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Synthesis of polycyclic scaffolds via a gold-catalysed dearomative cyclisation cascade

Aimee K. Clarke\*, James A. Rossi-Ashton, Richard J. K. Taylor and William P. Unsworth\*

Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK



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Synthesis of polycyclic scaffolds via a gold-catalysed dearomative cyclisation cascade

Aimee K. Clarke\*, James A. Rossi-Ashton, Richard J. K. Taylor and William P. Unsworth\*

aDepartment of Chemistry, University of York, Heslington, York, YO10 5DD, UK

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| ARTICLE INFO | ABSTRACT |
| Article history:ReceivedReceived in revised formAcceptedAvailable online | Polycyclic scaffolds found in akuammiline alkaloid natural products can be synthesised from ynone-tethered indoles, via a gold(I)-catalyzed dearomative cyclisation cascade sequence. The ynone starting materials are themselves made via a two-step modular synthesis from simple tryptamine and tryptophol derivatives.2009 Elsevier Ltd. All rights reserved. |
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The akuammiline alkaloids (*e.g.* **1**–**5**, Figure 1) are a diverse family of bioactive polycyclic natural products with a broad range of interesting biological properties.1 Accordingly, the total synthesis of various members of this family, and the development of methods to prepare the core scaffold **6**, have attracted considerable attention from synthetic and medicinal chemists over the years.2,3



Figure 1. Akuammiline alkaloids **1–5** and core scaffold **6**. E = CO2Me

One such method, developed in our groups at the University of York, is summarised in Scheme 1a.3 Thus, an enantioselective procedure for the preparation of polycyclic akuammiline scaffolds of the form **10** was reported, that is catalysed by SPINOL-based chiral phosphoric acid Ag-CPA-**8**.4,5 The reaction operates via an initial dearomatising spirocyclisation reaction6 of indole-tethered ynone **7**,7,8 to form an intermediate **9** which then cyclises *in situ*,to form the polycyclic product **10** in one-pot.9 Mechanistic studies support the idea that Ag-CPA-**8** catalyses both the dearomatisation and cyclisation steps, and the reactions typically proceed with high enantioselectivity (up to 99% *ee* in some cases).10,11



Scheme 1. a) Previous work: enantioselective Ag(I)-catalysed formation of polycycles **10**. b) This work: Au(I)-catalysed formation of racemic polycycles **13**.

For many applications, it is not necessary to prepare enantioenriched products, and indeed in some cases the formation of racemic products can be desirable (*e.g.* when making racemic analytical standards, or to evaluate the biological properties of both enantiomers simultaneously).Therefore, to complement the reported enantioselective process, we considered it valuable to develop a non-enantioselective process for the formation of racemic products. Thus, in this manuscript, a Au(I)-catalysed cascade12 reaction for the synthesis of racemic polycycles **13** is described (Scheme 1b).13 A major advantage to the new protocol, compared with the enantioselective variant, is that it uses a simpler, cheaper catalyst system, namely the commercially available Gagosz catalyst Au(PPh3)NTf2.13f,g The new protocol also uses a lower catalyst loading, proceeds in higher yields in many cases, and offers increased substrate scope, including the formation of non-trapped dienone scaffolds of the form **12**.

1. Results and discussion

All of the ynone cyclisation precursors used in this study were prepared via the simple two step synthesis described in our previous report (Scheme 2).3 Using a xanthate-mediated radical alkylation approach, tryptamine and tryptophol derivatives **14** underwent reaction with xanthates **15** to directly install a Weinreb amide handle at the C2-position of the indole ring. Subsequent reaction with Grignard alkyne reagents **17** promoted formation of the desired ynone cyclisation precursors **11** in good to excellent yields.



Scheme 2. Two-step preparation of ynone precursors. DLP = dilauroyl peroxide

Attention then turned to optimisation of the dearomative cyclisation cascade, with phenyl-tethered ynone **11a** used as a model substrate. To begin, we investigated the cyclisation cascade using a variety of metal catalysts known to facilitate alkyne activation (Table 1). Using 10 mol% catalyst loading, palladium, copper, silver and gold catalysts were tested (entries 1–7) and it was found that generally the silver and gold catalysts were the most effective, with palladium salts (*e.g.* Pd(OAc)2, entry 1) performing the worst overall in terms of product yield. Catalysts which furnished the desired tetracyclic product **13a** in the highest yields were then examined using 5 mol% loading (entries 8–10). Interestingly, when lowering the catalyst loading, yields increased for Cu(BF4)2·xH2O, Au(Me2S)Cl and Au(PPh3)NTf2 catalysts compared to their 10 mol% reactions, indicating that having too high a catalyst loading has a detrimental effect on the yield. It was found that using 5 mol% Au(PPh3)NTf2 in CHCl3 at RT promoted the reaction most efficiently, furnishing the desired product **13a** in 98% yield, and these were the conditions chosen for subsequent substrate scoping studies.14 Note that Au(I) catalysis (Ph3PAuSbF6, toluene, 60 °C) was also shown to be effective in a related study by Wang and coworkers, in which similar reactivity is demonstrated for indoles tethered to aliphatic alkynes rather than ynones.15

**Table 1**. Dearomative cyclisation catalyst screen.



|  |  |  |  |
| --- | --- | --- | --- |
| **Entry[a]** | **Catalyst** | **Loading/mol%** | **Yield/%[b]** |
| 1 | Pd(OAc)2 | 10 | 30 |
| 2 | Cu(BF4)2·xH2O | 10 | 73 |
| 3 | AgBF4 | 10 | 59 |
| 4 | AgSbF6 | 10 | 77 |
| 5[c] | IPrAuCl | 10 | 41 |
| 6 | Au(PPh3)NTf2 | 10 | 77 |
| 7[c] | Au(Me2S)Cl | 10 | 83 |
| 8 | Cu(BF4)2·xH2O | 5 | 92 |
| 9[d] | Au(SMe2)Cl | 5 | 92 |
| 10 | Au(PPh3)NTf2 | 5 | 98 |

aAll reactions were performed on 0.05 mmol scale in CHCl3 (0.1 mL/mmol) at RT for 24 h; bYields based on trimethoxybenzene internal standard; c10 mol% AgOTf added; d5 mol% AgOTf added.

The scope of the reaction was first examined by varying the protecting group on the tryptamine tether (Scheme 3). Commonly used electron withdrawing amine protecting groups all furnished the corresponding products (**13a–c**) in good to excellent yields. Substituents at the ynone terminus were then investigated; both electron-withdrawing and electron-donating aryl groups were tolerated (**13d** and **13e**), as well as a range of alkyl groups, protected alcohol and sulfide groups attached to the ynone terminus (**13g-k**). Substituents in any of the four positions around the indole phenyl ring were also tolerated (**13l-q**). Both indole and ynone tethers could be substituted with alkyl groups (**13r-t**); a slightly reduced yield of 75% was observed for the Me-substituted product **13t** as a result of the formation of minor, unidentified side-products. It was also possible to use oxygen trapping nucleophiles and vary the length of the trapping tether to generate the 5- and 6-membered oxa-cyclic analogues **13u** and **13v** in 95% and 99% yields, respectively.



Scheme 3. Substrate scope of dearomative cyclisation cascade.

Substrates which did not possess a suitably reactive tethered nucleophile, but had an alkyl substituent in the C3-position, could still undergo the initial dearomative cyclisation reaction, furnishing the corresponding dienone products (Scheme 4, **12w**–**12z**); three indoles with functionalised alkyl tethers, including alcohol, malonate and tertiary amine groups were found to react in this way, as was the simple 3-methyl substituted indole **11z**.



Scheme 4. Formation of dienone intermediates.

Furthermore, benzylated polycycle **13y** was accessed in 78% yield by treating dearomatised dienone product **12y** with TFA (Scheme 5). This polycycle could not be accessed directly from the corresponding *N*-Bn ynone using the standard dearomatisation cascade, presumably as the secondary amine is too nucleophilic.



Scheme 5. Formation of polycycle **13y**.

1. Conclusions

In summary, a Au(I)-catalysed protocol for the synthesis of racemic polycycles **13** and dienones **12** has been developed to complement our previously reported enantioselective Ag(I)-CPA variant.3 For applications in which enantioenriched products are not needed, we anticipate that this new Au(I)-catalysed method will be more widely adopted, in view of it using a commercially available catalyst and lower catalyst loading than the asymmetric variant. The reactions are also operationally more straightforward than their enantioselective analogues in which the conditions used involved prolonged cooling of the reaction (0 °C) to maximise *ee*, whereas all the reactions in the present study were performed at RT and do not require the use of an inert atmosphere. Furthermore, when comparing cases in which the same product has been prepared by both methods, modest improvements in yield are generally observed for the non-enantioselective system (*e.g.* products **13f–k, 13u, 13v**). We are currently exploring applications of both methods in target synthesis.

1. Experimental
	1. General aspects

Except where stated, all reagents were purchased from commercial sources and used without further purification and all experimental procedures were carried out under an atmosphere of argon unless stated otherwise. Anhydrous THF was obtained from an Innovative Technology Inc. PureSolv® solvent purification system. 1H NMR and 13C NMR spectra were recorded on a JEOL ECX400 or JEOL ECS400 spectrometer, operating at 400 MHz and 100 MHz, respectively. All spectral data was acquired at 295 K. Chemical shifts (δ) are quoted in parts per million (ppm). The residual solvent peaks, δH 7.27 and δC 77.0 for CDCl3 were used as a reference. Coupling constants (*J*) are reported in Hertz (Hz) to the nearest 0.5 Hz. The multiplicity abbreviations used are: s singlet, d doublet, t triplet, q quartet, m multiplet. Signal assignment was achieved by analysis of DEPT, COSY, HMBC and HSQC experiments where required. Infrared (IR) spectra were recorded on a PerkinElmer UATR 2 Spectrometer as a thin film dispersed from either CH2Cl2 or CDCl3. Mass spectra (high-resolution) were obtained by the University of York Mass Spectrometry Service, using Electrospray Ionisation (ESI) or Liquid Injection Field Desorption Ionisation (LIFDI) on a Bruker Daltonics, Micro-tof spectrometer. Melting points were determined using Gallenkamp apparatus and are uncorrected. Thin layer chromatography was carried out on Merck silica gel 60F254 pre-coated aluminium foil sheets and were visualised using UV light (254 nm) and stained with basic aqueous potassium permanganate. Flash column chromatography was carried out using slurry packed Fluka silica gel (SiO2), 35–70 μm, 60 Å, under a slight positive pressure, eluting with the specified solvent system.

* 1. General procedure A: Preparation of Weinreb amides

To a solution of indole (10.0 mmol) in degassed dichloroethane (DCE) (75.0 mL) under argon was added xanthate (18.0 mmol) and dilauroyl peroxide (DLP) (13.0–18.0 mmol) at RT. This reaction mixture was then refluxed for 1 h. The DCE was then removed *in vacuo* and the crude material was purified by column chromatography to afford the Weinreb amide product.

General procedure B: Ynone synthesis

To a stirred solution of alkyne (2.50–6.00 mmol) in THF (6.50 mL) at 0 °C under argon was added *i*PrMgCl (2.50–6.00 mmol, 2.00 M in THF) dropwise (quantities of reagents used for specific products are provided, along with their spectroscopic data) . The mixture was stirred at 0 °C for 1 h and then transferred via cannula to a −20 °C solution of Weinreb amide (1.00 mmol) in THF (5.00 mL). The reaction mixture was then stirred at the specified temperature until complete reaction was observed by TLC. The reaction was quenched by the addition of sat. aq. NH4Cl (10.0 mL). The organics were separated and the aqueous layer extracted with Et2O (3 x 10.0 mL). The organics were combined, washed with brine (10.0 mL), dried over MgSO4, concentrated *in vacuo* and purified by column chromatography to afford the ynone product.

General procedure C: Gold-catalysed diaromatic cyclisation cascade

To a solution of ynone (0.250 mmol) in CHCl3 (2.50 mL) was added Au(PPh3)NTf2 (9.80 mg, 6.25 µmol). The reaction mixture was stirred under air at RT for the specified amount of time until completion was observed by TLC. The reaction mixture was concentrated *in vacuo* and then purified by column chromatography to afford the dearomatised/cyclised products.

* 1. Experimental procedures
		1. tert-Butyl (2-(2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1H-indol-3-yl)ethyl)carbamate (**16a**)

Prepared according to general procedure A using *tert*-butyl (2-(1*H*-indol-3-yl)ethyl)carbamate16 (2.47 g, 9.50 mmol), *O*-ethyl *S*-(2-(methoxy(methyl)amino)-2-oxoethyl) carbonodithioate17 (3.80 g, 17.1 mmol), dilauroyl peroxide (4.90 g, 12.4 mmol) in degassed DCE (70.0 mL). Purification by flash chromatography on silica gel (100% Et2O) afforded the title compound **16a** as an brown foam (1.62 g, 47% yield); R*f* 0.12 (8:2 Et2O:hexane); δH (400 MHz, CDCl3) 8.89 (br s, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.15 (dd, *J* = 7.8, 7.6 Hz, 1H), 7.08 (dd, *J* = 7.9, 7.6 Hz, 1H), 4.72 (br s, 1H), 3.93 (s, 2H), 3.73 (s, 3H), 3.44–3.35 (m, 2H), 3.22 (s, 3H), 2.94 (t, *J* = 6.6 Hz, 2H), 1.44 (s, 9H); HRMS (ESI+): Found: 384.1894; C19H27N3NaO4+ (MNa+) Requires 384.1894 (0.1 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. Benzyl (2-(2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1H-indol-3-yl)ethyl)carbamate (**16b**)

Prepared according to general procedure A using benzyl (2-(1*H*-indol-3-yl)ethyl)carbamate18 (2.82 g, 9.58 mmol), *O*-ethyl *S*-(2-(methoxy(methyl)amino)-2-oxoethyl) carbonodithioate17 (3.85 g, 17.2 mmol), dilauroyl peroxide (4.96 g, 12.5 mmol) in degassed DCE (72.0 mL). Purification by flash chromatography on silica gel (9:1 Et2O:hexane, then 100% Et2O) afforded the title compound **16b** as a yellow foam (1.55 g, 41% yield); R*f* 0.26 (9:1 Et2O:hexane); δH (400 MHz, CDCl3) 8.84 (br s, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.37–7.28 (m, 6H), 7.18–7.12 (m, 1H), 7.11–7.05 (m, 1H), 5.17–5.03 (m, 3H), 3.89 (s, 2H), 3.70 (s, 3H), 3.53–3.43 (m, 2H), 3.18 (s, 3H), 2.97 (t, *J* = 6.6 Hz, 2H); HRMS (ESI+): Found: 418.1733; C22H25N3NaO4+ (MNa+) Requires 418.1737 (1.1 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. N-Methoxy-N-methyl-2-(3-(2-(4-methylphenylsulfonamido)ethyl)-1H-indol-2-yl)acetamide (**16c**)

