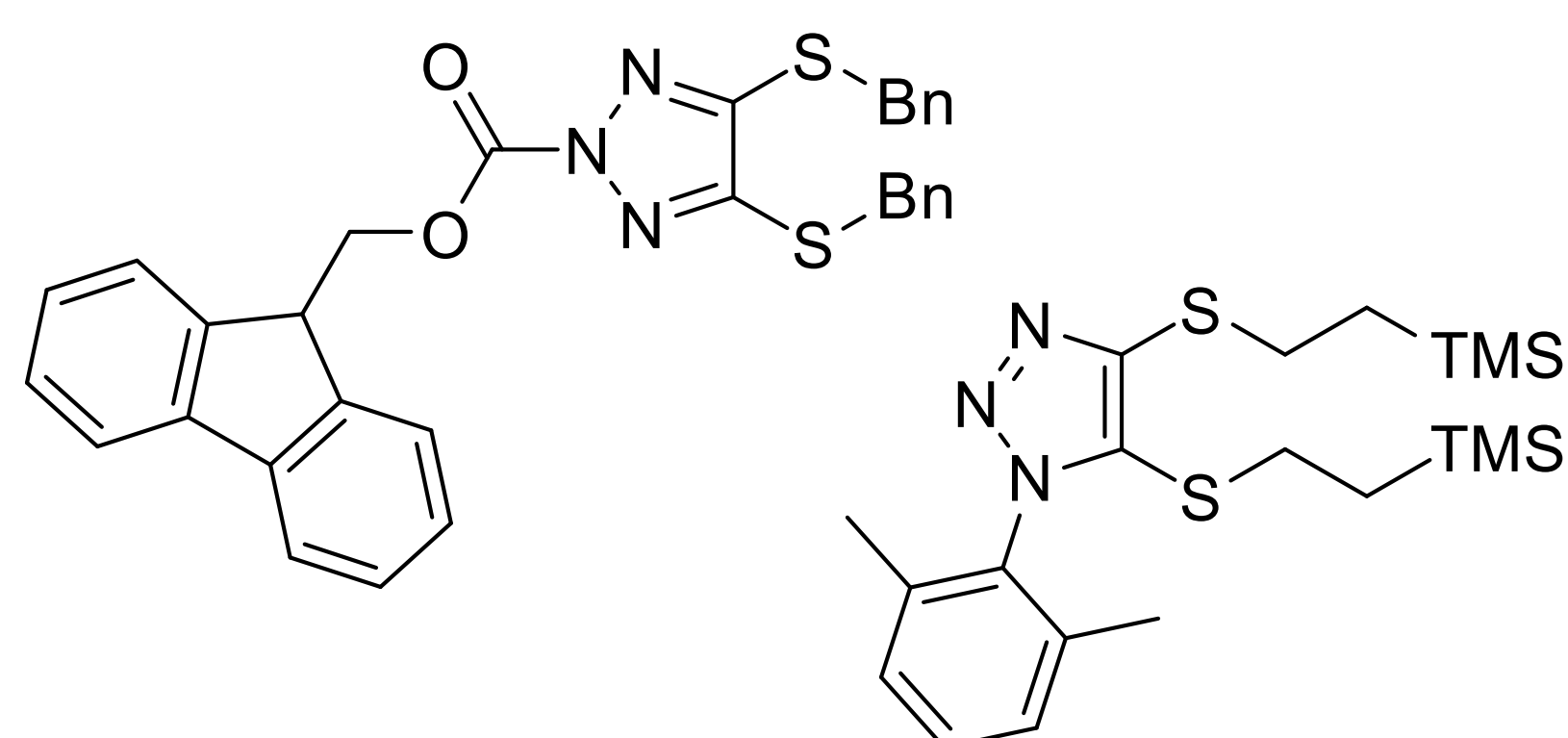




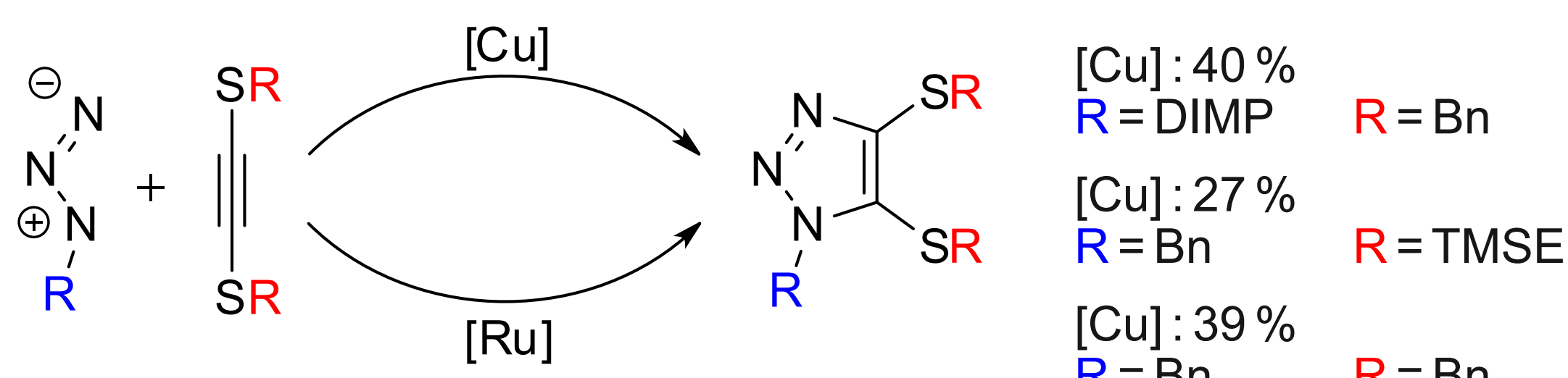
# Structure and Coordination Behaviour of 1*H*-1,2,3-Triazole Ligands with a Dithiolene Backbone

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Dithiolene complexes are well-known for delocalized electronics states, which involve both metal centres and ligands. In conjunction with a multistep redox variability dithiolene complexes represent versatile building blocks for materials with interesting electronic properties.



