Application of a *Grubbs–Hoveyda* Metathesis Catalyst Noncovalently Immobilized by Fluorous–Fluorous Interactions

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A *Grubbs–Hoveyda* metathesis catalyst bearing a tris(perfluoroalkyl)silyl tag for efficient noncovalent attachment to fluorous silica gel (FSG) was synthesized and employed in ring-closing metathesis (RCM) reactions in CH_2Cl_2. After the reaction, a solvent switch to a polar system allowed for recovery of the catalyst by filtration and its reuse. The approach was demonstrated for a number of different substrates. Furthermore, it was shown that the application of this catalytic system yielded products with low ruthenium content.

Introduction. – Homogeneous catalytic reactions are widely used in organic synthesis. Their major drawback however, is the difficult separation of the metal complexes from the products after the reaction. Immobilization techniques are a method to overcome this problem [1]. One of these technologies is the application of perfluoro-tagged catalysts in perfluorinated solvents [2]. These solvents are immiscible with most organic solvents at room temperature and hence, allow reactions to be performed under fluorous biphasic conditions [3]. Thus, the perfluoro-tagged catalyst can be recovered after the reaction by a simple liquid-liquid extraction and reused in consecutive runs. Despite the advantages offered by the approach, the needed fluorous solvents are expensive and environmentally persistent [4].

For this reason, *Curran* and *Luo* developed the so-called light fluorous technology [5]. In this method, the reaction is carried out in an organic solvent, and the perfluoro-tagged compound is afterwards separated from the products by solid-phase extraction on fluorous silica gel (FSG). One advantage of this technique is that the tagged molecules require lower F-content than normally needed for fluorous biphasic applications. In this respect, *Matsugi* and *Curran* have recently reported a light fluorous *Grubbs–Hoveyda* catalyst and demonstrated its use in ring-closing metathesis (RCM) reactions applying different substrates [6].

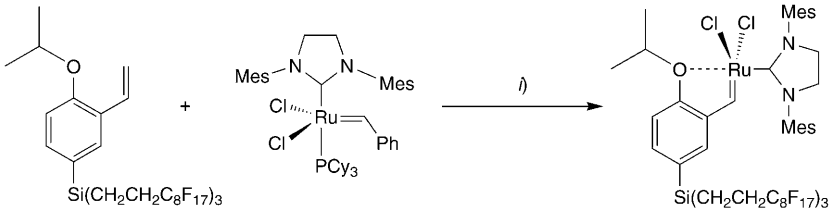
As an alternative approach to omit perfluorinated solvents, we have used FSG as support for the noncovalent immobilization of perfluorinated catalysts to be applied in organic solvents. After the reaction, the catalyst can be removed by a simple filtration step and can be reapplied to further reactions. This technology was successfully demonstrated for Pd-mediated *Suzuki* and *Sonogashira* couplings [7].

Perfluoro-tagged compounds can exhibit strong interactions with perfluorinated stationary phases. These interactions depend on the chain length of the perfluoro entity

and especially on the number of the perfluoro tags, the reason for this being cooperativity. In HPLC experiments, we could corroborate these effects by investigating and comparing retention times of different perfluoro tag-modified compounds on different FSGs [8]. The results led to our preference for $(C_8F_{17}CH_2CH_2)_3Si$ tags for the noncovalent immobilization of ligands and complexes on FSG. These tags have the further advantage that they can be easily introduced into aromatic systems which are rampant in many ligands of catalysts. We have been able to demonstrate this in a recent report on the synthesis of perfluoro-tagged salen ligands, binap, and the styrene derivative **1** [9].

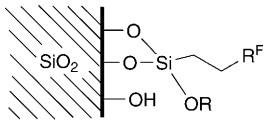
Results and Discussion. – According to *Scheme 1*, the ligand **1** was transformed into the perfluoro-tagged *Grubbs–Hoveyda* metathesis catalyst **3** by reacting it with *Grubbs* catalyst **2** (second generation) [10]. In this reaction, the addition of (trifluoromethyl)-benzene (BTF) was necessary to ensure homogeneous conditions. After the reaction, catalyst **3** was isolated by column chromatography in pure form.

