

**Electronic supplementary information**

**for**

**Novel Au<sup>I</sup> polyynes and their high optical power limiting performances in both solution and prototype device†**

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## Experimental

### Synthesis

#### L-2P

Under a N<sub>2</sub> atmosphere, to the mixture of THF (40 mL) and 1,4-diiodobenzene (1.32 g, 4.00 mmol), *n*-BuLi (3.52 mL, 2.5 M in hexane) was added slowly with a syringe at -78 °C. After addition, the reaction mixture was allowed to stir for 30 min at this temperature. Then, chlorodiphenyl phosphine (1.58 ml, 8.80 mmol) was added. The reaction temperature was raised to room temperature slowly and the reaction mixture was stirred for 1 h. After water quenching, the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After concentration, the crude product was purified by preparative TLC on silica eluting with petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> (9/1, v/v) to obtain the product as white solid (0.82 g, 46%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.35–7.29 (m, 20H), 7.25–7.22 (m, 4H); <sup>31</sup>P NMR (161.9 MHz, CDCl<sub>3</sub>): -5.70; FAB-MS (m/z): 446 [M]<sup>+</sup>.

#### L-2Au

NaAuCl<sub>4</sub> (0.50g, 1.39 mmol) was dissolved in mixed solvent EtOH/H<sub>2</sub>O (10 mL, v:v =1:1) and methyl sulfide was added drop wisely until white precipitation appeared. The white product was obtained by filtration and dried (0.39 g). Under a N<sub>2</sub> flow, the white solid (0.39 g, 1.33 mmol) and L-2P (0.28g, 0.63 mmol) were added to CH<sub>2</sub>Cl<sub>2</sub> (15 mL) at room temperature. After stirring for 1.5 h, the solvent was removed and the white solid was washed with ether (5×10 mL). The product was obtained as white solid (0.53 g, 84%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.59–7.49 (m, 24H); <sup>31</sup>P NMR (161.9 MHz, CDCl<sub>3</sub>): δ (ppm) 33.04; FAB-MS (m/z): 910 [M]<sup>+</sup>.

#### 2,7-Dibromo-9,9-didodecyl-fluorene

The mixture of 2,7-dibromofluorene (5.0 g, 15.4 mmol), NaOH (1.7 g, 42.5 mmol), 1-

bromododecane (11.5 g, 46.3 mmol) and DMSO (30 mL) were stirred at 90 °C for 24 h. After cooling to room temperature, the reaction mixture was extracted with petroleum ether (4×20 mL). The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated to dryness. The crude product was further purified by column chromatography on silica gel using petroleum ether as the eluent to afford the title product as yellow oil (8.21 g, 80.6%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.52 (d, *J* = 8.4 Hz, 2H), 7.46–7.44 (m, 4H), 1.93–1.88 (m, 4H), 1.26–1.04 (m, 36H), 0.87 (t, *J* = 6.8 Hz, 6H), 0.56 (m, 4H); FAB-MS (*m/z*): 660 [M]<sup>+</sup>.

### **1-Bromo-4-(dodecyloxy)benzene**

4-Bromophenol (5.0 g, 28.9 mmol), 1-bromododecane (16.3 g, 65.2 mmol) and K<sub>2</sub>CO<sub>3</sub> (6.0 g, 43.4 mmol) were mixed in ethanol (50 mL) at 80 °C and stirred for 24 h. After cooling to room temperature, water (50 mL) was added and mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (4×30 mL). The collected organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated to dryness. The liquid residue was purified by column chromatography on silica gel with petroleum ether to obtain colorless oil (5.8 g, 78%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.36 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 3.91 (t, *J* = 6.8 Hz, 2H), 1.80–1.73 (m, 2H), 1.37–1.26 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H); FAB-MS (*m/z*): 340, 342 [M]<sup>+</sup>.

### **4-(Dodecyloxy)-*N,N*-diphenylbenzenamine**

Under N<sub>2</sub> atmosphere, 1-bromo-4-(dodecyloxy)benzene (6.0 g, 43.4 mmol) diphenylamine (4.5 g, 26.7 mmol), *t*-BuOK (3.6 g, 32.1 mmol), Pd(OAc)<sub>2</sub> (0.2 g, 0.9 mmol), and *t*-Bu<sub>3</sub>P (1.8 mmol) were mixed in *p*-xylene, and then mixture was stirred at 120 °C for 16 h. After cooling to room temperature, the reaction mixture was filtrated, concentrated under vacuum. Then concentrated liquid was purified by column chromatography on silica gel with petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> (3/1, v/v) to get white solid (5.1 g, 65%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.22–7.18 (m, 4H),

7.06–7.18 (m, 6H), 6.94 (t,  $J = 7.4$  Hz, 2H), 6.83 (d,  $J = 8.8$  Hz, 2H), 3.93 (t, 2H,  $J = 6.6$  Hz), 1.81–1.74 (m, 2H), 1.35–1.27 (m, 18H), 0.88 (t, 3H,  $J = 7.2$  Hz); FAB-MS ( $m/z$ ): 429  $[M]^+$ .

#### **4-(Dodecyloxy)-4',4''-(dibromo)triphenylamine**

4-(Dodecyloxy)-*N,N*-diphenyl-benzenamine (2.0 g, 4.5 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (15 mL) and glacial acetic acid (0.5 mL) was added. NBS (1.7 g, 9.6 mmol) was added by portions at 0 °C. After addition, the reaction mixture was stirred at room temperature for 12 h. After removing a small amount of white solid through filtration, the reaction mixture was concentrated and purified by column chromatography on silica gel with petroleum ether/ $\text{CH}_2\text{Cl}_2$  (5/1, v/v) to get pale yellow oil (2.4 g, 92%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.29 (d,  $J = 8.8$  Hz, 4H), 7.01 (d,  $J = 8.8$  Hz, 2H), 6.94 (d,  $J = 7.4$  Hz, 4H), 6.83 (d,  $J = 8.8$  Hz, 2H), 3.92 (t,  $J = 6.4$  Hz, 2H), 1.81–1.73 (m, 2H), 1.34–1.26 (m, 18H), 0.88 (t,  $J = 7.0$  Hz, 3H); FAB-MS ( $m/z$ ): 585  $[M]^+$ .

#### ***N*-Dodecyl-carbazole**

Carbazole (5.0 g, 30.0 mmol), KOH (5.0 g, 89.3 mmol) and DMSO (30 mL) were mixed in round-bottom flask. The mixture was heated to reflux for 10 min. 1-Bromododecane (11.5 g, 46.3 mmol) was added slowly. After addition, the reaction mixture was refluxed for 2 h and then was cooled to room temperature, and poured into ice water (100 mL). The brown oily precipitate was collected, washed with water (5×30 mL) and dissolved with  $\text{CH}_2\text{Cl}_2$  (80 mL). After drying over anhydrous  $\text{Na}_2\text{SO}_4$ , the solvent was removed. The crude product was purified by column chromatography silica gel with petroleum ether/ $\text{CH}_2\text{Cl}_2$  (5/1, v/v) to obtain yellow oil (9.9 g, 93%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.10 (d,  $J = 8.0$  Hz, 2H), 7.49–7.40(m, 4H), 7.22 (t,  $J = 7.2$  Hz, 2H), 4.30 (t,  $J = 7.2$  Hz, 2H), 1.90–1.83 (m, 2H), 1.41–1.24 (m, 18H), 0.88 (t,  $J = 6.8$  Hz, 3H); FAB-MS ( $m/z$ ): 335  $[M]^+$ .

### ***N*-Dodecyl-3,6-diiodo-carbazole**

*N*-Dodecyl-carbazole (5.0 g, 14.9 mmol) and KI (3.2 g, 19.4 mmol) were added in acetic acid (50 mL), and the mixture was heated to reflux for 30 min. After cooling for a while, KIO<sub>3</sub> (4.8 g, 22.4 mmol) was slowly added under stirring. After gradual disappearance of purple color, the reaction mixture was reheated to reflux for 30 min. After cooling to room temperature, the mixture was poured into ice water (100 mL). The mixture was extracted by petroleum ether (4×40 mL) and the organic phase was washed with 0.5 M Na<sub>2</sub>CO<sub>3</sub> (30 mL). After drying over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed. The crude product were purified by column chromatography on silica gel with petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> (5/1, v/v) to give the brown solid (4.3 g, 81%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.33 (s, 2H), 7.71(d, *J* = 8.6 Hz, 2H), 7.17 (t, *J* = 8.8 Hz, 2H), 4.23 (t, *J* = 7.2 Hz, 2H), 1.90–1.83 (m, 2H), 1.41–1.24 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H); FAB-MS (*m/z*): 587 [M]<sup>+</sup>.