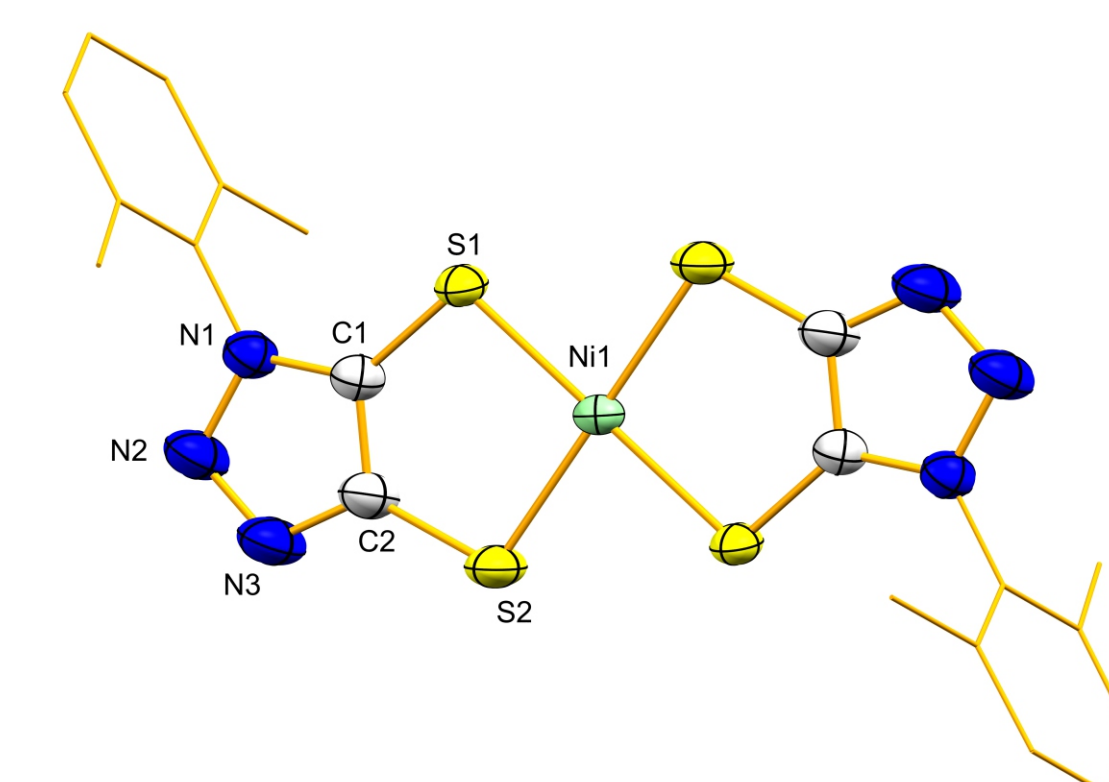
## Introduction



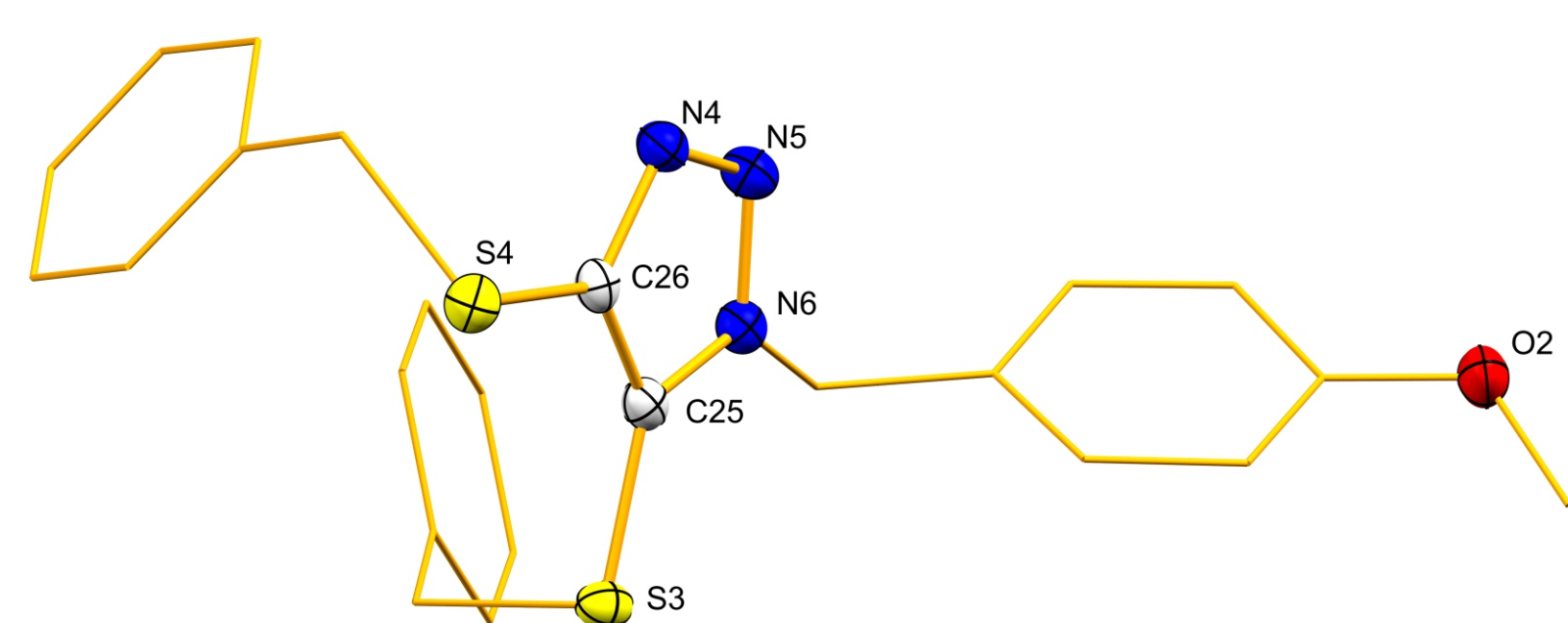
Triazole-5,6-dithiolate seems to be a perfect bridging dithiolate ligand, because coordination polymers can be formed by subsequent N-coordination in a very flexible way. First triazole-4,5-dithiolates and their complexes have been prepared by Schallenberg in our research group. [1]