Scheme 1. *Synthesis of the Perfluoro-Tagged Catalyst* **3**



i) CuCl, CH_2Cl_2/BTF, reflux, 4 h, 48%.

The FSG used for the noncovalent attachment of catalyst **3** is shown in *Fig. 1*. For the attachment, catalyst **3** was dissolved in Et_2O in which the FSG **4** had been suspended. Removal of the solvent yielded the supported catalyst as a greenish, free-flowing powder with a loading value of 5 μmol/g.



4a $R^F = C_6F_{13}$
4b $R^F = C_8F_{17}$
R = H, Et, SiR'_3

Fig. 1. *Fluorous silica gels* (FSG) **4** *for the noncovalent immobilization of catalyst* **3**

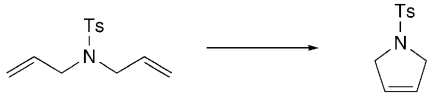
Preliminary experiments had revealed that **3** shows a high solubility even in relatively polar solvents like MeOH. For this reason, we envisaged a so-called solvent switch which we had previously successfully employed in a multistep synthesis starting

from $(C_8F_{17}CH_2CH_2)_3Si$-modified benzyl alcohol [11]. For metathesis reactions, we envisaged that this approach would be implemented in such a way that the reaction would be performed in CH_2Cl_2 and after reaction, the solvent would be evaporated, with subsequent washings with a polar solvent to remove the product from the immobilized catalyst. Incidentally, *Matsugi* and *Curran* also described the solvent switch approach for their light fluorous metathesis catalyst [6]. The reaction was carried out in CH_2Cl_2 and, thereafter, the catalyst was re-adsorbed on the support material in MeOH/H_2O 4:1.

We had found independently that MeOH/H_2O 4:1 was suitable for our perfluoro-tagged catalyst since washing steps with this mixture (same amounts as in the metathesis experiments) on the immobilized catalyst (FSG **4a** or **4b**) had led to a leaching of Ru of only 1% into the solvent mixture. A two-fold repetition resulted in the same amount of released ruthenium. We also tested the leaching of the catalyst when immobilized on unmodified silica gel. The result showed a slightly higher leaching of 3% which can still be regarded as very low. This was a clear indication that insolubility of the catalyst in MeOH/H_2O 4:1 was the main driving force for the adsorption to the support, and that fluorous-fluorous interactions contributed only marginally.

Next, we examined the influence of the support material during actual catalytic reactions. Equal amounts of catalyst were immobilized on FSGs **4a** and **4b** and also on unmodified silica gel. As a benchmark test, the RCM of **5a** leading to **6a** was carried out with 1 mol-% of catalyst corresponding to 1 mg of catalyst on 100 mg of silica gel or FSG (*Scheme 2*). As shown in *Fig. 2*, the nature of the support had, as expected, only a minor impact on the conversion rates in the different cycles. All conversions were in the same range, with FSG **4b** showing slightly better results than the other supports. The results with standard silica gel as support are in contrast to *Matsugi*'s and *Curran*'s observation that their light fluorous catalyst gave 'inferior' results [6]. The generally reduced conversion in runs 2 and 3 are attributed to decomposition of the catalyst since the decrease is much higher than the leaching values that were found in the initial washing experiments. It is known that *Grubbs* catalysts are especially prone to decomposition in the presence of MeOH and H_2O [12]. The conversions after recycling were by no means comparable to our covalently immobilized catalyst [13].

