Well-defined silica-supported molybdenum nitride species: Silica grafting triggers alkyne metathesis activity.

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Supporting Information

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1) General procedures:

All experiments were conducted under a strict inert atmosphere using standard Schlenk and glove box techniques for the organometallic synthesis and grafting processes. Solvents were purified and dried according to standard procedures. 4-decyne and 1-phenyl-1-propyne were distilled over $LiAlH_4$, degassed and stored in a glove-box.

GC analyses were performed on a Shimadzu GC2014 equiped with a FID detector and using N_2 as carrier gas. A Supelco Equity-5 column (95% methylpolysiloxane + 5% phenylsiloxane, 30m × 0.32mm × 0.25µm) was used with the following temperature programs:

For 4-decyne or 1-phenyl-1-propyne metathesis:

Rate [°C/min]	Temperature [°C]	Time [min]
-	100	5
20	200	5

For compounds **9** and **11** cross-metathesis:

Rate [°C/min]	Temperature [°C]	Time [min]
-	50	5
10	170	0
20	350	15

GC-MS analyses were performed on a Shimadzu GC–MS-QP2010 equipped with a Sulpelco SLB-5MS column (95% methylpolysiloxane + 5% phenylpolysiloxane, 30m × 0.25mm × 0.25µm) with Helium as carrier gas. Ionization was done by electronic impact at 70eV. The same temperature programs were used as for GC.

Mo contents determinations were performed at IRCELYON by ICP-AES (Activa Jobin Yvon) spectroscopy from a solution obtained by treatment of the solid catalyst with a mixture of HF, HNO_3 and H_2SO_4 in a Teflon reactor at 150°C. C, H and N measurement were performed at the London Metropolitan University. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer by using a DRIFT cell equipped with CaF_2 windows. The samples were prepared under Ar within a glove-box. Typically, 64 scans were accumulated for each spectrum (resolution 4 cm^{-1}). Confocal Raman spectra were acquired using the 488nm line of a Ar-ion laser (Melles Griot). The excitation beam was focused on the sample by a 50X long working distance microscope and the scattered light was analyzed by an air-cooled CCD (Labram HR, Horiba Jobin Yvon). The fluorescence was subtracted from the spectra for clarity. Solution NMR spectra were recorded on an Avance-300 Bruker spectrometer. All chemical shifts were measured relative to residual ^{1}H or ^{13}C resonance in the deuterated solvent: C_6D_6, δ 7.15 ppm for ^{1}H, 128 ppm for ^{13}C. Solid-state NMR spectra were acquired on Bruker Avance II 800 (^{1}H: 800.13 MHz, ^{13}C: 201.21 MHz) and Avance 400 spectrometers (^{1}H: 400.1 MHz, ^{13}C: 100.6 MHz). For ^{1}H experiments (18.8T), the spinning frequency was 20 kHz, the recycle delay was 5 s and 16 scans were collected using a 90° pulse excitation of 3 μs. The two-dimensional homonuclear experiment (DQ-MAS) was obtained using excitation and reconversion pulse blocks of two rotor periods each (100 μs), and at a spinning frequency of 20 kHz. The 90° pulse length was 3 μs, the recycle delay was 5 s and 16 scans were collected. The ^{13}C CP MAS experiment (9.4T) was obtained at a spinning frequency of 10 kHz, with a recycle delay of 5 s and 13300 scans were collected. Chemical shifts were given in ppm with respect to TMS as external reference for ^{1}H and ^{13}C NMR.

2) Preparation and characterization of catalyst 2

Preparation of $SiO_{2\text{-}700}$:

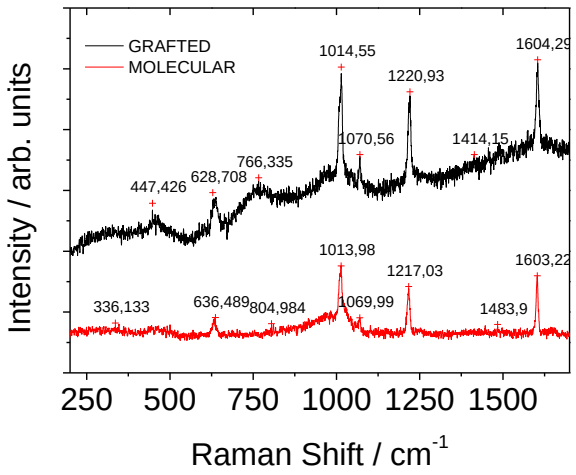
Aerosil silica from Degussa with a specific area of 200m²/g was placed in a tube connected to a diffusion pump. This silica was heated under vacuum (10^{-6}mbar) at a rate of 10°C/min up to 500°C and maintained at 500°C for 15h. Then the temperature was increased at a rate of 10°C/min up to 700°C and heating was maintained for another 4h. After this treatment, the specific area was about 200 m^2/g with an OH density of 0.7 OH/nm^2.

