Phosphonium Salt Catalyzed Addition of Diethylzinc to Aldehydes

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Abstract: The addition of diethylzinc to aromatic, heteroaromatic, and aliphatic aldehydes at room temperature is efficiently catalyzed by 1–7 mol% tetrabutylphosphonium chloride. The corresponding addition products are obtained in good to excellent yields of up to 99%. Moreover, polymer bond phosphonium salts can be used to catalyze this reaction with excellent recovery of the polymer bond catalyst up to three cycles. The application of chiral bifunctional phosphonium salts revealed a remarkable counter anion effect. Changing the anion, the activity of the tetrabutylphosphonium salt decreased in the order $Cl^- > Br^- > I^- \approx TsO^- > BF_4^- \approx PF_6^-$. However, the nature of the cation had also significant influence. Tetraalkylammonium chlorides showed similar activity compared to phosphonium chlorides, while alkaline metal chlorides proved to be considerably less active.

Key words: catalysis, phosphonium salt, addition, diethylzinc, aldehydes

Among the organic transformations carbon–carbon bond-forming processes are of considerable importance. In particular, the nucleophilic addition reaction of organozinc reagents to carbonyl compounds offers elegant opportunities for the synthesis of a variety of multifunctional substrates. Although organozinc compounds are long known,[1] their application in organic synthesis has been developed only over the past three decades[2] and led to significant success regarding chemical yields and enantiomeric purities of the addition products.[3] Nevertheless, this research area remains an object of intensive research.[4] Chiral ligands such as amino alcohols as well as Lewis acid chiral transition-metal complexes are typically employed as catalysts. The term Lewis acid catalysts generally refers to metal salts like aluminum, titanium, or iron chloride.[5] However, not only metal centers can function as Lewis acids,[6] but compounds containing for example carbenium,[7] imidazolinium,[8] imidazolium,[9] or phosphonium[10] cations also exhibit Lewis acidity. Only very few examples for the addition of alkylzinc reagents to aldehydes catalyzed by onium salts are known.[11] McNulty et al. reported the addition of diethylzinc to benzaldehyde in the presence of a phosphonium salt presumably acting as a mild Lewis acidic catalyst.[11d] To the best of our knowledge this is the only example for the addition of an organozinc reagent to a carbonyl group catalyzed by a phosphonium salt. We are generally interested in the use of (chiral) phosphonium salts as Lewis acidic catalysts.[6a]

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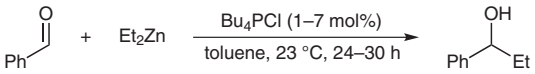
This provoked us to evaluate the potential of inexpensive and commercially available phosphonium salts as Lewis acidic catalysts for the addition of organozinc reagents to aldehydes. The frequently used benchmark for the evaluation of new catalysts is the addition of diethylzinc to benzaldehyde (**1a**). Herein we report the application of commercially available tetrabutylphosphonium chloride as a catalyst for this conversion. As expected the reaction proceeded very sluggishly in the absence of a catalyst.[11d,12] Even at room temperature the conversion was <20% after 24 hours (Table 1, entry 1). However, to our delight quantitative conversion was observed after 24 hours at room temperature in the presence of 7 mol% of Bu_4PCl (entry 2). If lower amounts of catalyst (1 and 5 mol%) were employed the desired alcohol **2a** could still be isolated in up to 90% yield (entries 3 and 4).

Table 1 Bu_4PCl-Catalyzed Addition of Et_2Zn to Benzaldehyde (**1a**)



1a **2a**

Entry	Bu_4PCl (mol%)	Et_2Zn (equiv)	Time (h)	Yield (%)
1	–	2.0	24	11[a]
2	7	2.0	24	95[a]
3	5	2.0	24	90[b]
4	1	2.0	24	90[a]
5	5	1.0	24	53[b]
6	5	0.5	24	80[b]
7	7	1.0	30	93[b]
8	7	0.5	30	67[b]

[a] Determined by GC with hexadecane as internal standard.
[b] Isolated yield.

The conversion of **1a** with 1.0 and even 0.5 equivalents of diethylzinc and 5 mol% of the catalyst gave **2a** in 80 and 53% yield, respectively (entries 5 and 6). In both cases the yields could be improved by increasing the amount of catalyst to 7 mol% and an extended reaction time of 30 hours (entries 7 and 8). For further evaluation of the scope of this catalyst a range of aromatic aldehydes were employed (Table 2). First, we were interested in the selectivity of the reaction concerning 1,2- versus 1,4-addition as well as the selectivity with respect to aldehydes and ketones. To explore the chemoselectivity of the reaction, initially

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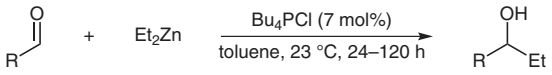
1 mol% Bu_4PCl of the catalyst and one equivalent of diethylzinc in the conversion of cinnamaldehyde (**1b**) and 4-acetylbenzaldehyde (**1c**) were used. However, the reaction proceeded very slowly under these conditions. When two equivalents of diethylzinc were utilized the conversion was quantitative after 72 hours. The addition occurred selectively to the carbonyl group of the aldehyde and the corresponding products **2b** and **2c** were isolated in excellent yields (Table 2, entries 1 and 2). In order to generally achieve full conversion in a reasonable reaction time, 7 mol% of the catalyst was used. Several 4-substituted benzaldehyde derivatives were converted under these conditions and the corresponding alcohols **2d–i** were obtained in good to excellent yields (entries 3–8). If 2-chloro- (**1j**) or 3-chlorobenzaldehyde (**1k**) is used instead of the 4-isomer **1h**, the addition product could be isolated in 85 and 91% yield, respectively (entries 9 and 10). The conversion of 1-naphthyl **1l** (entry 11) as well as of the sterically crowded di- and trisubstitued aromatic aldehydes **1m** and **1n** was also succesfully accomplished (entries 12 and 13). Though yields were slightly lower, it is noteworthy that even the hydroxy derivative **2n** was obtained in 80% yield. Our attention was next turned to the conversion of aliphatic and heteroaromatic substrates. Under our standard conditions the reaction of Et_2Zn and heptanal (**1o**) gave the desired product in a moderate yield of 51% (entry 14). Beside unreacted starting material **1o**, the corresponding alcohol and aldol products were observed. The heteroaromatic substrates **1p** and **1q**, however, reacted very sluggishly. To achieve full conversion a much longer reaction time was needed. Nevertheless, alcohol **2p** was obtained in 72% yield whereas the conversion of **1q** gave **2q** in 74% yield (entries 15 and 16).

