Tetrahedron Letters 54 (2013) 392–396

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Expeditious synthesis of fluorinated styrylbenzenes and polyaromatic hydrocarbons

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ARTICLE INFO

Article history:
Received 8 October 2012
Revised 4 November 2012
Accepted 5 November 2012
Available online 21 November 2012

Keywords:
Mizoroki–Heck
One-pot Reactions
Photocyclization
Fluorinated styrylbenzenes
Fluorinated polyaromatic hydrocarbons

ABSTRACT

A series of fluorinated styrylbenzene derivatives were synthesized by the Mizoroki–Heck reaction using phosphine-free catalytic conditions or by adopting the one-pot Wittig–Heck reaction sequence. The fluorinated styrylbenzenes were converted into polyaromatic hydrocarbons such as phenanthrenes, [4]helicenes, and benzo[*ghi*]perylene by a modified photocyclization procedure involving I_2-THF condition.

Fluorinated polyaromatic hydrocarbons (F-PHCs) play an important role in understanding the action and the mechanism of carcinogenesis of this class of compounds. Presence of fluorine at different positions of the PHC helps to narrow the possible active sites to bind with DNA[1] or in modulating the carcinogenicity from the remote sites[2] or understanding other conformational parameters.[3] The study has established that certain F-PHCs have lower biological activity due to the presence of fluorine at the crucial section of the molecular framework and hence are less tumorigenic than the parent PHCs.[1b,4] The derivatives of F-PHCs also have a significant role in the study of reactions of standard nucleophiles with radical cations.[5] Recently polyaromatic compounds such as hexabenzocoronenes with the presence of a number of fluorine substituents have shown novel metastable molecular conformations.[6] Besides these the F-PHCs have a wide range of applications in molecular recognition, Host–Guest interactions, material chemistry, biologically important compounds,[7] medicinal chemistry,[8] liquid crystals,[9] and crystal engineering.[10]

The area of chemistry of fluorinated organic molecules has been a subject of immense research and several monograms and books are now available for reference.[11] Generally the fluorine atom is introduced by various special fluorinating methods on the substrate molecules.[12] This approach of accessing F-PHCs often has a drawback of formation of unwanted isomers.[12c,13–16] The other option is to select an appropriately fluorinated starting molecule and build the structure of F-PHC and has been successfully demonstrated in some cases.[17–21]

Recently we have developed phosphine-free catalyst systems for efficient Mizoroki–Heck reaction[22] as well as a one-pot Wittig–Heck reaction sequence.[23] One of the useful methods of synthesis of phenanthrenes, benzo[*c*]phenanthrenes, and helicenes is photocyclization of the corresponding stilbene derivatives.[24] In our earlier studies we have also developed an efficient modification of this photocyclization procedure by replacing the conventionally preferred propylene oxide as the acid scavenger with readily available tetrahydrofuran.[25] In this communication we present a combination of these two methods to synthesize fluorinated polyaromatic hydrocarbons.

The Path A of Scheme 1 describes the basic Mizoroki–Heck reaction to construct styrylbenzene derivative. The phosphine free catalyst system [comprising of the in situ mixture of ligand 1-(α-aminobenzyl)-2-naphthols **L** and $Pd(OAc)_2$] was screened for standard Mizoroki–Heck reaction with fluorinated aromatic bromo compounds **1**, **7,** or **10** with good conversions, Scheme 2. The stilbenes obtained are isolated in excellent yield under the experimental conditions.

However, this approach is limited to the availability of the corresponding styrene derivatives. To overcome this limitation we had developed the one-pot approach of in situ synthesis of styrene from the aldehydes by the Wittig reaction and utilized it for the subsequent Mizoroki–Heck reaction.[23] The advantage of this reaction is the availability of a range of aldehydes with varied functional groups and the elimination of the need of purification of

