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Synthesis of Multisubstituted 1-Naphthoic Acids via Ru-Catalyzed C−H Activation and Double Alkyne Annulation Under Air

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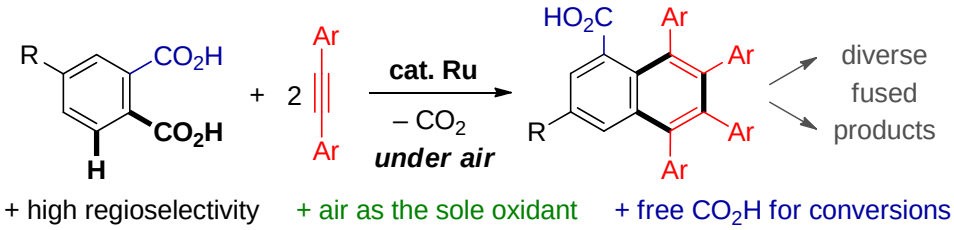


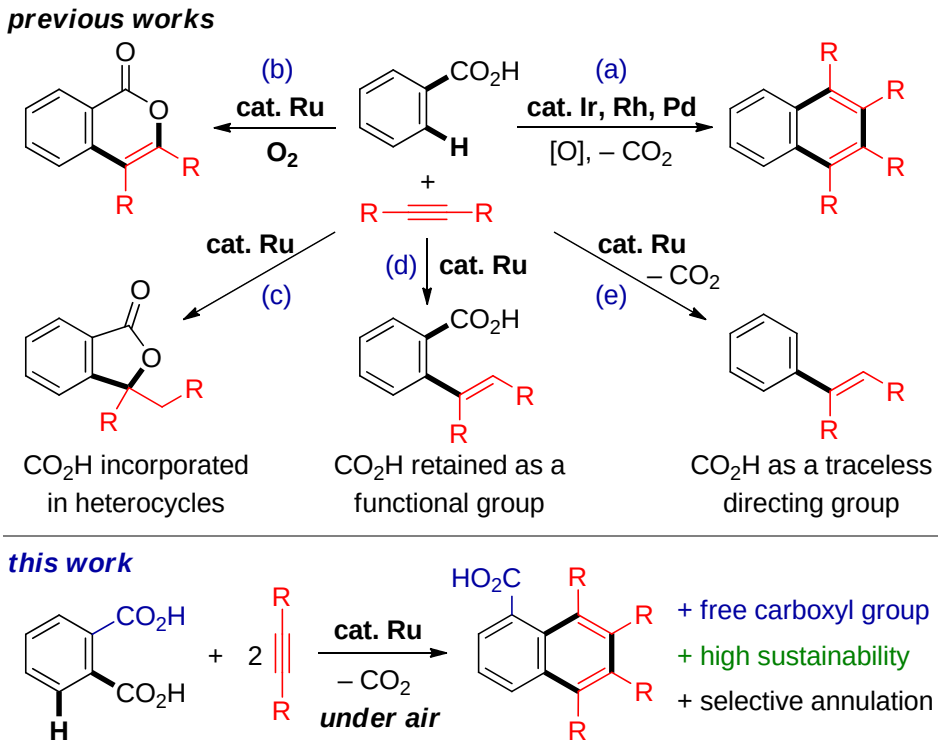
Abstract: An efficient [2+2+2] benzannulation of phthalic acids/anhydrides with two alkynes was developed for synthesis of multisubstituted 1-naphthoic acids via Ru-catalyzed C−H activation. The reaction preceded well using atmospheric oxygen as the sole oxidant with high atom/step economies. Facilitated by the free carboxyl group, the products can be easily converted to diverse polycyclic molecules.

Introduction

Owing to their unique electronic properties and geometries, multisubstituted naphthalenes have been widely used as key components for fluorophores and semiconductors[1], as well as structural units or precursors of unusual aromatic architectures[2]. Meanwhile, functionalized naphthalenes including 1-naphthoic acid are core substructures in some natural products and bioactive molecules.[3] Therefore, modular synthetic methods are highly desirable to access multisubstituted and functionalized naphthalenes from readily available building blocks.

The combination of C–H activation and alkyne annulation has been established as a powerful strategy for construction of heterocycles and carbocycles.[4] Since pioneer works of Miura and Satoh,[5] much progress has been made for oxidative [2+2+2] benzannulation,[5-7] by which multisubstituted naphthalenes can be obtained from simple aromatics such as benzoic acids (**Scheme 1a**). These reactions are commonly catalyzed by Ir, Rh, or Pd, while Ru catalysis seems to be favored for other coupling modes (**Scheme 1b–e**).[4c,8,9] In particular, Ackermann et al.[9a] developed a synthesis of isocoumarins using O_2 as the sole oxidant. Zhao et al.[9c] reported a decarboxylative hydroarylation of alkynes, and trace amount of tetraphenyl naphthalene was detected as a by-product. These works inspired us to quest which reaction modes would occur by using phthalic acid and alkynes.[10] We envisioned that one carboxyl group in phthalic acid may be activated by the other one, thus selective decarboxylative coupling would be possible to afford annulated products with a free carboxyl group.[11]

Scheme 1. Coupling Modes of Aromatic Acids and Alkynes



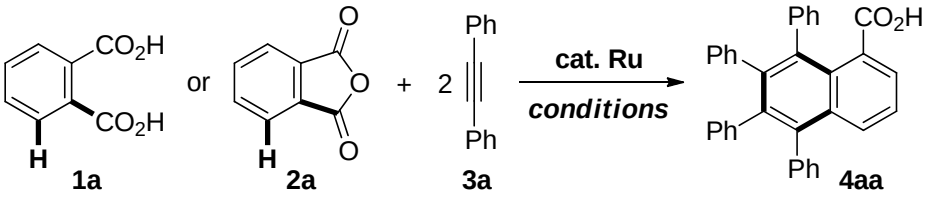
With our continuous interests in C–H functionalization and cyclization,[4d,12] we disclosed herein a Ru(II)-catalyzed decarboxylative [2+2+2] benzannulation for rapid and modular assembly of multisubstituted 1-naphthoic acids from readily available phthalic acids (**Scheme 1**). In this reaction, one carboxyl group serves as an auto-cleavable and traceless directing group for C–H functionalization,[13] while the other one is kept in the product as an easily transformable functional group. Notably, this reaction enables air as the sole oxidant, which improves the atom economy, sustainability and functional group tolerance.[14]

Results and Discussion

We commenced the study by employing phthalic acid (**1a**) and diphenylacetylene (**3a**) as the substrates with $[Ru(p\text{-cymene})Cl_2]_2$ as the catalyst precursor (**Table 1**). When the reaction was carried out in DMF at 100 °C under air, a 1:2 coupling product **4aa** was obtained in 28% yield with ~60% conversion of **3a** (entry 1). After survey of a variety of additives, halide salts were found to increase the reactivity and selectivity, among which tetrabutylammonium bromide (TBAB)[15] showed to be the most effective (entry 2–5). Other types of additives such as PPh_3, KPF_6, NaOAc or HOAc gave lower yields (< 20%). DMAc and NMP gave no improvement, while DMSO and toluene gave inferior results (entry 6–9). To our delight, a biomass-derived green solvent γ-valerolactone (GVL)[16] was found to be quite suitable for this reaction (entry 10). The high boiling point and flash point nature of GVL can improve the convenience and safety for reaction under air. As detected by TLC, significant side products with smaller R_f were detected by using DMF as solvent, while a little side product with high polarity was detected by using GVL. With mixed solvent of GVL and DMF as a reaction

medium, the selectivity of the reaction can be tuned to afford **4aa** up to 81% yield (entry 11–13).

