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PAPER

Copper-catalyzed dimerization fragmentation cyclization reactions of (*E*)-1-en-4-yn-3-ols as a versatile approach for the synthesis of multisubstituted 1*H*-cyclopenta[*b*]naphthalenes†

Xiang-Chuan Wang,[a] Jie Hu,[a] Peng-Shuai Sun,[a] Mei-Jin Zhong,[a] Shaukat Ali[a] and Yong-Min Liang*[a,b]

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An intermolecular condensation reaction of 1,3,5-triarylenynols catalyzed by copper is developed. This reaction is a straightforward method for the synthesis of highly conjugated 1*H*-cyclopenta[*b*]naphthalene. Fluorescent properties have been determined for some of the products.

Introduction

As multifunctional molecules, indene moieties are key substructures in both targets and building blocks for various biologically active molecules[1] and functional materials, such as fluorescent materials.[2] Consequently, much attention has been paid to the synthesis of indene derivatives. In this context, it is relevant that Tian and co-workers reported the regioselective $FeCl_3$-catalyzed synthesis of structurally diverse indene derivatives from readily accessible *N*-benzylic sulfonamides and disubstituted alkynes.[3] In the same year, Chatterjee and Roy reported the Ir–Sn-catalyzed propargylic alcohols to substituted indenes.[4] The one-step synthesis of highly conjugated carbon-rich indenes, π-electron-rich species which have special chemical and physical properties,[5] has been rarely reported.

In the context of our ongoing efforts to synthesise indene derivatives,[6] we found that the 1-en-4-yn-3-ol substrate might be perfect in a domino process.[7] We envisioned that (*E*)-1,3,5-triphenylpent-1-en-4-yn-3-ol derivatives could realize an isomerization/Friedel–Crafts type reaction and [4 + 2] cyclization to afford highly conjugated carbon-rich indenes in the presence of a Lewis acid. Herein, we report a Cu(I)-catalyzed tandem isomerization/Friedel–Crafts reaction/[4 + 2] cyclization to give cyclopenta[*b*]naphthalenes. In this reaction, several new carbon–carbon bonds were achieved, along with one carbon–carbon bond cleavage.

Results and discussion

We started by using 0.5 mmol of (*E*)-1,3,5-triphenylpent-1-en-4-yn-3-ol **1a** and 5 mol% of CuOTf in $MeNO_2$ at 80 °C and achieved a 92% yield of the desired product 1*H*-cyclopenta[*b*]naphthalene **2a** after 1 h (Table 1, entry 1). In an attempt to accelerate this transformation, the amount of catalyst was increased to 10 mol%, but the yield of the desired product was reduced to 84%. We then reduced CuOTf to 2 mol%, but this also reduced the yield. Using $Cu(OAc)_2$, $CuBr_2$, $Cu(OTf)_2$ and $CuSO_4$ as catalysts, slightly lower yields of **2a** were obtained (Table 1, entries 4–7). $Cu(acac)_2$ or CuBr was completely ineffective (Table 1, entries 8 and 9). Other Lewis acids and Brønsted acids did not give an improved result (Table 1, entries 10–15). Solvents, such as CH_3CN, CH_2Cl_2, toluene and THF, were also tested in the presence of CuOTf, however, no superior result was obtained (Table 1, entries 16–19). Thus, enynol **1a** (0.5 mmol), CuOTf (5 mol%) and CH_3NO_2 (5 mL) at 80 °C under Ar atmosphere was chosen as the standard conditions.

Under the optimized reaction conditions, various enynols bearing different aryl substituents were then subjected to this condensation reaction. All reactions were complete within 3 h in moderate to high yields (76–92%), as shown in Table 2. Substrates bearing electron-donating aryl substituents (Table 2, entries 2–4) reacted smoothly to give the expected products in high yields. When electron-withdrawing groups (Table 2, entries 5–7) were employed, slightly lower yields were obtained. When either R^2 or R^3 in **1** was an electron-donating group (Table 2, entries 8–9) the reaction gave a slightly lower yield. But when R^2 or R^3 in **1** is an electron-withdrawing group (Table 2, entries 10–15) the desired products were afforded in good yields. In order to expand the substrate scope, enynols with 2-thienyl, 2-furyl and 2-naphthyl substituents were also tested. As can be seen in Scheme 1, the expected highly conjugated products were isolated in moderate to high yields (52–95%)

Considering the highly conjugated structure obtained by our method, we assumed that these products might be useful in fluorescent materials chemistry.[8] We then tested the fluorescent properties for product **2a**, **2p**, **1q**, **2r**, **2s** and **3n** (Table 3). As illustrated in Fig. 1, the absorption band near the UV region shows strong fluorescence. The compounds thus prepared emitted blue light when excited at 365 nm (Fig. 2). It makes them extremely useful for sensing and labeling purposes. The fluorescence quantum yields of

[a]*State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou, 730000, P. R. China. E-mail: liangym@lzu.edu.cn; Fax: 0086-931-8912582*
[b]*Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Science, Lanzhou, 730000, P.R. China*
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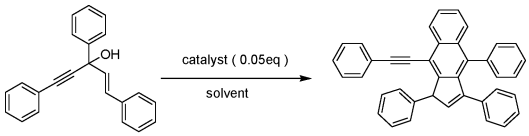
Table 1 Optimization of the reaction conditions[a]

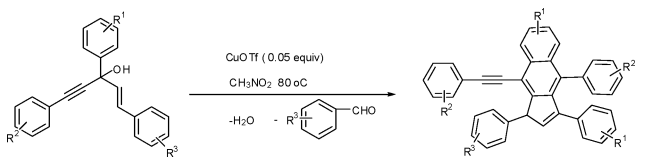


1a **2a**

Entry	Catalyst	Solvent	T/h	Yield (%)[b]
1	CuOTf	CH_3NO_2	1.5	92
2	CuOTf (10%)	CH_3NO_2	1.5	92
3	CuOTf (2%)	CH_3NO_2	1.5	92
4	$Cu(OAc)_2$	CH_3NO_2	2	85
5	$CuBr_2$	CH_3NO_2	2	78
6	$CuSO_4$	CH_3NO_2	2	72
7	$Cu(OTf)_2$	CH_3NO_2	2	81
8	$Cu(acac)_2$	CH_3NO_2	2	N.R.[c]
9	CuBr	CH_3NO_2	2	N.R.[c]
10	$ZnCl_2$	CH_3NO_2	3	65
11	$FeCl_3$	CH_3NO_2	2	71
12	$TiCl_4$	CH_3NO_2	0.5	Trace
13	$BF_3{\cdot}Et_2O$	CH_3NO_2	1	30
14	TsOH	CH_3NO_2	5	38
15	TsOH	CH_3NO_2	5	38
16	CuOTf	CH_3CN	3	86
17	CuOTf	CH_2Cl_2	4	51
18	CuOTf	toluene	2	45
19	CuOTf	THF	3	40

[a] *Reaction conditions*: enynol **1a** (0.5 mmol), catalyst (5 mol%) and solvent (5 mL) at 80 °C under Ar atmosphere. [b] Isolated yield. [c] No Reaction.

