Waste-Free Catalytic Propargylation/Allenylation of Aryl and Heteroaryl Nucleophiles and Synthesis of Naphthopyrans

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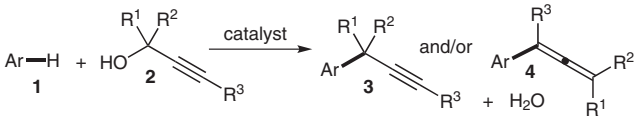
Abstract: A general method for the substitution of propargylic alcohols with electron-rich aromatic carbocycles and heterocycles has been developed. The reaction occurs under simple, mild conditions, and employs an inexpensive environmentally benign and recoverable arylboronic acid catalyst, perfluorophenylboronic acid, producing water as the only byproduct. High yields and selectivities are observed for propargyl- or allenyl-substituted products, including furans, indoles, and pyrroles, as well as methoxy-substituted benzenes and naphthalenes. Reaction with 2-naphthol affords substituted naphthopyrans as products. Preliminary evidence suggests a Friedel–Crafts-like substitution mechanism, which occurs via an in situ generated carbocation.

Key words: organocatalysis, boronic acids, propargylic alcohols, Friedel–Crafts reaction

The nucleophilic substitution of propargylic alcohols is a powerful tool in the synthesis of complex organic structures. This is due in part to the ease with which diverse starting materials can be prepared (i.e., by addition of acetylides to aldehydes and ketones) as well as the variety of transformations available to manipulate the alkyne or allene functionality in the products. The cobalt-mediated Nicholas reaction has therefore found wide application, particularly in the context of carbon–carbon bond-forming reactions,[1] and is featured prominently in several total syntheses.[2] Although a mild and useful method, the reaction suffers from the use of stoichiometric quantities of $Co(CO)_8$, which is necessary for stabilization of the carbocation intermediates. The direct catalytic substitution of propargylic alcohols with carbon nucleophiles remains a significant challenge, due in part to the poor leaving group ability of hydroxide, as well as the propensity of the resulting unstabilized carbocations to form polymerization products.

Recently, several reports on catalytic, cobalt-free direct substitution of propargylic alcohols **2** with aromatic nucleophiles **1** to afford coupled products **3**, have emerged (Scheme 1).[3] These studies have focused primarily on the use of transition-metal complexes,[4] and conventional Brønstead or Lewis acids as catalysts.[5] This approach is particularly attractive, since the aryl nucleophile requires no pre-activation (halides, etc.) and only water is produced as stoichiometric waste.[6] However, several drawbacks still need to be addressed, including the high cost and toxicity associated with transition-metal complexes, and the harsh nature of strongly Lewis acidic catalysts. Furthermore, methods to date have focused primarily on secondary alcohol substrates, and yield primarily propargyl-substituted products **3**. The intermediacy of propargylic cations in many of these reactions suggests that, in principle, allenyl arylation products **4** are also possible.[7,8]



Scheme 1 Direct aromatic substitution of propargylic alcohols

Diversely substituted arylboronic acids are inexpensive and widely available, primarily due to their use as coupling partners in the Suzuki–Miyaura reaction.[9] They possess several useful properties, including air and moisture stability, high solubility in organic solvents and Lewis acidity of the boron atom, which can be modulated by ring substituents.[10] Despite this, there are only sporadic reports of their use as catalysts.[11]

We have recently reported on the direct coupling of allylic and benzylic alcohols with electron-rich aromatics and heteroaromatics catalyzed by an electron-deficient arylboronic acid.[12] In our efforts to extend the applicability of this unique class of organocatalysts, we wish to report its use in the efficient, regioselective coupling of propargylic alcohols with electron-rich aromatic and heteroaromatic rings under simple, mild conditions.[13]

We began by applying our optimized conditions for the allylation reaction, treating a 1:1 mixture of 2-methylfuran (**5**) and diphenyl propargylic alcohol **2a** in dichloromethane with 4 Å molecular sieves and perfluorophenylboronic acid (**6**) at room temperature for 16 hours (Table 1, entry 1). We were pleased to observe the formation of propargyl derivative **3a**, although in modest yield, with recovery of starting materials. Heating the same mixture in 1,2-dichloroethane affords the product **3a** in good yield (entry 2). Moderately electron-poor derivative **2b** behaves similarly at room temperature, affording **3b** in comparably modest yield (entry 3). Electron-rich alcohol **2c** undergoes coupling much more efficiently under the same conditions to afford **3c** in near quantitative yield (entry 4). In all four cases, the propargyl derivatives are

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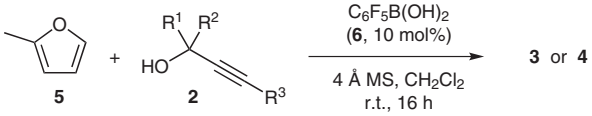
formed exclusively, with no evidence of isomeric products in the crude reaction mixtures

In contrast, triphenyl tertiary alcohol **2d** affords allenyl derivative **4d** exclusively under the same reaction conditions (entry 5). Similarly, the electron-rich tertiary alcohol **2e** undergoes substitution to afford tetraarylallene **4e** in high yield (entry 6). The analogous electron-poor derivative **2f** also affords exclusively the allene product **4f**, but in somewhat decreased isolated yield (entry 7).

Table 1 Propargylation of 2-Methylfuran



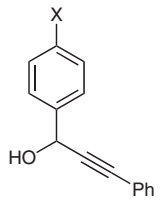
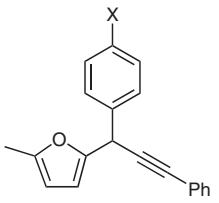
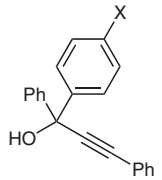
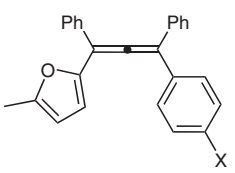
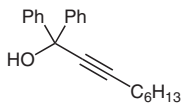
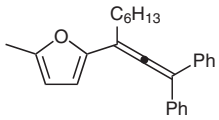
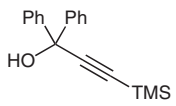
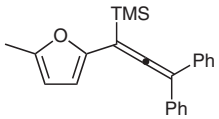
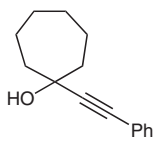
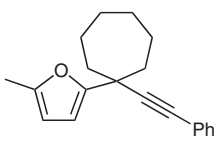
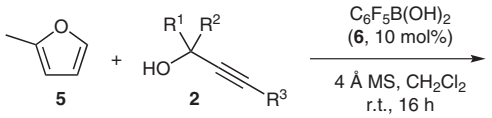
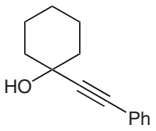
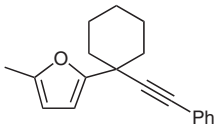
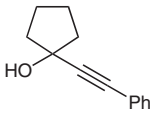
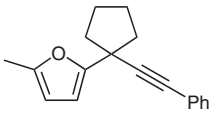
Entry	Alcohol **2**	Product **3** or **4**	Yield[a] (%)
1	 **2a**: X = H	 **3a**: X = H	41
2	**2a**: X = H	**3a**: X = H	79[b]
3	**2b**: X = F	**3b**: X = F	43
4	**2c**: X = OMe	**3c**: X = OMe	96
5	 **2d**: X = H	 **4d**: X = H	91
6	**2e**: X = OMe	**4e**: X = OMe	93
7	**2f**: X = CF_3	**4f**: X = CF_3	76
8	 **2g**	 **4g**	86
9	 **2h**	 **4h**	98
10	 **2i**	 **3i**	39[c]

Table 1 Propargylation of 2-Methylfuran (continued)



Entry	Alcohol **2**	Product **3** or **4**	Yield[a] (%)
11	 **2j**	 **3j**	10
12	 **2k**	 **3k**	38[d]

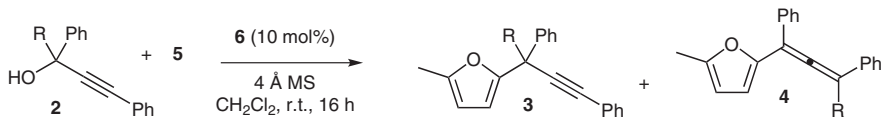
[a] Isolated yields.
[b] The reaction was run in DCE at reflux.
[c] 59% yield of dehydration product isolated.
[d] 57% yield of dehydration product isolated.

Non-aryl alkyne substituents at R^3 are well tolerated, including alkyl **2g** (entry 8) and silyl derivatives **2h** (entry 9). Similarly to the triaryl derivatives, subjecting **2g** or **2h** to the reaction conditions affords exclusively the allenyl products **4g** or **4h**, respectively.

The reaction is notably less effective for cyclic substrates **2i–k**. In the case of **2i** and **2k**, significant amounts of conjugated enyne dehydration products are formed (entries 10 and 12). Surprisingly, cyclohexyl derivative **2j** failed to react to any significant extent, with high recovery of starting materials (entry 11). This lack of reactivity suggests that steric effects arising from the conformation of the cyclohexane ring in **2j** are either inhibiting interaction with **6**, or the resulting carbocation is not in a configuration suitable for elimination or nucleophilic attack. In contrast to the acyclic tertiary alcohol substrates **2d–h**, derivatives **2i–k** (entries 10–12) react to form the propargylated derivatives **3i–k** as the only coupled products. This marked reversal of selectivity can be attributed to steric differences between the substrates at R^1 and R^2 (vide infra), and/or the strain associated with the exocyclic allenyl carbocations that would be formed from **2i–k**. For all of the examples shown in Table 1, high selectivity for either the alkyne or allene products is observed, with no evidence of the corresponding isomeric products in the crude reaction mixtures.

When we attempted to extend the scope of the reaction to include diarylalkyl derivatives **2l–n**, however, we observed formation of isomeric mixtures of **3** and **4** (Table 2). In the case of methyl derivative **2l**, the alkyne derivative **3l** is favored over the allene derivative **4l** by a factor of 7:3, affording an inseparable mixture of isomeric products in high combined yield (entry 1). Modification of the alkyl group from methyl to ethyl to isopropyl (entries 2 and 3), results in a steady decrease in this ratio,

Table 2 Alkyne/Allene Selectivity



Entry	R	2	Ratio[a] 3/4	Total yield[b] (%)
1	Me	**2l**	70:30	89
2	Et	**2m**	55:45	93
3	*i*-Pr	**2n**	50:50	95

[a] Determined by ^{1}H NMR.
[b] Isolated yields.

where in the case that R = *i*-Pr, the allene product **4n** is formed in equal amount with the alkyne product **3n** (entry 4).

Such mixtures of allenyl and propargyl products have been observed previously in conventional Friedel–Crafts reactions with propargylic electrophiles.[14] The carbocations derived from such substrates have been studied extensively and are well known to exist as resonance structures with the corresponding allenyl carbocations.[7] Of the two forms, the sp^3 hybridized propargylic carbocation is more highly stabilized than the sp^2 hybridized allylic one and thus the resonance hybrid should exhibit more positive character at the propargylic position. The results from Table 2 suggest that as the steric bulk of R increases, nucleophilic attack at the favored propargylic position is inhibited, resulting in attack on the electronically less favored allenyl position. These observations are also consistent with the results in Table 1. For example, the reversal of selectivity observed between reaction of secondary alcohol **2c** with **5**, (entry 4) and the tertiary alcohol **2e** with **5** (entry 6) can be explained by the lower steric demand of the hydrogen as compared to the phenyl group.

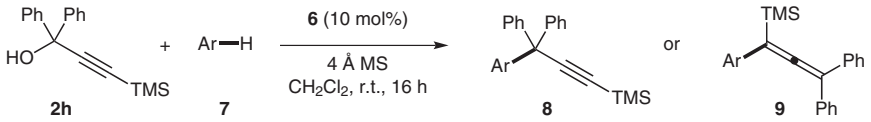
Having established the scope of the reaction with furan substrate **5**, we turned our attention to the reaction of various other aromatic heterocycles and carbocycles **7** with a propargylic alcohol **2h**, in order to test further the selectivity of the reaction (Table 3). Similarly to the reaction of **5** with **2h** (Table 1, entry 9), pyrrole (**7a**) affords allenyl products exclusively (entry 1); in this case, an inseparable mixture of C^2- and C^3-allenylated products **9a** and **9a′** results in high combined yield. Similarly, thiophene (**7b**) reacts with **2h** to form a mixture of allenylated products **9b** (entry 2), but in this case the minor product is the symmetrical disubstituted product **9b′**. The only nucleophile in this series that affords a propargylic product is indole (**7c**). It is unclear why some five-membered ring heterocycles (e.g., **7c**) form propargyl products with **2h** under these conditions, whereas others (e.g., **5**, **7b**) form allene products. However, these results suggest that in addition to the steric and electronic effects discussed above, subtle differences in the nucleophilicity of the heteroaromatic substrates may be contributing to the divergence in selectivity. Benzene- and naphthalene-based nucleophiles **7d–g** all afford allene-substituted products **9d–g**, respectively in high to near quantitative yields (entries 4–7).

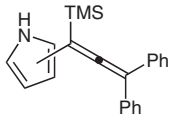
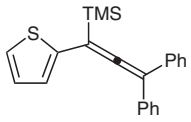
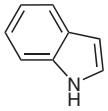
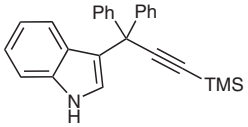
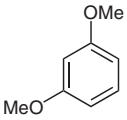
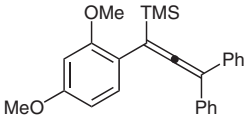
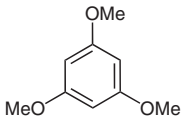
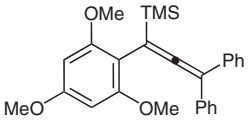
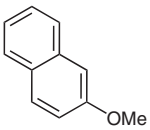
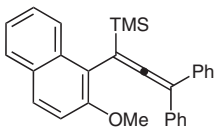
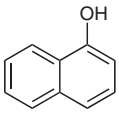
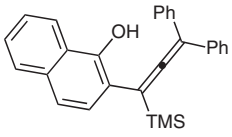
This method compares favorably with other propargylation reactions. While it does not compete in terms of catalyst loading with many of the transition-metal-based catalysts,[4] the lower cost, simplicity, and non-toxic nature of the boronic acid catalyst are significant advantages. A comparable Lewis acid, boron trifluoride–diethyl ether complex, has only been shown to be effective at mediating these reactions in stoichiometric quantities.[4i] Simple Bronstead acids (e.g., TsOH) are effective catalysts, but require harsh reaction conditions (refluxing MeCN).[5f]

Previous mechanistic studies on the related reaction of allylic and benzylic alcohols with aromatic nucleophiles, under similar conditions are in support of an S_N1/Friedel–Crafts-like mechanism,[14] involving the intermediacy of a resonance-stabilized carbocation. Although alternative mechanisms have been proposed for similar substitution reactions,[5d] our results suggest that an S_N1-type substitution mechanism is indeed operative. For example, the observation that electron-neutral and electron-poor secondary alcohols behave sluggishly in the reaction (Table 1, entries 1 and 3), whereas electron-rich substrates react completely under identical conditions (entry 4) is consistent with rate-determining carbocation formation via departure of the hydroxide as a leaving group. Furthermore, propargyl- vs. allenyl-substitution product distributions can be attributed to the formation of a delocalized propargylic carbocation. This intermediate undergoes nucleophilic attack at one of two positions, depending on the nature of the substituents, as well as the structure of the nucleophile.

Interestingly, reaction of **10** with **2h** under these conditions results in the clean formation of naphthopyran **11a** in excellent yield (Table 4, entry 1). Given that reaction of closely related **7f** forms allene product **9f**, we propose that reaction of **10** with **2h** results in initial formation of an allene, followed by protonation of the double bond to form a stabilized carbocation and intramolecular attack of oxygen.

Table 3 Propargylation of Other Nucleophiles



Entry	Ar-H	Product	Yield[a] (%)
1	 **7a**	 **9a/9a′**	85[b]
2	 **7b**	 **9b**	52[c]
3	 **7c**	 **8c**	83
4	 **7d**	 **9d**	86
5	 **7e**	 **9e**	99
6	 **7f**	 **9f**	94
7	 **7g**	 **9g**	87

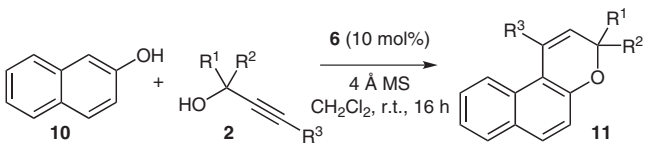
[a] Isolated yields.
[b] Inseparable 7:3 mixture of C^2- and C^3-substituted products **9a** and **9a′** as determined by ^1H NMR.
[c] 23% of C^2,C^4-disubstituted product **9b′** isolated.

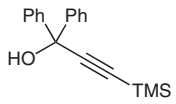
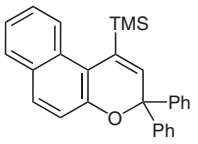
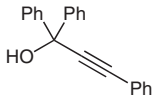
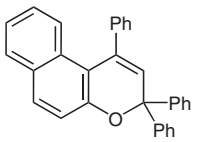
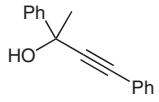
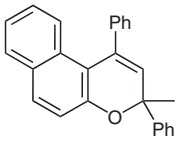
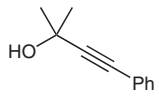
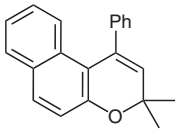
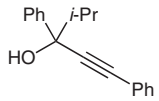
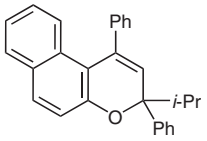
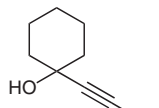
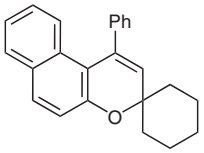
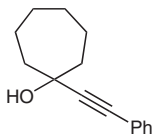
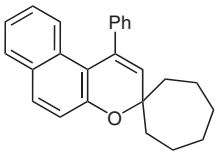
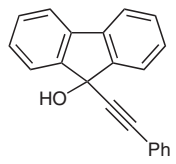
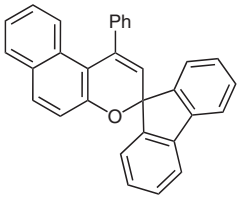
Benzopyran derivatives are of significant biological and medicinal value,[15] and have useful photochromic properties.[16] We therefore attempted a preliminary examination the scope of this reaction using a selection of propargylic alcohols **2** (Table 4). Annulation reactions of this type have been previously reported, but generally rely on harsh conventional Brønstead or Lewis acids that result in moderate yields, or costly transition-metal-based catalysts.[17]

We were pleased to find that tertiary propargylic alcohols bearing various combinations of aliphatic and aromatic substituents **2d**,**l**,**o**,**n** lead to regioselective formation of naphthopyrans **11b–e** in good to excellent yields (entries 2–5). Spironaphthopyran products bearing six-, seven-, and five-membered rings **11f–h** are also available by this method (entries 6–8). The moderate yield of **11f** (entry 7), even under reflux heating is consistent with our observation that **2j** has limited reactivity with other nucleophiles under these conditions (Table 1, entry 11).

In summary, we have developed an efficient, mild, and catalytic method for the direct propargylation and/or alle-

Table 4 One-Pot Synthesis of Naphthopyrans



Entry	2	Product	Yield[a] (%)
1	 **2h**	 **11a**	95
2	 **2d**	 **11b**	97
3	 **2l**	 **11c**	71
4	 **2o**	 **11d**	72
5	 **2n**	 **11e**	88
6	 **2j**	 **11f**	57[b]
7	 **2i**	 **11g**	79
8	 **2p**	 **11h**	91

[a] Isolated yields.
[b] Reaction run at reflux in DCE; product contaminated with conjugated enyne dehydration product (inseparable; 40% by ^{1}H NMR).

nylation of a variety of aromatic and heteroaromatic substrates. 2-Naphthols are efficiently annulated under these conditions. The catalyst is commercially available as well as being air and moisture stable and does not require any special handling. A wide variety of propargylic alcohol substrates are tolerated, the catalyst is recoverable and the reaction produces only water as a byproduct. Preliminary evidence suggests a Friedel–Crafts-like mechanism, involving rate-determining carbocation formation. Extension of the scope of this reaction, and further mechanistic studies are ongoing in our laboratory and will be reported in due course.

^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance III 400 spectrometer at 400 and 100 MHz, respectively. NMR shifts are reported relative to a TMS or $CDCl_3$ internal standard. IR spectra were obtained using a Varian Scimitar Series 1000 FT-IR spectrophotometer. HRMS were obtained using the Manitoba/Sciex prototype MALDI quadrupole/TOF (QqTOF) mass spectrometer.[18] Flash chromatography was performed using Merck silica gel Si 60 (40–63 μm) purchased from EMD chemicals. All solvents were purchased as ACS reagents and used without further purification. All other chemicals were purchased from Aldrich or Alfa Aesar and were used as received.

Acetylenes 3, 8, Allenes 4, 9, and 3H-Naphtho[2,1-b]pyrans 11; General Procedure

To a vial containing the alcohol (0.5 mmol) in CH_2Cl_2 (2.5 mL) was added freshly dried powdered 4 Å molecular sieves (500 mg), the nucleophile (1.0 equiv), and pentafluorophenylboronic acid (**6**, 11 mg, 0.1 equiv). The vial was capped and the mixture allowed to stir at r.t. for 16 h. The suspension was filtered through a 1-inch plug of silica gel (CH_2Cl_2), and the eluent concentrated in vacuo. The residue was purified (if necessary) by flash chromatography (EtOAc–hexanes).

2-(1,3-Diphenylprop-2-ynyl)-5-methylfuran (3a)

FTIR (neat): 3057, 2929, 2202, 1960, 1890, 1708, 1598, 1223, 1020, 701 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50–7.46 (m, 4 H), 7.37–7.32 (m, 2 H), 7.31–7.27 (m, 4 H), 6.13–6.11 (d, *J* = 3.0 Hz, 1 H), 5.89–5.87 (d, *J* = 3.0 Hz, 1 H), 5.20 (s, 1 H), 2.24 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.9, 151.8, 139.1, 131.7, 128.5, 128.2, 128.0, 127.8, 127.2, 123.3, 107.3, 106.1, 87.7, 83.7, 37.8, 13.6.

HRMS: *m*/*z* [M]$^+$ calcd for $C_{20}H_{16}O$: 272.1201; found: 272.1178.

2-[1-(4-Fluorophenyl)-3-phenylprop-2-ynyl]-5-methylfuran (3b)

FTIR (neat): 3060, 2924, 2199, 1599, 1508, 1158, 840, 758 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.46 (m, 4 H), 7.35–7.32 (m, 2 H), 7.10–7.04 (t, *J* = 8.5 Hz, 2 H), 6.18–6.16 (d, *J* = 2.8 Hz, 1 H), 5.95–5.93 (d, *J* = 2.8 Hz, 1 H), 5.22 (s, 1 H), 2.28 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.2–160.8 (d, *J* = 246 Hz), 152.0, 151.5, 134.88–134.85 (d, *J* = 2.9 Hz), 131.7, 129.4–129.3 (d, *J* = 8.0 Hz), 128.2–128.15 (d, *J* = 5.1 Hz), 123.0, 115.5, 115.2, 107.3, 106.2, 87.4, 83.9, 37.1, 13.6.

HRMS: *m*/*z* [M – H]$^+$ calcd for $C_{20}H_{14}FO$: 289.1029; found: 289.1015.

2-[1-(4-Methoxyphenyl)-3-phenylprop-2-ynyl]-5-methylfuran (3c)

FTIR (neat): 2954, 2836, 2199, 1302, 1109, 1034, 758, 692 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.43 (m, 2 H), 7.40–7.37 (d, *J* = 8.5 Hz, 2 H), 7.26–7.23 (m, 3 H), 6.87–6.83 (d, *J* = 8.5 Hz, 2 H), 6.11–6.09 (d, *J* = 3.0 Hz, 1 H), 5.87–5.85 (d, *J* = 3.0 Hz, 1 H), 5.14 (s, 1 H), 3.72 (s, 3 H), 2.20 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.9, 152.3, 151.9, 131.8, 131.4, 129.0, 128.3, 128.2, 123.4, 114.1, 107.2, 106.3, 88.3, 83.7, 55.3, 37.2, 13.7.

HRMS: *m*/*z* [M – H]$^+$ calcd for $C_{21}H_{17}O$: 301.1229; found: 301.1221.

2-Methyl-5-(1,3,3-triphenylpropa-1,2-dienyl)furan (4d)
FTIR (neat): 3055, 2928, 1957, 1893, 1715, 1596, 1447, 1273, 1019, 770 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.44 (d, *J* = 7.3 Hz, 2 H), 7.39–7.36 (d, *J* = 7.5 Hz, 4 H), 7.26–7.21 (m, 6 H), 7.20–7.15 (m, 3 H), 6.13–6.11 (d, *J* = 3.3 Hz, 1 H), 5.92–5.90 (d, *J* = 3.3 Hz, 1 H), 2.20 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.4, 152.4, 146.9, 136.4, 135.0, 128.6, 128.5, 128.4, 128.2, 127.8, 127.5, 113.7, 110.3, 107.5, 104.9, 13.8.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{21}O$: 349.1592; found: 349.1594.

2-[3-(4-Methoxyphenyl)-1,3-diphenylpropa-1,2-dienyl]-5-methylfuran (4e)
FTIR (neat): 3055, 2931, 2835, 1715, 1509, 1247, 1032, 831, 697 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.53 (d, *J* = 8.5 Hz, 2 H), 7.49–7.45 (d, *J* = 8.5 Hz, 2 H), 7.41–7.38 (d, *J* = 8.8 Hz, 2 H), 7.37–7.32 (m, 4 H), 7.30–7.26 (m, 2 H), 6.90–6.87 (d, *J* = 9.0 Hz, 2 H), 6.22–6.20 (d, *J* = 3.3 Hz, 1 H), 6.02–6.00 (d, *J* = 3.3 Hz, 1 H), 3.79 (s, 3 H), 2.31 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.2, 154.1, 152.3, 147.2, 136.7, 135.2, 129.7, 128.62, 128.58, 128.44, 128.39, 128.2, 127.7, 127.5, 113.8, 113.3, 110.1, 107.5, 104.7, 55.3, 13.8.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{23}O_2$: 379.1698; found: 371.1711.

2-{1,3-Diphenyl-3-[4-(trifluoromethyl)phenyl]-propa-1,2-dienyl}-5-methylfuran (4f)
FTIR (neat): 3059, 2927, 1718, 1493, 1326, 1167, 1067, 844, 699 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63–7.55 (m, 6 H), 7.49–7.45 (d, *J* = 7.3 Hz, 2 H), 7.43–7.34 (m, 6 H), 6.27–6.25 (d, *J* = 3.0 Hz, 1 H), 6.08–6.06 (d, *J* = 3.0 Hz, 1 H), 2.36 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.9, 152.8, 146.4, 140.5, 135.8, 134.6, 130.0–129.0 (q, *J* = 32.3 Hz), 128.8, 128.7, 128.63, 128.57, 128.3, 128.1, 127.9, 125.5–125.4 (q, *J* = 3.7 Hz), 122.9, 113.0, 110.9, 107.7, 105.7, 13.9.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{20}F_3O$: 417.1466; found: 417.1477.

2-[2-(Diphenylvinylidene)heptyl]-5-methylfuran (4g)
FTIR (neat): 3058, 2927, 1710, 1598, 1446, 910, 763, 735, 699 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.39 (m, 4 H), 7.34–7.29 (m, 4 H), 7.27–7.21 (m, 2 H), 6.19–6.17 (d, *J* = 3.0 Hz, 1 H), 5.98–5.96 (d, *J* = 3.0 Hz, 1 H), 2.49–2.44 (t, *J* = 7.5 Hz, 2 H), 2.26 (s, 3 H), 1.66–1.58 (q, *J* = 7.5 Hz, 2 H), 1.33–1.24 (m, 2 H), 1.24–1.16 (m, 4 H), 0.82–0.77 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.2, 151.9, 148.3, 137.2, 128.5, 128.2, 127.1, 113.5, 107.4, 107.3, 101.6, 31.6, 29.8, 29.1, 28.0, 22.6, 14.0, 13.8.

HRMS: *m*/*z* [M – H]$^+$ calcd for $C_{26}H_{27}O$: 355.2062; found: 355.2045.

2-[3,3-Diphenyl-1-(trimethylsilyl)propa-1,2-dienyl]-5-methylfuran (4h)
FTIR (neat): 3058, 2956, 2855, 1715, 1598, 1250, 1023, 874, 766 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64–7.61 (d, *J* = 7.3 Hz, 4 H), 7.55–7.50 (t, *J* = 7.3 Hz, 4 H), 7.45–7.41 (t, *J* = 7.3 Hz, 2 H), 6.45–6.43 (d, *J* = 3.0 Hz, 1 H), 6.18–6.16 (d, *J* = 3.0 Hz, 1 H), 2.47 (s, 3 H), 0.54 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.4, 151.9, 147.5, 137.2, 128.7, 128.5, 127.1, 108.9, 107.9, 107.7, 95.1, 14.0, –0.2.

HRMS: *m*/*z* [M]$^+$ calcd for $C_{23}H_{24}OSi$: 344.1596; found: 344.1583.

1-(5-Methylfuran-2-yl)-1-(phenylethynyl)cycloheptane (3i)
FTIR (neat): 3059, 2929, 2860, 2201, 1598, 1489, 1460, 1274, 757, 691 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.38 (m, 2 H), 7.29–7.23 (m, 3 H), 6.09–6.07 (d, *J* = 3.0 Hz, 1 H), 5.86–5.84 (d, *J* = 3.0 Hz, 1 H), 2.26 (s, 3 H), 2.18–2.12 (m, 2 H), 2.06–1.98 (m, 2 H), 1.88–1.79 (m, 2 H), 1.74–1.67 (m, 2 H), 1.63–1.56 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.8, 150.7, 131.6, 128.1, 127.5, 123.8, 105.6, 104.2, 93.7, 82.3, 41.0, 39.8, 28.2, 23.4, 13.6.

1-(5-Methylfuran-2-yl)-1-(phenylethynyl)cyclohexane (3j)
FTIR (neat): 3056, 2930, 2856, 2224, 1598, 1490, 1219, 1020, 781, 691 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.48 (m, 2 H), 7.34–7.31 (m, 3 H), 6.17–6.15 (d, *J* = 3.0 Hz, 1 H), 5.95–5.93 (d, *J* = 3.0 Hz, 1 H), 2.33 (s, 3 H), 2.15–2.10 (m, 2 H), 1.91–1.85 (m, 4 H), 1.79–1.72 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.5, 150.6, 131.5, 128.1, 127.6, 123.7, 105.8, 104.4, 92.4, 83.5, 38.2, 37.0, 25.8, 22.8, 13.6.

1-(5-Methylfuran-2-yl)-1-(phenylethynyl)cyclopentane (3k)
FTIR (neat): 3060, 2953, 2872, 2221, 1598, 1492, 1382, 1318, 1026, 915, 757, 692 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.40 (m, 2 H), 7.29–7.24 (m, 3 H), 6.14–6.12 (d, *J* = 3.0 Hz, 1 H), 5.88–5.86 (d, *J* = 3.0 Hz, 1 H), 2.28 (s, 3 H), 2.20–2.15 (m, 4 H), 1.97–1.91 (m, 2 H), 1.84–1.78 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.6, 151.0, 131.6, 128.1, 127.6, 123.8, 105.8, 105.3, 94.0, 81.1, 43.2, 40.2, 24.2, 13.7.

2-(2,4-Diphenylbut-3-yn-2-yl)-5-methylfuran (3l) and 2-(1,3-Diphenylbuta-1,2-dienyl)-5-methylfuran (4l)
FTIR (neat): 3059, 2985, 1771, 1447, 1267, 1026, 698, 588 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.47 (m, 4 H), 7.35–7.27 (m, 5 H), 7.25–7.21 (m, 1 H), 6.21–6.19 (d, *J* = 3.0 Hz, 0.3 H), 6.18–6.16 (d, *J* = 3.0 Hz, 0.7 H), 6.02–6.00 (d, *J* = 3.0 Hz, 0.3 H), 5.91–5.89 (d, *J* = 3.0 Hz, 0.7 H), 2.29 (s, 0.9 H), 2.28 (s, 0.9 H), 2.24 (s, 2.1 H), 1.97 (s, 2.1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.0, 155.4, 152.2, 151.8, 147.5, 144.4, 136.5, 135.6, 131.7, 128.41, 128.37, 128.25, 128.21, 128.15, 127.9, 127.5, 127.1, 126.8, 126.3, 126.0, 123.4, 109.8, 107.3, 106.7, 105.9, 104.8, 103.9, 92.5, 83.5, 41.5, 29.4, 17.1, 13.8, 13.7.

HRMS: *m*/*z* [M – H]$^+$ calcd for $C_{21}H_{17}O$: 285.1280; found: 285.1266.

2-(1,3-Diphenylpent-1-yn-3-yl)-5-methylfuran (3m) and 2-(1,3-Diphenylpenta-1,2-dienyl)-5-methylfuran (4m)
FTIR (neat): 3059, 2973, 2877, 1689, 1491, 1220, 1024, 758, 699 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.48 (m, 4 H), 7.34–7.27 (m, 5 H), 7.24–7.18 (m, 1 H), 6.23–6.21 (d, *J* = 3.0 Hz, 0.55 H), 6.20–6.18 (d, *J* = 3.0 Hz, 0.45 H), 6.01–5.99 (d, *J* = 3.0 Hz, 0.45 H), 5.90–5.88 (d, *J* = 3.0 Hz, 0.55 H), 2.65–2.59 (q, *J* = 7.3 Hz, 0.9 H), 2.45–2.35 (m, 0.55 H), 2.28 (s, 1.35 H), 2.23 (s, 1.65 H), 2.22–2.13 (m, 0.55 H), 1.26–1.21 (t, *J* = 7.3 Hz, 1.35 H), 1.03–0.97 (t, *J* = 7.3 Hz, 1.65 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.4, 154.8, 152.1, 151.6, 147.7, 142.9, 136.3, 135.7, 131.7, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.5, 127.0, 126.9, 126.7, 126.2, 123.5, 111.8, 109.5, 107.32, 107.30, 105.9, 90.9, 85.2, 47.2, 34.1, 23.7, 13.8, 13.7, 12.5, 9.8.

HRMS: *m*/*z* $[M - H]^+$ calcd for $C_{22}H_{19}O$: 299.1436; found: 299.1429.

2-Methyl-5-(4-methyl-1,3-diphenylpent-1-yn-3-yl)-5-methylfuran (3n) and 2-Methyl-5-(4-methyl-1,3-diphenylpenta-1,2-dienyl)furan (4n)
FTIR (neat): 3058, 2965, 2873, 1953, 1449, 1378, 784 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.78–7.74 (d, *J* = 8.5 Hz, 1 H), 7.58–7.55 (m, 1 H), 7.53–7.47 (m, 2 H), 7.33–7.25 (m, 5 H), 7.22–7.17 (t, *J* = 7.3 Hz, 1 H), 6.33–6.31 (d, *J* = 3.0 Hz, 0.5 H), 6.20–6.18 (d, *J* = 3.3 Hz, 0.5 H), 6.00 –5.98 (d, *J* = 3.3 Hz, 0.5 H), 5.85–5.83 (d, *J* = 3.0 Hz, 0.5 H), 3.06–2.95 (h, *J* = 6.8 Hz, 0.5 H), 2.86–2.75 (h, *J* = 6.8 Hz, 0.5 H), 2.28 (s, 1.5 H), 2.26 (s, 1.5 H), 1.27–1.24 (d, *J* = 6.8 Hz, 1.5 H), 1.23–1.20 (d, *J* = 6.8 Hz, 1.5 H), 1.08–1.05 (d, *J* = 6.8 Hz, 1.5 H), 0.87–0.84 (d, *J* = 6.8 Hz, 1.5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.8, 154.9, 152.1, 151.4, 147.9, 142.7, 136.3, 135.8, 131.8, 128.6, 128.5, 128.4, 128.2, 128.1, 127.5, 127.2, 127.1, 126.9, 126.7, 123.7, 117.4, 109.5, 107.8, 107.4, 106.2, 106.0, 88.9, 87.1, 52.6, 36.9, 29.5, 22.47, 22.46, 19.6, 18.4, 13.9.

HRMS: *m*/*z* $[M + H]^+$ calcd for $C_{23}H_{23}O$: 315.1749; found: 315.1751.

2-[3,3-Diphenyl-1-(trimethylsilyl)propa-1,2-dienyl]-1*H*-pyrrole (9a) 3-[3,3-Diphenyl-1-(trimethylsilyl)propa-1,2-dienyl]-1*H*-pyrrole (9a′)
FTIR (neat): 3058, 2957, 2169, 1598, 1491, 1445, 1248, 842, 754, 698 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.35 (s, br, 0.7 H), 8.29 (s, br, 0.3 H), 7.48–7.44 (m, 3 H), 7.43–7.38 (m, 3 H), 7.38–7.36 (m, 2 H), 7.35–7.31 (m, 2 H), 6.84–6.82 (m, 0.3 H), 6.82–6.79 (m, 0.7 H), 6.33–6.30 (m, 1.4 H), 6.22–6.19 (m, 0.3 H), 5.78–5.75 (m, 0.3 H), 0.42 (s, 6.3 H), 0.33 (s, 2.7 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.1, 197.4, 144.4, 136.7, 133.7, 128.5, 128.2, 128.04, 128.01, 127.0, 124.9, 118.4, 117.5, 109.6, 109.4, 108.9, 108.7, 108.4, 108.2, 96.1, 89.5, 0.0, –0.3.

2-[3,3-Diphenyl-1-(trimethylsilyl)propa-1,2-dienyl]thiophene (9b) and 2,5-Bis[3,3-diphenyl-1-(trimethylsilyl)propa-1,2-dienyl]thiophene (9b′)
Monosubstituted 9b
FTIR (neat): 3058, 2957, 1897, 1598, 1492, 1250, 868, 767, 630 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.30 (m, 7 H), 7.27–7.22 (m, 2 H), 7.16–7.14 (m, 1 H), 6.99–6.95 (m, 2 H), 0.32 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.5, 140.3, 136.6, 128.5, 128.2, 127.4, 127.0, 124.6, 124.4, 107.4, 98.2, –0.3.

Disubstituted 9b′
FTIR (neat): 2957, 2896, 1888, 1596, 1491, 1250, 1074, 768, 692, 626 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.21 (m, 20 H), 6.88–6.85 (m, 2 H), 0.31 (s, 18 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.8, 139.3, 136.6, 128.5, 128.3, 127.0, 125.3, 107.6, 98.4, –0.2.

3-[1,1-Diphenyl-3-(trimethylsilyl)prop-2-ynyl]-1*H*-indole (8c)
FTIR (neat): 3401, 3083, 3058, 2959, 2168, 1597, 1352, 1250, 1064, 859, 622 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.86 (s, br, 1 H), 7.51–7.47 (d, *J* = 8.0 Hz, 1 H), 7.41–7.37 (m, 4 H), 7.27–7.11 (m, 9 H), 6.50 (s, 1 H), 0.14 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.7, 137.0, 128.7, 128.0, 126.8, 126.2, 124.6, 122.2, 122.1, 121.2, 119.3, 111.2, 110.7, 88.9, 50.5, 0.1.

1-(2,4-Dimethoxyphenyl)-3,3-diphenyl-1-(trimethylsilyl)allene (9d)
FTIR (neat): 3002, 2966, 2837, 1600, 1503, 1282, 1032, 762, 558 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.38 (m, 4 H), 7.33–7.28 (m, 4 H), 7.22–7.15 (m, 3 H), 6.45–6.42 (m, 2 H), 3.75 (s, 3 H), 3.72 (s, 3 H), 0.19 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.8, 159.9, 157.3, 137.4, 130.3, 128.4, 128.2, 126.5, 118.7, 104.7, 100.4, 98.8, 55.4, 54.9, –0.1.

1,1-Diphenyl-3-(2,4,6-trimethoxyphenyl)-3-(trimethylsilyl)allene (9e)
FTIR (neat): 2996, 2962, 2836, 1597, 1494, 1451, 1257, 1151, 1057, 800, 632 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.59–7.56 (d, *J* = 7.3 Hz, 4 H), 7.43–7.38 (t, *J* = 7.3 Hz, 4 H), 7.32–7.27 (t, *J* = 7.3 Hz, 2 H), 6.22 (s, 2 H), 3.86 (s, 3 H), 3.77 (s, 6 H), 0.25 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.1, 159.8, 157.8, 137.4, 128.4, 128.1, 126.2, 107.0, 103.3, 94.9, 90.9, 55.5, 55.4, –0.3.

HRMS: *m*/*z* $[M + H]^+$ calcd for $C_{27}H_{31}O_3Si$: 431.2042; found: 431.2033.

1-(2-Methoxy-1-naphthyl)-3,3-diphenyl-1-(trimethylsilyl)allene (8f)
FTIR (neat): 3063, 2958, 2835, 1591, 1492, 1453, 1266, 1086, 841, 628, 695 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.83 (d, *J* = 8.0 Hz, 1 H), 7.72–7.67 (t, *J* = 8.0 Hz, 2 H), 7.45–7.41 (m, 4 H), 7.33–7.27 (m, 5 H), 7.27–7.24 (d, *J* = 7.5 Hz, 1 H), 7.23–7.18 (m, 3 H), 3.85 (s, 3 H), 0.15 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.8, 153.0, 137.1, 132.8, 129.4, 128.6, 128.4, 128.0, 127.9, 126.6, 126.0, 125.9, 123.5, 120.3, 113.3, 104.0, 98.3, 56.2, –0.4.

1-(1-Hydroxy-2-naphthyl)-3,3-diphenyl-1-(trimethylsilyl)allene (8g)
FTIR (neat): 3403, 2956, 2897, 1921, 1738, 1492, 1450, 1149, 910, 638 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.33–8.30 (d, *J* = 8.3 Hz, 1 H), 8.11–8.07 (d, *J* = 8.5 Hz, 1 H), 7.57–7.51 (m, 5 H), 7.50–7.45 (m, 5 H), 7.40–7.36 (t, *J* = 7.3 Hz, 2 H), 7.30–7.27 (d, *J* = 7.5 Hz, 1 H), 6.87–6.84 (d, *J* = 7.8 Hz, 1 H), 5.61 (s, br, 1 H), 0.34 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.5, 150.3, 137.3, 132.8, 128.54, 128.45, 127.8, 126.8, 126.7, 126.2, 125.3, 125.1, 125.0, 121.9, 108.5, 104.3, 101.6, –0.6.

3,3-Diphenyl-1-(trimethylsilyl)-3*H*-naphtho[2,1-*b*]pyran (11a)
FTIR (neat): 3054, 2958, 1949, 1898, 1819, 1600, 1246, 839 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00–7.97 (d, *J* = 8.5 Hz, 1 H), 7.64–7.61 (d, *J* = 7.8 Hz, 1 H), 7.58–7.54 (d, *J* = 8.5 Hz, 1 H), 7.47–7.43 (d, *J* = 7.3 Hz, 4 H), 7.37–7.32 (dd, *J* = 8.5, 7.0 Hz, 1 H), 7.25–7.20 (m, 6 H), 7.17–7.12 (t, *J* = 7.3 Hz, 2 H), 6.55 (s, 1 H), 0.29 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.3, 144.3, 140.3, 135.3, 131.0, 129.7, 129.4, 128.3, 127.9, 127.3, 127.1, 125.5, 125.0, 123.3, 120.9, 119.0, 81.2, 1.4.

HRMS: *m*/*z* [M]$^+$ calcd for $C_{28}H_{26}OSi$: 406.1753; found: 406.1699.

1,3,3-Triphenyl-3*H*-naphtho[2,1-*b*]pyran (11b)
FTIR (neat): 3056, 1957, 1622, 1446, 1237, 1071, 959, 697, 526 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66–7.63 (d, *J* = 8.8 Hz, 1 H), 7.61–7.58 (d, *J* = 8.0 Hz, 1 H), 7.56–7.52 (m, 4 H), 7.34–7.27 (m, 6 H), 7.25–7.20 (m, 4 H), 7.17–7.12 (t, *J* = 7.3 Hz, 2 H), 7.11–7.07 (m, 2 H), 6.97–6.92 (m, 1 H), 6.19 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.7, 144.6, 141.4, 137.3, 131.0, 130.4, 129.9, 129.6, 128.6, 128.5, 128.2, 128.1, 127.8, 127.7, 126.6, 125.2, 123.3, 118.9, 116.7, 82.3.

3-Methyl-1,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran (11c)
FTIR (neat): 3056, 2931, 1624, 1490, 1344, 1235, 1101, 1073, 825, 698, 523 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68–7.65 (d, *J* = 8.8 Hz, 1 H), 7.64–7.61 (d, *J* = 8.0 Hz, 1 H), 7.59–7.55 (m, 2 H), 7.32–7.27 (m, 5 H), 7.24–7.19 (m, 3 H), 7.14–7.09 (t, *J* = 8.5 Hz, 2 H), 7.05–7.01 (d, *J* = 8.5 Hz, 1 H), 6.97–6.92 (m, 1 H), 6.07 (s, 1 H), 1.83 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.1, 141.6, 135.5, 130.6, 130.4, 130.2, 129.9, 128.4, 127.9, 127.3, 126.4, 125.0, 123.0, 118.9, 116.1, 75.4, 26.4.

3,3-Dimethyl-1-phenyl-3*H*-naphtho[2,1-*b*]pyran (11d)
FTIR (neat): 3056, 2925, 2856, 1627, 1456, 1264, 1147, 990, 818, 578 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72–7.69 (d, *J* = 8.5 Hz, 2 H), 7.30–7.27 (m, 3 H), 7.21–7.16 (m, 4 H), 7.11–7.08 (d, *J* = 8.3 Hz, 1 H), 7.04–6.99 (m, 1 H), 5.70 (s, 1 H), 1.50 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.1, 141.6, 135.5, 130.6, 130.4, 130.2, 129.9, 128.4, 127.9, 127.3, 126.4, 125.0, 123.0, 118.9, 116.1, 75.4, 26.4.

3-Isopropyl-1,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran (11e)
FTIR (neat): 3026, 2964, 1614, 1490, 1445, 1155, 1108, 749, 698 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.79 (d, *J* = 8.8 Hz, 1 H), 7.78–7.75 (d, *J* = 8.0 Hz, 1 H), 7.68–7.65 (d, *J* = 8.0 Hz, 2 H), 7.50–7.46 (m, 6 H), 7.36–7.31 (t, *J* = 7.5 Hz, 2 H), 7.27–7.22 (m, 2 H), 7.17–7.13 (d, *J* = 8.8 Hz, 1 H), 7.09–7.04 (t, *J* = 7.0 Hz, 1 H), 6.34 (s, 1 H), 2.58–2.47 (sept, *J* = 6.8 Hz, 1 H), 1.23–1.20 (d, *J* = 6.8 Hz, 3 H), 1.11–1.07 (d, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.6, 143.6, 142.0, 137.8, 130.6, 130.2, 130.0, 128.6, 128.4, 128.2, 127.6, 127.2, 126.8, 126.7, 126.6, 125.0, 118.8, 116.7, 83.4, 38.5, 18.0, 17.6.

1′-Phenylspiro[cyclohexane-1,3′-naphtho[2,1-*b*]pyran] (11f)
FTIR (neat): 2853, 2726, 2671, 1625, 1460, 1377, 1234, 816, 722 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72–7.68 (m, 1.2 H), 7.42–7.39 (m, 0.8 H), 7.29–7.17 (m, 6.4 H), 7.11–7.08 (d, *J* = 8.5 Hz, 0.6 H), 7.03–6.98 (t, *J* = 8.0 Hz, 0.6 H), 6.21–6.18 (m, 0.4 H), 5.72 (s, 0.6 H), 2.25–2.19 (m, 0.8 H), 2.15–2.09 (m, 0.8 H), 1.97–1.91 (m, 1.2 H), 1.77–1.48 (m, 6.4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.8, 141.8, 135.7, 135.2, 131.5, 130.3, 130.2, 130.05, 130.00, 128.45, 128.42, 128.3, 127.9, 127.8, 127.3, 126.4, 125.0, 123.8, 122.9, 120.8, 118.8, 116.8, 91.4, 86.9, 76.4, 34.6, 29.3, 25.8, 25.6, 22.4, 21.9, 21.6.

1′-Phenylspiro[cycloheptane-1,3′-naphtho[2,1-*b*]pyran] (11g)
FTIR (neat): 3055, 2923, 2852, 1624, 1458, 1240, 1073, 993, 813, 699, 577 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70–7.66 (d, *J* = 8.5 Hz, 2 H), 7.29–7.24 (m, 3 H), 7.22–7.15 (m, 4 H), 7.10–7.07 (d, *J* = 8.5 Hz, 1 H), 7.02–6.97 (m, 1 H), 5.71 (s, 1 H), 2.17–2.10 (m, 2 H), 1.90–1.83 (m, 2 H), 1.77–1.64 (m, 4 H), 1.63–1.56 (m, 2 H), 1.52–1.44 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.9, 141.9, 134.8, 131.5, 130.3, 130.2, 129.9, 128.5, 128.4, 127.9, 127.3, 126.4, 125.0, 122.9, 119.0, 116.5, 80.2, 37.8, 29.2, 21.9.

1′-Phenylspiro[fluorene-9,3′-naphtho[2,1-*b*]pyran] (11h)
FTIR (neat): 3052, 1623, 1491, 1369, 1237, 1003, 821, 738, 527 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.80 (d, *J* = 8.0 Hz, 1 H), 7.79–7.76 (d, *J* = 8.8 Hz, 1 H), 7.71–7.68 (d, *J* = 7.5 Hz, 2 H), 7.50–7.47 (d, *J* = 7.5 Hz, 2 H), 7.43–7.39 (t, *J* = 7.5 Hz, 2 H), 7.38–7.35 (m, 3 H), 7.33–7.31 (m, 3 H), 7.24–7.21 (d, *J* = 8.8 Hz, 1 H), 7.20–7.14 (m, 4 H), 5.96 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.5, 146.3, 141.2, 139.5, 138.1, 130.6, 130.5, 129.9, 129.7, 128.6, 128.4, 128.3, 127.8, 127.6, 126.4, 126.1, 125.2, 125.1, 123.3, 120.0, 118.9, 116.4, 84.4.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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