

SUPPORTING INFORMATION

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Title: An Approach to the Synthesis of Functionalized Polycyclic Aromatic Hydrocarbons

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Contents:

1 - General Remarks

2 - Synthetic Procedures

- 3.0 - 1,5-Bis(allyloxy)naphthalene (9)
- 3.1 - 2,6-Diallyl-1,5-dihydroxynaphthalene (10)
- 3.2 - 2,6-Diallyl-1,5-bis(2,2,2-trichloroacetyl)naphthalene (11)
- 3.3 - 4,10-Dichlorochrysene (12)
- 3.4 - Method A - 4,10-Dimethylchrysene (15)
 - 4,10-Diphenylchrysene (16)
 - 4,10-Bis(4-methoxyphenyl)chrysene (17)
- 4.5 - Method B - 4,10-Bis(1-naphthyl)chrysene (18)
 - 4,10-Bis(3-thienyl)chrysene (19)
- 4.6 - Method C - 4,10-Bis(phenylthio)chrysene (20)
 - 4,10-Bis(2-naphthylthio)chrysene (21)
- 4.8 - Method D - 4,10-Bis(phenyloxy)chrysene (22)
- 4.9 - Method E - 4,10-Bis(oct-1-yn-1-yl)chrysene (23)

3 - UV/vis Spectra

4 - CV Data

- 4.0 - Chrysene (24)
- 4.1 - 4,10-Dichlorochrysene (12)
- 4.2 - 4,10-Dimethylchrysene (15)
- 4.3 - 4,10-Diphenylchrysene (16)
- 4.4 - 4,10-Bis(4-methoxyphenyl)chrysene (17)
- 4.5 - 4,10-Bis(3-thienyl)chrysene (19)
- 4.6 - 4,10-Bis(phenylthio)chrysene (20)
- 4.7 - 4,10-Bis(2-naphthylthio)chrysene (21)
- 4.8 - 4,10-Bis(phenyloxy)chrysene (22)
- 4.9 - 4,10-Bis(Oct-1-yn-1-yl)chrysene (23)

5 - NMR Spectra

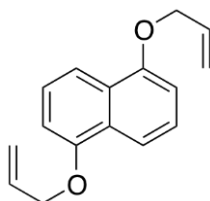
- 5.0 - 4,10-Dichlorochrysene (12)
- 5.1 - 4,10-Dimethylchrysene (15)
- 5.2 - 4,10-Diphenylchrysene (16)
- 5.3 - 4,10-Bis(4-methoxyphenyl)chrysene (17)
- 5.4 - 4,10-Bis(1-naphthyl)chrysene (18)
- 5.5 - 4,10-Bis(3-thienyl)chrysene (19)
- 5.6 - 4,10-Bis(phenylthio)chrysene (20)
- 5.7 - 4,10-Bis(2-naphthylthio)chrysene (21)
- 5.8 - 4,10-Bis(phenyloxy)chrysene (22)
- 5.9 - 4,10-Bis(Oct-1-yn-1-yl)chrysene (23)

6 - MO Calculations

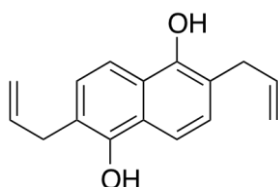
1.0 - General remarks.

