

## **Development of an Innovative, Green and Recyclable Switch-Molecule-Modified GO Electrode for Preventing Cu NPs Loss and Catalyst Deactivation in Electro-organic Reactions: Application in Castro–Stephens Coupling**

Abdulrahman A. Almehizia, Amer Alhaj Zen, Mohammed B. Alqaraguly, Aseel Smerat, Dilafruz Kholmurodova, Yuldash Takhirov, Abdullah Yahya Abdullah Alzahrani, Elyor Berdimurodov, Khasan Berdimuradov, Rasulbek Eshmetov, Ibrahim K. Alsulami, Raouf Hassan

### **Table of contents**

A) Overall approach for electro-organic synthesis of 1,2-diphenylethyne <i>via</i> Castro–Stephen’s coupling.....	S2
B) $^1\text{H}/^{13}\text{C}$ NMR data.....	S2
C) $^1\text{H}/^{13}\text{C}$ NMR spectroscopy.....	S4

## A) Overall approach for electro-organic synthesis of 1,2-diphenylethyne *via* Castro–Stephen’s coupling

The divided 100 mL electrolysis cell fitted with a magnetic stirring device, a hot plate stirrer, a graphite anode, and a GO-OHPN@Cu cathode was placed in a plastic chamber and kept in the dark. Subsequently, 15 mL of *i*PrOH, ethynylbenzene **1(a)** 0.5 g (0.005 mol), and chlorobenzene **2(a)** 0.55 g (0.005 mol) were added to the cell. The reaction was conducted under a continuous 8 mA current, and the mixture was maintained at 60 °C with stirring for 1.5 hours. Once TLC indicated completion, the reaction mixture was allowed to reach ambient temperature, and the current was discontinued. The reaction mixture was then irradiated with UV light for 30 minutes under vigorous stirring at room temperature. After irradiation, the electrodes were removed, 0.5 g of silica gel was added, and the mixture was thoroughly dried under vacuum at 60 °C using a rotary evaporator. The crude material was subjected to column chromatography on silica gel (glass column, 40 cm × 1.5 cm) using hexane/ethyl acetate (7:1 v/v) as the eluent to yield the purified compound (Figure 9)

## B) <sup>1</sup>H/<sup>13</sup>CNMR data

**1,2-Diphenylethyne (3a):** White solid, R<sub>f</sub> = 0.67 (7:1 Hexane: EtOAc), Yield = 94%; m.p= 56–58 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub>= 7.37–7.41 (m, 6H, Ar-H), 7.55–7.57 (m, 4H, Ar-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ= 89.2, 123.5, 128.4, 128.6, 131.4 ppm. Anal Calcd for C<sub>14</sub>H<sub>10</sub>: C, 94.34; H, 5.66 %. Found: C, 94.37; H, 5.66%.

**1,3-Dimethyl-2-(phenylethynyl)benzene (3b):** Liquid, R<sub>f</sub> = 0.65 (7:1 Hexane: EtOAc), Yield = 88%; m.p= 229–231 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>= 2.55 (s, 6H, 2Me), 7.11–7.17 (m, 3H, Ar-H), 7.36–7.38 (m, 3H, Ar-H), 7.56–7.58 (m, 2H, Ar-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ= 21.3, 87.2, 97.9, 122.8, 123.9, 126.8, 127.6, 128.1, 128.4, 131.4, 140.3 ppm. Anal Calcd for C<sub>16</sub>H<sub>14</sub>: C, 93.16; H, 6.84 %. Found: C, 93.21; H, 6.79 %.

**1-Methoxy-4-(4-tolyethynyl)benzene (3c):** White solid, R<sub>f</sub> = 0.65 (7:1 Hexane: EtOAc), Yield = 98%; m.p= 123–126 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>= 2.37 (s, 3H, Me), 3.83 (s, 3H, OMe), 6.87 (d, J = 8.9 Hz, 2H, Ar-H), 7.14 (d, J = 8.1 Hz, 2H, Ar-H), 7.42 (d, J = 8.3 Hz, 2H, Ar-H), 7.47 (d, J = 8.8 Hz, 2H, Ar-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ= 21.6, 55.4, 88.3, 88.8,

114.1, 115.7, 120.6, 129.2, 131.4, 133.1, 138.2, 159.6 ppm. Anal Calcd for C<sub>16</sub>H<sub>14</sub>O: C, 86.45; H, 6.35; O, 7.20 %. Found: C, 86.49; H, 6.32 %.

