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A Domino N_2-Extrusion-Cyclization of Alkynylarylketone Derivatives for the Synthesis of Indoloquinolines and Carbocycle-Fused Quinolines

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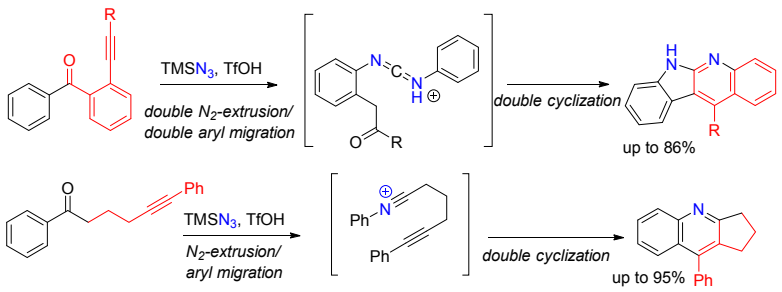
ABSTRACT

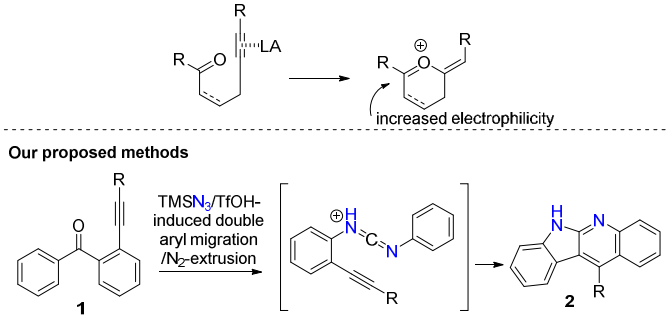


New synthetic approaches for the synthesis of indoloquinolines and carbocycle-fused quinolines have been developed employing alkynylketone substrates. These synthetic transformations involved the application of N_2-extrusion of azido complexes as a key step to generate carbodiimidium ion and nitrilium ion *in situ* which further cyclized intramolecularly with alkyne *via* a domino process to provide indoloquinolines and carbocycle-fused quinolines, respectively, in moderate to good yields.

■ INTRODUCTION

Activation of alkyne by Lewis acids, π-electrophilic Lewis acids or Brønsted acids is very useful in many organic transformations.[1] In addition, when a compound consists of both alkyne and ketone functional groups placed in proper orientation, the reaction of alkyne could be activated more efficiently under the assistance of the neighboring ketone moiety, while the electrophilicity of the ketone is also enhanced.[2] We envision that this dual alteration of reactivity can be employed to develop new synthetic methods. As our research group has been interested in the N_2-extrusion of azides for several years.[3] We therefore proposed the conceptually expedient method for the synthesis of indoloquinolines (**2**),[4] a well-established core structure showing a broad range of biological activities such as antibacterial, antifungal, antimicrobial, anti-HIV, anticancer and antimalarial activities.[5] Our method involves with the generation of carbodiimide intermediates *in situ* employing neighboring ketone participation to promote double aryl migration concurrently with N_2-extrusion of readily available alkynyl ketone precursor as shown in Scheme 1.

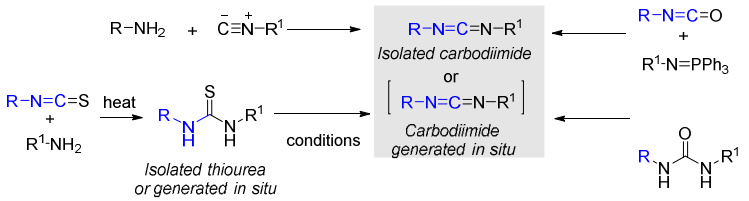
Scheme 1. Proposed method for synthesis of indoloquinolines.



In general, carbodiimide is one of the most important functional groups used in several applications in organic synthesis. The utilization of carbodiimides is very well-known as a coupling reagents to prepare amides, esters, acid anhydrides and is also commonly used in peptide synthesis.[6] In addition, the synthetic utility of carbodiimides has great impact in many transformations for the synthesis of *N*-containing compounds.[7] Carbodiimide could normally be prepared and stored for subsequent uses or could be generated and used *in situ* in the reactions.[8] The common precursors used in the preparation of

carbodiimides are thioureas, ureas, isonitriles and isocyanates under different conditions as shown in Scheme 2.[9]

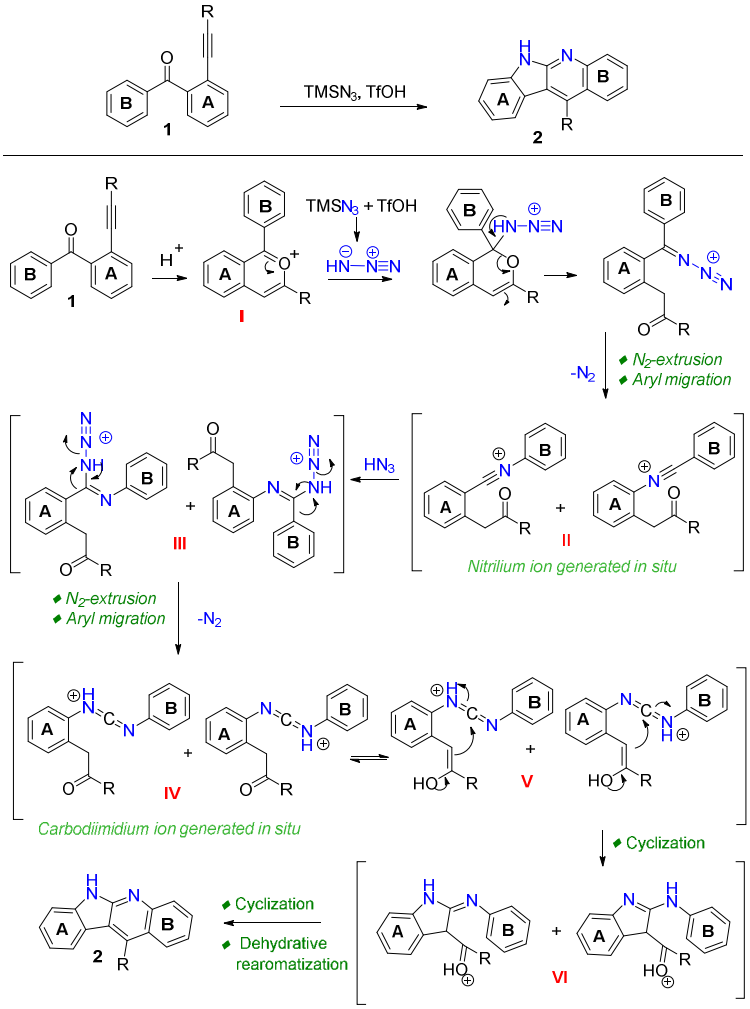
Scheme 2. Previous methods for generation of carbodiimide.



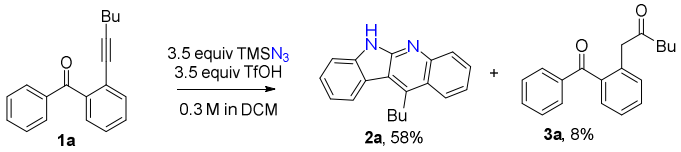
■ RESULTS AND DISCUSSION

In this work, the method for *in situ* generation of carbodiimides is very advantageous as the ketone precursors (**1**) are much more easily prepared and more diverse arrays of the compounds are available comparing to other precursors aforementioned. We proposed a new and challenging synthetic design to concisely construct indoloquinolines (**2**) employing domino reactions in one synthetic operation. A plausible mechanism is shown in Scheme 3. Under acidic conditions, *ortho*-alkynylarylketone (**1**) could undergo a protonation to form oxonium ion intermediate (**I**)[10] which further reacted with hydrazoic acid, generated *in situ* from $TMSN_3$/TfOH, to provide keto-nitrilium ion intermediate **II** *via* the N_2 extrusion and aryl migration reactions. Next, this intermediate was repeatedly attacked by hydrazoic acid and subsequently underwent a second N_2-extrusion (**III**) and aryl migration to give the reactive carbodiimidium ion **IV**. The intramolecular 5-endo-dig cyclization of enol intermediate **V** to carbodiimidium ion could ensue to intermediate **VI** which cyclized again by aromatic nucleophile ring B, followed by dehydrative rearomatization to obtain indoloquinolines (**2**).

Scheme 3. Proposed reaction mechanism.



Scheme 4. Optimal condition for synthesis of indoloquinolines.



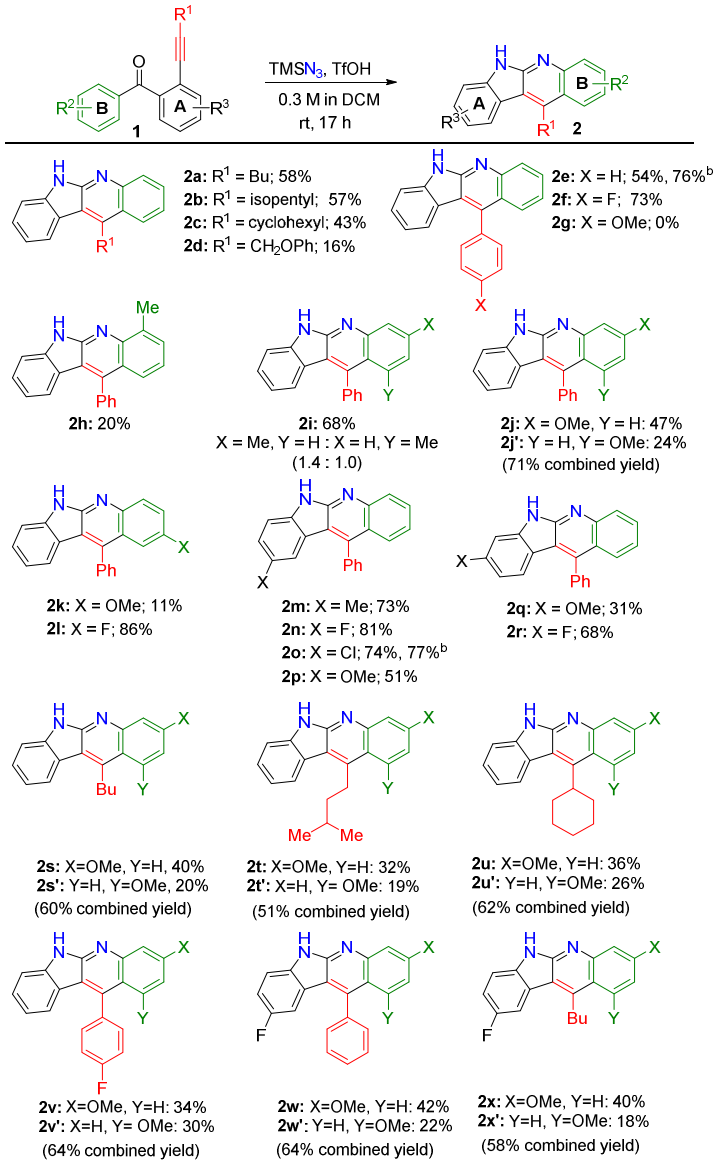
In our study, *ortho*-alkynylarylketones **1a** was employed as the screening substrate to optimize reaction conditions (see Table 1 in the Supporting Information). After screening several conditions, all cases

provided indoloquinoline **2a** as a major product along with the formation of compound **3a** as a minor product. The best result was obtained when the reaction was carried out using 3.5 equiv of both $TMSN_3$ and TfOH in dry DCM at 0.3 M concentration. This condition could provide highest yield (58%) of **2a** and could minimize the formation of side product **3a** could be minimized as shown in Scheme 4.

To explore the scope and limitation of our method for the synthesis of indoloquinolines (**2**), various *ortho*-alkynylarylketones (**1**) having different substituent groups were applied to the optimal conditions as shown in Scheme 5. Initially, alkyl substituents were examined. The substrates containing butyl (**1a**) and isopentyl (**1b**) groups provided the desired products in moderate yields (58% and 57% yields, respectively). In increasing the bulkiness of cyclohexyl substituent, the reaction showed less effectiveness than long linear side chain offering **2c** in 43% yield. However, the reaction of substrate tethering with phenylether side chain was not compatible with this procedure, the reaction of which led to low yield of indoloquinoline **2d**. Next, the study of substrate scope was extended by switching from alkyl to aryl side chain. The reaction of substrate bearing phenyl group at R^1 position furnished product **2e** in 54% yield whereas *para*-fluorophenyl substituent could offer desired product **2f** in higher yield (73%). In case of compound **1e** when the reaction was carried out in larger scale (1.0200 mmol), the reaction could provide the product **2e** in higher yield (76%). However, when the substrate containing *para*-methoxyphenyl group **1g** was employed, the reaction resulted in decomposition and provided none of the desired product. This result demonstrated that the electronic effect on R^1 played an important role towards the reactivity and stability of alkyne under these reaction conditions. Increasing the electron density of R^1 seemed to be non-beneficial for this transformation as it could increase the rate of decomposition of alkyne under the strong acidic conditions. Further study on the substrate scope was investigated by varying the substituent groups on aromatic ring B. With *ortho*-methyl group, the reaction gave the desired **2h** in low yield whereas the *meta*-methyl substituent gave **2i** as a regioisomeric mixture in good combined yield. This result implied that the steric effect of methyl group at the *ortho*-position played a significant role in hampering the cyclization process. In addition, we found that increasing the nucleophilicity of aromatic ring B did not significantly affect the product yields. In case of *meta*-methoxyphenyl precursor **1j**, the reaction provided separable regioisomeric

indoloquinolines **2j** and **2j'** in 71% combined yield which is comparable to the case of electronically neutral substituent **1i**. However, the reaction of **1k** was messy and afforded only 11% yield of the desired product. One of the possibilities is that the *para*-methoxyphenyl group could delocalize electron to the carbodiimidium intermediate which could undergo undesired reaction pathways. Surprisingly, the *para*-fluorophenyl **1l** was smoothly converted to the corresponding product in high yield (86%). In order to gain more information about the influence of substituents, we then expanded the scope of substrates by varying the substituents at R^3. In case of compound **1m**, containing *para*-methyl group with respect to aniline moiety, the reaction provided the desired product in 73% yield. When using *para*-fluoro (**1n**) and *para*-chloro (**1o**) substrates, the reaction in both cases could provide the corresponding products in high yields while substrate bearing *para*-methoxy group **1p** gave indoloquinoline product in lower yield. These results showed that the reactivity of carbonyl group towards nucleophile (HN_3) was decreased as the electron-donating group could delocalize electron into the ketone moiety resulting in lower yield of the desired product. Moreover, the reaction of compound **1o** was also examined in a larger scale which led to the product in slightly higher yield (77%). In case of substrate **1q**, containing a methoxy group at the *para*-position with respect to the alkyne moiety, the reaction gave only 31% yield of the desired product. The resonace effect of methoxy group directly increased the reactivity of alkyne towards acid leading to a decomposition. A similar effect of the methoxy group *para* to alkyne was also observed in substate **1g**. In contrast, the reaction of substrate containing electron-withdrawing substituent **1r** (*para*-fluoro) gave the corresponding product in good yield. Next, we also investigated the reaction by increasing the nucleophilicity of aromatic ring B. The reaction of both **1s** and **1t** were not significantly affected on the product yields. In both cases, the reactions gave separable regioisomeric products in moderate combined yields. Notably, the yield was improved dramatically in the case of cyclohexyl substituent, affording the separable **2u** and **2u'** in 62% combined yield. However, increasing the nucleophilicity on aromatic ring B of substrates **1v**, **1w**, and **1x** provided the corresponding products in slightly lower combined yields comparing to the substrates containing unsubstituted ring B.

Scheme 5. Substrate scope.[a]

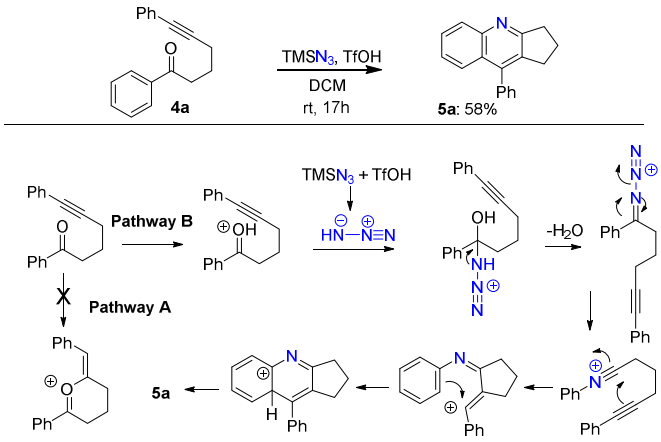


[a] Isolated Yields. [b]For examples of reaction carried out in larger scale, compounds **1e** and **1o** were carried out at 1.0200 mmol (228.9 mg) and 1.0120 mmol (256.8 mg) scales, respectively.

Furthermore, the effect of neighboring group participation on different structural alignment of alkynyl ketones was further studied. α-Alkynylketone **4a** was selected as a screening substrate. If the reaction were

to undergo the neighboring group participation mode, the carbonyl moiety would activate the alkyne to form the oxo-pyrylium ion and then reacted with hydrazoic acid as proposed in pathway A of Scheme 6. However, when compound **4a** was treated with 3.5 equiv of $TMSN_3$/TfOH, only carbocycle-fused quinoline **5a** was obtained in 58% yield. This result implied that ketone moiety could not participate in this transformation possibly due to high entropy effect of long linear chain of the substrate.[11] We therefore proposed the mechanism for the formation of compound **5a** as presented in pathway B of Scheme 6. Interestingly in this reaction, ketone moiety efficiently reacted with hydrazoic acid to generate nitrilium ion while the alkyne moiety still remained intact even though it was engulfed in strong acidic conditions. After the generation of the nitrilium ion intermediate, the alkyne moiety then underwent a domino cyclization/re-aromatization to provide fused tricyclic ring as the major product. Using this method, a library of fused quinolines **4a**, whose core structure has been found in compounds possessing various biological activities,[12] can be easily synthesized. We therefore optimized the reaction conditions (see Table 2 in the Supporting Information) and found that employing 1.2 equiv of $TMSN_3$/TfOH in 0.1 M dry DCM was the optimal condition in this conversion.

