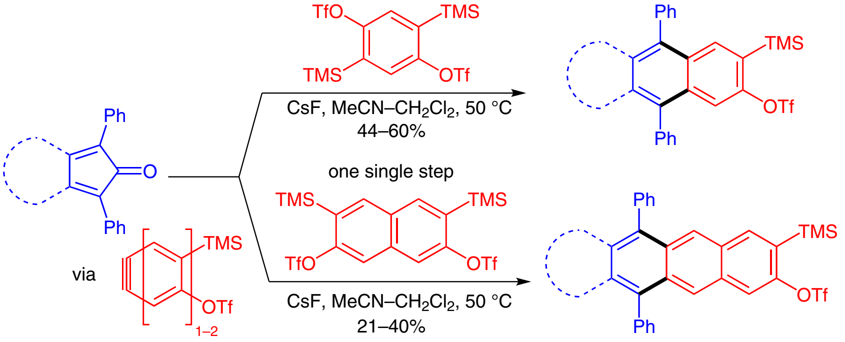
Straightforward Synthesis of Novel Acene-Based Aryne Precursors

Diego Rodríguez-Lojo
Diego Peña*
Dolores Pérez*
Enrique Guitián

Centro de Investigación en Química Biolóxica e Materiais
Moleculares (CIQUS) and Departamento de Química
Orgánica, Facultade de Química, Universidade de Santiago
de Compostela, 15782 Santiago de Compostela, Spain
diego.pena@usc.es
dolores.perez@usc.es

Dedicated to Prof. K. Peter C. Vollhardt



Received: 10.04.2015
Accepted after revision: 16.05.2015

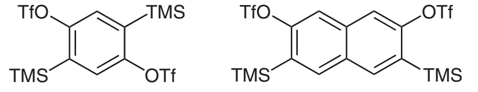
DOI: 10.1055/s-0034-1381005; Art ID: st-2015-b0262-l

Abstract Large polycyclic *o*-(trimethylsilyl)aryl triflates are easily obtained by reaction of commercially available bisaryne precursors with cyclopentadienones. The transformation involves controlled generation of one of the aryne functionalities, trapping by Diels–Alder reaction with a dienone, and chelotropic extrusion of CO. The newly synthesized triflates are precursors of acene-based arynes, including a didehydropentacene.

Key words arynes, polycyclic aromatic hydrocarbons, acenes, Diels–Alder reaction, cycloadditions

In recent years the chemistry of arynes[1] has experienced a significant resurgence mainly due to the availability of suitable methods for their generation.[2] Most of the work published in the last decade used the fluoride-induced elimination from *o*-(trimethylsilyl)aryl triflates for the generation of arynes and hetarynes under mild conditions. This method, first described by Kobayashi et al.[3] and further developed by our group and others, spelled the discovery of novel reaction venues, including metal-catalyzed transformations,[4,5] and facilitated the application of aryne chemistry to the synthesis of complex natural products[6] and novel polycyclic aromatic systems.[7]

The preparation of simple *o*-(trimethylsilyl)aryl triflates is usually achieved in one or two synthetic steps from the corresponding *o*-bromophenols[8] which, in many cases, are accessible by selective *o*-bromination of phenols. This procedure has been proved useful for the synthesis of a variety of benzyne, naphthyne, or phenanthryne precursors, starting from easily available phenols, naphthols, or phenanthrols. The preparation of slightly more complex polycyclic *o*-(trimethylsilyl)aryl triflates, such as the precursors of 2,3-triphenylyne,[9] 2,3-biphenylyne,[10] or corannulyne,[11] required longer, less efficient synthetic routes. Here we report a straightforward method for the synthesis of extended polycyclic *o*-(trimethylsilyl)aryl triflates by means of controlled [4+2] cycloadditions between cyclopentadienones and bistriflates **1**[12] or **2** (Figure 1),[13] which are formal precursors of the 1,4-benzodiyne and 2,6-naphthodiyne, respectively.