**1-[(4-Methoxyphenyl)ethynyl]-2-methylbenzene (3d):** White solid, R<sub>f</sub> = 0.69 (7:1 Hexane: EtOAc), Yield = 95%; m.p= 55-58 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>= 2.53 (s, 3H, Me), 3.84 (s, 3H, OMe), 6.88 (d, J = 8.9 Hz, 2H, Ar-H), 7.15–7.26 (m, 3H, Ar-H), 7.47–7.51 (m, 3H, Ar-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ= 20.7, 55.5, 87.2, 93.5, 114.2, 115.9, 123.3, 125.7, 128.1, 129.6, 131.8, 133.1, 140.2, 160.1 ppm. Anal Calcd for C<sub>16</sub>H<sub>14</sub>O: C, 86.45; H, 6.35; O, 7.20 %. Found: C, 86.48; H, 6.38 %.

**1-Methoxy-4-(phenylethynyl)benzene (3e):** Yellow solid, R<sub>f</sub> = 0.65 (7:1 Hexane: EtOAc), Yield = 96%; m.p= 74-76 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub>= 3.81 (s, 3H, OMe), 6.87 (d, J = 8.5 Hz, 2H, Ar-H), 7.31–7.33 (m, 3H, Ar-H), 7.47 (d, J = 8.7 Hz, 2H, Ar-H), 7.48–7.52 (m, 2H, AR-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ= 55.1, 88.2, 89.5, 114.1, 115.3, 123.6, 128.1, 128.4, 131.6, 133.2, 159.8 ppm. Anal Calcd for C<sub>15</sub>H<sub>12</sub>O: C, 86.51; H, 5.81; O, 7.68 %. Found: C, 88.54; H, 5.78%.

**1-Methyl-3-(phenylethynyl)benzene (3f):** White solid, R<sub>f</sub> = 0.68 (7:1 Hexane: EtOAc), Yield = 92%; m.p= 69-71 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub>= 2.37 (s, 3H, Me), 7.19 (d, J = 7.6 Hz, 1H, Ar-H), 7.24 (t, J = 7.5 Hz, 1H, Ar-H), 7.36–7.42 (m, 5H, Ar-H), 7.54–7.59 (m, 2H, Ar-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ= 21.3, 89.2, 89.7, 123.3, 123.5, 128.1, 128.3, 128.4, 128.8, 129.2, 131.5, 132.3, 138.1 ppm. Anal Calcd for C<sub>15</sub>H<sub>12</sub>: C, 93.71; H, 6.29 %. Found: C, 93.75; H, 5.25%.

**1-Methyl-2-(phenylethynyl)benzene (3g):** White solid, R<sub>f</sub> = 0.66 (7:1 Hexane: EtOAc), Yield = 94%; m.p= 73-76 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub>= 2.56 (s, 3H, Me), 7.16–7.22 (m, 1H, Ar-H), 7.26 (d, J = 4.3 Hz, 2H, Ar-H), 7.37–7.41 (m, 3H, Ar-H), 7.52–7.58 (m, 3H, Ar-H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ= 20.9, 88.3, 93.5, 123.2, 123.7, 125.5, 128.3, 128.4, 128.5, 129.6, 131.7, 131.9, 140.3 ppm. Anal Calcd for C<sub>15</sub>H<sub>12</sub>: C, 93.71; H, 6.29 %. Found: C, 93.77; H, 5.23%.

**N,N-Dimethyl-3-(phenylethynyl)aniline (3h):** White solid, R<sub>f</sub> = 0.64 (7:1 Hexane: EtOAc), Yield = 91%; m.p= 50-52 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>= 2.96 (s, 6H, NMe<sub>2</sub>), 6.72–6.75 (m, 1H, Ar-H), 6.93 (d, J = 7.3 Hz, 2H, Ar-H), 7.23 (t, J = 7.6 Hz, 1H, Ar-H), 7.31–7.36 (m, 3H,

Ar-H), 7.53–7.55 (m, 2H, Ar-H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ = 40.3, 88.3, 90.4, 112.9, 115.3, 119.8, 123.5, 123.6, 128.1, 128.3, 129.1, 131.6, 150.4 ppm. Anal Calcd for  $\text{C}_{16}\text{H}_{15}\text{N}$ : C, 86.84; H, 6.83; N, 6.33 %. Found: C, 86.87; H, 6.82; N, 6.31%.