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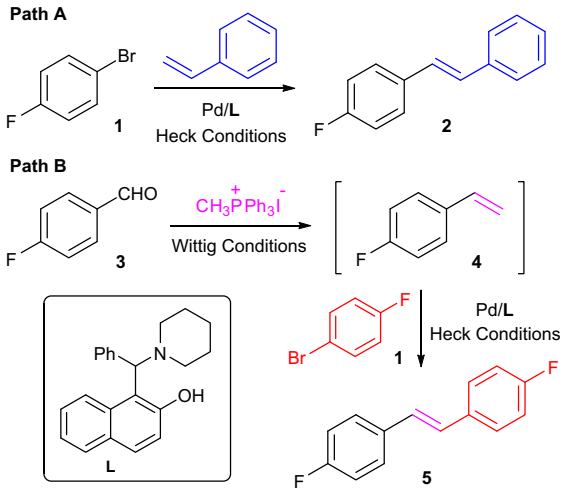
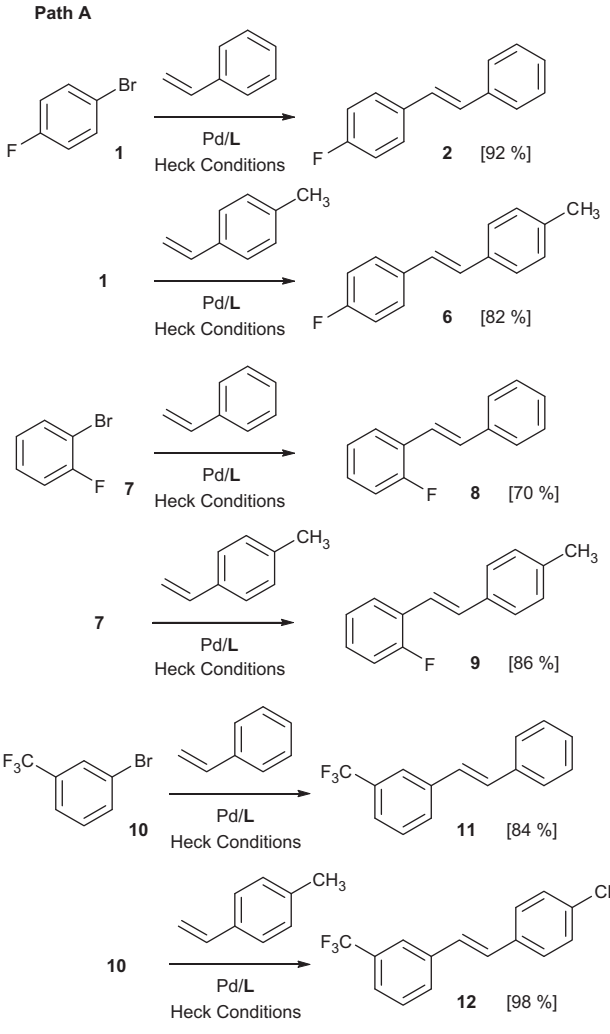
http://dx.doi.org/10.1016/j.tetlet.2012.11.022

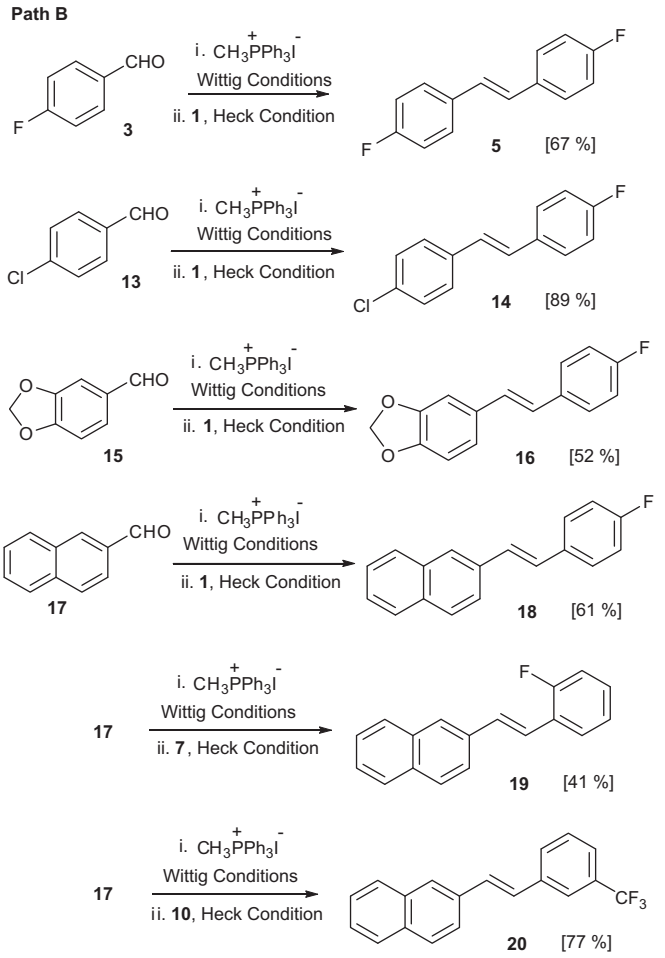


Scheme 1. Synthesis of fluorinated stilbenes.

