RSC Advances

PAPER

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Cite this: *RSC Adv.*, 2017, **7**, 29321

Metal triflate promoted synthesis of naphthalenes†

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Received 3rd May 2017
Accepted 30th May 2017

DOI: 10.1039/c7ra04960a

rsc.li/rsc-advances

A synthetic route to derive the skeleton of naphthalenes starting with isovanillin is described with modest total yields *via* the key transformation of metal triflate-mediated intramolecular benzannulation of *o*-formyl or *o*-benzoyl allylbenzenes in $MeNO_2$ at rt.

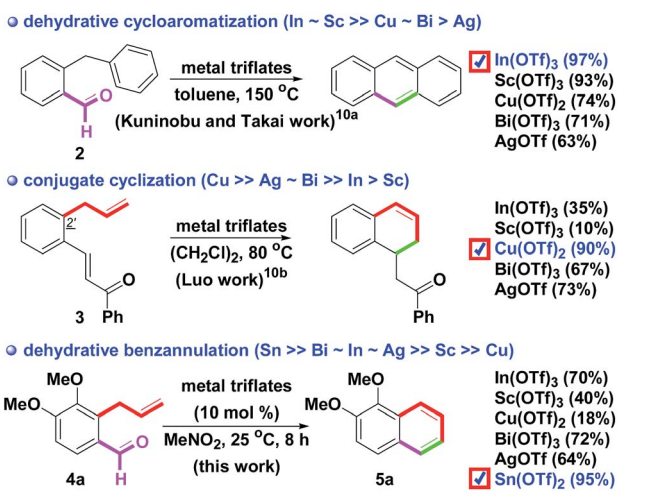
Introduction

A naphthalene ring system[1] is a key core skeleton for bioactive molecules,[2] natural products[3] and functionalized materials.[4] A considerable number of attempts have been developed to determine the synthetic routes of the bicyclic skeleton. Two major key transformations for the formation of a functionalized naphthalene skeleton include: (1) acids (or Lewis acids) promote intramolecular Friedel–Crafts type annulations,[5] and (2) bases promote intramolecular anionic annulations.[6] Transition metal (*e.g.*, Cr, Mn, Pd, W, Rh, Co, Ru, Ni, Co, Zn, Ti and Au) catalyzed benzannulations provide another approach for preparing the core structure.[7] Therefore, a new synthetic route for diverse naphthalenes *via* intramolecular annulation of the readily available starting materials is still a continuing need in the synthetic field.

As part of our efforts in the synthetic applications of dialkoxy *o*-formyl allylbenzenes **1**[8] and the development of metal triflate-promoted robust and efficient reactions,[9] we have now streamlined the facile synthesis of substituted naphthalenes *via* metal triflate-mediated intramolecular benzannulation of *o*-carbonyl synthon allylbenzenes, such as *o*-formyl or *o*-benzoyl allylbenzenes, in $MeNO_2$ at rt. To the best of our knowledge, few reports on the metal triflate-mediated intramolecular annulation of *o*-carbonyl synthon allylbenzenes have been documented.[10] In 2011, Kuninobu and Takai described that metal triflates-catalyzed the dehydrative cycloaromatization of *o*-benzylbenzaldehyde **2** provided tricyclic anthracene in a 97% yield.[10a] Among the metal triflates-mediated syntheses, $In(OTf)_3$ and $Sc(OTf)_3$ demonstrated excellent transformation. In 2014, Luo demonstrated that $Cu(OTf)_2$ provided a tetralin skeleton *via* the conjugate addition of 2′-allylchalcone **3** in a higher (90%) yield than the other scanned catalysts.[10b] The adopted synthetic routes are described in Scheme 1. Our aim was to find an optimal metal triflate as the catalyst for synthesizing naphthalenes **5** *via* the intramolecular benzannulation of *o*-formyl allylbenzene **4** (a hybrid combining the formyl motif of **2** and the allyl group of **3**).

Results and discussion

Initially, six metal triflates were chosen as the catalysts for examining the benzannulation of *o*-formyl allylbenzene **4a**.[11,12] In line with two preliminary studies, 10 mol% catalytic amounts of $In(OTf)_3$, $Sc(OTf)_3$, $Cu(OTf)_2$, $Bi(OTf)_3$, and AgOTf were first scanned for the formation of 1,2-dimethoxynaphthalene (**5a**) in $MeNO_2$ at rt for 8 h, as shown in Table 1 and entries 1–5. However, **5a** was isolated in a range of poor to moderate yields (18–72%). When $Sn(OTf)_2$ or $Fe(OTf)_3$ was applied to the reaction conditions, yields were increased to 95% or 88% (entries 6 and 7). Under the same conditions, treatment of **4a** with $Ga(OTf)_3$ provided **5a** in a 44% yield along with a 38% yield of **6a**



Scheme 1 Metal triflates-catalyzed annulations.

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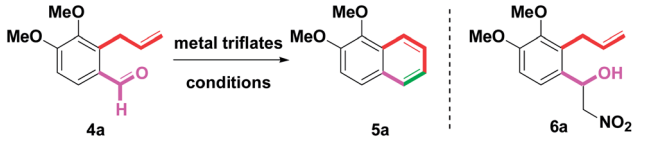
† Electronic supplementary information (ESI) available. CCDC 790259, 923282–923284, 1519809 and 1523594. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7ra04960a

Table 1 Metal triflates mediated reaction conditions[a]



Entry	Catalyst (mol%)	Solvent	Temp (°C)	Time (h)	5a[b] (%)
1	$Bi(OTf)_3$ (10)	$MeNO_2$	25	8	72
2	$In(OTf)_3$ (10)	$MeNO_2$	25	8	70
3	AgOTf (10)	$MeNO_2$	25	8	64
4	$Sc(OTf)_3$ (10)	$MeNO_2$	25	8	40[c]
5	$Cu(OTf)_2$ (10)	$MeNO_2$	25	8	18[c]
6	$Sn(OTf)_2$ (10)	$MeNO_2$	25	8	95
7	$Fe(OTf)_3$ (10)	$MeNO_2$	25	8	88
8	$Ga(OTf)_3$ (10)	$MeNO_2$	25	8	44 (38)[d]
9	$Sn(OTf)_2$ (5)	$MeNO_2$	25	8	72
10	$Sn(OTf)_2$ (10)	CH_2Cl_2	25	8	79
11	$Sn(OTf)_2$ (10)	Toluene	25	8	69
12	$Sn(OTf)_2$ (10)	$MeNO_2$	101	8	42[e]
13	$Sn(OTf)_2$ (10)	$MeNO_2$	25	20	83
14	$SnCl_2$ (10)	$MeNO_2$	25	8	<5
15	TfOH (10)	$MeNO_2$	25	8	60
16	$Sn(OTf)_2$ (10)[f]	$MeNO_2$	25	8	—[c,g]
17	$Sn(OTf)_2$ (10)[h]	$MeNO_2$	25	8	90

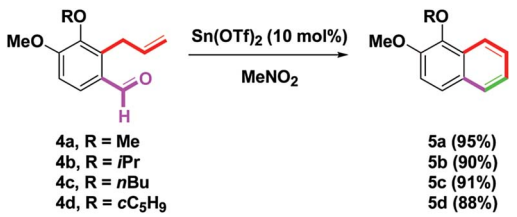
[a] Reactions were run on **4a** (0.5 mmol), solvent (5 mL). [b] Isolated yields. [c] **4a** was recovered (entry 5, 26%; entry 6, 54%; entry 14, 85%; entry 16, 80%). [d] **6a** (25%) was isolated. [e] Unknown product (35%) was formed. [f] Proton scavenger (2,6-di-*tert*-butylpyridine, 10 mol%) was added. [g] No reaction. [h] Water (10 mg) was added.

