SHORT COMMUNICATION

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Phosphane- and Amine-Catalyzed Ring-Opening Reactions of Cyclopropenones with Isatin Derivatives: Synthesis of Carboxylated 1*H*-Indoles and Multisubstituted 2*H*-Pyran-2-ones

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Keywords: Small ring systems / Organocatalysis / Ring opening reactions / Phosphanes / Amines

The phosphane- and amine-catalyzed ring-opening reactions of cyclopropenones with isatin derivatives give different reaction outcomes. Under phosphane catalysis, carboxylated 1*H*-indoles are afforded in good yields, and under amine catalysis, multisubstituted 2*H*-pyran-2-ones are provided in moderate yields. The mechanistic aspects of these reactions are discussed on the basis of control experiments.

Introduction

In 1959, the chemistry of cyclopropenone started as first reported independently by Breslow and Volpin.[1] Since then, cyclopropenones have drawn great attention from organic chemists as a result of their unique structure and reactivity.[2] According to the Hückel rule, cyclopropenones have a resonance form (aromatic cation) in which a negative charge lies on the oxygen atom, and the aromatic nature of the species makes the oxygen atom even more nucleophilic than other ordinary carbonyl compounds (Figure 1). Consequently, cyclopropenones are widely used as trapping agents for electrophiles;[3] moreover, they have also emerged as a powerful means to activate alcohols, aldoximes, and primary amides by acting as organocatalysts.[4] As α,β-unsaturated ketones, cyclopropenones are also treated as electrophiles in 1,2- and 1,4-nucleophilic addition reactions.[5] Moreover, the strain on cyclopropenones allows them to easily take part in cycloaddition reactions owing to their high activity.[6] Similar to other strained small ring molecules such as cyclopropenes, large ring strain[7] is another factor attributing to the high reactivity of cyclopropenones, and their transformations such as ring opening[8] and ring enlargement[9] are frequently found in the literature. However, though intensively investigated, the reaction of cyclopropenones catalyzed by organocatalysts is quite challenging, and only very few examples have been reported.[10] The difficulty of such reactions relies on the high reactivity of cyclopropenones, which causes either dimerization or further undesired transformations with other reagents during the process of the reaction.

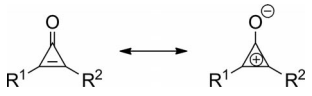

Figure 1. Aromatic stabilization of cyclopropenes.

In the context of our ongoing efforts to investigate the organocatalysis of diverse transformations of electron-deficient alkenes such as the Morita–Baylis–Hillman reaction[11] and other related reactions,[12] we attempted to find a new representative instead of acrylate derivatives, ketenes, or allenic esters. We envisaged that cyclopropenones would be a good alternative in such transformations. Herein, we wish to report the phosphane- and amine-catalyzed ring-opening reactions of cyclopropenones with isatin derivatives, which provides a facile synthetic method to construct carboxylated 1*H*-indoles and multisubstituted 2*H*-pyran-2-ones under mild conditions.

Results and Discussion

We started our investigation by optimizing the PPh_3-catalyzed nucleophilic addition of isatin derivative **2a** (Boc = *tert*-butoxycarbonyl) to cyclopropenone **1a**, and the results are shown in Table 1. Upon adding a solution of cyclopropenone **1a** (2 equiv.) to a mixture of **2a** and PPh_3 (20 mol-%) by using a syringe pump, all reactions proceeded smoothly in THF, CH_2Cl_2, MeCN, and toluene at 25 °C to deliver carboxylated 1*H*-indole **3a** in 82–93% yield

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(Table 1, entries 1–4). MeCN proved to be the best solvent in this reaction, as it gave corresponding product **3a** in 93% yield (Table 1, entry 3). The structure of analogue **3c** was unambiguously determined by X-ray diffraction (Figure 2).[13] Next, we studied the ratio of **1a**/**2a** by varying the loading of **1a**. Increasing the ratio of **1a**/**2a** to 2.5 or decreasing it to 1.5 or 1.0 impaired the production of **3a** dramatically (Table 1, entries 5–7). The optimal ratio was 2:1. Examination of the temperature revealed that **3a** was obtained in slightly lower yield at both 0 and 40 °C than at 25 °C (Table 1, entries 8 and 9). Upon adding 10 mol-% PPh_3, the yield of **3a** decreased to 80% (Table 1, entry 10). Moreover, if all the starting materials and catalyst were mixed together in one portion, the reaction became sluggish and **3a** was delivered in only 24% yield; this suggests that cyclopropenone is very reactive to undergo a self-reaction or polymerization with the formation of complex product mixtures (Table 1, entry 11).

