A One-pot Garratt-Braverman Cyclization and Scholl Oxidation Route to Acene-Helicene Hybrids

Tapobrata Mitra, Joyee Das, Manasi Maji, Ranjita Das, Uttam Kumar Das, Pratim K. Chattaraj* and Amit Basak*+

Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, India

+ absk@chem.iitkgp.ernet.in

SUPPORTING INFORMATION

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General Remarks:
All the reactions were monitored by TLC using polygram$^R$ SILG/UV$_{254}$ precoated (0.25 mm) silica gel TLC plates. Column chromatography was done with silica gel (60-120 or 230-400 mesh). NMR data were obtained with 200 MHz and 400 MHz Bruker NMR instruments. Proton and carbon spectra were referenced internally to solvent signals, using values of $\delta = 7.26$ ppm for proton and $\delta = 77.0$ for carbon (middle peak) in CDCl$_3$. The following abbreviations are used to describe peak patterns where appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, app. = apparently and b = broad signal. All coupling constants ($J$) are given in Hz. FT-IR spectra were obtained as KBr discs. Mass spectra were recorded in ESI$^+$ mode (70 eV). Melting points were determined in open capillary tubes and are uncorrected

General procedure for Sonogashira coupling:
The aromatic halide or triflate (1.0 eq.), PdCl$_2$(PPh$_3$)$_2$ (0.03 eq.) and propargyl alcohol (1.2 eq.) were added in succession to degassed triethylamine and refluxed at $80^\circ$C for 8 h. The reaction mixture was then poured into ethyl acetate and the organic layer was washed with saturated NH$_4$Cl solution and brine, dried over anhydrous sodium sulfate. Evaporation in vacuum gave a residue from which the product was isolated by column chromatography (Si-gel, petroleum ether-ethyl acetate mixture as eluent).

General procedure for synthesis of bromides 4, 7 and 9:
An ice-cold solution of the Sonogahira coupling product (1.0 eq.) and triethylamine (1.5 eq.) in THF was prepared. Mesyl chloride (1.5 eq., 5 times diluted with THF) was added dropwise. The reaction was complete within 5 mins. To the reaction mixture 5 equivalent of LiBr was added and the reactions took 2-3 hours to be complete depending on the substrates. The reaction mixture was then poured into water and extracted with DCM, washed with brine, dried over sodium sulfate, concentrated and subjected to column chromatography (Si-gel, 60-120 mesh, petroleum ether: ethyl acetate as eluent).
General procedure for the synthesis of sulfides:
The bromide (1.0 eq.) was taken into THF-water (5:1), TBAB (0.1 eq.) and Na₂S (0.5 eq.) were added to it at 0 °C. The reaction was complete at room-temperature within 1 h. The reaction mixture was extracted with DCM, washed with water and brine, dried over anhydrous sodium sulfate, concentrated in vacuum and subjected to column chromatography (Si-gel, petroleum ether-ethyl acetate mixture as eluent).

Synthesis of sulfones (2a, 2e-h):
To an ice-cold solution of sulfides (1.0 eq.) in dry DCM, m-CPBA (2.0 eq.) was added in succession under inert condition. After 20 minutes the ice was removed and the reaction mixtures were left to attain the room-temperature. The reactions were complete within 10-15 minutes. The reactions were quenched by diluting the reaction mixture with water and DCM and washed with saturated solutions of Na₂SO₃ and Na₂CO₃ successively. DCM layers were dried over anhydrous Na₂SO₄ and the solutions were concentrated under reduced pressure and subjected to column chromatography (Si-gel, pet ether-ethyl acetate mixture as eluent).

Synthesis of ether 2b:
9-bromophenanthrene (1.0 eq.), PdCl₂(PPh₃)₂ (0.03 eq.) and bis-propargyl ether alcohol (2.2 eq.) were added in succession to degassed triethylamine and refluxed at 80 °C for 10 min. The product was isolated by the procedure described earlier for the Sonogashira reactions.

Synthesis of 9-(3-Azido-prop-1-ynyl)-phenanthrene:
The bromide 4 (1 eq.) was treated with 5 eq. of NaN₃ in dry DMF for 4 h. The reaction was worked up with ethylacetate and water. Organic layer was washed with brine dried over sodium sulfate, evaporated and subjected to column chromatography (Si-gel 60-120 mesh, PE:EA = 20:1 as eluent).
Synthesis of 3-Phenanthren-9-yl-prop-2-ynylamine:

9-(3-Azido-prop-1-ynyl)-phenanthrene (1.0 eq.) was treated with PPh3 in THF: H2O = 15:1 for 8 h. The product was isolated by column chromatography (Si-gel 60-120 mesh, DCM:MeOH = 80:20 as eluent).

Synthesis of mono-propargyl sulfonamides 6c-d:

To an ice-cold solution of 9-(3-Azido-prop-1-ynyl)-phenanthrene (1.0 eq.) and triethylamine (1.0 eq.) in anhydrous DCM 1.0 eq. of tosyl chloride (for 6c) or nosyl chloride (for 6d) was added dropwise as a solution in DCM and the reaction was left to attain room temperature. The product was separated by column chromatography (Si-gel 60-120 mesh, PE-EA mixture as eluent).

