Platinum-Catalyzed Tandem Cyclization–Nazarov Cylization Reactions: An Easy Access to Complex Carbocyclic Molecules from 2-Alkenyl-(1′-hydroxyl-4-en-2-ynyl)benzenes

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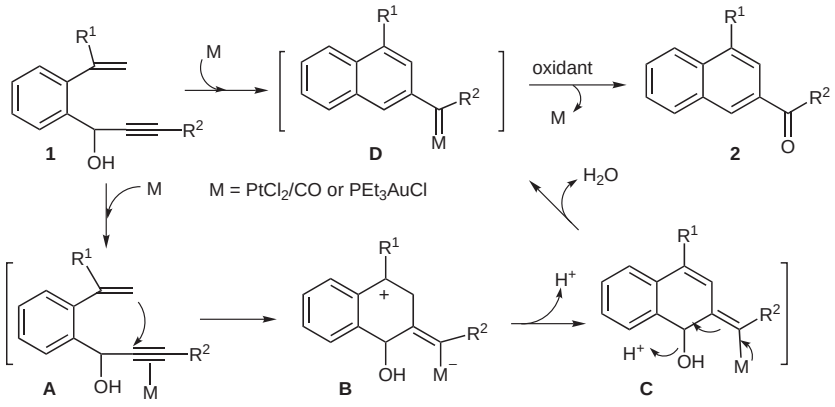
Abstract: In the presence of $PtCl_2$/CO catalyst, 2-alkenyl-(1′-hydroxyl-4-en-2-ynyl)benzenes undergo a tandem electrophilic 6-*exo-dig* cyclization–Nazarov cyclization sequence to give 1*H*-cyclopenta[*a*]naphthalenes efficiently and regioselectively.

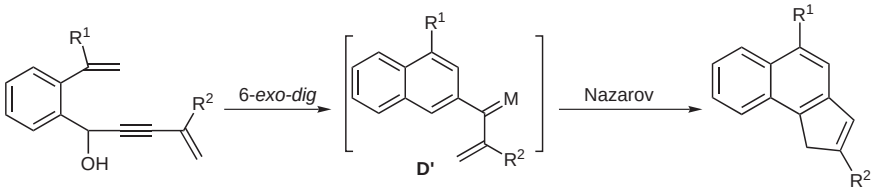
Key words: alcohols, alkynes, carbenoids, catalysis, tandem reactions

Tandem reactions have been the subject of intensive investigations in organic synthesis.[1] Their high efficiency and brief operation procedures are the beneficial features of these reactions. With a single workup, one can deliver a complicated molecule that would otherwise have to be prepared over the course of several individual steps. Transition-metal-catalyzed cyclizations of enynes[2–6] have emerged as powerful tools for the synthesis of carbocyclic compounds, and Pt(II) and Au(I) catalysts are commonly used to activate organic alkynes towards nucleophilic attack,[7] leading to new carbocyclizations. In this direction, we recently reported a novel oxidative cyclization[8] of dien-yn-ol **1** to 2-naphthyl aldehydes and ketones **2** via a tandem 6-*exo-dig* cyclization–oxidation sequence. Scheme 1 shows a proposed mechanism involving formation of 2-naphthylidene species **D**, which is subject to oxidation with H_2O_2 and H_2O to give desired product **2**, accompanied by regeneration of the catalysts.

To pursue additional value of this investigation, we envisage that such substrates bearing a vinylalkynol moiety would undergo unprecedented 6-*exo-dig*–Nazarov[9] tandem cyclizations, according to a protocol depicted in Scheme 2. A metal-catalyzed carbophilic activation of the carbon–carbon triple bond would trigger a 6-*exo-dig* cyclization, leading to formation of 2-naththylidene intermediate **D′**, thereby setting a protocol for Nazarov cyclization. In this paper we report an expedient cyclization of 2-alkenyl-(1′-hydroxyl-4-en-2-ynyl)benzenes to give 1*H*-cyclopenta[*a*]naphthalenes efficiently.



