$LiClO_4$-Promoted Addition of Alkyl Grignard and Alkynyllithium Reagents to Ketones. Comparison of a 5 M $LiClO_4$/Diethyl Ether Solution with $CeCl_3$

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The influence of a 5 M ethereal $LiClO_4$ solution as solvent on the addition of different alkyl Grignard and alkynyllithium reagents to highly enolizable ketones was studied. A comparison with the results in the presence of $CeCl_3$ shows a similar improvement in the yield.

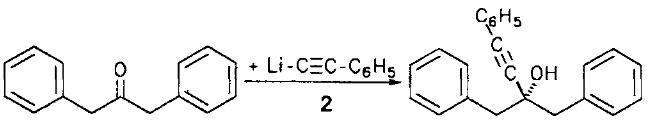
Cerium(III) chloride promotes the addition of organolithium and Grignard compounds to ketones by suppression of enolization, aldol condensation, and reduction[1]. Enhanced reactivity was observed regardless of whether $CeCl_3$ was first added to the organometalic reagent or to the ketone solution[2]. Ethereal solvents such as tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) were the solvents of choice[1a]. Addition products could be prepared by this simple procedure in yields as high as 99%, even though the yield was zero in the absence of the lanthanide salt[1].

Two arguments have been discussed for the improvement in yield caused by the addition of $CeCl_3$: On the one hand, it is postulated that primarily an organocerium compound is generated. However, no systematic studies of the structures of these organocerium reagents have been performed so far. These reagents are presumed to be σ-bonded $R-CeCl_2$ or ate complexes $(RCeCl_3)^-$[1a,3]. Other possibilities, such as weakly associated complexes $RLi \cdot CeCl_3$ or $RMgX \cdot CeCl_3$, however, cannot be excluded[1a]. On the other hand, it is postulated that $CeCl_3$ simply serves as a strongly oxophilic Lewis acid that effectively activates the carbonyl compound for the nucleophilic addition reaction by coordination, thus suppressing side reactions[2,4]. Recently, it was shown, that Grignards reagents react in the presence of anhydrous $CeCl_3$ effectively with 1,3-diketones to produce the corresponding β-hydroxy ketone in high yields[4a]. However, with "pregenerated" organocerium reagents it was not possible to obtain the expected β-hydroxy ketone. In most experiments only the starting materials were recovered[4a].

In order to gain more information on the role of $CeCl_3$ in the activation of carbonyl compounds, we studied the addition reactions of different alkyl Grignard compounds and alkynyllithium reagents with highly enolizable ketones in concentrated ethereal $LiClO_4$ solution and compared the results with reactions performed in the presence of $CeCl_3$ in THF. $LiClO_4$, like $CeCl_3$ is also a highly oxophilic Lewis acid, especially when concentrated solutions are used[5]. Ethereal solutions of $LiClO_4$ could be prepared in concentrations of up to approximately 6 M at 30 °C[6]. Due to the high polarity and the extremely high concentration of lithium ions, these solutions are excellent media for polar reactions. The usefulness of concentrated ethereal solutions of $LiClO_4$ was successfully demonstrated by the addition of different reagents such as ketene acetals[7], allylstannane[5,8], or trimethylsilyl cyanide[7,9] to the carbonyl compounds. Our results demonstrate a high degree of similarity between anhydrous $CeCl_3$ and $LiClO_4$ concerning the improvement in the yield obtained by the addition of organometallic reagents to ketones.

Results and Discussion

The reaction of dibenzyl ketone (**1**) with two equivalents of the lithium phenylacetylide (**2**) in THF at 0 °C afforded after 2 h the alcohol **3** in 29% yield. The yield increased to 99% when the addition of the acetylide was carried out for 15 min in 5 M $LiClO_4$/diethyl ether as the reaction medium. A similar improvement in the yield (98%, 30 min reaction time) was achieved in THF at 0 °C in the presence of two equivalents of $CeCl_3$ as activator.



