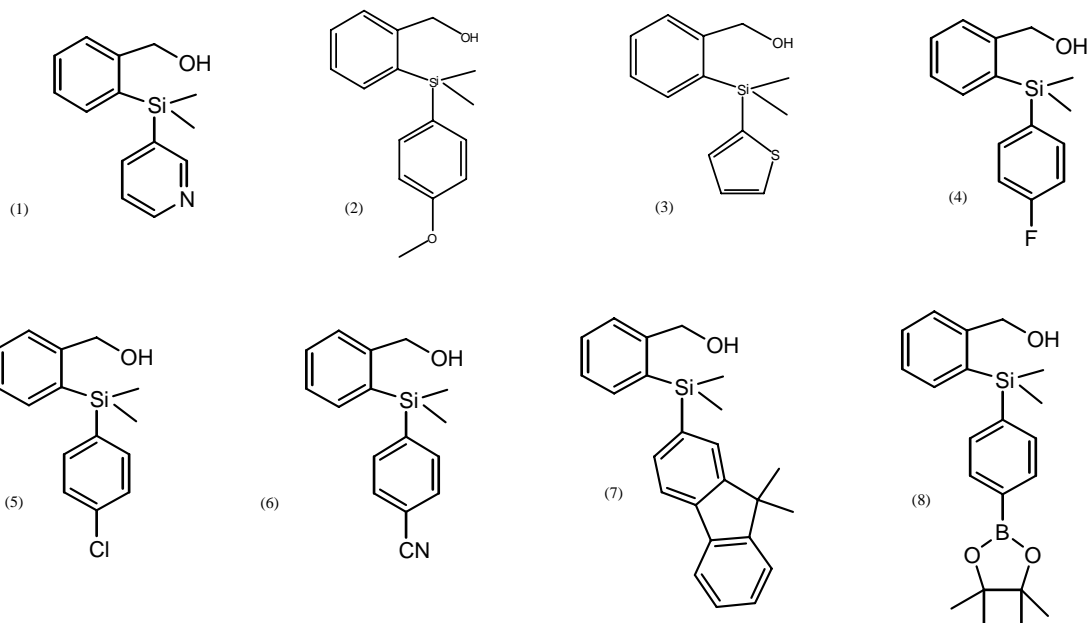
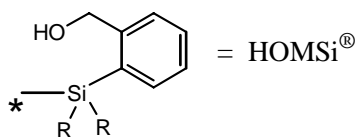
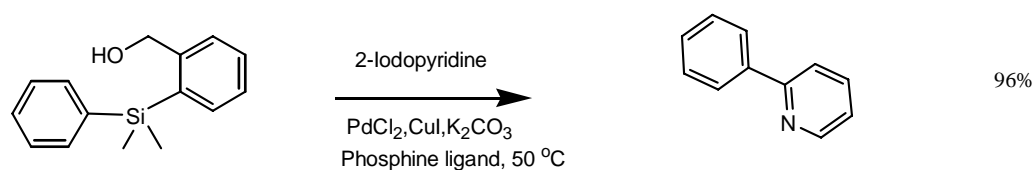
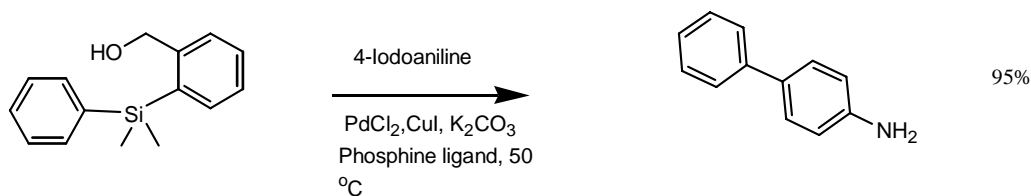
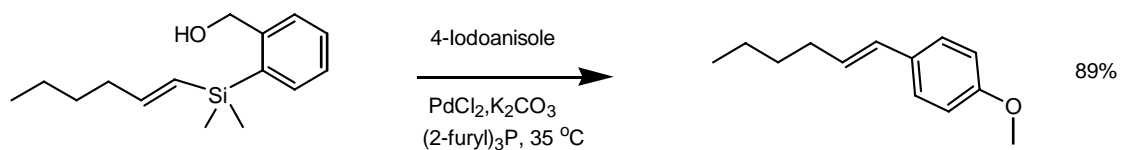


