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Aerobic C−H oxidation of arenes using a recyclable, heterogeneous rhodium catalyst

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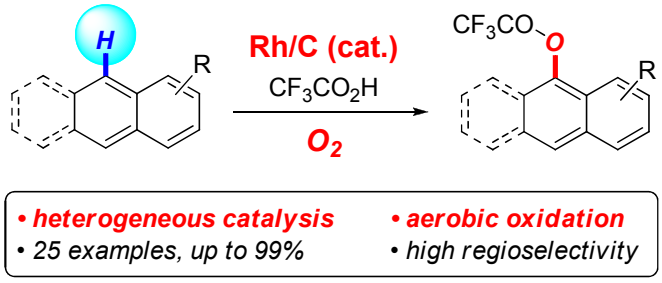
TOC/ Abstract Graphics:



Abstract:

A novel, practical protocol for the aerobic direct C−H acetoxylation of arenes, employing a recyclable heterogeneous rhodium catalyst, is reported herein. The trifluoroacetoxylation of 2-amido-substituted anthracenes proceeded at 9-position with exclusive regioselectivity. The oxidation of variously substituted anthracenes and other polycyclic aromatics with molecular oxygen as a terminal oxidant proceeded under mild conditions providing products in good to

excellent yields.

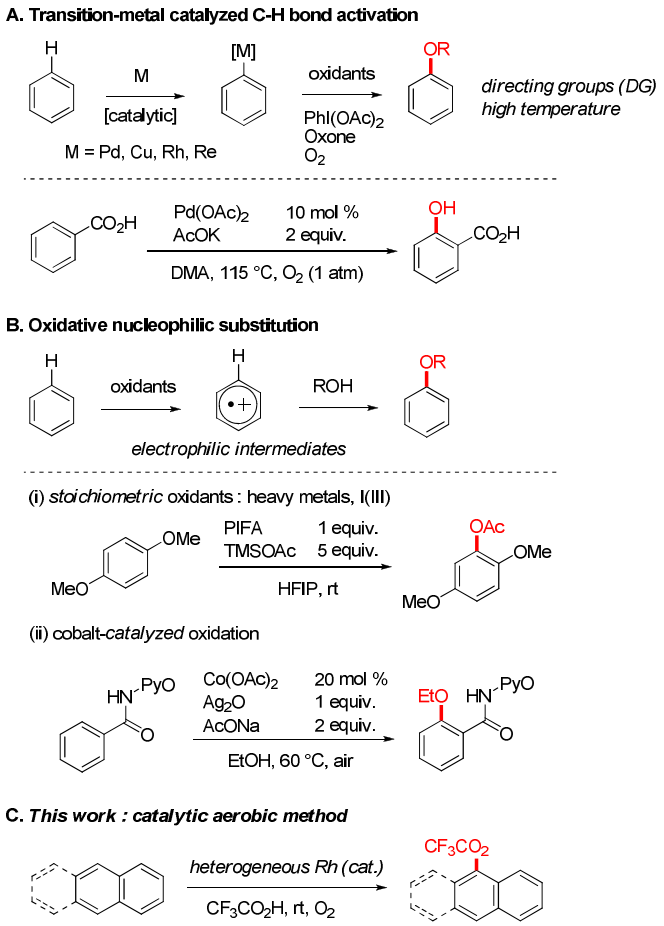
Introduction

Heterogeneous metal catalysts are a very important tool for the synthesis of fine chemicals and functional materials owing to their high efficiency, robustness, and facile recyclability.[1] Oxygenated aromatic compounds such as aryl ethers, aryl esters, and phenols are highly valuable in the pharmaceutical, agrochemical, and materials industries.[2] Recently, the direct C−H bond functionalization of arenes has received much attention as one of the most powerful methods for the formation of C−O bonds, because the reactants do not need prefunctionalization and because of the atom and step economy of the process.[3] However, despite these significant advances, the development of heterogeneous metal-catalyzed C−H oxygenation reactions amenable for application in environmentally sustainable chemistry still remains an unresolved challenge in organic chemistry.[4-7]

Most of the direct aromatic C−H oxygenation reactions reported are transition metal-promoted methods using various oxidants such as $PhI(OAc)_2$,[8,9] Oxone,[10] molecular oxygen,[11] and other reagents[12] (Scheme 1A). Since molecular oxygen has a clear advantage from the viewpoints of economic efficiency and environmental impact,[13] Yu has developed palladium-catalyzed aerobic hydroxylation of benzoic acids.[14] However, aerobic direct C−H oxygenation reactions are still problematic, rely on the use of directing groups, and require elevated temperatures in order to afford high efficiencies.[15]

In contrast, oxidative nucleophilic substitution reactions constitute an alternative method to directly synthesize oxygen-functionalized compounds (Scheme 1B). These processes are thought to proceed *via* radical cation intermediates, followed by nucleophilic substitution, to yield the oxygenated products under mild conditions. Although heavy-metal complexes such as $Tl(trifluoroacetate)_3$, $Mn(OAc)_3$, and $Pb(OAc)_4$ are traditionally employed as oxidants, hypervalent iodine reagents have recently received attention due to their lower toxicity and easy handling (Scheme 1B (i)).[16] In 1994, Kita reported the direct nucleophilic acetoxylation of electron-rich arenes through radical cation intermediates generated by phenyliodine(III) bis(trifluoroacetate) (PIFA).[17,18] However, they typically require stoichiometric oxidants; thus, alternative catalytic oxidation methods are desirable.[19] DiCosimo developed the first cobalt(III) trifluoroacetate catalyzed trifluoroacetoxylation of benzene with peroxide or peracid oxidants.[20] Niu recently reported the highly efficient cobalt-catalyzed alkoxylation of arenes by using a combination of Ag_2O as an oxidant and 2-aminopyridine-1-oxide as a directing group (Scheme 1B (ii)).[21] However, catalytic aerobic methods for direct aromatic C−H oxygenation still remain elusive. We report here the first examples of the direct, aerobic trifluoroacetoxylation and

dichloroacetoxylation of arenes achieved by employing a recyclable and commercially available heterogeneous rhodium catalyst (Scheme 1C).

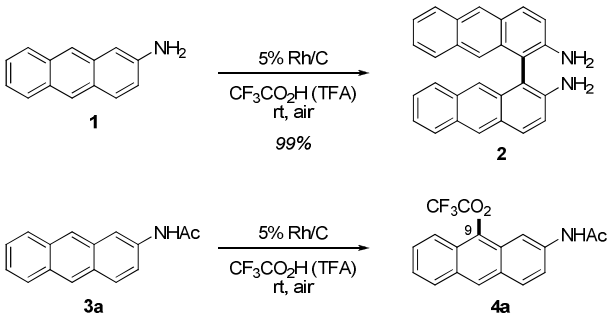


Scheme 1. Direct aromatic C−H oxygen-functionalization strategies. DMA = *N,N*-dimethylacetamide. PIFA = phenyliodine(III) bis(trifluoroacetate). HFIP = hexafluoroisopropanol. PyO = 2-aminopyridine-1-oxide.

Results and Discussion

Recently, we found that rhodium on carbon can function as an excellent catalyst for the oxidative homo-coupling of aryl amine **1** under acidic conditions to provide dehydrodimer **2** in high yield (Scheme 2).[22] We then developed a dehydrogenative cross-coupling of aryl amines using a heterogeneous catalyst.[23] It is worth noting that these reactions can be carried out with low catalyst loadings using air as a terminal oxidant. When the same reaction with acetylamino

derivative **3a** was carried out, surprisingly, the expected dehydrodimer was not observed at all; instead, a trifluoroacetoxylation reaction proceeded at the 9-position of the anthracene skeleton to provide **4a** with high selectivity. Previously reported acetoxylation protocols of anthracenes were usually hampered by over-oxidation reactions, which are often responsible for the low yields.[24,25] These by-processes readily occur due to the lower oxidation potentials of the oxidized products, which make them more reactive than the starting materials. In our case, the introduction of electron-withdrawing substituents such as amido groups moderated their oxidation potentials, and thus, over-oxidation was prevented, resulting in the preferential formation of mono-oxygenated products. To the best of our knowledge, this represents the first example of heterogeneously catalyzed trifluoroacetoxylation of polycyclic arenes under aerobic conditions.[26]

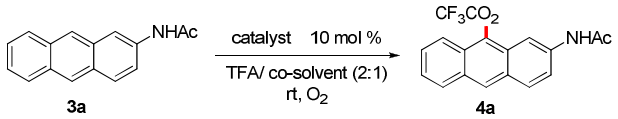


Scheme 2. Rh/C-catalyzed oxidative trifluoroacetoxylation.

These results prompted us to explore the direct trifluoroacetoxylation of *N*-2-anthracenylacetamide (**3a**) using various heterogeneous catalysts in trifluoroacetic acid (TFA) under oxygen (1 atm) (Table 1). In the presence of 5% Rh/C (10 mol % of rhodium, Sigma-Aldrich), the trifluoroacetoxylated product **4a** was obtained in 64% yield (entry 1). To decrease the amount of TFA, co-solvents were screened and benzotrifluoride was found to afford the best results (entries 2-6). To prevent the hydrolysis of the labile trifluoroacetate ester, trifluoroacetic anhydride (TFAA) and molecular sieves (MS 4 Å) were added as dehydrating agents, but no improvement in the yields was observed (entries 7 and 8). While a range of alternative heterogeneous catalysts were screened and proved inferior compared to Rh/C (entries 9-13), PtO_2 afforded a better yield of **4a** (entry 14). Interestingly, gold nanoparticles on TiO_2 were found to catalyze the trifluoroacetoxylation reaction of **3a** to give **4a** in 51% yield (entry 15).[27] In contrast, homogeneously catalyzed and non-metal-catalyzed reactions provided almost no products (entries 16-18). To verify the heterogeneous reaction, the following filtration

experiment was carried out. After Rh/C was stirred for 1 hour under the condition in Table 1, the catalyst was removed by filtration with a membrane filter. Then amide **3** was added to the filtrate, and the mixture was stirred at rt under O_2. No conversion was observed. This result suggests that this reaction is catalyzed by heterogeneous metal, not leaching metal.

Table 1. Oxidative trifluoroacetoxylation of amide 3a [a]



3a 4a

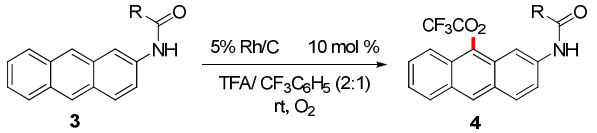
entry	catalyst	co-solvent	time (h)	yield (%) [b]
1	5% Rh/C	−	1	64
2	5% Rh/C	DMSO	80	No reaction
3	5% Rh/C	THF	80	33
4	5% Rh/C	CH_2Cl_2	6	64
5	5% Rh/C	Toluene	3	69
6	5% Rh/C	$CF_3C_6H_5$	3	76
7	5% Rh/C	TFAA	21	63
8 [c]	5% Rh/C	$CF_3C_6H_5$	3	73
9	5% Rh/Al_2O_3	$CF_3C_6H_5$	24	47
10	3% Cu/C	$CF_3C_6H_5$	24	63
11	5% Ru/C	$CF_3C_6H_5$	24	58
12	10% Pd/C	$CF_3C_6H_5$	24	14
13	5% Pt/C	$CF_3C_6H_5$	19	20
14	PtO_2	$CF_3C_6H_5$	25	73
15	1% AuNP/TiO_2	$CF_3C_6H_5$	28	51
16	$RhCl_3$	$CF_3C_6H_5$	30	No reaction
17	$Mn(OAc)_3$	$CF_3C_6H_5$	49	5
18	−	$CF_3C_6H_5$	38	No reaction

[a] Reaction conditions: **3a** (0.17 mmol), catalyst (10 mol %), TFA/ co-solvent (2: 1, 1 mL), rt, O_2 (balloon). [b] Yield of isolated product. [c] MS 4 Å were added.

