# Thieme Chemistry Journal Awardees – Where Are They Now? Pentafluorophenyl End-Capped Polyynes as Supramolecular Building Blocks

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Dedicated to Professor Herbert Meier on the occasion of his 70th birthday

**Abstract:** The synthesis of pentafluorophenyl end-capped polyynes up to an octayne has been developed based on the use of a Fritsch–Buttenberg–Wiechell rearrangement as the key step. UV/ Vis spectroscopic analysis shows little change in the electronic nature of these structures as phenyl is formally replaced by pentafluorophenyl. The ability of pentafluorophenyl polyynes to function as supramolecular building blocks in host–guest systems is demonstrated through the formation of an inclusion complex between triyne **5** and decafluorotolan.

**Key words:** alkynes, aromatic interactions, carbenes, carbenoids, crystal engineering, polyynes, supramolecular chemistry

The formation of conjugated polyynes can been a challenging synthetic problem on the way to developing carbon-rich structures, biologically active molecules, and unique molecular materials.<sup>1</sup> For the past few years, we have been one of the groups captivated by the potential of the polyyne skeleton and intrigued by the synthetic difficulties often encountered in polyyne formation. One such challenge is that of polyynes end-capped with pentafluorophenyl groups. The presence of the electrophilic pentafluorophenyl moiety can present unique synthetic challenges when combined with an acetylenic scaffold. For example, subjecting  $C_6F_5C=CSiMe_3$  to common desilylation conditions (methanolic KOH) produces the byproduct 4-MeOC<sub>6</sub>F<sub>4</sub>C=CH; a process optimized and put to good use by Marder and co-workers.<sup>2</sup>

On the other hand, the pentafluorophenyl group offers the prospect of solid-state organization through electrostatic interactions between the phenyl and pentafluorophenyl groups.<sup>3</sup> This concept was first introduced in 1960 by Patrick and Prosser who reported that the admixture of benzene and hexafluorobenzene resulted in the formation of a room temperature solid that was unique from either of its constituent parts.<sup>4</sup> Later experimental and theoretical studies have demonstrated this phenomenon can be explained by the fact that benzene and perfluorobenzene have quadrupolar moments that are nearly equal in magnitude but opposite in sign.<sup>5</sup> More recently, Grubbs and Dougherty used this predictable interaction to achieve supramolecular organization of diynes with the goal of facilitating topochemical polymerization.<sup>6</sup>



Rik R. Tykwinski was born in 1965 in Marshall, MN. He completed his B.Sc. degree in 1987 at the University of Minnesota - Duluth, where he also developed his passion for organic chemistry working as an undergraduate researcher with Prof. Ron Caple and Dr. Viktor Zhdankin. With Prof. Peter J. Stang at the University of Utah, he explored the chemistry of alkynyl iodonium salts and received his Ph.D. in 1994. He was awarded an Office of Naval Research Postdoctoral Fellowship and moved to ETH Zürich (1994-1997) to work with Prof. François Diederich on the chemistry and materials properties of functionalized tetraethynylethenes. In 1997, he joined the faculty at the University of Alberta, and he was promoted to Professor of Chemistry in 2005. In 2009, he began as Chair of Organic Chemistry at the University of Erlangen-Nürnberg in Germany, continuing the tradition of carbon-rich molecules established by John A. Gladysz and Paul von Ragu Schleyer. His current research interests focus on the development of synthetic methods for assembling conjugated carbonrich molecules, characterization of their electronic properties, applications of conjugated systems to nonlinear optics, polyynes/polyyne natural products, and mountain biking.

We,<sup>7</sup> and others,<sup>8</sup> have sought to build on the concept of organized acetylenic scaffolds based on arene/perfluoroarene interactions. In our particular case, we have used the carbene/carbenoid Fritsch–Buttenberg–Wiechell (FBW) rearrangement as a means to assemble polyynes endcapped with pentafluorophenyl group(s). Using this approach, a series of polyynes has been synthesized, and their solid-state structures examined by X-ray crystallography. The arene/perfluoroarene interactions previously documented for ethynyl- and butadiynyl-tethered systems<sup>2.6</sup> show a remarkable level of fidelity in longer analogues, providing predictable building-blocks for supramolecular chemistry. In this letter, we outline some of the successes (and failures) recently achieved from our efforts in this area.

The dibromoolefin **1** (Figure 1) was envisioned to be a valuable building block that could be easily synthesized<sup>9</sup> from the corresponding aldehyde. The product readily provided quality single crystals, and X-ray crystallographic analysis<sup>10</sup> showed a solid-state conformation in

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which the aryl ring and dibromoolefin were nearly orthogonal to each other, with a torsion angle of  $58^{\circ}$  as measured by planes generated from the aryl ring and atoms Br(1), Br(2), C(7), and C(8), respectively (Figure 1).