Table 1. Optimization of Conditions[a]



1a **2a** **3a** **4aa**

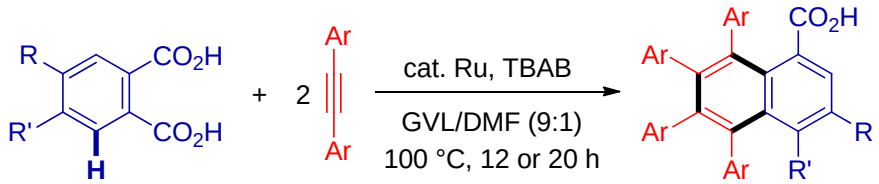
entry	substrate	additive	solvent	yield (%)[b]
1[c]	**1a**	-	DMF	28
2	**1a**	NaCl	DMF	40
3	**1a**	LiBr	DMF	51
4	**1a**	TMAB[d]	DMF	48
5	**1a**	TBAB	DMF	56
6	**1a**	TBAB	DMAc	52
7	**1a**	TBAB	NMP	51
8	**1a**	TBAB	DMSO	0
9	**1a**	TBAB	PhMe	38
10	**1a**	TBAB	GVL	70
11	**1a**	TBAB	GVL/DMF (4:1)	73
12	**1a**	**TBAB**	**GVL/DMF (9:1)**	**81**
13	**1a**	TBAB	GVL/DMF (19:1)	77
14[e]	**1a**	TBAB	GVL/DMF (9:1)	55
15[f]	**1a**	TBAB	GVL/DMF (9:1)	76
16	**1a**	$CuBr_2$	GVL/DMF (9:1)	0
17	**1a**	AgOAc	GVL/DMF (9:1)	0
18[c]	**2a**	TBAB	GVL/DMF (9:1)	77
19[g]	**2a**	**TBAB**	**GVL/DMF (9:1)**	**80**
20	**2a**	TBAB	H_2O	0
21	**2a**	TBAB	GVL/H_2O (9:1)	59
22[h]	**1a**	TBAB	GVL/DMF (9:1)	62
23[i]	**1a**	TBAB	GVL/DMF (9:1)	73
24[c, j]	**1a**	TBAB	GVL/DMF (9:1)	64

[a] Conditions: **1a** or **2a** (0.30 mmol), **3a** (0.40 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (0.01 mmol), additive (0.04 mmol), solvent (1.0 mL), 100 °C, 12 h, under air. [b] Isolated yield of **4aa** based on **3a**. [c] 20 h. [d] TMAB: tetramethylammonium bromide. [e] 6 mol% $RuCl_3 \cdot xH_2O$ (37% Ru) was used. [f] O_2 balloon was used. [g] H_2O (20 μL) was added. [h] 80 °C, 24 h. [i] 120 °C, 8 h. [j] **1a** (0.20 mmol) and **3a** (0.44 mmol) were used, the yield was based on **1a**.

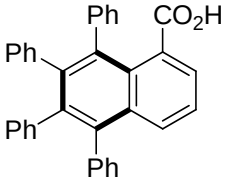
The reaction can also catalyzed by $RuCl_3$, yet an increased catalyst loading was needed for full conversion (entry 14). No desired product was detected by using $[Cp^*IrCl_2]_2$ (Cp* = pentamethylcyclopentadienyl), $[Cp^*RhCl_2]_2$, $[Cp^*Rh(OAc)_2]_2$, $PdCl_2$ or $Pd(OAc)_2$, though these catalysts have been widely used in reported naphthalene synthesis.[5,6] Reaction under O_2 could not further improve the yield, while the formation of **4aa** was completely inhibited by Cu(II) or Ag(I) salts (entry 15–17). Phthalic anhydride (**2a**) is an upstream industrial chemicals of **1a** and can also be obtained from renewable source.[17] The reaction using **2a** gave comparable yield in 20 h and can be accelerated by addition of 20 μL water, but using water as a sole solvent or cosolvent gave inferior results (entry 18–21). The reaction was sluggish at 80 °C, while side reactions were increased at 120 °C, affording **4aa** in lower yield (entry 22–23). Using excess of alkyne **3a** gave slower conversion and lower yield (entry 24).

With the optimized conditions in hand, a series of substituted phthalic acids **1** or anhydrides **2** were employed to couple with alkynes **3** to synthesize multisubstituted 1-naphthoic acids **4** (**Scheme 2**). Typically, comparable yields can be obtained by using the corresponding phthalic acids or anhydrides, while their commercial availability and prices were differed by the substituents. Various 4-substituted substrates successfully reacted with **3a** to afford products (73–90% yields) with alkyl or alkoxy groups (**4ba**–**4da**), halides (**4ea**, **4fa**), as well as strong electron-withdrawing groups such as CF_3 (**4ga**) and NO_2 (**4ha**). Trimellitic acid also reacted well to afford 1,3-naphthalic diacid **4ia** in 76% yield, while the corresponding anhydride gave an inferior result. Dihalogenated products **4ja** and **4ka** could be obtained from corresponding 4,5-disubstituted phthalic anhydrides. 2,3-Naphthalic diacid was also reactive and a multisubstituted 9-phenanthroic acid **4la** was obtained.

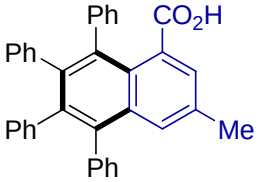
Scheme 2. Scope for Synthesis of 1-Naphthoic Acids[a]



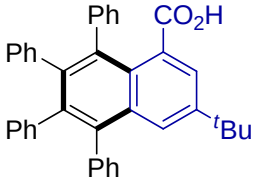
1 (or anhydrides **2**) **3** **4** (R' = H or R)



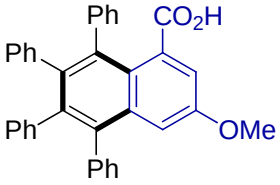
4aa, 81%, 80%[b,c]



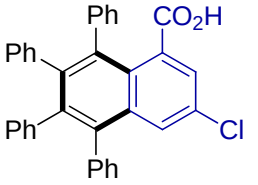
4ba, 84%, 82%[b,c]



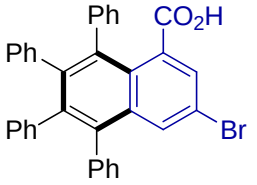
4ca, 77%[b,c]



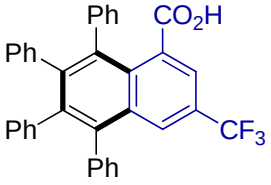
4da [X-ray], 85%



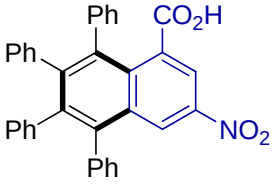
4ea, 83%, 85%[b]



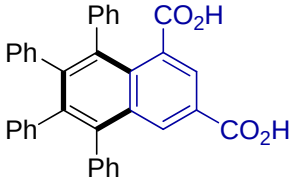
4fa, 84%, 90%[b]



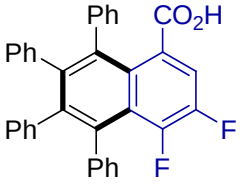
4ga, 86%



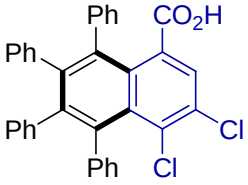
4ha, 73%[d]



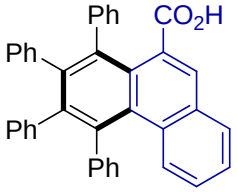
4ia, 76%



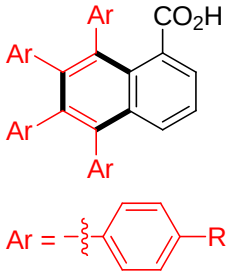
4ja, 78%[b]



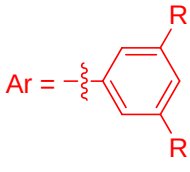
4ka, 41%[b,c,d]



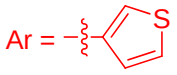
4la, 64%[d]



R = Me, **4ab**, 78%
OMe, **4ac**, 72%
F, **4ad,** 75%
Cl, **4ae**, 71%
Br, **4af**, 80%
CF_3, **4ag**, 76%
OCF_3, **4ah**, 69%[d]



R = Me, **4ai**, 72%[d]
R = Cl, **4aj**, 56%[d]



