# Supporting information Metallomicelle Catalyzed Aerobic Tandem Desilylation/Glaser Reaction in Waters

Shanyu Tang, Longjia Li, Xuanhe Ren, Jiao Li, Guanyu Yang, Heng Li, and Bingxin Yuan\*

College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou, Henan, China, 450001

| Contents   |    |
|--|----|
| General Information  | 3  |
| Typical Procedure to Synthesize L <sub>1</sub> -L <sub>4</sub> | 4  |
| Typical Procedure for Homocoupling of TMS-alkynes              | 4  |
| Typical Procedure for Homocoupling of terminal alkynes         | 4  |
| Procedure for the circulation of the mother liquor             | 5  |
| Preparation and Characterization of Micelles                   | 5  |
| Characterization Data of all products                          | 7  |
| References   | 12 |
| The NMR Spectra of all products                                | 14 |

|       |               | 1120,                    | 02,100 0, 01     |                      |        |                          |
|-------|---------------|--------------------------|------------------|----------------------|--------|--------------------------|
| Entry | CuI<br>(mol%) | L <sub>2</sub><br>(mol%) | NaOH<br>(equiv.) | O <sub>2</sub> (MPa) | T (°C) | Yield (%) <sup>[b]</sup> |
| 1     | 0             | 0                        | 1                | 0.3                  | 100    | 0                        |
| 2     | 1             | 1                        | 1                | 0.3                  | 100    | trace                    |
| 3     | 5             | 5                        | 1                | 0.3                  | 100    | 47                       |
| 4     | 10            | 10                       | 1                | 0.3                  | 100    | 98                       |
| 5     | 15            | 15                       | 1                | 0.3                  | 100    | 98                       |
| 6     | 5             | 10                       | 1                | 0.3                  | 100    | 49                       |
| 7     | 10            | 5                        | 1                | 0.3                  | 100    | 53                       |
| 8     | 10            | 10                       | 1                | 0.1                  | 100    | $47(34^{[c]}, 0^{[d]})$  |
| 9     | 10            | 10                       | 1                | 0.2                  | 100    | 91                       |
| 10    | 10            | 10                       | 1                | 0.3                  | r.t.   | 31                       |
| 11    | 10            | 10                       | 1                | 0.3                  | 60     | 69                       |
| 12    | 10            | 10                       | 1                | 0.3                  | 80     | 98                       |
| 13    | 10            | 10                       | 0.2              | 0.3                  | 80     | trace                    |
| 14    | 10            | 10                       | 0.4              | 0.3                  | 80     | 24                       |
| 15    | 10            | 10                       | 0.6              | 0.3                  | 80     | 59                       |
| 16    | 10            | 10                       | 0.8              | 0.3                  | 80     | 88                       |
| 17    | 10            | 10                       | 1.2              | 0.3                  | 80     | 98                       |

 $-SiMe_3 \xrightarrow{\text{catalyst, ligand, base}} \overline{H_2O, O_2, 100 \, ^{\circ}C, 6h}$ 

#### Table S1. Optimization of reaction reagents.<sup>[a]</sup>

<sup>[a]</sup> Reaction conditions: **1a** (0.3 mmol), Catalyst (x mol%), Ligand (y mol%), NaOH (1.0 equiv.), H<sub>2</sub>O (2 mL), O<sub>2</sub>, T °C, 6 h. <sup>[b]</sup> Isolated yield. <sup>[c]</sup> air. <sup>[d]</sup> N<sub>2</sub>.

#### **General Information**

All materials and catalysts were purchased from general merchant. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded at a Bruker Advance III HD spectrometer (Bremen, Germany) at 600 MHz (400 MHz) for <sup>1</sup>H NMR and 150 MHz (100 MHz) for <sup>13</sup>C NMR with CDCl<sub>3</sub> or  $d_6$ -DMSO as the solvent and TMS as the internal standard. High resolution mass spectra (HRMS) were measured with an Agilent 1290-6540 (Santa

Clara, USA). Low resolution mass spectra (LRMS) were recorded at an electron ionization (EI) conditions by using a Shimadzu GCMS-QP2010 Plus mass spectrometer (Kyoto, Japan). The melting points of the products were determined by an X-4 micro-melting point apparatus (Beijing, China). UV is measured by Agilent 8453 UV-visible Spectroscopy System. The average hydrodynamic size of micelles was measured by dynamic light scattering (DLS) on a Particle Size and Zeta Potential (Nanoplus-3, Micromeritics, USA), and transmission electron microscope (TEM, TECNAIG2F20-S-TWIN, FEI, USA) with a field emission gun at 200 kV. Surface tension was measured by BYZ-2 automated tensiometer (Shanghai, China) at 289.15 K.