HOMSi[®] REAGENTS FOR HIYAMA CROSS-COUPLING REACTIONS

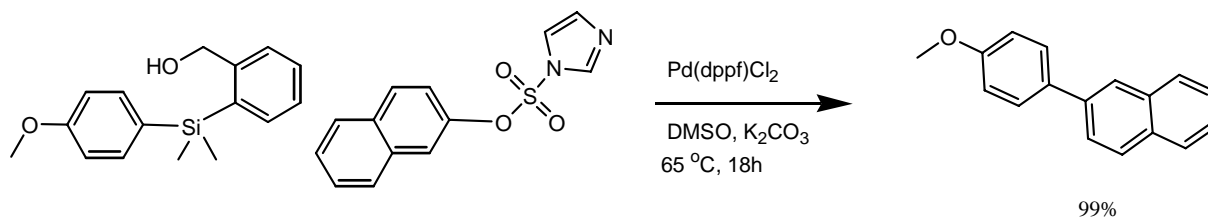
In 2008 AMT released a range of HOMSi[®] reagents developed by Professor Hiyama, Assistant Professor Nakao and co-workers.¹⁻⁹ We have grown this range to over 60 products over the past two years. A selection of HOMSi[®] reagents are shown below:



Silicon substituted HOMSi ((2-hydroxymethylphenyl)dimethylsilanes) reagents are excellent cross-coupling partners which can provide the desired coupled products under mild conditions and in high yields.²



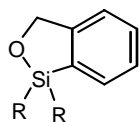
Recently HOMSi[®] reagents have been shown to cross couple with aryl imidazol-1-ylsulfonates which are alternative cross coupling partners to aryl halides. It is interesting to note that no copper iodide was required using these reagents.¹¹



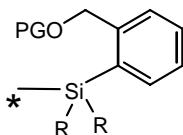
The cross-coupling reactions using HOMSi[®] reagents have the following characteristics:

1. High functional group compatibility (amino, cyano, hydroxy, ester, ketone, nitro etc.)
2. React with a variety of halide coupling partners including iodides, bromides and chlorides
3. A relatively mild base such as potassium carbonate is generally used
4. Can be performed under fluoride-free conditions
5. Mild reaction conditions (RT to 75 °C)
6. Organosilicon "by-product" can be recycled if required
7. The cross-coupling reactions can be turned "OFF" by the use of suitable protecting groups on the 2-hydroxymethyl group⁶

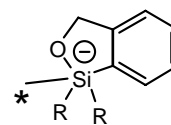
Protected HOMSi[®] Reagents



Organosilicon "by-product"

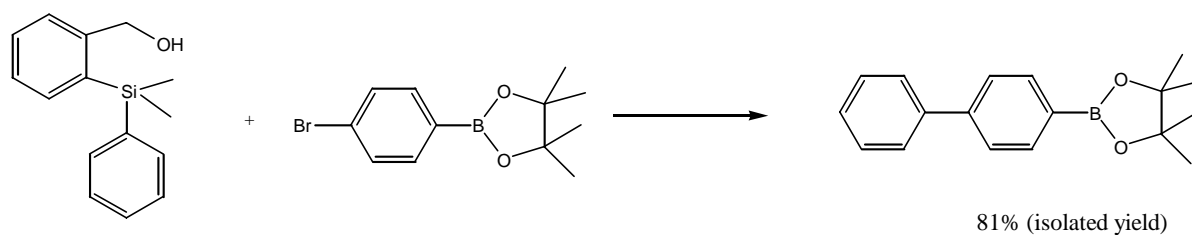


"OFF" position



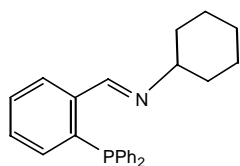
"ON" position

Another key advantage of the HOMSi reagents is that the cross-coupling reactions can be conducted in the presence of pinacol esters of aryl boronates as shown below.

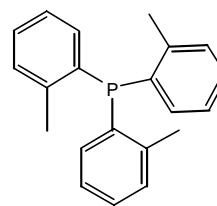


The HOMSi[®] reagents have been reported to undergo a number of other organic transformations.^{5,7,8}

The phosphine ligands that have been reported to work well in the cross coupling reactions include N-[2-(Diphenylphosphino)benzylidene] cyclohexylamine^{1-4,6,7} and tri(o-tolyl)phosphine.¹⁰ Both phosphines are available commercially from various suppliers.



N-[2-(Diphenylphosphino)benzylidene] cyclohexylamine



tri(o-Tolyl)phosphine

References

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- (2) Y. Nakao et al. *Pure Appl. Chem.* **2006**, *78*(2), 435-440
- (3) Y. Nakao et al. *Sci. Tech. Adv. Mat.* **2006**, *7*, 536-543.
- (4) Y. Nakao et al. *Chem. Lett.* **2007**, *36*(5), 606-607
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- (7) Y. Nakao et al. *J. Organometallic Chem.* **2007**, *692*, 585-603
- (8) Y. Nakao et al. *Chem. Lett.* **2008**, *37*(3), 290-291
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- (10) S. Marcuccio et al. Intersect 09, Melbourne Australia
- (11) S. Shirbin et al. *Tetrahedron letters*, **2010**, *51*, 2971-2974

For a full listing of reagents for Hiyama cross-couplings, visit www.amtechpl.com.

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