(entry 8). In addition, **6a** was generated *via* $Ga(OTf)_3$-mediated by the addition of **4a** with $MeNO_2$. With these results in mind, a series of commercially available lanthanide triflates ($Ln(OTf)_3$) were examined next, including: $La(OTf)_3$, $Ce(OTf)_3$, $Pr(OTf)_3$, $Nd(OTf)_3$, $Sm(OTf)_3$, $Eu(OTf)_3$, $Gd(OTf)_3$, $Tb(OTf)_3$, $Dy(OTf)_3$, $Ho(OTf)_3$, $Er(OTf)_3$, $Yb(OTf)_3$ and $Tm(OTf)_3$. However, no isolation of the desired **5a** was observed and only **4a** was recovered under $Ln(OTf)_3$-mediated reactions. With the results in hand, we found that $Sn(OTf)_2$ was among the most reactive and used catalyst compared to other metal triflate derivatives. Along this line, we planned to take advantage of the intrinsically high catalytic ability of $Sn(OTf)_2$ to construct the naphthalene system. After decreasing the catalytic amounts (10 → 5 mol%), a poor yield (72%) was observed (entry 9). Furthermore, we studied the factors of solvent and temperature. After changing the solvents (from $MeNO_2$ to CH_2Cl_2 and toluene), different results were observed (entries 10 and 11). In entry 12, the complex mixture occurred (35%) when elevating the temperature (25 → 101).

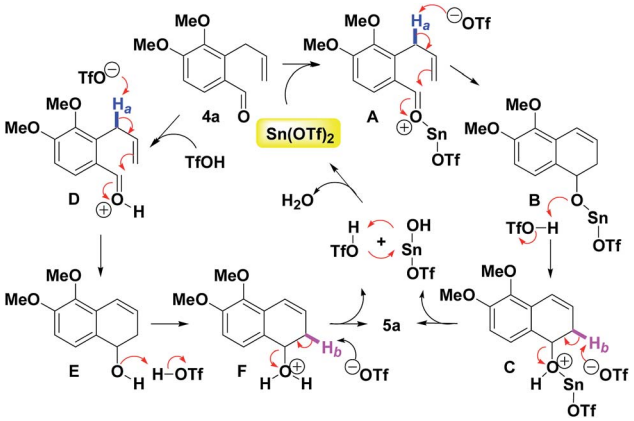
Next, $Sn(OTf)_2$ exhibited a low yield (83%) under an elongated reaction time (8 → 20 h), as shown in entry 13. Another type of tin(II) salt (*e.g.* $SnCl_2$) was examined. In entry 14, **5a** was isolated in trace amounts only. By the involvement of 10 mol% TfOH (entry 15), 60% of **5a** was generated. The control experiment revealed that the real catalyst was the trace amount of TfOH resulting from the hydrolysis of the metal triflates. In the other hand, proton scavenger (2,6-di-*tert*-butylpyridine, 10 mol%) was involved in the reaction system (entry 16). The resulting mixture failed to promote dehydrative benzannulation in the presence of **4a** due to the proton scavenger could block *in situ* generated TfOH. To examine the stability and reactivity of $Sn(OTf)_2$ in the presence of water, H_2O (10 mg) was added to the reaction condition and a 90% yield of **5a** was generated (entry 17). According to the results, a 10 mol% of $Sn(OTf)_2$/$MeNO_2$/rt condition would be an optimal combination for yielding **5a**.

Aside from the present benzannulation of *o*-formyl allylbenzene **4a**, $Sn(OTf)_2$ has also been reported as a catalyst for aldol reactions,[13a] Mannish-type reactions,[13b,c] rearrangements,[13d,e] (3 + 2) annulations,[13f–h] and other routes.[13i–k] For branched, linear and cyclic alkyl substituents of *o*-formyl allylbenzenes **4b–d** (R = Me, iPr, *n*Bu, and c-C_5H_9), **5b–d** provided good yields (90%, 91% or 88%) under the above-mentioned conditions (Scheme 2).

On the basis of the results, a plausible reaction mechanism is shown in Scheme 3. Mechanistically, two general distinctive activation modes of the *o*-allylbenzaldehydes can be proposed for intramolecular dehydrative benzannulations. The first one is a purely metallic-based Lewis acid pathway. The sequence initiates the formation of intermediate **A** by complexation of a carbonyl motif of **3a** with $Sn(OTf)_2$. The *in situ* generated triflate anion deprotonates the H_a (blue) of **A** to give **B** as the result of a tandem intramolecular electrophilic annulation. Following the protonation of **B** with the TfOH, **C** is obtained. On the basis of the triflate anion-mediated deprotonation of **C** (for H_b, pink), **5a** is provided *via* the removal of Sn(OH)OTf and TfOH. Subsequently, $Sn(OTf)_2$ is regenerated for the next catalytic cycle by the complexation of Sn(OH)OTf and TfOH. The second



Scheme 2 Synthesis of 5a–d.



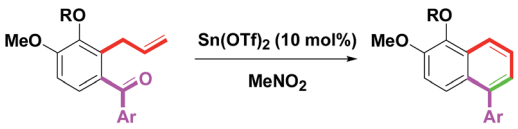
Scheme 3 Proposed mechanism.

possibility would involve a Brønsted acid catalysis. By $Sn(OTf)_2$ assisted *in situ* formed TfOH, **D** is generated.[17] Following the above similar route, **5a** is also produced *via* (i) the triflate anion deprotonates the H_a of **D**, (ii) protonation of **E** with the TfOH, (iii) triflate anion-mediated deprotonation of **F** (for H_b), (iv) the removal of water and the regeneration of TfOH. Although metal triflate-mediated transformations have been described proceeding *via* proton transfer, we think that the nature of the catalytic species may be still under debate.[18] For the overall benzannulation procedure, water is the only by-product. Therefore, it is important to use $Sn(OTf)_2$ that are stable and show high reactivity even in the presence of water.[9a,b,g,10a] Metal cations (*e.g.* Bi^{3+}, Al^{3+} or Sn^{2+}) in water exhibit strong acidic properties because of the acidification through coordination of water molecules present in the "inner-sphere" of the cation.[19] According to Duñach report,[18d] metal triflates such as $Bi(OTf)_3$ are generally obtained and used as its hydrate form and therefore presents indubitably a strong induced Brønsted acidity.