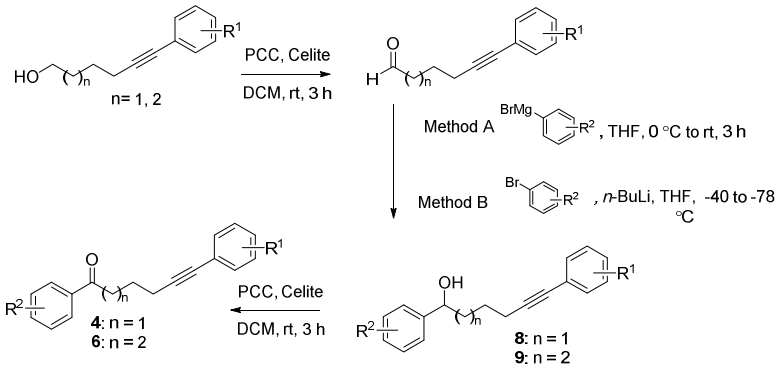
Scheme 6. Synthesis of carbocycle-fused quinolines.



The general method for the preparation of substrates **4** and **6** was elustrated in Scheme 7. The alkynyl alcohol derivatives were converted to aldehydes which were reacted with aryl Grignard or aryllithium

reagents without further purification to obtain compounds **8** and **9**. Next, these alcohols were oxidized with PCC to obtain the corresponding compounds.

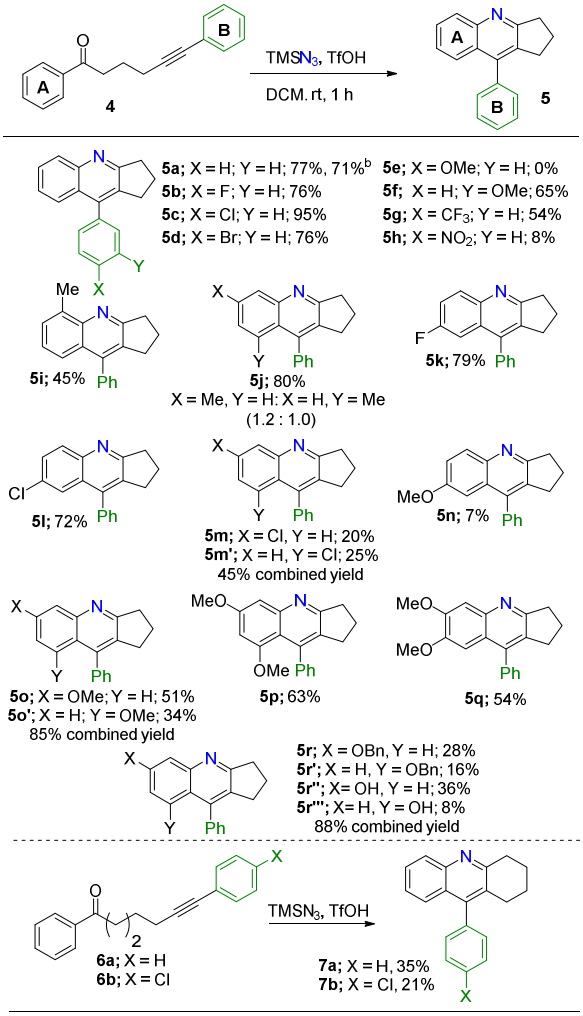
Scheme 7. The synthesis of compounds **4** and **6**



Next, the generality of the method was studied as shown in Scheme 8. A wide range of substrates with *para*-substituents on aromatic ring B with functional groups including hydrogen (**4a**), fluoride (**4b**), chloride (**4c**), and bromide (**4d**) smoothly converted to the corresponding products in good to excellent yields. In addition, compound **4a** was also carried out at 1.0051 mmol scale which could provide the desired product in camparable yield. However, the reaction of *para*-methoxyphenyl substrate (**4e**) failed to give the desired product because the resonance effect of the *para*-methoxy group accelerated rate of protonation of alkyne under this strong acid conditions leading to the decomposition of substrate. In contrast, the reaction of *meta*-methoxyphenyl substrate (**4f**) could provide carbocycle-fused quinoline in good yield. The effect of electron withdrawing groups was also evaluated resulting in lower yields of the corresponding products; *para*-nitro substituted substrate gave product in much lower yield comparing to *para*-trifluoromethyl substituent. We next examined the effect of substituent on aromatic ring A. The steric effect of *ortho*-methyl group (**4i**) offered the desired product in lower yield comparing with *meta*-methyl group substrate (**4j**). With other substituents at *para* position such as fluoro (**4k**) and chloro (**4l**) substituents, the reactions gave the desired products in good yields whereas the substrate containing

chlorine at *meta* position (**4m**) provided the corresponding product in lower yield. Next study, the resonance effect was also investigated in this conversion. Compound **4n** having *para*-methoxy group as the substituent was employed. The results showed that the resonance effect of methoxy group towards alkyne was not advantageous in this transformation. In this case, the yield of product was dramatically decreased. On the other hand, substrates containing *meta*-methoxy group (**4o**) efficiently furnished the corresponding products in good yields while substrates with dimethoxy groups, **4p** and **4q**, offered the desired products in moderate yields. Moreover, the reaction of substrate with benzyl protecting group (**4r**) provided separable regioisomeric products (**5r** and **5r'**) along with deprotected products (**5r"** and **5r"'**) in good combined yield (88%). Next, we also studied the effect of length on the side chain of precursor. Substrates **6a** and **6b** with one longer methylene unit were investigated. The reactions gave six-membered fused quinolines in much lower yields comparing to five-membered fused quinolines.

Scheme 8. Synthesis of carbocycle-fused quinolines.[a]



[a] Isolated Yields. [b]For examples of reaction carried out in larger scale, compound **4a** was carried at 1.0051 mmol (175.7 mg) scale.

■ CONCLUSIONS

In summary, we have developed new methods for the synthesis of indoloquinolines and carbocycle-fused quinolines from alkynyl ketone substrates. Indoloquinolines could be achieved by the domino N_2-extrusion/aryl migration of *ortho*-alkynylarylketones (**1**) to obtain the carbodiimidium ion key intermediate, followed by cyclization to obtain the desired products in moderate to good yields. This method provided a convenient route to synthesize a library of indoloquinolines from easily accessible precursors. For the synthesis of carbocycle-fused quinolines, linear alkynyl ketone (**3**) underwent the N_2-extrustion/aryl migration to generate nitrilium ion intermediate, followed by cyclization to give the carbocycle-fused quinolines in moderate to excellent yields.

■ EXPERIMENTAL SECTION

General Procedure. The commercial grade chemicals were used without further purification, unless otherwise specified. All solvents used were purified by the solvent purification system. The oven-dried glassware (110 °C at least for 2 h) was used for all reactions. Crude reaction mixtures were concentrated under reduced pressure by removing organic solvent with the rotary evaporator. Column chromatography was performed using silica gel 60 (particle size 0.06−0.2 mm; 70−230 mesh ASTM). Analytical thin layer chromatography (TLC) was performed with silica gel 60 F254 aluminum sheets. The nuclear magnetic resonance (NMR) spectra were recorded in deuterochloroform ($CDCl_3$) and deuterated dimethyl sulfoxide (DMSO-d_6) with 300, 400 and 600 MHz spectrometers. Chemical shifts for ^1H and ^{13}C NMR spectra were reported in part per million (ppm, δ), relative to tetramethylsilane (TMS) as the internal reference. Coupling constants (J) were reported in hertz (Hz). Infrared spectra were measured using an FT-IR spectrometer and were reported in cm^{-1}. High resolution mass spectra (HRMS) were obtained using time-of-flight (TOF).

General procedure for the synthesis of *ortho*-alkynylarylketones (1) **2**-(2-iodophenyl)(phenyl)methanone (609.3 mg, 1.9775 mmol, 1.0 equiv) was dissolved in NEt_3 (4.0 mL/mmol) in a sealed tube. A solution mixture was added $PdCl_2(PPh_3)_2$ (27.8 mg, 0.0396 mmol, 2 mol%), CuI (18.8 mg, 0.0989 mmol, 5 mol%), and PPh_3 (25.9 mg, 0.0989 mmol, 5 mol%) at room temperature, followed by bubbling with argon for 30 min at room temperature. The reaction was then added phenylacetylene (261

μL, 2.3730 mmol, 1.2 equiv) and stirred at 85 °C for 1 day. The reaction was quenched with sat. NH_4Cl, and then extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to provide crude product which was purified on silica gel (EtOAc/Hexane: 1:9) to yield product **1e** (541.0 mg, 97%). (**Note:** For the synthesis of compounds **1j**, **1m**, **1n**, **1p**, **1r**, **1s**, **1t**, **1u**, **1v**, **1w** and **1x**, the reactions employed 2-bromobenzophenone derivatives as starting material which were conducted in sealed tube at 85 °C for 2 days.)

(2-(Hex-1-yn-1-yl)phenyl)(phenyl)methanone (***1a***). Yield 958.0 mg (99%, brown oil); IR (neat): υ_{max} 2932, 1663, 1287, 927, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.83–7.79 (m, 2H), 7.60–7.51 (m, 1H), 7.49–7.34 (m, 6H), 2.10 (t, 2H, J = 6.9 Hz), 1.24–1.12 (m, 4H), 0.78 (t, 3H, J = 6.9 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ197.4, 141.7, 137.3, 132.9, 132.5, 130.1, 129.9, 128.2, 128.0, 127.3, 122.5, 96.6, 78.6, 30.2, 21.7, 18.9, 13.5;; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{19}O$ 263.1430; found 263.1429.

(2-(5-Methylhex-1-yn-1-yl)phenyl)(phenyl)methanone (***1b***). Yield 320.8 mg (81%, orange oil); IR (neat): υ_{max} 2956, 2869, 1668, 1316, 1288, 928, 704 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.84–7.80 (m, 2H), 7.56 (tt, 1H, J = 6.6, 1.5 Hz), 7.48–7.33 (m, 6H), 2.10 (t, 2H, J = 7.5 Hz), 1.46–1.33 (m, 1H), 1.15 (q, 2H, J = 7.2 Hz), 0.75 (d, 6H, J = 6.6 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 197.3, 141.7, 137.3, 132.9, 132.4, 130.1, 129.9, 128.2, 128.0, 127.3, 122.4, 96.6, 78.4, 36.9, 26.8, 22.0, 17.2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{20}H_{20}ONa$ 299.1406; found 299.1410.

(2-(Cyclohexylethynyl)phenyl)(phenyl)methanone (***1c***). Yield 392.7 mg (83%, brown oil); IR (neat): υ_{max} 2929, 2228, 1666, 1449, 1288, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, 2H, J = 7.7, 1.1 Hz), 7.55 (t, 1H, J = 7.4 Hz), 7.47–7.34 (m, 6H), 2.31–2.26 (m, 1H), 1.49–1.38 (m, 5H), 1.17–1.08 (m, 5H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 197.5, 141.8, 137.3, 133.0, 132.4, 130.2, 129.9, 128.2, 128.1, 127.4, 122.5, 100.7, 78.6, 31.9, 29.4, 25.7, 24.5; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{21}H_{20}ONa$ 311.1406; found 311.1408.

(2-(3-Phenoxyprop-1-yn-1-yl)phenyl)(phenyl)methanone (***1d***). Yield 313.6 mg (86%, yellow oil); IR (neat): υ_{max} 2923, 1665, 1597, 1494, 1214, 754 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.80-7.76 (m, 2H), 7.59-7.52 (m, 2H), 7.48-7.40 (m, 5H), 7.25-7.19 (m, 2H), 6.94 (tt, 1H, J = 7.2, 0.9 Hz), 6.83-6.79 (m, 2H), 4.62 (s, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 196.6, 157.6, 141.8, 137.1, 133.2, 133.1, 130.14, 130.11, 129.3,

128.38, 128.36, 138.32, 121.3, 120.9, 114.8, 89.4, 84.8, 56.2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{16}O_2Na$ 335.1043; found 335.1037.

Phenyl(2-(phenylethynyl)phenyl)methanone (***1e***). Yield 541.0 mg (97%, brown solid); mp 42−43 °C; IR (neat): υ_{max} 2216, 1663, 1287, 928, 753 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.90−7.86 (m, 2H), 7.63−7.40 (m, 7H), 7.26−7.16 (m, 3H), 7.06−7.02 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 197.0, 141.5, 137.3, 133.1, 132.5, 131.4, 130.3, 130.2, 128.6, 128.4, 128.1, 128.0, 122.6, 121.8, 95.1, 87.4; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{15}O$ 283.1117; found 283.1122.

(2-((4-Fluorophenyl)ethynyl)phenyl)(phenyl)methanone (***1f***). Yield 262.9 mg (80%, orange solid); mp 68–69 °C; IR (neat): υ_{max} 2923, 1665, 1508, 1288, 1232, 836, 701 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) *δ* 7.90–7.86 (m, 2H), 7.62–7.54 (m, 2H), 7.53–7.42 (m, 5H), 7.06–6.99 (m, 2H), 6.89 (tt, 2H, *J* = 8.7, 2.1 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) *δ* 196.6, 162.6 (d, J_{CF} = 248 Hz), 141.5, 137.4, 133.3 (d, J_{CF} = 8 Hz), 133.1, 132.5, 130.3, 130.2, 128.7, 128.4, 128.2, 121.7, 118.7 (d, J_{CF} = 4 Hz), 115.4, (d, J_{CF} = 22 Hz), 94.0, 87.2 (d, J_{CF} = 1 Hz); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{21}H_{13}FONa$ 323.0843; found 323.0838.

(2-((4-Methoxyphenyl)ethynyl)phenyl)(phenyl)methanone (***1g***). Yield 186.0 mg (56%, yellow solid); mp 91–92 °C; IR (neat): υ_{max} 2215, 1664, 1511, 1288, 1249, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.89–7.87 (m, 2H), 7.60–7.56 (m, 2H), 7.53–7.40 (m, 5H), 6.97 (dt, 2H *J* = 8.8, 2.4 Hz), 6.73 (dt, 2H, *J* = 8.8, 2.8 Hz), 3.77 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) *δ* 197.2, 159.7, 141.3, 137.4, 133.1, 132.9, 132.3, 130.3, 130.2, 128.7, 128.3, 127.8, 122.2, 114.7, 113.7, 95.4, 86.3, 55.2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{16}O_2Na$ 335.1043; found 335.1037.

(2-(Phenylethynyl)phenyl)(o-tolyl)methanone (***1h***). Yield 243.7 mg (81%, brown oil); IR (neat): υ_{max} 2922, 1622, 1634, 1300, 927, 755 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) *δ* 7.61–7.57 (m, 2H), 7.49 (td, 1H, *J* = 7.5, 1.5 Hz), 7.44–7.34 (m, 3H), 7.29–7.14 (m,7H), 2.51 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) *δ* 198.8, 142.0, 138.6, 138.3, 133.2, 131.6, 131.4, 131.3, 130.83, 130.76, 129.5, 128.4, 128.10, 128.05, 125.4, 122.7, 122.4, 95.0, 87.3, 20.8; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{16}ONa$ 319.1093; found 319.1090.

2-(Phenylethynyl)phenyl)(m-tolyl)methanone (***1i***). Yield 326.1 mg (78%, brown oil); IR (neat): υ_{max} 2922, 1662, 1443, 1291, 755 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) *δ* 7.72–7.70 (m, 1H), 7.64–7.60 (m, 2H), 7.53–7.43 (m, 3H), 7.41–7.31 (m, 2H), 7.25–7.17 (m, 3H), 7.10–7.06 (m, 2H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (75

MHz, $CDCl_3$) δ 197.2, 141.8, 138.2, 137.5, 133.9, 132.5, 131.4, 130.4, 130.2, 128.6, 128.3, 128.2, 128.1, 128.0, 127.6, 122.7, 121.8, 94.9, 87.5, 21.3; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{17}O$ 297.1274; found 297.1273.

(3-Methoxyphenyl)(2-(phenylethynyl)phenyl)methanone (***1j***). Yield 203.3 mg (98%, brown oil); IR (neat): υ_{max} 2940, 2217, 1664, 1289, 756 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.63–7.59 (m, 1H), 7.53–7.32 (m, 6H), 7.28–7.18 (m, 3H), 7.14–7.09 (m, 3H), 3.83 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 196.8, 159.7, 141.6, 138.7, 132.5, 131.4, 130.2, 129.3, 128.5, 128.4, 128.08, 128.05, 123.4, 122.7, 121.8, 119.8, 113.9, 94.9, 87.4, 55.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{17}O_2$ 313.1223; found 313.1235.