*Preparation of complex **1**:*

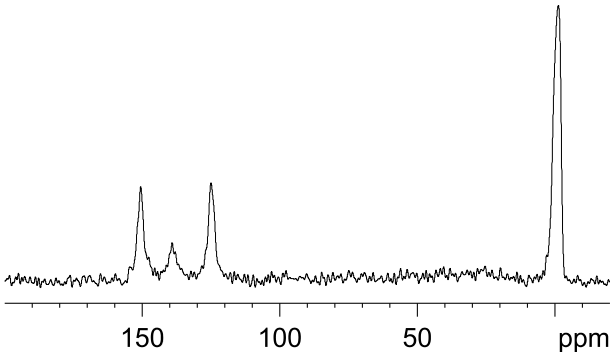
Complex **1** was prepared according to literature[1]: to a suspension of Na_2MoO_4 (0.95g, 4.5mmol) in dimethoxyethane (25mL), TMSCl (1.96g, 18.0mmol) is added dropwise. The mixture is then refluxed overnight. The obtained white suspension is evaporated under vacuum to afford a blue-green solid which is suspended in pentane (20mL). A solution of LiHMDS (1.5g, 9.0mmol) in pentane (5mL) is added causing the suspension to turn black. The stirring is maintained at room temperature for 2h then the mixture is filtrated over a pad of Celite® to afford an orange solution which is evaporated. A solution of pyridine (0.89g, 11.3mmol) in pentane (25mL) is then added under stirring to the resulting orange solid. The solution is stirred overnight. The solvent is removed under vacuum giving a yellow solid which is recrystallized in pentane to afford complex **1** as yellow crystals. ^1H and ^{13}C NMR are in accordance with literature data.

*Characterization of catalyst **2**:*

Raman spectra of **1** (red) and **2** (black):



^{13}C CP MAS spectrum of **2** (100.6 MHz, rotation speed 10 kHz, 13300 transients, recycle delay 5s):



Elemental analyses of **2**:

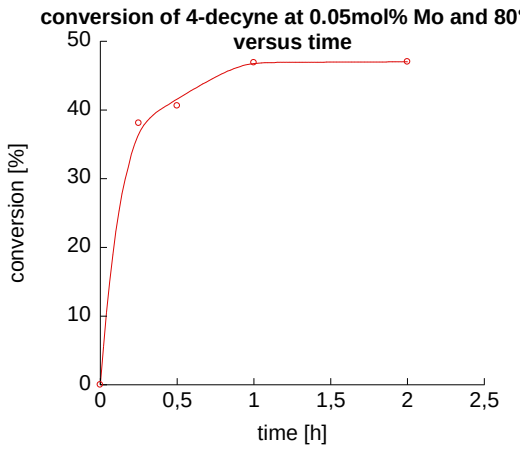
Element	Measure [wt%]	Molar ratio to Mo (calc.)
Mo	3,88 – 3,88	-
C	4,63 – 4,68	9,58 (11)
H	0,95 – 0,92	22,94 (23)
N	1,21 – 1,14	2,07 (2)

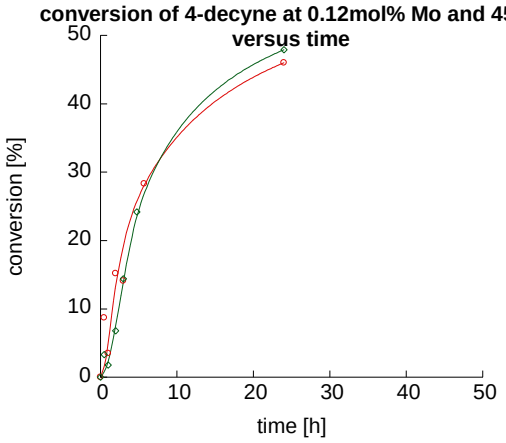
3) Self-metathesis reactions

With 4-decyne:

In a glovebox, a storage tube equipped with a screw cap is loaded with 4-decyne (345mg, 2.5mmol), catalyst **2** (3.7mg, 0.05mol% Mo) and toluene (2.5mL). The reaction mixture is heated at 80°C outside the glovebox. Kinetic monitoring of the reaction is performed through regular sampling by opening of the tube inside the glovebox after a fast entry/exit (5min overall). Conversion is measured referring to an external standard (decane) by GC. The relative error is estimated to be 5%. To ensure good reliability of the results, two independent experiments were generally carried out.

