Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Synthesis of Unsymmetrical 1,3-Butadiynes via Diyne Cross-Metathesis

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1. Crystallographic Details

Crystal data for molecule 4-(1,4-octadiynyl)toluene: Monoclinic, space group $P2_1/n$, a = 7.5687(3), b = 16.9200(5), c = 9.6449(4) Å, β = 109.885(4)°, Z = 4, V = 1161.50(7) Å^3, μ = 0.468 mm^{-1}. Data were recorded at 100 K on an Oxford Diffraction Nova diffractometer using mirror focused Cu-K_α radiation (λ = 1.54184 Å). The structure was refined on F^2 using the program SHELXL-97 (G.M. Sheldrick, University of Göttingen, Germany). Hydrogen atoms were included with a riding model, except for the CH_3 groups, which were incorporated as idealised methyl groups allowed to rotate but not tip. The final *wR*2 was 0.1088, with a conventional *R*1 of 0.0377, for 19029 mixed reflections and 2410 independent reflections. Complete data have been deposited at the Cambridge Crystallographic Data Centre under the number CCDC-935939. These data can be obtained free of charge from www.ccdc.cam.ac.uk/data_request/cif.

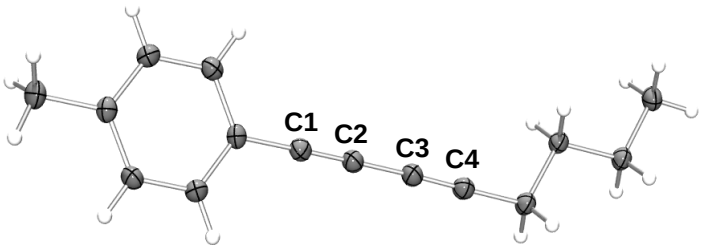


Figure S1. ORTEP presentation of the molecular structure of 4-(1,4-octadiynyl)toluene with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å] and angles [°]: C1-C2 1.2061(13), C2-C3 1.3783(12), C3-C4 1.2060(13); C1-C2-C3 178.87(9), C2-C3-C4 177.94(9).

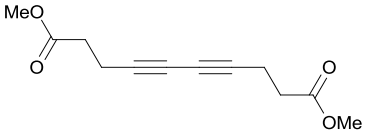
2. Synthetic and Analytical Details

2.1. Copper-catalysed homocoupling

General procedure for the copper-catalyzed homocoupling of terminal alkynes: To a solution of the alkyne (1 M) in DMSO was added CuCl or CuBr (10 mol%), and the reaction mixture was stirred under an oxygen atmosphere at 90 °C. The progress of the reactions was monitored by TLC, while the colour of the reaction mixtures changed from bright yellow to black. After completion, diethyl ether was added, and the mixtures were filtered through Celite. The DMSO phase was extracted with additional diethyl ether, and the combined ether phases were washed with a saturated NaCl solution. The ether phase was dried over $NaSO_4$,

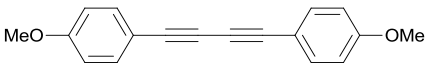
and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using hexane as eluent if not stated otherwise.

5,7-Dodecadiyne: This compound was prepared from 1-hexyne (6 g, 73 mmol) and copper(I) bromide (1.05 g, 7.3 mmol) in DMSO (73 mL). Isolated yield: 4.90 g (30.20 mmol, 83%); ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 0.90 (t, ^{3}J = 7.2 Hz, 6H, CH_3), 1.36-1.52 (m, 8H, CH_2), 2.24 (t, ^{3}J = 6.9 Hz, 4H, C≡CCH_2); ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz, 298 K): δ = 13.7 (s, *C*H_3), 19.0 (s, *n*Pr-*C*H_2), 22.1 (s, Me-*C*H_2), 30.5 (s, Et-*C*H_2), 65.4 (s, CH_2-C≡*C*), 77.6 (s, CH_2-*C*≡C). The analytical and spectroscopic data are in agreement with those reported in the literature.[1]



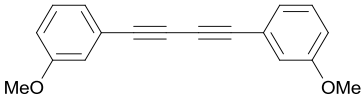
Dimethyl 4,6-decadiyne-1,10-dioate: The synthesis of the diester started with the esterification of 4-pentynoic acid.[2] Therefore, a few drops of sulfuric acid were added to a solution of 4-pentynoic acid (2.5 g, 25.49 mmol) in 50 mL of methanol, and the reaction mixture was refluxed for 12 h under an argon atmosphere. After completion of the reaction, the volume of the solvent was reduced, and a saturated $NaHCO_3$ solution was added. The aqueous phase was extracted three times with CH_2Cl_2, and the CH_2Cl_2 layer was washed with a saturated NaCl solution and dried over Na_2SO_4. Evaporation of CH_2Cl_2 afforded methyl-4-pentynoate as a colourless liquid. Isolated yield: 2.46 g (21.94 mmol, 86%); ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 1.91 (t, ^{4}J = 2.4 Hz, 1H, C≡C*H*), 2.40-2.53 (m, 4H, CH_2CH_2), 3.64 (s, 3H, OCH_3); ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz, 298 K): δ = 14.3 (s, C≡C*C*H_2), 33.1 (s, C=O*C*H_2), 51.8 (s, O*C*H_3), 69.0 (s, C≡*C*H), 82.4 (s, *C*≡CH), 172.1 (s, *C*=O).

The homocoupling to the 1,3-diyne was performed as described in the general procedure above. 2.46 g (21.94 mmol) of 4-pentynoate and 0.22 g (2.2 mmol) copper(I) chloride were dissolved in 21.9 mL of DMSO. A mixture of hexane/ethyl acetate (4:1, *v*/*v*) was used as eluent for purification by column chromatography. Isolated yield: 1.65 g (7.43 mmol, 68%); ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 2.43 (m, 8H, CH_2CH_2), 3.57 (s, 6H, OCH_3); ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz, 298 K): δ = 15.2 (s, C≡C-*C*H_2), 32.9 (s, C=O*C*H_2), 51.9 (s, O*C*H_3), 65.9 (s, CH_2-C≡*C*), 75.8 (s, CH_2-*C*≡C), 171.9 (s, *C*=O). The analytical and spectroscopic data are in agreement with those reported in the literature.[1]

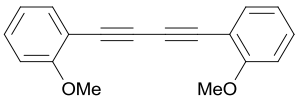


1,4-Bis(4-methoxyphenyl)-1,3-butadiyne: This compound was prepared from 4-ethynylanisole (3 g, 22.7 mmol) and copper(I) bromide (0.33 g, 2.3 mmol) in DMSO (22.7 mL). A mixture of hexane/ethyl acetate (4:1, *v*/*v*) was used as eluent for the purification by column

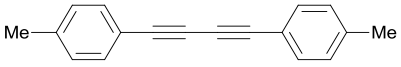
chromatography. Isolated yield: 2.70 g (10.29 mmol, 90%); ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 3.72 (s, 6H, OCH_3), 6.76 (d, ^{3}J = 9.0 Hz, 4H, Ph-H_m), 7.37 (d, ^{3}J = 8.9 Hz, 4H, Ph-H_o); ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz, 298 K): δ = 55.5 (s, OCH_3), 73.1 (s, *p*-AnisolC≡*C*), 81.4 (s, *p*-Anisol-*C*≡C), 114.1 (s, *p*-Anisol-C_i-C≡C), 114.3 (s, *p*-Anisol-C_m), 134.2 (s, *p*-Anisol-C_o), 160.4 (s, 6H, *p*-Anisol-C_pOCH_3). The analytical and spectroscopic data are in agreement with those reported in the literature.[3]



1,4-Bis(3-methoxyphenyl)-1,3-butadiyne: This compound was prepared from 3-ethynylanisole (2 g, 15.1 mmol) and copper(I) chloride (0.15 g, 1.5 mmol) in DMSO (15.1 mL). A mixture of hexane/ethyl acetate (4:1, *v*/*v*) was used as eluent for purification by column chromatography. Isolated yield: 1.51 g (5.76 mmol, 76%); ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 3.72 (s, 6H, OCH_3), 6.83-6.87 (m, 2H, *m*-Anisol-*H-4*), 6.96-6.97 (m, 2H, *m*-Anisol-*H-6*), 7.03-7.06 (m, 2H, *m*-Anisol-*H-5*), 7.14-7.19 (m, 2H, *m*-Anisol-*H-2*); ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz, 298 K): δ = 55.4 (s, OCH_3), 73.8 (s, *m*-Anisol-C≡*C*), 81.7 (s, *m*-Anisol-*C*≡C), 116.2 (s, *m*-Anisol-*C-4*), 117.2 (s, *m*-Anisol-*C-2*), 122.8 (s, *m*-Anisol-*C-1*), 125.2 (s, *m*-Anisol-*C-6*), 129.7 (*m*-Anisol-*C-5*), 159.5 (s, *m*-Anisol-*C-3*). The analytical and spectroscopic data are in agreement with those reported in the literature.[3]

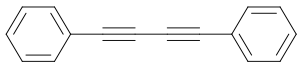


1,4-Bis(2-methoxyphenyl)-1,3-butadiyne: This compound was prepared from 2-ethynylanisole (1 g, 7.6 mmol) and copper(I) chloride (0.08 g, 0.8 mmol) in DMSO (7.6 mL). A mixture of hexane/ethyl acetate (4:1, *v*/*v*) was used as eluent for purification by column chromatography. Isolated yield: 810 mg (3.09 mmol, 81%); ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 3.82 (s, 6H, OCH_3), 6.79-6.86 (m, 4H, *o*-Anisol-*H-3*, *H-5*), 7.21-7.27 (m, 2H, *o*-Anisol-*H-4*), 7.39-7.42 (m, 2H, *o*-Anisol-*H-6*); ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz, 298 K): δ = 56.0 (s, OCH_3), 78.1 (s, *o*-Anisol-C≡*C*), 78.8 (s, *o*-Anisol-*C*≡C), 110.8 (s, *o*-Anisol-*C-3*), 111.5 (s, *o*-Anisol-*C-1*), 120.6 (s, *o*-Anisol-*C-5*), 130.7 (s, *o*-Anisol-*C-4*), 134.5 (*o*-Anisol-*C-6*), 161.5 (s, *o*-Anisol-*C-2*). The analytical and spectroscopic data are in agreement with those reported in the literature.[3]

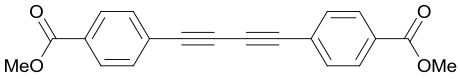


1,4-Bis(4-methylphenyl)-1,3-butadiyne: This compound was prepared from 4-ethynyltoluene (2 g, 17.2 mmol) and copper(I) chloride (0.17 g, 1.7 mmol) in DMSO (17.2 mL). Isolated yield: 1.3 g (5.6 mmol, 66%); ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 2.37 (s, 6H, CH_3), 7.13-7.16 (dm, ^{3}J = 7.9 Hz, 4H, Ph-H_m), 7. 41-7.44 (dm, ^{3}J = 8.1 Hz, 4H, Ph-H_o); ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz, 298

K): δ = 21.9 (s, *p*-Tol-CH_3), 73.6 (s, *p*-Tol-C≡*C*), 81.7 (s, *p*-Tol-*C*≡C), 118.9 (s, *p*-Tol-C_iC≡C), 129.4 (s, *p*-Tol-C_m), 132.5 (s, *p*-Tol-C_o), 139.6 (s, *p*-Tol-$C_p$$CH_3$). The analytical and spectroscopic data are in agreement with those reported in the literature.[3]



1,4-Diphenyl-1,3-butadiyne: This compound was prepared from ethynylbenze (5 g, 49 mmol) and copper(I) chloride (0.49 g, 4.9 mmol) in DMSO (49 mL). Isolated yield: 2,97 g (14.69 mmol; 60%); ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 7.22-7.32 (m, 6H, Ph-*H*), 7.43-7.47 (m, 4H, Ph-*H*); ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz, 298 K): δ = 74.1 (s, Ph-C≡*C*), 81.7 (s, Ph-*C*≡C), 122.0 (s, Ph-C_i), 128.6 (s, Ph-C_m), 129.3 (s, Ph-C_p), 132.6 (s, Ph-C_o). The analytical and spectroscopic data are in agreement with those reported in the literature.[3]

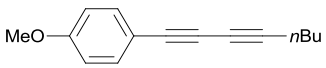


Dimethyl 4,4'-(1,3-butadiyne-1,4-diyl)dibenzoate: This compound was prepared from methyl 4-ethynylbenzoate (1 g, 6.24 mmol) and copper(I) chloride (0.06 g, 0.6 mmol) in DMSO (6.2 mL). Ethyl acetate was added after completion of the reaction instead of diethyl ether. For purification by column chromatography, toluene was used as eluent. Isolated yield: 616 mg (1.93 mmol, 62%); ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 3.93 (s, 6H, OCH_3), 7.59 (d, ^3J = 8.7 Hz, 4H, *p*-Carbomethoxyphenyl-H_o), 8.03 (d, ^3J, = 8.7 Hz, 4H, *p*-Carbomethoxyphenyl-H_m) ; ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz, 298 K): δ = 52.5 (s, O*C*H_3), 76.4 (s, *p*-Carbomethoxyphenyl-C≡*C*), 82.0 (s, *p*-Carbomethoxyphenyl-*C*≡C), 126.3 (s, *p*-Carbomethoxyphenyl-C_iC≡C), 129.7 (s, *p*-Carbomethoxyphenyl-C_m), 130.7 (s, *p*-Carbomethoxyphenyl-C_p), 132.6 (s, *p*-Carbomethoxyphenyl-C_o), 166.4 (s, *C*=O). The analytical and spectroscopic data are in agreement with those reported in the literature.[4]

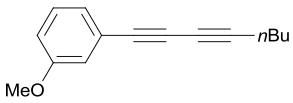
2.2. Diyne cross-metathesis

General procedure for diyne cross-metathesis: 2 mol% of the tungsten benzylidyne catalyst **1** were added to a solution of substrate **2** (0.025 M) and substrate **2'** (0.1 M), which is used in excess (4x), in dichloromethane. The reaction mixture was stirred at room temperature and after completion of the reaction, was filtered through alumina and washed with dichloromethane. The solvent was removed *in vacuo* and dried under high vacuum. The 1,3-diynes were separated by flash chromatography using silica gel as stationary and hexane as mobile phase if not stated otherwise. The yields of **3** are based on the conversion of the minor starting material **2**, the recovery rates of the starting materials **2** and **2'** are based on the maximum amounts (100%) that could be re-isolated based on the yields of **3**. The entry

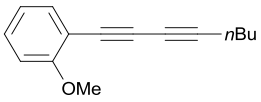
numbers refer to Table 1 in the manuscript. In some cases, where quantitative recovery rates (quant.) are stated, the calculated values actually slightly exceed 100%, which suggests an incorrect mass balance. However, this can be easily explained by weighing errors or incomplete evaporation of the solvent after purification by chromatography.