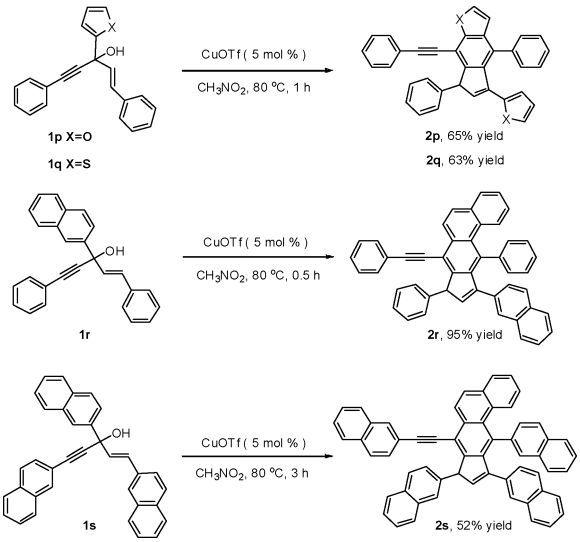
Table 2 Copper-Catalyzed condensation of various enynols[a]



Entry	Products	T/h	Yield (%)[b]
1	**2a** $R^1 = R^2 = R^3 = H$	1.5	92
2	**2b** $R^1 = p\text{-}CH_3$, $R^2 = R^3 = H$	2	88
3	**2c** $R^1 = p\text{-}OCH_3$, $R^2 = R^3 = H$	1.5	84
4	**2d** $R^1 = p\text{-}NHAc$, $R^2 = R^3 = H$	1	86
5	**2e** $R^1 = p\text{-}F$, $R^2 = R^3 = H$	1	88
6	**2f** $R^1 = p\text{-}Cl$, $R^2 = R^3 = H$	2	76
7	**2g** $R^1 = p\text{-}Br$, $R^2 = R^3 = H$	2	80
8	**2h** $R^1 = H$, $R^2 = R^3 = o\text{-}CH_3$	2	77
9	**2i** $R^1 = H$, $R^2 = R^3 = p\text{-}CH_3$	1.5	76
10	**2j** $R^1 = H$, $R^2 = R^3 = o\text{-}Cl$	2.5	82
11	**2k** $R^1 = H$, $R^2 = R^3 = p\text{-}Cl$	1.5	88
12	**2l** $R^1 = H$, $R^2 = R^3 = p\text{-}Br$	2	86
13	**2m** $R^1 = R^2 = H$, $R^3 = p\text{-}CN$	2	90
14	**2n** $R^1 = R^2 = H$, $R^3 = p\text{-}NO_2$	2	92
15	**2o** $R^1 = p\text{-}Cl$, $R^2 = p\text{-}CH_3$, $R^3 = p\text{-}NO_2$	2	91

[a] *General conditions*: enynol **1** (0.5 mmol), CuOTf (5 mol%), and CH_3NO_2 (5 mL) at 80 °C under Ar. [b] Isolated yield.

these products were found to be up to 0.66, which is much higher than for many known fluorescent compounds. It indicates that these compounds are good candidates for fluorescent materials. For example, **2n** can react with amino acids after a simple functional transformation (Scheme 2). Specific recognition properties by the target biomolecules are essential for the development of sensitive fluorescence-based probes[9]



Scheme 1 Cu(I)-Catalyzed condensation cyclization reaction of enynols.

Table 3 Selected photophysical parameters of compounds

Compound	λ_{exc}[a]	λ_{em}[b]	$\Delta\lambda$[c]	Φ_f[d]
2a	360	400	40	0.43
2p	333	393	60	0.08
2q	339	395	57	0.11
2r	372	401	29	0.25
2s	366	416	50	0.66
3n	348	399	51	0.22

[a] Excitation wavelength. [b] Emission wavelength. [c] Stokes shift, computed as $\Delta\lambda = \lambda_{exc} - \lambda_{em}$. [d] Fluorescence quantum yield CH_2Cl_2 at 25 °C.

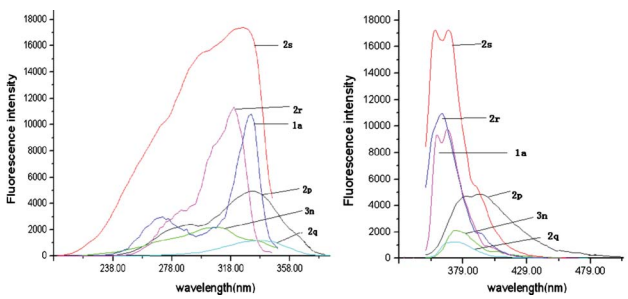


Fig. 1 Fluorescence excitation and emission spectrum for **2a**, **2p**, **1q**, **2r**, **2s** and **3n** in CH_2Cl_2 (1×10^{-5} M) at 293 K.

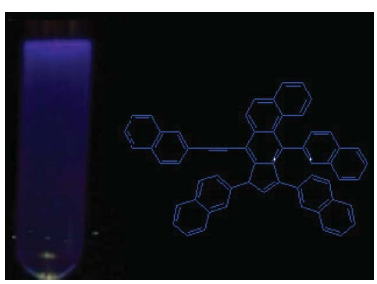
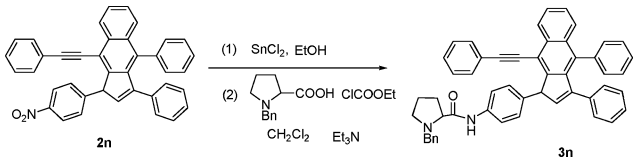
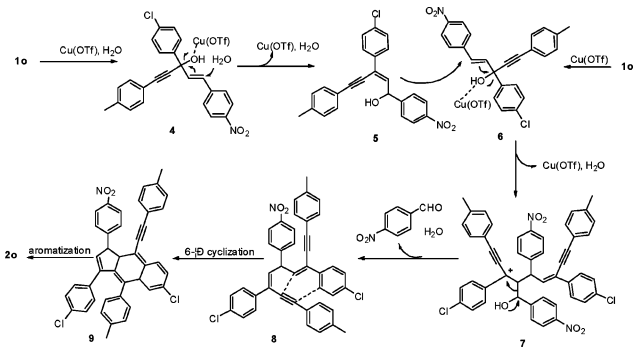


Fig. 2 Compound **2s** emitted blue light when excited at 365 nm.

Based on the above experimental results, a plausible mechanism for the Cu-catalyzed tandem reactions is proposed (Scheme 3). Initially, **1o** undergoes a rearrangement to furnish the intermediate



Scheme 2 Reaction of compound **2n** with amino acids.



Scheme 3 Plausible mechanism.

5.[10] Coordination of the other **1o** to the copper catalyst gives complex **6**. Then, electrophilic addition of the allylic cation center of **6** to enynol **5** gives the propargylic carbocation **7** and CuOTf is released for the next catalytic cycle. Subsequently, **7** undergoes a stereoselective Grob fragmentation to furnish the intermediate **8** along with elimination of R^3PhCHO.[11] Then [4 + 2] cyclization and aromatization reaction gives the final product.[12]

Conclusions

In summary, we have developed a novel intermolecular condensation reaction of 1,3,5-triarylenynols catalyzed by copper, which involves dimerization fragmentation and 6-π cyclization and aromatization. This reaction is a straightforward method for the synthesis of highly conjugated aromatic 1*H*-cyclopenta[*b*]naphthalenes. These products are extremely useful in materials chemistry.