All reactants and reagents were purchased from Sigma-Aldrich (UK) and were used without further purification. Solvents used were purified by standard methods. All reactions, unless otherwise noted, were carried out under N₂ gas using flame-dried glassware. MWI-assisted reactions were performed with a Biotage Initiator microwave reactor. NMR spectra were acquired using a B400 Bruker Avance III 400 MHz or B500 Bruker Avance II+ 500 MHz spectrometers, using TMS as an internal standard (0.00 ppm). Mass measurements were acquired with a Micromass Trio 200 spectrometer, using electrospray (ES), atmospheric pressure chemical ionisation (APCI) or matrix-assisted laser desorption ionisation (MALDI) techniques, as stated. High resolution mass spectra were recorded on a Kratos Concept IS spectrometer. Ultraviolet-visible (UV-Vis) spectra were recorded on a Varian Cary 50 spectrometer (1 cm cuvette) in de-aerated DCM. Cyclic Voltammetry (CV) was performed on a BASi-Epsilon platform with a scan rate of 100 V/s using solutions of 5 -10 mM of analyte and 100 mM of tetrabutylammonium hexafluorophosphate in DCM. Top-gate bottom-contact organic field effect transistors (OFETs) were fabricated with lithographically defined gold electrodes on glass substrates. The OSC candidate materials were spin-coated as blends with PMS (9 : 1) from ortho-dichlorobenzene at a concentration of 1-7 mg/mL followed by a spin-coated fluoropolymer dielectric material (Lisocon®D139 from Merck Germany).

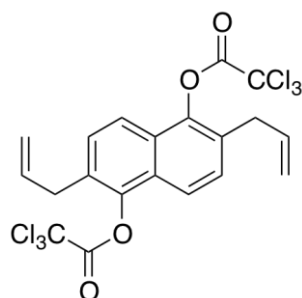
2 - Synthetic Procedures



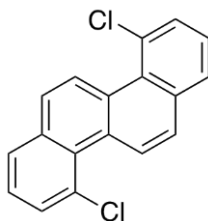
1,5-Bis(allyloxy)naphthalene (9). The allyl naphthyl ether was prepared by adaptation of a standard Williamson ether synthesis procedure. Allyl bromide (32.19 mL, 375 mmol) was added to a stirring suspension of 1,5-dihydroxynaphthalene (25 g, 156.25 mmol) and K_2CO_3 (51.75 g, 375 mmol) in dry acetone (400 mL) and stirred for 22 h at room temperature. The inorganic components were separated by filtration and the solvent removed in vacuo to afford a brown solid. Diethyl ether (500 mL) was added and the solution extracted with 1M NaOH solution (2 x 150 mL), followed by water (150 mL) and brine (150 mL). The organic phase was dried over $MgSO_4$ and concentrated in vacuo. The crude product was then recrystallized from methanol to afford the product 1,5-bis(allyloxy)naphthalene in 62% yield as a golden solid. m.p. 90 °C. 1H NMR (400 MHz, CHLOROFORM-d) δ 7.83 (2H, d, $J=8.5$ Hz, Np-H₄) 7.31 (2H, dd, $J=8.5, 7.5$ Hz, Np-H₃) 6.78 (2H, d, $J=7.5$ Hz, Np-H₂) 6.11 (2H, ddt, $J=17.5, 10.5, 5$ Hz, C-CH=C) 5.45 (2H, ddt, $J=17.5, 1.5, 1.5$ Hz, C=CH_(E)) 5.26 (2H, ddt, $J=10.5, 1.5, 1.5$ Hz, C=CH_(Z)) 5.0 (4H, dt, $J=5, 1.5$ Hz, O-CH₂-C) ppm. ^{13}C NMR (101 MHz, CHLOROFORM-d) δ 154.1, 133.3, 126.8, 125.1, 117.3, 114.5, 105.8, 68.9 ppm. IR ν_{max} 1590, 1507, 1406, 1379, 1266, 1208, 1109, 1076, 1034, 913, 772, 642 cm^{-1} . MS (APCI⁺) m/z 241 ([M+H]⁺, 100%), 200 ([M-C₃H₅]⁺, 40%). HRMS (EI⁺) C₁₆H₁₆O₂ requires 240.1145, found 240.1140.



