N-Heterocyclic Carbene Catalysed Oxygen-to-Carbon Carboxyl Transfer of Indolyl and Benzofuranyl Carbonates

Jennifer E. Thomson, Andrew F. Kyle, Katherine A. Gallagher, Philip Lenden, Carmen Concellón, Louis C. Morrill, Andrew J. Miller, Caroline Joannesse, Alexandra M. Z. Slawin, Andrew D. Smith*

EaStCHEM, School of Chemistry, University of St Andrews, North Haugh, St Andrews, KY16 9ST, UK

Received 29 March 2008

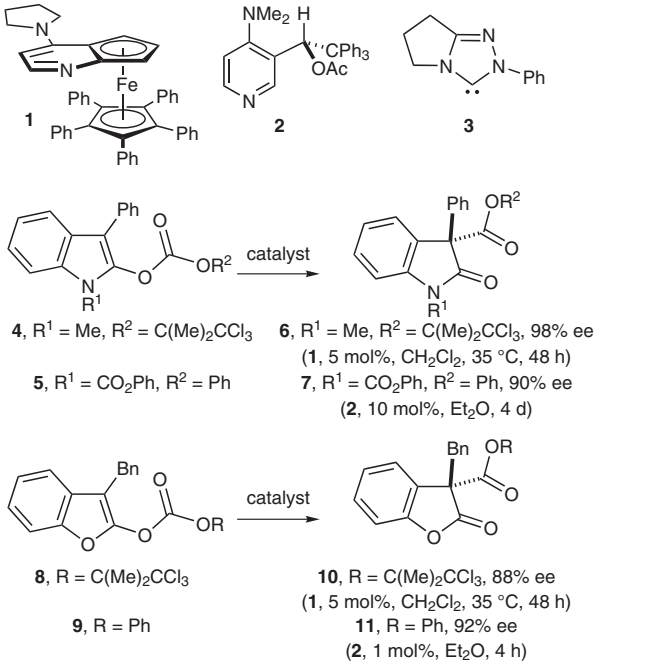
Abstract: The ability of N-heterocyclic carbenes to promote *O*-to-*C* carboxyl transfer on a range of indolyl and benzofuranyl carbonates is examined, and the scope and limitations of this process delineated.

Key words: N-heterocyclic carbene, catalysis, carboxyl transfer

N-Heterocyclic carbenes (NHCs) are versatile and efficient organocatalysts for a plethora of synthetic transformations.[1] Building upon their established use in polarity reversal or Umpolung techniques,[2,3] recent advances have seen NHCs used for the preparation of homoenolates[4] and enolates,[5] as well as applications as catalysts for trifluoromethylation,[6] cyanosilylation,[7] amidation,[8] hydroacylation,[9] redox reactions[10] and aziridine opening,[11] among others.[12] It is widely recognised that the development of efficient catalytic methodologies for the construction of all-carbon quaternary stereocentres represents a difficult challenge in synthetic chemistry. A variety of elegant catalytic asymmetric approaches to this problem have been developed,[13] including Diels–Alder reactions,[14] asymmetric alkylations,[15] Heck reactions,[16] rearrangement processes[17] and desymmetrisation reactions.[18] As part of a research programme concerned with the development of catalytically efficient methods for the preparation of this challenging structural motif, we have previously shown that N-heterocyclic carbene **3** can catalyse the Steglich rearrangement[19] of oxazolyl carbonates to their corresponding 4-carboxyazlactones, a reaction that generates a C–C bond and a quaternary stereocentre.[20,21] A number of asymmetric variants of this transformation have been developed,[22] and both Fu and Vedejs have extended this protocol to the asymmetric *O*-to-*C* carboxyl transfer of benzofuranyl and indolyl carbonates using catalysts **1** and **2** to generate 3,3′-disubstituted oxindole and 3,3′-benzofuranone derivatives respectively.[23] Despite high enantioselectivities being observed in these transformations, reactions in the indolyl series usually required relatively long reaction times, typically of the order of 48–96 hours, with 5–10 mol% of catalyst **1** or **2** (Scheme 1), while the rearrangement of highly substituted benzofuranyl carbonates has proven difficult with TADMAP **2**.

SYNTHESIS 2008, No. 17, pp 2805–2818
Advanced online publication: 06.08.2008
DOI: 10.1055/s-2008-1077890; Art ID: C03008SS

Given the high catalytic efficiency observed using NHCs as catalysts for *O*-to-*C* carboxyl transfer in the oxazolone series, we sought to probe the ability of NHC **3** to promote this transformation upon a range of indolyl and benzofuranyl derivatives. Herein we delineate our investigations within this area and showcase the generality and limitations of employing NHC-mediated catalysis in this transformation.



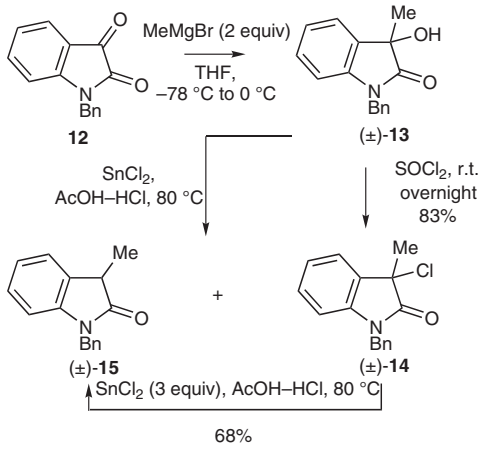
Scheme 1 Catalysts for *O*-to-*C* carboxyl transfer of indolyl and benzofuranyl carbonates

Model Studies: Preparation of Indolyl Substrates

Initial investigations set out to probe the variation in effectiveness of NHC-mediated catalysis within a series of indolyl carbonates that differed in bearing either an *N*-alkyl or *N*-phenoxycarbonyl protecting group upon the indole nitrogen. As indolyl carbonates are readily prepared from the corresponding 3-substituted oxindole, a robust method for the preparation of *N*-benzyl-3-methyloxindole [(±)-**15**] from *N*-benzylisatin (**12**) was necessary. Based upon a literature procedure,[22f] addition of methylmagnesium bromide to *N*-benzylisatin (**12**), followed by reduction of the crude product with tin(II) chloride (2 equiv) gave, after 90 minutes at 80 °C and at 75% conversion, a

50:50 mixture of chloride (±)-**14** and desired product (±)-**15**. Good conversion (>95%) to exclusively (±)-**15** required treatment with excess tin(II) chloride (3 equiv) for a prolonged period, giving (±)-**15** in 39% yield over two steps after purification. An authentic sample of chloride (±)-**14** was prepared from (±)-**13** by treatment with thionyl chloride in 83% isolated yield after chromatography, with X-ray crystal structure analysis proving unambiguously its molecular structure (Figure 1). Reduction of chloride (±)-**14** with tin(II) chloride (3 equiv) gave only (±)-**15**, which is consistent with chloride (±)-**14** being an intermediate in the preparation of (±)-**15** (Table 1).

Table 1 Preparation of Model Substrate Precursor (±)-**15**



$SnCl_2$ (equiv)	Time (h)	Conversion (%)[a]	Product distribution (±)-**14**:(±)-**15**
2	1.5	75	50:50
2	12	90	12:88
3	12	>95	<5:>95 (39%)[b]

[a] All product conversions and distributions were judged by ^{1}H NMR spectroscopic analysis of the crude reaction product.
[b] Isolated yield of homogeneous product over two steps after chromatography.

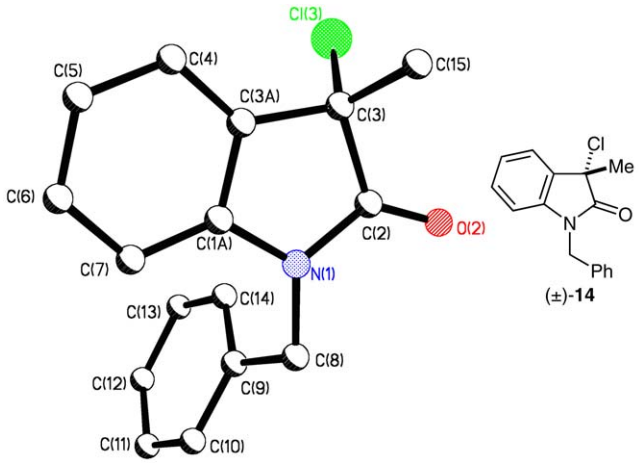
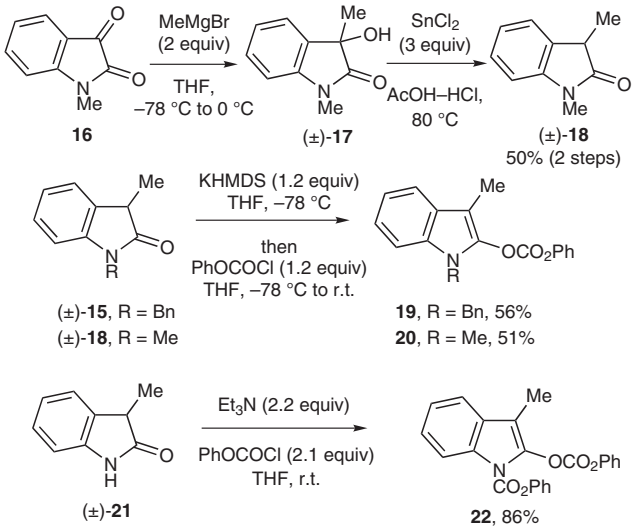


Figure 1 Molecular representation of the X-ray crystal structure of chloride (±)-**14** [one of two crystallographically independent molecules showing the major orientation of the disorder at C(3)]

An analogous series of transformations was used to prepare *N*-methyl-3-methyloxindole [(±)-**18**] from *N*-methylisatin (**16**), giving (±)-**18** in 50% yield over two steps. Deprotonation of both *N*-methyl and *N*-benzyl-3-methyloxindoles (±)-**15** and (±)-**18** with potassium hexamethyldisilazane (KHMDS) and subsequent addition of phenyl chloroformate gave the desired indolyl carbonates **19** and **20** respectively (Scheme 2). Bisphenoxycarbonyl **22** was simply prepared by treatment of commercially available 3-methyloxindole [(±)-**21**] with phenyl chloroformate and triethylamine, giving **22** in 86% yield. Compound **22** was characterised by X-ray crystal structure analysis, confirming that O- rather than C-carboxylation had occurred in this reaction (Figure 2).



Scheme 2 Preparation of model indolyl carbonate derivatives **19**, **20** and **22**

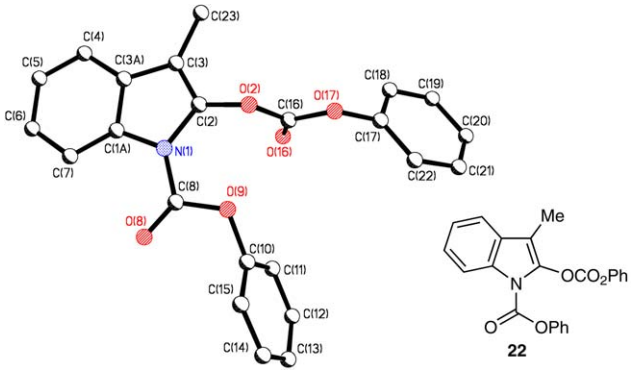
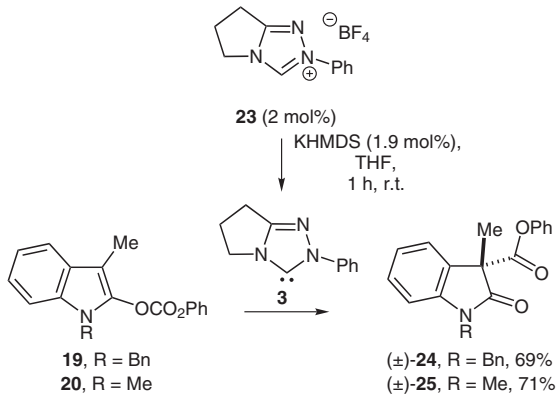


Figure 2 Molecular representation of the X-ray crystal structure of **22**

Model Studies: N-Protecting Group Effects upon NHC-Catalysed *O*-to-*C* Carboxyl Transfer of Indolyl Carbonates

Primary studies focused upon probing the ability of the NHC **3**, derived from in situ deprotonation of triazolium salt **23** (10 mol%) with KHMDS (9 mol%), to promote the *O*-to-*C* carboxyl rearrangement of *N*-benzyl or *N*-methyl

protected carbonates **19** and **20**, which proceeded to full conversion within one hour to give (±)-**24** and (±)-**25** respectively. Successively decreasing the catalyst loading indicated that 1.9 mol% of NHC **3** could be used to promote the desired rearrangement in both cases, giving (±)-**24** and (±)-**25** in 69% and 71% isolated yield respectively (Scheme 3).



Scheme 3 NHC-promoted *O*-to-*C* carboxyl transfer of **19** and **20**

Similar treatment of biscarbonate **22** with NHC **3** (9 mol%) gave, after complete conversion of **22** (1 h), a 60:40 mixture of *C*-phenoxycarbonyl (±)-**26** and oxindole (±)-**27**, with chromatographic purification furnishing (±)-**26** in 31% yield and (±)-**27** in 69% yield respectively (Table 2, entry 1). The molecular structure of (±)-**27** was confirmed by X-ray crystallography (Figure 3). Increasing the reaction time to two hours with 9 mol% of NHC **3** gave a 10:90 mixture of (±)-**26**:(±)-**27**, and allowed the isolation of diphenyl carbonate as a by-product of this reaction by chromatography. Decreasing the NHC loading to 4 mol% gave an 80:20 mixture of (±)-**26**:(±)-**27**, while treatment of an authentic homogeneous sample of (±)-**26** with NHC **3** (9 mol%) furnished a 60:40 mixture of (±)-**26**:(±)-**27** and diphenyl carbonate (Table 2, entry 4). The product distributions arising from both the crude reaction mixtures and isolated product mixtures indicate that although *O*-to-*C* carboxyl group rearrangement proceeds readily in this case, the *N*-phenoxycarbonyl group is labile to deprotection both upon silica and exposure to the NHC **3**. The formation of diphenyl carbonate as a by-product presumably requires the in situ generation of phenoxide, although at the present time a mechanism to account for this transformation has not been conclusively proven. Despite these problems, it is clear that NHC **3** promotes efficiently the *O*-to-*C* carboxyl transfer reaction of these model indolyl carbonate derivatives with good catalytic efficiency and reasonable reaction times.