Experimental section

General remarks

Column chromatography was carried out on silica gel. ^{1}H NMR spectra were recorded on 400 MHz in $CDCl_3$ and ^{13}C NMR spectra were recorded on 100 MHz in $CDCl_3$ using TMS as internal standard. IR spectra were recorded on a FT-IR spectrometer and only major peaks are reported in cm^{-1}. Melting points were determined on a microscopic apparatus and were uncorrected. All new compounds were further characterized by element analysis; copies of their ^{1}H NMR and ^{13}C NMR spectra are provided.

General procedure 1: Synthesis of 1,3,5-triaryl-1-en-4-yn-3-ols[10]

1a: silica gel column purification with hexane/ethyl acetate (10/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75–7.75 (m, 2H), 7.50–7.48 (m, 2H), 7.47–7.33 (m, 4H), 7.28–7.22 (m, 7H), 7.01–6.97 (d, J = 16 Hz, 2H), 6.99–6.93 (d, J = 16 Hz, 2H), 3.19 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$ ppm): δ 143.6, 136.3, 133.1, 132.2, 132.0, 129.2, 128.8, 128.7, 128.5, 128.5, 128.1, 128.1, 127.1, 126.1, 122.5, 90.2, 87.6, 73.39. IR (neat, cm^{-1}): 2867, 1594, 1432, 1220, 1021, 732. Anal. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85. Found: C, 89.09; H, 5.81.

1b: silica gel column purification with hexane/ethyl acetate (10/1, v/v);^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.4 Hz, 2H), 7.25–7.60 (m, 12H), 7.06 (d, J = 16 Hz, 1H), 6.52 (d, J = 16 Hz, 1H), 2.85 (brs, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 140.5, 137.6, 136.1, 133.0, 131.7, 129.0, 128.80, 128.4, 128.2, 127.8, 126.8, 125.7, 122.4, 90.1, 87.2, 73.0, 21.0. IR (neat, cm^{-1}): 2862, 1548, 1401, 1236, 1031, 698. Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.93; H, 6.16.

1c: silica gel column purification with hexane/ethyl acetate (10/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77–7.76 (m, 2H), 7.75–7.60 (m, 2H), 7.50–7.48 (m, 2H), 7.41–7.30 (m, 6H),7.09–7.05 (d, J = 16 Hz, 1H), 7.00–6.98 (m, 2H), 6.57–6.53 (d, J = 16 Hz, 1H), 3.85 (s, 3H), 3.22 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 159.1, 136.1, 135.6, 133.0, 131.7, 128.7, 128.537, 128.4 128.3, 128.2, 127.1, 126.8, 122.3, 113.6, 90.1, 87.2, 72.7, 55.2. IR (neat, cm^{-1}): 2912, 1521, 1392, 1190, 1019, 765. Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.59; H, 5.88.

1d: silica gel column purification with hexane/ethyl acetate (10/1, v/v); ^{1}H NMR (400 MHz, acetone): δ 9.25 (s, 1H), 7.83–7.70 (m, 1H), 7.56–7.07 (m, 3H), 7.56–7.54 (m, 2H), 7.50–7.45 (m, 2H), 7.40–7.39 m, 3H), 7.35–7.31 (m, 2H), 7.26–7.24 (m, 2H), 7.04–7.00 (d, J = 16 Hz, 1H), 6.57–6.53 (d, J = 16 Hz, 1H), 5.62 (brs, 1H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, acetone, ppm): δ 168.1, 143.4, 139.4, 138.9, 136.7, 134.4, 131.5, 128.6, 127.7, 126. 7, 126.3, 122.9, 118.8, 91.4, 86.1, 72.1, 23.4. IR (neat, cm^{-1}): 3059, 2989, 1498, 1384, 1179, 1002, 796. Anal. Calcd for $C_{25}H_{21}NO_2$: C, 81.72; H, 5.76; N, 3.81. Found: C, 81.61; H, 5.78, N, 3.86.

1e: silica gel column purification with hexane/ethyl acetate (10/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.80–7.79 (m, 2H), 7.61–7.58 (m, 2H), 7.49–7.46 (m, 2H), 7.42–7.31 (m, 5H), 7.15–7.11 (t, J = 8 Hz, 2H), 7.03 (d, J = 16 Hz, 1H), 6.47 (d, J = 16 Hz, 1H), 3.28 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 163.7, 161.3, 139.4, 139.4, 136.1, 132.9, 131.9, 129.4, 128.9, 128.7, 128.5, 128.2, 127.9, 127.9, 127.1, 122.3, 115.4, 115.2, 89.9, 87.8, 72.9. IR (neat, cm^{-1}): 3021, 1708, 1472, 1079, 1019, 765. Anal. Calcd for $C_{23}H_{17}O$ F: C, 84.12; H, 5.22. Found: C, 84.21; H, 5.26.

1f: silica gel column purification with hexane/ethyl acetate (10/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.08–8.07 (d, J = 1.6 Hz, 1H), 7.63–7.61 (m, 2H), 7.61–7.50 (m, 3H), 7.42–7.31 (m, 9H), 7.19–7.15(d, J = 16 Hz, 1H), 6.72–6.69 (d, J = 16 Hz, 1H), 3.61 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ139.7, 136.0, 132.2, 131.6, 131.2, 130.4, 129.5, 129.1, 128.5, 128.1, 127.4, 126.8, 126.8, 122.3, 88.9, 86.9, 72.0. IR (neat, cm^{-1}): 3026, 1721, 1452, 1076, 1032, 785. Anal. Calcd for $C_{23}H_{17}OCl$: C, 80.11; H, 4.97. Found: C, 80.18; H, 4.96.

1g: silica gel column purification with hexane/ethyl acetate (10/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.64–7.62 (d, J = 8.4 Hz, 1H), 7.47–7.45 (m, 2H), 7.38–7.34(m, 7H), 7.22–7.16 (m, 3H), 6.97–6.93(d, J = 16 Hz, 1H), 6.39–6.35 (d, J = 16 Hz, 1H), 3.40 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ141.9, 135.8, 133.6, 132.4, 131.7, 129.5, 128.7, 128.6, 128.5, 128.4, 128.3, 128.3, 128.0, 127.3, 126.9, 122.0, 89.5, 87.7, 72.7. IR (neat, cm^{-1}): 3054, 1703, 1439, 1055, 1022, 799. Anal. Calcd for $C_{23}H_{17}OBr$: C, 70.96; H, 4.40. Found: C, 71.01; H, 4.46.

