Synthesis of mono- and di-arylated acenaphthylenes and programmed access to dibenzo[: J, l] fluoranthenes via palladium-catalysed C-H bond functionalisation

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Synthesis of mono- and di-arylated acenaphthylenes and programmed access to dibenzo[*j*,*l*]fluoranthenes *via* palladium-catalysed C-H bond functionalisation

Xinzhe Shi,[a] Thierry Roisnel,[a] Jean-François Soulé,*[a] and Henri Doucet*[a]

Conditions allowing the C1-arylation and C1,C2-diarylation of acenaphthylene *via* palladium-catalysed direct arylation using either aryl bromides or benzenesulfonyl chlorides as aryl sources are reported. With aryl bromides, the mono-arylation was very selective; whereas, with benzenesulfonyl chlorides good yields in C1,C2-diarylated acenaphthylenes could be obtained. The reaction tolerates a wide variety of substituents including bromo or iodo. Moreover, the Pd-catalysed intramolecular C-H bond reaction of bromo-substituted C1,C2-diarylated acenaphthylenes provides the corresponding dibenzo[*j*,*l*]fluoranthenes.

Introduction

Polycyclic Aromatic Hydrocarbon (PAH) have emerged in the last decades as efficient molecular materials for opto-electronic applications.[1a] For example, perylenediimides are promising materials for solar applications.[b] Acenaphthylene is a polycyclic aromatic hydrocarbon, although the extent of aromaticity of its five-membered ring is very small (Fig. 1).[1c] Some 1,2-diarylacenaphthylene derivatives display photochromic properties,[1d,1e] and have been employed for the construction of donor-acceptor polymers *via* cyclopentannulation.[1f] Consequently, the development of fast and reliable methods for, access to substituted acenaphthylenes represents a major synthetic challenge.

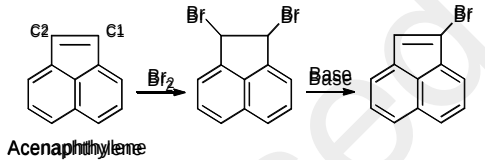
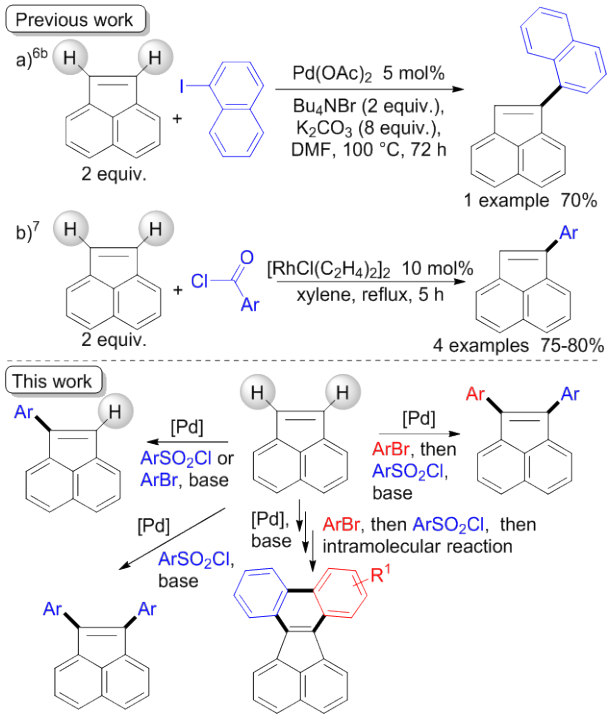


Figure 1 Synthesis of 1-bromoacenaphthylene

Acenaphthylene is a commercially available compound at an affordable price. The introduction of iodo- or bromo-substituents at C1 and/or C2 positions of acenaphthylene is possible by reaction with iodine or bromine,[2a,2b] but the selective preparation of the mono-halogenated acenaphthylenes in high yields requires two steps (bromination of acenaphthylene followed by dehydrobromination, Fig. 1).[2c] Moreover, the preparation of acenaphthylenes containing boron-substituents at C1 and/or C2 positions has not yet been reported. As a consequence, relatively few examples of synthesis of C1-arylated acenaphthylenes *via* Suzuki couplings have been reported.[3] Therefore, the direct functionalization of acenaphthylene *via* the activation of C-H bonds at C1 and/or C2 positions represent a very attractive pathway for the preparation of acenaphthylene derivatives.

The Pd-catalysed direct arylation of (hetero)aromatic compounds has recently emerged as a very effective tool for a simpler access to arylated (hetero)aromatics.[4,5] However, for these Pd-catalysed C-H bond arylation reactions, there are still important limitations in terms of yields, selectivity and substrate scope. To our knowledge, only a few examples of Pd-catalysed C-H bond functionalization of acenaphthylenes have been reported so far.[6-8] In 1993, Dyker described the reaction of acenaphthylene with 1-iodonaphthalene to prepare the corresponding C1-arylated acenaphthylene in good yield (Scheme 1, a).[6b] A single example of C1,C2-diarylation of acenaphthylene in a low 19% yield has also been reported by Dyker.[6d] Then in 2004, Miura et al. reported the coupling of acenaphthylene with benzoyl chlorides in the presence of a rhodium catalyst (Scheme 1, b).[7] Therefore, the discovery of effective procedures allowing the access to C1-arylated and especially C1,C2-diarylated acenaphthylenes using a low loading of easily available catalysts and tolerant to a wide range of functional groups remains an important challenge. Moreover, the synthesis of non-symmetrically substituted 1,2-diarylacenaphthylenes and to dibenzo[*j*,*l*]fluoranthenes *via* successive C-H bond functionalization reactions has not yet been reported (Scheme 1, bottom).



Scheme 1 Pd-catalysed direct arylation for access to C1-arylated acenaphthylenes, C1,C2-diarylated acenaphthylenes and dibenzo[*j*,*l*]fluoranthenes.

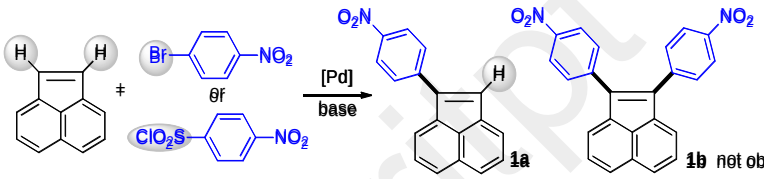
Herein, we report (i) on the influence of the aryl source and reaction conditions in the Pd-catalysed direct mono- or di-arylation at C1 and/or C2 positions of acenaphthylene, and (ii) on the programmed synthesis of dibenzo[*j*,*l*]fluoranthenes *via* successive Pd-catalysed C-H bond activation reactions (Scheme 1, bottom).

Results and discussion

We initially examined the influence of the nature of the aryl source, base and catalyst for the arylation of acenaphthylene, based on conditions employed for the direct arylation of various (hetero)aromatics in our previous work.[9] The use of 2 mol% $Pd(OAc)_2$ or $PdCl(C_3H_5)(dppb)$ as catalysts, KOAc as base in DMA with 1 equiv. of 4-bromonitrobenzene as aryl source resulted in the selective formation of the mono-arylation product **1a** in high yields (Table 1, entries 1 and 2). A lower catalyst loading of 0.5 mol% of $Pd(OAc)_2$ also provided selectively **1a** in a high 78% yield (Table 1, entry 3). The addition of phosphine ligands to the reaction mixture (Table 1, entries 4 and 5) or the use of NaOAc, CsOAc or Li_2CO_3 as bases did not allow to improve the yield in **1a** (Table 1, entries 6-8). Reactions performed in 1,4-dioxane, cyclopentyl methyl ether or diethyl carbonate gave no coupling product; whereas the "green" solvent pentan-1-ol afforded **1a** in 61% yield (Table 1, entries 9-12).