Scheme 2. *Benchmark Ring-Closing Metathesis* (RCM) *Reaction*



5a **6a**

To get a better understanding on the dependency of recycling on the amount of catalyst employed, we immobilized different amounts of **3** on **4b** to test consecutive RCMs with **5a** as substrate and 5, 2.5, 1 and 0.2 mol-% of catalyst. In contrast to *Matsugi* and *Curran*, we did not correct the loss of catalyst during the different runs [6]. This means that the same amount of substrate was used in all runs. As expected, the higher the catalyst loading, the more consecutive runs were possible (*Fig. 3*). With 5 and 2.5 mol-% of **3**, we were able to perform four runs with high conversions and then, we observed a drop in activity for both amounts. A catalyst loading of 1 mol-% showed a comparable

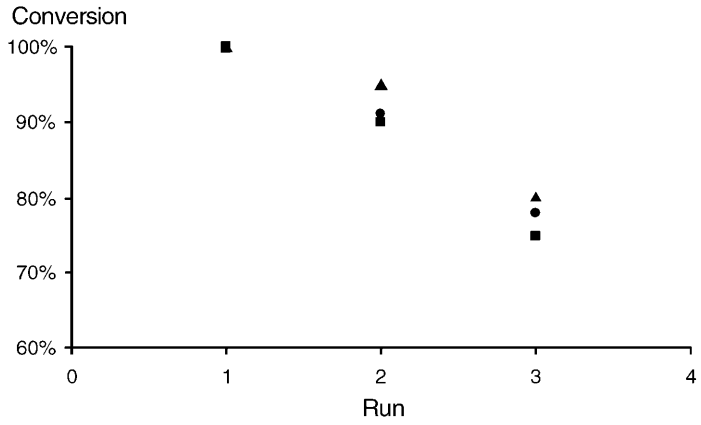


Fig. 2. *Recycling experiments with* **3** *immobilized on different supports:* FSG **4a** (■), FSG **4b** (▲), *unmodified silica gel* (●)

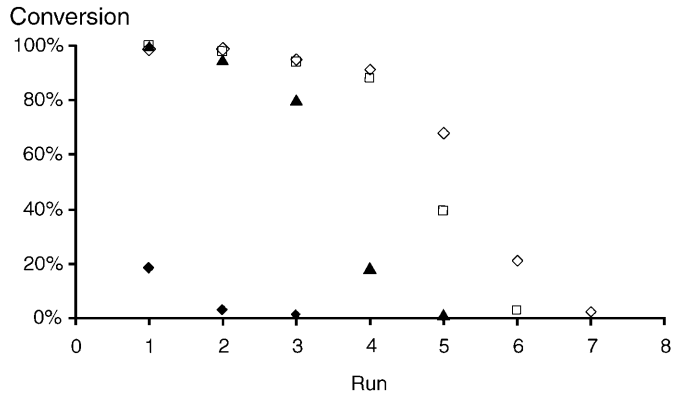


Fig. 3. *Recycling experiments with different catalyst amounts:* 5 mol-% (◇), 2.5 mol-% (□), 1 mol-% (▲), *and* 0.2 mol-% (◆)

conversion only in the first two runs. With 0.2 mol-% of **3**, no decent conversion was observed even in the first run. The accumulated turnover numbers are summarized in *Table 1*.

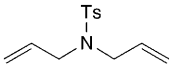
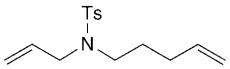
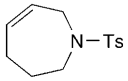
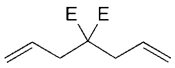
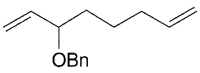
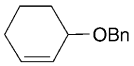
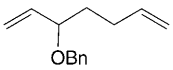
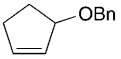
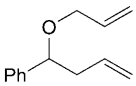
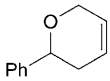
Table 1. *Turnover Numbers* (TON) *Obtained in Consecutive RCM of* **5a** *with Different Catalyst Amounts*

Catalyst amount [mol-%]	5	2.5	1	0.2
Number of runs	7	6	5	3
TON[a])	95	169	294	110

[a]) The values are accumulated TON.