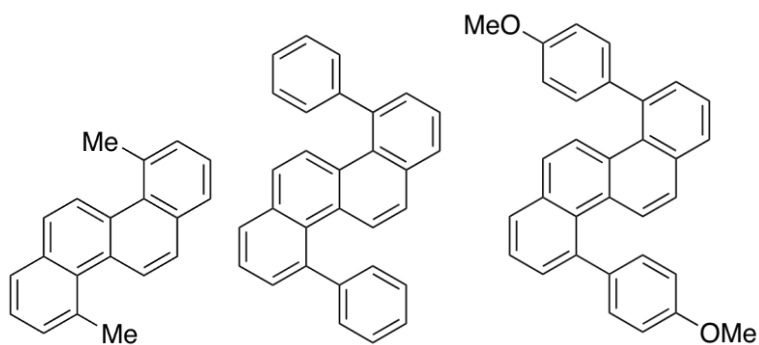
2,6-Diallyl-1,5-dihydroxynaphthalene (10). 1,5-bis(allyloxy)naphthalene was heated neat to 210 °C for 2h under N₂, affording the product in 99% yield. No purification was employed due to the title compound's sensitivity to oxidation. m.p. 135 °C. 1H NMR (500 MHz, CHLOROFORM-d) δ 7.73 (2H, d, $J=8.5$ Hz, Np-H₄) 7.24 (2H, d, $J=8.5$ Hz, Np-H₃) 6.09 (2H, ddt, $J=18, 10, 6.5$ Hz, C-CH=C) 5.51 (2H, s, OH) 5.26 (2H, ddt, $J=18, 2, 2$ Hz, C=CH_(E)) 5.25 (2H, ddt, $J=10, 2, 2$ Hz, C=CH_(Z)) 3.60 (4H, dt, $J=6.5, 2$ Hz, Np-CH₂-C) ppm. ^{13}C NMR (101 MHz, CHLOROFORM-d) δ 149.5, 136.2, 127.9, 125.2, 117.9, 117.0, 113.7, 35.7 ppm. IR ν_{max} 3310, 1636, 1606, 1496, 1355, 1240, 988, 900, 868, 812, 740, 673 cm^{-1} . MS (EI⁺) m/z 240 (M⁺, 100%). HRMS (ES⁺) C₁₆H₁₇O₂ requires 241.1223, found 241.1224.



2,6-Diallyl-1,5-bis(2,2,2-trichloroacetyl)naphthalene (11). 2,6-diallyl-1,5-dihydroxynaphthalene (15 g, 62.5 mmol) and pyridine (12.22 mL, 150 mmol) in dry diethyl ether (500 mL) were cooled to 0 °C. To this solution was added trichloroacetyl chloride (16.74 mL, 150 mmol) dropwise with rapid stirring. After 2 h the reaction was quenched by the slow addition of water (200 mL), the organic layer was collected and washed with sat. NaHCO₃ soln. (2 x 100 mL), water (2 x 100 mL) and brine (100 mL). The organic fraction was then dried over MgSO₄ and concentrated *in vacuo* to afford the title compound in 84% yield. No further purification was employed due to the title compound's instability. m.p. 133 °C. ¹H NMR (500 MHz, CHLOROFORM-*d*) δ 7.74 (2H, d, J=8.5 Hz, Np-H₄), 7.42 (2H, d, J=8.5 Hz, Np-H₃), 5.95 (2H, ddt, J=16.5, 10.5, 6.5 Hz, C-CH=C), 5.16 (2H, ddt, J=10.5, 1.5, 1.5 Hz, C=CH_(Z)), 5.15 (2H, ddt, J=16.5, 1.5, 1.5 Hz, C=CH_(E)), 3.52 (4H, dt, J=6.5, 1.5 Hz, Np-CH₂-C) ppm. ¹³C NMR (101 MHz, CHLOROFORM-*d*) δ 160.2, 143.6, 134.6, 129.3, 129.2, 126.6, 119.8, 117.5, 89.5, 34.1 ppm. IR ν_{max} 1777, 1379, 1191, 1169, 991, 960, 920, 878, 820, 792, 675 cm⁻¹. MS (APCI⁺) m/z 530 ([M(³⁵Cl₅ + ³⁷Cl₁)]⁺, 100%). HRMS (EI⁺) C₂₀H₁₄O₄Cl₆ requires 527.9018, found 527.9028.



