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An Investigation of the Solid-State Photochemistry of α-Mesitylacetophenone Derivatives: Asymmetric Induction Studies and Crystal Structure–Reactivity Relationships

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Abstract—The photochemical conversion of a series of α-mesitylacetophenone derivatives into 2-indanols via δ-hydrogen abstraction has been investigated in the solid state. A correlation between solid-state reactivity and crystal structure has been established for this type of reaction. For the seven compounds whose crystal structures were determined, the average value of **d** (C═O···H distance) and **L** (C═O···CH_3 distance) were 2.77±0.04 Å and 3.42±0.06 Å, and the value of ω (δ-H out of plane angle), Δ (C═O···H angle) and θ (C–H···O angle) were 59±2°, 80±7° and 123±3°, respectively. These parameters depended mainly on the magnitude of the deviation of the carbonyl group from the fully bisecting position over the mesityl ring, which ranged from 9–14° in the case of in the solid state reactive ketones and approached 0° for the unreactive compounds. Asymmetric induction studies were carried out by providing the reactants with carboxylic acid substituents to which ionic chiral auxiliaries were attached through salt formation with optically active amines. Irradiation of the salts (13 in total) in the crystalline state gave enantiomeric excesses of up to 90%. The crystal structures of three of the salts were determined and on this basis, the reasons for the selectivity in the crystalline state are discussed.

Introduction

Investigations of the photochemical behavior of organic compounds in a solid environment have been of interest to theoretical as well as synthetic chemists for some time now. Our interests have been centered around the pure crystalline state, since this medium makes it possible to determine the exact structure under study by using the very powerful technique of X-ray crystallography. We and others have carried out extensive research that has defined the role of the crystal lattice in controlling organic photoreactivity.[1] Through correlation of the reactivity pattern for a series of closely related compounds with their X-ray crystal structures, detailed mechanistic information on the preferred interatomic distances and angular requirements for a particular type of reaction can be obtained. This work has also shown that, compared to the results in fluid media, profound changes in reaction regio- and stereoselectivity can be achieved by irradiation of molecular crystals. Organic photochemistry offers a variety of reactions that transform achiral starting materials into chiral photoproducts, and to perform these reactions enantioselectively is one of the challenges facing organic photochemists these days. Our approach is based on the solid state irradiation of materials that crystallize in chiral space groups, where the chiral environment within the crystal takes on the role of an asymmetric inductor. Spontaneous crystallization of achiral compounds in chiral space groups, while well documented,[2] is rare and unpredictable and therefore unsuitable as a general method to perform asymmetric induction in the solid state. It occurred to us that one approach to overcome this problem lay in the use of ionic chiral auxiliaries.[3] By introducing a carboxylic acid group into the photoreactant and forming a salt with an optically pure amine, we obtain a compound that is required to crystallize in a chiral space group.

In this paper, we describe the application of the solid-state ionic chiral auxiliary approach to asymmetric induction. The reaction chosen for investigation was the photocyclization of α-mesitylacetophenone **1a** leading to 2-phenyl-2-hydroxy-4,6-dimethylindan (**2a**), which Wagner reported in 1991 to be highly efficient upon irradiation in solution as well as in the solid state.[4] The mechanism is similar to the Norrish/Yang type II sequence, and involves triplet-mediated δ-hydrogen abstraction via a seven membered transition state that generates a 1,5-biradical, which then undergoes ring closure[5] (Scheme 1).

A new stereogenic center is created from an achiral substrate during this reaction. Because only racemic mixtures were obtained by photolyzing pure α-mesitylacetophenone, this prompted us to investigate asymmetric induction using the ionic chiral auxiliary method.[6]

Keywords: photochemistry; cyclization; asymmetric induction.
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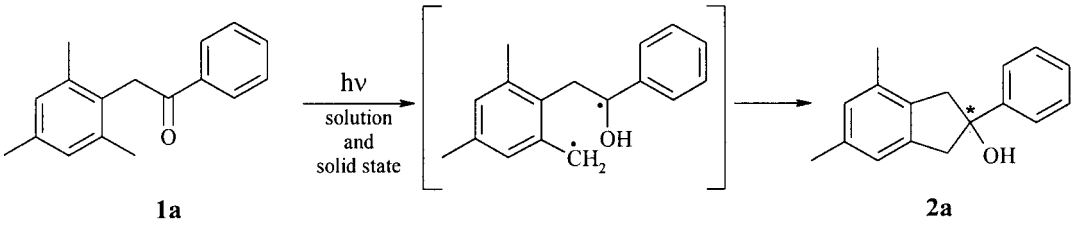


1a **2a**

Scheme 1. Photocyclization of α-mesitylacetophenone.

Although much is known about the geometric requirements for γ-hydrogen abstraction,[5] very little comparable data have been published on the δ-H-abstraction process.[7] We therefore decided to perform a crystal structure-solid state reactivity correlation study prior to the investigation of the chiral salts, in order to have a better understanding of the reaction under consideration.

Results and Discussion

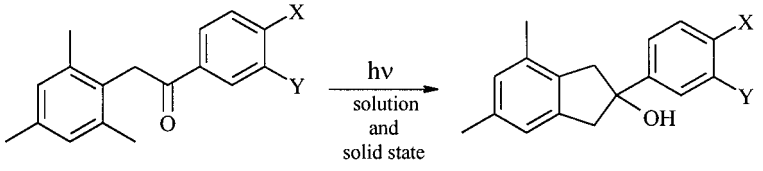
Crystal structure–solid-state reactivity

In developing crystal structure–solid-state reactivity relationships, it is desirable to have a series of closely related compounds to study, since this permits general trends to be detected. Accordingly, α-mesitylacetophenones **1b**–**k** (Scheme 2) were synthesized by standard procedures as outlined in the experimental section. All nine ketones were crystalline, and we were able to obtain the crystal structures of seven of them (**1b**–**d**, **1f**–**g**, **1j**–**k**). None of these ketones crystallized in a chiral space group, thus precluding absolute asymmetric synthesis studies.

Irradiation of ketones **1b**–**k** in solution led efficiently and exclusively to the corresponding 2-indanols **2b**–**k**. Similar results were obtained in the solid state, and Table 1 summarizes the conversions obtained as a function of irradiation temperature. The techniques used for solid-state irradiations are described in the Experimental Section. Low temperature photolyses were conducted in order to minimize the loss of topochemical control in the crystal lattice through melting, as observed in some cases.

The 2-indanols **2b**–**k** were the only photoproducts detectable by GC, with one exception. Upon photolysis of keto-ester **1j** to low conversion, we observed two photoproducts of similar retention time and identical molecular mass (GC/MS), with 2-indanol **2j** still being the major product. At higher overall conversion the ratio of indanol to unknown byproduct increases in favor of the former, until it becomes the only detectable product. Because of the very low yields we were unable to isolate the byproduct.[8]

The data collected in Table 1 are only a rough estimate of quantum yields in the solid state, and no rate constants could be obtained. Given the difficulties involved in making quantitative measurements in solids, the observation of efficient photocyclization merely indicates that hydrogen abstraction can occur.[9] Nevertheless, indanol formation could not occur unless these ketones exist in geometries that allow formation via δ-hydrogen abstraction of



1b-k **2b-k**

para-**1/2**: **(b)** X = F, Y = H
(c) X = CN , Y = H
(d) X = COOH , Y = H
(e) X = COOMe , Y= H

meta-**1/2**: **(f)** X = H ,Y = F
(g) X = H, Y = CN
(h) X = H, Y = COOH
(j) X = H, Y = $COOCH_3$
(k) X = H, Y = CH_3

Scheme 2.

Table 1. Temperature-dependent conversions in the solid-state photolysis of α-mesitylacetophenones **1b**–**k**

T (°C)[a]	*t* (h)	**1b** (%)	**1c** (%)	**1d** (%)	**1e** (%)	**1f** (%)	**1g** (%)	**1h** (%)	**1j**[b] (%)	**1k** (%)
Rt	2	0	96	31	58	76[c]	100	28	30 (73)	97[c]
−20	2	0	45	5	10	21	70	6	3 (100)	0

[a] rt=ambient temperature in photolysis box (30–40°C).
[b] % Yield of indanol in brackets (see text).
[c] Sample showed signs of melting upon photolysis.

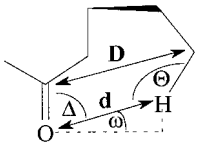


Figure 1.

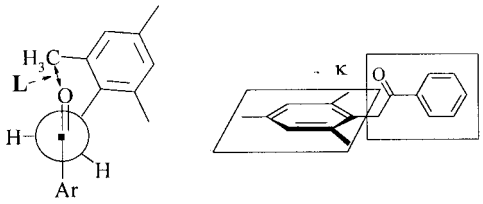


Figure 2.

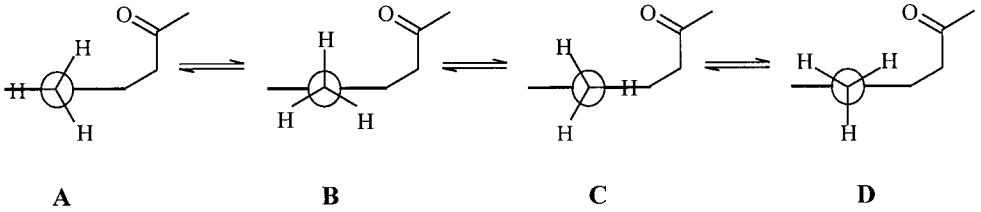
biradicals in conformations that can then cyclize without too much molecular motion.