Table 2 Bu_4PCl-Catalyzed Addition of Et_2Zn to Various Aldehydes **1**[a]



1b–q **2b–q**

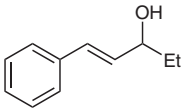
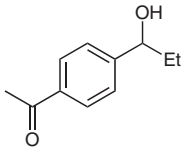
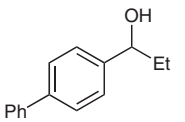
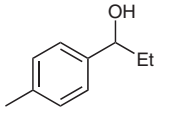
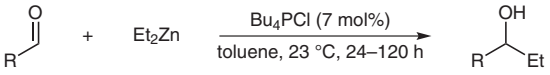
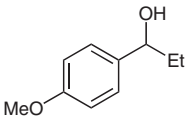
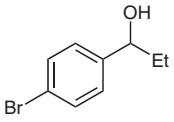
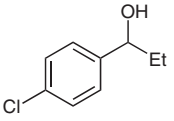
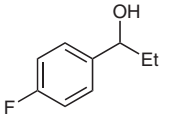
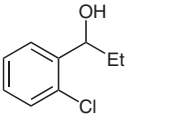
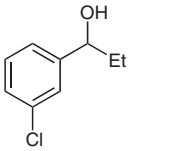
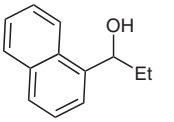
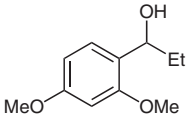
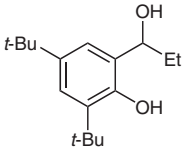
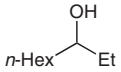
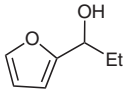
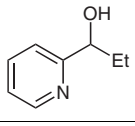
Entry	Aldehyde	Time (h)	Product		Yield (%)[b]
1	**1b**	72		**2b**	87[c]
2	**1c**	72		**2c**	89[c]
3	**1d**	30		**2d**	97
4	**1e**	30		**2e**	96

Table 2 Bu_4PCl-Catalyzed Addition of Et_2Zn to Various Aldehydes **1**[a] (continued)



1b–q **2b–q**

Entry	Aldehyde	Time (h)	Product		Yield (%)[b]
5	**1f**	30		**2f**	94
6	**1g**	30		**2g**	98
7	**1h**	30		**2h**	99
8	**1i**	24		**2i**	92
9	**1j**	30		**2j**	85
10	**1k**	30		**2k**	91
11	**1l**	30		**2l**	87
12	**1m**	30		**2m**	85
13	**1n**	30		**2n**	80
14	**1o**	30		**2o**	51
15	**1p**	120		**2p**	72[c]
16	**1q**	120		**2q**	74[c]

[a] Reaction conditions: Bu_4PCl (7 mol%), Et_2Zn (2 equiv), toluene, 23 °C.
[b] Isolated yields.
[c] Bu_4PCl used: 1 mol%.

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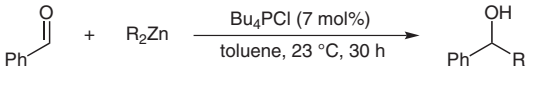
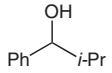
Our attention was then turned to the conversion of other commercially available organozinc reagents (Table 3). Under our standard conditions the reaction of Ph_2Zn with benzaldehyde (**1a**) yielded the desired product **2r** only in moderate yield (Table 3, entry 1). The conversion of **1a** with Bu_2Zn and *i*-Pr_2Zn gave the corresponding products **2s** and **2t** only in low isolated yield of 40 and 26%, respectively (entries 2 and 3). Interestingly, besides unreacted starting material significant amounts of benzyl alcohol were detected in the crude reaction mixture as a by-product in both cases. Moreover, in the addition of *i*-Pr_2Zn the corresponding ketone was isolated in 12% yield. The addition of Cy_2Zn to benzaldehyde (**1a**) lead to complex reaction mixtures (entry 4) and the desired product could not be detected.

Table 3 Bu_4PCl-Catalyzed Addition of R_2Zn to Benzaldehyde (**1a**)[a]



1a **2r–u**

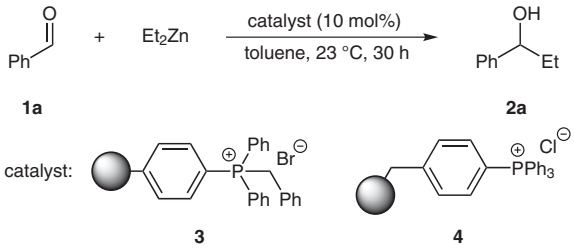
Entry	R	Product		Yield (%)[b]
1	Ph		**2r**	58
2	Bu		**2s**	40
3	*i*-Pr		**2t**	26
4	Cy		**2u**	–[c]

[a] Conditions: Bu_4PCl (7 mol%), R_2Zn (2 equiv), toluene, 24 h, 23 °C.
[b] Isolated yield.
[c] Not detected.

The possibility of employing immobilized phosphonium salts as recyclable catalysts in the addition of diethylzinc to aldehydes was explored further. Benzaldehyde (**1a**) was employed as a model substrate and polystyrene bond benzyltriphenylphosphonium bromide (**3**) and triphenylphosphonium chloride (**4**) as catalysts (Table 4). In the presence of 10 mol% of **3** based on the polymer loading the conversion after 30 hours at 23 °C was only 83% (Table 4, entry 1). In contrast the chloride salt **4** showed higher activity. In the indicated reaction time 99% conversion under selective formation of the desired product **2a** was observed (entry 2). The catalyst could be almost completely recovered from the reaction mixture and was reused. In the second cycle comparable results were obtained (entry 3). Again the catalyst was recovered and reused in a third cycle. Lower conversion was observed in this run but the desired product **2a** could still be isolated in 67% yield (entry 4).

Having established tetrabutylphosphonium chloride as an efficient catalyst for the addition of diethyl zinc to aldehydes we were interested in developing an asymmetric version of this reaction. Hence, bifunctional chiral phosphonium salts **6** and **8** were prepared (Scheme 1). The β-aminophosphonium salt **6** was readily prepared from L-prolinol (**5**) by treatment with triphenylphosphine and HBr as described by Anderson.[13] The reaction of (*R*)-BINAP (**7**) with one equivalent of MeI selectively afforded salt **8**.[14] It was envisioned that these compounds might show a dual mode of activation. Based on our results we presumed the activation of the carbonyl group by the Lewis acidic phosphonium cation and the activation of the zinc reagent by the second functional group.

Table 4 Polymer Bond Phosphonium Salt Catalyzed Addition of Et_2Zn to Benzaldehyde (**1a**)[a]

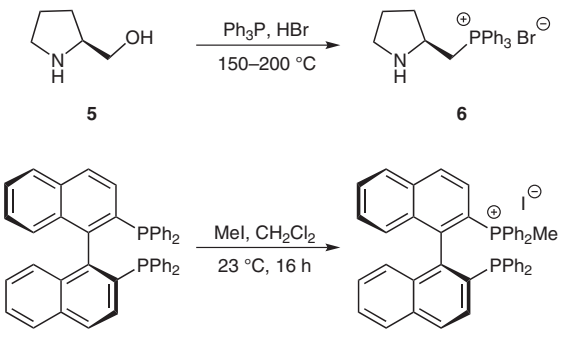


1a **2a**

3 **4**

Entry	Catalyst	Cycle	Recovery (%)	Conv. (%)[b]	Yield (%)[c]
1	**3**	1	99	83	62
2	**4**	1	99	99	99
3	**4**	2	99	90	90
4	**4**	3	63	77	67[b]

[a] Conditions: catalyst (10 mol%), R_2Zn (2 equiv), toluene, 30 h, 23 °C.
[b] Determined by GC with hexadecane as internal standard.
[c] Isolated yield.