4,10-Dichlorochrysene (12). 2,6-Diallyl-1,5-bis(2,2,2-trichloroacetyl)naphthalene (3 g, 7.58 mmol) and CuCl (5 mol%, 75 mg, 0.76 mmol) were dissolved in diglyme (3 mL) and were thoroughly degassed and purged with N₂. The solution was heated to reflux (162 °C) with gentle stirring for 2 h. The crude product mixture was then directly loaded onto a flash chromatography column and the product eluted with 1:5 DCM/Hexane. The product was isolated as colourless needles in 38% yield. m.p. 159 °C. ¹H NMR (500 MHz, CHLOROFORM-*d*) δ 9.45 (2H, d, J=9 Hz, H₅), 7.83 (2H, dd, J=8, 1.5 Hz, H₁), 7.77 (2H, d, J=9 Hz, H₆), 7.69 (2H, dd, J=8, 1.5 Hz, H₃), 7.46 (2H, t, J=8 Hz, H₂) ppm. ¹³C NMR (126 MHz, CHLOROFORM-*d*) δ 134.57, 131.42, 130.21, 129.86, 127.59, 127.47, 126.59, 126.43, 125.00 ppm. IR ν_{max} 1416, 1206, 1086, 929, 821, 723, 662 cm⁻¹. MS (APCI⁺) m/z 295 ([M-H]⁺, 100%), 296 (M⁺, 65%). HRMS (ES⁺) C₁₈H₁₀Cl₂ requires 296.0148, found 296.0154.

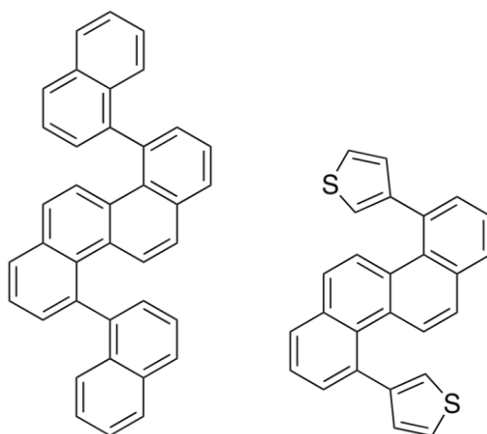


Method A (16, 17, 18). 4,10-Dichlorochrysene (200 mg, 0.68 mmol) and PEPPSI-iPr (5 mol%, 23 mg, 34 μ mol) were added to a Schlenk tube equipped with a magnetic stirrer bar and purged with N_2 . Thoroughly degassed THF (2 mL) was then added via cannula. With rapid stirring, the corresponding magnesiumbromide in THF (2.72 mmol) was added dropwise, with attention paid to the evolution of a red colour indicative of the activated catalyst species. The crude product was then filtered through silica with DCM to remove traces of palladium.

4,10-Dimethylchrysene (16). Product was isolated as orange crystals in 91% yield after recrystallisation from hexane. m.p. 102 °C. 1H NMR (500 MHz, CHLOROFORM-*d*) δ 8.59 (2H, d, $J=9$ Hz, H_5), 7.75 - 7.79 (4H, m), 7.46 (4H, m), 3.05 (6H, s, Me) ppm. ^{13}C NMR (126 MHz, CHLOROFORM-*d*) δ 135.04, 132.80, 130.97, 130.78, 130.69, 126.46, 126.00, 125.84, 125.42, 26.35 ppm. MS (MALDI-Dithranol) m/z 256 (M^+ , 19%). HRMS (EI^+) $C_{20}H_{16}$ requires 256.1247, found 256.1233.

