A Convenient Synthesis of Functionalised 1-Aryl-1,3-alkadiynes

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A two-step, one-pot synthesis of functionalised 1-arylalka-1,3-diynes is described. A key feature in this approach is exploitation of the "acetylene zipper" reaction to obtain terminal 1,3-alkadiynes **3** from internal isomers **1**. Without isolation, but after protonation, the 1,3-alkadiynes **3** are subjected to subsequent Pd/Cu-catalyzed Sonogashira cross-couplings with aryl iodides having both electron-withdrawing and electron-donating groups. The whole sequence takes place under mild reaction conditions to afford functionalised 1-arylalka-1,3-diynes **21**–**35** in high yields.

Introduction

Functionalized acetylene derivatives, due to their high synthetic potential, are often indispensable in pathways to complicated molecules. Additional applications followed from Castro's original discovery[1,2] that suitably positioned nucleophiles can undergo intramolecular cyclizations onto acetylene groups. Many studies have shown functionalised aryl- and heteraryl-acetylenes to be useful precursors for a wide variety of heterocyclic systems.[3–5] However, a careful review of the literature revealed that examples of similar reactions involving buta-1,3-diynyl-substituted arenes are limited[5,6–9] due to the lack of convenient preparative methods to the necessary functionalised aryldiynes. For example, the synthesis of arylbutadiynes from the corresponding 1,3-diketones[10] is unsuitable for the preparation of functionalised derivatives. The far-reaching synthetic applications of the Pd-Cu-catalyzed cross-coupling reaction between haloarenes and halo-heteroarenes with terminal acetylenes (the Sonogashira reaction).[11] have been demonstrated in many fields of chemistry, including polymer and supramolecular synthesis.[12–15] In comparison with 1-alkynes, applications of 1,3-diynes as the acetylenic component in such couplings is notably limited, mainly due to their lower stability and availability.[16,17]

The Cadiot–Chodkiewicz coupling,[18] consisting of the union of terminal alkynes with 1-bromoacetylenes in the presence of a copper(I) salt, is useful and important for the synthesis of unsymmetrically substituted diynes. A variety of other heterocoupling methods have also been developed.[19,20] However, a general problem associated with these is the prevalence of homo-coupling side reactions, arising by halogen-metal exchange. Dramatic increases in such by-product formation can occur in such reactions when these are applied to long-chain acetylenes. It is also relevant that cross-coupling methods require prior synthesis of the alkyne and especially the 1-bromoalkyne components. From these points of view, the development of new and convenient methods for the synthesis of conjugated diynes in general is clearly desirable. As a part of our program exploring the chemistry of functionalised diynes,[21,22] we report herein a method that allows the synthesis of functionalised 1-arylalka-1,3-diynes from simple starting materials in a convenient and efficient manner.

Results and Discussion

We have previously reported the first examples of an one-pot synthesis of 1-arylalka-1,3-diynes by sequential zipper and Sonogashira reactions.[23] Consequently, we have carried out a detailed study of the scope and limitations of this approach and herein, we report in full the results of our findings. The coupling reactivity of a series of iodo- and bromoarenes, having both electron-withdrawing and electron-donating substituents, has been tested in reactions with 1,3-diynes, formed in situ by "acetylene zipper" reactions (Scheme 1). Palladium acetate, $[PdCl_2(PPh_3)_2]$ and $[PdPPh_3)_4]$ in the presence of CuI, PPh_3 and Et_3N, have been used as catalytic systems for these Sonogashira reactions. The representative haloarene substrates **5**–**20** are depicted in Scheme 2.

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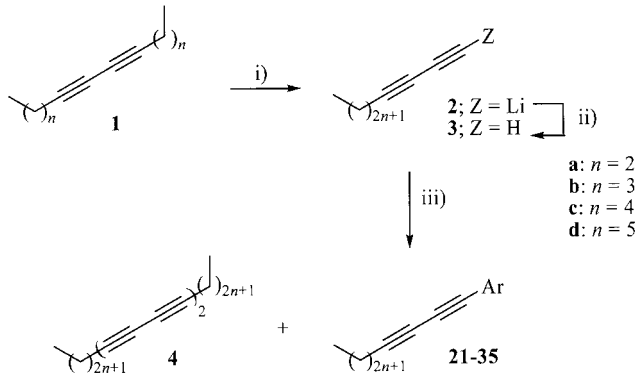
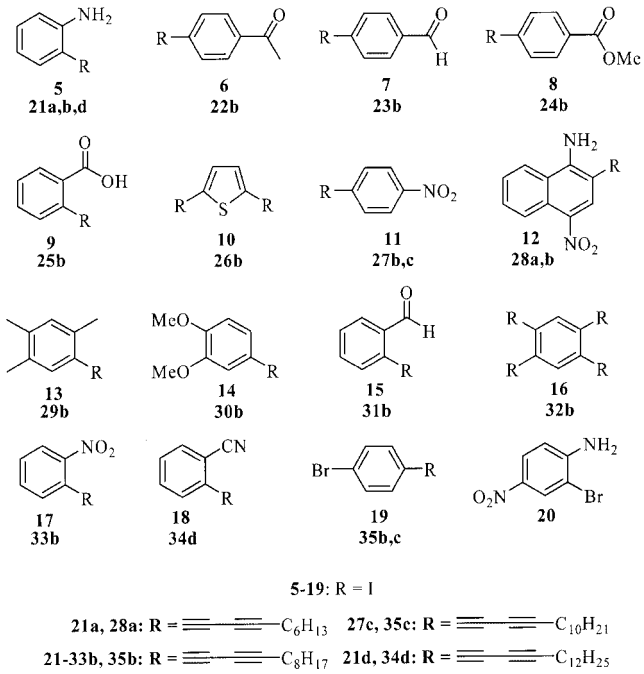


Scheme 1. i) 3 Equiv. lithium 2-aminoethylamide (LAETA), THF, C_6H_6, hexane, (1:1:1), 16° C, add diyne **1**, 10 min.; ii) add H_2O (0.2 mL mmol^{-1} of diyne **1**; iii) 0.8 equiv. ArI **5**–**20**, 0.08 equiv. Pd catalyst (see Table 2), Et_3N (2 mL mmol^{-1} of diyne **1**), 0.12 equiv. CuI, 0.5–12 h, 16– 40° C (see Table 1 and Table 2)



Scheme 2

1,3-Decadiyne (**3a**), 1,3-dodecadiyne (**3b**), 1,3-tetradecadiyne (**3c**) and 1,3-hexadecadiyne (**3d**) were obtained in situ from the internal diynes **1a**–**d** respectively, by treatment with three equivalents of lithium 2-aminoethylamide LAETA). This step is remarkably rapid, reaching completion within a few minutes at ambient temperature 16–18 °C).