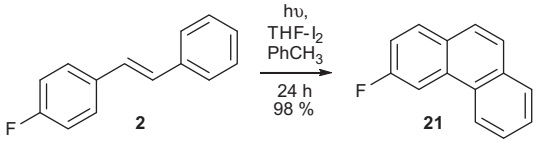


Scheme 2. Synthesis of stilbene derivatives by Path A. *Heck conditions*: Ar-Br (1.0 equiv), styrene (1.5 equiv), $Pd(OAc)_2$ (0.5 mol %), L (0.6 mol %), K_2CO_3 (2.5 equiv), TBAB (0.2 equiv), DMA, N_2 atm, 140 °C, 40 h.

the styrene for the coupling reactions. This strategy utilizes two aromatic moieties (Ar_1CHO and Ar_2X), to construct the stilbene unit and offers a variety of two different fluorine or fluorine containing substitutions as shown in Path B of Scheme 1.



Scheme 3. Synthesis of stilbene derivatives by Path B. *One-pot Wittig–Heck conditions*: Ar-CHO (1.5 equiv), CH_3PPh_3I (1.5 equiv), Ar-Br (1.0 equiv), $Pd(OAc)_2$ (0.5 mol %), L (0.6 mol %), K_2CO_3 (4.0 equiv), TBAB (0.2 equiv), DMA, N_2 atm, 140 °C, 40 h.



Scheme 4. Photodehydrocyclization of fluorinated stilbenes.

A series of fluorine containing styrylbenzenes were synthesized from corresponding aromatic aldehydes **3**, **13**, **15**, and **17** via their in situ conversion to styrenes and the subsequent Mizoroki–Heck reaction with suitable aryl halide as outlined in Scheme 3. As an example the reaction of 4-fluorobenzaldehyde **3** with one carbon phosphonium salt (Ph_3PCH_3I) and base will produce 4-fluorostyrene **4**, which will undergo in situ Mizoroki–Heck reaction with 1-bromo-4-fluorobenzene **1** to form 4,4′-difluoro stilbene **5** in moderate yield. Although the overall yields of such approach are slightly lower as the conditions are not currently fully optimized, this path offers wider scope for easy access to a variety of fluorinated stilbenes.

The standard method of photodehydrocyclization of stilbene in the presence of iodine as the oxidant produces phenanthrene and hydriodic acid, HI. Since this acid needs to be neutralized usually propylene oxide is used as an acid scavenger. However, the use of propylene oxide requires slight care as it has low boiling point

Table 1
Photocyclization of fluorinated stilbenes

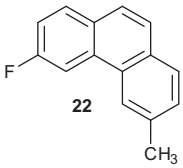
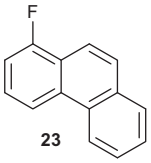
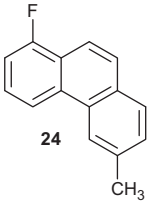
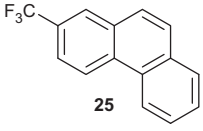
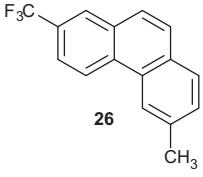
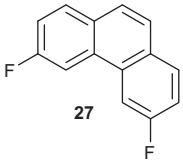
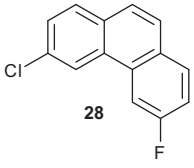
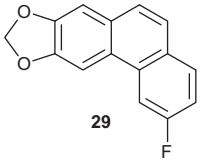
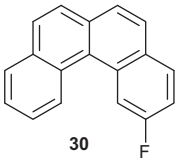
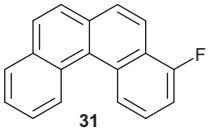
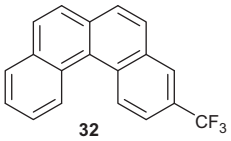
No.	Stilbene	Derivative	Cyclized product
1	**6**	96%	 **22**
2	**8**	97%	 **23**
3	**9**	95%	 **24**
4	**11**	98%	 **25**
5	**12**	84%	 **26**
6	**5**	98%	 **27**
7	**14**	96%	 **28**
8	**16**	28%	 **29**
9	**18**	71%	 **30**
10	**19**	81%	 **31**