4ak, 42%

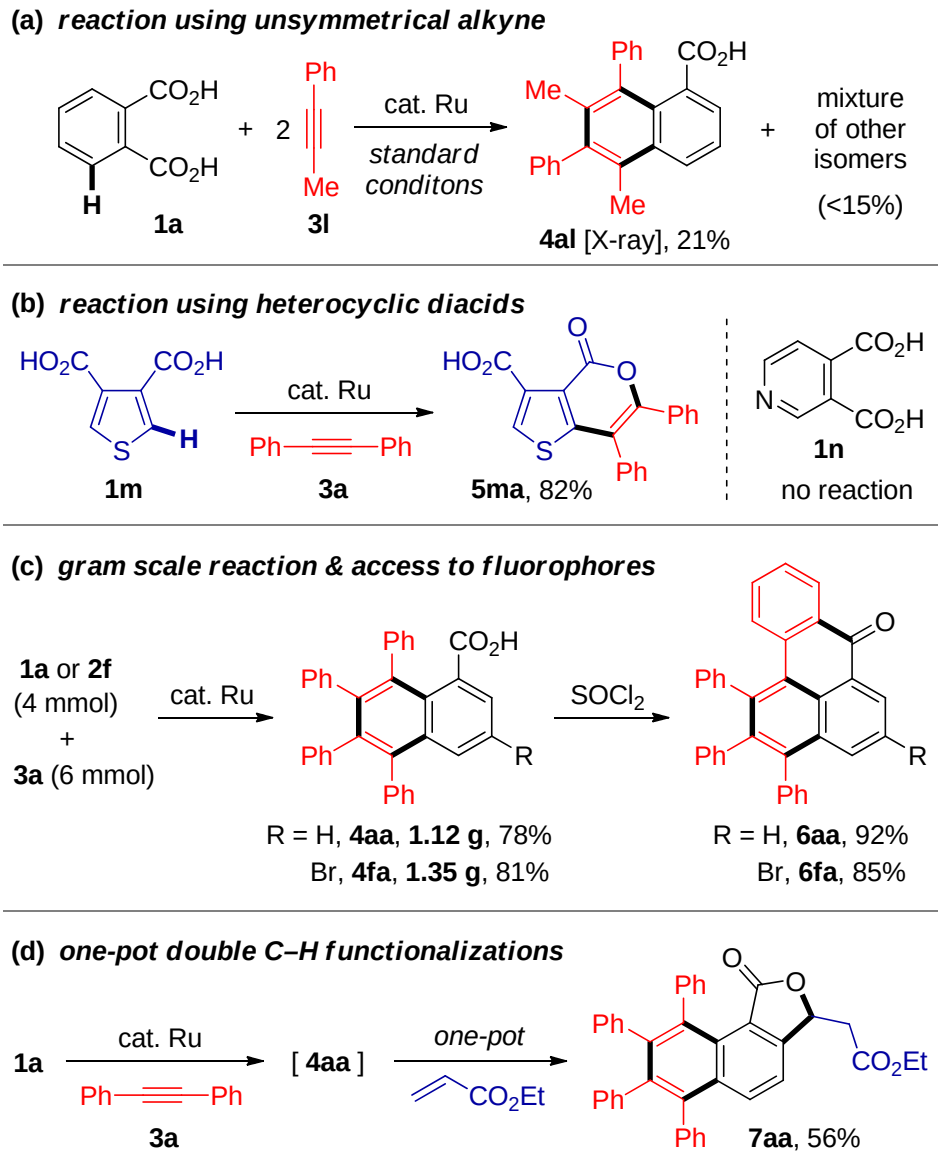
[a] Conditions: **1** (0.30 mmol), **3** (0.40 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (0.01 mmol), TBAB (0.04 mmol), GVL/DMF (9:1, 1.0 mL), 100 °C, 12 h, under air. [b] Anhydride **2** was used. [c] 20 μL H_2O was added. [d] 20 h.

Notably, the C–H site with less steric hindrance was more favorable for this reaction to afford 1-naphthoic acids with different substituents at 3-position with high regioselectivity (>25:1). Clear J_3 coupling of two hydrogen atoms on the naphthalene ring was observed in ^{1}H NMR spectrum of **4ca**, **4ea** and **4fa**. Furthermore, the structure of **4da** was unambiguously identified by single crystal X-ray analysis (**Figure S1a**), which confirmed the regioselectivity.

Symmetric diaryl alkynes with either electron-donating or -withdrawing groups as *para*-substituents reacted smoothly with phthalic acid to afford **4ab**–**4ah** in 69–80% yields. Diaryl alkynes with two methyl or chloride *meta*-substituents were also reactive for this reaction to afford **4ai** and **4aj**, respectively. Diaryl alkynes with *ortho*-substituents gave low conversion probably due to steric hindrance, while unsymmetrical diaryl alkynes gave messy results probably due to poor regioselectivity in both alkyne insertion steps.[18] When dialkyl alkynes such as 3-hexyne and 4-octyne were used, small amounts of side products were detected in TLC, but no expected products were obtained. When an aryl–alkyl unsymmetrical alkyne **3l** was used, one of the isomers **4al** can be isolated (**Scheme 3a**) and its structure was confirmed by X-ray analysis (**Figure S2a**).

Heterocyclic substrates were next explored to extend the scope of this reaction. Compound **4ak** with four thiophene rings could be obtained from bis(3-thienyl)ethyne in acceptable yield (**Scheme 2**), but only trace amount of product was obtained by using bis(2-thienyl)ethyne. When thiophene-3,4-dicarboxylic acid (**1m**) was used, [2+2+2] benzannulation did not occur. A 1:1 coupling product **5ma** with a fused heterocyclic skeleton was obtained in 82% yield (**Scheme 3b**), but this type of product was not detected using phthalic acids. Pyridine-containing substrates including **1n** were also tested, but no product was detected.

Scheme 3. Extension and Utilization of the Reaction



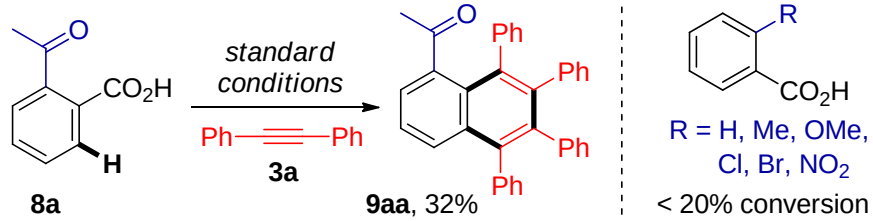
To demonstrate the practical use of this method, scale-up reactions were carried out to afford **4aa** and **4fa** in gram scale (**Scheme 3c**). The free carboxyl group in the products can serve as a handle for further transformations. Compound **4aa** can undergo intramolecular Friede-Crafts acylation to afford a multiaryl benzanthrone **6aa** (**Scheme 3c**), which is reported as a fluorophore synthesized from highly preactivated substrates.[19] Brominated benzanthrone **6fa** can also be obtained, which can be used for cross-coupling reactions to synthesize

complex benzanthrone fluorophores. The carboxyl group can be also employed as a directing group for further C−H functionalization. After the first step was finished, acrylate was added to the reaction tube for the second annulation in one-pot, and product **7aa** with a fused skeleton was obtained as expected (**Scheme 3d**).

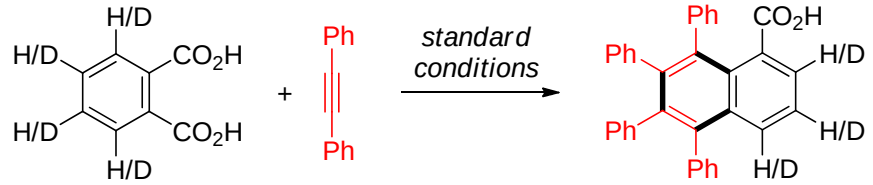
Several control experiments were conducted to unveil the mechanism of this [2+2+2] benzannulation. Only trace of **4aa** was detected under strictly deoxygenized conditions with either **1a** or **2a** as the substrate, while **4aa** could be obtained in moderate to good yield when the reaction tube was sealed or using diluted air (**Table S3**). These results illustrated the aerobic nature of the reaction and suggested that the catalyst turnover can be accomplished with a rather low concentration of oxygen. Benzoic acid, isophthalic acid and terephthalic acid, as well as benzoic acids with *ortho*-Me, OMe, Cl, Br, or NO_2 all showed low reactivity with **3a** under standard conditions. Similar [2+2+2] annulation can proceed by using 2-acetylbenzoic acid (**8a**) to afford **9aa** in 32% yield (**Scheme 4a**), which indicated that one carboxyl group may promote the decarboxylation of the other one. Either with or without **3a**, no H/D scrambling was observed by using **1a** with 50 μL D_2O or using deuterium labeling substrate **1a**-d_4, indicating that the cleavage of the C−H bond is irreversible. A primary kinetic isotope effect (KIE) was observed by independent reactions using **1a** or **1a**-d_4 as the substrate ($k_H/k_D \approx 3.8$) (**Scheme 4b**, see the Supporting Information for details). The KIE was also observed via parallel reactions or intermolecular competition, which product ratio n(**4aa**)/n(**4aa**-d_3) determined by HRMS analysis was 4.1 and 3.7, respectively. These results indicated that the cleavage of the C−H bond should be crucial for shaping the reaction kinetics.[20]

Scheme 4. Experiments for Preliminary Mechanism Studies

(a) ***reactions of related substrates***



(b) ***kinetic isotope effect***

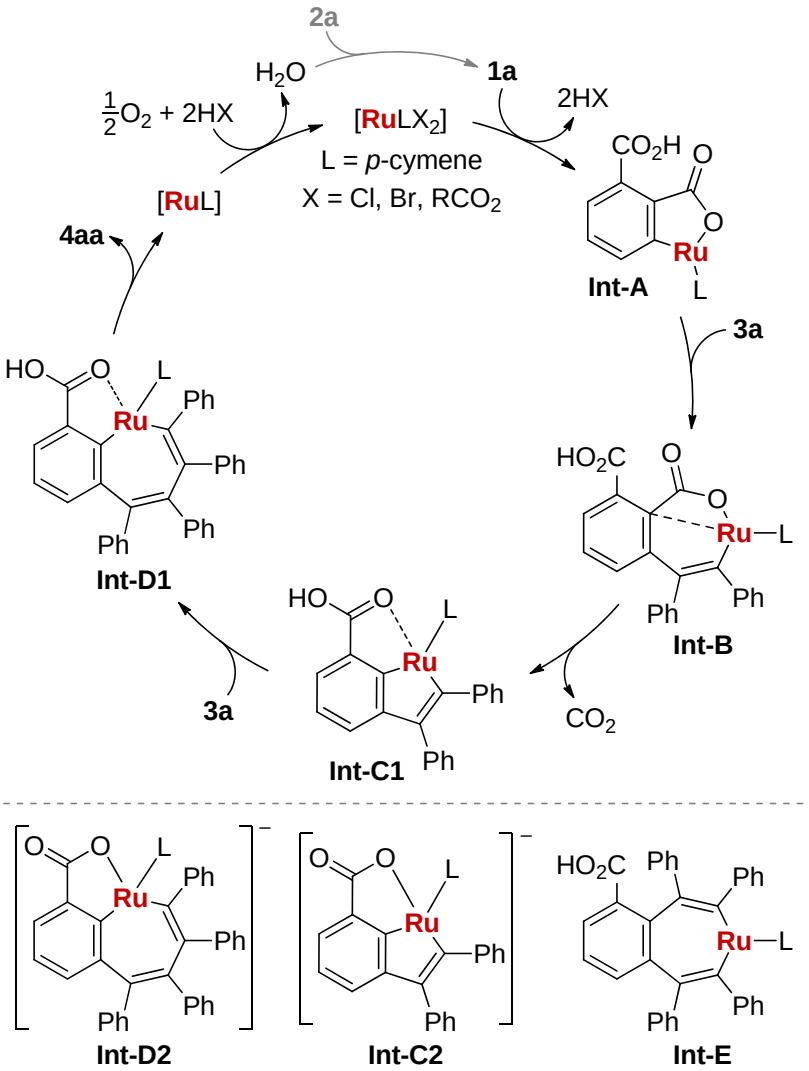


1a or **1a-*d*$_4$**	*kinetic measurement*	$k_H/k_D \approx 3.8$
1a or **1a-*d*$_4$**	*parallel reactions*	*n*(**4aa**)/*n*(**4aa-*d*$_3$**) = 4.1
1a + **1a-*d*$_4$**	*intermolecular competition*	*n*(**4aa**)/*n*(**4aa-*d*$_3$**) = 3.7

Based on these observations and related literatures,[5a,8,9,21] a catalytic cycle of this reaction is proposed (**Scheme 5**). Initially, de-dimerization of [Ru(*p*-cymene)Cl_2]$_2$ with TBAB and solvents forms active catalyst species, which undergoes ligand exchange and C−H bond cleavage to afford **Int-A**. Subsequent insertion of alkyne **3a** furnishes **Int-B**, which undergoes decarboxylation to afford **Int-C1** with weak coordination[8c] of the remained carboxyl group to Ru. The second alkyne insertion generates **Int-D1**, which undergoes reductive elimination to give the product **4aa**. Anionic complexes **Int-C2** and **Int-D2** with H^+ or tetrabutylammonium as the counterion may also be possible,[22] and **Int-E** with an alternative fashion for the second alkyne insertion cannot be ruled out. Finally, Ru(0) species can be oxidized to the active Ru(II) catalyst with air as oxidant. Phthalic anhydride **2a** can be hydrolyzed to **1a** by added water or trace of water in the solvent to enter the catalytic cycle, and the water formed by annulation could be recycled for the hydrolysis. Though the reaction is aerobic, an alternative reaction

pathway triggered by Ru-catalyzed decarbonylation of anhydride[23] cannot be completely ruled out (**Scheme S1**).

Scheme 5. Proposed Reaction Mechanism



In summary, we have developed a convenient method for synthesis of multisubstituted 1-naphthoic acids via Ru-catalyzed C−H activation and double alkyne annulations of phthalic acids/anhydrides. The reaction proceeds with high regioselectivity in moderate to good yields. The use of air as the sole oxidant improves the sustainability and practicability of this

synthetic method, while the free carboxyl group in the products enables further C−H functionalization and annulation to afford diverse polycyclic molecules. Future works are still in progress on extension the Ru catalytic systems for other aerobic annulations.

Experimental Section

General Methods. Unless otherwise noted, all organic compounds, inorganic salts and solvent were analytically pure and used directly after purchased. All new products were characterized by ^{1}H, $^{13}C\{^{1}H\}$ NMR, and HRMS. Nuclear magnetic resonance (NMR) spectra were recorded at 298 K. ^{1}H NMR (500 MHz) chemical shifts (δ) were referenced to internal standard TMS (δ = 0.00 ppm), and $^{13}C\{^{1}H\}$ NMR (126 MHz) chemical shifts were referenced to internal solvent $CDCl_3$ (δ = 77.16 ppm) or DMSO-d_6 (δ = 39.52 ppm). HRMS data were obtained on a high resolution magnetic sector mass spectrometer with electron spray ionization (ESI) source. The melting points were uncorrected and those below 300 °C were recorded.[24] Alkyne **3k** was prepared via Sonogashira reaction following the literature.[25]

Typical Procedure for Alkyne Annulation. To a 10 mL tube with a branch pipe, a magnetic stirrer, $[Ru(p\text{-cymene})Cl_2]_2$ (6.1 mg, 0.01 mmol), phthalic acid **1a** (49.8 mg, 0.3 mmol), diphenylacetylene **3a** (71.3 mg, 0.4 mmol), TBAB (12.9 mg, 0.04 mmol), 900 μL GVL and 100 μL DMF were added sequentially. The top of the tube was sealed and the branch pipe was open to air. The tube was put in a metallic heating mould (or immersed in an oil bath) at 100 °C and stirred for 12 h. The reaction mixture was then cool down, diluted with EtOAc and washed with water. After purification by flash column chromatography on silica gel with petroleum ether/EtOAc (gradient mixture ratio from 1:0 to 4:1) as eluant, **4aa** (77.5

mg, 81%) was obtained as a pale yellow solid. When phthalic anhydride **2a** (44.4 mg, 0.3 mmol) was used in place of **1a**, 20 μL water was added with the solvent, and **4aa** (76.2 mg, 80%) was obtained.

