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PAPER

Photoremovable chiral auxiliary†‡

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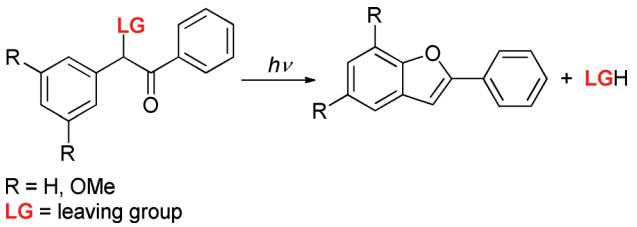
A new concept of a photoremovable chiral auxiliary (PCA), based on the chiral benzoin chromophore, is introduced. This moiety can control the asymmetric formation of a Diels–Alder adduct, and then be removed in a subsequent photochemical step in high chemical and quantum yields. Selective formation of the products at up to 96% ee was observed in the presence of a Lewis acid catalyst in the case of a 2-methoxybenzoinyl chiral auxiliary.

Introduction

Photoremovable protecting groups are chromophoric moieties which are released from species possessing desirable physical, chemical, or biological qualities upon irradiation. They have been successfully utilized in many applications in organic synthesis, solid-phase synthesis, biology, and surface sciences.[1–4] An obvious advantage of photochemical activation is the ability to precisely control the process in time and space, and the "reagentless" character of light.

A number of photoremovable protecting groups (PPG) are currently available, although only a few are used in practice. One of them, the benzoin (desyl alcohol) moiety, has gained importance in the past decade essentially because of its reasonable absorption coefficients in the near-UV region, a generally fast and efficient photorelease of leaving groups (LG), and formation of a relatively non-reactive benzofuran side-photoproduct (Scheme 1).[5–9] Pirrung, Givens, Wirz, and others have extensively investigated the photochemistry of this group.[10–15] They found that the photorelease from unsubstituted desyl esters generally occurs from the lowest excited triplet state, whereas that of 3′,5′-dimethoxybenzoinyl derivatives takes place *via* a singlet pathway. Phillips and his coworkers recently confirmed this observation and established the dominant reaction pathway.[16–18]

The presence of a stereogenic center in a PPG is generally considered a disadvantage. A pair of enantiomers of the benzoin group creates a mixture of diastereomers when the leaving group



Scheme 1 The benzoin chromophore as a PPG.

is chiral. For that reason, Pirrung and Shuey used chiral 3′,5′-dimethoxybenzoin for the protection of chiral alcohols to reduce the number of stereoisomers in the subsequent photochemical application.[10] On the other hand, Soldevilla and Griesbeck reported recently on a stereodifferentiation process that involved photoinduced decarboxylation of a chiral photoactivatable compound based on a phthalimide chromophore.[19]

Enantioselective construction of carbon-carbon bonds in synthetic organic chemistry is frequently mediated by chiral auxiliaries.[20–23] Such a group is temporarily covalently attached to the prochiral substrate to induce a diastereoselective transformation, and subsequently removed to liberate a chiral product. In this work, we introduce a novel strategy which combines the well-known concepts of a *chiral auxiliary* and a *photoremovable protecting group*. We show that the chromophoric auxiliary can also be removed photochemically from the chiral product after a stereoselective reaction has taken place, that is, without introducing any other reagent or heating. Hence, the group can be called a *photoremovable chiral auxiliary* (PCA). This approach is demonstrated through the asymmetric Diels–Alder reaction of cyclopentadiene with the acrylate **1** (*e.g.*, (*S*)-**1**), in which the chiral benzoin group is the PCA (Scheme 2, in red), yielding **2**. Asymmetric induction leads to the preferential formation of some stereoisomers out of the four possible. The final isomeric products, norbornene carboxylic acids **3**, are liberated upon irradiation of **2** in the subsequent step. To our knowledge the benzoin moiety, which can readily be synthesized in high enantiomeric purity, has never been used as a conventional chiral auxiliary before. A series of experiments and DFT-based

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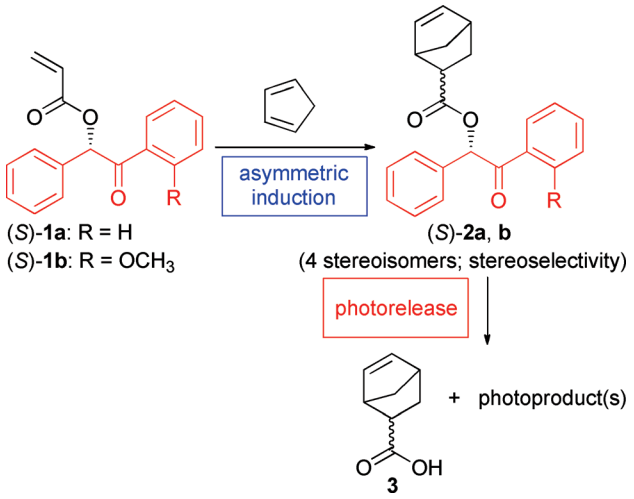


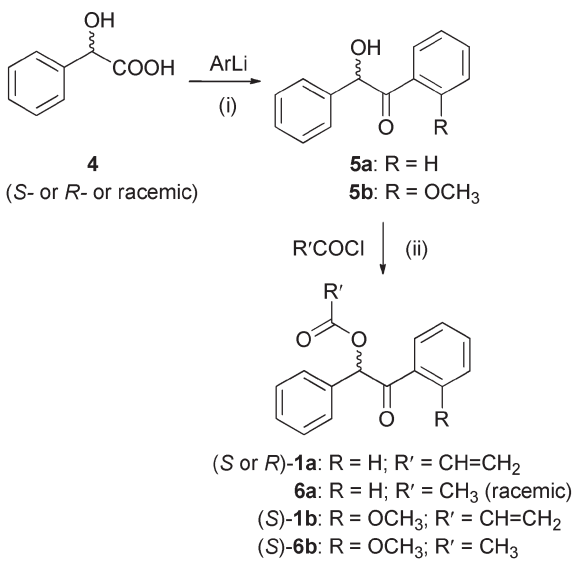
Scheme 2 The concept of a photoremovable chiral auxiliary.

quantum chemical calculations were performed to explain the asymmetric induction results.