Table 1 (*continued*)

No.	Stilbene	Derivative	Cyclized product
11	**20**	82%	 **32**

Conditions for photocyclization: iodine (1.1 equiv), THF (100 equiv), toluene, 125 W HPMV lamp, 24 h.

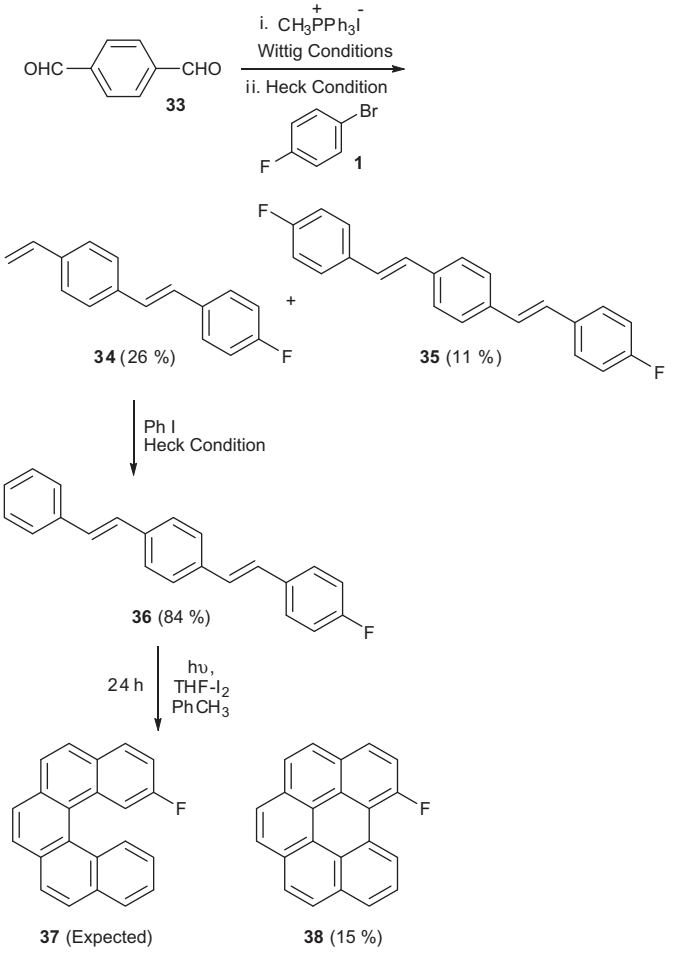
and proper cooling is necessary to prevent its loss during reaction. We have developed a modified method of similar photodehydrocyclization utilizing commonly available tetrahydrofuran as a readily available, less toxic acid scavenger with higher boiling point for practical applications.[25] The modified method is applied for the photodehydrocyclization of fluorinated stilbenes for the synthesis of corresponding fluorine containing phenanthrene derivatives, Scheme 4.

The photolysis is performed with iodine and excess of THF in degassed toluene under the irradiation of high pressure mercury vapor lamp till the cyclization is complete. The cyclization in most cases was complete in 24 h with excellent conversions as can be seen from the examples listed in Table 1. The 1,3-dioxolane containing derivative of stilbene **16** prepared from piperonal **15**, on photodehydrocyclization gave a linear product **29** instead of the angular product due to the steric constraints.[26] The fluorinated helical PHCs are also important compounds and a set of fluorinated [4]helicenes **30**, **31**, and **32** were prepared from the corresponding styrylnaphthalenes **18**, **19**, and **20**, respectively, in good chemical yields. In all the three cases the angular cyclization occurred and no linear products were detected.