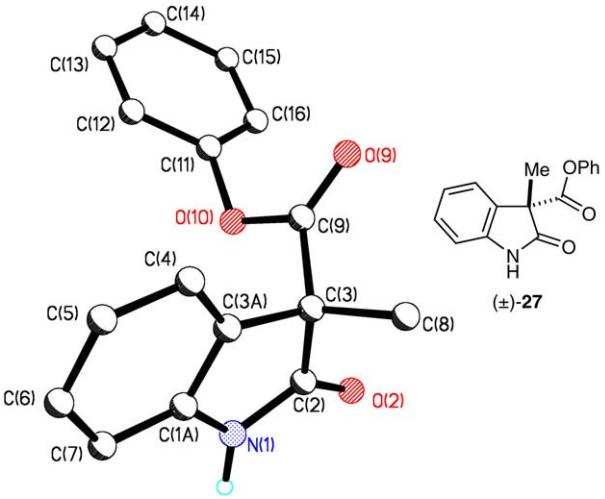
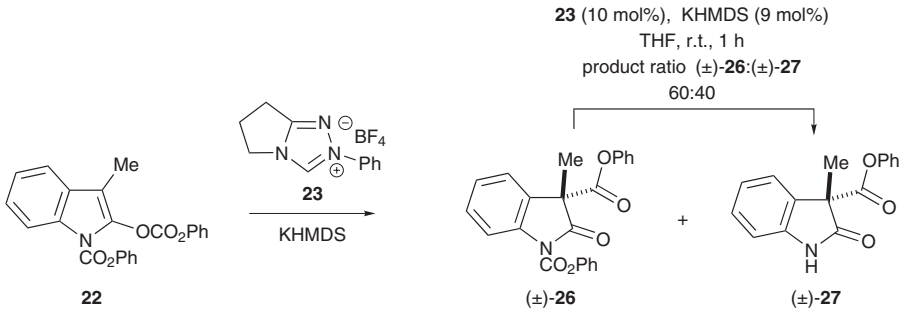


Figure 3 Molecular representation of the X-ray crystal structure of oxindole (±)-**27**

Table 2 NHC-Promoted *O*-to-*C* Carboxyl Rearrangement of **22**

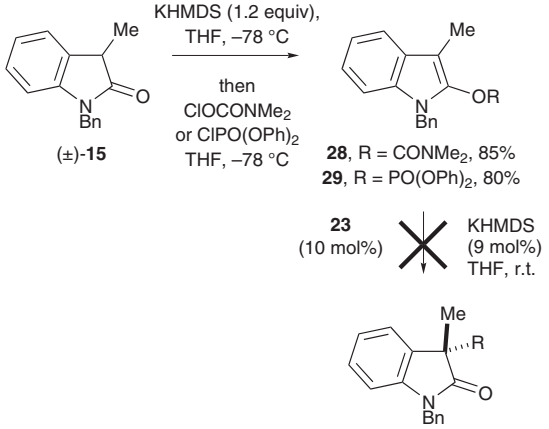


Entry	**23** (mol%)	KHMDS (mol%)	Time (min)	Product ratio[a] (±)-**26**:(±)-**27**
1	10	9	60	60:40
2	10	9	120	10:90
3	5	4	60	80:20
4	10	9	60	60:40

[a] Product distributions were judged by ^{1}H NMR spectroscopic analysis of the crude reaction mixture.

Probing the Generality of NHC-Mediated *O*-to-*C* Functional Group Transfer of Indolyl Derivatives

Given the product mixtures associated with the rearrangement of *N*-phenoxycarbonyl protected carbonate **22** with NHC **3**, subsequent studies utilised N-alkyl group protection of the indole nitrogen and sought to identify the scope and limitations of this rearrangement process with respect to both the migrating group and C(3)-substitution. Treatment of *N*-benzyl-3-methyloxindole [(±)-**15**] with KHMDS and subsequent derivatisation with dimethylcarbamoyl chloride or diphenyl phosphoryl chloride gave the corresponding indolyl carbamate **28** and phosphate **29** in good yield. Disappointingly, treatment of either **28** or **29** with NHC **3** (9 mol%) failed to promote rearrangement in either case,[24] returning only starting material after one hour (Scheme 4).



Scheme 4 Preparation and attempted NHC-promoted rearrangement of **28** and **29**

Subsequent studies focused predominantly upon the effect of variation in C(3)-substitution. *N*-Benzyl- and *N*-methyl-3-phenyloxindoles (±)-**30** and (±)-**31** were prepared by a similar route to that used for (±)-**15** and (±)-**18** respectively, with derivatisation using methyl or phenyl chloroformate under standard conditions giving carbonates **32**–**34** in good yields. X-ray crystal structure analysis of methyl carbonate **34** confirmed unambiguously that O- rather than C-carboxylation had occurred under these reaction conditions (Figure 4). Treatment of *N*-benzyl protected carbonates **32** and **33** with NHC **3** (9 mol%) gave full conversion to (±)-**35** and (±)-**36** respectively in both cases, with the structure of (±)-**35** confirmed by X-ray diffraction (Figure 5). However, a notable difference in the reactivity of the methyl and phenyl carbonate derivatives was observed upon decreasing the catalyst loading, with phenyl carbonate **33** rearranging readily to give (±)-**36** with 1.5 mol% of NHC **3**, while methyl carbonate **32** required 4 mol% of NHC **3** to achieve full reaction conversion to (±)-**35** within one hour. Further investigation showed that *N*-methyl protected phenyl carbonate **34** required 4 mol% of NHC **3** to give good conversion to (±)-**37** within one hour (Table 3). (±)-**37** was isolated in 74% yield and further characterised by X-ray crystallographic analysis (Figure 5). These studies confirm that phenyl carbonate derivatives are particularly reactive in this *O*-to-*C* carboxyl transfer reaction, although carbamate and phosphate derivatives are inert.

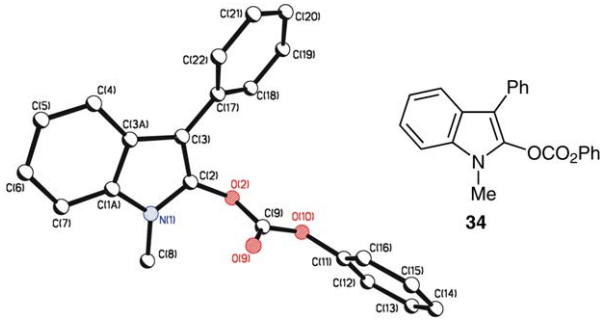
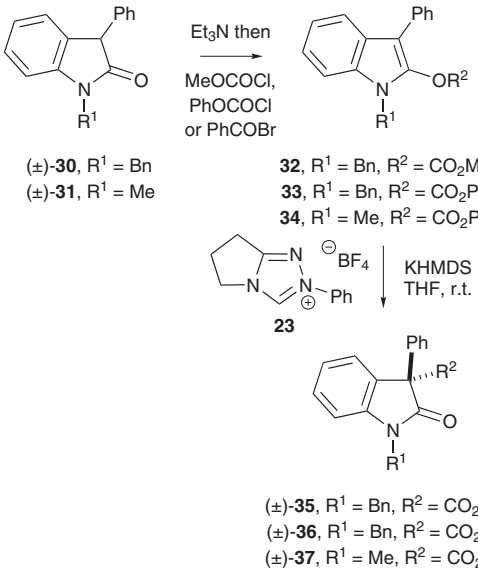


Figure 4 Molecular representation of the X-ray crystal structure of **34**

Table 3 NHC-Promoted *O*-to-*C* Carboxyl Transfer of **32**–**34**



Entry	**23** (mol%)	KHMDS (mol%)	Product	Yield (%)
1	10	9	(±)-**35**	49
2	2	1.5	(±)-**36**	91
3	5	4	(±)-**37**	74

To complete studies within the indolyl series, further C(3)-substituent modifications utilising *N*-benzyl indole protection was investigated. C(3)-Benzyl and C(3)-isopropyl substitution was envisaged to probe fully the limitations of this protocol, as the rearrangement of oxazolyl carbonates with C(3)-α-branched substituents is known to be difficult with DMAP derivatives.[22c] Following the standard protocol outlined above, *N*-benzylisatin (**12**) was converted into *N*-benzyl-3-benzyl and *N*-benzyl-3-isopropyloxindoles (±)-**40** and (±)-**41**, respectively. Isolation of the intermediate 3-hydroxyoxindoles (±)-**38** and (±)-**39** arising from Grignard addition was achieved by trituration of the crude reaction mixture with diethyl ether for characterisation purposes, giving (±)-**38** and (±)-**39** in good to moderate yields. In practice, however, the crude reaction product from the Grignard addition can be re-

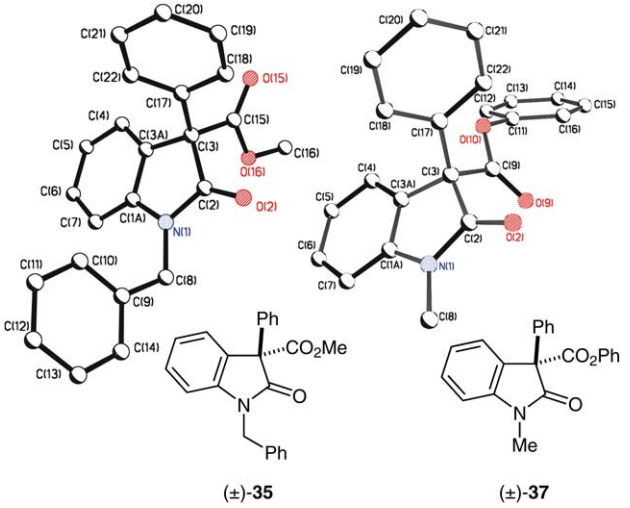
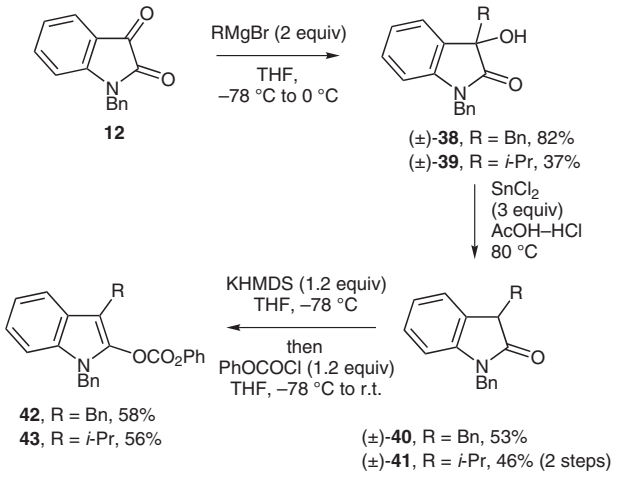


Figure 5 Molecular representations of the X-ray crystal structures of (±)-**35** and (±)-**37**

duced with tin(II) chloride directly to afford the desired 3-substituted oxindoles in respectable yield over two steps. Subsequent carbonate formation under standard conditions furnished **42** and **43** in 58% and 56% yield, respectively (Scheme 5). Once again, unambiguous proof of the *O*-phenoxycarbonyl linkage within **43** was proven by X-ray crystal structure analysis (Figure 6).

Treatment of C(3)-benzyl substituted carbonate **42** with NHC **3** (1.5 mol%) gave complete conversion to **44** within



Scheme 5 Preparation of indolyl carbonates **42** and **43**

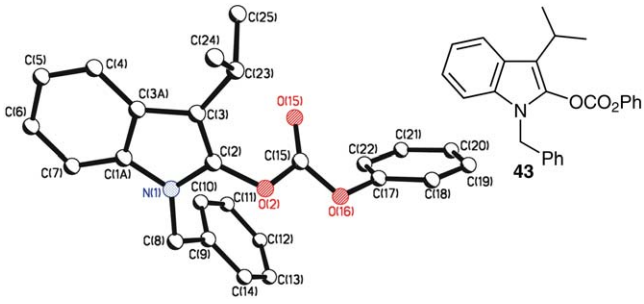
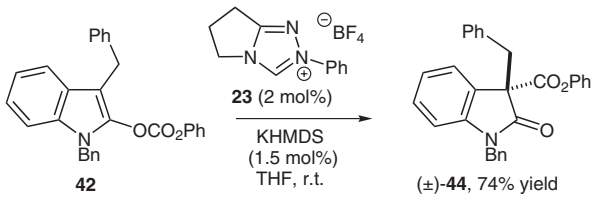


Figure 6 Molecular representation of the X-ray crystal structure of carbonate **43**

one hour, giving (±)-**44** in 74% isolated yield (Scheme 6), the structure of which was confirmed by X-ray crystallographic analysis (Figure 7).