There are four geometric parameters associated with the hydrogen abstraction process as established for the Norrish/Yang type II reaction sequence (Fig. 1).[10] The symbol **d** is given to the CO···H distance, and it seems reasonable to suggest that the optimum value should be close to the sum of the van der Waals radii for oxygen and hydrogen, which is 2.72 Å. The symbol ω refers to the angle by which the hydrogen atom lies outside the mean plane of the carbonyl group, and since the *n*-orbitals of oxygen, which are generally agreed to be involved in the abstraction process, lie in this plane, its ideal value is expected to be 0°. The angle Δ defines the CO···H angle, and its optimum value lies between 90–120°, depending on the hybridization of the non-bonding electrons on oxygen. The symbol θ refers to the CH···O angle, which according to theory, should have an optimum value of 180°.[12] Finally, the symbol **D** represents the interatomic distance between the two carbon atoms and is expected to be around 3.4 Å, the sum of the van der Waals radii of the two carbon atoms. In the case of α-mesitylacetophenones, one can expect the methyl groups to rotate around the single bond, even in the crystalline state, though they still spend most of the time at or near the energy minimum (conformation A or C in Scheme 3). Thus, the above discussed abstraction parameters are not necessarily fixed as in the case of more rigid compounds.

For this reason, we define a new parameter with reference to Fig. 2 to take the rotational freedom of the methyl groups in α-mesitylacetophenone derivatives into account. The distance **L** between the carbonyl oxygen atom and the methyl carbon atom does not change upon rotation of the methyl group and therefore seems to be more valuable for predicting hydrogen abstraction. The ideal value for **L** is 3.70 Å, given by the sum of $\mathbf{d}_{ideal}$=2.72 Å and the CH-bond length (0.98 Å) at the angle θ_{ideal}=180° (see Fig. 1). Another parameter, κ, has been defined to show the magnitude of the deviation of the carbonyl group from the fully bisecting position, which is best given by the value of the dihedral angle between the carbonyl plane and the plane defined by the mesityl ring carbon atoms. The ideal value for κ is 0°, which situates the carbonyl group closest to a δ-hydrogen by being in the same plane as one of the *m*-methyl groups. The least favorable value for κ is 90°, in which case the carbonyl group is totally bisecting the mesityl plane.

Hydrogen abstraction in the solid state is likely to occur with a minimum of motion in the carbon framework, and we assume that ground state geometric data derived from X-ray crystallography can be used to analyze the behavior of the excited molecule in the crystal lattice as well.[10] The values of **d**, **L**, ω, Δ, θ, κ and **D** derived from crystal structure analyses of ketones **1b–k** are summarized in Table 2.

The conformations of all these molecules are essentially the same. The central carbonyl moiety is approximately coplanar with the *p*- or *m*-substituted phenyl group and is pointed towards the mesityl ring. The most significant difference lies in the torsion angle κ. The two cyano ketones **1c** and **1g** show the shortest abstraction distances **d** and **L**, which is consistent with the observed torsion angle κ in both compounds deviating by 14° from its bisecting angle of 90°. The angles ω, Δ and θ lie within established values.[10] Ketones **1c** and **1g** are expected to show a high reactivity in the solid state, as was found (Table 1). The asymmetric unit of keto acid **1d** contains four independent molecules. Only two of these have the carbonyl oxygen tilted more towards one of the two *o*-methyl groups (κ=77 and 79°, Table 2) and the observed abstraction parameters predict hydrogen abstraction. The other two molecules have the carbonyl group almost bisecting the mesityl ring plane and the closest hydrogen (**d**)/methyl carbon (**L**) is too far from the carbonyl oxygen for abstraction to occur. This fact should reduce the reactivity of *p*-keto acid **1d**. In *m*-fluoro ketone **1f** and *m*-keto ester **1j** the closest methyl groups are disordered and only 77 and 67% of the hydrogens lie close enough for abstraction to occur (Scheme 2: conformer A versus C). Even if we expect the methyl groups to rotate during photolysis, the greater values for **L** predict a lower reactivity in comparison to the cyano ketones **1c** and **1g**, and that was also found (Table 1). Finally, the crystal structure of the *m*-methyl ketone **1k** suggests why it should be almost unreactive in the solid state. With the torsion angle κ between the carbonyl plane and the mesityl ring being



Scheme 3.

Table 2. Crystallographically derived C═O···H_δ-abstraction geometries for ketones **1b–k**

Ketone[a]	**d** (Å)	**L** (Å)	ω (°)	Δ (°)	θ (°)	κ (°)	**D** (Å)	Occ.[b]
1b	2.93	3.56	59	77	122	85	3.45	
1c	2.71	3.33	61	86	121	76	3.32	
1d[c]	3.31	3.84	42	86	117	90	3.78	
	2.79	3.38	59	88	119	76	3.37	
	2.77	3.46	56	65	118	79	3.53	
	3.15	3.77	60	61	122	88	3.31	
1f[d]	2.80	3.44	57	83	125	81	3.43	0.77
	3.10		48	66	102			0.23
1g	2.73	3.38	64	83	124	76	3.30	
1j[d]	2.83	3.52	59	74	128	81	3.40	0.67
	3.22		60	85	99			0.33
1k	3.03	3.66	61	69	123	87	3.39	
Average[e]	2.77±0.04	3.42±0.06	59±2	80±7	123±3	78±2	3.39±0.06	–
Ideal[10]	2.72	3.70	0	90–120	180	0	≤3.4	–
γ-H-Exp.[10]	2.54–2.90	–	34–64	76–92	113–117	–	2.95–3.10	–

[a] Only the parameters for the closest methyl group and its closest hydrogen are shown.
[b] Occupancy factor to signify population of the disordered component.
[c] Four independent molecules in the asymmetric unit.
[d] Rotational disorder in the *o*-methyl groups.
[e] Average of best values for reacting ketones **1c–j**.

close to 90°, the abstraction distances **d** and **L** are comparably long. In fact, ketone **1k** shows the longest abstraction distances in this series of compounds. The observed high yields for **1k** at room temperature are most likely due to melting with a concomitant loss of topochemical control resulting from the breakdown of the ordered crystal lattice. Upon photolysis at −20°C, where melting is suppressed, no reaction in ketone **1k** was observed. The lack of reactivity of the *p*-fluoro ketone **1b** in the solid state cannot be explained sufficiently by looking at the crystal structure. From the observed abstraction parameters it is predicted to react slowly, but a total lack of reactivity in the solid state is unexpected. Analysis of the crystal packing pattern of ketone **1b** in comparison with the other ketones **1c–k** does not show any difference in the free space around a molecule within the crystal. This excludes the possibility of steric interactions between two molecules in the crystal being responsible by preventing even the minimum motion required for reaction to occur. On the other hand, looking at the electronic features there is no reason to expect a *p*-fluoro substituent to have a large effect on the energy levels and therefore alter the photochemical behavior of a phenyl ketone.[11] The question why ketone **1b** does not react in the solid state remains unsolved.

By comparing the hydrogen abstraction geometries given in Table 2 with those from previous studies on the Norrish/Yang type II reaction in the solid state,[10] we find an excellent agreement. The abstraction distance **d**, as well as the angles ω, Δ and θ, come close to the previously reported values, and they show the same tendency as the two new parameters **L** and κ, introduced to take the rotational freedom of the methyl groups in α-mesitylacetophenones into account. It seems logical that cyclization occurs even though the distances between the two radical centers in 1,5 biradicals (**D**=3.30–3.53 Å) are longer than in the corresponding 1,4-biradicals (**D**=2.95–3.10 Å).[10] Unlike 1,4-biradicals, in which cleavage competes strongly with cyclization to a strained cyclobutane, 1,5 biradicals cyclize to relatively strain-free rings, and the possible competing 1,6-hydrogen shift to form an alkene has to overcome a more strained 7-membered transition state.

Asymmetric induction

Salts **S1–10** and **S11–13** formed between carboxylic acids **1d** and **1h** and a number of commercially available, enantiomerically pure amines (Table 3) were prepared and crystallized. X-Ray quality crystals were obtained for three of the salts—the *R*-(+)-α,4-dimethylbenzylamine salt (**S3**), the *R*-(+)-*N*,α-dimethylbenzylamine salt (**S4**) and the (1*S*,2*R*)-(+)-norephedrine salt (**S6**).

Solid state irradiations were conducted for various periods of time and at different temperatures on 5–10 mg crystalline samples of salts **S1–13** sandwiched between two Pyrex plates.[13] The extent of conversion was estimated by gas chromatography following workup with diazomethane, and the enantiomeric excesses in which photoproduct **2e** or **2j** was formed in each case was determined using chiral HPLC. The results of the photochemical studies in the solid state are compiled in Table 3.

In several cases high enantiomeric excesses with over 90% *ee* could be obtained. As expected, irradiation of salts **S1** and **S2** as well as **S5** and **S6** formed between carboxylic acid **1d** and the two optical antipodes of the same amine give rise to enantiomeric 2-indanols of similar *ee*. A well-behaved system like this allows access to both enantiomers by simple exchange of the ionic chiral auxiliary. An increase in conversion leads to decreasing *ee* values, due to the loss of topochemical control resulting from the breakdown of the ordered crystal lattice as starting material converts into photoproduct (although no melting was observable). As shown for some salts in Table 3, low temperature photolysis can be used to compensate this effect. By using different solvents for recrystallization we were able to obtain dimorphic crystals of salt **S13**, needles and flakes. Upon photolysis the needles reacted faster and led to better enantiomeric excess at low conversion. Comparison of

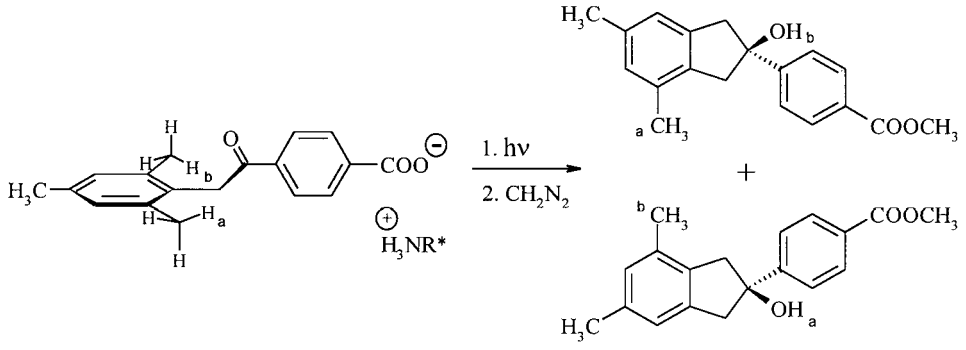
Table 3. Solid-state photolysis results for chiral salts of keto acid **1d** and **1h**

