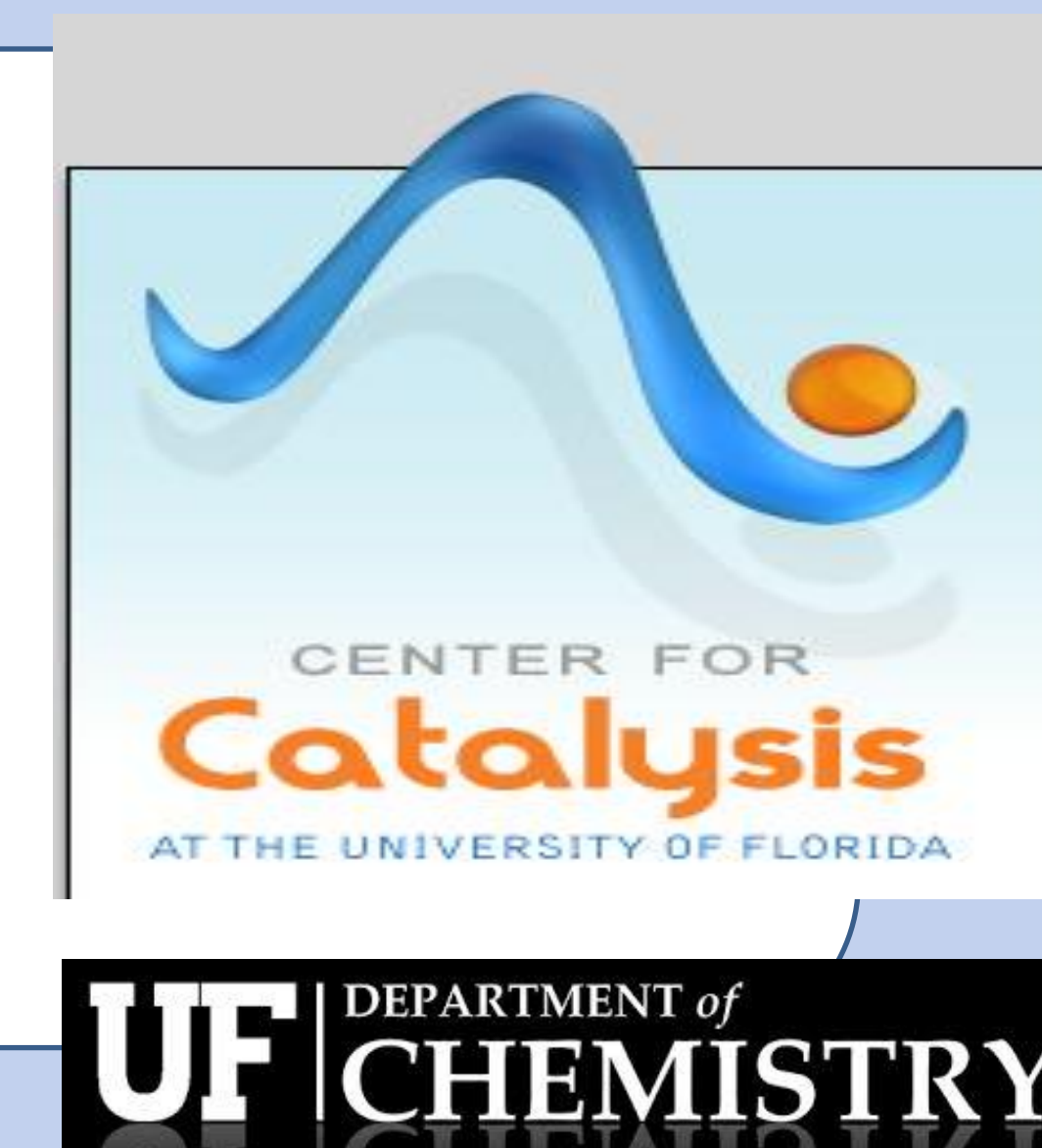




# Synthesis of metallo-polymers by forming C-N heterocyclic rings via iClick (inorganic click) reactions