Synthesis of bis-propargyl sulfonamides 2c-d:

1.0 eq. of bromide 4 was added to a solution of 5.0 eq. of dry K2CO3 and 1.0 eq. of 6c (for 2c) or 1.0 eq. of 6d (for 2d) in dry DMF. The reaction was stirred for 4h at room temperature and worked up with ethylacetate and water and brine. The organic layer was dried over sodium sulfate, evaporated and the product was purified by column chromatography (Si-gel 60-120 mesh, PE-EA mixture as eluent).

Synthesis of acenes 10a-j:

The sulfone starting materials 2a, 2e-h were treated with catalytic triethylamine in DCM at r.t. to furnish the GB products. The progress of the reactions were monitored by TLC. After the completion of GB, 25 eq. of anh. FeCl3 was added to the reaction mixture in two equal portions. The reaction mixtures were directly subjected to column chromatography (Si-gel 60-120 mesh, PE-EA mixture as eluent). The ether and sulfonamide starting materials 2b-d were refluxed at 110 °C in toluene with catalytic
DBU for 10 mins for GB reaction to occur then the reaction mixture was cooled to r.t.,
dry DCM was added to it and 25 eq. of anh. FeCl₃ was added to the reaction mixture in
two equal portions. The reactions were found to be complete within 5 mins. The spectral
data of the GB products were obtained from the aliquots collected prior to the addition of
FeCl₃ and purified by column chromatography (Si-gel 60-120 mesh, PE-EA mixture as
eluent). The reaction time and the timings of addition of FeCl₃ for various sulfone
starting materials are tabulated below.

<table>
<thead>
<tr>
<th>Bis-propargyl sulfone</th>
<th>Time of addition of 1st 12.5 eq. of anh. FeCl₃</th>
<th>Time of addition of 2nd 12.5 eq. of anh. FeCl₃</th>
<th>Reaction time</th>
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<tbody>
<tr>
<td>2a</td>
<td>15 min.</td>
<td>17 min.</td>
<td>20 min.</td>
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<tr>
<td>2e</td>
<td>5 min.</td>
<td>3 h</td>
<td>6 h</td>
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<tr>
<td>2f</td>
<td>5 min.</td>
<td>2 h</td>
<td>3 h</td>
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<td>2g</td>
<td>7 min.</td>
<td>6 h</td>
<td>24 h</td>
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<tr>
<td>2h</td>
<td>7 min.</td>
<td>6 h</td>
<td>24 h</td>
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**Table 1: One pot reaction condition**

**Spectral data:**

5: Yellow solid; Yield 95%; δ_H (CDCl₃, 200 MHz): 4.06 (s, 4H), 7.58-7.86 (m, 10H),
8.52-8.57 (m, 2H), 8.57-8.68 (m, 4H), δ_C (CDCl₃, 50 MHz): 20.9, 82.2, 89.4, 119.5,
122.8, 123.0, 127.0, 127.1, 127.2, 127.3,
127.7, 128.7, 130.3, 130.5, 131.3, 131.5,
132.4.

Bis-(1-naphthylpropargyl) sulfide: Yellow liquid; Yield 75%, δ_H (CDCl₃, 200 MHz):
4.07 (s, 4H), 7.44-7.55 (bm, 2H), 7.59-7.69
(bm, 4H), 7.82-7.94 (bm, 6H), 8.57 (d, J = 7.8
Hz, 2H); δ_C (CDCl₃, 50 MHz): 20.8, 82.1,
89.8, 120.8, 125.4, 126.3, 126.6, 127.1, 128.5,
129.0, 130.9, 133.4, 133.7.
Bis-(2-naphthylpropargyl) sulfide: Yellow liquid; Yield 75%, δH (CDCl3, 400 MHz): 3.90 (s, 2H), 3.91 (s, 2H), 7.52-7.61 (m, 6H), 7.81-7.89 (m, 6H), 8.06 (s, 2H). δC (CDCl3, 100 MHz) 20.6, 84.0, 85.2, 120.4, 126.6, 126.7, 127.8, 128.0, 128.6, 131.8, 132.9, 133.0 (1C signal was merged).

1-[3-(3-Phenyl-prop-2-ynylsulfanyl)-prop-1-ynyl]-naphthalene: Yellow liquid; Yield 95%, δH (CDCl3, 200 MHz): 3.84 (s, 2H), 3.94 (s, 2H), 7.35-7.88 (m, 11H), 8.39-8.42 (m, 1H); δC (CDCl3, 50 MHz) 20.5, 20.6, 81.9, 83.9, 84.8, 89.7, 120.8, 123.2, 125.4, 126.4, 126.6, 127.0, 128.5, 128.9, 130.8, 132.0, 133.4, 133.7 (2C signals were merged).

2-[3-(3-Phenyl-prop-2-ynylsulfanyl)-prop-1-ynyl]-naphthalene: Yellow liquid; Yield 95%, δH (CDCl3, 200 MHz): 3.81 (s, 2H), 3.83 (s, 2H), 7.35-7.55 (m, 7H), 7.79-7.83 (m, 4H), 8.01 (s, 1H); δC (CDCl3, 50 MHz) 20.6, 83.7, 84.0, 84.9, 85.2, 120.5, 122.6, 122.9, 123.2, 126.7, 126.8, 127.9, 128.1, 128.5, 128.8, 131.9, 132.0, 133.0, 133.2 (1C signal was merged).

