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Preparation of Highly Hindered Polyenynes[‡]

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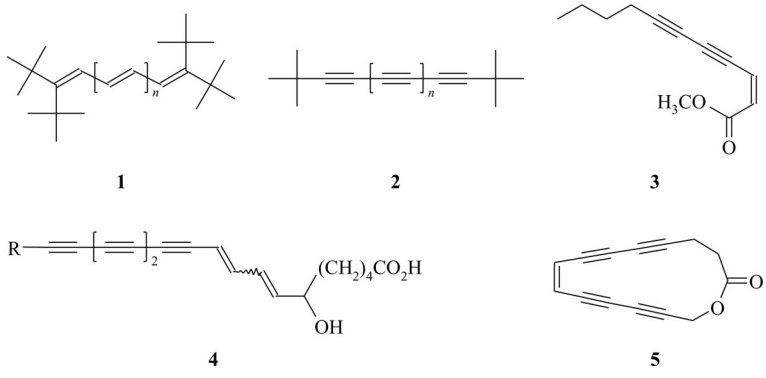
Dedicated to Professor Wolfgang Lüttke on the occasion of his 90th birthday

Keywords: Alkynes / Polyene/polyyne hybrid compounds / Carbon-rich compounds / Thiophenes

The terminal enynes **10**–**12** were prepared from the corresponding aldehydes **6**–**8** by applying conventional methods of acetylene chemistry. After exploratory study of the reactivity of these hydrocarbons (preparation of **13**, **18**, and **19** from **10**) these building blocks were subsequently oxidatively dimerized (Glaser coupling) to the sterically protected oligoenynes **22**–**25**; McMurry coupling of **13** yielded **26** as a mixture of diastereomers. Whereas **22** is inert towards sodium sulfide the higher vinylogs/ethynylogs **23**–**25** furnished the novel thiophene derivatives **28**–**31**. The structures of several (**22**–**25**, **28**, **29**) of the new highly unsaturated compounds were determined by single-crystal X-ray structural analysis.

Introduction

In a recent publication we described a general method for the preparation of the α,ω-tetra-*tert*-butylated polyolefins **1**, allowing the synthesis of these hydrocarbons with up to 13 consecutive double bonds (Scheme 1, **1**, n = 1 to 11).[1] It was shown that most of these hydrocarbons are stable under normal laboratory conditions, thus rendering a class of compounds known to be notoriously unstable in the presence of e.g. heat, light and oxygen – the unsubstituted parent systems[2] – amenable to structural and chemical investigation. Since the corresponding *tert*-butyl-capped polyacetylenes **2** are also stable hydrocarbons up to at least 12 consecutive triple bonds (Scheme 1, **2**, n = 10)[3] it seemed likely that hydrocarbons composed of a combination of C=C double and C≡C triple bonds would be stable provided they bear the bulky protecting groups in the "correct" positions. Indeed, a sizeable number of polyenynes have been isolated from natural sources, a typical representative being the lachnophyllin ester **3**, first isolated in 1935.[4] First reports on the isolation – not characterization – of natural products containing multiple triple and double bonds date back to the early 19th century,[5,6] and more recently the highly unsaturated fatty acid derivative



1 **2** **3** **4** **5**

Scheme 1. A selection of natural and nonnatural compounds containing both multiple double and triple bonds.

[‡] Highly Hindered Olefins and Polyolefins, XV. Part XIV: Ref.[1]

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caryoynencin **4**[7] has been isolated. Furthermore, macrocyclic entetraynes such as **5** have been prepared because they could cyclize by a Bergman type rearrangement and hence be of importance as model compounds for various anti-tumor antibiotics[8] (Scheme 1).

However, little is known about the preparation or the structural and chemical properties of relatively simple, unfunctionalized model compounds of this series. We therefore set out to apply the knowledge gained during our polyene work[1] to the synthesis of a selected number of basic polyene/polyyne hydrocarbon hybrids. First results are described in this contribution.

Preparation of Enyne Building Blocks

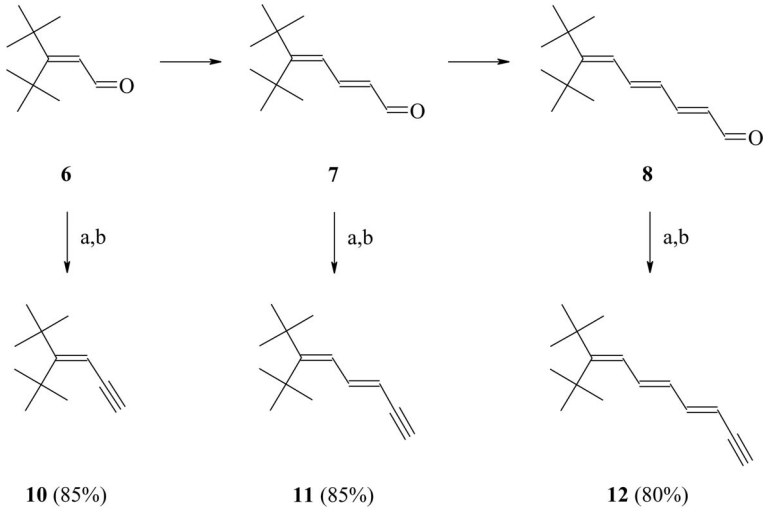
In the polyolefin work the α,β-unsaturated aldehyde **6** (Scheme 2) was of crucial importance.[1] This substrate was prepared in satisfactory manner from di-*tert*-butyl ketone and is available in multi-gram quantities. It could be chain-elongated without difficulty to the vinylogous aldehydes **7** and **8**.[1]

To prepare the terminal acetylenes **10** to **12** from these aldehydes we employed a variant of the protocol described by Michel and Rassat[9] which itself may be regarded as a simplification of the Corey–Fuchs method of converting an aldehyde into a terminal acetylene.[10] In the present case the ylid prepared by treatment of (bromomethyl)triphenylphosphonium bromide (**9**, Scheme 2) with potassium *tert*-butoxide at –78 °C was first quenched with the respective aldehyde **6** to **8**. Although the expected bromoalkene can be isolated if desired, for the preparation of the alkyne the reaction mixture was cooled again to –78 °C and subjected to a β-elimination. This provided the enynes **10**–**12** in good yields. The smallest acetylene **10** is a volatile colorless oil and its purification was carried out by chromatography on silica gel with pentane. The second acetylene, **11**, is also a colorless oil but is not as volatile as **10**. It could be purified easily by silica gel chromatography using higher boiling non-polar solvents such as hexane. The third member of the series, **12**, a pale yellow oil at room temperature and a solid below 0 °C, was again purified by silica gel chromatography with either pentane or hexane. The neat hydrocarbons **10** and **11** are stable for several weeks when kept under an inert gas atmosphere and in the cold, but exposure to air or to room temperature caused polymerization. The longest terminal acetylene **12** was less stable than its lower vinylogs even in the cold and under inert atmosphere and polymerized in a few days. The spectroscopic properties of these hydrocarbons are as expected and are listed in the experimental section. The ^{1}H NMR coupling constants at the respective double bonds of **11** and **12** demonstrate that these hydrocarbons have the *all-trans* configuration as shown.

Functionalization of the Monoenyne 10

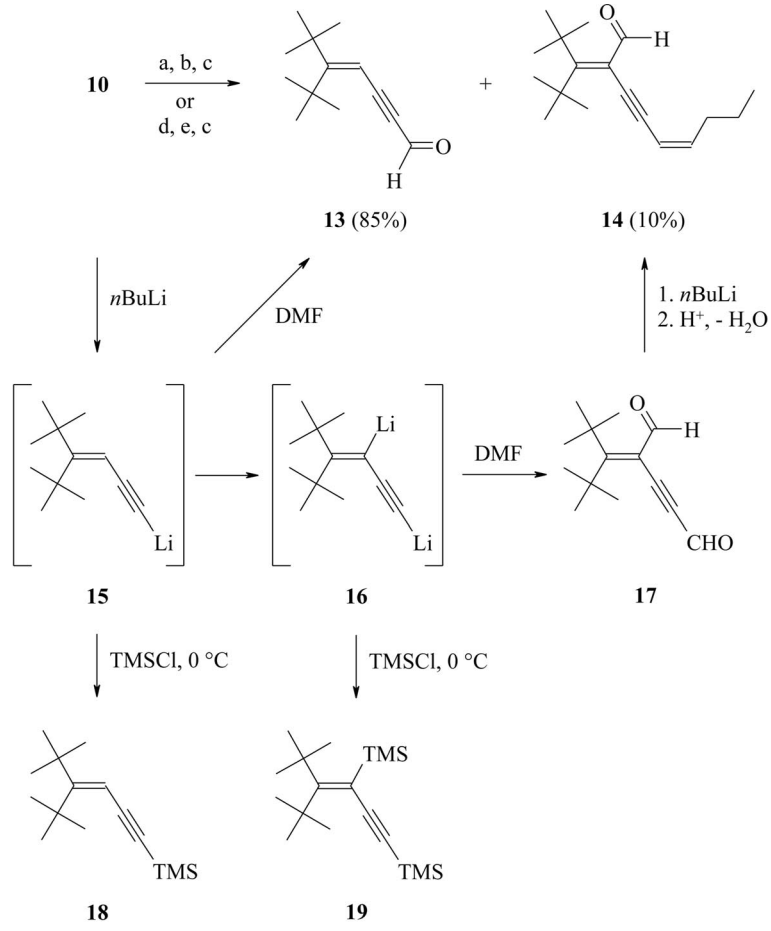
To learn about the reactivity of the vinylacetylene **10**, a few exploratory experiments were carried out; these are summarized in Scheme 3.

