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Trapping rhodium carbenoids with aminoalkynes for the synthesis of diverse *N*-heterocycles

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ABSTRACT

A convergent approach for the synthesis of diverse *N*-heterocycles is described. The reaction involves trapping of diazo-derived rhodium carbenoids with gold activated aminoalkynes, and accommodates both the donor/acceptor (D/A) as well as acceptor/acceptor (A/A) diazo carbonyls. Mechanistic investigations indicate that the Rh(II)/Au(I) catalyzed reaction of aminoalkynes with D/A diazos is concerted, while the reaction with A/A diazo is stepwise and proceeds with carbene N–H insertion and a subsequent Conia-ene cyclization.

1. Introduction

Diazo-derived rhodium carbenoids are versatile synthetic intermediates [1]. They offer sequential reactions with a nucleophile and an electrophile, and are ideal for cascade reactions, which are known to build molecular complexity with high efficiency, selectivity, and atom economy [2]. In continuation of our interest in rhodium carbenoid initiated cascade reactions [3], we herein report a cascade that provides direct access to diverse five membered *N*-heterocycles, which are common structural motifs in bioactive natural products and pharmaceuticals. This work is inspired from our previous work, in which, we efficiently trapped rhodium carbenoids with a variety of gold activated alkynoic acids and alkynols to access biologically relevant γ-butyrolactones, tetrahydrofurans, and spiroethers [3b,3d].

We envisioned trapping the rhodium carbenoids with amino alkynes using our previously reported synergistic Rh(II)/Au(I) catalytic system [3b] toward the synthesis of pyrrolidines and indolines. There have been reports of Conia-ene cyclizations on *N*-tethered compounds, but most of the transformations have been limited to the use of dicarbonyls such as amino-malonates [4]. The Sun group reported a dual catalysis Rh(II)/Zn(II) system for sequential diazo N–H insertion/Conia-ene cyclizations, however this chemistry was also found to be limited to the use of diazo-dicarbonyl compounds (Fig. 1a) [4f]. To overcome this limitation, we hypothesized that our previously developed synergistic Rh(II)/Au(I) catalyst system [3b] would provide the one pot diverted N–H insertion/Conia-ene cascade with amino alkynes, and accommodate both the acceptor/acceptor (A/A), as well as donor/acceptor (D/A) diazo compounds (Fig. 1b).

2. Results and discussion

To test our hypothesis, aminoalkyne **1a** and 2-tetralone diazo **2a** were selected as model substrates. The addition of 2-tetralone diazo **2a** to aminoalkyne **1a** in the presence of our previously optimized $Rh_2(esp)_2$/PPh_3AuCl/$AgSbF_6$ catalyst cocktail in dichloromethane at room temperature provided the major spiropyrrolidine product **3a** in 75% conversion with an isolated yield of 60% (Table 1, entry 1). Encouraged by the results of this cascade reaction, we examined the effect of different Lewis acids known for synthesizing *N*-heterocycles through alkyne cyclizations [4a,4c,4f]. Upon screening, it was realized that these metal complexes (**entries 2–5**) were ineffective and this cascade transformation was unique to the synergistic behavior of the Rh(II)/Au(I) catalytic cocktail. Next, we decided to examine the effect of different dirhodium

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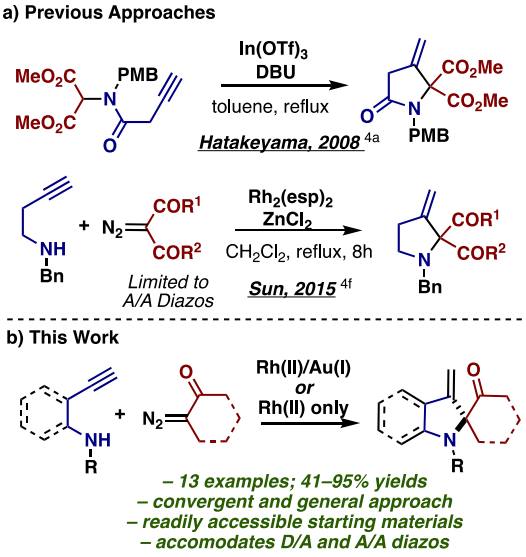
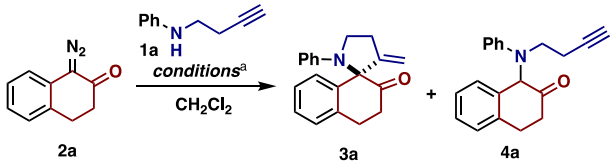


Fig. 1. a) Approaches for pyrrolidine and indoline synthesis using aminoalkynes; b) This work.

Table 1
Synergistic diazo N–H insertion/Conia-ene cascade.



entry	Rh(II)	Lewis Acid	3a %[b]	4a %[b]
1	**$Rh_2(esp)_2$**	**PPh_3AuSbF_6**	**75**	**25**
2	$Rh_2(esp)_2$	$ZnCl_2$	0	100
3	$Rh_2(esp)_2$	$In(OTf)_3$	0	100
4	$Rh_2(esp)_2$	PPh_3AuCl	0	100
5	$Rh_2(esp)_2$	$AgSbF_6$	0	100
6	$Rh_2(OAc)_4$	PPh_3AuSbF_6	0	100
7	$Rh_2(TFA)_4$	PPh_3AuSbF_6	40	60

[a] All reactions were performed by adding diazo compound **2a** (0.45 mmol, 1 equiv., 0.5 M CH_2Cl_2) dropwise via syringe to a solution of **1a** (0.50 mmol, 1.1 equiv.), $Rh_2(esp)_2$ (1 mol%), and $AgSbF_6/PPh_3AuCl$ (10 mol%) in 0.3 M CH_2Cl_2.
[b] Conversion (%) was determined from the crude ^1H NMR spectrum.

carboxylates known to decompose diazocarbonyls, but did not get much success (**entries 6**–**7**). These results further confirmed that $Rh_2(esp)_2$ is the most efficient catalyst for this cascade transformation [5].