We have recently reported that the use of benzenesulfonyl chlorides as aryl source[10-13] in Pd-catalysed direct arylation is very attractive as such reactions tolerate a variety of useful substituents, including halides.[14] Moreover, in some cases, their use drastically modify the reaction outcome of direct arylations, compared to the reactions performed with aryl halides, due to a change in the catalytic cycle.[14a] Based on our previous results on Pd-catalysed desulfitative coupling with arene derivatives,[14] the coupling reaction using 1.3 equiv. of acenaphthylene with 1 equiv. of 4-nitrobenzenesulfonyl chloride in the presence of 5 mol% $Pd(OAc)_2$ catalyst and Li_2CO_3 as the base at 140 °C was examined. Under these conditions, the formation of **1a** in 60% yield was obtained; however, the formation of some side-products was observed (Table 1, entry 13). The use of other bases or solvents gave no product **1a** showing the crucial role of reaction conditions in such desulfitative couplings (Table 1, entries 14-20).

Table 1. Influence of the reaction conditions for palladium-catalysed direct coupling of acenaphthylene with nitrobenzene derivatives.

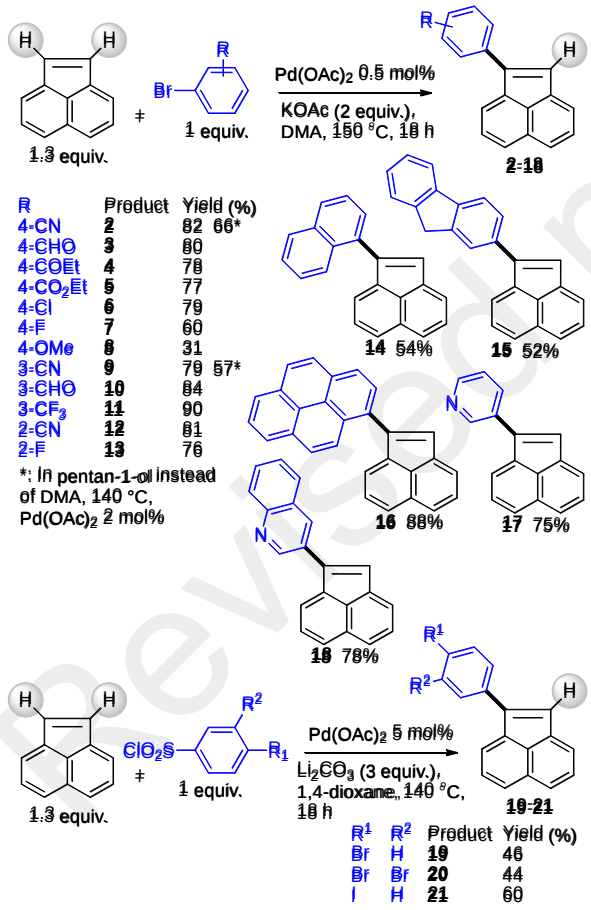


Entry	Catalyst (mol%)	Base (eq.)	Nitrobenzene substituent	Solvent	Yield in **1a** (%)
1	$Pd(OAc)_2$ (2)	KOAc (2)	Br	DMA	76
2	$PdCl(C_3H_5)(dppb)$ (2)	KOAc (2)	Br	DMA	74
3	$Pd(OAc)_2$ (0.5)	KOAc (2)	Br	DMA	78
4	$Pd(OAc)_2$ (0.5) / PPh_3 (1)	KOAc (2)	Br	DMA	71
5	$Pd(OAc)_2$ (0.5) / dppb (0.5)	KOAc (2)	Br	DMA	73
6	$Pd(OAc)_2$ (0.5)	NaOAc (2)	Br	DMA	77
7	$Pd(OAc)_2$ (0.5)	CsOAc (2)	Br	DMA	73
8	$Pd(OAc)_2$ (0.5)	Li_2CO_3 (2)	Br	DMA	67
9	$Pd(OAc)_2$ (0.5)	Li_2CO_3 (2)	Br	1,4-dioxane[a]	0
10	$Pd(OAc)_2$ (2)	KOAc (2)	Br	CPME[b]	0
11	$Pd(OAc)_2$ (2)	KOAc (2)	Br	DEC[c]	0
12	$Pd(OAc)_2$ (2)	KOAc (2)	Br	Pentan-1-ol[a]	61
13	$Pd(OAc)_2$ (5)	Li_2CO_3 (3)	SO_2Cl	1,4-dioxane[a]	60
14	$Pd(OAc)_2$ (5)	KOAc (3)	SO_2Cl	1,4-dioxane[a]	0
15	$Pd(OAc)_2$ (5)	CsOAc (3)	SO_2Cl	1,4-dioxane[a]	0
16	$Pd(OAc)_2$ (5)	K_2CO_3 (3)	SO_2Cl	1,4-dioxane[a]	0
17	$Pd(OAc)_2$ (5)	Li_2CO_3 (3)	SO_2Cl	DMF	0
18	$Pd(OAc)_2$ (5)	Li_2CO_3 (3)	SO_2Cl	DMA	0
19	$Pd(OAc)_2$ (5)	Li_2CO_3 (3)	SO_2Cl	CPME[b]	0
20	$Pd(OAc)_2$ (5)	Li_2CO_3 (3)	SO_2Cl	DEC[c]	0

Conditions: acenaphthylene (1.3 mmol), 4-bromonitrobenzene or 4-nitrobenzenesulfonyl chloride (1 mmol), under argon, 18 h, 150 °C, isolated yields. [a] 140 °C. [b] In CPME (cyclopentyl methyl ether) at 110 °C. [c] In DEC (diethyl carbonate) at 130 °C.