**Figure 1** Synthesis and ORTEP drawing of **1** (20% probability level). Selected bond angles [deg]: C(1)–C(7)–C(8) 126.0(6), Br(1)–C(8)–Br(2) 113.5(4), Br(1)–C(8)–C(7) 125.2(6), Br(2)–C(8)–C(7) 121.3(6).

Compound 1 was used in several subsequent experiments (Scheme 1), exploring a sequence of elimination followed by trapping with an electrophile in situ.<sup>8g</sup> Subjecting 1 to *n*-BuLi at low temperature afforded the lithium-acetylide, which was converted into the Grignard reagent and quenched with carbon dioxide to give acid 2 following acidic workup.<sup>11</sup> Formation of alcohol 3, as a triyne precursor, was attempted via the lithium-acetylide and quenching with ethyl formate. Unfortunately, this reaction failed to give the desired product, affording only baseline materials upon TLC analysis. Finally, synthesis of the 1,4-bis(pentafluorophenyl)diyne 4<sup>12</sup> was achieved via rearrangement of 1 to the acetylene, which was then subjected to Hay oxidative homocoupling conditions.<sup>13,14</sup>

The synthesis of triyne **5** (Scheme 2) was envisioned starting from dibromoolefin **6** via a FBW rearrangement.<sup>15–17</sup> The acylation reaction<sup>18</sup> of PhC=CSiMe<sub>3</sub> with the acid



**Scheme 1** Derivatization of dibromoolefin **1**. *Reagents and conditions*: (a) i. *n*-BuLi, hexanes, -78 °C to r.t.; ii. MgBr<sub>2</sub>; iii. CO<sub>2</sub>; iv. HCl, 28%; (b) *n*-BuLi, hexanes, -78 °C, then ethyl formate; (c) *n*-BuLi, hexanes, -78 °C, then CuCl, TMEDA, O<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 37%.



Scheme 3 Synthesis of tetraynes 10 and 12. *Reagents and conditions*: (a) AlCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C, 78%; (b) CBr<sub>4</sub>, Ph<sub>3</sub>P, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C, 60%; (c) *n*-BuLi, hexanes, -78 °C, 86%; (d) TBAF, THF, 0 °C; (e) Br-C=C-C=C-Ph, CuCl, NH<sub>2</sub>OH, *n*-Bu<sub>2</sub>NH, PhMe, r.t., 67% from 11; (f) CuCl, TMEDA, O<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 50% from 11.

chloride derived from 2 did not successfully give the expected ketone 7. The reverse process using  $8^{12,19}$  with excess acid chloride 9, however, readily gave 7 (Scheme 2). To our surprise, all attempts to form 6 via a standard dibromoolefination reaction<sup>20</sup> were unsuccessful, with a significant amount of baseline material observed from the reaction, suggesting decomposition of the ketone 7. Thus, an alternative route toward 5 was sought. With ketone 7 already in hand, a reaction with Colvin's reagent (lithium trimethylsilyldiazomethane, LiTMSD)<sup>21</sup> was the obvious choice, which gave triyne 5 in a rather low yield of 28%. This was, to our knowledge, the first synthesis of a polyyne using Colvin's reagent, and this protocol has subsequently been useful in other polyyne syntheses.<sup>22</sup>

A number of unsymmetrical tetraynes have been previously constructed based on the FBW rearrangement,  $^{16a,17a}$ providing several options for the synthesis of tetrayne **10** (Scheme 3). Ultimately, a route was developed using diyne **11**, since it would also provide easy access to the symmetrical tetrayne **12**. The synthesis of diyne **11** was readily developed in the usual way<sup>23</sup> from pentafluorobenzoyl chloride based on a sequence of Friedel–Crafts acylation to **13**, dibromoolefination to **14**, and a FBW rearrangement. Desilylation of **11** with tetrabutylammonium fluoride (TBAF) at 0 °C gave the deprotected diyne **15**, which was reacted immediately with Ph–C=C–C=C–Br



Scheme 2 Synthesis of tripne 5. *Reagents and conditions*: (a) PhC=CSiMe<sub>3</sub>, AlCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C; (b) AlCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C, 62%; (c) CBr<sub>4</sub>, Ph<sub>3</sub>P, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C; (d) LiTMSD, Et<sub>2</sub>O, 0 °C, 28%.

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(excess) under Cadiot–Chodkiewicz conditions<sup>24</sup> to give **10** in 67% yield over the two steps. Conversely, the homocoupling of **15** under Hay<sup>13</sup> conditions gave **12** in 50% yield over the two steps from **11**.



