

Unsymmetrically extended polyfused aromatics embedding coronene and perylene frameworks: their syntheses and properties

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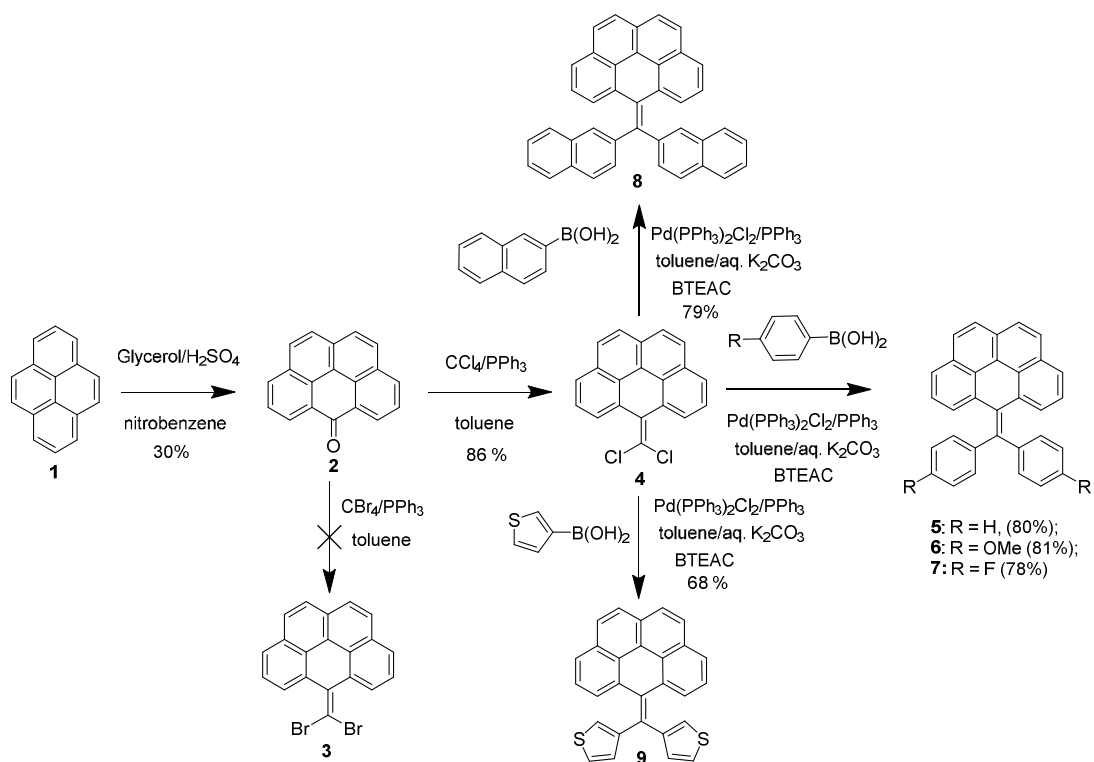
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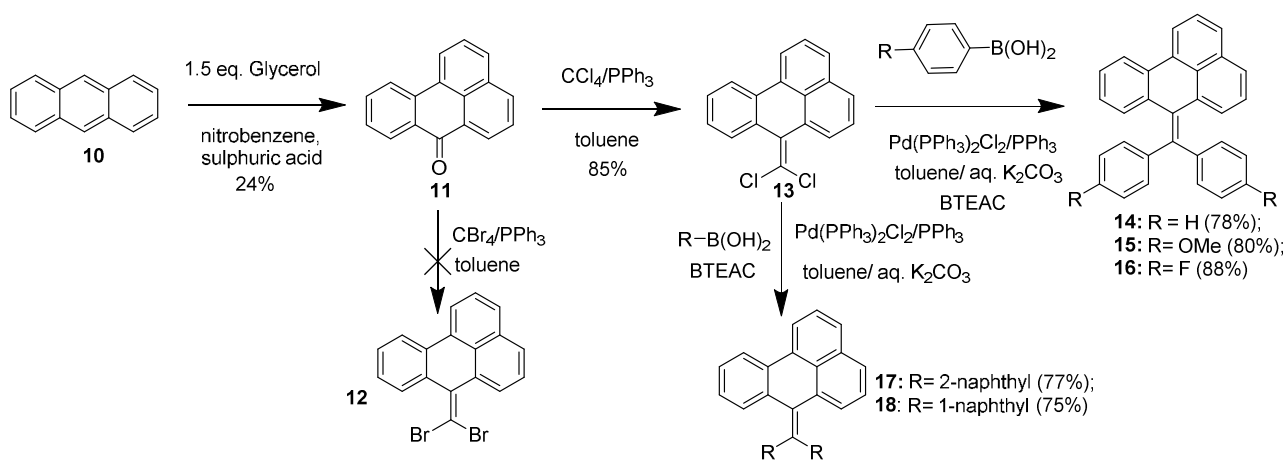
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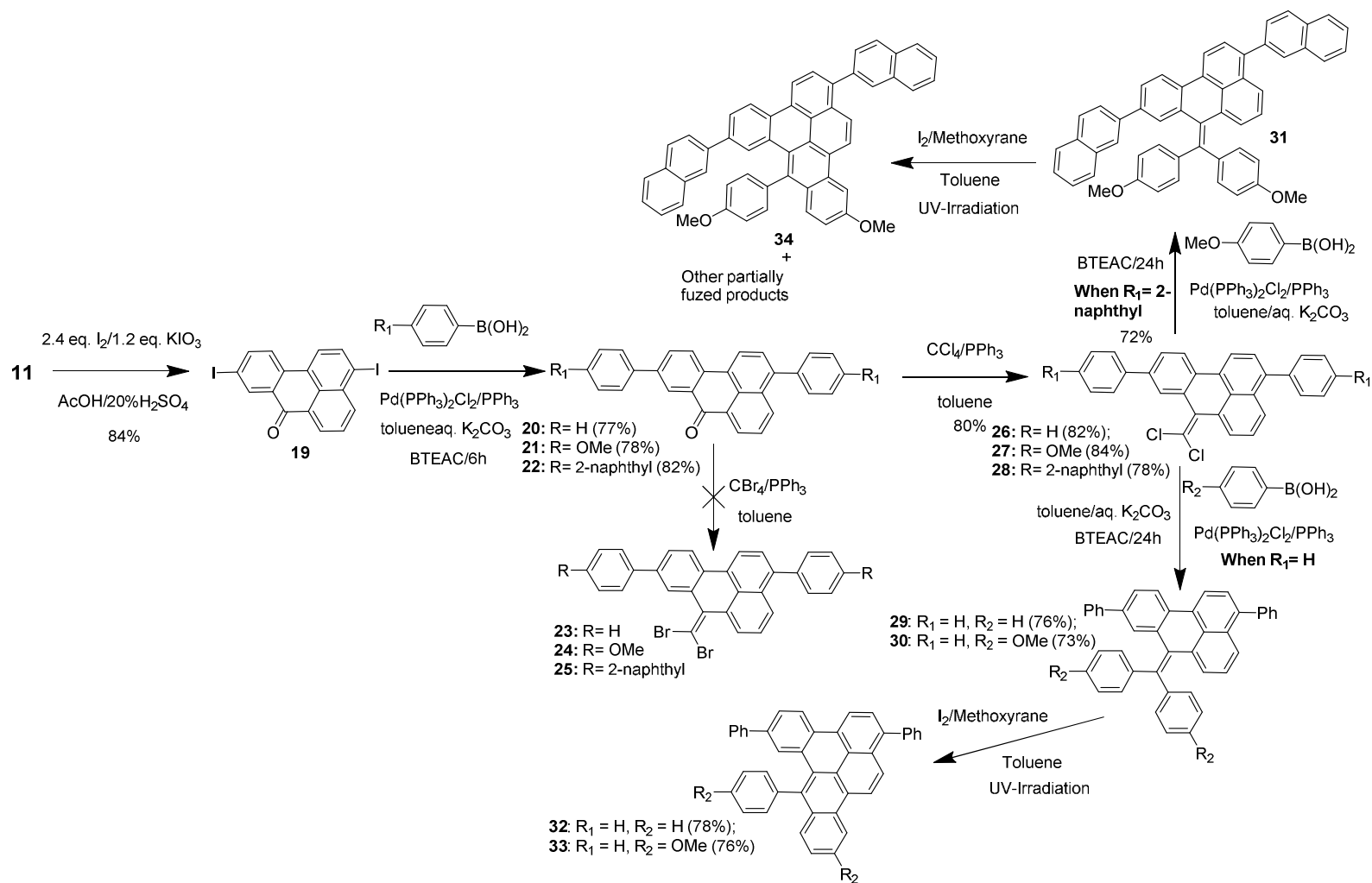
1. Synthetic Schemes, S1-S3 for the synthesis of aryl-derivatives (5-9, 14-18 and 31-34)



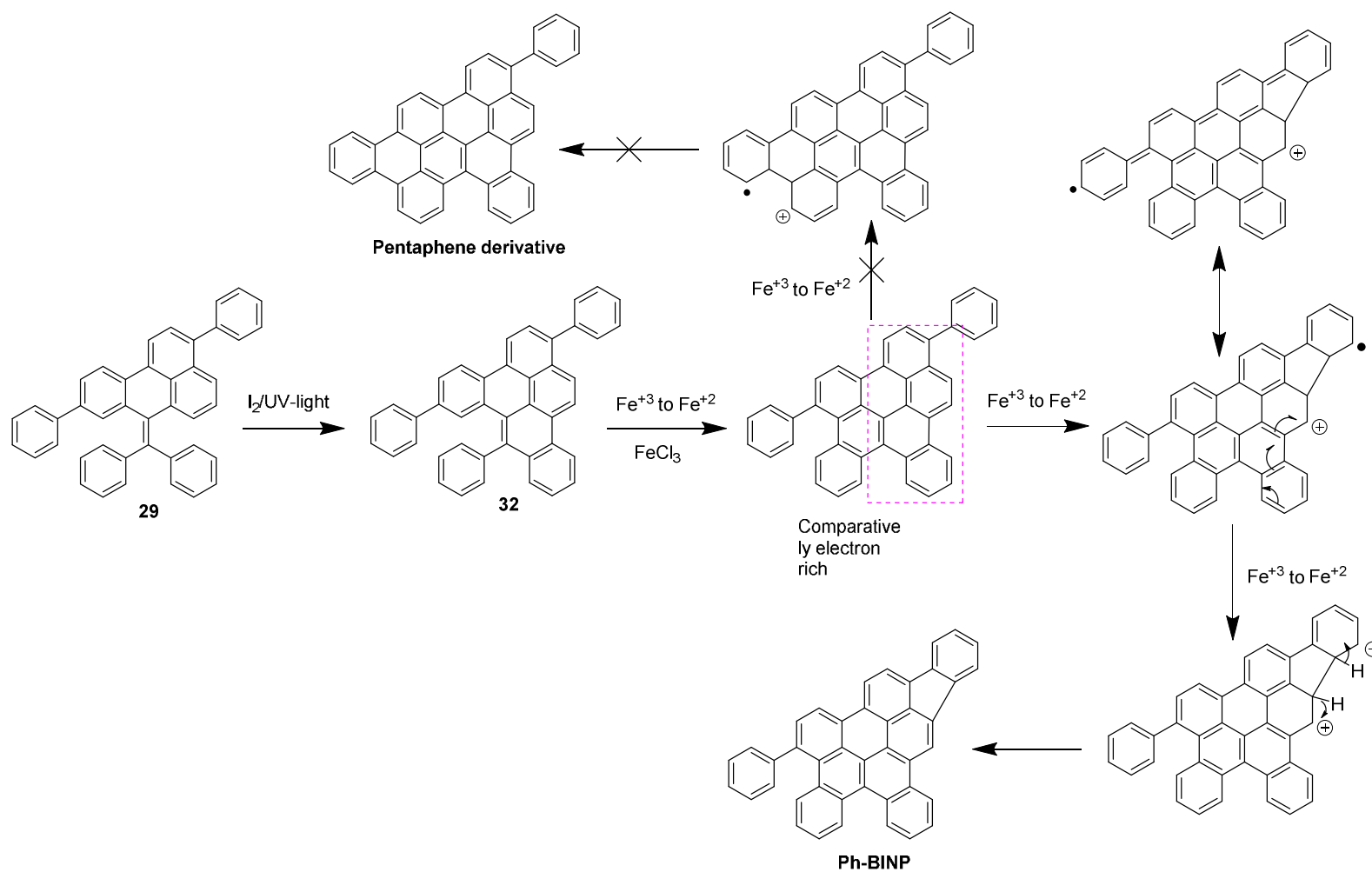
Scheme S1. Synthesis of diaryl-benzo[*cd*]pyrene derivatives (5-9)

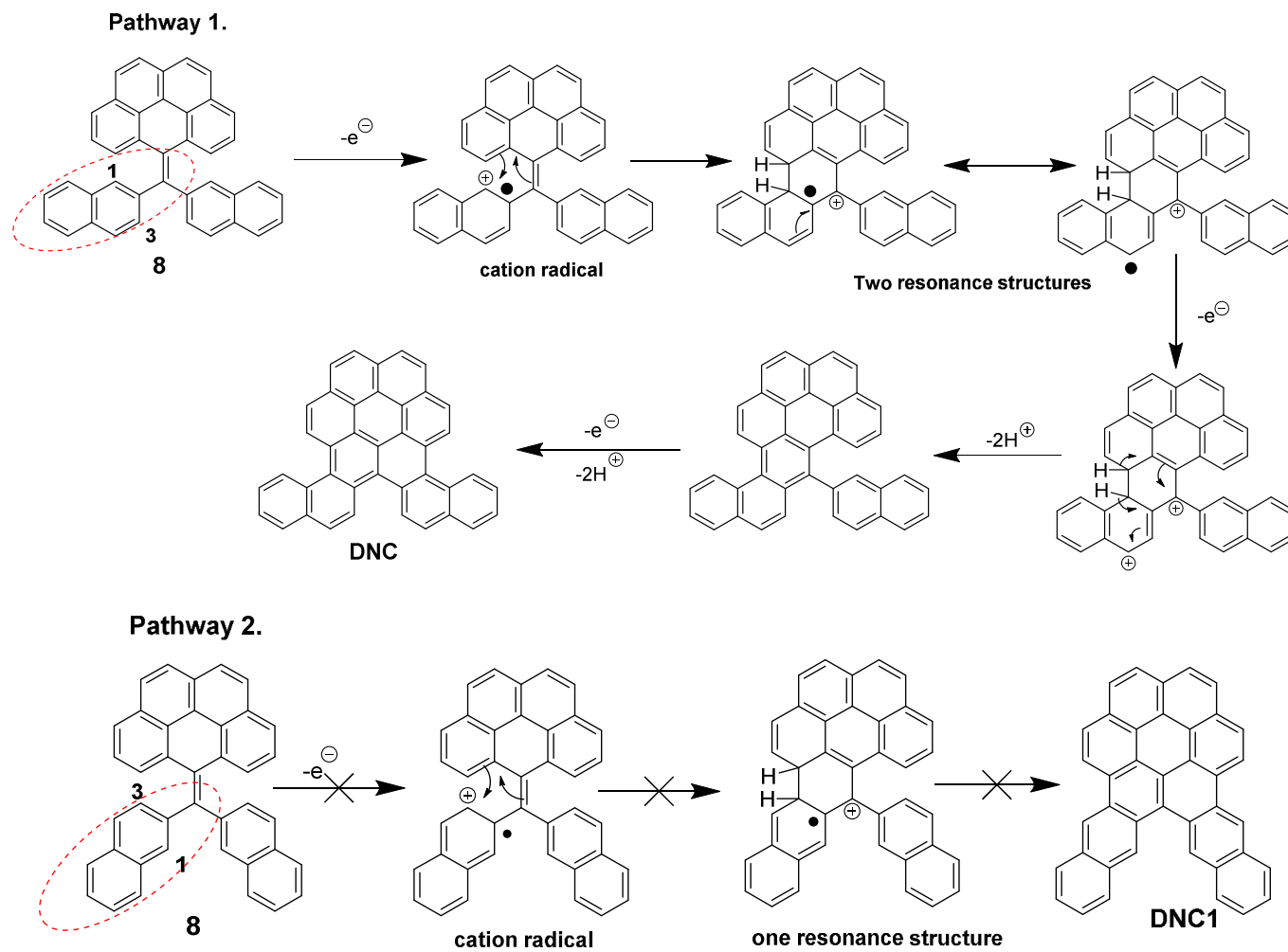


Scheme S2. Synthesis of diaryl-benzo[*de*]anthracene derivatives (14-18)



Scheme S3. Synthesis of partially fused derivatives (31-34)

2. Suggested mechanisms for the formation Ph-BINP and DNC



Scheme S5. Mechanism for the formation of DNC

3. Experimental Section

Starting materials were purchased from commercial sources. Solvents were distilled and dried prior to use for reaction, spectrophotometric, and spectrofluorimetric analyses. Suzuki couplings, iodine and FeCl₃ mediated oxidative reactions were conducted in N₂ atmosphere. Starting materials such as 6*H*-benzo[*cd*]pyren-6-one (**2**) and 7*H*-benzo[*de*]anthracen-7-one (**11**), 7*H*-benzo[*de*]anthracene-7-thione (**35**) and (diazomethylene)dibenzene (**36**) were prepared by procedures already reported in literature¹⁻³. Column chromatographic separations were performed by use of silica gel with 60-230 mesh size. ¹H NMR and ¹³C NMR were collected on a Bruker AMX400 O FT-NMR spectrometer in chloroform-*d* or DMSO-*d*₆ with tetramethylsilane (TMS) as the internal standard. V-550JASCO UV/VIS spectrophotometer and HITACHI F-4500 fluorescence spectrophotometer were used to carry out absorption and emission studies in dichloromethane. Thermal decomposition temperatures (T_d) of the **DBC** and **Flu-DBC** were measured by thermal gravimetric analyzer at a 10 °C/min in nitrogen atmosphere. HOMO-LUMO plots of the final derivatives were obtained by PC Spartan Pro software by semi-empirical method at AM1 level.

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2. a) Scheibye, S.; Shabana, R.; Lawesson, S.-O.; Romming, C. *Tetrahedron* **1982**, *38*, 993–1002; b) El-Barbary, A. A.; Shabana, R.; Lawesson, S.-O. *Phosphorus Sulfur Relat. Elem.* **1984**, *21*, 375–382.
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Preparation of 3,9-diiodo-7*H*-benzo[*de*]anthracen-7-one (19) 7*H*-benzo[*de*]anthracen-7-one (**11**) (0.23 g, 1.0 mmol), iodine (0.61 g, 2.4 mmol) and potassium iodate (0.26 g, 1.2 mmol) were taken in solvent mixtures of acetic acid (15 ml) and sulphuric acid (2.0 ml, 20%). The resulting mixture was heated at 90 °C for 6 h. On completion of the reaction, reaction mixture was cooled. The precipitated product was filtered and washed by methanol. The product was dried and recrystallized from dichloromethane and methanol to afford yellow powder. Yield: 0.40 g, 84%. Mp: 281 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 8.81-8.79 (m, 2H), 8.53-8.51 (m, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* =

8.0 Hz, 1H), 8.05-8.04 (m, 2H), 7.86 (t, $J = 7.6$ Hz, 1H). ^{13}C NMR could not be recorded due to poor solubility of the derivative. MALDI-TOF MS: calculated for $[\text{C}_{17}\text{H}_8\text{I}_2\text{O}+\text{H}]^+$: 482.8743, found: 482.8755.

General procedure for the Suzuki coupling on the 3,9-diiodo-7H-benzo[de]anthracen-7-one (19) 3,9-diiodo-7H-benzo[de]anthracen-7-one (**19**) (0.48 g, 1.0 mmol), aryl boronic acid (2.5 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (30 mg), PPh_3 (20 mg), potassium carbonate (1.38 g, 10.0 mmol) were taken in a mixture of toluene (50 ml) and water (10 ml). Reaction mixture was heated at 110 °C for 5 h in nitrogen atmosphere. On completion of reaction, reaction mixture was cooled and toluene layer was separated. Toluene was removed under vacuum, and product was purified by column chromatography using dichloromethane/hexane as eluent to afford product.

Preparation of 3,9-diphenyl-7H-benzo[de]anthracen-7-one (20) According to general reaction procedure, 3,9-diiodo-7H-benzo[de]anthracen-7-one (**19**) and phenylboronic acid (0.26 g, 2.5 mmol) were reacted to give product as yellow powder. Yield: 0.29 g, 77%. Mp: 180 °C. ^1H NMR (CDCl_3 , 400 MHz) δ : 8.84-8.78 (m, 2H), 8.52 (d, $J = 7.6$ Hz, 1H), 8.44 (d, $J = 8.4$ Hz, 1H), 8.32 (d, $J = 8.0$ Hz, 1H), 8.01 (dd, $J = 9.6, 2.0$ Hz, 1H), 7.80-7.72 (m, 3H), 7.66 (d, $J = 7.6$ Hz, 1H), 7.56-7.50 (m, 7H), 7.42 (t, $J = 7.2$ Hz, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 183.9, 142.7, 140.7, 139.7, 139.6, 134.9, 133.6, 131.7, 131.3, 131.1, 130.2, 129.8, 128.9, 128.7, 128.4, 128.1, 127.9, 127.8, 127.5, 128.0, 126.5, 126.1, 125.8, 125.7, 123.7. MALDI-TOF MS: calculated for $[\text{C}_{29}\text{H}_{18}\text{O}]^+$: 382.1385, found: 382.1370.

Preparation of 3,9-bis(4-methoxyphenyl)-7H-benzo[de]anthracen-7-one (21) According to general reaction procedure, 3,9-diiodo-7H-benzo[de]anthracen-7-one (**19**) and (4-methoxyphenyl)boronic acid (0.38 g, 2.5 mmol) were reacted to give product as yellow powder. Yield: 0.34 g, 78%. Mp: 167 °C. ^1H NMR (CDCl_3 , 400 MHz) δ : 8.83 (d, $J = 8.0$ Hz, 1H), 8.73 (d, $J = 2.4$ Hz, 1H), 8.50 (d, $J = 7.6$ Hz, 1H), 8.41 (d, $J = 8.4$ Hz, 1H), 8.35 (d, $J = 8.0$ Hz, 1H), 7.97 (dd, $J = 7.5, 2.4$ Hz, 1H), 7.77-7.72 (m, 3H), 7.63 (d, $J = 7.6$ Hz, 1H), 7.49-7.47 (m, 2H), 7.10-7.04 (m, 4H), 3.92 (s, 3H), 3.89 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 184.1, 159.7, 159.5, 142.4, 140.3, 134.5, 133.7, 132.2, 132.1, 131.6, 131.4, 131.2, 129.8, 128.9, 128.1, 127.6, 126.4, 125.7, 125.5, 123.7, 114.4, 114.0, 55.4. MALDI-TOF MS: calculated for $[\text{C}_{31}\text{H}_{22}\text{O}_3]^+$: 442.1563, found: 442.1550.

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Preparation of 3,9-di(naphthalen-2-yl)-7H-benzo[de]anthracen-7-one (22) According to general reaction procedure, 3,9-diiodo-7H-benzo[de]anthracen-7-one (**19**) and naphthalene-2-boronic acid (0.43 g, 2.5 mmol) were reacted to give product as yellow powder. Yield: 0.40 g, 82%. Mp: 204 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 8.92 (d, *J* = 2.0 Hz, 1H), 8.87 (d, *J* = 7.2 Hz, 1H), 8.57 (d, *J* = 7.6 Hz, 1H), 8.49 (d, *J* = 8.4 Hz, 1H), 8.38 (d, *J* = 8.4 Hz, 1H), 8.25 (s, 1H), 8.15 (dd, *J* = 10.4, 2.0 Hz, 1H), 8.02-7.92 (m, 8H), 7.78-7.66 (m, 3H), 7.60-7.52 (m, 4H). ¹³C NMR (CDCl₃, 100 MHz) δ: 184.1, 142.8, 140.8, 137.2, 137.0, 135.2, 133.9, 133.7, 133.3, 133.0, 132.8, 132.1, 131.6, 131.3, 130.1, 129.2, 128.9, 128.7, 128.4, 128.2, 128.1, 128.0, 127.8, 127.7, 126.7, 126.5, 126.3, 126.1, 126.0, 125.1, 123.9. MALDI-TOF MS: calculated for [C₃₇H₂₂O]⁺: 482.1665, found: 482.1657.

Preparation of 3',3'-diphenylspiro[benzo[de]anthracene-7,2'-thiirane (37) 7H-benzo[de]anthracene-7-thione (**35**) (1.23 g, 5.0 mmol) was dissolved in anhydrous THF (20 ml), and freshly prepared diazomethylenedibenzene (**36**) (1.36 g, 7.0 mmol) solution (in anhydrous THF, 20 ml) was added to it. The reaction mixture was stirred for 24 h in nitrogen atmosphere. On completion of reaction, the solvent was removed and product was purified by column chromatography using dcm/hexane as eluent to give light-yellow solid, 0.56 g, 27%. Mp: 256 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 8.30 (d, *J* = 7.2 Hz, 1H), 8.05 (d, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.34-7.23 (m, 3H), 7.11-6.74 (m, *J* = 1.6 Hz, 12H). ¹³C NMR (CDCl₃, 100 MHz) δ: 141.6, 141.4, 134.9, 133.5, 132.9, 131.6, 129.9, 129.7, 129.5, 129.2, 128.4, 127.6, 127.4, 127.1, 126.9, 126.3, 126.2, 126.0, 125.5, 123.2, 120.0, 72.8, 60.3. MALDI-TOF MS: calculated for [C₃₀H₂₀S]⁺: 412.1286, found: 412.1267.

Preparation of 7-(diphenylmethylene)-7H-benzo[de]anthracene (14) 3',3'-diphenylspiro[benzo[de]anthracene-7,2'-thiirane (**37**) (0.41 g, 1.0 mmol) and PPh₃ (0.52 g, 2.0 mmol) were taken in toluene (10 ml), and reaction mixture was heated to reflux for 12 h in nitrogen atmosphere. On completion of reaction, the mixture was cooled and toluene was removed. The product was obtained by column chromatography using dichloromethane/hexane as eluent to afford light-yellow solid. Yield: 0.26 g, 69%. Mp: 152 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 8.16 (d, *J* = 7.2 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.61-7.56 (m, 2H), 7.24-7.1201 (m, 13H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.90-6.86 (m, 1H). ¹³C NMR (CDCl₃, 100 MHz) δ: 144.0, 143.5, 134.6, 133.8,

133.5, 132.8, 132.5, 131.2, 130.6, 129.8, 129.7, 128.7, 128.5, 128.3, 127.8, 127.3, 127.1, 126.5, 126.4, 125.9, 125.8, 124.9, 123.7, 119.6. MALDI-TOF MS: calculated for $[C_{30}H_{20}]^+$: 380.1559, found: 380.1571.

General method for the preparation of chloromethylene derivatives (4, 13 and 26-28)

Aromatic ketones (**2**, **11** and **20-22**) (10.0 mmol), carbon tetrachloride (4.61 g, 30.0 mmol) and PPh_3 (15.72 g, 60.0 mmol) were taken in dry toluene (60 ml), and reaction mixture was heated at 100 °C for 24 h in nitrogen atmosphere. On completion of reaction, the reaction mixture was cooled and poured into dcm/hexane mixture (ratio= 1/4; 200 ml). The solution was filtered through short silica plug. Solvent was removed from the filtrate and product was re-precipitated by dcm/methanol to afford pure compound.

Preparation of 6-(dichloromethylene)-6H-benzo[cd]pyrene (4) According to general reaction procedure, 6H-benzo[cd]pyren-6-one (**2**) (2.54 g, 10.0 mmol), carbon tetrachloride and PPh_3 were reacted to give product as light-yellow solid. Yield: 2.76 g, 86%. Mp: 208 °C. 1H NMR ($CDCl_3$, 400 MHz) δ : 8.42 (d, $J = 7.6$ Hz, 2H), 7.97-7.90 (m, 6H), 7.69 (t, $J = 7.6$ Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 132.9, 130.7, 130.2, 129.5, 128.4, 128.1, 127.3, 126.9, 126.4, 125.3, 124.1, 120.7. MALDI-TOF MS: calculated for $[C_{20}H_{10}Cl_2]^+$: 320.0154, found: 320.0157.

Preparation of 7-(dichloromethylene)-7H-benzo[de]anthracene (13) According to general reaction procedure, 7H-benzo[de]anthracen-7-one (**11**) (2.30 g, 10.0 mmol), carbon tetrachloride and PPh_3 were reacted to give product as light-yellow solid. Yield: 2.52 g, 85%. Mp: 122 °C. 1H NMR ($CDCl_3$, 400 MHz) δ : 8.17 (s, 1H), 8.15 (s, 1H), 8.08-8.06 (m, 1H), 7.98 (d, $J = 8.4$ Hz, 1H), 7.86-7.83 (m, 2H), 7.62-7.55 (m, 2H), 7.47-7.43 (m, 1H), 7.38-7.34 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 133.4, 132.9, 132.7, 131.7, 130.3, 129.7, 129.4, 128.4, 128.3, 128.1, 127.7, 127.6, 126.3, 126.2, 125.1, 124.1, 120.4, 119.8. MALDI-TOF MS: calculated for $[C_{18}H_{10}Cl_2]^+$: 296.0154, found: 296.0158.

Preparation of 7-(dichloromethylene)-3,9-diphenyl-7H-benzo[de]anthracene (26)

According to general reaction procedure, 3,9-diphenyl-7H-benzo[de]anthracen-7-one (**20**) (3.82 g, 10.0 mmol), carbon tetra chloride and PPh_3 were reacted to give product as yellow solid. Yield: 3.68 g, 82%. Mp: 170 °C. 1H NMR ($CDCl_3$, 400 MHz) δ : 8.34 (s, 1H), 8.22 (d, $J = 7.6$ Hz, 1H), 8.18 (d, $J = 7.6$ Hz, 1H), 8.07 (d, $J = 8.4$ Hz, 1H), 7.93 (d, $J = 7.6$ Hz, 1H), 7.72-7.70 (m, 3H), 7.58-7.47 (m, 9H), 7.42 (t, $J = 6.4$ Hz, 2.0 Hz, 1H).

^{13}C NMR (CDCl_3 , 100 MHz) δ : 140.7, 140.4, 140.3, 138.9, 133.1, 132.3, 132.0, 131.0, 130.2, 129.8, 129.5, 128.9, 128.3, 128.2, 128.0, 127.9, 127.7, 127.6, 127.5, 127.4, 127.1, 127.0, 126.6, 125.0, 124.6, 120.2, 120.0. MALDI-TOF MS: calculated for $[\text{C}_{38}\text{H}_{18}\text{Cl}_2]^+$: 448.0780, found: 448.0793.

Preparation of 7-(dichloromethylene)-3,9-bis(4-methoxyphenyl)-7H-benzo[de]anthracene (27) According to general reaction procedure, 3,9-bis(4-methoxyphenyl)-7H-benzo[de]anthracen-7-one (**21**) (4.43 g, 10.0 mmol), carbon tetrachloride and PPh_3 were reacted to give product as yellow solid. Yield: 4.28 g, 84%. Mp: 205 °C. ^1H NMR (CDCl_3 , 400 MHz) δ : 8.28 (d, $J = 1.6$ Hz, 1H), 8.20-8.16 (m, 2H), 8.04 (d, $J = 8.4$ Hz, 1H), 7.50 (d, $J = 9.2$ Hz, 1H), 7.67-7.62- (m, 3H), 7.55-7.45 (m, 4H), 7.07-7.02 (m, 4H), 3.91 (s, 3H), 3.88 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 159.4, 159.2, 140.2, 138.5, 133.2, 132.9, 132.6, 131.9, 131.8, 131.2, 131.1, 129.8, 129.2, 128.0, 127.6, 127.3, 126.6, 124.9, 124.5, 120.1, 119.7, 114.4, 113.8, 55.4. MALDI-TOF MS: calculated for $[\text{C}_{32}\text{H}_{22}\text{Cl}_2\text{O}_2]^+$: 508.0991, found: 508.1003.

Preparation of 7-(dichloromethylene)-3,9-di(naphthalen-2-yl)-7H-benzo[de]anthracene (28) According to general reaction procedure, 3,9-di(naphthalen-2-yl)-7H-benzo[de]anthracen-7-one (**22**) (4.83 g, 10.0 mmol), carbon tetra chloride and PPh_3 were reacted to give product as yellow solid. Yield: 4.29 g, 78%. Mp: 220 °C. ^1H NMR (CDCl_3 , 400 MHz) δ : 8.49 (d, $J = 1.6$ Hz, 1H), 8.30 (d, $J = 7.2$ Hz, 1H), 8.22 (d, $J = 7.2$ Hz, 1H), 8.17-8.15 (m, 2H), 8.02-7.85 (m, 10H), 7.70-7.68 (m, 2H), 7.59-7.53 (m, 5H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 140.8, 137.8, 137.7, 133.8, 133.4, 133.1, 132.8, 132.7, 131.2, 130.0, 129.0, 128.7, 128.4, 128.3, 128.1, 127.9, 127.8, 127.7, 127.4, 126.7, 126.5, 126.3, 126.1, 125.8, 125.3, 125.2, 124.8, 120.3, 120.1. MALDI-TOF MS: calculated for $[\text{C}_{38}\text{H}_{22}\text{Cl}_2]^+$: 548.1093, found: 548.1090.

General reaction procedure of Suzuki coupling reaction on dichloromethylene derivatives (4, 13 and 26-28) with arylboronic acids Dichloromethylene derivative (1.0 mmol), aryl-boronic acid (2.5 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (30 mg) and PPh_3 (20 mg), potassium carbonate (1.38 g, 10.0 mmol) and benzyltriethyl ammonium chloride (0.5 g, 2.2 mmol) were taken in a mixture of toluene (20 ml) and water (10 ml). The reaction mixture was heated at 110 °C for 24 h in nitrogen atmosphere. On completion of reaction the mixture

was cooled, and toluene layer was separated. On removal of toluene the product was purified by column chromatography using dichloromethane/hexane as eluent.

Preparation of 6-(diphenylmethylene)-6*H*-benzo[*cd*]pyrene (5) According to general reaction procedure, 6-(dichloromethylene)-6*H*-benzo[*cd*]pyrene (**4**) (0.32 g, 1.0 mmol) and phenylboronic acid (0.26 g, 2.5 mmol) were reacted to give product as light-yellow solid. Yield: 0.32 g, 80%. Mp: 235 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 7.90 (s, 4H), 7.74-7.72 (m, 2H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.25-7.13 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz) δ: 145.7, 144.2, 133.5, 133.2, 130.9, 129.9, 129.0, 128.8, 128.6, 128.0, 127.2, 126.7, 126.4, 126.2, 125.2. MALDI-TOF MS: calculated for [C₃₂H₂₀]⁺: 404.1559, found: 404.1550.

Preparation of 6-(bis(4-methoxyphenyl)methylene)-6*H*-benzo[*cd*]pyrene (6) According to general reaction procedure, 6-(dichloromethylene)-6*H*-benzo[*cd*]pyrene (**4**) (0.32 g, 1.0 mmol) and (4-methoxyphenyl)boronic acid (0.38 g, 2.5 mmol) were reacted to give product as yellow solid. Yield: 0.38 g, 81%. Mp: 172 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 7.88 (s, 4H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 4H), 6.79-6.76 (m, 4H), 3.78 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ: 158.2, 145.2, 137.0, 133.7, 133.1, 131.2, 128.9, 128.5, 128.0, 127.1, 126.4, 126.1, 125.3, 114.1, 55.2. MALDI-TOF MS: calculated for [C₃₄H₂₄O₂]⁺: 464.1770, found: 464.1777.

Preparation of 6-(bis(4-fluorophenyl)methylene)-6*H*-benzo[*cd*]pyrene (7) According to general reaction procedure, 6-(dichloromethylene)-6*H*-benzo[*cd*]pyrene (**4**) (0.32 g, 1.0 mmol) and (4-fluorophenyl)boronic acid (0.35 g, 2.5 mmol) were reacted to give product as light-yellow solid. Yield: 0.34 g, 78%. Mp: 245 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 7.91 (s, 4H), 7.75 (d, *J* = 7.2 Hz, 2H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.19 (t, *J* = 8.0 Hz, 2H), 7.11-7.07 (m, 4H), 6.96-6.91 (m, 4H). ¹³C NMR (CDCl₃, 100 MHz) δ: 162.8, 160.4, 143.1, 140.0, 134.6, 132.8, 131.6, 131.5, 130.9, 129.2, 128.7, 127.8, 127.2, 127.0, 126.3, 125.2, 125.0, 115.8, 115.6. MALDI-TOF MS: calculated for [C₃₂H₁₈F₂]⁺: 440.1377, found: 440.1370.

Preparation of 6-(di(naphthalen-2-yl)methylene)-6*H*-benzo[*cd*]pyrene (8) According to general reaction procedure, 6-(dichloromethylene)-6*H*-benzo[*cd*]pyrene (**4**) (0.32 g, 1.0 mmol) and naphthalene-2-boronic acid (0.43 g, 2.5 mmol) were reacted to give

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product as yellow solid. Yield: 0.40 g, 79%. Mp: 230 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 7.93-7.92 (m, 4H), 7.80-7.66 (m, 10H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.44-7.41 (m, 4H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.05 (t, *J* = 8.0 Hz, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ: 145.3, 141.9, 134.1, 133.7, 133.2, 132.1, 131.0, 129.3, 129.1, 129.0, 128.4, 128.2, 127.9, 127.6, 127.2, 126.9, 126.2, 125.9, 125.8, 125.4, 125.2. MALDI-TOF MS: calculated for [C₄₀H₂₄]⁺: 504.1872, found: 504.1876.

Preparation of 3,3'-((6*H*-benzo[*cd*]pyren-6-ylidene)methylene)dithiophene (9)

According to general reaction procedure, 6-(dichloromethylene)-6*H*-benzo[*cd*]pyrene (4) (0.32 g, 1.0 mmol) and thiophene-3-boronic acid (0.32 g, 2.5 mmol) were reacted to give product as yellow solid. Yield: 0.28 g, 68%. Mp: 196 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 7.79 (s, 4H), 7.79-7.77 (m, 2H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 2H), 7.20-7.18 (m, 2H), 6.99 (dd, *J* = 8.0 Hz, 1.2 Hz, 2H), 6.67-6.65 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ: 143.8, 134.8, 134.3, 133.0, 130.9, 129.1, 128.9, 128.2, 127.7, 127.2, 126.9, 126.1, 125.4, 125.1, 123.7. MALDI-TOF MS: calculated for [C₂₈H₁₆S₂]⁺: 416.0687, found: 416.0678.

Preparation of 7-(diphenylmethylene)-7*H*-benzo[*de*]anthracene (14) According to general reaction procedure, 7-(dichloromethylene)-7*H*-benzo[*de*]anthracene (13) (0.30 g, 1.0 mmol) and phenylboronic acid (0.26 g, 2.5 mmol) were reacted to give product as light-yellow solid. Yield: 0.30 g, 78%.

Preparation of 7-(bis(4-methoxyphenyl)methylene)-7*H*-benzo[*de*]anthracene (15)

According to general reaction procedure, 7-(dichloromethylene)-7*H*-benzo[*de*]anthracene (13) (0.30 g, 1.0 mmol) and (4-methoxyphenyl)boronic acid (0.38 g, 2.5 mmol) were reacted to give product as yellow solid. Yield: 0.35 g, 80%. Mp: 150 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 8.15 (d, *J* = 7.2 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.61-7.55 (m, 2H), 7.25-7.22 (m, 3H), 7.10-7.06 (m, 3H), 7.03-7.01 (m, 2H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.80-6.72 (m, 4H), 3.78 (s, 3H), 3.75 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ: 158.1, 143.0, 136.8, 136.2, 135.1, 133.7, 133.1, 132.9, 131.3, 131.1, 130.9, 130.8, 128.7, 127.8, 126.9, 126.8, 126.3, 125.9, 125.8, 125.1, 123.8, 119.4, 114.0, 113.7, 55.1. MALDI-TOF MS: calculated for [C₃₂H₂₄O₂]⁺: 440.1770, found: 440.1768.

Preparation of 7-(bis(4-fluorophenyl)methylene)-7*H*-benzo[*de*]anthracene (16) According to general reaction procedure, 7-(dichloromethylene)-7*H*-

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benzo[*de*]anthracene (**13**) (0.30 g, 1.0 mmol) and (4-fluorophenyl)boronic acid (0.35 g, 2.5 mmol) were reacted to give product as yellow solid. Yield: 0.37 g, 88%. Mp: 245 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 8.16 (d, *J* = 7.2 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.65-7.57 (m, 2H), 7.29-7.25 (m, 1H), 7.18-7.05 (m, 7H), 7.05-6.88 (m, 5H). ¹³C NMR (CDCl₃, 100 MHz) δ: 162.8, 160.3, 141.0, 139.8, 139.2, 134.6, 134.2, 133.8, 132.8, 132.2, 131.5, 131.4, 131.3, 131.1, 130.5, 128.5, 128.0, 127.4, 127.2, 126.8, 126.0, 125.0, 123.8, 119.8, 115.7, 115.5, 115.4, 115.2. MALDI-TOF MS: calculated for [C₃₀H₁₈F₂]⁺: 416.1371, found: 416.1379.

Preparation of 7-(di(naphthalen-2-yl)methylene)-7*H*-benzo[*de*]anthracene (**17**)

According to general reaction procedure, 7-(dichloromethylene)-7*H*-benzo[*de*]anthracene (**13**) (0.30 g, 1.0 mmol) and naphthalene-2-boronic acid (0.43 g, 2.5 mmol) were reacted to give product as yellow solid. Yield: 0.37 g, 77%. Mp: 210 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 8.22 (d, *J* = 7.2 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.81-7.57 (m, 11H), 7.44-7.38 (m, 4H), 7.36-7.31 (m, 3H), 7.23-7.18 (m, 2H), 6.92 (t, *J* = 8.0 Hz, 1H), 6.780 (t, *J* = 8.0 Hz, 1H). ¹³C NMR (CDCl₃, 100 MHz) δ: 141.7, 141.1, 134.6, 134.1, 133.8, 133.6, 133.4, 132.9, 132.5, 132.0, 131.3, 130.8, 129.1, 128.9, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.6, 127.5, 127.4, 127.3, 126.7, 126.1, 126.0, 125.9, 125.8, 125.7, 125.2, 123.8, 119.7. MALDI-TOF MS: calculated for [C₃₈H₂₄]⁺: 480.1872, found: 480.1878.

Preparation of 7-(di(naphthalen-1-yl)methylene)-7*H*-benzo[*de*]anthracene (**18**)

According to general reaction procedure, 7-(dichloromethylene)-7*H*-benzo[*de*]anthracene (**13**) (0.30 g, 1.0 mmol) and naphthalene-1-boronic acid (0.43 g, 2.5 mmol) were reacted to give product as yellow solid. Yield: 0.36 g, 75%. Mp: 220 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 8.52-8.49 (m, 1H), 8.26-8.20 (m, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.84-7.82 (m, 1H), 7.77-7.73 (m, 2H), 7.66-7.57 (m, 4H), 7.50-7.44 (m, 3H), 7.38-7.12 (m, 8H), 6.79 (t, *J* = 8.0 Hz, 1H), 6.63 (t, *J* = 7.2 Hz, 1H). ¹³C NMR (CDCl₃, 100 MHz) δ: 142.1, 141.7, 137.7, 136.9, 134.9, 133.9, 133.8, 133.3, 132.8, 132.4, 130.9, 130.8, 128.9, 128.7, 128.4, 127.9, 127.3, 127.2, 127.0, 126.7, 126.5, 126.4, 126.2, 126.1, 125.9, 125.8, 125.6, 125.5, 125.4, 125.1, 125.0, 123.5, 119.9. MALDI-TOF MS: calculated for [C₃₈H₂₄]⁺: 480.1872, found: 480.1880.

Preparation of 7-(diphenylmethylene)-3,9-diphenyl-7*H*-benzo[*de*]anthracene (**29**)

According to general reaction procedure, 7-(dichloromethylene)-3,9-diphenyl-7*H*-

benzo[*de*]anthracene (**26**) (0.45 g, 1.0 mmol) and phenylboronic acid (0.26 g, 2.5 mmol) were reacted to give product as yellow solid. Yield: 0.40 g, 76%. Mp: 232 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 8.23 (d, *J* = 7.6 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 9.2 Hz, 1H), 7.57-7.44 (m, 8H), 7.37-7.17 (m, 14H), 7.04-6.97 (m, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ: 144.5, 143.8, 143.5, 140.7, 140.2, 138.5, 134.5, 133.7, 132.7, 132.5, 131.1, 130.4, 130.2, 129.8, 129.7, 129.5, 128.9, 128.7, 128.5, 128.4, 128.3, 127.8, 127.3, 127.1, 127.0, 126.4, 126.3, 125.8, 124.9, 124.1, 119.4. MALDI-TOF MS: calculated for [C₄₂H₂₈]⁺: 532.2185, found: 532.2200.

Preparation of 7-(bis(4-methoxyphenyl)methylene)-3,9-diphenyl-7H-benzo[*de*]anthracene (30) According to general reaction procedure, 7-(dichloromethylene)-3,9-diphenyl-7H-benzo[*de*]anthracene (**27**) (0.45 g, 1.0 mmol) and (4-methoxyphenyl)boronic acid (0.38 g, 2.5 mmol) were reacted to give product as yellow solid. Yield: 0.43 g, 73%. Mp: 240 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 8.22 (d, *J* = 7.6 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 9.2 Hz, 1H), 7.56-7.44 (m, 8H), 7.35-7.20 (m, 6H), 7.10-7.01 (m, 5H), 6.87-6.76 (m, 4H), 3.78 (s, 3H), 3.77 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ: 158.4, 158.1, 143.3, 140.8, 140.0, 138.4, 137.2, 136.1, 135.0, 133.3, 132.9, 132.6, 131.0, 131.0, 130.5, 130.1, 129.4, 129.0, 128.4, 128.2, 127.6, 127.2, 127.0, 125.6, 125.1, 124.7, 124.1, 119.3, 114.2, 113.9, 55.3, 55.1. MALDI-TOF MS: calculated for [C₄₄H₃₂O₂]⁺: 592.2396, found: 592.2384.