5 **6**

7 **8**

Scheme 1 Preparation of chiral phosphonium salts **6** and **8**

Subsequently **6**, **8**, and the commercially available [(2*S*)-3-hydroxy-2-methylpropyl](triphenyl)phosphonium bromide (**9**)[15] were employed as chiral catalysts for the conversion of benzaldehyde (**1a**) with diethylzinc (Table 5). In all three cases the isolated yields of the corresponding alcohol **2a** were slightly lower (68–77%) compared to the reaction in which tetrabutylphosphonium chloride was

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employed as catalyst. It is noteworthy that in case of catalyst **8** the lowest yield was obtained (Table 5, entry 2). Moreover, to our surprise and disappointment no enantiomeric excess was observed.

Table 5 Addition of Et_2Zn to Benzaldehyde (**1a**) Catalyzed by Chiral Phosphonium Salts[a]

Entry	Catalyst	Substrate	Product	Yield(%)[b]	ee (%)[c]
1	**6**	**1a**	**2a**	77	<5
2	**8**	**1a**	**2a**	68	<5
3	**9**	**1a**	**2a**	77[c]	<5

[a] Reaction conditions: catalyst (7 mol%), Et_2Zn (2 equiv), toluene, 23 °C.
[b] Isolated yield.
[c] Determined by Chiral HPLC.

A possible explanation would be the formation of a phosphorane along with EtZnCl after the addition of Et_2Zn to the aldehyde. EtZnCl itself is a Lewis acid and could catalyze further addition reactions. However, the only observed signal in the ^{31}P NMR spectrum was assigned to the phosphonium salt. The formation of a phosphorane was not observed in ^{31}P NMR spectrum. These findings provoked us to further investigate the influence of the phosphonium cation structure as well as the effect of the counter anion on the reactivity. In the presence of a range of structurally different phosphonium salts (7 mol%) **1a** was converted into **2a** with diethylzinc at 23 °C for 24 hours. The results are summarized in Table 6. Initial experiments were performed based on salts containing tetrabutylphosphonium as the cation. If the chloride or bromide salt were employed as the catalyst the conversion is almost quantitative and yields >90% were obtained (Table 6, entries 1 and 2). To clearly distinguish the reactivity of the chloride and the bromide salt the reaction time was reduced to 6 hours (entries 3 and 4). In the presence of tetrabutylphosphonium chloride 72% conversion and 71% yield were observed after 6 hours (entry 3), whereas the bromide gave significant lower conversion and yield (entry 4). Utilizing the iodide salt the yield and conversion after 24 hours were 82 and 79%, respectively (entry 5). Similar results were obtained with the tosylate (entry 6). However, the influence of the anion is even more significant when the less basic BF_4^- or PF_6^- salts were employed (entries 7 and 8). In these cases conversions and yields lay far below 50%. Based on these results the order of activation in respect to the anion is: $Cl^- > Br^- > I^- \approx TsO^- > BF_4^- \approx PF_6^-$. On the contrary, the structure of the cation seems to have no significant influence, since tetrabutyl-, tetraphenyl-, methyltriphenyl-, as well as benzyltriphenylphosphonium chloride gave conversions >99% and similar yields (entries 1, 9–11). However, if the nature of the cation is changed from phosphonium to ammonium the yield dropped from >99% (entry 1) to 76% (entry 12). If ammonium salts with sterically less demanding substituents were employed, higher yields up to 97% could be obtained (entries 13 and 14). It is noteworthy that, if simple lithium, sodium or potassium chloride was employed as catalyst, the desired product **1a** was obtained only in low yield <35% indicating the significant influence of the nature of the cation (entries 15–17).

Table 6 Conversion of **1a** in the Presence of Different Phosphonium Salt Catalysts[a]

Entry	Catalyst	Time (h)	Conv. (%)[b]	Yield(%)[b]
1	$[Bu_4P]Cl$	24	>99	97
2	$[Bu_4P]Br$	24	95	94
3	$[Bu_4P]Cl$	6	72	71
4	$[Bu_4P]Br$	6	57	57
5	$[Bu_4P]I$	24	82	79
6	$[Bu_4P]OTs$	24	77	74
7	$[Bu_4P]BF_4$	24	28	28
8	$[Bu_4P]PF_6$	24	34	25
9	$[Ph_4P]Cl$	24	>99	91
10	$[Ph_3PMe]Cl$	24	>99	93
11	$[Ph_3PBn]Cl$	24	>99	96
12	$[Bu_4N]Cl$	24	78	76
13	$[Et_4N]Cl$	24	97	96
14	$[Et_3NBn]Cl$	24	94	93
15	LiCl	24	35	33
16	NaCl	24	33	30
17	KCl	24	31	31

[a] Conditions: catalyst (7 mol%), Et_2Zn (2 equiv), toluene, 23 °C.
[b] Determined by GC with hexadecane as internal standard.

Tian and Plumet et al. described the addition of TMSCN to aldehydes and ketones catalyzed by simple phosphonium salts.[16] The authors proposed a double activation mechanism in which the Lewis acidic phosphonium cation coordinates to the carbonyl group of the ketone and thereby increases its electrophilicity. On the other hand IR spectroscopic experiments imply a Lewis basic activation of TMSCN by the anion.

So far our attempts to identify the activation mode by in situ IR and NMR spectroscopy were not successful. However, based on our results it can be concluded that beside the possible Lewis acidic activation by the phosphonium cation a second (nucleophilic) activation mode by the anion has to be taken into account as well. Halide effects are generally recognized in transition metal catalysis and have been observed even in the addition of organozinc reagents to aldehydes.[17] Knochel et al. reported the activation of diorganozinc reagents by $MgCl_2$ by the possible formation of ate complex intermediates in analogy to the

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Suzuki reaction where a boronic acid is converted into a boronate through the addition of a base.[18]

In conclusion, we have described a novel procedure for the addition of diethylzinc to aldehydes under mild conditions in the presence of catalytic amounts of inexpensive and commercially available tetrabutylphosphonium chloride. The desired products were usually obtained in good to excellent yields. Moreover, polymer bond phosphonium salts could be employed as recyclable catalysts. However, when chiral bifunctional catalysts based on phosphonium salts were employed, no asymmetric induction has been observed. In this context we explored the effect of the anion and cation on the catalyst activity. For tetrabutylphosphonium salts, activity strongly depended on the nature of the anion ($Cl^- > Br^- > I^- \approx TsO^- > BF_4^- \approx PF_6^-$). In addition, the nature of the cation had also significant influence. Tetraalkylammonium chlorides showed similar activity compared to phosphonium chlorides, while alkaline metal chlorides proved to be considerably less active.