Since Rh/C proved to be an effective catalyst, we next examined the direct trifluoroacetoxylation protocol with a selection of substituted benzamides **3** in order to understand the directing group potential of amido substituents at 2-position (Table 2). The

reaction of simple benzamide **3b** was much slower than that of **3a**, probably due to its low solubility (entry 1). When a methoxy substituent was introduced on the benzene ring at the *ortho* position, the reaction proceeded smoothly to afford the desired product **4c** in 83% yield (entry 2). Disubstituted analogs possessing additional fluoride (**3d**), nitro (**3e**), and methoxy (**3f**) groups at the *para* position also resulted in fast and highly selective transformations (entries 3-5). The other kinds of electron-rich, disubstituted analogs **3g** and **3h** also afforded good results (entries 6 and 7). The reaction of **3f** proceeded smoothly even using 1 mol % of 5% Rh/C (entry 5). To further explore the generality of this oxidative protocol, various substituted amides bearing *tert*-butyl, trifluoromethyl, and ethoxycarbonylmethyl groups were examined and the corresponding oxidized products **4i**, **4j**, and **4k** were obtained in high yields (entries 8-10). Heteroaromatic amides also afforded the desired products **4l** and **4m** in good yields (entries 11 and 12). Furthermore, the trifluoroacetoxylation of **3f** on a gram-scale gave 92% yield of **4f** with highly stereoselective manner, which was comparable to the result observed in the small-scale experiment (Scheme 3). This methodology can be applied to a wide range of amide groups and it should be noted that trifluoroacetoxylations of **3** are exclusive regioselective.

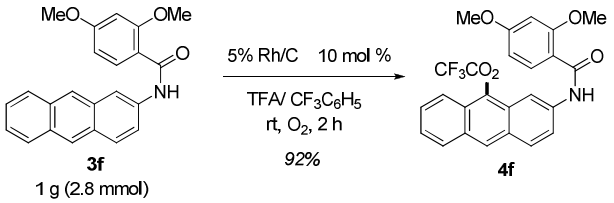
Table 2. Oxidative trifluoroacetoxylation of amides 3 [a]



3 4

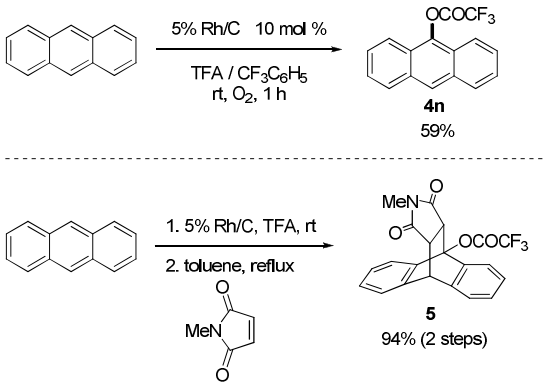
entry	R	3	time (h)	4	yield (%) [b]
1	C_6H_5	**3b**	42	**4b**	55
2	2-MeO-C_6H_4	**3c**	0.5	**4c**	83
3	2-MeO-4-F-C_6H_3	**3d**	1.5	**4d**	58
4	2-MeO-4-NO_2-C_6H_3	**3e**	1.5	**4e**	64
5	2,4-$(MeO)_2C_6H_3$	**3f**	1	**4f**	93 (77) [c]
6	2,5-$(MeO)_2C_6H_3$	**3g**	1	**4g**	86
7	3,4-$(MeO)_2C_6H_3$	**3h**	6	**4h**	85
8	*tert*-Bu	**3i**	2	**4i**	86
9	CF_3	**3j**	6	**4j**	quant.
10	CH_2CO_2Et	**3k**	2	**4k**	74
11	2-pyridyl	**3l**	23	**4l**	67
12	2-furyl	**3m**	24	**4m**	85

[a] Reaction conditions: **3** (0.12 mmol), 5% Rh/C (28 mg, 10 mol %), TFA/ $CF_3C_6H_5$ (2: 1, 1 mL), rt, O_2 (balloon). [b] Yield of isolated product. [c] The yield in parenthesis was obtained using 1 mol % of 5% Rh/C.



Scheme 3. Gram-scale reaction of **3f**

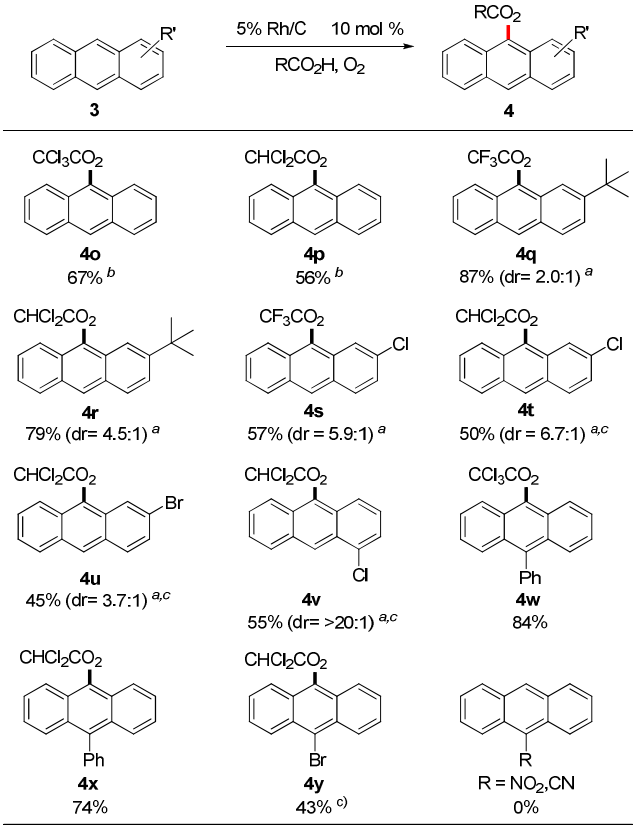
Besides amide analogs, simple anthracene was also efficiently trifluoroacetoxylated, but the yield of **4n** was moderate, probably due to the lack of stability of the product (Scheme 4). Therefore, under standard conditions, the crude trifluoroacetoxylated product **4n** was immediately refluxed in toluene with *N*-methylmaleimide (3 equiv) to give the Diels-Alder adduct **5** in 94% yield. This two-step protocol represented significant improvement and indicated that **4n** was unstable to silica gel column chromatography.



Scheme 4. Diels-Alder reaction of **4n** with *N*-methylmaleimide.

Using trichloroacetic acid and dichloroacetic acid as solvents, trichloroacetoxylation and dichloroacetoxylation took place to afford **4o** and **4p** in moderate yields, respectively (Scheme 5). These obtained products were more stable and easy to handle than **4n**. However, no

desired product was obtained with acetic acid, which showed that a highly acidic medium was necessary for this transformation to proceed. When 2-*tert*-butylanthracene was employed, the trifluoroacetoxylation and dichloroacetoxylation reactions took place smoothly, but the regioselectivity was decreased to give a mixture of products at 9- and 10-positions (**4q** and **4r**) in 87% and 79% yields, respectively. The halogenated anthracenes at 2-position also affoded oxidized products **4s**, **4t**, and **4u** with moderate selectivities. In contrast, 1-chloroanthracene was dichloroacetoxylated to give **4v** with highly stereoselective manner, probably due to the steric effect of chloride group at 1-position. The reactions of 9-phenyl and 9-bromoanthracene also afforded **4w**, **4x**, and **4y** but 9-nitro and 9-cyanoanthracene resulted in no desired products. The reaction described herein demonstrated to be applied to variously substituted anthracenes and the directing groups at 1- and 2-position were also found to play an important role in controlling the regioselectivity as well as the stability of the products.



Scheme 5. Oxidative acetoxylation of aromatics **3**. Reaction conditions for trifluoroacetoxylation: 5% Rh/C (10 mol %), TFA/ $CF_3C_6H_5$, rt, O_2 (balloon). Trichloroacetoxylation and dichloroacetoxylation: 5% Rh/C (10 mol %), CCl_3CO_2H or

$CHCl_2CO_2H$, 60 °C, O_2 (balloon). [a] The parenthetic number is a ratio for a mixture of products at 9- and 10-positions. [b] 15 mol %. [c] 20 mol %.

Considering the oxidation potential of several anthracenes (Figure 1),[28] the more easily oxidized anthracenes are smoothly acetoxylated, while those with higher potentials fail to react. Among 2-substituted anthracenes, trifluoroacetoxylation of analogs with amido and *tert*-butyl groups proceeds faster than those with electron-withdrawing halogens (2-*tert*-Bu: 10 min, **4a**: 3 h, 2-Cl: 48 h). Since the electron-donating substituents lower the oxidation potential of aromatic compounds, the mechanism can be speculated that radical cation intermediates, generated by a SET process, are directly attacked by acetate ion as a nucleophile.[29] However, although the addition of 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) as a radical quencher was attempted, TEMPO did not significantly inhibit the reaction (Scheme 6). From this result, in the case of amides, the reaction mechanism *via* an arylnitrenium ion can be envisaged (Scheme 7).[30] Amides **3** can be oxidized by the catalyst to produce radical cation intermediates **A** and the reduced rhodium species, which can undergo oxidation by molecular oxygen to regenerate the active catalyst. The generated cation radicals can immediately undergo successive one-electron transfer and rapid deprotonation to afford arylnitrenium ion intermediate **B**, probably due to the high acidity of amide proton. Amongst the allowed arylnitrenium intermediates, a resonance form **C** would be more reactive owing not only to the inherent nature of anthracene, but also to the electronic and steric properties of the amido substituents. For these reasons, TFA can readily react at the 9-position in a selective manner. In contrast, the reaction of anthracenes with *tert*-butyl group and halogens at 2-position afforded a mixture of products, which suggested that alkyl and halogen substituents cannot induce such a significant regiochemical bias because cation radical intermediates, not arylnitrenium, would be involved in these cases. However, the mechanistic details of the heterogeneous rhodium-catalyzed acetoxylation of arenes are still unclear and other mechanism such as direct C-H activation of rhodium catalyst cannot be ruled out.

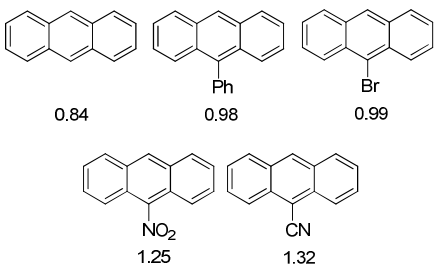
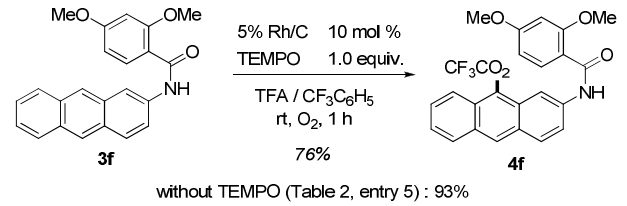
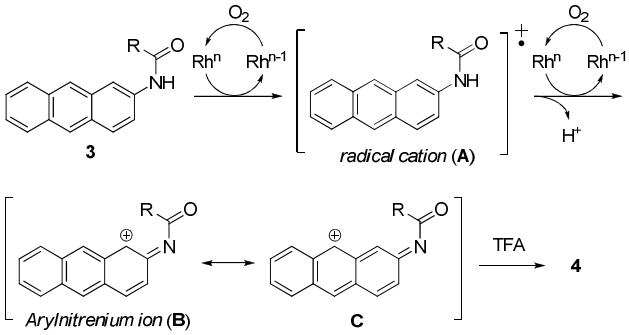


Figure 1. Oxidation potentials (V) referred from ref. 28.



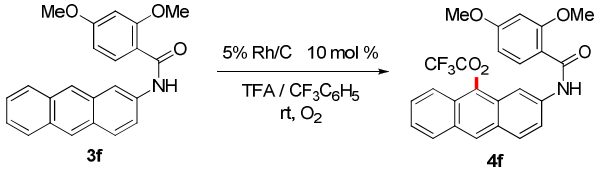
Scheme 6. Control experiment with TEMPO as a radical quencher.



Scheme 7. Proposed mechanism.

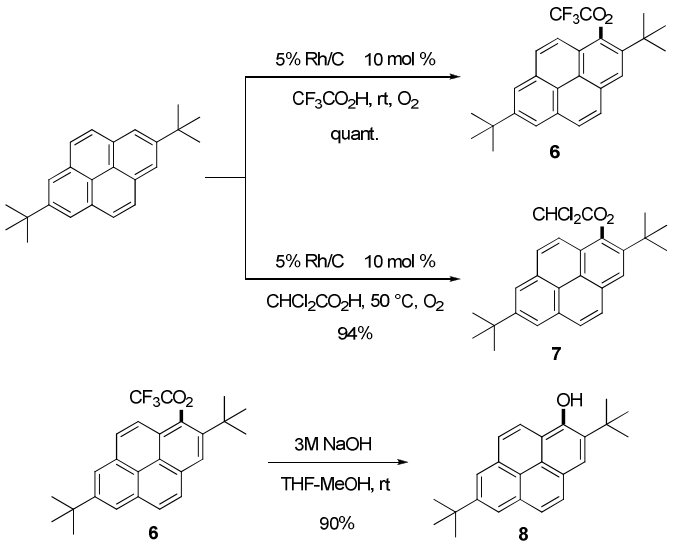
The easy catalyst recycle is one of the advantages for heterogeneous catalysts from the view of green chemistry. The recyclability of the Rh/C catalyst was examined during the trifluoroacetoxylation of **3f** (Table 3). After the reaction, Rh/C was recovered by centrifuged separation, washed with ethyl acetate, and then reused. Rh/C could be recycled for at least six times without the significant loss in the isolated yield of **4f**. However, its catalytic activity gradually decreased with consecutive runs, and hence the longer reaction times were required, probably due to chemical damage of catalysts under the acidic conditions.[31]

Table 3. Recyclability of Rh/C catalyst for trifluoroacetoxylation of 3f.