2a: Yellow solid; Yield 90%, δH (CDCl3, 200 MHz): 4.61 (s, 4H), 7.54-7.82 9m, 5H), 8.05 (s, 1H), 8.44-8.49 (m, 1H), 8.62-8.68 (m, 2H); δC (CDCl3, 50 MHz): 45.4, 80.5, 87.0, 118.0, 122.8, 123.0, 126.8, 127.3, 127.5, 127.6, 128.2, 128.9, 130.2, 130.8, 130.9, 131.1, 133.4.

2b: White solid; Yield 70%, δH (CDCl3, 200 MHz): 4.89 (s, 4H), 7.56-7.75 (m, 4H), 7.82-7.87 (m, 1H), 8.08 (s, 1H), 8.51-8.63 (m, 1H), 8.67-8.71 (m, 2H); δC (CDCl3, 50 MHz): 58.0, 85.5, 89.1, 119.1, 122.8, 122.9, 127.0, 127.1, 127.3, 128.8, 130.2, 130.5, 131.2, 132.7 (3C signals were merged).
2c: White solid; Yield 95%, $\delta_H$ (CDCl$_3$, 200 MHz): 2.14 (s, 3H), 4.80 (s, 4H), 7.22-7.31 (m, 3H), 7.56-7.80 (m, 12H), 7.95 (d, $J = 7.4$ Hz, 2H), 8.24 (d, $J = 8.4$ Hz, 2H), 8.65-8.69 (m, 3H).

2d: Yellowish solid; Yield 85%, $\delta_H$ (CDCl$_3$, 400 MHz): 4.81 (s, 4H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.54 (t, $J = 7.6$ Hz, 2H), 7.60-7.70 (m, 8H), 8.11 (d, $J = 8.0$ Hz, 2H), 8.17 (d, $J = 8.4$ Hz, 2H), 8.22 (d, $J = 8.8$ Hz, 2H), 8.61 (t, $J = 7.6$ Hz, 4H); $\delta_C$ (CDCl$_3$, 100 MHz): 38.6, 85.1, 85.4, 117.9, 122.5, 122.8, 124.1, 126.2, 127.0, 127.1, 127.2, 127.8, 128.4, 129.3, 129.9, 130.3, 130.5, 130.6, 132.6, 144.6 (1C signal was merged).

2e: Yellow solid; Yield 82%, $\delta_H$ (CDCl$_3$, 200 MHz): 4.57 (s, 4H), 7.40-7.56 (bm, 6H), 7.75-7.90 (bm, 6H), 8.41 (d, $J = 7.4$ Hz, 2H); $\delta_C$ (CDCl$_3$, 50 MHz) 45.0, 80.9, 86.6, 119.1, 125.2, 125.9, 126.8, 127.4, 128.5, 130.0, 131.4, 133.2, 133.5.

2f: Yellow solid; Yield 90%, $\delta_H$ (CDCl$_3$, 200 MHz): 4.45 (4H, s), 7.52-7.60 (6H, m), 7.78-7.88 (6H, m), 8.07 (2H, s); $\delta_C$ (CDCl$_3$, 50 MHz): 45.1, 88.8, 117.8, 124.8, 127.0, 127.4, 127.8, 128.0, 128.4, 128.8, 133.0, 135.6 (1C signal was merged).

2g: Yellow solid; Yield 95%, $\delta_H$ (CDCl$_3$, 200 MHz): 4.40 (s, 2H), 4.50 (s, 2H), 7.30-7.57 (m, 8H), 7.73-7.74 (m, 1H), 7.80-7.90 (m, 2H), 8.30-8.40 (m, 1H); 4.39 (m, 4H), 7.32-7.40 (m, 3H), 7.51-7.53 (m, 5H), 7.79-7.84 (m, 3H), 8.03 (s, 1H); $\delta_C$ (CDCl$_3$, 50 MHz): 44.9, 45.0, 76.2,
80.9, 86.6, 88.4, 119.2, 121.6, 125.3, 126.0, 126.8, 127.5, 128.6, 129.5, 130.0, 131.5, 132.2, 133.3, 133.7 (1C signal was merged).

2h: Yellow solid; Yield 93%, δ_H (CDCl_3, 200 MHz): 4.37-4.42 (m, 4H), 7.32-7.40 (m, 3H), 7.51-7.53 (m, 3H), 7.79-7.84 (m, 3H), 8.03 (s, 1H); δ_C (CDCl_3, 50 MHz): 44.8, 44.8, 76.1, 76.3, 88.2, 88.5, 118.8, 121.6, 126.9, 127.4, 127.9, 128.0, 128.3, 128.6, 129.4, 132.2, 132.6, 132.9, 133.3.

1a: White solid; Yield 95%, δ_H (CDCl_3, 400 MHz): 4.01 (d, J = 16.0 Hz, 1H), 4.06 (d, J = 16.0 Hz, 1H), 4.76 (s, 2H), 6.86 (t, J = 7.6 Hz, 1H), 7.46-7.60 (m, 4H), 7.62-7.64 (m, 2H), 7.73-7.75 (m, 1H), 7.80-7.94 (m, 6H), 7.95 (d, J = 8.4 Hz, 1H), 8.65 (d, J = 8.4 Hz, 1H), 8.72-8.81 (m, 3H), 8.91 (d, J = 8.8 Hz, 1H), 8.98 (d, J = 8.4 Hz, 1H); δ_C (CDCl_3, 100 MHz): 57.3, 57.9, 120.6, 120.7, 123.1, 123.3, 123.6, 123.7, 125.7, 126.1, 127.0, 127.1, 127.3, 127.5, 127.6, 127.9, 128.2, 128.4, 128.9, 129.1, 129.6, 129.8, 130.2, 130.4, 131.1, 131.7, 131.9, 132.4, 136.4, 138.4 (4C signals were merged); MS: m/z = 517.12 [MNa^+], 495.13 [MH^+].