(4-Methoxyphenyl)(2-(phenylethynyl)phenyl)methanone (***1k***). Yield 192.1 mg (≥99%, brown oil); IR (neat): υ_{max} 2940, 1580, 1412, 1330, 1122, 722 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.87 (dt, 2H, J = 9.0, 2.7 Hz), 7.62–7.59 (m, 1H), 7.51–7.40 (m, 3H), 7.27–7.17 (m, 3H), 7.12–7.08 (m, 2H), 6.94 (dt, 2H, J = 9.0, 2.7 Hz), 3.85 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 195.6, 163.7, 142.1, 132.6, 132.4, 131.4, 130.3, 129.9, 128.3, 128.2, 128.11, 128.06, 122.7, 121.6, 113.6, 94.7, 87.5, 55.5; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{16}O_2Na$ 335.1043; found 335.1048.

(4-Fluorophenyl)(2-(phenylethynyl)phenyl)methanone (***1l***). Yield 456.0 mg (97%, brown oil); IR (neat): υ_{max} 2927, 2217, 1664, 1596, 1235, 755 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94–7.89 (m, 2H), 7.63–7.61 (m, 1H), 7.53–7.49 (m, 2H), 7.47–7.43 (m, 1H), 7.28–7.20 (m, 3H), 7.14 (tt, 2H, J = 8.8, 2.8 Hz), 7.09–7.07 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 195.4, 165.8 (d, J_{CF} = 254 Hz), 141.2, 133.7 (d, J_{CF} = 3 Hz), 132.8 (d, J_{CF} = 9 Hz), 132.5, 131.3, 130.4, 128.5 (d, J_{CF} = 4 Hz), 128.2, 128.1, 122.4, 121.6, 115.6, 115.4, 95.2, 87.2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{21}H_{13}FONa$ 323.0843; found 323.0847.

(4-Methyl-2-(phenylethynyl)phenyl)(phenyl)methanone (***1m***). Yield 544.2 mg (≥99%, yellow solid); mp 96–97 °C; IR (neat): υ_{max} 2925, 1662, 1598, 1288, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.88–7.85 (m, 2H), 7.56 (tt, 1H, J = 6.3, 1.5 Hz), 7.47–7.42 (m, 4H), 7.25–7.16 (m, 4H), 7.07–7.02 (m, 2H), 2.42 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 196.9, 140.8, 138.6, 137.7, 133.1, 132.9, 131.4, 130.2, 129.1, 129.0, 128.3, 128.0, 122.7, 122.0, 94.8, 87.7, 21.2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{16}ONa$ 319.1093; found 319.1091.

(4-Fluoro-2-(phenylethynyl)phenyl)(phenyl)methanone (***1n***). Yield 524.9 mg (97%, orange solid); mp 87–88 °C; IR (neat): υ_{max} 2214, 1664, 1600, 1572, 1285, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82–7.85 (m, 2H), 7.61–7.53 (m, 2H), 7.49–7.46 (m, 2H), 7.31 (dd, 1H, J = 9.2, 2.8 Hz), 7.28–7.19 (m, 3H), 7.15 (td, 1H, J = 8.4, 2.4 Hz), 7.05–7.03 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 195.9, 163.4 (d, J_{CF} = 252 Hz), 137.6 (d, J_{CF} = 3 Hz), 137.4, 133.2, 131.5, 131.2 (d, J_{CF} = 9 Hz), 130.2, 128.8, 128.4, 128.1, 124.4 (d, J_{CF} = 10 Hz), 122.1, 119.3 (d, J_{CF} = 23 Hz), 115.6 (d, J_{CF} = 22 Hz), 96.3, 86.4 (d, J_{CF} = 3 Hz); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{14}FO$ 301.1023; found 301.1016.

(4-Chloro-2-(phenylethynyl)phenyl)(phenyl)methanone (***1o***). Yield 371.1 mg (≥99%, orange solid); mp 80–81 °C; IR (neat): υ_{max} 2218, 1666, 1584, 1285, 929, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87–7.85 (m, 2H), 7.61–7.57 (m, 2H), 7.49–7.45 (m, 3H), 7.41 (dd, 1H, J = 8.0 , 2.0 Hz), 7.27–7.18 (m, 3H), 7.04–7.02 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 195.9, 139.6, 137.1, 136.4, 133.3, 132.2, 131.5, 130.2, 130.1, 128.8, 128.45, 128.40, 128.1, 123.7, 122.0, 96.4, 86.2; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{14}ClO$ (Cl-35) 317.0728; found 317.0722.

(4-Methoxy-2-(phenylethynyl)phenyl)(phenyl)methanone (***1p***). Yield 162.5 mg (43%, orange solid); mp 68–69 °C; IR (neat): υ_{max} 2938, 1657, 1595, 1234, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, 2H, J = 8.0 Hz), 7.56–7.52 (m, 2H), 7.44 (t, 2H, J = 8.0 Hz), 7.25–7.17 (m, 3H), 7.11 (d, 1H, J = 2.4 Hz), 7.09–7.06 (m, 2H), 6.95 (dd, 1H, J = 8.8, 2.4 Hz), 3.87 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 196.3, 161.2, 138.1, 133.6, 132.6, 131.5, 131.4, 130.1, 128.4, 128.2, 128.0, 124.0, 122.5, 117.3, 114.4, 95.1, 87.7, 55.5; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{16}O_2Na$ 335.1043; found 335.1036.

(5-Methoxy-2-(phenylethynyl)phenyl)(phenyl)methanone (***1q***). Yield 307.4 mg (95%, orange solid); mp 90–91 °C; IR (neat): υ_{max} 2938, 1664, 1595, 1498, 1230, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, 2H, J = 8.0, 1.2 Hz), 7.58 (tt, 1H, J = 6.8, 1.2 Hz), 7.54 (dd, 1H, J = 8.0, 0.8 Hz), 7.49–7.45 (m, 2H), 7.23–7.15 (m, 3H), 7.05–7.02 (m, 2H), 6.99–6.97 (m, 2H), 3.86 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 196.9, 159.4, 143.0, 137.1, 133.9, 133.2, 131.1, 130.3, 128.4, 128.0, 122.9, 116.6, 113.9, 113.5, 93.7, 87.4, 55.5; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{16}O_2Na$ 335.1043; found 335.1040.

(5-Fluoro-2-(phenylethynyl)phenyl)(phenyl)methanone (***1r***). Yield 139.8 mg (42%, orange solid); mp 66–67 °C; IR (neat): υ_{max} 2171, 1668, 1597, 1497, 1289, 689 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.89–7.87

(m, 2H), 7.61–7.58 (m, 2H), 7.50–7.46 (m, 2H), 7.25–7.17 (m, 5H), 7.02–7.00 (m, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 195.5, 162.0 (d, J_{CF} = 252 Hz), 143.5 (d, J_{CF} = 7 Hz), 136.6, 134.5 (d, J_{CF} = 8 Hz), 133.5, 131.3, 130.2, 128.5, 128.4, 128.1, 122.3, 117.9 (d, J_{CF} = 4 Hz), 117.6 (d, J_{CF} = 22 Hz), 115.8, (d, J_{CF} = 23 Hz), 94.8, 86.3; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{21}H_{13}FONa$ 323.0843; found 323.0855.

(2-(Hex-1-yn-1-yl)phenyl)(3-methoxyphenyl)methanone (***1s***). Yield 459.7 mg (93%, brown oil); IR (neat): υ_{max} 2957, 2229, 1668, 1429, 1287, 755 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48–7.29 (m, 7H), 7.13–7.09 (m, 1H), 3.84 (s, 3H), 2.14 (t, 2H, *J* = 6.9 Hz), 1.26–1.16 (m, 4H), 0.79 (t, 3H, *J* = 6.9 Hz); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 197.1, 159.6, 141.8, 138.6, 132.5, 129.9, 129.2, 127.9, 127.2, 123.4, 122.5, 119.7, 113.6, 96.4, 78.5, 55.4, 30.3, 21.7, 19.0, 13.5; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{20}H_{20}O_2Na$ 315.1356; found 315.1350.

(3-Methoxyphenyl)(2-(5-methylhex-1-yn-1yl)phenyl)methanone (***1t***). Yield 371.4 mg (86%, brown oil); IR (neat): υ_{max} 2956, 2866, 1668, 1595, 1288, 1266, 756 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48–7.29 (m, 7H), 7.14–7.07 (m, 1H), 3.84 (s, 3H), 2.14 (t, 2H, *J* = 7.2 Hz),148–1.34 (m, 1H), 1.12 (q, 2H, *J* = 7.2 Hz), 0.76 (d, 6H, *J* = 6.6 Hz); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 197.0, 159.6, 141.7, 138.5, 132.4, 129.8, 129.1, 127.8, 127.2, 123.3, 122.3, 119.6, 113.6, 96.3, 78.4, 55.2, 37.0, 26.8, 21.9, 17.2; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{23}O_2$ 307.1693; found 307.1686.

(2-(Cyclohexylethynyl)phenyl)(3-methoxyphenyl)methanone (***1u***). Yield 214.6 mg (40%, yellow oil); IR (neat): υ_{max} 2930, 2229, 1667, 1449, 1288, 756 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48–7.28 (m, 7H), 7.14–7.07 (m, 1H), 3.84 (d, 3H, *J* = 0.9 Hz), 2.33 (br s, 1H), 1.63–1.40 (m, 5H), 1.26–1.13 (m, 5H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 197.3, 159.7, 141.8, 138.7, 132.5, 129.9, 129.2, 128.0, 127.3, 123.5, 122.5, 119.7, 113.7, 100.5, 78.6, 55.4, 31.9, 29.4, 25.8, 24.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{23}O_2$ 319.1693; found 319.1688.

(2-((4-Fluorophenyl)ethynyl)phenyl)(3-methoxyphenyl)methanone (***1v***). Yield 185.5 mg (65%, yellow solid); mp 84–85 °C; IR (neat): υ_{max} 2941, 1666, 1508, 1289, 1230, 836 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62–7.59 (m, 1H), 7.53–7.32 (m, 6H), 7.14–7.06 (m, 3H), 6.91 (tt, 2H, *J* = 9.3, 2.7 Hz), 3.83 (s, 3H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 196.7, 162.5 (d, J_{CF} = 248 Hz), 159.7, 141.5, 138.7, 133.3 (d, J_{CF} = 8

Hz), 132.5, 130.3, 129.3, 128.6, 128.1, 123.3, 121.7, 119.7, 118.8 (d, J_{CF} = 4 Hz), 115.4 (d, J_{CF} = 22 Hz), 113.9, 93.8, 87.1, 55.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{16}FO_2$ 331.1129; found 331.1131.

(4-Fluoro-2-(phenylethynyl)phenyl)(3-methoxyphenyl)methanone (***1w***). Yield 321.4 mg (99%, brown solid); mp 65–66 °C; IR (neat): υ_{max} 2940, 2214, 1667, 1598, 1288, 757 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.53 (dd, 1H, *J* = 8.4, 6.0 Hz), 7.44 (s, 1H), 7.36 (d, 2H, *J* = 4.7 Hz), 7.33–7.21 (m, 4H), 7.17–7.10 (m, 4H), 3.84 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 195.7, 163.4 (d, J_{CF} = 250 Hz), 159.8, 138.8, 137.7 (d, J_{CF} = 3 Hz), 131.6, 131.1 (d, J_{CF} = 9 Hz), 129.4, 128.8, 128.1, 124.5 (d, J_{CF} = 10 Hz), 123.3, 122.2, 119.8, 119.3 (d, J_{CF} = 23 Hz), 115.5 (d, J_{CF} = 21 Hz), 113.9, 96.1, 86.4 (d, J_{CF} = 4 Hz), 55.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{16}FO_2$ 331.1129; found 331.1138.

(4-Fluoro-2-(hex-1-yn-1-yl)phenyl)(3-methoxyphenyl)methanone (***1x***). Yield 261.5 mg (92%, orange solid); mp 64–65 °C; IR (neat): υ_{max} 2960, 1662, 1582, 1278, 1024, 755 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44–7.36 (m, 2H), 7.34–7.27 (m, 2H), 7.18–7.12 (m, 1H), 7.11–7.08 (m, 1H), 7.06–7.03 (m, 1H), 3.86 (s, 3H), 2.13 (t, 2H, *J* = 6.6 Hz), 1.29–1.13 (m, 4H), 0.82–0.78 (m, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 196.1, 163.3 (d, J_{CF} = 249 Hz), 159.7, 138.7, 137.9 (d, J_{CF} = 3 Hz), 130.5 (d, J_{CF} = 9 Hz), 129.2, 125.1 (d, J_{CF} = 10 Hz), 123.3, 119.7, 119.4 (d, J_{CF} = 23 Hz), 114.7 (d, J_{CF} = 22 Hz), 113.7, 97.9, 77.7 (d, J_{CF} = 3 Hz), 55.4, 30.1, 21.8, 19.0, 13.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{20}FO_2$ 311.1442; found 311.1444.

General procedure for the synthesis of indoloquinolines (2) (4-Chloro-2-(phenylethynyl)phenyl)(phenyl)methanone 1o (90.5 mg, 0.2857 mmol, 1.0 equiv) was dissolved in dry DCM (3.5 mL/mmol) under argon. A solution was added $TMSN_3$ (88.5 µL, 0.9999 mmol, 3.5 equiv), followed by TfOH (132.7 µL, 0.9999 mmol, 3.5 equiv). The reaction mixture was stirred at room temperature overnight. After completion, the reaction was quenched with sat. $NaHCO_3$ and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to provide crude product which was purified on silica gel (EtOAc/DCM: 1:9) to yield the corresponding indoloquinoline **2o** (69.8 mg, 74%).

11-Butyl-6H-indolo[2,3-b]quinoline (***2a***). Yield 48.6 mg (58%, white solid); mp 192–193 °C; IR (neat): υ_{max} 2955, 1611, 1398, 1231, 741 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 11.91 (br s, 1H), 8.30–8.16 (m, 3H),

7.79–7.74 (m, 1H), 7.58–7.48 (m, 3H), 7.32–7.27 (m, 1H), 3.69–3.64 (m, 2H), 1.96–1.86 (m, 2H), 1.74–1.62 (m, 2H), 1.06 (t, 3H, J = 7.2 Hz); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 153.4, 146.3, 144.6, 141.3, 128.7, 127.5, 127.1, 124.1, 123.4, 122.7, 121.4, 120.1, 116.5, 110.9, 31.7, 28.9, 23.4, 14.1; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{19}N_2$ 275.1543; found 275.1551.

11-Isopentyl-6H-indolo[2,3-b]quinoline (***2b***). Yield 57.8 mg (57%, yellow solid); mp 265–266 °C; IR (neat): υ_{max} 2921, 1633, 1471, 1399, 742 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.69 (s, 1H), 8.29 (d, 1H, J = 8.4 Hz), 8.17 (d, 1H, J = 7.6 Hz), 7.96 (d, 1H, J = 7.6 Hz), 7.73–7.69 (m, 1H), 7.55–7.49 (m, 3H), 7.32–7.28 (m, 1H), 3.65–3.61 (m, 2H), 2.02–1.92 (m, 1H), 1.68–1.62 (m, 2H), 1.09 (d, 6H, J = 6.8 Hz); $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 152.5, 146.4, 143.4, 141.3, 128.4, 127.7, 127.5, 123.8, 123.1, 122.6, 122.5, 120.3, 119.8, 115.1, 110.9, 38.3, 28.3, 26.3, 22.4; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{21}N_2$ 289.1699; found 289.1698.

11-Cyclohexyl-6H-indolo[2,3-b]quinoline (***2c***). Yield 38.5 mg (43%, yellow solid); mp 241–242 °C; IR (neat): υ_{max} 2926, 1607, 1400, 1256, 741 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.14 (br s, 1H), 8.62 (br s, 1H), 8.34 (br s, 1H), 8.24 (d, 1H, J = 8.4 Hz), 7.76 (t, 1H, J = 7.6 Hz), 7.59–7.46 (m, 3H), 7.36–7.28 (m, 1H), 4.31 (br s, 1H), 2.53 (br s, 2H), 2.10–1.98 (m, 5H), 1.73–1.64 (m, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 153.7, 149.4, 146.8, 141.5, 128.5, 128.3, 127.4, 127.3, 126.9, 123.8, 123.2, 121.5, 119.7, 116.8, 111.0, 42.8, 31.5, 27.6, 26.2; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{21}N_2$ 301.1699; found 301.1694.

11-(Phenoxymethyl)-6H-indolo[2,3-b]quinoline (***2d***). Yield 17.1 mg (16%, yellow solid); mp 265–266 °C; IR (neat): υ_{max} 2924, 1598, 1482, 1233, 751 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.86 (s, 1H), 8.44 (d, 1H, J = 8.4 Hz), 8.12 (d, 1H, J = 8.0 Hz), 8.03 (d, 1H, J = 8.4 Hz), 7.76 (t, 1H, J = 7.2 Hz), 7.57–7.52 (m, 3H), 7.35 (t, 2H, J = 8.0 Hz), 7.23–7.18 (m, 3H), 7.02 (t, 1H, J = 7.2 Hz), 6.09 (s, 2H) ; $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 158.5, 152.5, 146.3, 141.9, 134.9, 129.7, 128.7, 128.3, 127.6, 124.3, 124.1, 123.2, 122.5, 121.2, 119.8, 119.7, 117.0, 114.8, 111.0, 62.7; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{17}N_2O$ 325.1335; found 325.1343.

11-Phenyl-6H-indolo[2,3-b]quinoline (***2e***). Yield 57.5 mg (54%, yellow solid); mp 259–260 °C; IR (neat): υ_{max} 2846, 1611, 1584, 1402, 1250, 743 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.39 (br s, 1H), 8.24 (d, 1H,

J = 8.4 Hz), 7.77–7.69 (m, 2H), 7.67–7.63 (m, 3H), 7.53–7.48 (m, 3H), 7.40–7.33 (m, 2H), 7.05 (d, 1H, *J* = 7.5 Hz), 6.98–6.92 (m, 1H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 153.4, 146.2, 142.8, 141.6, 136.4 129.4, 128.94, 128.89, 128.5, 127.9, 126.6, 126.4, 123.7, 123.0, 122.8, 121.0, 119.7, 116.8, 110.8; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{15}N_2$ 295.1230; found 295.1220.

