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Polycyclic Ring Formation Using Bis-diazolactams for Cascade Stitching

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Supporting Information

ABSTRACT: The chemoselective reaction of donor/acceptor (D/A) and acceptor/acceptor (A/A) diazo moieties in the same molecule was examined using 3-diazo-1-(ethyl 2-diazomalonyl)-indolin-2-one under rhodium(II) catalysis. The metallo carbenoid derived from the D/A diazo group is preferentially formed and undergoes selective CH, NH, and OH insertion reactions, cyclopropanation, cyclopropenation, sulfur ylide formation/2,3-sigmatropic rearrangement, as well as nitrogen ylide formation followed by azetidine ring expansion. The initial reaction can be paired with a subsequent tandem cascade sequence involving dipole formation/cycloaddition in either an intra- or intermolecular sense to generate polycyclic *N*-heterocycles in one pot, with the formation up to three new rings in a single operation. Excellent diastereoselectivity was observed in the intramolecular cycloaddition reaction producing 5 to 7-membered rings.

INTRODUCTION

The total synthesis of alkaloids is an enduring pursuit of organic chemists.[1] These naturally occurring molecules are biologically and structurally intriguing, and they provide both inspiration and a proving ground for development of new reactions.[2] A strategy used in our research group for assembling polycyclic congested natural alkaloids has been to employ the Rh(II)-catalyzed cascade reactions of functionalized diazo compounds.[3] Tandem catalyzed reactions are often designed to exploit both catalyst and reagent selectivity so as to enforce the correct sequence of constituent reactions to produce the desired overall transformation.[4] By this means, cascade chemistry allows for a rapid increase in molecular complexity in a single synthetic step from carefully designed substrates, maximizing bond formations per operation. Over the years we have successfully applied a tandem Rh(II)-catalyzed dipole formation/dipolar cycloaddition strategy to construct complex nitrogen heterocycles in a single operation.[5] For example, a synthesis of the pentacyclic alkaloid (±)-aspidophytine **4** was carried out by making use of the domino dipole cascade sequence.[6] The key sequence of reactions involved a 1,3-dipolar cycloaddition of the "push−pull" dipole **2** derived from lactam **1** across the indole π-system. The *exo*-cycloadduct **3** was the exclusive product formed from the Rh(II)-catalyzed reaction of diazo ketoester **1**. A three-step sequence was then used to reductively open up the oxabicyclic ring system and remove both the ester and OH groups. Subsequent functional group manipulations allowed for the high-yielding conversion of compound **3** into (±)-aspidophytine **4** (Scheme 1).

In order to enhance the versatility of this approach, we sought to introduce a second diazo moiety within the starting material so as to increase the complexity of the Rh(II)-cascade reaction. This could result in the formation of two of the rings of a contiguously fused core in a single step starting from a bis-diazo compound and a bifunctionalized reaction partner. A plethora of possibilities exist for the cascade sequence. Variation of functionality at the tethered reactive site is certainly plausible. Ring size of the final product could also be controlled by simply changing the tether length. Prior to our foray into the cycloaddition chemistry of differentially substituted bis-diazo compounds, we recognized that there were a few isolated examples reported in the literature that were related to this proposition.[7] For example, Moody and Miller studied the OH insertion reaction of methanol with phosphono-diazoesters, such as **5** to give **6**, and noted the selectivity for insertion to take place at the monosubstituted diazo site, leaving the phosphono-diazoester moiety intact (Scheme 2).[8] In 2009, Muthusamy and Srinivasan probed the formal CH insertion

Scheme 1

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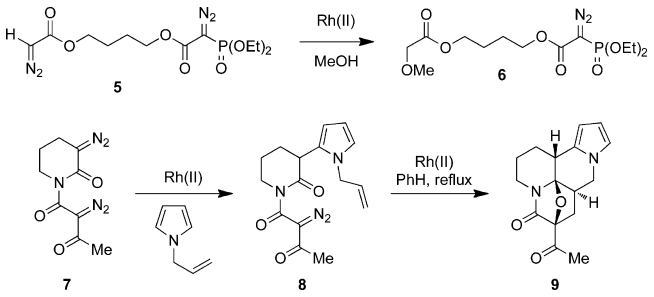
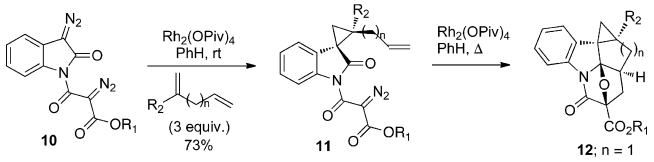
Scheme 2



chemistry of a bis-diazolactam with a *N*-allyl substituted indole and reported an interesting example of insertion into the aromatic framework (**7** → **8**) followed by intramolecular cycloaddition (**8** → **9**) across the tethered π-bond.[9]

In an earlier communication, we disclosed a preliminary study of the cyclopropanation reactions of bis-diazolactams containing both donor−acceptor (D/A) and acceptor-acceptor (A/A) substituted diazo groups.[10a,b] We noted complete selectivity for reaction at the D/A flanked diazo site (Scheme 3). This was followed by intramolecular cycloaddition across

Scheme 3

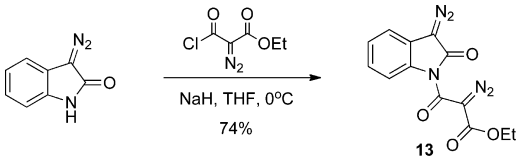


the neighboring π-bond via the 1,3-dipole formed by reaction of the Rh(II)-catalyst with the second diazo group. Herein we report a more detailed description of some cyclopropanations, XH-insertions, Stevens [1,2]-shift of ammonium ylides, and 2,3-sigmatropic rearrangement of sulfonium ylides of several bis-diazolactam systems[11] that we also studied and which produced complex polycyclic structures in a single operation.

RESULTS AND DISCUSSION

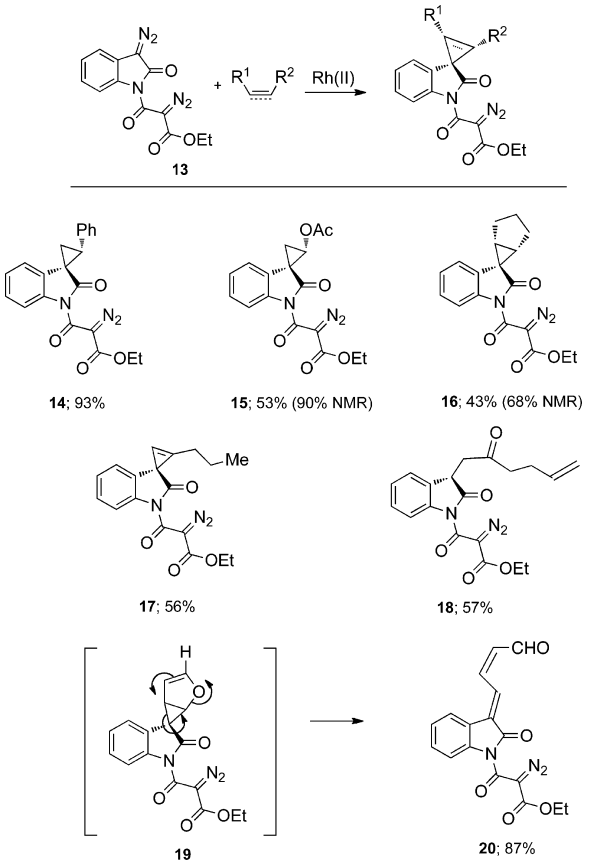
The question of whether it is possible to carry out a number of well-known Rh(II)-catalyzed transformations of a bis-diazolactam is interesting in itself, as there are not many examples of this type of reaction in the literature.[7] We initiated our studies by first examining the Rh(II)-catalyzed chemistry of 3-diazo-1-(ethyl 2-diazomalonyl)-indolin-2-one (**13**) for several reasons. First, it is already known that bis-diazo containing substrates are prone to undergo ring formation through a metathesis reaction at the diazo carbons.[12] By positioning the D/A diazo moiety in a ring having a 1,3-relationship to the other diazo group, ring formation is not geometrically feasible. Moreover, D/A−carbenoids are more easily formed under Rh(II) catalysis than A-carbenoids and they exhibit a substantial difference in reactivity and selectivity in the ensuing chemistry.[13] Thus, we anticipated that the D/A diazo site of **13** should react with the rhodium(II) catalyst much more rapidly than the A/A diazo site,[14] thereby enabling selective reaction of the D/A diazo moiety while the A/A diazo group was expected to remain intact. The 3-diazoindolin-2-one system had been studied previously and was found to perform well using a variety of metallocarbenoid induced reactions.[15] Bis-diazolactam **13** was easily prepared in 74% yield by acylation of the known 3-diazoindolin-2-one[16] with ethyl 2-diazomalonyl chloride,[17] providing **13** in 74% yield (Scheme 4).

Scheme 4



We began our studies by examining the Rh(II)-catalyzed cyclopropanation of **13** with styrene (Scheme 5). A solution of

Scheme 5



bis-diazolactam **13** was added over 1h to a dichloromethane solution containing one equivalent of styrene and a catalytic amount of $Rh_2(OPiv)_4$. The reaction was conducted at 0 °C in order to promote selective decomposition of the more reactive D/A diazo without impacting on the A/A diazo group. Pleasingly, cyclopropane **14** was produced in 93% yield, without any observation of products derived from decomposition at the A/A diazo site. The stereochemical assignment of **14** was based on literature precedent,[18] and was corroborated by the observation that the chemical shift of the proton at the 4-position of the indolinone ring is located at 5.92 ppm, indicative of anisotropic shielding by the *cis* phenyl substituent. Vinyl acetate, an electron deficient cyclopropanation substrate, also underwent the desired reaction in excellent yield as evidenced by ^{1}H NMR analysis of the crude reaction mixture. However, the isolated yield of **15** corresponded to only 53% due to its instability to chromatographic purification.