Scheme 6 NHC-promoted *O*-to-*C* carboxyl transfer of carbonate **42**

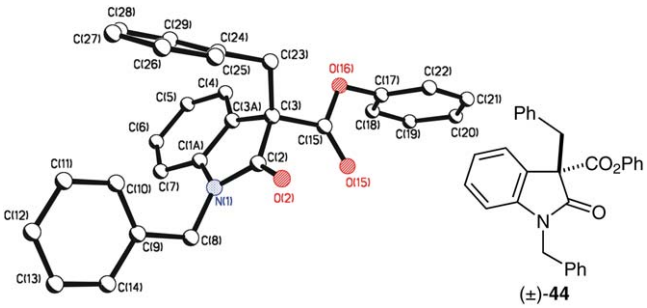
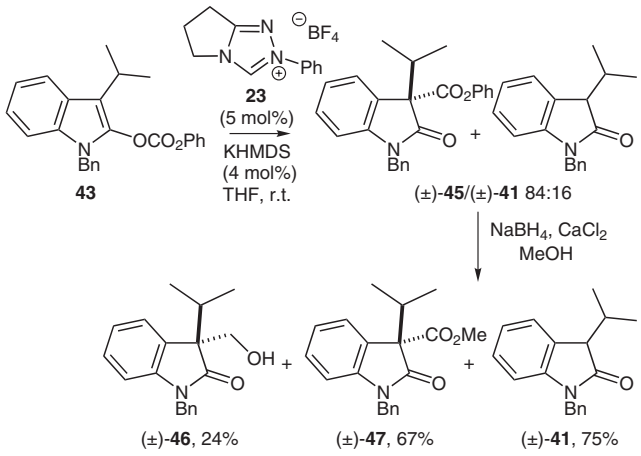


Figure 7 Molecular representation of the X-ray crystal structure of (±)-**44** (only one of two crystallographically independent molecules shown for clarity)

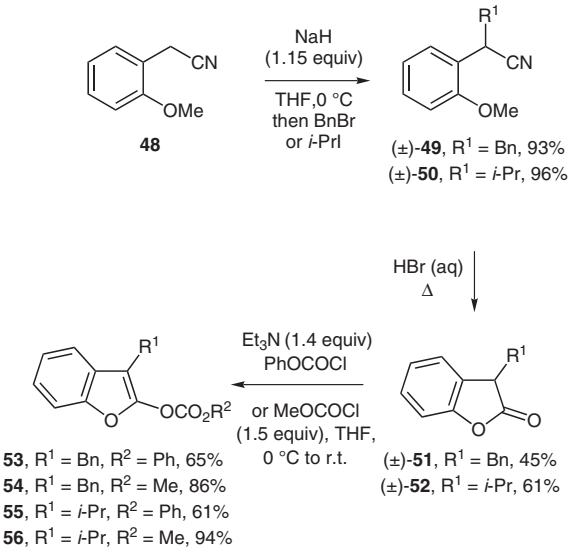
As expected, the C(3)-isopropyl substituted carbonate **43** proved the most difficult indolyl carbonate substrate to rearrange under NHC-mediated catalysis. Treatment of **43** with 4 mol% of NHC **3** gave an 81:19 mixture of the desired *C*-carboxyl product (±)-**45** to oxindole **41** at full conversion, giving an inseparable 84:16 mixture of (±)-**45**:(±)-**41** after chromatographic purification. Derivatisation of this 84:16 mixture of (±)-**45**:(±)-**41** by treatment with sodium borohydride and calcium chloride in methanol was investigated to allow full characterisation, giving a separable 22:62:16 mixture of alcohol (±)-**46**, methyl ester (±)-**47**, and oxindole (±)-**41**, respectively (Scheme 7).



Scheme 7 NHC-promoted *O*-to-*C* carboxyl transfer of carbonate **43** (isolated yields of (±)-**46** and (±)-**47** were calculated based upon the known 84:16 mixture of (±)-**45** and (±)-**41**, respectively).

NHC-Mediated *O*-to-*C* Carboxyl Group Transfer of Benzofuranyl Carbonates

Having demonstrated the scope of this NHC-mediated protocol in the indolyl series, we investigated its extension to benzofuranyl carbonates. The presence of a C(3)-branched substituent was again proposed to represent a significant challenge to the ability of NHC **3** to promote *O*-to-*C* carboxyl transfer in this system. The desired C(3)-benzyl and C(3)-isopropyl substituted benzofuranones were prepared following the method of Vedejs,[22c] with alkylation of commercially available nitrile **48** and subsequent hydrolysis generating (±)-**51** and (±)-**52** on a multigram scale. Treatment of (±)-**51** and (±)-**52** with triethylamine and either phenyl- or methyl chloroformate gave the desired substrates **53–56** in good isolated yield (Scheme 8).

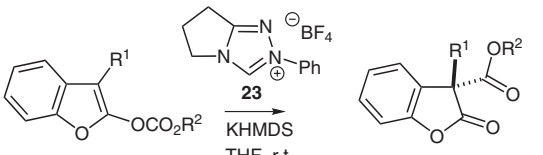


Scheme 8 Preparation of benzofuranyl carbonates **53–56**

The *O*-to-*C* carboxyl transfer of carbonates **53–56** was readily promoted upon treatment with 1.8–9 mol% NHC **3**, in each case giving good conversion to the desired products (±)-**57**–(±)-**60** within one hour, furnishing (±)-**57**–(±)-**60** in 65–88% isolated yield respectively. The trends in reactivity noted within this series of reactions mirrors that observed within the indolyl series, with lower catalyst loadings of NHC **3** giving full conversion to the corresponding C-carboxyl products with phenyl rather than methyl carbonate derivatives. Furthermore, C(3)-α-branched substituents are readily tolerated but require slightly higher catalyst loadings to achieve full reaction conversion within one hour (Table 4).

In conclusion, NHC **3** can promote the *O*-to-*C* carboxyl group rearrangement of indolyl and benzofuranyl carbonates with good catalytic efficiency (1.5–9 mol% of NHC **3**) and reasonable reaction times. Variation of carbonate functionality and C(3)-substitution within the indolyl and benzofuranyl skeleton is readily accommodated, although

Table 4 NHC-Promoted *O*-to-*C* Carboxyl Rearrangement of **53–56**



53, R^1 = Bn, R^2 = Ph
54, R^1 = Bn, R^2 = Me
55, R^1 = *i*-Pr, R^2 = Ph
56, R^1 = *i*-Pr, R^2 = Me

(±)-**57**, R^1 = Bn, R^2 = Ph
(±)-**58**, R^1 = Bn, R^2 = Me
(±)-**59**, R^1 = *i*-Pr, R^2 = Ph
(±)-**60**, R^1 = *i*-Pr, R^2 = Me

Entry	**23** (mol%)	KHMDS (mol%)	Product	Yield (%)
1	2	1.8	(±)-**57**	88
2	10	9	(±)-**58**	80
3	5	4	(±)-**59**	82
4	10	9	(±)-**60**	65

a change in product distribution was noted in the indolyl series with variation of the N-protecting group. The introduction of a C(3)-isopropyl group into both the indolyl and benzofuranyl skeleton is tolerated using NHC-mediated catalysis, which is indicative of the high reactivity of NHCs in this reaction manifold. Current studies are focused upon the preparation and optimisation of chiral NHCs to develop asymmetric versions of this transformation and probing new applications of NHCs in asymmetric catalysis.

Reactions were conducted under an Ar atmosphere using standard vacuum line techniques and with freshly dried solvents. Room temperature (r.t.) refers to 20–25 °C. In vacuo refers to the use of a Büchi Rotavapor R-2000 or a Heidolph Laborota 4001 rotary evaporator. Petroleum ether (PE), where used, had a boiling range of 40–60 °C. Flash column chromatography was performed on Kieselgel 60 silica in the solvent system stated. ^{1}H and ^{13}C NMR spectra were acquired on either a Bruker Avance 300 (300 MHz, ^{1}H; 75.4 MHz, ^{13}C) or Bruker Avance II 400 (400 MHz, ^{1}H; 100 MHz, ^{13}C) spectrometer in the deuterated solvent stated. Chemical shift values (δ, ppm) are reported relative to residual solvent peaks. The abbreviation Ar is used to denote aromatic. Infrared spectra (ν_{max}) were recorded on a Perkin–Elmer Spectrum GX FT-IR. Microanalyses were carried out on a Carlo Erba CHNS analyser. Melting points were recorded on an Electrothermal apparatus and are uncorrected. Mass spectrometric (*m/z*) data was acquired by electrospray ionisation (ESI), electron impact (EI) or chemical ionisation (CI), either at the University of St Andrews Mass Spectrometry facility or at the EPSRC National Mass Spectrometry Service Centre, Swansea.

Crystallographic data (excluding structure factors) for compounds (±)-**14**, **22**, (±)-**27**, **34**, (±)-**35**, (±)-**37**, **43** and (±)-**44** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers 683081–683088. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(1223)336033 or e-mail: deposit@ccdc.cam.ac.uk]

Grignard Addition to Isatins; General Procedure A

To a solution of the desired isatin in THF at –78 °C was slowly added a solution of Grignard reagent. The resulting solution was stirred at –78 °C for 10 min, then warmed to 0 °C and stirred for a further

20 min. After this time, sat. aq NH_4Cl (5 mL/mmol) was added, followed by EtOAc (5 mL/mmol) and the organic phase was removed. The aqueous phase was extracted into EtOAc (3 × 5 mL/mmol) and the combined organic fractions were washed with H_2O (1 × 5 mL/mmol) and brine (1 × 5 mL/mmol), dried ($MgSO_4$), filtered and concentrated.

$SnCl_2$ Reduction; General Procedure B

To a solution of starting material in a mixture of AcOH–HCl (concd) (15:1), was added $SnCl_2·2H_2O$ and the resulting suspension was heated at 80 °C overnight. After cooling, the solution was poured into H_2O (10 mL/mmol), extracted into Et_2O (3 × 5 mL/mmol) and the organic fractions combined, washed with aq NaOH (2 M, 2 × 10 mL/mmol), dried ($MgSO_4$), filtered and concentrated in vacuo to give the desired oxindole after chromatographic purification.

Formation of Indol-2-yl Carbonates Using KHMDS; General Procedure C

To a stirred solution of KHMDS in toluene (0.5 M, 1.2 equiv) at –78 °C, was added a solution of the desired oxindole (1 equiv) in THF at –78 °C. After 30 min the solution was added to a solution of phenyl chloroformate (1.2 equiv) in THF at –78 °C and the reaction was warmed slowly to r.t. overnight. After this time, HCl (0.1 M, 10 mL/mmol) was added and the mixture was extracted with Et_2O (3 × 10 mL/mmol). The combined organic phases were washed with brine (1 × 10 mL/mmol), dried ($MgSO_4$) then concentrated in vacuo. Chromatographic purification or recrystallisation gave the desired carbonate.

Formation of Indol-2-yl and Benzofuran-2-yl Carbonates with Et_3N; General Procedure D

To a stirred solution of the desired oxindole or benzofuranone in THF at 0 °C was added Et_3N followed by the selected chloroformate and the reaction was warmed slowly to r.t. overnight. After this time, work-up was carried out as described in general procedure C and subsequent purification gave the desired carbonate.

Rearrangement of Carbonates; General Procedure E

KHMDS was added to a solution of triazolium salt **23** in THF and the mixture was stirred at r.t. for 30 min. The desired carbonate was added, either as a solution in THF or as a solid, and stirred for the specified time before concentration in vacuo. Chromatographic purification (silica) gave the desired product.

1-Benzyl-3-hydroxy-3-methyl-2-oxo-2,3-dihydroindole [(±)-13]

Following general procedure A, *N*-benzylisatin (**12**; 5.00 g, 21.1 mmol), THF (100 mL) and methylmagnesium bromide (9.80 mL, 29.5 mmol, 3.0 M in Et_2O) gave, after recrystallisation (EtOH), (±)-**13** with spectroscopic data in accordance with the literature.[25]

Yield: 2.18 g (41%); yellow solid; mp 146–148 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.70 (s, 3 H, 3-CH_3), 3.14 (s, 1 H, O*H*), 4.85 (ABq, *J* = 15.7 Hz, 1 H, CH_AH$_B$Ph), 5.00 (ABq, *J* = 15.7 Hz, 1 H, CH$_A$$H_B$Ph), 6.75 (d, *J* = 7.8 Hz, 1 H, Ar*H*), 7.10 (td, *J* = 7.5, 0.9 Hz, 1 H, Ar*H*), 7.23 (td, *J* = 7.7, 1.3 Hz, 1 H, Ar*H*), 7.27–7.38 (m, 5 H, Ph*H*), 7.45 (dd, *J* = 7.3, 0.9 Hz, 1 H, Ar*H*).

1-Benzyl-3-chloro-3-methyl-2-oxo-2,3-dihydroindole [(±)-14]

Thionyl chloride (1.01 mL, 13.8 mmol) was added to (±)-**13** (0.500 g, 1.97 mmol) and the resultant solution was stirred at r.t. overnight before concentration in vacuo. Chromatographic purification (PE–Et_2O, 80:20) gave (±)-**14**.

Yield: 0.444 g (83%); yellow solid; mp 76–77 °C.

IR (KBr): 3032 (C–H), 1730 (C=O), 1613 (Ar C=C), 751 (C–Cl), 697 cm^{-1} (Ar C–H).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.89 (s, 3 H, 3-CH_3), 4.81 (ABq, *J* = 15.7 Hz, 1 H, CH_AH$_B$Ph), 4.90 (ABq, *J* = 15.7 Hz, 1 H, CH$_A$$H_B$Ph), 6.65 (d, *J* = 7.8 Hz, 1 H, Ar*H*), 7.01 (td, *J* = 7.5, 1.0 Hz, 1 H, Ar*H*), 7.14 (td, *J* = 7.8, 1.3 Hz, 1 H, Ar*H*), 7.17–7.28 (m, 5 H, Ar*H*), 7.36 (dd, *J* = 7.4, 0.9 Hz, 1 H, Ar*H*).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.0, 44.0, 61.9, 109.8, 123.5, 123.9, 127.2, 127.9, 129.0, 130.1, 131.1, 135.2, 141.2, 174.6.

MS (CI): *m*/*z* (%) = 236.1 (100) [M – Cl]$^+$, 272.1 (65) [M + H]$^+$.

HRMS (CI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{15}NOCl$: 272.0842; found: 272.0837.