Table 2. Couplings of 1,3-diynes **3a**–**d** with aryl iodides **5**–**19** (Scheme 2)

Entry	ArI	Product	Method	Ratio ArI:**1**	Yield of product [%]
1	**5**	**21b**	A	1:1	72
2	**6**	**22b**	A	1:1	86
3	**7**	**23b**	A	1:1	49
4	**8**	**24b**	A	1:1	69
5	**5**	**21b**	A	1:1.25	93–95
6	**5**	**21a**	A	1:1.25	77–87
7	**9**	**25b**	B	1:1.5	27
8	**10**	**26b**	B	1:2.5	99
9	**7**	**23b**	A	1:1.25	77
10	**11**	**27b**	A	1:1.25	72
11	**12**	**28b**	A	1:1.25	92
12	**12**	**28a**	A	1:1.25	77–88
13	**13**	**29b**	B	1:1.25	99
14	**14**	**30b**	B	1:1.25	98
15	**15**	**31b**	A	1:1.25	63
16	**15**	**31b**	B	1:1.25	71
17[b]	**16**	**32b**	A	1:5	93
18	**17**	**33b**	A	1:1.25	80
19	**19**	**35b**	B	1:1.25	96
20[a]	**19**	**35b**	B	1:1.5	95
21[a]	**19**	**35b**	B	1:2.5	54
22[b]	**19**	**35c**	B	1:1.5	92
23	**18**	**34d**	A	1:1.5	90
24	**5**	**21d**	A	1:1.5	67
25[b]	**11**	**27c**	B	1:1.5	77

[a] $[PdCl_2(PPh_3)_2]$ was used as a catalyst. [b] $[Pd(PPh_3)_4]$ was used as a catalyst. In other Entries $Pd(OAc)_2$ was used. All yields isolated.

The resulting lithium acetylides **2** were then quenched by the addition of water. With no further work-up, the subsequent Sonogashira couplings with iodoarenes **5**–**19** in the presence of the Pd-Cu catalyst system led to the desired products **21**–**35** in good to excellent yields. All reactions were carried out under argon at ambient temperature or with slight heating (40 °C) until TLC indicated complete conversion of the starting iodides. In general, iodoarenes having either electron-withdrawing or electron-donating groups readily reacted with the 1,3-diynes **3** to afford the expected cross-coupling products. The results are summarized and hence the scope of the method indicated in Table 2. Evidently, the presence of a small amount of water has no deleterious effect on the Sonogashira coupling step.

Homo-coupled products, the tetraynes **4**, were also isolated from the reaction mixtures, initially in yields of 8–14 %, with respect to the starting alkynes **1**. The formation of such products during Sonogashira reactions has been observed earlier and a mechanism which accounts for this has

Table 1. Influence of reaction conditions and temperature on the yield of products **21b** and **31b** (ratio ArI:diyne **1** = 1:1.25)

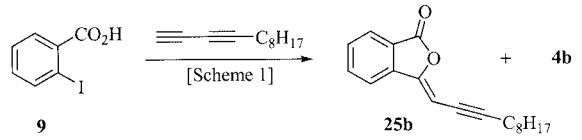
Entry	ArI	Time	*T* [°C]	Method	Yield of **4** [%]	Yield of product [%]
1, 2	**5**	12 h	room temp.	A	2–4	93–95
3	**5**	10 h	40 °C	A	4	77
4	**5**	6 h	room temp.	B	3	81
5	**5**	30 min	40 °C	B	2	92
6	**7**	12 h	40 °C	A	6	63
7	**7**	10 min	room temp.	B	2	71

been proposed.[15] In an attempt to increase the yields of the target products **3** and reduce this homo-coupling, the molar ratio of the starting diynes **1**, relative to the iodoarenes, was varied. We established that a 1.25 fold excess of diynes **1a**–**c** with respect to the iodoarene was necessary to complete the conversion. Fortunately, this molar ratio also led to a decrease in the yield of the tetrayne by-products **4** to 1–4 %. In contrast, reactions involving 1,3-hexadecadiyne (**3d**) and aryl iodides were completed only when a 1.5 fold excess of hexadeca-7,9-diyne (**1d**) was used initially.

Because the syntheses were carried out in a one-pot process (Procedure **A**, see Exp. Sect.), the resulting mixture of solvents contained ethylenediamine (EDA), benzene, hexane and THF. It is known that Pd^{II} can form stable complexes with EDA.[24] To elucidate the influence of EDA on the present Pd-catalyzed couplings, some experiments in which this component had been removed were conducted (Procedure **B**) in couplings with 1,3-dodecadiyne (**3b**). 2-Iodoaniline (**5**) and 4-iodobenzaldehyde (**7**) were chosen as model substrates. From the results presented in Table 1, it can be seen that, in the examples where EDA had been removed, the coupling reactions required significantly shorter reaction times and/or a lower reaction temperature. Removing the EDA also led to slightly increased yields. Despite this finding, the simplicity of the one-pot procedure (**A**) can make this preferable. Crucially, however, procedure **B** *had* to be used in reactions with less reactive iodoarenes, having several electron-donating groups [**13**, **14**], along with couplings to 2-iodobenzoic acid (**9**) and the polyhalogenated substrates **10**, **16** and **19**.

In an effort to extend this method to the synthesis of poly(butadiynes), we examined the reactions of 1,3-dodecadiyne **3b** with 2,5-diiodothiophene and 1,2,4,5-tetraiodobenzene (Table 2; Entries 8 and 17). This idea was successful: the reactions occurred rapidly at ambient temperature and 2,5-bis(dodeca-1,3-diynyl)thiophene (**26b**) and 1,2,4,5-tetrakis(dodeca-1,3-diynyl)benzene (**32b**) were obtained in high yields.

