Palladium-Catalyzed Tandem Reaction of Yne–Propargylic Carbonates with Boronic Acids: A Simple Method for the Synthesis of Fused Aromatic Rings through Allene-Mediated Electrocyclization

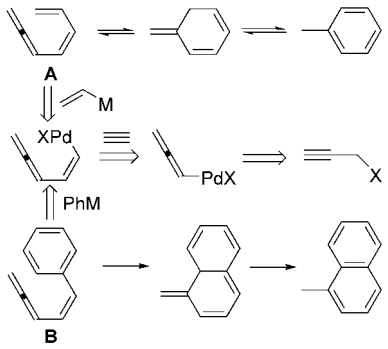
Feng Wang,[a] Xiaofeng Tong,[a] Jiang Cheng,[b] and Zhaoguo Zhang*[a]

Abstract: The palladium-catalyzed tandem reactions of yne–propargylic carbonates with aryl boronic acids, 2-furyl boronic acid, and 2-thiopheneboronic acid, followed by 6π-electrocyclization to give fused ring aromatic products such as naphthalene, benzofuran, and benzothiophene derivatives are realized. Screening of the reaction conditions revealed that the combination of $[Pd(PPh_3)_4]$ in THF gave the best results in terms of reactivity and product yields in the reaction of yne–propargylic carbonates with phenylboronic acid. The reaction is sensitive toward steric hindrance when substituted phenylboronic acids are emplyed. However, when we take 2-furyl boronic acid as the organometallic reagent, most substrates perform very well to give benzofuran derivatives. In addition, 2-thiopheneboronic acid is also a very effective coupling reagent to give bezothiophenes in high yields. A mechanism is proposed that involves the formation of an allenylpalladium complex from Pd^0 and propargylic carbonate, followed by insertion of an intramolecular triple bond and the Suzuki coupling reaction, and then electrocyclization.

Keywords: allenes · C–C coupling · electrocyclic reactions · fused-ring systems · heterogeneous catalysis · palladium

Introduction

Allene-mediated cyclization reactions have attracted much attention by chemists.[1] One type of cyclization product, isotoluene or its benzo analogues (Scheme 1), can be easily converted to toluene or naphthalenes, because of their unstable properties.[2] As a matter of fact, the electrocyclization of diene–allenes (**A**) were used as a key step in organic synthesis (Scheme 1).[3] This reaction could be extended to the arylvinylallene (**B**), which also takes place the 6π electrocyclization to give naphthalene.[4] However, these allenic compounds cannot be easily synthesized.[3b,5]



Scheme 1. Allene-mediated cyclization reactions.

It has been sporadically reported that the allenylpalladium complex could favorably insert into a triple bond to form an allenylvinylpalladium species that couples with the organometallic compounds to produce allene derivatives conveniently.[6,7]

On the basis of these foundations, we have designed a tandem reaction of yne–propargylic carbonates and aryl boronic acids catalyzed by palladium(0) to give the arylvinylallenes and followed by electrocyclization in situ to form the naphthalene, benzofuran, and benzothiophene derivatives. Herein, we report our preliminary results.

Results and Discussion

Tandem reaction of yne–propargylic carbonates with aryl boronic acids—synthesis of multisubstituted naphthalenes: Following the literature procedure,[6b] when we treated a mixture of **1**, Ph_2Zn, and $[Pd(dba)_2]$/4 TFP (TFP = trifurylphosphine) in refluxing Et_2O for 12 h, the starting material was recovered; no reaction occurred at all. However, when

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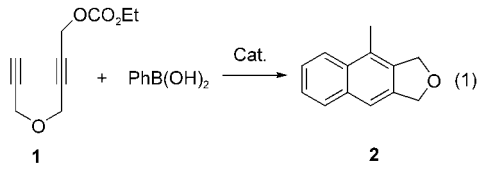
we employed $PhB(OH)_2$ instead of Ph_2Zn as the organometallic reagent for the coupling reaction, 4-methyl-1,3-dihydro-naphtho[2,3-*c*]furan (**2**) can be isolated in 19% yield within 1 h (Table 1, entry 1). By employing the commercially available catalyst $[Pd(PPh_3)_4]$, a better result was achieved (Table 1, entry 2).

Table 1. Tandem reaction of propargyl ethyl carbonates with phenylboronic acid.[a]



1 **2**

Entry	Catalyst (5 mol%)	Solvent	Yield [%][b]
1	$[Pd(dba)_2]$/4TFP	THF	19
2	$[Pd(PPh_3)_4]$	THF	42[c]
3	$Pd(OAc)_2$/3TFP	THF	7
4	$Pd(OAc)_2/3PPh_3$	THF	42
5	$Pd(OAc)_2/3P(OMe)_3$	THF	–
6	$Pd(OAc)_2/3P(o\text{-tol})_3$	THF	–
7	$Pd(OAc)_2$/2L	THF	–[d]
8	$[Pd(PPh_3)_4]$	5THF/H_2O	43
9	$[Pd(PPh_3)_4]$	toluene	29
10	$[Pd(PPh_3)_4]$	dioxane	42
11	$[Pd(PPh_3)_4]$	CH_3CN	trace
12	$[Pd(PPh_3)_4]$	DMF	trace
13	$[Pd(PPh_3)_4]$	THF	35[e]

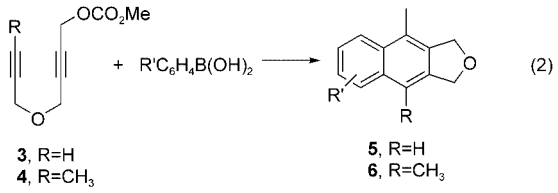
[a] All reactions were performed under argon atmosphere with **1** (0.30 mmol), palladium (5 mol%), and phenylboronic acid (0.45 mmol) in a specified solvent (3 mL) at 70°C for 1 h. [b] Yield of isolated product based on **1**. [c] At room temperature no reaction occurred. [d] L = BINAP, DPPE, DPPP or DPPB. The substrate **1** could be recovered; the reaction time was 12 h. [e] K_2CO_3 (0.6 mmol) was added as a base.

Recognizing that the phosphine ligands always play an important role in transition-metal-catalyzed reactions, the commercially available bidentate ligands (1,1′-binaphthalene-2,2′-diylbis(diphenylphosphine) (BINAP), 1,2-bis(diphenylphosphino)ethane (DPPE), 1,3-bis(diphenylphosphino)propane (DPPP), 1,4-bis(diphenylphosphino)butane(DPPB)) and monodentate ligands (PPh_3, $P(OMe)_3$, $P(o\text{-Tol})_3$) were tested for the reaction. $Pd(OAc)_2$ with bidentate phosphine ligands could not catalyze the reaction; no products were detected at all and the starting material **1** was recovered (entry 7). In contrast $Pd(OAc)_2$ with monodentate phosphine ligands could catalyze the reaction, giving **2** in the yields ranging from 0% to 42% (entries 3–6). Among the monophosphine ligands screened, PPh_3 gave the best result with 42% isolated yield. Compound **1** was consumed completely and no side product was detected in the ^1H spectrum of the solvent-free reaction mixture.