#### Typical Procedure to Synthesize L<sub>1</sub>-L<sub>4</sub>

A 25 mL Schlenk flask was charged with triethylene glycol MonoMethyl ether (3 mmol, 5.0 equiv), NaH (3.6 mmol, 6.0 equiv) and DMF (3 mL). The resulting mixture was stirred at room temperature for 10 minutes until no bubbles appeared in the reaction tube. And then 2,9-dibromo-1,10-phenanthroline (0.6 mmol, 1.0 equiv) was added. Finally, the schlenk tube was heated in 110 °C oil bath for 4 h. After the reaction was finished, the reaction mixture was extracted with dichloromethane ( $3 \times 50$  mL), and then dried over anhydrous sodium sulfate and filtered. After evaporation of the solvent under vacuum, the residue was subjected to flash column chromatography on silica gel to afford products L<sub>1</sub>-L<sub>4</sub>.

#### **Typical Procedure for Homocoupling of TMS-alkynes**

A 25 mL Schlenk flask was charged with 1-Phenyl-2-(triMethylsilyl)acetylene (51.3 mg, 0.3 mmol), CuI (5.7 mg, 0.03 mmol),  $L_2$  (15.1 mg, 0.03 mmol), NaOH (12.0 mg, 0.3 mmol), H<sub>2</sub>O (2 mL), 0.3 MPa O<sub>2</sub>, and then the resulting mixture was stirred at 80 °C for 6h. After the reaction was finished, the reaction mixture was extracted with dichloromethane (3 × 50 mL), and then dried over anhydrous sodium sulfate and filtered. After evaporation of the solvent under vacuum, the residue was subjected to flash column chromatography on silica gel to afford products **2a-21**.

#### Typical Procedure for Homocoupling of terminal alkynes

A 25 mL Schlenk flask was charged with ethynylbenzene (30.6 mg, 0.3 mmol), CuI (5.7 mg, 0.03 mmol),  $L_2$  (15.1 mg, 0.03 mmol),  $H_2O$  (2 mL), 0.3 MPa  $O_2$ , and then the resulting mixture was stirred at 80 °C for 6h. After the reaction was finished, the reaction mixture was extracted with dichloromethane (3 × 50 mL), and then dried over anhydrous sodium sulfate and filtered. After evaporation of the solvent under vacuum, the residue was subjected to flash column chromatography on silica gel to afford products **2a-p**.

#### Typical Procedure for the Cross-coupling reaction of TMS-Alkynes

A 25 mL Schlenk flask was charged with ((4-methoxyphenyl)ethynyl)trimethylsilane (61.2 mg, 0.3 mmol), 1-Phenyl-2-(triMethylsilyl)acetylene (153.9 mg, 0.9 mmol), CuI (5.7 mg, 0.03 mmol),  $L_2$  (15.1 mg, 0.03 mmol), NaOH (12.0 mg, 0.3 mmol), H<sub>2</sub>O (2

mL), 0.3 MPa  $O_2$ , and then the resulting mixture was stirred at 80 °C for 6h. After the reaction was finished, the reaction mixture was extracted with dichloromethane (3 × 50 mL), and then dried over anhydrous sodium sulfate and filtered. After evaporation of the solvent under vacuum, the residue was subjected to flash column chromatography on silica gel to afford products **4a-4d**.

#### Typical Procedure for the Cross-coupling reaction of terminal alkynes

A 25 mL Schlenk flask was charged with ethynylbenzene (30.6 mg, 0.3 mmol), 2methylbut-3-yn-2-ol (75.6 mg, 0.9 mmol), CuI (5.7 mg, 0.03 mmol),  $L_2$  (15.1 mg, 0.03 mmol), H<sub>2</sub>O (2 mL), 0.3 MPa O<sub>2</sub>, and then the resulting mixture was stirred at 80 °C for 6 h. After the reaction was finished, the reaction mixture was extracted with dichloromethane (3 × 50 mL), and then dried over anhydrous sodium sulfate and filtered. After evaporation of the solvent under vacuum, the residue was subjected to flash column chromatography on silica gel to afford products **5a-5c**.