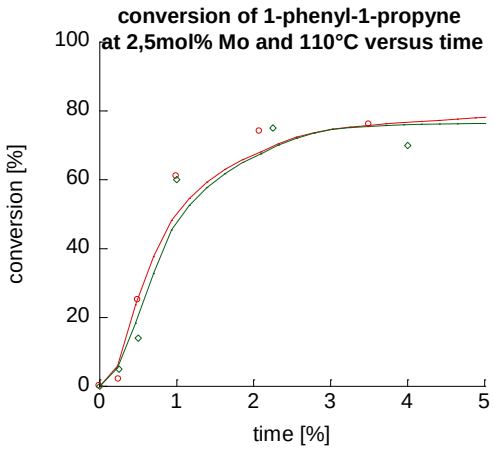
The same procedure is used for the experiment at 0,1mol% Mo and 45°C with 4-decyne (345mg, 2.5mmol), catalyst **2** (7.4mg, 0.12mol% Mo) and toluene (2.5mL).





With 1-phenyl-1-propyne:

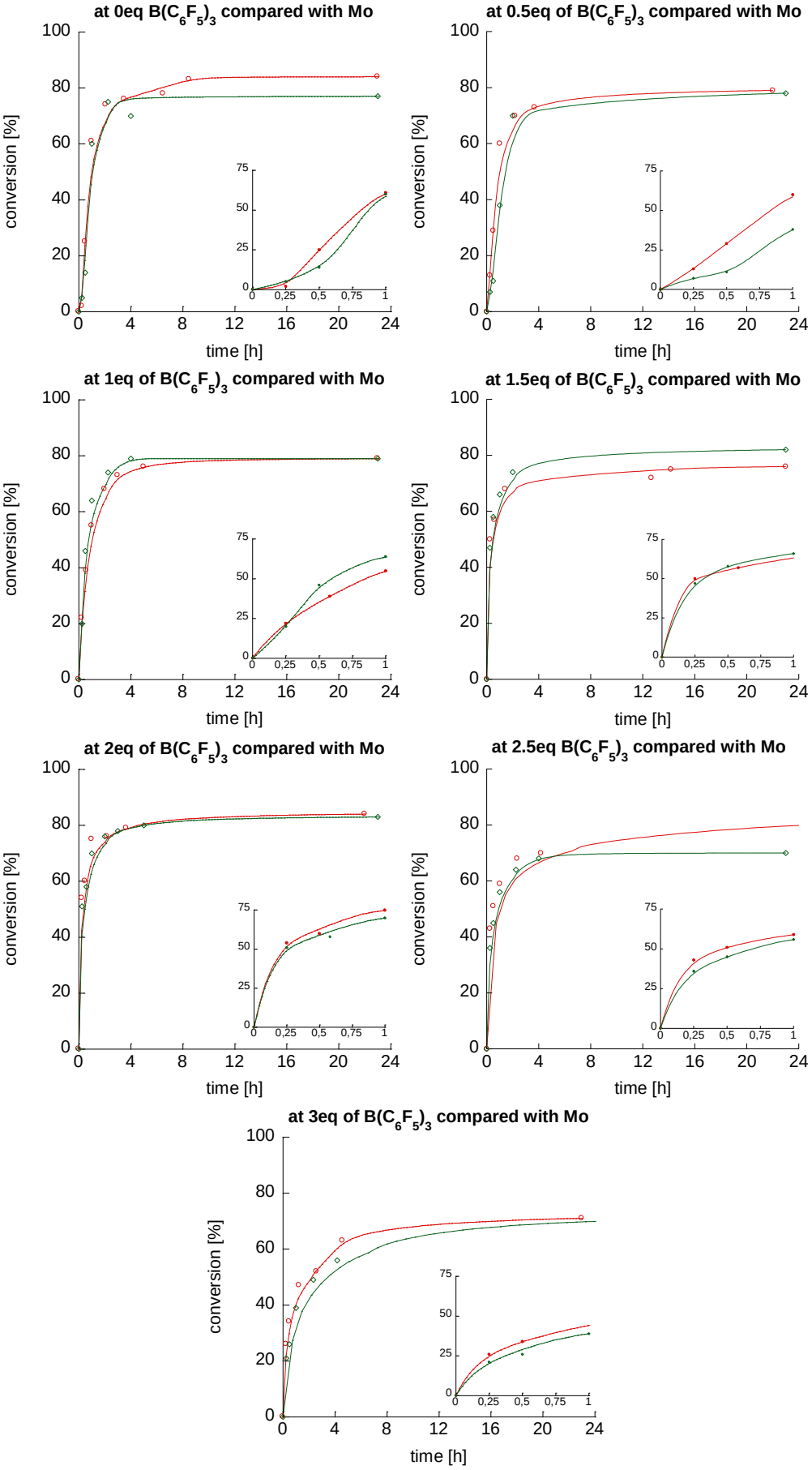
The same procedure described above is used with 1-phenyl-1-propyne (13.9mg, 0.12mmol), catalyst **2** (7.4mg, 2.5mol% Mo) and toluene (3mL) at 110°C to afford the following results:



4) Influence of the $B(C_6F_5)_3$ co-catalyst loading

The same protocol described before for self-metathesis is used except that $B(C_6F_5)_3$ is added in the reaction mixture as a solution in toluene (C=0.01M). In order to maintain the same range of concentration for all experiments, the amount of toluene is adjusted as follow:

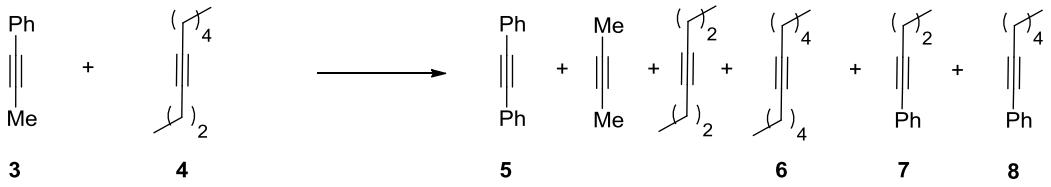
Number of equivalent of $B(C_6F_5)_3$ relative to Mo	Volume of $B(C_6F_5)_3$ solution (C=0,01M) [µL]	Volume of toluene added [mL]
0	0	3
0.5	150	3
1	293	3
1.5	449	2.5
2	599	2.5
2.5	748	2
3	879	2

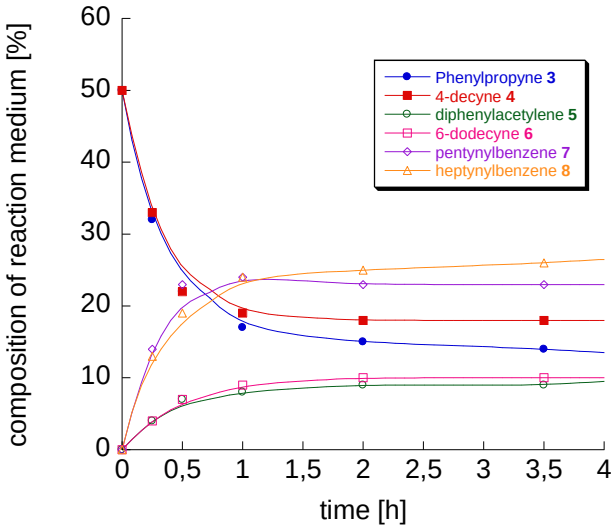


5) Cross-metathesis reactions:

Between 1-phenyl-1-propyne and 4-decyne:

In a glovebox, a storage tube equipped with a screw cap is loaded with 4-decyne (172.5mg, 1.25mmol), 1-phenyl-1-propyne (145mg, 1.25mmol), $B(C_6F_5)_3$ (12.8mg, 0.025mmol), catalyst **2** (30.5mg, 0.0125mmol Mo, 1mol% Mo) and toluene (2.5mL). The reaction mixture is heated at 80°C outside the glovebox. Kinetic monitoring of the reaction is performed through regular sampling by opening of the tube inside the glovebox after a fast entry/exit (5min overall). Conversion is measured referring to an external standard (decane) by GC. The relative error is estimated to be 5%. (The formation of 4-octyne could not be followed by GC because the retention time of this compound was too close from the solvent's one).