Besides THF, the reaction in other solvents, such as toluene, CH_3CN and DMF, were also investigated; under the catalysis with $[Pd(PPh_3)_4]$ compound **2** was separated in poor yields (Table 1, entries 9, 11, 12). The reaction proceeded in 1,4-dioxane similarly as in THF, the same yield was obtained (42%, Table 1, entry 10). When K_2CO_3 was added as a base, the yield decreased to 35% (Table 1, entry 13). It is noted that when the mixture of water and THF (1:5) was employed as the solvent, the yield of **2** did not change at all (Table 1, entry 8).

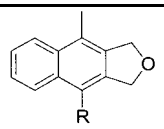
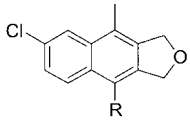
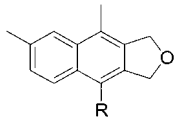
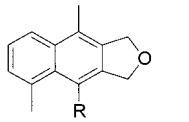
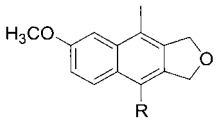
To improve the yields of products, we employed propargyl methyl carbonate **3** as reactant, and 48% of isolated yield of the product could be achieved (Table 2, entry 1). Other aryl boronic acids with electron-withdrawing, electron-donating groups, or an *ortho*-substituent, can also react with **3** to give the corresponding naphthalene derivatives **5b**–**5e** (Table 2, entries 2–5). When the terminal alkyne moiety of **3** is blocked by a methyl group, the resulting propargyl methyl carbonate **4** reacts with phenylboronic acid smoothly, and the isolated yield of naphthalene derivative (**6a**) is increased to 65% (Table 2, entry 1). The *para*-substituted phenylboronic acids also react with **4** to give the desired products in moderate yields (Table 2, entries 2, 3). It is not clear why a low yield of **6e** is obtained when electron-rich boronic acid **e** reacts with **4** (Table 2, entry 5).

Table 2. Tandem reaction of propargyl methyl carbonates with aryl boronic acids.[a]



3, R=H
4, R=CH_3

5, R=H
6, R=CH_3

Entry	$R'C_6H_4B(OH)_2$	*t* [h]	Product	Yield **5/6** [%][b]
1	**a** $B(OH)_2$	1		**5a/6a** 48/65
2	Cl, **b** $B(OH)_2$	2		**5b/6b** 61/61
3	**c** $B(OH)_2$	1		**5c/6c** 60/69
4	**d** $B(OH)_2$	1		**5d/6d** 45/–[c]
5	H_3CO, **e** $B(OH)_2$	2		**5e/6e** 61/34

[a] All reactions were performed under argon atmosphere with **3** (0.30 mmol), $[P(PPh_3)_4]$ (5 mol%), and aryl boronic acid (0.45 mmol) in refluxing THF (3 mL). [b] Yield of isolated product based on **3**. [c] Unidentified mixture.

However, no naphthalene product is detected when **4** reacts with $2\text{-}MeC_6H_4B(OH)_2$; this outcome is different from that found when propargyl methyl carbonate **3** was employed as the substrate. From the energy-minimized model of the allenic intermediate (Figure 1), the 6π system

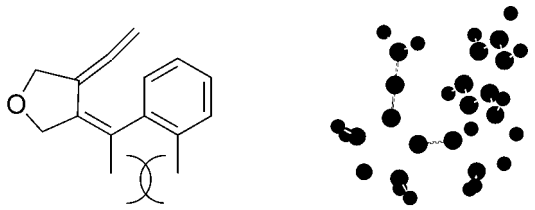
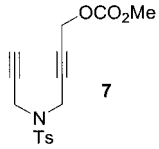
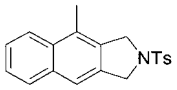
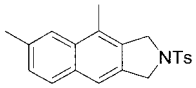
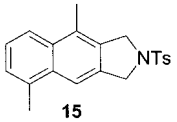
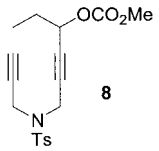
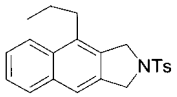
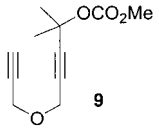
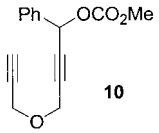
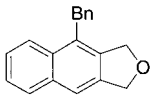
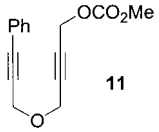
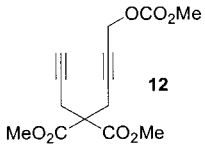
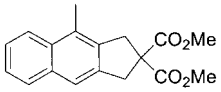


Figure 1. The energy-minimized (Chem3D ultra 6.0, MM2) model of the allenic intermediate.

cannot co-exist in one plane, due to the steric hindrance of two methyl groups, and this prevents the electrocyclization reaction.

The nitrogen-bridged substrate **7** reacts with phenylboronic acid smoothly to give **13** in 55% of yield (Table 3, entry 1). Like the oxygen-tethered substrate **3**, compound **7** could also react with other substituted aryl boronic acids, including *ortho*-substituted phenylboronic acid, to give the corresponding naphthalene derivatives as the products. When the α-position of the propargyl carbonates is substituted, for example, for an ethyl-substituted compound (**8**), the reaction even proceeds at room temperature. When a phenyl group is substituted at the α-position, the yield is much higher (entry 6). However, for the substrates **9** and **11**, mixtures of products are obtained that cannot be separated or identified. This may also be attributed to the same reason that a coplanar 6π system cannot be formed (Figure 1). The carbon-tethered substrate **12** with methyl carboxylate groups also reacts with phenylboronic acid to give a carbon-ring product, but with lower yields.

Table 3. Tandem reaction of yne–propargylic carbonates and aryl bronic acids.[a]

Entry	Carbonates	$ArB(OH)_2$[b]	*t* [h]	Products	Yield [%][c]
1	 **7**	**a**	1	 **13**	55
2	**7**	**c**	1	 **14**	64
3	**7**	**d**	2	 **15**	59
4	 **8**	**a**	1	 **16**	55
5	 **9**	**a**	2	mixture[d]	–
6	 **10**	**a**	1	 **17**	76
7	 **11**	**a**	1	mixture[d]	–
8	 **12**	**a**	1	 **18**	27(29)[e]

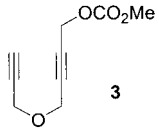
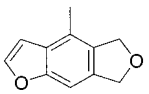
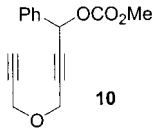
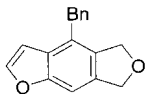
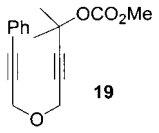
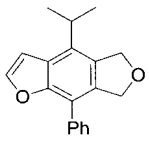
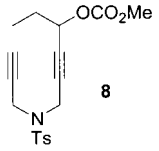
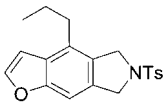
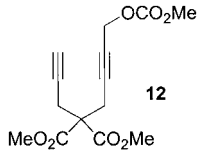
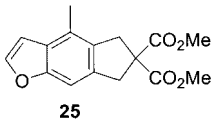
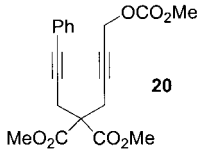
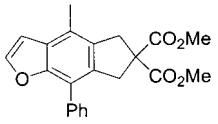
[a] The reaction conditions were the same as those in Table 1. [b] For structures of $ArB(OH)_2$ see Table 2. [c] Yield of isolated product. [d] Mixture products could not be separated or identified. [e] The yield in parenthesis is obtained with 5 mol% of $Pd(OAc)_2/3PPh_3$ as catalyst.