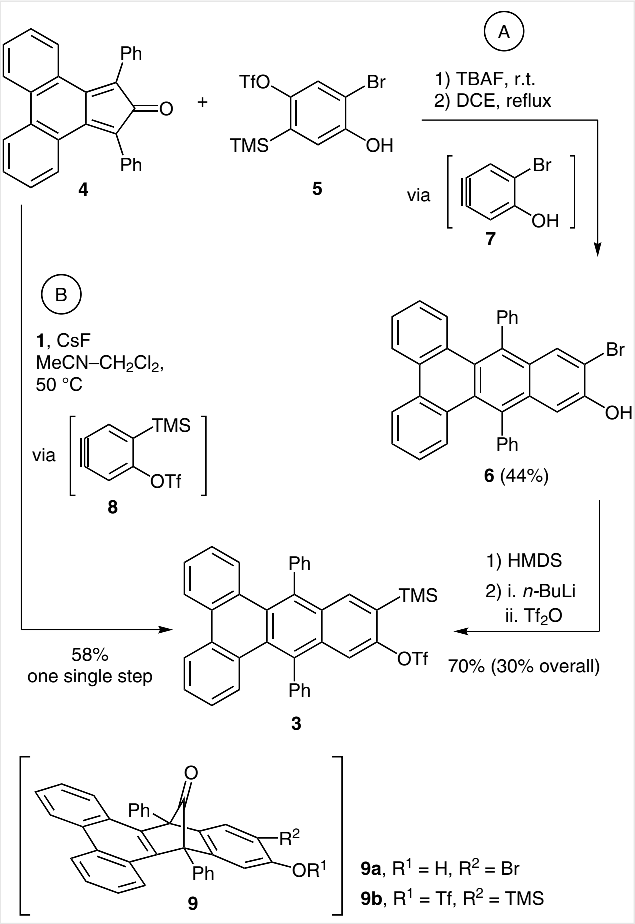
1 **2**

Figure 1

In the course of one of our research projects, focused to the synthesis of large polycyclic aromatic hydrocarbons (PAH) with application in organic electronics, we recently reported the use of the masked bisbenzyne approach for the synthesis of the benzotriphenylyne precursor **3**.[14]

Thus, treatment of cyclopentadienone **4**[15] with 3-bromo-4-hydroxy-6-(trimethylsilyl)phenyl triflate (**5**) and TBAF afforded bromophenol **6**, through a [4+2] cycloaddition of the dienone with aryne **7**, followed by chelotropic decarbonylation (Scheme 1, route A).

Transformation of **6** into the corresponding *o*-(trimethylsilyl)aryl triflate following our general established protocol,[8] afforded benzotriphenylyne precursor **3** in 30% overall yield, which was subsequently subjected to palladium-catalyzed cyclotrimerization to build a clover-shaped 16-ring nanographene. In an attempt to synthetize **3** more efficiently, we explored the reaction of **4** with 2,5-bis(trimethysilyl)-1,4-phenylene bis(triflate) (**1**), under controlled conditions for the selective generation and trapping of functionalized monoaryne **8**. Successfully, we found



Scheme 1 Synthesis of **3**. (A) Two-step procedure (masked bisbenzyne approach);[14] (B) one-step procedure using bistriflate **1**.

that treatment of **1** with 120 mol% anhydrous CsF in a MeCN–CH_2Cl_2 mixture (2:1), in the presence of 1,3-diphenyl-2*H*-cyclopenta[*l*]phenanthren-2-one (**4**), afforded triflate **3** in 58% yield (Scheme 1, route B).

The choice of the solvent mixture and the use of CsF as fluoride source seem to be crucial for the success of this chemoselective transformation.[17] On the one hand, CsF is only slightly soluble under these conditions, which allows the slow generation of the aryne. On the other hand, the lower solubility of the reaction products (with respect to the reagents) promotes their partial precipitation from the reaction mixture and minimizes the possibility of generating a second aryne.