Scheme 1



Scheme 2

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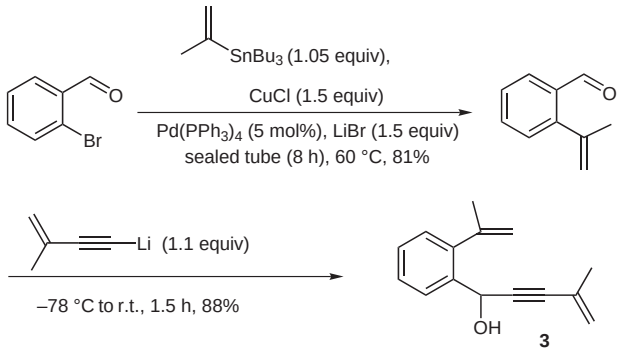
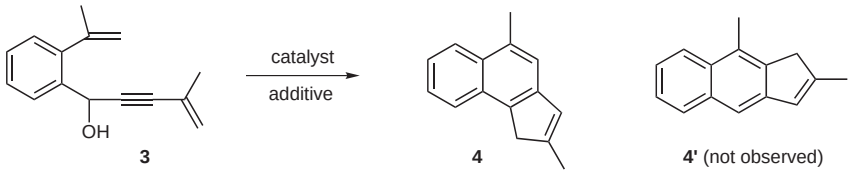


Scheme 3 Preparation of 2-alkenyl(1′-hydroxyl-4-en-2-ynyl)benzene **3**

To test the feasibility of this concept, we examined the $PtCl_2$-catalyzed cyclization of substrate **3**, which was readily prepared from commercially available 2-bromobenzaldehyde through Stille coupling[10] followed by an alkynylation reaction, as depicted in Scheme 3. Substrate **3** was subsequently treated with various gold and platinum catalysts in suitable solvents, each at 5% loading, to optimize the yields of desired 1*H*-cyclopenta[*a*]naphthalenes **4**, as shown in entries 1–7. Treatment of species **3** with $PtCl_2$ in THF (25 °C, 22 h) under N_2 gave compound **4** in 72% yield (Table 1, entry1); the yield increased to 89% under CO (1 atm,[11] entry 2). This $PtCl_2$/CO system became less efficient in CH_2Cl_2 and 1,2-dichloroethane than in THF upon comparison of their respective yields (entries 3 and 4). Both PPh_3AuSbF_6 and AuCl also catalyzed this tandem sequence, albeit with only modest yields (59–64%, entries 5 and 6) whereas $AuCl_3$ gave only a 24% yield (entry 7). Entries 8 and 9 showed our efforts to obtain 2-naphthyl vinyl ketone (R^1 = Me, R^2 = H_2C=CMe) through oxidation of 2-naphthyl carbenes **D′** with H_2O_2 and H_2O[8] according to the protocol in Scheme 1. These two oxidants either led to unreacted **3**[17] exclusively (entries 8), or gave the same 1*H*-cyclopenta[*a*]naphthalene **4**[18] over a long period (72 h, entry 9). Notably, we obtained no regioisomer **4′** from the screening of catalysts; this information implies that the Nazarov cyclization of the 2-naphthyl carbene intermediate **D′**, as depicted in Scheme 2, proceeds in a completely regioselective manner. The exclusive formation of compound **4** stems from the greater electron density at the C(1) carbon than at C(2) carbon.[12]

With optimized conditions, we prepared various alcohol substrates **5**–**13** to examine the scope and generality of this catalytic reaction sequence; the resulting 1*H*-cyclopenta[*a*]naphthalene derivatives **14**–**22** were obtained in satisfactory yields except for entry 9. As shown in Table 2, alcohol substrate **5** bearing a 1-phenylethenyl group was transformed into tricyclic compound **14** with a yield up to 87% (entry 1). This tandem cyclization is also suitable for substrates **6**–**9** bearing various phenyl X and Y substituents (X = OMe; Y = OMe or F, entries 2–5); the resulting cyclized products **15**–**18** were obtained with yields ranging from 53% to 96%. A high catalytic effi-