Tandem reaction of yne–propargylic carbonates with 2-furylboronic acid and 2-thiopheneboronic acids—synthesis of benzofurans and benzothiophenes: Besides the aryl boronic acids, we found that other heteroaryl boronic acids, such as 2-furylboronic acid and 2-thiopheneboronic acid, react more easily with the yne–propargylic carbonates to give the corresponding benzofurans and benzothiophenes (Tables 4 and 5).

Substrates **3** and **10** react with 2-furylboronic acid smoothly in higher yield than those with aryl boronic acids (Table 4, entries 1 and 2); even the α,α-dimethyl-substituted substrate **19** also gives benzofuran in moderate yield (Table 4, entry 3). Other substrates such as nitrogen- and carbon-tethered alkynyl propargylic carbonates react with 2-furylboronic acid to give the corresponding benzofurans (Table 4, entries 4–6).

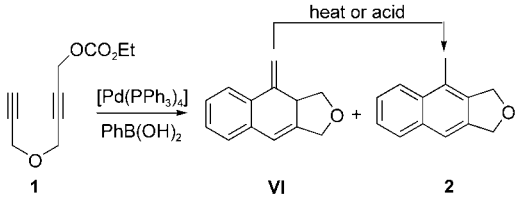
The best results are obtained when we take 2-thiopheneboronic acid as the coupling reagent. The yields are higher than those of when aryl and 2-furylboronic acid are employed and the reaction time is much shorter. For substrate **9**, which cannot form naphthalene when it reacts with phenylboronic acid (Table 3, entry 5), benzothiophene **30** is afforded in moderate yield in 30 minutes (Table 5, entry 4). It seems that the steric hindrance of carbonates does not have any effect on the reaction when 2-thiopheneboronic acid is applied (Table 5, entries 3–5 and 8).

Table 4. Tandem reaction of yne–propargylic carbonates with 2-furylboronic acid.[a]

Entry	Carbonates	t [h]	Products	Yield [%][b]
1	 **3**	0.5	 **21**	67
2	 **10**	0.5	 **22**	75
3	 **19**	1	 **23**	63
4	 **8**	1	 **24**	59
5	 **12**	0.5	 **25**	52
6	 **20**	3	 **26**	37(45)[c]

[a] The reaction conditions were the same as those in Table 1. [b] Yield of isolated product. [c] The yield in parenthesis is obtained with 5 mol% of $Pd(OAc)_2/3\,PPh_3$ as catalyst.

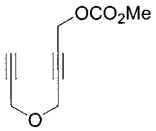
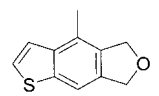
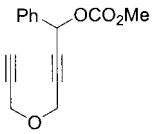
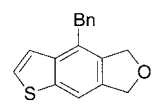
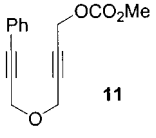
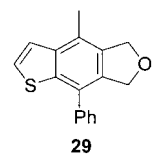
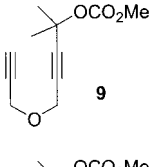
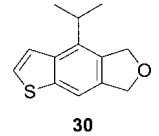
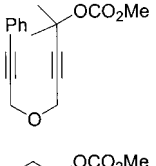
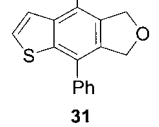
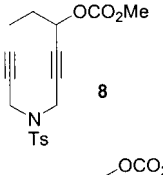
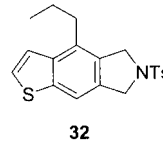
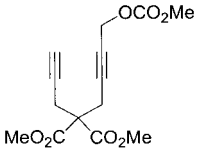
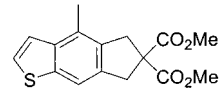
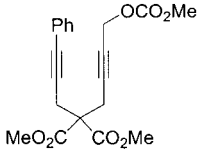
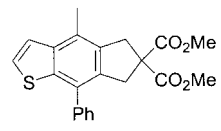
Mechanism investigation: In our initial experiment of yne–propargylic carbonate **1** with phenylboronic acid, we isolated another product **VI**, which is unstable. It directly changed slowly to **2** at room temperature, or very fast on heating or with catalytic amount of trifluoroacetic acid (Scheme 2). Therefore, we believe that the compound **VI** is one of the intermediates in the reaction.



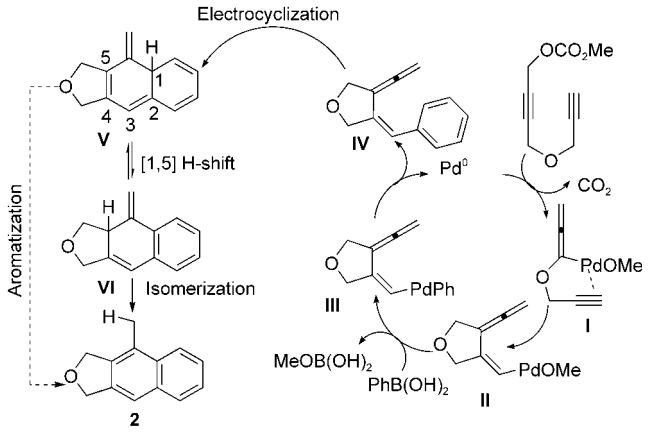
Scheme 2. Formation and subsequent reaction of intermediate **VI**.

On the basis of these results, we propose a possible reaction mechanism (Scheme 3). Palladium(0) attacks at propargylic carbonate through S_N2' substitution to form an allenylpalladium compound (**I**). Instead of direct coupling with phenylboronic acid,[7] the intermediate **I** inserts into the intramolecular triple bond to generate the alkenylpalladium intermediate **II**. The transmetalation of intermediate **II** with aryl boronic acid affords the intermediate **III**, which undergoes reductive elimination to give arylvinylallene **IV**. This allenic compound **IV** electrocylizes to form the highly conjugated intermediate **V**. Intermediate **V** either aromatizes directly to give the final product **2** or reacts through the [1,5] H-shift to afford the intermediate **VI**, which further isomerizes to give the product **2**. The isolation of compound **VI**[8] indicates that [1,5] H-shift must have taken place during the course of the product formation. Compound **VI** will covert to the naphthalene product in several hours in air at room temperature or in a few minutes in the presence of TFA.[1f]

Table 5. Tandem reaction of yne–propargylic carbonates with 2-thiopheneboronic acid.[a]

Entry	Carbonates	t [h]	Products	Yield [%][b]
1		0.1	 **27**	91
2	 **10**	0.5	 **28**	86
3	 **11**	0.5	 **29**	71
4	 **9**	0.5	 **30**	62
5		0.5	 **31**	82
6	 **8**	0.5	 **32**	86
7		0.5		58
8		1	 **34**	79

[a] The reaction conditions were the same as those in Table 1. [b] Yield of isolated product.



