One-pot synthesis of 3-naphtho[2,1-*b*]furanyl-2-oxindoles from 3-(arylethynyl)-3-hydroxyindolin-2-ones and 2-naphthols

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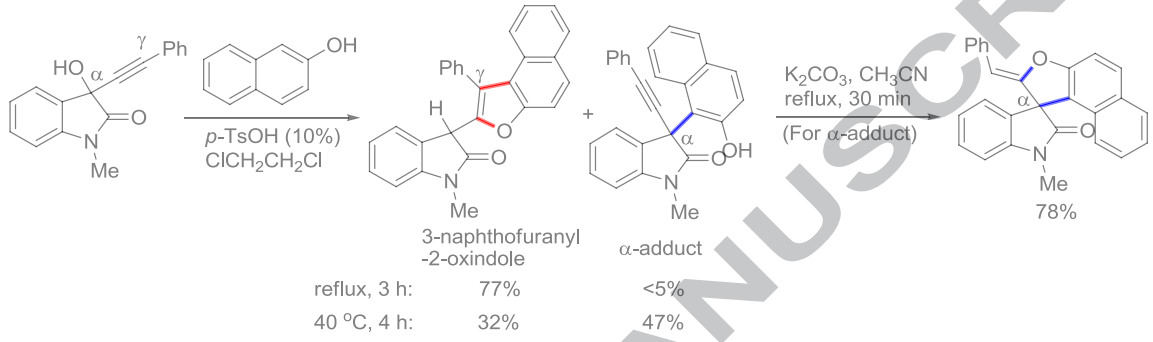

reflux, 3 h:	77%	<5%
40 °C, 4 h:	32%	47%

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One-pot synthesis of 3-naphtho[2,1-*b*]furanyl-2-oxindoles from 3-(arylethynyl)-3-hydroxyindolin-2-ones and 2-naphthols

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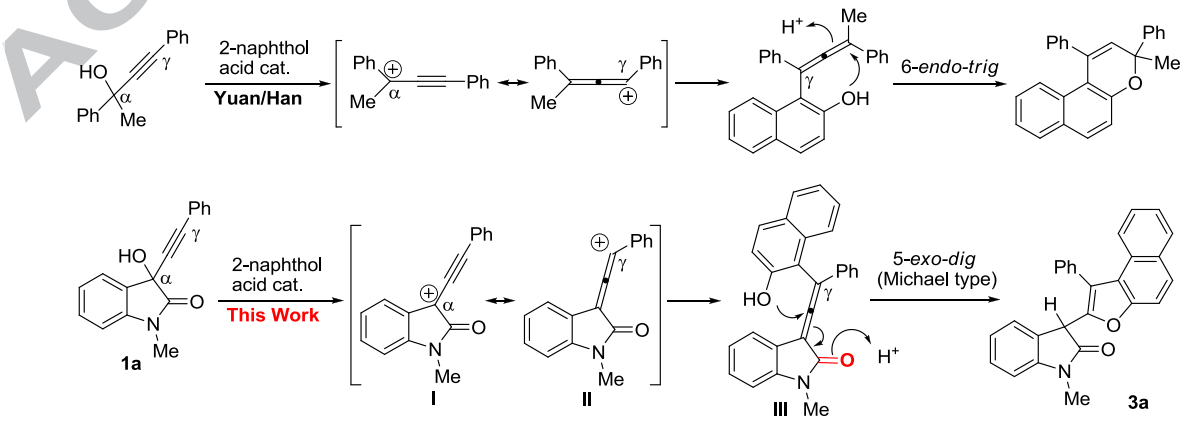
ABSTRACT

3-Naphthofuranyl-2-oxindoles were synthesized by the reaction of 3-(arylethynyl)-3-hydroxyindolin-2-ones and 2-naphthols via Friedel-Crafts reaction and a following Michael type 5-*exo-dig* cyclization. In addition, dihydrofuranyl-spirooxindoles were synthesized from 3-(*ortho*-hydroxyaryl)-2-oxindoles by base-catalyzed cyclization reaction.