All reactions were carried out under argon atmosphere using Schlenk techniques. Toluene was dried over Na and freshly distilled before use. All starting materials as well as the polymer bond phosphonium salt **9** were commercially available and used without further purification except benzaldehyde (**1a**), which was purified by distillation and then stored under argon atmosphere. TLC was performed on Macherey-Nagel silica gel plates 60 (UV 254). Preparative column chromatography was carried out using Macherey-Nagel M60 silica gel (0.04–0.063 mm) with cyclohexane and EtOAc as eluents for flash column chromatography. NMR spectra were recorded on a Bruker AV 400 or a Bruker AV 300 spectrometer. Multiplicities of carbon signals were determined by DEPT experiments. Mass spectra were recorded on an MAT 95XP mass spectrometer from Thermo. IR spectra were recorded on a Bruker Alpha P spectrophotometer. Elemental analyses were performed on a TruSpec CHNS micro analyzer from Leco. Chiral HPLC was performed on an Agilent 1100 HPLC System with a Chiralcel OD-H column.

Bu_4PCl Catalyzed Addition of Et_2Zn to Aldehydes 1; General Procedure

To a solution of aldehyde **1** (1.50 mmol, 1.0 equiv) in anhyd toluene (c = 2.5 mmol mL^{-1}) was added Bu_4PCl (1–7 mol%). The mixture was cooled to 0 °C, followed by dropwise addition of Et_2Zn in toluene (2.7 mL, 3.0 mmol, c = 1.1 mmol mL^{-1}, 2.0 equiv). The reaction mixture was allowed to warm to 23 °C and stirred for 24–120 h. The mixture was quenched with aq HCl (5 mL, c = 1 mmol mL^{-1}) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and all volatiles were removed in vacuo. The residue was purified by chromatography on silica gel (SiO_2) with cyclohexane and EtOAc as eluents.

Addition of Et_2Zn to Benzaldehyde (1a) Catalyzed by Polymer Bound Phosphonium Salts 3 and 4; General Procedure

To a solution of benzaldehyde (**1a**; 300 mg, 2.83 mmol, 1.0 equiv) in anhyd toluene (c = 0.38 mmol mL^{-1}) was added catalyst **3** or **4** (10 mol%). The mixture was cooled to 0 °C, followed by dropwise addition of Et_2Zn in toluene (5.1 mL, c = 1.1 mmol mL^{-1}, 5.61 mmol, 2.0 equiv). The mixture was allowed to warm to 23 °C and was then shaken for 30 h. Subsequently aq HCl (1 M, c = 3.1 mmol mL^{-1}) and CH_2Cl_2 (c = 3 mmol mL^{-1}) were added, the mixture was shaken for 1 min and the CH_2Cl_2 was carefully removed again. This procedure was repeated twice, and then the combined organic layers were dried ($MgSO_4$), and the solvent removed by rotary evaporation. The residue was purified by chromatography on silica gel (cyclohexane–EtOAc, 10:1) to yield the desired product **2a** as a colorless liquid. The aqueous phase of the extraction procedure was filtered and the residue was washed with aq HCl (1 M, 3 × 5 mL), distilled H_2O (3 × 5 mL), and then dried till constant weight to regain the polymer for recylization. When catalyst **3** was used, the residue was washed with aq HBr.

1-Phenylpropan-1-ol (2a)[19]

Benzaldehyde (**1a**; 159 mg, 1.50 mmol) was converted with Et_2Zn in toluene (2.7 mL, 3.0 mmol) in the presence of Bu_4PCl (22 mg, 0.075 mmol) into **2a**, which was isolated after chromatography (silica gel, cyclohexane–EtOAc, 10:1, R_f = 0.68) as a colorless oil (184 mg, 1.35 mmol, 90%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83 (t, ^3J = 7.3 Hz, 3 H), 1.59–1.79 (m, 2 H), 1.94 (br s, 1 H), 4.50 (t, ^3J = 6.9 Hz, 1 H), 7.16–7.29 (m, 5 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.27 (CH_3), 31.02 (CH_2), 76.13 (CH), 126.12 (2 CH), 127.61 (CH), 128.52 (2 CH), 144.79 (C).

MS (EI, 70 eV): m/z (%) = 136 ([M]$^+$, 12), 107 (100), 79 (70), 77 (39), 51 (26).

HRMS (EI, 70 eV): m/z [M]$^+$ calcd for $C_9H_{12}O$: 136.0883; found: 136.0887.

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.31; H, 8.70.

Chiral HPLC: Chiralcel OD-H, heptane–EtOH, 97:3, flow = 1.0 mL min^{-1}, t_R (enantiomer A) = 8.53 min, t_R (enantiomer B) = 9.82 min (Table 5).

(*E*)-1-Phenylpent-1-en-3-ol (2b)[20]

Aldehyde **1b** (198 mg, 1.50 mmol) was converted with Et_2Zn in toluene (2.7 mL, 3.0 mmol) in the presence of Bu_4PCl (4.4 mg, 0.015 mmol) into **2b**, which was isolated after chromatography (silica gel, cyclohexane–EtOAc, 20:1, R_f = 0.46) as a colorless oil (212 mg, 1.31 mmol, 87%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.02 (t, ^3J = 7.5 Hz, 3 H), 1.66–1.77 (m, 2 H,), 2.00 (br s, 1 H), 4.26 (ddt, ^3J = 1 Hz, ^3J = 6.5 Hz, ^3J = 6.6 Hz, 1 H), 6.26 (dd, ^3J = 15.7 Hz, ^3J = 6.5 Hz, 1 H), 6.63 (d, ^3J = 15.7 Hz, 1 H), 7.27–7.40 (m, 5 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.90 (CH_3), 30.32 (CH_2), 74.54 (CH), 126.57 (2 CH), 127.74 (CH), 128.35 (2 CH), 130.54 (CH), 132.34 (CH), 136.86 (C).

MS (EI, 70 eV): m/z (%) = 166 ([M]$^+$, 10), 148 (28), 147 (16), 137 (100), 109 (22), 94 (17), 77 (22).

1-[4-(1-Hydroxypropyl)phenyl]ethanone (2c)[21]

Aldehyde **1c** (148 mg, 1.00 mmol) was converted with Et_2Zn in toluene (1.8 mL, 2.0 mmol) in the presence of Bu_4PCl (2.9 mg, 0.010 mmol) into **2c**, which was isolated after chromatography (silica gel, cyclohexane–EtOAc, 20:1, R_f = 0.35) as a colorless oil (159 mg, 0.892 mmol, 89%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84 (t, ^3J = 7.5 Hz, 3 H), 1.18 (br s, 1 H), 1.66–1.73 (m, 2 H), 2.50 (s, 3 H), 4.59 (t, ^3J = 6.5 Hz, 1 H), 7.32–7.35 (m, 2 H, CH), 7.81–7.84 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.02 (CH_3), 26.72 (CH_3), 32.06 (CH_2), 75.38 (CH), 126.16 (2 CH), 128.59 (2 CH), 136.26 (C), 150.22 (C), 198.19 (C=O).