1b: Yellow solid; Yield 95%, δ_H (CDCl_3, 400 MHz): 4.64 (d, J = 13.2 Hz, 1H), 4.82 (d, J = 13.2 Hz, 1H), 5.44 (s, 2H), 6.77 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.61-7.82 (m, 6H), 7.90 (d, J = 8.4 Hz, 1H), 8.55 (d, J = 8.0 Hz, 1H), 8.63-8.65 (m, 1H), 8.70-8.74 (m, 2H), 8.83 (t, J = 9.2 Hz, 4H); δ_C (CDCl_3, 100 MHz): 74.3, 74.6, 115.6, 123.0, 123.3, 123.5, 123.8, 123.9, 126.2, 126.6, 126.9, 127.2, 127.4, 127.5, 127.6 (2C signals), 127.7, 128.5, 128.6, 129.1, 129.5, 130.2, 130.3, 130.4, 130.5, 130.9, 131.3, 131.8, 132.2, 132.3, 138.4, 139.4, 141.4; MS: m/z = 469.16 [MNa^+], 447.17 [MH^+].
1c: White solid; Yield 95%, $\delta_H$ (CDCl$_3$, 200 MHz): 4.22 (d, $J = 14.4$ Hz, 1H), 4.35 (d, $J = 14.4$ Hz, 1H), 4.98 (s, 2H), 6.77 (t, $J = 7.2$ Hz, 1H), 7.26-7.87 (m, 15H), 8.54-8.70 (m, 4H), 8.90 (t, $J = 6.8$ Hz, 2H); $\delta_C$ (CDCl$_3$, 50 MHz): 21.7, 54.4, 54.7, 117.2, 123.0, 123.2, 123.5, 123.7, 126.2, 126.9, 127.2, 127.4, 127.5, 127.7, 127.9, 128.5, 129.1, 130.0, 130.5, 130.9, 131.4, 132.0, 132.2, 133.8, 134.0, 135.3, 138.1, 138.6, 143.8 (10C signals were merged); MS: m/z = 622.18 [MNa$^+$], 600.20 [MH$^+$].

1d: White solid; Yield 90%, $\delta_H$ (CDCl$_3$, 400 MHz): 4.17 (d, $J = 14.4$ Hz, 1H), 4.33 (d, $J = 14.4$ Hz, 1H), 6.75 (t, $J = 7.6$ Hz, 1H), 7.26-7.39 (m, 2H), 7.45 (d, $J = 7.6$ Hz, 1H), 7.53 (s, 1H), 7.64-7.82 (m, 7H), 7.88 (d, $J = 8.8$ Hz, 2H), 8.27 (d, $J = 8.8$ Hz, 2H), 8.52 (d, $J = 8.0$ Hz, 1H), 8.59-8.65 (m, 3H), 8.84-8.89 (m, 2H). $\delta_C$ (CDCl$_3$, 100 MHz): 54.2, 54.5, 117.0, 118.9, 122.5, 122.8, 123.3, 123.5, 124.4, 126.1, 126.7, 127.0, 127.1, 127.2, 127.3, 127.4, 127.5, 127.8, 128.2, 128.4, 128.5, 128.8, 129.5, 129.7, 130.0, 131.2, 131.8, 131.9, 132.2, 133.6, 134.1, 136.9, 138.1, 142.7, 150.1 (3C signals were merged); MS: m/z = 653.15 [MNa$^+$], 631.17 [MH$^+$].

1e: Yellowish white solid; Yield 96%, $\delta_H$ (CDCl$_3$, 200 MHz): 4.01, 4.20 (ABq, $J = 16.2$ Hz, 2H), 4.73 (s, 2H), 7.21-7.32 (m, 3H), 7.36-7.42 (m, 1H), 7.49-7.58 (m, 2H), 7.62-7.72 (m, 3H), 7.79-7.83 (d, $J = 7.2$ Hz, 1H), 7.98-8.04 (t, $J = 6.4$ Hz, 2H), 8.68-8.72 (2H, m); $\delta_C$ (CDCl$_3$, 50 MHz): 56.5, 57.8, 120.0, 123.0, 124.5, 125.3, 125.8, 126.6, 127.2, 127.3, 127.5, 127.7, 128.1, 129.0, 129.4, 129.8, 130.0, 130.7, 131.4, 131.8, 132.0, 134.0, 135.3, 136.6 (2C signals were merged); MS: m/z = 417.09 [MNa$^+$], 395.11 [MH$^+$].
**1f**: Yellow solid; Yield 95%, $\delta_H$ (CDCl$_3$, 200 MHz): 4.02, 4.19 (ABq, $J = 16.5$ Hz, 2H), 4.58 (s, 2H), 6.93 (t, $J = 7.8$ Hz, 1H), 7.19-7.39 (m, 2H), 7.52-7.57 (m, 3H), 7.69-7.80 (m, 6H), 7.91-8.00 (m, 2H). $\delta_C$ (CDCl$_3$, 50 MHz): 57.6, 57.7, 125.9, 126.0, 126.6, 126.7, 126.9, 127.0, 127.3, 127.8, 128.2, 128.3, 128.9, 128.9, 129.1, 130.1, 130.3, 131.2, 132.9, 133.7, 133.8, 134.1, 138.1, 139.6 (2C signals were merged); MS: m/z = 417.08 [MNa$^+$], 395.12 [MH$^+$].