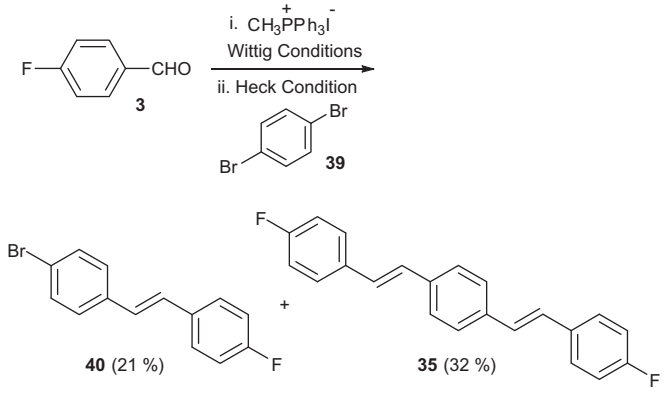
Having established the conditions for the improved procedure of photodehydrocyclization of fluorinated stilbenes it was envisaged to apply this strategy for the construction of larger F-PHCs by selecting fluorinated bis(stilbenes) or tris(stilbenes) as substrates. With this aim a number of such conjugated compounds were synthesized. The method of one-pot Wittig–Heck reaction developed in our laboratory[23] was extended for the synthesis of 1,4-bis(4-fluorostyryl)benzene **35**.[27] The process involved in situ synthesis of divinylbenzene starting from terephthalaldehyde **33** and the Wittig salt (Ph_3PCH_3I), which was trapped by the Mizoroki–Heck reaction with *p*-bromofluorobenzene **1** (Scheme 5). The reaction furnished a mixture of mono-Heck reaction product **34** and the expected double Heck reaction product **35**, the former was separated and further subjected to Mizoroki–Heck conditions[22] with iodobenzene to prepare 1-(4-fluorostyryl)-4-styrylbenzene **36** in excellent yield. The sample of **36** was subjected to the standard photocyclization condition, however the expected 2-fluoro[5]helicene **37** was not detected but 5-fluorobenzo[*ghi*]perylene **38** was isolated in small amount. Such type of further cyclization of [5]helicene is a common occurrence under photochemical conditions.[19a,28]

Synthesis of **35** by the above approach was less effective probably due to the polymerization and cross-linking of in situ formed divinylstyrene. Another approach for its synthesis was investigated where 4-fluorostyrene was in situ synthesized and subjected to a double Mizoroki–Heck reaction with 1,4-dibromobenzene **39** (Scheme 6). This approach was a better option for accessing the desired 1,4-bis(4-fluorostyryl)benzene **35**.

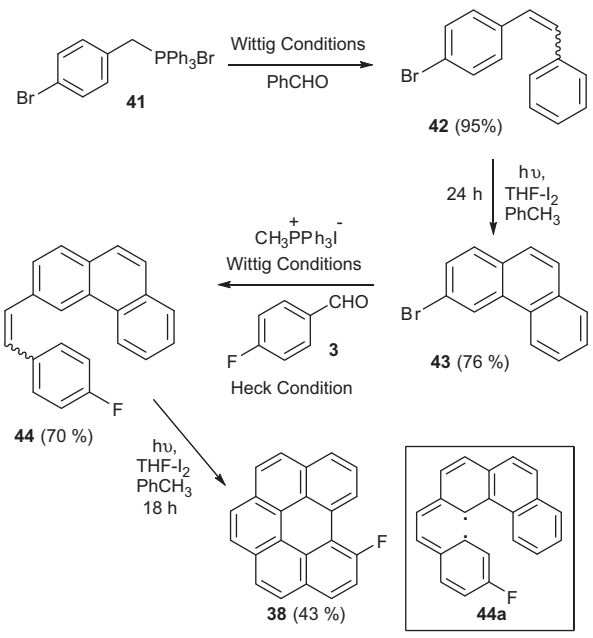
Another route for the preparation of 2-fluoro[5]helicene was investigated where 3-bromophenanthrene **43** was prepared from



Scheme 5. Attempted synthesis of 2-fluoro[5]helicene. *Conditions for Wittig–Heck step:* $Ar(CHO)_2$ **33** (1.0 equiv), CH_3PPh_3I (2.5 equiv), ArBr **1** (2.5 equiv), $Pd(OAc)_2$ (1.0 mol %), L (1.2 mol %), K_2CO_3 (8.0 equiv), TBAB (0.4 equiv), DMA, N_2 atm, 140 °C, 40 h. *Conditions for Mizoroki–Heck step*: **34** (1.2 equiv), PhI (1.0 equiv), $Pd(OAc)_2$ (0.5 mol %), L (0.6 mol %), K_2CO_3 (2.5 equiv), DMA, N_2 atm, 140 °C, 40 h.