### **General synthetic procedure for FLU-SiMe<sub>3</sub>, TPA-SiMe<sub>3</sub> and CAZ-SiMe<sub>3</sub>.**

The corresponding aromatic halide (1.0 equiv), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.05 equiv), CuI (0.05 equiv) and trimethylsilylacetylene (4.0 equiv) was mixed in the Et<sub>3</sub>N (20 mL) and stirred at room temperature for 0.5 h. Then, the reaction was allowed to proceed at 70 °C for 12 h. After cooling to room temperature, the precipitation was removed by filtration. The filtrate was concentrated under vacuum. The obtained crude product was further purified by column chromatography on silica gel with petroleum ether as eluent to get the pure product.

**FLU-SiMe<sub>3</sub>**: (Yield: 89%) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.59 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 6.4 Hz, 2H), 7.26 (s, 2H) 1.94–1.90 (m, 4H), 1.22-1.01 (m, 36H), 0.86 (t, *J* = 7.0 Hz, 6H), 0.51 (br, 4H), 0.28 (s, 18H); FAB-MS (*m/z*): 694 [M]<sup>+</sup>.

**TPA-SiMe<sub>3</sub>**: (Yield: 88%) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.30 (t, 4H, *J* = 8.8 Hz, 4H),

7.01 (d,  $J = 8.8$  Hz, 2H), 6.92 (d,  $J = 7.4$  Hz, 4H), 6.83 (d,  $J = 8.8$  Hz, 2H), 3.93 (t,  $J = 6.4$  Hz, 2H), 1.81–1.74 (m, 2H), 1.31–1.26 (m, 18H), 0.88 (t,  $J = 6.8$  Hz, 3H), 0.23 (s, 18H); FAB-MS (m/z): 621 [M]<sup>+</sup>.

**CAZ-SiMe<sub>3</sub>**: (Yield: 86%) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.20 (s, 2H), 7.57 (d,  $J = 8.0$  Hz, 2H), 7.28 (t,  $J = 8.4$  Hz, 2H), 4.23 (t,  $J = 7.2$  Hz, 2H), 1.84–1.80 (m, 2H), 1.41–1.22 (m, 18H), 0.89 (t,  $J = 6.8$  Hz, 3H), 0.30 (s, 18H); FAB-MS (m/z): 527 [M]<sup>+</sup>.

### General synthetic procedure for L-1, L-2 and L-3.

**FLU-SiMe<sub>3</sub>/TPA-SiMe<sub>3</sub>/CAZ-SiMe<sub>3</sub>** (1.0 equiv) and [*n*-Bu<sub>4</sub>N]F (2.1 equiv) were mixed in CH<sub>2</sub>Cl<sub>2</sub> (30 mL). The reaction mixture was stirred at room temperature for 30 min and then was washed with water (2×30 mL). The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum. The crude product was purified by column chromatography on silica gel with petroleum ether as eluent to get the pure product as colorless oil.

**L-1** (Yield: 92%) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.63 (d,  $J = 8.0$  Hz, 2H), 7.49–7.46 (m, 4H, Ar), 3.15 (s, 2H), 1.93 (m, 4H), 1.28–1.03 (m, 36H), 0.86 (t,  $J = 5.2$  Hz, 6H), 0.56 (m, 4H); <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 151.03, 140.97, 131.23, 126.53, 120.81, 119.96, 84.51, 55.19, 40.21, 31.90, 29.94, 29.59, 29.54, 29.32, 29.24, 23.65, 22.68; FAB-MS (m/z): 550 [M]<sup>+</sup>.

**L-2**: (Yield: 89%) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.33 (d,  $J = 8.4$  Hz, 4H), 7.04 (d,  $J = 8.0$  Hz, 2H), 6.96 (d,  $J = 8.4$  Hz, 4H), 6.85 (d,  $J = 8.0$  Hz, 2H), 3.94 (t,  $J = 6.4$  Hz, 2H), 3.03 (s, 2H), 1.78 (m, 2H, CH<sub>2</sub>), 1.47–1.26 (m, 18H), 0.88 (t,  $J = 6.4$  Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 154.78, 145.91, 137.10, 131.21, 126.16, 120.21, 113.67, 113.22, 81.89, 66.34, 30.04, 27.80, 27.77, 27.74, 27.53, 27.48, 27.42, 24.19, 20.82, 12.27; FAB-MS (m/z): 477 [M]<sup>+</sup>.

**L-3**: (Yield: 91%) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.20 (s, 2H), 7.59 (d,  $J = 8.4$  Hz, 2H), 7.28 (d,  $J = 8.4$  Hz, 2H), 4.25 (t,  $J = 7.2$  Hz, 2H), 3.07 (s, 2H), 1.83 (m, 2H), 1.29–1.21 (m, 18H),

0.88 (t,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 138.74, 128.22, 122.87, 120.32, 110.74, 107.06, 82.83, 73.56, 41.43, 30.01, 27.68, 27.63, 27.56, 27.43, 27.00, 25.32, 20.79, 12.24; FAB-MS ( $m/z$ ): 383  $[\text{M}]^+$ .

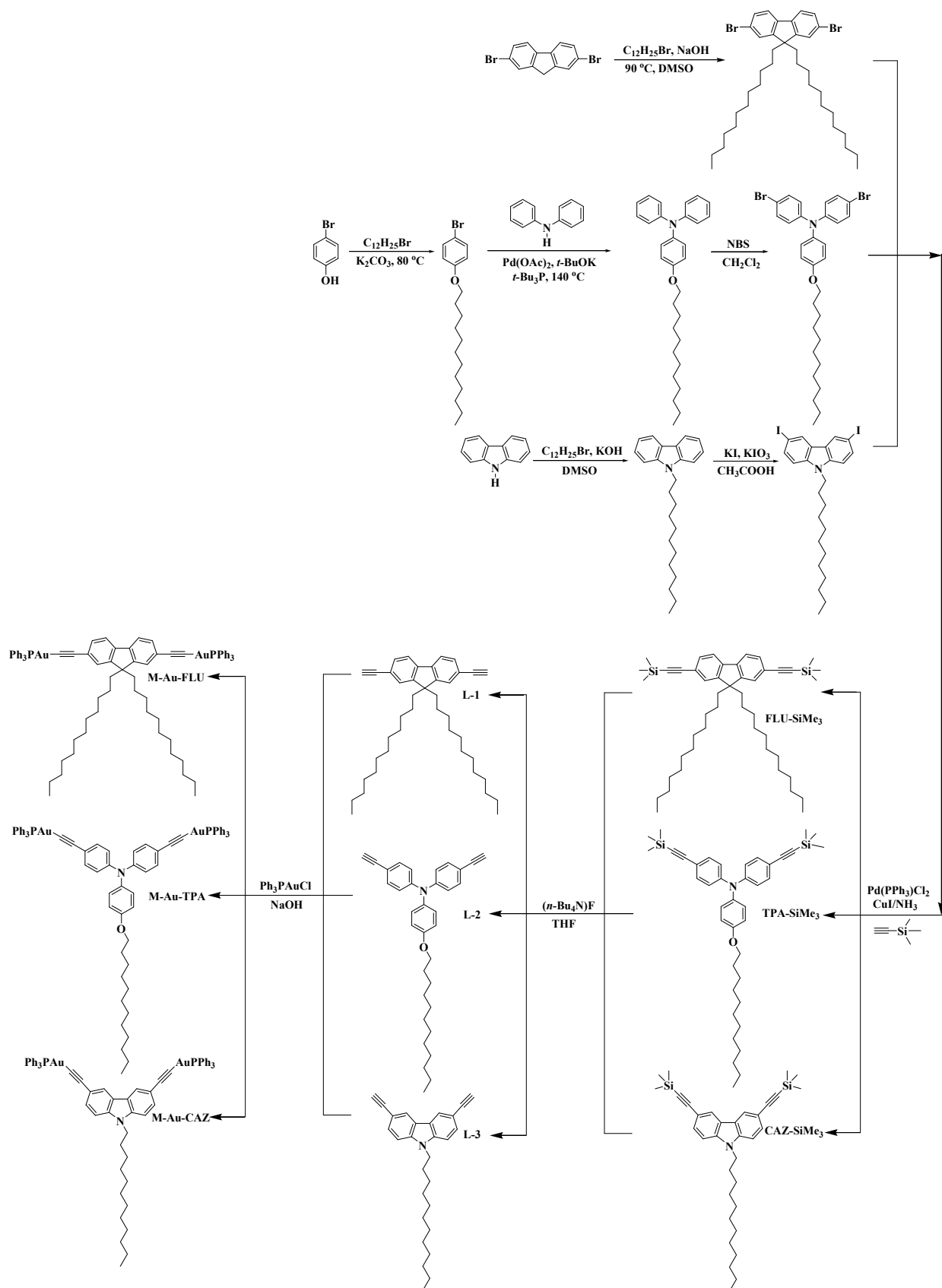
**General synthetic procedure for M-Au-FLU, M-Au-TPA and M-Au-CAZ.**