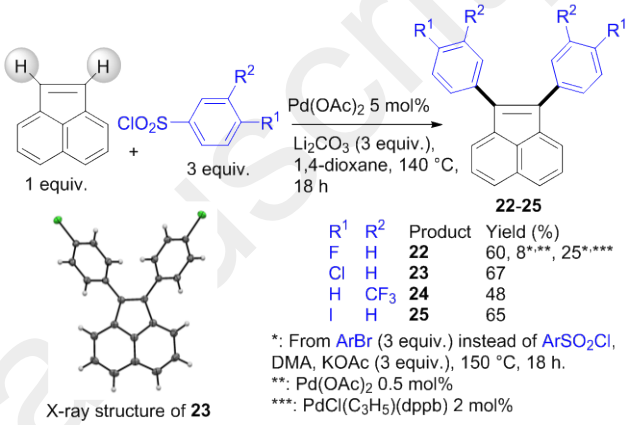
Next, the scope of the C1-arylation of acenaphthylene with various aryl bromides using 0.5 mol% $Pd(OAc)_2$ catalyst, KOAc base in DMA was investigated (Scheme 2, top). With aryl bromides bearing cyano, formyl, propionyl or ester *para*-substituents, high yields in **2**-**5** were obtained. High yields in **6** and **7** were also obtained using 4-chloro- and 4-fluoro-substituted aryl bromides; whereas, from 4-bromoanisole, **8** was only produced in 31% yield. The higher yields obtained with electron-deficient aryl bromides might come from their easier oxidative addition to palladium. Then, we examined the reactivity of a few *meta*-substituted aryl bromides. Good yields in

9-**11** were obtained from nitrile-, formyl- and trifluoromethyl-substituted aryl bromides. The use of 2-bromobenzonitrile and 2-bromofluorobenzene as coupling partners also provided the desired products **12** and **13** in high yields. Fluorene and pyrenes derivatives continue to attract the attention of synthetic organic chemists, due to their inherent physical properties. The reaction of 2-bromofluorene and 1-bromopyrene with acenaphthylene, under the same reaction conditions, afforded the target products **15** and **16** in 52% and 88% yields. Pyridines and quinolines are important azaheterocycles embedded in many natural products, active pharmaceuticals, and functional materials. Therefore, the coupling of 3-bromopyridine and 3-bromoquinoline with acenaphthylene was also studied. The desired compounds **17** and **18** were obtained in 75% and 78% yields, respectively. As the use of benzenesulfonyl chlorides as aryl source in Pd-catalysed direct arylations tolerates halo substituents,[14] the reactivity of 4-bromobenzenesulfonyl chloride and 3,4-dibromobenzenesulfonyl chloride for coupling with acenaphthylene was investigated (Scheme 2, bottom). Using 5 mol% $Pd(OAc)_2$ catalyst, Li_2CO_3 base in 1,4-dioxane, the expected products **19** and **20** were obtained in satisfactory yields without cleavage of the C-Br bonds, allowing further transformations. Even 4-iodobenzenesulfonyl chloride was successfully employed, affording **21** in 60% yield without cleavage of the C-I bond.



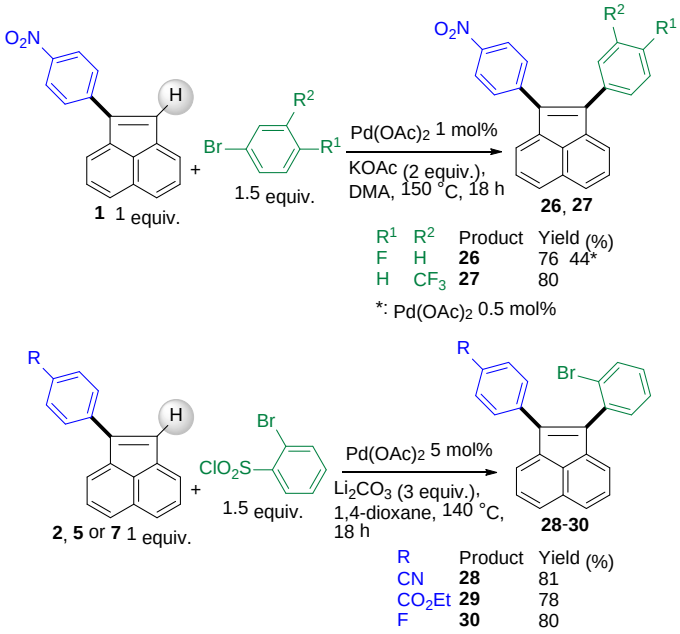
Scheme 2 Palladium-catalysed direct C1-arylation of acenaphthylene

Under the same reaction conditions than for C1-arylation of acenaphthylene, namely 0.5 mol% $Pd(OAc)_2$ in the presence of KOAc base -which favours a concerted-metallation-deprotonation (CMD) mechanism-, but using 3 equiv. of aryl bromides, the one-pot preparation of symmetrical 1,2-diarylacenaphthylenes was attempted (Scheme 3). However, using 4-bromofluorobenzene, we obtained the desired diarylated product **22** in only 8-25% yields, as large amount of mono-arylated product **7** were also produced. The second arylation was found to be sluggish. It is known that the reactions which proceed *via* a CMD type mechanism are sensitive to steric hindrance.[4k] Conversely, quite good yields in **22**-**24** were obtained using chloro-, fluoro- or trifluoromethyl-substituted benzenesulfonyl chlorides as aryl sources, $Pd(OAc)_2$ as catalyst and Li_2CO_3 as base. Such reactions likely proceed via a Pd(II)Pd(IV) mechanism.[14a] The structure of **23** was confirmed by X-ray analysis. Moreover, using this one-pot procedure from 4-iodobenzenesulfonyl chloride, the acenaphthylene **25** containing two 4-iodobenzene units at C1 and C2 positions was obtained in 65% yield.



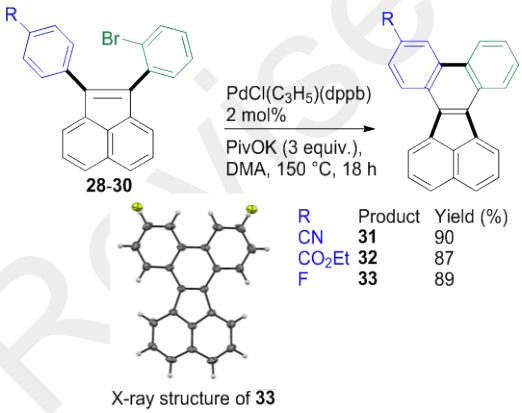
Scheme 3 Palladium-catalysed one-pot direct C1,C2-diarylation of acenaphthylene

Under similar reaction conditions than for the C1-arylations of acenaphthylene, the synthesis of non-symmetrical 1,2-diarylacenaphthylenes using both aryl bromides and benzenesulfonyl chlorides was studied (Scheme 4). From **1** and 4-fluorobromobenzene using 0.5 mol% $Pd(OAc)_2$ catalyst, **26** was isolated in only 44% yield (Scheme 4, top). The use of a higher catalyst loading (1 mol%) afforded **26** in a higher yield of 76%. The reaction of **1** with 3-trifluoromethyobromobenzene, using again 1 mol% $Pd(OAc)_2$ gave the desired product **27** in 80% yields (Scheme 4, top). 2-Bromobenzenesulfonyl chloride was also successfully employed as aryl source for this second arylation, allowing to prepare the products **28**-**30** in 78-81% yields, without cleavage of the C-Br bonds (Scheme 4, bottom).



Scheme 4 Palladium-catalysed direct C2-arylation of 1-arylacenaphthylenes

Very few examples of synthesis of dibenzo[*j*,*l*]fluoranthenes have been reported so far.[15] Among the rare examples, Klumpp, Olah et al. described in 1997 the synthesis of aryl pinacols which were treated with triflic acid to provide dibenzo[*j*,*l*]fluoranthenes.[15a] From **28**-**30**, Pd-catalysed intramolecular C-H bond reaction should provide the corresponding dibenzo[*j*,*l*]fluoranthenes (Scheme 5). Our first attempt to cyclize **28**, using 0.5 mol% $Pd(OAc)_2$ catalyst and KOAc as base was not successful, as **31** was obtained in a low yield due to a poor conversion of **28**. However, in the presence of 2 mol% of more stable $PdCl(C_3H_5)(dppb)$ catalyst,[16] and PivOK as base, the desired product **31** was obtained in a very high yield. The reaction of the ester- and fluoro-substituted 1,2-diarylacenaphthylenes **29** and **30** also afforded the desired dibenzo[*j*,*l*]fluoranthenes **32** and **33** in high yields. The structure of **33** was unambiguously assigned by X-ray analysis.



