Note

Transition-metal Controlled Diastereodivergent Radical Cyclization/Azidation Cascade of 1,7-Enynes

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Transition-metal Controlled Diastereodivergent Radical Cyclization/Azidation Cascade of 1,7-Enynes

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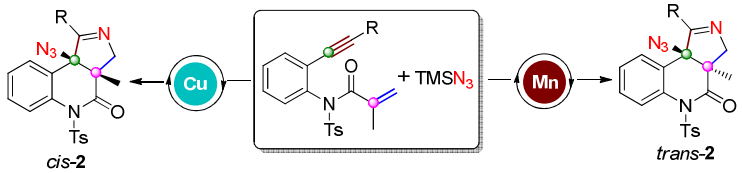
ABSTRACT



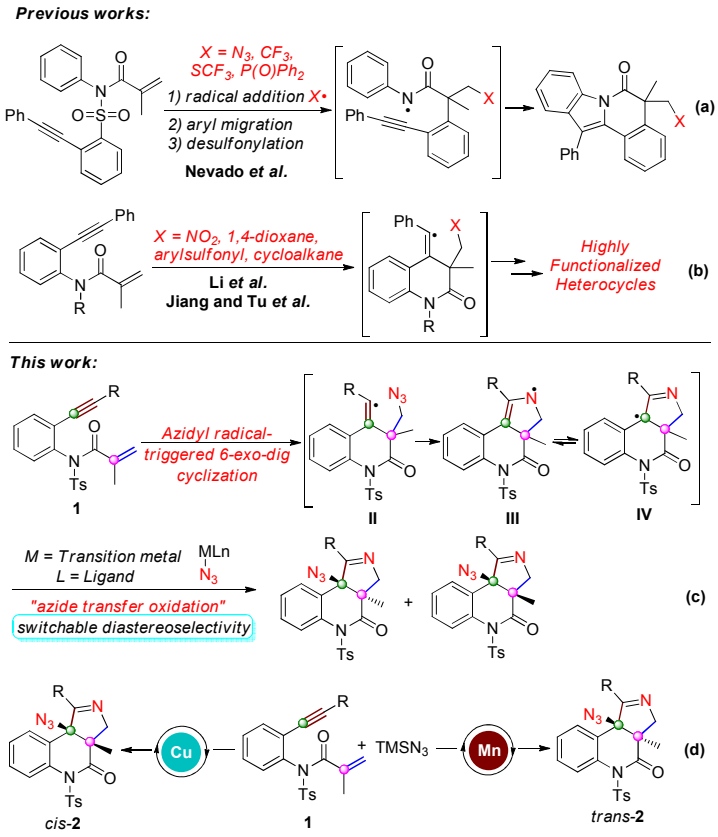
A strategy for achieving diastereodivergent azidations of enynes has been developed, employing azide transfer from M-N_3 complex to alkyl radicals. Following this concept, the diastereoselectivity has been switched by modulating the transition-metals and the ligands. Mn(III)-mediated radical cyclization/azidation cascade of 1,7-enynes afforded *trans*-fused pyrrolo[3,4-*c*]quinolinones, whereas Cu(II)/bipyridine system gave *cis*-products.

Diastereodivergent catalysis[1], aiming at attaining different diastereomers from the same substrates solely controlled by distinct catalysts, is the most straightforward and efficient tool to produce the complete set of diastereomers. This strategy has been extensively employed to selectively control the formation of stereocenters in asymmetric catalysis.[1b–f] On the other hand, azidation of alkenes has emerged as a promising alternative for the synthesis of useful organic azides, which are valuable

precursors of numerous nitrogen-containing compounds[2]. Therefore, the past decade has witnessed substantial achievements in this area.[3] Despite the impressive advances, the stereocontrol of the product distribution still remains a notable challenge, which may be due to the involvement of free radical process. In this context, diastereodivergent azidations to generate the complete set of diastereomers is of high demand. In the pioneering works of Kochi,[4] Fristad,[3d, 5] and Minisci[6], it is suggested that the terminating step of olefin diazidations proceeds through azide transfer from metal azide complex to alkyl radicals[7], namely "ligand-transfer oxidation" process. Besides, an iron-catalyzed diazidation was disclosed by Xu's group very recently, in which azido ligand transfer step was believed to be crucial for its high d.r. value.[3f] Intrigued by these seminal works and our interests in azide chemistry[8], we speculated that if a radical reaction was terminated by the azide transfer oxidation step, instead of free azidyl radical process, the diastereoselectivity possibly could be switched by modulating the transition-metals and the ligands.

In recent years, 1,*n*-enynes, which endowed with both C=C and C≡C unsaturated moieties, are privileged building blocks for assembling elaborate compounds via radical reaction cascades. For example, Nevado and co-workers[9] reported various radicals triggered domino cyclizations of enynes, providing highly complex aza-heterocycles through a radical addition/aryl migration/desulfonylation cascade pathway (Scheme 1a). Li[10], Jiang and Tu[11] *et al*. devoted to exploring the intriguing radical reactivity of *N*-tethered 1,7-enynes (Scheme 1b). As our continued efforts to exploit new reaction patterns of unsaturated precursors,[12] we envisioned that

enynes **1** could undergo azidyl radical-triggered cyclization/the loss of N_2/tautomerization cascade process to form alkyl radical **IV**, which can be intercepted by L_nM-N_3 species[3j], leading to alkyl azides with high diastereoselectivity (Scheme 1c). Indeed, Mn(III)-mediated azidations of *N*-sulfonyl tethered 1,7-enynes **1** afforded *trans*-fused pyrrolo[3,4-*c*]quinolinones (*trans*-**2**), whereas Cu(II)/bipyridine system gave *cis*-products (Scheme 1d). Although Li *et al.* has already reported an analogous Cu-catalyzed azidation of enynes for the synthesis of *cis*-**2**,[13] additional multi-step reactions were required to synthesize azido-benziodoxolone, which served as the azide source in the work. Besides, easily handled and commercial available $TMSN_3$ was proven to be ineffective for the reaction. Given the step-economy, simple operation and opposite selectivity of our protocol, we herein demonstrate Mn- and Cu-controlled diastereodivergence in radical bicyclization/azidation cascade of enynes.

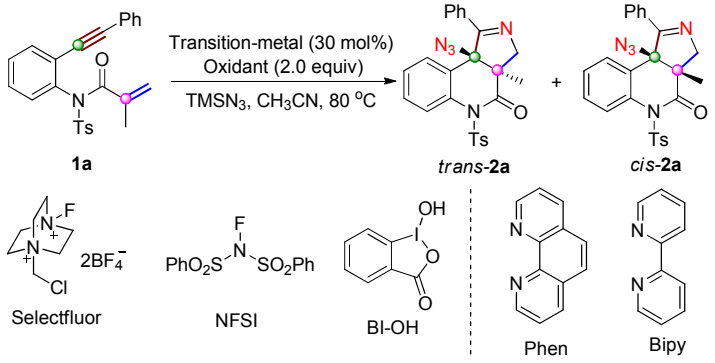


Scheme 1. Diastereodivergent radical cyclization/azidation cascade of 1,7-enynes.

We commenced our investigations using *N*-sulfonyl tethered 1,7-enyne **1a** as benchmark substrate and commercial available $TMSN_3$ as azide source. When 3.0 equivalent of $Mn(OAc)_3•2H_2O$ was employed as the radical initiator, to our delight, *trans*-fused pyrrolo[3,4-*c*]quinolinones **2a**[14] was obtained in 53% yield, albeit with moderate diastereoselectivity (Table 1, entry 1). In contrast, commonly used oxidant $K_2S_2O_8$ gave poor results, which possibly was ascribed to the free radical process in its terminating step (Table 1, entry 2). The utilization of TBPB as oxidant generated no desired product (Table 1, entry 3). Notably, treatment of **1a** with sub-stoichiometric $Mn(OAc)_3•2H_2O$ and 2.0 equivalent of TBPB also produced *trans*-**2a** in a comparable yield (Table 1, entry 4), which prompted us to evaluate other transition-metals. The

results demonstrated that Fe(II) could execute this reaction, but were inferior to Mn(III) (Table 1, entry 5). Surprisingly, *cis*-**2a** is predominant in the product mixture when $Cu(ClO_4)_2$•$6H_2O$ was introduced to the reaction (Table 1, entry 6). After screening of various oxidants, we were delighted to find that NFSI led to *trans*-**2a** in 15:1 d.r. and 67% yield (Table 1, entries 7–11). The introduction of ligands exerted a negative influence on the results (Table 1, entries 12, 13). In comparison, the combination of Cu(II) and N,N-bidentate ligand, such as phen and bipy, could drastically increase the selectivity and *cis*-**2a** was observed as the single isomer; the latter ligand yielded a slightly better result (Table 1, entries 14, 15).