Scheme 6. Improved Synthesis of 1,4-bis(4-fluorostyryl)benzene **35**. *One-pot Wittig–Heck conditions*: $Ar(Br)_2$ **39** (1.0 equiv), **3** (2.5 equiv), CH_3PPh_3I (2.5 equiv), $Pd(OAc)_2$ (2.0 mol %), L (2.4 mol %), K_2CO_3 (8.0 equiv), TBAB (0.4 equiv), DMA, N_2 atm, 140 °C, 40 h.

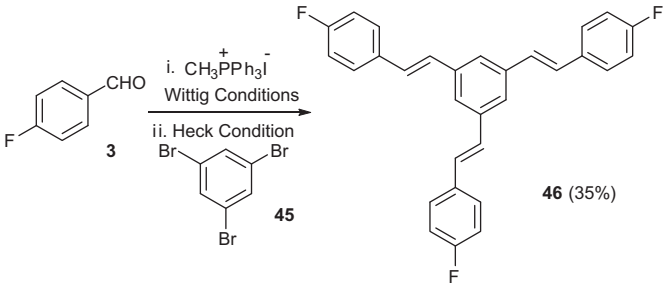


Scheme 7. Attempted synthesis fluoro[5]helicene. *Conditions for Wittig step*: PhCHO (1.0 equiv), **41** (1.1 equiv), Na (1.1 equiv), MeOH, rt, N_2 atm, 24 h. *Conditions for Wittig–Heck step*: **43** (1.0 equiv), **3** (1.5 equiv), CH_3PPh_3I (1.5 equiv), $Pd(OAc)_2$ (0.5 mol %), L (0.6 mol %), K_2CO_3 (2.5 equiv), TBAB (0.4 equiv), DMA, N_2 atm, 140 °C, 40 h.

the phosphonium salt **41** via an intermediate 4-bromostilbene **42**. This bromophenanthrene **43** was subjected to another one-pot Wittig–Heck reaction sequence to introduce fluorinated stilbene derivative **44**. However the photolysis of **44** also resulted in the formation of 5-fluorobenzo[*ghi*]perylene **38** as a major product (Scheme 7). It is noteworthy that photocyclization of distyrylbenzene **36** as well as styrylphenanthrene **44** gave the same product **38** but the latter case was more efficient possibly due to the formation of a more stable diradical intermediate **44a**.

In continuation with our efforts to construct highly conjugated fluorinated molecules a combination of Wittig–Heck reaction was performed on 4-fluorobenzaldehyde **3** to make in situ 4-fluorostyrene which was trapped by the triple Heck reaction with 1,3,5-tribromobenzene **45** (Scheme 8). The fluorinated tri-styrylbenzene **46** was isolated in all *E* form, but efforts to subject it to the photolysis to construct trifluoro benzo[*c*]naphtha[2,1-*p*]chrysene[29] were not successful. Under the present conditions several unidentifiable products were detected during the photochemical reaction of **46**.

In this Letter we present our initial results for the synthesis of fluorine containing styrylbenzene derivatives by the Mizoroki–Heck reaction and the one-pot Wittig–Heck reaction sequence. The fluorinated stilbene derivatives were then subjected to modified photodehydrocyclization reaction to efficiently prepare several fluorinated polyaromatic hydrocarbons.[30]



Scheme 8. Synthesis of tri-styrylbenzene derivative. *One-pot Wittig–Heck conditions*: $Ar(Br)_3$ **45** (1.0 equiv), **3** (3.6 equiv), CH_3PPh_3I (3.6 equiv), $Pd(OAc)_2$ (3.0 mol %), L (3.6 mol %), K_2CO_3 (12.0 equiv), TBAB (0.6 equiv), DMA, N_2 atm, 140 °C, 40 h.