Scheme 5 Intramolecular palladium-catalysed direct arylation for access to dibenzo[*j*,*l*]fluoranthenes

Conclusion

In summary, we have demonstrated that the Pd-catalysed C-H bond functionalisation of acenaphthylene can be performed using aryl bromides or benzenesulfonyl chlorides as aryl sources in the presence of phosphine-free $Pd(OAc)_2$ catalyst without additives. The reaction affords regioselectively the C1-arylated acenaphthylene in high yields. Moreover, using an excess of benzenesulfonyl chlorides, the formation of C1,C2-diarylated acenaphthylene also proceeded in good yields. From 1-arylacenaphthylene, the introduction of an other aryl at C2-position gives rise to non-symmetrical diarylacenaphthylenes. The protocol using benzenesulfonyl chlorides tolerates bromo and iodo substituents. This functional group tolerance was employed for the programmed synthesis of dibenzo[*j*,*l*]fluoranthenes *via* sequential Pd-catalysed C-H bond activation steps. Moreover, the functional group tolerance should allow the easy modification of these acenaphthylene derivatives, a strategy enabling the tuning of their properties.

Experimental

General. All reactions were perfomed in Schlenk tubes under argon. DMA or 1,4-dioxane analytical grade were not distilled before use. Potassium acetate 99+ and lithium carbonate 99% were used. Commercial acenaphthylene (>94%), aryl bromides and benzenesulfonyl chlorides were used without purification. ^1H (400 MHz), ^{13}C (100 MHz) spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm relative to $CDCl_3$ (^1H: 7.26 and ^{13}C: 77.0). Flash chromatography was performed on silica gel (230-400 mesh).

Preparation of the $PdCl(C_3H_5)(dppb)$ catalyst:[16] An oven-dried 40 mL Schlenk tube equipped with a magnetic stirring bar under argon atmosphere, was charged with $[Pd(C_3H_5)Cl]_2$ (182 mg, 0.5 mmol) and dppb (426 mg, 1 mmol). 10 mL of anhydrous dichloromethane were added, then, the solution was stirred at room temperature for twenty minutes. The solvent was removed in vacuum. The yellow powder was used without purification. ^{31}P NMR (81 MHz, $CDCl_3$) δ = 19.3 (s).

General procedure for the synthesis of 1-18
As a typical experiment, the reaction of the aryl bromide (1 mmol), acenaphthylene (>94%) (0.210 g, 1.3 mmol), KOAc (0.196 g, 2 mmol) at 150 °C during 18 h in DMA (5 mL) in the presence of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) under argon afford the corresponding arylation products after evaporation of the solvent and purification on silica gel. Solvent pentane:ethyl acetate 95:5 for **1**-**5**, **8**-**10**, **12**; pentane for **6**, **7**, **11**, **13**-**16**; pentane:ethyl acetate 7:3 for **17**; pentane:ethyl acetate 8:2 for **18**.

1-(4-Nitrophenyl)acenaphthylene (1)[17]
From 4-bromonitrobenzene (0.202 g, 1 mmol) and acenaphthylene (0.210 g, 1.3 mmol), **1** was obtained in 78% (0.213 g) yield as an orange solid: mp 129-132 °C.
^1H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, J = 8.7 Hz, 2H), 7.95 (d, J = 7.0 Hz, 1H), 7.94-7.91 (m, 3H), 7.89 (d, J = 8.1 Hz, 1H), 7.79 (d, J = 6.9 Hz, 1H), 7.65 (dd, J = 8.1, 7.0 Hz, 1H), 7.62 (dd, J = 8.1, 6.9 Hz, 1H), 7.35 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 142.8, 140.9, 138.3, 137.6, 129.3, 128.6, 128.5, 128.3, 128.2 (m), 127.7, 125.2, 124.5, 124.2.

4-(Acenaphthylen-1-yl)benzonitrile (2)
From 4-bromobenzonitrile (0.182 g, 1 mmol) and acenaphthylene (0.210 g, 1.3 mmol), **2** was obtained in 82% (0.207 g) yield as a yellow solid: mp 97-100 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.7 Hz, 2H), 7.88-7.82 (m, 3H), 7.78-7.71 (m, 3H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.28 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3, 140.7, 138.4, 137.6, 132.6, 129.3, 128.6, 128.3, 128.2, 128.1, 128.0, 127.9, 127.6, 125.0, 124.5, 119.1, 110.8.
Elemental analysis: calcd (%) for $C_{19}H_{11}N$ (253.30): C 90.09, H 4.38; found: C 90.17, H 4.21.

4-(Acenaphthylen-1-yl)benzaldehyde (3)
From 4-bromobenzaldehyde (0.185 g, 1 mmol) and acenaphthylene (0.210 g, 1.3 mmol), **3** was obtained in 80% (0.205 g) yield as an orange oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.06 (s, 1H), 7.99-7.83 (m, 7H), 7.75 (d, *J* = 6.9 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.32 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 191.8, 142.3, 141.9, 138.6, 137.9, 135.3, 130.3, 129.4, 128.5, 128.3, 128.1, 128.0, 127.9, 127.8, 127.6, 124.8, 124.6.
Elemental analysis: calcd (%) for $C_{19}H_{12}O$ (256.30): C 89.04, H 4.72; found: C 89.20, H 4.67.

1-(4-(Acenaphthylen-1-yl)phenyl)propan-1-one (4)
From 4-bromopropiophenone (0.213 g, 1 mmol) and acenaphthylene (0.210 g, 1.3 mmol), **4** was obtained in 78% (0.222 g) yield as an orange solid: mp 118-121 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.1 Hz, 2H), 7.95 (d, *J* = 6.9 Hz, 1H), 7.91-7.82 (m, 4H), 7.72 (d, *J* = 6.9 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.28 (s, 1H), 3.04 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 200.3, 142.1, 140.6, 138.7, 138.1, 135.7, 129.4, 128.6, 128.5, 128.1, 127.9, 127.8, 127.7, 127.6, 127.2, 124.6, 124.5, 31.8, 8.4.
Elemental analysis: calcd (%) for $C_{21}H_{16}O$ (284.36): C 88.70, H 5.67; found: C 88.47, H 5.60.

Ethyl 4-(acenaphthylen-1-yl)benzoate (5)
From ethyl 4-bromobenzoate (0.229 g, 1 mmol) and acenaphthylene (0.210 g, 1.3 mmol), **5** was obtained in 77% (0.231 g) yield as a yellow solid: mp 133-136 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 8.1 Hz, 2H), 7.95 (d, *J* = 6.9 Hz, 1H), 7.90-7.82 (m, 4H), 7.72 (d, *J* = 6.9 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.28 (s, 1H), 4.45 (q, *J* = 7.6 Hz, 2H), 1.45 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 142.3, 140.6, 138.7, 138.1, 130.1, 129.4, 129.3, 128.5, 128.1, 127.7, 127.6 (m), 124.6, 124.5, 61.0, 14.4.
Elemental analysis: calcd (%) for $C_{21}H_{16}O_2$ (300.36): C 83.98, H 5.37; found: C 84.21, H 5.48.