Results and discussion

Synthesis

The chiral or racemic benzoins **5a**, **b** were prepared from the corresponding stereoisomer of mandelic acid (**4**) and an aryllithium compound at −78 °C according to a known procedure[24] (Scheme 3). The subsequent esterification[5] of **5a**, **b** with acryloyl chloride or acetyl chloride gave **1a**, **b** or **6a**, **b**, respectively, in 85–90% overall yields. The enantiomeric purity of both chiral **5** and **1** (>98% ee) was verified by enantioselective HPLC analyses. The racemic derivative **6a**, prepared from **5a**, was utilized in the quantum yield measurements; therefore, its enantiomeric purity was not essential.

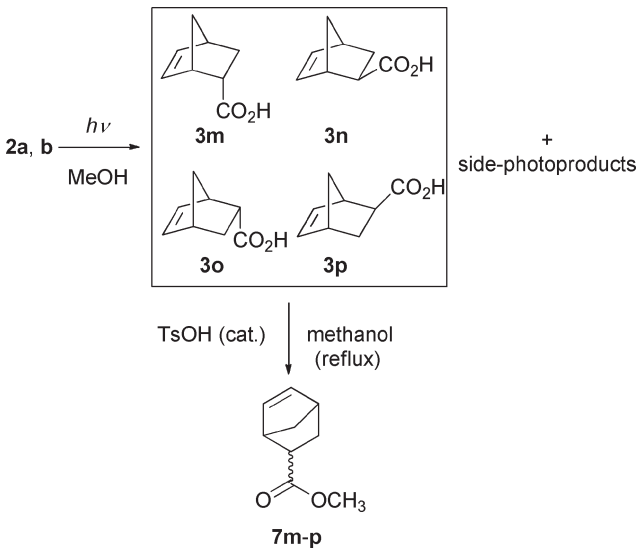


Reagents and conditions: (i) Ar = phenyl or 2-methoxyphenyl: 1. THF, −78 °C; 2. NH_4Cl, H_2O; (ii) R′ = $CH=CH_2$ or CH_3: triethylamine, dichloromethane, 20 °C.

Scheme 3 Synthesis of the benzoin derivatives **1** and **6**.

Cycloaddition

Various experimental conditions were used to achieve the best asymmetric induction in the cycloaddition reaction of **1** with cyclopentadiene, yielding 4 stereoisomers (**3m–p**; Scheme 4). The reactions were carried out at different temperatures in various solvents, and were either non-catalyzed or catalyzed by $EtAlCl_2$, $TiCl_4$, or $SnCl_4$ as Lewis acids (Table 1). Reaction times were adjusted to achieve optimum isolated chemical yields (85–95%; ESI‡). The reactions carried out in water (entries 2, 7) as well as the catalyzed reactions (entries 3–5, 8–15) were much faster than the non-catalyzed ones (entries 1 and 6). When the reaction was completed, a mixture of the isomeric adducts **2** was isolated and used in the subsequent photorelease step. In order to ensure that the absolute configuration of the starting material **1** is not lost in the course of a cycloaddition process, the reaction catalyzed by $SnCl_4$ was carried out in the absence of cyclopentadiene: After work-up, the identical unreacted pure enantiomer was recovered.



Scheme 4 Photochemical removal of the PCA from **2** and conversion of the acids **3** to their methyl esters **7**.

It has already been shown that the rate of the Diels–Alder reactions increases in water, in part from hydrophobic association of the reactants, but predominantly from enhanced hydrogen bonding with water molecules.[25–28] Indeed, rate enhancement by 2 orders of magnitude was observed in our experiments (entries 2, 7). The complexation of Lewis acids with various substrates is known to affect the course of the Diels–Alder reaction due to the increased electron deficiency (decreased LUMO energy) of the dienophile, which eventually leads to reaction rate enhancement.[29–34] We used DFT quantum chemical calculations at the B3LYP level of theory with the LANL2DZ basis set[35,36] to reveal the most favorable coordination interactions between (*S*)-**1b** and $SnCl_4$ that could be responsible for the cycloaddition rate enhancement. In case of 1 eq of $SnCl_4$, the catalyst molecule is coordinated to both the methoxy and carbonyl groups' oxygens in 9 different conformations (97% of the Botzmann population; one example is shown in Fig. 1a), in which the LUMO is located on the benzoin phenyl ring that is unfavorable

Table 1 Cycloaddition of **1** with cyclopentadiene and the subsequent PCA release from **2**