#### Procedure for the circulation of the mother liquor

To a reactor (70 mL) was added 1-Phenyl-2-(triMethylsilyl)acetylene **1a** (342 mg, 2 mmol), CuI (38 mg, 0.2 mmol), L<sub>2</sub> (100.8 mg, 0.2 mmol), NaOH (80 mg, 2 mmol), H<sub>2</sub>O (15 mL).The reactor was charged with O<sub>2</sub> up to 0.3 MPa three times. Subsequently, the reactor was stirred under 0.3 MPa O<sub>2</sub> at 80 °C for 12 h, replenishing oxygen up to 0.3 MPa promptly if the pressure declined during the reaction period. After cooling to room temperature, the reaction mixture was filtered and washed with 0.5 mL water. The filter cake was dried and the desired product **2a** was obtained, giving the yield up to 96%. The filtrate was reused directly in the next run. A fresh batch of ethynylbenzene (204 mg, 2 mmol) and NaOH (80 mg, 2 mmol) was added to the filtrate and the reaction was performed under the same reaction condition. We carried out the oxidation process successfully in 5 runs, with the yields varying as follow: 96%, 94%, 93%, 90%, 90%.

To a reactor (70 mL) was added ethynylbenzene **1a'** (204 mg, 2 mmol), CuI (38 mg, 0.2 mmol),  $L_2$  (100.8 mg, 0.2 mmol),  $H_2O$  (15 mL). The reactor was charged with  $O_2$  up to 0.3 MPa three times. Subsequently, the reactor was stirred under 0.3 MPa  $O_2$  at 80 °C for 12 h, replenishing oxygen up to 0.3 MPa promptly if the pressure declined during the reaction period. After cooling to room temperature, the reaction mixture was filtered and washed with 0.5 mL water. The filter cake was dried and the desired product **2a** was obtained, giving the yield up to 97%. The filtrate was reused directly as the solvent in the next run with the addition of fresh ethynylbenzene (204 mg, 2 mmol). We carried out the oxidation process successfully in 5 runs, with the yields varying as follow: 97%, 95%, 92%, 91%, 89%.

#### **Preparation and Characterization of Micelles**

#### **UV-Vis measurement of Micelles**

 $L_2$  was formulated into an aqueous solution of 0.015 mol/L. CuI was added in a corresponding ratio. The mixed solution was stirred at room temperature for 12 h and

then diluted to  $4 \times 10^{-5}$  mol/L. The measurement was carried out using water as a background solution.

#### **TEM mearsurement of Micelles**

#### 1) TEM of pure $L_2$

 $L_2$  (0.02 mmol, 10.1 mg) was dissolved in 2 mL of water and stirred at room temperature for 2 h to obtain a micelle solution. To prepare specimens for TEM observation, a drop of the micelle solution was deposited onto a carbon-coated copper grid. After deposition, excess solution was removed using a strip of filter paper. Then the carbon-coated copper grid dried in air.

#### 2) TEM of CuI/ $L_2$ (1:1)

 $L_2$  (0.02 mmol, 10.1 mg) and CuI (0.02 mmol, 3.8 mg) was dissolved in 2 mL of water and stirred at room temperature for 12h to obtain a micelle solution. To prepare specimens for TEM observation, a drop of the micelle solution was deposited onto a carbon-coated copper grid. After deposition, excess solution was removed using a strip of filter paper. Then the carbon-coated copper grid dried in air.

#### **DLS mearsurement of Micelles**

1. DLS measurement of  $Cu/L_2$  (Cu:L2 = 1:1)

CuI and  $L_2$  are mixed in 1:1 ratio to prepare a micelle solution of 0.015 mol/mL. The solution was stirred 12 h at room temperature. The average hydrodynamic size of micelles was measured by dynamic light scattering (DLS) on a on a Particle Size and Zeta Potential (Nanoplus-3, Micromeritics, USA).

2. DLS measurement of  $L_2$ 

A 0.015 mol/mL solution of  $L_2$  was prepared by stirring for 12 h at room temperature. The average hydrodynamic size of micelles was measured by dynamic light scattering (DLS) on a on a Particle Size and Zeta Potential (Nanoplus-3, Micromeritics, USA).

#### Surface tension measurement of Micelles

A micelle solution of  $3 \times 10^{-2}$  mol/L L<sub>2</sub> was prepared. The solution was stirred 2 h at room temperature and then diluted to  $2.5 \times 10^{-2}$  mol/L ,  $2 \times 10^{-2}$  mol/L ,  $1.5 \times 10^{-2}$  mol/L ,  $1.25 \times 10^{-2}$  mol/L ,  $1 \times 10^{-2}$  mol/L ,  $7.5 \times 10^{-3}$  mol/L ,  $6 \times 10^{-3}$  mol/L ,  $5 \times 10^{-3}$  mol/L ,  $3 \times 10^{-3}$  mol/L ,  $2.5 \times 10^{-3}$  mol/L ,  $1 \times 10^{-3}$  mol/L ,  $5 \times 10^{-4}$  mol/L ,  $2.5 \times 10^{-4}$  mol/L ,  $1 \times 10^{-4}$  mol/L , respectively. And then, the solutions was stirred 2 h at room temperature. The surface tensions of the solutions of micelles were determined by the Wilhelmy Plate method with an accuracy of  $\pm 0.01$  mN/m. The measurements were carried out at 286.15 K with an uncertainty of 0.1 K.