Treating **10** with 1.6 equiv. of *n*-BuLi in anhydrous Et_2O at –78 °C gave the lithium acetylide, the formation of which was easily observed by a pronounced color change of the solution from colorless to deep red during the addition of the base. At the same temperature DMF was added and after the reaction had reached room temperature, work-up gave **13** in 85% and the by-product **14** in 10% yield. The aldehyde **13** is a red oil and stable at low temperatures. The formation of the cross-conjugated aldehyde **14** can be explained by dimetalation of **10** to **16** via the monoacetylide **15**. Dimetalation of 1-butene-3-yne under strongly basic conditions (BuLi/*t*BuOK) has been investigated by Brandsma and co-workers.[11] In the present case, after di-



(a) $BrCH_2P^+Ph_3Br^-$ (**9**), *t*BuOK, THF, -78 °C → 20 °C; (b) *t*BuOK, THF, -78 °C

Scheme 2. Preparation of the oligoenyne building blocks.

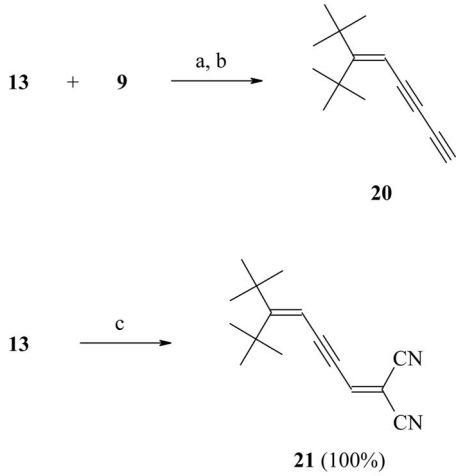


(a) *n*BuLi, Et_2O, -78 °C; (b) DMF, -78 °C → room temp.; (c) H^+, H_2O; (d) EtMgBr, THF, -40 °C; (e) DMF, -30 °C → room temp.

Scheme 3. Testing the reactivity of enyne **10**.

metalation, formylation evidently takes place at both sites, leading to **17**. This is finally attacked by excess *n*BuLi to provide – via the corresponding alcohol and its dehydration – the observed aldehyde **14**. The C5–C6 double bond of **14** was found to be *Z*-configured according to the ^{1}H NMR coupling constant (^3J = 3 Hz). In another metalation experiment **10** was treated with *n*-butyllithium as above and the reaction mixture trapped by trimethylsilyl chloride. The deep red color of the reaction mixture disappeared, and after work-up the formation of a mixture of the silylated compounds **18** and **19** was demonstrated by GC/MS-analysis (**18**: *m*/*z* = 236 [M$^+$]; **19**: *m*/*z* = 308 [M$^+$]). When the organolithium reagent was replaced by ethylmagnesium bromide (1.2 equiv., THF, –40 °C) for the metalation of **10** the only product isolated after quenching with DMF was the aldehyde **13** (85%).

To gain further impressions of the reactivity of **13**, the aldehyde was treated with the Wittig regent generated from **9** with *t*BuOK at –78 °C in THF. As above, the intermediate vinyl bromide was not isolated but subjected to dehydrobromination by excess base to give the diacetylene **20** (Scheme 4). This hydrocarbon is highly unstable and



(a) THF, -78 °C → room temp.; (b) *t*BuOK, -78 °C; (c) $CH_2(CN)_2$, β-alanine, EtOH

Scheme 4. Chain-extension reactions of the aldehyde **13**.

attempts to purify the crude product resulted in polymerization. For this reason the compound had to be characterized using the crude elimination mixture.

Knoevenagel condensation of **13** with malononitrile was carried out in 95% EtOH in the presence of a catalytic amount of β-alanine. After chromatographic purification on silica gel compound **21** was obtained in quantitative yield as a greenish-yellow oil. This polarized dienyne is characterized by an absorption band at 362 nm in its electronic spectrum (other analytical data: see Exp. Section).

Dimerization Reactions

Oxidative Coupling Reactions of Terminal Acetylenes 10–12

The three terminal acetylenes readily dimerized under typical Glaser/Hay conditions. Oxygen gas was passed through a mixture of 1 equiv. of the terminal acetylene and 0.3 equiv. of CuCl in pyridine for two hours. The first two diacetylenes **22** and **23** (Scheme 5) were purified by sublimation at 75 °C/ 4 mbar and 120 °C/ 4 mbar, respectively. The longest vinylog **24** was purified by chromatography on silica gel with pentane; all diacetylenes were formed in quantitative yield. Whereas **22** is a colorless solid, **23** and **24** are yellow solids. All compounds are stable and they are resistant both towards air/oxygen and higher temperatures; even after melting no decomposition was observed. Their spectroscopic data are summarized in the experimental section and their solid-state structures, determined by single-crystal X-ray diffraction, are discussed below.

When the diyne **20** was subjected to Glaser coupling the tetraacetylene **25** was produced in 65% yield. The lower yield in this case is probably associated with the instability of the substrate **20** (see above). The dimer is a yellow solid that could be handled in the same way as its analogous diynes (see above). Recrystallization of this hydrocarbon from ethanol also furnished crystals suitable for an X-ray structural analysis.

The Structures of 22–25 in the Solid State

All compounds crystallize solvent-free (see parts a of Figures 1, 2, 3, and 4). Each molecule displays crystallographic symmetry: twofold symmetry for **22** and inversion symmetry for **23**–**25**, although the latter all possess approximate *2/m* symmetry (r.m.s. deviations 0.17, 0.36, 0.19 Å respectively; the higher value for **24** is attributable to an S-shaped bowing of the central carbon chain, with e.g. C1···C7···C6′ 154°, Figure 3b). Compounds **23** and **25**, with similar C_{12} chains bearing the *t*Bu groups, are effectively

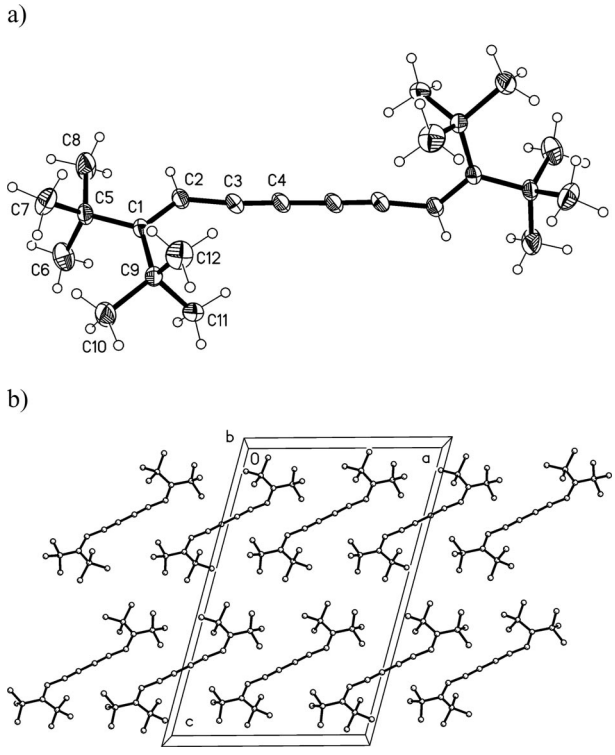
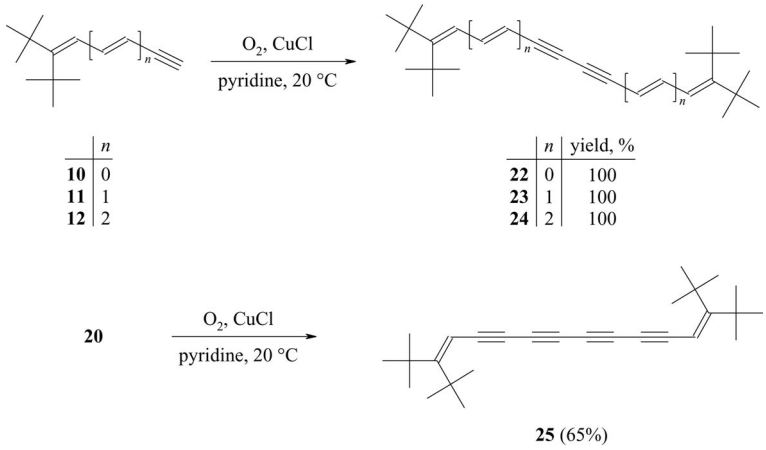


Figure 1. a) The molecule of compound **22** in the crystal. Ellipsoids represent 50% probability levels. b) Packing diagram of compound **22**; H atoms omitted for clarity.



Scheme 5. Preparation of di- and tetraacetylenes from terminal alkynes **10**–**12**.

isotypic. For the *polyene* portions of the chains, a similar general geometry is observed to that of the polyenes reported in our previous publication,[1] which may be summarised as follows: (i) The C–C bond lengths alternate, with formal double bonds of ca. 1.35 and formal single bonds of ca. 1.44 Å (scatter ca. 0.01 Å; for individual values of these and other dimensions, see the Supporting Information); (ii) the angle at the central carbon of the $(t\mathrm{Bu})_2$C=CH–CH grouping is very wide (129–132°), presumably for steric reasons; (iii) other angles are appreciably greater than 120° (123–125°). In the *polyyne* moieties, angles at sp carbons are essentially linear (range 173–179°), with C≡C bond lengths around 1.21 Å and C(sp)–C(sp) single-bond lengths around 1.36–1.37 Å. A search of the Cambridge Database[12] found 409 examples of the moiety C–C≡C–C≡C–C, with an average length of 1.376 Å for the central single bond (but with several severe outliers implying serious systematic errors).