1h: silica gel column purification with hexane/ethyl acetate (10/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.82–7.80 (d, J = 8.4 Hz, 1H), 7.50–7.45 (m, 4H), 7.38–7.35 (m, 3H), 7.21–7.16

(m, 4H), 7.06–7.02 (d, J = 16 Hz, 1H), 6.49–6.45 (d, J = 16 Hz, 1H), 2.81(brs, 1H), 2.42 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 143.5, 138.7, 137.7, 133.3, 131.9, 131.6, 131.6, 129.2, 129.0, 129. 7, 128.9, 128.5, 128.3, 127.8, 126.8, 126.7, 125.8, 119.2, 89.3, 87.6, 73.3, 21.4, 21.2 IR (neat, cm^{-1}): 2985, 1717, 1398, 1025, 985, 785. Anal. Calcd for $C_{25}H_{22}O$: C, 88.72; H, 6.55. Found: C, 88.65; H, 6.59.

1i: silica gel column purification with hexane/ethyl acetate (10/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.85–7.83 (d, J = 15.6 Hz, 1H), 7.51–7.37 (m, 7H), 7.22–7.18 (m, 4H), 7.09–7.05(d, J = 15.6 Hz, 1H), 6.51–6.48 (d, J = 15.6 Hz, 1H), 2.93(brs, 1H), 2.43 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ143.5, 138.8, 137.7, 133.3, 131.9, 131.6, 129.2, 129.0, 128.9, 128.4, 127.8, 126.8, 125.8, 119.2, 89.3, 87.6, 73.3, 21.5, 21.2. IR (neat, cm^{-1}): 3015, 1720, 1418, 1025, 985, 735. Anal. Calcd for $C_{25}H_{22}O$: C, 88.72; H, 6.55. Found: C, 88.69; H, 6.51.

1j: silica gel column purification with hexane/ethyl acetate (10/1, v/v);^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.85–7.83 (d, J = 7.6 Hz, 2H), 7.54–7.54 (d, J = 1.6 Hz, 1H), 7.53–7.37 (m, 4H), 7.36–7.35 (m, 2H), 7.30–7.23 (m, 4H), 6.96–6.92 (d, J = 15.6 Hz, 1H), 6.501–6.46 (d, J = 15.6 Hz, 1H), 3.20 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 142.9, 138.0, 134.6, 134.3, 134.1, 131.7, 130.0, 129.8, 129.7, 129.1, 128.6, 128.3, 128.0, 127.9, 126.8, 125.8, 125.2, 123.9, 91.0, 86.2, 73.1. IR (neat, cm^{-1}): 3038, 1761, 1432, 1001, 962, 712. Anal. Calcd for $C_{23}H_{16}OCl_2$: C, 72.83; H, 4.25. Found: C, 72.79; H, 4.21.

1k: silica gel column purification with hexane/ethyl acetate (10/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.87–7.85 (d, J = 4.8 Hz, 1H), 7.48–7.45 (m, 2H), 7.37–7.35 (m, 3H), 7.28–7.24 (m, 4H), 7.21–7.19 (m, 1H), 7.02–6.98 (d, J = 16 Hz, 1H), 6.50–6.46 (d, J = 16 Hz, 1H), 3.40 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 138.5, 135.835, 134.215, 133.1, 131.6, 130.8, 129.9, 128.7, 128.5, 128.4, 128.2, 128.1, 126.9, 122.1, 88.5, 87.1, 71.6. IR (neat, cm^{-1}):3031, 1758, 1429, 1012, 965, 694. Anal. Calcd for $C_{23}H_{16}OCl_2$: C, 72.83; H, 4.25. Found: C, 72.76; H, 4.28.

1l: silica gel column purification with hexane/ethyl acetate (10/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.77–7.73 (m, 2H), 7.51–7.49 (m, 3H), 7.46–7.40 (m, 6H), 7.29–7.27 (d, J = 8.8 Hz, 2H), 6.94–6.90(d, J = 16 Hz, 1H), 6.47–6.43 (d, J = 16 Hz, 1H), 2.85 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 142.9, 135.0, 133.3, 133.3, 133.0, 131.7, 131.7, 128.6, 128.5, 128.3, 128.1, 125.9, 125.8, 123.2, 121.9, 121.2, 90.8, 86.6, 73.2. IR (neat, cm^{-1}):3029, 1765, 1398, 1003, 945, 672. Anal. Calcd for $C_{23}H_{16}OBr_2$: C, 59.00; H, 3.44. Found: C, 58.95; H, 3.38.

1m: silica gel column purification with hexane/ethyl acetate (10/1, v/v);^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.80–7.79 (d, J = 4.4, 2H), 7.56–7.54 (d, J = 7.6 Hz, 4H), 7.46–7.38 (m, 8H), 7.05–7.01 (d, J = 15.6 Hz, 1H), 6.62–6.58 (d, J = 15.6 Hz, 1H), 3.45 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 142.7, 140.6, 136.5, 132.1, 131.6, 128.7, 128.4, 128.3, 128.1, 127.2, 126.9, 125.7, 121.9, 118.7, 110.7, 89.2, 87.7, 72.8. IR (neat, cm^{-1}): 3023, 1708, 1426, 1003, 672. Anal. Calcd for $C_{24}H_{17}NO$: C, 85.94; H, 5.11; N, 4.18. Found: C, 85.89; H, 5.17; N, 4.23.

1n: silica gel column purification with hexane/ethyl acetate (10/1, v/v);^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.17–8.15 (d, J = 8.4, 2H), 7.80–7.76 (m, 2H), 7.57–7.52 (m, 4H), 7.46–7.42 (m, 2H), 7.38–7.35 (m, 4H), 7.09–7.05 (d, J = 15.6 Hz, 1H), 6.54–6.61 (d, J = 15.6 Hz, 1H), 3.20 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 147.0, 142.7, 142.8, 137.4, 131.7, 128.9, 128.7, 128.6, 128.4, 128.3, 127.4, 126.6, 125.8, 123.8, 121.9, 89.1, 87.9, 73.0. IR (neat, cm^{-1}): 3029, 1740, 1471, 1203, 1075, 672. Anal. Calcd for $C_{23}H_{17}NO_3$: C, 77.73; H, 4.82; N, 3.94. Found: C, 77.69; H, 4.85; N, 3.89.

1o: silica gel column purification with hexane/ethyl acetate (10/1, v/v);^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.22(s, 1H), 8.09–8.06 (m, 1H), 7.70–7.68 (d, J = 8.8 Hz, 3H), 7.48–7.36 (m, 5H), 7.18–7.16 (d, J = 8 Hz, 4H), 7.04–7.00 (d, J = 15.6 Hz, 1H), 6.56–6.52 (d, J = 15.6 Hz, 1H), 3.26 (brs, 1H), 2.38(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.3, 141.4, 139.2, 137.7, 135.6, 133.9, 132.7, 131.6, 129.4, 129.1, 128.9, 128.6, 127.3, 126.7, 122.5, 121.4, 118.6, 88.3, 88.1, 72.5, 21.5. IR (neat, cm^{-1}): 3062, 1801, 1462, 1185, 1023, 705. Anal. Calcd for $C_{24}H_{18}ClNO_3$: C, 71.38; H, 4.49; N, 3.47. Found: C, 71.26; H, 4.52; N, 3.41.