**1g**: Yellowish white solid; Yield 96%, $^1$H NMR (Acetone-d$_6$, 400 MHz): $\delta$ 4.27 (s, 2H), 4.77 (s, 2H), 7.41-7.80 (m, 7H), 7.97 (d, $J = 8.0$ Hz, 1H), 8.88 (d, $J = 8.0$ Hz, 1H), 9.08 (s, 1H); MS: m/z = 367.08 [MNa$^+$], 345.09 [MH$^+$].

**1h**: Yellowish white solid; Yield 96%, $^1$H NMR (Acetone-d$_6$, 400 MHz): $\delta$ 4.16 (s, 2H), 4.71 (s, 2H), 7.09 (t, $J = 7.2$ Hz, 1H), 7.35-7.38 (m, 2H), 7.47 (t, $J = 7.2$ Hz, 1H), 7.57-7.65 (m, 4H), 7.88 (s, 2H), 7.92 (d, $J = 7.6$ Hz, 1H), 8.08 (s, 1H). MS: m/z = 367.07 [MNa$^+$], 345.08 [MH$^+$].

**10a**: Yellow crystals; m.p. >250 °C; Yield: 75%; $\delta_H$ (400 MHz, CDCl$_3$): 3.75 (d, $J = 16.4$ Hz, 1H), 4.64 (d, $J = 15.2$ Hz, 1H), 5.00 (d, $J = 16.4$, 1H), 5.07 (d, $J = 15.2$ Hz, 1H), 7.60-7.84 (m, 7H), 8.10 (t, $J = 8.0$ Hz, 1H), 8.71 (d, $J = 7.6$ Hz, 1H), 8.77-8.89 (m, 5H), 8.96 (d, $J = 8.0$ Hz, 1H), 9.05 (d, $J = 8.0$ Hz, 1H); $\delta_C$ (100 MHz, CDCl$_3$): 57.3, 60.5, 118.1, 121.5, 123.9, 124.0, 124.1, 124.2, 124.9, 126.1, 126.6, 126.7, 126.9, 127.0, 127.2, 127.4, 127.6, 127.7, 128.2, 128.6 (2C signals), 129.0, 129.2,
129.3, 129.5, 129.6, 130.0 (2C signals), 130.6, 130.8, 131.6, 131.8 (2C signals were merged); MS: m/z = 515.11 [MNa+], 493.12 [MH+]. HRMS: Calcd. for C₃₄H₂₀O₂S+H⁺ 493.1262 found 493.1263 [MH⁺].

10b: Yellow crystals: m. p. >250 °C; Yield: 74%; δ_H (400 MHz, CDCl₃): 4.52 (d, J = 13.2 Hz, 1H), 5.34 (d, J = 12.0 Hz, 1H), 5.68 (d, J = 12.0 Hz, 1H), 5.74 (d, J = 13.6 Hz, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.68-7.83 (m, 6H), 8.05 (t, J = 8.0 Hz, 1H), 8.69 (d, J = 8.0 Hz, 1H), 8.77 (d, J = 8.0 Hz, 1H), 8.88-8.84 (m, 4H), 8.93 (d, J = 7.6 Hz, 1H), 9.01 (d, J = 8.0 Hz, 1H), δ_C (100 MHz, CDCl₃): 73.9, 76.5, 113.0, 120.6, 123.4, 123.6, 123.7, 123.8 (2C signals), 124.6, 125.8, 126.4, 126.7, 126.8 (2C signals), 126.9 (2C signals), 127.6 (2C signals), 128.5, 128.7, 129.0, 129.2 (2C signals), 129.9 (2C signals), 130.0, 131.0, 131.3, 134.4, 134.6, 139.4 (2C signals were merged); MS: m/z = 467.14 [MNa⁺], 445.16 [MH⁺]. HRMS: Calcd. for C₃₄H₂₀O⁺H⁺ 445.1592 found 445.1599 [MH⁺].