Table 1. Optimization of the reaction conditions.[a]



Entry	Transition-metal	Oxidant	Yield[b] [%]	d.r.[b] (*trans*:*cis*)
1[c]	$Mn(OAc)_3$•$2H_2O$	–	53 (*trans*)	5.6:1
2[c]	–	$K_2S_2O_8$	25 (*trans*)	1.8:1
3[c]	–	TBPB	0	–
4	$Mn(OAc)_3$•$2H_2O$	TBPB	45 (*trans*)	8.6:1
5	$Fe(OAc)_2$	TBPB	30 (*trans*)	1:1
6	$Cu(ClO_4)_2$•$6H_2O$	TBPB	33 (*cis*)	1:3.6

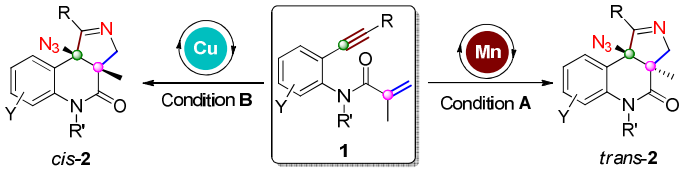
7	$Mn(OAc)_3•2H_2O$	$K_2S_2O_8$	14 (*trans*)	2.4:1
8	$Mn(OAc)_3•2H_2O$	TBHP	10 (*trans*)	6.6:1
9	$Mn(OAc)_3•2H_2O$	BI-OH	38 (*trans*)	5.7:1
10	$Mn(OAc)_3•2H_2O$	Selectfluor	38 (*trans*)	7.2:1
11	$Mn(OAc)_3•2H_2O$	NFSI	67 (*trans*)	15:1
12	$Mn(OAc)_3•2H_2O$ / Phen	NFSI	39 (*trans*)	4.4:1
13	$Mn(OAc)_3•2H_2O$ / Bipy	NFSI	35 (*trans*)	4.7:1
14	$Cu(ClO_4)_2•6H_2O$ /Phen	TBPB	59 (*cis*)	–[d]
15	$Cu(ClO_4)_2•6H_2O$ /Bipy	TBPB	64 (*cis*)	–[d]

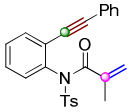
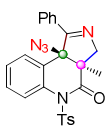
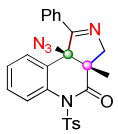
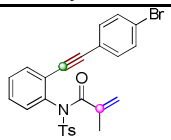
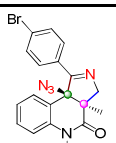
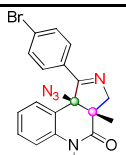
[a]Reaction conditions: **1a** (0.10 mmol), $Mn(OAc)_3•2H_2O$ (30 mol%), ligand (33 mol% when added), $TMSN_3$ (6.0 equiv), and oxidant (2.0 equiv) in CH_3CN (2.0 mL) at 80 °C for 22 h. [b]Determined by HPLC analysis of the crude reaction mixture before isolated. Naphthalene was used as the internal standard. [c]$Mn(OAc)_3•2H_2O$ or oxidant (3.0 equiv) was employed. [d]*cis*-**2a** was observed as the single isomer. TBPB = *tert*-Butyl peroxybenzoate. TBHP = *tert*-Butyl hydroperoxide.

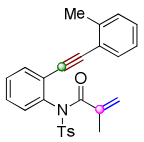
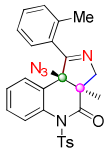
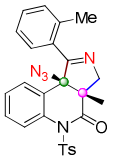
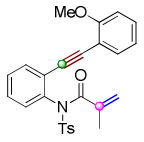
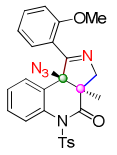
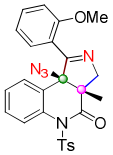
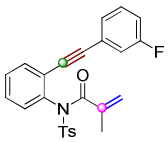
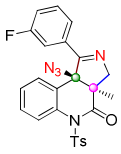
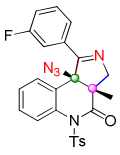
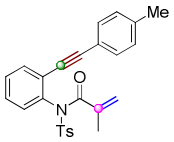
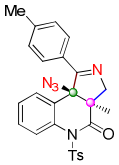
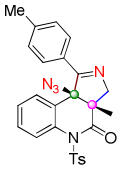
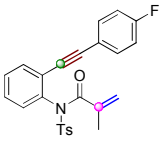
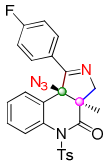
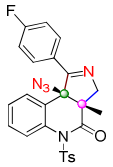
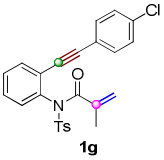
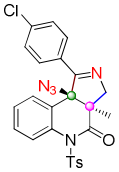
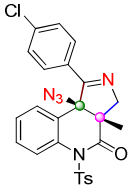
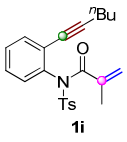
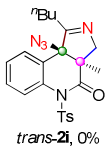
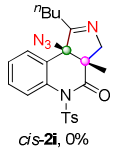
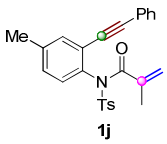
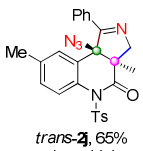
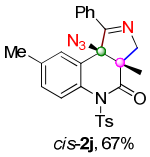
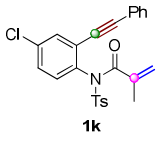
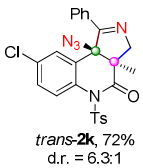
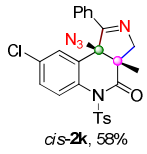
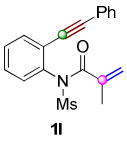
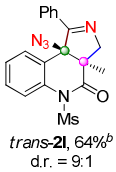
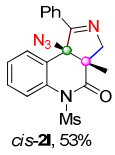
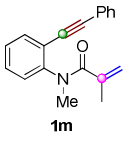
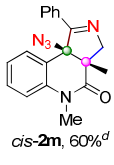
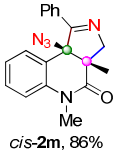
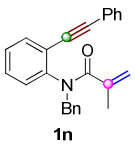
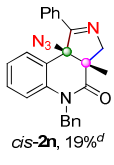
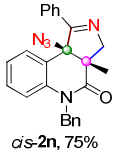
With the optimized conditions in hand, we next explored the scope and limitations of Mn(III)- and Cu(II)-mediated radical cyclization/azidation cascade of enynes **1**. As summarized in Table 2, variations of R at the terminal alkyne were first examined. A wide array of substituted aromatic groups were well tolerated, providing both *trans*- and *cis*-**2** in moderate to good yields (Table 2, entries 2–8). The electronic properties and the positions of the substituents on the phenyl ring had only minimal influence on the reactivity. For example, electron-rich substrates **1b**, **1c** and **1e** underwent this diastereodivergent reaction smoothly, furnishing the corresponding

diastereomers with good selectivity, regardless of the steric effects. Electron-deficient substituents, such as F, Cl and Br, on the phenyl ring were also compatible with the transformations (Table 2, entries 4, 6–8). It is worthwhile to mention that treatment of **1g** with Cu(II)/bipy/TBPB system only delivered *cis*-isomer in 38% yield and 75% conversion, which was owing to the poor solubility under the standard conditions. However, no desired products were observed when submitting butyl substituted enyne **1i** to the standard conditions. Substrates possessing different substituents on the aniline moiety were readily converted into the complete set of diastereomers in high efficiencies (Table 2, entries 10, 11). Notably, *N*-Ms tethered enyne **1l** afforded *trans*- and *cis*-**2l** in 64% and 54% yield under the optimized conditions, respectively. Surprisingly, both Mn(III)- and Cu(II)-mediated reactions of *N*-alkyl substrates **1m** and **1n** led to the formation of *cis*-products. Electron-donating alkyl substituent presumably changes the inherent properties of the substrates and its less steric hinderance tends to make the cyclized rings too flexible to facilitate the coordination of manganese complex and the nitrogen atoms, thus affording the same selectivity.