11-(4-Fluorophenyl)-6H-indolo[2,3-b]quinoline (***2f***). Yield 72.2 mg (73%, yellow solid); mp 296–297 °C; IR (neat): υ_{max} 2924, 1607, 1507, 1231, 743 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.21 (br s, 1H), 8.20 (d, 1H, *J* = 8.3 Hz), 7.80–7.74 (m, 2H), 7.57–7.35 (m, 7H), 7.11–7.00 (m, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 163.0 (d, J_{CF} = 246 Hz), 153.1, 146.4, 141.7, 141.4, 132.3 (d, J_{CF} = 3 Hz), 131.2 (d, J_{CF} = 8 Hz), 129.0, 128.1, 126.9, 126.3, 123.9, 123.1 (d, J_{CF} = 11 Hz), 121.1, 120.0, 116.8, 116.3, 116.1, 110.8; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{14}FN_2$ 313.1136; found 313.1132.

4-Methyl-11-phenyl-6H-indolo[2,3-b]quinoline (***2h***). Yield 21.5 mg (20%, yellow solid); mp 165–166 °C; IR (neat): υ_{max} 2974, 1610, 1599, 1396, 1245, 733 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.50 (br s, 1H), 7.69–7.61 (m, 5H), 7.57–7.52 (m, 2H), 7.41–7.27 (m, 3H), 7.04–6.93 (m, 2H), 2.97 (s, 3H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 152.3, 145.4, 143.2, 141.1, 136.8, 134.4, 129.4, 129.3, 128.9, 128.5, 127.7, 124.6, 123.7, 123.1, 122.6, 121.2, 119.9, 116.1, 110.6, 18.9; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{17}N_2$ 309.1386; found 309.1383.

3-Methyl-11-phenyl-6H-indolo[2,3-b]quinoline (***2i***) and 1-*Methyl-11-phenyl-6H-indolo[2,3-b]quinoline* (***2i'***). Yield 87.8 mg (68%, ratio **2i**:**2i'**; 1.4:1.0, yellow solid); mp 211–212 °C; IR (neat): υ_{max} 2926, 2853, 1598, 1461, 1394, 1236, 744 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.1 (br s, 1.8H), 8.06 (d, 1.0H, *J* = 8.4 Hz, minor), 7.84 (s, 1.4H, major), 7.63–7.45 (m, 17.2H), 7.38–7.31 (m, 3H), 7.20–7.15 (m, 2.7H), 7.00–6.84 (m, 3.9H), 6.40 (d, 1H, *J* = 7.8 Hz), 2.47 (s, 4.2H, major), 2.17 (s, 3H, minor) ; $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 153.4 (major), 152.2 (minor), 147.5, 146.3, 143.6, 142.6, 141.7, 141.6, 140.9, 139.2, 136.8, 136.6, 129.4, 128.9, 128.8, 128.7, 128.4, 128.2, 127.6, 127.5, 126.6, 126.1, 126.0, 125.6, 125.1, 123.2, 122.8, 122.1, 121.7, 121.6, 121.3, 119.6, 118.1, 116.0, 110.8, 110.7; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{17}N_2$ 309.1386; found 309.1390.

3-Methoxy-11-phenyl-6H-indolo[2,3-b]quinoline (***2j***). Yield 44.7 mg (47%, yellow solid); mp 233–234 °C; IR (neat): υ_{max} 2965, 1606, 1391, 1218, 744 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69–7.59 (m, 4H), 7.55–

7.50 (m, 4H), 7.41–7.36 (m, 1H), 7.07–6.95 (m, 3H), 3.95 (s, 3H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 160.6, 153.7, 148.1, 143.0, 141.0, 136.5, 129.3, 128.9, 128.5, 127.6, 127.1, 122.7, 121.6, 119.7, 118.8, 115.8, 114.7, 110.6, 105.0, 55.4; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{17}N_2O$ 325.1335; found 325.1339.

1-Methoxy-11-phenyl-6H-indolo[2,3-b]quinoline (***2j'***). Yield 23.3 mg (24%, yellow solid); mp 218–219 °C; IR (neat): υ_{max} 2834, 1599, 1579, 1395, 1244, 1099, 741 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, 1H, J = 8.4 Hz), 7.65 (t, 1H, J = 8.0 Hz), 7.58–7.50 (m, 4H), 7.43–7.35 (m, 3H), 6.94–6.89 (m, 1H), 6.74 (d, 1H, J = 7.8 Hz), 6.57 (d, 1H, J = 7.5 Hz), 3.51 (s, 3H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 158.1, 152.6, 147.5, 143.1, 141.3, 141.2, 129.3, 128.0, 127.6, 127.3, 126.9, 123.4, 121.7, 120.0, 119.4, 117.6, 115.4, 110.7, 103.3, 55.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{17}N_2O$ 325.1335; found 325. 1337.

2-Methoxy-11-phenyl-6H-indolo[2,3-b]quinoline (***2k***). Yield 9.3 mg (11%, yellow solid); mp 208 °C (decomp); IR (neat): υ_{max} 2956, 1611, 1402, 1227, 1034, 743 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.71 (br s, 1H), 8.08 (d, 1H, J = 9.3 Hz), 7.71–7.61 (m, 3H), 7.57–7.54 (m, 2H), 7.48–7.39 (m, 3H), 7.06–6.94 (m, 3H), 3.77 (s, 3H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 155.1, 151.6, 142.2, 141.6, 141.0, 136.6, 129.3, 129.1, 128.6, 128.2, 127.9, 124.5, 123.2, 121.2, 121.1, 119.9, 116.6, 110.6, 104.8, 55.4; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{17}N_2O$ 325.1335; found 325.1346.

2-Fluoro-11-phenyl-6H-indolo[2,3-b]quinoline (***2l***). Yield 71.2 mg (86%, yellow solid); mp 261–262 °C; IR (neat): υ_{max} 2928, 1631, 1612, 1403, 1227, 744 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.50 (br s, 1H), 8.16 (dd, 1H, J = 9.2, 5.6 Hz), 7.71–7.63 (m, 3H), 7.55–7.42 (m, 5H), 7.38 (dd, 1H, J = 10.0, 2.8 Hz), 7.07 (d, 1H, J = 7.6 Hz), 7.02–6.98 (m, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 158.4 (d, J_{CF} = 241 Hz), 152.8, 143.1, 142.0 (d, J_{CF} = 5 Hz), 141.6, 135.9, 129.2, 129.1, 128.8, 128.4 (d, J_{CF} = 9 Hz), 128.2, 124.1, 123.2, 120.6, 119.9, 118.8 (d, J_{CF} = 26 Hz), 117.1, 110.7, 109.6 (d, J_{CF} = 23 Hz); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{14}FN_2$ 313.1136; found 313.1134.

9-Methyl-11-phenyl-6H-indolo[2,3-b]quinoline (***2m***). Yield 62.6 mg (73%, yellow solid); mp 242–243 °C; IR (neat): υ_{max} 2858, 1599, 1484, 1381, 1253, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.95 (bs s, 1H), 8.24 (d, 1H, J = 8.4 Hz), 7.77–7.72 (m, 2H), 7.67–7.65 (m, 3H), 7.54–7.52 (m, 2H), 7.38 (t, 2H, J = 8.0 Hz), 7.19 (d, 1H, J = 8.0 Hz), 6.83 (s, 1H), 2.27 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 153.6, 146.3,

142.6, 139.5, 136.5, 129.4, 129.0, 128.93, 128.90, 128.8, 128.5, 126.6, 126.5, 123.7, 123.2, 122.7, 121.2, 116.7, 110.4, 21.4; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{17}N_2$ 309.1386; found 309.1383.

9-Fluoro-11-phenyl-6H-indolo[2,3-b]quinoline (***2n***). Yield 79.9 mg (81%, yellow solid); mp 278–279 °C; IR (neat): υ_{max} 2860, 1603, 1486, 1472, 1182, 757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.96 (br s, 1H), 8.17 (d, 1H, J = 8.4 Hz), 7.75 (t, 2H, J = 8.4 Hz), 7.71–7.64 (m, 3H), 7.51–7.48 (m, 2H), 7.41–7.36 (m, 2H), 7.09 (td, 1H, J = 8.8, 2.4 Hz), 6.70 (dd, 1H, J = 9.2, 2.4 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.2 (d, J_{CF} = 236 Hz), 153.7, 146.6, 143.5, 137.6, 135.8, 129.3, 129.2, 129.1, 128.9, 126.9, 126.5, 123.5, 123.1, 121.6 (d, J_{CF} = 10 Hz), 116.3 (d, J_{CF} = 4 Hz), 115.3 (d, J_{CF} = 25 Hz), 111.2 (d, J_{CF} = 9 Hz), 109.2 (d, J_{CF} = 25 Hz); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{14}FN_2$ 313.1136; found 313.1132.

9-Chloro-11-phenyl-6H-indolo[2,3-b]quinoline (***2o***). Yield 69.8 mg (74%, yellow solid); mp 303–304 °C; IR (neat): υ_{max} 2929, 1600, 1451, 1281, 759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.38 (br s, 1H), 8.12 (d, 1H, J = 8.4 Hz), 7.73–7.67 (m, 5H), 7.46–7.45 (m, 2H), 7.38 (t, 1H, J = 7.5 Hz), 7.24 (d, 1H, J = 9.2 Hz), 7.16 (d, 1H, J = 8.0), 6.94 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.1, 146.6, 143.6, 139.6, 135.7, 129.4, 129.2, 129.1, 129.0, 127.7, 126.7, 126.4, 125.1, 123.7, 123.2, 122.7, 122.2, 115.7, 111.6; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{14}ClN_2$ (Cl-35) 329.0840; found 329.0839.

9-Methoxy-11-phenyl-6H-indolo[2,3-b]quinoline (***2p***). Yield 43.8 mg (51%, yellow solid); mp 225–226 °C; IR (neat): υ_{max} 2930, 1600, 1588, 1486, 1205, 756 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 11.18 (br s, 1H), 8.20 (d, 1H, J = 8.4 Hz), 7.80–7.72 (m, 2H), 7.70–7.60 (m, 3H), 7.57–7.54 (m, 2H), 7.41–7.36 (m, 2H), 7.03 (dd, 1H, J = 8.7, 2.4 Hz), 6.55 (d, 1H, J = 2.4 Hz), 3.59 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 153.7, 153.6, 146.4, 142.8, 136.3, 135.9, 129.5, 128.95, 128.92, 128.6, 126.61, 126.56, 123.5, 122.8, 121.6, 116.8, 116.1, 111.3, 106.9, 55.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{17}N_2O$ 325.1335; found 325.1345.

8-Methoxy-11-phenyl-6H-indolo[2,3-b]quinoline (***2q***). Yield 26.4 mg (31%, yellow solid); mp 223–224 °C; IR (neat): υ_{max} 2934, 1618, 1602, 1402, 1162, 758 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.21 (br s, 1H), 8.17 (d, 1H, J = 8.4 Hz), 7.71 (d, 1H, J = 8.0 Hz), 7.67–7.60 (m, 4H), 7.50–7.48 (m, 2H), 7.37–7.33 (m, 1H), 6.90 (d, 1H, J = 8.4 Hz), 6.82 (s, 1H), 6.52 (dd, 1H, J = 8.8, 2.0 Hz), 3.70 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.3, 153.3, 145.3, 143.1, 140.9, 136.5, 129.5, 128.9, 128.4, 128.3, 126.3, 126.2, 123.83,

123.80, 122.8, 116.9, 114.3, 107.9, 95.1, 55.3; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{17}ON_2$ 325.1335; found 325.1330.

8-Fluoro-11-phenyl-6H-indolo[2,3-b]quinoline (***2r***). Yield 60.0 mg (68%, yellow solid); mp 245–246 °C; IR (neat): υ_{max} 2925, 1615, 1604, 1401, 1142, 756 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 12.67 (br s, 1H), 8.13 (d, 1H, J = 8.1 Hz), 7.71–7.62 (m, 5H), 7.47–7.44 (m, 2H), 7.40–7.34 (m, 1H), 7.05 (dd, 1H, J = 9.3, 2.1 Hz), 6.92 (dd, 1H, J = 8.7, 5.7 Hz), 6.62 (td, 1H, J = 9.3, 2.4 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 162.8 (d, J_{CF}= 244 Hz), 153.6, 145.8, 142.6 (d, J_{CF}= 13 Hz), 142.2 (d, J_{CF}= 2 Hz), 136.2, 129.4, 129.0, 128.7, 126.4, 126.2, 124.0 (d, J_{CF}= 10 Hz), 123.7, 123.2, 117.3 (d, J_{CF}= 2 Hz), 116.1, 107.5 (d, J_{CF}= 23 Hz), 98.0 (d, J_{CF}= 26 Hz); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{14}FN_2$ 313.1136; found 313.1136.

11-Butyl-3-methoxy-6H-indolo[2,3-b]quinoline (***2s***). Yield 58.9 mg (40%, white solid); mp 202–203 °C; IR (neat): υ_{max} 2922, 1610, 1578, 1457, 1220, 739 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 10.71 (br s, 1H), 8.17–8.13 (m, 2H), 7.56–7.46 (m, 3H), 7.33–7.27 (m, 1H), 7.17 (dd, 1H, J = 9.0, 2.4 Hz), 4.00 (s, 3H), 3.65–3.60 (m, 2H), 1.94–1.84 (m, 2H), 1.72–1.60 (m, 2H), 1.05 (t, 3H, J = 7.3 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 160.5, 153.6, 148.5, 144.7, 140.5, 126.8, 125.3, 123.0, 121.9, 120.2, 118.6, 115.7, 114.4, 110.7, 105.8, 55.5, 31.8, 29.0, 23.4, 14.1; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{21}N_2O$ 305.1648; found 305.1641.

11-Butyl-1-methoxy-6H-indolo[2,3-b]quinoline (***2s'***). Yield 29.2 mg (20%, white solid); mp 227–228 °C; IR (neat): υ_{max} 2928, 1605, 1581, 1394, 1240, 737 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, 1H, J = 7.9 Hz), 7.76 (d, 1H, J = 8.3 Hz), 7.63 (t, 1H, J = 7.9 Hz), 7.55–7.47 (m, 2H), 7.33–7.28 (m,1H), 6.85 (d, 1H, J = 7.7 Hz), 4.05–3.61 (m, 5H), 1.94 (quint, 2H, J = 7.1 Hz), 1.77–1.65 (m, 2H), 1.10 (t, 3H, J = 7.3 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 158.8, 152.0, 148.1, 147.4, 140.9, 129.0, 127.3, 123.6, 121.8, 120.4, 119.4, 117.3, 116.0, 111.1, 102.9, 55.6, 32.7, 31.9, 23.6, 14.1; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{21}N_2O$ 305.1648; found 305.1649.

11-Isopentyl-3-methoxy-6H-indolo[2,3-b]quinoline (***2t***). Yield 35.9 mg (32%, white solid); mp 244–245 °C; IR (neat): υ_{max} 2954, 1613, 1590, 1220, 1208, 738 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 10.85 (br s, 1H), 8.15–8.11 (m, 2H), 7.55–7.46 (m, 3H), 7.30 (t, 1H, J = 7.2 Hz), 7.17 (dd, 1H, J = 9.3, 2.7 Hz), 3.99 (s, 3H), 3.63–3.57 (m, 2H), 2.04–1.91 (m, 1H), 1.83–1.72 (m, 2H), 1.14 (d, 6H, J = 6.6 Hz); $^{13}C\{^1H\}$ NMR

(75 MHz, $CDCl_3$) δ 160.5, 153.6, 148.4, 145.0, 140.5, 126.8, 125.1, 122.9, 121.8, 120.2, 118.4, 115.8, 114.3, 110.7, 105.8, 55.5, 38.5, 29.1, 27.3, 22.6; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{23}N_2O$ 319.1805; found 319.1801.

11-Isopentyl-1-methoxy-6H-indolo[2,3-b]quinoline (***2t'***). Yield 22.1 mg (19%, white solid); mp 264–265 °C; IR (neat): υ_{max} 2924, 1606, 1580, 1393, 1242, 736 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 10.66 (br s, 1H), 8.21 (d, 1H, *J* = 7.9 Hz), 7.75 (d, 1H, *J* = 8.3 Hz), 7.62 (t, 1H, *J* = 8.0 Hz), 7.54–7.49 (m, 2H), 7.31–7.28 (m, 1H), 6.85 (d, 1H, *J* = 7.6 Hz), 4.04– 3.45 (m, 5H), 2.02–1.97 (m, 1H), 1.85 (q, 2H, *J* = 7.2 Hz), 1.15 (d, 6H, *J* = 6.6 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 158.8, 152.6, 148.7, 147.4, 140.9, 128.5, 127.1, 123.6, 122.2, 120.3, 120.2, 116.9, 116.2, 110.8, 102.7, 55.4, 38.7, 31.2, 29.5, 22.7; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{23}N_2O$ 319.1805; found 319.1808.