Scheme 4 Toward hexayne 17; attempted formation of dibromoolefin 20. *Reagents and conditions*: (a) AlCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C, 33%; (b) CBr<sub>4</sub>, Ph<sub>3</sub>P, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C.

In view of the successful sequence used to form diyne 11 (Scheme 3), an analogous approach was attempted toward triyne 16 as the precursor to hexayne 17 (Scheme 4). Acylation of diyne 18 via reaction with pentafluorobenzoyl chloride gave the desired ketone 19 in moderate yield. Unfortunately, conversion of 19 into dibromoolefin 20 was unsuccessful, so this approach was abandoned in favor of one based on the use of 8 and 21 (Scheme 5).

Thus, acylation of **8** with **21** gave diynone **22**, which was carried on to the dibromoolefin step and, gratifyingly, gave **23** in respectable yield. A FBW rearrangement then gave triyne **16**, and the ensuing sequence of desilylation and Hay homocoupling produced hexayne **17** in 44% yield over the two steps.

The synthesis of octayne 24 was approached in a fashion analogous to the synthesis of 17 (Scheme 6). Starting again from alkyne 8, acylation with 25a gave an unstable ketone, which was carried on directly, following workup, to the dibromoolefination step, giving 26a. Attempts to convert 26a into tetrayne 27a, however, were problematic, resulting in a mixture of products that severely hampered the isolation of the desired product. Furthermore, this product mixture slowly turned brown over a period of hours, suggesting decreased stability for this derivative. The complementary sequence of synthetic steps with the triisopropylsilyl protecting group starting with 25b, on the other hand, afforded the desired tetrayne 27b in decent yield, following the FBW rearrangement. Desilylation with TBAF and Hay homocoupling then gave 24 as a dark orange/red solid that slowly darkened over time (hours/ days).

The electronic absorption characteristics of the new diaryl polyynes have been evaluated in comparison to the unfluorinated analogues (Table 1). Even though the  $C_6F_5$  group might be considered to be a strong electron-acceptor, its presence at the terminus of a polyyne has seemingly little electronic influence based on UV/Vis analysis. As shown



Scheme 5 Synthesis of hexayne 17. *Reagents and conditions*: (a) AlCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C, 61%; (b) CBr<sub>4</sub>, Ph<sub>3</sub>P, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C, 58%; (c) *n*-BuLi, hexanes, -78 °C, 79%; (d) TBAF, THF, 0 °C; (e) CuCl, TMEDA, O<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 44% from 16.



Scheme 6 Synthesis of octayne 24. *Reagents and conditions*: (a) AlCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C; (b) CBr<sub>4</sub>, Ph<sub>3</sub>P, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C, 19% (26a), 18% (26b); (c) *n*-BuLi, hexanes, -78 °C, 0% (27a), 53% (27b); (d) TBAF, THF, 0 °C; (e) CuCl, TMEDA, O<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 19% from 27b.



Figure 2 UV/Vis spectra of 10, 12, and 28 measured in THF.

in Figure 2 for **10**, **12**, and **28**,<sup>17b</sup> there are two distinct absorption regions for each molecule, the first being characterized by strong bands at high energy (Region 1) and the second, a series of weaker absorptions, at lower energy (Region 2). The  $\lambda_{max}$  and  $\epsilon$  values for **10**, **12**, and **28** differ little as a function of substitution pattern, with  $\lambda_{max}$  in Region 1 centered at ca. 285 nm and the lowest energy absorptions found in Region 2 at 400±1 nm for all three

### Table 1 Selected UV/Vis Spectral Data for Diaryl Polyynes<sup>a</sup>

	)c	$\lambda_{max} (nm)^b$
	<sup>-1</sup> cm <sup>-1</sup> )	$\epsilon (L mol^{-1} cm^{-1})$
$h - (C \equiv C)_4 - Ph^d$	/00), 369 (34,700), 399 (22,000)	288 (143 000)
$h_F - (C \equiv C)_4 - Ph_F$	000), 368 (31,600), 399 (19,500)	284 (130,000)
$h-(C\equiv C)_4-Ph_F$	400), 370 (28,400), 401 (17,900)	286 (107,000)
$h - (C \equiv C)_6 - Ph^d$	600), 426 (16,400), 465 (8,000)	337 (155,000)
$h_F - (C \equiv C)_6 - Ph_F$	200), 423 (16,400), 461 (8,030)	327 (144,000)
h–(C≡C) <sub>8</sub> –Ph <sup>d</sup>	00), 433 (11,000), 469 (8,700), 512 (3,600)	344 (272,000)
$h_F - (C \equiv C)_8 - Ph_F$	, 461, 507 <sup>e</sup>	341 <sup>e</sup>
$h-(C\equiv C)_8-Ph^d$ $h_F-(C\equiv C)_8-Ph_F$	00), 433 (11,000), 469 (8,700), 512 (3,600) , 461, 507 <sup>e</sup>	344 (272,000) 341°

<sup>a</sup> Measured in THF.

