Grignard Reactions

DOI: 10.1002/anie.201409815

Catalytic Asymmetric Alkylation of Acylsilanes**

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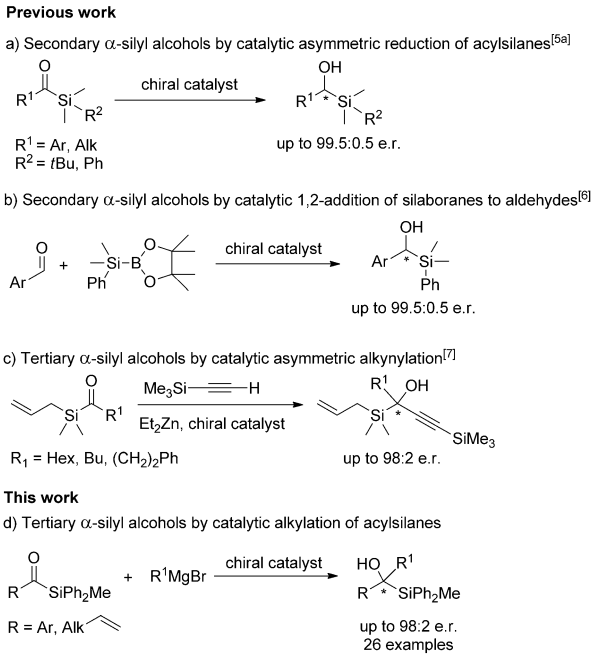
Abstract: *The highly enantioselective addition of Grignard reagents to acylsilanes is catalyzed by copper diphosphine complexes. This transformation affords α-silylated tertiary alcohols in up to 97% yield and 98:2 enantiomeric ratio. The competing Meerwein–Ponndorf–Verley reduction is suppressed by the use of a mixture of Lewis acid additives. The chiral catalyst can be recovered as a copper complex and used repeatedly without any loss of catalytic activity.*

Chiral organosilanes are important building blocks in stereoselective carbon–carbon bond formation and rearrangement reactions.[1] Furthermore, silicon isosteres, that is, compounds in which a carbon atom has been replaced by a silicon atom, have become popular in medicinal chemistry owing to their low toxicity and favorable metabolic profiles.[2] As a result, the development of synthetic methods for the enantioselective preparation of chiral organosilanes, in particular α-hydroxy- and α-aminosilanes, is increasingly important in synthetic and medicinal chemistry.[1–3]

Several strategies that are based on the asymmetric reduction of acylsilanes have been reported for the preparation of enantiopure secondary α-silyl alcohols;[4] however, catalytic methods are still scarce.[5] In 2008, the Ohkuma group reported the first example of a highly enantioselective ruthenium-catalyzed asymmetric hydrogenation of acylsilanes (Scheme 1 a).[5a] In 2013, the Riant group reported the synthesis of secondary α-silyl alcohols through a copper-catalyzed asymmetric addition of silaboranes to aldehydes (Scheme 1 b).[6]

Whereas these methods provide access to enantiopure secondary α-silyl alcohols, a general catalytic method to synthesize tertiary α-silyl alcohols is not yet available. The most straightforward approach for their synthesis would be the catalytic asymmetric addition of organometallic reagents to acylsilanes. Although Marek and co-workers have reported the catalytic enantioselective alkynylation of several acylsilanes (Scheme 1 c),[7] methods for the catalytic asymmetric alkylation using organometallic reagents are unprecedented. The main hurdle to achieve this is a single, formidable competing reaction, a non-catalytic Meerwein–Ponndorf–Verley (MPV)-type reduction,[8] which leads to the formation of racemic secondary α-silyl alcohols. For instance, in 2012, the Xu group applied the well-known titanium-catalyzed alkylation of aldehydes and ketones with diethylzinc to acylsilanes, but reduction of the carbonyl moiety was the major pathway.[9]



Scheme 1. Previous and current work.

