**Electronic Supplementary Information**

**Microwave-Assisted Regioselective Synthesis of Substituted-9-bromo-9,10-dihydro-9,10-ethanoanthracenes Via** **Diels-Alder Cycloaddition.**

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**Experimental Part**

*2.1. Synthesis of 10-bromo-9,10-dihydro-9,10-ethanoanthracene-11-carbonitrile* ***8a*** *and 9-bromo-9,10-dihydro-9,10-ethanoanthracene-11-carbonitrile* ***8b***

To a 10 mL microwave vessel, a stir bar, 9-bromoanthracene **1** (257 mg, 1 mmol) and three equivalent of acrylonitrile **2** (200 μL, 3 mmol) were added. After sealing the vessel with a plastic septum, it put into the Microwave CEM Discover SP system. The reaction was carried out under these conditions; high stirring, 250 W maximum power, 250 psi maximum pressure and 150 oC temperature for 48 hours providing mixture of **8a** and **8b**. The mixture was cooled to RT, then deliver for NMR analysis. 1H-NMR (CDCl3, JEOL 400 MHz):*δ* = 2.17-2.22 (m, 1H, H-11), 2.29-2.35 (m, 1H, H-11), 2.47-2.51 (m, 1H, H-12'), 2.64-2.70 (m, 1H, H-12'), 3.01-3.06 (m, 1H, H-11'), 3.281-3.31 (m, 1H, H-12), 4.37 (t, *J* = 2 Hz, 1H, H-10), 4.55 (d, *J* = 2 Hz, 1H, H-10'), 7.21-7.31 (m, 5H, H-Ar), 7.48-7.51 (m, 2H, H-Ar), 7.57-7.62 (m,2H, H-Ar), 7.78-7.87 ( m, 2H, H-Ar), 7.96-7.98 (m, 2H, H-Ar), 8.40 (s, 1H, H-Ar) 8.51-8.57 (m, 2H, H-Ar) ppm.

*2.2. Synthesis of 9-bromo-12-chloro-9,10-dihydro-9,10-ethanoanthracene-12-carbonitrile* ***9a*** *and 10-bromo-12-chloro-9,10-dihydro-9,10-ethanoanthracene-12-carbonitrile* ***9b***

To a 10 mL microwave vessel, a stir bar, 9-bromoanthracene **1** (512 mg, 2 mmol) and 2-chloroacrylonitrile **3** (0.5 ml, 6 mmol) were added. After sealing the vessel with a plastic septum, it put into the Microwave CEM Discover SP system. The reaction was carried out under these conditions; high stirring, 250 W maximum power, 250 psi maximum pressure and 150 0C temperature for 48 hours oC providing mixture of **9a** and **9b**. The mixture was cooled to RT, then deliver for NMR analysis. 1H-NMR (CDCl3, JEOL 400 MHz):*δ* = 2.61 (dd, *J* = 3.2, 3.2 Hz, 1H, H-11), 2.97 (dd, *J* = 2.8, 2.8 Hz, 1H, H-11), 4.36 (t, *J* = 2.4 Hz, 1H, H-10), 4.72 (s, 1H, H-10'), 7.24-7.30 (m, 6H, H-Ar) 7.83-7.85 (m, 1H, H-Ar), 7.96-7.98 (m, 1H, H-Ar) ppm.

*\* 1H-NMR values for ortho 9a only, except δ = 4.72(s, 1H, H-10*'*) for meta* ***9b***

*2.3. Synthesis of 10-bromo-12-cyano-9,10-dihydro-9,10-ethanoanthracen-12-yl acetate* ***10a*** *and 9-bromo-12-cyano-9,10-dihydro-9,10-ethanoanthracen-12-yl acetate* ***10b***

To a 10 mL microwave vessel, a stir bar, 9-bromoanthracene **1** (500 mg, 2 mmol), cyano vinyl acetate **4** (0.250 ml, 2.3 mmol) and (2 ml) xylene were added. After sealing the vessel with a plastic septum, it put into the Microwave CEM Discover SP system. The reaction was run with these conditions; high stirring, 250 W maximum power, 250 psi maximum pressure and 150 oC temperature for 48 hours providing mixture of **10a** and **10b**. The mixture was cooled to RT, then deliver for NMR analysis. 1H-NMR (CDCl3, JEOL 400 MHz):*δ* = 2.35 (s, 3H, H-OAc'), 2.42 (s,3H, H-OAc), 2.57 (d, *J* = 14, 1H, H-11'), 2.96 (d, *J* = 2.8 Hz, 1H, H-11), 3.00 (d, *J* = 2.8 Hz, 1H, H-11), 3.12 (d, *J* = 14 Hz, 1H, H-11'), 4.37 (t, *J* = 2.8 Hz, 1H, H-10), 5.07 (s, 1H, H-10'), 7.16-7.32 (m, 8H, H-Ar), 7.48 (d, *J* = 6.4 Hz, 1H, H-Ar), 7.66-7.83 (m, 4H, H-Ar), 7.93-7.98 (m, 2H, H-Ar), 8.29-8.32 (m, 1H, H-Ar) ppm.