1-(Biphenyl-4-yl)propan-1-ol (2d)[22]

Aldehyde **1d** (273 mg, 1.50 mmol) was converted with Et_2Zn in toluene (2.7 mL, 3.0 mmol) in the presence of Bu_4PCl (30 mg, 0.10

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mmol) into **2d**, which was isolated after chromatography (silica gel, cyclohexane–EtOAc, 10:1, R_f = 0.69) as colorless crystals (308 mg, 1.45 mmol, 97%); mp 58–59 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.97 (t, ^3J = 7.4 Hz, 3 H), 1.77–1.88 (m, 2 H), 1.92 (br s, 1 H, OH), 4.66 (dt, ^3J = 3.0 Hz, ^3J = 6.4 Hz, 1 H), 7.32–7.38 (m, 1 H), 7.40–7.47 (m, 4 H), 7.57–7.62 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.36 (CH_3), 32.10 (CH_2), 75.90 (CH), 126.56 (2 CH), 127.21 (2 CH), 127.29 (2 CH), 127.38 (CH), 128.89 (2 CH), 140.58 (C), 141.02 (C), 143.74 (C).

MS (EI, 70 eV): *m*/*z* (%) = 212 ([M]$^+$, 15), 194 (22), 184 (14), 183 (100), 178 (10), 155 (44), 154 (10), 153 (16), 152 (20), 77 (12).

HRMS (EI, 70 eV): *m*/*z* [M]$^+$ calcd for $C_{15}H_{16}O$: 212.1195; found: 212.1189.

Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 85.27; H, 7.17.

1-(4-Methylphenyl)propan-1-ol (2e)[22]

Aldehyde **1e** (180 mg, 1.50 mmol) was converted with Et_2Zn in toluene (2.7 mL, 3.0 mmol) in the presence of Bu_4PCl (30 mg, 0.10 mmol) into **2e**, which was isolated after chromatography (silica gel, cyclohexane–EtOAc, 20:1, R_f = 0.83) as a colorless oil (215 mg, 1.43 mmol, 96%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.96 (t, ^3J = 7.4 Hz, 3 H), 1.74–1.92 (m, 2 H), 1.98 (d, ^3J = 3.0 Hz, 1 H), 2.41 (s, 3 H), 4.60 (dt, ^3J = 2.6 Hz, ^3J = 6.8 Hz, 1 H), 7.20–7.23 (m, 2 H), 7.27–7.31 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.33 (CH_3), 21.23 (CH_3), 31.91 (CH_2), 76.00 (CH), 126.01 (2 CH), 129.34 (2 CH), 137.25 (C), 141.76 (C).

MS (EI, 70 eV): *m*/*z* (%) = 150 ([M]$^+$, 9), 121 (100), 93 (47), 91 (43), 77 (25), 65 (10).

HRMS (EI, 70 eV): *m*/*z* [M]$^+$ calcd for $C_{10}H_{14}O$: 150.1039; found: 150.1041.

1-(4-Methoxyphenyl)propan-1-ol (2f)[22]

Aldehyde **1f** (204 mg, 1.50 mmol) was converted with Et_2Zn in toluene (2.7 mL, 3.0 mmol) in the presence of Bu_4PCl (44 mg, 0.15 mmol) into **2f**, which was isolated after chromatography (silica gel, cyclohexane–EtOAc, 20:1, R_f = 0.66) as a colorless oil (234 mg, 1.41 mmol, 94%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, ^3J = 7.6 Hz, 3 H), 1.71–1.92 (m, 2 H), 1.99 (br s, 1 H), 3.85 (s, 3 H), 4.58 (dt, ^3J = 2.3 Hz, ^3J = 7.3 Hz, 1 H), 6.91–6.94 (m, 2 H), 7.29–7.33 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.42 (CH_3), 31.96 (CH_2), 55.39 (CH_3), 75.75 (CH), 114.08 (2 CH), 127.66 (2 CH), 137.15 (C), 159.45 (C).

MS (EI, 70 eV): *m*/*z* (%) = 166 ([M]$^+$, 10), 148 (28), 147 (16), 137 (100), 109 (22), 94 (17), 77 (22).

HRMS (EI, 70 eV): *m*/*z* [M]$^+$ calcd for $C_{10}H_{14}O_2$: 166.0988; found: 166.0994.

1-(4-Bromophenyl)propan-1-ol (2g)[23]

Aldehyde **1g** (277 mg, 1.50 mmol) was converted with Et_2Zn in toluene (2.7 mL, 3.0 mmol) in the presence of Bu_4PCl (30 mg, 0.11 mmol) into **2g**, which was isolated after chromatography (silica gel, cyclohexane–EtOAc, 20:1, R_f = 0.77) as a colorless oil (314 mg, 1.46 mmol, 98%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.82 (t, ^3J = 7.4 Hz, 3 H), 1.60–1.73 (m, 2 H), 1.91 (br s, 1 H), 4.48 (t, ^3J = 6.6 Hz, 1 H), 7.11–7.15 (m, 2 H), 7.37–7.41 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.11 (CH_3), 32.03 (CH_2), 75.42 (CH), 121.30 (C), 127.84 (CH), 131.57 (CH), 143.63 (C).

MS (EI, 70 eV): *m*/*z* (%) = 216 ([MH]$^+$, 11), 214 (10), 187 (94), 185 (100), 159 (15), 157 (20), 78 (29), 77 (58), 51 (10).

HRMS (EI, 70 eV): *m*/*z* [M]$^+$ calcd for $C_9H_{11}BrO$: 215.9967; found: 215.9966.

Anal. Calcd for $C_9H_{11}BrO$: C, 50.26; H, 5.15. Found: C, 50.32; H, 5.07.

1-(4-Chlorophenyl)propan-1-ol (2h)[22]

Aldehyde **1h** (210 mg, 1.49 mmol) was converted with Et_2Zn in toluene (2.7 mL, 3.0 mmol) in the presence of Bu_4PCl (30 mg, 0.10 mmol) into **2h**, which was isolated after chromatography (silica gel, cyclohexane–EtOAc, 20:1, R_f = 0.66) as a colorless oil (253 mg, 1.48 mmol, 99%).

^{1}H NMR (300 MHz, $CDCl_3$): d = 0.83 (t, ^3J = 7.4 Hz, 3 H), 1.61–1.74 (m, 2 H), 1.86 (br s, 1 H), 4.50 (dt, ^3J = 3.3 Hz, ^3J = 6.4 Hz, 1 H), 7.18–7.21 (m, 2 H), 7.22–7.26 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.12 (CH_3), 32.08 (CH_2), 75.42 (CH), 127.48 (2 CH), 128.65 (2 CH), 133.21 (C), 143.13 (C).

MS (EI, 70 eV): *m*/*z* (%) = 170 ([M]$^+$, 10), 143 (34), 142 (10), 141 (100), 139 (12), 117 (15), 115 (17), 113 (16), 77 (56), 51 (10), 32 (43).

HRMS (EI, 70 eV): *m*/*z* [M]$^+$ calcd for $C_9H_{11}ClO$: 170.0492; found: 170.0494.