4,10-Diphenylchrysene (17). Product was isolated as colourless crystals in 84% yield after recrystallisation from DCM/hexane. m.p. 204 °C. 1H NMR (400 MHz, CHLOROFORM-*d*) δ 7.80 (2H, dd, $J=8, 1.5$ Hz), 7.72 (2H, d, $J=9$ Hz), 7.59 (2H, t, $J=7$ Hz), 7.38 - 7.54 (14H, m) ppm. ^{13}C NMR (101 MHz, CHLOROFORM-*d*) δ 145.00, 140.36, 133.03, 130.61, 130.58, 129.19, 128.99, 128.96, 127.73, 127.66, 127.04, 125.80, 124.36 ppm. MS (MALDI-Dithranol) m/z 380 (M^+ , 95%). HRMS (EI^+) $C_{30}H_{20}$ requires 380.1560, found 380.1565.

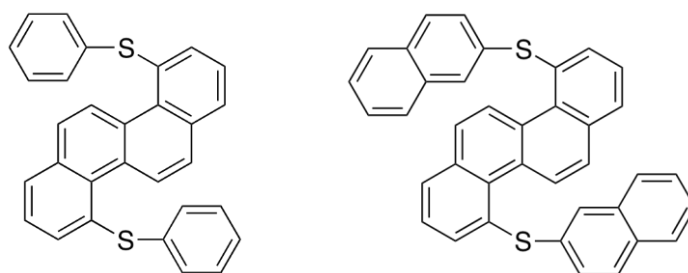
4,10-Bis(4-methoxyphenyl)chrysene (18). Product was isolated as colourless crystals in 69% yield after recrystallisation from hexane. m.p. 206 °C. 1H NMR (400 MHz, CHLOROFORM-*d*) δ 7.69 - 7.72 (4H, m), 7.40 - 7.53 (4H, m), 7.30 - 7.35 (6H, m), 6.93 (4H, d, $J=8.5$ Hz), 3.84 (6H, s, O-Me) ppm. ^{13}C NMR (101 MHz, CHLOROFORM-*d*) δ 158.80, 139.98, 137.41, 133.08, 130.74, 130.48, 130.19, 129.10, 127.49, 127.38, 125.77, 124.31, 114.35, 55.36 ppm. MS (APCI) m/z 441 ($[M + H]^+$, 100%). HRMS (EI^+) $C_{32}H_{24}O_2$ requires 440.1771, found 440.1753.



Method B (19, 20). PEPPSI-iPr (2 mol%, 9 mg, 13.6 μmol) and KO^tBu (197 mg, 1.78 mmol) were added to a Schlenk tube equipped with a magnetic stirrer bar and purged with N_2 . Thoroughly degassed anhydrous ethanol (3 mL) was added via cannula and the mixture stirred until a colour change from yellow to red was observed, signifying the activation of the catalyst. Without stirring and under a blanket of N_2 , 4,10-dichlorochrysene (200 mg, 0.68 mmol) and the corresponding boronic acid (1.62 mmol) were added. The tube was then resealed and stirred under N_2 for 30 min.

4,10-Bis(1-naphthyl)chrysene (19). Product was isolated as a white solid formed as a precipitate which was isolated by vacuum filtration and washing with water (10 mL), methanol (10 mL) and hexane (10 mL). Product is sparingly soluble in chlorinated solvents and toluene. The mono-coupled product is detectable in the ^1H NMR as a doublet at 9.55 ppm. 82% yield. m.p. 240 $^\circ\text{C}$. ^1H NMR (400 MHz, CHLOROFORM-*d*) δ 7.86 - 7.97 (4H, m), 7.70 (2H, dt, $J=7.5$, 2 Hz), 7.36 - 7.59 (14H, m), 7.07 - 7.24 (4H, m) ppm. ^{13}C NMR (101 MHz, CHLOROFORM-*d*) δ 138.15, 138.06, 132.78, 131.54, 131.45, 130.21, 128.30, 128.24, 128.11, 127.63, 126.98, 126.89, 126.35, 126.29, 126.21, 126.10, 126.04, 125.54, 125.28 ppm. **MS** (MALDI-DCTB) 481 ($[\text{M} + \text{H}]^+$, 100%). **HRMS** (EI^+) $\text{C}_{38}\text{H}_{24}$ requires 480.1873, found 480.1867.