Prepared according to general procedure A using *N*-(2-(1*H*-indol-3-yl)ethyl)-4-methylbenzenesulfonamide19 (1.57 g, 5.00 mmol), *O*-ethyl *S*-(2-(methoxy(methyl)amino)-2-oxoethyl) carbonodithioate17 (2.01 g, 9.00 mmol), dilauroyl peroxide (2.59 g, 6.50 mmol) in degassed DCE (38.0 mL). Purification by flash chromatography on silica gel (7:3 EtOAc:hexane) afforded the title compound **16c** as an orange foam (1.07 g, 52% yield); R*f* 0.22 (7:3 EtOAc:hexane); δH (400 MHz, CDCl3) 8.78 (br s, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.30 (dd, *J* = 7.7, 7.7 Hz, 2H), 7.18–7.09 (m, 3H), 7.00 (dd, *J* = 7.5, 7.5 Hz, 1H), 5.32–5.24 (m, 1H), 3.91 (s, 2H), 3.79 (s, 3H), 3.25–3.17 (m, 5H), 2.96 (t, *J* = 6.2 Hz, 2H), 2.35 (s, 3H); HRMS (ESI+): Found: 438.1458; C21H25N3NaO4S+ (MNa+) Requires 438.1458 (0.0 ppm error. Spectroscopic data matched those previously reported in the literature.3

* + 1. tert-Butyl (2-(4-bromo-2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1H-indol-3-yl)ethyl)carbamate (**16d**)

Prepared according to general procedure A using *tert*-butyl (2-(7-bromo-1*H*-indol-3-yl)ethyl)carbamate20 (2.88 g, 8.49 mmol), *O*-ethyl *S*-(2-(methoxy(methyl)amino)-2-oxoethyl) carbonodithioate17 (3.41 g, 15.3 mmol), dilauroyl peroxide (4.40 g, 11.0 mmol) in degassed DCE (64.0 mL). Purification by flash chromatography on silica gel (100% Et2O) afforded the title compound **16d** as a pale yellow oil (1.94 g, 52% yield); R*f* 0.27 (100% Et2O); δH (400 MHz, CDCl3) 9.31 (br s, 1H), 7.25–7.19 (m, 2H), 6.96–6.90 (m, 1H), 4.78 (br s, 1H), 3.97 (s, 2H), 3.76 (s, 3H), 3.47–3.37 (m, 2H), 3.22 (s, 3H), 3.18–3.12 (m, 2H), 1.42 (s, 9H); HRMS (ESI+): Found: 462.0994; C19H2679BrN3NaO4+ (MNa+) Requires 462.0999 (1.1 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. tert-Butyl (2-(4-(benzyloxy)-2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1H-indol-3-yl)ethyl)carbamate (**16e**)

Prepared according to general procedure A using *tert*-butyl (2-(4-(benzyloxy)-1*H*-indol-3-yl)ethyl)carbamate21(1.30 g, 3.55 mmol), *O*-ethyl *S*-(2-(methoxy(methyl)amino)-2-oxoethyl) carbonodithioate17 (1.43 g, 6.39 mmol), dilauroyl peroxide (1.84 g, 4.62 mmol) in degassed DCE (30.0 mL). Purification by flash chromatography on silica gel (100% Et2O) afforded the title compound **16e** as an orange oil (650 mg, 39% yield); R*f* 0.22 (100% Et2O); δH (400 MHz, CDCl3) 8.94 (br s, 1H), 7.51–7.46 (m, 2H), 7.44–7.39 (m, 2H), 7.39–7.34 (m, 1H), 7.08–7.02 (m, 1H), 6.99–6.93 (m, 1H), 6.56 (d, *J* = 7.7 Hz), 5.15 (s, 2H), 4.59 (br s, 1H), 3.90 (s, 2H), 3.72 (s, 3H), 3.35–3.27 (m, 2H), 3.22 (s, 3H), 3.02–2.93 (m, 2H), 1.39 (s, 9H); HRMS (ESI+): Found: 490.2316; C26H33N3NaO5+ (MNa+) Requires 490.2312 (−0.6 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. tert-Butyl (2-(5-bromo-2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1H-indol-3-yl)ethyl)carbamate (**16f**)

Prepared according to general procedure A using *tert*-butyl (2-(5-bromo-1*H*-indol-3-yl)ethyl)carbamate20 (696 mg, 2.05 mmol), *O*-ethyl *S*-(2-(methoxy(methyl)amino)-2-oxoethyl) carbonodithioate17 (825 mg, 3.69 mmol), dilauroyl peroxide (1.06 g, 2.67 mmol) in degassed DCE (15 mL). Purification by flash chromatography on silica gel (100% Et2O) afforded the title compound **16f** as a pale yellow foam (452 mg, 50% yield); R*f* 0.25 (100% Et2O); δH (400 MHz, CDCl3) 9.05 (br s, 1H), 7.63–7.61 (m, 1H), 7.23–7.15 (m, 2H,), 4.73–4.65 (m, 1H), 3.92 (s, 2H), 3.74 (s, 3H), 3.38–3.30 (m, 2H), 3.22 (s, 3H), 2.88 (t, *J* = 6.5 Hz, 2H), 1.43 (s, 9H); HRMS (ESI+): Found: 462.1006; C19H26BrN3NaO4+ (MNa+) Requires 462.0999 (−1.5 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. tert-Butyl (2-(5-methoxy-2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1H-indol-3-yl)ethyl)carbamate (**16g**)

Prepared according to general procedure A using *tert*-butyl (2-(5-methoxy-1*H*-indol-3-yl)ethyl)carbamate20 (1.54 g, 5.29 mmol), *O*-ethyl *S*-(2-(methoxy(methyl)amino)-2-oxoethyl) carbonodithioate17 (2.13 g, 9.52 mmol), dilauroyl peroxide (2.74 g, 6.88 mmol) in degassed DCE (40 mL). Purification by flash chromatography on silica gel (100% Et2O) afforded the title compound **16g** as an orange foam (851 mg, 41% yield); R*f* 0.26 (100% Et2O); δH (400 MHz, CDCl3) 8.81 (br s, 1H), 7.19 (d, *J* = 8.7 Hz, 1H), 6.99–6.96 (m, 1H), 6.80 (dd, *J* = 8.7, 2.5 Hz, 1H), 4.77 (br s, 1H), 3.91 (s, 2H), 3.85 (s, 3H), 3.72 (s, 3H), 3.45–3.35 (m, 2H), 3.22 (s, 3H), 2.95–2.87 (m, 2H), 1.42 (s, 9H); HRMS (ESI+): Found: 414.2012; C20H29N3NaO5+ (MNa+) Requires 414.1999 (−3.0 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. tert-Butyl (2-(6-chloro-2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1H-indol-3-yl)ethyl)carbamate (**16h**)

Prepared according to general procedure A using *tert-*butyl (2-(6-chloro-1*H*-indol-3-yl)ethyl)carbamate3 (930 mg, 3.15 mmol), *O*-ethyl *S*-(2-(methoxy(methyl)amino)-2-oxoethyl) carbonodithioate17 (1.27 g, 5.68 mmol), dilauroyl peroxide (1.63 g, 4.10 mmol) in degassed DCE (24 mL). Purification by flash chromatography on silica gel (100% Et2O) afforded the title compound **16h** as an orange oil (618 mg, 50% yield); R*f* 0.28 (100% Et2O); δH (400 MHz, CDCl3) 8.96 (br s, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.30–7.27 (m, 1H), 7.05–7.01 (m, 1H), 4.69 (br s, 1H), 3.91 (s, 2H), 3.74 (s, 3H), 3.40–3.30 (m, 2H), 3.23 (s, 3H), 2.94–2.85 (m, 2H), 1.42 (s, 9H); HRMS (ESI+): Found: 418.1505; C19H26ClN3NaO4+ (MNa+) Requires 418.1504 (−0.3 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. tert-Butyl (2-(2-(2-(methoxy(methyl)amino)-2-oxoethyl)-7-methyl-1H-indol-3-yl)ethyl)carbamate (**16i**)

Prepared according to general procedure A using *tert-*butyl (2-(7-methyl-1*H*-indol-3-yl)ethyl)carbamate3 (1.89 g, 6.89 mmol), *O*-ethyl *S*-(2-(methoxy(methyl)amino)-2-oxoethyl) carbonodithioate17 (2.77 g, 12.4 mmol), dilauroyl peroxide (3.57 g, 8.96 mmol) in degassed DCE (50 mL). Purification by flash chromatography on silica gel (9:1 Et2O:hexane, then 100% Et2O) afforded the title compound **16i** as a yellow foam (1.06 g, 41% yield); R*f* 0.40 (100% Et2O); δH (400 MHz, CDCl3) 8.83 (br s, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.04–6.98 (m, 1H), 6.97–6.93 (m, 1H), 4.78–4.69 (m, 1H), 3.96 (s, 2H), 3.74 (s, 3H), 3.44–3.34 (m, 2H), 3.23 (s, 3H), 2.98–2.88 (m, 2H), 2.45 (s, 3H), 1.43 (s, 9H); HRMS (ESI+): Found: 398.2059; C20H29N3NaO4+ (MNa+) Requires 398.2050 (−2.2 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. tert-Butyl (1-(2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1H-indol-3-yl)butan-2-yl)carbamate (**16j**)

Prepared according to general procedure A using *tert-*butyl (1-(1*H*-indol-3-yl)butan-2-yl)carbamate3 (2.24 g, 7.77 mmol), *O*-ethyl *S*-(2-(methoxy(methyl)amino)-2-oxoethyl) carbonodithioate17 (3.12 g, 14.0 mmol), dilauroyl peroxide (4.03 g, 10.1 mmol) in degassed DCE (55.0 mL). Purification by flash chromatography on silica gel (100% Et2O) afforded the title compound **16j** as a pale yellow foam (1.19 g, 39% yield); R*f* 0.33 (100% EtOAc); δH (400 MHz, CDCl3) 8.99 (br s, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.18–7.03 (m, 2H), 4.57–4.47 (m, 1H), 3.98 (s, 2H), 3.72 (s, 3H), 3.22 (s, 3H), 3.03–2.79 (m, 2H), 1.69–1.53 (m, 1H), 1.49–1.25 (m, 10H) 0.97–0.85 (m, 3H); HRMS (ESI+): Found: 412.2204; C21H31N3NaO4+ (MNa+) Requires 412.2207 (0.7 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. (S)-tert-Butyl (1-hydroxy-3-(2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1H-indol-3-yl)propan-2-yl)carbamate (**16k**)

Prepared according to general procedure A using *N*-α-(*tert*-butoxycarbonyl)-*L*-tryptophanol22 (1.75 g, 6.03 mmol), *O*-ethyl *S*-(2-(methoxy(methyl)amino)-2-oxoethyl) carbonodithioate17 (2.43 g, 10.9 mmol), dilauroyl peroxide (4.34 g, 10.9 mmol) in degassed DCE (32.0 mL). Purification by flash chromatography on silica gel (9:1 EtOAc:hexane, then 100% EtOAc) afforded the title compound **16k** as an orange foam (953 mg, 40% yield); R*f* 0.33 (100% EtOAc); νmax (thin film)/cm−1 3330, 2930, 1687, 1644, 1497, 1460, 1390, 1366, 1246, 1169, 1056, 738; δH (400 MHz, CDCl3, 55 °C) 8.70 (br s, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.17–7.12 (m, 1H), 7.11–7.05 (m, 1H), 5.08 (br d, *J* = 7.5 Hz, 1H), 4.06–3.88 (m, 4H), 3.80 (s, 3H), 3.53 (ddd, *J* = 14.8, 11.1, 3.8 Hz, 2H), 3.24 (s, 3H), 3.08–2.94 (m, 2H), 1.45 (s, 9H); δC (100 MHz, CDCl3, 55 °C) 171.3, 156.2, 136.1, 128.9, 128.5, 122.1, 119.7, 119.1, 110.9, 110.0, 79.5, 63.2, 61.8, 53.1, 29.8, 28.63, 28.60, 26.2; HRMS (ESI+): Found: 414.2005; C20H29N3NaO5+ (MNa+) Requires 414.1999 (−1.5 ppm error).

* + 1. tert-Butyl (2-(2-(1-(methoxy(methyl)amino)-1-oxopropan-2-yl)-1H-indol-3-yl)ethyl)carbamate (**16l**)

Prepared according to general procedure A using *tert*-butyl (2-(1*H*-indol-3-yl)ethyl)carbamate16 (905 mg, 3.48 mmol), *O*-ethyl *S*-(1-(methoxy(methyl)amino)-1-oxopropan-2-yl) carbonothioate23 (1.71 g, 6.25 mmol), dilauroyl peroxide (1.80 g, 4.52 mmol) in degassed DCE (30.0 mL). Note: An additional 0.65 equivalents of dilauroyl peroxide (900 mg, 2.26 mmol) was added after stirring at 90 °C for 1 h. The reaction mixture was then stirred at 90 °C for a further 1 h. Purification by flash chromatography on silica gel (8:2 Et2O:hexane) afforded the title compound **16l** as yellow oil (594 mg, 45% yield); R*f* 0.31 (8:2 Et2O:hexane); νmax (thin film)/cm−1 3331, 2975, 2933, 1693, 1644, 1460, 1365, 1249, 1169, 988, 733; δH (400 MHz, CDCl3) 8.86 (br s, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.18–7.12 (m, 1H), 7.11–7.05 (m, 1H), 4.74–4.62 (m, 1H), 4.62–4.51 (m, 1H), 3.66 (s, 3H), 3.59–3.43 (m, 1H), 3.41–3.27 (m, 1H), 3.20 (s, 3H), 3.02–2.89 (m, 2H), 1.53 (d, *J* = 7.0 Hz, 3H), 1.43 (s, 9H); δC (100 MHz, CDCl3) 174.5, 156.0, 135.8, 134.8, 127.9, 121.9, 119.4, 118.6, 111.1, 108.4, 79.2, 61.8, 41.1, 32.3, 32.0, 28.5, 24.9, 20.1; HRMS (ESI+): Found: 398.2057; C20H29N3NaO4+ (MNa+) Requires 398.2050 (−1.8 ppm error).

