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Anionic Cycloaromatization of 1-Aryl-3-hexen-1,5-diynes Initiated by Methoxide Addition: Synthesis of Phenanthridinones, Benzo[*c*]phenanthridinones, and Biaryls

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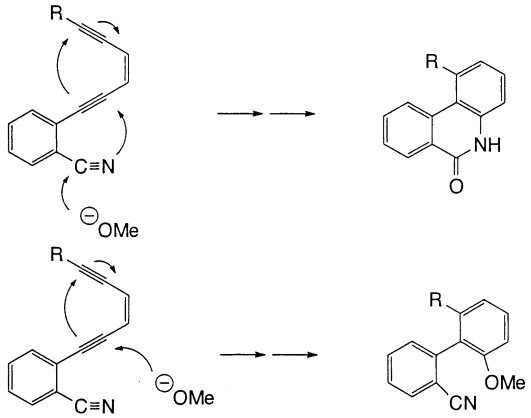
Treatment of 2-((*Z*)-6-substituted-3-hexene-1,5-diynyl)benzonitriles with sodium methoxide in refluxing methanol in the presence of a polar aprotic solvent, such as DMSO, HMPA, THF, or 18-crown-6, gave phenanthridinones in 21−77% yields. In these cases, addition of 10% DMSO into the reaction mixture gave the highest yield. On the other hand, methanolysis of 2-(2-(2-alkynylphenyl)ethynyl)benzonitriles under the same reaction conditions gave benzo[*c*]phenanthridinones in 31−57% yields. Methanolysis of (*Z*)-1-aryl-3-hexen-1,5-diynes in the presence of 2 equiv of tetrabutylammonium iodide gave biaryls in 14−64% yields. It is found that the reactions with aryl groups bearing electron-withdrawing groups proceeded at greater rates and gave better yields.

Introduction

Recently, we reported that treatment of 2-(6-substituted-3-hexen-1,5-diynyl)benzonitriles with sodium methoxide in methanol at reflux gives phenanthridinones and substituted biphenyl derivatives.[1] Although the chemical yields are low, this reaction constitutes a novel cycloaromatization of enediynes[2] and a new synthetic approach to phenanthridinones and biphenyls. Since phenanthridinones,[3] biphenyls,[4] and structurally related compounds are of current interest in the pharmaceutical area and for the preparation of new materials, methods for the selective preparation of these compounds have considerable synthetic value. A proposed mechanism for the formation of phenanthridinones is methoxide addition to the cyano group, followed by an anionic cascade cycloaromatization. In contrast, methoxide addition to C2 of the acetylenic moiety and the same type of cycloaromatization will give biphenyls (Scheme 1). We believe that the low yields in these reactions are due to poor regioselectivity in the nucleophilic addition of methoxide to the conjugated system. Thus, we anticipated that introducing a polar aprotic solvent into the reaction mixture would increase the nucleophilicity and the hardness of the nucleophile and therefore promote regioselectivity in the nucleophilic addition step to increase the chemical yield.

SCHEME 1



Results and Discussion

Our first attempt was carried out by treatment of 2-(3-nonen-1,5-diynyl)benzonitrile (**1a**) with 2 equiv of sodium methoxide in methanol containing 10% DMSO. The reaction mixture was stirred at 60 °C for 7 h, which gave phenanthridinone **2a** in 50% yield after chromatography. The addition of 30% DMSO gave a similar result. Other polar aprotic solvents were also examined, and the results are summarized in Table 1. The addition of 10% HMPA gave phenanthridine **2a** in 38% yield accompanied by ether **3a** in 22% yield. In the presence of 10% THF poor regioselectivity was observed; phenanthridinone **2a** was obtained in 30% yield, and biphenyl **4a** was obtained in 13% yield. A 2 equiv amount of 18-crown-6 were also employed in this study, and the reaction gave **2a** in 43% yield and **4a** in 6% yield. In the presence of 10% DMF no product was obtained.

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(1) Wu, M.-J.; Lin, C.-F.; Chen, S.-H. *Org. Lett*. **1999**, *1*, 767.

(2) For examples for nonradical cycloaromatization of enediynes, see: (a) Magnus, P.; Eisenbeis, S. A.; Rose, W. C.; Zein, N.; Solomon, W. *J. Am. Chem. Soc*. **1993**, *115*, 12627. (b) Sugiyama, H.; Yamashita, K.; Nishi, M.; Saito, I. *Tetrahedron Lett*. **1992**, *33*, 515.

(3) Lewis, J. R. *Nat. Prod. Rep*. **1997**, *14*, 303.

(4) (a) Bringmann, G.; Water, R.; Weirich, R. *Angew. Chem., Int. Ed. Engl*. **1990**, *29*, 977. (b) Acton, U.; Goltner, C.; Mullen, K. *Chem. Ber*. **1992**, *125*, 2325. (c) Rosin, C.; Franzin, L.; Rafaeli, A.; Salvadori, P. *Synthesis* **1992**, *6*, 503. (d) Tamao, K.; Yamamoto, H.; Matsumoto, H.; Miyake, N.; Hayashi, Y.; Kumada, M. *Tetrahedron Lett*. **1977**, *47*, 1389. (e) Miyashita, A.; Karino, H.; Shimamura, J. I.; Chiba, T.; Nagano, K.; Nohira, H.; Takaya, H. *Chem. Lett*. **1989**, 1849.

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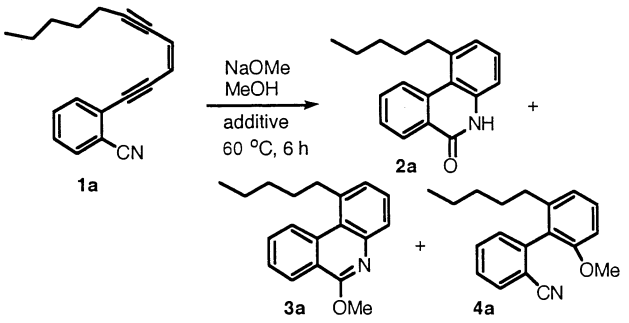
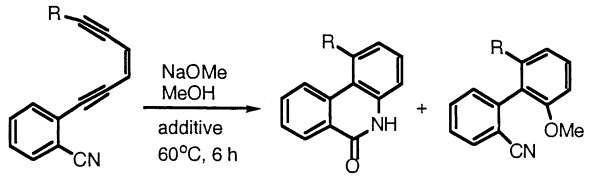
TABLE 1. Additive Effects on Methanolysis of 1a



	yields of products (%)[a]		
additive	**2a**	**3a**	**4a**
10% DMSO	50		
10% THF	30		13
10% HMPA	38	22	
18-crown-6	43		6
10% DMF	no reacn		

[a] Yields refer to isolated yields.

TABLE 2. Methanolysis of 1b−d



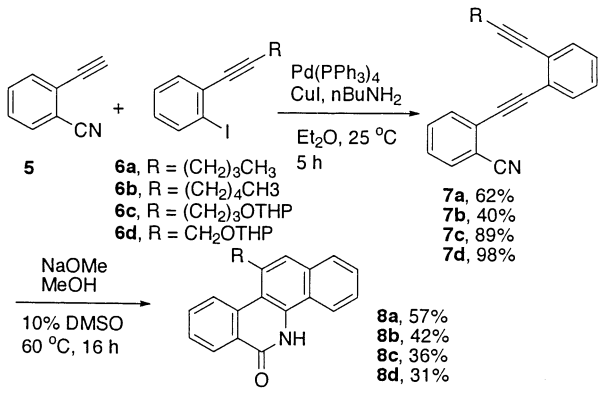
compds	additive	products (yields, %)[a]
1b, R = $(CH_2)_3CH_3$	10% DMSO	**2b** (77)
1b	10% THF	**2b** (60), **4b** (5)
1b	18-crown-6	**2b** (65)
1c, R = $(CH_2)_3OTHP$	10% DMSO	**2c** (50)
1c	10% THF	**2c** (43)
1c	18-crown-6	**2c** (56)
1d, R = CH_2OTHP	10% DMSO	**2d** (21)
1d	18-crown-6	**2d** (17)

[a] Yields refer to isolated yields.