Entry	Keto-acid	Ionic chiral auxiliary	Time (min)	Temp. (°C)[a]	Convers. (%)[b]	ee of **2e/2j** (%)[c]	HPLC Peak[d]
S1	**1d**	(*S*)-(−)-α-Methylbenzylamine	30	rt	69	69	1
			08	rt	16	94	
			120	−20	61	83	
S2	**1d**	(*R*)-(+)-α-Methylbenzylamine	30	rt	53	66	2
			06	rt	18	92	
			120	−20	74	75	
S3[e]	**1d**	(*R*)-(+)-α,4-Dimethyl-benzylamine	180	rt	89	83	1
			07	rt	32	92	
S4[e]	**1d**	(*R*)-(+)-*N*,α-Dimethyl-benzylamine	280	rt	14	0	
S5	**1d**	(1*R*,2*S*)-(−)-Norephedrine	60	rt	56	82	1
			06	rt	12	97	
			140	−19	21	95	
S6[e]	**1d**	(1*S*,2*R*)-(+)-Norephedrine	130	rt	80	80	2
			06	rt	12	90	
			62	−19	30	98	
S7	**1d**	(1*S*,2*S*)-(+)-2-Amino-1-phenyl-1,3-propanediol	60	rt	62	4	2
			08	rt	12	16	
			120	−19	38	12	
S8	**1d**	(1*R*,2*S*)-(+)-Aminoindanol	240	rt	13	39	1
S9	**1d**	*cis*-(−)-Myrtanylamine	240	rt	81	13	2
			60	rt	40	19	
S10	**1h**	(*S*)-(−)-α-Methylbenzylamine	120	rt	63	43	1
			16	rt	12	69	
			310	−19	10	77	
S11	**1h**	(*R*)-(+)-*N*,α-Dimethyl-benzylamine	210	rt	2	0	–
S12	**1h**	(1*R*,2*S*)-(−)-Norephedrine	90	rt	69	37	2
			30	rt	36	48	
			90	−18	17	55	
S13	**1h**	(1*R*,2*S*)-(+)-Aminoindanol, needles	60	rt	86	18	2
		Needles	05	rt	32	79	
		Flakes	45	rt	26	47	
		Flakes	335	rt	73	37	

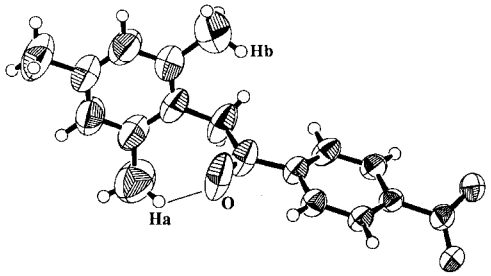
[a] rt=ambient temperature in photolysis box (30–40°C).
[b] Percentage of total GC integral due to compound **1e** or **1j**. Remaining integral due >98% within experimental error to photoproduct **2e** or **2j**.
[c] Enantiomeric excesses measured by chiral HPLC.
[d] Peak 1 indicates major enantiomer is first peak eluted from chiral HPLC column.
[e] Crystal structure obtained.

salts **S1–10** prepared from *para*-carboxylic acid **1d**, and salts **S11–13** formed between the same optically pure amines and *meta*-carboxylic acid **1h** reveals that enantioselectivity depends not only on the chiral ionic auxiliary but on the location of the carboxylic acid group in the reactant as well. Small structural changes in the acid as well as in the chiral base have a considerable influence on reactivity and selectivity in the δ-hydrogen abstraction-cyclization sequence of α-mesitylacetophenones in the solid state. By optimizing the chiral auxiliary used we were able to achieve over 80% *ee* at 80–90% conversion, which indicates synthetic value.

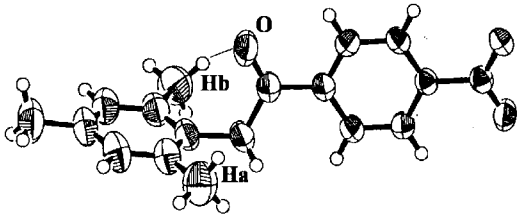
There is a plausible explanation as to how the observed solid state enantioselectivity is governed by structural factors. In mesitylacetophenone there are two 'enantiotopic' methyl groups available for δ-hydrogen abstraction by the excited ketone to form the 1,5-biradical. If we label the methyl



Scheme 4.



S3



S6

Figure 3.

group proximal to the *re* face of the carbonyl group as *a* and the methyl group proximal to the *si* face as *b* as shown in Scheme 4, abstraction of a hydrogen atom from group *a*(*b*) should lead to the S(R)-enantiomer, assuming that, with molecular motions severely restricted in the crystalline state, rotation at the biradical stage around the single bonds between the carbonyl group and the mesityl ring to form the opposite enantiomer does not occur. The reactant may adopt a conformation in the crystal lattice that situates the carbonyl oxygen closer to one *o*-methyl group than the other. In fact, the previously discussed crystal structures of ketones **1b**–**k** showed that the carbonyl group is indeed not always perfectly perpendicular to the mesityl ring plane as indicated by $\kappa \neq 90°$ (Table 2).

Fig. 3 shows the molecular conformations of α-mesityl-4-carboxyacetophenone in the chiral crystal lattices of salts **S3** and **S6**. Since the absolute configurations of the ammonium cations are known, the absolute conformations of the reacting ketones can be assigned unequivocally. The abstraction parameters are compiled in Table 4, together with those for salt **S4**.

The X-ray crystal structure of salt **S3** clearly shows a hydrogen atom on methyl group *a* being in a favorable position for δ-hydrogen abstraction (Table 4). The distance **d** between the carbonyl oxygen and H_a is over 1 Å shorter than the corresponding distance to H_b, and the angles are also at better settings for abstraction. The twisted conformation is emphasized by the 15° deviation of the dihedral angle κ from its bisecting angle of 90°. According to the observed crystal structure data, hydrogen abstraction should occur preferentially from methyl group *a*, and this predicts that the (*S*)-enantiomer of photoproduct **2e** should be formed in excess. Formation of the (*R*)-enantiomer would require a 180° rotation of the acyl group, which is topochemically unlikely in the crystalline state. These findings clearly explain the high enantioselectivity observed for salt **S3**. By comparison with the geometric parameters for ketones **1b**–**k**, salt **S3** shows the shortest distances and best angular values observed in this series. This no doubt helps to account for the relatively short photolysis times needed (Table 3).

Support for the picture presented above comes from the crystal structure of salt **S6**. In this case, the absolute conformation of the reacting molecule shows the carbonyl group pointing towards H_b rather than H_a, as suggested by the dihedral angle κ being 102°, and hydrogen H_b is clearly favored to be abstracted. Therefore photolysis of salt **S6** leads to the optical antipode (peak 2) of indanol **2e**, and the assumption that was made earlier concerning the restricted motion of the biradical in the solid state appears justified.

Finally, the crystal structure of salt **S4** explains why photolysis of this material in the solid state gives only racemic product **2e**. Crystals of the *R*-(+)-*N*,α-dimethylbenzylamine salt (**S4**) contain equal amounts of two independent conformational isomers of the mesitylacetophenone moiety in the asymmetric unit. The two conformers have a near mirror image relationship and each slightly favors abstraction of the opposite δ-hydrogen. Thus abstraction of H_a is favored for one molecule and abstraction of H_b for the other,

Table 4. Crystallographically derived C═O···H_δ-abstraction geometries

Salt	δ-Hydrogen	**d** (Å)	**L** (Å)	ω (°)	Δ (°)	θ (°)	κ-90 (°)	**D** (Å)
S3	H_a	2.60	3.29	50	90	128	−15	3.46
	H_b	3.66		45	53	114		3.69
S4[a]	H_a	3.07	3.74	58	60	126	−1	3.32
	H_b	3.14		37	80	126		3.79
	H_a'	3.11	3.71	34	90	124	+2	3.79
	H_b'	3.05		51	52	126		3.26
S6	H_a	3.68	3.38	53	68	108	+12	3.72
	H_b	2.69		56	84	127		3.45
Aver.[b]	δ-H	2.85±0.21	3.53±0.20	54±3	72±16	127±1	|7|±6	3.37±0.08

[a] Two independent molecules in the asymetric unit.
[b] Average values with standard deviations taken from the six reacting ketones **1c**–**j**.

and the overall result is formation of racemic product **2e**. Similar observations have been made by us previously, although in those cases some asymmetric induction was still observed (ee<30% at low conversion) due to the reaction taking place in the chiral environment of the crystal lattice.[14] A totally racemic outcome of the photolysis of salt **S4** was unexpected and may be due to a non-stereospecific reaction course after all. It should also be noted that, with the carbonyl group almost bisecting the mesityl ring (κ=89/92°), the overall observed geometric parameters are poor for hydrogen abstraction to occur, and this explains the lower reactivity of salt **S4** compared to salts **S3** and **S6**.

Conclusion

In summary this paper demonstrates once more the extent to which reactivity and selectivity in the solid state are controlled by the conformation adopted by each component in the crystal lattice. As a result, the ionic chiral auxiliary method allows us to govern enantioselectivity in solid state photochemical reactions in a straightforward way.

Experimental

General information

Commercial spectral grade solvents were used for photochemical experiments unless otherwise stated. For synthetic use tetrahydrofuran, diethyl ether, hexane and benzene were dried over sodium/benzophenone complex; dimethyl sulfate and dichloro methane were dried over calcium hydride. Most starting materials were purchased from Sigma-Aldrich Canada, Ltd., and some were bought from Lancaster Synthesis, Inc.

