2,2,4,6-Tetraaryl-2H-benzo[h]chromenes: the influence of electronic communication between aryl substituents on their photochromism

Stuart Aiken, Georgina K. Armitage, Orlando D. C. C. de Azevedo, Daniel, L. Crossley, Rhianne Dobson, Christopher D. Gabbutt, B. Mark Heron, Denis Jacquemin, Craig R. Rice and Nicola Soltowska

*a Department of Chemical Sciences, School of Applied Sciences, University of Huddersfield, Queensgate, Huddersfield, HD1 3DH, UK

Email: o.carvalhocoutodeazevedo2@hud.ac.uk

Email: m.heron@hud.ac.uk

b Université de Nantes, CNRS, CEISAM UMR 6230, Nantes, France.

Email: Denis.Jacquemin@univ-nantes.fr

Highlights

- A series of 2,2,4,6-tetraaryl-2H-benzo[h]chromenes have been succinctly synthesised by two complementary strategies.
- The most efficient route employed the Suzuki cross-coupling reaction of arylboronic acids to 6-bromo-2,2,4-triaryl-2H-benzo[h]chromenes.
- Photochromism was observed for the tetraarylbenzochromenes which possessed a strong aryl withdrawing group at C-4 and a strong aryl donor group at C-6.
- Inverting the electronic nature of the C-4 and C-6 aryl groups switched off the photochromism in favour of fluorescence.
Abstract – A series of photochromic 2,2,4,6-tetraaryl-2H-benzo[h]chromenes have been efficiently synthesised by two complementary strategies employing the condensation of 1,1,3-triarylprop-2-yn-1-ols with 4-substituted 1-naphthols and Suzuki cross-coupling chemistry. The novel 1,1,3-triarylpropynols were readily obtained either by the addition of an arylacetylide to the requisite benzophenones or by a Sonogashira coupling of a halobenzene with a preformed 1,1-diarylprop-2-yn-1-ol. The tetraarylbenzochromenes which possessed a strong electron withdrawing aryl moiety at C-4 exhibited good room temperature photochromism. The combination of a strong electron donating aryl group at C-6 with a strong electron withdrawing aryl group at C-4 resulted in the generation of a photomerocyanine which exhibited two absorption bands in the visible region of the electromagnetic spectrum, rather than one broad band when the C-6 aryl group was only weakly electron donating. Remarkably inverting the electronic nature of the C-4 and C-6 aryl groups resulted in the inhibition of photochromism and instead led to fluorescence. TD-DFT calculations were used to rationalise the shift from photochromism to fluorescence.

**Keywords:** 2H-benzo[h]chromene, 2H-naphtho[1,2-b]pyran, photochromism, Suzuki cross-coupling, propynol, fluorescence.
Introduction

The phenomenon of photochromism has attracted significant academic and commercial attention over the last few decades.[1-4] Perhaps the most widespread and commercially successful photochromic systems are those which incorporate the diaryl-2H-pyran moiety [5-7] which is typically fused to a naphthalene ring to afford the benzochromenes (naphthopyrans) 1 and 2; though fusion to other carbocycles to afford polycyclic 2H-pyran containing systems e.g. 3 – 8, is widespread (Figure 1).[8-13] The fusion of the 2H-pyran unit to heterocyclic ring systems has also attracted attention in the search for attractive photochromic properties.[6]

![Figure 1: Selected examples of pyran containing photochromic systems](image)

The photochromic response of pyran derived systems, illustrated for the most commonly encountered commercially significant 2H-benzo[h]chromene and 3H-benzo[f]chromene units (Figure 2), stems from the electrocyclic ring-opening – ring-closing of the 2H-pyran unit to generate a mixture of transient photomerocyanine isomers; the hue and persistence of which can be controlled by judicious placement of substituents.[5,6]
Figure 2: Reversible electrocyclic ring-opening of the 2\textit{H}-pyran unit to form isomeric photomerocyanines

There has been a significant amount of interest in substitution effects which impact upon the formation and persistence of the various isomeric photomerocyanines. In particular, for the 2\textit{H}-benzo[\textit{h}]chromene system, academic studies have revealed that substitution at the 5-position [14-17] and 5,6-positions [18] offer significant improvement in the fading of the photomerocyanines. An extensive series of 2\textit{H}-benzo[\textit{h}]chromenes have been prepared by Coelho et al., in which the 4,5-positions have been linked with either carbocyclic rings [19-22] or with a lactone unit [23-25] and which offer much improved rates of fade of the photomerocyanines and retain good colourability. We have previously prepared selected examples of substituted 2\textit{H}-benzo[\textit{h}]chromenes which possess an aryl group at C-4; the location of which significantly impacts upon the photochromic response, [26-29] and in this current work we were keen to explore the synergistic influence of aryl substituents at C-4 and C-6 upon the photochromic response of the 2\textit{H}-benzo[\textit{h}]chromenes 9 (Figure 3). A thorough examination of the literature has revealed that there is only one example of a 2,2,4,6-tetraaryl-2\textit{H}-benzo[\textit{h}]chromene which was isolated as a by-product (6%), resulting from nucleophilic displacement of an activated 6-methoxy group with phenyllithium, and was studied no further.[22] The aryl substituents Ar\textsubscript{3} and Ar\textsubscript{4} of 9 are in conjugation in the photomerocyanines and thus their electronic characteristics are expected to have a marked influence on both the hue and persistence of the photomerocyanines 10 and 11. Furthermore, the steric demands of Ar\textsubscript{3} in the photomerocyanine pentadienone chain will additionally impact upon the photochromic response of 9.
Results and Discussion

The synthesis of the 2H-benzo[h]chromenes 9 can be accomplished by two complementary strategies. In the first route, Route A, commercially available 4-bromo-1-naphthol is condensed with a 1,1,3-triarylprop-2-yn-1-ol 12 to afford the 6-bromo-2,2,4-triaryl-2H-benzo[h]chromenes 13 into which the fourth aryl group can be subsequently introduced by a late-stage Suzuki cross-coupling with a commercially available arylboronic acid to afford 9. The alternative route, Route B, relies upon an initial Suzuki cross-coupling to 4-bromo-1-naphthol to afford the 4-aryl-1-naphthols 14 which can then undergo ‘chromenization’ with a 1,1,3-triarylprop-2-yn-1-ol 12 to afford 9 (Scheme 1). Given our experience concerning the synthesis of triaryl substituted 2H-benzo[h]chromenes [27,28] and Suzuki cross-couplings to bromo substituted benzochromenes [29-32] we elected to initially examine Route A with the late-stage Suzuki cross-coupling reaction.
The 1,1,3-triarylprop-2-yn-1-ols **12** required for this study were prepared by either the addition of an arylethynyllithium, from *n*-butyllithium and the requisite substituted ethynylbenzene, to a benzophenone or, where the substituent on the ethynylbenzene was incompatible with *n*-butyllithium, by a Sonogashira coupling reaction [33,34] between a halobenzene and a preformed 1,1-diarylprop-2-yn-1-ol **15** (Scheme 2).[28,29] The benzophenones of choice were either 4,4′-dimethoxybenzophenone or 2,4,4′-trimethoxybenzophenone; the latter provides for a benzochromene in which one of the C-2 aryl groups contains an ortho-methoxy substituent, a feature which has proven beneficial for increasing the half-life of the photomerocyanines.[35-37]

The addition of the arylethynyllithium to the benzophenones proceeded smoothly to afford propynols **12a** – **12h** in generally good to excellent yields (Scheme 2). Of note is that the addition of the arylethynyllithium to the more sterically congested carbonyl function of 2,4,4′-trimethoxybenzophenone proceeded in lower yields (52 – 85%) and required lengthy reaction times. Obtaining the pyridyl substituted analogue **12h** (16%) was particularly problematic as a consequence of commencing from 4-ethynylpyridine hydrochloride which required prior *in situ* neutralisation with excess *n*-BuLi. The diarylpropynols **15a**, b were isolated in excellent yield by the addition of lithium trimethylsilylacetylide to the benzophenones with subsequent base-mediated unmasking of the terminal alkyne function according to literature procedures.[28,32] Propynols **12i** – **12k** were obtained in typically excellent yields by the Sonogashira coupling protocol. The ¹H NMR spectra of the new triaryl substituted propynols **12a** – **c** and **k** exhibited a singlet at *ca.* δ 3.8 assigned to the equivalent MeO groups and an exchangeable signal at δ 2.8 due to the tertiary OH group. The remaining propynols **12d** – **j** derived from 2,4,4′-trimethoxybenzophenone typically exhibited a singlet at δ 2.8 accounting for two MeO groups with a second singlet in this chemical shift region accounting for the o-MeO group in their ¹H NMR spectra. The presence of the o-MeO group in close proximity to the OH group resulted in a downfield shift of the OH signal to *ca.* δ 4.8 as a consequence of H-bonding. The acetylenic C-atoms resonated at *ca.* δ 86 and δ 92 in the ¹³C NMR spectra.
Scheme 2: Preparation of 1,1,3-triarylprop-2-yn-1-ol precursors

With the range of propynols to hand their acid-catalysed reaction with 4-bromo-1-naphthol was investigated. A variety of acidic catalysts and solvent systems have been employed to prepare benzochromenes with the most widely used examples being pyridinium-p-toluenesulfonate (PPTS) with (MeO)₃CH in 1,2-DCE under reflux [38], p-toluenesulfonic acid in refluxing toluene [37] or acidic alumina in refluxing PhMe [28]. Thus, refluxing a solution of 12a (1 eq.) with 4-bromo-1-naphthol (1 eq.) containing PPTS (5 mol%), (MeO)₃CH (2 eq.) in 1,2-DCE gave the 6-bromo-2H-benzo[h]chromene 16a in 38% yield after column chromatography. A second component was isolated from the reaction mixture and characterised as the known α,β-unsaturated ketone 17a (27%) resulting from a Meyer-Schuster rearrangement of 12a.[28] Key evidence to support the formation of 17a was accrued from ¹H NMR spectroscopy which exhibited a singlet at δ 6.13 (3-H) and ¹³C NMR spectroscopy which revealed a signal at δ 82.9
(C-2), the chemical shifts of which were in good agreement with reported NMR data.[6] The signal for 5-H was obscured by the signals for the other aromatic protons. The signals furthest downfield in the $^1$H NMR spectrum were assigned to 10-H (ca. $\delta$ 8.4), peri- to the pyran ring O-atom, and 7-H (ca. $\delta$ 8.1) peri- to the bromine atom. Applying the foregoing reaction conditions with the remaining series of propynols 12b – g and 12i – k afforded the bromobenzochromenes 16b – j in 33 – 55% yield after column chromatography (Scheme 3). No bromobenzochromene could be obtained from the reaction between 12h and 4-bromo-1-naphthol.

Fortuitously, 16c crystallised as translucent yellow crystals from the column chromatography eluent (20% EtOAc / n-hexane) and the crystals (P21/c space group) were suitable for examination by X-ray crystallography (Figure 4). The pyran ring was puckered with the C-2 – C-3 unit out of plane with the remaining naphthalene moiety. The bond angle between the C-2 geminal aryl rings is 108.1 $^\circ$ in accord with the sp$^3$ hybridisation of C-2. The C-4 aryl unit is twisted out of the plane of the naphthalene ring, with a torsion angle of 48.9 $^\circ$ [C12-C13-C14-C15 (crystallographic atom numbering)], thereby minimising steric interactions between the

Scheme 3: Preparation of 6-bromo-2H-benzo[h]chromene intermediates

![Scheme 3: Preparation of 6-bromo-2H-benzo[h]chromene intermediates](image-url)
ortho protons of the CF₃C₆H₄ ring and 5-H. Full lists of bond angles and bond lengths together with a ‘checkcif’ file can be accessed from the Cambridge Crystallographic Data Centre using reference number CCDC2092387.

Figure 4: X-ray crystal structure of bromobenzochromene 16c (thermal ellipsoids shown at 50% probability level)

In previous work, we have performed many Suzuki cross-coupling reactions on a wide range of either bromo- or trifluoromethoxy- substituted benzochromenes with a multitude of boronic acids and derivatives.[30-32, 39] Recently, we revealed that the choice of cross-coupling conditions, particularly the base, was critical for an efficient, clean cross-coupling reaction. A competing base-mediated ring-contraction of the benzochromene unit to afford a naphthofuran was observed and conditions were optimised such that either selective cross-coupling or ring-contraction could be achieved.[29] Thus heating a solution [PhMe/anhyd. EtOH (1:1)] containing 6-bromobenzochromene 16a (1.0 eq.), 4-methoxyphenylboronic acid (1.5 eq.), Pd(PPh₃)₄ (5 mol%) and KF (1.9 eq.) under nitrogen for ca. 20 h gave the tetraarylbenzochromene 18a in 73% yield after elution from silica with neat dichloromethane; pleasingly there was no evidence of naphthofuran formation (Scheme 4). The ¹H NMR spectrum of 18a exhibited the expected singlet for 3-H at δ 6.16 and a singlet was now resolved for 5-H at δ 7.13. The chemical shift of 10-H remained largely unaffected by the introduction of the C-6 aryl group and resonated at δ 8.51, whereas 7-H was now shifted upfield by ca. 0.3 ppm, relative to that in the bromo-precursor 16a, to resonate at δ 7.80 as a consequence of its proximity to the aromatic ring current of the C-6 aryl group. The C-2 aryl methoxy substituents are equivalent and afford a singlet at δ 3.78 and the remaining methoxy group resonated at δ 3.85. C-2 of the pyran ring again resonated in the expected region at ca. δ 8.3.
Employing the foregoing Suzuki cross-coupling reaction conditions to the remaining series of bromobenzochromenes 16 with a variety of arylboronic acids afforded an extensive array of analogues 18b – v in generally very good to excellent yields (Scheme 4 and Scheme 5).

![Scheme 4: Preparation of 4,6-diaryl substituted 2,2-bis(4-methoxyphenyl)-2H-benzo[h]chromenes 18a – g](image)

Surveying the $^1$H NMR data for the series 18a – v reveals that 3-H resonates in the range δ 6.1 – 6.5 and 5-H in the range δ 6.9 – 7.3, with the chemical shifts varying in accord with the electronic nature of the adjacent aryl groups at C-4 and C-6, respectively. The ca. 0.3 ppm upfield shift in the signal for 7-H upon replacement of the bromine substituent with the aryl group was apparent and 7-H resonated at ca. δ 7.8. The signal for 10-H resonated as expected at ca. δ 8.5. The presence of the nitrophenyl moiety [18g, r – t and 18w (Scheme 6)] was evidenced by a low field signal integrating for 2H at δ 8.26 due to the H-atoms ortho to the NO$_2$ group. NMR spectra ($^1$H, $^{13}$C and $^{19}$F) along with mass spectral data for the tetraarylbenzochromenes are presented in the electronic supplementary information.
The overall yield for the two-step conversion 4-bromo-1-naphthol → 16 → 18 ranged from 19% (16c, 18e combination) to 44% (16f, 18k combination).

Reagents: (i) Pd(PPh₃)₄ (5 mol%), KF (1.9 eq), PhMe/anhyd. EtOH (1:1), N₂, reflux
We thought it worthwhile to also examine the alternative strategy (Route B, Scheme 1) which involves initial Suzuki cross-coupling of 4-bromo-1-naphthol with the appropriate boronic acid to afford a 4-aryl-1-naphthol which is then condensed with a propynol 12 to afford the benzochromene 18.

Thus, stirring a mixture of 4-bromo-1-naphthol (1 eq.), 4-methoxyphenylboronic acid (1.5 eq.) in aqueous NaOH solution containing Pd(OAc)$_2$ (2.7 mol%) at room temperature under air gave naphthol 19a in 47% yield. Using the identical reaction conditions with phenylboronic acid similarly gave 19b in 47% yield (Scheme 6).

The chromenization of naphthol 19a with propynol 12d gave 18i in 44% yield which had identical physical and spectroscopic properties to the same material obtained by Route A. A marginally improved yield of 50% was obtained for 18w from 19b and 12i. The NMR spectral data for 18i and 18w was comparable with that for the other members of the series of 18 obtained via Route A. Comparison of the overall two-step yield for the formation of 18i from Route A (30% via 16e) and Route B (21% via 19a) reveals that the late stage coupling approach (Route A) is most efficient. It should be noted that yields for all of the transformations are unoptimized.

With the extensive series of 18 to hand their photochromic response was next examined. Preliminary assessment of the photochromism was undertaken by visual examination of dilute

Scheme 5: Preparation of 4,6-diaryl substituted 2-(2,4-dimethoxyphenyl)-2-(4-methoxyphenyl)-2H-benzo[h]chromenes 18h – v

Scheme 6: Synthesis of tetraaryl-2H-benzo[h]chromenes 18i and 18w by Route B
toluene solutions of $18a - g$ under 365 nm irradiation. Unfortunately, all of these benzochromenes containing 4-methoxyphenyl groups at C-2, with the exception of $18g$, failed to exhibit a discernible photochromic response at room temperature; indeed, cooling the solutions of $18a - f$ down to ca. -10 – 0 °C resulted in the observation of only a transient red hue which faded immediately upon cessation of the UV irradiation. The absorption spectra of $18g$ are presented in Figure 5a along with images of the solution during the irradiation process (Figure 5b). The unirradiated solution of $18g$ was essentially colourless and developed a pleasing dull red hue upon UV irradiation as a consequence of the presence of two broad overlapping bands with the maximum wavelength of absorption at the photostationary state ($\lambda_{\text{PSS}}$) at 446 and 530 nm. The presence of two absorption maxima for $2H$-benzo[h]chromenes is in accord with literature observations.[6] The photocolorability factor ($\Delta A_{\text{Conc.}}$) was unexpectedly high ($1.4 \times 10^4 \text{ M}^{-1}$ at 446 nm and $1.6 \times 10^4 \text{ M}^{-1}$ at 530 nm) and the half-life ($t_{1/2}$) for the persistence of the red hue was determined as 488 s, after irradiation to a steady state absorption (Table 1).

It is interesting to note that, for $18g$, the combined presence of a strong aryl donor at C-6 with a strong aryl acceptor at C-4 has a marked impact upon the photocolorability of the photochromic dye in solution. It may be the case that when the communication between these two aryl groups is ‘turned-on’ by the electrocyclic ring-opening of the pyran ring, an additional donor-acceptor system is formed (Figure 6), which has opposing conjugation (cross-
conjugation [40,41]) to that of the traditional photomerocyanine. The generation of this second donor-acceptor system results in the disruption of the traditional photomerocyanine $\pi$-system, imparting some degree of stability which is sufficient to increase its population at the photostationary state. The existence of the donor-acceptor systems is supported by the presence of the two overlapping absorptions bands in the UV-Vis spectrum, centred at 446 nm and 530 nm.