 $^{b}\,\lambda_{max}$  defined as the most intense absorption in Region 1.

 $^{c}\,\lambda_{max}$  defined as the lowest energy absorptions in Region 2.

<sup>d</sup> Data from reference 17b.

<sup>e</sup> Sample did not give reliable ε-values, likely due to decomposition.

derivatives. For hexyane **17** and octayne **24**, the comparison to their unfluorinated cousins<sup>17b</sup> reveals muted differences, although in each case the perfluorinated derivatives show slightly blue-shifted  $\lambda_{max}$  values.

The solid-state structure of two polyyne building blocks has been explored by X-ray crystallography. Crystals of diyne **11** were obtained from pentane,<sup>25</sup> whereas crystals of tetrayne **27b** were obtained from chloroform (Figure 3).<sup>26</sup> In both cases, the molecules pack in a herringbone fashion that effectively separates the pentafluorophenyl units and precludes either face-to-face or edgeto-face  $\pi$ -stacking. While the bond lengths were rather unremarkable, the bond angles along each polyyne chain deviated somewhat from linearity, culminating in angles of



**Figure 3** ORTEP drawing of **11** (top) and **27b** (bottom) at 20% probability level. Selected bond angles [deg] for **11**: Si–C(1)–C(2) 176.36(14), C(1)–C(2)–C(3) 178.55(17), C(2)–C(3)–C(4) 179.25(18), C(3)–C(4)–C(11) 178.47(18) and for **27b**: Si–C(1)–C(2) 173.5(2), C(1)–C(2)–C(3) 178.1(2), C(2)–C(3)–C(4) 178.9(3), C(3)–C(4)–C(5) 179.5(3), C(4)–C(5)–C(6) 179.1(2), C(5)–C(6)–C(7) 179.5(2), C(6)–C(7)–C(8) 179.4(3), C(7)–C(8)–C(21) 179.1(2).

 $176.36(14)^{\circ}$  and  $173.5(2)^{\circ}$  for Si-C(1)-C(2) of **11** and **27b**, respectively.

The solid-state structures of **5**, **10**, and **12**·**28** have been previously reported,<sup>7</sup> and each show a remarkably similar solid-state structure dominated by phenyl–pentafluorophenyl interactions. This is demonstrated for **5** in Figure 4. The triyne segment is nearly linear, and each molecule is effectively planar [the dihedral angle between planes formed of terminal aryl rings is only 4.61(7)°]. Neighboring molecules in the solid-state pack to form centrosymmetric, dimeric pairs, separated by 3.46 Å.<sup>27</sup> The center-to-center distance (*d*) between each molecule is d = 3.7 Å and is nearly identical to those of the analogous monoyne (Ph<sub>F</sub>–C=C–Ph),<sup>2</sup> diyne (Ph<sub>F</sub>–C=C–C=C–Ph),<sup>6</sup> and tetrayne (**10**).<sup>7</sup>

Given the predictability observed in the solid-state packing of derivatives such as **5**, it is of interest to explore their use as supramolecular building blocks toward forming inclusion complexes with guest molecules. One such exam-



**Figure 4** ORTEP drawing of **5** (20% probability level) showing orientation of four neighboring molecules; arrows show center-to-center distances *d*. Selected bond angles [deg]: C(1)-C(2)-C(11) 179.8(3), C(1)-C(2)-C(3) 179.0(2), C(2)-C(3)-C(4) 179.7(2), C(3)-C(4)-C(5) 179.5(2), C(4)-C(5)-C(6) 178.8(2), C(5)-C(6)-C(21) 179.4(2).

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ple is shown in Figure 5. Allowing a binary mixture of triyne **5** and decafluorotolan in carbon tetrachloride/cy-clohexane to evaporate at 4 °C produced crystals that con-

tained a 4:1 mixture of **5**:decafluorotolan.<sup>28</sup> As predicted, the overall packing motif was dominated by the phenyl– pentafluorophenyl interactions, although the molecular



