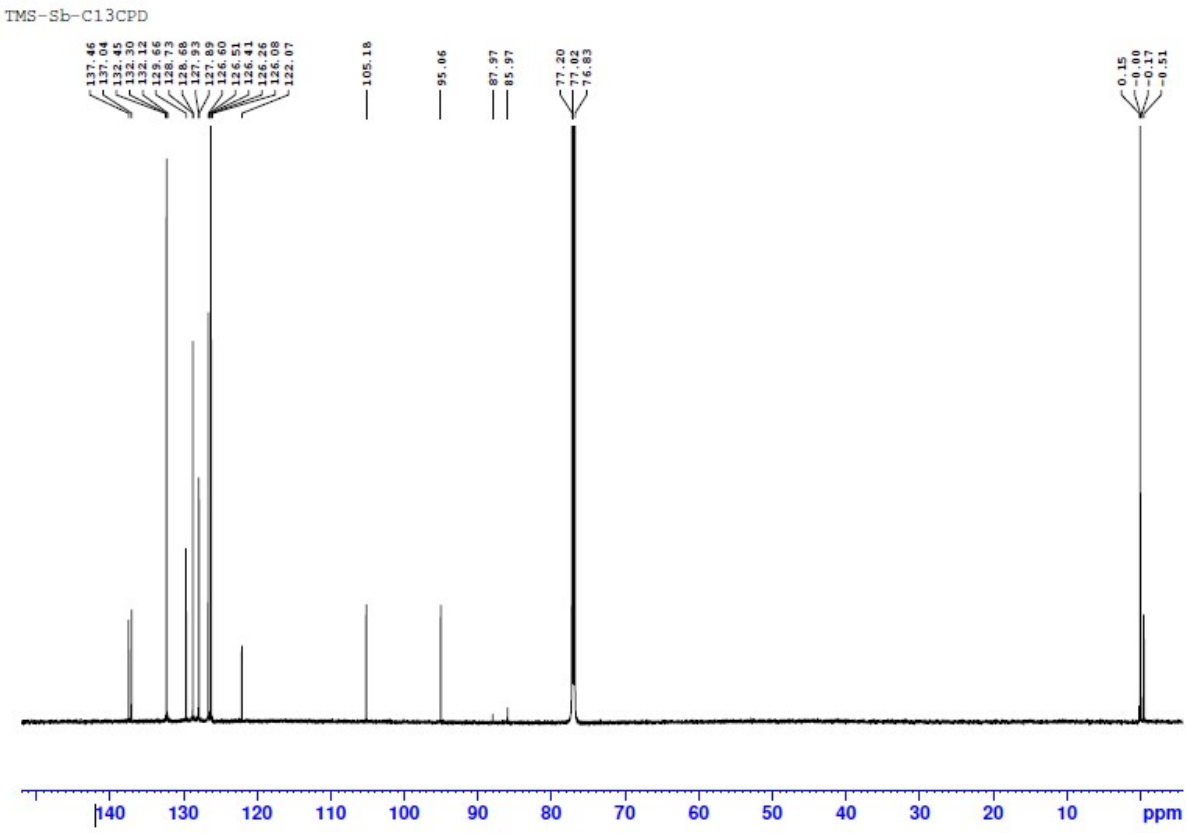



**Figure S11**. $^{13}C$ spectrum of **2a**.

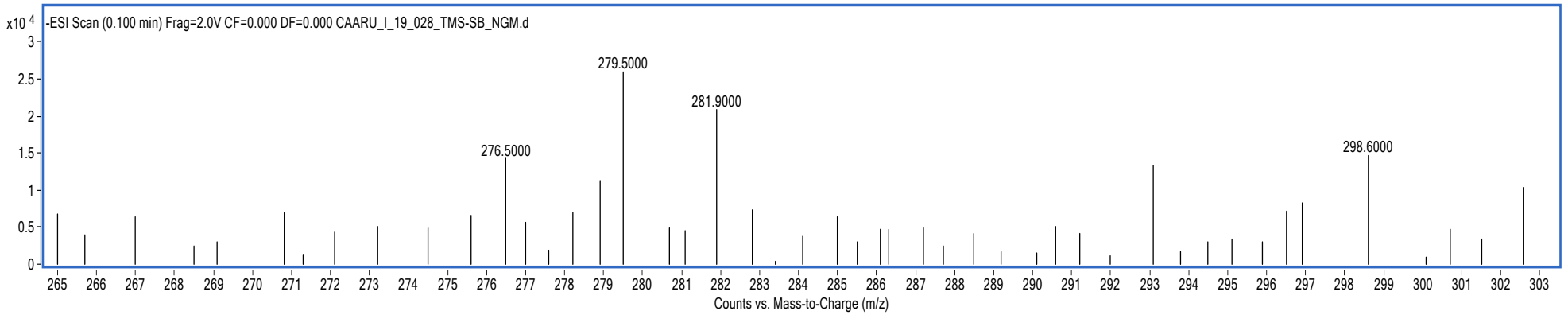



**Figure S12**. ESI-MS spectrum of **2a**.

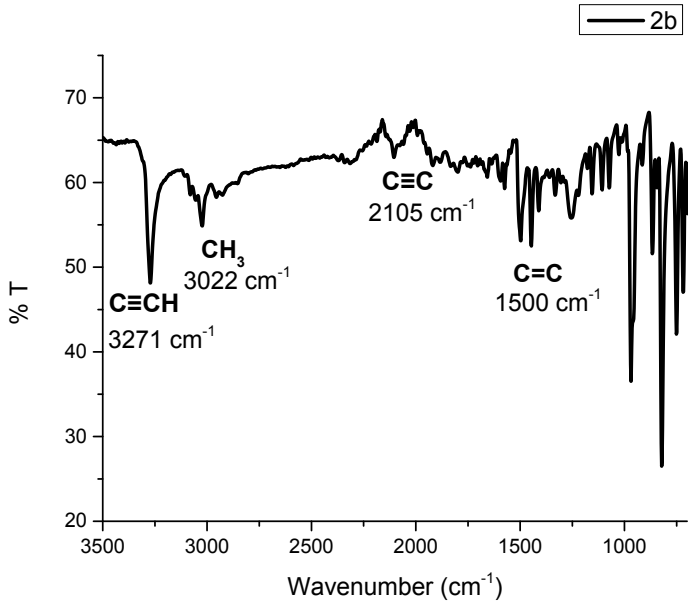



**Figure S13.** FTIR spectrum of **2b.**

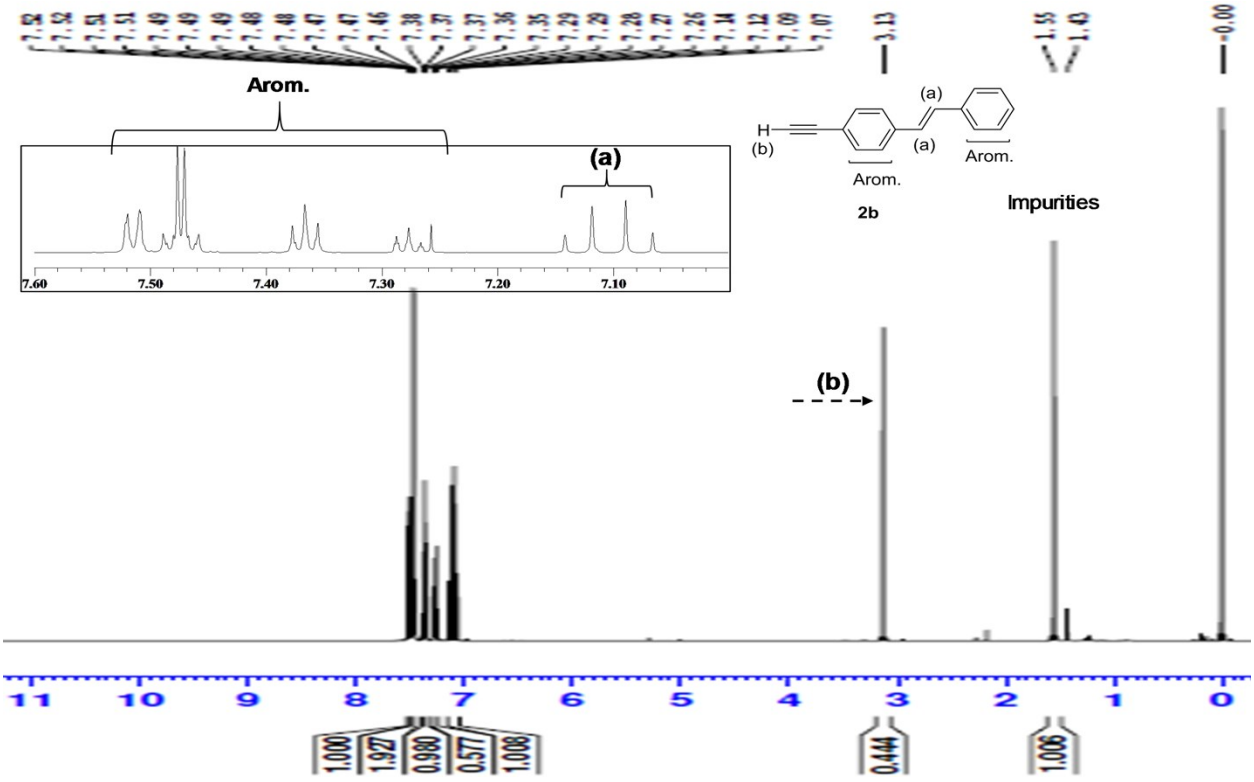



**Figure S14**. [1]H-NMR spectrum of **2b**.

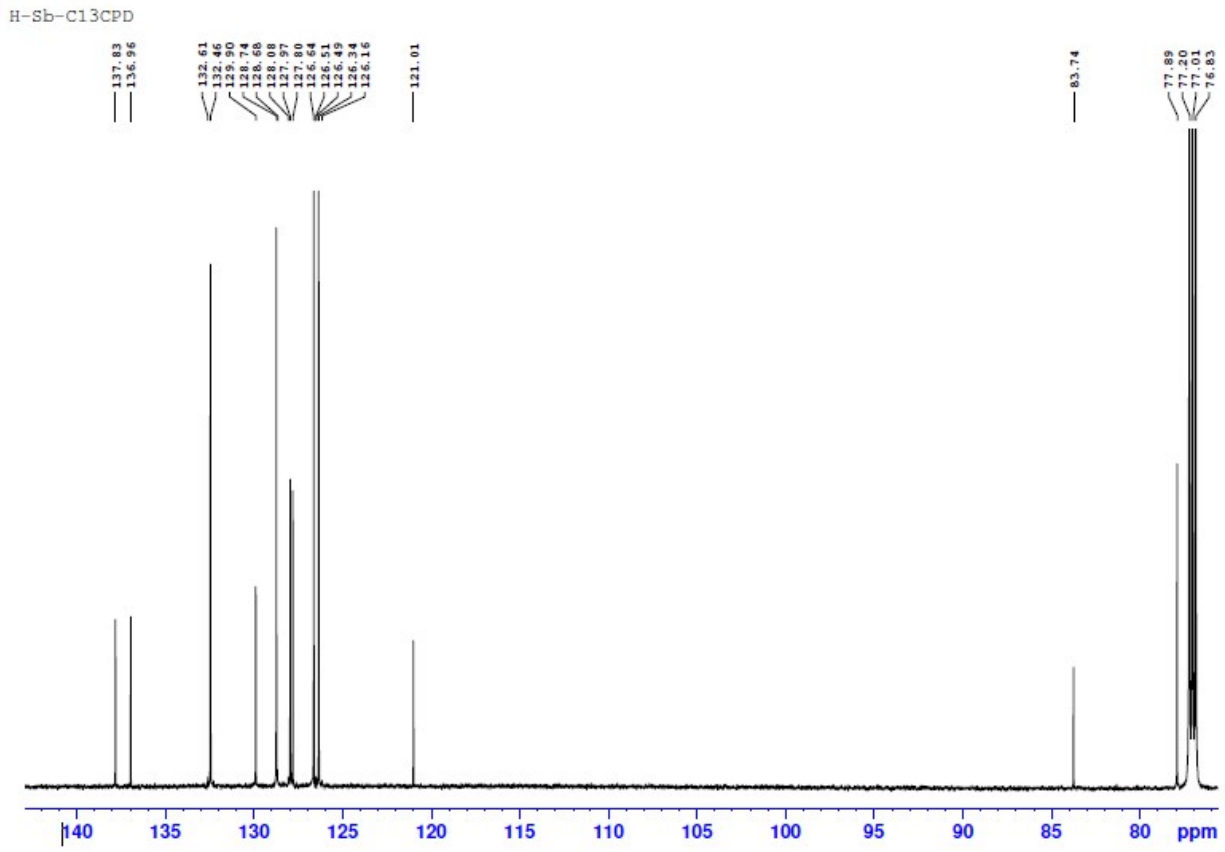



**Figure S15**. $^{13}$C-NMR spectrum of **2b**.

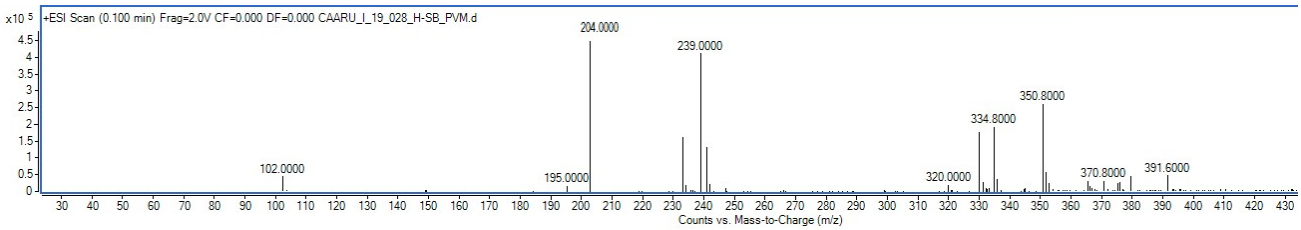



**Figure S16**. ESI-MS spectrum of **2b**.

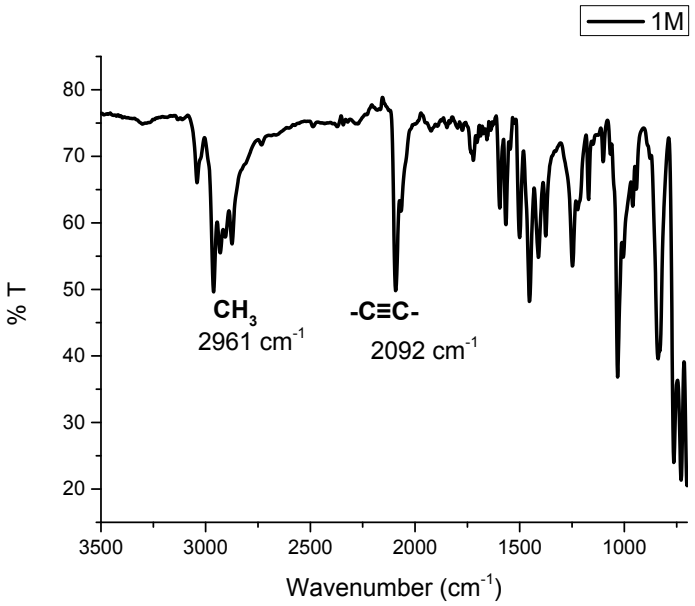