With the optimized conditions in hand, we investigated the applicability of this cascade reaction as shown in Fig. 2. Fused aromatic phenanthrenone diazo **2b** also participated in the cascade to provide spiropyrrolidine **3b** in good yield. In hopes of applying the system to the more stable acceptor/acceptor diazos, methylbenzoylacetate diazo **2c** was exposed to aminoalkyne **1a** in the presence of our catalytic cocktail. At room temperature this electron deficient A/A diazo did not decompose because of preferred complexation of $Rh_2(esp)_2$ with the aminoalkyne. Due to the ineffectiveness of the catalyst at room temperature, the reaction was refluxed in order to obtain the desired transformation, providing the pyrrolidine **3c** in low yield. To optimize the yield of **3c**, methylbenzoylacetate diazo **2c** was added to aminoalkyne **1a** in the presence of $Rh_2(esp)_2$ alone in refluxing dichloromethane. After

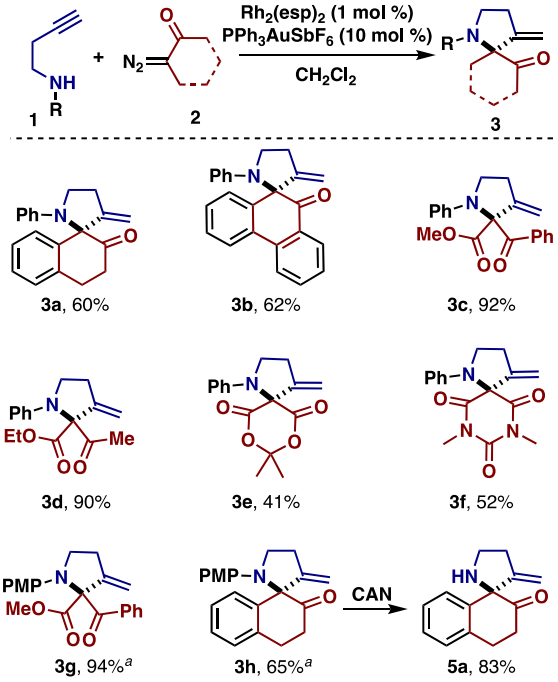


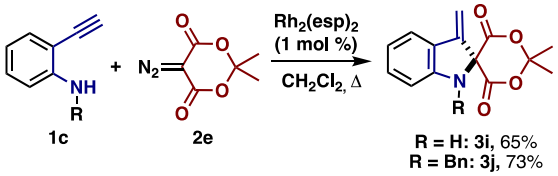
Fig. 2. Substrate scope of the Rh(II)/Au(I) catalyzed diazo N–H insertion/Conia-ene cyclization. Substrates **3a**–**3b, 3h** were prepared using General Procedure A. Substrates **3c**–**3d, 3g** were prepared using General Procedure B. Substrates **3e**–**3f** were prepared using General Procedure C. [a]See Supporting Information for structure of aminoalkyne (**1b**) used to synthesize **3g**–**3h**.

5 min the desired insertion product was visualized via thin layer chromatography and subsequently PPh_3AuCl and $AgSbF_6$ were added to the same pot to provide **3c** in 92% yield. This protocol was also used to synthesize pyrrolidine **3d.** When attempting to extend this modified protocol to A/A cyclic diazos, Meldrum's acid and barbituric acid diazos, it was observed that the stepwise Conia-ene reaction was unsuccessful. Therefore, to synthesize compounds **3e**–**3f**, the diazo was added to a solution of aminoalkyne, $Rh_2(esp)_2$, and $PPh_3AuCl/AgSbF_6$ then refluxed until complete. The decreased yield for spiropyrrolidine **3e** can be attributed to the instability of the Meldrum's acid tethered products to the Lewis acidic reaction conditions as observed previously [3d].

To demonstrate the utility of this transformation, it was necessary to identify a removable protecting group that would provide access to the free N–H pyrrolidine. Using aminoalkyne **1b** synthesized from *N*-methyl 4-methoxyaniline, we were able to obtain the PMP-protected pyrrolidines **3g** and **3h**. Compound **3h** was then taken forward and exposed to CAN (ceric ammonium nitrate) to give the secondary spiropyrrolidine **5a** in 83% yield.

Next we desired to expand our system to accommodate other aminoalkynes. Easily accessible 2-ethynylaniline **1c** was synthesized and exposed to Meldrum's acid diazo **2e**. In the presence of our catalytic cocktail the desired product **3i** was obtained but in a decreased yield similar to **3e**. However, we hypothesized that aromatic restraint found within 2-ethynylaniline could facilitate the Conia-ene cyclization step with $Rh_2(esp)_2$ alone. Our hypothesis was proven correct and 2-ethynylaniline **1c** reacted with Meldrum's Acid diazo **2e** in the presence of only $Rh_2(esp)_2$ to provide the desired product **3i** in 65% yield (Scheme 1). The benzyl protected compound **3j** was also successfully synthesized using this modified method.

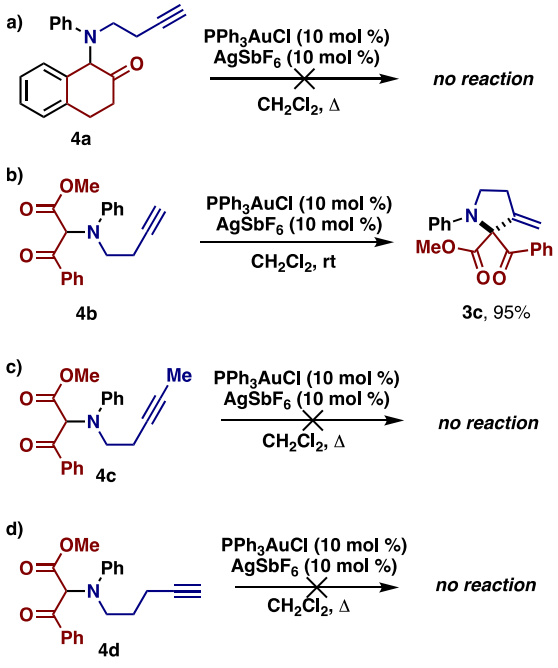
To gain further insights into the mechanism, insertion products were synthesized with both the D/A 2-tetralone diazo and A/A methylbenzoylacetate diazo using $Rh_2(esp)_2$ as a catalyst. When the