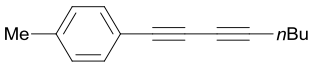
1-(4-Methoxyphenyl)-1,3-octadiyne (Entry 1): This compound was prepared from 1,4-bis(4-methoxyphenyl)-1,3-butadiyne (**2**, 170 mg, 0.65 mmol), 5,7-dodecadiyne (**2'**, 422 mg, 2.6 mmol) and the tungsten benzylidyne catalyst (**1**, 69 mg, 0.065 mmol) in DCM (26 mL). Isolated yield of **3**: 211 mg (0.99 mmol, 76%). Recovered starting materials: **2** (39 mg, 0.15 mmol, 96%); **2'** (290 mg, 1.8 mmol, 86%). ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 0.85 (t, ^{3}J = 7.2 Hz, 3H, CH_3), 1.31-1.53 (m, 4H, Me-CH_2, Et-CH_2), 2.28 (t, ^{3}J = 6.9 Hz, *n*Pr-CH_2), 3.73 (s, 3H, *p*-Anisol-OCH_3), 6.75 (d, ^{3}J = 9.0 Hz, 2H, *p*-Anisol-H_m), 7.33 (d, ^{3}J = 9.0 Hz, 2H, *p*-Anisol-H_o); ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz, 298 K): δ = 13.7 (s, *C*H$_3$), 19.4 (s, *n*Pr-*C*H$_2$), 22.1 (s, Me-*C*H$_2$), 30.5 (s, Et-*C*H$_2$), 55.4 (s, *p*-Anisol-O*C*H$_3$), 65.3 (s, *n*Bu-C≡*C*), 73.3 (s, *p*-Anisol-C≡*C*), 75.0 (s, *n*Bu-*C*≡C), 84.3 (s, *p*-Anisol-*C*≡C), 114.17 (s, *p*-Anisol-C_iC≡C), 114.21 (s, *p*-Anisol-C_m), 134.2 (s, *p*-Anisol-C_o), 160.2 (s, *p*-Anisol-C_pOCH$_3$); Elemental analysis calcd. for $C_{15}H_{16}O$: C 84.87, H 7.60; found C 84.69, H 7.71.



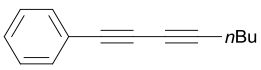
1-(3-Methoxyphenyl)-1,3-octadiyne (Entry 2): This compound was prepared from 1,4-bis(3-methoxyphenyl)-1,3-butadiyne (**2**, 170 mg, 0.65 mmol), 5,7-dodecadiyne (**2'**, 422 mg, 2.6 mmol) and the tungsten benzylidyne catalyst (**1**, 69 mg, 0.065 mmol) in DCM (26 mL). Isolated yield of **3**: 229 mg (1.08 mmol, 83%). Recovered starting materials: **2** (27 mg, 0.10 mmol, 91%); **2'** (330 mg, 2.03 mmol, 99%). ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 0.85 (t, ^{3}J = 7.2 Hz, 3H, CH_3), 1.31-1.53 (m, 4H, Me-*C*H$_2$, Et-CH_2), 2.28 (t, ^{3}J = 6.9 Hz, 2H, *n*Pr-CH_2), 3.70 (s, 3H, *m*-Anisol-OCH_3), 6.79-6.83 (m, 1H, *m*-Anisol-*H-4*), 6.91-6.92 (m, 1H, *m*-Anisol-*H-6*), 6.97-7.00 (m, 1H, *m*-Anisol-*H-5*), 7.10-7.18 (m, 1H, *m*-Anisol-*H-2*); ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz, 298 K): δ= 13.7 (s, *C*H$_3$), 19.4 (s, *n*Pr-*C*H$_2$), 22.1 (s, Me-*C*H$_2$), 30.4 (s, Et-*C*H$_2$), 55.4 (s, *m*-Anisol-O*C*H$_3$), 65.1 (s, *n*Bu-C≡*C*), 74.4 (s, *m*-Anisol-C≡*C*), 74.7 (s, *n*Bu-*C*≡C), 85.0 (s,*m*-Anisol-*C*≡C), 115.7 (s, *m*-Anisol-C-4), 117.2 (s, *m*-Anisol-C-2), 123.2 (s, *m*-Anisol-C-1), 125.2 (s, *m*-Anisol-C-6), 129.5 (*m*-Anisol-C-5), 159.4 (s, *m*-Anisol-C-3); Elemental analysis calcd. for $C_{15}H_{16}O$: C 84.87, H 7.60; found: C 85.17, H 7.88. The analytical and spectroscopic data are in agreement with those reported in the literature.[5]



1-(2-Methoxyphenyl)-1,3-octadiyne (Entry 3): This compound was prepared from 1,4-bis(2-methoxyphenyl)-1,3-butadiyne (**2**, 170 mg, 0.65 mmol), 5,7-dodecadiyne (**2'**, 422 mg, 2.6 mmol) and the tungsten benzylidyne catalyst (**1**, 69 mg, 0.065 mmol) in DCM (26 mL). After re-isolation of dodecadiyne, the mobile phase was switched to a mixture of hexane/ethyl acetate (5:95, *v*/*v*). Isolated yield of **3**: 178 mg (0.84 mmol, 65%). Recovered starting materials: **2** (60 mg, 0.23 mmol, 100%); **2'** (330 mg, 2.03 mmol, 93%). ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 0.85 (t, ^{3}J = 7.2 Hz, 3H, CH_3), 1.31-1.53 (m, 4H, Me-CH_2, Et-CH_2), 2.29 (t, ^{3}J = 6.9 Hz, *n*Pr-CH_2), 3.79 (s, 3H, *o*-Anisol-OCH_3), 6.76-6.83 (m, 2H, *o*-Anisol-*H-3*, *o*-Anisol-*H-5*), 7.18-7.24 (m, 1H, *o*-Anisol-*H-4*), 7.34-7.37 (m, 1H, *o*-Anisol-*H-6*); ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz, 298 K): δ = 13.7 (s, CH_3), 19.5 (s, *n*Pr-CH_2), 22.1 (s, Me-CH_2), 30.4 (s, Et-CH_2), 55.9 (s, *o*-Anisol-OCH_3), 65.4 (s, *n*Bu-C≡*C*), 71.2 (s, *o*-Anisol-C≡*C*), 78.3 (s, *n*Bu-*C*≡C), 85.5 (s, *o*-Anisol-*C*≡C), 110.7 (s, *o*-Anisol-*C-3*), 111.5 (s, *o*-Anisol-*C-1*), 120.6 (s, *o*-Anisol-*C-5*), 130.3 (s, *o*-Anisol-*C-4*), 134.6 (*o*-Anisol-*C-6*), 161.5 (s, *o*-Anisol-*C-2*); Elemental analysis calcd. for $C_{15}H_{16}O$: C 84.87, H 7.60; found: C 84.41, H 7.74.

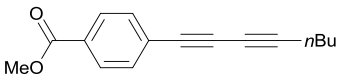


1-(4-Methylphenyl)-1,3-octadiyne (Entry 4): This compound was prepared from 1,4-bis(4-methylphenyl)-1,3-butadiyne (**2**, 150 mg, 0.65 mmol), 5,7-dodecadiyne (**2'**, 422 mg, 2.6 mmol) and the tungsten benzylidyne catalyst (**1**, 69 mg, 0.065 mmol) in DCM (26 mL). Isolated yield of **3**: 191 mg (0.97 mmol, 75%). Recovered starting materials: **2** (32 mg, 0.14 mmol, 85%); **2'** (288 mg, 1.77 mmol, 84%). ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 0.85 (t, ^{3}J = 7.2 Hz, 3H, CH_3), 1.31-1.53 (m, 4H, Me-CH_2, Et-CH_2), 2.26 (s, 3H, PhCH_3), 2.26 (t,^{3}J = 6.8 Hz, 2H, *n*Pr-CH_2), 7.01-7.04 (dm, ^{3}J = 7.9 Hz, 2H, *p*-Tol-*H*$_m$), 7.27-7.31 (dm, ^{3}J = 8.1 Hz, 2H, *p*-Tol-*H*$_o$); ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz, 298 K): δ = 13.7 (s, CH_3), 19.4 (s, *n*Pr-CH_2), 21.7 (s, Ph-CH_3), 22.1 (s, Me-CH_2), 30.5 (s, Et-CH_2), 65.3 (s, *n*Bu-C≡*C*), 73.9 (s, *p*-Tol-C≡*C*), 75.1 (s, *n*Bu-*C*≡C), 84.6 (s, *p*-Tol-*C*≡C), 119.1 (s, *p*-Tol-*C*$_i$C≡C), 129.3 (s, *p*-Tol-*C*$_m$), 132.5 (s, *p*-Tol-*C*$_o$), 139.2 (s, *p*-Tol-*C*$_p$CH$_3$); Elemental analysis calcd. for $C_{15}H_{16}$: C 91.78, H 8.22; found C 91.72, H 8.41.

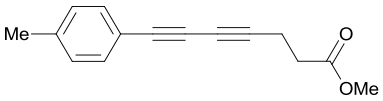


1-Phenyl-1,3-octadiyne (Entry 5): This compound was prepared from 1,4-diphenyl-1,3-butadiyne (**2**, 131 mg, 0.65 mmol), 5,7-dodecadiyne (**2'**, 422 mg, 2.6 mmol) and the tungsten benzylidyne catalyst (**1**, 69 mg, 0.065 mmol) in DCM (26 mL). Isolated yield of **3**: 147 mg (0.81 mmol, 62%). Recovered starting materials: **2** (19 mg, 0.09 mmol, 36%); **2'** (260 mg, 1.6 mmol, 73%). ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 0.86 (t, ^{3}J = 7.2 Hz, 3H, CH_3), 1.34-1.52 (m, 4H, Me-CH_2, Et-CH_2), 2.29 (t, ^{3}J = 6.9 Hz,

2H, *n*Pr-C*H*$_2$), 7.17-7.24 (m, 3H, Ph-*H*), 7.38-7.41 (m, 2H, Ph-*H*); ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz, 298 K): δ = 13.5 (s, *C*H$_3$), 19.3 (s, *n*Pr-*C*H$_2$), 21.9 (s, Ph-*C*H$_3$), 30.3 (s, Etl-*C*H$_2$), 65.0 (s, *n*Bu-*C*≡*C*), 74.4 (s, Ph-*C*≡*C*), 74.7 (s, Ph-*C*≡*C*), 84.8 (s, *n*Bu-*C*≡*C*), 122.1 (s, Ph-*C*$_i$C≡C), 128.3 (s, Ph-*C*$_m$), 128.8 (s, Ph-*C*$_p$), 132.5 (s, Ph-*C*$_o$); Elemental analysis calcd. for $C_{14}H_{14}$: C 92.26, H 7.74; found: C 91.53, H 8.01.

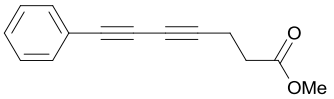


Methyl 4-(5,7-octadiynyl)benzoate (Entry 6): This compound was prepared from dimethyl 4,4'-(1,3-butadiyne-1,4-diyl)dibenzoate (**2**, 131 mg, 0.41 mmol), 5,7-dodecadiyne (**2'**, 265 mg, 1.64 mmol) and the tungsten benzylidyne catalyst (**1**, 44 mg, 0.041 mmol) in DCM (16.4 mL). After re-isolation of dodecadiyne, the mobile phase was switched to dichloromethane. Isolated yield of **3**: 149 mg (0.62 mmol, 76%). Recovered starting materials: **2** (32 mg, 0.10 mmol, quant.); **2'** (197 mg, 1.21 mmol, 91%). ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 0.86 (t, ^3J = 7.2 Hz, 3H, C*H*$_3$), 1.32-1.55 (m, 4H, Me-C*H*$_2$, Et-C*H*$_2$), 2.31 (t, ^3J = 6.9 Hz, 2H, *n*Pr-C*H*$_2$), 3.84 (s, 3H, OC*H*$_3$), 7.43-7.47 (dm, ^3J = 8.7 Hz, 2H, *p*-Carbomethoxyphenyl-*H*$_o$), 7.87-7.91 (dm, ^3J = 8.6 Hz, 2H, *p*-Carbomethoxyphenyl-*H*$_m$); ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz, 298 K): δ = 13.7 (s, *C*H$_3$), 19.5 (s, *n*Pr-*C*H$_2$), 22.1 (s, Me-*C*H$_2$), 30.3 (s, Et-*C*H$_2$), 52.4 (s, O*C*H$_3$), 65.0 (s, *n*Bu-C≡*C*), 73.9 (s, *p*-Carbomethoxyphenyl-C≡*C*), 77.5 (s, *n*Bu-*C*≡C), 86.7 (s, *p*-Carbomethoxyphenyl-*C*≡C), 127.1 (s, *p*-Carbomethoxyphenyl-*C*$_i$C≡C), 129.6 (s, *p*-Carbomethoxyphenyl-*C*$_m$), 130.1 (s, *p*-Carbomethoxyphenyl-*C*$_p$), 132.5 (s, *p*-Carbomethoxyphenyl-*C*$_o$), 166.5 (s, C=O); Elemental analysis calcd. for $C_{16}H_{16}O_2$: C 79.97, H 6.71; found C 79.54, H 6.70.

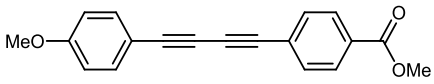


Methyl 7-(4-methylphenyl)-4,6-heptadiynoate (Entry 7): This compound was prepared from 1,4-bis(4-methylphenyl)-1,3-butadiyne (**2**, 150 mg, 0.65 mmol), dimethyl 4,6-decadiyne-1,10-dioate (**2'**, 578 mg, 2.6 mmol) and the tungsten benzylidyne catalyst (**1**, 69 mg, 0.065 mmol) in DCM (26 mL). After re-isolation of dodecadiyne, the mobile phase was switched to a mixture of hexane/ethyl acetate (5:95, *v*/*v*). Isolated yield of **3**: 239 mg (1.06 mmol, 81%). Recovered starting materials: **2** (31 mg, 0.13 mmol, quant.); **2'** (439 mg, 1.98 mmol, 95%).^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ = 2.27 (s, 3H, C*H*$_3$), 2.47-2.66 (m, 4H, C=OC*H*$_2$C*H*$_2$), 3.64 (s, 3H, OC*H*$_3$), 7.01-7.05 (dm, ^3J = 7.9 Hz, 2H, *p*-Tol-*H*$_m$), 7. 27-7.33 (dm, ^3J = 8.2 Hz, 2H, *p*-Tol-*H*$_o$); ^{13}C {^{1}H} NMR ($CDCl_3$, 50 MHz, 298 K): δ = 15.6 (s, C≡C*C*H$_2$), 21.7 (s, *p*-Tol-*C*H$_3$), 32.9 (s, C=O*C*H$_2$), 52.0 (s, O*C*H$_3$), 66.1 (s, MeOCOEt-C≡*C*), 73.5 (s,*p*-Tol-C≡*C*), 75.8 (s, MeOCOEt-*C*≡C), 81.9 (s, *p*-Tol-*C*≡C), 118.8 (s, *p*-Tol-*C*$_i$C≡C),

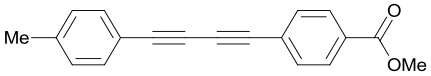
129.3 (s, *p*-Tol-C_m), 132.6 (s, *p*-Tol-C_o), 139.5 (s, *p*-Tol-$C_p$$CH_3$), 171.9 (s, *C*=O); Elemental analysis calcd. for $C_{15}H_{14}O_2$: C 79.62, H 6.24; found C 79.15, H 6.30.