1-(4-Chlorophenyl)acenaphthylene (6)
From 4-bromochlorobenzene (0.192 g, 1 mmol) and acenaphthylene (0.210 g, 1.3 mmol), **6** was obtained in 79% (0.207 g) yield as a yellow solid: mp 92-95 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 6.9 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.74-7.68 (m, 3H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.17 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 138.9, 138.3, 134.7, 133.5, 129.3, 129.1, 129.0, 128.5, 128.1, 127.8, 127.6, 127.3, 126.0, 124.3, 124.2.
Elemental analysis: calcd (%) for $C_{18}H_{11}Cl$ (262.74): C 82.29, H 4.22; found: C 82.17, H 4.10.

1-(4-Fluorophenyl)acenaphthylene (7)[18]
From 4-bromofluorobenzene (0.175 g, 1 mmol) and acenaphthylene (0.210 g, 1.3 mmol), **7** was obtained in 60% (0.148 g) yield as a yellow solid: mp 60-63 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 6.9 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.80-7.72 (m, 2H), 7.70 (d, *J* = 6.9 Hz, 1H), 7.65-7.54 (m, 2H), 7.20 (t, *J* = 8.5 Hz, 2H), 7.14 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5 (d, *J* = 247.1 Hz), 142.4, 139.0, 138.6, 128.6, 129.5 (d, *J* = 7.9 Hz), 129.2, 128.4, 128.0, 127.7, 127.5, 127.1, 125.4 (d, *J* = 1.3 Hz), 124.2, 123.9, 115.7 (d, *J* = 21.5 Hz).

1-(4-Methoxyphenyl)acenaphthylene (8)[17]
From 4-bromoanisole (0.187 g, 1 mmol) and acenaphthylene (0.210 g, 1.3 mmol), **8** was obtained in 31% (0.080 g) yield as a brown solid: mp 69-71 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 6.9 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.80-7.72 (m, 3H), 7.65 (d, *J* = 6.7 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.09 (s, 1H), 7.04 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 143.1, 139.3, 138.9, 129.3, 129.1, 128.8, 128.3, 128.0, 127.5, 127.4, 126.6, 124.3, 124.2, 123.4, 114.3, 55.4.

3-(Acenaphthylen-1-yl)benzonitrile (9)
From 3-bromobenzonitrile (0.182 g, 1 mmol) and acenaphthylene (0.210 g, 1.3 mmol), **9** was obtained in 79% (0.200 g) yield as an orange solid: mp 98-101 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.93 (d, *J* = 7.2 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.87-7.82 (m, 2H), 7.72 (d, *J* = 6.8 Hz, 1H), 7.64-7.51 (m, 4H), 7.23 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 140.8, 138.4, 137.6, 137.4, 132.0, 131.2, 130.8, 129.6, 129.2, 128.5, 128.2, 128.1, 127.9, 127.6, 127.2, 124.8, 124.2, 118.9, 113.0
Elemental analysis: calcd (%) for $C_{19}H_{11}N$ (253.30): C 90.09, H 4.38; found: C 90.01, H 4.47.

3-(Acenaphthylen-1-yl)benzaldehyde (10)
From 3-bromobenzaldehyde (0.185 g, 1 mmol) and acenaphthylene (0.210 g, 1.3 mmol), **10** was obtained in 84% (0.215 g) yield as an orange oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.07 (s, 1H), 8.24 (s, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.91 (d, *J* = 7.0 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.86-7.82 (m, 2H), 7.69 (d, *J* = 6.9 Hz, 1H), 7.63-7.55 (m, 3H), 7.21 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 192.3, 141.7, 138.7, 138.0, 137.1, 136.9, 133.6, 129.5, 129.3, 128.8 (m) , 128.5, 128.1, 127.9, 127.6, 127.5, 126.7, 124.5, 124.4.
Elemental analysis: calcd (%) for $C_{19}H_{12}O$ (256.30): C 89.04, H 4.72; found: C 89.02, H 4.87.

1-(3-(Trifluoromethyl)phenyl)acenaphthylene (11)
From 1-bromo-3-(trifluoromethyl)benzene (0.225 g, 1 mmol) and acenaphthylene (0.210 g, 1.3 mmol), **11** was obtained in 90% (0.266 g) yield as a yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.97-7.87 (m, 3H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.74 (d, *J* = 6.9 Hz, 1H), 7.68-7.56 (m, 4H), 7.24 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7, 138.1, 137.0, 131.0, 131.2 (q, *J* = 32.1 Hz), 131.0, 129.3, 128.5, 128.1, 127.9, 127.7, 127.6, 126.7, 124.6 (m), 124.5, 124.4, 124.3 (q, *J* = 272.4 Hz), 124.2 (q, *J* = 3.8 Hz).
Elemental analysis: calcd (%) for $C_{19}H_{11}F_3$ (296.29): C 77.02, H 3.74; found: C 76.87, H 3.68.

2-(Acenaphthylen-1-yl)benzonitrile (12)[19]
From 2-bromobenzonitrile (0.182 g, 1 mmol) and acenaphthylene (0.210 g, 1.3 mmol), **12** was obtained in 81% (0.205 g) yield as a yellow solid: mp 167-170 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.81 (d, *J* = 6.8 Hz, 1H), 7.78-7.74 (m, 2H), 7.71 (td, *J* = 7.5, 1.3 Hz, 1H), 7.64-7.58 (m, 2H), 7.51 (s, 1H), 7.47 (td, *J* = 7.7, 1.2 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 139.4, 138.8, 138.5, 138.3, 134.3, 132.6, 130.4, 129.8, 128.8, 128.5, 128.2, 128.1, 128.0, 127.6, 127.5, 125.4, 124.2, 119.0, 111.4.

1-(2-Fluorophenyl)acenaphthylene (13)
From 2-bromofluorobenzene (0.175 g, 1 mmol) and acenaphthylene (0.210 g, 1.3 mmol), **13** was obtained in 76% (0.187 g) yield as a yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89-7.82 (m, 3H), 7.77-7.72 (m, 2H), 7.63-7.56 (m, 2H), 7.40-7.32 (m, 1H), 7.32-7.22 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5 (d, *J* = 248.9 Hz), 139.3, 139.0, 136.9, 131.0 (d, *J* = 3.6 Hz), 129.1 (d, *J* = 8.2 Hz), 129.0, 128.9 (d, *J* = 4.8 Hz), 128.5, 128.1, 127.8, 127.7, 127.5, 124.8 (d, *J* = 3.0 Hz), 124.5, 124.4 (d, *J* = 1.6 Hz), 124.1 (d, *J* = 14.5 Hz), 116.4 (d, *J* = 22.5 Hz).
Elemental analysis: calcd (%) for $C_{18}H_{11}F$ (246.28): C 87.78, H 4.50; found: C 87.60, H 4.39.