According to our results, the nature of the substituents (i. e. electron-withdrawing or -donating) on the iodoarenes did not have a great influence on the course of the cross-coupling Sonogashira reactions. One exception was in the case of an *ortho*-carboxylic acid group. Thus, reaction of 2-iodobenzoic acid (**9**) with 1,3-dodecadiyne (**3b**), in the presence of the $[Pd(PPh_3)_2Cl_2]$ – CuI – Et_3N catalyst system using procedure **B**, was complete in 10 min at ambient temperature. However, there was an unexpected increase in the yield of the tetrayne by-product **4b** and a low yield of a cross–coupled product. This turned out to be the ylidenephthalide **25b**, due to a subsequent and additional cyclisation (Scheme 3). The phthalide **25b** and tetrayne **4b** were separated from the reaction mixture in yields of 27 % and 15 % respectively (Table 2, Entry 7). The Castro reaction of copper acetylides with 2-iodobenzoic acid can afford either or both isocoumarins or phthalides, depending upon the exact conditions and nature of the acetylenes.[2,5,25] The synthesis of phthalides by $[Pd(PPh_3)_2Cl_2]$ – CuI – Et_3N catalysed cross coupling of terminal acetylenes with 2-iodobenzoic acid has also been reported, together with formation of the corresponding isocoumarins, as minor products;[26] no traces of isocoumarin or non-cyclized cross-coupling products were detected in the present case. It should be noted that similar cyclizations did not occur in reactions with *ortho*-amino derivatives.



Scheme 3

We also tested the reactivity of bromoarenes in this process. In contrast to iodoarenes, which reacted readily in the presence of either $Pd(OAc)_2$ or $[PdCl_2(PPh_3)_2]$, 1,3-dodecadiyne (**3b**) did not react with bromoarenes using procedure **A** or **B**. This result is not surprising, given the established lower reactivity of bromides in comparison with iodoarenes. Usually, cross-couplings of terminal alkynes with bromo derivatives requires significantly higher temperatures and prolonged reaction times (12–72h). Even 2-bromo-4-nitroaniline did not react with 1,3-dodecadiyne **3b** in the presence of $Pd(OAc)_2$ at 40 °C. Increasing the temperature to 80 °C resulted in decomposition of the unstable 1,3-diyne **3b** and only homocoupled product **4b** and starting material **20** were detected by TLC monitoring. Of course, this lack of reactivity can be utilised in a positive sense. Thus, 1-bromo-4-iodobenzene (**19**) afforded only 1-(4-bromophenyl)dodeca-1,3-diyne (**35b**) in the presence of $Pd(OAc)_2$ or $[PdCl_2(PPh_3)_2]$ (Table 2; Entries 19, 20). Using a 2.5 molar excess of starting diyne and $[PdCl_2(PPh_3)_2]$ as catalyst, at 80 °C also led to the bromophenyl derivative **35b**, which was obtained in 54 % yield (Table 2, Entry 21). The yield decrease was a consequence of decomposition of the unstable terminal diyne **1b** under these conditions. A similar product **35c** was separated from the reaction of 1,3-tetradecadiyne **2c** with 1-bromo-4-iodobenzene in the presence the more active catalyst $[Pd(PPh_3)_4]$ (Table 2, Entry 22), but now in excellent yield.

Conclusions

A novel and synthetically convenient approach to functionalised 1-aryl-1,3-alka-diynes has been developed which can be applied to a wide range of electronically diverse aryl iodides.

Experimental Section

General Remarks: All reactions were performed under dry argon and all solvents were dried according to standard methods. Deca-4,6-diyne (**1a**), dodeca-5,7-diyne (**1b**), tetradeca-6,8-diyne (**1c**) and hexadeca-7,9-dyne (**1d**) were prepared by an oxidative coupling method.[27] $[PdCl_2(PPh_3)_2]$, $Pd(OAc)_2$, $[Pd(PPh_3)_4]$, CuI and Et_3N were used as purchased. IR spectra were recorded using a Specord-M80. ^1H and ^{13}C NMR spectra were recorded with a Bruker AX-300 spectrometer at 300 and 75 MHz, respectively. Solvent reso-

nances were used as internal standards. Thin layer chromatography was performed on glass plates, pre-coated with Merck Kieselgel 60 to 0.5 mm thickness. CHN analyses were performed in the analytical laboratory of the Saint-Petersburg State University using a Perkin–Elmer B18 instrument. GC/MS analysis was performed an Agilent 68–90, MS detector Agilent 5973 (ionization voltage 70eV). Tetraynes **4** have been characterized earlier.[28] Starting iodides **5**–**7**, **10**, **11**, **17** and **19** are commercially available. Other iodides were prepared by known methods.[29–32]

General Acetylene Zipper Procedure: LAETA was obtained by the reaction of lithium metal (53 mg, 7.5 mmol) with absolute ethylene diamine (0.6 mL, 7.5 mmol) in dry THF (1.8 mL). After lithium dissolution, benzene (1.8 mL) and hexane (1.8 mL) were added to the resulting straw-coloured suspension of LAETA. The resulting mixture was cooled to 16 °C, the diyne **1** (2.5 mmol) added by syringe and the final mixture stirred at 16–18 °C for 10 min.

General in situ 1,3-Diyne Coupling. Procedure A: When the "acetylene zipper" reaction was complete, water (0.5 mL) was added to the dark-brown reaction mixture. An aryl iodide (2 mmol), the palladium catalyst (0.2 mmol, see Table 2), triphenylphosphane (52.5 mg, 0.2 mmol), triethylamine (5 mL) and copper(I) iodide (57 mg, 0.3 mmol) were then added sequentially, in this order, to the stirred reaction mixture. TLC was used to monitor the progress of the reaction. Upon completion, the reaction mixture was poured into ice-water and the resulting mixture extracted with dichloromethane (4 × 25 mL). The combined organic extracts were washed with water and dried with $MgSO_4$. After solvent evaporation, the product was isolated by flash chromatography on silica gel, eluting with hexane, then hexane/CH_2Cl_2 mixtures. The reactions are scalable: only a slight decrease in yields were observed using 5 g of the diynes **1**.

1,3-Diyne Coupling after Removal of Ethylene Diamine. Procedure B: When the "acetylene zipper" reaction was complete, the dark-brown reaction mixture was poured into ice-water and the mixture shaken. The organic layer was separated, returned to the flask, then the coupling reaction was carried out as described in Procedure A.