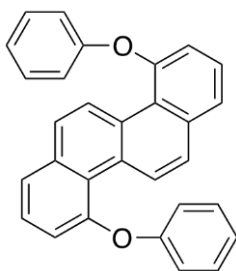
4,10-Bis(3-thienyl)chrysene (20). Product was isolated as colourless crystals in 60% yield after column chromatography from DCM/hexane. m.p. 195 $^\circ\text{C}$. ^1H NMR (400 MHz, CHLOROFORM-*d*) δ 7.72 - 7.91 (4H, m), 7.55 - 7.69 (4H, m), 7.50 (2H, d, $J=9$ Hz), 7.38 - 7.44 (4H, m), 7.07 (2H, dd, $J=4$, 2.5 Hz) ppm. ^{13}C NMR (101 MHz, CHLOROFORM-*d*) δ 145.3, 134.9, 133.0, 130.6, 130.2, 129.3, 127.9, 126.8, 126.0, 125.8, 124.5, 121.6, 119.8 ppm. **MS** (MALDI-Dithranol) m/z 392 (M^+ , 65%). **HRMS** (EI^+) $\text{C}_{26}\text{H}_{16}\text{S}_2$ requires 392.0688, found 392.0671.



Method C (21, 22). 4,10-Dichlorochrysene (100 mg, 0.34 mmol), potassium carbonate (141 mg, 1.01 mmol), the corresponding thiol (0.81 mmol) and dry DMF (1 mL) were added to a Schlenk tube and purged with N₂. The tube was then heated to 100 °C in a sand-bath for 6 h, until 100% conversion by ¹H NMR. The product mixture was then diluted with DCM (10 mL), filtered through a plug of cotton wool and concentrated *in vacuo*.

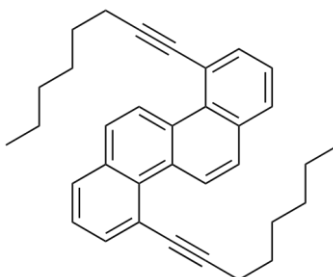
4,10-Bis(phenylthio)chrysene (21). Product was isolated as a white solid in 86% yield after recrystallization from methanol. The mono-coupled product is detectable in the ¹H NMR as a doublet at δ 9.50 ppm. m.p. 178 °C. **¹H NMR** (400 MHz, CHLOROFORM-*d*) δ 9.36 (2H, d, H₅, J=9 Hz), 7.89 (2H, dd, J=8, 1.5 Hz), 7.84 (2H, d, H₆, J=9 Hz), 7.66 (2H, dd, J=7.5, 1.5 Hz), 7.50 (2H, t, H₂, J=7.5 Hz), 7.18 - 7.31 (10H, m, S-Ph) ppm. **¹³C NMR** (101 MHz, CHLOROFORM-*d*) δ 136.04, 132.58, 132.01, 129.76, 129.27, 128.23, 126.91, 125.97, 125.95, 125.26, 123.95 ppm. **MS** (MALDI-Dithranol) m/z 444 (M⁺, 100%). **HRMS** (EI⁺) C₃₀H₂₀S₂. requires 444.1001 found 444.0994.

4,10-Bis(1-naphthylthio)chrysene (22). Product was isolated as an orange solid in 40% yield after multiple recrystallization from toluene. m.p. 201-203 °C. **¹H NMR** (500 MHz, CHLOROFORM-*d*) δ 9.36 (2H, d, J=9 Hz) 7.84 - 7.91 (6H, m) 7.77 - 7.82 (2H, m) 7.69 - 7.74 (4H, m) 7.67 (2H, dd, J=7.5, 1 Hz) 7.44 - 7.49 (6H, m) 7.25 (2H, dd, J=8.5, 1.5 Hz) ppm. **¹³C NMR** (126 MHz, CHLOROFORM-*d*) δ ppm 134.47, 133.85, 133.63, 133.50, 133.24, 132.30, 130.93, 130.35, 129.84, 129.04, 128.59, 127.89, 127.75, 127.49, 127.13, 126.61, 126.36, 126.24, 125.10 ppm. **MS** (APCI) m/z 545 ([M + H]⁺, 100%). **HRMS** (EI⁺) C₃₈H₂₄S₂. requires 544.1314 found 544.1335.