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3

29% (THF)
98% ($CeCl_3$/THF)
99% ($LiClO_4$/ether)

The yield of the alcohols **6** and **7** obtained by the addition of acetylide **2** to indanones **4** and **5**, respectively, was also significantly increased by using 5 M $LiClO_4$/diethyl ether as reaction medium and is quite comparable to results obtained in the presence of anhydrous $CeCl_3$. Similarly comparable is the yield of the alcohols **9** and **11** obtained by the addition of **2** to the ketones **8** and **10**, when the reaction was carried in the presence of $CeCl_3$ or in 5 M

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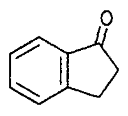
$LiClO_4$/diethyl ether as solvent. In Table 1 the results are summarized. Obviously, there is a direct proportionality between the pK_s values of the ketones and the improvement of the product yield by $CeCl_3$ or $LiClO_4$. The higher the acidity of the ketones, the lower is the yield of the inactivated addition of acetylides and the more pronounced is the increase of the yield in the presence of $CeCl_3$ or $LiClO_4$[10].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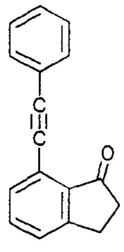
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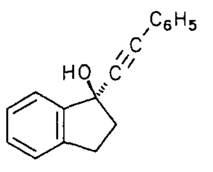
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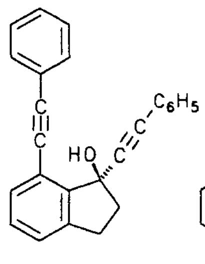
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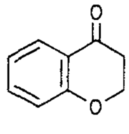
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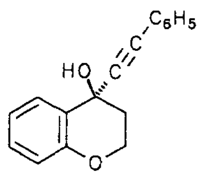
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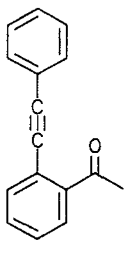
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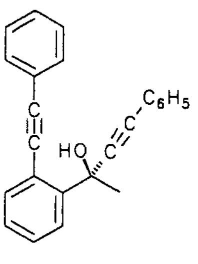
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A remarkable increase of the yield by means of 5 M ethereal solution of $LiClO_4$ was also observed in the addition of *n*-butylmagnesium bromide to dibenzyl ketone as well as to β-tetralone or by the addition of isopropylmagnesium chloride to cyclohexanone. Although this improvement of the yield by 5 M $LiClO_4$ was lower compared to the reactions performed in the presence of $CeCl_3$ in the case of β-tetralone (see Table 2). Similar to $CeCl_3$ also 5 M ethereal $LiClO_4$ suppresses the reduction of 2,4-dimethyl-3-pentanone during the addition of *n*-propylmagnesium bromide in favor of the addition product. Presumably, due to higher sterical demand, $LiClO_4$ shows no effect on the ratio of addition to reduction product in the reaction of 2,4-dimethyl-3-pentanone with isopropylmagnesium bromide[11]. In this case $CeCl_3$ is superior to $LiClO_4$.

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Table 1. Addition of lithium phenylacetylide (**2**) to ketones **1**, **4**, **5**, **8** and **10**

Ketone	Medium	Temp. (°C)	Time (h)	Product	yield (%)
1	$LiClO_4$/Ether	20	0.25	**3**	99
1	$CeCl_3$/THF	0	0.5	**3**	98
1	THF	0	2	**3**	29
4	$LiClO_4$/Ether	20	0.25	**6**	71
4	$CeCl_3$/THF	0	0.5	**6**	77
4	THF	0	2	**6**	40
5	$LiClO_4$/Ether	20	0.25	**7**	70
5	$CeCl_3$/THF	0	0.5	**7**	73
5	THF	0	2	**7**	45
8	$LiClO_4$/Ether	20	0.25	**9**	42
8	$CeCl_3$/THF	0	0.5	**9**	44
8	THF	0	2	**9**	16
10	$LiClO_4$/Ether	20	0.25	**11**	97
10	$CeCl_3$/THF	0	0.5	**11**	99
10	THF	0	2	**11**	66

Experimental

Elemental analyses: Carlo Erba Modell 1104. – IR: Bruker IFS 25. – UV: Hewlett-Packard 8452A Diode array spectrophotometer. – ^1H and ^{13}C NMR: Bruker AM 400 or AC 200, respectively. – MS: Varian MAT 311A or Varian MAT 111. – $LiClO_4$ (Fluka) was dried at 140°C for 24 h at 0.5 Torr. Perfluoro-1-octanesulfonyl fluoride and 4-chromanone (Aldrich), 2-hydroxyacetophenone and phenylacetylene (Janssen), 7-hydroxyindanone[12], and bis(triphenylphosphane)palladium(II) chloride[13]. All reactions were carried out under argon.

