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Assisted Tandem Catalytic Cross Metathesis–Oxidation: In One Flask from Styrenes to 1,2-Diketones and Further to Quinoxalines

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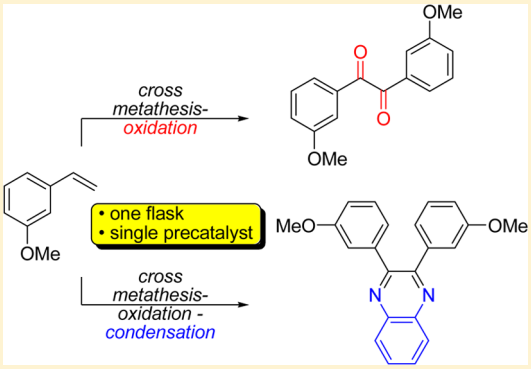
Supporting Information

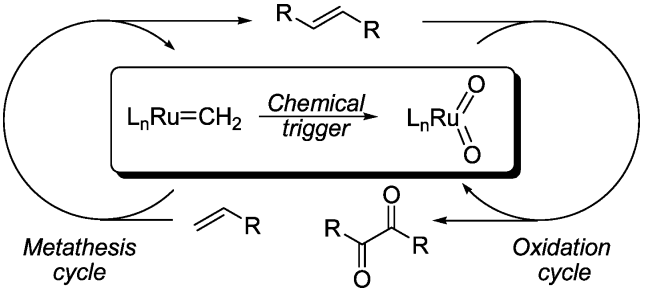
ABSTRACT: 1,2-Diketones were synthesized from styrenes by combining a cross metathesis and a Ru-catalyzed alkene oxidation to an assisted tandem catalytic sequence. The synthesis relies on the use of just one metathesis precatalyst, which was in situ converted to the oxidation catalyst by addition of an alkyl hydroperoxide as a chemical trigger and oxidant. The one-flask sequence can be extended beyond 1,2-diketones to quinoxalines, by condensation of the oxidation products with *ortho*-phenylenediamine.



INTRODUCTION

Olefin metathesis reactions were found to be ideally suited for incorporation in domino sequences[1,2] shortly after the discovery of stable and defined homogeneous precatalysts[3−5] for this transformation. In these reaction sequences, often referred to as ring rearrangement metathesis (RRM),[6,7] two or more olefin metathesis steps are coupled in a defined way, leading ultimately to an alkene or cycloalkene. A completely different class of sequential metathesis reactions is characterized by the combination of an olefin metathesis reaction with a subsequent nonmetathesis transformation of the newly generated C−C double bond.[8,9] These reaction sequences have been described as "assisted tandem catalysis", if both transformations are catalyzed through different mechanisms, but with just one precatalyst.[10] Metathesis−nonmetathesis sequences of this type require an organometallic conversion of one catalytic species into another, to link the two originally independent catalytic cycles. This organometallic conversion, and hence the connection of the catalytic cycles, is normally accomplished by a suitable reagent, which is added to the reaction mixture in due course. Several reaction sequences have been developed along these lines over the past decade, such as metathesis−hydrogenation,[11,12] metathesis−isomerization,[13−15] metathesis−di-[16−18] and ketohydroxylation,[17,19] metathesis−atom transfer radical addition,[20,21] metathesis−aromatization,[22,23] and metathesis−allylic oxidation.[24,25] The two latter reaction sequences, recently developed in our group, rely on the use of alkyl hydroperoxides as both a chemical trigger and an oxidant. Most likely, the Ru-metathesis catalyst is converted into a Ru(IV)-dioxo species, which mediates the subsequent aromatization or allylic oxidation. We assume that the course of the reaction is primarily governed by the substitution pattern of the alkene, rather than the reaction conditions, and were therefore intrigued by recent reports describing the oxidative transformation of alkenes[26,27] and alkynes[28,29] into 1,2-diketones, using Ru(II)-complexes such as $[Ru(cymene)Cl_2]_2$ as precatalysts and *tert*-butyl hydroperoxide as the oxidant. Previously, only Pd-catalyzed oxidations of alkynes[30−33] or a sequence of Brønsted acid mediated alkyne hydration in combination with subsequent α-oxidation[34] had been described as methods for transforming C−C multiple bonds into 1,2-diketones. Although typical Ru-based metathesis catalysts had to the best of our knowledge not been used as precatalysts for these alkene or alkyne oxidations, we were optimistic that the combination of an oxidative diketone formation with an olefin metathesis reaction as outlined in Scheme 1 should be possible.

Scheme 1. Concept of Assisted Tandem Catalytic Metathesis−Nonmetathesis Transformations



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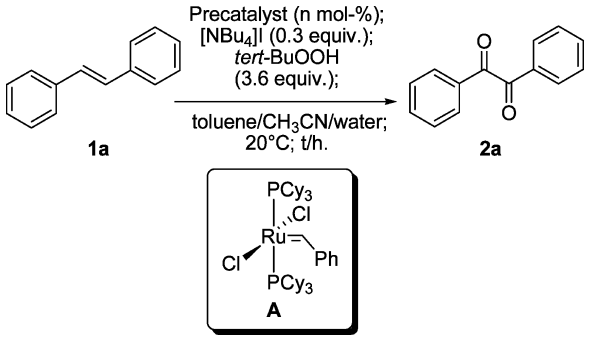
In this paper we describe the successful connection of a cross metathesis reaction and the subsequent oxidative diketone formation of the intermediate CM products, using only one precatalyst. As 1,2-diketones play a prominent role in heterocyclic chemistry, opportunities for extending the catalytic sequence by condensation reactions have also been investigated. As a result, styrenes can be converted in a one-flask fashion into quinoxalines and imidazole derivatives.

RESULTS AND DISCUSSION

Initially we tested whether a typical Ru-carbene complex can catalyze the oxidative conversion of a stilbene into a 1,2-diketone under conditions similar to those published by Wan et al. for the precatalyst $[Ru(cymene)Cl_2]_2$.[26] Thus, *E*-stilbene (**1a**) was treated with a catalytic amount of first generation Grubbs' catalyst (**A**) and an aqueous solution of *tert*-BuOOH as the oxidant in a solvent system consisting of toluene, acetonitrile, and water. Although the effective catalyst loading in our experiment (2.5 mol % of Ru, entry 3) was similar to that used by Wan et al. (1.0 mol % of $[Ru(cymene)Cl_2]_2$, corresponding to 2.0 mol % of Ru, entry 1),[26] we obtained a significantly lower yield of benzil (**2a**). From our previous experience with *tert*-BuOOH as a reagent for allylic oxidations, we knew that uncatalyzed background reactions occur to some extent, in particular after prolonged reaction times. For this reason we reproduced the control experiment performed by Wan et al. (entry 2), but with an extended reaction time of 36 h (entry 4). Even after this time period, the substrate was found to be completely inert to oxidation in the absence of Ru-catalysts, and stilbene was quantitatively recovered (Table 1).