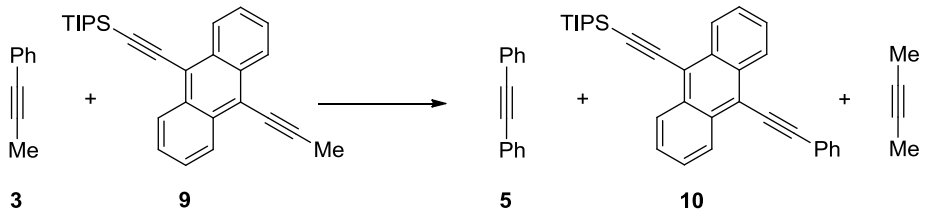


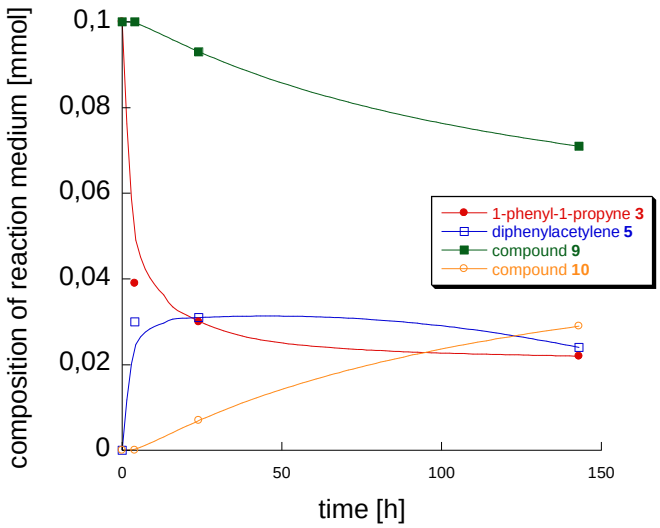


*Between 1-phenyl-1-propyne and compound **9**:*

In a glovebox, a storage tube equipped with a screw cap is loaded with compound **9** (39.6mg, 0.1mmol), 1-phenyl-1-propyne (11.6mg, 0.1mmol), $B(C_6F_5)_3$ (10.2mg, 0.02mmol), catalyst **2**

(24.6mg, 0.01mmol Mo, 10mol% Mo) and toluene (3mL). The reaction mixture is heated at 110°C outside the glovebox. Kinetic monitoring of the reaction is performed through regular sampling by opening of the tube inside the glovebox after a fast entry/exit (5min overall). Conversion is measured referring to an external standard (decane) by GC. The relative error is estimated to be 5%. Products were identified by comparison (retention time and fragmentation in GCMS) with pure samples prepared by alternative method (see below).

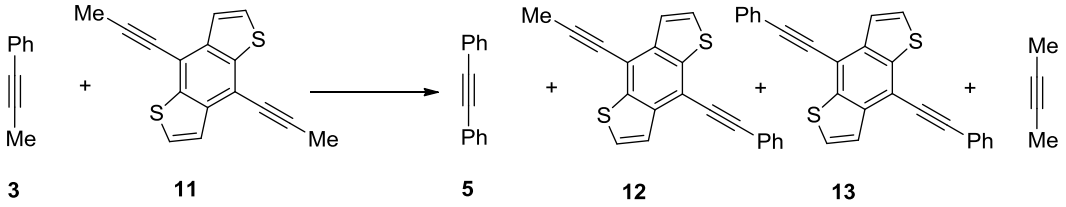


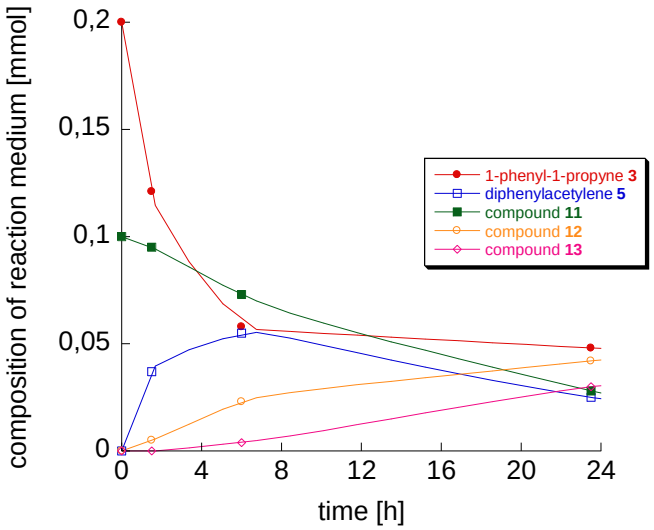


*Between 1-phenyl-1-propyne and compound **11**:*

In a glovebox, a storage tube equipped with a screw cap is loaded with compound **11** (26.6mg, 0.1mmol), 1-phenyl-1-propyne (23.2mg, 0.2mmol), $B(C_6F_5)_3$ (10.2mg, 0.02mmol), catalyst **2** (24.6mg, 0.01mmol Mo, 10mol% Mo) and toluene (3mL). The reaction mixture is heated at 110°C outside the glovebox. Kinetic monitoring of the reaction is performed through regular sampling by opening of the tube inside the glovebox after a fast entry/exit

