

Synthesis of **Natural** Polyacetylenes Bearing Furan Ring

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SUPPORTING INFORMATION

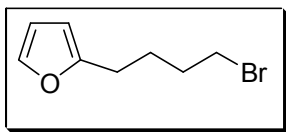
CONTENTS

Materials and Methods	2
General Procedure for the Preparation of the 2-(n-bromo-n-alkyl)-furan derivatives	2
General Procedure for the Preparation of the Alcohols derivatives	3
General Procedure for the Preparation of the Terminal Alkynes derivatives	5
General Procedure for the Preparation of the Alkynyl Iodides derivatives	6
General Procedure for the Preparation of the Pentadec-14-yn-1-ol derivative	7
General Procedure for the Copper-Catalyzed Coupling Reaction of Alkynes with Iodides derivatives	7
General Procedure for the Preparation of the 19-Furan-2-yl-nonadeca-5,7-diynoic Acid	8
General Procedure for the Preparation of the 19-Furan-2-yl-nonadeca-5,7-diynoic Acid Methyl Ester	9
Selected Spectra	10

Materials and Methods

Proton nuclear magnetic resonance spectra (^1H NMR) were obtained at 400 MHz. Spectra were recorded in CDCl_3 solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of CHCl_3 or tetramethylsilane (TMS) as the external reference. Data are reported as follows: chemical shift (δ), multiplicity, coupling constant (J) in Hertz and integrated intensity. Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained at 100 MHz. Spectra were recorded in CDCl_3 solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of CHCl_3 . Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sex (sextet) and m (multiplet). High resolution mass spectra were recorded on a double focusing magnetic sector mass spectrometer using EI at 70 eV. Column chromatography was performed using silica gel (230-400 mesh) following the methods described by Still.¹ Thin layer chromatography (TLC) was performed using silica gel GF₂₅₄, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine vapor, or acidic vanillin. The following solvents were dried and purified by distillation from the reagents indicated: tetrahydrofuran from sodium with a benzophenone ketyl indicator. All other solvents were ACS or HPLC grade unless otherwise noted. Air- and moisture-sensitive reactions were conducted in flame-dried or oven dried glassware equipped with tightly fitted rubber septa and under a positive atmosphere of dry nitrogen or argon. Reagents and solvents were handled using standard syringe techniques. Temperatures above room temperature were maintained by use of a mineral oil bath with an electrically heated coil connected to a controller.

General Procedure for the Preparation of the 2-(*n*-bromo-*n*-alkyl)-furan derivatives²: Dry THF (40 mL) was cooled to $-20\text{ }^\circ\text{C}$ in a 100 mL two-necked flask and *n*-butyl lithium (10 mL of 2.4M solution in hexane, 24 mmol) was added with stirring under argon. Freshly distilled furan (1.7 mL, 24 mmol) was added, dropwise, into the *n*-butyl lithium solution. The mixture was stirred for 4 h at $-20\text{ }^\circ\text{C}$, then, the appropriate alkyl bromide (20 mmol) was added dropwise with vigorous stirring and the mixture was left overnight at room temperature. The reaction was quenched by the addition of saturated NH_4Cl aqueous solution (20 mL) and extracted with ethyl acetate (3 X 20 mL). The organic phase was separated, dried over MgSO_4 , and the solvent removed under reduced pressure using a rotary evaporator. The residue was purified by column chromatography on silica gel using hexane as eluent to give 2-(*n*-bromo-*n*-alkyl)-furan.

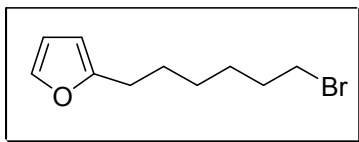


2-(4-Bromo-butyl)-furan (7a): This compound was prepared in 3.555 g (88%) as yellow oil, from 1,4-dibromobutane according to the already described procedure. ^1H NMR (CDCl_3 , 200 MHz): δ 7.33-7.27 (m, 1H), 6.32-6.24 (m, 1H), 6.03-5.95 (m, 1H), 3.42 (t, $J = 6.5$ Hz, 2H), 2.66 (t, $J = 6.5$ Hz, 2H), 2.07-1.64 (m, 4H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 155.3, 140.9, 110.0, 105.0, 33.4, 32.0, 27.0, 26.5. MS (EI, 70 eV) m/z (relative intensity):

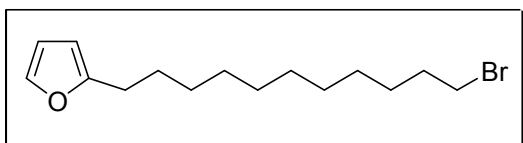
¹ Still, W.C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925.

² Lissi, A. E.; Encinas, V. M.; Castañeda, F.; Olea, A. F. *J. Phys. Chem.* **1980**, *84*, 251-255.

201 (23), 122 (17), 94 (26), 80 (100), 53 (34). HRMS: m/z calcd for $C_8H_{11}BrO$ 201.9993, found 201.9998.