1-Benzyl-3-methyl-2-oxo-2,3-dihydroindole [(±)-15]

Following general procedure B, (±)-**13** (5.34 g, 21.1 mmol), AcOH (185 mL), concd HCl (12 mL) and $SnCl_2·2H_2O$ (14.3 g, 63.3 mmol) gave, after chromatographic purification (PE–Et_2O, 80:20), (±)-**15** with spectroscopic data in accordance with the literature.[26]

Yield: 1.94 g (39% over two steps); yellow solid; mp 112–114 °C (Lit.[26] 117–118 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.53 (d, *J* = 7.6 Hz, 3 H, 3-CH_3), 3.58 (q, *J* = 7.6 Hz, 1 H, C*H*), 4.95 (s, 2 H, NCH_2Ph), 6.76 (td, *J* = 7.8 Hz, 1 H, Ar*H*), 7.03–7.39 (m, 8 H, Ar*H*).

3-Hydroxy-1,3-dimethyl-2-oxo-2,3-dihydroindole [(±)-17]

Following general procedure A, *N*-methylisatin (**16**; 2.00 g, 8.44 mmol), THF (40 mL) and methylmagnesium bromide (3.90 mL, 11.8 mmol, 3.0 M in Et_2O) gave crude (±)-**17** as a dark orange solid (2.96 g) which was used without further purification.

1,3-Dimethyl-2-oxo-2,3-dihydroindole [(±)-18]

Following general procedure B, crude (±)-**17** (5.49 g, 30.9 mmol), AcOH (280 mL), concd HCl (20 mL) and $SnCl_2·2H_2O$ (13.9 g, 61.7 mmol) gave, after chromatographic purification (PE–Et_2O, 70:30), (±)-**18** with spectroscopic data in accordance with the literature.[27]

Yield: 2.50 g (50% over two steps); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.48 (d, *J* = 7.6 Hz, 3 H, CH_3), 3.21 (s, 3 H, NCH_3), 3.43 (q, *J* = 7.4 Hz, 1 H, *H*-3), 6.82 (d, *J* = 7.8 Hz, 1 H, Ar*H*), 7.03–7.08 (m, 1 H, Ar*H*), 7.22–7.30 (m, 2 H, Ar*H*).

1-Benzyl-3-methylindol-2-yl Phenyl Carbonate (19)

Following general procedure C, KHMDS (5.00 mL, 2.52 mmol), oxindole (±)-**15** (0.500 g, 2.10 mmol), THF (4.20 mL), phenyl chloroformate (0.320 mL, 2.52 mmol) and THF (4.20 mL) gave, after chromatographic purification (PE–Et_2O, 90:10), carbonate **19** with spectroscopic data in accordance with the literature.[22c]

Yield: 0.420 g (56%); colourless solid; mp 67–69 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.20 (s, 3 H, CH_3), 5.21 (s, 2 H, CH_2), 7.00–7.17 (m, 7 H, Ar*H*), 7.19–7.25 (m, 3 H, Ar*H*), 7.28–7.37 (m, 3 H, Ar*H*), 7.48–7.52 (m, 1 H, Ar*H*).

1,3-Dimethylindol-2-yl Phenyl Carbonate (20)

Following general procedure C, KHMDS (16.8 mL, 8.42 mmol), oxindole (±)-**18** (1.13 g, 7.02 mmol), THF (14 mL), phenyl chloroformate (1.06 mL, 8.42 mmol) and THF (14 mL) gave a pale-yellow solid. NMR analysis of this material indicated that it was a 2:1 mixture of O- and C-carboxylated product. This residue was then triturated with Et_2O and the solid material filtered off to give the desired carbonate **20** with spectroscopic data in accordance with the literature.[22c]

Yield: 1.00 g (51%); pale-yellow solid; mp 115–117 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.27 (s, 3 H, 3-CH_3), 3.67 (s, 3 H, NCH_3), 7.12–7.20 (m, 1 H, Ar*H*), 7.24–7.34 (m, 5 H, Ar*H*), 7.40–7.49 (m, 2 H, Ar*H*), 7.53–7.58 (m, 1 H, Ar*H*).

3-Methyl-1-phenoxycarbonylindol-2-yl Phenyl Carbonate (22)
Following general procedure D, 3-methyloxindole (±)-**21** (1.50 g, 10.2 mmol), THF (30 mL), Et_3N (3.10 mL, 22.4 mmol) and phenyl chloroformate (2.70 mL, 21.6 mmol) gave, after trituration (PE), the product **22**, with spectroscopic data in accordance with the literature.[22c]

Yield: 3.40 g (86%); pale-yellow solid; mp 93–96 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.28 (s, 3 H, 3-CH_3), 7.10–7.25 (m, 3 H, Ar*H*), 7.29–7.56 (m, 10 H, Ar*H*), 8.14–8.19 (m, 1 H, Ar*H*).

Phenyl 1-Benzyl-3-methyl-2-oxo-2,3-dihydroindole-3-carboxylate [(±)-24]
Following general procedure E, KHMDS (0.018 mL, 0.0090 mmol, 1.9 mol%), triazolium salt **23** (0.0030 g, 0.0090 mmol, 2.0 mol%), THF (0.4 mL) and carbonate **19** (0.17 g, 0.46 mmol) gave, after 1 h and chromatographic purification (PE–Et_2O, 60:40), (±)-**24** with spectroscopic data in accordance with the literature.[22c]

Yield: 0.12 g (69%); colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.76 (s, 3 H, CH_3), 4.77 (ABq, *J* = 15.8 Hz, 1 H, CH_AH$_B$Ph), 5.09 (ABq, *J* = 15.8 Hz, 1 H, CH$_A$$H_B$Ph), 6.69 (d, *J* = 7.8 Hz, 1 H, Ar*H*), 6.90 (d, *J* = 7.6 Hz, 2 H, Ar*H*), 7.01 (td, *J* = 7.6, 0.7 Hz, 1 H, Ar*H*), 7.10–7.22 (m, 5 H, Ar*H*), 7.22–7.31 (m, 5 H, Ar*H*).

Phenyl 1,3-Dimethyl-2-oxo-2,3-dihydroindole-3-carboxylate [(±)-25]
Following general procedure E, KHMDS (0.014 mL, 0.0070 mmol, 1.9 mol%), triazolium salt **23** (0.0020 mg, 0.0070 mmol, 2 mol%), THF (0.3 mL) and carbonate **20** (0.10 g, 0.35 mmol) gave, after 1 h and chromatographic purification (PE–Et_2O, 50:50), (±)-**25** with spectroscopic data in accordance with the literature.[22c]

Yield: 0.071 g (71%); colourless solid; mp 93–95 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.77 (s, 3 H, 3-CH_3), 3.30 (s, 3 H, NCH_3), 6.90–6.96 (m, 3 H, Ar*H*), 7.11–7.21 (m, 2 H, Ar*H*), 7.28–7.40 (m, 4 H, Ar*H*).

Diphenyl 3-Methyl-2-oxo-2,3-dihydroindole-1,3-dicarboxylate [(±)-26]
Following general procedure E, KHMDS (0.116 mL, 0.0581 mmol, 9 mol%), triazolium salt **23** (0.0176 g, 0.0645 mmol, 10 mol%), THF (2.5 mL) and carbonate **22** (0.250 g, 0.645 mmol) gave, after 1 h, a 60:40 mixture of (±)-**26**:(±)-**27**. Subsequent chromatographic purification (PE–Et_2O, 90:10→50:50), afforded (±)-**26** (0.077 g, 31%) as a yellow oil with spectroscopic data in accordance with the literature,[22c] and (±)-**27** (0.119 g, 69%) as an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.90 (s, 3 H, CH_3), 6.94–7.01 (m, 2 H, Ar*H*), 7.17–7.50 (m, 11 H, Ar*H*), 8.05 (d, *J* = 8.1 Hz, 1 H, Ar*H*).

Phenyl-3-methyl-2-oxoindole-3-carboxylate [(±)-27]
Mp 220–223 °C.

IR (KBr): 3083 (N–H), 1755 (C=O), 1708 (C=O), 1192 (C–O), 745 cm^{-1} (Ar C–H).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.73 (s, 3 H, 3-CH_3), 6.88–6.92 (m, 3 H, Ar*H*), 7.01–7.29 (m, 6 H, Ar*H*), 8.16 (br s, 1 H, N*H*).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.6, 55.1, 110.1, 121.1, 122.2, 123.2, 126.3, 129.2, 129.7, 130.3, 142.2, 150.0, 168.4, 175.3.

MS (ESI+): *m*/*z* (%) = 290.1 (100) $[M + Na]^+$.

HRMS (ESI+): *m*/*z* $[M + Na]^+$ calcd for $C_{16}H_{13}NO_3Na$: 290.0793; found: 290.0792.

1-Benzyl-3-methylindol-2-yl Dimethylcarbamate (28)
To a stirred solution of oxindole (±)-**15** (0.200 g, 0.850 mmol) in THF (1.70 mL) at –78 °C was added KHMDS (2.05 mL, 1.02 mmol) followed by dimethylcarbamoyl chloride (0.0820 mL, 0.900 mmol) and the reaction warmed slowly to r.t. overnight. After this time, H_2O (2 mL) was added and the organic phase was extracted with Et_2O (3 × 2 mL). The organic extracts were combined, washed with HCl (0.1 M, 1 × 6 mL), sat. aq $NaHCO_3$ (1 × 6 mL) and brine (1 × 6 mL), dried ($MgSO_4$) then concentrated in vacuo. Chromatographic purification (PE–Et_2O, 25:75) gave carbamate **28**.

Yield: 0.222 g (85%); colourless solid; mp 135–136 °C.

IR (KBr): 3053 (C–H), 2930 (C–H), 1739 (C=O), 1645 (Ar C=C), 1266 (C–O), 731 (C–H), 695 cm^{-1} (C–H).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.11 (s, 3 H, 3-CH_3), 2.90 [s, 3 H, N(CH_3)$_2$], 2.93 [s, 3 H, N(CH_3)$_2$], 5.07 (s, 2 H, CH_2), 7.21–7.00 (m, 8 H, Ar*H*), 7.45–7.42 (m, 1 H, Ar*H*).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 7.9, 37.0, 34.5, 46.4, 97.5, 109.7, 119.0, 119.8, 121.6, 127.1, 127.5, 127.7, 129.0, 132.8, 138.1, 140.2, 153.6.

MS (EI+): *m*/*z* (%) = 309 (100) $[M + H]^+$.

HRMS (EI+): *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{21}N_2O_2$: 309.1598; found: 309.1595.

1-Benzyl-3-methylindol-2-yl Diphenyl Phosphate (29)
To a stirred solution of oxindole (±)-**15** (0.200 g, 0.85 mmol) in THF (1.70 mL) at –78 °C was added KHMDS (2.05 mL, 1.02 mmol) followed by diphenyl phosphoroyl chloride (0.170 mL, 0.900 mmol) and the reaction warmed slowly to r.t. overnight. After this time, H_2O (2 mL) was added and the organic phase was extracted with Et_2O (3 × 2 mL). The organic extracts were combined, washed with 0.1 M HCl (1 × 6 mL), sat. aq $NaHCO_3$ (1 × 6 mL) and brine (1 × 6 mL), dried ($MgSO_4$) then concentrated in vacuo. Chromatographic purification (PE–Et_2O, 25:75) gave phosphate **29**.

Yield: 0.320 g (80%); colourless oil.

IR (thin film): 3061 (C–H), 2900 (C–H), 1301 (P=O), 1627 (Ar C=C), 1185 (C–O), 951 (P–O–C), 739 (C–H), 688 cm^{-1} (C–H).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.21 (d, *J* = 2.1 Hz, 3 H, 3-CH_3), 5.11 (s, 2 H, CH_2), 6.88–6.90 (m, 2 H, Ar*H*), 7.00–7.19 (m, 16 H, Ar*H*), 7.40–7.44 (m, 1 H, Ar*H*).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 7.7, 45.8, 95.9 (d, *J* = 3.0 Hz), 109.7, 119.0, 120.0, 120.3 (d, *J* = 3.9 Hz), 122.0, 126.0, 126.6, 126.9, 127.4, 128.7, 130.0, 132.1, 137.4, 138.1 (d, *J* = 7.7 Hz), 150.5 (d, *J* = 7.3 Hz).

^{31}P NMR (121 MHz, $CDCl_3$): δ = –16.

MS (CI+): *m*/*z* (%) = 470 (100) $[M + H]^+$.

HRMS (CI+): *m*/*z* $[M + H]^+$ calcd for $C_{28}H_{25}NO_4P$: 470.1521; found: 470.1520.

1-Benzyl-2-oxo-3-phenyl-2,3-dihydroindole [(±)-30]
Following general procedure B, crude 1-benzyl-3-hydroxy-2-oxo-3-phenyl-2,3-dihydroindole (1.99 g, 6.33 mmol), AcOH (56 mL), concd HCl (4 mL) and $SnCl_2·2H_2O$ (2.86 g, 12.7 mmol) gave, after chromatographic purification (PE–Et_2O, 80:20), (±)-**30** with spectroscopic data in accordance with the literature.[28]

Yield: 1.42 g (75% over two steps); yellow solid; mp 108–110 °C (Lit.[28] 115–116 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.63 (s, 1 H, *H*-3), 4.83 (ABq, *J* = 15.6 Hz, 1 H, CH_AH$_B$Ph), 4.93 (ABq, *J* = 15.6 Hz, 1 H, CH$_A$$H_B$Ph), 6.71 (d, *J* = 7.8 Hz, 1 H, Ar*H*), 6.94 (td, *J* = 7.6, 0.9 Hz, 1 H, Ar*H*), 7.08–7.30 (m, 12 H, Ar*H*).