catalyzed by [(NHC)Cu]<sub>2</sub>  
complicated catalyst

However, the most interacting prototype system with NH-triazole is still missing. The latter would allow the formation of neutral coordination polymers by N-deprotonation and subsequent coordination.



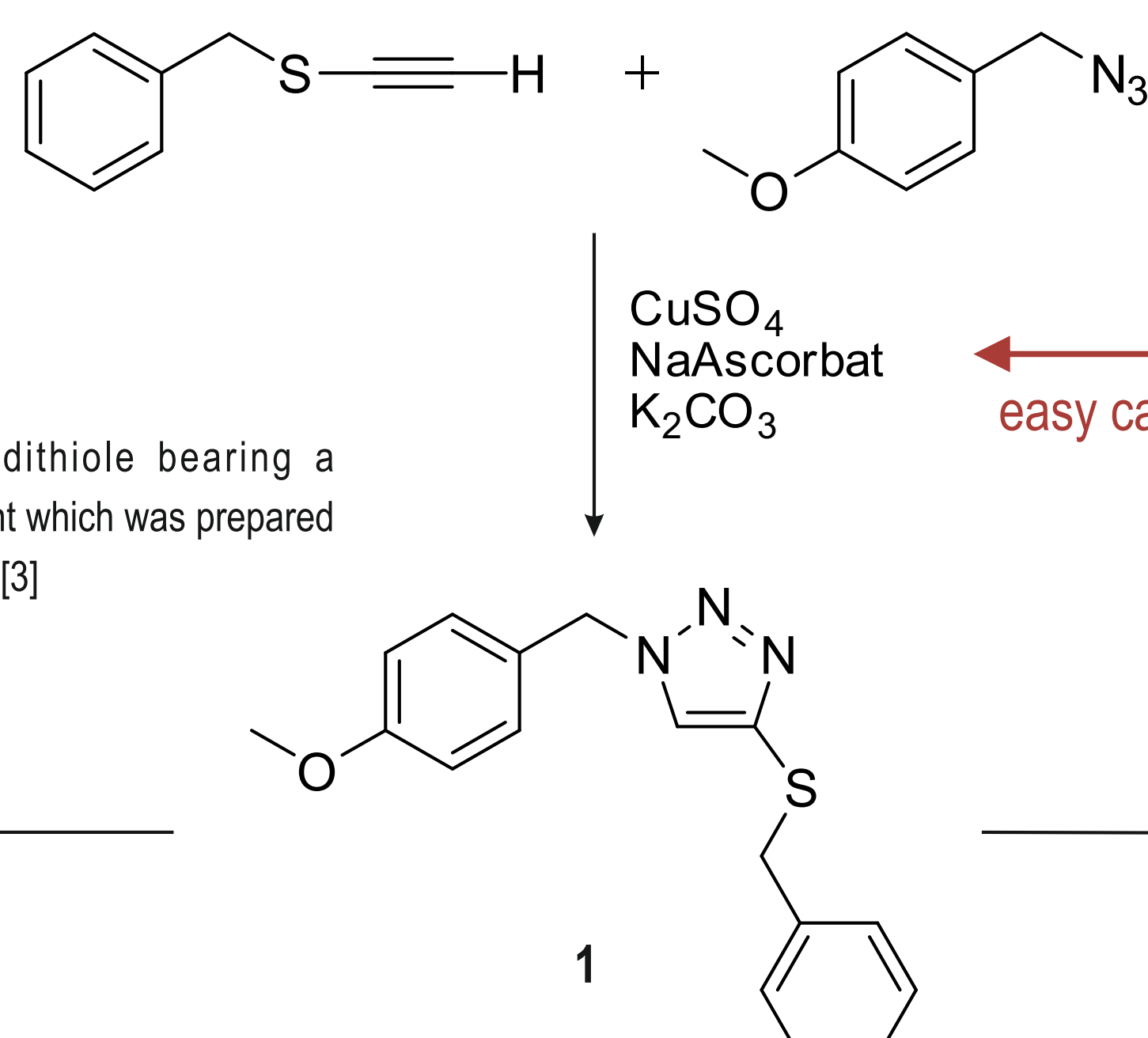
## Results



bond/torsions angle	
C1-S1	1.7495(19) Å
C2-S2	1.739(2) Å
S2-C2-C1-S1	-0.4(3)°

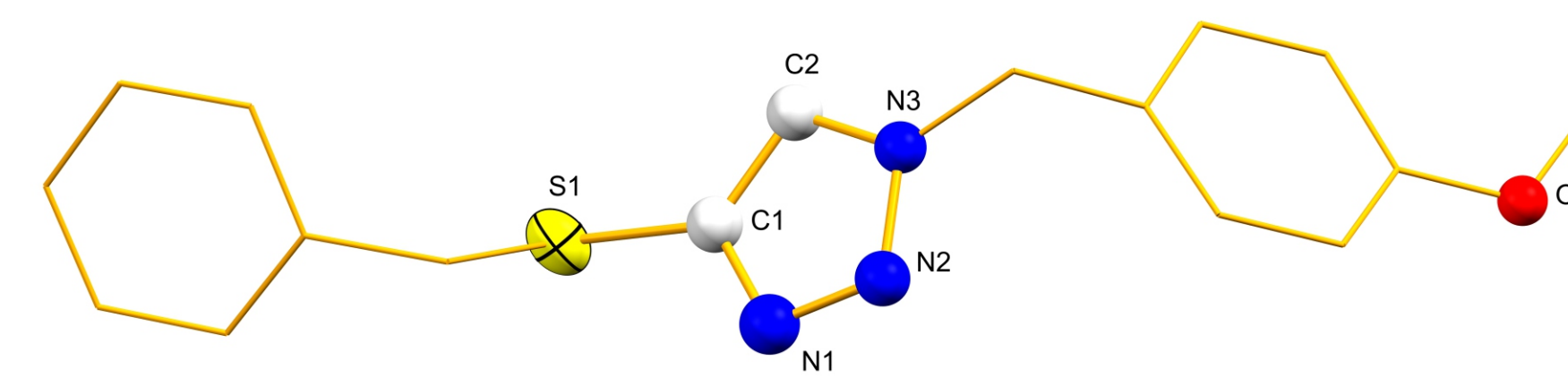