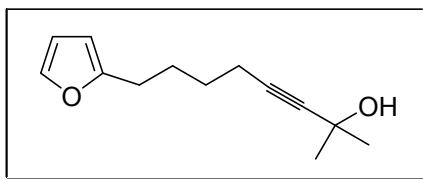


2-(6-Bromo-hexyl)-furan (15): This compound was prepared in 4.278 g (93%) yield from 1,6-dibromohexane as described. 1H NMR ($CDCl_3$, 200 MHz): δ 7.34-7.25 (m, 1H), 6.33-6.20 (m, 1H), 6.02-5.92 (m, 1H), 3.43-3.33 (m, 2H), 2.68-2.54 (m, 2H), 1.96-1.76 (m, 2H), 1.74-1.53 (m, 2H), 1.52-1.25 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.3, 140.5, 109.9, 104.6, 33.8, 32.5, 28.1, 27.8, 27.7, 27.2. MS (EI, 70 eV) m/z (relative intensity): 229 (14), 150 (14), 122 (8), 94 (14), 80 (100), 52 (10). HRMS: m/z calcd for $C_{10}H_{15}BrO$ 230.0306, found 230.0309.



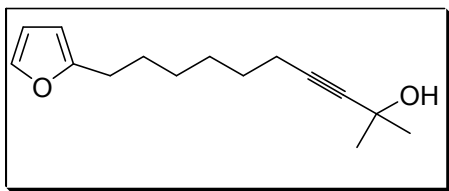
2-(11-Bromo-undecyl)-furan (7b): In a reaction similar to that of (7a), 1,11-dibromoundecane yielded 5.760 g (96%) of (7b). 1H NMR ($CDCl_3$, 400 MHz): δ 7.30-7.27 (m, 1H), 6.29-6.25 (m, 1H), 5.98-5.94 (m, 1H), 3.40 (t, $J = 6.8$ Hz, 2H), 2.60 (t, $J = 7.5$ Hz, 2H), 1.85 (quint, $J = 7.1$ Hz, 2H), 1.62 (quint, $J = 7.1$ Hz, 2H), 1.37-1.15 (m, 14H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.4, 140.4, 109.9, 104.4, 33.8, 32.7, 29.4, 29.3, 29.3, 29.2, 29.0, 28.6, 28.1, 27.9, 27.9. MS (EI, 70 eV) m/z (relative intensity): 299 (26), 218 (17), 136 (14), 122 (32), 94 (87), 80 (100), 52 (22). HRMS: m/z calcd for $C_{15}H_{25}BrO$ 300.1088, found 300.1091.

General Procedure for the Preparation of the alcohols derivatives³: To a solution of the appropriate alcohol (10 mmol) in THF (20 mL) and HMPA (10 mL, 60 mmol) at $-78^\circ C$, under argon atmosphere and magnetic stirring, was added *n*-butyl lithium (8 mL of 2.4M solution in hexane, 20 mmol). The temperature was progressively raised to $-30^\circ C$ and maintained for 45 min. The appropriate bromide (10 mmol) was added dropwise at $-30^\circ C$. After this the solution was stirred at room temperature for 18 hours. The solution was diluted by saturated NH_4Cl aqueous solution (20 mL) and extracted with ethyl acetate (3 X 20 mL). The organic phase was separated, dried over $MgSO_4$, and the solvent removed under reduced pressure using a rotary evaporator. The residue was purified by column chromatography on silica gel using ethyl acetate/hexane as eluent.

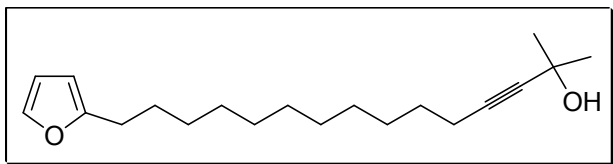


8-Furan-2-yl-2-methyl-oct-3-yn-2-ol (9a): Yield: 1.442 g (70%). 1H NMR ($CDCl_3$, 400 MHz): δ 7.34-7.28 (m, 1H), 6.33-6.22 (m, 1H), 6.02-5.95 (m, 1H), 2.64 (t, $J = 7.3$ Hz, 2H), 2.21 (t, $J = 7.3$ Hz, 2H), 2.00 (s, 1H), 1.73 (quint, $J = 7.3$ Hz, 2H), 1.59-1.50 (m, 2H), 1.49 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.9, 140.7, 110.0, 104.7, 85.3, 82.0, 65.2, 31.6, 27.9, 27.3, 27.0, 18.2. MS (EI, 70 eV) m/z (relative intensity): 189 (8), 144 (56), 118 (44), 106 (56), 94 (45), 80 (100), 52 (65). HRMS: m/z calcd for $C_{13}H_{18}O_2$ 206.1307, found 206.1311.

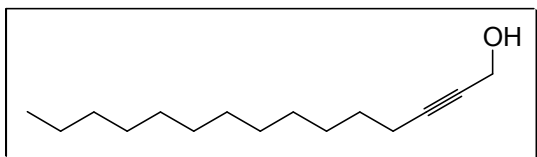
³ Cossy, J.; Pete, J. P. *Tetrahedron Lett.* **1986**, 27, 573-574.