		Cycloaddition reaction conditions[b]			Photorelease of the PCA[f]		
Entry	Ester[a]	Catalyst	*T*/°C	Time/h	de (%)[g]	ee (*endo*) (%)[g]	ee (*exo*) (%)[g]
1	(*S*)-**1a**	—[c]	20	36	46	35	−36
2		—[e]	20	0.2	36	29	−32
3		$EtAlCl_2$ (1 eq)[d]	−20	2	85	12	9
4		$SnCl_4$ (1 eq)[c]	20	1	70	13	41
5		$SnCl_4$ (2 eq)[c]	−78	6	62	46	58
6	(*S*)-**1b**	—[c]	20	72	46	31	−42
7		—[e]	20	0.5	−7	27	−33
8		$TiCl_4$ (2 eq)[c]	−65	6	79	53	52
9		$EtAlCl_2$ (1 eq)[d]	−20	2	73	54	50
10		$SnCl_4$ (1 eq)[c]	20	2	58	25	50
11		$SnCl_4$ (2 eq)[c]	20	2	34	11	40
12		$SnCl_4$ (1 eq)[c]	0	3	50	11	54
13		$SnCl_4$ (2 eq)[c]	0	2	18	−19	66
14		$SnCl_4$ (1 eq)[c]	−78	3	70	−35	**90**
15		$SnCl_4$ (2 eq)[c]	−78	5	53	−43	**96**

[a] The purity of the starting material was >98% ee. [b] Asymmetric induction step: A solution of **1** ($c \approx 0.05$ M) and cyclopentadiene ($c \approx 0.1$ M) in [c] toluene or [d] dichloromethane, or [e] a mixture of **1** with water (1 : 20, w/w), was stirred during the time and the temperature (*T*) given. [f] Photorelease step: A solution of **2** ($c = 0.005$ M) in methanol was irradiated at $\lambda = 313$ nm to release the acids **3m–p**. [g] The acids **3** were converted to their methyl esters **7** (Scheme 4) and *de* and *ee* were calculated from the measured concentrations of the *endo* **7m**, **o** and *exo* **7n**, **p** isomers according to the standard equations. All data are the average of at least two measurements. $\text{de} = \frac{([\mathbf{7m}]+[\mathbf{7o}])-([\mathbf{7n}]+[\mathbf{7p}])}{[\mathbf{7m}]+[\mathbf{7o}]+[\mathbf{7n}]+[\mathbf{7p}]} \times 100$; $\text{ee}\ (endo) = \frac{[\mathbf{7m}]-[\mathbf{7o}]}{[\mathbf{7m}]+[\mathbf{7o}]} \times 100$; $\text{ee}\ (exo) = \frac{[\mathbf{7n}]-[\mathbf{7p}]}{[\mathbf{7n}]+[\mathbf{7p}]} \times 100$.

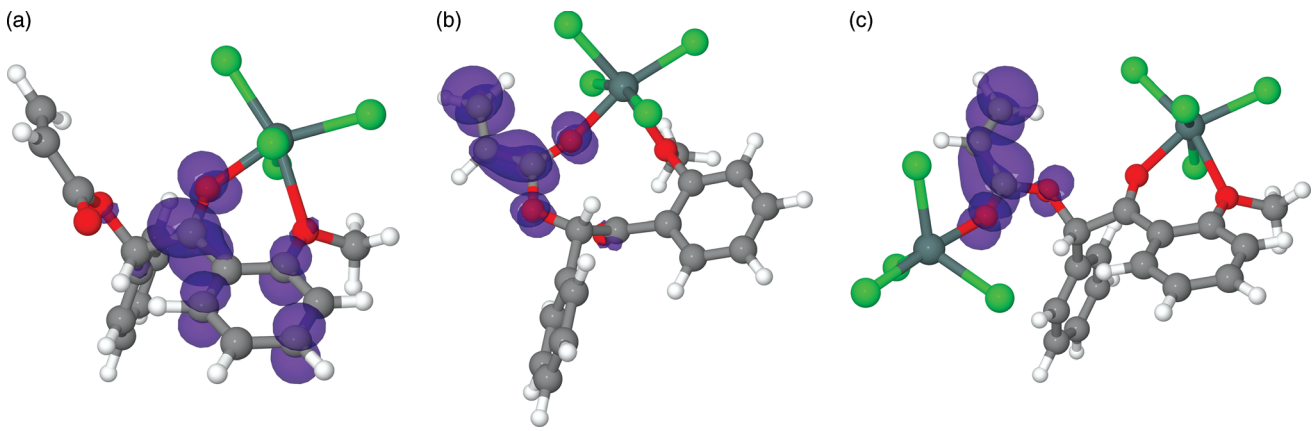


Fig. 1 Localization of the LUMO (in violet) in (*S*)-**1** coordinated with 1 and 2 molecules of $SnCl_4$. The calculated interaction energies between $SnCl_4$ and (*S*)-**1** using DFT B3LYP/LANL2DZ are (a) −27.62, (b) −18.94, and (c) −45.18 kcal mol^{-1}.

for the Diels–Alder reaction. Only 4 conformers with the catalyst coordinated to both the carboxyl group and the methoxy group (representing 3% of the Botzmann population; Fig. 1b) have the LUMO located favorably on the acrylic double bond (dienophile). Two $SnCl_4$ molecules are then coordinated to all three oxygen atoms (99.95% of the Boltzmann population; Fig. 1c) and the LUMO is located on the dienophile moiety. We therefore assume that only the conformers, which have the catalyst coordinated with the carboxyl group, undergo fast reaction.

Photorelease and photoproducts

Despite the fact that desyl esters are easily hydrolyzed under both acidic and basic conditions,[37–39] we decided to use this chromophore to prove the concept of a photoremovable chiral auxiliary because the photochemistry of benzoin derivatives has already been thoroughly studied,[10–18] and pure stereoisomers of **5** are easily synthetized.