1-(4-Fluorophenyl)propan-1-ol (2i)[22]

Aldehyde **1i** (186 mg, 1.50 mmol) was converted with Et_2Zn in toluene (2.7 mL, 3.0 mmol) in the presence of Bu_4PCl (30 mg, 0.10 mmol) into **2i**, which was isolated after chromatography (silica gel, cyclohexane–EtOAc, 20:1, R_f = 0.47) as a colorless oil (213 mg, 1.38 mmol, 92%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.81 (t, ^3J = 7.4 Hz, 3 H), 1.57–1.76 (m, 2 H), 2.00 (br s, 1 H), 4.48 (t, ^3J = 6.6 Hz, 1 H), 6.91–6.98 (m, 2 H), 7.18–7.24 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.17 (CH_3), 32.09 (CH_2), 75.45 (CH), 115.28 (d, $^2J_{C,F}$ = 21.3 Hz, 2 CH), 127.70 (d, $^3J_{C,F}$ = 7.9 Hz, 2 CH), 140.39 (d, $^4J_{C,F}$ = 3.0 Hz, C), 162.2 (d, $^1J_{C,F}$ = 245.2 Hz, C).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –115.0.

MS (EI, 70 eV): *m*/*z* (%) = 154 ([M]$^+$, 6), 125 (100), 97 (46), 95 (14), 77 (14).

HRMS (EI, 70 eV): *m*/*z* [M]$^+$ calcd for $C_9H_{11}FO$: 154.0788; found: 154.0787.

Anal. Calcd for $C_9H_{11}FO$: C, 70.11; H, 7.19. Found: C, 70.15; H, 7.59.

1-(2-Chlorophenyl)propan-1-ol (2j)[22]

Aldehyde **1j** (210 mg, 1.49 mmol) was converted with Et_2Zn in toluene (2.7 mL, 3.0 mmol) in the presence of Bu_4PCl (30 mg, 0.10 mmol) into **2j**, which was isolated after chromatography (silica gel, cyclohexane–EtOAc, 20:1, R_f = 0.55) as a colorless oil (216 mg, 1.27 mmol, 85%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, ^3J = 7.4 Hz, 3 H), 1.60–1.80 (m, 2 H), 2.02 (br s, 1 H), 4.96–5.00 (m, 1 H), 7.08–7.14 (m, 1 H), 7.18–7.26 (m, 2 H), 7.44–7.47 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.18 (CH_3), 30.59 (CH_2), 72.07 (CH), 127.14 (CH), 127.27 (CH), 128.46 (CH), 129.48 (CH), 132.09 (C), 142.10 (C).

MS (EI, 70 eV): *m*/*z* (%) = 170 ([M]$^+$, 7), 143 (34), 142 (9), 141 (100), 113 (15), 77 (52), 51 (9).

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HRMS (EI, 70 eV): *m/z* $[M]^+$ calcd for $C_9H_{11}ClO$: 170.0492; found: 170.0489.

Anal. Calcd for $C_9H_{11}ClO$: C, 63.35; H, 6.50. Found: C, 63.15; H, 6.80.

1-(3-Chlorophenyl)propan-1-ol (2k)[22]

Aldehyde **1k** (210 mg, 1.50 mmol) was converted with Et_2Zn in toluene (2.7 mL, 3.0 mmol) in the presence of Bu_4PCl (30 mg, 0.10 mmol) into **2k**, which was isolated after chromatography (silica gel, cyclohexane–EtOAc, 20:1, $R_f = 0.48$) as a yellow oil (233 mg, 1.37 mmol, 91%).

^1H NMR (300 MHz, $CDCl_3$): δ = 0.96 (t, ^3J = 7.4 Hz, 3 H), 1.72–1.88 (m, 2 H), 2.05 (br s, 1 H), 4.62 (t, ^3J = 6.5 Hz, 1 H), 7.23–7.28 (m, 1 H), 7.29–7.35 (m, 2 H), 7.38–7.40 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.11 (CH_3), 32.04 (CH_2), 75.44 (CH), 124.25 (CH), 126.28 (CH), 127.69 (CH), 129.79 (CH), 134.41 (C), 146.78 (C).

MS (EI, 70 eV): *m/z* (%) = 170 ($[M]^+$, 12), 143 (33), 142 (8), 141 (100), 115 (15), 113 (14), 77 (66), 51 (8).

HRMS (EI, 70 eV): *m/z* $[M]^+$ calcd for $C_9H_{11}ClO$: 170.0493; found: 170.0491.

Anal. Calcd for $C_9H_{11}ClO$: C, 63.35; H, 6.50. Found: C, 63.20; H, 6.37.

1-(Naphthalen-1-yl)propan-1-ol (2l)[22]

Aldehyde **1l** (234 mg, 1.50 mmol) was converted with Et_2Zn in toluene (2.7 mL, 3.0 mmol) in the presence of Bu_4PCl (30 mg, 0.10 mmol) into **2l**, which was isolated after chromatography (silica gel, cyclohexane–EtOAc, 25:1, $R_f = 0.71$) as a pale yellow oil (242 mg, 1.30 mmol, 87%).

^1H NMR (300 MHz, $CDCl_3$): δ = 1.04 (t, ^3J = 7.4 Hz, 3 H), 1.86–2.03 (m, 2 H), 2.05 (br s, 1 H), 5.37–5.42 (m, 1 H), 7.46–7.56 (m, 3 H), 7.63–7.65 (m, 1 H), 7.77–7.80 (m, 1 H), 7.86–7.91 (m, 1 H), 8.09–8.15 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.65 (CH_3), 31.20 (CH_2), 72.70 (CH), 123.02 (CH), 123.36 (CH), 125.52 (CH), 125.60 (CH), 126.03 (CH), 128.99, (CH) 129.00 (CH), 130.62 (C), 133.93 (C), 140.36 (C).

MS (EI, 70 eV): *m/z* (%) = 186 ($[M]^+$, 29), 168 (12), 158 (12), 157 (100), 153 (24), 152 (12), 130 (11), 129 (99), 128 (55), 127 (32).

HRMS (EI, 70 eV): *m/z* $[M]^+$ calcd for $C_{13}H_{14}O$: 186.1039, found: 186.1033.

1-(2,4-Dimethoxyphenyl)propan-1-ol (2m)[24]

Aldehyde **1m** (249 mg, 1.50 mmol) was converted with Et_2Zn in toluene (2.7 mL, 3.0 mmol) in the presence of Bu_4PCl (44 mg, 0.15 mmol) into **2m**, which was isolated after chromatography (silica gel, cyclohexane–EtOAc, 10:1, $R_f = 0.38$) as a colorless oil (249 mg, 1.27 mmol, 85%).

^1H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, ^3J = 7.4 Hz, 3 H), 1.70–1.76 (m, 2 H), 2.40 (br s, 1 H), 3.73 (s, 3 H), 3.74 (s, 3 H), 4.65 (q, ^3J = 6.0 Hz, 1 H), 6.38–6.39 (m, 1 H), 6.40–6.41(m, 1 H), 7.10–7.13 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.68 (CH_3), 30.25 (CH_2), 55.39 (CH_3), 55.48 (CH_3), 72.16 (CH), 98.78 (CH), 104.10 (CH), 125.06 (C), 127.78 (CH), 157.88 (C), 160.10 (C).

MS (EI, 70 eV): *m/z* (%) = 196 ($[M]^+$, 5), 178 (11), 168 (10), 167 (100), 151 (14), 137 (18).