Methanolysis of 2-(6-substituted 3(*Z*)-hexen-1,5-diynyl)benzonitriles **1b−d** was also carried out and gave the results summarized in Table 2. Cyclization of **1b,c** was carried out under three different reaction conditions, in the presence of 10% DMSO, 10% THF, or 2 equiv of 18-crown-6. All of these reactions gave phenanthridinones **2b,c** in good chemical yields. However, **1d** gave a low yield of **2d**, possibly due to the reactivity of the propargylic alcohol moiety under such strongly basic conditions.

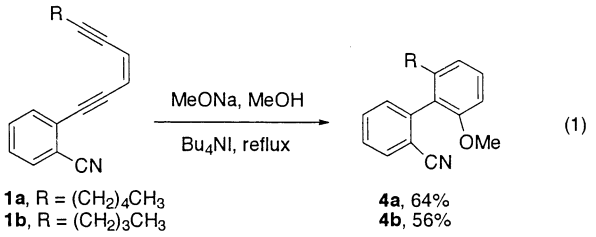
Benzo[*c*]phenanthridinones are also pharmaceutically interesting molecules, and much attention have been given to the development of new synthetic methods.[5] We have successfully applied the anionic cycloaromatization method to prepare four benzo[*c*]phenanthridinones. Compounds **7a−d** were obtained in 40−98% yields by the palladium-catalyzed coupling reaction of 2-ethynylbenzonitrile (**5**) with 2-alkynyliodobenzenes **6a−d** using the reported procedure.[6] Methanolysis of **7a−d** with 2 equiv

SCHEME 2



of sodium methoxide in methanol containing 10% DMSO at 60 °C for 16 h gave benzo[*c*]phenanthridinones **8a−d** in 31−57% yields (Scheme 2),

When 2 equiv of tetrabutylammonium iodide was added to the reaction of **1a** with sodium methoxide in methanol at reflux, biphenyl **4a** was obtained in 64% yield. A similar result obtained in the methanolysis of **1b** under the same reaction conditions gave biphenyl **4b** in 56% yield (eq 1).

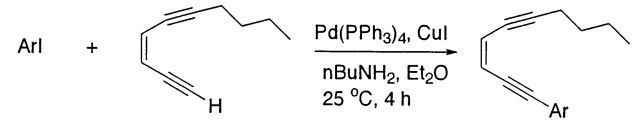


Since we could select different reaction conditions for the anionic cycloaromatization of 2-(6-substituted-3(*Z*)-hexen-1,5-diynyl)benzonitriles to prepare phenanthridinones or biphenyls in good yield, extension of this strategy to the cycloaromatization of other enediynes were carried out. Thus, a series of (*Z*)-1-aryl-3-decen-1,5-diynes **1e−m** was synthesized by the palladium-catalyzed coupling reaction of aryl iodides **9e−m** with (*Z*)-3-decen-1,5-diyne (**10**) (Scheme 3). The yields are from 31 to 99%. Various reaction conditions were employed for the anionic cycloaromatization of (*Z*)-1-(4-(trifluoromethyl)phenyl)-3-decen-1,5-diyne (**1e**) to give biphenyl **4e** (Table 3). The optimal reaction conditions were found to be the following: treatment of compound **1e** with 2 equiv of tetrabutylammonium iodide and 2 atom equiv of sodium metal in methanol at reflux for 16 h gave compound **4e** in 43% yield. Under these reaction conditions, methanolysis of **1f−m** gave biphenyls **4f−m** in 14−56% yields (Table 4). It was found that aryl groups bearing an electron-withdrawing group reacted faster and gave better yields (entries 1−3) than the examples in which the aryl group is unsubstituet or is thienyl. Pyridinyl- and pyrazinyl-substituted enediynes **1k,l** cyclized faster and give better yields than a thienyl-substituted enediyne (**1m**). When an aryl group substituted with a nitro, ester, or keto group, e.g. **1n−p**, was

(5) (a) Mackay, S. P.; Meth-Cohn, O.; Waich, R. D. *Advances in Hetreocyclic Chemistry*; Katritzky, A. R., Ed.; Academic Press: San Diego, CA, 1997; Vol. 67, pp 345−389. (b) Janin, Y. L.; Bisagni, E. *Tetrahedron* **1993**, 10305.

(6) (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467. (b) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627.

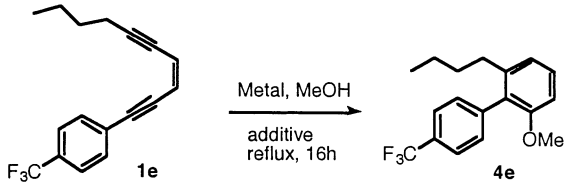
SCHEME 3



5e, Ar = *p*-$CF_3C_6H_4$
5f, Ar = *o*-$CF_3C_6H_4$
5g, Ar = *m*-$CF_3C_6H_4$
5h, Ar = *p*-CNC_6H_4
5i, Ar = *p*-ClC_6H_4
5j, Ar = C_6H_5
5k, Ar = pyridinyl
5l, Ar = thienyl
5m, Ar = pyrazinyl
5n, Ar = *p*-$NO_2C_6H_4$
5o, Ar = *p*-$CH_3CO_2C_6H_4$
5p, Ar = *p*-$CH_3COC_6H_4$

1e, 46%
1f, 33%
1g, 46%
1h, 46%
1i, 31%
1j, 67%
1k, 84%
1l, 53%
1m, 99%
1n, 59%
1o, 31%
1p, 96%

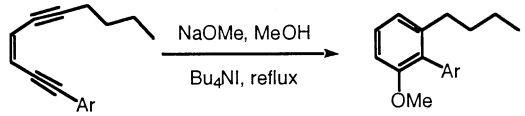
TABLE 3. Methanolysis of 1e under Various Conditions



metal[a]	additive	yield (%)	metal[a]	additive	yield (%)
Na	none	20	Na	10% DMSO	35
K	none	32	Na	10% THF	21
Li	none	no reacn	Na	18-crown-6 (2 equiv)	30
Na	Bu_4NI (2 equiv)	43	K	Bu_4NI (2 equiv)	43

[a] A 2 atom equiv amount of metal was used. [b] Isolated yields.