Scheme 3. The possible mechanism of the tandem reaction of yne–propargylic carbonates and aryl boronic acids.

We have no proof to support the direct aromatization of **V** to give the product.

Conclusion

In summary, we found a novel method for the synthesis of poly-substituted naphthalenes, benzofurans, and benzothiophenes by means of the palladium-catalyzed tandem reaction of yne–propargylic carbonates with boronic acids followed by electrocyclization. This is an efficient way to build complex fused ring system from linear molecules. It should be noted that this method can be used especially for the synthesis of multi-substituted naphthalenes, benzofurans, and benzothiophenes with regioselectivity. The searching for the catalyst/ligands to achieve a more efficient coupling of the yne–propargylic carbonate with aryl boronic acids, and the application of the method in highly fused aromatic ring synthesis are in progress in our laboratory.

Experimental Section

General: All reactions and manipulations were conducted under Ar atmosphere by using standard Schlenk techniques. All solvents were purified according to standard procedures. Column chromatography was performed using silica gel (200–300 mesh). Melting points were not corrected. NMR spectra were recorded at 300 MHz for ^{1}H and 75 MHz for ^{13}C spectra, with tetramethylsilane as the internal standard for ^{1}H spectra and the residual solvent signals as the standard for ^{13}C spectra. Chemical shifts were downfield reported in ppm. MS, HRMS, IR spectra, and microanalysis were performed by the State-authorized Analytical Center in Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. All catalysts and phosphine ligands were purchased from commercial sources. The substrates were prepared similarly according to the literature.

General procedure for the palladium-catalyzed tandem reaction of yne–propargylic carbonates with aryl boronic acids (Method A): A Schlenk tube was charged a solution of aryl boronic acid (0.45 mmol) and [P(PPh$_3$)$_4$] (17.3 mg, 0.015 mmol) in THF (2.0 mL) under argon atmosphere. With stirring, a solution of yne–propargylic carbonate (0.3 mmol) in THF (1.0 mL) was introduced into the tube by syringe in one portion. The reaction mixture was heated at reflux until the carbonate was consumed as monitored by TLC. The reaction mixture was cooled to room temperature, and one drop of trifluoroacetic acid was added; the mixture was then stirred for about 30 minutes. After evaporation of the solvent under reduced pressure, the mixture was purified by chromatography on silica gel with hexane and ethyl acetate as eluent to afford the product.

4-Methyl-1,3-dihydronaphtho[2,3-*c*]furan (5a/2): 48%, white solid; m.p. 50–51°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00–7.96 (m, 2H), 7.81–7.78 (m, 1H), 7.51–7.44 (m, 3H), 5.23–5.22 (m, 4H), 2.53 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.4, 136.6, 133.5, 132.1, 128.5, 126.2, 125.5, 125.3, 123.5, 117.2, 73.5, 72.8, 15.4 ppm; MS (EI, 70 eV): *m/z* (%): 184 (100) [M^+], 169 (40), 155 (92), 141 (57), 128 (20), 115 (23); IR (KBr): $\tilde{\nu}$ = 2854 (w), 1048 (s), 908 (m), 747 cm^{-1} (s); elemental analysis calcd (%) for $C_{13}H_{12}O$: C 84.75, H 6.57; found: C 84.73, H 6.77.

6-Chloro-4-methyl-1,3-dihydronaphtho[2,3-*c*]furan (5b): 61%, white solid; m.p. 125–126°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (d, J = 2.1 Hz, 1H), 7.74 (d, J = 8.7 Hz, 1H), 7.50 (s, 1H), 7.40 (dd, J = 2.1, 8.7 Hz, 1H), 5.23 (s, 4H), 2.50 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.8, 137.8, 132.9, 131.8, 131.4, 129.9, 126.1, 125.6, 122.7, 117.2, 73.4, 72.7, 15.4 ppm; MS (EI, 70 eV): *m/z* (%): 218 (100) [M^+(^{35}Cl)], 189 (90), 175 (38), 153 (54), 139 (14); IR (KBr): $\tilde{\nu}$ = 2858 (w), 1495 (m), 1081 (m), 1044 (s), 900 (s), 865 cm^{-1} (s); elemental analysis calcd (%) for $C_{13}H_{11}ClO$: C 71.40, H 5.07; found: C 71.32, H 5.15.

6-Methyl-4-methyl-1,3-dihydronaphtho[2,3-*c*]furan (5c): 60%, white solid; m.p. 100–101°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74–7.69 (m, 2H), 7.48 (s, 1H), 7.31–7.25 (m, 1H), 5.22 (s, 4H), 2.54 (s, 3H), 2.52 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.6, 136.4, 135.1, 132.3, 131.7, 128.3, 127.5, 125.4, 122.6, 117.0, 73.5, 72.8, 22.0, 15.4 ppm; MS (EI, 70 eV): *m/z* (%): 198 (60) [M^+], 183 (32), 169 (100), 155 (68), 141 (14), 128 (18), 115 (15); IR (KBr): $\tilde{\nu}$ = 2850 (w), 1505 (w), 1340 (m), 1048 (s), 901 (s), 800 (s), 521 cm^{-1} (m); elemental analysis calcd (%) for $C_{14}H_{14}O$: C 84.81, H 7.12; found: C 84.84, H 7.25.

4,8-Dimethyl-1,3-dihydronaphtho[2,3-*c*]furan (5d): 45%, white solid; m.p. 83–84°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86 (d, J = 8.4 Hz, 1H), 7.71 (s, 1H), 7.41–7.36 (m, 1H), 7.30 (d, J = 6.6 Hz, 1H), 5.28 (s, 2H), 5.24 (s, 2H), 2.68 (s, 3H), 2.54 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.2, 136.2, 134.5, 132.6, 132.1, 126.7, 126.2, 125.0, 121.8, 113.4, 73.8, 72.9, 20.0, 15.8 ppm; MS (EI, 70 eV): *m/z* (%): 198 (98) [M^+], 183 (39), 169 (100), 155 (74), 141 (18), 128 (23), 115 (24), 91 (16); IR (KBr): $\tilde{\nu}$ = 2838 (m), 1448 (m), 1341 (m), 1048 (s), 904 (s), 793 (s), 750 cm^{-1} (s); elemental analysis calcd (%) for $C_{14}H_{14}O$: C 84.81, H 7.12; found: C 84.79, H 7.32.