Next, we extended our study to the RCM of several α,ω-dienes employing 1 mol-% of catalyst **3** (*Table 2*). After 2 h, the conversion of all substrates was complete. For the

Table 2. *RCM of Different α,ω-Dienes with Catalyst* **3**

Substrate	Product	Conversion [%] run 1, run 2[a])
 **5a**	 **6a**	>98, >98
 **5b**	 **6b**	>98, >98
 **5c**[b])	 **6c**[b])	>98, 92
 **5d**	 **6d**	>98, 84
 **5e**	 **6e**	>98, 10 >98, 55[c])
 **5f**	 **6f**	>98, 16 >98, 62[c])

[a]) Conversions determined by ^{1}H-NMR. [b]) E = COOEt. [c]) 2.5 mol-% of **3**.

formation of **6a**–**d**, high conversions were obtained after recycling but not for the formation of **6e** and **6f**. These RCMs were repeated with 2.5 mol-% of **3**, but even then only moderate conversions were observed in the second run.

In general, a major limitation of metathesis reactions with *Grubbs* catalysts is the high leaching of Ru into the product. Several groups reported that applying the *Hoveyda*-type catalyst, the leaching of Ru could be decreased substantially [14]. We ourselves reported recently that performing olefin metathesis in supercritical carbon dioxide results in a Ru content in the product as low as 20 ppm [15]. Due to the low solubility of **3** in MeOH/H_2O, we envisaged that in this case too, we would be able to reduce the leaching strongly. So, we performed the RCM of **5a** on a larger scale and then determined the Ru in the crude product by atomic absorption spectroscopy (AAS). A clear trend was not observed. The lowest Ru-content in the product, 86 ppm, was found with **3** on FSG **4b**. With **3** on FSG **4a**, 137 ppm, and with **3** on normal silica gel, 119 ppm of Ru were found.

Conclusion. – We prepared a $(C_8F_{17}CH_2CH_2)_3Si$-modified *Grubbs–Hoveyda* olefin metathesis catalyst, which was highly active in ring-closing metathesis reactions. The catalyst was noncovalently immobilized on fluorous silica gel and applied in CH_2Cl_2 as solvent. After the reaction, a solvent switch to $MeOH/H_2O$ was applied to re-attach the catalyst to the FSG, which allowed its separation from the product by filtration. The thus isolated supported catalyst could be reused in further cycles. This was demonstrated in RCMs for a number of different substrates. Furthermore, the aqueous workup yielded products of high purity. We found only 86–137 ppm of Ru in the crude product.

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Experimental Part

General. All reagents were obtained from *Aldrich*, *Fluka*, or *Lancaster* and were of the highest purity available. CH_2Cl_2 was dried over CaH_2. The solvents used for the catalytic reactions and the workup were reaction-grade solvents. FSGs **4a** and **4b** were prepared based on silica gel (100–300 μm particle size, 500 Å pore size, 70–90 m^2/g specific surface) obtained from *Grace* as described earlier [7]. Column chromatography (CC): commercially available *MN* silica gel *60* (0.063–0.2 mm/70–230 mesh) *ASTM* for CC from *Baker*. HPLC: *Agilent-1100* system with binary pump, sample changer, column oven, and diode array detector.

NMR Spectra at 300, 400, and 500 MHz (^1H) and at 100.6 and 125.7 MHz (^{13}C); chemical shifts δ in ppm rel. to Me_4Si (=0 ppm) for ^1H and rel. to $CHCl_3$ (=77.0 ppm) for ^{13}C, resp., *J* in Hz. MS: *TSQ-700* mass spectrometer (EI, CI, ESI); in *m*/z (rel. %).