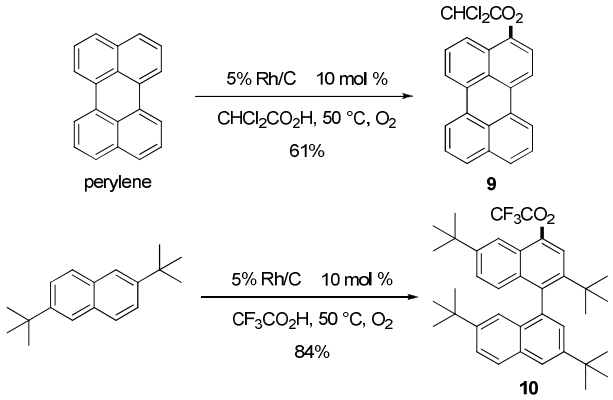


reaction run	time (h)	isolated yield (%)
0	1	89
1	3	92
2	3	85
3	7	82
4	10	76
5	10	82
6	24	78

This direct trifluoroacetoxylation protocol can be applied to the oxidation of pyrenes (Scheme 8). 2,7-Di-*tert*-butylpyrene was converted into trifluoroacetoxylated product **6** in quantitative yield. Dichloroacetoxylated product **7** was also obtained in excellent yield when TFA was replaced by dichloroacetic acid. Moreover, trifluoroacetic acid ester of **6** was easily hydrolyzed to afford hydroxypyrene **8** in 90% yield. Perylene was also dichloroacetoxylated under standard conditions to give **9** in 61% yield (Scheme 9). In contrast, naphthalene failed to react. Probably because the cation radical of naphthalene is much more reactive than those of the condensed ring aromatics such as perylene and anthracene, the control of reactivity is too difficult and thus the reaction results in its polymerization or decomposition. On the other hand, the introduction of sterically bulky substituents is generally useful method for the control of reactivity and increase of stability of cation radicals. Therefore, when 2,6-di-*tert*-butylnaphthalene with the bulky alkyl group was employed under TFA conditions, tandem dimerization-tifluoroacetoxylation proceeded smoothly to give **10** in 84% yield as a sole product. These results demonstrate the potential for furthering the scope and utility of the novel reactions described above.



Scheme 8. Oxidative trifluoroacetoxylation and dichloroacetoxylation of pyrene.



Scheme 9. Oxidative transformations of perylene and naphthalene.

Conclusion

In summary, we have reported a novel, direct acetoxylation of aromatics with molecular oxygen as the terminal oxidant catalyzed by rhodium. This method is more advantageous compared to the existing C−H bond oxygenation reactions owing to the mild conditions employed and the facile recyclability of the heterogeneous catalyst used. Our protocol provides an operationally simple and efficient approach for the synthesis of valuable organic compounds and is expected to be applicable to a range of diverse dehydrogenative C−O couplings. Further studies regarding synthetic applications and mechanistic details are underway in our laboratory.

Experimental Section

General Methods. NMR spectra were recorded on a JEOL AL-400, Varian 400-MR, Varian 500-MR, Bruker AVANCE III HD-500, or JEOL JNM-ECA-600 spectrometer, and as the referenced standard (^{1}H NMR at 0.00 ppm (TMS), ^{13}C NMR at 77.0 ppm ($CDCl_3$)). Chemical sifts are reported in ppm. Peak multiplicities are used the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sept, septet; m, multiplet; br, broadend. IR spectra were recorded on a JASCO FT/IR-4200 or Shimadzu FT/IR-8300 spectrometer. Mass spectra and high resolution mass spectra were obtained on a JEOL JMS-K9, JEOL JMS-700, or Waters SYNAPT G2-Si HDMS mass spectrometer. Elemental analyses were performed with PerkinElmer 2400 series II CHNS/O analyzer. Melting points were recorded on a Yanaco MP-500D or SRS Opti Melt MPA 100 apparatus and are uncorrected. Analytical TLC was performed on precoated plates (0.25 mm, Merck silica gel 60 F_{254}). Column chromatography was performed on silica gel (40−50 and 63−210 μm).

Representative Procedure A for synthesis of *N*-2-anthracenyl amide: *N*-(2'-Anthracenyl)-2-methoxy-4-nitrobenzamide (3e)

To a solution of 2-methoxy-4-nitrobenzoic acid (591 mg, 3.0 mmol) in CH_2Cl_2 (20 mL) were added oxalyl chloride (0.26 mL, 3.0 mmol) and DMF (0.1 mL) at 0 °C and then stirred for 1 h. 2-Aminoanthrathene (386 mg, 2.0 mmol) and triethylamine (0.83 mL, 6.0 mmol) were added at 0 °C, and the resulting mixture was stirred at rt for 24 h. The reaction was quenched by the addition of a saturated $NaHCO_3$ solution and extracted with AcOEt. The combined organic layer was washed with brine, dried over with Na_2SO_4, filtered and concentrated in vacuo to give a crude product, which was purified by recrystallization from AcOEt to afford 600 mg (81%) of **3e** as red prisms (mp. 238−245 °C). ^{1}H-NMR (400 MHz, DMSO-*d6*) δ: 10.65 (1H, s), 8.68 (1H, d, *J* = 2.0 Hz), 8.50 (2H, s), 8.07 (1H, d, *J* = 8.2 Hz), 8.06-8.02 (2H, m), 7.94 (1H, dd, *J* = 2.8, 8.2 Hz), 7.93 (1H, s), 7.86 (1H, d, *J* = 9.2 Hz), 7.67 (1H, dd, *J* = 2.0, 9.2 Hz), 7.52-7.44 (2H, m), 4.02 (3H, s). ^{13}C-NMR (100 MHz, DMSO-*d6*) δ: 163.6 (s), 156.8 (s), 149.3 (s), 135.7 (s), 131.8 (s), 131.7 (s), 131.5 (s), 130.6 (s), 130.2 (d), 128.9 (d), 128.7 (s), 128.0 (d), 127.7 (d), 125.9 (d), 125.6 (d), 125.3 (d), 125.1 (d), 121.1 (d), 115.5 (d), 114.8 (d), 106.8 (d), 56.6 (q). IR (KBr): 3369, 3099, 3053, 2947, 1674, 1562, 1522, 1018 cm^{-1}. MS (EI) *m/z*: 372 (M^+, 100%). HRMS (EI) *m/z* calcd for $C_{22}H_{16}N_2O_4$ (M^+): 372.1110, found: 372.1110.

***N*-2-Anthracenylacetamide (3a)** [32]

To a solution of 2-aminoanthrathene (3.1 g, 16 mmol) in CH_2Cl_2 (160 mL) were added acetyl chloride (1.7 mL, 24 mmol) and pyridine (3.9 mL, 48 mmol) at rt and then stirred for 15 h. The reaction mixture was filtered and concentrated in vacuo to give a crude product, which was purified by reprecipitation from THF-MeOH to afford 2.4 g (64%) of **3a** as colorless needles (mp. 246−248 °C). ^{1}H-NMR (400 MHz, DMSO-*d6*) δ: 10.17 (brs, 1H), 8.47 (s, 1H), 8.47 (s, 1H), 8.42 (s, 1H), 8.02 (d, *J* = 9.2 Hz, 3H), 7.54 (d, *J* = 9.2 Hz, 1H), 7.50-7.42 (m, 2H), 2.12 (s, 3H). MS (EI) *m/z*: 235 (M^+), 193 (M^+-CH_2C=O, 100%). HRMS (EI) *m/z* calcd for $C_{16}H_{13}NO$ (M^+): 235.0997, found: 235.0998.

***N*-2-Anthracenylbenzamide (3b)** [33]

Yield 268 mg (23%) from 2-aminoanthrathene (772 mg, 4.0 mmol) using Representative Procedure A. Pale gray solids (mp. 270 °C (dec.); AcOEt). ^{1}H-NMR (600 MHz, DMSO-*d6*) δ: 10.57 (1H, s), 8.68 (1H, s), 8.51 (1H, s), 8.48 (1H, s), 8.07-8.01 (5H, m), 7.85 (1H, d, *J* = 8.9 Hz), 7.62-7.45 (5H, m). ^{13}C-NMR (150 MHz, DMSO-*d6*) δ: 166.0 (s), 136.3 (s), 134.9 (s), 131.7 (d), 131.6 (s), 130.5 (s), 128.7 (s), 128.6 (d), 128.4 (d), 128.1 (d), 127.79 (d), 127.75 (d), 125.8 (d), 125.6 (d), 125.2 (d), 125.0 (d), 121.9 (d), 115.3 (d). IR (KBr): 3259, 3051, 1643, 1564, 1546 cm^{-1}. MS (EI) *m/z*: 297 (M^+), 105 (PhC=O, 100%). HRMS (EI) *m/z* calcd for $C_{21}H_{15}NO$ (M^+): 297.1154, found: 297.1153.

***N*-(2'-Anthracenyl)-2-methoxybenzamide (3c)**

To a solution of 2-aminoanthrathene (386 mg, 2.0 mmol) and 2-methoxybenzoic acid (685 mg, 4.5 mmol) in CH_2Cl_2 (20 mL) were added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (863 mg, 4.5 mmol) and DMAP (540 mg, 4.5 mmol) at rt and then stirred for 21 h. 1M HCl was added and the resulting mixture was extracted with AcOEt. The combined organic layer was washed with brine, dried over with Na_2SO_4, filtered and concentrated in vacuo to give a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 30%) to afford 367 mg (56%) of **3c** as pale brown solids (mp. 166−168 °C). ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 10.03 (1H, s), 8.66 (1H, s), 8.41 (1H, s), 8.37 (1H, s), 8.36 (1H, d, *J* = 8.2 Hz), 8.00-7.95 (3H, m), 7.53 (1H, t, *J* = 8.2 Hz), 7.50 (1H, d, *J* = 9.0 Hz), 7.48-7.40 (2H, m), 7.18 (1H, t, *J* = 8.2 Hz), 7.07 (1H, d, *J* = 8.2 Hz), 4.11 (3H, s). ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 163.5 (s), 157.3 (s), 135.1 (s), 133.3 (d), 132.6 (d), 132.22 (s), 132.19 (s), 131.1 (s), 129.3 (s), 129.1 (d), 128.2 (d), 128.0 (d), 126.0 (d), 125.8 (d), 125.5 (d), 125.0 (d), 121.8 (d),

121.4 (d), 116.2 (d), 111.6 (d), 56.3 (q). IR (KBr): 3300, 1672, 1568, 1462 cm^{-1}. MS (EI) *m/z*: 327 (M^+, 100%), 135 (2-$MeOC_6H_4C$=O). HRMS (EI) *m/z* calcd for $C_{22}H_{17}NO_2$ (M^+): 327.1259, found: 327.1259.

_N_-(2'-Anthracenyl)-4-fluoro-2-methoxybenzamide (3d)

Yield 300 mg (43%) from 2-aminoanthrathene (386 mg, 2.0 mmol) using Representative Procedure A. Pale brown solids (mp. 188−190 °C; AcOEt). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 9.84 (1H, brs), 8.63 (1H, s), 8.41-8.35 (3H, m), 8.01-7.96 (3H, m), 7.51-7.42 (3H, m), 6.88 (1H, ddd, J = 2.4, 8.0 Hz, J_{C-F} = 8.0 Hz), 6.80 (1H, dd, J = 2.4 Hz, J_{C-F} = 8.0 Hz), 4.12 (3H, s). ^{13}C-NMR (150 MHz, DMSO-*d6*) δ: 164.4 (s, d: J_{C-F} = 246 Hz), 164.0 (s), 158.4 (s, d: J_{C-F} = 10 Hz), 135.9 (s), 131.7 (s), 131.6 (d, d: J_{C-F} = 5.7 Hz), 130.5 (s), 128.74 (d), 128.66 (s), 128.1 (d), 127.7 (d), 125.8 (d), 125.6 (d), 125.1 (d), 125.0 (d), 121.5 (d), 121.4 (s), 114.6 (d), 107.1 (d, d: J_{C-F} = 22 Hz), 100.3 (d, d: J_{C-F} = 26 Hz), 56.6 (q). IR (KBr): 3350, 1670, 1589, 1250 cm^{-1}. MS (EI) *m/z*: 345 (M^+, 100%), 153. HRMS (EI) *m/z* calcd for $C_{22}H_{16}FNO_2$ (M^+): 345.1165, found: 345.1165.