1*H*-1,2,3-triazole-4,5-dithiole bearing a methoxybenzyl substituent which was prepared by a novel synthetic route. [3]

1.) *n*-BuLi  
2.) ClPPh<sub>2</sub>



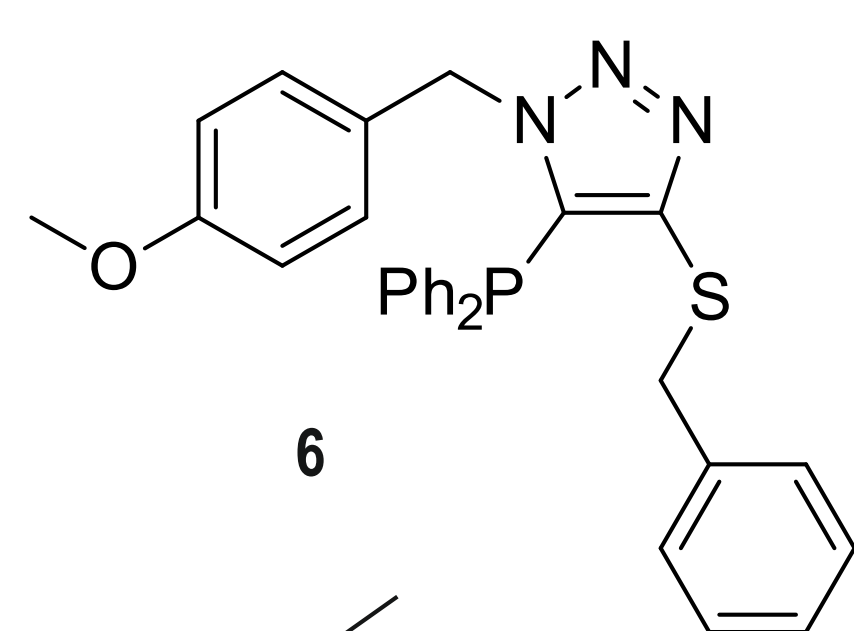
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1.) *n*-BuLi  
2.) 1/8 S<sub>8</sub>

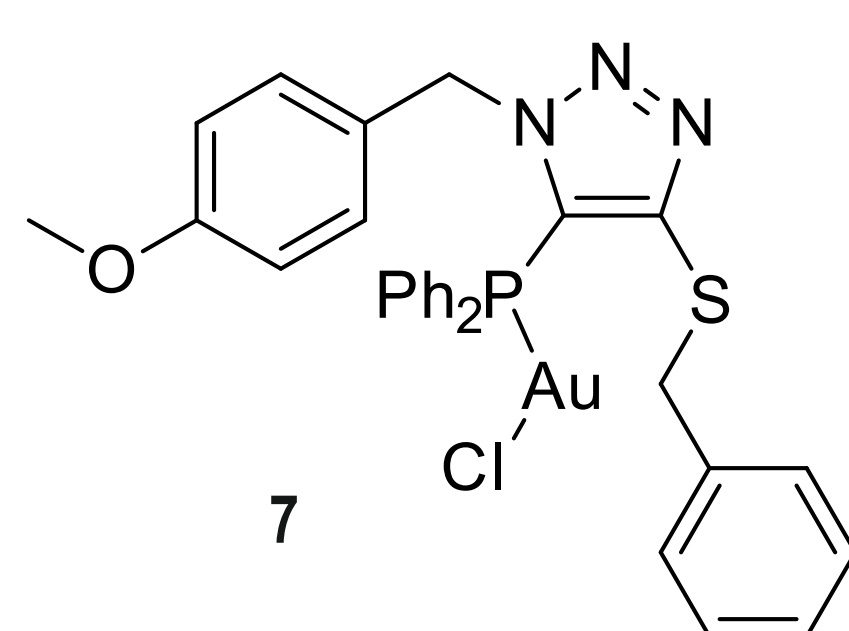


It was shown that the 4-substituted benzylthio 1*H*-1,2,3-triazole **1** was isolated with very good yields by literature-known copper catalyzed cycloaddition. [2].