**Characterization Data of all products** 



**2,9-bis(2-(2-(2-methoxyethoxy)ethoxy)-1,10-phenanthroline (L<sub>1</sub>).** colorless oil (272.7 mg, 90% yield) (ethyl acetate as eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.06 (d, *J* = 8.7 Hz, 2H), 7.58 (s, 2H), 7.11 (d, *J* = 8.7 Hz, 2H), 4.93-4.80 (m, 4H), 4.08-3.96 (m, 4H), 3.83-3.77 (m, 4H), 3.73-3.68 (m, 4H), 3.68-3.61 (m, 4H), 3.56-3.50 (m, 4H), 3.36 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 162.1, 142.9, 139.0, 125.2, 123.4, 113.6, 71.9, 70.6, 70.6, 70.5, 69.9, 65.1, 59.0. HRMS (ESI): m/z calcd for C<sub>26</sub>H<sub>37</sub>N<sub>2</sub>O<sub>8</sub> [M+H]<sup>+</sup>, 505.2544; found, 505.2543.



**4,7-bis(2-(2-(2-methoxyethoxy)ethoxy)-1,10-phenanthroline (L<sub>2</sub>).** orange oil (284.9 mg, 94% yield) (methyl alcohol as eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.99 (d, *J* = 5.2 Hz, 2H), 8.20 (s, 2H), 6.99 (d, *J* = 5.3 Hz, 2H), 4.48-4.31 (m, 4H), 4.08-4.02 (m, 4H), 3.90-3.77 (m, 4H), 3.74-3.69 (m, 4H), 3.69-3.64 (m, 4H), 3.57-3.52 (m, 4H), 3.37 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 161.4, 151.1, 146.9, 120.9, 119.1, 103.5, 71.9, 71.1, 70.7, 70.6, 69.4, 68.1, 59.1. HRMS (ESI): m/z calcd for C<sub>26</sub>H<sub>37</sub>N<sub>2</sub>O<sub>8</sub> [M+H]<sup>+</sup>, 505.2544; found, 505.2548.



**6,6'-bis(2-(2-(2-methoxyethoxy)ethoxy)-2,2'-bipyridine** (L<sub>3</sub>). Yellow oil (284.9 mg, 89% yield) (ethyl acetate as eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.04-7.85 (m, 2H), 7.75-7.58 (m, 2H), 6.82-6.74 (m, 2H), 4.61 (t, *J* = 3.8 Hz, 4H), 3.95-3.7 (m, 4H), 3.79-3.73 (m, 4H), 3.71-3.63 (m, 8H), 3.58-3.51 (m, 4H), 3.37 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 162.8, 153.2, 139.3, 113.7, 111.3, 71.9, 70.7, 70.7, 70.6, 69.8, 64.9, 59.1. HRMS (ESI): m/z calcd for C<sub>24</sub>H<sub>37</sub>N<sub>2</sub>O<sub>8</sub> [M+H]<sup>+</sup>, 481.2544; found, 481.2549.



4,4'-bis(2-(2-(2-

**methoxyethoxy)ethoxy)-2,2'-bipyridine** (L<sub>4</sub>): Yellow oil (284.9 mg, 89% yield) (ethyl acetate as eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.45 (d, *J* = 5.7 Hz, 2H), 7.98 (d, *J* = 2.4 Hz, 2H), 6.89-6.83 (m, 2H), 4.31-4.24 (m, 4H), 3.92-3.84 (m, 4H), 3.77-3.71 (m, 4H), 3.69-3.60 (m, 8H), 3.55-3.51 (m, 4H), 3.36 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 165.9, 157.8, 150.1, 111.5, 106.6, 71.9, 70.9, 70.7, 70.6, 69.4, 67.5, 59.1. HRMS (ESI): m/z calcd for C<sub>24</sub>H<sub>37</sub>N<sub>2</sub>O<sub>8</sub> [M+H]<sup>+</sup>, 481.2544; found, 481.2549.