1p: silica gel column purification with hexane/ethyl acetate (10/1, v/v);^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.59–7.57 (m, 2H), 7.51–7.49 (d, J = 3.6 Hz, 3H), 7.39–7.30 (m, 6H), 7.13–7.09 (d, J = 16 Hz, 1H), 6.68–6.64 (d, J = 16 Hz, 1H), 6.59–6.58 (d, J = 3.2 Hz, 1H), 6.42–6.40 (m, 1H), 3.55 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 154.5, 142.9, 135.9, 131.9, 131.8, 131.8, 130.8, 129.2, 128.7, 128.5, 128.5, 128.3, 128.0, 126.9, 125.8, 122.0, 110.3, 107.1, 87.7, 86.5, 68.5. IR (neat, cm^{-1}): 3012, 1719, 1401, 1064, 962, 691. Anal. Calcd for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 83.95; H, 5.41.

1q: silica gel column purification with hexane/ethyl acetate (10/1, v/v);^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.64–7.63 (m, 2H), 7.62–7.53 (m, 2H), 7.51–7.34 (m, 8H), 7.19–7.13 (d, J = 15.6 Hz, 1H), 7.08–7.06 (m, 1H), 6.68–6.65 (d, J = 15.6 Hz, 1H), 3.31 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.4, 135.8, 131.8, 131.7, 129.4, 128.7, 128.5, 128.3, 128.90, 126.9, 126.7, 125.8, 124.8, 121.9, 89.2, 86.7, 70.4. IR (neat, cm^{-1}):3009, 1703, 1415, 1035, 978, 645. Anal. Calcd for $C_{21}H_{16}OS$: C, 79.71; H, 5.10. Found: C, 79.65; H, 5.11.

1i: silica gel column purification with hexane/ethyl acetate (10/1, v/v);^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.31(s, 1H), 7.95–7.91 (m, 4H), 7.64–7.62(m, 2H), 7.61–7.54 (m, 2H), 7.49–7.47 (m, 2H), 7.42–7.27 (m, 6H), 7.16–7.12 (d, J = 15.6 Hz, 1H), 6.63–6.59 (d, J = 15.6 Hz, 1H), 3.07 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 140.7, 136.2, 133.2, 133.1, 132.8, 131.9, 129.6, 128.8, 128.7, 128.5, 128.5, 128.4, 128.1, 127.7, 127.1, 126.4, 126.3, 124.4, 124.4, 122.4, 90.0, 87.8, 73.5. IR (neat, cm^{-1}): 2975, 1707, 1385, 1015, 979, 765. Anal. Calcd for $C_{27}H_{20}O$: C, 89.97; H, 5.59. Found: C, 90.03; H, 5.61.

1s: silica gel column purification with hexane/ethyl acetate (10/1, v/v);^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.71(s, 1H), 8.07–8.05(m, 1H), 7.89–7.87 (m, 1H), 7.78–7.76 (m, 2H), 7.70–7.64 (m, 7H), 7.50–7.41 (m, 1H), 7.40–7.28 (m, 9H), 7.20–7.16 (d, J = 16 Hz, 1H), 6.78–6.74 (d, J = 16 Hz, 1H), 2.95 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 138.0, 134.7, 133.6, 133.5, 133.2, 133.0, 132.9, 132.8, 131.7, 131.0 130.3, 129.6, 128.8, 128.3, 128.2, 128.0, 128.0, 127.8, 127.7, 127.6, 127.2, 126.8, 126.7, 126.5, 126.3, 126.0, 125.6, 125.5, 125.0, 124.1, 123.8, 119.7, 90.9, 88.4, 73.2. IR (neat, cm^{-1}):2965, 1718, 1379, 1020, 962, 755. Anal. Calcd for $C_{35}H_{24}O$: C, 91.27; H, 5.25. Found: C, 91.23; H, 5.29.

General procedure for the preparation of 2

To a solution of 1,3,5-triaryl-1-en-4-yn-3-ol derivatives **1** (0.50 mmol) in CH_3NO_2 (5.0 mL) was added 5 mmol% CuOTf

at 80 °C under Ar. When the reaction was considered complete, as determined by TLC analysis, the reaction mixture was quenched by addition of saturated aqueous NH_4Cl and diluted with ethyl ether (40 mL), washed with water, saturated brine, dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford the corresponding 1*H*-cyclopenta[*b*]naphthalenes **2a–2s**

2a: silica gel column purification with hexane/ethyl acetate (100/1, v/v);, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.39–8.37 (d, J = 12.8 Hz, 1H), 7.65–7.64 (m, 1H), 7.45–7.44 (m, 1H), 7.43–7.16 (m, 9H), 7.10–7.06 (m, 4H), 7.05–7.04 (m, 2H), 6.98–6.85 (m, 2H), 6.84–6.74 (m, 2H), 6.51–6.50 (d, J = 2.4 Hz, 1H), 5.04–5.03 (d, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 149.2, 143.9, 142.4, 140.3, 138.1, 135.9, 135.0, 133.7, 132.3, 132.2, 132.0, 131.7, 131.5, 131.2, 131.1, 130.3, 129.4, 129.3, 128.8, 128.5, 128.5, 128.3, 127.7, 127.6, 127.6, 127.2, 127.1, 126.8, 126.7, 125.6, 123.0, 116.5, 99.5, 85.0, 55.0. IR (neat, cm^{-1}): 3062, 1708, 1592, 1076, 755. Anal. Calcd for $C_{39}H_{26}$: C, 94.70; H, 5.30. Found: C, 94.76; H, 5.25.

2b: silica gel column purification with hexane/ethyl acetate (100/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.48–8.46(m, 1H), 7.67 (s, 1H), 7.56–7.32(m, 11H), 7.27–7.12(m, 4H), 6.85–6.79 (m, 4H), 6.56–6.55 (d, J = 2.4 Hz, 1H), 5.04–5.03(d, J = 2.4 Hz, 1H), 2.35 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.5, 145.3, 141.0, 139.7, 139.0, 136.9, 135.5, 135.3, 134.0, 132.9, 132.6, 131.5, 131.3, 131.2, 130.2, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.6, 127.2, 126.5, 126.4, 125.8, 125.7, 123.5, 116.1, 98.7, 85.9, 54.9, 21.8, 21.1. IR (neat, cm^{-1}):2923, 1693, 1445, 820, 735. Anal. Calcd for $C_{41}H_{30}$: C, 94.21; H, 5.79. Found: C, 94.28; H, 5.71.

2c: silica gel column purification with hexane/ethyl acetate (100/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.37–7.22 (m, 12H), 7.16–7.02(m, 6H), 6.84–6.82 (d, J = 8.8 Hz,, 9H), 6.05 (s, 1H), 5.08–5.07 (d, J = 2.4 Hz, 1H), 3.76 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 157.7, 147.3, 144.8, 141.3, 140.1, 139.1, 136.9, 134.1, 132.1, 131.4, 131.2, 131.1, 129.4, 129.1, 128.5, 128.4, 128.4, 128.2, 127.4, 127.3, 127.3, 126.7, 126.5, 123.5, 117.5, 112.7, 106.1, 98.7, 85.9, 55.2, 55.1, 54.8. IR (neat, cm^{-1}):2926, 1598, 1498, 1071, 755, 696. Anal. Calcd for $C_{41}H_{30}O_2$: C, 88.78; H, 5.45. Found: C, 88.71; H, 5.39.