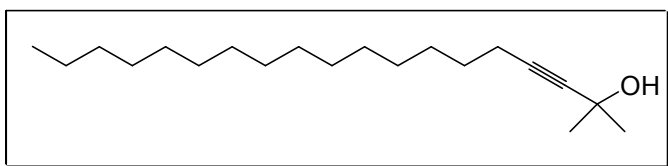
10-Furan-2-yl-2-methyl-dec-3-yn-2-ol (9b): Yield: 1.170 g (50%). ^1H NMR (CDCl_3 , 400 MHz): δ 7.30-7.27 (m, 1H), 6.29-6.24 (m, 1H), 5.98-5.95 (m, 1H), 2.61 (t, $J = 7.3$ Hz, 2H), 2.17 (t, $J = 7.3$ Hz, 2H), 2.13 (s, 1H), 1.64 (quint, $J = 7.3$ Hz, 2H), 1.53-1.44 (m, 8H), 1.43-1.31 (m, 4H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 156.2, 140.5, 109.9, 104.5, 85.1, 82.3, 65.1, 31.6, 28.4, 28.4, 28.3, 27.7, 27.7, 18.4. MS (EI, 70 eV) m/z (relative intensity): 213 (14), 199 (34), 158 (27), 106 (27), 94 (33), 80 (100), 53 (84). HRMS: m/z calcd for $\text{C}_{15}\text{H}_{22}\text{O}_2$ 234.1620, found 234.1623.



15-Furan-2-yl-2-methyl-pentadec-3-yn-2-ol (16): Yield: 1.307 g (43%). ^1H NMR (CDCl_3 , 200 MHz): δ 7.33-7.27 (m, 1H), 6.32-6.24 (m, 1H), 6.00-5.94 (m, 1H), 2.61 (t, $J = 7.5$ Hz, 2H), 2.17 (t, $J = 6.9$ Hz, 2H), 1.90 (s, 1H), 1.72-1.55 (m, 4H), 1.54-1.45 (s, 6H), 1.49 (s, 6H), 1.40-1.21 (m, 14H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 156.5, 140.5, 109.9, 104.4, 85.0, 82.6, 65.2, 31.7, 29.5, 29.4, 29.4, 29.3, 29.1, 29.0, 28.7, 28.6, 28.0, 27.9, 18.5. MS (EI, 70 eV) m/z (relative intensity): 286 (59), 240 (47), 118 (24), 106 (31), 94 (38), 80 (100), 52 (20). Anal. (%) Calc for $\text{C}_{20}\text{H}_{32}\text{O}_2$: C 78.90, H 10.59. Found: C 79.02, H 10.43.



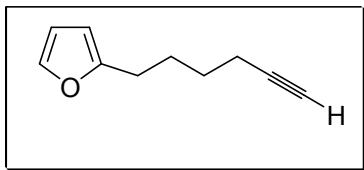
Pentadec-2-yn-1-ol (12): Yield: 1.904 g (85%). ^1H NMR (CDCl_3 , 400 MHz): δ 4.27-4.23 (m, 2H), 2.24-2.18 (m, 2H), 1.58 (s, 1H), 1.55-1.45 (m, 2H), 1.42-1.32 (m, 2H), 1.31-1.22 (m, 16H), 0.88 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 86.6, 78.2, 51.4, 31.8, 29.6, 29.6, 29.6, 29.4, 29.3, 29.1, 28.8, 28.5, 22.6, 18.7, 14.0. MS (EI, 70 eV) m/z (relative intensity): 191 (2), 134 (14), 120 (23), 92 (66), 80 (100), 66 (52), 54 (90). HRMS: m/z calcd for $\text{C}_{15}\text{H}_{28}\text{O}$ 224.2140, found 224.2145.



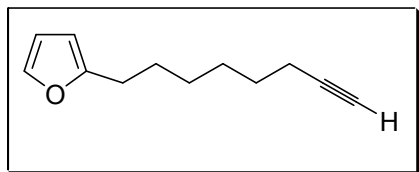
2-Methyl-nonadec-3-yn-2-ol (17): Yield: 1.456 g (65%). ^1H NMR (CDCl_3 , 400 MHz): δ 2.17 (t, $J = 7.0$ Hz, 2H), 1.85 (s, 1H), 1.54-1.44 (s, 6H), 1.40-1.12 (m, 26H), 0.88 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (CDCl_3 , 50 MHz): δ 85.0, 82.4, 65.1, 31.8, 31.6, 29.5, 29.5, 29.5, 29.4, 29.2, 29.0, 28.7, 28.6, 22.5, 18.4, 13.9. MS (EI, 70 eV) m/z (relative intensity): 276 (100), 124 (8), 110 (9), 94 (17), 81 (15), 67 (8). HRMS: m/z calcd for $\text{C}_{20}\text{H}_{38}\text{O}$ 294.2923, found 294.2928.