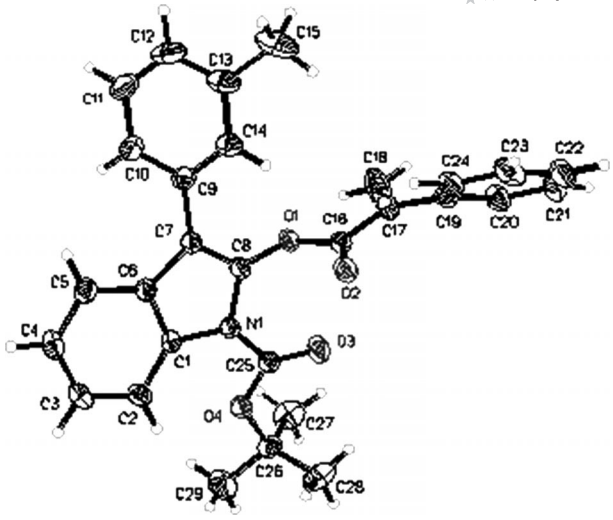
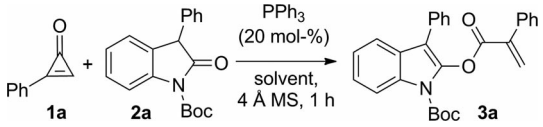


Figure 2. ORTEP drawing of **3c**.

Table 1. Screening of the reaction conditions catalyzed by PPh_3.[a]

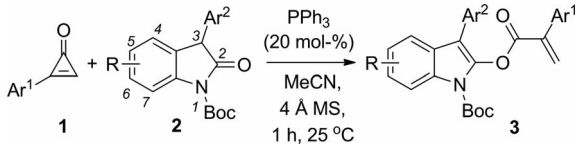


Entry	**1a**/**2a**	Solvent	*t* [°C]	**3a**, yield [%][b]
1	2:1	THF	25	91
2	2:1	CH_2Cl_2	25	82
3	2:1	MeCN	25	93
4	2:1	toluene	25	91
5	1.5:1	MeCN	25	77
6	1:1	MeCN	25	21
7	2.5:1	MeCN	25	43
8	2:1	MeCN	0	87
9	2:1	MeCN	40	80
10[c]	2:1	MeCN	25	80
11[d]	2:1	MeCN	25	24

[a] Conditions (unless otherwise specified): **2a** (0.2 mmol), PPh_3 (20 mol-%), solvent (1.5 mL), molecular sieves (4 Å, 50 mg); **1a** (0.4 mmol in 1.5 mL solvent) was added by syringe pump over 30 min. [b] Yield of isolated product. [c] Loading of PPh_3: 10 mol-%. [d] **1a**, **1b**, and PPh_3 were added in one pot.

With the best reaction conditions in hand, we next turned our efforts to study the scope and limitations of this phosphane-catalyzed nucleophilic addition reaction (Table 2). By using **1a** as the model substrate, isatins **2** with different aryl substituents at the C3 position (R = H) were tested, and the corresponding carboxylated 1*H*-indoles **3a**–**g** were obtained in excellent yields without the observation of a significant electronic impact (Table 2, entries 1–7). As for substrates **2h** (5-F, Ar^2 = 4-FC_6H_4) and **2j** (5-MeO, Ar^2 = C_6H_5), the reactions also proceeded smoothly and delivered corresponding products **3h** and **3j** in 79 and 85% yield, respectively (Table 2, entries 8 and 10). Treatment of 3-naphthyl-substituted substrate **2i** under the standard reaction conditions gave desired product **3i** in 97% yield (Table 2, entry 9). Other cyclopropenones were also employed as substrates, such as **1b** (Ar^1 = 4-MeC_6H_4) and **1c** (Ar^1 = 4-FC_6H_4), which led to products **3k** and **3l** in 88% and 86% yield, respectively (Table 2, entries 11 and 12).