11-Cyclohexyl-3-methoxy-6H-indolo[2,3-b]quinoline (***2u***). Yield 35.2 mg (36%, white solid); mp 229–230 °C; IR (neat): υ_{max} 2923, 1600, 1568, 1464, 1240, 1095, 739 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.60 (br s, 1H), 8.47 (d, 1H, *J* = 8.1 Hz), 8.31 (br s, 1H), 7.57–7.55 (m, 1H), 7.50–7.44 (m, 2H), 7.31–7.26 (m, 1H), 7.13 (dd, 1H, *J* = 9.3, 2.4 Hz), 4.24 (br s, 1H), 3.99 (s, 3H), 2.46 (br s, 2H), 2.10–1.87 (m, 5H), 1.73–1.65 (m, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 160.0, 154.0, 149.7, 149.1, 140.9, 127.9, 126.7, 123.5, 121.9, 119.8, 118.4, 114.7, 110.8, 105.8, 55.4, 42.7, 31.7, 27.6, 26.2; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{23}N_2O$ 331.1805; found 331.1809.

11-Cyclohexyl-1-methoxy-6H-indolo[2,3-b]quinoline (***2u'***). Yield 25.6 mg (26%, white solid); mp 226–227 °C; IR (neat): υ_{max} 2919, 1601, 1568, 1464, 1240, 1095, 730 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 11.01 (br s, 1H), 8.36 (d, 1H, *J* = 7.8 Hz), 7.76 (dd, 1H, *J* = 8.4, 0.9 Hz), 7.63 (t, 1H, *J* = 7.9 Hz), 7.54–7.46 (m, 2H), 7.33–7.27 (m, 1H), 6.85 (d, 1H, *J* = 7.1 Hz), 4.40–4.31 (m, 1H), 4.07 (s, 3H), 2.64–2.52 (m, 2H), 2.04–1.89 (m, 5H), 1.67–1.56 (m, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 157.7, 153.3, 151.4, 148.8, 141.2, 128.3, 127.1, 125.6, 121.8, 120.1, 119.7, 118.0, 116.8, 110.9, 102.7, 54.8, 43.7, 28.6, 27.2, 26.1; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{23}N_2O$ 331.1805; found 331.1808.

11-(4-Fluorophenyl)-3-methoxy-6H-indolo[2,3-b]quinoline (***2v***). Yield 37.7 mg (34%, yellow solid); mp 244–245 °C; IR (neat): υ_{max} 2923, 2853, 1609, 1221, 1029, 800 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 11.74 (br s, 1H), 7.59 (d, 1H, *J* = 9.3 Hz), 7.50–7.44 (m, 3H), 7.40–7.31 (m, 4H), 7.07–6.97 (m, 3H), 3.86 (s, 3H);

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 163.0 (d, J_{CF} = 246 Hz), 160.7, 153.5, 148.2, 141.8, 140.9, 132.4 (d, J_{CF} = 4 Hz), 131.2 (d, J_{CF} = 8 Hz), 127.3, 122.5, 121.4, 119.9, 118.9, 116.2 (d, J_{CF} = 9 Hz), 116.0, 114.8, 110.7, 105.2, 55.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{16}FN_2O$ 343.1241; found 343.1240.

11-(4-Fluorophenyl)-1-methoxy-6H-indolo[2,3-b]quinoline (***2v'***). Yield 32.4 mg (30%, yellow solid); mp 242–243 °C; IR (neat): υ_{max} 2934, 1601, 1582, 1396, 1245, 1100, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.99 (br s, 1H), 7.82 (d, 1H, *J* = 8,4 Hz), 7.62 (t, 1H, *J* = 8.0 Hz), 7.49 (d, 1H, *J* = 8.0 Hz), 7.38–7.35 (m, 3H), 7.82–7.22 (m, 2H), 6.94 (t, 1H, *J* = 7.4 Hz), 6.72 (d, 1H, *J* = 7.7 Hz), 6.63 (d, 1H, *J* = 7.9 Hz), 3.54 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.0 (d, J_{CF} = 245 Hz), 157.8, 152.9, 148.0, 141.5, 141.3, 137.3 (d, J_{CF} = 4 Hz), 129.10, 129.05 (d, J_{CF} = 8 Hz), 127.7, 123.2, 121.5, 119.8, 119.6, 117.6, 115.3, 114.9 (d, J_{CF} = 21 Hz), 110.8, 103.0, 55.4; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{16}FN_2O$ 343.1241; found 343.1254.

9-Fluoro-3-methoxy-11-phenyl-6H-indolo[2,3-b]quinoline (***2w***). Yield 44.1 mg (42%, yellow solid); mp 267–268 °C; IR (neat): υ_{max} 2923, 1608, 1493, 1258, 1142, 803 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.64–7.60 (m, 4H), 7.45–7.41 (m, 2H), 7.39–7.35 (m, 2H), 7.10–7.02 (m, 2H), 6.65 (dd, 1H, *J* = 9.3, 2.4 Hz), 3.87 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 161.1, 157.3 (d, J_{CF} = 235 Hz), 153.6, 147.9, 144.0, 137.0, 135.8, 129.09, 129.06, 128.9, 127.9, 122.0 (d, J_{CF} = 10 Hz), 118.5, 116.1, 114.6 (d, J_{CF} = 25 Hz), 111.1 (d, $J_{C\,F}$ = 9 Hz), 108.8 (d, J_{CF} = 25 Hz), 104.6, 55.4; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{16}FN_2O$ 343.1241; found 343.1249.

9-Fluoro-1-methoxy-11-phenyl-6H-indolo[2,3-b]quinoline (***2w'***). Yield 22.8 mg (22%, yellow solid); mp 291–292 °C; IR (neat): υ_{max} 2933, 1602, 1582, 1471, 1251, 1098, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, 1H, *J* = 7.9 Hz), 7.63 (t, 1H, *J* = 7.8 Hz), 7.59–7.52 (m, 3H), 7.39–7.34 (m, 3H), 7.08 (td, 1H, *J* = 8.9, 2.6 Hz), 6.72 (d, 1H, *J* = 7.3 Hz), 6.19 (dd, 1H, *J* = 9.6, 2.6 Hz), 3.51 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 158.1, 157.2 (d, $J_{C\,F}$ = 234 Hz), 153.2, 148.3, 143.4, 140.9, 137.2, 129.5, 128.1, 127.2, 127.1, 122.4 (d, J_{CF} = 10 Hz), 119.7, 117.0 (d, J_{CF} = 4 Hz), 115.3, 114.9 (d, J_{CF} = 25 Hz), 110.9 (d, J_{CF} = 9 Hz), 109.6 (d, J_{CF} = 25 Hz), 103.2, 55.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{16}FN_2O$ 343.1241; found 343.1240.

11-Butyl-9-fluoro-3-methoxy-6H-indolo[2,3-b]quinoline (***2x***). Yield 40.9 mg (40%, yellow solid); mp 216–217 °C; IR (neat): υ_{max} 2957, 1617, 1591, 1478, 1259, 1161, 811 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 11.62 (s, 1H), 8.19 (d, 1H, J = 9.3 Hz), 7.86 (dd, 1H, J = 9.6, 2.1 Hz), 7.47 (dd, 1H, J = 8.7, 4.5 Hz), 7.37–7.31 (m, 2H), 7.13 (dd, 1H, J = 9.0, 2.4 Hz), 3.93 (s, 3H), 3.54 (t, 2H, J = 7.6 Hz), 1.73 (quint, 2H, J = 9.3 Hz), 1.60–1.50 (m, 2H), 0.95 (t, 3H, J = 7.2 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6) δ 160.0, 156.8 (d, J_{CF} = 232 Hz), 153.5, 148.8, 144.4, 137.1, 125.6, 121.2 (d, J_{CF} = 9 Hz), 117.7, 115.3, 114.1 (d, J_{CF} = 25 Hz), 113.1 (d, J_{CF} = 3 Hz), 111.5 (d, J_{CF} = 9 Hz), 108.7 (d, J_{CF} = 25 Hz), 106.2, 55.3, 31.7, 27.8, 22.4, 13.9; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{20}FN_2O$ 323.1554; found 323.1559.

11-Butyl-9-fluoro-1-methoxy-6H-indolo[2,3-b]quinoline (***2x'***). Yield 18.1 mg (18%, brown solid); mp 223–224 °C; IR (neat): υ_{max} 2958, 1606, 1582, 1465, 1246, 1159, 765 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 11.67 (s, 1H), 7.86 (dd, 1H, J = 10.1, 2.4 Hz), 7.61–7.46 (m, 3H), 7.37 (td, 1H, J = 9.2, 2.4 Hz), 6.92 (dd, 1H, J = 7.6, 1.2 Hz), 3.99–3.55 (m, 5H), 1.80 (quint, 2H, J = 7.7 Hz), 1.70–1.58 (m, 2H), 1.04 (t, 3H, J = 7.2 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6) δ 158.2, 156.6 (d, J_{CF} = 232 Hz), 152.6, 149.0, 146.0, 137.6, 128.8, 121.1 (d, J_{CF} = 9 Hz), 120.5, 115.5 (d, J_{CF} = 4 Hz), 115.0, 114.5 (d, J_{CF} = 24 Hz), 111.6 (d, J_{CF} = 9 Hz), 109.2 (d, J_{CF} = 25 Hz), 102.8, 55.7, 31.8, 31.6, 22.8, 13.9; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{20}FN_2O$ 323.1554; found 323.1560.

1-(2-Benzoylphenyl)hexan-2-one (***3a***). Yield 6.4 mg (8%, brown oil); IR (neat): υ_{max} 2958, 1716, 1659, 1447, 1268, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.82–7.78 (m, 2H), 7.60–7.54 (m, 1H), 7.50–7.30 (m, 4H), 7.34–7.26 (m, 2H), 3.95 (s, 2H), 2.45 (t, 2H, J = 7.2 Hz), 1.56–1.46 (m, 2H), 1.31–1.19 (m, 2H), 0.85 (t, 3H, J = 7.5 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 207.7, 198.2, 138.0, 137.9, 134.5, 132.8, 132.0, 130.9, 130.3, 130.1, 128.3, 126.2, 47.2, 42.3, 25.8, 22.2, 13.8; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{21}O_2$ 281.1536; found 281.1525.

General procedure for the synthesis of α-alkynylalcohols (8) and (9) Method A: 6-phenylhex-5-yn-1-ol (401.1 mg, 2.3020 mmol, 1.0 equiv) was dissolved in DCM (AR grade) (3.0 mL/mmol) at room temperature. The solution was added Celite and PCC (595.5 mg, 2.7624 mmol, 1.2 equiv) and stirred at room temperature. After completion, the reaction was filtered through Celite and silica gel, followed by

concentration under reduced pressure to obtain crude product aldehyde which was used without further purification. The crude aldehyde was dissolved in dry THF (2.3 mL/mmol) and cooled to 0 °C under argon atmosphere. The solution was then added 4-fluorophenylmagnesium bromide (1.3 mL, 2.6415 mmol, 1.2 equiv) and then the reaction was allowed to warm to room temperature. After completion, the reaction was quenched with sat. NH_4Cl and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to provide the crude product which was purified on silica gel (EtoAc/Hexane: 2:8) to yield the product **8k** (445.3 mg, 75%).

Method B: 4-Bromoveratrole (109.8 µL, 0.7631 mmol, 1.3 equiv) was dissolved in dry THF (3.4 mL/mmol) and cooled to -40 °C under argon atmosphere. The solution was then added n-BuLi (0.6 mL, 0.7044 mmol, 1.2 equiv) and stirred for 30 min and then cooled to -78 °C. The reaction mixture was added with the crude aldehyde in dry THF (3.4 mL/mmol), prepared from the oxidation of alcohol with PCC as described in method A. After completion, the reaction was quenched with H_2O and extracted with EtOAc. The combined organic layers were then washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to provide the crude product which was purified on silica gel (EtOAc/Hexane: 3:7) to yield the □-alkynylalcohols **8q** (104 mg, 55%). (Note: For the synthesis of comcound 8m which used iodobenzene derivatives as strating material, the temperature was cooled to -78 °C throughout the reaction.)

1,6-Diphenylhex-5-yn-1-one (***8a***). Yield 351.5 mg (64 %, colorless oil); IR (neat): υ_{max} 3385, 2935, 1490, 1066, 754 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39–7.32 (m, 6H), 7.30–7.25 (m, 4H), 4.73 (dd, 1H, J = 7.2, 5.7 Hz), 2.44 (t, 2H, J = 6.9 Hz), 2.03–1.48 (m, 4H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 144.6, 131.6, 128.5, 128.2, 127.7, 127.6, 125.9, 123.9, 89.8, 81.0,74.2, 38.1, 25.0, 19.3; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{18}H_{18}ONa$ 273.1250; found 273.1259.

6-(4-Fluorophenyl)-1-phenylhex-5-yn-1-ol (***8b***). Yield 484.9 mg (67%, colorless oil); IR (neat): υ_{max} 3385, 2936, 1506, 1454, 1229, 834 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.36–7.23 (m, 7H), 6.98–6.92 (m, 2H), 4.72–4.67 (m, 1H), 2.40 (t, 2H, J = 6.9 Hz), 2.09 (br s, 1H), 2.00–1.82 (m, 2H), 1.80–1.66 (m, 1H), 1.64–1.50 (m, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 162.0 (d, J_{CF} = 247 Hz), 144.5, 133.3 (d, J_{CF} = 8 Hz), 128.5, 127.6, 125.8, 119.9 (d, J_{CF} = 4 Hz), 115.3 (d, J_{CF} = 22 Hz), 89.4, 79.9, 74.1, 38.1, 24.9,19.2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{18}H_{17}FONa$ 291.1156; found 291.1157.

6-(4-Chlorophenyl)-1-phenylhex-5-yn-1-ol (***8c***). Yield 507.4 mg (65%, colorless oil); IR (neat): υ_{max} 3383, 2936, 2236, 1489, 1090, 826 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.37–7.22 (m, 9H), 4.74 (t, 1H, J = 6.3 Hz), 2.43 (t, 2H, J = 6.9 Hz), 2.04–1.59 (m, 5H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 144.5, 133.5, 132.8, 128.54, 128.48, 127.7, 125.9, 122.4, 90.9, 79.9, 74.2, 38.1, 24.9, 19.3; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{18}H_{17}ClONa$ (Cl-35) 307.0860; found 307.0858.

6-(4-Bromophenyl)-1-phenylhex-5-yn-1-ol (***8d***). Yield 513.9 mg (72%, colorless oil); IR (neat): υ_{max} 3369, 2935, 2228, 1485, 823 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40–7.34 (m, 6H), 7.30–7.20 (m, 3H), 4.72 (t, 1H, J = 6.3 Hz), 2.41 (t, 2H, J = 6.9 Hz), 2.01– 1.80 (m, 3H), 1.77–1.68 (m, 1H), 1.66–1.52 (m, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 144.5, 133.0, 131.4, 128.5, 127.6, 125.8, 122.8, 121.6, 91.1, 80.0, 74.2, 38.1, 24.8, 19.3; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{18}H_{17}BrONa$ (Br-79) 351.0355; found 351.0350.

6-(4-Methoxyphenyl)-1-phenylhex-5-yn-1-ol (***8e***). Yield 503.0 mg (64%, colorless oil); IR (neat): υ_{max} 3421, 2935, 1606, 1508, 1244, 831 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.36–7.26 (m, 7H), 6.82–6.77 (m, 2H), 4.73 (dd, 1H, J = 7.2, 6.0 Hz), 3.78 (s, 3H), 2.42 (t, 2H, J = 7.2 Hz), 1.98–1.83(m, 3H), 1.79–1.52 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 159.0, 144.6, 132.8, 128.5, 127.6, 125.9, 116.0, 113.8, 88.1, 80.7, 74.2, 55.2, 38.1, 25.0, 19.3; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{19}H_{20}O_2Na$ 303.1356; found 303.1361.

6-(3-Methoxyphenyl)-1-phenylhex-5-yn-1-ol (***8f***). Yield 249.3 mg (33%, colorless oil); IR (neat): υ_{max} 3421, 2938, 1598, 1575, 1286, 1043, 687 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35–7.24 (m, 5H), 7.17 (t, 1H, J = 8.1 Hz), 6.97 (dt, 1H, J = 7.5, 0.9 Hz), 6.91–6.90 (m, 1H), 6.81 (ddd, 1H, J = 8.4, 2.7, 0.9), 4.72 (dd, 1H, J = 7.2, 5.7 Hz), 3.77 (s, 3H), 2.43 (t, 2H, J = 6.9 Hz), 2.04–1.83 (m, 3H), 1.80–1.47 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 159.2, 144.5, 129.2, 128.5, 127.6, 125.8, 124.9, 124.1, 116.4, 114.1, 89.7, 80.9, 74.1, 55.2, 38.1, 24.9, 19.2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{19}H_{20}O_2Na$ 303.1356; found 303.1360.

1-Mhenyl-6-(4-(trifluoromethyl)phenyl)hex-5-yn-1-ol (***8g***). Yield 424.7 mg (49%, colorless oil); IR (neat): υ_{max} 3364, 2937, 2237, 1616, 1321, 1066, 841 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, 2H, J = 8.4 Hz), 7.46 (d, 2H, J = 8.4 Hz), 7.40–7.27 (m, 5H), 4.74 (dd, 1H, J = 7.2, 6.0 Hz), 2.46 (t, 2H, J = 7.2 Hz), 2.04–1.83 (m, 3H), 1.81–1.69 (m, 1H), 1.67–1.57 (m, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 144.5, 131.8,

129.4 (d, J_{CF} = 33 Hz), 128.6, 127.7, 125.9, 125.1 (d, J_{CF} = 4 Hz), 120.4 (d, J_{CF} = 270 Hz), 92.7, 79.9, 74.2, 38.1, 29.7, 24.8, 19.3; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{19}H_{17}F_3ONa$ 341.1124; found 341.1110.