General Procedure for the Preparation of the Terminal Alkynes derivatives⁴:

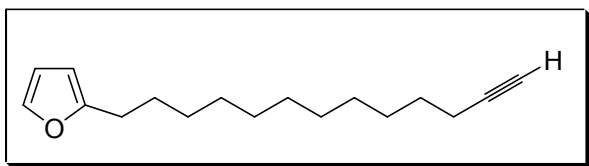
Powdered NaOH (0.6 g, 15 mmol) was added to a two-neck round bottomed flask equipped with a reflux condenser, containing a solution of the appropriate alcohol (5 mmol) in toluene (20 mL) under an argon atmosphere. The mixture was then heated at reflux for 12 hours. After this time, the solution was allowed to reach room temperature and was then diluted with NH₄Cl aqueous solution (20 mL) and extracted with ethyl acetate (3 X 10 mL). The organic phase was separated, dried over MgSO₄, and the solvent removed under reduced pressure using a rotary evaporator. The residue was purified by column chromatography on silica gel using hexane as eluent.



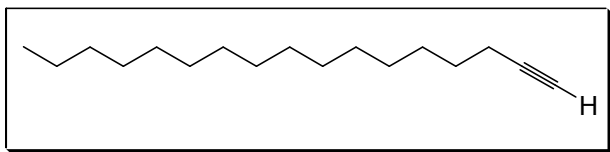
2-Hex-5-ynyl-furan (10a): Yield: 0.429g (58%). ¹H NMR (CDCl₃, 200 MHz): δ 7.31-7.27 (m, 1H), 6.29-6.24 (m, 1H), 6.01-5.95 (m, 1H), 2.64 (t, *J* = 7.4 Hz, 2H), 2.21 (td, *J* = 7.0, 2.6 Hz, 2H), 1.94 (t, *J* = 2.5 Hz, 1H), 1.80-1.70 (m, 2H), 1.63-1.52 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ 155.8, 140.7, 110.0, 104.8, 84.2, 68.3, 27.8, 27.3, 27.0, 18.1. MS (EI, 70 eV) *m/z* (relative intensity): 146 (11), 132 (11), 118 (36), 91 (100), 80 (82), 52 (44). HRMS: *m/z* calcd for C₁₀H₁₂O 148.0888, found 148.0891.



2-Oct-7-ynyl-furan (14): Yield: 0.572 g (65%). ¹H NMR (CDCl₃, 400 MHz): δ 7.31-7.27 (m, 1H), 6.33-6.24 (m, 1H), 6.02-5.91 (m, 1H), 2.61 (t, *J* = 7.5 Hz, 2H), 2.18 (td, *J* = 7.0, 2.6 Hz, 2H), 1.93 (t, *J* = 2.6 Hz, 1H), 1.65 (quint, *J* = 7.5 Hz, 2H), 1.58-1.48 (m, 2H), 1.47-1.30 (m, 4H). ¹³C NMR (CDCl₃, 100 MHz): δ 156.3, 140.6, 109.9, 104.5, 84.5, 68.1, 28.5, 28.3, 28.3, 27.8, 18.3. MS (EI, 70 eV) *m/z* (relative intensity): 174 (2), 146 (20), 118 (19), 106 (58), 94 (71), 80 (100), 52 (38). IR (neat) (ν max, cm⁻¹) 3300, 9934, 2858, 2116, 1795, 1597, 1508, 1460, 1148, 1009, 885. HRMS: *m/z* calcd for C₁₂H₁₆O 176.1201, found 176.1206.



2-Tridec-12-ynyl-furan (10b): Yield: 1.008 g (82%). ¹H NMR (CDCl₃, 200 MHz): δ 7.32-7.26 (m, 1H), 6.30-6.22 (m, 1H), 6.01-5.92 (m, 1H), 2.61 (t, *J* = 7.5 Hz, 2H), 2.18 (td, *J* = 6.9, 2.6 Hz, 2H), 1.93 (t, *J* = 2.6 Hz, 1H), 1.72-1.44 (m, 4H), 1.43-1.11 (m, 14H). ¹³C NMR (CDCl₃, 100 MHz): δ 156.5, 140.5, 109.9, 104.4, 84.7, 68.0, 29.5, 29.4, 29.4, 29.3, 29.1, 29.0, 28.7, 28.4, 28.0, 27.9, 18.3. MS (EI, 70 eV) *m/z* (relative intensity): 243 (10), 146 (18), 106 (54), 94 (72), 80 (100), 52 (34). Anal. (%) Calc for C₁₇H₂₆O: C 82.87, H 10.64. Found: C 82.58, H 10.32.