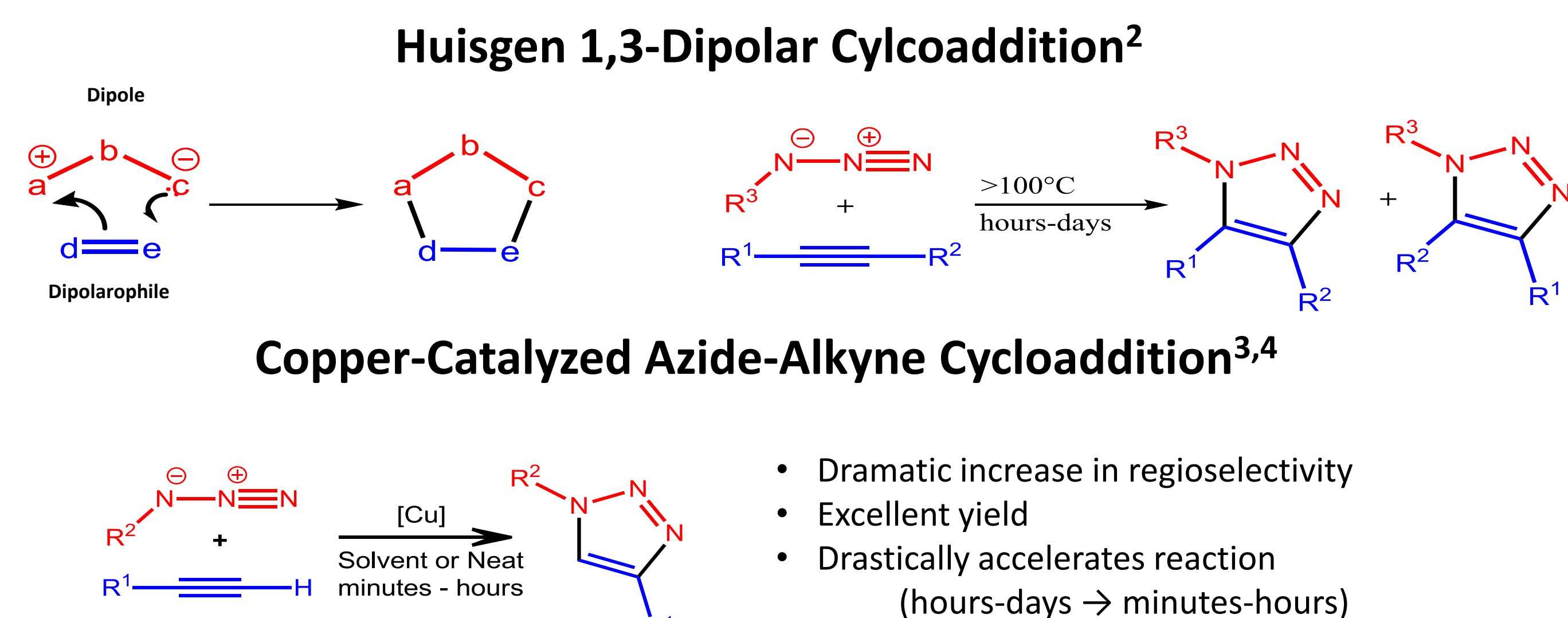
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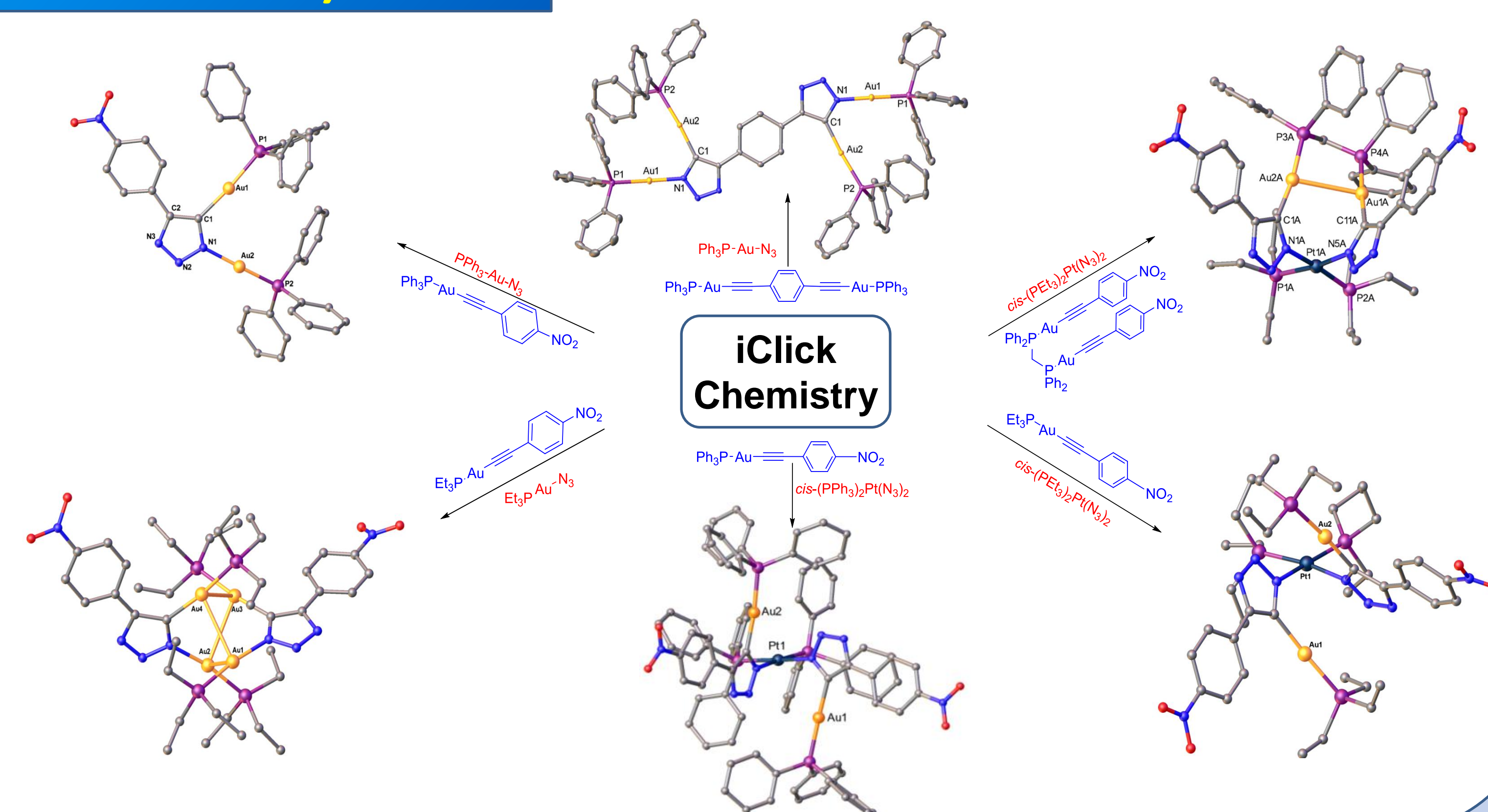
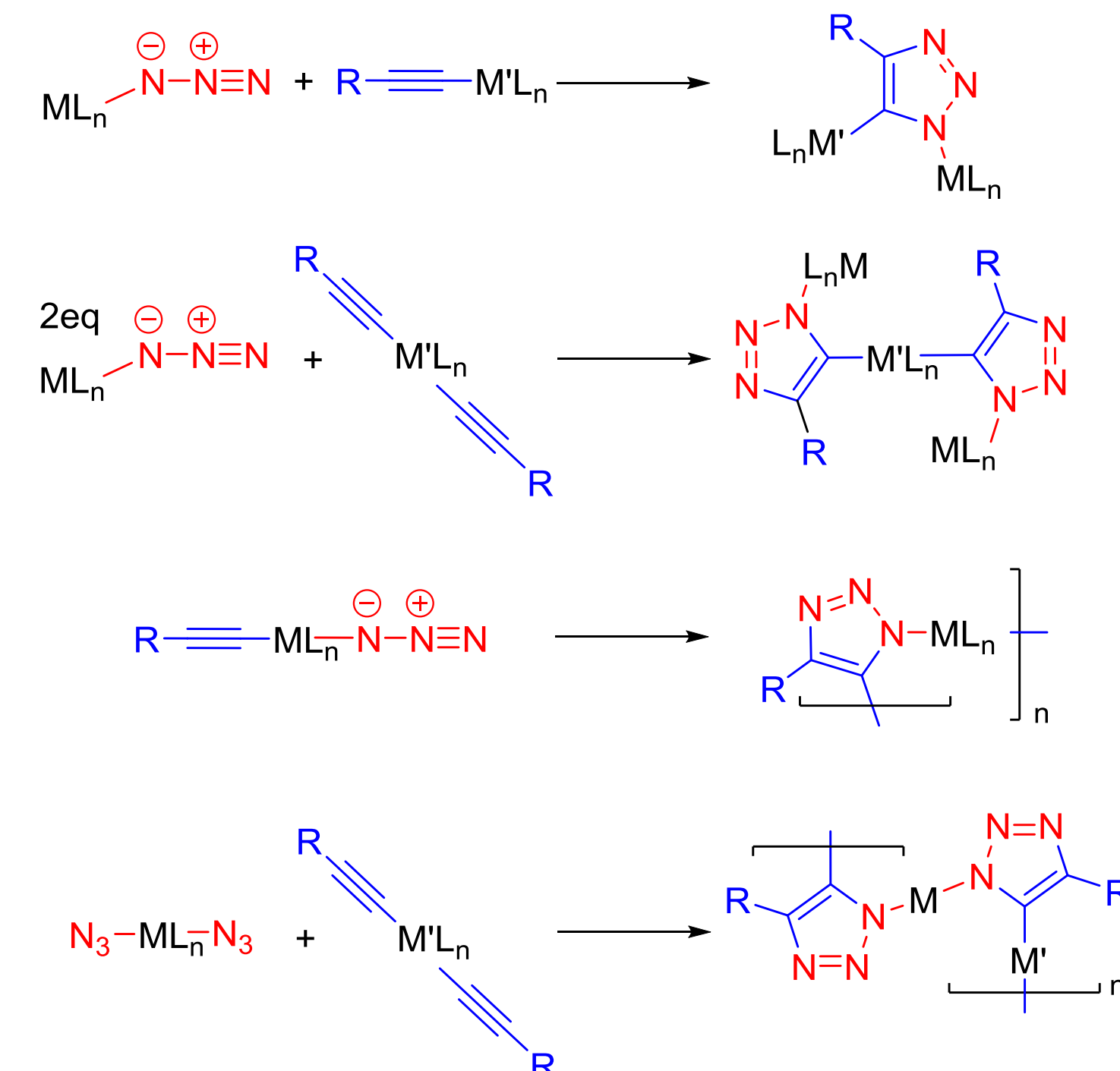