TABLE 4. Anionic Cycloaromatization of 1-Aryl-3-decen-1,5-diynes

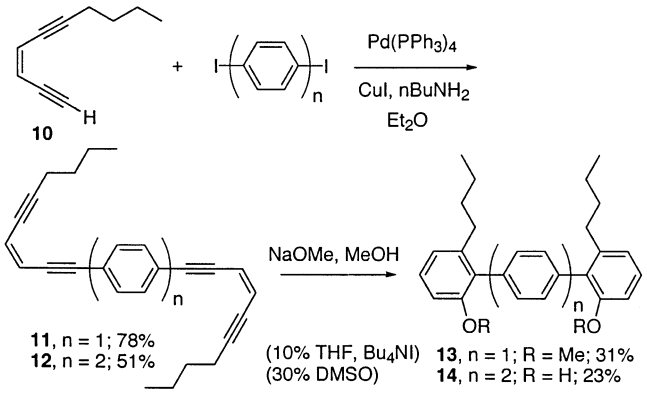


Compds	time (h)	products (yields, %)	compds	time (h)	products (yields, %)
1f	16	**4f** (34)	**1j**	24	**4j** (14)
1g	16	**4g** (37)	**1k**	16	**4k** (34)
1h	16	**4h** (56)	**1l**	16	**4l** (20)
1i	16	**4i** (31)	**1m**	16	**4m** (34)

subjected to methanolysis, a complex mixture of products was obtained from which none of the desired biphenyls could be isolated. All of the above results agree well with the proposed anionic cycloaromatization mechanism.

We have also extended this methodology to the cyclization of compounds **11** and **12** to give oligobenzene derivatives. Compounds **11** and **12** were prepared in 78% and 51% yields by palladium-catalyzed coupling reaction of (*Z*)-3-decen-1,5-diyne (**10**) with 1,4-diiodobenzene and 4,4′-diiodobiphenyl, respectively. Reaction of **11** with sodium methoxide in methanol in the presence of 10% THF and 2.5 equiv of tetrabutylammonium iodide gave **13** in 31% yield. Due to the poor solubility of **12** in methanol, methanolysis of **12** was carried out in the presence of 30% DMSO to give **14** in 23% yield (Scheme 4).

SCHEME 4



In conclusion, we have developed a novel anionic cycloaromatization of enediynes and related molecules. In contrast to published methods which require multisteps synthesis,[5,7] this one-step cyclization reaction provides an efficient method for the synthesis of phenanthridinones, benzo[*c*]phenanthridinones, and biaryls. This method has also been extended to the synthesis of oligobenzene derivatives.

Experimental Section

General Procedure for Methanolysis of 1a−d and 7a−b (Method A). To a solution of 2-(6-substituted-3-henxen-1,5-diynyl)benzonitrile (1.1 mmol) in 20 mL of methanol containing 2 mL of polar aprotic sovent (or 2 equiv of 18-crown-6) was added freshly cut sodium metal (2 mmol atom). The resulting solution was heated to 60 °C and stirred at this temperature for 6 h. After cooling of the solution to room temperature, the methanol was removed in vacuo. Water was added to the residue, and it was extracted with EtOAc. The combined organic extracts were dried over anhydrous $MgSO_4$. After filtration and removal of solvent, the residue was purified by flash chromatography on silica gel to give the products.

General Procedure for the Coupling Reaction of 2-Alkynyliodobenzene (6a−d) with 2-Ethynylbenzonitrile (Method B). A degassed solution of 2-alkynyliodobenzene (12 mmol) in dry ether (30 mL) containing $Pd(PPh_3)_4$ (0.8 mmol) and CuI (3.2 mmol) was added to a solution of 2-ethynylbenzonitrile (24 mmol) containing *n*-butylamine (34 mmol). The resulting solution was stirred for 6 h at 25 °C, quenched with saturated aqueous NH_4Cl and Na_2CO_3 solutions, and extracted with EtOAc. The organic layer was separated and dried over $MgSO_4$. After filtration, the solvent was evaporated in vacuo. The residue was purified by flash chromatography to give the products.

2-(3(*Z*)-Undecen-1,5-diynyl)benzonitrile (1a): obtained as an oil according to method B; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.67 (dd, 1H, J = 7.2, 1.1 Hz), 7.57−7.53 (m, 2H), 7.49−7.36 (m, 1H), 6.06−5.99 (m, 2H), 2.47 (td, 2H, J = 6.9, 1.5 Hz), 1.64−1.25 (m, 6H), 0.85 (t, 3H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 132.7, 132.6, 132.2, 128.3, 127.1, 122.7, 117.3, 116.9, 115.0, 101.3, 93.3, 91.4, 78.1, 31.0, 28.2, 22.2, 19.9, 13.9; MS (EI) [*m*/*z* (relative intensity)] 247 (M^+, 14), 217 (49), 204 (100), 190 (68); HRMS calcd for $C_{18}H_{17}N$ 247.1362, found 247.1357.

2-(3(*Z*)-Decen-1,5-diynyl)benzonitrile (1b): obtained as an oil according to method B; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.66 (dd, 1H, J = 7.8, 1.0 Hz), 7.59−7.49 (m, 2H), 7.43−7.35

(7) For the transition metal-catalyzed coupling reaction to prepare biaryls, see: (a) Hong, R.; Hoen, R.; Zhang, J.; Lin, G.-q. *Synlett* **2001**, *10*, 1527. (b) Zhang, N.; Thomas, L.; Wu, B. *J. Org. Chem*. **2001**, *66*, 1500 and references therein.

(m, 1H), 6.03−5.98 (m, 2H), 2.47 (td, 2H, J = 6.8, 1.5 Hz), 1.61−1.39 (m, 4H), 0.89 (t, 3H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 132.7, 132.6, 132.2, 128.3, 127.1, 122.7, 117.3, 116.9, 115.0, 101.2, 93.3, 91.4, 78.1, 30.6, 21.9, 19.6, 13.6; MS (EI) [m/z (relative intensity)] 233 (M^+, 22), 218 (55), 204 (100), 190 (73), 164 (36); HRMS calcd for $C_{17}H_{15}N$ 233.1205, found 233.1210.

2-(9-(Tetrahydropyranyloxy)-3(*Z*)-nonen-1,5-diynyl)-benzonitrile (1c): obtained as an oil according to method B; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67−7.63 (m, 2H), 7.58−7.50 (m, 2H), 7.43−7.35 (m, 2H), 6.03 (d, 1H, J = 10.9 Hz), 5.96 (dt, 1H, J = 10.9, 1.7 Hz), 4.58 (t, 1H, J = 3.8 Hz), 3.90−3.76 (m, 2H), 3.57−3.46 (m, 2H), 2.60 (td, 2H, J = 7.3, 1.7 Hz), 1.95−1.48 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 132.8, 132.7, 132.6, 132.4, 132.2, 128.4, 122.5, 117.1, 115.0, 100.4, 98.7, 93.2, 91.7, 78.3, 66.0, 62.1, 30.6, 28.7, 25.4, 19.5, 16.8; MS (EI) [m/z (relative intensity)] 319 (M^+, 11), 235 (68), 216 (100), 203 (38), 190 (71); HRMS calcd for $C_{21}H_{21}NO_2$ 319.1573, found 319.1576.

2-(7-(Tetrahydropyranyloxy)-3(*Z*)-hepten-1,5-diynyl)-benzonitrile (1d): obtained as an oil according to method B; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.59−7.66 (m, 2H), 7.54 (td, 1H, J = 7.5, 1.3 Hz), 7.41 (td, 1H, J = 7.5, 1.3 Hz), 6.10 (d, 1H, J = 10.8 Hz), 6.02 (td, 1H, J = 10.8, 2.0 Hz), 4.87 (t, 1H, J = 3.5 Hz), 4.56 (dd, 1H, J = 6.3, 1.9 Hz), 4.49 (dd, 1H, J = 6.3, 1.9 Hz), 3.82−3.88 (m, 1H), 3.50−3.55 (m, 1H), 1.50−1.83 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 132.8, 132.7, 132.2, 128.6, 128.5, 121.7, 121.3, 118.6, 96.8, 94.8, 92.7, 92.5, 82.9, 61.9, 55.0, 51.0, 30.2, 25.3, 18.9; MS (EI) [m/z (relative intensity)] 291 (M^+, 1.8), 190 (100), 85 (45); HRMS calcd for $C_{19}H_{17}NO_2$ 291.1260, found 291.1255.