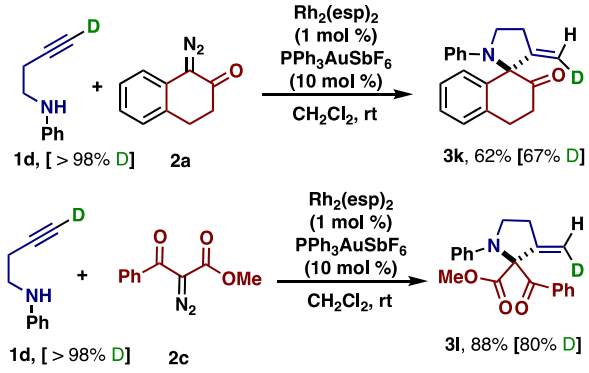
Scheme 1. $Rh_2(esp)_2$ catalyzed N–H insertion/Conia-ene cascade of 2-ethynylanilines.

insertion products were subjected to the gold-catalyzed Conia-ene cyclization [6], we did not observe any cyclization for the 2-tetralone insertion product **4a** even after refluxing in dichloromethane for 12 h (Scheme 2a). However, for the methylbenzoylacetate insertion product **4b**, cyclization occurred with equal efficiency as observed in our one pot, tandem cyclization protocol (Scheme 2b). Next we examined if non-terminal alkynes were tolerated in this transformation. When insertion product **4c** was exposed to PPh_3AuSbF_6 no cyclization occurred even after the reaction was refluxed for 12 h (Scheme 2c). Lastly, in an attempt to access piperidines, insertion product **4d** was synthesized and exposed to PPh_3AuSbF_6, however no cyclization occurred (Scheme 2d).

Given the results from the control experiments, we decided to probe the reaction mechanism using deuterium-labeling experiments with 2-tetralone diazo **2a** and methylbenzoylacetate diazo **2c** (Scheme 3). When the deuterium labeling experiment was conducted using 2-tetralone diazo **2a** and deuterated aminoalkyne **1d**, the desired product was obtained in 62% yield, proving there was no effect of deuterium on the overall reaction efficiency. However, deuterium scrambling was observed, an observation inconsistent with studies reported by our own laboratory and the Toste group for gold-catalyzed Cona-ene carbocyclizations [3d,6]. When the experiment was conducted using methylbenzoylacetate diazo, deuterium scrambling was also observed. The results from



Scheme 2. a) Insertion product from D/A diazo (**4a**) exposed to Conia-ene cyclization conditions, no reaction. b) Insertion product from A/A diazo (**4b**) exposed to Conia-ene cyclization conditions, cyclization proceeded efficiently. c) Attempted cyclization of non-terminal alkyne (**4c**), no reaction d) Attempted cyclization of 6-membered alkyne (**4d**), no reaction.



Scheme 3. Deuterium labeling experiments.

the control and deuterium labeling experiments suggest the possibility of gold-acetylide as a reactive intermediate that is in equilibrium with an alkyne π–complex with gold [7].

These findings allow us to propose a reaction mechanism depicted in Fig. 3. Specifically, Rh(II) decomposes the diazo compounds **2** to form a Rh-carbenoid that undergoes nitrogen addition to provide a zwitterionic intermediate, which undergoes a keto-enol tautomerism to provide a reactive intermediate, which undergoes a Conia-ene cyclization with the mono-carbonyl compounds in presence of a gold activated alkyne complex. In the stepwise mechanism, the zwitterionic intermediate undergoes 1,2-proton transfer to provide the insertion product **4**. As expected, no Conia-ene cyclization was observed with monocarbonyl (pKa ~20) presumably due to non-enolization, while dicarbonyls (pKa ~12) undergoes Conia-ene cyclization in good yields under gold conditions (Fig. 3).

3. Conclusion

In summary, the reported trapping of rhodium carbenoids with aminoalkynes is convergent in nature and uses readily available starting materials for the synthesis of a variety of *N*-heterocycles. An important feature of this transformation is its high chemo- and regio-selectivity. Further mechanistic analyses using computational tools are ongoing and will be reported in due course.

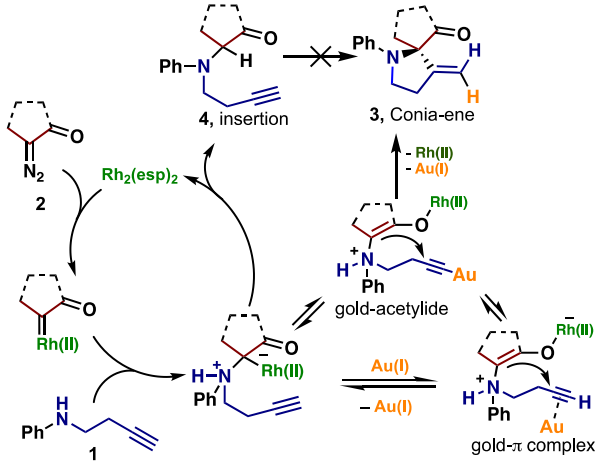


Fig. 3. Plausible reaction mechanism for the stepwise and synergistic Rh(II/Au(I)-catalyzed diazo N–H insertion/Conia-ene cascade.

4. Experimental section

4.1. General information

All reactions were performed in flame-dried glassware under positive N_2 pressure with magnetic stirring unless otherwise noted. Reagents and solvents were obtained from Sigma-Aldrich, Chem-Impex, VWR International, and Acros Organics and used without further purification unless otherwise indicated. Dichloromethane and Acetonitrile were distilled over CaH under N_2 unless otherwise indicated. Tetrahydrofuran was distilled over Na under N_2 with benzophenone indicator. Thin layer chromatography (TLC) was performed on 0.25 mm E. Merck silica gel 60 F254 plates and visualized under UV light (254 nm) or by staining with potassium permanganate ($KMnO_4$), cerium ammonium molybdate (CAM), phosphomolybdic acid (PMA), and ninhydrin. Silica flash chromatography was performed on Sorbtech 230–400 mesh silica gel 60. Syringe pump addition reactions were conducted using a Harvard Apparatus (Model: 55-1111) or a New Era Pump Systems, Inc. (Model: NE-300) syringe pump. Sonication was performed using a Bransonic Ultrasonic Cleaner (Model: M5800H). NMR spectra were recorded on a Varian VNMRS 300, 400, 500, and 600 MHz NMR spectrometer at 20 °C in $CDCl_3$ unless otherwise indicated. Chemical shifts are expressed in ppm relative to solvent signals: $CDCl_3$ (^{1}H, 7.26 ppm, ^{13}C, 77.0 ppm); coupling constants are expressed in Hz. IR spectra were recorded on a Cary 760 FTIR spectrometer with peaks reported in cm^{-1}. Mass spectra were obtained on an Advion Expression CMS TLC Mass Spectrometer.