## Click Chemistry and iClick (Inorganic Click)

In 2001 Sharpless and coworkers grouped the Huisgen 1,3-dipolar cycloaddition, as well as the related copper-catalyzed azide-alkyne cycloaddition (CuAAC) into a set of bond-forming reactions that were 'near-perfect' for the rapid assembly of complicated, functionalized molecules through the linking or "clicking" of smaller, modular building blocks.<sup>1</sup>

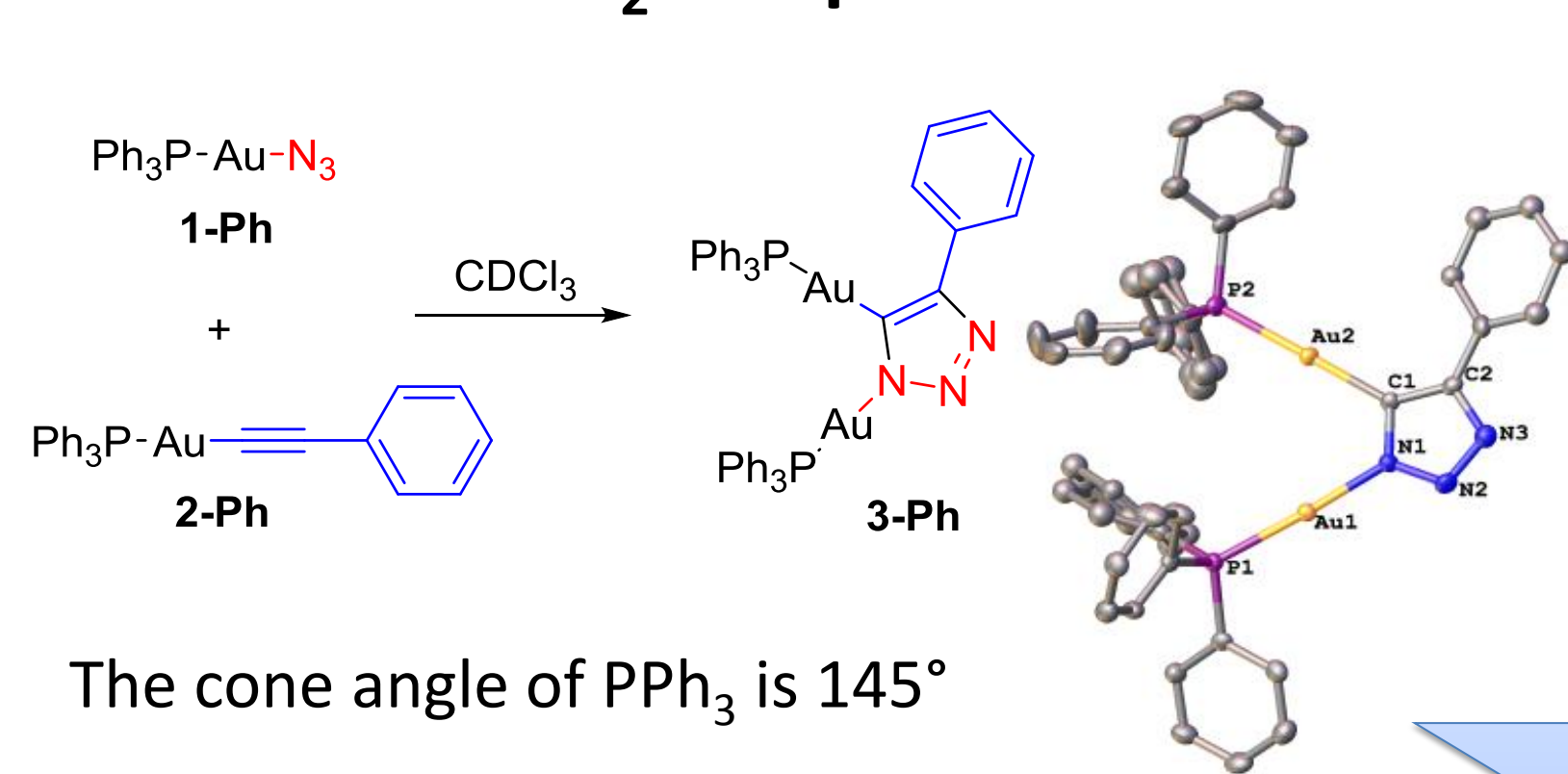


### Extension to iClick



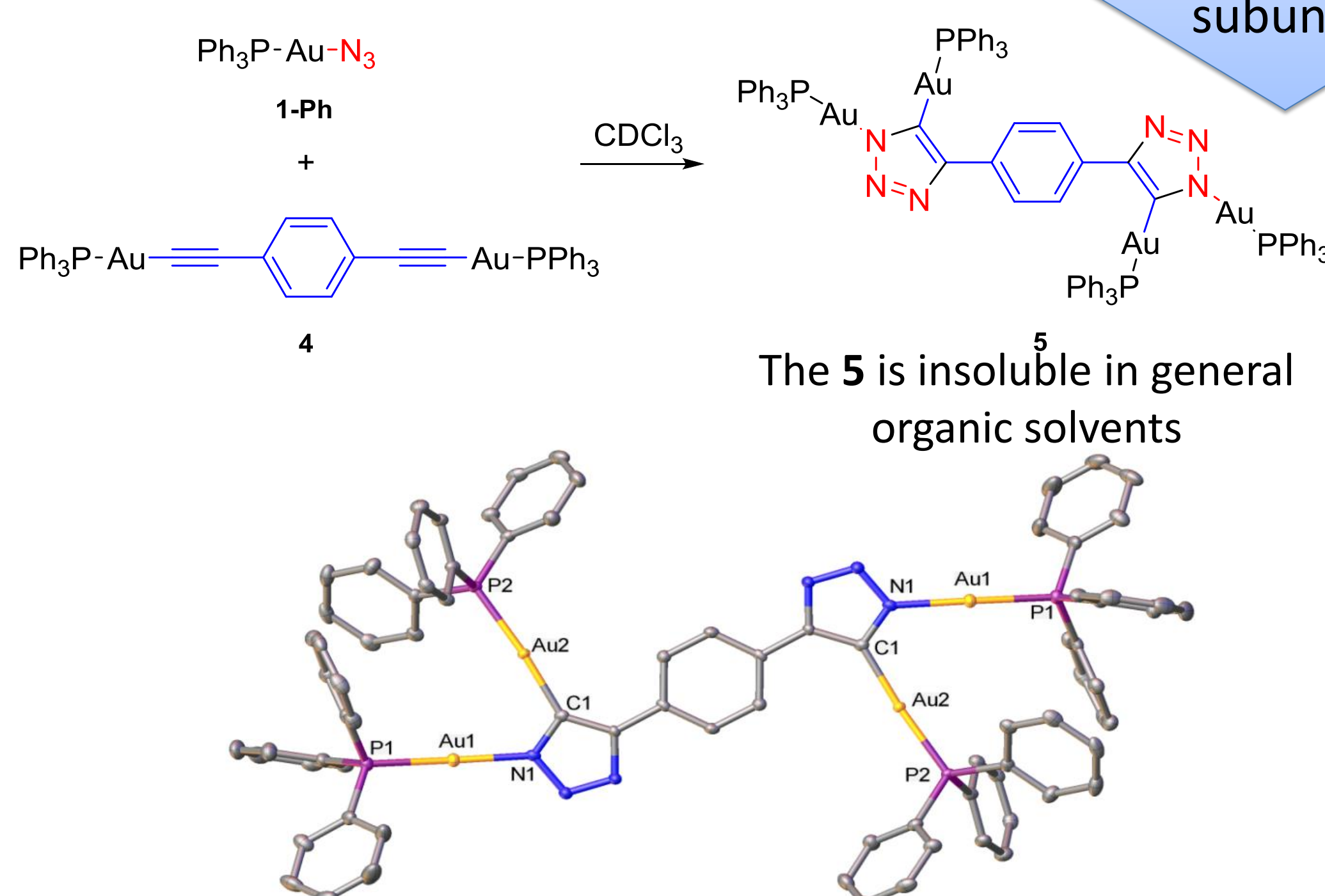
## Type I: triazolate ring based gold metallooligomers formed by aurophilicity

### Dinuclear Au<sup>I</sup><sub>2</sub> complex<sup>5</sup>



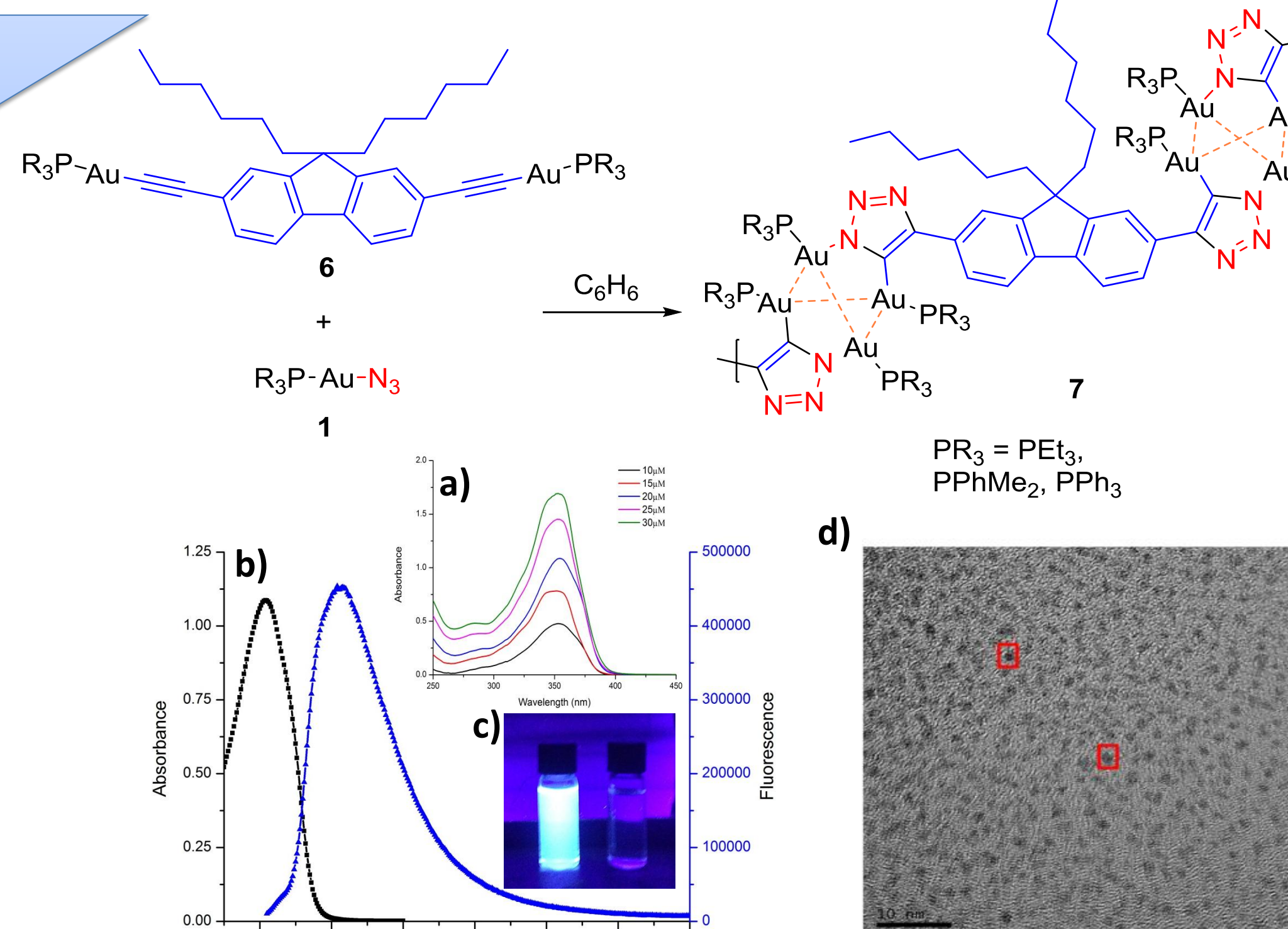
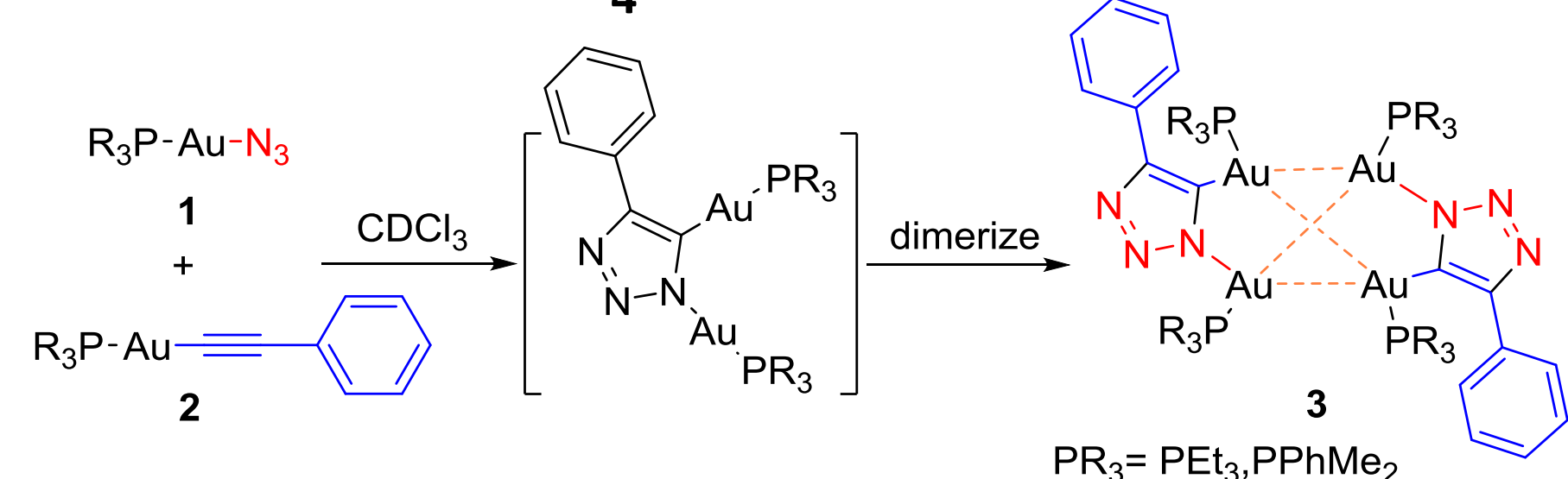
Decrease phosphine steric bulk to generate aurophilic interactions