Furthermore, $Sn(OTf)_2$-mediated conversion of *o*-aroyl allylbenzenes **4e–l** into arylnaphthalenes **5e–l** was examined, as shown in Scheme 4. The starting materials **4e–l** (R = H, allyl; Ar = Ph, 4-FC_6H_4, 2-MeC_6H_4, 2-$MeOC_6H_4$, 3-$MeOC_6H_4$, 4-$MeOC_6H_4$, 3,4-$CH_2O_2C_6H_3$) were prepared by our previous reports.[8p] The substituents of R and Ar on **4e–l** did not affect the yield outcome for the benzannulation procedure and no obvious yield changes were observed for the generation of **5e–l**. The isolated yields were provided in the range of 88–95%. The structures of **5e** and **5f** were determined by single-crystal X-ray crystallography.[14]

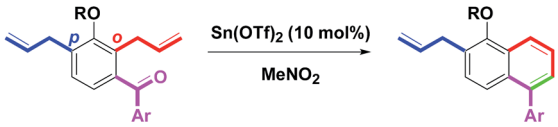
As an extension of the benzannulation, the skeleton of aroylbenzene having two allyl arms (*ortho* and *para* positions) was studied (Scheme 5). Treatment of **4m–o** (R = H, Me; Ar = 4-$MeOC_6H_4$, 3,4-$CH_2O_2C_6H_3$)[8p] with $Sn(OTf)_2$ provided **5m–o** in 95%, 90% and 91% yields, respectively. Notably, the *p*-allyl substituent was unaffected. With the results in hands, 10 mol% of $Sn(OTf)_2$ was applied to the annulation of two substrates **4j** (Ar = 4-$MeOC_6H_4$) or **4l** (Ar = 3,4-$CH_2O_2C_6H_3$) having two allyl arms: one *o*-allyl group (blue) and one *C*-allyl group (red). Under a two-step procedure of $Sn(OTf)_2$-mediated reaction and then *O*-methylation (K_2CO_3, MeI), we observed *C*-allyl isomers **7a** or **7b** were produced in only 21% and 15% yields, respectively *via* a one-pot tandem intramolecular dehydrative benzannulation and Claisen rearrangement (Scheme 6). By increasing the use of $Sn(OTf)_2$ from catalytic amounts (10 mol%) to stoichiometric amounts (1.0 equivalent),[15] the yields of **7a** or **7b** were enhanced to 85% and 80% yields, respectively *via* the two-step route. The non-catalytic amounts (1.0 equivalent) of $Sn(OTf)_2$ which mediated the tandem intramolecular procedure included: (1) benzannulation of *o*-allyl and aroyl groups and (2) double Claisen rearrangement of the *o*-allyl group. In particular, the present double Claisen rearrangement occurred at room temperature. In comparison with the literature reports (150–200 °C),[16] a few examples were described.

To change the position of the aryl group on the naphthalene skeleton, eight **4p–v** (Ar = Ph, 4-FC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-$CF_3C_6H_4$, 2-$MeOC_6H_4$, 4-PhC_6H_4) were investigated next. By this synthetic protocol, **8a–g** were synthesized in 74–81% yields, as shown in Scheme 7. By the removal of the *m*-oxygenated group, **4w–x** having the *o*-allyl side arms (Y = H, MeO) were then examined. When benzannulation of **4w–x** was treated with $Sn(OTf)_2$, the yields of **9a** (61%) and **9b** (40%) provide good results (Scheme 8). The structures of **8d**, **8g**, **9a** and **9b** were determined by single-crystal X-ray crystallography.[14] By a one-pot two-step route (Suzuki–Miyaura coupling and our method),[8p] a simple naphthalene **10a** could be obtained from *o*-formyl phenyl boronic acids in a 70% yield *via* the formation of



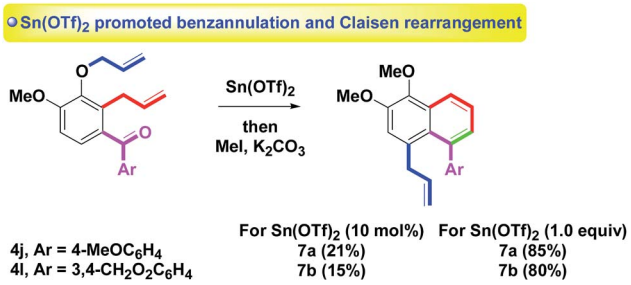
4e, R = H, Ar = Ph — 5e (95%)
4f, R = H, Ar = 4-FC_6H_4 — 5f (90%)
4g, R = allyl, Ar = 2-MeC_6H_4 — 5g (91%)
4h, R = allyl, Ar = 2-$MeOC_6H_4$ — 5h (88%)
4i, R = allyl, Ar = 3-$MeOC_6H_4$ — 5i (95%)
4j, R = allyl, Ar = 4-$MeOC_6H_4$ — 5j (90%)
4k, R = allyl, Ar = 4-FC_6H_4 — 5k (91%)
4l, R = allyl, Ar = 3,4-$CH_2O_2C_6H_4$ — 5l (88%)

Scheme 4 Synthesis of 5e–l.



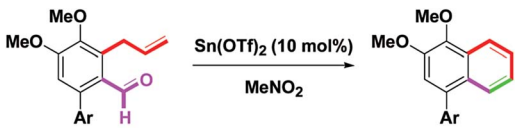
4m, R = H, Ar = 4-$MeOC_6H_4$ — 5m (95%)
4n, R = Me, Ar = 4-$MeOC_6H_4$ — 5n (90%)
4o, R = Me, Ar = 3,4-$CH_2O_2C_6H_4$ — 5o (91%)

Scheme 5 Synthesis of 5m–o.



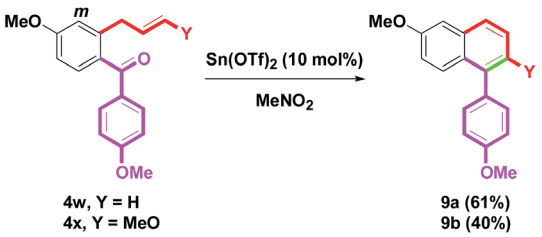
	For $Sn(OTf)_2$ (10 mol%)	For $Sn(OTf)_2$ (1.0 equiv)
4j, Ar = 4-$MeOC_6H_4$	7a (21%)	7a (85%)
4l, Ar = 3,4-$CH_2O_2C_6H_4$	7b (15%)	7b (80%)

Scheme 6 Synthesis of 7a–b.