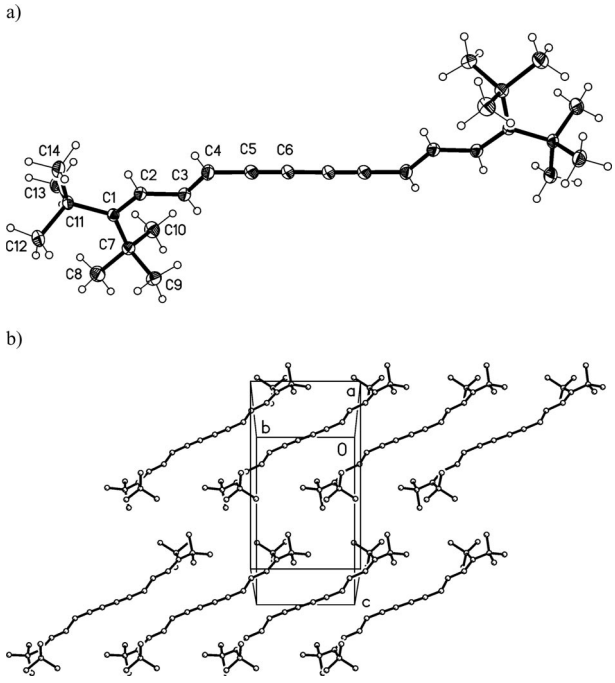


Figure 2. a) The molecule of compound **23** in the crystal. Ellipsoids represent 50% probability levels. b) Packing diagram of compound **23**; H atoms omitted for clarity.

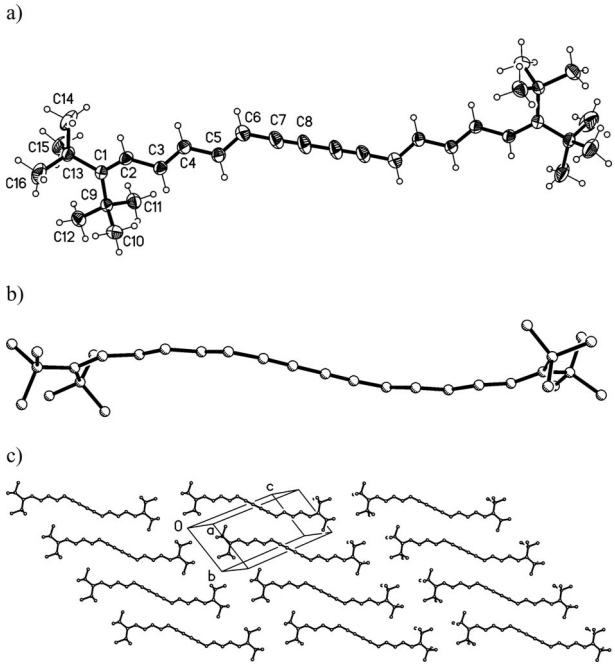


Figure 3. a) The molecule of compound **24** in the crystal. Ellipsoids represent 50% probability levels. b) The molecule of compound **24**; alternative view showing the bowing of the central chain. Radii are arbitrary; H atoms omitted. c) Packing diagram of compound **24**; H atoms omitted for clarity. View direction perpendicular to ($\bar{1}02$).

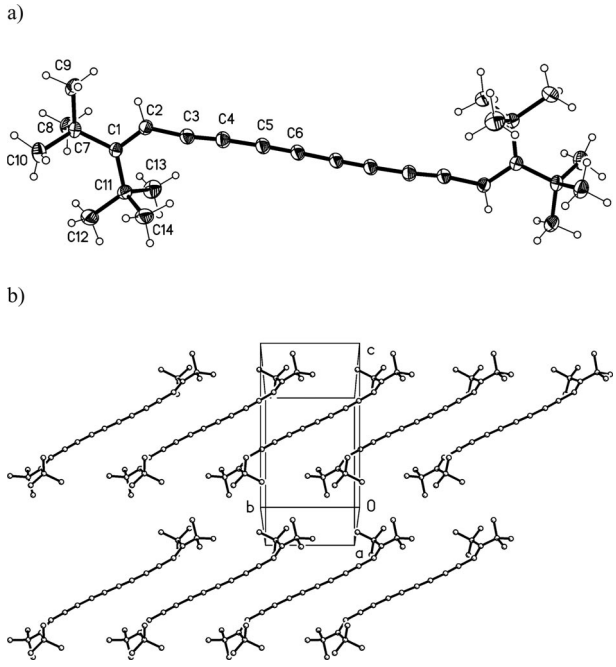
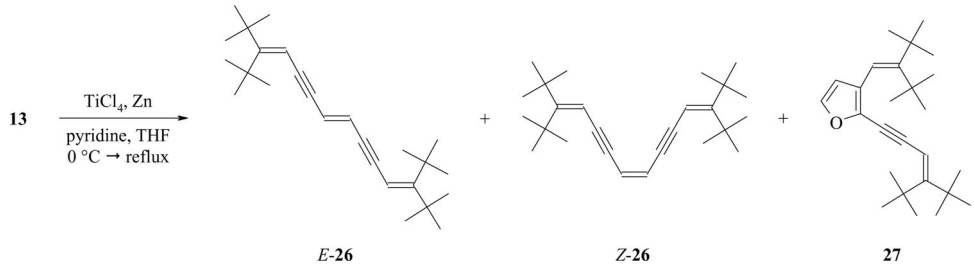


Figure 4. a) The molecule of compound **25** in the crystal. Ellipsoids represent 50% probability levels. b) Packing diagram of compound **25**; H atoms omitted for clarity.

The packing of the hydrocarbons **22**–**25** is to some extent similar, involving layers of molecules. For **22** (Figure 1, b) the neighbouring molecules in the horizontal rows are mutually displaced by **b**/4 out of the plane. For **23** and **25**, all molecules are at the same level ($x \approx 0$) and the next layer is at $x \approx 1/2$ (see parts b of Figures 2 and 4). For **24** (Figure 3, c) the packing involves only translational symmetry.

McMurry Coupling of the Aldehyde 13

The McMurry coupling reaction of **13** was performed by treatment of the aldehyde with Ti(0) prepared from $TiCl_4$ with Zn in the presence of pyridine in THF at 0 °C.[13] Purification/separation of the product mixture, which consisted of three components (total yield 70%, ratio 3:1:1 according to ^{1}H NMR analysis), by column chromatography on silica gel yielded only one component in analytically pure form: the triendiyne ***E*-26** (Scheme 6). The structure of this hydrocarbon follows from its spectra data (see Exp. Section).



Scheme 6. McMurry coupling of aldehyde **13**.

It was not possible to separate the other two products from each other by various separation techniques (column chromatography on silica gel; silica gel impregnated with silver nitrate; high-vacuum sublimation). According to NMR- and GC/MS results (see Exp. Section) one of these inseparable products is probably the *Z*-diastereomer ***Z*-26**. The third product was tentatively identified as the furan derivative **27** according to its ^{1}H and ^{13}C NMR spectroscopic data (see Exp. Section). A similar furan formation in McMurry coupling reactions of acetylenic aldehydes has been reported by Krüger[14] and Srinivasan.[15]

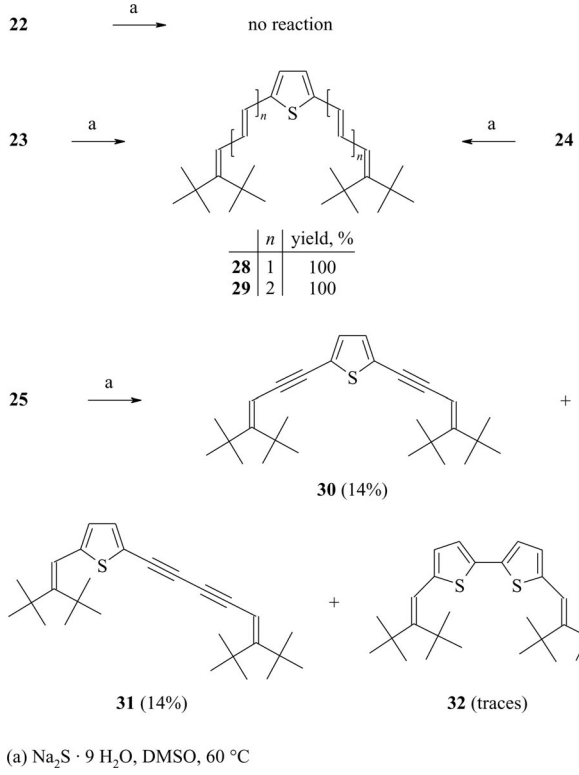
Thiophene Derivatives from 23–25

In a common reaction of diacetylenes, thiophenes are produced by hydrogen sulfide addition to the termini of the conjugated triple bonds. This formal 1,4-addition process has been used to prepare numerous thiophene derivatives of vastly differing structural complexity,[6,16] and $Na_2S{\cdot}9H_2O$ may be employed with good success as the sulfur source.[17]

When the diacetylenes **22**–**24** were stirred for 20 min in the presence of excess sodium sulfide nonahydrate and potassium hydroxide in DMSO at 60 °C for 20 min, the first hydrocarbon did not react. Changing the solvent to methanol and increasing both reaction temperature (reflux) and reaction time had no effect. We assume that this inertness is due to steric hindrance by the four flanking *tert*-butyl moieties, which are too close to the reactive part of the substrate. Increasing this distance by lengthening the olefinic side-arms, as in **23** and **24**, removes this steric barrier and the two thiophene derivatives **28** and **29** are produced in quantitative yield (Scheme 7).