Utilizing organic linkers to connect two iClick subunits



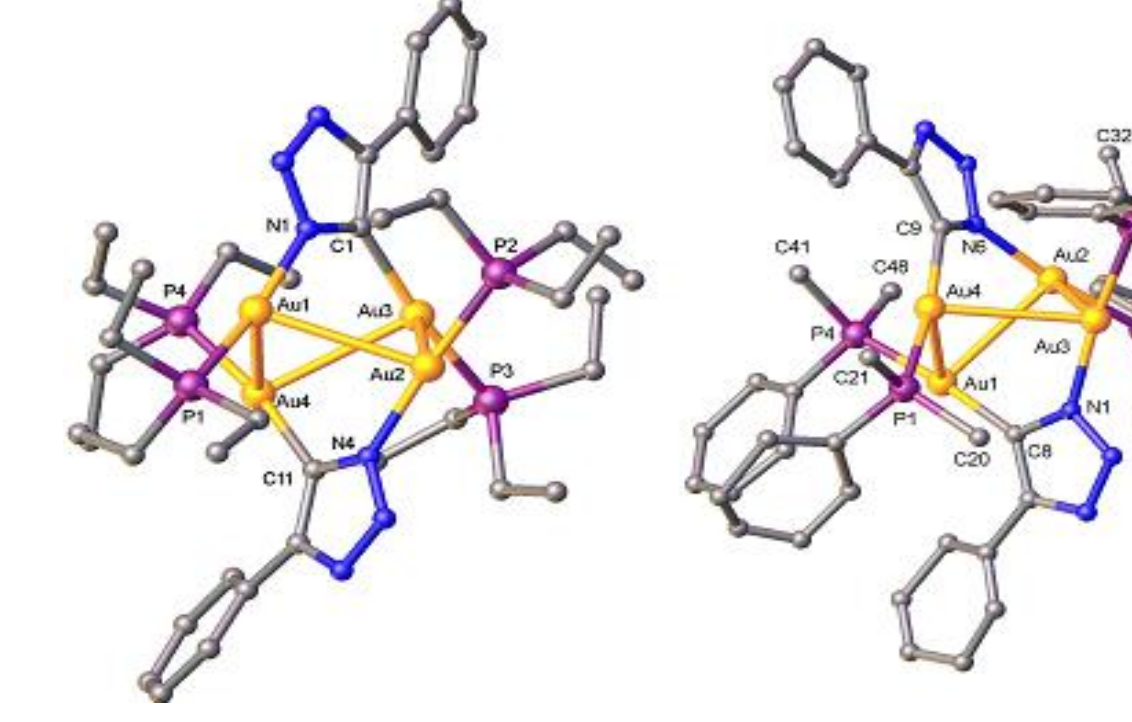
The torsion angles between triazolate rings and central phenyl ring are only about 2° which indicate that there is an electron delocalization across the whole organic motif.