* + 1. 2-(3-(2-Hydroxyethyl)-1H-indol-2-yl)-N-methoxy-N-methylacetamide (**16m**)

Prepared according to general procedure A using 2-(1*H*-indol-3-yl)ethanol (967 mg, 6.00 mmol), *O*-ethyl *S*-(2-(methoxy(methyl)amino)-2-oxoethyl) carbonodithioate17 (2.41 g, 10.8 mmol), dilauroyl peroxide (3.11 g, 7.80 mmol) in degassed DCE (45.0 mL). Purification by flash chromatography on silica gel (99:1 Et2O:MeOH) afforded the title compound **16m** as an orange oil (771 mg, 49% yield); R*f* 0.20 (100% EtOAc); δH (400 MHz, CDCl3) 8.73 (br s, 1H), 7.60–7.51 (m, 1H), 7.32 (dd, *J* = 7.1, 0.9 Hz, 1H), 7.20–7.13 (m, 1H), 7.09 (ddd, *J* = 8.1, 7.2, 1.1 Hz, 1H), 3.97 (s, 2H), 3.86 (t, *J* = 6.0 Hz, 2H), 3.77 (s, 3H), 3.23 (s, 3H), 3.01 (t, *J* = 6.0 Hz, 2H); HRMS (ESI+): Found: 285.1206; C14H18N2NaO3+ (MNa+) Requires 285.1210 (1.3 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. 2-(3-(3-Hydroxypropyl)-1H-indol-2-yl)-N-methoxy-N-methylacetamide (**16n**)

Prepared according to general procedure A using 3-(1*H*-indol-3-yl)propan-1-ol (526 mg, 3.00 mmol), *O*-ethyl *S*-(2-(methoxy(methyl)amino)-2-oxoethyl) carbonodithioate17 (1.21 g, 5.40 mmol), dilauroyl peroxide (1.55 g, 3.90 mmol) in degassed DCE (23.0 mL). Purification by flash chromatography on silica gel (100% EtOAc) afforded the title compound **16n** as an orange oil (434 mg, 52% yield); R*f* 0.33 (100% EtOAc); δH (400 MHz, CDCl3) 8.73 (br s, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.17–7.11 (m, 1H), 7.08 (dd, *J* = 7.8, 0.9 Hz, 1H), 3.93 (s, 2H), 3.77 (s, 3H), 3.57 (t, *J* = 6.0 Hz, 2H), 3.24 (s, 3H), 2.89 (t, *J* = 7.0 Hz, 2H), 1.98–1.87 (m, 2H); HRMS (ESI+): Found: 299.1357; C15H20N2NaO3+ (MNa+) Requires 299.1366 (2.9 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. 2-(3-(4-Hydroxybutyl)-1H-indol-2-yl)-N-methoxy-N-methylacetamide (**16o**)

Prepared according to general procedure A using 4-(1*H*-indol-3-yl)butan-1-ol24 (1.51 g, 8.00 mmol), *O*-ethyl *S*-(2-(methoxy(methyl)amino)-2-oxoethyl) carbonodithioate17 (3.22 g, 14.4 mmol), dilauroyl peroxide (4.15 g, 10.4 mmol) in degassed DCE (60.0 mL). Purification by flash chromatography on silica gel (100% Et2O, then 95:5 CH2Cl2:MeOH) afforded the title compound **16o** as an orange oil (1.28 g, 55% yield); R*f* 0.34 (100% EtOAc); νmax (thin film)/cm−1 3407, 3319, 2934, 2858, 1641, 1459, 1387, 1177, 1058, 1000, 741; δH (400 MHz, CDCl3) 8.80 (br s, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.32–7.28 (m, 1H), 7.12 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.09–7.04 (m, 1H), 3.91 (s, 2H), 3.70 (s, 3H), 3.65 (t, *J* = 6.4 Hz, 2H), 3.22 (s, 3H), 2.78 (t, *J* = 7.3 Hz, 2H), 1.77–1.59 (m, 5H); δC (100 MHz, CDCl3) 171.1, 135.8, 128.2, 127.5, 121.6, 119.1, 118.6, 113.3, 110.9, 61.9, 61.7, 32.6, 32.3, 29.3, 27.0, 23.9; HRMS (ESI+): Found: 313.1515; C16H22N2NaO3+ (MNa+) Requires 313.1523 (2.6 ppm error).

* + 1. Dimethyl 2-(2-(2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1H-indol-3-yl)ethyl)malonate (**16p**)

Prepared according to general procedure A using dimethyl 2-(2-(1*H*-indol-3-yl)ethyl)malonate25 (830 mg, 3.01 mmol), *O*-ethyl *S*-(2-(methoxy(methyl)amino)-2-oxoethyl) carbonodithioate17 (1.21 g, 5.42 mmol), dilauroyl peroxide (1.56 g, 3.91 mmol) in degassed DCE (23.0 mL). Purification by flash chromatography on silica gel (9:1 Et2O:hexane) afforded the title compound **16p** as an orange oil (542 mg, 48% yield); R*f* 0.27 (9:1 Et2O:hexane); νmax (thin film)/cm−1 3393, 2953, 2855, 1730, 1651, 1460, 1435, 1242, 1197, 1154, 1002, 745; δH (400 MHz, CDCl3) 8.91 (br s, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.17–7.05 (m, 2H), 3.93 (s, 2H), 3.73 (s, 3H), 3.71 (s, 6H), 3.43 (t, *J* = 7.4 Hz, 1H), 3.23 (s, 3H), 2.85–2.76 (m, 2H), 2.30–2.23 (m, 2H); δC (100 MHz, CDCl3) 171.1, 170.0, 135.8, 128.3, 127.9, 121.8, 119.3, 118.4, 111.4, 111.0, 61.8, 52.6, 51.2, 32.2, 29.8, 28.9, 21.9; HRMS (ESI+): Found: 399.1532; C19H24N2NaO6+ (MNa+) Requires 399.1527 (−1.4 ppm error).

* + 1. tert-Butyl benzyl(2-(2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1H-indol-3-yl)ethyl)carbamate (**16q**)

Prepared according to general procedure A using *tert*-butyl (2-(1*H*-indol-3-yl)ethyl)(benzyl)carbamate26 (1.16 g, 3.31 mmol), *O*-ethyl *S*-(2-(methoxy(methyl)amino)-2-oxoethyl) carbonodithioate17 (1.33 g, 5.96 mmol), dilauroyl peroxide (1.72 g, 4.30 mmol) in degassed DCE (25.0 mL). Purification by flash chromatography on silica gel (100% Et2O) afforded the title compound **16q** (as a 5:1 mixture of rotamers) as an orange foam (557 mg, 37% yield); R*f* 0.31 (100% Et2O); νmax (thin film)/cm−1 3320, 2973, 2929, 1666, 1661, 1414, 1365, 1243, 1163, 1120, 739; δH (400 MHz, CDCl3, 55 °C) 8.83 (br s, 1H), 7.47–7.41 (m, 1H), 7.31–7.27 (m, 3H), 7.25–7.17 (m, 3H), 7.15–7.10 (m, 1H), 7.07–7.02 (m, 1H), 4.36 (br s, 2H), 3.90 (s, 2H), 3.69 (s, 3H), 3.45–3.35 (m, 2H), 3.22 (s, 3H), 3.00–2.89 (m, 2H), 1.49 (s, 9H). Only peaks for major rotamer listed. δC (100 MHz, CDCl3) 170.9, 156.1, 138.6, 135.8, 128.6 (2 x C), 128.1, 127.5, 127.2, 121.8, 119.3, 118.3, 111.0, 110.2, 79.8, 61.7, 50.6, 47.3, 32.2, 29.8, 28.6, 23.5; HRMS (ESI+): Found: 474.2365; C26H33N3NaO4+ (MNa+) Requires 474.2363 (−0.4 ppm error).

* + 1. N-Methoxy-N-methyl-2-(3-methyl-1H-indol-2-yl)acetamide (**16r**)

Prepared according to general procedure A using 3-methyl-1*H*-indole(468 mg, 3.57 mmol), *O*-ethyl *S*-(2-(methoxy(methyl)amino)-2-oxoethyl) carbonodithioate17 (1.44 g, 6.43 mmol), dilauroyl peroxide (2.56 g, 6.43 mmol) in degassed DCE (40.0 mL). Purification by flash chromatography on silica gel (100% Et2O) afforded the title compound **16r** as an orange solid (420 mg, 51% yield); mp 57–59 °C; R*f* 0.27 (9:1 Et2O:hexane); νmax (thin film)/cm−1 3320, 2923, 1645, 1462, 1385, 1132, 1006, 742; δH (400 MHz, CDCl3) 8.73 (br s, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.14 (dd, *J* = 8.1, 7.5 Hz, 1H), 7.08 (dd, *J* = 7.8, 7.5 Hz, 1H), 3.93 (s, 2H), 3.69 (s, 3H), 3.22 (s, 3H), 2.29 (s, 3H); δC (100 MHz, CDCl3) 171.3, 135.7, 128.9, 127.5, 121.7, 119.1, 118.4, 110.8, 108.4, 61.7, 32.2, 29.2, 8.7; HRMS (ESI+): Found: 255.1109; C13H16N2NaO2+ (MNa+) Requires 255.1104 (−1.9 ppm error).

* + 1. tert-Butyl (2-(2-(2-oxo-4-phenylbut-3-yn-1-yl)-1H-indol-3-yl)ethyl)carbamate (**11a**)

Prepared according to general procedure B using phenylacetylene (1.54 mL, 14.0 mmol), THF (40.0 mL), *i*PrMgCl (7.02 mL, 14.0 mmol, 2.00 M in THF) and *tert*-butyl (2-(2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1*H*-indol-3-yl)ethyl)carbamate **16a** (1.45 g, 4.01 mmol) stirring at 0 °C for 2 h. Purification by flash chromatography on silica gel (1:1 Et2O:hexane) afforded the title compound **11a** as a brown foam (1.20 g, 74% yield); R*f* 0.31 (1:1 Et2O:hexane); δH (400 MHz, CDCl3) 8.50 (br s, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.52–7.47 (m, 2H), 7.47–7.43 (m, 1H), 7.39–7.33 (m, 3H), 7.19 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.11 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 4.65 (br s, 1H), 4.15 (s, 2H), 3.46–3.33 (m, 2H), 3.03–2.92 (m, 2H), 1.43 (s, 9H); HRMS (ESI+): Found: 425.1837; C25H26N2NaO3+ (MNa+) Requires 425.1836 (−0.4 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. Benzyl (2-(2-(2-oxo-4-phenylbut-3-yn-1-yl)-1H-indol-3-yl)ethyl)carbamate (**11b**)

Prepared according to general procedure B using phenylacetylene (0.690 mL, 6.33 mmol), THF (18.5 mL), *i*PrMgCl (3.16 mL, 6.33 mmol, 2.00 M in THF) benzyl (2-(2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1*H*-indol-3-yl)ethyl)carbamate **16b** (715 mg, 1.81 mmol) stirring at 0 °C for 30 min. Purification by flash chromatography on silica gel (1:1 Et2O:hexane, then 95:5 CH2Cl2:EtOAc) afforded the title compound **11b** as a yellow solid (524 mg, 66% yield); mp 108–110 °C; R*f* 0.71 (9:1 Et2O:hexane); δH (400 MHz, CDCl3) 8.44 (br s, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.49–7.42 (m, 3H), 7.38–7.28 (m, 9H), 7.20–7.15 (m, 1H), 7.12–7.06 (m, 1H), 5.07 (s, 2H), 4.87 (br s, 1H), 4.08 (s, 2H), 3.53–3.43 (m, 2H), 3.00 (t, *J* = 6.7 Hz, 2H); HRMS (ESI+): Found: 459.1677; C28H24N2NaO3+ (MNa+) Requires 459.1679 (0.4 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. 4-Methyl-N-(2-(2-(2-oxo-4-phenylbut-3-yn-1-yl)-1H-indol-3-yl)ethyl)benzenesulfonamide (**11c**)

Prepared according to general procedure B using phenylacetylene (1.05 mL, 9.60 mmol), THF (20.0 mL), *i*PrMgCl (4.80 mL, 9.60 mmol, 2.00 M in THF) and *N*-methoxy-*N*-methyl-2-(3-(2-(4-methylphenylsulfonamido)ethyl)-1*H*-indol-2-yl)acetamide **16c** (1.14 mg, 2.74 mmol) stirring at 0 °C for 30 min. Purification by flash chromatography on silica gel (6:4 Et2O:hexane) afforded the title compound **11c** as a yellow foam (815 mg, 65% yield); R*f* 0.57 (8:2 Et2O:hexane); δH (400 MHz, CDCl3) 8.43 (br s, 1H), 7.64–7.59 (m, 2H), 7.56–7.52 (m, 2H), 7.51–7.45 (m, 1H), 7.42–7.31 (m, 4H), 7.15–7.22 (m, 3H), 7.08–7.03 (m, 1H), 4.51 (t, *J* = 6.6 Hz, 1H), 4.13 (s, 2H), 3.26 (app. q, *J* = 6.6 Hz, 2H), 2.99 (t, *J* = 6.6 Hz, 2H), 2.37 (s, 3H); HRMS (ESI+): Found: 479.1397; C27H24N2NaO3S+ (MNa+) Requires 479.1400 (0.5 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. tert-Butyl (2-(2-(4-(4-fluorophenyl)-2-oxobut-3-yn-1-yl)-1H-indol-3-yl)ethyl)carbamate (**11d**)

Prepared according to general procedure B using 1-ethynyl-4-fluorobenzene (357 mg, 3.50 mmol), THF (8.30 mL), *i*PrMgCl (1.75 mL, 3.50 mmol, 2.00 M in THF) and *tert*-butyl (2-(2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1*H*-indol-3-yl)ethyl)carbamate **16a** (361 mg, 1.00 mmol) stirring at 0 °C for 1 h. Purification by flash chromatography on silica gel (1:1 Et2O:hexane) afforded the title compound **11d** as a yellow foam (309 mg, 73% yield); R*f* 0.32 (1:1 Et2O:hexane); δH (400 MHz, CDCl3) 8.53 (br s, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.50–7.44 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.21–7.16 (m, 1H), 7.14–7.09 (m, 1H), 7.08–7.01 (m, 1H), 4.66 (br s, 1H), 4.13 (s, 2H), 3.45–3.33 (m, 2H), 3.03–2.92 (m, 2H), 1.44 (s, 9H); HRMS (ESI+): Found: 443.1734; C25H25FN2NaO3+ (MNa+) Requires 443.1741 (1.6 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. tert-Butyl (2-(2-(4-(4-methoxyphenyl)-2-oxobut-3-yn-1-yl)-1H-indol-3-yl)ethyl)carbamate (**11e**)

Prepared according to general procedure B using 1-ethynyl-4-methoxybenzene (463 mg, 3.50 mmol), THF (10.0 mL), *i*PrMgCl (1.75 mL, 3.50 mmol, 2.00 M in THF) and *tert*-butyl (2-(2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1*H*-indol-3-yl)ethyl)carbamate **16a** (361 mg, 1.00 mmol) stirring at 0 °C for 1 h. Purification by flash chromatography on silica gel (6:4 hexane:Et2O, then 1:1 Et2O:hexane) afforded the title compound **11e** as a yellow foam (352 mg, 81% yield); R*f* 0.16 (6:4 hexane:Et2O); δH (400 MHz, CDCl3) 8.54 (br s, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.45–7.41 (m, 2H), 7.34 (app. dt, *J* = 8.0, 0.9 Hz, 1H), 7.18 (ddd, *J* = 8.1, 7.1, 1.2 Hz, 1H), 7.11 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 6.88–6.84 (m, 2H), 4.66 (br s, 1H), 4.12 (s, 2H)k, 3.44–3.33 (m, 2H), 3.02–2.94 (m, 2H), 1.44 (s, 9H); HRMS (ESI+): Found: 455.1937; C26H28N2NaO4+ (MNa+) Requires 455.1941 (0.8 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. tert-Butyl (2-(2-(2-oxobut-3-yn-1-yl)-1H-indol-3-yl)ethyl)carbamate (**11f**)

To a solution of Weinreb amide **16a** (1.45 g, 4.00 mmol) in THF (20.0 mL) under argon at −78 °C was added ethynylmagnesium chloride (56.0 mL, 28.0 mmol, 0.500 M in THF) dropwise over 40 min. The reaction mixture was then warmed to 0 °C and stirred 2 h. The reaction was quenched by the addition of aq. 1 M NaHSO4 (20.0 mL). The organics were separated and the aqueous layer extracted with EtOAc (3 x 20.0 mL). The organics were then combined, washed with brine (10.0 mL), dried over Na2SO4 and concentrated *in vacuo*. The crude material was then purified by flash chromatography on silica gel (1:1 EtOAc:hexane) to afford the title compound **11f** as a yellow oil (990 mg, 76% yield); R*f* 0.80 (7:3 EtOAc:hexane); δH (400 MHz, CDCl3) 8.42 (br s, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.19 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.11 (dd, *J* = 7.8, 7.2 Hz, 1H), 4.64 (br s, 1H), 4.05 (s, 2H), 3.44–3.36 (m, 2H), 3.34 (s, 1H), 2.93 (t, *J* = 6.6 Hz, 2H), 1.44 (s, 9H); HRMS (ESI+): Found: 327.1707; C19H23N2O3+ (MH+) Requires 327.1703 (−1.2 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. tert-Butyl (2-(2-(2-oxopent-3-yn-1-yl)-1H-indol-3-yl)ethyl)carbamate (**11g**)

To a solution of Weinreb amide **16a** (712 mg, 1.97 mmol) in THF (8.00 mL) under argon at −20 °C was added methylmagnesium bromide (13.8 mL, 6.89 mmol, 0.500 M in THF) dropwise over 15 min. The reaction mixture was then stirred at −20 °C for 2 h. The reaction was quenched by the addition of sat. aq. NH4Cl (20.0 mL). The organics were separated and the aqueous layer extracted with Et2O (3 x 20.0 mL). The organics were then combined, washed with brine (10.0 mL), dried over MgSO4 and concentrated *in vacuo*. The crude material was then purified by flash chromatography on silica gel (7:3 Et2O:hexane) to afford the title compound **11g** as an orange foam (380 mg, 57% yield); R*f* 0.25 (7:3 Et2O:hexane); δH (400 MHz, CDCl3, 55 °C) 8.43 (br s, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.16 (app. t, *J* = 8.0 Hz, 1H), 7.10 (app. t, *J* = 7.8 Hz, 1H), 4.59 (br s, 1H), 4.00 (s, 2H), 3.44–3.33 (m, 2H), 2.94 (t, *J* = 6.8 Hz, 2H), 2.01 (s, 3H), 1.46 (s, 9H); HRMS (ESI+): Found: 341.1857; C20H25N2O3+ (MH+) Requires 341.1860 (0.7 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. tert-Butyl (2-(2-(2-oxooct-3-yn-1-yl)-1H-indol-3-yl)ethyl)carbamate (**11h**)

Prepared according to general procedure B using hex-1-yne (0.800 mL, 7.00 mmol), THF (20.0 mL), *i*PrMgCl (3.50 mL, 7.00 mmol, 2.00 M in THF) and *tert*-butyl (2-(2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1*H*-indol-3-yl)ethyl)carbamate **16a** (723 mg, 2.00 mmol) stirring at 0 °C for 1 h. Purification by flash chromatography on silica gel (7:3 hexane:Et2O, then 1:1 Et2O:hexane) afforded the title compound **11h** as a pale orange foam (510 mg, 66% yield); R*f* 0.26 (1:1 Et2O:hexane); δH (400 MHz, CDCl3) 8.55 (br s, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.32 (app. dt, *J* = 8.1, 0.9 Hz, 1H), 7.17 (ddd, *J* = 8.1, 7.1, 1.2 Hz, 1H), 7.10 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 4.66 (br s, 1H), 4.00 (s, 2H), 3.43–3.30 (m, 2H), 2.93 (t, *J* = 6.6 Hz, 2H), 2.35 (t, *J* = 7.1 Hz, 2H), 1.55–1.41 (m, 11H), 1.41–1.30 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); HRMS (ESI+): Found: 405.2142; C23H30N2NaO3+ (MNa+) Requires 405.2149 (1.5 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. tert-Butyl (2-(2-(2-oxo-4-(phenylthio)but-3-yn-1-yl)-1H-indol-3-yl)ethyl)carbamate (**11i**)

Prepared according to general procedure B using ethynyl(phenyl)sulfane27 (939 mg, 7.00 mmol), THF (20.0 mL), *i*PrMgCl (3.50 mL, 7.00 mmol, 2.00 M in THF) and *tert*-butyl (2-(2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1*H*-indol-3-yl)ethyl)carbamate **16a** (723 mg, 2.00 mmol) stirring at 0 °C for 30 min. Purification by flash chromatography on silica gel (1:1 Et2O:hexane) afforded the title compound **11i** as a yellow foam (602 mg, 69% yield); R*f* 0.24 (1:1 Et2O:hexane); δH (400 MHz, CDCl3) 8.48 (br s, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.25–7.10 (m, 7H), 4.57 (br s, 1H), 4.02 (s, 2H), 3.40–3.28 (m, 2H), 2.92 (t, *J* = 6.6 Hz, 2H), 1.43 (s, 9H); HRMS (ESI+): Found: 457.1566; C23H26N2NaO3S+ (MNa+) Requires 457.1556 (−2.1 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. tert-Butyl (2-(2-(4-cyclopropyl-2-oxobut-3-yn-1-yl)-1H-indol-3-yl)ethyl)carbamate (**11j**)

Prepared according to general procedure B using ethynylcyclopropane (0.440 mL, 5.25 mmol), THF (16.0 mL), *i*PrMgCl (2.63 mL, 5.25 mmol, 2.0 M in THF) and *tert*-butyl (2-(2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1*H*-indol-3-yl)ethyl)carbamate **16a** (542 mg, 1.50 mmol) stirring at 0 °C for 1 h. Purification by flash chromatography on silica gel (6:4 Et2O:hexane) afforded the title compound **11j** as an orange oil (309 mg, 56% yield); R*f* 0.80 (100% Et2O; δH (400 MHz, CDCl3) 8.42 (br s, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.17 (app. t, *J* = 8.0 Hz, 1H), 7.10 (app. t, *J* = 7.9 Hz, 1H), 4.62 (br s, 1H), 3.98 (s, 2H), 3.42–3.29 (m, 2H), 2.92 (t, *J* = 6.6 Hz, 2H), 1.45 (s, 9H), 1.42–1.35 (m, 1H), 1.02–0.96 (m, 2H), 0.90–0.85 (m, 2H); HRMS (ESI+): Found: 389.1833; C22H26N2NaO3+ (MH+) Requires 389.1836 (0.6 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. tert-Butyl (2-(2-(5-((tert-butyldiphenylsilyl)oxy)-2-oxopent-3-yn-1-yl)-1H-indol-3-yl)ethyl)carbamate (**11k**)

Prepared according to general procedure B using *tert*-butyldiphenyl(prop-2-yn-1-yloxy)silane28 (1.55 g, 5.25 mmol), THF (16 mL), *i*PrMgCl (2.63 mL, 5.25 mmol, 2.00 M in THF) and *tert*-butyl (2-(2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1*H*-indol-3-yl)ethyl)carbamate **16a** (542 mg, 1.50 mmol) stirring at 0 °C for 45 min. Purification by flash chromatography on silica gel (7:3 hexane:Et2O) afforded the title compound **11k** as a yellow foam (643 mg, 72% yield); R*f* 0.15 (7:3 hexane:Et2O); δH (400 MHz, CDCl3) 8.24 (br s, 1H), 7.72–7.66 (m, 4H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.49–7.36 (m, 6H), 7.32–7.27 (m, 1H), 7.20–7.08 (m, 2H), 4.63 (br s, 1H), 4.45 (s, 2H), 3.92(s, 2H), 3.41–3.29 (m, 2H), 2.93–2.85 (m, 2H), 1.44 (s, 9H), 1.07 (s, 9H); HRMS (ESI+): Found: 617.2815; C36H42N2NaO4Si+ (MNa+) Requires 617.2806 (−1.4 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. tert-Butyl (2-(4-bromo-2-(2-oxo-4-phenylbut-3-yn-1-yl)-1H-indol-3-yl)ethyl)carbamate (**11l**)

Prepared according to general procedure B using phenylacetylene (1.06 mL, 9.64 mmol), THF (28.0 mL), *i*PrMgCl (4.82 mL, 9.64 mmol, 2.00 M in THF) and *tert*-butyl (2-(4-bromo-2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1*H*-indol-3-yl)ethyl)carbamate**16d** (1.21 g, 2.76 mmol) stirring at 0 °C for 45 min. Purification by flash chromatography on silica gel (1:1 Et2O:hexane) afforded the title compound **11l** as a yellow foam (721 mg, 54% yield); R*f* 0.33 (1:1 Et2O:hexane); δH (400 MHz, CDCl3) 8.88 (br s, 1H), 7.58–7.44 (m, 3H), 7.41–7.34 (m, 2H), 7.30–7.23 (m, 2H), 6.98 (app. t, *J* = 7.9 Hz, 1H), 4.74 (br s, 1H), 4.19 (s, 2H), 3.50–3.39 (m, 2H), 3.29–3.12 (m, 2H), 1.44 (s, 9H); HRMS (ESI+): Found: 503.0939; C25H25BrN2NaO3+ (MNa+) Requires 503.0941 (0.3 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. tert-Butyl (2-(4-(benzyloxy)-2-(2-oxo-4-phenylbut-3-yn-1-yl)-1H-indol-3-yl)ethyl)carbamate (**11m**)

Prepared according to general procedure B using phenylacetylene (0.410 mL, 3.74 mmol), THF (11.0 mL), *i*PrMgCl (1.87 mL, 3.74 mmol, 2.00 M in THF) and *tert-*butyl (2-(4-(benzyloxy)-2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1*H*-indol-3-yl)ethyl)carbamate **16e** (500 mg, 1.07 mmol) stirring at 0 °C for 45 min. Purification by flash chromatography on silica gel (1:1 Et2O:hexane) afforded the title compound **11m** as a yellow foam (345 mg, 63% yield); R*f* 0.29 (1:1 Et2O:hexane); δH (400 MHz, CDCl3) 8.48 (br s, 1H), 7.61–7.31 (m, 10H), 7.11–7.04 (m, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.58 (d, *J* = 7.8 Hz, 1H), 5.16 (s, 2H), 4.50 (br s, 1H), 4.12 (s, 2H), 3.39–3.20 (m, 2H), 3.07–2.91 (m, 2H), 1.40 (s, 9H); HRMS (ESI+): Found: 531.2265; C32H32N2NaO4+ (MNa+) Requires 531.2254 (−2.1 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. tert-Butyl (2-(5-bromo-2-(2-oxo-4-phenylbut-3-yn-1-yl)-1H-indol-3-yl)ethyl)carbamate (**11n**)

Prepared according to general procedure B using phenylacetylene (0.370 mL, 3.35 mmol), THF (10.0 mL), *i*PrMgCl (1.67 mL, 3.35 mmol, 2.00 M in THF) and *tert*-butyl (2-(5-bromo-2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1*H*-indol-3-yl)ethyl)carbamate **16f** (421 mg, 0.960 mmol) stirring at 0 °C for 1 h. Purification by flash chromatography on silica gel (1:1 Et2O:hexane) afforded the title compound **11n** as a yellow foam (285 mg, 62% yield); R*f* 0.24 (1:1 Et2O:hexane); δH (400 MHz, CDCl3) 8.74 (br s, 1H), 7.67–7.64 (m, 1H), 7.51–7.44 (m, 3H), 7.39–7.33 (m, 2H), 7.26–7.18 (m, 2H), 4.71–4.62 (m, 1H), 4.13 (s, 2H), 3.44–3.28 (m, 2H), 2.92 (t, *J* = 6.4 Hz, 2H), 1.44 (s, 9H); HRMS (ESI+): Found: 503.0943; C25H25BrN2NaO3+ (MNa+) Requires 503.0941 (−0.4 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. tert-Butyl (2-(5-methoxy-2-(2-oxo-4-phenylbut-3-yn-1-yl)-1H-indol-3-yl)ethyl)carbamate (**11o**)

Prepared according to general procedure B using phenylacetylene (0.800 mL, 7.24 mmol), THF (20.0 mL), *i*PrMgCl (3.62 mL, 7.24 mmol, 2.00 M in THF) and *tert*-butyl (2-(5-methoxy-2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1*H*-indol-3-yl)ethyl)carbamate **16g** (810 mg, 2.07 mmol) stirring at 0 °C for 45 min. Purification by flash chromatography on silica gel (1:1 Et2O:hexane) afforded the title compound **11o** as a yellow foam (704 mg, 79% yield); R*f* 0.24 (1:1 Et2O:hexane); δH (400 MHz, CDCl3) 8.40 (br s, 1H), 7.52–7.42 (m, 3H), 7.39–7.33 (m, 3H), 7.25–7.22 (m, 1H), 7.02–6.98 (m, 1H), 6.85 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.67 (br s, 1H), 4.12 (s, 2H), 3.86 (s, 3H), 3.47–3.29 (m, 2H), 3.02–2.88 (m, 2H), 1.43 (s, 9H); HRMS (ESI+): Found: 455.1945; C26H28N2NaO4+ (MNa+) Requires 455.1941 (−0.9 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. tert-Butyl (2-(6-chloro-2-(2-oxo-4-phenylbut-3-yn-1-yl)-1H-indol-3-yl)ethyl)carbamate (**11p**)

Prepared according to general procedure B using phenylacetylene (0.590 mL, 5.34 mmol), THF (16.0 mL), *i*PrMgCl (2.67 mL, 5.34 mmol, 2.00 M in THF) and *tert*-butyl (2-(6-chloro-2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1*H*-indol-3-yl)ethyl)carbamate **16h** (604 mg, 1.53 mmol) stirring at 0 °C for 45 min. Purification by flash chromatography on silica gel (1:1 Et2O:hexane) afforded the title compound **11p** as a yellow foam (509 mg, 76% yield); R*f* 0.28 (1:1 Et2O:hexane); δH (400 MHz, CDCl3) 8.58 (br s, 1H), 7.53–7.44 (m, 4H), 7.40–7.35 (m, 2H), 7.32 (d, *J* = 3.0 Hz, 1H), 7.07 (dd, *J* = 8.4, 1.8 Hz, 1H), 4.63 (br s, 1H), 4.13 (s, 2H), 3.42–3.28 (m, 2H), 2.94 (t, *J* = 6.6 Hz, 2H), 1.43 (s, 9H); HRMS (ESI+): Found: 459.1447; C25H25ClN2NaO3+ (MNa+) Requires 459.1446 (−0.2 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. tert-Butyl (2-(7-methyl-2-(2-oxo-4-phenylbut-3-yn-1-yl)-1H-indol-3-yl)ethyl)carbamate (**11q**)

Prepared according to general procedure B using phenylacetylene (1.05 mL, 9.60 mmol), THF (28.0 mL), *i*PrMgCl (4.80 mL, 9.60 mmol, 2.00 M in THF) and *tert*-butyl (2-(2-(2-(methoxy(methyl)amino)-2-oxoethyl)-7-methyl-1*H*-indol-3-yl)ethyl)carbamate **16i** (1.03 g, 2.74 mmol) stirring at 0 °C for 45 min. Purification by flash chromatography on silica gel (1:1 Et2O:hexane) afforded the title compound **11q** as a light brown foam (526 mg, 46% yield); R*f* 0.31 (1:1 Et2O:hexane); δH (400 MHz, CDCl3) 8.39 (br s, 1H), 7.54–7.40 (m, 4H), 7.39–7.33 (m, 2H), 7.08–6.97 (m, 2H), 4.65 (br s, 1H), 4.16 (s, 2H), 3.47–3.32 (m, 2H), 2.99 (t, *J* = 6.6 Hz, 2H), 2.48 (s, 3H), 1.44 (s, 9H); HRMS (ESI+): Found: 439.1996; C26H28N2NaO3+ (MNa+) Requires 439.1992 (−0.9 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. tert-Butyl (1-(2-(2-oxo-4-phenylbut-3-yn-1-yl)-1H-indol-3-yl)butan-2-yl)carbamate (**11r**)

Prepared according to general procedure B using phenylacetylene (0.930 mL, 8.34 mmol), THF (24.0 mL), *i*PrMgCl (4.17 mL, 8.34 mmol, 2.00 M in THF) and *tert*-butyl (1-(2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1*H*-indol-3-yl)butan-2-yl)carbamate **16j** (928 mg, 2.38 mmol) stirring at 0 °C for 45 min. Purification by flash chromatography on silica gel (1:1 hexane:Et2O) afforded the title compound **11r** as a yellow foam (541 mg, 53% yield); R*f* 0.27 (1:1 hexane:Et2O); δH (400 MHz, CDCl3) 8.58 (br s, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.53–7.42 (m, 3H), 7.40–7.31 (m, 3H), 7.20–7.14 (m, 1H), 7.14–7.08 (m, 1H), 4.52–4.37 (m, 1H), 4.18 (s, 2H), 3.89–3.70 (m, 1H), 3.12–2.78 (m, 2H), 1.68–1.55 (m, 1H), 1.48–1.23 (m, 10H), 0.94–0.84 (t, *J* = 7.3 Hz, 3H); HRMS (ESI+): Found: 453.2143; C27H30N2NaO3+ (MNa+) Requires 453.2149 (1.3 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. (S)-tert-Butyl (1-hydroxy-3-(2-(2-oxo-4-phenylbut-3-yn-1-yl)-1H-indol-3-yl)propan-2-yl)carbamate (**11s**)

Prepared according to general procedure B using phenylacetylene (0.830 mL, 7.56 mmol), THF (20.0 mL), *i*PrMgCl (3.78 mL, 7.56 mmol, 2.00 M in THF) and *(S)-tert-*butyl (1-hydroxy-3-(2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1*H*-indol-3-yl)propan-2-yl)carbamate **16k** (658 mg, 1.68 mmol) stirring at 0 °C for 2 h. Purification by flash chromatography on silica gel (6:4 hexane:EtOAc) afforded the title compound **11s** as a pale orange foam (394 mg, 54% yield); R*f* 0.71 (100% EtOAc); νmax (thin film)/cm−1 3395, 2977, 2930, 2201, 1666, 1490, 1366, 1168, 1077, 909, 738; δH (400 MHz, CDCl3, 55 °C) 8.40 (br s, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.56–7.49 (m, 2H), 7.49–7.43 (m, 1H), 7.40–7.31 (m, 3H), 7.18 (dd, *J* = 7.8, 7.5 Hz, 1H), 7.12 (dd, *J* = 7.8, 7.5 Hz, 1H), 4.88 (br s, 1H), 4.20 (s, 2H), 4.02–3.91 (m, 1H), 3.65 (dd, *J* = 10.9, 3.9 Hz, 1H), 3.56 (dd, *J* = 10.9, 4.5 Hz, 1H), 3.12–2.98 (m, 2H), 1.44 (s, 9H); δC (100 MHz, CDCl3, 55 °C) 183.9, 156.2, 136.4, 133.4, 131.2, 128.8, 128.6, 127.8, 122.4, 120.0, 119.7, 119.0, 111.0, 110.7, 93.6, 88.1, 79.8, 63.9, 53.4, 42.5, 28.6, 26.2; HRMS (ESI+): Found: 433.2125; C26H29N2O4+ (MH+) Requires 433.2122 (−0.7 ppm error).

* + 1. tert-Butyl (2-(2-(3-oxo-5-phenylpent-4-yn-2-yl)-1H-indol-3-yl)ethyl)carbamate (**11t**)

Prepared according to general procedure B using phenylacetylene (0.520 mL, 4.77 mmol), THF (14.0 mL), *i*PrMgCl (2.39 mL, 4.77 mmol, 2.00 M in THF) and *tert*-butyl (2-(2-(1-(methoxy(methyl)amino)-1-oxopropan-2-yl)-1*H*-indol-3-yl)ethyl)carbamate **16l** (5.12 g, 1.36 mmol) stirring at RT for 1 h. Purification by flash chromatography on silica gel (1:1 Et2O:hexane) afforded the title compound **11t** as a yellow foam (4.15 g, 73% yield); R*f* 0.39 (1:1 Et2O:hexane); νmax (thin film)/cm−1 3332, 2977, 2931, 2196, 1689, 1664, 1507, 1490, 1459, 1366, 1271, 1250, 1166, 1044, 758, 736; δH (400 MHz, CDCl3) 8.33 (br s, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.50–7.40 (m, 3H), 7.39–7.30 (m, 3H), 7.18 (app. t, *J* = 7.4 Hz, 1H), 7.11 (app. t, *J* = 7.4 Hz, 1H), 4.75–4.61 (br s, 1H), 4.39 (q, *J* = 7.1 Hz, 1H), 3.62–3.30 (m, 2H), 3.20–2.94 (m, 2H), 1.63 (d, *J* = 7.1 Hz, 3H), 1.44 (s, 9H); δC (100 MHz, CDCl3) 187.2, 156.1, 136.2, 133.4, 132.5, 131.2, 128.8, 128.2, 122.4, 119.7, 119.6, 118.8, 111.1, 111.0, 93.7, 87.6, 79.3, 46.0, 41.4, 28.5, 25.0, 17.0; HRMS (ESI+): Found: 439.1996; C26H28N2NaO3+ (MNa+) Requires 439.1992 (−0.8 ppm error).

* + 1. 1-(3-(2-Hydroxyethyl)-1H-indol-2-yl)-4-phenylbut-3-yn-2-one (**11u**)

Prepared according to general procedure B using phenylacetylene (0.130 mL, 1.18 mmol), THF (4.00 mL), *i*PrMgCl (0.590 mL, 1.18 mmol, 2.00 M in THF) and 2-(3-(2-hydroxyethyl)-1*H*-indol-2-yl)-*N*-methoxy-*N*-methylacetamide **16m** (100 mg, 0.381 mmol) stirring at 0 °C for 30 min. Purification by flash chromatography on silica gel (8:2 Et2O:hexane) afforded the title compound **11u** as a yellow foam (67.0 mg, 58% yield); R*f* 0.23 (8:2 Et2O:hexane); δH (400 MHz, CDCl3) 8.53 (s, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.53–7.40 (m, 3H), 7.40–7.30 (m, 3H), 7.19 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 7.15–7.09 (m, 1H), 4.16 (s, 2H), 3.89 (t, *J* = 6.3 Hz, 2H), 3.05 (t, *J* = 6.3 Hz, 2H); HRMS (ESI+): Found: 326.1156; C20H17NNaO2+ (MNa+) Requires 326.1151 (−1.4 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. 1-(3-(3-Hydroxypropyl)-1H-indol-2-yl)-4-phenylbut-3-yn-2-one (**11v**)

Prepared according to general procedure B using phenylacetylene (0.840 mL, 7.62 mmol), THF (19.0 mL), *i*PrMgCl (3.81 mL, 7.62 mmol, 2.00 M in THF) and 2-(3-(3-hydroxypropyl)-1*H*-indol-2-yl)-*N*-methoxy-*N*-methylacetamide **16n** (421 mg, 1.52 mmol) stirring at −20 °C for 1.5 h. Purification by flash chromatography on silica gel (9:1 hexane:EtOAc, then 1:1 hexane:EtOAc) afforded the title compound **11v** as an orange foam (342 mg, 71% yield); R*f* 0.45 (1:1 hexane:EtOAc); δH (400 MHz, CDCl3) 8.38 (br s, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.51–7.40 (m, 3H), 7.38–7.30 (m, 3H), 7.20–7.15 (m, 1H), 7.13–7.08 (m, 1H), 4.14 (s, 2H), 3.66 (t, *J* = 6.2 Hz, 2H), 2.90 (t, *J* = 7.3 Hz, 2H), 2.00–1.90 (m, 2H); HRMS (ESI+): Found: 340.1308; C21H19NNaO2+ (MNa+) Requires 340.1308 (0.0 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. 1-(3-(4-Hydroxybutyl)-1H-indol-2-yl)-4-phenylbut-3-yn-2-one (**11w**)

Prepared according to general procedure B using phenylacetylene (0.990 mL, 9.00 mmol), THF (22.0 mL), *i*PrMgCl (4.50 mL, 9.00 mmol, 2.00 M in THF) and 2-(3-(4-hydroxybutyl)-1*H*-indol-2-yl)-*N*-methoxy-*N*-methylacetamide **16o** (436 mg, 1.50 mmol) stirring at −20 °C for 1.5 h. Purification by flash chromatography on silica gel (7:3 Et2O, hexane) afforded the title compound **11w** as pale orange oil (275 mg, 55% yield); R*f* 0.29 (7:3 Et2O:hexane); νmax (thin film)/cm−1 3544, 3398, 2934, 2858, 2201, 1660, 1489, 1459, 1443, 1305, 1074, 758, 742; δH (400 MHz, CDCl3) 8.31 (br s, 1H), 7.59–7.55 (m, 1H), 7.51–7.43 (m, 3H), 7.39–7.32 (m, 3H), 7.20–7.15 (m, 1H), 7.13–7.07 (m, 1H), 4.11 (s, 2H), 3.67–3.59 (m, 2H), 2.82 (t, *J* = 7.4 Hz, 2H), 1.81–1.70 (m, 2H), 1.70–1.60 (m, 2H); δC (100 MHz, CDCl3) 184.0, 136.2, 133.3, 131.3, 128.8, 128.2, 125.9, 122.1, 119.5, 119.4, 118.8, 114.9, 111.0, 93.4, 87.9, 63.0, 42.6, 32.8, 27.1, 24.1; HRMS (ESI+): Found: 354.1466; C22H21NNaO2+ (MNa+) Requires 354.1464 (−0.5 ppm error).

* + 1. Dimethyl 2-(2-(2-(2-oxo-4-phenylbut-3-yn-1-yl)-1H-indol-3-yl)ethyl)malonate (**11x**)

Prepared according to general procedure B using phenylacetylene (0.960 mL, 8.73 mmol), THF (25.0 mL), *i*PrMgCl (4.37 mL, 8.73 mmol, 2.00 M in THF) and dimethyl 2-(2-(2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1*H*-indol-3-yl)ethyl)malonate **16p** (939 mg, 2.50 mmol) stirring at 0 °C for 1.5 h. Purification by flash chromatography on silica gel (1:1 Et2O, hexane) afforded the title compound **11x** as yellow oil (840 mg, 80% yield); R*f* 0.34 (1:1 Et2O, hexane); νmax (thin film)/cm−1 3392, 2953, 2202, 1731, 1665, 1459, 1443, 1260, 1154, 1076, 760, 745; δH (400 MHz, CDCl3) 8.43 (br s, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.51–7.42 (m, 3H), 7.39–7.31 (m, 3H), 7.21–7.15 (m, 1H), 7.15–7.09 (m, 1H), 4.12 (s, 2H), 3.70 (s, 6H), 3.45 (t, *J* = 7.3 Hz, 1H), 2.85 (t, *J* = 7.6 Hz, 2H), 2.35–2.26 (m, 2H); δC (100 MHz, CDCl3) 183.9, 170.0, 136.1, 133.4, 131.2, 128.8, 127.9, 126.6, 122.3, 119.6, 119.5, 118.7, 113.0, 111.0, 93.4, 87.9, 52.6, 51.2, 42.3, 29.8, 22.0; HRMS (ESI+): Found: 440.1471; C25H23NNaO5+ (MNa+) Requires 440.1468 (−0.5 ppm error).

* + 1. tert-Butyl benzyl(2-(2-(2-oxo-4-phenylbut-3-yn-1-yl)-1H-indol-3-yl)ethyl)carbamate (**11y**)

Prepared according to general procedure B using phenylacetylene (0.300 mL, 2.77 mmol), THF (7.00 mL), *i*PrMgCl (1.39 mL, 2.77 mmol, 2.00 M in THF) and *tert*-butyl benzyl(2-(2-(2-(methoxy(methyl)amino)-2-oxoethyl)-1*H*-indol-3-yl)ethyl)carbamate **16q** (500 mg, 1.11 mmol) initially stirring at −20 °C and warming to 0 °C over 2 h. Purification by flash chromatography on silica gel (1:1 Et2O:hexane) afforded the title compound **11y** as an orange foam (385 mg, 71% yield); R*f* 0.74 (100% EtOAc); νmax (thin film)/cm−1 3319, 2975, 2201, 1664, 1460, 1416, 1366, 1245, 1162, 1074, 738; δH (400 MHz, CDCl3, 55 °C) 8.37 (br s, 1H), 7.56–7.42 (m, 4H), 7.39–7.18 (m, 8H), 7.19–7.14 (m, 1H), 7.11–7.04 (m, 1H), 4.38 (br s, 2H), 4.04 (br s, 2H), 3.43 (br s, 2H), 2.97 (br s, 2H), 1.52 (s, 9H); δC (100 MHz, CDCl3, 55 °C) 183.6, 156.0, 138.9, 136.3, 133.3, 131.2, 128.8, 128.6, 128.3, 128.0, 127.4, 126.9, 122.3, 119.8, 119.7, 118.7, 112.0, 111.0, 93.3, 88.0, 79.9, 51.4, 48.0, 42.4, 28.8, 23.5; HRMS (ESI+): Found: 493.2491; C32H33N2O3+ (MH+) Requires 493.2486 (−1.0 ppm error).

* + 1. 1-(3-Methyl-1H-indol-2-yl)-4-phenylbut-3-yn-2-one (**11z**)

Prepared according to general procedure B using phenylacetylene (1.13 mL, 10.3 mmol), THF (35.0 mL), *i*PrMgCl (5.16 mL, 10.3 mmol, 2.00 M in THF) and *N*-methoxy-*N*-methyl-2-(3-methyl-1*H*-indol-2-yl)acetamide **16r** (958 mg, 4.12 mmol) stirring at 0 °C for 30 min. Purification by flash chromatography on silica gel (6:4 hexane:Et2O) afforded the title compound **11z** as a yellow solid (885 mg, 81% yield); mp 98–100 °C; R*f* 0.69 (9:1 Et2O:hexane); νmax (thin film)/cm−1 3397, 3064, 2923, 2199, 1658, 1489, 1459, 1259, 1073, 756, 739; δH (400 MHz, CDCl3) 8.26 (br s, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.50–7.43 (m, 3H), 7.39–7.30 (m, 3H), 7.21–7.14 (m, 1H), 7.14–7.07 (m, 1H), 4.11 (s, 2H), 2.35 (s, 3H); δC (100 MHz, CDCl3) 183.8, 136.0, 133.3, 131.2, 129.0, 128.8, 125.9, 122.2, 119.6, 119.4, 118.7, 110.8, 110.2, 93.2, 87.9, 42.7, 8.8; HRMS (ESI+): Found: 296.1048; C19H15NNaO+ (MNa+) Requires 296.1046 (−0.7 ppm error).

* + 1. (4bS,8aR)-tert-Butyl 7-oxo-5-phenyl-8,9-dihydro-7H-8a,4b-(epiminoethano)carbazole-10-carboxylate (**13a**)

Prepared according to general procedure C using ynone **11a** (101 mg, 0.250 mmol), Au(PPh3)NTf2 (9.80 mg, 6.25 µmol) and CHCl3 (2.50 mL) stirring at RT for 22 h. Purification by flash chromatography on silica gel (9:1 CH2Cl2:EtOAc) afforded the title compound **13a** (as a 6:4 mixture of rotamers) as a brown foam (98.2 mg, 98% yield); R*f* 0.55 (9:1 CH2Cl2:EtOAc); δH (400 MHz, CDCl3) 7.40–7.30 (m, 6H, both rotamers), 7.11–6.98 (m, 6H, both), 6.69–6.61 (m, 2H, both), 6.57–6.48 (m, 2H, both), 6.26–6.19 (m, 2H, both), 6.00 (br s, 1H, major rotamer), 5.95–5.92 (m, 2H, both), 5.34 (br s, 1H, minor rotamer), 3.82–3.65 (m, 3H, both + major), 3.53–3.46 (m, 1H, minor), 3.15–3.01 (m, 2H, both), 2.82–2.68 (m, 4H, both), 2.63–2.53 (m, 2H, both), 1.56 (s, 9H, minor), 1.41 (s, 9H, major). Only peaks for major rotamer listed. HRMS (ESI+): Found: 425.1838; C25H26N2NaO3+ (MNa+) Requires 425.1836 (−0.6 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. (4bS,8aR)-Benzyl 7-oxo-5-phenyl-8,9-dihydro-7H-8a,4b-(epiminoethano)carbazole-10-carboxylate (**13b**)

Prepared according to general procedure C using ynone **11b** (109 mg, 0.250 mmol), Au(PPh3)NTf2 (9.80 mg, 6.25 µmol) and CHCl3 (2.50 mL) stirring at RT for 22 h. Purification by flash chromatography on silica gel (9:1 CH2Cl2:EtOAc) afforded the title compound **13b** (as a 7:3 mixture of rotamers) as an off-white foam (77.0 mg, 71% yield); R*f* 0.34 (98:2 CH2Cl2:EtOAc); δH (400 MHz, CDCl3) 7.46–7.27 (m, 16H, both rotamers), 7.10–6.99 (m, 6H, both), 6.67 (d, *J* = 7.8 Hz, 1H, major rotamer), 6.56–6.49 (m, 2H, both), 6.45 (d, *J* = 7.8 Hz, 1H, minor rotamer), 6.25–6.19 (m, 2H, both), 5.98 (br s, 1H, major), 5.96–5.91 (m, 2H, both), 5.37 (d, *J* = 12.2 Hz, 1H, minor), 5.29 (br s, 1H, minor), 5.19–5.12 (m, 2H, both), 3.88–3.71 (m, 3H, both + major), 3.51 (d, *J* = 16.2 Hz, 1H, minor), 3.23–3.10 (m, 2H, both), 2.83–2.73 (m, 4H, both), 2.68–2.55 (m, 2H, both). Only peaks for major rotamer listed. HRMS (ESI+): Found: 459.1679; C28H24N2NaO3+ (MNa+) Requires 459.1679 (0.1 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. (4bS,8aR)-5-Phenyl-10-tosyl-8,9-dihydro-7H-8a,4b-(epiminoethano)carbazol-7-one (**13c**)

Prepared according to general procedure C using ynone **11c** (114 mg, 0.250 mmol), Au(PPh3)NTf2 (9.80 mg, 6.25 µmol) and CHCl3 (2.50 mL) stirring at RT for 24 h. Purification by flash chromatography on silica gel (8:2 Et2O:hexane) afforded the title compound **13c** as a yellow oil (110 mg, 96% yield); R*f* 0.36 (7:3 Et2O:hexane); δH (400 MHz, CDCl3) 7.59 (d, *J* = 8.5 Hz, 2H), 7.40–7.29 (m, 3H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.03–6.94 (m, 3H), 6.53 (d, *J* = 7.8 Hz, 1H), 6.48 (td, *J* = 7.5, 0.7 Hz, 1H), 6.13 (d, *J* = 7.5 Hz, 1H), 5.91 (s, 1H), 5.62 (s, 1H), 3.72 (d, *J* = 16.0 Hz, 1H), 3.63 (t, *J* = 8.4 Hz, 1H), 3.06–2.96 (m, 1H), 2.90 (d, *J* = 16.0 Hz, 1H), 2.78–2.70 (m, 1H), 2.68–2.57 (m, 1H), 2.37 (s, 3H); HRMS (ESI+): Found: 479.1412; C27H24N2NaO3S+ (MNa+) Requires 479.1400 (−2.5 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. (4bS,8aR)-tert-Butyl 5-(4-fluorophenyl)-7-oxo-8,9-dihydro-7H-8a,4b-(epiminoethano)carbazole-10-carboxylate (**13d**)

Prepared according to general procedure C using ynone **11d** (135 mg, 0.321 mmol), Au(PPh3)NTf2 (12.6 mg, 8.02 µmol) and CHCl3 (3.20 mL) stirring at RT for 22 h. Purification by flash chromatography on silica gel (100% CH2Cl2, then 97:3 CH2Cl2:EtOAc) afforded the title compound **13d** (as a 6:4 mixture of rotamers) as a pale brown oil (120 mg, 89% yield); R*f* 0.43 (95:05 CH2Cl2:EtOAc); δH (400 MHz, CDCl3) 7.08–7.00 (m, 10H, both rotamers), 6.69–6.62 (m, 2H, both), 6.59–6.51 (m, 2H, both), 6.27–6.21 (m, 2H, both), 5.99 (br s, 1H, major rotamer), 5.92–5.90 (m, 2H, both), 5.33 (br s, 1H, minor rotamer), 3.81–3.65 (m, 3H, both + major), 3.49 (d, *J* = 16.3 Hz, 1H, minor), 3.15–3.01 (m, 2H, both), 2.81–2.65 (m, 4H, both), 2.60–2.50 (m, 2H, both), 1.55 (s, 9H, minor), 1.40 (s, 9H, major). Only peaks for major rotamer listed. HRMS (ESI+): Found: 443.1749; C25H25FN2NaO3+ (MNa+) Requires 443.1741 (−1.7 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. (4bS,8aR)-tert-Butyl 5-(4-methoxyphenyl)-7-oxo-8,9-dihydro-7H-8a,4b-(epiminoethano)carbazole-10-carboxylate (**13e**)

Prepared according to general procedure C using ynone **11e** (108 mg, 0.250 mmol), Au(PPh3)NTf2 (9.80 mg, 6.25 µmol) and CHCl3 (2.50 mL) stirring at RT for 24 h. Purification by flash chromatography on silica gel (100% CH2Cl2, then 95:5 CH2Cl2:EtOAc) afforded the title compound **13e** (as a 6:4 mixture of rotamers) as a pale orange foam (107 mg, 99% yield); R*f* 0.50 (9:1 CH2Cl2:EtOAc); δH (400 MHz, CDCl3) 7.06–6.99 (m, 6H, both rotamers), 6.89–6.82 (m, 4H, both), 6.67–6.60 (m, 2H, both), 6.58–6.50 (m, 2H, both), 6.34–6.28 (m, 2H, both), 5.99 (br s, 1H, major rotamer), 5.94–5.92 (m, 2H, both), 5.33 (br s, 1H, minor rotamer), 3.83 (s, 6H, both), 3.79–3.63 (m, 3H, both + major), 3.48 (d, *J* = 16.3 Hz, 1H, minor), 3.16–3.02 (m, 2H, both), 2.83–2.67 (m, 4H, both), 2.63–2.51 (m, 2H, both), 1.56 (s, 9H, minor), 1.40 (s, 9H, major). Only peaks for major rotamer listed. HRMS (ESI+): Found: 455.1948; C26H28N2NaO4+ (MNa+) Requires 455.1941 (−1.5 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. (4bS,8aR)-tert-Butyl 7-oxo-8,9-dihydro-7H-8a,4b-(epiminoethano)carbazole-10-carboxylate (**13f**)

Prepared according to general procedure C using ynone **11f** (54.3 mg, 0.166 mmol), Au(PPh3)NTf2 (6.50 mg, 4.16 µmol) and CHCl3 (1.70 mL) stirring at RT for 2 h. Purification by flash chromatography on silica gel (95:5 CH2Cl2:EtOAc) afforded the title compound **13f** (as a 3:2 mixture of rotamers) as a yellow oil (46.0 mg, 85% yield); R*f* 0.34 (95:5 CH2Cl2:EtOAc); δH (400 MHz, CDCl3) 7.24–7.19 (m, 2H, both rotamers), 7.17–7.10 (m, 2H, both), 6.91–6.82 (m, 2H, both), 6.70–6.59 (m, 2H, both), 5.99–5.90 (m, 3H, both + major rotamer), 5.29 (br s, 1H, minor rotamer), 3.77–3.59 (m, 3H, both + major rotamer), 3.43 (d, *J* = 16.5 Hz, 1H, minor), 3.20–3.06 (m, 2H, both), 2.67 (d, *J* = 14.0 Hz, 1H, minor), 2.62 (d, *J* = 16.5Hz, 1H, major), 2.58–2.46 (m, 2H, both), 2.29–2.16 (m, 2H, both), 1.54 (s, 9H, minor), 1.41 (s, 9H, major). Only peaks for major rotamer listed. HRMS (ESI+): Found: 349.1522; C19H22N2NaO3+ (MNa+) Requires 349.1523 (0.2 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. (4bS,8aR)-tert-Butyl 5-methyl-7-oxo-8,9-dihydro-7H-8a,4b-(epiminoethano)carbazole-10-carboxylate (**13g**)

Prepared according to general procedure C using ynone **11g** (85.0 mg, 0.250 mmol), Au(PPh3)NTf2 (9.80 mg, 6.25 µmol) and CHCl3 (2.50 mL) stirring at RT for 4 h. Purification by flash chromatography on silica gel (9:1 CH2Cl2:Et2O) afforded the title compound **13g** (as a 3:2 mixture of rotamers) as a yellow oil (79.0 mg, 93% yield); R*f* 0.72 (9:1 CH2Cl2:Et2O); δH (400 MHz, CDCl3, 55 °C) 7.27–7.22 (m, 2H, both rotamers), 7.12 (app. t, *J* = 7.6 Hz, 2H, both), 6.88–6.79 (m, 2H, both), 6.68–6.61 (m, 2H, both), 5.90 (s, 1H, major rotamer), 5.84 (s, 2H, both), 5.25 (s, 1H, minor rotamer), 3.77–3.68 (m, 1H, minor), 3.65–3.57 (m, 2H, 2 × major), 3.43–3.33 (m, 1H, minor), 3.19–3.03 (m, 2H, both), 2.70–2.48 (m, 4H, both), 2.21–2.10 (m, 2H, both), 2.03 (s, 6H, both), 1.54 (s, 9H, minor), 1.40 (s, 9H, major). Only peaks for major rotamer listed. HRMS (ESI+): Found: 363.1676; C20H24N2NaO3+ (MNa+) Requires 363.1679 (0.9 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. (4bS,8aR)-tert-Butyl 5-butyl-7-oxo-8,9-dihydro-7H-8a,4b-(epiminoethano)carbazole-10-carboxylate (**13h**)

Prepared according to general procedure C using ynone **11h** (139 mg, 0.360 mmol), Au(PPh3)NTf2 (14.3 mg, 9.08 µmol) and CHCl3 (3.60 mL) stirring at RT for 21 h. Purification by flash chromatography on silica gel (9:1 CH2Cl2:Et2O) afforded the title compound **13h** (as a 11:9 mixture of rotamers) as a pale yellow foam (136 mg, 98% yield); R*f* 0.72 (9:1 CH2Cl2:Et2O); δH (400 MHz, CDCl3) 7.28 (d, *J* = 7.6 Hz, 2H, both rotamers), 7.12 (app. t, *J* = 7.6 Hz, 2H, both), 6.84 (app. td, *J* = 8.2, 0.7 Hz, 2H, both), 6.65 (app. t, *J* = 8.2 Hz, 2H, both), 5.94–5.86 (m, 3H, both + major rotamer), 5.26 (br s, 1H, minor rotamer), 3.70 (dd, *J* = 10.5, 8.6 Hz, 1H, minor), 3.64–3.55 (m, 2H, 2 x major), 3.37 (d, *J* = 16.2 Hz, 1H, minor), 3.16–3.01 (m, 2H, both), 2.70–2.57 (m, 3H, both + minor), 2.53 (d, *J* = 16.2 Hz, 1H, major), 2.40–2.28 (m, 4H, both), 2.22–2.09 (m, 2H, both), 1.60–1.44 (m, 10H, both + minor), 1.44–1.23 (m, 16H, both + major), 0.89 (t, *J* = 7.1 Hz, 6H, both). Only peaks for major rotamer listed. HRMS (ESI+): Found: 405.2149; C23H30N2NaO3+ (MNa+) Requires 405.2149 (0.0 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. (4bS,8aR)-tert-Butyl 7-oxo-5-(phenylthio)-8,9-dihydro-7H-8a,4b-(epiminoethano)carbazole-10-carboxylate (**13i**)

Prepared according to general procedure C using ynone **11i** (54.3 mg, 0.125 mmol), Au(PPh3)NTf2 (4.90 mg, 3.13 µmol) and CHCl3 (1.30 mL) stirring at RT for 20 h. Purification by flash chromatography on silica gel (95:05 CH2Cl2:EtOAc) afforded the title compound **13i** (as a 11:9 mixture of rotamers) as a yellow oil (54.0 mg, 99% yield); R*f* 0.63 (9:1 CH2Cl2:EtOAc); δH (400 MHz, CDCl3) 7.54 (d, *J* = 7.5 Hz, 2H, both rotamers), 7.45–7.35 (m, 10H, both), 7.21–7.16 (m, 2H, both), 6.96–6.88 (m, 2H, both), 6.68 (app. t, *J* = 8.2 Hz, 2H, both), 5.93 (br s, 1H, major rotamer), 5.40–5.36 (m, 2H, both), 5.27 (br s, 1H, minor rotamer), 3.80–3.72 (m, 1H, minor), 3.69–3.62 (m, 1H, major), 3.59 (d, *J* = 16.4 Hz, 1H, major), 3.37 (d, *J* = 16.4 Hz, 1H, minor), 3.22–3.08 (m, 2H, both), 2.99–2.85 (m, 2H, both), 2.64 (d, *J* = 16.4 Hz, 1H, minor), 2.57 (d, *J* = 16.4 Hz, 1H, major), 2.47–2.36 (m, 2H, both), 1.53 (s, 9H, minor), 1.40 (s, 9H, major). Only peaks for major rotamer listed. HRMS (ESI+): Found: 457.1560; C25H26N2NaO3S+ (MNa+) Requires 457.1556 (−0.8 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. (4bS,8aR)-tert-Butyl 5-cyclopropyl-7-oxo-8,9-dihydro-7H-8a,4b-(epiminoethano)carbazole-10-carboxylate (**13j**)

Prepared according to general procedure C using ynone **11j** (55.0 mg, 0.150 mmol), Au(PPh3)NTf2 (5.90 mg, 3.75 µmol) and CHCl3 (1.50 mL) stirring at RT for 23 h. Purification by flash chromatography on silica gel (9:1 CH2Cl2:EtOAc) afforded the title compound **13j** (as a 11:9 mixture of rotamers) as a yellow oil (49.6 mg, 90% yield); R*f* 0.48 (9:1 CH2Cl2:EtOAc); δH (400 MHz, CDCl3) 7.37 (d, *J* = 7.6 Hz, 2H, both rotamers), 7.17–7.11 (m, 2H, both), 6.88–6.80 (m, 2H, both), 6.70–6.63 (m, 2H, both), 5.90 (s, 1H, major rotamer), 5.57–5.53 (m, 2H, both), 5.25 (s, 1H, minor rotamer), 3.76–3.68 (m, 1H, minor), 3.65–3.55 (m, 2H, both), 3.39–3.33 (m, 1H, major), 3.20–3.04 (m, 2H, both), 2.84–2.71 (m, 2H, both), 2.62–2.48 (m, 2H, both), 2.28–2.16 (m, 2H, both), 1.75–1.66 (m, 2H, both), 1.53 (s, 9H, minor), 1.41 (s, 9H, major), 1.09–0.97 (m, 2H, both), 0.89–0.80 (m, 2H, both), 0.67–0.54 (m, 4H, both). Only peaks for major rotamer listed. HRMS (ESI+): Found: 389.1836; C22H26N2NaO3+ (MNa+) Requires 389.1836 (−0.2 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. (4bR,8aR)-tert-Butyl 5-(((tert-butyldiphenylsilyl)oxy)methyl)-7-oxo-8,9-dihydro-7H-8a,4b-(epiminoethano)carbazole-10-carboxylate (**13k**)

Prepared according to general procedure C using ynone **11k** (149 mg, 0.250 mmol), Au(PPh3)NTf2 (9.80 mg, 6.25 µmol) and CHCl3 (2.50 mL) stirring at RT for 24 h. Purification by flash chromatography on silica gel (97:03 CH2Cl2:EtOAc) afforded the title compound **13k** (as a 11:9 mixture of rotamers) as a pale yellow foam (144 mg, 97% yield); R*f* 0.19 (98:02 CH2Cl2:EtOAc); δH (400 MHz, CDCl3) 7.70–7.64 (m, 4H, both rotamers), 7.60–7.56 (m, 4H, both), 7.49–7.32 (m, 12H, both), 7.12–7.05 (m, 2H, both), 6.94–6.89 (m, 2H, both), 6.74–6.59 (m, 4H, both), 6.37–6.30 (m, 2H, both), 5.90 (br s, 1H, major rotamer), 5.25 (br s, 1H, minor rotamer), 4.42–4.37 (m, 4H, both), 3.68–3.59 (m, 2H, both), 3.58–3.52 (m, 1H, major), 3.40 (d, *J* = 15.7 Hz, 1H, minor), 3.08–2.94 (m, 2H, both), 2.61 (d, *J* = 16.3 Hz, 1H, minor), 2.55 (d, *J* = 16.3 Hz, 1H, major), 2.50–2.42 (m, 2H, both), 2.06–1.93 (m, 2H, both), 1.53 (s, 9H, minor), 1.38 (s, 9H, major), 1.08–1.03 (m, 18H, both). Only peaks for major rotamer listed. HRMS (ESI+): Found: 617.2819; C36H42N2NaO4Si+ (MNa+) Requires 617.2806 (−2.0 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. (4bS,8aR)-tert-Butyl 4-bromo-7-oxo-5-phenyl-8,9-dihydro-7H-8a,4b-(epiminoethano)carbazole-10-carboxylate (**13l**)

Prepared according to general procedure C using ynone **11l** (120 mg, 0.250 mmol), Au(PPh3)NTf2 (9.80 mg, 6.25 µmol) and CHCl3 (2.50 mL) stirring at RT for 24 h. Purification by flash chromatography on silica gel (95:5 CH2Cl2:EtOAc) afforded the title compound **13l** (as a 13:7 mixture of rotamers) as an off-white foam (120 mg, >99% yield); R*f* 0.41 (95:5 CH2Cl2:EtOAc); δH (400 MHz, CDCl3) 7.39–7.27 (m, 6H, both rotamers), 6.97–6.86 (m, 6H, both), 6.79–6.72 (m, 2H, both), 6.68–6.60 (m, 2H, both), 6.04 (br s, 1H, major rotamer), 5.88–5.84 (m, 2H, both), 5.36 (br s, 1H, minor rotamer), 3.82–3.76 (m, 1H, minor), 3.73–3.53 (m, 4H, 2 x major + both), 3.41 (d, *J* = 16.3 Hz, 1H, minor), 3.22–3.06 (m, 2H, both), 2.76 (d, *J* = 16.3 Hz, 1H, minor), 2.68 (d, *J* = 16.3 Hz, 1H, major), 2.41–2.25 (m, 2H, both), 1.54 (s, 9H, minor), 1.40 (s, 9H, major). Only peaks for major rotamer listed. HRMS (ESI+): Found: 503.0940; C25H25BrN2NaO3+ (MNa+) Requires 503.0941 (0.2 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. (4bS,8aR)-tert-Butyl 4-(benzyloxy)-7-oxo-5-phenyl-8,9-dihydro-7H-8a,4b-(epiminoethano)carbazole-10-carboxylate (**13m**)

Prepared according to general procedure C using ynone **11m** (127 mg, 0.250 mmol), Au(PPh3)NTf2 (9.80 mg, 6.25 µmol) and CHCl3 (2.50 mL) stirring at RT for 24 h. Purification by flash chromatography on silica gel (95:5 CH2Cl2:EtOAc) afforded the title compound **13m** (as a 6:4 mixture of rotamers) as an orange oil (123 mg, 97% yield); R*f* 0.27 (95.5 CH2Cl2:EtOAc); δH (400 MHz, CDCl3) 7.35–7.26 (m, 6H, both rotamers), 7.22–7.07 (m, 6H, both), 7.04–6.90 (m, 10H, both), 6.35 (d, *J* = 7.7 Hz, 1H, major rotamer), 6.31 (d, *J* = 7.7 Hz, 1H, minor rotamer), 6.18–6.10 (m, 2H, both), 5.94 (s, 1H, major), 5.87–5.80 (m, 2H, both), 5.33 (s, 1H, minor), 4.62–4.54 (m, 2H, both), 4.15 (d, *J* = 12.5 Hz, 1H, minor), 4.09 (d, *J* = 12.5 Hz, 1H, major), 3.85–3.76 (m, 1H, minor), 3.76–3.62 (m, 2H, 2 x major), 3.46–3.34 (m, 3H, both + minor), 3.32–3.16 (m, 2H), 2.74 (d, *J* = 16.3 Hz, 1H, minor), 2.67 (d, *J* = 16.3 Hz, 1H, major), 2.45–2.28 (m, 2H, both), 1.55 (s, 9H, minor), 1.42 (s, 9H, major). Only peaks for major rotamer listed. HRMS (ESI+): Found: 531.2260; C32H32N2NaO4+ (MNa+) Requires 531.2254 (−1.0 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. (4bS,8aR)-tert-Butyl 3-bromo-7-oxo-5-phenyl-8,9-dihydro-7H-8a,4b-(epiminoethano)carbazole-10-carboxylate (**13n**)

Prepared according to general procedure C using ynone **11n** (120 mg, 0.250 mmol), Au(PPh3)NTf2 (9.80 mg, 6.25 µmol) and CHCl3 (2.50 mL) stirring at RT for 22 h. Purification by flash chromatography on silica gel (9:1 hexane:Et2O, then 1:1 hexane:Et2O) afforded the title compound **13n** (as a 13:7 mixture of rotamers) as a pale yellow foam (119 mg, 99% yield); R*f* 0.66 (1:1 hexane:Et2O); δH (400 MHz, CDCl3) 7.44–7.34 (m, 6H, both rotamers), 7.17–7.11 (m, 2H, both), 7.05–6.99 (m, 4H, both), 6.57–6.51 (m, 2H, both), 6.28–6.23 (m, 2H, both), 6.02 (br s, 1H, major rotamer), 5.97–5.94 (m, 2H, both), 5.34 (br s, 1H, minor rotamer), 3.83–3.75 (m, 1H, minor), 3.75–3.65 (m, 2H, 2 x major), 3.48 (d, *J* = 16.3 Hz, 1H, minor), 3.17–3.03 (m, 2H, both), 2.78 (d, *J* = 16.3 Hz, 1H, minor), 2.74–2.51 (m, 5H, both + major), 1.55 (s, 9H, minor), 1.41 (s, 9H, major). Only peaks for major rotamer listed. HRMS (ESI+): Found: 503.0934; C25H25BrN2NaO3+ (MNa+) Requires 503.0941 (1.3 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. (4bS,8aR)-tert-Butyl 3-methoxy-7-oxo-5-phenyl-8,9-dihydro-7H-8a,4b-(epiminoethano)carbazole-10-carboxylate (**13o**)

Prepared according to general procedure C using ynone **11o** (108 mg, 0.250 mmol), Au(PPh3)NTf2 (9.80 mg, 6.25 µmol) and CHCl3 (2.50 mL) stirring at RT for 4 days. Purification by flash chromatography on silica gel (9:1 CH2Cl2:EtOAc) afforded the title compound **13o** (as a 6:4 mixture of rotamers) as a yellow foam (105 mg, 97% yield); R*f* 0.38 (95:5 CH2Cl2:EtOAc); δH (400 MHz, CDCl3) 7.40–7.30 (m, 6H, both rotamers), 7.10–7.04 (m, 4H, both), 6.65–6.53 (m, 4H, both), 5.97–5.93 (m, 2H, both), 5.84 (br s, 1H, major rotamer), 5.80–5.76 (m, 2H, both), 5.18 (br s, 1H, minor rotamer), 3.82–3.74 (m, 1H, minor), 3.73–3.64 (m, 2H, 2 x major), 3.47 (d, *J* = 16.3 Hz, 1H, minor), 3.42 (s, 6H, both), 3.17–3.02 (m, 2H, both), 2.81–2.65 (m, 4H, both), 2.61–2.49 (m, 2H, both), 1.55 (s, 9H, minor), 1.41 (s, 9H, major). Only peaks for major rotamer listed. HRMS (ESI+): Found: 455.1950; C26H28N2NaO4+ (MNa+) Requires 455.1941 (−2.0 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. (4bS,8aR)-tert-Butyl 2-chloro-7-oxo-5-phenyl-8,9-dihydro-7H-8a,4b-(epiminoethano)carbazole-10-carboxylate (**13p**)

Prepared according to general procedure C using ynone **11p** (109 mg, 0.250 mmol), Au(PPh3)NTf2 (9.80 mg, 6.25 µmol) and CHCl3 (2.5 mL) stirring at RT for 24 h. Purification by flash chromatography on silica gel (100% CH2Cl2, then 9:1 CH2Cl2:EtOAc) afforded the title compound **13p** (as a 13:7 mixture of rotamers) as an off-white foam (98.0 mg, 90% yield); R*f* 0.52 (9:1 CH2Cl2:EtOAc); δH (400 MHz, CDCl3) 7.40–7.30 (m, 6H, both rotamers), 7.08–7.01 (m, 4H, both), 6.65–6.61 (m, 2H, both), 6.53–6.44 (m, 2H, both), 6.13–6.08 (m, 2H, both), 6.04 (br s, 1H, major rotamer), 5.97–5.91 (m, 2H, both), 5.37 (br s, 1H, minor rotamer), 3.83–3.76 (m, 1H, minor), 3.76–3.65 (m, 2H, 2 x major), 3.48 (d, *J* = 16.4 Hz, 1H, minor), 3.18–3.00 (m, 2H, both), 2.82–2.64 (m, 4H, both), 2.63–2.51 (m, 2H, both), 1.56 (s, 9H, minor), 1.42 (s, 9H, major). Only peaks for major rotamer listed. HRMS (ESI+): Found: 459.1454; C25H25ClN2NaO3+ (MNa+) Requires 459.1446 (−1.7 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. (4bS,8aR)-tert-Butyl 1-methyl-7-oxo-5-phenyl-8,9-dihydro-7H-8a,4b-(epiminoethano)carbazole-10-carboxylate (**13q**)

Prepared according to general procedure C using ynone **11q** (104 mg, 0.250 mmol), Au(PPh3)NTf2 (9.80 mg, 6.25 µmol) and CHCl3 (2.5 mL) stirring at RT for 24 h. Purification by flash chromatography on silica gel (95:5 CH2Cl2:EtOAc) afforded the title compound **13q** (as a 1:1 mixture of rotamers) as a light brown foam (104 mg, >99% yield); R*f* 0.45 (95:5 CH2Cl2:EtOAc); δH (400 MHz, CDCl3) 7.41–7.28 (m, 6H, both rotamers), 7.10–7.02 (m, 4H, both), 6.87 (d, *J* = 7.5 Hz, 2H, both), 6.46 (dd, *J* = 7.4, 7.4 Hz, 2H, both), 6.08 (app. t, *J* = 6.8 Hz, 2H, both), 5.96 (br s, 1H, rotamer A), 5.94 (d, *J* = 2.6 Hz, 2H, both), 5.36 (br s, 1H, rotamer B), 3.80–3.72 (m, 2H, 2 x A), 3.71–3.62 (m, 1H, B), 3.52 (d, *J* = 15.9 Hz, 1H, B), 3.15–2.96 (m, 2H, both), 2.84–2.67 (m, 4H, both), 2.63–2.51 (m, 2H, both), 2.11 (d, *J* = 4.4 Hz, 6H, both), 1.57 (s, 9H, B), 1.40 (s, 9H, A). Only peaks for rotamer A listed. HRMS (ESI+): Found: 439.1992; C26H28N2NaO3+ (MNa+) Requires 439.1992 (0.1 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. (4bS,8aR)-tert-Butyl 11-ethyl-7-oxo-5-phenyl-8,9-dihydro-7H-8a,4b-(epiminoethano)carbazole-10-carboxylate (**13r**)

Prepared according to general procedure C using ynone **11r** (108 mg, 0.250 mmol), Au(PPh3)NTf2 (9.80 mg, 6.25 µmol) and CHCl3 (2.50 mL) stirring at RT for 24 h. Purification by flash chromatography on silica gel (95:5 CH2Cl2:EtOAc) afforded the title compound **13r** as an off-white foam as a mixture of diastereomers (1: 1.3 *dr* based on HPLC) with each diastereomer existing as two rotamers (106 mg, 98% yield); R*f* (major diastereomer) 0.22 (95.5 CH2Cl2:EtOAc); δH (400 MHz, CDCl3) 7.41–7.29 (m, 3H, all rotamers/diastereomers), 7.11–6.99 (m, 3H, all), 6.71–6.56 (m, 1H, all), 6.55–6.45 (m, 1H, all), 6.32–5.30 [3H, 2 x m and 2 x s, 6.32–6.17, 5.95–5.85, 5.54, 5.30, all), 4.05–3.03 (m, 2H, all), 2.99–1.38 [13H, 2 x m and 4 x s, 2.99–2.60, 2.40–1.88, 1.57, 1.54, 1.43, 1.38, all] 0.94–0.43 (m, 4H, all); HRMS (ESI+): Found: 453.2156; C27H30N2NaO3+ (MNa+) Requires 453.2149 (−1.7 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. (4bS,8aR)-tert-Butyl 11-(hydroxymethyl)-7-oxo-5-phenyl-8,9-dihydro-7H-8a,4b-(epiminoethano)carbazole-10-carboxylate (**13s**)

Prepared according to general procedure C using ynone **11s** (108 mg, 0.250 mmol), Au(PPh3)NTf2 (9.80 mg, 6.25 µmol) and CHCl3 (2.50 mL) stirring at RT for 24 h. Purification by flash chromatography on silica gel (6:4 EtOAc:hexane) afforded the title compound **13s** as an orange oil as a mixture of diastereomers (3:2 *dr* based on HPLC) with each diastereomer existing as two rotamers (108 mg, >99% yield); R*f* 0.38 (6:4 EtOAc:hexane); νmax (thin film)/cm−1 3378, 2976, 1668, 1467, 1394, 1368, 1332, 1198, 1155, 1136, 1062, 733; δH (400 MHz, CDCl3) 7.41–7.29 (m, 3H, all rotamers/diastereoisomers), 7.11–6.99 (m, 3H, all), 6.69–6.61 (m, 1H, all), 6.57–6.48 (m, 1H, all), 6.28–6.19 (m, 1H, all), 6.00–5.27 [2H, 1 x m and 2 x s, 5.98–5.79, 5.52, 5.27, all], 4.42–2.62 [7H, 7 x m, 4.40–4.24, 4.11–4.00, 3.95–3.84, 3.76–3.40, 3.20–3.11, 3.05–2.91, 2.90–2.62, all] 1.63–1.38 [9H, 4 x s, 1.58, 1.57, 1.45, 1.40, all]; δC (100 MHz, CDCl3) 195.9–195.0 (m, 1 x C), 157.9–157.1 (m, 1 x C), 155.4–154.6 (m, 1 x C), 148.1–147.2 (m, 1 x C), 138.5–137.9 (m, 1 x C), 129.5–127.0 (m, 6 x C), 126.1–125.3 (m, 1 x C), 120.0–119.4 (m, 1 x C), 110.9–109.8 (m, 1 x C), 88.5–87.5 (m, 1 x C), 83.0–82.5 (m, 1 x C), 68.2–57.5 (m, 3 x C), 45.1–42.0 (m, 1 x C), 36.3–35.0 (m, 1 x C), 29.0–28.4 (m, 1 x C); HRMS (ESI+): Found: 455.1940; C26H28N2NaO4+ (MNa+) Requires 455.1941 (0.2 ppm error).

* + 1. (4bS,8aR)-tert-Butyl 8-methyl-7-oxo-5-phenyl-8,9-dihydro-7H-8a,4b-(epiminoethano)carbazole-10-carboxylate (**13t**)

Prepared according to general procedure C using ynone **11t** (104 mg, 0.250 mmol), Au(PPh3)NTf2 (9.80 mg, 6.25 µmol) and CHCl3 (2.50 mL) stirring at 60 °C for 22 h. Purification by flash chromatography on silica gel (9:1 CH2Cl2:EtOAc) afforded the title compound **13t** (as a 6:4 mixture of rotamers) as a yellow foam (78.0 mg, 75% yield); R*f* 0.31 (9:1 CHCl3:Et2O); νmax (thin film)/cm−1 3373, 2976, 2934, 1674, 1466, 1383, 1367, 1162, 1135, 945, 910, 757, 731; δH (400 MHz, CDCl3) 7.40–7.31 (m, 6H, both rotamers), 7.12–7.07 (m, 4H, both), 7.06–7.00 (m, 2H, both), 6.66–6.58 (m, 2H, both), 6.55–6.47 (m, 2H, both), 6.22–6.15 (m, 2H, both), 5.92 (br s, 1H, major rotamer), 5.85 (s, 2H, both), 5.29 (br s, 1H, minor rotamer), 3.88–3.80 (m, 1H, minor), 3.77–3.69 (m, 1H, major), 3.70–3.63 (m, 1H, major), 3.42 (q, *J* = 7.6 Hz, 1H, minor), 3.24–3.10 (m, 2H, both), 2.75–2.60 (m, 4H, both), 1.56 (s, 9H, minor), 1.43 (s, 9H, major), 1.32–1.23 (m, 6H, both). Only peaks for major rotamer listed. δC (100 MHz, CDCl3) 201.0, 155.9, 153.7, 148.4, 138.6, 129.0, 128.6, 128.4, 128.2 (2 x C), 125.5, 124.8, 119.0, 110.2, 89.4, 80.4, 58.6, 46.96, 46.93, 33.0, 28.6, 15.8; HRMS (ESI+): Found: 439.1996; C26H28N2NaO3+ (MNa+) Requires 439.1992 (−0.8 ppm error).

* + 1. (4bS,8aR)-5-Phenyl-8,9-dihydro-7H-8a,4b-(epoxyethano)carbazol-7-one (**13u**)

Prepared according to general procedure C using ynone **11u** (91.0 mg, 0.300 mmol), Au(PPh3)NTf2 (11.8 mg, 7.50 µmol) and CHCl3 (3.00 mL) stirring at RT for 48 h. Purification by flash chromatography on silica gel (9:1 CH2Cl2:EtOAc, then 100% EtOAc) afforded the title compound **13u** as a yellow foam (86.4 mg, 95% yield); R*f* 0.25 (9:1 CH2Cl2:EtOAc); δH (400 MHz, CDCl3) 7.41–7.33 (m, 3H), 7.21–7.17 (m, 2H), 7.02 (app. td, *J* = 7.7, 1.2 Hz, 1H), 6.61 (d, *J* = 7.7 Hz, 1H), 6.51 (app. td, *J* = 7.5, 1.0 Hz, 1H), 6.22 (d, *J* = 7.5 Hz, 1H), 5.98 (s, 1H), 4.77 (br s, 1H), 4.17 (m, 1H), 3.66 (m, 1H), 3.07 (d, *J* = 16.1 Hz, 1H), 2.89 (d, *J* = 16.1 Hz, 1H), 2.85–2.79 (m, 2H); HRMS (ESI+): Found: 326.1146; C20H17NNaO2+ (MNa+) Requires 326.1151 (1.7 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. (4bS,8aR)-5-Phenyl-8,9-dihydro-7H-8a,4b-(epoxypropano)carbazol-7-one (**13v**)

Prepared according to general procedure C using ynone **11v** (91.5 mg, 0.290 mmol), Au(PPh3)NTf2 (11.4 mg, 7.21 µmol) and CHCl3 (3.00 mL) stirring at RT for 24 h. Purification by flash chromatography on silica gel (95:5 CH2Cl2:MeOH, then 9:1 CH2Cl2:MeOH) afforded the title compound **13v** as a yellow oil (90.5 mg, 99% yield); R*f* 0.22 (95:5 CH2Cl2:MeOH); δH (400 MHz, CDCl3) 7.33–7.27 (m, 1H), 7.24–7.19 (m, 2H), 7.13 (app. td, *J* = 7.6, 1.1 Hz, 1H), 6.74 (d, *J* = 7.6 Hz, 1H), 6.70–6.63 (m, 3H), 6.37 (d, *J* = 7.5 Hz, 1H), 5.87 (s, 1H), 4.46 (br s, 1H), 3.80–3.72 (m, 1H), 3.54 (app. td, *J* = 11.7, 2.8 Hz, 1H), 3.28 (d, *J* = 16.4 Hz, 1H), 2.72 (d, *J* = 16.4 Hz, 1H), 2.61–2.52 (m, 1H), 2.05–1.93 (m, 1H), 1.62–1.48 (m, 2H); HRMS (ESI+): Found: 340.1304; C21H19NNaO2+ (MNa+) Requires 340.1308 (1.1 ppm error). Spectroscopic data matched those previously reported in the literature.3

* + 1. 4a-(4-Hydroxybutyl)-4-phenyl-4a,9-dihydro-2H-carbazol-2-one (**12w**)

Prepared according to general procedure C using ynone **11w** (66.5 mg, 0.200 mmol), Au(PPh3)NTf2 (7.90 mg, 5.02 µmol) and CHCl3 (2.00 mL) stirring at RT for 24 h. Purification by flash chromatography on silica gel (95:5 CH2Cl2:MeOH) afforded the title compound **12w** as a yellow foam (64.5 mg, 97% yield); R*f* 0.36 (95:5 CH2Cl2:MeOH); νmax (thin film)/cm−1 3167, 2945, 1639, 1596, 1551, 1468, 1234, 1205, 732, 702; δH (400 MHz, CDCl3) 9.48 (s, 1H), 7.47–7.39 (m, 3H), 7.25–7.23 (m, 2H), 7.13 (dd, *J* = 7.7, 1.1 Hz, 1H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.71 (dd, *J* = 7.6, 0.9 Hz, 1H), 6.36 (d, *J* = 7.6 Hz, 1H), 6.08 (d, *J* = 1.5 Hz, 1H), 5.80 (d, *J* = 1.5 Hz, 1H), 3.60–3.46 (m, 2H), 2.10–2.03 (m, 2H), 1.45–1.31 (m, 3H), 1.15–1.03 (m, 1H); δC (100 MHz, CDCl3) 187.7, 175.5, 156.9, 144.3, 138.1, 131.8, 129.9, 128.8, 128.4 (2 x C), 128.3, 125.0, 121.2, 110.9, 97.3, 62.1, 58.3, 50.2, 31.9, 19.8; HRMS (ESI+): Found: 354.1463; C22H21NNaO2+ (MNa+) Requires 354.1464 (0.3 ppm error).

* + 1. Dimethyl 2-(2-(2-oxo-4-phenyl-4a,9-dihydro-2H-carbazol-4a-yl)ethyl)malonate (**12x**)

Prepared according to general procedure C using ynone **11x** (181 mg, 0.430 mmol), Au(PPh3)NTf2 (17.0 mg, 10.8 µmol) and CHCl3 (4.30 mL) stirring at RT for 48 h. Purification by flash chromatography on silica gel (100% EtOAc) afforded the title compound **12x** as a yellow oil (170 mg, 94% yield); R*f* 0.31 (100% EtOAc); νmax (thin film)/cm−1 3031, 2953, 1733, 1642, 1562, 1468, 1234, 1200, 1157, 753, 733, 703; δH (400 MHz, CDCl3) 8.65–8.54 (m, 1H), 7.48–7.42 (m, 3H), 7.33–7.28 (m, 2H), 7.17–7.11 (m, 1H), 6.90 (d, *J* = 7.7 Hz, 1H), 6.71 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.33 (d, *J* = 7.0 Hz, 1H), 6.10 (d, *J* = 1.5 Hz, 1H), 5.78 (d, *J* = 1.5 Hz, 1H), 3.69 (s, 3H), 3.66 (s, 3H), 3.20 (t, *J* = 6.9 Hz, 1H), 2.19–2.09 (m, 1H), 2.04–1.94 (m, 2H), 1.75–1.65 (m, 1H); δC (100 MHz, CDCl3) 187.1, 173.8, 169.4, 155.9, 144.0, 137.9, 131.4, 130.4, 128.8, 128.7, 128.4, 128.3, 125.1, 121.3, 110.8, 98.4, 57.1, 52.8, 50.9, 46.1, 22.9; HRMS (ESI+): Found: 440.1472; C25H23NNaO5+ (MNa+) Requires 440.1468 (−0.9 ppm error).

* + 1. tert-Butyl benzyl(2-(2-oxo-4-phenyl-4a,9-dihydro-2H-carbazol-4a-yl)ethyl)carbamate (**12y**)

Prepared according to general procedure C using ynone **11y** (123 mg, 0.250 mmol), Au(PPh3)NTf2 (9.80 mg, 10.8 µmol) and CHCl3 (2.50 mL) stirring at RT for 50 h. Purification by flash chromatography on silica gel (7:3 EtOAc:hexane) afforded the title compound **12y** as a yellow oil (85.0 mg, 69% yield); R*f* 0.25 (7:3 EtOAc:hexane); νmax (thin film)/cm−1 3233, 2976, 1640, 1559, 1468, 1366, 1233, 1202, 1188, 1163, 1131, 909, 729, 700; δH (400 MHz, CDCl3, 55 °C) 8.41–7.92 (br s, 1H), 7.47–7.31 (m, 4H), 7.30–7.21 (m, 3H), 7.18–7.06 (m, 4H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.69 (t, *J* = 7.6, 1H), 6.28 (d, *J* = 7.4 Hz, 1H), 6.02 (d, *J* = 1.5 Hz, 1H), 5.70 (d, *J* = 1.5 Hz, 1H), 4.32–4.16 (m, 2H), 3.40–3.11 (br s, 1H), 2.91–2.67 (br s, 1H), 2.25–2.10 (m, 2H), 1.40 (s, 9H); δC (100 MHz, CDCl3, 55 °C) 186.7, 173.5, 155.6, 144.1, 138.3, 138.0, 129.9, 128.8, 128.7 (2 x C), 128.5 (2 x C), 128.4 (2 x C), 128.1, 127.5, 125.3, 121.5, 110.6, 98.4, 80.3, 65.1, 56.3, 51.3, 42.4, 28.6; HRMS (ESI+): Found: 515.2303; C32H32N2NaO3+ (MNa+) Requires 515.2305 (0.5 ppm error).

* + 1. 4a-Methyl-4-phenyl-4a,9-dihydro-2H-carbazol-2-one (**12z**)

Prepared according to general procedure C using ynone **11z** (68.3 mg, 0.250 mmol), Au(PPh3)NTf2 (9.80 mg, 6.25 µmol) and CHCl3 (2.50 mL) stirring at RT for 48 h. Purification by flash chromatography on silica gel (100% EtOAc) afforded the title compound **12z** as a yellow oil (70.0 mg, >99% yield); R*f* 0.24 (100% EtOAc); νmax (thin film)/cm−1 3159, 2927, 1640, 1551, 1467, 1371, 1198, 908, 749, 730, 700; δH (400 MHz, CDCl3) 9.81 (s, 1H), 7.50–7.41 (m, 3H), 7.32 (m, 2H), 7.13 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.70 (dd, *J* = 7.5, 1.1 Hz, 1H), 6.41 (d, *J* = 7.5 Hz, 1H), 6.05 (d, *J* = 1.6 Hz, 1H), 5.80 (d, *J* = 1.6 Hz, 1H), 1.83 (s, 3H); δC (100 MHz, CDCl3) 187.1, 177.8, 158.2, 143.6, 138.0, 132.8, 129.0, 128.7, 128.41, 128.37, 128.3, 124.7, 121.2, 111.2, 96.2, 54.2, 39.9; HRMS (ESI+): Found: 274.1221; C19H16NO+ (MH+) Requires 274.1226 (2.0 ppm error).

* + 1. (4bR,8aS)-10-Benzyl-5-phenyl-8,9-dihydro-7H-8a,4b-(epiminoethano)carbazol-7-one (**13y**)

To a solution of *tert*-butyl benzyl(2-(2-oxo-4-phenyl-4a,9-dihydro-2*H*-carbazol-4a-yl)ethyl)carbamate **12y** (96.0 mg, 0.190 mmol) in CH2Cl2 (0.600 mL) at 0 °C was added TFA (0.200 mL, 0.290 mmol) dropwise. The reaction mixture was then warmed to RT and stirred for 1.5 h. The reaction was quenched by the addition of sat. aq. NaHCO3 (2.00 mL). The organics were separated and the aqueous layer extracted with EtOAc (3 x 2.00 mL). The organics were then combined, washed with brine (2.00 mL), dried over MgSO4 and concentrated *in vacuo*. The crude material was then purified by flash chromatography on silica gel (95:05 CH2Cl2:MeOH) to afford the title compound **13y** as a yellow solid (75.0 mg, 78% yield); mp 150–152 °C; R*f* 0.52 (95:05 CH2Cl2:MeOH); νmax (thin film)/cm−1 3346, 2925, 2804, 1662, 1606, 1494, 1292, 1027, 946, 908, 730, 698; δH (400 MHz, CDCl3) 7.45–7.22 (m, 9H), 7.02 (td, *J* = 7.7, 1.2 Hz, 1H), 6.57 (d, *J* = 7.7 Hz, 1H), 6.51 (td, *J* = 7.4, 0.9 Hz, 1H), 6.26 (d, *J* = 7.4 Hz, 1H), 5.99 (s, 1H), 4.38 (br s, 1H), 3.87 (d, *J* = 13.4 Hz, 1H), 3.66 (d, *J* = 13.4 Hz, 1H), 3.01–2.85 (m, 3H), 2.78–2.56 (m, 3H); δC (100 MHz, CDCl3) 197.4, 159.5, 148.5, 139.3, 139.1, 130.4, 128.7, 128.6 (2 x C), 128.5, 128.3, 128.2, 127.3, 126.8, 125.4, 118.9, 109.3, 88.2, 60.1, 52.6, 51.1, 43.7, 35.2; HRMS (ESI+): Found: 393.1961; C27H25N2O+ (MH+) Requires 393.1961 (0.2 ppm error).

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