Following this procedure, other products **4** in **Scheme 2** were synthesized from corresponding diacids **1** or anhydrides **2** (0.3 mmol) and alkynes **3** (0.4 mmol), of which the yields were based on alkynes, i.e., 0.2 mmol expected products. Similarly, product **4al** was obtained by reaction of **1a** (0.6 mmol) and **3l** (0.8 mmol) for 20 h. Product **5ma** was obtained by reaction of **1m** (0.3 mmol) and **3a** (0.4 mmol) for 16 h, and the yield was based on **1m**. Product **9aa** was obtained by reaction of **8a** (0.45 mmol) and **3a** (0.6mmol) for 24 h. Large scale synthesis of **4aa** and **4fa** were conducted in a 50 mL round-bottom flask using 6 mmol **3a** and 4 mmol **1a** or **2f** with other chemicals scale-up proportionally based on **3a**.

*5,6,7,8-Tetraphenyl-1-naphthoic acid (**4aa**).* Pale yellow solid (77.5 mg, 81%, from diacid; 76.2 mg, 80%, from anhydride; 1.121 g, 78%, large scale): mp 282–284 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (dd, J = 8.6, 1.3 Hz, 1H), 7.66 (dd, J = 7.0, 1.3 Hz, 1H), 7.39 (dd, J = 8.5, 7.0 Hz, 1H), 7.25–7.22 (m, 2H), 7.21–7.16 (m, 3H), 7.09–7.04 (m, 5H), 6.86–6.80 (m, 6H), 6.78–6.76 (m, 2H), 6.73–6.71 (m, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 174.4, 141.3, 140.35, 140.32, 140.27, 140.1, 139.4, 139.0, 137.3, 133.5, 132.4, 131.5, 131.4, 131.3, 131.1, 130.8, 129.0, 128.3, 127.8, 127.2, 126.8, 126.74, 126.69, 126.5, 125.6, 125.5, 124.5; HRMS (ESI) calcd for $C_{35}H_{24}O_2$ $[M - H]^-$ 475.1704, found 475.1712.

*3-Methyl-5,6,7,8-tetraphenyl-1-naphthoic acid (**4ba**).* Pale yellow solid (82.2 mg, 84%, from diacid; 80.1 mg, 82%, from anhydride): mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (s, 2H), 7.23–7.22 (m, 2H), 7.19–7.15 (m, 3H), 7.07–7.01 (m, 5H), 6.85–6.80 (m, 6H),

6.76–6.74 (m, 2H), 6.72–6.70 (m, 2H), 2.42 (s, 3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ = 175.0, 140.49, 140.47, 140.4, 140.3, 140.1, 139.6, 138.4, 137.1, 134.3, 133.7, 132.4, 131.5, 131.45, 131.43, 131.1, 130.4, 129.6, 127.7, 127.4, 127.1, 126.7, 126.6, 126.5, 125.5, 125.4, 21.6; HRMS (ESI) calcd for $C_{36}H_{26}O_2$ $[M - H]^-$ 489.1860, found 489.1869.

*3-(tert-Butyl)-5,6,7,8-tetraphenyl-1-naphthoic acid (**4ca**).* Pale yellow solid (81.8 mg, 77%): mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, J = 2.0 Hz, 1H), 7.68 (d, J = 2.0 Hz, 1H), 7.25–7.22 (m, 2H), 7.19–7.17 (m, 3H), 7.10–7.02 (m, 5H), 6.86–6.80 (m, 6H), 6.77–6.76 (m, 2H), 6.73–6.71 (m, 2H), 1.28 (s, 9H); $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) δ 170.2, 146.7, 140.12, 140.05, 139.9, 139.4, 139.2, 139.1, 138.2, 136.9, 134.0, 132.5, 132.0, 130.9, 130.8, 130.7, 127.5, 126.6, 126.5, 126.4, 126.34, 126.30, 126.0, 125.4, 125.2, 123.6, 34.3, 30.5; HRMS (ESI) calcd for $C_{39}H_{32}O_2$ $[M - H]^-$ 531.2330, found 531.2337.

*3-Methoxy-5,6,7,8-tetraphenyl-1-naphthoic acid (**4da**).* Pale yellow solid (86.2 mg, 85%): mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 2.7 Hz, 1H), 7.25–7.22 (m, 2H), 7.18–7.16 (m, 3H), 7.08–7.02 (m, 6H), 6.86–6.81 (m, 6H), 6.77–6.75 (m, 2H), 6.72–6.70 (m, 2H), 3.70 (s, 3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 173.5, 156.0, 140.6, 140.43, 140.37, 139.7, 139.0, 137.9, 137.3, 135.1, 133.1, 132.4, 131.5, 131.3, 131.1, 127.9, 127.1, 126.8, 126.70, 126.65, 126.58, 125.5, 125.4, 124.5, 120.6, 109.1, 55.5; HRMS (ESI) calcd for $C_{36}H_{26}O_3$ $[M - H]^-$ 505.1809, found 505.1820.

*3-Chloro-5,6,7,8-tetraphenyl-1-naphthoic acid (**4ea**).* Pale yellow solid (85.1 mg, 83%, from diacid; 86.6 mg, 85%, from anhydride): mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 2.2 Hz, 1H), 7.58 (d, J = 2.2 Hz, 1H), 7.25–7.19 (m, 3H), 7.16–7.14 (m, 2H), 7.07–7.03 (m, 5H), 6.87–6.81 (m, 6H), 6.76–6.73 (m, 2H), 6.73–6.71 (m, 2H); $^{13}C\{^{1}H\}$ NMR

(126 MHz, $CDCl_3$) δ 173.6, 141.6, 141.2, 139.9, 139.85, 139.81, 138.7, 138.4, 137.4, 134.5, 133.3, 132.3, 131.3, 131.2, 130.9, 130.5, 129.1, 128.7, 128.0, 127.5, 127.3, 127.1, 126.81, 126.79, 126.76, 125.8, 125.7; HRMS (ESI) calcd for $C_{35}H_{23}ClO_2$ $[M - H]^-$ 509.1314, found 509.1319.

*3-Bromo-5,6,7,8-tetraphenyl-1-naphthoic acid (**4fa**).* Pale yellow solid (93.2 mg, 84%, from diacid; 100.1 mg, 90%, from anhydride; 1.354 g, 81%, large scale): mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, J = 2.1 Hz, 1H), 7.70 (d, J = 2.1 Hz, 1H), 7.26–7.19 (m, 3H), 7.15–7.14 (m, 2H), 7.07–7.03 (m, 5H), 6.86–6.80 (m, 6H), 6.76–6.72 (m, 2H), 6.71–6.68 (m, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 173.6, 141.7, 141.2, 139.9, 139.82, 139.81, 138.6, 138.3, 137.5, 134.8, 133.3, 132.4, 132.3, 131.3, 131.2 (overlapped), 130.9, 128.0, 127.7, 127.3, 127.1, 126.81, 126.79, 126.76, 125.8, 125.7, 118.5; HRMS (ESI) calcd for $C_{35}H_{23}BrO_2$ $[M - H]^-$ 553.0809, found 553.0821.

*5,6,7,8-Tetraphenyl-3-(trifluoromethyl)-1-naphthoic acid (**4ga**).* Pale yellow solid (93.3 mg, 86%): mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (m, 1H), 7.80 (d, J = 1.7 Hz, 1H), 7.28–7.21 (m, 3H), 7.17–7.15 (m, 2H), 7.08–7.04 (m, 5H), 6.88–6.83 (m, 6H), 6.76–6.74 (m, 2H), 6.72–6.70 (m, 2H); ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.5; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 174.0, 143.6, 141.6, 140.2, 139.7, 139.63, 139.61, 138.3, 137.6, 132.9, 132.8, 132.4, 131.3, 131.1, 130.9, 130.3, 128.1 (q, J = 4.5 Hz), 128.0, 127.4, 126.91 (overlapped), 126.86, 126.5 (q, J = 33.1 Hz), 125.94, 125.90, 125.0, 123.9 (q, J = 272.2 Hz), 123.7 (q, J = 2.8 Hz); HRMS (ESI) calcd for $C_{36}H_{23}F_3O_2$ $[M - H]^-$ 543.1577, found 543.1588.