The isolated PCA esters **2** were photolyzed at $\lambda = 313$ nm in methanol to release **3m–p**, which were separated from the reaction mixtures as the sodium salts, and the mixture was subsequently neutralized to obtain free acids. The yields of acids (**3**) released were 84–87% for both **2a** and **2b** at 85–90% conversion (GC). The products started to decompose upon further irradiation. To simplify GC analysis of the mixture of stereoisomers,[40] **3m–p** were esterified with methanol in the presence of TsOH to the corresponding methyl esters **7m–p** (Scheme 4). The absolute stereochemistry of **7** was determined by comparing it with that of the authentic compounds[41–43] (ESI‡). For comparison, the methyl esters **7m–p** were also directly produced by treating the Diels–Alder reaction adducts **2a**, **b** with K_2CO_3 in aqueous methanol. The same product distributions (within the

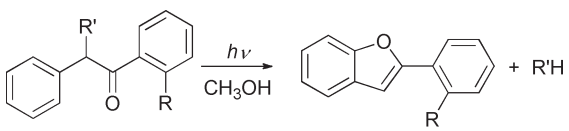
Table 2 Photodecomposition quantum yields of **6a**, **b**[a]

Compound	Quantum yield (Φ)
6a	0.36 ± 0.01
6b	0.43 ± 0.01

[a] Degassed solutions (≈3 × 10^{-4} M) in methanol were irradiated at λ = 313 ± 5 nm (optical bench). Run in triplicate; standard deviation of the mean given. 2-Nitrobenzaldehyde was the actinometer (Φ (methanol) = 0.41).[47] Product yields were determined by GC.

experimental error) as those obtained by the photolysis/esterification reaction sequence were observed in all cases.

Two reaction paths of photodissociation of benzoin derivatives, a cyclization-elimination process leading to 2-phenylbenzofuran **7** or to heterolytic dissociation *via* the corresponding carbocation, have been proposed.[13,14,17,18] Benzoin substitution is known to influence the photoproduct distribution considerably.[44] Analogous to this known photochemistry, benzofurans **8a** and **8b** (Scheme 5) were isolated as major side-photoproducts by irradiation of **2a** and **2b**, respectively, in methanol in 64–74% yields at ≈70% conversion. Benzofurans started to decompose upon prolonged irradiation. Only traces of α-cleavage photoproducts, such as the corresponding benzaldehyde[45,46] and methyl benzoate, were detected in extensively irradiated methanolic degassed solutions. The quantum yields of the acetates **6a**, **b** (Scheme 3) disappearance were determined (Table 2). They are comparable to those obtained for **6a** in non-polar benzene (Φ = 0.33;[45] where α-cleavage dominates), or for the corresponding desyl phosphate in methanol (Φ = 0.39)[6] or aqueous acetonitrile (Φ = 0.37).[7,8]



2a: R = H
2b: R = OCH_3
8a: R = H
8b: R = OCH_3
R' = norbornenyl-5-carboxylate or OAc

Scheme 5 Photolysis of **2a**, **b**.

Asymmetric induction

Table 1 demonstrates the effect of catalysts and temperature on the asymmetric Diels–Alder reaction of **1**. Diastereoselectivity fluctuated between 85 and −7% de. The highest excesses (85–73%, *i.e.*, when the *endo* derivatives are preferentially formed; entries 3, 8, 9 in Table 1) were obtained in the presence of $EtAlCl_2$ or $TiCl_4$. In contrast, the reactions carried out in water exhibited a low diastereoselectivity (entries 2 and 7). Enantioselectivity was observed in all experiments. Generally lower ee (*endo*) values (<53%) were obtained. The opposite *endo* enantiomers (−43 to −19% ee) were preferentially formed from **1b** in the presence of $SnCl_4$ (entries 13–15) compared to all other experimental arrangements. The highest ee (*exo*) values, 90 and 96%, were obtained in the presence of 1 and 2 eq of $SnCl_4$, respectively, at −78 °C (entries 14 and 15). The values were reversed in the absence of the catalyst (entries 1, 2, 6, 7). To verify the results, (*R*)-**1a** instead of (*S*)-**1a** was used in selected experiments (entries 3–5; not shown); the opposite enantiomers were formed as expected.

Table 3 The calculated enantioselectivity of cycloaddition of **1b** with cyclopentadiene[a]

Entry[b]	$SnCl_4$ amount	*T*/°C	ee (*endo*)/%	ee (*exo*)/%
10	1 eq	20	−63	57
11	2 eq	20	−12	68
12	1 eq	0	−66	64
13	2 eq	0	−13	71
14	1 eq	−78	−76	78
15	2 eq	−78	−18	84

[a] The ee values were calculated by using B3LYP/LANL2DZ transition state localization. [b] The entry numbers correspond to those of Table 1.

The starting ester **1** is a rather conformationally flexible molecule and the stereogenic carbon in the benzoin moiety is relatively distant from the acrylic double bond. Therefore, we anticipated that a diene might approach the reaction center with rather low facial selectivity. The methoxy substitution on the phenyl ring of **5b** was originally designed to provide an additional potential coordination site on the chiral auxiliary group to enhance its rigidity when more than one catalyst molecule is used. However, Table 1 reveals that the stereoselectivity was affected only moderately by the second molecule of a catalyst. The methoxy derivative **1b** exhibited much higher enantioselectivity (*exo*) in the presence of $SnCl_4$ than **1a**; therefore, DFT B3LYP/LANL2DZ computational methods were used to localize the transition states for possible orientations of the ester **1b** with cyclopentadiene. This enabled us to determine the theoretical enantiomeric excesses (Table 3 and ESI‡). As discussed above, the complexation of Lewis acids with the acrylate (dienophile) group enhances the Diels–Alder reaction rates significantly.[29–34] In case of 1 eq of $SnCl_4$, only the conformers with the *catalyst coordinated to the carboxyl carbonyl group* were thus considered. The calculated ee (*exo*) values and their trends are well in accord with the experimental results shown in Table 1. Those of ee (*endo*) are more pronounced (more negative), but they still unambiguously support the experimental findings according to which the opposite enantiomers are favored for the *endo* and *exo* approaches. It should be noted that the optimization process did not include a solvent; the experiments were carried out in nonpolar toluene. We conclude that the temperature-dependent enhanced enantioselectivity in $SnCl_4$ catalyzed reactions results from decreased steric hindrance of the diene approach in the transition state, principally involving conformers in which the catalyst is coordinated directly to the dienophile (Fig. 2).