6-(4-Nitrophenyl)-1-phenylhex-5-yn-1-ol (***8h***). Yield 219.3 mg (37%, brown oil); IR (neat): υ_{max} 3394, 2933, 2225, 1594, 1516, 1342, 854 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, 2H, *J* = 9 Hz), 7.49 (d, 2H, *J* = 9 Hz), 7.41–7.28 (m, 5H), 4.76–4.72 (m, 1H), 2.48 (t, 2H, *J* = 6.9 Hz), 2.04–1.82 (m, 3H), 1.80–1.56 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 146.6, 144.4, 132.2, 131.0, 128.6, 127.7, 125.8, 123.5, 96.1, 79.6, 74.1, 38.1, 24.7, 19.4; HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ calcd for $C_{18}H_{21}N_2O_3$ 313.1547; found 313.1550.

6-Phenyl-1-(o-tolyl)hex-5-yn-1-ol (***8i***). Yield 406.6 mg (55%, brown oil); IR (neat): υ_{max} 3394, 2931, 1598, 1489, 1442, 1068, 754 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.49 (dd, 1H, *J* = 7.4, 1.3 Hz), 7.40–7.34 (m, 2H), 7.32–7.12 (m, 6H), 5.04–4,99 (m, 1H), 2.48 (td, 2H, *J* = 7.1, 2.3 Hz), 2.36 (s, 3H), 1.95–1.74 (m, 3H), 1.72–1.63 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 142.8, 134.5, 131.5, 130.4, 128.2, 127.5, 127.2, 126.3, 125.1, 123.9, 89.8, 81.0, 70.3, 37.0, 25.1, 19.3, 19.1; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{19}H_{20}ONa$ 287.1406; found 287.1407.

6-Phenyl-1-(m-tolyl)hex-5-yn-1-ol (***8j***). Yield 435.7 mg (70%, light yellow oil); IR (neat): υ_{max} 3329, 2922, 1599, 1490, 1442, 1069, 755 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40–7.34 (m, 2H), 7.27–7.20 (m, 4H), 7.16–7.07 (m, 3H), 4.67 (t, 1H, *J* = 6.4 Hz), 2.42 (t, 2H, *J* = 6.9 Hz), 2.34 (s, 3H), 2.01 (br s, 1H), 1.99–1.81 (m, 2H), 1.79–1.54 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 144.5, 138.1, 131.5, 128.4, 128.3, 128.1, 127.5, 126.5, 123.9, 122.9, 89.8, 80.9, 74.2, 38.0, 25.0, 21.4, 19.2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{19}H_{20}ONa$ 287.1406; found 287.1407.

1-(4-Fluorophenyl)-6-phenylhex-5-yn-1-ol (***8k***). Yield 445.3 mg (75%, light yellow oil); IR (neat): υ_{max} 3373, 2936, 1603, 1508, 1490, 1221, 755 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39–7.35 (m, 2H), 7.34–7.24 (m, 5H), 7.02 (tt, 2H, *J* = 8.7, 2.9 Hz), 4.70 (t, 1H, *J* = 6.6 Hz), 2.43 (t, 2H, *J* = 6.9 Hz), 2.03 (br s,1H), 1.98–1.79 (m, 2H), 1.77–1.50 (m, 2H) ; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 162.2 (d, J_{CF} = 244 Hz), 140.3 (d, J_{CF} = 3 Hz), 131.5, 128.2, 127.6, 127.5 (d, J_{CF} = 8 Hz), 123.8, 115.3 (d, J_{CF} = 21 Hz), 89.7, 81.1, 73.5, 38.2, 24.9, 19.2; HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ calcd for $C_{18}H_{21}FNO$ 286.1602; found 286.1608.

1-(4-Chlorophenyl)-6-phenylhex-5-yn-1-ol (***8l***). Yield 460.8 mg (73%, light yellow oil); IR (neat): υ_{max} 3392, 2935, 1598, 1490, 1090, 1014, 755 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.38–7.33 (m, 2H), 7.31–7.25 (m, 7H), 4.68 (t, 1H, J = 6.9 Hz), 2.42 (t, 2H, J = 6.9 Hz), 2.14 (br s, 1H), 1.97–1.78 (m, 2H), 1.76–1.51 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 143.0, 133.1, 131.5, 128.6, 128.2, 127.6, 127.2, 123.8, 89.6, 81.1, 73.4, 38.1, 24.7, 19.2; HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ calcd for $C_{18}H_{21}ClNO$ (Cl-35) 302.1306; found 302.1307.

1-(3-Chlorophenyl)-6-phenylhex-5-yn-1-ol (***8m***). Yield 316.4 mg (37%, yellow oil); IR (neat): υ_{max} 3395, 2936, 1598, 1490, 1432, 1069, 754 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40–7.35 (m, 3H), 7.31–7.21 (m, 6H), 4.74 (dd, 1H, J = 6.9, 6.0 Hz), 2.45 (t, 2H, J = 6.9 Hz), 1.99–1.81 (m, 3H), 1.80–1.69 (m, 1H), 1.67–1.55 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.7, 134.4, 131.5, 129.8, 128.2, 127.7, 127.6, 126.1, 124.0, 123.8, 89.6, 81.1, 73.5, 38.1, 24.8, 19.2; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{18}ClO$ (Cl-35) 285.1041; found 285.1029.

1-(4-Methoxyphenyl)-6-phenylhex-5-yn-1-ol (***8n***). Yield 427.7 mg (72%, light yellow oil); IR (neat): υ_{max} 3398, 2935, 1611, 1512, 1246, 1033, 756 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.38–7.34 (m, 2H), 7.29–7.23 (m, 5H), 6.88–6.84 (m, 2H), 4.64 (t, 1H, J = 6.6 Hz), 3.77 (s, 3H), 2.14 (t, 2H, J = 7.1 Hz), 2.08 (br s, 1H), 2.01–1.84 (m, 4H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 159.0, 136.7, 131.5, 128.1, 127.5, 127.1, 123.8, 113.8, 89.8, 80.9, 73.6, 55.2, 37.9, 25.0, 19.2; HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ calcd for $C_{19}H_{24}NO_2$ 298.1802; found 298.1813.

1-(3-Methoxyphenyl)-6-phenylhex-5-yn-1-ol (***8o***). Yield 496.9 mg (67%, light yellow oil); IR (neat): υ_{max} 3358, 2937, 1591, 1489, 1450, 1247, 755 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40–7.35 (m, 2H), 7.29–7.24 (m, 4H), 6.94–6.92 (m, 2H), 6.83–6.80 (m, 1H), 4.71 (t, 1H, J = 6.0 Hz), 3.79 (s, 3H), 2.43 (t, 2H, J = 6.8 Hz), 2.00–1.85 (m, 3H), 1.79–1.55 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 159.8, 146.3, 131.5, 129.5, 128.1, 127.5, 123.8, 118.2, 113.0, 111.3, 89.8, 81.0, 74.1, 55.2, 38.0, 24.9, 19.2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{19}H_{20}O_2Na$ 303.1356; found 303.1360.

1-(3,5-Dimethoxyphenyl)-6-phenylhex-5-yn-1-ol (***8p***). Yield 361.8 mg (52%, colorless oil); IR (neat): υ_{max} 3421, 2936, 1596, 1429, 1152, 756 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39–7.35 (m, 2H), 7.27–7.24 (m, 3H), 6.53 (d, 2H, J = 2.1 Hz), 6.38 (t, 1H, J = 2.1 Hz), 4.68 (br t, 1H, J = 6.3 Hz), 3.78 (s, 6H), 2.45 (t, 2H,

J = 6.9 Hz), 1.97–1.83 (m, 3H), 1.81–1.62 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 160.9, 147.2, 131.5, 128.2, 127.5, 123.9, 103.8, 99.5, 89.8, 81.0, 74.2, 55.3, 38.0, 24.9, 19.3; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{20}H_{22}O_3Na$ 333.1461; found 333.1473.

1-(3,4-Dimethoxyphenyl)-6-phenylhex-5-yn-1-ol (***8q***). Yield 104.0 mg (55%, light yellow solid); mp 77–78 °C; IR (neat): υ_{max} 3481, 2934, 1515, 1260, 1137, 1027, 757 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39–7.34 (m, 2H), 7.28–7.23 (m, 3H), 6.91–6.80 (m, 3H), 4.67 (t, 1H, J = 6.3 Hz), 3.86 (s, 6H), 2.43 (t, 2H, J = 7.2 Hz), 2.08 (br s, 1H), 2.02–1.82 (m, 2H), 1.79–1.51 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 149.0, 148.4, 137.2, 131.4, 128.1, 127.5, 123.8, 118.1, 110.9, 108.9, 89.8, 80.9, 73.9, 55.85, 55.76, 38.0, 25.0, 19.2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{20}H_{22}O_3Na$ 333.1461; found 333.1460.

1-(3-(Benzyloxy)phenyl)-6-phenylhex-5-yn-1-ol (***8r***). Yield 353.5 mg (42%, light yellow oil); IR (neat): υ_{max} 2934, 1683, 1581, 1439, 1255, 1026, 691 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.44–7.36 (m, 6H), 7.34–7.31 (m, 1H), 7.30–7.25 (m, 4H), 7.02–7.01 (m, 1H), 6.95 (d, 1H, J = 7.6 Hz), 6.89 (dd, 1H, J = 8.4, 2.4 Hz), 5.06 (s, 2H), 4.72 (t, 1H, J = 6.4 Hz), 2.43 (t, 2H, J = 6.4 Hz), 2.00–1.85 (m, 3H), 1.78–1.67 (m, 1H), 1.65–1.54 (m, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 159.0, 146.3, 136.9, 131.5, 129.6, 128.5, 128.2, 127.9, 127.53, 127.50, 123.8, 118.5, 113.9, 112.3, 89.8, 81.0, 74.6, 69.9, 38.0, 24.9, 19.2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{25}H_{24}O_2Na$ 379.1669; found 379.1682.

1,7-Diphenylhept-6-yn-1-ol (***9a***). Yield 318.5 mg (62%, light yellow oil); IR (neat): υ_{max} 3373, 2937, 1490, 1453, 1027, 755 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37–7.31 (m, 6H), 7.30–7.24 (m, 4H), 4.67 (t, 1H, J = 6.8 Hz), 2.39 (t, 2H, J = 6.8 Hz), 1.95 (s, 1H), 1.89–1.70 (m, 2H), 1.66–1.52 (m, 3H), 1.51–1.38 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.7, 131.5, 128.4, 128.1, 127.51, 127.46, 125.9, 123.9, 90.0, 80.8, 74.5, 38.5, 28.5, 25.1, 19.3; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{19}H_{20}ONa$ 287.1406; found 287.1408.

7-(4-Chlorophenyl)-1-phenylhept-6-yn-1-ol (***9b***). Yield 405.8 mg (56%, colorless oil); IR (neat): υ_{max} 3379, 2938, 2228, 1489, 1091, 827 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34–7.21 (m, 9H), 4.66 (t, 1H, J = 6.6 Hz), 2.37 (t, 2H, J = 6.6 Hz), 2.00 (br s, 1H), 1.88–1.68 (m, 2H), 1.66–1.51 (m, 3H), 1.47–1.37 (m, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, CDCl3) δ 144.6, 133.3, 132.7, 128.4, 127.5, 125.8, 122.4, 91.1, 79.7, 74.4, 38.4, 28.4, 25.0, 19.2; HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ calcd for $C_{19}H_{23}ClNO$ 316.1463; found 316.1460.

General procedure for the synthesis of α-alkynylketones (4) and (6) Compound **9a** (286.0 mg, 1.0818 mmol, 1.0 equiv) was dissolved in DCM (AR grade) (4.6 mL/mmol) at room temperature. Celite and PCC (279.8 mg, 1.2982 mmol, 1.2 equiv) were added to the solution and stirred for 3 h. The reaction was filtered through Celite and silica gel followed by concentration under reduced pressure to obtain crude product. The crude product was purified on silica gel (EtOAc/Hexane: 3:7) to yield the α-alkynylketone **6a** (277.5 mg, 98%).

1,6-Diphenylhex-5-yn-1-one (***4a***). Yield 199.2 mg (85 %, colorless oil); IR (neat): υ_{max} 2938, 1683, 1448, 1229, 755 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.01–7.97 (m, 2H), 7.55 (tt, 1H, J = 7.2, 1.5 Hz), 7.47–7.35 (m, 4H), 7.31–7.24 (m, 3H), 3.17 (t, 2H, J = 7.2 Hz), 2.55 (t, 2H, J = 6.9 Hz), 2.05 (quint, 2H, J = 6.9 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 199.7, 136.9, 133.0, 131.5, 128.5, 128.2, 128.0, 127.6, 123.7, 89.3, 81.4, 37.2, 23.1, 18.9; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{18}H_{16}ONa$ 271.1093; found 271.1096.

6-(4-Fluorophenyl)-1-phenylhex-5-yn-1-one (***4b***). Yield 358.9 mg (87%, white solid); mp 50–51 °C; IR (neat): υ_{max} 2938, 1683, 1599, 1506, 1449, 1228, 835 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.01–7.98 (m, 2H), 7.59–7.53 (m, 1H), 7.49–7.43 (m, 2H), 7.38–7.31 (m, 2H), 7.00–6.93 (m, 2H), 3.17 (t, 2H, J = 6.9 Hz), 2.54 (t, 2H, J = 6.9 Hz), 2.05 (quint, 2H, J = 6.9 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 199.6, 162.1 (d, J_{CF} = 247 Hz), 137.0, 133.3 (d, J_{CF} = 8 Hz), 133.0, 128.6, 128.0, 119.8 (d, J_{CF} = 3 Hz), 115.4 (d, J_{CF} = 22 Hz), 88.9, 80.4, 37.2, 23.1, 18.9; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{18}H_{15}FONa$ 289.0999; found 289.1005.

6-(4-Chlorophenyl)-1-phenylhex-5-yn-1-one (***4c***). Yield 431.7 mg (98%, white solid); mp 53–54 °C; IR (neat): υ_{max} 2939, 1683, 1597, 1489, 1091, 827 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.99 (dd, 2H, J = 8.4, 1.2 Hz), 7.60–7.54 (m, 1H), 7.46 (t, 2H, J = 7.5 Hz), 7.31–7.23 (m, 4H), 3.17 (t, 2H, J = 7.2 Hz), 2.54 (t, 2H, J = 6.9 Hz), 2.06 (quint, 2H, J = 6.9 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 199.6, 137.0, 133.6, 133.1, 132.8, 128.6, 128.5, 128.0, 122.3, 90.4, 80.4, 37.2, 23.1, 18.9; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{18}H_{15}ClONa$ (Cl-35) 305.0704; found 305.0694.

6-(4-Bromophenyl)-1-phenylhex-5-yn-1-one (***4d***). Yield 390.5 mg (≥99%, white solid); mp 60–61 °C; IR (neat): υ_{max} 2938, 2223, 1683, 1485, 1230, 1070, 822 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.00–7.96 (m,

2H), 7.55 (tt, 1H, J = 7.2, 1.5 Hz), 7.50–7.37 (m, 4H), 7.24–7.19 (m, 2H), 3.15 (t, 2H, J = 6.9 Hz), 2.53 (t, 2H, J = 6.9 Hz), 2.05 (quint, 2H, J = 7.2 Hz); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 199.4, 136.9, 132.99, 132.95, 131.4, 128.5, 128.0, 122.7, 121.7, 90.6, 80.4, 37.1, 22.9, 18.9; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{18}H_{15}BrONa$ (Br-79) 349.0199; found 349.0200.

6-(4-Methoxyphenyl)-1-phenylhex-5-yn-1-one (***4e***). Yield 379.9 mg (96%, white solid); mp 69–70 °C; IR (neat): υ_{max} 2936, 1683, 1508, 1244, 1172, 830 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02–7.98 (m, 2H), 7.56 (tt, 1H, J = 7.2, 1.2 Hz), 7.49–7.43 (m, 2H), 7.34–7.29 (m, 2H), 6.83–6.78 (m, 2H), 3.79 (s, 3H), 3.17 (t, 2H, J = 7.2 Hz), 2.53 (t, 2H, J = 6.9 Hz), 2.05 (quint, 2H, J = 6.9 Hz) ; $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 199.8, 159.1, 137.0, 133.0, 132.9, 128.6, 128.0, 115.9, 113.8, 87.6, 81.2, 55.2, 37.3, 23.3, 18.9; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{19}H_{18}O_2Na$ 301.1199; found 301.1209.

6-(3-Methoxyphenyl)-1-phenylhex-5-yn-1-one (***4f***). Yield 171.0 mg (79%, colorless oil); IR (neat): υ_{max} 2939, 1683, 1597, 1286, 1164, 687 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02–7.98 (m, 2H), 7.56 (tt, 1H, J = 7.2, 1.2 Hz), 7.49–7.43 (m, 2H) , 7.19 (t, 1H, J = 8.1 Hz), 6.98 (d, 1H, J = 7.5 Hz), 6.92–6.91 (m, 1H), 6.83 (ddd, 1H, J = 8.1, 2.4, 0.6 Hz), 3.78 (s, 3H), 3.18 (t, 2H, J = 7.2 Hz), 2.55 (t, 2H, J = 6.9 Hz), 2.06 (quint, 2H, J = 6.9 Hz); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 199.6, 159.2, 136.9, 133.0, 129.2, 128.5, 128.0, 124.7, 124.0, 116.4, 114.2, 89.2, 81.3, 55.1, 37.2, 23.1, 18.9; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{19}H_{18}O_2Na$ 301.1199; found 301.1207.