Both thiophenes are stable compounds and no decomposition was observed even upon melting. Their recrystallization from ethanol gave crystals suitable for X-ray structure analyses (see below).

The tetraacetylene **25** was also treated with $Na_2S{\cdot}9H_2O$ in DMSO and the products obtained were purified and separated by chromatography on silica gel with ethyl acetate/hexane (1:10). Two of the three thiophene derivatives produced were monoadducts according to their spectroscopic and analytical data (see Exp. Section). For the formation of the first product, **30** (14%, Scheme 7), an internal diyne moiety has been attacked, whereas the second, **31** (14%, Scheme 7), results from cyclization of a terminal diyne unit. As can be seen from the yields, these two modes of addition



Scheme 7. Novel thiophene derivatives from the oligoacetylenes **23**–**25**.

occur with equal ease. Both adducts possess an intensely orange color. To the third adduct, detected by TLC and produced in minute amounts only, we assign structure **32**, since its mass spectrum clearly indicates the presence of a second sulfur atom plus two additional hydrogen atoms.

Structures of 28 and 29 in the Solid State

The thiophene derivatives **28** and **29** (see Figures 5 and 6) display twofold symmetry, exact and approximate (r.m.s.d. 0.07 Å), respectively. For **28**, the atoms S and C2–7 are coplanar (r.m.s.d. 0.03 Å); for **29**, the atoms S, C2–6 and C20–25 are coplanar (r.m.s.d. 0.02 Å) but the chain C7–11 is angled at 12° to this plane, lying from 0.25 Å (C7) to 1.02 Å (C11) outside it. The geometry of the polyene chains is similar to that noted above, whereby the angles adjacent to the thiophene rings (at C4 in **28**, C6 and C20 in **29**) are widened to 126–127°.

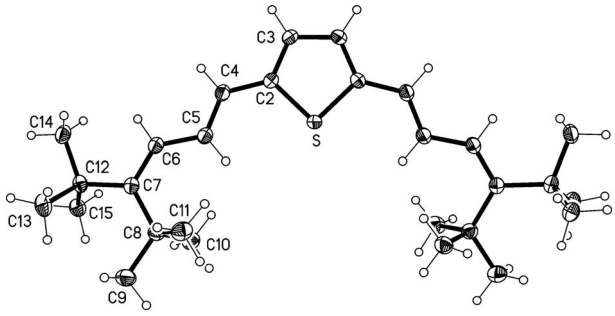


Figure 5. The molecule of compound **28** in the crystal. Ellipsoids represent 50% probability levels.

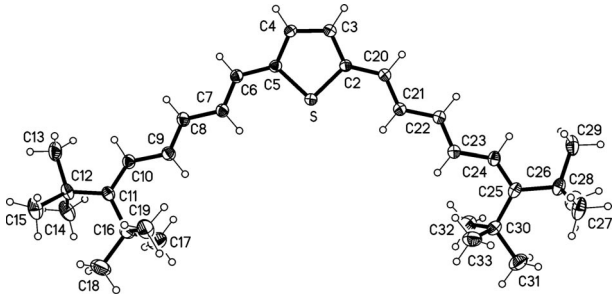


Figure 6. The molecule of compound **29** in the crystal. Ellipsoids represent 30% probability levels.

The packing of **28** and **29** is complex and without any clearly defined features such as layer formation.

Conclusion

In summary we have shown that the stabilization of long conjugated π-systems by terminal *tert*-butyl groups is not restricted to polyolefins and polyacetylenes but can be extended to hybrids of these two types of fundamental hydrocarbons making polyenynes also available for further structural and chemical studies.

Experimental Section

1. General: Melting points below 200 °C: Büchi 510 apparatus; above 200 °C: Kofler apparatus. NMR: Bruker AC-200: ^{1}H NMR (200.1 MHz), ^{13}C NMR (50.3 MHz); Bruker AM-400: ^{1}H NMR (400.1 MHz), ^{13}C NMR (100.6 MHz); Bruker DRX-400: ^{1}H NMR (400.1 MHz), ^{13}C NMR (100.6 MHz) in deuteriochloroform. Chemical shifts in ppm downfield from internal tetramethylsilane. IR: Nicolet 320 FT-IR spectrometer as KBr pellets or thin films. UV/Vis: HP 8452A Diode Array spectrophotometer. MS: Finnigan MAT 8430 (EI, 70 eV and FAB). GC/MS: Finnigan MAT 4515 (EI, 40 eV) attached to a Carlo Erba HRGC 5160. Elemental analysis: Institut für Pharmazeutische Chemie, TU Braunschweig. X-ray analysis: see below. The aldehydes **6**–**8** were prepared according to the procedure described in ref.[1] All other reagents were commercial compounds.

2. 4-*tert*-Butyl-5,5-dimethylhex-3-en-1-yne (10): To a stirred suspension of (bromomethyl)triphenylphosphonium bromide (**9**, 9.73 g, 22.3 mmol) in anhydrous THF (80 mL) was added at –78 °C *t*BuOK (2.50 g, 22.3 mmol) under N_2, and the mixture was stirred for 30 min. With the ylide formation the color changed from white to yellow. A solution of **6** (3.00 g, 17.9 mmol) in anhydrous THF (115 mL) was added dropwise during 1 h at the same temperature, and the mixture was left to warm to room temp. Subsequently *t*BuOK (2.50 g, 22.3 mmol) was added and the mixture was refluxed for 1.5 h. Another portion of *t*BuOK (1.25 g, 11.2 mmol) was added and refluxing was continued for an additional 1.5 h. The reaction mixture was stirred overnight at room temp, quenched with water, and the phases were separated. The aqueous phase was extracted several times with ethyl ether, the combined organic phases were dried with anhydrous $MgSO_4$, and the solvent was removed in a rotary evaporator. The oily residue was purified by column chromatography on silica gel with hexane. The acetylene **10** was obtained as a colorless, highly volatile oil (2.49 g, 85%). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 5.66 (d, J = 2.8 Hz, 1 H, 3-H), 3.38 (d, J = 2.8 Hz, 1 H, 1-H), 1.51 and 1.47 (s, 18 H, *t*Bu) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 171.40 (s, C-4), 103 ppm. 37 (d, C-3), 85.87 (s, C-2), 84.34 (d, C-1), 39.50 and 38.85 (s, C-5,-9), 32.29, 31.56 (q, *t*Bu) ppm. IR (film): $\tilde{\nu}$ = 3314 (m), 2958 (s), 2090 (w), 1729 (w), 1485 (w), 1366 (m), 1237 (m), 1219 (m), 1196 (m), 835 (w) cm^{-1}. MS (GC/MS): *m*/*z* (%) = 164 [M$^+$], 149, 135, 121, 107, 99, 91, 79, 65, 57. UV (CH_3CN): λ_{max} (lg ε) = 234 (4.02), 260 nm (3.36). The spectroscopic data are consistent with the proposed structure; however, the elemental analysis of this hydrocarbon did not yield a satisfactory composition.

3. 6-*tert*-Butyl-7,7-dimethylocta-3,5-dien-1-yne (11): To a stirred suspension of (bromomethyl)triphenylphosphonium bromide (**9**, 4.51 g, 10.0 mmol) in anhydrous THF (25 mL) at –78 °C was added *t*BuOK (1.16 g, 10.0 mmol) under N_2, and the mixture was stirred for 30 min (color change to yellow). A solution of **7** (1.00 g, 5.18 mmol) in anhydrous THF (10 mL) was added dropwise at the same temperature over 1 h, and the mixture was left to warm to room temp. Subsequently *t*BuOK (1.74 g, 10.0 mmol) was added and the mixture was first refluxed for 3 h followed by overnight stirring at room temp. Work-up as above yielded **11** as a colorless oil (0.84 g, 85%). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.36, 1.22 (s, 18 H, *t*Bu), 3.03 (d, J = 1.9 Hz, 1 H, 1-H), 5.41 (dd, J_1 = 15.2, J_2 = 2.0 Hz, 1 H, 3-H), 6.02 (d, J = 11.6 Hz, 1 H, 5-H), 7.33 (dd, J_1 = 15.2, J_2 = 11.6 Hz, 1 H, 4-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 142.81 (d, C-4), 122.78 (d, C-5), 108.55 (d, C-3), 84.00 (s, C-2), 78.97 (d, C-1), 39.09, 38.06 (s, C-7,-9), 33.91, 31.59 (q, C-8,-10) ppm; C-6 signal too weak to be detected. IR (film): $\tilde{\nu}$ = 2929 (s), 2039 (w), 1637 (m), 1380 (m), 1254 (m), 1201 (m), 1172 (m) cm^{-1}. MS (GC/MS): *m*/*z* (%) = 190 [M$^+$] (13), 133 (66), 119 (57), 105 (57), 91 (68), 84 (10), 77 (16), 69 (13), 57 (100). UV (CH_3CN): λ_{max} (lg ε) = 222 (3.70), 276 (4.30), 286 (4.24, sh), 288 (4.23), 304 nm (3.54). The spectroscopic data are consistent with the proposed structure; however, the elemental analysis of this hydrocarbon did not yield a satisfactory composition.