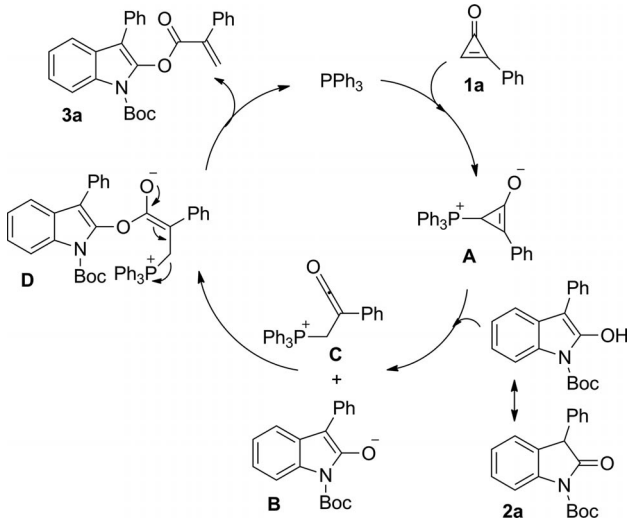
Table 2. Scope of the reaction catalyzed by PPh_3.[a]



Entry	**1**, Ar^1	**2**, R/Ar^2	**3**, yield [%][b]
1	**1a**, C_6H_5	**2a**, H/C_6H_5	**3a**, 93
2	**1a**, C_6H_5	**2b**, H/2-MeC_6H_4	**3b**, 97
3	**1a**, C_6H_5	**2c**, H/3-MeC_6H_4	**3c**, 83
4	**1a**, C_6H_5	**2d**, H/4-MeC_6H_4	**3d**, 93
5	**1a**, C_6H_5	**2e**, H/3,5-$Me_2C_6H_3$	**3e**, 98
6	**1a**, C_6H_5	**2f**, H/4-FC_6H_4	**3f**, 98
7	**1a**, C_6H_5	**2g**, H/3-FC_6H_4	**3g**, 96
8	**1a**, C_6H_5	**2h**, 5-F/4-FC_6H_4	**3h**, 79
9	**1a**, C_6H_5	**2i**, $C_{10}H_7$	**3i**, 97
10	**1a**, C_6H_5	**2j**, 5-MeO/C_6H_5	**3j**, 85
11	**1b**, 4-MeC_6H_4	**2a**, H/C_6H_5	**3k**, 88
12	**1c**, 4-FC_6H_4	**2a**, H/C_6H_5	**3l**, 86

[a] Conditions (unless otherwise specified): **2a** (0.2 mmol), PPh_3 (20 mol-%), solvent (1.5 mL), molecular sieves (4 Å, 50 mg); **1a** (0.4 mmol in 1.5 mL solvent) was added by syringe pump over 30 min. [b] Yield of isolated product.

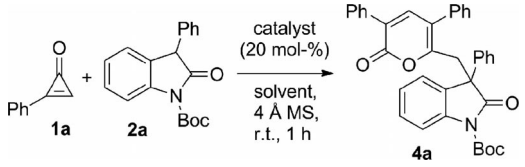
An explanation for the reaction sequence is depicted in Scheme 1 by using **1a** and **2a** as models. The 1,4-addition of PPh_3 with **1a** gives zwitterionic intermediate **A**, which abstracts a proton from the enolate resonance structure of **2a** to deliver enolate **B** and cationic intermediate **C**. Intermolecular nucleophilic addition of **B** and **C** produces zwitterionic intermediate **D**, which undergoes elimination to give the corresponding carboxylated 1*H*-indole **3a** together with the regenerated PPh_3 catalyst.



Scheme 1. Plausible mechanism for the reaction catalyzed by PPh_3.