4.2. General Procedures for N-H insertion/Conia-ene

General Procedure A: Rh/Au catalyzed (but-3-yn-1-yl)-aniline trapping with diazos: To a 4.0 mL vial equipped with a magnetic stir bar was added $Rh_2(esp)_2$ (1 mol %), PPh_3AuCl (10 mol %), and $AgSbF_6$ (10 mol %) directly into the reaction vessel. A solution of (but-3-yn-1-yl)-aniline (1.1 equiv.) was then added. Lastly, the diazo (1.0 equiv.) in dichloromethane (0.3 M) was added. The reaction vessel was sealed, and allowed to stir at room temperature until bubbling ceased and the diazo was consumed via TLC (approximately 30 min). (Take caution when opening reaction flask. Evolution of N_2 gas creates pressurized system.) Once the reaction was complete, the crude reaction mixture was filtered through a slurry of celite/silica gel, concentrated, and analyzed via crude ^{1}H NMR. The crude mixture was then purified via flash chromatography to furnish functionalized spiropyrrolidines.

General Procedure B: Rh catalyzed insertion of (but-3-yn-1-yl)-aniline with sequential Au catalyzed Conia-ene: To a 4.0 mL vial equipped with a magnetic stir bar was added $Rh_2(esp)_2$ (1 mol %) and a solution of (but-3-yn-1-yl)-aniline (1.1 equiv.). The diazo (1.0 equiv.) in dichloromethane (0.3 M) was added and the reaction vessel was sealed, and allowed to stir at reflux until bubbling ceased and the diazo was consumed via TLC (approximately 5 min). (Take caution when opening reaction flask. Evolution of N_2 gas creates pressurized system.) Once the insertion product had formed PPh_3AuCl (10 mol %), and $AgSbF_6$ (10 mol %) were added directly into the reaction vessel and this solution was allowed to stir an additional 30 min until the insertion product was no longer visible on TLC and a new, more polar spot had formed (the cyclization product). Once the reaction was complete, the crude reaction mixture was filtered through a slurry of celite/silica gel, concentrated, and analyzed via crude ^{1}H NMR. The crude mixture was then purified via flash chromatography to furnish functionalized pyrrolidines.

General Procedure C: Rh/Au catalyzed (but-3-yn-1-yl)-aniline trapping with diazos: To a 4.0 mL vial equipped with a magnetic stir bar was added $Rh_2(esp)_2$ (1 mol %), PPh_3AuCl (10 mol %), and $AgSbF_6$ (10 mol %) directly into the reaction vessel. A solution of (but-3-yn-1-yl)-aniline (1.1 equiv.) was then added. Lastly, the diazo (1.0 equiv.) was added. The reaction vessel was sealed and allowed to stir at reflux for 16 h (Take caution when opening reaction flask. Evolution of N_2 gas creates pressurized system.) After this time, the crude reaction mixture was filtered through a slurry of celite/silica gel, concentrated, and analyzed via crude ^{1}H NMR. The crude mixture was then purified via flash chromatography to furnish functionalized spiropyrrolidines.

General Procedure D: Rh catalyzed 2-ethynylaniline trapping with diazos: To a 4.0 mL vial equipped with a magnetic stir bar was added $Rh_2(esp)_2$ (1 mol %) directly into the reaction vessel. A solution of 2-ethynylaniline (1.1 equiv.) was then added. Lastly, the diazo (1.0 equiv.) was added. The reaction vessel was sealed and allowed to stir at reflux for 16 h (Take caution when opening reaction flask. Evolution of N_2 gas creates pressurized system.) After this time, the crude reaction mixture was filtered through a slurry of celite/silica gel, concentrated, and analyzed via crude ^{1}H NMR. The crude mixture was then purified via flash chromatography to furnish functionalized spiropyrrolidines.

4.2.1. 3′-methylene-1′-phenyl-3,4-dihydro-2H-spiro[naphthalene-1,2′-pyrrolidin]-2-one (**3a**)

Prepared from 1-diazo-3,4-dihydronaphthalen-2(1H)-one and N-(but-3-yn-1-yl)aniline using General Procedure A (Reaction time = 10 min) Yellow oil (32 mg, 60%). TLC: R_f 0.52 (20% ethyl acetate in hexanes). IR (NaCl): 3289, 3065, 2922, 2859, 2367, 2320, 1719. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (td, J = 7.3, 1.5 Hz, 1H), 7.18–7.12 (m, 1H), 7.10 (dd, J = 7.9, 1.5 Hz, 1H), 7.06–6.99 (m, 2H), 6.59 (tt, J = 7.3, 1.0 Hz, 1H), 6.29 (dt, J = 7.8, 1.0 Hz, 2H), 5.15 (dd, J = 2.6, 1.3 Hz, 1H), 4.61 (dd, J = 2.9, 1.2 Hz, 1H), 3.95–3.85 (m, 2H), 3.49–3.16 (m, 4H), 3.03–2.88 (m, 1H), 2.84–2.75 (m, 1H), 2.74–2.62 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.6, 152.9, 145.1, 140.0, 135.6, 128.6 (2C), 128.1, 127.8, 127.7, 127.3 (2C), 116.7, 113.7 (2C), 111.6, 49.02, 36.73, 29.89, 28.62. HRMS (ESI) m/z calcd for $C_{20}H_{20}NO$ ($[M+H]^+$) 290.1545; found 290.1537.