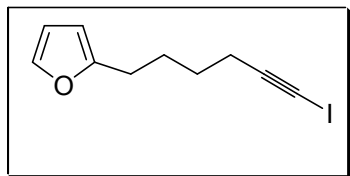


Heptadec-1-yne (18): Yield: 0.802 g (68%). ¹H NMR (CDCl₃, 200 MHz): δ 2.18 (td, *J* = 6.9, 2.5 Hz, 2H), 1.94 (t, *J* = 2.6 Hz, 1H), 1.60-1.54 (m, 6H), 1.32-1.21 (m, 20H), 0.88 (t, *J* = 6.7 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 84.7, 63.9, 31.9, 29.7, 29.6, 29.6, 29.6, 29.5, 29.3, 29.1, 28.7,

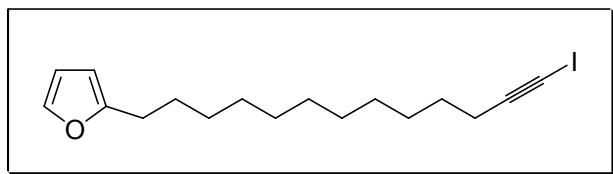
⁴ Neenan, T. X.; Whitesides, G. M. *J. Org. Chem.* **1988**, 53, 2489.

28.5, 22.6, 18.3, 14.0. MS (EI, 70 eV) m/z (relative intensity): 108 (15), 95 (78), 81 (100), 67 (29), 55 (26). HRMS: m/z calcd for $C_{17}H_{32}$ 236.2504, found 236.2509.

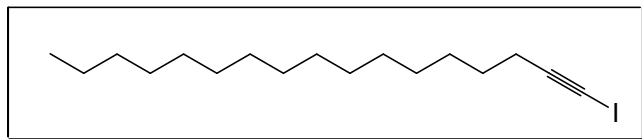
General Procedure for the Preparation of the Alkynyl Iodides derivatives⁵: To a solution of the appropriate alkynyl (5 mmol) in THF (10 mL) at -20°C , under argon atmosphere and magnetic stirring, was slowly added *n*-butyl lithium (2 mL of 2.4M solution in hexane, 5 mmol). The mixture was stirred for 1 h at -20°C , then, the temperature was decreased to -40°C and iodine (1.40 g, 5.5 mmol, 1.1 eq) dissolved in 5 mL of THF was added. The reaction mixture was allowed to stir at room temperature overnight. Excess I_2 was removed by washing with saturated aq $\text{Na}_2\text{S}_2\text{O}_3$. The product was then extracted by ethyl acetate (3 X 10 mL). The organic phase was separated, dried over MgSO_4 , and the solvent removed under reduced pressure using a rotary evaporator. The residue was purified by column chromatography on silica gel using hexane as eluent.



2-(6-Iodo-hex-5-ynyl)-furan (5a): Yield: 1.096 g (80%). ^1H NMR (CDCl_3 , 200 MHz): δ 7.35-7.27 (m, 1H), 6.32-6.22 (m, 1H), 6.04-5.94 (m, 1H), 2.64 (t, $J = 7.0$ Hz, 2H), 2.38 (t, $J = 7.0$ Hz, 2H), 1.81-1.46 (m, 4H). ^{13}C NMR (CDCl_3 , 50 MHz): δ 155.7, 140.7, 110.0, 104.8, 94.3, 68.8, 27.8, 27.3, 27.0, 20.5. MS (EI, 70 eV) m/z (relative intensity): 146 (84), 118 (24), 106 (21), 90 (100), 80 (84), 52 (56). IR (neat) (ν max, cm^{-1}) 3298, 3113, 2941, 2860, 2185, 1595, 1506, 1460, 1429, 1147, 1005, 883, 482. HRMS: m/z calcd for $\text{C}_{10}\text{H}_{11}\text{IO}$ 273.9855, found 273.9859.



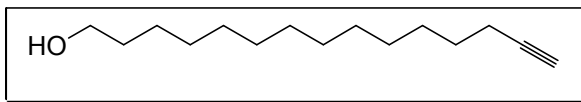
2-(13-Iodo-tridec-12-ynyl)-furan (5b): Yield: 1.525 g (82%). ^1H NMR (CDCl_3 , 200 MHz): δ 7.32-7.26 (m, 1H), 6.30-6.23 (m, 1H), 5.99-5.92 (m, 1H), 2.60 (t, $J = 7.5$ Hz, 2H), 2.35 (t, $J = 6.9$ Hz, 2H), 1.71-1.41 (m, 4H), 1.40-1.19 (m, 14H). ^{13}C NMR (CDCl_3 , 50 MHz): δ 156.5, 140.5, 109.9, 104.4, 94.7, 29.4, 29.4, 29.3, 29.2, 29.1, 28.9, 28.7, 28.4, 27.9, 27.9, 20.7. MS (EI, 70 eV) m/z (relative intensity): 242 (94), 106 (17), 94 (26), 80 (100), 66 (14), 52 (22). IR (neat) (ν max, cm^{-1}) 2929, 2851, 2187, 1593, 1505, 1469, 1425, 1167, 999, 930, 883, 795, 511. HRMS: m/z calcd for $\text{C}_{17}\text{H}_{25}\text{IO}$ 372.0950, found 372.0953.