1-Methyl-2-oxo-3-phenyl-2,3-dihydroindole [(±)-31]
To a solution of crude 3-hydroxy-1-methyl-2-oxo-3-phenyl-2,3-dihydroindole (4.49 g, 18.7 mmol) in anhydrous CH_2Cl_2 (40 mL) at 0 °C was added triethylsilane (5.96 mL, 37.4 mmol) followed by $BF_3{\cdot}OEt_2$ (4.74 mL, 37.4 mmol). The reaction mixture was stirred at 0 °C for 20 min and then allowed to warm slowly to r.t. overnight. The reaction was quenched with sat. aq $NaHCO_3$ (40 mL) and, once gas evolution had subsided, extracted with CH_2Cl_2 (3 × 40 mL). The organic extracts were combined, washed with H_2O (1 × 40 mL) and brine (1 × 40 mL), dried ($MgSO_4$) and concentrated in vacuo. Chromatographic purification (PE–Et_2O, 90:10) afforded (±)-**31** with spectroscopic data in accordance with the literature.[29]

Yield: 2.50 g (60% over two steps); pale-yellow solid; mp 116–118 °C (Lit.[30] 118–119 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.30 (s, 3 H, N-C*H*$_3$), 4.65 (s, 1 H, *H*-3), 6.94 (d, *J* = 7.8 Hz, 1 H, Ar*H*), 7.11 (t, *J* = 7.5 Hz, 1 H, Ar*H*), 7.20–7.26 (m, 3 H, Ar*H*), 7.30–7.40 (m, 4 H, Ar*H*).

1-Benzyl-3-phenylindol-2-yl Methyl Carbonate (32)
Following general procedure D, oxindole (±)-**30** (1.00 g, 3.34 mmol), THF (15 mL), Et_3N (0.510 mL, 3.68 mmol) and methyl chloroformate (0.270 mL, 3.55 mmol) gave, after chromatographic purification (PE–Et_2O, 90:10), carbonate **32**.

Yield: 1.67 g (93%); pale-yellow gum.

IR (thin film): 3059 (C–H), 3032 (C–H), 2957 (C–H), 2925 (C–H), 1781 (C=O), 1619 (C=C), 1244 (C–O), 1213 (C–O), 700 cm^{-1} (Ar C–H).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.64 (s, 3 H, OCH_3), 5.19 (s, 2 H, CH_2Ph), 7.07–7.27 (m, 9 H, Ar*H*), 7.34–7.40 (m, 2 H, Ar*H*), 7.52–7.56 (m, 2 H, Ar*H*), 7.72–7.78 (m, 1 H, Ar*H*).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 46.2, 56.2, 103.7, 110.0, 119.8, 120.9, 122.5, 125.1, 126.4, 126.9, 127.7, 128.4, 128.9 (× 2), 132.4, 133.0, 136.7, 138.8, 152.6.

MS (ESI+): *m*/*z* (%) = 380.1 (100) [M + Na]$^+$.

HRMS (ESI+): *m*/*z* [M + Na]$^+$ calcd for $C_{23}H_{19}NO_3Na$: 380.1263; found: 380.1256 (–1.8 ppm).

1-Benzyl-3-phenylindol-2-yl Phenyl Carbonate (33)
Following general procedure D, oxindole (±)-**30** (1.50 g, 5.02 mmol), THF (23 mL), Et_3N (0.770 mL, 5.52 mmol) and phenyl chloroformate (0.670 mL, 5.32 mmol) gave, after recrystallisation (CH_2Cl_2–MeOH), carbonate **33**.

Yield: 1.82 g (87%); pale-yellow solid; mp 116–118 °C.

IR (KBr): 3060 (C–H), 3033 (C–H), 2925 (C–H), 1793 (C=O), 1620 (C=C), 1228 (C–O), 1192 (C–O), 742 (Ar C–H), 700 cm^{-1} (Ar C–H).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.30 (s, 2 H, CH_2Ph), 6.72–6.77 (m, 2 H, Ar*H*), 7.09–7.28 (m, 12 H, Ar*H*), 7.38–7.44 (m, 2 H, Ar*H*), 7.59–7.63 (m, 2 H, Ar*H*), 7.74–7.80 (m, 1 H, Ar*H*).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 46.2, 103.8, 110.0, 119.8, 120.5, 120.9, 122.6, 125.0, 126.5, 126.6, 126.9, 127.8, 128.4, 128.9 (× 2), 129.6, 132.4, 132.9, 136.6, 138.7, 150.2, 150.7.

MS (CI): *m*/*z* (%) = 420.2 (100) [M + H]$^+$.

HRMS (CI): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{22}NO_3$: 420.1600; found: 420.1589 (–2.5 ppm).

1-Methyl-3-phenylindol-2-yl Phenyl Carbonate (34)
Following general procedure D, oxindole (±)-**31** (0.600 g, 2.69 mmol), THF (7 mL), Et_3N (0.390 mL, 2.96 mmol) and phenyl chloroformate (0.360 mL, 2.85 mmol) gave, after chromatographic purification (PE–Et_2O, 90:10), carbonate **34**.

Yield: 0.757 g (82%); pale-yellow solid; mp 78–80 °C.

IR (KBr): 3052 (C–H), 2925 (C–H), 1777 (C=O), 1619 (Ar C=C), 1601 (Ar C=C), 1249 (C–O), 1138 (C–O), 748 cm^{-1} (Ar C–H).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.65 (s, 3 H, N-C*H*$_3$), 6.99–7.03 (m, 2 H, Ar*H*), 7.09–7.30 (m, 7 H, Ar*H*), 7.37–7.42 (m, 2 H, Ar*H*), 7.56–7.59 (m, 2 H, Ar*H*), 7.74 (d, *J* = 8.0 Hz, 1 H, Ar*H*).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.6, 29.8, 103.3, 109.4, 119.8, 120.6, 120.8, 122.3, 124.7, 126.4, 126.7, 128.4, 128.9, 129.7, 132.7, 133.0, 138.7, 150.8.

MS (CI+): *m*/*z* (%) = 344.1 (70) [M + H]$^+$.

HRMS (CI+): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{18}NO_3$: 344.1287; found: 344.1293 (+1.8 ppm).

Methyl 1-Benzyl-2-oxo-3-phenyl-2,3-dihydroindole-3-carboxylate [(±)-35]
Following general procedure E, KHMDS (0.10 mL, 0.050 mmol, 9 mol%), triazolium salt **23** (0.015 mg, 0.056 mmol, 10 mol%), THF (2 mL) and carbonate **32** (0.20 g, 0.56 mmol) gave, after 1 h and chromatographic purification (PE–Et_2O, 80:20), compound (±)-**35**.

Yield: 0.098 g (49%); colourless solid; mp 140–142 °C.

IR (KBr): 2952 (C–H), 1746 (C=O), 1720 (C=O), 1609 (Ar C=C), 1232 (C–O), 696 cm^{-1} (Ar C–H).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.69 (s, 3 H, OC*H*$_3$), 4.75 (ABq, *J* = 15.8 Hz, 1 H, C*H*$_A$H$_B$Ph), 4.95 (ABq, *J* = 15.8 Hz, 1 H, CH$_A$*H*$_B$Ph), 6.68–6.71 (m, 1 H, Ar*H*), 7.01–7.07 (m, 1 H, Ar*H*), 7.14–7.30 (m, 11 H, Ar*H*), 7.35–7.39 (m, 1 H, Ar*H*).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 44.1, 53.4, 64.1, 109.9, 123.1, 126.0, 127.1 (× 2), 127.7, 128.0, 128.4, 128.7, 128.8, 129.6, 135.4, 135.8, 143.5, 169.8, 173.1.

MS (ESI+): *m*/*z* (%) = 380.0 (100) [M + Na]$^+$.

HRMS (ESI+): *m*/*z* [M + Na]$^+$ calcd for $C_{23}H_{19}NO_3Na$: 380.1263; found: 380.1268 (+1.3 ppm).

Phenyl 1-Benzyl-2-oxo-3-phenyl-2,3-dihydroindole-3-carboxylate [(±)-36]
Following general procedure E, KHMDS (0.028 mL, 0.014 mmol, 1.5 mol%), triazolium salt **23** (0.0050 mg, 0.019 mmol, 2.0 mol%), THF (0.4 mL) and carbonate **33** (0.40 g, 0.96 mmol) gave, after 1 h and subsequent chromatographic purification (PE–Et_2O, 90:10), (±)-**36**.

Yield: 0.36 g (91%); colourless solid; mp 85–87 °C.

IR (KBr): 3061 (C–H), 3032 (C–H), 2936 (C–H), 1768 (C=O), 1714 (C=O), 1608 (Ar C=C), 1189 (C–O), 752 (C–H), 695 cm^{-1} (Ar C–H).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.86 (ABq, *J* = 15.8 Hz, 1 H, C*H*$_A$H$_B$Ph), 5.15 (ABq, *J* = 15.8 Hz, 1 H, CH$_A$*H*$_B$Ph), 6.84–6.87 (m, 1 H, Ar*H*), 7.05–7.09 (m, 2 H, Ar*H*), 7.19–7.54 (m, 15 H, Ar*H*), 7.61–7.65 (m, 1 H, Ar*H*).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 44.2, 64.4, 110.2, 121.2, 123.3, 126.0, 126.3, 126.7, 127.2, 127.8, 128.2, 128.6, 128.8, 128.9, 129.5, 130.0, 135.4, 143.7, 150.6, 167.8, 172.7.

MS (ESI+): *m*/*z* (%) 442.1 (100) [M + Na]$^+$.

HRMS (ESI+): *m*/*z* [M + Na]$^+$ calcd for $C_{28}H_{21}NO_3Na$: 442.1419; found: 442.1422 (+0.7 ppm).

Phenyl 1-Methyl-2-oxo-3-phenyl-2,3-dihydroindole-3-carboxylate [(±)-37]
Following general procedure E, KHMDS (0.058 mL, 0.029 mmol, 4 mol%), triazolium salt **23** (0.010 g, 0.036 mmol, 5 mol%), THF (1.6 mL) and carbonate **34** (0.25 g, 0.73 mmol) gave, after 1 h and chromatographic purification (PE–Et_2O, 60:40), (±)-**37**.

Yield: 0.19 g (74%); colourless oil.

IR (thin film): 3061 (C–H), 2937 (C–H), 1763 (C=O), 1720 (C=O), 1609 (Ar C=C), 1187 (C–O), 750 (Ar C–H), 736 cm^{-1} (Ar C–H).

^1H NMR (400 MHz, $CDCl_3$): δ = 3.13 (s, 3 H, NCH_3), 6.86 (d, J = 7.8 Hz, 1 H, ArH), 6.88–6.92 (m, 2 H, ArH), 7.05–7.14 (m, 2 H, ArH), 7.18–7.29 (m, 5 H, ArH), 7.32–7.38 (m, 3 H, ArH), 7.48–7.51 (m, 1 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.9, 64.1, 109.1, 121.2, 123.2, 126.1, 126.3, 126.5, 128.0, 128.5, 128.7, 129.5, 130.1, 135.5, 144.6, 150.6, 167.7, 172.4.

MS (EI): m/z (%) = 343.1 (10) $[M]^+$.

HRMS (EI): m/z $[M]^+$ calcd for $C_{22}H_{17}NO_3$: 343.1208; found: 343.1211 (+0.7 ppm).

1,3-Dibenzyl-3-hydroxy-2-oxo-2,3-dihydroindole [(±)-38]

Following general procedure A, *N*-benzylisatin **12** (3.50 g, 14.8 mmol), THF (60 mL) and benzylmagnesium bromide (8.12 mL, 16.2 mmol, 2.0 M in THF) gave, after trituration with Et_2O, (±)-**38** with spectroscopic data in accordance with the literature.[31]

Yield: 3.97 g (82%); pale-yellow solid; mp 164–165 °C (Lit.[31] 188–190 °C).

^1H NMR (300 MHz, $CDCl_3$): δ = 3.30 (ABq, J = 12.7 Hz, 1 H, CH_AH$_B$Ph), 3.43 (ABq, J = 12.7 Hz, 1 H, CH$_A$$H_B$Ph), 4.45 (ABq, J = 16.0 Hz, 1 H, NCH_AH$_B$Ph), 5.00 (ABq, J = 16.0 Hz, 1 H, NCH$_A$$H_B$Ph), 6.42–6.46 [m, 1 H, C(7)H], 6.69–6.74 (m, 2 H, ArH), 6.93–6.98 (m, 2 H, ArH), 7.04–7.24 (m, 8 H, ArH), 7.35–7.40 (m, 1 H, ArH).

1-Benzyl-3-hydroxy-2-oxo-3-isopropyl-2,3-dihydroindole [(±)-39]

Following general procedure A, *N*-benzylisatin **12** (4.00 g, 16.9 mmol), THF (65 mL) and isopropylmagnesium chloride (9.28 mL, 18.6 mmol, 2.0 M in THF) gave, after trituration with Et_2O, (±)-**39**.

Yield: 1.77 g (37%); pale-yellow solid; mp 142–144 °C.

IR (KBr): 3366 (O–H), 3030 (C–H), 2966 (C–H), 1699 (C=O), 1616 (Ar C=C), 1466 (Ar C=C), 1181 (C–O), 754 cm^{-1} (Ar C–H).

^1H NMR (300 MHz, $CDCl_3$): δ = 0.80 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 1.13 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 2.32 [sept, J = 6.8 Hz, 1 H, CH(CH$_3$)$_2$], 2.70 (s, 1 H, OH), 4.74 (ABq, J = 15.6 Hz, 1 H, NCH_AH$_B$Ph), 5.03 (ABq, J = 15.6 Hz, 1 H, NCH$_A$$H_B$Ph), 6.71–6.76 [m, 1 H, C(7)H], 7.01–7.08 (m, 1 H, ArH), 7.18–7.25 (m, 1 H, ArH), 7.25–7.33 (m, 5 H, ArH), 7.37–7.41 (m, 1 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.0, 16.5, 36.2, 43.9, 79.3, 109.3, 122.9, 124.8, 127.4, 127.7, 128.6, 128.8, 129.5, 135.6, 143.2, 178.7.