*2.4. Synthesis of 10-bromo-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic acid* ***11a*** *and 9-bromo-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic acid* ***11b***

To a 10 mL microwave vessel, a stir bar, 9-bromoanthracene **1** (257 mg, 1 mmol) and acrylic acid **5** (75 μL, 1.1 mmol) were added. After sealing the vessel with a plastic septum, it put into the Microwave CEM Discover SP system. The reaction was run with these conditions; high stirring, 250 W maximum power, 250 psi maximum pressure and 150 oC temperature for 24 hours 0C providing mixture of **11a** and **11b**. The mixture was cooled to RT, then deliver for NMR analysis. 1H-NMR (CDCl3, JEOL 400 MHz):*δ* = 2.03-2.07 (m, 1H, H-11), 2.29-2.34 (m, 1H, H-11), 2.53-2.59 (m, 1H, H-12'), 2.73-2.77 (m, 1H, H-12'), 3.04-3.08 (m, 1H, H-11'), 3.19-3.23 (m, 1H, H-12), 4.3 9 (t, *J* = 2.4 Hz, 1H, H-10), 4.74 (d, *J* = 2 Hz, 1H, H-10'), 7.18-7.35 (m, 8H, H-Ar), 7.51-7.65 (m, 1H, H-Ar), 7.61-7.65 (m, 1H, H-Ar) 7.75-7.83 (m, 4H, H-Ar), 8.01 (d, *J* = 8 Hz, 1H, H-Ar), 8.56 (d, *J* = 8.8 Hz, 1H, H-Ar), 11.39 (weak, broad s, H-COOH) ppm.

*2.5. Synthesis of 9-bromo-12-methyl-9,10-dihydro-9,10-ethanoanthracene-12-carbonyl chloride* ***12a*** *and 10-bromo-12-methyl-9,10-dihydro-9,10-ethanoanthracene-12-carbonyl chloride* ***12b***

To a 10 mL microwave vessel, a stir bar, 9-bromoanthracene **1,** (257 mg, 1 mmol) and methacryloyl chloride **6** (108 μL, 1.1 mmol) were added. After sealing the vessel with a plastic septum, it put into the Microwave CEM Discover SP system. The reaction was run with these conditions; high stirring, 250 W maximum power, 250 psi maximum pressure and 150 oC temperature for 24 hours providing mixture of **12a** and **12b**. The mixture was cooled to RT, then deliver for NMR analysis. 1H-NMR (CDCl3, JEOL 400 MHz):*δ* = 1.084 (s, 3H, H-CH3), 1.13 (s, 3H, H-CH3), 1.17 (dd, *J* = 2.8, 3.2 Hz, 1H, H-11), 1.96 (d, *J* = 13.2 Hz, 1H, H-12'), 2.50 (dd, *J* = 2.8, 2.4 Hz, 1H, H-11), 3.16 (d, *J* = 13.2 Hz, 1H, H-12'), 4.29 (t, *J* = 2.4 Hz, 1H, H-10), 4.42 (s,1H, H-10'), 7.15-7.30 (m, 8H, H-Ar), 7.48-7.52 (t, *J* = 7.6 Hz, 1H, H-Ar), 7.58-7.62 (t, *J* = 8.8 Hz, 1H, H-Ar), 7.717.78 (m, 3H, H-Ar), 7.98 (d, *J* = 8 Hz, 1H, H-Ar), 8.43 (s, 1H, H-Ar), 8.52 (d, *J* = 8.8 Hz, 1H, H-Ar) ppm.

*2.6. Synthesis of 10-bromo-12-(phenylsulfonyl)-9,10-dihydro-9,10-ethanoanthracene* ***13b***

To a 10 mL microwave vessel, a stir bar, 9-bromoanthracene **1** (875 mg, 3.4 mmol), phenyl vinyl sulfone **7** (600 mg, 3.7 mmol) and (2 mL) xylene. After sealing the vessel with a plastic septum, it put into the Microwave CEM Discover SP system. The reaction was run with these conditions; high stirring, 250 W maximum power, 250 psi maximum pressure and 150 oC temperature for 48 hours providing only single isomer **13b**. The reaction was cooled to RT, then deliver for NMR analysis.1H-NMR (CDCl3, JEOL 400 MHz):*δ* = 2.44-2.50 (m, 1H, H-12'), 2.67-2.71 (m, 1H, H-12'), 3.52-3.27 (m, 1H, H-11'), 4.91 (d, *J* = 1.6 Hz, 1H, H-10'), 7.15-7.27 (m, 4H, H-Ar), 7.39-7.41 (m, 2H, H-Ar), 7.55 (d, *J* = 8 Hz, 1H, H-Ar), 7.96 (d, *J* = 8.8 Hz, 2H, H-Ar), 8.41 (s, 2H, H-Ar), 8.49 (d, *J* = 8.8 Hz, 2H, H-Ar) ppm.