3-Aryloxindoles are important intermediates for the synthesis of many biologically important 3,3-disubstituted oxindoles and indolines.[1,2] Thus, numerous synthetic approaches for 3-aryloxindoles have been developed.[2] The aryl moiety of 3-aryloxindoles included phenyl, substituted phenyl, and heteroaryls such as thienyl[2e,o,q] or indolyl.[2e,r] 3-Aryloxindoles have been prepared by cyclization of α-aryl acetanilides,[2a-d] arylation of isatins using aryl Grignard reagents and subsequent reduction,[2e-h] palladium or nickel-catalyzed arylation of oxindoles,[2i-n] or arylation of 3-diazooxindoles with arenes or aryl boron reagents.[2o-s]

The reactions of propargylic alcohols and 2-naphthols afforded naphthopyrans and naphthofurans depending on the reaction conditions as well as the structure of propargylic alcohols.[3] Recently, Yuan and Han reported the synthesis of naphthopyran derivative by the reaction of a tertiary propargylic alcohol and 2-naphthol as shown in Scheme 1.[3a] A propargylic alcohol **1a**, derived from *N*-methylisatin and phenylacetylene, has been reported;[4] however, the synthetic application of this compound has not been studied much.[4f-k] We reasoned out that the reaction of **1a** and 2-naphthol (**2a**) could afford the corresponding allene intermediate **III**, which could be converted



Scheme 1. Synthetic rationale of 3-naphthofuranyl-2-oxindole **3a**.

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Table 1. Optimization of reaction conditions for the synthesis of **3a**.

Entry	Conditions	**3a** (%)[a]
1	*p*-TsOH (10 mol%), DCE, 40 °C, 4 h	32[b]
2	*p*-TsOH (10 mol%), DCE, reflux, 3 h	77
3	*p*-TsOH (10 mol%), toluene, reflux, 3 h	65
4	CF_3COOH (10 equiv.), DCE, reflux, 3 h	74
5	Montmorillonite K-10 (300 %*w*/*w*), DCE, reflux, 4 h	64
6	$FeCl_3$ (20 mol%), DCE, reflux, 3 h	68
7	$FeCl_3$ (20 mol%), CH_3CN, reflux, 3 h	66
8	$InCl_3$ (10 mol%), DCE, reflux, 3 h	79
9	$Yb(OTf)_3$ (5 mol%), CH_3NO_2, 80 °C, 3 h	71
10	$AlCl_3$ (30 mol%), DCE, reflux, 12 h	15
11[c]	*p*-TsOH (10 mol%), DCE, reflux, 3 h	78
12[c]	$Yb(OTf)_3$ (5 mol%), CH_3NO_2, 80 °C, 3 h	75

[a]Isolated yield. [b]α-Adduct **4a** was isolated (47%).
[c]The corresponding Boc carbonate of **1a** was used.

to 3-naphthofuranyl-2-oxindole **3a** via more favorable Michael type 5-*exo*-*dig* cyclization.[5] The carbonyl group of oxindole moiety would facilitate the Michael type cyclization.

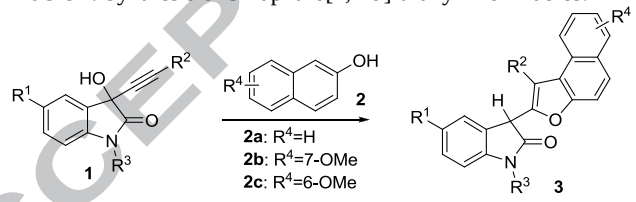
3-(Phenylethynyl)-3-hydroxyindolin-2-one **1a** was prepared by introduction of phenylacetylene to *N*-methylisatin according to the reported methods.[4] To our delight, the reaction of **1a** and **2a** in the presence of *p*-TsOH (10 mol%) in 1,2-dichloroethane (DCE, reflux, 3 h) afforded **3a** in good yield (77%), as expected (Entry 2, Table 1). In the reaction, 2-naphthol was used as a 1,3-*C*,*O*-bisnucleophile.[6] The carbon atom of C-1 position of **2a** was used in the Friedel-Crafts type reaction to form **III**, and the oxygen atom of **2a** was involved in a following Michael type cyclization step. The structure of **3a** was unequivocally confirmed by its crystal structure (see, Table 1).[7]