6-Methoxy-4-methyl-1,3-dihydronaphtho[2,3-*c*]furan (5e): 61%, white solid; m.p. 119–120°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70 (d, J = 9.0 Hz, 1H), 7.45 (s, 1H), 7.21 (d, J = 2.4 Hz, 1H), 7.13 (dd, J = 2.4, 9.0 Hz, 1H), 5.22 (s, 4H), 3.94 (s, 3H), 2.48 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.4, 137.1, 135.0, 133.1, 129.9, 128.8, 124.8, 127.5, 117.0, 102.3, 73.5, 72.9, 55.2, 15.5 ppm; MS (EI, 70 eV): *m/z* (%): 214 (74) [M^+], 199 (15), 185 (100), 171 (41), 152 (24), 141 (86), 128 (41), 115 (87); IR (KBr): $\tilde{\nu}$ = 2858 (w), 1618 (s), 1506 (s), 1233 (s), 1180 cm^{-1} (s), 1045 (s); HRMS (MALDI): *m/z* calcd for $C_{14}H_{15}O_2^+$ [M^++H]: 215.1072; found: 215.1067.

4,9-Dimethyl-1,3-dihydronaphtho[2,3-*c*]furan (6a): 65%, white solid; m.p. 139–141°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01–7.98 (m, 2H), 7.52–7.49 (m, 2H), 5.26 (s, 4H), 2.51 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.8, 132.5, 125.1, 123.9, 123.8, 73.5, 15.3 ppm; MS (EI, 70 eV): *m/z* (%): 198 (100) [M^+], 183 (81), 169 (74), 155 (91), 141 (31), 128 (27), 115 (27), 91 (15); IR (KBr): $\tilde{\nu}$ = 2839 (w), 1457 (m), 1335 (m), 1038 (s), 908 (s), 759 cm^{-1} (s); elemental analysis calcd (%) for $C_{14}H_{14}O$: C 84.81, H 7.12; found: C 84.45, H 7.08.

6-Chloro-4,9-dimethyl-1,3-dihydronaphtho[2,3-*c*]furan (6b): 61%, white solid; m.p. 114–115°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91–7.86 (m, 2H), 7.40 (d, J = 8.7 Hz, 1H), 5.21(s, 4H), 2.45 (s, 3H), 2.43 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.0, 136.1, 133.5, 131.1, 130.8, 125.7, 125.5, 124.0, 123.2, 123.0, 73.4, 73.4, 15.3, 15.3 ppm; MS (EI, 70 eV): *m/z* (%): 232 (100) [M^+(^{35}Cl)], 217 (81), 203 (72), 189 (45), 165 (36), 153 (55), 91 (44); IR (KBr): $\tilde{\nu}$ = 2847 (m), 1604 (m), 1501 (m), 1461 (m), 1382 (m), 1338 (m), 1096 (m), 1041 (s), 910 (s), 871 (s), 805 cm^{-1} (s); elemental analysis calcd (%) for $C_{13}H_{11}ClO$: C 72.26, H 5.63; found: C 72.28, H 5.75.

4,6,9-Trimethyl-1,3-dihydronaphtho[2,3-*c*]furan (6c): 69%, white solid; m.p. 95–96°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90 (d, J = 8.7 Hz, 1H),

7.77 (s, 1H), 7.34 (d, J=8.7 Hz, 1H), 5.26 (s, 4H), 2.55 (s, 3H), 2.50 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=135.7, 134.8, 134.5, 132.7, 130.6, 127.1, 123.7, 123.6, 123.1, 123.0, 73.5, 73.4, 21.8, 15.3, 15.2 ppm; MS (EI, 70 eV): m/z (%): 212 (100) [M^+], 197 (77), 183 (71), 169 (56), 153 (34), 141 (15), 128 (16), 115 (14); IR (KBr): $\tilde{\nu}$=2837 (w), 1337 (m), 1041 (s), 909 (s), 810 cm^{-1} (s); HRMS (EI): m/z calcd for $C_{15}H_{16}O$: 212.1201; found: 212.1191.

6-Methoxy-4,9-dimethyl-1,3-dihydronaphtho[2,3-*c*]furan (6e): 34%, white solid; m.p. 135–136°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.91 (d, J=9.3 Hz, 1H), 7.24 (d, J=2.7 Hz, 1H), 7.17 (dd, J=2.7, 9.3 Hz, 1H), 5.25 (s, 4H), 3.95 (s, 3H), 2.48 (s, 3H), 2.46 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=157.1, 136.4, 133.7, 133.5, 127.8, 125.5, 123.9, 122.5, 116.9, 102.9, 73.6, 73.5, 55.2, 15.5, 15.4 ppm; MS (EI, 70 eV): m/z (%): 228 (100) [M^+], 213 (64), 199 (58), 185 (36), 153 (16), 141 (20), 115 (14); IR (KBr): $\tilde{\nu}$=1617 (s), 1423 (m), 1224 (s), 1043 (s), 838 (s), 811 cm^{-1} (m); HRMS (EI): m/z calcd for $C_{15}H_{16}O_2$: 228.1150; found: 228.1151.

4-Methyl-2-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-benzo[*f*]isoindole (13): 55%, white solid; m.p. 172–173°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.93 (d, J=8.1 Hz, 1H), 7.81 (d, J=8.1 Hz, 2H), 7.75 (d, J=8.1 Hz, 1H), 7.50–7.46 (m, 3H), 7.32 (d, J=8.1 Hz, 2H), 4.74 (s, 2H), 4.72 (s, 2H), 2.50 (s, 3H), 2.39 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=143.7, 134.0, 133.4, 133.3, 133.2, 131.9, 129.8, 128.4, 128.0, 127.6, 125.8, 125.7, 123.5, 119.2, 53.6, 53.0, 21.5, 15.2 ppm; MS (EI, 70 eV): m/z (%): 337 (13) [M^+], 181 (100), 167 (12), 155 (12), 91 (15); IR (KBr): $\tilde{\nu}$=1348 (s), 1160 (s), 1098 (m), 670 (s), 546 cm^{-1} (s); HRMS (EI): m/z calcd for $C_{20}H_{19}NO_2S$: 337.1136; found: 337.1145.

4,6-Dimethyl-2-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-benzo[*f*]isoindole (14): 64%, white solid; m.p.>250°C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.81 (d, J=8.4 Hz, 2H), 7.69 (s, 1H), 7.65 (d, J=8.4 Hz, 1H), 7.43 (s, 1H), 7.31 (dd, J=8.4 Hz, 3H), 4.73 (s, 2H), 4.71 (s, 2H), 2.52 (s, 3H), 2.48 (s, 3H), 2.39 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=143.7, 135.4, 133.4, 133.2, 133.0, 132.1, 131.5, 129.8, 128.1, 127.9, 127.6, 127.2, 122.6, 118.9, 53.6, 53.0, 22.0, 21.5, 15.1 ppm; MS (EI, 70 eV): m/z (%): 351 (15) [M^+], 195 (100); IR (KBr): $\tilde{\nu}$=1346 (s), 1160 (s), 1098 (s), 667 (s), 547 cm^{-1} (s); HRMS (EI): m/z calcd for $C_{20}H_{19}NO_2S$: 351.1293; found: 351.1290.