Infrared spectra were recorded on a Perkin–Elmer 1710 Fourier transform spectrometer. Solid samples were ground in KBr (1–5%) and pelleted in an evacuated die (Perkin–Elmer 186-0002) at 17 000 psi. Liquid samples were run neat as thin films between two NaCl plates. Melting points were determined on a Fisher–Johns hot-stage apparatus and are uncorrected. Nuclear magnetic resonance spectra were recorded in deuterated solvents from Aldrich on 200, 400, and 500 MHz (Bruker) and 300 MHz (Varian) instruments. ^{13}C spectra were run under broadband $^{13}C\{^1H\}$ decoupling and assignments, where given, are supported by the attached proton test. For APT, (+) signifies C or CH_2 and (−) signifies CH or CH_3. Low- and high-resolution mass spectra were obtained from a Kratos MS 50 instrument at 70 eV. FAB mass spectra were recorded on an AEI MS-9 spectrometer with xenon bombardment of an alcohol matrix as noted. Ultraviolet spectra were recorded on a Perkin–Elmer Lambda-4B spectrometer in the solvents indicated. Elemental analyses were performed by the departmental microanalyst, Mr. P. Borda. Gas chromatographic analysis was performed on a Hewlett-Packard 5890 instrument fitted with a flame ionization detector and a Hewlett-Packard 3392 integrator. The following 15 m×0.25 mm capillary columns from J & W Scientific, Inc. were used: DB-5, HP-5. Analytical thin-layer chromatography was carried out on commercial precoated silica gel plates (Merck, type 5554). Column chromatography was performed by using 230–400 mesh silica gel (Merck 9384 or Silicycle) slurry packed with the eluting solvent. For flash chromatography compressed air was used. High-pressure liquid chromatography was performed on a Waters 600E system controller connected to a tunable UV detector (Waters 486). For the determination of enantiomeric excesses, a Chiralcel® OD column (250×4.4 mm^2) from Chiral Technologies, Inc. was used.

Preparation of starting materials

Mesitylacetic acid was prepared as described in *Organic Synthesis*,[15] and its acid chloride derivative was prepared according to the procedure of Lutz and Hinkley.[16] As far as we are aware, the remainder of the compounds described below are new.

α-Mesityl-4-fluoroacetophenone (1b). Following the procedure described by Leibovitch et al.,[3b] 10 g (50 mmol) of mesitylacetic acid chloride in 200 mL of anhydrous THF was added to 31 mL of a 2 M diethyl ether solution of 4-fluorobenzenemagnesium bromide (61 mmol) at −78°C. After slow warming to room temperature, the red-brown mixture was carefully hydrolized with water and acidified with 50% aqueous HCl. Standard workup (extraction with diethyl ether, washing, drying, and removal of the solvents) and recrystallization from ethanol afforded 9.2 g (36 mmol, 72%) of the desired ketone **1b** as light yellow needles: mp 131–133°C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.11–8.07 (2H, m, aryl-H), 7.19–7.13 (2H, m, aryl-H), 6.89 (2H, s, mesityl-H), 4.29 (2H, s, CH_2), 2.27 (3H, s, *p*-CH_3), 2.17 (6H, s, *o*-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.24 (−), 20.90 (−), 39.18 (+), 115.55 and 115.84 ($^2J_{C-F}$=22 Hz, negative), 128.10 (−), 128.89 (−), 130.59 and 130.71 ($^3J_{C-F}$=6 Hz, negative), 133.49 and 133.54 ($^4J_{C-F}$=3 Hz, positive), 136.39 (+), 136.72 (+), 164.03 and 167.40 ($^1J_{C-F}$= 225 Hz, positive), 195.53(+); IR (KBr) 2916, 1680 (C=O), 1600, 1506, 1486, 1413, 1327, 1229 (C–F), 1201, 1159, 994, 852, 841, 815, 604 cm^{-1}; MS (EI) *m/z* 256 (M+), 133 (base) 123, 95; HRMS 256.12601 (calcd for $C_{17}H_{17}FO$, 256.12634). Anal. Calcd for $C_{17}H_{17}FO$: C, 79.66; H, 6.69. Found: C, 79.55; H, 6.61.

α-Mesityl-4-cyanoacetophenone (1c). In a flame-dried 100 mL flask equipped with condenser and stirrer, 2.69 g (10.5 mmol) of ketone **1b** and 1.08 g (21.6 mmol) of sodium cyanide were dissolved in 70 mL of anhydrous dimethyl sulfoxide. The mixture was stirred at 120°C for 18 h until no starting material remained, as indicated by TLC (20% ethyl acetate–petroleum ether 35–60). The dark red solution was poured into 100 mL of water and extracted with ether (3×200 mL). Standard workup afforded a yellow solid, which was purified by flash chromatography (SiO_2, 15% ethyl acetate–petroleum ether 35–60). Recrystallization from methanol afforded 2.13 g (8.1 mmol, 77%) of the desired ketone **1c** as light yellow prisms: mp 129–131°C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (2H, d, *J*=8 Hz, aryl-H), 7.79 (2H, d, *J*=8 Hz, aryl-H), 6.90 (2H, s, mesityl-H), 4.32 (2H, s, CH_2), 2.28 (3H, s, *p*-CH_3), 2.17 (6H, s, *o*-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.2 (−), 20.9 (−), 39.6 (+), 116.3 (+), 117.9 (+), 128.9 (−), 128.4 (−), 128.5 (−) 132.5 (+), 136.6 (+), 136.7 (+),

139.8 (+), 196.0 (+); IR (KBr) 2921, 2232 (CN), 1686 (C═O), 1608, 1485, 1404, 1327, 1292, 1214, 995, 858, 838, 823, 700, 584 cm^{-1}; MS (EI) *m/z* 263 (M+), 133 (base) 115, 91; HRMS 263.13056 (calcd for $C_{18}H_{17}NO$, 263.13101). Anal. Calcd for $C_{18}H_{17}NO$: C, 82.09; H, 6.51; N, 5.32. Found: C, 82.10; H, 6.36; N, 5.21.

α-Mesityl-4-carboxyacetophenone (1d). To a 500 mL flask equipped with a condenser and stirrer was added 2.7 g (10.3 mmol) of ketone **1c**, 75 mL of a 25% aqueous sodium hydroxide solution and 250 mL of methanol. The mixture was refluxed for 4 h, cooled to room temperature and strongly acidified with 50% aqueous HCl. The aqueous layer was extracted with diethyl ether (1.5 L), and standard workup afforded after recrystallization from benzene 2.85 g (8.0 mmol, 78%) of the desired keto acid **1d** as colorless fine needles: mp 185–188°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.1 (1H, s (br), COOH), 8.59 (2H, d, *J*=8 Hz, aryl-H), 8.49 (2H, d, *J*=8 Hz, aryl-H), 7.24 (2H, s, mesityl-H), 4.71 (2H, s, CH_2), 2.63 (3H, s, *p*-CH_3), 2.55 (6H, s, *o*-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3 (−), 20.9 (−), 39.8 (+), 128.1 (−), 128.8 (−), 128.9 (−), 130.6 (−) 133.0 (+), 136.6 (+), 136.8 (+), 141.1 (+), 171.2 (+), 196.9 (+); IR (KBr) 2918, 2601, 2454, 1689 (C═O, COOH), 1425, 1291, 1214, 995 cm^{-1}; MS (EI) *m/z* 282 (M+), 149, 133 (base); HRMS 282.12609 (calcd for $C_{18}H_{18}O_3$, 282,12558). Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.37; H, 6.47.

α-Mesityl-4-carbomethoxyacetophenone (1e). A solution of 284 mg (1.0 mmol) of keto acid **1d** and 100 mg of *p*-toluensulfonic acid in 15 mL of methanol was refluxed for 4.5 h until no starting material remained as indicated by TLC (20% ethyl acetate–petroleum ether 35–60). The desired keto ester **1e** crystallized in fine needles from the reaction mixture. Recrystallization from methanol afforded 191 mg (0.7 mmol, 64%) of the desired keto-ester as colorless fine needles: mp 127–128°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16–8.08 (4H, m, aryl-H), 6.89 (2H, s, mesityl-H), 4.33 (2H, s, CH_2), 3.95 (3H, s, $COOCH_3$), 2.27 (3H, s, *p*-CH_3), 2.17 (6H, s, *o*-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3 (−), 20.9 (−), 39.7 (+), 52.4 (−), 127.9 (−), 128.9 (−), 129.9 (−), 133.9 (+), 136.5 (+), 136.7 (+), 140.4 (+), 166.2 (+), 196.8 (+); IR (KBr) 2953, 1718 ($COOCH_3$), 1685 (C═O), 1486, 1440, 1407, 1328, 1288 (CH_3), 1213, 1198, 1114, 995, 856, 766, 696 cm^{-1}; MS (EI) *m/z* 296 (M+), 163, 133 (base); HRMS 296.14156 (calcd for $C_{19}H_{20}O_3$, 296.14124). Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 76.84; H, 6.75.

α-Mesityl-3-fluoroacetophenone (1f). To 260 mg of magnesium turnings, activated with 10 μL of 1,2-dibromoethane or iodine, in 5 mL of anhydrous ether was added 1.04 g (5.9 mmol) of 1-bromo-3-fluoro benzene at a rate to keep the ether at reflux. After the addition was complete, the mixture was refluxed for another 20 min. An additional 15 mL of anhydrous ether was added and the solution was cooled to −78°C (acetone/dry ice), whereupon 825 mg (4.2 mmol) of mesitylacetic acid chloride dissolved in 5 mL of ether was transferred into the cooled flask. After slow warming to room temperature the mixture was carefully hydrolized with 15 mL 1N hydrochloric acid. The aqueous layer was extracted with diethyl ether and standard workup afforded after chromatography (silica gel, 2% ethyl acetate–petroleum ether 35–60) and recrystallization from methanol 444 mg (1.7 mmol, 41%) of the desired ketone **1f** as colorless cubes: mp 110–113°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (1H, dt, *J*=8, 1 Hz, aryl-H), 7.74–7.71 (1H, m, aryl-H), 7.50–7.45 (1H, m, aryl-H), 7.31–7.26 (1H, m, aryl-H), 6.89 (2H, s, mesityl-H), 4.29 (2H, s, CH_2), 2.27 (3H, s, *p*-CH_3), 2.17 (6H, s, *o*-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.26 (−), 20.94 (−), 39.45 (+), 114.70 and 114.99 ($^2J_{C-F}$=22 Hz, negative), 120.00 and 120.28 ($^2J_{C-F}$=22 Hz, negative), 123.74 and 123.78 ($^4J_{C-F}$=3 Hz, negative), 128.85 (−), 130.28 and 130.39 ($^3J_{C-F}$=8 Hz, negative), 136.51 (+), 136.73 (+), 139.09 and 139.17 ($^3J_{C-F}$=6 Hz, positive), 161.22 and 164.51 ($^1J_{C-F}$=248 Hz, positive), 195.92(+); IR (KBr) 2915, 1682 (C═O), 1589, 1486, 1442, 1413, 1331, 1251 (C–F), 1169, 1152, 875, 787, 681 cm^{-1}; MS (EI) *m/z* 256 (M+), 133 (base), 123; HRMS 256.12615 (calcd for $C_{17}H_{17}FO$, 256.12634). Anal. Calcd for $C_{17}H_{17}FO$: C, 79.66; H, 6.69. Found: C, 79.58; H, 6.77.

α-Mesityl-3-cyanoacetophenone (1g). 2-Mesitylethanol (5.8 g, 35.4 mmol) was converted into the corresponding mesitylacetaldehyde by standard Swern oxidation (4.5 g, 78% after flash chromatography on silica gel, eluent 10% ethyl acetate–petroleum ether 35–60).[17] A solution of 1.0 g (6.4 mmol) of mesitylacetaldehyde in 5 mL of THF was added slowly at −90°C (diethyl ether–liquid nitrogen) to a THF–hexane solution of 3-cyanophenyl lithium (freshly prepared from 3-bromobenzonitrile (1.2 g) and 4.3 mL of a 1.6 M in THF solution of *n*-butyl lithium following the procedures described by Parham et al.[18]). After slow warming to room temperature the mixture was carefully hydrolized with water and acidified with 50% aqueous HCl. Standard workup afforded 1.6 g (6.1 mmol, 95%) of the secondary alcohol as a yellow oil. Without further purification, this material was converted into ketone **1g** by standard pyridinium chlorochromate oxidation (PCC on Celite in dichloro methane).[19] Flash chromatography (10–20% ethyl acetate–petroleum ether 35–60) yielded 1.0 g (3.8 mmol, 58%) of ketone **1g** as a light yellow powder. Recrystallization from ethanol gave colorless prisms: mp 134–136°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (1H, t, *J*=1 Hz, aryl-H), 8.27 (1H, dt, *J*=8, 1 Hz, aryl-H), 7.86 (1H, dt, *J*=8, 1 Hz, aryl-H), 7.63 (1H, t, *J*=8 Hz, aryl-H), 6.90 (2H, s, mesityl-H), 4.31 (2H, s, CH_2), 2.26 (3H, s, *p*-CH_3), 2.16 (6H, s, *o*-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.2 (2C, negative), 20.9 (−), 39.4 (+), 113.2 (+), 117.9 (+), 128.3 (+), 128.9 (−), 129.7 (−) 131.7 (−), 132.0 (−), 136.0 (−), 136.6 (+), 136.7 (+), 137.7 (+), 195.2 (+); IR (KBr) 2915, 2230 (CN), 1699 (C═O), 1482, 1451, 1337, 1239, 1172, 1006, 856, 803, 739, 682 cm^{-1}; MS (EI) *m/z* 263 (M+), 133 (base) 115, 91; HRMS 263.13069 (calcd for $C_{18}H_{17}NO$, 263.13101). Anal. Calcd for $C_{18}H_{17}NO$: C, 82.09; H, 6.51; N, 5.32. Found: C, 81.96; H, 6.61; N, 5.36.

α-Mesityl-3-carboxyacetophenone (1h). To a 500 mL flask equipped with a condenser and stirrer was added 958 mg (4.6 mmol) of ketone **1g**, 25 mL of a 25% aqueous sodium hydroxide solution and 85 mL of methanol. The mixture was refluxed for 4 days, then cooled to room temperature and strongly acidified with aqueous 50% HCl. The aqueous layer was extracted with diethyl ether (0.5 L)

and standard workup afforded 1.56 g (4.4 mmol, 95%) of desired keto acid **1h** as a white powder. Recrystallization from benzene gave colorless fine needles: mp 197–199°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (1H, t, J=1 Hz, aryl-H), 8.34 (H, dt, J=8, 1 Hz, aryl-H), 8.30 (1H, dt, J=8, 1 Hz, aryl-H), 7.63 (1H, t, J=8 Hz, aryl-H), 6.90 (2H, s, mesityl-H), 4.39 (2H, s, CH_2), 2.19 (3H, s, p-CH_3), 2.17 (6H, s, o-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.2 (−), 20.9 (−), 39.9 (+), 128.8 (−), 128.9 (−), 129.2 (−), 130.0 (−) 133.0 (−), 136.5 (+), 136.8 (+), 137.6 (+), 170.8 (+), 196.3 (+); IR (KBr) 2918, 2654, 2590, 1685/1604 (C═O, COOH), 1446, 1413, 1312, 1216, 752 cm^{-1}; MS (EI) m/z 282 (M+), 149, 133 (base); HRMS 282.12521 (calcd for $C_{18}H_{18}O_3$, 282.12558). Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.61; H, 6.55.

α-Mesityl-3-carbomethoxyacetophenone (1j). A sample of 400 mg of keto acid **1h** (1.4 mmol) was treated with an approximately 0.5 M solution of diazomethane in diethyl ether. Radial chromatography afforded 379 mg of keto ester **1j** (1.3 mmol, 90%) as a white powder. Recrystallization from diisopropyl ether gave colorless cubes: mp 123–125°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72–8.71 (1H, m, aryl-H), 8.27–822 (2H, m, aryl-H), 7.58 (1H, t, J=8 Hz, aryl-H), 6.89 (2H, s, mesityl-H), 4.36 (2H, s, CH_2), 3.96 (3H, s, $COOCH_3$), 2.27 (3H, s, p-CH_3), 2.18 (6H, s, o-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3 (−), 20.9 (−), 39.5 (+), 52.4 (−), 128.8 (−), 128.9 (−), 129.1 (−), 130.7 (+), 132.2 (−), 133.7 (−), 136.4 (+), 136.7 (+), 166.3 (+), 196.3 (+); IR (KBr) 2909, 1724 ($COOCH_3$), 1693 (C═O), 1488, 1441, 1327, 1306, 1276 (CH_3), 1210, 1190, 1117, 1075, 1000, 958, 853, 753, 683 cm^{-1}; MS (EI) m/z 296 (M+), 163, 133 (base); HRMS 296.14093 (calcd for $C_{19}H_{20}O_3$, 296.14124). Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 77.32; H, 6.68.

α-Mesityl-3-methylacetophenone (1k). To 931 mg (4.7 mmol) of mesitylacetic acid chloride in 20 mL of anhydrous THF was added 5.2mL of a 1 M solution of 3-tolylmagnesium chloride (61mmol) in THF at −78°C. After slow warming to room temperature, the red–brown mixture was carefully hydrolyzed with water and acidified with aqueous 50% HCl. Standard workup and purification by flash chromatography (silica gel, 2% ethyl acetate–petroleum ether 35–60) afforded 426 mg (1.7 mmol, 36%) of the desired ketone **1k**. Recrystallization from ethanol afforded colorless cubes: mp 75–78°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.87 (2H, m, aryl-H), 7.43–7.37 (2H, m, aryl-H), 6.90 (2H, s, mesityl-H), 4.36 (2H, s, CH_2), 2.45 (3H, s, aryl-CH_3), 2.27 (3H, s, p-mesityl-CH_3), 2.17 (6H, s, o-mesityl-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.2 (−), 20.9 (−),21.4 (−) 39.3 (+), 125.2 (−), 128.5 (−), 128.7 (−), 129.3 (+), 133.8 (−), 136.2 (−), 136.8 (−), 137.1 (+), 138.4 (+), 197.2 (+); IR (KBr) 2918, 1683 (C═O), 1601, 1486, 1423, 1324, 1246, 1158, 861, 790, 692 cm^{-1}; MS (EI) m/z 252 (M+), 133, 119 (base). 91; HRMS 252.15211 (calcd for $C_{18}H_{20}O$, 252.15141). Anal. Calcd for $C_{19}H_{20}O_3$: C, 85.67; H, 7.99. Found: C, 85.79; H, 8.02.

Photochemical procedures

All photolyses were performed using a 450 W Hanovia medium-pressure mercury lamp placed in a water-cooled, Pyrex immersion well. For preparative-scale liquid-phase photolyses, Pyrex tubes were used and the solution was purged with nitrogen for at least 30 min prior to photolysis. Workup consisted of solvent removal in vacuum followed by silica gel radial chromatography. For solid-state photolyses, 5–10 mg samples were placed between two Pyrex microscope slides, and by sliding the top and bottom plates back and forth, the sample was distributed over the surface in a thin, even layer. The microscope plates were Scotch-taped together at the top and bottom ends, place in a polyethylene bag, and thoroughly degassed with nitrogen. The bag was then sealed under a positive pressure of nitrogen with a heat-sealing device and placed 5 cm from the immersion well. Low temperature solid-state photolyses were performed by placing the double sealed bags as close as possible to the immersion well in a cryostated methanol bath (Neslab Cryocool CC-100 II). Temperatures were maintained within 2°C of the designated values. Workup of the solid-state photolysis samples consisted of washing the solid off the plate with ether into a suitable container and determining the conversion by gas chromatography.