10c: Yellow powder: m. p. >250 °C; Yield: 80%; δ_H (400 MHz, CDCl₃): 4.00 (d, J = 14.4 Hz, 1H); 4.89 (d, J = 13.2 Hz, 1H), 5.08 (d, J = 13.2 Hz, 1H), 5.18 (d, J = 14.8, 1H), 7.12 (d, J = 8.0 Hz, 1H), 7.62-7.47 (m, 3H), 7.81-7.72 (m, 6H), 7.6 Hz, 1H), 8.01 (t, J = 8.0 Hz, 8.71-8.65 (m, 3H), 8.84-8.78 (m, 3H), 8.87 (d, J = 8.0 Hz, 1H), 8.98 (d, J = 8.0 Hz, 1H); δ_C (100 MHz, CDCl₃): 21.2, 54.4, 57.1, 114.3, 120.7, 123.5, 123.7, 123.8, 124.1, 124.3, 126.0, 126.3, 126.4, 126.5, 126.9, 127.0 (2C signals), 127.3, 127.7, 127.8, 127.9, 128.4, 128.7, 128.8, 128.9, 129.0, 129.1, 129.2, 129.4, 129.5, 129.9, 130.0, 130.3, 131.4, 131.6, 132.9, 136.1, 143.5 (1C signal was merged); MS: m/z = 620.17 [MNa⁺], 598.18 [MH⁺]. HRMS: Calcd. for C₄₁H₂₇NO₂S+H⁺ 598.1841 found 598.1843 [MH⁺].
10d: Yellow powder; m. p. >250 °C; Yield: 80%; δH (400 MHz, CDCl3): 4.1 (d, J = 11.6 Hz, 1H), 4.96 (d, J = 13.2 Hz, 1H), 5.21 (d, J = 13.6 Hz, 1H), 5.29 (d, J = 17.6 Hz, 1H), 743-7.82 (m, 13H), 8.04 (d, J = 8.8 Hz, 1H), 7.73-7.83 (m, 4H), 8.88 (d, J = 8.0 Hz, 1H), 8.95 (d, J = 7.6 Hz, 1H), 9.04 (d, J = 8.0 Hz, 1H). MS: m/z = 651.38 [MNa⁺], 629.51[MH⁺]. HRMS: Calcd. for C₄₀H₂₅N₂O₄S⁺H⁺ 629.1535 found 629.1536 [MH⁺].

10e: State: yellowish solid; m. p. >250 °C, yield: 30%; δH (CDCl₃, 400 MHz), 3.96, 4.25 (ABq, J = 16 Hz, 2H), 4.86 (s, 2H), 7.25 (d, J = 8.8 Hz, 1H), 7.31 (s, 1H), 7.41-7.45 (m, 1H), 7.59-7.62 (m, 2H), 7.76-7.80 (m, 1H), 7.87-7.94 (m, 2H), 8.13 (bd, J = 8 Hz, 1H), 8.18 (bd, J = 8.4 Hz, 1H), 8.35-8.37 (m, 1H), 9.06 (bd, J = 8 Hz, 1H), 9.16 (s, 1H). δC (CDCl₃, 100 MHz) 55.9, 57.2, 120.6, 123.9, 124.0, 124.6, 125.1, 126.0, 126.7, 127.3, 128.1, 128.6, 129.0, 129.3, 129.8, 130.7, 131.3, 131.4, 131.8, 132.0, 132.3, 134.2, 134.7, 135.6 (1C signal was merged). MS: m/z = 415.08 [MNa⁺], 393.23, [MH⁺]. HRMS: Calcd. for C₂₆H₁₇O₂S⁺H⁺ 393.0949 found 393.0943 [MH⁺].

10f: Yellow solid; m. p. >250 °C, Yield 95%, δH (CDCl₃, 400 MHz): 4.00, 4.30 (ABq, J = 16.4 Hz, 2H), 4.85 (s, 2H), 7.10-7.33 (m, 2H), 7.52-7.56 (m, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.76-7.80 (m, 1H), 7.86-7.91 (m, 1H), 7.94 (d, J = 7.6 Hz, 1H), 8.35-8.38 (m, 1H), 8.46 (bd, J = 8.4 Hz, 1H), 9.05-9.07 (m, 1H), 9.17 (s, 1H). δC (CDCl₃, 100 MHz) 55.9, 57.2, 121.0, 123.9, 123.9, 125.0, 125.2, 126.0, 126.6, 128.1, 128.2, 128.4, 128.6, 128.7, 129.3, 129.8, 130.7, 131.2, 131.3, 131.6, 132.1, 132.5, 133.1, 134.5, 134.6 (1C signal was merged); MS: m/z = 415.05 [MNa⁺], 393.15, [MH⁺]. HRMS: Calcd. for C₂₆H₁₇O₂S⁺H⁺ 393.0949 found 393.0941 [MH⁺].
10g: White solid; Yield 90%, mp 240 °C; δ_H (CDCl₃, 400 MHz): δ 4.88 (s, 2H), 5.32 (s, 2H), 7.81 (t, J = 7.8 Hz, 1H), 7.87 (t, J = 7.4 Hz, 2H), 8.10 (d, J = 8.8 Hz, 1H), 8.20 (d, J = 9.6 Hz, 1H), 8.34 (s, 1H), 8.40-8.45 (m, 4H), 8.89-8.92 (m, 2H). δ_C (CDCl₃, 100 MHz) 55.6, 60.4, 121.9, 123.5, 123.8, 124.1, 124.7, 124.9, 125.2, 125.7, 125.8, 126.0, 126.8, 127.0, 127.3, 127.5, 127.6, 127.9, 128.1, 128.7, 129.3, 129.9, 130.4, 130.5, 130.6, 130.7; MS: m/z = 415.03 [MNa⁺], 393.10, [MH⁺]. HRMS: Calcd. for C₂₆H₁₇O₂S+H⁺ 393.0949 found 393.0953 [MH⁺].