**Figure S17**. FTIR spectrum of **1M.**

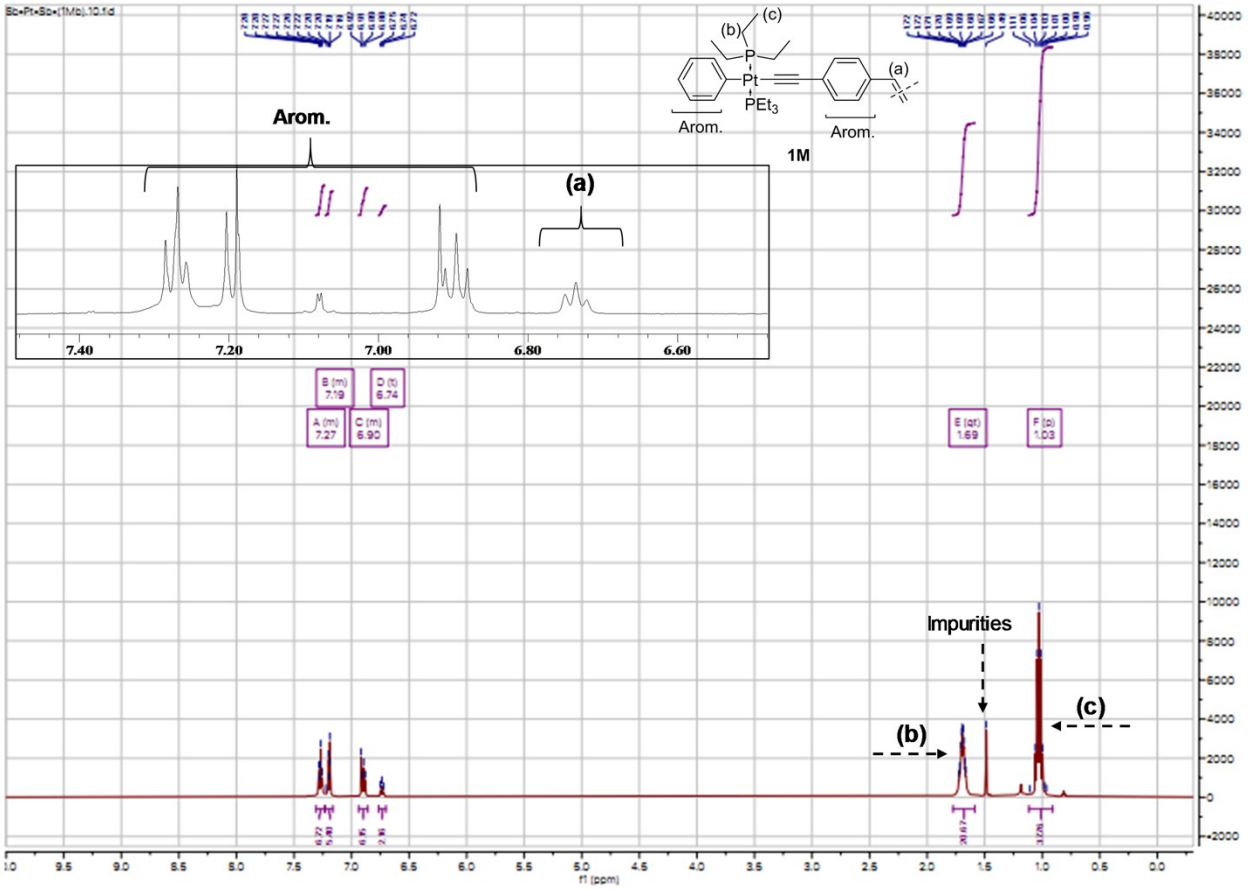



**Figure S18**. $^{1}$H-NMR spectrum of **1M.**

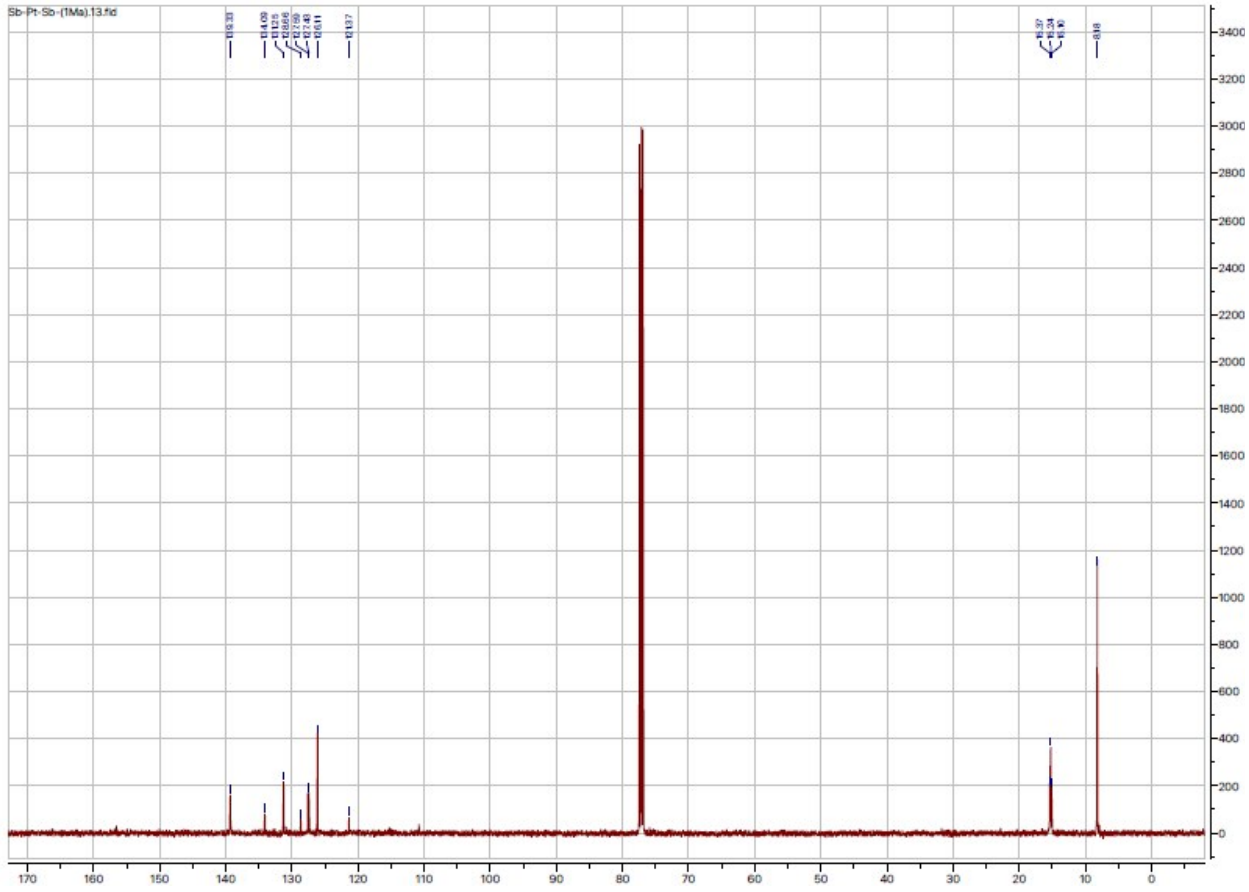



**Figure S19**. $^{13}$C-NMR spectrum of **1M.**

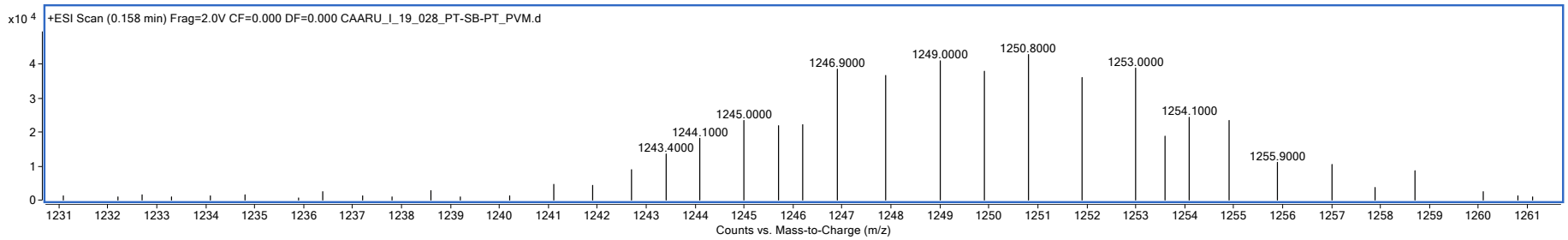



**Figure S20**. ESI-MS spectrum of **1M** .

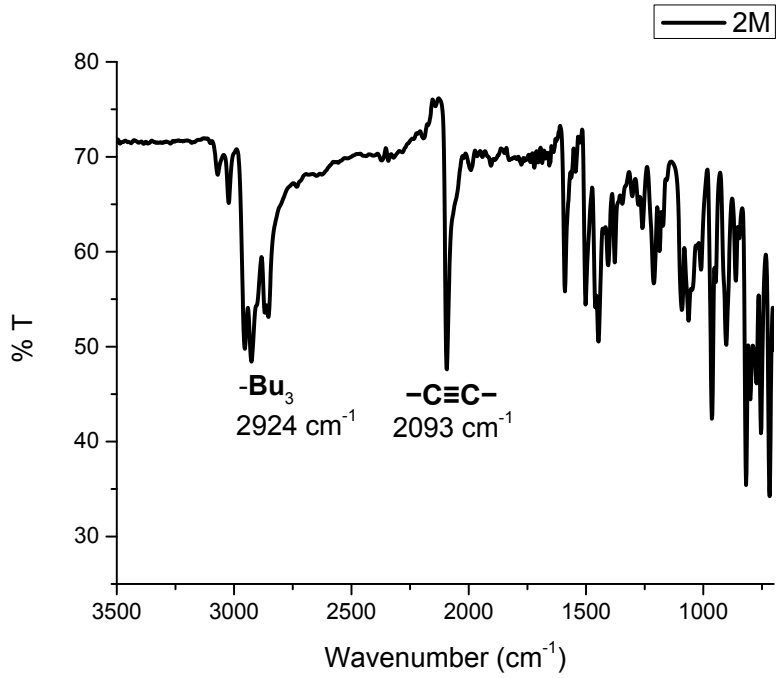



**Figure S21**. FTIR spectrum of **2M.**

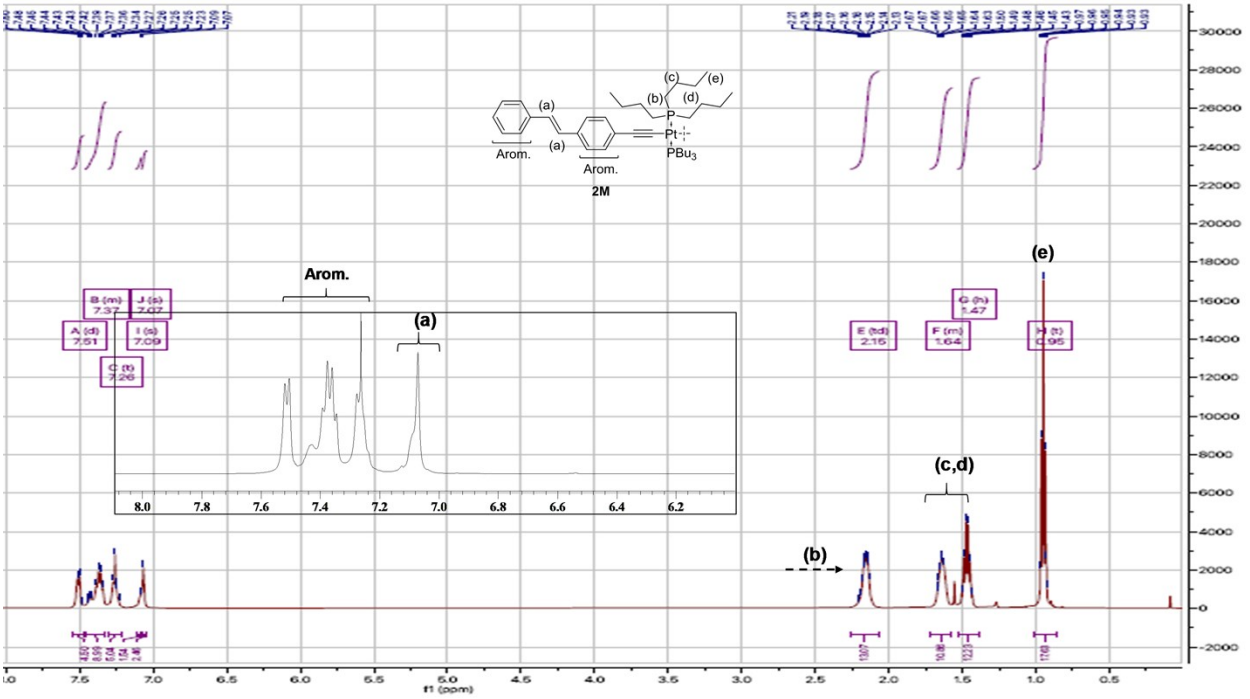



**Figure S22**. $^{1}$H-NMR spectrum of **2M**.

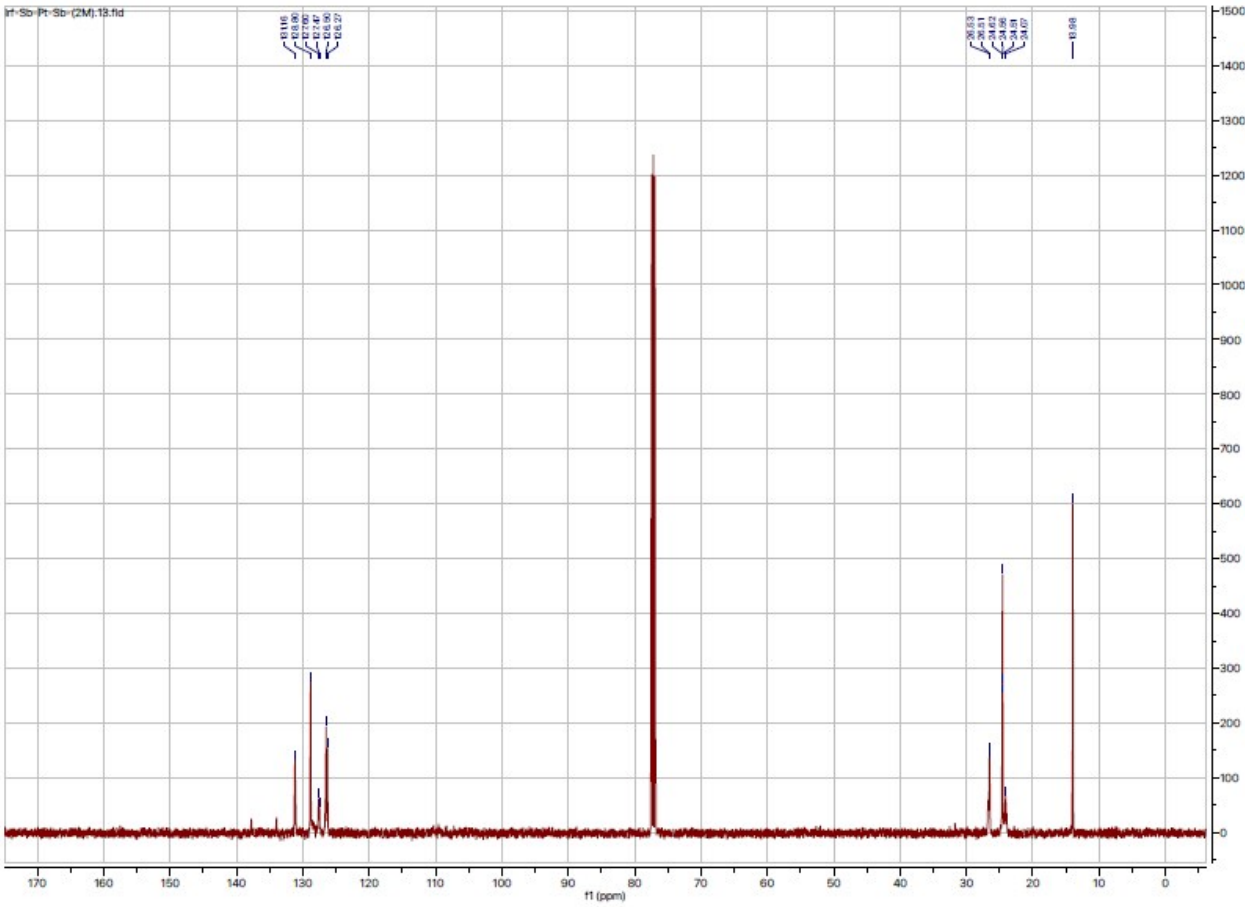