Conclusions

In conclusion, a new concept of a photoremovable chiral auxiliary was introduced in this work. It was shown that chiral benzoin auxiliaries can control asymmetric formation of Diels–Alder adducts, and then be removed in a subsequent photochemical step in high chemical yields. Selective formation of the products at up to 96% ee was observed in the presence of $SnCl_4$ as a Lewis acid catalyst in the case of the 2-methoxybenzoinyl derivative. Photoinitiated ("reagentless") removal of a chromophoric chiral auxiliary could be an attractive alternative to conventional steps used in asymmetric synthesis.

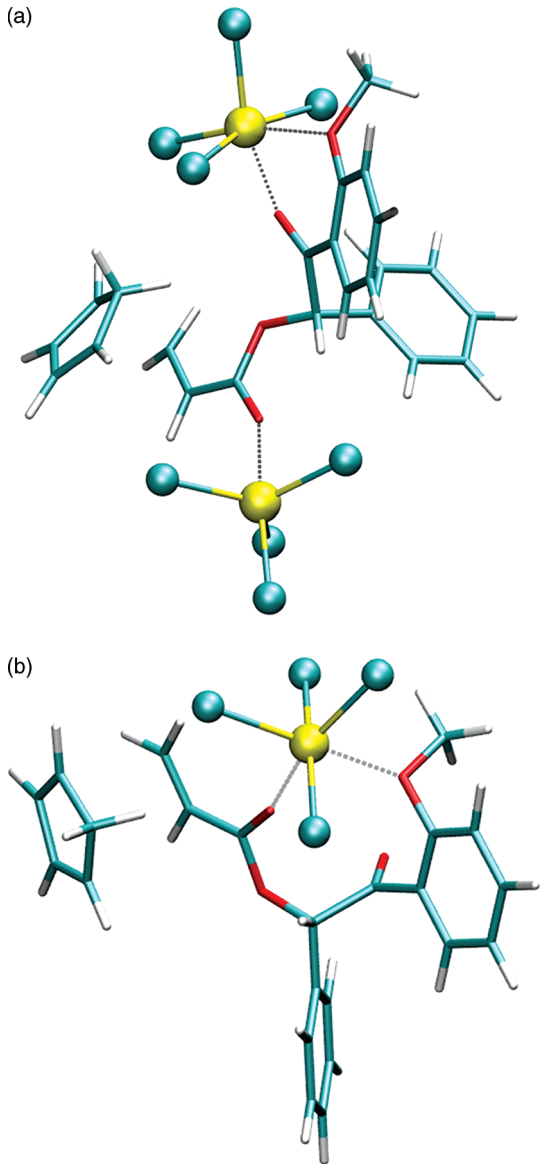


Fig. 2 The calculated structure of **1b** coordinated with (a) 2 and (b) 1 eq of $SnCl_4$ and the preferential approach of cyclopentadiene to give the major *exo* product **3n**.

Experimental

General method for the preparation[24] of enantiopure benzoins (5)

A solution of aryllithium in dry diethyl ether (60 mL) was prepared from the corresponding freshly distilled bromoarene (0.15 mol) and lithium wire (2.3 g, 0.33 mol) at 20 °C. The solution was cooled to −78 °C, and enantiopure mandelic acid (**4**, 5.0 g, 32.9 mmol) in dry tetrahydrofuran (35 mL) was added dropwise under vigorous stirring. The mixture was then allowed to warm to 20 °C, stirred for 3 h, and poured into a mixture of ice (150 g) and solid ammonium chloride (20 g) under vigorous stirring. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (3 × 50 mL). The combined organic layers were washed with aq $NaHCO_3$ (10%, 2 × 30 mL) and brine (3 × 25 mL), dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. Column chromatography (diethyl ether/petroleum ether, 3 : 7) gave the title compound.

2-Hydroxy-1,2-diphenylethanone ((*S*)-5a or (*R*)-5a). Prepared from (*S*)-**4** or (*R*)-**4**, respectively, and bromobenzene in 77% yield; white crystals; mp 125.0–127.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 4.57 (d, 1H, -OH, J = 6.3 Hz), 5.98 (d, 1H, J = 6.0 Hz), 7.26–7.37 (m, 5H), 7.41 (t, 2H, J = 7.4 Hz), 7.54 (t, 1H, J = 7.4 Hz), 7.94 (d, 2H, J = 7.3 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 76.4, 128.0, 128.8, 128.9, 129.3, 129.4, 133.8, 134.1, 139.2, 199.2. MS (EI, *m*/*z*): 212 (5), 105 (100), 107 (40), 77 (60), 51 (25). FTIR (KBr, cm^{-1}): 3415, 3379, 3057, 3031, 2895, 1678, 1593, 1446, 1385, 1259, 1221, 1178, 1080, 974, 847, 766, 696, 602. Anal. calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70%. Found: C, 78.89; H, 5.69%.