10h: Yellow solid; Yield 95%, mp 242 °C. δ_H (CDCl₃, 400 MHz): 4.98 (s, 2H), 5.52 (s, 2H), 7.85-7.95 (m, 4H), 8.21 (d, J = 8.8 Hz, 1H), 8.30 (s, 1H), 8.47 (d, J = 7.6 Hz, 2H), 8.59 (s, 1H), 8.61 (s, 1H), 8.94 (d, J = 8.4 Hz, 1H), 9.01 (d, J = 8.4 Hz, 1H); δ_C (CDCl₃, 100 MHz) 56.0, 59.6, 123.8, 124.8, 124.9, 125.4, 125.5, 125.6, 125.8, 127.1, 127.3, 127.4, 127.5, 127.6, 128.0, 128.1, 128.2, 128.4, 128.9, 129.0, 129.5, 130.7, 130.9, 131.1, 131.4, 131.6; MS: m/z = 415.05 [MNa⁺], 393.09, [MH⁺]. HRMS: Calcd. for C₂₆H₁₇O₂S+H⁺ 393.0949 found 393.0951 [MH⁺].

10i: Yellow solid; Yield 95%, mp 240 °C. δ_H (CDCl₃, 400 MHz): 4.15 (s, 2H), 4.69 9s, 2H), 7.20-7.22 (m, 2H), 7.45-7.46 (m, 3H), 7.75-7.77 (m, 2h, 8.41-8.44 (m, 1H), 8.64-8.67 (m, 1H), 8.71 (s, 1H); δ_C (CDCl₃, 100 MHz): 57.9, 58.0, 124.1, 124.7, 126.4, 127.5, 127.9, 128.1, 128.3, 128.5, 128.7, 128.7, 129.1, 129.3, 130.0 130.1, 130.4, 130.5, 130.7, 132.2, 133.3, 138.7, 142.0 ; MS: m/z = 365.10 [MNa⁺], 343.08 [MH⁺]; HRMS: Calcd. for C₁₆H₁₂O₄S+H⁺ 343.0793 found 343.0788.
10j: Yellow solid; Yield 95%, mp 240 °C; δ_H (CDCl₃, 400 MHz): 4.19 (s, 2H), 4.70 (s, 2H), 7.09 (t, J = 8.4 Hz, 1H), 7.28 (s, 1H), 7.44-7.74 (m, 5H), 7.75 (d, J = 7.6 Hz, 1H), 7.94 (s, 1H), 8.47 (s, 1H); δ_C (CDCl₃, 100 MHz): 56.8, 58.8, 119.7, 123.0, 124.0, 125.5, 126.2, 127.9, 128.1, 128.2, 128.6, 128.9, 129.2, 129.4, 129.5, 129.6, 129.8, 130.4, 130.7, 132.1, 137.1, 138.0; MS: m/z = 365.11 [MNa⁺], 343.07 [MH⁺]; HRMS: Calcd. for C₁₆H₁₂O₄S+H⁺ 343.0793 found 343.0798.
$^1$H and $^{13}$C NMR spectra of all compounds (all were recorded in CDCl$_3$ unless otherwise specified)
$^{1}H$ NMR (200 MHz)

$^{13}C$ NMR (50 MHz)
$^1$H NMR (200 MHz)

$^{13}$C NMR (50 MHz)
Br

$^1$H NMR (200 MHz)

Br

$^{13}$C NMR (50 MHz)
$^1$H NMR (200 MHz)

$^{13}$C NMR (50 MHz)
$^1\text{H NMR (200 MHz)}$

$^{13}\text{C NMR (50 MHz)}$
$^1$H NMR (200 MHz)

$^1$C NMR (50 MHz)
$^1$H NMR (200 MHz)

$^{13}$C NMR (50 MHz)
$^1$H NMR in d$_4$-Methanol (200 MHz)

$^1$H NMR (200 MHz)
13C NMR in d₆-Acetone + CDCl₃ (50 MHz)
$^1$H NMR in d$_6$-Acetone (200 MHz)

$^{13}$C NMR in d$_6$-Acetone (50 MHz)
$^1$H NMR (200 MHz)

$^{13}$C NMR (50 MHz)
$^1$H NMR (200 MHz)

$^{13}$C NMR (50 MHz)
$^1$H NMR (200 MHz)

$^{13}$C NMR (100 MHz)
$^1$H NMR (200 MHz)

$^{13}$C NMR (50 MHz)
$^{1}H$ NMR (200 MHz)

$^{13}C$ NMR (50 MHz)
$^1$H NMR (400 MHz)

$^{13}$C NMR (100 MHz)
$^{13}$C NMR (100 MHz) expanded
DEPT-135 (100 MHz)

DEPT-135 (100 MHz) expanded
$^1\text{H NMR (400 MHz)}$

$^{13}\text{C NMR (100 MHz)}$
$^{13}$C NMR (100 MHz) expanded

DEPT-135 (100 MHz)
13C NMR (50 MHz) expanded
$^{13}$C NMR (100 MHz) expanded

DEPT-135 (100 MHz)
$^1$H NMR (400 MHz)
$^1$H NMR (400 MHz)
$^{13}$C NMR (100 MHz)

DEPT-135 (100 MHz)
$^1$H NMR (400 MHz)
$^{13}$C NMR (100 MHz) expanded

DEPT-135 (100 MHz)

DEPT-135 (100 MHz) expanded
$^1$H NMR (400 MHz)

DEPT-135 (100 MHz) expanded
$^{13}$C NMR (100 MHz)
$^{13}$C NMR (100 MHz) expanded
DEPT-135 (100 MHz)

$^1$H NMR (400 MHz)
$^1$H NMR (400 MHz) in d$_6$-Acetone
$^1$H NMR (400 MHz) in d$_6$-Acetone expanded