In order to find a better reaction condition, various acid catalysts were examined as shown in Table 1. The reaction at lower temperature (40 °C, entry 1) in the presence of *p*-TsOH (10 mol%) afforded **3a** in low yield (32%) along with α-adduct **4a** (47%, *vide infra*). The reaction in refluxing toluene was less efficient (entry 3), and the formation of some unidentified side products was observed. The use of trifluoroacetic acid (entry 4), montmorillonite K-10 (entry 5), $FeCl_3$ (entries 6 and 7), $InCl_3$ (entry 8), or $Yb(OTf)_3$ (entry 9) also afforded **3a** in variable yields (64-79%). The reaction using $AlCl_3$ was much less efficient (entry 10). When we use the corresponding Boc carbonate instead of **1a**, a similar result was observed (entries 11 and 12). Although the yield of **3a** was slightly higher when we use $InCl_3$ (entry 8), we decided to use *p*-TsOH as a cheap acid catalyst in 1,2-dichloroethane (entry 2) throughout the whole entries.

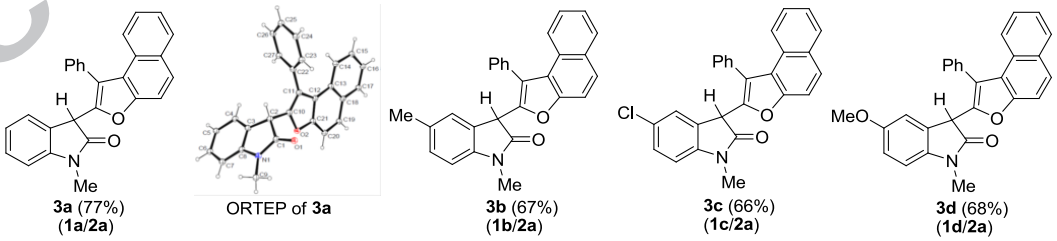
Encouraged by the result, various 3-(arylethynyl)-3-hydroxyindolin-2-ones **1b**-**1g** were prepared according to the reported methods,[4] and the reactions with 2-naphthols were examined. The results are summarized in Table 2.[8] The reactions of **1b**-**1f** afforded the corresponding products **3b**-**3f** in good yields (66-78%). Besides 2-naphthol, both 7-methoxynaphthalene-2-ol (**2b**) and 6-methoxynaphthalene-2-ol (**2c**) afforded the corresponding products **3g** and **3h**, respectively, in moderate yields (47 and 45%). The reaction of *N*-unsubstituted derivative **3i** was obtained in low yield (32%) under typical reaction condition; however, the yield could be increased up to 53% by using $InCl_3$ (50 mol%).

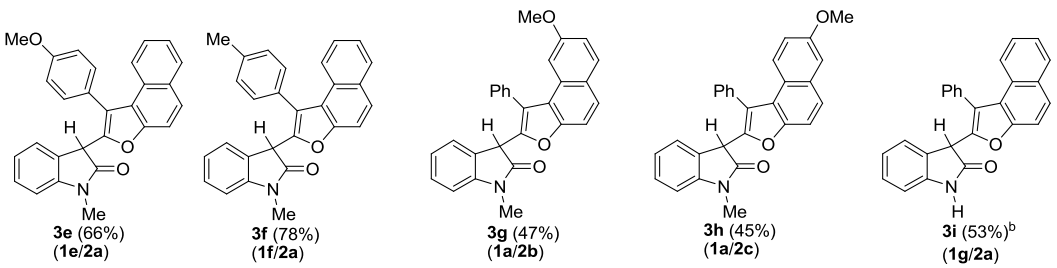
As shown in Scheme 2, the reaction of **1a** and **2a** at low temperature (40 °C) afforded α-adduct **4a** in moderate yield (47%) along with **3a** in low yield (32%) for 4 h (*vide supra*, Entry 1, Table 1). This compound **4a** could be converted to **3a** under refluxing 1,2-dichloroethane in the presence of *p*-TsOH for 6 h in moderate yield (56%), as shown Scheme 2. The result stated that **4a** could be converted to an allene intermediate **III**, and eventually to **3a**, via an acid-catalyzed retro-Friedel-Crafts reaction.[9]