4.2.2. 3′-methylene-1′-phenyl-10H-spiro[phenanthrene-9,2′-pyrrolidin]-10-one (**3b**)

Prepared from 10-diazophenanthren-9(10H)-one and N-(but-3-yn-1-yl)aniline using General Procedure A (Reaction time = 10 min). Yellow oil (33 mg, 62%). TLC: R_f 0.55 (20% ethyl acetate in hexanes). IR (NaCl): 3065, 3036, 2959, 2926, 2363, 2350, 1684. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, J = 8.1 Hz, 1H), 8.10–8.05 (m, 2H), 7.73 (td, J = 7.7, 1.5 Hz, 1H), 7.46–7.40 (m, 1H), 7.37 (td, J = 8.0, 7.6, 1.4 Hz, 1H), 7.31 (dd, J = 7.9, 1.3 Hz, 1H), 7.23 (d, J = 7.0 Hz, 1H), 7.00 (dd, J = 8.5, 7.2 Hz, 2H), 6.61–6.53 (m, 1H), 6.26 (d, J = 8.1 Hz, 2H), 4.86 (t, J = 2.1 Hz, 1H), 4.54 (t, J = 2.1 Hz, 1H), 4.03 (td, J = 8.2, 6.8 Hz, 1H), 3.99 (td, J = 8.9, 4.9 Hz, 1H), 3.06–2.97 (m, 1H), 2.89–2.82 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.1, 150.1, 145.2, 141.4, 137.4, 134.8 (2C), 129.9, 129.8, 128.7, 128.5 (2C), 128.2, 127.9, 127.0, 124.0, 123.1, 116.7, 114.4 (2C), 109.8, 76.6, 49.0, 29.5. HRMS (ESI) m/z calcd for $C_{24}H_{20}NO$ ($[M+H]^+$) 338.1545; found 338.1544.

4.2.3. Methyl-2-benzoyl-3-methylene-1-phenylpyrrolidine-2-carboxylate (**3c**)

Prepared from methyl 2-diazo-3-oxo-3-phenylpropanoate and N-(but-3-yn-1-yl)aniline using General Procedure B (Reaction time = 20 min). Yellow oil (54 mg, 92%). TLC: R_f 0.41 (20% ethyl acetate in hexanes). IR (NaCl): 3059, 2949, 2916, 2849, 2320, 1740, 1678. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (dd, J = 8.4, 1.4 Hz, 2H), 7.35 (ddt, J = 8.8, 7.3, 1.3 Hz, 1H), 7.24–7.19 (m, 2H), 7.11–7.05 (m, 2H), 6.67 (td, J = 7.3, 1.0 Hz, 1H), 6.61 (dq, J = 7.3, 1.5, 1.0 Hz, 2H),

5.31–5.24 (m, 2H), 3.87 (dt, $J = 8.9$, 7.5 Hz, 1H), 3.73 (s, 3H), 3.64 (dt, $J = 8.7$, 7.2 Hz, 1H), 2.98 (tt, $J = 7.3$, 2.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.2, 169.2, 146.4, 145.1, 136.0, 132.2, 128.8 (2C), 128.7 (2C), 127.9 (2C), 118.2, 113.7, 112.8, 80.3, 74.8, 52.7, 47.8, 30.0. HRMS (ESI) m/z calcd for $C_{20}H_{19}NO_3Na$ ($[M+Na]^+$) 344.1263; found 344.1272.

4.2.4. Ethyl-2-acetyl-3-methylene-1-phenylpyrrolidine-2-carboxylate (**3d**)

Prepared from ethyl 2-diazo-3-oxobutanoate and N-(but-3-yn-1-yl)aniline using General Procedure B (Reaction time = 20 min). Faint yellow oil (50 mg, 90%). TLC: R_f 0.44 (20% ethyl acetate in hexanes). IR (NaCl): 2978, 2926, 2855, 2363, 2324, 1751, 1734, 1601. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25–7.14 (m, 2H), 6.78 (tt, $J = 7.3$, 1.0 Hz, 1H), 6.56 (dt, $J = 7.9$, 1.0 Hz, 2H), 5.34 (td, $J = 2.3$, 0.7 Hz, 1H), 5.27 (td, $J = 2.2$, 0.7 Hz, 1H), 4.19–4.01 (m, 2H), 3.80 (ddd, $J = 8.6$, 7.3, 6.0 Hz, 1H), 3.64 (dt, $J = 8.6$, 7.5 Hz, 1H), 2.93–2.83 (m, 2H), 2.13 (s, 3H), 1.07 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.8, 168.5, 145.4, 129.1 (2C), 118.2, 113.2 (2C), 111.4, 80.3, 61.4, 48.1, 30.6, 26.1, 13.8. HRMS (ESI) m/z calcd for $C_{16}H_{19}NO_3Na$ ($[M+Na]^+$) 296.1263; found 296.1247.

4.2.5. 8,8-Dimethyl-4-methylene-1-phenyl-7,9-dioxa-1-azaspiro[4.5]decane-6,10-dione (**3e**)

Prepared from 5-diazo-2,2-dimethyl-1,3-dioxane-4,6-dione and N-(but-3-yn-1-yl)aniline using General Procedure C (Reaction time = 16 h). Yellow oil (24 mg, 41%). TLC: R_f 0.26 (20% ethyl acetate in hexanes). IR (NaCl): 2926, 2845, 2359, 2162, 1684. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (d, $J = 8.0$ Hz, 2H), 6.85 (t, $J = 7.3$ Hz, 1H), 6.61 (d, $J = 8.1$ Hz, 2H), 5.37 (t, $J = 2.1$ Hz, 2H), 3.79 (t, $J = 6.9$ Hz, 2H), 2.96 (tt, $J = 6.9$, 2.0 Hz, 2H), 1.91 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.6, 148.8, 144.3, 134.2, 132.0, 129.3, 129.2, 119.9, 114.6, 111.1, 107.1, 72.1, 48.8, 31.3, 30.5, 29.2. HRMS (ESI) m/z calcd for $C_{16}H_{17}NO_4Na$ ($[M+Na]^+$) 310.1055; found 310.1107.