*3-Nitro-5,6,7,8-tetraphenyl-1-naphthoic acid (**4ha**).* Yellow solid (76.4 mg, 73%): mp >300 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.75 (brs, 1H), 8.40 (d, J = 1.7 Hz, 1H), 8.19

(d, J = 1.7 Hz, 1H), 7.33–7.28 (m, 5H), 7.15–7.12 (m, 1H), 7.09–7.06 (m, 2H), 7.04–7.02 (m, 2H), 6.90–6.86 (m, 8H), 6.80–6.79 (m, 2H); $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) δ 168.2, 144.6, 143.6, 141.5, 140.5, 139.12, 139.11, 138.3, 137.9, 137.6, 136.3, 131.9, 130.9, 130.6, 130.4 (overlapped), 127.9, 127.5, 127.0, 126.8, 126.6, 126.5, 125.9, 125.8, 124.4, 120.1; HRMS (ESI) calcd for $C_{35}H_{23}NO_4$ $[M - H]^-$ 520.1554, found 520.1566.

*5,6,7,8-Tetraphenylnaphthalene-1,3-dicarboxylic acid (**4ia**).* Pale yellow solid (104.0 mg, 76%): mp >300 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.77 (brs, 2H), 8.24 (s, 1H), 7.99 (s, 1H), 7.29–7.24 (m, 5H), 7.10–7.03 (m, 5H), 6.88–6.79 (m, 10H); $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) δ 169.5, 166.6, 142.9, 140.4, 139.73, 139.68, 138.9, 138.5, 137.5, 134.8, 132.3, 132.1, 131.0, 130.71, 130.67, 130.0, 127.8, 127.2, 127.0, 126.8, 126.7, 126.6, 125.8, 125.7; HRMS (ESI) calcd for $C_{36}H_{24}O_4$ $[M - H]^-$ 519.1602, found 519.1613.

*3,4-Difluoro-5,6,7,8-tetraphenyl-1-naphthoic acid (**4ja**).* Pale yellow solid (119.8 mg, 78%): mp >300 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.49 (s, 1H), 7.74 (s, 1H), 7.19–7.10 (m, 10H), 6.82–6.74 (m, 10H); $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) δ 168.0, 145.9 (dd, J = 245.9, 13.5 Hz), 145.8 (dd, J = 258.4, 12.8 Hz), 142.1, 141.1, 140.3 (d, J = 4.0 Hz), 139.4, 139.0, 138.6, 137.7, 134.3 (d, J = 4.9 Hz), 132.2, 131.7 (dd, J = 5.3, 5.3 Hz), 130.64, 130.60, 129.72 (d, J = 3.1 Hz), 126.9, 126.82, 126.79, 126.7, 126.5, 126.4, 126.3, 125.6, 125.5, 123.5 (d, J = 4.5 Hz), 118.3 (d, J = 21.8 Hz); ^{19}F NMR (471 MHz, DMSO-d_6) δ -132.13 (d, J = 18.9 Hz), -140.86 (d, J = 19.1 Hz); HRMS (ESI) calcd for $C_{35}H_{22}F_2O_2$ $[M - H]^-$ 511.1515, found 511.1519.

*3,4-Dichloro-5,6,7,8-tetraphenyl-1-naphthoic acid (**4ka**).* Pale yellow solid (44.4 mg, 41%): mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.10–7.07 (m, 3H), 7.05–6.98 (m,

7H), 6.84–6.80 (m, 6H), 6.64–6.61 (m, 4H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 172.5, 143.4, 141.7, 141.0, 139.62, 139.59, 139.5, 138.0, 137.6, 133.1, 132.9, 132.0, 131.9, 131.5, 131.4, 131.1, 131.0, 130.2, 128.9, 127.3, 127.2, 127.0, 126.8, 126.7, 126.6, 125.8, 125.7; HRMS (ESI) calcd for $C_{35}H_{22}Cl_2O_2$ $[M - H]^-$ 543.0924, found 543.0935.

*5,6,7,8-Tetraphenylphenanthrene-9-carboxylic acid (**4la**).* Pale brown solid (67.6 mg, 64%): mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.85–7.84 (m, 1H), 7.51 (d, J = 8.7 Hz, 1H), 7.44–7.41 (m, 1H), 7.17–7.15 (m, 3H), 7.11–7.08 (m, 3H), 7.05–7.02 (m, 5H), 6.86–6.82 (m, 6H), 6.70–6.67 (m, 4H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 174.2, 143.0, 141.5, 140.5, 140.4, 140.3, 140.2, 138.4, 137.9, 133.3, 132.1, 131.6, 131.5, 131.4, 130.88, 130.86, 130.25, 129.1, 128.9, 128.5, 128.1, 127.1, 127.0, 126.74, 126.68, 126.65, 126.63, 126.56, 125.5, 125.4; HRMS (ESI) calcd for $C_{39}H_{26}O_2$ $[M - H]^-$ 525.1860, found 525.1868.

*5,6,7,8-Tetra-p-tolyl-1-naphthoic acid (**4ab**).* Pale yellow solid (83.2 mg, 78%): mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (dd, J = 8.6, 1.2 Hz, 1H), 7.62 (dd, J = 7.0, 1.2 Hz, 1H), 7.32 (dd, J = 8.5, 7.0 Hz, 1H), 7.03–7.01 (m, 4H), 6.92–6.90 (m, 2H), 6.84–6.83 (m, 2H), 6.65–6.61 (m, 6H), 6.58–6.57 (m, 2H), 2.30 (s, 3H), 2.15 (s, 3H), 2.093 (s, 3H), 2.086 (s, 3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 175.2, 141.4, 140.3, 138.8, 137.7, 137.5, 137.4, 137.2, 136.7, 136.02, 136.00, 134.60, 134.56, 133.8, 132.2, 131.5, 131.3, 131.1, 130.9, 130.8, 129.4, 128.4, 128.0, 127.8, 127.41, 127.36, 124.0, 21.45, 21.37, 21.2 (overlapped); HRMS (ESI) calcd for $C_{39}H_{32}O_2$ $[M - H]^-$ 531.2330, found 531.2341.

*5,6,7,8-Tetrakis(4-methoxyphenyl)-1-naphthoic acid (**4ac**).* Pale yellow solid (86.3 mg, 72%): mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (dd, J = 8.6, 1.1 Hz, 1H), 7.68 (dd, J = 7.0, 1.1 Hz, 1H), 7.37 (dd, J = 8.6, 7.0 Hz, 1H), 7.06–7.04 (m, 2H), 6.97–6.96 (m, 2H),

6.79–6.78 (m, 2H), 6.65–6.64 (m, 2H), 6.62–6.59 (m, 4H), 6.43–6.41 (m, 4H), 3.79 (s, 3H), 3.63–3.62 (m, 9H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 174.8, 158.3, 158.2, 157.14, 157.12, 141.4, 140.3, 138.8, 137.0, 133.8, 133.5, 133.2, 133.1, 133.0, 132.5, 132.3, 132.14, 132.08, 131.5, 130.6, 129.4, 128.1, 124.3, 113.3, 112.7, 112.4, 55.3, 55.14, 55.08, 55.05; HRMS (ESI) calcd for $C_{39}H_{32}O_6$ $[M - H]^-$ 595.2126, found 595.2139.

*5,6,7,8-Tetrakis(4-fluorophenyl)-1-naphthoic acid (**4ad**).* Pale yellow solid (109.6 mg, 75%): mp 296–298 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72–7.71 (m, 2H), 7.48–7.45 (m, 1H), 7.12–7.09 (m, 2H), 7.074–7.01 (m, 2H), 6.98–6.95 (m, 2H), 6.80–6.76 (m, 2H), 6.70–6.58 (m, 8H); ^{19}F NMR (471 MHz, DMSO-d_6) δ -115.3, -115.6, -116.4, -116.5; $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) δ 170.2, 161.0 (d, J = 244.0 Hz), 160.9 (d, J = 243.5 Hz), 160.1 (d, J = 243.0 Hz), 160.0 (d, J = 243.1 Hz), 139.9, 138.6, 137.7, 136.6, 136.2 (d, J = 2.5 Hz, overlapped), 135.4 (d, J = 2.9 Hz), 135.0 (d, J = 3.1 Hz), 134.1, 133.9 (d, J = 8.1 Hz), 132.73 (d, J = 8.2 Hz), 132.65 (d, J = 8.2 Hz), 132.6, 132.5 (d, J = 8.1 Hz), 128.4, 127.9, 127.8, 125.5, 114.7 (d, J = 21.3 Hz), 113.7 (d, J = 21.2 Hz), 113.6 (d, J = 21.2 Hz), 113.5 (d, J = 21.1 Hz); HRMS (ESI) calcd for $C_{35}H_{20}F_4O_2$ $[M - H]^-$ 547.1327, found 547.1339.