[1,3-Bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene]dichloro{2-(isopropoxy-κO)-5-[tris(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)silyl]benzylidene-κC}ruthenium (**3**). *Grubbs* catalyst **2** (109 mg, 128 μmol) was dissolved under Ar in anh. CH_2Cl_2 (8 ml). Then, **1** (130 mg, 85.0 μmol) dissolved in degassed BTF (3 ml) and CuCl (13 mg, 131 μmol) were added, and the mixture was heated for 4 h at 60° (oil bath). After cooling to r.t., the mixture was filtered over silica gel and the filtrate was purified by CC (cyclohexane → cyclohexane/CH_2Cl_2 1:1): **3** (80.0 mg, 48%). Green solid. ^1H-NMR (500 MHz, $CDCl_3$): 1.05–1.09 (*m*, $(C_8F_{17}CH_2CH_2)_3Si$); 1.27 (*d*, *J*=6.2, Me_2CH); 1.95–2.06 (*m*, $(C_8F_{17}CH_2CH_2)_3$); 2.36–2.45 (*m*, 6 Me); 4.18 (*s*, NCH_2CH_2N); 4.91 (*sept.*, *J*=6.1, Me_2CH); 6.88 (*d*, *J*=8.3, 1 arom. H); 6.99 (*d*, *J*=1.5, 1 arom. H); 7.05 (*s*, 4 arom. H); 7.52 (*dd*, *J*=8.1, 1.5, 1 arom. H); 16.53 (*s*, Ru=CHAr). ^{13}C-NMR (125.7 MHz, $CDCl_3$): 0.1; 1.6; 20.9; 21.2; 22.2; 25.3; 25.5; 25.6; 27.0; 75.9; 113.9; 116.1; 118.0; 120.8; 124.0; 127.4; 128.4; 129.5; 130.3; 134.7; 139.0; 145.3; 154.4; 210.3; 295.1. EI-MS: 2000 (3), 1999 (6), 1998 (13), 1997 (19), 1996 (31), 1995 (29), 1994 (37, M^+), 1993 (29), 1992.4 (19), 1992.0 (16), 1991 (10), 1990 (5), 1920 (2), 1919 (3), 1918 (5), 1917 (6), 1916 (9), 1915 (79), 1914 (6), 1913 (4), 1912 (3), 1883 (7), 1882 (16), 1881 (18), 1880 (33), 1879 (33), 1878 (31), 1877 (31), 1876 (17), 1875 (12), 1874 (11), 1873 (6), 1530 (6), 1518 (18), 1475 (14), 1457 (6), 940 (5), 939 (5), 620 (7), 619 (7), 499 (12), 445 (4), 444 (9), 443 (11), 442 (21), 441 (20), 440 (22), 439 (20), 438 (14), 437 (9), 436 (8), 435 (4), 409 (10), 408 (31), 407 (44), 406 (75), 405 (96), 404 (100), 403 (88), 402 (71), 401 (43), 400 (42), 399 (34), 398 (24), 397 (17), 396 (12), 395 (12), 394 (9), 393 (8), 392 (10), 391 (12), 390 (13), 389 (19), 388 (13), 387 (7), 386 (6), 385 (6), 363 (13), 345 (15), 339 (29), 308 (6), 307.0 (22), 306.9 (17), 305 (37), 304 (50), 303 (63), 301 (26), 299 (6), 297 (17), 296 (7), 295 (43), 289 (12), 287 (9), 281 (7), 278 (9), 275 (7), 245 (7), 244 (12), 243 (9), 242 (38), 239 (7), 231 (9), 217 (6), 216 (20), 215 (25), 214 (82), 213 (9), 204 (7). ESI-MS (pos.): 2000 (100), 1999 (86), 1998 (65), 1997 (46), 1996 (33), 1995 (24), 1994 (25, M^+), 1993 (7), 1992, (5), 1991 (4), 1985 (7), 1984 (6), 1983 (10), 1982 (10), 1981 (11), 1980 (15), 1979

(11), 1978 (21), 1977 (13), 1976 (11), 1975 (7), 1964 (4), 1963 (5), 1962 (10), 1961 (14), 1960 (12), 1959 (18), 1958 (14), 1957 (14), 1956 (11), 1955 (10), 1954 (7), 1953 (7), 1928 (3), 1927 (6), 1926 (9), 1925 (14), 1924 (12), 1923 (13), 1922 (10), 1921 (5), 1920 (4), 1919 (2), 1918 (1), 1904 (1), 1903 (4), 1902 (5), 1901 (6), 1900 (8), 1899 (6), 1898 (4), 1897 (3), 1896 (2), 1895 (1), 1894 (2), 765 (5), 764 (14), 681 (4), 680 (10), 663 (6), 549 (7), 548 (24), 475 (6), 439 (11), 438 (6), 437 (19), 436 (12), 435 (11), 434 (11), 422 (4), 407 (5), 405 (6), 307 (5).