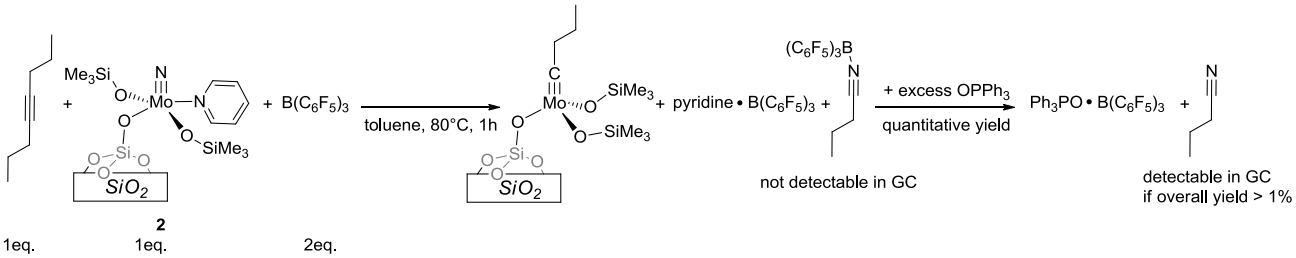
(5min overall). Conversion is measured referring to an external standard (decane) by GC. The relative error is estimated to be 5%. Products were identified by comparison (retention time and fragmentation in GCMS) with pure samples prepared by alternative method (see below).



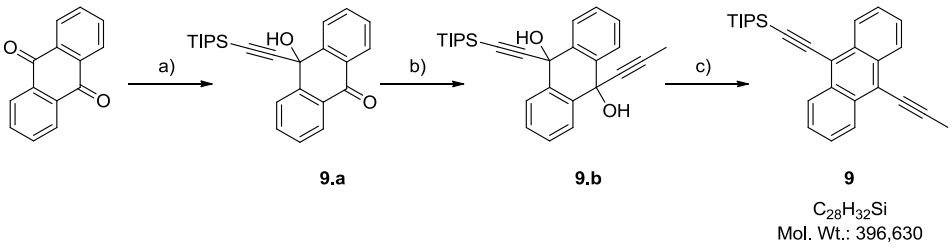


6) Description of attempts to observe nitrile by-products

As direct detection of nitriles from 4-decyne or 1-phenyl-1propyne was unsuccessful, symmetrical 4-octyne was used as substrate and reacted with 1eq of catalyst **2** and 2eq of $B(C_6F_5)_3$ per Mo in toluene at 80°C for 1h. The amount of 4-octyne and the concentration was adjusted so that 1% of formation of nitrile would have been detected by our GC method, as shown by injection of a standard solution. As $B(C_6F_5)_3$ could coordinate the nitrile, $OPPh_3$ was then added in excess to cleave the butyronitrile-$B(C_6F_5)_3$ adduct which is not observable in GC, from previous tests done to ensure that this deprotection is quantitative. Butyronitrile was not observed thus suggesting that less than 1% of the pre-catalyst **2** turns into active carbyne.



7) Synthesis and characterization of triisopropyl((10-(prop-1-yn-1-yl)anthracen-9-yl)ethynyl)silane 9:



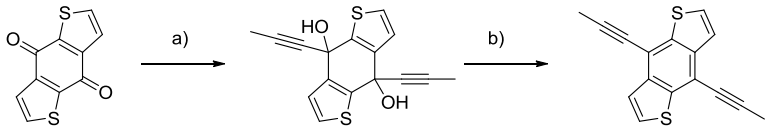
a) *n*-BuLi (3.28 mL, 5.25 mmol, 1.05 eq., 1.6M/hexanes) was dropwise added to a solution of triisopropylsilylacetylene (1.16 mL, 5.25 mmol, 1.05 eq.) in THF (10 mL) at -78°C under argon and the mixture was allowed to warm to room temp. After 15 min., this solution was dropwise added to a solution of anthraquinone (1.04 g, 5 mmol) in THF (100 mL) at -78°C under argon. The mixture was allowed to warm to room temp and stirred for 4 hours. The

reaction was then partitioned between 40 mL of NH_4Cl sat. and Et_2O (50 mL), and the layers separated. Aqueous phase was extracted with 2x30 mL of AcOEt. Organic phases where mixed and evaporated *in vacuo*. The residue has been purified by flash chromatography (Cyclohexane/EtOAc 9/1) to yield **9.a** (1.66 g, 4.25 mmol, 85 %) as a white solid.

b) A solution of 1-propynylmagnesium bromide (18 ml, 9 mmol, 3 eq., 0.5 M) in THF was added to a concentrated solution of **9.a** (1.17 g, 3 mmol) in THF (5 mL) a -78°C under argon. The mixture was allowed to warm to room temp. and stirred for 6 h. The reaction was then partitioned between $NH_4Cl_{sat.}$ (20 mL) and Et_2O (30 mL). Layers were separated, and the aqueous phase was extracted once with EtOAc (20 mL). Organic layers were mixed, dried over $MgSO_4$ and concentrated *in vacuo*. The crude residue **9.b** was directly taken to the next step.