Acknowledgment

Financial support for this work by the Council of Scientific and Industrial Research (CSIR), New Delhi [No. 01(2386)/10/EMR-II] is gratefully acknowledged. We also thank CSIR, New Delhi for the award of research fellowship to ARC, Navin Fluorine International Limited for providing samples of fluorinated reagents and Professor B.V. Kamath, Head, Department of Chemistry for the infrastructural facilities and constant encouragements.

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30. Representative procedure for the one pot Wittig–Heck reaction:
E-2-[2-(4-Fluorophenyl)vinyl]naphthalene (**18**):
In dry N_2 flushed two-necked r.b. flask a mixture of *p*-bromofluorobenzene (0.50 g, 2.857 mmol), 2-naphthaldehyde (0.67 g, 4.286 mmol), triphenylmethylphosphonium iodide (1.73 g, 4.286 mmol), palladium acetate (0.0032 g, 0.014 mmol) and **L** (0.0055 mg, 0.017 mmol), TBAB (0.184 g, 0.571 mmol), and K_2CO_3 (1.591 g, 11.43 mmol) in dry N,N-dimethylacetamide (20 mL) was taken and kept under N_2 atmosphere. The reaction mixture heated to 140 °C for 40 h. The cooled mixture was then poured into water (25 mL) and extracted with ethyl acetate (3 × 25 mL). The combined organic layer was washed with water (2 × 20 mL), dried with anhydrous sodium sulfate, concentrated in vacuum and purified by column chromatography over silica gel and petroleum ether as eluent to give *E*-2-[2-(4-fluorophenyl)vinyl]naphthalene **18** as white solid (0.428 g, 61%); mp 148–150 °C (Lit.[21] 151–152 °C).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.89–7.83 (m, 4H), 7.77–7.74 (dd, J = 8.8, 1.6 Hz, 1H), 7.6–7.46 (m, 4H), 7.22 (s, 2H), 7.12–7.07 (m, 2H).
Mass (EI) 248.5 $(M)^+$ (40), 247.8 (98), 247 (55), 246 (100), 245 (39), 229 (23).
IR (KBr) 3051, 3017, 2926, 2354, 1897, 1666, 1596, 1509, 1411, 1238, 1158, 1097, 966, 903, 855, 826, 740, 694, 641 cm^{-1}.
General procedure for photodehydrocyclization:
2-Fluorobenzo[*c*] phenanthrene (**30**):
To a solution of *E*-2-[2-(4-fluorophenyl)vinyl]naphthalene **18** (0.20 g, 0.806 mmol) in toluene (550 mL) was added iodine (225 mg, 0.887 mmol) and dry tetrahydrofuran (6.6 mL, 80.64 mmol) in a standerd immersion photo reactor. The mixture is degassed (15 min.) by sonication and irradiated with 125 W high pressure mercury vapor lamp for 24 h. The reaction mixture was washed with aquous sodium thiosulfate (3 × 150 mL), dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The residue was chromatograhed on silica gel column by eluting with petroleum ether to afford 2-fluorobenzo[*c*]phenanthrene **30** as white solid (0.14 g, 71%), mp 64–66 °C (Lit.[31] 63.7–64.1 °C).
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09–9.07 (d, J = 8.4 Hz, 1H), 8.84–8.80 (dd, J = 12.4, 2.4 Hz, 1H), 8.05–8.99 (m, 2H), 7.94–7.89 (m, 2H), 7.85–7.79 (m, 2H), 7.74–7.69 (m, 1H), 7.68–7.63 (m, 1H), 7.43–7.38 (td, J = 8.8, 2.8 Hz, 1H).
Mass (EI) 246.3 (100), 245.2 (93), 243.8 (80), 241.7 (15), 228.3 (20), 227.2 (20), 226.1(18), 225.2 (11), 121.9 (60), 113.1 (12), 112.1 (11), 110.1 (11), 98.7 (10).
IR (KBr) υ 3046, 1684, 1598, 1499, 1429, 1357, 1289, 1247, 1216, 1199, 1176, 1124, 1010, 974, 885, 837, 784, 744 cm^{-1}.
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