The reaction proceeds via [4+2] cycloaddition reaction of monoaryne **8** to cyclopentadienone **4**, followed by chelotropic extrusion of carbon monoxide. In some experiments, the intermediate cycloadduct **9** can be detected and forced to evolve towards **3** upon additional heating. It is worth to note that bistriflate **1** had been previously used as 1,4-bisbenzyne synthon equivalent in a double Diels–Alder reaction to build a stable twistacene,[12] but – to the best of our knowledge – no example of an efficient single fluoride-induced elimination to generate intermediate **8** had been described prior to our work.[18]

Application of the same protocol to the reaction of **1** with other dienones, such as the commercially available 2,3,4,5-tetraphenylcyclopentadienone (**10**) and the easily accessible 9,11-diphenyl-10*H*-cyclopenta[*e*]pyren-10-one (**11**),[19] afforded the corresponding *o*-(trimethylsilyl)aryl triflates **12** and **13** in 60% and 44% yields, respectively (Table 1, entries 1 and 3). As mentioned above, compound **3** is a convenient precursor of the dibenzofused 2,3-didehydroanthracene **15** as demonstrated in the synthesis of a [16]cloverphene.[14] On the other hand, the tetraphenylnapthyne **14**, which can be generated from **12**, and the bisbenzotetracyne **16**, available through **13**, had been obtained before from other precursors[20,21] and employed in Diels–Alder reactions for the synthesis of stable, phenyl-substituted and/or benzoannulated large acenes.

In order to extend the polycyclic aryne core towards larger acenes, we explored the reactions of the 2,6-naphthodiyne precursor **2**. Satisfyingly, treatment of **2** with 120 mol% CsF in the presence of dienes **4**, **10**, and **11** under similar controlled conditions, afforded the corresponding *o*-(trimethylsilyl)aryl triflates **17**–**19** as major products in reasonable yields (Table 1, entries 4–6).[22] Remarkably, triflate **19** is a stable, functionalized pentacene[23] and a potential precursor of the large pentacene-based aryne **22**. The UV/vis spectra of **19** showed the lowest-energy absorption band at λ_{onset} = 484 nm, with a band gap of 2.56 eV, slightly lower than the HOMO–LUMO gap of a previously described pyrene-terminated pentacene (Figure 2).[24] On the other hand, cyclic voltammetry (CV) showed a reversible reduction process at $E_{1/2}^{red}$ = –1.48 V.

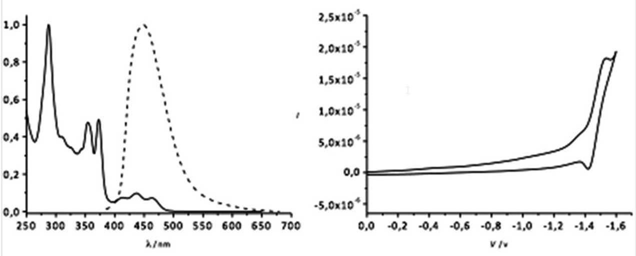
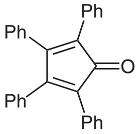
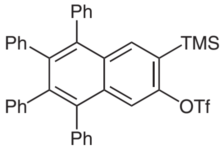
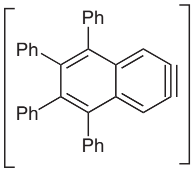
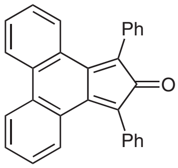
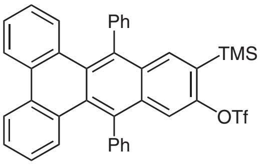
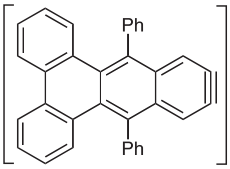
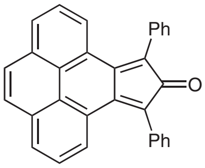
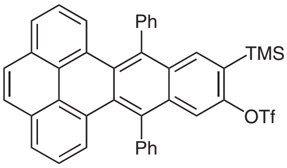
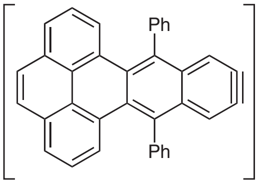
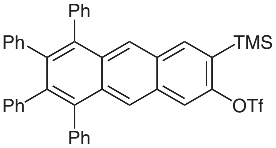
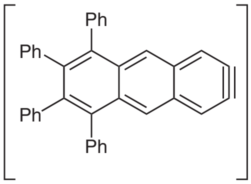
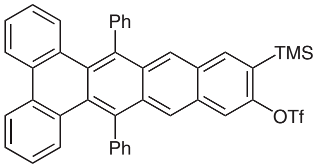
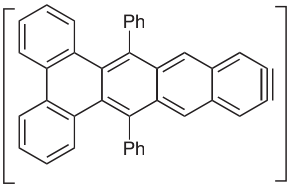
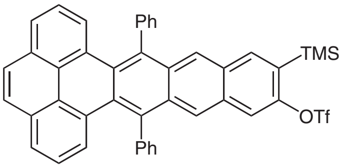
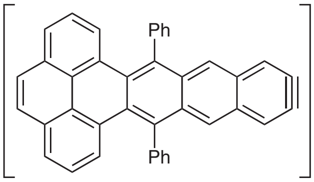