_N_-(2'-Anthracenyl)-2,4-dimethylbenzamide (3f)

Yield 139 mg (25%) from 2-aminoanthrathene (386 mg, 2.0 mmol) using Representative Procedure A. Pale brown needles (mp. 209−211 °C; AcOEt). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 9.91 (1H, s), 8.64 (1H, d, J = 2.0 Hz), 8.39 (1H, s), 8.36 (1H, s), 8.33 (1H, d, J = 8.7 Hz), 8.00-7.95 (3H, m), 7.49 (1H, dd, J = 2.0, 9.2 Hz), 7.46-7.40 (2H, m), 6.69 (1H, dd, J = 2.4, 8.7 Hz), 6.57 (1H, d, J = 2.4 Hz), 4.08 (3H, s), 3.89 (3H, s). ^{13}C-NMR (100 MHz, DMSO-*d6*) δ: 163.9 (s), 163.0 (s), 158.4 (s), 135.9 (s), 132.0 (d), 131.68 (s), 131.65 (s), 130.4 (s), 128.64 (d), 128.62 (s), 128.0 (d), 127.7 (d), 125.8 (d), 125.6 (d), 125.0 (d), 124.9 (d), 121.8 (d), 116.0 (s), 114.5 (d), 105.8 (d), 98.6 (d), 56.2 (q), 55.6 (q). IR (KBr): 3354, 2841, 1656, 1585 cm^{-1}. MS (FAB) *m/z*: 358 (M^++H), 357 (M^+). HRMS (FAB) *m/z* calcd for $C_{23}H_{19}NO_3$ (M^+): 357.1365, found: 357.1369.

_N_-(2'-Anthracenyl)-2,5-dimethylbenzamide (3g)

To a solution of 2-aminoanthrathene (386 mg, 2.0 mmol) and 2,5-dimethoxybenzoic acid (728 mg, 4.0 mmol) in CH_2Cl_2 (20 mL) were added 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (575 mg, 3.0 mmol) and DMAP (360 mg, 3.0 mmol) at rt and then stirred for 73 h. 1M HCl was added and the resulting mixture was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over with Na_2SO_4, filtered and concentrated in

vacuo to give a crude product, which was purified by reprecipitation from AcOEt to afford 403 mg (56%) of **3g** as yellow brown solids (mp. 203−205 °C). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 10.15 (1H, s), 8.65 (1H, s), 8.38 (1H, s), 8.34 (1H, s), 7.96-7.94 (3H, m), 7.89 (1H, d, *J* = 2.9 Hz), 7.45-7.42 (3H, m), 7.08 (1H, dd, *J* = 2.9, 9.2 Hz), 7.00 (1H, d, *J* = 9.2 Hz), 4.01 (3H, s), 3.85 (3H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 163.1 (s), 154.2 (s), 151.5 (s), 135.0 (s), 132.16 (s), 132.14 (s), 131.1 (s), 129.3 (s), 129.0 (d), 128.1 (d), 127.9 (d), 126.0 (d), 125.7 (d), 125.5 (d), 124.9 (d), 122.2 (s), 121.3 (d), 119.9 (d), 116.0 (d), 115.6 (d), 113.2 (d), 56.8 (q), 55.8 (q). IR (KBr): 3300, 2988, 2839, 1676 cm^{-1}. MS (EI) *m/z*: 357 (M^+), 165 ($(MeO)_2C_6H_3C$=O, 100%). HRMS (EI) *m/z* calcd for $C_{23}H_{19}NO_3$ (M^+): 357.1365, found: 357.1365.

_N_-(2'-Anthracenyl)-3,4-dimethoxybenzamide (3h)

To a solution of 2-aminoanthrathene (386 mg, 2.0 mmol) and 3,4-dimethoxybenzoic acid (1.1 g, 6.0 mmol) in CH_2Cl_2 (20 mL) were added *N*,*N*-diisopropylcarbodiimide (0.92 mL, 6.0 mmol) and DMAP (49 mg, 0.40 mmol) at rt and then stirred for 42 h. 1M HCl was added and the resulting mixture was extracted with AcOEt. The combined organic layer was washed with brine, dried over with Na_2SO_4, filtered and concentrated in vacuo to give a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 30%) to afford 637 mg (89%) of **3h** as pale yellow solids (mp. 214−216 °C). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.51 (1H, s), 8.38 (2H, s), 8.02-7.95 (4H, m), 7.57-7.56 (2H, m), 7.47-7.45 (3H, m), 6.93 (1H, d, *J* = 8.2 Hz), 3.98 (3H, s), 3.96 (3H, s). ^{13}C-NMR (100 MHz, DMSO-*d6*) δ: 165.2 (s), 151.7 (s), 148.3 (s), 136.3 (s), 131.63 (s), 131.55 (s), 130.5 (s), 128.6 (s), 128.4 (d), 128.0 (d), 127.7 (d), 126.9 (s), 125.8 (d), 125.5 (d), 125.0 (d), 124.9 (d), 122.0 (d), 121.1 (d), 115.3 (d), 111.1 (d), 111.0 (d), 55.6 (q). IR (KBr): 3238, 2827, 1666 cm^{-1}. MS (EI) *m/z*: 357 (M^+, 100%), 165 ($(MeO)_2C_6H_3C$=O). HRMS (EI) *m/z* calcd for $C_{23}H_{19}NO_3$ (M^+): 357.1365, found: 357.1367.

_N_-2-Anthracenylpivalamide (3i)

To a solution of 2-aminoanthrathene (386 mg, 2.0 mmol) in CH_2Cl_2 (20 mL) were added pivaloyl chloride (0.36 mL, 3.0 mmol) and pyridine (0.24 mL, 3.0 mmol) at rt and then stirred for 12 h. The reaction was quenched by the addition of 1M HCl and extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over with Na_2SO_4, filtered and concentrated in vacuo to give a crude product, which was purified by recrystallization from $CHCl_3$ to afford 392 mg (77%) of **3i** as brown needles (mp. 253−255 °C). ^{1}H-NMR (600 MHz, DMSO-*d6*) δ: 9.44 (1H, s), 8.48 (1H, s), 8.46 (1H, s), 8.41 (1H, s), 8.05-8.00 (3H, m), 7.71 (1H, d, *J* = 9.6 Hz), 7.50-7.42 (2H, m), 1.28 (9H, s). ^{13}C-NMR (150 MHz, DMSO-*d6*) δ: 176.9 (s),

136.4 (s), 131.6 (s), 130.4 (s), 128.5 (s), 128.3 (d), 128.0 (d), 127.7 (d), 125.7 (d), 125.5 (d), 124.89 (d), 124.86 (d), 122.0 (d), 115.0 (d), 39.3 (s), 27.2 (q). IR (KBr): 3313, 2974, 1666, 1566, 1225 cm^{-1}. MS (EI) *m/z*: 277 (M^+, 100%), 193. HRMS (EI) *m/z* calcd for $C_{19}H_{19}NO$ (M^+): 277.1467, found: 277.1468.

_N_-(2-Anthracenyl)-trifluoroacetamide (3j)

To a solution of 2-aminoanthrathene (386 mg, 2.0 mmol) in CH_2Cl_2 (6 mL) were added trifluoroacetic anhydride (0.42 mL, 3.0 mmol) and pyridine (0.24 mL, 3.0 mmol) at rt and then stirred for 1 h. The reaction was quenched by the addition of H_2O and extracted with AcOEt. The combined organic layer was washed with brine, dried over with Na_2SO_4, filtered and concentrated in vacuo to give a crude product, which was purified by recrystallization from $CHCl_3$-AcOEt to afford 420 mg (73%) of **3j** as brown powder (mp. 214 ℃ (dec.)). ^{1}H-NMR (400 MHz, DMSO-*d6*) δ: 11.51 (1H, brs), 8.55 (2H, s), 8.51 (1H, s), 8.12 (1H, d, J = 9.2 Hz), 8.10-8.04 (2H, m), 7.72 (1H, d, J = 9.2 Hz), 7.54-7.47 (2H, m). ^{13}C-NMR (100 MHz, DMSO-*d6*) δ: 154.7 (s, q: $J_{C\text{-}F}$ = 37 Hz), 133.4 (s), 131.7 (s), 131.0 (s), 130.8 (s), 129.1 (d), 129.0 (s), 128.0 (d), 127.8 (d), 126.0 (d), 125.87 (d), 125.83 (d), 125.5 (d), 121.0 (d), 117.49 (d), 115.8 (s, q: $J_{C\text{-}F}$ = 289 Hz). IR (KBr): 3246, 1720, 1539, 1462 cm^{-1}. MS (EI) *m/z*: 289 (M^+, 100%), 165. HRMS (EI) *m/z* calcd for $C_{16}H_{10}F_3NO$ (M^+): 289.0714, found: 289.0715.

Ethyl 3-(2'-anthracenylamino)-3-oxopropanoate (3k)

To a solution of 2-aminoanthrathene (386 mg, 2.0 mmol) in CH_2Cl_2 (20 mL) were added ethyl malonyl chloride (452 mg, 3.0 mmol) and pyridine (0.24 mL, 3.0 mmol) at rt and then stirred for 48 h. The reaction was quenched by the addition of 1M HCl and extracted with CH_2Cl_2. The combined organic layer was filtered and concentrated in vacuo to give a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 30%) to afford 488 mg (79%) of **3k** as pale brown solids (mp. 193−195 ℃). ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 9.48 (1H, brs), 8.46 (1H, s), 8.38 (1H, s), 8.36 (1H, s), 8.00-7.95 (3H, m), 7.48-7.42 (3H, m), 4.30 (2H, q, J = 7.2 Hz), 3.55 (2H, s), 1.36 (3H, t, J = 7.2 Hz). ^{13}C-NMR (150 MHz, ACETONE-*d6*) δ: 168.5 (s), 165.0 (s), 136.8 (s), 133.2 (s), 133.0 (s), 132.0 (s), 130.1 (s), 129.8 (d), 129.0 (d), 128.7 (d), 126.9 (d), 126.4 (d), 126.2 (d), 125.8 (d), 121.6 (d), 115.5 (d), 61.6 (t), 44.5 (t), 14.4 (q). IR (KBr): 3230, 3084, 2982, 1743, 1659, 1574 cm^{-1}. MS (EI) *m/z*: 307 (M^+, 100%), 219 (M^+-AcOEt), 193. HRMS (EI) *m/z* calcd for $C_{19}H_{17}NO_3$ (M^+): 307.1208, found: 307.1197.

***N*-(2-Anthracenyl)picolinamide (3l)**

Yield 318 mg (53%) from 2-aminoanthrathene (386 mg, 2.0 mmol) using Representative Procedure A. Pale brown solids (mp. 237−239 °C; AcOEt). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 10.25 (1H, brs), 8.73 (1H, s), 8.67 (1H, d, *J* = 4.3 Hz), 8.43 (1H, s), 8.40 (1H, s), 8.37 (1H, d, *J* = 8.0 Hz), 8.04 (1H, d, *J* = 9.2 Hz), 8.03-7.92 (3H, m), 7.66 (1H, d, *J* = 9.2 Hz), 7.52 (1H, dd, *J* = 4.3, 8.0 Hz), 7.50-7.42 (2H, m). ^{13}C-NMR (150 MHz, DMSO-*d6*) δ: 162.9 (s), 149.9 (s), 148.5 (d), 138.2 (d), 135.4 (s), 131.7 (s), 131.5 (s), 130.6 (s), 128.8 (s), 128.7 (d), 128.1 (d), 127.8 (d), 127.0 (d), 125.9 (d), 125.7 (d), 125.3 (d), 125.1 (d), 122.5 (d), 121.8 (d), 115.4 (d). IR (KBr): 3325, 3053, 1624, 1570 cm^{-1}. MS (FAB) *m/z*: 299 (M^++H), 298 (M^+). HRMS (FAB) *m/z* calcd for $C_{20}H_{14}N_2O$ (M^+): 298.1106, found: 298.1109.