2-(Deca-1,3-diynyl)aniline (21a): Deca-4,6-diyne (**1a**, 335 mg, 2.5 mmol) was used to obtain 1,3-decadiyne (**3a**) which was reacted with 2-iodoaniline (**5**, 438 mg, 2 mmol) (Procedure A). Chromatography on silica gel (hexane/CH_2Cl_2, 2:1) afforded the diyne **21a** (435 mg, 87 %) as a light yellow oil. R_f = 0.27 (hexanes/CH_2Cl_2, 4:1). ^{1}HNMR (300 MHz, $CDCl_3$): δ = 0.90 (t, J = 7 Hz, 3 H), 1.18–1.32 (m, 8 H), 2.35 (t, J = 7 Hz, 2 H), 4.44 (s, 2 H, NH_2), 6.65–6.72 (m, 2 H), 7.11 (t, J = 7 Hz, 1 H), 7.27 (t, J = 7 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.3, 20.0, 23.1, 28.7, 29.5, 32.3 65.7, 71.7, 80.0, 86.3, 107.2, 114.5, 118,0, 130.4, 133.3, 149.3 ppm. IR (CCl_4): $\tilde{\nu}$ = 3495, 3390 (NH_2), 3070, 2960, 2230, 2140, 1620, 1560, 1470, 1400, 1255, 840 cm^{-1}. MS (EI): *m*/*z* (%) = 225 (100) [M$^+$], 196 (30), 186 (40), 182 (30), 154 (70), 144 (10), 130 (33), 117 (33). $C_{16}H_{19}N$ (225.3): calcd. C 85.28, H 8.50, N 6.22; found C 85.29, H 8.45, N 6.03.

2-(Dodeca-1,3-diynyl)aniline (21b): Dodeca-5,7-diyne (**1b**, 405 mg, 2.5 mmol) was used to obtain 1,3-dodecadiyne (**3b**) which was reacted with 2-iodoaniline (**5**, 438 mg, 2 mmol) (Procedure A). Chromatography on silica gel (hexane/CH_2Cl_2, 2:1) afforded the diyne **21b** (481 mg, 95 %) as an oil. Using Procedure B, the product **21b** was obtained in 92 % yield (466 mg, 1.84 mmol). R_f = 0.22 (hexanes/CH_2Cl_2, 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, J = 7 Hz, 3 H), 1.21–1.42 (m, 10 H), 1.57 (quint., J = 7 Hz, 2 H), 2.39 (t, J = 7 Hz, 2 H), 4.29 (s, 2 H, NH_2), 6.66–6.71 (m, 2 H), 7.14 (t, J = 7 Hz, 1 H), 7.31 (t, J = 7, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 20.1, 23.1, 28.7, 29.3, 29.5, 29.6, 32.3, 65.4, 72.0, 80.0, 86.4, 107.1, 114.9, 118.4, 130.6, 133.5, 149.6 ppm. IR (CCl_4): $\tilde{\nu}$ = 3500, 3400, 3080, 2925, 2850, 2240, 2150, 1610, 1470, 1400, 1255, 840 cm^{-1}. MS (EI): *m*/*z* (%) = 253 (100) [M$^+$], 224 (23), 210 (34), 196 (22), 184 (56), 160 (17), 146 (28), 130 (53), 106 (35). $C_{18}H_{23}N$ (253.4): calcd. C 85.32, H 9.15, N 5.53; found C 85.24, H 9.13, N 5.63.

The separation of 2-(dodeca-1,3-diynyl)aniline (**21b**) was also modified: upon completion, the reaction mixture was concentrated in vacuo. The dark residue was re-dissolved in dry hexane and dry hydrogen chloride gas was passed through the solution for 30 min. The resulting hydrochloric salt of **21b** was filtered and dried. This separation has the advantage of removing the requirement for purification by chromatography. The yield of the salt was 74 %; however, it is more stable when compared with aniline **21b** and could be stored for a longer time.

2-(Hexadeca-1,3-diynyl)aniline (21d): Hexadeca-7,9-diyne (**1d**, 654 mg, 3 mmol) was used to obtain 1,3-hexadecadiyne (**3d**) which was reacted with 2-iodoaniline (**5**, 438 mg, 2 mmol) using procedure A. Chromatography on silica gel (hexanes/CH_2Cl_2, 2:1) afforded the diyne **21d** (409 mg, 67 %) as a light yellow oil, R_f = 0.24 (hexanes/CH_2Cl_2, 4:1), which slowly crystallised, m. p. 31 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, J = 7 Hz, 3 H), 1.21–1.67 (m, 20 H), 2.39 (t, J = 7 Hz, 2 H), 4.28 (s, 2 H, NH_2), 6.65–6.69 (m, 2 H), 7.14 (t, J = 7 Hz, 1 H), 7.28 (t, J = 7 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.6, 20.1, 23.1, 28.7, 29.3, 29.5, 29.8, 29.9, 30.0, 30.1, 30.2, 32.3, 65.5, 72.1, 80.0, 86.3, 106.9, 114.7, 118.3, 130.6, 133.5, 149.9 ppm. IR (CCl_4): $\tilde{\nu}$ = 3505, 3405, 3080, 3030, 2950, 2850, 2230, 2150, 1600, 1480, 1455, 1300, 900 cm^{-1}. MS (EI): *m*/*z* (%) = 309 (100) [M$^+$], 224 (11), 196 (26), 182 (23), 168 (23), 167 (22), 156 (57), 154 (51), 130 (34), 117 (26), 106 (37). $C_{22}H_{31}N$ (309.5): calcd. C 85.38, H 10.10, N 4.53; found C 85.23, H 10.02, N 4.57.

4-(Dodeca-1,3-diynyl)acetophenone (22b): Dodeca-5,7-diyne (**1b**, 405 mg, 2.5 mmol) was used to obtain 1,3-dodecadiyne (**3b**) which was reacted with 4-iodoacetophenone (**6**, 492 mg, 2 mmol) (Procedure A). Chromatography on silica gel (hexanes/CH_2Cl_2, 4:1) afforded the diyne **22b** (482 mg, 86 %) as a light yellow oil. R_f = 0.37 (hexanes/CH_2Cl_2, 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, J = 7 Hz, 3 H), 1.09–1.55 (m, 10 H), 1.60 (quint., J = 7 Hz, 2 H), 2.37 (t, J = 7 Hz, 2 H), 2.58 (s, 3 H), 7.53 (d, J = 9 Hz, 2 H), 7.65 (d, J = 9 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 20.0, 23.0, 28.6, 29.3, 29.4, 29.5, 32.2, 27.0, 65.3, 74.1, 78.1, 87.2, 127.5, 128.6, 133.0, 136.9, 197.4 ppm. IR (CCl_4): $\tilde{\nu}$ = 3090, 2245, 1680, 1600, 1470, 1430, 1400, 1250 cm^{-1}. MS (EI): *m*/*z* (%) = 280 (48) [M$^+$], 251 (21), 237 (42), 223 (37), 199 (54), 185 (44), 171 (17), 167 (100), 139 (19). $C_{20}H_{24}O$ (280.4): calcd. C 85.67, H 8.63; found C 85.66, H 8.57.