General Procedure for the Recycling Experiments. The catalyst **3** loaded on FSG **4b** was placed in a reaction tube, and olefin **5a** was added from a 0.05M stock soln. in CH_2Cl_2 (1 ml, 50 μmol). The mixture was shaken for 2 h at 60° (oil bath). Then, a sample of the mixture was taken to determine the conversion by HPLC. After this, Et_2O (2 ml) was added, and the solvents were evaporated. The RCM product **6a** was obtained by washing the silica gel with MeOH/H_2O 4:1 (5×1 ml). After the washing with MeOH/H_2O 4:1, the silica gel was dried by washing with Et_2O and was reused.

General Procedure for the Ring-Closing Metathesis. To a 0.05M stock soln. of the α,ω-diene in CH_2Cl_2 (1 ml, 50 μmol) was added the catalyst noncovalently immobilized on FSG **4b**. The mixture was shaken for 2 h at 60° (oil bath). After cooling to r.t., Et_2O (2 ml) was added, and the solvents were evaporated. The RCM product was obtained by washing the silica gel with MeOH/H_2O 4:1 (5×1 ml). After the washing with MeOH/H_2O 4:1, the silica gel was dried by washing with Et_2O and was reused.

*2,5-Dihydro-1-[(4-methylphenyl)sulfonyl]-1*H*-pyrrole* (**6a**) [16]. ^{1}H-NMR ($CDCl_3$): 2.42 (*s*, *Me*C_6H_4); 4.12 (*s*, 4 H, CH_2CH=CHCH_2); 5.65 (*s*, CH_2CH=CHCH_2); 7.32 ($m_{AA'BB'}$, $J_{app.}$=8.1, 2 arom. H); 7.72 ($m_{AA'BB'}$, $J_{app.}$=8.1, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 21.6; 54.9; 125.5; 127.5; 129.8; 134.4; 143.5. MS: 223 (50, M^+), 155 (52), 91 (92), 86 (13), 84 (20), 68 (100), 65 (24), 41 (24).

*2,3,4,7-Tetrahydro-1-[(4-methylphenyl)sulfonyl]-1*H*-azepine* (**6b**) [17]. ^{1}H-NMR ($CDCl_3$): 1.80 (*m*, 2 H); 2.18 (*m*, 2 H); 2.41 (*s*, *Me*C_6H_4); 3.39 (*t*, *J*=6.1, NCH_2CH_2); 3.83 (*d*, *J*=4.5, NCH_2CH=CH); 5.64 (*dt*, *J*=10.6, 5.1, H–C(5) or H–C(6)); 5.77 (*dt*, *J*=10.9, 5.3, H–C(6) or H–C(5)); 7.28 ($m_{AA'BB'}$, J_{app}=8.2, 2 arom. H); 7.68 ($m_{AA'BB'}$, J_{app}=8.1, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 21.5; 26.9; 31.0; 46.4; 49.7; 126.7; 127.3; 129.6; 133.0; 136.5; 143.1. MS: 251 (100, M^+), 236 (7), 184 (85), 155 (40), 96 (87), 91 (37), 69 (35), 67 (30), 41 (24).

Cyclopent-3-ene-1,1-dicarboxylic Acid Diethyl Ester (**6c**) [18]. ^{1}H-NMR ($CDCl_3$): 1.25 (*t*, *J*=7.1, 2 *Me*CH_2); 3.01 (*s*, CH_2CH=CHCH_2); 4.20 (*q*, *J*=7.1, 2 MeCH_2); 5.61 (*s*, CH_2CH=CHCH_2). ^{13}C-NMR ($CDCl_3$): 14.0; 40.9; 58.9; 61.2; 127.8; 172.3. MS: 212 (63, M^+), 166 (60), 138 (100), 111 (38), 93 (32), 79 (40), 66 (54).