***N*-(2'-Anthracenyl)furan-2-carboxamide (3m)**

Yield 322 mg (56%) from 2-aminoanthrathene (386 mg, 2.0 mmol) using Representative Procedure A. Brown solids (mp. 214−216 °C; AcOEt). ^{1}H-NMR (400 MHz, DMSO-*d6*) δ: 10.45 (1H, brs), 8.62 (1H, s), 8.49 (1H, s) 8.47 (1H, s), 8.08-7.96 (4H, m), 7.83 (1H, d, *J* = 8.7 Hz), 7.50-7.40 (3H, m), 6.73 (1H, s). ^{13}C-NMR (100 MHz, DMSO-*d6*) δ: 156.5 (s), 147.5 (s), 145.9 (d), 135.6 (s), 131.7 (s), 131.5 (s), 130.6 (s), 128.7 (s), 128.6 (d), 128.1 (d), 127.7 (d), 125.8 (d), 125.6 (d), 125.2 (d), 125.0 (d), 121.7 (d), 115.4 (d), 114.9 (d), 112.2 (d). IR (KBr): 3290, 3049, 1672, 1560, 1539 cm^{-1}. MS (EI) *m/z*: 287 (M^+, 100%), 165. HRMS (EI) *m/z* calcd for $C_{19}H_{13}NO_2$ (M^+): 287.0946, found: 287.0946.

Representative Procedure B for the Aerobic Oxidative Trifluoroacethoxylation: 2-Acetamido-9-anthracenyl trifluoroacetate (4a)

To a solution of **3a** (40 mg, 0.17 mmol) in TFA-benzotrifluoride (2: 1, 1 mL) was added 5% Rh/C (34 mg, 0.017 mmol, 10 mol %) was added. After stirred at rt under O_2 (balloon) for 3 h, the reaction was quenched by the addition of a saturated $NaHCO_3$ solution and extracted with AcOEt. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and the solvent was evaporated to afford the crude product, which was purified by silica gel column chromatography (AcOEt/hexane = 20%) to yield 45 mg (76%) of **4a** as yellow green solids. ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.22 (1H, s), 8.05 (1H, s), 7.94-7.90 (2H, m), 7.81 (1H, d, *J* = 8.4 Hz), 7.77 (1H, d, *J* = 8.4 Hz), 7.54 (1H, t, *J* = 8.4 Hz), 7.45 (1H, t, *J* = 8.4 Hz), 7.34 (1H, d, *J* = 8.4 Hz), 2.16 (3H, s). ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 151.8 (s), 140.5 (s, q: J_{C-F} = 35 Hz), 126.8 (s), 124.1 (s), 120.2 (s), 119.2 (d), 118.7 (s), 118.3 (d), 117.5 (d), 116.3 (d), 115.9 (d), 114.1 (s), 113.8 (s), 112.1 (d), 111.1 (d), 107.4 (s, q: J_{C-F} = 229 Hz), 101.7 (d), 34.7 (q). IR

(KBr): 3273, 1793, 1668 cm^{-1}. MS (EI) *m/z*: 347 (M^+, 100%), 223, 208. HRMS (EI) *m/z* calcd for $C_{18}H_{12}F_3NO_3$ (M^+): 347.0769, found: 347.0771. The regioselectivity of **4a** was determined by HMBC correlation.

Representative Procedure C: 2-Benzamido-9-anthracenyl trifluoroacetate (4b)

To a solution of **3b** (36 mg, 0.12 mmol) in TFA-benzotrifluoride (2: 1, 1 mL) was added 5% Rh/C (28 mg, 0.012 mmol) and then stirred at rt under O_2 (balloon) for 42 h. The reaction mixture was filtered and concentrated in vacuo to give a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 10%) to yield 34 mg (55%) of **4b** as yellow solids. ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.28 (1H, s), 8.22 (1H, s), 8.13 (1H, brs), 7.94 (2H, t, J = 8.6 Hz), 7.86 (2H, d, J = 8.2 Hz), 7.79 (1H, d, J = 8.9 Hz), 7.62 (1H, dd, J = 2.4, 8.9 Hz), 7.56-7.52 (2H, m), 7.48-7.42 (2H, m). ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 166.1 (s), 156.3 (s, q: $J_{C\text{-}F}$ = 43 Hz), 139.2 (s), 136.7 (s), 134.5 (s), 132.1 (d), 131.0 (s), 129.7 (d), 129.2 (s), 128.8 (d), 128.6 (d), 127.6 (d), 127.1 (d), 126.2 (d), 125.5 (d), 123.5 (s), 123.3 (s), 121.4 (d), 119.7 (d), 115.0 (s, q: $J_{C\text{-}F}$ = 286 Hz), 107.7 (d). IR (KBr): 3339, 3062, 1803, 1651 cm^{-1}. MS (EI) *m/z*: 409 (M^+, 100%), 312 (M^+-CF_3CO). HRMS (EI) *m/z* calcd for $C_{23}H_{14}F_3NO_3$ (M^+): 409.0926, found: 409.0930.

2-(2'-Methoxybenzamido)-9-anthracenyl trifluoroacetate (4c)

Yield 44 mg (83%) from **3c** (39 mg, 0.12 mmol) according to Representative Procedure C (conditions: rt under O_2 for 0.5 h). Yellow solids. ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 10.14 (1H, s), 8.43 (1H, s), 8.35 (1H, d, J = 7.8 Hz), 8.33 (1H, s), 8.08-8.03 (2H, m), 7.85 (1H, d, J = 7.8 Hz), 7.78 (1H, d, J = 7.8 Hz), 7.60-7.49 (3H, m), 7.18 (1H, t, J = 7.8 Hz), 7.08 (1H, d, J = 7.8 Hz), 4.12 (3H, s). ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 163.6 (s), 157.2 (s), 156.2 (s, q: $J_{C\text{-}F}$ = 43 Hz), 139.2 (s), 137.2 (s), 133.5 (d), 132.7 (d), 130.8 (s), 129.6 (d), 129.3 (s), 128.6 (d), 127.4 (d), 126.1 (d), 125.4 (d), 123.6 (s), 123.5 (s), 122.0 (d), 121.8 (d), 121.5 (s), 119.8 (d), 115.1 (s, q: $J_{C\text{-}F}$ = 286 Hz), 111.5 (d), 107.5 (d), 56.2 (q). IR (KBr): 3336, 2947, 2845, 1803, 1674 cm^{-1}. MS (EI) *m/z*: 439 (M^+), 135 (2-$MeOC_6H_4CO$, 100%). HRMS (EI) *m/z* calcd for $C_{24}H_{16}F_3NO_4$ (M^+): 439.1031, found: 439.1030.

2-(2'-Methoxy-4'-fluorobenzamido)-9-anthracenyl trifluoroacetate (4d)

Yield 32 mg (58%) from **3d** (41 mg, 0.12 mmol) according to Representative Procedure C (conditions: rt under O_2 for 1.5 h). Yellow solids. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 9.93 (1H, brs),

8.43 (1H, s), 8.37 (1H, dd, J = 8.7 Hz, $J_{C\text{-}F}$ = 6.8 Hz), 8.32 (1H, d, J = 1.9 Hz), 8.08-8.02 (2H, m), 7.85 (1H, d, J = 8.7 Hz), 7.73 (1H, dd, J = 1.9, 8.7 Hz), 7.61-7.46 (2H, m), 6.88 (1H, ddd, J = 1.9, 8.7 Hz, $J_{C\text{-}F}$ = 10.0 Hz), 6.79 (1H, dd, J = 1.9 Hz, $J_{C\text{-}F}$ = 10.8 Hz), 4.11 (3H, s). ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 165.8 (s, d: $J_{C\text{-}F}$ = 253 Hz), 162.7 (s), 158.6 (s, d: $J_{C\text{-}F}$ = 10 Hz), 156.2 (s, q: $J_{C\text{-}F}$ = 43 Hz), 139.3 (s), 137.0 (s), 134.8 (d, d: $J_{C\text{-}F}$ = 10 Hz), 130.9 (s), 129.6 (d), 129.3 (s), 128.6 (d), 127.5 (d), 126.1 (d), 125.5 (d), 123.6 (s), 123.5 (s), 121.9 (d), 119.8 (d), 117.8 (s, d: $J_{C\text{-}F}$ = 2.9 Hz), 115.1 (s, q: $J_{C\text{-}F}$ = 286 Hz), 108.79 (d, d: $J_{C\text{-}F}$ = 22 Hz), 107.6 (d), 99.7 (d, d: $J_{C\text{-}F}$ = 27 Hz), 56.6 (q). IR (KBr): 3344, 1791, 1670, 1600, 1152 cm^{-1}. MS (EI) *m/z*: 457 (M^+), 153 (100%). HRMS (EI) *m/z* calcd for $C_{24}H_{15}F_4NO_4$ (M^+): 457.0937, found: 457.0934.

2-(2'-Methoxy-4'-Nitrobenzamido)-9-anthracenyl trifluoroacetate (4e)

Yield 37 mg (64%) from **3e** (45 mg, 0.12 mmol) according to Representative Procedure C (conditions: rt under O_2 for 1.5 h). Yellow solids. ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 9.88 (1H, brs), 8.51 (1H, d, J = 8.9 Hz), 8.40 (2H, s), 8.05 (1H, d, J = 8.9 Hz), 8.03 (1H, d, J = 8.9 Hz), 8.00 (1H, dd, J = 1.8, 8.9 Hz), 7.91 (1H, d, J = 1.8 Hz), 7.85 (1H, d, J = 8.9 Hz), 7.63 (1H, d, J = 8.9 Hz), 7.59 (1H, dd, J = 7.2, 8.9 Hz), 7.51 (1H, dd, J = 7.2, 8.9 Hz), 4.20 (3H, s). ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 161.4 (s), 157.2 (s), 156.2 (s, q: $J_{C\text{-}F}$ = 43 Hz), 150.7 (s), 139.4 (s), 136.4 (s), 134.0 (d), 131.1 (s), 129.9 (d), 129.3 (s), 128.6 (d), 127.7 (d), 126.9 (s), 126.2 (d), 125.7 (d), 123.6 (s), 123.4 (s), 121.6 (d), 119.9 (d), 116.4 (d), 115.1 (s, q: $J_{C\text{-}F}$ = 286 Hz), 108.3 (d), 107.0 (d), 57.1 (q). IR (KBr): 3352, 1788, 1670, 1522 cm^{-1}. MS (FAB) *m/z*: 485 (M^++H), 484 (M^+), 154 (100%). HRMS (FAB) *m/z* calcd for $C_{24}H_{15}F_3N_2O_6$ (M^+): 484.0882, found: 484.0882.

2-(2',4'-Dimethoxybenzamido)-9-anthracenyl trifluoroacetate (4f)

Yield 52 mg (93%) from **3f** (43 mg, 0.12 mmol) according to Representative Procedure B (conditions: rt under O_2 for 1 h). Yellow solids. ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 10.00 (1H, s), 8.37 (1H, s), 8.31 (1H, s), 8.30 (1H, d, J = 9.7 Hz), 8.03-7.98 (2H, m), 7.83 (1H, d, J = 8.4 Hz), 7.71 (1H, dd, J = 2.0, 9.7 Hz), 7.58-7.44 (2H, m), 6.67 (1H, dd, J = 2.4, 8.4 Hz), 6.53 (1H, d, J = 2.4 Hz), 4.05 (3H, s), 3.88 (3H, s). ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 163.9 (s), 163.3 (s), 158.5 (s), 156.2 (s, q: $J_{C\text{-}F}$ = 43 Hz), 139.0 (s), 137.4 (s), 134.3 (d), 130.6 (s), 129.4 (d), 129.1 (s), 128.6 (d), 127.3 (d), 126.0 (d), 125.2 (d), 123.6 (s), 123.4 (s), 121.9 (d), 119.7 (d), 115.1 (s, q: $J_{C\text{-}F}$ = 286 Hz), 114.3 (s), 107.0 (d), 105.8 (d), 98.6 (d), 56.1 (q), 55.5 (q). IR (KBr): 3348, 3008, 1793, 1670, 1550 cm^{-1}. MS (EI) *m/z*: 469 (M^+), 165 (2,4-$(MeO)_2C_6H_3CO$, 100%). HRMS (EI) *m/z* calcd for $C_{25}H_{18}F_3NO_5$ (M^+): 469.1137, found: 469.1138.