**Figure 5** ORTEP drawings of **5** co-crystallized with decafluorotolan (4:1 molecular ratio, respectively), shown at 20% probability level; crystallographic molecules A and B are designated with A and B, respectively; blue denotes  $C_6F_5$ , orange  $C_6H_5$ , and purple decafluorotolan. (a) relative packing position of the three unique molecules in the crystal lattice; (b) orientation of four neighboring molecules; arrows show center-to-center distances *d*; (c) packing as viewed down the c-axis. Selected bond angles [deg]: C(1A)–C(2A)–C(11A) 179.8(2), C(1A)–C(2A)–C(3A) 179.1(2), C(2A)–C(3A)–C(4A) 178.8(2), C(3A)–C(4A)–C(5A) 179.0(2), C(4A)–C(5A)–C(6A) 178.8(2), C(5A)–C(6A)–C(21A) 179.54(19) and C(1B)–C(2B)–C(11B) 179.8(2), C(1B)–C(2B)–C(3B) 179.6(2), C(2B)–C(3B) 179.6(2), C(3B)–C(4B)–C(5B) 179.5(2), C(4B)–C(5B)–C(6B) 179.6(2), C(5B)–C(6B)–C(21B) 179.7(2).

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organization was somewhat different to that found for pure 5. In this case, two crystallographically independent molecules of 5 pack in the unit cell: molecules A and B (Figure 5a). Each forms a centrosymmetric dimeric pair with its nearest neighbor separated by 3.43 Å (A–A pair) and 3.46 Å (B–B pair).<sup>27</sup> Likewise, neighboring A–B pairs are packed at an analogous distance of 3.46 Å. Whereas pure 5 shows a lateral offset of neighboring molecules, the inclusion of decafluorotolan gives rise to an alternating pattern of molecules A-A-B (Figure 5b), with center-to-center distances of d = 3.76 Å (A–A) and 3.65 Å (A–B). The next series of three molecules is then offset, with d = 3.72 (B–B). Thus, the same overall relative packing is observed with respect to pure 5, but with a slightly different lateral arrangement. Finally, the incorporation of the decafluorotolan can be best appreciated as viewed down the crystallographic c axis, which shows each 'guest' molecule sandwiched between ca. four molecules of 5 in neighboring tiers of the structure.

In summary, several synthetic routes toward pentafluorophenyl polyynes have been explored and developed.<sup>32</sup> In the course of this investigation, it has become clear that the presence of pentafluorophenyl groups can present unique synthetic challenges. Transformations that have historically worked well with other substitution patterns can fail in the presence of the pentafluorophenyl moiety, often without an obvious explanation. Furthermore, the presence of the C<sub>6</sub>H<sub>5</sub> group does not generally complicate the FBW rearrangement; i.e., no substantial addition of *n*-BuLi to the C<sub>6</sub>H<sub>5</sub> group is observed and the reaction rate for the rearrangement in the presence of this group is not altered to any great extent.

Solid-state structural analysis of a number of systems reveals that the interactions between pentafluorophenyl and phenyl polyynes offer a powerful mode of supramolecular organization, including the formation of inclusion complexes. Our study of these molecules continues.

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- (25) Data for **11** ( $C_{16}H_{15}F_5Si$ ),  $F_w = 330.37$ ; monoclinic crystal system; space group  $P_{21}/c$  (No. 14), a = 8.3640(5), b = 18.3726(11), c = 10.9822(7) Å;  $\beta = 104.5167(9)^\circ$ ; V = 1633.74(17) Å<sup>3</sup>; Z = 4;  $\rho_{calcd} = 1.343$  g cm<sup>-3</sup>;  $2\theta_{max} = 52.76^\circ$ ;  $\mu = 0.186$  mm<sup>-1</sup>; T =  $-80^\circ$ C; total data collected = 12874;  $R_1 = 0.0381$  [2844 observed reflections with  $F_o^2 \ge 2\sigma(F_o^2)$ ];  $wR_2 = 0.1125$  for 201 variables and 3346 unique reflections with  $F_o^2 \ge -3\sigma(F_o^2)$ ; residual electron density = 0.210 and -0.241 e Å<sup>-3</sup>. CCDC 725483.
- (26) Data for **27b** ( $C_{23}H_{21}F_{5}Si$ ),  $F_w = 420.49$ ; triclinic crystal system; space group  $P\overline{1}$  (No. 2), a = 7.5471(8), b = 16.2227(18), c = 18.215(2) Å; a = 83.2514(15),  $\beta = 81.0827(16)$ ,  $\gamma = 84.9478(16)^{\circ}$ ; V = 2182.3(4) Å<sup>3</sup>; Z = 4;  $\rho_{calcd} = 1.280$  g cm<sup>-3</sup>;  $2\theta_{max} = 52.00^{\circ}$ ;  $\mu = 0.155$  mm<sup>-1</sup>; T = -80 °C; total data collected = 14651;  $R_1 = 0.0460$  [6050 observed reflections with  $F_0^2 \ge 2\sigma(F_0^2)$ ];  $wR_2 = 0.1342$  for 523 variables and 8490 unique reflections with  $F_0^2 \ge -3\sigma(F_0^2)$ ; residual electron density = 0.329 and -0.165 e Å<sup>-3</sup>. CCDC 725482.
- (27) Intermolecular distances are based on the separation of planes generated from all non-hydrogen atoms of neighboring molecules using Mercury 1.3.
- (28) Data for **5**-decafluorotolan (4:1,  $C_{86}H_{20}F_{30}$ ),  $F_w = 1623.02$ ; triclinic crystal system; space group P1 (No. 2), a = 7.2628(8), b = 13.1573(14), c = 18.0306(19) Å;  $a = 80.3101(17), \beta = 82.1018(17), \gamma = 81.9049(18)^\circ$ ; V = 1670.0(3) Å<sup>3</sup>; Z = 1;  $\rho_{calcd} = 1.614$  g cm<sup>-3</sup>;  $2\theta_{max} = 52.80^\circ$ ;  $\mu = 0.152$  mm<sup>-1</sup>; T = -80 °C; total data collected = 13414;  $R_1 = 0.0460$  [4226 observed reflections with  $F_o^2 \ge 2\sigma(F_o^2)$ ];  $wR_2 = 0.1494$  for 523 variables and 6819 unique reflections with  $F_o^2 \ge -3\sigma(F_o^2)$ ; residual electron density = 0.397 and -0.189 e Å<sup>-3</sup>. CCDC 725484.
- (29) The synthesis of **5**, **10**, **12**, **17**, and **24** has been communicated, see ref. 7.
- (30) TLC analysis often indicated that reactions were complete soon after addition of base (ca. 30 min), although warming