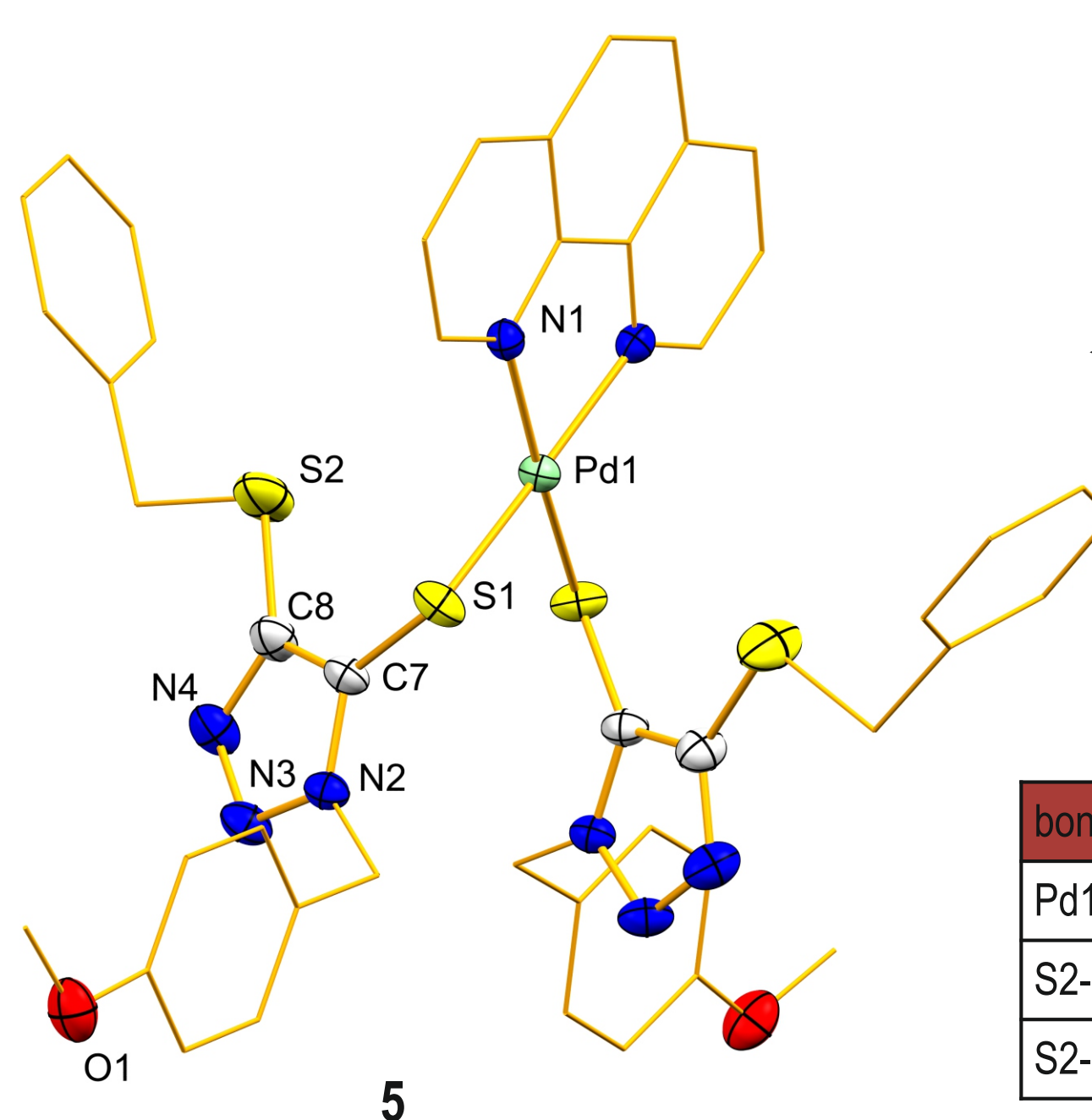
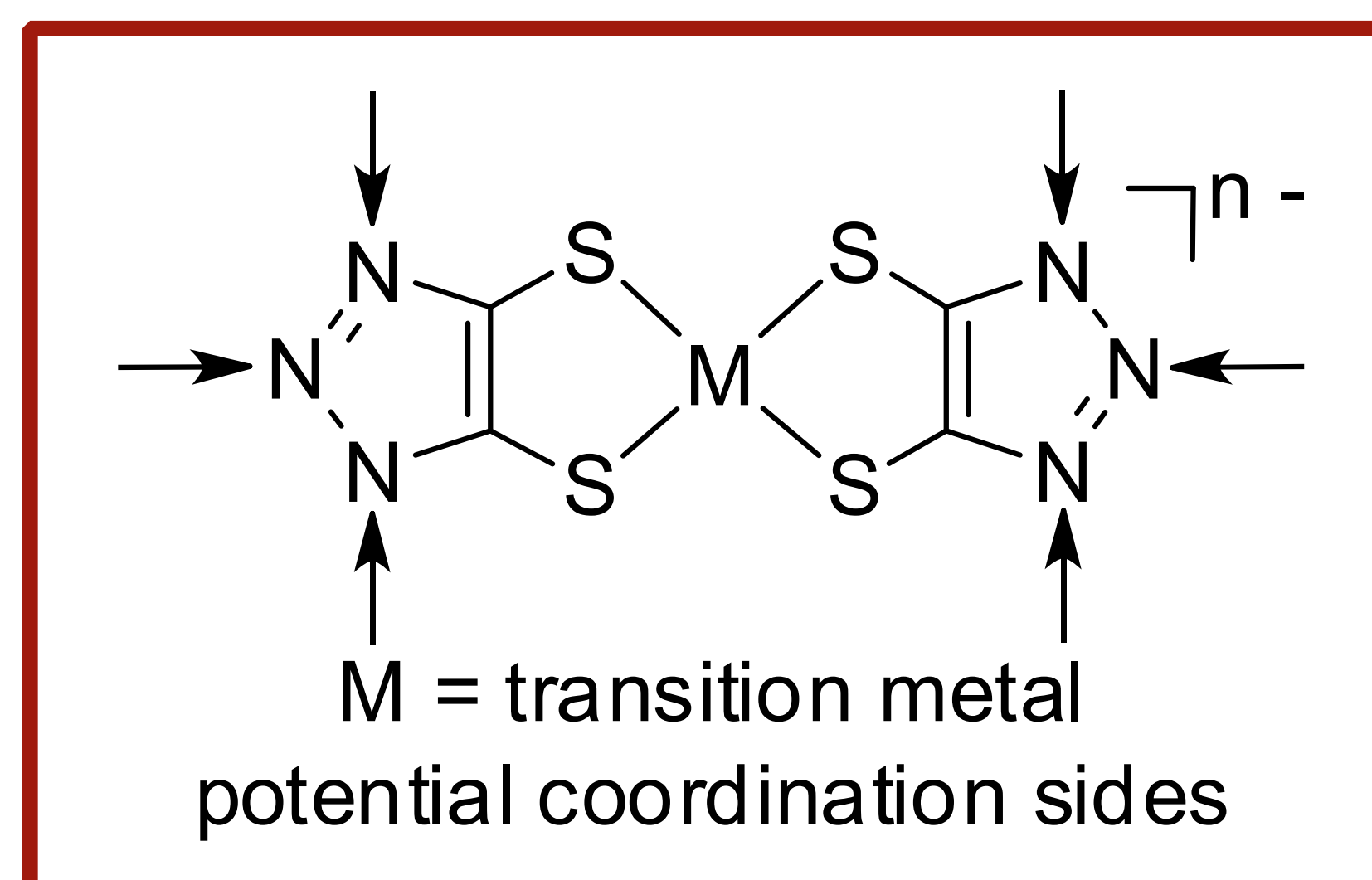
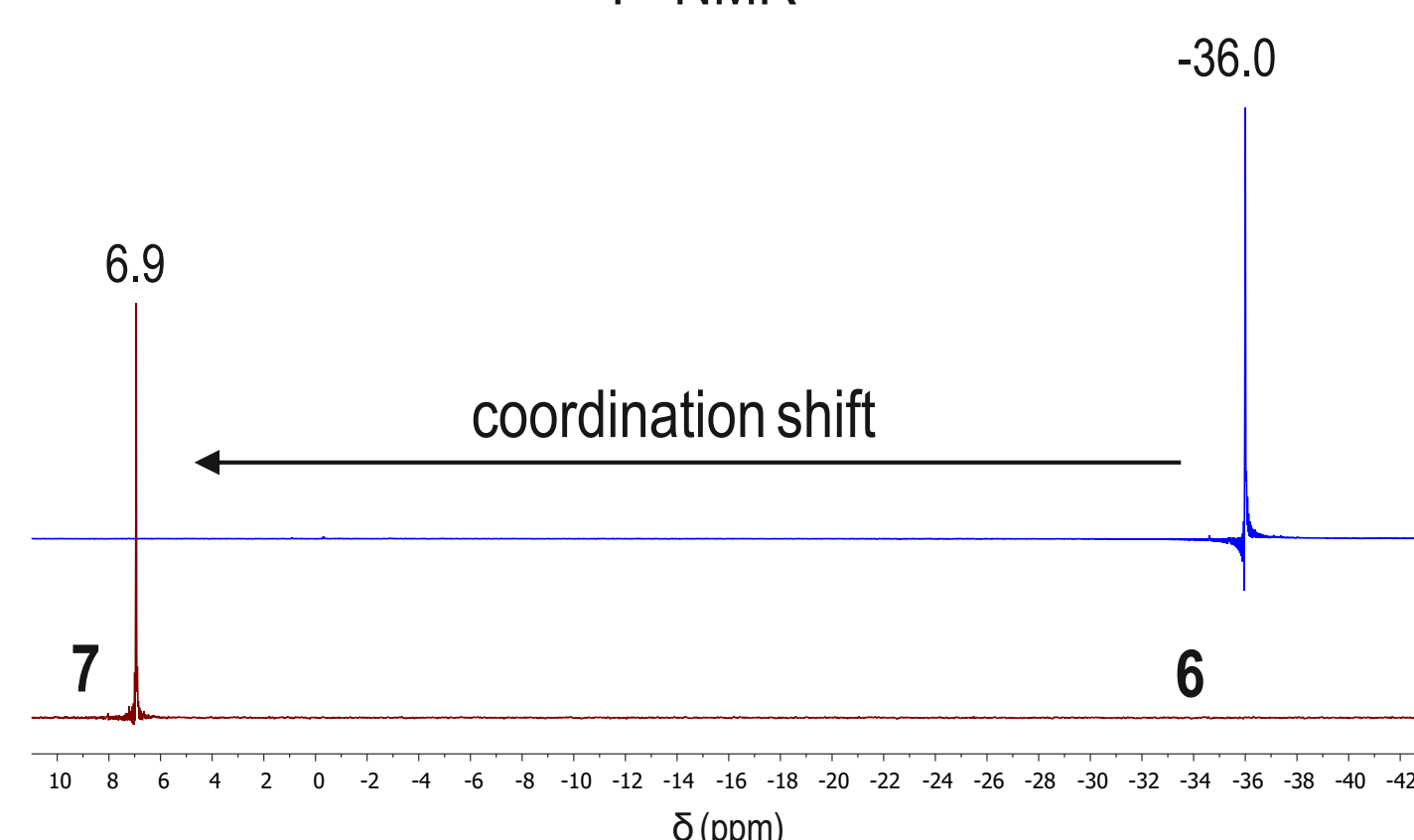
In addition to the benzylthio-substituent we tried to introduce another donor at the 5-position. After deprotonation, the triazole **1** reacts with chlorodiphenylphosphane and the first 4-sulfur-5-phosphorus-1*H*-1,2,3-triazole (**6**) could be isolated and analyzed. To investigate the coordination behaviour of triazole **6** we coordinated the ligand to gold(I).