Figure 2 Electronic properties of pentacene **19**. (a) Absorption (solid line) and emission (dashed line) spectra in CH_2Cl_2; (b) cyclic voltammogram in CH_2Cl_2/0.1 M Bu_4NPF_6 using AgCl/Ag as the reference electrode.

In conclusion, an expeditious method for the synthesis of novel polycyclic *o*-(trimethylsilyl)aryl triflates, based on the controlled reaction of a formal bisaryne precursor with cyclopentadienones, has been described. The application of these compounds to the synthesis of novel acene, phene, and starphene derivatives by means of aryne cycloaddition reactions will be reported in due course.

Table 1 Reaction of Bistriflates **1** and **2** with Cyclopentadienones[16]

Entry	Bisaryne precursor	Cyclopentadienone	Product	Yield (%)	Derived aryne
1	**1**	 **10**	 **12**	60	 **14**
2	**1**	 **4**	 **3**	58	 **15**
3	**1**	 **11**	 **13**	44	 **16**
4	**2**	**10**	 **17**	40	 **20**
5	**2**	**4**	 **18**	21	 **21**
6	**2**	**11**	 **19**	24	 **22**

Acknowledgment

Financial support from the Spanish Ministry of Science and Competitiveness (MINECO, CTQ2013-44142-P and MAT2013-46593-C6-6-P), the European Union (Project PAMS, contract no. 610446), Xunta de Galicia (GPC2014/25), and FEDER is gratefully acknowledged. D.R.-L. thanks the Spanish Ministry of Education for the award of an FPU fellowship.

Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1381005.

References and Notes

(1) General reviews on aryne chemistry: (a) Hoffmann, R. W. *Dehydrobenzene and Cycloalkynes*; Academic Press: New York, **1967**. (b) Hart, H. *The Chemistry of Triple-Bonded Functional Groups*, In *Arynes and Heteroarynes*; Patai, S.; Rappoport, Z., Eds.; Wiley: Chichester, **1994**, Suppl. C2 1017. (c) Pellisier, H.; Santelli, M. *Tetrahedron* **2003**, *59*, 701. (d) Sanz, R. *Org. Prep. Proced. Int.* **2008**, *40*, 215.

(2) Kitamura, T. *Aust. J. Chem.* **2010**, *98*, 987.

(3) Himeshima, Y.; Sonoda, T.; Kobayashi, H. *Chem. Lett.* **1983**, 1211.

(4) Representative metal-catalyzed transformations involving arynes: (a) Peña, D.; Escudero, S.; Pérez, D.; Guitián, E.; Castedo, L. *Angew. Chem. Int. Ed.* **1998**, *37*, 2659. (b) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *J. Am. Chem. Soc.* **1999**, *121*, 5827. (c) Yokinawa, E.; Yamamoto, Y. *Angew. Chem. Int. Ed.* **2000**, *39*, 173. (d) Peña, D.; Pérez, D.; Guitián, E. *Palladium-Catalyzed Cycloaddition Reactions of Arynes*, In *Palladium in Organic Synthesis*; Vol. 14; Tsuji, J., Ed.; Springer: Weinheim, **2005**, 109. (e) Liu, Z.; Larock, R. C. *J. Org. Chem.* **2007**, *72*, 223. (f) Yoshida, H.; Ohshita, J.; Kunai, A. *Bull. Chem. Soc. Jpn.* **2010**, *83*, 199. (g) Worlikar, S. A.; Larock, R. C. *Current. Org. React.* **2011**, *15*, 3214.