$^{13}$C NMR (100 MHz) in d$_6$-Acetone expanded

$^{13}$C NMR (100 MHz) in d$_6$-Acetone
DEPT-135 (100 MHz) in d$_6$-Acetone
$^1$H NMR (400 MHz) in d$_6$-Acetone

$^1$H NMR (400 MHz) in d$_6$-Acetone expanded
\[ ^{13}\text{C NMR (100 MHz) in d}_6\text{-Acetone} \]

\[ ^{13}\text{C NMR (100 MHz) in d}_6\text{-Acetone expanded} \]
DEPT-135 (100 MHz) in d6-Acetone expanded
$^1$H NMR (400 MHz) in d$_6$-Acetone

$^1$H NMR (400 MHz)
DEPT-135 (50 MHz)

$^1$H NMR (400 MHz)
$^{13}$C NMR (100 MHz)

DEPT-135 (100 MHz)
DEPT-135 (100 MHz)
Electrochemical data:

Fig. 1: Cyclic voltammogram of 10a

7a; \( E_{\text{ox onset}} = 0.9 \text{ V} \)

Fig. 2: Cyclic voltammogram of 10b

7b; \( E_{\text{ox onset}} = 1.05 \text{ V} \)
Fig. 3: Cyclic voltammogram of 10c

10c; \( E_{\text{onset}}^{\text{ox}} = 1.00 \text{ V} \)

Fig. 4: Cyclic voltammogram of 10d

10d; \( E_{\text{onset}}^{\text{ox}} = 1.25 \text{ V} \)
Fig. 5: Cyclic voltammogram of 10e

Fig. 6: Cyclic voltammogram of 10f
**Fig. 7:** Cyclic voltammogram of 10g

**Fig. 8:** Cyclic voltammogram of 10h
**Fig. 9:** Cyclic voltammogram of 10i

10i; $E_{\text{onset, red}}^\text{red} = -0.71$ V

**Fig. 10:** Cyclic voltammogram of 10j

10j; $E_{\text{onset, red}}^\text{red} = -0.41$ V
Computational details:

The HOMA is obtained from the following equation

\[ HOMA = 1 - \frac{\alpha}{n} \sum_{i=1}^{n} \left( R_{opt} - R_i \right)^2 \quad \ldots \ldots \ldots (1) \]

where \( n \) is the number of bonds considered, and \( \alpha \) is an empirical constant (for C-C bonds, \( \alpha = 257.7 \)) \((\text{Ref: Jordi Poater, Miquel Solà, Rosario G. Viglione, Riccardo Zanas J. Org. Chem. 2004, 69, 7537-7542})\) chosen in such a way that HOMA = 0 for model nonaromatic systems and HOMA = 1 for systems having all bonds equal to an optimal value \( R_{opt} \), presumed to be achieved for completely aromatic systems (for C-C bonds, \( R_{opt} \) is equal to 1.388 Å) and \( R_i \) is the running bond length. The calculated HOMA
indices for individual rings of each compound are listed in Table 2. The HOMA, structural indicator of aromaticity, provides a parallel trend to NICS (in most cases). The trend of aromaticity of individual rings of 10(a-c) are almost similar (both HOMA and NICS indices). In the same way the trend is similar for 10(e-h) compounds with a very few exceptions. The HOMA and NICS indices are appeared to be in good agreement with the Clar’s sextet structures.

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<th>Ring</th>
<th>Compound</th>
<th>10a</th>
<th>10b</th>
<th>10c</th>
<th>10d</th>
<th>10e</th>
<th>10f</th>
<th>10g</th>
<th>10h</th>
<th>10i</th>
<th>10j</th>
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<td>HOMA</td>
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<td>0.906</td>
<td>0.908</td>
<td>0.908</td>
<td>0.872</td>
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<td>0.245</td>
<td>0.237</td>
<td>0.237</td>
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<td>0.891</td>
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|                              | C        | -0.21  | -0.18  | -0.17  | -0.284 | -4.43  | -4.08  | -4.11  | -4.48  | -4.309  | -4.024  |
|                              | D        | 16.13  | 16.11  | 15.92  | 16.129 | 3.10   | 4.43   | 2.93   | 1.87   | 2.500   | 5.410   |
|                              | G        | -8.91  | -8.84  | -9.28  | -9.230 | -6.74  | 5.00   | -0.68  | 1.89   | 0.262   | -5.589  |
|                              | I        | -0.82  | -0.77  | -0.89  | -0.870 | -6.29  | -4.21  | -5.92  | -8.08  | -6.700  | -7.454  |
|                              | J        | 11.87  | 13.82  | 13.54  | 13.509 | -4.01  | -3.04  | -2.80  | -10.0  | -6.098  | -5.088  |

Table 2: HOMA and NICS values for the PAHs studied at B3LYP/6-311+G (d, p) level
**Fig. 12:** Structures with individual rings labeled

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<th>Compd</th>
<th>Optical band gap (1240/(\lambda_{\text{edge}})) (eV)</th>
<th>Theoretical band gap (eV)</th>
<th>HOMO energy (Expt) (eV)</th>
<th>HOMO energy (Calcd) (eV)</th>
<th>LUMO energy (Expt) (eV)</th>
<th>LUMO energy Calcd (eV)</th>
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**Table 3:** Experimental and Calculated Band gap and HOMO-LUMO Energy Values
Trend in Band gap and HOMO-LUMO Energies (Experimental and Calculated)

Band Gap Expt

Band gap Calcd

HOMO Expt

HOMO Calcd