Methyl 7-phenyl-4,6-heptadiynoate (Entry 8): This compound was prepared from 1,4-diphenyl-1,3-butadiyne (**2**, 131 mg, 0.65 mmol), dimethyl 4,6-decadiyne-1,10-dioate (**2'**, 578 mg, 2.6 mmol) and the tungsten benzylidyne catalyst (**1**, 69 mg, 0.065 mmol) in DCM (26 mL). After re-isolation of dodecadiyne, the mobile phase was switched to a mixture of hexane/ethyl acetate (5:95, v/v). Isolated yield of **3**: 218 mg (1.03 mmol, 79%). Recovered starting materials: **2** (26 mg, 0.13 mmol, 96%); **2'** (439 mg, 1.98 mmol, 95%). ^{1}H NMR (CDCl3, 200 MHz, 298 K): δ = 2.48-2.71 (m, 4H, C=OCH2CH2), 3.65 (s, 3H, OCH3), 7.17-7.34 (m, 3H, Ph-H), 7.36-7.44 (m, 2H, Ph-H); ^{13}C{1H} NMR (CDCl3, 50 MHz, 298 K): δ = 15.6 (s, C≡CCH2), 32.9 (s, C=OCH2), 52.1 (s, OCH3), 66.0 (s, MeOCOEt-C≡C), 74.2 (s, Ph-C≡C), 75.6 (s, MeOCOEt-C≡C), 82.3 (s, Ph-C≡C), 122.0 (s, Ph-Ci), 128.5 (s, Ph-Cm), 129.1 (s, Ph-Cp), 132.7 (s, Ph-Co), 172.0 (s, C=O); Elemental analysis calcd. for C19H14O2: C 79.22, H 5.70; found.: C 78.82, H 5.82.



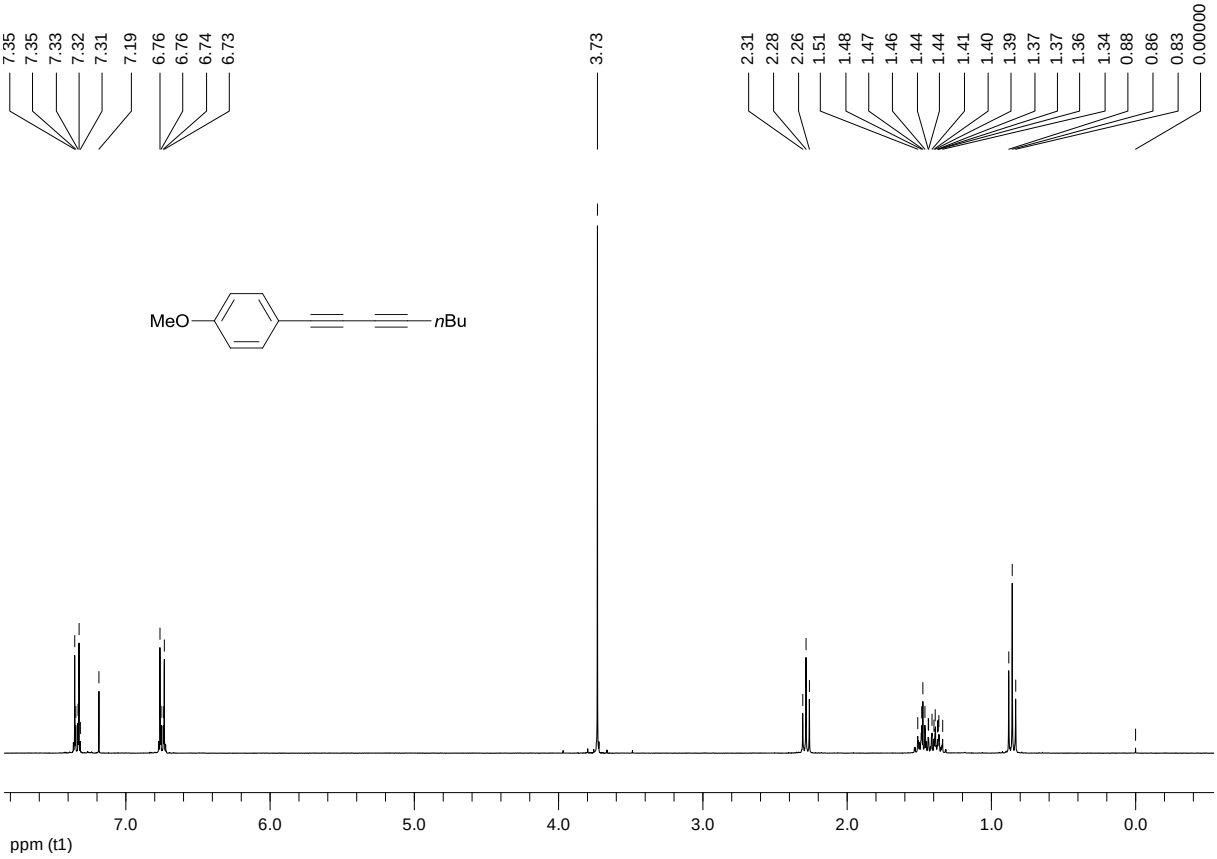
Methyl 4-(4-methoxyphenyl-1,3-butadiynyl)benzoate (Entry 9): This compound was prepared from dimethyl 4,4'-(1,3-butadiyne-1,4-diyl)dibenzoate (**2**, 207 mg, 0.65 mmol), 1,4-bis(4-methoxyphenyl)-1,3-butadiyne (**2'**, 682 mg, 2.60 mmol) and the tungsten benzylidyne catalyst (**1**, 69 mg, 0.065 mmol) in DCM (26 mL). After re-isolation of dodecadiyne, the mobile phase was switched to a mixture of hexane/ethyl acetate (5:95, v/v). Isolated yield of **3**: 306 mg (1.05 mmol, 87%). Recovered starting materials: **2** (30 mg, 0.09 mmol, 72%); **2'** (532 mg, 2.03 mmol, 98%). ^{1}H-NMR ($CDCl_3$, 300 MHz, 298 K): δ [ppm] = 3.84 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 6.96 (d, $^3J_{HH}$ = 7.9 Hz, 2H, *p*-Anisol-H_m), 7.45 (d, $^3J_{HH}$ = 8.1 Hz, 2H, *p*-Anisol-H_o); 7.67 (d, $^3J_{HH}$ = 8.7 Hz, 2H, *p*-Carbomethoxyphenyl-H_o), 7.92 (d, $^3J_{HH}$ = 8.7 Hz, 2H, *p*-Carbomethoxyphenyl-H_m);^{13}C {^{1}H}-NMR ($CDCl_3$, 75 MHz, 298 K): δ [ppm] = 52.3 (s, OCH_3), 55.8 (s, OCH_3),72.0 (s, *C*≡*C*), 75.2 (s, *C*≡*C*), 79.9 (s, *C*≡*C*), 83.0 (s, *C*≡*C*), 113.3 (s, *p*-Anisol-C_iC≡C), 125.6 (s, *p*-Carbomethoxyphenyl-C_iC≡C), 128.3 (s, *p-Carbomethoxy-phenyl-*C_m), 132.5 (s, *p*-Carbomethoxy-phenyl-C_p), 130.2 (s, *p*-Carbomethoxyphenyl-C_p), 132.3 (s, *p*-Tol-C_o), 132.5 (s, *p*-Carbomethoxyphenyl-C_o), 162.0 (s, *p*-Anisol-C_p -OCH_3), 165.3 (s, *C*=O); Elementaranalyse ber. für $C_{19}H_{14}O_3$: C 78.61, H 4.86; found: C 78.95, H 5.17.

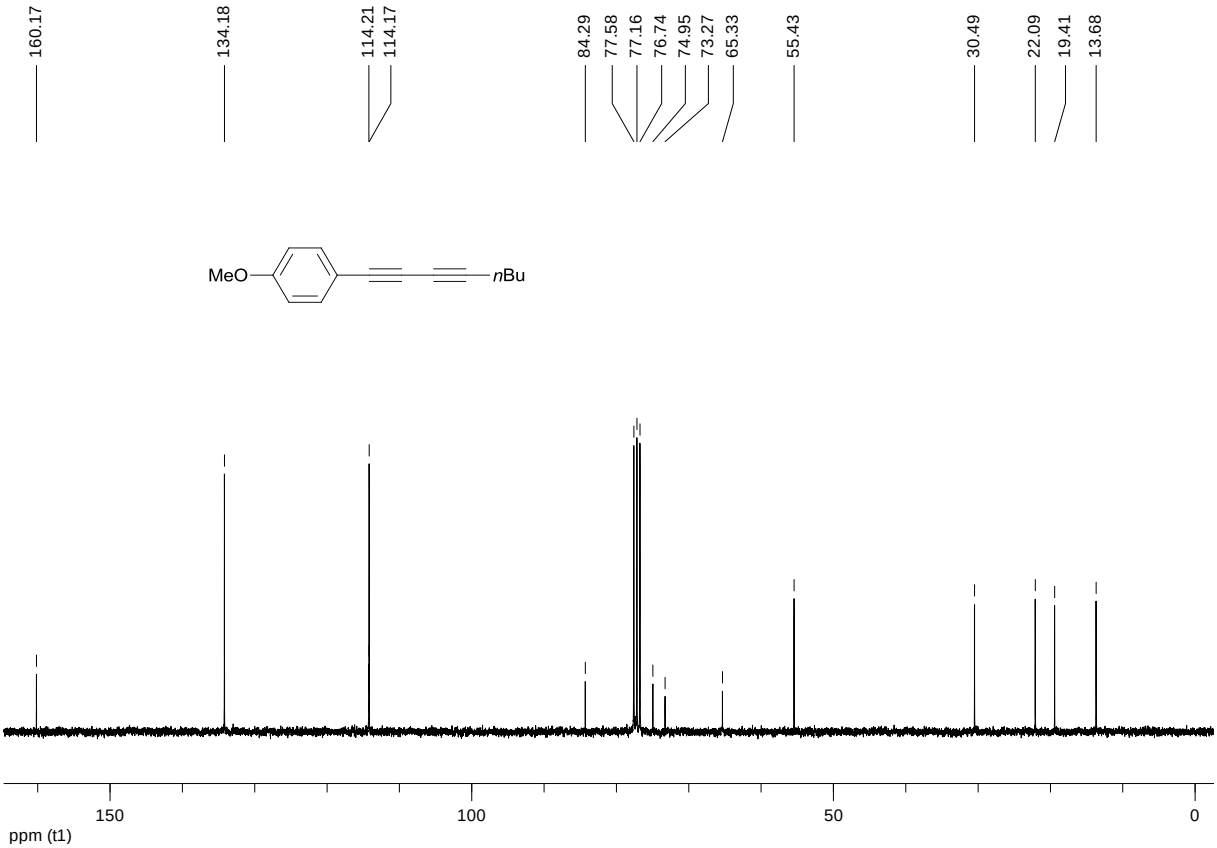


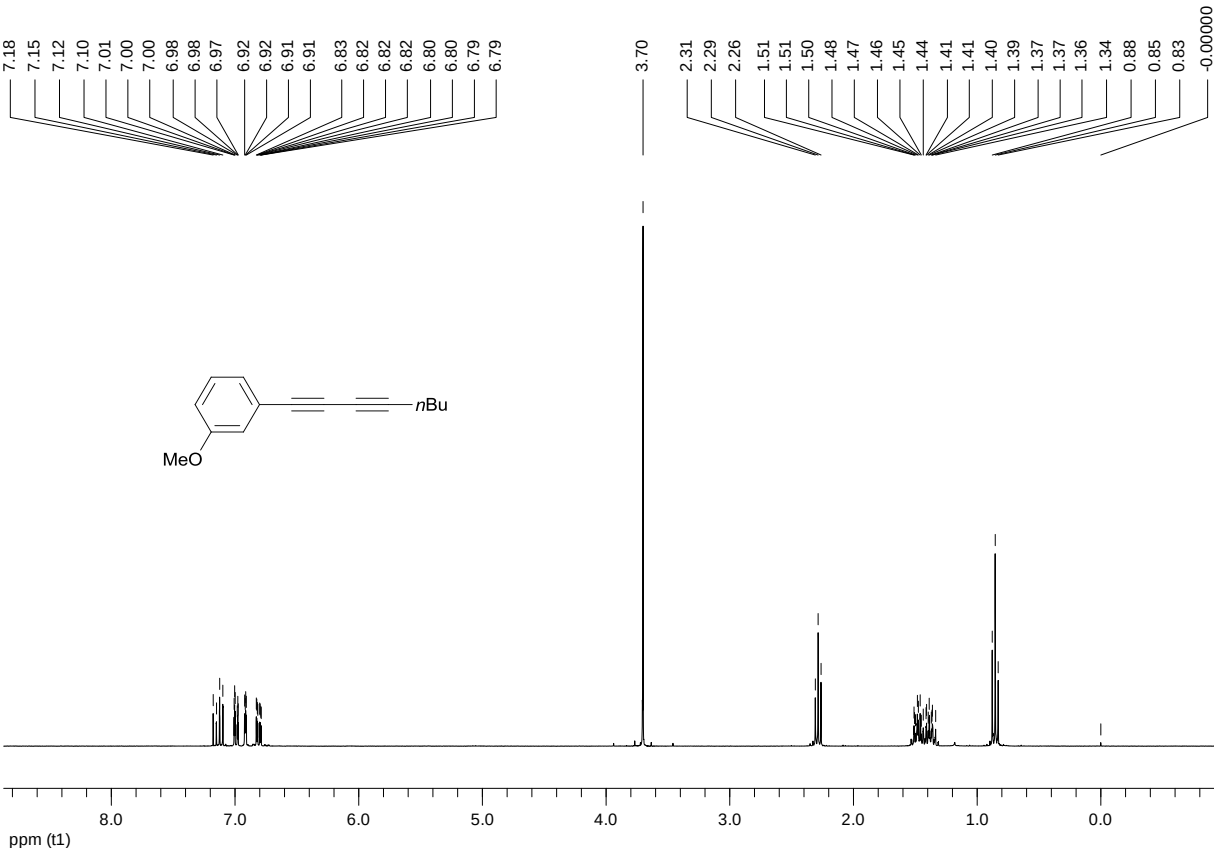
Methyl 4-(4-methylphenyl-1,3-butadiynyl)benzoate (Entry 10): This compound was prepared from dimethyl 4,4'-(1,3-butadiyne-1,4-diyl)dibenzoate (**2**, 131 mg, 0.41 mmol), 1,4-bis(4-methylphenyl)-1,3-butadiyne (**2'**, 376 mg, 1.64 mmol), and the tungsten benzylidyne catalyst (**1**, 44 mg, 0.041 mmol) in DCM (16.4 mL). After re-isolation of dodecadiyne, the mobile phase was switched to a mixture of hexane/ethyl acetate (5:95, *v*/*v*). Isolated yield of **3**: 191 mg (0.70 mmol, 85%). Recovered starting materials: **2** (16 mg, 0.05 mmol, 83%); **2'** (302 mg, 1.31 mmol, quant.). ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 2.29 (s, 3H, PhCH_3), 3.84 (s, 3H, OCH_3), 7.05-7.09 (dm, ^{3}J = 7.9 Hz, 2H, *p*-Tol-H_m), 7.33-7.37 (dm, ^{3}J = 8.1 Hz, 2H, *p*-Tol-H_o); 7.47-7.51 (dm, ^{3}J = 8.7 Hz, 2H, *p*-Carbomethoxyphenyl-H_o), 7.90-7.94 (dm, ^{3}J = 8.7 Hz, 2H, *p*-Carbomethoxyphenyl-H_m); ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz, 298 K): δ = 21.8 (s, Ph-CH$_3$), 52.4 (s, OCH$_3$), 73.2 (s, C≡C), 77.1 (s, C≡C), 80.3 (s, C≡C), 83.6 (s, C≡C), 118.5 (s, *p*-Tol-C_iC≡C), 126.8 (s, *p*-Carbomethoxyphenyl-C_iC≡C), 129.4 (s, *p*-Tol-C_m), 129.7 (s, *p*-Carbomethoxy-phenyl-C_m), 130.3 (s, *p*-Carbomethoxyphenyl-C_p), 132.5 (s, *p*-Tol-C_o), 132.6 (s, *p*-Carbomethoxyphenyl-C_o), 140.1 (s, *p*-Tol-C_pCH$_3$), 166.5 (s, C=O); Elemental analysis calcd. for $C_{19}H_{14}O_2$: C 83.19, H 5.14; found C 83.07, H 5.37.