**Methyl 4-(phenylethynyl)benzoate (3i):** Yellow solid,  $R_f$  = 0.66 (7:1 Hexane: EtOAc), Yield = 93%; m.p= 117-120 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ = 3.91 (s, 3H, OMe), 7.35 (t,  $J$  = 4.2 Hz, 3H, Ar-H), 7.54–7.58 (m, 2H, Ar-H), 7.58 (d,  $J$  = 8.4 Hz, 2H, Ar-H), 8.03 (d,  $J$  = 8.5 Hz, 2H, Ar-H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ = 52.3, 88.6, 92.4, 122.7, 127.8, 128.5, 128.6, 129.5, 129.6, 131.3, 131.5, 166.7 ppm. Anal Calcd for  $\text{C}_{16}\text{H}_{12}\text{O}_2$ : C, 81.34; H, 5.12; O, 13.54 %. Found: C, 81.38; H, 5.09 %.

**1-Nitro-4-(phenylethynyl)benzene (3j):** Yellow solid,  $R_f$  = 0.68 (7:1 Hexane: EtOAc), Yield = 91%; m.p= 111-113 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ = 7.38–7.42 (m, 3H, Ar-H), 7.55–7.58 (m, 2H, Ar-H), 7.66–7.69 (m, 2H, Ar-H), 8.21–8.24 (m, 2H, Ar-H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ = 87.5, 94.6, 122.2, 123.5, 128.6, 129.4, 130.4, 131.8, 132.3, 147.1 ppm. Anal Calcd for  $\text{C}_{14}\text{H}_9\text{NO}_2$ : C, 75.33; H, 4.06; N, 6.27; O, 14.33 %. Found: C, 75.37; H, 4.08; N, 6.29 %.

**4-(Phenylethynyl)benzonitrile (3k):** Yellow solid,  $R_f$  = 0.67 (7:1 Hexane: EtOAc), Yield = 92%; m.p= 103-106 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ = 7.36–7.39 (m, 3H, Ar-H), 7.54–7.56 (m, 2H, Ar-H), 7.57–7.63 (m, 4H, Ar-H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ = 87.7, 93.9, 111.6, 118.7, 122.4, 128.2, 128.5, 129.3, 131.9, 132.2, 132.3 ppm. Anal Calcd for  $\text{C}_{15}\text{H}_9\text{N}$ : C, 88.64; H, 4.46; N, 6.89 %. Found: C, 88.61; H, 4.49; N, 6.90 %.

**1-(Phenylethynyl)-3-(trifluoromethyl)benzene (3l):** White solid,  $R_f$  = 0.69 (7:1 Hexane: EtOAc), Yield = 90%; m.p= 70-72 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ = 7.38 (t,  $J$  = 2.9 Hz, 3H, Ar-H), 7.46–7.52 (m, 1H, Ar-H), 7.55–7.62 (m, 3H, Ar-H), 7.72 (d,  $J$  = 7.5 Hz, 2H, Ar-H), 7.83 (s, 1H, Ar-H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ = 88.3, 91.4, 123.1, 124.3, 124.8, 125.3, 128.7, 128.8, 129.3, 129.5, 131.5, 132.2, 135.0 ppm. Anal Calcd for  $\text{C}_{15}\text{H}_9\text{F}_3$ : C, 73.17; H, 3.68; F, 23.15 %. Found: C, 73.19; H, 3.65 %.

**16-((2,3,5,6,8,9,11,12-octahydrobenzo[b][1,4,7,10,13]pentaoxacyclopentadecin-15-yl)diazanyl)-2,3,5,6,8,9,11,12-octahydrobenzo[b][1,4,7,10,13]pentaoxacyclopentadecin-14-amine (OHPN):** White solid,  $R_f$  = 0.52 (2:1 Hexane: EtOAc),  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ )  $\delta_{\text{H}}$ = 3.81 (s, 16 H,  $\text{CH}_2$ ), 3.82-3.85 (m, 8H,  $\text{CH}_2$ ), 4.12-4.16 (m, 8H,  $\text{CH}_2$ ), 7.01 (s, 1H, Ar-H),

7.11 (d,  $J = 9$  Hz, 1H, Ar-H), 7.83 (s, 1H, Ar-H) ppm. Anal Calcd for  $C_{28}H_{39}N_3O_{10}$ : C, 58.22; H, 6.81; N, 7.27; O, 27.70%. Found: C, 58.25; H, 6.77; N, 7.31 %.

**C)  $^1H/^{13}CNMR$  spectroscopy**

