2-(2',5'-Dimethoxybenzamido)-9-anthracenyl trifluoroacetate (4g)

Yield 48 mg (86%) from **3g** (43 mg, 0.12 mmol) according to Representative Procedure C (conditions: rt under O_2 for 1 h). Yellow solids. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 10.26 (1H, s), 8.39 (1H, s), 8.34 (1H, d, *J* = 1.9 Hz), 8.02 (2H, d, *J* = 8.7 Hz), 7.88 (1H, d, *J* = 2.9 Hz), 7.84 (1H, d, *J* = 8.7 Hz), 7.71 (1H, dd, *J* = 1.9, 8.7 Hz), 7.57 (1H, dd, *J* = 6.8, 8.7 Hz), 7.48 (1H, dd, *J* = 6.8, 8.7 Hz), 7.07 (1H, dd, *J* = 2.9, 9.7 Hz), 6.99 (1H, d, *J* = 9.7 Hz), 4.05 (3H, s), 3.88 (3H, s). ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 163.3 (s), 156.2 (s, q: $J_{C\text{-}F}$ = 43 Hz), 154.2 (s), 151.5 (s), 139.2 (s), 137.2 (s), 130.8 (s), 129.6 (d), 129.3 (s), 128.6 (d), 127.4 (d), 126.1 (d), 125.4 (d), 123.6 (s), 123.5 (s), 122.0 (s), 121.9 (d), 120.3 (d), 119.8 (d), 115.6 (d), 115.1 (s, q: $J_{C\text{-}F}$ = 284 Hz), 113.3 (d), 107.5 (d), 56.8 (q), 55.9 (q). IR (KBr): 3315, 2827, 1795, 1631, 1481 cm^{-1}. MS (EI) *m/z*: 469 (M^+), 165 (2,5-$(MeO)_2C_6H_3CO$, 100%). HRMS (EI) *m/z* calcd for $C_{25}H_{18}F_3NO_5$ (M^+): 469.1137, found: 469.1139.

2-(3',4'-Dimethoxybenzamido)-9-anthracenyl trifluoroacetate (4h)

Yield 48 mg (85%) from **3h** (43 mg, 0.12 mmol) according to Representative Procedure C (conditions: rt under O_2 for 6 h). Yellow solids. ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.39 (1H, s), 8.25 (1H, s), 8.04 (1H, d, *J* = 8.9 Hz), 8.03 (1H, d, *J* = 8.9 Hz), 8.01 (1H, brs), 7.84 (1H, d, *J* = 8.9 Hz), 7.70 (1H, dd, *J* = 1.8, 8.9 Hz), 7.58 (1H, dd, *J* = 6.6, 8.9 Hz), 7.54 (1H, d, *J* = 1.8 Hz), 7.50 (1H, dd, *J* = 6.6, 8.9 Hz), 7.42 (1H, dd, *J* = 1.8, 8.2 Hz), 6.90 (1H, d, *J* = 8.2 Hz), 3.98 (3H, s), 3.95 (3H, s). ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 165.6 (s), 156.3 (s, q: $J_{C\text{-}F}$ = 43 Hz), 152.4 (s), 149.4 (s), 139.3 (s), 136.9 (s), 131.0 (s), 129.8 (d), 129.2 (s), 128.7 (d), 127.6 (d), 127.2 (s), 126.2 (d), 125.6 (d), 123.6 (s), 123.5 (s), 121.5 (d), 119.8 (d), 119.5 (d), 115.1 (s, q: $J_{C\text{-}F}$ = 286 Hz), 110.9 (d), 110.4 (d), 107.5 (d), 56.2 (q), 56.1 (q). IR (KBr): 3325, 2960, 2839, 1782, 1647, 1591 cm^{-1}. MS (EI) *m/z*: 469 (M^+, 100%), 165 (3,4-$(MeO)_2C_6H_3CO$). HRMS (EI) *m/z* calcd for $C_{25}H_{18}F_3NO_5$ (M^+): 469.1137, found: 469.1139.

2-Pivalamido-9-anthracenyl trifluoroacetate (4i)

Yield 50 mg (86%) from **3i** (43 mg, 0.12 mmol) according to Representative Procedure B (conditions: rt under O_2 for 2 h). Yellow solids. ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.35 (1H, s), 8.11 (1H, s), 8.00 (1H, d, *J* = 8.9 Hz), 7.97 (1H, d, *J* = 8.9 Hz), 7.80 (1H, d, *J* = 8.9 Hz), 7.61-7.45 (4H, m), 1.36 (9H, s). ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 176.9 (s), 156.2 (s, q: $J_{C\text{-}F}$ = 43 Hz), 139.2 (s), 136.8 (s), 130.9 (s), 129.6 (d), 129.2 (s), 128.6 (d), 127.5 (d), 126.1 (d), 125.5 (d), 123.5 (s), 121.5 (d), 119.8 (d), 115.0 (s, q: $J_{C\text{-}F}$ = 286 Hz), 107.3 (d), 39.8 (s), 27.6 (q). IR

(KBr): 3348, 2966, 1799, 1660 cm^{-1}. MS (EI) *m/z*: 389 (M^+, 100%). HRMS (EI) *m/z* calcd for $C_{21}H_{18}F_3NO_3$ (M^+): 389.1239, found: 389.1238.

2-Trifluoroacetamido-9-anthracenyl trifluoroacetate (4j)

Yield 48 mg (quant.) from **3j** (35 mg, 0.12 mmol) according to Representative Procedure C (conditions: rt under O_2 for 6 h). Yellow solids. ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.47 (1H, s), 8.31 (1H, s), 8.12-8.05 (3H, m), 7.87 (1H, d, *J* = 8.9 Hz), 7.64-7.54 (3H, m). ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 156.2 (s, q: J_{C-F} = 43 Hz), 155.0 (s, q: J_{C-F} = 38 Hz), 139.7 (s), 133.7 (s), 131.7 (s), 130.4 (d), 129.4 (s), 128.6 (d), 128.0 (d), 126.4 (d), 126.2 (d), 123.7 (s), 122.8 (s), 120.1 (d), 119.9 (d), 115.6 (s, q: J_{C-F} = 287 Hz), 114.9 (s, q: J_{C-F} = 284 Hz), 109.4 (d). IR (KBr): 3340, 3169, 2926, 1801, 1722, 1595 cm^{-1}. MS (EI) *m/z*: 401 (M^+, 100%), 304 (M^+-CF_3CO). HRMS (EI) *m/z* calcd for $C_{18}H_9F_6NO_3$ (M^+): 401.0487, found: 401.0486.

Ethyl 3-oxo-[(9-trifluoroacetoxyanthracen-2-yl)amino]propanoate (4k)

Yield 93 mg (74%) from **3k** (92 mg, 0.30 mmol) according to Representative Procedure C (conditions: rt under O_2 for 2 h). Yellow solids. ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 9.60 (1H, s), 8.36 (1H, s), 8.35 (1H, s), 8.00 (1H, d, *J* = 8.9 Hz), 7.98 (1H, d, *J* = 8.9 Hz), 7.82 (1H, d, *J* = 8.2 Hz), 7.58-7.47 (3H, m), 4.29 (2H, q, *J* = 7.2 Hz), 3.54 (2H, s), 1.35 (3H, t, *J* = 7.2 Hz). ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 170.1 (s), 163.3 (s), 156.2 (s, q: J_{C-F} = 43 Hz), 139.4 (s), 136.1 (s), 131.0 (s), 129.7 (d), 129.2 (s), 128.6 (d), 127.5 (d), 126.1 (d), 125.5 (d), 123.6 (s), 123.4 (s), 121.2 (d), 119.8 (d), 115.0 (s, q: J_{C-F} = 286 Hz), 107.6 (d), 62.1 (t), 41.4 (t), 14.0 (q). IR (KBr): 3350, 2997, 2368, 1791, 1708, 1639 cm^{-1}. MS (EI) *m/z*: 419 (M^+, 100%), 322 (M^+-CF_3CO), 208. HRMS (EI) *m/z* calcd for $C_{21}H_{16}F_3NO_5$ (M^+): 419.0981, found: 419.0981.

2-Picolinamido-9-anthracenyl trifluoroacetate (4l)

Yield 33 mg (67%) from **3l** (36 mg, 0.12 mmol) according to Representative Procedure B (conditions: rt under O_2 for 23 h). Yellow solids. ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 10.31 (1H, s), 8.67-8.64 (1H, m), 8.52 (1H, d, *J* = 2.1 Hz), 8.40 (1H, s), 8.35 (1H, d, *J* = 7.6 Hz), 7.06 (1H, d, *J* = 8.9 Hz), 8.03 (1H, d, *J* = 8.9 Hz), 7.94 (1H, dt, *J* = 2.4, 7.6 Hz), 7.84 (1H, d, *J* = 8.9 Hz), 7.77 (1H, dd, *J* = 2.1, 8.9 Hz), 7.60-7.47 (3H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 162.4 (s), 156.2 (s, q: J_{C-F} = 43 Hz), 149.4 (s), 148.0 (d), 139.3 (s), 137.8 (d), 136.4 (s), 130.9 (s), 129.8 (d), 129.2 (s), 128.6 (d), 127.5 (d), 126.7 (d), 126.2 (d), 125.5 (d), 123.55 (s), 123.52 (s), 122.6 (d), 121.1 (d), 119.8 (d), 115.1 (s, q: J_{C-F} = 286 Hz), 107.1 (d). IR (KBr): 3309, 3057, 1793, 1689, 1521,

cm^{-1}. MS (EI) *m/z*: 410 (M^+, 100%), 313 (M^+-CF_3CO). HRMS (EI) *m/z* calcd for $C_{22}H_{13}F_3N_2O_3$ (M^+): 410.0878, found: 410.0878.

2-(2'-Furancarboxamido)-9-anthracenyl trifluoroacetate (4m)

Yield 41 mg (85%) from **3m** (34 mg, 0.12 mmol) according to Representative Procedure C (conditions: rt under O_2 for 20 h). Yellow solids. ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.31 (1H, s), 8.30 (1H, s), 8.26 (1H, s), 7.96 (1H, d, *J* = 8.9 Hz), 7.95 (1H, d, *J* = 8.9 Hz), 7.81 (1H, d, *J* = 8.9 Hz), 7.60-7.42 (4H, m), 7.28 (1H, d, *J* = 3.4 Hz), 6.57-6.53 (1H, m). ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 156.2 (s, q: J_{C-F} = 43 Hz), 156.2 (s), 147.4 (s), 144.4 (d), 139.2 (s), 136.1 (s), 130.9 (s), 129.8 (d), 129.1 (s), 128.6 (d), 127.5 (d), 126.1 (d), 125.5 (d), 123.5 (s), 123.3 (s), 121.0 (d), 119.7 (d), 115.7 (d), 115.0 (s, q: J_{C-F} = 284 Hz), 112.7 (d), 107.2 (d). IR (KBr): 3381, 1789, 1683, 2597 cm^{-1}. MS (EI) *m/z*: 399 (M^+, 100%), 302 (M^+-CF_3CO). HRMS (EI) *m/z* calcd for $C_{21}H_{12}F_3NO_4$ (M^+): 399.0718, found: 399.0718.

9-Anthracenyl trifluoroacetate (4n)

Yield 28 mg (59%) from anthracene (36 mg, 0.20 mmol) according to Representative Procedure C (conditions: rt under O_2 for 1 h). Recrystallization from hexane afforded **4n** as colorless needles (mp. 125-127 °C). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.49 (1H, s), 8.07 (2H, d, *J* = 8.7 Hz), 7.88 (2H, d, *J* = 8.7 Hz), 7.61-7.50 (4H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 155.7 (s, q: J_{C-F} = 43 Hz), 139.8 (s), 131.6 (s), 128.5 (d), 127.3 (d), 126.4 (d), 125.9 (d), 123.0 (s), 120.0 (d), 115.0 (s, q: J_{C-F} = 285 Hz). IR (ATR): 1792, 1338, 1224, 1137 cm^{-1}. MS (EI) *m/z*: 290 (M^+), 193 (M^+-CF_3CO, 100%). HRMS (EI) *m/z* calcd for $C_{16}H_9F_3O_2$ (M^+): 290.0555, found: 290.0561. Anal. calcd for $C_{16}H_9F_3O_2$: C, 66.21; H, 3.13, found: C, 65.87; H, 3.23.

9-Anthracenyl trichloroacetate (4o)

A mixture of anthracene (178 mg, 1.0 mmol), 5% Rh/C (309 mg, 0.15 mmol) and trichloroacetic acid (4 g) was heated to 60 °C and stirred under O_2 for 15 h. The reaction was quenched by the addition of a saturated $NaHCO_3$ solution. The resulting mixture was filtrated through a celite pad and then extracted with AcOEt. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered, concentrated in vacuo to give a crude product, which was purified by silica gel column chromatography (CH_2Cl_2/ hexane = 10-20%) to yield 227 mg (67%) of **4o**. Recrystallization from acetonitrile afforded **4o** as colorless powder (mp. 162-165 °C). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.45 (1H, s), 8.05 (2H, d, *J* = 7.5 Hz), 8.03 (2H, d,

J = 7.5 Hz), 7.59-7.49 (4H, m). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 160.7 (s), 141.0 (s), 131.7 (s), 128.5 (d), 127.1 (d), 126.1 (d), 125.8 (d), 123.4 (s), 120.3 (d), 89.8 (s). IR (ATR): 1784, 1340, 1218 cm^{-1}. MS (EI) *m/z*: 340 (M^++2), 338 (M^+), 193 (M^+-CCl_3CO, 100%). HRMS (EI) *m/z* calcd for $C_{16}H_9Cl_3O_2$ (M^+): 337.9668, found: 337.9677.