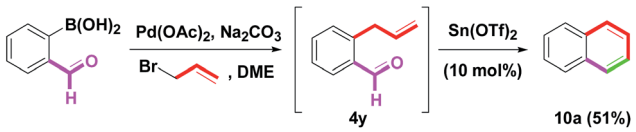


4p, Ar = Ph — 8a (81%)
4q, Ar = 4-FC_6H_4 — 8b (74%)
4r, Ar = 4-MeC_6H_4 — 8c (77%)
4s, Ar = 4-$MeOC_6H_4$ — 8d (76%)
4t, Ar = 4-$CF_3C_6H_4$ — 8e (80%)
4u, Ar = 2-$MeOC_6H_4$ — 8f (80%)
4v, Ar = 4-PhC_6H_4 — 8g (75%)

Scheme 7 Synthesis of 8a–g.



Scheme 8 Synthesis of 9a–b.



Scheme 9 Synthesis of 10a.

o-allylbenzaldehyde **4y** (Scheme 9). Although the isolated yield of **10a** was low, it still provided a novel and efficient transformation from *o*-formyl phenylboronic acid to naphthalene.

Conclusion

In summary, we have successfully presented a synthetic route for the synthesis of substituted naphthalenes in good yields *via* $Sn(OTf)_2$-mediated benzannulation of *o*-formyl or *o*-aroyl allylbenzenes. The use of various metal triflates was investigated for the one-pot facile approach and efficient transformation. Further investigations regarding the synthetic application of metal triflates will be conducted and published in due course.

Experimental

General

All reagents and solvents were obtained from commercial sources and used without further purification. Reactions were routinely carried out under an atmosphere of dry air with magnetic stirring. Products in organic solvents were dried with anhydrous magnesium sulfate before concentration *in vacuo*. Melting points were determined with a SMP3 melting apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 spectrometer operating at 400 and at 100 MHz, respectively. Chemical shifts (δ) are reported in parts per million (ppm) and the coupling constants (J) are given in Hertz. High resolution mass spectra (HRMS) were measured with a mass spectrometer Finnigan/Thermo Quest MAT 95XL. X-ray crystal structures were obtained with an Enraf-Nonius FR-590 diffractometer (CAD4, Kappa CCD).

A representative procedure of skeleton 5 and compound 6a is as follows

$Sn(OTf)_2$ (42 mg, 0.1 mmol) was added to a solution of **4a–o** (1.0 mmol) in $MeNO_2$ (5 mL) at 25 °C. The reaction mixture was stirred for 8 h at 25 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product. Purification on silica gel (hexanes/EtOAc = 100/1–10/1) afforded **5** and **6a**.

1,2-Dimethoxynaphthalene (5a). Yield = 95% (179 mg); colorless oil; HRMS (ESI, M^+ + 1) calcd for $C_{12}H_{13}O_2$ 189.0916, found 189.0919; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.62 (d, J = 8.8 Hz, 1H), 7.52–7.48 (m, 1H), 7.40–7.36 (m, 1H), 7.31 (d, J = 8.8 Hz, 1H), 4.03 (s, 3H), 4.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.28, 142.84, 129.63, 128.98, 127.61, 126.05, 124.17, 124.01, 121.23, 115.15, 61.06, 56.83.

1-(2-Allyl-3,4-dimethoxyphenyl)-2-nitroethanol (6a). For $Ga(OTf)_3$ promoted reaction, **6a** was generated in 38% (101 mg); colorless solid; mp = 78–80 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{13}H_{18}NO_5$ 268.1185, found 268.1188; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, J = 8.4 Hz, 1H), 6.87 (d, J = 8.4 Hz, 1H), 6.02–5.92 (m, 1H), 5.60 (dd, J = 2.8, 10.0 Hz, 1H), 5.60 (dq, J = 1.6, 10.0 Hz, 1H), 4.93 (dq, J = 1.6, 17.2 Hz, 1H), 4.49 (q, J = 13.2 Hz, 1H), 4.48 (q, J = 13.2 Hz, 1H), 3.87 (s, 3H), 3.80 (s, 3H), 3.53 (t, J = 5.6 Hz, 2H), 2.41 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.87, 147.13, 136.98, 130.59, 129.66, 121.95, 115.74, 110.93, 80.88, 67.28, 60.89, 55.66, 29.86.

1-Isopropoxy-2-methoxynaphthalene (5b). Yield = 90% (194 mg); colorless oil; HRMS (ESI, M^+ + 1) calcd for $C_{14}H_{17}O_2$ 217.1229, found 217.1230; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.59 (d, J = 9.2 Hz, 1H), 7.49–7.45 (m, 1H), 7.38–7.34 (m, 1H), 7.30 (d, J = 8.8 Hz, 1H), 4.72–4.65 (m, 1H), 3.98 (s, 3H), 1.40 (d, J = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.53, 140.93, 130.40, 129.72, 127.43, 125.67, 123.88, 123.67, 122.17, 115.36, 75.30, 56.84, 22.71 (2x).

1-Butoxy-2-methoxynaphthalene (5c). Yield = 91% (209 mg); colorless oil; HRMS (ESI, M^+ + 1) calcd for $C_{15}H_{19}O_2$ 231.1385, found 231.1388; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.60 (d, J = 8.8 Hz, 1H), 7.50–7.46 (m, 1H), 7.39–7.35 (m, 1H), 7.30 (d, J = 8.8 Hz, 1H), 4.16 (t, J = 6.4 Hz, 2H), 3.99 (s, 3H), 1.94–1.87 (m, 2H), 1.67–1.58 (m, 2H), 1.04 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.36, 142.34, 129.77, 129.45, 127.55, 125.88, 123.98, 123.86, 121.52, 115.53, 73.43, 57.00, 32.50, 19.34, 13.94.

1-Cyclopentyloxy-2-methoxynaphthalene (5d). Yield = 88% (213 mg); colorless oil; HRMS (ESI, M^+ + 1) calcd for $C_{16}H_{19}O_2$ 243.1385, found 243.1382; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 8.8 Hz, 1H), 7.47–7.43 (m, 1H), 7.37–7.33 (m, 1H), 7.29 (d, J = 8.8 Hz, 1H), 5.09–5.05 (m, 1H), 3.97 (s, 3H), 2.04–1.92 (m, 4H), 1.80–1.72 (m, 2H), 1.70–1.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.33, 141.15, 130.34, 129.81, 127.48, 125.70, 123.95, 123.55, 121.98, 115.71, 84.79, 57.00, 32.91 (2x), 23.78 (2x).