Herein, we report the first general method for the enantioselective synthesis of tertiary α-silyl alcohols through the copper-catalyzed addition of alkyl Grignard reagents to acylsilanes (Scheme 1 d). This method provides access to a range of aryl- and vinyl-substituted α-hydroxysilanes bearing a tetrasubstituted chiral carbon atom, with yields of up to 97% and enantiomeric ratios (e.r.) of up to 98:2.

To tackle the synthesis of chiral tertiary α-silyl alcohols, we built on our experience with the copper-catalyzed synthesis of chiral alcohols using Grignard reagents that we recently developed.[10] We envisioned that a similar strategy could be applied for the alkylation of acylsilanes, despite a number of potential problems: 1) The increased bulkiness of the silyl group is expected to impede the formation of the hindered tetrasubstituted chiral carbon atom; 2) the reduction of the carbonyl moiety is a common side reaction in this type of transformations; and 3) a Brook rearrangement of the final product could occur.

We began our studies by investigating the catalytic asymmetric alkylation of acylsilane **1a** (Table 1). Initial

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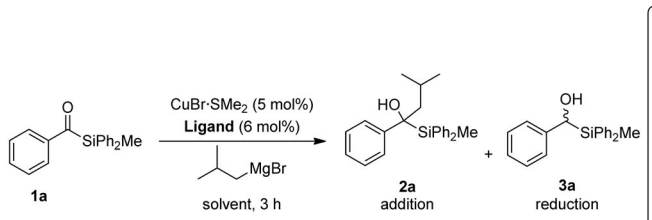
[**] Financial support from The Netherlands Organization for Scientific Research (NWO-Vidi, to S.R.H.), the China Scholarship Council (CSC, to J.R.), and the Ministry of Education, Culture and Science (Gravity program 024.001.035) is acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201409815.

Table 1: Catalytic asymmetric alkylation of acylsilanes: selected optimization results.[a]



Entry	Ligand	Solvent	T [°C]	Lewis acid (equiv)	**2a**/**3a**[b]	e.r. (**2a**)[c]
1	**L1**	*t*BuOMe	−78	–	1:2	95:5
2	**L2**	*t*BuOMe	−78	–	1:8.5	81:19
3	**L3**–**L7**	*t*BuOMe	−78	–	0:1	n.d.
4	**L1**	CH_2Cl_2	−78	–	1:2.2	72:28
5	**L1**	toluene	−78	–	1:3.2	92:8
6	**L1**	Et_2O or THF	−78	–	0:1	n.d.
7	**L1**	*t*BuOMe	−100	–	1:5	95:5
8	**L1**	*t*BuOMe	−30	–	1:9	85:15
9	**L1**	*t*BuOMe	−78	$CeCl_3$ (1.3)	1:1.5	96:4
10	**L1**	*t*BuOMe	−78	TMSCl (2)	1:1.2	96:4
11	**L1**	*t*BuOMe	−78	$CeBr_3$ (1)	1:1.5	95:5
12	**L1**	*t*BuOMe	−78	$MgCl_2$ (2)	1:2	96:4
13	**L1**	*t*BuOMe	−78	$BF_3{\cdot}Et_2O$ (2)	3:1	93:7
14	**L1**	*t*BuOMe	−78	$BF_3{\cdot}Et_2O/CeCl_3$ (1:1)	5:1	95:5

[a] Conditions: *i*BuMgBr (1.2–1.5 M in *t*BuOMe) was added over 2 hours. Full conversion was achieved in all cases. [b] The ratio of **2a**/**3a** was determined by ^{1}H NMR spectroscopy. [c] The e.r. value was determined by HPLC analysis on a chiral stationary phase. Cy = cyclohexyl, TMS = trimethylsilyl.

attempts focused on the use of *i*BuMgBr (2 equiv, 2 h addition time), CuBr·SMe_2 (5 mol%), and various chiral ligands **L** (6 mol%) in *t*BuOMe at −78 °C.