[(Cyclohex-2-en-1-yloxy)methyl]benzene (**6d**) [19]. ^{1}H-NMR ($CDCl_3$): 1.51–1.59 (*m*, 1 H); 1.71–1.89 (*m*, 3 H); 1.91–1.99 (*m*, 1 H); 2.02–2.10 (*m*, 1 H); 3.93–3.98 (*m*, H–C(1)); 4.55 ($d_{AA'}$, *J*=12.0, 1 H, CH_2O); 4.61 ($d_{AA'}$, *J*=12.0, 1 H, CH_2O); 5.79–5.89 (*m*, H–C(2), H–C(3)); 7.24–7.37 (*m*, 5 arom. H). ^{13}C-NMR ($CDCl_3$): 19.3; 25.3; 28.4; 70.0; 72.2; 127.4; 127.6; 127.8; 128.3; 130.9; 139.1. MS: 188 (5, M^+), 130 (9), 97 (48), 91 (100), 84 (8), 81 (13), 79 (13), 77 (7), 69 (22), 65 (11), 55 (10), 41 (15).

[(Cyclopent-2-en-1-yloxy)methyl]benzene (**6e**) [20]. ^{1}H-NMR ($CDCl_3$): 1.82–1.89 (*m*, 1 H, CH_2(4)); 2.12–2.19 (*m*, 1 H, CH_2(4)); 2.23–2.30 (*m*, 1 H, CH_2(5)); 2.47–2.55 (*m*, 1 H, CH_2(5)); 4.51 (*d*, J_{AB}=11.7, 1 H, CH_2O); 4.55 (*d*, J_{AB}=11.7, 1 H, CH_2O); 4.67 (*m*, H–C(1)); 5.88–5.91 (*m*, H–C(3)); 6.01–6.04 (*m*, H–C(2)); 7.24–7.37 (*m*, Ph). ^{13}C-NMR ($CDCl_3$): 29.8; 31.1; 70.6; 84.5; 127.4; 127.8; 128.3; 130.8; 135.7; 138.9. MS: 192 (12, $[M+NH_4]^+$), 175 (4, $[M+H]^+$), 157 (10), 126 (21), 108 (17), 91 (36), 84 (100), 67 (7).

*2-Phenyl-3,6-dihydro-2*H*-pyran* (**6f**) [21]. ^{1}H-NMR ($CDCl_3$): 2.20–2.44 (*m*, 2 H); 4.33–4.39 (*m*, 2 H); 4.56 (*dd*, *J*=10.0, 3.8, H–C(2)); 5.77–5.85 (*m*, 1 H); 5.88–5.96 (*m*, 1 H); 7.25–7.41 (*m*, Ph). ^{13}C-NMR ($CDCl_3$): 32.9; 66.6; 75.7; 124.5; 125.9; 126.4; 127.5; 128.4; 142.6. MS: 160 (16, M^+), 105 (100), 77 (18), 54 (75).

REFERENCES

[1] C. C. Tzschucke, C. Markert, W. Bannwarth, S. Roller, A. Hebel, R. Haag, *Angew. Chem.* **2002**, *114*, 4136; *Angew. Chem., Int. Ed.* **2002**, *41*, 3964; J. Yoshida, K. Itami, *Chem. Rev.* **2002**, *102*, 3693; D. J. Cole-Hamilton, *Science (Washington, D.C.)* **2003**, *299*, 1702.

[2] I. T. Horváth, J. Rábai, *Science (Washington, D.C.)* **1994**, *266*, 72; D. P. Curran, *Angew. Chem.* **1998**, *110*, 1230; *Angew. Chem., Int. Ed.* **1998**, *37*, 1174; I. T. Horváth, *Acc. Chem. Res.* **1998**, *31*, 641; J. A. Gladysz, D. P. Curran, *Tetrahedron* **2002**, *58*, 3823.