2-(4′-Fluorophenyl)-2-hydroxy-4,6-dimethylindane (2b). A solution of 254 mg of ketone **1b** in 40 mL of acetonitrile was irradiated through Pyrex for 7 h. GC indicated a 100% conversion, and radial chromatography (silica gel, 20% ethyl acetate–petroleum ether 35–60) of the reaction mixture afforded 163 mg of indanol **2b** (64%) as a colorless oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.50 (2H, m, aryl-H), 7.10–7.02 (2H, m, aryl-H), 6.90 (1H, s, indanyl-H), 6.87 (1H, s, indanyl-H), 3.31 (2H, AB quart., J=16 Hz, CH_2), 3.24 (2H, AB quart., J=16 Hz, CH_2), 2.35 (3H, s, CH_3), 2.25 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.98 (−), 21.19 (−), 47.4 (+), 49.48 (+), 82.68 (+), 114.86 and 115.07 ($^2J_{C-F}$=21 Hz, negative), 122.97 (−), 126.84 and 126.92 ($^3J_{C-F}$=8 Hz, negative), 128.75 (−), 134.07 (+), 136.51 (+), 136.87 (+), 140.59 (+), 141.68 (+), 160.65 and 163.09 ($^1J_{C-F}$=245 Hz, positive); IR (neat) 3401 (OH), 2916, 1604, 1510, 1481, 1230 (C–F), 1161, 1046, 837, 815, 574 cm^{-1}; MS (EI) m/z 256 (M+), 133 (base) 123, 95; HRMS 256.12647 (calcd for $C_{17}H_{17}FO$, 256.12634). Anal. Calcd for $C_{17}H_{17}FO$: C, 79.66; H, 6.69. Found: C, 79.70; H, 6.67.

2-(4′-Cyanophenyl)-2-hydroxy-4,6-dimethylindane (2c). A solution of 200 mg of ketone **1c** in 40 mL of acetonitrile was irradiated through Pyrex for 4 h. GC indicated a 100% conversion, and after evaporation of the solvent, recrystallization of the resulting yellow oil from hexane afforded 120 mg of indanol **2c** (60%) as a colorless solid: mp 131–132°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68–7.61 (4H, m, aryl-H), 6.91 (1H, s, indanyl-H), 6.88 (1H, s, indanyl-H), 3.33 (2H, AB quart., J=16 Hz, CH_2), 3.26 (2H, AB quart., J=16 Hz, CH_2), 2.31 (3H, s, CH_3), 2.22 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.0 (−), 21.2 (−), 48.4 (+), 49.6 (+), 82.7 (+), 110.8 (+), 118.8 (+), 123.0 (−), 125.9 (−), 129.0 (−), 132.1 (−), 134.2 (+), 135.9 (+), 137.2 (+), 140.0 (+), 151.4 (+); IR (KBr) 3408 (OH), 2947, 2901, 2234 (CN), 1610, 1505, 1478, 1406, 1377, 1219, 1051, 960, 852, 830, 591, 565 cm^{-1}; MS (EI) m/z 263 (M+), 133 (base); HRMS 263.13135 (calcd for $C_{18}H_{17}NO$, 263.13101). Anal. Calcd for $C_{18}H_{17}NO$: C, 82.09; H, 6.51; N, 5.32. Found: C, 81.88; H, 6.61; N, 5.38.

2-(4′-Carbomethoxyphenyl)-2-hydroxy-4,6-dimethylindane (2e). A solution of 200 mg of ketone **1e** in 40 mL of acetonitrile was irradiated through Pyrex for 4 h. GC indicated a 100% conversion, and radial chromatography (silica gel, 10% ethyl acetate–petroleum ether 35–60) of the reaction mixture afforded 120 mg of indanol **2e** (60%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (2H, dt, J=9, 2 Hz, aryl-H), 7.63 (2H, dt, J=9, 2 Hz, aryl-H), 6.91 (1H, s, indanyl-H), 6.87 (1H, s, indanyl-H), 3.90 (3H, s, OCH_3), 3.35 (2H, AB quart., J=16 Hz, CH_2), 3.31 (2H, AB quart., J=16 Hz, CH_2), 2.38 (1H, s (br), OH), 2.31 (3H, s, CH_3), 2.22 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.0 (−), 21.2 (−), 48.1 (+), 49.8 (+), 52.0 (−), 82.9 (+), 122.9 (−), 125.1 (−), 128.8 (−), 129.6 (−), 134.1 (+), 136.3 (+), 136.9 (+), 140.4 (+), 151.2 (+), 166.9 (+); IR (neat) 3441 (OH), 2949, 1723 (COOMe), 1610, 1436, 1407, 1280, 1192, 1110, 1020, 857, 776, 710 cm^{-1}; MS (EI) m/z 296 (M+), 278, 263, 163 (base), 133; HRMS 296.14158 (calcd for $C_{19}H_{20}O_3$, 296.14124). Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 77.01; H, 6.77.

2-(4′-Carboxyphenyl)-2-hydroxy-4,6-dimethylindane (2c). A solution of 30 mg of ketone **1d** in 5 mL of acetonitrile was irradiated through Pyrex for 1 h. GC indicated, after treatment with diazomethane (0.5 M in diethyl ether), a 100% conversion, and radial chromatography (silica gel, 10% ethyl acetate–petroleum ether 35–60) of the reaction mixture afforded ester indanol **2e**.

2-(3′-Fluorophenyl)-2-hydroxy-4,6-dimethylindane (2f). A solution of 110 mg of ketone **1f** in 40 mL of acetonitrile was irradiated through Pyrex for 1 h. GC indicated a 100% conversion, and radial chromatography (silica gel, 5% ethyl acetate–petroleum ether 35–60) of the reaction mixture afforded 105 mg of indanol **2f** (96%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.29 (3H, m, aryl-H), 6.99–6.94 (1H, m, aryl-H), 6.93 (1H, s, indanyl-H), 6.88 (1H, s, indanyl-H), 3.34 (2H, AB quart., J=16 Hz, CH_2), 3.26 (2H, AB quart., J=16 Hz, CH_2), 2.33 (3H, s, CH_3), 2.24 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.98 (−), 21.19 (−), 47.95 (+), 49.59 (+), 82.66 (+), 112.32 and 112.61 ($^2J_{C-F}$=22 Hz, negative), 113.67 and 113.92 ($^2J_{C-F}$=21 Hz, negative), 120.65 and 120.69 ($^4J_{C-F}$= 3 Hz, negative), 122.93 (−), 128.76, 129.66 and 129.77 ($^3J_{C-F}$=8 Hz, negative), 134.06 (+), 136.35 (+), 136.91 (+), 140.41 (+), 148.69 and 148.76 ($^3J_{C-F}$=7 Hz, negative), 161.16 and 164.42 ($^1J_{C-F}$=244 Hz, positive); IR (neat) 3370 (OH), 2916, 1615, 1588, 1484, 1442, 1377, 1273, 1214, 1046, 873, 843, 786, 696 cm^{-1}; MS (EI) m/z 256 (M+), 238, 223, 133 (base) 123; HRMS 256.12610 (calcd for $C_{17}H_{17}FO$, 256.12634). Anal. Calcd for $C_{17}H_{17}FO$: C, 79.66; H, 6.69. Found: C, 79.58; H, 6.77.

2-(3′-Cyanophenyl)-2-hydroxy-4,6-dimethylindane (2g). A solution of 121 mg of ketone **1g** in 40 mL of acetonitrile was irradiated through Pyrex for 21 h. GC indicated a 95% conversion, and radial chromatography (silica gel, 10% ethyl acetate–petroleum ether 35–60) of the reaction mixture afforded 68 mg of indanol **1g** (57%) as a light yellow solid: mp 107–110°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (1H, t, J=1 Hz, aryl-H), 7.78 (1H, dt, J=8, 1 Hz, aryl-H), 7.55 (1H, dt, J=8, 1 Hz, aryl-H), 7.45 (1H, t, J=8 Hz, aryl-H), 6.91 (1H, s, indanyl-H), 6.88 (1H, s, indanyl-H), 3.33 (2H, AB quart., J=16 Hz, CH_2), 3.25 (2H, AB quart., J=16 Hz, CH_2), 2.31 (3H, s, CH_3), 2.22 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.0 (−), 21.2 (−), 48.1 (+), 49.7 (+), 82.4 (+), 112.2 (+), 118.9 (+), 122.6 (−), 128.9 (−), 129.0 (−), 129.7 (−), 130.7 (−), 134.1 (+), 135.9 (+), 137.2 (+), 140.0 (+), 147.6 (+); IR (KBr) 3450 (OH), 2916, 2227 (CN), 1477, 1438, 1376, 1342, 1320, 1284, 1247, 1152, 1048, 904, 847, 802, 693, 606, 543, 523 cm^{-1}; MS (EI) m/z 263 (M+), 245, 133 (base); HRMS 263.13097 (calcd for $C_{18}H_{17}NO$, 263.13101). Anal. Calcd for $C_{18}H_{17}NO$: C, 82.09; H, 6.51; N, 5.32. Found: C, 81.95; H, 6.40; N, 5.22.

2-(3′-Carbomethoxyphenyl)-2-hydroxy-4,6-dimethylindane (2j). A solution of 114 mg of ketone **1j** in 35 mL of acetonitrile was irradiated through Pyrex for 2.5 h. GC indicated a 100% conversion, and radial chromatography (silica gel, 5% ethyl acetate–petroleum ether 35–60) of the reaction mixture afforded 85 mg of indanol **2j** (75%) as a colorless solid: mp 151–153°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (1H, t, J=2 Hz, aryl-H), 7.95 (1H, dt, J=8, 1 Hz, aryl-H), 7.80–7.78 (1H, m, aryl-H), 7.43 (1H, t, J=8 Hz, aryl-H), 6.93 (1H, s, indanyl-H), 6.87 (1H, s, indanyl-H), 3.90 (3H, s, OCH_3), 3.37 (2H, AB quart., J=16 Hz, CH_2), 3.29 (2H, AB quart., J=16 Hz, CH_2), 2.31 (3H, s, CH_3), 2.26 (1H, s (br), OH), 2.23 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.0 (−), 21.2 (−), 48.0 (+), 49.6 (+), 52.1 (−), 82.8 (+), 123.0 (−), 126.4 (−), 128.3 (−), 128.4 (−), 128.8 (−), 129.8 (−), 130.1 (+), 134.1 (+), 136.4 (+), 136.9 (+), 140.4 (+), 146.3 (+), 167.1 (+); IR (KBr) 3461 (OH), 1697 (COOMe), 1447, 1347, 1294, 1232, 1209, 848, 763, 695 cm^{-1}; MS (EI) m/z 296 (M+), 278, 263, 163 (base), 133; HRMS 296.14064 (calcd for $C_{19}H_{20}O_3$, 296.14124). Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 76.89; H, 6.66.

2-(3′-Carboxyphenyl)-2-hydroxy-4,6-dimethylindane (2h). A solution of 30 mg of ketone **1h** in 5 mL of acetonitrile was irradiated through Pyrex for 1h. GC indicated, after treatment with diazomethane (0.5 M in diethyl ether), a 100% conversion, and radial chromatography (silica gel, 5% ethyl acetate–petroleum ether 35–60) of the reaction mixture afforded ester indanol **2j**.

2-(3′-Methylphenyl)-2-hydroxy-4,6-dimethylindane (2k). A solution of 136 mg of ketone **1k** in 35 mL of acetonitrile was irradiated through Pyrex for 1 h 45 min. GC indicated a 98% conversion, and radial chromatography (silica gel, 5% ethyl acetate–petroleum ether 35–60) of the reaction mixture afforded 129 mg of indanol **2j** (95%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (1H, s, aryl-H), 7.38 (1H, d, J=8 Hz, aryl-H), 7.28 (1H, t, J=8 Hz, aryl-H), 7.12 (1H, d, J=8 Hz, aryl-H), 6.95 (1H, s, indanyl-H), 6.90 (1H, s, indanyl-H), 3.37 (2H, AB quart., J=16 Hz, CH_2), 3.29 (2H, AB quart., J=16 Hz, CH_2), 2.40 (3H, s, aryl-CH_3), 2.33 (3H, s, indanyl-CH_3), 2.26 (3H, s, indanyl-CH_3), 2.05(1H, s (br), OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.0 (−), 21.2 (−), 21.6 (−), 47.7 (+), 49.4 (+), 83.0 (+), 122.1 (−), 122.9 (−), 125.9 (−), 127.8 (−), 128.2 (−), 128.6 (−), 134.0 (+), 136.7 (+), 136.7 (+), 137.8 (+), 140.8 (+), 145.8 (+); IR (KBr) 3392 (OH), 2916, 1608, 1482, 1377, 1251, 1212, 1046, 901, 849, 829, 786, 706 cm^{-1}; MS (EI) m/z 296 (M+), 278, 263, 163 (base), 133; HRMS 252.15157

(calcd for $C_{18}H_{20}O$, 252.15141). Anal. Calcd for $C_{19}H_{20}O_3$: C, 85.67; H, 7.99. Found: C, 85.45; H, 8.02.

Preparation of salts

Salts were prepared by dissolving equimolar amounts of keto acid and amine in the solvent indicated. The initial precipitates were collected and recrystallized from the indicated solvents. Satisfactory NMR and IR spectra were recorded for all salts. The NMR spectra showed the change in the carboxylic acid carbonyl signal expected for a carboxylate anion. In the IR, salt formation resulted in a characteristic change in the carboxylic acid OH stretching band at 3500–2400 cm^{-1}, which was replaced by multiple combination bands for ammonium in the 3200–2220 cm^{-1} region. In addition, the carboxylic acid carbonyl stretching vibration at 1690 cm^{-1} was replaced by two bands characteristic for carboxylate: a strong absorption in the 1650–1550 cm^{-1} region, and a weaker one near 1400 cm^{-1}.

(*S*)-(−)- and (*R*)-(+)-α-Methylbenzylamine salt S1 and S2 of keto acid 2d. To a solution of 50 mg (0.18 mmol) of keto acid **2d** in 5 mL of diethyl ether was added 50 μL of optically pure (*S*)-(−)-α-methylbenzylamine (Aldrich). The resulting precipitate was filtered off and washed with ether to give 59 mg (0.15 mmol, 83%) of salt **S1** (colorless powder, ethyl acetate): mp 142–145°C (CH_3CN), MS (FAB, +LSIMS) *m/z* 404 (M^++1), 283, 230, 149, 133, 122, 105 (matrix: thioglycerol); Anal. Calcd for $C_{26}H_{29}NO_3$: C, 77.38; H, 7.25; N, 3.47. Found: C, 77.60; H, 7.27; N, 3.32.

The (*R*)-(+)-α-methylbenzylamine salt **S2** was prepared analogously (90% yield) and also gave satisfactory MS and elemental analysis results.

(*R*)-(+)-α,4-Dimethylbenzylamine salt S3 of keto acid 2d. To a solution of 92 mg (0.33 mmol) of keto acid **2d** in 5 mL of diethyl ether was added 60 μL of optically pure (*R*)-(+)-α,4-dimethylbenzylamine (Aldrich). The resulting precipitate was filtered off and washed with ether to give 121 mg (0.15 mmol, 88%) of salt **S3**: mp 170–172°C (plates, benzene/isopropanol 2:1), MS (FAB, +LSIMS) *m/z* 418 (M^++1), 283, 271, 136, 133, 119 (matrix: thioglycerol); Anal. Calcd for $C_{27}H_{31}NO_3$: C, 77.67; H, 7.48; N, 3.35. Found: C, 77.72; H, 7.32; N, 3.35.

(*R*)-(+)-*N*,α-Dimethylbenzylamine salt S4 of keto acid 2d. To a solution of 84 mg (0.30 mmol) of keto acid **2d** in 5 mL of diethyl ether was added 60 μL of optically pure (*R*)-(+)-*N*,α-dimethylbenzylamine (Aldrich). The resulting precipitate was filtered off and washed with ether to give 115 mg (0.28 mmol, 93%) of salt **S4**: mp 144–146°C (cubes, ethyl acetate), MS (FAB, +LSIMS) *m/z* 418 (M^++1), 307, 283, 265, 136, 133, 105 (matrix: thioglycerol); Anal. Calcd for $C_{27}H_{31}NO_3$: C, 77.67; H, 7.48; N, 3.35. Found: C, 77.41; H, 7.67; N, 3.37.

(1*R*,2*S*)-(−)- and (1*S*,2*R*)-(+)-Norephedrine salt S5 and S6 of keto acid 2d. A solution of 87 mg (0.31 mmol) of keto acid **2d** in 5 mL of diethyl ether was added to a solution of 53 mg of (1*R*,2*S*)-(−)-norephedrine (Aldrich) in 5 mL of diethyl ether. The resulting precipitate was filtered off and washed with ether to give 129 mg (0.30 mmol, 96%) of salt **S5** (colorless powder, methanol): mp 168–170°C (isopropanol), MS (FAB, +LSIMS) *m/z* 434 (M^++1), 283, 260, 152, 134, 118 (matrix: thioglycerol); Anal. Calcd for $C_{27}H_{31}NO_4$: C, 74.79; H, 7.21; N, 3.23. Found: C, 74.77; H, 7.14; N, 3.20.

The (1*S*,2*R*)-(+)-norephedrine salt **S6** was prepared analogously (95% yield) and also gave satisfactory MS and elemental analysis results. X-Ray quality crystals were grown by dissolving the crude salt in a mixture of methanol/ethanol 3:1 and slow evaporation of the solvents.

(1*S*,2*S*)-(+)-2-Amino-1-phenyl-1,3-propandiol salt S7 of keto acid 2d. A solution of 67 mg (0.24 mmol) of keto acid **2d** in 5 mL of diethyl ether was added to a solution of 49 mg of (1*S*,2*S*)-(+)-2-amino-1-phenyl-1,3-propandiol (Aldrich) in 5 mL of diethyl ether. The resulting precipitate was filtered off and washed with ether to give 91 mg (0.20 mmol, 87%) of salt **S7**: mp 176–178°C (needles, benzene/ethyl acetate 1:1), MS (FAB, +LSIMS) *m/z* 450 (M^++1), 283, 265, 168, 150, 133, 120 (matrix: thioglycerol); Anal. Calcd for $C_{27}H_{31}NO_5$: C, 72.12; H, 6.95; N, 3.12. Found: C, 71.82; H, 6.94; N, 3.07.

(1*R*,2*S*)-(+)-*cis*-1-Amino-2-indanol salt S8 of keto acid 2d. To a solution of 88 mg (0.31 mmol) of keto acid **2d** in 5 mL of diethyl ether was added a solution of 51 mg of (1*R*,2*S*)-(+)-*cis*-1-amino-2-indanol (Aldrich) in methanol/ethyl acetate. The resulting precipitate was filtered off and washed with ether to give 101 mg (0.23 mmol, 74%) of salt **S8**: mp 170–173°C (needles, isopropanol), MS (FAB, +LSIMS) *m/z* 432 (M^++1), 283, 271, 150, 133, 105 (matrix: thioglycerol); Anal. Calcd for $C_{27}H_{29}NO_4$: C, 75.14; H, 6.78; N, 3.25. Found: C, 75.07; H, 6.64; N, 3.21.

