**SUPPORTING INFORMATION**

# Synthesis and photochromic properties of benzofuran-phenanthrene and benzofuran-pyrene hybrids

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I) **NMR Spectra**

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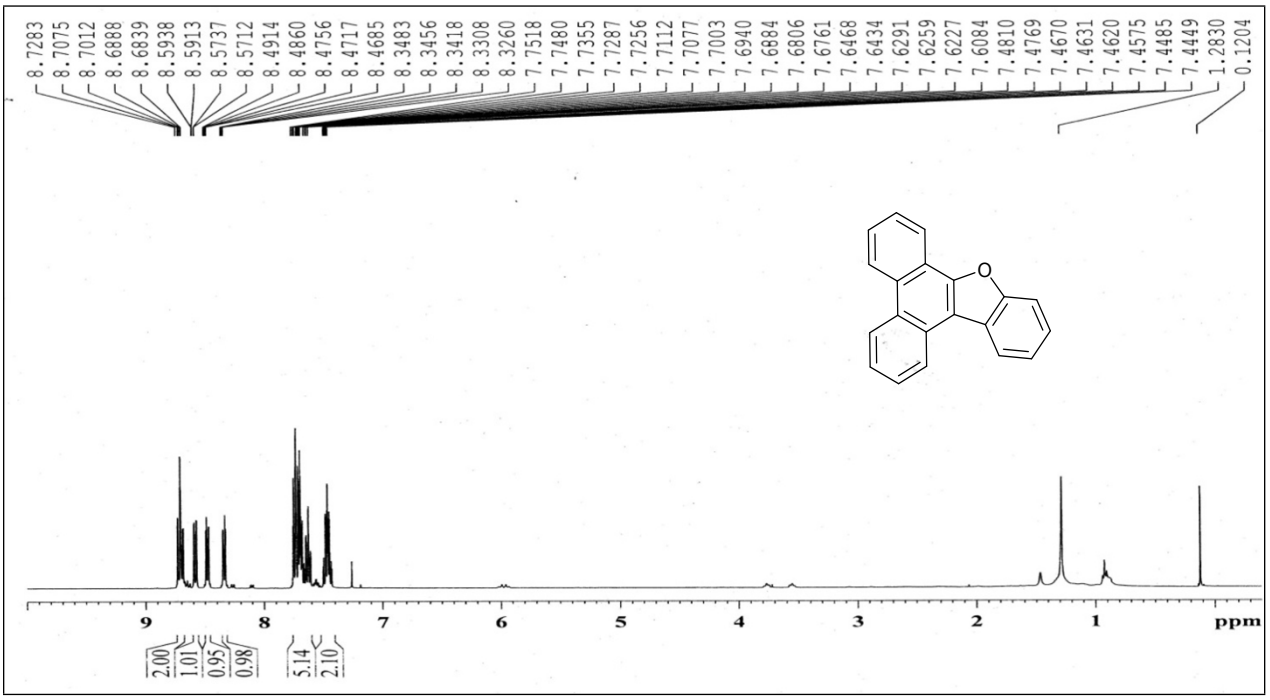
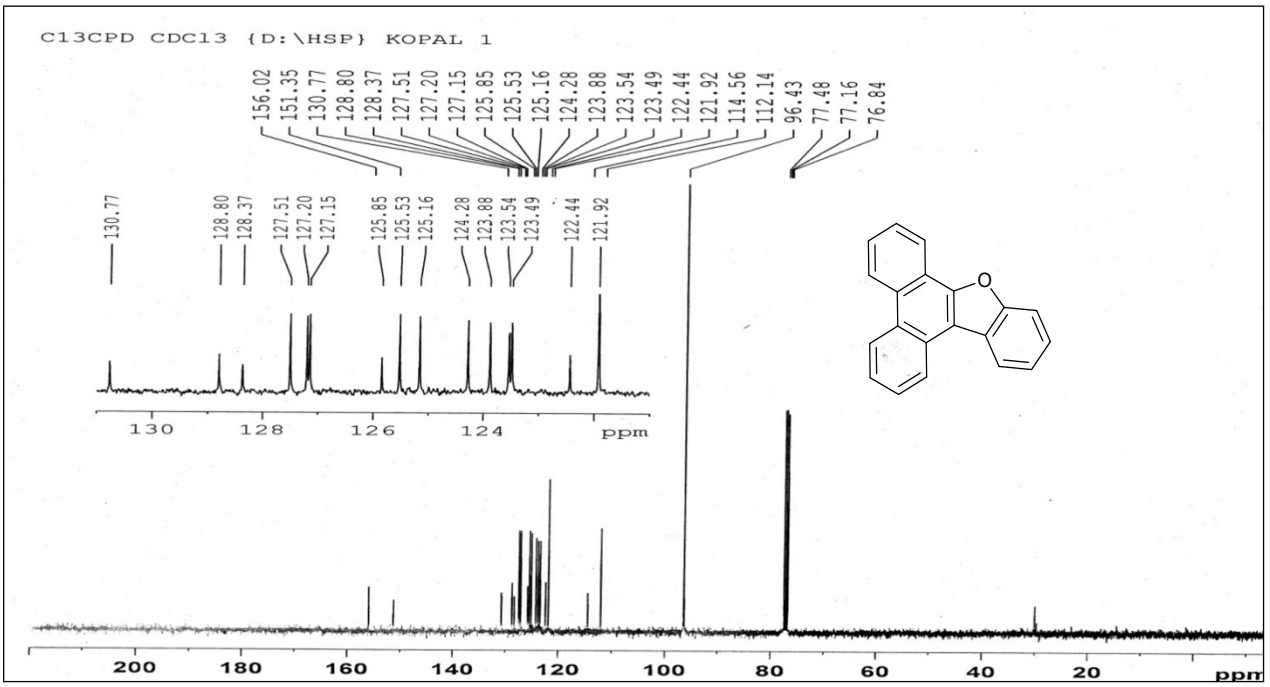
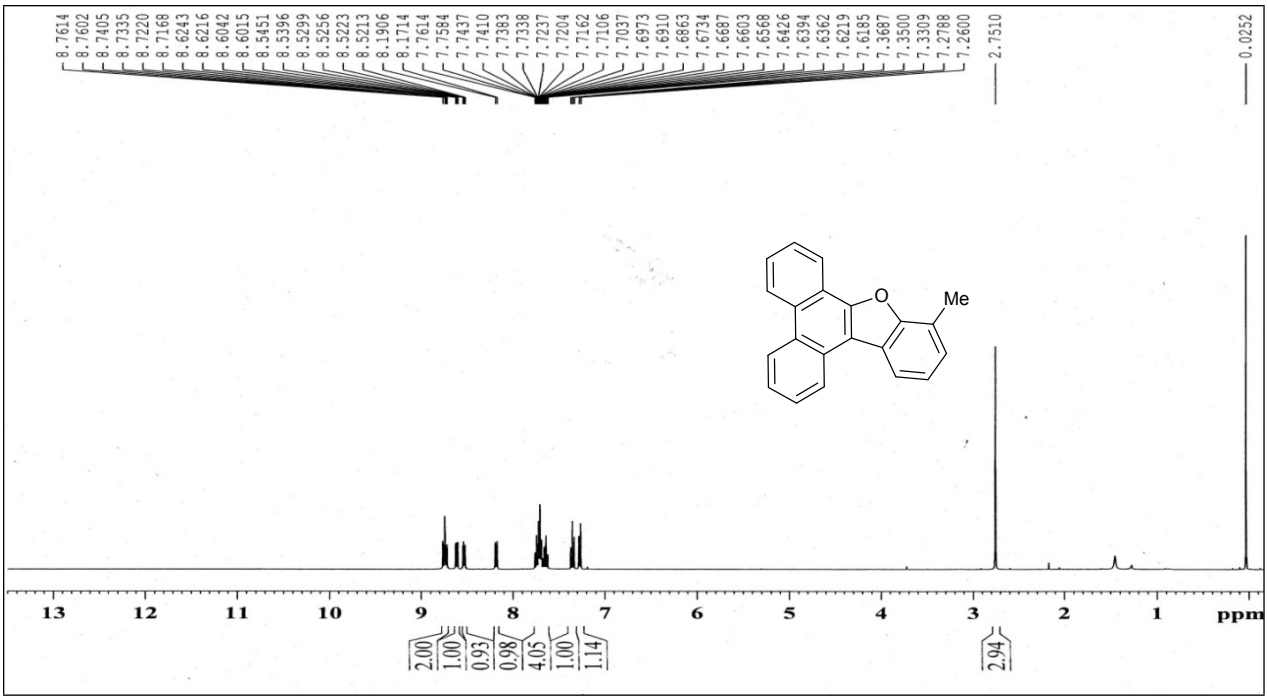
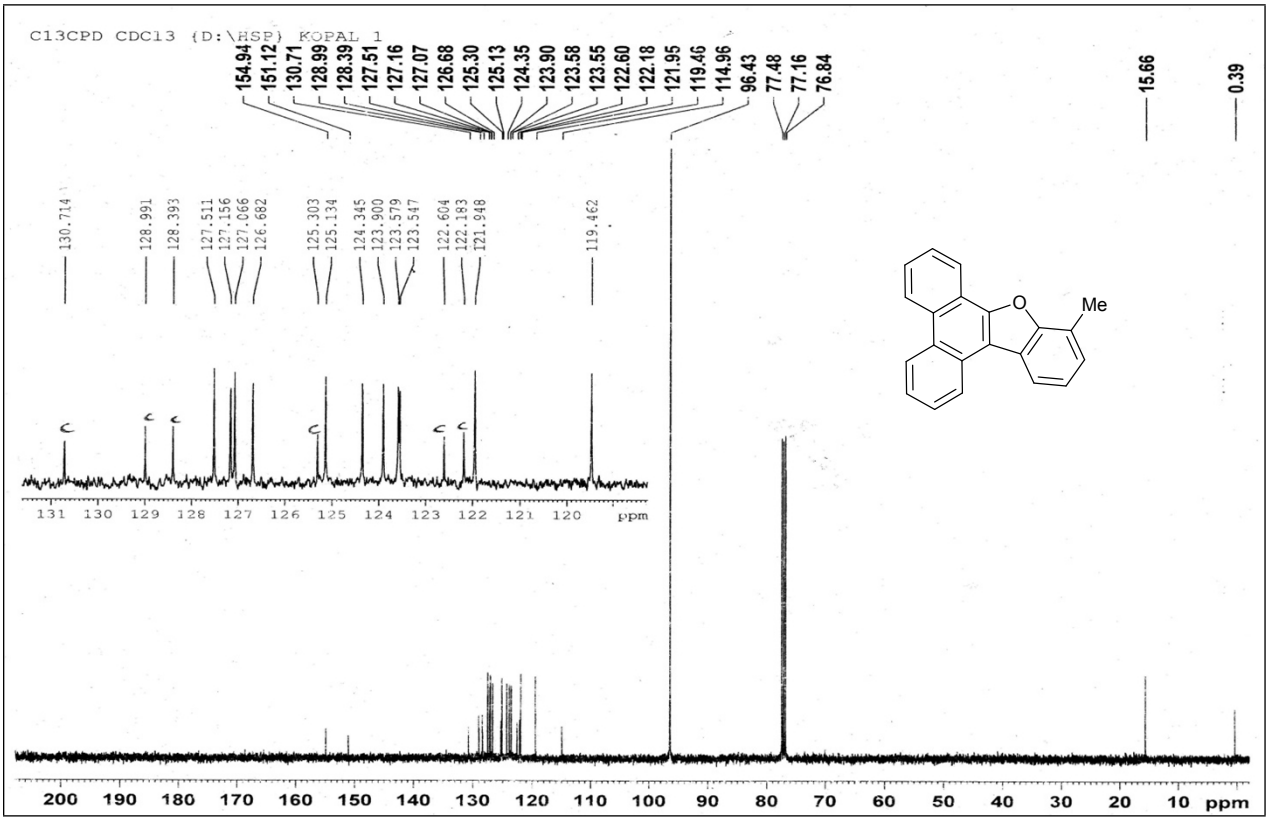


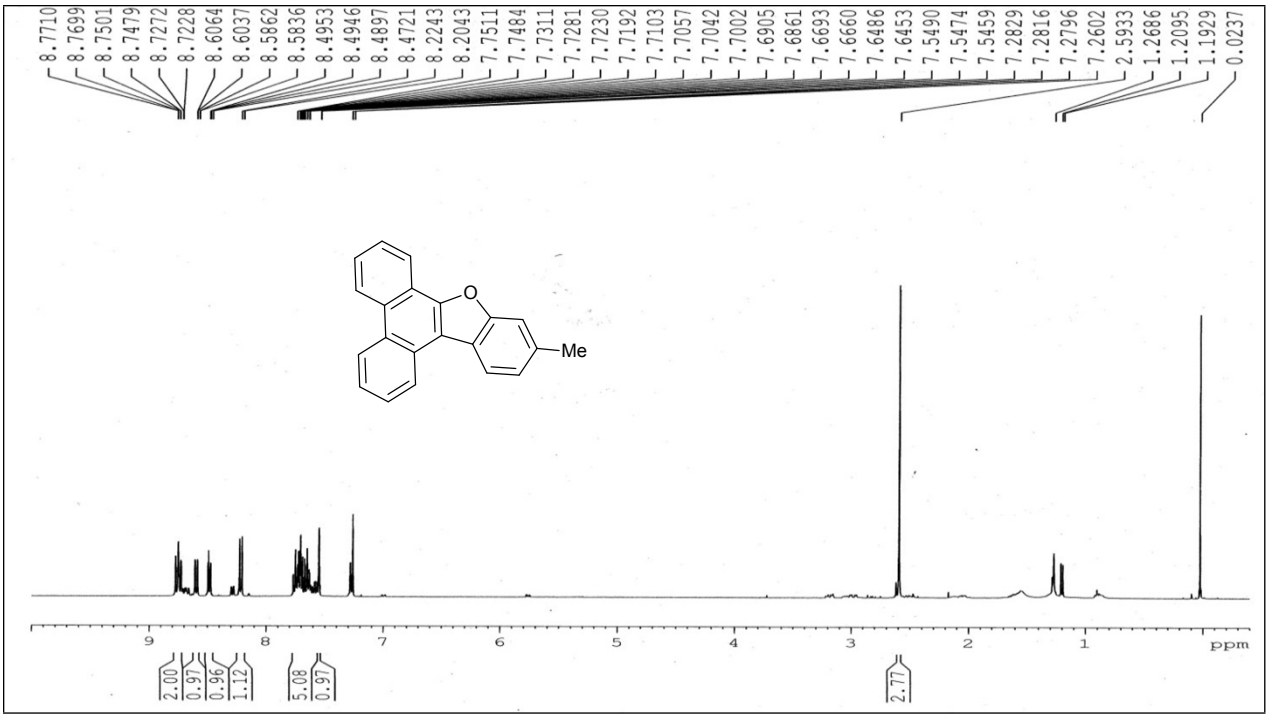



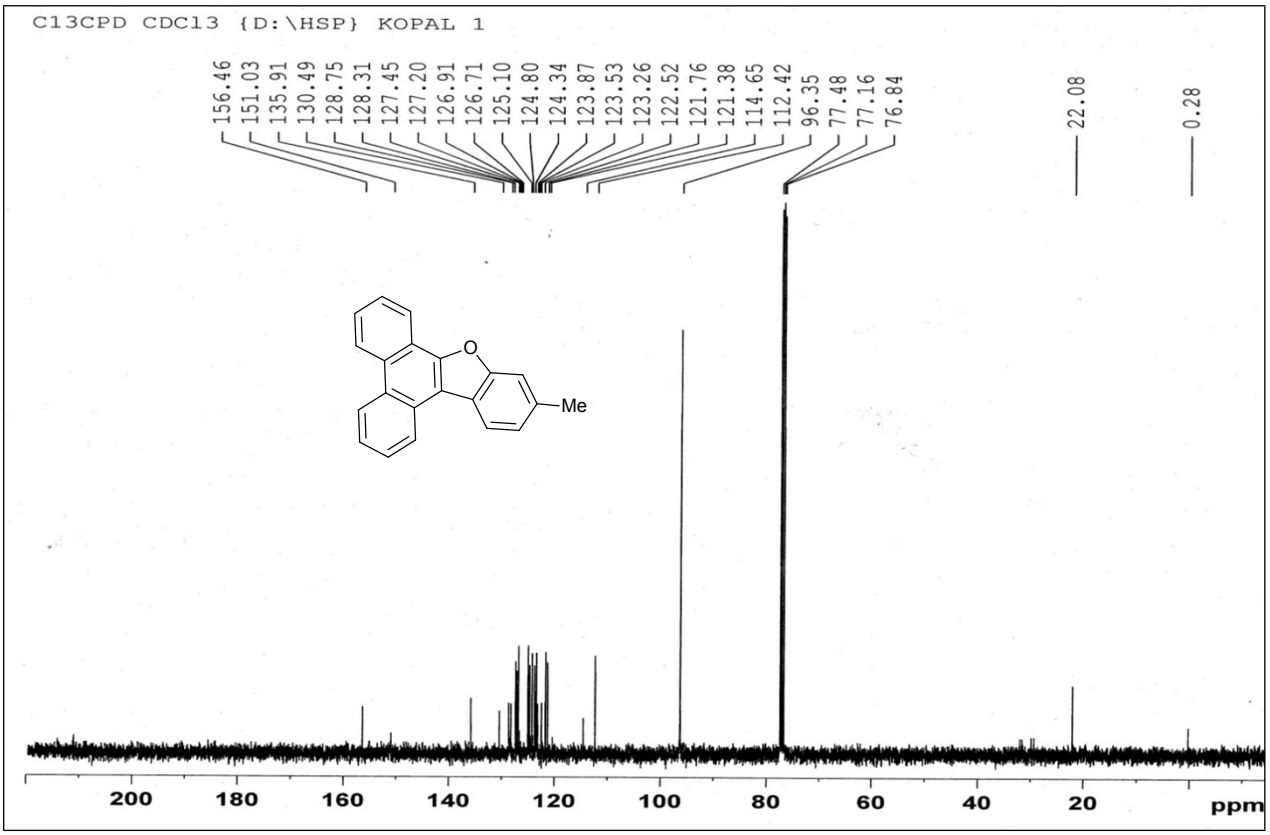

1) $^{1}H$ (400 MHz, $CDCl_3 + CCl_4$) and $^{13}C$ (100 MHz, $CDCl_3 + CCl_4$) NMR spectra of benzo[*d*]phenanthro[9,10-*b*]furan **6a**.