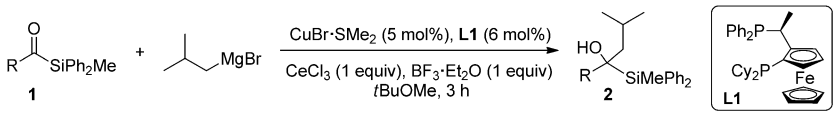
The chiral ferrocenyl diphosphine ligands **L1**–**L5**, BINAP **L6**, as well as phosphoramidite **L7** were studied in this reaction (Table 1). The combination of chiral ferrocenyl diphosphine ligand **L1** and CuBr·SMe_2 as the copper salt proved to be an efficient catalyst system for this reaction, and the desired α-hydroxysilane **2a** was obtained with high e.r. (95:5). As expected, the product selectivity of the reaction was disappointing, with a large amount of **3a** originating from the non-catalyzed reduction pathway (entry 1). In the absence of a copper catalyst, only the reduction product was observed.

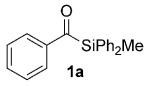
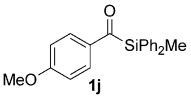
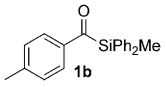
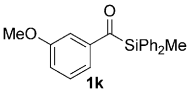
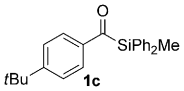
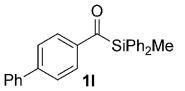
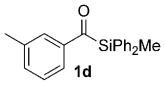
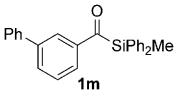
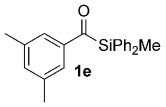
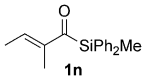
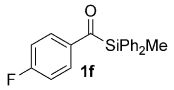
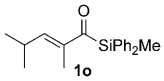
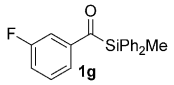
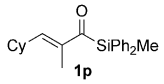
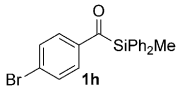
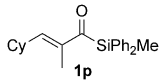
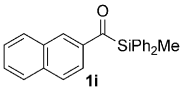
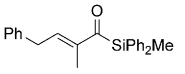
When ligand **L2**, in which the alkyl and aryl phosphine groups have swapped positions, was used instead of **L1**, product **2a** was obtained with lower selectivity (**2a**/**3a** = 1:8.5) and e.r. (entry 2). Unfortunately, with all other ligands tested (**L3**–**L7**), alkylation products were not formed. Instead of the desired product **2a**, the secondary racemic α-silyl alcohols **3a** was obtained (entry 3).

Having established **L1** as the optimal chiral ligand for this reaction and with the aim to improve the selectivity, we studied the effect of the solvent on the reaction outcome. Dichloromethane and toluene provided product **2a** with slightly lower enantiomeric ratios than *t*BuOMe but with a similar product selectivity (entries 4 and 5). In Et_2O and THF (entry 6), however, only the reduction product was obtained. Increasing or decreasing the reaction temperature from −78 °C to −100 °C or to −30 °C did not improve the selectivity either (entries 7 and 8). To test the role of the bulkiness of the silyl moiety, we evaluated related substrates with $SiMe_2Ph$, $SiPh_3$, and $SiEt_3$ moieties.[3e] With $SiMe_2Ph$, an e.r. of 90:10 was obtained, and the selectivity was improved to 1:1.3. Surprisingly, both the acylsilane with the more bulky $SiPh_3$ and the acylsilane with the less bulky $SiEt_3$ moiety provided the reduction products only. Assuming that the reduction reaction is a result of the activation of the carbonyl moiety of the acylsilane through coordination with the magnesium ion of the Grignard reagent followed by β-hydride transfer,[8] we predicted that reduction could be avoided by using Lewis acid additives.[8a] Lewis acids are expected to prevent the coordination of the magnesium to the carbonyl moiety, thereby allowing the catalytic pathway to outcompete reduction.[11] A survey of Lewis acids (entries 9–13), demonstrated that in the presence of $CeCl_3$, both the selectivity and the enantioselectivity improved (compare entries 1 and 9). The best selectivity (**2a**/**3a** = 3:1) was obtained when $BF_3{\cdot}Et_2O$ was used as an additive, but at the cost of a drop in e.r. to 93:7 (entry 13). Remarkably, a mixture of $BF_3{\cdot}Et_2O/CeCl_3$ (1:1) resulted in a dramatic decrease in reduction and provided both a high selectivity and enantiomeric ratio (entry 14).