Table 1 Catalyst Screening for Alcohol **3** under Various Conditions



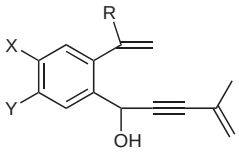
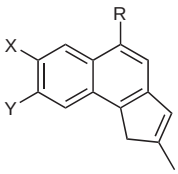
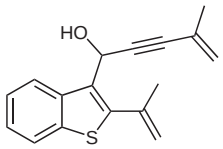
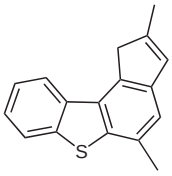
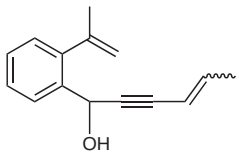
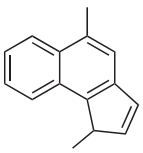
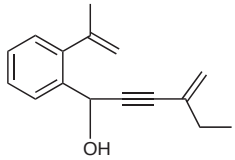
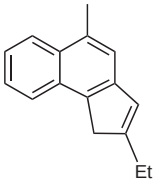
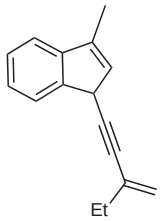
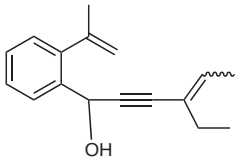
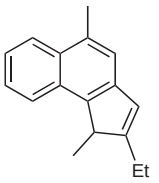
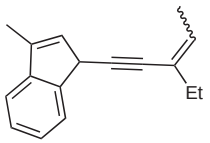
Entry[a]	Catalyst	Additive	Solvent	Temp (time, h)	Yield (%)[b]
1	$PtCl_2$	–	THF	r.t. (22)	72
2	$PtCl_2$/CO	–	THF	r.t. (20)	89
3	$PtCl_2$/CO	–	CH_2Cl_2	r.t. (20)	72
4	$PtCl_2$/CO	–	DCE	r.t. (21)	74
5	$AuCl(PPh_3)/AgSbF_6$	–	CH_2Cl_2	0 °C to r.t. (8)	64
6	AuCl	–	CH_2Cl_2	r.t. (10)	59
7	$AuCl_3$	–	CH_2Cl_2	r.t. (20)	24
8[c,d]	$AuClPEt_3$	H_2O_2	DCE	r.t. (50)	n.r.[e]
9[f,g]	$PtCl_2$/CO	H_2O	THF	r.t. (72)	69

[a] [Substrate] = 0.23 M and 5 mol% metal catalyst.
[b] Yield of isolated product after silica gel column chromatography.
[c] With 4 equiv of H_2O_2.
[d] Starting material (89%) was recovered.
[e] No reaction.
[f] Starting material (24%) was recovered.
[g] With 20 equiv of H_2O.

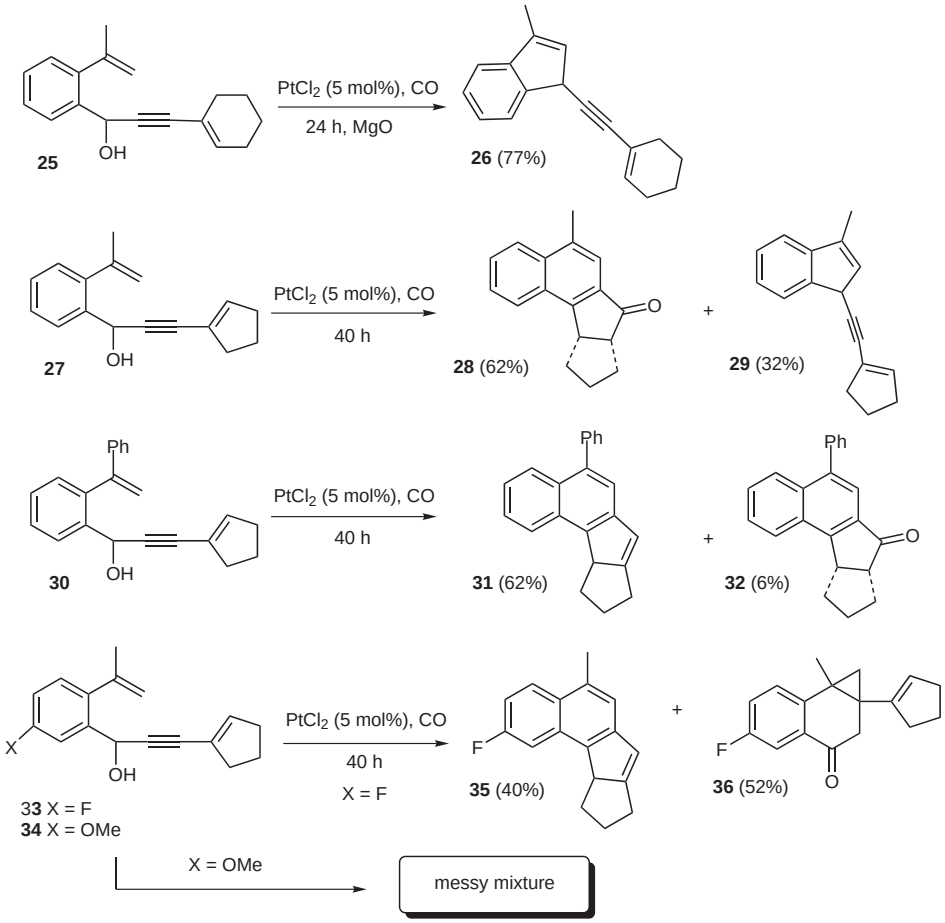
ciency was maintained for alcohol **10** bearing a benzothienyl group, which afforded the cyclized product **19** in 74% yield. The cyclization efficiency is sensitive to the types of vinylalkynyl substituents; the examples are manifested in entries 7–9. Substrates **11** and **12**, bearing 1,2-disubstituted and 1,1-disubstituted alkenes, respectively, are applicable to this cyclization and give the corresponding desired products **20** and **21** in 68% and 84% yields, respectively. For substrate **13** bearing a trisubstituted alkene, the reaction was plagued by undesired indene product **24**, produced by a single Nazarov cyclization even in the presence of proton scavenger MgO;[13] the expected 1*H*-cyclopenta[*a*]naphthalene **22** was obtained in a 12% yield in this case.