**Figure S23**. $^{13}$C-NMR spectrum of **2M**.

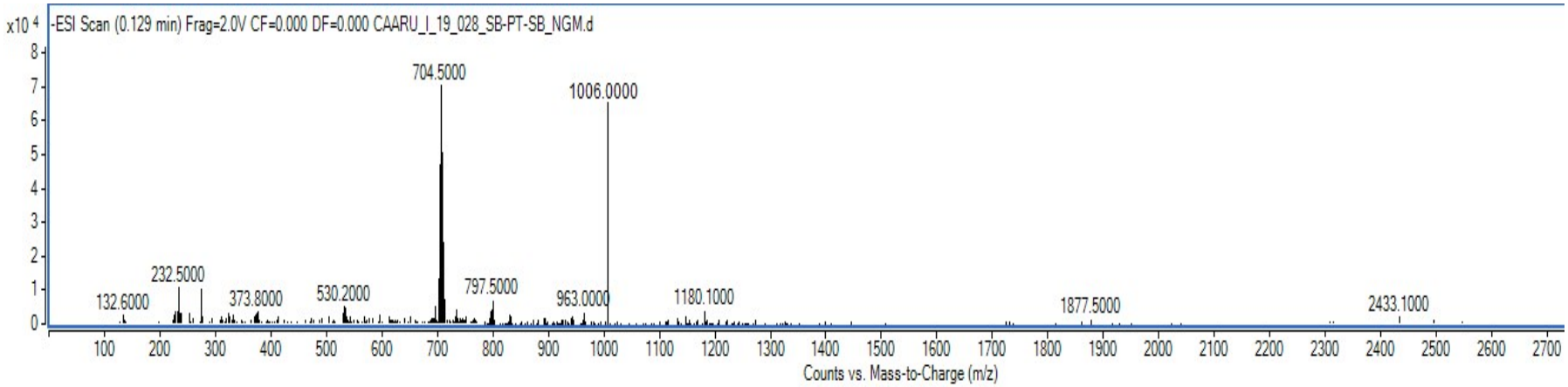



**Figure S24**. ESI-MS of **2M**.

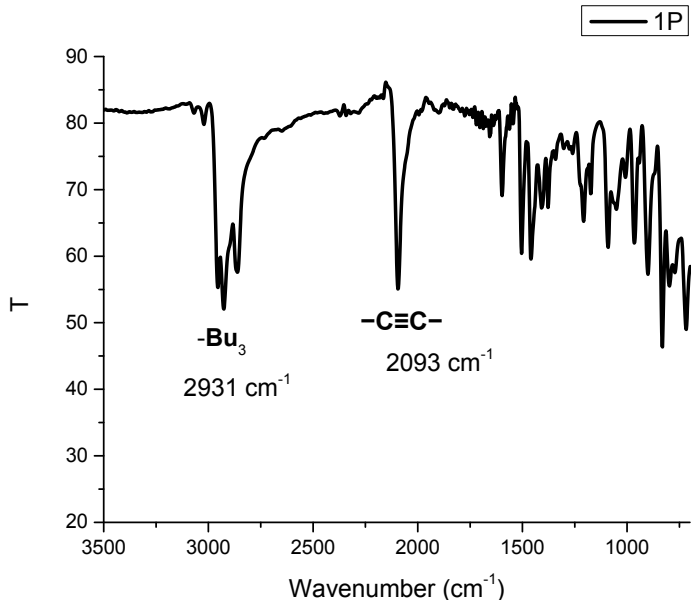



**Figure S25**. FTIR spectrum of **1P**.

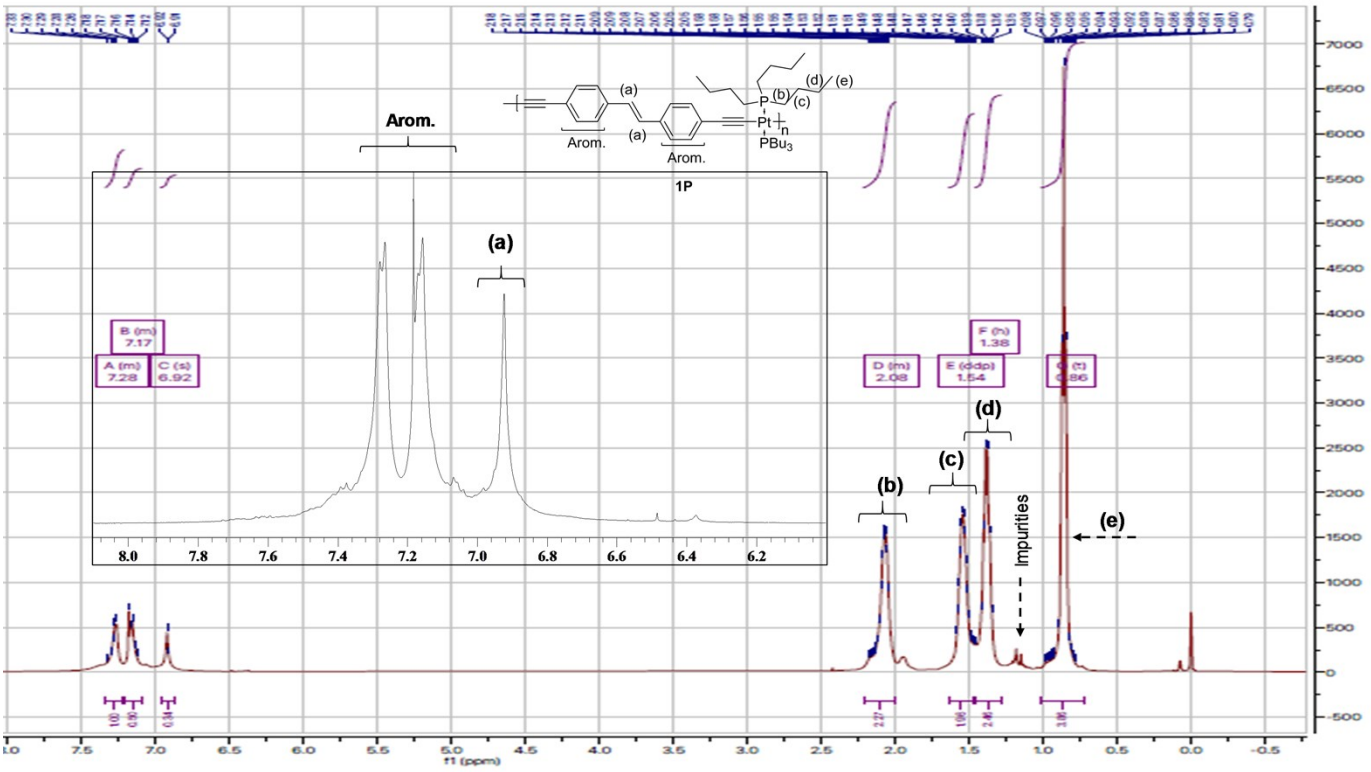



**Figure S26**. $^{1}$H-NMR spectrum of **1P**.

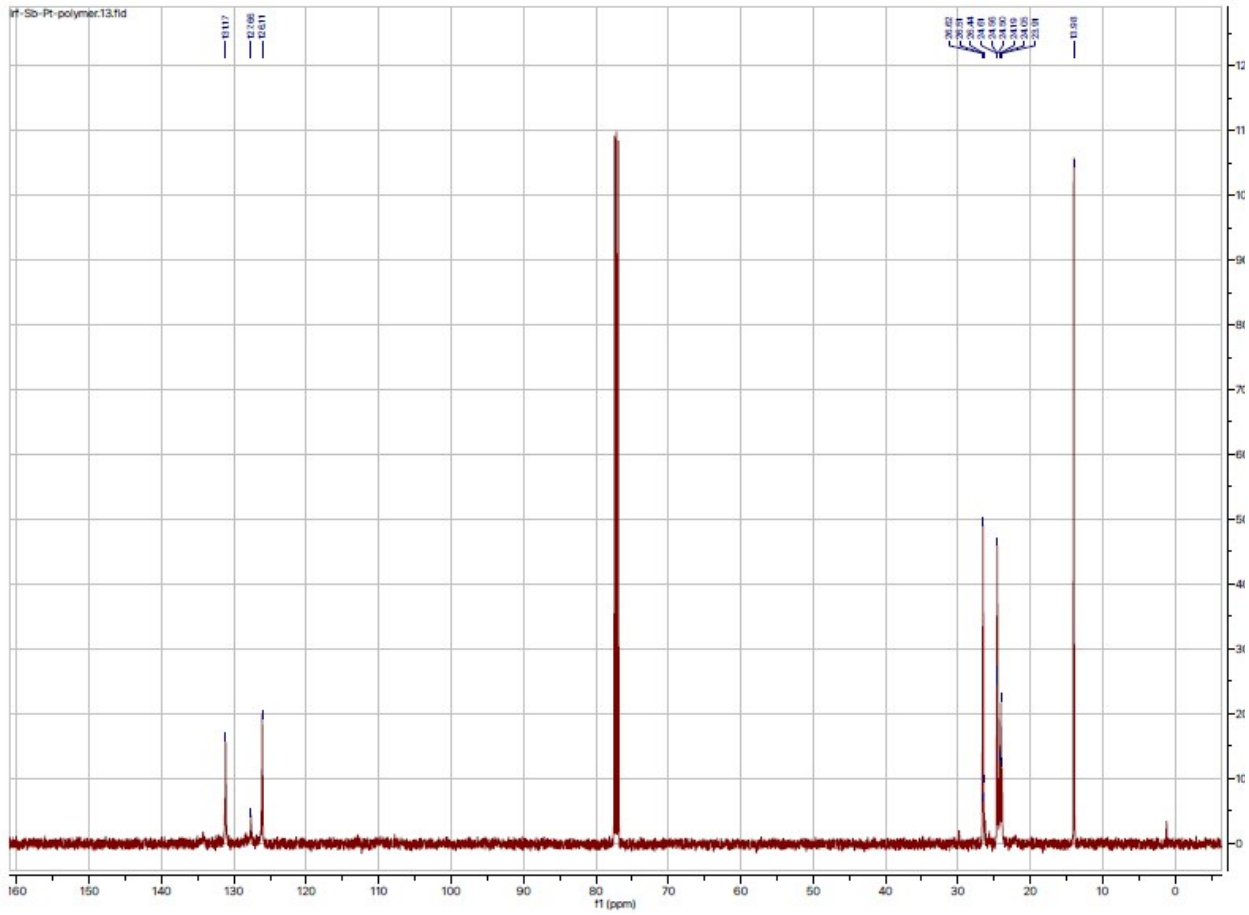



**Figure S27**. $^{13}$C-NMR spectrum of **1P**.

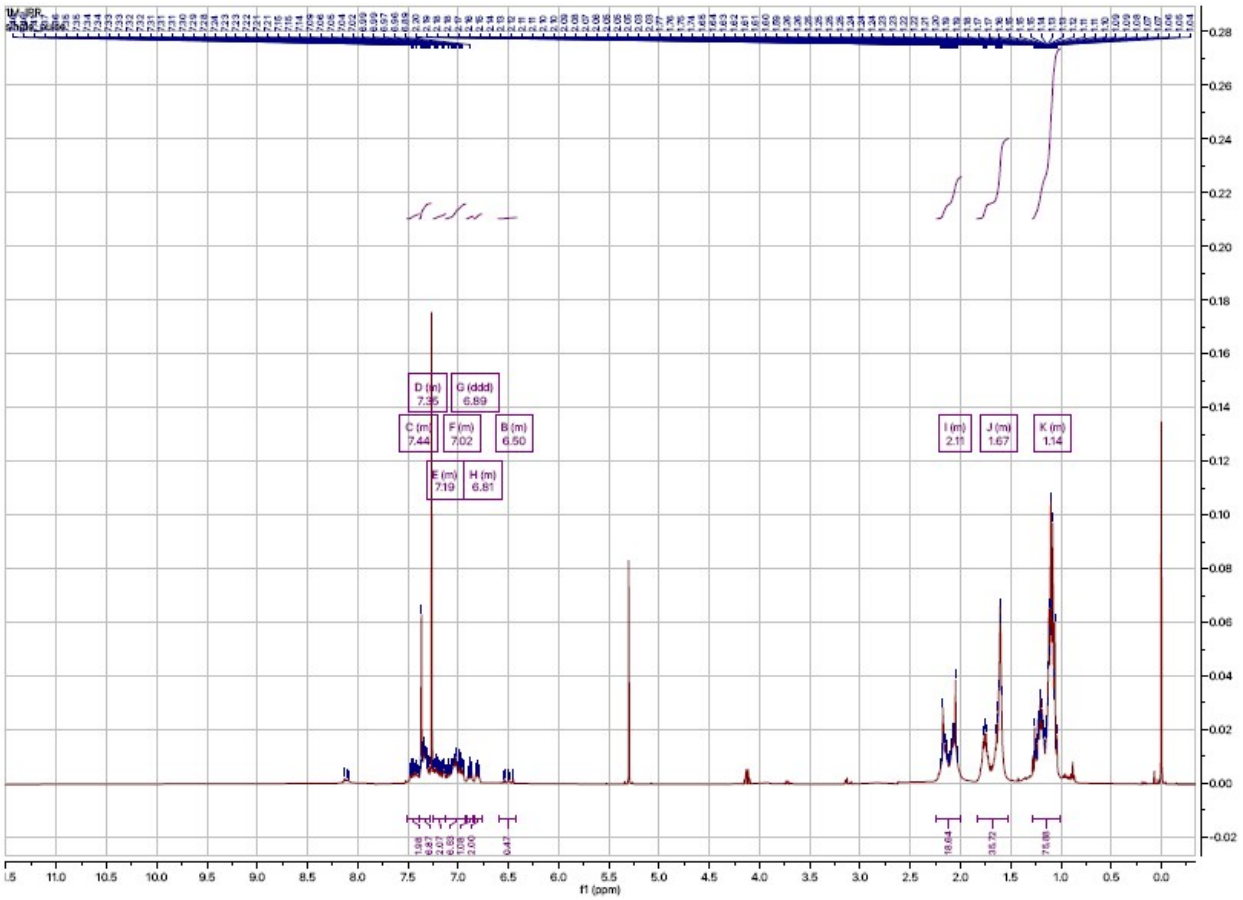



**Figure S28**. $^{1}$H NMR of **1M** after it was irradiated at 365 nm for 25 min. (spectrum obtained with sample in $CDCl_3$ as a solvent).


**Figure S29**. Aromatic region $^{1}H$ NMR of **2M** after it was irradiated at 365 nm for 25 min. Insets: $^{1}H$ NMR spectrum of olefinic hydrogen atoms (spectrum obtained with sample in $CDCl_3$ as a solvent).

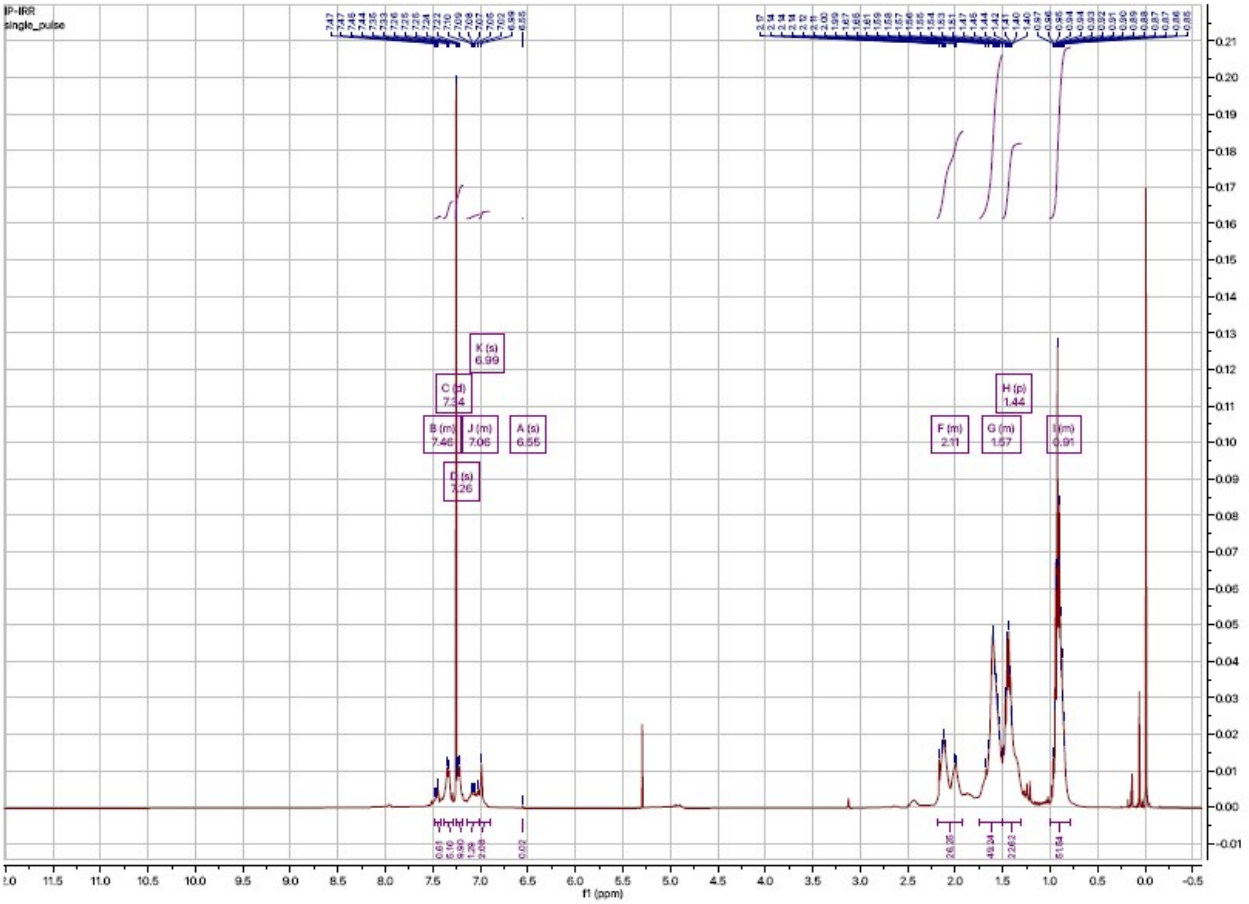



**Figure S30**. $^{1}$H NMR of **1P** after it was irradiated at 365 nm for 25 min. (spectrum obtained with sample in $CDCl_3$ as a solvent)

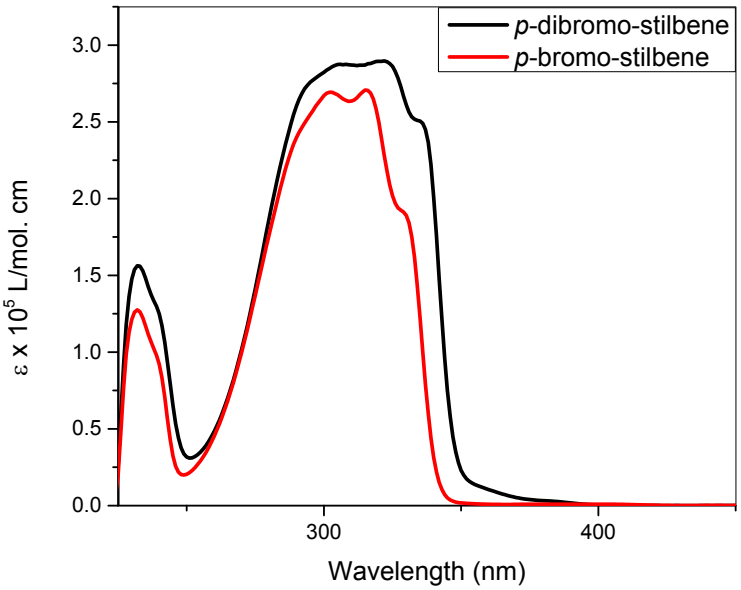


**Figure S31.** Electronic spectra of the stilbene ligands.

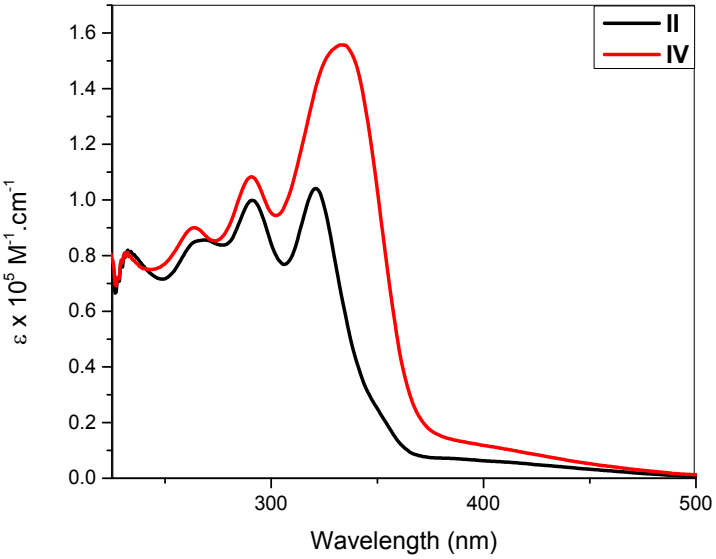



**Figure S32.** Electronic absorption spectra of meta-azobenzene diyne (**II**) and poly-yne (**IV**) systems.

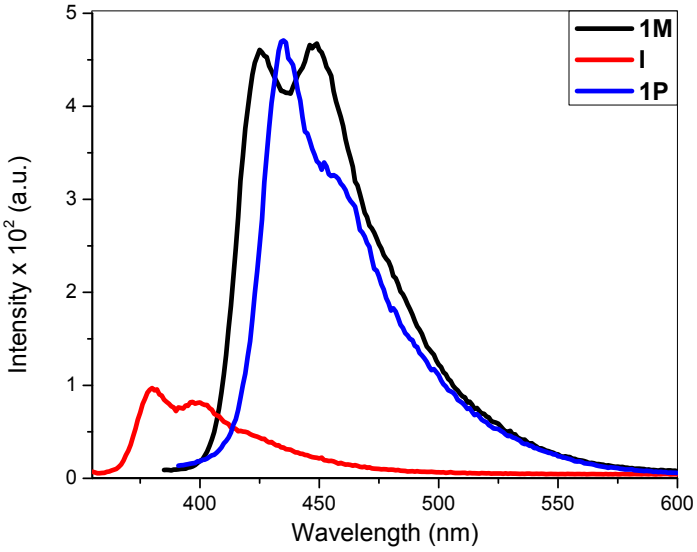



**Figure S33**. Emission spectra of azobenzene emitted species along with **1M** and **1P**. Excitation was at 380 nm for **1M** and **1P** and 340 nm for **I**.

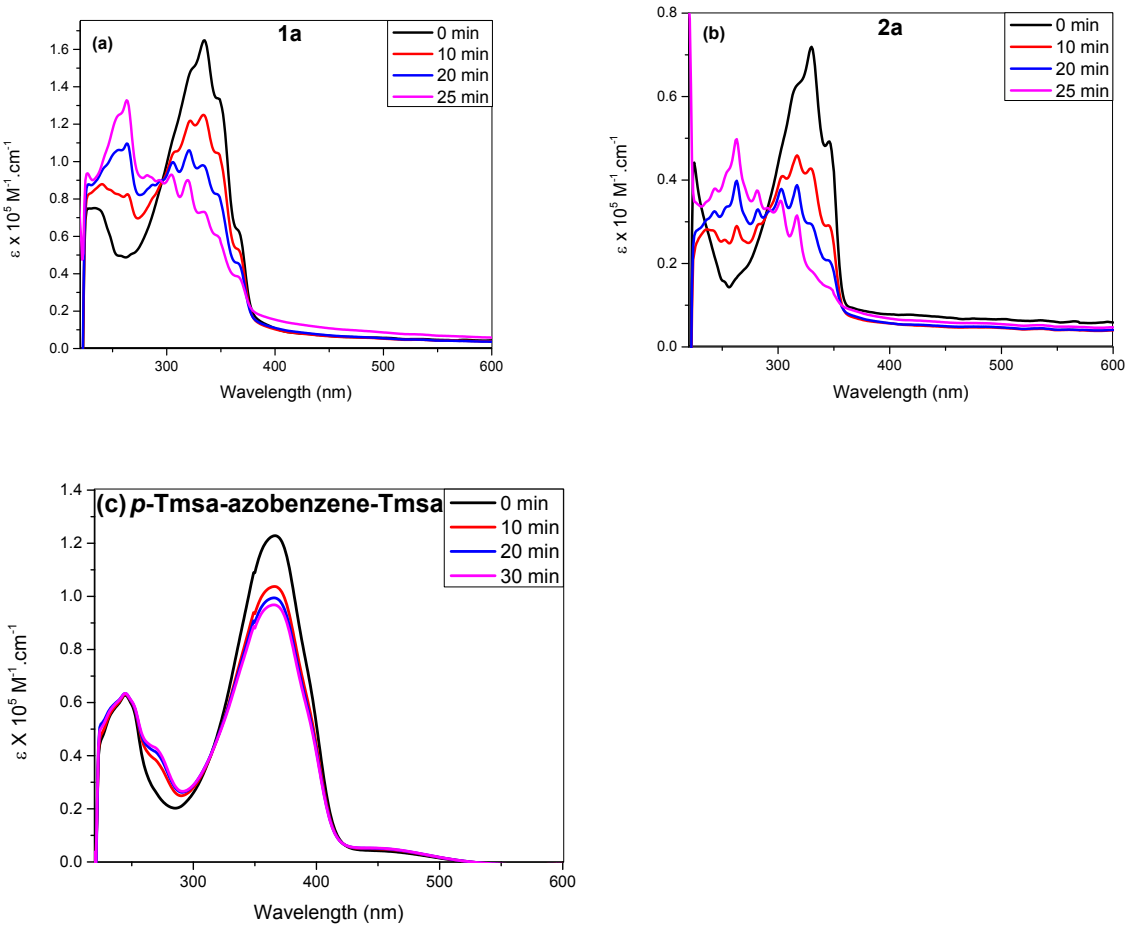



**Figure S34.** Changes in absorption spectral profile of compounds **1a** (a), **2a** (b) and *p*-Tmsa-aznbenzene-Tmsa (c) upon irradiation with light at 254 nm at different exposure times.

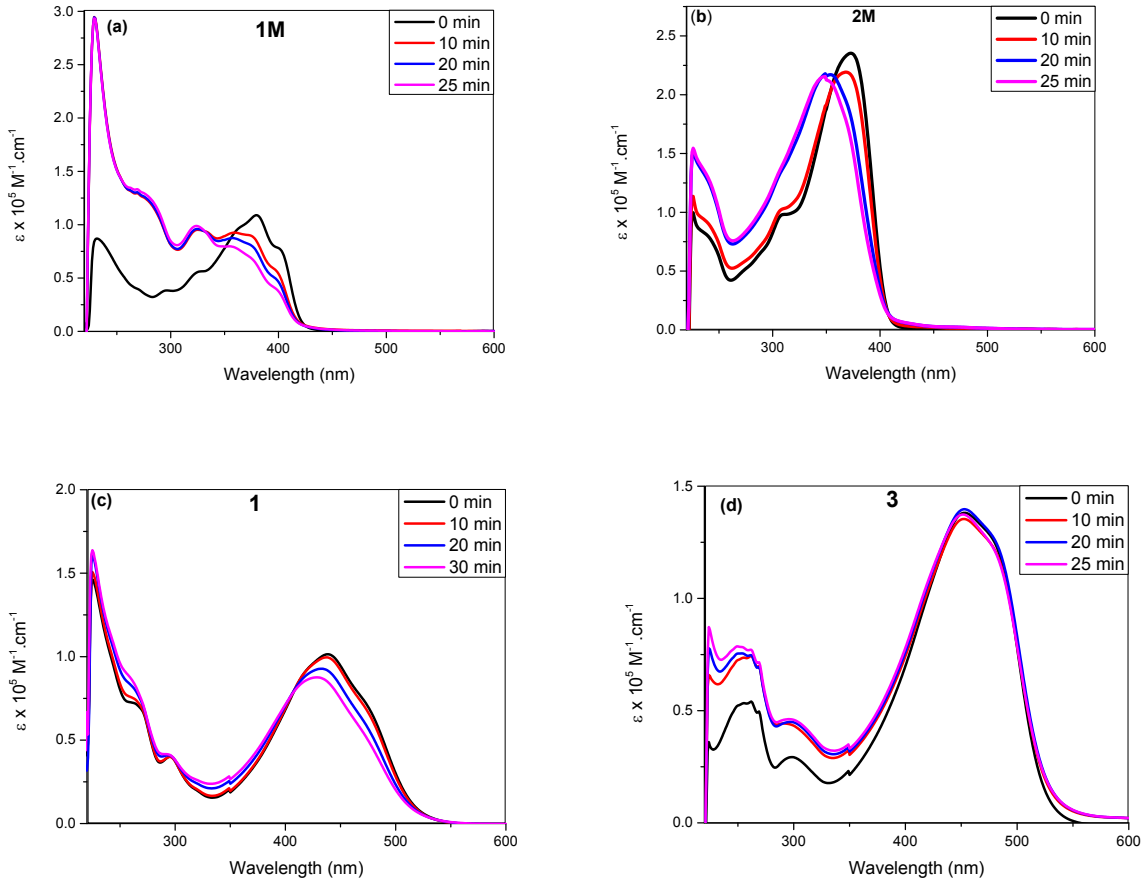



**Figure S35.** Changes in absorption spectral profile of compounds 1M (a), 2M (b) 1 (Pt(II) di-yne with para-azobenzene spacer group) (c) and 3 (Pt(II) poly-yne with para-azobenzene spacer group) upon irradiation with light at 254 nm at different exposure times.

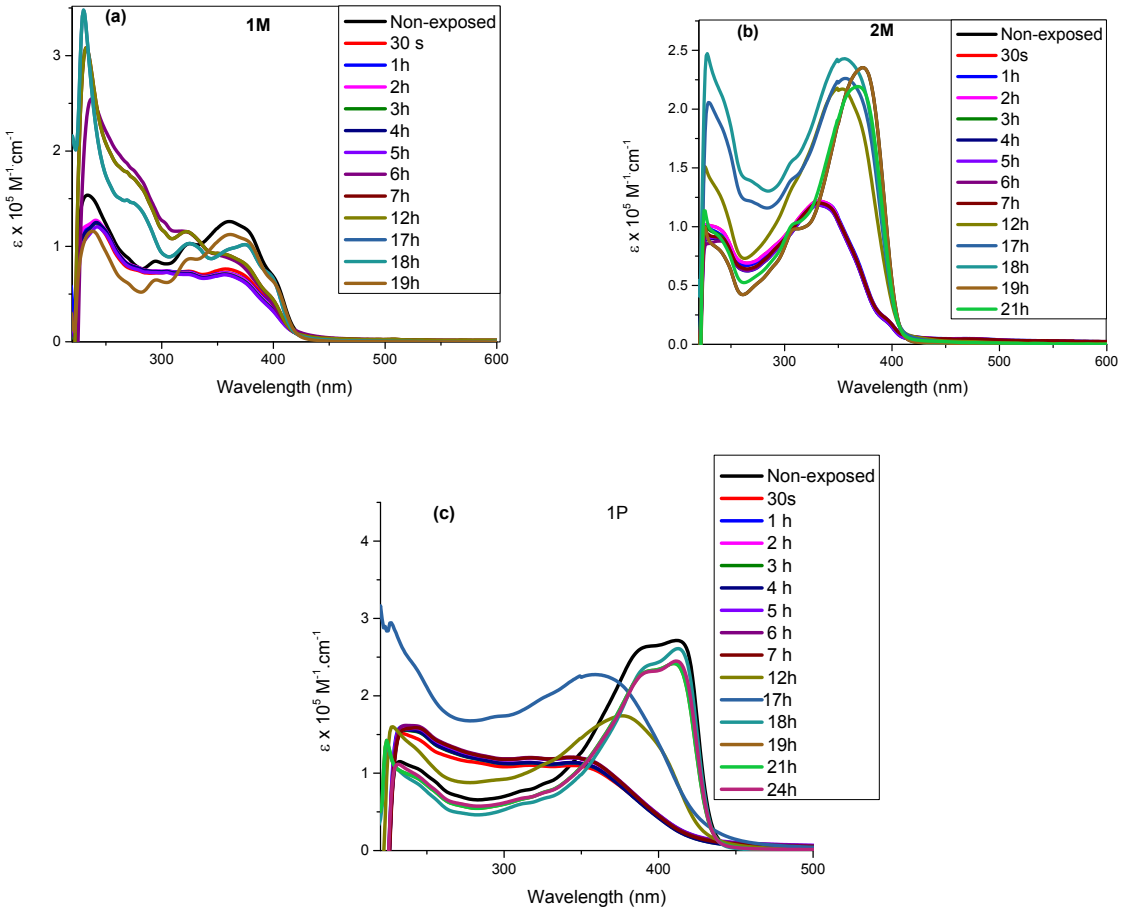



**Figure S36.** Absorption spectra profile with recovery time required for **1M (a), 2M (b)** and **1P (c)** after 25 minutes irradiation at 365 nm.

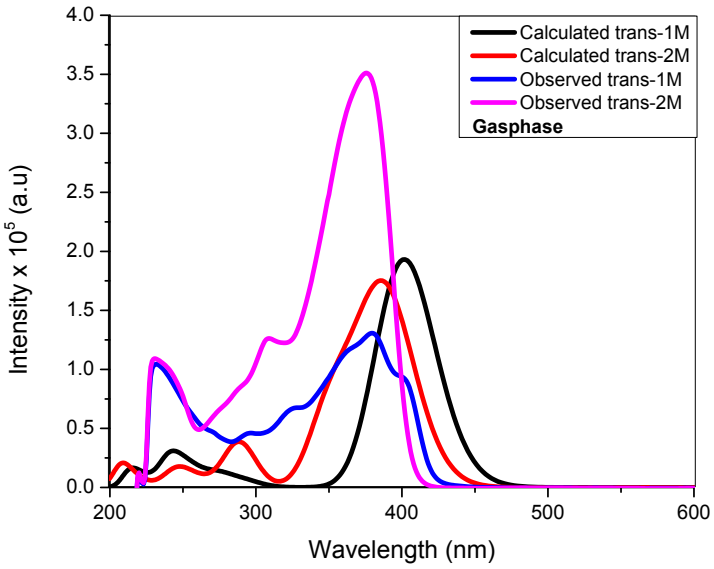



**Figure S37.** Comparison of simulated *trans*-configurations of **1M** and **2M** optical absorption spectra versa the experimental observed spectra of *trans*-**1M** and **2M**. The simulated spectra are in gas phase simulations.

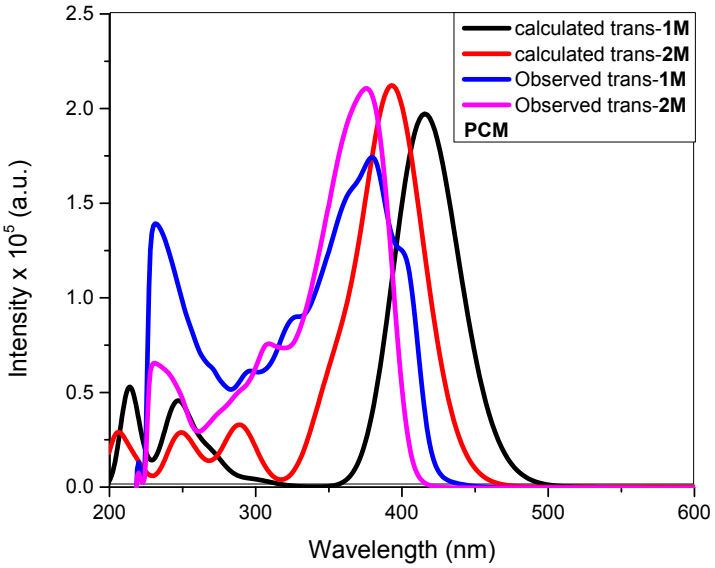



**Figure S38**. Comparison of simulated *trans*-configurations of **1M** and **2M** optical absorption spectra versa the experimental observed spectra of *trans*-**1M** and **2M**. The calculated spectra are in PCM simulations.

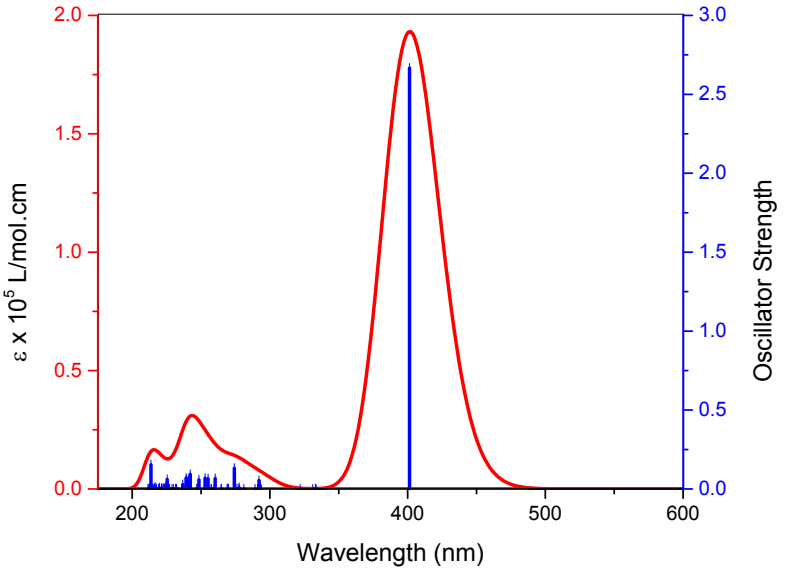



**Figure S39**. Convoluted spectra and line spectra of *trans*-**1M** in gas phase showing the lowest 100 spin-allowed transitions. The convoluted spectra were produced using Gaussian peaks with a FWHM of 3000 $cm^{-1}$.

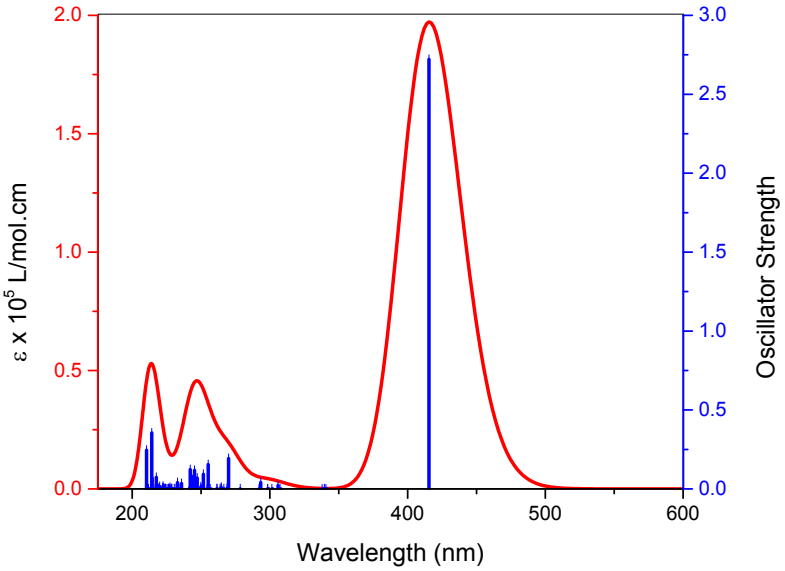



**Figure S40**. Convoluted spectra and line spectra of *trans*-**1M** in PCM showing the lowest 100 spin-allowed transitions. The convoluted spectra were produced using Gaussian peaks with a FWHM of 3000 $cm^{-1}$.

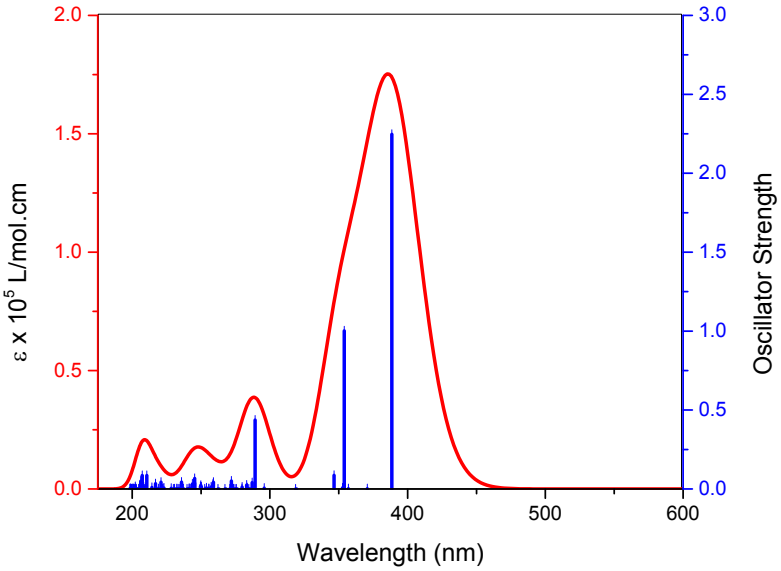



**Figure S41**. Convoluted spectra and line spectra of *trans*-**2M** in gas phase showing the lowest 100 spin-allowed transitions. The convoluted spectra were produced using Gaussia peaks with a FWHM of 3000 $cm^{-1}$.

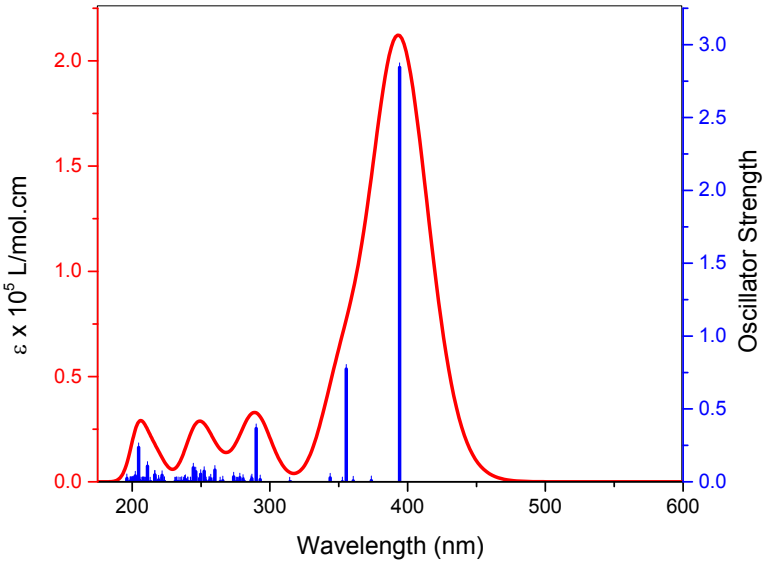



**Figure S42**. Convoluted spectra and line spectra of *trans*-**2M** in PCM showing the lowest 100 spin-allowed transitions. The convoluted spectra were produced using Gaussian peaks with a FWHM of 3000 $cm^{-1}$.

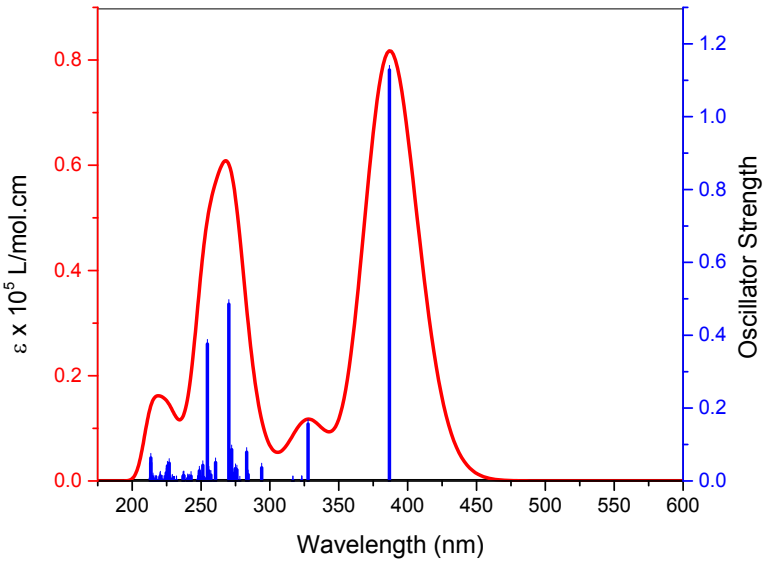



**Figure S43**. Convoluted spectra and line spectra of *cis*-**1M** in gas phase showing the lowest 100 spin-allowed transitions. The convoluted spectra were produced using Gaussian peaks with a FWHM of 3000 $cm^{-1}$.

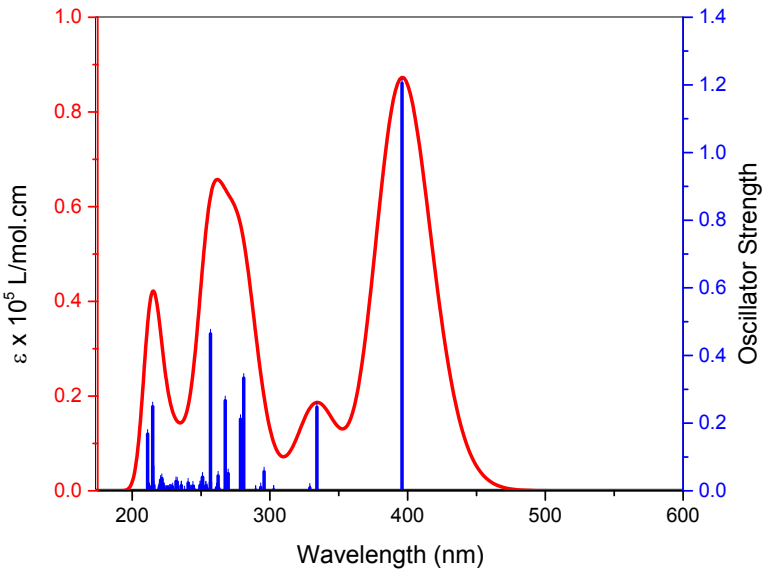



**Figure S44**. Convoluted spectra and line spectra of *cis*-**1M** in PCM showing the lowest 100 spin-allowed transitions. The convoluted spectra were produced using Gaussian peaks with a FWHM of 3000 $cm^{-1}$.

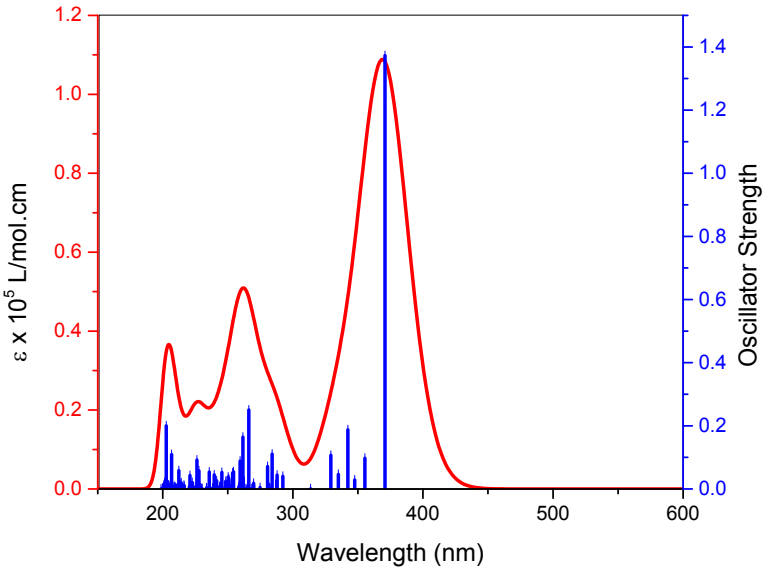



**Figure S45**. Convoluted spectra and line spectra of *cis*-**2M** in gas phase showing the lowest 100 spin-allowed transitions. The convoluted spectra were produced using Gaussian peaks with a FWHM of 3000 $cm^{-1}$.

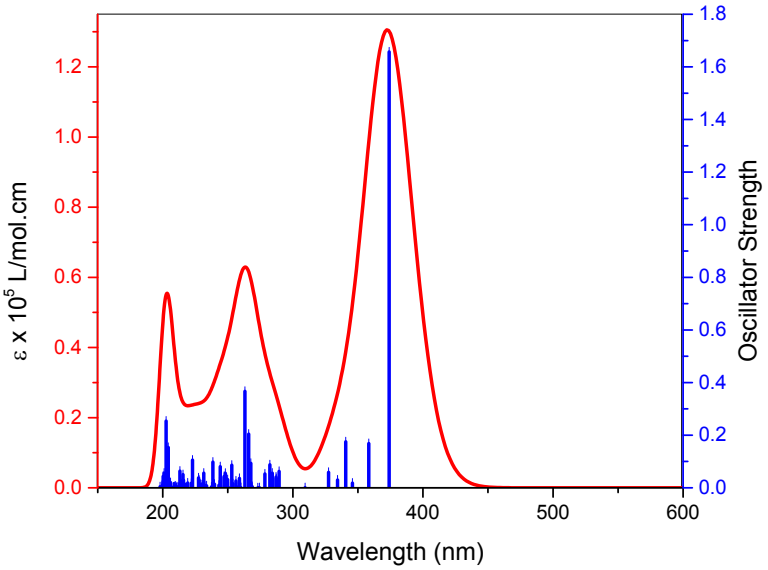
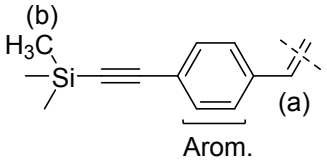
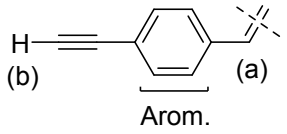


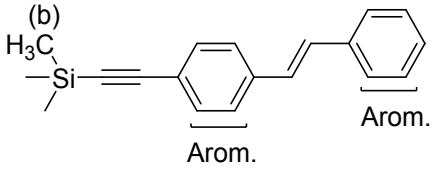

**Figure S46**. Convoluted spectra and line spectra of *cis*-**2M** in PCM showing the lowest 100 spin-allowed transitions. The convoluted spectra were produced using Gaussian peaks with a FWHM of 3000 $cm^{-1}$.



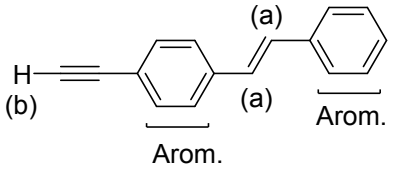

**1a**



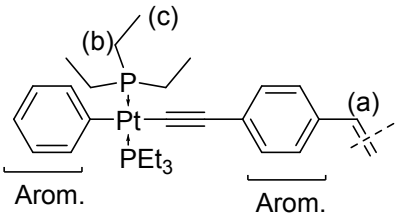

**1b**



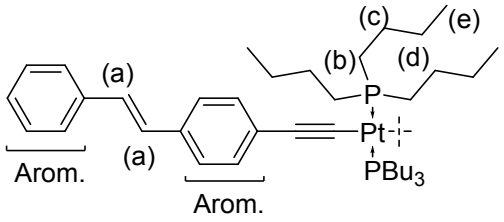

**2a**



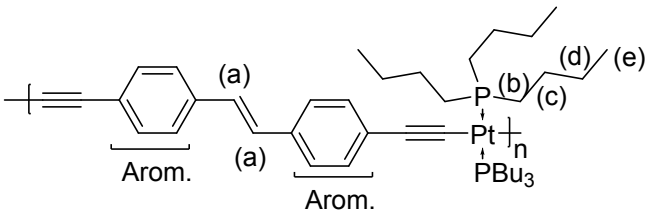

**2b**




**1M**




**2M**




**1P**

**Figure S47**. Labelled (numbered) chemical structures used in proton-resonance assignments.

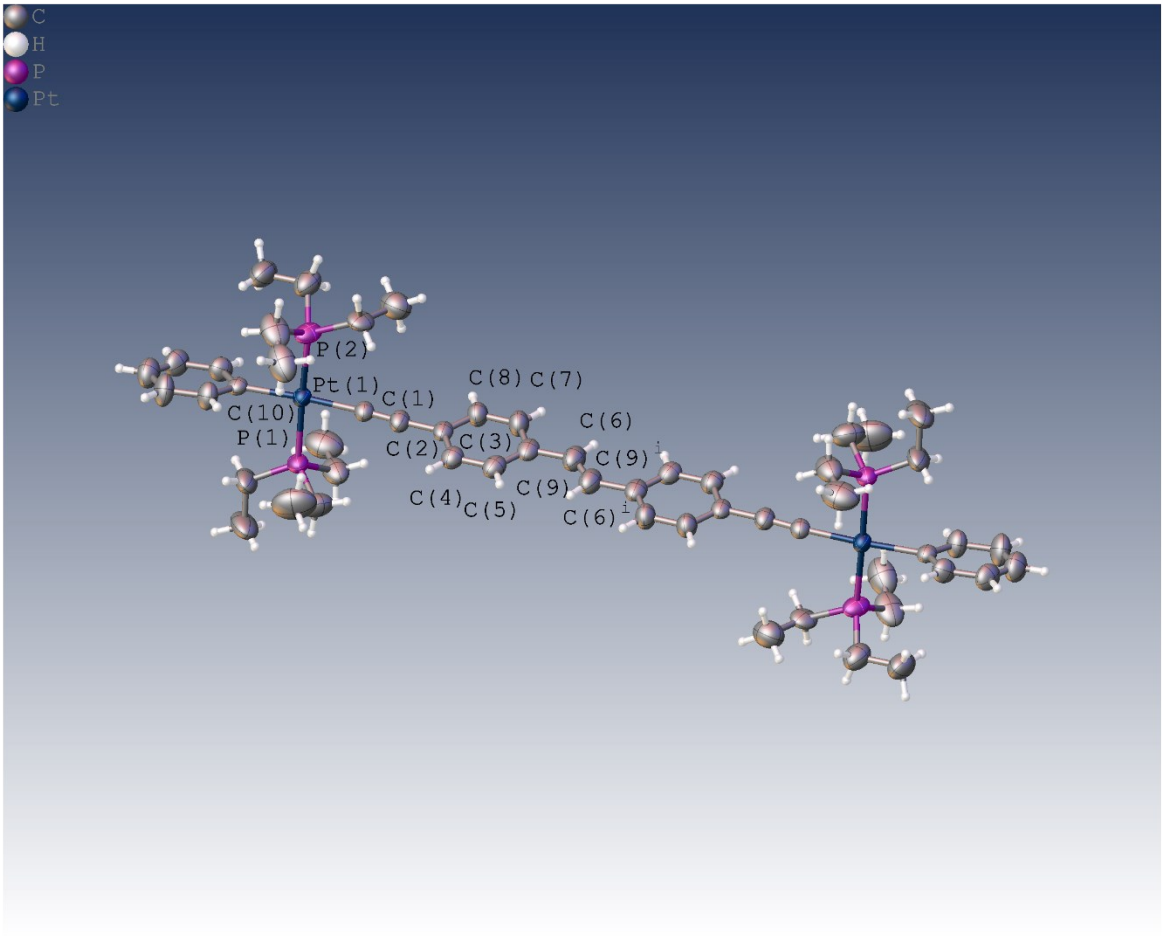



**Table ST1.** Crystal data and structure refinement for PtStil1.

| | |
|---|---|
| CCDC ID number | 2035894 |
| Identification code | shelx |
| Empirical formula | C27H40P2Pt |
| Formula weight | 621.62 |
| Temperature/K | 296.15 |
| Crystal system | monoclinic |
| Space group | P21/c |
| a/Å | 9.7774(5) |
| b/Å | 9.2190(5) |
| c/Å | 30.2215(16) |
| α/° | 90 |
| β/° | 91.884(2) |
| γ/° | 90 |
| Volume/Å3 | 2722.6(2) |
| Z | 4 |

| | |
|---|---|
| ρcalcg/cm3 | 1.517 |
| μ/mm-1 | 5.282 |
| F(000) | 1240.0 |
| Crystal size/mm3 | 0.2 × 0.2 × 0.2 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.992 to 50.998 |
| Index ranges | -11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -36 ≤ l ≤ 36 |
| Reflections collected | 38985 |
| Independent reflections | 5056 [Rint = 0.0501, Rsigma = 0.0278] |
| Data/restraints/parameters | 5056/285/344 |
| Goodness-of-fit on F2 | 1.372 |
| Final R indexes [I>=2σ (I)] | R1 = 0.0513, wR2 = 0.0999 |
| Final R indexes [all data] | R1 = 0.0569, wR2 = 0.1018 |
| Largest diff. peak/hole / e Å-3 | 1.28/-2.88 |

Table ST2 Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for shelx. Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Pt1 | 3503.1(3) | 3914.7(3) | 6260.5(2) | 41.22(14) |
| P1 | 5271(2) | 2386(3) | 6438.6(8) | 51.6(6) |
| P2 | 1816(11) | 5588(12) | 6106(5) | 61.3(8) |
| C1 | 4886(8) | 5113(9) | 5939(3) | 45.6(18) |
| C2 | 5727(9) | 5864(9) | 5779(3) | 53(2) |
| C3 | 6699(8) | 6813(9) | 5574(3) | 47.2(15) |
| C4 | 7566(9) | 7701(10) | 5824(3) | 56.6(18) |
| C5 | 8492(9) | 8620(9) | 5624(3) | 58.4(18) |
| C6 | 8581(9) | 8644(9) | 5165(3) | 58.5(18) |
| C7 | 7722(10) | 7774(11) | 4926(3) | 65(2) |
| C8 | 6804(10) | 6875(11) | 5120(3) | 60(2) |
| C9 | 9562(10) | 9575(11) | 4927(4) | 72(3) |
| C10 | 2157(7) | 2705(8) | 6626(3) | 41.1(15) |
| C11 | 1926(10) | 3019(11) | 7062(3) | 63(2) |
| C12 | 1062(11) | 2220(12) | 7322(4) | 79(3) |
| C13 | 362(12) | 1067(12) | 7146(4) | 80(3) |
| C14 | 550(10) | 716(10) | 6721(4) | 70(2) |

| | | | | | |
|---|---|---|---|---|---|
| C15 | 1431(10) | 1510(10) | 6460(3) | 61(2) | |
| C16 | 6702(12) | 3404(15) | 6714(5) | 98(3) | |
| C17 | 6289(17) | 4260(20) | 7103(6) | 146(7) | |
| C18 | 6103(12) | 1651(13) | 5953(4) | 83(3) | |
| C19 | 5201(15) | 614(16) | 5697(5) | 116(5) | |
| C20 | 4929(12) | 869(13) | 6796(4) | 91(3) | |
| C21 | 6136(14) | -169(16) | 6903(5) | 118(5) | |
| C23 | 2190(20) | 7129(19) | 6873(5) | 109(5) | |
| C25 | 2480(40) | 6960(40) | 5284(7) | 103(9) | |
| C22 | 1194(19) | 6409(16) | 6594(5) | 100(5) | |
| C24 | -530(30) | 4060(40) | 5895(10) | 101(7) | |
| C29 | 2320(17) | 7236(15) | 5802(5) | 67(4) | |
| C27 | 439(17) | 5100(20) | 5696(6) | 86(5) | |
| P2A | 1858(15) | 5626(16) | 6092(6) | 61.2(8) | |
| C23A | 2990(70) | 7250(80) | 6776(17) | 109(19) | |
| C25A | 2860(50) | 7390(60) | 5365(12) | 104(10) | |
| C22A | 2220(50) | 7310(30) | 6362(15) | 107(13) | |
| C24A | -400(40) | 4130(50) | 5731(13) | 101(7) | |
| C29A | 1720(30) | 6300(30) | 5517(8) | 99(8) | |
| C27A | 61(18) | 5010(30) | 6126(9) | 86(7) | |

Table ST3 Anisotropic Displacement Parameters (Å2×103) for shelx. The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+…].

| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Pt1 | 37.32(19) | | 40.06(19) | | 46.6(2) | 3.53(15) 6.12(12) 1.52(15) |
| P1 | 41.3(11) | 56.2(14) | 57.8(13) | 10.4(11) | 6.6(10) | 12.9(10) |
| P2 | 46.9(14) | 39.8(14) | 97(2) | 0.5(14) | -1.9(14) | 10.8(12) |
| C1 | 44(3) | 40(4) | 52(5) | 5(3) | 8(3) | 7(3) |
| C2 | 50(3) | 44(4) | 67(5) | 11(4) | 12(3) | 6(3) |
| C3 | 42(3) | 37(3) | 63(3) | 11(3) | 10(2) | 11(2) |
| C4 | 51(4) | 50(4) | 70(4) | 3(3) | 9(3) | 5(3) |
| C5 | 49(4) | 44(4) | 82(4) | 3(3) | 8(3) | 5(3) |
| C6 | 50(4) | 44(4) | 83(4) | 13(3) | 13(3) | 13(3) |
| C7 | 67(4) | 62(5) | 68(4) | 15(3) | 16(3) | -3(4) |
| C8 | 61(4) | 56(5) | 63(3) | 11(3) | 11(3) | -1(3) |
| C9 | 60(5) | 57(5) | 99(7) | 19(5) | 15(5) | 4(4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C10 | 35(3) | 38(3) | 51(3) | 3(3) | 4(3) | 8(2) |
| C11 | 70(5) | 63(5) | 56(3) | -4(3) | 19(3) | -9(4) |
| C12 | 90(6) | 76(5) | 72(5) | 1(4) | 36(4) | -12(5) |
| C13 | 82(6) | 63(5) | 96(5) | 13(4) | 24(4) | -8(4) |
| C14 | 68(5) | 46(5) | 96(5) | 6(4) | 7(4) | -10(4) |
| C15 | 64(5) | 50(4) | 69(4) | 1(3) | -2(3) | -9(3) |
| C16 | 70(7) | 97(7) | 126(8) | 2(6) | -21(6) | 5(5) |
| C17 | 127(13) | 162(15) | 144(10) | -51(10) | -43(9) | 9(11) |
| C18 | 85(7) | 83(7) | 83(6) | 15(4) | 22(5) | 40(5) |
| C19 | 125(10) | 105(8) | 117(10) | -13(7) | -12(8) | 48(7) |
| C20 | 77(6) | 90(7) | 106(8) | 57(7) | 19(6) | 22(4) |
| C21 | 106(9) | 125(11) | 123(11) | 69(9) | 24(8) | 53(8) |
| C23 | 160(15) | 81(11) | 89(10) | -2(8) | 43(8) | 30(9) |
| C25 | 100(20) | 110(20) | 91(8) | 9(10) | -2(9) | 19(15) |
| C22 | 141(13) | 59(8) | 103(7) | 10(6) | 36(7) | 43(8) |
| C24 | 64(7) | 103(9) | 137(17) | 33(11) | 6(9) | -4(6) |
| C29 | 63(8) | 47(7) | 90(8) | 16(7) | -6(7) | 22(5) |
| C27 | 64(9) | 75(10) | 120(9) | 11(8) | 14(9) | 5(7) |
| P2A | 46.9(15) | 39.8(14) | 97(2) | 0.6(14) | -1.7(14) | 10.7(12) |
| C23A | 90(20) | 110(30) | 129(19) | 2(15) | 6(14) | 4(17) |
| C25A | 84(16) | 120(20) | 110(18) | 42(15) | -13(14) | -9(14) |
| C22A | 100(20) | 90(20) | 135(18) | 7(14) | 1(19) | 5(11) |
| C24A | 64(8) | 103(9) | 137(17) | 33(12) | 6(9) | -4(6) |
| C29A | 79(14) | 107(19) | 111(14) | 38(10) | 6(8) | 6(14) |
| C27A | 49(11) | 83(13) | 124(16) | 43(11) | 3(7) | 19(7) |

Table ST4 Bond Lengths for shelx.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Pt1 | P1 | 2.281(2) | C9 | C91 | 1.23(2) |
| Pt1 | P2 | 2.295(8) | C10 | C11 | 1.378(12) |
| Pt1 | C1 | 2.019(8) | C10 | C15 | 1.395(12) |
| Pt1 | C10 | 2.070(8) | C11 | C12 | 1.383(13) |
| Pt1 | P2A | 2.298(11) | C12 | C13 | 1.362(15) |
| P1 | C16 | 1.859(12) | C13 | C14 | 1.345(15) |
| P1 | C18 | 1.831(11) | C14 | C15 | 1.393(13) |
| P1 | C20 | 1.805(10) | C16 | C17 | 1.484(19) |

| | | | | | |
|---|---|---|---|---|---|
| P2 | C22 | 1.781(19) | C18 | C19 | 1.499(18) |
| P2 | C29 | 1.852(15) | C20 | C21 | 1.546(14) |
| P2 | C27 | 1.855(15) | C23 | C22 | 1.43(2) |
| C1 | C2 | 1.190(11) | C25 | C29 | 1.60(2) |
| C2 | C3 | 1.446(12) | C24 | C27 | 1.49(2) |
| C3 | C4 | 1.385(12) | P2A | C22A | 1.78(2) |
| C3 | C8 | 1.380(12) | P2A | C29A | 1.846(16) |
| C4 | C5 | 1.392(12) | P2A | C27A | 1.852(17) |
| C5 | C6 | 1.393(13) | C23A | C22A | 1.44(3) |
| C6 | C7 | 1.354(14) | C25A | C29A | 1.57(3) |
| C6 | C9 | 1.489(13) | C24A | C27A | 1.50(3) |
| C7 | C8 | 1.368(12) | | | |

12-X,2-Y,1-Z

Table ST5 Bond Angles for shelx.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| P1 | Pt1 | P2 | 175.8(3) | C7 | C6 | C5 | 117.7(9) |
| P1 | Pt1 | P2A | 174.8(5) | C7 | C6 | C9 | 118.8(10) |
| C1 | Pt1 | P1 | 86.4(2) | C6 | C7 | C8 | 122.3(10) |
| C1 | Pt1 | P2 | 91.3(4) | C7 | C8 | C3 | 121.5(10) |
| C1 | Pt1 | C10 | 176.4(3) | C91 | C9 | C6 | 130.2(16) |
| C1 | Pt1 | P2A | 89.6(5) | C11 | C10 | Pt1 | 121.7(6) |
| C10 | Pt1 | P1 | 91.8(2) | C11 | C10 | C15 | 114.3(8) |
| C10 | Pt1 | P2 | 90.3(4) | C15 | C10 | Pt1 | 124.0(6) |
| C10 | Pt1 | P2A | 92.0(5) | C10 | C11 | C12 | 123.6(10) |
| C16 | P1 | Pt1 | 110.3(4) | C13 | C12 | C11 | 120.2(10) |
| C18 | P1 | Pt1 | 113.1(4) | C14 | C13 | C12 | 118.6(10) |
| C18 | P1 | C16 | 101.5(6) | C13 | C14 | C15 | 121.3(10) |
| C20 | P1 | Pt1 | 117.8(4) | C14 | C15 | C10 | 122.0(9) |
| C20 | P1 | C16 | 106.0(6) | C17 | C16 | P1 | 113.8(10) |
| C20 | P1 | C18 | 106.8(6) | C19 | C18 | P1 | 112.4(9) |
| C22 | P2 | Pt1 | 112.3(7) | C21 | C20 | P1 | 116.7(8) |
| C22 | P2 | C29 | 99.6(9) | C23 | C22 | P2 | 116.1(13) |
| C22 | P2 | C27 | 113.3(11) | C25 | C29 | P2 | 113.1(14) |
| C29 | P2 | Pt1 | 116.8(7) | C24 | C27 | P2 | 110.2(15) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C29 | P2 | C27 | 93.8(9) | C22A | P2A | Pt1 | 111.7(14) |
| C27 | P2 | Pt1 | 118.3(8) | C22A | P2A | C29A | 98.4(16) |
| C2 | C1 | Pt1 | 175.3(8) | C22A | P2A | C27A | 114.5(19) |
| C1 | C2 | C3 | 177.5(9) | C29A | P2A | Pt1 | 117.8(11) |
| C4 | C3 | C2 | 121.6(8) | C29A | P2A | C27A | 96.7(12) |
| C8 | C3 | C2 | 121.4(9) | C27A | P2A | Pt1 | 115.9(10) |
| C8 | C3 | C4 | 117.0(8) | C23A | C22A | P2A | 117(3) |
| C3 | C4 | C5 | 121.2(9) | C25A | C29A | P2A | 117.4(19) |
| C4 | C5 | C6 | 120.3(9) | C24A | C27A | P2A | 112.5(18) |
| C5 | C6 | C9 | 123.6(10) | | | | |

12-X,2-Y,1-Z

Table ST6 Torsion Angles for shelx.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| Pt1 | P1 | C16 | C17 | 53.7(13) | C11 | C10 | C15 | C14 | 0.0(13) |
| Pt1 | P1 | C18 | C19 | -68.9(9) | C11 | C12 | C13 | C14 | 1.2(18) |
| Pt1 | P1 | C20 | C21 | 178.7(9) | C12 | C13 | C14 | C15 | -0.5(17) |
| Pt1 | P2 | C22 | C23 | 57.5(15) | C13 | C14 | C15 | C10 | -0.1(16) |
| Pt1 | P2 | C29 | C25 | 77.6(19) | C15 | C10 | C11 | C12 | 0.7(14) |
| Pt1 | P2 | C27 | C24 | 75(2) | C16 | P1 | C18 | C19 | 172.9(9) |
| Pt1 | C10 | C11 | C12 | -178.4(8) | C16 | P1 | C20 | C21 | -57.4(13) |
| Pt1 | C10 | C15 | C14 | 179.1(7) | C18 | P1 | C16 | C17 | 173.9(12) |
| Pt1 | P2A | C22A | C23A | -28(5) | C18 | P1 | C20 | C21 | 50.2(13) |
| Pt1 | P2A | C29A | C25A | -75(4) | C20 | P1 | C16 | C17 | -74.8(13) |
| Pt1 | P2A | C27A | C24A | -78(3) | C20 | P1 | C18 | C19 | 62.2(10) |
| C2 | C3 | C4 | C5 | -179.5(8) | C22 | P2 | C29 | C25 | -161.2(18) |
| C2 | C3 | C8 | C7 | 179.9(8) | C22 | P2 | C27 | C24 | -59(2) |
| C3 | C4 | C5 | C6 | -1.2(13) | C29 | P2 | C22 | C23 | -66.9(14) |
| C4 | C3 | C8 | C7 | 0.0(13) | C29 | P2 | C27 | C24 | -162(2) |
| C4 | C5 | C6 | C7 | 1.4(13) | C27 | P2 | C22 | C23 | -165.3(13) |
| C4 | C5 | C6 | C9 | -178.8(8) | C27 | P2 | C29 | C25 | -46.8(18) |
| C5 | C6 | C7 | C8 | -1.0(14) | C22A | P2A | C29A | C25A | 45(4) |
| C5 | C6 | C9 | C91 | 1(2) | C22A | P2A | C27A | C24A | 150(3) |
| C6 | C7 | C8 | C3 | 0.3(15) | C29A | P2A | C22A | C23A | -153(5) |
| C7 | C6 | C9 | C91 | -179.0(15) | C29A | P2A | C27A | C24A | 47(3) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C8 | C3 | C4 | C5 | 0.4(12) | C27A | P2A | C22A | C23A | 106(5) |
| C9 | C6 | C7 | C8 | 179.2(9) | C27A | P2A | C29A | C25A | 161(3) |
| C10 | C11 | C12 | C13 | -1.3(18) | | | | | |

12-X,2-Y,1-Z

Table ST7 Hydrogen Atom Coordinates (Å×$10^4$) and Isotropic Displacement Parameters (Å$^2$×$10^3$) for shelx.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H4 | 7529.06 | 7683.18 | 6131.49 | 68 |
| H5 | 9053.9 | 9220.35 | 5798.16 | 70 |
| H7 | 7756.65 | 7786.89 | 4618.94 | 78 |
| H8 | 6237.09 | 6292.73 | 4942.55 | 71 |
| H9 | 9502.98 | 9502.6 | 4620.26 | 86 |
| H11 | 2375.76 | 3811.59 | 7190.13 | 75 |
| H12 | 959.02 | 2470.46 | 7616.85 | 94 |
| H13 | -233.14 | 535.31 | 7316.68 | 96 |
| H14 | 83.23 | -73.75 | 6597.61 | 84 |
| H15 | 1537.69 | 1234.33 | 6167.17 | 73 |
| H16A | 7407.53 | 2721.52 | 6809.35 | 118 |
| H16B | 7096.38 | 4053.36 | 6500.45 | 118 |
| H17A | 5674.98 | 5022.15 | 7006.71 | 218 |
| H17B | 7086.52 | 4684.56 | 7245.68 | 218 |
| H17C | 5839.44 | 3643.56 | 7307.46 | 218 |
| H18A | 6353.69 | 2443.91 | 5761.07 | 100 |
| H18B | 6937.06 | 1154.89 | 6048.38 | 100 |
| H19A | 5690.27 | 226.4 | 5453.35 | 174 |
| H19B | 4399.42 | 1114.41 | 5586.18 | 174 |
| H19C | 4934.47 | -163.52 | 5887.13 | 174 |
| H20A | 4603.87 | 1246.47 | 7072.9 | 109 |
| H20B | 4189.33 | 306.68 | 6659.61 | 109 |
| H21A | 6418.58 | -624.08 | 6634.91 | 176 |
| H21B | 5852.35 | -898.55 | 7106.96 | 176 |
| H21C | 6887.08 | 370.35 | 7032.47 | 176 |
| H23A | 2548.25 | 7950.06 | 6719.25 | 164 |
| H23B | 2921.43 | 6469.22 | 6947.85 | 164 |
| H23C | 1769.66 | 7449.42 | 7138.02 | 164 |

| | | | | |
|---|---|---|---|---|
| H25A | 2685.78 | 7861.11 | 5140.89 | 154 |
| H25B | 1636.02 | 6578.96 | 5159.5 | 154 |
| H25C | 3202.95 | 6281.13 | 5240.3 | 154 |
| H22A | 494.32 | 7107.51 | 6505.89 | 120 |
| H22B | 757.7 | 5664.25 | 6766.56 | 120 |
| H24A | -528.11 | 4198.63 | 6209.93 | 152 |
| H24B | -261.44 | 3086.81 | 5829.86 | 152 |
| H24C | -1438.61 | 4233 | 5773.28 | 152 |
| H29A | 1637.11 | 7983.46 | 5842.17 | 80 |
| H29B | 3182.97 | 7590.25 | 5926.76 | 80 |
| H27A | -47.78 | 5966.3 | 5601 | 103 |
| H27B | 837.11 | 4660.13 | 5438.57 | 103 |
| H23D | 2632.65 | 6496.94 | 6958.6 | 164 |
| H23E | 3934.35 | 7046.74 | 6719.9 | 164 |
| H23F | 2926.35 | 8164.34 | 6925.1 | 164 |
| H25D | 2578.71 | 7807.65 | 5085.78 | 157 |
| H25E | 3704.1 | 6880.47 | 5335.79 | 157 |
| H25F | 2972.32 | 8143.44 | 5582.29 | 157 |
| H22C | 2713.08 | 7914.23 | 6160.21 | 129 |
| H22D | 1354.61 | 7782.9 | 6415.19 | 129 |
| H24D | -730.71 | 4767.9 | 5500.44 | 152 |
| H24E | -1119.44 | 3486.9 | 5813.45 | 152 |
| H24F | 356.57 | 3576.56 | 5627.79 | 152 |
| H29C | 1730.7 | 5465.41 | 5321.03 | 119 |
| H29D | 840.77 | 6766.29 | 5475.15 | 119 |
| H27C | -30.67 | 4431.91 | 6391.16 | 103 |
| H27D | -529.09 | 5850.64 | 6149.5 | 103 |

Table ST8 Atomic Occupancy for shelx.

| Atom | Occupancy | Atom | Occupancy | Atom | Occupancy |
|---|---|---|---|---|---|
| P2 | 0.582(14) | C23 | 0.8 | H23A | 0.8 |
| H23B | 0.8 | H23C | 0.8 | C25 | 0.582(14) |
| H25A | 0.582(14) | H25B | 0.582(14) | H25C | 0.582(14) |
| C22 | 0.8 | H22A | 0.8 | H22B | 0.8 |
| C24 | 0.582(14) | H24A | 0.582(14) | H24B | 0.582(14) |
| H24C | 0.582(14) | C29 | 0.582(14) | H29A | 0.582(14) |

| | | | | | |
|---|---|---|---|---|---|
| H29B | 0.582(14) | C27 | 0.582(14) | H27A | 0.582(14) |
| H27B | 0.582(14) | P2A | 0.418(14) | C23A | 0.2 |
| H23D | 0.2 | H23E | 0.2 | H23F | 0.2 |
| C25A | 0.418(14) | H25D | 0.418(14) | H25E | 0.418(14) |
| H25F | 0.418(14) | C22A | 0.2 | H22C | 0.2 |
| H22D | 0.2 | C24A | 0.418(14) | H24D | 0.418(14) |
| H24E | 0.418(14) | H24F | 0.418(14) | C29A | 0.418(14) |
| H29C | 0.418(14) | H29D | 0.418(14) | C27A | 0.418(14) |
| H27C | 0.418(14) | H27D | 0.418(14) | | |

**Experimental**

Single crystals of $(C_{27}H_{40}P_2Pt)_2$ were recrystallised from a hexane/$CH_2Cl_2$ mixture. A suitable crystal was selected and glued on to a glass fibre on a diffractometer. The crystal was kept at 296 K during data collection. Using Olex2 [1] and WinGX [2], the structure was solved with the by direct methods using WinGX [2] and refined by full-matrix least-squares (SHELXL-2014) on $F^2$ [3].


1. O.V. Dolomanov, et al., J Appl Cryst, 2009, 42, 339-341
2. L. Farrugia, J. Appl. Crystallogr, 1999, 32, 837-838.
3. G. M. Sheldrick, Acta Crystallographica a-Foundation and Advances, 2015, 71, 3-8.


**Crystal structure determination of $(C_{27}H_{40}P_2Pt)_2$**

**Crystal Data** for $C_{27}H_{40}P_2Pt$ ($M$ =621.62 g/mol): monoclinic, space group $P2_1/c$ (no. 14), $a$ = 9.7774(5) Å, $b$ = 9.2190(5) Å, $c$ = 30.2215(16) Å, $\beta$ = 91.884(2)°, $V$ = 2722.6(2) Å$^3$, $Z$ = 4, $T$ = 296.15 K, μ(MoKα) = 5.282 mm$^{-1}$, *Dcalc* = 1.517 g/cm$^3$, 38985 reflections measured (5.992° ≤ 2Θ ≤ 50.998°), 5056 unique ($R_{int}$ = 0.0501, $R_{sigma}$ = 0.0278) which were used in all calculations. The final $R_1$ was 0.0513 (I > 2σ(I)) and $wR_2$ was 0.1018 (all data).

**Refinement model description**

Number of restraints - 285.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2. Restrained distances
 P2-C27 ≈ P2-C29
 with sigma of 0.02
 Pt1-P2 ≈ Pt1-P2A
 with sigma of 0.02
 P2-C22 ≈ P2A-C22A
 with sigma of 0.02
 P2-C29 ≈ P2A-C29A
 with sigma of 0.02
 P2-C27 ≈ P2A-C27A
 with sigma of 0.02
 C29-C27 ≈ C29A-C27A
 with sigma of 0.04
 C23-C22 ≈ C23A-C22A
 with sigma of 0.02
 C22-C27 ≈ C22A-C27A
 with sigma of 0.04
 C25-C29 ≈ C25A-C29A
 with sigma of 0.02
 C24-C27 ≈ C24A-C27A
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 with sigma of 0.02
 C22-C29 ≈ C22A-C29A
 with sigma of 0.04
 Pt1-C22 ≈ Pt1-C22A
 with sigma of 0.04
 Pt1-C29 ≈ Pt1-C29A
 with sigma of 0.04
 Pt1-C27 ≈ Pt1-C27A
 with sigma of 0.04
 P2-C23 ≈ P2A-C23A
 with sigma of 0.04
 P2-C25 ≈ P2A-C25A
 with sigma of 0.04
 P2-C24 ≈ P2A-C24A
 with sigma of 0.04
3. Uiso/Uaniso restraints and constraints
C24A ≈ C24: within 2A with sigma of 0.001 and sigma for terminal atoms of
0.002 within 2A
C25 ≈ C25A: within 2A with sigma of 0.01 and sigma for terminal atoms of
0.02 within 2A
P2A ≈ P2: within 2A with sigma of 0.001 and sigma for terminal atoms of
0.002 within 2A
Uanis(C23A) ≈ Ueq: with sigma of 0.01 and sigma for terminal atoms of 0.02
4. Rigid body (RIGU) restrains
 Pt1, P1, P2, C1, C10, P2A, C16, C18, C20, C22, C29, C27, C2, C11, C15, C22A,
 C29A, C27A, C17, C19, C21, C23, C25, C24, C3, C12, C14, C23A, C25A, C24A, C4,
 C8, C13, C5, C7, C6, C9
 with sigma for 1-2 distances of 0.001 and sigma for 1-3 distances of 0.001
5. Others
 Sof(P2A)=Sof(C25A)=Sof(H25D)=Sof(H25E)=Sof(H25F)=Sof(C24A)=Sof(H24D)=
 Sof(H24E)=Sof(H24F)=Sof(C29A)=Sof(H29C)=Sof(H29D)=Sof(C27A)=Sof(H27C)=
 Sof(H27D)=1-FVAR(1)
 Sof(P2)=Sof(C25)=Sof(H25A)=Sof(H25B)=Sof(H25C)=Sof(C24)=Sof(H24A)=Sof(H24B)=
 Sof(H24C)=Sof(C29)=Sof(H29A)=Sof(H29B)=Sof(C27)=Sof(H27A)=Sof(H27B)=FVAR(1)
 Fixed Sof: C23(0.8) H23A(0.8) H23B(0.8) H23C(0.8) C22(0.8) H22A(0.8)
 H22B(0.8) C23A(0.2) H23D(0.2) H23E(0.2) H23F(0.2) C22A(0.2) H22C(0.2) H22D(0.2)
6.a Riding coordinates:
 C23A(H23D,H23E,H23F)
6.b Secondary CH2 refined with riding coordinates:
 C16(H16A,H16B), C18(H18A,H18B), C20(H20A,H20B), C22(H22A,H22B), C29(H29A,
 H29B), C27(H27A,H27B), C22A(H22C,H22D), C29A(H29C,H29D), C27A(H27C,H27D)
6.c Aromatic/amide H refined with riding coordinates:
 C4(H4), C5(H5), C7(H7), C8(H8), C9(H9), C11(H11), C12(H12), C13(H13),
 C14(H14), C15(H15)
6.d Idealised Me refined as rotating group:
 C17(H17A,H17B,H17C), C19(H19A,H19B,H19C), C21(H21A,H21B,H21C), C23(H23A,H23B,
 H23C), C25(H25A,H25B,H25C), C24(H24A,H24B,H24C), C25A(H25D,H25E,H25F),
 C24A(H24D,H24E,H24F)
```

**Table ST9.** The quantitative analysis of reduction and enhancement in A and B bands, respectively for **1a**.

| Irradiation time (min) | A-band (ε x $10^5$ $M^{-1}.cm^{-1}$) (λ (nm)) | B-band (ε x $10^5$ $M^{-1}.cm^{-1}$) (λ(nm)) | % reduction in A-band | % enhancement in B-band |
|---|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| 0 (non-exposed) | 1.65 (334) | 0.50 (257) | - | - |
| 10 | 1.25 (333) | 0.83 (263) | 24 | 66 |
| 20 | 1.06 (320) | 1.10 (263) | 36 | 120 |
| 25 | 0.90 (319) | 1.32 (263) | 45 | 164 |

**Table ST10.** The quantitative analysis of reduction and enhancement in A and B bands, respectively for **2a**.

| Irradiation time (min) | A-band (ε x 105 M-1.cm-1) (λ) | B-band (ε x 105 M-1.cm-1)(λ) | % reduction in A-band | % enhancement in B-band |
|---|---|---|---|---|
| 0 (non-exposed) | 0.72 (328) | 0.17 (263) | - | - |
| 10 | 0.46 (317) | 0.28 (262) | 36 | 64 |
| 20 | 0.39 (316) | 0.40 (262) | 45 | 135 |
| 25 | 0.31 (315) | 0.49 (262) | 56 | 188 |

**Table ST11.** The quantitative analysis of reduction and enhancement in A and B bands, respectively for **1M**.

| Irradiation time (min) | A-band (ε x $10^5$ $M^{-1}.cm^{-1}$) | B-band (ε x $10^5$ $M^{-1}.cm^{-1}$) | % reduction in A-band | % enhancement in B-band |
|---|---|---|---|---|
| 0 (non-exposed) | 1.07 (380) | 0.38 (292) | - | - |
| 10 | 0.90 (372) | 1.21 (280) | 15 | 218 |
| 20 | 0.83 (372) | 1.22 (280) | 22 | 221 |
| 25 | 0.72 (372) | 1.28 (280) | 32 | 280 |

**Table ST12.** The quantitative analysis of reduction and enhancement in A and B bands, respectively for **2M**.

| Irradiation time (min) | A-band (ε x $10^5$ $M^{-1}.cm^{-1}$) | B-band (ε x $10^5$ $M^{-1}.cm^{-1}$) | % reduction in A-band | % enhancement in B-band |
|---|---|---|---|---|
| 0 (non-exposed) | 2.35 (376) | 1.00 (225) | - | - |
| 10 | 2.19 (366) | 1.12 (224) | 6 | 12 |
| 20 | 2.17 (353) | 1.49 (226) | 7 | 49 |
| 25 | 2.14 (348) | 1.53 (225) | 9 | 53 |

**Table ST13.** The quantitative analysis of reduction and enhancement in A and B bands, respectively for **1P**.

| Irradiation time (min) | A-band (ε x $10^5$ $M^{-1}.cm^{-1}$) | B-band (ε x $10^5$ $M^{-1}.cm^{-1}$) | % reduction in A-band | % enhancement in B-band |
|---|---|---|---|---|
| 0 (non-exposed) | 2.62 (413) | 0.95 (230) | - | - |
| 10 | 2.54 (378) | 2.43 (231) | 3 | 155 |
| 20 | 2.09 (352) | 2.52 (231) | 20 | 165 |
| 25 | 1.81 (342) | 2.61 (231) | 30 | 174 |

**Table ST14.** Electronic transitions in the *cis*- and *trans*-stilbene isomers of the Pt(II) complexes **1M** and **2M** in gas phase.

| System (Gas phase) | E[eV] (nm) | $f$ | Assignment |
|---|---|---|---|
| ***Trans*-1M** | 3.09(401) | 2.70 | HOMO--> LUMO<br>+HOMO-1---> LUMO+1 |
| | 4.53(274) | 0.13 | HOMO--> LUMO |
| | 5.12(242) | 0.092 | HOMO--> LUMO |
| | 5.82(213) | 0.15 | HOMO--> LUMO |
| ***Trans*-2M** | 3.20(388) | 2.25 | HOMO--> LUMO<br>+HOMO-1---> LUMO+1 |
| | 3.51(353) | 1.00 | HOMO--> LUMO<br>+HOMO-1---> LUMO+1 |
| | 4.29(289) | 0.44 | HOMO--> LUMO |
| | 4.98(249) | 0.023 | HOMO--> LUMO |
| | 5.90(210) | 0.085 | HOMO--> LUMO |
| ***Cis*-1M** | 3.21(386) | 1.13 | HOMO--> LUMO<br>+HOMO-1---> LUMO+1 |
| | 3.79(327) | 0.16 | HOMO--> LUMO<br>+HOMO-1---> LUMO+1 |
| | 4.59(270) | 0.49 | HOMO--> LUMO |
| | 4.88(254) | 0.38 | HOMO--> LUMO |

| | | | |
|---|---|---|---|
| | 5.82(213) | 0.050 | HOMO--> LUMO |
| ***Cis*-2M** | 3.35(370) | 1.37 | HOMO--> LUMO +HOMO-1---> LUMO+1 |
| | 4.66(266) | 0.25 | HOMO--> LUMO |
| | 5.46(227) | 0.058 | HOMO--> LUMO |
| | 6.14(202) | 0.20 | HOMO--> LUMO |

**Table ST15**. Electronic transitions in the *cis*- and *trans*-stilbene isomers of the Pt(II) complexes **1M** and **2M** in PCM.

| System (PCM) | E[eV] (nm) | $f$ | Assignment |
|---|---|---|---|
| ***Trans*-1M** | 2.99(415) | 2.72 | HOMO--> LUMO +(HOMO-1---> LUMO+1) |
| | 4.49(270) | 0.19 | HOMO--> LUMO |
| | 4.94(251) | 0.093 | HOMO--> LUMO |
| | 5.79(214) | 0.35 | HOMO--> LUMO |
| ***Trans*-2M** | 3.15(394) | 2.84 | HOMO--> LUMO +(HOMO-1---> LUMO+1) |
| | 3.49(334) | 0.77 | HOMO--> LUMO +(HOMO-1---> LUMO+1) |
| | 4.29(290) | 0.37 | HOMO--> LUMO |
| | 5.04(246) | 0.069 | HOMO--> LUMO |
| | 6.01(204) | 0.24 | HOMO--> LUMO |
| ***Cis*-1M** | 3.14(395) | 1.20 | HOMO--> LUMO +HOMO-1---> LUMO+1 |
| | 3.79(327) | 0.25 | HOMO--> LUMO + HOMO-1---> LUMO+1 |
| | 4.41(281) | 0.33 | HOMO--> LUMO |
| | 4.64(267) | 0.27 | HOMO--> LUMO |
| | 5.79(214) | 0.25 | HOMO--> LUMO |

| | | | |
|---|---|---|---|
| ***Cis*-2M** | 3.35(374) | 1.66 | MLCT + π-----π* |
| | 4.66(263) | 0.37 | HOMO--> LUMO |
| | 6.14(202) | 0.25 | HOMO--> LUMO |