### Tetranuclear Au<sup>I</sup><sub>4</sub> cluster



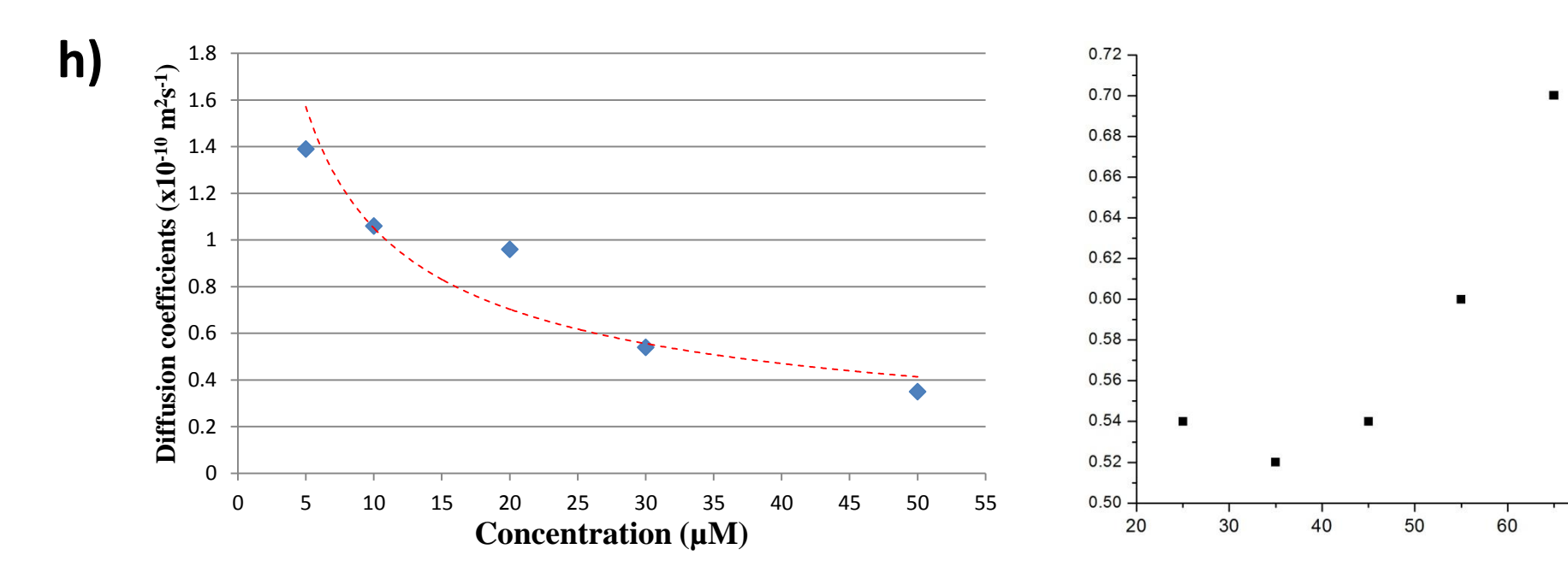
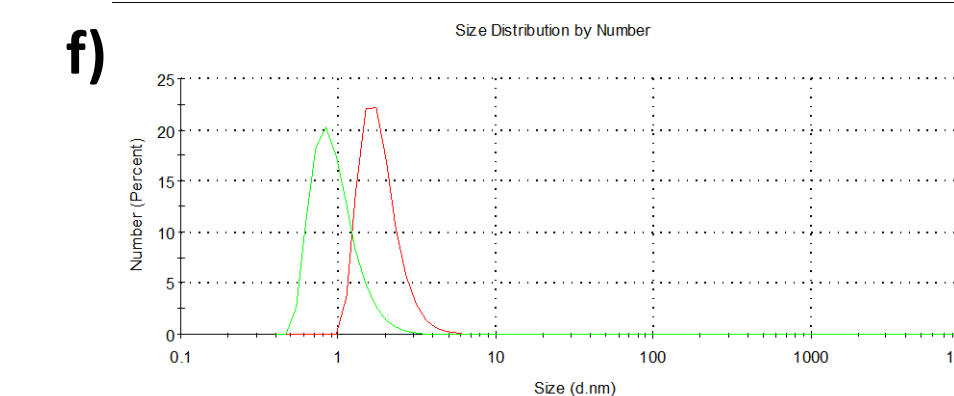
Complex	Diffusion coefficient (D (x10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup> ))	Radius derived from Diffusion coefficient (Å)	Radius derived from Crystal structure data (Å)
3-Ph	6.96	6.6	6.55
3-Et	6.98	6.6	6.60
3-PhMe <sub>2</sub>	6.25	7.1	6.63

The DOSY NMR data and radius simulation indicate that both 3-Et and 3-PhMe<sub>2</sub> maintain the aurophilic bonding in CDCl<sub>3</sub> at room temperature. 3-Et has an equilibrium between monomer and dimer in DMSO-d<sub>6</sub> and variable temperature NMR indicated that 3-Et converts completely to the monomeric species at 80 °C while 3-PhMe<sub>2</sub> remained as the dimer in DMSO even at 80 °C.



Complex	Diffusion coefficient (D (x10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup> ))	DLS (nm)
7-Ph	3.50	0.6
7-Et	1.70	1.6
7-PhMe <sub>2</sub>	1.88	-

The experiments were done in CDCl<sub>3</sub> with concentration as 5μM



Concentration (μM)	5	10	20	30	50
D of 7-Et (x 10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup> )	1.39 ± 0.10	1.06 ± 0.06	0.93 ± 0.05	0.54 ± 0.04	0.35 ± 0.01
D of TMS (x 10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup> )	21.25 ± 0.32	20.78 ± 0.64	20.78 ± 0.64	20.78 ± 0.64	20.78 ± 0.64