4,8-Dimethyl-2-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-benzo[*f*]isoindole (15): 59%, white solid; m.p. 183–184°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.81 (dd, J=8.4 Hz, 3H), 7.64 (s, 1H), 7.39–7.25 (m, 4H), 4.78 (s, 2H), 4.73 (s, 2H), 2.63 (s, 3H), 2.50 (s, 3H), 2.39 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=143.7, 134.5, 133.8, 133.5, 132.9, 132.5, 132.0, 129.8, 128.5, 127.6, 126.5, 125.4, 121.8, 115.4, 53.9, 53.1, 21.5, 19.9, 15.6 ppm; MS (EI, 70 eV): m/z (%): 351 (16) [M^+], 195 (100); IR (KBr): $\tilde{\nu}$=1346 (s), 1160 (s), 1098 (s), 667 (s), 547 cm^{-1} (s); HRMS (EI): m/z calcd for $C_{20}H_{19}NO_2S$: 351.1293; found: 351.1287.

4-Propyl-2-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-benzo[*f*]isoindole (16): 55%, white solid; m.p. 135–136°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.95 (d, J=7.8 Hz, 1H), 7.81 (d, J=8.1 Hz, 2H), 7.77–7.74 (m, 1H), 7.49–7.42 (m, 3H), 7.31 (d, J=8.1 Hz, 2H), 4.74 (s, 4H), 2.90–2.85 (m, 2H), 2.40 (s, 3H), 1.69–1.61 (m, 2H), 1.02 ppm (t, J=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=143.7, 134.1, 133.7, 133.4, 133.0, 131.2, 129.8, 128.5, 127.6, 125.7, 125.5, 123.5, 119.4, 115.2, 53.5, 52.8, 31.9, 23.4, 21.5, 14.4 ppm; MS (EI, 70 eV): m/z (%): 365 (17) [M^+], 209 (71), 180 (100), 167 (19), 152 (20), 91 (41); IR (KBr): $\tilde{\nu}$=1345 (s), 1160 (s), 1100 (s), 669 (s), 547 cm^{-1} (s); elemental analysis calcd (%) for $C_{22}H_{23}NO_2S$: C 72.30, H 6.34, N 3.83; found: C 72.54, H 6.49, N 3.63.

4-Benzyl-1,3-dihydro-naphtho[2,3-*c*]furan (17): 76%, white solid; m.p. 63–65°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.97–7.94 (m, 1H), 7.85–7.82 (m, 1H), 7.52 (s, 1H), 7.61 (s, 1H), 7.46–7.38 (m, 1H), 7.23–7.15 (m, 1H), 7.12–7.07 (m, 1H) 5.27 (s, 2H), 5.19 (s, 2H), 4.33 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=139.4, 137.8, 137.6, 133.9, 131.9, 128.6, 128.6, 128.5, 128.1, 126.2, 125.8, 125.4, 124.0, 118.4, 73.4, 72.7, 35.4 ppm; MS (EI, 70 eV): m/z (%): 260 (100) [M^+], 215 (75), 182 (93), 169 (83), 153 (60), 141 (86), 115 (32), 78 (23); IR (KBr): $\tilde{\nu}$=2838 (m), 1056 (s), 909 (m), 740 (s), 705 (s), 509 cm^{-1}(m); HRMS (EI): m/z calcd for $C_{19}H_{17}O^+$: 261.1279; found: 261.1274.

Dimethyl ester of 4-methyl-1,3-dihydrocyclopenta[*b*]naphthalene-2,2-dicarboxylic acid (18): 27%, yellow oil. 1H NMR (300 MHz, $CDCl_3$): δ= 7.95 (d, J=8.4 Hz, 1H), 7.75 (d, J=8.4 Hz, 1H), 7.52 (s, 1H), 7.45–7.33 (m, 3H), 3.76 (s, 6H), 3.74 (s, 2H), 3.72 (s, 2H), 2.59 ppm (s, 2H); ^{13}C NMR (75 MHz, CDCl3): δ=172.1, 138.2, 137.1, 133.4, 132.1, 128.7, 128.2, 125.1, 125.0, 123.6, 120.5, 60.2, 53.0, 40.5, 39.7, 15.3 ppm; MS (EI, 70 eV): m/z (%): 298 (25) [M^+], 238 (57), 179 (100), 165 (37), 84 (74), 47 (18); IR ($CHCl_3$): $\tilde{\nu}$=2955 (w), 1736 (brs), 1435 (s), 1256 (brs), 1073 (m), 734 cm^{-1} (m); HRMS (EI): m/z calcd for $C_{18}H_{18}O_4$: 298.1205; found: 298.1204.

General procedure for the palladium-catalyzed tandem reaction of yne-propargylic carbonates with furylboronic acid and thiopheneboronic acid (Method B): A Schlenk tube was charged a solution of furyl boronic acid or thiopheneboronic acid (0.45 mmol) and [$P(PPh_3)_4$] (17.3 mg, 0.015 mmol) in THF (2.0 mL) under argon atmosphere, with stirring; a solution of yne–propargylic carbonate (0.3 mmol) in THF (1.0 mL) was added to the tube by syringe in one portion. The reaction mixture was heated at reflux until carbonate was consumed as detected by TLC. The reaction mixture was cooled, evaporated under reduced pressure, and purified by chromatography on silica gel with hexane and ethyl acetate as eluent to afford the product.

4-Methyl-5,7-dihydro-1,6-dioxa-*s*-indacene (21): 67%, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.60 (d, J=2.4 Hz, 1H), 7.17 (s, 1H), 6.76 (d, J=2.4 Hz, 1H), 5.23 (s, 2H), 5.18 (s, 2H), 2.37 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=154.9, 145.0, 135.1, 131.6, 127.1, 123.4, 104.9, 101.4, 73.7, 72.5, 15.7 ppm; MS (EI, 70 eV): m/z (%): 174 (35) [M^+], 159 (41), 145 (100), 131 (23), 115 (28); IR ($CHCl_3$): $\tilde{\nu}$=2852 (s), 1382 (s), 1297 (s), 1141 (s), 1038 (s), 908 (s), 770 (s), 725 ppm (s); HRMS (EI): m/z calcd for $C_{11}H_{10}O_2$: 174.0681; found: 174.0664.