4-(Dodeca-1,3-diynyl)benzaldehyde (23b): Dodeca-5,7-diyne (**1b**, 405 mg, 2.5 mmol) was used to obtain 1,3-dodecadiyne (**3b**) which was reacted with 4-iodobenzaldehyde (**7**, 464 mg, 2 mmol) (Procedure A). Chromatography on silica gel (hexanes/CH_2Cl_2, 4:1) afforded the diyne **23b** (410 mg, 77 %), m. p. 34–36 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, J = 7 Hz, 3 H), 1.29–1.44 (m, 10 H), 1.59 (quint., J = 7 Hz, 2 H), 2.38 (t, J = 7 Hz, 2 H), 7.61 (d, J = 9 Hz, 2 H), 7.82 (d, J = 9 Hz, 2 H), 10.00 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 20.0, 23.0, 28.5, 29.3, 29.4, 29.5, 32.2, 65.2, 73.9, 78.8, 87.8, 128.9, 129.9, 133.4, 136.1, 191.6 ppm. IR (CCl_4): $\tilde{\nu}$ = 3090, 2950, 2930, 2850, 2245, 1680, 1600, 1470, 1430, 1400, 1250 cm^{-1}. MS [EI]: *m*/*z* (%) = 266 (31) [M$^+$], 239 (29), 225 (100), 211 (44), 209 (46, 181 (98), 165 (78), 155 (50), 139 (99), 107 (45), 104 (79), 77 (71). $C_{19}H_{22}O$ (266.4): calcd. C 85.67, H 8.32; found C 85.39, H 8.25.

Methyl 4-(Dodeca-1,3-diynyl)benzoate (24b): Dodeca-5,7-diyne (**1b**, 405 mg, 2.5 mmol) was used to obtain 1,3-dodecadiyne (**3b**) which was reacted with methyl 4-iodobenzoate (**8**, 524 mg, 2 mmol) (Procedure A). Chromatography on silica gel (hexanes/CH_2Cl_2, 4:1) afforded the diyne **24b** (408 mg, 69 %) as an oil. R_f = 0.43 (hexanes/CH_2Cl_2, 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, J = 7 Hz, 3 H), 1.30–1.62 (m, 12 H), 2.48 (t, J = 7 Hz, 2 H), 4.02 (s, 3 H), 7.53 (d, J = 8 Hz, 2 H), 7.71 (d, J = 8 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 21.0, 23.0, 28.5, 29.4, 29.5, 29.6, 32.3, 51.5, 65.6, 74.5, 78.5, 89.3, 125.0, 130.5, 130.6, 133.7, 177.1 ppm. IR (CCl_4): $\tilde{\nu}$ = 3095, 2955, 2920, 2850, 2245, 1730, 1600, 1470, 1430, 1400, 1240 cm^{-1}. MS (EI): *m*/*z* (%) = 298 (15) [M$^+$], 239 (68), 186 (100), 181 (95), 91 (10). $C_{20}H_{24}O_2$ (296.4): calcd. C 81.04, H 8.16; found C 81.15, H 8.31.

3-(Undec-2-ynylidene)phthalide (25b): Dodeca-5,7-diyne (**1b**, 405 mg, 2.5 mmol) was used to obtain 1,3-dodecadiyne (**3b**) which was reacted with 2-iodobenzoic acid (**9**, 496 mg, 2 mmol) according to Procedure B. Chromatography on silica gel (hexane/CH_2Cl_2, 1:1) separated the ylidenephthalide **25b** as a light brown oil (149 mg, 27 %). R_f = 0.48 (hexanes/CH_2Cl_2, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, J = 7 Hz, 3 H), 1.23–1.49 (m, 10 H), 1.60 (quint., J = 7 Hz, 2 H), 2.45 (td, J = 7 and 2.8 Hz, 2 H), 5.68 (t, J = 2.8 Hz, 1 H), 7.55 (t, J = 7 Hz, 1 H), 7.64–7.74 (m, 2 H), 7.90 (d, J = 8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 20.5, 23.1, 29.0, 29.4, 29.5, 29.6, 32.2, 74.3, 89.0, 102.2, 120.2, 124.6, 126.0, 130.8, 134.9, 139.0, 152.9, 166.4 ppm. IR (CCl_4): $\tilde{\nu}$ = 3115, 3065, 2975, 2940, 2870, 2220, 2065, 1990, 1950, 1850, 1800, 1765, 1660, 1625, 1475, 1360, 1280, 1210, 1180, 1100, 980, 770, 695 cm^{-1}. MS (EI): *m*/*z* (%) = 282 (17) [M$^+$], 267 (7), 253 (9), 239 (8), 225 (8), 211 (11), 197 (100), 183 (22), 170 (40), 146 (43), 91 (56). $C_{19}H_{22}O_2$ (282.4): calcd. C 80.82, H 7.85; found C 80.57; H 7.88.

2,5-Bis(dodeca-1,3-diynyl)thiophene (26b): Dodeca-5,7-diyne (**1b**, 810 mg, 5 mmol) was used to obtain 1,3-dodecadiyne (**3b**) which was reacted with 2,5-diiodothiophene (**10**, 772 mg, 2 mmol) (Procedure B). Chromatography on silica gel (hexane) afforded the bis(diynylthiophene) **26b** (801 mg, 99 %) as a light yellow oil. R_f = 0.8 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, J = 6 Hz, 6 H), 1.22–1.61 (m, 24 H), 2.39 (t, J = 7 Hz, 4 H), 7.09 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 20.2, 23.1, 28.6, 29.3, 29.5, 29.6, 32.3, 65.4, 67.4, 80,1, 88.5, 124.8, 133.8 ppm. IR (CCl_4): $\tilde{\nu}$ = 3100, 2245, 1515, 1410, 1280, 740 cm^{-1}. MS (EI): *m*/*z* (%) = 404 (100) [M$^+$], 370 (95), 336 (70), 313 (32), 273 (50), 219 (46, 91 (30), 82 (98). $C_{28}H_{36}S$ (404.7): calcd. C 83.11, H 8.97; found C 83.31, H 9.13.