(*S*)-2-Hydroxy-1-(2-methoxyphenyl)-2-phenylethanone ((*S*)-5b). Prepared from (*S*)-**4** and 2-methoxybromobenzene in 65% yield; yellow crystals; mp 142.0–146.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.84 (s, 3H), 4.61 (d, 1H, -OH, J = 6.0 Hz), 6.10 (d, 1H, J = 6.0 Hz), 6.87 (d, 1H, J = 8.4 Hz), 6.95 (dt, 1H, J_1 = 7.7 Hz, J_2 = 0.9 Hz), 7.20–7.28 (m, 5H), 7.43 (ddd, 1H, J_1 = 8.4 Hz, J_2 = 7.4 Hz, J_3 = 1.8 Hz), 7.68 (dd, 1H, J_1 = 7.7 Hz, J_2 = 1.8 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 55.5, 79.3, 111.7, 121.0, 124.8, 127.7, 128.2, 128.7, 131.3, 134.7, 139.1, 158.5, 201.2. MS (EI, *m*/*z*): 242 (5), 135 (100), 107 (40), 105 (30), 77 (50), 51 (20). FTIR (KBr, cm^{-1}): 3467, 3066, 3031, 2956, 2928, 1725, 1665, 1599, 1487, 1465, 1292, 1249, 1021, 975, 759, 701, 601. Anal. calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82%. Found: C, 74.52; H, 5.96%.

General method for esterification of enantiopure benzoins

A solution of carboxylic acid chloride (13.2 mmol) in dry dichloromethane (15 mL) was added dropwise to a solution of **5** (9.4 mmol) and triethylamine (3.8 mL, 14.1 mmol) in dry dichloromethane (40 mL) cooled to 0 °C. The solution was allowed to warm to 20 °C and stirred for additional 18 h. The resulting yellow solution was diluted with water (30 mL) and aq HCl (5 M, 25 mL), and the product was extracted with dichloromethane (3 × 30 mL). The combined organic layers were washed with saturated aq Na_2CO_3 (25 mL) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure, and the title compound was separated from the mixture by column chromatography (diethyl ether/petroleum ether, 3 : 7).

2-Oxo-1,2-diphenylethyl acrylate ((*S*)-1a or (*R*)-1a). Prepared from (*S*)-**5a** or (*R*)-**5a**, respectively, and acryloyl chloride in 86% yield; white solid; mp 73.5–74.2 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 5.88 (dd, 1H, J_1 = 10.2 Hz, J_2 = 1.3 Hz), 6.29 (dd, 1H, J_1 = 17.3 Hz, J_2 = 10.2 Hz), 6.53 (dd, 1H, J_1 = 17.3 Hz, J_2 = 1.3 Hz), 7.04 (s, 1H), 7.30–7.41 (m, 5H), 7.48 (t, 1H, J = 7.1 Hz), 7.56 (d, 2H, J = 6.6 Hz), 7.94–7.99 (m, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 77.7, 127.6, 128.6, 128.7, 128.7, 129.1, 129.3, 132.0, 133.4, 133.6, 134.6, 165.4, 193.6. MS (EI, *m*/*z*): 266 (4), 211 (1), 161 (20), 105 (100), 77 (40), 55 (50). FTIR (KBr, cm^{-1}): 3059, 2949, 2927, 1724, 1685, 1594, 1450, 1408, 1273, 1250, 1176, 1064, 970, 862, 760, 700, 586. Anal. calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30%. Found: C, 76.56; H, 5.46%.

(*S*)-2-(2-Methoxyphenyl)-2-oxo-1-phenylethyl acrylate (1b). Prepared from (*S*)-**5b** and acryloyl chloride in 83% yield; white crystals; mp 96.9–98.7 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.83 (s, 3H) 5.88 (dd, 1H, J_1 = 10.3 Hz, J_2 = 1.4 Hz), 6.25 (dd, 1H, J_1 = 17.4 Hz, J_2 = 10.3 Hz), 6.50 (dd, 1H, J_1 = 17.4 Hz, J_2 = 1.4 Hz), 6.87 (d, 1H, J = 8.3 Hz), 6.96 (t, 1H, J = 7.7 Hz), 7.13 (s, 1H), 7.31–7.45 (m, 6H), 7.78 (dd, 1H, J_1 = 7.7 Hz, J_2 = 1.6 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 55.6, 80.9, 111.8, 121.1, 125.9, 128.3, 128.8, 129.0, 129.1, 131.5, 131.7, 134.5 (broad), 158.5, 165.7, 195.1. MS (EI, *m*/*z*): 296 (2), 161 (10), 135 (100), 77 (30), 55 (30). FTIR (KBr, cm^{-1}): 3068, 2937, 2837, 1714, 1674, 1597, 1485, 1404, 1292, 1238, 1201, 1022, 976, 756, 698. Anal. calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44%. Found: C, 73.06; H, 5.66%.

2-Oxo-1,2-diphenylethyl acetate (6a). Prepared from **5a** and acetyl chloride in 95% yield; white solid; mp 85.3–87.1 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 2.22 (s, 3H), 6.87 (s, 1H), 7.35–7.55 (m, 8H), 7.92–7.97 (m, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 21.0, 77.9, 128.8, 128.9, 129.0, 129.3, 129.5, 133.7, 133.9, 134.9, 170.7, 194.0. MS (EI, *m*/*z*): 254 (1), 211 (4), 195 (1), 194 (1), 165 (10), 167 (2), 149 (25), 107(30), 105 (100), 77 (25), 43 (30). FTIR (KBr, cm^{-1}): 3062, 2956, 1730, 1691, 1593, 1448, 1369, 1230, 1051, 986, 758, 696, 523. UV (CH_3OH): ε_{313} = 1200 dm^3 mol^{-1} cm^{-1}. Anal. calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55%. Found: C, 75.12; H, 5.55%.