4-Benzyl-5,7-dihydro-1,6-dioxa-*s*-indacene (22): 75%, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.58 (d, J=2.1 Hz, 1H), 7.29–7.13 (m, 6H), 6.69 (dd, J=1.2, 2.1 Hz, 1H), 5.18 (s, 2H), 5.04 (s, 2H), 4.11 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=155.2, 145.1, 139.2, 136.4, 132.9, 128.6, 128.4, 127.1, 126.3, 126.2, 105.1, 102.2, 73.5, 72.3, 36.8 ppm; MS (EI, 70 eV): m/z (%): 250 (82) [M^+], 221 (38), 172 (100), 159 (34), 131 (35), 115 (47), 78 (40), 51 (41); IR ($CHCl_3$): $\tilde{\nu}$=2849 (m), 1379 (s), 1297 (s), 1139 (s), 1043 (s), 909 (m), 735 (m), 701 cm^{-1} (m); HRMS (EI): m/z calcd for $C_{17}H_{14}O_2$: 250.0994; found: 250.0980.

4-Isopropyl-8-phenyl-5,7-dihydro-1,6-dioxa-*s*-indacene (23): 63%, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.60 (d, J=2.1 Hz, 1H), 7.57–7.54 (m, 2H), 7.50–7.45 (m, 2H), 7.40–7.36 (m, 1H), 6.91 (d, J=2.1 Hz, 1H), 5.26 (s, 2H), 5.20 (s, 2H), 3.15 (h, J=6.9 Hz, 1H), 1.40 ppm (d, J= 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=152.9, 144.7, 134.8, 134.6, 133.4, 131.6, 129.0, 128.5, 127.7, 125.5, 117.7, 106.0, 72.9, 72.6, 31.8, 22.0 ppm; MS (EI, 70 eV): m/z (%): 278 (100) [M^+], 263 (14), 249 (50), 235 (36), 207 (52), 178 (50), 43 (56); IR ($CHCl_3$): $\tilde{\nu}$=2963 (s), 1481 (s), 1375 (s), 1146 (s), 1067 (s), 744 (s), 698 cm^{-1} (s); HRMS (EI): m/z calcd for $C_{19}H_{18}O_2$: 278.1307; found: 278.1328.

4-Propyl-6-(toluene-4-sulfonyl)-6,7-dihydro-5*H*-1-oxa-6-aza-*s*-indacene (24): 59%, white solid; m.p. 166–168°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.79 (d, J=8.1 Hz, 2H), 7.56 (d, J=2.1 Hz, 1H), 7.31 (d, J=8.1 Hz, 2H), 7.12 (s, 1H), 6.72 (d, J=2.1 Hz, 2H), 4.69 (s, 2H), 4.65 (s, 2H), 2.67 (t, J=7.2 Hz, 2H), 2.39 (s, 3H), 1.67–1.57 (m, 2H), 0.94 ppm (t, J= 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=154.9, 145.0, 143.6, 133.5, 132.6, 129.9, 129.8, 128.9, 127.6, 126.8, 105.0, 103.3, 53.6, 52.2, 32.8, 23.1, 21.5, 14.1 ppm; MS (EI, 70 eV): m/z (%): 355 (5) [M^+], 199 (42), 170 (58), 115 (54), 91 (100), 71 (71), 39 (68); IR (KBr): $\tilde{\nu}$=1340 (s), 1163 (s), 1098 (m), 667 (s), 607 (m), 551 cm^{-1} (m); elemental analysis calcd (%) for $C_{20}H_{21}NO_3S$: C 67.58, H 5.95, N 3.94; found: C 67.47, H 6.17, N 3.57.

4-Methyl-5,7-dihydro-1-oxa-*s*-indacene-6,6-dicarboxylic acid dimethyl ester (25): 52%, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.53 (d, J= 1.8 Hz, 1H), 7.17 (s, 1H), 6.71 (d, J=1.8 Hz, 1H), 3.76 (s, 6H), 3.68 (s, 2H), 3.58 ppm (s, 2H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ= 172.1, 154.7, 144.3, 136.5, 132.8, 126.6, 125.8, 105.0, 104.6, 60.5, 53.0, 40.5, 38.5, 15.8 ppm; MS (EI, 70 eV): m/z (%): 288 (35) [M^+], 228 (100), 197 (22), 169 (94), 141 (17), 115 (20), 84 (17); IR ($CHCl_3$): $\tilde{\nu}$=2956 (w), 1740 (s), 1435 (m), 1251 (s), 1201 cm^{-1} (m); HRMS (EI): m/z calcd for $C_{16}H_{16}O_5$: 288.0998; found: 288.0970.

Dimethyl ester of 4-methyl-8-phenyl-5,7-dihydro-1-oxa-*s*-indacene-6,6-dicarboxylic acid (26): 37%, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.59–7.54 (m, 3H), 7.51–7.47 (m, 2H), 7.1–7.35 (m, 1H), 6.77 (d, J= 2.1 Hz, 1H), 3.73 (s, 6H), 3.69 (s, 2H), 3.65 (s, 2H), 2.45 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=172.1, 144.6, 143.3, 135.2, 134.5, 134.4, 133.5, 129.5, 128.4, 127.4, 125.0, 119.8, 105.2, 60.5, 53.0, 39.8, 38.8,

15.8 ppm; MS (EI, 70 eV): *m/z* (%): 364 (64) [M^+], 304 (71), 245 (66), 202 (21), 84 (100); IR ($CHCl_3$): $\tilde{\nu}$ = 2955 (w), 1736 (s), 1256 (s), 757 cm^{-1} (s); HRMS (MALDI): *m/z* calcd for $C_{22}H_{20}O_5Na^+$: 387.1208; found: 387.1203.

4-Methyl-5,7-dihydro-6-oxa-1-thia-*s*-indacene (27): 91%, white solid; m.p. 69–70 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (s, 1H), 7.41 (d, *J* = 5.7 Hz, 1H), 7.36 (dd, *J* = 1.8, 5.7 Hz, 1H), 5.21 (s, 2H), 5.17 (s, 2H), 2.47 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.5, 138.7, 136.2, 134.8, 125.8, 125.3, 121.3, 111.9, 73.5, 72.6, 16.3 ppm; MS (EI, 70 eV): *m/z* (%): 190 (35) [M^+], 175 (47), 161 (100), 147 (20), 128 (20), 115 (18); IR (KBr): $\tilde{\nu}$ = 2848 (w), 1046 (s), 904 (s), 764 (s), 697 cm^{-1} (s); HRMS (EI): *m/z* calcd for $C_{11}H_{10}OS$: 190.0452; found: 190.0449.

4-Benzyl-5,7-dihydro-6-oxa-1-thia-*s*-indacene (28): 86%, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 (s, 1H), 7.39–7.33 (m, 2H), 7.27–7.16 (m, 3H), 7.12–7.09 (m, 2H), 5.19 (s, 2H), 5.07 (s, 2H), 4.21 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.0, 139.2, 138.8, 136.6, 135.6, 128.5, 128.2, 128.0, 126.3, 126.2, 121.6, 112.9, 73.3, 72.4, 37.0 ppm; MS (EI, 70 eV): *m/z* (%): 266 (100) [M^+], 250 (16), 237 (39), 221 (50), 188 (68), 175 (37), 147 (38), 115 (19); IR ($CHCl_3$): $\tilde{\nu}$ = 2857 (w), 1493 (w), 1054 (s), 740 (m), 699 cm^{-1} (s); HRMS (EI): *m/z* calcd for $C_{17}H_{14}OS$: 266.0765; found: 266.0763.