2d: silica gel column purification with hexane/ethyl acetate (100/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.45–8.43(d, J = 8.8 Hz, 1H), 7.94–7.91(m, 1H), 7.60(s, 2H), 7.37–7.26 (m, 9H), 7.12–7.00 (m, 6H), 7.00–6.88 (m, 5H),6.53–6.52 (d, J = 2 Hz, 1H), 5.08 (d, J = 2.4 Hz, 1H), 2.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 168.5, 148.5, 145.2, 141.9, 140.0, 138.8, 136.8, 136.6, 136.02 133.2, 132.5, 131.5, 131.2, 131.2, 129.1, 128.6, 128.5, 128.3, 128.3, 128.1, 127.4, 127.4, 127.1, 127.0, 126.9, 126.7, 126.0, 123.4, 120.0, 116.2, 115.6, 99.1, 85.6, 55.0, 29.7. IR (neat, cm^{-1}):2924, 1654, 1486, 1073, 755, 697. Anal. Calcd for $C_{43}H_{32}ON_2$: C, 84.84; H, 5.30; N, 4.60. Found: C, 84.81; H, 5.30; N, 4.52.

2e: silica gel column purification with hexane/ethyl acetate (100/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.54–8.50 (m, 1H), 7.47–7.32 (m, 12H), 7.23–7.21 (m, 1H), 7.16–7.13 (m, 3H), 7.07–7.05 (m, 1H), 6.90–6.88 (m, 2H), 6.86–6.64 (m, 2H), 6.57–6.56 (d, J = 2 Hz, 1H), 5.11–5.10 (d, J = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 162.6, 162.3, 160.1, 159.9, 148.4, 144.1, 142.3, 140.3, 138.4, 136.2, 134.2, 134.1, 132.6, 132.6, 132.5, 132.4, 131.7, 131.5, 131.1, 131.0, 130.7, 129.7, 129.7, 128.9, 128.8, 128.6, 128.5, 128.4, 128.3, 128.3, 127.9, 127.7, 127.6, 127.5, 127.2, 126.9, 126.8, 123.2, 116.5, 115.9, 115.6, 114.1, 114.0, 113.9, 113.8, 110.6, 110.4, 99.4, 85.3, 55.0. IR (neat, cm^{-1}):2926, 1614, 1508, 1248, 71034, 697. Anal. Calcd for $C_{39}H_{24}F_2$: C, 88.28; H, 4.56. Found: C, 88.31; H, 4.61.

2f: silica gel column purification with hexane/ethyl acetate (100/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.29–8.26 (d, J = 8.8 Hz, 1H), 7.545–7.540 (d, J = 2 Hz, 1H), 7.34–7.31 (m, 1H), 7.31–7.16 (m, 5H), 7.13–7.07 (m, 7H), 6.97–6.95 (m, 3H), 6.94–6.93 (m, 1H), 6.76–6.74 (d, J = 8 Hz, 2H), 6.64–6.62 (d, J = 8 Hz, 2H), 6.383–6.378 (d, J = 2 Hz, 2H), 4.915–4.91 (d, J = 2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 149.2, 143.9, 142.4, 140.3, 138.1, 135.9, 135.0, 133.7, 132.3, 132.2, 132.1, 131.5, 131.1, 131.1, 130.3, 129.3, 128.5, 128.5, 128.5, 128.2, 127.6, 127.6, 127.6, 127.2, 126.8, 126.8, 126.7, 125.6, 123.1, 116.5, 99.6, 85.1, 55.1. IR (neat, cm^{-1}): 3056, 1458, 1377, 1248, 756, 697. Anal. Calcd for $C_{39}H_{24}Cl_2$: C, 83.12; H, 4.29. Found: C, 83.15; H, 4.21.

2g: silica gel column purification with hexane/ethyl acetate (100/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.40–8.38 (d, J = 8.8 Hz, 1H), 7.90 (s, 1H), 7.66–7.63 (m, 1H), 7.63–7.25 (m, 11H), 7.17–7.02(m, 5H), 6.64–6.62 (d, J = 8.4 Hz, 2H), 6.57–6.56 (d, J = 2 Hz, 2H), 5.09–5.08 (d, J = 2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 149.4, 143.9, 142.3, 140.2, 138.0, 135.8, 135.5, 134.1, 132.2, 131.5, 131.1, 131.1, 130.5, 130.2, 129.6, 129.3, 128.8, 128.6, 128.5, 128.5, 128.4, 128.3, 127.7, 127.6, 127.6, 127.2, 126.8, 123.1, 120.6, 120.2, 116.6, 99.7, 85.0, 55.1. IR (neat, cm^{-1}):3023, 1599, 1490, 1027, 732, 696. Anal. Calcd for $C_{39}H_{24}Br_2$: C, 71.80; H, 3.71. Found: C, 71.86; H, 3.68.

2h: silica gel column purification with hexane/ethyl acetate (100/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.51–8.49 (d, J = 8 Hz, 1H), 7.80–7.78 (d, J = 8.4 Hz, 1H), 7.57–7.53 (m, 1H), 7.41–7.30(m, 2H), 7.23–7.19 (m, 4H), 7.14–7.12 (m, 2H), 7.04–6.84 (m, 9H), 6.52–6.51 (d, J = 2.4 Hz, 2H), 5.09–5.08 (d, J = 2.4 Hz, 1H), 2.42 (s, 3H), 2.36 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 149.6, 145.1, 141.4, 139.8, 138.3, 137.0, 136.3, 136.1, 135.6, 133.7, 133.0, 132.7, 131.9, 131.6, 131.4, 131.1, 131.0, 129.1, 129.0, 128.8, 128.5, 128.3, 128.2, 128.0, 127.8, 127.8, 126.9, 126.8, 125.8, 125.7, 125.7, 125.4, 120.5, 116.2, 99.1, 85.2, 54.6, 21.6, 21.1, 21.09. IR (neat, cm^{-1}): 2924, 1600, 1488, 1092, 755, 700. Anal. Calcd for $C_{42}H_{32}$: C, 93.99; H, 6.01. Found: C, 94.05; H, 6.07.

2i: silica gel column purification with hexane/ethyl acetate (100/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.47–8.45 (d, J = 8.4 Hz, 1H), 7.59–7.75 (m, 1H), 7.47–7.44 (m, 1H), 7.38–7.36 (m, 2H), 7.26–7.23 (m, 4H), 7.19–7.17 (m, 1H), 7.10–6.87 (m, 9H), 6.57 (s, 1H), 5.12 (s, 1H), 2.46 (s, 3H), 2.41 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 149.4, 145.2, 141.4, 139.6, 138.2, 137.0, 136.3, 136.0, 135.7, 133.7, 133.7, 133.0, 132.8, 131.9, 131.5, 131.4, 131.1, 131.0, 129.0, 129.0, 128.5, 128.2, 127.8, 127.8, 126.9, 126.8, 125.8, 125.7, 125.4, 120.5, 116.2, 99.2, 54.6, 21.5, 21.1, 21.1. IR (neat, cm^{-1}):3026, 1617, 1446, 1027, 819, 732. Anal. Calcd for $C_{42}H_{32}$: C, 93.99; H, 6.01. Found: C, 93.94; H, 5.95.