Scheme 4 shows additional examples to assess the effect of vinylalkynyl substituents of substrates **25**, **27**, **30**, **33**, and **34** bearing a cycloalkyl substituent at the alkyne group; herein, we observed substrate-dependent chemoselectivities. Similar to species **13**, indene product **26** was obtained in 77% yield. The same tandem catalysis on alcohol substrate **27** gave tetracyclic ketone **28** in 62% yield together with indene product **29** (32%). This ketone syn-

Table 2 Tandem 6-*exo*-*dig*–Nazarov Cyclization of Alcohol Substrates

Entry	Substrate[a]	Time (h)	Product (yield,[b] %)
			
1	**5**: X = Y = H, R = Ph	7	**14** (87)
2	**6**: X = OMe, Y = H, R = Me	20	**15** (53)
3	**7**: X = H, Y = OMe, R = Me	6	**16** (96)
4	**8**: X = Y = OMe, R = Me	6	**17** (87)
5	**9**: X = H, Y = F, R = Me	10	**18** (90)
6	 **10**	19	 **19** (74)
7	 **11**	16	 **20** (68)
8	 **12**	19	 **21** (84)  **23** (14)
9	 **13**	22	 **22** (12)  **24** (78)

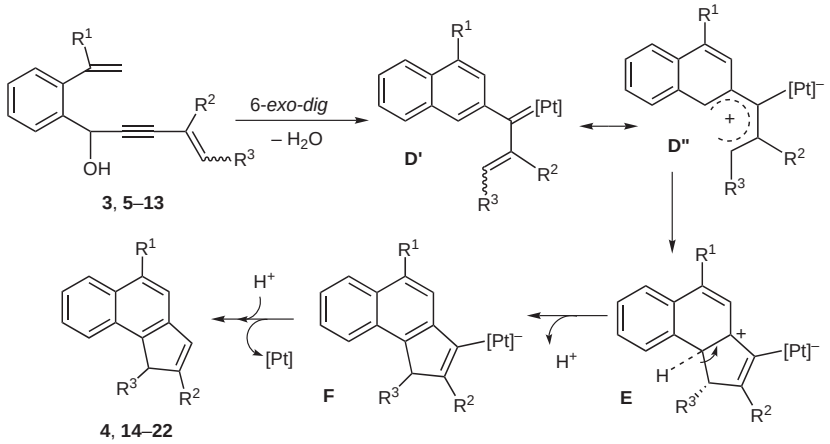
[a] Isolated yield after the purification by silica gel column chromatography.
[b] Conditions: 25 °C, CO (1 atm), [substrate] = 0.23 M, 5 mol% $PtCl_2$.