With the optimized reaction conditions in hand, the acylsilane scope[12] was explored (Table 2). Subjecting a wide range of substituted acylsilanes to the optimized reaction

Table 2: Substrate scope.[a]



Entry	1	2	2 [%][b]	e.r. (2)[c]	Entry	1	2	2 [%][b]	e.r. (2)[c]
1	 1a	**2a**	74	95:5	10	 1j	**2j**	67	63:37
2	 1b	**2b**	70	94:6	11	 1k	**2k**	73	93:7
3[f]	 1c	**2c**	85	95:5	12	 1l	**2l**	76	95:5
4	 1d	**2d**	53	96:4	13	 1m	**2m**	56	95:5
5	 1e	**2e**	59	92:8	14[e]	 1n	**2n**	90	98:2
6	 1f	**2f**	60	95:5	15[e]	 1o	**2o**	91	98:2
7[d]	 1g	**2g**	52	96:4	16[e]	 1p	**2p**	90	98:2
8[d]	 1h	**2h**	52	96:4	17[e,f]	 1p	**2p**	92	98:2
9	 1i	**2i**	57	90:10	18[e]	 1q	**2q**	66	97:3

[a] Conditions: *i*BuMgBr (1.2–1.5 M in *t*BuOMe) was added over 2 hours. Full conversion was achieved in all cases. [b] The ratio of **2a**/**3a** was determined by ^{1}H NMR spectroscopy. [c] The e.r. value was determined by HPLC analysis on a chiral stationary phase. [d] CuBr·SMe_2 (15 mol%), **L1** (18 mol%). [e] $CeCl_3$ (0.25 equiv), BF_3·Et_2O (0.25 equiv). [f] The reaction was performed with a chiral catalyst recovered from a previous reaction.

conditions afforded the alkylation products in moderate to excellent yields and with good to excellent enantiomeric ratios.

For instance, aromatic acylsilanes bearing alkyl substituents in the *para* or *meta* position provided the corresponding tertiary α-silyl alcohols with good yields and enantiomeric ratios of up to 96:4 (entries 1–5). The presence of halogens on the aromatic ring decreased the selectivity of the alkylation, while maintaining high levels of stereoselectivity (entries 6–8). Unexpectedly, the presence of a *para*-methoxy substituent in acylsilane **2j** resulted in a decrease in e.r. to 63:37, whereas for *meta*-methoxy-substituted **2k**, an e.r. of 93:7 was obtained (entries 10 and 11). With the *ortho*-methyl-substituted substrate, neither alkylation nor reduction was observed. Aryl acylsilanes bearing phenyl substituents in the *para* or *meta* position furnished the corresponding tertiary α-silyl alcohols with good yields and e.r. values of 95:5 (Table 2, entries 12 and 13). Aliphatic acylsilanes with the $SiPh_2Me$ moiety provided the reduction products only.

Further expansion of the substrate scope was carried out with α,β-unsaturated acylsilanes (enoylsilanes).[12] Notably, for these substrates, the conjugate addition of the Grignard reagent is another potential pathway, in addition to the reduction and alkylation reactions. However, using our catalytic system, only the desired 1,2-addition product was observed. Remarkably, the corresponding tertiary vinylic α-silyl alcohols were obtained with excellent yields and enantiomeric ratios (entries 14–18).[13a] Furthermore, as Meerwein–Ponndorf–Verley reduction was less pronounced for these substrates, the amount of the Lewis acid mixture could be reduced to 0.25 equivalents.

Variations of the Grignard reagent were subsequently studied using **1p** and **1c** as the substrates (Table 3). We found that the reaction tolerated linear, β-branched, as well as functionalized Grignard reagents (entries 1–11). In all cases, high yields and good to excellent stereoselectivities were obtained. Low conversion and racemic product were obtained with MeMgBr.