4.2.6. 7,9-Dimethyl-4-methylene-1-phenyl-1,7,9-triazaspiro[4.5]decane-6,8,10-trione (**3f**)

Prepared from 5-diazo-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione and N-(but-3-yn-1-yl)aniline using General Procedure C (Reaction time = 16 h). Yellow oil (33 mg, 52%) TLC: R_f 0.22 (20% ethyl acetate in hexanes). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 (dd, $J = 8.7$, 7.4 Hz, 2H), 6.79–6.75 (m, 1H), 6.32 (dt, $J = 7.7$, 1.0 Hz, 2H), 5.20 (q, $J = 2.1$ Hz, 1H), 5.01 (q, $J = 2.2$ Hz, 1H), 3.86 (t, $J = 7.0$ Hz, 2H), 3.40 (s, 6H), 2.96 (tt, $J = 6.9$, 2.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.4 (2C), 149.3, 144.3, 129.5 (2C), 118.7 (2C), 112.9 (2C), 108.5, 90.0, 48.5, 31.0, 29.7, 29.5. HRMS (ESI) m/z calcd for $C_{16}H_{17}N_3O_3Na$ ($[M+Na]^+$); 322.1168; found 322.1204.

4.2.7. Methyl-2-benzoyl-1-(4-methoxyphenyl)-3-methylenepyrrolidine-2-carboxylate (**3g**)

Prepared from methyl 2-diazo-3-oxo-3-phenylpropanoate and N-(but-3-yn-1-yl)-4-methoxyaniline using General Procedure B (Reaction time = 20 min). Vibrant yellow oil (80 mg, 94%). TLC: R_f 0.47 (30% ethyl acetate in hexanes). IR (NaCl): 2955, 2835, 1740, 1682. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78–7.71 (m, 2H), 7.41–7.33 (m, 1H), 7.25–7.22 (m, 2H), 6.71–6.62 (m, 2H), 6.61–6.53 (m, 2H), 5.25 (qd, $J = 2.3$, 0.8 Hz, 2H), 3.82 (ddd, $J = 8.7$, 7.9, 6.2 Hz, 1H), 3.71 (s, 3H), 3.66 (s, 3H), 3.58 (td, $J = 8.5$, 6.6 Hz, 1H), 2.99–2.91 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.3, 169.3, 152.3, 146.7, 139.3, 136.1, 132.2, 128.9 (2C), 127.9 (2C), 115.0 (2C), 114.3 (2C), 112.8, 80.8, 55.5, 52.6, 48.2, 30.1. HRMS (ESI) m/z calcd for $C_{21}H_{21}NO_4Na$ ($[M+Na]^+$) 374.1368; found 374.1375.

4.2.8. 1'-(4-methoxyphenyl)-3'-methylene-3,4-dihydro-2H-spiro[naphthalene-1,2'-pyrrolidin]-2-one (**3h**)

Prepared from 1-diazo-3,4-dihydronaphthalen-2(1H)-one and N-(but-3-yn-1-yl)-4-methoxyaniline using General Procedure A (Reaction time = 10 min). Yellow oil (70 mg, 65%). TLC: R_f 0.60 (30% ethyl acetate in hexanes). IR (NaCl): 2926, 2859, 2359, 2324, 2124, 1792, 1753. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.21 (m, 2H), 7.17–7.15 (m, 2H), 6.70–6.61 (m, 2H), 6.31–6.19 (m, 2H), 5.13 (dd, $J = 2.6$, 1.4 Hz, 1H), 4.60 (dd, $J = 2.9$, 1.3 Hz, 1H), 3.90–3.84 (m, 2H), 3.66 (s, 3H), 3.39–3.30 (m, 1H), 3.27–3.14 (m, 2H), 2.93 (dddt, $J = 15.0$, 10.1, 7.6, 2.7 Hz, 1H), 2.82–2.74 (m, 1H), 2.69–2.61 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.4, 153.2, 151.3, 140.3, 139.8, 135.7, 128.3, 128.1, 128.0, 127.7, 127.3, 114.7 (2C), 114.4 (2C), 111.4, 55.6, 49.4, 37.1, 30.0, 28.6. HRMS (ESI) m/z calcd for $C_{21}H_{22}NO_2$ ($[M+H]^+$) 320.1651; found 320.1652.

4.2.9. 2',2'-dimethyl-3-methylenespiro[indoline-2,5'-[1,3]dioxane]-4',6'-dione (**3i**)

2,2-dimethyl-1,3-dioxane-4,6-dione and 2-ethynylaniline using General Procedure D (Reaction time = 16 h). Faint yellow oil (50 mg, 65%). TLC: R_f 0.14 (20% ethyl acetate in hexanes). IR (NaCl): 3327, 2922, 2855, 2363, 2324, 1790, 1740. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35–7.32 (m, 1H), 7.25–7.22 (m, 1H), 6.91 (t, $J = 7.3$ Hz, 2H), 5.65 (d, $J = 2.3$ Hz, 1H), 5.37 (d, $J = 2.4$ Hz, 1H), 4.66 (s, 1H), 1.90 (s, 3H), 1.78 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7 (2C), 152.3, 147.8, 131.4 (2C), 123.5, 121.6, 112.8, 106.1, 104.2, 71.6, 31.1, 27.3. HRMS (ESI) m/z calcd for $C_{14}H_{13}NO_4Na$ ($[M+Na]^+$) 282.0742; found 282.1021.

4.2.10. 1-Benzyl-2',2'-dimethyl-3-methylenespiro[indoline-2,5'-[1,3]dioxane]-4',6'-dione (**3j**)

Prepared from 5-diazo-2,2-dimethyl-1,3-dioxane-4,6-dione and N-benzyl-2-ethynylaniline using General Procedure D (Reaction time = 16 h). Faint yellow oil (30 mg, 73%). TLC: R_f 0.38 (20% ethyl acetate in hexanes). IR (NaCl): 2926, 2855, 2359, 2324, 2124, 1792, 1753. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55–7.51 (m, 2H), 7.37–7.33 (m, 2H), 7.29 (t, $J = 6.7$ Hz, 2H), 7.12–7.08 (m, 1H), 6.76 (td, $J = 7.5$, 0.9 Hz, 1H), 6.40 (d, $J = 8.1$ Hz, 1H), 5.62 (d, $J = 2.3$ Hz, 1H), 5.34 (d, $J = 2.3$ Hz, 1H), 4.47 (s, 2H), 1.85 (s, 3H), 1.52 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.8 (2C), 153.5, 147.0, 136.2, 131.4, 128.7, 128.2 (2C), 127.8 (2C), 123.2, 121.2, 119.4, 109.0, 106.2, 103.4, 51.6, 31.1, 29.7, 28.0. HRMS (ESI) m/z calcd for $C_{21}H_{19}NO_4Na$ ($[M+Na]^+$]) 372.1212; found 372.1204.

