SUPPORTING INFORMATION

Title: A Novel Multicomponent Reaction Involving Isocyanide, Dimethyl acetylenedicarboxylate (DMAD) and Electrophilic Styrenes: Facile Synthesis of Highly Substituted Cyclopentadienes.

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Experimental Section

General: All reactions were carried out in oven-dried glasswares. Progress of reactions were monitored by Thin Layer Chromatography while purification was effected using silica gel column chromatography. NMR data were collected at room temperature in CDCl₃ at operating frequency 300 MHz. IR spectra were recorded in Bomem MB Series FT-IR spectrophotometer. Melting points were recorded on a Buchi melting point apparatus and are uncorrected. Arylidinemalononitriles and Aryl cyanoacrylates were prepared by the Knoevenagel condensation of corresponding aromatic aldehydes with malononitrile and ethyl cyanoacetate respectively.

Synthesis of fully substituted Cyclopentadiene derivatives from Isocyanides DMAD and Electrophilic styrenes. General Procedure: To a refluxing solution of DMAD **2** (1.0 mmol) and styrene **3** or **5** (1.1 mmol) in dry THF was added isocyanide **1** or **1'** (1.0 mmol). The resulting solution was refluxed for 24 hours. On completion of the reaction, the the solvent was removed on a rotavapor and the residue subjected to column chromatography on silica gel column using hexane – ethylacetate solvent mixture (95:5) to afford the products, which were recrystallised from hexane-dichloromethane solvent mixture.

Cyclopentadiene 4b.

Yellow crystalline solid **Mp** 137-139 °C; **IR** (KBr) ν_{max} : 3343, 3265, 3084, 2944, 2862, 2360, 2246, 1744, 1677, 1605, 1532, 1455, 1352, 1222, 1144, 1082, 788 cm⁻¹; **¹H NMR**:; δ 1.32-1.86 (m, 8H, CyH), 2.21 (broad s, 2H, CyH), 3.65 (s, 3H, OCH₃), 3.90 (broad s, 4H, OCH₃ and CHN), 7.63 (t, 1H, J = 8.0, ArH), 7.88 (d, 1H, J = 7.1, ArH), 8.38 (d, 1H, J = 7.5, ArH), 8.44 (s, 1H, NH, exchangeable by D₂O); **¹³C NMR**: δ 24.5, 24.9, 34.0, 51.8, 52.8, 56.3, 99.6, 109.7, 114.8, 122.1, 123.2, 130.3, 131.3, 132.1, 141.4, 148.8, 157.3, 164.4, 164.6.

Cyclopentadiene 4c.

Yellow crystalline solid **Mp** 107-108 °C; **IR** (KBr) ν_{max} : 3477, 3224, 3131, 2981, 2950, 2251, 1750, 1667, 1595, 1450, 1356, 1217, 1093. cm^{-1} ; **^1H NMR**: δ 1.65 (s, 9H, C(CH₃)₃), 3.76 (s, 3H, OCH₃), 3.78 (s, 3H, OCH₃), 7.39 (d, 2H J = 8.4 ArH), 7.49 (d, 2H, J = 8.4 ArH), 8.90 (s, 1H, NH, exchangeable with D₂O); **^{13}C NMR**: δ 31.2, 48.7, 51.7, 52.5, 56.8, 103.3, 110.8, 119.8, 127.9, 129.3, 129.7, 135.6, 138.2, 157.6, 164.7, 164.8. Elemental analysis calculated for C₂₁H₂₀ClN₃O₄: Calculated: C, 60.95, H, 4.87, N, 10.15. Found: C, 60.98, H, 4.90, N, 10.20.

Cyclopentadiene 4e.

Yellow crystalline solid **Mp** 129-130 °C; **IR** (KBr) ν_{max} : 3467, 3213, 3131, 2981, 2950, 2246, 1744, 1682, 1594, 1450, 1362, 1222. cm^{-1} ; **^1H NMR**: δ 1.66 (s, 9H, C(CH₃)₃), 3.75 (s, 3H, OCH₃), 3.78 (s, 3H, OCH₃), 7.36-7.57 (m, 5H, ArH), 8.87 (s, 1H, NH, exchangeable by D₂O); **^{13}C NMR**: δ 31.3, 44.1, 51.8, 52.5, 56.8, 103.6, 111.1, 128.4, 129.0, 129.4, 129.6, 146.2, 164.9, 165.1. Elemental analysis calculated for C₂₁H₂₁N₃O₄: Calculated: C, 66.48, H, 5.58, N, 11.08. Found: C, 66.63, H, 5.33, N, 11.19.