1-Iodo-heptadec-1-yne (13): Yield: 1.339 g (74%). ^1H NMR (CDCl_3 , 200 MHz): δ 2.35 (t, $J = 6.9$ Hz, 2H), 1.44-1.116 (m, 26H), 0.88 (t, $J = 6.7$ Hz, 3H). ^{13}C NMR (CDCl_3 , 50 MHz): δ 94.8, 31.9, 29.6, 29.6, 29.6, 29.5, 29.4, 29.3, 29.0, 28.7, 28.4, 22.6, 20.8, 14.0. MS (EI, 70 eV) m/z (relative intensity): 122 (11), 108 (31), 94 (78), 80 (100), 66 (44), 54 (51). IR (KBr) (ν max, cm^{-1}) 4322, 2942, 2838, 2185, 1470, 1426, 1370, 1279, 716, 563, 501. HRMS: m/z calcd for $\text{C}_{17}\text{H}_{31}\text{I}$ 362.1470, found 362.1475.

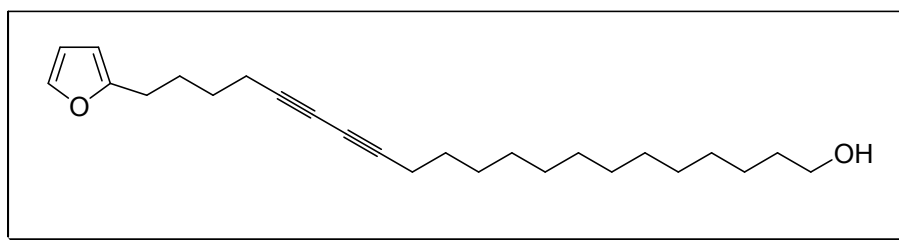
⁵ Coleman, B. E.; Cwynar, V.; Hart, D. J.; Havas, F.; Mohan, J. M.; Patterson, S.; Ridenour, S.; Schmidt, M.; Smith, E.; Wells, A. J. *Synlett*, **2004**, 1339.

General Procedure for the Preparation of the Pentadec-14-yn-1-ol derivative⁶



(6b): To a two-neck round-bottomed flask, under argon, containing 1,3-diaminopropane (15 mL) was added lithium (0.23 g, 33 mmol). The mixture was heated and stirred at 70°C for 2 h until the blue colour had discharged, and a milky white suspension of the lithium salt was obtained. The mixture was cooled to room temperature and potassium *tert*-butoxide (2.24 g, 20 mmol) was added all at once, affording a pale yellow solution. After stirring for 15 min pentadec-14-yn-1-ol (1.12 g, 5 mmol) was added in one portion. Stirring was continued for 12 h and the mixture poured into water. The product was extracted with ethyl acetate (3X). The combined organic phases were washed successively with water, and dilute HCl solution, dried over MgSO₄, and the solvent removed under reduced pressure using a rotary evaporator. The residue was purified by column chromatography on silica gel using ethyl acetate/hexane (20:80) as eluent. Yield: 0.784 g (70%). ¹H NMR (CDCl₃, 200 MHz): δ 3.64 (t, *J* = 6.5 Hz, 2H), 2.18 (td, *J* = 6.9, 2.5 Hz, 2H), 1.94 (t, *J* = 2.6 Hz, 1H), 1.64 (s, 1H), 1.59-1.45 (m, 4H), 1.44-1.19 (m, 18H). ¹³C NMR (CDCl₃, 100 MHz): δ 84.8, 68.0, 63.0, 32.7, 29.5, 29.5, 29.5, 29.4, 29.4, 29.0, 28.7, 28.4, 25.7, 18.3. MS (EI, 70 eV) *m/z* (relative intensity): 204 (5), 187 (41), 126 (44), 116 (64), 104 (100), 90 (97), 76 (47). HRMS: *m/z* calcd for C₁₅H₂₈O 224.2140, found 224.2144.

General Procedure for the Copper-Catalyzed Coupling Reaction of Alkynes with Iodides derivatives⁷: To a two-neck round-bottomed flask, under argon, were added the appropriate iodide (1 mmol), the pyrrolidine (3 mL) and the appropriate alkyne (1.2 mmol) at room temperature. The temperature was decreased to 0°C and copper iodide (0.038 g, 0.2 mmol) was added. The reaction mixture was allowed to stir at room temperature overnight. After this time, the solution was diluted by saturated NH₄OH/NH₄Cl aqueous solution (20 mL) and extracted with ethyl acetate (3 X 20 mL). The organic phase was separated, dried over MgSO₄, and the solvent removed under reduced pressure using a rotary evaporator. The residue was purified by column chromatography on silica gel using ethyl acetate/hexane as eluent.



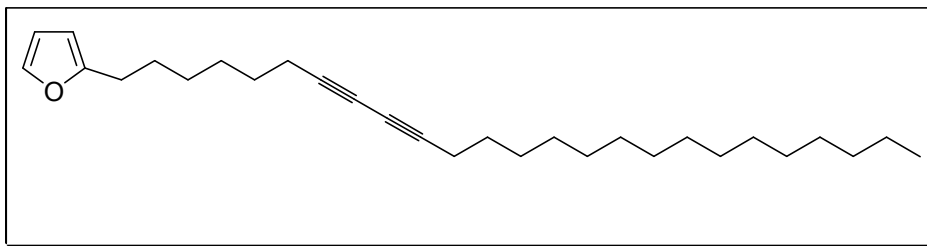
21-Furan-2-yl-henicosa-14,16-diyn-1-ol (4): Yield: 0.240 g (65%). ¹H NMR (CDCl₃, 200 MHz): δ 7.30-7.27 (m, 1H), 6.30-6.25 (m, 1H), 6.01-5.96 (m, 1H), 3.66-3.58 (m, 2H), 2.63 (t, *J* = 7.3

Hz, 2H), 2.30-2.20 (m, 4H), 1.77-1.70 (m, 2H), 1.61-1.46 (m, 10H), 1.41-1.22 (m, 14H). ¹³C NMR (CDCl₃, 100 MHz): δ 155.7, 140.7, 110.0, 104.8, 77.7, 68.0, 65.5, 65.1, 63.0, 32.8, 29.5, 29.5, 29.5, 29.4, 29.4, 29.4, 29.0, 28.8, 28.3, 27.7, 27.3, 27.1, 25.7, 19.1, 18.9. IR (KBr) (ν max, cm⁻¹) 3420, 3124, 2922, 2846, 2183, 2140, 1597, 1506, 1467, 1415, 1176, 1141, 1058, 1035, 1003, 883. MS (EI,

⁶ Abrams, S. R. *Can. J. Chem.* **1984**, 62, 1333-1334.

⁷ Alami, M.; Ferri, F. *Tetrahedron Lett.* **1996**, 37, 2763-2766.

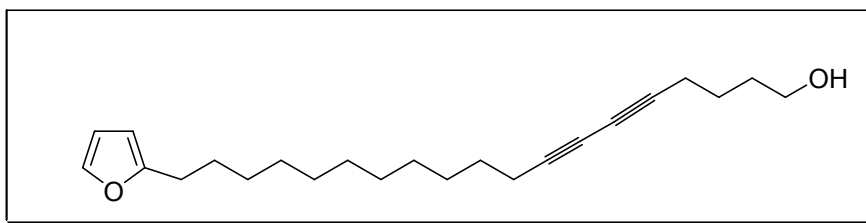
70 eV) m/z (relative intensity): 366 (27), 350 (4), 224 (14), 182 (67), 157 (100), 128 (94), 80 (80), 54 (46). HRMS: m/z calcd for $C_{25}H_{38}O_2$ 370.2872, found 370.2877.



2-Pentacosadiynyl-furan (3):

Yield: 0.356 g (89%). 1H NMR ($CDCl_3$, 400 MHz): δ 7.31-7.27 (m, 1H), 6.29-6.25 (m, 1H),

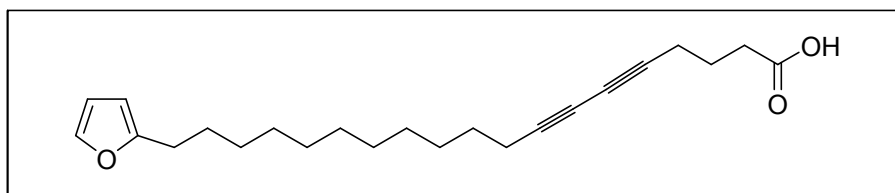
5.99-5.95 (m, 1H), 2.61 (t, $J = 7.4$ Hz, 2H), 2.24 (t, $J = 6.7$ Hz, 4H), 1.68-1.59 (m, 2H), 1.58-1.47 (m, 4H), 1.46-1.31 (m, 6H), 1.30-1.21 (m, 22H), 0.88 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.3, 140.6, 109.9, 104.5, 77.5, 77.2, 65.3, 65.2, 31.9, 29.6, 29.6, 29.6, 29.6, 29.6, 29.4, 29.3, 29.0, 28.8, 28.5, 28.4, 28.3, 28.1, 27.8, 27.8, 22.6, 19.1, 19.1, 14.0. MS (EI, 70 eV) m/z (relative intensity): 406 (21), 210 (30), 130 (40), 104 (36), 90 (53), 80 (100), 54 (25). IR (KBr) (ν max, cm^{-1}) 3128, 2911, 2843, 2180, 2141, 1599, 1506, 1469, 1418, 1175, 1138, 1069, 1005, 883. Anal. (%) Calc for $C_{29}H_{46}O$: C 84.81, H 11.29. Found: C 84.61, H 10.87.



19-Furan-2-yl-nonadeca-5,7-diynol (11):

Yield: 0.256 g (75%). 1H NMR ($CDCl_3$, 200 MHz): δ 7.33-7.27 (m, 1H), 6.20-6.24 (m, 1H),

5.99-5.92 (m, 1H), 3.67 (t, $J = 6.2$ Hz, 2H), 2.61 (t, $J = 7.4$ Hz, 2H), 2.39-2.16 (m, 5H), 1.75-1.54 (m, 6H), 1.39-1.19 (m, 16H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.6, 140.5, 109.9, 104.4, 77.6, 76.8, 65.6, 65.1, 62.1, 31.6, 29.4, 29.4, 29.3, 29.2, 29.0, 28.9, 28.7, 28.2, 27.9, 27.8, 24.5, 19.0, 18.9. MS (EI, 70 eV) m/z (relative intensity): 342 (1), 310 (5), 156 (22), 130 (29), 94 (53), 80 (100), 66 (19). Anal. (%) Calc for $C_{23}H_{34}O_2$: C 80.65, H 10.01. Found: C 80.44, H 9.78.