[(SMe<sub>2</sub>)AuCl]



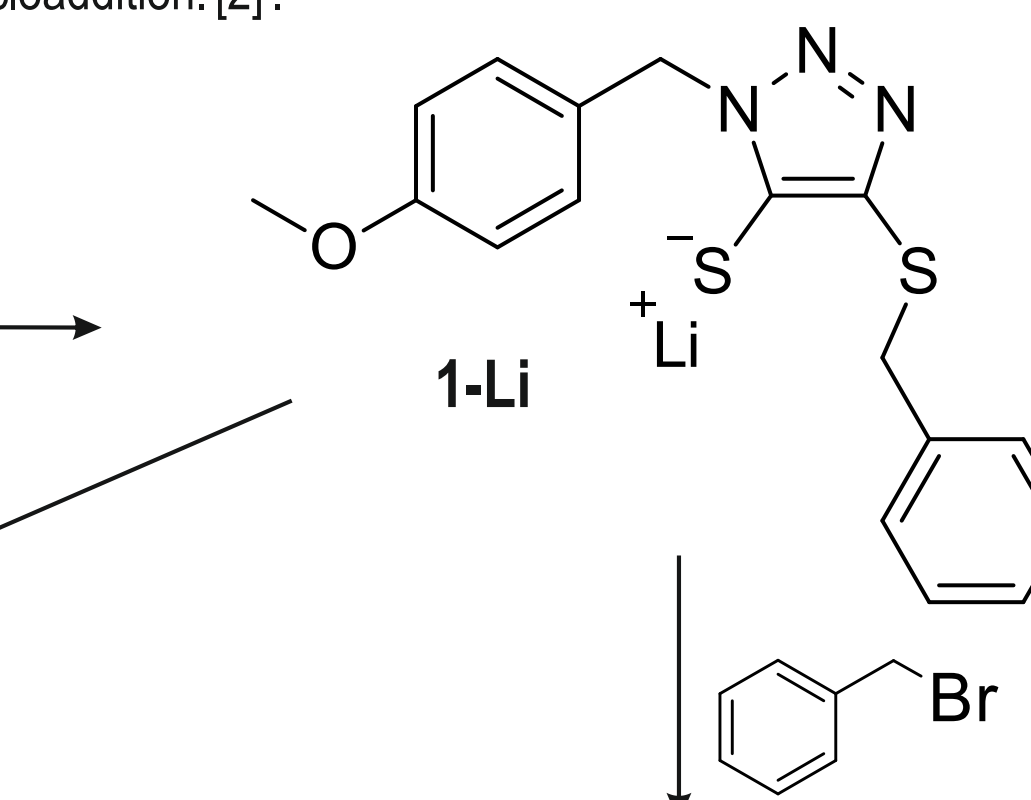
<sup>31</sup>P-NMR



bond/torsions angle	
Pd1-S2	2.2861(8) Å
S2-C1	1.733(3) Å
S2-C1-C2-S1	4.9(5)°

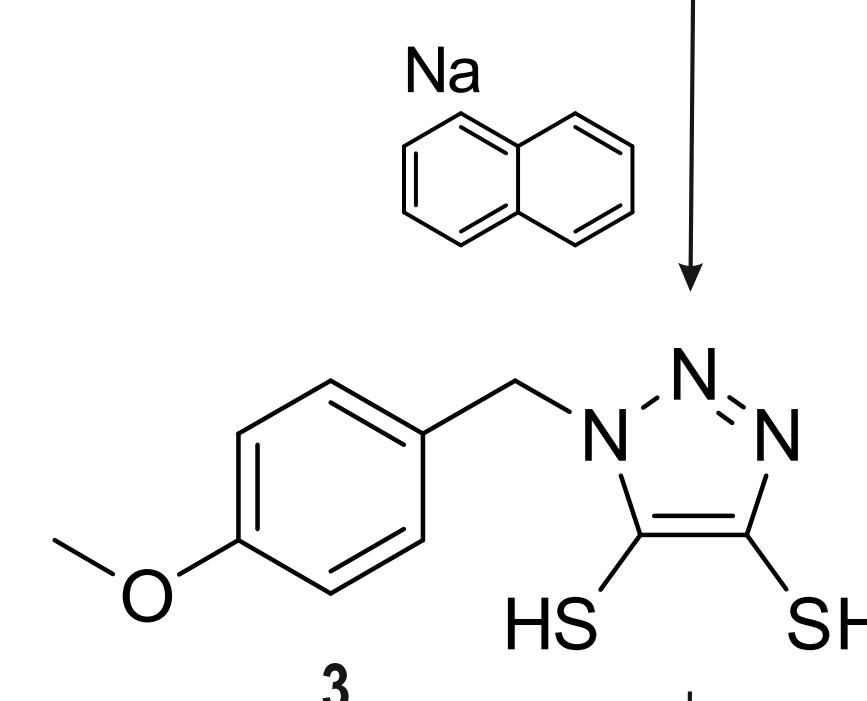
The thiolate intermediate **1-Li** can also be strapped with [(phen)PdCl<sub>2</sub>] (**5**).