**1,4-diphenylbuta-1,3-diyne (2a)**<sup>[1]</sup>. White solid (30.0 mg, 99% yield) (hexane as eluent); mp 86-87°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.55-7.51 (m, 5H), 7.38-7.30 (m, 5H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 132.5, 129.3, 128.5, 121.8, 81.6, 74.0. LRMS (EI) : m/z calcd for C<sub>16</sub>H<sub>10</sub> [M]<sup>+</sup>, 202; found, 202.

**1,4-di-***p***-tolylbuta-1,3-diyne (2b)**<sup>[1]</sup>. White solid (32.4 mg, 94% yield) (hexane as eluent); mp 189-190 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.41 (d, *J* = 8.1 Hz, 4H), 7.14 (d, *J* = 7.9 Hz, 4H), 2.36 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 139.5, 132.4, 129.2, 118.8, 81.6, 73.5, 21.7. LRMS (EI): m/z calcd for C<sub>18</sub>H<sub>14</sub> [M]<sup>+</sup>, 230; found, 230.



**1,4-di-m-tolylbuta-1,3-diyne (2c)**<sup>[1]</sup>. White solid (28.6 mg, 83% yield) (hexane as eluent); mp 69-70 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.35-7.33 (m, 4H), 7.25-7.15 (m, 4H), 2.34 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 138.2, 133.0, 130.2, 129.6, 128.4, 121.6, 81.6, 73.6, 21.3. LRMS (EI): m/z calcd for C<sub>18</sub>H<sub>14</sub> [M]<sup>+</sup>, 230; found, 230.



**1,4-di-***o***-tolylbuta-1,3-diyne (2d)**<sup>[2]</sup>. White solid (33.1 mg, 96% yield) (hexane as eluent); mp 72-74 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.45 (d, *J* = 7.6 Hz, 2H), 7.22 - 7.14 (m, 4H), 7.10 (t, *J* = 7.4 Hz, 2H), 2.44 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 141.7, 132.9, 129.6, 129.1, 125.7, 121.7, 81.2, 77.5, 20.8. LRMS (EI): m/z calcd for C<sub>18</sub>H<sub>14</sub> [M]<sup>+</sup>, 230; found, 230.



**1,4-bis(4-(***tert***-butyl)phenyl)buta-1,3-diyne (2e)<sup>[3]</sup>.** White solid (42.9 mg, 91% yield) (hexane as eluent); mp 193-194 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.46 (d, *J* = 8.8 Hz, 4H), 7.35 (d, *J* = 8.4 Hz, 4H), 1.31 (s, 18H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 152.6, 132.3, 125.5, 118.8, 81.5, 73.5, 34.9, 31.1. LRMS (EI): m/z calcd for C<sub>24</sub>H<sub>26</sub> [M]<sup>+</sup>, 314; found, 314.



**1,4-bis(4-methoxyphenyl)buta-1,3-diyne (2f)** <sup>[1]</sup>. Pale yellow solid (38.1 mg, 97% yield) (hexane as eluent); mp 139-140 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.46 (d, *J* = 8.8 Hz, 4H), 6.85 (d, *J* = 8.8 Hz, 4H), 3.82 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 160.3, 134.1, 114.2, 113.9, 81.3, 73.0, 55.4. LRMS (EI): m/z calcd for C<sub>18</sub>H<sub>14</sub>O<sub>2</sub> [M]<sup>+</sup>, 262; found, 262.



**1,4-bis(2-chlorophenyl)buta-1,3-diyne (2g)**<sup>[1]</sup>. White solid (39.7 mg, 98% yield) (hexane as eluent); mp 138-140 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.60-7.55 (m, 2H), 7.45-7.39 (m, 2H), 7.34-7.28 (m, 2H), 7.27-7.20 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 137.0, 134.4, 130.3, 129.5, 126.6, 121.8, 79.5, 78.4. LRMS (EI): m/z calcd for C<sub>16</sub>H<sub>8</sub>Cl<sub>2</sub> [M]<sup>+</sup>, 270; found, 270.



**1,4-bis(2-bromophenyl)buta-1,3-diyne (2h)**<sup>[4]</sup>. Pale yellow solid (46.7 mg, 87% yield) (hexane as eluent); mp 180-182 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.63-7.54 (m, 4H), 7.33-7.18 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 134.6, 132.6, 130.5, 127.2, 126.3, 124.1, 81.1, 77.9. LRMS (EI): m/z calcd for C<sub>16</sub>H<sub>8</sub>Br<sub>2</sub> [M]<sup>+</sup>, 358; found, 358.