Table 2. Substrate scope of diastereodivergent radical cyclization/azidation cascade of 1,7-enynes.[a]



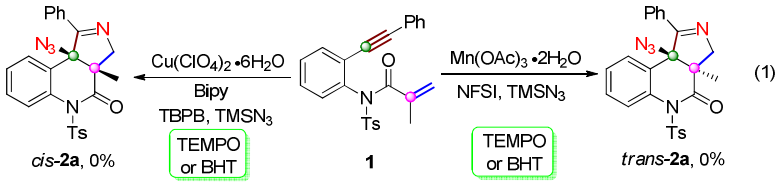
Entry	Enyne **1**	Condition **A**	Condition **B**	Entry	Enyne **1**	Condition **A**	Condition **B**
1	 **1a**	 *trans*-**2a**, 59% d.r. = 15:1	 *cis*-**2a**, 59%	8	 **1h**	 *trans*-**2h**, 57% d.r. = 7.3:1	 *cis*-**2h**, 46%

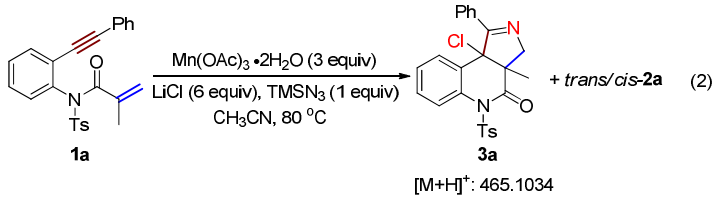
2	 **1b**	 *trans*-**2b**, 59% d.r. = 16:1	 *cis*-**2b**, 54%
3	 **1c**	 *trans*-**2c**, 49%[b] d.r. = 13:1	 *cis*-**2c**, 44%
4	 **1d**	 *trans*-**2d**, 65% d.r. = 12:1	 *cis*-**2d**, 78%
5	 **1e**	 *trans*-**2e**, 60% d.r. = 16:1	 *cis*-**2e**, 55%
6	 **1f**	 *trans*-**2f**, 66% d.r. = 16:1	 *cis*-**2f**, 63%
7	 **1g**	 *trans*-**2g**, 64% d.r. = 10:1	 *cis*-**2g**, 38%[c]
9	 **1i**	 *trans*-**2i**, 0%	 *cis*-**2i**, 0%
10	 **1j**	 *trans*-**2j**, 65% d.r. = 14:1	 *cis*-**2j**, 67%
11	 **1k**	 *trans*-**2k**, 72% d.r. = 6.3:1	 *cis*-**2k**, 58%
12	 **1l**	 *trans*-**2l**, 64%[b] d.r. = 9:1	 *cis*-**2l**, 53%
13	 **1m**	 *cis*-**2m**, 60%[d]	 *cis*-**2m**, 86%
14	 **1n**	 *cis*-**2n**, 19%[d]	 *cis*-**2n**, 75%

[a]Condition **A**: **1** (0.20 mmol), $Mn(OAc)_3$•$2H_2O$ (30 mol%), NFSI (2.0 equiv), $TMSN_3$ (6.0 equiv), CH_3CN (4.0 mL), 80 °C for 22 h; d.r. (*trans*/*cis*) value was determined by HPLC analysis of the crude reaction mixture before isolated. Condition **B**: **1** (0.20 mmol), $Cu(ClO_4)_2$•$6H_2O$ (30 mol%), Bipy (33 mol%), TBPB (2.0 equiv), $TMSN_3$ (6.0 equiv), CH_3CN (4.0 mL), 80 °C for 22 h; *cis*-**2** was observed as the single isomer. [b]$Mn(OAc)_3$•$2H_2O$ (3.0 equiv) was employed in the reaction. [c]Yield was calculated on the basis of 0.20 mmol of the product and 25% of starting substrate **1g** was recovered. [d]*trans*-isomer was not observed.

To gain further insights into the diastereodivergent azidation reaction, some

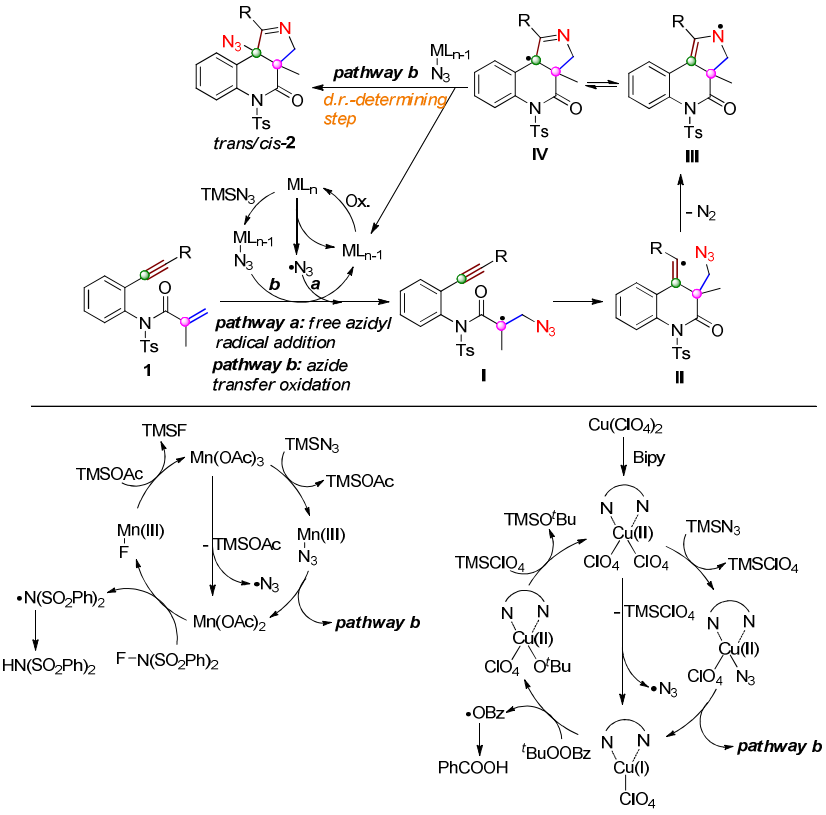
mechanistic experiments were conducted. Subjecting TEMPO or BHT, well-known radical scavengers, to the reaction system led to complete inhibition of this diastereodivergent process, implying that a free radical-mediated pathway is involved (Eq. 1). Additionally, when a mixture of LiCl (6.0 equiv), $Mn(OAc)_3•2H_2O$ (3.0 equiv) and $TMSN_3$ (1.0 equiv) was introduced to the reaction system, chloro-substituted product **3a** was observed, explicitly illustrating that Mn(III)-Cl complex is formed and then undergoes chloro-ligand transfer oxidation process to deliver **3a** (Eq. 2). As a consequence, we believe that L_nM-N_3 species is in situ formed and then involved in the d.r.-determining step, which is in accordance with our initial hypothesis.





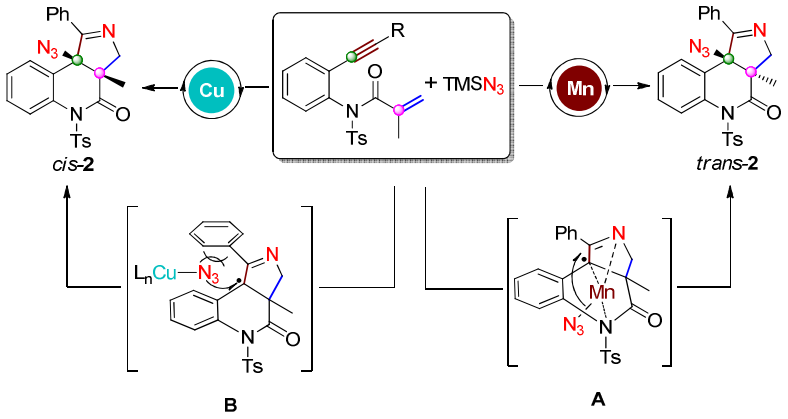
On the basis of these experimental observations, a plausible mechanism is presented in Scheme 2. Initially, $TMSN_3$ is oxidized by high-valent transition-metals to produce a free azidyl radical, which then attacks the alkene moiety of enyne **1**, giving alkyl radical **I** (pathway a). It is noteworthy that direct azide transfer from metal azide complex to alkene cannot be ruled out (pathway b). Radical-triggered 6-*exo*-*dig* cyclization of **I** affords vinyl radical **II**, which can be further trapped by azidyl group, followed by releasing one molecule of nitrogen to generate aminyl radical **III**. The tautomer of **III**, alkyl radical **IV**, undergoes inner-sphere azide

transfer oxidation process, rather than free azidyl radical pathway, to deliver the desired product **2**. The oxidation of low-valent metals Mn(II) and Cu(I) by NFSI and TBPB regenerates the catalysts.