Cyclopentadiene 4f.

Yellow crystalline solid **Mp** 123-124°C; **IR** (KBr) ν_{max} : 3467, 3270, 2960, 2862, 2251, 1750, 1677, 1594, 1455, 1263, 1222, 1150, 1072. cm^{-1} ; **^1H NMR**: δ 1.30-1.90 (m, 8H, CyH), 2.23-2.20 (m, 2H, CyH), 3.80 (s, 3H, OCH₃), 3.82 (broad s, 4H, OCH₃ and CHN), 7.37-7.57 (m, 5H, ArH), 8.31 (d, 1H, J = 11.0 NH, exchangeable by D₂O); **^{13}C NMR**: δ 24.5, 24.9, 34.1, 42.5, 51.6, 52.5, 55.9, 99.9, 110.0, 119.4, 127.5, 129.0, 129.1, 129.7, 138.6, 156.9, 164.6, 165.1. Elemental analysis calculated for C₂₃H₂₃N₃O₄: Calculated: C, 68.13, H, 5.72, N, 10.36. Found: C, 67.72, H, 5.54, N, 10.29.

Cyclopentadiene 4h.

Yellow crystalline solid **Mp** 140-141 °C; **IR** (KBr) ν_{max} : 3467, 3270, 2955, 2929, 2856, 2220, 1750, 1672, 1605, 1512, 1459, 1351, 1253, 1217, 1144. cm^{-1} ; **^1H NMR**: δ 1.25-1.86 (m, 8H, CyH), 2.15-2.18 (m, 2H, CyH), 3.75 (broad s, 4H, OCH₃ and CHN), 3.77 (s, 3H, OCH₃), 3.82 (s, 3H, OCH₃), 6.91 (d, 2H, J = 8.6 ArH), 7.45 (d,

2H, $J = 8.6$ ArH), 8.20 (d, 1H, $J = 11.0$ NH, exchangeable with D₂O).; ¹³C NMR: δ 24.5, 25.0, 34.2, 51.6, 52.5, 55.2, 55.9, 99.5, 110.3, 112.7, 114.6, 118.7, 122.0, 129.2, 137.0, 156.5, 160.2, 164.7, 165.2. Elemental analysis calculated for C₂₄H₂₅N₃O₅: Calculated: C, 66.19, H, 5.79, N, 9.65. Found: C, 66.47, H, 5.74, N, 9.73.

Cyclopentadiene 6a.

Yellow crystalline solid **Mp** 120-121 °C; **IR** (KBr) ν_{max} : 3462, 3208, 3125, 3089, 2950, 2215, 1740, 1662, 1595, 1527, 1450, 1356, 1051.cm⁻¹; ¹H NMR:; δ 1.11(t, 3H, $J = 7.1$ CH₂CH₃), 1.53 (s, 9H, C(CH₃)₃), 3.77 (s, 3H, OCH₃), 3.79 (s, 3H, OCH₃), 4.18 (q, 2H, $J = 7.1$ CH₂CH₃), 7.55 (t, 1H, $J = 8.0$ ArH), 7.89 (d, 1H, $J = 7.9$ ArH), 8.16 (d, 1H, $J = 8.2$ ArH), 8.27 (s, 1H, ArH), 9.23 (s, 1H, NH, exchangeable by D₂O); ¹³C NMR: δ 13.7, 30.7, 51.4, 52.4, 56.0, 64.2, 102.4, 114.1, 119.4, 123.0, 123.4, 132.7, 134.3, 148.3, 161.3, 162.8, 165.3, 165.4. Elemental analysis calculated for C₂₃H₂₅N₃O₈: Calculated: C, 58.59, H, 5.34, N, 8.91. Found: C, 58.32, H, 5.15, N, 8.84.