2-Methoxy-5-phenylnaphthalen-1-ol (5e). Yield = 95% (238 mg); colorless solid; HRMS (ESI, M^+ + 1) calcd for $C_{17}H_{15}O_2$ 251.1072, found 251.1078; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 8.4 Hz, 1H), 7.56–7.41 (m, 7H), 7.32 (d, J = 6.8 Hz, 1H), 7.19 (d, J = 9.2 Hz, 1H), 6.13 (br s, 1H), 3.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.02, 139.83, 139.69, 129.98 (2x), 128.90, 128.12 (2x), 127.70, 127.11, 125.33, 124.92, 124.34, 120.72, 117.93, 112.93, 57.00. Single-crystal X-ray diagram: crystal of

compound **5e** was grown by slow diffusion of EtOAc into a solution of compound **5e** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the orthorhombic crystal system, space group *Fdd*2, a = 13.3885(3) Å, b = 66.3135(18) Å, c = 5.5816(2) Å, V = 4955.6(2) Å^3, Z = 16, d_{calcd} = 1.342 g cm^{-3}, $F(000)$ = 2112, 2θ range 1.23–26.39°, R indices (all data) R_1 = 0.0428, wR_2 = 0.1154.

5-(4-Fluorophenyl)-2-methoxynaphthalen-1-ol (5f). Yield = 90% (241 mg); colorless solid; HRMS (ESI, M^+ + 1) calcd for $C_{17}H_{14}FO_2$ 269.0978, found 269.0983; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 8.4 Hz, 1H), 7.53–7.39 (m, 4H), 7.7.29 (dd, J = 1.2, 6.8 Hz, 1H), 7.22–7.17 (m, 3H), 6.18 (br s, 1H), 3.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.16 (d, J = 244.1 Hz), 141.08, 139.74, 138.71, 136.87 (d, J = 3.0 Hz), 131.46 (d, J = 17.5 Hz, 2x), 127.71, 125.41, 124.87, 124.35, 120.92, 117.65, 115.02 (d, J = 21.2 Hz, 2x), 113.01, 56.94. Single-crystal X-ray diagram: crystal of compound **5f** was grown by slow diffusion of EtOAc into a solution of compound **5f** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the triclinic crystal system, space group $P\bar{1}$, a = 6.7021(11) Å, b = 7.9371(12) Å, c = 12.170(2) Å, V = 631.92(18) Å^3, Z = 2, d_{calcd} = 1.410 g cm^{-3}, $F(000)$ = 280, 2θ range 1.70–26.38°, R indices (all data) R_1 = 0.0431, wR_2 = 0.1097.

1-Allyloxy-2-methoxy-5-*o*-tolylnaphthalene (5g). Yield = 91% (277 mg); colorless gum; HRMS (ESI, M^+ + 1) calcd for $C_{21}H_{21}O_2$ 305.1542, found 305.1549; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (dt, J = 0.4, 8.4 Hz, 1H), 7.51 (dd, J = 6.8, 8.4 Hz, 1H), 7.38–7.16 (m, 7H), 6.30–6.20 (m, 1H), 5.49 (dq, J = 1.6, 17.2 Hz, 1H), 5.30 (dq, J = 1.6, 10.4 Hz, 1H), 4.71 (dt, J = 1.6, 6.0 Hz, 2H), 3.97 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.20, 141.77, 140.33, 139.58, 136.76, 134.49, 130.30, 129.81, 129.61, 128.23, 127.50, 125.68, 125.48, 124.89, 122.60, 121.00, 117.39, 114.90, 74.33, 56.80, 20.01.

1-Allyloxy-2-methoxy-5-(2-methoxyphenyl)naphthalene (5h). Yield = 88% (282 mg); colorless gum; HRMS (ESI, M^+ + 1) calcd for $C_{21}H_{21}O_3$ 321.1491, found 321.1496; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (dt, J = 1.2, 8.4 Hz, 1H), 7.52 (dd, J = 7.2, 8.8 Hz, 1H), 7.43 (ddd, J = 1.6, 7.2, 9.2 Hz, 1H), 7.34 (dd, J = 0.8, 9.2 Hz, 1H), 7.30–7.27 (m, 2H), 7.18 (d, J = 9.2 Hz, 1H), 7.09 (dd, J = 0.8, 7.2 Hz, 1H), 7.05 (d, J = 7.2 Hz, 1H), 6.30–6.20 (m, 1H), 5.49 (dq, J = 1.6, 17.2 Hz, 1H), 5.29 (dq, J = 1.6, 10.4 Hz, 1H), 4.70 (dt, J = 1.6, 6.0 Hz, 2H), 3.97 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.19, 148.08, 141.68, 136.74, 134.56, 131.91, 129.64, 129.57, 128.92, 128.36, 125.67, 125.60, 122.94, 121.22, 120.50, 117.34, 114.76, 111.01, 74.33, 56.82, 55.59.

1-Allyloxy-2-methoxy-5-(3-methoxyphenyl)naphthalene (5i). Yield = 95% (304 mg); colorless gum; HRMS (ESI, M^+ + 1) calcd for $C_{21}H_{21}O_3$ 321.1491, found 321.1499; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, J = 8.4 Hz, 1H), 7.68 (d, J = 9.2 Hz, 1H), 7.51 (dd, J = 7.2, 8.4 Hz, 1H), 7.40 (t, J = 8.0 Hz, 1H), 7.31 (dd, J = 0.8, 6.8 Hz, 1H), 7.23 (d, J = 9.2 Hz, 1H), 7.09–7.06 (m, 1H), 7.04 (t, J = 2.4 Hz, 1H), 6.98 (ddd, J = 0.8, 2.8, 8.4 Hz, 1H), 6.29–6.19 (m, 1H), 5.48 (dq, J = 1.6, 17.2 Hz, 1H), 5.29 (dq, J = 1.6, 10.0 Hz, 1H), 4.70 (dt, J = 1.6, 6.0 Hz, 2H), 3.98 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.41, 148.23, 142.27, 141.63, 139.95, 134.41, 129.87, 129.15, 127.76, 125.65, 125.03, 122.65, 122.51, 121.21, 117.52, 115.52, 114.87, 112.86, 74.33, 56.78, 55.28.

1-Allyloxy-2-methoxy-5-(4-methoxyphenyl)naphthalene (5j). Yield = 90% (288 mg); colorless gum; HRMS (ESI, M^+ + 1) calcd for $C_{21}H_{21}O_3$ 321.1491, found 321.1493; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (dt, J = 0.8, 8.4 Hz, 1H), 7.66 (dd, J = 0.8, 9.2 Hz, 1H), 7.48 (dd, J = 7.2, 8.8 Hz, 1H), 7.40 (d, J = 8.8 Hz, 2H), 7.27 (dd, J = 0.8, 7.2 Hz, 1H), 7.21 (d, J = 9.2 Hz, 1H), 7.01 (d, J = 8.8 Hz, 2H), 6.27–6.17 (m, 1H), 5.46 (dq, J = 1.6, 17.2 Hz, 1H), 5.27 (dq, J = 1.6, 10.4 Hz, 1H), 4.68 (dt, J = 1.6, 6.0 Hz, 2H), 3.96 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.90, 148.19, 141.66, 139.76, 134.43, 133.24, 131.03 (2x), 129.93, 128.05, 125.73, 125.18, 122.67, 120.84, 117.49, 114.76, 113.64 (2x), 74.32, 56.79, 55.32.