The complex **5** crystallized in I 4/a with an axis of symmetry through the palladium. By comparison to the literature, the bondlength of S2-C1 is equal with other triazole-dithiolate complexes, but the torsion angle is larger, which is explained with steric demand of the 1*H*-1,2,3-triazole ligands. [1, 4]



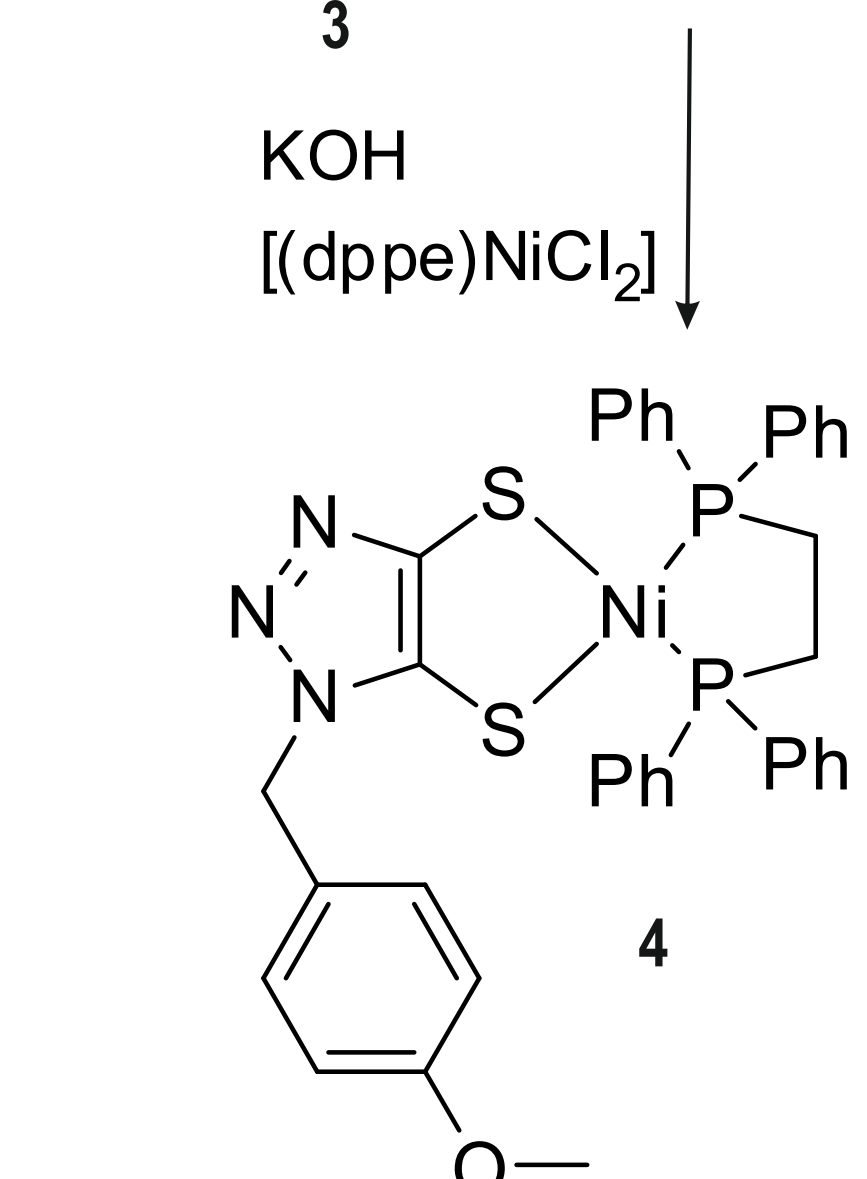
2

At the 5-position, the second benzylthio group was generated by deprotonation and alkylation (**2**).



3

The deprotection of the dithiolene group can be performed reductively with sodium naphthalide (**3**).



4

Starting from triazoldithiole **3** a coordination can be achieved by deprotonation of dithiole and reaction with a metal precursor like [(dppe)NiCl<sub>2</sub>]. The coordination via the dithiolate unit can be observed by <sup>1</sup>H- and <sup>31</sup>P-NMR-spectroscopy.

[1] D. Schallenberg, *Dissertation 2013, Universität Rostock*.

[2] A. S. Kumar, V. D. Ghule, S. Subrahmanyam, A. K. Sahoo, *Chem. Eur. J.* 2013, 19, 509-518.

[3] W. W. Seidel, M. J. Meel, M. Schaffrath, T. Pape, *Eur. J. Org. Chem.* 2007, 21, 3526-3532.

[4] P. Pyykkö, M. Atsumi, *Chem. Eur. J.* 2009, 15, 12770-12779.