HRMS (EI, 70 eV): *m/z* $[M]^+$ calcd for $C_{11}H_{16}O_3$: 196.1094; found: 196.1095.

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.45; H, 8.62.

2,4-Di-*tert*-butyl-6-(1-hydroxypropyl)phenol (2n)[25]

Aldehyde **1n** (351 mg, 1.50 mmol) was converted with Et_2Zn in toluene (2.7 mL, 3.0 mmol) in the presence of Bu_4PCl (44 mg, 0.15 mmol) into **2n**, which was isolated after chromatography (silica gel, cyclohexane–EtOAc, 25:1, $R_f = 0.86$) as a colorless oil (316 mg, 1.20 mmol, 80%).

^1H NMR (300 MHz, $CDCl_3$): δ = 1.00 (t, ^3J = 7.3 Hz, 3 H), 1.30 (s, 9 H), 1.44 (s, 9 H), 1.83–2.01 (m, 2 H), 2.44 (d, ^3J = 2.3 Hz, 1 H), 4.74–4.73 (m, 1 H), 6.81 (d, ^4J = 2.4 Hz, 1 H), 7.25 (d, ^4J = 2.4 Hz, 1 H), 8.19 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.50 (CH_3), 29.87 (CH_2), 29.89 (3 CH_3), 31.77 (3 CH_3), 34.32 (CH), 35.21 (C), 79.24 (CH), 122.25 (CH), 123.47 (CH), 126.53 (C), 137.02 (C), 141.20 (C), 152.71 (C).

MS (EI, 70 eV): *m/z* (%) = 246 ($[M - H_2O]^+$, 21), 232 (18), 231 (100).

HRMS (EI, 70 eV): *m/z* $[M - H_2O]^+$ calcd for $C_{17}H_{26}O$: 246.1978; found: 246.1978.

Anal. Calcd for $C_{17}H_{28}O_2$: C, 77.22; H, 10.67. Found: C, 77.38; H, 10.70.

Nonan-3-ol (2o)[24]

Aldehyde **1o** (171 mg, 1.50 mmol) was converted with Et_2Zn in toluene (2.7 mL, 3.0 mmol) in the presence of Bu_4PCl (30 mg, 0.11 mmol) into **2o**, which was isolated after chromatography (silica gel, cyclohexane–EtOAc, 25:1, $R_f = 0.86$) as a colorless oil (110 mg, 0.763 mmol, 51%).

^1H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, ^3J = 7.3 Hz, 3 H), 0.98 (t, ^3J = 7.5 Hz, 3 H), 1.28–1.37 (m, 8 H), 1.37–1.59 (m, 4 H), 3.53–3.59 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.99 (CH_3), 14.19 (CH_3), 22.75 (CH_2), 25.75 (CH_2), 29.52 (CH_2), 30.26 (CH_2), 32.98 (CH_2), 37.09 (CH_2), 73.43 (CH).

MS (EI, 70 eV): *m/z* (%) = 144 ($[M]^+$, 10), 115 (30), 97 (72), 69 (18), 59 (100), 58 (11), 57 (16), 55 (73), 43 (22), 41 (30), 31 (14), 29 (16).

1-(Furan-2-yl)propan-1-ol (2p)[22]

Aldehyde **1p** (144 mg, 1.50 mmol) was converted with Et_2Zn in toluene (2.7 mL, 3.0 mmol) in the presence of Bu_4PCl (30 mg, 0.10 mmol) over 5 d into **2p**, which was isolated after chromatography (silica gel, cyclohexane–EtOAc, 20:1, $R_f = 0.68$) as a pale yellow oil (136 mg, 1.08 mmol, 72%).

^1H NMR (300 MHz, $CDCl_3$): δ = 0.95 (t, ^3J = 7.5 Hz, 3 H), 1.83–1.90 (m, 2 H), 2.0 (br s, 1 H), 4.59 (t, ^3J = 6.6 Hz, 1 H), 6.22–6.23 (m, 1 H), 6.32–6.33 (m, 1 H), 7.36–7.37 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.06 (CH_3), 28.72 (CH_2), 69.32 (CH), 106.05 (CH), 110.24 (CH), 142.05 (CH), 156.84 (C).

MS (EI, 70 eV): *m/z* (%) = 126 ($[M]^+$, 15), 97 (100), 69 (12), 41 (18), 39 (12).

HRMS (ESI): *m/z* $[M - H]^-$ calcd for $C_7H_9O_2$: 125.0608; found: 125.0607.

1-(Pyridin-2-yl)propan-1-ol (2q)[26]

Aldehyde **1q** (160 mg, 1.50 mmol) was converted with Et_2Zn in toluene (2.7 mL, 3.0 mmol) in the presence of Bu_4PCl (30 mg, 0.10 mmol) over 5 d into **2q**, which was isolated after chromatography (silica gel, cyclohexane–EtOAc, 20:1, $R_f = 0.68$) as a pale yellow oil (106 mg, 0.773 mmol, 52%).

^1H NMR (300 MHz, $CDCl_3$): δ = 0.85 (t, ^3J = 7.5 Hz, 3 H), 1.55–1.69 (m, 1 H), 1.72–1.86 (m, 1 H), 4.21 (br s, 1 H), 4.58–4.62 (m, 1 H), 7.07–7.12 (m, 1 H), 7.15–7.17 (m, 1 H), 7.55–7.61 (m, 1 H), 8.43–8.44 (m, 1 H).

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^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.52 (CH_3), 31.44 (CH_2), 73.88 (CH), 120.50 (CH), 122.32 (CH), 136.90 (CH), 148.25 (CH), 162.12 (C).

MS (EI, 70 eV): *m*/*z* (%) = 137 ([M]$^+$, 12), 120 (14), 109 (77), 108 (100), 106 (12), 80 (21), 79 (20), 78 (36), 53 (12), 52 (14), 51 (11).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_8H_{12}NO$: 138.0913; found: 138.0914.

Diphenylmethanol (2r)[27]

Benzaldehyde (**1a**; 75 mg, 0.74 mmol) in toluene (1.5 mL) was converted with Ph_2Zn (325 mg, 1.48 mmol) in the presence of Bu_4PCl (15 mg, 0.06 mmol) over 24 h into **2r**, which was isolated after chromatography (silica gel, cyclohexane–EtOAc, 20:1 → 10:1; R_f = 0.58, cyclohexane–EtOAc, 1:1) as colorless crystals (80 mg, 0.43 mmol, 58%); mp 65 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.41 (s, 1 H), 5.78 (s, 1 H), 7.20–7.38 (m, 10 H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 76.16 (CH), 126.50 (4 CH), 127.50 (2 CH), 128.74 (4 CH), 143.87 (2 C).

MS (EI, 70 eV): *m*/*z* (%) = 184 ([M]$^+$, 26), 167 (11), 168 (5), 152 (7), 105 (100), 77 (56), 51 (20).