1-(Naphthalen-1-yl)acenaphthylene (14)[20]
From 1-bromonaphthalene (0.207 g, 1 mmol) and acenaphthylene (0.210 g, 1.3 mmol), **14** was obtained in 54% (0.150 g) yield as a yellow solid: mp 88-91 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.93-7.88 (m, 2H), 7.80 (d, *J* = 6.9 Hz, 1H), 7.73 (d, *J* = 7.0 Hz, 1H), 7.68-7.53 (m, 5H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.25 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 142.4, 140.6, 139.5, 134.1, 134.0, 132.3, 128.9, 128.5, 128.4, 128.3, 128.1, 128.0, 127.7, 127.6, 127.4, 127.2, 126.6, 126.0, 125.9, 125.5, 124.5, 124.1.

2-(Acenaphthylen-1-yl)-9H-fluorene (15)
From 2-bromofluorene (0.245 g, 1 mmol) and acenaphthylene (0.210 g, 1.3 mmol), **15** was obtained in 52% (0.164 g) yield as an orange solid: mp 186-189 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 6.9 Hz, 1H), 7.97 (s, 1H), 7.93-7.80 (m, 5H), 7.70 (d, *J* = 6.8 Hz, 1H), 7.67-7.54 (m, 3H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.23 (s, 1H), 4.01 (s, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 143.8, 143.5, 141.5, 141.4, 139.3, 138.8, 134.8, 129.4, 128.4, 128.0, 127.6, 127.5, 126.9 (m), 126.8, 125.3, 125.1, 124.5, 124.4, 123.7, 120.2, 120.0, 37.1.
Elemental analysis: calcd (%) for $C_{25}H_{16}$ (316.40): C 94.90, H 5.10; found: C 94.65, H 5.30.

1-(Acenaphthylen-1-yl)pyrene (16)
From 1-bromopyrene (0.281 g, 1 mmol) and acenaphthylene (0.210 g, 1.3 mmol), **16** was obtained in 88% (0.310 g) yield as an orange solid: mp 215-218 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, *J* = 8.7 Hz, 1H), 8.28 (d, *J* = 7.9 Hz, 1H), 8.25-8.15 (m, 3H), 8.15-8.10 (m, 2H), 8.06-8.00 (m, 2H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.81 (d, *J* = 6.9 Hz, 1H), 7.68-7.62 (m, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.34 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 142.8, 140.7, 139.5, 131.5, 131.1, 130.9, 129.4, 129.1, 128.9, 128.5, 128.1, 127.8, 127.7 (m), 127.6, 127.5, 127.3, 127.2, 126.1, 126.0, 125.3, 125.2, 125.0, 124.9, 124.7, 124.2.
Elemental analysis: calcd (%) for $C_{28}H_{16}$ (352.44): C 95.42, H 4.58; found: C 95.61, H 4.39.

3-(Acenaphthylen-1-yl)pyridine (17)
From 3-bromopyridine (0.158 g, 1 mmol) and acenaphthylene (0.210 g, 1.3 mmol), **17** was obtained in 75% (0.172 g) yield as an orange oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.07 (s, 1H), 8.62 (d, *J* = 4.5 Hz, 1H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.90 (d, *J* = 6.9 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 6.9 Hz, 1H), 7.64-7.55 (m, 2H), 7.40 (dd, *J* = 7.9, 4.5 Hz, 1H), 7.23 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 148.8, 148.6, 139.8, 138.7, 138.0, 134.9, 132.0, 129.2, 128.5, 128.1, 128.0, 127.7, 127.6, 126.8, 124.5, 124.3, 123.7.
Elemental analysis: calcd (%) for $C_{17}H_{11}N$ (229.28): C 89.05, H 4.84; found: C 89.12, H 4.89.

3-(Acenaphthylen-1-yl)quinoline (18)
From 3-bromoquinoline (0.208 g, 1 mmol) and acenaphthylene (0.210 g, 1.3 mmol), **18** was obtained in 78% (0.218 g) yield as a brown oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.35 (d, *J* = 2.0 Hz, 1H), 8.49 (d, *J* = 2.0 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 6.9 Hz, 1H), 7.93-7.89 (m, 2H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 6.9 Hz, 1H), 7.75-7.71 (m, 1H), 7.67-7.56 (m, 3H), 7.37 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 147.4, 139.8, 138.8, 138.2, 133.5, 129.4, 129.3 (m), 129.2, 128.5, 128.2, 128.1, 128.0 (m), 127.6 (m), 127.1, 127.0, 124.6, 124.4.
Elemental analysis: calcd (%) for $C_{21}H_{13}N$ (279.34): C 90.29, H 4.69; found: C 90.20, H 4.75.

General procedure for the synthesis of 19-21
As a typical experiment, the reaction of the benzenesulfonyl chloride (1 mmol), acenaphthylene (>94%) (0.210 g, 1.3 mmol), Li_2CO_3 (0.222 g, 3 mmol) at 140 °C during 18 h in 1,4-dioxane (5 mL) in the presence of $Pd(OAc)_2$ (11.2 mg, 0.05 mmol) under argon afford the corresponding arylation products after evaporation of the solvent and purification on silica gel. Solvent pentane.

1-(4-Bromophenyl)acenaphthylene (19)
From 4-bromobenzenesulfonyl chloride (0.255 g, 1 mmol) and acenaphthylene (0.210 g, 1.3 mmol), **19** was obtained in 46% (0.141 g) yield as an orange solid: mp 74-77 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 6.9 Hz, 1H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 6.9 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.63-7.54 (m, 4H), 7.18 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 138.9, 138.2, 135.1, 131.9, 129.4, 129.3, 128.5, 128.1, 127.8, 127.5, 127.3, 126.0, 124.3, 124.2, 121.6.
Elemental analysis: calcd (%) for $C_{18}H_{11}Br$ (307.19): C 70.38, H 3.61; found: C 70.27, H 3.70.

1-(3,4-Dibromophenyl)acenaphthylene (20)
From 3,4-dibromobenzenesulfonyl chloride (0.334 g, 1 mmol) and acenaphthylene (0.210 g, 1.3 mmol), **19** was obtained in 44% (0.170 g) yield as a yellow solid: mp 84-87 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 1.8 Hz, 1H), 7.89 (d, *J* = 7.2 Hz, 2H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.74-7.69 (m, 2H), 7.65-7.54 (m, 3H), 7.21 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 138.5, 137.8, 136.9, 133.9, 132.6, 129.2, 128.5, 128.1, 128.0, 127.8, 127.7, 127.6, 126.8, 125.2, 124.6, 124.2, 123.6.
Elemental analysis: calcd (%) for $C_{18}H_{10}Br_2$ (386.09): C 56.00, H 2.61; found: C 55.87, H 2.42.

1-(4-Iodophenyl)acenaphthylene (21)
From 4-iodobenzenesulfonyl chloride (0.303 g, 1 mmol) and acenaphthylene (0.210 g, 1.3 mmol), **19** was obtained in 60% (0.212 g) yield as an orange solid: mp 102-105 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 6.9 Hz, 1H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.85-7.77 (m, 3H), 7.70 (d, *J* = 6.9 Hz, 1H), 7.63-7.54 (m, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.18 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 138.8, 138.2, 137.9, 135.6, 129.6, 129.3, 128.5, 128.1, 127.8, 127.5, 127.3, 126.0, 124.3, 124.2, 93.1.
Elemental analysis: calcd (%) for $C_{18}H_{11}I$ (354.19): C 61.04, H 3.13; found: C 61.17, H 3.30.