Table 3: Variation of the Grignard reagent.[a]

Entry	1	RMgBr	2	Yield [%][b]	e.r. (2)[c]
1	**1p**		**2r**	95	92:8
2	**1p**		**2s**	93	92:8
3[d]	**1p**		**2p**	90	98:2
4[e]	**1p**		**2t**	89 (98)	93:7 (93:7)
5[f]	**1p**		**2u**	95	91:9
6	**1p**		**2v**	97	93:7
7	**1p**		**2w**	96	95:5
8[g]	**1c**		**2c**	85	96:4
9[g]	**1c**		**2x**	88	85:15
10[g]	**1c**		**2y**	52	80:20
11[g]	**1c**		**2z**	96	85:15

[a] Conditions: The Grignard reagent (1.2–1.5 M in *t*BuOMe) was added over 2 hours. Full conversion was achieved in all cases. [b] The ratio of **2a**/**3a** was determined by ^{1}H NMR spectroscopy. [c] The e.r. value was determined by HPLC analysis on a chiral stationary phase. [d] $CeCl_3$ (0.25 equiv), $BF_3{\cdot}Et_2O$ (0.25 equiv). [e] Values in brackets correspond to the results obtained on a preparative scale (0.5 g of **1p**). [f] $CeCl_3$ (1 equiv). [g] $CeCl_3$ (1 equiv), $BF_3{\cdot}Et_2O$ (1 equiv).

To further demonstrate the potential of this method, the alkylation of **1p** with *i*PentMgBr was carried out on 500 mg scale; product **2t** was obtained in an excellent 98% yield with 93:7 e.r. (Table 2, entry 4). The catalyst was recovered as the copper complex by column chromatography in 87% yield and used repeatedly without any loss of catalytic activity (Table 1, entries 3 and 17).[13b]

The effect of the Lewis acid mixture is remarkable, in particular, the high e.r. values and selectivities obtained in the presence of $BF_3{\cdot}Et_2O$ and three metals (Mg, Cu, Ce). Performing the addition of *i*BuMgBr to **1c** in the absence of the copper catalyst and the Lewis acid mixture exclusively led to the reduction product. A similar result was obtained in the presence of only the Lewis acid mixture, albeit at a slower reaction rate. Whereas it is not yet possible to provide a detailed mechanistic picture, the involvement of an organocerium species as a nucleophile and $BF_3{\cdot}Et_2O$ as the Lewis acid should be considered. To test this hypothesis, the isobutylcerium reagent was synthesized[14] and tested. The reduction product was obtained both in the presence and in the absence of the copper catalyst. These results indicate that organocerium species are probably not involved, but instead, a new Lewis acidic species compatible with the copper catalyst is formed upon mixing $BF_3{\cdot}Et_2O$ and $CeCl_3$. Future studies will elucidate the precise role of the Lewis acids.

In summary, we have developed an unprecedented catalytic asymmetric strategy to access valuable aryl- and vinyl-substituted α-hydroxysilanes with tetrasubstituted chiral carbon centers in high yields and enantioselectivities. The competing Meerwein–Ponndorf–Verley reduction can be suppressed by the use of a mixture of Lewis acid additives. The chiral catalyst can be recovered as a copper complex and used repeatedly without any loss of catalytic activity. Studies towards synthetic applications of the newly synthesized tertiary α-silyl alcohols, the elucidation of the mechanism of this transformation, and understanding the effect of the Lewis acid mixture are currently in progress.