Table 2. Synthesis of 3-naphtho[2,1-*b*]furanyl-2-oxindoles.[a]

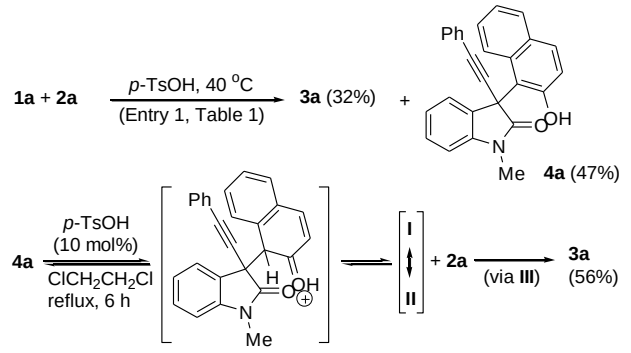


1a: R^1=H, R^2=Ph, R^3=Me
1b: R^1=Me, R^2=Ph, R^3=Me
1c: R^1=Cl, R^2=Ph, R^3=Me
1d: R^1=OMe, R^2=Ph, R^3=Me
1e: R^1=H, R^2=4-$MeOC_6H_4$, R^3=Me
1f: R^1=H, R^2=4-MeC_6H_4, R^3=Me
1g: R^1=H, R^2=Ph, R^3=H



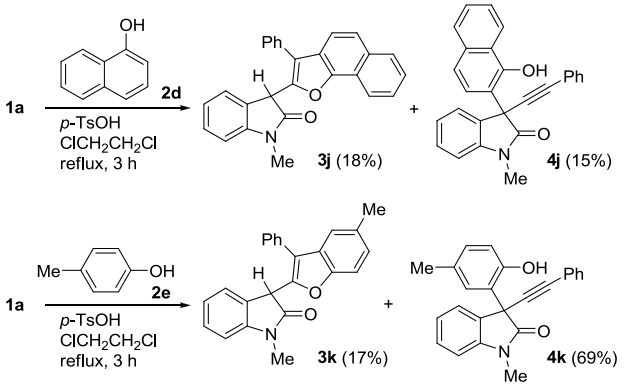


[a]Conditions: propargyl alcohol **1** (0.5 mmol), 2-naphthol derivative **2** (0.5 mmol), $ClCH_2CH_2Cl$, *p*-TsOH (10%), reflux, 3h.
[b]$InCl_3$ (50 mol%) was used.



Scheme 2. Formation of **3a** from **4a** via retro-Friedel-Crafts reaction.

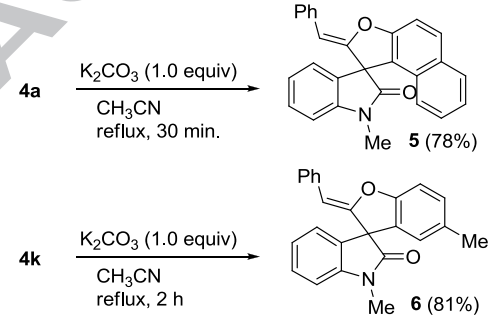
As a next entry, the reaction of **1a** with 1-naphthol (**2d**) was



Scheme 3. The reaction of **1a** with 1-naphthol (**2d**) and *p*-cresol (**2e**).

examined, as shown in Scheme 3. Desired product **3j** was obtained in low yield (18%) along with α-adduct **4j** (15%). The formation of many intractable side products was observed, to our surprise.[10] In addition, the reaction of **1a** and *p*-cresol (**2e**) also afforded **3k** in low yield (17%) along with α-adduct **4k** as a major product (69%).[11] The reason for low yield of **3k** might be attributed to steric reason in part, as already observed by Sanz and co-workers in their regioselective alkylations of indoles and 2-arylindoles with tertiary propargylic alcohols.[11b,c] Sterically less hindered *p*-cresol might react preferentially with propargylic cation **I** while 2-naphthol react with allenic cation intermediate **II** (see, Scheme 1). Another reason would be a difficult retro-Friedel-Crafts reaction of **4k** presumably due to loss of larger resonance energy as compared to that of the case of **4a** (see, Scheme 2).