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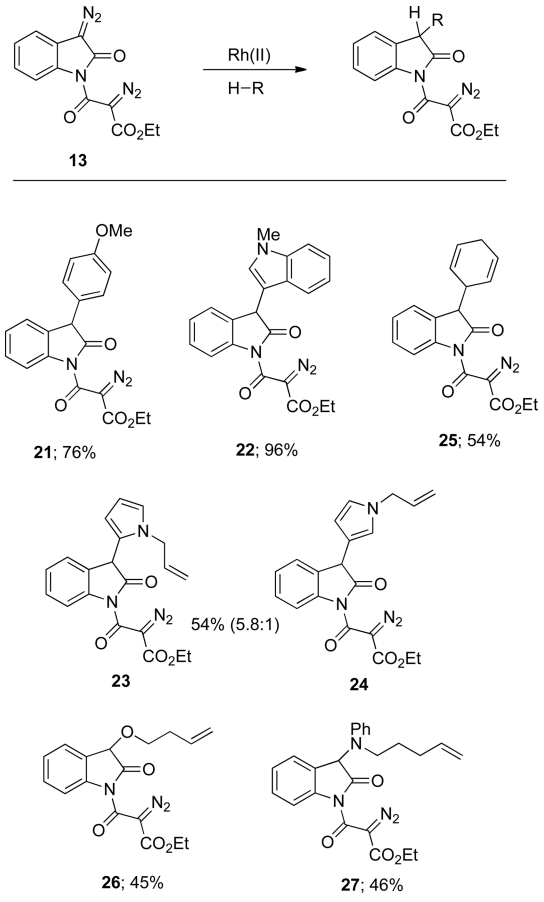
The Rh(II)-catalyzed reaction of **13** with cyclopentene afforded compound **16** in 68% yield by NMR spectroscopy analysis but could only be isolated in 43% yield. Cyclopropenation using an alkyne also occurred, although this somewhat more difficult transformation required that the reaction be performed at room temperature rather than 0 °C.[19] Thus, cyclopropenation of **13** with 1-pentyne at ambient temperature furnished compound **17** in 56% yield, again with no apparent reaction at the A/A diazo location despite the increase in temperature. The reaction of **13** with 2-trimethylsiloxy-1,5-hexadiene gave indolinone **18** in 57% isolated yield by a cyclopropanation/ring opening sequence. We also examined the Rh(II) catalyzed reaction of **13** with furan which afforded **20** in 87% yield. Presumably this reaction also proceeds via an initial cyclopropanation reaction to give **19** as a transient intermediate which was rapidly transformed into **20**, a reorganization known to occur with related systems.[20]

We next investigated the possibility that the D/A carbenoid derived from **13** would undergo both CH and XH insertion chemistry (Scheme 6). Indeed CH insertion occurred smoothly

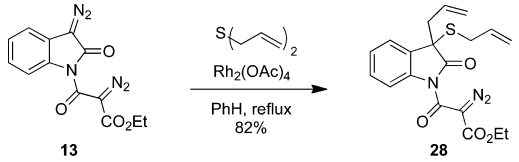
Scheme 6



with anisole and *N*-methylindole, furnishing compounds **21** and **22** in 76% and 96% yield. In the case of anisole, this electron-rich aromatic compound was employed as the solvent. Reaction of **13** with *N*-methylindole proceeded more readily and only three equivalents of the indole was necessary. When *N*-allyl pyrrole was used, the catalyst loading was raised to 1 mol%, and the temperature was increased to reflux in benzene in order to effect complete diazo decomposition. We believe this to be the result of an interaction of the pyrrole with the catalyst in an inhibitory manner. In this case, a 5.8:1 mixture of **23** and **24** was isolated in 54% yield. Although CH insertion reactions with tetrahydrofuran and cyclohexene failed to occur, bis-diazolactam **13** reacted readily with 1,4-cyclohexadiene,[21] to afford the CH-insertion product **25** in 54% yield. Although XH insertion reactions can possibly suffer from catalyst quenching by the heteroatom, we had previously found that OH insertion with **13** and 3-butene-1-ol gave **26** in 45% yield, and NH-insertion took place with *N*-(1-pentene-5-yl)aniline to give **27** in 46% yield.[22]

In contrast to the above observations, the Rh(II)-catalyzed reaction of **13** with allyl sulfide resulted first in sulfonium ylide formation and this was followed by a [2,3]-sigmatropic rearrangement to give compound **28** in 82% yield (Scheme 7). An elevated temperature (80 °C) was required in order to

Scheme 7



effect decomposition of the bis-diazolactam **13** in the presence of allyl sulfide. Electron rich substrates are known to inhibit Rh(II)-catalysis,[23] and the interaction of the sulfur atom with the catalyst could explain the observed temperature effect. Although the A/A-diazo moiety might have been expected to decompose in the presence of $Rh_2(OAc)_4$ at this temperature,[23] compound **28** proved to be stable within the time frame required to consume the starting bis-diazolactam **13**.

After demonstrating that selective cyclopropanation, cyclopropenation, CH and XH insertion, as well as Doyle like reactions[11] of bis-diazolactam **13** proceed by selective D/A-diazo decomposition, we next examined the dipole formation-cycloaddition pathway at the A/A-diazo site. The previously synthesized diazo-cyclopropane **14** was treated with $Rh_2(OPiv)_4$ in the presence of three equivalents of dimethyl acetylenedicarboxylate (DMAD) in benzene at reflux temperature. Under these conditions, cycloadduct **29** was isolated in 59% yield (Scheme 8). The intramolecular dipole/cycloaddition cascade of compound **28** provided cycloadduct **30** in 80% yield. It is notable that the reaction conditions employed for the formation of **30** are identical to those used for the synthesis of **28**, but required prolonged heating (36 h) relative to the more facile formation of **28** (1 h). Indoles **22** and **23** are devoid of a substituent group at the C−3 carbon of the indolinone ring, and therefore there is a possibility that proton elimination can become competitive with cycloaddition once dipole formation occurs.[24] Indeed, in the case using compound **22**, intermolecular dipolar cycloaddition of the resulting 1,3-dipole with DMAD did not occur. Instead, proton transfer of the transient dipole gave the 2,3-dihydrooxazole ring of compound **31** in near quantitative yield. On the other hand, when diazolactam **23** was heated in the presence of the Rh(II)-catalyst, intramolecular dipolar cycloaddition was found to be much faster than proton transfer and cycloadduct **32** was isolated in 79% yield.

At this stage of our studies, we attempted to induce a one-pot multicomponent cyclopropanation/cycloaddition cascade reaction. We were pleased to find that cycloadduct **29** could be obtained in 70% yield from the reaction of bis-diazolactam **13**

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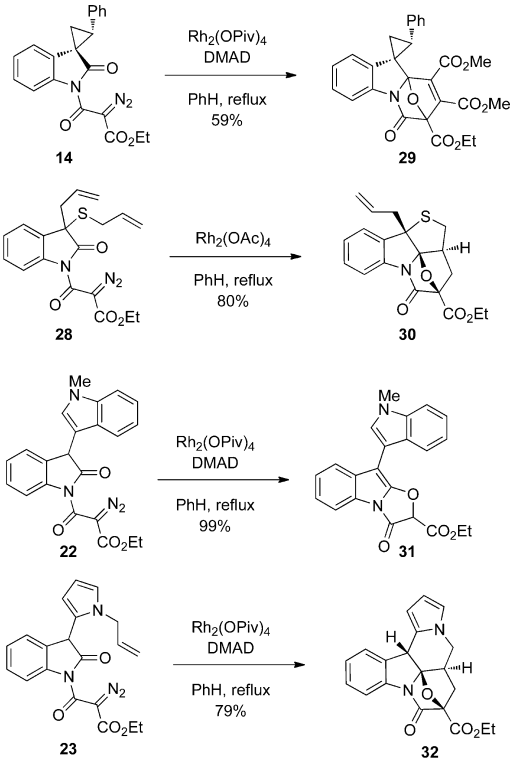
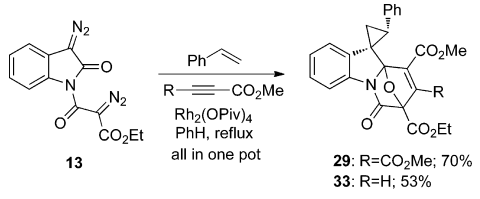
Scheme 8



with a slight excess of styrene and in the presence of three equivalents of DMAD in refluxing benzene (Scheme 9).

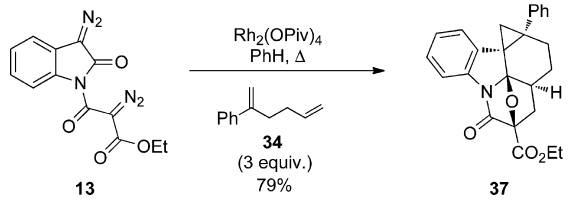
Scheme 9



Changing the acetylenic dipolarophile to the less reactive methyl propiolate, afforded the analogous cycloadduct **30** in 53% yield. In this particular case, the Rh(II)-catalyzed reaction was conducted at an elevated temperature where decomposition of both the diazo groups occur. It is not crystal clear whether selective reaction of the D/A-diazo moiety occurs prior to reaction of the A/A-diazo group at the elevated temperatures employed, though this is most probable.