1-Allyloxy-5-(4-fluorophenyl)-2-methoxynaphthalene (5k). Yield = 91% (280 mg); colorless gum; HRMS (ESI, M^+ + 1) calcd for $C_{20}H_{18}FO_2$ 309.1291, found 309.1293; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (dt, J = 0.8, 8.4 Hz, 1H), 7.60 (dd, J = 0.8, 9.2 Hz, 1H), 7.51 (dd, J = 6.8, 8.4 Hz, 1H), 7.47–7.42 (m, 2H), 7.27 (dd, J = 1.2, 7.2 Hz, 1H), 7.24 (d, J = 9.2 Hz, 1H), 7.21–7.15 (m, 2H), 6.30–6.20 (m, 1H), 5.49 (dq, J = 1.6, 17.2 Hz, 1H), 5.30 (dq, J = 1.6, 10.4 Hz, 1H), 4.72 (dt, J = 1.6, 6.0 Hz, 2H), 3.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.21 (d, J = 244.1 Hz), 148.26, 141.69, 138.97, 136.76 (d, J = 3.0 Hz), 134.36, 131.46 (d, J = 7.5 Hz, 2x), 129.90, 127.82, 125.64, 125.25, 122.31, 121.32, 117.52, 115.09 (d, J = 21.2 Hz, 2x), 114.99, 74.31, 56.75.

5-(5-Allyloxy-6-methoxynaphthalen-1-yl)benzo[1,3]dioxole (5l). Yield = 88% (294 mg); colorless gum; HRMS (ESI, M^+ + 1) calcd for $C_{21}H_{19}O_4$ 335.1283, found 335.1288; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (dt, J = 1.2, 8.4 Hz, 1H), 7.68 (dd, J = 1.2, 9.2 Hz, 1H), 7.48 (dd, J = 6.8, 8.4 Hz, 1H), 7.26 (dd, J = 1.2, 7.2 Hz, 1H), 7.23 (d, J = 9.2 Hz, 1H), 6.96 (br s, 1H), 6.93 (br s, 2H), 6.27–6.17 (m, 1H), 6.04 (s, 2H), 5.47 (dq, J = 1.6, 16.8 Hz, 1H), 5.28 (dq, J = 1.6, 10.4 Hz, 1H), 4.68 (dt, J = 1.6, 6.0 Hz, 2H), 3.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.23, 147.42, 141.66, 139.66, 134.74, 134.41, 129.92, 127.96, 126.01, 125.67, 125.16, 123.35, 122.58, 121.06, 117.52, 114.85, 110.57, 108.17, 101.09, 74.33, 56.81.

2-Allyl-5-(4-methoxyphenyl)naphthalen-1-ol (5m). Yield = 95% (276 mg); colorless gum; HRMS (ESI, M^+ + 1) calcd for $C_{20}H_{19}O_2$ 291.1385, found 291.1386; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (dt, J = 1.2, 8.4 Hz, 1H), 7.51 (dd, J = 6.8, 8.4 Hz, 1H), 7.46 (dd, J = 0.8, 8.4 Hz, 1H), 7.42 (d, J = 8.8 Hz, 2H), 7.38 (dd, J = 1.2, 6.8 Hz, 1H), 7.17 (d, J = 8.4 Hz, 1H), 7.03 (d, J = 8.8 Hz, 2H), 6.14–6.04 (m, 1H), 5.60 (br s, 1H), 5.30–5.23 (m, 2H), 3.90 (s, 3H), 3.58 (dt, J = 1.6, 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.88, 149.77, 139.59, 136.05, 133.35, 132.19, 131.07 (2x), 128.27, 126.89, 125.24, 124.86, 120.60, 118.65, 117.57, 117.05, 113.63 (2x), 55.33, 35.73.

2-Allyl-1-methoxy-5-(4-methoxyphenyl)naphthalene (5n). Yield = 90% (274 mg); colorless gum; HRMS (ESI, M^+ + 1) calcd for $C_{21}H_{21}O_2$ 305.1542, found 305.1548; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (dt, J = 1.2, 8.4 Hz, 1H), 7.69 (dd, J = 0.8, 8.4 Hz, 1H), 7.56 (dd, J = 7.2, 8.4 Hz, 1H), 7.43 (d, J = 8.8 Hz, 2H), 7.40 (dd, J = 1.6, 6.8 Hz, 1H), 7.29 (d, J = 8.8 Hz, 1H), 7.05 (d, J = 8.8 Hz, 2H), 6.12–6.02 (m, 1H), 5.16–5.11 (m, 2H), 3.99 (s, 3H), 3.91 (s, 3H), 3.64 (dt, J = 1.6, 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.89, 153.47, 140.10, 137.11, 133.18, 132.25, 131.03 (2x), 128.55, 128.18, 127.76, 126.64, 125.45, 122.25, 121.25, 115.85, 113.64 (2x), 62.14, 55.29, 33.82.

5-(6-Allyl-5-methoxynaphthalen-1-yl)benzo[1,3]dioxole (5o). Yield = 91% (289 mg); colorless gum; HRMS (ESI, $M^+ + 1$) calcd for $C_{21}H_{19}O_3$ 319.1334, found 319.1336; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (dt, J = 1.2, 8.4 Hz, 1H), 7.67 (d, J = 8.8 Hz, 1H), 7.52 (dd, J = 7.2, 8.4 Hz, 1H), 7.37 (dd, J = 1.2, 6.8 Hz, 1H), 7.27 (d, J = 8.8 Hz, 1H), 6.97 (t, J = 1.6 Hz, 1H), 6.93 (br s, 2H), 6.04 (s, 2H), 6.10–6.00 (m, 1H), 5.14–5.08 (m, 2H), 3.96 (s, 3H), 3.61 (dt, J = 1.6, 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.50, 147.44, 146.86, 140.04, 137.10, 134.70, 132.21, 128.56, 128.30, 127.86, 126.64, 125.41, 123.37, 122.16, 121.48, 115.90, 110.58, 108.17, 101.10, 62.18, 33.82.

A representative procedure of skeleton 7 is as follows

$Sn(OTf)_2$ (420 mg, 1.0 mmol) was added to a solution of **4j** or **4l** (1.0 mmol) in $MeNO_2$ (5 mL) at 25 °C. The reaction mixture was stirred for 8 h at 25 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product. Without further purification, K_2CO_3 (276 mg, 2.0 mmol) was added to a solution of the resulting products in acetone (10 mL) at 25 °C for 10 min. MeI (426 mg, 3.0 mmol) was added to the reaction mixture. The reaction mixture was stirred for 8 h at reflux, cooled to 25 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product. Purification on silica gel (hexanes/EtOAc = 100/1–10/1) afforded **7**.

4-Allyl-1,2-dimethoxy-5-(4-methoxyphenyl)naphthalene (7a). Yield = 85% (284 mg); colorless gum; HRMS (ESI, $M^+ + 1$) calcd for $C_{22}H_{23}O_3$ 335.1647, found 335.1652; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (dt, J = 1.2, 8.4 Hz, 1H), 7.44 (dd, J = 6.8, 8.4 Hz, 1H), 7.24 (d, J = 8.8 Hz, 2H), 7.17 (dd, J = 1.2, 6.8 Hz, 1H), 7.13 (s, 1H), 6.93 (d, J = 8.8 Hz, 2H), 5.70–5.60 (m, 1H), 4.92 (dq, J = 1.6, 10.0 Hz, 1H), 4.73 (dq, J = 1.6, 17.2 Hz, 1H), 4.01 (s, 3H), 3.98 (s, 3H), 3.88 (s, 3H), 3.13 (dt, J = 1.6, 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.64, 147.29, 141.43, 139.61, 138.20, 137.16, 134.02, 131.03, 130.21 (2x), 128.53, 124.70, 121.42, 117.95, 115.56, 113.64, 113.17 (2x), 61.08, 56.69, 55.28, 39.75.

5-(8-Allyl-5,6-dimethoxynaphthalen-1-yl)benzo[1,3]dioxole (7b). Yield = 80% (278 mg); colorless gum; HRMS (ESI, $M^+ + 1$) calcd for $C_{22}H_{21}O_4$ 349.1440, found 349.1450; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (dd, J = 1.2, 8.4 Hz, 1H), 7.43 (dd, J = 7.2, 8.4 Hz, 1H), 7.17 (dd, J = 1.6, 7.2 Hz, 1H), 7.14 (s, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.81 (d, J = 1.6 Hz, 1H), 6.77 (dd, J = 1.6, 8.0 Hz, 1H), 6.05 (d, J = 1.2 Hz, 1H), 6.01 (d, J = 1.2 Hz, 1H), 5.74–5.64 (m, 1H), 4.96 (dq, J = 1.6, 10.4 Hz, 1H), 4.78 (dq, J = 1.6, 17.2 Hz, 1H), 4.00 (s, 3H), 3.98 (s, 3H), 3.19 (d, J = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.35, 147.02, 146.57, 141.44, 139.42, 138.54, 138.18, 133.88, 130.75, 128.40, 126.69, 124.66, 122.54, 121.63, 118.03, 115.65, 110.02, 107.77, 101.03, 61.09, 56.69, 39.61.

A representative procedure of skeleton 8 is as follows

$Sn(OTf)_2$ (42 mg, 0.1 mmol) was added to a solution of **4p–v** (1.0 mmol) in $MeNO_2$ (5 mL) at 25 °C. The reaction mixture was stirred for 8 h at 25 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product. Purification on silica gel (hexanes/EtOAc = 100/1–10/1) afforded **8**.

1,2-Dimethoxy-4-phenylnaphthalene (8a). Yield = 81% (214 mg); colorless gum; HRMS (ESI, $M^+ + 1$) calcd for $C_{18}H_{17}O_2$ 265.1229, found 265.1230; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 8.8 Hz, 1H), 7.81 (d, J = 8.8 Hz, 1H), 7.53–7.43 (m, 6H), 7.34–7.30 (m, 1H), 7.27 (s, 1H), 4.06 (s, 3H), 4.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.55, 142.32, 140.49, 136.89, 130.07 (2x), 129.32, 128.26 (2x), 127.74, 127.28, 126.05 (2x), 124.14, 121.54, 116.40, 61.14, 56.91.

4-(4-Fluorophenyl)-1,2-dimethoxynaphthalene (8b). Yield = 74% (209 mg); colorless gum; HRMS (ESI, $M^+ + 1$) calcd for $C_{18}H_{16}FO_2$ 283.1134, found 283.1139; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 8.8 Hz, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.52–7.48 (m, 1H), 7.47–7.42 (m, 2H), 7.34–7.30 (m, 1H), 7.21 (s, 1H), 7.20–7.16 (m, 2H), 4.05 (s, 3H), 4.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.28 (d, J = 244.9 Hz), 147.54, 142.51, 136.39 (d, J = 3.1 Hz), 135.75, 131.59 (d, J = 7.6 Hz, 2x), 129.35, 127.83, 126.12, 125.81, 124.31, 121.63, 116.57, 115.21 (d, J = 21.2 Hz, 2x), 61.16, 56.99.

1,2-Dimethoxy-4-*p*-tolylnaphthalene (8c). Yield = 77% (214 mg); colorless gum; HRMS (ESI, $M^+ + 1$) calcd for $C_{19}H_{19}O_2$ 279.1385, found 279.1388; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23–8.20 (m, 1H), 7.85–7.82 (m, 1H), 7.50 (ddd, J = 1.2, 6.8, 8.4 Hz, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.34–7.29 (m, 3H), 7.25 (s, 1H), 4.06 (s, 3H), 4.02 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.57, 142.17, 137.55, 137.01, 136.91, 129.94 (2x), 129.32, 128.98 (2x), 127.83, 126.13, 125.99, 124.05, 121.51, 116.33, 61.13, 56.88, 21.19.

1,2-Dimethoxy-4-(4-methoxyphenyl)naphthalene (8d). Yield = 76% (223 mg); colorless solid; mp = 118–120 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, $M^+ + 1$) calcd for $C_{19}H_{19}O_3$ 295.1334, found 295.1338; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.51–7.47 (m, 1H), 7.35 (d, J = 8.4 Hz, 2H), 7.33–7.29 (m, 1H), 7.23 (s, 1H), 7.41 (d, J = 8.8 Hz, 2H), 4.05 (s, 3H), 4.01 (s, 3H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.00, 147.57, 142.10, 136.60, 132.85, 131.11 (2x), 129.34, 127.96, 126.12, 125.99, 124.05, 121.52, 116.36, 113.74 (2x), 61.14, 56.90, 55.36. Single-crystal X-ray diagram: crystal of compound **8d** was grown by slow diffusion of EtOAc into a solution of compound **8d** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group $P2_1/c$, a = 13.3450(12) Å, b = 15.2538(14) Å, c = 7.5723(7) Å, V = 1518.9(2) Å^3, Z = 4, d_{calcd} = 1.287 g cm^{-3}, $F(000)$ = 624, 2θ range 2.045–26.421°, R indices (all data) R_1 = 0.1172, wR_2 = 0.1285.

1,2-Dimethoxy-4-(4-trifluoromethylphenyl)naphthalene (8e). Yield = 80% (266 mg); colorless gum; HRMS (ESI, $M^+ + 1$) calcd for $C_{19}H_{16}F_3O_2$ 333.1102, found 333.1108; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 8.0 Hz, 2H), 7.55–7.51 (m, 1H), 7.37–7.33 (m, 1H), 4.09 (s, 3H), 4.04 (s, 3H), 7.27 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.54, 144.19, 142.97, 135.19, 130.41 (2x),

129.51 (d, J = 31.9 Hz), 129.40, 127.44, 126.26, 125.48, 125.23 (q, J = 3.8 Hz, 2x), 124.58, 124.28 (d, J = 270.6 Hz), 121.74, 116.60, 61.14, 56.97.

1,2-Dimethoxy-4-(2-methoxyphenyl)naphthalene (8f). Yield = 80% (235 mg); colorless gum; HRMS (ESI, M^+ + 1) calcd for $C_{19}H_{19}O_3$ 295.1334, found 295.1336; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20–8.17 (m, 1H), 7.51–7.46 (m, 2H), 7.44 (dd, J = 1.6, 8.0 Hz, 1H), 7.31–7.264 (m, 2H), 7.24 (s, 1H), 7.10 (dd, J = 1.2, 7.6 Hz, 1H), 7.07 (d, J = 8.0 Hz, 1H), 4.06 (s, 3H), 4.00 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.22, 147.56, 142.21, 133.41, 132.04, 129.18, 129.06, 129.02, 128.23, 126.42, 125.80, 123.76, 121.38, 120.53, 116.74, 111.03, 61.11, 56.81, 55.56.

4-Biphenyl-4-yl-1,2-dimethoxynaphthalene (8g). Yield = 75% (255 mg); colorless solid; mp = 118–120 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{24}H_{21}O_2$ 341.1542, found 341.1548; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24–8.21 (m, 1H), 7.90–7.88 (m, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.71–7.69 (m, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.54–7.48 (m, 3H), 7.42–7.38 (m, 1H), 7.36–7.32 (m, 1H), 7.30 (s, 1H), 4.07 (s, 3H), 4.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.62, 142.42, 140.77, 140.21, 139.48, 136.47, 130.51 (2x), 129.39, 128.85 (2x), 127.76, 127.40, 127.12 (2x), 127.02 (2x), 126.11, 126.06, 124.23, 121.60, 116.42, 61.18, 56.95. Single-crystal X-ray diagram: crystal of compound **8g** was grown by slow diffusion of EtOAc into a solution of compound **8g** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the triclinic crystal system, space group $P\bar{1}$, a = 6.6111(3) Å, b = 9.8830(5) Å, c = 14.4700(8) Å, V = 867.14(8) Å^3, Z = 2, d_{calcd} = 1.304 g cm^{-3}, F(000) = 360, 2θ range 1.488–26.356°, R indices (all data) R_1 = 0.0460, wR_2 = 0.1231.

A representative procedure of skeleton 9 is as follows

$Sn(OTf)_2$ (42 mg, 0.1 mmol) was added to a solution of **4w–x** (1.0 mmol) in $MeNO_2$ (5 mL) at 25 °C. The reaction mixture was stirred for 8 h at 25 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product. Purification on silica gel (hexanes/EtOAc = 100/1–10/1) afforded **9**.

6-Methoxy-1-(4-methoxyphenyl)naphthalene (9a). Yield = 61% (161 mg); colorless solid; mp = 83–85 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{18}H_{17}O_2$ 265.1229, found 265.1229; ^{1}H NMR (400 MHz): δ 7.84 (d, J = 9.2 Hz, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.50–7.40 (m, 3H), 7.27 (dd, J = 1.2, 6.8 Hz, 1H), 7.20 (d, J = 2.8 Hz, 1H), 7.10 (dd, J = 2.8, 9.2 Hz, 1H), 7.05–7.01 (m, 2H), 3.95 (s, 3H), 3.90 (s, 3H); ^{13}C NMR (100 MHz): δ 158.89, 157.39, 139.89, 135.10, 133.23, 131.02 (2x), 127.70, 127.23, 126.16, 126.03, 124.75, 118.52, 114.14, 113.67 (2x), 55.34, 55.30. Single-crystal X-ray diagram: crystal of compound **9a** was grown by slow diffusion of EtOAc into a solution of compound **9a** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group $P12_1/c1$, a = 7.654(4) Å, b = 13.820(8) Å, c = 13.657(8) Å, V = 1429.0(14) Å^3, Z = 4, d_{calcd} = 1.229 g cm^{-3}, F(000) = 560, 2θ range 2.11–26.46°, R indices (all data) R_1 = 0.0711, wR_2 = 0.1581.

2,6-Dimethoxy-1-(4-methoxyphenyl)naphthalene (9b). Yield = 40% (118 mg); colorless solid; mp = 65–67 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{19}H_{19}O_3$ 295.1334, found 295.1335; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 8.8 Hz, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.51–7.41 (m, 2H), 7.27 (dd, J = 1.2, 6.8 Hz, 1H), 7.21 (d, J = 2.4 Hz, 1H), 7.11 (dd, J = 2.8, 9.2 Hz, 1H), 7.02–6.96 (m, 2H), 3.98 (s, 3H), 3.97 (s, 3H), 3.90 (s, 3H). Single-crystal X-ray diagram: crystal of compound **9b** was grown by slow diffusion of EtOAc into a solution of compound **9b** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group $C1c1$, a = 8.6905(3) Å, b = 21.9250(7) Å, c = 8.2652(3) Å, V = 1494.97(9) Å^3, Z = 4, d_{calcd} = 1.308 g cm^{-3}, F(000) = 624, 2θ range 1.86–26.52°, R indices (all data) R_1 = 0.0291, wR_2 = 0.0743.

Naphthalene (10a). Na_2CO_3 (106 mg, 1.0 mmol) was added to a solution of allyl bromide (240 mg, 2.0 mmol) in dimethoxyethane (DME, 5 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 5 min. Then, *o*-formylphenylboronic acid (150 mg, 1.0 mmol) was added to the reaction mixture at 25 °C. The reaction mixture was stirred at 25 °C for 5 min. $Pd(OAc)_2$ (11 mg, 0.05 mmol) was added to the reaction mixture at 25 °C. The reaction mixture was stirred at 80 °C for 5 h. The reaction mixture (*in situ* formed **4y**) was cooled to 25 °C and $Sn(OTf)_2$ (42 mg, 0.1 mmol) was added to the reaction mixture. The reaction mixture was stirred for 8 h at 25 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product. Purification on silica gel (hexanes/EtOAc = 100/1–10/1) afforded **10a** (51%, 65 mg).

Acknowledgements

The authors would like to thank the Ministry of Science and Technology of the Republic of China for its financial support (MOST 105-2113-M-037-001).

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