Method D (23). 4,10-Dichlorochrysene (50 mg, 0.17 mmol), cesium carbonate (143 mg, 0.44 mmol), the corresponding phenol (0.40 mmol), copper iodide (75 mg, 0.40 mmol) and diglyme (2 mL) were added to a Schlenk tube equipped with a magnetic stirrer bar and purged under N₂. The tube was then heated to 150 °C in a sand-bath for 48 h, until 100% conversion by ¹H NMR. The product mixture was then diluted with DCM (10 mL) and filtered through a plug of silica and concentrated *in vacuo*.

4,10-Bis(phenoxy)chrysene (24). Product was isolated as a white solid in 78% yield after column chromatography with 1:9 EtOAc/hexane. m.p. 216 °C. ¹H NMR (400 MHz, CHLOROFORM-*d*) δ 9.51 (2H, d, H₅, *J*=9.5 Hz), 7.83 (2H, d, H₆, *J*=9.5 Hz), 7.67 (2H, dd, *J*=8, 1.5 Hz), 7.45 (2H, t, H₂, *J*=8 Hz), 7.20 - 7.29 (4H, m, O-Ph), 7.14 (2H, dd, *J*=8, 1.5 Hz), 6.95 - 7.06 (6H, m, O-Ph) ppm. ¹³C NMR (101 MHz, CHLOROFORM-*d*) δ 157.61, 155.27, 134.61, 129.89, 129.56, 127.09, 126.65, 126.56, 124.40, 118.56, 118.26, 116.47 ppm. MS (APCI) *m/z* 413 ([M + H]⁺, 100%). HRMS (EI⁺) C₃₀H₂₀O₂. requires 412.1458 found 412.1451.