4.2.11. 3'-(methylene-d)-1'-phenyl-3,4-dihydro-2H-spiro[naphthalene-1,2'-pyrrolidin]-2-one (**3k**)

Prepared from 1-diazo-3,4-dihydronaphthalen-2(1H)-one and N-(but-3-yn-1-yl-4-d)aniline using General Procedure A (Reaction time = 10 min). Faint yellow oil (43 mg, 67%). TLC: R_f 0.77 (30% ethyl acetate in hexanes). IR (NaCl): 3032, 2922, 2849, 1719, 1600. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (t, $J = 6.7$ Hz, 1H), 7.21 (t, $J = 7.4$ Hz, 1H), 7.13 (t, $J = 7.5$ Hz, 1H), 7.08 (d, $J = 7.9$ Hz, 1H), 7.02 (t, $J = 7.9$ Hz, 2H), 6.58 (t, $J = 7.3$ Hz, 1H), 6.27 (d, $J = 8.0$ Hz, 2H), 5.15–5.10 (m, 1H), 4.59 (t, $J = 1.8$ Hz, 0.44H), 3.91–3.84 (m, 2H), 3.35 (dt, $J = 13.8$, 6.7 Hz, 1H), 3.29–3.15 (m, 2H), 2.97–2.87 (m, 1H), 2.76 (dt, $J = 15.2$, 5.6 Hz, 1H), 2.72–2.63 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.6, 152.8, 152.7, 145.1, 140.0, 135.6, 135.6, 128.6, 128.3, 128.0, 127.7, 127.7, 127.4, 116.7, 113.7, 111.6, 111.37, 111.2, 49.4, 36.7, 29.9. HRMS (ESI) m/z calcd for $C_{20}H_{20}DNO$ ($[M+H]^+$) 291.1608; found 291.1608.

4.2.12. Methyl-2-benzoyl-3-(methylene-d)-1-phenylpyrrolidine-2-carboxylate (**3l**)

Prepared from methyl 2-diazo-3-oxo-3-phenylpropanoate and N-(but-3-yn-1-yl-4-d)aniline using General Procedure B (Reaction time = 20 min). Yellow oil (50 mg, 95%). TLC: R_f 0.59 (30% ethyl acetate in hexanes). IR (NaCl): 3059, 2949, 2855, 2363, 1748, 1680. ^{1}H NMR (500 MHz, benzene d^6) δ 7.85–7.74 (m, 2H), 7.06–6.99 (m, 2H), 6.94–6.84 (m, 3H), 6.83–6.77 (m, 2H), 6.61 (ddt, $J = 8.4$, 7.4,

1.1 Hz, 1H), 5.34 (t, $J = 2.2$ Hz, 0H), 4.93–4.88 (m, 1H), 3.44 (dq, $J = 11.4$, 4.3, 2.4 Hz, 1H), 3.37 (s, 3H), 3.29 (td, $J = 9.0$, 5.3 Hz, 1H), 2.54 (ddt, $J = 10.9$, 8.6, 4.3 Hz, 1H), 2.46–2.36 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.2, 169.2, 146.3, 145.1, 136.0, 132.2, 128.8, 128.7, 127.9, 118.2, 113.7, 112.7, 112.6, 112.4, 80.3, 53.4, 52.7, 47.8, 30.1, 30.0. HRMS (ESI) *m/z* calcd for $C_{20}H_{18}DNO_3Na$ ($[M+Na]^+$) 345.1325; found 345.1330.

4.3. General Procedure for aminoalkyne insertion

General Procedure for aminoalkyne insertion into diazos: To a 4.0 mL vial equipped with a magnetic stir bar was added $Rh_2(esp)_2$ (1 mol %). A solution of (but-3-yn-1-yl)-aniline (1.1 equiv.) was then added. Lastly, the diazo (1.0 equiv.) in dichloromethane (0.3 M) was added. The reaction vessel was sealed, and allowed to stir at room temperature (for acceptor/donor diazos) or heated to reflux (for acceptor/acceptor diazos) until the diazo was consumed via TLC (5–20 min). Once the reaction was complete, the crude reaction mixture was filtered through a slurry of celite/silica gel, concentrated, and analyzed via crude ^{1}H NMR. The crude mixture was then purified via flash chromatography to furnish *N*-alkylated aminoalkynes.

4.3.1. 1-(but-3-yn-1-yl(phenyl)amino)-3,4-dihydronaphthalen-2(1H)-one (**4a**)

Prepared from 1-diazo-3,4-dihydronaphthalen-2(1H)-one and N-(pent-4-yn-1-yl)aniline. Orange oil (30 mg, 69%). TLC: R_f 0.82 (20% ethyl acetate in hexanes). IR (NaCl): 3294, 2926, 2363, 1699, 1653. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16–7.11 (m, 2H), 6.86 (dt, $J = 7.8$, 1.1 Hz, 3H), 6.81 (tt, $J = 7.2$, 1.1 Hz, 2H), 6.64–6.60 (m, 2H), 3.98 (dt, $J = 14.0$, 7.0 Hz, 2H), 3.42 (dt, $J = 13.5$, 6.5 Hz, 2H), 3.10–2.99 (m, 2H), 2.92 (ddd, $J = 15.6$, 6.9, 4.5 Hz, 2H), 2.76 (ddd, $J = 16.5$, 13.7, 6.9 Hz, 2H), 2.55–2.48 (m, 2H), 2.06 (t, $J = 2.6$ Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 147.4, 133.5, 132.5, 129.6 (2C), 127.6, 126.5, 124.8, 121.2, 118.6, 114.1, 113.2 (2C), 82.4, 70.5, 48.6, 27.8, 25.7, 18.6. HRMS (ESI) *m/z* calcd for $C_{20}H_{19}NONa$ ($[M+Na]^+$) 312.1364; found 312.1379.