[3] R. L. Scott, *J. Am. Chem. Soc.* **1948**, *70*, 4090; J. H. Hildebrand, D. R. F. Cochran, *J. Am. Chem. Soc.* **1949**, *71*, 22; R. L. Scott, *J. Phys. Chem.* **1958**, *62*, 136.
[4] A. R. Ravishankara, S. Solomon, A. A. Turnipseed, R. F. Warren, *Science (Washington, D.C.)* **1993**, *259*, 194; D. J. Wuebbles, J. M. Calm, *Science (Washington, D.C.)* **1997**, *278*, 1090.
[5] D. P. Curran, Z. Luo, *J. Am. Chem. Soc.* **1999**, *121*, 9069; Q. Zhang, Z. Luo, D. P. Curran, *J. Org. Chem.* **2000**, *65*, 8866; D. P. Curran, *Synlett* **2001**, 1488.
[6] M. Matsugi, D. P. Curran, *J. Org. Chem.* **2005**, *70*, 1636.
[7] C. C. Tzschucke, C. Markert, H. Glatz, W. Bannwarth, *Angew. Chem.* **2002**, *114*, 4678; *Angew. Chem., Int. Ed.* **2002**, *41*, 4500; C. C. Tzschucke, W. Bannwarth, *Helv. Chim. Acta* **2004**, *87*, 2882.
[8] H. Glatz, C. Blay, H. Engelhardt, W. Bannwarth, *Chromatographia* **2004**, *59*, 567.
[9] V. Andrushko, D. Schwinn, C. C. Tzschucke, F. Michalek, J. Horn, C. Mössner, W. Bannwarth, *Helv. Chim. Acta* **2005**, *88*, 936.
[10] J. S. Kingsbury, J. P. A. Harrity, P. J. Bonitatebus Jr., A. H. Hoveyda, *J. Am. Chem. Soc.* **1999**, *121*, 791; S. B. Garber, J. S. Kingsbury, B. L. Gray, A. H. Hoveyda, *J. Am. Chem. Soc.* **2000**, *122*, 8168.
[11] D. Schwinn, W. Bannwarth, *Helv. Chim. Acta* **2002**, *85*, 255.
[12] T. M. Trnka, J. P. Morgan, M. S. Sanford, T. E. Wilhelm, M. Scholl, T.-L. Choi, S. Ding, M. W. Day, R. H. Grubbs, *J. Am. Chem. Soc.* **2003**, *125*, 2546; M. B. Dinger, J. C. Mol, *Organometallics* **2003**, *22*, 1089; M. B. Dinger, J. C. Mol, *Eur. J. Inorg. Chem.* **2003**, 2827.
[13] F. Koç, F. Michalek, L. Rumi, W. Bannwarth, R. Haag, *Synthesis* **2005**, 3362.
[14] M. Mayr, B. Mayr, M. R. Buchmeiser, *Angew. Chem.* **2001**, *113*, 3957; *Angew. Chem., Int. Ed.* **2001**, *40*, 3839; D. Fischer, S. Blechert, *Adv. Synth. Catal.* **2005**, *347*, 1329; J. C. Conrad, H. H. Parnas, J. L. Snelgrove, D. E. Fogg, *J. Am. Chem. Soc.* **2005**, *127*, 11882.
[15] F. Michalek, D. Mädge, J. Rühe, W. Bannwarth, *Eur. J. Org. Chem.* **2006**, 577.
[16] A. Fürstner, A. F. Hill, M. Liebl, J. D. E. T. Wilton-Ely, *Chem. Commun.* **1999**, 601.
[17] M. S. Visser, N. M. Heron, M. T. Didiuk, J. F. Sagal, A. H. Hoveyda, *J. Am. Chem. Soc.* **1996**, *118*, 4291.
[18] D. F. Taber, K. J. Frankowski, *J. Org. Chem.* **2003**, *68*, 6047.
[19] S. E. Denmark, J. P. Edwards, *J. Org. Chem.* **1991**, *56*, 6974.
[20] J. J. Tufariello, A. C. Bayer, J. J. Spadaro Jr., *J. Am. Chem. Soc.* **1979**, *101*, 3309.
[21] B. Schmidt, *J. Chem. Soc., Perkin Trans. 1* **1999**, 2627.

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