1-(4-Nitrophenyl)dodeca-1,3-diyne (27b): Dodeca-5,7-diyne (**1b**, 405 mg, 2.5 mmol) was used to obtain 1,3-dodecadiyne (**3b**) which was reacted with 1-iodo-4-nitrobenzene (**11**, 498 mg, 2 mmol) (Procedure A). Chromatography on silica gel (hexanes/CH_2Cl_2, 4:1) afforded the diyne **27b** (408 mg, 72 %) as an oil. R_f = 0.43 (hexanes/CH_2Cl_2, 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, J = 7 Hz, 3 H), 1.31–1.51 (m, 10 H), 1.59 (quint., J = 7 Hz, 2 H), 2.46 (t, J = 7 Hz, 2 H), 7.73 (d, J = 8 Hz, 2 H), 8.23 (d, J = 8 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8, 19.4, 22.8, 28.1, 28.7, 29.1, 29.3, 32.0, 64.5, 65.7, 72.8, 88.9, 125.2, 128.9, 132.5, 139.2 ppm. IR (CCl_4): $\tilde{\nu}$ = 3100, 2960, 2930, 2860, 2240, 1590, 1470, 1400, 1255, 840 cm^{-1}. MS (EI): *m*/*z* (%) = 283 (15) [M$^+$], 254 (13), 240 (22), 226 (74), 212 (32), 201 (29), 179 (45), 173 (52), 165 (100), 152 (61), 139 (57), 126 (38). $C_{18}H_{21}NO_2$ (283.4): calcd. C 76.29, H 7.47, N 7.94; found C 76.20, H 7.55, N 4.91.

1-(4-Nitrophenyl)tetradeca-1,3-diyne (27c): Tetradeca-6,8-diyne (**1c**, 476 mg, 2.5 mmol) was used to obtain 1,3-tetradecadiyne (**3c**) which was reacted with 1-iodo-4-nitrobenzene **11** (498 mg, 2 mmol) (Procedure B). Chromatography on silica gel (hexanes/CH_2Cl_2, 4:1) afforded the diyne **27c** (480 mg, 77 %) as an oil. R_f = 0.43 (hexanes/CH_2Cl_2, 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, J = 7 Hz, 3 H), 1.30–1.43 (m, 14 H), 1.60 (quint., J = 7 Hz, 2 H), 2.37 (t, J = 7 Hz, 2 H), 7.34 (d, J = 8 Hz, 2 H), 7.46 (d, J = 8 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 20.0, 23.1, 28.4, 28.6, 29.3, 29.5, 29.7, 29.9, 30.0, 32.3, 65.4, 73.9, 76.1, 86.0, 121.6, 123.6, 132.1, 134.2 ppm. IR (CCl_4): $\tilde{\nu}$ = 3120, 2230, 1585, 1475, 1450, 1260, 850 cm^{-1}. MS (EI): *m*/*z* (%) = 311 (25) [M$^+$], 207 (19), 283 (24), 269 (54), 255 (29), 241 (37), 227 (53), 213 (51), 199 (100), 123 (77). $C_{20}H_{25}NO_2$ (311.4): calcd. C 77.13, H 8.09, N 4.50; found C 77.05, H 8.22, N 4.37.

2-(Deca-1,3-diynyl)-4-nitro-1-naphthylamine (28a): Deca-4,6-diyne (**1a**, 335 mg, 2.5 mmol) was used to obtain 1,3-decadiyne (**3a**) which was reacted with 2-iodo-4-nitro-1-naphthylamine (**12**, 628 mg, 2 mmol) (Procedure A). Chromatography on silica gel (hexanes/CH_2Cl_2, 2:1) afforded the amine **28a** (563 mg, 88 %) as a solid, m. p. 134–136 °C. R_f = 0.56 (hexane/CH_2Cl_2, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, J = 7 Hz, 3 H), 1.22–1.38 (m, 6 H), 1.57 (quint., J = 7 Hz, 2 H), 2.47 (t, J 7 Hz, 2 H), 5.86 (s, 2 H, NH_2), 7.62 (t, J = 8 Hz, 1 H), 7.77 (t, J = 8 Hz, 1 H), 7.89 (d, J = 8 Hz, 1 H), 8.39 (s, 1 H), 8.89 (d, J = 8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 20.1, 23.1, 29.3, 29.5, 32.2, 66.1, 70.0, 81.3, 87.9, 116.9, 121.3, 122.2, 124.8, 126.9, 127.4, 130.1, 130.9, 136.1, 153.1. IR (CCl_4): $\tilde{\nu}$ = 3535, 3480, 3425, 2290, 2260, 2150, 1630, 1370. MS (EI): *m*/*z* (%) = 320 (28) [M$^+$], 303 (10), 188 (14), 97 (100). $C_{20}H_{20}N_2O_2$ (320.4): calcd. C 74.98, H 6.29, N 8.74; found C 74.72, H 6.33, N 8.69.

2-(Dodeca-1,3-diynyl)-4-nitro-1-naphthylamine (28b): Dodeca-5,7-diyne (**1b**, 405 mg, 2.5 mmol) was used to obtain 1,3-dodecadiyne (**3b**) which was reacted with 2-iodo-4-nitro-1-naphthylamine (**12**, 628 mg, 2 mmol) (Procedure A). Chromatography on silica gel (hexanes/CH_2Cl_2, 2:1) afforded the amine **28b** (640 mg, 92 %) as a solid, m. p. 112–114 °C. R_f = 0.59 (hexanes/CH_2Cl_2, 1:1). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 0.92 (t, J = 7 Hz, 3 H), 1.21–1.46 (m, 10 H), 1.63 (quint., J = 7 Hz, 2 H), 2.45 (t, J = 7 Hz, 2 H), 5.90 (s, 2 H, NH_2) 7.61(t, J = 8 Hz, 1 H), 7.76 (t, J = 8 Hz, 1 H), 7.91 (d, J = 8 Hz, 1 H), 8.42 (s, 1 H), 8.83 (d, J = 8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 14.8, 19.7, 22.9, 28.5, 29.2, 29.3, 29.4, 32.1, 66.4, 71.7, 87.8, 96.5, 113.0, 121.6, 124.4, 124.7, 127.0, 127.8, 131.9, 132.9, 142.8, 155.8 ppm. IR (CCl_4): $\tilde{\nu}$ = 3540, 3430, 2995, 2895, 2300, 2150, 1640, 1475, 1375, 710 cm^{-1}. MS (EI): *m*/*z* (%) = 348 (5) [M$^+$], 314 (7), 168 (8), 97 (100). $C_{22}H_{24}N_2O_2$ (348.4): calcd. C 75.84, H 6.94, N 8.04; found C 75.65, H 7.16, N 7.91.

1-(2,4,5-Trimethylphenyl)dodeca-1,3-diyne (29b): Dodeca-5,7-diyne (**1b**, 405 mg, 2.5 mmol) was used to obtain a 1,3-dodecadiyne (**3b**) which was reacted with 1-iodo-2,4,5-trimethylbenzene (**13**, 492 mg, 2 mmol) (Procedure B). Chromatography on silica gel (hexane) afforded the diyne **29b** as an oil (555 mg, 99 %), R_f = 0.83 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, J = 7 Hz, 3 H), 1.22–1.51 (m, 10 H), 1.60 (quint., J = 7 Hz, 2 H), 2.20 (s, 3 H), 2.24 (s, 3 H), 2.39 (s, 3 H), 2.38 (t, J = 7 Hz, 2 H), 6.97 (s, 1 H), 7.24 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 19.4, 20.06, 20.09, 20.11, 20.4, 23.1, 28.7, 29.3, 29.5, 32.2, 65.7, 74.5, 77.4, 85.2, 119.4, 131.3, 134.2, 134.3, 138.2, 139.3 ppm. IR (CCl_4): $\tilde{\nu}$ = 3070, 2240, 1690, 1590, 1470, 1430, 1400, 1255, 900 cm^{-1}. MS (EI): *m*/*z* (%) = 281 (24) [M + 1], 280 (100) [M$^+$], 223 (50), 209 (31), 195 (31), 183 (72), 179 (41), 165 (98), 152 (31), 133(34), 91 (20), 67 (28), 55 (21). $C_{21}H_{28}$ (280.5): calcd. C 89.93, H 10.06; found C 89.49, H 10.43.

1-(3,4-Dimethoxyphenyl)dodeca-1,3-diyne (30b): Dodeca-5,7-diyne (**1b**, 405 mg, 2.5 mmol) was used to obtain 1,3-dodecadiyne (**3b**)

which was reacted with 4-iodo-1,2-dimethoxybenzene (**14**) (528 mg, 2 mmol) (Procedure B). Chromatography on silica gel (hexanes/CH_2Cl_2, 2:1) afforded the diyne **30b** (584 mg, 98 %) as an oil. R_f = 0.45 (hexanes/CH_2Cl_2, 2:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, J = 7 Hz, 3 H), 1.25–1.49 (m, 10 H), 1.57 (quint., J = 7 Hz, 2 H), 2.36 (t, J = 7 Hz, 2 H), 3.82 (s, 3 H), 3.86 (s, 3 H), 6.42 (s, 1 H), 6.45 (d, J = 8 Hz, 1 H), 7.37 (d, J = 8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 20.1, 23.1, 28.7, 29.3, 29.5, 29.6, 32.2, 55.8, 56.2, 65.8, 71.7, 77.3, 85.2, 98.7, 104.2, 105.4, 135.7, 162.0, 163.1 ppm. IR (CCl_4): $\tilde{\nu}$ = 3075, 2955, 2875, 2250, 1680, 1585, 1475, 1420, 1400, 1265, 1110, 890 cm^{-1}. MS (EI): *m*/*z* (%) = 298 (22) [M$^+$], 255 (32), 213 (15), 186 (100), 138 (24), 91 (32). $C_{20}H_{26}O_2$ (298.5): calcd. C 80.50, H 8.78; found C 80.48, H 8.77.

2-(Dodeca-1,3-diynyl)benzaldehyde (31b): Dodeca-5,7-diyne (**1b**, 405 mg, 2.5 mmol) was used to obtain 1,3-dodecadiyne (**3b**) which was reacted with 2-iodobenzaldehyde (**15**, 464 mg, 2 mmol) (Procedure A). Chromatography on silica gel (hexanes/CH_2Cl_2, 2:1) afforded the diyne **31b** (335 mg, 63 %). Using Procedure B, the same product **31b** was obtained in 71 % isolated yield (378 mg, 1.42 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, J = 7 Hz, 3 H), 1.27–1.66 (m, 12 H), 2.40 (t, J = 7 Hz, 2 H), 7.46 (t, J = 7 Hz, 1 H), 7.52–7.62 (m, 2 H), 7.92 (d, J = 8 Hz, 1 H), 10.50 (app. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 20.1, 23.0, 28.5, 29.3, 29.4, 29.5, 32.2, 65.1, 70.4, 81.7, 87.9, 126.2, 127.7, 129.4, 134.0, 134.7, 137.8, 191.5 ppm. IR (CCl_4): $\tilde{\nu}$ = 3070, 2950, 2930, 2850, 2230, 1690, 1590, 1470, 1430, 1400, 1255, 900 cm^{-1}. MS (EI): *m*/*z* (%) = 266 (17) [M$^+$], 237 (9), 223 (100), 209 (40), 200 (25), 181 (73), 161 (39), 141 (22), 133 (19), 105 (41), 91 (38). $C_{19}H_{22}O$ (266.4): calcd. C 85.67, H 8.32; found C 85.61, H 8.40.

1,2,4,5-Tetrakis(dodeca-1,3-diynyl)benzene (32b): Dodeca-5,7-diyne (**1b**, 1.62 g, 10 mmol) was used to obtain 1,3-dodecadiyne (**3b**) which was reacted with 1,2,4,5-tetraiodobenzene (**16**, 1.163 g, 2 mmol) by Procedure A. Chromatography on silica gel (hexane) afforded the *tetrayne* **32b** (1,337 g, 93 %) as a solid, m. p. 45–46 °C. R_f = 0.5 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, J = 6 Hz, 12 H), 1.20–1.49 (m, 40 H), 1.60 (quint., J = 7 Hz, 8 H), 2.39 (t, J = 7 Hz, 8 H), 7.51 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 20.2, 23.1, 28.6, 29.3, 29.4, 29.5, 32.2, 65.5, 71.9, 81.3, 88.4 125.8, 137.8 ppm. IR (CCl_4): $\tilde{\nu}$ = 2950, 2850, 2260, 1475, 1455, 900, 710 cm^{-1}. $C_{54}H_{70}$ (719.1): calcd. C 90.19, H 9.81; found C 90.09, H 9.82.

1-(2-Nitrophenyl)dodeca-1,3-diyne (33b): Dodeca-5,7-diyne (**1b**, 405 mg, 2.5 mmol) was used to obtain 1,3-dodecadiyne (**3b**) which was reacted with 1-iodo-2-nitrobenzene (**17**, 498 mg, 2 mmol) (Procedure A). Chromatography on silica gel (hexanes/CH_2Cl_2, 4:1) afforded the diyne **33b** (453 mg, 80 %) as a solid, m. p. 14–16 °C. R_f = 0.5 (hexanes/CH_2Cl_2, 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, J = 6 Hz, 3 H), 1.18–1.47 (m, 10 H), 1.58 (quint., J = 7 Hz, 2 H), 2.39 (t, J = 7 Hz, 2 H), 7.48 (t, J = 7 Hz, 1 H), 7.58 (t, J = 7 Hz, 1 H), 7.67 (d, J = 7 Hz, 1 H), 8.06 (d, J = 7 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 20.1, 23.1, 28.5, 29.3, 29.4, 29.5, 32.2, 65.4, 69.7, 82.7, 89.1, 118.4, 125.2, 129.4, 133.3, 136.3, 150.6 ppm. IR (CCl_4): $\tilde{\nu}$ = 2950, 2850, 2235, 1600, 1560, 1525 cm^{-1}. MS (EI): *m*/*z* (%) = 283 (5) [M$^+$], 238 (10), 223 (26), 210 (40), 196 (40), 172 (33), 160 (100), 148 (30), 140 (26), 132 (36), 115 (40), 104 (43), 95 (30), 91 (26). $C_{18}H_{21}NO_2$ (283.4): calcd. C 76.30, H 7.47, N 4.94; found C 76.28, H 7.63, N 4.82.

2-(Hexadeca-1,3-diynyl)benzonitrile (34d): Hexadeca-7,9-diyne (**1c**, 654 mg, 3 mmol) was used to obtain 1,3-hexadecadiyne (**3d**) which was reacted with 2-iodobenzonitrile (**18**, 458 mg, 2 mmol) (Procedure A). Chromatography on silica gel (hexanes/CH_2Cl_2, 2:1) afforded the diyne **34d** (283 mg, 90 %) as a light yellow oil which slowly crystallised, m. p. 34.5 °C. R_f = 0.21 (hexanes/CH_2Cl_2, 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, J = 7 Hz, 3 H), 1.23–1.64 (m, 20 H), 2.38 (t, J = 7 Hz, 2 H), 7.43 (t, J = 7 Hz, 1 H), 7.51–7.59 (m, 2 H), 7.28 (d, J 7 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8, 19.3, 27.7, 28.6, 28.7, 29.0, 29.1, 29.27, 29.29, 29.31, 29.32, 31.6, 65.1, 70.6, 81.2, 88.6, 116.3, 117.6, 126.6, 129.1, 132.7, 133.2, 133.8 ppm. IR (CCl_4): $\tilde{\nu}$ = 3075, 2930, 2855, 2240 (strong; alkyne and CN), 1470, 1460 cm^{-1}. MS (EI): *m*/*z* (%) = 319 (6) [M$^+$], 248 (10), 234 (19), 220 (35), 207 (64), 206 (100), 193 (35), 192 (35), 179 (52), 167 (40), 164 (43), 153 (27). $C_{23}H_{29}N$ (319.5): calcd. C 86.46, H 9.15, N 4.38; found C 86.62, H 9.22, N 4.15.

1-(4-Bromophenyl)dodeca-1,3-diyne (35b): Dodeca-5,7-diyne **1b** (405 mg, 2.5 mmol) was used to obtain 1,3-dodecadiyne (**3b**) which was reacted with 1-bromo-4-iodobenzene (**19**, 566 mg, 2 mmol) (Procedure B). Chromatography on silica gel (hexane) afforded the diyne **35b** (533 mg, 84 %) as an oil. R_f = 0.8 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, J = 6 Hz, 3 H), 1.23–1.61 (m, 12 H), 2.37 (t, J = 7 Hz, 2 H), 7.34 (d, J = 5 Hz, 2 H), 7.45 (d, J = 5 Hz 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 20.0, 23.1, 28.6, 29.3, 29.5, 29.6, 32.2, 65.3, 73.9, 76.0, 86.1, 121.5, 123.6, 132.1, 134.3 ppm. IR (CCl_4): $\tilde{\nu}$ = 2955, 2935, 2240, 1475, 1100, 1055 cm^{-1}. MS (EI): *m*/*z* (%) = 318 (13) [M$^+$ (^{81}Br)], 316 (10) [M$^+$ (^{79}Br)], 290 (21), 288 (22), 261 (33), 259 (31), 219 (57), 217 (49), 206 (26), 165 (100), 152 (55), 137 (32), 125 (31), 84 (65). $C_{18}H_{21}Br$ (317.3): calcd. C 68.14, H 6.67; found C 68.05, H 6.74.

1-(4-Bromophenyl)tetradeca-1,3-diyne (35c): Tetradeca-6,8-diyne (**1c**, 476 mg, 2.5 mmol) was used to obtain 1,3-dodecadiyne (**3c**) which was reacted with 1-bromo-4-iodobenzene (**19**, 566 mg, 2 mmol) (Procedure B). Chromatography on silica gel (hexane) afforded the diyne **35c** (635 mg, 92 %). R_f = 0.8 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, J = 6 Hz, 3 H), 1.29–1.54 (m, 14 H), 1.60 (quint., J = 7 Hz, 2 H), 2.37 (t, J = 7 Hz, 2 H), 7.34 (d, J = 5 Hz, 2 H), 7.46 (d, J = 5 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 20.0, 23.1, 28.6, 29.3, 29.5, 29.7, 29.9, 30.0, 32.3, 65.3, 73.9, 76.5, 86.1, 121.5, 123.6, 132.1, 134.3 ppm. IR (CCl_4): $\tilde{\nu}$ = 2955, 2935, 2250, 1470, 1130, 1075 cm^{-1}. MS (EI): *m*/*z* (%) = 346 (23) [M$^+$ (^{81}Br)], 344 (20) [M$^+$ (^{79}Br)], 316 (24), 302 (31), 288 (30), 274 (21), 260 (15), 232 (18), 156 (100), 137 (32), 125 (31), 84 (65). $C_{20}H_{25}Br$ (345.3): calcd. C 69.56, H 7.30; found C 69.55, H 7.28.

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