General Procedure for Coupling of Aryl Iodides with (*Z*)-3-Decen-1,5-diyne (Method C). A degassed solution of (*Z*)-3-hexen-1,5-diyne (2.3 mmol) in dry ether (5 mL) containing $Pd(PPh_3)_4$ (0.1 mmol) and CuI (0.6 mmol) was added to a solution of aryl iodide (4.5 mmol) containing *n*-butylamine (5 mmol). The resulting solution was stirred for 6 h at 25 °C, quenched with saturated aqueous NH_4Cl and Na_2CO_3 solutions, and extracted with EtOAc. The organic layer was separated and dried over $MgSO_4$. After filtration, the solvent was evaporated in vacuo. The residue was purified by flash chromatography to give the products.

4-(3(*Z*)-Decen-1,5-diynyl)(trifluoromethyl)benzene (1e): obtained in 46% yield as an oil according to method C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.57 (s, 4H), 5.95 (d, 2H, J = 1.6 Hz), 2.46 (t, 2H, J = 6.8 Hz), 1.58−1.49 (m, 4H), 0.90 (t, 3H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) 146.9, 134.6, 131.8, 127.0, 125.3, 121.6, 117.4, 112.1, 100.2, 89.4, 78.3, 30.6, 21.9, 19.5, 13.5; MS (EI) [m/z (relative intensity)] 276 (M^+, 100), 233 (59), 207 (31), 192 (24), 165 (47), 49 (43); HRMS calcd for $C_{17}H_{15}F_3$, M_r = 276.1129, found 276.1174.

2-(3(*Z*)-Decen-1,5-diynyl)(trifluoromethyl)benzene (1f): obtained in 33% yield as an oil according to method C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.64 (td, 2H, J = 7.8, 1.8 Hz), 7.39−7.37 (m, 2H), 6.02−5.87 (m, 2H), 2.45 (t, 2H, J = 7.0 Hz), 1.60−1.51 (m, 4H), 0.90 (t, 3H, J = 7.0 Hz); ^{13}CNMR ($CDCl_3$, 50 MHz) δ 146.3, 134.2, 131.2, 128.0, 125.8, 125.7, 121.6, 117.5, 112.1, 100.3, 92.5, 91.5, 78.0, 30.6, 21.9, 19.5, 13.5; MS (EI) [m/z (relative intensity)] 276 (M^+, 100), 233 (34), 232 (29), 221 (48), 214 (22), 183 (29), 165 (14); HRMS calcd for $C_{17}H_{15}F_3$, M_r = 276.1174, found 276.1174.

3-(3(*Z*)-Decen-1,5-diynyl)(trifluoromethyl)benzene (1g): obtained in 46% yield as an oil according to method C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.72 (s, 1H), 7.61 (d, 1H, J = 7.6 Hz), 7.55 (d, 1H, J = 8.0 Hz), 7.45 (t, 1H, J = 7.6 Hz), 5.97 (d, 1H, J = 10.8 Hz), 5.92 (d, 1H, J = 10.8 Hz), 2.46 (t, 2H, J = 6.8 Hz), 1.62−1.45 (m, 4H), 0.90 (t, 3H, J = 7.2 Hz); ^{13}CNMR ($CDCl_3$ 50 MHz) δ 146.9, 134.6, 128.8, 128.5, 124.8, 124.8, 124.2, 121.5, 117.4, 100.1, 94.2, 88.6, 78.3, 30.6, 21.8, 19.5, 13.4; MS (EI) [m/z (relative intensity)] 276 (M^+, 100), 261 (30), 246 (34), 233 (84), 207 (47), 183 (62), 178 (37), 165 (68); HRMS calcd for $C_{17}H_{15}F_3$, M_r = 276.1125, found 276.1174.

4-(3(*Z*)-Decen-1,5-diynyl)benzonitrile (1h): obtained in 46% yield as an oil according to method C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.61 (d, 2H, J = 6.4 Hz), 7.53 (d, 2H, J = 8.4 Hz), 5.95 (d, 2H, J = 1.6 Hz), 2.44 (t, 2H, J = 6.8 Hz), 1.59−1.44 (m, 4H), 0.9 (t, 3H, J = 7.2 Hz); ^{13}CNMR ($CDCl_3$, 50 MHz) δ 132.0, 131.9, 128.1, 122.2, 118.4, 117.1, 111.5, 100.6, 93.9, 91.3, 78.2, 30.5, 21.8, 19.4, 13.5; MS (EI) [m/z (relative intensity)] 233 (M^+, 51), 203 (51), 190 (100), 177 (35), 164 (46), 140 (28); HRMS calcd for $C_{17}H_{15}N$, M_r = 233.1206, found 233.1205.

4-(3(*Z*)-Decen-1,5-diynyl)benzochloride (1i): obtained in 31% yield as an oil according to method C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.36 (d, 2H, J = 8.8 Hz), 7.31 (d, 2H, J = 8.6 Hz), 5.97−5.84 (m, 2H), 2.45 (t, 2H, J = 6.8 Hz), 1.61−1.45 (m, 4H), 0.9 (t, 3H, J = 7.0 Hz); ^{13}CNMR ($CDCl_3$, 50 MHz) δ 134.4, 132.8, 128.6, 121.7, 120.7, 117.7, 99.7, 94.7, 88.1, 78.3, 30.7, 21.8, 19.5, 13.5; MS (EI) [m/z (relative intensity)] 242 (M^+, 100), 201 (16), 199 (40), 192 (78), 165 (63), 164 (45), 163 (52); HRMS calcd for $C_{16}H_{15}Cl$, M_r = 242.0859, found 242.0863.

(3*Z*)-Decen-1,5-diynylbenzene (1j): obtained in 67% yield as an oil according to method B; ^{1}HNMR($CDCl_3$, 200 MHz) δ 7.49−7.43 (m, 2H), 7.35−7.29 (m, 3H), 5.94 (d, 1H, J = 10.8 Hz), 5.87 (d, 1H, J = 10.8 Hz), 2.45 (t, 2H, J = 6.8 Hz), 1.63−1.43 (m, 4H), 0.9 (t, 3H, J = 7.0 Hz); ^{13}CNMR ($CDCl_3$, 50 MHz) δ 131.7 128.3, 128.2, 123.2, 120.3, 118.1, 99.4, 96.0, 87.2, 78.4, 30.7, 21.9, 19.5, 13.6; MS (EI) [m/z (relative intensity)] 208 (M^+, 67), 179 (26), 178 (63), 165 (100), 163 (28), 152 (27), 139 (39), 115 (28); HRMS calcd for $C_{16}H_{16}$, M_r = 208.1255, found 208.1252.

2-(3(*Z*)-Decen-1,5-diynyl)pyridine (1k): obtained in 84% yield as an oil according to method B; ^{1}HNMR($CDCl_3$, 200 MHz) δ 8.58 (dt, 1H, J = 5.0, 1.0 Hz), 7.63 (td, 1H, J = 7.6, 1.8 Hz), 7.42 (td, 1H, J = 7.6, 1.0 Hz), 7.23−7.16 (m, 2H), 5.99−5.93 (m, 2H), 2.43 (td, 2H, J = 7.0, 1.6 Hz), 1.92−1.43 (m, 4H), 0.87 (t, 3H, J = 7.0 Hz); ^{13}CNMR ($CDCl_3$, 50 MHz) δ 150.5, 143.3, 135.9, 127.2, 122.7, 122.1, 117.3, 100.3, 94.7, 86.8, 78.2, 30.6, 21.8, 19.5, 13.5; MS (EI) [m/z (relative intensity)] 209 (M^+, 19), 180 (100), 78 (18), 51 (18); HRMS calcd for $C_{15}H_{15}N$, M_r = 209.1209, found 209.1205.