The α-adduct **4a** could be converted to dihydrofuranyl-spirooxindole **5** in good yield (78%),[12] as shown in Scheme 4.



Scheme 4. Synthesis of spirooxindoles **5** and **6**.

Spirooxindole **5** was obtained in the presence of K_2CO_3 in CH_3CN (reflux) in short time (30 min) via base-catalyzed 5-*exo*-*dig* cyclization.[13] Similarly, compound **4k** (see, Scheme 3) was converted to spirooxindole **6** in good yield (81%).[14]

In summary, various 3-naphthofuranyl-2-oxindoles have been synthesized by the reaction of isatin propargylic alcohols and 2-naphthols. In addition, dihydrofuranyl-spirooxindoles could also be synthesized from 3-(*ortho*-hydroxyaryl)-2-oxindoles by base-catalyzed cyclization reaction.

Acknowledgments

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6. Moghaddam and co-workers reported that 2-naphthol can used as 1,3-*C*,*O*-bisnucleophile in the reaction with quinolinium salt to form naphthooxazocine skeleton.[6a] For similar 1,3-*C*,*O*-bisnucleophiles in the reaction with propargylic alcohol derivatives,[6b,c] see: (a) Moghaddam, F. M.; Taheri, S.; Mirjafary, Z.; Saeidian, H.; Kiamehr, M.; Tafazzoli, M. *Helv. Chim. Acta*. **2011**, *94*, 142; (b) Hu, J.; Wei, Y.; Tong, X. *Org. Lett*. **2011**, *13*, 3068; (c) Li, C.; Zhang, Q.; Tong, X. *Chem. Commun*. **2010**, *46*, 7828.

7. CCDC 1455352 (**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. It is interesting to note that the phenyl group at 2-position of naphtho[2,1-*b*]furanyl moiety did not rotate freely at room temperature and 27 carbon peaks appeared in ^{13}C NMR spectrum ($CDCl_3$). When we took ^{13}C NMR at 77 ^{o}C in DMSO-d_6, 25 carbon peaks appeared including two large peaks corresponding *ortho*- and *meta*-carbon atoms (see, Supporting Information).

8. **Typical procedure for the synthesis of 3a**: A stirred solution of **1a** (132 mg, 0.5 mmol), **2a** (72 mg, 0.5 mmol), and *p*-TsOH monohydrate (10 mg, 10 mol%) in 1,2-dichloroethane (1.5 mL) was heated to reflux for 3 h. After the usual aqueous extractive workup and column chromatographic purification process (hexanes/EtOAc, 4:1) compound **3a** was obtained as a pale yellow solid, 150 mg (77%). Other compounds were synthesized similarly, and the selected spectroscopic data of **3a**, **3b**, and **5** are as follows.

Compound **3a**: 77%; pale yellow solid, mp 206-208 ^{o}C; IR (KBr) 1718, 1612, 1492, 1470, 1370, 1348 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.16 (s, 3H), 4.80 (s, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.28-7.34 (m, 2H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.44-7.50 (m, 2H), 7.51-7.56 (m, 1H), 7.55 (d, *J* = 9.0 Hz, 1H), 7.60-7.66 (m, 2H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 26.71, 45.18, 108.50, 112.51, 122.07, 122.88, 123.23, 123.25, 124.42, 124.57, 125.87, 126.10, 127.03, 128.14, 128.26, 128.63, 128.87, 128.97, 129.00, 130.63, 130.85, 131.02, 132.88, 144.35, 147.92, 152.01, 173.78; ^{13}C NMR (DMSO-d_6, 125 MHz, 77 ^{o}C) δ 25.94, 44.31, 108.35, 111.84, 120.98, 121.87, 121.89, 122.02, 123.63, 124.09, 125.54, 125.77, 126.20, 127.02, 127.90, 128.27, 128.35, 128.62, 129.90, 130.18, 131.74, 143.87, 148.13, 150.86, 172.40; ESIMS *m/z* 390 [M+H]$^{+}$. Anal. Calcd for $C_{27}H_{19}NO_2$: C, 83.27; H, 4.92; N, 3.60. Found: C, 83.08; H, 5.10; N, 3.71.