Methyl 4,6-undecadiynoate (Entry 11): This compound was prepared from dimethyl 4,6-decadiyne-1,10-dioate (**2**, 144 mg, 0.65 mmol, 5,7-dodecadiyne (**2'**, 422 mg, 2.6 mmol) and the tungsten benzylidyne catalyst (**1**, 69 mg, 0.065 mmol) in DCM (26 mL). After re-isolation of dodecadiyne, the mobile phase was switched to dichloromethane. Isolated yield of **3**: 209 mg (1.09 mmol, 84%). Recovered starting materials: **2** (30 mg, 0.14 mmol, quant.); **2'** (332 mg, 2.05 mmol, 100%). ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 0.83 (t, ^{3}J = 7.1 Hz, 3H, CH_3), 1.27-1.48 (m, 4H, Me-CH_2, Et-CH_2), 2.18 (t, ^{3}J = 6.7 Hz, 2H, *n*Pr-CH_2), 2.42-2.60 (m, 4H, C=OCH_2CH_2), 3.63 (s, 3H, OCH_3); ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz, 298 K): δ = 13.6 (s, CH$_3$), 15.3 (s, C≡CCH$_2$), 19.0 (s, *n*Pr-CH$_2$), 22.0 (s, Me-CH$_2$), 30.4 (s, Et-CH$_2$), 33.0 (s, C=OCH$_2$), 52.0 (s, OCH$_3$), 65.1 (s, *n*Bu-C≡C), 66.2 (s, MeOCOEt-C≡C), 75.0 (s, *n*Bu-C≡C), 78.4 (s, MeOCOEt-C≡C), 172.1 (s, C=O); Elemental analysis calcd. for $C_{12}H_{16}O_2$: C 74.97, H 8.39; found C 74.69, H 8.44.

3. ^{1}H and ^{13}C NMR spectra of unsymmetrical diynes



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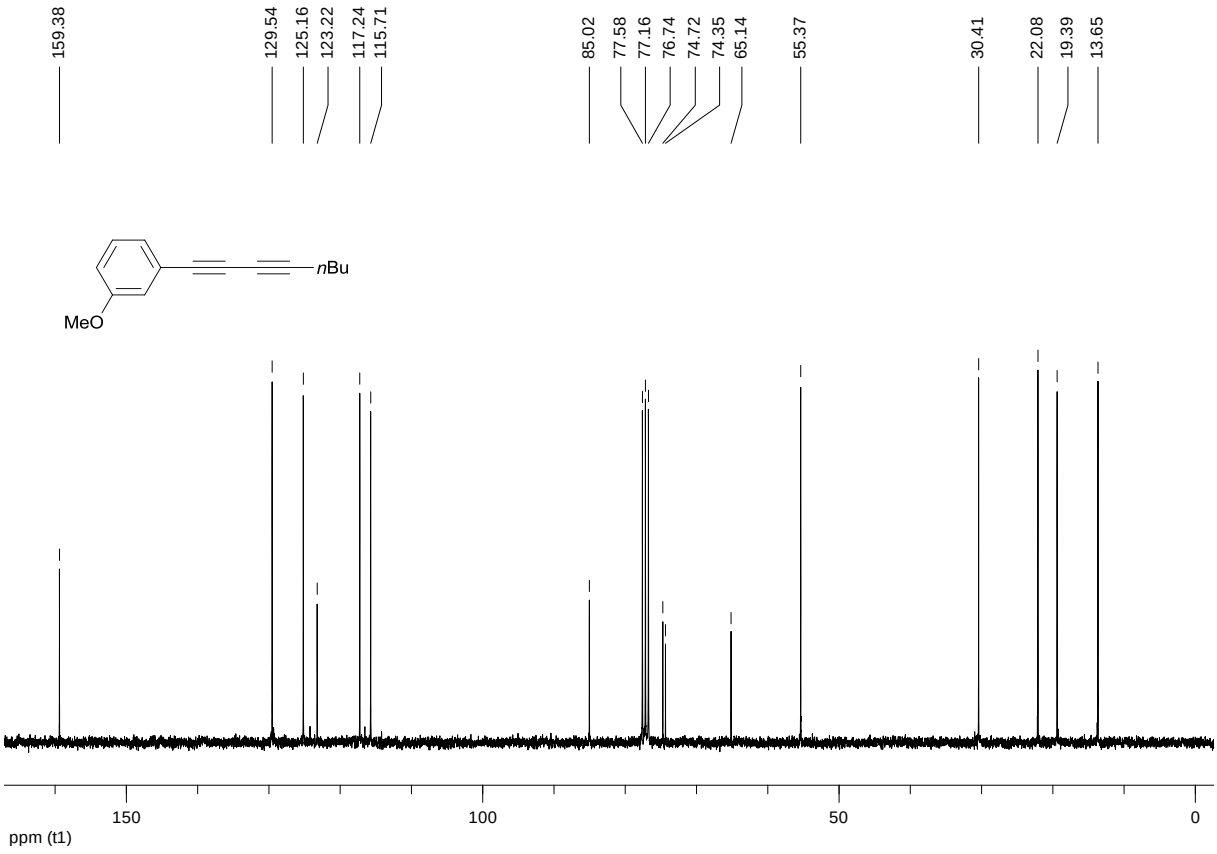
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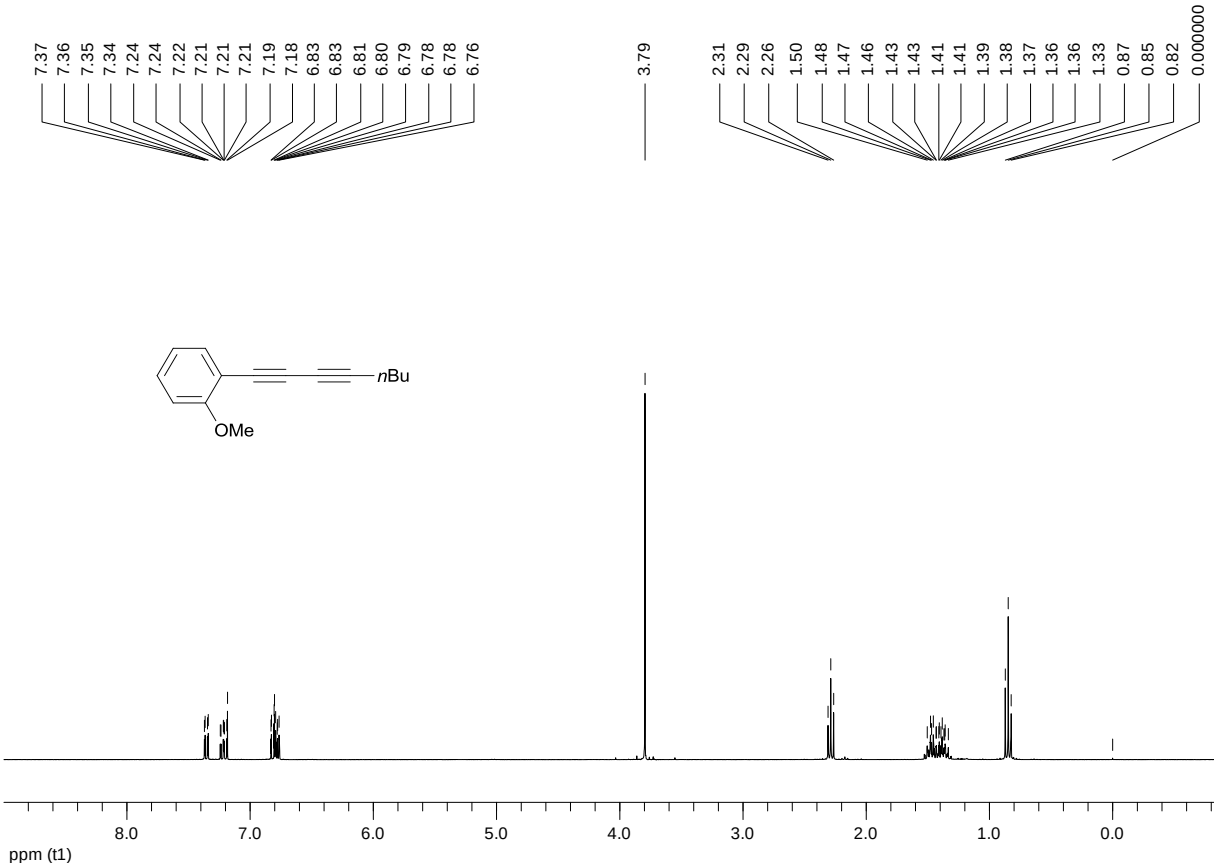