(*S*)-(−)-Myrtanylamine salt S9 of keto acid 2d. To a solution of 91 mg (0.32 mmol) of keto acid **2d** in 5 mL of diethyl ether was added 90 μL (*S*)-(−)-myrtanylamine (Aldrich). The resulting precipitate, which was formed after 30 min, was filtered off and washed with ether to give 98 mg (0.23 mmol, 71%) of salt **S9**: mp 154–157°C (powder, ethanol), MS (FAB, +LSIMS) *m/z* 436 (M^++1), 343, 295, 283, 265, 154, 133, 95, 81 (matrix: thioglycerol); Anal. Calcd for $C_{28}H_{37}NO_3$: C, 77.19; H, 8.57; N, 3.22. Found: C, 77.49; H, 8.52; N, 3.22.

(*S*)-(−)-α-Methylbenzylamine salt S10 of keto acid 2h. To a solution of 62 mg (0.22 mmol) of keto acid **2h** in 5 mL of diethyl ether/ethyl acetate (2:1) was added 70 μL of optically pure (*S*)-(−)-α-methylbenzylamine (Aldrich). A white precipitate formed after reducing the volume of solvent by 50%. The solid was filtered off and washed with ether to give 47 mg (0.12 mmol, 55%) of salt **S10**: mp 136–138°C (needles, ethyl acetate); MS (FAB, +LSIMS) *m/z* 404 (M^++1), 305, 283, 265, 133, 122, 105 (matrix: thioglycerol); Anal. Calcd for $C_{26}H_{29}NO_3$: C, 77.38; H, 7.25; N, 3.47. Found: C, 77.01; H, 7.45; N, 3.41.

(*R*)-(+)-*N*,α-Dimethylbenzylamine salt S11 of keto acid 2h. To a solution of 51 mg (0.18 mmol) of keto acid **2h** in 5 mL of diethyl ether was added 50 μL of optically pure (*R*)-(+)-*N*,α-dimethylbenzylamine (Aldrich). The resulting

precipitate was filtered off and washed with ether to give 57 mg (0.14 mmol, 77%) of salt **S11**: mp 141–144°C (cubes, ethyl acetate); MS (FAB, +LSIMS) *m/z* 418 (M^++1), 307, 283, 265, 136, 105 (matrix: thioglycerol); Anal. Calcd for $C_{27}H_{31}NO_3$: C, 77.67; H, 7.48; N, 3.35. Found: C, 77.29; H, 7.50; N, 3.35.

(1*R*,2*S*)-(−)-(+)-Norephedrine salt S12 of keto acid 2h. A solution of 61 mg (0.22 mmol) of keto acid **2h** in 5 mL of diethyl ether was added to a solution of 62 mg of (1*R*,2*S*)-(−)-norephedrine (Aldrich) in 5 mL of diethyl ether. The resulting precipitate was filtered off and washed with ether to give 75 mg (0.17 mmol, 77%) of salt **S12**: mp 85–90°C (powder, isopropanol), MS (FAB, +LSIMS) *m/z* 434 (M^++1), 283, 265, 214, 152, 134, 133, 105 (matrix: thioglycerol); Anal. Calcd for $C_{27}H_{31}NO_4$: C, 74.79; H, 7.21; N, 3.23. Found: C, 75.00; H, 7.06; N, 3.16.

(1*R*,2*S*)-(+)-*cis*-1-Amino-2-indanol salt S13 of keto acid 2h. To a solution of 60 mg (0.21 mmol) of keto acid **2h** in 5 mL of diethyl ether was added a solution of 57 mg of (1*R*,2*S*)-(+)-*cis*-1-amino-2-indanol (Aldrich) in methanol/diethyl ether. The solvent was removed by rotary evaporation and the resulting oil recrystallized from isopropanol/petroleum ether 35–60 to give fine needles (49 mg, 0.10 mmol, 48%). Recrystallisation of the resulting oil from acetonitrile afforded a flaky solid: mp 100–103°C, MS (FAB, +LSIMS) *m/z* 432 (M^++1), 283, 271, 150, 133, 105 (matrix: thioglycerol); Anal. Calcd for $C_{27}H_{29}NO_4$: C, 75.14; H, 6.78; N, 3.25. Found: C, 74.84; H, 6.64; N, 3.39.

Photolysis of salts S1–13

Crystals of salts **S1**–**S13** (5–10 mg) were photolyzed between Pyrex microscope slides for varying lengths of time and at different temperatures (see Table 3) as described under Photochemical Procedures. The solid mixtures were removed from the slides with methanol, and after removal of the solvent, treated with an excess ethereal diazomethane to convert the acids into the corresponding methyl esters. The extent of conversion was analyzed by GC. Only starting materials and 2-indanols were observed. The enantiomeric excesses were determined on chiral HPLC (eluent hexane/isopropanol, Ciralcel® OD column).

X-Ray crystallographic analyses

The crystals were grown by slow evaporation of the listed solvents. The crystallographic data were obtained with a Rigaku AFC-6 four cycle diffractometer (Cu-K_α-radiation, graphite-monochromator) at 293 K. The structures were solved using direct methods and refined on F using teXsan.[20] The atomic coordinates were deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge CB2 IEZ, UK.

Crystal data for ***1b****:* $C_{17}H_{17}FO$, M=256.32, transparent, colorless plate 0.50×0.25×0.10 (ethanol); monoclinic; $P2_1/a$; a=10.151(3) Å, b=8.687(4) Å, c=16.802(4) Å, β=104.99(2)°, V=1431.1(7) Å^3, Z=4, ρ_{calcd}=1.19 g/cm^3, 3275 reflections collected, R=4.3%.

Crystal data for ***1c****:* $C_{18}H_{17}NO$, M=263.34, transparent, yellow pyramid 1.00×1.00×0.50 (methanol), monoclinic, $P2_1/a$; a=10.586(1) Å, b=8.377(2) Å, c=17.539(2) Å, β=107.325(8)°, V=1484.9 9(4) Å^3, Z=4, ρ_{calcd}=1.18 g/cm^3, 3437 reflections collected, R=4.5%.

Crystal data for ***1d****:* $C_{18}H_{18}O_3$, M=282.34, transparent, yellow prism 0.30×0.25×0.20 (methanol); monoclinic, $P2_1/c$, a=12.590(1) Å, b=9.201(1) Å, c=52.835(4) Å, β=94.451(8)°, V=6102(1) Å^3, Z=16, ρ_{calcd}=1.23 g/cm^3, 13816 reflections collected, R=4.6%, four independent molecules in the unit cell.

Crystal data for ***1f****:* $C_{17}H_{17}FO$, M=256.32, transparent, colorless cube 0.25×0.25×0.25 (methanol), orthorhombic, *Pbca*, a=99.985(3) Å, b=33.586(7) Å, c=8.457(4) Å, V=2836(1) Å^3, Z=8, ρ_{calcd}=1.20 g/cm^3, 2951 reflections collected, R=4.9%.

Crystal data for ***1g****:* $C_{18}H_{17}NO$, M=263.34, transparent, colorless prism 0.40×0.25×0.15 (ethanol), monoclinic, $P2_1/a$, a=7.962(1) Å, b=15.840(3) Å, c=12.119(3) Å, β=107.40(1)°, V=1458.5(5) Å^3, Z=4, ρ_{calcd}=1.20 g/cm^3, 3294 reflections collected, R=4.9%.

Crystal data for ***1j****:* $C_{19}H_{20}NO_3$, M=296.37, transparent, colorless prism 0.20×0.10×0.10 (isopropyl ether/ethyl acetate), triclinic, $P\bar{1}$, a=9.099(2) Å, b=11.302(2) Å, c=8.406(2) Å; α=100.84(2)° β=109.16(1)°, γ=78.88(2)°, V=794.0(3) Å^3, Z=2, ρ_{calcd}=1.24 g/cm^3, 3460 reflections collected, R=5.3%.

Crystal data for ***1h****:* $C_{18}H_{20}O$, M=252.36, transparent, colorless cube 0.25×0.25×0.25 (ethanol), monoclinic, *C*2/*c*, a=10.554(4) Å, b=15.238(4) Å, c=18.885(3) Å; β=95.88(2)°; V=3021(1) Å^3, Z=8, ρ_{calcd}=1.11 g/cm^3, 3395 reflections collected, R=5.3%.

Crystal data for ***S3****:* $C_{27}H_{31}NO_3$, M=417.55, transparent, colorless plate 0.65×0.30×0.10 (benzene/isopropanol), monoclinic, $P2_1$, a=7.182(1) Å, b=6.048(1) Å, c=27.779(2) Å, β=97.094(9)°, V=1197.4(2) Å^3, Z=2, ρ_{calcd}=1.16 g/cm^3, 2911 reflections collected, R=4.4%.

Crystal data for ***S4****:* $C_{27}H_{31}NO_3$, M=417.55, transparent, colorless prism 0.50×0.25×0.25 (ethyl acetate), triclinic, $P1$, a=10.519(3) Å, b=13.927(5) Å, c=9.501(3) Å, α=99.57(3)°, β=114.97(2)°, γ=101.68(3)°; V=1184.9(8) Å^3, Z=2, ρ_{calcd}=1.17 g/cm^3, 5103 reflections collected, R=6.2%; two independent molecules in the unit cell.

Crystal data for ***S6****:* $C_{27}H_{31}NO_3$, M=433.55, transparent, colorless prism 0.35×0.10×0.05 (methanol/ethanol 3:1), monoclinic, *C*2; a=17.732(5) Å, b=5.612(2) Å, c=25.720(4) Å, β=109.18(2)°, V=2417(1)Å, Z=4, ρ_{calcd}=1.19 g/cm^3, 2841 reflections collected, R=4.5%.

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9. The possibility of reverse hydrogen transfer, although shown by Wagner to be small in α-mesitylacetophenone (**1a**),[4] is another unknown factor affecting the quantum yields for ketones **1b–k**.
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