2-(3(*Z*)-Decen-1,5-diynyl)thiophene (1l): obtained in 53% yield as an oil according to method B; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.29 (d, 1H, J = 5.2 Hz), 7.22 (d, 1H, J = 2.6 Hz), 7.00 (t, 1H, J = 5.2 Hz), 5.94 (d, 1H, J = 10.4 Hz), 5.86 (d, 1H, J = 10.8 Hz), 2.45 (d, 2H, J = 6.8 Hz), 1.63−1.47 (m, 4H), 0.92 (t, 3H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 132.1, 127.7, 127.2, 123.3, 120.1, 117.7, 99.8, 91.2, 89.1, 78.4, 30.6, 21.9, 19.5, 13.5; MS (EI) [m/z (relative intensity)] 214 (M^+, 100), 184 (41), 171 (80), 165 (53); HRMS calcd for $C_{14}H_{14}S$, M_r = 214.0811, found 214.0817.

2-(3(*Z*)-Decen-1,5-diynyl)pyrazine (1m): obtained in 99% yield as an oil according to method B; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.66 (d, 1H, J = 1.6 Hz), 8.55 (s, 1H), 8.45 (d, 1H, J = 2.4 Hz), 5.98 (m, 2H), 2.44 (t, 2H, J = 6.8 Hz), 1.58−1.43 (m, 4H), 0.88 (t, 3H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 147.8, 144.4, 142.6, 140.3, 123.5, 116.5, 101.3, 91.7, 90.8, 78.1, 30.5, 21.8, 19.5, 13.5; MS (EI) [m/z (relative intensity)] 210 (M^+, 39), 181 (100), 168 (14), 127 (17); HRMS calcd for $C_{14}H_{14}N_2$, M_r = 210.1154, found 210.1158.

4-(3(*Z*)-Decen-1,5-diynyl)benzonitride (1n): obtained in 59% yield as an oil according to method B; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.16 (d, 2H, J = 9.0 Hz), 7.60 (d, 2H, J = 9.0 Hz), 5.97 (s, 2H), 2.45 (t, 2H, J = 6.4 Hz), 1.61−1.45 (m, 4H), 0.9 (t, 3H, J = 7.0 Hz); ^{13}CNMR ($CDCl_3$, 50 MHz) δ 147.0, 132.1, 123.5, 122.6, 118.3, 117.0, 100.9, 93.6, 92.2, 78.2, 30.6, 21.8, 19.5, 13.5; MS (EI) [m/z (relative intensity)] 253 (M^+, 100), 238 (16), 210 (16), 192 (14), 165 (13), 163 (21); HRMS calcd for $C_{16}H_{15}NO_2$, M_r = 253.1105, found 253.1103.

2-(3(*Z*)-Decen-1,5-diynyl)benzoate (1o): obtained in 31% yield as an oil according to method B; ^{1}HNMR ($CDCl_3$, 200 MHz) δ 7.95 (d, 1H, J = 7.8 Hz), 7.57 (d, 1H, J = 7.4 Hz), 7.46−7.31 (m, 2H), 6.00 (d, 1H, J = 10.8 Hz), 5.91 (d, 1H, J = 10.8 Hz, 3.91 (s, 2H), 2.45 (t, 2H, J = 6.8 Hz), 1.62−1.42 (m, 4H), 0.87 (t, 3H, J = 7.0 Hz); ^{13}CNMR ($CDCl_3$, 50 MHz) δ 166.5,

134.3 131.6, 131.5, 130.3, 127.9, 123.7, 120.8, 118.1, 99.6, 94.6, 78.4, 52.0, 30.6, 21.9, 19.5, 13.5; MS (EI) [*m*/*z* (relative intensity)] 266 (M^+, 71), 237 (75), 224 (51), 223 (70), 209 (82), 191 (21), 181 (49), 176 (24); HRMS calcd for $C_{18}H_{18}O_2$, M_r = 266.1305, found 266.1307.

4-(3(*Z*)-Decen-1,5-diynyl)benzonone (1p): obtained in 96% yield as an oil according to method B; ^{1}HNMR ($CDCl_3$, 200 MHz) δ 7.92 (d, 2H, J = 8.4 Hz), 7.54 (d, 2H, J = 8.4 Hz), 5.99−5.90 (m, 2H), 2.60 (s, 3H), 2.45 (t, 2H, J = 7.2 Hz), 1.63−1.46 (m, 4H), 0.91 (t, 3H, J = 7.2 Hz); ^{13}CNMR ($CDCl_3$, 50 MHz) δ 197.2, 136.3, 131.7, 128.2, 128.1, 121.6, 117.6, 100.3, 95.0, 90.4, 78.4, 30.7, 26.6, 21.9, 19.5, 13.6; MS (EI) [*m*/*z* (relative intensity)] 250 (M^+, 100), 235 (37), 165 (29); HRMS calcd for $C_{18}H_{18}O$, M_r = 250.1372, found 250.1358.

1-Pentyl-6-phenanthridone (2a). Methanolysis of **1a** according to method A gave **2a** as a white solid: mp 177−178 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.23 (bs, 1H), 8.62 (dd, 1H, J = 7.7, 1.3 Hz), 8.40 (d, 1H, J = 8.4 Hz), 7.79 (td, 1H, J = 8.6, 1.7 Hz), 7.61 (t, 1H, J = 7.9 Hz), 7.37 (t, 1H, J = 7.7 Hz), 7.16 (d, 1H, J = 7.4 Hz), 7.06 (d, 1H, J = 8.0 Hz), 3.24 (t, 2H, J = 8.0 Hz), 1.85−1.20 (m, 6H), 0.95 (t, 3H, J = 7.1 Hz); MS (EI) [*m*/*z* (relative intensity)] 265 (M^+, 53), 209 (100), 180 (55), 165 (75); HRMS calcd for $C_{18}H_{19}NO$, M_r = 265.1467, found 265.1472.

1-Butyl-6-phenanthridone (2b). Methanolysis of **1b** according to method A gave **2b** as a white solid: mp 160−161 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.83 (bs, 1H), 8.67 (dd, 1H, J = 8.1, 1.6 Hz), 8.43 (d, 1H, J = 8.4 Hz), 7.81 (td, 1H, J = 7.1, 1.5 Hz), 7.28 (dd, 1H, J = 8.0, 1.3 Hz), 7.17 (dd, 1H, J = 7.5, 1.3 Hz), 3.26 (t, 2H, J = 7.8 Hz), 1.80−1.78 (m, 2H), 1.57−1.51 (m, 2H), 1.02 (t, 3H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.1, 162.1, 141.1, 136.8, 135.7, 13.3, 128.6, 128.4, 127.1, 126.9, 126.5, 117.7, 115.3, 37.0, 32.4, 22.8, 13.9; MS (EI) [*m*/*z* (relative intensity)] 251 (M^+, 73), 209 (100), 208 (60), 190 (30), 165 (40), 152 (24); HRMS calcd for $C_{17}H_{17}NO$, M_r = 251.1311, found 251.1316

1-(3-(2-Tetrahydropyranyloxy)propyl)-6-methoxyphenanthridone (2c). Methanolysis of **1c** according to method A gave **2c** as a white solid: mp 179−180 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.60 (bs, 1H), 8.71 (dd, 1H, J = 7.6, 1.2 Hz), 8.62 (d, 1H, J = 8.0 Hz), 7.75 (td, 1H, J = 7.6, 1.4 Hz), 7.62 (td, 1H, J = 7.8, 1.2 Hz), 7.53 (d, 2H, J = 0.6 Hz), 7.45−7.31 (m, 1H), 4.92 (t, 1H, J = 3.6 Hz), 4.13 (t, 2H, J = 7.8 Hz), 4.10−3.91 (m, 2H), 3.67−3.40 (m, 2H), 2.10−1.55 (m, 8H); MS (EI) [*m*/*z* (relative intensity)] 337 (M^+, 15), 224 (35), 209 (100), 186 (29), 145 (21), 124 (40); HRMS calcd for $C_{21}H_{23}NO_3$, M_r = 337.1679, found 337.1671.