*5,6,7,8-Tetrakis(4-chlorophenyl)-1-naphthoic acid (**4ae**).* Pale yellow solid (87.5 mg, 71%): mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, J = 7.0, 1.1 Hz, 1H), 7.68 (dd, J = 8.6, 1.1 Hz, 1H), 7.46 (dd, J = 8.6, 7.0 Hz, 1H), 7.26–7.25 (m, 2H), 7.07–7.05 (m, 4H), 6.98–6.96 (m, 2H), 6.91–6.88 (m, 4H), 6.67–6.61 (m, 4H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 175.3, 139.8, 138.6, 138.5, 138.4, 138.12, 138.07, 137.3, 136.6, 133.5, 133.39, 133.36, 133.2, 132.5, 132.4, 132.3, 132.2, 132.1, 131.1, 130.6, 129.6, 128.9, 128.4, 127.7, 127.6, 127.5, 125.4; HRMS (ESI) calcd for $C_{35}H_{20}Cl_4O_2$ $[M - H]^-$ 611.0145, found 611.0156.

*5,6,7,8-Tetrakis(4-bromophenyl)-1-naphthoic acid (**4af**).* Pale yellow solid (126.7 mg, 80%): mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 6.8 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.47–7.40 (m, 3H), 7.22–7.20 (m, 2H), 7.07–6.99 (m, 6H), 6.91–6.89 (m, 2H), 6.61–6.54 (m, 4H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 175.3, 139.6, 138.9, 138.51, 138.46, 138.410, 138.406, 137.7, 136.5, 133.8, 133.3, 132.8, 132.7, 132.4, 131.4, 131.0, 130.7, 130.6, 130.54, 130.48, 129.9, 128.9, 125.4, 121.6, 121.5, 120.6, 120.5; HRMS (ESI) calcd for $C_{35}H_{20}{}^{79}Br_2{}^{81}Br_2O_2$ $[M - H]^-$ 790.8083, found 790.8101.

*5,6,7,8-Tetrakis(4-(trifluoromethyl)phenyl)-1-naphthoic acid (**4ag**).* Pale yellow solid (113.3 mg, 76%): mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 6.7 Hz, 1H), 7.67 (d, J = 8.3 Hz, 1H), 7.56–7.50 (m, 3H), 7.33–7.30 (m, 4H), 7.18–7.14 (m, 6H), 6.88–6.80 (m, 4H); ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.4, -62.7, -62.86, -62.89; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 175.3, 143.5, 143.0, 142.9, 142.2, 139.4, 138.6, 138.2, 136.7, 133.3, 132.4, 131.5, 131.4, 131.2, 130.9, 130.8, 130.3, 129.9 (q, J = 32.9 Hz), 129.3 (q, J = 32.4 Hz), 128.87 (q, J = 32.6 Hz), 128.85, 128.82 (q, J = 32.6 Hz), 126.0, 125.2 (m), 124.4–124.3 (m, overlapped), 124.2 (q, J = 3.8 Hz), 124.1 (q, J = 272.3 Hz, overlapped), 123.90 (q, J = 272.0 Hz), 123.88 (q, J = 272.1 Hz); HRMS (ESI) calcd for $C_{39}H_{20}F_{12}O_2$ $[M - H]^-$ 747.1199, found 747.1200.

*5,6,7,8-Tetrakis(4-(trifluoromethoxy)phenyl)-1-naphthoic acid (**4ah**).* Pale yellow solid (112.0 mg, 69%): mp 250–252 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77–7.76 (m, 2H), 7.50 (t, J = 7.6 Hz, 1H), 7.19–7.06 (m, 6H), 6.93–6.92 (m, 2H), 6.78–6.68 (m, 8H); ^{19}F NMR (471 MHz, $CDCl_3$) δ -58.0, -58.1, -58.4, -58.5; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 175.6, 148.5, 148.3, 147.6, 139.9, 138.7, 138.6, 138.5, 138.4, 138.3, 137.4, 136.6, 133.6, 133.4, 132.6, 132.4, 132.2, 131.1, 130.7, 129.6, 128.8, 125.6, 120.63, 120.60 (q, J = 257.4 Hz), 120.5 (q, J

= 257.3 Hz), 120.4 (q, J = 257.0 Hz, overlapped), 119.9 (overlapped), 119.8; HRMS (ESI) calcd for $C_{39}H_{20}F_{12}O_6$ $[M - H]^-$ 811.0996, found 811.0990.

*5,6,7,8-Tetrakis(3,5-dimethylphenyl)-1-naphthoic acid (**4ai**).* Pale yellow solid (85.1 mg, 72%): mp 299–301 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (dd, J = 8.5, 1.1 Hz, 1H), 7.58 (dd, J = 7.0, 1.1 Hz, 1H), 7.38 (dd, J = 8.5, 7.0 Hz, 1H), 6.79–6.78 (m, 3H), 6.68 (s, 2H), 6.64 (s, 1H), 6.42–6.37 (m, 6H), 2.21 (s, 6H), 2.08 (s, 6H), 1.97 (s, 6H), 1.95 (s, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 175.2, 141.6, 140.4, 140.18, 140.14, 140.0, 139.5, 138.7, 136.9, 136.7, 136.2, 135.25, 135.21, 133.4, 131.9, 130.7, 130.3, 129.4, 129.3, 129.2, 128.7, 128.0, 127.7, 127.3, 126.7, 126.6, 124.0, 21.34, 21.27, 21.1 (overlapped); HRMS (ESI) calcd for $C_{43}H_{40}O_2$ $[M - H]^-$ 587.2956, found 587.2961.

*5,6,7,8-Tetrakis(3,5-dichlorophenyl)-1-naphthoic acid (**4aj**).* Pale yellow solid (84.0 mg, 56%): mp 287–290 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, J = 7.0, 1.1 Hz, 1H), 7.71 (dd, J = 8.5, 1.1 Hz, 1H), 7.61 (dd, J = 8.5, 7.1 Hz, 1H), 7.33 (t, J = 1.8 Hz, 1H), 7.14 (t, J = 1.8 Hz, 1H), 7.09 (d, J = 1.8 Hz, 2H), 7.05 (t, J = 1.8 Hz, 1H), 7.03 (t, J = 1.8 Hz, 1H), 7.00 (d, J = 1.8 Hz, 2H), 6.75 (d, J = 1.8 Hz, 2H), 6.72 (d, J = 1.8 Hz, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 174.4, 141.8, 141.24, 141.17, 140.7, 137.9, 137.6, 136.8, 135.8, 135.2, 134.5, 134.42, 134.39, 133.0, 131.4, 130.4, 130.3, 129.9, 129.23, 129.17, 129.0, 128.5, 128.2, 127.43, 127.40, 127.3, 126.7; HRMS (ESI) calcd for $C_{35}H_{16}Cl_8O_2$ $[M - H]^-$ 746.8586, found 746.8573.

*5,6,7,8-Tetra(thiophen-3-yl)-1-naphthoic acid (**4ak**).* Pale yellow solid (42.4 mg, 42%): mp >300 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.20 (brs, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.59 (d, J = 6.8 Hz, 1H), 7.49–7.46 (m, 2H), 7.29 (brs, 1H), 7.20–7.18 (m, 1H), 7.10–7.07 (m, 3H),

6.97 (brs, 1H), 6.84 (m, 1H), 6.77 (s, 1H), 6.58–6.57 (m, 2H), 6.51–6.50 (m, 1H); $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) δ 169.7, 139.9, 139.7, 139.6, 138.6, 136.2, 135.5, 134.1, 133.9, 133.2, 132.9, 130.6, 130.2, 129.7, 128.9, 128.3, 127.6, 125.6, 125.21, 125.20, 125.0, 123.99, 123.97, 123.55, 123.52, 123.47; HRMS (ESI) calcd for $C_{27}H_{16}O_2S_4$ $[M - H]^-$ 498.9960, found 498.9969.