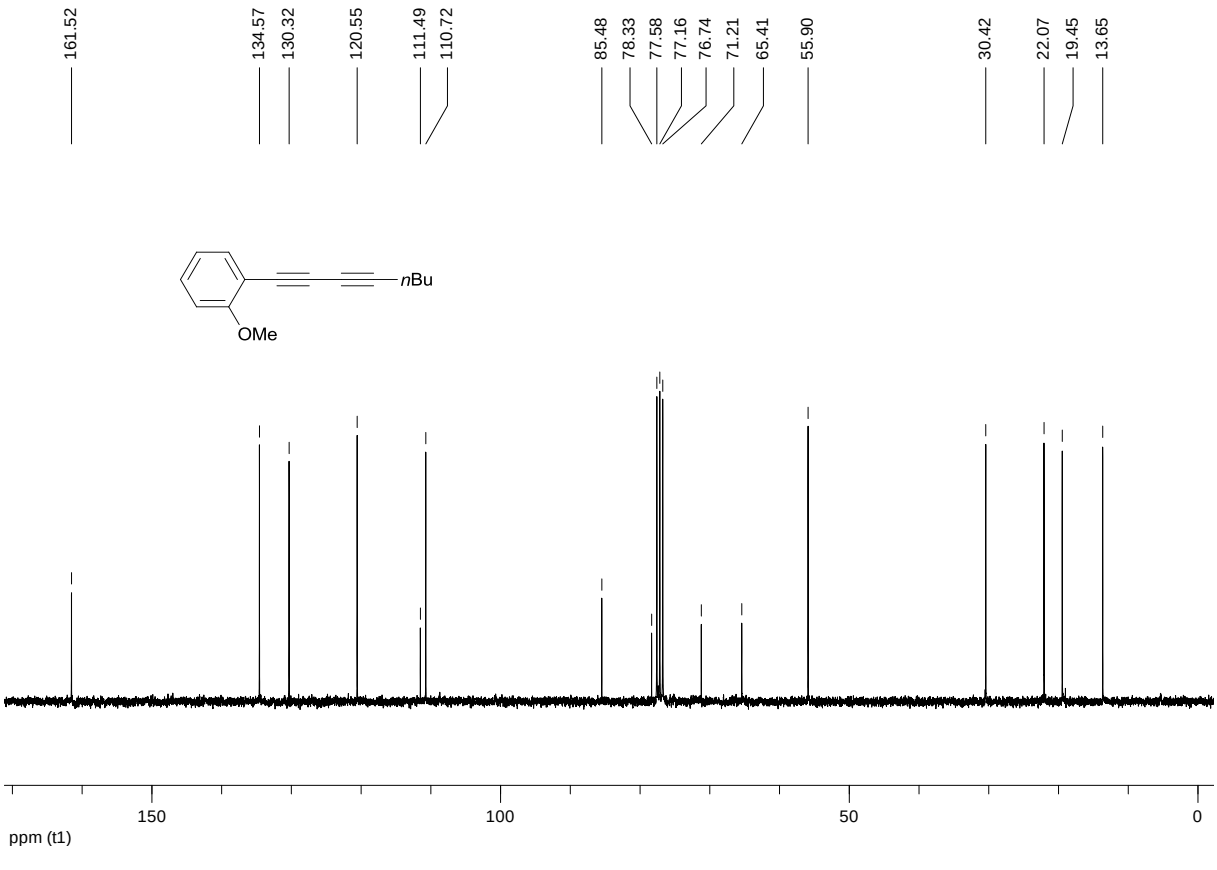

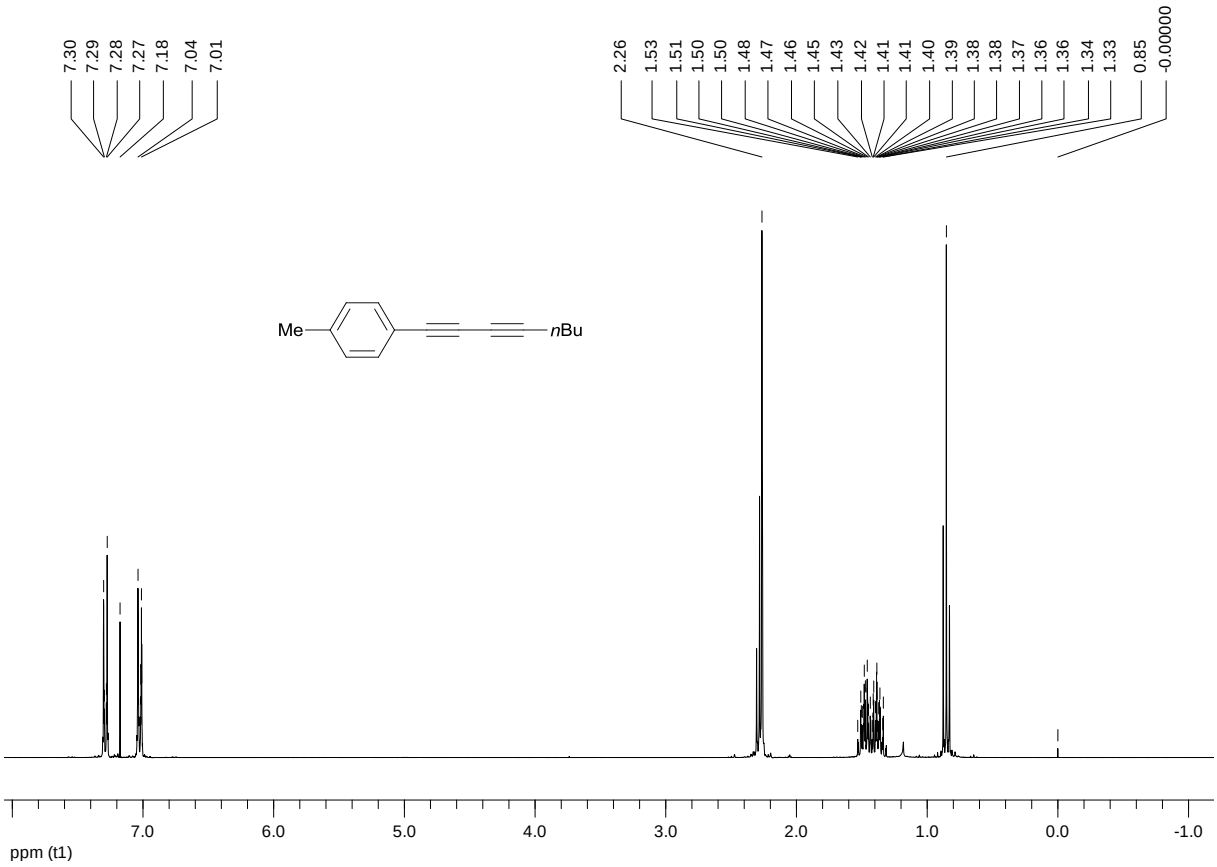

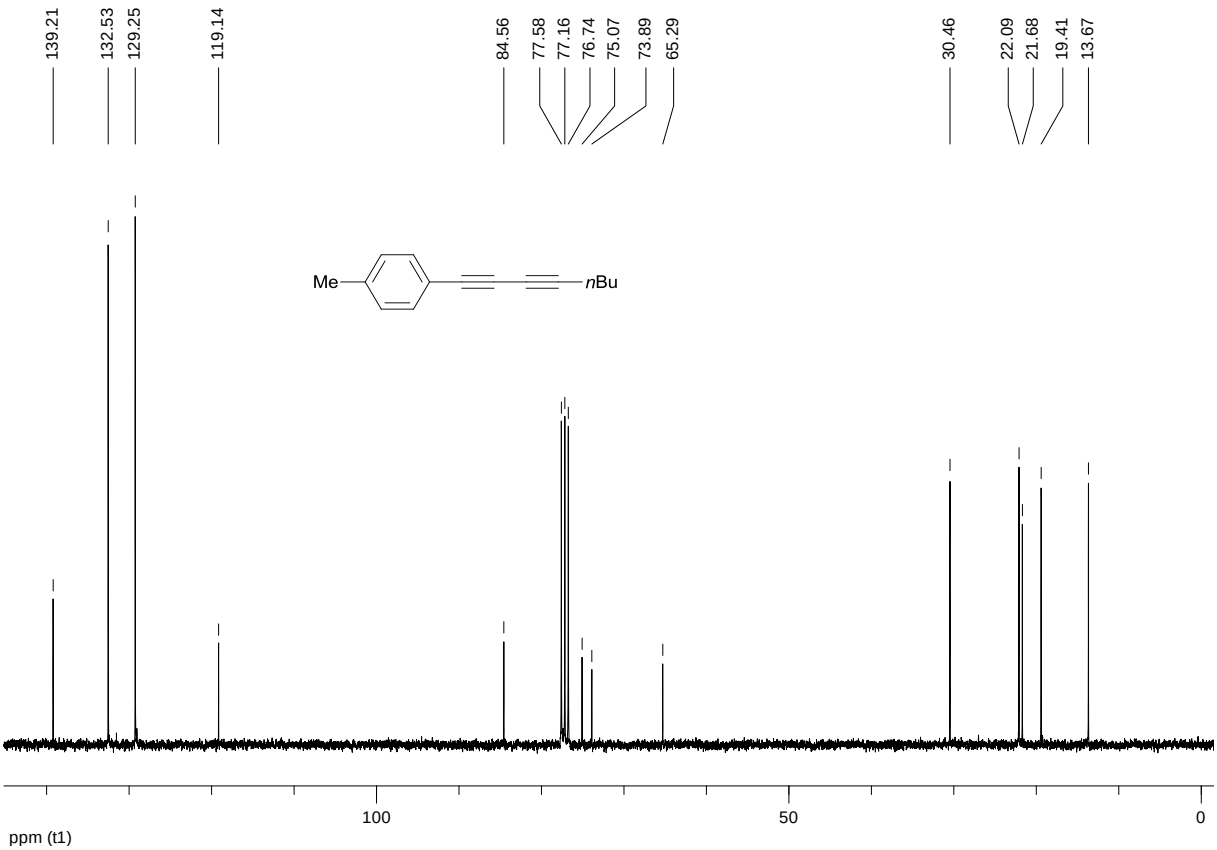

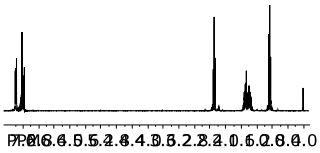

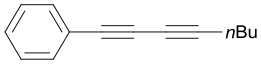
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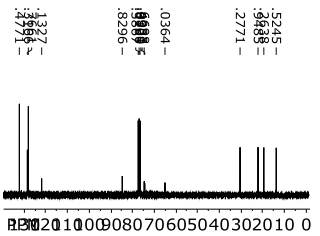