Received: October 6, 2014
Published online: November 17, 2014

Keywords: acylsilanes · alkylation · asymmetric synthesis · copper catalysis · Grignard reactions

[1] a) M. A. Brook, *Silicon in Organic, Organometallic and Polymer Chemistry*, Wiley, New York, **2000**; b) H.-J. Zhang, D. L. Priebbenow, C. Bolm, *Chem. Soc. Rev.* **2013**, *42*, 8540–8571; c) A. Ricci, A. Degl'Innocenti, *Synthesis* **1986**, 647–660; d) J. M. O'Brien, A. H. Hoveyda, *J. Am. Chem. Soc.* **2011**, *133*, 7712–7715; e) L. B. Delvos, D. J. Vyas, M. Oestreich, *Angew. Chem. Int. Ed.* **2013**, *52*, 4650–4653; *Angew. Chem.* **2013**, *125*, 4748–4751; f) D. J. Vyas, M. Oestreich, *Angew. Chem. Int. Ed.* **2010**, *49*, 8513–8515; *Angew. Chem.* **2010**, *122*, 8692–8694; g) M. Mortensen, R. Husmann, E. Veri, C. Bolm, *Chem. Soc. Rev.* **2009**, *38*, 1002–1010; h) J.-P. Picard, *Adv. Organomet. Chem.* **2004**, *52*, 175–375; i) A. Hensel, K. Nagura, L. B. Delvos, M. Oestreich, *Angew. Chem. Int. Ed.* **2014**, *53*, 4964–4967; *Angew. Chem.* **2014**, *126*, 5064–5067; j) D. M. Ballweg, R. C. Miller, D. L. Gray, K. A. Scheidt, *Org. Lett.* **2005**, *7*, 1403–1406; k) L. Nielsen, T. J. Skrydstrup, *J. Am. Chem. Soc.* **2008**, *130*, 13145–13151; l) Y. Bo, S. Singh, H. Q. Duong, C. Cao, S. M. Sieburth, *Org. Lett.* **2011**, *13*, 1787–1789.

[2] a) A. K. Franz, S. O. Wilson, *J. Med. Chem.* **2013**, *56*, 388–405; b) W. Bains, R. Tacke, *Curr. Opin. Drug Discovery Dev.* **2003**, *6*, 526–543; c) S. Gately, R. West, *Drug Dev. Res.* **2007**, *68*, 156–163; d) G. K. Min, D. Hernańdez, T. Skrydstrup, *Acc. Chem. Res.* **2013**, *46*, 457–470; e) P. K. Pooni, G. A. Showell, *Mini-Rev. Med. Chem.* **2006**, *6*, 1169–1177; f) M. W. Mutahi, T. Nittoli, L. Guo, S. M. Sieburth, *J. Am. Chem. Soc.* **2002**, *124*, 7363–7375.

[3] For examples of the use of chiral α-hydroxysilanes, see: a) R. J. Linderman, A. Ghannam, I. Badejo, *J. Org. Chem.* **1991**, *56*, 5213–5216; b) R. E. Ireland, M. D. Varney, *J. Am. Chem. Soc.* **1984**, *106*, 3668–3670; c) P. A. Jacobi, C. Tassa, *Org. Lett.* **2003**, *5*, 4879–4882; d) S. Perrone, P. Knochel, *Org. Lett.* **2007**, *9*, 1041–1044; e) J. R. Huckins, S. D. Rychnovsky, *J. Org. Chem.* **2003**, *68*, 10135–10145.

[4] a) J. D. Buynak, J. B. Strickland, T. Hurd, A. Phan, *J. Chem. Soc. Chem. Commun.* **1989**, 89–90; b) J. A. Soderquist, C. L. Anderson, E. I. Miranda, I. Rivera, G. W. Kabalka, *Tetrahedron Lett.* **1990**, *31*, 4677–4680; c) K. Takeda, Y. Ohnishi, T. Koisumi, *Org. Lett.* **1999**, *1*, 237–239; d) R. Tacke, H. Hengersberg, H. Zilch, B. J. Stumpf, *Organomet. Chem.* **1989**, *379*, 211–216.

[5] a) N. Arai, K. Suzuki, S. Sugisaki, H. Sorimachi, T. Ohkuma, *Angew. Chem. Int. Ed.* **2008**, *47*, 1770–1773; *Angew. Chem.* **2008**, *120*, 1794–1797; b) J.-I. Matsuo, Y. Hattori, H. Ishibashi, *Org. Lett.* **2010**, *12*, 2294–2297.

[6] V. Cirriez, C. Rasson, T. Hermant, J. Petrignet, J. Díaz Álvarez, K. Robeyns, O. Riant, *Angew. Chem. Int. Ed.* **2013**, *52*, 1785–1788; *Angew. Chem.* **2013**, *125*, 1829–1832.

[7] a) R. Unger, F. Weisser, N. Chinkov, A. Stanger, T. Cohen, I. Marek, *Org. Lett.* **2009**, *11*, 1853–1856; b) P. Smirnov, J. Mathew, A. Nijs, E. Katan, M. Karni, C. Bolm, Y. Apeloig, I. Marek, *Angew. Chem. Int. Ed.* **2013**, *52*, 13717–13721; *Angew. Chem.* **2013**, *125*, 13962–13966.

[8] a) M. Hatano, S. Suzuki, K. Ishihara, *J. Am. Chem. Soc.* **2006**, *128*, 9998–9999; b) M. Hatano, S. Suzuki, K. Ishihara, *Synlett* **2010**, 321–324; c) M. Hatano, T. Matsumura, K. Ishihara, *Org. Lett.* **2005**, *7*, 573–576; d) G. Giacomelli, L. Lardicci, R. Santi, *J. Org. Chem.* **1974**, *39*, 2736–2739.

[9] G. Gao, X. Bai, F. Li, L. Zheng, Z. Zheng, G. Lai, K. Jiang, F. Li, L. Xu, *Tetrahedron Lett.* **2012**, *53*, 2164 – 2166.

[10] a) A. V. R. Madduri, S. R. Harutyunyan, A. J. Minnaard, *Angew. Chem. Int. Ed.* **2012**, *51*, 3164 – 3167; *Angew. Chem.* **2012**, *124*, 3218 – 3221; < lit b > A. V. R. Madduri, A. J. Minnaard, S. R. Harutyunyan, *Chem. Commun.* **2012**, *48*, 1478 – 1480; c) A. V. R. Madduri, A. J. Minnaard, S. R. Harutyunyan, *Org. Biomol. Chem.* **2012**, *10*, 2878 – 2884; d) R. Oost, J. Rong, A. J. Minnaard, S. R. Harutyunyan, *Catal. Sci. Technol.* **2014**, *4*, 1997 – 2005; e) F. Caprioli, M. Lutz, A. Meetsma, A. J. Minnaard, S. R. Harutyunyan, *Synlett* **2013**, 2419 – 2422.

[11] The catalytic alkylation pathway requires the following sequence of events: transmetalation of the Grignard reagent to the copper complex, π-complexation with the carbonyl group of the acylsilane, and finally, transfer of the alkyl group from the copper center to the carbonyl carbon atom of the acylsilane; for references, see: a) S. R. Harutyunyan, F. López, W. R. Browne, A. Correa, D. Peña, R. Badorrey, A. Meetsma, A. J. Minnaard, B. L. Feringa, *J. Am. Chem. Soc.* **2006**, *128*, 9103 – 9118; b) S. H. Bertz, R. A. Hardin, C. A. Ogle, *J. Am. Chem. Soc.* **2013**, *135*, 9656 – 9658; c) S. H. Bertz, R. A. Hardin, T. J. Heavey, C. A. Ogle, *Angew. Chem. Int. Ed.* **2013**, *52*, 10250 – 10252; *Angew. Chem.* **2013**, *125*, 10440 – 10442.

[12] For the synthesis of the acylsilanes and corresponding references, see the Supporting Information.

[13] a) Performing the addition reaction with an α-H-substituted enoylsilane provided exclusively the 1,2-addition product. However, the corresponding tertiary alcohol was obtained in nearly racemic form; b) for the structure of the Cu complex, see Ref. [10d].

[14] T. Imamoto, N. Takiyama, K. Nakamura, T. Hatajima, Y. Kamiya, *J. Am. Chem. Soc.* **1989**, *111*, 4392 – 4398.