In general, the nitrogen atom is more electronegative and more basic than the phosphorus atom. These two factors can majorly account for the differences between nitrogen- and phosphane-containing organocatalysts. With respect to this aspect, we also attempted to investigate the catalytic behavior of nitrogen-containing catalysts (tertiary amines and pyridine) in the reaction of **1** with **2**. To our delight, upon treating **1a** and **2a** in the presence of *N*,*N*-diisopropylethylamine (DIPEA, 20 mol-%) in THF for 1 h, new product **4a** was obtained in 57% yield (Table 3, entry 1). Its structure was identified by X-ray diffraction of analogue **4d** (Figure 3).[14] The structure contains a 2*H*-pyran-2-one moiety, which is built at the 3-carbon of the indoline backbone. Other nitrogen-containing catalysts such as Et_3N, 1,8-diazabicyclo[5,4,0]-7-undecene (DBU), 4-*N*,*N*-dimethylpyridine (DMAP), and 1,4-diazabicyclo[2,2,2]octane (DABCO) all showed good catalytic activity in this reaction, but DABCO gave the best result and furnished **4a** in 86% yield (Table 3, entries 2–5). Next, with the use of DABCO as the catalyst, a survey aimed at finding the optimal ratio of **1a**/**2a** was conducted (Table 3, entries 6–10). The results indicated that the addition of 1.5 equiv. **1a** by syringe pump to a mixture of **2a** and DABCO in THF resulted in the highest yield (90%) of **4a** (Table 3, entry 7). Solvent effects were then investigated. Changing the solvent to CH_2Cl_2, toluene, 1,4-dioxane, and DMF significantly reduced the yield of **4a** (Table 3, entries 11–13 and 15). Notably, the use of MeCN produced **4a** in 91% yield (Table 3, entry 14). However, the addition of **1a** or **2a** by syringe pump over 30 min decreased the yield of **4a** significantly (Table 3, entries 16 and 17). Noteworthy is that a trace amount of byproduct **5a** (an analogue of **5g** shown in Figure 4), which could not be completely separated from **4a**, was observed on the basis of the NMR spectroscopic data. Fortunately, after recrystallization, **4a** was obtained in pure form, and the recrystallization yields are all indicated in Table 3.

Table 3. Screening of the reaction conditions catalyzed by amines.[a]



Entry	**1a**/**2a**	Catalyst	Solvent	Yield [%] isolated product	Yield [%] after recrystallization
1	2.5:1	DIPEA	THF	57	10
2	2.5:1	Et_3N	THF	82	19
3	2.5:1	DBU	THF	85	19
4	2.5:1	DMAP	THF	79	17
5	2.5:1	DABCO	THF	86	20
6	2:1	DABCO	THF	82	23
7	1.5:1	DABCO	THF	90	25
8	1:1	DABCO	THF	88	15
9	1:1.5	DABCO	THF	80	15
10	1:2	DABCO	THF	74	7
11	1.5:1	DABCO	CH_2Cl_2	53	10
12	1.5:1	DABCO	toluene	60	15
13	1.5:1	DABCO	1,4-dioxane	52	10
14	1.5:1	DABCO	MeCN	91	35
15	1.5:1	DABCO	DMF	73	9
16[b]	1.5:1	DABCO	MeCN	61	20
17[c]	1.5:1	DABCO	MeCN	29	8

[a] The reaction was performed on a 0.2 mmol scale (for **2a**) in solvent (2 mL) at room temperature (25 °C). [b] **1a** was added by syringe pump over 30 min. [c] **2a** was added by syringe pump over 30 min.

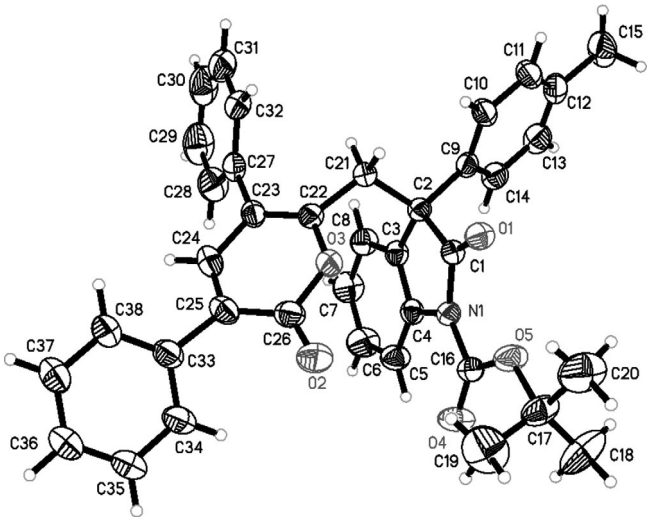
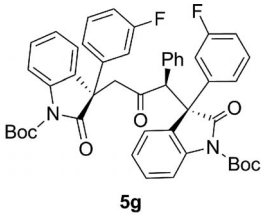


Figure 3. ORTEP drawing of **4d**.