General procedure for the synthesis of 22-25
As a typical experiment, the reaction of the benzenesulfonyl chloride (3 mmol), acenaphthylene (>94%) (0.162 g, 1 mmol), Li_2CO_3 (0.222 g, 3 mmol) at 140 °C during 18 h in 1,4-dioxane (5 mL) in the presence of $Pd(OAc)_2$ (11 mg, 0.05 mmol) under argon afford the corresponding diarylation products after evaporation of the solvent and purification on silica gel. Solvent pentane.

1,2-Bis(4-fluorophenyl)acenaphthylene (22)[21]
From 4-fluorobenzenesulfonyl chloride (0.585 g, 3 mmol) and acenaphthylene (0.162 g, 1 mmol), **22** was obtained in 60% (0.204 g) yield as an orange solid: mp 154-157 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 6.9 Hz, 2H), 7.61 (dd, *J* = 8.1, 6.9 Hz, 2H), 7.40 (dd, *J* = 8.5, 5.5 Hz, 4H), 7.07 (t, *J* = 8.5 Hz, 4H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 162.1 (d, *J* = 247.0 Hz), 139.7, 137.1, 131.6 (d, *J* = 7.9 Hz), 131.0 (d, *J* = 3.4 Hz), 128.4, 128.0, 127.9, 127.5, 123.8, 115.6 (d, *J* = 21.5 Hz).

1,2-Bis(4-chlorophenyl)acenaphthylene (23)
From 4-chlorobenzenesulfonyl chloride (0.633 g, 3 mmol) and acenaphthylene (0.162 g, 1 mmol), **23** was obtained in 67% (0.250 g) yield as an orange solid: mp 214-217 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 6.9 Hz, 2H), 7.60 (dd, *J* = 8.1, 6.9 Hz, 2H), 7.36 (s, 8H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 139.3, 137.2, 133.4, 133.3, 131.2, 128.8, 128.5, 128.1, 127.9, 127.7, 124.0.
Elemental analysis: calcd (%) for $C_{24}H_{14}Cl_2$ (373.28): C 77.23, H 3.78; found: C 77.11, H 3.87.

1,2-Bis[3-(trifluoromethyl)phenyl]acenaphthylene (24)
From 3-(trifluoromethyl)benzenesulfonyl chloride (0.735 g, 3 mmol) and acenaphthylene (0.162 g, 1 mmol), **24** was obtained in 48% (0.211 g) yield as an orange solid: mp 180-183 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 6.9 Hz, 2H), 7.72 (s, 2H), 7.66 (dd, *J* = 8.1, 6.9 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.50 (t, *J* = 8.2 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 137.6, 135.5, 133.2, 131.1 (q, *J* = 32.3 Hz), 129.1, 128.6, 128.1, 128.0, 126.7 (q, *J* = 3.8 Hz), 124.3, 124.1 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.5 Hz).
Elemental analysis: calcd (%) for $C_{26}H_{14}F_6$ (440.39): C 70.91, H 3.20; found: C 71.04, H 3.08.

1,2-Bis(4-iodophenyl)acenaphthylene (25)
From 4-iodobenzenesulfonyl chloride (0.909 g, 3 mmol) and acenaphthylene (0.162 g, 1 mmol), **25** was obtained in 65% (0.361 g) yield as an orange solid: mp 240-243 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.75-7.67 (m, 6H), 7.60 (t, *J* = 7.5 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 4H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 139.2, 137.7, 137.3, 134.4, 131.8, 128.5, 128.1, 128.0, 127.8, 124.1, 93.2.
Elemental analysis: calcd (%) for $C_{24}H_{14}I_2$ (556.18): C 51.83, H 2.54; found: C 51.60, H 2.38.

General procedure for the synthesis of 26 and 27
As a typical experiment, the reaction of the aryl bromide (1.5 mmol), 1-(4-nitrophenyl)acenaphthylene **1** (0.273 g, 1 mmol), KOAc (0.196 g, 2 mmol) at 150 °C during 18 h in DMA (5 mL) in the presence of $Pd(OAc)_2$ (2.2 mg, 0.01 mmol) under argon afford the corresponding arylation products after evaporation of the solvent and purification on silica gel. Solvent pentane:ethyl acetate 95:5.

1-(4-Nitrophenyl)-2-(4-fluorophenyl)acenaphthylene (26)
From 4-bromofluorobenzene (0.262 g, 1.5 mmol) and 1-(4-nitrophenyl)acenaphthylene **1** (0.273 g, 1 mmol), **26** was obtained in 76% (0.279 g) yield as an orange solid: mp 203-206 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.8 Hz, 2H), 7.96 (d, *J* = 7.2 Hz, 1H), 7.93 (d, *J* = 7.2 Hz, 1H), 7.76(d, *J* = 6.9 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.68-7.62 (m, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.42-7.35 (m, 2H), 7.11 (t, *J* = 8.0 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8 (d, *J* = 248.2 Hz), 146.7, 142.3, 139.6, 139.2, 138.7, 135.7, 131.6 (d, *J* = 8.0 Hz), 130.7, 130.3 (d, *J* = 3.5 Hz), 128.7, 128.4, 128.2, 128.1, 128.0, 127.9, 124.8, 124.0, 123.8, 115.9 (d, *J* = 21.5 Hz).
Elemental analysis: calcd (%) for $C_{24}H_{14}FNO_2$ (367.38): C 78.46, H 3.84; found: C 78.25, H 3.67.

1-(4-Nitrophenyl)-2-[3-(trifluoromethyl)phenyl]acenaphthylene (27)
From 1-bromo-3-(trifluoromethyl)benzene (0.338 g, 1.5 mmol) and 1-(4-nitrophenyl)acenaphthylene **1** (0.273 g, 1 mmol), **27** was obtained in 80% (0.334 g) yield as an orange solid: mp 174-177 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.8 Hz, 2H), 7.99-7.94 (m, 2H), 7.77 (d, *J* = 6.9 Hz, 2H), 7.74 (s, 1H), 7.70-7.61 (m, 3H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.56-7.47 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 141.8, 138.8, 138.7, 138.5, 136.7, 135.3, 133.2, 131.2 (q, *J* = 32.4 Hz), 130.7, 129.3, 128.7, 128.6, 128.4, 128.2, 128.1, 128.0, 126.6 (q, *J* = 3.8 Hz), 124.8, 124.5 (q, *J* = 3.8 Hz), 124.4, 123.9, 123.8 (q, *J* = 272.5 Hz).
Elemental analysis: calcd (%) for $C_{25}H_{14}F_3NO_2$ (417.39): C 71.94, H 3.38; found: C 71.75, H 3.21.

General procedure for the synthesis of 28-30
As a typical experiment, the reaction of the benzenesulfonyl chloride (1.5 mmol), 1-arylacenaphthylene derivative (1 mmol), Li_2CO_3 (0.222 g, 3 mmol) at 140 °C during 18 h in 1,4-dioxane (5 mL) in the presence of $Pd(OAc)_2$ (11.2 mg, 0.05 mmol) under argon afford the corresponding arylation products after evaporation of the solvent and purification on silica gel. Solvent pentane:ethyl acetate 95:5 for **28** and **29**; pentane for **30**.