1-Phenyl-6-(4-(trifluoromethyl)phenyl)hex-5-yn-1-one (***4g***). Yield 341.5 mg (88%, white solid); mp 68–69 °C; IR (neat): υ_{max} 2897, 2220, 1682, 1327, 1119, 842 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01–7.97 (m, 2H), 7.58–7.50 (m, 3H), 7.47–7.42 (m, 4H), 3.16 (t, 2H, J = 7.2 Hz), 2.57 (t, 2H, J = 6.9 Hz), 2.08 (quint, 2H, J = 6.9 Hz); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 199.3, 136.9, 133.0, 131.7, 129.3 (d, J_{CF} = 32 Hz), 128.6, 128.0, 127.6, 125.1 (d, J_{CF} = 4 Hz), 123.9 (d, J_{CF} = 270 Hz), 92.2, 80.3, 37.1, 22.9, 18.9; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{16}F_3O$ 317.1148; found 317.1154.

6-(4-Nitrophenyl)-1-phenylhex-5-yn-1-one (***4h***). Yield 109.0 mg (55%, light yellow solid); mp 108–110 °C; IR (neat): υ_{max} 2940, 2216, 1683, 1592, 1508, 1346, 852 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (dt, 2H, J = 9.0, 2.1 Hz), 8.02–7.98 (m, 2H), 7.61–7.55 (m, 1H), 7.52–7.44 (m, 4H), 3.18 (t, 2H, J = 7.2 Hz), 2.61 (t, 2H, J = 6.9 Hz), 2.10 (quint, 2H, J = 6.9 Hz); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 199.3, 146.7, 136.9,

133.1, 132.3, 130.8, 128.6, 128.0, 123.5, 95.5, 80.0, 37.1, 22.7, 19.1; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{16}NO_3$ 294.1125; found 294.1123.

6-Phenyl-1-(o-tolyl)hex-5-yn-1-one (***4i***). Yield 236.6 mg (71%, light yellow oil); IR (neat): υ_{max} 2929, 1683, 1599, 1489, 1228, 754 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.71–7.68 (m, 1H), 7.40–7.34 (m, 3H), 7.29–7.23 (m, 5H), 3.11 (t, 2H, J = 7.2 Hz), 2.54 (t, 2H, J = 6.9 Hz), 2.51 (s, 3H), 2.03 (quint, 2H, J = 6.9 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 203.8, 137.9, 131.9, 131.5, 131.1, 128.4, 128.1, 127.6, 125.6, 123.7, 89.2, 81.4, 40.1, 23.1, 21.2, 18.8; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{19}H_{18}ONa$ 285.1250; found 285.1260.

6-Phenyl-1-(m-tolyl)hex-5-yn-1-one (***4j***). Yield 325.8 mg (88%, light yellow oil); IR (neat): υ_{max} 2938, 1682, 1586, 1490, 1251, 1156, 755 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.80–7.77 (m, 2H), 7.40–7.33 (m, 4H), 7.31–7.24 (m, 3H), 3.15 (t, 2H, J = 7.2 Hz), 2.54 (t, 2H, J = 6.9 Hz), 2.39 (s, 3H), 2.05 (quint, 2H, J = 6.9 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 199.9, 138.3, 137.0, 133.7, 131.5, 128.5, 128.4, 128.2, 127.6, 125.2, 123.8, 89.3, 81.4, 37.3, 23.2, 21.3, 18.9; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{19}H_{18}ONa$ 285.1250; found 285.1252.

1-(4-Fluorophenyl)-6-phenylhex-5-yn-1-one (***4k***). Yield 302.2 mg (75%, light yellow solid); mp49–50 °C; IR (neat): υ_{max} 2939, 1683, 1597, 1229, 1156, 756 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.05–7.98 (m, 2H), 7.39–7.35 (m, 2H), 7.32–7.25 (m, 3H), 7.16–7.08 (m, 2H), 3.15 (t, 2H, J = 7.2 Hz), 2.55 (t, 2H, J = 6.6 Hz), 2.05 (quint, 2H, J = 6.9 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 198.1, 165.7 (d, J_{CF} = 253 Hz), 133.4 (d, J_{CF} = 3 Hz), 131.5, 130.7 (d, J_{CF} = 9 Hz), 128.2, 127.7, 123.7, 115.6 (d, J_{CF} = 22 Hz), 89.2, 81.5, 37.1, 23.1, 18.9 ; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{18}H_{15}FONa$ 289.0999; found 289.0993.

1-(4-Chlorophenyl)-6-phenylhex-5-yn-1-one (***4l***). Yield 370.7 mg (92%, yellow solid); mp 79–80 °C; IR (neat): υ_{max} 2939, 1684, 1589, 1228, 1091, 755 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.93 (dt, 2H, J = 9.0, 2.4 Hz), 7.42 (dt, 2H, J = 8.7, 2,4 Hz), 7.39–7.35 (m, 2H), 7.30–7.25 (m, 3H), 3.14 (t, 2H, J = 7.2 Hz), 2.55 (t, 2H, J = 6.6 Hz), 2.05 (quint, 2H, J = 6.9 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 198.4, 139.4, 135.3, 131.5, 129.5, 128.9, 128.2, 127.7, 123.7, 89.1, 81.6, 37.2, 23.0, 18.9; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{16}ClO$ (Cl-35) 283.0884; found 283.0881.

1-(3-Chlorophenyl)-6-phenylhex-5-yn-1-one (***4m***). Yield 173.3 mg (59%, yellow oil); IR (neat): υ_{max} 2939, 1687, 1571, 1422, 1224, 1197, 755 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.87 (d, 1H, J = 8.0 Hz), 7.55–7.52 (m, 1H), 7.43–7.38 (m, 3H), 7.31–7.27 (m, 3H), 3.61 (t, 2H, J = 7.2 Hz), 2.56 (t, 2H, J = 6.8 Hz), 2.06 (quint, 2H, J = 7.2 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.4, 138.5, 134.9, 132.9, 131.5, 129.9, 128.21, 128.18, 127.7, 126.1, 123.6, 89.0, 81.6, 37.3, 23.0, 18.8; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{16}ClO$ (Cl-35) 283.0884; found 283.0884.

1-(4-Methoxyphenyl)-6-phenylhex-5-yn-1-one (***4n***). Yield 349.9 mg (92%, light yellow solid); mp 59–61 °C; IR (neat): υ_{max} 2937, 1675, 1599, 1236, 1170, 757 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.99–7.98 (m, 2H), 7.40–7.36 (m, 2H), 7.29–7.24 (m, 3H), 6.94–6.89 (m, 2H), 3.85 (s, 3H), 3.11 (t, 2H, J = 7.5 Hz), 2.54 (t, 2H, J = 6.9 Hz), 2.04 (quint, 2H, J = 6.9 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 198.2, 163.4, 131.5, 130.2, 130.0, 128.1, 127.6, 123.7, 113.6, 89.4, 81.3, 55.4, 36.8, 23.3, 18.9; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{19}O_2$ 279.1380; found 279.1383.

1-(3-Methoxyphenyl)-6-phenylhex-5-yn-1-one (***4o***). Yield 300.2 mg (79%, colorless solid); mp 62–64 °C; IR (neat): υ_{max} 2939, 1683, 1597, 1429, 1257, 1043, 755 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.58 (dt, 1H, J = 7.5, 0.9 Hz), 7.52–7.50 (m, 1H), 7.40–7.36 (m, 3H), 7.28–7.24 (m, 3H), 7.10 (ddd, 1H, J = 8.1, 2.7, 0.9 Hz), 3.83 (s, 3H), 3.16 (t, 2H, J = 7.2 Hz), 2.54 (t, 2H, J = 6.9 Hz), 2.05 (quint, 2H, J = 6.9 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 199.5, 159.8, 138.2, 131.5, 129.5, 128.2, 127.6, 123.7, 120.7, 119.4, 112.2, 89.2, 81.4, 55.3, 37.3, 23.2, 18.9; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{19}O_2$ 279.1380; found 279.1384.

1-(3,5-Dimethoxyphenyl)-6-phenylhex-5-yn-1-one (***4p***). Yield 232.1 mg (73%, colorless oil); IR (neat): υ_{max} 2939, 1683, 1592, 1205, 1153, 1153, 756, 691 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40–7.36 (m, 2H), 7.28–7.24 (m, 3H), 7.12 (d, 2H, J = 2.1 Hz), 6.64 (t, 1H, J = 2.4 Hz), 3.81 (s, 6H), 3.13 (t, 2H, J = 7.2 Hz), 2.54 (t, 2H, J = 6.9Hz), 2.04 (quint, 2H, J = 6.9 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 199.4, 160.9, 138.9, 131.5, 128.2, 127.6, 123.7, 105.9, 105.3, 89.2, 81.5, 55.5, 37.3, 23.3, 18.9; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{20}H_{20}O_3Na$ 331.1305; found 331.1316.

11-(3,4-Dimethoxyphenyl)-6-phenylhex-5-yn-1-one (***4q***). Yield 260.7 mg (93%, light yellow solid); mp 55–56 °C; IR (neat): υ_{max} 2921, 1672, 1586, 1261, 1151, 1023, 757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64

(dd, 1H, *J* = 8.4, 2.0 Hz), 7.55 (d, 1H, *J* = 1.6 Hz), 7.40–7.37 (m, 2H), 7.28–7.26 (m, 3H), 6.88 (d, 1H, *J* = 8.4 Hz), 3.95 (s, 3H), 3.92 (s, 3H), 3.14 (t, 2H, *J* = 7.2 Hz), 2.55 (t, 2H, *J* = 6.8 Hz), 2.05 (quint, 2H, *J* = 6.8 Hz); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 198.4, 153.2, 149.0, 131.5, 130.2, 128.2, 127.6, 123.8, 122.7, 110.1, 110.0, 89.4, 81.4, 56.0, 55.9, 36.8, 23.5, 19.0; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{20}H_{20}O_3Na$ 331.1305; found 331.1303.

1,7-Diphenylhept-6-yn-1-one (***6a***). Yield 277.5 mg (98%, light yellow oil); IR (neat): υ_{max} 2938, 1683, 1598, 1448, 1223, 754, 689 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, 2H, *J* = 8.0, 1.6 Hz), 7.57–7.53 (m, 1H), 7.45 (t, 2H, *J* = 8.0 Hz), 7.39–7.36 (m, 2H), 7.30–7.26 (m, 3H), 3.04 (t, 2H, *J* = 7.6 Hz), 2.48 (t, 2H, *J* = 6.8 Hz), 1.93 (quint, 2H, *J* = 7.2 Hz), 1.71 (quint, 2H, *J* = 7.2 Hz); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 200.0, 137.0, 132.9, 131.5, 128.6, 128.2, 128.0, 127.5, 123.9, 89.7, 81.0, 38.0, 28.3, 23.5, 19.3; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{19}O$ 263.1430; found 263.1436.

7-(4-Chlorophenyl)-1-phenylhept-6-yn-1-one (***6b***). Yield 301.5 mg (94%, white solid); mp 60–61 °C; IR (neat): υ_{max} 2939, 1683, 1489, 1223, 1090, 827 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99–7.95 (m, 2H) ,7.56 (tt, 1H, *J* = 7.5, 1.2 Hz), 7.48–7.43 (m, 2H), 7.31–7.28 (m, 2H), 7.26–7.22 (m, 2H), 3.04 (t, 2H, *J* = 7.2 Hz), 2.47 (t, 2H, *J* = 6.9 Hz), 1.98–1.88 (m, 2H), 1.75–1.66 (m, 2H) ; $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 199.8, 136.8, 133.4, 132.9, 132.7, 128.5, 128.4, 127.9, 122.3, 90.8, 79.9, 37.9, 28.1, 23.4, 19.2; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{18}ClO$ (Cl-35) 297.1041; found 297.1043.

General procedure for the synthesis of carbocycle-fused quinolines (5) and (7) α-Alkynylketone (**4l**) (100.9 mg, 0.3568 mmol, 1.0 equiv) was dissolved in dry DCM (10.0 mL/mmol) under argon. The solution was added $TMSN_3$ (56.8 µL, 0.4282 mmol, 1.2 equiv), followed by TfOH (37.9 µL, 0.4282 mmol, 1.2 equiv). The mixture was stirred at room temperature for 1 h. The reaction was then quenched by sat. $NaHCO_3$ and extracted with EtOAc. The combined organic layers were then washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to provide the crude product which was purified on silica gel (EtOAc/Hexane: 3:7) to yield the carbocycle-fused quinolines **5l** (72.2 mg, 72%).

9-Phenyl-2,3-dihydro-1H-cyclopenta[b]quinoline (***5a***). Yield 60.5 mg (77%, white solid); mp 133–134 °C; IR (neat): υ_{max} 2957, 1572, 1491, 1384, 763 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09–8.06 (m, 1H), 7.64–

7.59 (m, 2H), 7.55–7.43 (m, 3H), 7.40–7.34 (m, 3H), 3.24 (t, 2H, J = 7.8 Hz), 2.91 (t, 2H, J = 7.5 Hz), 2.16 (quint, 2H, J = 7.5 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 167.4, 147.8, 142.8, 136.7, 133.7, 129.3, 128.7, 128.5, 128.2, 128.0, 126.2, 125.6, 125.5, 35.2, 30.3, 23.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{16}N$ 246.1277; found 246.1287.

9-(4-Fluorophenyl)-2,3-dihydro-1H-cyclopenta[b]quinoline (***5b***). Yield 90.5 mg (76%, white solid); mp 134–135 °C; IR (neat): υ_{max} 2959, 1580, 1495, 1220, 1159, 756 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, 1H, J = 8.4 Hz), 7.65–7.57 (m, 2H), 7.41–7.31 (m, 3H), 7.26–7.18 (m, 2H), 3.23 (t, 2H, J = 7.5 Hz), 2.89 (t, 2H, J = 7.2 Hz), 2.17 (quint, 2H, J = 7.5 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 167.4, 162.5 (d, J_{CF} = 246 Hz), 147.9, 141.6, 133.8, 132.6 (d, J_{CF} = 3 Hz), 131.0 (d, J_{CF} = 8 Hz), 128.9, 128.3, 126.2, 125.6, 125.3, 115.6 (d, J_{CF} = 21 Hz), 35.2, 30.3, 23.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{15}FN$ 264.1183; found 264.1192.

9-(4-Chlorophenyl)-2,3-dihydro-1H-cyclopenta[b]quinoline (***5c***). Yield 94.4 mg (95%, white solid); mp 139–140 °C; IR (neat): υ_{max} 2957, 1602, 1487, 1381, 1088, 765 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, 1H, J = 8.1 Hz), 7.65–7.56 (m, 2H), 7.53–7.48 (m, 2H), 7.41–7.36 (m, 1H), 7.32–7.29 (m, 2H), 3.23 (t, 2H, J = 7.8 Hz), 2.89 (t, 2H, J = 7.5 Hz), 2.17 (q, 2H, J = 7.5 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 167.4, 147.9, 141.4, 135.2, 134.1, 133.7, 130.7, 128.9, 128.8, 128.3, 125.9, 125.7, 125.2, 35.1, 30.3, 23.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{15}ClN$ (Cl-35) 280.0888; found 280.0897.

9-(4-Bromophenyl)-2,3-dihydro-1H-cyclopenta[b]quinoline (***5d***). Yield 83.4 mg (76%, white solid); mp 137–138 °C; IR (neat): υ_{max} 2958, 1603, 1486, 1380, 1011, 764 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, 1H, J = 8.1 Hz), 7.66–7.56 (m, 4H), 7.38 (t, 2H, J = 7.8 Hz), 7.26–7.22 (m, 2H), 3.23 (t, 2H, J = 7.8 Hz), 2.88 (t, 2H, J = 7.2 Hz), 2.16 (quint, 2H, J = 7.2 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 167.4, 147.9, 141.3, 135.6, 133.6, 131.7, 130.9, 128.9, 128.3, 125.8, 125.7, 125.2, 122.2, 35.1, 30.2, 23.4; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{15}BrN$ (Br-79) 324.0382; found 324.0384.

9-(3-Methoxyphenyl)-2,3-dihydro-1H-cyclopenta[b]quinoline (***5f***). Yield 64.8 mg (65%, white solid); mp 148–149 °C; IR (neat): υ_{max} 2960, 1593, 1582, 1426, 1250, 1037, 760 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, 1H, J=8.4 Hz), 7.66–7.59 (m, 2H), 7.46–7.36 (m, 2H), 7.01 (ddd, 1H, J = 8.4, 2.7, 0.9), 6.96–6.89 (m, 2H), 3.85 (s, 3H), 3.23 (t, 2H, J = 7.8 Hz), 2.92 (t, 2H, J = 7.2 Hz), 2.17(quint, 2H, J = 7.8 Hz);

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 167.4, 159.6, 147.9, 142.6, 138.1, 133.6, 129.6, 128.8, 128.2, 126.2, 125.7, 125.5, 121.7, 114.9, 113.4, 55.3, 35.2, 30.3, 23.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{18}NO$ 276.1383; found 276.1395.

9-(4-(Trifluoromethyl)phenyl)-2,3-dihydro-1H-cyclopenta[b]quinoline (***5g***). Yield 58.8 mg (54%, white solid); mp 144–145 °C; IR (neat): υ_{max} 2960, 1603, 1322, 1124, 1066, 765 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, 1H, J = 8.1 Hz), 7.80 (d, 2H, J = 8.1 Hz), 7.67–7.62 (m, 1H), 7.54–7.49 (m, 3H), 7.42–7.37 (m, 1H), 3.25 (t, 2H, J = 7.5 Hz), 2.88 (t, 2H, J = 7.2 Hz), 2.19 (quint, 2H, J = 7.5 Hz); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 167.4, 147.9, 141.1, 140.6, 133.6, 130.3 (d, J_{CF} = 32 Hz), 129.7, 129.0, 128.5, 125.9, 125.7, 125.6 (d, J_{CF} = 4 Hz), 125.1, 120.5 (d, J_{CF} = 270 Hz), 35.1, 30.2, 23.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{15}F_3N$ 314.1151; found 314.1164.