Preparation of 7-(bis(4-methoxyphenyl)methylene)-3,9-di(naphthalen-2-yl)-7H-benzo[*de*]anthracene (31) According to general reaction procedure, 7-(dichloromethylene)-3,9-di(naphthalen-2-yl)-7H-benzo[*de*]anthracene (**28**) (0.55 g, 1.0 mmol) and (4-methoxyphenyl)boronic acid (0.38 g, 2.5 mmol) were reacted to give product as yellow solid. Yield: 0.50 g, 72%. Mp: 267 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 8.27 (d, *J* = 7.6 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.99 (s, 1H), 7.95-7.92 (m, 3H), 7.84-7.65 (m, 7H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.57-7.48 (m, 4H), 7.39-7.27 (m, 5H), 7.11-7.05 (m, 3H), 6.96-6.94 (m, 2H), 6.81-6.79 (m, 2H), 3.81 (s, 3H), 3.78 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ: 158.3, 158.1, 143.4, 140.0, 138.4, 138.3, 138.2, 137.3, 136.2, 135.0, 133.7, 133.4, 133.2, 132.9, 132.7, 132.6, 132.5, 131.2, 131.1, 130.9, 130.6, 129.8, 129.1, 128.8, 128.6, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 126.3, 126.1,

126.0, 125.9, 125.8, 125.4, 125.2, 124.8, 124.2, 119.4, 114.3, 114.0, 55.2, 55.1. MALDI-TOF MS: calculated for $[C_{52}H_{36}O_2]^+$: 692.2710, found: 692.2696.

General procedure for I₂ mediated oxidative coupling and FeCl₃ promoted Scholl reactions for the synthesis of coronene and perylene derivatives Diarylmethylene derivatives (**5-9** and **14-18**) or tetraarylmethylene derivatives (**29-31**) (1.0 mmol), iodine (0.64 g, 2.5 mmol) and methyloxirane (10 ml) were taken in anhydrous toluene (30 ml). The mixture was irradiated under UV-light for 12 h in nitrogen atmosphere. On completion of reaction, the excessive iodine was removed by treating with saturated sodium thiosulphate solution. Toluene was removed under vacuum, and product mixture (partially and completely annulated products, in case of **5-9** and **14-18** and **34**) or pure partially fused products (in case of **29-30**) were dried.

Mixture or pure partially fused derivatives (**32-33**) were dissolved in anhydrous dichloromethane (60 ml) and stirred in nitrogen atmosphere. Iron chloride (20.0-40.0 mmol) as dissolved in nitromethane (10 ml) was added via syringe, and reaction mixture was further stirred at room temperature for 4-36 h depending on the reactivity of the substrate. On completion of reaction, the reaction mixture was quenched by adding methanol, and the precipitated product was filtered. It was successively washed with methanol, hydrochloric acid and water then dried. Depending on the solubility, it was purified either by recrystallization or by column chromatography.

Preparation of dibenzo[*a,d*]coronene (DBC) According to general reaction procedure, 6-(diphenylmethylene)-6*H*-benzo[*cd*]pyrene (**5**) (0.40 g, 1.0 mmol), iodine and methyloxirane were reacted to furnish a mixture of partially and completely annulated products, then product mixture was treated with iron chloride (3.24 g, 20.0 mmol) for 24 h. Product was obtained by re-crystallization with benzene, Yield: 0.30 g, 76%. Mp: >300 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 9.53 (d, *J* = 8.8 Hz, 2H), 9.49 (d, *J* = 8.4 Hz, 2H), 9.38 (d, *J* = 8.4 Hz, 2H), 8.81 (d, *J* = 8.8 Hz, 2H), 8.71-8.65 (m, 4H), 8.02 (t, *J* = 7.2 Hz, 2H), 7.93 (t, *J* = 7.2 Hz, 2H). ¹³C NMR could not be recorded due to poor solubility of the derivative. MALDI-TOF MS: calculated for $[C_{32}H_{16}]^+$: 400.1246, found: 400.1249.

Preparation of 8,13-dimethoxydibenzo[*a,d*]coronene (Met-DBC) According to general reaction procedure, 6-(bis(4-methoxyphenyl)methylene)-6*H*-benzo[*cd*]pyrene (**6**) (0.46 g, 1.0 mmol), iodine and methyloxirane were reacted to furnish the mixture of partially and

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completely annulated products, then product mixture was treated with iron chloride (3.24 g, 20.0 mmol) for 6 h. Product was purified by column chromatography using dichloromethane as eluent to afford yellow solid. Yield: 0.36 g, 80%. Mp: 275 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 9.36 (d, *J* = 8.8 Hz, 2H), 9.29 (d, *J* = 9.2 Hz, 2H), 8.71 (d, *J* = 8.8 Hz, 2H), 8.65-8.62 (m, 6H), 7.54 (dd, *J* = 11.6 Hz, 2.4 Hz, 2H), 4.24 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz) δ: 158.2, 131.7, 131.4, 129.8, 128.8, 126.5, 126.1, 125.5, 124.7, 123.8, 123.5, 123.2, 123.0, 121.2, 119.8, 115.6, 104.5, 55.7. MALDI-TOF MS: calculated for [C₃₄H₂₀O₂]⁺: 460.1463, found: 460.1457.

Preparation of 8,13-difluorodibenzo[*a,d*]coronene (Flu-DBC) According to general reaction procedure, 6-(Bis(4-methoxyphenyl)methylene)-6*H*-benzo[*cd*]pyrene (**6**) (0.44 g, 1.0 mmol), iodine and methyloxirane were reacted to furnish the mixture of partially and completely annulated products, then product mixture was treated with iron chloride (3.24 g, 20.0 mmol) for 20 h. Product was purified by vacuum sublimation at 420 °C (5*10⁻⁵ torr) to afford yellow solid. Yield: 0.30 g, 65%. Mp: >300 °C. Due to low solubility of the derivative, NMR data could not be obtained. MALDI-TOF MS: calculated for [C₃₂H₁₄F₂]⁺: 436.1058, found: 436.1047.

Preparation of dinaphtho[1,2-*a*:2',1'-*d*]coronene (DNC) According to general reaction procedure, 6-(Di(naphthalen-2-yl)methylene)-6*H*-benzo[*cd*]pyrene (**8**) (0.50 g, 1.0 mmol), iodine and methyloxirane were reacted to furnish the mixture of partially and completely annulated products, then product mixture was treated with iron chloride (3.24 g, 20.0 mmol) for 12 h. Product was obtained by re-crystallization with benzene to give light yellow solid. Yield: 0.39 g, 77%. Mp: >300 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 10.04 (d, *J* = 8.8 Hz, 2H), 9.50 (d, *J* = 8.4 Hz, 2H), 9.18 (d, *J* = 8.8 Hz, 2H), 8.91 (d, *J* = 9.2 Hz, 2H), 8.84 (s, 4H), 8.26 (d, *J* = 7.2 Hz, 2H), 8.12 (d, *J* = 8.8 Hz, 2H), 7.92-7.82 (m, 4H). ¹³C NMR could not be recorded due to poor solubility of the derivative. MALDI-TOF MS: calculated for [C₄₀H₂₀]⁺: 500.1559, found: 500.1552.

Preparation of coroneno[1,2-*b*:4,3-*b'*]dithiophene (DTC) According to general reaction procedure, 3,3'-((6*H*-benzo[*cd*]pyren-6-ylidene)methylene)dithiophene (**9**) (0.42 g, 1.0 mmol), iodine and methyloxirane were reacted to furnish the mixture of partially and completely annulated products, then product mixture was treated with iron chloride

(3.24 g, 20.0 mmol) for 12 h. A mixture of product and by-products was obtained that could not be purified.

Preparation of benzo[*b*]naphtho[1,2,3,4-*pqr*]perylene (BNP) According to general reaction procedure, 7-(diphenylmethylene)-7*H*-benzo[*de*]anthracene (**14**) (0.38 g, 1.0 mmol), iodine and methyloxirane were reacted to furnish the mixture of partially and completely annulated products, then product mixture was treated with iron chloride (3.24 g, 20.0 mmol) for 24 h. Product was obtained by re-crystallization from benzene to afford light-yellow solid. Yield: 0.26 g, 70%. Mp: 295 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 9.15 (d, *J* = 7.2 Hz, 1H), 9.05 (d, *J* = 9.2 Hz, 1H), 8.77-8.70 (m, 4H), 8.63 (d, *J* = 8.4 Hz, 1H), 8.59 (d, *J* = 8.0 Hz, 1H), 8.20 (d, *J* = 7.2 Hz, 1H), 8.06 (s, 1H), 8.04 (s, 1H), 7.96-7.92 (m, 1H), 7.78-7.74 (m, 1H), 7.64-7.61 (m, 1H), 7.45-7.35 (m, 2H). ¹³C NMR could not be recorded due to poor solubility of the derivative. MALDI-TOF MS: calculated for [C₃₀H₁₆]⁺: 376.1246, found: 376.1241.

Preparation of 2,7-dimethoxybenzo[*b*]naphtho[1,2,3,4-*pqr*]perylene (Met-BNP) According to general reaction procedure, 7-(bis(4-methoxyphenyl)methylene)-7*H*-benzo[*de*]anthracene (**15**) (0.44 g, 1.0 mmol), iodine and methyloxirane were reacted to furnish the mixture of partially and completely annulated products, then product mixture was treated with iron chloride (3.24 g, 20.0 mmol) for 6 h. Product was purified by column chromatography using dichloromethane as eluent to afford yellow solid. Yield: 0.37 g, 85%. Mp: 211 °C. ¹H NMR (DMSO-*D*, 400 MHz) δ: 9.17 (d, *J* = 9.2 Hz, 1H), 9.09-9.06 (m, 2H), 9.01 (d, *J* = 7.6 Hz, 1H), 8.97 (d, *J* = 9.2 Hz, 1H), 8.75 (d, *J* = 8.8 Hz, 1H), 8.57 (d, *J* = 2.0 Hz, 1H), 8.39-8.30 (m, 3H), 8.08-8.02 (m, 2H), 7.53 (dd, *J* = 11.6 Hz 2.4Hz, 1H), 7.41 (dd, *J* = 11.6 Hz 2.4Hz, 1H), 4.16 (s, 3H), 4.10 (s, 3H). ¹³C NMR (DMSO-*D*, 100 MHz) δ: 158.9, 158.3, 132.8, 132.5, 131.6, 131.3, 130.5, 130.2, 129.9, 129.3, 129.2, 127.6, 127.2, 125.3, 125.2, 125.1, 124.8, 123.4, 123.0, 122.7, 122.1, 121.4, 119.7, 117.1, 116.1, 106.5, 104.2, 56.0. MALDI-TOF MS: calculated for [C₃₂H₂₀O₂]⁺: 436.1457, found: 436.1455.

Preparation of 2,7-difluorobenzo[*b*]naphtho[1,2,3,4-*pqr*]perylene (Flu-BNP) According to general reaction procedure, 7-(bis(4-fluorophenyl)methylene)-7*H*-benzo[*de*]anthracene (**16**) (0.41 g, 1.0 mmol), iodine and methyloxirane were reacted to furnish a mixture of partially and completely annulated products, then product mixture

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was treated with iron chloride (3.24 g, 20.0 mmol) for 24 h. Product was obtained by re-crystallization from benzene to afford a light-yellow solid. Yield: 0.28 g, 69%. Mp: >300 °C. ¹H NMR (DMSO-D, 400 MHz) δ: 9.34 (d, *J* = 10.0 Hz, 1H), 9.02 (d, *J* = 9.6 Hz, 1H), 8.91-8.86 (m, 2H), 8.69 (d, *J* = 8.4 Hz, 1H), 7.95-7.91 (m, 2H), 7.68 (t, *J* = 8.8 Hz, 1H), 7.63-7.48 (m, 5H), 7.15 (t, *J* = 7.6 Hz, 1H). ¹³C NMR could not recorded due to poor solubility of the derivative. MALDI-TOF MS: calculated for [C₃₀H₁₄F₂]₂⁺: 824.2128, found: 824.2302.

Preparation of naphtho[2,1-*b*]phenanthro[4,3,2,1-*pqr*]perylene (NPP) According to general reaction procedure, 7-(di(naphthalen-2-yl)methylene)-7*H*-benzo[*de*]anthracene (**17**) (0.48 g, 1.0 mmol), iodine and methyloxirane were reacted to furnish a mixture of partially and completely annulated products, then product mixture was treated with iron chloride (3.24 g, 20.0 mmol) for 12 h. Product was obtained by re-crystallization in benzene to afford a light yellow solid. Yield: 0.34 g, 71%. Mp: 253 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 9.38 (d, *J* = 9.2 Hz, 1H), 9.32 (d, *J* = 8.0 Hz, 1H), 9.21 (t, *J* = 8.0 Hz, 2H), 9.03 (t, *J* = 7.2 Hz, 2H), 8.88 (d, *J* = 9.2, 1H), 8.80 (d, *J* = 8.8, 1H), 8.25 (d, *J* = 8.8, 2H), 8.17-7.96 (m, 6H), 7.82-7.68 (m, 4H). ¹³C NMR could not recorded due to poor solubility of the derivative. MALDI-TOF MS: calculated for [C₃₈H₂₀]⁺: 476.1559, found: 476.1570.

Preparation of 1,6,8-triphenyldibenzo[*f,pqr*]tetraphene (32) According to general reaction procedure, 7-(diphenylmethylene)-3,9-diphenyl-7*H*-benzo[*de*]anthracene (**29**) (0.53 g, 1.0 mmol), iodine and methyloxirane were reacted to furnish the partially annulated product as light-yellow solid. Yield: 0.41 g, 78 %. Mp: 245 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 9.00 (t, *J* = 7.6 Hz, 2H), 8.80 (d, *J* = 8.0 Hz, 1H), 8.69 (d, *J* = 8.4 Hz, 1H), 8.36 (d, *J* = 9.6 Hz, 1H), 8.30 (s, 1H), 7.95-7.92 (m, 2H), 7.80-7.53 (m, 13H), 7.37-7.31 (m, 3H), 7.14-7.11 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ: 144.5, 143.8, 143.5, 140.7, 140.2, 138.5, 134.5, 133.7, 132.7, 132.5, 131.1, 130.4, 130.2, 129.8, 129.7, 129.5, 128.9, 128.7, 128.5, 128.4, 128.3, 127.8, 127.3, 127.1, 127.0, 126.4, 126.3, 125.4, 124.9, 124.1, 119.4. MALDI-TOF MS: calculated for [C₄₂H₂₆]⁺: 530.2029, found: 530.2029.

Preparation of 11-methoxy-8-(4-methoxyphenyl)-1,6-diphenyldibenzo[*f,pqr*]tetraphene (33) According to general reaction procedure, 7-(bis(4-methoxyphenyl)methylene)-3,9-diphenyl-7*H*-benzo[*de*]anthracene (**30**) (0.59 g, 1.0

mmol), iodine and methyloxirane were reacted to furnish the partially annulated product as light-yellow solid. Yield: 0.45 g, 76%. Mp: 300 °C. ^1H NMR (CDCl_3 , 400 MHz) δ : 8.87 (d, $J = 8.8$ Hz, 1H), 8.79 (d, $J = 8.4$ Hz, 1H), 8.68 (d, $J = 7.6$ Hz, 1H), 8.33-8.28 (m, 2H), 8.21 (d, $J = 2.0$ Hz, 1H), 7.95-7.92 (m, 2H), 7.72 (dd, $J = 13.0$ Hz, 2.0 Hz, 1H), 7.69-7.52 (m, 7H), 7.39-7.33 (m, 4H), 7.22-7.19 (m, 4H), 4.09 (s, 3H), 3.99 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 159.3, 158.0, 141.2, 140.8, 138.9, 138.0, 135.8, 135.3, 132.7, 131.7, 131.0, 130.5, 130.2, 129.6, 129.5, 128.4, 127.6, 127.5, 127.3, 127.1, 125.9, 129.7, 125.4, 124.7, 123.9, 121.9, 119.4, 117.8, 115.1, 102.5, 55.5. MALDI-TOF MS: calculated for $[\text{C}_{44}\text{H}_{30}\text{O}_2]^+$: 590.2240, found: 590.2226.

Preparation of 18-phenylbenzo[*b*]indeno[1,2,3-*lm*]naphtho[1,2,3,4-*pqr*]perylene (Ph-BINP) According to general reaction procedure, 1,6,8-triphenyldibenzo[*f,pqr*]tetraphene (**32**) (0.53 g, 1.0 mmol) and iron chloride (4.86 g, 30.0 mmol) were reacted for 36 h. The product was purified by column chromatography using dcm/hexane eluent to afford a yellow-orange solid. Yield: 0.42 g, 80%. Mp: >300 °C. ^1H NMR (CDCl_3 , 400 MHz) δ : 9.18 (d, $J = 8.4$ Hz, 1H), 9.08 (s, $J = 9.6$ Hz, 1H), 9.00 (d, $J = 8.4$ Hz, 1H), 8.80 (d, $J = 8.0$ Hz, 1H), 8.49 (d, $J = 8.4$ Hz, 1H), 8.04-7.75 (m, 7H), 7.64-7.45 (m, 8H), 7.19 (t, $J = 8.0$ Hz, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 144.7, 138.7, 135.1, 134.3, 131.6, 131.0, 130.9, 130.8, 130.5, 130.3, 129.8, 129.6, 129.5, 129.4, 129.2, 128.0, 127.8, 127.2, 127.0, 126.4, 126.2, 125.4, 125.0, 123.2, 122.1, 121.9, 121.7, 121.6, 120.8, 120.1, 115.9. MALDI-TOF MS: calculated for $[\text{C}_{42}\text{H}_{22}]^+$: 526.1716, found: 526.1717.

Preparation of 2,7-dimethoxy-9,14-diphenylbenzo[*b*]naphtho[1,2,3,4-*pqr*]perylene (Met-PhBNP) According to general reaction procedure, 11-methoxy-8-(4-methoxyphenyl)-1,6-diphenyldibenzo[*f,pqr*]tetraphene (**33**) (0.59 g, 1.0 mmol) and iron chloride (3.24g, 20.0 mmol) were reacted for 4 h. The product was purified by column chromatography using dcm/hexane as eluent to afford an orange solid. Yield: 0.48 g, 81%. Mp: 295 °C. ^1H NMR (CDCl_3 , 400 MHz) δ : 9.02 (d, $J = 9.2$ Hz, 1H), 8.78-8.75 (m, 3H), 8.56 (d, $J = 9.2$ Hz, 1H), 8.30 (d, $J = 2.8$ Hz, 1H), 8.26 (d, $J = 9.6$ Hz, 1H), 7.88-7.84 (m, 2H), 7.71-7.42 (m, 12H), 7.05 (dd, $J = 11.6$ Hz 2.8Hz, 1H), 4.13 (s, 3H), 3.33 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 156.4, 145.0, 141.1, 138.8, 138.2, 132.3, 131.3, 131.1, 130.7, 130.4, 130.1, 130.0, 129.8, 129.6, 129.2, 128.9, 128.4, 127.8, 127.6, 127.3, 127.1, 126.7, 125.8, 125.2, 125.0, 124.7, 123.2, 122.3, 122.0, 121.6, 120.6, 120.2, 116.2,

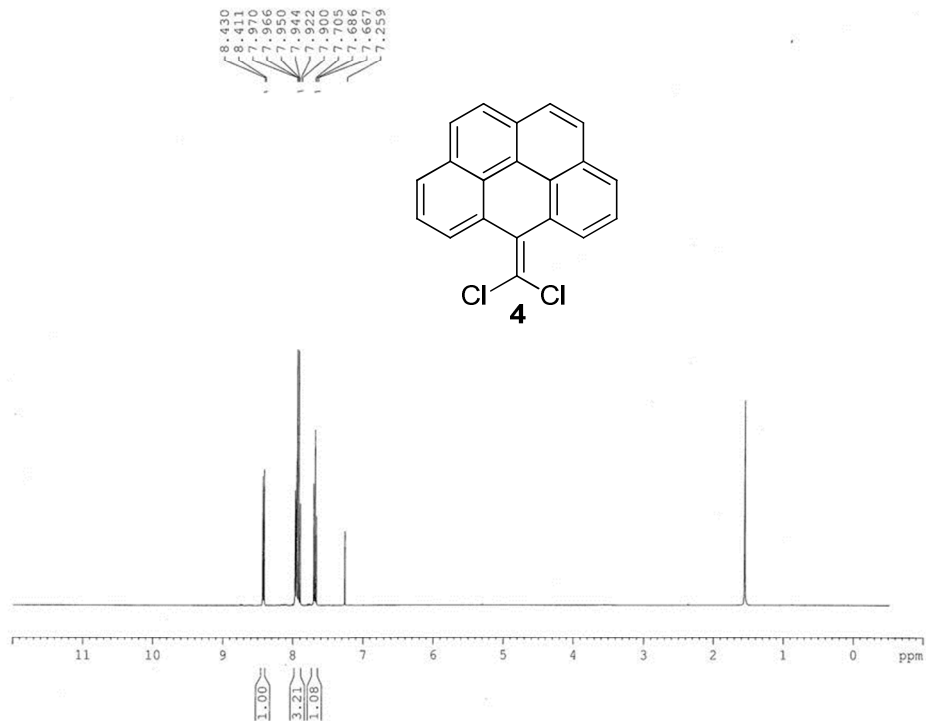
111.4, 103.6, 55.5. MALDI-TOF MS: calculated for $[C_{44}H_{28}O_2]^+$: 588.2083, found: 588.2099.

Preparation of 5,10-dimethyltribenzo[*a,ghi,k*]fluorantheno[2,3,4-*cde*]perylene (Met-BFP) According to general reaction procedure, 11-Methoxy-8-(4-methoxyphenyl)-1,6-diphenyldibenzo[*f,pqr*]tetraphene (**33**) (0.59 g, 1.0 mmol) and iron chloride (4.86 g, 30.0 mmol) were reacted for 12 h. Product was purified by column chromatography using dcm/hexane eluent to afford an orange solid. Yield: 0.48 g, 82%. Mp: 180 °C. 1H NMR ($CDCl_3$, 400 MHz) δ : 9.95 (s, 1H), 9.71 (d, $J = 8.0$ Hz, 1H), 9.44 (s, 1H), 9.31 (s, 1H), 9.18-9.08 (m, 4H), 8.85 (s, 1H), 8.63 (d, $J = 7.2$, 1H), 8.55 (d, $J = 6.4$, 1H), 8.29 (d, $J = 6.8$, 1H), 7.97 (d, $J = 8.4$, 1H), 7.88-7.81 (m, 2H), 7.63-7.59 (m, 3H), 4.34 (s, 3H), 4.26 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 157.3, 132.2, 130.4, 129.8, 129.4, 128.9, 128.4, 127.1, 126.3, 123.4, 121.8, 121.3, 119.7, 115.2, 102.8, 55.9, 55.3. MALDI-TOF MS: calculated for $[C_{44}H_{24}O_2]^+$: 584.1770, found: 584.1777.

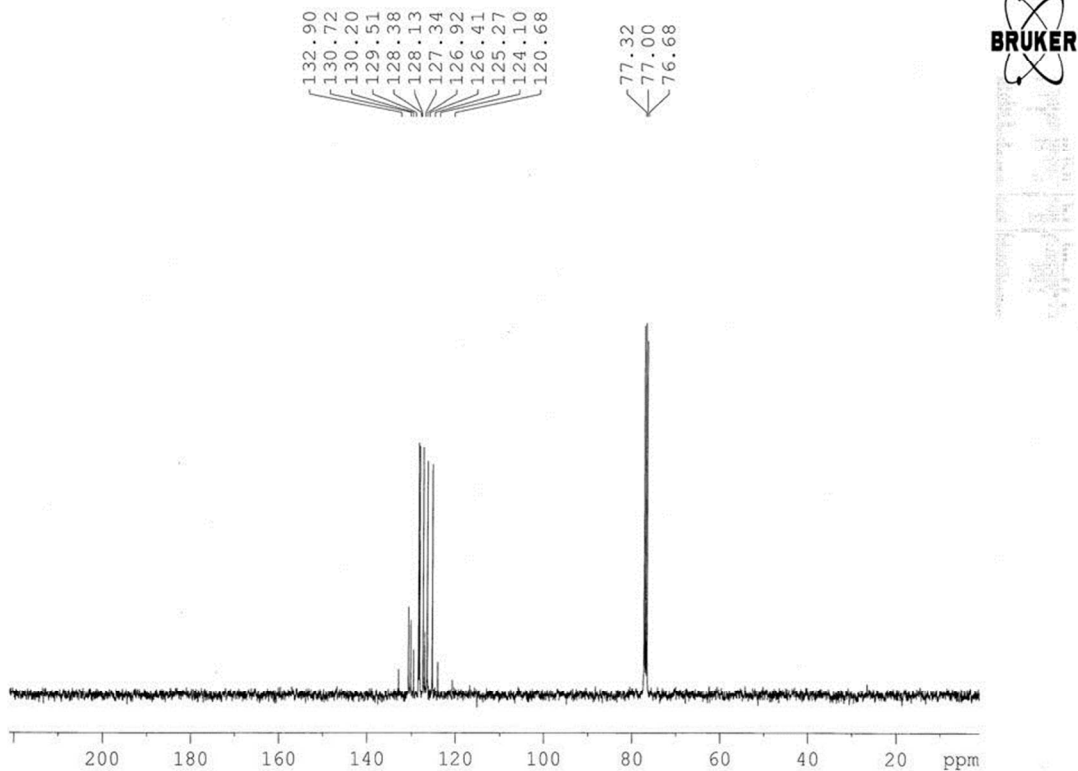
Preparation of 5,10-dimethoxydibenzo[*a,ghi*]benzo[8,9]fluorantheno[2,3,4-*cde*]naphtho[2,1-*k*]perylene (Met-BBFNP) According to general reaction procedure, 7-(bis(4-methoxyphenyl)methylene)-3,9-di(naphthalen-2-yl)-7*H*-benzo[*de*]anthracene (**31**) (0.69 g, 1.0 mmol), iodine and methyloxirane were reacted to furnish the partially annulated product (**34**) along with other fused derivatives, then product mixture was treated with iron chloride (4.86 g, 30.0 mmol) for 24 h. Product was found to be weakly soluble to characterize by NMR spectroscopy, therefore it could only characterize by mass spectroscopy. Fab HRMS: calculated for $[C_{52}H_{28}O_2]^+$: 684.2089, found: 684.2097.

4. NMR spectra of the derivatives

pyreneketo2cl A

**Figure S1.** ¹H NMR spectrum of 6-(dichlorolmethylene)-6H-benzo[cd]pyrene (4)

pyreneketo2cl Ac13

**Figure S2.** ¹³C NMR spectrum of 6-(dichlorolmethylene)-6H-benzo[cd]pyrene (4)

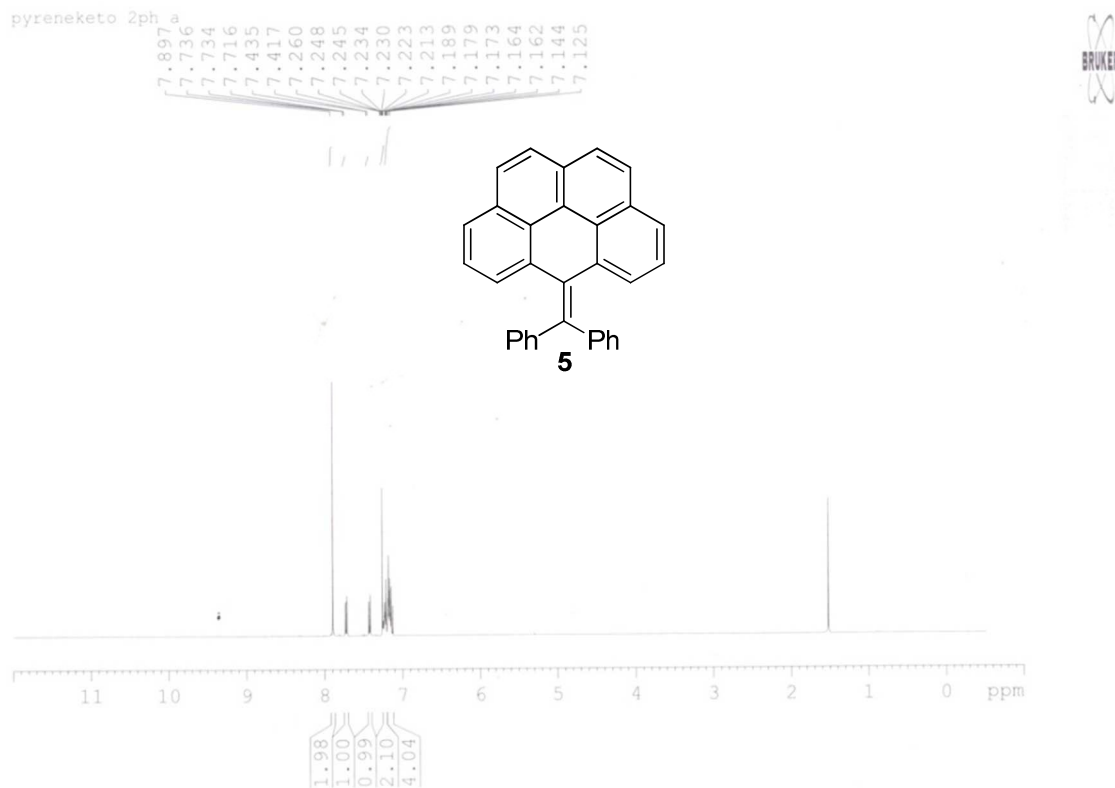


Figure S3. ^1H NMR spectrum of 6-(diphenylmethylene)-6*H*-benzo[*cd*]pyrene (**5**)

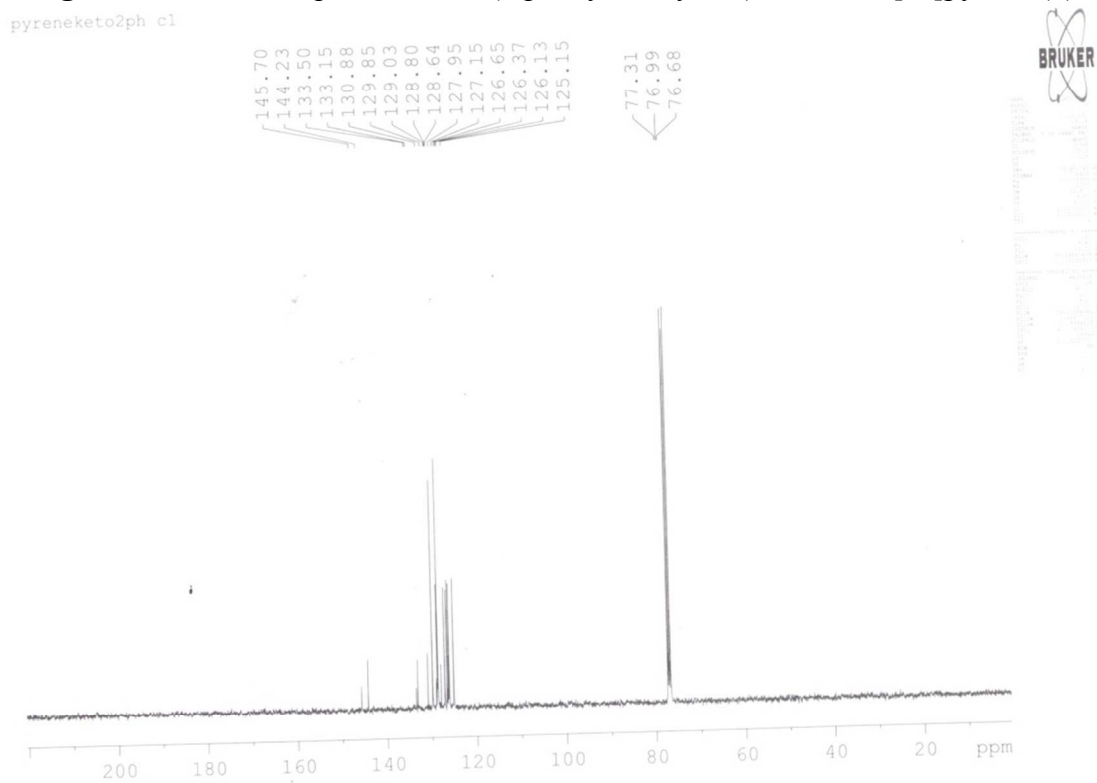


Figure S4. ^{13}C NMR spectrum of 6-(diphenylmethylene)-6*H*-benzo[*cd*]pyrene (**5**)

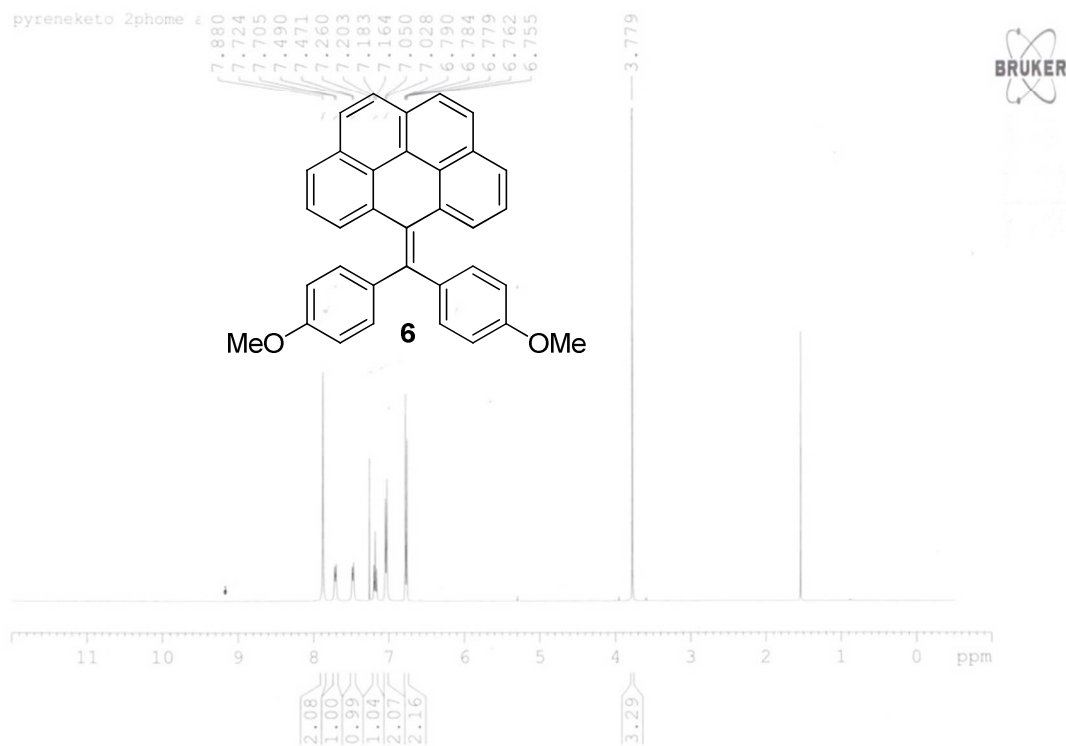


Figure S5. ¹H NMR spectrum of 6-(bis(4-methoxyphenyl)methylene)-6H-benzo[*cd*]pyrene (**6**)

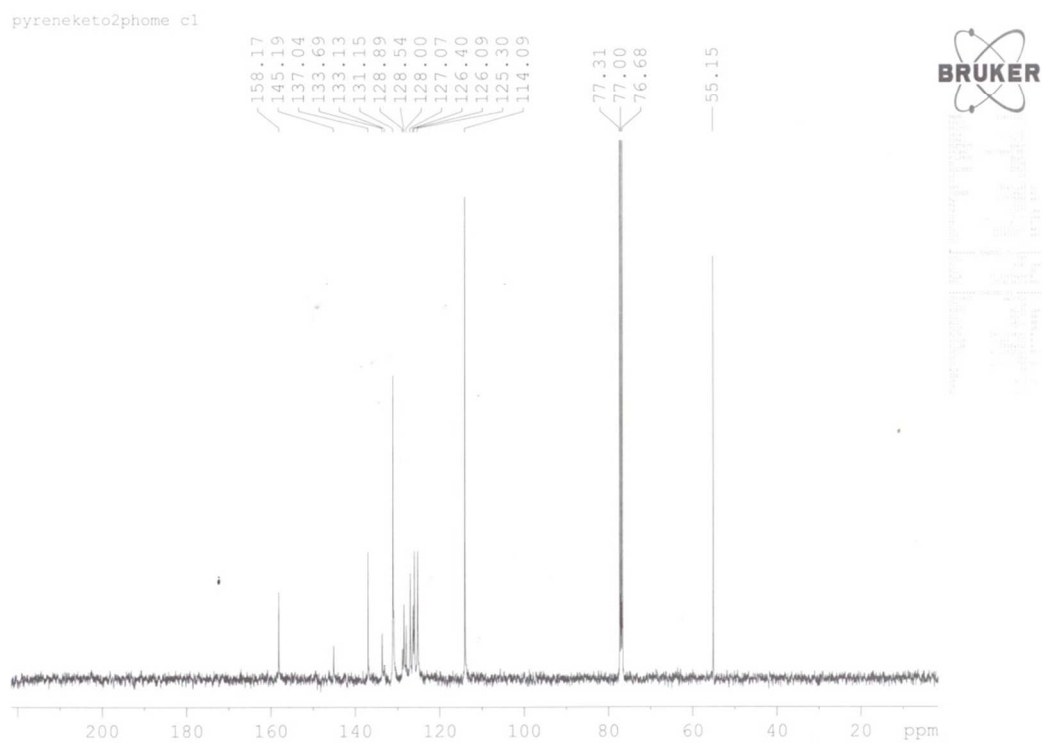


Figure S6. ¹³C NMR spectrum of 6-(bis(4-methoxyphenyl)methylene)-6H-benzo[*cd*]pyrene (**6**)

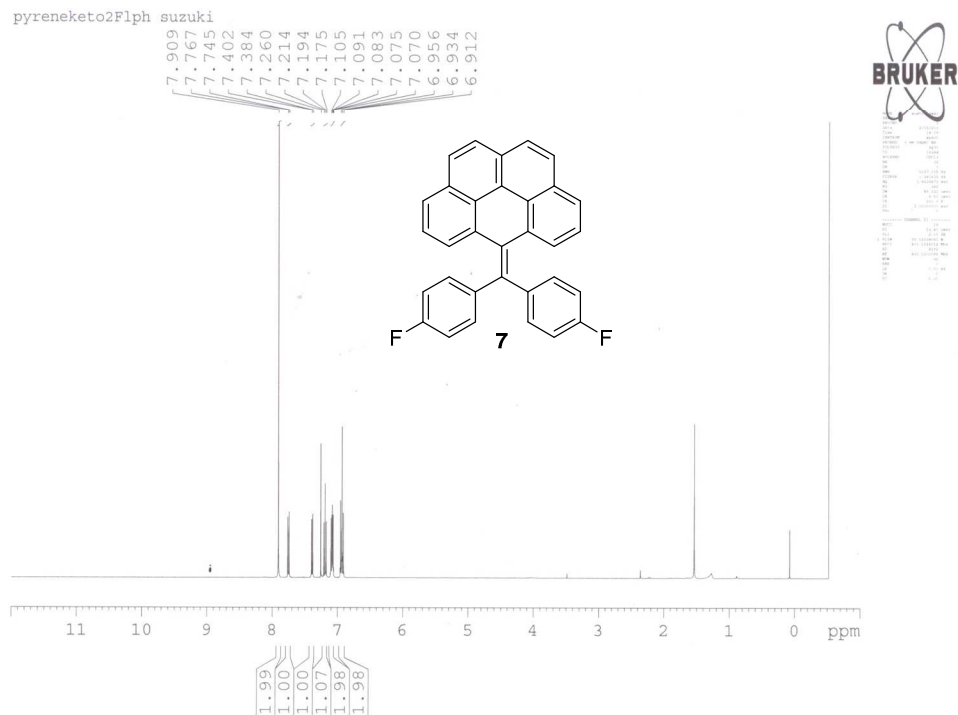


Figure S7. ^1H NMR spectrum of 6-(bis(4-fluorophenyl)methylene)-6*H*-benzo[*cd*]pyrene (7)

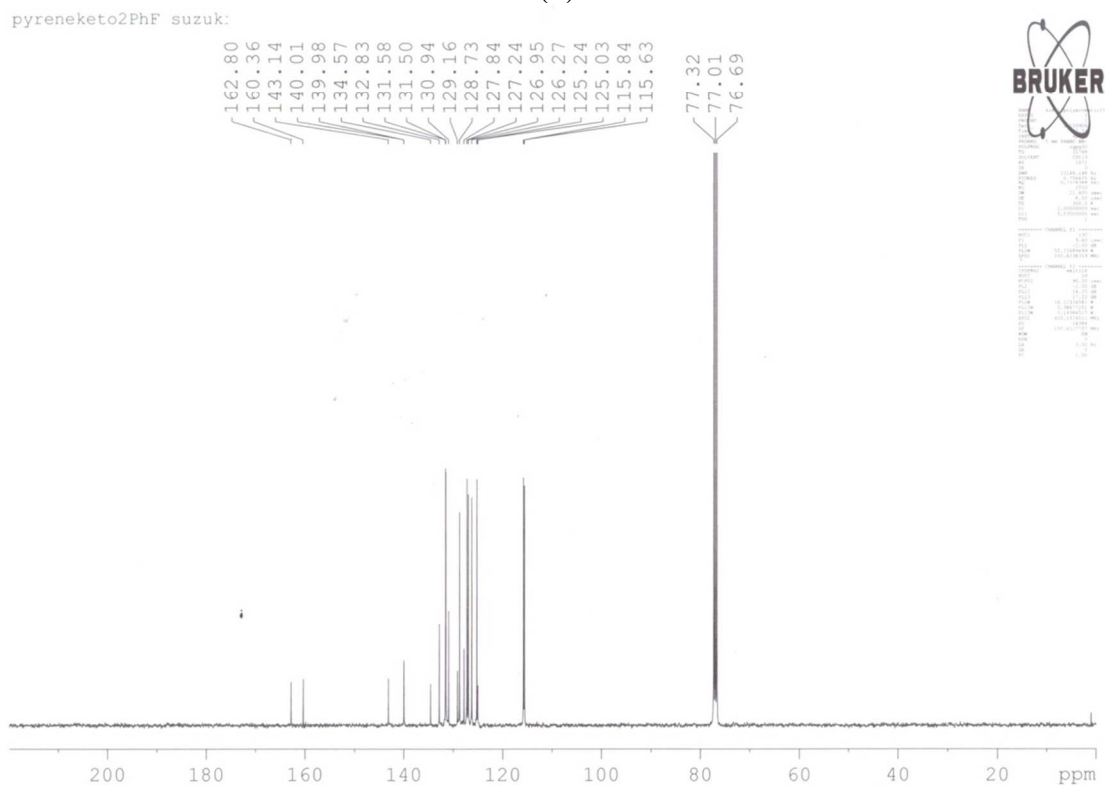


Figure S8. ^{13}C NMR spectrum of 6-(bis(4-fluorophenyl)methylene)-6*H*-benzo[*cd*]pyrene (7)

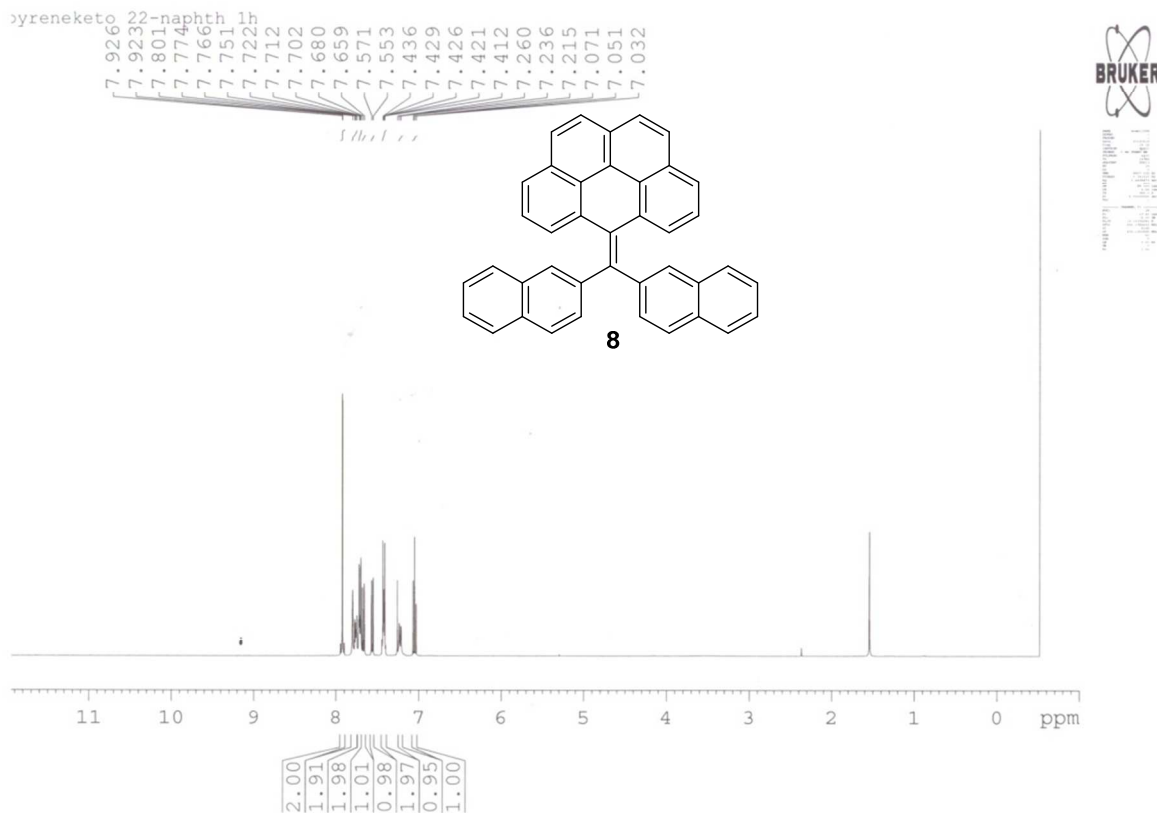


Figure S9. ^1H NMR spectrum of 6-(di(naphthalen-2-yl)methylene)-6*H*-benzo[*cd*]pyrene (**8**)

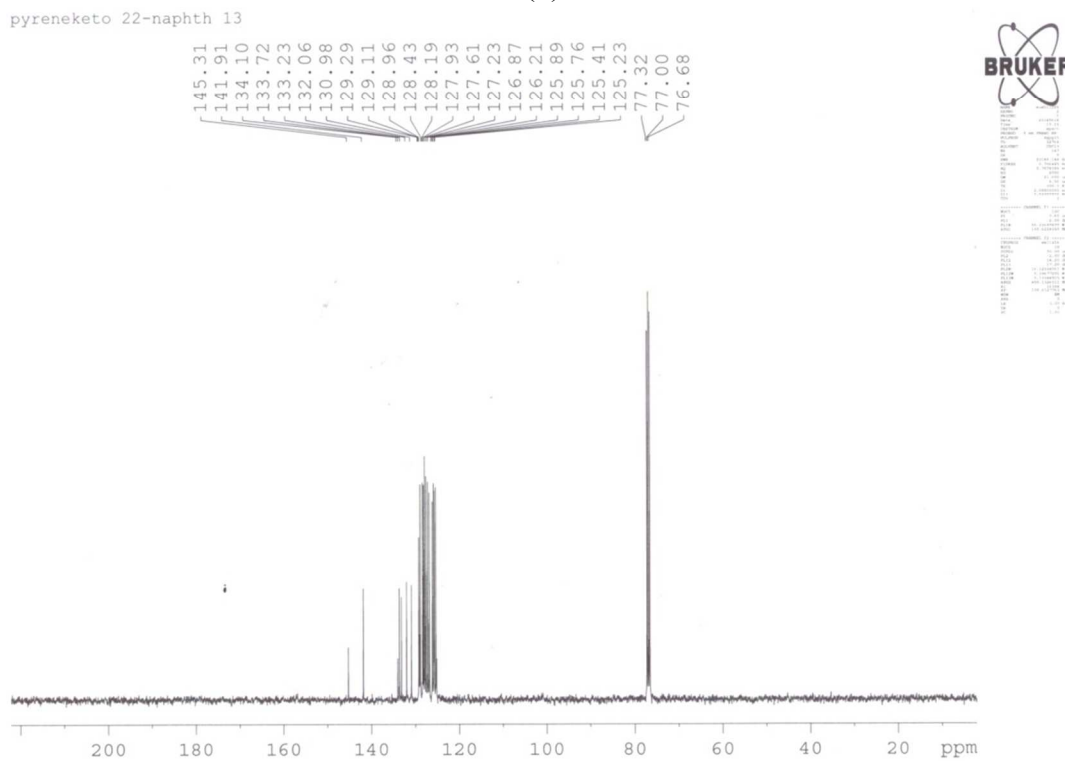


Figure S10. ^{13}C NMR spectrum of 6-(di(naphthalen-2-yl)methylene)-6*H*-benzo[*cd*]pyrene (**8**)

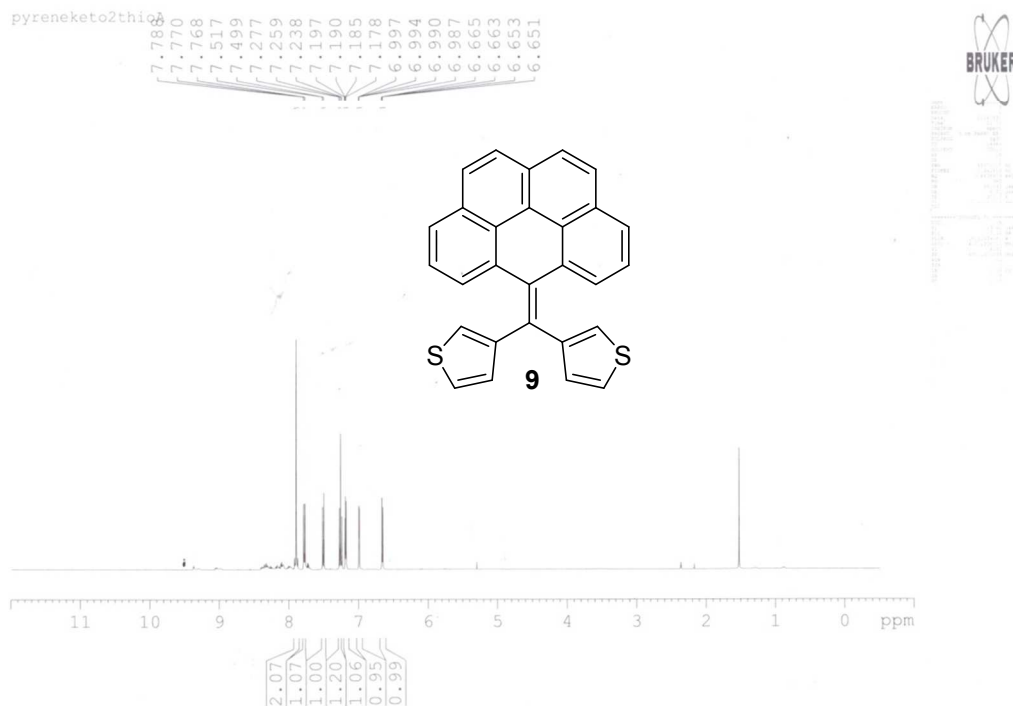


Figure S11. ^1H NMR spectrum of 3,3'-((6*H*-benzo[*cd*]pyren-6-ylidene)methylene)dithiophene (**9**)

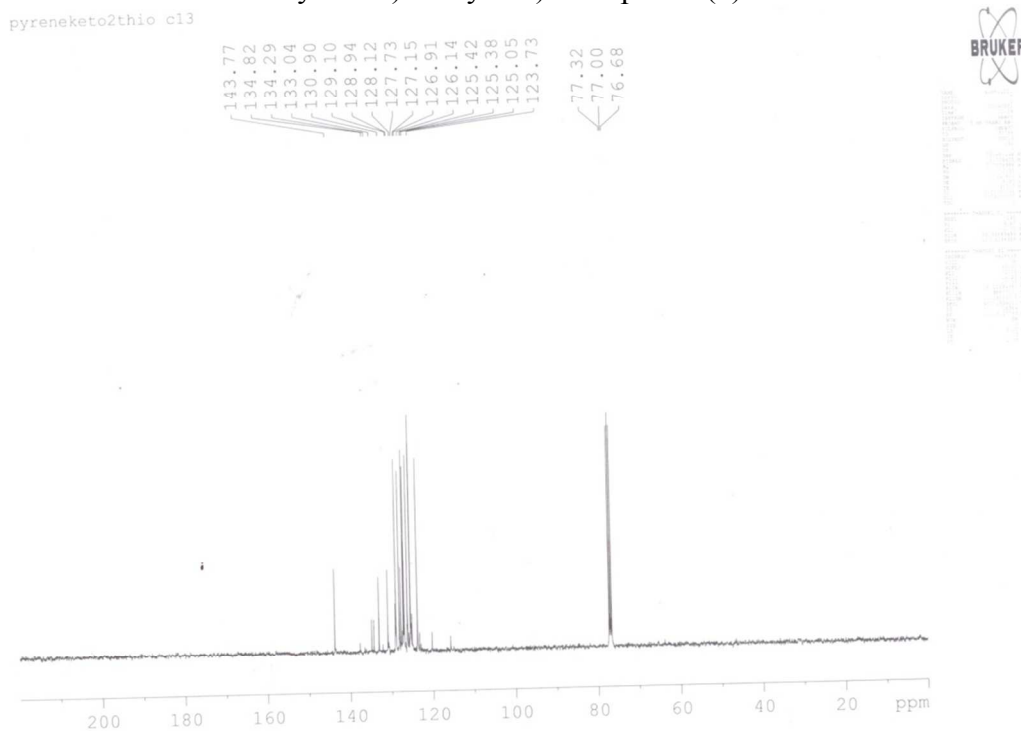
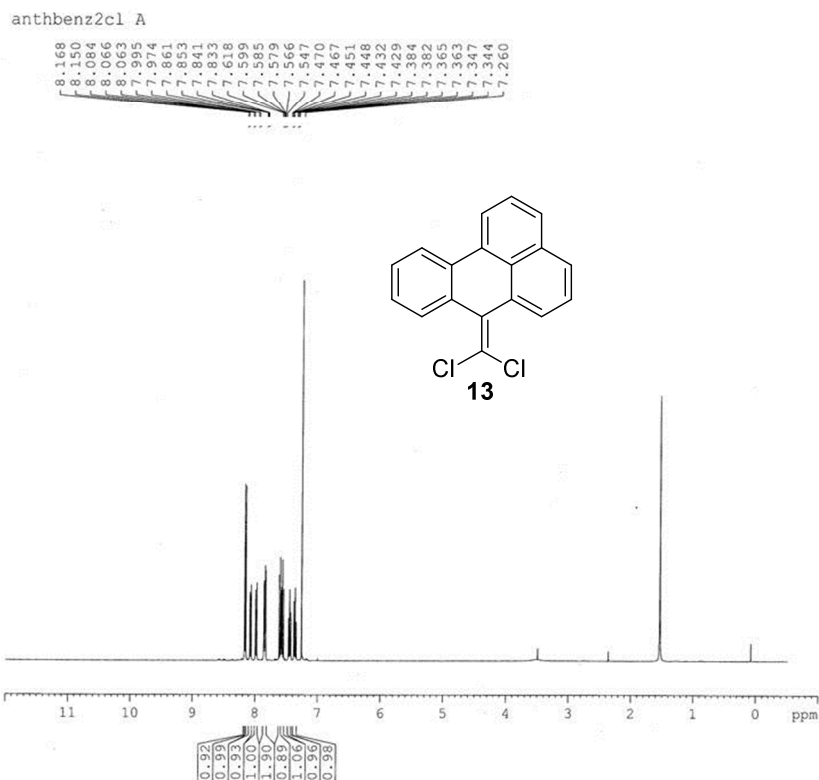
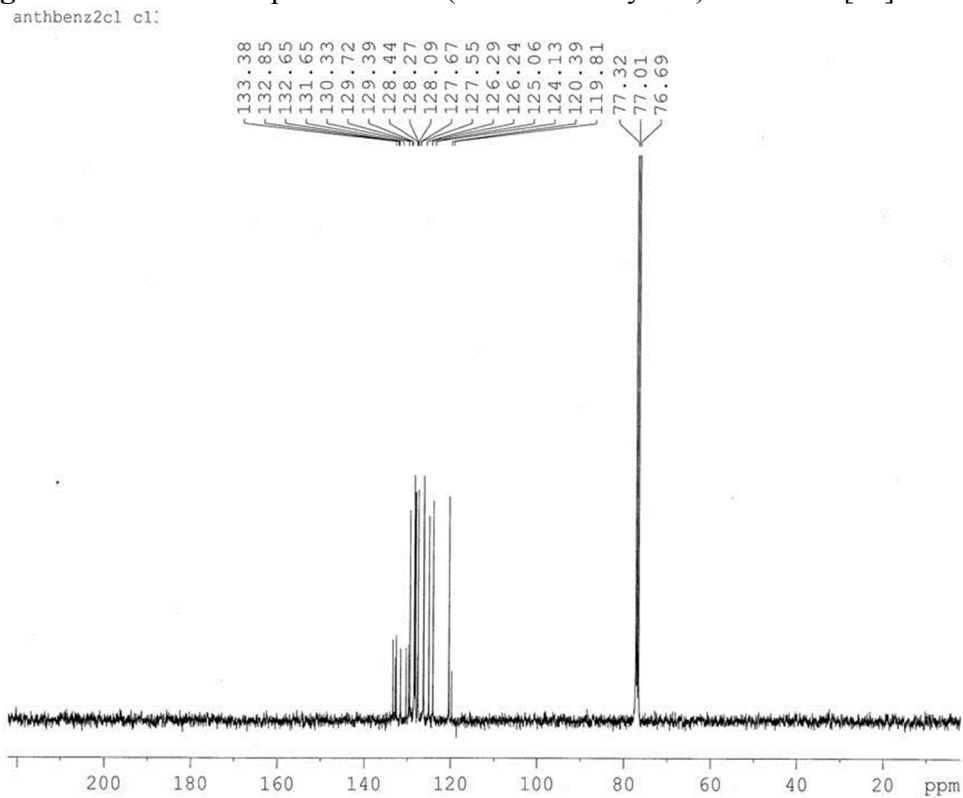


Figure S12. ^{13}C NMR spectrum of 3,3'-((6*H*-benzo[*cd*]pyren-6-ylidene)methylene)dithiophene (**9**)



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Figure S13. ^1H NMR spectrum of 7-(dichloromethylene)-7H-benzo[de]anthracene (**13**)



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Figure S14. ^{13}C NMR spectrum of 7-(dichloromethylene)-7H-benzo[de]anthracene (**13**)

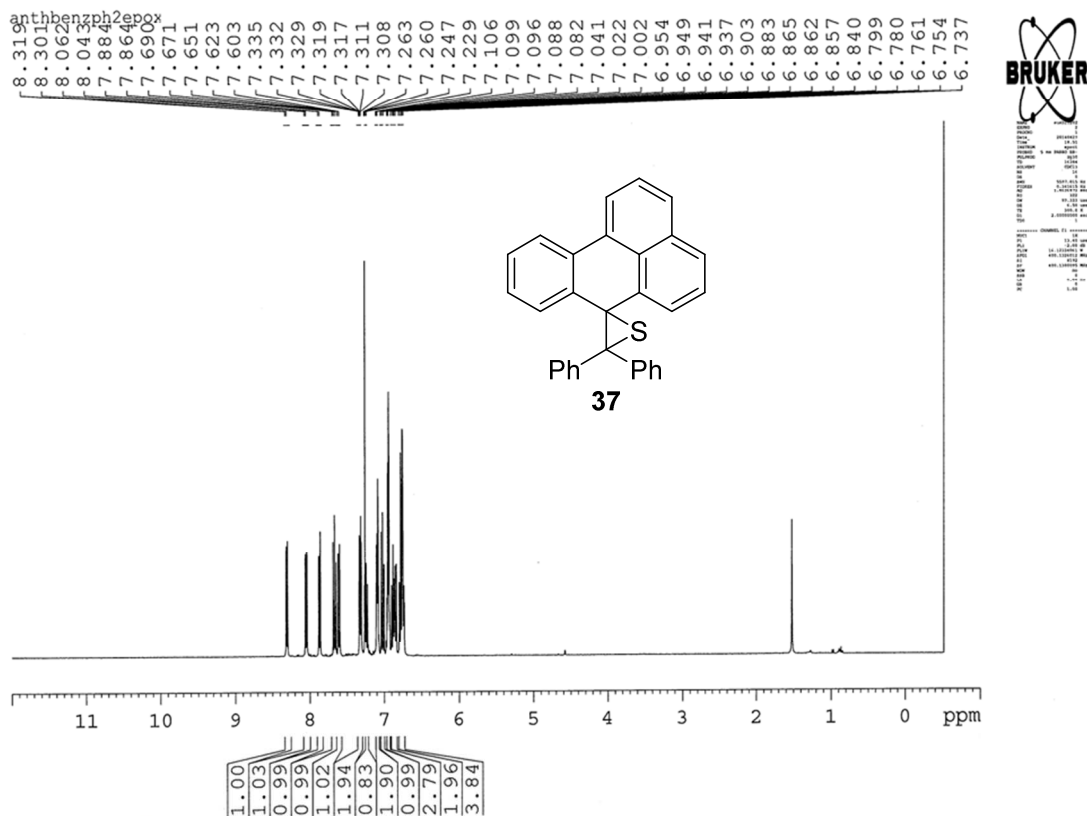


Figure S15. ^1H NMR spectrum of 3',3'-diphenylspiro[benzo[*de*]anthracene-7,2'-thiirane] (**37**)

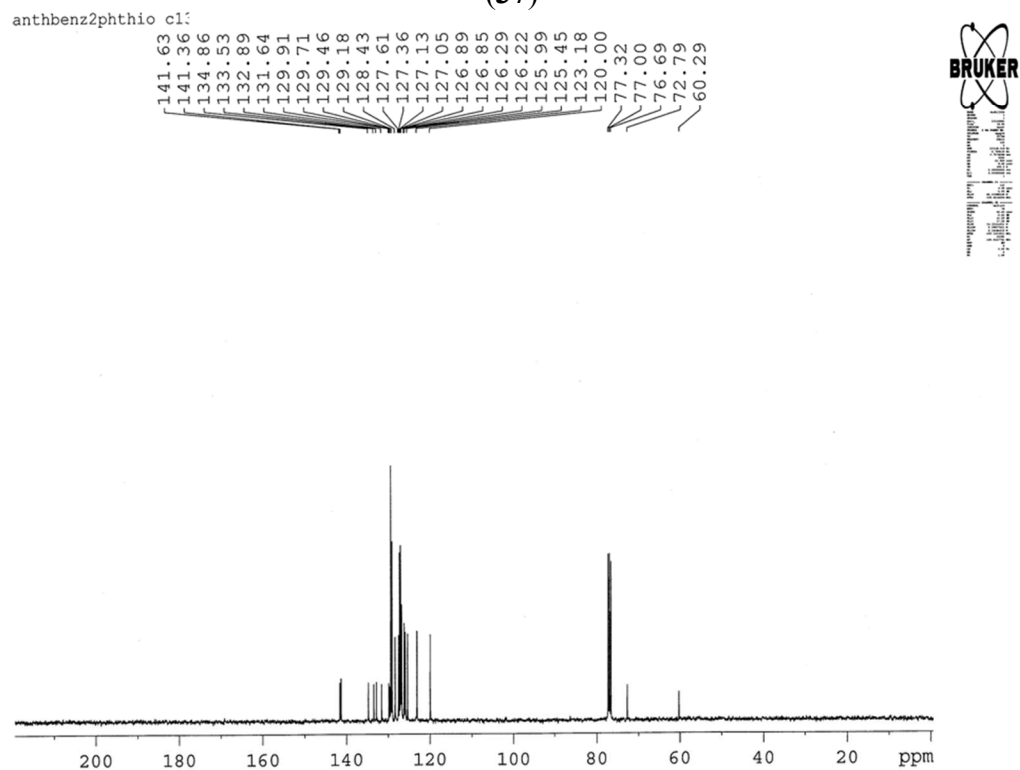


Figure S16. ^{13}C NMR spectrum of 3',3'-diphenylspiro[benzo[*de*]anthracene-7,2'-thiirane] (**37**)

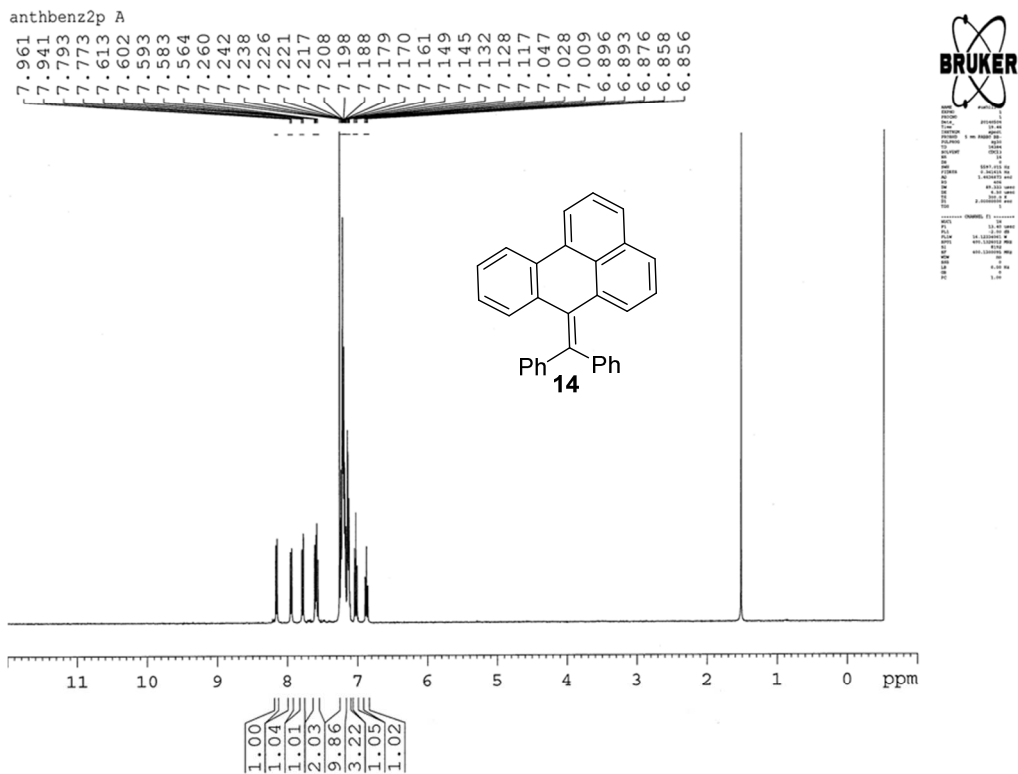


Figure S17. ^1H NMR spectrum of 7-(diphenylmethylene)-7*H*-benzo[*de*]anthracene (**14**)

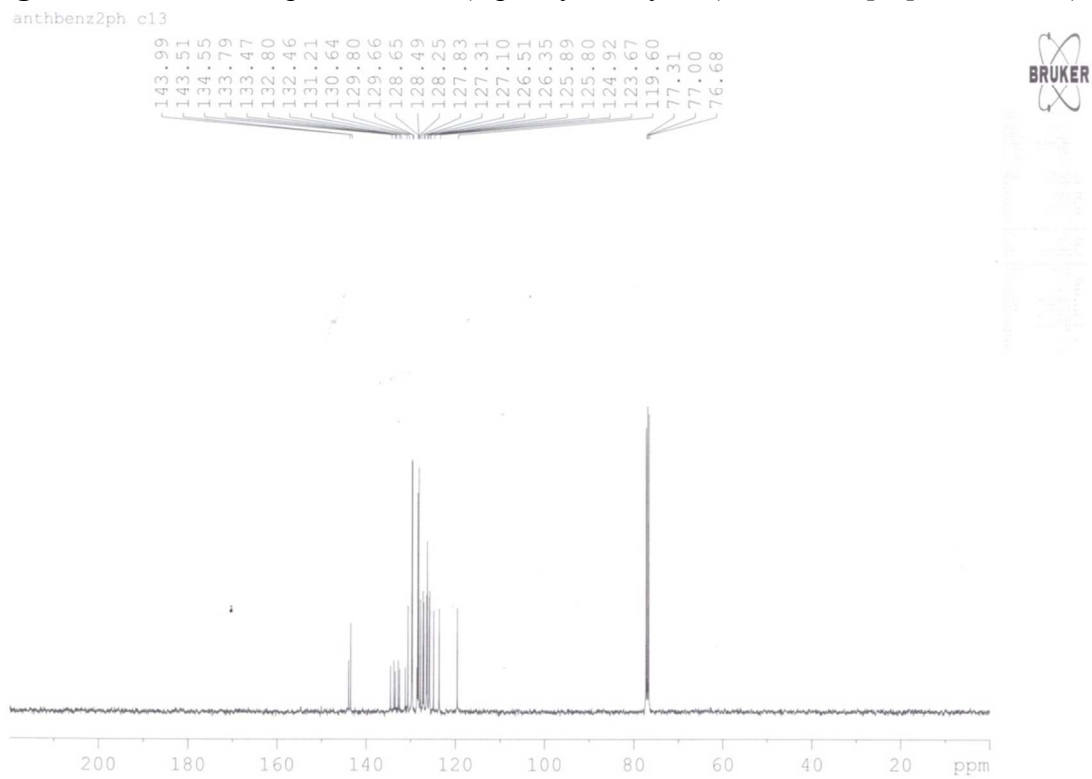


Figure S18. ^{13}C NMR spectrum of 7-(diphenylmethylene)-7*H*-benzo[*de*]anthracene (**14**)

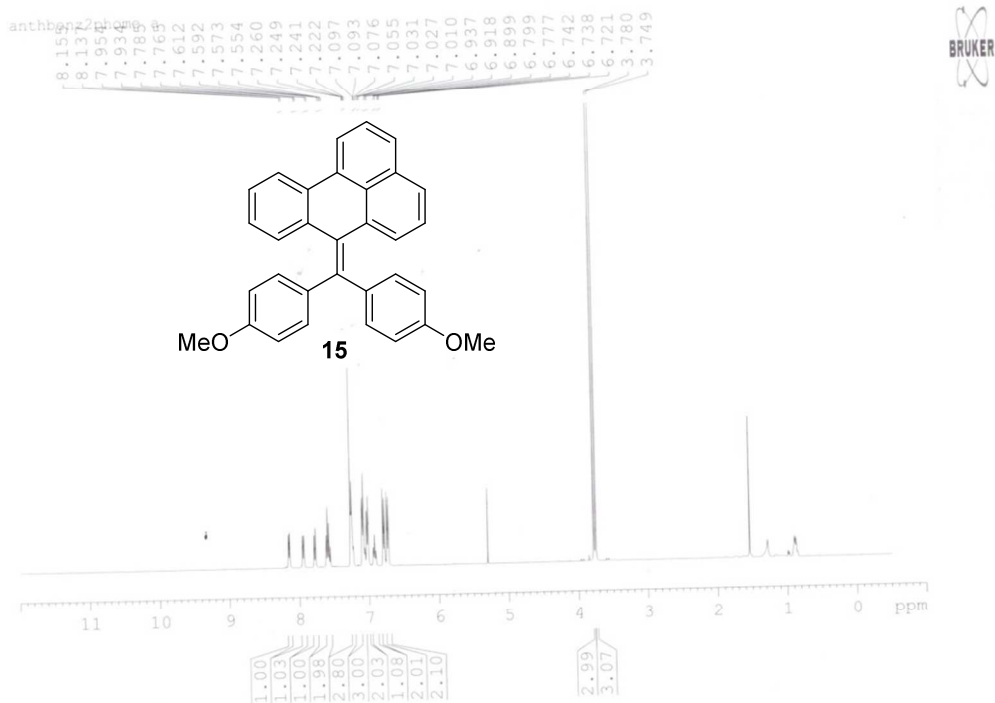


Figure S19. ¹H NMR spectrum of 7-(bis(4-methoxyphenyl)methylene)-7H-benzo[de]anthracene (**15**)

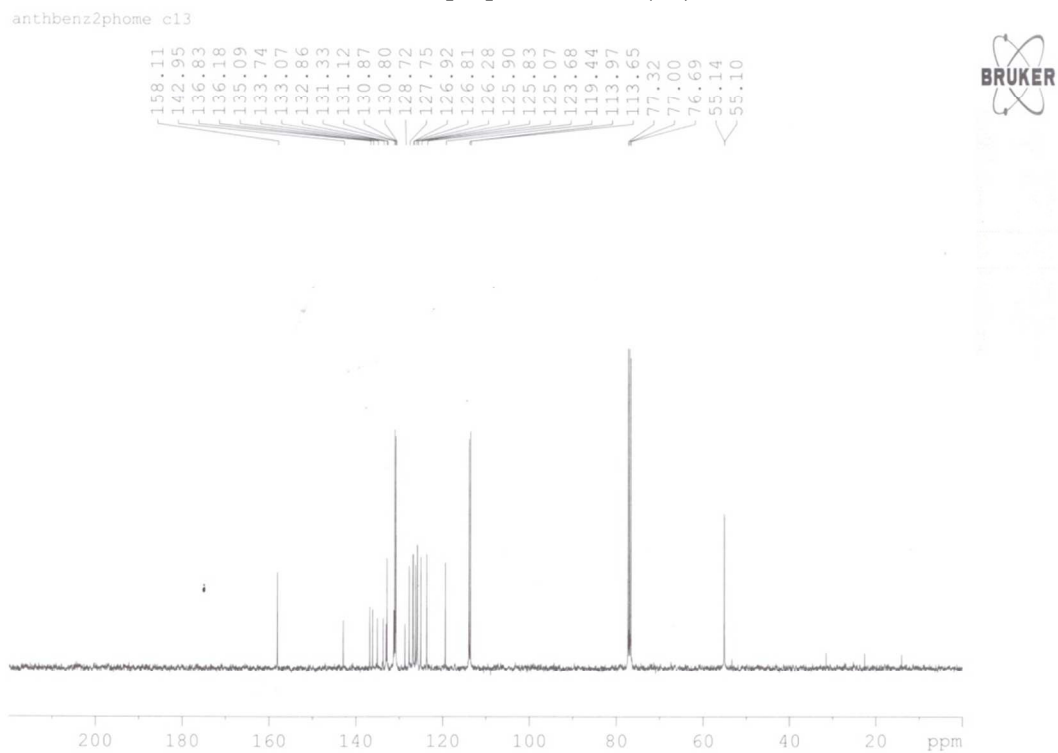


Figure S20. ¹³C NMR spectrum of 7-(bis(4-methoxyphenyl)methylene)-7H-benzo[de]anthracene (**15**)

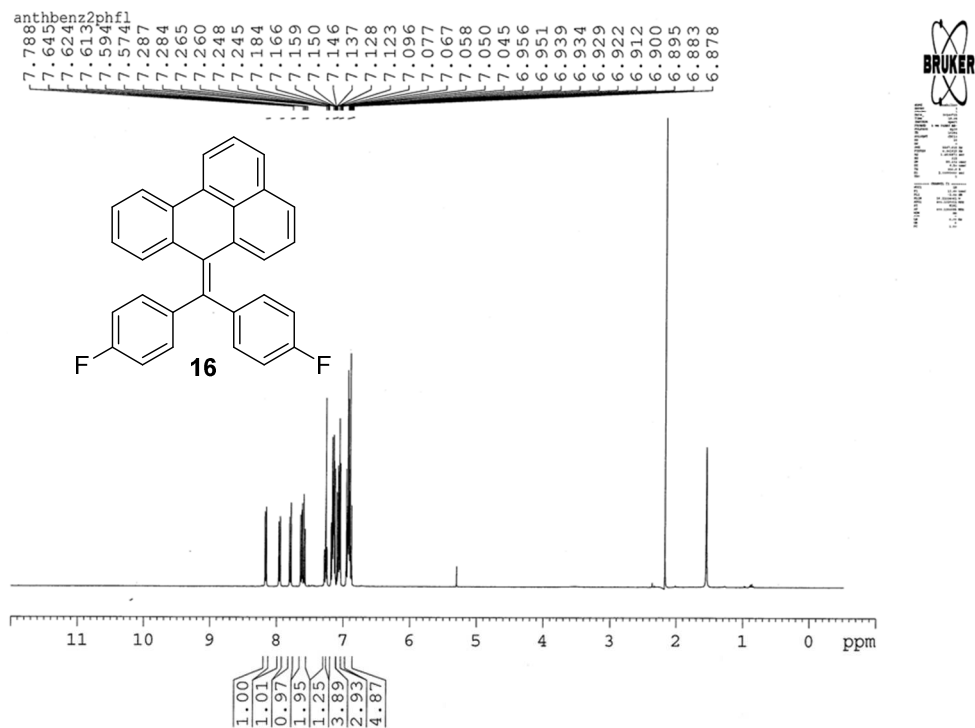


Figure S21. ^1H NMR spectrum of 7-(bis(4-fluorophenyl)methylene)-7H-benzo[de]anthracene (**16**)

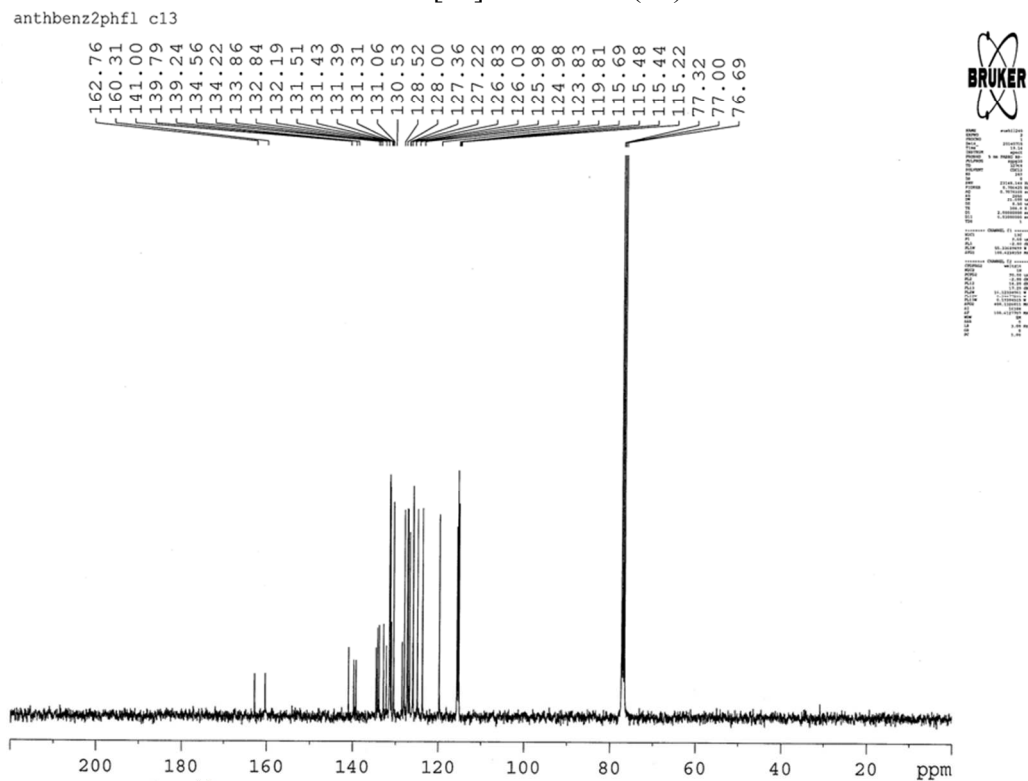


Figure S22. ^{13}C NMR spectrum of 7-(bis(4-fluorophenyl)methylene)-7H-benzo[de]anthracene (**16**)

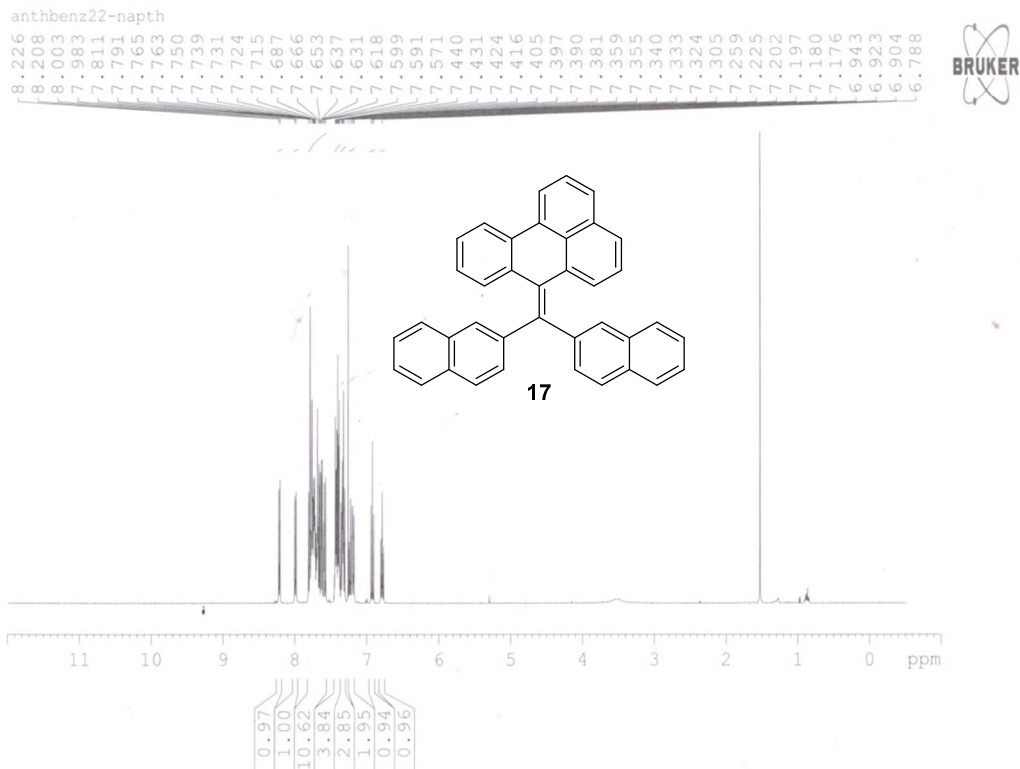


Figure S23. ^1H NMR spectrum of 7-(di(naphthalen-2-yl)methylene)-7H-benzo[de]anthracene (**17**)

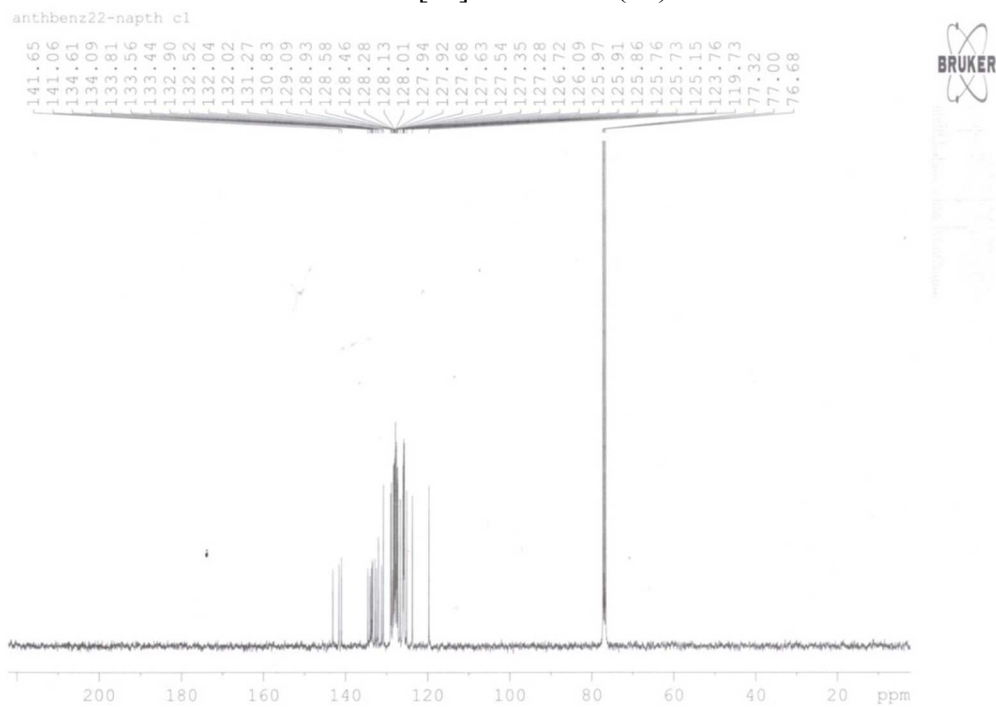


Figure S24. ^{13}C NMR spectrum of 7-(di(naphthalen-2-yl)methylene)-7H-benzo[de]anthracene (**17**)

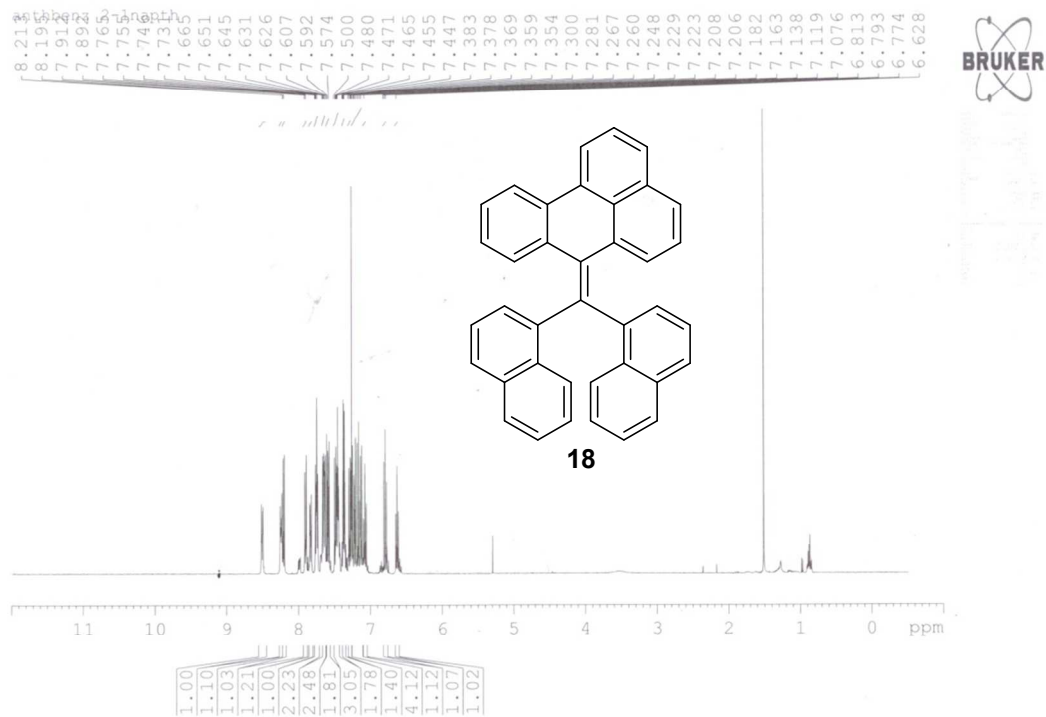


Figure S25. ¹H NMR spectrum of 7-(di(naphthalen-1-yl)methylene)-7H-benzo[de]anthracene (**18**)

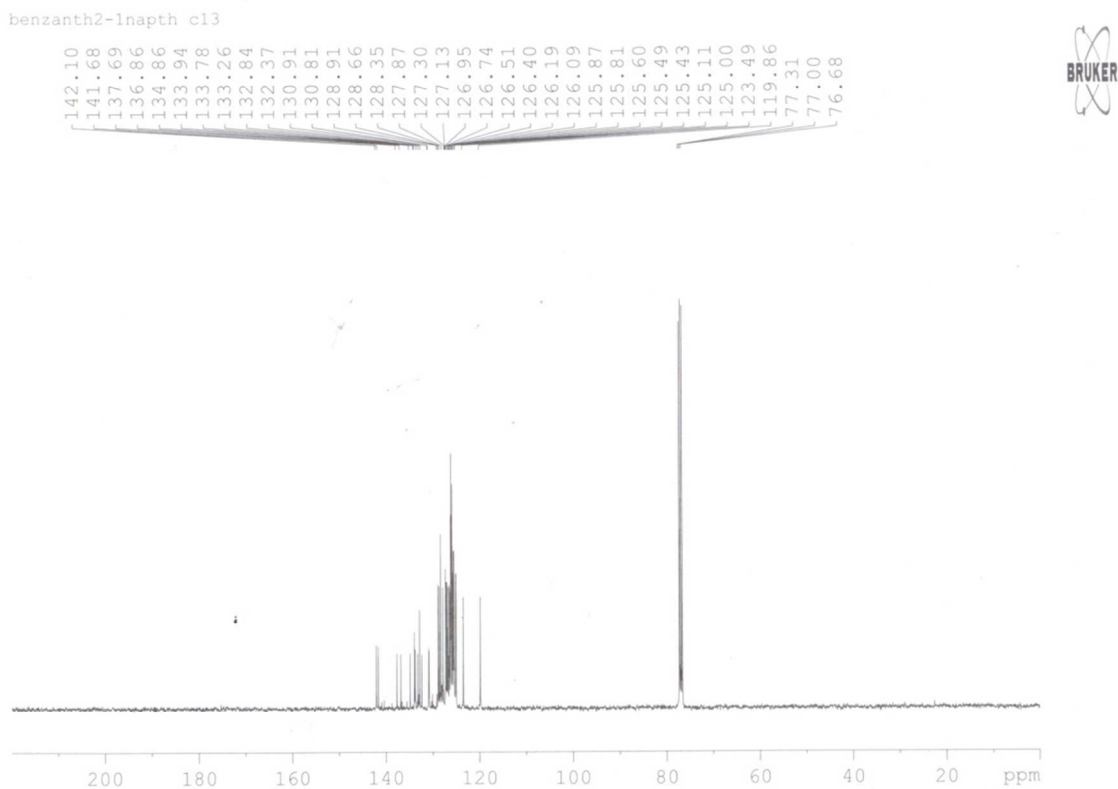


Figure S26. ¹³C NMR spectrum of 7-(di(naphthalen-1-yl)methylene)-7H-benzo[de]anthracene (**18**)

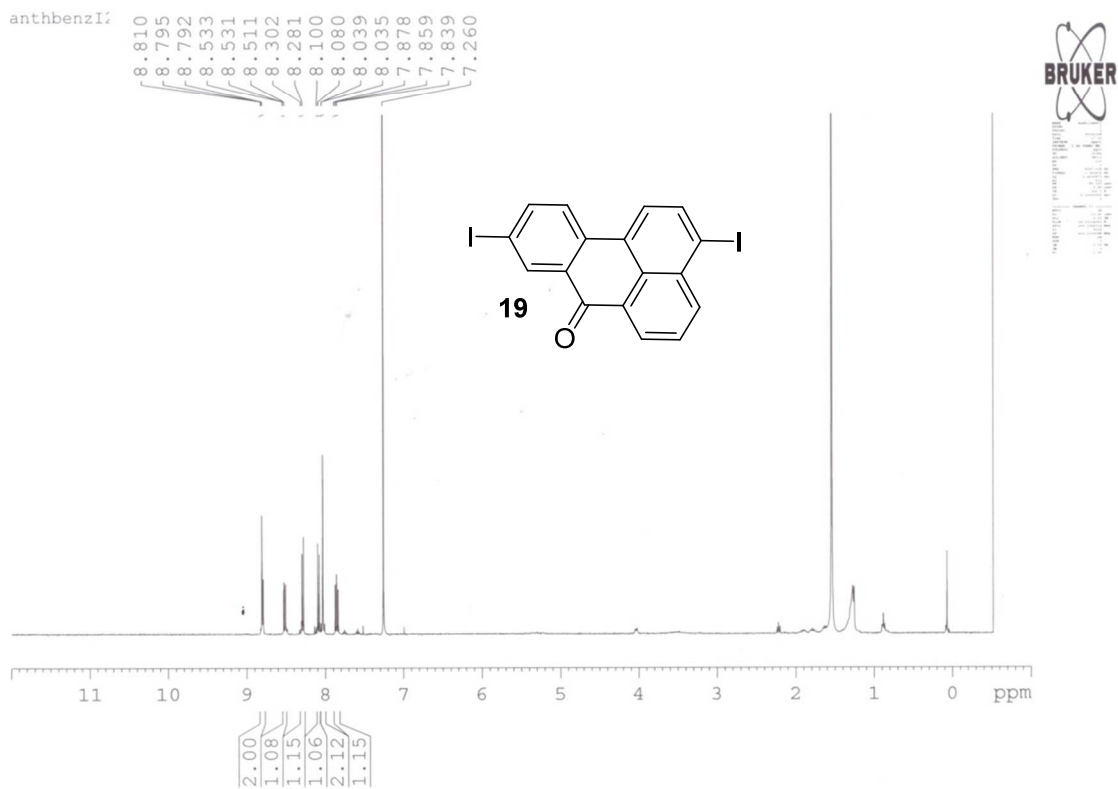


Figure S27. ^1H NMR spectrum of 3,9-diiodo-7*H*-benzo[*de*]anthracen-7-one (**19**)

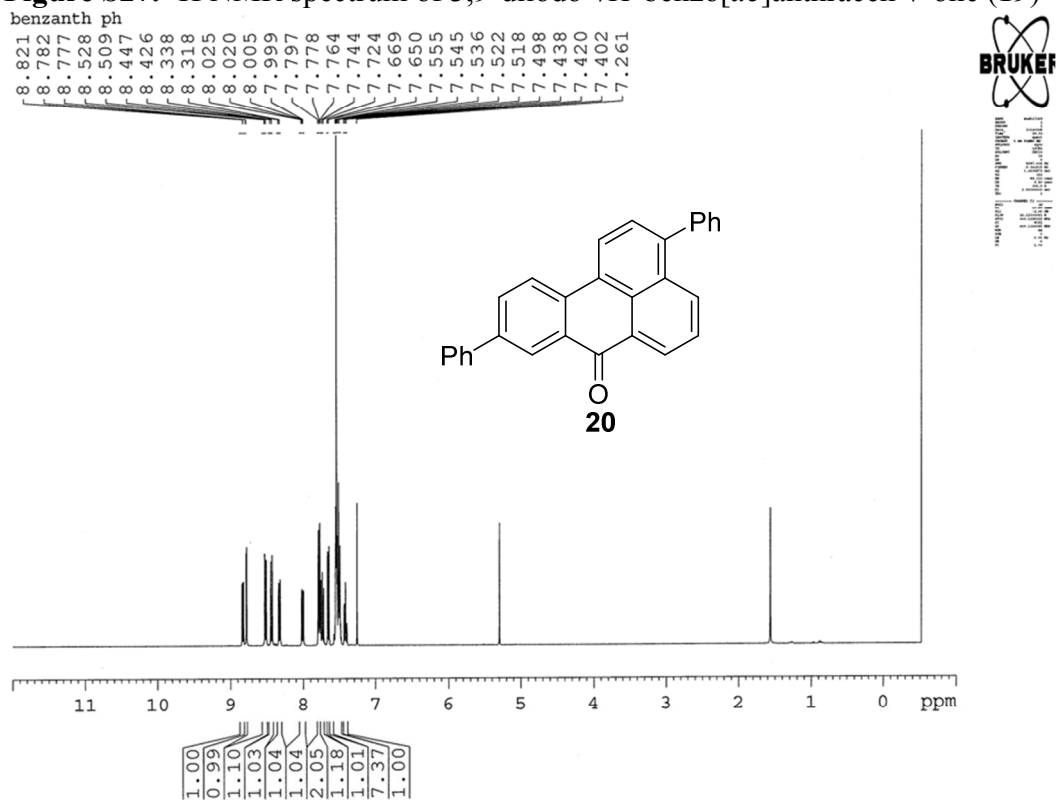


Figure S28. ^1H NMR spectra of 3,9-diphenyl-7*H*-benzo[*de*]anthracen-7-one (**20**)

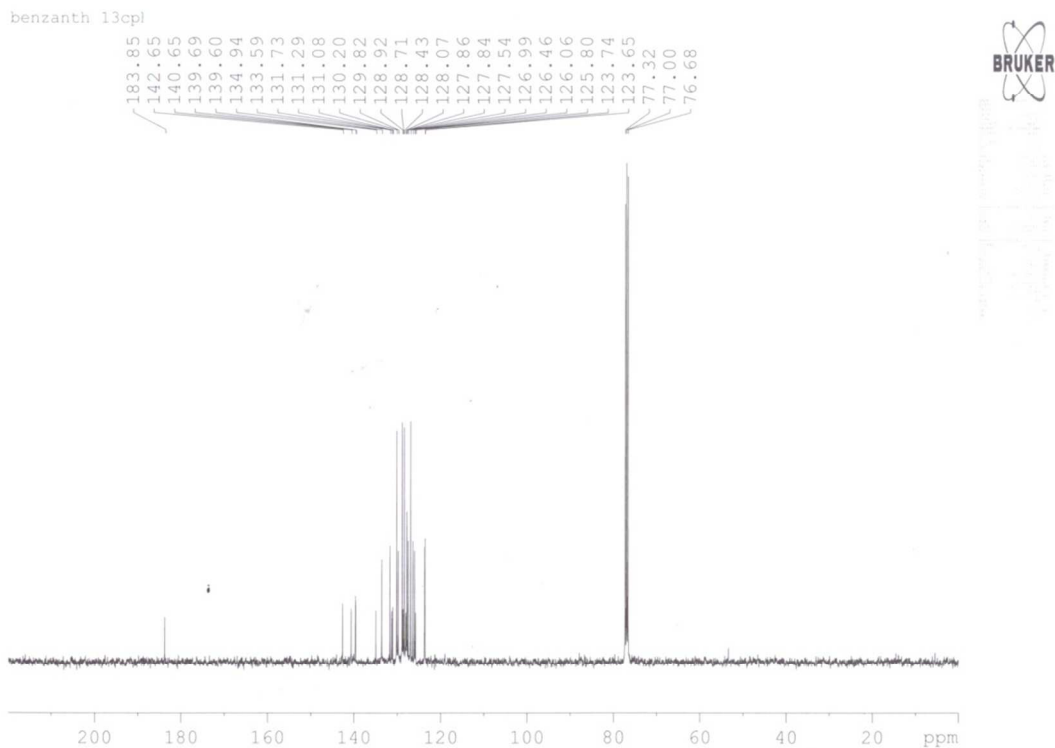


Figure S29. ^{13}C NMR spectra of 3,9-diphenyl-7*H*-benzo[*de*]anthracen-7-one (**20**)

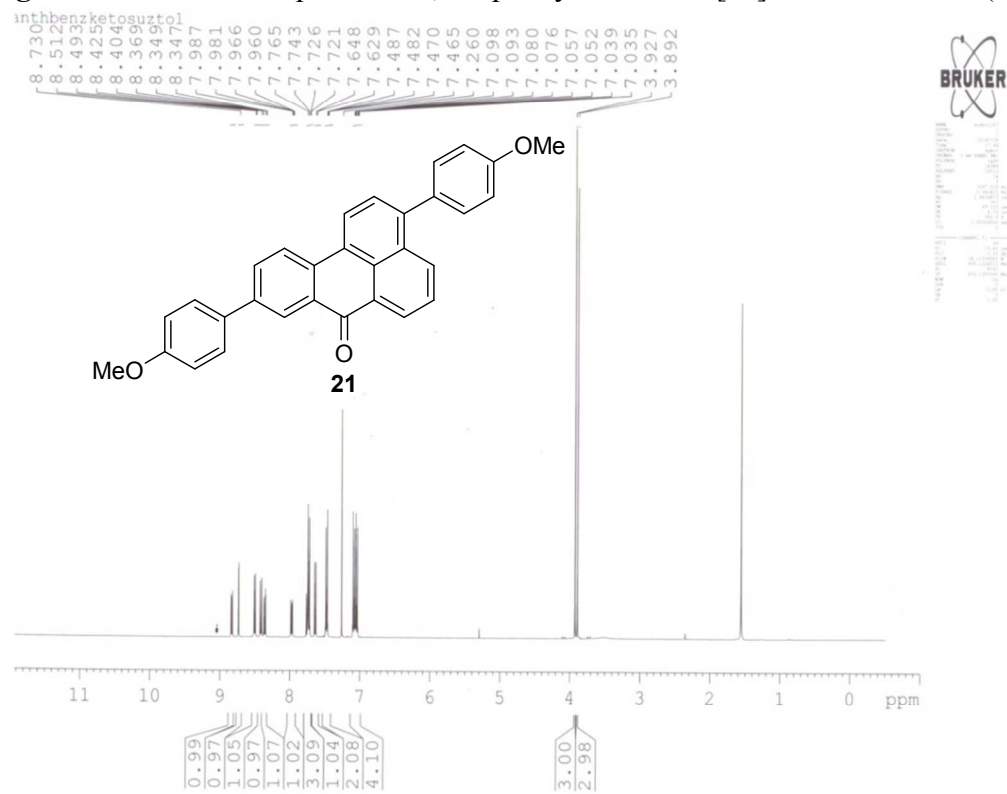


Figure S30. ^1H NMR spectrum of 3,9-bis(4-methoxyphenyl)-7*H*-benzo[*de*]anthracen-7-one (**21**)

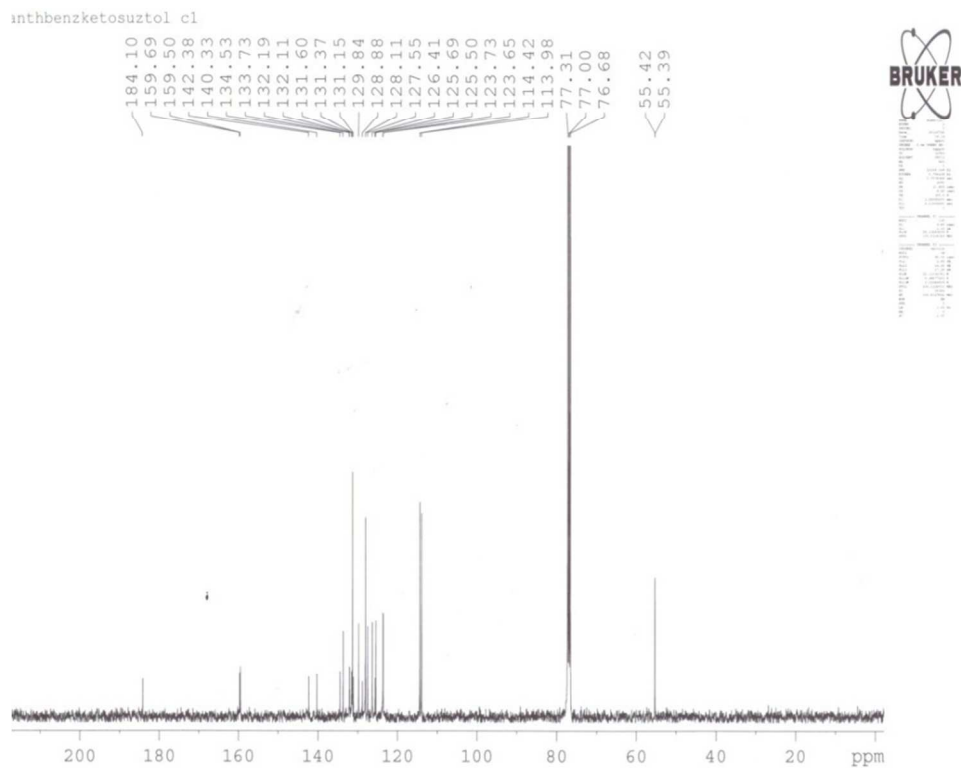


Figure S31. ^{13}C NMR spectrum of 3,9-bis(4-methoxyphenyl)-7H-benzo[de]anthracen-7-one (21)

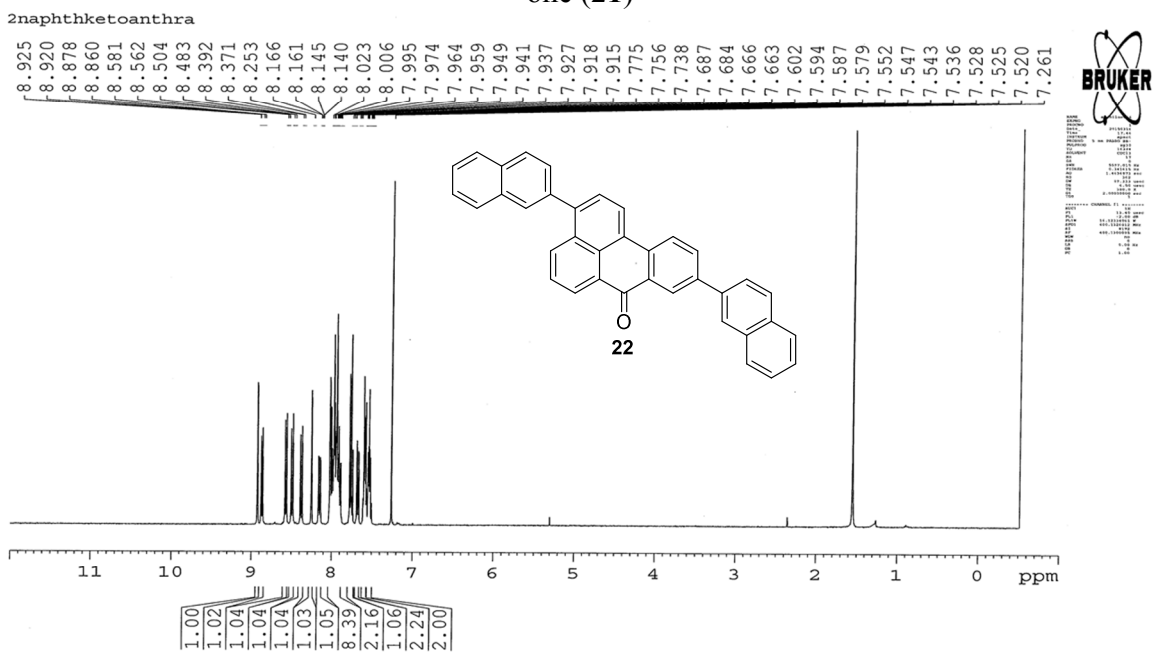


Figure S32. ^1H NMR spectrum of 3,9-di(naphthalen-2-yl)-7H-benzo[de]anthracen-7-one (22)

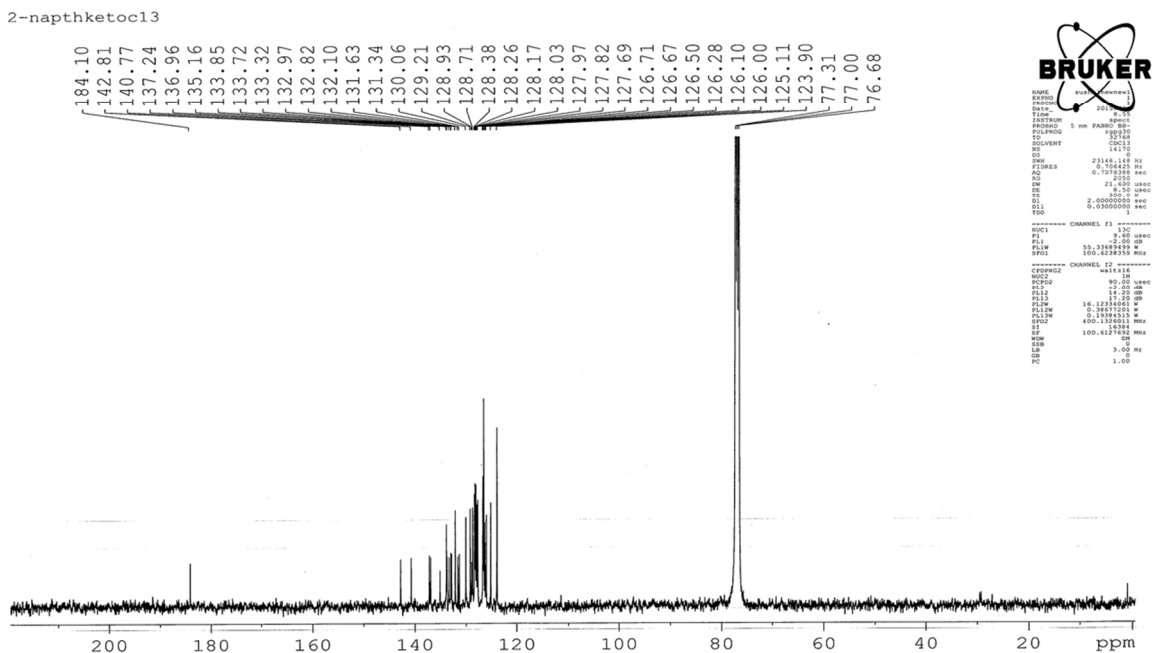


Figure S33. ^{13}C NMR spectrum of 3,9-di(naphthalen-2-yl)-7H-benzo[de]anthracen-7-one (22)

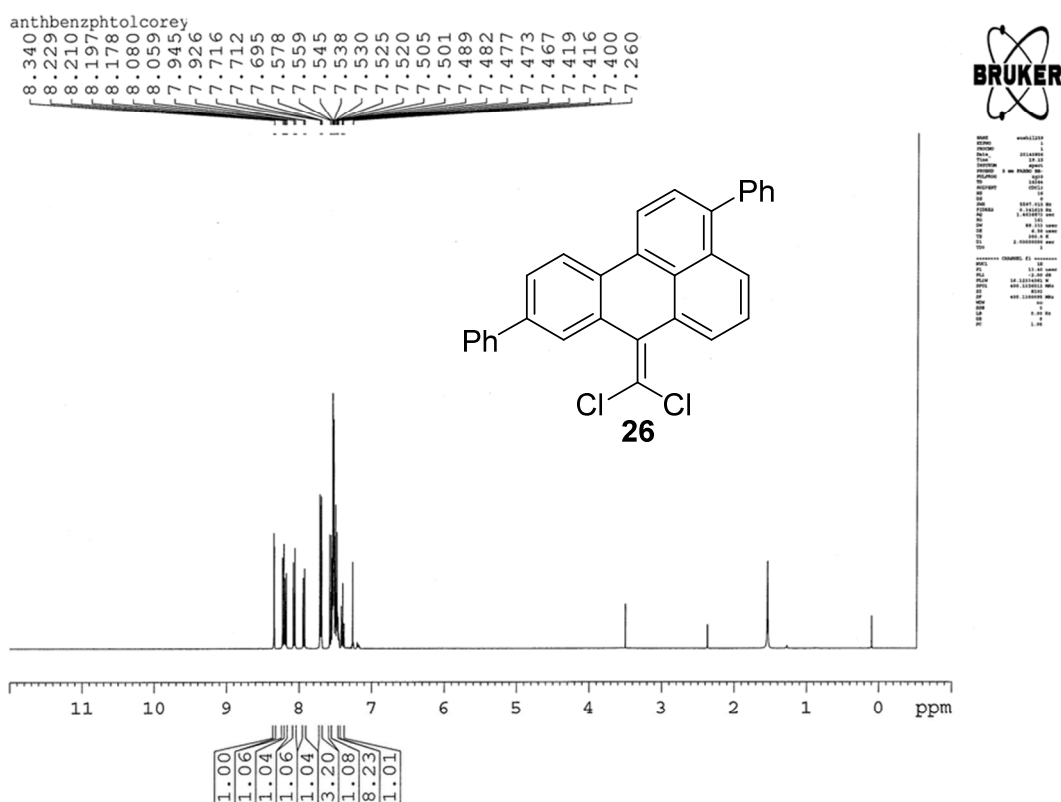


Figure S34. ^1H NMR spectrum of 7-(dichloromethylene)-3,9-diphenyl-7H-benzo[de]anthracene (26)

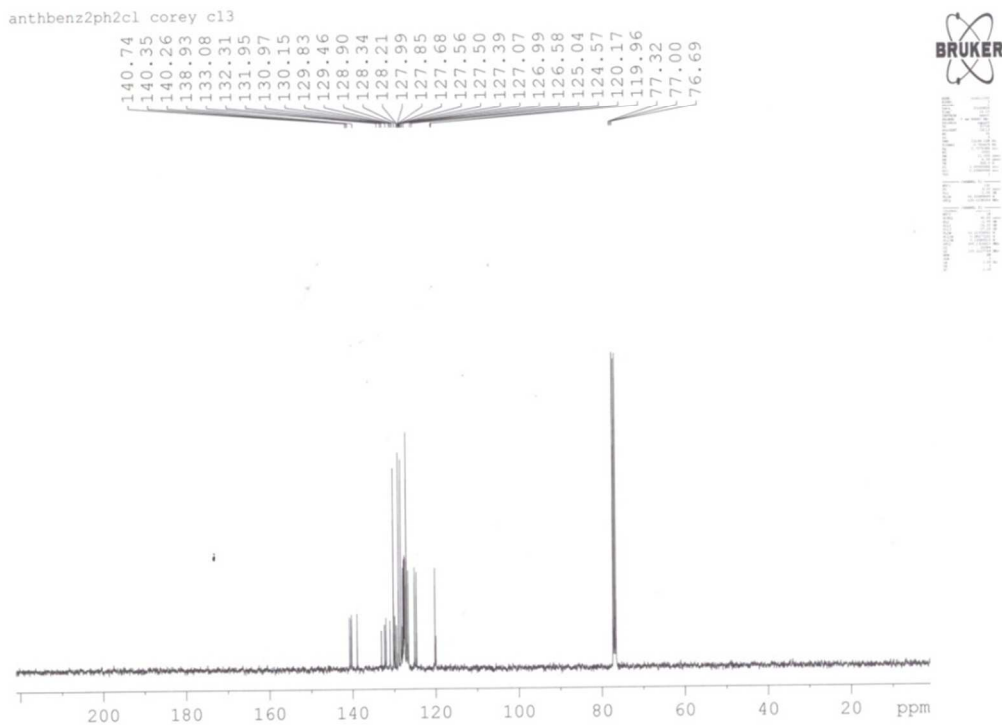


Figure S35. ^{13}C NMR spectrum of 7-(dichloromethylene)-3,9-diphenyl-7H-benzo[*de*]anthracene (**26**)

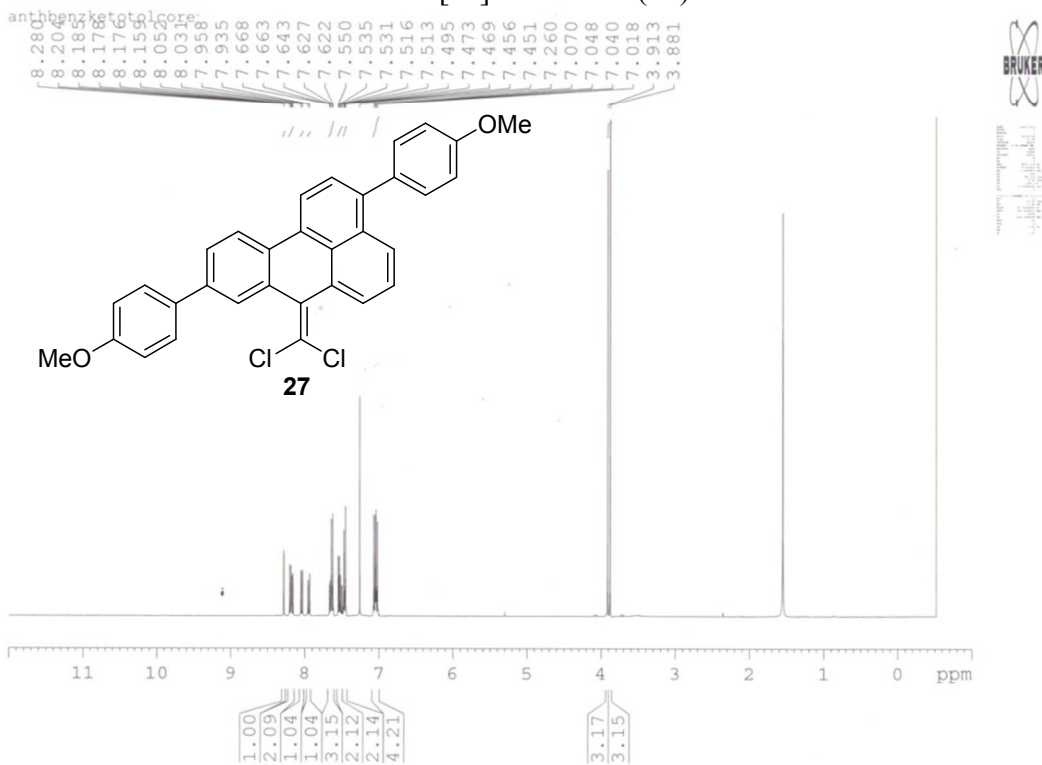


Figure S36. ^1H NMR spectrum of 7-(dichloromethylene)-3,9-bis(4-methoxyphenyl)-7H-benzo[*de*]anthracene (**27**)

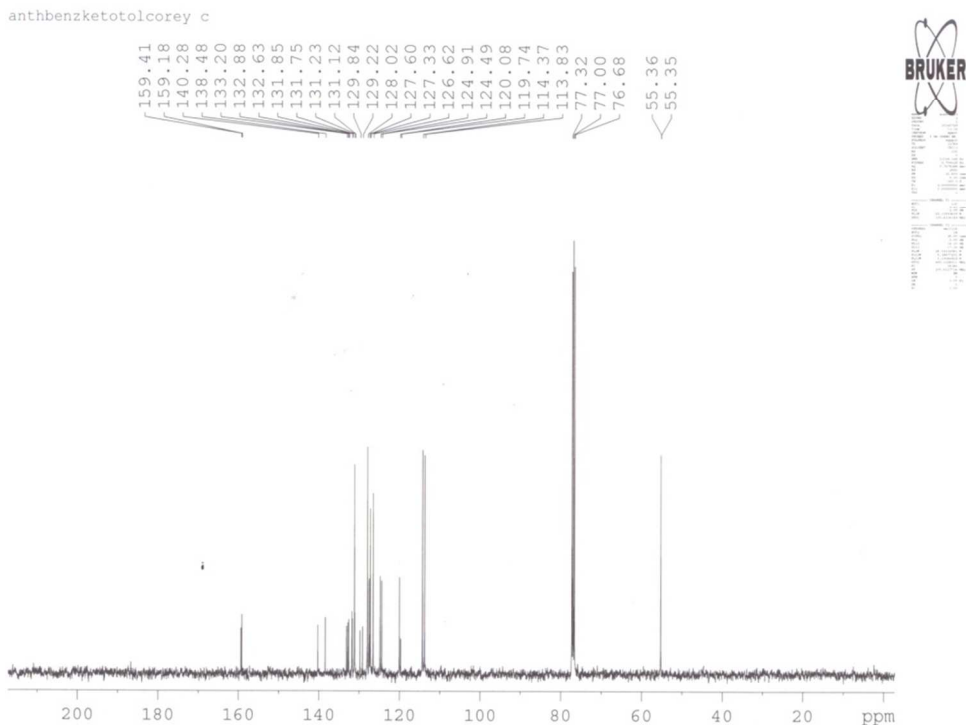


Figure S37. ^{13}C NMR spectrum of 7-(dichloromethylene)-3,9-bis(4-methoxyphenyl)-7H-benzo[de]anthracene (**27**)

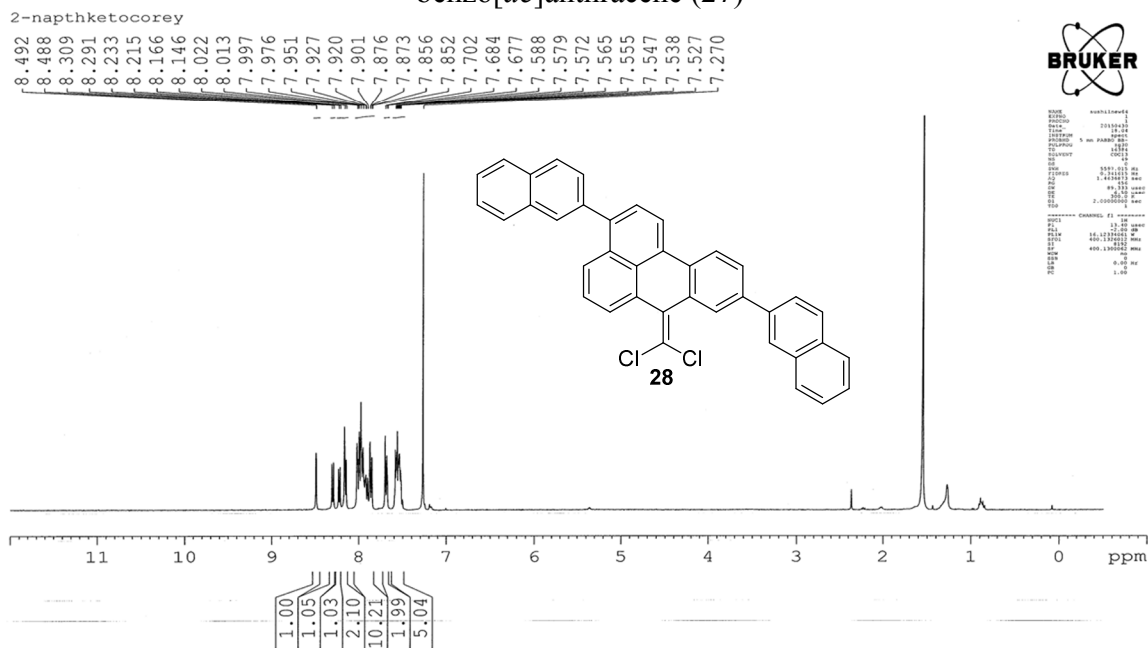


Figure S38. ^1H NMR spectrum of 7-(dichloromethylene)-3,9-di(naphthalen-2-yl)-7H-benzo[de]anthracene (**28**)

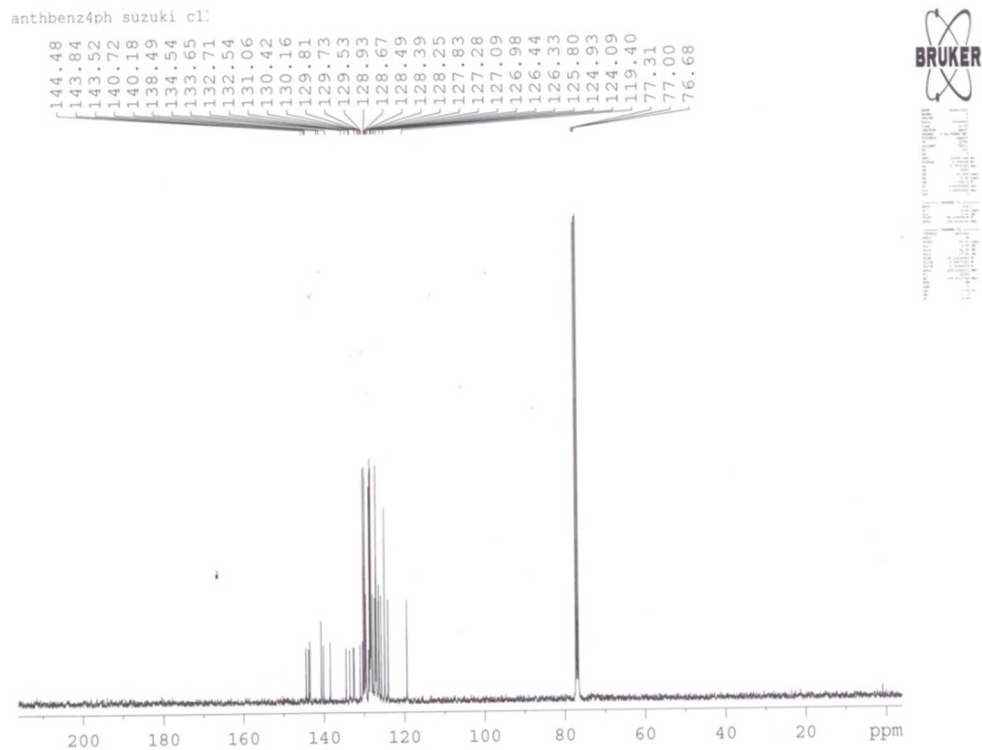


Figure S41. ^{13}C NMR spectrum of 7-(diphenylmethylene)-3,9-diphenyl-7H-benzo[*de*]anthracene (**29**)

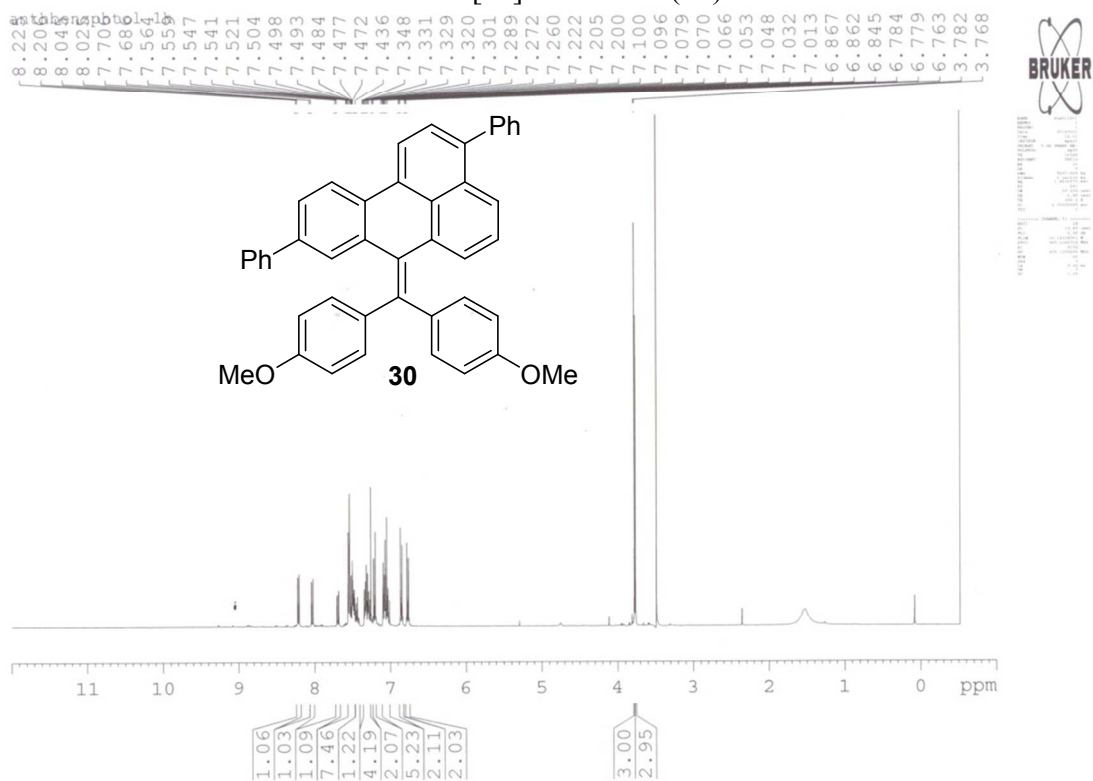


Figure S42. ^1H NMR spectrum of 7-(bis(4-methoxyphenyl)methylene)-3,9-diphenyl-7H-benzo[*de*]anthracene (**30**)

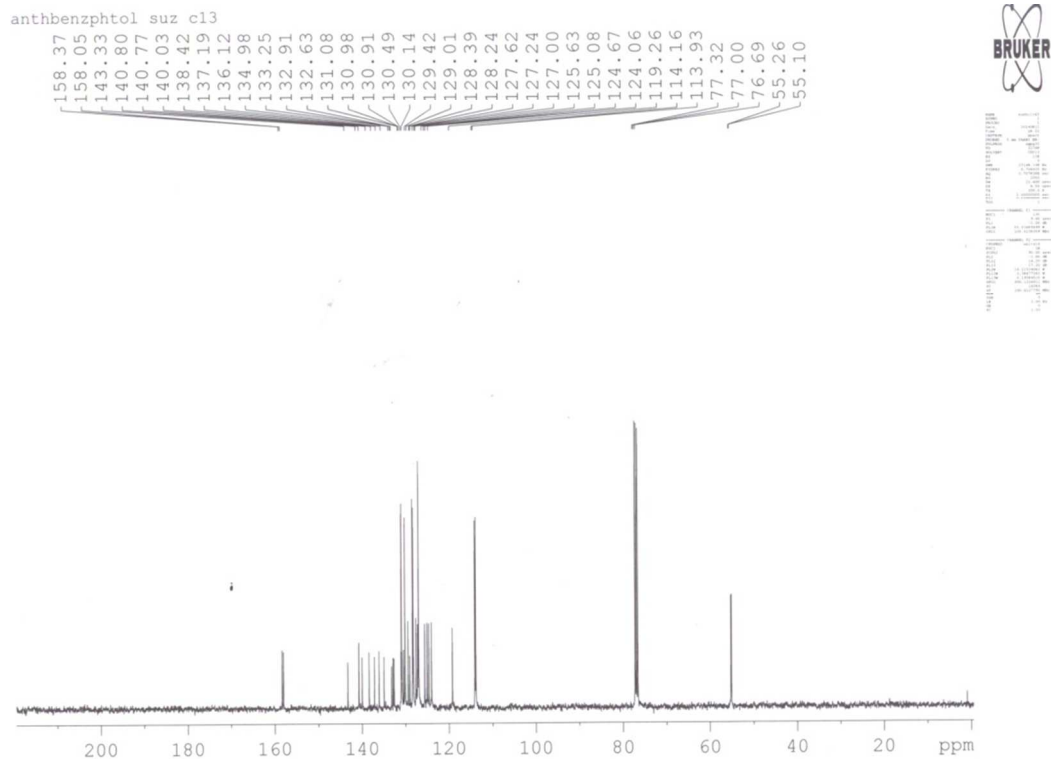


Figure S43. ^{13}C NMR spectrum of 7-(bis(4-methoxyphenyl)methylene)-3,9-diphenyl-7*H*-benzo[*de*]anthracene (**30**)

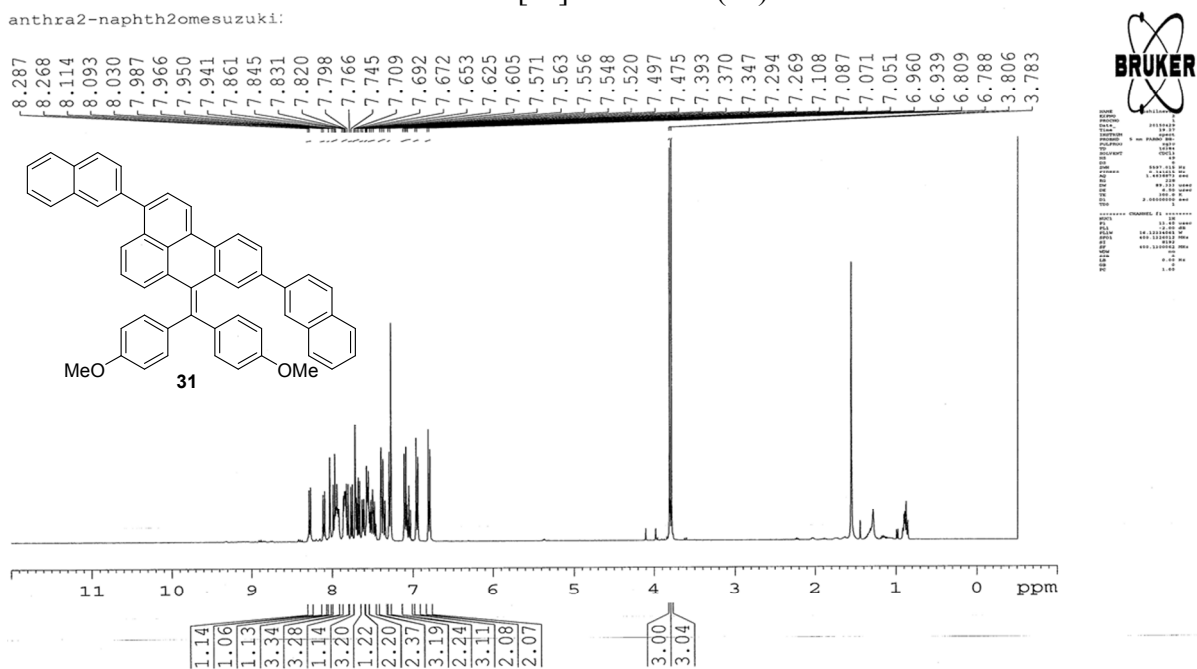


Figure S44. ^1H NMR spectrum of 7-(dichloromethylene)-3,9-di(naphthalen-2-yl)-7*H*-benzo[*de*]anthracene (**31**)

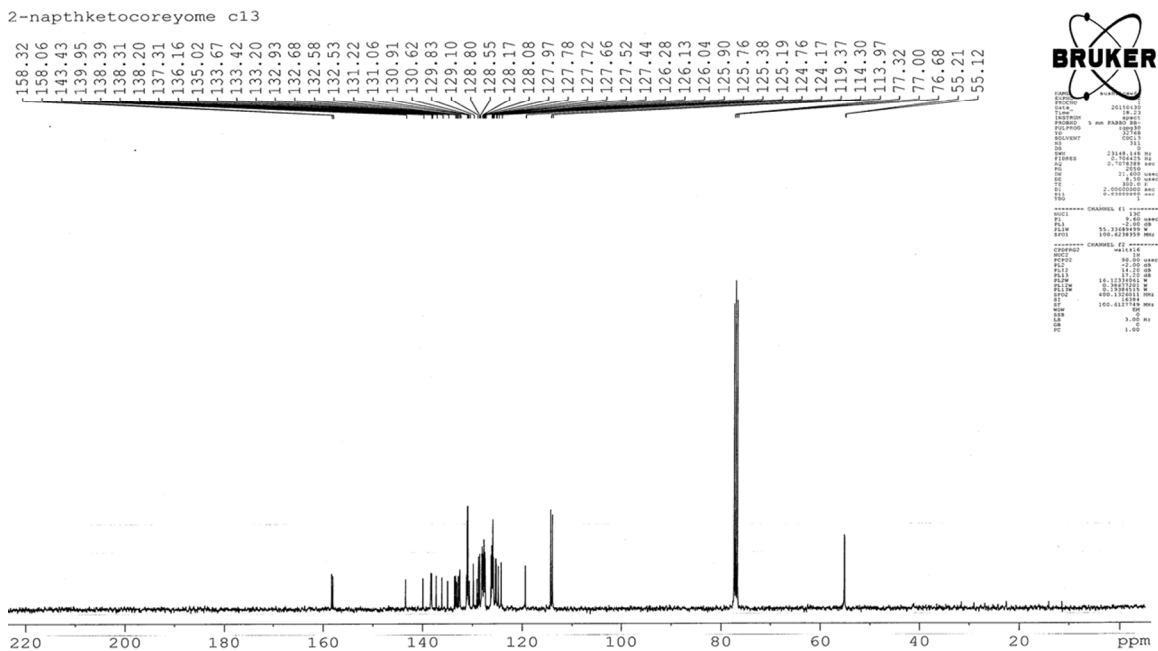


Figure S45. ^{13}C NMR spectrum of 7-(dichloromethylene)-3,9-di(naphthalen-2-yl)-7H-benzo[de]anthracene (**31**)

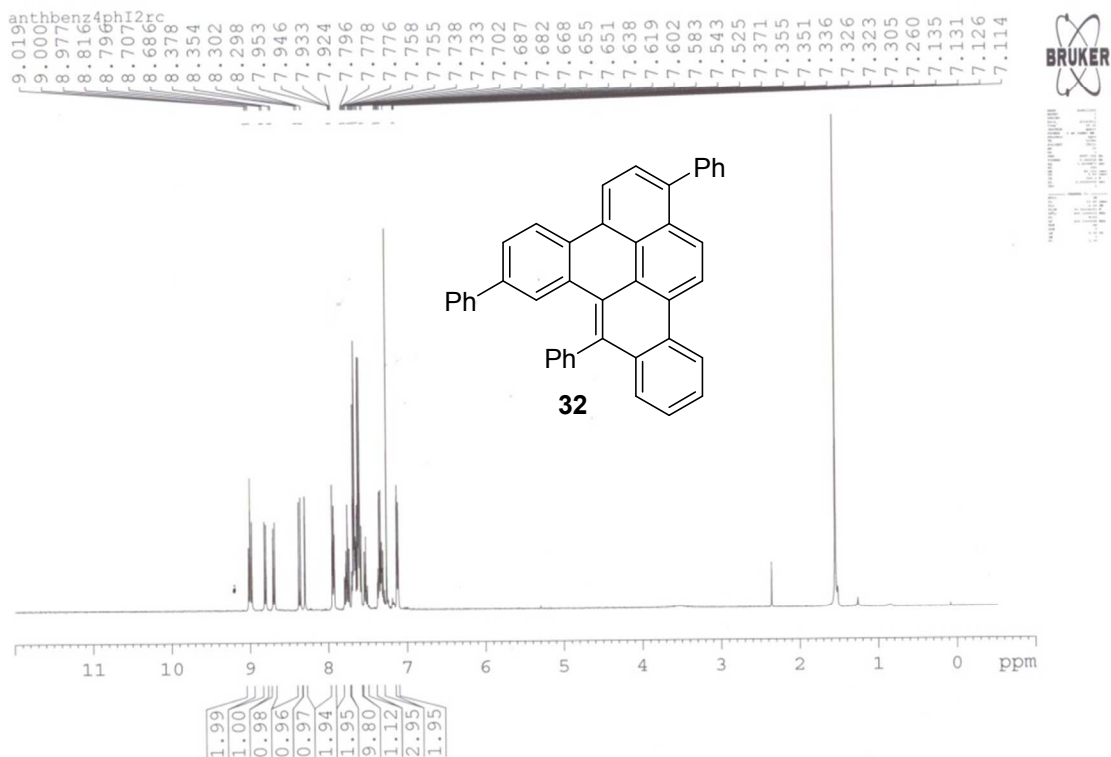


Figure S46. ^1H NMR spectrum of 1,6,8-triphenyldibenzo[*f,pqr*]tetraphene (**32**)

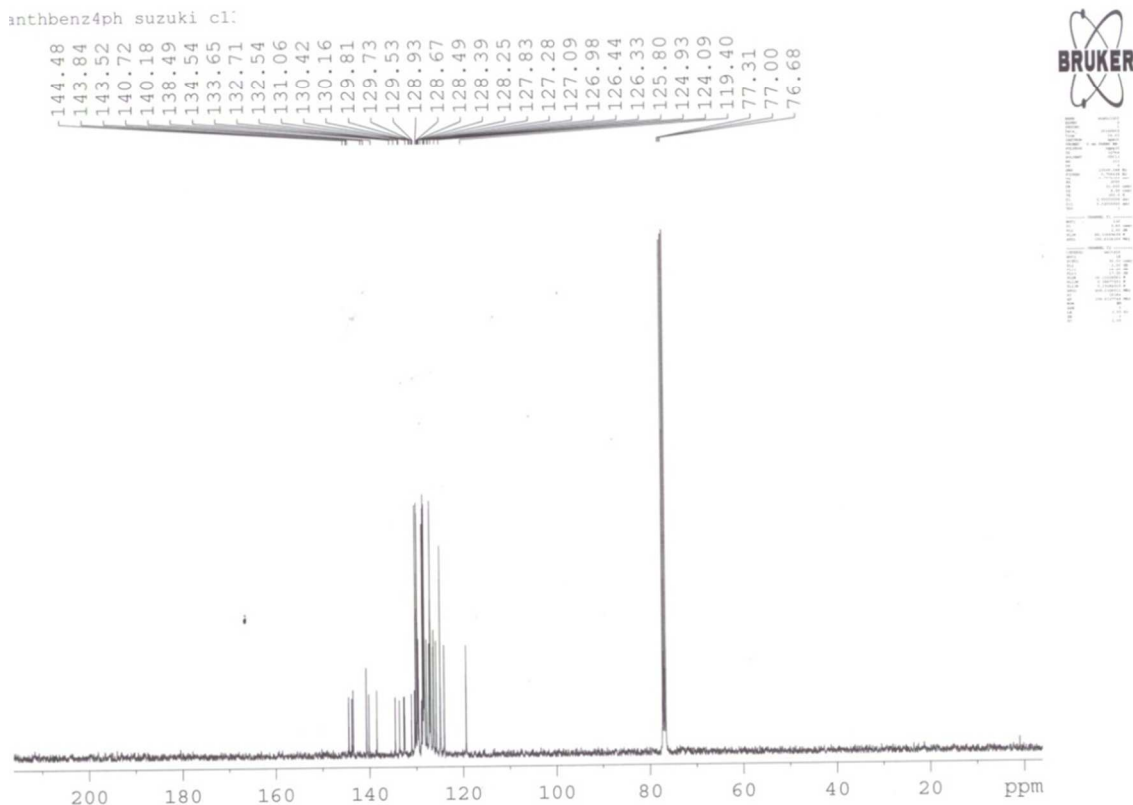


Figure S47. ^{13}C NMR spectrum of 1,6,8-triphenyldibenzo[*f,pqr*]tetraphene (**32**)

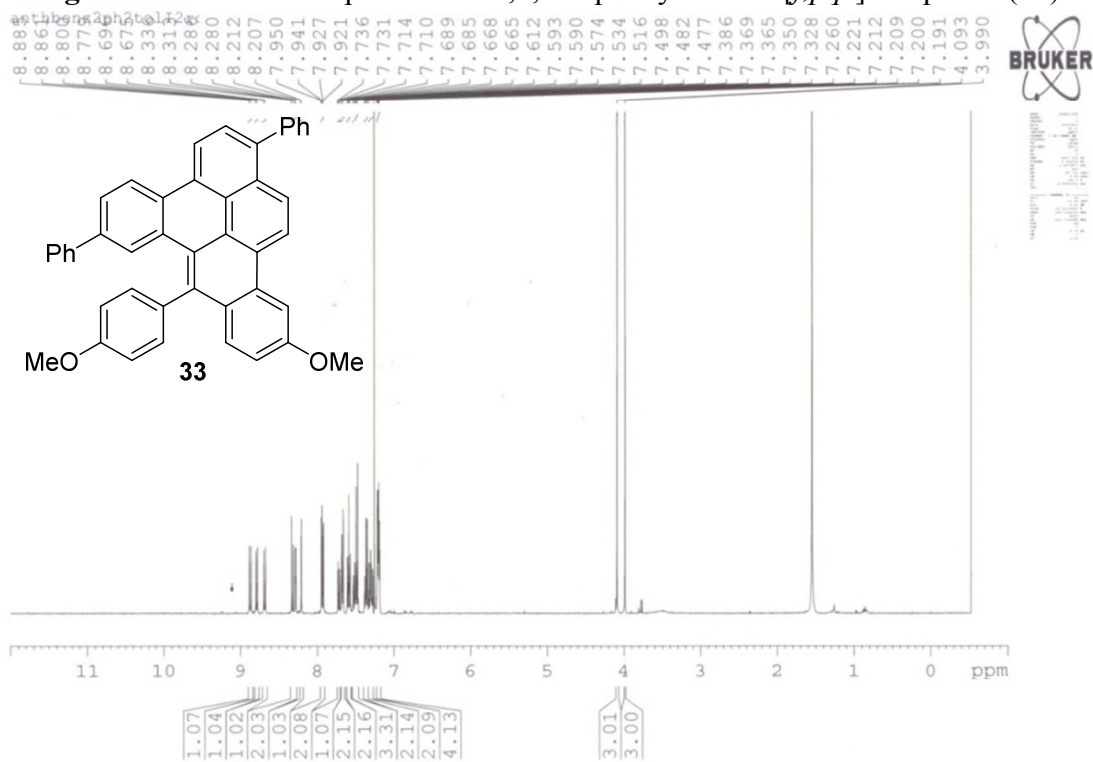


Figure S48. ^1H NMR spectrum of 3,11-dimethoxy-8-(4-methoxyphenyl)-1,6-diphenyldibenzo[*f,pqr*]tetraphene (**33**)

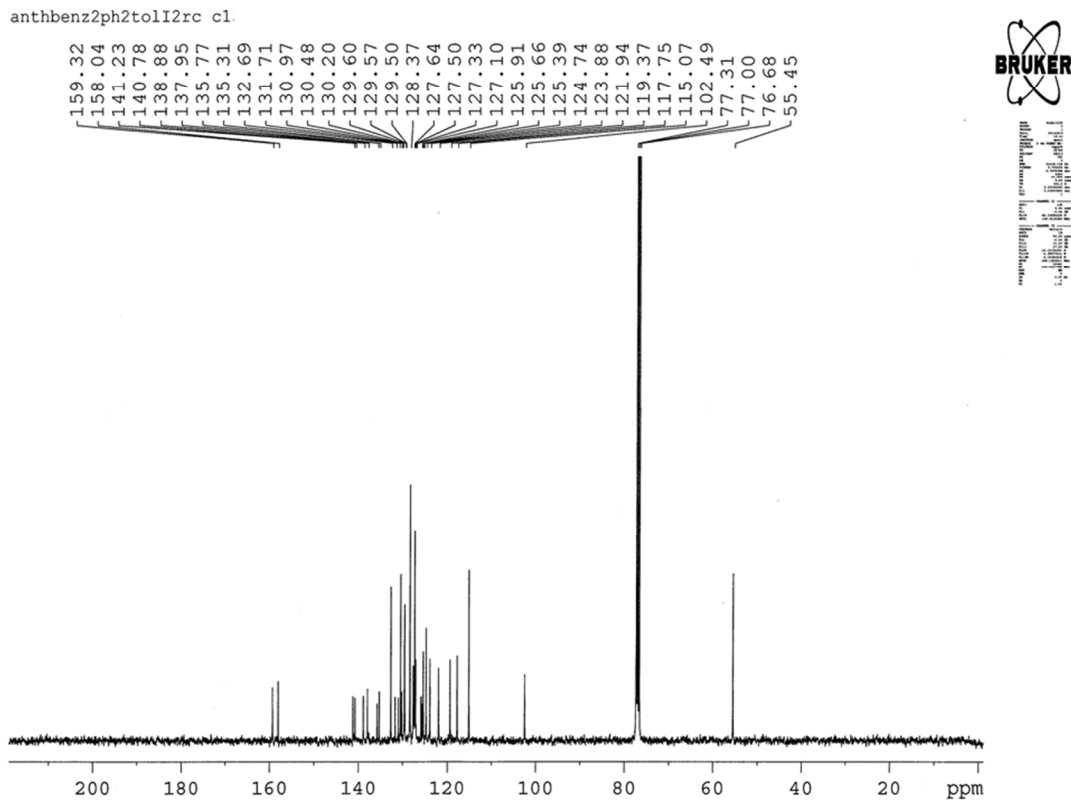


Figure S49. ^{13}C NMR spectrum of 3,11-dimethoxy-8-(4-methoxyphenyl)-1,6-diphenyldibenzo[*f,pqr*]tetraphene (**33**)

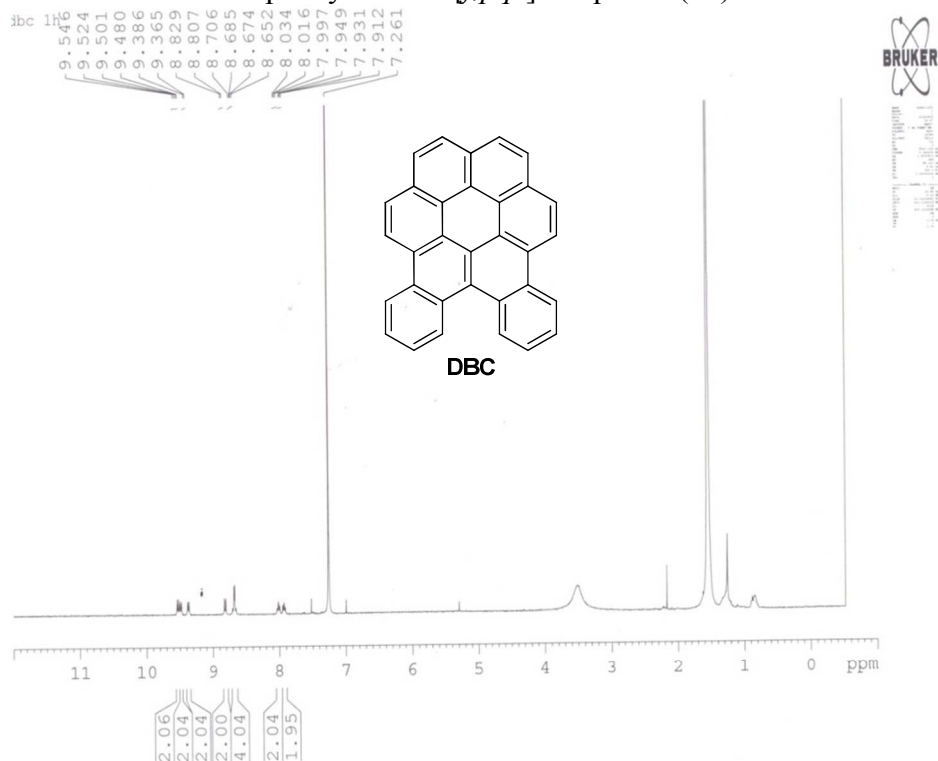


Figure S50. ^1H NMR spectrum of dibenzo[*a,d*]coronene (**DBC**)

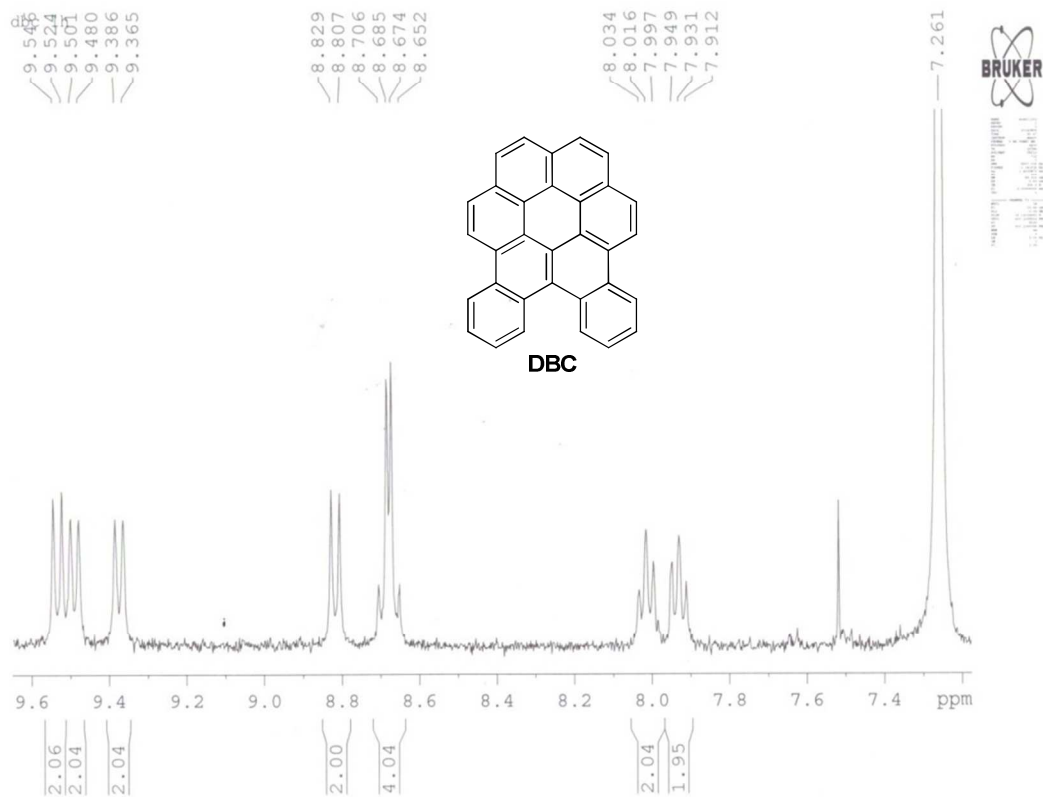


Figure S51. ¹H NMR spectrum (expansion) of dibenzo[*a,d*]coronene (DBC)

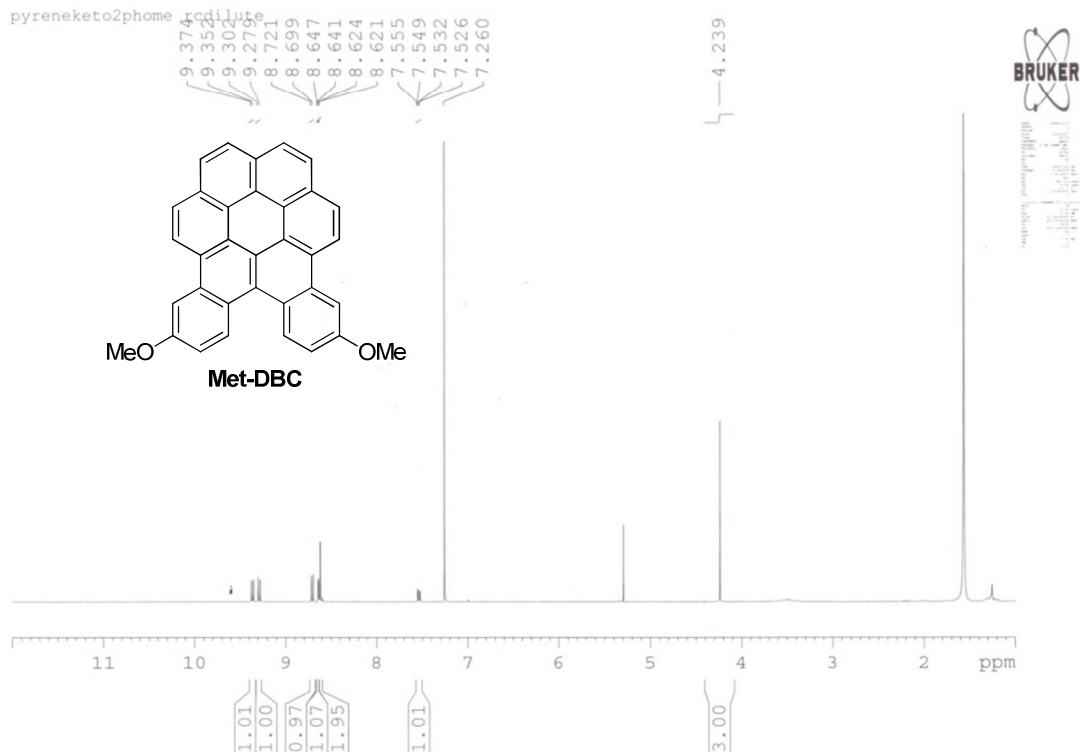


Figure S52. ¹H NMR spectrum of 8,13-dimethoxydibenzo[*a,d*]coronene (Met-DBC)

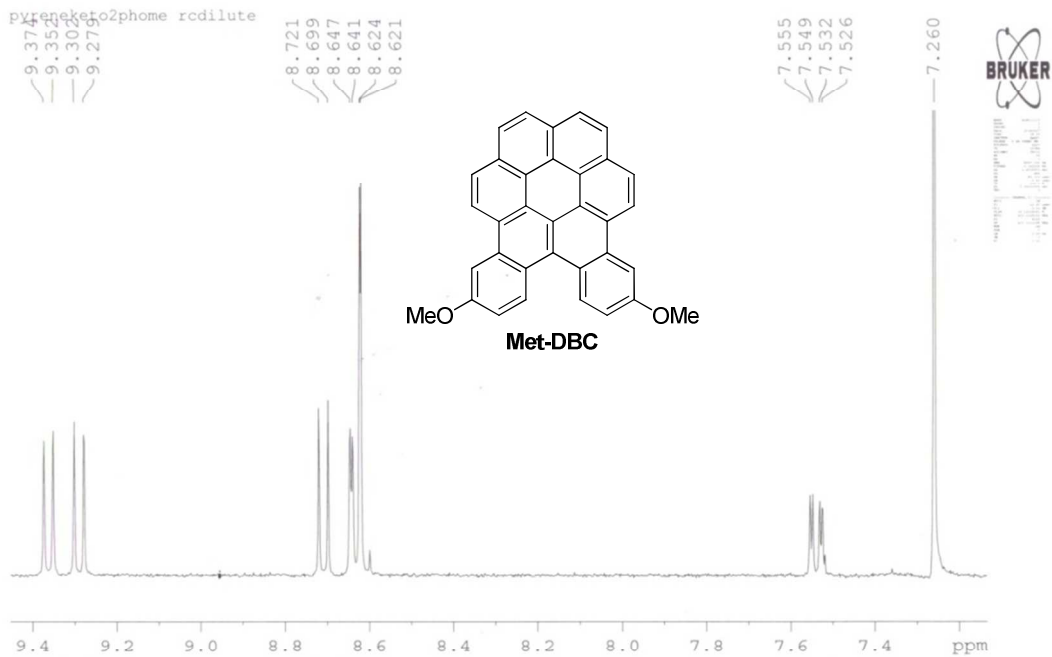


Figure S53. ^1H NMR spectrum (expansion) of 8,13-dimethoxydibenzo[*a,d*]coronene (Met-DBC)

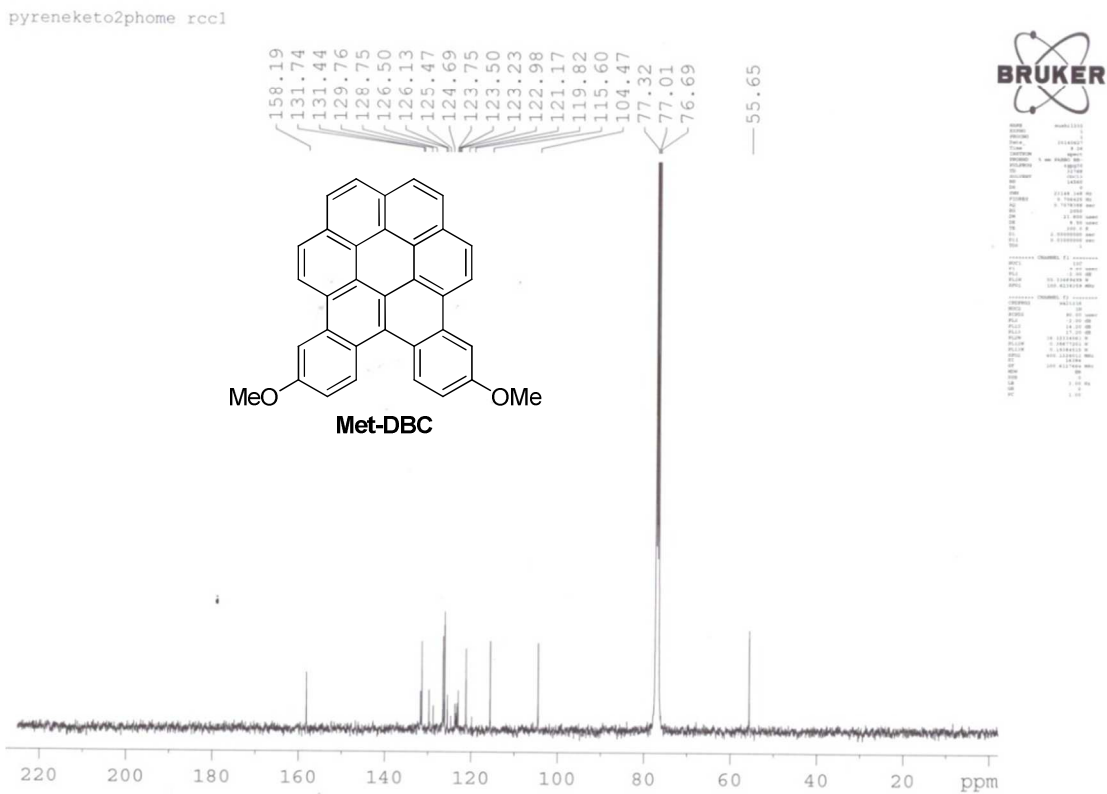


Figure S54. ^{13}C NMR spectrum of 8,13-dimethoxydibenzo[*a,d*]coronene (Met-DBC)

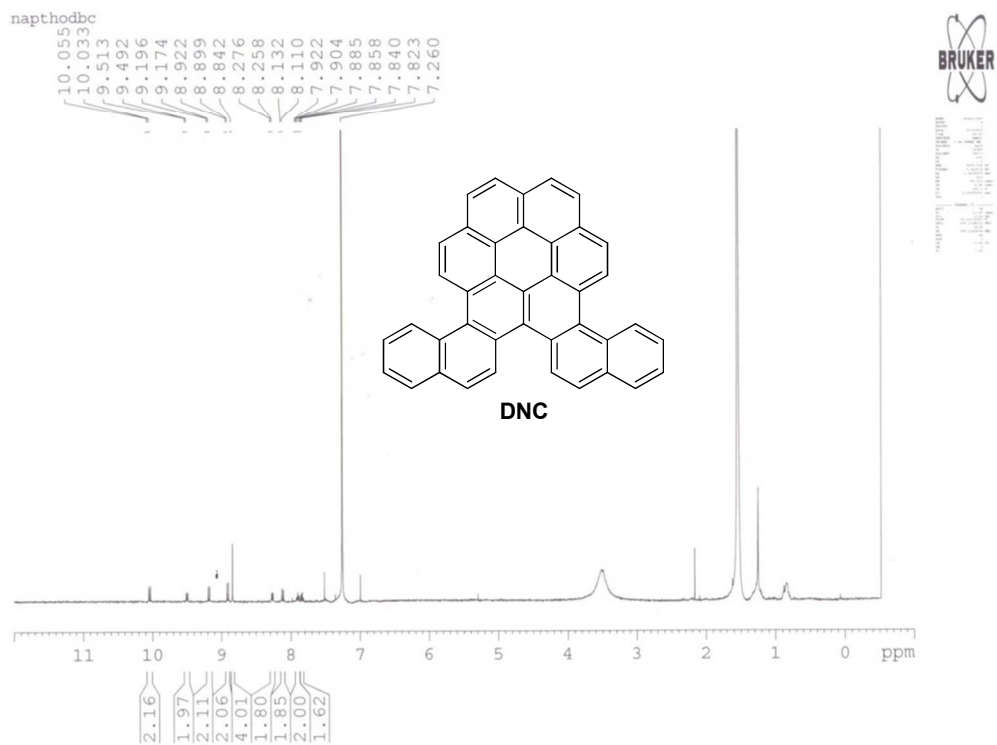


Figure S55. ^1H NMR spectrum of dinaphtho[1,2-*a*:2',1'-*d*]coronene (**DNC**)

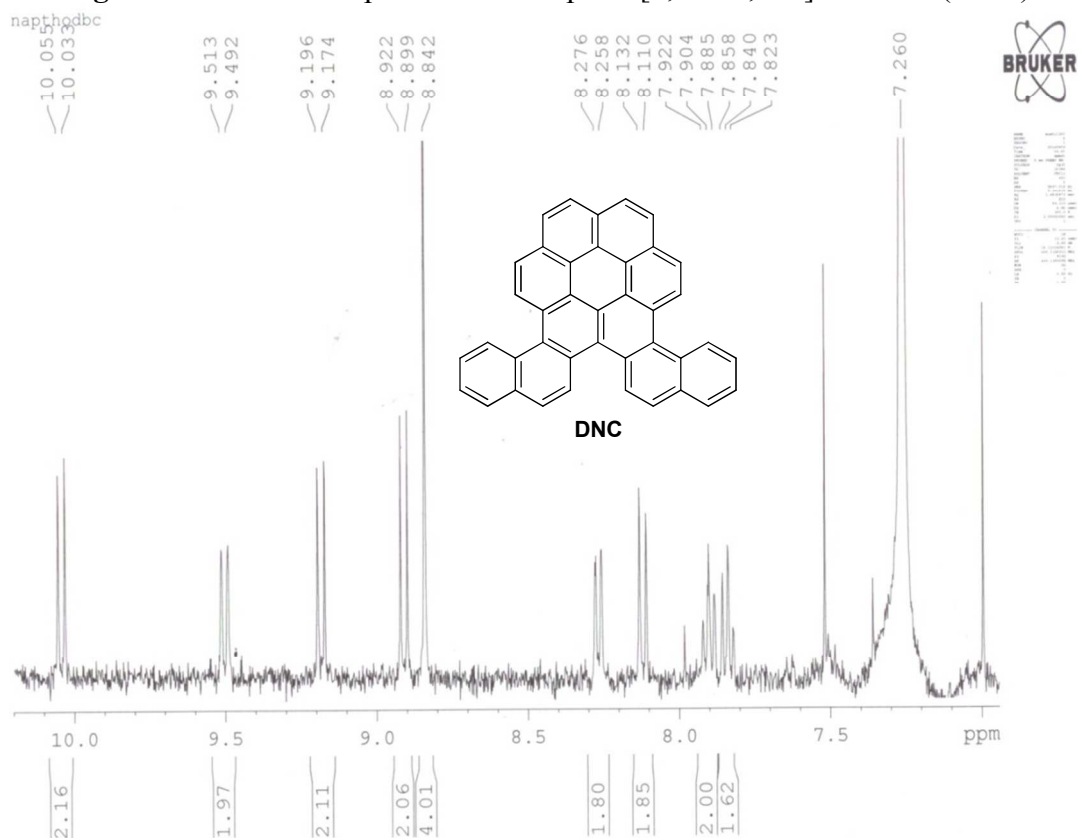


Figure S56. ^1H NMR spectrum (expansion) of dinaphtho[1,2-*a*:2',1'-*d*]coronene (**DNC**)

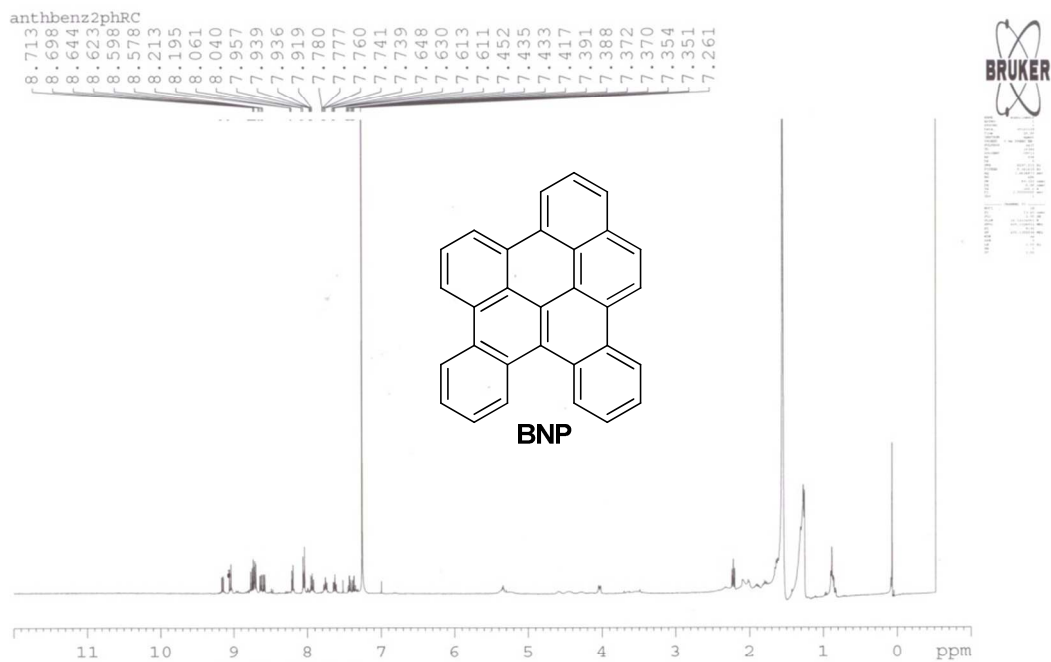


Figure S57. ^1H NMR spectrum of benzo[*b*]naphtho[1,2,3,4-*pqr*]perylene (BNP)

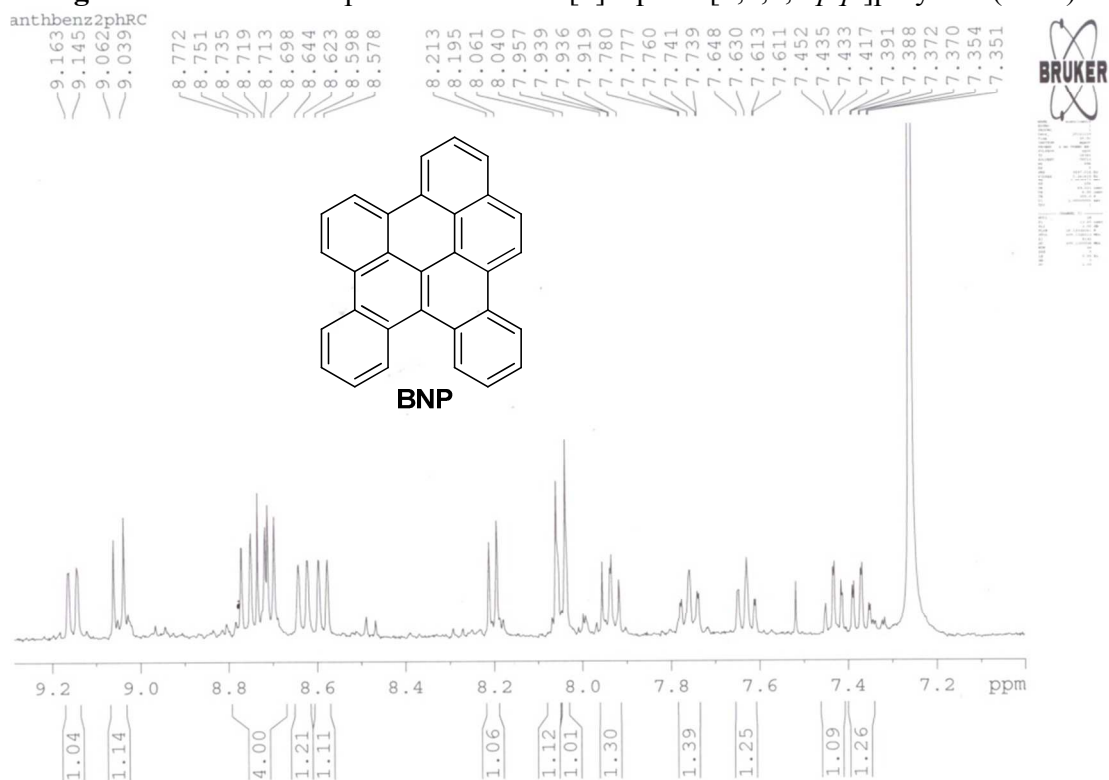


Figure S58. ^1H NMR spectrum (expansion) of benzo[*b*]naphtho[1,2,3,4-*pqr*]perylene (BNP)

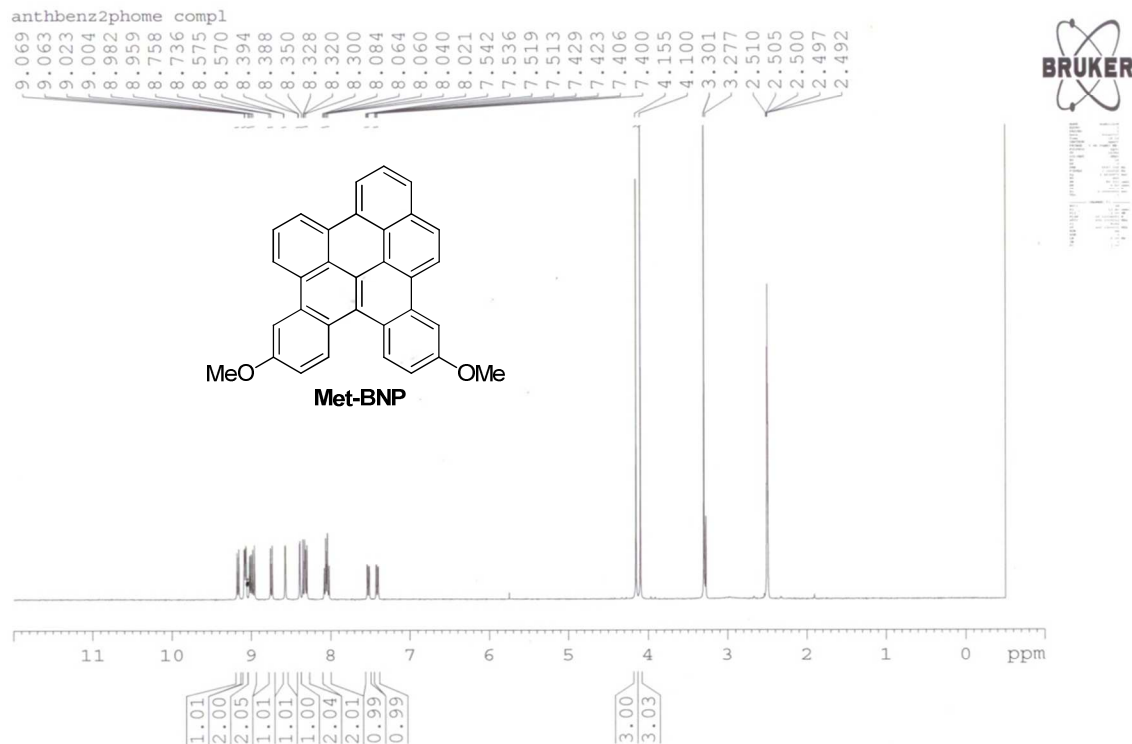


Figure S59. ^1H NMR spectrum of 2,7-dimethoxybenzo[*b*]naphtho[1,2,3,4-*pqr*]perylene (Met-BNP)

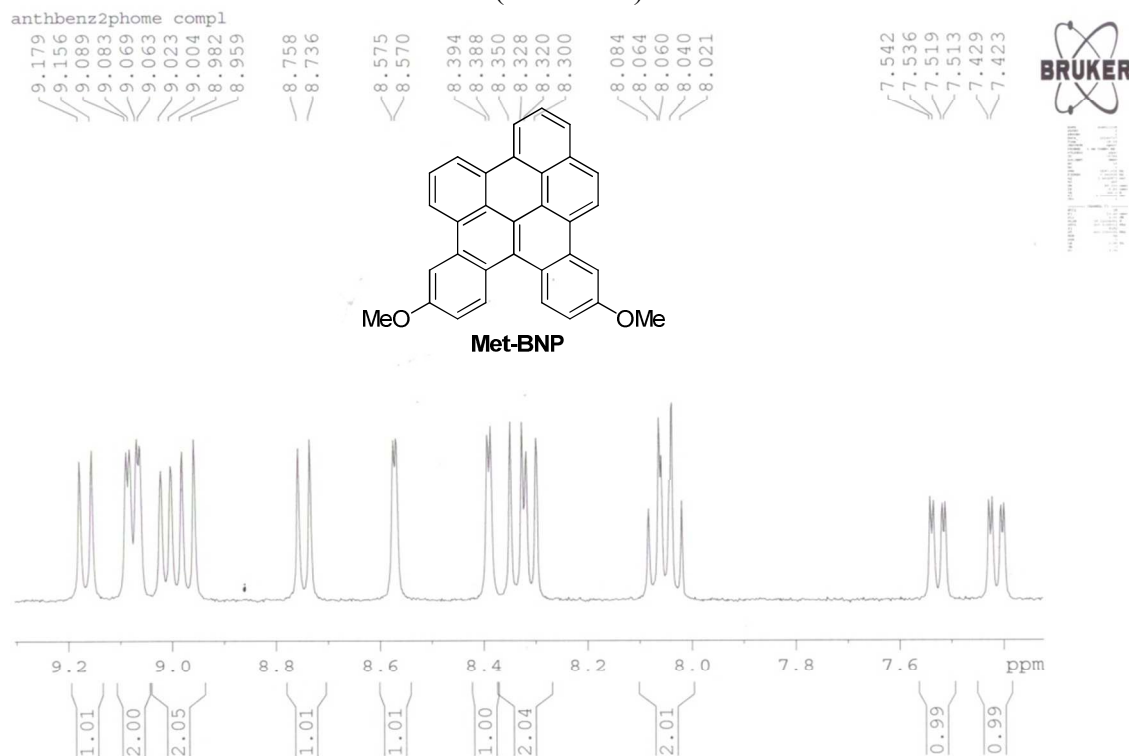


Figure S60. ^1H NMR spectrum (expansion) of 2,7-dimethoxybenzo[*b*]naphtho[1,2,3,4-*pqr*]perylene (Met-BNP)

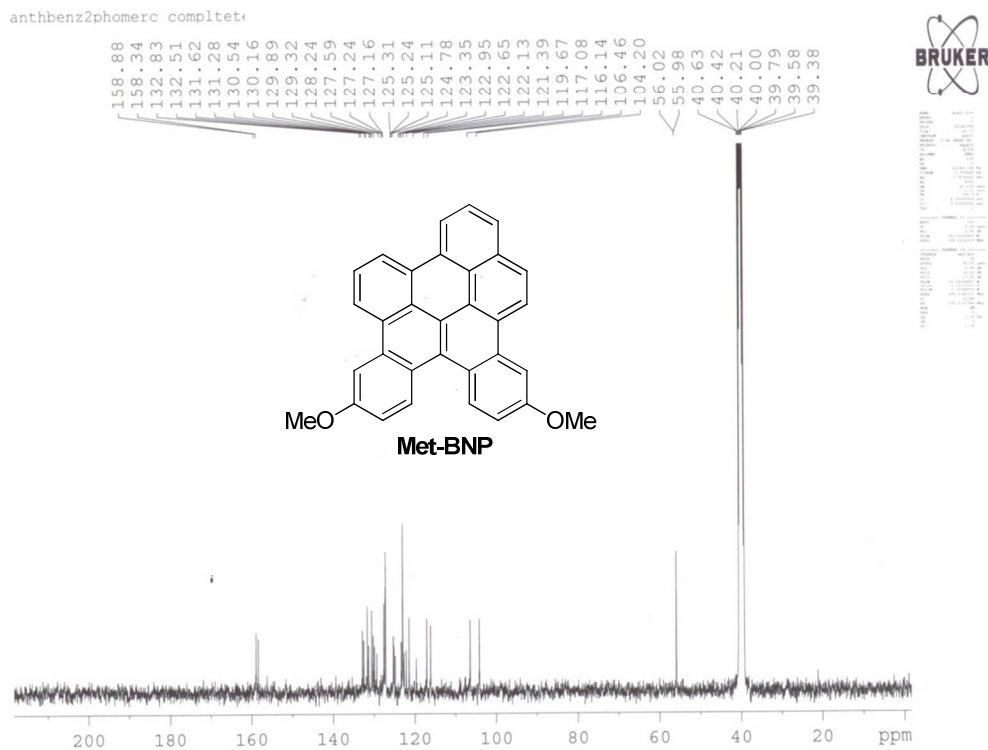


Figure S61. ^{13}C NMR spectrum of 2,7-dimethoxybenzo[*b*]naphtho[1,2,3,4-*pqr*]perylene (Met-BNP)

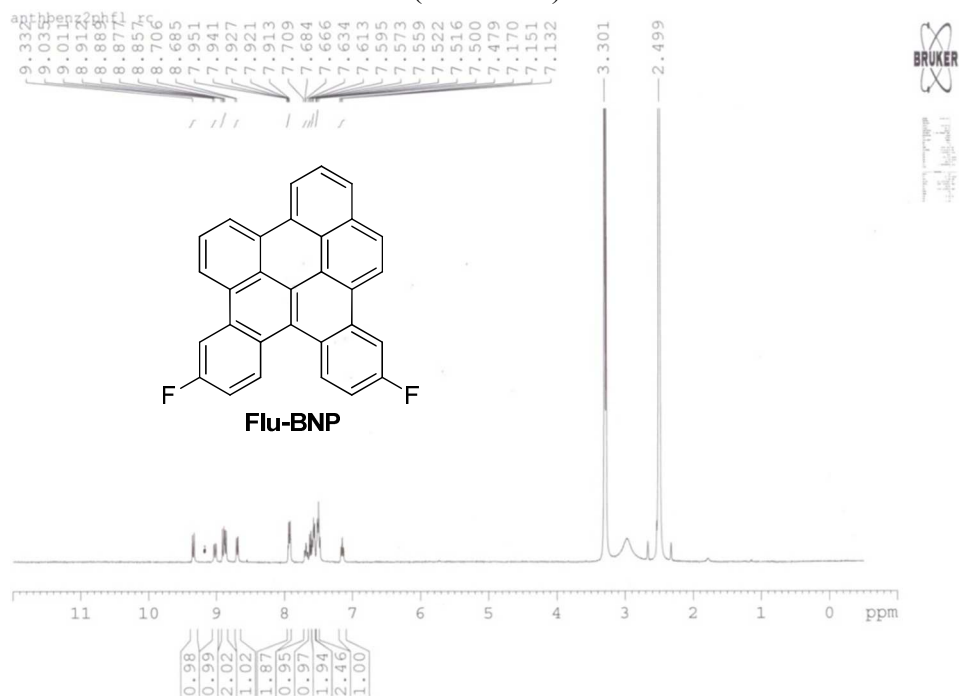


Figure S62. ^1H NMR spectrum of 2,7-difluorobenzo[*b*]naphtho[1,2,3,4-*pqr*]perylene (Flu-BNP)

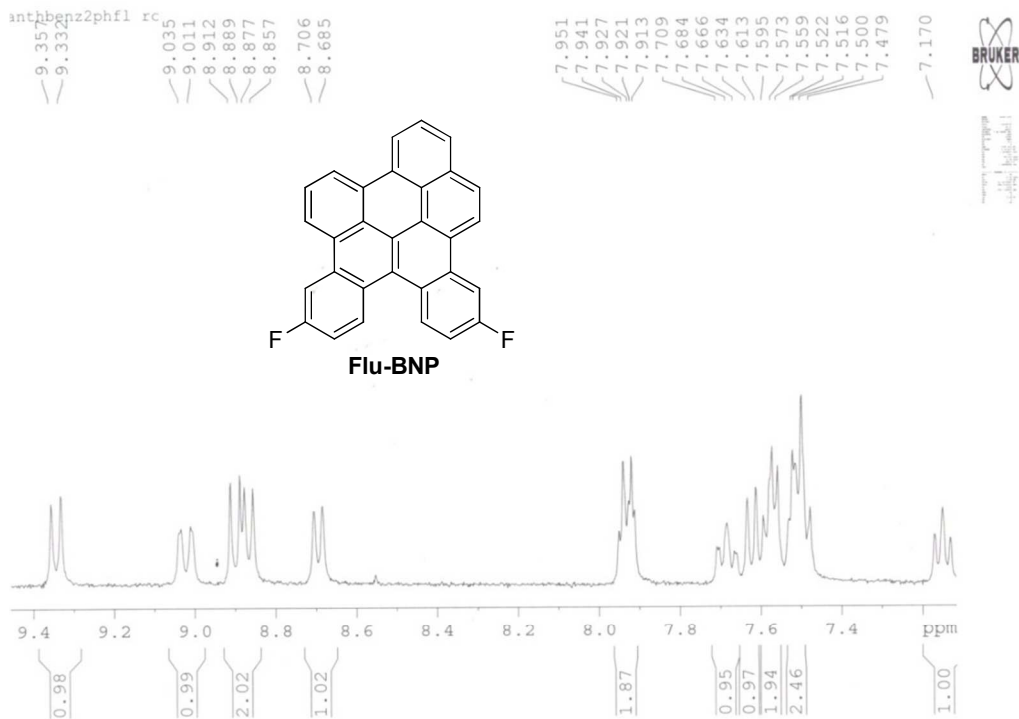


Figure S63. ^1H NMR spectrum (expansion) of 2,7-difluorobenzo[*b*]naphtho[1,2,3,4-*pqr*]perylene (**Flu-BNP**)

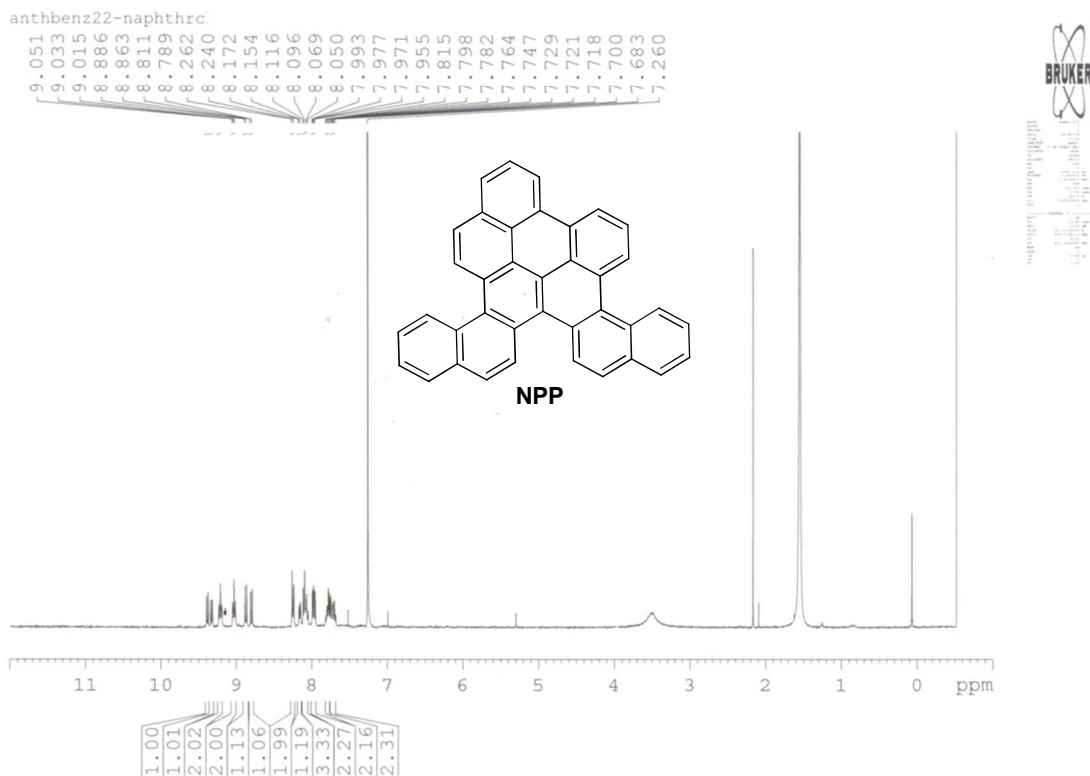


Figure S64. ^1H NMR spectrum of naphtho[2,1-*b*]phenanthro[4,3,2,1-*pqr*]perylene (**NPP**)

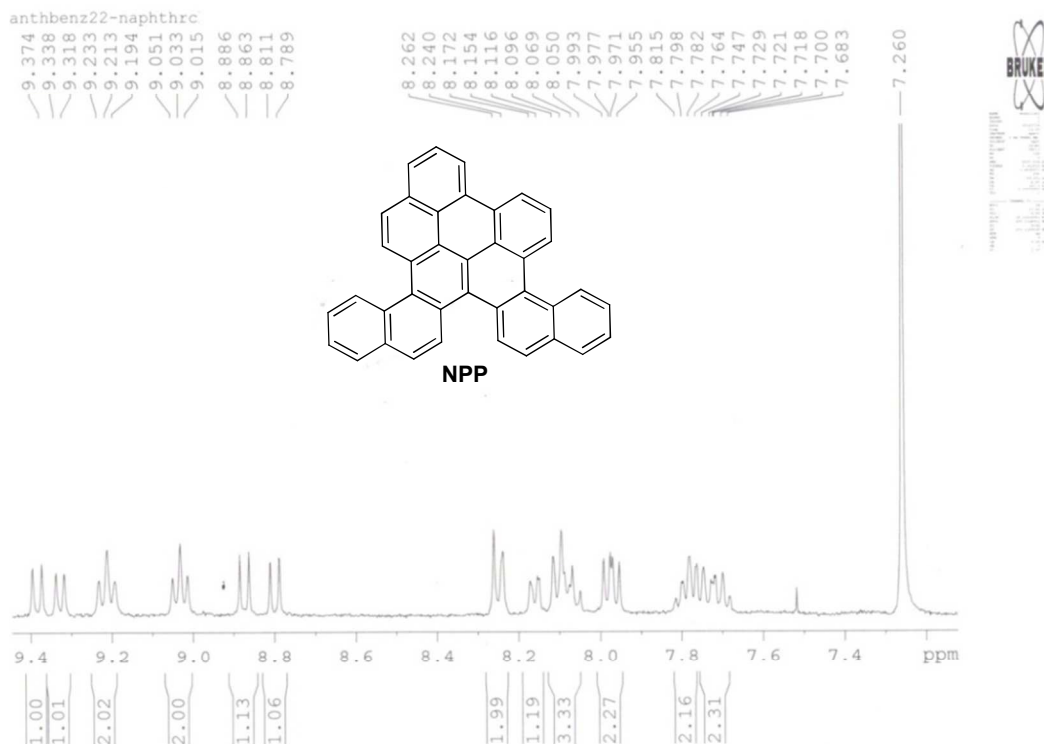


Figure S65. ^1H NMR spectrum (expansion) of naphtho[2,1-*b*]phenanthro[4,3,2,1-*pqr*]perylene (NPP)

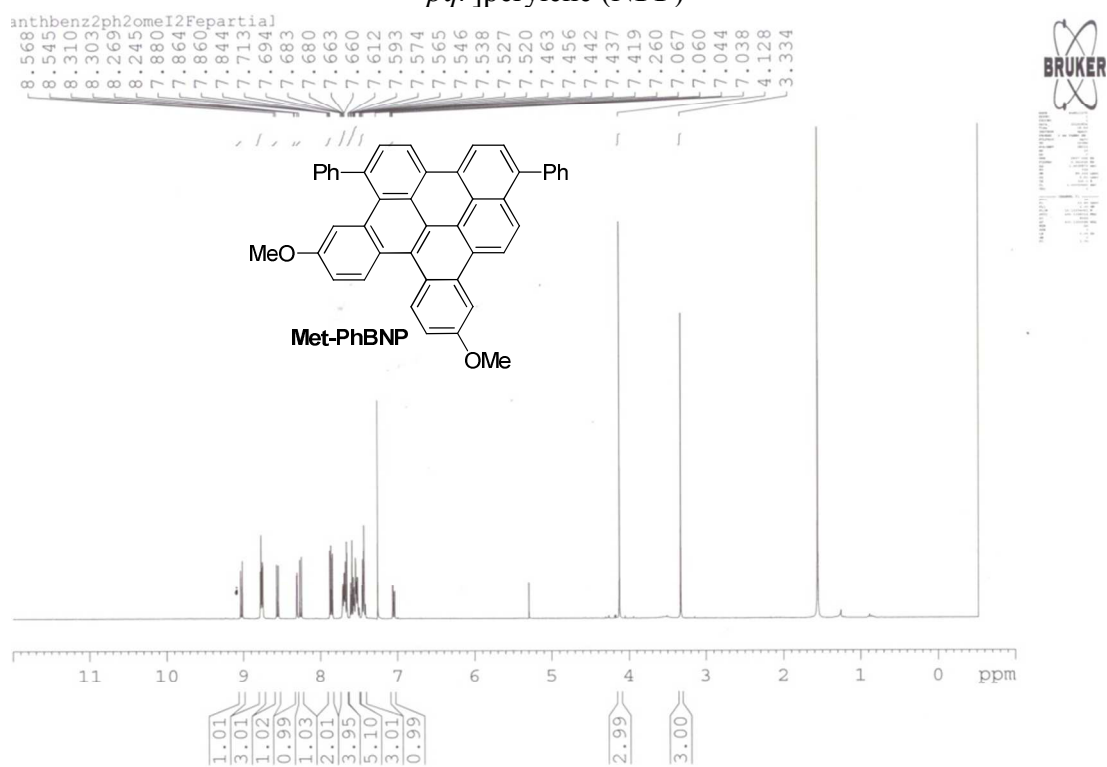


Figure S66. ^1H NMR spectrum of 2,7-dimethoxy-9,14-diphenylbenzo[*b*]naphtho[1,2,3,4-*pqr*]perylene (Met-PhBNP)

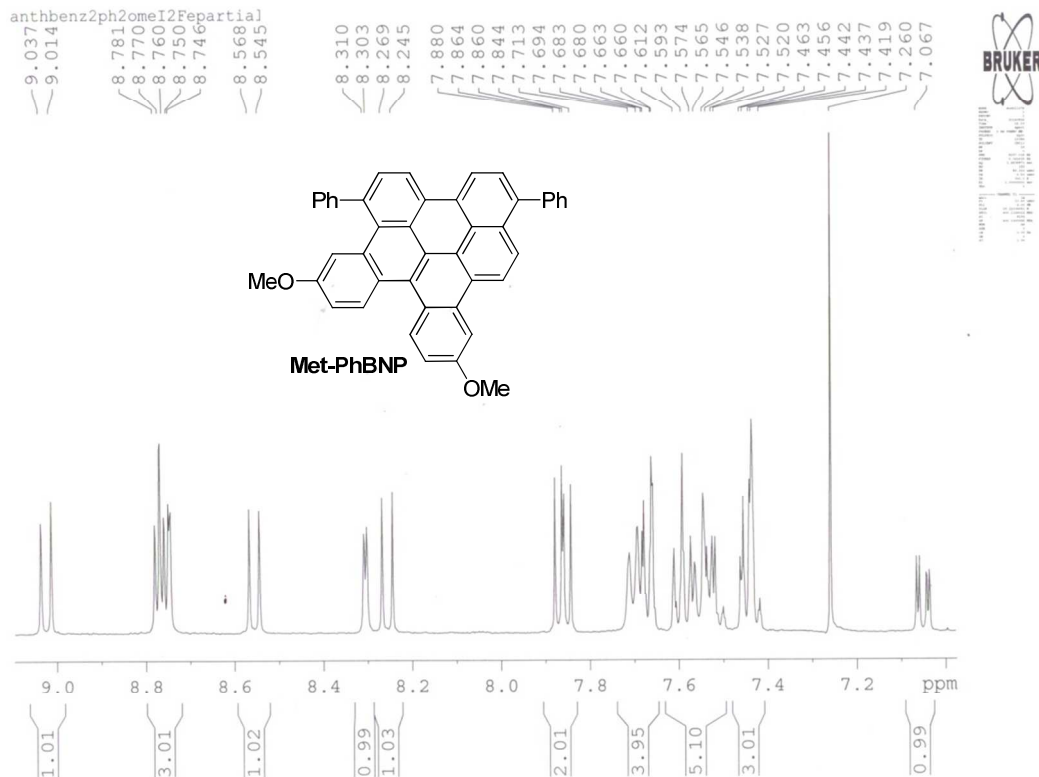


Figure S67. ^1H NMR spectrum (expansion) of 2,7-dimethoxy-9,14-diphenylbenzo[*b*]naphtho[1,2,3,4-*pqr*]perylene (Met-PhBNP)

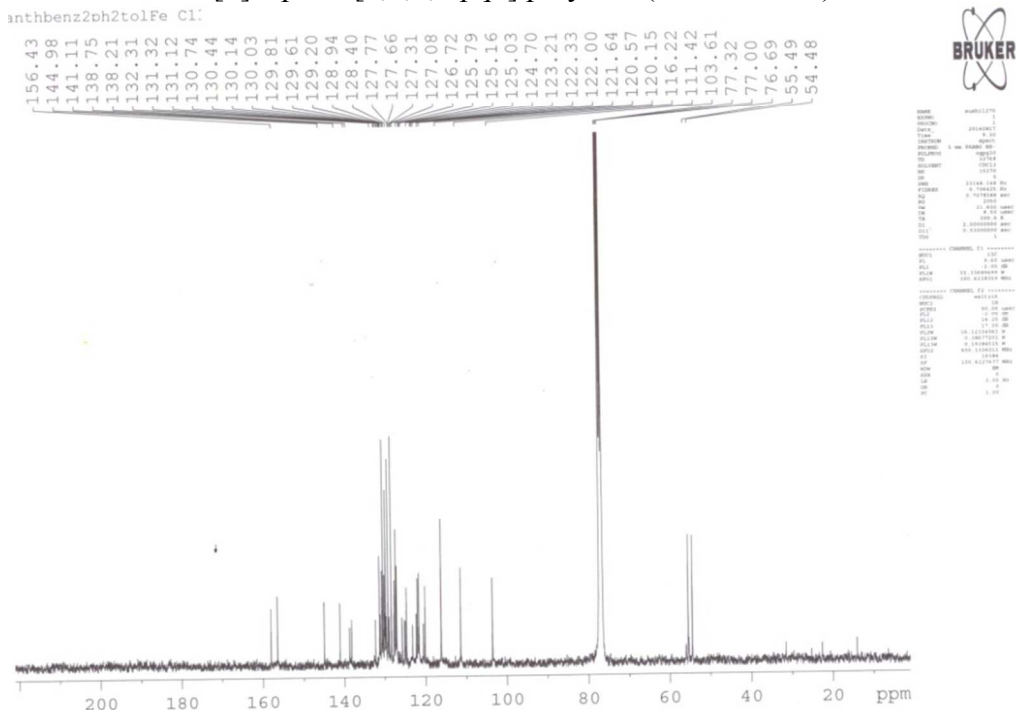


Figure S68. ^{13}C NMR spectrum of 2,7-dimethoxy-9,14-diphenylbenzo[*b*]naphtho[1,2,3,4-*pqr*]perylene (Met-PhBNP)

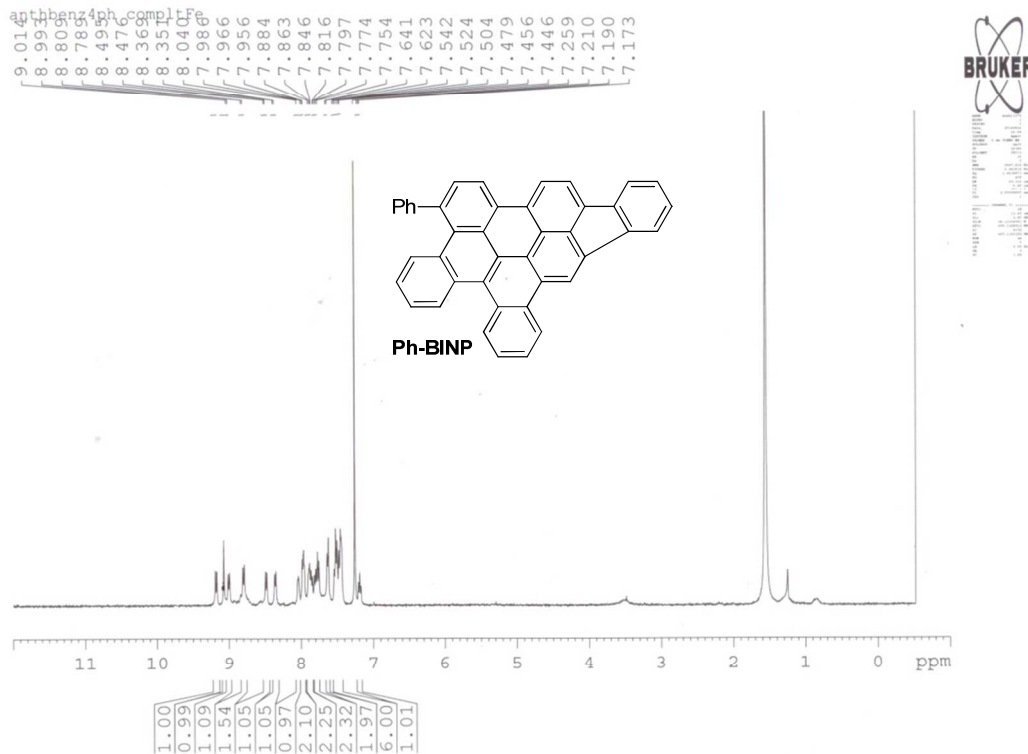


Figure S69. ^1H NMR spectrum of 18-phenylbenzo[*b*]indeno[1,2,3-*lm*]naphtho[1,2,3,4-*pqr*]perylene (**Ph-BINP**)

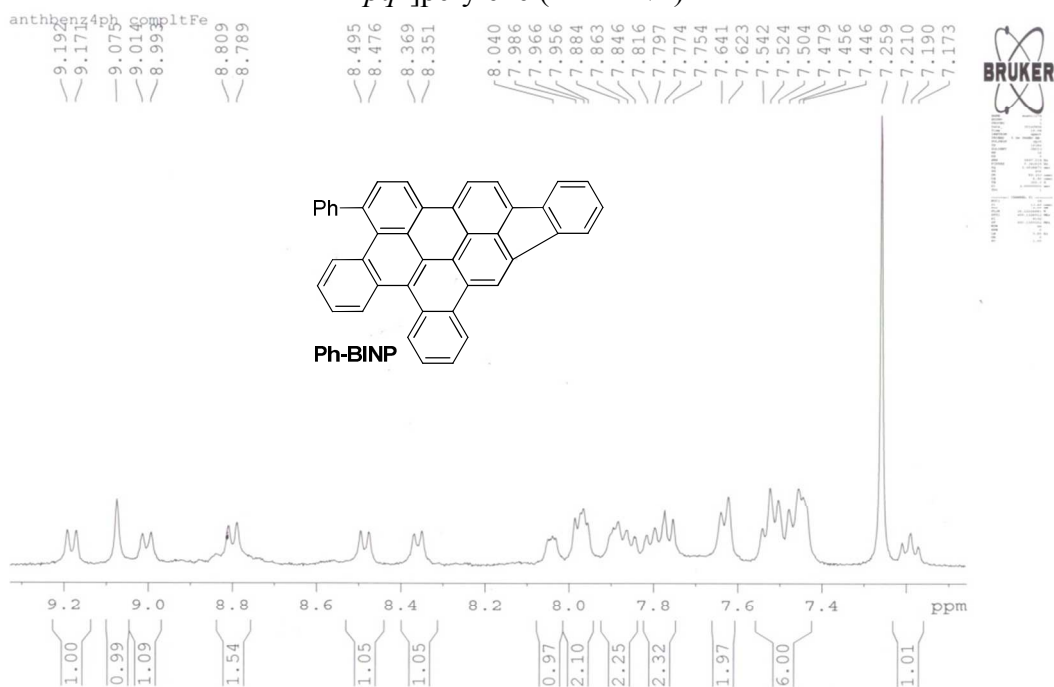


Figure S70. ^1H NMR spectrum (expansion) of 18-phenylbenzo[*b*]indeno[1,2,3-*lm*]naphtho[1,2,3,4-*pqr*]perylene (**Ph-BINP**)

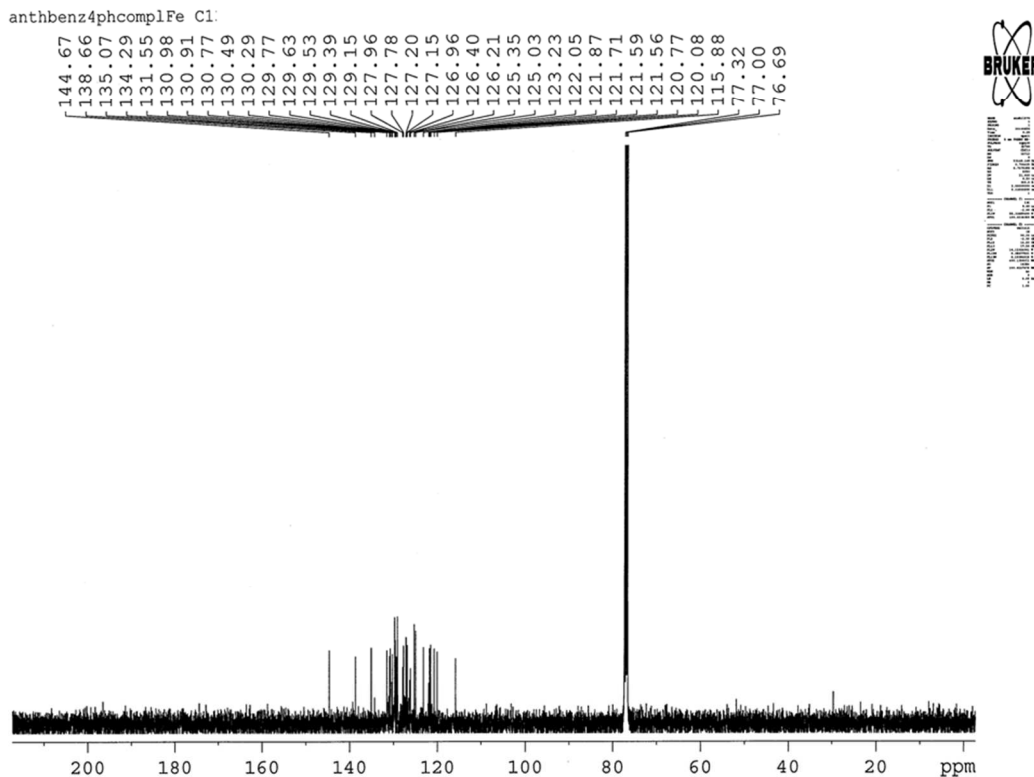


Figure S71. ^{13}C NMR spectrum of 18-phenylbenzo[*b*]indeno[1,2,3-*lm*]naphtho[1,2,3,4-*pqr*]perylene (**Ph-BINP**)

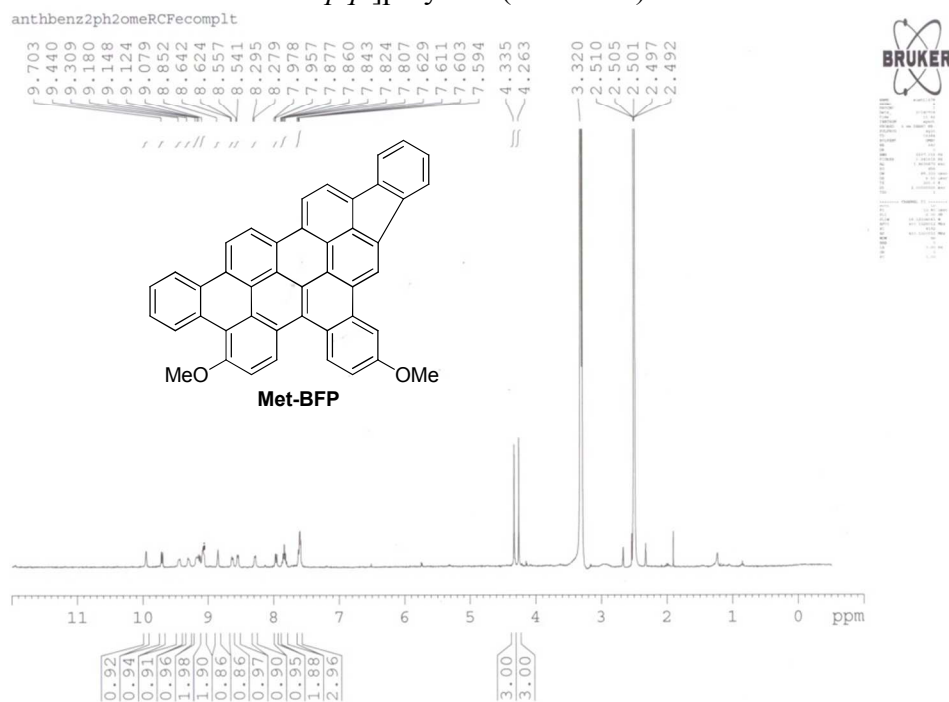


Figure S72. ^1H NMR spectrum of 5,10-dimethoxytribenzo[*a,ghi,k*]fluorantheno[2,3,4-*cde*]perylene (**Met-BFP**)

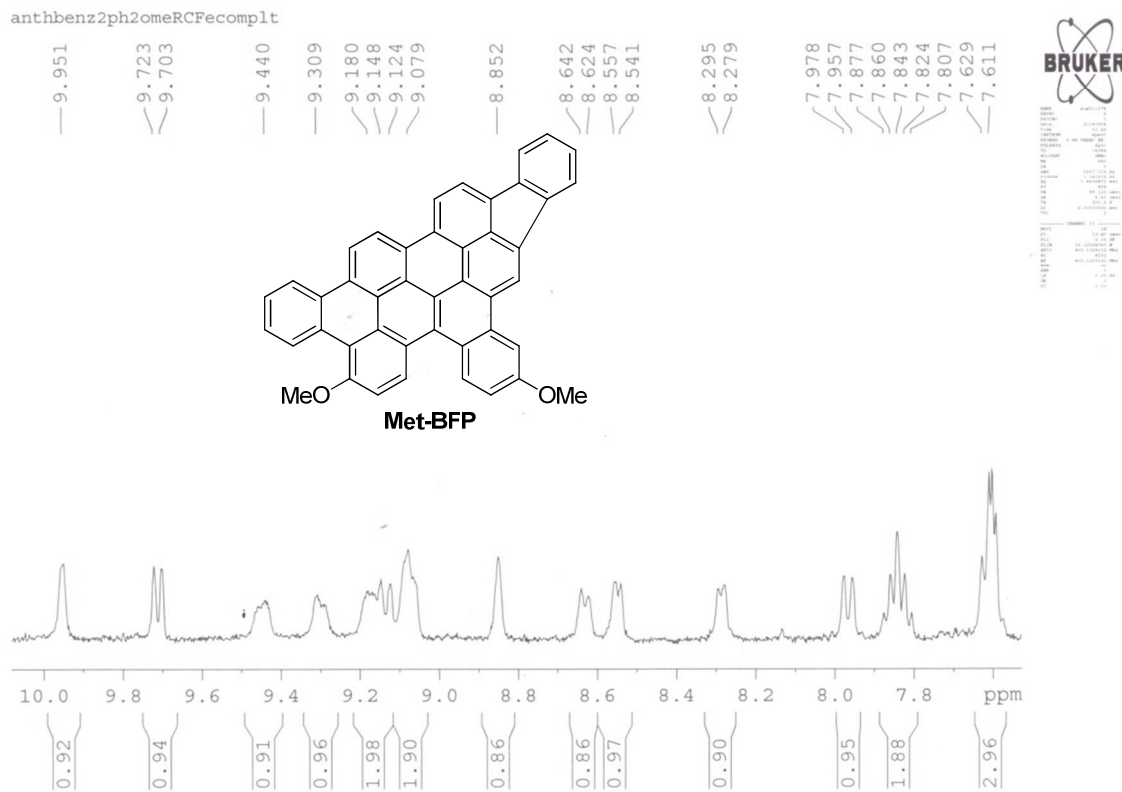


Figure S73. ^1H NMR spectrum (expansion) of 5,10-dimethoxytribenzo[*a,ghi,k*]fluorantheno[2,3,4-*cde*]perylene (**Met-BFP**)

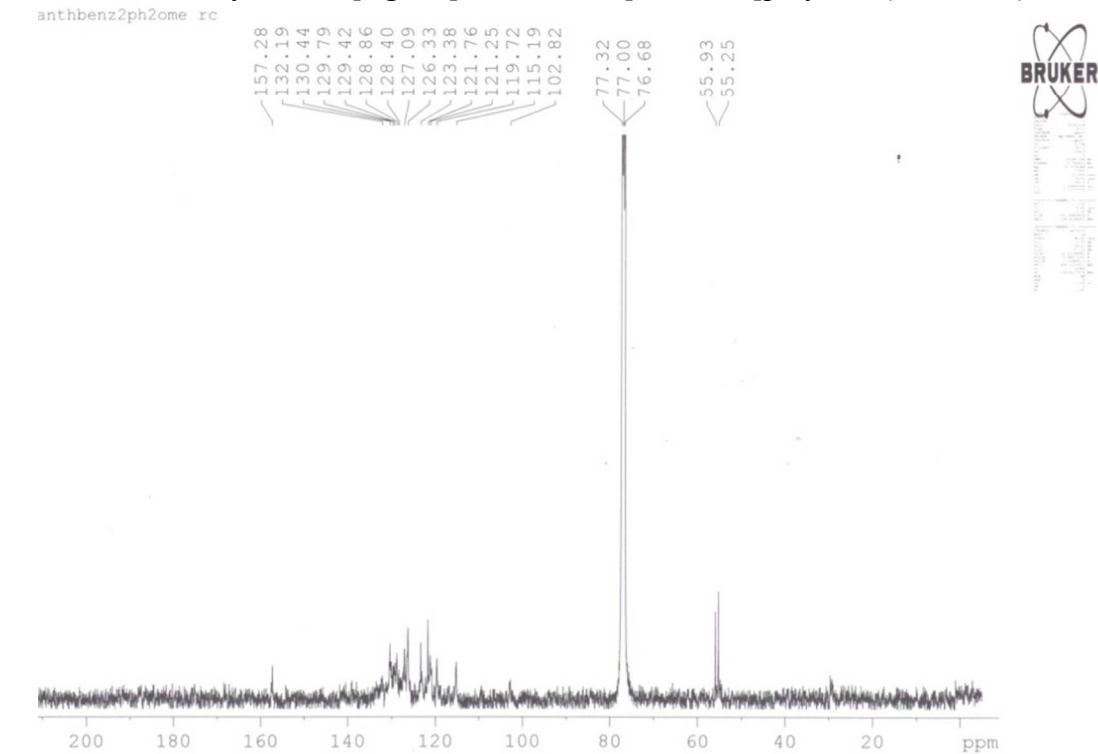
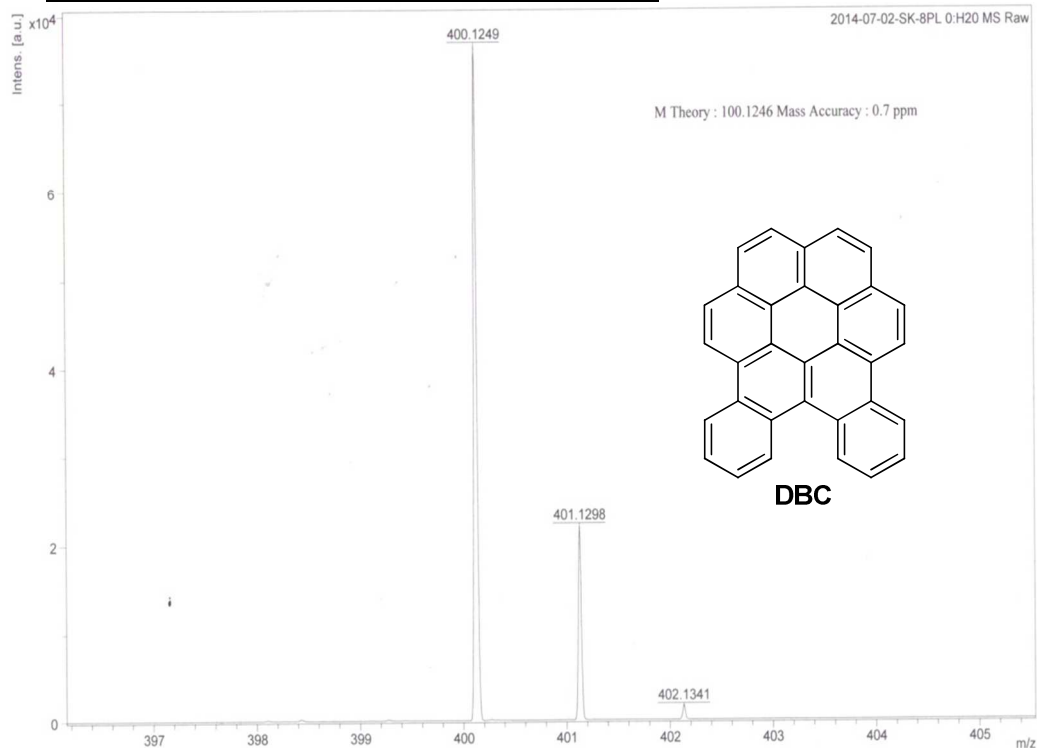
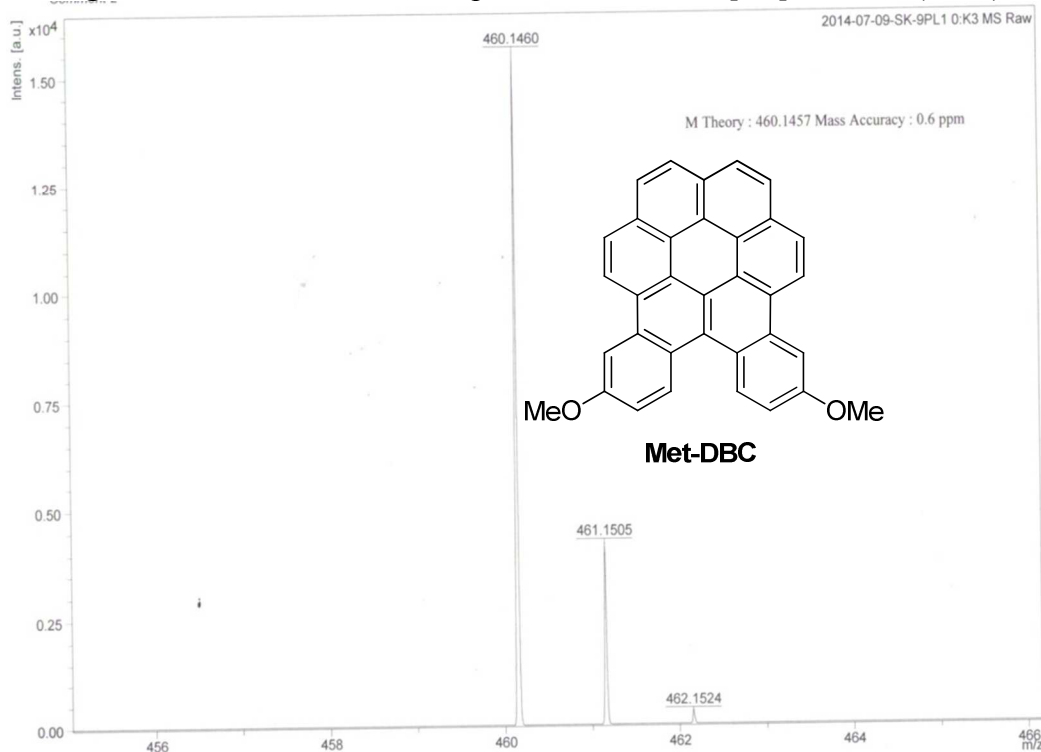


Figure S74. ^{13}C NMR spectrum of 5,10-dimethoxytribenzo[*a,ghi,k*]fluorantheno[2,3,4-*cde*]perylene (**Met-BFP**)

5. MALDI-TOF MS spectra of final derivatives

Figure S75. MALDI-TOF MS spectrum of Dibenzo[*a,d*]coronene (DBC)Figure S76. MALDI-TOF MS spectrum of 8,13-dimethoxydibenzo[*a,d*]coronene (Met-DBC)

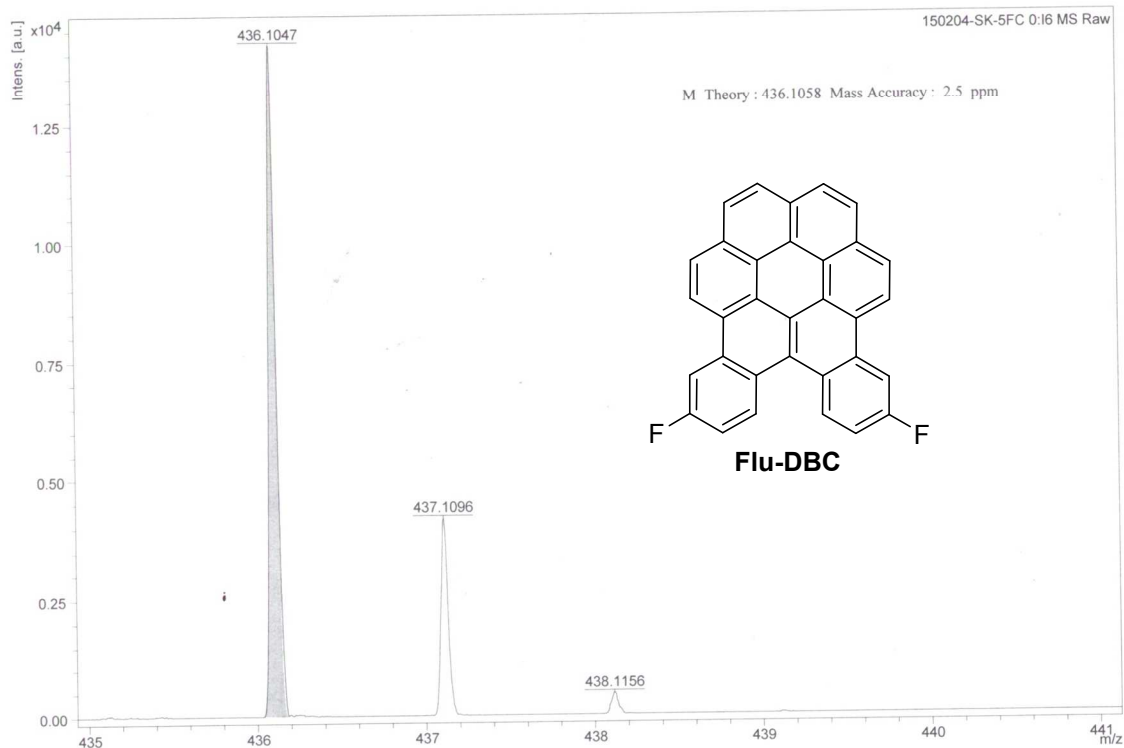


Figure S77. MALDI-TOF MS spectrum of 8,13-dimethoxydibenzo[*a,d*]coronene (**Flu-DBC**)

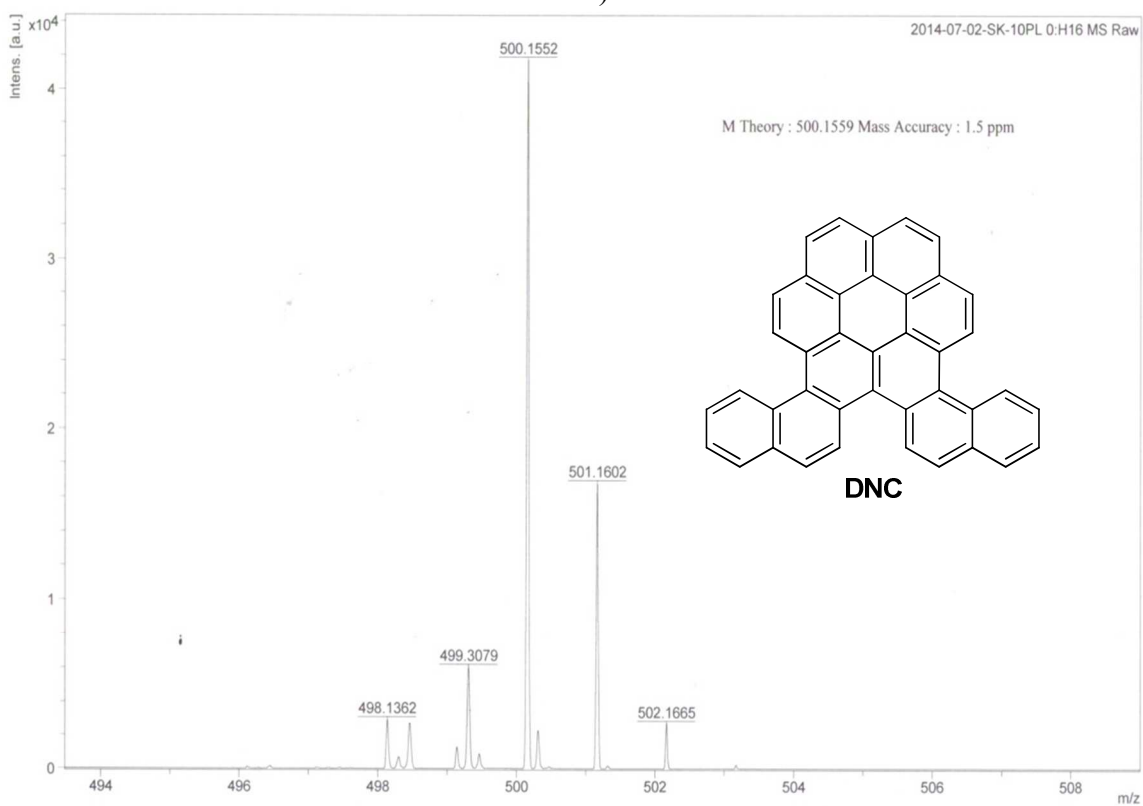


Figure S78. MALDI-TOF MS spectrum of dinaphtho[1,2-*a*:2',1'-*d*]coronene (**DNC**)

Supporting Information

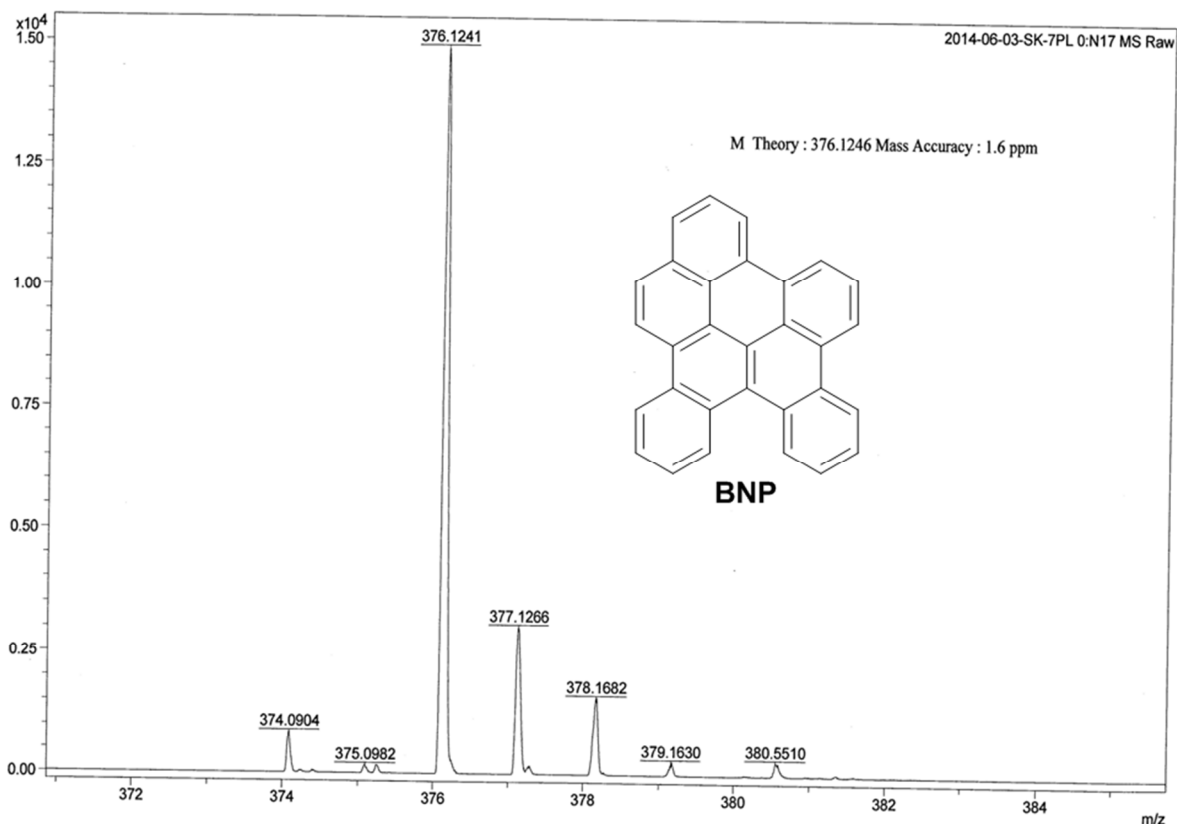


Figure S79. MALDI-TOF MS spectrum of benzo[*b*]naphtho[1,2,3,4-*pqr*]perylene (BNP)

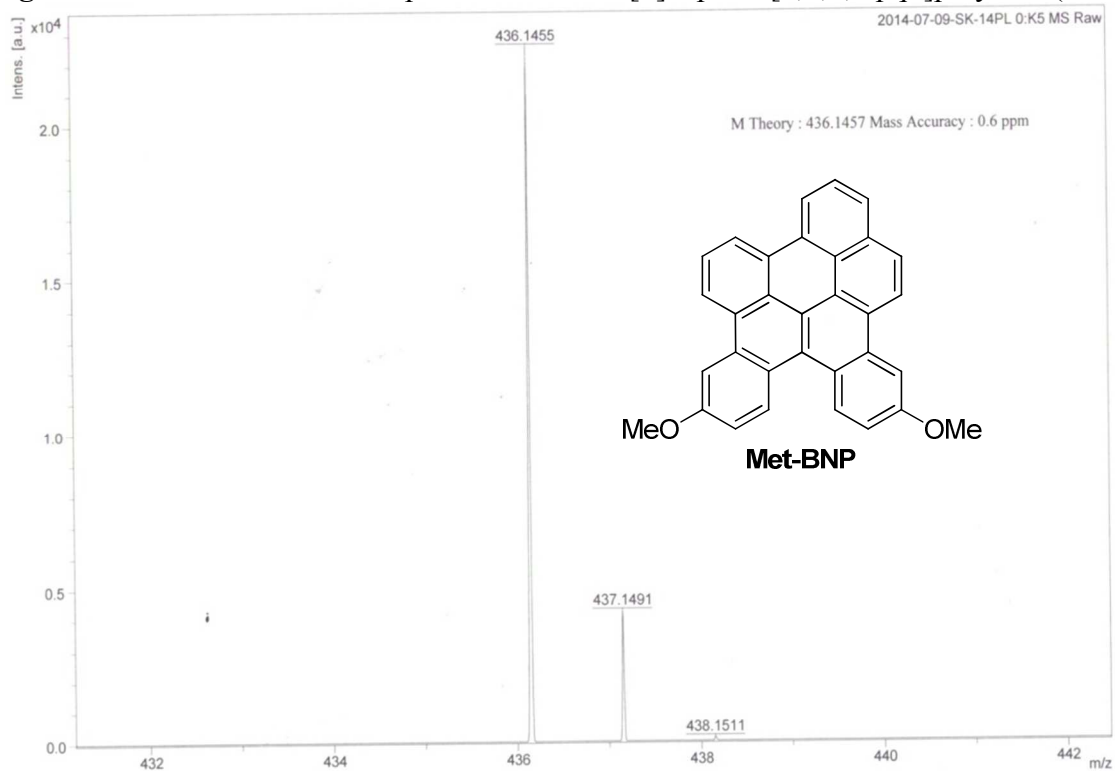


Figure S80. MALDI-TOF MS spectra of 2,7-dimethoxybenzo[*b*]naphtho[1,2,3,4-*pqr*]perylene (Met-BNP)

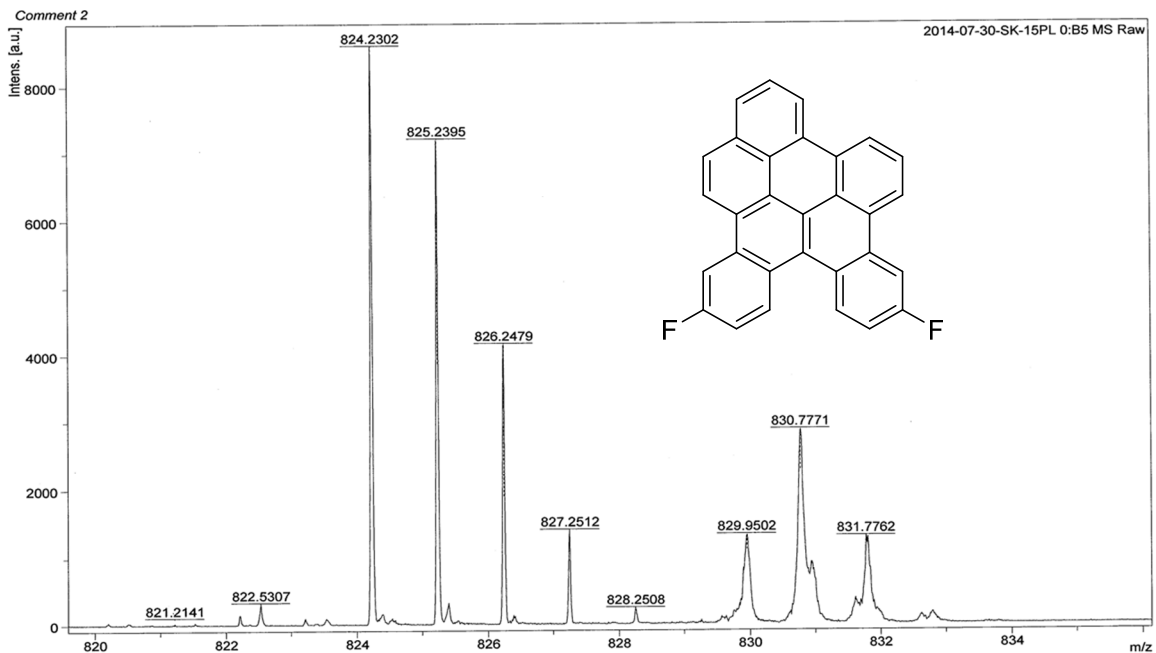


Figure S81. Maldi-Tof mass spectrum of 2,7-difluorobenzo[*b*]naphtho[1,2,3,4-*pqr*]perylene (**Flu-BNP**)

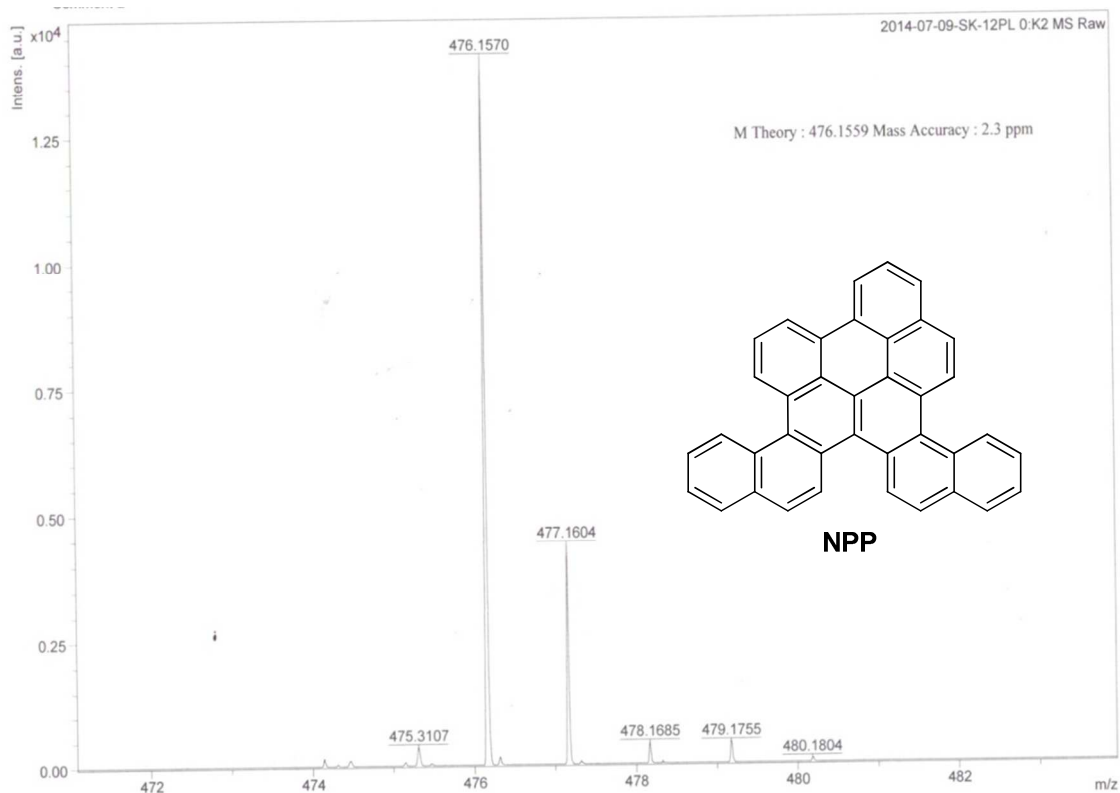


Figure S82. MALDI-TOF MS spectrum of naphtho[2,1-*b*]phenanthro[4,3,2,1-*pqr*]perylene (**NPP**)

Supporting Information

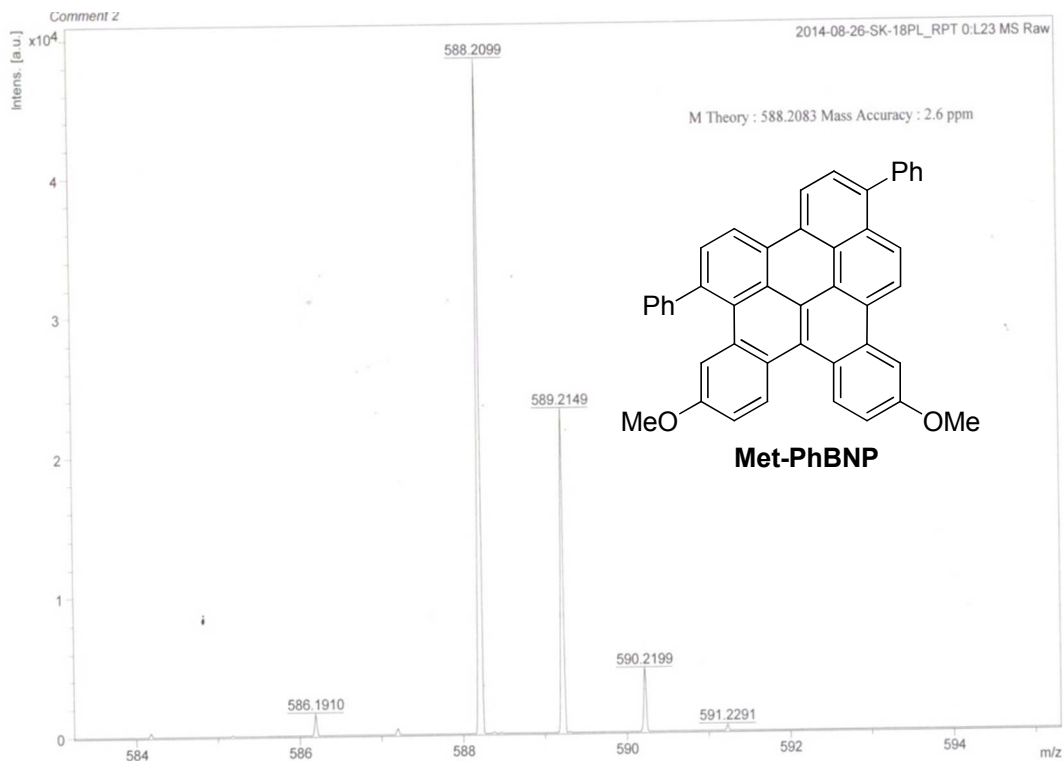


Figure S83. MALDI-TOF MS spectrum of 2,7-dimethoxy-9,14-diphenylbenzo[*b*]naphtho[1,2,3,4-*pqr*]perylene (**Met-PhBNP**)

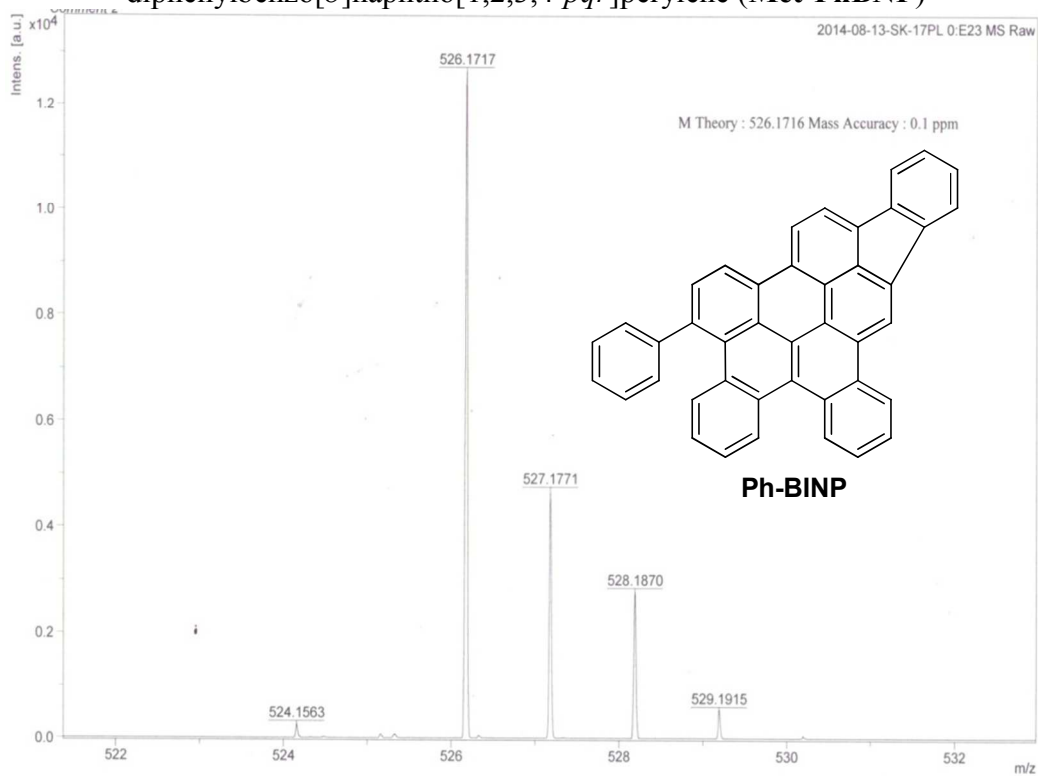


Figure S84. MALDI-TOF MS spectrum of 18-phenylbenzo[*b*]indeno[1,2,3-*lm*]naphtho[1,2,3,4-*pqr*]perylene (**Ph-BINP**)

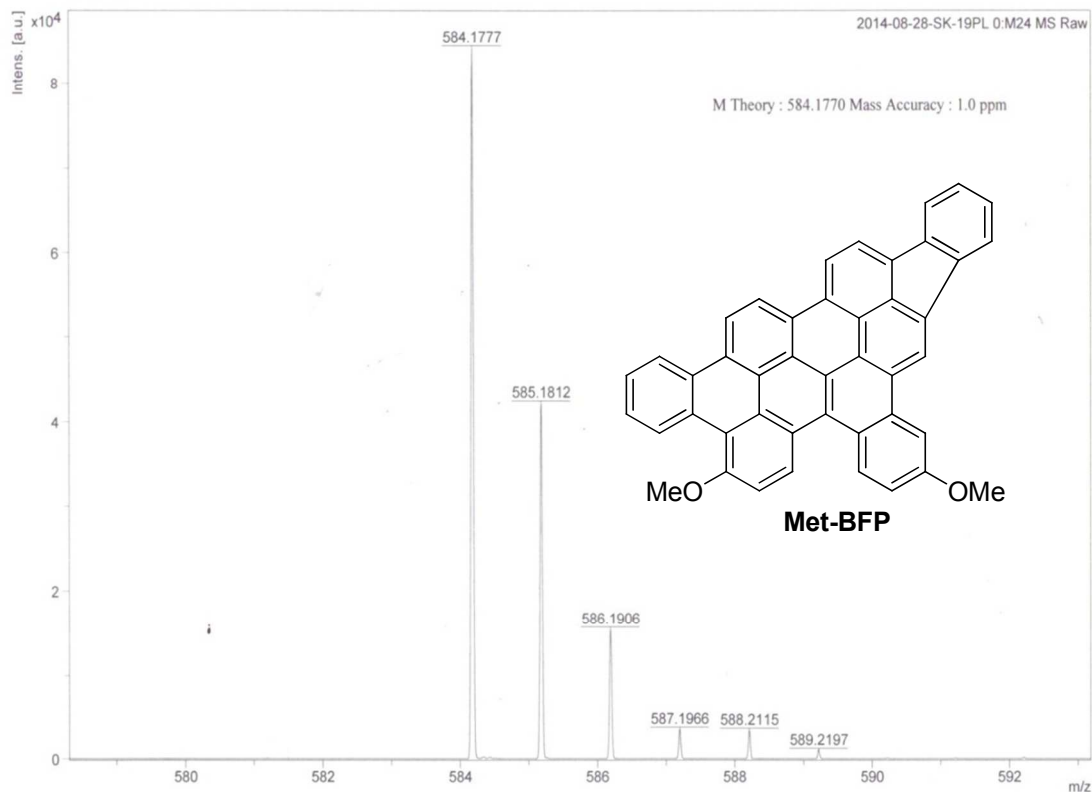


Figure S85. MALDI-TOF MS spectrum of 5,10-dimethoxytribenzo[*a,ghi,k*]fluorantheno[2,3,4-*cde*]perylene (**Met-BFP**)

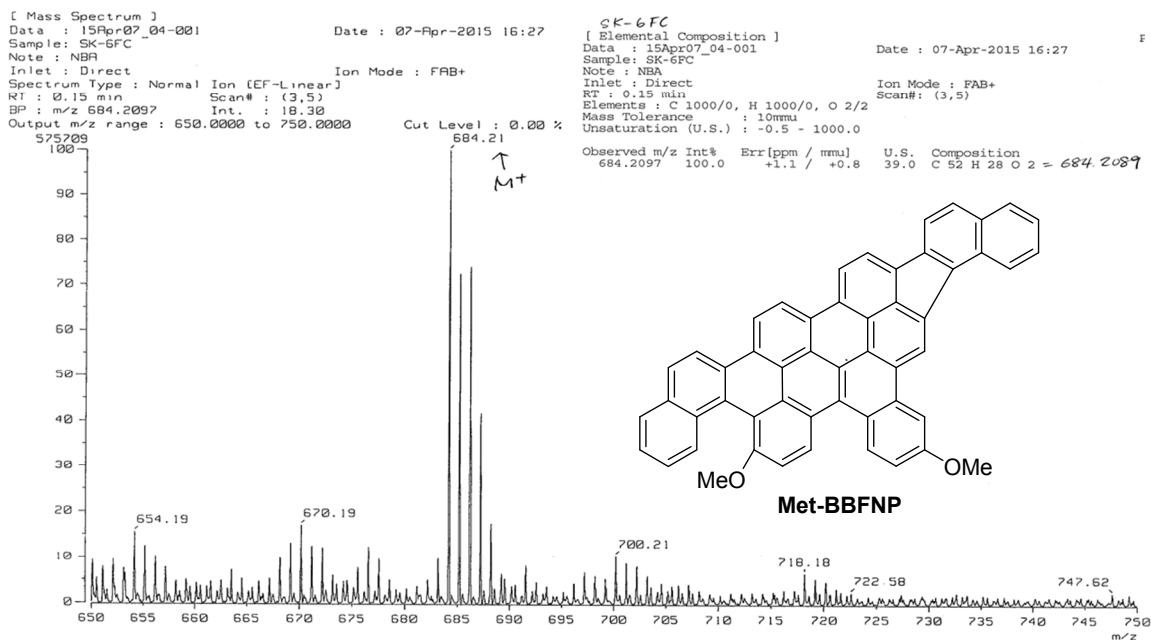


Figure S86. High resolution Fab-spectrum 5,10-dimethoxy dibenzo[*a,ghi*] benzo[9,10]fluorantheno[2,3,4-*cde*]naphtho[2,1-*k*]perylene (**Met-BBFNP**)

6. Single-crystal data and packing in DBC, Flu-DBC, DNC and Ph-BINP molecules.

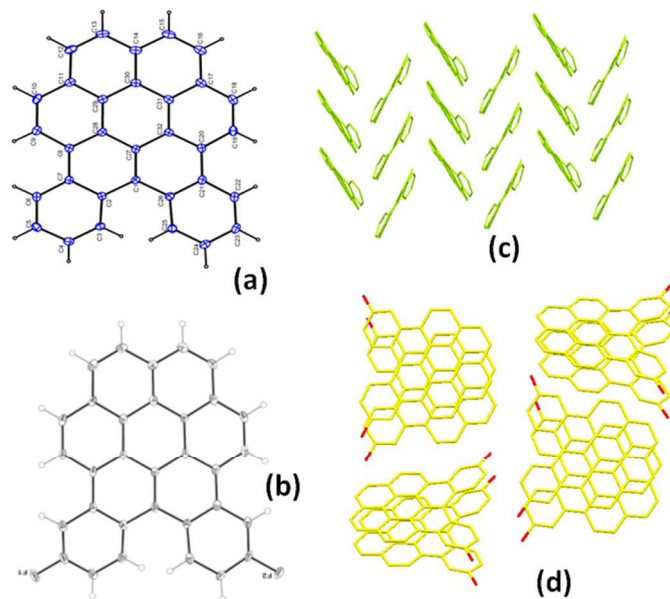


Figure S87 (a-b). Thermal ellipsoids of **DBC** (52%) and **Flu-DBC** (48%); **(c-d)** Packing of molecules in **DBC** and **Flu-DBC**

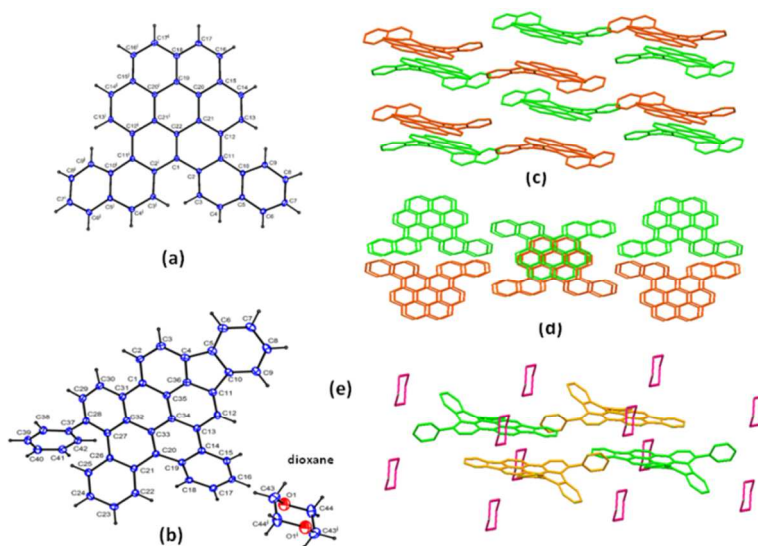


Figure S88. (a-b) ORTEP plots of **DNC** (51%) and **Ph-BINP** (46%); **(c-d)** Packing arrangement in **DNC**; **(e)** Packing arrangement in **Ph-BINP**.

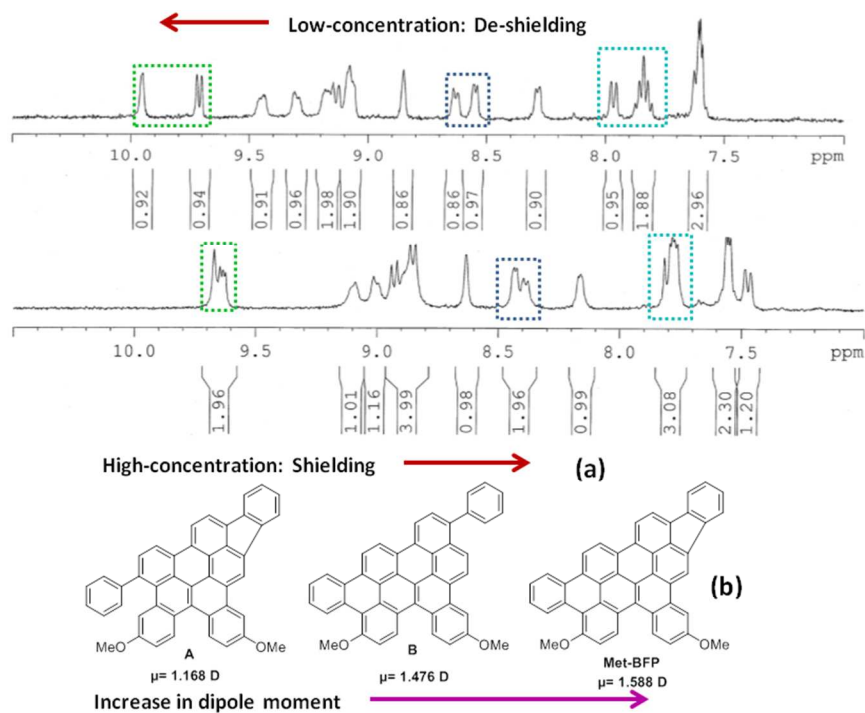


Figure S89. NMR spectra of **Met-BFP** recorded at different concentrations in DMSO-d_6 ; (b) estimated dipole moment change upon fusion into planar **Met-BFP** from its precursors.

7. Absorption/emission spectra of final derivatives as recorded in dichloromethane

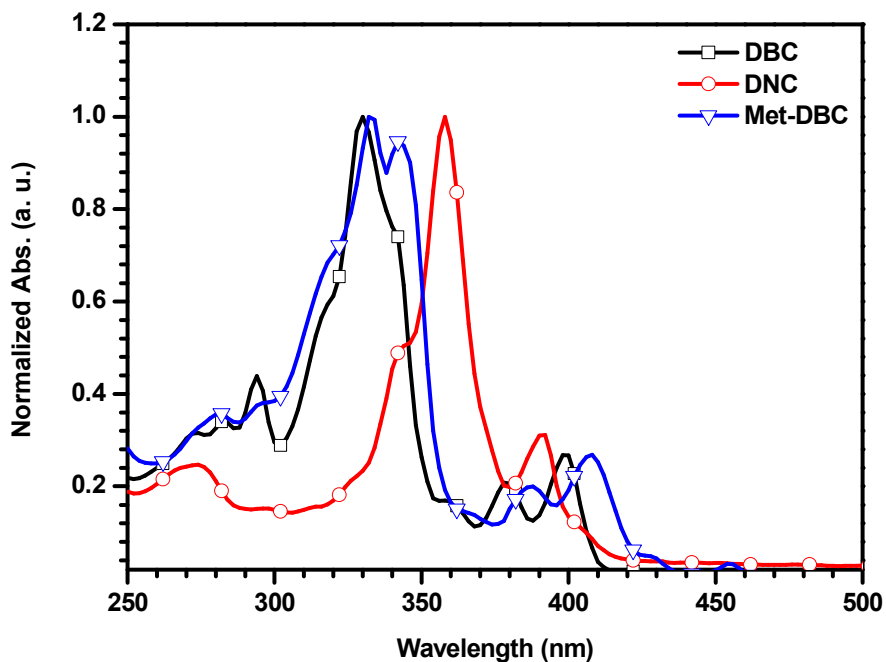


Figure S90. Normalized absorption spectra of coronene derivatives

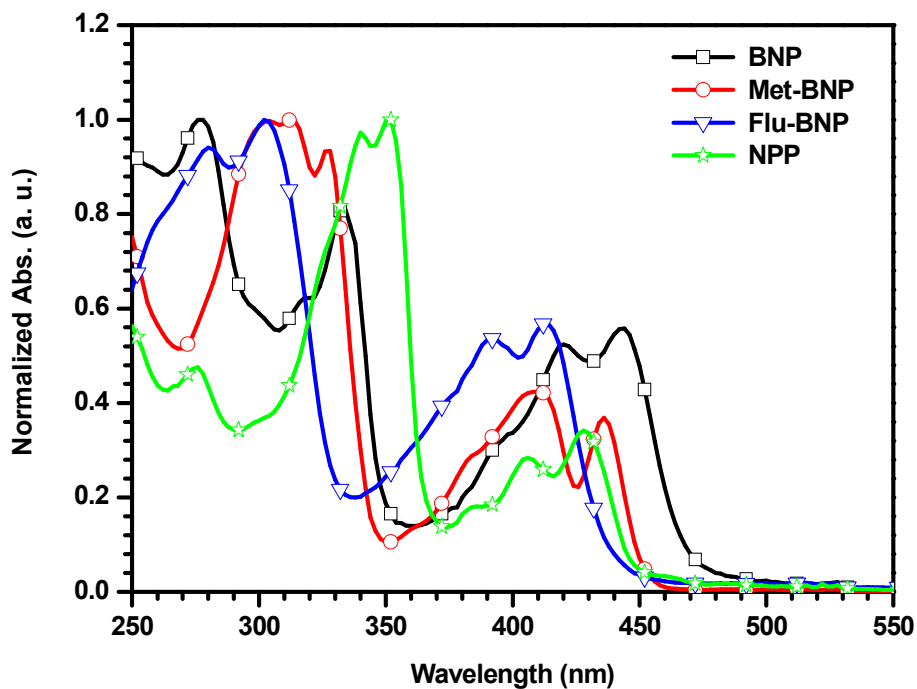


Figure S91. Normalized absorption spectra of perylene derivatives

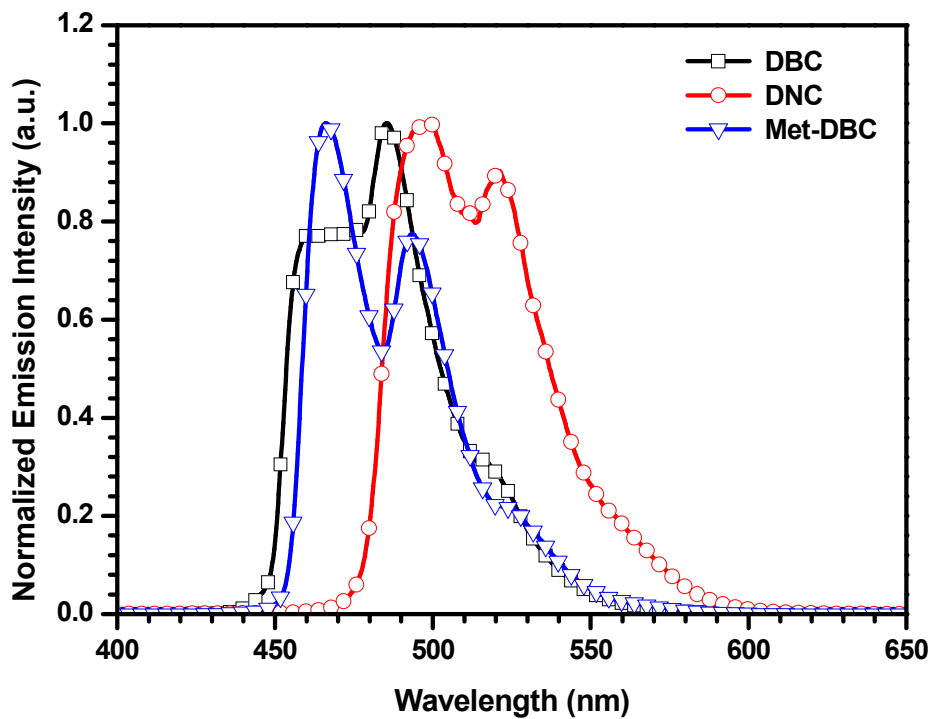


Figure S92. Normalized emission spectra of coronene derivatives

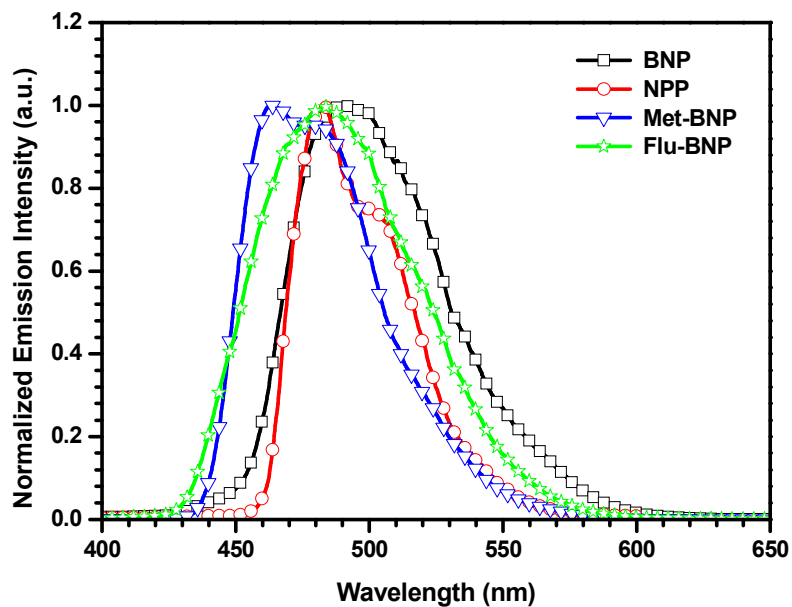


Figure S93. Normalized emission spectra of perylene derivatives

8. Thermogravimetric plots of DBC and Flu-DBC

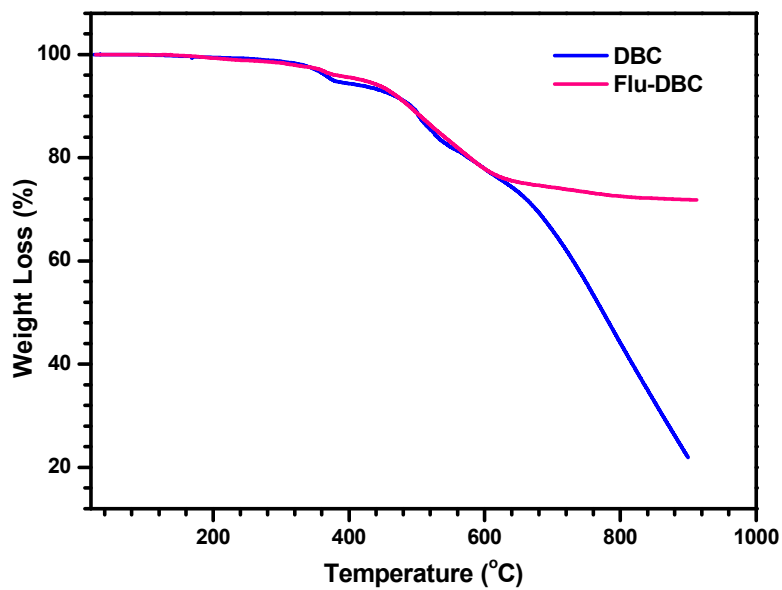


Figure S94. Thermogravimetric plot of DBC and Flu-DBC

9. HOMO/LUMO plots of coronene- and perylene-embedded derivatives

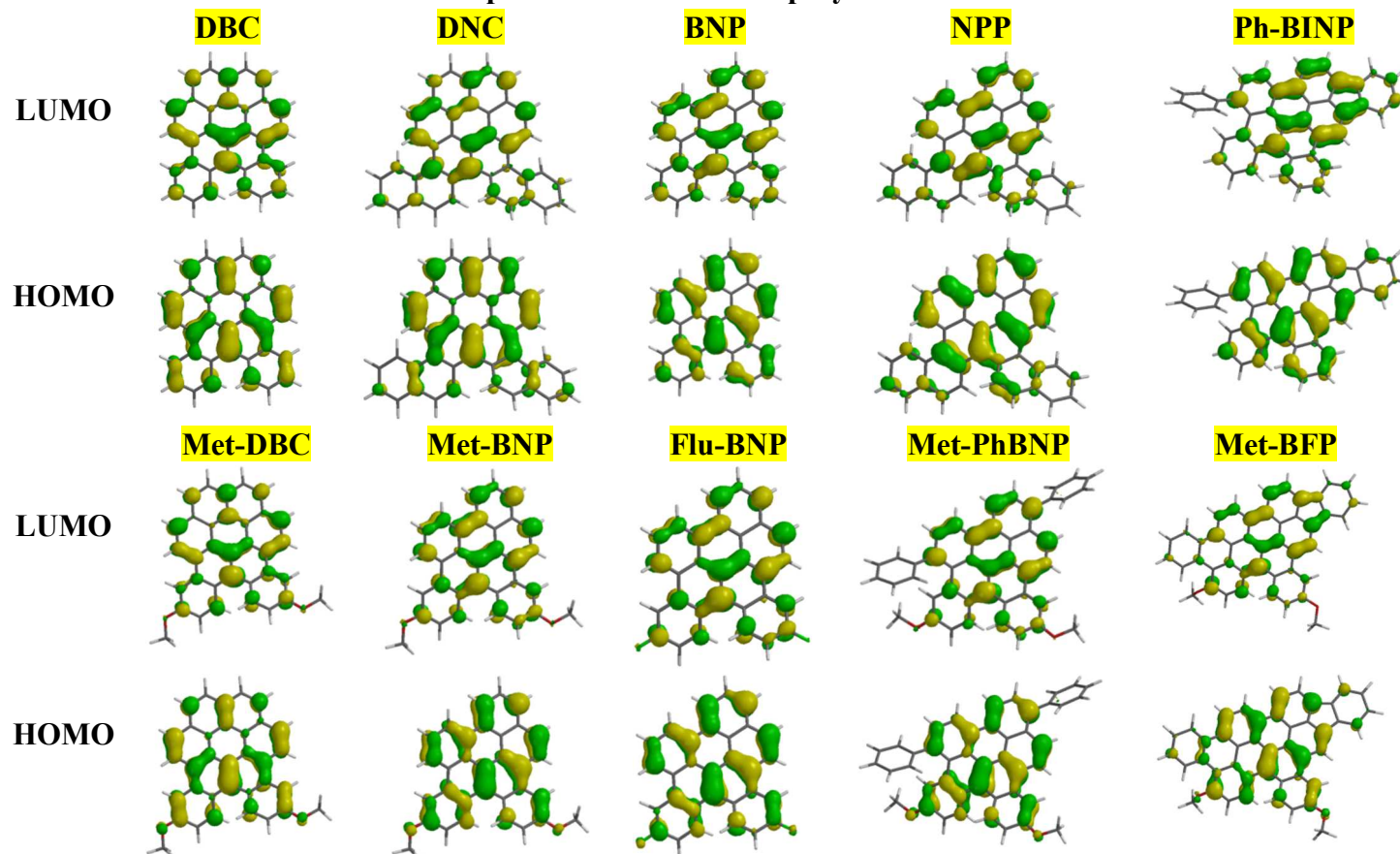


Figure S95. HOMO/LUMO plots of coronene and perylene derivatives (Obtained by Spartan pro software by semi-empirical method at level AM1)

10. Single-crystal data, packing and device performance data for the DBC and Flu-DBC

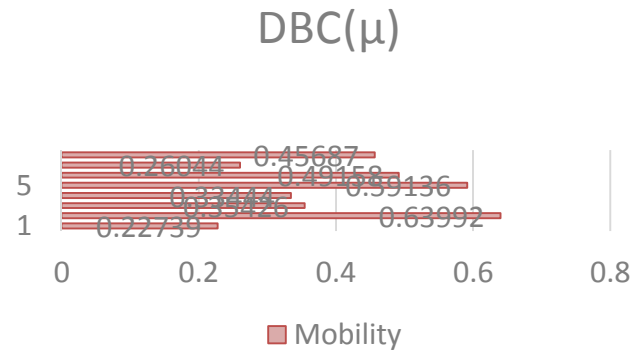


Figure S96. The mobility data obtained for different devices made by using **DBC**

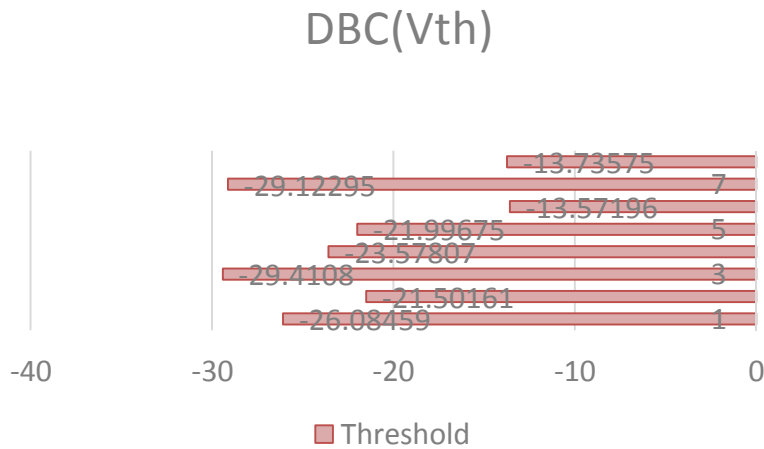


Figure S97. The threshold voltage data obtained for different devices made by using **DBC**

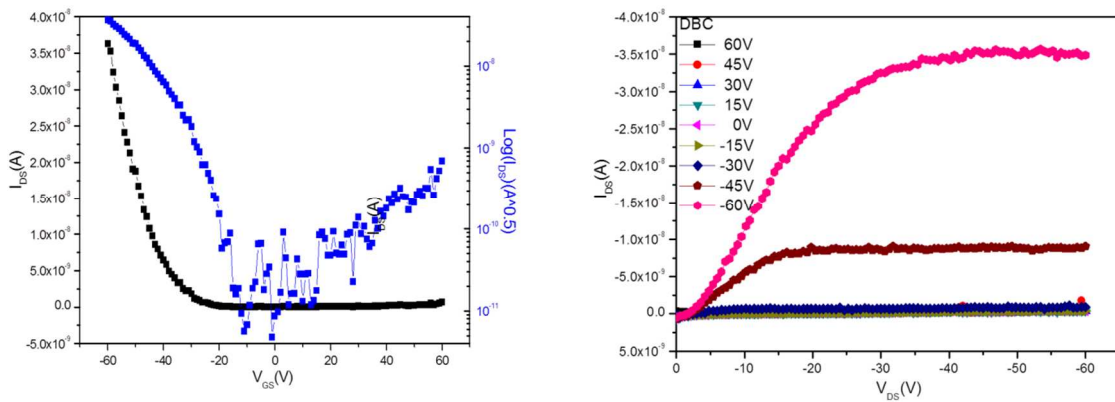


Figure S98. I_d/V curve for **DBC**

Table S1. Photo-physical data for coronene- and perylene-embedded derivatives

Compd.	$\lambda_{\text{abs.}}$, nm	$\lambda_{\text{em.}}$, nm	Stokes shift (cm^{-1})	E_g
DBC	399, 379, 330, 293	486, 460 (max)	3324	3.061
DNC	392, 358, 275	520, 500 (max)	5510	3.031
Met-DBC	408, 387, 342, 332, 281	494, 466 (max)	3051	2.988
BNP	444, 421, 334, 277	493	2239	2.707
NPP	428, 406, 351, 340, 276	482	2618	2.818
Met-BNP	436, 411, 327, 312,	463	1338	2.786
Flu-BNP	413, 391, 303, 281	483	3509	2.910
Met-PhBNP	450, 419, 312	494	1979	2.684
Ph-BINP	479, 421, 345, 285	536 (max), 526	1865	2.520
Met-BFP	511, 480, 447, 358, 288	548	1321	2.362

E_g , the optical band-gap

Table S2. Single-crystal OFET performance of **DBC**.

	μ	μ_{average}	On/off	Threshold
	(Cm^2/Vs)	(Cm^2/Vs)	ratio	Voltage
				(V_{th} , V)
DBC	0.23-0.64	0.42 ± 0.15	10^3 - 10^4	(-13)-(-29)

10. Single-Crystal data of Ph-BINP, DNC, DBC and Flu-DBC**Single-crystal data for Ph-BINP**Table 1. Crystal data and structure refinement for **Ph-BINP**.

Identification code	i15298	
Empirical formula	C44 H26 O	
Formula weight	570.65	
Temperature	100.0(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 6.8964(6) Å b = 14.2616(13) Å c = 14.9139(13) Å	$\alpha = 113.498(5)^\circ$ $\beta = 97.210(5)^\circ$ $\gamma = 91.404(5)^\circ$
Volume	1330.1(2) Å ³	
Z	2	
Density (calculated)	1.425 Mg/m ³	
Absorption coefficient	0.083 mm ⁻¹	
F(000)	596	
Crystal size	0.180 x 0.140 x 0.040 mm ³	
Theta range for data collection	1.562 to 27.102°	
Index ranges	-8<=h<=8, -18<=k<=18, -19<=l<=19	
Reflections collected	61961	
Independent reflections	5862 [R(int) = 0.1746]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9705 and 0.681	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5862 / 0 / 407	
Goodness-of-fit on F ²	1.020	
Final R indices [I>2sigma(I)]	R1 = 0.0718, wR2 = 0.1727	
R indices (all data)	R1 = 0.1436, wR2 = 0.2141	
Extinction coefficient	0.004(2)	
Largest diff. peak and hole	0.463 and -0.542 e.Å ⁻³	

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for i15298. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7570(4)	5556(2)	6992(2)	22(1)
C(2)	7663(4)	6625(2)	7323(2)	24(1)
C(3)	7689(4)	7126(3)	6683(2)	27(1)
C(4)	7626(4)	6557(2)	5681(2)	24(1)
C(5)	7589(4)	6764(2)	4782(2)	25(1)
C(6)	7568(4)	7675(3)	4649(3)	28(1)
C(7)	7491(4)	7624(3)	3690(3)	30(1)
C(8)	7449(4)	6699(3)	2897(3)	29(1)
C(9)	7455(4)	5780(3)	3014(2)	26(1)
C(10)	7516(4)	5808(2)	3957(2)	23(1)
C(11)	7496(4)	4989(2)	4317(2)	21(1)
C(12)	7393(4)	3944(2)	3890(2)	23(1)
C(13)	7342(4)	3365(2)	4484(2)	20(1)
C(14)	7021(4)	2268(2)	4052(2)	21(1)
C(15)	6700(4)	1696(2)	3015(2)	26(1)
C(16)	6051(4)	675(2)	2595(2)	26(1)
C(17)	5651(4)	177(2)	3194(2)	25(1)
C(18)	6086(4)	691(2)	4201(2)	24(1)
C(19)	6879(4)	1722(2)	4664(2)	22(1)

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C(20)	7379(4)	2266(2)	5730(2)	20(1)
C(21)	7933(4)	1741(2)	6380(2)	21(1)
C(22)	8625(4)	752(2)	6024(2)	23(1)
C(23)	9444(4)	332(2)	6652(2)	25(1)
C(24)	9662(5)	899(3)	7668(2)	31(1)
C(25)	8989(5)	1852(3)	8037(2)	29(1)
C(26)	8075(4)	2294(2)	7415(2)	21(1)
C(27)	7562(4)	3353(2)	7815(2)	21(1)
C(28)	7168(4)	3871(2)	8803(2)	24(1)
C(29)	7057(4)	4923(2)	9176(2)	27(1)
C(30)	7256(4)	5478(2)	8613(2)	25(1)
C(31)	7471(4)	4989(2)	7617(2)	22(1)
C(32)	7552(4)	3900(2)	7202(2)	21(1)
C(33)	7492(4)	3329(2)	6144(2)	19(1)
C(34)	7443(4)	3877(2)	5519(2)	19(1)
C(35)	7540(4)	4967(2)	5963(2)	19(1)
C(36)	7560(4)	5488(2)	5353(2)	22(1)
C(37)	6719(5)	3323(3)	9423(2)	29(1)
C(38)	7725(5)	3617(3)	10374(2)	31(1)
C(39)	7351(5)	3090(3)	10946(2)	35(1)
C(40)	5897(5)	2300(3)	10604(3)	38(1)
C(41)	4797(5)	2022(3)	9670(2)	34(1)
C(42)	5215(5)	2531(3)	9090(2)	31(1)
O(1)	8280(4)	56(2)	443(2)	63(1)
C(43)	9973(6)	788(3)	907(3)	53(1)
C(44)	8194(6)	-302(4)	-595(3)	52(1)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for i15298.