(*S*)-2-(2-Methoxyphenyl)-2-oxo-1-phenylethyl acetate (6b). Prepared from (*S*)-**5b** and acetyl chloride in 92% yield; white solid; mp 109.5–112.1 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 2.18 (s, 3H), 3.81 (s, 3H), 6.86 (d, 1H, J = 8.4 Hz), 6.95 (dt, 1H, J_1 = 7.6 Hz, J_2 = 1.0 Hz), 7.01 (s, 1H), 7.28–7.43 (m, 6H), 7.75 (dd, 1H, J_1 = 7.8 Hz, J_2 = 1.8 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 20.9, 55.3, 80.6, 111.6, 120.8, 127.8, 128.5, 128.8, 128.9, 131.3, 134.2, 134.6, 158.2, 170.8, 198.8. MS (EI, *m*/*z*): 284 (3), 241 (2), 225 (2), 210 (3), 181 (4), 149 (1), 135 (100), 107 (10), 77 (30), 43 (25). FTIR (KBr, cm^{-1}): 3070, 1969, 2937, 2839, 1734, 1676, 1595, 1483, 1367, 1238, 1045, 1020, 862, 760, 704, 536. UV (CH_3OH): ε_{313} = 5500 dm^3 mol^{-1} cm^{-1}. HRMS (APCI−): calcd for $C_{17}H_{15}O_4$ (M–H$^+$) 283.0976, found 283.0980. Anal. calcd for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67%. Found: C, 71.88; H, 5.81%.

General procedures for asymmetric Diels–Alder reaction between chiral benzoin acrylates (1a, b) and cyclopentadiene

(a) Non-catalyzed reaction (toluene). A solution of cyclopentadiene (170 μL, 2 mmol) in dry toluene (5 mL) was added to a solution of **1** (1 mmol) in dry toluene. The reaction mixture was vigorously stirred at the given temperature (Table 1) until the starting material was consumed (TLC). The solvent was removed under reduced pressure, and the residue was dissolved in dichloromethane (25 mL) and washed with water (20 mL) and brine (20 mL). The organic layer was dried over $MgSO_4$ and dichloromethane was removed under reduced pressure.

(b) Non-catalyzed reaction (water). Cyclopentadiene (170 μL, 2 mmol) and **1** (1 mmol) were added to water (20 mL). The reaction mixture was vigorously stirred at the given temperature (Table 1) until the starting material was consumed (TLC), and the products were extracted to dichloromethane (25 mL). The organic layer was separated and dried over $MgSO_4$, and dichloromethane was removed under reduced pressure.

(c) Catalyzed reaction. A catalyst (1 or 2 eq, Table 1) was added dropwise to a solution of a dienophile (**1**, 1 mmol) in dry solvent (25 mL) at the given temperature (Table 1), and the mixture was stirred for 20 min. A solution of cyclopentadiene (170 μL, 2 mmol) in the same dry solvent (5 mL) was added dropwise. The mixture was stirred at the given temperature (until the starting material was consumed; TLC) and subsequently treated according to the following procedures.

$SnCl_4$. The reaction mixture was quenched with the addition of aq HCl (10%, 30 mL). The organic layer was separated, washed with aq Na_2CO_3 (10%, 25 mL), water (2 × 20 mL) and brine (20 mL), and dried over $MgSO_4$. The solvent was evaporated under reduced pressure.

$TiCl_4$. The reaction mixture was quenched with saturated aq $NaHCO_3$ (25 mL). The organic phase was separated and washed with water (2 × 20 mL) and brine (20 mL), and dried over $MgSO_4$. The solvent was removed under reduced pressure.

$EtAlCl_2$. The reaction mixture was quenched with aq NaOH (10%, 25 mL). The organic layer was separated and washed with water (2 × 20 mL) and brine (20 mL), and dried over $MgSO_4$. The solvent was evaporated under reduced pressure.

Finally, the product **2** (four stereoisomers) was purified by column chromatography (diethyl ether/petroleum ether, 3 : 7) in all procedures.

(*S*)-2-Oxo-1,2-diphenylethylbicyclo[2.2.1]hept-5-ene-2-carboxylate (2a). Prepared from **1a**; yield 85–95%; white solid; mp 89.7–96.5 °C; a mixture of diastereomers (Table 1). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.29 (d, 1H, J = 8.3 Hz), 1.40–1.55 (m, 2H), 1.87–2.01 (m, 1H), 2.92 (bs, 1H), 3.07–3.19 (m, 1H), 3.26 (bs, 0.4H), 3.39 (bs, 0.6H), 5.85 (dd, 0.4H, J_1 = 5.4 Hz, J_2 = 2.8 Hz), 6.08 (dd, 0.6H, J_1 = 5.4 Hz, J_2 = 2.8 Hz), 6.18 (dd, 1H, J_1 = 5.3 Hz, J_2 = 2.9 Hz), 6.80 (d, 1H, J = 5.9 Hz), 7.33–7.42 (m, 5H), 7.44–7.53 (m, 3H), 7.92 (d, 2H, J = 7.6 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 29.5, 29.6, 42.8, 42.8, 43.2, 43.4, 46.0, 46.6, 49.9, 77.4, 77.5, 128.7, 128.8, 129.0, 129.2, 129.3, 132.5, 132.9, 133.5, 133.5, 134.1, 134.2, 135.1, 135.1, 137.6, 138.0, 174.5, 174.5, 194.4, 194.4. FTIR (KBr, cm^{-1}): 3062, 2976, 2870, 1736, 1687, 1595, 1448, 1338, 1225, 1176, 1105, 943, 756, 698, 538. Anal. calcd for $C_{22}H_{20}O_3$: C, 79.50; H, 6.06%. Found: C, 79.15; H, 6.13%. HRMS (MS ES+): cald for $C_{22}H_{21}O_3$ (M + H$^+$) 333.1491, found 333.1485.