4. 8-*tert*-Butyl-9,9-dimethyldeca-3,5,7-trien-1-yne (12): To a stirred suspension of (bromomethyl)triphenylphosphonium bromide (**9**, 3.76 g, 8.63 mmol) in anhydrous THF (22 mL) at –78 °C was added 0.96 g (8.60 mmol) of *t*BuOK under N_2, and the mixture was stirred for 30 min (color change to bright yellow). A solution of **8** (1.00 g, 4.54 mmol) in anhydrous THF (10 mL) was added dropwise during 20 min at the same temperature, and the mixture was left to warm to room temp. Then another portion of *t*BuOK (1.45 g, 12.9 mmol) was added and the mixture was first refluxed for 3 h followed by overnight stirring at room temp. Work-up as above furnished **12** as a colorless oil (0.79 g, 80%). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 6.86 (dd, J_1 = 14.4, J_2 = 11.7 Hz, 1 H, 6-H), 6.70 (dd, J_1 = 15.5, J_2 = 11.1 Hz, 1 H, 4-H), 6.04 (dd, J_1 =

14.4, J_2 = 11.1 Hz, 1 H, 5-H), 5.97 (d, J = 11.7 Hz, 1 H, 7-H), 5.46 (dd, J_1 = 15.5, J_2 = 2.4 Hz, 1 H, 3-H), 2.98 (d, J = 2.4 Hz, 1 H, 1-H), 1.29 and 1.15 (s, 18 H, *t*Bu) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 160.55 (s, C-8), 144.38 (d, C-6), 135.75 (d, C-4), 130.84 (d, C-7), 123.74 (d, C-5), 108.71 (d, C-3), 83.86 (s, C-2), 80.01 (d, C-1), 39.43 and 38.34 (s, C-9,-13), 34.10 and 32.01 (q, C-10,-16) ppm. IR (film): $\tilde{\nu}$ = 3312 (m), 2957 (s), 2094 (w), 1598 (m), 1484 (m), 1459 (m), 1366 (m), 1217 (m), 988 (s) cm^{-1}. UV (CH_3CN): λ_{max} (lgε) = 242 (3.62), 288 (4.30), 310 (4.60), 322 (4.58), 350 (3.97), 364 nm (2.91). During spectrometric analysis the compound started to polymerize.

5. 5-*tert*-Butyl-6,6-dimethylhept-4-en-2-ynal (13): *n*BuLi (6.10 mL, 1.6 M solution in hexane) was slowly (30 min) added to a stirred solution of **10** (1.0 g, 6.1 mmol) in anhydrous diethyl ether (40 mL) at –78 °C. The colorless solution turned red. The mixture was left to warm to room temp. slowly, then cooled back to –78 °C, and DMF (0.79 mL, 1.0 mmol) was added. After warming up to room temp. again, stirring was continued overnight. The reaction mixture was quenched by addition of water and the layers were separated. The aqueous phase was extracted several times with diethyl ether; the combined organic layers were dried with anhydrous $MgSO_4$ and the solvent was removed in vacuo. The remaining residue was purified by column chromatography on silica gel with ethyl acetate/hexane = 1:10 (v/v). Aldehyde **13** was obtained as a red oil (1.00 g, 85%).

(*Z*)-2-(1-*tert*-Butyl-2,2-dimethylpropylidene)non-5-en-3-ynal (14) was obtained as a by-product (0.16 g, 10%).

In another experiment, freshly prepared EtMgBr (0.47 g, 3.7 mmol) in THF (3 mL) was added slowly (20 min) to a cooled solution (–40 °C) of **10** (0.500 g, 3.05 mmol) in THF (5 mL) under N_2. A first white, then gray suspension formed. The mixture was left to warm to room temp. and stirred for an additional 1 h, then cooled to –30 °C and DMF (0.267 g, 3.66 mmol) in THF (2 mL) was added. Stirring was continued overnight at room temp. The reaction mixture was quenched by addition of water and worked-up as described above. After chromatographic purification (see above) **13** was obtained in 85% yield (0.50 g). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.47, 1.24 (s, 18 H, *t*Bu), 5.80 (d, J = 1.0 Hz, 1 H, 4-H), 9.36 (d, J = 1.2 Hz, 1 H, 1-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 179.79 (s, C-5), 176.87 (d, C-1), 101.65 (d, C-4), 97.06, 96.01 (s, C-2,-3), 40.02, 39.46 (s, C-6,-10), 32.35 and 31.02 (q, C-7,-13) ppm. IR (film): $\tilde{\nu}$ = 2960 (m), 2164 (s), 1660 (s), 1569 (w), 1485 (w), 1367 (w), 1152 (m) cm^{-1}. MS (70 eV): *m*/*z* (%) = 192 (2) [M$^+$], 136 (34), 121 (13), 105 (11), 92 (28), 91 (32), 84 (28), 79 (11), 77 (15), 69 (17), 65 (10), 57 (100). UV (CH_3CN): λ_{max} (lgε) = 198 (3.83), 216 (3.86), 292 (4.01), 328 (3.27), 334 (3.11), 344 (2.93), 356 nm (2.73). The aldehyde is an unstable compound that did not provide a satisfactory elemental analysis. The intensity of the molecular ion peak was too small to carry out a HRMS measurement. By-product **14**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.4 Hz, 3 H, 9-H), 1.18, 1.41 (s, 18 H, 12-, 14-H; the lower signal overlaps with a m, 2 H, 8-H), 2.35 (m, 2 H, 7-H), 5.82 (d, J = 3.0 Hz, 1 H, 5-H), 6.45 (d, J = 3.0 Hz, 1 H, 6-H), 9.39 (s, 1 H, 1-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 193.96 (d, C-1), 173.07 (s, C-10), 150.53 (s, C-2), 130.32 (d, C-6), 103.74 (d, C-5), 39.58, 38.90 (s, C-11,-13), 32.16, 31.16 (q, C-12,-14), 28.22 (t, C-7), 21.93 (t, C-8), 13.96 (q, C-9) ppm; the acetylenic carbon atoms could not be detected. IR (film): $\tilde{\nu}$ = 2960 (vs), 2931 (s), 2873 (s), 2167 (s), 1683 (vs), 1665 (s), 1604 (w), 1561 (w), 1485 (w), 1392 (m), 1366 (s), 1187 (m) cm^{-1}. MS (70 eV): *m*/*z* (%) = 260 (30) [M$^+$], 203 (94), 189 (26), 175 (25), 161 (62), 147 (46), 133 (48), 131 (37), 119 (90), 117 (14), 105 (26), 91 (34), 84 (9), 77 (18), 69 (14), 57 (100), 55 (20). HRMS $C_{18}H_{28}O$ calcd. 260.2140; found 260.2133 ± 2 ppm.

6. 6-*tert*-Butyl-7,7-dimethyloct-5-ene-1,3-diyne (20): To a suspension of (bromomethyl)triphenylphosphonium bromide (**9**, 1.00 g, 2.27 mmol) in THF (8 mL), cooled to –78 °C, *t*BuOK (0.255 g, 2.27 mmol) was added under N_2, and the mixture was stirred for 30 min; a solution of the aldehyde **13** (0.350 g, 1.82 mmol) in THF (12 mL) was added dropwise over 30 min, and the mixture was left to reach room temp. Then *t*BuOK (0.255 g, 2.27 mmol) was added, and the mixture was refluxed for 3 h. Stirring was continued overnight at room temp. The reaction mixture was hydrolyzed (20 mL of water), and the phases were separated. The aqueous phase was extracted several times with diethyl ether, the combined organic phases were dried with $MgSO_4$, and the solvent was removed in a rotary evaporator. The remaining residue was purified by column chromatography on silica gel with pentane. After purification 0.184 g (54%) of **20** was obtained. The compound was highly unstable and polymerized to some extent during purification, making it impossible to determine its elemental composition. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.45 and 1.20 (s, 18 H, 8-, 10-H), 2.58 (d, J = 1.2 Hz, 1 H, 1-H), 5.65 (d, J = 1.0 Hz, 1 H, 5-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 175.83 (s, C-6), 102.16 (d, C-5), 81.36 (s, C-4), 75.25, 72.63 (s, C-2,-3,-4), 68.67 (d, C-1), 39.49, 39.07 (s, C-7,-9), 32.27 and 31.14 (q, C-8,-10) ppm. IR (KBr): $\tilde{\nu}$ = 3312 (m), 2959 (s), 2186 (m), 1571 (w), 1484 (m), 1366 (m), 1233 (m), 1214 (m), 1195 (m), 665 (w) cm^{-1}. MS (70 eV): the compound ($C_{14}H_{20}$, mol. weight: 188.30) displayed the mass spectrum of the dimerized product **25**: *m*/*z* (%) = 374 [M$^+$] (24), 317 (16), 245 (12), 229 (14), 215 (20), 191 (14), 177 (14), 157 (14), 141 (12), 119 (14), 109 (10), 91 (18), 83 (10), 57 (100). UV ($CHCl_3$): λ_{max} (lgε) = 214 (4.16), 220 (4.19), 250 (3.79), 260 (3.91), 274 (4.02), 290 (4.00), 308 (3.69), 328 (3.52), 348 (3.31), 364 (3.14), 378 (3.08), 412 nm (2.81).