C(1)-C(2)	1.399(4)
C(1)-C(35)	1.423(4)
C(1)-C(31)	1.463(4)
C(2)-C(3)	1.404(4)
C(2)-H(2)	0.9500
C(3)-C(4)	1.382(4)
C(3)-H(3)	0.9500
C(4)-C(36)	1.401(4)
C(4)-C(5)	1.481(4)
C(5)-C(6)	1.390(4)
C(5)-C(10)	1.420(4)
C(6)-C(7)	1.397(5)
C(6)-H(6)	0.9500
C(7)-C(8)	1.373(5)
C(7)-H(7)	0.9500
C(8)-C(9)	1.389(4)
C(8)-H(8)	0.9500
C(9)-C(10)	1.386(4)
C(9)-H(9)	0.9500
C(10)-C(11)	1.468(4)
C(11)-C(12)	1.363(4)
C(11)-C(36)	1.413(4)
C(12)-C(13)	1.434(4)
C(12)-H(12)	0.9500
C(13)-C(34)	1.412(4)
C(13)-C(14)	1.434(4)
C(14)-C(15)	1.417(4)
C(14)-C(19)	1.426(4)
C(15)-C(16)	1.372(4)
C(15)-H(15)	0.9500
C(16)-C(17)	1.393(4)
C(16)-H(16)	0.9500

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C(17)-C(18)	1.371(4)
C(17)-H(17)	0.9500
C(18)-C(19)	1.412(4)
C(18)-H(18)	0.9500
C(19)-C(20)	1.454(4)
C(20)-C(33)	1.386(4)
C(20)-C(21)	1.464(4)
C(21)-C(22)	1.414(4)
C(21)-C(26)	1.415(4)
C(22)-C(23)	1.374(4)
C(22)-H(22)	0.9500
C(23)-C(24)	1.389(4)
C(23)-H(23)	0.9500
C(24)-C(25)	1.365(4)
C(24)-H(24)	0.9500
C(25)-C(26)	1.412(4)
C(25)-H(25)	0.9500
C(26)-C(27)	1.456(4)
C(27)-C(32)	1.418(4)
C(27)-C(28)	1.426(4)
C(28)-C(29)	1.384(4)
C(28)-C(37)	1.482(4)
C(29)-C(30)	1.380(4)
C(29)-H(29)	0.9500
C(30)-C(31)	1.396(4)
C(30)-H(30)	0.9500
C(31)-C(32)	1.430(4)
C(32)-C(33)	1.454(4)
C(33)-C(34)	1.433(4)
C(34)-C(35)	1.422(4)
C(35)-C(36)	1.386(4)
C(37)-C(38)	1.390(4)
C(37)-C(42)	1.402(5)
C(38)-C(39)	1.384(5)
C(38)-H(38)	0.9500
C(39)-C(40)	1.376(5)
C(39)-H(39)	0.9500
C(40)-C(41)	1.397(5)
C(40)-H(40)	0.9500
C(41)-C(42)	1.382(5)
C(41)-H(41)	0.9500
C(42)-H(42)	0.9500
O(1)-C(44)	1.417(5)
O(1)-C(43)	1.447(5)
C(43)-C(44)#1	1.492(6)
C(43)-H(43A)	0.9900
C(43)-H(43B)	0.9900
C(44)-C(43)#1	1.492(6)
C(44)-H(44A)	0.9900
C(44)-H(44B)	0.9900
C(2)-C(1)-C(35)	117.7(3)
C(2)-C(1)-C(31)	125.3(3)
C(35)-C(1)-C(31)	117.0(3)
C(1)-C(2)-C(3)	122.8(3)
C(1)-C(2)-H(2)	118.6
C(3)-C(2)-H(2)	118.6
C(4)-C(3)-C(2)	119.8(3)
C(4)-C(3)-H(3)	120.1
C(2)-C(3)-H(3)	120.1
C(3)-C(4)-C(36)	117.3(3)
C(3)-C(4)-C(5)	137.0(3)

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C(36)-C(4)-C(5)	105.7(3)
C(6)-C(5)-C(10)	120.4(3)
C(6)-C(5)-C(4)	131.5(3)
C(10)-C(5)-C(4)	108.0(3)
C(5)-C(6)-C(7)	118.4(3)
C(5)-C(6)-H(6)	120.8
C(7)-C(6)-H(6)	120.8
C(8)-C(7)-C(6)	120.9(3)
C(8)-C(7)-H(7)	119.5
C(6)-C(7)-H(7)	119.5
C(7)-C(8)-C(9)	121.5(3)
C(7)-C(8)-H(8)	119.2
C(9)-C(8)-H(8)	119.2
C(10)-C(9)-C(8)	118.7(3)
C(10)-C(9)-H(9)	120.7
C(8)-C(9)-H(9)	120.7
C(9)-C(10)-C(5)	120.1(3)
C(9)-C(10)-C(11)	131.7(3)
C(5)-C(10)-C(11)	108.2(3)
C(12)-C(11)-C(36)	118.9(3)
C(12)-C(11)-C(10)	135.3(3)
C(36)-C(11)-C(10)	105.8(3)
C(11)-C(12)-C(13)	120.3(3)
C(11)-C(12)-H(12)	119.9
C(13)-C(12)-H(12)	119.9
C(34)-C(13)-C(14)	117.8(3)
C(34)-C(13)-C(12)	120.1(3)
C(14)-C(13)-C(12)	121.9(3)
C(15)-C(14)-C(19)	117.7(3)
C(15)-C(14)-C(13)	121.9(3)
C(19)-C(14)-C(13)	120.3(3)
C(16)-C(15)-C(14)	122.1(3)
C(16)-C(15)-H(15)	119.0
C(14)-C(15)-H(15)	119.0
C(15)-C(16)-C(17)	119.8(3)
C(15)-C(16)-H(16)	120.1
C(17)-C(16)-H(16)	120.1
C(18)-C(17)-C(16)	119.2(3)
C(18)-C(17)-H(17)	120.4
C(16)-C(17)-H(17)	120.4
C(17)-C(18)-C(19)	122.7(3)
C(17)-C(18)-H(18)	118.6
C(19)-C(18)-H(18)	118.6
C(18)-C(19)-C(14)	117.5(3)
C(18)-C(19)-C(20)	123.1(3)
C(14)-C(19)-C(20)	119.2(3)
C(33)-C(20)-C(19)	118.9(3)
C(33)-C(20)-C(21)	118.2(3)
C(19)-C(20)-C(21)	122.6(3)
C(22)-C(21)-C(26)	118.1(3)
C(22)-C(21)-C(20)	122.0(3)
C(26)-C(21)-C(20)	119.1(3)
C(23)-C(22)-C(21)	121.8(3)
C(23)-C(22)-H(22)	119.1
C(21)-C(22)-H(22)	119.1
C(22)-C(23)-C(24)	119.7(3)
C(22)-C(23)-H(23)	120.2
C(24)-C(23)-H(23)	120.2
C(25)-C(24)-C(23)	120.0(3)
C(25)-C(24)-H(24)	120.0
C(23)-C(24)-H(24)	120.0
C(24)-C(25)-C(26)	122.0(3)

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C(24)-C(25)-H(25)	119.0
C(26)-C(25)-H(25)	119.0
C(25)-C(26)-C(21)	118.3(3)
C(25)-C(26)-C(27)	121.2(3)
C(21)-C(26)-C(27)	119.8(3)
C(32)-C(27)-C(28)	119.0(3)
C(32)-C(27)-C(26)	117.9(3)
C(28)-C(27)-C(26)	123.0(3)
C(29)-C(28)-C(27)	118.7(3)
C(29)-C(28)-C(37)	118.3(3)
C(27)-C(28)-C(37)	122.8(3)
C(30)-C(29)-C(28)	122.1(3)
C(30)-C(29)-H(29)	118.9
C(28)-C(29)-H(29)	118.9
C(29)-C(30)-C(31)	121.0(3)
C(29)-C(30)-H(30)	119.5
C(31)-C(30)-H(30)	119.5
C(30)-C(31)-C(32)	118.3(3)
C(30)-C(31)-C(1)	121.9(3)
C(32)-C(31)-C(1)	119.8(3)
C(27)-C(32)-C(31)	120.1(3)
C(27)-C(32)-C(33)	118.9(3)
C(31)-C(32)-C(33)	120.9(3)
C(20)-C(33)-C(34)	119.9(3)
C(20)-C(33)-C(32)	120.9(3)
C(34)-C(33)-C(32)	119.1(3)
C(13)-C(34)-C(35)	119.5(3)
C(13)-C(34)-C(33)	121.8(3)
C(35)-C(34)-C(33)	118.7(3)
C(36)-C(35)-C(34)	118.0(3)
C(36)-C(35)-C(1)	117.9(3)
C(34)-C(35)-C(1)	124.0(3)
C(35)-C(36)-C(4)	124.5(3)
C(35)-C(36)-C(11)	123.2(3)
C(4)-C(36)-C(11)	112.3(3)
C(38)-C(37)-C(42)	118.1(3)
C(38)-C(37)-C(28)	120.5(3)
C(42)-C(37)-C(28)	121.3(3)
C(39)-C(38)-C(37)	120.7(3)
C(39)-C(38)-H(38)	119.6
C(37)-C(38)-H(38)	119.6
C(40)-C(39)-C(38)	120.5(3)
C(40)-C(39)-H(39)	119.7
C(38)-C(39)-H(39)	119.7
C(39)-C(40)-C(41)	119.8(3)
C(39)-C(40)-H(40)	120.1
C(41)-C(40)-H(40)	120.1
C(42)-C(41)-C(40)	119.5(3)
C(42)-C(41)-H(41)	120.3
C(40)-C(41)-H(41)	120.3
C(41)-C(42)-C(37)	121.2(3)
C(41)-C(42)-H(42)	119.4
C(37)-C(42)-H(42)	119.4
C(44)-O(1)-C(43)	108.3(3)
O(1)-C(43)-C(44)#1	110.7(3)
O(1)-C(43)-H(43A)	109.5
C(44)#1-C(43)-H(43A)	109.5
O(1)-C(43)-H(43B)	109.5
C(44)#1-C(43)-H(43B)	109.5
H(43A)-C(43)-H(43B)	108.1
O(1)-C(44)-C(43)#1	110.3(3)
O(1)-C(44)-H(44A)	109.6

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C(43)#1-C(44)-H(44A)	109.6
O(1)-C(44)-H(44B)	109.6
C(43)#1-C(44)-H(44B)	109.6
H(44A)-C(44)-H(44B)	108.1

Symmetry transformations used to generate equivalent atoms:
 #1 -x+2,-y,-z

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for i15298. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
C(1)	19(1)	23(2)	22(2)	8(1)	4(1)	4(1)
C(2)	24(2)	21(2)	22(2)	3(1)	4(1)	3(1)
C(3)	22(2)	23(2)	32(2)	8(2)	4(1)	1(1)
C(4)	15(1)	23(2)	34(2)	13(2)	2(1)	1(1)
C(5)	14(1)	29(2)	33(2)	15(2)	3(1)	1(1)
C(6)	18(2)	25(2)	40(2)	13(2)	5(1)	2(1)
C(7)	22(2)	31(2)	42(2)	21(2)	1(2)	1(1)
C(8)	21(2)	39(2)	34(2)	23(2)	1(1)	2(1)
C(9)	19(2)	33(2)	32(2)	18(2)	5(1)	4(1)
C(10)	15(1)	28(2)	29(2)	15(2)	2(1)	3(1)
C(11)	15(1)	25(2)	24(2)	11(2)	3(1)	3(1)
C(12)	16(1)	33(2)	19(2)	12(2)	2(1)	2(1)
C(13)	17(1)	24(2)	19(2)	7(1)	4(1)	2(1)
C(14)	17(1)	25(2)	22(2)	9(1)	4(1)	4(1)
C(15)	28(2)	31(2)	20(2)	11(2)	3(1)	7(1)
C(16)	31(2)	23(2)	16(2)	1(1)	1(1)	6(1)
C(17)	24(2)	23(2)	24(2)	4(2)	1(1)	1(1)
C(18)	24(2)	24(2)	24(2)	10(2)	7(1)	6(1)
C(19)	18(1)	25(2)	21(2)	7(1)	5(1)	5(1)
C(20)	17(1)	22(2)	20(2)	7(1)	5(1)	3(1)
C(21)	19(2)	24(2)	19(2)	7(1)	4(1)	1(1)
C(22)	21(2)	25(2)	22(2)	9(1)	5(1)	2(1)
C(23)	25(2)	24(2)	30(2)	12(2)	8(1)	7(1)
C(24)	34(2)	37(2)	27(2)	17(2)	5(1)	13(2)
C(25)	33(2)	34(2)	22(2)	12(2)	7(1)	10(2)
C(26)	19(1)	26(2)	19(2)	10(1)	3(1)	2(1)
C(27)	15(1)	25(2)	23(2)	9(1)	-1(1)	0(1)
C(28)	22(2)	29(2)	18(2)	7(1)	1(1)	4(1)
C(29)	28(2)	29(2)	19(2)	5(2)	3(1)	1(1)
C(30)	25(2)	20(2)	24(2)	4(1)	3(1)	2(1)
C(31)	15(1)	28(2)	20(2)	7(1)	1(1)	4(1)
C(32)	15(1)	24(2)	20(2)	5(1)	2(1)	3(1)
C(33)	13(1)	23(2)	18(2)	7(1)	2(1)	1(1)
C(34)	14(1)	22(2)	21(2)	9(1)	2(1)	-1(1)
C(35)	13(1)	23(2)	20(2)	7(1)	1(1)	0(1)
C(36)	15(1)	22(2)	26(2)	9(1)	1(1)	-1(1)
C(37)	36(2)	28(2)	18(2)	5(2)	5(1)	6(2)
C(38)	31(2)	33(2)	25(2)	8(2)	2(1)	2(2)
C(39)	43(2)	40(2)	21(2)	10(2)	4(2)	9(2)
C(40)	49(2)	40(2)	31(2)	19(2)	11(2)	8(2)
C(41)	39(2)	32(2)	31(2)	12(2)	6(2)	5(2)
C(42)	34(2)	32(2)	23(2)	8(2)	2(1)	8(2)
O(1)	56(2)	76(2)	57(2)	29(2)	10(2)	-1(2)
C(43)	63(3)	40(2)	42(2)	4(2)	2(2)	1(2)
C(44)	44(2)	72(3)	39(2)	27(2)	-8(2)	-14(2)

Single-crystal data for DNCTable 1. Crystal data and structure refinement for **DNC**.

Identification code	i15472	
Empirical formula	C20 H10	
Formula weight	250.28	
Temperature	100.0(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 25.1911(10) Å	$\alpha = 90^\circ$.
	b = 12.5917(5) Å	$\beta = 94.052(2)^\circ$.
	c = 7.2168(3) Å	$\gamma = 90^\circ$.
Volume	2283.44(16) Å ³	
Z	8	
Density (calculated)	1.456 Mg/m ³	
Absorption coefficient	0.083 mm ⁻¹	
F(000)	1040	
Crystal size	0.220 x 0.100 x 0.060 mm ³	
Theta range for data collection	1.621 to 27.101°.	
Index ranges	-32 ≤ h ≤ 32, -16 ≤ k ≤ 16, -9 ≤ l ≤ 9	
Reflections collected	42938	
Independent reflections	2526 [R(int) = 0.0594]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9705 and 0.9104	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2526 / 0 / 184	
Goodness-of-fit on F ²	1.294	
Final R indices [I > 2σ(I)]	R1 = 0.0543, wR2 = 0.1845	
R indices (all data)	R1 = 0.0594, wR2 = 0.1877	
Extinction coefficient	0.0040(8)	
Largest diff. peak and hole	0.559 and -0.384 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å² × 10³) for i15472. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5000	2564(2)	2500	11(1)
C(2)	4537(1)	2007(2)	3081(3)	12(1)
C(3)	4567(1)	935(2)	3749(3)	13(1)
C(4)	4132(1)	408(2)	4276(3)	14(1)
C(5)	3615(1)	858(2)	3951(3)	14(1)
C(6)	3153(1)	245(2)	4159(3)	18(1)
C(7)	2658(1)	647(2)	3658(3)	20(1)
C(8)	2610(1)	1673(2)	2910(3)	19(1)
C(9)	3054(1)	2298(2)	2748(3)	16(1)
C(10)	3570(1)	1925(2)	3331(3)	13(1)
C(11)	4052(1)	2555(2)	3196(3)	12(1)
C(12)	4058(1)	3694(2)	3276(3)	12(1)
C(13)	3626(1)	4298(2)	3910(3)	13(1)
C(14)	3638(1)	5378(2)	3980(3)	13(1)
C(15)	4083(1)	5955(2)	3431(3)	13(1)
C(16)	4093(1)	7083(2)	3404(3)	15(1)
C(17)	4534(1)	7619(2)	2946(3)	16(1)
C(18)	5000	7068(2)	2500	13(1)
C(19)	5000	5944(2)	2500	12(1)

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C(20)	4537(1)	5380(2)	2959(3)	12(1)
C(21)	4530(1)	4249(2)	2926(3)	11(1)
C(22)	5000	3675(2)	2500	11(1)

Table 3. Bond lengths [Å] and angles [°] for i15472.

C(1)-C(22)	1.399(4)
C(1)-C(2)#1	1.448(2)
C(1)-C(2)	1.448(2)
C(2)-C(11)	1.412(3)
C(2)-C(3)	1.434(3)
C(3)-C(4)	1.357(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.424(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.414(3)
C(5)-C(10)	1.418(3)
C(6)-C(7)	1.370(3)
C(6)-H(6)	0.9500
C(7)-C(8)	1.402(3)
C(7)-H(7)	0.9500
C(8)-C(9)	1.379(3)
C(8)-H(8)	0.9500
C(9)-C(10)	1.417(3)
C(9)-H(9)	0.9500
C(10)-C(11)	1.458(3)
C(11)-C(12)	1.436(3)
C(12)-C(21)	1.418(3)
C(12)-C(13)	1.429(3)
C(13)-C(14)	1.361(3)
C(13)-H(13)	0.9500
C(14)-C(15)	1.415(3)
C(14)-H(14)	0.9500
C(15)-C(20)	1.415(3)
C(15)-C(16)	1.422(3)
C(16)-C(17)	1.360(3)
C(16)-H(16)	0.9500
C(17)-C(18)	1.420(2)
C(17)-H(17)	0.9500
C(18)-C(19)	1.415(4)
C(18)-C(17)#1	1.420(2)
C(19)-C(20)	1.425(2)
C(19)-C(20)#1	1.425(2)
C(20)-C(21)	1.425(3)
C(21)-C(22)	1.438(2)
C(22)-C(21)#1	1.438(2)
C(22)-C(1)-C(2)#1	118.99(12)
C(22)-C(1)-C(2)	118.99(12)
C(2)#1-C(1)-C(2)	122.0(2)
C(11)-C(2)-C(3)	117.67(17)
C(11)-C(2)-C(1)	119.96(19)
C(3)-C(2)-C(1)	122.00(18)
C(4)-C(3)-C(2)	122.07(18)
C(4)-C(3)-H(3)	119.0
C(2)-C(3)-H(3)	119.0
C(3)-C(4)-C(5)	120.36(19)
C(3)-C(4)-H(4)	119.8
C(5)-C(4)-H(4)	119.8
C(6)-C(5)-C(10)	120.11(19)

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C(6)-C(5)-C(4)	121.04(19)
C(10)-C(5)-C(4)	118.78(18)
C(7)-C(6)-C(5)	120.8(2)
C(7)-C(6)-H(6)	119.6
C(5)-C(6)-H(6)	119.6
C(6)-C(7)-C(8)	119.58(19)
C(6)-C(7)-H(7)	120.2
C(8)-C(7)-H(7)	120.2
C(9)-C(8)-C(7)	120.7(2)
C(9)-C(8)-H(8)	119.7
C(7)-C(8)-H(8)	119.7
C(8)-C(9)-C(10)	121.14(19)
C(8)-C(9)-H(9)	119.4
C(10)-C(9)-H(9)	119.4
C(9)-C(10)-C(5)	117.37(18)
C(9)-C(10)-C(11)	123.35(18)
C(5)-C(10)-C(11)	119.13(18)
C(2)-C(11)-C(12)	118.89(17)
C(2)-C(11)-C(10)	117.85(18)
C(12)-C(11)-C(10)	123.17(17)
C(21)-C(12)-C(13)	117.57(18)
C(21)-C(12)-C(11)	119.47(17)
C(13)-C(12)-C(11)	122.54(18)
C(14)-C(13)-C(12)	121.83(18)
C(14)-C(13)-H(13)	119.1
C(12)-C(13)-H(13)	119.1
C(13)-C(14)-C(15)	121.25(18)
C(13)-C(14)-H(14)	119.4
C(15)-C(14)-H(14)	119.4
C(20)-C(15)-C(14)	118.31(18)
C(20)-C(15)-C(16)	119.48(18)
C(14)-C(15)-C(16)	122.17(18)
C(17)-C(16)-C(15)	121.01(18)
C(17)-C(16)-H(16)	119.5
C(15)-C(16)-H(16)	119.5
C(16)-C(17)-C(18)	121.0(2)
C(16)-C(17)-H(17)	119.5
C(18)-C(17)-H(17)	119.5
C(19)-C(18)-C(17)#1	119.24(13)
C(19)-C(18)-C(17)	119.24(13)
C(17)#1-C(18)-C(17)	121.5(3)
C(18)-C(19)-C(20)	119.90(13)
C(18)-C(19)-C(20)#1	119.90(13)
C(20)-C(19)-C(20)#1	120.2(3)
C(15)-C(20)-C(21)	120.46(17)
C(15)-C(20)-C(19)	119.34(19)
C(21)-C(20)-C(19)	120.19(18)
C(12)-C(21)-C(20)	119.88(17)
C(12)-C(21)-C(22)	120.30(19)
C(20)-C(21)-C(22)	119.81(18)
C(1)-C(22)-C(21)	120.14(12)
C(1)-C(22)-C(21)#1	120.14(12)
C(21)-C(22)-C(21)#1	119.7(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for i15472. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

U¹¹

U²²

U³³

U²³

U¹³

U¹²

Supporting Information

C(1)	10(1)	14(1)	7(1)	0	0(1)	0
C(2)	12(1)	13(1)	10(1)	-2(1)	1(1)	-1(1)
C(3)	12(1)	14(1)	13(1)	-1(1)	2(1)	2(1)
C(4)	18(1)	12(1)	14(1)	0(1)	2(1)	0(1)
C(5)	14(1)	16(1)	13(1)	-1(1)	4(1)	-2(1)
C(6)	19(1)	16(1)	20(1)	0(1)	6(1)	-4(1)
C(7)	16(1)	22(1)	24(1)	-4(1)	6(1)	-6(1)
C(8)	11(1)	24(1)	23(1)	-4(1)	1(1)	-1(1)
C(9)	14(1)	16(1)	17(1)	-1(1)	2(1)	0(1)
C(10)	12(1)	15(1)	14(1)	-2(1)	3(1)	-1(1)
C(11)	11(1)	14(1)	10(1)	1(1)	1(1)	0(1)
C(12)	10(1)	15(1)	10(1)	1(1)	-1(1)	1(1)
C(13)	10(1)	18(1)	12(1)	1(1)	2(1)	0(1)
C(14)	12(1)	17(1)	12(1)	-1(1)	1(1)	3(1)
C(15)	13(1)	15(1)	10(1)	-1(1)	-1(1)	1(1)
C(16)	16(1)	14(1)	14(1)	-2(1)	0(1)	5(1)
C(17)	21(1)	12(1)	14(1)	-1(1)	0(1)	2(1)
C(18)	17(1)	13(1)	8(1)	0	-1(1)	0
C(19)	14(1)	12(1)	9(1)	0	-1(1)	0
C(20)	13(1)	13(1)	9(1)	0(1)	0(1)	1(1)
C(21)	10(1)	13(1)	9(1)	0(1)	0(1)	1(1)
C(22)	9(1)	15(1)	10(1)	0	-1(1)	0

Single-crystal data for DBC

Table 1. Crystal data and structure refinement for **DBC**.

Identification code	i15505	
Empirical formula	C ₃₂ H ₁₆	
Formula weight	400.45	
Temperature	100.0(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 5.2697(2) Å b = 14.6808(6) Å c = 11.6839(4) Å	α = 90°. β = 96.013(2)°. γ = 90°.
Volume	898.93(6) Å ³	
Z	2	
Density (calculated)	1.479 Mg/m ³	
Absorption coefficient	0.084 mm ⁻¹	
F(000)	416	
Crystal size	0.100 x 0.080 x 0.040 mm ³	
Theta range for data collection	1.753 to 27.103°	
Index ranges	-6 ≤ h ≤ 6, -18 ≤ k ≤ 18, -14 ≤ l ≤ 14	
Reflections collected	35392	
Independent reflections	3962 [R(int) = 0.0541]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9705 and 0.9086	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3962 / 1 / 290	
Goodness-of-fit on F ²	1.044	
Final R indices [I > 2σ(I)]	R1 = 0.0406, wR2 = 0.0957	
R indices (all data)	R1 = 0.0565, wR2 = 0.1058	
Absolute structure parameter	0.5	
Extinction coefficient	0.013(3)	
Largest diff. peak and hole	0.229 and -0.188 e.Å ⁻³	

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Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for i15505. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
C(1)	3381(5)	4994(2)	6681(2)	16(1)
C(2)	2265(5)	4331(2)	7406(2)	16(1)
C(3)	3385(5)	4104(2)	8526(2)	19(1)
C(4)	2245(5)	3514(2)	9224(2)	21(1)
C(5)	-83(5)	3109(2)	8832(2)	22(1)
C(6)	-1105(5)	3248(2)	7718(2)	20(1)
C(7)	70(5)	3829(2)	6965(2)	15(1)
C(8)	-811(5)	3880(2)	5756(2)	16(1)
C(9)	-2940(5)	3367(2)	5263(2)	19(1)
C(10)	-3636(5)	3362(2)	4107(2)	21(1)
C(11)	-2279(5)	3875(2)	3349(2)	20(1)
C(12)	-2993(5)	3883(2)	2146(2)	24(1)
C(13)	-1692(6)	4389(2)	1423(3)	25(1)
C(14)	417(6)	4934(2)	1863(2)	20(1)
C(15)	1753(5)	5486(2)	1129(2)	25(1)
C(16)	3765(6)	6006(2)	1556(2)	24(1)
C(17)	4593(5)	6022(2)	2756(2)	20(1)
C(18)	6715(5)	6541(2)	3218(3)	22(1)
C(19)	7470(5)	6549(2)	4370(3)	21(1)
C(20)	6119(5)	6050(2)	5155(2)	17(1)
C(21)	6749(5)	6129(2)	6388(2)	17(1)
C(22)	8735(5)	6705(2)	6873(3)	21(1)
C(23)	9064(5)	6888(2)	8032(3)	24(1)
C(24)	7357(5)	6527(2)	8746(2)	23(1)
C(25)	5485(5)	5936(2)	8312(2)	19(1)
C(26)	5232(5)	5668(2)	7138(2)	17(1)
C(27)	2661(5)	4974(2)	5495(2)	15(1)
C(28)	569(5)	4408(2)	5022(2)	15(1)
C(29)	-170(5)	4403(2)	3813(2)	17(1)
C(30)	1180(5)	4942(2)	3058(2)	18(1)
C(31)	3259(5)	5497(2)	3517(2)	17(1)
C(32)	4015(5)	5517(2)	4729(2)	16(1)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for i15505.

C(1)-C(27)	1.398(4)
C(1)-C(26)	1.452(4)
C(1)-C(2)	1.455(4)
C(2)-C(3)	1.417(4)
C(2)-C(7)	1.421(4)
C(3)-C(4)	1.371(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.396(4)
C(4)-H(4)	0.9500
C(5)-C(6)	1.371(4)
C(5)-H(5)	0.9500
C(6)-C(7)	1.414(4)
C(6)-H(6)	0.9500
C(7)-C(8)	1.442(4)
C(8)-C(28)	1.413(4)
C(8)-C(9)	1.422(4)
C(9)-C(10)	1.362(4)
C(9)-H(9)	0.9500
C(10)-C(11)	1.413(4)
C(10)-H(10)	0.9500
C(11)-C(29)	1.415(4)

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C(11)-C(12)	1.416(4)
C(12)-C(13)	1.363(4)
C(12)-H(12)	0.9500
C(13)-C(14)	1.421(4)
C(13)-H(13)	0.9500
C(14)-C(30)	1.412(4)
C(14)-C(15)	1.419(4)
C(15)-C(16)	1.358(4)
C(15)-H(15)	0.9500
C(16)-C(17)	1.424(4)
C(16)-H(16)	0.9500
C(17)-C(18)	1.412(4)
C(17)-C(31)	1.418(4)
C(18)-C(19)	1.363(4)
C(18)-H(18)	0.9500
C(19)-C(20)	1.422(4)
C(19)-H(19)	0.9500
C(20)-C(32)	1.405(4)
C(20)-C(21)	1.448(4)
C(21)-C(22)	1.417(4)
C(21)-C(26)	1.418(4)
C(22)-C(23)	1.374(4)
C(22)-H(22)	0.9500
C(23)-C(24)	1.394(4)
C(23)-H(23)	0.9500
C(24)-C(25)	1.370(4)
C(24)-H(24)	0.9500
C(25)-C(26)	1.420(4)
C(25)-H(25)	0.9500
C(27)-C(32)	1.441(4)
C(27)-C(28)	1.443(3)
C(28)-C(29)	1.426(3)
C(29)-C(30)	1.429(4)
C(30)-C(31)	1.424(4)
C(31)-C(32)	1.431(3)

C(27)-C(1)-C(26)	118.8(2)
C(27)-C(1)-C(2)	118.6(2)
C(26)-C(1)-C(2)	122.6(2)
C(3)-C(2)-C(7)	117.3(2)
C(3)-C(2)-C(1)	122.7(2)
C(7)-C(2)-C(1)	119.9(2)
C(4)-C(3)-C(2)	122.1(3)
C(4)-C(3)-H(3)	119.0
C(2)-C(3)-H(3)	119.0
C(3)-C(4)-C(5)	119.9(3)
C(3)-C(4)-H(4)	120.0
C(5)-C(4)-H(4)	120.0
C(6)-C(5)-C(4)	119.5(3)
C(6)-C(5)-H(5)	120.2
C(4)-C(5)-H(5)	120.2
C(5)-C(6)-C(7)	121.8(3)
C(5)-C(6)-H(6)	119.1
C(7)-C(6)-H(6)	119.1
C(6)-C(7)-C(2)	118.6(2)
C(6)-C(7)-C(8)	121.6(2)
C(2)-C(7)-C(8)	119.7(2)
C(28)-C(8)-C(9)	118.7(2)
C(28)-C(8)-C(7)	119.3(2)
C(9)-C(8)-C(7)	121.9(2)
C(10)-C(9)-C(8)	121.5(3)
C(10)-C(9)-H(9)	119.2

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C(8)-C(9)-H(9)	119.2
C(9)-C(10)-C(11)	121.2(3)
C(9)-C(10)-H(10)	119.4
C(11)-C(10)-H(10)	119.4
C(10)-C(11)-C(29)	118.7(2)
C(10)-C(11)-C(12)	121.8(3)
C(29)-C(11)-C(12)	119.5(3)
C(13)-C(12)-C(11)	121.4(3)
C(13)-C(12)-H(12)	119.3
C(11)-C(12)-H(12)	119.3
C(12)-C(13)-C(14)	120.5(3)
C(12)-C(13)-H(13)	119.7
C(14)-C(13)-H(13)	119.7
C(30)-C(14)-C(15)	119.0(3)
C(30)-C(14)-C(13)	119.5(3)
C(15)-C(14)-C(13)	121.5(3)
C(16)-C(15)-C(14)	121.1(3)
C(16)-C(15)-H(15)	119.5
C(14)-C(15)-H(15)	119.5
C(15)-C(16)-C(17)	121.2(3)
C(15)-C(16)-H(16)	119.4
C(17)-C(16)-H(16)	119.4
C(18)-C(17)-C(31)	118.6(3)
C(18)-C(17)-C(16)	122.2(3)
C(31)-C(17)-C(16)	119.1(3)
C(19)-C(18)-C(17)	121.3(3)
C(19)-C(18)-H(18)	119.4
C(17)-C(18)-H(18)	119.4
C(18)-C(19)-C(20)	121.2(3)
C(18)-C(19)-H(19)	119.4
C(20)-C(19)-H(19)	119.4
C(32)-C(20)-C(19)	119.3(2)
C(32)-C(20)-C(21)	119.1(2)
C(19)-C(20)-C(21)	121.5(2)
C(22)-C(21)-C(26)	118.5(3)
C(22)-C(21)-C(20)	121.8(2)
C(26)-C(21)-C(20)	119.5(2)
C(23)-C(22)-C(21)	121.5(3)
C(23)-C(22)-H(22)	119.2
C(21)-C(22)-H(22)	119.2
C(22)-C(23)-C(24)	119.5(3)
C(22)-C(23)-H(23)	120.2
C(24)-C(23)-H(23)	120.2
C(25)-C(24)-C(23)	120.2(3)
C(25)-C(24)-H(24)	119.9
C(23)-C(24)-H(24)	119.9
C(24)-C(25)-C(26)	121.6(3)
C(24)-C(25)-H(25)	119.2
C(26)-C(25)-H(25)	119.2
C(21)-C(26)-C(25)	117.6(2)
C(21)-C(26)-C(1)	119.8(2)
C(25)-C(26)-C(1)	122.4(2)
C(1)-C(27)-C(32)	120.2(2)
C(1)-C(27)-C(28)	120.6(2)
C(32)-C(27)-C(28)	119.2(2)
C(8)-C(28)-C(29)	119.6(2)
C(8)-C(28)-C(27)	120.3(2)
C(29)-C(28)-C(27)	120.1(2)
C(11)-C(29)-C(28)	120.3(2)
C(11)-C(29)-C(30)	119.3(2)
C(28)-C(29)-C(30)	120.4(2)
C(14)-C(30)-C(31)	120.3(2)

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C(14)-C(30)-C(29)	119.8(2)
C(31)-C(30)-C(29)	119.8(2)
C(17)-C(31)-C(30)	119.2(2)
C(17)-C(31)-C(32)	120.3(2)
C(30)-C(31)-C(32)	120.5(2)
C(20)-C(32)-C(31)	119.3(2)
C(20)-C(32)-C(27)	120.8(2)
C(31)-C(32)-C(27)	119.9(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for i15505. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	14(1)	15(1)	18(1)	-1(1)	0(1)	2(1)
C(2)	15(1)	15(1)	17(1)	0(1)	3(1)	2(1)
C(3)	21(1)	19(1)	18(1)	-4(1)	1(1)	1(1)
C(4)	26(1)	19(2)	18(1)	0(1)	2(1)	2(1)
C(5)	27(2)	18(2)	23(2)	3(1)	7(1)	0(1)
C(6)	17(1)	17(1)	25(2)	0(1)	4(1)	-1(1)
C(7)	16(1)	11(1)	19(1)	-2(1)	3(1)	2(1)
C(8)	14(1)	13(1)	20(1)	0(1)	2(1)	3(1)
C(9)	17(1)	15(1)	26(2)	-1(1)	0(1)	1(1)
C(10)	17(1)	14(1)	30(2)	-5(1)	-2(1)	0(1)
C(11)	20(1)	18(1)	21(1)	-5(1)	-3(1)	5(1)
C(12)	21(1)	24(2)	24(2)	-7(1)	-6(1)	8(1)
C(13)	28(2)	29(2)	16(2)	-5(1)	-4(1)	12(1)
C(14)	24(1)	20(2)	17(2)	-2(1)	2(1)	12(1)
C(15)	31(2)	29(2)	17(2)	2(1)	4(1)	15(1)
C(16)	28(2)	24(2)	21(2)	4(1)	9(1)	11(1)
C(17)	22(1)	19(2)	20(2)	3(1)	7(1)	7(1)
C(18)	22(1)	18(1)	27(2)	6(1)	11(1)	4(1)
C(19)	17(1)	15(1)	31(2)	1(1)	5(1)	0(1)
C(20)	16(1)	12(1)	23(2)	1(1)	4(1)	4(1)
C(21)	14(1)	12(1)	25(2)	1(1)	0(1)	2(1)
C(22)	16(1)	16(1)	30(2)	0(1)	3(1)	-1(1)
C(23)	19(1)	20(2)	31(2)	-3(1)	-3(1)	-5(1)
C(24)	25(1)	22(2)	22(2)	-5(1)	-1(1)	-1(1)
C(25)	19(1)	18(1)	20(2)	1(1)	1(1)	-2(1)
C(26)	14(1)	17(1)	18(2)	-1(1)	0(1)	2(1)
C(27)	13(1)	12(1)	19(1)	-1(1)	1(1)	3(1)
C(28)	14(1)	12(1)	19(1)	-2(1)	0(1)	3(1)
C(29)	16(1)	15(1)	20(2)	-2(1)	2(1)	6(1)
C(30)	19(1)	16(1)	17(1)	-2(1)	2(1)	7(1)
C(31)	19(1)	15(1)	19(2)	2(1)	5(1)	7(1)
C(32)	16(1)	15(1)	16(2)	0(1)	4(1)	4(1)

Single-crystal data for Flu-DBC:

Table 1. Crystal data and structure refinement for **Flu-DBC**.

Identification code	ch17382
Empirical formula	C32 H14 F2
Formula weight	436.43
Temperature	200(2) K
Wavelength	0.71073 \AA
Crystal system	Orthorhombic
Space group	P 21 21 21

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Unit cell dimensions	a = 3.8133(15) Å	$\alpha = 90^\circ$.
	b = 20.154(7) Å	$\beta = 90^\circ$.
	c = 23.688(9) Å	$\gamma = 90^\circ$.
Volume	1820.5(12) Å ³	
Z	4	
Density (calculated)	1.592 Mg/m ³	
Absorption coefficient	0.105 mm ⁻¹	
F(000)	896	
Crystal size	0.79 x 0.04 x 0.01 mm ³	
Theta range for data collection	1.33 to 25.10°	
Index ranges	-4<=h<=3, -24<=k<=23, -28<=l<=27	
Reflections collected	9342	
Independent reflections	3238 [R(int) = 0.0772]	
Completeness to theta = 25.10°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9989 and 0.9214	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3238 / 0 / 307	
Goodness-of-fit on F ²	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0737, wR2 = 0.1840	
R indices (all data)	R1 = 0.1202, wR2 = 0.2278	
Absolute structure parameter	-1(2)	
Largest diff. peak and hole	0.584 and -0.603 e.Å ⁻³	

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for flu-dbc. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	11164(16)	10230(2)	9047(3)	31(2)
C(2)	11614(15)	10166(2)	8481(2)	26(1)
C(3)	10374(13)	9586(2)	8204(2)	19(1)
C(4)	9063(14)	9059(2)	8538(2)	19(1)
C(5)	8428(15)	9181(2)	9117(2)	26(1)
C(6)	9537(15)	9756(2)	9372(3)	28(1)
C(7)	10237(14)	9544(2)	7599(2)	19(1)
C(8)	11442(15)	10073(2)	7254(2)	25(1)
C(9)	11054(15)	10056(2)	6684(2)	27(1)
C(10)	9460(14)	9509(2)	6407(2)	21(1)
C(11)	8993(15)	9489(3)	5813(2)	28(1)
C(12)	7517(15)	8961(2)	5561(2)	26(1)
C(13)	6361(14)	8407(2)	5874(2)	21(1)
C(14)	6789(13)	8413(2)	6466(2)	18(1)
C(15)	8347(14)	8968(2)	6739(2)	20(1)
C(16)	8743(13)	8989(2)	7338(2)	17(1)
C(17)	7680(14)	8419(2)	7674(2)	18(1)
C(18)	6148(13)	7850(2)	7394(2)	18(1)
C(19)	5706(14)	7858(2)	6793(2)	17(1)
C(20)	4151(14)	7308(2)	6517(2)	22(1)
C(21)	3736(15)	7314(2)	5922(2)	26(1)
C(22)	4804(14)	7850(3)	5617(2)	27(1)
C(23)	3018(14)	6762(2)	6844(2)	25(1)
C(24)	3431(15)	6760(2)	7417(2)	26(1)
C(25)	5132(14)	7295(2)	7707(2)	20(1)
C(26)	5902(15)	7268(2)	8303(2)	23(1)
C(27)	5231(14)	6688(2)	8620(2)	24(1)

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C(28)	6365(17)	6652(2)	9159(2)	28(1)
C(29)	8320(15)	7142(2)	9422(2)	23(1)
C(30)	8874(15)	7722(2)	9122(2)	24(1)
C(31)	7526(14)	7821(2)	8570(2)	20(1)
C(32)	8071(15)	8433(2)	8262(2)	22(1)
F(1)	12371(10)	10792(1)	9305(1)	41(1)
F(2)	5653(11)	6087(1)	9467(1)	42(1)

Table 3. Bond lengths [Å] and angles [°] for flu-dbc.

C(1)-C(2)	1.358(7)
C(1)-F(1)	1.367(6)
C(1)-C(6)	1.375(7)
C(2)-C(3)	1.422(7)
C(2)-H(2)	0.9500
C(3)-C(4)	1.415(7)
C(3)-C(7)	1.437(7)
C(4)-C(5)	1.414(7)
C(4)-C(32)	1.470(6)
C(5)-C(6)	1.373(7)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-C(16)	1.399(7)
C(7)-C(8)	1.420(7)
C(8)-C(9)	1.358(7)
C(8)-H(8)	0.9500
C(9)-C(10)	1.420(7)
C(9)-H(9)	0.9500
C(10)-C(15)	1.410(7)
C(10)-C(11)	1.419(7)
C(11)-C(12)	1.345(7)
C(11)-H(11)	0.9500
C(12)-C(13)	1.410(7)
C(12)-H(12)	0.9500
C(13)-C(22)	1.409(7)
C(13)-C(14)	1.412(7)
C(14)-C(19)	1.422(7)
C(14)-C(15)	1.423(7)
C(15)-C(16)	1.428(7)
C(16)-C(17)	1.455(7)
C(17)-C(32)	1.402(7)
C(17)-C(18)	1.447(6)
C(18)-C(25)	1.396(7)
C(18)-C(19)	1.435(7)
C(19)-C(20)	1.415(7)
C(20)-C(23)	1.412(7)
C(20)-C(21)	1.419(7)
C(21)-C(22)	1.363(7)
C(21)-H(21)	0.9500
C(22)-H(22)	0.9500
C(23)-C(24)	1.367(7)
C(23)-H(23)	0.9500
C(24)-C(25)	1.435(7)
C(24)-H(24)	0.9500

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C(25)-C(26)	1.443(7)
C(26)-C(27)	1.412(7)
C(26)-C(31)	1.423(7)
C(27)-C(28)	1.349(7)
C(27)-H(27)	0.9500
C(28)-F(2)	1.381(5)
C(28)-C(29)	1.386(7)
C(29)-C(30)	1.385(7)
C(29)-H(29)	0.9500
C(30)-C(31)	1.419(7)
C(30)-H(30)	0.9500
C(31)-C(32)	1.448(6)

C(2)-C(1)-F(1)	118.5(5)
C(2)-C(1)-C(6)	123.0(5)
F(1)-C(1)-C(6)	118.5(5)
C(1)-C(2)-C(3)	119.4(5)
C(1)-C(2)-H(2)	120.3
C(3)-C(2)-H(2)	120.3
C(4)-C(3)-C(2)	118.4(5)
C(4)-C(3)-C(7)	120.0(5)
C(2)-C(3)-C(7)	121.4(5)
C(5)-C(4)-C(3)	118.2(5)
C(5)-C(4)-C(32)	122.4(5)
C(3)-C(4)-C(32)	119.1(5)
C(6)-C(5)-C(4)	121.4(5)
C(6)-C(5)-H(5)	119.3
C(4)-C(5)-H(5)	119.3
C(5)-C(6)-C(1)	118.5(5)
C(5)-C(6)-H(6)	120.8
C(1)-C(6)-H(6)	120.8
C(16)-C(7)-C(8)	118.6(5)
C(16)-C(7)-C(3)	120.1(5)
C(8)-C(7)-C(3)	121.2(5)
C(9)-C(8)-C(7)	121.1(5)
C(9)-C(8)-H(8)	119.4
C(7)-C(8)-H(8)	119.4
C(8)-C(9)-C(10)	121.8(5)
C(8)-C(9)-H(9)	119.1
C(10)-C(9)-H(9)	119.1
C(15)-C(10)-C(11)	119.6(5)
C(15)-C(10)-C(9)	118.1(5)
C(11)-C(10)-C(9)	122.3(5)
C(12)-C(11)-C(10)	121.0(5)
C(12)-C(11)-H(11)	119.5
C(10)-C(11)-H(11)	119.5
C(11)-C(12)-C(13)	121.6(5)
C(11)-C(12)-H(12)	119.2
C(13)-C(12)-H(12)	119.2
C(22)-C(13)-C(12)	122.3(5)
C(22)-C(13)-C(14)	119.0(5)
C(12)-C(13)-C(14)	118.7(5)
C(13)-C(14)-C(19)	120.1(4)
C(13)-C(14)-C(15)	120.4(4)
C(19)-C(14)-C(15)	119.5(5)
C(10)-C(15)-C(14)	118.7(5)

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C(10)-C(15)-C(16)	120.0(5)
C(14)-C(15)-C(16)	121.3(4)
C(7)-C(16)-C(15)	120.3(4)
C(7)-C(16)-C(17)	120.3(5)
C(15)-C(16)-C(17)	119.4(4)
C(32)-C(17)-C(18)	120.9(4)
C(32)-C(17)-C(16)	119.8(4)
C(18)-C(17)-C(16)	119.2(5)
C(25)-C(18)-C(19)	120.2(5)
C(25)-C(18)-C(17)	120.2(5)
C(19)-C(18)-C(17)	119.6(4)
C(20)-C(19)-C(14)	119.0(5)
C(20)-C(19)-C(18)	119.9(4)
C(14)-C(19)-C(18)	121.0(4)
C(23)-C(20)-C(19)	119.0(5)
C(23)-C(20)-C(21)	121.0(5)
C(19)-C(20)-C(21)	119.9(5)
C(22)-C(21)-C(20)	120.0(5)
C(22)-C(21)-H(21)	120.0
C(20)-C(21)-H(21)	120.0
C(21)-C(22)-C(13)	121.9(5)
C(21)-C(22)-H(22)	119.0
C(13)-C(22)-H(22)	119.0
C(24)-C(23)-C(20)	120.7(5)
C(24)-C(23)-H(23)	119.6
C(20)-C(23)-H(23)	119.6
C(23)-C(24)-C(25)	121.7(5)
C(23)-C(24)-H(24)	119.2
C(25)-C(24)-H(24)	119.2
C(18)-C(25)-C(24)	118.3(5)
C(18)-C(25)-C(26)	119.6(5)
C(24)-C(25)-C(26)	122.2(5)
C(27)-C(26)-C(31)	119.4(5)
C(27)-C(26)-C(25)	120.9(5)
C(31)-C(26)-C(25)	119.5(4)
C(28)-C(27)-C(26)	119.2(5)
C(28)-C(27)-H(27)	120.4
C(26)-C(27)-H(27)	120.4
C(27)-C(28)-F(2)	118.8(5)
C(27)-C(28)-C(29)	124.1(5)
F(2)-C(28)-C(29)	117.1(5)
C(30)-C(29)-C(28)	116.9(5)
C(30)-C(29)-H(29)	121.6
C(28)-C(29)-H(29)	121.6
C(29)-C(30)-C(31)	122.4(5)
C(29)-C(30)-H(30)	118.8
C(31)-C(30)-H(30)	118.8
C(30)-C(31)-C(26)	117.2(4)
C(30)-C(31)-C(32)	122.1(5)
C(26)-C(31)-C(32)	120.4(5)
C(17)-C(32)-C(31)	117.9(4)
C(17)-C(32)-C(4)	119.1(4)
C(31)-C(32)-C(4)	123.0(5)

Symmetry transformations used to generate equivalent atoms:

Supporting Information

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for flu-dbc. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
C(1)	34(4)	18(3)	41(4)	-7(2)	-7(3)	-3(3)
C(2)	26(3)	17(2)	34(4)	0(2)	-2(3)	2(2)
C(3)	14(3)	13(2)	31(3)	-1(2)	-3(3)	4(2)
C(4)	14(3)	17(2)	25(3)	-2(2)	-3(2)	6(2)
C(5)	31(3)	20(2)	27(3)	2(2)	4(3)	4(3)
C(6)	30(3)	23(3)	30(3)	-7(2)	-1(3)	3(2)
C(7)	15(3)	13(2)	30(3)	5(2)	2(2)	0(2)
C(8)	24(3)	13(2)	39(4)	5(2)	-3(3)	-2(2)
C(9)	25(3)	19(3)	38(4)	8(2)	2(3)	1(2)
C(10)	21(3)	17(2)	26(3)	8(2)	0(3)	2(2)
C(11)	24(3)	27(3)	34(4)	8(2)	3(3)	4(3)
C(12)	24(3)	34(3)	21(3)	6(2)	-5(3)	9(3)
C(13)	13(3)	25(3)	24(3)	1(2)	4(3)	5(2)
C(14)	8(3)	19(3)	28(3)	2(2)	0(2)	1(2)
C(15)	16(3)	16(2)	28(3)	3(2)	2(3)	4(2)
C(16)	13(3)	11(2)	27(3)	2(2)	1(2)	-1(2)
C(17)	16(3)	15(2)	23(3)	0(2)	0(2)	5(2)
C(18)	12(3)	10(2)	32(3)	0(2)	1(3)	-1(2)
C(19)	16(3)	15(2)	22(3)	-1(2)	4(2)	4(2)
C(20)	17(3)	17(2)	31(3)	-6(2)	1(3)	4(2)
C(21)	26(3)	23(3)	28(3)	-10(2)	-5(3)	2(3)
C(22)	21(3)	33(3)	26(3)	-4(3)	0(3)	5(3)
C(23)	21(3)	16(2)	38(4)	-6(2)	-3(3)	1(2)
C(24)	27(3)	14(2)	38(4)	0(2)	6(3)	-3(2)
C(25)	15(3)	15(2)	29(3)	2(2)	4(2)	4(2)
C(26)	21(3)	18(2)	30(3)	1(2)	2(3)	2(2)
C(27)	23(3)	13(2)	35(4)	-1(2)	5(3)	3(2)
C(28)	41(4)	15(2)	29(3)	9(2)	14(3)	1(3)
C(29)	29(3)	19(2)	22(3)	6(2)	9(3)	5(2)
C(30)	23(3)	18(2)	31(3)	-5(2)	5(3)	4(2)
C(31)	19(3)	16(2)	25(3)	2(2)	-1(3)	3(2)
C(32)	24(3)	14(2)	28(3)	2(2)	-5(3)	1(2)
F(1)	53(2)	24(2)	47(2)	-13(1)	-9(2)	-7(2)
F(2)	68(3)	23(2)	34(2)	12(1)	8(2)	-4(2)