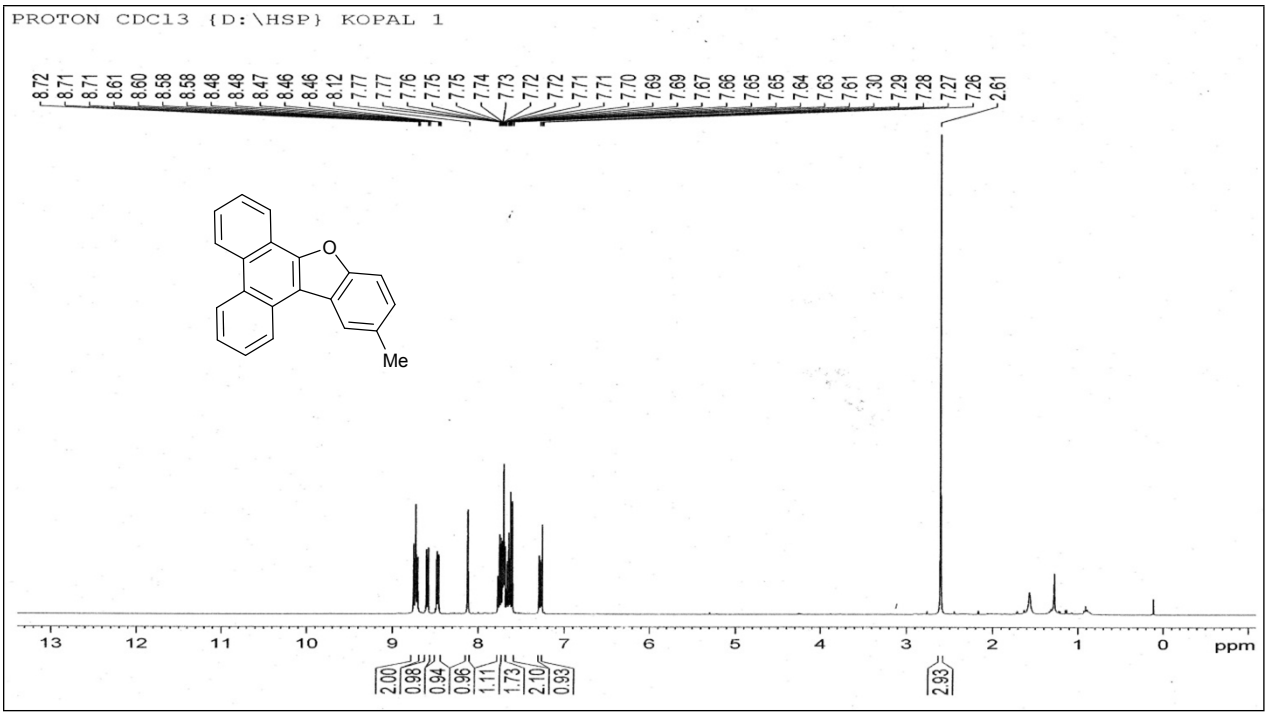



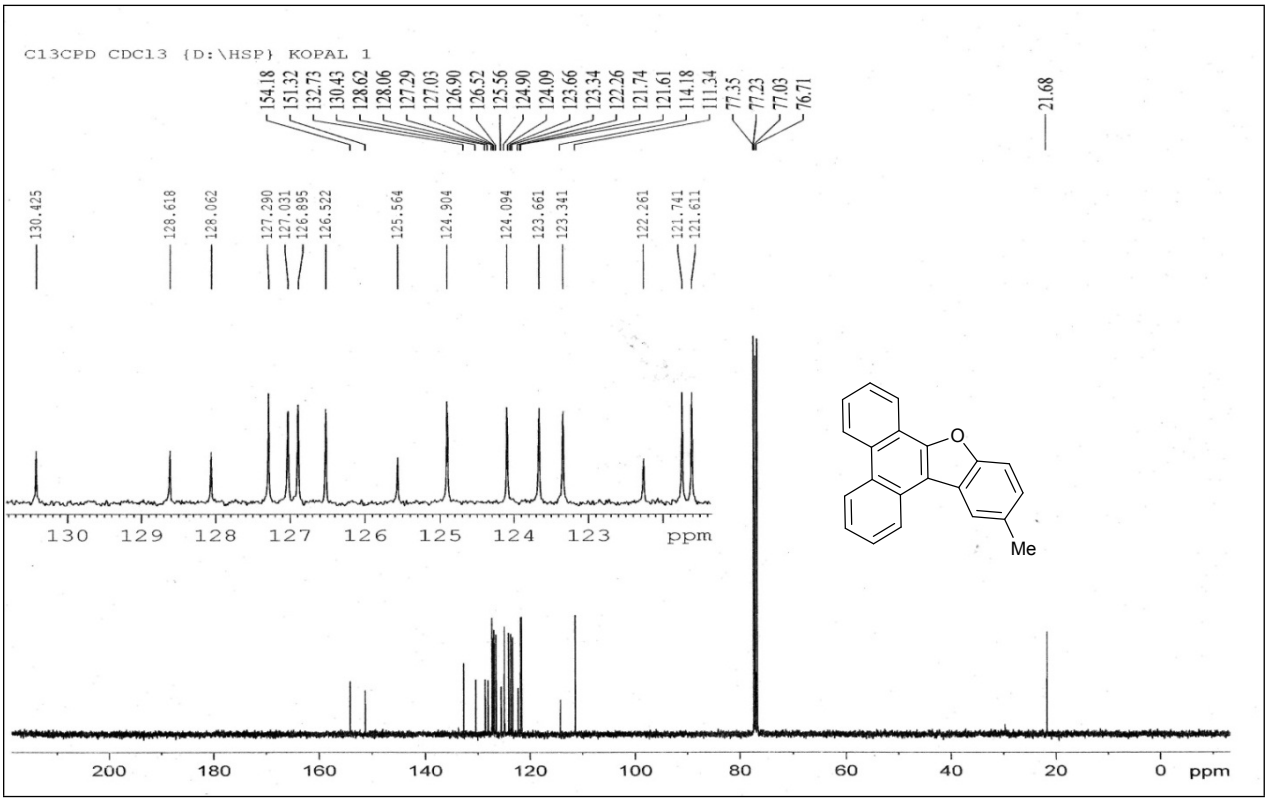

2) $^{1}H$ (400 MHz, $CDCl_3 + CCl_4$) and $^{13}C$ (100 MHz, $CDCl_3 + CCl_4$) NMR spectra of 10-methylbenzo[*d*]phenanthro[9,10-*b*]furan **6b**.



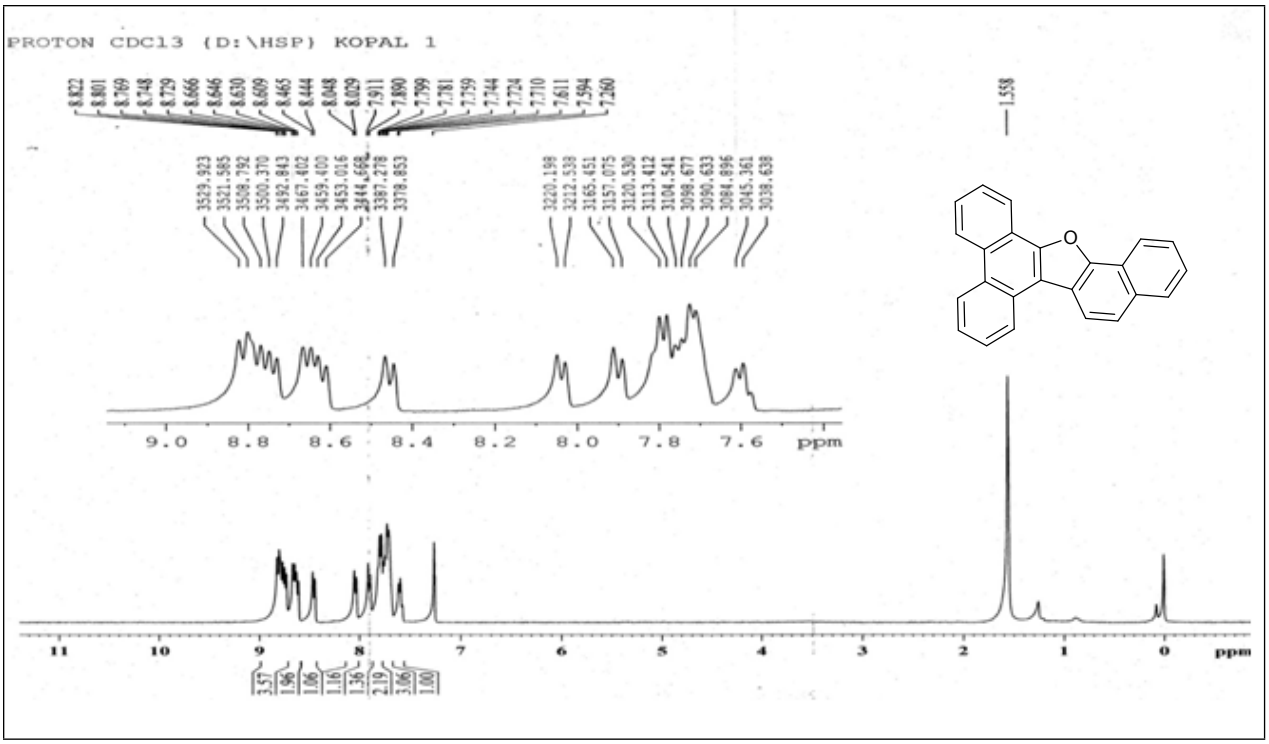



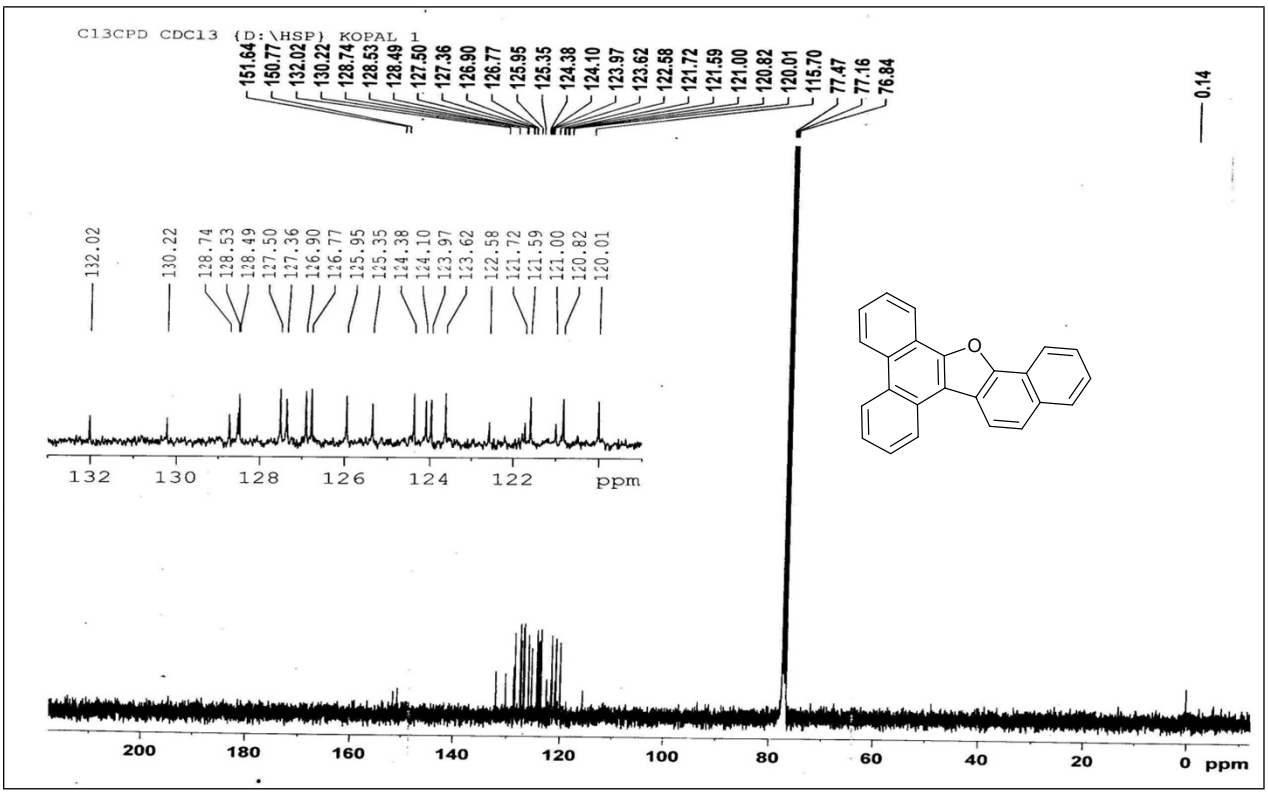

3) $^{1}H$ (400 MHz, $CDCl_3 + CCl_4$) and $^{13}C$ (100 MHz, $CDCl_3 + CCl_4$) NMR spectra of 11-methylbenzo[*d*]phenanthro[9,10-*b*]furan **6c**.



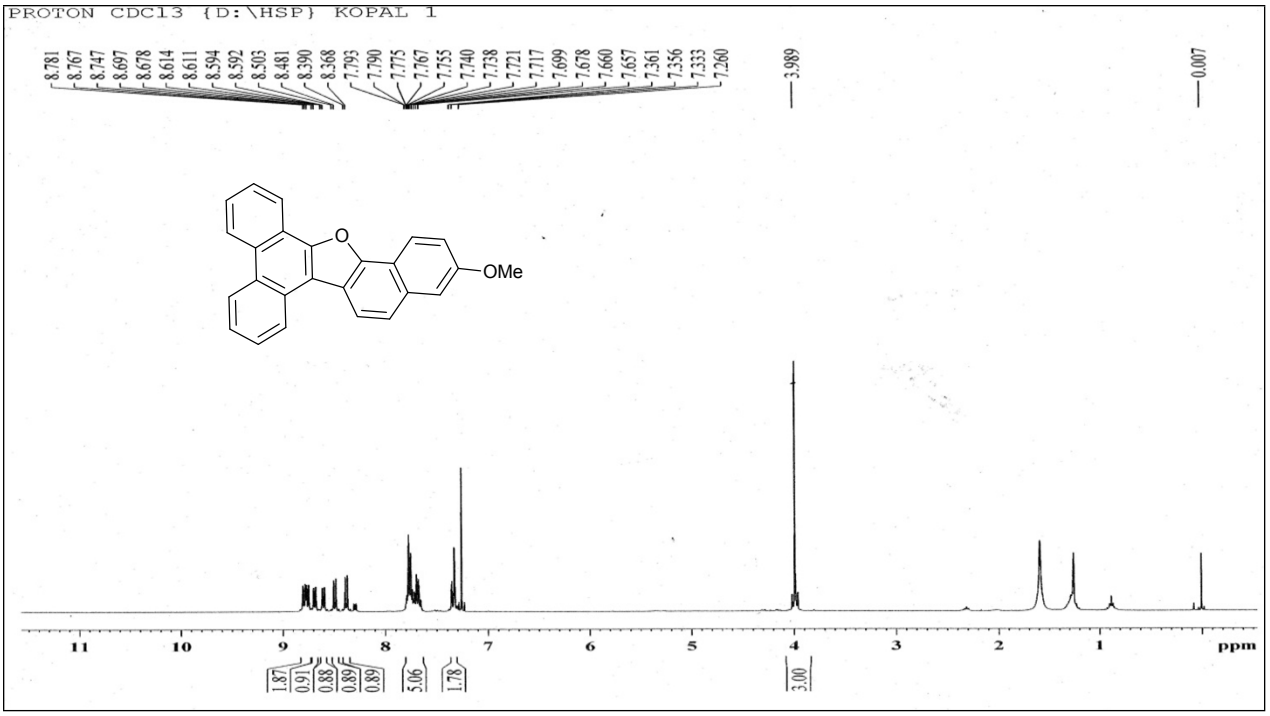



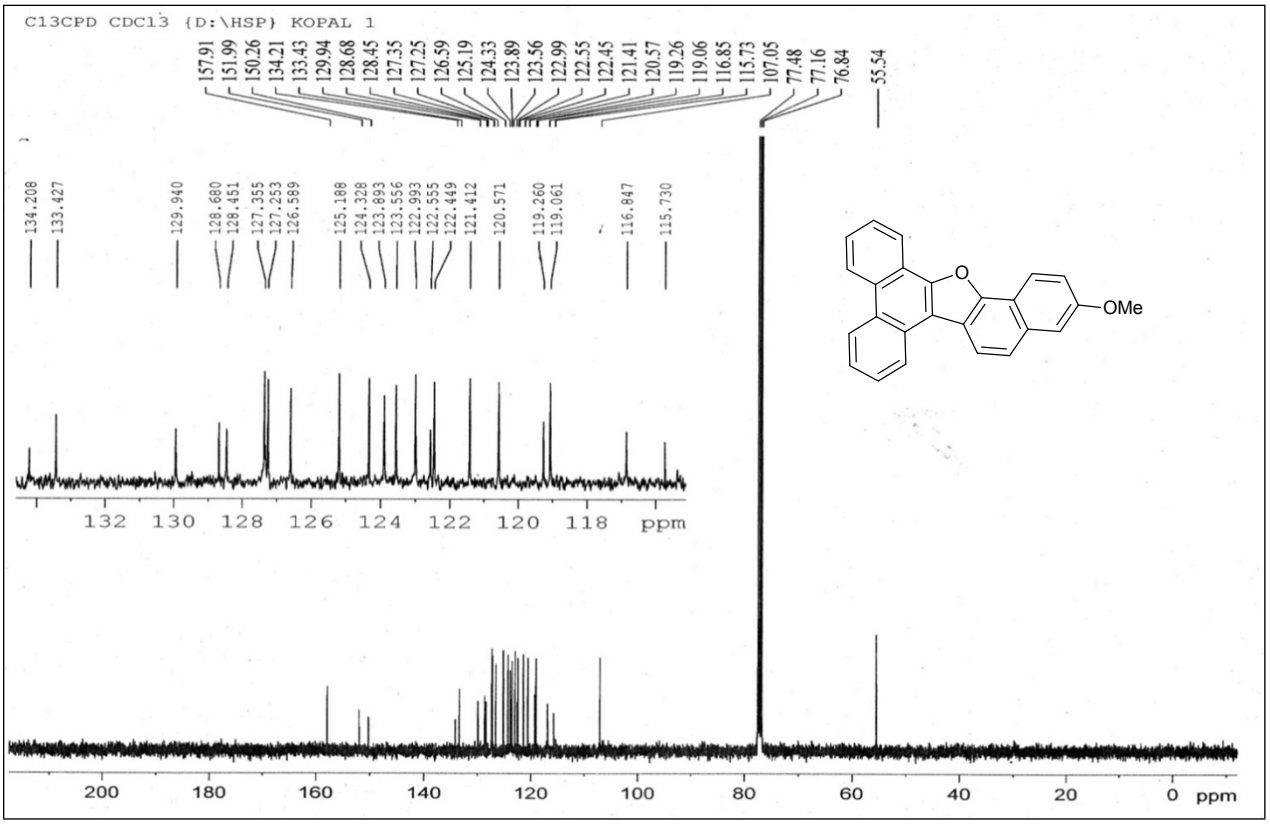

4) $^{1}H$ (400 MHz, $CDCl_3$) and $^{13}C$ (100 MHz, $CDCl_3$) NMR spectra of 12-methylbenzo[*d*]phenanthro[9,10-*b*]furan **6e.**



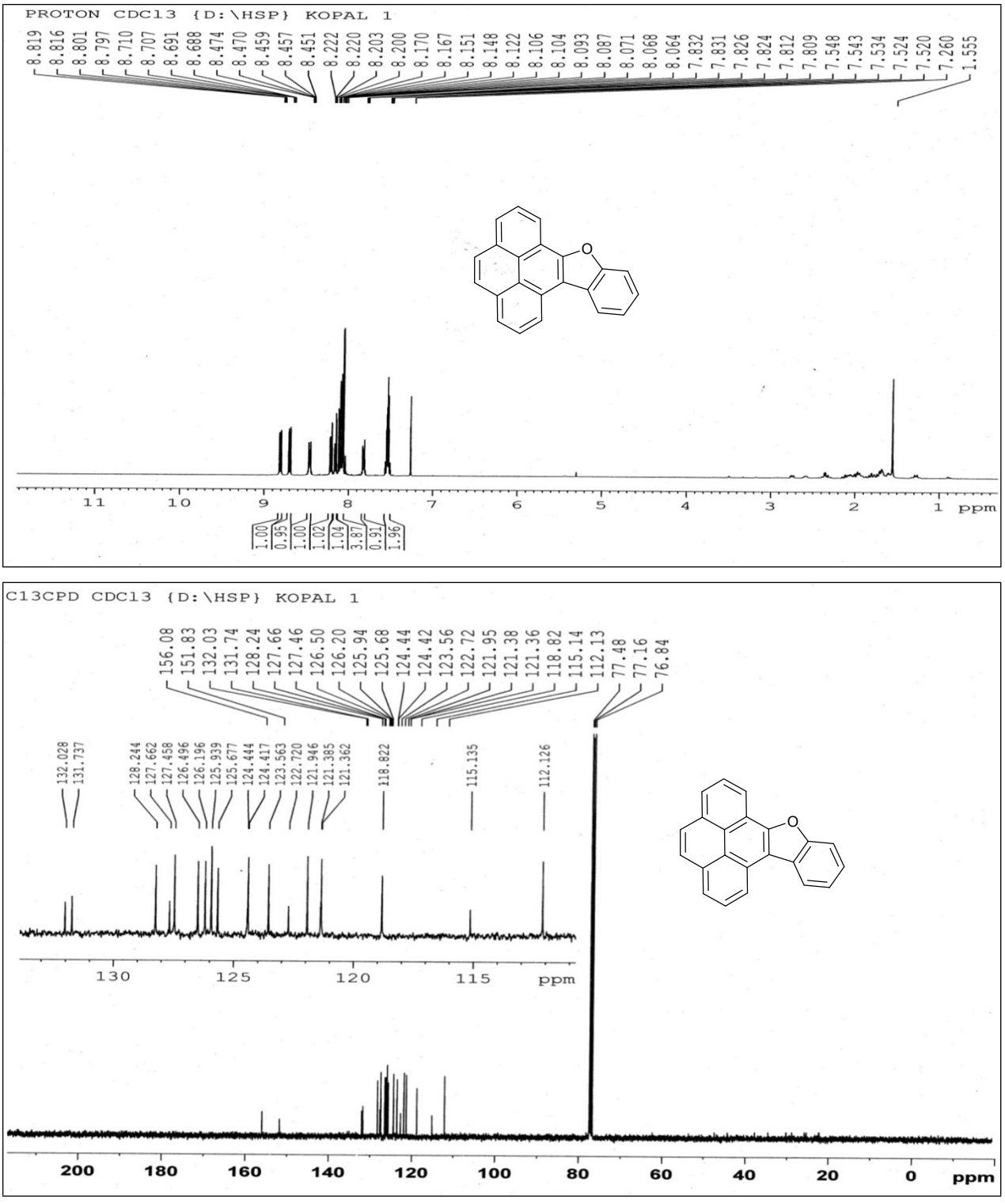




5) $^{1}H$ (400 MHz, $CDCl_3$) and $^{13}C$ (100 MHz, $CDCl_3$) NMR spectra of naphtho[2,1-*d*]phenanthro[9,10-*b*]furan **6f** .

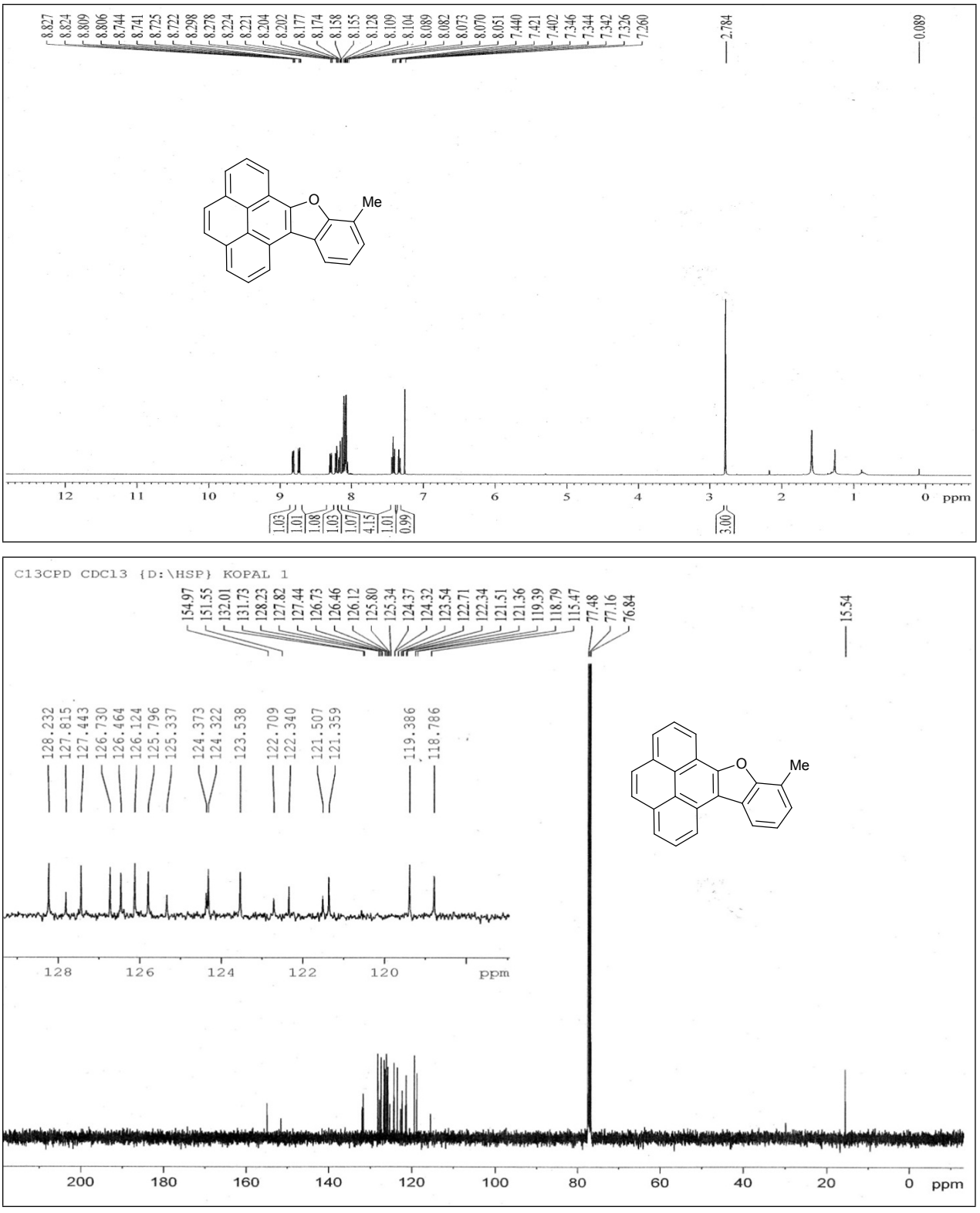


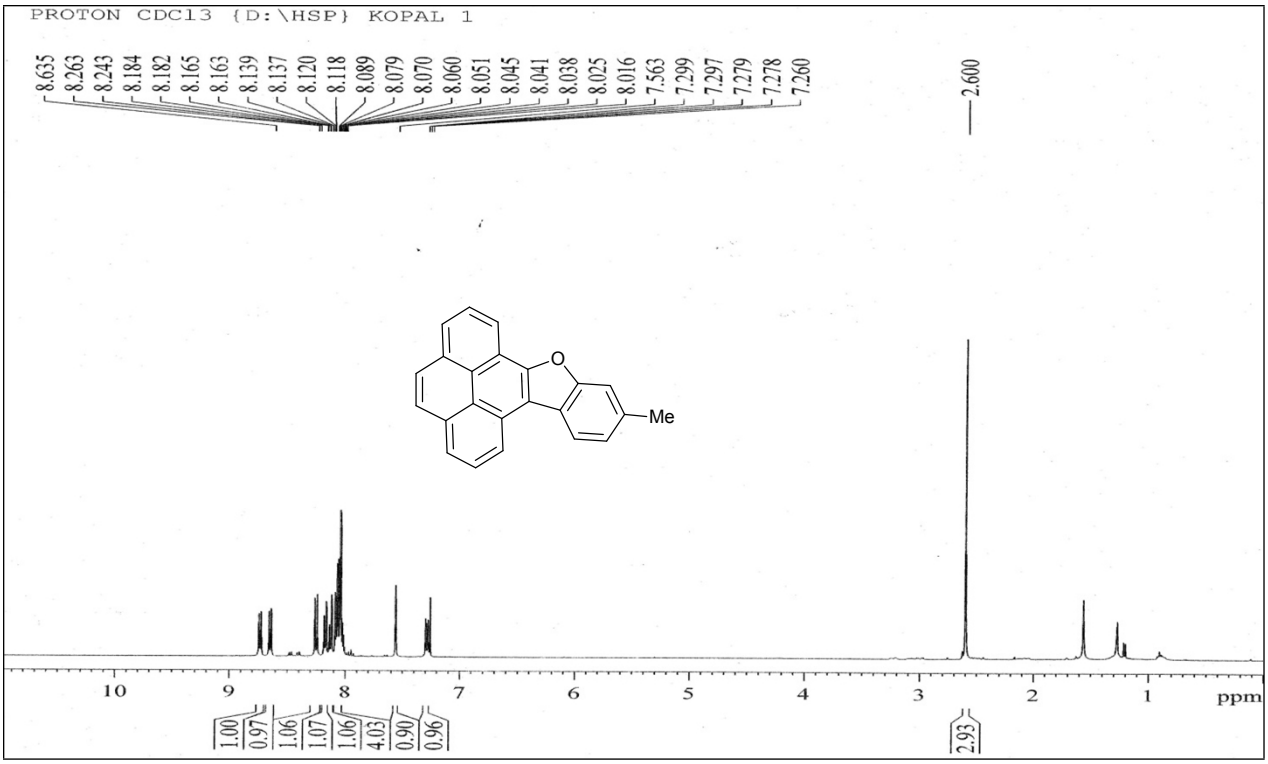

6) $^{1}H$ (400 MHz, $CDCl_3$) and $^{13}C$ (100 MHz, $CDCl_3$) NMR spectra of 12-methoxynaphtho[2,1-*d*]phenanthro[9,10-*b*]furan **6g**.

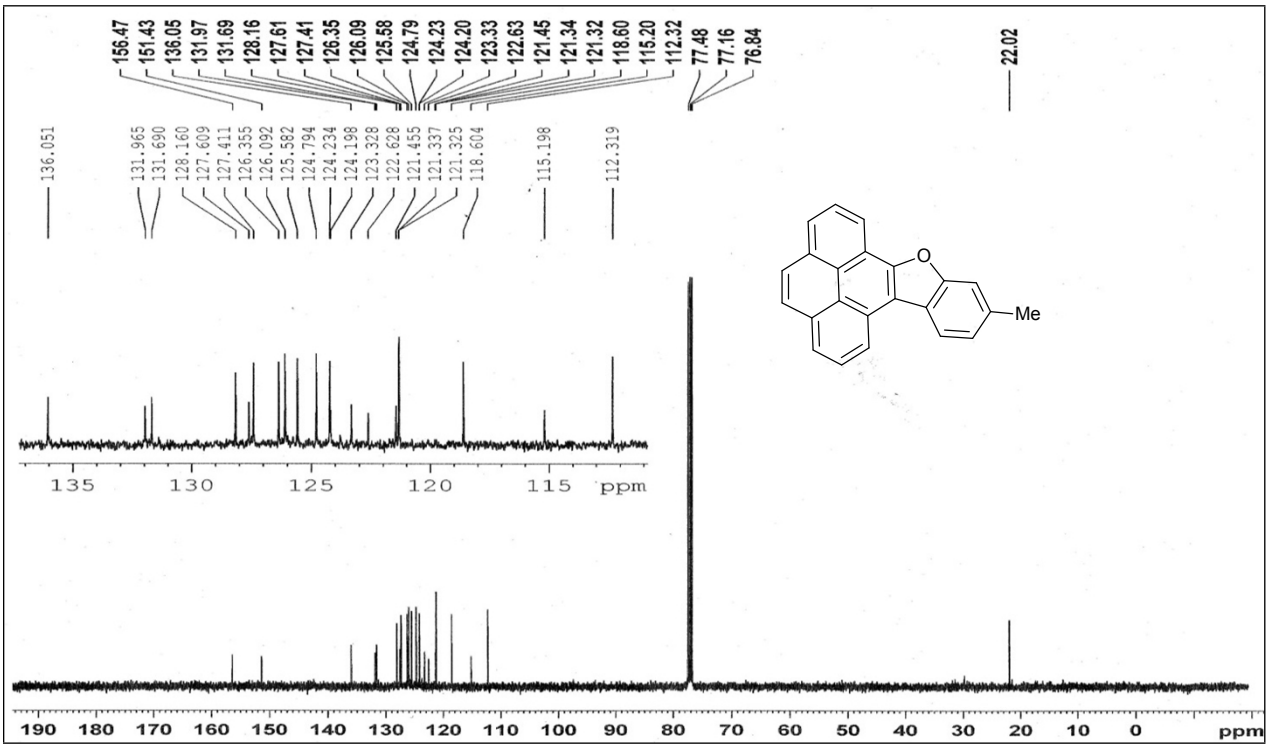



7) $^{1}H$ (400 MHz, $CDCl_3$) and $^{13}C$ (100 MHz, $CDCl_3$) NMR spectra of benzo[*d*]pyreno[4,5-*b*]furan **8a**.

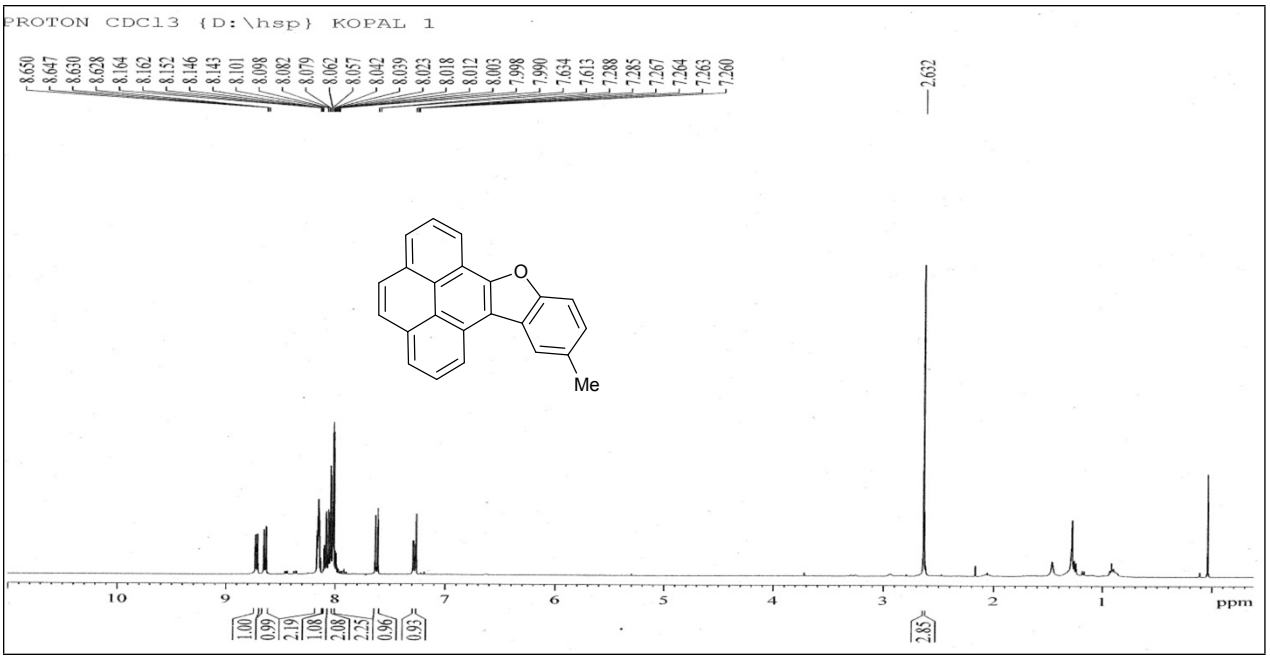


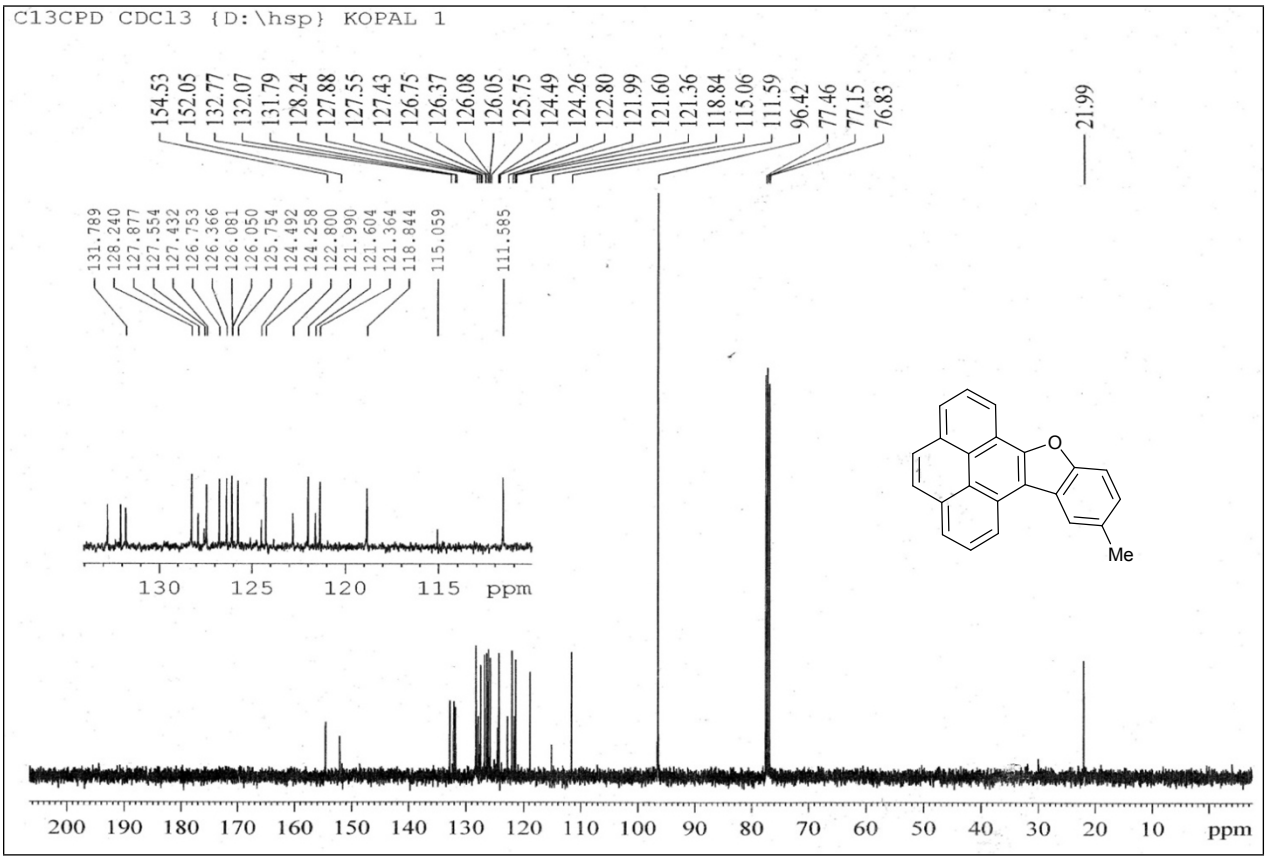

8) $^{1}H$ (400 MHz, $CDCl_3$) and $^{13}C$ (100 MHz, $CDCl_3$) NMR spectra of 10-methylbenzo[*d*]pyreno[4,5-*b*]furan **8b**.



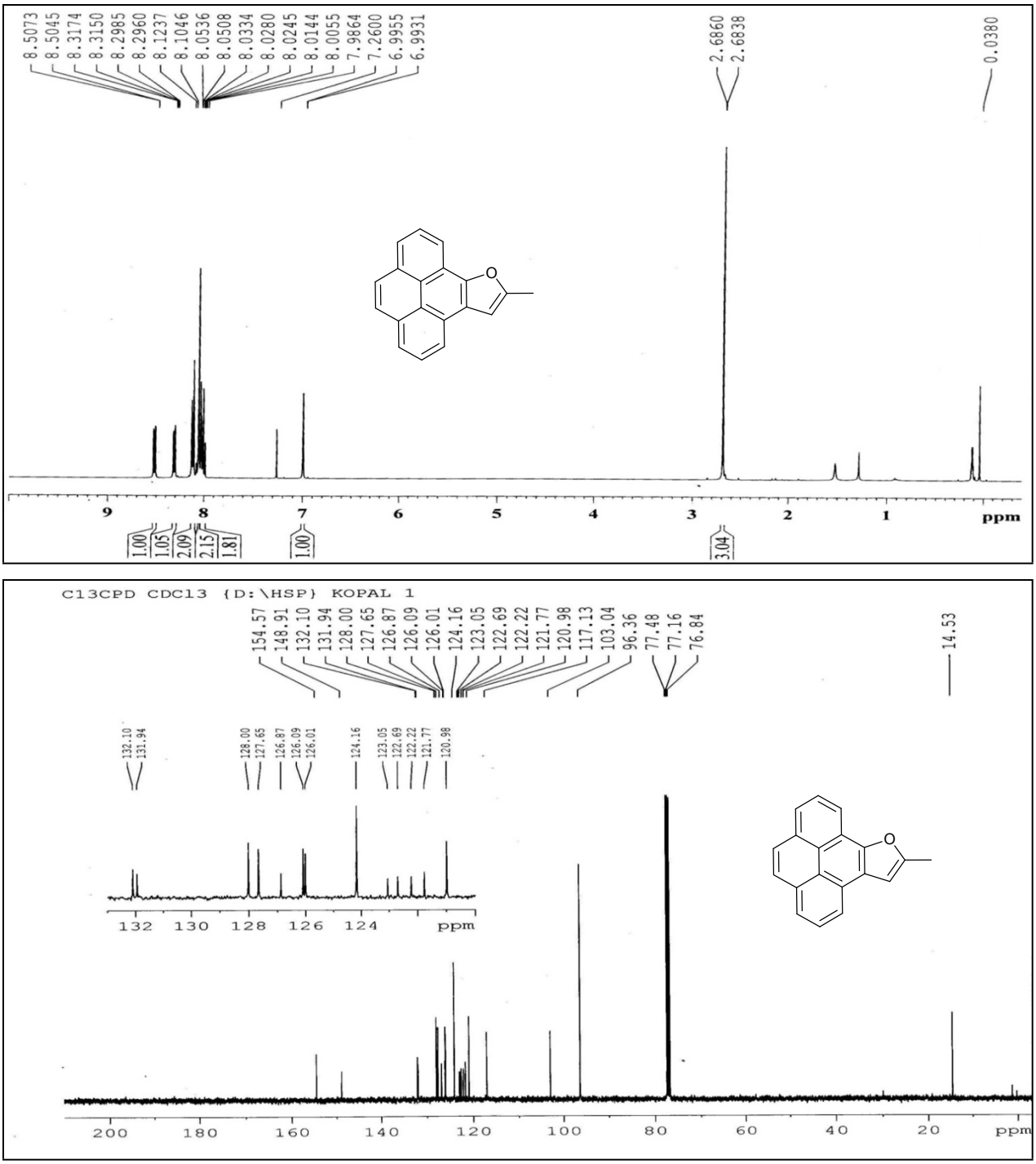




9) $^{1}H$ (400 MHz, $CDCl_3$) and $^{13}C$ (100 MHz, $CDCl_3$) NMR spectra of 11-methylbenzo[*d*]pyreno[4,5-*b*]furan **8c**.

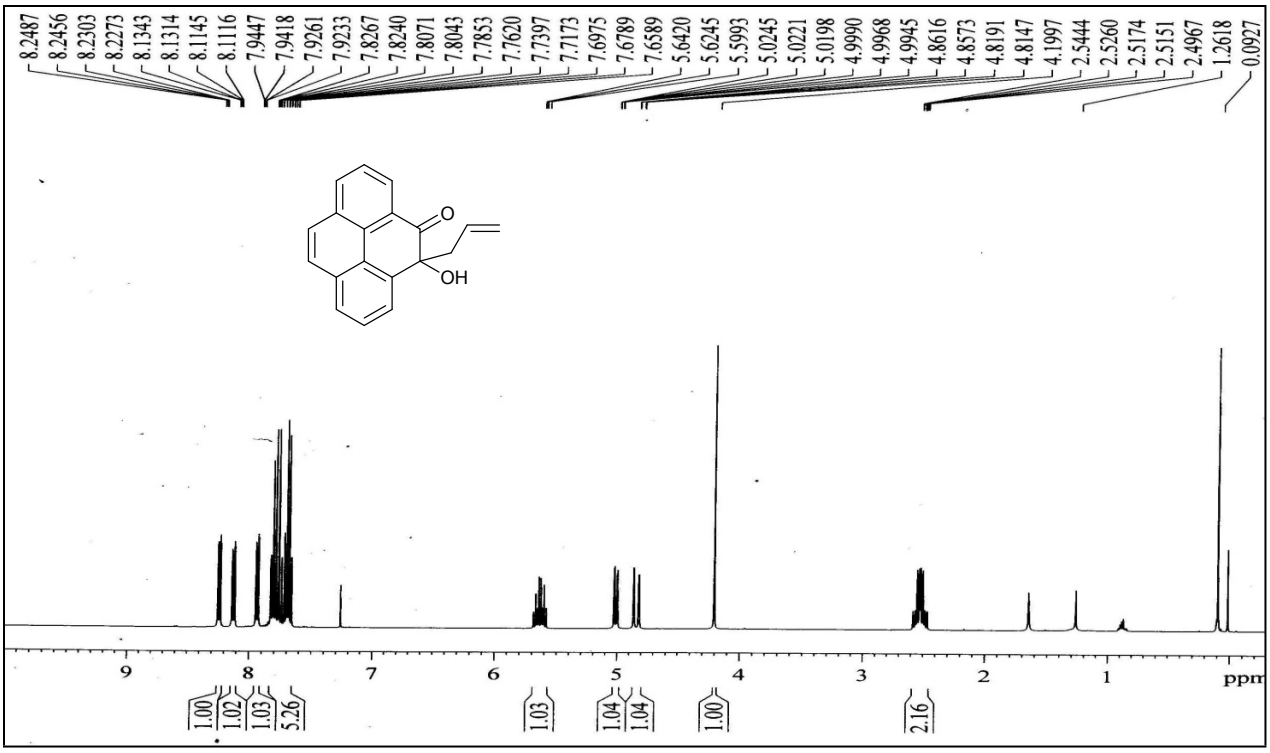


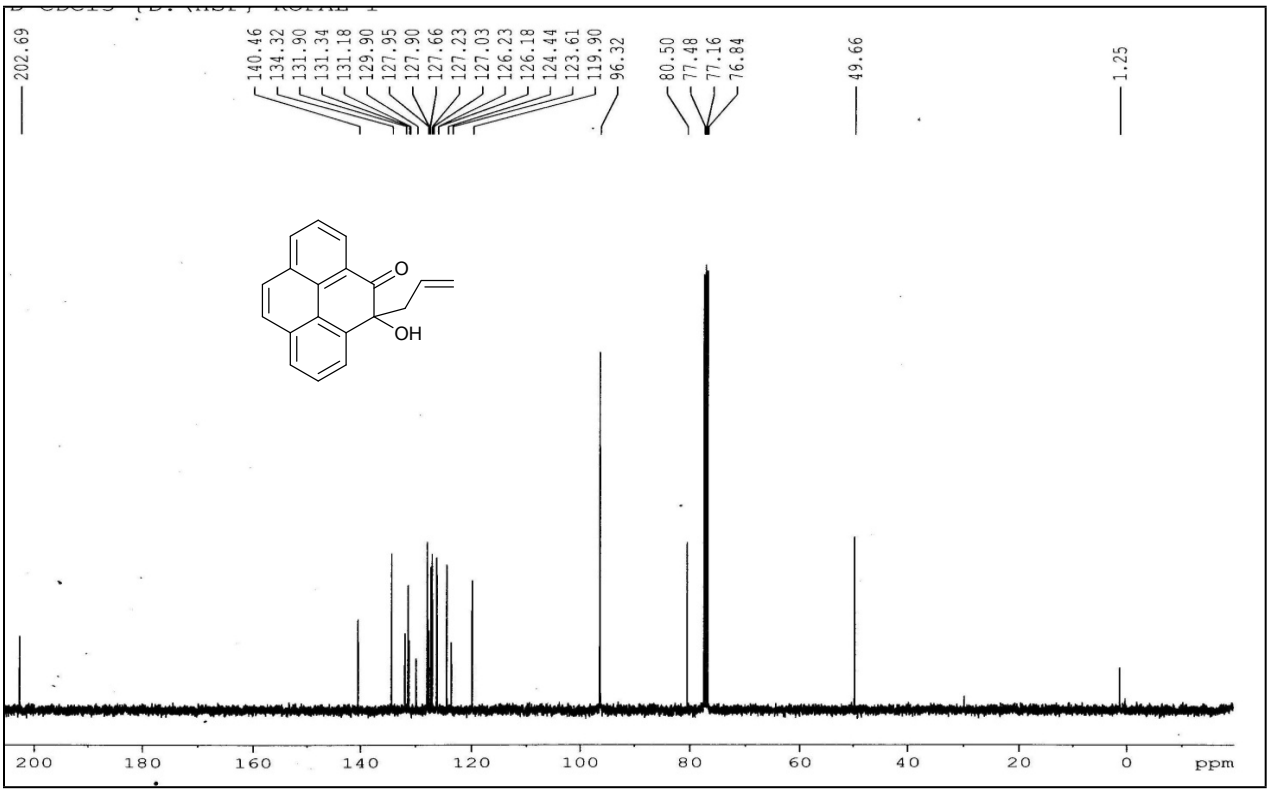




10) $^{1}H$ (400 MHz, $CDCl_3 + CCl_4$) and $^{13}C$ (100 MHz, $CDCl_3 + CCl_4$) NMR spectra of 12-methylbenzo[*d*]pyreno[4,5-*b*]furan **8d**.

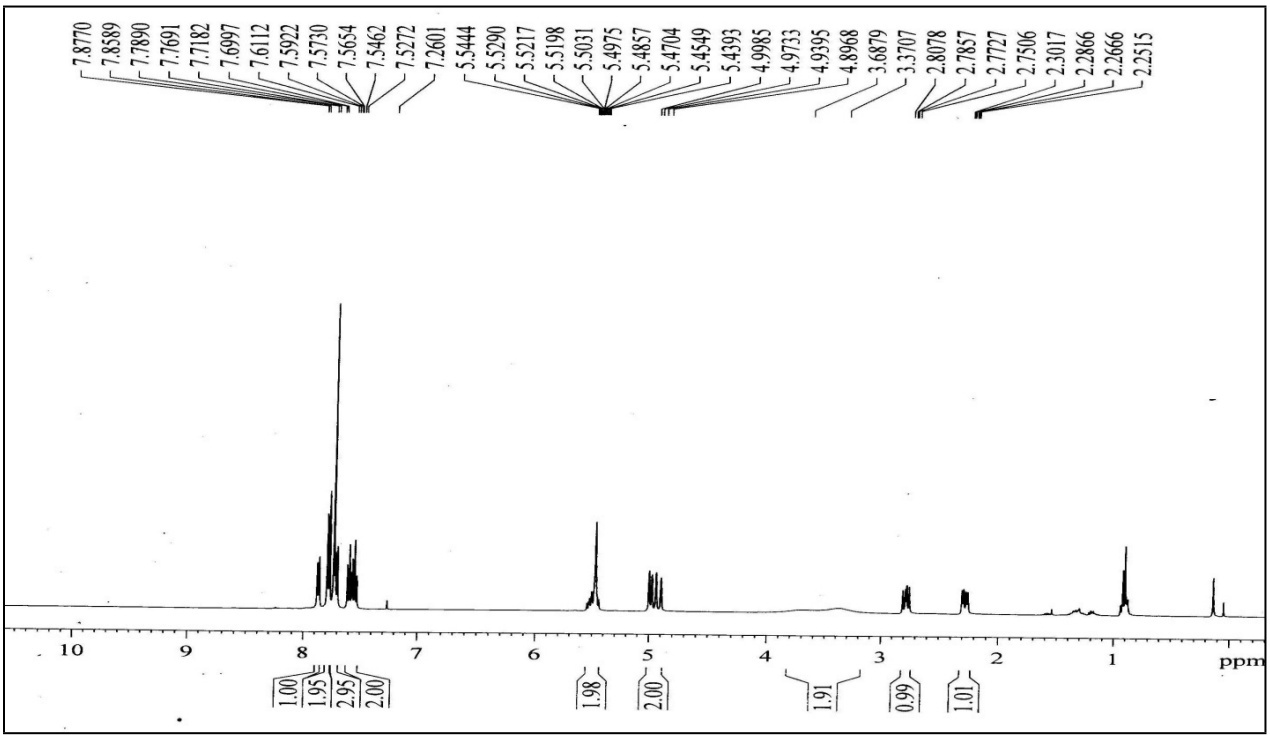


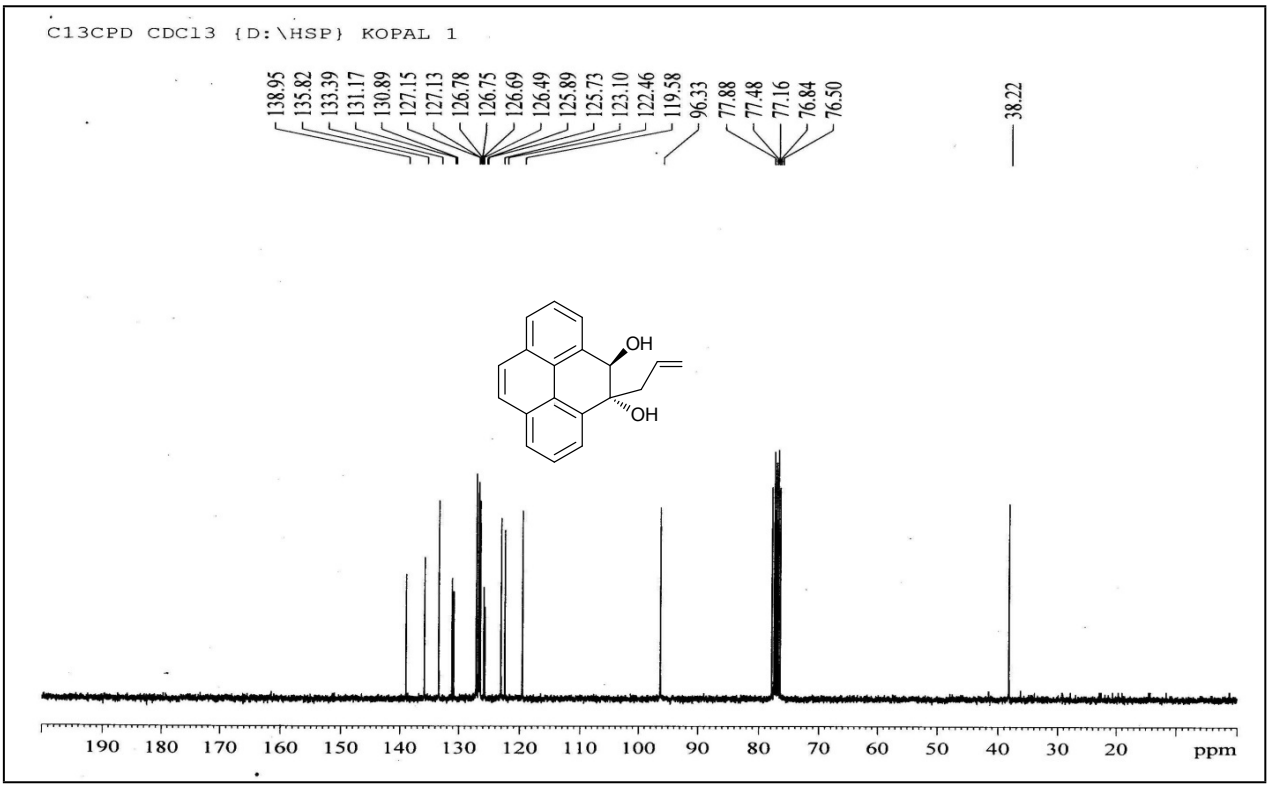

11) $^{1}H$ (400 MHz, $CDCl_3 + CCl_4$) and $^{13}C$ (100 MHz, $CDCl_3 + CCl_4$) NMR spectra of 10-Methylpyreno[4,5-*b*]furan **9**.



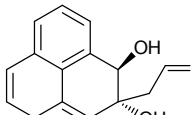

12) $^{1}H$ (400 MHz, $CDCl_3 + CCl_4$) and $^{13}C$ (100 MHz, $CDCl_3 + CCl_4$) NMR spectra of 5-allyl-5-hydroxypyren-4(5*H*)-one **10**.

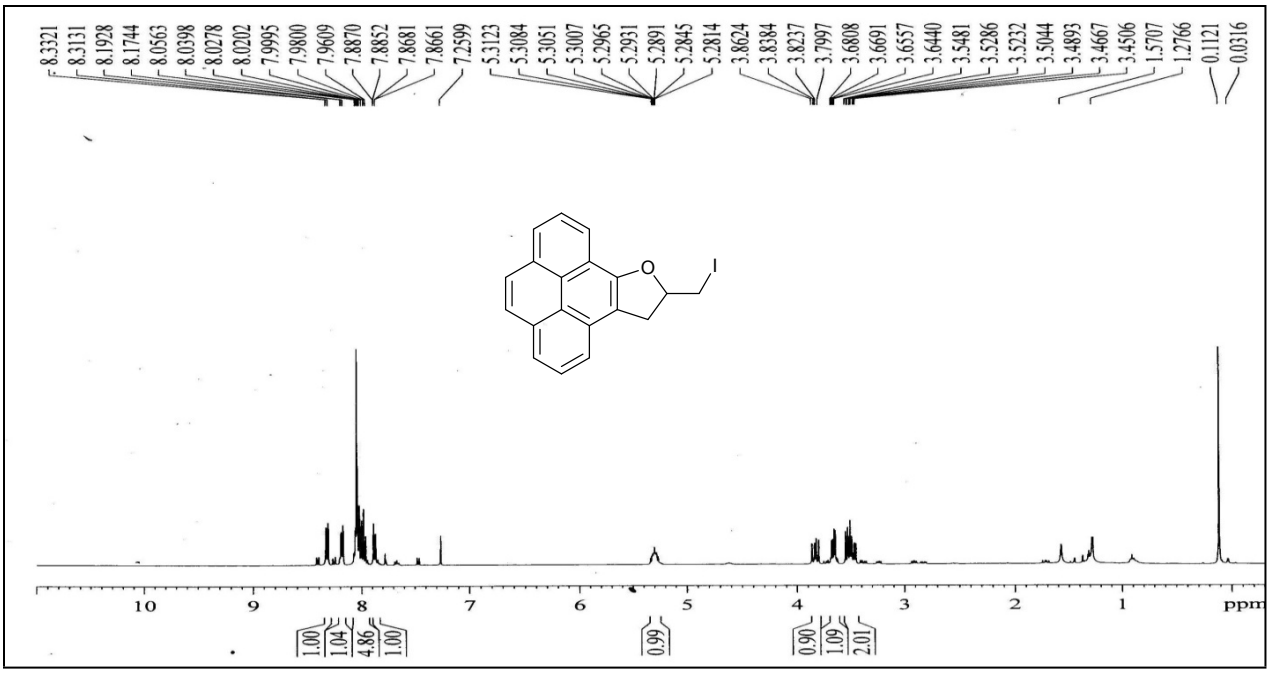


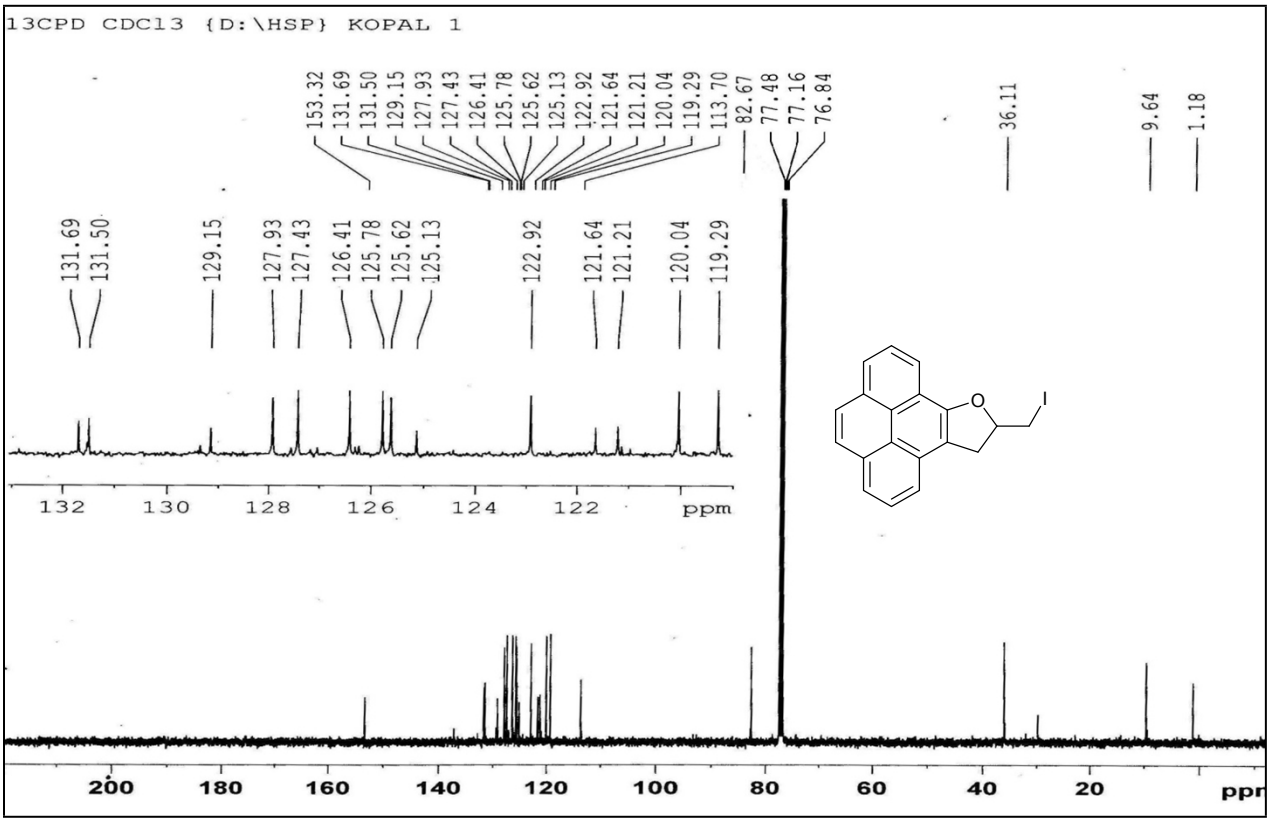




13) $^{1}H$ (400 MHz, $CDCl_3 + CCl_4$) and $^{13}C$ (100 MHz, $CDCl_3 + CCl_4$) NMR spectra of (4*R*,5*R*)-4-allyl-4,5-dihydropyrene-4,5-diol **11**.

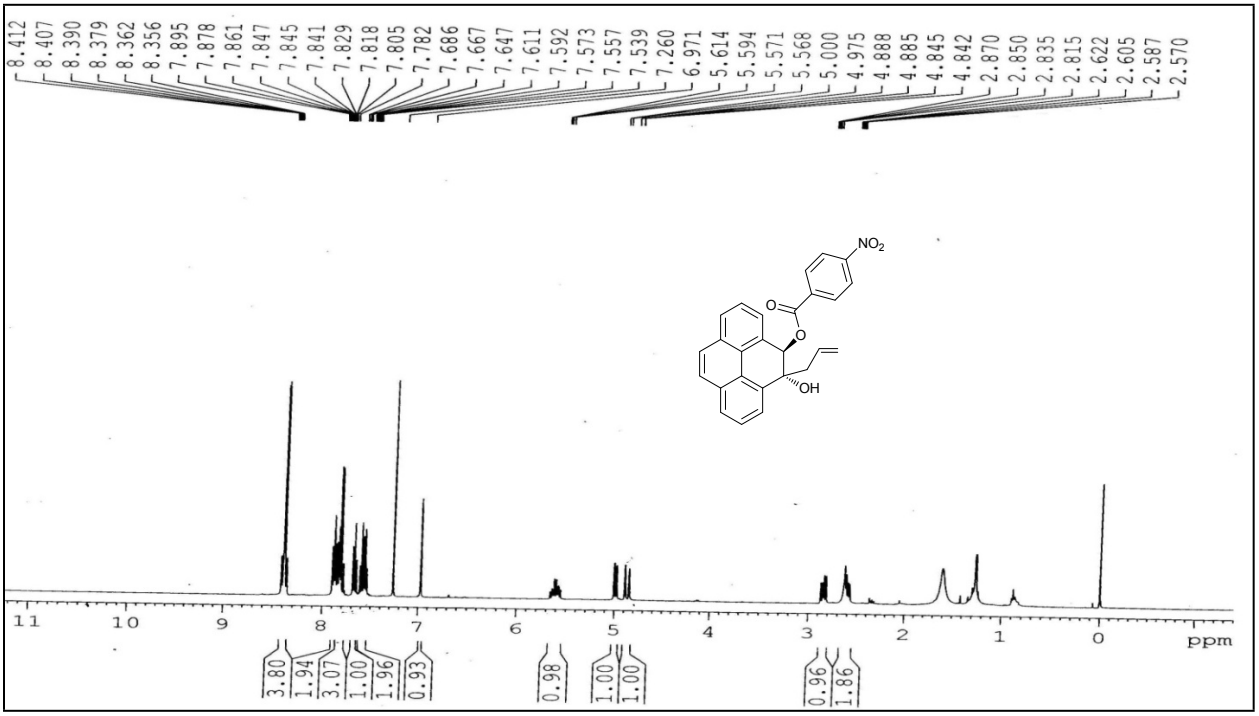


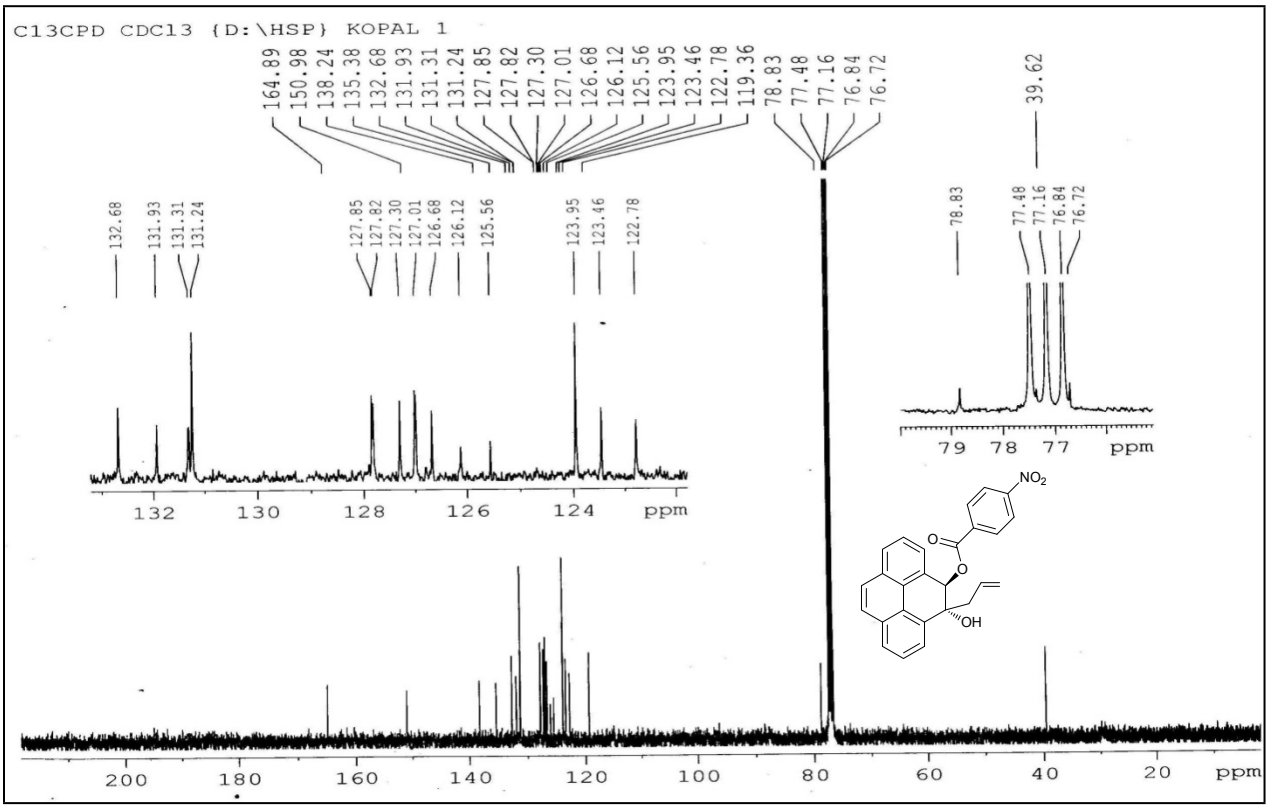





14) $^{1}H$ (400 MHz, $CDCl_3$) and $^{13}C$ (100 MHz, $CDCl_3$) NMR spectra of 10-(iodomethyl)-10,11-dihydropyreno[4,5-*b*]furan **12.**




15) $^{1}H$ (400 MHz, $CDCl_3$) and $^{13}C$ (100 MHz, $CDCl_3$) NMR spectra of (4*R*,5*R*)-5-allyl-5-hydroxy-4,5-dihydropyren-4-yl 4-nitrobenzoate **13.**

II) Assignment of signals in $^{1}H$ and $^{13}C$ NMR spectra of **6a-g**, **8a-d**, **9-13**

(Color indicates the chemical shifts of different protons in a molecule. The signals of these protons appeared together as multiplets)

**Table 1.** $^{1}H$ NMR spectral assignemtns for **6a-e**.

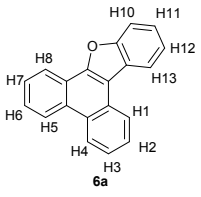
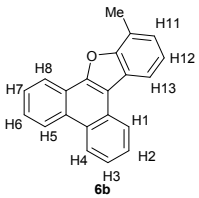
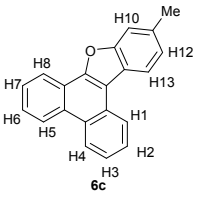
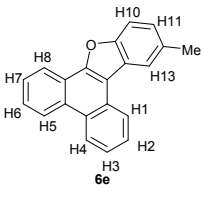
| Hydrogen number |   **6a** |   **6b** |   **6c** |   **6e** |
|---|---|---|---|---|
| H1 | 8.58 (dd, *J* = 8.0, 1.0 Hz, 1H, Ar-CH) | 8.61 (dd, *J* = 8.1, 1.1 Hz, 1H, Ar-CH), | 8.60 (dd, *J* = 8.1, 1.1 Hz, 1H, Ar-CH) | 8.59 (dd, *J* = 8.1, 1.0 Hz, 1H, Ar-CH) |
| H2 | 7.75-7.60 (m, 5H, Ar-CH) | 7.76-7.62 (m, 4H, Ar-CH) | 7.77-7.64 (m, 5H, Ar-CH) | 7.77-7.61 (m, 5H, Ar-CH) |
| H3 | 7.75-7.60 (m, 5H, Ar-CH) | 7.76-7.62 (m, 4H, Ar-CH) | 7.77-7.64 (m, 5H, Ar-CH) | 7.77-7.61 (m, 5H, Ar-CH) |
| H4 | 8.72-8.68 (m, 2H, Ar-CH) | 8.76-8.72 (m, 2H, Ar-CH) | 8.77-8.72 (m, 2H, Ar-CH) | 8.77-8.71 (m, 2H, Ar-CH) |
| H5 | 8.72-8.68 (m, 2H, Ar-CH) | 8.76-8.72 (m, 2H, Ar-CH) | 8.77-8.72 (m, 2H, Ar-CH) | 8.77-8.71 (m, 2H, Ar-CH) |
| H6 | 7.75-7.60 (m, 5H, Ar-CH) | 7.76-7.62 (m, 4H, Ar-CH) | 7.77-7.64 (m, 5H, Ar-CH) | 7.77-7.61 (m, 5H, Ar-CH) |
| H7 | 7.75-7.60 (m, 5H, Ar-CH) | 7.76-7.62 (m, 4H, Ar-CH) | 7.77-7.64 (m, 5H, Ar-CH) | 7.77-7.61 (m, 5H, Ar-CH) |
| H8 | 8.49-8.47 (m, 1H, Ar-CH), | 8.55-8.52 (m, 1H, Ar-CH) | 8.50-8.47 (m, 1H, Ar-CH) | 8.48-8.46 (m, 1H, Ar-CH) |
| H10 | 7.75-7.60 (m, 5H, Ar-CH) | - | 7.54 (s, 1H, Ar-CH), | 7.77-7.61 (m, 5H, Ar-CH) |
| H11 | 7.50-7.43 (m, 2H, Ar-CH) | 7.28 (d, *J* = 7.5 Hz, 1H, Ar-CH) | - | 7.29 (dd, *J* = 8.3, 1.1 Hz, 1H, Ar-CH) |
| H12 | 7.50-7.43 (m, 2H, Ar-CH) | 7.35 (t, *J* = 7.6 Hz, 1H, Ar-CH) | 7.77-7.64 (m, 5H, Ar-CH) | - |
| H13 | 8.35-8.33 (m, 1H, Ar-CH), | 8.18 (d, *J* = 7.7 Hz, 1H, Ar-CH), | 8.21 (d, *J* = 8.0 Hz, 1H, Ar-CH) | 8.12 (s, 1H, Ar-CH) |
| Methyl | - | 2.75 (s, 3H, $CH_3$) | 2.59 (s, 3H, $CH_3$) | 2.61 (s, 3H, $CH_3$) |

**Table 2.** $^{1}$H NMR spectral assignemtns for **6f-g**.

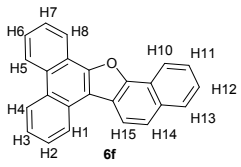
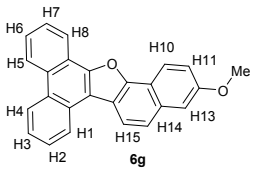
| Hydrogen number |  **6f** |  **6g** |
|---|---|---|
| H1 | 8.67-8.61 (m, 2H, Ar-CH) | 8.69 (d, *J* = 7.8 Hz, 1H, Ar-CH) |
| H2 | 7.80-7.59 (m, 6H, Ar-CH) | 7.79-7.66 (m, 5H, Ar-CH) |
| H3 | 7.80-7.59 (m, 6H, Ar-CH) | 7.79-7.66 (m, 5H, Ar-CH) |
| H4 | 8.82-8.73 (m, 3H, Ar-CH) | 8.76 (d, *J* = 8.3 Hz, 2H, Ar-CH) |
| H5 | 8.82-8.73 (m, 3H, Ar-CH) | 8.76 (d, *J* = 8.3 Hz, 2H, Ar-CH) |
| H6 | 7.80-7.59 (m, 6H, Ar-CH) | 7.79-7.66 (m, 5H, Ar-CH) |
| H7 | 7.80-7.59 (m, 6H, Ar-CH) | 7.79-7.66 (m, 5H, Ar-CH) |
| H8 | 8.67-8.61 (m, 2H, Ar-CH) | 8.60 (dd, *J* = 8.0, 1.0 Hz, 1H, Ar-CH)) |
| H10 | 8.82-8.73 (m, 3H, Ar-CH) | 7.79-7.66 (m, 5H, Ar-CH) |
| H11 | 7.80-7.59 (m, 6H, Ar-CH) | 7.36-7.33 (m, 2H, Ar-CH) |
| H12 | 7.80-7.59 (m, 6H, Ar-CH) | - |
| H13 | 8.45 (d, *J* = 8.4 Hz, 1H, Ar-CH) | 7.36-7.33 (m, 2H, Ar-CH) |
| H14 | 7.90 (d, *J* = 7.7 Hz, 1H, Ar-CH) | 8.38 (d, *J* = 8.7 Hz, 1H, Ar-CH) |
| H15 | 8.04 (d, *J* = 7.7 Hz, 1H, Ar-CH) | 8.49 (d, *J* = 8.7 Hz, 1H, Ar-CH) |
| O-Me | | 3.99 (s, 3H, $OCH_3$) |

**Table 3.** $^{1}$H NMR spectral assignemtns for **8a-d**.

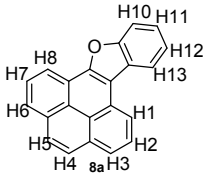
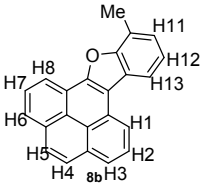
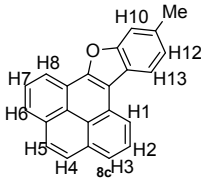
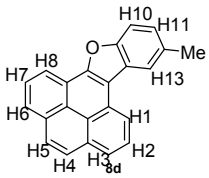
| Hydrogen number |  |  |  |  |
|---|---|---|---|---|
| H1 | 8.12-8.06 (m, 4H, Ar-CH) | 8.18-8.05 (m, 5H, Ar-CH) | 8.18-8.02 (m, 5H, Ar-CH) | 8.10-8.00 (m, 5H, Ar-CH |
| H2 | 8.12-8.06 (m, 4H, Ar-CH) | 8.18-8.05 (m, 5H, Ar-CH) | 8.18-8.02 (m, 5H, Ar-CH) | 8.10-8.00 (m, 5H, Ar-CH |
| H3 | 8.81 (dd, *J* = 7.6, 1.2 Hz, 1H, Ar-CH) | 8.82 (dd, *J* = 7.6, 1.2 Hz, 1H, Ar-CH) | 8.74 (dd, *J* = 7.5, 1.1 Hz, 1H, Ar-CH) | 8.72 (dd, *J* = 7.5, 1.1 Hz, 1H, Ar-CH) |
| H4 | 8.21 (dd, *J* = 7.7, 1.0 Hz, 1H, Ar-CH), | 8.29 (d, *J* = 7.6 Hz, 1H, Ar-CH) | 8.25 (d, *J* = 8.0 Hz, 1H, Ar-CH) | 8.17-8.14 (m, 2H, Ar-CH) |
| H5 | 8.16 (dd, *J* = 7.7, 1.2 Hz, 1H, Ar-CH) | 8.21 (dd, *J* = 7.7, 1.1 Hz, 1H, Ar-CH) | 8.17 (dd, *J* = 7.6, 0.9 Hz, 1H, Ar-CH) | 8.17-8.14 (m, 2H, Ar-CH) |
| H6 | 8.70 (dd, *J* = 7.7, 1.1 Hz, 1H, Ar-CH) | 8.73 (dd, *J* = 7.7, 1.1 Hz, 1H, Ar-CH) | 8.65 (dd, *J* = 7.7, 1.0 Hz, 1H, Ar-CH) | 8.64 (dd, *J* = 7.7, 1.1 Hz, 1H, Ar-CH) |
| H7 | 8.12-8.06 (m, 4H, Ar-CH) | 8.18-8.05 (m, 5H, Ar-CH) | 8.18-8.02 (m, 5H, Ar-CH) | 8.10-8.00 (m, 5H, Ar-CH |
| H8 | 8.12-8.06 (m, 4H, Ar-CH) | 8.18-8.05 (m, 5H, Ar-CH) | 8.18-8.02 (m, 5H, Ar-CH) | 8.10-8.00 (m, 5H, Ar-CH |
| H10 | 7.83-7.81 (m, 1H, Ar-CH) | - | 7.56 (s, 1H, Ar-CH) | 7.62 (d, *J* = 8.3 Hz, 1H, Ar-CH) |
| H11 | 7.55-7.52 (m, 2H, Ar-CH) | 7.33 (d, *J* = 7.2 Hz, 1H, Ar-CH) | - | 7.28 (dd, *J* = 8.3, 1.1 Hz, 1H, Ar-CH) |
| H12 | 7.55-7.52 (m, 2H, Ar-CH) | 7.42 (t, *J* = 7.5 Hz, 1H, Ar-CH) | 7.29 (d, *J* = 7.9 Hz, 1H, Ar-CH) | - |
| H13 | 8.47-8.45 (m, 1H, Ar-CH), | 8.18-8.05 (m, 5H, Ar-CH) | 8.18-8.02 (m, 5H, Ar-CH) | 8.10-8.00 (m, 5H, Ar-CH |
| Methyl | | 2.78 (s, 3H, $CH_3$) | 2.60 (s, 3H, $CH_3$) | 2.63 (s, 3H, $CH_3$) |

**Table 4.** $^{1}$H NMR spectral assignemtns for **10, 11$^{\$}$ and 13**

$^{\$}$ Numbering is for comparison and convenience; different from IUPAC system

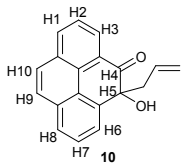
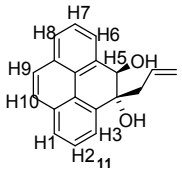
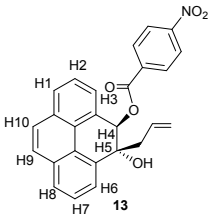
| Hydrogen number |   **10** |   **11** |   **13** |
|---|---|---|---|
| H1 | 8.12 (dd, *J* = 7.9, 1.2 Hz, 1H**,** Ar-CH) | 7.74-7.69 (m, 3H, Ar-CH) | 7.90-7.78 (m, 5H, Ar-CH) |
| H2 | 7.83-7.66 (m, 5H, Ar-CH) | 7.61-7.52 (m, 2H, Ar-CH) | 7.59-7.54 (m, 2H, Ar-CH) |
| H3 | 8.24 (dd, *J* = 7.3, 1.2 Hz, 1H**,** Ar-CH) | 7.87 (d, *J* = 7.2 Hz, 1H, Ar-CH) | 7.90-7.78 (m, 5H, Ar-CH) |
| H6 | 7.83-7.66 (m, 5H, Ar-CH) | 7.74-7.69 (m, 3H, Ar-CH) | 7.90-7.78 (m, 5H, Ar-CH) |
| H7 | 7.83-7.66 (m, 5H, Ar-CH) | 7.61-7.52 (m, 2H, Ar-CH) | 7.59-7.54 (m, 2H, Ar-CH) |
| H8 | 7.83-7.66 (m, 5H, Ar-CH) | 7.74-7.69 (m, 3H, Ar-CH) | 7.68-7.61 (m, 1H, Ar-CH) |
| H9 | 7.83-7.66 (m, 5H, Ar-CH) | 7.78 (d, *J* = 7.9 Hz, 2H, Ar-CH) | 7.90-7.78 (m, 5H, Ar-CH) |
| H10 | 7.93 (dd, *J* = 7.4, 1.2 Hz, 1H**,** Ar-CH) | 7.78 (d, *J* = 7.9 Hz, 2H, Ar-CH) | 7.90-7.78 (m, 5H, Ar-CH) |
| Remaining $^{1}$H NMR signals | 5.01 (dd, *J* = 9.2, 0.9 Hz, 1H, $CH_2$), 4.84 (dd, *J* = 17.0, 1.7 Hz, 1H, $CH_2$), 4.20 (s, 1H, OH), 2.58-2.48 (m, 2H, $CH_2$) | 5.54-5.44 (m, 2H, 2CH), 4.99 (d, *J* = 10.1 Hz, 1H, $CH_2$), 4.92 (d, *J* = 17.1 Hz, 1H, $CH_2$), 3.76 (s, 1H, OH), 3.37 (s, 1H, OH), 2.78 (dd, *J* = 14.1, 8.8 Hz, 1H, $CH_2$), 2.28 (dd, *J* = 14.0, 6.0 Hz, 1H, $CH_2$) | 8.41-8.35 (m, 4H, Ar-CH) (Nitro benzoate) 6.97 (s, 1H, CH), 5.61-5.57 (m, 1H, CH), 4.99 (d, *J* = 10.0 Hz, 1H, $CH_2$), 4.86 (d, *J* = 17.2 Hz, 1H, $CH_2$), 2.87-2.81 (m, 1H, $CH_2$), 2.62-2.57 (m, 2H, 1H in $CH_2$, OH) |

**Table 5.** $^{1}$H NMR spectral assignemtns for **9** and **12**.

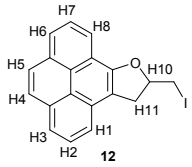
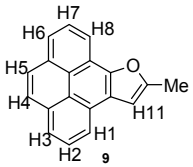
| Hydrogen number |  |  |
|---|---|---|
| H1 | 8.07-7.96 (m, 5H, Ar-CH) | 8.05-7.99 (m, 4H, Ar-CH) |
| H2 | 8.07-7.96 (m, 5H, Ar-CH) | 8.05-7.99 (m, 4H, Ar-CH) |
| H3 | 8.32 (d, *J* = 7.6 Hz, 1H, Ar-CH) | 8.52 (dd, *J* = 7.6, 1.1 Hz, 1H, Ar-CH) |
| H4 | 8.07-7.96 (m, 5H, Ar-CH) | 8.12-8.10 (m, 2H, Ar-CH) |
| H5 | 8.07-7.96 (m, 5H, Ar-CH) | 8.12-8.10 (m, 2H, Ar-CH) |
| H6 | 8.18 (d, *J* = 7.4 Hz, 1H, Ar-CH) | 8.31 (dd, *J* = 7.6, 1.0 Hz, 1H, Ar-CH) |
| H7 | 8.07-7.96 (m, 5H, Ar-CH) | 8.05-7.99 (m, 4H, Ar-CH) |
| H8 | 7.87 (d, *J* = 7.6 Hz, 1H, Ar-CH) | 8.05-7.99 (m, 4H, Ar-CH) |
| H11 | | 6.99 (s, 1H, Ar-CH) |
| Remaining $^{1}$H NMR signals | 5.34-5.26 (m, 1H, CH), 3.83 (dd, *J* = 15.5, 7.6 Hz, 1H, $CH_2$), 3.67 (dd, *J* = 10.0, 4.7 Hz, 1H, $CH_2$), 3.55-3.45 (m, 2H, $CH_2$) | 2.69 (s, 3H, $CH_3$) |

**Table 6**. $^{13}C$ NMR spectral assignemtns for **6a-e**.

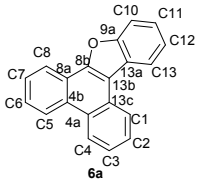
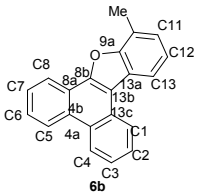
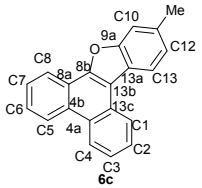
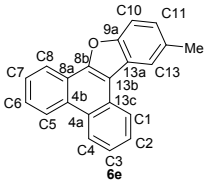
| Carbon number |  **6a** |  **6b** |  **6c** |  **6e** |
|---|---|---|---|---|
| C1 | 127.5 (CH) | 127.5 (CH) | 127.2 (CH) | 127.3 (CH) |
| C2 | 125.5 (CH) | 127.1 (CH) | 126.6 (CH) | 126.9 (CH) |
| C3 | 124.3 (CH) | 125.1 (CH) | 124.5 (CH) | 124.1 (CH) |
| C4 | 121.9 (CH) | 122.0 (CH) | 121.5 (CH) | 121.7 (CH) |
| C4a | 130.8 (C) | 130.7 (C) | 130.2 (C) | 130.4 (C) |
| C4b | 128.8 (C) | 129.0 (C) | 128.5 (C) | 128.6 (C) |
| C5 | 121.9 (CH) | 119.5 (CH) | 121.1 (CH) | 121.6 (CH) |
| C6 | 123.9 (CH) | 124.4 (CH) | 124.1 (CH) | 123.7 (CH) |
| C7 | 123.9 (CH) | 126.7 (CH) | 124.8 (CH) | 126.5 (CH) |
| C8 | 127.20 (CH) | 127.2 (CH) | 126.9 (CH) | 127.0 (CH) |
| C8a | 114.6 (C) | 115.0 (C) | 114.4 (C) | 114.2 (C) |
| C8b | 151.4 (C) | 151.1 (C) | 150.8 (C) | 151.3 (C) |
| C9a | 156.0 (C) | 154.9 (C) | 156.2 (C) | 154.2 (C) |
| C10 | 112.1 (CH) | 122.2 (C) | 112.1 (CH) | 111.3 (CH) |
| C11 | 127.15 (CH) | 123.9 (CH) | 135.6 (C) | 124.9 (CH) |
| C12 | 123.54 (CH) | 123.58 (CH) | 123.6 (CH) | 132.7 (C) |
| C13 | 123.49 (CH) | 123.55 (CH) | 123.3 (CH) | 123.3 (CH) |
| C13a | 122.4 (C) | 122.6 (C) | 122.2 (C) | 122.3 (C) |
| C13b | 125.9 (C) | 125.3 (C) | 123.0 (C) | 125.6 (C) |
| C13c | 128.4 (C) | 128.4 (C) | 128.0 (C) | 128.1 (C) |
| Methyl | | 15.7 | 21.8 ($CH_3$) | 21.7 ($CH_3$) |