7. 8-*tert*-Butyl-9,9-dimethyldeca-1,7-dien-3,5-diyne-1,1-dicarbonitrile (21): A mixture of **13** (0.1 g, 0.52 mmol), malononitrile (0.034 g, 0.52 mmol), and a catalytic amount of β-alanine (0.001 g, 0.11 mmol) in 95% EtOH (25 mL) was stirred for 30 min at room temp. The mixture was diluted with water and extracted several times with diethyl ether. The combined organic phases were dried with $MgSO_4$ and the solvent was removed in vacuo. The remaining residue was purified by column chromatography on silica gel with diethyl ether/pentane = 1:2 (v/v). Compound **21** was obtained as a greenish yellow oil (0.124 g, 100%). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.48, 1.26 (s, 18 H, 8-, 10-H), 5.97 (d, J = 3.3 Hz, 1 H, 5-H), 7.11 (d, J = 3.3 Hz, 1 H, 2-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 182.01 (s, C-6), 141.70 (d, C-2), 116.35, 112.83, 111.73 (s, C-1, -a, -b), 102.78 (d, C-5), 93.34, 91.46 (s, C-3,-4), 40.38, 39.86 (s, C-7,-9), 32.55, 30.97 (q, C-8,-10) ppm. IR (film): $\tilde{\nu}$ = 2962 (m), 2233 (w), 2158 (s), 1537 (s), 1485 (w), 1367 (w), 1198 (w), 992 (w), 674 (w) cm^{-1}. MS (70 eV): *m*/*z* (%) = 240 (4) [M$^+$], 184 (40), 169 (18), 157 (7), 140 (8), 128 (7), 115 (6), 84 (27), 69 (12), 57 (100). UV (CH_3CN): λ_{max} (lgε) = 218 (3.92), 306 (3.93), 322 (4.01), 362 (4.28), 418 nm (2.81). $C_{16}H_{20}N_2$ (240.43): calcd. C 79.96, H 8.39, N 11.66; found C 79.82, H 8.37,N 11.09.

8. 3,10-Di-*tert*-butyl-2,2,11,11-tetramethyldodeca-3,9-diene-5,7-diyne (22): Oxygen gas was bubbled for 2 h through a stirred suspension of **10** (0.923 g, 5.63 mmol) and CuCl (0.167 g, 1.69 mmol) in pyridine (15 mL). The pyridine was removed in vacuo, the remaining precipitate was dissolved by the addition of aqueous NH_4Cl solution and the solution extracted several times with diethyl ether. The combined organic phases were dried with $MgSO_4$ and the solvent was removed in a rotary evaporator. The crude mixture was first filtered through silica gel using hexane as the eluent, and purification was completed by sublimation at 75 °C/4 mbar. The compound was obtained in 100% yield (0.915 g) as a yellow solid, m.p. 105–106 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.45 and 1.20 (s,

36 H, 1-, 12-, 14-, 16-H), 5.76 (s, 2 H, 4-, 9-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 173.17 (s, C-3,-13), 103.24 (d, C-4,-9), 83.13 (s, C-6,-7), 82.7 (s, C-5,-8), 39.41 and 38.95 (s, C-2,-11,-13,-15), 32.25, 31.25 (q, 1,-12,-14,-16) ppm. IR (KBr): $\tilde{\nu}$ = 2953 (s), 2120 (w), 1561 (w), 1482 (m), 1387 (m), 1362 (s), 1216 (s), 829 (m), 664 (m) cm^{-1}. MS (70 eV): *m*/*z* (%) = 326 (50) [M$^+$], 270 (16), 269 (68), 213 (19), 197 (24), 185 (27), 171 (17), 167 (12), 157 (18), 143 (35), 133 (11), 128 (19), 119 (50), 107 (19), 57 (100). **UV** ($CHCl_3$): λ_{max} (lg ε) = 194 (4.15), 202 (4.15), 208 (4.16), 216 (4.24), 238 (4.48), 246 (4.53), 252 (4.55), 264 (4.49), 276 (4.01), 294 (4.23), 312 (4.41), 332 nm (4.32). $C_{24}H_{38}$ (326.54): calcd. C 88.27, H 11.73; found C 88.19, H 11.70.

9. 3,14-Di-*tert*-butyl-2,2,15,15-tetramethylhexadeca-3,5,11,13-tetraene-7,9-diyne (23): Oxygen gas was passed for 2 h through a stirred suspension of **11** (0.200 g, 1.05 mmol) and CuCl (0.031 g, 0.315 mmol) in pyridine (15 mL). The pyridine was removed in vacuo, the remaining precipitate was dissolved by the addition of aqueous NH_4Cl solution and extracted several times with diethyl ether. The combined organic phases were dried with $MgSO_4$ and the solvent was removed in a rotary evaporator. The crude mixture was first filtered through silica gel using hexane as the eluent, and purification was completed by sublimation at 120 °C/4 mbar: yellow solid (0.179 g, 95%), m.p. 136 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.36, 1.22 (s, 36 H, 1-, 16-, 18-, 20-H), 5.53 (d, *J* = 14.9 Hz, 2 H, 4-, 9-H), 6.06 (d, *J* = 11.8 Hz, 2 H, 4-, 13-H), 7.39 (dd, J_1 = 14.9, J_2 = 11.8 Hz, 2 H, 5-, 12-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 162.08 (s, C-3,-14), 144.13 (d, C-5,-12), 123.07 (d, C-4,-13), 108.56 (d, C-6,-11), 83.22 (s, C-8,-9), 77.20 (s, C-7,-10), 39.26, 38.26 (s, C-2,-15,-17,-19), 33.98, 31.58 (q, C-1,-16,-18,-20) ppm. IR (KBr): $\tilde{\nu}$ = 3037 (w), 2935 (s), 2135 (w), 1605 (m), 1461 (m), 1378 (m), 1196 (s), 953 (s), 739 (m) cm^{-1}. MS (70 eV): *m*/*z* (%) = 378 (86) [M$^+$], 321 (6), 265 (10), 249 (17), 235 (14), 222 (13), 207 (15), 194 (16), 179 (10), 145 (16), 133 (11), 57 (100). UV ($CHCl_3$): λ_{max} (lg ε) = 218 (3.85), 222 (3.89), 248 (3.80), 262 (3.90), 276 (4.01), 292 (4.04), 314 (4.10), 328 (4.16), 336 (4.18), 358 (4.28), 384 nm (4.23). $C_{28}H_{42}$ (378.62): calcd. C 88.82, H 11.18; found C 88.66, H 11.30.

10. 3,18-Di-*tert*-butyl-2,2,19,19-tetramethylicosa-3,5,7,13,15,17-hexaene-9,11-diyne (24): Oxygen gas was passed for 2 h through a stirred suspension of **12** (0.100 g, 0.463 mmol) and CuCl (0.014 g, 0.140 mmol) in pyridine (5 mL). Work-up as above furnished **24** (98 mg, 98%) as a yellow solid, m.p. 148 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.29, 1.15 (s, 36 H, 1-, 20-, 22-, 24-H), 5.58 (d, *J* = 15.1 Hz, 2 H, 8-, 13-H), 5.98 (d, *J* = 11.8 Hz, 2 H, 4-, 17-H), 6.07 (dd, J_1 = 14.3, J_2 = 11.3 Hz, 2 H, 6-, 15-H), 6.74 (dd, J_1 = 15.4, J_2 = 11.3 Hz, 2 H, 7-, 14-H), 6.89 (dd, J_1 = 14.3, J_2 = 11.8 Hz, 2 H, 5-, 16-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 161.03 (s, C-3,-18), 145.18 (d, C-5,-16), 136.10 (d, C-7,-14), 130.81 (d, C-6,-15), 123.57 (d, C-4,-17), 108.45 (d, C-8,-13), 84.03 (s, C-10,-11), 77.46 (s, C-9,-12), 39.20, 38.13 (s, C-2,-19,-21,-23), 33.87, 31.67 (q, C-1,-20,-22,-24) ppm. IR (KBr): $\tilde{\nu}$ = 3064 (w), 2957 (s), 2115 (w), 1586 (m), 1480 (w), 1367 (m), 1280 (w), 1216 (m), 986 (s) cm^{-1}. MS (70 eV): *m*/*z* (%) = 430 (86) [M$^+$], 317 (15), 301 (4), 289 (5), 274 (5), 261 (7), 246 (8), 232 (12), 205 (7), 171 (7), 117 (7), 61 (12), 57 (100). UV ($CHCl_3$): λ_{max} (lg ε) = 268 (4.22), 296 (4.30), 308 (4.37), 318 (4.45), 338 (4.52), 370 (4.78), 392 (4.82), 422 nm (4.76). HRMS: $C_{32}H_{46}$: calcd. 430.3599; found 430.3588 ± 2 ppm.