Table 1. Control Experiments and Comparison with Data from the Literature

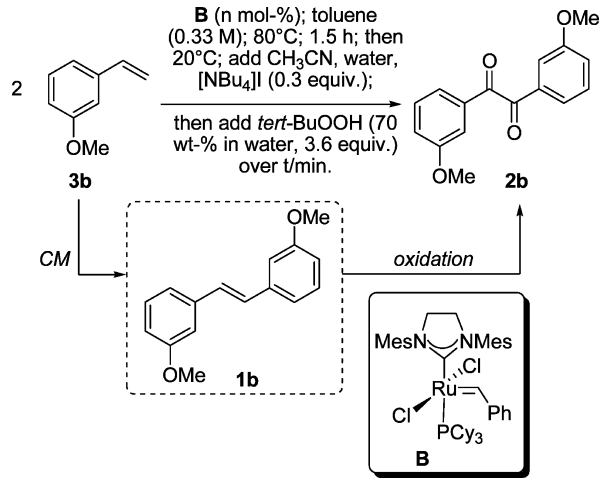


entry	precatalyst (mol %)	*t*/h	yield of **2**	ref.
1	$[Ru(cymene)Cl_2]_2$ (1.0)	1	91%	26
2	none	1	"not detected"	26
3	**A** (2.5)	1	50%	this work
4	none	36	<1%[a]	this work

[a]Stilbene (**1a**) was recovered in 99% yield.

From the initial test experiment with first generation Grubbs' catalyst (**A**) it became evident that Ru carbenes should in principle be suitable catalysts for this nonmetathesis transformation, but that there is still a considerable activity gap between **A** and the dimeric Ru-cymene complex used by Wan et al. Therefore, we thought that the development of an assisted tandem catalytic CM–oxidation sequence as outlined in Scheme 1 should be promising, but that in particular the second step would require optimization. It turned out that the cross metathesis of styrene is difficult to monitor by TLC, which prompted us to choose 3-methoxy styrene **3b** as a test substrate. Literature precedence for the cross or self-metathesis of two styrenes[35−37] to symmetrical or unsymmetrical stilbenes[38] is scarce compared to the plethora of successful examples for cross metathesis reactions in general.[39−42] However, the examples described so far in the literature suggest that second generation catalysts give significantly better conversions at lower catalyst loadings, although Noels et al. reported a very promising GC-yield for one example with a moderate loading of first generation catalyst **A**.[36] Initially, we tested this catalyst but could not observe any self-metathesis of **3b** within 1.5 h and with a catalyst loading of 5 mol % at a reaction temperature of 80 °C (Table 2, entry 1). This

Table 2. Optimization of Conditions for the CM–Oxidation of 3b



entry	catalyst and catalyst loading	Addition time *t*	yield[a]
1	**A** (5.0 mol %)	–	–[b]
2	**B** (2.5 mol %)	0.8 min.	38%
3	**B** (5.0 mol %)	0.8 min.	48%
4	**B** (2.5 mol %)	5.0 min.	57%
5	**B** (5.0 mol %)	5.0 min.	55%
6	**B** (2.5 mol %)	10.0 min.	82%
7	**B** (5.0 mol %)	10.0 min.	65%
8	**B** (2.5 mol %)	10.0 min.	30%[c]

[a]Isolated yield of 1,2-diketone **2b**. [b]No stilbene formation observed after 1.5 h at 80 °C. [c]3,5-Di-*tert*-butyl-4-hydroxy toluene (BHT, 1.0 equiv) was added to the reaction mixture prior to addition of the *tert*-butyl hydroperoxide.

prompted us to switch to the second generation catalyst **B**, which resulted in a complete conversion of **3b** to **1b** under otherwise identical conditions. Even with a reduced catalyst loading of 2.5 mol %, full conversion was observed by TLC after 1.5 h at 80 °C. After the metathesis reaction cooled to ambient temperature and the addition of the required cosolvents and the additive $[NBu_4]I$, the aqueous *tert*-butyl hydroperoxide solution was added within less than 1 min. Under these conditions, a moderate yield of 38% of **2b** was obtained with 2.5 mol % of precatalyst **B** (entry 2), which could be slightly improved to 48% by increasing the amount of catalyst to 5.0 mol % (entry 3). Under both conditions gas evolution was observed during the addition of the oxidant, indicating the formation of oxygen through Ru-catalyzed decomposition of the *tert*-butyl hydroperoxide, which might also explain the moderate yields. A similar observation has been

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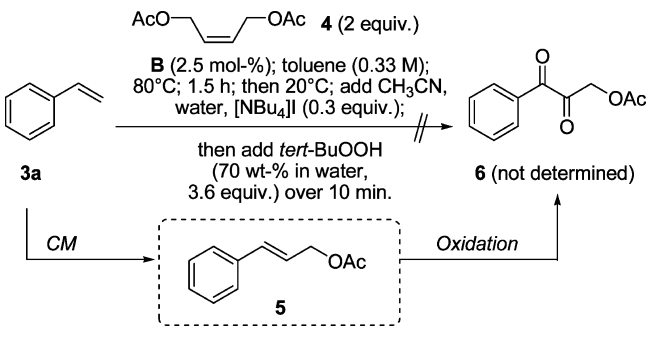
made by us during the development of the RCM−allylic oxidation sequence.[24] In this case, we found that competing decomposition of the oxidant is suppressed by slow addition of the oxidant to the reaction mixture. We could indeed observe a significant improvement by extending the addition time to 5 min. Interestingly, the yield of **2b** was virtually unaffected by the catalyst loading at this addition time (entries 4 and 5). The best yields were obtained when the oxidant was added slowly over a period of 10 min using a syringe pump. With this addition time, a higher catalyst loading is clearly detrimental, as the yield drops from 82% to 65% when the catalyst loading is increased from 2.5 to 5.0 mol % (entries 6 and 7).

The reason for the adverse effect of a higher catalyst loading at prolonged addition times might be a more efficient competition of the unproductive hydroperoxide decomposition with the intended alkene oxidation in this case. Alternatively, an oxidative scission of the C−C σ-bond may occur as another competing reaction. Although the expected 3-methoxy benzaldehyde was not detected under these particular conditions, there is ample precedence for oxidative fragmentation of alkenes to carbonyl compounds from the literature on Ru-catalyzed dihydroxylation reactions.[43−47] To test whether radical pathways play a significant role in the oxidation step or not, we performed a control experiment similar to that used by Murahashi et al. for investigating the mechanism of Ru-catalyzed allylic and benzylic oxidation[48] (entry 8). Adding 1 equiv of the radical scavenger BHT immediately before addition of the hydroperoxide leads to a decreased yield of 30%, but not to a complete inhibition of the second step. We conclude from this observation that a mechanism proceeding exclusively or predominantly via a radical pathway is unlikely, but that the oxidation catalyst is intercepted to a considerable extent by the radical scavenger.

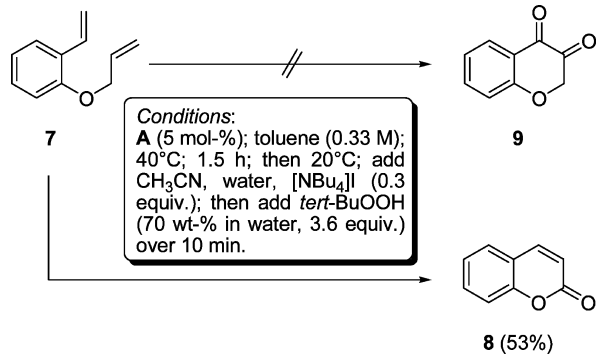
As outlined in the introduction, we have previously developed other oxidative metathesis sequences under different conditions but by using hydroperoxides as a chemical trigger and as an oxidizing agent.[23,24] In these cases, the substrates contained allylic hydrogen atoms and the oxidation step proceeded via abstraction of this hydrogen, resulting in the formation of five-membered aromatic heterocycles or lactones. To check whether Ru-catalyzed diketone formation can efficiently compete with allylic oxidation under the optimized conditions, we performed two additional experiments. First, styrene (**3a**) was reacted with 2 equiv of *Z*-2-butene-1,4-diacetate (**4**) under the optimized CM−oxidation conditions (Scheme 2). This experiment led to a quantitative conversion of the intermediate CM product **5**[49] to a complex mixture of products with no identifiable major component. To exclude the possibility that the complexity of the mixture was caused by residual **4**, the cross metathesis product **5** was isolated and separately subjected to the oxidation conditions using 2.5 mol % of Ru-carbene complex **B**. This experiment also resulted in the formation of a mixture with no defined major product.