Given this interesting photochromic behaviour exhibited by 18g we next explored the photochromism of the tetraaryl 2H-benzo[h]chromenes 18h – v which possessed a 4-methoxyphenyl and a 2,4-di(4-methoxyphenyl) unit at C-2. For this series, we would predict that more pronounced photochromism would be observed at room temperature since it is well established that the presence of an ortho-substituent on at least one of the gem-aryl rings
hinders the ring closure of the photomerocyanines leading to a steady state with a higher population of photomerocyanines and thus the perception of more intense colour.[35,36]

A preliminary survey of the photochromism of $18h - v$ was made in the same manner as that for the examples $18a - g$ and then further by irradiation using a bespoke irradiation spectrophotometer system (Oriel 300 W xenon arc lamp source set at 150 W with irradiation delivery to the stirred sample in a cuvette via a liquid light guide – see experimental for full description of equipment). For each benzochromene solution examined the UV-Vis spectra were recorded at higher dilution for the pre-irradiated benzochromene (blue spectra in each figure) to enable the wavelength of the intense maxima ($\lambda_{\text{max}}$) in the UV region at ca. 345 nm to be ascertained. UV-Vis spectra were recorded at higher concentration for the UV-irradiated sample solutions (red spectra in each figure) to enable the maximum wavelength of the relatively low population of the photomerocyanines at the photostationary state ($\lambda_{\text{PSS}}$) to be ascertained. Examples $18h, k - m$ failed to exhibit any discernible photochromism in the visible region of the spectrum under irradiation at room temperature; behaviour which was further confirmed by UV-Vis spectrophotometry (Figure 7a,b).

Figure 7a: Absorption spectra of a solution of $18h, k - m$ in aerated toluene [pre-irradiated solution concentration $10^{-2}$ mM range (blue spectra); post-irradiation ($\lambda_{\text{air}}$ 325 nm; $P_{\text{lamp}}$ 150 W) concentration $10^{-1}$ to $10^{0}$ mM range (red spectra)]; Figure 7b: Images of solutions of $18h, k - m$, (1) before UV irradiation, (2) under UV irradiation (365 nm) and (3) immediately after cessation of UV irradiation
Whilst only a very weak photochromic response could be discerned for benzochromenes 18i, j, n – q and u, λ_{PSS} was obtained for the low steady state concentration of the photomerocyanines using our irradiation – spectrophotometer system (Figure 8a,b) and the thermal bleaching rate constant and half-life for the fade of the low steady state concentration of the photomerocyanine form was determined (Figure 10, Table 1).

Figure 8a: Absorption spectra of a solution of 18i, j, n – q and u in toluene [pre-irradiated solution concentration 10^{-2} mM range (blue spectra); post-irradiation (λ_{air} 325 nm; P_{lamp} 150 W) concentration 10^{-1} to 10^{0} mM range (red spectra)]; before and after irradiation; Figure 8b:
Images of solutions of \(18i, j, n - q\) and \(u\), (1) before UV irradiation, (2) under UV irradiation (365 nm) and (3) immediately after cessation of UV irradiation

With the exception of \(18v\), the remaining benzochromenes \(18r - t\) and \(w\) agreeably exhibited good photochromism at room temperature generating very intensely coloured solutions at their photostationary states (PSS) unlike the benzochromenes \(18i, j, n - q\) and \(u\); \(\lambda_{\text{PSS}}\) and thermal bleaching kinetic data for the photomerocyanines were readily obtained (Figure 9a,b, Figure 10, Table 1).

![Absorption spectra](image)

Figure 9a: Absorption spectra of a solution of \(18r - t\) and \(w\) in toluene [pre-irradiated solution concentration \(10^{-2}\) mM range (blue spectra); post-irradiation (\(\lambda_{\text{air}} 325\) nm; P\(_{\text{lamp}} 150\) W) concentration \(10^{-1}\) to \(10^{-2}\) mM range (red spectra)]; before and after irradiation; Figure 9b: Images of solutions of \(18r - t\) and \(w\), (1) before UV irradiation, (2) under UV irradiation (365 nm) and (3) immediately after cessation of UV irradiation

Thermal bleaching data for the benzochromenes \(18g, i, j, n - u\) and \(w\) are presented in Figure 10.
Figure 10: Thermal bleaching plots (absorbance at $\lambda_{PSS}$ versus time) for the photochromic benzochromenes 18g, i, j, n – u and 18w

As a preliminary indication of the cyclability of the series 18r – t and w three irradiation – bleaching cycles were recorded due to relatively slow bleaching kinetics of the respective photomerocyanines (Figure 11). From the available data we tentatively infer that the photochromic compounds 18r – t and w offer good performance though further examination in a polymer matrix is required.

Figure 11: Irradiation – bleaching cycles for benzochromenes 18r – t and 18w
Table 1: Summary of the spectrokinetic data of naphthopyrans $18g - 18w$ and respective photomerocyanines obtained after continuous UV irradiation ($\lambda_{irr}$ 325 nm, $P_{lamp}$ 150 W) to a photostationary state (PSS) in aerated toluene solution

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<th>Entry</th>
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<th>$R^3$</th>
<th>$\lambda_{ssa}$ / nm ($\epsilon$ / M$^{-1}$cm$^{-1}$)</th>
<th>$\lambda_{ss}$ / nm</th>
<th>$\Delta A_{conc}$ / M$^{-1}$</th>
<th>$k_b$ / s$^{-1}$</th>
<th>$t_{1/2}$ / s</th>
<th>$\lambda_{em}$ / nm ($\Phi$ / %)</th>
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<td>Ph</td>
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<td>454</td>
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<td>1.5 × 10$^3$</td>
<td>384</td>
<td>N/A</td>
</tr>
<tr>
<td>$18t$</td>
<td>OMe</td>
<td>4-NO$_2$Ph</td>
<td>4-NEt$_2$Ph</td>
<td>348 (6.1 × 10$^3$)</td>
<td>448</td>
<td>4.4 × 10$^3$</td>
<td>4.7 × 10$^3$</td>
<td>296</td>
<td>N/A</td>
</tr>
<tr>
<td>$18u$</td>
<td>OMe</td>
<td>4-CNPh</td>
<td>4-NMe$_2$Ph</td>
<td>348 (7.5 × 10$^3$)</td>
<td>508</td>
<td>6.8 × 10$^3$</td>
<td>2.0 × 10$^3$</td>
<td>240</td>
<td>N/A</td>
</tr>
<tr>
<td>$18v$</td>
<td>OMe</td>
<td>4-NMe$_2$Ph</td>
<td>4-NO$_2$Ph</td>
<td>354 (9.8 × 10$^3$)</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>554 (1.3)</td>
</tr>
<tr>
<td>$18w$</td>
<td>OMe</td>
<td>4-NO$_2$Ph</td>
<td>Ph</td>
<td>346 (5.8 × 10$^3$)</td>
<td>496</td>
<td>2.5 × 10$^4$</td>
<td>4.4 × 10$^4$</td>
<td>1727</td>
<td>N/A</td>
</tr>
</tbody>
</table>

$k_{em}$ = maximum wavelength of absorption at the closed state. $\epsilon$ = molar attenuation coefficient. $\lambda_{ssa}$ = maximum wavelength of absorption at the photostationary state (PSS). $\Delta A_{conc}$ = colour generated at the photostationary state after continuous UV irradiation of 1 molar of a given naphthopyran in solution, calculated as $\Delta A_{conc} = \Delta A_{closed} - \Delta A_{open}$. With $\Delta A_{closed}$ and $\Delta A_{open}$ being the induced optical density at $t = 0$ and $t = conc$, respectively. $\Delta A_{closed}$ being the concentration of the naphthopyran in solution prior to UV irradiation. $k_b$ = thermal bleaching rate constant. $\lambda_{em}$ = maximum wavelength of emission of the naphthopyrans in aerated toluene. $\Phi$ = quantum yield of emission. *Compound $18v$ is fluorescent and non-photochromic.

From the spectra presented in Figures 5, 7, 8 – 11 and data summarised in Table 1 some observations can be noted for the benzochromenes $18g - u$ and $18w$. The maximum of absorption of the closed (pre-irradiated) state occurs in the narrow range 342 – 350 nm with
molar extinction coefficient $\varepsilon = 3.3 \times 10^3$ to $1.0 \times 10^4 \text{M}^{-1}\text{cm}^{-1}$, and the toluene solutions appear colourless.

For the C-2 unsymmetrically substituted benzochromenes which exhibit weak photochromism, the combination of a donor aryl group at C-6 and an acceptor aryl group at C-4 results in a bathochromically shifted weak absorption maxima with, for example, $18q$ [4-(4-F$_3$CC$_6$H$_4$-), 6-(4-Me$_2$NC$_6$H$_4$-)] and $18u$ [4-(4-NCC$_6$H$_4$-, 6-(4-Me$_2$NC$_6$H$_4$-)] affording maxima at 506 and 508 nm, respectively; whereas retaining a 4-(4-F$_3$CC$_6$H$_4$-) group but decreasing the donor group strength of the aryl group at C-6 to either an anisyl (An) group ($18o$) or a phenyl group ($18n$) results in a hypsochromic shift in $\lambda_{PSS}$ to 500 nm and 486 nm, respectively. The most hypsochromically shifted absorption maxima, 476 nm, occurs for $18j$ with a C-4 phenyl ring and a 4-F$_3$CC$_6$H$_4$- moiety at C-6. For these weakly photochromic examples with $\Delta A_{\text{conc}}$ below ca. $2.8 \times 10^2 \text{M}^{-1}$ the smallest thermal bleaching rate constant of $4.0 \times 10^{-4} \text{s}^{-1}$ was noted for $18j$ and the biggest ($2.0 \times 10^{-3} \text{s}^{-1}$) for $18u$; this trend suggests that a stronger aryl donor group at C-6 results in faster bleaching kinetics. Whilst the data recorded reveals a mono-exponential decay of the photogenerated colour it is likely that this decay profile results from either (i) very rapid cyclisation ($k_1 >10^{-1} \text{s}^{-1}$) of the E-photomerocyanine relative to the cyclisation of the Z-photomerocyanine (Figure 6), or (ii) the PSS population, whilst extremely low, is predominantly the slower fading Z-photomerocyanine as a consequence of the longer UV irradiation times (Figure 6). For the C-2 unsymmetrically substituted benzochromenes which exhibit good photochromism at room temperature with half-lives in the range 296 – 1727 s, for $18r$ – $t$ and $w$, it is clear that the presence of a strong electron withdrawing 4-nitrophenyl group at C-4 is essential for stabilising the red coloured photomerocyanines. The photocolourability factor, $\Delta A_{\text{conc}}$, is significantly enhanced ($2.5 \times 10^3 - 1.0 \times 10^4 \text{M}^{-1}$) for $18r$ – $t$ and $w$, relative to that of the other benzochromenes with either weaker electron withdrawing ($18n$ – $q$, CF$_3$; $18u$, CN) or electron donating (H or OMe) aryl groups at C-4 where $\Delta A_{\text{conc}}$ is in the ‘not measurable’ to $2.8 \times 10^2 \text{M}^{-1}$ range. Furthermore, coupling the C-4 electron deficient ring with an aryl ring at C-6 which is substituted with a very strong electron donating substituent e.g., NMe$_2$ ($18s$) or NEt$_2$ ($18t$), results in the generation of a relatively stable photomerocyanine which possesses two absorption bands with a weaker shorter wavelength band appearing at ca. 447 nm and the major band at ca. 534 nm (Figure 9a). This contrasts with the formation of a sharp absorption band at ca. 498 nm for $18r$ and $18w$ (Figure 9a) that contain weaker donor groups at C-6. Thus, the development of these two absorption bands in the UV-Vis spectra of the photostationary states occurs exclusively when coupling a strong aryl donor group at C-6.
and a strong acceptor at C-4 (18s, 18t and also 18g) which is a strong indicator of the existence of an additional donor-acceptor system that involves the aryl donor group at C-6. An additional comment would be that the $\Delta A_{\text{conc}}$ is diminished for each absorption band of the more electron donating NEt$_2$ substituted analogue (18t) relative to those of 18s with the NMe$_2$ substituent. The spectrokinetic data for this series, 18r – t and w, reveals that as the electron donor strength of the C-6 aryl group increases the thermal bleaching rate constant from Ph (18w) → An (18r) → Me$_2$NC$_6$H$_4$- (18t) → Et$_2$NC$_6$H$_4$- (18s) increases from $9.3 \times 10^{-4}$ s$^{-1}$ to $1.5 \times 10^{-3}$ s$^{-1}$.

It is noteworthy that the C-2 symmetrically diaryl substituted benzochromene 18g, which lacks the important ortho-methoxy group but possesses a strong electron withdrawing C-4 4-nitrophenyl ring together with a C-6 4-dimethylaminophenyl ring also exhibits good photochromism with the absorption spectrum displaying two broad overlapping bands with $\lambda_{\text{PSS}}$ at 446 nm ($\Delta A_{\text{conc}} = 1.4 \times 10^4$ M$^{-1}$) and 530 nm ($\Delta A_{\text{conc}} = 1.6 \times 10^4$ M$^{-1}$). This latter observation is important and leads to the conclusion that for good room temperature photochromism to be observed in the studied series of benzochromenes an electron withdrawing group at C-4 is essential and this holds irrespective of the presence of a sterically demanding ortho-substituent in one of the C-2 aryl rings.

Independent of the other tetra-aryl benzochromenes, the initial toluene solution of 18v (the isomer of 18s in which the NO$_2$ and the NMe$_2$ groups are transposed) was noticeably pale yellow. However, upon excitation with UV irradiation from a LED portable UV flashlight (Weltool M2-BF 2W, $\lambda_{\text{max}}$ 365 nm) the solution exhibited a moderate yellow fluorescence. In contrast, the toluene solution of the isomer 18s exhibited a strong photochromic response with the development of an intense persistent cherry-red hue. The absorption spectrum of a PhMe solution of 18v is presented in Figure 12a. The spectra confirm the pale-yellow colour (Figure 12b) of the initial solution, and its intensification upon irradiation, which is due to absorption bands in the UV region tailing into the visible region.
Figure 12a: Normalised absorption spectrum (blue), excitation spectrum (red, $\lambda_{em}$ 554 nm) and emission spectrum (yellow, $\lambda_{ex}$ 354 nm) of an aerated toluene solution of 18v ($10^{-1}$ mM).

Figure 12b: Images of solutions of 18v, 1) before UV irradiation, 2) under UV irradiation (365 nm) and 3) immediately after cessation of UV irradiation.

The fluorescence of the toluene solution of 18v was confirmed with an emission maximum ($\lambda_{em}$) measured to be 554 nm (Figure 12a) and a typically short lifetime of emission of 0.61 ns ($\tau_1$) and 3.0 ns ($\tau_2$). The relative fluorescence quantum yield for 18v was determined to be 1.3% (versus anthracene $\Phi = 36\%$ in cyclohexane under air) with a Stokes shift determined to be 191 nm. Given the starkly contrasting behaviour between the isomers 18s and 18v, which differ by transposition of the 4-dimethylaminophenyl and 4-nitrophenyl substituents at the 4- and 6-positions we sought to employ TD-DFT to account for the differences. For 18s, the lowest vertical TD-DFT transitions are located at 359 nm ($f = 0.007; S_0-S_1$) and 325 nm ($f = 0.186; S_0-S_2$). By following Kasha’s rule, 18s will relax to $S_1$ after absorption to any other electronic state. Considering that $S_1$ is nearly dark, radiative relaxation through fluorescence is extremely unlikely. In any case, the two first electronic transitions encompass a very complex MO blend, and we have resorted to Electron Density Difference (EDD) plots for representation. As can be seen from Figure 13, the lower-lying transition (359 nm) has a clear CT character (direction of the dimethylaminophenyl to nitrophenyl) but considering the spatial arrangement of the two groups it is logical that the transition probability is low. In fact, Le Bahers’ CT model predicts a transfer of almost 1 electron ($q_{CT} = 0.99 e$) over quite a large distance ($d_{CT} = 3.69$ Å). For the second transition (325 nm), this CT character is conserved but less pronounced ($q_{CT} = 0.75 e$ and $d_{CT} = 2.95$ Å), with density changes more centred on the core of the dye, explaining the higher transition probability. For 18v, the lowest transition 349 nm ($f = 0.280$) is much brighter than in 18s, and its relaxation will lead to a bright state that can be potentially emissive, consistent with the emergence of fluorescence experimentally. The EDD plot shows a strong
CT character ($q^{CT} = 0.82$ e and $d^{CT} = 3.51$ Å) but with a very different localization as compared to 18s. Indeed, in 18v, the lowest excitation triggers a CT from the core of the dye towards the nitro group, but with no involvement of the Ph-NMe$_2$ moiety that is passive in the absorption process according to theory. Moreover, there are also remarkable differences of the density changes on the C-O bond upon $S_0$-$S_1$ transition for the two systems (Figure 13). The change of density is much more marked for 18s than for 18v, which is consistent with the breaking of the C-O bond in 18s but not in 18v. To further ascertain this qualitative observation, we have optimized the $S_1$ geometries of both compounds with TD-DFT. For 18s, the C-O distance is greatly increased as compared to $S_0$ (1.445 to 1.477 Å, a +0.032 Å increase) and the state remains dark ($f = 0.001$ at the end of the optimization), hinting that bond breaking is indeed more likely to occur than fluorescence. In contrast in 18v, the C-O bond only increases by +0.011 Å (1.450 to 1.461 Å) during the optimization and the state remains very bright ($f = 0.417$), which supports the emergence of fluorescence.

Figure 13: Density difference plot for the lowest two electronic transitions of 18s (upper) and the two lowest transitions of closed 18v (lower). On the rightmost part, close up views of the
density changes for the $S_0$-$S_1$ transitions on the CO bond of $18s$ (upper) and $18v$ (lower) are depicted. The blue and red regions indicate zones of decrease and increase of electron density upon excitation, respectively. Contour: 0.001 au

**Conclusion**

Two complementary strategies have been successfully employed to synthesise a series of photochromic $2,2,4,6$-tetraaryl-$2H$-benzo$[h]$chromenes. In the former route, $1,1,3$-triarylprop-2-yn-1-ols were condensed with 4-bromo-1-naphthol to afford 6-bromo-1,1,3-triaryl-$2H$-benzo$[h]$chromenes which underwent efficient Suzuki cross-coupling with a range aryl boronic acids to the target benzochromenes. In the latter route, 4-aryl-1-naphthols were obtained by Suzuki cross-coupling followed by condensation with 1,1,3-triarylprop-2-yn-1-ols. The novel 1,1,3-triarylpropynols were readily obtained either by the addition of an arylacetylide to the requisite benzophenones or by a Sonogashira coupling of a halobenzene with a preformed 1,1-diarylprop-2-yn-1-ol. For the observation of good room temperature photochromism, it was essential to have a strong electron withdrawing aryl moiety at C-4; indeed, this structural feature dominated over the established requirement of a sterically demanding ortho-substituted C-2 aryl group for good photocolourability. The presence of a strong electron donating aryl group at C-6 communicating with an electron withdrawing aryl group at C-4 in the photomerocyanine resulted in the appearance of two absorption bands in the visible region of the electromagnetic spectrum, rather than one broad band when the C-6 aryl group was weakly electron donating i.e. wherein only a weak donor-acceptor secondary chromophore was generated. Remarkably, inverting the donor-acceptor character of the C-4 and C-6 aryl groups resulted in the inhibition of photochromism and instead gave rise to fluorescence. TD-DFT computational studies were performed to rationalise the change from photochromism to fluorescence. We anticipate that the new structure–colour relationships disclosed herein will be of value in the design of future generations of photochromic pyran derived systems for commercial applications.