11. 3,14-Di-*tert*-butyl-2,2,15,15-tetramethylhexadeca-3,13-diene-5,7,9,11-tetrayne (25): Oxygen gas was bubbled for 1 h through a stirred suspension of **20** (40.0 mg, 0.213 mmol) and CuCl (6.0 mg, 0.07 mmol) in pyridine (5 mL). Work-up as above yielded **25** (26 mg, 65%), yellow solid, m.p. 124 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.35, 1.20 (s, 36 H, 1-, 16-, 18-, 20-H), 5.64 (s, 2 H, 4-, 13-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 178.34 (s, C-3,-15), 101.99 (d, C-4,-13), 82.29, 77.81, 69.10, 64.84 (s, C-5,-6,-7,-8,-9,-10,-11,-12), 39.72, 39.43 (s, C-2,-15,-17,-19), 32.40, 31.11 (q, C-1,-16,-18,-20) ppm. IR (KBr): $\tilde{\nu}$ = 2958 (s), 2179 (s), 1559 (m), 1483 (m), 1466 (m), 1391 (m), 1231 (m), 1195 (m), 1049 (m), 992 (m), 992 (m), 825 (m) cm^{-1}. MS (70 eV): *m*/*z* (%) = 374 (63) [M$^+$], 317 (51), 287 (6), 259 (7), 245 (26), 231 (32), 229 (27), 215 (38), 191 (24), 189 (15), 165 (12), 155 (10), 143 (9), 129 (13), 119 (12), 91 (8), 57 (100). UV ($CHCl_3$): λ_{max} (lg ε) = 208 (4.29), 216 (4.28), 236 (4.34), 246 (4.45), 254 (4.57), 262 (4.61), 282 (4.76), 296 (4.93), 314 (4.83), 330 (4.19), 354 (4.23), 380 (4.28), 412 nm (4.07). HRMS: $C_{28}H_{38}$: calcd. 374.2973; found 374.2964 ± 2 ppm.

12. 3,12-Di-*tert*-butyl-2,2,13,13-tetramethyltetradeca-3,7,11-triene-5,9-diyne (26): To anhydrous THF (5 mL), cooled to 0 °C, $TiCl_4$ (0.218 g, 1.15 mmol) was added under nitrogen, followed by Zn powder (0.155 g, 2.38 mmol), and finally pyridine (0.076 g, 0.96 mmol). The dark gray mixture was stirred for 30 min, then a solution of **13** (0.200 g, 1.04 mmol) in THF (5 mL) was added dropwise. Cooling was removed and the reaction mixture was refluxed for 15 min. The mixture was quenched by addition of 1 N aqueous HCl which dissolved the black residue completely. After extraction with ether, the organic phase was neutralized with saturated $NaHCO_3$ solution, the layers were separated, and the organic layer was dried with $MgSO_4$. The solvent was removed by rotary evaporation and the residue was purified by column chromatography on silica gel with hexane: 0.153 g (42%) of ***E*-26**. Furthermore, a 1:1-mixture of 3,12-di-*tert*-butyl-2,2,13,13-tetramethyltetradeca-3,7-*Z*,11-triene-5,9-diyne (***Z*-26**, see below) and 3-(2-*tert*-butyl-3,3-dimethylbut-1-enyl)-2-(4-*tert*-butyl-5,5-dimethylhex-3-en-1-ynyl)furan (**27**, see below) were formed as by-products. ***E*-26**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.21, 1.44 (s, 36 H, 1-, 14-, 16-, 18-H), 5.76 (s, 2 H, 4-, 11-H), 6.09 (s, 2 H, 7-, 8-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 170.35 (s, C-3,-15), 119.68 (d, C-7,-8), 103.87 (d, C-4,-11), 96.50 (s, C-6,-9), 95.12 (s, C-5,-10), 39.34, 38.73 (s, C-2,-13,-15,-17), 32.13, 31.32 (q, C-1,-14,-16,-18) ppm. IR (KBr): $\tilde{\nu}$ = 2956 (vs), 2186 (m), 1484 (m), 1467 (m), 1397 (m), 1365 (m), 1236 (m), 1197 (m), 1179 (m), 928 (m) cm^{-1}. UV ($CHCl_3$): λ_{max} (lg ε) = 318 (4.42, sh), 332 (4.50), 334 (4.49), 352 nm (4.36, sh). MS (70 eV): *m*/*z* (%) = 352 (65) [M$^+$], 295 (63), 209 (11), 193 (16), 181 (14), 169 (26), 165 (12), 145 (20), 143 (9), 129 (11), 119 (21), 105 (13), 91 (12), 57 (100). HRMS $C_{26}H_{40}$ (352.60) calcd. 352.3130; found 352.3120 ± 2 ppm.

3,12-Di-*tert*-butyl-2,2,13,13-tetramethyltetradeca-3*Z*,7,11-triene-5,9-diyne (*Z*-26): ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.15, 1.41 (s, 36 H, 1-, 14-, 16-, 18-H), 5.74 (s, 2 H, 4-, 11-H), 5.84 (d, *J* = 1.0 Hz, 2 H, 7-, 8-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 169.9 (s, C-3,-12), 118 (d, C-7-,-8), 104.35 (d, C-4,-11), 97.25 (s, C-6,-9), 95.82 (s, C-5,-10), 39.34, 38.69 (s, C-2,-13,-15,-17), 32.15, 31.33 (q, C-1,-14,-16,-18) ppm. MS (GC/MS): *m*/*z* (%) = 352 [M$^+$] (10), 295 (20), 281, 265, 211, 193, 181, 169 (20), 156, 145 (10), 133, 119 (20), 105 (10), 91, 79, 69, 57(100).

3-(2-*tert*-Butyl-3,3-dimethylbut-1-enyl)-2-(4-*tert*-butyl-5,5-dimethylhex-3-en-1-ynyl)furan (27): ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.15, 1.18, 1.20, 1.41 (s, 36 H, 13-, 15-, 17-, 19-H), 5.79 (s, 1 H, 8-H), 6.17 (s, 1 H, 10-H), 6.25 (d, *J* = 1.9 Hz, 1 H, 4-H), 7.21 (s, *J* = 1.9 Hz, 1 H, 5-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 169.1 (s, C-9), 159.9 (s, C-11), 142 (d, C-5), 129 (s, C-2,-3), 114.89 (d, C-10), 114.1 (d, C-4), 103.44 (d, C-8), 96.64 (s, C-7), 87.77 (s, C-6), 39.51, 39.34, 39.28, 38.74 (s, C-12,-14,-16,-18), 32.32, 32.34, 33.48 (q, C-13,-15,-17,-19) ppm. MS (GC/MS): *m*/*z* (%) = 368 [M$^+$], 312, 297, 199 (10), 185 (40), 171, 151, 109 (10), 95 (30), 83, 57 (100).

13. 2,5-Bis(4-*tert*-butyl-5,5-dimethylhexa-1,3-dienyl)thiophene (28): A stirred mixture of **23** (40 mg, 0.105 mmol), $Na_2S·9H_2O$ (56.0 mg, 0.233 mmol), and KOH (12 mg, 0.21 mmol) in DMSO (25 mL) was heated to 55 °C. The reaction was monitored by TLC and after 10 min conversion of **23** to the product was complete. The DMSO was removed by vacuum distillation, the remaining residue was dissolved by addition of water and the mixture was extracted several times with diethyl ether. The combined organic phases were dried with $MgSO_4$ and the solvent was removed by rotary evaporation. After purification of the residue by column chromatography on silica gel with ethyl acetate/hexane = 1:10 (v/v), **28** was obtained in 100% yield (43 mg) as a yellow solid, m.p. 159 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.36, 1.17 (s, 36 H, 6-, 12-, 14-, 16-H), 6.03 (d, J = 11.4 Hz, 2 H, 3-, 9-H), 6.38 (d, J = 14.9 Hz, 2 H, 1-, 7-H), 6.69 (s, 2 H, 3′-, 4′-H), 7.06 (dd, J_1 = 14.9, J_2 = 11.4 Hz, 2 H, 2-, 8-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 157.82 (s, C-4,-10), 142.11 (s, C-2′,-5′), 128.40 (d, C-2,-8); 126.22 (d, C-3′,-4′), 124.52 (d, C-1,-7), 123.59 (d, C-3,-9), 39.02, 38.00 (s, C-5,-11,-13,-15), 33.99, 31.82 (q, C-6,-12,-14,-16) ppm. IR (KBr): $\tilde{\nu}$ = 3442 (br), 3070 (w), 2956 (s), 1740 (w), 1629 (w), 1481 (m), 1366 (m), 1214 (m), 964 (m), 784 (m) cm^{-1}. MS (70 eV): *m*/*z* (%) = 412 (100) [M$^+$], 355 (65), 298 (39), 283 (39), 270 (24), 189 (10), 57 (40). UV ($CHCl_3$): λ_{max} (lgε) = 236 (4.12), 260 (4.20), 266 (4.30), 274 (4.31), 286 (3.93), 376 (4.46), 392 (4.56), 412 nm (4.43, sh). $C_{28}H_{44}S$ (412.73): calcd. C 81.49, H 10.75, S 7.75; found C 80.90, H 10.88, S 7.68.