With this issue in mind, we decided to examine the reaction of bis-diazolactam **13** with 2-phenyl-1,5-hexadiene (**34**) in order to provide some confirmation of the ordering of events in Scheme 9. If the dipole is formed first, it should not result in a bimolecular cycloaddition reaction because the simple terminal alkene is not suitably activated for a dipolar intermolecular cycloaddition reaction, although it can undergo an intramolecular one. When a disubstituted alkene such as **34** is to be employed as the trapping partner, it would be expected that two different stereoisomers would be formed from the cyclopropanation reaction. With 2-phenyl-1,5-hexadiene (**34**) as the reaction partner, the size difference between the phenyl and butenyl groups should first lead to preferential formation of the cyclopropane where the butenyl group is oriented adjacent to the incipient dipole (i.e., compound **35**, *vide infra*). This geometrical arrangement would allow for a subsequent intramolecular cycloaddition in the second step of the cascade. With the other stereoisomer (i.e., compound **36**, *vide infra*), the butenyl group will be oriented away from the incipient dipole, and therefore cannot be a part of the tether for a successful cycloaddition step. What we actually observed was that when the bis-diazolactam **13** was allowed to react with diene **34** using $Rh_2(OPiv)_4$ in refluxing benzene, the only product formed as a single diastereomer was cycloadduct **37** isolated in 73% isolated yield (Scheme 10). The relative stereochemistry of **37** was

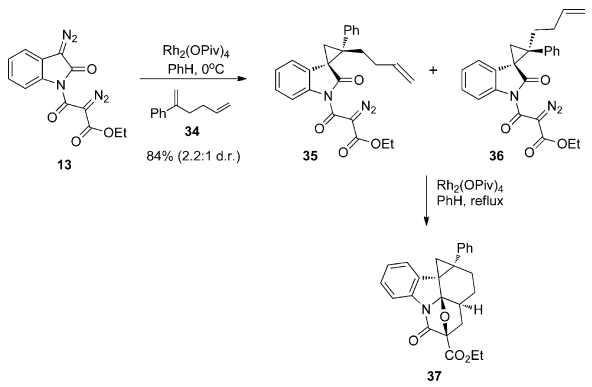
Scheme 10



determined by X-ray crystallographic analysis. The formation of cycloadduct **37** seemingly requires an initial cyclopropanation reaction to produce a cyclopropane with a tethered π-bond correctly oriented and thus the dipolar cycloaddition step must follow after cyclopropanation for these types of cascade reactions.

Interestingly, when the Rh(II)-catalyzed reaction of **13** with diene **34** was carried out at 0 °C, the two expected diastereomeric cyclopropanes (i.e., **35** and **36**) were formed with a combined yield of 84% in a 2.2:1 ratio and cycloadduct **37** was not detected in the reaction mixture (Scheme 11). The

Scheme 11



stereochemistry assignment was based on the upfield shift of the proton at the 4-position of the indolinone ring for diastereomer **35** (δ 5.50) due to anisotropic shielding by the *cis* phenyl group. As expected, diastereomer **35** afforded cycloadduct **37** in 88% yield when heated in refluxing benzene in the presence of the Rh(II) catalyst. What was surprising was that the other diastereomer **36** also produced **37** in a comparable yield when treated under identical conditions.

At first glance it would seem as though the diastereoselectivity of the initial cyclopropanation step involved in the formation of cycloadduct **37** is not important to the outcome of the cycloaddition reaction. The fact that the *cis* diasteromer **36** also produced **37** can best be explained by a thermal isomerization about the cyclopropane ring prior to cyclo-

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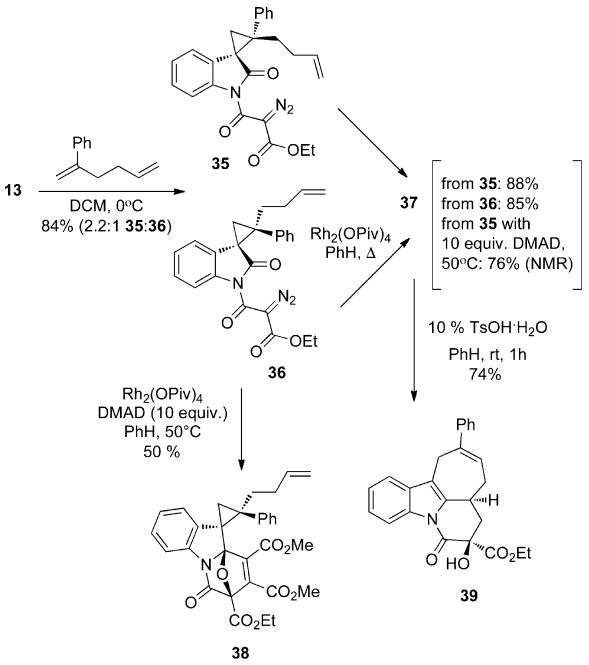
addition step.[25] Furthermore, when the minor diastereomer **36** is treated with the Rh(II) catalyst and 10 equiv of DMAD at 50 °C in benzene, bimolecular cycloaddition with the acetylenic dipolarophile occurred to give **38** as the exclusive product as evidenced by NMR but was only obtained in 50% isolated yield (Scheme 12). In contrast, diastereomer **35** underwent intra-

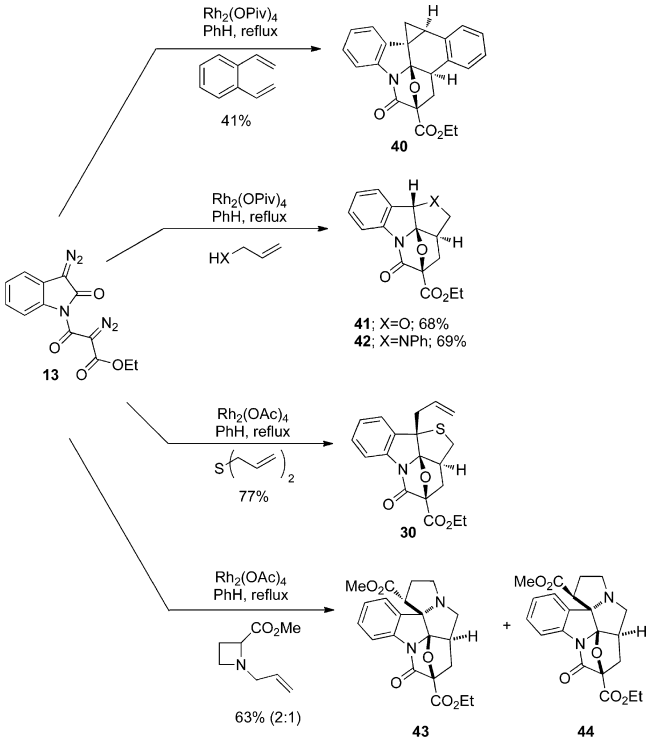
Scheme 12



molecular cycloaddition with the tethered π-bond at a faster rate than the bimolecular reaction with DMAD. This observation provides strong support that cyclopropane isomerization for **36** is necessary for the subsequent intramolecular cycloaddition, and that it occurs at a slower rate than the bimolecular cycloaddition with DMAD. We also noted that the bridging oxabicyclic ring in adduct **37** was easily cleaved in the presence of catalytic acid to give alcohol **39** in 74% yield.

We next conducted a survey of some additional tandem cycloaddition reactions of the bis-diazolactam **13** (Scheme 13). When **13** was treated with *o*-divinylbenzene in the presence of the Rh(II) catalyst at 80 °C, cycloadduct **40** was formed in 41% yield. As was discussed above, epimerization about the initially formed mixture of cyclopropanes is most likely involved in the subsequent production of **40**. Insertion of the carbenoid into an XH group (X = O or N) was also compatible with the tandem process. Thus, OH insertion into allyl alcohol afforded the 5-membered ring ether **41** in 68% yield. The NH insertion reaction with *N*-(1-buten-4-yl)aniline was found to be similarly efficient and produced cycloadduct **42** in 69% yield. Sufonium ylide formation followed by a [2,3]-rearrangement/cycloaddition reaction was carried out as a 1-pot sequence, with **30** being formed in 77% yield, as compared to an overall yield of 65% when the cycloaddition was performed after isolation of the intermediate sulfide **28**. Azetidines are known to react with both A and A/A diazo compounds to afford pyrrolidines as ring expansion products via a transient ammonium ylide.[26] Pleasingly, the reaction of methyl *N*-allyl-azetidine-3-carboxylate with the D/A diazo group in **13** proceeded smoothly to give a 2:1-mixture of hexacyclic amines **43** and **44** in a combined yield of 63%. The stereochemistry of the minor

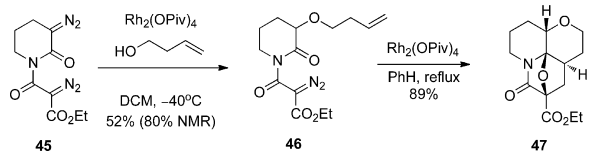
Scheme 13



diastereomer **44** was confirmed by X−ray crystallographic analysis.

Having characterized the major reactions of the D/A, A/A bis(diazo) system **13**, we became interested in exploring whether a related insertion/cycloaddition sequence would occur with other bis(diazo)lactams and chose piperidone **45** for this study. As was the case with bis-diazolactam **13**, the diazo groups are geometrically precluded from an intramolecular methathesis reaction. However, in contrast to **13**, the diazo functionality contained within the piperidone lactam ring of **45** does possess hydrogens alpha to the carbenoid site and this might result in a rapid deprotonation of the metallocarbene intermediate. To probe this possibility, bis(diazo)lactam **45** was easily synthesized from 3-diazo-2-piperidone in 80% yield (Scheme 14) and its subsequent

Scheme 14



chemistry was examined. In order to minimize the chance of deprotonation, we paired bis(diazo)lactam **45** with 3-buten-1-ol since OH insertion reactions with this alcohol was expected to be very facile. The Rh(II)-catalyzed OH insertion using **45** was carried out at −40 °C and the expected insertion product **46** was formed in 60% isolated yield. When **46** was further subjected to the Rh(II)-catalyst in refluxing benzene, a smooth cycloaddition reaction occurred to form tetracycle **47** in 89% yield. This compound was obtained as a single diastereomer, in congruence with the reactions observed with bis(diazo)lactam **13**. There was no evidence of any eliminative quenching of the

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dipole intermediate. Since compound **46** was unstable toward chromatographic purification, we sought to perform the overall transformation of **45** to **47** as a one-pot tandem sequence. However, it was necessary to carry out the cascade reaction in two stages, since the OH insertion reaction of **45** is incompatible with the elevated temperature required to effect the dipolar cycloaddition. After completion of the OH insertion step as evidenced by TLC analysis, benzene was added to the reaction mixture, and the solution was heated to reflux in the presence of the catalyst to effect the dipole formation/cycloaddition cascade, producing **47** in 89% yield by NMR analysis.

In summary, we have investigated the tandem cascade chemistry of two different bis(diazo)lactams with a variety of reaction partners. These unique molecules undergo preferential reaction at the cyclic D/A or A-diazo site under Rh(II) catalysis, and the ensuing transient metallocarbenoid undergoes CH, NH, and OH insertion reactions, cyclopropanation, cyclopropenation, sulfur ylide formation/2,3-sigmatropic rearrangement, as well as nitrogen ylide formation followed by azetidine ring expansion. This initial reaction can be paired with a subsequent tandem cascade sequence involving dipole formation/cycloaddition in either an intra- or intermolecular sense to generate polycyclic *N*-heterocycles in one pot, with the formation up to three new rings in a single operation. Excellent diastereoselectivity was observed in the intramolecular cycloaddition reaction producing 5 to 7-membered rings. In the case of the cyclopropanation/cycloaddition sequence with aryl alkenes, stereoconvergence due to a cyclopropane epimerization during the dipole formation step yields the cycloadducts as single diastereomers.

EXPERIMENTAL SECTION

General Procedures. Melting points are uncorrected. Mass spectra were determined at an ionizing voltage of 70 eV. The mass analyzer type used for the HRMS measurements was TOF with electrospray as the ionization method. Unless otherwise noted, all reactions were performed in flame-dried glassware under an atmosphere of either dry nitrogen or argon. All solvents were distilled prior to use. Solutions were evaporated under reduced pressure with a rotary evaporator and the residue was chromatographed on a silica gel column (0.04−0.062 mm) using an ethyl acetate/hexane mixture as the eluent. All solids were recrystallized from ethyl acetate/hexane for analytical data. Yields refer to isolated, spectroscopically pure compounds.

2-Phenyl-1′-(ethyl diazomalonyl)spiro[cyclopropane-1,3′-indolin]-2′-one (14). A catalytic amount (0.3 mg) of $Rh_2(OPiv)_4$, dichloromethane (1.0 mL) and styrene (11.5 μL, 0.1 mmol) was cooled in an ice/water bath, and a solution of 1-(ethyl diazomalonyl)-3-diazoindolin-2-one (**13**)[16] (30 mg, 0.1 mmol) in dichloromethane (1.0 mL) was added over 1 h via a syringe pump. The resulting pale yellow solution was concentrated under reduced pressure and purified by flash column chromatography to give 35 mg (93%) of the titled compound **14** as a white solid, mp 48−51 °C; IR (KBr) 2983, 2931, 2137, 1724, 1659, 1604, 1481, and 1465 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, 3H, *J* = 7.1 Hz), 2.04 (dd, 1H, *J* = 8.2, 4.8 Hz), 2.26 (dd, 1H, *J* = 9.2,4.7 Hz), 3.34 (t, 1H, *J* = 8.7 Hz), 4.28 (q, 2H, *J* = 7.1 Hz), 5.92 (d, 1H, *J* = 7.6 Hz), 6.75 (t, 1H, *J* = 7.5 Hz), 7.13 (t, 1H, *J* = 7.9 Hz), 7.16−7.19 (m, 2H), 7.22−7.30 (m, 3H), and 7.62 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 23.9, 33.9, 38.4, 62.2, 72.5, 113.7, 120.9, 124.1, 126.9, 127.1, 128.0, 128.7, 130.3, 134.3, 139.6, 160.5, 160.8, and 175.4; HRMS calcd for $[C_{21}H_{17}N_3O_4+H^+]$: 376.1292; found: 376.1295.

2-Acetoxy-1′-(ethyl diazomalonyl)spiro[cyclopropane-1,3′-indolin]-2′-one (15). 2-Acetoxy-1′-(ethyl diazomalonyl)spiro-[cyclopropane-1,3′-indolin]-2′-one was prepared in a similar manner to give 48 mg (53%) of **15** as a thick oil; IR (film) 2984, 2141, 1755, 1702, 1661, 1610, and 1466 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, 3H, *J* = 7.1 Hz), 1.95 (dd, 1H, *J* = 6.4, 5.5 Hz), 2.03 (s, 3H), 2.19 (t, 1H, *J* = 6.8 Hz), 4.25−4.34 (m, 2H), 4.71 (dd, 1H, *J* = 7.0, 5.4 Hz), 6.98 (d, 1H, *J* = 7.4 Hz), 7.14 (t, 1H, *J* = 7.1 Hz), 7.31 (t, 1H, *J* = 7.7 Hz), and 7.69 (d, 1H, *J* = 8.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 20.6, 22.3, 32.9, 61.0, 62.3, 72.3, 114.5, 120.7, 124.6, 125.3, 128.0, 140.1, 160.1, 160.8, 170.1, and 173.5; HRMS calcd for $[C_{17}H_{15}N_3O_6+H^+]$: 358.1039; found: 358.1038.

3′-Spiro[bicyclo[3.1.0]heptane-6,3′-indolin]-2′-one (16). This compound was prepared in a similar manner to give 49 mg (43%) of **16** as a white solid; mp 100−101 °C; IR (KBr) 2958, 2876, 2134, 1727, 1658, 1607, and 1463 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, 3H, *J* = 7.2 Hz), 1.89−2.11 (m, 3H), 2.21−2.32 (m, 3H), 2.52−2.57 (m, 2H), 4.27 (q, 2H, *J* = 7.2 Hz), 6.89 (d, 1H, *J* = 7.5 Hz), 7.17 (t, 1H, *J* = 7.4 Hz), 7.31 (t, 1H, *J* = 8.0 Hz), and 7.75 (d, 1H, *J* = 8.1 Hz); ^{13}C NMR (100 MHz,$CDCl_3$) δ 14.5, 24.8, 29.0, 40.9, 62.1, 114.3,, 121.9, 124.2, 126.4, 126.9, 140.5, 160.8, and 174.5; HRMS calcd for $[C_{18}H_{17}N_3O_4+H^+]$: 340.1292, found: 340.1293.

2-Propyl-1′-(ethyl diazomalonyl)spiro[cyclopropene-1,3′-indolin]-2′-one (17). To a mixture containing dichloromethane (1.0 mL), 1-pentyne (30 μL, 0.30 mmol), and a catalytic amount of $Rh_2(OAc)_4$ (0.2 mg) was added a solution of bis-diazolactam **13** (30 mg, 0.1 mmol) in dichloromethane (1.0 mL) via a syringe pump over 3 h at rt. The resulting yellow solution was concentrated under reduced pressure and purified by flash column chromatography to give the titled compound **17** (56%) as a yellow gum; IR (neat) 3126, 2964, 2873, 2132, 1727, 1652, 1608, and 1462 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, *J* = 7.4 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.61 (sextet, *J* = 7.4 Hz, 2H), 2.54 (t, *J* = 7.3 Hz, 2H), 4.34−4.21 (m, 2H), 6.43 (s, 1H), 6.88 (d, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.26 (t, *J* = 7.8 Hz, 1H), and 7.69 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 14.5, 20.6, 26.1, 34.4, 62.0, 72.2, 92.3, 114.2, 114.5, 119.8, 124.6, 127.3, 131.4, 138.9, 160.6, 160.9, and 177.1; HRMS calcd for $[C_{18}H_{17}N_3O_4+Na^+]$: 362.1111; found; 362.1112.

1-(Ethyl diazomalonyl)-3-(5-hexen-2-one-1-yl)indolin-2-one (18). A sample of 2-trimethylsiloxy-1,5-hexadiene[27] (46 mg, 0.3 mmol), benzene (1.0 mL), and 0.3 mg of $Rh_2(OPiv)_4$ was heated to reflux and then a solution of **13** (30 mg, 0.10 mmol) in benzene (1.0 mL) was added over a 1 h period via syringe at 80 °C. The solution was concentrated under reduced pressure and purified by flash column chromatography to give 19 mg (57%) of the titled compound **18** as a pale yellow oil: IR (film) 3079, 2981, 2909, 2141, 1718, 1661, 1608, 1481, and 1465 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7.2 Hz, 1H), 1.31 (t, *J* = 7.2 Hz, 1H), 2.37−2.30 (m, 2H), 2.59−2.53 (m, 2H), 3.01 (dd, *J* = 18.3, 7.7 Hz, 1H), 3.24 (dd, *J* = 18.3, 3.7 Hz, 1H), 4.03 (dd, *J* = 7.6, 3.5 Hz, 1H), 4.29 (ABX_3, 2H, $\Delta\delta_{AB}$ = 0.02, J_{AB} = 10.5 Hz, J_{AX} = J_{BX} = 7.4 Hz), 5.05−4.96 (m, 2H), 5.77 (ddt, *J* = 16.8, 10.6, 6.6 Hz, 1H), 7.14 (ABX, 2H, $\Delta\delta_{AB}$ = 0.06, J_{AB} = 7.2 Hz, J_{AX} = 0, J_{BX} = 7.4 Hz), 7.29 (t, *J* = 7.6 Hz, 1H), and 7.61 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 27.8, 41.7, 41.9, 43.9, 62.2, 72.6, 114.1, 115.9, 124.0, 125.0, 128.2, 128.6, 136.8, 140.1, 160.2, 160.7, 176.6, and 206.5; MS calcd for $[C_{19}H_{19}N_3O_5+H^+]$: 370.1403; found; 370.1407.

1-(Ethyl diazomalonyl)-3-((2*Z*)-2-butenalidene)indolin-2-one (20). 1-(Ethyl diazomalonyl)-3-((2*Z*)-2-butenalidene)indolin-2-one (**20**) was prepared according to the general procedure described above and was obtained as a thick oil in 87% yield; IR (film) 3057, 2982, 2854, 2138, 1724, 1667, 1598, and 1462 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, *J* = 7.1 Hz, 3H), 4.29 (q, *J* = 7.1 Hz, 2H), 6.34 (dd, *J* = 11.1, 8.1 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.79 (dd, *J* = 13.1, 11.2 Hz, 1H), 8.09 (d, *J* = 13.3 Hz, 1H), and 10.46 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 62.3, 72.8, 114.8, 121.9, 124.9, 125.2, 127.9, 130.7, 131.6, 135.1, 138.1, 140.9, 160.3, 160.5, 166.2, and 189.9; HRMS calcd for $[C_{17}H_{13}N_3O_5+H^+]$: 340.0928; found: 340.0929.

1-(Ethyl 2-diazomalonyl)-3-(4-methoxyphenyl)indolin-2-one (21). To a mixture containing a catalytic amount (0.3 mg) of $Rh_2(OPiv)_4$, and anisole (1.0 mL) was added a solution of bis-

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diazolactam **13** (30 mg, 0.10 mmol) in anisole (1.0 mL) over 1 h via a syringe pump. The solution was concentrated under reduced pressure to give a thick oil which was purified by flash column chromatography to afford 29 mg (76%) of **21** as a pale yellow gum; IR (film) 2981, 2837, 2139, 1754, 1725, 1652, 1608, and 1511 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.17 (t, 3H, J = 7.1 Hz), 3.78 (s, 3H), 4.16 (ABX_3, 2H, $\Delta\delta_{AB}$ = 0.06, J_{AB} = 10.7 Hz, J_{AX} = J_{BX} = 7.1 Hz), 4.73 (s, 1H), 6.84−6.89 (m, 4H), 7.09−7.37 (m, 1H), and 7.67 (d, 1H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 52.0, 55.5, 62.2, 114.3, 114.6, 125.3, 125.4, 128.0, 128.6, 128.8, 130.0, 140.2, 159.6, 160.6, 160.7, and 175.0; HRMS calcd for $[C_{20}H_{17}N_3O_5+H^+]$: 380.1241; found: 380.1240.

1-(Ethyl 2-diazomalonyl)-3-(indole-3-yl)indolin-2-one (22). 1-(Ethyl 2-diazomalonyl)-3-(indole-3-yl)indolin-2-one (**22**) was prepared in a similar manner (39 mg, 96%) and obtained as a white solid, mp 70−71 °C; IR (KBr) 3053, 2981, 2137, 1725, 1606, and 1478 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.16 (t, 3H, J = 7.1 Hz), 3.75 (s, 3H), 4.12 (ABX_3, 2H, $\Delta\delta_{AB}$ = 0.03, J_{AB} = 10.7 Hz, J_{AX} = J_{BX} = 7.1 Hz), 5.08 (s, 1H), 6.99 (s, 1H), 7.04 (t, 1H, J = 7.5 Hz), 7.13 (t, 1H, J = 7.5 Hz), 7.19−7.25 (m, 2H), 7.26−7.31 (m, 2H), 7.35 (t, 1H, J = 7.8 Hz), and 7.73 (d, 1H, J = 8.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.3, 33.1, 45.1, 62.1, 108.8, 109.7, 114.3, 119.5, 119.8, 122.4, 125.2, 126.9, 128.3, 128.6, 128.7, 137.5, 140.0, 160.7, 160.8, and 175.2; HRMS calcd for $[C_{22}H_{18}N_4O_4+H^+]$: 403.1401; found: 403.1404.

1-(Ethyl 2-diazomalonyl)-3-(*N*-allylpyrrole-2-yl)indolin-2-one (23) and 1-(Ethyl 2-diazomalonyl)-3-(*N*-allylpyrrole-3-yl)indolin-2-one (24). A mixture of *N*-allylpyrrole (13 mg, 0.12 mmol), benzene (1.0 mL), and a catalytic amount (0.5 mg) of $Rh_2(OPiv)_4$ was heated to reflux and then a solution of **13** (30 mg, 0.10 mmol) in benzene (1.0 mL) was added via a syringe pump. The solution was subjected to flash column chromatography to give 18 mg (47%) of **23**, followed by 2.5 mg (7%) of **24** as clear oils; Compound **23**: IR(neat) 2981, 2138, 1752, 1726, 1699, 1607, 1480, and 1463 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.17 (t, 3H, J = 7.1 Hz), 4.15 (ABX_3, 2H, $\Delta\delta_{AB}$ = 0.08, J_{AB} = 10.7 Hz, J_{AX} = J_{BX} = 7.1 Hz), 4.52 (d, 1H, J = 16.6 Hz), 4.76 (dd, 1H, J = 16.6, 5.6 Hz), 4.92 (s, 1H), 4.99 (d, 1H, J = 17.3 Hz), 5.18 (d, 1H, J = 10.2 Hz), 5.91 (s, 1H), 5.91−6.02 (m, 1H), 6.08 (t, 1H, J = 3.2 Hz), 6.69−6.70 (m, 1H), 7.19 (t, 1H, J = 7.5 Hz), 7.27 (d, 1H, J = 7.5 Hz), 7.36 (t, 1H, J = 7.9 Hz), and 7.65 (d, 1H, J = 8.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 45.1, 50.1, 62.3, 107.8, 109.5, 114.2, 117.1, 123.1, 125.2, 125.5 125.6, 127.1, 129.0, 134.6, 140.1, 160.6, and 160.8, 173.6

Compound **24**: IR (film) 2982, 2924, 2140, 1756, 1729, 1656, 1607, 1479, and 1464 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.22 (t, 3H, J = 7.1 Hz), 4.22 (ABX_3, 2H, $\Delta\delta_{AB}$ = 0.05, J_{AB} = 10.8 Hz, J_{AX} = J_{BX} = 7.1 Hz), 4.42 (d, 2H, J = 5.9 Hz), 4.75 (s, 1H), 5.14 (d, 1H, J = 17.0 Hz), 5.19 (d, 1H, J = 10.2 Hz), 5.91−5.98 (m, 1H), 6.07−6.08 (m, 1H), 6.58−6.59 (m, 1H), 6.60−6.62 (m, 1H), 7.18 (t, 1H, J = 7.6 Hz), 7.30−7.34 (m, 1H), and 7.66 (d, 1H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 25.9, 52.5, 62.2, 108.3, 114.2, 117.5, 118.1, 119.8, 121.6, 125.0, 125.2, 128.4, 129.1, 134.2, 140.0, 160.7, 160.8, and 175.5.

3-(1,4-Cyclohexadien-3-yl)-1-(ethyl 2-diazomalonyl)indolin-2-one (25). To a mixture of $Rh_2(OPiv)_4$ (1 mg, 0.002 mmol), dichloromethane (1.0 mL), and 1,4-cyclohexadiene (95 μL, 1.0 mmol) was added a solution of **13** (30 mg, 0.10 mmol) in benzene (1.0 mL) over 1 h via a syringe pump. After heating at reflux for 3 h the solution was concentrated under reduced pressure to give 19 mg (54%) of the titled compound **25** as a white solid, mp 81−83 °C; IR (KBr) 3021, 2982, 2817, 2136, 1724, 1656, 1607, 1479, and 1464 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.32 (t, 3H, J = 7.1 Hz), 2.49−2.65 (m, 2H), 3.68 (d, 1H, J = 3.5 Hz) 3.69−3.74 (m, 1H), 4.30 (ABX_3, 2H, $\Delta\delta_{AB}$ = 0.02, J_{AB} = 10.8 Hz, J_{AX} = J_{BX} = 7.1 Hz), 5.45−5.50 (m, 1H), 5.66−5.71 (m, 1H), 5.72−5.76 (m, 1H), 5.93−5.97 (m, 1H), 7.10 (td, 1H, J = 7.6, 0.8 Hz, 1H), 7.28 (t, 1H, J = 7.5 Hz,), 7.37 (d, 1H, J = 7.5 Hz), and 7.59 (d, 1H, J = 8.0 Hz); (150 MHz, $CDCl_3$) δ 14.5, 26.5, 38.7, 50.7, 62.2, 114.0, 123.8, 124.6, 124.7, 126.1, 127.0, 127.6, 128.1, 128.4, 140.3, 160.4, 160.6, and 175.5; HRMS calcd for $[C_{19}H_{17}N_3O_4+H^+]$: 352.1292; found; 352.1293.

3-Allyl-3-allylthio-1-(ethyl 2-diazomalonyl)indolin-2-one (28). A mixture of $Rh_2(OAc)_4$ (0.9 mg, 0.002 mmol), benzene (1.0 mL), and allyl sulfide (14 μL, 0.1 mmol) was heated to reflux and then a solution of **13** (30 mg, 0.10 mmol) in benzene (1.0 mL) was added via a syringe pump. After being heated for an additional 1 h the solution was concentrated under reduced pressure and purified by flash column chromatography to give 32 mg (82%) of the titled compound **28** as a colorless gum; IR (film) 2981, 2136, 1727, 1703, 1659, 1604, 1478, and 1465 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.32 (t, 3H, J = 7.1 Hz), 2.84 (ABX, 2H, $\Delta\delta_{AB}$ = 0.05, J_{AB} = 13.9 Hz, J_{AX} = 7.8 Hz, J_{BX} = 6.6 Hz), 3.08 (dd, 1H, J = 12.9, 6.4 Hz), 3.20 (dd, 1H, J = 12.9, 8.0 Hz), 4.31 (q, 2H, J = 7.1 Hz), 4.93−4.98 (m, 2H), 5.02 (d, 1H, J = 10.0 Hz), 5.06 (d, 1H, J = 16.9 Hz), 5.53 (ddt, 1H, J = 17.1, 10.0, 7.3 Hz), 5.67 (dddd, 1H, J = 16.7, 10.0, 7.9, 6.4 Hz), 7.22 (t, 1H, J = 7.5 Hz), 7.33 (td, 1H, J = 7.8, 1.2 Hz), 7.37 (d, 1H, J = 7.5 Hz), and 7.62 (d, 1H, J = 8.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 32.8, 40.9, 55.1, 62.2, 114.6, 118.6, 120.7, 124.6, 125.4, 128.3, 129.5, 130.8, 133.2, 139.0, 159.9, 160.5, and 175.3; HRMS calcd for $[C_{19}H_{19}N_3O_4S+H^+]$: 386.1169, found: 386.1170.

(2a*S*,2a^1*R*,4*R*,10b*S*)-Ethyl 10*b*-Allyl-5-oxo-2,2*a*,3,4,5,10*b*-hexahydro-2*a*^{1},4-epoxybenzo[*b*] thieno[4,3,2-*hi*]indolizine-4-carboxylate (30). A mixture of $Rh_2(OAc)_4$ (0.9 mg, 0.002 mmol), benzene (1.0 mL), allyl sulfide (14 μL, 0.10 mmol), and bis-diazolactam **13** (30 mg, 0.10 mmol) was heated at reflux for 14 h. The mixture was concentrated under reduced pressure and purified by flash column chromatography to give 28 mg (80%) of the titled compound **30** as a white solid, mp 113−114 °C; IR (KBr) 2980, 1728, 1640, 1604, 1475, and 1444 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.39 (3H, J = 7.2 Hz), 2.21 (dd, 1H, J = 12.8, 4.2 Hz), 2.51 (dd, 1H, J = 12.8, 7.2 Hz), 2.80 (ABX, 2H, $\Delta\delta_{AB}$ = 0.10, J_{AB} = 14.0 Hz, J_{AX} = 6.7 Hz, J_{BX} = 7.7 Hz), 2.91−3.05 (m, 3H), 4.41 (ABX_3, 2H, $\Delta\delta_{AB}$ = 0.06, J_{AB} = 10.8 Hz, J_{AX} = J_{BX} = 7.2 Hz), 5.04 (d, 1H, J = 17.1 Hz), 5.11 (d, 1H, J = 10.0 Hz), 5.90 (ddt, 1H, J = 17.1, 10.0, 7.2 Hz), 7.13 (t, 1H, J = 7.6 Hz), 7.25 (d, 1H, J = 7.6 Hz), 7.30 (t, 1H, J = 7.6 Hz), and 7.39 (d, 1H, J = 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 33.6, 35.9, 42.2, 54.0, 57.1, 62.7, 94.9, 113.9, 114.1, 120.2, 125.4, 126.7, 129.5, 132.8, 132.9, 138.4, 162.0, and 164.6; HRMS calcd for $[C_{19}H_{19}NO_4S+H^+]$: 358.1108, found: 358.1104.

Ethyl 3-oxo-9-(1-Methylindol-3-yl)-2,3-dihydrooxazolo[3,2-*a*]indole-2-carboxylate (31). A mixture of 1-(ethyl 2-diazomalonyl)-3-(indole-3-yl)indolin-2-one (**22**) (25 mg, 0.062 mmol), benzene (1.2 mL), DMAD (23 μL, 0.19 mmol), and $Rh_2(OPiv)_4$ (0.2 mg) was heated at reflux for 1 h. The solution was allowed to cool, concentrated under reduced pressure, and purified by flash column chromatography to give 23 mg (99%) of the titled compound **31** as a pale pink solid, mp 200−201 °C; IR (KBr) 2924, 1752, 1727, 1668, 1611, 1537, and 1458 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.40 (t, 3H, J = 7.1 Hz), 3.88 (s, 1H), 4.34−4.47 (m, 2H), 5.62 (s, 1H), 7.19 (t, 1H, J = 7.2 Hz), 7.27−7.41 (m, 5H), 7.63 (d, 1H, J = 7.7 Hz), 7.89 (d, 1H, J = 7.8 Hz), and 7.92 (d, 1H, J = 8.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 33.2, 63.6, 84.7, 88.1, 104.4, 109.6, 113.6, 119.8, 120.2, 121.1, 122.4, 123.0, 125.7, 126.0, 127.0, 127.2, 135.3, 137.1, 150.8, 159.5, and 163.7; HRMS calcd for $[C_{22}H_{18}N_2O_4+H^+]$: 375.1339, found: 375.1336.

(5a*R*,5a^1*R*,7*R*,13b*R*)-Ethyl 8-oxo-5,5*a*,6,7,8,13b-hexahydro-5*a*^{1},7-epoxyindolo[3,2,1-*ij*]-pyrrolo[1,2-*g*][1,6]naphthyridine-7-carboxylate (32). A mixture containing 1-(ethyl 2-diazomalonyl)-3-(*N*-allylpyrrole-2-yl)indolin-2-one (**23**) (18 mg, 0.048 mmol), benzene (1.0 mL), and $Rh_2(OAc)_4$ (2 mg) was heated at reflux for 12 h. The mixture was allowed to cool to rt, concentrated under reduced pressure, and purified by flash column to give 13 mg (79%) of the titled compound **32** as a white solid, mp 167−168 °C; IR (KBr) 2982, 1732, 1605, 1479, 1464, and 1394 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.39 (t, 3H, J = 7.2 Hz), 2.09 (dd, 1H, J = 13.0, 3.8 Hz), 2.64 (dd, 1H, J = 13.0, 8.0 Hz), 2.71−2.80 (m, 1H), 3.78 (t, 1H, J = 12.2 Hz), 4.21 (dd, 1H, J = 12.4, 5.3 Hz), 4.36−4.48 (m, 2H), 5.00 (s, 1H), 6.19 (t, 1H, J = 3.2 Hz), 6.39 (s, 1H), 6.62 (s, 1H), 7.18 (t, 1H, J = 7.6 Hz), 7.30 (t, 1H, J = 7.7 Hz), 7.41 (d, 1H, J = 7.8 Hz), and 7.60 (d, 1H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 30.9, 39.3, 41.7, 47.8, 62.9, 89.9, 102.9, 106.4, 108.6, 113.8, 120.1, 124.9, 125.4,

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126.6, 129.2, 132.8, 136.1, 164.9, and 165.4; HRMS calcd for $[C_{20}H_{18}N_2O_4+H^+]$: 351.1339; found: 351.1338.

(1′*S*,2′*R*)-7-Ethyl 8,9-dimethyl 6-oxo-2′-phenyl-6,7-dihydrospiro[7,9*a*-epoxypyrido[1,2-*a*]indole-10,1′-cyclopropane]-7,8,9-tricarboxylate (29). A mixture containing $Rh_2(OPiv)_4$ (0.3 mg), benzene (1.0 mL), styrene (35 μL, 0.30 mmol), DMAD (35 μL, 0.30 mmol), and **13** (30 mg, 0.10 mmol) was heated to reflux for 1 h. Concentration under reduced pressure followed by flash column chromatography gave 37 mg (75%) of the titled product **29** as an off-white solid, mp 66−68 °C; IR (KBr) 2986, 2952, 2277, 1724, 1602, 1550, and 1441 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.37 (t, 3H, *J* = 7.1 Hz) 1.99−2.05 (m, 1H), 2.10−2.15 (m, 1H), 3.29 (dd, 1H, *J* = 9.4, 7.3 Hz), 3.77 (s, 3H), 3.91 (s, 3H), 4.31−4.42 (m, 2H), 6.84 (d, 1H, *J* = 7.7 Hz), 6.89−6.95 (m, 2H), 7.00−7.05 (m, 1H), 7.07−7.13 (m, 4H), and 7.46 (dd, 1H, *J* = 7.7, 1.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.3, 20.6, 30.3, 30.7, 52.4, 53.2, 62.0, 115.2, 123.2, 125.5, 126.16, 126.18, 126.8, 127.9, 128.0, 129.1, 130.5, 133.4, 134.7, 136.1, 139.3, 157.2, 161.5, 163.3, and 163.8; HRMS calcd for $[C_{27}H_{23}NO_8+H^+]$: 490.1496; found: 490.1495.

(1′*S*,2′*R*)-7-Ethyl 9-methyl 6-oxo-2′-phenyl-6,7-dihydrospiro[7,9a-epoxypyrido[1,2*a*]-indole-10,1′-cyclopropane]-7,9-dicarboxylate (33). A mixture containing a catalytic amount of $Rh_2(OPiv)_4$ (0.3 mg), benzene (1.0 mL), styrene (13 μL, 0.11 mmol), methyl propiolate (27 μL, 0.3 mmol), and **13** (30 mg, 0.10 mmol) was heated at reflux for 4 h. The solution was concentrated under reduced pressure and purified by flash column chromatography to give 23 mg (53%) of the titled compound **33** as a colorless oil; IR (neat) 2983, 2279, 1717, 1597, and 1538 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.38 (t, 3H, *J* = 7.7 Hz), 2.03 (dd, 1H, *J* = 9.3, 6.0 Hz, 1H), 2.12 (t, 1H, *J* = 6.7 Hz), 3.32 (dd, 1H, *J* = 9.3, 7.3 Hz), 3.80 (s, 3H), 4.32−4.40 (m, 2H), 6.83 (dd, 1H, *J* = 7.7, 1.3 Hz), 6.93−6.97 (m, 2H), 7.07−7.13 (m, 4H), 7.37 (s, 1H), 7.53 (dd, 1H, *J* = 7.6, 1.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 20.7, 30.5, 30.7, 52.0, 61.5, 116.4, 119.2, 123.1, 125.5, 125.9, 126.6, 127.8, 128.0, 128.9, 131.3, 133.5, 134.6, 136.4, 142.5, 158.3, 162.7, and 164.1 HRMS calcd for $[C_{25}H_{21}NO_6+H^+]$: 432.1442, found: 432.1438.

***trans*-2-(1-Buten-4-yl)-2-phenyl-1′-(ethyl diazomalonyl)-spiro[cyclopropane-1,3′-indolin]-2′-one (35) and *cis*-2-(1-Buten-4-yl)-2-phenyl-1′-(ethyl diazomalonyl)spiro-[cyclopropane-1,3′-indolin]-2′-one (36).** These compounds were prepared by using the general procedure described above and purified by flash column chromatography give 174 mg (61%) of the *trans* isomer **35** as a colorless gum and 71 mg (23%) of the *cis* isomer as a white solid. Compound **35**: IR (film) 3059, 2979, 2135, 1724, 1660, 1607, and 1480 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.32 (t, 3H, *J* = 7.2 Hz), 1.94−2.08 (m, 3H), 2.14 (d, 1H, *J* = 4.9 Hz), 2.20 (d, 1H, *J* = 4.9 Hz), 2.44−2.57 (m, 1H), 4.29 (ABX_3, 2H, $\Delta\delta_{AB}$ = 0.08, J_{AB} = 10.7 Hz, J_{AX} = J_{BX} = 7.1 Hz), 4.90−4.99 (m, 2H), 5.50 (d, 1H, *J* = 7.7 Hz), 5.72−5.84 (m, 1H), 6.66 (t, 1H, *J* = 7.7 Hz), 6.75−6.83 (m, 1H), 7.10 (t,1H, *J* = 7.7 Hz), 7.08−7.18 (m, 1H), 7.23−7.30 (m, 1H), 7.44−7.37 (m, 2H), and 7.62 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 30.8, 31.6, 31.8, 32.1, 36.8, 49.1, 62.1, 72.1, 113.2, 115.0, 121.7, 123.5, 126.7, 127.8, 128.2, 128.5, 128.7, 129.7, 131.8, 138.3, 138.7, 139.0, 160.7, 160.8, and 174.7; HRMS calcd for $[C_{25}H_{23}N_3O_4+H^+]$: 430.1761; found: 430.1760.

Compound **36**: mp 120−121 °C; IR (KBr) 3059, 2979, 2925, 2136, 1733, 1698, 1661, 1606, and 1480 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.22 (t, 3H, *J* = 7.1 Hz), 1.81−1.91 (m, 1H), 1.93 (d, 1H, *J* = 5.1 Hz), 1.95−2.10 (m, 3H), 2.48 (d, 1H, *J* = 5.1 Hz), 4.13−4.26 (m, 2H), 4.89−4.97 (m, 2H), 5.67−5.79 (m, 1H), 7.16−7.22 (m, 3H), 7.24−7.36 (m, 5H), and 7.70 (d, 1H, *J* = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 29.8, 31.4, 35.3, 38.2, 48.2, 61.9, 114.5, 115.5, 122.0, 124.1, 127.4, 127.5, 127.6, 128.5, 129.9, 137.8, 138.8, 140.1, 160.0, 160.6, and 172.6; HRMS calcd for $[C_{25}H_{23}N_3O_4+H^+]$: 430.1761; found: 430.1762.

(2a*S*,2a^1*R*,4*R*,10b*S*,11a*R*)-Ethyl 5-oxo-11*a*-phenyl-1,2,2*a*,3,4,5,11,11*a*-octahydro-2*a*^{1},4-epoxycyclopropa[*d*]-pyrido[1,2,3-*lm*]carbazole-4-carboxylate (37). A mixture of 2-phenyl-1,5-hexadiene[28] (106 mg, 0.67 mmol), benzene (1.7 mL), a catalytic amount (0.5 mg) of $Rh_2(OPiv)_4$, and bis-diazolactam **13** (50 mg, 0.17 mmol) was heated at reflux for 1 h. The solution was concentrated under reduced pressure and purified by flash column chromatography to give 54 mg (79%) of the titled compound **37** as a white solid, mp 141−143 °C; IR (KBr) 3055, 2934, 2855, 1745, 1604, 1478, and 1460 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.36 (t, 3H, *J* = 7.1 Hz), 1.26−1.39 (m, 1H), 1.67 (d, 1H, *J* = 6.0 Hz), 1.80−1.89 (m, 1H), 1.95 (dd, 1H, *J* = 13.0, 3.7 Hz), 2.02 (d, 1H, *J* = 6.0 Hz), 1.99−2.09 (m, 1H), 2.24−2.32 (m, 1H), 2.38 (ddd, 1H, *J* = 14.5, 3.9, 2.6 Hz), 2.64 (dd, 1H, *J* = 13.0, 8.0 Hz), 4.38 (ABX_3, 2H, $\Delta\delta_{AB}$ = 0.04, J_{AB} = 11.0 Hz, J_{AX} = J_{BX} = 7.1 Hz), 5.62 (d, 1H, *J* = 7.7 Hz), 6.67 (app t, 1H, *J* = 7.7 Hz), 7.20−7.30 (m, 3H), and 7.39 (d, 1H, *J* = 7.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 18.5, 25.0, 31.4, 33.4, 33.9, 34.6, 40.2, 62.6, 87.2, 102.7, 112.9, 123.1, 123.8, 127.3, 128.7, 130.5, 132.4, 140.0, 141.7, 165.7, and 170.8; HRMS (EI, M+H) calcd for $[C_{25}H_{23}NO_4+H^+]$: 402.1700; found: 402.1701.

(1′*S*,2′*S*,7*R*,9a*S*)-7-Ethyl 8,9-dimethyl 2′-(but-3-en-1-yl)-6-oxo-2′-phenyl-6,7-dihydrospiro[7,9*a*-epoxypyrido[1,2-*a*]-indole-10,1′-cyclopropane]-7,8,9-tricarboxylate (38). A mixture of *cis*-2-(1-buten-4-yl)-2-phenyl-1′-(ethyl diazomalonyl)spiro-[cyclopropane-1,3′-indolin]-2′-one (**36**) (18 mg, 0.042 mmol), benzene (0.84 mL), DMAD (52 μL, 0.42 mmol) and $Rh_2(OPiv)_4$ (0.1 mg) was heated at 50 °C for 3 h. The solution was allowed to cool, concentrated under reduced pressure and purified by flash column chromatography to give 14 mg (50%) of the titled compound **38** as a colorless oil; IR (film) 2951, 2261, 1722, 1603, 1547, and 1440 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 0.92−0.99 (m, 1H), 1.31 (t, 3H, *J* = 7.1 Hz), 1.68 (d, 1H, *J* = 6.2 Hz), 1.83−1.94 (m, 2H), 2.47−2.55 (m, 2H), 3.76 (s, 3H), 3.77 (s, 3H), 4.19−4.30 (m, 2H), 4.77−4.82 (m, 2H), 5.57−5.65 (m, 1H), 7.08−7.15 (m, 2H), 7.16−7.26 (m, 4H), 7.41 (d, 2H, *J* = 7.7 Hz), and 7.77 (d, 1H, *J* = 7.5 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, 50 °C) δ 14.3, 25.3, 31.6, 33.5, 29.8, 52.2, 52.9, 61.6, 114.9, 116.4, 124.4, 125.5, 126.2, 127.1, 127.2, 128.2, 129.2, 129.5, 132.9, 133.3, 134.5, 138.4,139.4,157.0, 161.6, and 163.6; HRMS calcd for $[C_{31}H_{29}NO_8+Na^+]$: 566.1785; found: 566.1790.

(4a*S*,6*R*)-Ethyl 6-hydroxy-7-oxo-2-phenyl-1,4,4*a*,5,6,7-hexahydrobenzo[*b*]cyclohepta-[*hi*]indolizine-6-carboxylate (39). To a solution of compound **37** (54 mg, 0.13 mmol) in benzene (2.7 mL) was added $TsOH·H_2O$ (2.5 mg, 0.013 mmol). The solution was allowed to stir at rt for 1 h and then quenched by the addition of a saturated aqueous sodium bicarbonate. The aqueous layer was extracted with dichloromethane and the combined extracts were washed with water then brine, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. Purification by flash column chromatography gave 45 mg (74%) of the titled compound **39** as a white solid; mp 66−68 °C; IR (KBr) 3550−3300, 2928, 2853, 1739, 1694, 1621, 1460, and 1383 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.24−1.29 (m, 4H), 2.15 (t, 1H, *J* = 13.5 Hz), 2.46−2.59 (m, 2H), 2.66−2.76 (m, 1H), 3.25−3.36 (m, 1H), 3.95 (ABq, 2H, $\Delta\delta_{AB}$ = 0.10, J_{AB} = 19.0 Hz), 4.22−4.32 (m, 2H), 4.41 (s, 1H), 6.23−6.29 (m, 1H), 7.22−7.44 (m, 7H), 7.47−7.54 (m, 1H), and 8.40−8.48 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 27.9, 31.3, 32.8, 39.3, 63.0, 76.5, 114.8, 116.7, 118.1, 124.9, 125.3, 126.3, 127.4, 128.7, 131.2, 134.1, 136.8, 141.9, 143.8, 168.0, and 170.4; HRMS calcd for $[C_{25}H_{23}NO_4+Na^+]$: 424.1519; found: 424.1518.

(2*R*,4^1*R*,8b*S*,9a*S*,13b*R*)-Ethyl 3-oxo-1,2,3,9,9a,13b-hexahydro-2,4^1-epoxybenzo[*b*]cyclo-propa[*d*]pyrido[1,2,3-*lm*]-carbazole-2-carboxylate (40). This compound was prepared using the standard Rh(II)-catalyzed procedure and was purified by flash column chromatography to give 27 mg (41%) of **40** as a white solid, mp 94−95 °C; IR (KBr) 2983, 2254, 1732, 1607, 1485, and 1411 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.36 (t, 3H, *J* = 7.1 Hz), 1.60−1.67 (m, 2H), 2.61 (dd, 1H, *J* = 12.7, 4.7 Hz), 2.73 (dd, 1H, *J* = 8.9, 6.0 Hz), 2.99 (dd, 1H, *J* = 12.7, 8.5 Hz), 3.58 (dd, 1H, *J* = 8.2, 4.8 Hz), 4.38 (ABX_3, 2H, $\Delta\delta_{AB}$ = 0.03, J_{AB} = 10.7 Hz, J_{AX} = J_{BX} = 7.1 Hz), 6.93 (d, 1H, *J* = 7.6 Hz), 7.10−7.14 (m, 2H), 7.21−7.30 (m, 3H), 7.43−7.46 (m, 1H), and 7.48 (d, 1H, *J* = 7.9 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.4, 23.0, 24.5, 26.5, 34.2, 43.9, 62.7, 89.9, 102.9, 113.6, 120.5, 125.1, 127.4, 127.5, 128.3, 130.0, 134.8, 135.1, 135.4, 137.0, 165.2, and 166.7; HRMS calcd for $[C_{23}H_{19}NO_4+H^+]$: 374.1387; found: 374.1390.

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(2a*R*,2a^1*R*,4*R*,10b*S*)-Ethyl 5-oxo-2,2*a*,3,4,5,10b-hexahydro-2a^1,4-epoxybenzo[*b*]furo-[4,3,2-*hi*]indolizine-4-carboxylate (41). This compound was prepared using the standard procedure and after purification of the reaction mixture by flash column chromatography gave 70 mg (68%) of **41** as a pale yellow oil; IR (film) 2984, 2871, 1731, 1607, 1468, and 1411 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (t, 3H, J = 7.2 Hz), 2.27 (dd, 1H, J = 12.6, 5.8 Hz), 2.55 (dd, 1H, J = 12.6, 8.2 Hz, 1H), 2.61−2.71 (m, 1H), 3.67 (dd, 1H, J = 11.6, 8.3 Hz), 3.67 (dd, 1H, J = 11.6, 8.3 Hz, 1H), 4.18 (t, 1H, J = 7.7 Hz), 4.42 (q, 2H, J = 7.2 Hz), 5.56 (s, 1H), 7.19 (td, 1H, J = 1.8 Hz), 7.37−7.44 (m, 2H), and 7.49 (d, 1H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 31.5, 50.4, 62.9, 71.7, 74.5, 97.3, 111.8, 114.7, 125.6, 128.1, 131.0, 132.2, 135.5, 161.7, and 164.4; HRMS calcd for $[C_{16}H_{15}NO_5+H^+]$: 302.1023; found: 302.1022.