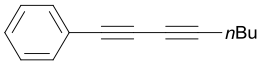
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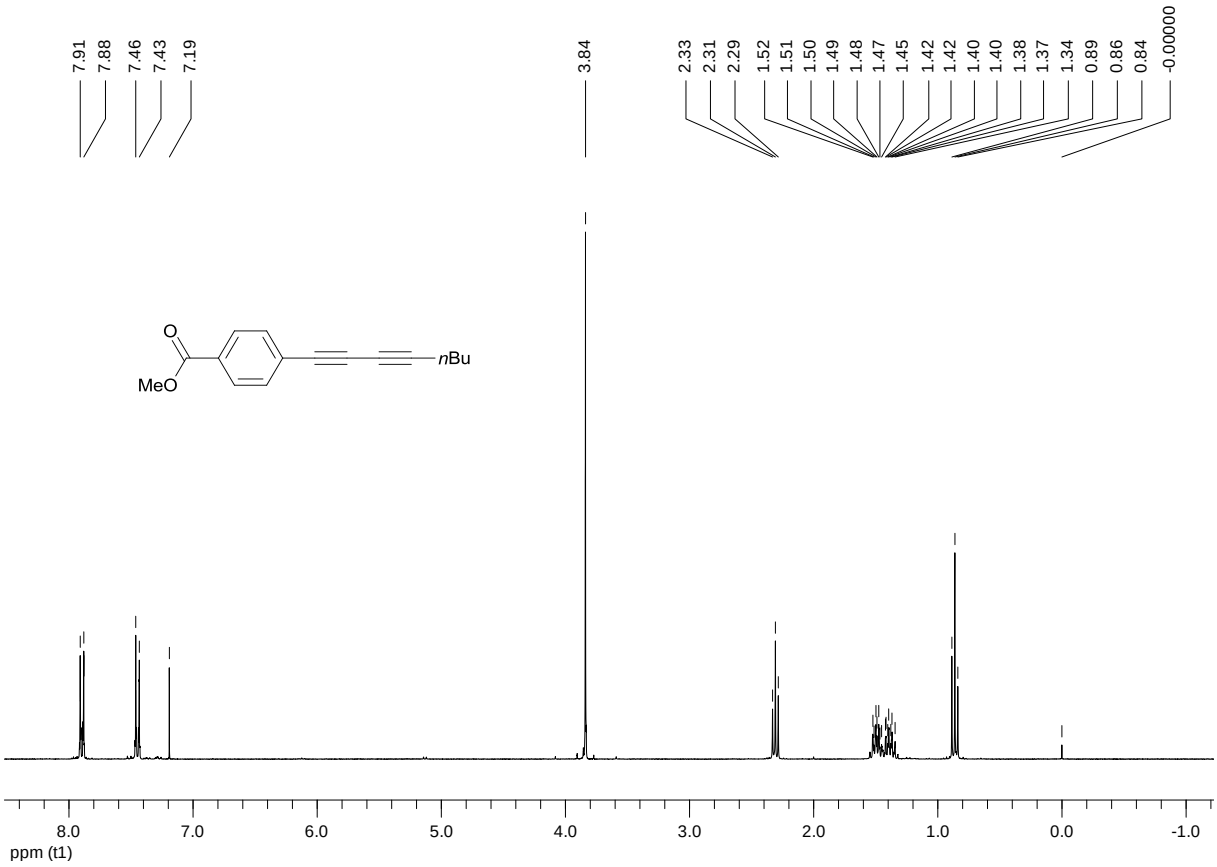
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2.31
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1.48
1.47
1.45
1.42
1.42
1.40
1.40
1.38
1.37
1.34
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0.84
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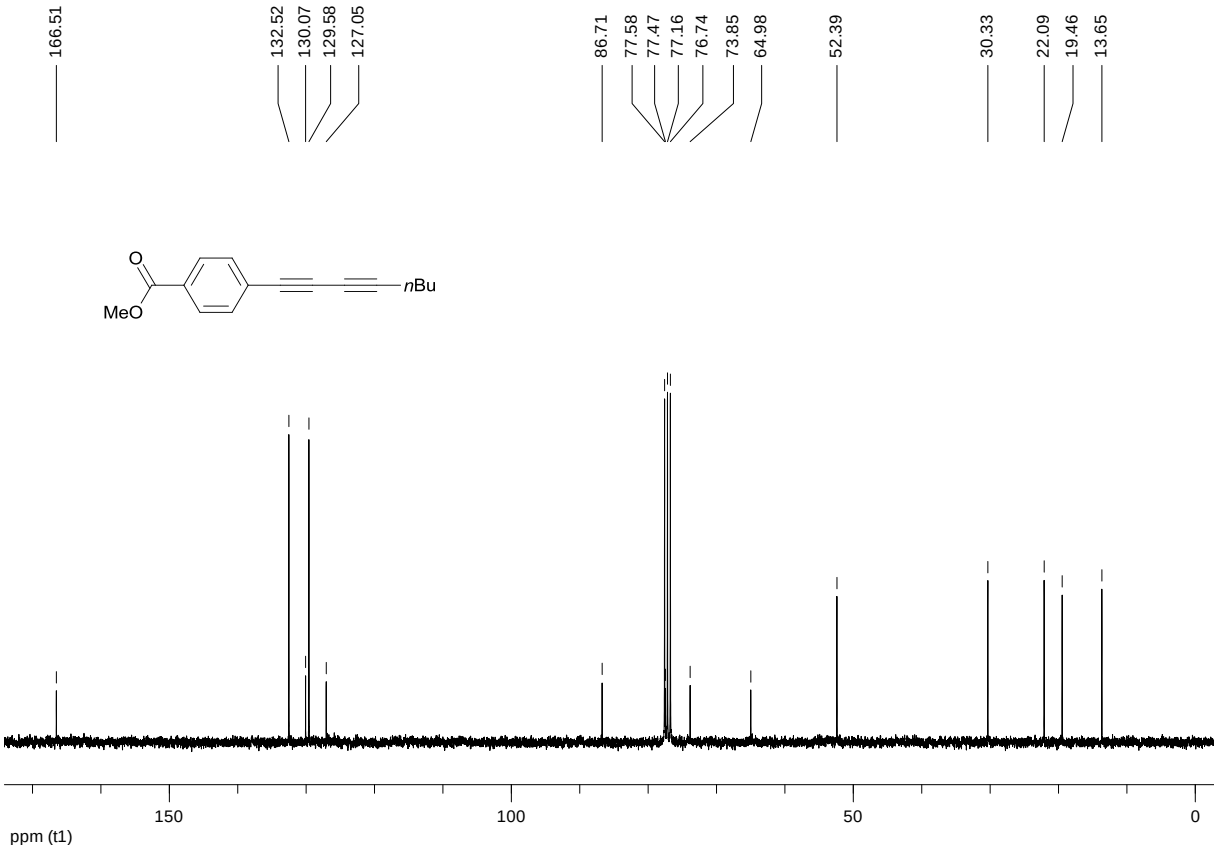
ppm (t1)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30.33
22.09
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nBu
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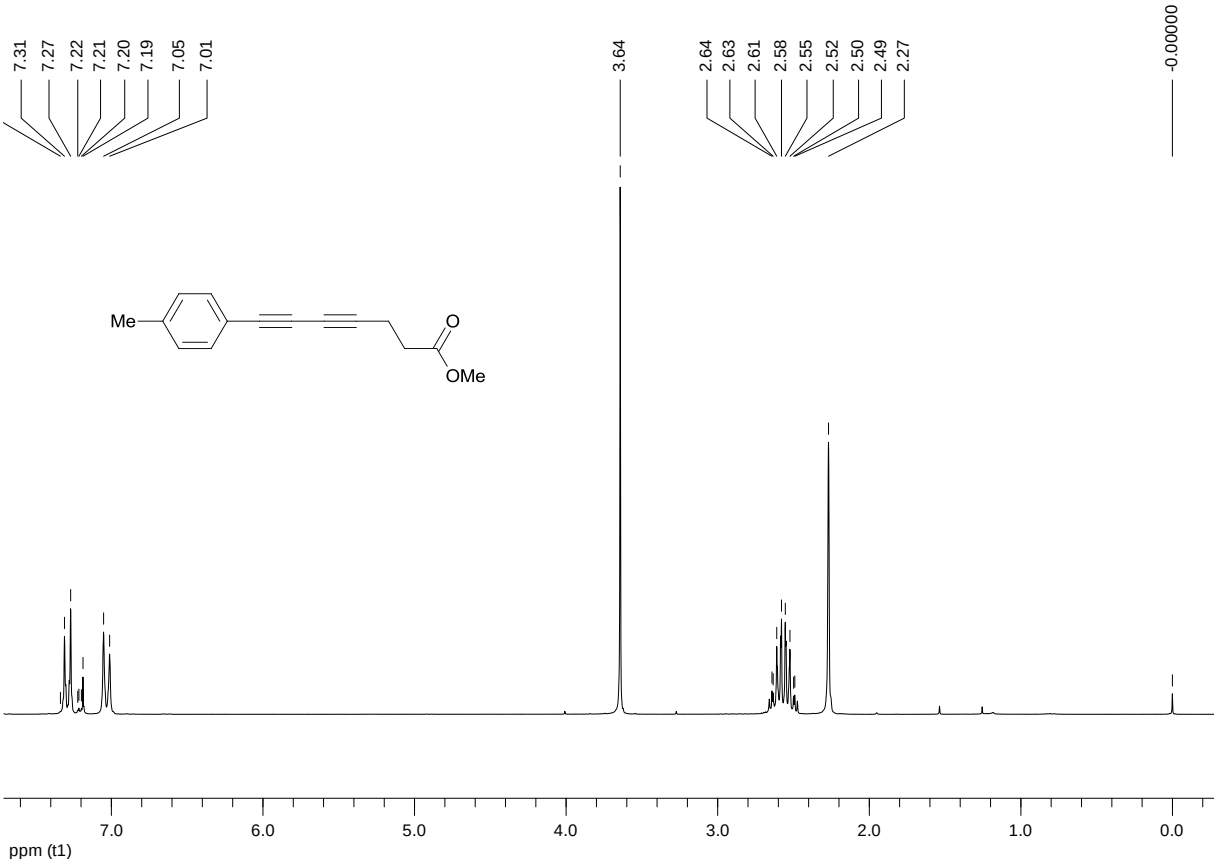
100
50
0
ppm (t1)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2.58
2.55
2.52
2.50
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OMe
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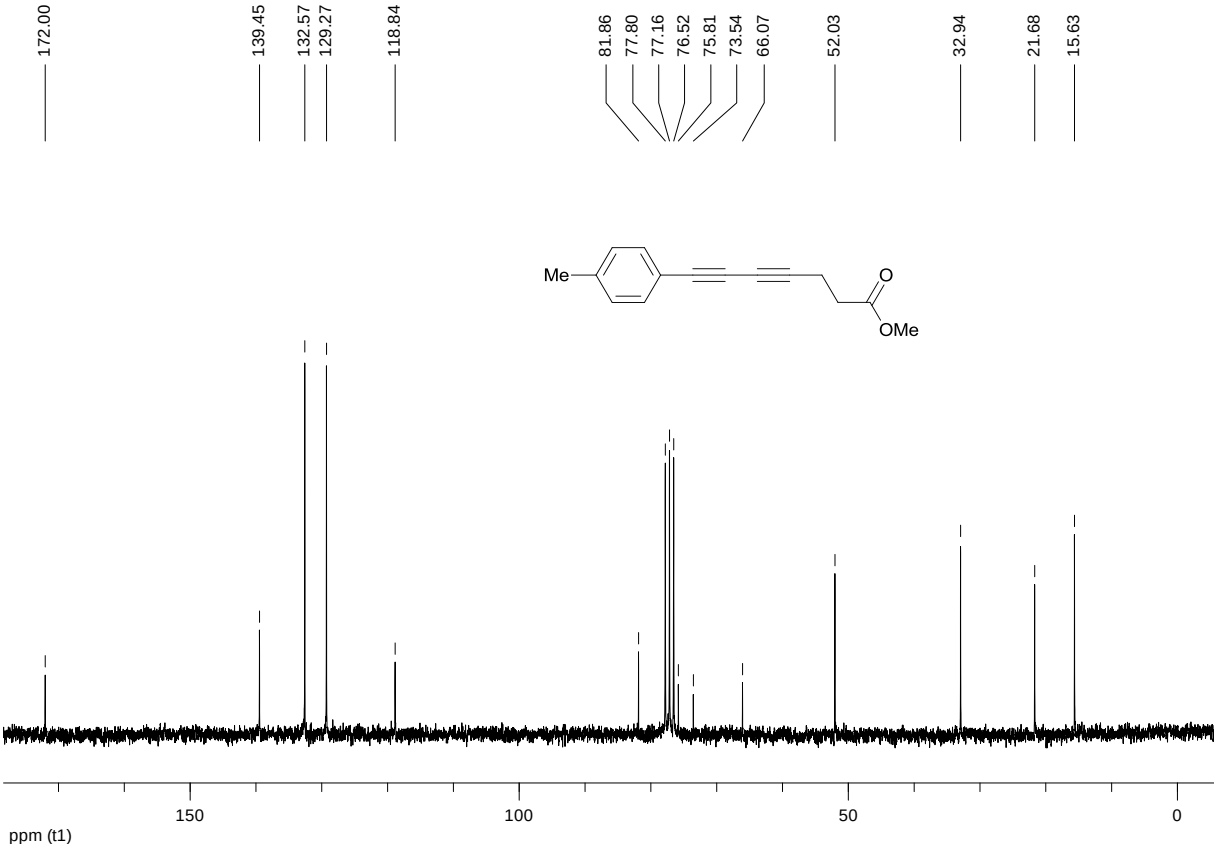
0.0
ppm (t1)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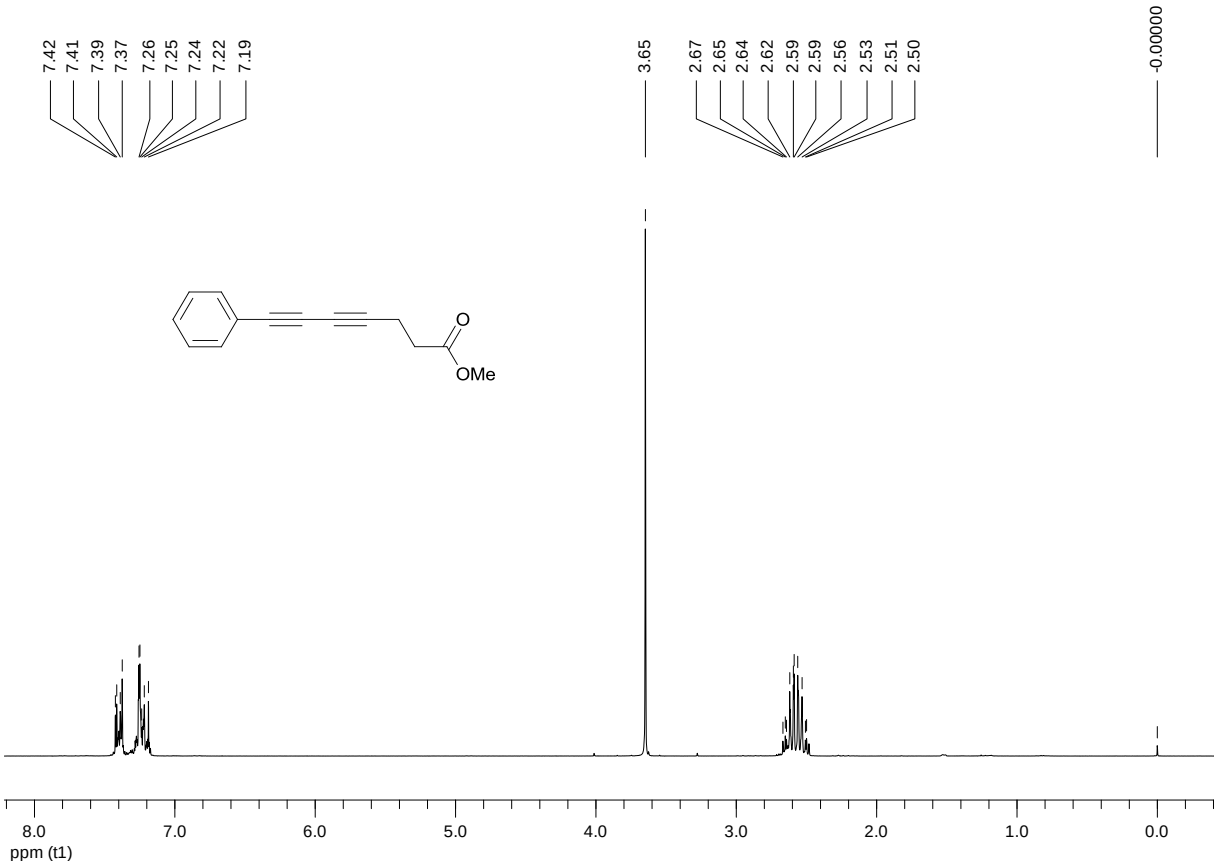
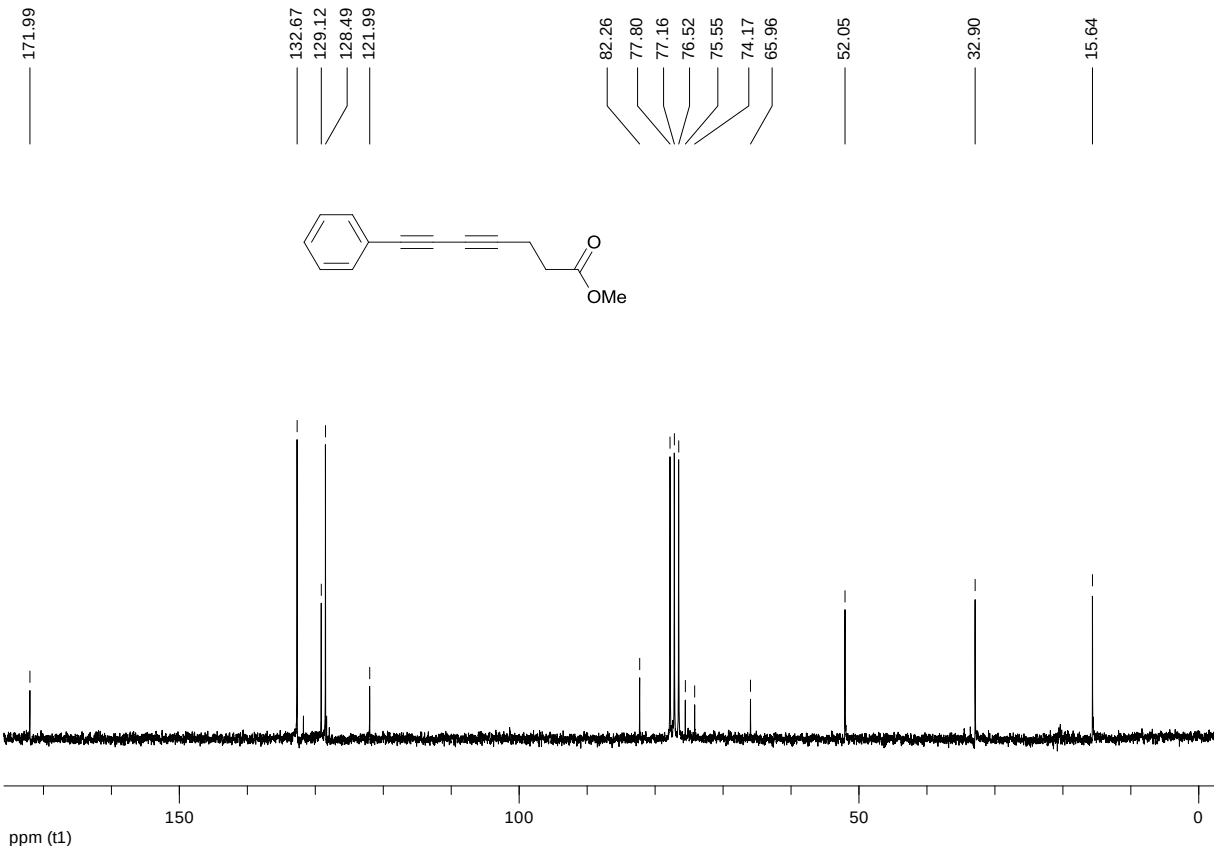
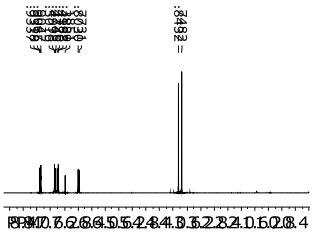
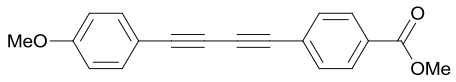
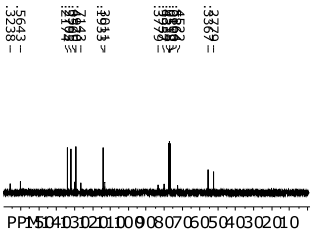
ppm (t1)