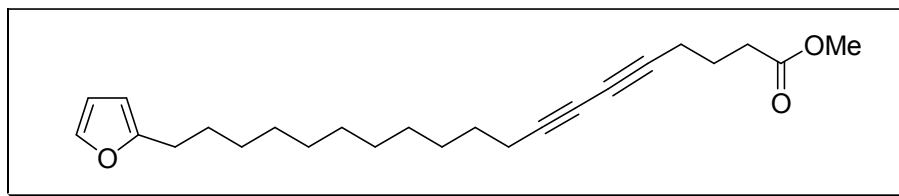
General Procedure for the Preparation of the 19-Furan-2-yl-nonadeca-5,7-diynoic Acid⁸ (1):

Pyridinium dichromate (PDC) (0.66 g, 1.75 mmol)

was added to the solution of alcohol (11) (0.17 g, 0.5 mmol) in DMF (1 mL). The mixture was stirred for 4 h and poured into water. The product was extracted with ethyl ether (3X). The organic extract was washed successively with water, and dilute HCl solution, dried over $MgSO_4$, and the solvent removed under reduced pressure using a rotary evaporator. The residue was purified by column chromatography on silica gel using ethyl acetate/hexane (40:60) as eluent. Yield: 0.872 g (49%). 1H NMR ($CDCl_3$, 400 MHz): δ 7.30-7.27 (m, 1H), 6.30-6.23 (m, 1H), 5.99-5.93 (m, 1H), 2.60 (t, $J =$

⁸ Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, 5, 399-402.

7.5 Hz, 2H), 2.49 (t, $J = 7.4$ Hz, 2H), 2.35 (t, $J = 6.9$ Hz, 2H), 2.24 (t, $J = 7.0$ Hz, 2H), 1.84 (quint, $J = 7.1$ Hz, 2H), 1.62 (quint, $J = 7.1$ Hz, 2H), 1.51 (quint, $J = 7.3$ Hz, 2H), 1.35-1.23 (m, 14H). ^{13}C NMR (CDCl_3 , 50 MHz): δ 179.1, 156.5, 140.5, 109.9, 104.4, 78.0, 75.6, 66.3, 64.9, 32.5, 29.5, 29.4, 29.4, 29.3, 29.1, 29.0, 28.7, 28.2, 27.9, 27.9, 23.1, 19.1, 18.5. IR (KBr) (ν_{max} , cm^{-1}) 3446-2370, 2918, 2846, 2150, 1690, 1598, 1508, 1463, 1443, 1412, 1205, 1180, 1009, 885. Anal. (%) Calc for $\text{C}_{23}\text{H}_{32}\text{O}_3$: C 77.49, H 9.05. Found: C 77.82, H 8.83.



General Procedure for the Preparation of the 19-Furan-2-yl-nonadeca-5,7-diynoic Acid Methyl Ester⁹ (2): To a solution of **1** (0.178 g, 0.5 mmol) in absolute

MeOH (1 mL) were added 0.03 mL of SOCl_2 . The reaction mixture was stirred at room temperature for 15 h, and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel using ethyl acetate/hexane (20:80) as eluent. Yield: 0.121 g (65%). ^1H NMR (CDCl_3 , 200 MHz): δ 7.30-7.27 (m, 1H), 6.29-6.25 (m, 1H), 5.98-5.94 (m, 1H), 3.67 (s, 3H), 2.60 (t, $J = 7.5$ Hz, 2H), 2.44 (t, $J = 7.3$ Hz, 2H), 2.33 (t, $J = 6.8$ Hz, 2H), 2.23 (t, $J = 7.0$ Hz, 2H), 1.84 (quint, $J = 7.0$ Hz, 2H), 1.62 (quint, $J = 7.3$ Hz, 2H), 1.50 (quint, $J = 7.3$ Hz, 2H), 1.34-1.22 (m, 14H). ^{13}C NMR (CDCl_3 , 50 MHz): δ 173.3, 156.5, 140.5, 109.9, 104.4, 77.9, 75.8, 66.2, 65.0, 51.5, 32.6, 29.4, 29.4, 29.3, 29.2, 29.1, 29.0, 28.7, 28.2, 27.9, 27.9, 23.4, 19.1, 18.6. IR (neat) (ν_{max} , cm^{-1}) 3462, 3115, 2924, 2852, 2256, 2164, 1597, 1506, 1462, 1435, 1159, 1148, 1074, 1074, 1107, 885. Anal. (%) Calc for $\text{C}_{24}\text{H}_{34}\text{O}_3$: C 77.80, H 9.25. Found: C 77.52, H 8.79.

⁹ Kazemi, F.; Kiasat, A. R.; Mombaini, B. *Phosphorus, Sulfur Silicon Relat. Elem.* **2004**, 179, 1187.

SELECTED SPECTRA