(2a*R*,2a^1*R*,4*R*,10b*S*)-ethyl-5-oxo-1-phenyl-2,2a,3,4,5,10b-hexahydro-1*H*-2a^1,4-epoxybenzo[*b*]pyrrolo[4,3,2-*hi*]-indolizine-4-carboxylate (42). A catalytic amount (0.6 mg) of $Rh_2(OPiv)_4$, benzene (1.0 mL), and *N*-allylaniline (13 mg, 0.10 mmol) was added sequentially to a 10 mL flask with a side arm, which was stoppered with a septum, equipped with a condenser. The resulting solution was heated at reflux, and a solution of bis-diazo compound **1** (30 mg, 0.10 mmol) in benzene (1.0 mL) was added through the side arm over a 1 h period using a syringe pump. Stirring was continued at this temperature for an additional 3 h and the solution was then concentrated under reduced pressure. Purification by flash column chromatography gave 27 mg (69%) of the titled compound **42** as an off-white solid, mp 196−198 °C; IR (film) 2982, 2845, 1728, 1602, 1502, and 1466 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.40 (t, 3H, J = 7.2 Hz), 2.36 (dd, 1H, J = 12.7 and 5.5 Hz), 2.61 (dd, 1H, J = 12.7 and 8.2 Hz), 2.80−2.86 (m, 1H), 3.09 (dd, 1H, J = 11.1 and 9.0 Hz), 3.97 (t, 1H, J = 8.1 Hz), 4.42 (q, 2H, J = 7.2 Hz), 6.85−6.92 (m, 3H), 7.15 (t, 1H, J = 7.6 Hz), 7.34 (t, 2H, J = 7.7 Hz), 7.34 (t, 1H, J = 7.8 Hz), and 7.63 (d, 1H, J = 7.7 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.4, 33.0, 46.2, 53.0, 60.2, 62.8, 96.2, 108.8, 113.1, 114.7, 118.7, 125.7, 127.9, 129.9, 130.4, 134.6, 135.3, 148.1, 161.8, and 164.5; HRMS calcd for $[C_{22}H_{20}N_2O_4+H^+]$: 377.1496; found: 377.1501.

(1*R*,5a*R*,5a^1*R*,7*R*,13b*S*)-7-Ethyl 1-methyl 8-oxo-1,2,3,5,5a,6,7,8-octahydro-5a^1,7-epoxy-benzo[*b*]pyrrolizino-[2,1-*hi*]indolizine-1,7-dicarboxylate (43) and (1*S*,5a*R*,5a^1*R*,7*R*,13b*S*)-7-Ethyl 1-Methyl 8-oxo-1,2,3,5,5a,6,7,8-octahydro-5a^1,7-epoxybenzo[*b*]-pyrrolizino[2,1-*hi*]indolizine-1,7-dicarboxylate (44). A mixture of methyl *N*-allylazetidine-2-carboxylate (39 mg, 0.25 mmol), benzene (2.5 mL), and $Rh_2(OAc)_4$ was heated to reflux, and a solution of **13** (75 mg, 0.25 mmol) in benzene (2.5 mL) was added over 1 h via a syringe pump, and heating was continued for an additional 3 h. The brown solution was concentrated under reduced pressure and purified by flash column chromatography to give 43 mg (43%) of **43** and 21 mg (20%) of **44**.

Compound **43** was obtained as a yellow oil from the above reaction; IR (film) 2950, 1729, 1605, 1469, and 1410 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.41 (t, 3H, J = 7.1 Hz), 2.27−2.35 (m, 2H), 2.49−2.54 (m, 2H), 2.60−2.67 (m, 1H), 2.70−2.77 (m, 1H), 2.89 (dt, 1H, J = 10.9, 6.8 Hz), 3.20 (s, 3H), 3.43 (dd, 1H, J = 8.1, 6.7 Hz), 3.56 (t, 1H, J = 7.6 Hz), 3.53 (dt, 1H, J = 10.9, 6.3 Hz), 4.43 (q, 2H, J = 7.1 Hz), 7.11 (t, 1H, J = 7.7 Hz), 7.27−7.32 (m, 2H), and 7.38 (d, 1H, J = 7.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 30.5, 33.7, 46.6, 49.9, 51.8, 53.8, 59.0, 62.7, 74.5, 95.9, 108.6, 114.1, 125.5, 126.3, 130.1, 134.4, 136.8, 161.8, 164.7, and 171.9; HRMS calcd for $[C_{21}H_{22}N_2O_6+H^+]$: 399.1551; found: 399.1554.

Compound **44** was also obtained (21 mg, 20%) from the above reaction as an off-white solid; mp 180−182 °C; IR (KBr) 2950, 1722, 1606, 1472, and 1411 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.35 (t, 3H, J = 7.2 Hz), 2.18−2.26 (m, 2H), 2.34−2.47 (m, 2H), 2.55−2.63 (m, 2H), 3.15 (dd, 1H, J = 12.4, 6.7 Hz), 3.21−3.27 (m, 2H), 3.36 (dd, 1H, J = 6.0, 3.9 Hz), 3.62 (s, 3H), 4.36 (ABX_3, 2H, $\Delta\delta_{AB}$ = 0.07, J_{AB} = 10.8 Hz, J_{AB} = J_{BX} = 7.2 Hz), 7.21 (t, 1H, 7.7 Hz), 7.35 (t, 1H, J = 8.0 Hz), 7.38 (d, 1H, J = 7.6 Hz), 7.42 (d, 1H, J = 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 30.5, 33.7, 46.6, 49.9, 51.8, 53.8, 59.0, 63.0, 74.5, 95.9, 108.6, 114.1, 125.5, 126.3, 130.1, 134.4, 136.8, 161.8, 164.7, and 171.9; HRMS calcd for $[C_{21}H_{22}N_2O_6+H^+]$: 399.1551; found: 399.1553.

3-Diazo-1-(ethyl diazomalonyl)-2-piperidone (45). A sample of 3-diazo-2-piperidone[29] (300 mg, 2.40 mmol) was dissolved in 12 mL dry THF. The solution was cooled in an ice/water bath, and 192 mg (4.8 mmol) of sodium hydride (60% dispersion in mineral oil) was added and the resulting suspension was allowed to stir for 10 min. Ethyl diazomalonyl chloride[1] (640 mg, 3.6 mmol) was added via syringe, and the mixture was allowed to stir for 30 min at rt. Water was added and the aqueous layer was extracted with ethyl acetate. The combined extracts were washed with water then brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Flash column chromatography of the resulting residue gave 509 mg (80%) of the titled compound **45** as a bright yellow solid, mp 60−61 °C; IR (KBr) 2981, 2127, 2085, 1723, 1698, and 1637 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (t, J = 7.0 Hz, 3H), 2.02−1.94 (m, 2H), 2.80 (t, J = 6.7 Hz, 2H), 3.70−3.64 (m, 2H), and 4.24 (q, J = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 21.2, 22.0, 44.9, 58.1, 61.8, 72.3, 161.4, 163.9, 166.0; HRMS calcd for $[C_{10}H_{11}N_5O_4+H^+]$: 266.0884; found 266.0885.

3-(3-Buten-1-oxy)-1-(ethyl 2-diazomalonyl)-2-piperidone (46). A mixture of $Rh_2(OPiv)_4$ (0.2 mg), dichloromethane (0.75 mL), 3-buten-1-ol (6.5 μL, 0.075 mmol), and 20 mg (0.075 mmol) of **45** was stirred for 1 h at rt. The mixture was concentrated under reduced pressure and purified by flash column chromatography to give 12 mg (52%) of the titled compound **46** as a pale yellow oil; IR (neat) 2956, 2131, 1715, and 1651 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (t, 3H, J = 7.1 Hz), 1.81−2.04 (m, 3H), 2.17−2.25 (m, 1H), 2.36 (q, 2H, J = 6.9 Hz), 3.49−3.58 (m, 2H), 3.68−3.76 (m, 1H), 3.92 (dt, 1H, J = 9.3, 6.8 Hz), 4.06 (dd, 1H, J = 10.2, 6.2 Hz), 4.13−4.74 (m, 2H), 5.01 (d, 1H, J = 10.2 Hz), 5.08 (dq, 1H, J = 17.1, 1.6 Hz), and 5.82 (ddt, 1H, J = 17.1, 10.2, 6.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 21.3, 29.7, 34.5, 46.7, 61.7, 70.9 72.0, 77.8, 116.6, 135.3, 161.1, 165.5, and 174.9.

(3a*S*,3a^1*R*,5*R*,10a*S*)-Ethyl 6-oxodecahydro-3a^1,5-epoxypyrano[2,3,4-*ij*]quinolizine-5-carboxylate (47). A sample of the above diazo-2-piperidone **46** (23 mg, 0.074 mmol), benzene (1.5 mL), and $Rh_2(OAc)_4$ (0.3 mg) was heated at reflux for 1 h. The solution was allowed to cool to rt and then concentrated under reduced pressure. Recrystallization of the residue from ethyl acetate and hexane provide 19 mg (89%) of the titled compound **47** as a white solid, mp 149−150 °C; IR (KBr) 2951, 2872, 1747, 1716, and 1097 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (t, 3H, J = 7.1 Hz), 1.58−1.77 (m, 2H), 1.79−2.00 (m, 5H), 2.24−2.33 (m, 2H), 2.65 (td, 1H, J = 13.0, 3.4 Hz), 3.63−3.73 (m, 2H), 3.77 (dd, 1H, J = 13.4, 4.6 Hz), 4.26 (dd, 1H, J = 11.0, 6.6 Hz), and 4.30−4.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 22.1, 24.9, 31.9, 35.9, 36.1, 38.7, 59.9, 62.5, 70.5, 86.1, 91.7, 165.8, and 169.8; HRMS calcd for $[C_{14}H_{19}NO_5+H^+]$: 282.1336; found: 282.1335.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02663.

^{1}H and ^{13}C NMR data of various key compounds (PDF)

X-ray crystallographic data for compounds **37** and **44** (ZIP)

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The authors declare no competing financial interest.

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