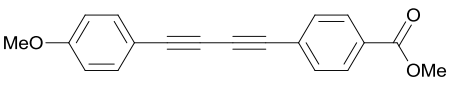


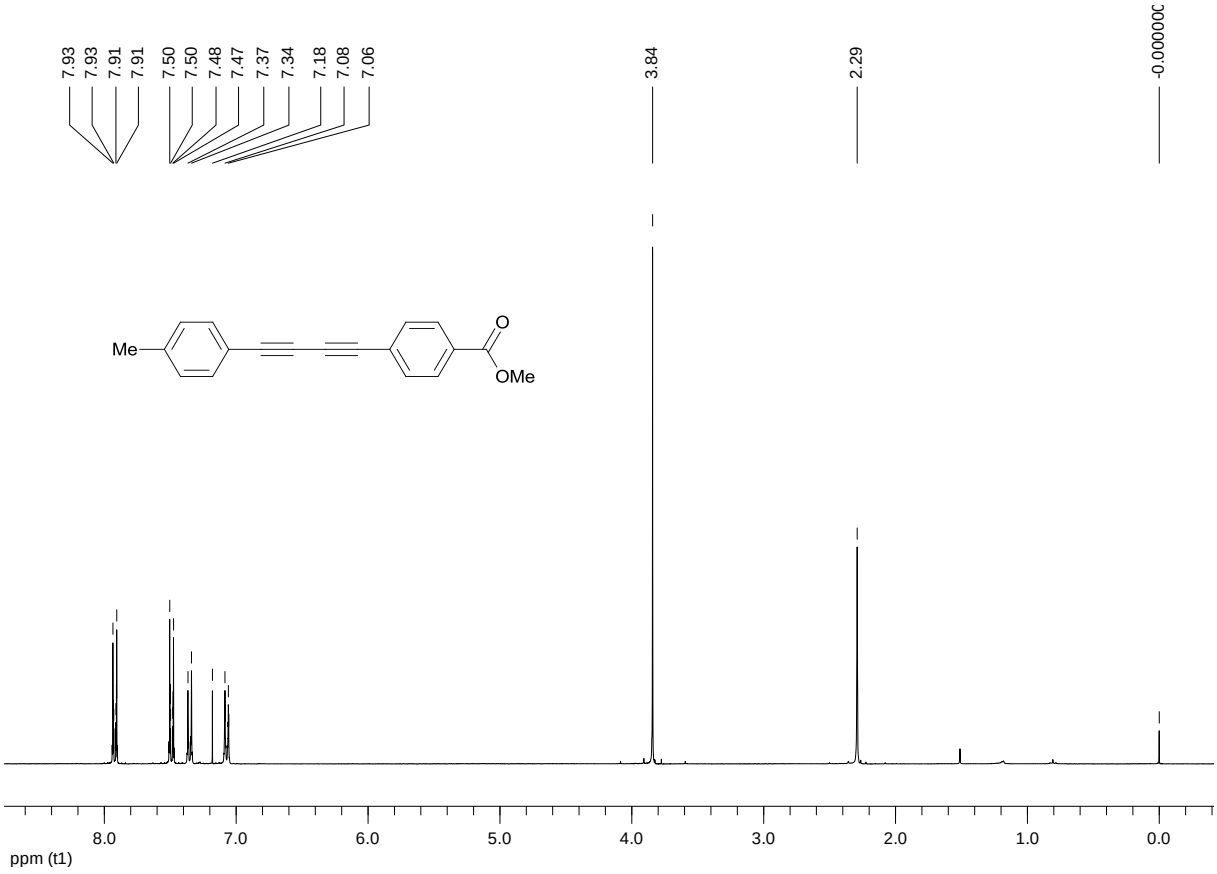


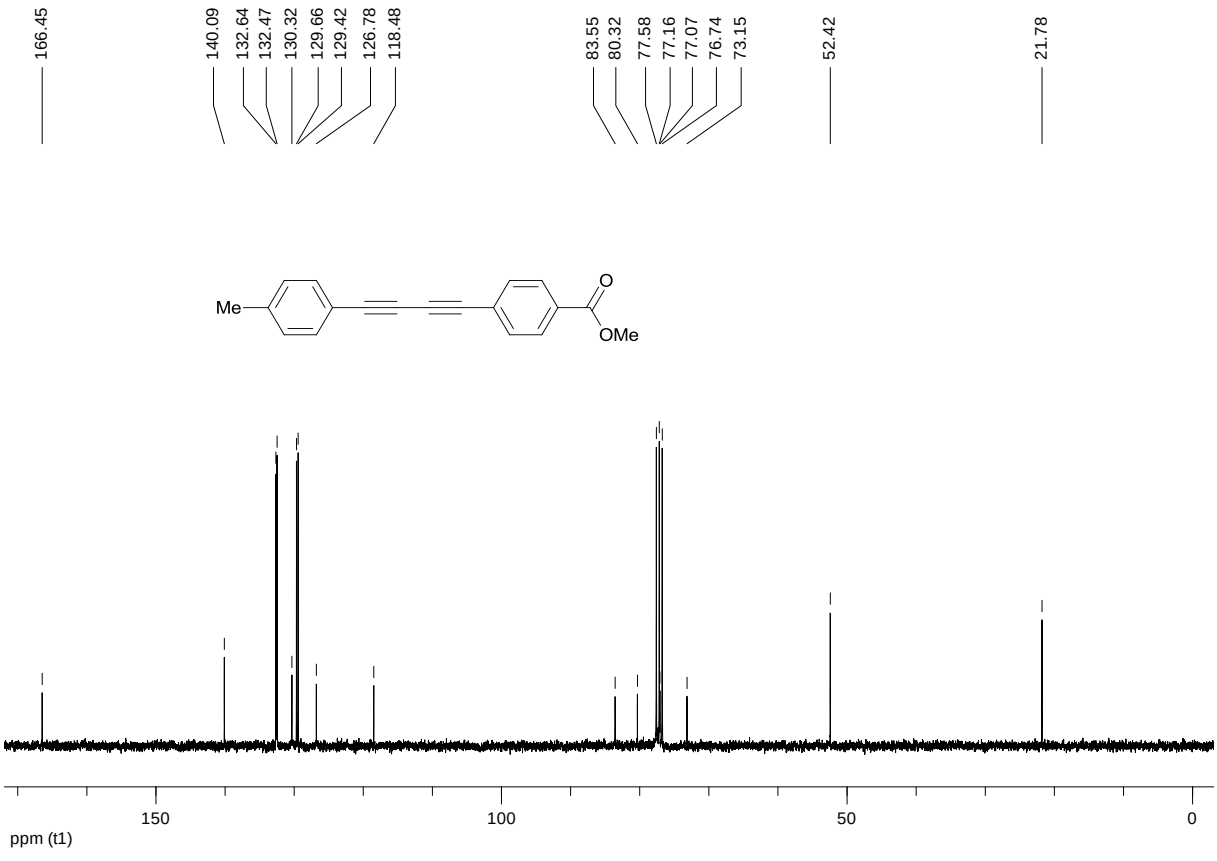


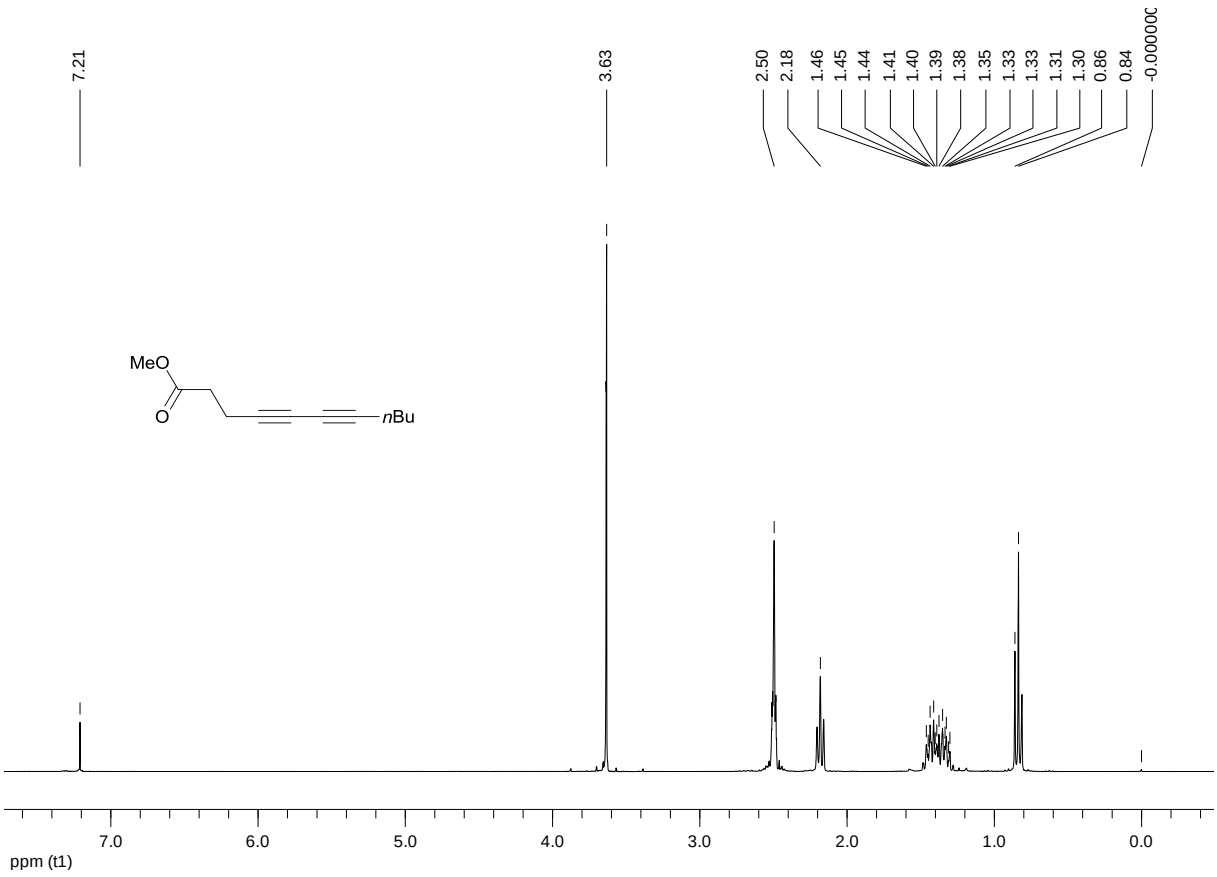








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3.63
2.50
2.18
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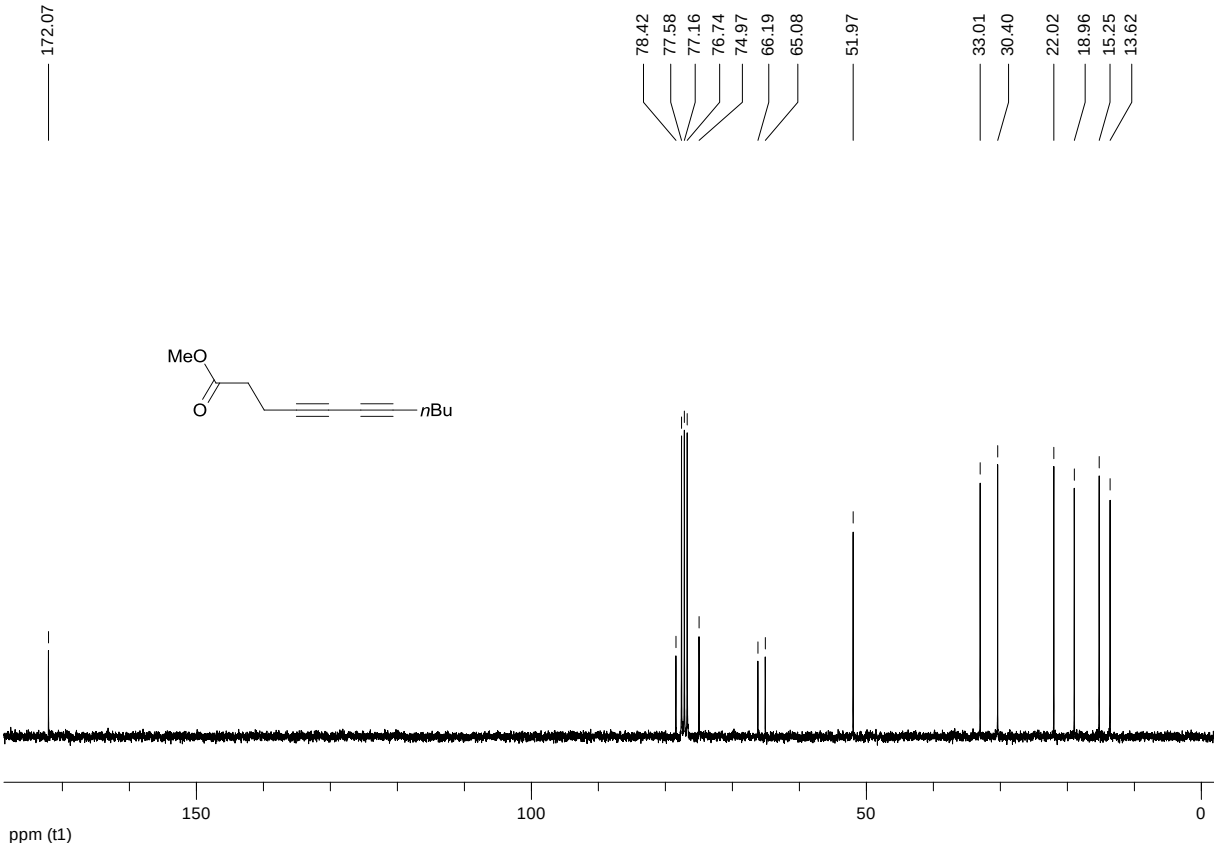
1.45
1.44
1.41
1.40
1.39
1.38
1.35
1.33
1.33
1.31
1.30
0.86
0.84
-0.000000
MeO
O
nBu
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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65.08
51.97
33.01
30.40
22.02
18.96
15.25
13.62
MeO
O
nBu
150
100
50
0
ppm (t1)

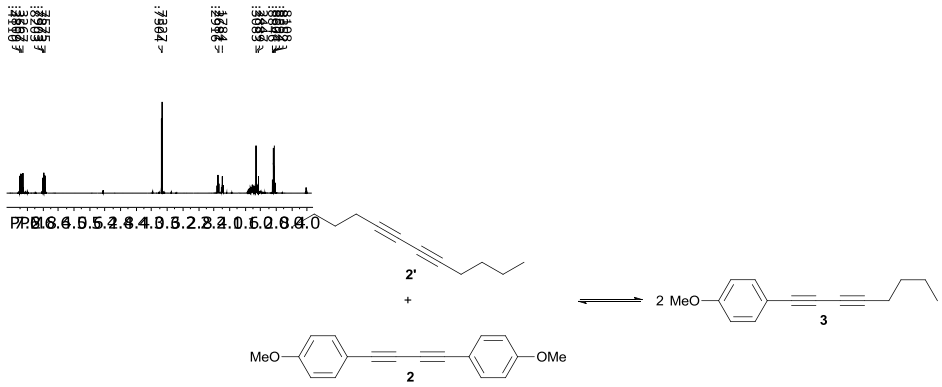
4. NMR study of the DYCM equilibrium reaction

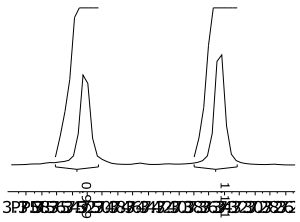
0.1 M CD_2Cl_2 solutions of 1,4-bis(4-methoxyphenyl)-1,3-butadiyne (**2**) and 5,7-dodecadiyne (**2'**) were prepared by dissolving 26.23 mg (0.1 mmol) of **2** in CD_2Cl_2 (V = 1 mL) and 40.57 mg (0.25 mmol) of **2'** in CD_2Cl_2 (V = 2.5 mL). A 0.01 M solution of catalyst **1** was obtained by dissolving 6.34 mg (6 μmol) of **1** in CD_2Cl_2 (V = 0.6 mL). The NMR samples were prepared by mixing the solutions in the following fashion:

- 1:1 mixture: 300 μL (**2**), 300 μL (**2'**), 100 μL (**1**);
- 1:2 mixture: 200 μL (**2**), 400 μL (**2'**), 100 μL (**1**);
- 1:3 mixture: 150 μL (**2**), 450 μL (**2'**), 100 μL (**1**);
- 1:4 mixture: 120 μL (**2**), 480 μL (**2'**), 100 μL (**1**).

This results in a total alkyne concentration of 0.086 M and a catalyst concentration of 1.4 mM (catalyst loading = 1.7 mol%). After 4.5 h, ^{1}H NMR spectra were recorded, and the [**3**]:[**2**] ration was determined by integration of the OCH_3 ^{1}H NMR signals in **3** (3H) and **2** (6H). The full spectra and excerpts from these spectra showing the OCH_3 signals are shown below.