Representative Procedure D for the Aerobic Oxidative Dichloroacethoxylation:

9-Anthracenyl dichloroacetate (4p)

To a solution of anthracene (534 mg, 3.0 mmol) in dichloroacetic acid (6 ml) was added 5% Rh/C (926 mg, 0.45 mmol) and stirred at 60 °C under O_2 for 18 h. The reaction was quenched by the addition of a saturated $NaHCO_3$ solution. The resulting mixture was filtrated through a celite pad and then extracted with AcOEt. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered, concentrated in vacuo to give a crude product, which was purified by silica gel column chromatography (CH_2Cl_2/ hexane = 10 to 20%) to yield 512 mg (56%) of **4p**. Recrystallization from ethanol afforded **4p** as a pale brown plate (mp. 128-130 °C). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.43 (1H, s), 8.04 (2H, d, *J* = 8.0 Hz), 8.00 (2H, d, *J* = 8.0 Hz), 7.57-7.47 (4H, m). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 163.1 (s), 140.6 (s), 131.7 (s), 128.5 (d), 126.9 (d), 125.8 (d), 125.7 (d), 123.5 (s), 120.5 (d), 64.3 (d). IR (ATR): 1756, 1360, 1274, 1156 cm^{-1}. MS (EI) *m/z*: 306 (M^++2), 304 (M^+), 193 (M^+-$CHCl_2CO$, 100%). HRMS (EI) *m/z* calcd for $C_{16}H_{10}Cl_2O_2$ (M^+): 304.0058, found: 304.0061.

2-*tert*-Butyl-9-anthracenyl trifluoroacetate/ 2-*tert*-Butyl-10-anthracenyl trifluoroacetate (4q)

Yield 60 mg (87%) as inseparable 2 : 1 mixture of 9- and 10-isomer from 2-*tert*-buthylanthracene (47 mg, 0.2 mmol) according to Representative Procedure C (conditions: rt under O_2 for 10 min). Pale brown oil. 9-isomer: ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.39 (1H, s), 8.02 (1H, d, *J* = 8.9 Hz), 7.98 (1H, d, *J* = 8.9 Hz), 7.85 (1H, d, *J* = 8.9 Hz), 7.74 (1H, s), 7.61 (1H, d, *J* = 8.9 Hz), 7.56-7.46 (2H, m), 1.42 (9H, s). 10-isomer: ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.41 (0.5H, s), 8.02 (0.5H, d, *J* = 8.9 Hz), 7.93 (0.5H, s), 7.85 (0.5H, d, *J* = 8.9 Hz), 7.81 (0.5H, d, *J* = 8.9 Hz), 7.68 (0.5H, d, *J* = 8.9 Hz), 7.56-7.46 (1H, m), 1.44 (4.5H, s). 9-isomer: ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 156.2 (s, q: J_{C-F} = 43 Hz), 150.1 (s), 139.7 (s), 131.2 (s), 130.4 (s), 128.5 (d), 128.3 (d), 127.1 (d), 126.1 (d), 125.6 (d), 125.5 (d), 123.1 (s), 122.9 (s), 120.0 (d), 115.08 (s, q: J_{C-F} = 286 Hz), 113.9 (d), 35.3 (s), 30.6 (q). IR (neat): 2964, 2906, 1801, 1670, 1597, 1226, 1128 cm^{-1}. MS (EI) *m/z*: 346 (M^+, 100%), 249 (M^+-CF_3CO). HRMS (EI) *m/z* calcd for $C_{20}H_{17}F_3O_2$ (M^+): 346.1181, found: 346.1180.

2-*tert*-Butyl-9-anthracenyl dichloroacetate (4r)

Yield 285 mg (79%) from 2-*tert*-butylanthracene (234 mg, 1.0 mmol) according to the procedure for Representative Procedure D (conditions: 60 °C under O_2 for 12 h) using and 5% Rh/C (204 mg, 0.10 mmol) to of **4r**. Recrystallization from hexane afforded **4r** as colorless needles (mp. 138-139 °C). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.36 (1H, s), 8.01 (1H, d, J = 9.0 Hz), 7.97 (1H, d, J = 9.0 Hz), 7.94 (1H, d, J = 9.0 Hz), 7.92 (1H, d, J = 2.0 Hz), 7.60 (1H, dd, J = 2.0, 9.0 Hz), 7.54-7.44 (2H, m), 1.42 (9H, s). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 163.1 (s), 149.6 (s), 140.4 (s), 131.3 (s), 130.5 (s), 128.5 (d), 128.2 (d), 126.7 (d), 125.5 (d), 125.3 (d), 125.1 (d), 123.6 (s), 123.5 (s), 120.4 (d), 114.5 (d), 64.3 (d), 35.5 (s), 30.8 (q). IR (ATR): 1779, 1277, 1137 cm^{-1}. MS (EI) *m/z*: 362 (M^++2), 360 (M^+), 249 (M^+-$CHCl_2CO$, 100%). HRMS (EI) *m/z* calcd for $C_{20}H_{18}Cl_2O_2$ (M^+): 360.0684, found: 360.0690. The regioselectivity of **4r** was determined by HMBC correlation.

2-Chloro-9-anthracenyl trifluoroacetate (4s)

Yield 75 mg (57%) from 2-chloroanthracene (85 mg, 0.40 mmol) according to General Procedure C (conditions: rt under O_2 for 48 h). Brown solids. ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.35 (1H, s), 7.98 (1H, d, J = 8.7 Hz), 7.92 (1H, d, J = 8.7 Hz), 7.80 (1H, d, J = 8.7 Hz), 7.78 (1H, s), 7.59-7.48 (2H, m), 7.39 (1H, d, J = 8.7 Hz). ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 156.0 (s, q: $J_{C\text{-}F}$ = 43 Hz), 138.9 (s), 133.5 (s), 131.7 (s), 130.3 (d), 129.6 (s), 128.6 (d), 128.0 (d), 127.3 (d), 126.5 (d), 126.2 (d), 123.5 (s), 123.2 (s), 119.9 (d), 118.7 (d), 114.9 (s, q: $J_{C\text{-}F}$ = 285 Hz). IR (KBr): 3059, 2374, 1797, 1624 cm^{-1}. MS (EI) *m/z*: 326 (M^++2), 324 (M^+, 100%), 227 (M^+-CF_3CO). HRMS (EI) *m/z* calcd for $C_{16}H_8F_3O_2Cl$ (M^+): 324.0165, found: 324.0166.

2-Chloro-9-anthracenyl dichloroacetate (4t)

Yield 85 mg (50%) from 2-chloroanthracene (106 mg, 0.50 mmol) according to Representative Procedure D (conditions: 60 °C under O_2 for 40 h). Recrystallization from EtOH afforded **4t** as pale yellow needles (mp. 144-146 °C). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.35 (1H, s), 7.99 (1H, d, J = 8.5 Hz), 7.95 (1H, d, J = 8.5 Hz), 7.94 (1H, d, J = 2.0 Hz), 7.93 (1H, d, J = 8.5 Hz), 7.58-7.48 (2H, m), 7.39 (1H, dd, J = 2.0, 8.5 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 163.0 (s), 139.7 (s), 133.1 (s), 131.8 (s), 130.2 (d), 129.7 (s), 128.6 (d), 127.6 (d), 127.1 (d), 126.1 (d), 126.0 (d), 124.1 (s), 123.7 (s), 120.4 (d), 119.2 (d), 64.1 (d). IR (ATR): 1761, 1291, 1151 cm^{-1}. MS (EI) *m/z*: 340 (M^++2), 338 (M^+), 227 (M^+-$CHCl_2CO$, 100%). HRMS (EI) *m/z* calcd for

$C_{16}H_9Cl_3O_2$ (M^+): 337.9668, found: 337.9671. The regioselectivity of **4t** was determined by HMBC correlation.

2-Bromo-9-anthracenyl dichloroacetate (4u)

Yield 86 mg (45%) from 2-bromoanthracene (129 mg, 0.50 mmol) according to Representative Procedure D (conditions: 60 °C under O_2 for 48 h). Recrystallization from EtOH afforded **4u** as brown needles (mp. 166-168 °C). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.37 (1H, s), 8.15 (1H, s), 8.01 (1H, d, *J* = 8.5 Hz), 7.97 (1H, d, *J* = 8.5 Hz), 7.88 (1H, d, *J* = 8.5 Hz), 7.59-7.50 (3H, m), 6.46 (1H, s). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 163.0 (s), 139.6 (s), 131.9 (s), 130.1 (d), 129.8 (s), 129.4 (d), 128.6 (d), 127.6 (d), 126.2 (d), 126.1 (d), 124.2 (s), 124.0 (s), 122.7 (d), 121.5 (s), 120.5 (d), 64.1 (d). IR (ATR): 1763, 1290, 1137 cm^{-1}. MS (EI) *m/z*: 386 (M^++4), 384 (M^++2), 382 (M^+), 273 (M^++2-$CHCl_2CO$, 100%), 271 (M^+-$CHCl_2CO$). HRMS (EI) *m/z* calcd for $C_{16}H_9BrCl_2O_2$ (M^+): 381.9163, found: 381.9159. The regioselectivity of **4u** was determined by HMBC correlation.

1-Chloro-10-anthracenyl dichloroacetate (4v)

Yield 187 mg (55%) from 1-chloroanthracene (213 mg, 1.0 mmol) according to Representative Procedure D (conditions: 60 °C under O_2 for 48 h). Recrystallization from AcOEt-hexane afforded **4v** as colorless needles (mp. 125-127 °C). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.89 (1H, s), 8.14 (1H, d, *J* = 8.5 Hz), 8.01 (1H, d, *J* = 8.5 Hz), 7.95 (1H, d, *J* = 8.5 Hz), 7.63 (1H, d, *J* = 7.0 Hz), 7.63-7.55 (2H, m) 7.45 (1H, dd, *J* = 7.0, 8.5 Hz), 6.46 (1H, s). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 162.9 (s), 140.9 (s), 132.5 (s), 132.0 (s), 129.0 (d), 127.7 (d), 126.4 (d), 126.2 (d), 125.7 (d), 124.4 (s), 123.8 (s), 123.1 (d), 120.4 (d), 119.8 (d), 64.2 (d). IR (ATR): 1764, 1292, 1145 cm^{-1}. MS (EI) *m/z*: 340 (M^++2), 338 (M^+), 227 (M^+-$CHCl_2CO$, 100%). HRMS (EI) *m/z* calcd for $C_{16}H_9Cl_3O_2$ (M^+): 337.9668, found: 337.9677. The regioselectivity of **4v** was determined by HMBC correlation.

10-Phenyl-9-anthracenyl trichloroacetate (4w)

A mixture of 9-phenylanthracene (254 mg, 1.0 mmol), 5% Rh/C (204 mg, 0.10 mmol) and trichloroacetic acid (4 g) was heated to 60 °C and then stirred under O_2 for 21 h. The reaction was quenched by the addition of a saturated $NaHCO_3$ solution. The resulting mixture was filtrated through a celite pad and then extracted with $CHCl_3$. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered, concentrated in vacuo to give a crude product,

which was purified by silica gel column chromatography (CH_2Cl_2/ hexane = 5%) to yield 350 mg (84%) of **4w**. Recrystallization from AcOEt-hexane afforded **4w** as pale yellow powder (mp. 244-246 °C). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.09 (1H, d, *J* = 8.5 Hz), 7.70 (1H, d, *J* = 8.5 Hz), 7.62-7.52 (5H, m), 7.45-7.36 (4H, m). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 160.8 (s), 140.8 (s), 137.9 (s), 137.2 (s), 131.2 (d), 130.4 (s), 128.5 (d), 127.8 (d), 127.4 (d), 126.9 (d), 125.7 (d), 123.0 (s), 120.2 (d), 89.8 (s). IR (ATR): 1786, 1770, 1371, 1201 cm^{-1}. MS (EI) *m/z*: 416 (M^++2), 414 (M^+), 269 (M^+-CCl_3C=O, 100%). HRMS (EI) *m/z* calcd for $C_{22}H_{13}Cl_3O_2$ (M^+): 413.9981, found: 413.9972.