General Method for Preparation of 7-(Phenylethynyl)-1-indanone (**5**) *and 2-(Phenylethynyl)acetophenone* (**10**): 10 mmol of 7-hydroxyindanone or 2-hydroxyacetophenone, 5.53 g (11 mmol) of perfluoro-1-octanesulfonyl fluoride, 1.2 g (15 mmol) of phenylacetylene, 210 mg (3 mol-%) of bis(triphenylphosphane)palladium(II) chloride, and 115 mg (6 mol-%) of CuI were heated at 80°C for 20 h in a mixture of 10 ml of DMF and 10 ml of triethylamine. After addition of 80 ml of a 0.5 N HCl solution the organic layer was extracted with diethyl ether. The ethereal phase was washed with water and dried with $MgSO_4$. After removal of the solvent the crude product was purified by silica gel column chromatography (CH_2Cl_2). Yield: 1.74 g (75%) of **5**, m.p. 67°C. – IR (KBr pellet): $\tilde{\nu}$ = 3060 cm^{-1} (aryl-H), 2978 (alkyl-H), 2209 (C≡C), 1714 (C=O), 1597, 1582 (C=C), 1491, 779, 763, 693. – UV (ethanol): λ_{max} (lg ε) = 230 nm (4.26), 246 (4.33), 280 (4.00), 288 (4.04), 296 (4.17), 332 (4.09). – ^1H NMR ($CDCl_3$): δ = 2.7–2.66 (m, 2 H), 3.10–3.05 (m, 2 H), 7.36–7.31 (m, 3 H), 7.38 (d, 1 H), 7.46 (d, 1 H), 7.49 (dd, 1 H), 7.65–7.62 (m, 2 H). – ^{13}C NMR ($CDCl_3$): δ = 25.28 (CH_2), 36.44 (CH_2), 86.64 (C), 95.47 (C), 120.33 (C), 123.14 (C), 126.26 (CH), 128.27 (2 × CH), 128.62 (CH), 131.55 (CH), 132.05 (2 × CH), 133.64 (CH), 136.36 (C), 155.69 (C), 204.61 (C=O). – MS (70 eV), *m/z* (%): 232 (100), 202 (41). – $C_{17}H_{12}O$: calcd. 232.0900; found 232.0875 (MS). – $C_{17}H_{12}O$ (232.3): calcd. C 87.90, H 5.21; found C 88.20, H 5.16.

Ketone **10**: 1.35 g (61%), light yellow oil. – IR (neat): $\tilde{\nu}$ = 3060 cm^{-1} (aryl-H), 2932 (alkyl-H), 2215 (C≡C), 1686 (C=O), 1592 (C=C), 1490, 1357, 1279, 1246, 757, 681. – UV (ethanol): λ_{max} (lg ε) = 204 nm (4.37), 222 (4.28), 248 (4.27), 290 (4.20), 308 (3.96). – ^1H NMR ($CDCl_3$): δ = 2.79 (s, 3 H), 7.38–7.33 (m, 3 H), 7.39 (ddd, 1 H), 7.46 (ddd, 1 H), 7.58–7.51 (m, 2 H), 7.62 (dd, 1 H), 7.75 (dd, 1 H). – ^{13}C NMR ($CDCl_3$): δ = 29.94 (CH_3), 88.46 (C), 95.01 (C), 121.67 (C), 122.88 (C), 128.24 (CH), 128.43 (CH), 128.65 (2 × CH), 128.72 (CH), 131.24 (CH), 131.49 (2 × CH), 133.84 (CH),