(S)-2-(2-Methoxyphenyl)-2-oxo-1-phenylethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (2b). Prepared from **1b**; yield 85–95%; white crystals; mp 51.9–59.8 °C; a mixture of diastereomers (Table 1). ^{1}H NMR (300 MHz, $CDCl_3$): see Fig. S9 (ESI‡). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) major diastereomer (*endo*): 29.2, 42.6, 42.9, 46.3, 49.5, 55.3, 80.1, 111.5, 120.7, 126.9, 128.4, 128.5, 128.6, 131.0, 132.8, 133.9, 134.2, 137.0, 158.1, 174.1, 195.1; minor diastereomer (*exo*): 29.3, 42.5, 43.1, 46.3, 49.5, 55.3, 80.2, 111.4, 120.7, 126.8, 128.4, 128.4, 128.5, 131.0, 132.3, 133.9, 134.5, 137.5, 158.0, 174.0, 195.3. FTIR (KBr, cm^{-1}): 3059, 2976, 2941, 1872, 2834, 1730, 1676, 1595, 1485, 1460, 1288, 1246, 1171, 1022, 758, 704. UV (CH_3OH):

ε_{313} = 4100 dm^3 mol^{-1} cm^{-1}. HRMS (MS ES^+): cald for $C_{23}H_{22}O_4$ (M + H+) 363.1591, found 363.1584.

Photolysis of 2a and 2b: Formation of 8a and 8b

A solution of **2a** or **2b** (5 mmol) in degassed methanol (100 mL) was irradiated using a 400 W Hg lamp through a 313 nm bandpass glass filter. When the conversion reached 70–90% (TLC), methanol was removed under reduced pressure. The residue was dissolved in dichloromethane (25 mL), and the solution was washed with aq NaOH (10%; 3 × 25 mL). The side-products **8a** or **8b**, respectively, were isolated from the dichloromethane solution (see below), and the basic aqueous layers were processed according the instructions in the following paragraph.

The *dichloromethane solution* was washed with water (25 mL) and brine (20 mL), and dried over $MgSO_4$. The title compound was separated from the mixture by column chromatography (diethyl ether/petroleum ether, 1 : 9).

2-Phenyl-1-benzofuran (8a). Prepared from **2a**; 73% yield; white solid; mp 112.2–115.1 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.03 (s, 1H), 7.23 (dt, 1H, J_1 = 7.3 Hz, J_2 = 1.0 Hz), 7.29 (dt, 1H, J_1 = 7.3 Hz, J_2 = 1.7 Hz), 7.34–7.39 (m, 1H), 7.42–7.49 (m, 2H), 7.53 (dd, 1H, J_1 = 7.6 Hz, J_2 = 0.7 Hz), 7.59 (dd, 1H, J_1 = 7.3 Hz, J_2 = 1.3 Hz), 7.87 (td, 2H, J_1 = 7.2 Hz, J_2 = 1.7 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 101.5, 111.4, 121.1, 123.2, 124.5, 125.2, 128.8, 129.0, 129.5, 130.8, 155.2, 156.2. MS (EI, *m*/*z*): 194 (100), 117 (60), 77 (80). FTIR (KBr, cm^{-1}): 3051, 2966, 1639 (br), 1473, 1452, 1259, 1099, 1018, 916, 804, 744, 688, 494. This compound has been characterized before.[8]

2-(2-Methoxyphenyl)-1-benzofuran (8b). Prepared from **2b**; 64% yield; white solid; mp 75.6–76.8 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm), 4.04 (s, 3H) 7.04 (d, 1H, J = 8.3 Hz), 7.11 (dt, 1H, J_1 = 7.6 Hz, J_2 = 0.9 Hz), 7.33–7.23 (m, 3H), 7.38 (s, 1H), 7.53 (dd, 1H, J_1 = 8.0 Hz, J_2 = 1.1 Hz), 7.61 (dd, 1H, J_1 = 7.3 Hz, J_2 = 1.6 Hz), 8.10 (dd, 1H, J_1 = 8.0 Hz, J_2 = 1.7 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 55.7, 106.5, 111.0, 111.3, 119.7, 121.0, 121.2, 122.9, 124.3, 127.3, 129.5, 130.0, 152.4, 154.1, 156.8. MS (EI, *m*/*z*): 224 (100), 209 (20), 118 (50), 91 (30), 77 (30). FTIR (KBr, cm^{-1}): 1730, 1639, 1602, 1493, 1448, 1281, 1250, 1163, 1018, 918, 818, 744, 698, 660. This compound has been characterized before.[48]

The *basic aqueous layer* (see title procedure) was cautiously acidified to pH = 3 with concentrated aq HCl, and extracted with dichloromethane (20 mL). The organic layer was washed with water (25 mL), dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure at 20 °C. To simplify the subsequent GC analyses, the acids were converted to their methyl esters **7** according to the following procedure.[40]

Methyl ester of bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (7, four stereoisomers). The stereoisomers of **3**, present in the irradiated mixture, were converted to the corresponding methyl norbornenates **7** according to a known procedure.[40] *p*-Toluenesulfonic acid (6 mg) was added to a solution of **3** (50 mg) in methanol (10 mL) and the resulting solution was refluxed overnight. It was then cooled to 20 °C, poured into cold water (20 mL), and extracted with n-hexane (15 mL). The organic layer was washed with cold water (15 mL), saturated aq $NaHCO_3$ (15 mL), and brine (20 mL), dried over $MgSO_4$, and analyzed. Product **7** identification was based on comparison with the GC retention times and mass spectra of the synthesized authentic compounds (ESI‡).

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