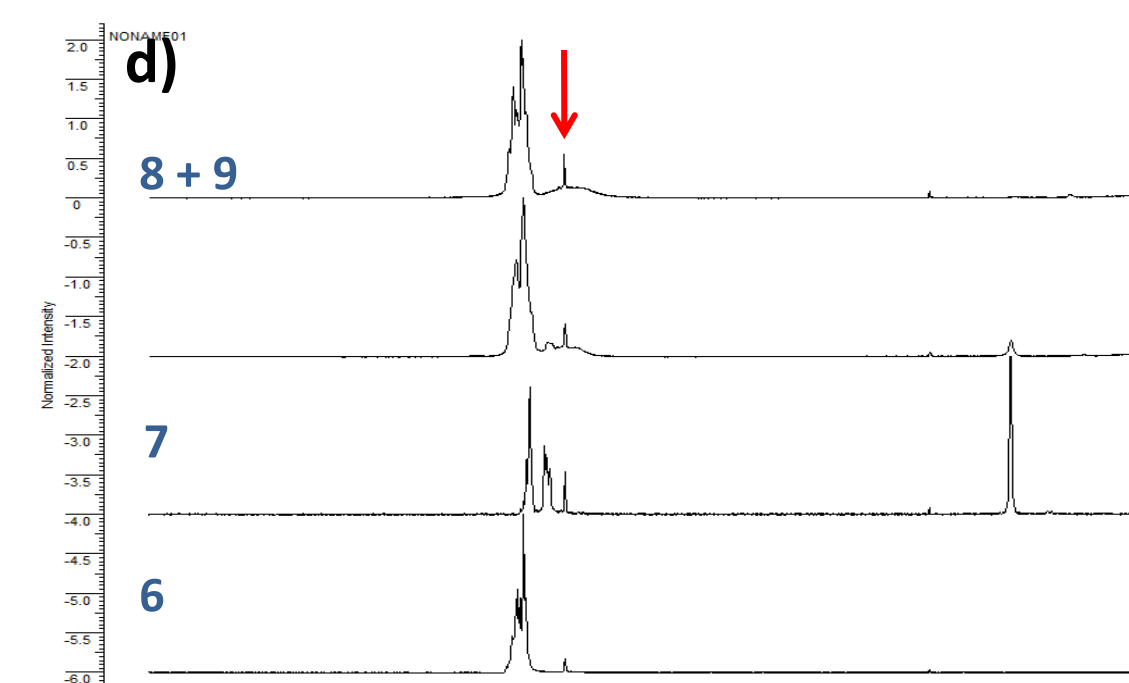
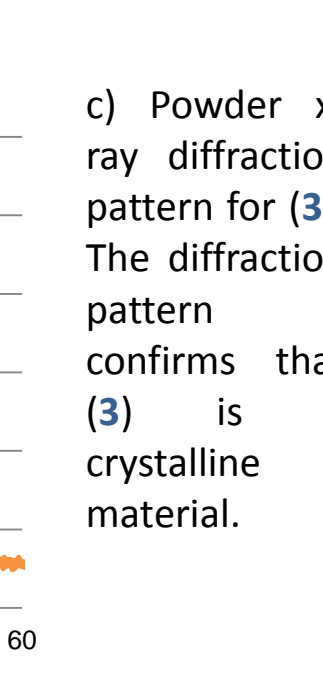
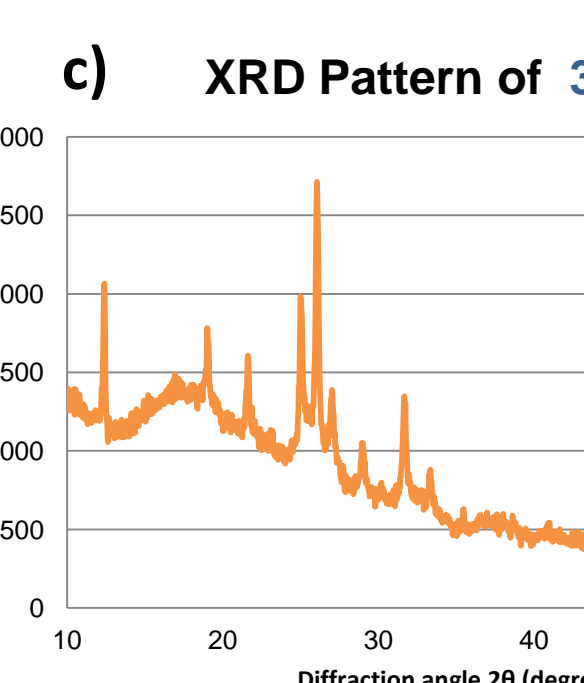
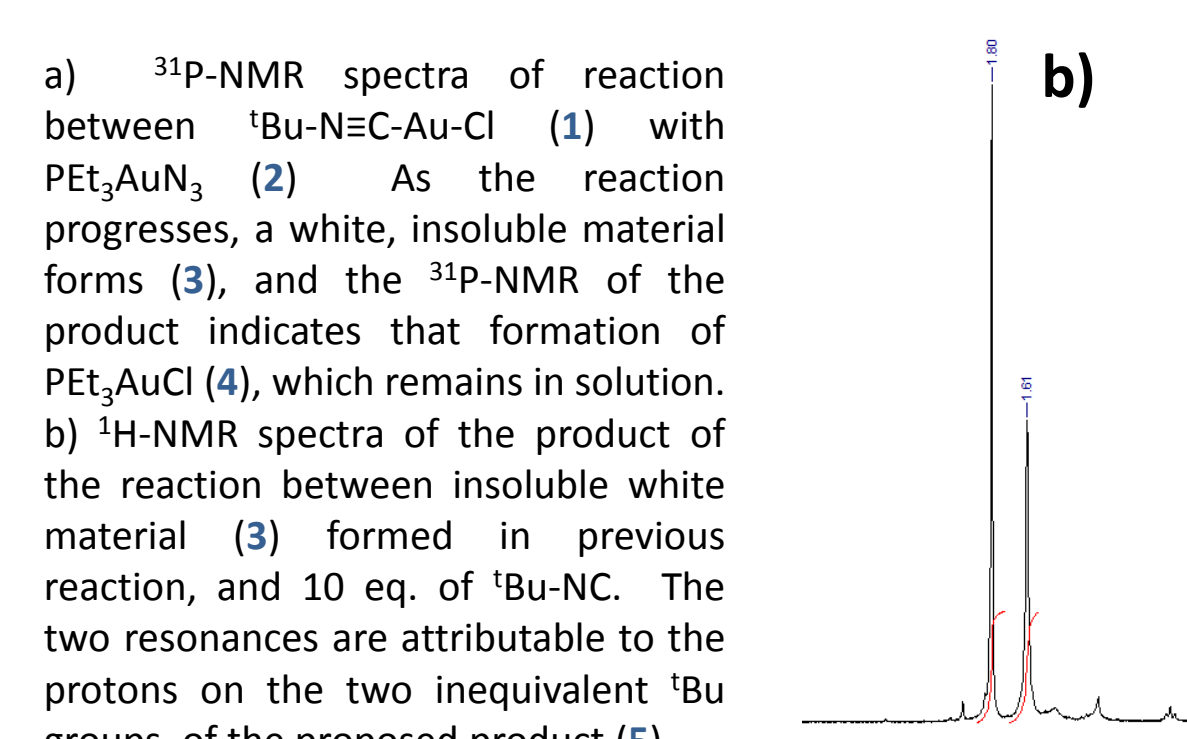
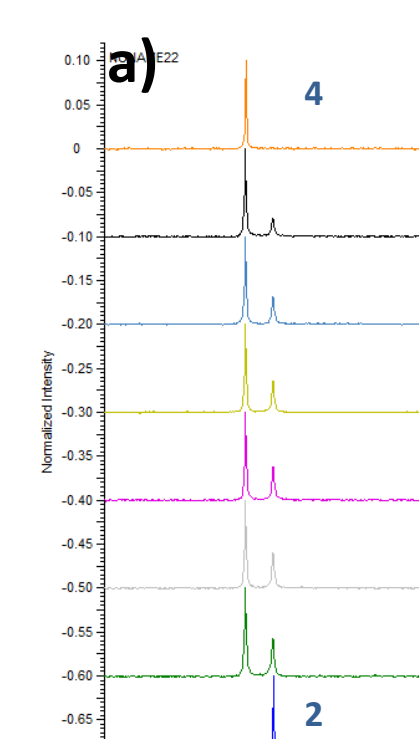
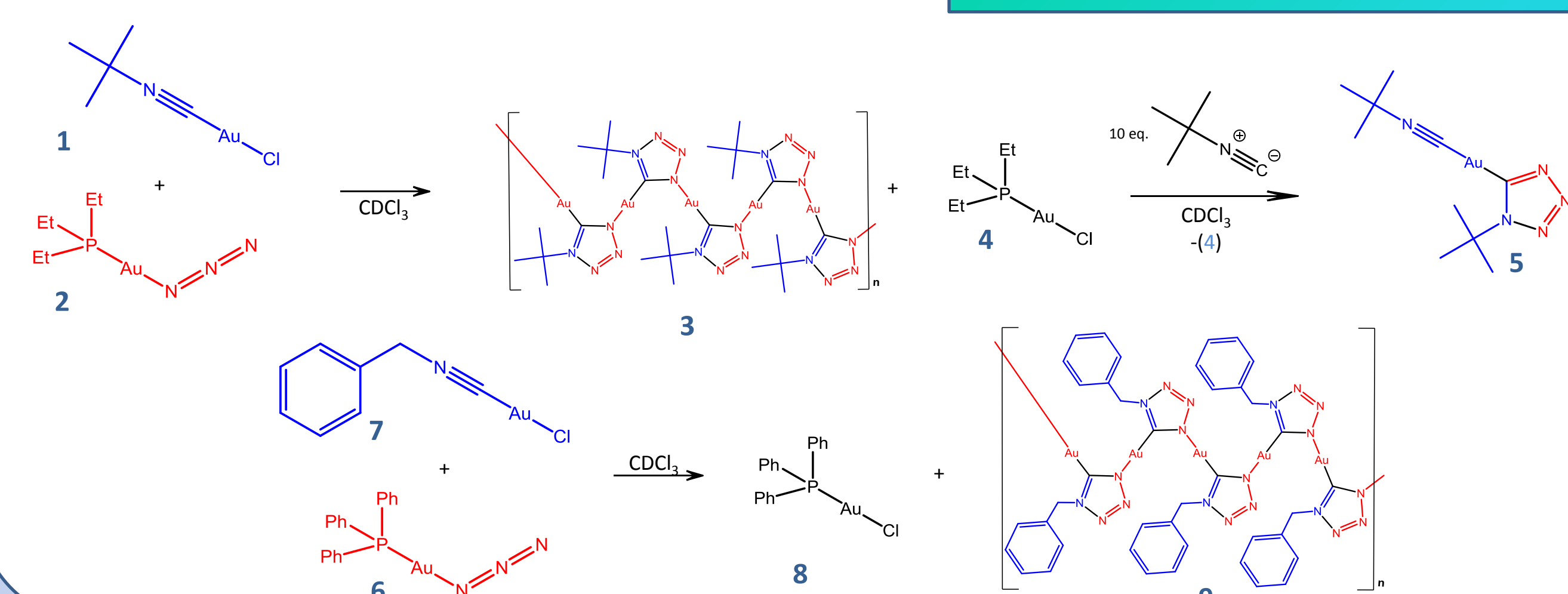
<sup>1</sup>H DOSY NMR was measured in C<sub>6</sub>D<sub>6</sub> at 25 °C. nm = not measured.