**1,4-bis(4-fluorophenyl)buta-1,3-diyne (2i)**<sup>[1]</sup>. White solid (31.2 mg, 87% yield) (hexane as eluent); mp 190-191 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.55-7.48 (m, 4H), 7.09-6.99 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 164.3 (d, *J* = 250.1 Hz), 134.6 (d, *J* = 8.6 Hz), 117.8 (d, *J* = 3.6 Hz), 116.0 (d, *J* = 22.3 Hz), 80.44, 73.53. LRMS (EI): m/z calcd for C<sub>16</sub>H<sub>8</sub>F<sub>2</sub> [M]<sup>+</sup>, 238; found, 238.

**1,4-bis(4-(trifluoromethyl)phenyl)buta-1,3-diyne (2j)**<sup>[5]</sup>. Pale yellow solid (47.2 mg, 93% yield) (hexane as eluent); mp 167-168 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.65-7.60 (m, 8H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 132.8, 131.0 (q, *J* = 32.0 Hz), 125.2, 125.4 (q, *J* = 4.0 Hz), 123.7 (q, *J* = 271.0 Hz), 81.0, 75.6. LRMS (EI): m/z calcd for C<sub>18</sub>H<sub>8</sub>F<sub>6</sub> [M]<sup>+</sup>, 338; found, 338.



**1,4-di(naphthalen-1-yl)buta-1,3-diyne (2k)**<sup>[6]</sup>. White solid (42.1 mg, 93% yield) (hexane as eluent); mp 169-171 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.43 (d, *J* = 8.3 Hz, 2H), 7.92-7.80 (m, 6H), 7.68-7.60 (m, 2H), 7.58-7.52 (m, 2H), 7.49-7.42 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 133.9, 133.1, 132.1, 129.8, 128.5, 127.3, 126.8, 126.2, 125.3, 119.5, 81.0, 78.7. LRMS (EI): m/z calcd for C<sub>24</sub>H<sub>14</sub> [M]<sup>+</sup>, 302; found, 302.



**1,4-di(thiophen-2-yl)buta-1,3-diyne (2l)**<sup>[1]</sup>. White solid (26.0 mg, 81% yield) (hexane as eluent); mp 90-91 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.39-7.25 (m, 4H), 7.07-6.88 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 134.5, 129.0, 127.3, 121.9, 77.9, 76.7. LRMS (EI): m/z calcd for C<sub>12</sub>H<sub>6</sub>S<sub>2</sub> [M]<sup>+</sup>, 214; found, 214.

**deca-4,6-diyne (2m)**<sup>[7]</sup>: Colorless oil (15.1 mg, 75% yield) (hexane as eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 2.23 (t, *J* = 7.0 Hz, 4H), 1.62-1.47 (m, 4H), 0.99 (t, *J* = 7.4 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 77.2, 65.4, 21.9, 21.1, 13.4. LRMS (EI): m/z calcd for C<sub>10</sub>H<sub>14</sub> [M]<sup>+</sup>, 134; found, 134.

## $\triangleright = = \checkmark$

**1,4-dicyclopropylbuta-1,3-diyne (2n)**<sup>[8]</sup>. Colorless oil (14.4 mg, 74% yield) (hexane as eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.34-1.23 (m, 2H), 0.81-0.73 (m, 8H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 80.0, 60.8, 8.7, 0.1. LRMS (EI): m/z calcd for C<sub>10</sub>H<sub>10</sub> [M]<sup>+</sup>, 130; found, 130.

**2,7-dimethylocta-3,5-diyne-2,7-diol (20)**<sup>[5]</sup>. White solid (21.0 mg, 84% yield) (hexane as eluent); mp 130-132 °C. <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  = 5.55 (s, 2H), 1.37 (s, 12H). <sup>13</sup>C NMR (100 MHz, DMSO)  $\delta$  = 86.1, 65.5, 64.1, 31.5. LRMS (EI): m/z calcd for C<sub>10</sub>H<sub>14</sub>O<sub>2</sub> [M]<sup>+</sup>, 166; found, 166.

(H<sub>3</sub>C)<sub>3</sub>Si----------Si(CH<sub>3</sub>)<sub>3</sub>

**1,4-bis(trimethylsilyl)buta-1,3-diyne (2p)**<sup>[7]</sup>. White solid (24.5 mg, 84% yield) (hexane as eluent); mp 107-109 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 0.19 (s, 18H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 88.0, 85.9, -0.5. LRMS (EI): m/z calcd for C<sub>10</sub>H<sub>18</sub>Si<sub>2</sub> [M]<sup>+</sup>, 194; found, 194.