Table 2. Addition of Grignard reagents to ketones

Ketone	Grignard	Medium	Temp. (°C)	Time (h)	Product(s)	yield (%)
1	n-C_4H_9MgBr	$LiClO_4/Et_2O$	20	0.25	$(PhCH_2)_2C(OH)(n$-$C_4H_9)$[a]	74
1	n-C_4H_9MgBr	$CeCl_3$/THF	0	0.5	$(PhCH_2)_2C(OH)(n$-$C_4H_9)$[a]	82
1	n-C_4H_9MgBr	THF[14]	0	2	$PhCH_2)_2C(OH)(n$-$C_4H_9)$[a]	20
β-Tetralone	n-C_4H_9MgBr	$LiClO_4/Et_2O$	20	0.25	$(\pm)$-β-$(n$-$C_4H_9)$-β-Tetralol[a]	37
β-Tetralone	n-C_4H_9MgBr	$CeCl_3$/THF	0	0.5	$(\pm)$-β-$(n$-$C_4H_9)$-β-Tetralol[a]	75
β-Tetralone	n-C_4H_9MgBr	THF[14]	0	2	$(\pm)$-β-$(n$-$C_4H_9)$-β-Tetralol[a]	6
Cyclohexanone	i-C_3H_7MgCl	$LiClO_4/Et_2O$	20	0.25	1-$(i$-$C_3H_7)$-Cyclohexanol[b]	63
Cyclohexanone	i-C_3H_7MgCl	$CeCl_3$/THF[2]	0	0.5	1-$(i$-$C_3H_7)$-Cyclohexanol[b]	72
Cyclohexanone	i-C_3H_7MgCl	THF[2]	0	2	1-$(i$-$C_3H_7)$-Cyclohexanol[b]	30
$(i$-$C_3H_7)_2CO$	n-C_3H_7MgBr	$LiClO_4/Et_2O$	20	0.25	$(i$-$C_3H_7)_2C(OH)(n$-$C_3H_7)$[b]	71
					$(i$-$C_3H_7)_2CH(OH)$[b]	29
$(i$-$C_3H_7)_2CO$	n-C_3H_7MgBr	$CeCl_3$/THF	0	0.5	$(i$-$C_3H_7)_2C(OH)(n$-$C_3H_7)$[b]	25
$(i$-$C_3H_7)_2CO$	n-C_3H_7MgBr	THF	0	2	$(i$-$C_3H_7)_2C(OH)(n$-$C_3H_7)$[b]	35
					$(i$-$C_3H_7)_2CH(OH)$[b]	65
$(i$-$C_3H_7)_2CO$	i-C_3H_7MgCl	$LiClO_4/Et_2O$	20	0.25	$(i$-$C_3H_7)_3C(OH)$[b]	9
					$(i$-$C_3H_7)_2CH(OH)$[b]	56
$(i$-$C_3H_7)_2CO$	i-C_3H_7MgCl	$CeCl_3$/THF[2]	0	0.5	$(i$-$C_3H_7)_3C(OH)$[b]	52
					$(i$-$C_3H_7)_2CH(OH)$[b]	31
$(i$-$C_3H_7)_2CO$	i-C_3H_7MgCl	THF[2]	0	2	$(i$-$C_3H_7)_3C(OH)$[b]	3
					$(i$-$C_3H_7)_2CH(OH)$[b]	58

[a] Isolated yields. – [b] Yields determined by ^1H NMR and GC MS.

140.79 (C), 200.26 (C=O). – MS (70 eV), m/z (%): 220 (83), 205 (100), 176 (40). – $C_{16}H_{12}O$: calcd. 220.0888; found 220.0877 (MS). – $C_{16}H_{12}O$ (220.3): calcd. C 87.25, H 5.49; found C 87.05, H 5.21.

General Procedure for the Reaction of the Ketones **1**, **4**, **5**, **8**, *and* **10** *with Lithium Phenylacetylide in 5* M *$LiClO_4$/Diethyl Ether:* A solution of 0.216 g (2 mmol) of the acetylide in 5 ml of 5 M $LiClO_4$/diethyl ether was added to 1 mmol of the ketone in 4 ml of 5 M $LiClO_4$ in diethyl ether at 20°C. After 15 min, 50 ml of a saturated NH_4Cl solution was added. The Product was extracted with diethyl ether, the extract washed with a saturated NaCl solution and dried with $MgSO_4$.

1,3-Diphenyl-2-(phenylethynyl)-2-propanol (**3**): 309 mg (99%), light yellow oil after chromatography on neutral Al_2O_3 (diethyl ether/pentane, 3:1). – IR (neat): $\tilde{\nu}$ = 3441 cm^{-1} (OH), 3061, 3029 (aryl-H), 2921 (alkyl-H), 2228 (C≡C), 1599 (C=C), 1494, 1454, 1085 (C–O), 1031, 756, 701. – UV (ethanol): λ_{max} (lg ε) = 210 nm (4.41), 244 (4.25), 254 (4.18). – ^1H NMR ($CDCl_3$): δ = 2.13 (s, 1 H), 3.10 (s, 4 H), 7.36–7.26 (m, 11 H), 7.43–7.39 (m, 4 H). – ^{13}C NMR ($CDCl_3$): δ = 48.23 (2 × CH_2), 71.52 (C), 87.10 (C), 91.15 (C), 122.70 (C), 126.94 (2 × CH), 128.03 (4 × CH), 128. 32 (CH), 130.97 (4 × CH), 131.47 (2 × CH), 136.28 (2 × C). – MS (70 eV), m/z (%): 312 (3), 294 (6), 221 (80), 129 (46), 91 (100). – $C_{23}H_{20}O$: calcd. 312.1514; found 312.1508 (MS). – $C_{23}H_{20}O$ (312.4): calcd. C 88.42, H 6.45; found C 88.15, H 6.19.

1-(Phenylethynyl)-1-indanol (**6**): 166 mg (71%), light yellow oil after chromatography on neutral Al_2O_3 (diethyl ether). – IR (neat): $\tilde{\nu}$ = 3372 cm^{-1} (OH), 3068 (aryl-H), 2974, 2935 (alkyl-H), 2226 (C≡C), 1598 (C=C), 1490, 1070, 1039, 944, 757, 691. – UV (ethanol): λ_{max} (lg ε) = 204 nm (4.35), 244 (4.21), 254 (4.14), 272 (3.10). – ^1H NMR ($CDCl_3$): δ = 2.33 (s, 1 H), 2.56–2.49 (m, 1 H), 2.70–2.61 (m, 1 H), 3.00–2.91 (m, 1 H), 3.21–3.11 (m, 1 H), 7.32–7.26 (m, 6 H), 7.46–7.42 (m, 2 H), 7.62–7.56 (m, 1 H). – ^{13}C NMR ($CDCl_3$): δ = 29.64 (CH_2), 43.27 (CH_2), 76.79 (C), 84.91 (C), 91.06 (C), 122.66 (C), 123.28 (CH), 125.08 (CH), 127.13 (CH), 128.23 (CH), 128.38 (2 × CH), 129.02 (CH), 131.72 (2 × CH), 143.08 (C), 145.78 (C). – MS (70 eV), m/z (%): 234 (4), 233 (7), 215 (83). – $C_{17}H_{14}O$: calcd. 234.1045; found 234.1031 (MS). – $C_{17}H_{14}O$ (234.3): calcd. C 87.15, H 6.02; found C 86.99, H 5.85.

1,7-Bis(phenylethynyl)-1-indanol (**7**): 234 mg (70%), light yellow oil after chromatography on neutral Al_2O_3 (CH_2Cl_2). – IR (neat): $\tilde{\nu}$ = 3550 cm^{-1}, 3440 (OH), 3054 (aryl-H), 2946 (alkyl-H), 2210 (C≡C), 1599 (C=C), 1491, 1443, 1070, 755, 690. – UV (ethanol): λ_{max} (lg ε) = 205 nm (4.57), 226 (4.49), 248 (4.34), 274 (4.14), 288 (4.29), 296 (4.17), 306 (4.25). – ^1H NMR ($CDCl_3$): δ = 2.59–2.50 (m, 1 H), 2.86–2.78 (m, 1 H), 3.12–2.96 (m, 2 H), 3.52 (s, 1 H), 7.33–7.18 (m, 8 H), 7.37–7.34 (m, 2 H), 7.43 (d, 1 H), 7.55–7.50 (m, 2 H). – ^{13}C NMR ($CDCl_3$): δ = 29.32 (CH_2), 42.11 (CH_2), 76.95 (C), 85.37 (C), 86.16 (C), 91.00 (C), 95.58 (C), 118.38 (C), 122.79 (C), 122.89 (C), 125.47 (CH), 128.10 (2 × CH), 128.17 (2 × CH), 128.37 (CH), 128.60 (CH), 128.75 (CH), 130.83 (CH), 131.59 (2 × CH), 131.76 (2 × CH), 143.14 (C), 146.38 (C). – MS (70 eV), m/z (%): 334 (100), 315 (63). – $C_{25}H_{18}O$: calcd. 334.1357; found 334.1448 (MS). – $C_{25}H_{18}O$ (334.4): calcd. C 89.79, H 5.42; found C 89.99, H 5.52.