Compound **3b**: 67%; white solid, mp 198-200 ^{o}C; IR (KBr) 1715, 1499, 1349 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.28 (s, 3H), 3.20 (s, 3H), 4.83 (s, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.93 (s, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.30 (t, *J* = 8.5 Hz, 1H), 7.40 (t, *J* = 8.5 Hz, 1H), 7.44-7.51 (m, 2H), 7.52-7.55 (m, 1H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.60-7.68 (m, 2H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.15, 26.74, 45.24, 108.21, 112.55, 122.09, 123.19, 123.28, 124.41, 125.41, 125.83, 126.09, 127.05, 128.18, 128.24, 128.63, 128.97, 129.08, 130.63, 130.88, 131.09, 132.47, 132.97, 142.01, 148.14, 152.03, 173.70 (one carbon is overlapped); ESIMS *m/z* 404 [M+H]$^{+}$. Anal. Calcd for $C_{28}H_{21}NO_2$: C, 83.35; H, 5.25; N, 3.47. Found: C, 83.54; H, 5.16; N, 3.46.

Compound **5**: 78%; white solid, mp 232-234 ^{o}C; IR (KBr) 1722, 1683, 1610, 1469, 1342, 1252 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.45 (s, 3H), 5.23 (s, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 2H), 7.16-7.25 (m, 2H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 27.24, 62.23, 103.81, 108.77, 112.11, 118.58, 121.22, 124.04, 124.12, 125.18, 126.70, 127.87, 128.42, 128.66, 129.26, 129.41, 129.57, 130.82, 131.61, 132.14, 134.49, 143.77, 157.04, 157.41, 175.24; ESIMS *m/z* 390 [M+H]$^{+}$. Anal. Calcd for $C_{27}H_{19}NO_2$: C, 83.27; H, 4.92; N, 3.60. Found: C, 83.25; H, 5.18; N, 3.33.

9. For retro-Friedel-Crafts reaction, see: (a) Bacci, J. P.; Kearney, A. M.; Van Vranken, D. L. *J. Org. Chem*. **2005**, *70*, 9051; (b) Sun, Y.; Chen, P.; Zhang, D.; Baunach, M.; Hertweck, C.; Li, A. *Angew. Chem. Int. Ed*. **2014**, *53*, 9012; (c) Sun, Y.; Meng, Z.; Chen, P.; Zhang, D.; Baunach, M.; Hertweck, C.; Li, A. *Org. Chem. Front*. **2016**, *3*, 368; (d) Frost, J. R.; Cheong, C. B.; Akhtar, W. M.; Caputo, D. F. J.; Stevenson, N. G.; Donohoe, T. J. *J. Am. Chem. Soc*. **2015**, *137*, 15664.

10. The formation of many intractable side products was observed in the reaction of **1a** and 1-naphthol (**2d**) even at low temperature (40 ^{o}C).

11. For regioselective introduction of carbon nucleophiles at the α- and γ-positions of propargylic alcohols, see: (a) Zhang, X.; Teo, W. T.; Chan, P. W. H. *Org. Lett.* **2009**, *11*, 4990; (b) Sanz, R.; Miguel, D.; Martinez, A.; Gohain, M.; Garica-Garcia, P.; Fernandez-Rodriguez, M. A.; Alvarez, E.; Rodriguez, F. *Eur. J. Org. Chem.* **2010**, 7027; (c) Sanz, R.; Gohain, M.; Miguel, D.; Martinez, A.; Rodriguez, F. *Synlett* **2009**, 1985; (d) Zhan, Z.; Wang, S.; Cai, X.; Liu, H.; Yu, J.; Cui, Y. *Adv. Synth. Catal.* **2007**, *349*, 2097; (e) Detz, R. J.; Hiemstra, H.; van Maarseveen, J. H. *Eur. J. Org. Chem.* **2009**, 6263; (f) Zhang, L.; Zhu, Y.; Yin, G.; Lu, P.; Wang, Y. *J. Org. Chem*. **2012**, *77*, 9510; (g) See also references 3a, 3e and 3m.