4-Methyl-8-phenyl-5,7-dihydro-6-oxa-1-thia-*s*-indacene (29): 71%, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53–7.39 (m, 7H), 5.23 (s, 2H), 5.15 (s, 2H), 2.50 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.7, 139.5, 138.6, 135.7, 134.2, 128.8, 128.2, 128.0, 127.5, 126.4, 124.3, 121.7, 73.3, 72.9, 16.2 ppm; MS (EI, 70 eV): *m/z* (%): 266 (100) [M^+], 251 (8), 237 (90), 221 (65), 189 (20), 111 (10); IR ($CHCl_3$): $\tilde{\nu}$ = 2856 (w), 1443 (m), 1361 (m), 1054 (s), 763 (m), 734 (s), 703 cm^{-1} (s); elemental analysis calcd (%) for $C_{17}H_{14}OS$: C 76.66, H 5.30; found: C 76.55, H 5.17.

4-Isopropyl-5,7-dihydro-6-oxa-1-thia-*s*-indacene (30): 62%, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (s, 1H), 7.50 (d, *J* = 5.4 Hz, 1H), 7.39 (d, *J* = 5.4 Hz, 1H), 5.26 (s, 2H), 5.16 (s, 2H), 3.40 (h, *J* = 7.5 Hz, 1H), 1.37 ppm (d, *J* = 7.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.3, 137.1, 137.0, 136.3, 133.2, 125.3, 122.0, 112.2, 72.7. 72.4, 31.8, 21.8 ppm; MS (EI, 70 eV): *m/z* (%): 218 (100) [M^+], 203 (12), 189 (57), 175 (34), 235 (84), 161 (18), 147 (57); IR ($CHCl_3$): $\tilde{\nu}$ = 2964 (s), 1463 (m), 1364 (s), 1059 (s), 918 (s), 841 (s), 777 (s), 702 cm^{-1} (s); HRMS (MALDI): *m/z* calcd for $C_{13}H_{15}OS^+$: 219.0844; found: 219.0838.

4-Isopropyl-8-phenyl-5,7-dihydro-6-oxa-1-thia-*s*-indacene (31): 82%, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57–7.38 (m, 7H), 5.32 (s, 2H), 5.08 (s, 2H), 3.44 (h, *J* = 7.2 Hz, 1H), 1.42 ppm (d, *J* = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.7, 138.6, 138.0, 135.3, 135.0, 134.2, 128.8, 128.2, 128.0, 127.7, 126.0, 122.5, 72.8, 72.4, 31.9, 21.9 ppm; MS (EI, 70 eV): *m/z* (%): 294 (100) [M^+], 279 (15), 265 (27), 251 (34), 235 (21), 223 (71), 84 (21); IR ($CHCl_3$): $\tilde{\nu}$ = 2964 (s), 1359 (m), 1062 (s), 720 (m), 732 (s), 701 cm^{-1} (s); HRMS (EI): *m/z* calcd for $C_{19}H_{18}OS$: 294.1078; found: 294.1064.

4-Propyl-6-(toluene-4-sulfonyl)-6,7-dihydro-5*H*-1-thia-6-aza-*s*-indacene (32): 86%, white solid; m.p. 166–168 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.4 Hz, 2H), 7.50 (s, 1H), 7.41–7.30 (m, 4H), 4.71 (s, 2H), 4.69 (s, 2H), 2.77 (t, *J* = 7.8 Hz, 2H), 2.39 (s, 3H), 1.69–1.57 (m, 2H), 0.97 ppm (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.7, 139.9, 138.4, 133.4, 132.9, 131.8, 131.2, 129.8, 127.6, 126.2, 121.4, 113.9, 53.5, 52.4, 33.2, 23.3, 21.5, 14.3 ppm; MS (EI, 70 eV): *m/z* (%): 371 (5) [M^+], 215 (56), 186 (100), 173 (22), 115 (17), 91 (46), 65 (14); IR (KBr): $\tilde{\nu}$ = 2951 (w), 1338 (s), 1162 (s), 1095 (m), 666 (s), 602 cm^{-1} (m); elemental analysis calcd (%) for $C_{20}H_{22}O_2S_2$: C 64.66, H 5.70, N 3.77; found: C 64.16, H 5.58, N 3.77.

Dimethyl ester of 4-methyl-5,7-dihydro-1-thia-*s*-indacene-6,6-dicarboxylic acid (33): 58%, white solid; m.p. 108–110 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54 (s, 1H), 7.36–7.32 (m, 2H), 3.76 (s, 6H), 3.69 (s, 2H), 3.63 (s, 2H), 2.51 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.1, 139.1, 138.5, 136.9, 135.2, 127.9, 125.1, 121.6, 115.1, 60.5, 53.0, 40.4, 38.9, 16.3 ppm; MS (EI, 70 eV): *m/z* (%): 304 (33) [M^+], 244 (85), 185 (100), 171 (31); IR (KBr): $\tilde{\nu}$ = 2952 (w), 1740 (s), 1722 (s), 1252 (s), 1156 (s), 1071 (m), 766 (m), 701 cm^{-1} (m); HRMS (MALDI): *m/z* calcd for $C_{16}H_{16}O_4SNa^+$: 327.0667; found: 327.0662.

Dimethyl ester of 4-methyl-8-phenyl-5,7-dihydro-1-thia-*s*-indacene-6,6-dicarboxylic acid (34): 79%, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55–7.46 (m, 4H), 7.43–7.34 (m, 3H), 3.73 (s, 6H), 3.71 (s, 2H), 3.60 (s, 2H), 2.59 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.0, 139.6, 139.1, 139.0, 135.9, 134.7, 129.9, 128.7, 128.6, 127.7, 127.0, 125.9, 122.0, 60.4, 53.0, 39.8, 39.2, 16.3 ppm; MS (EI, 70 eV): *m/z* (%): 380 (79) [M^+], 320 (73), 289 (15), 261 (100), 247 (22), 84 (54); IR ($CHCl_3$): $\tilde{\nu}$ = 2954 (w), 1736 (s), 1436 (s), 1249 (s), 1073 (m), 703 cm^{-1} (m); HRMS (MALDI): *m/z* calcd for $C_{22}H_{20}O_4SNa^+$: 403.0980; found: 403.0975.

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[8] Data of **VI**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84–7.81 (m, 1H), 7.31–7.27 (m, 3H), 5.67 (s, 1H), 4.94–4.92 (m, 2H), 4.82–4.81 (m, 2H), 4.77 (s, 1H), 3.61–3.60 ppm (m, 2H); After 24 h in $CDCl_3$ or add one drop of TFA for several minutes, **VI** will change to **2** completely without formation of any other side products.

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