1-Phenylpentanol (2s)[28]

Benzaldehyde (**1a**; 160 mg, 1.51 mmol) in toluene (0.4 mL) was converted with Bu_2Zn (3.0 ml, 1 M in heptane, 3.0 mmol) in the presence of Bu_4PCl (30 mg, 0.11 mmol) over 24 h into **2s**, which was isolated after chromatography (silica gel, cyclohexane–EtOAc 20:1 → 10:1; R_f = 0.07, cyclohexane–EtOAc, 20:1) as a colorless oil (100 mg, 0.609 mmol, 40%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85–0.91 (m, 3 H), 1.19–1.46 (m, 4 H), 1.63–1.90 (m, 3 H), 4.66 (dd, ^3J = 5.9 Hz, ^3J = 7.5 Hz, 1 H), 7.23–7.31 (m, 1 H), 7.31–7.37 (m, 4 H).

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 13.95 (CH_3), 22.54 (CH_2), 27.91 (CH_2), 38.72 (CH_3), 74.56 (CH), 125.85 (2 CH), 127.35 (CH), 128.31 (2 CH), 144.89 (C).

MS (EI, 70 eV): *m*/*z* (%) = 164.1 ([M]$^+$, 6), 107 (100), 79 (44), 77 (23), 51 (5).

2-Methyl-1-phenylpropanol (2t)[29]

Benzaldehyde (**1a**; 106 mg, 1.15 mmol) in toluene (1 mL) was converted with *i*-Pr_2Zn (2 mL, 1 M in toluene, 2.0 mmol) in the presence of Bu_4PCl (21 mg, 0.07 mmol) over 24 h into **2t**, which was isolated after chromatography (silica gel, cyclohexane–EtOAc, 20:1 → 10:1 → EtOAc; R_f = 0.27, cyclohexane–EtOAc, 10:1) as a colorless oil (45 mg, 0.30 mmol, 26%). Phenyl isopropyl ketone (20 mg, 0.13 mmol, 12%, R_f = 0.50 in cyclohexane–EtOAc, 10:1) was isolated as a by-product (see below).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.79 (d, ^3J = 6.9 Hz, 3 H), 1.00 (d, ^3J = 6.7 Hz, 3 H), 1.88–2.03 (m, 2 H), 4.35 (dd, ^3J = 2.0 Hz, ^3J = 6.8 Hz, 1 H), 7.22–7.36 (m, 5 H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 18.20 (CH_3), 18.95 (CH_3), 35.21 (CH), 80.00 (CH), 126.52 (2 CH), 127.37 (CH), 128.14 (2 CH), 143.59 (C).

MS (EI, 70 eV): *m*/*z* (%) = 150 ([M]$^+$, 7), 107 (100), 79 (54), 77 (32), 51 (8).

Phenyl Isopropyl Ketone[30]

Phenyl isopropyl ketone (20 mg, 0.13 mmol, 12%; R_f = 0.50, cyclohexane–EtOAc, 10:1) was obtained as a by-product in the synthesis of **2t**.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22 (d, ^3J = 6.9 Hz, 6 H), 3.56 (hept, ^3J = 6.8 Hz, 1 H), 7.42–7.57 (m, 3 H), 7.93–7.99 (m, 2 H).

MS (EI, 70 eV): *m*/*z* (%) = 148 ([M]$^+$, 9), 105 (100), 77 (38), 51 (12).

(*S*)-(2-Pyrrolidinylmethyl)triphenylphosphonium Bromide (6)[13]

L-Prolinol (**5**; 1.40 g, 13.8 mmol) and Ph_3P (3.63 g, 13.8 mmol) were dissolved in toluene (6 mL). The mixture was cooled to 5 °C and aq 48% HBr (9.0 mL, 166 mmol) was added portionwise (cautiously at first). The reaction mixture was heated to 150 °C, which caused the toluene and most of the H_2O to evaporate to give a melt. The melt was heated to 200–210 °C and stirred for 1 h and then 3 h at 150 °C. The reaction mixture was allowed to cool to r.t., quenched with H_2O (50 mL), and extracted with EtOAc (3 × 25 mL). The acidic aqueous fraction was basified to pH 8 with aq Na_2CO_3/$NaHCO_3$, extracted with CH_2Cl_2 (6 × 40 mL), dried (Na_2SO_4), and concentrated in vacuo to give **6** (2.95 g, 6.91 mmol, 50%) as a yellow hygroscopic solid.

IR (KBr): 2856 (m, br), 2177 (w), 1586 (w), 1484 (w), 1436 (s), 1109 (s), 919 (s), 719 (vs), 687 (vs), 639 (s), 494 cm^{-1} (vs).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.63–1.78 (m, 1 H), 1.78–1.99 (m, 3 H), 2.79–2.92 (m, 1 H), 2.95–3.07 (m, 1 H), 3.71–3.97 (m, 2 H), 4.06 (ddd, ^3J = 5.4 Hz, ^2J = 12.4 Hz, $^2J_{H,P}$ = 15.6 Hz, 1 H), 4.30 (ddd, ^3J = 8.2 Hz, ^2J = 12.4 Hz, $^2J_{H,P}$ = 15.7 Hz, 1 H), 7.59–9.00 (m, 15 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.95 (CH_2), 26.39 (d, $^1J_{C,P}$ = 53.2 Hz, CH_2), 31.77 (d, $^3J_{C,P}$ = 7.0 Hz, CH_2), 44.87 (CH_2), 54.17 (d, $^2J_{C,P}$ = 1.7 Hz, CH), 117.33 (d, $^1J_{C,P}$ = 86.7 Hz, 3 C), 130.45 (d, $^2J_{C,P}$ = 12.8 Hz, 6 CH), 133.71 (d, $^3J_{C,P}$ = 10.5 Hz, 6 CH), 135.17 (d, $^4J_{C,P}$ = 2.9 Hz, 3 CH).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 21.85 (1 P, P$^+$).

HRMS (ESI): *m*/*z* [M]$^+$ calcd for $C_{23}H_{25}NP$: 346.1719; found: 346.1715.

Methylbinapium Iodide (8)[14]

MeI (227 mg, 1.60 mmol) was added to (*S*)-BINAP (**7**; 1.00 g, 1.65 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred for 16 h at 23 °C. Et_2O (20 mL) was added and the precipitate was collected by filtration, washed with Et_2O (40 mL), and dried in vacuo to give **8** (1.11 g, 1.45 mmol, 91%) as a white amorphous solid; mp >200 °C (dec.).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.99 (d, $^2J_{P,H}$ = 13.4 Hz, 3 H), 6.57–6.61 (m, 1 H), 6.72–6.93 (m, 6 H), 7.00–7.07 (m, 2 H), 7.14–7.30 (m, 4 H), 7.38–7.44 (m, 2 H), 7.44–7.56 (m, 8 H), 7.56–7.69 (m, 3 H), 7.74–7.79 (m, 1 H), 7.79–7.83 (m, 1 H), 7.89–7.91 (m, 1 H), 7.92–7.95 (m, 1 H), 7.95–7.97 (m, 1 H), 8.16–8.22 (m, 1 H).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 22.65 (1 P, P$^+$), –14.55 (1 P, P).

HRMS (ESI): *m*/*z* [M]$^+$ calcd for $C_{45}H_{35}OP_2$: 653.2158; found: 653.2158.

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