*5,7-Dimethyl-6,8-diphenyl-1-naphthoic acid (**4al**).* Pale yellow solid (30.1 mg, 21%): mp 261–262 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.01 (s, 1H), 8.20 (dd, J = 8.3, 1.1 Hz, 1H), 7.54–7.48 (m, 4H), 7.43–7.40 (m, 1H), 7.35–7.34 (m, 3H), 7.26–7.24 (m, 2H), 7.18–7.16 (m, 2H), 2.38 (s, 3H), 1.73 (s, 3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) δ 170.3, 141.4, 140.3, 139.8, 135.7, 134.0, 133.4, 131.6, 131.5, 130.8, 129.1, 128.6, 128.1, 127.4, 126.97, 126.93, 126.86, 126.4, 124.2, 20.1, 17.1.; HRMS (ESI) calcd for $C_{25}H_{20}O_2$ $[M - H]^-$ 351.1391, found 351.1390.

*4-Oxo-6,7-diphenyl-4H-thieno[3,2-c]pyran-3-carboxylic acid (**5ma**).* Pale yellow solid (85.6 mg, 82%): mp >300 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.49 (brs, 1H), 8.26 (s, 1H), 7.50–7.47 (m, 3H), 7.42–7.40 (m, 2H), 7.38–7.30 (m, 5H); $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) δ 163.0, 156.9, 156.2, 152.0, 133.7, 133.2, 132.8, 131.4, 129.8, 129.4, 129.1, 128.9, 128.3, 119.1, 114.9; HRMS (ESI) calcd for $C_{20}H_{12}O_4S$ $[M - H]^-$ 347.0384, found 347.0385.

*1-(5,6,7,8-Tetraphenylnaphthalen-1-yl)ethanone (**9aa**).* Pale yellow solid (45.5 mg, 32%): mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (dd, J = 8.4, 1.4 Hz, 1H), 7.41 (dd, J = 7.0, 1.4 Hz, 1H), 7.35 (dd, J = 8.4, 7.0 Hz, 1H), 7.25–7.22 (m, 2H), 7.20–7.17 (m, 3H), 7.13–7.10 (m, 3H), 7.08–7.06 (m, 2H), 6.87–6.82 (m, 6H), 6.79–6.77 (m, 2H), 6.74–6.72 (m, 2H), 2.01

(s, 3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 204.4, 142.2, 141.1, 141.0, 140.4, 140.3, 140.0, 139.5, 139.1, 137.4, 133.6, 132.9, 131.4, 131.3, 131.1, 129.8, 129.3, 127.7, 127.5, 127.0, 126.77, 126.74, 126.71, 125.7, 125.6, 125.5, 124.6, 30.7; HRMS (ESI) calcd for $C_{36}H_{26}O$ [M + H]$^+$ 475.2056, found 475.2052.

Procedure for Synthesis of 6. To a 50 mL Schlenk flask equipped with a magnetic stirrer, **4aa** (190.6 mg, 0.4 mmol), 16 mL DCM, and 4 mL $MeNO_2$ were added sequentially. The flask was charged with N_2 and $SOCl_2$ (120 μL, 1.6 mmol) was added. The flask was stirred at room temperature for 6 h. The reaction mixture was then diluted with DCM and washed with $NaHCO_3$ aqueous solution and water. After purification by flash column chromatography on silica gel with petroleum ether/EtOAc (gradient mixture ratio from 1:0 to 15:1) as eluant, **6aa** (168.3 mg, 92%) was obtained as a yellow solid. Similarly, **6fa** was synthesized from **4fa**.

*1,2,3-Triphenyl-7H-benzo[de]anthracen-7-one (**6aa**).*[19] Yellow solid (168.3 mg, 92%): mp 260–261 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (dd, J = 7.2, 1.1 Hz, 1H), 8.46 (dd, J = 7.8, 1.1 Hz, 1H), 7.93 (dd, J = 8.3, 1.1 Hz, 1H), 7.67–7.64 (m, 1H), 7.34–7.31 (m, 1H), 7.25–7.20 (m, 3H), 7.17–7.08 (m, 7H), 7.06–7.04 (m, 2H), 6.90–6.88 (m, 3H), 6.75–6.74 (m, 2H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 184.5, 142.0, 141.9, 141.25, 141.22, 139.6, 138.9, 137.5, 134.4, 132.9, 132.0, 131.7, 131.4, 131.2, 131.1, 130.2, 129.7, 128.8, 128.5, 128.4, 127.7, 127.6, 127.4, 127.1, 127.0, 126.9, 126.4, 125.8, 125.3.

*5-Bromo-1,2,3-triphenyl-7H-benzo[de]anthracen-7-one (**6fa**).* Yellow solid (183.2 mg, 85%): mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.80 (d, J = 2.2 Hz, 1H), 8.41 (d, J = 7.7 Hz, 1H), 8.02 (d, J = 2.2 Hz, 1H), 7.34–7.31 (m, 1H), 7.26–7.22 (m, 3H), 7.17–7.10 (m, 7H), 7.03–7.02 (m, 2H), 6.90–6.89 (m, 3H), 6.73–6.71 (m, 2H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

δ 183.4, 142.4, 142.1, 141.7, 140.4, 139.3, 138.1, 137.3, 135.7, 133.8, 132.4, 132.3, 132.1, 131.2, 131.03, 130.99, 130.3, 130.0, 128.5, 127.9, 127.8, 127.7, 127.31, 127.25, 126.9, 125.9, 125.6, 121.1; HRMS (ESI) calcd for $C_{35}H_{21}BrO$ $[M + H]^+$ 537.0849, found 537.0845.

Procedure for One-pot Synthesis of 7aa. To a 10 mL tube with a branch pipe, a magnetic stirrer, $[Ru(p\text{-cymene})Cl_2]_2$ (6.1 mg, 0.01 mmol), phthalic acid **1a** (39.9 mg, 0.24 mmol), diphenylacetylene **3a** (71.3 mg, 0.4 mmol), TBAB (12.9 mg, 0.04 mmol), 900 μL GVL and 100 μL DMF were added sequentially. The top of the tube was sealed and leave the branch pipe open to air. After reaction at 100 °C for 12 h, the tube was cool down, following by addition of KOAc (19.6 mg, 0.20 mmol) and ethyl acrylate (44 μL, 0.40 mmol). After reaction at 100 °C for additional 16 h, the reaction mixture was cool down, diluted with EtOAc and washed with water. After purification by flash column chromatography on silica gel with petroleum ether/EtOAc (gradient mixture ratio from 1:0 to 12:1) as eluant, **7aa** (64.6 mg, 56%) was obtained as a pale yellow solid.

*Ethyl 2-(1-oxo-6,7,8,9-tetraphenyl-1,3-dihydronaphtho[1,2-c]furan-3-yl)acetate (**7aa**).* Pale yellow solid (64.6 mg, 56%): mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 8.7 Hz, 1H), 7.37 (d, J = 8.7 Hz, 1H), 7.25–7.15 (m, 5H), 7.12–7.07 (m, 5H), 6.87–6.82 (m, 6H), 6.79–6.69 (m, 4H), 5.81 (dd, J = 7.0, 5.9 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 2.90 (dd, J = 16.2, 5.8 Hz, 1H), 2.84 (dd, J = 16.2, 7.2 Hz, 1H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 169.5, 166.9, 152.5, 143.1, 141.6, 140.8, 140.04, 139.96, 139.5, 139.3, 137.6, 135.3, 133.8, 131.31, 131.29, 131.26, 131.22, 131.18, 131.03, 130.99, 130.97, 128.8, 127.85, 127.83, 127.1, 127.0, 126.8, 126.7, 126.4, 125.7, 125.6, 121.8, 118.4, 74.8, 61.4, 40.1, 14.3; HRMS (ESI) calcd for $C_{40}H_{30}O_4$ $[M + H]^+$ 575.2217, found 575.2214.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.xxxxxxx.

X-ray structural details, mechanism studies, and copies of NMR spectra (PDF)

X-ray crystallography data for compound **4da** (CIF)

X-ray crystallography data for compound **4al** (CIF)

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Notes

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