To examine the substrate scope of this reaction, several isatin derivatives **2** with different aryl substituents Ar^2 were first investigated by using **1a** as a model substrate (Table 4). The Ar^2 substituents did not have a significant electronic or steric impact on this reaction, and corresponding products **4a**–**h** were afforded in good yields (Table 4, entries 1–8). As for substrates **2i** (R = 6-Br, $Ar^2 = C_6H_5$), **2j** (R = 5-MeO, $Ar^2 = C_6H_5$), and **2k** (R = 5-F, Ar^2 = 4-FC_6H_4), corresponding products **4i**, **4j**, and **4k** were also obtained in



5g

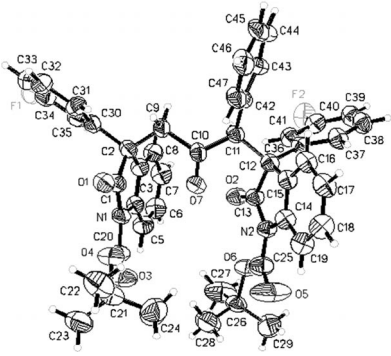
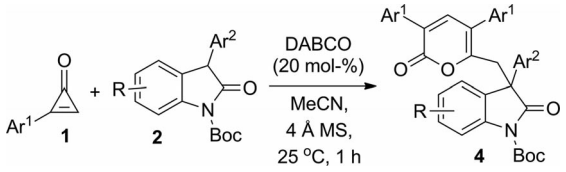


Figure 4. The X-ray structure of **5g**.

46, 80, and 67% yield, respectively (Table 4, entries 9–11). Next, by using **2a** as the model substrate, a variety of cyclopropenones **1** were investigated. Similar to the phosphane-catalyzed reaction, substituents with different electronic properties did not significantly affect the reaction outcome, and 2*H*-pyran-2-ones **4l**–**n** were furnished in 70–85% yield (Table 4, entries 12–14). In all cases, the yield of **4** after recrystallization is indicated in Table 4.

Table 4. Scope of the reaction catalyzed by DABCO.[a]

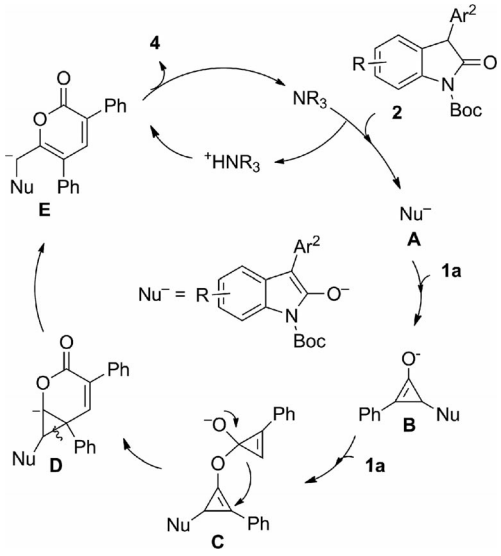


Entry	**1**, Ar^1	**2**, R/Ar^2	Product	Yield [%] isolated product	Yield [%] after recryst.
1	**1a**, C_6H_5	**2a**, H/C_6H_5	**4a**	91	35
2	**1a**, C_6H_5	**2b**, $H/2\text{-}MeC_6H_4$	**4b**	69	42
3	**1a**, C_6H_5	**2c**, $H/3\text{-}MeC_6H_4$	**4c**	70	25
4	**1a**, C_6H_5	**2d**, $H/4\text{-}MeC_6H_4$	**4d**	74	15
5	**1a**, C_6H_5	**2e**, $H/3,5\text{-}Me_2C_6H_3$	**4e**	92	44
6	**1a**, C_6H_5	**2f**, $H/4\text{-}FC_6H_4$	**4f**	81	30
7	**1a**, C_6H_5	**2g**, $H/3\text{-}FC_6H_4$	**4g**	90	13
8	**1a**, C_6H_5	**2h**, $H/C_{10}H_7$	**4h**	72	23
9	**1a**, C_6H_5	**2i**, $6\text{-}Br/C_6H_5$	**4i**	46	15
10	**1a**, C_6H_5	**2j**, $5\text{-}MeO/C_6H_5$	**4j**	80	12
11	**1a**, C_6H_5	**2k**, $5\text{-}F/4\text{-}FC_6H_4$	**4k**	67	11
12	**1c**, $4\text{-}FC_6H_4$	**2a**, H/C_6H_5	**4l**	70	15
13	**1d**, $3\text{-}ClC_6H_4$	**2a**, H/C_6H_5	**4m**	85	18
14	**1e**, $3\text{-}MeC_6H_4$	**2a**, H/C_6H_5	**4n**	77	20