**Acknowledgments**

N.S. thanks the University of Huddersfield for financial support for this research study. D.J. is deeply indebted to the CCIPL computational centre installed in Nantes for the very generous allocation of computational time.
**Experimental Section**

Unless otherwise stated, reagents and solvents were purchased from major chemical catalogue companies and were used as supplied. For reactions requiring heating, DrySyn® aluminium heating blocks in conjunction with electrical stirrer hotplates were used as the heat source. $^1$H NMR, $^{13}$C{$^1$H} NMR and $^{19}$F{$^1$H} spectra were recorded on a Bruker Avance DPX300, DPX400 and DPX600 in CDCl$_3$ unless stated otherwise. Chemical shifts are provided in parts per million (ppm) using either the residual solvent peak or TMS as the internal reference. Coupling constants ($J$) are provided in Hz. FT-IR spectra were recorded on a Nicolet 380 FTIR spectrophotometer equipped with a diamond ATR attachment (neat sample). Flash column chromatography was performed on chromatography silica gel (either Sigma-Aldrich, 40 – 63 micron particle size distribution or Fluorochem Silica gel 40 – 63 micron particle size distribution). All final compounds were homogeneous by TLC using a range of eluent systems of differing polarity (either Merck TLC aluminium sheets silica gel 60 F254 (cat. No 105554) or Fluorochem cat. No. LC0927). Melting points were determined in capillary tubes, using a Stuart SMP10 melting point apparatus, and are uncorrected. Accurate mass measurements were obtained from the Innovative Physical Organic Solutions (IPOS) centre at the University of Huddersfield.

UV-visible spectra were recorded for toluene solutions of the samples (10 mm path length quartz cuvette, PTFE capped, concentration in the range $10^{-3}$ – $10^{-5}$ moldm$^{-3}$). A bespoke Shimadzu UV-3600 Plus UV-Vis-NIR spectrophotometer was used and equipped with a single cell Peltier temperature controlled (23 °C) magnetically stirred fluorescence cell holder attachment. The spectrophotometer sample chamber door was modified to accept activating irradiation delivered from the light source by liquid light guides (Newport 77557, Newport 77569). Irradiation was provided by a xenon ozone free arc lamp (Newport 6255) powered by an Oriel 300-Watt xenon arc lamp source (Newport 66906) (set in Power Mode 150 W). An in-line distilled water liquid filter (Newport 6177), multiple filter holder (Newport 62020), fibre optic coupler (Newport 77799) completed the irradiation equipment. Activation of the colourless closed forms of the photochromic compounds to a photostationary state was achieved by UV irradiation using the UG11 filter (Newport FSO-UG11). Bleaching of the coloured (opened forms) when required was effected by irradiation with visible light using the Newport filter (GG420, Cut-On 420 nm). In a first experiment, spectra (300 – 700 nm) were recorded prior to (ground state) and immediately after cessation of activating irradiation to a photostationary state. In a second experiment, the decrease of absorbance, Abs, at the
wavelength of maximum absorption of the photostationary state, \( \lambda_{\text{PSS}} \), under UV irradiation (Newport FSQ-UG11) was recorded over time (in Kinetic Mode). The kinetic data was fitted by employing OriginPro 2021 NLFit (ExpDec 1 or ExpDec 2) functions – Iteration Algorithm Levenberg Marquardt.

Emission and excitation spectra were acquired on a Horiba Scientific Fluoromax-4 Spectrophotometer. Quantum yields (\( \Phi \)) were calculated by applying the equation:

\[
\Phi = \frac{\text{Integral}}{\text{Integral (R)}} \times \frac{1 - 10^{-\text{Abs}(R)}}{1 - 10^{-\text{Abs}}} \times \frac{\eta^2}{\eta^2(R)}
\]

The standard (R) used was anthracene (\( \Phi(R) = 36\% \) in cyclohexane under air determined by a relative optical method [42]; excitation window: 310 – 365 nm), \( \eta \) is the refractive index of the solvent (cyclohexane = 1.427, PhMe = 1.497).

Emission lifetime was recorded by time-correlated single-photon counting using an Edinburgh Instruments Mini-Tau spectrometer (EPL-405).

Single crystal X-ray diffraction data was collected on a Bruker Venture diffractometer equipped with a graphite monochromated Cu(K\(\alpha\)) radiation source and a cold stream of N\(_2\) gas. Crystal structure data for compound \( \mathbf{16c} \) has been deposited at the Cambridge Crystallographic Data Centre with deposition number CCDC2092387.

To perform our simulations, we have selected the Gaussian16 program.[43] The \textit{ab initio} simulations consisted of: i) DFT geometry optimisations of the \( S_0 \) structures; ii) calculations of the vibrational frequencies on these structures; and iii) subsequent vertical TD-DFT calculations of the singlet excited states on these structures. We have applied default procedures, integration grids, algorithms and parameters, except for tighten energy (typically \( 10^{-10} \text{ a.u.} \)) convergence threshold and the use of the \textit{ultrafine} integration DFT grid at all steps (including CPKS). The ground-state geometrical parameters have been determined with the M06 hybrid exchange-correlation functional.[44] For all nuclei, we have selected Pople’s 6-311G(d,p) basis set. The vibrational spectra determined analytically at the same level of theory and it has been checked that all structures correspond to true minima of the potential energy surface. At least, the first fifteen low-lying excited-states have been determined within the vertical TD-DFT approximation using the CAM-B3LYP functional, [45] that is suited when CT states are at play. The TD-DFT calculations are performed with the 6-311+G(2d,p) basis set. During all steps, a modelling of bulk solvent effects (Toluene) through the Polarizable Continuum Model (PCM),[46] using the (default) linear-response non-equilibrium approach
for the TD-DFT part of the calculation. We use the well-known Le Bahers model for quantifying the CT strength.[47]

The prop-2-yn-1-ols 15a and 15b were obtained by literature protocols.[32]

Preparation of intermediates

Preparation of 1,1,3-triarylprop-2-yn-1-ols – Arylacetylide addition protocol

1,1-Bis(4-methoxyphenyl)-3-phenylprop-2-yn-1-ol 12a

n-BuLi (2.5 M in hexanes) (38 mL, 95 mmol, 1.15 eq.) was added via syringe, over ca. 10 minutes, to a cold (ca. 0 °C) stirred solution of phenyl acetylene (9.7 mL, 95 mmol, 1.15 eq.) in anhydrous THF (ca. 180 mL) under nitrogen. The resulting pale-yellow solution was left to stir for 30 minutes before the 4,4'-dimethoxybenzophenone (20.0 g, 82.6 mmol, 1.0 eq.) was added in a single portion. The resulting mixture was warmed to room temperature and left to react ca. 3.5 hours, monitored by TLC (20% EtOAc in n-hexane) until no starting material remained. The solution was quenched with water (100 mL) before being extracted into EtOAc (ca. 4 × 75 mL). The combined organic extracts were washed with water (ca. 50 mL), then dried (anhydrous MgSO₄). The excess solvent was removed under vacuum to afford the title product as a viscous golden yellow oil (27.8 g, 98%); ν_max (neat) 3428, 2956, 2836, 1606, 1506, 1462, 1442, 1369, 1299, 1246, 1165, 1109, 1031, 981, 905, 829, 808, 759, 664, 587, 564 cm⁻¹; ¹H NMR (CDCl₃) δ 2.83 (1H, broad s, OH), 3.80 (6H, s, OMe), 6.85 - 6.88 (4H, m, Ar-H), 7.1 - 7.36 (3H, m, Ar-H), 7.48 - 7.51 (2H, m, Ar-H), 7.55 - 7.61 (4H, m, Ar-H); ¹³C{¹H} NMR (CDCl₃) δC 55.3, 74.2, 86.9, 92.1, 113.6, 122.6, 127.4, 128.3, 128.6, 131.8, 137.6, 159.1; HRMS found [M]+ = 344.1416. C₂₃H₂₀O₃ requires [M]+ = 344.1412.

1,1,3-Tris(4-methoxyphenyl)prop-2-yn-1-ol 12b

n-BuLi (2.5 M in hexanes) (38 mL, 95 mmol, 1.15 eq.) was added via syringe, over ca. 10 minutes, to a cold (ca. 0 °C) stirred solution of 4-methoxyphenyl acetylene (12.6 g, 95 mmol, 1.15 eq.) in anhydrous THF (ca. 180 mL) under nitrogen. The resulting yellow solution was left to stir for 30 minutes before the 4,4'-dimethoxybenzophenone (20.0 g, 82.6 mmol, 1.0 eq.) was added in a single portion. The resulting mixture was warmed to room temperature and left to stir for ca. 3 hours, until TLC revealed no starting material remained (20% EtOAc in n-hexane). The solution was quenched with water (100 mL), extracted into EtOAc (ca. 4 × 75 mL), washed with water (50 mL), and dried (MgSO₄). Removal of the solvent gave the title product as a viscous dark orange oil (31.9 g, 99%); ν_max (neat) 3447, 2956, 2837, 1604, 1506,
1,1-Bis(4-methoxyphenyl)-3-[4-(trifluoromethyl)phenyl]prop-2-yn-1-ol 12c

$n$-BuLi (2.5 M in hexanes) (11.6 mL, 29.1 mmol, 1.24 eq.) was added via syringe, over ca. 10 minutes, to a cold (ca. 0 °C) stirred solution of 4-(trifluoromethyl)phenylacetylene (ca. 4.0 g, 24 mmol, 1.15 eq.) in anhydrous THF (ca. 150 mL) under nitrogen. The resulting yellow solution was left to stir for 30 minutes before the 4,4’-dimethoxybenzophenone (6.13 g, 25.3 mmol, 1.08 eq.) was added in a single portion. The resulting mixture was warmed to room temperature and left to stir for ca. 3.5 hours, until no benzophenone remained (via TLC). The reaction was quenched with water (ca. 150 mL), extracted into EtOAc (4 x 75 mL), washed with water (50 mL), and dried (MgSO₄). Removal of the solvent gave the title product as a viscous yellow oil (9.82 g, 99%); ν_max (neat) 3431, 2933, 2839, 1609, 1584, 1507, 1463, 1320, 1302, 1247, 1165, 1123, 1005, 1068, 1032, 1015, 988, 901, 829, 812, 748, 591, 515 cm⁻¹; ¹H NMR (CDCl₃) δ_H 2.76 (1H, s, OH), 3.80 (6H, s, OMe), 3.82 (3H, s, OMe), 6.83 – 6.90 (6H, m, Ar-H), 7.41 – 7.46 (2H, m, Ar-H), 7.54 – 7.59 (4H, m, Ar-H); ¹³C{¹H} NMR (CDCl₃) δ 55.3, 74.2, 85.9, 86.8, 90.8, 113.5, 113.9, 114.6, 127.4, 133.2, 137.8, 159.0, 159.8; HRMS found [M]+ = 374.1525. C_{24}H_{22}O₄ requires [M]+ = 374.1518.

1-(2,4-Dimethoxyphenyl)-1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-ol 12d

$n$-BuLi (2.5 M in hexanes) (9.76 mL, 24.4 mmol) was added portionwise via syringe to a cold (-70 °C) stirred solution of phenylacetylene (2.68 mL, 2.49 g, 24.4 mmol) in anhydrous THF (50 mL) under N₂. The cold solution was stirred for 30 minutes and then (2,4-dimethoxyphenyl)(4-methoxyphenyl)methanone (6.00 g, 22.0 mmol) was added in a single portion. The cooling bath was removed and the mixture stirred for 20 h at room temperature under N₂. The reaction mixture was diluted with water (100 mL) and extracted with EtOAc (3 × 100 mL). The combined organic extracts were washed with water (100 mL), dried with anhydrous sodium sulfate and evaporated to a viscous yellow oil. Elution from silica with 5 % EtOAc/PhMe afforded the title compound as a yellow gum (4.25 g, 52%); ν_max (neat) 3500,
2380, 2150, 1155, 1012, 751, 689, 634, 510 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta_{H}\) 3.80 (6H, s, 2 × OMe), 3.82 (3H, s, OMe), 4.83 (1H, s, OH), 6.44 (1H, dd, \(J = 8.6, 2.4\) Hz, Ar-H), 6.52 (1H, d, \(J = 2.4\) Hz, Ar-H), 6.86 – 6.90 (2H, m, Ar-H), 7.24 (1H, d, \(J = 6.4\) Hz, Ar-H), 7.27 – 7.31 (3H, m, Ar-H), 7.44 – 7.48 (2H, m, Ar-H), 7.49 – 7.54 (2H, m, Ar-H); \(^{13}\)C\{\(^1\)H\} NMR (75 MHz, CDCl\(_3\)) \(\delta_{C}\) 55.29, 55.43, 55.93, 74.08, 86.26, 91.65, 100.11, 103.96, 113.27, 123.02, 125.70, 127.73, 128.17, 128.26, 129.15, 131.75, 136.78, 157.91, 158.93, 160.70; HRMS (ESI) found [M+H]\(^+\) = 375.1590 C\(_{24}\)H\(_{22}\)O\(_4\) requires [M+H]\(^+\) = 375.1596.

**1-(2,4-Dimethoxyphenyl)-1,3-bis(4-methoxyphenyl)prop-2-yn-1-ol 12e**

\(n\)-BuLi (2.5 M in hexanes) (9.76 mL, 24.4 mmol) was added portionwise via a syringe to a cold (-70 °C) stirred solution of 4-methoxyphenylacetylene (3.16 mL, 3.22 g, 24.4 mmol) in anhydrous THF (50 mL) under N\(_2\). The cold solution was stirred for 30 minutes and then (2,4-dimethoxyphenyl)(4-methoxyphenyl)methanone (6.00 g, 22.0 mmol) was added in a single portion. The cooling bath was removed and the mixture stirred for 20 h at room temperature under N\(_2\). TLC examination of the reaction mixture after this time indicated that some of the (2,4-dimethoxyphenyl)(4-methoxyphenyl)methanone remained. Thus further ((4-methoxyphenyl)ethynyl)lithium solution was prepared [from 4-methoxyphenylacetylene (0.98 mL, 7.6 mmol) and \(n\)-BuLi (3.04 mL, 7.8 mmol)] at -10 °C and added via syringe to the foregoing alkynol reaction mixture. The resulting mixture was stirred for an additional 17 h at room temperature and then diluted with water (100 mL) and extracted with EtOAc (3 × 100 mL). The combined organic extracts were washed with water (100 mL), dried with anhydrous sodium sulfate and evaporated to afford a yellow oil. Gradient elution from silica with 10 % EtOAc/\(n\)-hexane \(\rightarrow\) 30 % EtOAc/\(n\)-hexane \(\rightarrow\) 50 % EtOAc/\(n\)-hexane afforded the title compound as a viscous yellow oil (6.26 g, 70 %); \(\nu_{\text{max}}\) (neat) 3509, 2935, 2835, 2223, 1604, 1506, 1243, 1125, 1026, 828, 586 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta_{H}\) 3.79 (3H, s, OMe), 3.80 (3H, s, OMe), 3.81 (3H, s, OMe), 3.82 (3H, s, OMe), 4.79 (1H, s, OH), 6.44 (1H, dd, \(J = 8.6, 2.4\) Hz Ar-H), 6.52 (1H, d, \(J = 2.4\) Hz, Ar-H), 6.80 – 6.84 (2H, m, Ar-H), 6.86 – 6.89 (2H, m, Ar-H), 7.27 (1H, d, \(J = 8.6\) H, Ar-H), 7.38 – 7.42 (2H, m, Ar-H), 7.49 – 7.52 (2H, m, Ar-H); \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)) \(\delta_{C}\) 55.28, 55.42, 55.91, 74.15, 86.25, 90.25, 100.14, 103.99, 113.23, 113.78, 115.17, 125.90, 127.68, 129.17, 133.18, 137.09, 157.91, 158.87, 159.57, 160.67; HRMS (ESI) found [M+H]\(^+\) = 405.1702 C\(_{25}\)H\(_{24}\)O\(_3\) requires [M+H]\(^+\) = 405.1702.
1-(2,4-Dimethoxyphenyl)-1-(4-methoxyphenyl)-3-[4-(trifluoromethyl)phenyl]prop-2-yn-1-ol 12f

$n$-BuLi (2.5 M in hexanes) (8.92 mL, 22.3 mmol) was added portionwise via syringe to a cold (-10 °C) stirred solution of 4-(trifluoromethyl)phenylacetylene (3.60 mL, 3.76 g, 22.1 mmol) in anhydrous THF (50 mL) under N$_2$. The cold solution was stirred for 30 minutes and then (2,4-dimethoxyphenyl)(4-methoxyphenyl)methanone (5.00 g, 18.4 mmol) was added in a single portion. The cooling bath was removed and the mixture stirred for 20 h at room temperature under N$_2$ and then diluted with water (100 mL) and extracted with EtOAc (3 × 100 mL). The combined organic extracts were washed with water (100 mL), dried with anhydrous sodium sulfate and evaporated to afford yellow oil. Elution from silica with 10 % EtOAc/PhMe afforded the title compound as a pale yellow microcrystals (4.92 g, 60 %); m.p. = 106 – 108 °C; $\nu_{\text{max}}$ (neat) 3545, 3010, 2180, 1606, 1320, 1251, 1207, 1156, 1123, 1029, 843, 523 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$) δ$_{\text{H}}$ 3.80 (6H, s, 2 × OMe), 3.81 (3H, s, OMe), 4.83 (1H, s, OH), 6.44 (1H, dd, $J = 8.6, 2.4$ Hz Ar-H), 6.52 (1H, d, $J = 2.3$ Hz, Ar-H), 6.88 (2H, d, $J = 8.8$ Hz, Ar-H), 7.19 (1H, d, $J = 8.6$ Hz, Ar-H), 7.48 – 7.51 (2H, m, Ar-H), 7.53 – 7.56 (4H, m, Ar-H); δ$_{\text{F}}$ (376 MHz, CDCl$_3$) -62.8; $^{13}$C($^1$H) NMR (150 MHz, CDCl$_3$) δ$_{\text{C}}$ 55.30, 55.44, 55.91, 74.02, 84.77, 94.25, 100.14, 104.07, 113.38, 123.94 (q, $J = 272.5$ Hz, C$_3$F), 125.14 (q, $J = 3.8$ Hz, =CH-C$_3$F), 125.27, 126.86 (q, $J = 1.3$ Hz, =CH=CH-C$_3$F$_3$), 127.72, 129.07, 129.99 (q, $J = 32.5$ Hz, =CH=CF$_2$), 131.97, 136.30, 157.91, 159.10, 160.86; HRMS (ESI) found [M-H$_2$O+H]$^+$ = 425.1358 C$_{25}$H$_{19}$F$_3$O$_3$ requires [M-H$_2$O+H]$^+$ = 425.1364.