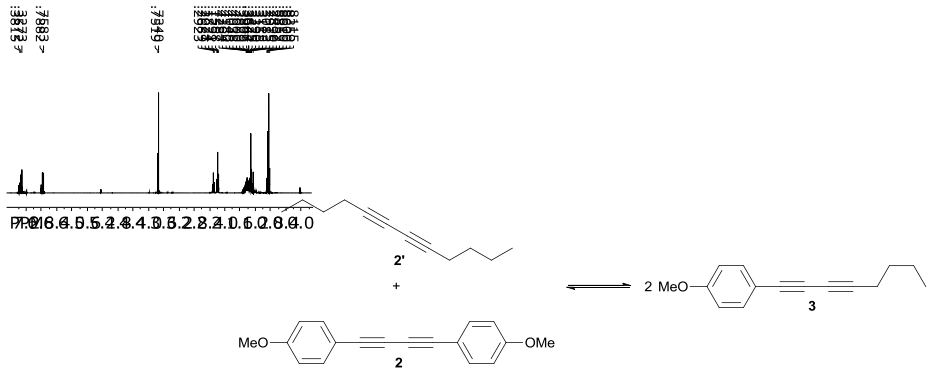
1:1

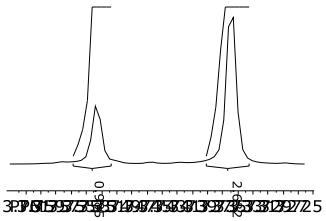




2 **3**

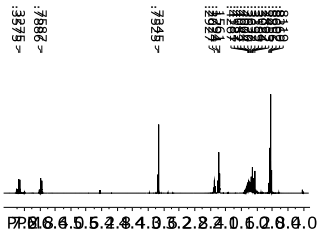
1:2

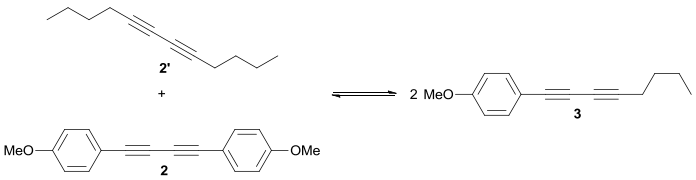


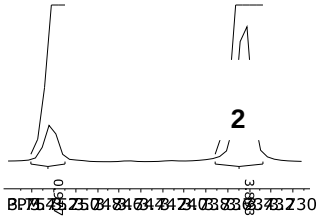


2 **3**

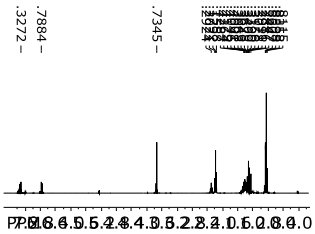
1:3

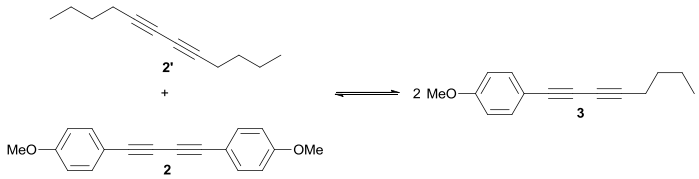


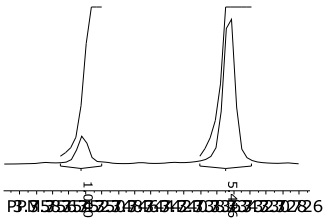




1:4







2 **3**

5. Conversion-time diagrams for diyne disproportionation

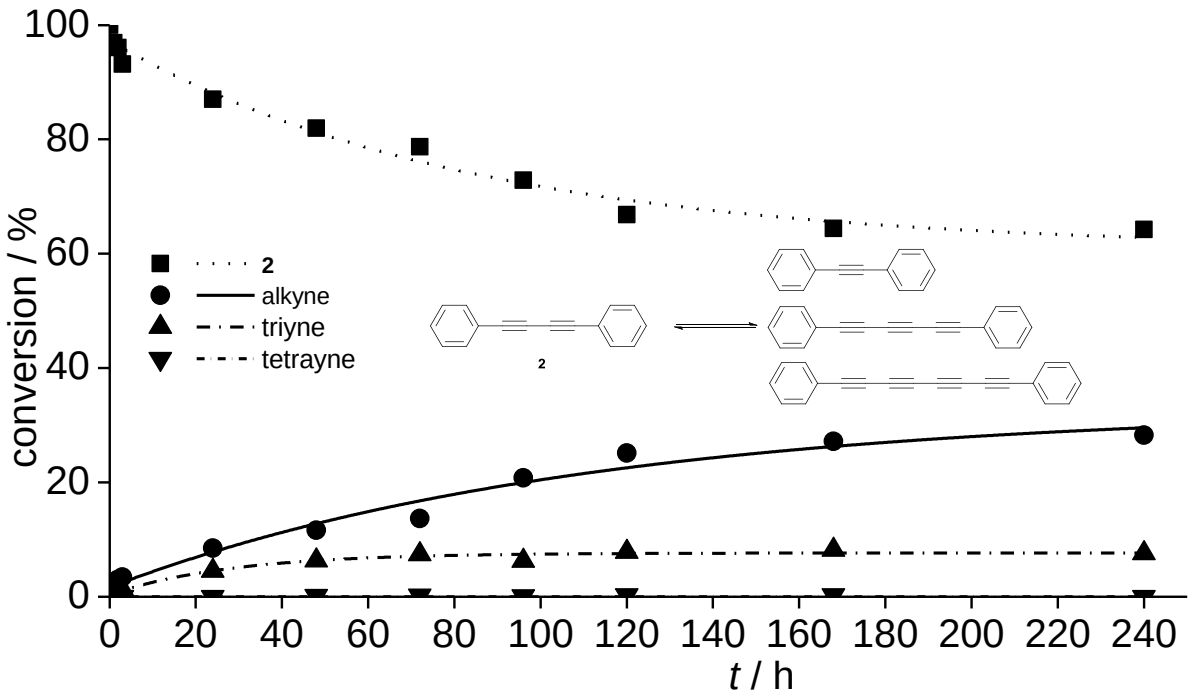


Figure S2. Conversion-time diagram for the disproportionation of diphenylbutadiyne into the corresponding monoyne, triyne and tetrayne; conditions: diyne (0.25 mmol), catalyst 1 (5 μmol, 2 mol%), CH_2Cl_2 (2 mL), room temperature.

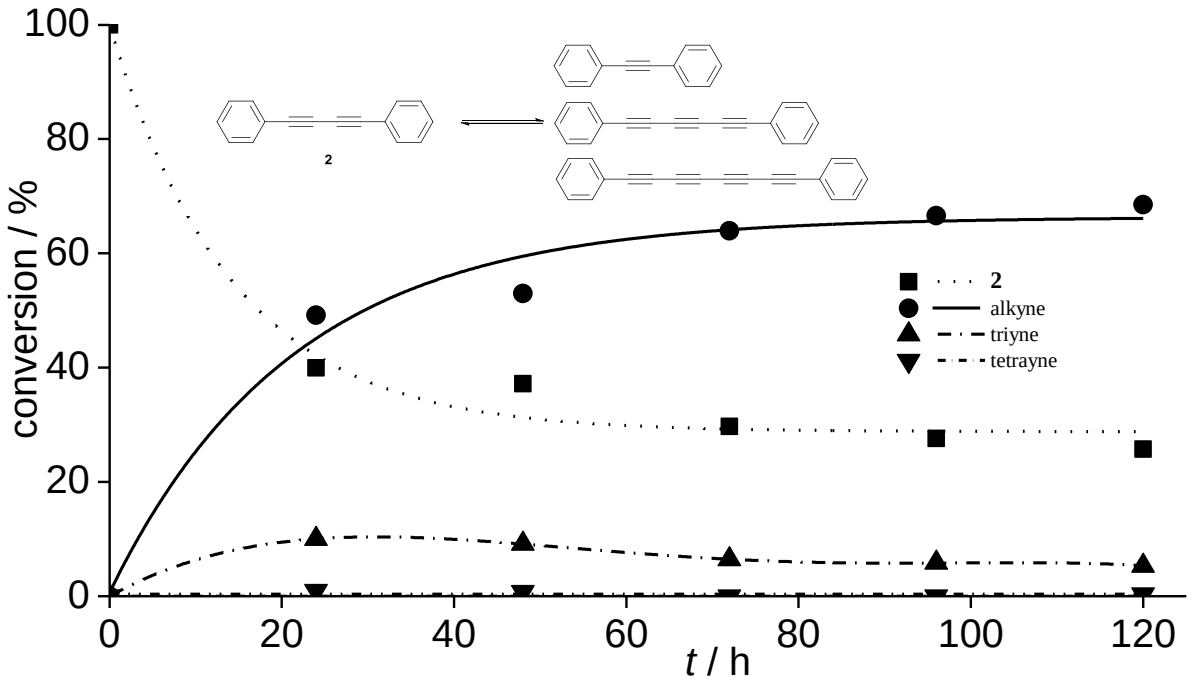


Figure S3. Conversion-time diagram for the disproportionation of diphenylbutadiyne into the corresponding monoyne, triyne and tetrayne; conditions: diyne (0.74 mmol), catalyst 1 (74 μmol, 10 mol%), toluene (5.93 mL), T = 333 K.

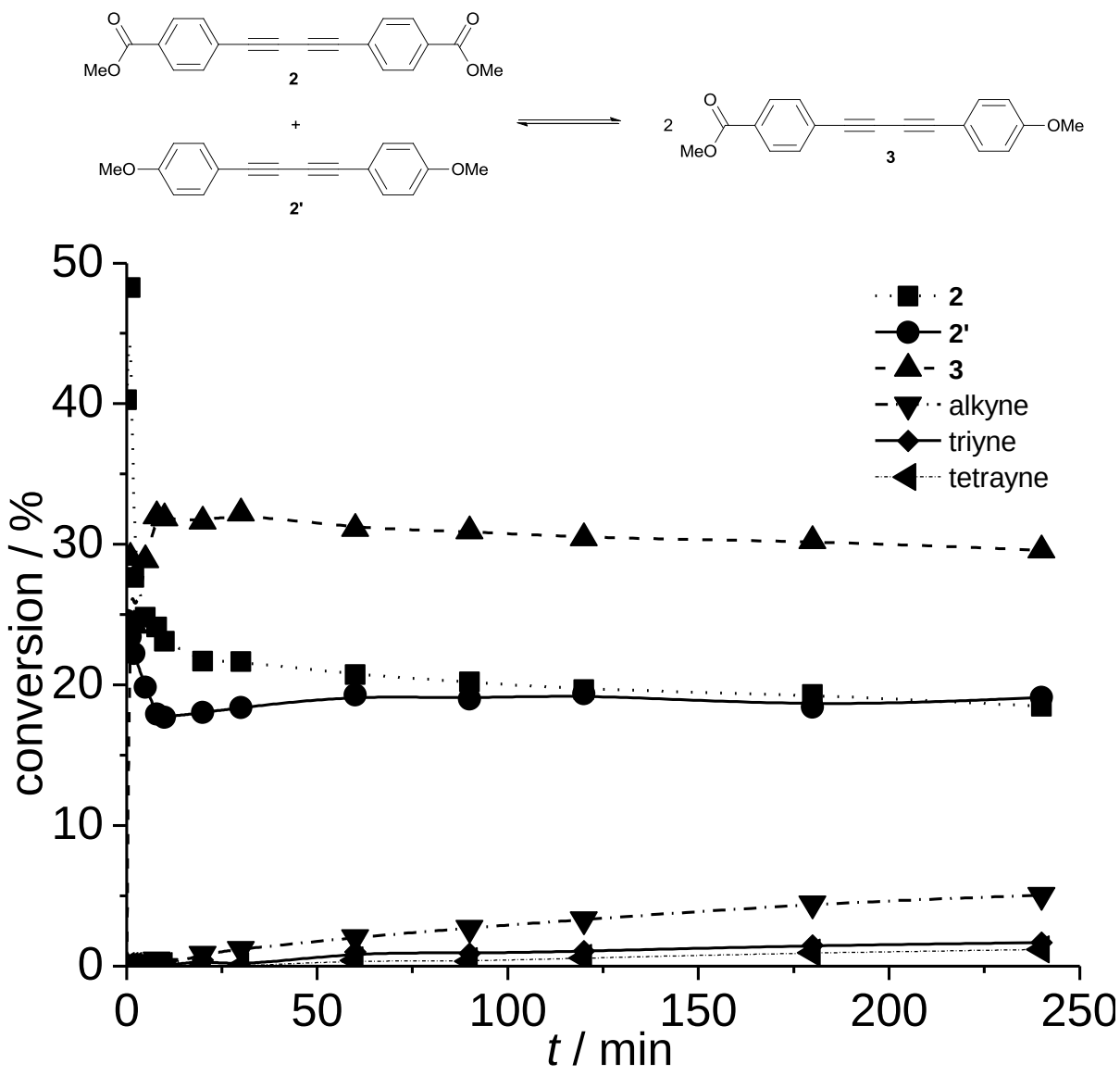


Figure S4. Conversion-time diagram for the 1 : 1 mixture of dimethyl 4,4'-(1,3-butadiyne-1,4-diyl)dibenzoate **2** and 1,4-bis(4-methoxyphenyl)-1,3-butadiyne **2'**. The conversion of **2** and **2'** into the unsymmetrical diyne **3** and the formation of monoyne, triyne and tetrayne species was followed by GC; conditions: **2** (50 mg, 0.16 mmol), **2'** (41.2 mg, 0.16 mmol), catalyst **1** (6.68 mg, 6.28 μmol, 2 mol%), toluene (1.8 mL), room temperature.

6. Computational Details

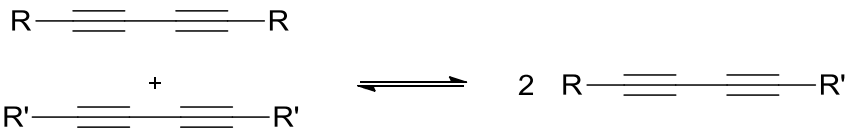
The calculations were performed using the GAUSSIAN09 package.[6] All structures were fully optimized on the DFT level employing the B97-D functional,[7] and represent global minima on the potential energy surface. For all main-group elements (C, H and O) the all-electron triple-ζ basis set (6-311G**) was used.[8]

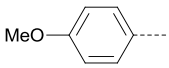
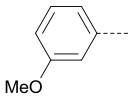
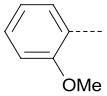
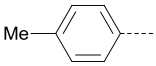
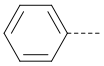
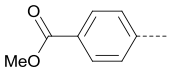
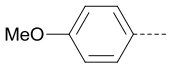
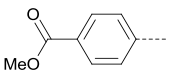
Table S1. Energies for all optimized structures

	E(0 K)[a]/[Ha]	H(298 K)[b]/[Ha]	G(298 K)[b]/[Ha]
*n*Bu-CC-CC-*n*Bu	-467.537195	-467.520626	-467.58205
Ph-CC-CC-Ph	-615.094711	-615.080474	-615.136045
*p*MePh-CC-CC-*p*MePh	-693.641498	-693.623361	-693.690519
*o*MeOPh-CC-CC-*o*MeOPh	-843.997667	-843.97824	-844.047041
*m*MeOPh-CC-CC-*m*MeOPh	-843.998555	-843.979066	-844.047839
*p*MeOPh-CC-CC-*p*MeOPh	-844.001412	-843.981948	-844.050902
*p*MeOOCPh-CC-CC- *p*MeOOCPh	-1070.61151	-1070.588011	-1070.668053
Ph-CC-CC-*n*Bu	-541.315964	-541.300499	-541.360456
*p*MePh-CC-CC-*n*Bu	-580.589222	-580.571821	-580.636968
*o*MeOPh-CC-CC-*n*Bu	-655.76722	-655.749185	-655.814703
*m*MeOPh-CC-CC-*n*Bu	-655.767906	-655.749821	-655.816138
*p*MeOPh-CC-CC-*n*Bu	-655.769055	-655.751047	-655.816545
*p*MeOOCPh-CC-CC- *n*Bu	-769.074581	-769.054542	-769.125582
*p*MeOOCPh-CC-CC- *p*MeOPh	-957.307106	-957.285631	-957.359933

[a] DFT energy incl. ZPE.
[b] standard conditions T = 298.15 K and p = 1 atm.

Table S2. Calculated values for the diyne cross-metathesis of selected 1,3-butadiynes



Entry	R	R'	ΔG [kJ·mol^{-1}]	K
1		*n*Bu-----	-0.36	1.16
2		*n*Bu-----	-6.27	12.56
3		*n*Bu-----	-0.83	1.40
4		*n*Bu-----	-3.59	4.26
5		*n*Bu-----	-7.40	19.82
6		*n*Bu-----	-2.79	3.08
9			-2.39	2.62

6. References

[1] K. R. Deaton and M. S. Gin, *Org. Lett.*, 2003, **5**, 2477.

[2] H. Shimotahira, S. Fusazaki, I. Ikeda and Y. Ozoe, *Bioorg. Med. Chem. Lett.*, 2011, **21**, 1598.

[3] T.-M. Wu, S.-H. Huang and F.-Y. Tsai, *Appl. Organometal. Chem.*, 2011, **25**, 395.

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