Temperature (°C)	25	35	45	55	65
D of 7-Et (x 10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup> )	0.54 ± 0.02	0.61 ± 0.03	0.74 ± 0.03	0.96 ± 0.04	1.26 ± 0.05
D of TMS (x 10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup> )	20.78 ± 0.64	24.38 ± 0.52	28.78 ± 0.77	33.23 ± 1.10	37.29 ± 1.26
normalized D (x 10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup> )	0.54 ± 0.02	0.52 ± 0.03	0.54 ± 0.03	0.6 ± 0.04	0.7 ± 0.04

<sup>1</sup>H DOSY NMR was measured in C<sub>6</sub>D<sub>6</sub> with concentration of 30μM.

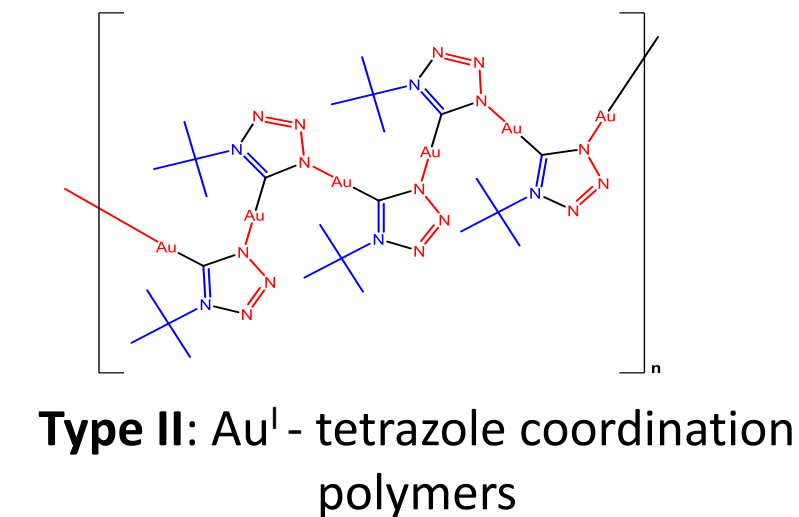
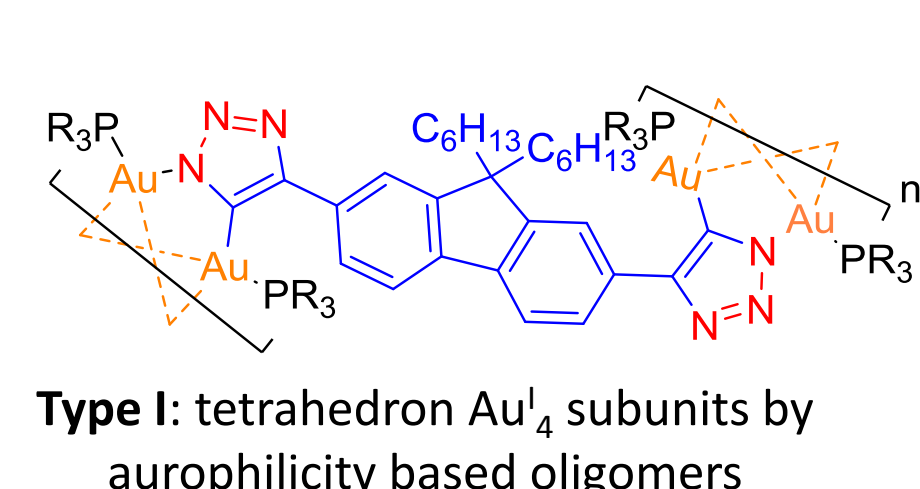
h) Variable concentration DOSY NMR experiments (Table 1), and variable temperature DOSY NMR experiments (Table 2) of 7-Et showed that the complex behaved like a supramolecular self-assembly system. It is an oligomeric and its size is concentration dependent as well as its structure is stable when temperature is below 50 °C.

## Type II: tetrazolate ring based gold metallo-oligomers



## Conclusions

Though utilizing click reactions to synthesize organic molecules having triazolate or tetrazolate rings are well known, applying the heterocyclic ring formation process to assemble organometallic polymers/oligomers is still rare. The inorganic click (iClick) synthetic method provides a promising way to achieve this type of materials in which metal centers are linked by newly formed heterocyclic rings.



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- Dr. Ion Ghiviriga (NMR)
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  - DOE
  - UF



### References

1. Kolb, H. C.; Finn, M. D.; Sharpless, K. *Angewandte Chemie-International Edition* 2001, 40 (11), 2004-2021.
2. Huisgen, R. *Angewandte Chemie-International Edition in English* 1963, 2 (10), 565-598.
3. Rostovtsev, V. V.; Green, L.; Fokin, V. V.; Sharpless, K. *Angewandte Chemie-International Edition* 2002, 41 (24), 2596-2599.
4. Tornøe, C. W.; Christensen, C.; Meldal, M. *The Journal of Organic Chemistry* 2002, 67 (9), 3057-3064.
5. Del Castello, T.; Sarker, S.; Abboud, K.; Veige, A. *Dalton Transactions* 2013, 48932, 8140-8144.
6. Hemmelgich, A.; Fink, M.; Raub, S. *Angewandte Chemie-International Edition* 2011, 50, 2628.
7. Powers, A. R.; Yang, X.; Del Castello, T. J.; Ghiviriga, I.; Abboud, K. A.; Veige, A. S. *Dalton Transactions* 2013, 42421, 14963-14966.