Scheme 2. A plausible mechanism.

Although we have no direct rationale on the coordination modes between transition-metal complex and the substrate, a tentative model for the diastereodivergence is depicted (Scheme 3). In the case of Mn-mediated reaction, Mn-N_3 possibly also coordinates with the nitrogen atoms of intermediate **IV**, following azide transfer to produce *trans*-**2**. When Cu was introduced to the reaction, the pronounced steric repulsion between phenyl and azide group enables the azide attack on the opposite side, thus providing *cis*-**2**.



Scheme 3. A tentative model for transition-metal controlled diastereodivergence.

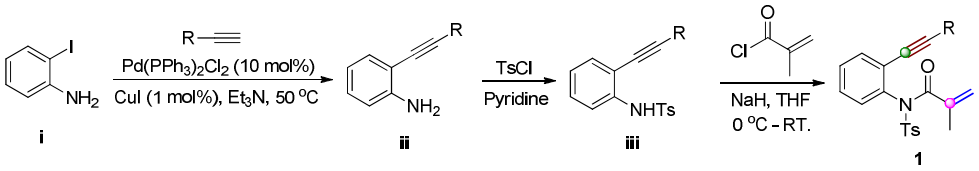
In summary, we have developed a strategy for achieving diastereodivergent azidations of enynes, employing azide transfer from M-N_3 complex to alkyl radicals. Following this concept, the diastereoselectivity has been switched by modulating the transition-metals and the ligands. Mn(III)-mediated radical cyclization/azidation cascade of 1,7-enynes afforded *trans*-fused pyrrolo[3,4-*c*]quinolinones, whereas Cu(II)/bipyridine system gave *cis*-products. Further studies on the azide transfer oxidation mechanism are underway in our laboratory.

EXPERIMENTAL SECTION

General Information. Unless otherwise stated, all manipulations and reactions were performed under inert atmosphere using standard Schlenk techniques or in an argon-filled glove-box. All chemicals were purchased from commercial sources and were used without further purification. Solvents were treated prior to use according to the standard methods. Column chromatography was carried out on silica gel (200–300 mesh) using a forced flow of eluent at 0.3–0.5 bar pressure. NMR Spectra were recorded at room temperature in $CDCl_3$ on 400 MHz spectrometers. The chemical shifts for ^1H NMR were recorded in ppm downfield from tetramethylsilane (TMS)

with $CDCl_3$ (7.26 ppm) as the internal standard. The chemical shifts for ^{13}C NMR were recorded in ppm downfield using the central peak of $CDCl_3$ (77.16 ppm) as the internal standard. Coupling constants (J) are reported in hertz and refer to apparent peak multiplications. The abbreviations *s*, *d*, *t*, *q* and *m* stand for singlet, doublet, triplet, quartet and multiplet in that order. HRMS data were obtained by ESI on a Q-TOF mass spectrometer.

General procedure for the synthesis of enynes 1



Ts-protected 2-(phenylethynyl)aniline **iii** was prepared according to the reported method[15]. 60% NaH in mineral oil (2 equiv, 20 mmol, 0.80 g) was slowly added to a solution of **iii** (10 mmol) in 40 mL THF and the mixture was stirred 30 minutes at 0 °C, then the methacryloyl chloride (2 equiv, 20 mmol, 2.0 mL) was added, and stirred overnight. The reaction was quenched with saturated NH_4Cl, and the solution was extracted with ethyl acetate three times. The combined organic phases were dried with anhydrous Na_2SO_4, the solvent was concentrated via rotary evaporation. The crude residue was recrystallized with EtOH to afford **1** as a white or yellow solid.

***N*-(2-(phenylethynyl)phenyl)-*N*-tosylmethacrylamide (1a):** white solid; 6.0 g (in 16.0 mmol scale); 86% yield; mp 127–128 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.3 Hz, 2H), 7.66 – 7.59 (m, 1H), 7.50 – 7.44 (m, 1H), 7.44 – 7.41 (m, 1H), 7.41 – 7.36 (m, 1H), 7.27 (d, J = 7.5 Hz, 1H), 7.21 (t, J = 7.4 Hz, 2H), 7.05 (d, J = 8.3 Hz, 4H), 5.23 (s, 2H), 2.08 (s, 3H), 1.77 (s, 3H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 170.6, 144.8, 139.2, 138.9, 136.3, 132.8, 132.7, 131.5, 130.0, 129.2, 129.01, 128.97,

128.8, 128.1, 123.8, 123.5, 122.09, 94.9, 85.6, 21.5, 19.3. HRMS (ESI) calcd for $C_{25}H_{22}NO_3S$ $[M+H]^+$ 416.1315, found 416.1317.

***N*-(2-(o-tolylethynyl)phenyl)-*N*-tosylmethacrylamide (1b):** white solid; 833.0 mg (in 3.2 mmol scale); 53% yield; mp 125–126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.57 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.51 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.46 – 7.35 (m, 2H), 7.22 – 7.15 (m, 1H), 7.12 (d, *J* = 7.4 Hz, 1H), 7.07 – 7.00 (m, 3H), 6.91 (d, *J* = 7.6 Hz, 1H), 5.26 (s, 1H), 5.22 (s, 1H), 2.30 (s, 3H), 2.10 (s, 3H), 1.77 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.5, 144.8, 139.9, 139.2, 138.5, 136.3, 133.0, 132.5, 132.3, 130.0, 129.3, 129.2, 129.0, 128.89, 128.87, 125.5, 124.0, 123.5, 121.9, 94.0, 89.4, 21.5, 20.6, 19.4. HRMS (ESI) calcd for $C_{26}H_{24}NO_3S$ $[M+H]^+$ 430.1471, found 430.1478.

***N*-(2-((2-methoxyphenyl)ethynyl)phenyl)-*N*-tosylmethacrylamide (1c):** light yellow solid; 1.25 g (in 4.1 mmol scale); 69% yield; mp 114–115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.62 – 7.51 (m, 2H), 7.45 – 7.34 (m, 2H), 7.28 – 7.20 (m, 1H), 7.04 (d, *J* = 8.2 Hz, 2H), 6.86 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.78 (t, *J* = 7.9 Hz, 2H), 5.25 (s, 1H), 5.18 (s, 1H), 3.77 (s, 3H), 2.09 (s, 3H), 1.77 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.5, 159.9 144.6, 139.2, 138.5, 136.4, 133.7, 133.1, 132.5, 130.3, 130.1, 129.2, 128.9, 128.7, 124.0, 123.1, 120.2, 111.3, 110.2, 91.8, 89.6, 55.5, 21.5, 19.4. HRMS (ESI) calcd for $C_{26}H_{24}NO_4S$ $[M+H]^+$ 446.1421, found 446.1424.

***N*-(2-((3-fluorophenyl)ethynyl)phenyl)-*N*-tosylmethacrylamide (1d):** white solid; 700 mg (in 1.9 mmol scale); 79% yield; mp 112–113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.51 – 7.36 (m, 3H), 7.19 (dd, *J* = 14.0, 7.7 Hz, 1H), 7.10 (d, *J* = 8.1 Hz, 2H), 7.03 – 6.95 (m, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 9.2 Hz, 1H), 5.25 (s, 1H), 5.23 (s, 1H), 2.14 (s, 3H), 1.76 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.6, 162.1 (d, *J* = 246.7 Hz), 144.9, 139.1, 139.1, 136.4, 132.9, 132.7, 130.1, 129.7 (d, *J* = 8.6 Hz), 129.3 (d, *J* = 7.9 Hz), 129.0, 127.4 (d, *J* = 3.0 Hz), 124.0, 123.8, 123.7, 123.0, 118.2 (d, *J* = 23.0 Hz), 116.2 (d, *J* = 21.2 Hz), 93.5, 86.4, 21.4, 19.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.80. HRMS (ESI)

calcd for $C_{25}H_{21}FNO_3S$ $[M+H]^+$ 434.1221, found 434.1229.

***N*-(2-(p-tolylethynyl)phenyl)-*N*-tosylmethacrylamide (1e):** white solid; 1.2 g (in 3.6 mmol scale); 78% yield; mp 182–183 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.50 – 7.34 (m, 3H), 7.06 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.1 Hz, 2H), 5.23 (s, 1H), 5.21 (s, 1H), 2.34 (s, 3H), 2.10 (s, 3H), 1.76 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.6, 144.7, 139.2, 139.1, 138.9, 136.4, 132.73, 132.66, 131.5, 130.1, 129.2, 129.0, 128.9, 128.8, 123.8, 123.7, 119.0, 95.3, 85.1, 21.7, 21.5, 19.3. HRMS (ESI) calcd for $C_{26}H_{24}NO_3S$ $[M+H]^+$ 430.1471, found 430.1472.