<sup>1</sup>3 1-methoxy-4-(phenylbuta-1,3-diyn-1-

**yl)benzene (4a)**<sup>[9]</sup>. White solid (46.6 mg, 67% yield) (hexane as eluent); mp 95-96 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.46-7.41 (m, 2H), 7.39 (d, *J* = 8.7 Hz, 2H), 7.28-7.21 (m, 3H), 6.78 (d, *J* = 8.7 Hz, 2H), 3.73 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 160.4, 134.2, 132.5, 129.1, 128.5, 122.0, 114.2, 113.7, 81.9, 81.1, 74.2, 72.8, 55.4. LRMS (EI): m/z calcd for C<sub>17</sub>H<sub>12</sub>O [M]<sup>+</sup>, 232; found, 232.

 $\mathsf{F} - \swarrow - \bigcirc - \bigcirc \mathsf{OCH}_3$ 

#### 1-fluoro-4-((4-methoxyphenyl)buta-1,3-

**diyn-1-yl)benzene (4b)**<sup>[1]</sup>. White solid (47.3 mg, 63% yield) (hexane as eluent); mp 119-121 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.53-7.43 (m, 4H), 7.09-6.97 (m, 2H), 6.91-6.80 (m, 2H), 3.82 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 164.2, 161.7, 160.4, 134.5, 134.4, 134.2, 118.2, 118.1, 116.0, 115.8, 114.2, 113.6, 81.8, 79.9, 74.0, 74.0, 72.6, 55.4. LRMS (EI): m/z calcd for C<sub>17</sub>H<sub>11</sub>FO [M]<sup>+</sup>, 250; found, 250.



**2-((4-methoxyphenyl)buta-1,3-diyn-1-yl)thiophene (4c)**<sup>[10]</sup>. White solid (50.7 mg, 71% yield) (hexane as eluent); mp 67-69 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.49-7.43 (m, 2H), 7.33-7.29 (m, 2H), 7.00-6.98 (m, 1H), 6.89-6.82 (m, 2H), 3.82 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 160.5, 134.2, 134.1, 128.5, 127.2, 122.3, 114.2, 113.6,

83.9, 78.2, 74.0, 72.6, 55.4. LRMS (EI): m/z calcd for  $C_{15}H_{10}OS [M]^+$ , 238; found, 238.

**1-(cyclopropylbuta-1,3-diyn-1-yl)-4-methoxybenzene (4d)**<sup>[11]</sup>. Pale yellow oil (30.6 mg, 52% yield) (hexane as eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.45-7.36 (m, 2H), 6.85-6.77 (m, 2H), 3.80 (s, 3H), 1.45-1.34 (m, 1H), 0.92-0.76 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 159.6, 133.7, 113.7, 86.8, 73.9, 72.9, 60.2, 54.9, 8.6, 0.00. LRMS (EI): m/z calcd for C<sub>14</sub>H<sub>12</sub>O [M]<sup>+</sup>, 196; found, 196.

**2-methyl-6-phenylhexa-3,5-diyn-2-ol (5a)**<sup>[9]</sup>. White solid (36.4 mg, 66% yield) (hexane as eluent); mp 54-56 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.51-7.44 (m, 2H), 7.38-7.28 (m, 3H), 2.18 (s, 1H), 1.58 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 132.5, 129.3, 128.5, 121.5, 86.7, 78.8, 73.1, 67.1, 65.8, 31.1. LRMS (EI): m/z calcd for C<sub>13</sub>H<sub>12</sub>O [M]<sup>+</sup>, 184; found, 184.

**2-methyl-6-**(*p*-tolyl)hexa-3,5-diyn-2-ol (5b)<sup>[9]</sup>. Pale yellow solid (35.1 mg, 59% yield) (hexane as eluent); mp 78-79 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.38 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 2.35 (s, 3H), 2.03 (s, 1H), 1.58 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 139.7, 132.5, 129.2, 118.4, 86.3, 79.1, 72.5, 67.2, 65.8, 31.2, 21.7. LRMS (EI): m/z calcd for C<sub>14</sub>H<sub>14</sub>O [M]<sup>+</sup>, 198; found, 198.