1-(3-(2-Tetrahydropyranyloxy)methyl)-6-methoxyphenanthridone (2d). Methanolysis of **1d** according to method A gave **2d** as a white solid: mp 164−165 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 10.55 (bs, 1H), 8.66 (dd, 1H, J = 7.6, 1.4 Hz), 8.59 (d, 1H, J = 8.1 Hz), 7.84 (td, 1H, J = 7.2, 1.4 Hz), 7.65 (td, 1H, J = 8.0, 1.0 Hz), 7.49 (d, 2H, J = 0.7 Hz), 7.48−7.33 (m, 1H), 5.29 (d, 1H, J = 12.1 Hz), 4.97 (d, 1H, J = 12.1 Hz), 4.91 (t, 1H, J = 3.8 Hz), 4.10−3.94 (m, 1H), 3.68−3.48 (m, 1H), 1.95−1.54 (m, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 162.2, 136.8, 135.5, 135.0, 132.6, 128.6, 128.2, 127.6, 127.5, 126.6, 126.5, 118.6, 116.9, 97.8, 69.1, 62.5, 30.6, 25.4, 19.4; MS (EI) [*m*/*z* (relative intensity)] 309 (M^+, 9), 225 (20), 209 (100), 190 (22), 180 (22), 165 (35); HRMS calcd for $C_{19}H_{19}NO_3$, M_r = 309.1366, found 309.1365

1-Pentyl-6-methoxyphenanthridine (3a). Methanolysis of **1a** according to method A gave **3a** as an oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.63 (d, 1H, J = 8.4 Hz), 8.43 (dd, 1H, J = 8.1, 1.5 Hz), 7.81 (td, 1H, J = 7.1, 1.6 Hz), 7.64 (td, 1H, J = 8.1, 1.1 Hz), 7.50 (t, 1H, J = 7.3 Hz), 7.33 (dd, 1H, J = 7.5, 1.5 Hz), 7.27−7.21 (m, 1H), 4.24 (s, 3H), 3.36 (t, 2H, J = 7.8 Hz), 1.87−1.25 (m, 6H), 0.96 (t, 3H, J = 7.3 Hz); MS (EI) [*m*/*z* (relative intensity)] 279 (M^+, 13), 250 (53), 222 (16), 207 (15), 190 (11); HRMS calcd for $C_{19}H_{21}NO$, M_r = 279.1624, found 279.1620.

2-(2-Pentyl-6-methoxyphenyl)benzonitrile (4a): obtained in 64% yield as an oil according to method A except 2 equiv of Bu_4NI added; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.74 (ddd, 1H, J = 7.7, 1.3, 0.4 Hz), 7.62 (td, 1H, J = 7.7, 1.3 Hz), 7.43 (td, 1H, J = 7.5, 1.1 Hz), 7.34−7.31 (m, 2H), 6.94 (td, 1H, J = 7.7, 0.6 Hz), 6.84 (d, 1H, J = 8.2 Hz), 3.73 (s, 3H), 2.41−2.24 (m, 2H), 1.41−1.38 (m, 2H), 1.16−1.11 (m, 4H), 0.77 (t, 3H, J = 7.9 Hz); MS (EI) [*m*/*z* (relative intensity)] 279 (M^+, 38), 222 (100), 190 (56), 165 (25); HRMS calcd for $C_{19}H_{21}NO$, M_r = 279.1624, found 279.1623.

2-(2-Butyl-6-methoxyphenyl)benzonitrile (4b): obtained in 56% yield as an oil according to method A except 2 equiv of Bu_4NI added; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.74 (dd, 1H, J = 7.7, 1.2 Hz), 7.62 (td, 1H, J = 7.6, 1.4 Hz), 7.47−7.39 (m, 1H), 7.37−7.29 (m, 2H), 6.94 (d, 1H, J = 7.6 Hz), 6.84 (d, 1H, J = 8.3 Hz), 3.73 (s, 3H), 2.45−2.23 (m, 2H), 1.42−1.31 (m, 2H), 1.25−1.14 (m, 2H), 0.74 (t, 3H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 49.9 MHz) δ 156.7, 142.2, 141.9, 132.5, 132.1, 131.2, 129.5, 127.2, 126.6, 121.7, 118.2, 114.4, 108.4, 55.7, 33.0, 32.7, 22.3, 13.7; MS (EI) [*m*/*z* (relative intensity)] 265 (M^+, 58), 223 (100), 190 (24), 180 (15); HRMS calcd for $C_{18}H_{19}NO$, M_r = 265.1468, found 265.1474.

4-(2-Butyl-6-methoxyphenyl)benzotriflouride (4e): obtained in 43% yield as an oil according to method A except 2 equiv of Bu_4NI added; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65 (d, 2H, J = 8.4 Hz), 7.34 (t, 1H, J = 8.4 Hz), 7.29 (d, 2H, J = 8.0 Hz), 6.94 (d, 1H, J = 7.2 Hz), 6.83 (d, 1H, J = 8.0 Hz), 3.69 (s, 3H), 2.32 (t, 2H, J = 7.6 Hz), 1.40−1.20 (m, 4H), 0.75 (t, 3H, J = 7.2 Hz); MS (EI) [*m*/*z* (relative intensity)] 308 (M^+, 100), 266 (61), 250 (37), 235 (29), 233 (47), 197 (57), 181 (36), 165 (69); HRMS calcd for $C_{18}H_{19}F_3O$, M_r = 308.1385, found 308.1436.

2-(2-Butyl-6-methoxyphenyl)benzotriflouride(4f): obtained in 34% yield as an oil according to method A except 2 equiv of Bu_4NI added; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76 (d, 1H, J = 8.4 Hz), 7.52 (t, 1H, J = 7.2 Hz), 7.48 (t, 1H, J = 7.6 Hz), 7.30 (t, 1H, J = 8.0 Hz), 7.20 (d, 1H, J = 6.8 Hz), 6.92 (d, 1H, J = 7.6 Hz), 6.79 (d, 1H, J = 7.6 Hz), 3.67 (s, 3H), 2.27−2.11 (m, 2H), 1.55−1.40 (m, 2H), 1.26−1.14 (m, 2H), 0.77 (t, 3H, J = 7.6 Hz); MS (EI) [*m*/*z* (relative intensity)] 308 (M^+, 100), 266 (63), 245 (10), 215 (10), 197 (100), 183 (19), 181 (27), 165 (27); HRMS calcd for $C_{18}H_{19}F_3O$, M_r = 308.1391, found 308.1436.

3-(2-Butyl-6-methoxyphenyl)benzotriflouride(4g): obtained in 37% yield as an oil according to method A except 2 equiv of Bu_4NI added; ^{1}HNMR($CDCl_3$, 400 MHz) δ 7.60 (d, 1H, J = 8.0 Hz), 7.52 (t, 1H, J = 7.6 Hz), 7.48 (s, 1H), 7.41 (d, 1H, J = 7.6 Hz), 7.28 (t, 1H, J = 8.0 Hz), 6.93 (d, 1H, J = 6.8 Hz), 6.82 (d, 1H, J = 7.6 Hz), 3.69 (s, 3H), 1.37−1.17 (m, 4H), 0.88 (t, 3H, J = 5.2 Hz); MS (EI) [*m*/*z* (relative intensity)] 308 (M^+, 100), 266 (85), 250 (45), 235 (44), 233 (38), 197 (44), 183 (20); HRMS calcd for $C_{18}H_{19}F_3O$, M_r = 308.1391, found 308.1436.

4-(2-Butyl-6-methoxyphenyl)benzonitrile (4h): obtained in 56% yield as an oil according to method A except 2 equiv of Bu_4NI added; ^{1}HNMR ($CDCl_3$, 400 MHz) δ 7.22 (t, 1H, J = 8.0 Hz), 7.00 (d, 2H, J = 8.8 Hz), 6.90 (d, 1H, J = 7.2 Hz), 6.79 (d, 1H, J = 7.6 Hz), 6.75 (d, 2H, J = 8.4 Hz), 3.69 (s, 3H), 1.41−1.19 (m, 4H), 0.78 (t, 3H, J = 6.8 Hz); MS (EI) [*m*/*z* (relative intensity)] 265 (M^+, 65), 223 (85), 250 (100), 190 (30); HRMS calcd for $C_{18}H_{19}NO$, M_r = 265.1474, found 265.1468.

4-(2-Butyl-6-methoxyphenyl)benzochloride(4i): obtained in 31% yield as an oil according to method A except 2 equiv of Bu_4NI added; ^{1}HNMR ($CDCl_3$, 400 MHz) δ 7.39 (d, 1H, J = 6.4 Hz), 7.37 (t, 1H, J = 8.4 Hz), 7.16 (d, 1H, J = 8.8 Hz), 6.92 (d, 2H, J = 8.0 Hz), 6.82 (d, 2H, J = 8.4 Hz), 3.70 (s, 3H), 2.38 (t, 2H, J = 8.0 Hz), 1.39−1.19 (m, 4H), 0.78 (t, 3H, J = 7.2 Hz); MS (EI) [*m*/*z* (relative intensity)] 274 (M^+, 100), 232 (53), 201 (18), 119 (17), 197 (75), 181 (41), 165 (27), 152 (44); HRMS calcd for $C_{17}H_{19}ClO$, M_r = 274.1120, found 274.1125.

(2-Butyl-6-methoxyphenyl)benzene (4j): obtained in 14% yield as an oil according to method A except 2 equiv of

Bu_4NI added; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.40 (t, 1H, J = 6.8 Hz), 7.38 (t, 1H, J = 6.0 Hz), 7.34−7.28 (m, 4H), 6.92 (d, 1H, J = 6.8 Hz), 6.82 (d, 1H, J = 7.2 Hz), 3.69 (s, 3H), 1.37−1.25 (m, 4H), 0.75 (t, 3H, J = 8.0 Hz); MS (EI) [*m*/*z* (relative intensity)] 240 (M^+, 100), 198 (35), 197 (53), 182 (34), 167 (52), 165 (83), 152 (50); HRMS calcd for $C_{17}H_{20}O$, M_r = 240.1512, found 240.1515.

(2-Butyl-6-methoxyphenyl)pyridine(4k): obtained in 34% yield as an oil according to method A except 2 equiv of Bu_4NI added; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.71 (d, 1H, J = 4.0 Hz), 7.73 (td, 1H, J = 6.0, 2.0 Hz), 7.30−7.22 (m, 3H), 6.91 (d, 1H, J = 7.6 Hz), 6.82 (d, 1H, J = 7.6 Hz), 3.69 (s, 3H), 2.35 (t, 2H, J = 7.6 Hz), 1.37−1.16 (m, 4H), 0.73 (t, 3H, J = 7.2 Hz); MS (EI) [*m*/*z* (relative intensity)] 241 (M^+, 45), 212 (100), 197 (41), 154 (22); HRMS calcd for $C_{15}H_{15}N$, M_r = 241.1461, found 241.1467.

(2-Butyl-6-methoxyphenyl)thiophene(4l): obtained in 20% yield as an oil according to method A except 2 equiv of Bu_4NI added; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.39 (dd, 1H, J = 5.2, 1.2 Hz), 7.28 (d, 1H, J = 8.0 Hz), 7.10 (dd, 1H, J = 4.8, 3.2 Hz), 6.89 (t, 1H, J = 2.4 Hz), 6.80 (d, 1H, J = 0.8 Hz), 6.78 (d, 1H, J = 0.8 Hz), 3.74 (s, 3H), 2.46 (t, 2H, J = 8.0 Hz), 1.46−1.26 (m, 4H), 0.81 (t, 3H, J = 7.2 Hz); MS (EI) [*m*/*z* (relative intensity)] 246 (M^+, 100), 203 (45), 188 (24), 173 (35); HRMS calcd for $C_{15}H_{18}OS$, M_r = 246.1074, found 246.1079.

(2-Butyl-6-methoxyphenyl)pyrazine (4m): obtained in 34% yield as an oil according to method A except 2 equiv of Bu_4NI added; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.67 (dd, 1H, J = 2.5, 1.2 Hz), 8.66 (d, 1H, J = 1.6 Hz), 8.50 (d, 1H, J = 1.5 Hz), 7.33 (t, 1H, J = 8.0 Hz), 6.94 (td, 1H, J = 6.8, 2.0 Hz), 6.84 (dd, 1H, J = 8.4, 0.8 Hz), 3.70 (s, 3H), 2.38 (t, 2H, J = 8.0 Hz), 1.39−1.35 (m, 2H), 1.33−1.13 (m, 2H), 0.74 (t, 3H, J = 7.6 Hz); MS (EI) [*m*/*z* (relative intensity)] 242 (M^+, 49), 241 (50), 213 (75), 199 (100), 184 (34); HRMS calcd for $C_{14}H_{14}N_2$, M_r = 242.1421, found 242.1420.

2-(2-(2-Hexynylphenyl)ethynyl)benzonitrile (7a): obtained in 62% yield as an oil according to method B; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.71−7.52 (m, 4H), 7.47−7.37 (m, 2H), 7.33−7.25 (m, 2H), 2.52 (t, 2H, J = 7.6 Hz), 1.66−1.43 (m, 4H), 0.89 (t, 3 H, J = 7.6 Hz); HRMS (EI) calcd for $C_{21}H_{17}N$, M_r = 283.1362, found 283.1326.

2-(2-(2-Heptynylphenyl)ethynyl)benzonitrile (7b): obtained in 40% yield as an oil according to method B; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.70−7.53 (m, 4H), 7.47−7.34 (m, 2H), 7.30−7.25 (m, 2H), 2.51 (t, 2H, J = 7.6 Hz), 1.69−1.25 (m, 6H), 0.85 (t, 3 H, J = 7.6 Hz); HRMS (EI) calcd for $C_{22}H_{19}N$, M_r = 297.1518, found 297.1515.

2-(2-(3-Tetrahydropyranyl-5-oxy-1-pentynylphenyl)-ethynyl)benzonitrile (7c): obtained in 57% yield as an oil according to method B; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.70−7.51 (m, 4H), 7.47−7.34 (m, 2H), 7.31−7.28 (m, 2H), 4.59−4.56 (m, 1H), 3.95−3.81 (m, 1H), 3.62−3.47 (m, 1H), 2.64 (t, 2H, J = 7.4 Hz), 1.97−1.46 (m, 10H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 132.7, 132.6, 132.5, 132.3, 132.1, 132.0, 128.9, 128.2, 127.4, 127.3, 126.4, 124.3, 117.5, 115.2, 98.8, 94.9, 88.6, 79.3, 66.1, 62.2, 30.7, 28.9, 25.5, 19.5, 16.6; HRMS (EI) calcd for $C_{25}H_{23}NO_2$, M_r = 369.1729, found 369.1725.

2-(2-(3-Tetrahydropyranyl-2-oxy-1-propynylphenyl)-ethynyl)benzonitrile (7d): obtained in 63% yield as an oil according to method B; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.84−7.37 (m, 8H), 5.08−5.04 (m, 1H), 4.70 (d, 2H, J = 2.2 Hz), 4.21−3.93 (m, 1H), 3.69−3.61 (m, 1H), 1.93−1.58 (m, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 132.7, 132.6, 132.5, 132.3, 132.2, 128.9, 128.4, 127.1, 125.6, 124.9, 117.4, 115.1, 96.8, 94.4, 89.1, 84.0, 61.9, 54.9, 30.3, 25.4, 19.0; HRMS (EI) calcd for $C_{23}H_{19}NO_2$, M_r = 341.1414, found 341.1452.

1-Butylbenzo[*c*]phenanthridinone (8a): obtained in 57% yield as a white solid according to method A using 10% DMSO as the cosolvent; mp 230 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 10.26 (bs, 1H); 8.68 (dd, 1H, J = 8.0, 1.6 Hz); 8.52 (d, 1H, J = 8.4 Hz); 8.30 (d, 1H, J = 8.4 Hz); 7.86−7.80 (m, 2H), 7.67−7.58 (m, 4H), 3.38 (t, 2H, J = 8.0 Hz); 1.90−1.82 (m, 2H); 1.58−1.49 (m, 2H), 0.89 (t, 3H, J = 8.0 Hz); HRMS (EI) calcd for $C_{21}H_{19}NO$, M_r = 301.1467, found 301.1467.

1-Pentylbenzo[*c*]phenanthridinone (8b): obtained in 42% yield as a white solid according to method A using 10% DMSO as the cosolvent; mp 214 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 10.85 (bs, 1H), 8.67 (dd, 1H, J = 8.0, 1.6 Hz), 8.55 (d, 1H, J = 8.4 Hz), 8.37 (d, 1H, J = 8.0 Hz), 7.88−7.84 (m, 2H), 7.67−7.58 (m, 4H), 3.39 (t, 2H, J = 8.0 Hz), 1.90−1.84 (m, 2H), 1.53−1.39 (m, 4H), 0.94 (t, 3H, J = 8.0 Hz); HRMS (EI) calcd for $C_{22}H_{21}NO$, M_r = 315.1624, found 315.1623.

11-(Tetrahydropyranyl-5-oxypropyl)-5*H*-benzo[*c*]phenanthridinone (8c): obtained in 36% yield as a white solid according to method A using 10% DMSO as the cosolvent; mp 157−158 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.81 (bs, 1H), 8.17 (dd, 1H, J = 8.0, 2.0 Hz), 7.87−7.79 (m, 3H), 7.66−7.54 (m 5H), 4.65−4.63 (m, 1H), 3.96−3.82 (m, 1H), 3.63−3.50 (m, 1H), 2.17 (t, 2H, J = 8.4 Hz), 1.78−1.24 (m, 10H); HRMS (EI) calcd for $C_{25}H_{25}NO_3$, M_r = 387.1839, found 387.1871.

11-(Tetrahydropyranyl-2-oxymethyl)-5*H*-benzo[*c*]phenanthridinone (8d): obtained in 31% yield as a white solid according to method A using 10% DMSO as the cosolvent; mp 203−204 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.95 (bs, 1H), 8.69 (d, 1H, J = 8.0 Hz), 8.20 (d, 1H, J = 7.6 Hz), 7.92 (dd, 1H, J = 7.6, 1.2 Hz), 7.86 (s, 1H), 7.83 (t, 1H, J = 7.6 Hz), 7.69−7.60 (m, 3H), 5.38 (d, 1H, J = 12 Hz), 5.05 (d, 1H, J = 12 Hz), 4.96−4.94 (m, 1H), 4.03−4.00 (m, 1H); 3.65−3.62 (m, 1H), 1.79−1.50 (m, 6H); HRMS (EI) calcd for $C_{23}H_{21}NO_3$, M_r = 359.1523, found 359.1558.

1,4-Bis(3-(*Z*)-dodecen-1,5-diynyl)benzene (11): obtained in 78% yield as an oil according to method B; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.41 (s, 2H); 6.02−5.58 (m, 4H), 2.45 (t, 2H, J = 7.2 Hz), 1.70−1.47 (m, 8H), 0.90 (t, 6H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 131.5, 122.2, 120.8, 117.9, 99.9, 95.7, 89.2, 78.4, 30.7, 21.9, 19.6, 13.6; HRMS (EI) calcd for $C_{26}H_{26}$, M_r = 338.2035, found 338.2017.

4,4′-Bis(3-(*Z*)-dodecen-1,5-diynyl)biphenyl (12): obtained in 51% yield as an oil according to method B; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.58−7.51 (m, 8H); 5.98−5.86 (m, 4H), 2.45 (td, 4H, J = 7.2, 2.0 Hz), 1.65−1.48 (m, 8H), 0.91 (t, 6H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 140.1, 132.2, 126.8, 122.6, 120.4, 116.1, 99.6, 95.9, 88.3, 78.5, 31.5, 30.7, 21.9, 14.2; HRMS (EI) calcd for $C_{32}H_{30}$, M_r = 414.2349, found 414.2346.

1,4-Bis(2-methoxy-6-butylphenyl)benzene (13): obtained in 31% yield as a white solid according to method A using 10% THF as the cosolvent; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.25 (t, 2H, J = 7.8 Hz), 7.24 (s, 4H), 6.92 (d, 2H, J = 7.8 Hz), 6.82 (dd, 2H, J = 8.2, 1.2 Hz), 3.72 (s, 6H), 2.43 (t, 4H, J = 7.6 Hz), 1.41−1.16 (m, 8H), 0.77 (t, 6H, J = 7.6 Hz); HRMS (EI) calcd for $C_{28}H_{34}O_2$, M_r = 402.2560, found 402.2560.

4,4′-Bis(2-hydroxy-6-butylphenyl)biphenyl (14): obtained in 23% yield as a white solid according to method A using 30% DMSO as the cosolvent; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.80 (dd, 4H, J = 6.0, 1.6 Hz), 7.24 (s, 4H), 7.41 (dd, 4H, J = 6.4, 2.0 Hz), 7.22 (t, 2H, J = 7.6 Hz), 6.91−6.85 (m, 4H), 4.74 (bs, 2H), 2.42 (t, 4H, J = 7.6 Hz), 1.45−1.20 (m, 8H), 0.79 (t, 6H, J = 7.2 Hz); HRMS (EI) calcd for $C_{32}H_{34}O_2$, M_r = 450.2560, found 450.2562.

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