2j: silica gel column purification with hexane/ethyl acetate (100/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.47–8.45 (d, J = 8 Hz, 1H), 7.70–7.67 (m, 1H), 7.67–7.59 (m, 1H), 7.57–7.46 (m, 1H), 7.44–7.30 (m, 6H), 7.13–7.00 (m, 9H), 6.97–6.93 (m, 2H), 6.51–6.50 (d, J = 1.6 Hz, 2H), 5.04–5.03 (d, J = 2 Hz,

1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.7, 145.5,140.7, 139.4, 138.2, 136.2, 134.2, 133.4, 132.5, 132..0, 131.8, 131.4, 131.4, 131.3, 129.8,129.5, 129.3, 129.2, 128.7, 128.6, 127.9, 127.3, 127.2, 127.1, 126.4, 126.3, 125.8, 124.7, 116.4, 98.0, 86.4, 54.5. IR (neat, cm^{-1}):2924, 1600, 1488, 1092, 825, 700. Anal. Calcd for $C_{39}H_{23}Cl_3$: C, 78.34; H, 3.88. Found: C, 78.39; H, 3.92.

2k: silica gel column purification with hexane/ethyl acetate (100/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.45–8.43 (d, J = 8.4 Hz, 1H), 7.70–7.68 (d, J = 8.4 Hz, 1H), 7.60–7.57 (m, 1H), 7.46–7.42 (m, 2H), 7.30–7.26 (m, 5H), 7.20–7.13 (m, 2H), 7.02–6.95 (m, 5H), 6.87–6.85 (m, 2H), 6.50–6.49 (d, J = 2 Hz, 2H), 5.05–5.04 (d, J = 2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.8, 145.3, 140.9, 139.6, 137.2, 136.3, 134.9, 134.5, 133.1, 132.6, 132.6, 132.5, 132.4, 132.1, 131.8, 130.8, 129.8, 128.9, 128.7, 128.6, 128.6, 128.3, 128.2, 127.4, 127.34, 127.3, 126.5, 126.3, 126.3, 126.2, 125.8, 121.6, 116.3, 98.3, 86.3, 54.2. IR (neat, cm^{-1}): 2854, 1644, 1446, 1074, 756, 698. Anal. Calcd for $C_{39}H_{23}Cl_3$: C, 78.34; H, 3.88. Found: C, 78.29; H, 3.91.

2l: silica gel column purification with hexane/ethyl acetate (100/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.44–8.42 (d, J = 8.4 Hz, 1H), 7.70–7.68 (m, J = 8.8 Hz, 1H), 7.59–7.51 (m, 3H), 7.42–7.40 (m, 3H), 7.20–7.13 (m, 7H), 7.00–6.97 (m, 3H), 6.90–6.84 (m, 3H), 6.49–6.48 (d, J = 2.4 Hz, 2H), 5.03–5.02 (d, J = 2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.7, 145.4, 140.8, 139.6, 137.8, 136.3, 135.4, 132.9, 132.8, 132.7, 132.5, 132.1, 131.8, 131.7, 131.6, 131.5, 130.4, 130.3, 130.2, 128.2, 127.4, 126.5, 126.3, 126.3, 126.2, 125.8, 122.8, 122.0, 121.4, 120.4, 116.4, 98.4, 86.5, 54.4. IR (neat, cm^{-1}): 3026, 1598, 1491, 1028, 760, 696. Anal. Calcd for $C_{39}H_{23}Br_3$: C, 64.05; H, 3.17. Found: C, 64.01; H, 3.23.

2m: silica gel column purification with hexane/ethyl acetate (100/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.50–8.48(d, J = 8.4 Hz, 1H), 7.75–7.73 (d, J = 8.4 Hz, 1H), 7.60–7.56 (m, 3H), 7.46–7.36 (m, 8H), 7.15–7.00 (m, 5H), 7.00–6.89 (m, 4H), 6.47–6.46 (d, J = 2.4 Hz, 2H), 5.14–5.13 (d, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.0, 146.7, 145.1, 139.7, 139.0, 136.4, 133.9, 133.0, 132.3, 132.0, 131.3, 131.2, 129.4, 128.7, 128.5, 128.1, 127.4, 127.3, 127.2, 127.1, 127.0, 125.9, 123.0, 119.0, 116.6, 110.4, 99.5, 85.4, 54.8. IR (neat, cm^{-1}): 2854, 1460, 1376, 1073, 757, 696. Anal. Calcd for $C_{40}H_{25}N$: C, 92.46; H, 4.85; N, 2.70. Found: C, 92.41; H, 4.81; N, 2.63.

2n: silica gel column purification with hexane/ethyl acetate (100/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.52–8.50 (d, J = 8.4 Hz, 1H), 8.18–8.16 (d, J = 8.4 Hz, 2H), 7.77–7.75 (m, 1H), 7.59–7.57 (m, 1H), 7.47–7.38 (m, 8H), 7.17–7.00 (m, 6H), 6.99–6.90 (m, 4H), 6.48–6.47 (d, J = 2 Hz, 2H), 5.19–5.18 (d, J = 2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.0, 147.3, 146.9, 146.9, 139.5, 138.9, 136.3, 134.0, 133.1, 132.0, 131.3, 131.2, 131.2, 129.4, 128.7, 128.5, 128.1, 127.4, 127.4, 127.3, 127.1, 127.0, 126.4, 125.9, 123.7, 123.0, 116.7, 99.5, 85.5, 54.5. IR (neat, cm^{-1}): 2924, 1489, 1312, 1028, 803, 724. Anal. Calcd for $C_{39}H_{25}NO_2$: C, 86.80; H, 4.67; N, 2.60. Found: C, 86.72; H, 4.76; N, 2.52.

2o: silica gel column purification with hexane/ethyl acetate (100/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.42–8.41(d, J = 8.4 Hz, 1H), 8.21–8.22 (m, 1H), 8.11–8.10 (d, J = 1.2 Hz, 1H), 7.76–7.61 (m, 1H), 7.61–7.40 (m, 1H), 7.35–7.34 (m, 4H), 7.24–7.22 (m, 1H), 7.18–7.16 (m, 4H), 6.99–6.92 (m, 5H), 6.89–6.77 (m, 3H), 6.50–6.49 (d, J = 2.4 Hz, 1H), 5.15–5.18 (d, J = 2.4 Hz, 1H), 2.40 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.4, 147.7, 145.7, 141.0, 140.1, 139.9, 139.2, 137.6, 134.7, 134.5, 134.2, 134.0, 133.0, 132.6, 132.4, 132.3, 131.2, 131.0, 130.9, 130.4, 129.4, 129.2, 129.1, 128.60, 128.3, 127.6, 127.0, 125.8, 123.8, 122.0, 119.5, 116.7, 100.3, 84.1, 54.4, 21.5, 21.1. IR (neat, cm^{-1}): 2924, 1710, 1261, 1030, 802, 697. Anal. Calcd for $C_{41}H_{27}Cl_2NO_2$: C, 77.36; H, 4.28; N, 2.20. Found: C, 77.32; H, 4.21; N, 2.23.