4-(Phenylethynyl)-4-chromanol (**9**): 105 mg (42%), light yellow oil after chromatography on neutral Al_2O_3 (diethyl ether). – IR (neat): $\tilde{\nu}$ = 3448 cm^{-1} (OH), 3060 (aryl-H), 2965, 2928 (alkyl-H), 2216 (C≡C), 1607, 1582 (C=C), 1488, 1452, 1224, 1107, 1053, 756, 691. – UV (ethanol): λ_{max} (lg ε) = 206 nm (4.67), 244 (4.43), 252 (4.40), 278 (3.77), 284 (3.71). – ^1H NMR ($CDCl_3$): δ = 2.40–2.24 (m, 4 H), 2.50 (s, 1 H), 6.77–6.72 (dd, 1 H), 6.88–6.83 (ddd, 1 H), 7.15 (ddd, 1 H), 7.22–7.17 (m, 3 H), 7.36–7.31 (m, 2 H), 7.65–7.62 (dd, 1 H). – ^{13}C NMR ($CDCl_3$): δ = 37.27 (CH_2), 62.42 (CH), 64.21 (C), 84.86 (C), 91.54 (C), 117.31 (CH), 120.86 (CH), 122.36 (C). 125.26 (C), 128.30 (3 × CH), 128.60 (CH), 130.15 (CH), 131.73 (2 × CH), 153.53 (C). – MS (70 eV), m/z (%): 250 (15), 232 (100). – $C_{17}H_{14}O_2$: calcd. 250.0994; found 250.0984 (MS). – $C_{17}H_{14}O_2$ (250.3): calcd. C 81.58, H 5.64; found C 81.45, H 5.51.

1-(Phenylethynyl)-1-[2-(phenylethynyl)phenyl]ethanol (**11**): 312 mg (97%), light yellow oil after chromatography on neutral Al_2O_3 (CH_2Cl_2/pentane, 1:1). – IR (neat): $\tilde{\nu}$ = 3416 cm^{-1} (OH), 3057 (aryl-H), 2981, 2931 (alkyl-H), 2232 (C≡C), 1598 (C=C), 1491, 1442, 1069, 755, 690. – UV (ethanol): λ_{max} (lg ε) = 222 nm (4.13), 244 (4.17), 254 (4.17), 272 (4.00), 286 (4.17), 294 (4.03), 304 (4.15). – ^1H NMR ($CDCl_3$): δ = 2.01 (s, 3H), 3.59 (s, 1H), 7.13–7.05 (m, 3H), 7.21–7.13 (m, 4H), 7.29–7.21 (m, 3H), 7.44–7.39 (m, 2H), 7.51 (dd, 1H), 7.68 (dd, 1H). – ^{13}C NMR ($CDCl_3$): δ = 30.12 (CH_3), 69.84 (C), 84.50 (C), 88.47 (C), 92.41 (C), 96.59 (C), 120.25 (C), 122.73 (C), 123.02 (C), 124.75 (CH), 127.48 (CH), 128.10 (2 × CH), 128.20 (2 × CH), 128.37 (2 × CH), 128.51 (CH), 131.36 (2 × CH), 131.71 (2 × CH), 134.13 (CH), 146.37 (C). – MS (70 eV), *m/z* (%): 322 (43), 321 (100), 307 (78). – $C_{24}H_{18}O$: calcd. 322.1358; found 322.1325 (MS). – $C_{24}H_{18}O$ (322.4): calcd. C 89.41, H 5.63; found C 89.17, H 5.33.

General Procedure for the Reaction of the Ketones **1**, **4**, **5**, **8**, *and* **10** *with Lithium Phenylacetylide in the Presence of $CeCl_3$:* 745 mg (2 mmol) of $CeCl_3 \cdot 7\, H_2O$ (Fluka) was dried at 140°C and 0.5 Torr for 4h, then cooled to 0°C and stirred with 4 ml of THF for 12h. After addition of 1 mmol of the respective ketone in 2 ml of THF and stirring of the mixture for 2h, 2 mmol of phenylacetylide in 2 ml of THF was added. After 30 min, 20 ml of a saturated NH_4Cl solution was added. Further procedure as above. – **3**: 306 mg (98%); **6**: 180 mg (77%); **7**: 245 mg (73%); **9**: 110 mg (44%); **11**: 319 mg (99%).

General Procedure for the Reaction of the Ketones **1**, **4**, **5**, **8**, *and* **10** *with Lithium Phenylacetylide without a Lewis Acid in THF:* 2 mmol of phenylacetylide in 2 ml of THF was added to a solution of 1 mmol of the respective ketone in 2 ml of THF at 0°C. After 2h, 20 ml of a saturated NH_4Cl solution was added. Further procedure as above. – **3**: 91 mg (29%); **6**: 96 mg (41%); **7**: 150 mg (45%); **9**: 40 mg (16%); **11**: 213 mg (66%).

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