(5) Representative novel metal-free transformations: (a) Peña, D.; Pérez, D.; Guitián, E. *Angew. Chem. Int. Ed.* **2006**, *45*, 3579. (b) Bhunia, A.; Yetra, S. R.; Biju, A. T. *Chem. Soc. Rev.* **2012**, *41*, 3140. (c) Bhunia, A.; Biju, A. T. *Synlett* **2014**, *25*, 608. (d) Criado, A.; Vilas-Varela, M.; Cobas, A.; Pérez, D.; Peña, D.; Guitián, E. *J. Org. Chem.* **2013**, *78*, 12637. (e) Dubrovskiy, A. V.; Markina, N. A.; Larock, R. C. *Org. Biomol. Chem.* **2013**, *11*, 191.

(6) (a) Tadross, P. M.; Stoltz, B. M. *Chem. Rev.* **2012**, *112*, 3550. (b) Gampe, C. M.; Carreira, E. M. *Angew. Chem. Int. Ed.* **2012**, *51*, 3766.

(7) (a) Pérez, D.; Peña, D.; Guitián, E. *Eur. J. Org. Chem.* **2013**, 5981. (b) Li, J.; Zhang, Q. *Synlett* **2013**, *24*, 686.

(8) Peña, D.; Cobas, A.; Pérez, D.; Guitián, E.; Castedo, L. *Synthesis* **2002**, 1454.

(9) Romero, C.; Peña, D.; Pérez, D.; Guitián, E. *Chem. Eur. J.* **2006**, *12*, 5677.

(10) Iglesias, B.; Cobas, A.; Pérez, D.; Guitián, E.; Vollhardt, K. P. C. *Org. Lett.* **2004**, *6*, 3557.

(11) Sygula, A.; Sygula, R.; Kobryn, L. *Org. Lett.* **2008**, *10*, 3927.

(12) Duong, H. M.; Bendikov, M.; Steiger, D.; Zhang, Q.; Sonmez, G.; Yamada, J.; Wudl, F. *Org. Lett.* **2003**, *5*, 4433.

(13) Kitamura, C.; Abe, Y.; Ohara, T.; Yoneda, A.; Kawase, T.; Kobayashi, T.; Naito, H.; Komatsu, T. *Chem. Eur. J.* **2010**, *16*, 890.

(14) Alonso, J. M.; Díaz-Álvarez, A. E.; Criado, A.; Peña, D.; Pérez, D.; Guitián, E. *Angew. Chem. Int. Ed.* **2012**, *51*, 173.

(15) Wooi, G. Y.; White, J. M. *Org. Biomol. Chem.* **2005**, *3*, 972.

(16) **General Procedure**

To a solution of bisaryne precursor **1** or **2** and cyclopentadienone **4**, **10**, or **11** (110 mol%), in 2:1 MeCN–CH_2Cl_2, finely powdered anhydrous CsF (120 mol%) was added, and the mixture was stirred at 50 °C under argon atmosphere for 12 h. The solvent was evaporated under reduced pressure, and the resulting mixture was purified by column chromatography (SiO_2, hexanes–CH_2Cl_2) to isolate the corresponding *o*-(trimethylsilyl)aryl triflate. In some experiments, the intermediate Diels–Alder adduct (e.g., **9**) was detected in other fractions eluted from the column, which were collected, concentrated under vacuum, dissolved in tetrachloroethane, and refluxed for 12 h. Evaporation of the solvent under vacuum and column chromatography (SiO_2, hexanes–CH_2Cl_2) of the residue afforded an additional portion of *o*-(trimethylsilyl)aryl triflate.

9,14-Diphenyl-12-(trimethylsilyl)benzo[*f*]tetraphen-11-yl Trifluoromethanesulfonate (3)