Scheme 2. Attempted CM−Oxidation Sequence with 2-Butene-1,4-diacetate (4)



In the second experiment we used the RCM precursor **7** as a substrate and very similar metathesis−oxidation conditions (Scheme 3). In this case, first generation catalyst **A** is sufficiently active to promote the RCM and was therefore used instead of **B**. Under metathesis−oxidation conditions, a defined product could be isolated from the reaction mixture in 53% yield, which was discovered to be coumarin (**8**) rather than the diketone **9**. The strong preference for the allylic oxidation reaction under the conditions of the metathesis−oxidation sequence is somewhat surprising, as Wan et al.[26] could successfully convert alkenes with allylic hydrogen atoms into the corresponding diketones in high yields, using $[Ru(cymene)Cl_2]_2$ as the precatalyst. We also checked whether the preference for allylic oxidation was caused by the choice of catalyst and repeated the metathesis−oxidation sequence for substrate **7** with second generation catalyst **B** under otherwise identical conditions. The outcome was very similar, with a yield of 35% of **8** and no indication for the formation of any diketone **9**.

Scheme 3. Attempted RCM−Oxidation of Styrenyl Ether 7



Having identified this obvious limitation of the cross metathesis−oxidation sequence, we tested the optimized conditions for a variety of other styrenes (Table 3).

High yields of the corresponding diketones **2a−c** were obtained with styrene (**3a**) and its 3-methoxy- (**3b**) and 3-methyl- (**3c**) derivatives (entries 1−3). A significantly lower yield and a comparatively sluggish reaction was observed with the benzyl ether **3d** (entry 4), which is most likely caused by a competing benzylic oxidation. Successful CM−oxidations could also be accomplished for the *para*-substituted styrenes **3e−h**, although the isolated yields are generally lower than those for the analogous *meta*-substituted styrenes. While the isolated yield of *m*-methyl derivative **2e** (entry 5) is comparable to that of unsubstituted **2a**, a more strongly electron-donating substituent such as 4-methoxy (entry 6) or isopropyl (entry 8) leads to a significantly decreased isolated yield. Monitoring the reaction by TLC revealed nearly complete consumption of the intermediate stilbene and high selectivity; thus, the rather low yields must most likely be attributed to loss of material upon chromatography on silica. In the case of 4-chlorostyrene **3g** the NMR spectra of the reaction mixture suggested that the desired diketone **2g** was formed to a considerable extent, but it

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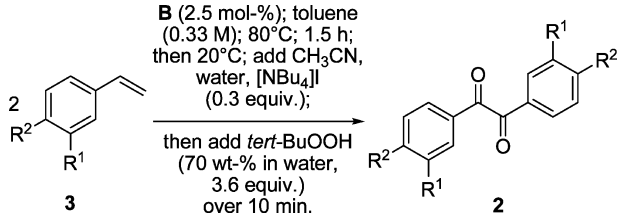
Table 3. Scope and Limitations of the Assisted Tandem Catalytic CM−Oxidation Sequence



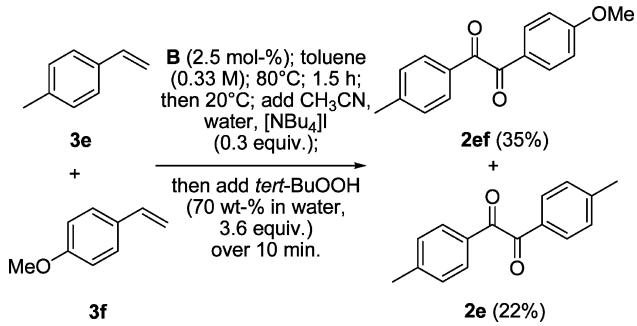
entry	3	R^1	R^2	2	yield[a]
1	**3a**	-H	-H	**2a**	75%
2	**3b**	-OMe	-H	**2b**	82%
3	**3c**	-Me	-H	**2c**	81%
4	**3d**	-OBn	-H	**2d**	40%
5	**3e**	-H	-Me	**2e**	67%
6	**3f**	-H	-OMe	**2f**	44%
7	**3g**	-H	-Cl	**2g**	n. d.[b]
8	**3h**	-H	-*iso*-Pr	**2h**	46%
9	**3i**	-H	$-CO_2Me$	**2i**	–[c]
10	**3j**	-H	-Ph	**2j**	–[c]
11	**3k**	-CH=CH-CH=CH-		**2k**	–[c]
12	**3l**	$-NO_2$	-H	**2l**	–[c]
13	**3m**	-H	$-NO_2$	**2m**	–[c]

[a]Isolated yields of diketones **2**. [b]Inseparable mixture of products. [c]Precipitate formed after completed CM step; no conversion to diketones **2** under standard conditions.

could not be purified by chromatography or crystallization (entry 7). When we applied the optimized CM−oxidation conditions to styrenes **3i−m** (entries 9−13), we encountered an unexpected difficulty: after completion of the cross metathesis step a precipitate was formed which could not be dissolved by the addition of more toluene or acetonitrile, the cosolvent required for the second step of the sequence. For each styrene **3i−m** the reaction mixtures were therefore evaporated after the cross metathesis step and analyzed by NMR spectroscopy. In all cases the precipitates were found to be only sparingly soluble in all solvents commonly used for NMR spectroscopy, such as $CDCl_3$, C_6D_6, acetone-d_6, methanol-d_4, or DMSO-d_6. Although solubility problems are sometimes observed for compounds with aromatic substituents, this observation was surprising in these cases, because the expected stilbenes **1i−m** had previously been synthesized via other methods, and NMR spectroscopical data were reported in either $CDCl_3$ or C_6D_6 for all of them (e.g., **1i**,[50] **1j**,[51] **1k**,[52] **1l**,[53] **1m**[54]). The ^{1}H NMR spectra obtained by us from the cross metathesis reaction mixtures suggested that the expected stilbenes were formed only to a very small extent, along with minor amounts of other unidentified low-molecular weight products and unreacted starting materials. This result points at a polymerization of styrenes **3i−m** under the cross metathesis conditions, presumably through a radical pathway. The sensitivity toward polymerization might be enhanced in these cases because the C−C double bond is connected to electron-deficient aryl substituents or extended π-systems, leading to a better stabilization of a benzylic radical.

Encouraged by previous reports describing a remarkable selectivity in the cross metathesis reactions of differently substituted styrenes,[36,37] we applied the tandem CM−oxidation conditions to an equimolar mixture of *para*-substituted styrenes **3e** and **3f**. We could only isolate 35% of the desired unsymmetrical 1,2-diketone **2ef**, along with 22% of **2e**. The methoxy substituted product **2f** was formed in very minor quantities and could not be isolated (Scheme 4). This

Scheme 4. Unsymmetrical Tandem CM−Oxidation Sequence



observation suggests that the selectivity of the cross metathesis step is much lower than expected on the basis of the literature reports. The complete absence of **2f** most likely results from the lower reactivity of the 4,4′-dimethoxy stilbene (**1f**) compared to its dimethyl analogue **1e**, which becomes evident from a comparison of the yields obtained for the symmetrical diketones **2e** and **2f** via self-metathesis−oxidation of **3e** and **3f** (Table 3, entries 5, 6) respectively. To investigate whether the ratio of diketones obtained through CM−oxidation of **3e** and **3f** reflects the selectivity of the cross metathesis or the different reactivity of the stilbenes in the oxidation step, we monitored the cross metathesis reaction by GC-MS. The CM products were formed in a statistical ratio of 1:2:1, with the unsymmetrical stilbene resulting from cross metathesis of **3e** and **3f** accounting for 50% of the mixture. We conclude from this result that the isolated yields of CM−oxidation products **2ef** (35%), **2e** (22%), and **2f** (<5%) indeed mirror the lower reactivity of electron-rich C−C double bonds in the oxidative diketone formation.

To functionalize the 1,2-diketones obtained from the CM−oxidation sequence further, we considered an extension of the one-flask sequence by a condensation step with 1,2-diamines, e.g. phenylene diamine (**10**). The resulting products are 2,3-diaryl quinoxalines **11**, which have attracted attention for a manifold of applications, such as dyes (e.g., for dye-sensitized solar cells),[55−57] drugs (e.g., the antihypertensive brimonidine[58] or potential influenza NS1A protein inhibitors[59]), and organic semiconductors.[60,61] The established method for the synthesis of 2,3-diaryl quinoxalines is the condensation of phenylene diamines and benzil or substituted derivatives in glacial acetic acid.[56,59,62] Alternatively, catalytic amounts of Lewis acids such as ceric ammonium nitrate have been used in water as a solvent.[63] Recently, an organocatalytic one-flask synthesis of 2,3-diaryl quinoxalines from benzaldehydes via benzoin condensation, oxidation, and condensation with diamines has been described.[64] One of the most important tasks in the development of tandem or one-flask sequences is to avoid using an excess of reagents in all steps, because these will accumulate as impurities and cause serious problems in the isolation of the final product. Another important requirement is to ensure the compatibility of all reaction steps with the solvent or solvent mixture used in the previous steps. If this is not the case, solvents have to be evaporated in between and the reaction mixture has to be redissolved prior to the last steps of the sequence. This procedure is inconvenient and limits the

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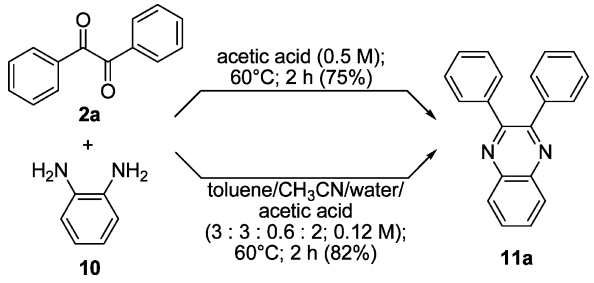
synthetic utility of a one-flask reaction. For these reasons we started this investigation by testing the solvent mixture from the CM–oxidation sequence for the condensation of equimolar amounts of benzil (**2a**) and phenylene diamine (**10**). Under standard conditions, i.e. by heating a 1:1 mixture of **2a** and **10** in acetic acid at 60 °C, the desired 2,3-diphenyl quinoxaline (**11a**) was obtained in 75% yield at an initial substrate concentration of 0.5 M after 2 h. We then simulated the final step of the projected CM–oxidation–condensation sequence by dissolving equimolar amounts of **2a** and **10** in a mixture of toluene, acetonitrile, and water. Glacial acetic acid was added to this mixture as an additional cosolvent, resulting in an overall initial substrate concentration of 0.12 M, and the reaction mixture was again heated to 60 °C for 2 h. Gratifyingly, the yield of quinoxaline **11a** was even higher under these simulated one-flask conditions compared to the standard conditions using glacial acetic acid as a solvent (Scheme 5).

Scheme 5. Condensation of 2a and 10 under Simulated One-Flask Conditions



With this promising result in hand, we repeated the CM–oxidation reaction for styrene (**3a**) and extended the sequence, simply by adding 1 equiv of phenylene diamine (**10**) and acetic acid as a cosolvent and heating the mixture to 60 °C for another 2 h. 2,3-Diphenyl quinoxaline (**11a**) was obtained following this protocol in 45% yield, which corresponds to an average yield of 67% per step, whereas the average yield for the two-step protocol is 78%. This difference does not indicate an adverse effect of the Ru-catalyst on the condensation step but is more likely caused by the necessity to remove Ru-residues from the reaction mixtures.

Similarly, substituted 2,3-diarylquinoxalines **11b–h** were isolated in comparable yields starting from styrenes **3b–h**. Notably, the isolated yields of the quinoxalines **11d** and **11h** were considerably higher than those of the underlying 1,2-diketones **2d** and **2h**. Another remarkable example is the 4-chloro derivative **11g**, which could be isolated in 47% yield, in contrast to the corresponding 1,2-diketone **2g**, which was obtained as an inseparable mixture. This example illustrates that sometimes extending a one-flask sequence by additional steps does not complicate, but facilitates, the isolation of the final product. This might explain why the isolated yields of quinoxalines **11d–h** are higher than expected considering the isolated yields of the 1,2-diketones reported in Table 3 (Scheme 6 and Table 4).

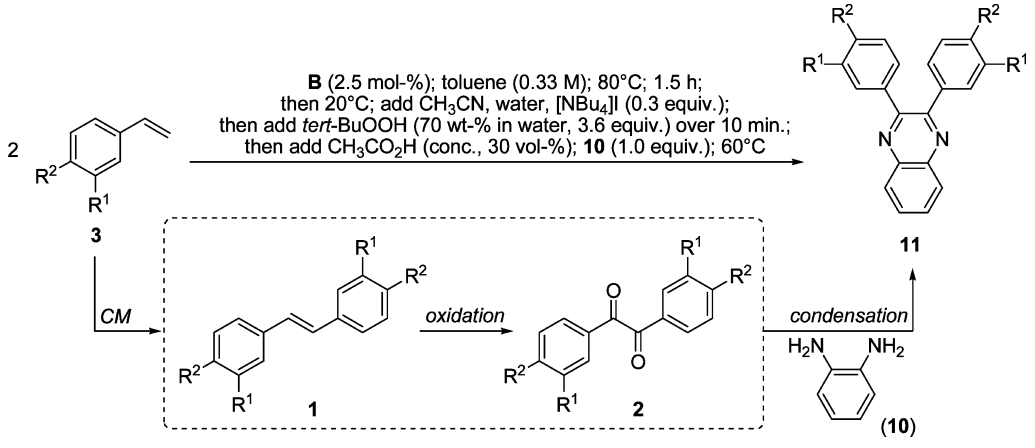
Table 4. Quinoxalines via One-Flask CM–Oxidation–Condensation (see Scheme 6 for details)

entry	3	R^1	R^2	11	yield[a]
1	**3a**	-H	-H	**11a**	45%
2	**3b**	-OMe	-H	**11b**	51%
3	**3c**	-Me	-H	**11c**	47%
4	**3d**	-OBn	-H	**11d**	54%
5	**3e**	-H	-Me	**11e**	45%
6	**3f**	-H	-OMe	**11f**	44%
7	**3g**	-H	-Cl	**11g**	47%
8	**3h**	-H	-*iso*-Pr	**11h**	51%

[a]Isolated yields of quinoxalines **11**.