12. For similar dihydro- and tetrahydrofuranyl-spirooxindoles, see: (a) Cerisoli, L.; Lombardo, M.; Trombini, C.; Quintavalla, A. *Chem. Eur. J*. **2016**, *22*, 3865; (b) Shanmugam, P.; Vaithiyanathan, V. *Tetrahedron* **2008**, *64*, 3322; (c) Shanmugam, P.; Viswambharan, B. *Synlett* **2008**, 2763; (d) Liu, Z.; Fang, J.; Yan, C. *Chin. J. Chem.* **2013**, *31*, 1054; (e) Chung, C.-P.; Hsu, C.-Y.; Lin, J.-H.; Kuo, Y.-H.; Chiang, W.; Lin, Y.-L. *J. Agric. Food Chem.* **2011**, *59*, 1185; (f) Wang, L.; Li, Z.; Lu, L.; Zhang, W. *Tetrahedron* **2012**, *68*, 1483; (g) Nair, V.; Treesa, P. M.; Rath, N. P.; Kunwar, A. C.; KiranKumar, K. S.; RaviSankar, A.; Vairamani, M.; Prabhakar, S. *Tetrahedron* **2002**, *58*, 7221.

13. For similar metal-free 5-*exo*-*dig* cyclizations, see: (a) Ma, Q.; Wang, Y.; Zhao, Y.; Liao, P.; Sun, B.; Bi, X. *Eur. J. Org. Chem*. **2014**, 4999 and further references cited therein; (b) Taylor, C.; Bolshan, Y. *Tetrahedron Lett*. **2015**, *56*, 4392; (c) Kraus, G. A.; Wie, J.; Thite, A. *Synthesis* **2008**, 2427; (d) Chenevert, R.; Page, J.; Plante, R.; Beaucage, D. *Synthesis* **1982**, 75.

14. As expected, the reaction of **1a** and phenol (**2f**) afforded the corresponding *para*-isomer as a major product (69%) along with a trace amount of *ortho*-isomer, and a treatment of the *para*-isomer with K_2CO_3 showed no reaction.

Supplementary Data

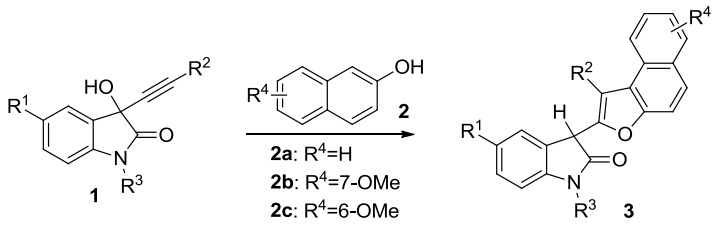
Supplementary data (experimental procedures and characterization data for the compounds **1b**, **1d**, **1e**, **3a**-**3k**, **4a**, **4j**, **4k**, **5** and **6**) associated with this article can be found, in the online version, at xxxxxxxxxxxx.

Table 1. Optimization of reaction conditions for the synthesis of **3a**.

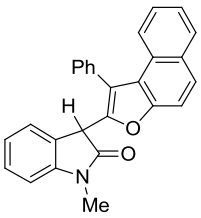
Entry	Conditions	**3a** (%)[a]
1	*p*-TsOH (10 mol%), DCE, 40 ^{o}C, 4 h	32[b]
2	*p*-TsOH (10 mol%), DCE, reflux, 3 h	77
3	*p*-TsOH (10 mol%), toluene, reflux, 3 h	65
4	CF_3COOH (10 equiv.), DCE, reflux, 3 h	74
5	Montmorillonite K-10 (300 %*w*/*w*), DCE, reflux, 4 h	64
6	$FeCl_3$ (20 mol%), DCE, reflux, 3 h	68
7	$FeCl_3$ (20 mol%), CH_3CN, reflux, 3 h	66
8	$InCl_3$ (10 mol%), DCE, reflux, 3 h	79
9	$Yb(OTf)_3$ (5 mol%), CH_3NO_2, 80 ^{o}C, 3 h	71
10	$AlCl_3$ (30 mol%), DCE, reflux, 12 h	15
11[c]	*p*-TsOH (10 mol%), DCE, reflux, 3 h	78
12[c]	$Yb(OTf)_3$ (5 mol%), CH_3NO_2, 80 ^{o}C, 3 h	75