9-(4-Nitrophenyl)-2,3-dihydro-1H-cyclopenta[b]quinoline (***5h***). Yield 6.1 mg (8%, white crystal); mp 141–143 °C; IR (neat): υ_{max} 2921, 1597, 1520, 1462, 1348, 766 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 (dt, 2H, J = 8.7, 2.4 Hz), 8.10 (d, 1H, J = 8.1 Hz), 7.69–7.64 (m, 1H), 7.57 (dt, 2H, J = 9.0, 2.1 Hz), 7.50–7.39 (m, 2H), 3.26 (t, 2H, J = 7.5 Hz), 2.89 (t, 2H, J = 7.5 Hz), 2.21 (quint, 2H, J = 7.5 Hz); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 167.5, 147.9, 147.7, 143.8, 140.2, 133.5, 130.4, 129.2, 128.7, 126.1, 125.3, 124.7, 123.9, 35.1, 30.2, 23.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{15}N_2O_2$ 291.1128; found 291.1131.

5-Methyl-9-phenyl-2,3-dihydro-1H-cyclopenta[b]quinoline (***5i***). Yield 57.9 mg (45%, light yellow solid); mp 159–160 °C; IR (neat): υ_{max} 2924, 1464, 1260, 1095, 1018, 799 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54–7.42 (m, 5H), 7.36–7.33 (m, 2H), 7.28–7.23 (m, 1H), 3.26 (t, 2H, J = 7.5 Hz), 2.91–2.85 (m, 5H), 2.20–2.10 (m, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 166.2, 147.0, 142.8, 137.2, 136.3, 133.1, 129.2, 128.5, 128.3, 127.7, 126.0, 124.9, 123.7, 35.4, 30.3, 23.5, 18.6; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{18}N$ 260.1434; found 260.1444.

6-methyl-9-phenyl-2,3-dihydro-1H-cyclopenta[b]quinoline (***5j***) and *8-methyl-9-phenyl-2,3-dihydro-1H-cyclopenta[b]quinoline* (***5j'***). Yield 78.7 mg (80%, ratio **5j**:**5j'**; 1.2:1.0, yellow oil); IR (neat): υ_{max} 2958, 1597, 1574, 1443, 1343, 702 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, 1H, J = 8.4 Hz, minor), 7.58 (s, 1.2H, major), 7.53–7.39 (m, 8.9H), 7.36–7.33 (m, 2.5H), 7.26–7.14 (m, 4.4H), 3.20 (t, 4.3H, J = 7.8 Hz), 2.87 (t, 2.4H, J = 7.2 Hz, major), 2.69 (t, 2H, J = 7.5 Hz, minor), 2.52 (s, 3.6H, major), 2.18–2.04 (m,

4.6H), 1.96 (s, 3H, minor); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 167.2 (major), 165.8 (minor), 149.1, 148.1, 143.3, 142.5, 141.1, 138.2, 136.9, 135.29, 135.27, 132.6, 129.2, 129.0, 128.41, 128.37, 128.1, 128.0, 127.9, 127.81, 127.77, 127.5, 127.4, 125.2, 125.0, 124.1, 35.1, 34.9, 30.6, 30.2, 24.3, 23.4, 23.1, 21.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{18}N$ 260.1434; found 260.1429.

7-Fluoro-9-phenyl-2,3-dihydro-1H-cyclopenta[b]quinoline (***5k***). Yield 82.1 mg (79%, colorless crystal); mp 112–114 °C; IR (neat): υ_{max} 2915, 1624, 1509, 1493, 1205, 831 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (dd, 1H, J = 9.0, 5.4 Hz), 7.55–7.43 (m, 3H), 7.40–7.32 (m, 3H), 7.24 (dd, 1H, J = 10.2, 2.7 Hz), 3.21 (t, 2H, J = 7.8 Hz), 2.90 (t, 2H, J = 7.2 Hz), 2.15 (quint, 2H, J = 7.5 Hz); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 166.8 (d, J_{CF} = 3 Hz), 160.1 (d, J_{CF} = 244 Hz), 144.9, 142.1 (d, J_{CF} = 5 Hz), 136.2, 134.4, 130.9 (d, J_{CF} = 9 Hz), 129.0, 128.6, 128.1, 127.0 (d, J_{CF} = 9 Hz), 117.9 (d, J_{CF} = 25 Hz), 109.1 (d, J_{CF} = 23 Hz), 34.9, 30.3, 23.4; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{15}FN$ 264.1183; found 264.1182.

7-Chloro-9-phenyl-2,3-dihydro-1H-cyclopenta[b]quinoline (***5l***). Yield 72.2 mg (72%, white solid); mp 84–85 °C; IR (neat): υ_{max} 2959, 1605, 1488, 1388, 1077, 828, 702 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, 1H, J = 8.7 Hz), 7.58–7.46 (m, 5H), 7.35–7.33 (m, 2H), 3.22 (t, 2H, J = 7.8 Hz), 2.90 (t, 2H, J = 7.5 Hz), 2.16 (quint, 2H, J = 7.5 Hz) ; $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 167.8, 146.3, 141.9, 136.0, 134.6, 131.3, 130.3, 129.1, 128.9, 128.7, 128.2, 127.0, 124.4, 35.1, 30.3, 23.4; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{15}ClN$ (Cl-35) 280.0888; found 280.0880.

6-Chloro-9-phenyl-2,3-dihydro-1H-cyclopenta[b]quinoline (***5m***). Yield 13.9 mg (20%, brown oil); IR (neat): υ_{max} 2925, 1599, 1569, 1486, 1393, 1073, 937 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, 1H, J = 2.1 Hz), 7.56–7.44 (m, 4H), 7.35–7.29 (m, 3H), 3.22 (t, 2H, J = 7.5 Hz), 2.89 (t, 2H, J = 7.2 Hz), 2.16 (quint, 2H, J = 7.5 Hz); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 168.7, 148.4, 142.7, 136.2, 133.99, 133.97, 129.1, 128.6, 128.2, 127.8, 126.9, 126.3, 124.7, 35.2, 30.2, 23.4; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{15}ClN$ 280.0888; found 280.0880.

8-Chloro-9-phenyl-2,3-dihydro-1H-cyclopenta[b]quinoline (***5m'***). Yield 17.3 mg (25%, white solid); mp 116–117 °C; IR (neat): υ_{max} 2923, 1660, 1561, 1424, 1371, 1092, 707 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (dd, 1H, J = 7.8, 1.5 Hz), 7.53–7.39 (m, 5H), 7.25–7.22 (m, 2H), 3.23 (t, 2H, J = 7.8 Hz), 2.74 (t, 2H, J = 7.5 Hz), 2.13 (quint, 2H, J = 7.8 Hz); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 167.3, 149.7, 142.4, 139.6,

137.0, 130.7, 128.9, 128.7, 128.5, 127.90, 127.85, 127.4, 123.5, 35.1, 30.8, 23.1; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{15}ClN$ (Cl-35) 280.0888; found 280.0885.

7-Methoxy-9-phenyl-2,3-dihydro-1H-cyclopenta[b]quinoline (***5n***). Yield 6.6 mg (7%, colorless crystal); mp 131–132 °C; IR (neat): υ_{max} 2955, 1602, 1507, 1495, 1226, 831 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, 1H, J = 9.0 Hz), 7.55–7.43 (m, 3H), 7.38–7.35 (m, 2H), 7.28 (dd, 1H, J = 9.3, 2.7 Hz), 6.93 (d, 1H, J = 2.7 Hz), 3.73 (s, 3H), 3.20 (t, 2H, J = 7.8 Hz), 2.87 (t, 2H, J = 7.5 Hz), 2.15 (quint, 2H, J = 7.5 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 164.9, 157.1, 143.8, 141.7, 137.0, 134.0, 130.1, 129.1, 128.6, 127.9, 127.0, 119.9, 104.4, 55.3, 34.9, 30.4, 23.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{18}NO$ 276.1383; found 276.1385.

6-Methoxy-9-phenyl-2,3-dihydro-1H-cyclopenta[b]quinoline (***5o***). Yield 51.0 mg (51%, colorless crystal); mp 138–139 °C; IR (neat): υ_{max} 2920, 1618, 1413, 1220, 1026, 711 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.53–7.41 (m, 5H), 7.36–7.32 (m, 2H), 7.03 (dd, 1H, J = 9.0, 2.7 Hz), 3.94 (s, 3H), 3.20 (t, 2H, J = 7.8 Hz), 2.87 (t, 2H, J = 7.5 Hz), 2.15 (quint, 2H, J = 7.5 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 167.6, 159.8, 149.7, 142.7, 136.9, 131.4, 129.2, 128.4, 127.9, 126.7, 121.1, 118.0, 107.3, 55.4, 35.2, 30.1, 23.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{18}NO$ 276.1383; found 276.1379.

8-Methoxy-9-phenyl-2,3-dihydro-1H-cyclopenta[b]quinoline (***5o'***). Yield 34.3 mg (34%, colorless crystal); mp 124–126 °C; IR (neat): υ_{max} 2956, 1575, 1466, 1258, 1232, 759 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.69 (dd, 1H, J = 8.4, 0.9 Hz), 7.51 (t, 1H, J = 7.8 Hz), 7.42–7.29 (m, 3H), 7.20–7.17 (m, 2H), 6.73 (d, 1H, J = 7.8 Hz), 3.41 (s, 3H), 3.19 (t, 2H, J = 7.8 Hz), 2.73 (t, 2H, J = 7.5 Hz), 2.09 (quint, 2H, J = 7.5 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 167.0, 156.6, 149.7, 142.0, 141.6, 134.7, 128.2, 127.4, 127.2, 126.2, 121.8, 117.9, 105.7, 55.4, 35.1, 30.5, 23.1; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{18}NO$ 276.1383; found 276.1382.

6,8-Dimethoxy-9-phenyl-2,3-dihydro-1H-cyclopenta[b]quinoline (***5p***). Yield 56.1 mg (63%, white solid); mp 127–128 °C; IR (neat): υ_{max} 2956, 1617, 1582, 1403, 1206, 1153, 832 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40–7.32 (m, 3H), 7.18 (d, 2H, J = 6.6 Hz), 7.07 (d, 1H, J = 2.1 Hz), 6.39 (d, 1H, J = 2.4 Hz), 3.93 (s, 3H), 3.39 (s, 3H), 3.16 (t, 2H, J = 7.8 Hz), 2.70 (t, 2H, J = 7.5Hz), 2.09 (quint, 2H, J = 7.5Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 167.1, 160.0, 157.4, 151.0, 142.4, 141.5, 132.6, 127.4, 127.2, 126.3,

113.5, 100.4, 98.5, 55.4, 55.3, 35.1, 30.3, 23.1; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{20}NO_2$ 306.1489; found 306.1486.

6,7-dimethoxy-9-phenyl-2,3-dihydro-1H-cyclopenta[b]quinoline (***5q***). Yield 51.0 mg (54%, brown solid); mp 138–139 °C; IR (neat): υ_{max} 2955, 1507, 1495, 1427, 1243, 1144, 707 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54–7.51 (m, 2H), 7.48–7.44 (m, 2H), 7.38 (d, 2H, J = 6.8 Hz), 6.90 (s, 1H), 4.03 (s, 3H), 3.77 (s, 3H), 3.19 (t, 2H, J = 7.6 Hz), 2.86 (t, 2H, J = 7.2 Hz), 2.14 (quint, 2H, J = 7.2 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.8, 151.2, 148.7, 144.6, 141.6, 137.1, 131.8, 129.0, 128.5, 127.9, 121.0, 107.7, 103.7, 56.0, 55.7, 34.9, 30.3, 23.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{20}NO_2$ 306.1489; found 306.1500.

6-(Benzyloxy)-9-phenyl-2,3-dihydro-1H-cyclopenta[b]quinoline (***5r***). Yield 26.4 mg (28%, yellow oil); IR (neat): υ_{max} 2925, 1618, 1443, 1416, 1222, 1026, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54–7.43 (m, 7H), 7.41–7.31 (m, 5H), 7.12 (dd, 1H, J = 8.8, 2.4 Hz), 5.20 (s, 2H), 3.20 (t, 2H, J = 8.0 Hz), 2.87 (t, 2H, J = 7.2 Hz), 2.15 (quint, 2H, J = 7.6 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.6, 159.0, 149.4, 143.0, 136.8, 136.6, 131.6, 129.2, 128.6, 128.5, 128.04, 127.95, 127.6, 126.8, 121.3, 118.4, 108.4, 70.1, 35.2, 30.1, 23.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{25}H_{22}NO$ 352.1696; found 352.1692.

8-(Benzyloxy)-9-phenyl-2,3-dihydro-1H-cyclopenta[b]quinoline (***5r'***). Yield 15.2 mg (16%, yellow solid); mp 139–140 °C; IR (neat): υ_{max} 2925, 1572, 1453, 1258, 1230, 1061, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, 1H, J = 7.6 Hz), 7.50 (t, 1H, J = 8.0 Hz), 7.23–7.16 (m, 7H), 7.13–7.09 (m, 1H), 6.85–6.82 (m, 3H), 4.78 (s, 2H), 3.20 (t, 2H, J = 7.6 Hz), 2.69 (t, 2H, J = 7.2 Hz), 2.09 (quint, 2H, J = 7.6 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.9, 155.6, 149.8, 142.2, 141.4, 136.2, 135.1, 128.2, 128.1, 127.41, 127.35, 127.26, 126.4, 122.0, 117.9, 106.7, 70.6, 35.1, 30.6, 23.1; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{25}H_{22}NO$ 352.1696; found 352.1690.

9-Phenyl-2,3-dihydro-1H-cyclopenta[b]quinolin-6-ol (***5r''***). Yield 25.1 mg (36%, brown solid); mp 239 °C (decomp); IR (neat): υ_{max} 2925, 1615, 1584, 1417, 1232, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54–7.40 (m, 6H), 7.31–7.29 (m, 2H), 6.91 (dd, 1H, J = 9.2, 2.0 Hz), 3.18 (t, 2H, J = 7.6 Hz), 2.83 (t, 2H, J = 7.6 Hz), 2.11 (quint, 2H, J = 7.6 HZ); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.5, 158.4, 147.8, 144.3,

136.5, 131.2, 129.2, 128.5, 128.1, 127.1, 120.6, 118.5, 108.9, 34.3, 30.0, 23.5; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{16}NO$ 262.1226; found 262.1226.

9-Phenyl-2,3-dihydro-1H-cyclopenta[b]quinolin-8-ol (***5r'''***). Yield 5.7 mg (8%, brown solid); mp 202–204 °C; IR (neat): υ_{max} 2924, 1575, 1464, 1334, 1267, 1033, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, 1H, J = 8.0 Hz), 7.60–7.49 (m, 4H), 7.44–7.41 (m, 2H), 6.86 (d, 1H, J = 7.6 Hz), 5.40 (br s, 1H), 3.21 (t, 2H, J = 8.0 Hz), 2.71 (t, 2H, J = 7.6 Hz), 2.13 (quint, 2H, J = 7.6 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.8, 152.9, 149.5, 139.4, 137.9, 134.4, 129.5, 129.2, 129.1, 128.4, 121.6, 115.6, 111.5, 35.0, 29.9, 23.1; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{16}NO$ 262.1226; found 262.1236.

9-Phenyl-1,2,3,4-tetrahydroacridine (***7a***). Yield 34.2 mg (35%, white solid); mp 137–138 °C; IR (neat): υ_{max} 2935, 1572, 1485, 1432, 1399, 759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, 1H, J = 8.4 Hz), 7.61–7.57 (m, 1H), 7.53–7.44 (m, 3H), 7.33–7.28 (m, 2H), 7.23 (d, 2H, J = 6.8 Hz), 3.20 (t, 2H, J = 6.4 Hz), 2.60 (t, 2H, J = 6.4 Hz), 1.96 (quint, 2H, J = 6.4 Hz), 1.78 (quint, 2H, J = 6.0 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.0, 146.4, 146.3, 137.1, 129.0, 128.5, 128.31, 128.27, 127.7, 126.6, 125.7, 125.3, 34.2, 28.0, 23.0, 22.9; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{18}N$ 260.1434; found 260.1432.

9-(4-Chlorophenyl)-1,2,3,4-tetrahydroacridine (***7b***). Yield 20.8 mg (21%, white solid); mp 176–177 °C; IR (neat): υ_{max} 2936, 1575, 1486, 1399, 1088, 762 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, 1H, J = 8.4 Hz), 7.64–7.58 (m, 1H), 7.53–7.49 (m, 2H), 7.36–7.30 (m, 2H), 7.20–7.16 (m, 2H), 3.20 (t, 2H, J = 6.6 Hz), 2.59 (t, 2H, J = 6.6 Hz), 2.01–1.93 (m, 2H), 1.84–1.76 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, CDCl3) δ 159.1, 146.3, 145.1, 135.5, 133.8, 130.5, 128.9, 128.47, 128.46, 128.4, 126.4, 125.6, 125.4, 34.2, 28.0, 22.9, 22.8; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{17}ClN$ (Cl-35) 294.1044; found 294.1052.

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■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra of all prepared products. This material is available free of charge via the Internet at http://pubs.acs.org/.

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