**6-(4-fluorophenyl)-2-methylhexa-3,5-diyn-2-ol (5c)**<sup>[9]</sup>. White solid (43.0 mg, 71% yield) (hexane as eluent); mp 82-84 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.49-7.43 (m, 2H), 7.05-6.98 (m, 2H), 2.12 (s, 1H), 1.58 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 164.3, 161.8, 134.6, 134.5, 117.7, 117.6, 116.0, 115.8, 86.7, 77.7, 72.9, 72.9, 66.9, 65.8, 31.1. LRMS (EI): m/z calcd for C<sub>13</sub>H<sub>11</sub>FO [M]<sup>+</sup>, 202; found, 202.

#### References

- Zhang, L.; Wang, Y.; Liu, J.; Xu, M.; Zhang, X.; *RSC Adv.* 2016, 6, 28653-28657.
- [2] Kusuda, A.; Xu, X.; Wang, X.; Tokunaga, E.; Shibata, N.; *Green Chem.* 2011,13, 843-846.
- [3] Szadkowska, A.; Staszko, S.; Zaorska, E.; Pawłowski, R.; *RSC Adv.* **2016**, 6, 44248-44253.
- [4] Toshihiro, O.; Kenichi, K.; Atsushi, W.; Shigehiro, Y.; Org. Lett. 2005, 7(23), 5301-5304.
- [5] Xu, H.; Wu, K.; Tian, J.; Zhu L.; Yao, X.; Green Chem. 2018, 20(4), 793-797.
- [6] Gong, Y.; Liu, J.; Tetrahedron Lett. 2016, 57, 2143-2146.

- [7] Fateh, V.; Mônica, F.; Hélio, A.; *Tetrahedron Lett.* 2009, 50, 2636-2639.
- [8] Yin, Kun.; Li, C.; Lia, J.; Jia, X.; Green Chem. 2011, 13, 591-593.
- [9] Weng, Y.; Cheng, B.; He, C.; Lei A.; Angew. Chem. Int . Ed. 2012, 51, 9547-9551.
- [10] Mo, S.; Shao, X.; Zhang, G.; Li, Q.; RSC Adv., 2017, 7, 27243-27247.
- [11]Liu, Y.; Wang, C.; Wang, X.; Wan, J.; Tetrahedron Lett. 2013, 54, 3953-3955.

## The NMR Spectra of all products

 $\label{eq:2.9-bis} \textbf{(2-(2-methoxy)ethoxy)ethoxy)-1,10-phenanthroline (L_1):}$ 





4,7-bis(2-(2-methoxyethoxy)ethoxy)-1,10-phenanthroline (L<sub>2</sub>):





6,6'-bis(2-(2-(2-methoxy)ethoxy)ethoxy)-2,2'-bipyridine (L<sub>3</sub>):





4,4'-bis(2-(2-(2-methoxy)ethoxy)ethoxy)-2,2'-bipyridine (L<sub>4</sub>):





1,4-diphenylbuta-1,3-diyne (2a):





1,4-di-*p*-tolylbuta-1,3-diyne (2b):





1,4-di-*m*-tolylbuta-1,3-diyne (2c):





1,4-di-o-tolylbuta-1,3-diyne (2d):





1,4-bis(4-(*tert*-butyl)phenyl)buta-1,3-diyne (2e):





1,4-bis(4-methoxyphenyl)buta-1,3-diyne (2f):





1,4-bis(2-chlorophenyl)buta-1,3-diyne (2g):





1,4-bis(2-bromophenyl)buta-1,3-diyne (2h):





1,4-bis(4-fluorophenyl)buta-1,3-diyne (2i):





1,4-bis(4-(trifluoromethyl)phenyl)buta-1,3-diyne (2j):





1,4-di(naphthalen-1-yl)buta-1,3-diyne (2k):





1,4-di(thiophen-2-yl)buta-1,3-diyne (2l):





deca-4,6-diyne (2m):





# 1,4-dicyclopropylbuta-1,3-diyne (2n):





2,7-dimethylocta-3,5-diyne-2,7-diol (20):





1,4-bis(trimethylsilyl)buta-1,3-diyne (2p):





1-methoxy-4-(phenylbuta-1,3-diyn-1-yl)benzene (4a):





1-fluoro-4-((4-methoxyphenyl)buta-1,3-diyn-1-yl)benzene (4b):





## 2-((4-methoxyphenyl)buta-1,3-diyn-1-yl)thiophene (4c):





1-(cyclopropylbuta-1,3-diyn-1-yl)-4-methoxybenzene (4d):



2-methyl-6-phenylhexa-3,5-diyn-2-ol (5a):



2-methyl-6-(p-tolyl)hexa-3,5-diyn-2-ol (5b):





## 6-(4-fluorophenyl)-2-methylhexa-3,5-diyn-2-ol (5c):

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm