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Synthesis of spirooxindoles *via* formal acetylene insertion into a common palladacycle intermediate†

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A palladium-catalyzed spirocyclization reaction is reported, which is proposed to arise *via* insertion of an oxabicyclic into a palladacycle, formed from carbocyclization and a C–H functionalization sequence. Mechanistic studies suggest the insertion is diastereoselective and a post-catalytic retro-Diels–Alder step furnishes an alkene, wherein the oxibicyclic has served as an acetylene surrogate. Aryl iodides and carbamoyl chlorides were compatible as starting materials under the same reaction conditions, enabling the convergent and complementary synthesis of spirooxindoles, as well as other azacycles. These spirooxindoles allowed further transformations that were previously inaccessible.

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Introduction

Combining carbopalladation and C–H functionalization has proven to be an attractive entry into palladacyclic species.¹ These reactive intermediates have been shown to undergo a variety of transformations, leading to carbo- and heterocyclic

compounds including spirooxindoles, spiroindolines and spirodihydrobenzofurans (Scheme 1I).^{2–4}

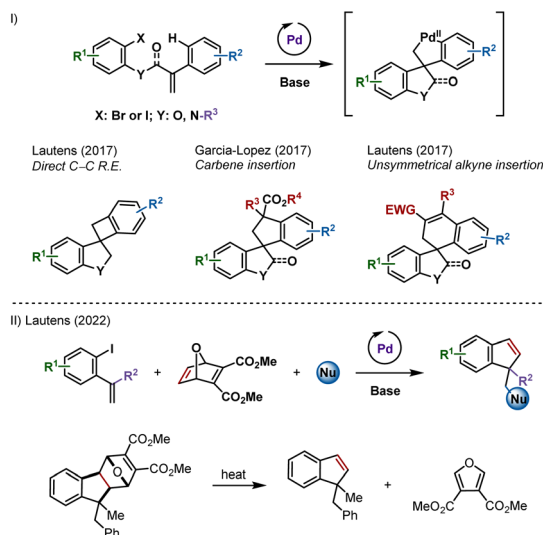
We reported that unsymmetrical polarized alkynes insert into these palladacyclic species (Scheme 1I, right example).^{4f} However, internal symmetrical alkynes failed to react, likely due to a higher activation energy for the requisite insertion step.⁵ Acetylene, the simplest symmetrical alkyne, was not studied as a potential partner out of concerns for side reactions.

Recently, we described a palladium-catalyzed multicomponent synthesis of indenenes and benzofulvenes, using an oxabicyclic as an acetylene surrogate, *via* a post-catalytic retro-Diels–Alder reaction (Scheme 1II).⁶ Acetylene itself is not well-suited for metal-catalyzed domino processes due to difficulty in handling and has reactive C–H groups that can be favoured over addition to the π -bond.⁷ Herein, we report the synthesis of spirocycles resulting from formal acetylene insertion using this strategy.

Results and discussion

Reaction optimization

Reacting aryl iodide **1** with oxabicyclic **2**, catalytic Pd(PPh₃)₄, base (Cs₂CO₃) in toluene at 120 °C for 16 h gave the desired product **3a** in 55% yield (Table 1, entry 1). Reaction at higher concentration (0.2 M) was detrimental to the transformation, giving **3a** in 47% yield (entry 2). Conversely, diluting the mixture to 0.05 M resulted in an improved yield of 69% (entry 3). Conducting the reaction at 130 °C led to a dramatic increase in product formation, and **3a** was isolated in 75% yield (entry 4). The combination of higher temperature and lower concentration proved to be best, leading to the product in 85% yield (entry 5). Further reducing the catalyst loading from **10** to 7.5 mol% furnished the desired spirooxindole in an optimized isolated yield of 88% (entry 6).



Scheme 1 (I) Palladium-catalyzed spirocyclizations *via* remote C–H activation. (II) Palladium-catalyzed synthesis of indenenes and benzofulvenes using an oxabicyclic as an acetylene surrogate.

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Table 1 Optimization of reaction conditions

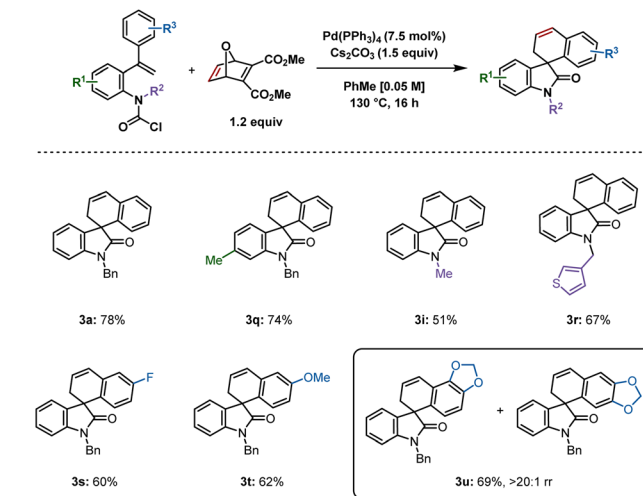
Entry	Variation	Yield ^a (%)
1	None	59 (55) ^b
2	PhMe [0.2 M]	47
3	PhMe [0.05 M]	69
4	130 °C	75
5	PhMe [0.05 M], 130 °C	85
6	Pd(PPh ₃) ₄ (7.5 mol%), PhMe [0.05 M], 130 °C	92 (88) ^b

^a Reactions were performed on a 0.2 mmol scale; yields were determined by ¹H NMR spectroscopy analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

^b Isolated yield.

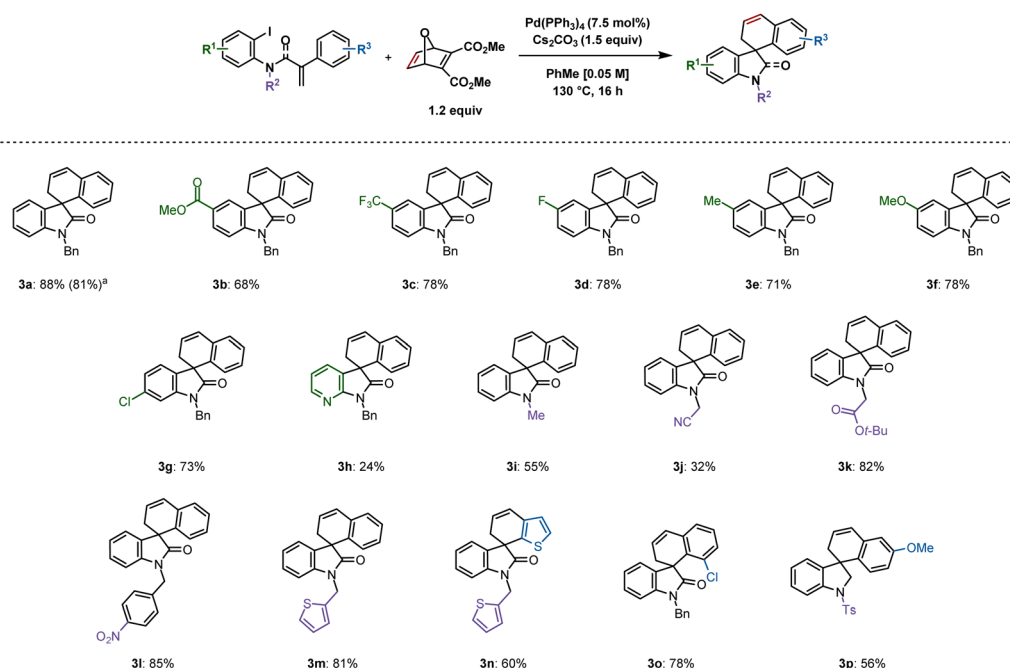
Substrate scope

Following optimization, an exploration of the substrate scope was undertaken by varying the substituents on the iodoarene ring (Scheme 2). A variety of 5-substituted spirooxindoles were formed following this protocol: **3b** (methoxycarbonyl), **3c** (trifluoromethyl), **3d** (fluoro), **3e** (methyl) and **3f** (methoxy) were synthesized in yields ranging from 68 to 78%. A chloro substituent on the 6-position resulted in 73% yield (**3g**). A more challenging substrate containing a pyridine moiety resulted in the corresponding spirooxazaindole (**3h**) in only 24% yield. Modifying substituents on the nitrogen atom was also explored. Less

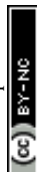


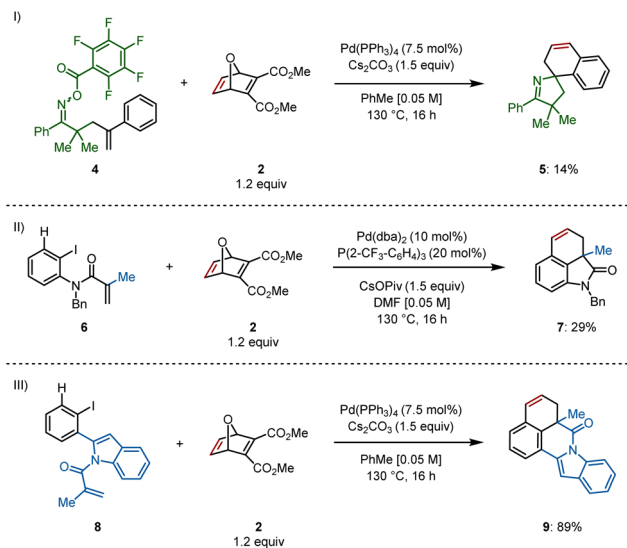
Scheme 3 Spirooxindoles synthesized from carbamoyl chlorides. Reactions were performed on a 0.2 mmol scale; isolated yields are shown.

steric bulk seemed to disfavour the desired reactivity, as the relatively small methyl and cyanomethyl groups gave the products in 55% (**3i**) and 32% (**3j**) yields respectively. In contrast, a yield of 82% was obtained with the *tert*-butyl-ester derivative **3k**. A substrate bearing a nitro group reacted, generating **3l** in 85% yield. Thiophene-derived compounds **3m** and **3n** were both generated in good yields of 81% and 60%, the latter resulting from C–H activation at the 3-position of the corresponding substrate's tethered thiophene ring. An *ortho*-chloro group on the aryl ring undergoing C–H activation gave rise to **3o** in 78% yield.



Scheme 2 Spirooxindoles synthesized from aryl iodides. Reactions were performed on a 0.2 mmol scale; isolated yields are shown. ^aReaction was performed on a 1 mmol scale.





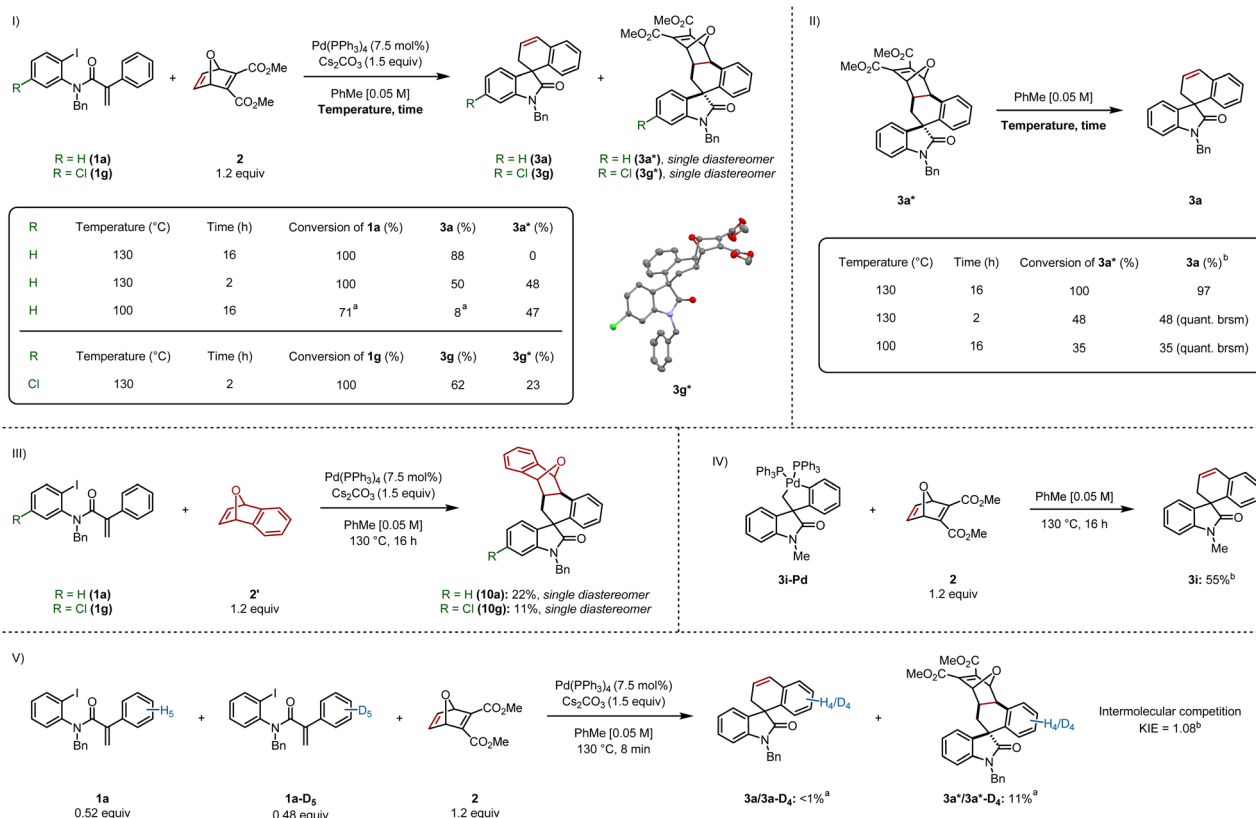
Scheme 4 Synthesis of analogous azacycles. (I) Spirocyclic pyrroline. (II) Dihydrobenzindolone. (III) Indolo[2,1-a]isoquinolinone. Reactions were performed on a 0.2 mmol scale; isolated yields are shown.

A 1 mmol scale reaction of **1a** was performed, which provided **3a** in 81% yield. We were also able to synthesize spiroindoline **3p** in 56% yield from the corresponding

sulfonamide. Unfortunately, spirodihydrobenzofurans could not be accessed using this methodology (see ESI† for unsuccessful substrates).

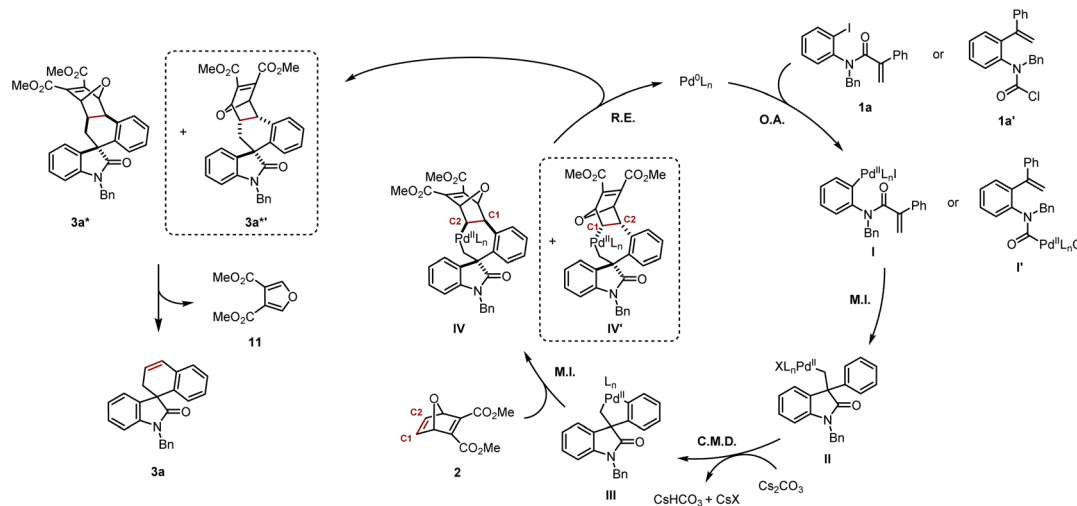
Based on our studies using carbamoyl chlorides as reactive precursors,⁸ and those of Qu and Chen, wherein carbamoyl chlorides were used to access spirooxindoles following insertion of benzyne or an unsymmetrical alkyne,⁹ we attempted to synthesize **3a** using the previously optimized reaction conditions (Scheme 3). The product was isolated in 78% yield, which was comparable to that reported from the aryl iodide **1**. A methyl group at the 6-position generated **3q** in 74% yield. The smaller the substituent on the nitrogen, the lower the yield, as demonstrated by isolation of **3i** in 51% yield, whereas 3-thiophene derivative **3r** was produced in 67% yield. Fluoro and methoxy substituents at the *para* position of the aryl ring undergoing C–H activation gave similar yields of **3s** (60%) and **3t** (62%) respectively. Interestingly, a benzodioxol-derived substrate provided **3u** in 69% yield in >20:1 rr, the major regioisomer resulting from C–H activation at the benzodioxole moiety's 6-position. This result is in contrast to a related example in our previous report on benzyne insertion,^{4c} where the major spirodihydrobenzofuran resulted from C–H activation at the 4-position (6.7:1 rr).

Access to different types of scaffolds *via* insertion of oxabicyclo **2** was also of interest. The spirocyclic pyrroline **5** was



Scheme 5 Mechanistic studies. (I) Isolation of pre-retro-Diels–Alder intermediates **3a*** and **3g***. (II) Confirmation of **3a*** as a precursor to **3a**. (III) Insertion of an oxabicyclo that cannot undergo a retro-Diels–Alder step. (IV) Palladacycle **3i-Pd** as a competent intermediate in the catalytic cycle. (V) KIE experiment. Reactions were performed on a 0.2 mmol scale; isolated yields are shown. ^aYield was determined by ¹H NMR spectroscopic analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. ^bReaction was performed on a 0.1 mmol scale.





Scheme 6 Proposed mechanism.

formed, though only in 14% yield, from γ,δ -unsaturated oxime ester **4** through a domino Narasaka–Heck/C–H activation reaction (Scheme 4I).¹⁰ Spirocyclic synthesis is only feasible *via* remote C(sp²)–H activation, that is, when an aryl ring is bound to the alkene on the starting material, allowing for formation of a spiropalladacycle. In the absence of the aryl group on the alkene, the only C(sp²)–H bond available is located at the *ortho* position of the aryl iodide, providing a fused palladacycle and ultimately, fused rings following insertion of an unsaturated system.¹¹

For example, methyl-derived **6** provided dihydrobenzoindolone **7** in 29% yield (Scheme 4II, see ESI† for optimization) and indole-derived substrate **8** delivered indolo [2,1-*a*]isoquinolinone **9** in 89% yield using the standard reaction conditions (Scheme 4III).¹² This final example demonstrates successful formation of a six-membered N-heterocycle prior to C–H activation and insertion into the π system of the oxabicyclic.

Mechanistic studies

Based on our previous work on the synthesis of indenes,⁶ we set out to isolate the pre-retro-Diels–Alder intermediate, by stopping the reaction after less time elapsed. In a parallel experiment, the reaction was run at a lower temperature (Scheme 5I). Stopping the reaction after 2 h formed the final product **3a** and intermediate cycloadduct **3a*** in 50% and 48% yields respectively. Running the reaction at 100 °C led to incomplete conversion of **1a**, resulting in the formation of **3a** in 8%, as judged by ¹H NMR, whereas **3a*** was formed in 47% yield. We dissolved cycloadduct **3a*** in toluene followed by heating at 130 °C for 16 h, which led to full conversion and provided **3a** in 97% yield (Scheme 5II). This experiment also suggests that heat is solely responsible for the retro-Diels–Alder step (see ESI† for control experiments). We also heated **3a*** at 130 °C for only 2 h, and separately, at 100 °C for 16 h, which resulted in 48% and 35% consumption of **3a***, providing **3a** in quantitative yield (based on recovered starting material).

Interestingly, **3a*** was isolated as a single diastereomer. The relative configuration between the spirocenter and the four stereocenters on the oxabicyclic moiety was elucidated *via* single crystal X-ray diffraction of an analogous chlorinated compound **3g*** (Scheme 5I), which revealed the aryl backbone is on the same side of the bridging oxygen.

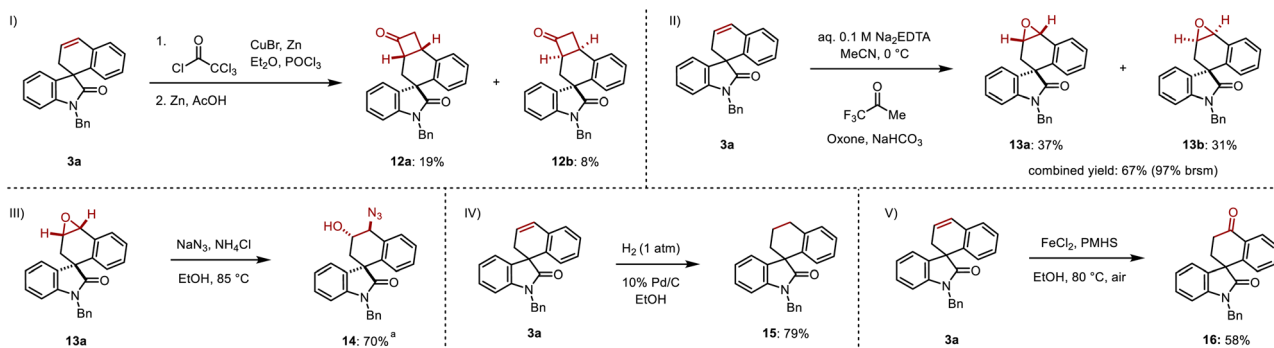
We sought to generate an adduct that was unable to undergo the retro-Diels–Alder step (Scheme 5III).¹³ Spirooxindoles **10a** and **10g** were formed by reacting **1a** and **1g** respectively with benzooxabicyclo **2'**, which were generated as a single diastereomer.

We independently synthesized palladacycle **3i-Pd** and reacted it with **2**, providing **3i** in 55% yield, confirming that the five-membered palladacycle is a competent intermediate in the catalytic cycle (Scheme 5IV). Based on this experiment, and other reports,^{4c,4f,5} we suggest that C–H activation precedes oxabicyclic insertion.

An intermolecular competition experiment was carried out between **1a** and **1a-D₅** with a reaction time of 8 minutes (Scheme 5V). A KIE value of 1.08 was observed, demonstrating C–H activation does not constitute the turnover-limiting step when using an aryl iodide as the substrate (see ESI† for the analogous carbamoyl chloride KIE experiment), which is consistent with previous findings by our group involving benzyne insertion.^{4c}

Based on the mechanistic data presented in Scheme 5, and previous work from our group and others,^{4c,4f,5} a plausible mechanism is shown in Scheme 6. Aryl iodide **1a** or carbamoyl chloride **1a'** would undergo oxidative addition to provide respectively arylpalladium(II) **I** or acylpalladium(II) **I'**. Both of these species converge to the same neopentylpalladium(II) intermediate **II** following intramolecular carbopalladation. Subsequently, a Cs₂CO₃-assisted concerted metalation–deprotonation (CMD) step gives rise to the key five-membered palladacycle **III**. Insertion of the strained alkene in **2** occurs not only in *exo* fashion, but also preferentially into the Csp²–Pd bond, leading to seven-membered palladacycle **IV** with the palladium





Scheme 7 Derivatizations. (I) Ketene [2 + 2] cycloaddition then dehalogenation. (II) Epoxidation. (III) Epoxide ring opening with sodium azide. (IV) Hydrogenation. (V) Iron-catalyzed Wacker oxidation. Reactions were performed on a 0.15 mmol scale; isolated yields are shown. ^aReaction was performed on a 0.029 mmol scale.

atom being bound to the C2 of the oxabicyclic. We cannot at this stage exclude the formation of the *exo*-diastereomer **IV'** with the palladium atom being bound to the C1 of the oxabicyclic resulting from its opposite regioselective insertion into **III**.¹⁴ Reductive elimination closes the catalytic cycle, thereby regenerating Pd(0) and releasing **3a*** and potentially its diastereomer **3a'**. Thereafter, a retro-Diels–Alder process delivers product **3a** and the furan **11**. It is possible that the rate of the retro-Diels–Alder reaction of **3a*** is significantly faster than its analogue **3a'**, which might explain why it was never isolated. However, the experiment at 100 °C/16 h would suggest if **3a'** is formed, it would clearly be the minor diastereomer (Scheme 5I).

The resulting cyclic alkene offers multiple opportunities to further diversify the products. A [2 + 2] cycloaddition between **3a** and *in situ*-formed dichloroketene followed by dehalogenation in the presence of zinc and acetic acid was highly regioselective but gave cyclobutanones **12a** and **12b** in 19% and 8% yields with minimal diastereoselectivity over two steps (Scheme 7I).¹⁵ Epoxidation of **3a** using *in situ*-formed methyl(trifluoromethyl)dioxirane gave the diastereomeric epoxides **13a** and **13b** in 37% and 31% yields respectively, corresponding to a 97% combined yield (based on recovered starting material) (Scheme 7II).¹⁶ A regioselective ring opening of **13a** with sodium azide gave the 1,2-azido alcohol **14** in 70% yield, resulting in a formal difunctionalization of the olefin in **3a** (Scheme 7III). Direct hydrogenation converted **3a** to its saturated spirocyclic analogue **15** in 79% yield (Scheme 7IV). Finally, **3a** was subjected to an iron-catalyzed Wacker oxidation to provide **16** in 58% yield (Scheme 7V).¹⁷

Conclusions

In summary, we have successfully utilized a surrogate to formally insert acetylene in the synthesis of spirooxindoles. Two access points were identified; one using aryl iodides, and the other using carbamoyl chlorides under identical reaction conditions. We determined the oxabicyclic acted as a C2-donor by undergoing a thermal post-catalytic retro-Diels–Alder reaction from the corresponding cycloadduct. Various derivatizations were carried out on the resulting alkene, demonstrating its use as an efficient synthetic handle.

Data availability

All experimental procedures, characterization, and computational data for this study can be found in the ESI†

Author contributions

X. A.-S., and M. L. conceived and led the project. X. A.-S., C. E. J. and B. I. performed the experiments. X. A.-S., C. E. J. and M. L. analyzed the data and discussed the results. X. A.-S. prepared the ESI† and a first draft of the manuscript, which was edited by all authors.

Conflicts of interest

There are no conflicts to declare.

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