MS (EI$^+$): m/z (%) = 91.1 (100) $[CH_2Ph]^+$, 238.2 (28) $[M - CH(CH_3)_2]^+$, 281.2 (27) $[M]^+$, 282.3 (5) $[M + H]^+$.

HRMS (ESI$^+$): m/z $[M + NH_4]^+$ calcd for $C_{18}H_{23}N_2O_2$: 299.1754; found: 299.1759 (+1.8 ppm).

1,3-Dibenzyl-2-oxo-2,3-dihydroindole [(±)-40]

Following general procedure B, (±)-**38** (2.00 g, 6.07 mmol), AcOH (58 mL), concd HCl (3.7 mL) and $SnCl_2·2H_2O$ (4.10 g, 18.2 mmol) gave, after chromatographic purification (PE–Et_2O, 90:10), (±)-**40** with spectroscopic data in accordance with the literature.[32]

Yield: 1.00 g (53%); pale-yellow solid; mp 93–95 °C (Lit.[32] 98–99 °C).

^1H NMR (300 MHz, $CDCl_3$): δ = 3.14 [dd (ABX), J = 8.1 Hz, $J_{A–B}$ = 13.6 Hz, 1 H, CH_AH$_B$Ph], 3.51 (dABq, J = 4.4 Hz, $J_{A–B}$ = 13.6 Hz, 1 H, CH$_A$$H_B$Ph), 3.85 [dd, J = 4.4, 8.1 Hz, 1 H, C(3)H], 4.64 [dd (ABX), J = 15.8 Hz, 1 H, NCH_AH$_B$Ph], 5.04 (ABq, J = 15.8 Hz, 1 H, NCH$_A$$H_B$Ph), 6.55 [d, J = 7.8 Hz, 1 H, C(7)H], 6.90–7.00 (m, 4 H, ArH), 7.06–7.17 (m, 3 H, ArH), 7.19–7.24 (m, 6 H, ArH).

1-Benzyl-2-oxo-3-isopropyl-2,3-dihydroindole [(±)-41]

Following general procedure B, crude (±)-**39** (3.56 g, 12.7 mmol), AcOH (120 mL), concd HCl (8 mL) and $SnCl_2·2H_2O$ (8.57 g, 38.0 mmol) gave, after chromatographic purification (PE–Et_2O, 90:10), (±)-**41** with spectroscopic data in accordance with the literature.[33]

Yield: 1.55 g (46% over two steps); crimson oil.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.93 [d, J = 7.0 Hz, 3 H, CH(CH_3)$_2$], 1.12 [d, J = 7.0 Hz, 3 H, CH(CH_3)$_2$], 2.51–2.63 [m, 1 H, CH(CH$_3$)$_2$], 3.47 [d, J = 3.5 Hz, 1 H, C(3)H], 4.79 (ABq, J = 15.6 Hz, 1 H, NCH_AH$_B$Ph), 5.03 (ABq, J = 15.6 Hz, 1 H, NCH$_A$$H_B$Ph), 6.68–6.73 [m, 1 H, C(7)H], 6.97–7.03 (m, 1 H, ArH), 7.12–7.20 (m, 1 H, ArH), 7.21–7.32 (m, 6 H, ArH).

1,3-Dibenzylindol-2-yl Phenyl Carbonate (42)

Following general procedure C, KHMDS (6.50 mL, 3.25 mmol), oxindole (±)-**40** (0.850 g, 2.71 mmol), THF (8 mL), phenyl chloroformate (0.410 mL, 3.26 mmol) and THF (5 mL) gave, after recrystallisation (Et_2O–hexane), carbonate **42**.

Yield: 0.680 g (58%); colourless solid; mp 97–99 °C.

IR (KBr): 3062 (C–H), 3029 (C–H), 2933 (C–H), 1778 (C=O), 1623 (Ar C=C), 1495 (Ar C=C), 1225 (C–O), 1198 (C–O), 742 cm^{-1} (Ar C–H).

^1H NMR (300 MHz, $CDCl_3$): δ = 4.03 (s, 2 H, CCH_2Ph), 5.21 (s, 2 H, NCH_2Ph), 6.85–6.92 (m, 2 H, ArH), 6.96–7.04 (m, 1 H, ArH), 7.05–7.30 (m, 15 H, ArH), 7.32–7.38 (m, 1 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.8, 46.5, 101.2, 110.0, 120.0, 120.5, 121.0, 122.5, 124.8, 126.5, 127.0, 127.1, 128.1, 128.8, 129.1, 129.3, 130.0, 132.9, 137.3, 139.7, 140.5, 150.9, 151.1.

MS (CI): m/z (%) = 314.2 (100) $[M + H – CO_2Ph]^+$, 434.2 (34) $[M + H]^+$.

HRMS (ESI$^+$): m/z $[M + H]^+$ calcd for $C_{29}H_{24}NO_3$: 434.1751; found: 434.1751 (+0.1 ppm).

1-Benzyl-3-isopropylindol-2-yl Phenyl Carbonate (43)

Following general procedure C, KHMDS (14.0 mL, 7.00 mmol), (±)-**41** (1.55 g, 5.84 mmol), THF (14.5 mL), phenyl chloroformate (0.880 mL, 7.00 mmol) and THF (9 mL) gave, after recrystallisation (Et_2O–hexane), carbonate **43**.

Yield: 1.26 g (56%); colourless solid; mp 86–89 °C.

IR (KBr): 3064 (C–H), 2961 (C–H), 2926 (C–H), 1792 (C=O), 1622 (Ar C=C), 1466 (Ar C=C), 1225 (C–O), 1194 (C–O), 740 cm^{-1} (Ar C–H).

^1H NMR (400 MHz, $CDCl_3$): δ = 1.45 [d, J = 7.1 Hz, 6 H, CH(CH_3)$_2$], 3.21 [sept, J = 7.1 Hz, 1 H, CH(CH$_3$)$_2$], 5.25 (s, 2 H, NCH_2Ph), 7.04–7.25 (m, 8 H, ArH), 7.27–7.41 (m, 5 H, ArH), 7.69–7.73 (m, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.4, 25.1, 46.0, 107.8, 109.8, 119.7, 120.2, 120.6, 121.9, 125.0, 126.6, 126.8, 127.6, 128.9, 129.7, 132.7, 137.1, 137.6, 150.9, 151.08.

MS (ESI$^+$): m/z (%) = 408.2 (100) $[M + Na]^+$.

HRMS (ESI$^+$): m/z $[M + Na]^+$ calcd for $C_{25}H_{23}NNaO_3$: 408.1576; found: 408.1579 (+0.9 ppm).

Phenyl 1,3-Dibenzyl-2-oxo-2,3-dihydroindole-3-carboxylate [(±)-44]

Following general procedure E, KHMDS (0.0210 mL, 0.0107 mmol, 1.5 mol%), triazolium salt **23** (0.00390 g, 0.0143 mmol, 2 mol%), THF (0.55 mL) and carbonate **42** (0.310 g, 0.715 mmol) gave, after 1 h and chromatographic purification (PE–Et_2O, 90:10), (±)-**44**.

Yield: 0.228 g (74%); colourless solid; mp 104–105 °C.

IR (KBr): 3060 (C–H), 3033 (C–H), 2933 (C–H), 1759 (C=O), 1721 (C=O), 1613 (Ar C=C), 1491 (Ar C=C), 1193 (C–O), 742 cm^{-1} (Ar C–H).

^1H NMR (400 MHz, $CDCl_3$): δ = 3.72 (ABq, *J* = 13.4 Hz, 1 H, C$H_A$$H_B$Ph), 3.78 (ABq, *J* = 13.4 Hz, 1 H, CH$_A$$H_B$Ph), 4.63 (ABq, *J* = 16.1 Hz, 1 H, NC$H_A$$H_B$Ph), 4.95 (ABq, *J* = 16.1 Hz, 1 H, NCH$_A$$H_B$Ph), 6.42–6.46 [m, 1 H, C(7)*H*], 6.67–6.72 (m, 2 H, Ar*H*), 6.94–7.25 (m, 13 H, Ar*H*), 7.32–7.38 (m, 2 H, Ar*H*), 7.49–7.53 (m, 1 H, Ar*H*).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 39.2, 43.8, 61.1, 109.9, 121.3, 122.8, 123.8, 126.2, 126.6, 127.0 (× 2), 127.3, 128.1, 128.7, 129.4 (× 2), 130.4, 134.3, 134.8, 143.6, 150.5, 168.1, 173.1.

MS (CI): *m*/*z* (%) = 314.2 (68) [M + H – CO_2Ph]$^+$, 434.2 (100) [M + H]$^+$, 451.2 (50) [M + NH_4]$^+$.

HRMS (ESI$^+$): *m*/*z* [M + NH_4]$^+$ calcd for $C_{29}H_{27}N_2O_3$: 451.2016; found: 451.2008 (–1.7 ppm).

Phenyl 1-Benzyl-2-oxo-3-isopropyl-2,3-dihydroindole-3-carboxylate [(±)-45]

Following general procedure E, KHMDS (0.046 mL, 0.023 mmol, 4 mol%), triazolium salt **23** (0.0079 g, 0.029 mmol, 5 mol%), THF (1.11 mL) and carbonate **43** (0.222 g, 0.576 mmol) gave, after 1 h and chromatographic purification (PE–Et_2O, 90:10), an inseparable 84:16 mixture of (±)-**45**:(±)-**41** (estimated by ^1H NMR) as a colourless solid (0.172 g).

^1H NMR (400 MHz, $CDCl_3$): δ = 0.93 [d, *J* = 6.8 Hz, 3 H, CH(CH_3)$_2$], 1.27 [d, *J* = 6.8 Hz, 3 H, CH(CH_3)$_2$], 2.96 [sept, *J* = 6.8 Hz, 1 H, C*H*(CH$_3$)$_2$], 4.93 (ABq, *J* = 15.7 Hz, 1 H, NC$H_A$$H_B$Ph), 5.04 (ABq, *J* = 15.7 Hz, 1 H, NCH$_A$$H_B$Ph), 6.74–6.77 [m, 1 H, C(7)*H*], 7.00–7.04 (m, 2 H, Ar*H*), 7.06–7.11 (m, 1 H, Ar*H*), 7.20–7.37 (m, 9 H, Ar*H*), 7.42–7.45 (m, 1 H, Ar*H*).

1-Benzyl-3-(hydroxymethyl)-2-oxo-3-isopropyl-2,3-dihydroindole [(±)-46]

$NaBH_4$ (0.0400 g, 1.06 mmol) was added to a suspension of a 84:16 mixture of (±)-**45**:(±)-**41** (0.121 g) and $CaCl_2$ (0.0590 g, 0.530 mmol) in anhydrous MeOH (1 mL), cooled to 0 °C and stirred at this temperature for 2 h. The reaction was then allowed to warm to r.t. and stirred overnight before concentration in vacuo. 3 N citric acid was added dropwise until pH 2–3 before extracting with CH_2Cl_2 (3 × 20 mL). The organic extracts were combined, dried (Na_2SO_4) and concentrated in vacuo to give, after chromatography (PE–Et_2O, 90:10), (±)-**46** as a colourless solid (0.0200 g, 24%) and (±)-**47** (0.0600 g, 67%) as a colourless gum. Unreacted (±)-**41** was also recovered from the reaction mixture (0.0104 g, 75%).

Mp 137–140 °C.

IR (KBr): 3424 (O–H), 2964 (C–H), 1695 (C=O), 1611 (Ar C=C), 1466 (Ar C=C), 1177 (C–O), 697 cm^{-1} (Ar C–H).

^1H NMR (300 MHz, $CDCl_3$): δ = 0.72 [d, *J* = 6.9 Hz, 3 H, CH(CH_3)$_2$], 1.11 [d, *J* = 6.9 Hz, 3 H, CH(CH_3)$_2$], 2.32–2.42 (m, 1 H, O*H*), 2.54 [sept, *J* = 6.9 Hz, 1 H, C*H*(CH$_3$)$_2$], 3.79–3.88 (m, 1 H, CH_2OH), 4.02–4.14 (m, 1 H, CH_2OH), 4.91 (ABq, *J* = 15.7 Hz, 1 H, NC$H_A$$H_B$Ph), 4.97 (ABq, *J* = 15.7 Hz, 1 H, NCH$_A$$H_B$Ph), 6.72–6.78 [m, 1 H, C(7)*H*], 7.00–7.08 (m, 1 H, Ar*H*), 7.15–7.34 (m, 7 H, Ar*H*).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.3, 17.5, 31.2, 43.7, 57.6, 65.5, 109.2, 122.5, 123.9, 127.3, 127.6, 128.3, 128.7, 128.8, 135.8, 143.8, 180.0.

MS (ESI$^+$): *m*/*z* (%) = 318.2 (100) [M + Na]$^+$.

HRMS (ESI$^+$): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{21}NO_2Na$: 318.1470; found: 318.1465 (–1.5 ppm).

Methyl 1-Benzyl-2-oxo-3-isopropyl-2,3-dihydroindole-3-carboxylate [(±)-47]

IR (thin film): 2964 (C–H), 1745 (C=O), 1715 (C=O), 1610 (Ar C=C), 1466 (Ar C=C), 1259 (C–O), 750 cm^{-1} (Ar C–H).

^1H NMR (300 MHz, $CDCl_3$): δ = 0.85 [d, *J* = 6.9 Hz, 3 H, CH(CH_3)$_2$], 1.16 [d, *J* = 6.9 Hz, 3 H, CH(CH_3)$_2$], 2.86 [sept, *J* = 6.9 Hz, 1 H, C*H*(CH$_3$)$_2$], 3.74 (s, 3 H, OCH_3), 4.93 (ABq, *J* = 15.7 Hz, 1 H, NC$H_A$$H_B$Ph), 4.98 (ABq, *J* = 15.7 Hz, 1 H, NCH$_A$$H_B$Ph), 6.71–6.75 [m, 1 H, C(7)*H*], 7.02–7.09 (m, 1 H, Ar*H*), 7.17–7.25 (m, 1 H, Ar*H*), 7.25–7.37 (m, 6 H, Ar*H*).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.2, 17.3, 34.8, 43.8, 52.9, 63.2, 109.1, 122.7, 124.1, 127.3, 127.60, 127.63, 128.7, 128.8, 135.7, 143.2, 169.8, 173.4.