Under  $\text{N}_2$  atmosphere,  $\text{AuPPh}_3\text{Cl}$  (2.05 equiv) was added to the solution of the corresponding organic ligand **L-1/L-2/L-3** (1.0 equiv) in methanol containing NaOH (2.05 equiv). The reaction mixture was stirred for 10 h at room temperature. The reaction mixture was concentrated under vacuum. Then, the residue was dissolved in small amount  $\text{CH}_2\text{Cl}_2$  and added into methanol. The precipitate was collected and washed with methanol ( $2 \times 10$  mL). The title compounds were obtained in high yield.

**M-Au-FLU:** (Yield: 89%)  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.51–7.43 (m, 36H, Ar), 1.92–1.85 (m, 4H,  $\text{CH}_2$ ), 1.28–0.83 (m, 36H,  $\text{CH}_2$ ), 0.86 (t,  $J = 7.2$  Hz, 6H), 0.54 (br, 4H);  $^{31}\text{P}$  NMR (161.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 42.37.

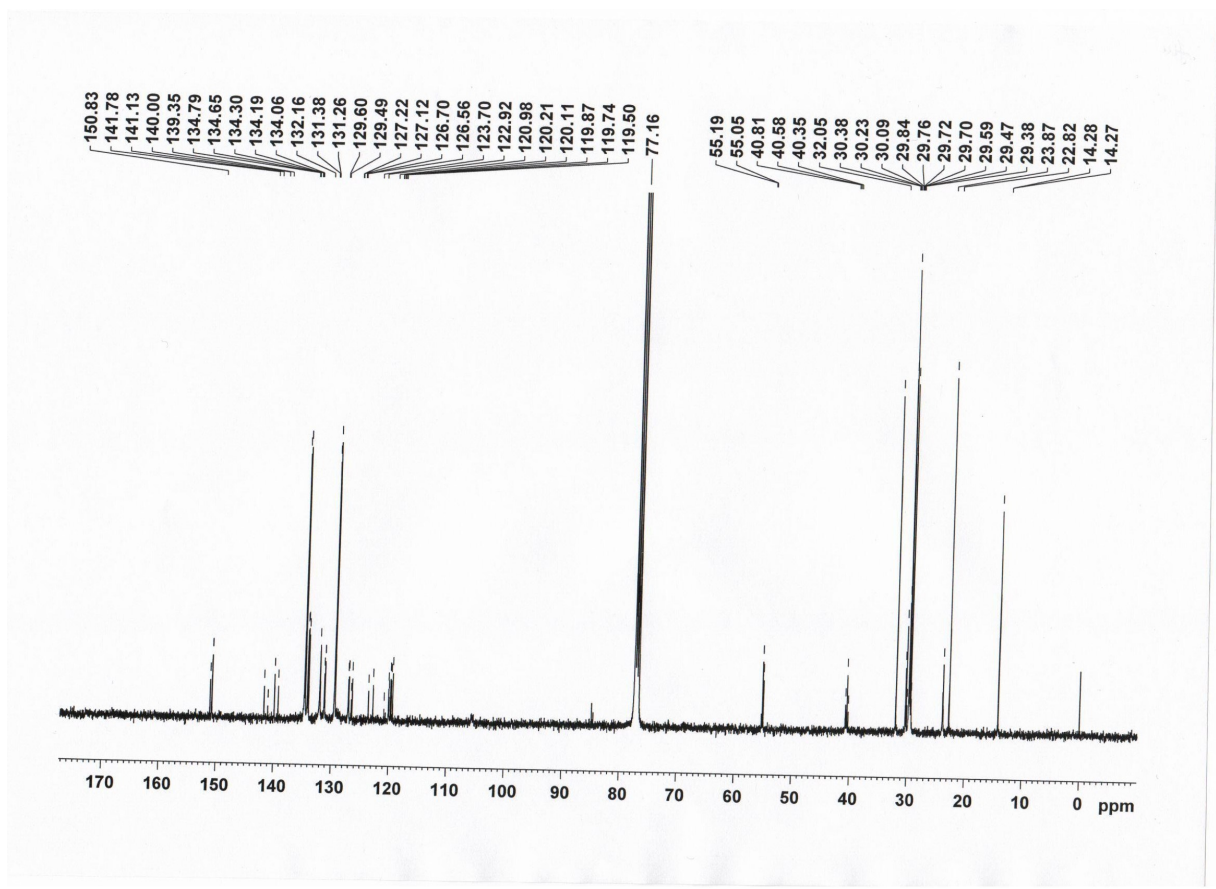
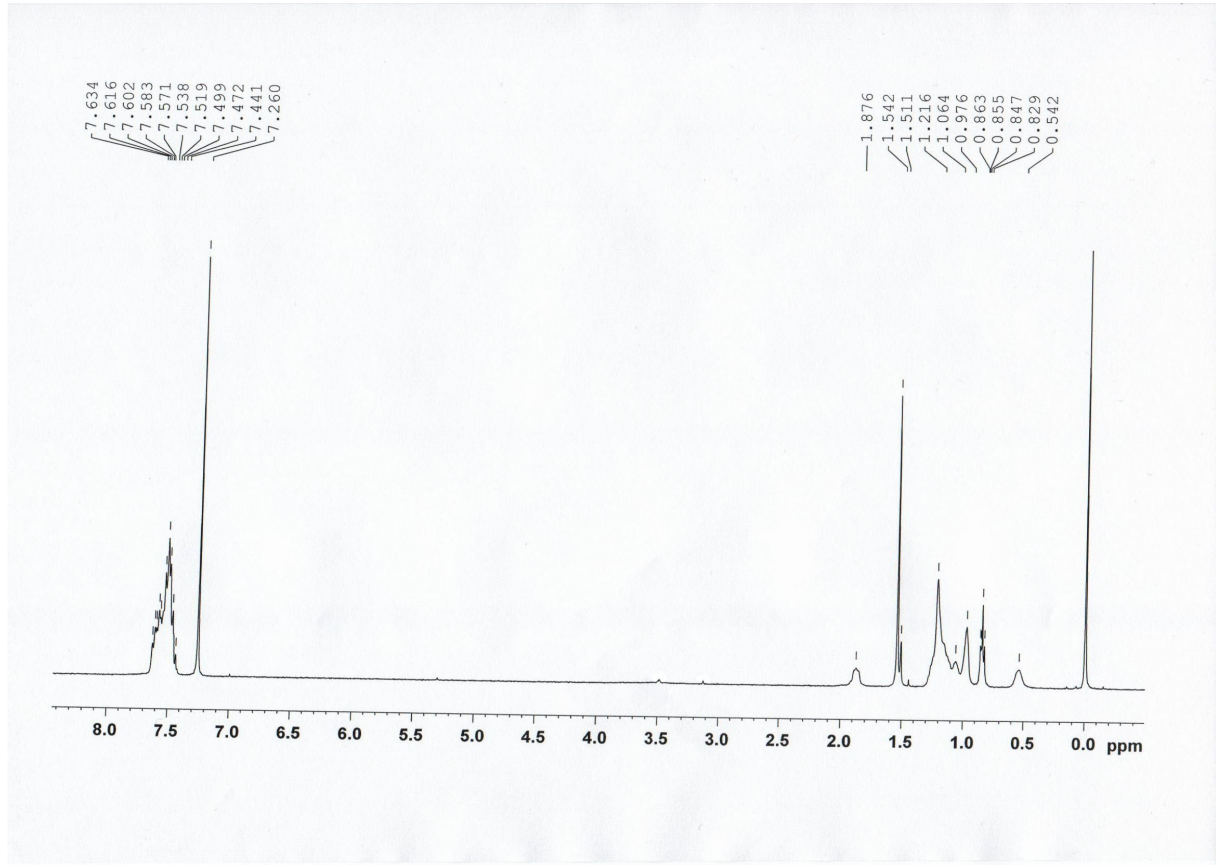
**M-Au-TPA:** (Yield: 88%)  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.57–7.42 (m, 30H), 7.33 (d,  $J = 8.4$  Hz, 4H), 7.03 (d,  $J = 8.8$  Hz, 2H), 6.89 (d,  $J = 6.0$  Hz, 4H), 6.81 (d,  $J = 8.8$  Hz, 2H), 3.91 (t,  $J = 6.4$  Hz, 2H), 1.80–1.72 (m, 2H), 1.44–1.25 (m, 18H), 0.87 (t,  $J = 6.0$  Hz, 3H);  $^{31}\text{P}$  NMR (161.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 42.34.