Reaction of 1,3-diphenyl-2*H*-cyclopenta[*l*]phenanthren-2-one (**4**, 243 mg, 0.637 mmol), 2,5-bis(trimethylsilyl)-1,4-phenylene bis(trifluoromethanesulfonate) (**1**, 300 mg, 0.579 mmol), and CsF (105 mg, 0.695 mmol) in MeCN–CH_2Cl_2 (2:1; 9 mL) afforded **3** (218 mg, 58%) as a greenish solid; mp 219–221 °C. ^{1}H NMR (250 MHZ, $CDCl_3$): δ = 8.29 (d, *J* = 7.3 Hz, 2 H), 8.13 (s, 1 H), 7.85 (s, 1 H), 7.59 (d, *J* = 8.5 Hz, 2 H), 7.54 (m, 5 H), 7.54 (m, 5 H), 7.41–7.36 (m, 2 H), 7.04–6.98 (m, 2 H), 0.33 (s, 9 H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 152.6 (C), 140.9 (C), 140.5 (C), 136.8 (CH), 135.4 (C), 135.2 (C), 132.7 (C), 132.3 (2 CH), 132.2 (C), 132.1 (2 CH), 132.1 (C), 131.9 (C), 130.8 (C), 130.6 (C), 130.55 (C), 130.50 (CH), 130.4 (CH), 129.8 (C), 129.3 (C), 129.1 (2 CH), 129.0 (2 CH), 128.0 (CH), 127.9 (CH), 127.3 (CH), 127.2 (CH), 125.9 (2 CH), 123.3 (2 CH), 115.7 (CH), –0.8 (3 CH_3) ppm. MS (EI): *m/z* (%) = 650 (30). HRMS (EI): *m/z* calcd for $C_{38}H_{29}F_3O_3SSi$: 650.1559; found: 650.1563.

5,6,7,8-Tetraphenyl-3-(trimethylsilyl)naphthalen-2-yl Trifluoromethanesulfonate (12)

Reaction of 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one (**10**, 329 mg, 0.858 mmol), 2,5-bis(trimethylsilyl)-1,4-phenylene bis(trifluoromethanesulfonate) (**1**, 404 mg, 0.780 mmol), and CsF (142 mg, 0.936 mmol) in MeCN–CH_2Cl_2 (2:1; 11 mL) afforded **12** (305 mg, 60%) as a white solid; mp 249–251 °C. ^{1}H NMR (300 MHZ, $CDCl_3$): δ = 7.89 (s, 1 H), 7.59 (s, 1 H), 7.32–7.20 (m, 10 H), 6.92–6.87 (m, 10 H), 0.30 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.8 (C), 140.7 (C), 139.9 (4C), 138.7 (2 C), 138.5 (C), 138.3 (C), 136.9 (CH), 133.4 (C), 131.1 (3 CH), 131.1 (4 CH), 130.9 (2 CH), 130.5 (C), 127.7 (2 CH), 127.6 (2 CH), 126.9 (CH), 126.7 (4 CH), 125.7 (CH), 125.6 (CH), 118.4 (q, *J* = 320 Hz, CF_3), 116.3 (CH), –0.9 (3 CH_3) ppm. MS (EI): *m/z* (%) = 652.3 (70) [M$^+$], 504.3 (14), 293.3 (41), 147.1 (43). HRMS (EI): *m/z* calcd for $C_{38}H_{31}F_3O_3SSi$: 652.1715; found: 652.1713.

9,14-Diphenyl-12-(trimethylsilyl)dibenzo[*de,qr*]tetracen-11-yl Trifluoromethanesulfonate (13)

Reaction of 9,11-diphenyl-10*H*-cyclopenta[*e*]pyren-10-one (**11**, 100 mg, 0.246 mmol), 2,5-bis(trimethylsilyl)-1,4-phenylene bis(trifluoromethanesulfonate) (**1**, 116 mg, 0.224 mmol), and CsF (41 mg, 0.269 mmol) in MeCN–CH_2Cl_2 (2:1; 9 mL) afforded **13** (66 mg, 40%) as a yellow solid; mp 279–281 °C. ^{1}H NMR (500 MHZ, $CDCl_3$): δ = 8.11 (s, 1 H), 7.90–7.85 (m, 6 H), 7.82 (s, 1 H), 7.56–7.48 (m, 10 H), 7.35 (td, *J* = 7.9, 2.2 Hz, 2 H), 0.32 (s, 9 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 153.0 (C), 141.7 (C), 141.4 (C), 137.3 (CH), 136.9 (C), 136.6 (C), 133.2 (C), 132.4 (2 CH), 132.2 (2 CH), 131.0 (C), 131.0 (C), 130.99 (C) 130.97 (C), 130.3 (C), 130.2 (C), 130.1 (C), 129.9 (C), 129.5 (2 CH), 129.4 (2 CH), 129.1 (CH), 129.0 (CH), 128.2 (CH), 128.1 (CH), 127.1 (CH), 127.1 (CH), 126.6 (CH), 126.4 (CH), 126.2 (C), 126.1 (C), 125.1 (CH), 125.0 (CH), 118.5 (q, *J* = 325 Hz, CF_3), 116.1 (CH), –0.6 (3 CH_3) ppm. MS (EI): *m/z* (%) = 674 (100) [M$^+$], 541 (53), 448 (16).