of the reaction solution in the TLC capillary could influence this analysis.

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- (32) General procedure for FBW rearrangements<sup>29</sup> Unless otherwise noted in the individual procedures, in a flame-dried flask, a solution of the dibromoolefin (2.00 mmol) in anhydrous hexanes (30 mL, freshly distilled from CaH<sub>2</sub>) was cooled to -78 °C under a positive pressure of N<sub>2</sub>. n-BuLi (2.5 M in hexanes, 1.05 equiv) was slowly added dropwise over a period of ca. 5 min. The reaction was allowed to warm to r.t. over ~1 h, stirred for 3 h,<sup>30</sup> and then quenched through the addition of aqueous NH<sub>4</sub>Cl (50 mL). Et<sub>2</sub>O (50 mL) was added, and the organic layer was separated, washed with distilled  $H_2O(3 \times 25 \text{ mL})$ , dried over MgSO<sub>4</sub>, filtered, and the solvent removed in vacuo. Column chromatography (silica gel) gave the desired product. 3-Pentafluorophenyl-2-propynoic acid (2) Using the general procedure, 1 (0.500 g, 1.42 mmol) in hexanes (30 mL) was reacted with n-BuLi (1.15 mL, 2.90 mmol, 2.5 M in hexanes) for 1 h and then warmed to r.t. MgBr<sub>2</sub> (0.29 g, 1.6 mmol) was added in one portion, and the inhomogeneous mixture was stirred for 15 min. Dry CO<sub>2</sub> gas was bubbled through the solution as it was allowed to warm to r.t. and stirred overnight. Et<sub>2</sub>O (50 mL) and aqueous 10% HCl (50 mL) were added and the organic phase was separated and washed with distilled H<sub>2</sub>O, followed by 10% aqueous NaOH ( $3 \times 30$  mL). The aqueous phases were collected and acidified with aqueous 10% HCl (50 mL).  $Et_2O$  (3 × 30 mL) was added and the organic phases were separated, dried over MgSO<sub>4</sub>, treated with activated charcoal, and filtered. Solvent removal gave 2 (0.182 g, 28%) as a colorless solid. Data were consistent with those reported.11 Mp 96-98 °C (Lit.11 105-106 °C). IR (neat): 3055 (s), 2987 (s), 2241 (s), 1694 (s), 1522 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 10.19 (br); <sup>19</sup>F (376 MHz, CDCl<sub>3</sub>):  $\delta = -132.9$  to -133.0 (m, 2 F), -146.6 (tt,  ${}^{3}J = 21$ Hz,  ${}^{5}J = 4$  Hz, 1 F), -160.2 to -160.4 (m, 2 F);  ${}^{13}C{}^{1}H$  NMR  $(125 \text{ MHz}, \text{CDCl}_3): \delta = 157.0, 148.4 \text{ (d mult, } {}^1J = 258 \text{ Hz}),$ 143.8 (d mult,  ${}^{1}J = 260 \text{ Hz}$ ), 137.8 (d mult,  ${}^{1}J = 260 \text{ Hz}$ ), 96.8 (app td, J = 17.4, 3.9 Hz), 90.1–90.0 (m), 72.4–72.2 (m); EIMS: m/z (%) = 192.0 (100) [M – CO<sub>2</sub>]<sup>+</sup>; HRMS: m/z[M – CO<sub>2</sub>]<sup>+</sup> calcd for C<sub>8</sub>HF<sub>5</sub>: 191.9998; found: 191.9974. Anal. Calcd for C<sub>9</sub>HF<sub>5</sub>O<sub>2</sub>: C, 45.76; H, 0.42. Found: C, 45.98; H, 0.67.
  - **1,4-[Bis(pentafluorophenyl)]-1,3-butadiyne (4)** Using the general procedure, **1** (0.700 g, 1.99 mmol) in hexanes (30 mL) was reacted with *n*-BuLi (1.7 mL, 4.1 mmol, 2.4 M in hexanes). Aqueous work up gave a faintyellow oil that was immediately dissolved in CH<sub>2</sub>Cl<sub>2</sub> (ca. 5 mL) and added dropwise over 30 min to a solution of Hay catalyst [CuCl (0.200 g, 2.04 mmol) and TMEDA (1.21 g, 10.4 mmol, 1.6 mL)] in CH<sub>2</sub>Cl<sub>2</sub> (50 mL). The reaction was stirred overnight, Et<sub>2</sub>O (50 mL) and aqueous 10% HCl (50 mL) were added, and the organic phase was separated, washed with distilled H<sub>2</sub>O (3 × 50 mL), dried over MgSO<sub>4</sub>, filtered, and the solvent removed in vacuo. Column chromatography (pentane) gave **4** (0.146 g, 37%) as a colorless solid. Spectral data for this compound were consistent with those reported.<sup>12</sup>