***N*-(2-((4-fluorophenyl)ethynyl)phenyl)-*N*-tosylmethacrylamide (1f):** light yellow solid; 1.3 g (in 3.7 mmol scale); 84% yield; mp 184–185 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.49 – 7.36 (m, 3H), 7.11 – 7.02 (m, 4H), 6.92 (t, *J* = 8.7 Hz, 2H), 5.25 (s, 1H), 5.23 (s, 1H), 2.13 (s, 3H), 1.76 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.7, 162.9 (d, *J* = 250.8 Hz), 144.7, 139.1, 139.0, 136.5, 133.6 (d, *J* = 8.5 Hz), 132.7, 130.1, 129.3, 129.1, 129.0, 124.0, 123.4, 118.2(d, *J* = 3.4 Hz), 115.5 (d, *J* = 22.1 Hz), 93.9, 85.4, 21.5, 19.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.80. HRMS (ESI) calcd for $C_{25}H_{21}FNO_3S$ $[M+H]^+$ 434.1221, found 434.1223.

***N*-(2-((4-chlorophenyl)ethynyl)phenyl)-*N*-tosylmethacrylamide (1g):** white solid; 1.5 g (in 3.4 mmol scale); 98% yield; mp 200–201 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.50 – 7.36 (m, 3H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 8.2 Hz, 2H), 5.24 (s, 1H), 5.23 (s, 1H), 2.13 (s, 3H), 1.75 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.7, 144.8, 139.1, 136.4, 135.0, 132.7, 132.7, 130.1, 129.3, 129.3, 129.0, 128.5, 124.0, 123.2, 120.5, 93.7, 86.6, 21.5, 19.2. HRMS (ESI) calcd for $C_{25}H_{21}ClNO_3S$ $[M+H]^+$ 450.0925, found 450.0925.

***N*-(2-((4-bromophenyl)ethynyl)phenyl)-*N*-tosylmethacrylamide (1h):** white solid; 400 mg (in 1.2 mmol scale); 71% yield; mp 206–207 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.42 (d, *J* =

8.1 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 5.27 (s, 1H), 5.24 (s, 1H), 2.15 (s, 3H), 1.77 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.7, 144.8, 139.1 136.4, 132.9, 132.7, 131.4, 130.1, 129.3, 129.3, 129.0, 124.1, 123.3, 123.2, 121.0, 93.8, 86.8, 21.5, 19.3. HRMS (ESI) calcd for $C_{25}H_{21}BrNO_3S$ $[M+H]^+$ 494.0420, found 494.0422.

***N*-(2-(hex-1-ynyl)phenyl)-N-tosylmethacrylamide (1i):** white solid; 476 mg (in 1.7 mmol scale); 71% yield; mp 142–143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.45 – 7.21 (m, 5H), 5.22 (s, 1H), 5.21 (s, 1H), 2.50 (s, 3H), 2.54 – 1.84 (m, 2H), 1.77 (s, 3H), 1.50 – 1.06 (m, 4H), 0.86 (t, *J* = 6.3 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.5, 144.5, 139.2, 138.8, 136.6, 133.1, 132.2, 130.1, 129.1, 129.0, 128.2, 124.5, 123.4, 96.9, 76.6, 30.2, 22.3, 21.8, 19.3, 19.1, 13.7. HRMS (ESI) calcd for $C_{23}H_{26}NO_3S$ $[M+H]^+$ 396.1628, found 396.1631.

***N*-(4-methyl-2-(phenylethynyl)phenyl)-*N*-tosylmethacrylamide (1j):** white solid; 415 mg (in 2.3 mmol scale); 42% yield; mp 166–167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.44 (s, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 7.0 Hz, 1H), 7.20 (t, *J* = 7.3 Hz, 3H), 7.08 – 7.00 (m, 4H), 5.23 (s, 2H), 2.44 (s, 3H), 2.08 (s, 3H), 1.77 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.7, 144.8, 139.6, 139.2, 138.7, 136.4, 133.2, 132.5, 131.4, 130.2, 130.1, 129.0, 128.6, 128.1, 123.7, 122.2, 120.5, 94.2, 85.8, 21.6, 21.5, 19.3. HRMS (ESI) calcd for $C_{26}H_{24}NO_3S$ $[M+H]^+$ 430.1471, found 430.1473.

***N*-(4-chloro-2-(phenylethynyl)phenyl)-*N*-tosylmethacrylamide (1k):** white solid; 520 mg (in 2.0 mmol scale); 58% yield; mp 176–177 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 1.8 Hz, 1H), 7.43 – 7.34 (m, 2H), 7.32 – 7.19 (m, 3H), 7.05 (t, *J* = 7.9 Hz, 4H), 5.30 (s, 1H), 5.25 (s, 1H), 2.09 (s, 3H), 1.79 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.3, 145.1, 139.9, 139.0, 136.1, 134.5, 133.4, 132.7, 131.6, 130.0, 129.7, 129.12, 129.07, 128.2, 124.3, 122.1, 121.7, 95.8, 84.7, 21.5, 19.3. HRMS (ESI) calcd for $C_{25}H_{21}ClNO_3S$ $[M+H]^+$ 450.0925, found 450.0929.

***N*-(methylsulfonyl)-*N*-(2-(phenylethynyl)phenyl)methacrylamide (1l):** light yellow

solid; 710 mg (in 2.3 mmol scale); 90% yield; mp 127–128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 4H), 7.46 – 7.36 (m, 5H), 5.35 (s, 1H), 5.33 (s, 1H), 3.52 (s, 3H), 1.89 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.0, 138.9, 138.2, 133.0, 132.5, 131.5, 129.5, 129.4, 129.4, 128.9, 124.6 123.1, 122.0, 95.6, 85.7, 42.4, 19.3. HRMS (ESI) calcd for $C_{19}H_{18}NO_3S$ $[M+H]^+$ 340.1002, found 340.1002.

***N*-methyl-*N*-(2-(phenylethynyl)phenyl)methacrylamide (1m):** known compound[10a]; white solid; 200 mg (in 3.4 mmol scale); 21% yield; mp 85–86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.48 (m, 3H), 7.39 – 7.27 (m, 5H), 7.18 (d, *J* = 7.6 Hz, 1H), 5.03 (s, 1H), 5.00 (s, 1H), 3.38 (s, 3H), 1.84 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.4, 146.5, 140.5, 133.0, 131.8, 129.4, 128.9, 128.6, 128.3, 127.6, 122.7, 122.4, 119.1, 94.9, 85.8, 37.0, 20.3. HRMS (ESI) calcd for $C_{19}H_{18}NO$ $[M+H]^+$ 276.1383, found 276.1387.

***N*-benzyl-*N*-(2-(phenylethynyl)phenyl)methacrylamide (1n):** white solid; 261 mg (in 1.2 mmol scale); 62% yield; mp 178–179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.44 (m, 3H), 7.34 – 7.23 (m, 5H), 7.22 – 7.09 (m, 5H), 6.86 (d, *J* = 7.4 Hz, 1H), 5.51 (d, *J* = 14.3 Hz, 1H), 5.02 (s, 1H), 4.98 (s, 1H), 4.60 (d, *J* = 14.3 Hz, 1H), 1.86 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.8, 144.3, 140.3, 137.0, 132.7, 131.5, 129.1, 129.0, 128.7, 128.6, 128.3, 128.1, 127.3, 127.2, 122.6, 122.4, 119.0, 94.7, 86.1, 52.3, 20.1. HRMS (ESI) calcd for $C_{25}H_{22}NO$ $[M+H]^+$ 352.1696, found 352.1702.

Representative procedure for the synthesis of *trans*-product

To a sealed tube were added enynes **1** (0.2 mmol), $Mn(OAc)_3$•$2H_2O$ (30 mol%), NFSI (2 equiv.), and MeCN (4 mL) in sequence. Subsequently $TMSN_3$ (6 equiv.) was introduced. The resulting dark solution was stirred at 80 ^{o}C for 22 h. Upon completion, remove the solvent and purification by flash chromatography on silica gel (petroleum ether/EtOAc: 5/1) afforded the desired products *trans*-**2**.

***trans*-9b-azido-3a-methyl-1-phenyl-5-tosyl-5,9b-dihydro-3*H*-pyrrolo[3,4-*c*]quinolin-4(3a*H*)-one (*trans*-2a):** white solid; 55.3 mg; 59% yield; mp 178–179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 7.0 Hz, 2H), 7. 59 – 7.44 (m, 4H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.19 – 7.10 (m, 2H),

4.05 (d, *J* = 16.4 Hz, 1H), 3.89 (d, *J* = 16.4 Hz, 1H), 2.45 (s, 3H), 0.80 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.3, 168.7, 145.6, 137.5, 135.3, 133.7, 131.4, 129.9, 129.7, 129.2, 129.1, 128.0, 126.32, 126.29, 126.26, 126.0, 79.7, 63.4, 57.5, 21.9, 20.9. HRMS (ESI) calcd for $C_{25}H_{22}N_5O_3S$ $[M+H]^+$ 472.1438, found 472.1439.

***trans*-9b-azido-3a-methyl-1-*o*-tolyl-5-tosyl-5,9b-dihydro-3*H*-pyrrolo[3,4-*c*]quinolin-4(3a*H*)-one (*trans*-2b):** white solid; 57.5 mg; 59% yield; mp 156–157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 10.5, 8.7 Hz, 3H), 7.47 – 7.30 (m, 7H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 4.07 (d, *J* = 16.0 Hz, 1H), 3.96 (d, *J* = 15.9 Hz, 1H), 2.45 (s, 3H), 2.37 (s, 3H), 0.94 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.3, 169.7, 145.6, 137.3, 136.8, 135.4, 133.8, 131.7, 130.1, 129.8, 129.6, 129.2, 127.3, 126.4, 125.8, 125.4, 125.1, 79.7, 63.6, 56.5, 21.9, 20.8, 20.4. HRMS (ESI) calcd for $C_{26}H_{24}N_5O_3S$ $[M+H]^+$ 486.1594, found 486.1594.

***trans*-9b-azido-1-(2-methoxyphenyl)-3a-methyl-5-tosyl-5,9b-dihydro-3*H*-pyrrolo[3,4-*c*]quinolin-4(3a*H*)-one (*trans*-2c):** white solid; 48.4 mg; 49% yield; mp 158–159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 2H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.57 – 7.50 (m, 1H), 7.47 – 7.40 (m, 1H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.14 – 7.02 (m, 3H), 6.98 (d, *J* = 7.6 Hz, 1H), 4.10 (d, *J* = 15.4 Hz, 1H), 3.86 – 3.80 (m, 4H), 2.46 (s, 3H), 0.82 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.6, 169.7, 157.2, 145.5, 136.9, 135.8, 132.5, 129.7, 129.5, 129.3, 126.2, 125.6, 125.3, 124.8, 121.6, 111.4, 78.4, 65.7, 63.0, 56.2, 21.9, 19.9. HRMS (ESI) calcd for $C_{26}H_{24}N_5O_4S$ $[M+H]^+$ 502.1544, found 502.1549.

***trans*-9b-azido-1-(3-fluorophenyl)-3a-methyl-5-tosyl-5,9b-dihydro-3*H*-pyrrolo[3,4-*c*]quinolin-4(3a*H*)-one (*trans*-2d):** white solid; 63.1 mg; 65% yield; mp 173–174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.58 – 7.46 (m, 1H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.26 (m, 1H), 7.19 – 7.11 (m, 2H), 4.05 (d, *J* = 16.5 Hz, 1H), 3.91 (d, *J* = 16.5 Hz, 1H), 2.45 (s, 3H), 0.79 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.1, 167.6, 163.0 (d, *J* = 248.6 Hz), 145.7, 137.5, 135.8 (d, *J* = 7.3 Hz), 135.3, 130.8 (d, *J* = 8.1 Hz), 129.94, 129.85, 129.2, 126.4, 126.1, 125.8, 123.7 (d, *J* = 3.2 Hz), 118.5 (d, *J* = 21.2 Hz), 115.2 (d, *J* =

23.1 Hz), 79.8, 63.5, 57.5, 21.9, 21.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.76. HRMS (ESI) calcd for $C_{25}H_{21}FN_5O_3S$ $[M+H]^+$ 490.1344, found 490.1342.

***trans*-9b-azido-3a-methyl-1-*p*-tolyl-5-tosyl-5,9b-dihydro-3*H*-pyrrolo[3,4-c]quinoli n-4(3a*H*)-one (*trans*-2e):** white solid; 56.0 mg; 60% yield; mp 181–182 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 8.4 Hz, 4H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 4.02 (d, *J* = 16.3 Hz, 1H), 3.87 (d, *J* = 16.3 Hz, 1H), 2.45 (s, 3H), 2.44 (s, 3H), 0.78 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.4, 168.3, 145.5, 141.8, 137.5, 135.2, 130.7, 129.9, 129.7, 129.6, 129.1, 127.9, 126.5, 126.20, 126.17, 126.1, 79.7, 63.2, 57.4, 21.8, 21.6, 20.9. HRMS (ESI) calcd for $C_{26}H_{24}N_5O_3S$ $[M+H]^+$ 486.1594, found 486.1596.

***trans*-9b-azido-1-(4-fluorophenyl)-3a-methyl-5-tosyl-5,9b-dihydro-3*H*-pyrrolo[3, 4-*c*]quinolin-4(3a*H*)-one (*trans*-2f):** white solid; 64.5 mg; 66% yield; mp 190–191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.79 (dd, *J* = 8.6, 5.3 Hz, 2H), 7.52 – 7.45 (m, 1H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.22 (t, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 3.9 Hz, 2H), 4.04 (d, *J* = 16.5 Hz, 1H), 3.88 (d, *J* = 16.4 Hz, 1H), 2.45 (s, 3H), 0.78 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.2, 167.4, 164.6 (d, *J* = 252.9 Hz), 145.7, 137.5, 135.2, 130.2 (d, *J* = 8.6 Hz), 123.0, 129.8, 129.2, 126.4 (d, *J* = 8.1 Hz), 126.3, 125.8, 116.4 (d, *J* = 22.0 Hz), 79.8, 63.4, 57.6, 21.9, 21.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.78. HRMS (ESI) calcd for $C_{25}H_{21}FN_5O_3S$ $[M+H]^+$ 490.1344, found 490.1346.

***trans*-9b-azido-1-(4-chlorophenyl)-3a-methyl-5-tosyl-5,9b-dihydro-3*H*-pyrrolo[3, 4-*c*]quinolin-4(3a*H*)-one (*trans*-2g):** white solid; 65.0 mg; 64% yield; mp 184–185 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.53 – 7.46 (m, 3H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.18 – 7.12 (m, 2H), 4.04 (d, *J* = 16.5 Hz, 1H), 3.89 (d, *J* = 16.5 Hz, 1H), 2.44 (s, 3H), 0.78 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.2, 167.6, 145.7, 137.7, 137.5, 135.2, 132.1, 129.94, 129.85, 129.5, 129.4, 129.2, 126.41, 126.35, 126.2, 125.8, 79.8, 63.5, 57.5, 21.9, 21.0. HRMS (ESI) calcd for $C_{25}H_{21}ClN_5O_3S$ $[M+H]^+$ 506.1048, found

506.1049.

***trans*-9b-azido-1-(4-bromophenyl)-3a-methyl-5-tosyl-5,9b-dihydro-3*H*-pyrrolo[3,4-*c*]quinolin-4(3a*H*)-one (*trans*-2h):** white solid; 56.1 mg; 57% yield; mp 172–173 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.70 – 7.63 (m, 4H), 7.52 – 7.46 (m, 1H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.20 – 7.12 (m, 2H), 4.03 (d, *J* = 16.6 Hz, 1H), 3.89 (d, *J* = 16.5 Hz, 1H), 2.45 (s, 3H), 0.78 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.1, 167.7, 145.7, 137.5, 135.2, 132.5, 132.4, 130.0, 129.9, 129.5, 129.2, 126.42, 126.36, 126.2, 126.1, 125.8, 79.8, 63.6, 57.5, 21.9, 21.0. HRMS (ESI) calcd for $C_{25}H_{21}BrN_5O_3S$ $[M+H]^+$ 550.0543, found 550.0546.

***trans*-9b-azido-3a,8-dimethyl-1-phenyl-5-tosyl-5,9b-dihydro-3*H*-pyrrolo[3,4-*c*]quinolin-4(3a*H*)-one (*trans*-2j):** white solid; 62.6 mg; 65% yield; mp 145–146 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 6.7 Hz, 3H), 7.58 – 7.49 (m, 3H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 7.3 Hz, 1H), 4.02 (d, *J* = 16.3 Hz, 1H), 3.87 (d, *J* = 16.3 Hz, 1H), 2.44 (d, *J* = 8.1 Hz, 6H), 0.79 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.5, 168.9, 145.6, 140.1, 137.4, 135.4, 133.7, 131.3, 129.9, 129.14, 129.07, 128.0, 127.0, 126.8, 125.9, 123.2, 79.7, 63.4, 57.4, 21.9, 21.8, 20.9. HRMS (ESI) calcd for $C_{26}H_{24}N_5O_3S$ $[M+H]^+$ 486.1594, found 486.1597.

***trans*-9b-azido-8-chloro-3a-methyl-1-phenyl-5-tosyl-5,9b-dihydro-3*H*-pyrrolo[3,4-*c*]quinolin-4(3a*H*)-one (*trans*-2k):** white solid; 72.7 mg; 72% yield; mp 153–154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 1.4 Hz, 1H), 7.77 – 7.71 (m, 2H), 7.61 – 7.49 (m, 3H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.16 – 7.04 (m, 2H), 4.04 (d, *J* = 16.5 Hz, 1H), 3.90 (d, *J* = 16.4 Hz, 1H), 2.45 (s, 3H), 0.82 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.0, 168.2, 145.9, 138.5, 135.5, 134.9, 133.4, 131.5, 130.0, 129.2, 127.9, 126.7, 126.5, 126.2, 124.9, 79.3, 63.4, 57.4 21.9, 21.0. HRMS (ESI) calcd for $C_{25}H_{21}ClN_5O_3S$ $[M+H]^+$ 506.1048, found 506.1058.

***trans*-9b-azido-3a-methyl-5-(methylsulfonyl)-1-phenyl-5,9b-dihydro-3*H*-pyrrolo[3,4-*c*]quinolin-4(3a*H*)-one (*trans*-2l):** white solid; 50.6 mg; 64% yield; mp

177–178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 6.9 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.63 – 7.52 (m, 3H), 7.47 – 7.41 (m, 1H), 7.22 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 4.33 (d, *J* = 16.3 Hz, 1H), 4.06 (d, *J* = 16.3 Hz, 1H), 3.59 (s, 3H), 0.86 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.9, 168.7, 136.8, 133.7, 131.5, 129.8, 129.2, 127.9, 126.5, 126.3, 126.0, 125.8, 79.7, 63.5, 57.6, 42.8, 20.7. HRMS (ESI) calcd for $C_{19}H_{18}N_5O_3S$ $[M+H]^+$ 396.1125, found 396.1124

Representative procedure for the synthesis of *cis*-product

To a sealed tube were added enynes **1** (0.2 mmol), $Cu(ClO_4)_2$•$6H_2O$ (30 mol%), bipyridine (33 mol%), and MeCN (4 mL) in sequence. Subsequently TBPB (2 equiv.) and $TMSN_3$ (6 equiv.) were introduced to the mixture. The resulting dark solution was stirred at 80 ^{o}C for 22 h. Upon completion, the reaction was quenched by saturated $NaHCO_3$ and extracted with ethyl acetate three times. The combined organic layers were dried with anhydrous Na_2SO_4. Then remove the solvent and purification by flash chromatography on silica gel (petroleum ether/EtOAc: 10/1) afforded the desired products *cis*-**2**.

***cis*-9b-azido-3a-methyl-1-phenyl-5-tosyl-5,9b-dihydro-3*H*-pyrrolo[3,4-*c*]quinolin-4(3a*H*)-one (*cis*-2a):** known compound[13]; yellow oil; 55.3 mg; 59% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.2 Hz, 1H), 7.73 – 7.66 (m, 3H), 7.61 (d, *J* = 7.5 Hz, 2H), 7.50 – 7.41 (m, 2H), 7.40 – 7.32 (m, 3H), 7.21 (d, *J* = 8.1 Hz, 2H), 4.32 (d, *J* = 16.5 Hz, 1H), 3.79 (d, *J* = 16.5 Hz, 1H), 2.42 (s, 3H), 1.22 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.8, 170.3, 145.7, 134.9, 133.0, 132.5, 131.4, 129.8, 129.40, 129.36, 128.8, 128.5, 128.2, 126.6, 124.1, 122.7, 78.6, 69.3, 61.1, 21.9, 14.2.

***cis*-9b-azido-3a-methyl-1-*o*-tolyl-5-tosyl-5,9b-dihydro-3*H*-pyrrolo[3,4-*c*]quinolin-4(3a*H*)-one (*cis*-2b):** white solid; 52.8 mg; 54% yield; mp 154–155 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.27 – 7.25 (m, 2H), 7.24 – 7.19 (m, 2H), 7.12 – 7.06 (m, 1H), 4.43 (d, *J* = 16.4 Hz, 1H), 3.98 (d, *J* = 16.4 Hz, 1H), 2.43 (s, 3H), 2.40 (s, 3H), 1.32 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.9, 171.0, 145.7, 138.6, 135.8, 133.4, 131.8, 131.7, 130.0, 129.7, 129.1, 128.32, 128.28, 126.4, 125.4, 122.9,

121.8, 79.4, 70.1, 59.6, 21.9, 20.8, 15.8. HRMS (ESI) calcd for $C_{26}H_{24}N_5O_3S$ $[M+H]^+$ 486.1594, found 486.1596.

***cis*-9b-azido-1-(2-methoxyphenyl)-3a-methyl-5-tosyl-5,9b-dihydro-3*H*-pyrrolo[3,4-*c*]quinolin-4(3a*H*)-one (*cis*-2c):** white solid; 43.5 mg; 44% yield; mp 140–141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.44 – 7.35 (m, 3H), 7.31 – 7.26 (m, 3H), 7.22 – 7.16 (m, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 8.3 Hz, 1H), 4.37 (d, *J* = 16.8 Hz, 1H), 3.84 (d, *J* = 16.8 Hz, 1H), 3.48 (s, 3H), 2.40 (s, 3H), 1.31 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.0, 171.7, 157.3, 145.5, 135.8, 133.2, 132.0, 130.8, 129.6, 129.03, 128.98, 128.0, 125.7, 123.5, 122.0, 121.4, 120.7, 110.9, 80.0, 71.4, 59.9, 54.9, 21.8, 15.6. HRMS (ESI) calcd for $C_{26}H_{24}N_5O_4S$ $[M+H]^+$ 502.1544, found 502.1545.

***cis*-9b-azido-1-(3-fluorophenyl)-3a-methyl-5-tosyl-5,9b-dihydro-3*H*-pyrrolo[3,4-*c*]quinolin-4(3a*H*)-one (*cis*-2d):** white solid; 76.5 mg; 78% yield; mp 161–162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 3H), 7.53 – 7.45 (m, 1H), 7.42 – 7.34 (m, 3H), 7.35 – 7.27 (m, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.18 – 7.11 (m, 1H), 4.35 (d, *J* = 16.7 Hz, 1H), 3.80 (d, *J* = 16.7 Hz, 1H), 2.44 (s, 3H), 1.22 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.7, 169.3, 162.7 (d, *J* = 247.3 Hz), 145.9, 134.9, 134.4 (d, *J* = 7.6 Hz), 133.0, 130.5 (d, *J* = 8.1 Hz), 130.0, 129.4, 128.4, 126.8, 123.9 (d, *J* = 3.0 Hz), 123.7, 122.9, 118.6 (d, *J* = 21.2 Hz), 115.3 (d, *J* = 23.4 Hz), 78.5, 69.3, 61.3, 21.9, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.32. HRMS (ESI) calcd for $C_{25}H_{21}FN_5O_3S$ $[M+H]^+$ 490.1344, found 490.1346.

***cis*-9b-azido-3a-methyl-1-*p*-tolyl-5-tosyl-5,9b-dihydro-3*H*-pyrrolo[3,4-*c*]quinolin-4(3a*H*)-one *(cis*-2e):** white solid; 53.2 mg; 55% yield; mp 145–146 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.7 Hz, 1H), 7.69 (t, *J* = 8.3 Hz, 3H), 7.52 (d, *J* = 7.9 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 4.29 (d, *J* = 16.4 Hz, 1H), 3.76 (d, *J* = 16.4 Hz, 1H), 2.43 (s, 3H), 2.36 (s, 3H), 1.20 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.9, 170.2, 145.7, 141.9, 134.9, 133.0, 129.7, 129.70, 129.56, 129.5, 129.4, 128.6, 128.2, 126.6, 124.3, 122.8, 78.6, 69.1, 61.1, 21.9, 21.6, 14.2. HRMS (ESI) calcd for $C_{26}H_{24}N_5O_3S$

$[M+H]^+$ 486.1594, found 486.1603.