c) Crude **9.b** (considered as 3 mmol) was dissolved in a minimum of dioxane (2 mL) and was added to a solution of $SnCl_2.2H_2O$ (1.69 g, 7.5 mmol, 2.5 eq.) in $AcOH.H_2O$ (23 mL 1:1). The mixture was stirred for 15 min. and was then diluted with Et_2O (300 mL). Solid Na_2CO_3 (10 g) was portion-wise added. The mixture was filtered over Celite® and over a silica pad. The filtrate was concentrated *in vacuo* and the crude residue was purified by flash chromatography (Cyclohexane:CH_2Cl_2) to afford **9** (0.99 g, 2.49 mmol, 83 % from **9.a**) as a yellow powder. TLC R*f* 0.38 (Cyclohexane/CH_2Cl_2 8/2); mp 140-142°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.26-1.28 (s, 21H), 2.42 (s, 3H), 7.54-7.61 (m, 4H), 8.54-8.66 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 5.5, 11.7, 19.1, 77.9, 78.1, 99.4, 103.6, 117.9, 119.9, 125.4, 126.6, 127.0, 127.4, 127.5, 132.3;

8) Synthesis and characterization of: 4,8-di(prop-1-yn-1-yl)benzo[1,2-b:4,5-b']dithiophene 11:



11.a **11**

$C_{16}H_{10}S_2$

Mol. Wt.: 266,381

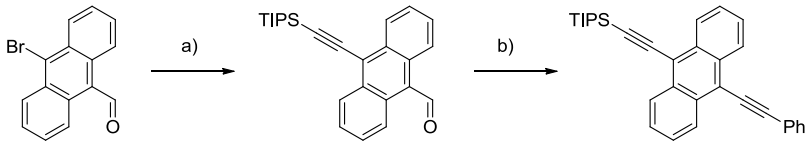
a) A solution of 1-propynylmagnesium bromide (18 ml, 9 mmol, 3 eq., 0.5 M) in THF was added to a solution of benzo[1,2-b:4,5-b']dithiophene-4,8-dione[2] (3 mmol) in THF (40 mL) at -78°C under argon. The mixture was allowed to warm to room temp and stirred for 4 hours. The reaction was partitioned between 40 mL of NH_4Cl sat. and Et_2O (50 mL) and the layers separated. Aqueous phase was extracted with 2x30 mL of AcOEt. Organic phases where mixed and evaporated *in vacuo*. The crude **11.a** was directly taken to the next step.

b) Crude **11.a** (considered as 3 mmol) was dissolved in dioxane (3 mL) and was added to a solution of $SnCl_2.2H_2O$ (1.69 g, 7.5 mmol, 2.5 eq.) in $AcOH.H_2O$ (23 mL 1:1). The mixture was stirred for 15 min. and was then diluted with Et_2O (300 mL). Solid Na_2CO_3 (10 g) was portionwise added. The mixture was filtered over Celite® and over a silica pad. The filtrate was concentrated *in vacuo* and the crude residue was purified by flash chromatography (Cyclohexane:CH_2Cl_2) to afford **11** (783 mg, 2.94 mmol, 98 % from benzo[1,2-b:4,5-b']dithiophene-4,8-dione) as a yellow powder.

TLC R*f* 0.36 (Cyclohexane/CH_2Cl_2 8/2); mp 192°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 2.29 (s, 6H), 7.50 (d, *J* = 5.6 Hz, 2H), 7.59 (d, *J* = 5.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 5.2, 76.4, 95.9, 112.4, 123.4, 127.8, 138.5, 140.3.

9) Independent synthesis of 10 and 13:

*triisopropyl((10-(phenylethynyl)anthracen-9-yl)ethynyl)silane **10**:*



10.a **10**

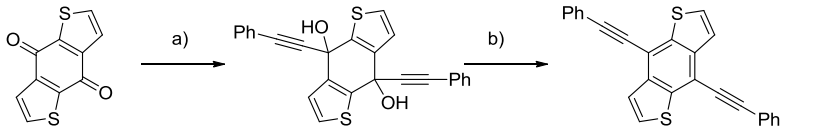
$C_{33}H_{34}Si$
Mol. Wt.: 458,709

a) TIPS-acetylene (1.2 equiv., 539 µL, 2.4 mmol), $Pd(PPh_3)_4$ (69 mg, 3 mol%) and CuI (23 mg, 6 mol%) were added to a solution of 9-bromo-10-anthracenecarboxaldehyde (570 mg , 2 mmol) in THF (5 mL), NEt_3 (5 mL) was added and the mixture was stirred at 80°C for 16 h. After cooling to room temp., the mixture was diluted in Et_2O (20 mL) and filtered on a short pad of silica. The mixture was concentrated *in vacuo* and the residue has been purified by flash chromatography (Cyclohexane/EtOAc 9/1) to yield **10.a** (742 mg, 1.92 mmol, 96%**)** as a bright yellow powder.