[a] Conditions: **1** (0.75 mmol), **2** (0.5 mmol), DABCO (20 mol-%), molecular sieves (4 Å, 100 mg), MeCN (5 mL), 25 °C, 1 h.

Upon using **2g** and **1a** as substrates, the structure of by-product **5g** was identified by X-ray diffraction,[15] which indicated that two molecules of isatin and one molecule of cyclopropenone were incorporated into the structure (Figure 4, also see the Supporting Information).

A plausible mechanism for the formation of **4** is proposed in Scheme 2 by using **1a** as a model. First, DABCO abstracts one proton from **2** to generate anionic species **A** (Nu^-), which then initiates a 1,4-addition to the C=C bond of **1a** on the less sterically hindered side to furnish enolate intermediate **B**. Subsequent intermolecular nucleophilic addition of intermediate **B** to another molecule of **1a** takes place to give intermediate **C**. After a ring-opening process and intramolecular nucleophilic addition, intermediate **C** is transformed into cyclopropane-containing anionic intermediate **D** through a concerted manner, and it then undergoes another ring-opening process to generate intermediate **E**. After protonation, final product **4** is formed together with the regenerated catalyst.



Scheme 2. Plausible mechanism for the reaction catalyzed by amines.

Conclusions

In summary, we developed phosphane- and amine-catalyzed ring-opening reactions of cyclopropenones with isatin derivatives to afford carboxylated 1*H*-indoles and multisubstituted 2*H*-pyran-2-ones in moderate to excellent yields. These two products are the key intermediates in the synthesis of biologically active compounds.[16] The methodology displayed broad substrate scope and functional group compatibility, and the desired products were obtained under very mild conditions. The unique activity of the cyclopropenones under the organocatalysis conditions was explicated by proposed mechanisms. Further investigations to examine the mechanistic details more extensively are underway in our laboratory.

Experimental Section

General Procedure for the Preparation of 3: A flame-dried Schlenk flask was charged with substrate **2** (0.2 mmol), PPh_3 (11 mg,

0.04 mmol), and molecular sieves (4 Å, 50 mg). Then, dry MeCN (1.5 mL) was added. Compound **1** (0.4 mmol) in MeCN (1.5 mL) was added by syringe over 30 min. The reaction mixture was stirred at room temperature under an atmosphere of argon. Upon completion of the reaction, the mixture was evaporated under reduced pressure, and the residue was purified by silica gel flash column chromatography (petroleum/ethyl acetate, 20:1 v/v) to afford **3**.

General Procedure for the Preparation of 4: A flame-dried Schlenk flask was charged with substrate **1** (0.75 mmol), substrate **2** (0.5 mmol), DABCO (9 mg, 0.15 mmol), and molecular sieves (4 Å, 100 mg). Then, dry MeCN (1.5 mL) was added. The reaction mixture was stirred at room temperature under an atmosphere of argon. Upon completion of the reaction, the mixture was evaporated under reduced pressure, and the residue was purified by silica gel flash column chromatography (petroleum/ethyl acetate, 4:1 v/v) to afford a light yellow solid that was further purified by recrystallization (petroleum ether, with a few drops of dichloromethane).

Supporting Information (see footnote on the first page of this article): General experimental procedures; ^{13}C NMR and ^{1}H NMR spectroscopic data and analytic data for **3** and **4**; and crystallographic details of **3c**, **4d**, and **5g**.

Acknowledgments

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[14] CCDC-914709 (for **4d**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. See also the Supporting Information.

[15] CCDC-931360 (for **5g**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. See also the Supporting Information.

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