2p: silica gel column purification with hexane/ethyl acetate (100/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.34–7.28 (m, 14H), 7.23–7.18 (m, 4H), 7.00–6.98 (m, 1H), 6.67–6.66 (d, J = 2.4 Hz, 2H), 6.59–6.57 (m, 1H), 6.30–6.28 (m, 1H), 5.03–5.028 (d, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 147.7, 142.2, 139.3, 138.1, 137.8, 137.4, 131.7, 131.6, 130.0, 130.0, 128.7, 128.5, 128.2, 127.4, 127.0, 126.8, 126.6, 125.9, 124.5, 123.8, 123.1, 113.4, 98.3, 85.1, 54.7. IR (neat, cm^{-1}): 2922, 1489, 1260, 1094, 800, 694. Anal. Calcd for $C_{35}H_{22}O_2$: C, 88.58; H, 4.67. Found: C, 88.71; H, 4.69.

2q: silica gel column purification with hexane/ethyl acetate (100/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.365–7.25 (m, 14H), 7.22–7.18 (m, 4H), 6.99–6.98 (d, J = 4.4 Hz, 2H), 6.66–6.65 (d, J = 2 Hz, 2H), 6.58–6.56 (m, 1H), 6.29–6.28 (d, J = 3.2 Hz, 1H), 5.02–5.01 (d, J = 2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 147.6, 142.2, 140.7, 139.3, 138.1, 137.9, 137.8, 137.4, 131.7, 131.6, 131.6, 130.0, 128.7, 128.4, 128.2, 127.4, 126.9, 126.9, 126.8, 126.6, 125.9, 124.5, 123.8, 123.0, 113.4, 98.3, 85.1 54.7. IR (neat, cm^{-1}): 2960, 1447, 1226, 1029, 862, 731. Anal. Calcd for $C_{35}H_{22}S_2$: C, 82.97; H, 4.38. Found: C, 82.89; H, 4.41.

2r: silica gel column purification with hexane/ethyl acetate (100/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.60–8.58 (m, 1H), 7.88–7.86 (d, J = 8.4 Hz, 2H), 7.78–7.76 (d, J = 8.4 Hz, 2H), 7.67–7.66 (m, 1H), 7.48–7.33 (m, 16H), 7.27–7.26 (m, 1H), 7.17–7.16 (m, 1H), 7.07–7.06 (d, J = 7.2 Hz, 1H), 7.00–6.96(m, 1H), 6.89 (s, 1H), 6.83–6.81 (m, 1H), 6.72 (s, 1H), 6.64 (s, 1H), 5.17–5.16 (d, J = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 149.2, 145.7, 142.4, 141.4, 140.0, 138.3, 135.7, 134.5, 133.7, 132.6, 132.1, 131.5, 128.6, 128.5, 128.3, 128.2, 127.7, 127.3, 126.9, 126.7, 126.7, 126.4, 125.6, 125.4, 125.3, 124.7, 124.4, 123.4, 117.2, 99.1, 86.2, 54.8. IR (neat, cm^{-1}): 3079, 1598, 1491, 1073, 760, 696. Anal. Calcd for $C_{47}H_{30}$: C, 94.92; H, 5.08. Found: C, 94.96; H, 5.05.

2s: silica gel column purification with hexane/ethyl acetate (100/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.58–8.56 (d, J = 8 Hz, 1H), 8.05 (s, 1H), 7.87–7.77 (m, 7H), 7.69–7.62 (m, 1H), 7.60–7.40 (m, 16H), 7.40–7.25 (m, 2H), 6.90–6.87 (m, 2H), 6.62–6.57 (m, 4H), 5.34–5.33 (d, J = 2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 149.2, 145.6, 141.2, 136.4, 133.8, 132.9, 132.8, 132.7, 132.6, 132.3, 132.0, 131.4, 129.1, 128.3, 128.2, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6, 127.7, 127.4, 126.9, 126.8, 126.8, 126.7, 126.6, 126.4, 126.1, 126.0, 126.0, 125.7, 125.65, 125.6, 125.5, 120.5, 116.7, 99.7, 85.9, 55.3. IR (neat, cm^{-1}): 3058, 1642, 1449, 1028, 911, 760. Anal. Calcd for $C_{47}H_{30}$: C, 95.13; H, 4.87. Found: C, 95.02; H, 4.93.

Typical procedure for synthesis of 3n and characterization data of 3n

To a solution of **2n** (1.07 g 2 mmol) in EtOH (20 mL) was added 2 eq $SnCl_2$ at 50 °C. When the reaction was considered complete, as determined by TLC analysis, the reaction mixture was quenched by addition 20% NaOH and diluted with ethyl ether (40 mL), washed with water, saturated brine, dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified

by chromatography on silica gel to afford the corresponding reaction intermediate (773 mg, yield 76%).

1-Benylpyrrolidione-2-carboxylic acid (307 mg, 1.5 mmol) was dissolved in CH_2Cl_2 (10 ml) and cooled to −15 °C. Et_3N was added (151 mg, 1.5 mmol), followed by ethyl chloroformate (162 mg, 1.5 mmol). The suspension was stirred for 30 min, then the reaction intermediate from the first step (509 mg, 1 mmol) was added and stirring was continued for 6 h. the reaction mixture was quenched by addition of water and diluted with CH_2Cl_2 (100 mL), washed with water, saturated brine, dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford corresponding compounds **3n** (591 mg, yield 85%).

3n: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.40–9.38 (d, J = 8.8 Hz, 1H), 8.48–8.46 (d, J = 8 Hz, 1H), 7.69–7.67 (d, J = 8.4 Hz, 1H), 7.53–7.41 (m, 5H), 7.37–7.21 (m, 12H), 7.10–6.85 (m, 10H), 6.46–6.45 (d, J = 2 Hz, 1H), 5.06–5.05 (d, J = 2 Hz, 1H), 3.92–3.89 (m, 1H), 3.57–3.53 (m, 1H), 3.33–3.29 (m, 1H), 3.10–3.08 (m, 1H), 2.45–2.40 (m, 1H), 2.30–3.24 (m, 1H), 2.02–1.98 (m, 1H), 1.78–1.72 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 172.6, 149.4, 145.4, 141.5, 139.4, 138.5, 138.4, 136.9, 136.7, 136.4, 134.4, 133.3, 132.9, 132.0, 131.6, 131.58, 131.3, 131.2, 129.2, 128.7, 128.67, 128.3, 128.2, 127.5, 127.3, 126.8, 126.9, 126.0, 125.9, 119. 5, 116.4, 99.3, 85.8, 68.0, 60.1, 54.5, 54.1, 30.8, 24.3. IR (neat, cm^{-1}): 3062, 1708, 1592, 1076, 761, 732. Anal. Calcd for $C_{51}H_{40}N_2O$: C, 87.90; H, 5.79; N, 4.02. Found: C, 87.82; H, 5.76; N, 4.07.

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