1-(2,4-Dimethoxyphenyl)-3-[4-(dimethylamino)phenyl]-1-(4-methoxyphenyl)prop-2-yn-1-ol 12g

$n$-BuLi (2.5 M in hexanes) (11.80 mL, 29.4 mmol) was added portionwise via syringe to a cold (-70 °C) stirred solution of 4-ethynyl-$N,N$-dimethylaniline (4.27 g, 29.4 mmol) in anhydrous THF (30 mL) under N$_2$. The cold solution was stirred for 30 minutes and then (2,4-dimethoxyphenyl)(4-methoxyphenyl)methanone (4.00 g, 14.7 mmol) was added in a single portion. The cooling bath was removed and the mixture stirred for 20 h at room temperature under N$_2$. The reaction mixture was diluted with water (150 mL) and extracted with EtOAc (3 × 75 mL). The combined organic extracts were washed with water (150 mL), dried with anhydrous sodium sulfate and evaporated to afford a brown oil. Elution from silica with 20 % EtOAc/petroleum ether afforded the title compound as an orange powder (0.87 g, 85 %); m.p. = 49 – 50 °C; $\nu_{\text{max}}$ (neat) 3506, 2932, 2834, 2217, 1605, 1503, 1245, 1206, 1156, 1028, 816,
586 and 523 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) \(\text{H} 2.95 (6\text{H}, \text{s}, \text{NMe}_2)\), 3.78 (3\text{H}, \text{s}, \text{OMe})\), 3.80 (3\text{H}, \text{s}, \text{OMe})\), 3.81 (3\text{H}, \text{s}, \text{OMe})\), 4.77 (1\text{H}, \text{dd}, \text{J} = 8.6, 2.4 \text{ Hz, Ar-H})\), 6.51 (1\text{H}, \text{d, J} = 2.4 \text{ Hz, Ar-H})\), 6.58 – 6.62 (2\text{H}, \text{m, Ar-H})\), 6.84 – 6.88 (2\text{H}, \text{m, Ar-H})\), 7.30 – 7.35 (3\text{H}, \text{m, Ar-H})\), 7.49 – 7.53 (2\text{H}, \text{m, Ar-H})\); \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)) \(\delta\) C 40.24, 55.27, 55.41, 55.93, 74.27, 87.39, 89.35, 100.16, 103.97, 109.97, 111.69, 113.17, 126.25, 127.71, 129.22, 132.82, 137.45, 150.12, 157.94, 158.78, 160.58; HRMS (ESI) found [M+H]\(^+\) = 418.2002 \(\text{C}_{26}\text{H}_{27}\text{NO}_4\) requires [M+H]\(^+\) = 418.2018.

1-(2,4-Dimethoxyphenyl)-1-(4-methoxyphenyl)-3-(pyridin-4-yl)prop-2-yn-1-ol 12h

\(n\)-BuLi (2.5 M in hexanes) (14.70 mL, 36.7 mmol) was added portionwise via a syringe to a cold (-70 °C) stirred suspension of 4-ethynylpyridine hydrochloride (3.08 g, 22.0 mmol) in anhydrous THF (30 mL) under N\(_2\). The cold solution was stirred for 30 minutes and then (2,4-dimethoxyphenyl)(4-methoxyphenyl)methanone (4.00 g, 14.7 mmol) was added in a single portion. The cooling bath was removed and the mixture stirred for 20 h at room temperature under N\(_2\). TLC examination of the reaction mixture after this time indicated that some of the (2,4-dimethoxyphenyl)(4-methoxyphenyl)methanone remained. Thus further (pyridin-4-ylethynyl)lithium solution was prepared [from 4-ethynylpyridine hydrochloride (1.03 g, 7.33 mmol) and \(n\)-BuLi (4.90 mL, 12.2 mmol)] at -70 °C and added to the foregoing alkynol reaction mixture. The resulting mixture was stirred for an additional 20 h at room temperature and then diluted with water (300 mL) and extracted with EtOAc (3 \(\times\) 100 mL). The combined organic extracts were washed with water (200 mL), dried with anhydrous sodium sulfate and evaporated to afford a brown gum. Elution from silica with 50 % EtOAc/petroleum ether afforded the title compound as a brown powder (0.89 g, 16 %); m.p. = 42 – 43 °C; \(\nu\)\(_{\text{max}}\) (neat) 3108, 2955, 2834, 2360, 1584, 1500, 1246, 1207, 1029, 820 and 588 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) \(\text{H} 3.80 (6\text{H}, \text{s}, 2\text{x OMe})\), 3.82 (3\text{H}, \text{s}, \text{OMe})\), 4.93 (1\text{H}, \text{s}, \text{OH})\), 6.45 (1\text{H}, \text{dd, J} = 8.6 \text{ Hz, Ar-H})\), 6.53 (1\text{H}, \text{d, J} = 2.4 \text{ Hz, Ar-H})\), 6.87 – 6.91 (2\text{H}, \text{m, Ar-H})\), 7.17 (1\text{H}, \text{d, J} = 8.6 \text{ Hz, Ar-H})\), 7.30 – 7.32 (2\text{H}, \text{m, Ar-H})\), 7.48 – 7.52 (2\text{H}, \text{m, Ar-H})\), 8.54 (2\text{H}, \text{d, J} = 4.2 \text{ Hz, Py-H})\); \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)) \(\delta\) C 55.29, 55.44, 55.89, 73.87, 83.35, 96.70, 100.13, 104.08, 113.41, 125.02, 125.76, 127.72, 128.97, 131.31, 135.96, 149.58, 157.88, 159.15, 160.92; HRMS (ESI) found [M+H]\(^+\) = 376.1539 \(\text{C}_{23}\text{H}_{21}\text{NO}_4\) requires [M+H]\(^+\) = 376.1549.

**General procedure for synthesis of 1,1,3-triarylprop-2-yn-1-ols via a Sonogashira cross-coupling reaction**
The requisite 1,1-diaryl prop-2-yn-1-ol (1.0 eq.), the appropriate aryl halide (1.0 eq.), copper(I) iodide (7.5 mol %), PPh$_3$ (15 mol %) and Pd(PPh$_3$)$_4$ (3 mol %) were added to an oven dried 3 neck flask under nitrogen and freshly distilled anhydrous Et$_3$N (7 mL/mmol) was added. The mixture was heated under reflux until TLC examination of the reaction mixture indicated no further change (up to 20 h). The cooled mixture was evaporated to dryness and the crude was diluted with DCM (75 mL), washed with water (200 mL) and neutralised with 2M aq. HCl (15 mL). The aqueous layer was extracted with DCM (3 × 20 mL). The combined organic extracts were washed with water (100 mL), dried with anhydrous sodium sulfate and solvent evaporated under reduced pressure to afford the crude mixture that was eluted from silica to provide the pure product. The following compounds were obtained by using this method.

**1-(2,4-Dimethoxyphenyl)-1-(4-methoxyphenyl)-3-(4-nitrophenyl)prop-2-yn-1-ol 12i**

From 1-(2,4-dimethoxyphenyl)-1-(4-methoxyphenyl)prop-2-yn-1-ol (3.20 g, 10.7 mmol) and 1-bromo-4-nitrobenzene (2.17 g, 10.7 mmol) after elution from silica with 20 % EtOAc/petroleum ether afford the title compound as a pale brown waxy solid (3.10 g, 69 %); m.p. = 54 – 56 °C; ν$_{max}$ (neat) 3500, 2935, 2836, 2362, 1584, 1505, 1340, 1246, 1027, 855, 749, 587 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ$_H$ 3.81 (3H, s, OMe), 3.82 (3H, s, OMe), 3.83 (3H, s, OMe), 4.88 (1H, s, OH), 6.45 (1H, dd, $J = 8.6, 2.4$ Hz, Ar-H), 6.54 (1H, d, $J = 2.4$ Hz, Ar-H), 6.86 – 6.92 (2H, s, Ar-H), 6.89 – 6.95 (2H, s, Ar-H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ$_C$ 55.31, 55.46, 55.90, 74.03, 84.24, 97.18, 100.10, 104.07, 113.44, 123.50, 124.88, 127.70, 129.05, 129.96, 132.47, 135.91, 147.09, 157.87, 159.18, 160.95; HRMS (ESI) found [M-H$_2$O+H]$^+$ = 402.1336 C$_{24}$H$_{21}$NO$_6$ requires [M-H$_2$O+H]$^+$ = 402.1341.

**4-[3-(2,4-Dimethoxyphenyl)-3-hydroxy-3-(4-methoxyphenyl)prop-1-yn-1-yl]benzonitrile 12j**

From 1-(2,4-dimethoxyphenyl)-1-(4-methoxyphenyl)prop-2-yn-1-ol (1.50 g, 5.03 mmol) and 4-iodobenzonitrile (1.15 g, 5.03 mmol) after elution from silica with 30 % EtOAc/petroleum ether afford the title compound as a brown powder (1.96 g, 98 %); m.p. = 76 – 77 °C; ν$_{max}$ (neat) 3655, 2980, 2889, 1603, 1382, 1250, 1157, 955, 834 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ$_H$ 3.81 (6H, s, 2 × OMe), 3.82 (3H, s, OMe), 4.87 (1H, s, OH), 6.45 (1H, dd, $J = 8.6, 2.3$ Hz, Ar-H), 6.53 (1H, d, $J = 2.2$ Hz, Ar-H), 6.89 (2H, d, $J = 8.8$ Hz, Ar-H), 7.17 (1H, d, $J = 8.6$ Hz, Ar-H), 7.49 (2H, d, $J = 8.8$ Hz, Ar-H), 7.53 – 7.60 (4H, s, Ar-H); $^{13}$C{$^1$H} NMR (100 MHz,
CDCl$_3$ $\delta_C$ 55.31, 55.46, 55.90, 74.01, 84.48, 96.27, 100.10, 104.06, 111.60, 113.41, 118.51, 124.97, 127.69, 127.96, 129.04, 131.93, 132.25, 136.02, 157.86, 159.14, 160.91; HRMS (ESI) found [M-H$_2$O+H]$^+$ = 382.1435 C$_{23}$H$_{21}$NO$_4$ requires [M-H$_2$O+H]$^+$ = 382.1643.

1,1-Bis(4-methoxyphenyl)-3-(4-nitrophenyl)prop-2-yn-1-ol 12k

From 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol (2.00 g, 7.45 mmol) and 1-bromo-4-nitrobenzene (1.51 g, 7.45 mmol) after elution from silica with 20 % EtOAc/petroleum ether afford the title compound as a brown oil (2.75 g, 95 %); $\nu_{\text{max}}$ (neat) 3500, 2940, 1592, 1517, 1340, 1237, 1171, 855, 775, 588 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta_H$ 2.85 (1H, s, OH), 3.81 (6H, s, 2 × OMe), 6.89 (4H, d, $J$ = 8.6 Hz, Ar-H), 7.53 (4H, d, $J$ = 8.6 Hz, Ar-H), 7.64 (2H, d, $J$ = 8.6 Hz, Ar-H), 8.20 (2H, d, $J$ = 8.6 Hz, Ar-H); $^{13}$C{$_1$H} NMR (100 MHz, CDCl$_3$) $\delta_C$ 55.34, 74.24, 84.83, 97.41, 113.71, 123.59, 127.41, 129.45, 132.52, 136.75, 147.28, 159.30; HRMS (ESI) found [M-H$_2$O+H]$^+$ = 372.1228 C$_{23}$H$_{19}$NO$_5$ requires [M-H$_2$O+H]$^+$ = 372.1236.

Procedure for the Suzuki cross-coupling to 4-bromo-1-naphthol

A mixture of 4-bromo-1-naphthol (1 eq.), arylboronic acid (1.5 eq.), NaOH (4 eq.) and Pd(OAc)$_2$ (2.7 mol %) in water (4.5 mL/mmol) was stirred in a closed flask at room temperature until TLC examination of the reaction mixture indicated no further change in composition (20 h). The suspension was neutralised with HCl (2M aq.) and then extracted into EtOAc (3 × 100 mL). The combined organic extracts were washed with water (200 mL), dried with anhydrous sodium sulfate and evaporated to afford the crude product that required further purification by flash chromatography to afford the pure target compound. The following 4-substituted 1-naphthols were obtained from 4-bromo-1-naphthol by using this protocol:

4-(4-Methoxyphenyl)naphthalen-1-ol 19a

From (4-methoxyphenyl)boronic acid (3.07 g, 20.2 mmol) and 4-bromo-1-naphthol (3.00 g, 13.5 mmol) after gradient elution from silica with 10 % EtOAc/petroleum ether → 20 % EtOAc/petroleum ether to afford the title compound as a beige powder (1.57 g, 47 %); m.p. = 130 – 131 °C; $\nu_{\text{max}}$ (neat) 3309, 3057, 1579, 1343, 1230, 1044, 1019, 825, 785, 762, 419 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta_H$ 3.90 (3H, s, OMe), 5.34 (1H, s, OH), 6.86 (1H, d, $J$ = 7.6 Hz, 2H), 7.01 – 7.04 (2H, m, Ar-H), 7.24 (1H, d, $J$ = 7.6 Hz, 3-H), 7.38 – 7.41 (2H, m, Ar-H), 7.43 – 7.53 (2H, m, 6-H, 7-H), 7.88 – 7.90 (1H, m, 5-H), 8.25 – 8.27 (1H, m, 8-H); $^{13}$C{$_1$H} NMR (100 MHz, CDCl$_3$) $\delta_C$ 55.40, 108.19, 113.71, 121.82, 124.45, 125.14, 126.06, 126.48, 126.76, 131.27, 132.92, 132.92, 133.19, 150.67, 158.68; HRMS (ESI) found [M+H]$^+$ = 251.1064
C_{17}H_{14}O_2 requires [M+H]^+ = 251.1072. Spectroscopic data were comparable with that reported in the literature.\(^{[48]}\)

**4-Phenylnaphthalen-1-ol 19b**

From phenylboronic acid (2.87 g, 23.5 mmol) and 4-bromo-1-naphthol (3.50 g, 15.7 mmol) after elution from silica with 15 % EtOAc/petroleum ether to afford the title compound as a brown microcrystalline powder (1.62 g, 47 %); m.p. = 145 - 146 °C (lit. m.p. 139 - 140 °C \(^{[49]}\)); \(\nu_{\text{max}}\) (neat) 3325, 2980, 1509, 1343, 1244, 1175, 1031, 820, 760, 560 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 5.33 (1H, s, OH), 6.88 (1H, d, \(J = 7.6\) Hz, 2-H), 7.27 (1H, d, \(J = 7.4\) Hz, 3-H), 7.39 - 7.54 (7H, m, Ar-H), 7.88 - 7.90 (1H, m, 5-H), 8.26 - 8.29 (1H, m, 8-H); \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)) \(\delta\) C 108.16, 121.84, 124.43, 125.19, 126.00, 126.57, 126.84, 126.94, 128.26, 130.28, 132.70, 133.29, 140.78, 150.91; HRMS (ESI) found [M+H]^+ = 221.0966 C_{16}H_{12}O requires [M+H]^+ = 221.0966.

**Preparation of [4-(diethylamino)phenyl]boronic acid**

A solution of 4-diethylaminophenylmagnesium bromide was prepared by the addition of 4-bromo-\(N,N\)-diethylaniline (4.00 g, 17.5 mmol) in dry THF (25 mL) to magnesium (0.469 g, 19.3 mmol) previously treated with iodine (50 mg), continuously stirred under N\(_2\). After 20 h of stirring at room temperature, the 4-diethylaminophenylmagnesium bromide solution was added dropwise to the solution of trimethyl borate (2.00 g, 19.3 mmol) in dry THF (25 mL) at -70 °C under N\(_2\). The ice bath was removed and the mixture stirred at room temperature under N\(_2\) for 20 h. The resulting suspension was dissolved in aqueous HCl (6M, 10 mL) and then aqueous ammonia solution (~25 % v/v) was added to obtain a neutral pH. The resulting solution was extracted with Et\(_2\)O (3 × 100 mL). The combined organic extracts were washed with water (100 mL), dried over magnesium sulfate. The solvent was reduced, petroleum ether added and the precipitate filtered to give the title compound as a dark blue powder (1.04 g, 31 %); m.p. = 229 - 230 °C; \(\nu_{\text{max}}\) (neat) 3211, 2967, 2928, 1596, 1307, 1263, 1183, 1153, 748, 695 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) H 1.23 (6H, t, \(J = 6.4\) Hz, 2 × CH\(_3\)), 3.45 (4H, q, \(J = 6.7\) Hz, 2 × CH\(_2\)), 6.75 (2H, d, \(J = 7.8\) Hz, Ar-H), 8.08 (2H, d, \(J = 7.8\) Hz, Ar-H); HRMS (ESI) found [M+H]^+ = 194.1346 C\(_{10}\)H\(_{16}\)BNO\(_2\) requires [M+H]^+ = 194.1352.

**Preparation of 2H-Benzol[h]chromenes (2H-Naphtho[1,2-b]pyrans)**

**General method for the synthesis of substituted 6-bromo-2H-naphtho[1,2-b]pyrans (6-bromo-2H-benzo[h]chromenes)**
A stirred solution of the 4-bromo-1-naphthol (1.0 eq.) and the requisite 1,1,3-triaryl prop-2-yn-1-ol (1.0 eq.) in the presence of pyridinium 4-toluenesulfonate (PPTS) (5 mol %) and trimethyl orthoformate (2.0 eq.) in 1,2-dichloroethane (6 mL/mmol) was heated under reflux for up to 5 hours (until none of the prop-2-yn-1-ol remained by TLC examination of the reaction mixture). Removal of the solvent under reduced pressure from the cooled reaction mixture and gave either a dark red or green gum that was eluted from silica to afford the pure products. The following compounds were obtained by using this general method.

6-Bromo-2,2-bis(4-methoxyphenyl)-4-phenyl-2H-benzo[h]chromene 16a

From 1,1-bis(4-methoxyphenyl)-3-phenylprop-2-yn-1-ol (4.82 g, 13.4 mmol) and 4-bromo-1-naphthol (3.00 g, 13.4 mmol) after elution from silica with 20% EtOAc in n-hexane to afford:
Fraction 1: the title compound as a pale purple powder after washing with n-hexane (2.83 g, 38%), m.p. = 154 – 164 °C; v max (neat) 2956, 2839, 1604, 1507, 1443, 1372, 1350, 1297, 1252, 1220, 1173, 1100, 1032, 975, 905, 828, 758, 698, 614, 581, 524 cm⁻¹; ¹H NMR (CDCl₃) δH 3.76 (6H, s, OMe), 6.13 (1H, s, 3-H), 6.78 – 6.87 (4H, m, Ar-H), 7.37 – 7.50 (10H, m, Ar-H), 7.51 – 7.61 (3H, m, Ar-H), 8.04 – 8.12 (1H, m, Ar-H), 8.38 – 8.46 (1H, m, Ar-H); ¹³C{¹H} NMR (CDCl₃) δC 55.3, 82.9, 113.4, 113.5, 117.9, 122.8, 126.4, 126.5, 126.8, 127.1, 127.2, 127.9, 128.3, 128.8, 132.4, 135.5, 136.9, 137.7, 148.2, 159.0; HRMS found [M]+ = 548.0986. C₃₃H₂₅BrO₃ requires [M]+ = 548.0987. Fraction 2: 1,1-di(4-methoxyphenyl)-3-phenylprop-2-en-3-one 17a as an orange – brown powder (1.24 g, 27%), m.p. = 92 – 93 °C (lit. m.p. = 94 – 95 °C); v max (neat) 3009, 2933, 2839, 1650, 1603, 1554, 1507, 1424, 1379, 1290, 1245, 1213, 1186, 1173, 1160, 961, 831, 822, 788, 764, 704, 652, 574, 551, 511 cm⁻¹; ¹H NMR (CDCl₃) δH 3.79 (3H, s, OMe), 3.85 (3H, s, OMe), 6.80 (2H, dt, J = 2.4, 8.8 Hz, Ar-H), 6.90 (2H, dt, J = 2.5, 8.8 Hz, Ar-H), 7.01 (1H, s, C=CH), 7.13 (2H, dt, J = 2.3, 8.6 Hz, Ar-H), 7.37 (4H, dt, J = 2.0, 9 Hz, Ar-H), 7.39 (2H, d, J = 7.7 Hz, Ar-H), 7.47 (1H, tt, J = 1.2, 7.4 Hz, Ar-H), 7.91 (2H, app. d, J = 8.0 Hz, Ar-H); ¹³C{¹H} NMR (CDCl₃) δC 55.2, 55.4, 113.4, 113.8, 121.4, 128.3, 128.7, 130.3, 131.5, 132.4, 134.3, 138.8, 155.1, 159.8, 160.8, 192.5; HRMS found [M]+ = 344.1411. C₂₃H₂₀O₃ requires [M]+ = 344.1412.

6-Bromo-2,2,4-tris(4-methoxyphenyl)-2H-benzo[h]chromene 16b

From 1,1,3-tris(4-methoxyphenyl)prop-2-yn-ol (5.04 g, 13.4 mmol) and 4-bromo-1-naphthol (3.00 g, 13.4 mmol) after elution from silica with 20% → 40% EtOAc in n-hexane to afford:
Fraction 1: the title compound, a pale purple ‘fluffy’ solid after washing with n-hexane (3.02 g, 40%); m.p. = 187 – 190 °C; v max (neat) 2933, 2837, 1606, 1509, 1439, 1372, 1345, 1296,
1249, 1175, 1096, 1028, 959, 933, 905, 879, 826, 765, 588, 565, 550 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\)H 3.75 (6H, s, OMe) 3.87 (3H, s, OMe), 6.08 (1H, s, 3-H), 6.83 (4H, dt, \(J = 2.6, 8.9\) Hz, Ar-H), 6.94 – 7.02 (2H, m, Ar-H), 7.35 – 7.49 (7H, m, Ar-H), 7.51 – 7.57 (2H, m, Ar-H), 8.07 (1H, dd, \(J = 1.8, 7.8\) Hz, Ar-H), 8.41 (1H, dd, \(J = 1.8, 7.8\) Hz, Ar-H); \(^{13}\)C\{\(^1\)H\} NMR (CDCl\(_3\)) 55.2, 55.4, 82.9, 113.3, 113.5, 114.0, 118.1, 122.8, 126.3, 126.4, 126.9, 127.1, 127.8, 128.2, 129.9, 130.0, 132.4, 135.0, 137.0, 148.3, 158.9, 159.6; HRMS found [M]+ \(m/z = 578.1093\). C\(_{34}\)H\(_{27}\)BrO\(_4\) requires [M]+ \(m/z = 578.1093\).

6-Bromo-2,2-bis(4-methoxyphenyl)prop-2-en-3-one 17b as a viscous red gum (1.5 g, 30%); \(\nu_{\text{max}}\) (neat) 2933, 2837, 1651, 1596, 1576, 1556, 1506, 1460, 1443, 1374, 1290, 1245, 1215, 1172, 1023, 959, 829, 732, 702, 574, 551, 510 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) 3.79 (3H, s, OMe), 3.85 (6H, s, OMe), 6.80 (2H, dt, \(J = 2.4, 8.8\) Hz, Ar-H), 6.91 – 6.85 (4H, m, Ar-H), 6.97 (1H, s, 3-H), 7.12 (2H, dt, \(J = 2.5, 8.8\) Hz, Ar-H), 7.35 – 7.30 (2H, m, Ar-H), 7.92 (2H, dt, \(J = 2.4, 9.0\) Hz, Ar-H);

\(\nu_{\text{max}}\) (neat) 2953, 2834, 1607, 1509, 1327, 1247, 1222, 1175, 1156, 1122, 1099, 1068, 1032, 965, 906, 828, 758, 622, 571, 522 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\)H 3.75 (6H, s, OMe), 6.16 (1H, s, 3-H), 6.79 – 6.89 (4H, m, Ar-H), 7.12 (2H, dt, \(J = 2.4, 9.0\) Hz, Ar-H), 7.72 (1H, s, 5-H), 7.39 – 7.49 (4H, m, Ar-H), 7.50 – 7.65 (4H, m, Ar-H), 7.71 (2H, d, \(J = 8.1\) Hz, Ar-H), 8.08 (1H, dd, \(J = 2.1, 8.0\) Hz, Ar-H), 8.42 (1H, dd, \(J = 2.3, 8.0\) Hz, Ar-H); \(^{13}\)C\{\(^1\)H\} NMR (CDCl\(_3\)) \(\delta\)C 55.3, 83.0, 113.6, 113.7, 117.2, 122.8, 124.1 (q, \(J = 270.5\) Hz, CF\(_3\)), 125.7 (q, \(J = 3.7\) Hz, CH-C-CF\(_3\)), 126.3, 126.4, 126.6, 127.2, 128.1, 128.2, 129.1, 130.4 (q, \(J = 32.4\) Hz, C-CF\(_3\)), 132.6, 134.5, 136.6, 141.4 (q, \(J = 1.4\) Hz, C-CH=CH-C-CF\(_3\)), 148.4, 159.1; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\)F = -62.5; HRMS found [M]+ = 374.1514. C\(_{24}\)H\(_{22}\)O\(_4\) requires [M]+ = 374.1518.[50]

6-Bromo-2,2-bis(4-methoxyphenyl)-4-(4-nitrophenyl)-2H-benzo[h]chromene 16c

From 1,1-bis(4-methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ol (7.4 g, 18 mmol) and 4-bromo-1-naphthol (4.00 g, 17.9 mmol) after elution from silica with 20% EtOAc in n-hexane to afford the title product after washing with n-hexane as translucent yellow crystals (3.64 g, 33%); m.p. = 215 – 217 °C; \(\nu_{\text{max}}\) (neat) 2953, 2834, 1607, 1509, 1327, 1247, 1222, 1175, 1156, 1122, 1099, 1068, 1032, 965, 906, 828, 758, 622, 571, 522 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\)H 3.75 (6H, s, OMe), 6.16 (1H, s, 3-H), 6.79 – 6.89 (4H, m, Ar-H), 7.23 (1H, s, 5-H), 7.39 – 7.49 (4H, m, Ar-H), 7.50 – 7.65 (4H, m, Ar-H), 7.71 (2H, d, \(J = 8.1\) Hz, Ar-H), 8.08 (1H, dd, \(J = 2.1, 8.0\) Hz, Ar-H), 8.42 (1H, dd, \(J = 2.3, 8.0\) Hz, Ar-H); \(^{13}\)C\{\(^1\)H\} NMR (CDCl\(_3\)) \(\delta\)C 55.3, 83.0, 113.6, 113.7, 117.2, 122.8, 124.1 (q, \(J = 270.5\) Hz, CF\(_3\)), 125.7 (q, \(J = 3.7\) Hz, CH-C-CF\(_3\)), 126.3, 126.4, 126.6, 127.2, 128.1, 128.2, 129.1, 130.4 (q, \(J = 32.4\) Hz, C-CF\(_3\)), 132.6, 134.5, 136.6, 141.4 (q, \(J = 1.4\) Hz, C-CH=CH-C-CF\(_3\)), 148.4, 159.1; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\)F = -62.5; HRMS found [M]+ = 616.0858. C\(_{34}\)H\(_{24}\)BrF\(_3\)O\(_3\) requires [M]+ = 616.0861.

6-Bromo-2,2-bis(4-methoxyphenyl)-4-(4-nitrophenyl)-2H-benzo[h]chromene 16d

From 1,1-bis(4-methoxyphenyl)-3-(4-nitrophenyl)prop-2-yn-1-ol (1.69 g, 4.34 mmol) and 4-bromo-1-naphthol (0.97 g, 4.3 mmol) after elution from silica with 60 % DCM/petroleum ether to afford the title compound as a pale yellow powder (0.47 g, 40%); m.p. = 245 – 246 °C; \(\nu_{\text{max}}\)
(neat) 2980, 1595, 1507, 1342, 1247, 1168, 1096, 1032, 978, 825, 751, 586 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$H 3.76 (6H, s, 2 × OMe), 6.21 (1H, s, 3-H), 6.83 – 6.86 (4H, m, Ar-H), 7.31 (1H, s, 5-H), 7.41 – 7.43 (4H, m, Ar-H), 7.55 – 7.61 (2H, m, Ar-H), 7.64 – 7.66 (2H, m, Ar-H), 8.09 – 8.10 (1H, m, 7-H), 8.31 – 8.33 (2H, m, Ar-H), 8.41 – 8.43 (1H, m, 10-H); $^{13}$C{$^1$H} NMR (150 MHz, CDCl$_3$) $\delta$C 55.27, 83.00, 113.67, 113.83, 116.68, 122.81, 124.03, 125.94, 126.40, 126.75, 127.21, 128.16, 128.30, 129.64, 132.70, 134.01, 136.28, 144.50, 147.76, 148.43, 159.20; HRMS (ESI) found [M+H]$^+$ = 594.0891 C$_{33}$H$_{24}$BrNO requires [M+H]$^+$ = 594.0916.

6-Bromo-2-(2,4-dimethoxyphenyl)-2-(4-methoxyphenyl)-4-phenyl-2H-benzo[h]chromene 16e

From 1-(2,4-dimethoxyphenyl)-1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-ol (7.47 g, 19.9 mmol) and 4-bromo-1-naphthol (4.45 g, 19.9 mmol) after elution from silica with 80 % DCM/n-hexane to afford the title compound as feathery pale pink microcrystals (4.81 g, 42 %); m.p. = 86 – 88 °C; $\nu_{\text{max}}$ (neat) 1606, 1501, 1248, 1206, 1161, 1029, 827, 758, 699, 577 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$H 3.62 (3H, s, OMe), 3.76 (3H, s, OMe), 3.78 (3H, s, OMe), 6.43 (1H, s, 3-H), 6.45 – 6.48 (2H, m, Ar-H), 6.78 – 6.82 (2H, m, Ar-H), 7.41 – 7.48 (8H, m, Ar-H), 7.51 – 7.58 (2H, m, Ar-H), 7.65 – 7.67 (1H, m, Ar-H), 8.08 – 8.10 (1H, m, 7-H), 8.41 – 8.44 (1H, m, 10-H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$C 55.17, 55.32, 55.51, 82.29, 100.19, 103.70, 113.10, 113.21, 117.91, 122.82, 124.48, 126.23, 126.42, 126.80, 126.89, 127.06, 127.63, 127.89, 127.98, 128.21, 128.60, 128.78, 132.30, 134.27, 136.79, 138.21, 148.05, 157.23, 158.75, 160.52; HRMS (ESI) found [M]$^+$ = 578.1086 C$_{34}$H$_{27}$BrO$_4$ requires [M]$^+$ = 578.1093.

6-Bromo-2-(2,4-dimethoxyphenyl)-2,4-bis(4-methoxyphenyl)-2H-benzo[h]chromene 16f

From 1-(2,4-dimethoxyphenyl)-1,3-bis(4-methoxyphenyl)prop-2-yn-1-ol (5.01 g, 12.4 mmol) and 4-bromo-1-naphthol (2.77 g, 12.4 mmol) after elution from silica with neat DCM to afford the title compound as pale pink feathery needles (3.66 g, 48 %); m.p. = 105 – 107 °C; $\nu_{\text{max}}$ (neat) 1606, 1505, 1244, 1029, 826, 756, 532 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$H 3.74 (3H, s, OMe), 3.76 (3H, s, OMe), 3.87 (3H, s, OMe), 6.36 (1H, s, 3-H), 6.44 – 6.47 (2H, m, Ar-H), 6.77 – 6.80 (2H, m, Ar-H), 6.97 – 7.01 (2H, m, Ar-H), 7.38 – 7.45 (4H, m, Ar-H), 7.48 (1H, s, 5-H), 7.51 – 7.58 (2H, m, Ar-H), 7.64 – 7.66 (1H, m, Ar-H), 8.07 – 8.10 (1H, m, 7-H), 8.40 – 8.43 (1H, m, 10-H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$C 55.16, 55.31, 55.37, 55.49, 82.27, 100.21, 103.70, 113.07, 113.13, 113.99, 118.16, 122.80, 124.60, 126.16,
126.86, 127.02, 127.55, 127.87, 128.18, 129.91, 130.53, 132.24, 133.78, 136.89, 148.07, 157.25, 158.72, 159.43, 160.48; HRMS (ESI) found [M+H]⁺ = 609.1267 C_{35}H_{29}BrO_{5} requires [M+H]⁺ = 609.1276.

6-Bromo-2-(2,4-dimethoxyphenyl)-2-(4-methoxyphenyl)-4-[4-(trifluoromethyl)-phenyl]-2H-benzo[h]chromene 16g

From 1-(2,4-dimethoxyphenyl)-1-(4-methoxyphenyl)-3-[4-(trifluoromethyl)phenyl]prop-2-yn-1-ol (4.80 g, 10.8 mmol) and 4-bromo-1-naphthol (2.41 g, 10.8 mmol) after elution from silica with 60 % DCM/n-hexane to afford the title compound as colourless feathery needles (3.37 g, 48 %); m.p. = 97 – 98 °C; \( \nu_{\text{max}} \) (neat) 1607, 1503, 1162, 1121, 1066, 1032, 828, 758 cm⁻¹; \(^1\)H NMR (400 MHz, CDCl₃) \( \delta_H \) 3.62 (3H, s, OMe), 3.76 (3H, s, OMe), 3.78 (3H, s, OMe), 6.45 – 6.46 (2H, m, Ar-H), 6.47 (1H, s, 3-H), 6.78 – 6.82 (2H, m, Ar-H), 7.37 (1H, s, 5-H), 7.40 – 7.43 (2H, m, Ar-H), 7.53 – 7.64 (5H, m, Ar-H), 7.72 (2H, d, \( J = 8.1 \) Hz, Ar-H), 8.09 – 8.11 (1H, m, 7-H), 8.41 – 8.43 (1H, m, 10-H); \(^{13}\)C \{\(^1\)H\} NMR (100 MHz, CDCl₃) \( \delta_C \) 55.19, 55.34, 55.52, 82.32, 100.21, 103.81, 113.19, 113.45, 117.16, 122.81, 124.07, 124.18 (q, \( J = 272.5 \) Hz, CF₃), 125.62 (q, \( J = 3.8 \) Hz, =CH-C-CF₃), 126.26, 126.37, 126.47, 127.14, 127.87, 127.89, 128.05, 128.17, 129.10, 130.11 (q, \( J = 32.5 \) Hz, C-CF₃), 132.45, 133.23, 136.40, 141.95 (q, \( J = 1.3 \) Hz, C-CH=CH-C-CF₃), 148.12, 157.15, 158.88, 160.63; \(^1^9\)F NMR (376 MHz, CDCl₃) \( \delta_F \) -62.5; HRMS (ESI) found [M]+ = 646.0959 C_{35}H_{26}BrF_{3}O_{4} requires [M]+ = 646.0967.

6-Bromo-2-(2,4-dimethoxyphenyl)-2-(4-methoxyphenyl)-4-(4-nitrophenyl)-2H-benzo[h]chromene 16h

From 1-(2,4-dimethoxyphenyl)-1-(4-methoxyphenyl)-3-(4-nitrophenyl)prop-2-yn-1-ol (1.50 g, 3.58 mmol) and 4-bromo-1-naphthol (0.80 g, 3.58 mmol) after elution from silica with 20 % EtOAc/petroleum ether to afford the title compound as a pale orange powder (0.76 g, 33 %); m.p. = 173 – 175 °C; \( \nu_{\text{max}} \) (neat) 1596, 1504, 1342, 1248, 1025, 825, 754 cm⁻¹; \(^1\)H NMR (400 MHz, CDCl₃) \( \delta_H \) 3.63 (3H, s, OMe), 3.76 (3H, s, OMe), 3.77 (3H, s, OMe), 6.44 – 6.47 (2H, m, Ar-H), 6.52 (1H, s, 3-H), 6.80 (2H, d, \( J = 8.9 \) Hz, Ar-H), 7.32 (1H, s, 5-H), 7.40 (2H, d, \( J = 8.8 \) Hz, Ar-H), 7.54 – 7.64 (5H, m, Ar-H), 8.09 – 8.11 (1H, m, 7-H), 8.32 (2H, d, \( J = 8.7 \) Hz, Ar-H), 8.41 – 8.43 (1H, m, 10-H); \(^{13}\)C \{\(^1\)H\} NMR (100 MHz, CDCl₃) \( \delta_C \) 55.20, 55.35, 55.56, 82.34, 100.23, 103.89, 113.25, 113.62, 116.69, 122.82, 123.76, 123.98, 125.97, 126.36, 126.62, 127.20, 127.88, 128.08, 128.15, 128.95, 129.59, 132.54, 132.67, 136.11, 145.05, 147.56,
148.22, 157.13, 158.97, 160.71; HRMS (ESI) found [M+H]^+ = 624.1017 C_{34}H_{26}^{81}BrNO_6 requires [M+H]^+ = 624.1022.

**4-[6-Bromo-2-(2,4-dimethoxyphenyl)-2-(4-methoxyphenyl)-2H-benzo[h]chromen-4-yl]benzonitrile 16i**

From 4-[3-(2,4-dimethoxyphenyl)-3-hydroxy-3-(4-methoxyphenyl)prop-1-yn-1-yl]benzonitrile (1.10 g, 2.75 mmol) and 4-bromo-1-naphthol (0.61 g, 2.8 mmol) after elution from silica with 70 % DCM/petroleum ether to afford the title compound as a pale green crystalline powder (0.60 g, 36 %); m.p. = 128 – 129 °C; \( \nu_{\text{max}} \) (neat) 2227, 1605, 1503, 1248, 1206, 1102, 1031, 827, 760, 557 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta_H \) 3.61 (3H, s, OMe), 3.75 (3H, s, OMe), 3.76 (3H, s, OMe), 6.43 – 6.46 (2H, m, Ar-H), 6.47 (1H, s, 3-H), 6.79 (2H, m, Ar-H), 7.30 (1H, s, 5-H), 7.39 (2H, m, Ar-H), 7.50 – 7.60 (5H, m, Ar-H), 7.75 (2H, d, \( J = 8.8 \) Hz, Ar-H), 8.08 – 8.10 (1H, m, 7-H), 8.39 – 8.42 (1H, m, 10-H); \(^13\)C{\(^1\)H} NMR (100 MHz, CDCl\(_3\)) \( \delta_C \) 55.19, 55.35, 55.55, 82.32, 100.23, 103.87, 111.77, 113.22, 113.56, 116.76, 118.77, 122.81, 123.84, 126.01, 126.37, 126.58, 127.17, 127.87, 128.03, 128.15, 128.62, 129.45, 132.50, 132.52, 132.98, 136.19, 143.07, 148.21, 157.13, 158.94, 160.69; HRMS (ESI) found [M+H]^+ = 604.1114 C_{35}H_{32}^{81}BrNO_4 requires [M+H]^+ = 604.1123.

**4-[6-Bromo-2-(2,4-dimethoxyphenyl)-2-(4-methoxyphenyl)-2H-benzo[h]chromen-4-yl]-N,N-dimethylaniline 16j**

From 1-(2,4-dimethoxyphenyl)-3-(4-(dimethylamino)phenyl)-1-(4-methoxyphenyl)prop-2-yn-1-ol (1.85 g, 4.43 mmol) and 4-bromo-1-naphthol (0.98 g, 4.4 mmol) after elution from silica with 50 % DCM/petroleum ether to afford the title compound as a pale brown crystalline powder (1.51 g, 55 %); m.p. = 225 – 226 °C; \( \nu_{\text{max}} \) (neat) 2160, 2027, 1606, 1501, 1246, 1206, 1028, 820, 588 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta_H \) 3.01 (6H, s, NMe\(_2\)), 3.59 (3H, s, OMe), 3.74 (3H, s, OMe), 3.75 (3H, s, OMe), 6.33 (1H, s, 3-H), 6.43 – 6.44 (2H, m, Ar-H), 6.77 (2H, d, \( J = 8.8 \) Hz, Ar-H), 6.79 (2H, d, \( J = 8.6 \) Hz, Ar-H), 7.34 (2H, d, \( J = 8.6 \) Hz, Ar-H), 7.42 (2H, d, \( J = 8.8 \) Hz, Ar-H), 7.49 – 7.54 (2H, m, Ar-H), 7.56 (1H, s, 5-H), 7.63 – 7.65 (1H, m, Ar-H), 8.07 (1H, d, \( J = 8.3 \) Hz, 7-H), 8.40 (1H, d, \( J = 8.3 \) Hz, 10-H); \(^13\)C{\(^1\)H} NMR (150 MHz, CDCl\(_3\)) \( \delta_C \) 40.54, 55.13, 55.27, 55.45, 82.28, 100.16, 103.60, 112.32, 113.00, 118.47, 122.79, 124.77, 125.26, 125.96, 126.03, 126.46, 126.96, 127.13, 127.40, 127.86, 128.22, 129.51, 132.15, 134.06, 137.10, 148.09, 150.27, 157.27, 158.64, 160.39; HRMS (ESI) found [M+H]^+ = 622.1590 C_{36}H_{32}^{81}BrNO_4 requires [M+H]^+ = 622.1593.
General method for the synthesis of 2,2,4,6-tetraaryl substituted 2H-naphtho[1,2-b]pyrans (2,2,4,6-tetraaryl substituted 2H-benzo[h]chromenes) from a preformed 4-aryl-1-naphthol

A stirred solution of the 4-aryl-1-naphthol (1.0 eq.) and the requisite 1,1,3-triaryl prop-2-yn-1-ol (1.0 eq.) in the presence of pyridinium 4-toluenesulfonate (PPTS) (5 mol %) and trimethyl orthoformate (2.0 eq.) in 1,2-dichloroethane (6 mL/mmol) was heated under reflux for up to 5 hours until none of the prop-2-yn-1-ol remained by TLC examination of the reaction mixture. Removal of the solvent under reduced pressure from the cooled reaction mixture and gave a dark red gum that was eluted from silica to afford the pure products. The following compounds were obtained by using this method.

2-(2,4-Dimethoxyphenyl)-2,6-bis(4-methoxyphenyl)-4-phenyl-2H-benzo[h]chromene 18i

From 1-(2,4-dimethoxyphenyl)-1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-ol (1.50 g, 4.01 mmol) and 4-(4-methoxyphenyl)-1-naphthol (1.00 g, 4.01 mmol) after elution from silica with 60 % DCM/petroleum ether afford the title compound as an off-white microcrystalline powder (1.09 g, 44 %); m.p. = 81 – 82 °C; νmax (neat) 1606, 1504, 1245, 1030, 763, 700, 587 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δH 3.62 (3H, s, OMe), 3.77 (3H, s, OMe), 3.79 (3H, s, OMe), 3.84 (3H, s, OMe), 6.43 (1H, s, 3-H), 6.47 – 6.51 (2H, m, Ar-H), 6.81 (2H, d, J = 8.8 Hz, Ar-H), 6.94 (2H, d, J = 8.6 Hz, Ar-H), 7.11 (1H, s, 5-H), 7.29 (2H, d, J = 8.6 Hz, Ar-H), 7.35 – 7.43 (4H, m, Ar-H), 7.47 – 7.50 (5H, m, Ar-H), 7.75 (1H, d, J = 8.5 Hz, Ar-H), 7.79 (1H, d, J = 8.3 Hz, 7-H), 8.48 (1H, d, J = 8.3 Hz, 10-H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δC 55.17, 55.31 (× 2), 55.51, 81.97, 100.20, 103.76, 113.05, 113.56, 116.14, 122.67, 124.19, 125.09, 125.19, 125.28, 125.94, 126.26, 126.43, 127.63, 128.02, 128.26, 128.39, 128.86, 131.23, 131.94, 132.63, 133.24, 135.02, 137.39, 138.84, 147.51, 157.27, 158.60, 158.65, 160.42; HRMS (ESI) found [M]+ = 606.2396 C₄₁H₃₄O₅ requires [M]+ = 606.2406.

2-(2,4-Dimethoxyphenyl)-2-(4-methoxyphenyl)-4-(4-nitrophenyl)-6-phenyl-2H-benzo[h]chromene 18w

From 1-(2,4-dimethoxyphenyl)-1-(4-methoxyphenyl)-3-(4-nitrophenyl)prop-2-yn-1-ol (1.00 g, 2.38 mmol) and 4-phenyl-1-naphthol (0.53 g, 2.4 mmol) after elution from silica with 20 % EtOAc/petroleum ether to afford the title compound as a bright yellow powder (0.74 g, 50 %); m.p. = 116 – 117 °C; νmax (neat) 2980, 1508, 1344, 1247, 1173, 1031, 827, 765, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δH 3.64 (3H, s, OMe), 3.76 (3H, s, OMe), 3.78 (3H, s, OMe), 6.48 –
6.50 (2H, m, Ar-H), 6.53 (1H, s, 3-H), 6.82 (2H, d, J = 8.8 Hz, Ar-H), 6.98 (1H, s, 5-H), 7.34 – 7.46 (8H, m, Ar-H), 7.50 – 7.54 (1H, m, Ar-H), 7.65 (2H, d, J = 8.8 Hz, Ar-H), 7.68 – 7.70 (1H, m, Ar-H), 7.80 (1H, d, J = 8.4 Hz, 7-H), 8.27 (2H, d, J = 8.8 Hz, Ar-H), 8.48 (1H, d, J = 8.4 Hz, 10-H); ^13^C{^1^H} NMR (100 MHz, CDCl\textsubscript{3}) δ 55.20, 55.35, 55.58, 82.08, 100.23, 103.93, 113.21, 114.99, 122.67, 123.41, 123.83, 124.31, 125.15, 125.75, 126.05, 126.82, 127.05, 128.01, 128.22, 128.44, 129.65, 130.13, 132.64, 132.86, 133.46, 136.68, 140.46, 145.71, 147.35, 147.87, 157.15, 158.88, 160.63; HRMS (ESI) found [M+H]^+ = 622.2222 \text{C}_{40}\text{H}_{31}\text{NO}_6 \text{requires [M+H]^+} = 622.2229.

**General method for the Suzuki cross-coupling reaction of 4-aryl-6-bromo-2H-benzo[h]chromenes**

A 4-aryl-6-bromo-2H-benzo[h]chromene (1.0 eq.), arylboronic acid (1.5 – 3.0 eq.) and potassium fluoride (1.9 eq.) were dissolved in a mixture of EtOH and PhMe (1:1) (15 mL/mmol) and the mixture was degassed with N\textsubscript{2} for 20 minutes. Pd(PPh\textsubscript{3})\textsubscript{4} catalyst (5 mol %) was added to the reaction mixture and mixture was heated at reflux under N\textsubscript{2} for up to 20 h until no further change was noted by TLC examination of the reaction mixture. The cooled mixture was diluted with water (250 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with water (2 × 100 mL), dried with anhydrous sodium sulfate and the solvent evaporated under reduced pressure to afford the crude product that required further purification by flash chromatography to afford the pure target compound. The following 2H-benzo[h]chromenes were obtained by using this protocol:

**2,2,6-Tris(4-methoxyphenyl)-4-phenyl-2H-benzo[h]chromene 18a**

From 6-bromo-2,2-di(4-methoxyphenyl)-4-phenyl-2H-benzo[h]chromene (0.80 g, 1.5 mmol) and 4-methoxyphenylboronic acid (0.33 g, 2.2 mmol) after elution from silica with neat DCM to afford the title compound as a white foam (0.61 g, 73%); m.p. = 107 – 111 °C; ν\textsubscript{max} (neat) 3657, 2982, 2932, 1607, 1507, 1462, 1442, 1396, 1372, 1245, 1170, 1159, 1098, 1031, 945, 828, 771, 699, 589, 532 cm\textsuperscript{-1}; ^1^H NMR (CDCl\textsubscript{3}) δ 3.78 (6H, s, OMe), 3.85 (3H, s, OMe), 6.16 (1H, s, 3-H), 6.87 (4H, dt, J = 2.8, 8.8 Hz, Ar-H), 6.95 (2H, dt, J = 3.0, 8.8 Hz, Ar-H), 7.13 (1H, s, 5-H), 7.28 – 7.33 (2H, m, Ar-H), 7.34 – 7.46 (4H, m, Ar-H), 7.50 – 7.56 (7H, m, Ar-H), 7.80 (1H, d, J = 8.3 Hz, Ar-H), 8.51 (1H, dd, J = 0.6, 8.4 Hz, Ar-H); ^13^C{^1^H} NMR (CDCl\textsubscript{3}) δ 55.2, 55.3, 82.6, 113.5, 113.6, 116.2, 122.6, 124.2, 125.2, 125.5, 126.0, 126.5, 126.8, 127.9, 128.3, 128.5, 128.8, 131.2, 132.2, 132.8, 133.1, 136.2, 137.5, 138.4, 147.7, 158.6, 158.9; HRMS found [M]^+ = 576.2293. \text{C}_{40}\text{H}_{32}\text{O}_4 \text{requires [M]^+} = 576.2301.
**2,2,4-Tris(4-methoxyphenyl)-6-phenyl-2H-benzo[h]chromene 18b**

From 6-bromo-2,2,4-tris(4-methoxyphenyl)-2H-benzo[h]chromene (0.80 g, 1.4 mmol) and phenylboronic acid (0.25 g, 2.1 mmol) after elution from silica with neat DCM to afford the title compound as a white foam (0.64 g, 80%); m.p. = 134 – 135 °C; \( \nu_{\text{max}} \) (neat) 2981, 1607, 1509, 1454, 1396, 1372, 1325, 1302, 1247, 1172, 1160, 1105, 1029, 929, 829, 776, 702, 602, 567, 528 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \( \delta \)H 3.78 (6H, s, OMe), 3.84 (3H, s, OMe), 6.11 (1H, s, 3-H), 6.86 (4H, d, \( J = 8.8 \) Hz, Ar-H), 6.95 (2H, d, \( J = 8.6 \) Hz, Ar-H), 7.16 (1H, s, 5-H), 7.30 – 7.47 (8H, m, Ar-H), 7.47 – 7.57 (5H, m, Ar-H), 7.79 (1H, d, \( J = 8.4 \) Hz, Ar-H), 8.50 (1H, d, \( J = 8.3 \) Hz, Ar-H); \(^{13}\)C\({}^{1}\)H NMR (CDCl\(_3\)) \( \delta \)C 55.2, 55.3, 82.6, 113.5, 113.9, 116.4, 122.6, 124.3, 125.2, 125.5, 125.9, 126.1, 126.5, 126.8, 128.1, 128.3, 130.0, 130.2, 130.6, 132.4, 132.5, 135.7, 137.6, 140.8, 148.0, 158.9, 159.4; HRMS found [M]\(^+\) = 576.2296. C\(_{40}\)H\(_{32}\)O\(_4\) requires [M]\(^+\) = 576.2301.

**2,2,4,6-Tetra(4-methoxyphenyl)-2H-benzo[h]chromene 18c**

From 6-bromo-2,2,4-tris(4-methoxyphenyl)-2H-benzo[h]chromene (0.80 g, 1.4 mmol) and 4-methoxyphenylboronic acid (0.31 g, 2.1 mmol) after elution from silica with neat DCM to afford the title compound as a beige powder (0.42 g, 50%); m.p. = 184 – 187 °C; \( \nu_{\text{max}} \) (neat) 2982, 2835, 1607, 1509, 1453, 1396, 1369, 1300, 1245, 1175, 1159, 1119, 1106, 1033, 969, 829, 769, 575, 537 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \( \delta \)H 3.78 (6H, s, OMe), 3.86 (3H, s, OMe), 6.11 (1H, s, 3-H), 6.86 (4H, d, \( J = 8.8 \) Hz, Ar-H), 6.95 (4H, d, \( J = 8.6 \) Hz, Ar-H), 7.14 (1H, s, 5-H), 7.30 (2H, d, \( J = 8.5 \) Hz, Ar-H), 7.38 – 7.46 (3H, m, Ar-H), 7.48 – 7.53 (5H, m, Ar-H), 7.79 (1H, d, \( J = 8.4 \) Hz, Ar-H), 8.49 (1H, d, \( J = 8.3 \) Hz, Ar-H); \(^{13}\)C\({}^{1}\)H NMR (CDCl\(_3\)) \( \delta \)C 55.2, 55.3, 55.4, 82.6, 113.3, 113.6, 113.9, 116.4, 122.6, 124.3, 125.2, 125.4, 126.0, 126.1, 126.4, 128.3, 130.0, 130.7, 131.2, 132.1, 132.7, 133.2, 135.7, 137.6, 147.7, 158.6, 158.9, 159.4; HRMS found [M]\(^+\) = 606.2400. C\(_{41}\)H\(_{34}\)O\(_5\) requires [M]\(^+\) = 606.2406.

**4-[2,2,4-Tris(4-methoxyphenyl)-2H-benzo[h]chromen-6-yl]benzonitrile 18d**

From 6-bromo-2,2,4-tris(4-methoxyphenyl)-2H-benzo[h]chromene (0.60 g, 1.0 mmol) and 4-cyanophenylboronic acid (0.23 g, 1.6 mmol) after elution from silica with neat DCM to afford the title compound as a pale yellow powder after washing with \( n \)-hexane (0.24 g, 39%); m.p. = 175 – 183 °C; \( \nu_{\text{max}} \) (neat) 2932, 2836, 2227, 1606, 1507, 1442, 1370, 1318, 1300, 1242, 1169, 1109, 1098, 1029, 972, 829, 769, 725, 622, 542 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \( \delta \)H 3.78 (6H, s, OMe), 3.86 (3H, s, OMe), 6.16 (1H, s, 3-H), 6.88 (4H, d, \( J = 8.8 \) Hz, Ar-H), 6.99
(2H, d, J = 8.4 Hz, Ar-H), 7.42 – 7.59 (10H, m, Ar-H), 7.66 – 7.73 (3H, m, Ar-H), 8.55 (1H, d, J = 8.4 Hz, Ar-H); $^{13}$C NMR (CDCl$_3$) δC 55.3, 55.4, 83.0, 110.6, 113.5, 114.0, 116.6, 119.1, 122.9, 124.7, 125.1, 125.4, 125.9, 126.4, 127.2, 128.3, 129.9, 130.3, 130.4, 130.9, 131.4, 132.1, 135.4, 137.3, 145.7, 148.9, 159.0, 159.6; HRMS found [M]$^+$ = 601.2248. C$_{41}$H$_{31}$NO$_4$ requires [M]$^+$ = 601.2253.

2,2,6-Tris(4-methoxyphenyl)-4-[4-(trifluoromethyl)phenyl]-2H-benzo[h]chromene 18e

From 6-bromo-2,2-di(4-methoxyphenyl)-4-[4-(trifluoromethyl)phenyl]-2H-benzo[h]chromene (0.80 g, 1.3 mmol) and 4-methoxyphenylboronic acid (0.30 g, 1.9 mmol) after elution from silica with 35 % EtOAc in n-hexane to afford the title compound as a pale green solid (0.48 g, 57%); m.p. = 206 – 211 °C; ν$_{max}$ (neat) 2953, 2833, 1607, 1509, 1463, 1396, 1373, 1326, 1300, 1250, 1240, 1173, 1160, 1068, 1026, 1018, 975, 929, 861, 832, 776, 712, 602, 567, 527; $^1$H NMR (CDCl$_3$) δH 3.79 (6H, s, OMe), 3.88 (3H, s, OMe), 6.36 (1H, s, 3-H), 6.97 (4H, app. d, J = 8.8 Hz, Ar-H), 7.01 – 7.09 (3H, m, Ar-H), 7.42 (2H, d, J = 8.6 Hz, Ar-H), 7.51 (1H, t, J = 7.6 Hz, Ar-H), 7.63 (1H, t, J = 7.6 Hz, Ar-H), 7.68 (4H, app. d, J = 8.8 Hz, Ar-H), 7.75 – 7.78 (4H, m, Ar-H), 7.98 (1H, d, J = 8.5 Hz, Ar-H), 8.70 (1H, d, J = 8.4 Hz, Ar-H); $^{13}$C NMR (CDCl$_3$) δC 55.2, 55.3, 44.4, 82.6, 113.6, 113.7, 114.2, 115.6, 122.7, 123.6, 124.2 (q, J = 270.0 Hz, CF$_3$), 125.3, 125.5 (q, J = 3.8 Hz, CH-C-CF$_3$), 125.7, 126.2, 126.8, 127.77, 127.81, 128.2, 129.2, 130.0 (q, J = 32.1 Hz, C-F), 131.2, 132.5, 132.9, 133.0, 133.5, 135.3, 137.2, 142.1 (q, J = 1.3 Hz, C=CH=CH-C-CF$_3$), 147.8, 158.7, 158.8, 159.0; $^{19}$F NMR (376 MHz, CDCl$_3$) δF -62.1; HRMS found [M]$^+$ = 644.2169. C$_{41}$H$_{31}$F$_3$O$_4$ requires [M]$^+$ = 644.2174.

4-{2,2-Bis(4-methoxyphenyl)-4-[4-(trifluoromethyl)phenyl]-2H-benzo[h]chromen-6-yl}-N,N-dimethylaniline 18f

From 6-bromo-2,2-di(4-methoxyphenyl)-4-[4-(trifluoromethyl)phenyl]-2H-benzo[h]chromene (0.80 g, 1.3 mmol) and 4-(dimethylamino)phenylboronic acid (0.30 g, 1.9 mmol) after elution from silica with 35 % EtOAc in n-hexane to afford the title compound as a pale yellow foam (0.62 g, 73%); m.p. = 101 – 104 °C; ν$_{max}$ (neat) 2930, 2835, 1609, 1507, 1454, 1397, 1322, 1247, 1163, 1120, 1105, 1066, 1033, 976, 822, 768, 581, 528 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δH 3.05 (6H, s, NMe$_2$), 3.82 (6H, s, OMe), 6.30 (1H, s, 3-H), 6.88 (2H, d, J = 8.8 Hz, Ar-H), 6.94 – 6.98 (4H, m, Ar-H), 7.17 (1H, s, 5-H), 7.38 (2H, d, J = 8.7 Hz, Ar-H), 7.51 (1H, td, J = 1.2, 7.6 Hz, Ar-H), 7.60 – 7.65 (5H, m, Ar-H), 7.74 – 7.78 (4H, m, Ar-H), 8.02 (1H, d, J = 8.3 Hz, Ar-H), 8.63 (1H, d, J = 8.2 Hz, Ar-H); $^{13}$C NMR (CDCl$_3$) δC 40.6, 55.3, 82.6,
112.2, 113.1, 113.6, 122.6, 123.5, 125.2, 125.5 (q, J = 271.0 Hz, C-F), 125.5 (q, J = 3.7 Hz, CH-C-CF₃), 126.3, 126.6, 127.0, 127.6, 128.2, 128.5, 129.2, 129.9 (q, J = 32.3 Hz, C-CF₃), 130.8, 133.1, 135.4, 137.3, 142.2 (q, J = 1.4 Hz, CH=CH-C-CF₃), 147.4, 149.3, 149.6, 159.0; ¹⁹F NMR (CDCl₃) δF -62.2; HRMS found [M]+ = 657.2484. C₄₂H₃₄F₃NO₃ requires [M]+ = 657.2491.

4-[2,2-Bis(4-methoxyphenyl)-4-(4-nitrophenyl)-2H-benzo[h]chromen-6-yl]-N,N-dimethylaniline 18g

From 6-bromo-2,2-bis(4-methoxyphenyl)-4-(4-nitrophenyl)-2H-benzo[h]chromene (0.25 g, 0.42 mmol) and 4-(dimethylamino)phenylboronic acid (0.17 g, 1.1 mmol) after elution from silica with 20 % EtOAc/petroleum ether to afford the title compound as an orange powder (0.24 g, 90 %); m.p. = 149 – 150 °C; νmax (neat) 2956, 2363, 2342, 1610, 1510, 1342, 1253, 1173, 830, 817, 770 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δH 2.97 (6H, s, NMe₂), 3.77 (6H, s, 2 × OMe), 6.20 (1H, s, 3-H), 6.77 (2H, d, J = 8.8 Hz, Ar-H), 6.84 – 6.88 (2H, m, Ar-H), 6.95 (1H, s, 5-H), 6.24 – 7.22 (2H, m, Ar-H), 7.39 – 7.43 (1H, m, Ar-H), 7.46 – 7.52 (5H, m, Ar-H), 7.65 – 7.68 (2H, m, Ar-H), 7.88 (1H, d, J = 8.4 Hz, 7-H), 8.25 – 8.27 (2H, m, Ar-H), 8.47 (1H, d, J = 7.9 Hz, 10-H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δC 40.60, 55.26, 82.53, 112.21, 113.60, 115.10, 122.58, 123.14, 123.83, 125.25, 125.69, 126.36, 126.74, 128.20, 128.30, 128.35, 129.72, 130.77, 133.15, 133.30, 134.90, 136.98, 145.33, 147.46, 147.49, 149.66, 159.05; HRMS (ESI) found [M+H]+ = 635.2542 C₄₁H₃₄N₂O₅ requires [M+H]+ = 635.2546.

2-(2,4-Dimethoxyphenyl)-2-(4-methoxyphenyl)-4,6-diphenyl-2H-benzo[h]chromene 18h

From 6-bromo-2-(2,4-dimethoxyphenyl)-2-(4-methoxyphenyl)-4-phenyl-2H-benzo[h]-chromene (1.00 g, 1.73 mmol) and phenylboronic acid (0.32 g, 2.6 mmol) after elution from silica with 10 % EtOAc/petroleum ether to afford the title compound as an off-white microcrystalline powder (0.89 g, 89 %); m.p. = 84 – 87 °C; νmax (neat) 1605, 1503, 1247, 1207, 1158, 1029, 972, 829, 771, 700, 579 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δH 3.61 (3H, s, OMe), 3.76 (3H, s, OMe), 3.78 (3H, s, OMe), 6.42 (1H, s, 3-H), 6.45 – 6.50 (2H, m, Ar-H), 6.79 – 6.81 (2H, m, Ar-H), 7.12 (1H, s, 5-H), 7.31 – 7.41 (9H, m, Ar-H), 7.46 – 7.50 (5H, m, Ar-H), 7.73 (1H, d, J = 8.5 Hz, Ar-H), 7.76 (1H, d, J = 8.4 Hz, 7-H), 8.47 – 8.49 (1H, m, 10-H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δC 55.17, 55.31, 55.52, 82.03, 100.21, 103.77, 113.06, 116.13, 122.68, 124.24, 125.06, 125.17, 125.34, 125.89, 126.35, 126.45, 126.77, 127.65, 128.02, 128.10, 128.26, 128.41, 128. 85, 130.25, 132.31, 132.41, 134.98, 137.37, 138.80,
140.85, 147.73, 157.27, 158.66, 160.43; HRMS (ESI) found [M+H]^+ = 577.2365 \text{C}_{40}\text{H}_{32}\text{O}_4 \\
requires [M+H]^+ = 577.2379.

**2-(4-Dimethoxyphenyl)-2,6-bis(4-methoxyphenyl)-4-phenyl-2H-benzo[h]chromene 18i**

From 6-bromo-2-(4-dimethoxyphenyl)-2-(4-methoxyphenyl)-4-phenyl-2H-benzo[h]-chromene (1.00 g, 1.73 mmol) and 4-methoxyphenylboronic acid (0.40 g, 2.6 mmol) after elution from silica with 20 % EtOAc/n-hexane as a colourless gum that solidified when scratched with n-pentane to give the title compound as off-white crystalline powder (0.76 g, 72 %). This compound had near identical physical and spectroscopic properties to the material obtained from 4-(4-methoxyphenyl)-1-naphthol and 1-(2,4-dimethoxyphenyl)-1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-ol.

**2-(2,4-Dimethoxyphenyl)-2-(4-methoxyphenyl)-6-[4-(trifluoromethyl)-phenyl]-2H-benzo[h]chromene 18j**

From 6-bromo-2-(4-dimethoxyphenyl)-2-(4-methoxyphenyl)-4-phenyl-2H-benzo[h]-chromene (1.00 g, 1.73 mmol) and (4-trifluoromethyl)phenylboronic acid (0.49 g, 2.6 mmol) after elution from silica with 20 % EtOAc/n-hexane to afford the title compound as a peach coloured microcrystalline powder (0.95 g, 85 %); m.p. = 53 – 56 °C; \nu_{\text{max}} (neat) 1607, 1502, 1321, 1248, 1159, 1118, 1065, 829, 700, 578 cm\(^{-1}\); \text{\textsuperscript{1}H} NMR (400 MHz, CDCl\(_3\)) \(\delta\)H 3.63 (3H, s, OMe), 3.77 (3H, s, OMe), 3.79 (3H, s, OMe), 6.46 (1H, s, 3-H), 6.47 – 6.51 (2H, m, Ar-H), 6.80 – 6.84 (2H, m, Ar-H), 7.12 (1H, s, 5-H), 7.36 – 7.44 (4H, m, Ar-H), 7.47 – 7.54 (7H, m, Ar-H), 7.65 (2H, d, J = 8.1 Hz, Ar-H), 7.70 – 7.75 (2H, m, Ar-H), 8.51 (1H, d, J = 8.3 Hz, 10-H); \text{\textsuperscript{13}C\{\text{\textsuperscript{1}H}\}} NMR (100 MHz, CDCl\(_3\)) \(\delta\)C 55.18, 55.33, 55.53, 82.20, 100.19, 103.75, 113.08, 116.20, 122.87, 124.36 (q, J = 272 Hz, CF\(_3\)), 124.47, 124.86, 125.11 (q, J = 3.8 Hz, =CH-C-CF\(_3\)), 125.22, 125.37, 125.63, 126.63, 126.78, 127.80, 127.97, 128.26, 128.49, 128.80, 128.95 (q, J = 32.5 Hz, C-CF\(_3\)), 130.52, 130.75, 132.01, 134.76, 137.18, 138.59, 144.58 (q, J = 13 Hz, C-CH=CH-C-CF\(_3\)), 148.33, 157.26, 158.71, 160.49; \text{\textsuperscript{19}F} NMR (376 MHz, CDCl\(_3\)) \(\delta\)F -62.3; HRMS (ESI) found [M+H]^+ = 645.2236 \text{C}_{41}\text{H}_{31}\text{F}_3\text{O}_4 requires [M+H]^+ = 645.2252.

**2-(2,4-Dimethoxyphenyl)-2,4-bis(4-methoxyphenyl)-6-phenyl-2H-benzo[h]chromene 18k**

From 6-bromo-2-(2,4-dimethoxyphenyl)-2,4-bis(4-methoxyphenyl)-2H-benzo[h]chromene (1.00 g, 1.64 mmol) and phenylboronic acid (0.30 g, 2.5 mmol) after elution from silica with 30 % EtOAc/petroleum ether afforded the title compound as pale yellow microcrystalline powder (0.92 g, 92 %); m.p. = 101 – 103 °C; \nu_{\text{max}} (neat) 1606, 1504, 1245, 1207, 1173, 1030,
828, 701 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.63 (3H, s, OMe), 3.77 (3H, s, OMe), 3.79 (3H, s, OMe), 3.84 (3H, s, OMe), 6.40 (1H, s, 3-H), 6.47 – 6.51 (2H, m, Ar-H), 6.80 – 6.83 (2H, m, Ar-H), 6.93 – 6.97 (2H, m, Ar-H), 7.16 (1H, s, 5-H), 7.33 – 7.45 (8H, m, Ar-H), 7.47 – 7.52 (3H, m, Ar-H), 7.75 (1H, d, \(J = 8.4\) Hz, Ar-H), 7.79 (1H, d, \(J = 8.4\) Hz, 7-H), 8.49 (1H, d, \(J = 7.9\) Hz, 10-H); \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)) \(\delta\)C 55.17, 55.32, 55.33, 55.52, 82.02, 100.19, 103.71, 113.03, 113.83, 116.38, 122.69, 124.34, 125.11, 125.18, 125.33, 125.77, 125.88, 126.33, 126.78, 127.99, 128.12, 128.28, 129.98, 130.27, 131.13, 132.26, 132.34, 134.49, 137.43, 140.89, 147.76, 157.26, 158.63, 159.19, 160.39; HRMS (ESI) found [M+H]\(^+\) = 607.2475 C\(_{41}\)H\(_{34}\)O\(_5\) requires [M+H]\(^+\) = 607.2484.

2-(2,4-Dimethoxyphenyl)-2,4,6-tris(4-methoxyphenyl)-2\(H\)-benzo[\(h\)]chromene 18l

From 6-bromo-2-(2,4-dimethoxyphenyl)-2,4-bis(4-methoxyphenyl)-2\(H\)-benzo[\(h\)]chromene (1.00 g, 1.64 mmol) and (4-methoxyphenyl)boronic acid (0.37 g, 2.5 mmol) after elution from silica with 30 % EtOAc/petroleum ether to afford the title compound as a pale yellow microcrystalline powder (0.89 g, 86 %); m.p. = 110 – 112 °C; \(\nu\)max (neat) 1606, 1510, 1242, 1170, 1030, 828, 570 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\)H 3.62 (3H, s, OMe), 3.76 (3H, s, OMe), 3.78 (3H, s, OMe), 3.84 (3H, s, OMe), 3.85 (3H, s, OMe), 6.39 (1H, s, 3-H), 6.47 – 6.50 (2H, m, Ar-H), 6.80 – 6.82 (2H, m, Ar-H), 6.93 – 6.96 (4H, m, Ar-H), 7.13 (1H, s, 5-H), 7.29 – 7.31 (2H, m, Ar-H), 7.37 – 7.43 (3H, m, Ar-H), 7.47 – 7.50 (3H, m, Ar-H), 7.74 (1H, d, \(J = 8.4\) Hz, Ar-H), 7.79 (1H, d, \(J = 8.3\) Hz, 7-H), 8.47 – 8.49 (1H, m, 10-H); \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)) \(\delta\)C 55.16, 55.32, 55.33 (× 2), 55.51, 81.97, 100.20, 103.74, 113.02, 113.56, 113.82, 116.41, 122.67, 124.27, 125.17, 125.20, 125.25, 125.74, 125.93, 126.22, 128.00, 128.26, 129.97, 131.18, 131.23, 131.88, 132.57, 133.29, 134.52, 137.48, 147.53, 157.28, 158.59, 158.63, 159.19, 160.38; HRMS (ESI) found [M+H]\(^+\) = 637.2581 C\(_{42}\)H\(_{36}\)O\(_6\) requires [M+H]\(^+\) = 637.2590.

2-(2,4-Dimethoxyphenyl)-2,4-bis(4-methoxyphenyl)-6-[4-(trifluoromethyl)phenyl]-2\(H\)-benzo[\(h\)]chromene 18m

From 6-bromo-2-(2,4-dimethoxyphenyl)-2,4-bis(4-methoxyphenyl)-2\(H\)-benzo[\(h\)]chromene (1.00 g, 1.64 mmol) and (4-trifluoromethyl)phenylboronic acid (0.47 g, 2.5 mmol) after elution from silica with 20 % EtOAc/petroleum ether to afford the title compound as a colourless gum that solidified when scratched with \(n\)-pentane and gave a very pale yellow microcrystalline powder (0.81 g, 73 %); m.p. = 120 – 122 °C; \(\nu\)max (neat) 1608, 1504, 1323, 1247, 1121, 1031, 830, 768 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\)H 3.62 (3H, s, OMe), 3.77 (3H, s, OMe), 3.78
(3 H, s, OMe), 3.84 (3 H, s, OMe), 6.40 (1 H, s, 3-H), 6.46 – 6.50 (2 H, m, Ar-H), 6.79 – 6.83 (2 H, m, Ar-H), 6.93 – 6.96 (2 H, m, Ar-H), 7.13 (1 H, s, 5-H), 7.40 – 7.43 (3 H, m, Ar-H), 7.44 – 7.51 (5 H, m, Ar-H), 7.65 (2 H, d, J = 8.1 Hz, Ar-H), 7.70 – 7.73 (2 H, m, Ar-H), 8.49 (1 H, d, J = 8.3 Hz, 10-H); 13C {1H} NMR (100 MHz, CDCl3) δc 55.17, 55.31, 55.51, 82.21, 100.21, 103.75, 113.06, 113.88, 116.44, 122.87, 124.36 (q, J = 272.0 Hz, CF3), 124.55, 124.99, 125.09 (q, J = 3.8 Hz, =CH-C-CF3), 125.23, 125.34, 125.57, 125.93, 126.71, 127.95, 128.25, 128.93 (q, J = 32.5 Hz, C=CH–CH–C-CF3), 129.92, 130.51, 130.68, 130.91, 131.96, 134.26, 137.29, 144.64 (q, J = 1.2 Hz, C–CH=CH–C-CF3), 148.36, 157.28, 158.69, 159.30, 160.46; 19F NMR (376 MHz, CDCl3) δF -62.3; HRMS (ESI) found [M+H]+ = 675.2347 C42H33F3O5 requires [M+H]+ = 675.2358.

2-(2,4-Dimethoxyphenyl)-2-(4-methoxyphenyl)-6-phenyl-4-[4-(trifluoromethyl)phenyl]-2H-benzo[h]chromene 18n

From 6-bromo-2-(2,4-dimethoxyphenyl)-2-(4-methoxyphenyl)-4-[4-(trifluoromethyl)phenyl]-2H-benzo[h]chromene (0.80 g, 1.2 mmol) and phenylboronic acid (0.23 g, 1.9 mmol) after elution from silica with 10 % EtOAc/petroleum ether to afford the title compound as a pale yellow microcrystalline powder (0.65 g, 81 %); m.p. = 76 – 78 °C; νmax (neat) 1606, 1503, 1322, 1249, 1121, 1066, 1031, 829, 702 cm⁻¹; 1H NMR (400 MHz, CDCl3) δH 3.63 (3 H, s, OMe), 3.77 (3 H, s, OMe), 3.79 (3 H, s, OMe), 6.48 (1 H, s, 3-H), 6.49 – 6.51 (2 H, m, Ar-H), 6.80 – 6.84 (2 H, m, Ar-H), 7.03 (1 H, s, 5-H), 7.35 – 7.53 (9 H, m, Ar-H), 7.59 – 7.61 (2 H, m, Ar-H), 7.66 – 7.68 (2 H, m, Ar-H), 7.71 (1 H, d, J = 8.4 Hz, Ar-H), 7.78 (1 H, d, J = 8.4 Hz, 7-H), 8.48 (1 H, d, J = 8.3 Hz, 10-H); 13C {1H} NMR (100 MHz, CDCl3) δc 55.19, 55.33, 55.53, 82.06, 100.20, 103.83, 113.14, 115.41, 122.67, 123.68, 124.61, 125.13, 125.44 (q, J = 3.8 Hz, =CH-C-CF3), 125.59, 125.98, 126.62, 126.91 (q, J = 272 Hz, C=CF3), 126.95, 127.56, 127.99, 128.19, 128.24, 129.14, 129.78 (q, J = 32.5 Hz, C=CF3), 130.19, 132.56, 132.64, 133.97, 136.96, 140.62, 142.54 (q, J = 1.3 Hz, C=CH–CH–C-CF3), 147.77, 157.17, 158.78, 160.53; 19F NMR (376 MHz, CDCl3) δF -62.5; HRMS (ESI) found [M+H]+ = 645.2244 C41H31F3O4 requires [M+H]+ = 645.2252.

2-(2,4-Dimethoxyphenyl)-2,6-bis(4-methoxyphenyl)-4-[4-(trifluoromethyl)phenyl]-2H-benzo[h]chromene 18o

From 6-bromo-2-(2,4-dimethoxyphenyl)-2-(4-methoxyphenyl)-4-[4-(trifluoromethyl)phenyl]-2H-benzo[h]chromene (0.80 g, 1.2 mmol) and (4-methoxyphenyl)boronic acid (0.28 g, 1.9 mmol) after elution from silica with 20 % EtOAc/petroleum ether to afford the title compound
as a pale yellow gum that solidified when scratched with n-pentane and gave pale yellow microcrystalline powder (0.68 g, 81 %); m.p. = 99 – 101 °C; νmax (neat) 1607, 1509, 1322, 1245, 1159, 1104, 1031, 972, 829, 768 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δH 3.63 (3H, s, OMe), 3.77 (3H, s, OMe), 3.79 (3H, s, OMe), 3.85 (3H, s, OMe), 6.48 (1H, s, 3-H), 6.48 – 6.51 (2H, m, Ar-H), 6.82 (2H, d, J = 8.8 Hz, Ar-H), 6.95 (2H, d, J = 8.6 Hz, Ar-H), 7.00 (1H, s, 5-H), 7.29 (2H, d, J = 8.6 Hz, Ar-H), 7.40 – 7.53 (4H, m, Ar-H), 7.59 – 7.61 (2H, m, Ar-H), 7.66 – 7.68 (2H, m, Ar-H), 7.71 (1H, d, J = 8.5 Hz, Ar-H), 7.79 (1H, d, J = 8.4 Hz, 7-H), 8.48 (1H, d, J = 8.2 Hz, 10-H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δC 55.19, 55.32, 55.33, 55.53, 82.00, 100.20, 103.83, 113.13, 113.63, 114.81, 115.43, 116.02, 122.65, 123.64, 124.22 (q, J = 272.5 Hz, CF₃), 124.64, 125.15, 125.43 (q, J = 3.8 Hz, =CH-C-CF₃), 125.53, 126.04, 126.54, 127.99, 128.24, 129.16, 129.60, 129.79 (q, J = 32.5 Hz, C-CF₃), 129.92, 131.18, 132.29, 132.78, 132.98, 134.01, 136.99, 142.58 (q, J = 1.2 Hz, C-CH=CH-C-CF₃), 147.56, 157.17, 158.70, 158.77, 160.52; δF (376 MHz, CDCl₃) -62.4; HRMS (ESI) found [M+H]+ = 675.2352 C₄₂H₃₃F₃O₅ requires [M+H]+ = 675.2358.