b) A solution of LiHMDS in THF (5 equiv., 6 mL, 6 mmol, 1M/THF) was added to a mixture of **10.a** (445 mg , 1.15 mmol,), benzyl phenyl sulfone ($PhSO_2Bn$) (1.2 equiv., 320 mg, 1.38 mmol) and diethyl chlorophosphate (1.2 equiv., 201 µL, 1.38 mmol) in THF (35 mL) at 0°C. The mixture was then stirred for 24 h protected from light. An aqueous solution of NH_4Cl (sat.) (1 mL) was added and the mixture was concentrated in *vacuo*. The crude residue was purified by flash chromatography (Cyclohexane:CH_2Cl_2) to afford **10** (438 mg, 0.96 mmol, 83% from **10a**) as a yellow powder. TLC R*f* 0.36 (Cyclohexane/CH_2Cl_2 9/1); mp 100-101°C; IR ν_{max} 3057, 2940, 2888, 2862, 2721, 2128, 1619, 1595, 1571, 1518, 1492, 1459, 1442, 1436, 1387, 1366, 1328, 1296, 1243, 1177, 1147, 1069, 1027, 1016, 994, 960, 916, 881, 853, 837, 817 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 1.31 and 1.32 (s, 21H), 7.42-7.50 (m, 3H), 7.63-7.68 (m, 4H), 7.79-7.81 (m, 2H), 8.68-8.73 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$)

δ (ppm) 11.8, 19.1, 86.7, 102.6, 103.7, 105.1, 118.7, 118.9, 123.7, 129.9, 127.1, 127.4, 127.5, 128.8, 128.9, 131.9, 132.2, 132.7; HR-MS 481.232 ($C_{33}H_{34}Si$ + Na calcd 481.232).

*4,8-bis(phenylethynyl)benzo[1,2-b:4,5-b']dithiophene **13**:*



13.a **13**

Chemical Formula: $C_{26}H_{14}S_2$
Molecular Weight: 390,519

a) *n*-BuLi (2 mmol, 1.25 mL 4 eq., 1.6 M/hexanes) was dropwise added to a solution of phenylacetylene (2 mmol, 219 µL, 4 eq.) in THF (4 mL) at -78°C under argon and the mixture was allowed to warm to room temp. After 15 min., this solution was dropwise added to a solution of benzo[1,2-b:4,5-b']dithiophene-4,8-dione[2] (0.5 mmol, 110,1 mg) in THF (10 mL) at -78°C under argon. The mixture was allowed to warm to room temp and stirred for 4 hours. The reaction was partitioned between 40 mL of NH_4Cl sat. and Et_2O (50 mL) and the layers separated. Aqueous phase was extracted with 2x20 mL of AcOEt. The organic phases where mixed and evaporated *in vacuo* and the crude residue was directly taken to the next step.

b) Crude **13.a** (781 mg) was dissolved in dioxane (4 mL) and poured to a solution a $SnCl_2.2H_2O$ (4.6 mmol, 1.04 g, 2.5 eq.) in $AcOH.H_2O$ (1:1; 25 mL). The mixture was stirred for 30 min. The mixture was diluted with Et_2O (100 mL) and solid Na_2CO_3 was slowly added. Layers were separated and the mixture was concentrated *in vacuo*. The residue was taken up in Et_2O and carefully extracted with 3x30 mL of aqueous Na_2CO_3 (sat.). The organic phase was concentrated *in vacuo* and the product was purified by flash chromatography (Cyclohexane:CH_2Cl_2; 70:30) to afford **13** (1.74 mmol, 690 mg, 87 % over two steps) as a bright yellow powder. TLC R*f* 0.28 (Cyclohexane/CH_2Cl_2 7/3); mp 204°C; IR ν_{max} 3104, 3080, 3046, 2921, 2852, 1594, 1598, 1513, 1488, 1462, 1440, 1388, 1330, 1311, 1284, 1245,

1179, 1168, 1156, 1136, 1104, 1081, 1070, 1025, 999, 984, 952, 913, 876, 841, 829, 810 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.39-7.46 (m, 6H), 7.60 (d, *J* = 5.6 Hz, 2H), 7.68-7.71 (m, 4H), 7.72 (d, *J* = 5.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 85.7, 99.3, 112.1, 122.9, 123.3, 128.2, 128.5, 128.9, 131.8, 138.3, 140.4; HR-MS 413.043 ($C_{26}H_{14}S_2$ + Na calcd 413.043).

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