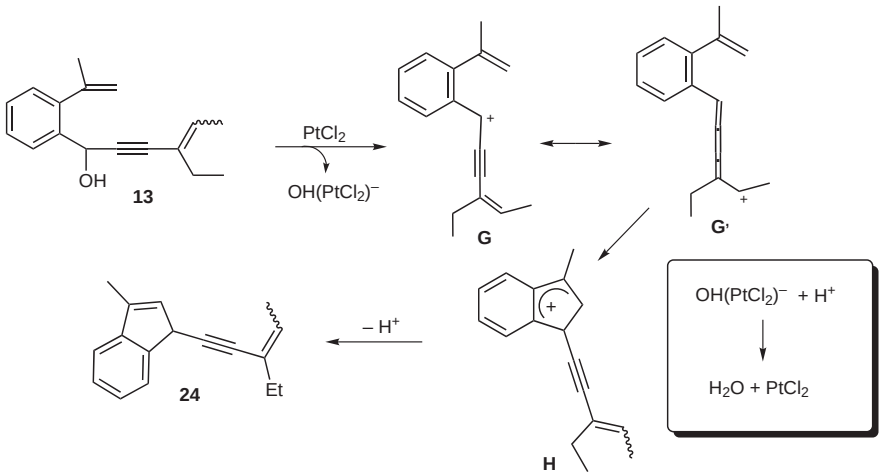
Scheme 4

thesis lacks the generality in chemoselectivities; for instance, its 1-phenylethenyl and 5-fluorobenzene analogues **30** and **33** gave tetracyclic olefins **31** (62%), **35** (40%), and cyclohexanone **36** (52%). Formation of ketone derivative **36** apparently proceeded through a distinct 6-*endo-dig* cyclization pathway.[14]

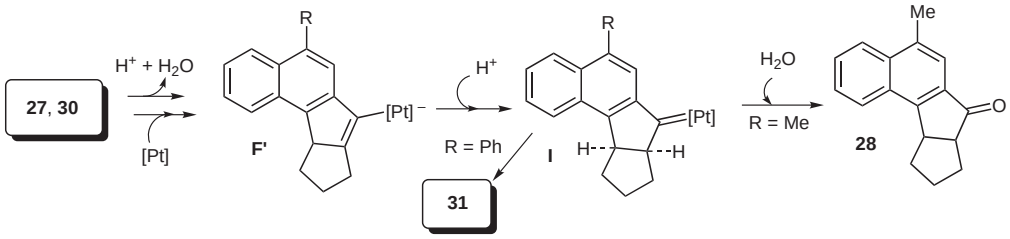
Finally, we obtained a messy mixture of products for the 5-methoxyphenyl analogue **34**. In this tandem catalysis, 1*H*-cyclopenta[*a*]naphthalenes **4**, **14**–**22** are produced exclusively from most substrates that we tested in Table 2; and the mechanism of their formation is depicted in Scheme 5. We envisage that one molecule of water to be produced as starting alcohol substrates **3** and **5**–**13** become transformed by $PtCl_2$ into carbenium intermediate **D′**, which possesses a cationic pentadienyl resonance to initiate Nazarov cyclization to form species **E**, ultimately giving desired products through hydrodemetalation. For species **13** and **25** bearing a trisubstituted alkenylalkynol, their corresponding cyclizations preferably gave indene derivatives **24** and **26**. Scheme 6 shows the rationalization



Scheme 5



Scheme 6



Scheme 7

of this substituent effect on cyclization chemoselectivity. We propose that initial treatment of alcohol **13** with $PtCl_2$ forms propargyl cation **G**, which subsequently gave cyclopentenyl cation **H** through Nazarov cyclization, and ultimately produced compound **24** with release of one proton. Regeneration of the catalyst was achieved by reaction of $PtCl_2(OH)^-$ with proton. For species **13** and **25**, the 1-methyl and cyclohexyl substituents stabilize resonance form **G′**, which will enhance this chemoselectivity.

Although tetracyclic ketone **28** was produced exclusively only from substrate **27**, its mechanism of formation deserves attention (see Scheme 7). Herein, we only obtained a 32% yield of indene species **29** because its corresponding resonance structure **G′** is less stabilized by its nonplanar cyclopentyl framework. One molecule of water and proton are expected to be released in the transformation of species **27** into intermediate **F′**, of which the highly strained bicyclo[3.3.0]octene core becomes subsequently protonated to give carbene species **I**, finally rendering desired ketone **26** through H_2O oxidation. For its phenyl analogue **30**, we envisage that the corresponding carbene species **I** preferably undergoes 1,2-hydride shift to give tetracyclic alkene **31**. This hydrogen shift also inhibits the ketone synthesis in addition to the competitive indene formation (see Scheme 5). At the present stage, we do not know the exact reason for the formation of tetracyclic ketone **28** from species **27**.