2-(2,4-Dimethoxyphenyl)-2-(4-methoxyphenyl)-4,6-bis[4-(trifluoromethyl)phenyl]-2H-benzo[h]chromene 18p

From 6-bromo-2-(2,4-dimethoxyphenyl)-2-(4-methoxyphenyl)-4-[4-(trifluoromethyl)phenyl]-2H-benzo[h]chromene (0.80 g, 1.2 mmol) and (4-trifluoromethyl)phenylboronic acid (0.35 g, 1.9 mmol) after elution from silica with 20 % EtOAc/petroleum ether to afford the title compound as pale yellow gum that solidified when scratched with n-pentane and gave a white microcrystalline powder (0.79 g, 90 %); m.p. = 111 – 114 °C; νmax (neat) 1608, 1503, 1321, 1160, 1105, 830, 768 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δH 3.64 (3H, s, OMe), 3.77 (3H, s, OMe), 3.79 (3H, s, OMe), 6.49 (1H, s, 3-H), 6.50 – 6.51 (2H, m, Ar-H), 6.82 – 6.85 (2H, m, Ar-H), 7.02 (1H, s, 5-H), 7.44 – 7.61 (8H, m, Ar-H), 7.66 – 7.73 (6H, m, Ar-H), 8.50 (1H, d, J = 8.4 Hz, 10-H); ¹³C{¹H} NMR (150 MHz, CDCl₃) δC 55.19, 55.34, 55.55, 82.26, 100.24, 103.89, 113.20, 115.49, 122.87, 123.42, 123.88, 124.17 (q, J = 272.0 Hz, C-CF₃), 124.34 (q, J = 272 Hz, C-CF₃), 124.49, 125.07, 125.20 (q, J = 3.5 Hz, =CH-C-CF₃), 125.48, 125.52 (q, J = 3.5 Hz, =CH-C-CF₃), 125.86, 127.04, 127.79, 127.97, 128.23, 129.11, 129.15 (q, J = 32.5 Hz, C-CF₃), 129.95 (q, J = 32.5 Hz, C-CF₃), 130.48, 131.10, 132.20, 133.76, 136.82, 142.36 (q, J = 1.5 Hz, C-CH=CH-C-CF₃), 144.36 (q, J = 1.5 Hz, C-CH=CH-C-CF₃), 148.40, 157.21, 158.87, 160.63; δF (376 MHz, CDCl₃) -62.4, -62.5; HRMS (ESI) found [M+H]+ = 713.2125 C₄₂H₃₀F₆O₄ requires [M+H]+ = 713.2126.
4-{2-(2,4-Dimethoxyphenyl)-2-(4-methoxyphenyl)-4-(4-(trifluoromethyl)phenyl)-2{H}benzo[h]chromen-6-yl}-N,N-dimethylaniline 18q

From 6-bromo-2-(2,4-dimethoxyphenyl)-2-(4-methoxyphenyl)-4-(4-(trifluoromethyl)phenyl)-2{H}benzo[h]chromene (0.35 g, 0.54 mmol) and 4-(dimethylamino)phenylboronic acid (0.22 g, 1.4 mmol) after elution from silica with 20 % EtOAc/petroleum ether to afford the title compound as a pale yellow microcrystalline powder (0.30 g, 80 %); m.p. = 227 – 228 °C; \(\nu_{\text{max}}\) (neat) 2981, 1608, 1504, 1324, 1256, 1177, 1110, 1065, 1031, 971, 823, 767 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 2.97 (6H, s, NMe\(_2\)), 3.61 (3H, s, OMe), 3.75 (3H, s, OMe), 3.77 (3H, s, OMe), 6.46 (1H, s, 3-H), 6.46 – 6.49 (2H, m, Ar-H), 6.76 – 6.78 (2H, m, Ar-H), 6.79 – 6.82 (2H, m, Ar-H), 7.00 (1H, s, 5-H), 7.23 – 7.25 (2H, m, Ar-H), 7.37 – 7.40 (1H, m, Ar-H), 7.44 – 7.46 (2H, m, Ar-H), 7.47 – 7.49 (1H, m, Ar-H), 7.59 (2H, d, \(J = 8.1\) Hz, Ar-H), 7.65 (2H, d, \(J = 8.1\) Hz, Ar-H), 7.71 (1H, d, \(J = 8.5\) Hz, Ar-H), 7.87 (1H, d, \(J = 8.4\) Hz, 7-H), 8.46 (1H, d, \(J = 8.4\) Hz, 10-H); \(^{13}\)C\{\(^1\)H\} NMR (150 MHz, CDCl\(_3\)) \(\delta\) 40.61, 55.19, 55.33, 55.54, 81.94, 100.22, 103.87, 112.20, 113.14, 115.50, 122.60, 123.49, 124.26 (q, \(J = 272.0\) Hz, CF\(_3\)), 124.78, 125.19, 125.40 (q, \(J = 3.8\) Hz, \(=\)CH-C-CF\(_3\)), 126.31, 126.33, 127.40, 128.03, 128.25, 128.66, 129.20, 129.71 (q, \(J = 32.5\) Hz, \(\equiv\)CH-C-CF\(_3\)), 130.85, 132.90, 132.95, 133.97, 134.15, 137.11, 142.70 (q, \(J = 1.3\) Hz, \(\equiv\)CH=CH-C-CF\(_3\)), 147.21, 149.59, 157.20, 158.77, 160.52; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -62.5; HRMS (ESI) found \([M+H]^{+}\) = 688.2666 C\(_{43}\)H\(_{36}\)F\(_3\)NO\(_4\) requires \([M+H]^{+}\) = 688.2674.

2-(2,4-Dimethoxyphenyl)-2,6-bis(4-methoxyphenyl)-4-(4-nitrophenyl){-2H}benzo[h]chromene 18r

From 6-bromo-2-(2,4-dimethoxyphenyl)-2-(4-methoxyphenyl)-4-(4-nitrophenyl)-2{H}benzo[h]chromene (0.30 g, 0.48 mmol) and 4-methoxyphenylboronic acid (0.11 g, 0.72 mmol) after elution from silica with 20 % EtOAc/petroleum ether to afford the title compound as an orange oil that solidified on standing to give orange powder (0.20 g, 63 %); m.p. = 133 – 135 °C; \(\nu_{\text{max}}\) (neat) 2930, 2834, 2361, 1607, 1511, 1344, 1244, 1101, 1030, 828, 710 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.64 (3H, s, OMe), 3.77 (3H, s, OMe), 3.79 (3H, s, OMe), 3.84 (3H, s, OMe), 6.48 – 6.50 (2H, m, Ar-H), 6.53 (1H, s, 3-H), 6.80 – 6.84 (2H, m, Ar-H), 6.93 – 6.97 (2H, m, Ar-H), 6.96 (1H, s, 5-H), 7.27 – 7.30 (2H, m, Ar-H), 7.41 – 7.47 (3H, m, Ar-H), 7.50 – 7.54 (1H, m, Ar-H), 7.64 – 7.67 (2H, m, Ar-H), 7.68 – 7.71 (1H, m, Ar-H), 7.80 (1H, d, \(J = 8.3\) Hz, 7-H), 8.26 – 8.29 (2H, m, Ar-H), 8.47 (1H, d, \(J = 7.9\) Hz, 10-H); \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)) \(\delta\) 55.20, 55.33, 55.35, 55.57, 82.02, 100.22, 103.92, 113.19, 113.68, 115.00,
122.66, 123.35, 123.81, 124.32, 125.69, 126.10, 126.72, 128.00, 128.22, 128.41, 129.65, 131.12, 132.50, 132.81, 132.86, 133.49, 136.70, 145.77, 147.33, 147.64, 157.15, 158.76, 158.86, 160.61; HRMS (ESI) found [M+H]$^+$ = 652.2323 C$_{41}$H$_{33}$NO$_7$ requires [M+H]$^+$ = 652.2335.

4-[2-(2,4-Dimethoxyphenyl)-2-(4-methoxyphenyl)-4-(4-nitrophenyl)-2H-benzo[h]chromen-6-yl]-N,N-dimethylaniline 18s

From 6-bromo-2-(2,4-dimethoxyphenyl)-2-(4-methoxyphenyl)-4-(4-nitrophenyl)-2H-benzo[h]chromene (0.30 g, 0.48 mmol) and 4-(dimethylamino)phenylboronic acid (0.12 g, 0.72 mmol) after elution from silica with 20 % EtOAc/petroleum ether to afford the title compound as an orange oil that solidified when scratched with n-pentane and gave an orange powder (0.27 g, 85 %); m.p. = 126 – 128 °C; $\nu_{max}$ (neat) 2932, 2834, 2159, 1608, 1514, 1444, 1248, 823, 414 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$H 2.98 (6H, s, NMe$_2$), 3.64 (3H, s, OMe), 3.77 (3H, s, OMe), 3.79 (3H, s, OMe), 4.68 – 6.50 (2H, m, Ar-H), 6.53 (1H, s, 3-H), 6.77 – 6.83 (4H, m, Ar-H), 6.97 (1H, s, 5-H), 7.25 (2H, d, $J$ = 9.1 Hz, Ar-H), 7.40 – 7.53 (4H, m, Ar-H), 7.65 (2H, d, $J$ = 8.6 Hz, Ar-H), 7.70 (1H, d, $J$ = 9.2 Hz, Ar-H), 7.89 (1H, d, $J$ = 8.4 Hz, 7-H), 8.27 (2H, d, $J$ = 8.6 Hz, Ar-H), 8.47 (1H, d, $J$ = 8.3 Hz, 10-H); $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$) $\delta$C 40.62, 40.85, 55.20, 55.35, 55.57, 81.94, 100.22, 103.91, 112.22, 113.18, 115.06, 115.06, 122.60, 123.20, 123.78, 124.42, 125.19, 125.57, 126.35, 126.51, 128.03, 128.23, 128.28, 128.45, 129.69, 130.79, 133.00, 133.11, 133.62, 136.79, 145.88, 147.27, 149.63, 157.15, 158.83, 160.58; HRMS (ESI) found [M+H]$^+$ = 665.2640 C$_{42}$H$_{36}$N$_2$O$_6$ requires [M+H]$^+$ = 655.2651.

4-[2-(2,4-Dimethoxyphenyl)-2-(4-methoxyphenyl)-4-(4-nitrophenyl)-2H-benzo[h]chromen-6-yl]-N,N-diethylaniline 18t

From 6-bromo-2-(2,4-dimethoxyphenyl)-2-(4-methoxyphenyl)-4-(4-nitrophenyl)-2H-benzo[h]chromene (0.30 g, 0.51 mmol) and (4-(diethylamino)phenyl)boronic acid (0.24 g, 1.3 mmol) after elution from silica with 20 % EtOAc/petroleum ether to afford the title compound as an orange powder (0.30 g, 94 %); m.p. = 260 – 261 °C; $\nu_{max}$ (neat) 2962, 2359, 1608, 1519, 1347, 1252, 1174, 1159, 1036, 831 and 817 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$H 1.18 (6H, t, $J$ = 7.0 Hz, NEt$_2$), 3.37 (4H, q, $J$ = 7.0 Hz, NEt$_2$), 3.62 (3H, s, OMe), 3.75 (3H, s, OMe), 3.77 (3H, s, OMe), 6.47 – 6.49 (2H, m, Ar-H), 6.51 (1H, s, 3-H), 6.70 (2H, d, $J$ = 8.6 Hz, Ar-H), 6.81 (2H, d, $J$ = 8.8 Hz, Ar-H), 6.96 (1H, s, 5-H), 7.20 (2H, d, $J$ = 8.6 Hz, Ar-H), 7.39 – 7.51 (4H, m, Ar-H), 7.65 (2H, d, $J$ = 8.6 Hz, Ar-H), 7.70 (1H, d, $J$ = 9.2 Hz, Ar-H), 7.93 (1H, d, $J$ = 8.4 Hz, Ar-H), 8.27 (2H, d, $J$ = 8.6 Hz, Ar-H), 8.47 (1H, d, $J$ = 8.3 Hz, 10-H); $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$) $\delta$C 40.62, 40.85, 55.20, 55.35, 55.57, 81.94, 100.22, 103.91, 112.22, 113.18, 115.06, 122.60, 123.20, 123.78, 124.42, 125.19, 125.57, 126.35, 126.51, 128.03, 128.23, 128.28, 128.45, 129.69, 130.79, 133.00, 133.11, 133.62, 136.79, 145.88, 147.27, 149.63, 157.15, 158.83, 160.58; HRMS (ESI) found [M+H]$^+$ = 665.2640 C$_{42}$H$_{36}$N$_2$O$_6$ requires [M+H]$^+$ = 655.2651.
= 8.4 Hz, 7-H), 8.26 (2H, d, J = 8.6 Hz, Ar-H), 8.46 (1H, d, J = 8.2 Hz, 10-H); $^{13}$C $^{1}$H} NMR (100 MHz, CDCl$_3$) δc 12.68, 44.35, 55.19, 55.34, 55.57, 81.93, 100.25, 103.96, 111.29, 113.19, 115.06, 122.57, 123.12, 123.76, 124.50, 125.21, 125.52, 126.43, 126.46, 127.20, 128.05, 128.22 (× 2), 129.70, 130.99, 133.05, 133.28, 133.66, 136.86, 145.93, 146.85, 147.15, 147.30, 157.17, 158.84, 160.59; HRMS (ESI) found [M+H]$^+$ = 693.2951 C$_{44}$H$_{40}$N$_2$O$_6$ requires [M+H]$^+$ = 693.2964.

4-{$^{2}$-(2,4-Dimethoxyphenyl)-6-{$^{4}$-(dimethylamino)phenyl}-2-(4-methoxyphenyl)-2H-benzo[h]chromen-4-yl}benzonitrile 18u

From 4-{$^{6}$-bromo-2-(2,4-dimethoxyphenyl)-2-(4-methoxyphenyl)-2H-benzo[h]chromen-4-yl}benzonitrile (100 mg, 0.165 mmol) and 4-(dimethylamino)phenylboronic acid (68.2 mg, 0.414 mmol) after elution from silica with 20 % EtOAc/petroleum ether to afford the title compound as a beige powder (0.10 g, 94 %); m.p. = 148 – 149 °C; $\nu_{\text{max}}$ (neat) 2845, 1897, 1607, 1504, 1249, 1208, 1161, 1033, 948, 824, 768, 446 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$) δH 2.98 (6H, s, NMe$_2$), 3.62 (3H, s, OMe), 3.76 (3H, s, OMe), 3.77 (3H, s, OMe), 6.46 (1H, s, 3-H), 6.47 – 6.48 (2H, m, Ar-H), 6.77 (2H, d, J = 8.5 Hz, Ar-H), 6.81 (2H, d, J = 8.6 Hz, Ar-H), 6.95 (1H, s, 5-H), 7.23 (2H, d, J = 8.4 Hz, Ar-H), 7.40 (1H, t, J = 7.3 Hz, Ar-H), 7.44 (2H, d, J = 8.6 Hz, Ar-H), 7.49 (1H, t, J = 7.6 Hz, Ar-H), 7.59 (2H, d, J = 8.0 Hz, Ar-H), 7.68 – 7.70 (3H, m, Ar-H), 7.87 (1H, d, J = 8.4 Hz, 7-H), 8.45 (1H, d, J = 8.3 Hz, 10-H); $^{13}$C $^{1}$H} NMR (100 MHz, CDCl$_3$) δc 40.61, 55.19, 55.34, 55.56, 81.92, 100.24, 103.92, 111.32, 112.20, 113.16, 115.10, 118.89, 122.59, 123.21, 124.54, 125.20, 125.51, 126.33, 126.45, 127.95, 128.02, 128.21, 128.51, 129.57, 130.80, 132.29, 132.99, 133.02, 133.91, 136.89, 143.87, 147.27, 149.62, 157.16, 158.81, 160.56; HRMS (ESI) found [M+H]$^+$ = 645.2745 C$_{43}$H$_{36}$N$_2$O$_4$ requires [M+H]$^+$ = 645.2753.

4-{$^{2}$-(2,4-Dimethoxyphenyl)-2-(4-methoxyphenyl)-6-(4-nitrophenyl)-2H-benzo[h]chromen-4-yl-N,N-dimethylaniline 18v

From 4-{$^{6}$-bromo-2-(2,4-dimethoxyphenyl)-2-(4-methoxyphenyl)-2H-benzo[h]chromen-4-yl)-N,N-dimethylaniline (0.40 g, 0.64 mmol) and 4-nitrophenylboronic acid (0.22 g, 1.3 mmol) after elution from silica with 20 % EtOAc/petroleum ether to afford the title compound as an orange powder (0.34 g, 79 %); m.p. = 154 – 155 °C; $\nu_{\text{max}}$ (neat) 1608, 1514, 1343, 1249, 1208, 1159, 1034, 829 and 767 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$) δH 3.00 (6H, s, NMe$_2$), 3.64 (3H, s, OMe), 3.78 (3H, s, OMe), 3.80 (3H, s, OMe), 6.41 (1H, s, 3-H), 6.48 – 6.50 (2H, m, Ar-H), 6.79 (2H, d, J = 8.6 Hz, Ar-H), 6.82 (2H, d, J = 8.7 Hz, Ar-H), 7.27 (1H, s, 5-H), 7.38 (2H, d,
$J = 8.5 \text{ Hz, Ar-H}$), 7.44 (1H, t, $J = 7.4 \text{ Hz, Ar-H}$), 7.49 (2H, d, $J = 8.6 \text{ Hz, Ar-H}$), 7.53 (1H, t, $J = 7.7 \text{ Hz, Ar-H}$), 7.57 (2H, d, $J = 8.5 \text{ Hz, Ar-H}$), 7.71 – 7.74 (2H, m, Ar-H), 8.27 (2H, d, $J = 8.5 \text{ Hz, Ar-H}$), 8.53 (1H, d, $J = 8.4 \text{ Hz, 10-H}$); $^{13}$C{$_1^1$}H NMR (150 MHz, CDCl$_3$) δc 40.49, 55.15, 55.29, 55.48, 82.38, 100.16, 103.66, 112.22, 113.01, 116.81, 123.01, 123.44, 124.93, 125.02, 125.09, 129.19, 125.33, 125.64, 126.15, 126.88, 127.91, 128.26, 129.50, 129.54, 130.98, 131.53, 134.34, 137.35, 146.67, 148.03, 148.93, 150.18, 157.30, 158.65, 160.41; HRMS (ESI) found [M+H]$^+$ = 665.2644 C$_{42}$H$_{36}$N$_2$O$_6$ requires [M+H]$^+$ = 665.2651.

References