To further evaluate the opportunities for extending the CM–oxidation sequence by other condensation steps, we investigated a synthesis of spirocyclic bisimines **14**. For example, **14a** had previously been synthesized from benzil (**2a**), cyclohexanone (**12**), and NH_4OAc (**13**) in acetic acid. The spirocycle **14a** served as a precursor for enantiomerically pure C_2-symmetric 1,2-diamines, which were used as chiral ligands for Lewis acidic catalysts, e.g. for Diels–Alder reactions.[65] Similar to the optimization of conditions for the one-flask quinoxaline synthesis, we compared the condensation of benzil (**2a**), cyclohexanone (**12**), and NH_4OAc (**13**) in acetic acid under the published conditions[65] with the conditions given by the tandem protocol (Scheme 7). In contrast to the condensation of benzil and phenylenediamine, the condensation leading to **14a** is less tolerant toward the modified solvent system. If acetic acid is replaced by a mixture of toluene, acetonitrile, water, and acetic acid, the reaction becomes

Scheme 6. From Styrenes 3 to Quinoxalines 11 via One-Flask CM–Oxidation–Condensation



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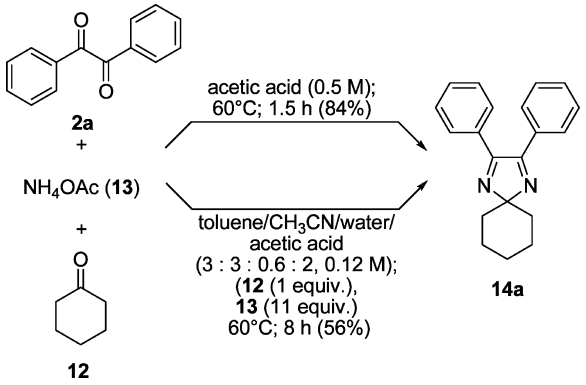
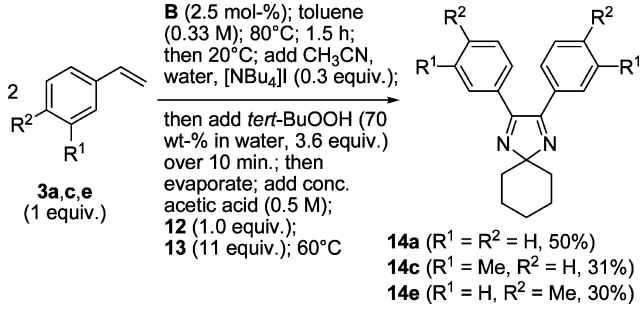
Scheme 7. Condensation of 2a, 12, and NH_4OAc under Simulated One-Flask Conditions



considerably slower and remains incomplete even after 8 h. The isolated yield of **14a** from this experiment was 56%, compared to 84% obtained under standard conditions in neat acetic acid within 1.5 h.

This rather slow reaction and the decreased isolated yield prompted us to modify the conditions for the one-flask synthesis of spirocycles **14** from styrenes **3** by evaporating the solvent mixture after the CM−oxidation step and redissolving the residue in acetic acid prior to the addition of cyclohexanone and NH_4OAc (Scheme 8). While **14a** could be synthesized

Scheme 8. From Styrenes 3 to Spirodiimines 14 via One-Flask CM−Oxidation−Condensation



from styrene via this protocol in a fair yield of 50%, two further examples, starting from methyl substituted styrenes **3c** and **3e**, gave the corresponding spirocycles **14c** and **14e**, respectively, only in a significantly lower yield of ca. 30%.

CONCLUSIONS

In summary, we demonstrated that the Ru-catalyzed cross metathesis of styrenes and the Ru-catalyzed oxidation of the intermediate stilbenes to 1,2-diketones can be coupled in an assisted tandem catalytic transformation, using the oxidant required for the second step as a chemical trigger to convert the metathesis active carbene into an oxidation catalyst, presumably a Ru-dioxo-species. The sequence does not require the removal of solvents or byproducts in the first step before the second step is initiated. Instead, the addition of appropriate cosolvents after completion of the first catalytic step, together with the oxidant, is sufficient. The CM−oxidation sequence can be extended by an uncatalyzed condensation step under one-flask conditions. While the reaction with phenylene diamine produces quinoxalines efficiently without a solvent exchange, the three-component condensation leading to spirocyclic bisimines is significantly less effective and provides the products only in moderate yields after an intermediate exchange of solvents. The potential of the sequence, in particular for the synthesis of polyarylated quinoxalines with interesting optical and electronical properties, will be the subject of future investigations.

EXPERIMENTAL SECTION

General Methods. All experiments were conducted in dry reaction vessels under an atmosphere of dry nitrogen. Solvents were purified by standard procedures. ^1H NMR spectra were obtained at 300 MHz in $CDCl_3$ with tetramethylsilane (δ = 0.00 ppm) as an internal standard. Coupling constants (J) are given in Hz. ^{13}C NMR spectra were recorded at 75 MHz in $CDCl_3$ with $CDCl_3$ (δ = 77.0 ppm) as an internal standard. The number of coupled protons was analyzed by APT-experiments and is denoted by a number in parentheses following the chemical shift value. IR spectra were recorded as neat films on NaCl or KBr plates or as KBr discs. Wavenumbers (ν) are given in cm^{-1}. The peak intensities are defined as strong (s), medium (m), or weak (w). Low and high resolution mass spectra were obtained by EI/TOF.

General Procedure for the Synthesis of 1,2-Diketones 2 from Styrenes 3. To a solution of the appropriate styrene **3** (1.0 mmol) in toluene (3.0 mL) was added Ru-catalyst **B** (20.6 mg, 2.5 mol %). The solution was stirred for 1.5 h at 80 °C. After cooling to ambient temperature, acetonitrile (3.0 mL), water (0.6 mL), and tetrabutylammonium iodide (55 mg, 0.15 mmol) were added. Then *tert*-butyl hydroperoxide (70 wt % in water, 500 μL, 1.8 mmol) was added dropwise via a syringe pump within 10 min. After stirring for 1.0 h at ambient temperature the solution was diluted with methyl *tert*-butyl ether (75 mL) and washed with a saturated aqueous solution of Na_2SO_3 (5 mL). After phase separation the organic layer was dried with $MgSO_4$ and filtered, and all volatiles were removed in vacuo. The residue was purified by column chromatography.

Benzil (2a).[66] Following the general procedure, **2a** was obtained from **3a** (104 mg, 1.0 mmol) as a yellowish solid (79 mg, 0.38 mmol, 75%). Mp 78−80 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.94−7.87 (4H), 7.63−7.54 (2H), 7.49−7.40 (4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.5 (0), 134.9 (1), 133.0 (0), 129.9 (1), 129.0 (1); IR (KBr-disc) ν 3065 (w), 1616 (s), 1594 (m), 1580 (w), 1451 (m), 1326 (w); HRMS (EI) calcd for $C_{14}H_{10}O_2$ $[M]^+$: 210.0681, found: 210.0699; MS (EI) m/z 210 (M^+, 3), 105 (100), 77 (48), 51 (18), 43 (8).

1,2-Bis(3-methoxyphenyl)ethane-1,2-dione (2b).[67] Following the general procedure, **2b** was obtained from **3b** (134 mg, 1.0 mmol) as a yellowish solid (110 mg, 0.41 mmol, 82%). Mp 80−82 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.54 (dd, 2H, J = 2.4, 1.6), 7.47 (ddd, 2H, J = 7.6, 1.2, 1.2), 7.39 (dd, 2H, J = 7.9, 7.7), 7.20 (ddd, 2H, J = 8.0, 2.6, 1.0), 3.86 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.3 (0), 160.1 (0), 134.3 (0), 130.0 (1), 123.1 (1), 121.8 (1), 112.9 (1), 55.5 (3); IR (KBr-disc) ν 2918 (m), 2850 (w), 1720 (m), 1670 (m), 1596 (m), 1582 (m), 1486 (s), 1432 (m), 1259 (s); HRMS (EI) calcd for $C_{16}H_{14}O_4$ $[M]^+$: 270.0892, found: 270.0888; MS (EI) m/z 270 (M^+, 8), 135 (100), 107 (20), 92 (14), 77 (16).

1,2-Di-*m*-tolylethane-1,2-dione (2c).[68] Following the general procedure, **2c** was obtained from **3c** (118 mg, 1.0 mmol) as a yellowish solid (96 mg, 0.41 mmol, 81%). Mp 90−92 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.80 (s (br), 2H), 7.79 (d, 2H, J = 8.1), 7.49 (d, 2H, J = 7.5), 7.41 (dd, J = 7.6, 7.5), 2.42 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.9 (0), 139.0 (0), 135.7 (1), 133.1 (0), 130.2 (1), 128.9 (1), 127.2 (1), 21.2 (3); IR (KBr-disc) ν 3030 (w), 2923 (w), 1669 (s), 1603 (m), 1584 (m), 1452 (w); HRMS (EI) calcd for $C_{16}H_{14}O_2$ $[M]^+$: 238.0994, found: 238.0978; MS (EI) m/z 238 (M^+, 10), 136 (20), 119 (78), 91 (35), 85 (80), 83 (100), 71 (19), 57 (22), 47 (24), 43 (27).

1,2-Bis(3-(benzyloxy)phenyl)ethane-1,2-dione (2d). Following the general procedure, **2d** was obtained from **3d** (210 mg, 1.0 mmol) as a yellowish solid (84 mg, 0.20 mmol, 40%). Mp 111−113 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.60 (dd, 2H, J = 2.3, 1.5), 7.49 (ddd, 2H, J = 7.5, 2.5, 1.1) 7.48−7.34 (14H), 7.30 (ddd, 2H, J = 8.2,

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2.6, 1.1), 5.10 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.3 (0), 159.2 (0), 136.2 (0), 134.3 (0), 130.1 (1), 128.6 (1), 128.2 (1), 127.5 (1), 123.2 (1), 122.4 (1), 114.4 (1), 70.3 (2); IR (KBr-disc) ν 3066 (w), 3033 (w), 2921 (w), 2873 (w), 1668 (s), 1589 (s), 1483 (s), 1440 (s), 1382 (w); HRMS (EI) calcd for $C_{28}H_{22}O_4$ $[M]^+$: 422.1518, found: 422.1521; MS (EI) m/z 422 (M^+, 1), 211 (40), 91 (100), 83 (52).

1,2-Di-*p*-tolylethane-1,2-dione (2e).[68] Following the general procedure, **2e** was obtained from **3e** (118 mg, 1.0 mmol) as a yellowish solid (80 mg, 0.34 mmol, 67%). Mp 101−103 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, 4H, J = 8.2), 7.22 (d, 4H, J = 7.9), 2.35 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.5 (0), 146.0 (0), 130.7 (1), 130.0 (1), 129.7 (0), 21.2 (3); IR (KBr-disc) ν 2924 (w), 1667 (s), 1602 (m), 1584 (m), 1484 (w), 1451 (w); HRMS (EI) calcd for $C_{16}H_{14}O_2$ $[M]^+$: 238.0994, found: 238.0984; MS (EI) m/z 238 (M^+, 1), 119 (100), 91 (46), 65 (32), 39 (20).

1,2-Bis(4-methoxyphenyl)ethane-1,2-dione (2f).[68] Following the general procedure, **2f** was obtained from **3f** (134 mg, 1.0 mmol) as a yellowish solid (59 mg, 0.22 mmol, 44%). Mp 125−127 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, 4H, J = 8.9), 6.97 (d, 4H, J = 9.0), 3.88 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.4 (0), 164.8 (0), 132.2 (1), 114.3 (1), 114.3 (0), 55.6 (3); IR (KBr-disc) ν 3067 (w), 2956 (w), 2846 (w), 2654 (w), 1691 (w), 1655 (s), 1596 (s), 1572 (s), 1509 (m), 1423 (m); HRMS (EI) calcd for $C_{16}H_{14}O_4$ $[M]^+$: 270.0892, found: 270.0904; MS (EI) m/z 270 (M^+, 5), 135 (100), 107 (6), 92 (4), 77 (10).

1,2-Bis(4-isopropylphenyl)ethane-1,2-dione (2h).[69] Following the general procedure, **2h** was obtained from **3h** (146 mg, 1.0 mmol) as a yellowish solid (68 mg, 0.23 mmol, 46%). Mp 74−76 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, 4H, J = 8.4), 7.35 (d, 4H, J = 8.2), 2.97 (sept, 2H, J = 6.9), 1.26 (d, 12H, J = 6.9); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.5 (0), 156.6 (0), 131.1 (0), 130.1 (1), 127.1 (1), 34.5 (1), 23.5 (3); IR (KBr-disc) ν 2962 (m), 2930 (w), 2872 (w), 1720 (w), 1670 (s), 1601 (s), 1460 (m); HRMS (EI) calcd for $C_{20}H_{22}O_2$ $[M]^+$: 294.1620, found: 294.1614; MS (EI) m/z 294 (M^+, 4), 147 (100), 91 (10).

1-(4-Methoxyphenyl)-2-*p*-tolylethane-1,2-dione (2ef).[70] Following the general procedure, **2ef** was obtained from **3e** (59 mg, 0.5 mmol) and **3f** (67 mg, 0.5 mmol) as a yellowish solid (44 mg, 0.17 mmol, 35%), along with **2e** (26 mg, 0.11 mmol, 22%). Mp 103−105 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, 2H, J = 8.9), 7.88 (d, 2H, J = 8.2), 7.31 (d, 2H, J = 8.0), 6.99 (d, 2H, J = 8.9), 3.89 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.6 (0), 193.3 (0), 164.9 (0), 145.9 (0), 132.3 (1), 130.8 (0), 130.0 (1), 129.6 (1), 126.2 (0), 114.3 (1), 55.6 (3), 21.9 (3); IR (KBr-disc) ν 2936 (w), 2842 (w), 1664 (s), 1595 (s), 1573 (m), 1511 (m), 1309 (w); HRMS (EI) calcd for $C_{16}H_{14}O_3$ $[M]^+$: 254.0943, found: 254.0937; MS (EI) m/z 254 (M^+, 5), 135 (100), 119 (22), 91 (12).

Coumarin (8). Following the general procedure, **8** was obtained from **7** (160 mg, 1.0 mmol) as a colorless solid (77 mg, 0.53 mmol, 53%), mp 70−72 °C. Analytical data are identical to those previously reported by us.[24]

General Procedure for the Synthesis of Quinoxalines 11 from Styrenes 3. To a solution of the appropriate styrene **3** (1.0 mmol) in toluene (3.0 mL) was added Ru-catalyst **B** (20.6 mg, 2.5 mol %). The solution was stirred for 1.5 h at 80 °C. After the solution cooled to ambient temperature, acetonitrile (3.0 mL), water (0.6 mL), and tetrabutylammonium iodide (55 mg, 0.15 mmol) were added. Then *tert*-butyl hydroperoxide (70 wt % in water, 500 μL, 1.8 mmol) was added dropwise via a syringe pump within 10 min. After stirring for 1.0 h at ambient temperature, the solution was diluted with glacial acetic acid (2 mL) and heated to 60 °C. At this temperature *o*-phenylene diamine (**10**, 59 mg, 0.5 mmol) was added and the mixture was stirred for an additional 2 h. After the mixture cooled to ambient temperature, all volatiles were removed in vacuo and the residue was treated with aqueous NaOH (1 M, 10 mL). The aqueous layer was extracted three times with ethyl acetate (each time 20 mL). The combined organic layers were dried with $MgSO_4$ and filtered, and all volatiles were removed in vacuo. The residue was purified by column chromatography.

2,3-Diphenylquinoxaline (11a).[71] Following the general procedure, **11a** was obtained from **3a** (104 mg, 1.0 mmol) as a yellowish solid (64 mg, 0.23 mmol, 45%). Mp 118−120 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (dd, 2H, J = 6.4, 3.5), 7.75 (dd, 2H, J = 6.4, 3.5), 7.56−7.48 (4H), 7.39−7.27 (6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4 (0), 141.2 (0), 139.1 (0), 129.8 (1), 129.2 (1), 128.7 (1), 128.2 (1); IR (KBr-disc) ν 3059 (m), 1558 (w), 1477 (m), 1442 (m), 1396 (m), 1344 (m); HRMS (EI) calcd for $C_{20}H_{14}N_2$ $[M]^+$: 282.1157 found: 282.1156; MS (EI) m/z 282 (M^+, 100), 181 (65), 179 (20), 178 (18).

2,3-Bis(3-Methoxyphenyl)quinoxaline (11b).[72] Following the general procedure, **11b** was obtained from **3b** (134 mg, 1.0 mmol) as a yellowish solid (87 mg, 0.26 mmol, 51%). Mp 108−110 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (dd, 2H, J = 6.4, 3.5), 7.79 (dd, 2H, J = 6.4, 3.5), 7.30−7.21 (2H), 7.15−7.08 (4H), 6.93 (ddd, 2H, J = 8.2, 2.6, 0.9), 3.73 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5 (0), 153.2 (0), 141.2 (0), 140.3 (0), 129.9 (1), 129.3 (1), 129.2 (1), 122.3 (1), 115.2 (1), 114.8 (1), 55.2 (3); IR (KBr-disc) ν 2937 (w), 2834 (w), 1580 (s), 1489 (m), 1460 (m), 1426 (m), 1339 (m); HRMS (EI) calcd for $C_{22}H_{18}O_2N_2$ $[M]^+$: 342.1368, found: 342.1350; MS (EI) m/z 342 (M^+, 100), 311 (30), 299 (18), 85 (18), 83 (27).

2,3-Di-*m*-tolylquinoxaline (11c).[73] Following the general procedure, **11c** was obtained from **3c** (118 mg, 1.0 mmol) as a yellowish solid (73 mg, 0.24 mmol, 47%). Mp 109−111 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (dd, 2H, J = 6.4, 3.4), 7.77 (dd, 2H, J = 6.4, 3.5), 7.47−7.43 (2H), 7.19−7.15 (6H), 2.35 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.7 (0), 141.2 (0), 139.1 (0), 138.0 (0), 130.4 (1), 129.7 (1), 129.5 (1), 129.2 (1), 127.9 (1), 127.1 (1), 21.4 (3); IR (KBr-disc) ν 3057 (m), 2922 (w), 1719 (w), 1605 (w), 1479 (w), 1340 (s), 1276 (w); HRMS (EI) calcd for $C_{22}H_{18}N_2$ $[M]^+$: 310.1470, found: 310.1489; MS (EI) m/z 310 (M^+, 28), 195 (22), 192 (24), 165 (31), 147 (38), 116 (71), 91 (50), 90 (54), 76 (100), 65 (72), 57 (62), 50 (74).

2,3-Bis(3-(benzyloxy)phenyl)quinoxaline (11d). Following the general procedure, **11d** was obtained from **3d** (210 mg, 1.0 mmol) as a yellowish solid (133 mg, 0.27 mmol, 54%). Mp 138−140 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (dd, 2H, J = 6.4, 3.4), 7.77 (dd, 2H, J = 6.4, 3.5), 7.41−7.21 (12H), 7.19 (dd, 2H, J = 2.2, 1.7), 7.10 (ddd, 2H, J = 7.5, 1.4, 0.8), 6.99 (ddd, 2H, J = 8.2, 2.5, 0.9), 4.94 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.8 (0), 153.2 (0), 141.2 (0), 140.4 (0), 136.9 (0), 130.0 (1), 129.3 (1), 129.2 (1), 128.5 (1), 127.9 (1), 127.4 (1), 122.6 (1), 116.1 (1), 116.1 (1), 70.2 (2); IR (KBr-disc) ν 3062 (w), 3033 (w), 2866 (w), 1736 (w), 1582 (m), 1487 (m), 1434 (m), 1338 (m); HRMS (EI) calcd for $C_{34}H_{26}O_2N_2$ $[M]^+$: 494.1994, found: 494.1991; MS (EI) m/z 494 (M^+, 28), 403 (18), 91 (100).

2,3-Di-*p*-tolylquinoxaline (11e).[64] Following the general procedure, **11e** was obtained from **3e** (118 mg, 1.0 mmol) as a yellowish solid (70 mg, 0.23 mmol, 45%). Mp 139−145 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (dd, 2H, J = 6.4, 3.5), 7.74 (dd, 2H, J = 6.4, 3.4), 7.43 (d, 4H, J = 8.1), 7.15 (d, 4H, J = 7.9), 2.37 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5 (0), 141.2 (0), 138.7 (0), 136.5 (0), 129.8 (1), 129.6 (1), 129.1 (1), 128.9 (1), 21.3 (3); IR (KBr-disc) ν 3058 (m), 3029 (m), 2976 (m), 2920 (m), 1717 (w), 1613 (w), 1342 (s); HRMS (EI) calcd for $C_{22}H_{18}N_2$ $[M]^+$: 310.1470, found: 310.1472; MS (EI) m/z 310 (M^+, 100), 295 (46), 192 (20), 165 (16), 146 (10), 116 (9), 91 (8), 90 (7).

2,3-Bis(4-methoxyphenyl)quinoxaline (11f).[64] Following the general procedure, **11f** was obtained from **3f** (134 mg, 1.0 mmol) as a yellowish solid (76 mg, 0.22 mmol, 44%). Mp 143−145 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (dd, 2H, J = 6.4, 3.4), 7.72 (dd, 2H, J = 6.4, 3.4), 7.50 (d, 4H, J = 8.9), 6.88 (d, 4H, J = 8.8), 3.83 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.2 (0), 153.0 (0), 141.1 (0), 131.8 (0), 131.3 (1), 129.5 (1), 129.0 (1), 113.8 (1), 55.3 (3); IR (KBr-disc) ν 3061 (w), 2934 (w), 1836 (w), 1735 (w), 1606 (s), 1513 (s), 1460 (m); HRMS (EI) calcd for $C_{22}H_{18}O_2N_2$ $[M]^+$: 342.1368, found: 342.1372; MS (EI) m/z 342 (M^+, 100), 311 (22), 299 (8), 209 (7), 166 (23), 135 (16), 133 (24).

2,3-Bis(4-chlorophenyl)quinoxaline (11g).[64] Following the general procedure, **11g** was obtained from **3g** (138 mg, 1.0 mmol) as a yellowish solid (83 mg, 0.24%, 47%). Mp 186−188 °C; ^{1}H NMR

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(300 MHz, $CDCl_3$) δ 8.15 (dd, 2H, J = 6.4, 3.4) 7.77 (dd, 2H, J = 6.4, 3.5), 7.46 (d, 4H, J = 8.5), 7.33 (dd, 4H, J = 8.6); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.9 (0), 141.2 (0), 137.3 (0), 135.3 (0), 131.2 (1), 130.3 (1), 129.2 (1), 128.7 (1); IR (KBr-disc) ν 3062 (w), 1593 (m), 1556 (m), 1396 (m), 1342 (m), 1220 (m), 1090 (s); HRMS (EI) calcd for $C_{20}H_{12}N_2[35]Cl_2$ $[M]^+$: 350.0378, found: 350.0372; MS (EI) m/z 332 (M^+, 68), 350 (M^+, 100), 349 (100), 315 (46), 178 (42).

2,3-Bis(4-isopropylphenyl)quinoxaline (11h).[69] Following the general procedure, **11h** was obtained from **3h** (146 mg, 1.0 mmol) as a yellowish solid (94 mg, 0.26 mmol, 51%). Mp 149−151 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (dd, 2H, J = 6.3, 3.4), 7.71 (dd, 2H, J = 6.4, 3.4), 7.47 (d, 4H, J = 8.2), 7.19 (d, 4H, J = 8.2), 2.91 (sept, 2H, J = 6.8), 1.25 (d, 12H, J = 6.9); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5 (0), 149.6 (0), 141.1 (0), 136.7 (0), 129.7 (1), 129.5 (1), 129.1 (1), 126.3 (1), 33.9 (1), 23.8 (3); IR (KBr-disc) ν 2960 (s), 1720 (w), 1609 (w), 1460 (m), 1390 (w), 1340 (m); HRMS (EI) calcd for $C_{26}H_{26}N_2$ $[M]^+$: 366.2096, found: 366.2090; MS (EI) m/z 366 (M^+, 100), 351 (24), 323 (50), 281 (16), 147 (20).

General Procedure for the Synthesis of Spirocyclic Bisimines 14 from Styrenes 3. To a solution of the appropriate styrene **3** (1.0 mmol) in toluene (3.0 mL) was added catalyst **B** (20.6 mg, 2.5 mol %). The solution was stirred for 1.5 h at 80 °C. After the solution cooled to ambient temperature, acetonitrile (3.0 mL), water (0.6 mL), and $[NBu_4]I$ (55 mg, 0.15 mmol) were added. Then *tert*-butyl hydroperoxide (70 wt % in water, 500 μL, 1.8 mmol) was added dropwise via a syringe pump within 10 min. After the solution stirred for 1.0 h at ambient temperature, all volatiles were removed in vacuo. The residue was dissolved in glacial acetic acid (2 mL), and cyclohexanone (98 mg, 1.0 mmol) and NH_4OAc (806 mg, 10.9 mmol) were added. The solution was heated to 100 °C for 2 h. After the solution cooled to ambient temperature, all volatiles were removed in vacuo and the residue was treated with aqueous NaOH (1 M, 10 mL). The aqueous layer was extracted three times with methyl *tert*-butyl ether (each time 20 mL). The combined organic layers were dried with $MgSO_4$ and filtered, and all volatiles were removed in vacuo. The residue was purified by column chromatography.

2,3-Diphenyl-1,4-diazaspiro[4.5]deca-1,3-diene (14a).[74] Following the general procedure, **14a** was obtained from **3a** (104 mg, 1.0 mmol) as a yellowish solid (72 mg, 0.25 mmol, 50%). Mp 103−105 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54−7.47 (4H), 7.46−7.39 (2H), 7.39−7.30 (4H), 2.03−1.89 (4H), 1.87−1.78 (4H), 1.78−1.68 (2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.0 (0), 133.2 (0), 129.9 (1), 128.8 (1), 128.2 (1), 104.1 (0), 34.7 (2), 25.7 (2), 24.1 (2); IR (KBr-disc) ν 3059 (w), 2932 (s), 2854 (s), 1547 (m), 1448 (w), 1444 (s), 1274 (m); HRMS (EI) calcd for $C_{20}H_{20}N_2$ $[M]^+$: 288.1626, found: 288.1614; MS (EI) m/z 288 (M^+, 1), 186 (16), 185 (100), 184 (12), 104 (32), 103 (26), 67 (16).

2,3-Di-*m*-tolyl-1,4-diazaspiro[4.5]deca-1,3-diene (14c).[75] Following the general procedure, **14c** was obtained from **3c** (118 mg, 1.0 mmol) as a yellowish solid (98 mg, 0.15 mmol, 31%). Mp 78−80 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (s, 2H), 7.25−7.17 (6H), 2.34 (s, 6H), 2.03−1.88 (4H), 1.88−1.66 (6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2 (0), 138.0 (0), 133.1 (0), 130.6 (1), 129.5 (1), 127.9 (1), 126.0 (1), 103.9 (0), 34.8 (2), 25.7 (2), 24.1 (2), 21.3 (3); IR (KBr-disc) ν 2929 (m), 2854 (w), 1730 (w), 1606 (w), 1543 (w), 1481 (w), 1445 (w), 1283 (m); HRMS (EI) calcd for $C_{22}H_{24}N_2$ $[M]^+$: 316.1939, found: 316.1949; MS (EI) m/z 316 (M^+, 1), 199 (100), 118 (15), 118 (15). Anal. Calcd for $C_{22}H_{24}N_2$ (316.19): C, 83.5; H, 7.6; N, 8.9. Found: C, 83.9; H, 7.8; N, 8.7.

2,3-Di-*p*-tolyl-1,4-diazaspiro[4.5]deca-1,3-diene (14e).[75] Following the general procedure, **14e** was obtained from **3e** (118 mg, 1.0 mmol) as a yellowish solid (95 mg, 0.15 mmol, 30%). Mp 120−122 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, 4H, J = 8.1), 7.16 (d, 4H, J = 7.9), 2.38 (s, 6H), 2.02−1.88 (4H), 1.84−1.66 (6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.0 (0), 140.0 (0), 130.5 (0), 128.9 (1), 128.9 (1), 103.7 (0), 34.8 (2), 25.8 (2), 24.2 (2), 21.4 (3); IR (KBr-disc) ν 3028 (w), 2928 (m), 2854 (m), 1614 (w), 1550 (w), 1501 (m), 1444 (m), 1273 (m); HRMS (EI) calcd for $C_{22}H_{24}N_2$ $[M]^+$: 316.1939, found: 316.1952; MS (EI) m/z 316 (M^+, 2), 199 (100), 118 (15). Anal. Calcd for $C_{22}H_{24}N_2$ (316.19): C, 83.5; H, 7.6; N, 8.9. Found: C, 83.5; H, 7.8; N, 8.7.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for all reaction products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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