In summary, we have developed a convenient preparation of 1*H*-cyclopenta[*a*]naphthalene derivatives from readily prepared 2-alkenyl(1′-hydroxyl-4-en-2-ynyl)benzenes.[15,16] This catalytic sequence comprises tandem 6-*exo-dig* cyclization–Nazarov cyclizations. Current studies focus on the asymmetric version of this tandem sequence.

Acknowledgment

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(14) See ref. 7d for the formation mechanism of the ketone product **36**.

(15) **Typical Procedure for the Synthesis of 4-Methyl-1-[2-(prop-1-en-2-yl)phenyl]pent-4-en-2-yn-1-ol (3)**
To a THF (15 mL) solution of 2-bromobenzaldehyde (1.00 g, 5.40 mmol) was added tributyl(prop-1-en-2-yl)stannane (1.87 g, 1.05 mmol), $Pd(PPh_3)_4$ (311 mg, 0.27 mmol), CuCl (0.80 g, 8.10 mmol) and LiBr (0.7 g, 8.10 mmol); the mixture was heated in a sealed tube at 60 °C for 8 h. The resulting solution was concentrated under reduced pressure, and the residues were eluted through a silica column (hexane–EtOAc, 98:2) to afford 2-(prop-1-en-2-yl)benzaldehyde (639 mg, 4.37 mmol, 81%) as colorless oil. To a THF (8 mL) solution of 2-methylbut-1-en-3-yne (0.29 g, 4.45 mmol) was slowly added *n*-BuLi (1.6 mL, 2.5 M in hexane) at –78 °C; the solution was stirred for 30 min at –78 °C before addition of a THF solution (2 mL) of 2-(prop-1-en-2-yl)benzaldehyde (0.50 g, 3.42 mmol). After 30 min, to this solution was added H_2O (3 mL); the solution was extracted with EtOAc, and concentrated to afford crude alcohol. The crude product was eluted through a silica column (hexane–EtOAc, 5:1) to afford substrate **3** (640 mg, 3.01 mmol, 88%) as a light yellow oil.

(16) **Typical Procedure for the 6-*exo*-*dig*–Nazarov tandem cyclization of 4-Methyl-1-(2-prop-1-en-2-yl)phenylpent-4-en-2-yn-1-ol(1) to 1,5-Dimethyl-1*H*-cyclopenta[*a*]naphthalene (4)**
A long tube containing $PtCl_2$ (6.3 mg, 0.023 mmol) was evacuated and backfilled with CO. After repeating this procedure twice, the tube was charged with alcohol substrate **3** (100 mg, 0.472 mmol) and dry THF (2 mL). The resulting mixture was stirred at 23 °C for 20 h. The solution was concentrated and eluted through a silica column (hexane) to give compound **4** (81 mg, 0.417 mmol, 89%) as viscous oil.

(17) **4-Methyl-1-[2-(prop-1-en-2-yl)phenyl])pent-4-en-2-yn-1-ol (3)**
IR (neat): 3654 (m), 1624 (m), 1610 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 7.0 Hz, 1 H), 7.33–7.29 (m, 2 H), 7.17 (d, *J* = 7.0 Hz, 1 H), 5.79 (s, 1 H), 5.32 (s, 1 H), 5.25 (s, 1 H), 5.24 (s, 1 H), 4.99 (s, 1 H), 2.12 (s, 3 H), 1.89 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.0, 142.4, 137.5, 128.0, 127.8, 127.4, 127.1, 126.1, 122.1, 116.0, 88.7, 87.1, 61.8, 25.3, 23.1. HRMS: *m/z* calcd for $C_{15}H_{16}O$: 212.1201; found: 212.1204.

(18) **1,5-Dimethyl-1*H*-cyclopenta[*a*]naphthalene (4)**
IR (neat): 1598 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.0 Hz, 1 H), 7.68 (d, *J* = 8.0 Hz, 1 H), 7.44 (t, *J* = 8.0 Hz, 1 H), 7.36 (t, *J* = 8.0 Hz, 1 H), 7.31 (s, 1 H), 6.53 (s, 1 H), 3.58 (s, 2 H), 2.69 (s, 3 H), 2.22 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.6, 142.9, 137.2, 133.0, 129.9, 129.8, 127.6, 125.6, 125.1, 123.7, 123.6, 120.8, 41.5, 19.7, 16.8. HRMS: *m/z* calcd for $C_{15}H_{14}$: 194.1096; found: 194.1092.