MS (ESI$^+$): *m*/*z* (%) = 346.2 (100) [M + Na]$^+$.

HRMS (ESI$^+$): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{21}NO_3Na$: 346.1419; found: 346.1412 (–2.1 ppm).

2-(2-Methoxyphenyl)-3-phenylpropiononitrile [(±)-49]

2-Methoxyphenyl acetonitrile (**48**; 2.00 g, 13.6 mmol) was added in a single portion to a stirred slurry of NaH (0.626 g, 15.6 mmol, 60% wt in mineral oil) in DMF (3 mL) and stirred at r.t. for 1 h. The solution was then cooled to 0 °C, benzyl bromide (1.62 mL, 13.6 mmol) was added, and the mixture warmed slowly to r.t. overnight. The solution was quenched with sat. aq NH_4Cl (50 mL), H_2O (50 mL) was added and the mixture was extracted with Et_2O (3 × 50 mL). The organic extracts were combined, dried ($MgSO_4$) and concentrated in vacuo to give nitrile (±)-**49**, which was used without further purification.

Yield: 2.99 g (93%); yellow oil.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.04–3.10 (m, 2 H, CH_2Ph), 3.85 (s, 3 H, OCH_3), 4.39–4.45 (m, 1 H, C*H*CN), 6.88–7.40 (m, 9 H, Ar*H*).

2-(2-Methoxyphenyl)-3-methylbutyronitrile [(±)-50]

2-Methoxyphenyl acetonitrile (**48**; 2.00 g, 13.6 mmol) was added in a single portion to a stirred slurry of NaH (0.626 g, 15.6 mmol, 60% wt in mineral oil) in DMF (3 mL) and stirred at r.t. for 1 h. The solution was then cooled to 0 °C, 2-iodopropane (1.36 mL, 13.6 mmol) was added, and the mixture was warmed slowly to r.t. overnight. The solution was quenched with sat. aq NH_4Cl (50 mL), H_2O (50 mL) was added and the mixture was extracted with Et_2O (3 × 50 mL). The organic extracts were combined, dried ($MgSO_4$) and concentrated in vacuo to give nitrile (±)-**50**, which was used without further purification.

Yield: 2.30 g (96%); pale-yellow oil.

IR (thin film): 2970 (C–H), 1750 (C≡N), 1620 cm^{-1} (C=C).

^1H NMR (400 MHz, $CDCl_3$): δ = 0.99 [m, 6 H, (CH_3)$_2$], 2.08 [m, 1 H, C*H*(CH$_3$)$_2$], 3.73 (s, 3 H, OCH_3), 4.03 (d, *J* = 6.4 Hz, 1 H, C*H*CN), 6.78–6.97 (m, 2 H, Ar*H*), 7.16–7.30 (m, 2 H, Ar*H*).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.8, 20.9, 29.7, 39.0, 55.5, 110.7, 120.3, 120.7, 123.6, 129.2, 129.3, 156.2.

MS (ESI+): *m*/*z* (%) = 212.1 (100) [M + Na]$^+$.

HRMS (ESI+): *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{15}NONa$: 212.1051; found: 212.1047 (+1.9 ppm).

3-Benzyl-2-oxo-2,3-dihydrobenzofuran [(±)-51]

Nitrile (±)-**49** (4.60 g, 20.5 mmol) was poured onto aq HBr (48%, 100 mL) and heated to reflux for 5 d. The reaction was then cooled 0 °C, and excess acid was neutralised by slow addition of 3 M aq NaOH, then extracted with Et_2O (3 × 75 mL). The organic layers were combined, dried ($MgSO_4$) and concentrated in vacuo to give, after chromatographic purification (PE–Et_2O, 90:10), benzofura-

none (±)-**51** with spectroscopic data in accordance with the literature.[34]

Yield: 2.09 g (45%); pale-orange oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.95 (dd, *J* = 13.7, 9.0 Hz, 1 H, C*H*$_A$H$_B$Ph), 3.43 (dd, *J* = 13.7, 4.8 Hz, 1 H, CH$_A$*H*$_B$Ph), 3.93 (dd, *J* = 9.0, 4.8 Hz, 1 H, C*H*CH$_2$Ph), 6.66–7.43 (m, 9 H, Ar*H*).

2-Oxo-3-isopropyl-2,3-dihydrobenzofuran [(±)-52]

Nitrile (±)-**50** (17.4 g, 91.9 mmol) was poured onto aq HBr (48%, 500 mL) and heated to reflux for 5 d. The reaction was then cooled 0 °C, and excess acid was neutralised by slow addition of 10 M aq NaOH, then extracted with Et_2O (3 × 250 mL). The organic layers were combined, dried ($MgSO_4$) and concentrated in vacuo to give, after chromatographic purification (PE–Et_2O, 90:10), benzofuranone (±)-**52**.

Yield: 9.86 g (61%); pale-yellow oil.

IR (thin film): 3010 (C–H), 1820 cm^{-1} (C=O).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.9 Hz, 3 H, C*H*$_3$), 1.01 (t, *J* = 6.9 Hz, 3 H, C*H*$_3$), 2.41 [sept, *J* = 6.9, 3.6 Hz, 1 H, C*H*(CH$_3$)$_2$], 3.56 [d, *J* = 3.9 Hz, 1 H, C(3)*H*], 7.00–7.10 (m, 2 H, Ar*H*), 7.18–7.27 (m, 2 H, Ar*H*).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.5, 19.4, 31.4, 49.7, 110.6, 123.9, 124.6, 126.1, 128.8, 154.1, 176.5.

MS (ESI+): *m*/*z* (%) = 199.1 (100) [M + Na]$^+$.

HRMS (ESI+): *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{12}O_2Na$: 199.0735; found: 199.0732 (–1.8 ppm).

3-Benzylbenzofuran-2-yl Phenyl Carbonate (53)

Following general procedure D, benzofuranone (±)-**51** (2.00 g, 8.92 mmol), THF (50 mL), Et_3N (1.87 mL, 13.0 mmol) and phenyl chloroformate (1.68 mL, 13.0 mmol) gave, after chromatographic purification (hexane–Et_2O, 95:5), carbonate **53** with spectroscopic data in accordance with the literature.[22c]

Yield: 2.01 g (65%); off-white solid; mp 78–80 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.02 (s, 2 H, C*H*$_2$Ph), 7.17 (td, *J* = 7.5, 1.0 Hz, 1 H, Ar*H*), 7.20–7.33 (m, 10 H, Ar*H*), 7.39–7.45 (m, 3 H, Ar*H*).

3-Benzylbenzofuran-2-yl Methyl Carbonate (54)

Following general procedure D, benzofuranone (±)-**51** (4.00 g, 17.8 mmol), THF (100 mL), Et_3N (3.73 mL, 27.0 mmol) and methyl chloroformate (2.07 mL, 27.0 mmol) gave, after chromatographic purification (PE–Et_2O, 90:10), carbonate **54**.

Yield: 4.32 g (86%); yellow oil.

IR (thin film): 1704 (C=O), 1444 (C=C), 1250 (C–O), 749 cm^{-1} (Ar C–H).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.00 (s, 3 H, OC*H*$_3$), 4.10 (s, 2 H, C*H*$_2$Ph), 7.25–7.44 (m, 8 H, Ar*H*), 7.52–7.56 (m, 1 H, Ar*H*).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.5, 56.4, 101.8, 111.2, 120.1, 123.1, 124.2, 126.5, 128.5, 128.57, 128.64, 138.4, 149.8, 150.0, 152.4.

MS (ESI+): *m*/*z* (%) = 305.0 (100) [M + Na]$^+$.

HRMS (ESI+): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{14}O_4Na$: 305.0790; found: 305.0796 (+2.1 ppm).

Phenyl 3-Isopropylbenzofuran-2-yl Carbonate (55)

Following general procedure D, benzofuranone (±)-**52** (4.00 g, 22.7 mmol), THF (40 mL), Et_3N (4.75 mL, 34.0 mmol) and phenyl chloroformate (4.28 mL, 34.0 mmol) gave, after chromatographic purification (hexane–Et_2O, 95:5), carbonate **55**.

Yield: 4.10 g (61%); pale-yellow oil.

IR (thin film): 2968 (C–H), 1797 (C=O), 1653 (C=C), 1225 (C–O), 746 cm^{-1} (Ar C–H).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 [d, *J* = 6.9 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.23 [d, *J* = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$], 2.93 [sept, *J* = 6.8 Hz, 1 H, C*H*(CH$_3$)$_2$], 7.01–7.05 (m, 2 H, Ar*H*), 7.18 (d, *J* = 8.1 Hz, 1 H, Ar*H*), 7.21–7.27 (m, 2 H, Ar*H*), 7.33–7.43 (m, 3 H, Ar*H*), 7.47 (dd, *J* = 1.0 Hz, 1 H, Ar*H*).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.7, 24.3, 108.7, 111.4, 120.5, 120.7, 122.9, 124.1, 126.8, 128.0, 129.8, 147.8, 149.8, 150.6, 150.9.

MS (ESI+): *m*/*z* (%) = 319.1 (100) [M + Na]$^+$.

HRMS (ESI+): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{16}O_4Na$: 319.0946; found: 319.0942 (–1.3 ppm).

Methyl 3-Isopropylbenzofuran-2-yl Carbonate (56)

Following general procedure D, benzofuranone (±)-**52** (3.17 g, 18.0 mmol), THF (40 mL), Et_3N (3.73 mL, 27.0 mmol) and methyl chloroformate (2.07 mL, 27.0 mmol) gave, after chromatographic purification (PE–Et_2O, 95:5), carbonate **56**.

Yield: 3.96 g (94%); colourless oil.

IR (thin film): 2965 (C–H), 1650 (C=C), 1247 cm^{-1} (C–O).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29 [d, *J* = 7.2 Hz, 6 H, CH(C*H*$_3$)$_2$], 2.98 [sept, *J* = 7.2 Hz, 1 H, C*H*(CH$_3$)$_2$], 3.88 (s, 3 H, OC*H*$_3$), 7.03–7.13 (m, 2 H, Ar*H*), 7.30–7.32 (m, 1 H, Ar*H*), 7.49–7.51 (m, 1 H, Ar*H*).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 24.1, 56.4, 108.2, 111.2, 120.3, 122.7, 123.8, 127.9, 148.0, 149.7, 152.6.

MS (CI+): *m*/*z* (%) = 234.1 (75) [M]$^+$, 235.1 (40) [M + H]$^+$.

HRMS (CI+): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{15}O_4$: 235.0970; found: 235.0968 (–1.0 ppm).

Phenyl 3-Benzyl-2-oxo-2,3-dihydrobenzofuran-3-carboxylate [(±)-57]

Following general procedure E, KHMDS (0.0520 mL, 0.0260 mmol, 1.8 mol%), triazolium salt **23** (0.00800 g, 0.0290 mmol, 2 mol%), THF (5 mL) and carbonate **53** (0.500 g, 1.45 mmol) gave, after 1 h and chromatographic purification (PE–Et_2O, 90:10), (±)-**57** with spectroscopic data in accordance with the literature.[22c]

Yield: 0.440 g (88%); colourless solid; mp 106–108 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.63 (s, 2 H, C*H*$_2$Ph), 6.85–7.40 (m, 14 H, Ar*H*).

Methyl 3-Benzyl-2-oxo-2,3-dihydrobenzofuran-3-carboxylate [(±)-58]

Following general procedure E, KHMDS (0.12 mL, 0.060 mmol, 9 mol%), triazolium salt **23** (0.019 g, 0.070 mmol, 10 mol%), THF (5 mL) and carbonate **54** (0.20 g, 0.71 mmol) gave, after 1 h and chromatographic purification (PE–Et_2O, 90:10), (±)-**58**.

Yield: 0.16 g (80%); pale-yellow oil.

IR (thin film): 2965 (C–H), 1762 (C=O), 1630 cm^{-1} (Ar C=C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.58 (ABq, *J* = 13.6 Hz, 1 H, C*H*$_A$H$_B$Ph), 3.62 (ABq, *J* = 13.6 Hz, 1 H, CH$_A$*H*$_B$Ph), 3.76 (s, 3 H, OC*H*$_3$), 6.87–6.93 (m, 3 H, Ar*H*), 7.06–7.14 (m, 3 H, Ar*H*), 7.18 (td, *J* = 7.6, 1.0 Hz, 1 H, Ar*H*), 7.25–7.30 (m, 1 H, Ar*H*), 7.35–7.38 (m, 1 H, Ar*H*).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 40.4, 53.6, 60.0, 110.9, 124.3, 124.4, 125.8, 127.4, 128.2, 130.0, 130.1, 133.4, 153.4, 168.2, 172.8.

MS (ESI+): *m*/*z* (%) = 305.1 (100) [M + Na]$^+$.

HRMS (ESI+): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{14}O_4Na$: 305.0790; found: 305.0787 (–1.0 ppm).

Phenyl 3-Isopropyl-2-oxo-2,3-dihydrobenzofuran-3-carboxylate [(±)-59]

Following general procedure E, KHMDS (0.14 mL, 0.068 mmol, 4 mol%), triazolium salt **23** (0.023 g, 0.084 mmol, 5 mol%), THF (5 mL) and carbonate **55** (0.50 g, 1.7 mmol) gave, after 1 h and chromatographic purification (PE–Et_2O, 90:10), (±)-**59**.

Yield: 0.41 g (82%); colourless oil.

IR (thin film): 2970 (C–H), 1813 (C=O), 1756 (C=O), 1190 (C–O), 754 cm^{-1} (Ar C–H).

^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 [d, *J* = 7.0 Hz, 3 H, $CH(CH_3)_2$], 1.13 [d, *J* = 7.0 Hz, 3 H, $CH(CH_3)_2$], 2.83 [sept, *J* = 7.0 Hz, 1 H, $CH(CH_3)_2$], 6.96–7.40 (m, 9 H, Ar*H*).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.3, 17.4, 35.7, 62.8, 111.0, 121.2, 124.6, 124.8, 126.0, 126.5, 129.6, 130.2, 150.4, 153.7, 166.4, 171.7.

MS (ESI): *m*/*z* (%) = 391.1 (100) $[M + Na]^+$.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{18}H_{16}O_4Na$: 319.0946; found: 319.0943 (–1.0 ppm).

Methyl 3-Isopropyl-2-oxo-2,3-dihydrobenzofuran-3-carboxylate [(±)-60]

Following general procedure E, KHMDS (0.384 mL, 0.192 mmol, 9 mol%), triazolium salt **23** (0.058 g, 0.213 mmol, 10 mol%), THF (5 mL) and carbonate **56** (0.500 g, 2.13 mmol) gave, after 1 h and chromatographic purification (PE–Et_2O, 90:10), (±)-**60**.

Yield: 0.323 g (65%); colourless oil.

IR (thin film): 2969 (C–H), 1811 (C=O), 1748 (C=O), 1187 (C–O), 749 cm^{-1} (Ar C–H).

^1H NMR (400 MHz, $CDCl_3$): δ = 0.85 [d, *J* = 6.8 Hz, 3 H, $CH(CH_3)_2$], 1.10 [d, *J* = 6.8 Hz, 3 H, $CH(CH_3)_2$], 2.80 [sept, *J* = 6.8 Hz, 1 H, $CH(CH_3)_2$], 3.75 (s, 3 H, OCH_3), 7.10–7.14 (m, 1 H, Ar*H*), 7.16–7.21 (m, 1 H, Ar*H*), 7.33–7.38 (m, 2 H, Ar*H*).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.1, 17.3, 35.6, 53.3, 62.5, 110.7, 124.45, 124.47, 126.1, 129.8, 153.4, 168.2, 172.0.

MS (CI): *m*/*z* (%) = 175.1 (100) $[M - COOMe]^+$, 235.1 (13) $[M + H]^+$.

HRMS (CI): *m*/*z* $[M + H]^+$ calcd for $C_{13}H_{15}O_4$: 235.0970; found: 235.0972 (+0.7 ppm).

Acknowledgment

The authors would like to thank the Royal Society for a University Research Fellowship (A.D.S.) and a Summer Studentship (K.A.G.), the EPSRC (C.C. and C.J.), EaStCHEM and the University of St Andrews (J.E.T. and A.J.M.), and AstraZeneca (Research Support Grant) for funding (L.C.M.).

References

(1) For recent reviews, see: (a) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5606. (b) Marion, N.; Díez-González, S.; Nolan, S. P. *Angew. Chem. Int. Ed.* **2007**, *46*, 2988.

(2) Mattson, A. E.; Bharadwaj, A. R.; Zuhl, A. M.; Scheidt, K. A. *J. Org. Chem.* **2006**, *71*, 5715.

(3) (a) Teles, J. H.; Melder, J.-P.; Ebel, K.; Schneider, R.; Gehrer, E.; Harder, W.; Brode, S.; Enders, D.; Breuer, K.; Raabe, G. *Helv. Chim. Acta* **1996**, *79*, 61. (b) Enders, D.; Breuer, K.; Teles, J. H. *Helv. Chim. Acta* **1996**, *79*, 1217. (c) Enders, D.; Breuer, K.; Runsink, J.; Teles, J. H. *Helv. Chim. Acta* **1996**, *79*, 1899. (d) Enders, D.; Kallfass, U. *Angew. Chem. Int. Ed.* **2002**, *41*, 1743. (e) Kerr, M. S.; Read de Alaniz, J.; Rovis, T. *J. Am. Chem. Soc.* **2002**, *124*, 10298. (f) Chow, K. Y.-K.; Bode, J. W. *J. Am. Chem. Soc.* **2004**, *126*, 8126. (g) Reynolds, N. T.; Read de Alaniz, J.; Rovis, T. *J. Am. Chem. Soc.* **2004**, *126*, 9518. (h) Myers, M. C.; Bharadwaj, A. R.; Milgram, B. C.; Scheidt, K. A. *J. Am. Chem. Soc.* **2005**, *127*, 14675. (i) Suzuki, Y.; Toyota, T.; Imada, F.; Sato, M.; Miyashita, A. *Chem. Commun.* **2003**, 1314.

(4) For select examples, see: (a) Burstein, C.; Glorius, F. *Angew. Chem. Int. Ed.* **2004**, *43*, 6205. (b) Sohn, S. S.; Rosen, E. L.; Bode, J. W. *J. Am. Chem. Soc.* **2004**, *126*, 14370. (c) Chan, A.; Scheidt, K. A. *Org. Lett.* **2005**, *7*, 905.

(5) For the direct formation of enolates from ketenes, see: (a) Duguet, N.; Campbell, C. D.; Slawin, A. M. Z.; Smith, A. D. *Org. Biomol. Chem.* **2008**, *6*, 1108. (b) Zhang, Y.-R.; He, L.; Wu, X.; Shao, P.-L.; Ye, S. *Org. Lett.* **2008**, *10*, 277.

(6) Song, J. J.; Tan, Z.; Reeves, J. T.; Gallou, F.; Yee, N. K.; Senanayake, C. H. *Org. Lett.* **2005**, *7*, 2193.

(7) (a) Song, J. J.; Gallou, F.; Reeves, J. T.; Tan, Z.; Yee, N. K.; Senanayake, C. H. *J. Org. Chem.* **2006**, *71*, 1273. (b) Suzuki, Y.; Abu Bakar, M. D.; Muramatsu, K.; Sato, M. *Tetrahedron* **2006**, *62*, 4227. (c) Kano, T.; Sasaki, K.; Konishi, T.; Mii, H.; Maruoka, K. *Tetrahedron Lett.* **2006**, *47*, 4615.

(8) (a) Vora, H. U.; Rovis, T. *J. Am. Chem. Soc.* **2007**, *129*, 13796. (b) Bode, J. W.; Sohn, S. S. *J. Am. Chem. Soc.* **2007**, *129*, 13798.

(9) Chan, A.; Scheidt, K. A. *J. Am. Chem. Soc.* **2006**, *128*, 4558.

(10) (a) Zeitler, K. *Angew. Chem. Int. Ed.* **2005**, *44*, 7506. (b) Reynolds, N. T.; Rovis, T. *J. Am. Chem. Soc.* **2005**, *127*, 16406. (c) Sohn, S. S.; Bode, J. W. *Angew. Chem. Int. Ed.* **2006**, *45*, 6021.

(11) (a) Sun, X.; Ye, S.; Wu, J. *Eur. J. Org. Chem.* **2006**, 4787. (b) Wu, J.; Sun, X.; Ye, S.; Sun, W. *Tetrahedron Lett.* **2006**, *47*, 4813.

(12) (a) Fukada, Y.; Maeda, Y.; Kondo, K.; Aoyama, T. *Chem. Pharm. Bull.* **2006**, *54*, 397. (b) Song, J. J.; Tan, Z.; Reeves, J. T.; Yee, N. K.; Senanayake, C. H. *Org. Lett.* **2007**, *9*, 1013.

(13) For a review, see: Douglas, C. J.; Overman, L. E. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 5363.

(14) (a) Corey, E. J. *Angew. Chem. Int. Ed.* **2002**, *41*, 1650. (b) Maruoka, K. In *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed.; Wiley-VCH: New York, **2000**, 467–491. (c) Kozmin, S. A.; Iwama, T.; Huang, Y.; Rawal, V. H. *J. Am. Chem. Soc.* **2002**, *124*, 4628. (d) Ryu, D. H.; Corey, E. J. *J. Am. Chem. Soc.* **2003**, *125*, 6388. (e) Evans, D. A.; Wu, J. *J. Am. Chem. Soc.* **2003**, *125*, 10162.

(15) (a) O'Donnell, M. J. In *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed.; Wiley-VCH: New York, **2000**, 727–755. (b) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. (c) Hodous, B. L.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 1578. (d) d'Angelo, J.; Desmaële, D.; Dumas, F.; Guingant, A. *Tetrahedron: Asymmetry* **1992**, *3*, 459. (e) Trost, B. M.; Jiang, C. *J. Am. Chem. Soc.* **2001**, *123*, 12907. (f) Austin, J. F.; Kim, S.-G.; Sinz, C. J.; Xiao, W.-J.; MacMillan, D. W. C. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 5482. (g) Bella, M.; Kobbelgaard, S.; Jørgensen, K. A. *J. Am. Chem. Soc.* **2005**, *127*, 3670.

(16) (a) Dounay, A. B.; Overman, L. E. *Chem. Rev.* **2003**, *103*, 2945. (b) Donde, Y.; Overman, L. E. In *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed.; Wiley-VCH: New York, **2000**, 675–697. (c) Lebsack, A. D.; Link, J. T.; Overman, L. E.; Stearns, B. A. *J. Am. Chem. Soc.* **2002**, *124*, 9008.

(17) (a) Lachia, M.; Poriel, C.; Slawin, A. M. Z.; Moody, C. J. *Chem. Commun.* **2007**, 286. (b) Menozzi, C.; Dalko, P. I.; Cossy, J. *Heterocycles* **2007**, *72*, 199. (c) Kawasaki, T.; Shinada, M.; Kamimura, D.; Ohzono, M.; Ogawa, A. *Chem. Commun.* **2006**, 420.
(18) (a) Eder, U.; Sauer, G.; Wiechert, R. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 496. (b) Hajos, Z. G.; Parrish, D. R. *J. Org. Chem.* **1974**, *39*, 1615. (c) Davies, S. G.; Sheppard, R. L.; Smith, A. D.; Thomson, J. E. *Chem. Commun.* **2005**, 3802. (d) Ohshima, T.; Kagechika, K.; Adachi, M.; Sodeoka, M.; Shibasaki, M. *J. Am. Chem. Soc.* **1996**, *118*, 7108. (e) Wu, M. H.; Hansen, K. B.; Jacobsen, E. N. *Angew. Chem. Int. Ed.* **1999**, *38*, 2012.
(19) Steglich, W.; Höfle, G. *Tetrahedron Lett.* **1970**, *11*, 4727.
(20) Thomson, J. E.; Rix, K.; Smith, A. D. *Org. Lett.* **2006**, *8*, 3785.
(21) Thomson, J. E.; Campbell, C. D.; Concellón, C.; Duguet, N.; Rix, K.; Slawin, A. M. Z.; Smith, A. D. *J. Org. Chem.* **2008**, *73*, 2784.
(22) For asymmetric versions of this reaction, see: (a) Ruble, J. C.; Fu, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 11532. (b) Shaw, S. A.; Aleman, P.; Vedejs, E. *J. Am. Chem. Soc.* **2003**, *125*, 13368. (c) Shaw, S. A.; Aleman, P.; Christy, J.; Kampf, J. W.; Va, P.; Vedejs, E. *J. Am. Chem. Soc.* **2006**, *128*, 925. (d) Nguyen, H. Y.; Butler, D. C. D.; Richards, C. J. *Org. Lett.* **2006**, *8*, 769. (e) Seitzberg, J. G.; Dissing, C.; Søtofte, I.; Norrby, P.-O.; Johannsen, M. *J. Org. Chem.* **2005**, *70*, 8332. (f) For the application of this methodology to the preparation of oxindole and benzofuran derivatives, see: Hills, I. D.; Fu, G. C. *Angew. Chem. Int. Ed.* **2003**, *42*, 3921.
(23) For the seminal work of Black upon the rearrangement of benzofuranyl carbonates with DMAP, see: (a) Black, T. H.; Arrivo, S. M.; Schumm, J. S.; Knobeloch, J. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1524. (b) Black, T. H.; Arrivo, S. M.; Schumm, J. S.; Knobeloch, J. M. *J. Org. Chem.* **1987**, *52*, 5425. (c) Moody, C. J.; Doyle, K. J.; Elliott, M. C.; Mowlem, T. J. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2413.
(24) Wiemer et al. have demonstrated extensively the base-catalysed rearrangement of vinyl phosphates to the corresponding β-keto phosphonates; a process driven under thermodynamic control by the formation of a stabilised anion. For an example, see: Calogeropoulou, T.; Hammond, G. B.; Wiemer, D. F. *J. Org. Chem.* **1987**, *52*, 4185.
(25) Connolly, T. J.; Durst, T. *Can. J. Chem.* **1997**, *75*, 542.
(26) Takigawa, Y.; Ito, H.; Omodera, K.; Ito, M.; Taguchi, T. *Tetrahedron* **2004**, *60*, 1385.
(27) Shaughnessy, K. H.; Hamann, B. C.; Hartwig, J. F. *J. Org. Chem.* **1998**, *63*, 6546.
(28) Trost, B. M.; Frederiksen, M. U. *Angew. Chem. Int. Ed.* **2005**, *44*, 308.
(29) Nishio, T. J. *Chem. Soc., Perkin Trans. 1* **1991**, 1717.
(30) Speeter, M. E. U.S. Patent 2759935, **1956**; *Chem. Abstr.* **1956**, *51*, 9613.
(31) Kafka, S.; Klásek, A.; Košmrlj, J. *J. Org. Chem.* **2001**, *66*, 6394.
(32) Balasubramanian, K. K.; Dhathathreyon, K. S.; Munusamy, R.; Venkatachalam, C. S. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1154.
(33) Huang, A.; Kodanko, J. J.; Overman, L. E. *J. Am. Chem. Soc.* **2004**, *126*, 14043.
(34) Yoneda, E.; Sugioka, T.; Hirao, K.; Zhang, S.-W.; Takahashi, S. *J. Chem. Soc., Perkin Trans. 1* **1998**, 477.