10-Phenyl-9-anthracenyl dichloroacetate (4x)

Yield 142 mg (74%) from 9-phenylanthracene (127 mg, 0.50 mmol) according to Representative Procedure D (conditions: 60 °C under O_2 for 63 h). Recrystallization from CCl_4−hexane afforded **4x** as pale yellow powder (mp. 165-168 °C). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.05 (1H, d, *J* = 8.8 Hz), 7.69 (1H, d, *J* = 8.8 Hz), 7.62-7.52 (5H, m), 7.45-7.36 (4H, m), 6.50 (1H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 163.2 (s), 140.4 (s), 138.0 (s), 136.8 (s), 131.2 (d), 130.4 (s), 128.4 (d), 127.8 (d), 127.3 (d), 126.7 (d), 125.6 (d), 123.1 (s), 120.3 (d), 64.3 (d). IR (ATR): 1754, 1373, 1242, 1052 cm^{-1}. MS (EI) *m/z*: 384 (M^++4), 382 (M^++2), 380 (M^+), 269 (M^+-$CHCl_2C$=O, 100%). HRMS (EI) *m/z* calcd for $C_{22}H_{14}Cl_2O_2$ (M^+): 380.0371, found: 380.0367.

10-Bromo-9-anthracenyl dichloroacetate (4y)

Yield 167 mg (43%) from 9-bromoanthracene (257 mg, 1.0 mmol) according to Representative Procedure D (conditions: 60 °C under O_2 for 5 days). Recrystallization from EtOH afforded **4y** as pale yellow needles (mp. 151-154 °C). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.58 (2H, d, *J* = 8.5 Hz), 8.02 (2H, d, *J* = 8.5 Hz), 7.67-7.56 (4H, m), 6.46 (1H, s). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 162.8 (s), 140.8 (s), 130.6 (s), 128.2 (d), 127.6 (d), 127.3 (d), 124.2 (s), 121.5 (s), 120.8 (d), 64.1 (d). IR (ATR): 1752, 1331, 1273, 1184, 745 cm^{-1}. MS (EI) *m/z*: 386 (M^++4), 384 (M^++2), 382 (M^+), 273 (M^++2-$CHCl_2CO$, 100%), 271 (M^+-$CHCl_2CO$). HRMS (EI) *m/z* calcd for $C_{16}H_9BrCl_2O_2$ (M^+): 381.9163, found: 381.9150.

Diels-Alder adduct 5

To a solution of anthracene (36 mg, 0.20 mmol) in TFA-benzotrifluoride (2: 1, 1.5 mL) was added 5% Rh/C (47 mg, 0.020 mmol) at rt and then stirred under O_2 for 1 h. The reaction

mixture was filtered and concentrated in vacuo to give a crude product **4n**, which was used without further purification. **4n** was diluted with toluene (2 mL) and then *N*-methylmaleimide (67 mg, 0.60 mmol) was added. The mixture was refluxed under argon for 17 h. The resulting mixture was concentrated in vacuo to give a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 3%) to yield 75 mg (94%) of **5** as colorless solids (mp. 211-214 °C). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.57 (1H, d, J = 7.6 Hz), 7.48-7.42 (1H, m), 7.33-7.10 (6H, m), 4.80 (1H, d, J = 3.6 Hz), 4.55 (1H, d, J = 8.8 Hz), 3.43 (1H, dd, J = 3.6, 8.8 Hz), 2.51 (3H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 175.6 (s), 173.8 (s), 156.0 (s, q: $J_{C\text{-}F}$ = 43 Hz), 138.9 (s), 137.3 (s), 136.0 (s), 135.8 (s), 128.1 (d), 127.8 (d), 127.4 (d), 126.8 (d), 124.7 (d), 124.6 (d), 121.2 (d), 120.5 (d), 114.6 (s, q: $J_{C\text{-}F}$ = 284 Hz), 86.1 (s), 47.4 (d), 44.7 (d), 44.2 (d), 24.4 (q). IR (KBr): 3074, 2949, 1793, 1705, 1460, 1150 cm^{-1}. MS (EI) *m/z*: 401 (M^+), 290 (M^+-$C_5H_5NO_2$, 100%), 193. HRMS (EI) *m/z* calcd for $C_{21}H_{14}F_3NO_4$ (M^+): 401.0875, found: 401.0874.

2,7-Di-*tert*-butyl-1-(trifluoroacetoxy)pyrene (6)

To a solution of 2,6-di-*tert*-butylpyrene (126 mg, 0.40 mmol) in TFA (1 mL) was added 5% Rh/C (82 mg, 0.040 mmol) and stirred at rt under O_2 for 3.5 h. The reaction was quenched by the addition of a saturated $NaHCO_3$ solution and extracted with AcOEt. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered, concentrated in vacuo to give a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 10%) to yield 179 mg (quant.) of **6**. Recrystallization from EtOH afforded **6** as a colorless plate (mp. 126−129 °C). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.25 (1H, d, J = 2.0 Hz), 8.22 (1H, d, J = 2.0 Hz), 8.22 (1H, s), 8.11 (1H, d, J = 8.8 Hz), 8.07 (1H, d, J = 8.8 Hz), 8.02 (1H, d, J = 8.8 Hz), 7.67 (1H, d, J = 8.8 Hz), 1.59 (9H, s), 1.58 (9H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 156.5 (s, q: $J_{C\text{-}F}$ = 43 Hz), 150.0 (s), 141.5 (s), 138.7 (s), 130.7 (s), 130.1 (s), 129.8 (s), 129.4 (d), 128.0 (d), 127.0 (d), 124.1 (s), 123.6 (d), 123.3 (d), 122.9 (d), 122.8 (s), 122.3 (s), 119.0 (d), 115.0 (s, q: $J_{C\text{-}F}$ = 285 Hz), 35.29 (s), 35.28 (s), 31.9 (q), 30.7 (q). IR (ATR): 1794, 11220, 1171, 1120 cm^{-1}. MS (EI) *m/z*: 427 (M^++H), 426 (M^+, 100%), 411 (M^+-CH_3). HRMS (EI) *m/z* calcd for $C_{26}H_{25}F_3O_2$ (M^+): 426.1807, found: 426.1805.

2,7-Di-*tert*-butyl-1-(dichloroacetoxy)pyrene (7)

Yield 166 mg (94%) from 2,6-di-*tert*-butylpyrene (126 mg, 0.40 mmol) according to Representative Procedure D (conditions: 50 °C under O_2 for 48 h). Recrystallization from AcOEt−hexane afforded **7** as colorless powder (mp. 152−154 °C). ^{1}H-NMR (400 MHz, $CDCl_3$)

δ: 8.23 (1H, d, *J* = 1.6 Hz), 8.22 (1H, s), 8.20 (1H, d, *J* = 1.6 Hz), 8.08 (1H, d, *J* = 8.8 Hz), 8.05 (1H, d, *J* = 8.8 Hz), 8.02 (1H, d, *J* = 8.8 Hz), 7.89 (1H, d, *J* = 8.8 Hz), 6.44 (1H, s), 1.61 (9H, s), 1.57 (9H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 163.2 (s), 149.5 (s), 142.4 (s), 138.8 (s), 130.7 (s), 130.2 (s), 129.5 (s), 129.0 (d), 127.7 (d), 127.0 (d), 124.1 (s), 123.5 (d), 123.4 (s), 123.0 (d), 122.7 (d), 122.4 (s), 119.4 (d), 64.5 (d), 35.4 (s), 35.2 (s), 31.9 (q), 30.7 (q). IR (ATR): 1761, 1224, 1130 cm^{-1}. MS (EI) *m/z*: 444 (M^++4), 442 (M^++2), 440 (M^+, 100%), 329 (M^+-$CHCl_2C$=O). HRMS (EI) *m/z* calcd for $C_{26}H_{26}Cl_2O_2$ (M^+): 440.1310, found: 440.1308. Anal. calcd for $C_{26}H_{26}Cl_2O_2$: C, 70.75; H, 5.94, found: C, 70.34; H, 6.10.

2,7-Di-*tert*-butyl-1-hydroxypyrene (8) [34]

To a solution of **6** (213 mg, 0.50 mmol) in THF-MeOH (1:1, 10 mL) was added 3M NaOH (1.6 ml, 5.0 mmol) at rt and then stirred for 1 h. The reaction mixture was extracted with AcOEt. The combined organic layer was washed with brine, dried over with $MgSO_4$, filtered and concentrated in vacuo to give a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 5%) to yield 148 mg (90%) of **8**. Recrystallization from hexane afforded **8** as a brown plate (mp. 226−231 °C). ^{1}H-NMR (400 MHz, DMSO-*d6*) δ: 9.81 (1H, s), 8.40 (1H, d, *J* = 8.4 Hz), 8.17 (1H, d, *J* = 2.0 Hz), 8.16 (1H, d, *J* = 2.0 Hz), 8.14 (1H, s), 8.03 (1H, d, *J* = 8.4 Hz), 8.01 (1H, d, *J* = 8.4 Hz), 7.91 (1H, d, *J* = 8.4 Hz), 1.62 (9H, s), 1.53 (9H, s). IR (ATR): 3564, 2953, 1170 cm^{-1}. MS (EI) *m/z*: 330 (M^+, 100%), 315 (M^+-CH_3). HRMS (EI) *m/z* calcd for $C_{24}H_{26}O$ (M^+): 330.1984, found: 330.1991.

1-Dichloroacetoxyperylene (9)

Yield 229 mg (61%) from perylene (252 mg, 1.0 mmol) according to Representative Procedure D (conditions: 50 °C under O_2 for 6 h). Recrystallization from $CHCl_3$ afforded **9** as yellow powder (mp. 223 °C (dec.)). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.24 (1H, d, *J* = 8.0 Hz), 8.21 (1H, d, *J* = 8.0 Hz), 8.17 (2H, d, *J* = 8.0 Hz), 7.79 (1H, d, *J* = 8.0 Hz), 7.71 (2H, d, *J* = 8.0 Hz), 7.58-7.46 (3H, m), 7.36 (1H, d, *J* = 8.0 Hz), 6.33 (1H, s). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 162.9 (s), 145.2 (s), 134.6 (s), 131.7 (s), 130.54 (s), 130.50 (s), 130.4 (s), 129.8 (s), 128.37 (d), 128.35 (s), 128.28 (d), 127.5 (d), 127.3 (s), 126.6 (d), 120.9 (d), 120.8 (d), 120.7 (d), 120.1 (d), 119.4 (d), 118.2 (d), 64.3 (d). IR (ATR): 1771, 1385, 1226 cm^{-1}. MS (EI) *m/z*: 380 (M^++2), 378 (M^+), 267 (M^+-$CHCl_2C$=O, 100%). HRMS (EI) *m/z* calcd for $C_{22}H_{12}Cl_2O_2$ (M^+): 378.0214, found: 378.0211.

2,3',6,7'-Tetra-*tert*-butyl-1,1'-binaphthyl-4-yl trifluoroacetate (10)

To a solution of 2,6-di-*tert*-butylnaphthalene (240 mg, 1.0 mmol) in TFA (3 mL) was added 5% Rh/C (204 mg, 0.10 mmol) and stirred at 50 °C under O_2 for 14 h. The reaction was quenched by the addition of a saturated $NaHCO_3$ solution and extracted with AcOEt. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered, concentrated in vacuo to give a crude product, which was purified by silica gel column chromatography (CH_2Cl_2/ hexane = 5%) to yield 250 mg (84%) of **10** as colorless amorphous. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.87 (1H, d, J = 8.0 Hz), 7.85 (1H, d, J = 2.0 Hz), 7.72-7.64 (4H, m), 7.62-7.59 (2H, m), 7.57 (1H, dd, J = 2.0, 8.0 Hz), 1.48 (9H, s), 1.46 (9H, s), 1.22 (9H, s), 1.19 (9H, s). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 156.5 (s, q: J_{C-F} = 43 Hz), 148.8 (s), 148.1 (s), 147.1 (s), 142.2 (s), 137.8 (s), 136.8 (s), 136.2 (s), 132.6 (s), 132.2 (s), 130.7 (s), 128.1 (d), 128.0 (d), 126.2 (d), 124.8 (d), 124.7 (d), 122.6 (d), 122.0 (d), 120.7 (d), 120.0 (d), 115.0 (s, q: J_{C-F} = 284 Hz), 35.1 (s), 34.9 (s), 34.8 (s), 31.3 (q), 31.2 (q), 31.0 (q), 30.8 (q). IR (ATR): 1800, 1223, 1171, 1124 cm^{-1}. MS (EI) *m/z*: 590 (M^+, 100%), 575 (M^+-CH_3). HRMS (EI) *m/z* calcd for $C_{38}H_{45}F_3O_2$ (M^+): 590.3372, found: 590.3370. The regioselectivity of **10** was determined by INADEQUATE correlation.

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Supporting Information

^{1}H, ^{13}C spectra for all new compounds

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