#### 1-Pentafluorophenyl-5-(*tert*-butyldimethylsilyl)-2,4pentadiyn-1-one (19)

To anhydrous  $CH_2Cl_2$  (100 mL, freshly distilled from  $CaH_2$ ) was added pentafluorophenyl benzoyl chloride (1.61 g, 11.4 mmol) and **18** (1.50 g, 6.35 mmol). The temperature of the solution was lowered to 0 °C under a positive pressure of N<sub>2</sub>, and AlCl<sub>3</sub> (1.01 g, 7.63 mmol) was added portion-wise over

5 min. The reaction was stirred at 0 °C, monitored by TLC until starting material was no longer observed (typically ca. 3 h), and then carefully poured into aqueous 10% HCl (50 mL) in ice (50 g); CAUTION: exothermic. Pentane (50 mL) was added and the organic layer was separated, washed with distilled H<sub>2</sub>O ( $3 \times 50$  mL), dried over MgSO<sub>4</sub>, treated with activated charcoal, filtered, and the solvent removed in vacuo. Column chromatography (CH<sub>2</sub>Cl<sub>2</sub>-pentane, 1:4) gave 19 (0.754 g, 2.11 mmol, 33%), as a clear pale-yellow oil.  $R_f = 0.35$  (CH<sub>2</sub>Cl<sub>2</sub>-pentane, 1:4). IR (neat): 2955 (m), 2193 (s), 2099 (s), 1659 (s), 1522 (m) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 0.97$  (s, 9 H), 0.19 (s, 6 H); <sup>19</sup>F (376 MHz, CDCl<sub>3</sub>):  $\delta = -140.3$  to -140.4 (m, 2 F), -146.8 (tt,  ${}^{3}J = 21$ Hz,  ${}^{5}J = 6$  Hz, 1 F), -160.3 to -160.5 (m, 2 F);  ${}^{13}C{}^{19}F{}$ NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 166.9, 145.6, 144.0, 137.8, 113.9, 100.5–100.4 (m), 86.1, 79.3, 72.6, 25.5 (q sept, J = 126, 6 Hz), 16.9–16.8 (m), -5.2 (q mult,  ${}^{1}J = 126$  Hz); HRMS (EI): *m/z* [M<sup>+</sup>] calcd. for C<sub>17</sub>H<sub>15</sub>F<sub>5</sub>OSi: 358.0812; found: 358.0809. Anal. Calcd for C<sub>17</sub>H<sub>15</sub>F<sub>5</sub>OSi: C, 56.98; H, 4.19. Found: C, 57.35; H, 4.20.

#### 5-tert-Butyldimethylsilyl-2,4-butynoic acid

1-(*tert*-Butyldimethylsilyl)butadiyne<sup>31</sup> (1.30 g, 7.93 mmol) was added to anhydrous THF (75 mL) and the mixture was cooled to -78 °C under a positive pressure of N2. CH3Li (6.0 mL, 9.0 mmol, 1.5 M in Et<sub>2</sub>O) was added and the mixture was stirred for 1 h. Dry CO<sub>2</sub> gas was bubbled through the solution as it was allowed to warm to r.t. and stirred overnight. Et<sub>2</sub>O (50 mL) and aqueous 10% HCl were added and the organic phase was separated, washed with distilled water ( $3 \times 50$  mL), dried over MgSO<sub>4</sub>, treated with activated charcoal, and filtered. Solvent removal in vacuo gave 5-tertbutyldimethylsilyl-2,4-butynoic acid (1.35 g, 82%) as a pale-yellow solid. Mp 52-53 °C. IR (neat): 3400-2700 (br), 2955 (s), 2248 (m), 2206 (s), 2108 (s), 1691 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 10.28$  (s), 0.96 (s, 9 H), -0.17 (s, 6 H);  ${}^{13}C$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 156.8, 95.5, 86.0,$ 73.7, 65.4, 26.0, 16.8, -5.2; MS (EI): *m*/*z* (%) = 208.1 (8)  $[M^+]$ , 151.0 (64)  $[M - t - Bu]^+$ , 107.0 (100)  $[M - t - Bu - CO_2]^+$ ;

HRMS: m/z [M<sup>+</sup>] calcd. for C<sub>11</sub>H<sub>16</sub>O<sub>2</sub>Si: 208.0920; found: 208.0922. Anal. Calcd for C<sub>11</sub>H<sub>16</sub>O<sub>2</sub>Si: C, 63.46; H, 7.69. Found: C, 63.28; H, 7.96.

## 1-*tert*-Butyldimethylsilyl-5-dibromomethylene-7pentafluorophenyl-1,3,6-heptatriyne (26a)

SOCl<sub>2</sub> (1.49 g, 0.9 mL, 12.5 mmol) was added to 5-tertbutyldimethylsilyl-2,4-butynoic acid (0.520 g, 2.50 mmol) in a flask protected from moisture with a drying tube containing CaCl<sub>2</sub>. The mixture was stirred at r.t. overnight. The excess SOCl<sub>2</sub> was removed in vacuo to provide 25a, which was subjected to acylation with acetylene 8 (0.580 g,2.20 mmol) and AlCl<sub>3</sub> (0.351 g, 2.64 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (75 mL) as described for compound 19. The ketone product was immediately dissolved in anhydrous CH2Cl2 (50 mL, freshly distilled from CaH<sub>2</sub>) and carried on to the next step. CBr<sub>4</sub> (0.476 g, 1.44 mmol) and Ph<sub>3</sub>P (0.754 g, 2.88 mmol) were added to  $CH_2Cl_2$  (50 mL) and allowed to stir for 5 min at r.t. until the mixture turned bright orange. This solution was cooled to 0 °C, the reserved ketone was slowly added over a period of 20 min, and the reaction was stirred overnight. The solvent was reduced to ca. 10 mL, pentane (100 mL) was added and the inhomogeneous mixture was filtered through a plug of Celite and the solvent removed in vacuo. Column chromatography (pentane) gave 26a (0.219 g, 0.407 mmol, 19%) as a pale-yellow solid. Mp 104-105 °C.  $R_f$  = 0.66 (pentane). IR (neat): 2954 (m), 2197 (w), 2098 (m), 1502 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.97 (s, 9 H), 0.18 (s, 6 H);  ${}^{19}$ F (376 MHz, CDCl<sub>3</sub>):  $\delta$  = -134.8 to -134.9 (m, 2 F), -150.7 (app t, J = 21 Hz, 1 F), -161.6 to -161.7 (m, 2 F); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz,  $CDCl_3$ ):  $\delta = 147.0$  (d mult,  ${}^{1}J = 256$  Hz), 142.6 (dtt,  ${}^{1}J = 259$ Hz, J = 14 Hz, J = 5 Hz), 137.6 (d mult,  ${}^{1}J = 252$  Hz), 114.4 (br), 112.4, 99.2 (app td, *J* = 18 Hz, *J* = 4 Hz), 96.3 (app q, *J* = 4 Hz), 94.8, 87.5, 81.4, 79.9 (app q, *J* = 4 Hz), 70.7, 26.0, 16.8, -5.0; HRMS (EI): m/z [M<sup>+</sup>] calcd. for  $C_{20} H_{15}{}^{79} Br^{81} Br F_5 Si:$  537.9210; found: 537.9213. Anal.  $Calcd \ for \ C_{20}H_{15}Br_2F_5Si: C, 44.61; H, 2.79. \ Found: C, 45.01;$ H, 3.06.

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