1-(2-Bromophenyl)-2-(4-cyanophenyl)acenaphthylene (28)
From 2-bromobenzenesulfonyl chloride (0.382 g, 1.5 mmol) and 4-(acenaphthylen-1-yl)benzonitrile **2** (0.253 g, 1 mmol), **28** was obtained in 81% (0.330 g) yield as a yellow solid: mp 112-115 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 6.9 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.67-7.57 (m, 4H), 7.55-7.47 (m, 3H), 7.38-7.26 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 140.1, 139.9, 139.3, 138.3, 137.5, 136.1, 133.3, 132.2, 132.1, 129.9, 129.6, 128.6, 128.2, 128.1, 128.0, 127.9, 127.6, 124.9, 124.4, 124.1, 119.0, 110.6.
Elemental analysis: calcd (%) for $C_{25}H_{14}BrN$ (408.30): C 73.54, H 3.46; found: C 73.67, H 3.27.

1-(2-Bromophenyl)-2-[(4-(ethoxycarbonyl)phenyl)]acenaphthylene (29)

From 2-bromobenzenesulfonyl chloride (0.382 g, 1.5 mmol) and ethyl 4-(acenaphthylen-1-yl)benzoate **5** (0.300 g, 1 mmol), **29** was obtained in 78% (0.355 g) yield as a yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 6.9 Hz, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.53-7.48 (m, 3H), 7.36-7.29 (m, 2H), 7.28-7.22 (m, 1H), 4.40 (q, *J* = 7.6 Hz, 2H), 1.41 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 139.9, 139.6, 139.2, 138.8, 138.6, 136.5, 133.2, 132.2, 129.6, 129.4, 129.3, 129.0, 128.6, 128.1, 128.0, 127.9, 127.8, 127.7, 127.5, 124.6, 124.5, 124.2, 61.0, 14.4.
Elemental analysis: calcd (%) for $C_{29}H_{19}BrO_2$ (455.35): C 71.22, H 4.21; found: C 71.35, H 4.04.

1-(2-Bromophenyl)-2-(4-fluorophenyl)acenaphthylene (30)
From 2-bromobenzenesulfonyl chloride (0.382 g, 1.5 mmol) and 1-(4-fluorophenyl)acenaphthylene **7** (0.246 g, 1 mmol), **30** was obtained in 80% (0.321 g) yield as a yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 6.9 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.48 (d, *J* = 6.9 Hz, 1H), 7.43-7.36 (m, 2H), 7.35-7.22 (m, 3H), 7.08-7.01 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5 (d, *J* = 247.1 Hz), 139.7, 139.2, 138.6, 137.9, 136.7, 133.1, 132.3, 131.1 (d, *J* = 3.4 Hz), 131.0 (d, *J* = 8.0 Hz), 129.2, 128.5, 128.0, 127.9, 127.8, 127.7, 127.4, 127.3, 124.3, 123.9, 115.4 (d, *J* = 21.4 Hz).
Elemental analysis: calcd (%) for $C_{24}H_{14}BrF$ (401.28): C 71.84, H 3.52; found: C 71.98, H 3.64.

General procedure for the synthesis of 31-33
As a typical experiment, the reaction of the 1,2-diarylacenaphthylene derivative (0.5 mmol), PivOK (0.210 g, 1.5 mmol) at 150 °C during 18 h in DMA (5 mL) in the presence of $PdCl(C_3H_5)$(dppb) (6.1 mg, 0.01 mmol) under argon afford the corresponding arylation products after evaporation of the solvent and purification on silica gel. Solvent pentane:ethyl acetate 95:5 for **31** and **32**; pentane for **32**.

Dibenzo[*j,l*]fluoranthene-9-carbonitrile (31)
From 1-(2-bromophenyl)-2-(4-cyanophenyl)acenaphthylene **28** (0.204 g, 0.5 mmol), **31** was obtained in 90% (0.147 g) yield as a yellow solid: mp 257-260 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (s, 1H), 8.48 (d, *J* = 7.8 Hz, 1H), 8.33 (d, *J* = 8.3 Hz, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 8.21 (d, *J* = 7.0 Hz, 1H), 7.99 (d, *J* = 6.9 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.62-7.46 (m, 5H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 136.4, 136.2, 136.0, 132.0, 131.5, 131.2, 129.6, 129.5, 129.3, 129.1, 128.3, 128.2, 127.8, 127.7 (m), 126.7, 125.5, 125.0, 124.7, 124.6, 123.0, 119.6, 108.4.
Elemental analysis: calcd (%) for $C_{25}H_{13}N$ (327.39): C 91.72, H 4.00; found: C 91.57, H 3.89.

Ethyl dibenzo[*j,l*]fluoranthene-9-carboxylate (32)
From 1-(2-bromophenyl)-2-[(4-(ethoxycarbonyl)phenyl)]acenaphthylene **29** (0.228 g, 0.5 mmol), **32** was obtained in 87% (0.162 g) yield as an orange solid: mp 126-129 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.19 (s, 1H), 8.59-8.50 (m, 2H), 8.44 (d, *J* = 8.6 Hz, 1H), 8.21 (d, *J* = 7.1 Hz, 1H), 8.10 (d, *J* = 7.0 Hz, 1H), 8.05 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.76-7.68 (m, 2H), 7.59-7.45 (m, 4H), 4.51 (q, *J* = 7.6 Hz, 2H), 1.54 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 137.0, 136.9, 135.5, 132.7, 132.1, 131.7, 130.8, 129.8, 129.6, 129.1, 127.8, 127.7, 127.6, 127.4, 127.2, 127.0, 126.6, 126.4, 125.6, 125.2, 124.8, 124.7, 124.5, 123.5, 61.1, 14.6.
Elemental analysis: calcd (%) for $C_{27}H_{18}O_2$ (374.44): C 86.61, H 4.85; found: C 86.47, H 4.67.

9-Fluorodibenzo[*j,l*]fluoranthene (33)
From 1-(2-bromophenyl)-2-(4-fluorophenyl)acenaphthylene **30** (0.201 g, 0.5 mmol), **33** was obtained in 89% (0.142 g) yield as a yellow solid: mp 207-210 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80-8.69 (m, 2H), 8.55 (d, *J* = 8.4 Hz, 1H), 8.42 (d, *J* = 7.0 Hz, 1H), 8.35 (d, *J* = 7.0 Hz, 1H), 8.29 (dd, *J* = 11.3, 2.4 Hz, 1H), 7.87-7.82 (m, 2H), 7.74-7.58 (m, 4H), 7.40 (t, *J* = 7.8 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2 (d, *J* = 245.6 Hz), 137.5, 137.4, 133.4, 133.0, 132.6 (d, *J* = 8.0 Hz), 131.7, 130.1 (m), 129.3, 128.0, 127.8, 127.7 (m), 127.5, 127.0, 126.8, 126.5, 126.2, 125.0, 124.9, 124.7, 123.7, 116.0 (d, *J* = 23.6 Hz), 108.7 (d, *J* = 22.2 Hz).
Elemental analysis: calcd (%) for $C_{24}H_{13}F$ (320.37): C 89.98, H 4.09; found: C 89.79, H 4.00.

Conclusions

The conclusions section should come in this section at the end of the article, before the acknowledgements.

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