5,6,7,8-Tetraphenyl-3-(trimethylsilyl)anthracen-2-yl Trifluoromethanesulfonate (17)

Reaction of 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one (**10**, 126 mg, 0.329 mmol), 3,6-bis(trimethylsilyl)-naphthalene-2,7-diyl bis(trifluoromethanesulfonate) (**2**, 115 mg, 0.299 mmol), and CsF (55 mg, 0.359 mmol) in MeCN–CH_2Cl_2 (2:1; 9 mL) afforded **17** (84 mg, 40%) as a white solid; mp 223–225 °C. ^{1}H NMR (300 MHZ, $CDCl_3$): δ = 8.27 (s, 1 H), 8.22 (s, 1 H), 8.04 (s, 1 H), 7.82 (s, 1 H), 7.39–7.21 (m, 10 H), 7.01–6.78 (m, 10 H), 0.43 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.4 (C), 140.5 (2 C), 139.91 (C), 139.59 (C), 139.52 (C), 139.4 (C), 139.0 (CH),

138.6 (C), 138.3 (C), 132.1 (C), 131.7 (C), 131.6 (CH), 131.6 (CH), 131.4 (CH), 129.6 (C), 128.1 (CH), 128.0 (CH), 127.0 (CH), 126.9 (CH), 126.9 (CH), 126.8 (CH), 126.4 (CH), 125.7 (CH), 116.2 (CH), –0.4 (3 CH_3) ppm. MS (MALDI-TOF): $m/z = 702$ [M^+].

9,16-Diphenyl-13-(trimethylsilyl)dibenzo[*a*,*c*]tetracen-12-yl Trifluoromethanesulfonate (18)

Reaction of 1,3-diphenyl-2*H*-cyclopenta[*l*]phenanthren-2-one (**4**, 148 mg, 0.388 mmol), 3,6-bis(trimethylsilyl)-naphthalene-2,7-diyl bis(trifluoromethanesulfonate) (**2**, 200 mg, 0.353 mmol), and CsF (65 mg, 0.424 mmol) in MeCN–CH_2Cl_2 (2:1; 9 mL) afforded **18** (50 mg, 21%) as a yellow solid. ^1H NMR (500 MHZ, $CDCl_3$): δ = 8.51 (s, 1 H), 8.46 (s, 1 H), 8.18 (d, *J* = 7.9 Hz, 2 H), 8.05 (s, 1 H), 7.84 (s, 1 H), 7.66–7.54 (m, 10 H), 7.42 (t, *J* = 8.0 Hz, 2 H), 7.32 (t, *J* = 7.5 Hz, 2 H), 6.95 (t, *J* = 7.7 Hz, 2 H), 0.43 (s, 9 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 152.4 (C), 141.6 (2 C), 141.5 (2 C), 139.0 (CH), 135.4 (C), 135.0 (C), 133.0 (2 CH), 133.0 (2 CH), 132.6 (C), 132.6 (C), 131.8 (C), 131.5 (C), 131.5 (C), 131.4 (C), 131.2 (C), 131.0 (CH), 130.9 (CH), 130.0 (C), 129.6 (2 CH), 129.5 (2 CH), 128.3 (CH), 128.2 (CH), 128.06 (C), 127.6 (CH), 127.6 (CH), 126.5 (CH), 126.3 (CH), 126.0 (CH), 123.7 (CH), 118.2 (q, *J* = 321 Hz, CF_3), 116.3 (CH), –0.4 (CH_3) ppm. MS (MALDI-TOF): $m/z = 700$ [M^+].