14. 2,5-Bis(6-*tert*-butyl-7,7-dimethylocta-1,3,5-trienyl)thiophene (29): A stirred mixture of **24** (30.0 mg, 0.069 mmol), $Na_2S·9H_2O$ (37.0 mg, 0.153 mmol) and KOH (8.0 mg, 0.14 mmol) in DMSO (20 mL) was heated to 55 °C. The reaction was monitored by TLC and after 5 min, conversion of the starting material to product was complete. Work-up as above furnished **29** in 100% yield (32 mg) as an orange solid, m.p. 188–189 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.32, 1.16 (s, 36 H, 8-, 16-, 18-, 20-H), 6.02 (d, J = 11.7 Hz, 2 H, 5-, 13-H), 6.10 (dd, J_1 = 14.3, J_2 = 10.5 Hz, 2 H, 3-, 11-H), 6.49 (d, J = 15.0 Hz, 2 H, 1-, 9-H), 6.58 (dd, J_1 = 15.1, J_2 = 10.5 Hz, 2 H, 2-, 10-H), 6.71 (s, 2 H, 3′-, 4′-H), 6.84 (dd, J_1 = 14.3, J_2 = 11.7 Hz, 2 H, 4-, 12-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 158.11 (s, C-6,-14), 142.05 (s, C-2′,-5′), 133.21, 131.73, 129.75, 126.56, 124.22, 123.91 (d, C-3′,-4′,-1,-2,-3,-4,-5,-9,-10,-11,-12,-13), 39.04, 37.99 (s, C-7,-15,-17,-19), 33.81, 31.80 (q, C-8,-16,-18,-20) ppm. IR (KBr): $\tilde{\nu}$ = 3419 (br), 2959 (s), 1618 (w), 1459 (w), 1389 (w), 1261 (s), 1217 (m), 1097 (s), 1031 (s), 980 (s), 802 (s) cm^{-1}. MS (70 eV): *m*/*z* (%) = 464 (18) [M$^+$], 401 (10), 369 (8), 350 (8), 297 (100), 281 (8), 242 (26), 221 (29), 207 (35), 203 (19), 147 (69), 133 (13), 73 (85), 57 (40). UV ($CHCl_3$): λ_{max} (lgε) = 224 (3.49), 272 (4.01), 288 (3.94), 298 (3.99), 310 (4.09), 322 (4.13), 364 (3.74), 406 (4.30), 426 (4.44), 452 nm (4.34). HRMS: $C_{32}H_{48}S$: calcd. 464.3476; found 464.3466 ±2 ppm.

15. 2,5-Bis(4-*tert*-butyl-5,5-dimethylhex-3-en-1-ynyl)thiophene (30) and 2-(2-*tert*-butyl-3,3-dimethylbut-1-enyl)-5-(6-*tert*-butyl-7,7-dimethyloct-5-ene-1,3-diynyl)thiophene (31): A mixture of **25** (60.0 mg, 0.021 mmol), $Na_2S·9H_2O$ (225 mg, 0.941 mmol), and KOH (48.0 mg, 0.856 mmol) in DMSO (50 mL) was stirred for 30 min at 80 °C. The DMSO was removed by vacuum distillation, the remaining precipitate was dissolved by the addition of water and the mixture was extracted several times with diethyl ether. The combined organic phases were dried with $MgSO_4$ and the solvent was removed in vacuo. Purification of the residue on silica gel using ethyl acetate/hexane = 1:10 (v/v) furnished 12 mg (14%) **30** and 12 mg (14%) of **31** as orange solids.

2,5-Bis(4-*tert*-butyl-5,5-dimethylhex-3-en-1-ynyl)thiophene (30): ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.21, 1.28 (s, 36 H, 6-, 11-, 14-, 16-H), 6.29 (s, 2 H, 3-, 9-H), 6.72 (s, 2 H, 3′-, 4′-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 158.66 (s, C-4,-10), 151.46 (s, C-1,-7),

Table 1. Crystallographic data for compounds **22**, **23**, **24**, **25**, **28** and **29**.

Compound	**22**	**23**	**24**	**25**	**28**	**29**
Formula	$C_{24}H_{38}$	$C_{28}H_{42}$	$C_{32}H_{46}$	$C_{28}H_{38}$	$C_{28}H_{44}S$	$C_{32}H_{48}S$
M_r	326.54	378.62	430.69	374.58	412.69	464.76
Habit	colourless plate	yellow prism	yellow prism	yellow tablet	yellow needle	orange tablet
Crystal size [mm]	0.45×0.25×0.1	0.28×0.16×0.13	0.55×0.4×0.25	0.33×0.25×0.12	0.4×0.14×0.12	0.7×0.4×0.2
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	tetragonal	monoclinic
Space group	*C*2/*c*	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$I4_1/acd$	$P2_1/c$
Cell constants						
a [Å]	15.339(2)	11.645(3)	6.0630(8)	11.4627(14)	22.7579(16)	11.648(5)
b [Å]	6.1571(10)	7.967(2)	8.1408(12)	8.1292(10)	22.7579(16)	33.917(6)
c [Å]	23.483(3)	13.572(4)	15.623(2)	13.4476(18)	19.6508(18)	8.202(4)
α [°]	90	90	75.944(8)	90	90	90
β [°]	105.328(6)	106.559(10)	79.759(10)	107.906(3)	90	109.08(4)
γ [°]	90	90	71.949(10)	90	90	90
V [Å^3]	2138.8	1206.9	706.78	1192.4	10177.6	3062.3
Z	4	2	1	2	16	4
D_x [Mg m^{-3}]	1.014	1.042	1.012	1.043	1.077	1.008
μ [mm^{-1}]	0.06	0.06	0.06	0.06	0.14	0.12
F(000)	728	420	238	412	3648	1024
T [°C]	–130	–130	–130	–130	–130	–100
$2\theta_{max}$	56.6	56.6	50	56.6	57	50
Refl. measured	10802	8547	2728	12132	74536	5635
Refl. independent	2649	2997	2472	2955	3244	5634
R_{int}	0.061	0.098	0.016	0.029	0.083	
Parameters	115	133	152	133	138	310
$wR(F^2$, all refl.)	0.138	0.143	0.118	0.120	0.107	0.101
$R[F, >4\sigma(F)]$	0.048	0.057	0.044	0.040	0.038	0.045
S	1.03	0.95	1.00	1.07	1.00	0.83
max. $\Delta\rho$ (e Å^{-3})	0.30	0.43	0.18	0.32	0.28	0.20

144.45 (s, C-2′,-5′), 142.94 (s, C-2,-8), 126.61 (d, C-3′,-4′), 97.11 (d, C-3), 38.97, 38.78 (s, C-5,-11,-13,-15), 32.26, 31.88 (q, C-6,-11,-14,-16) ppm. IR (KBr): $\tilde{\nu}$ = 2960 (s), 2925 (vs), 2869 (m), 2855 (m), 2038 (vw), 1637 (w), 1459 (w), 1261 (m), 1098 (m), 1022 (m), 803 (m) cm^{-1}. MS (70 eV): *m*/*z* (%) = 408 (100) [M^+], 393 (8), 351 (40), 337 (12), 295 (40), 279 (10), 267 (12), 202 (7), 57 (100). UV ($CHCl_3$): λ_{max} (lgε) = 242 (3.60), 288 (3.74), 370 (3.60), 416 (3.63), 448 nm (3.58). Because of the very small quantity of the substance no elemental analysis could be obtained.

2-(2-*tert*-Butyl-3,3-dimethylbut-1-enyl)-5-(6-*tert*-butyl-7,7-dimethyloct-5-ene-1,3-diynyl)thiophene (31): ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.16, 1.22, 1.29, 1.39 (s, 36 H, 4′-, 6′-, 8-, 10-H), 5.77 (s, 1 H, 5-H), 6.27 (d, J = 0.5 Hz, 1 H, 1′-H), 6.75 [dd, J_1 = 3.8, J_2 = 0.5 Hz, 1 H, 3-H (thiophene)], 6.89 [d, J = 3.8 Hz, 1 H, 4-H (thiophene)] ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 170.00 (s, C-6), 159.78 (s, C-2′), 151.91 (s, C-2), 145.44 [s, C-2 (thiophene)], 144.16 (s, C-1), 131.20 [d, C-3 (thiophene)], 125.33 [d, C-4 (thiophene)], 123.67 [s, C-5 (thiophene)], 103.68 (d, C-5), 96.26 (d, C-1′), 95.46 (s, C-3), 91.38 (s, C-4), 39.37, 39.11, 38.86, 38.77 (s, C-3′,-5′,-7,-9), 32.17, 31.35 (q, C-8,-10), 32.11, 31.87 (C-4′,-6′) ppm. IR (KBr): $\tilde{\nu}$ = 2996 (s), 2961 (m), 2923 (m), 2180 (m), 1636 (m), 1630 (m), 1560 (w), 1484 (m), 1261 (s), 1096 (s), 1049 (s), 803 (s), 792 (s) cm^{-1}. MS (70 eV): *m*/*z* (%) = 408 (100) [M^+], 393 (12), 351 (100), 295 (9), 279 (19), 267 (6), 111 (7), 97 (8), 57 (24). UV ($CHCl_3$): λ_{max} (lgε) = 234 (3.70), 274 (3.76), 322 (3.47), 344 (3.72), 366 (4.01), 386 (4.14), 400 nm (4.10).

16. X-ray Structure Determinations: Numerical details are presented in Table 1. *Data collection and reduction*: Crystals were mounted in inert oil on glass fibres and transferred to the cold gas stream of the diffractometer (**22**, **23**, **25**, **28**: Bruker SMART 1000 CCD; **24**, **29**: Siemens P4, with appropriate low-temperature equipment). Measurements were performed with monochromated Mo-K_α radiation (λ = 0.71073 Å). No absorption corrections were performed. *Structure refinement*: The structures were refined anisotropically against F^2 (program SHELXL-97).[18] Hydrogen atoms were included as rigid methyl groups or with a riding model.

CCDC-742714 (for **22**), -742715 (for **23**), -742716 (for **24**), -742717 (for **25**), -742718 (for **28**), -742719 (for **29**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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