**Table 7**. $^{13}C$ NMR spectral assignemtns for **6f-g**.

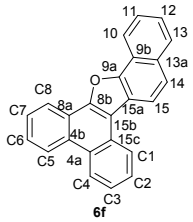
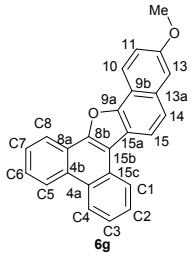
| Carbon number |  **6f** |  **6g** |
|---|---|---|
| C1 | 127.5 (CH) | 127.3 (CH) |
| C2 | 126.0 (CH) | 125.2 (CH) |
| C3 | 124.4 (CH) | 123.9 (CH) |
| C4 | 124.0 (CH) | 123.0 (CH) |
| C4a | 130.2 (C) | 134.2 (C) |
| C4b | 128.7 (C) | 133.4 (C) |
| C5 | 123.6 (CH) | 122.5 (CH) |
| C6 | 124.1 (CH) | 123.6 (CH) |
| C7 | 125.4 (CH) | 124.3 (CH) |
| C8 | 127.1 (CH) | 126.8 (CH) |
| C8a | 115.7 (C) | 115.7 (C) |
| C8b | 151.6 (C) | 152.0 (C) |
| C9a | 150.8 (C) | 150.3 (C) |
| C9b | 121.0 (C) | 116.9 (C) |
| C10 | 121.6 (CH) | 127.4 (CH) |
| C11 | 126.9 (CH) | 119.2 (CH) |
| C12 | 126.8 (CH) | 157.9 (C) |
| C13 | 128.49 (CH), | 107.1 (CH) |
| C13a | 132.0 (C), | 129.9 (C) |
| C14 | 120.0 (CH) | 120.6 (CH) |
| C15 | 120.8 (CH) | 121.4 (C) |
| C15a | 122.6 (C) | 128.5 (C) |
| C15b | 121.7 (C) | 119.1 (C) |
| C15c | 128.53 (C) | 128.7 (C) |
| O-Me | | 55.5 ($CH_3$) |

**Table 8**. $^{13}C$ NMR spectral assignemtns for **8a-d**.

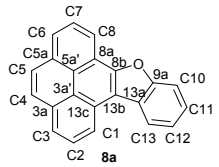
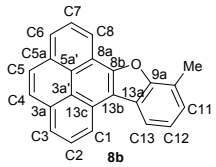
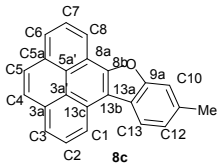
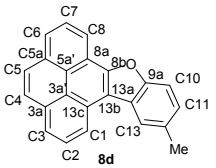
| Carbon number |  **8a** |  **8b** |  **8c** |  **8d** |
|---|---|---|---|---|
| C1 | 123.6 (CH) | 121.4 (CH) | 121.34 (CH) | 122.0 (CH) |
| C2 | 125.7 (CH) | 125.8 (CH) | 125.6 (CH) | 126.08 (CH) |
| C3 | 128.2 (CH) | 128.2 (CH) | 128.2 (CH) | 128.2 (CH) |
| C3a | 132.0 (C) | 132.0 (C) | 132.0 (C) | 132.8 (C) |
| C3a[1] | 124.44 (C) | 124.4 (C) | 123.3 (C) | 124.5 (C) |
| C4 | 126.5 (CH) | 126.7 (CH) | 126.4 (CH) | 126.8 (CH) |
| C5 | 126.2 (CH) | 126.5 (CH) | 126.1 (CH) | 126.4 (CH) |
| C5a | 131.7 (C) | 131.7 (C) | 131.7 (C) | 132.1 (C) |
| C5a[1] | 122.7 (C) | 122.7 (C) | 122.6 (C) | 122.8 (C) |
| C6 | 127.5 (CH) | 127.4 (CH) | 127.4 (CH) | 127.4 (CH) |
| C7 | 124.42 (CH) | 124.3 (CH) | 124.23 (CH) | 124.3 (CH) |
| C8 | 122.0 (CH) | 119.4 (CH) | 121.32 (CH) | 121.4 (CH) |
| C8a | 115.1 (C) | 115.5 (C) | 115.2 (C) | 115.1 (C) |
| C8b | 151.8 (C) | 151.6 (C) | 151.4 (C) | 152.1 (C) |
| C9a | 156.1 (C) | 155.0 (C) | 156.5 (C) | 154.5 (C) |
| C10 | 112.1 (CH) | 122.3 (C) | 112.3 (CH) | 111.6 (CH) |
| C11 | 125.9 (CH) | 126.1 (CH) | 136.1 (C) | 125.8 (CH) |
| C12 | 121.36 (CH) | 123.5 (CH) | 124.8 (CH) | 131.8 (C) |
| C13 | 118.8 (CH) | 118.8 (CH) | 118.6 (CH) | 118.8 (CH) |
| C13a | 127.7 (C) | 127.8 (C) | 127.6 (C) | 127.9 (C) |
| C13b | 125.9 (C) | 125.3 (C) | 124.20 (C) | 126.05 (C) |
| C13c | 121.38 (C) | 121.5 (C) | 121.5 (C) | 121.6 (C) |
| Methyl | | 15.5 ($CH_3$) | 22.0 ($CH_3$) | 22.0 ($CH_3$) |

**Table 9**. $^{13}C$ NMR spectral assignemtns for **10, 11[$] and 13**.
[$] Numbering is for comparison and convenience; different from IUPAC system

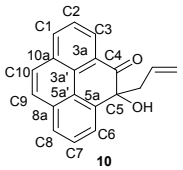
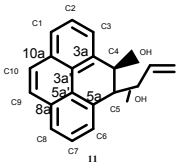
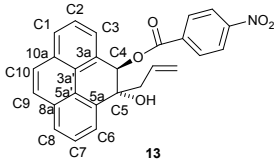
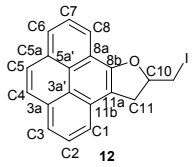
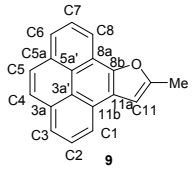
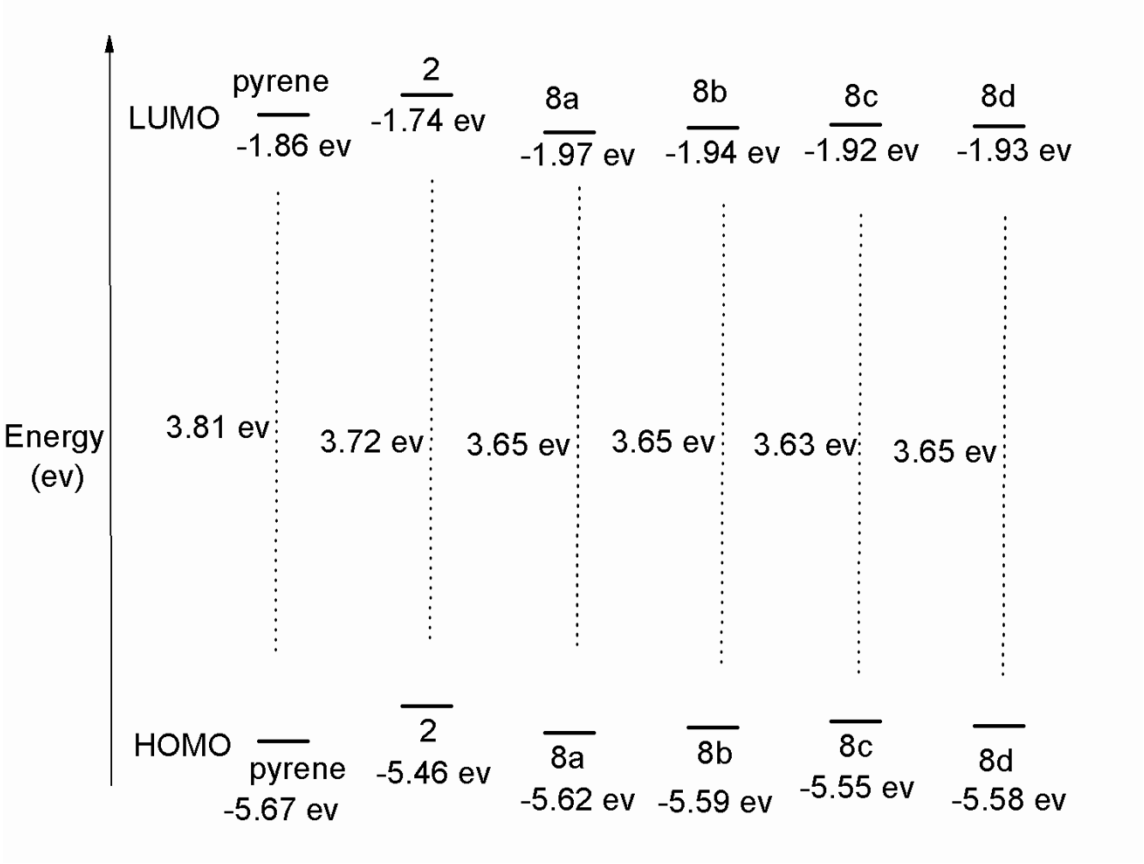
| Carbon number |  **10** |  **11** |  **13** |
|---|---|---|---|
| C1 | 131.2 (CH) | 126.5 (CH) | 126.7 (CH) |
| C2 | 124.4 (CH) | 127.15 (CH) | 127.9 (CH) |
| C3 | 127.9 (CH) | 126.7 (CH) | 127.0 (CH) |
| C3a | 128.0 (C) | 130.9 (C) | 131.3 (C) |
| C3a[1] | 123.6 (C) | 125.9 (C) | 126.1 (C) |
| C4 | 202.7 (C=O) | 76.5 (CH) | 78.8 (CH), |
| C5 | 80.5 (C) | 77.9 (C) | 76.7 (C) |
| C5a | 129.9 (C) | 139.0 (C) | 138.2 (C) |
| C5a[1] | 131.3 (C) | 125.7 (C) | 125.6 (C) |
| C6 | 127.7 (CH) | 123.1 (CH) | 122.8 (CH) |
| C7 | 127.0 (CH) | 127.13 (CH) | 127.3 (CH) |
| C8 | 127.2 (CH) | 122.5 (CH) | 123.5 (CH) |
| C8a | 140.5 (C) | 131.2 (C) | 131.3 (C) |
| C9 | 126.23 (CH) | 126.78 (CH) | 127.8 (CH) |
| C10 | 126.18 (CH) | 126.75 (CH) | 127.8 (CH) |
| C10a | 131.9 (C) | 135.8 (C) | 131.9 (C) |
| Remaining $^{13}C$ NMR signals | 134.3 (CH) 119.9 ($CH_2$)<br>49.7 ($CH_2$) | 133.4 (CH)<br>119.6 ($CH_2$)<br>38.2 ($CH_2$) | 164.9 (COO),<br>151.0 (C-$NO_2$), 135.4 (C), 131.2 (2CH) 124.0 (2CH)<br>132.7 (CH), 119.4 ($CH_2$) 39.6 ($CH_2$) |

**Table 10**. $^{13}C$ NMR spectral assignemtns for **9 and 12**.

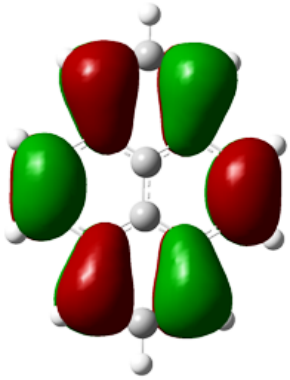
| Carbon number |  |  |
|---|---|---|
| C1 | 120.0 (CH) | 121.0 (CH) |
| C2 | 125.6 (CH) | 124.2 (CH) |
| C3 | 127.9 (CH) | 128.0 (CH) |
| C3a | 131.7 (C) | 132.1 (C) |
| C3a[1] | 121.6 (C) | 126.9 (C) |
| C4 | 126.4 (CH) | 126.1 (CH) |
| C5 | 125.8 (CH) | 126.0 (CH) |
| C5a | 131.5 (C) | 131.9 (C) |
| C5a[1] | 121.2 (C) | 123.1 (C) |
| C6 | 127.4 (CH) | 127.7 (CH) |
| C7 | 122.9 (CH) | 124.2 (CH) |
| C8 | 119.3 (CH) | 117.1 (CH) |
| C8a | 129.1 (C) | 121.8 (C) |
| C8b | 153.3 (C) | 154.6 (C) |
| C10 | 82.7 (CH) | 148.9 (C) |
| C11 | 36.1 ($CH_2$) | 103.0 (CH) |
| C11a | 113.7 (C) | 122.2 (C) |
| C11b | 125.1 (C) | 122.7 (C) |
| Remaining $^{13}C$ NMR signal | 9.6 ($CH_2$) | 14.0 ($CH_3$) |

**III) Theoretical data**

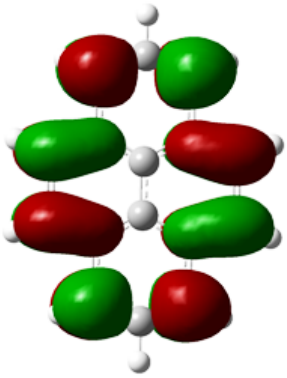



1) Energy potential diagram of **2**, **9**, **8a-d** in frontier orbitals (caliculated by TD-DFT B3LYP/6-311G(d,p))

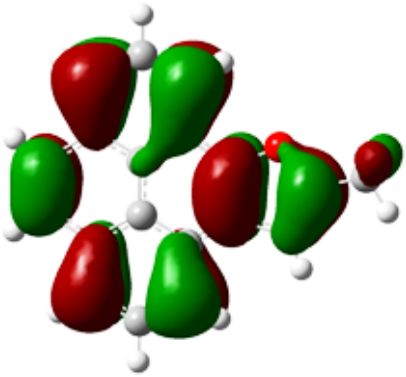
2) Molecular orbitals of **2, 9, 8a-d.**



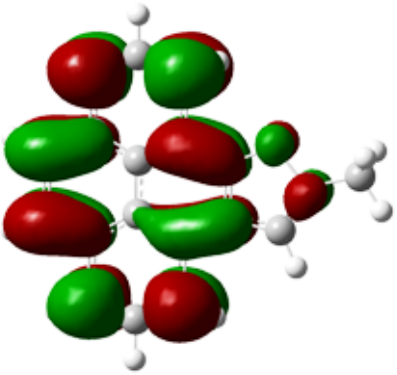
HOMO **2**



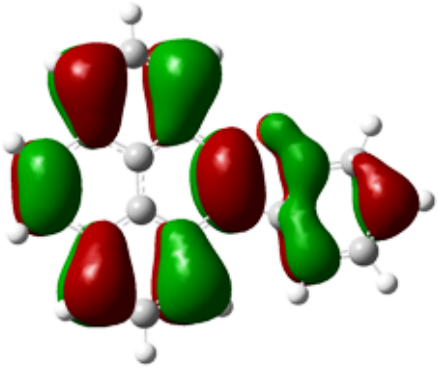
LUMO **2**



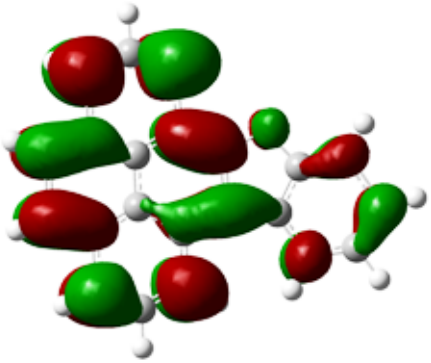
HOMO **9**



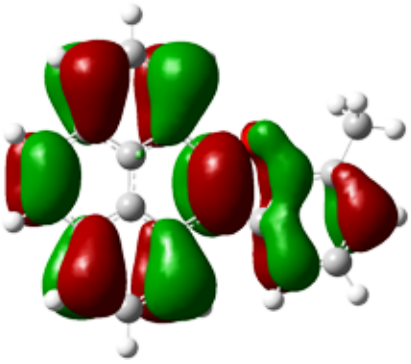
LUMO **9**



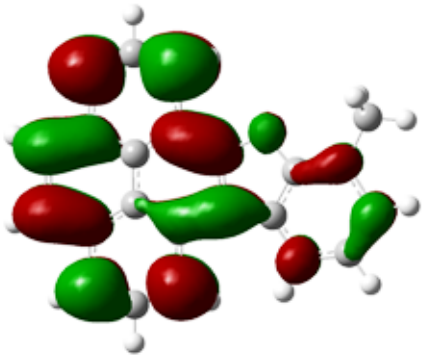
HOMO **8a**



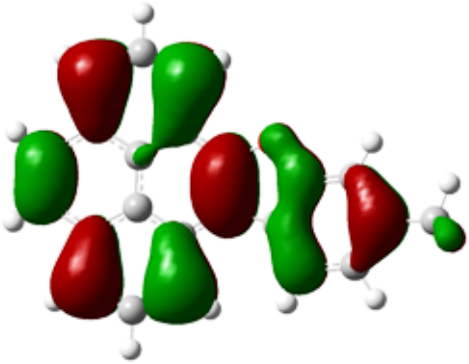
LUMO **8a**



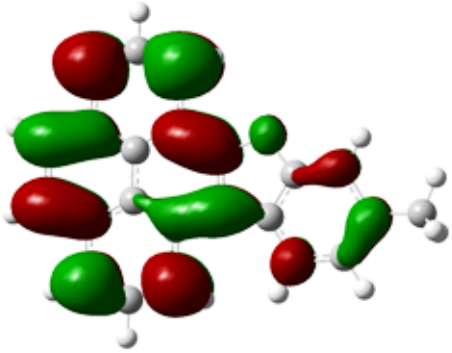
HOMO **8b**



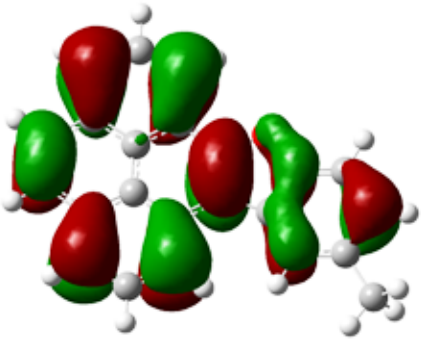
LUMO **8b**



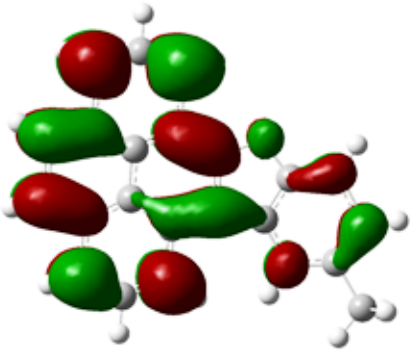
HOMO **8c**



LUMO **8c**



HOMO **8d**



LUMO **8d**

2) Molecular orbitals of **2**, **9**, **8a-d**.

3) Atom coordinates and absolute energies of **2**, **9**, **8a-d** in ground state theoretical calculations.

**2** (ground): E (B3LYP/6-311G(d,p) = -615.91612861 A.U.

| Centre | | Coordinate (Angstroms) | | |
|---|---|---|---|---|
| Number | Atom | X | Y | Z |
| 1 | C | 0.0000 | 1.2091 | -2.8298 |
| 2 | C | 0.0000 | 1.2345 | -1.4274 |
| 3 | C | 0.0000 | 0.0000 | -0.7127 |
| 4 | C | 0.0000 | -1.2345 | -1.4274 |
| 5 | C | 0.0000 | -1.2091 | -2.8298 |
| 6 | C | 0.0000 | 0.0000 | -3.5195 |
| 7 | C | 0.0000 | 0.0000 | 0.7127 |
| 8 | C | 0.0000 | -1.2345 | 1.4274 |
| 9 | C | 0.0000 | -2.4612 | 0.6796 |
| 10 | C | 0.0000 | -2.4612 | -0.6796 |
| 11 | C | 0.0000 | 1.2345 | 1.4274 |
| 12 | C | 0.0000 | 1.2091 | 2.8298 |
| 13 | C | 0.0000 | 0.0000 | 3.5195 |
| 14 | C | 0.0000 | -1.2091 | 2.8298 |
| 15 | C | 0.0000 | 2.4612 | -0.6796 |
| 16 | C | 0.0000 | 2.4612 | 0.6796 |
| 17 | H | 0.0000 | 2.1464 | -3.3761 |
| 18 | H | 0.0000 | -2.1464 | -3.3761 |
| 19 | H | 0.0000 | 0.0000 | -4.6038 |
| 20 | H | 0.0000 | -3.3981 | 1.2270 |
| 21 | H | 0.0000 | -3.3981 | -1.2270 |
| 22 | H | 0.0000 | 2.1464 | 3.3761 |
| 23 | H | 0.0000 | 0.0000 | 4.6038 |
| 24 | H | 0.0000 | -2.1464 | 3.3761 |
| 25 | H | 0.0000 | 3.3981 | -1.2270 |
| 26 | H | 0.0000 | 3.3981 | 1.2270 |

**9** (ground): E (B3LYP/6-311G(d,p) = -806.71494887 A.U.

| Centre | | Coordinate (Angstroms) | | |
|---|---|---|---|---|
| Number | Atom | X | Y | Z |
| 1 | C | -1.9341 | 2.9752 | 0.0000 |
| 2 | C | -2.0761 | 1.5778 | 0.0000 |
| 3 | C | -0.9109 | 0.7561 | 0.0000 |
| 4 | C | 0.3745 | 1.3846 | 0.0000 |
| 5 | C | 0.4762 | 2.7805 | 0.0000 |
| 6 | C | -0.6749 | 3.5645 | 0.0000 |
| 7 | C | -1.0388 | -0.6725 | 0.0000 |
| 8 | C | 0.1130 | -1.5219 | 0.0000 |
| 9 | C | 1.4009 | -0.8799 | 0.0000 |
| 10 | C | 1.4843 | 0.4945 | 0.0000 |
| 11 | C | -2.3381 | -1.2625 | 0.0000 |
| 12 | C | -2.4604 | -2.6612 | 0.0000 |
| 13 | C | -1.3326 | -3.4721 | 0.0000 |
| 14 | C | -0.0572 | -2.9103 | 0.0000 |
| 15 | C | -3.3662 | 0.9473 | 0.0000 |
| 16 | C | -3.4902 | -0.4051 | 0.0000 |
| 17 | C | 2.7606 | -1.3522 | 0.0000 |
| 18 | C | 3.5566 | -0.2495 | 0.0000 |
| 19 | O | 2.7899 | 0.8942 | 0.0000 |
| 20 | C | 5.0285 | -0.0531 | 0.0000 |
| 21 | H | -2.8247 | 3.5946 | 0.0000 |
| 22 | H | 1.4563 | 3.2418 | 0.0000 |
| 23 | H | -0.5865 | 4.6451 | 0.0000 |
| 24 | H | -3.4507 | -3.1039 | 0.0000 |
| 25 | H | -1.4437 | -4.5507 | 0.0000 |
| 26 | H | 0.8144 | -3.5548 | 0.0000 |
| 27 | H | -4.2480 | 1.5796 | 0.0000 |
| 28 | H | -4.4728 | -0.8654 | 0.0000 |
| 29 | H | 3.1084 | -2.3731 | 0.0000 |
| 30 | H | 5.3528 | 0.5060 | -0.8832 |
| 31 | H | 5.3528 | 0.5059 | 0.8832 |

**8a** (ground): E (B3LYP/6-311G(d,p) = -921.06807521 A.U.

| Centre | | Coordinate (Angstroms) | | |
|---|---|---|---|---|
| Number | Atom | X | Y | Z |
| 1 | C | -1.2960 | -3.8949 | 0.0000 |
| 2 | C | -0.0607 | -3.2270 | 0.0000 |
| 3 | C | -0.0381 | -1.8013 | 0.0000 |
| 4 | C | -1.2799 | -1.0957 | 0.0000 |
| 5 | C | -2.4925 | -1.7948 | 0.0000 |
| 6 | C | -2.4929 | -3.1872 | 0.0000 |
| 7 | C | 1.2105 | -1.0985 | 0.0000 |
| 8 | C | 1.2579 | 0.3338 | 0.0000 |
| 9 | C | 0.0000 | 1.0371 | 0.0000 |
| 10 | C | -1.1790 | 0.3234 | 0.0000 |
| 11 | C | 2.4291 | -1.8406 | 0.0000 |
| 12 | C | 3.6545 | -1.1558 | 0.0000 |
| 13 | C | 3.6872 | 0.2315 | 0.0000 |
| 14 | C | 2.5051 | 0.9699 | 0.0000 |
| 15 | C | 1.1863 | -3.9378 | 0.0000 |
| 16 | C | 2.3718 | -3.2756 | 0.0000 |
| 17 | C | -0.3928 | 2.4356 | 0.0000 |
| 18 | C | -1.8011 | 2.4228 | 0.0000 |
| 19 | O | -2.2812 | 1.1368 | 0.0000 |
| 20 | C | 0.2542 | 3.6800 | 0.0000 |
| 21 | C | -0.5160 | 4.8386 | 0.0000 |
| 22 | C | -1.9177 | 4.7843 | 0.0000 |
| 23 | C | -2.5872 | 3.5627 | 0.0000 |
| 24 | C | -1.3067 | -4.9796 | 0.0000 |
| 25 | H | -3.4240 | -1.2426 | 0.0000 |
| 26 | H | -3.4353 | -3.7230 | 0.0000 |
| 27 | H | 4.5780 | -1.7248 | 0.0000 |
| 28 | H | 4.6399 | 0.7492 | 0.0000 |
| 29 | H | 2.5575 | 2.0499 | 0.0000 |
| 30 | H | 1.1619 | -5.0224 | 0.0000 |
| 31 | H | 3.3070 | -3.8257 | 0.0000 |
| 32 | H | 1.3334 | 3.7547 | 0.0000 |
| 33 | H | -0.0231 | 5.8039 | 0.0000 |
| 34 | H | -2.4891 | 5.7051 | 0.0000 |
| 35 | H | -3.6680 | 3.4977 | 0.0000 |

**8b** (ground): E (B3LYP/6-311G(d,p) = -960.39673332 A.U.

| Centre | | Coordinate (Angstroms) | | |
|---|---|---|---|---|
| Number | Atom | X | Y | Z |
| 1 | C | 3.1928 | -2.7397 | 0.0000 |
| 2 | C | 3.1283 | -1.3369 | 0.0000 |
| 3 | C | 1.8541 | -0.6967 | 0.0000 |
| 4 | C | 0.6789 | -1.5082 | 0.0000 |
| 5 | C | 0.7814 | -2.9040 | 0.0000 |
| 6 | C | 2.0351 | -3.5099 | 0.0000 |
| 7 | C | 1.7636 | 0.7332 | 0.0000 |
| 8 | C | 0.4939 | 1.3984 | 0.0000 |
| 9 | C | -0.6865 | 0.5713 | 0.0000 |
| 10 | C | -0.5554 | -0.8005 | 0.0000 |
| 11 | C | 2.9615 | 1.5083 | 0.0000 |
| 12 | C | 2.8776 | 2.9094 | 0.0000 |
| 13 | C | 1.6424 | 3.5419 | 0.0000 |
| 14 | C | 0.4636 | 2.7982 | 0.0000 |
| 15 | C | 4.3103 | -0.5225 | 0.0000 |
| 16 | C | 4.2291 | 0.8328 | 0.0000 |
| 17 | C | -2.1169 | 0.8260 | 0.0000 |
| 18 | C | -2.7180 | -0.4458 | 0.0000 |
| 19 | O | -1.7665 | -1.4389 | 0.0000 |
| 20 | C | -2.9536 | 1.9521 | 0.0000 |
| 21 | C | -4.3289 | 1.7534 | 0.0000 |
| 22 | C | -4.8841 | 0.4648 | 0.0000 |
| 23 | C | -4.0889 | -0.6830 | 0.0000 |
| 24 | C | -4.6521 | -2.0786 | 0.0000 |
| 25 | H | 4.1650 | -3.2210 | 0.0000 |
| 26 | H | -0.1210 | -3.5026 | 0.0000 |
| 27 | H | 2.1080 | -4.5915 | 0.0000 |
| 28 | H | 3.7915 | 3.4937 | 0.0000 |
| 29 | H | 1.5902 | 4.6249 | 0.0000 |
| 30 | H | -0.4862 | 3.3149 | 0.0000 |
| 31 | H | 5.2767 | -1.0156 | 0.0000 |
| 32 | H | 5.1309 | 1.4362 | 0.0000 |
| 33 | H | -2.5540 | 2.9570 | 0.0000 |
| 34 | H | -4.9909 | 2.6118 | 0.0000 |
| 35 | H | -5.9631 | 0.3521 | 0.0000 |
| 36 | H | -5.7431 | -2.0552 | -0.0000 |
| 37 | H | -4.3212 | -2.6394 | -0.8792 |
| 38 | H | -4.3213 | -2.6393 | 0.8792 |

**8c** (ground): E (B3LYP/6-311G(d,p) = -960.39540671 A.U.

| Centre | | Coordinate (Angstroms) | | |
|---|---|---|---|---|
| Number | Atom | X | Y | Z |
| 1 | C | 3.5585 | -2.5272 | -0.0001 |
| 2 | C | 3.3546 | -1.1377 | -0.0000 |
| 3 | C | 2.0232 | -0.6273 | 0.0001 |
| 4 | C | 0.9339 | -1.5516 | 0.0002 |
| 5 | C | 1.1752 | -2.9305 | 0.0001 |
| 6 | C | 2.4829 | -3.4085 | -0.0000 |
| 7 | C | 1.7916 | 0.7866 | 0.0002 |
| 8 | C | 0.4624 | 1.3225 | 0.0003 |
| 9 | C | -0.6297 | 0.3829 | 0.0002 |
| 10 | C | -0.3640 | -0.9695 | 0.0000 |
| 11 | C | 2.9064 | 1.6772 | 0.0001 |
| 12 | C | 2.6830 | 3.0630 | 0.0002 |
| 13 | C | 1.3908 | 3.5697 | 0.0003 |
| 14 | C | 0.2921 | 2.7122 | 0.0003 |
| 15 | C | 4.4499 | -0.2099 | -0.0001 |
| 16 | C | 4.2347 | 1.1308 | -0.0000 |
| 17 | C | -2.0776 | 0.4937 | 0.0002 |
| 18 | C | -2.5497 | -0.8303 | -0.0000 |
| 19 | O | -1.5081 | -1.7245 | -0.0002 |
| 20 | C | -3.0322 | 1.5217 | -0.0006 |
| 21 | C | -4.3809 | 1.1900 | -0.0015 |
| 22 | C | -4.8301 | -0.1464 | -0.0014 |
| 23 | C | -3.8910 | -1.1788 | -0.0010 |
| 24 | C | -6.3097 | -0.4475 | 0.0020 |
| 25 | H | 4.5738 | -2.9091 | -0.0002 |
| 26 | H | 0.3369 | -3.6161 | 0.0001 |
| 27 | H | 2.6627 | -4.4776 | -0.0001 |
| 28 | H | 3.5341 | 3.7356 | 0.0001 |
| 29 | H | 1.2315 | 4.6422 | 0.0003 |
| 30 | H | -0.7052 | 3.1303 | 0.0004 |
| 31 | H | 5.4605 | -0.6049 | -0.0002 |
| 32 | H | 5.0723 | 1.8205 | -0.0001 |
| 33 | H | -2.7400 | 2.5636 | -0.0012 |
| 34 | H | -5.1174 | 1.9870 | -0.0027 |
| 35 | H | -4.1916 | -2.2198 | -0.0017 |
| 36 | H | -6.8097 | 0.0152 | -0.8545 |
| 37 | H | -6.7899 | -0.0593 | 0.9058 |
| 38 | H | -6.4976 | -1.5219 | -0.0407 |

**8d** (ground): E (B3LYP/6-311G(d,p) = -960.39496086 A.U.

| Centre | | Coordinate (Angstroms) | | |
|---|---|---|---|---|
| Number | Atom | X | Y | Z |
| 1 | C | 3.8775 | -2.1107 | 0.0000 |
| 2 | C | 3.4641 | -0.7686 | 0.0000 |
| 3 | C | 2.0702 | -0.4674 | 0.0000 |
| 4 | C | 1.1354 | -1.5471 | 0.0000 |
| 5 | C | 1.5838 | -2.8729 | 0.0000 |
| 6 | C | 2.9492 | -3.1459 | 0.0000 |
| 7 | C | 1.6251 | 0.8945 | -0.0000 |
| 8 | C | 0.2293 | 1.2208 | -0.0000 |
| 9 | C | -0.7070 | 0.1250 | -0.0000 |
| 10 | C | -0.2367 | -1.1712 | -0.0000 |
| 11 | C | 2.5913 | 1.9444 | 0.0000 |
| 12 | C | 2.1598 | 3.2801 | -0.0000 |
| 13 | C | 0.8055 | 3.5835 | -0.0000 |
| 14 | C | -0.1499 | 2.5686 | -0.0000 |
| 15 | C | 4.4050 | 0.3154 | 0.0000 |
| 16 | C | 3.9875 | 1.6074 | 0.0000 |
| 17 | C | -2.1554 | 0.0120 | -0.0000 |
| 18 | C | -2.4157 | -1.3689 | -0.0000 |
| 19 | O | -1.2486 | -2.0932 | -0.0000 |
| 20 | C | -3.2495 | 0.8913 | -0.0000 |
| 21 | C | -4.5487 | 0.3858 | -0.0000 |
| 22 | C | -4.7520 | -1.0090 | -0.0000 |
| 23 | C | -3.6910 | -1.9082 | -0.0000 |
| 24 | C | -5.7404 | 1.3156 | 0.0001 |
| 25 | H | 4.9392 | -2.3332 | 0.0000 |
| 26 | H | 0.8600 | -3.6783 | 0.0000 |
| 27 | H | 3.2902 | -4.1750 | 0.0000 |
| 28 | H | 2.8985 | 4.0743 | -0.0000 |
| 29 | H | 0.4842 | 4.6191 | -0.0000 |
| 30 | H | -1.1987 | 2.8313 | -0.0000 |
| 31 | H | 5.4639 | 0.0795 | 0.0000 |
| 32 | H | 4.7098 | 2.4170 | 0.0000 |
| 33 | H | -3.1021 | 1.9638 | -0.0000 |
| 34 | H | -5.7669 | -1.3928 | -0.0000 |
| 35 | H | -3.8475 | -2.9797 | -0.0000 |
| 36 | H | -6.3696 | 1.1542 | -0.8806 |
| 37 | H | -6.3686 | 1.1553 | 0.8818 |
| 38 | H | -5.4285 | 2.3618 | -0.0008 |