4.3.2. Methyl 2-(but-3-yn-1-yl(phenyl)amino)-3-oxo-3-phenylpropanoate (**4b**)

Prepared from methyl 2-diazo-3-oxo-3-phenylpropanoate and N-(but-3-yn-1-yl)aniline. Orange oil (25 mg, 96%). TLC: R_f 0.76 (20% ethyl acetate in hexanes). IR (NaCl): 3298, 3065, 2949, 1643. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.99 (s, 1H), 7.64–7.58 (m, 2H), 7.41–7.35 (m, 1H), 7.32–7.25 (m, 4H), 6.82 (tt, $J = 7.3$, 1.0 Hz, 1H), 6.77–6.72 (m, 2H), 3.71 (s, 3H), 3.44 (ddd, $J = 14.4$, 9.9, 5.6 Hz, 1H), 3.32 (ddd, $J = 14.4$, 9.9, 6.0 Hz, 1H), 2.33–2.12 (m, 2H), 1.92 (t, $J = 2.7$ Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.61, 171.61, 148.25, 133.11, 130.87, 129.47 (2C), 128.24 (2C), 127.92 (2C), 117.76, 112.48 (2C), 109.03, 81.95, 69.50, 52.21, 51.39, 17.05. HRMS (ESI) *m/z* calcd for $C_{20}H_{19}NO_3Na$ ($[M+Na]^+$) 344.1263; found 344.1255.

4.3.3. Methyl 3-oxo-2-(pent-3-yn-1-yl(phenyl)amino)-3-phenylpropanoate (**4c**)

Prepared from methyl 2-diazo-3-oxo-3-phenylpropanoate and N-(pent-3-yn-1-yl)aniline. Orange oil (55 mg, 90%). TLC: R_f 0.78 (20% ethyl acetate in hexanes). IR (NaCl): 3062, 2854, 2594, 2358, 2341, 1728, 1614. ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.99 (s, 1H), 7.64–7.60 (m, 2H), 7.39–7.35 (m, 1H), 7.30–7.23 (m, 4H), 6.80 (tt, $J = 7.3$, 1.0 Hz, 1H), 6.76–6.72 (m, 2H), 3.69 (s, 3H), 3.37 (ddd, $J = 14.3$, 10.1, 5.5 Hz, 1H), 3.27 (ddd, $J = 14.4$, 10.1, 6.0 Hz, 1H), 2.24–2.07 (m, 2H), 1.71 (t, $J = 2.6$ Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.7, 171.5, 148.5, 133.2, 130.8, 129.4 (2C), 128.3, 128.2 (2C), 128.0 (2C), 117.6, 112.5 (2C), 109.1, 52.2, 51.9, 17.3, 3.4, 1.0. HRMS (ESI) *m/z* calcd for $C_{21}H_{21}NO_3Na$ ($[M+Na]^+$) 358.1419; found 358.1501.

4.3.4. Methyl 3-oxo-2-(pent-4-yn-1-yl(phenyl)amino)-3-phenylpropanoate (**4d**)

Prepared from methyl 2-diazo-3-oxo-3-phenylpropanoate and N-(pent-4-yn-1-yl)aniline. Orange oil (27 mg, 90%). TLC: R_f 0.81 (20% ethyl acetate in hexanes). IR (NaCl): 2958, 2920, 2891, 2358, 2331, 1780, 1610. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.00 (s, 1H), 7.62 (d, $J = 8.1$ Hz, 2H), 7.40–7.34 (m, 1H), 7.31–7.27 (m, 2H), 7.25 (s, 1H), 6.79 (dd, $J = 13.9$, 7.7 Hz, 4H), 3.72 (d, $J = 1.7$ Hz, 3H), 3.28 (ddd, $J = 12.4$, 8.9, 6.1 Hz, 2H), 2.00 (td, $J = 7.1$, 3.3 Hz, 2H), 1.94 (d, $J = 2.5$ Hz, 1H), 1.61–1.50 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 171.6, 149.1, 133.3, 130.7, 129.3 (2C), 128.2 (2C), 128.0 (2C), 117.4, 112.6 (2C), 109.3, 83.6, 68.8, 52.2, 51.4, 25.9, 16.0. HRMS (ESI) *m/z* calcd for $C_{21}H_{21}NO_3Na$ ($[M+Na]^+$) 358.1419; found 358.1420.

4.4. Procedure for CAN deprotection of PMP protecting group

Substrate 3i PMP deprotection with Ceric Ammonium Nitrate (CAN): To a 15 mL round bottom flask equipped with a magnetic stir bar was added the PMP-protected pyrrolidine (1 equiv.) in MeCN (0.08 M). This solution was cooled to 0 °C then CAN (3 equiv.) as a 0.5 M solution in H_2O was added dropwise via syringe to the flask. After 1 h, $NaHCO_3$ was added until pH = 6 was achieved then sodium sulfite was added until a brown slurry crashed out. The crude mixture was transferred to a separatory funnel and diluted with brine and ethyl acetate. The organic layer was extracted and dried over Na_2SO_4 and concentrated to yield the crude compound. The crude was loaded to a column and purified with a 20%–50% Hex/EtOAc gradient column.

4.4.1. 3′-methylene-3,4-dihydro-2H-spiro[naphthalene-1,2′-pyrrolidin]-2-one (**5a**)

Prepared 1'-(4-methoxyphenyl)-3′-methylene-3,4-dihydro-2*H*-spiro[naphthalene-1,2′-pyrrolidin]-2-one. Clear viscous oil (24 mg, 83%). TLC: R_f 0.34 (30% ethyl acetate in hexanes). IR (NaCl): 2926, 2855, 2359, 1725. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, $J = 7.9$ Hz, 1H), 7.23 (s, 1H), 7.20 (t, $J = 7.3$ Hz, 1H), 7.12 (d, $J = 7.6$ Hz, 1H), 5.19 (t, $J = 1.8$ Hz, 1H), 4.68 (t, $J = 1.9$ Hz, 1H), 3.41 (dt, $J = 10.0$, 6.6 Hz, 1H), 3.30–3.05 (m, 4H), 2.62 (dt, $J = 13.8$, 5.0 Hz, 1H), 2.59–2.55 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 209.9, 154.8, 142.7, 135.4, 128.6, 127.4, 127.3, 127.2, 116.1, 111.4, 45.9, 35.24, 33.4, 29.6. HRMS (ESI) *m/z* calcd for $C_{14}H_{16}NO$ ($[M+H]^+$) 214.1232; found 214.1236.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.tet.2018.06.042.

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