9,16-Diphenyl-13-(trimethylsilyl)dibenzo[*de*,*uv*]pentacen-12-yl Trifluoromethanesulfonate (19)

Reaction of 9,11-diphenyl-10*H*-cyclopenta[*e*]pyren-10-one (**11**, 118 mg, 0.290 mmol), 3,6-bis(trimethylsilyl)-naphthalene-2,7-diyl bis(trifluoromethanesulfonate) (**2**, 150 mg, 0.264 mmol), and CsF (48 mg, 0.317 mmol) in MeCN–CH_2Cl_2 (2:1; 9 mL) afforded **19** (46 mg, 24%) as a yellow solid. ^1H NMR (500 MHZ, $CDCl_3$): δ = 8.52 (s, 1 H), 8.47 (s, 1 H), 8.06 (s, 1 H), 7.85 (m, 3 H), 7.82 (d, *J* = 7.7 Hz, 2 H), 7.73 (t, *J* = 8.4 Hz, 2 H), 7.65–7.57 (m, 10 H), 7.29 (td, *J* = 7.9, 1.2 Hz, 2 H), 0.44 (s, 9 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 152.4 (C), 142.1 (C), 142.0 (C), 139.1 (CH), 136.6 (C), 136.6 (C), 132.8 (2 CH), 132.76 (2 CH), 132.0 (C), 131.6 (C), 131.6 (C), 131.3 (C), 131.0 (C), 130.9 (C), 130.4 (C), 130.1 (C), 129.7 (CH), 129.6 (CH), 129.4 (CH), 129.3 (CH), 128.2 (CH), 128.1 (CH), 127.0 (CH), 127.0 (CH), 126.7 (CH), 126.6 (CH), 126.6 (CH), 126.4 (C), 126.3 (C), 126.1 (CH), 125.1 (CH), 125.1 (C), 118.2 (q, *J* = 322 Hz, CF_3), 116.29 (CH), 116.28 (CH), –0.43 (3 CH_3) ppm. MS (MALDI-TOF): $m/z = 724$ [M^+].

(17) The use of neat MeCN or CH_2Cl_2 resulted in lower conversions due to the poor solubility of either the diene (in MeCN) or the CsF (in CH_2Cl_2). On the other hand the use of TBAF as the fluoride source afforded lower yields of the expected triflates.

(18) In parallel to the work described in this article, we also studied the generation of a naphtho[1,2,3,4-*ghi*]perylyne precursor by reaction of **8** with perylene: Schuler, B.; Collazos, S.; Gross, L.; Meyer, G.; Pérez, D.; Guitián, E.; Peña, D. *Angew. Chem. Int. Ed.* **2014**, *53*, 9004.

(19) Pascal, R. A. Jr.; McMillan, W. D.; Van Engen, D.; Eason, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4660.

(20) Miao, Q.; Chi, X.; Xiao, S.; Zeis, R.; Lefernfeld, M.; Siegrist, T.; Steigerwald, M. L.; Nuckolls, C. *J. Am. Chem. Soc.* **2006**, *128*, 1340.

(21) (a) Zhang, Q.; Divayana, Y.; Xiao, J.; Wang, Z.; Tiekink, E. R. T.; Doung, H. M.; Zhang, H.; Boey, F.; Sun, X. W.; Wudl, F. *Chem. Eur. J.* **2010**, *16*, 7422. (b) Xiao, J.; Liu, S.; Liu, Y.; Ji, L.; Liu, X.; Zhang, H.; Sun, X.; Zhang, Q. *Chem. Asian J.* **2012**, *7*, 561. (c) Xiao, J.; Duong, H. M.; Liu, Y.; Shi, W.; Ji, L.; Li, G.; Li, S.; Liu, X.-W.; Ma, J.; Wudl, F.; Zhang, Q. *Angew. Chem. Int. Ed.* **2012**, *51*, 6094.

(22) We have already employed triflate **17** as an efficient precursor of tetraphenylanthracyne **20**, in the synthesis of large benzo-fused acenes: Rodríguez-Lojo, D. R.; Pérez, D.; Peña, D.; Guitián, E. *Chem. Commun.* **2015**, *51*, 5418.

(23) Pentacene and larger acenes are paradigmatic organic semiconductors, although their poor solubility and low stability limit their application: Anthony, J. E. *Angew. Chem. Int. Ed.* **2008**, *47*, 452.

(24) Xiao, J.; Divayana, Y.; Zhang, Q.; Doung, H. M.; Zhang, H.; Boey, F.; Sun, X. W.; Wudl, F. *J. Mat. Chem.* **2010**, *20*, 8617.