[a]Isolated yield. [b]α-Adduct **4a** was isolated (47%).
[c]The corresponding Boc carbonate of **1a** was used.

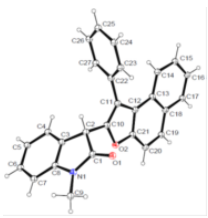
Table 2. Synthesis of 3-naphtho[2,1-*b*]furanyl-2-oxindoles.[a]



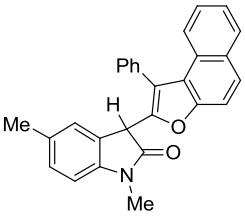
1a: R^1=H, R^2=Ph, R^3=Me
1b: R^1=Me, R^2=Ph, R^3=Me
1c: R^1=Cl, R^2=Ph, R^3=Me
1d: R^1=OMe, R^2=Ph, R^3=Me
1e: R^1=H, R^2=4-MeOC$_6$H$_4$, R^3=Me
1f: R^1=H, R^2=4-MeC$_6$H$_4$, R^3=Me
1g: R^1=H, R^2=Ph, R^3=H



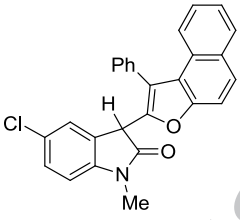
3a (77%)
(**1a**/**2a**)



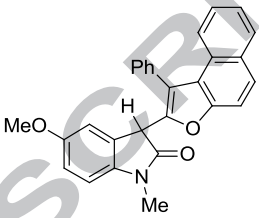
ORTEP of **3a**



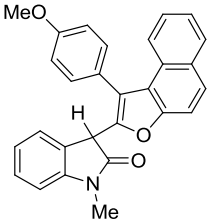
3b (67%)
(**1b**/**2a**)



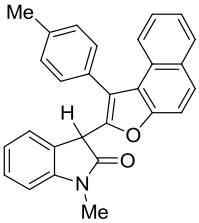
3c (66%)
(**1c**/**2a**)



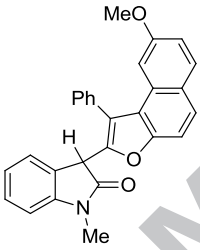
3d (68%)
(**1d**/**2a**)



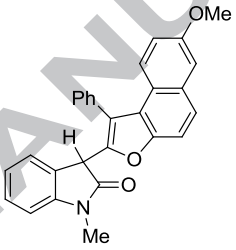
3e (66%)
(**1e**/**2a**)



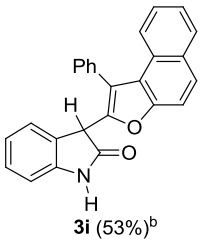
3f (78%)
(**1f**/**2a**)



3g (47%)
(**1a**/**2b**)



3h (45%)
(**1a**/**2c**)



3i (53%)[b]
(**1g**/**2a**)

[a]Conditions: propargyl alcohol **1** (0.5 mmol), 2-naphthol derivative **2** (0.5 mmol), $ClCH_2CH_2Cl$, *p*-TsOH (10%), reflux, 3 h.
[b]$InCl_3$ (50 mol%) was used.

Highlights

*One-pot synthesis of 3-naphtho[2,1-*b*]furanyl-2-oxindoles
*Efficient synthesis of dihydrofuranyl-spirooxindoles
*2-Naphthol can be used as a 1,3-*C*,*O*-bisnucleophile