**M-Au-CAZ:** (Yield: 91%)  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.22 (s, 2H, Ar), 7.63–7.55 (m, 14H), 7.53–7.43 (m, 18H, Ar), 7.24 (d,  $J = 8.8$  Hz, 2H), 4.20 (t,  $J = 7.6$  Hz, 2H), 1.83 (m, 2H), 1.33–1.23 (m, 18H), 0.88 (t,  $J = 6.4$  Hz, 3H);  $^{31}\text{P}$  NMR (161.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 42.50.



**Scheme S1** Synthetic scheme for the diethynyl aromatic ligands and the Au<sup>I</sup> acetylides.





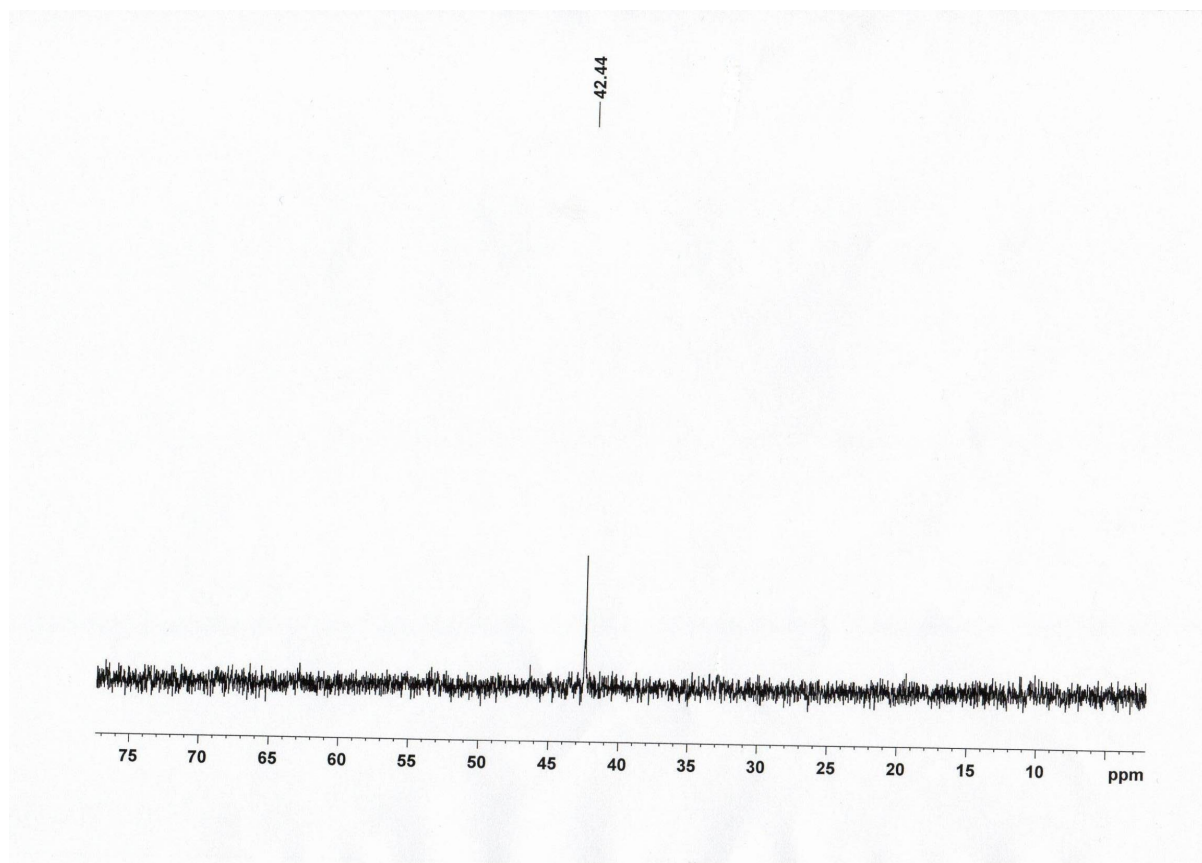
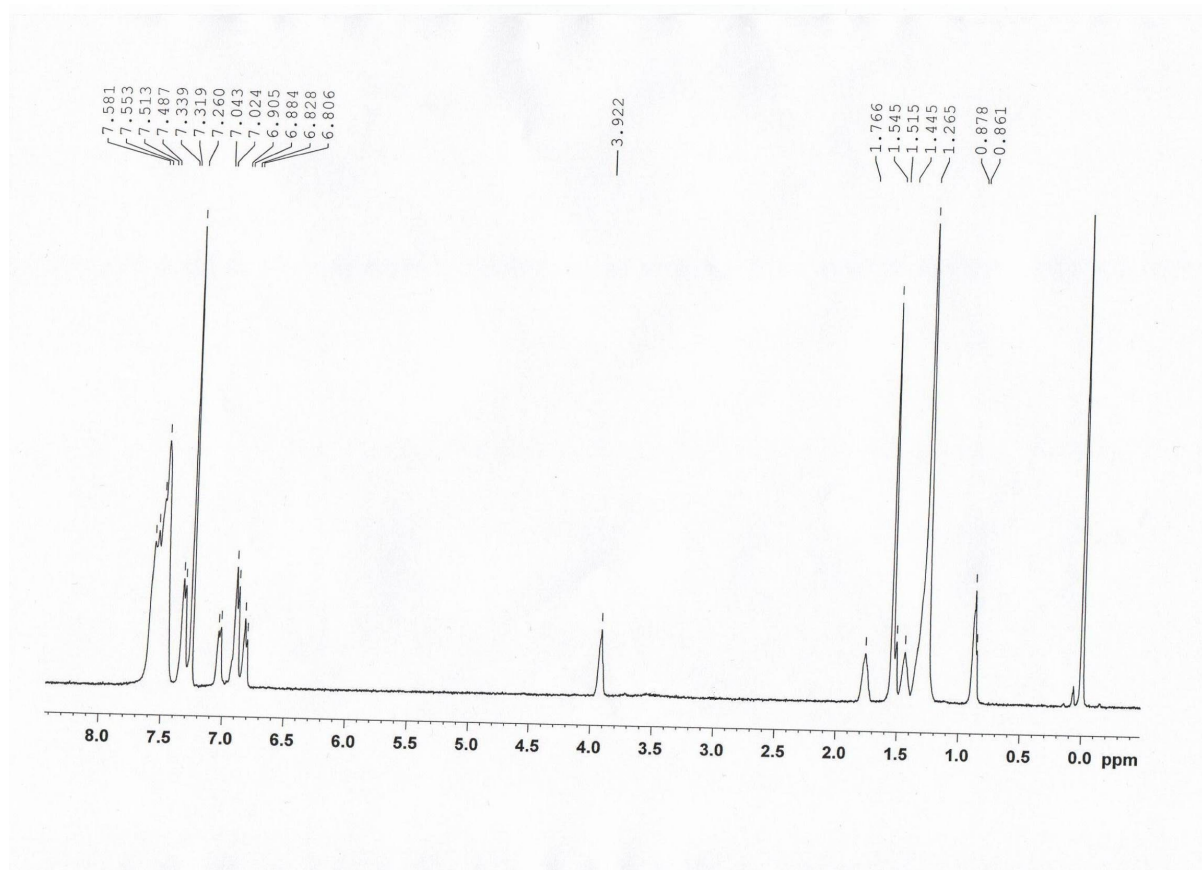


Fig. S1  $^1\text{H}$ -,  $^{13}\text{C}$ - and  $^{31}\text{P}$ -NMR spectra for P-Au-FLU.



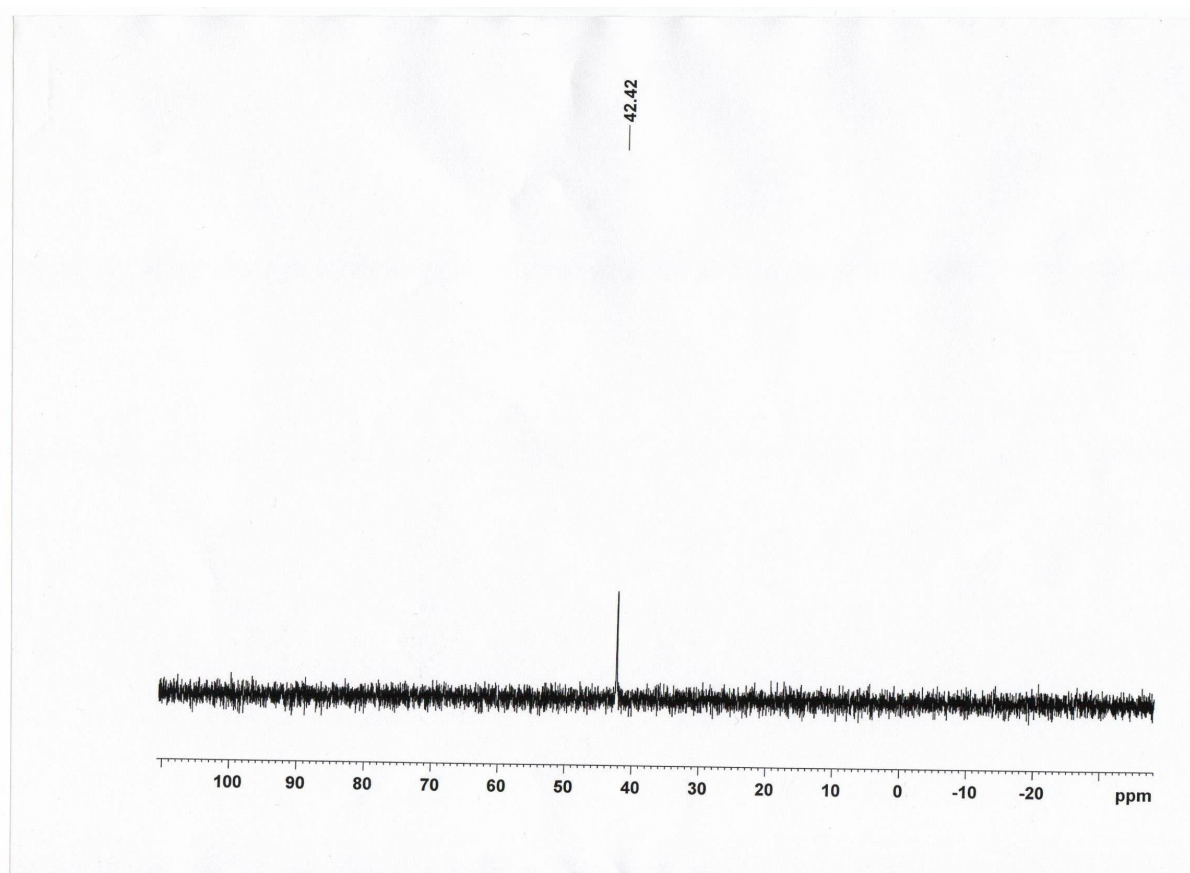
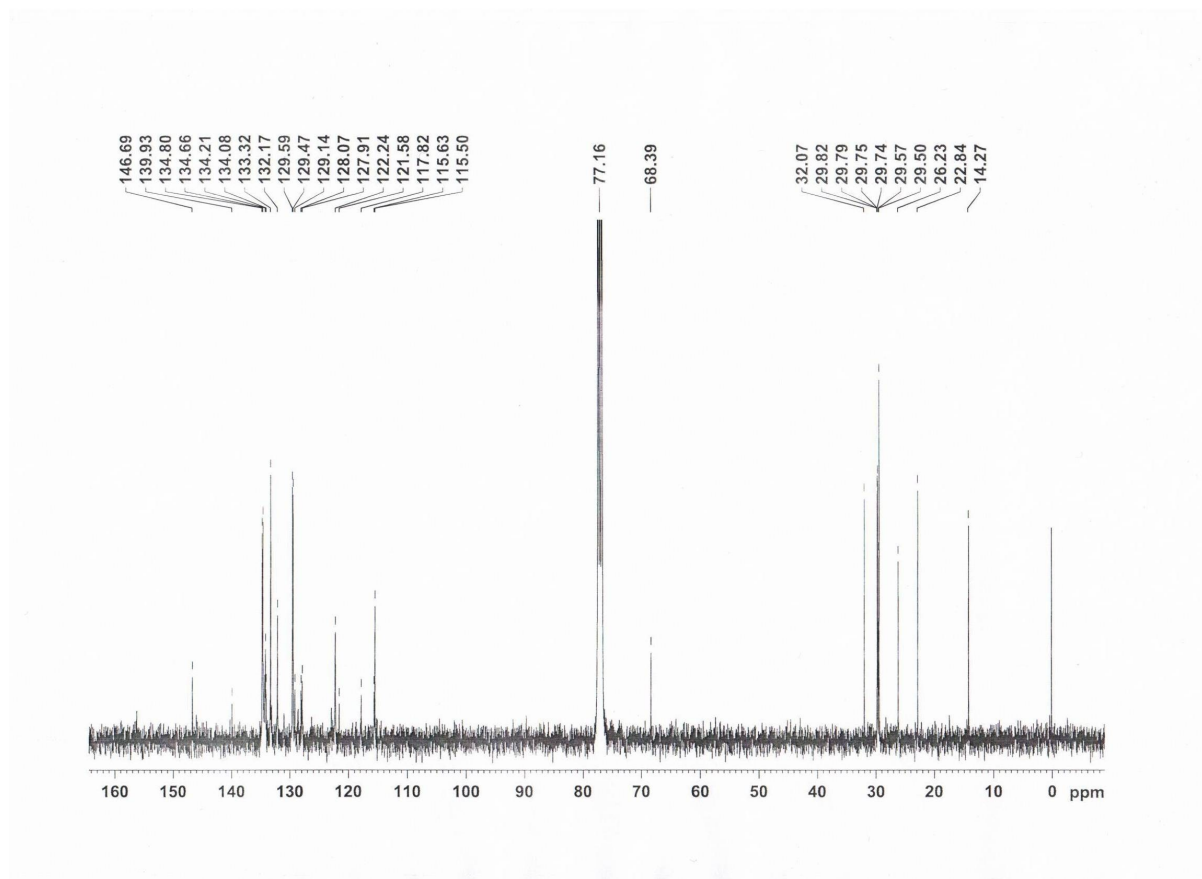
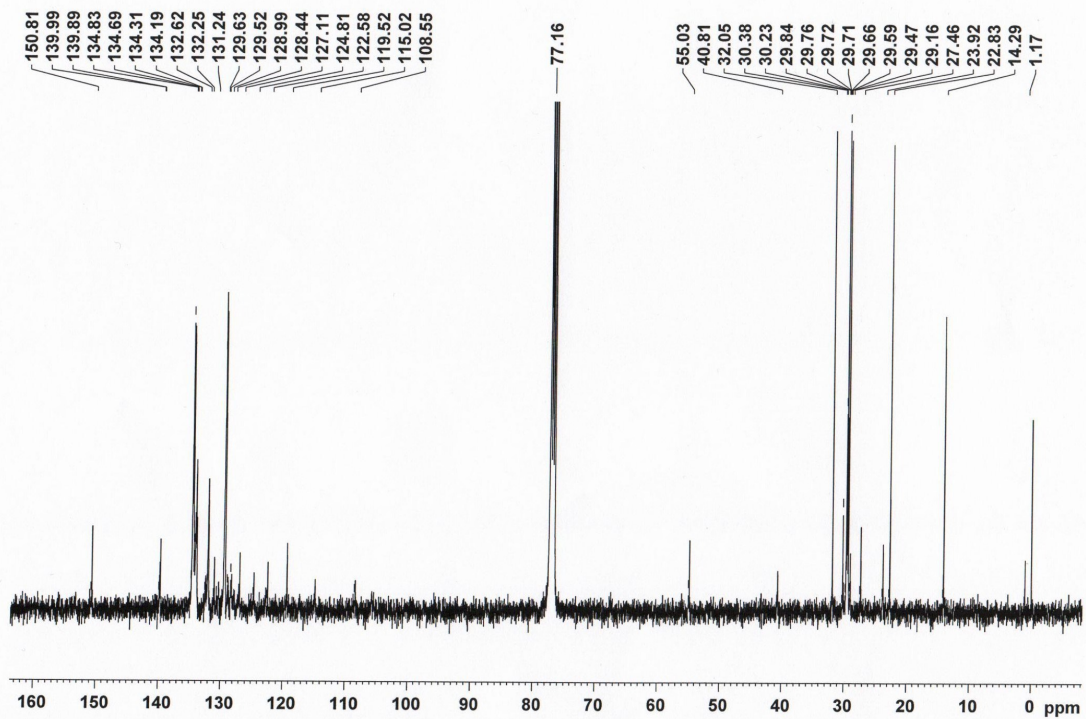
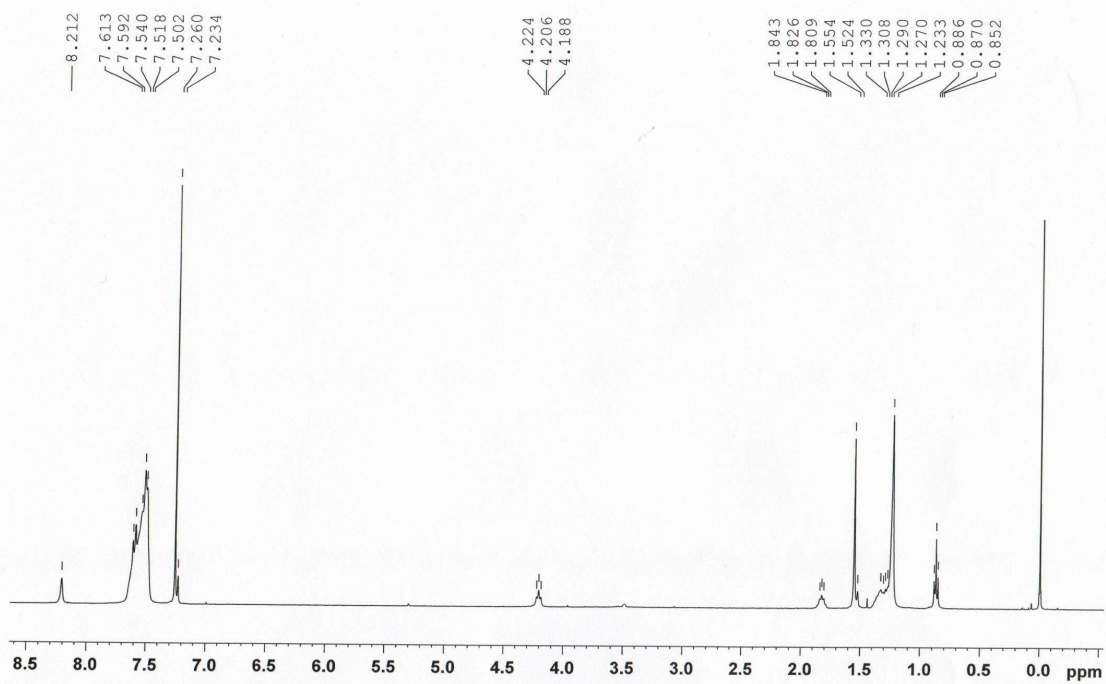


Fig. S2 <sup>1</sup>H-, <sup>13</sup>C- and <sup>31</sup>P-NMR spectra for P-Au-TPA.



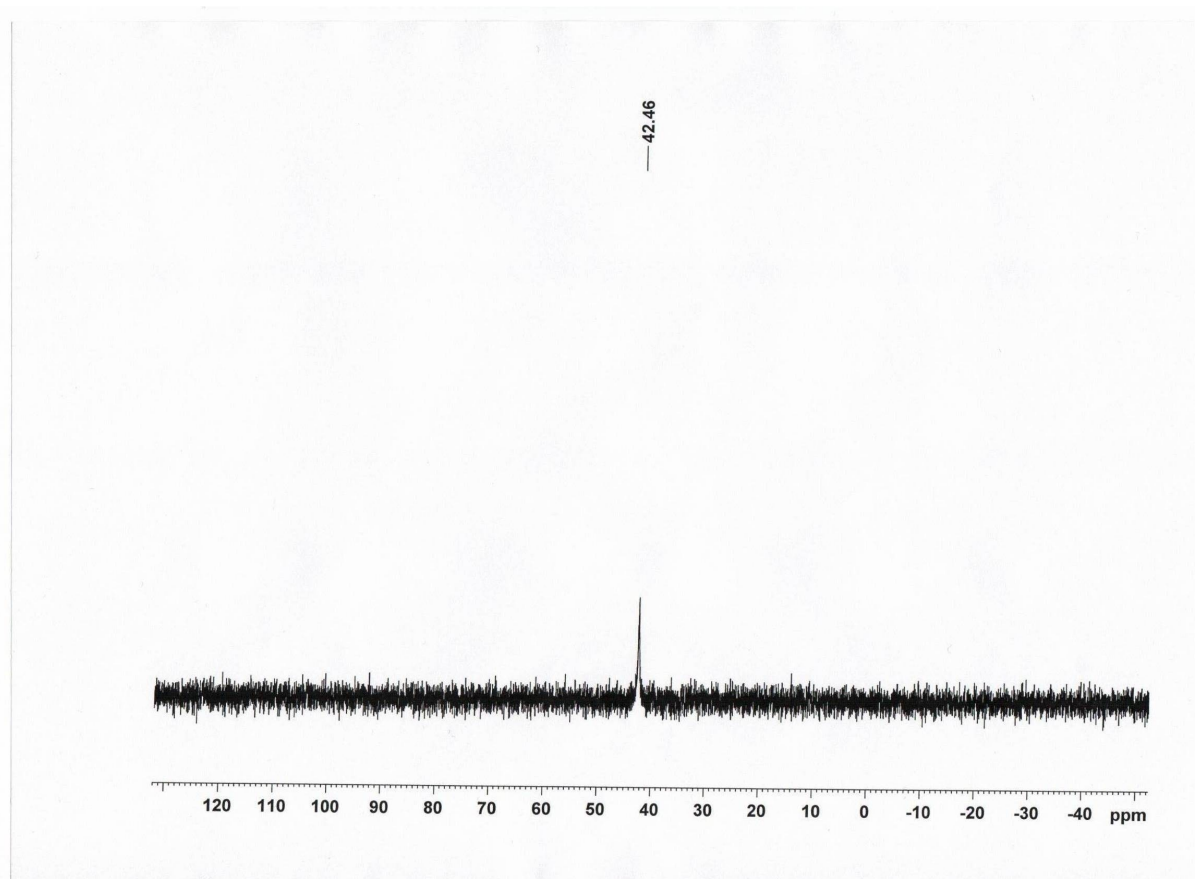


Fig. S3  $^1\text{H}$ -,  $^{13}\text{C}$ - and  $^{31}\text{P}$ -NMR spectra for P-Au-CAZ.

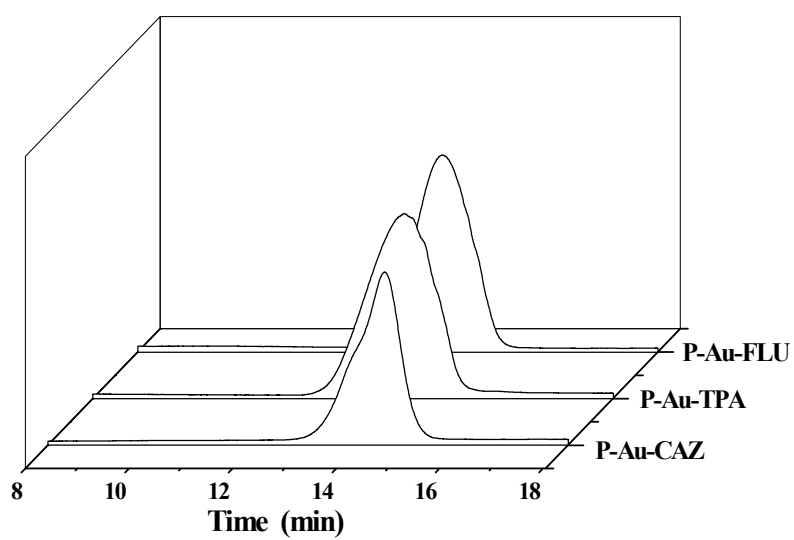
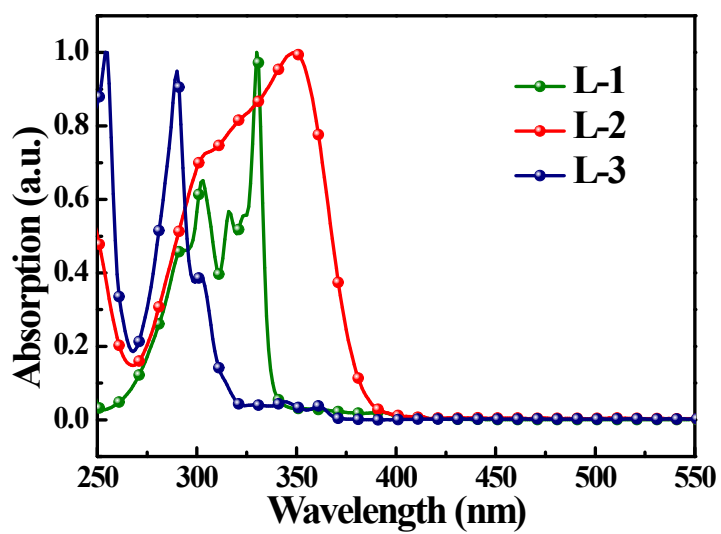
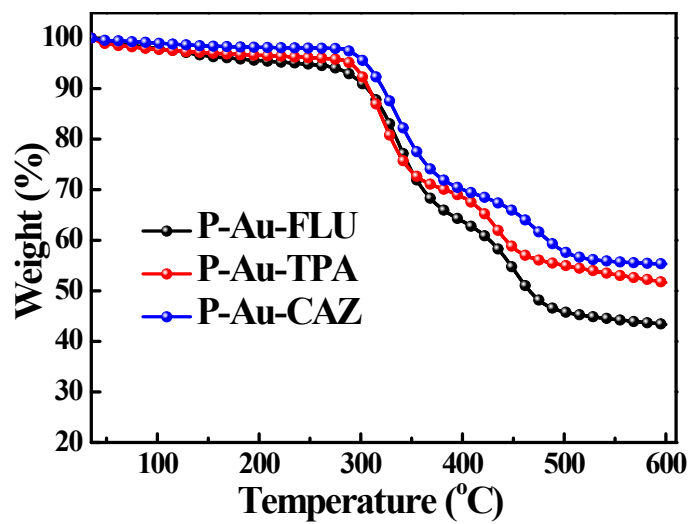


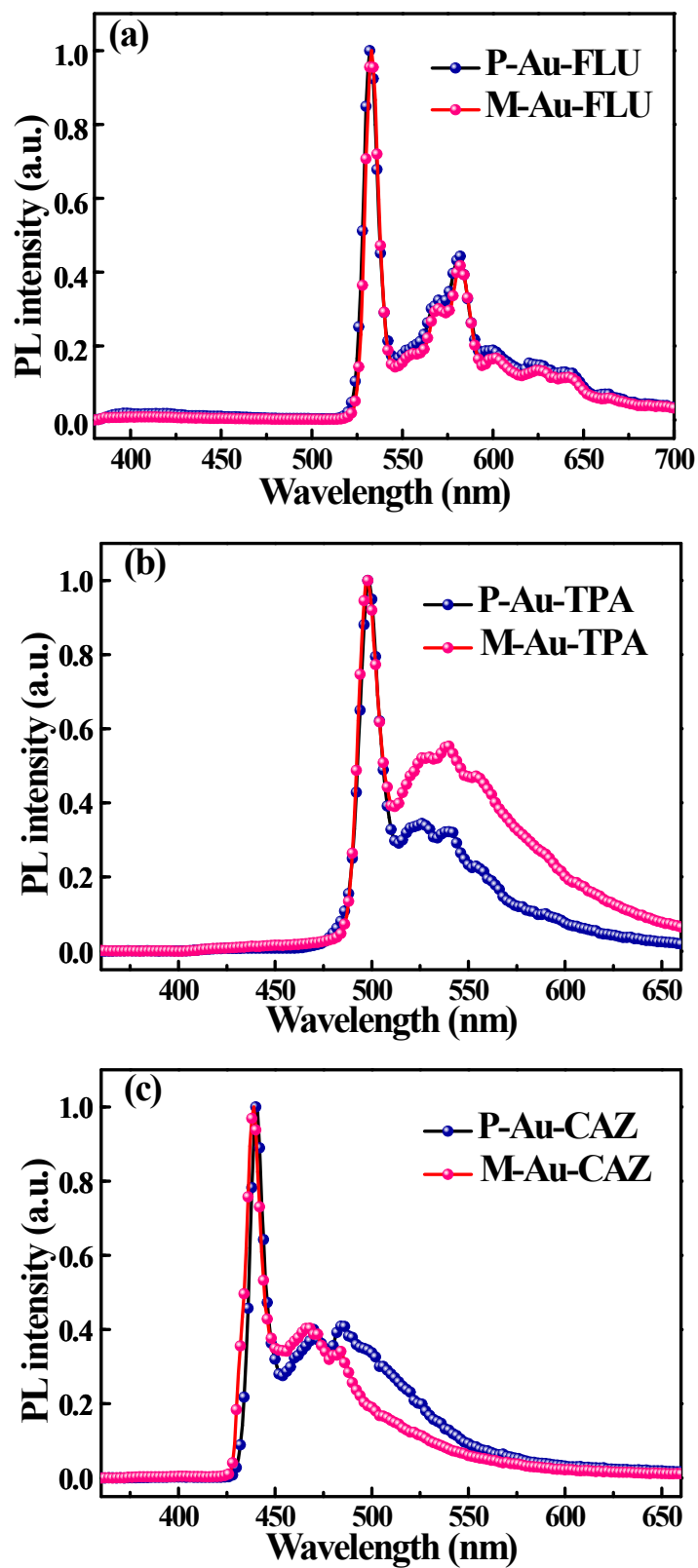
Fig. S4 GPC curves for P-Au-FLU, P-Au-TPA and P-Au-CAZ.