***cis*-9b-azido-1-(4-fluorophenyl)-3a-methyl-5-tosyl-5,9b-dihydro-3*H*-pyrrolo[3,4-*c*]quinolin-4(3a*H*)-one (*cis*-2f):** white solid; 61.6 mg; 63% yield; mp 201–202 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.70 (t, *J* = 8.6 Hz, 3H), 7.63 (dd, *J* = 8.8, 5.4 Hz, 2H), 7.52 – 7.45 (m, 1H), 7.39 (dd, *J* = 11.1, 4.1 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.03 (t, *J* = 8.6 Hz, 2H), 4.33 (d, *J* = 16.5 Hz, 1H), 3.79 (d, *J* = 16.5 Hz, 1H), 2.43 (s, 3H), 1.22 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.8, 169.2, 164.6 (d, *J* = 253.1 Hz), 145.8, 135.0, 133.0, 130.5 (d, *J* = 8.7 Hz), 129.9, 129.4 (d, *J* = 3.8 Hz), 128.4, 126.7, 124.0, 122.8, 116.0 (d, *J* = 21.8 Hz), 78.6, 69.3, 61.4, 21.9, 14.2. HRMS (ESI) calcd for $C_{25}H_{21}FN_5O_3S$ $[M+H]^+$ 490.1344, found 490.1349.

***cis*-9b-azido-1-(4-chlorophenyl)-3a-methyl-5-tosyl-5,9b-dihydro-3*H*-pyrrolo[3,4-*c*]quinolin-4(3a*H*)-one (*cis*-2g):** white solid; 37.9 mg; 38% yield; mp 179–180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.74 – 7.67 (m, 3H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.51 – 7.45 (m, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 4.34 (d, *J* = 16.6 Hz, 1H), 3.80 (d, *J* = 16.6 Hz, 1H), 2.43 (s, 3H), 1.22 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.8, 169.4, 145.8, 137.8, 135.0, 133.0, 130.9, 130.0, 129.6, 129.42, 129.37, 129.2, 128.3, 126.7, 123.9, 122.8, 78.5, 69.5, 61.3, 21.9, 14.2. HRMS (ESI) calcd for $C_{25}H_{21}ClN_5O_3S$ $[M+H]^+$ 506.1048, found 506.1052.

***cis*-9b-azido-1-(4-bromophenyl)-3a-methyl-5-tosyl-5,9b-dihydro-3*H*-pyrrolo[3,4-*c*]quinolin-4(3a*H*)-one (*cis*-2h):** white solid; 50.8 mg; 46% yield; mp 183–184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.70 (t, *J* = 9.1 Hz, 3H), 7.52 – 7.45 (m, 5H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 4.33 (d, *J* = 16.6 Hz, 1H), 3.79 (d, *J* = 16.6 Hz, 1H), 2.44 (s, 3H), 1.22 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.8, 169.5, 145.9, 135.0, 133.0, 132.1, 131.3, 130.0, 129.7, 129.43, 129.38, 128.4, 126.8, 126.3, 123.8, 122.8, 78.5, 69.5, 61.3, 21.9, 14.2. HRMS (ESI) calcd for $C_{25}H_{21}BrN_5O_3S$ $[M+H]^+$ 550.0543, found 550.0547.

***cis*-9b-azido-3a,8-dimethyl-1-phenyl-5-tosyl-5,9b-dihydro-3*H*-pyrrolo[3,4-*c*]quin**

olin-4(3a*H*)-one (*cis*-2j): white solid; 64.8 mg; 67% yield; mp 208–209 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.64 (m, 4H), 7.63 (s, 1H), 7.52 (s, 1H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 8.6 Hz, 3H), 4.27 (d, *J* = 16.4 Hz, 1H), 3.76 (d, *J* = 16.5 Hz, 1H), 2.43 (d, *J* = 4.6 Hz, 6H), 1.20 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.9, 170.5, 145.7, 140.1, 134.9, 132.8, 132.6, 131.4, 129.4, 129.3, 128.8, 128.3, 128.2, 127.5, 123.3, 121.0, 78.5, 69.0, 60.9, 21.9, 21.59, 14.3. HRMS (ESI) calcd for $C_{26}H_{24}N_5O_3S$ $[M+H]^+$ 486.1594, found 486.1600.

***cis*-9b-azido-8-chloro-3a-methyl-1-phenyl-5-tosyl-5,9b-dihydro-3*H*-pyrrolo[3,4-*c*] quinolin-4(3a*H*)-one (*cis*-2k):** white solid; 58.8 mg; 58% yield; mp 216–217 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.5 Hz, 1H), 7.72 (d, *J* = 1.9 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.61 – 7.56 (m, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.40 – 7.33 (m, 3H), 7.22 (d, *J* = 8.2 Hz, 2H), 4.35 (d, *J* = 16.6 Hz, 1H), 3.78 (d, *J* = 16.6 Hz, 1H), 2.43 (s, 3H), 1.22 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.5, 169.9, 146.0, 135.5, 134.5, 133.8, 132.2, 131.6, 129.7, 129.5, 129.4, 128.9, 128.1, 126.8, 122.9, 122.6, 78.3, 69.4, 61.1, 21.9, 14.1. HRMS (ESI) calcd for $C_{25}H_{21}ClN_5O_3S$ $[M+H]^+$ 506.1048, found 506.1050.

***cis*-9b-azido-3a-methyl-5-(methylsulfonyl)-1-phenyl-5,9b-dihydro-3*H*-pyrrolo[3,4 -*c*]quinolin-4(3a*H*)-one (*cis*-2l):** white solid; 42.0 mg; 53% yield; mp 149–150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.4 Hz, 1H), 7.59 (d, *J* = 7.4 Hz, 2H), 7.47 – 7.27 (m, 6H), 4.70 (d, *J* = 16.3 Hz, 1H), 4.01 (d, *J* = 16.3 Hz, 1H), 3.39 (s, 3H), 1.34 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.8, 171.4, 132.6, 132.4, 131.4, 129.8, 128.8, 128.6, 128.0, 126.7, 124.2, 122.0, 78.5, 69.40, 61.8, 43.5, 14.3. HRMS (ESI) calcd for $C_{19}H_{18}N_5O_3S$ $[M+H]^+$ 396.1125, found 396.1125.

***cis*-9b-azido-3a,5-dimethyl-1-phenyl-5,9b-dihydro-3*H*-pyrrolo[3,4-*c*]quinolin-4(3 a*H*)-one (*cis*-2m):** known compound[13]; light yellow solid; 56.7 mg; 86% yield; mp 109–110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 3H), 7.43 – 7.36 (m, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.14 – 7.09 (m, 1H), 7.06 (d, *J* = 8.2 Hz, 1H), 4.62 (d, *J* = 16.1 Hz, 1H), 3.95 (d, *J* = 16.1 Hz, 1H), 3.36 (s, 3H), 1.41 (s, 3H). ^{13}C {^{1}H} NMR

(100 MHz, $CDCl_3$) δ 171.2, 171.0, 138.3, 133.5, 130.7, 130.4, 129.3, 128.4, 128.3, 123.6, 119.5, 114.8, 78.9, 68.6, 56.2, 30.5, 16.0.

***cis*-9b-azido-5-benzyl-3a-methyl-1-phenyl-5,9b-dihydro-3H-pyrrolo[3,4-c]quinoli n-4(3aH)-one (*cis*-2n):** known compound[13]; yellow oil; 61.1 mg; 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 3H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.23 – 7.14 (m, 4H), 7.10 – 7.02 (m, 3H), 6.94 (d, *J* = 8.2 Hz, 1H), 5.37 (d, *J* = 16.1 Hz, 1H), 5.06 (d, *J* = 16.2 Hz, 1H), 4.79 (d, *J* = 16.0 Hz, 1H), 4.01 (d, *J* = 16.0 Hz, 1H), 1.49 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.5, 171.3, 137.3, 136.0, 133.4, 130.8, 130.3, 129.5, 128.9, 128.5, 128.4, 127.3, 126.3, 123.7, 119.8, 115.9, 79.1, 68.6, 56.5, 46.3, 15.9.

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Notes

The authors declare no competing financial interest.

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ASSOCIATED CONTENT

Supporting information

The Supporting Information is available free of charge on the ACS Publications

website. Details of mechanistic studies, X-ray structure, NMR spectra (PDF).

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