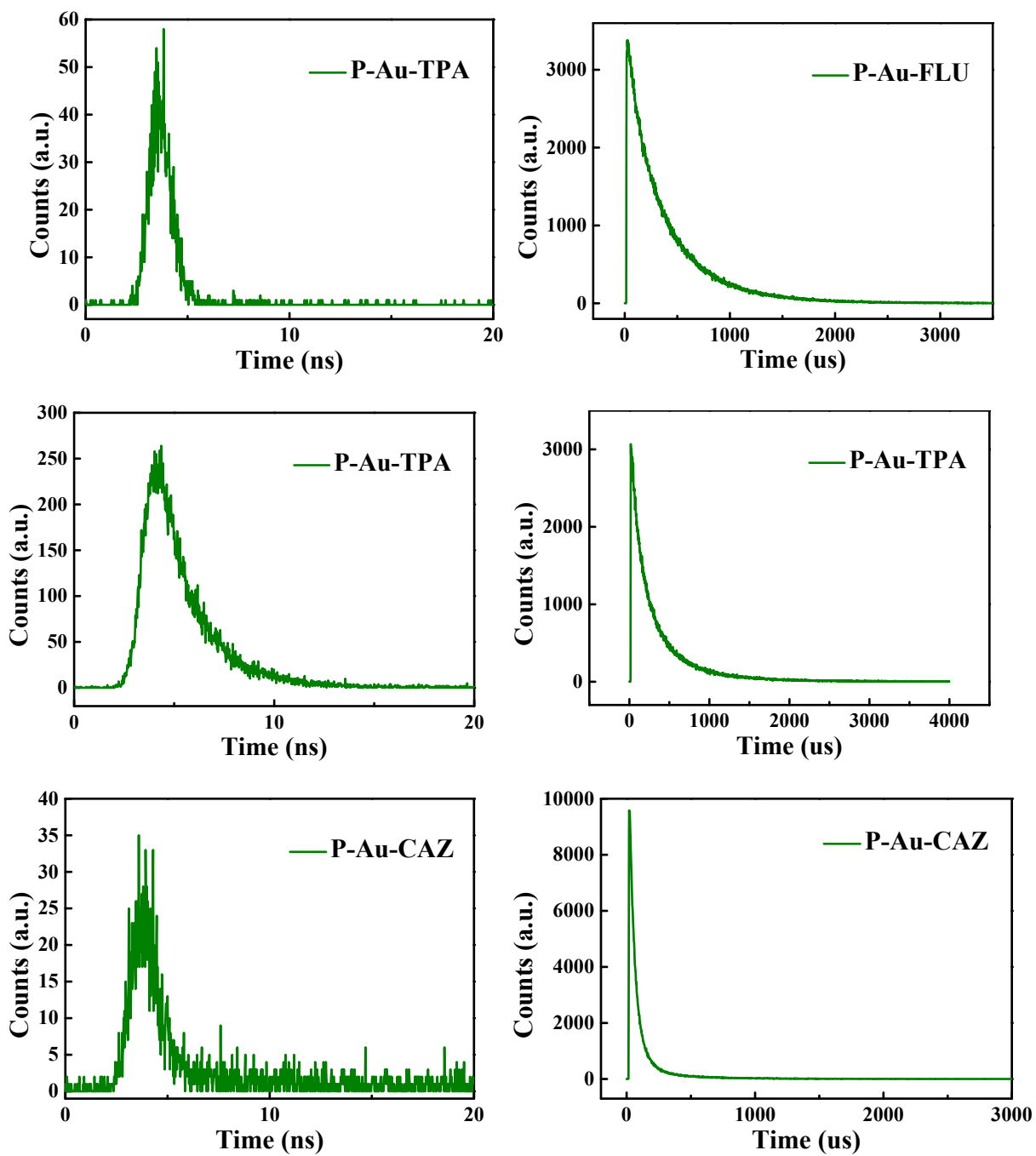
**Fig. S5** UV-vis absorption spectra for the organic ligands in  $\text{CH}_2\text{Cl}_2$  at 298 K.



**Fig. S6** TGA curves for P-Au-FLU, P-Au-TPA and P-Au-CAZ.

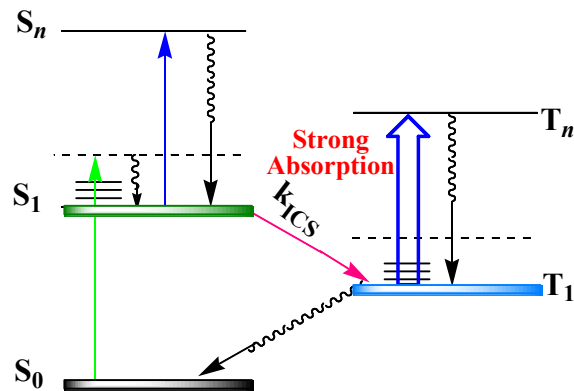


**Fig. S7** PL spectra of the Au<sup>I</sup> polyynes and their model Au<sup>I</sup> acetylides in CH<sub>2</sub>Cl<sub>2</sub> glass at 77 K. (a) P-Au-FLU and M-Au-FLU, (b) P-Au-TPA and M-Au-TPA, (c) P-Au-CAZ and M-Au-CAZ

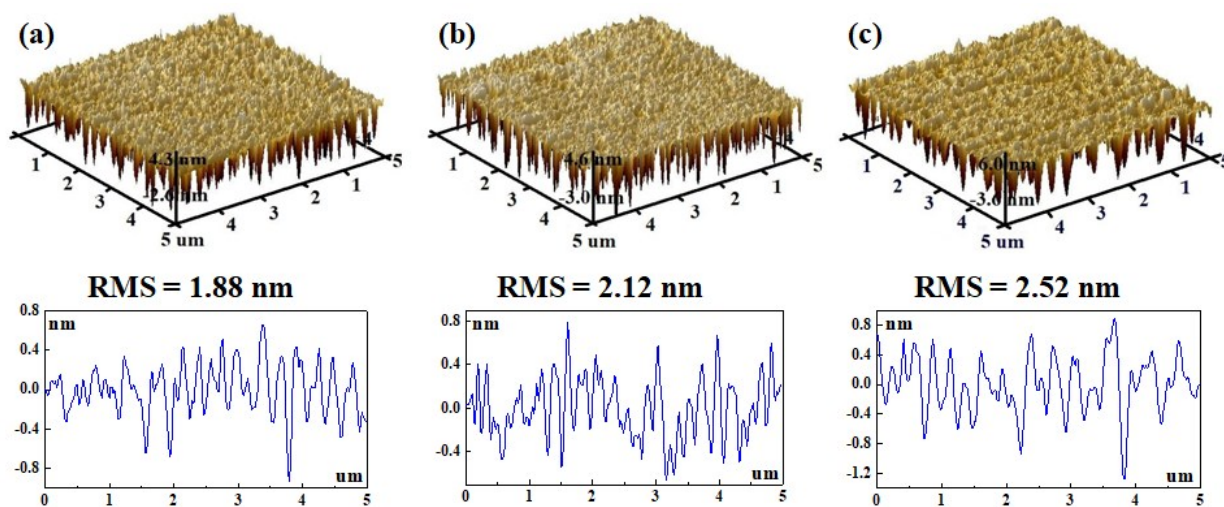


**Fig. S8** Fluorescence decay signals at 298 K and phosphorescence decay signal at 77 K of the Au<sup>I</sup> polyynes in CH<sub>2</sub>Cl<sub>2</sub>.

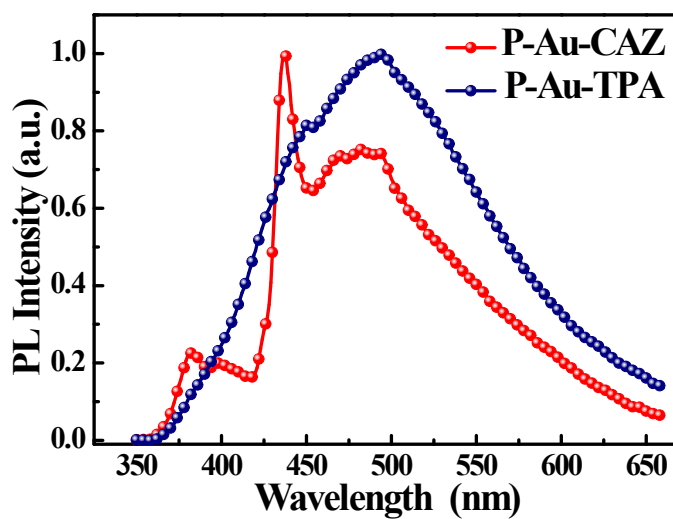




**Fig. S9** OPL mechanism of reverse saturable absorption (RSA) mechanism of the  $T_1$  states for nano-second laser.



**Fig. S10** Atomic force microscopy (AFM) images of the surfaces for the  $Au^I$  polyynes films together with the RMS values. (a) P-Au-FLU, (b) P-Au-TPA and (c) P-Au-CAZ.



**Fig. S11** PL spectra for P-Au-TPA and P-Au-CAZ doped in polystyrene (PS) solid film (ca. 3.0-wt% doping level) at 298 K.