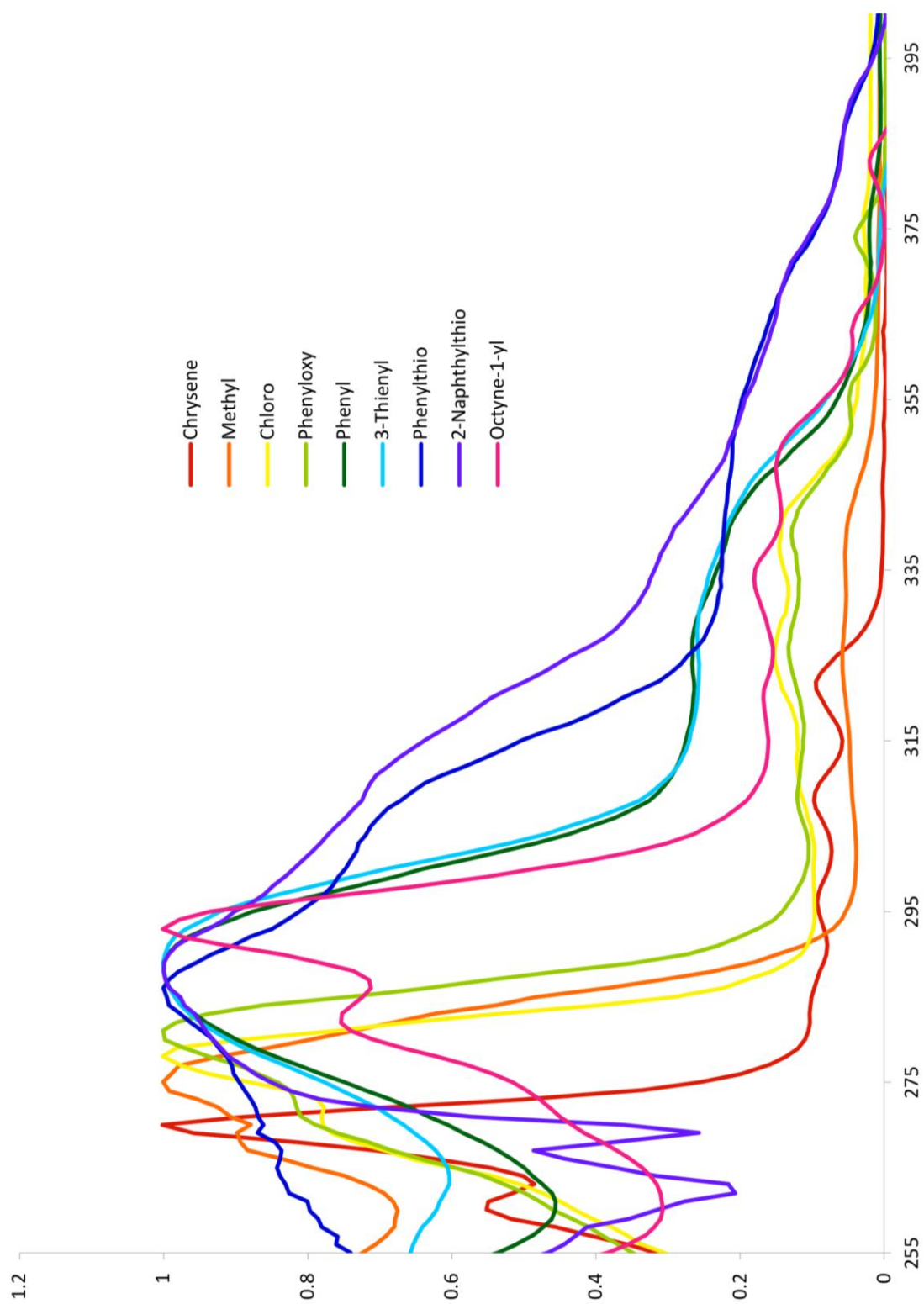


Method E (25). 4,10-Dichlorochrysene (50 mg, 0.17 mmol), the corresponding terminal alkyne (0.36 mmol), cesium carbonate (121 mg, 0.38 mmol), bis(triphenylphosphine)palladium(II) dichloride (6 mol-%, 7 mg, 10 μmol), tri(cyclohexyl)phosphine (15 mol%, 7 mg, 25 μmol) and dry DMF (0.5 mL) were added to a Schlenk tube and purged with N₂. The mixture was then heated to 110 °C in sand-bath for 40 h, until 100% conversion by ¹H NMR. The product mixture was then diluted with DCM (10 mL), filtered through a plug of silica and concentrated *in vacuo*.

4,10-Bis(oct-1-yn-1-yl)chrysene (23). The *title compound* was isolated as a waxy orange solid in 61% yield after column chromatography with hexane and recrystallization from hot hexane. 4-oct-1-yn-1-ylchrysene is detectable in the ¹H NMR spectrum at δ 8.80 and 10.05 ppm as a product of dehalogenation. m.p. 50 °C. ¹H NMR (400 MHz, CHLOROFORM-*d*) δ 10.22 (2H, d, H₅, *J*=9 Hz), 7.77 - 7.86 (6H, m, H₁, H₃, H₆), 7.46 (2H, t, H₂, *J*=7.5 Hz), 2.56 (4H, t, C≡C-CH₂, *J*=7 Hz), 1.70 (4H, quin, *J*=7.5 Hz), 1.52 (4H, quin, *J*=7.5 Hz), 1.25 - 1.38 (4H, m), 1.19 (4H, m), 0.76 - 0.92 (6H, m) ppm. ¹³C NMR (125 MHz, CHLOROFORM-*d*) δ 134.73, 132.96, 130.15, 129.81, 128.43, 125.82, 125.49, 125.20, 120.57, 96.43, 83.40, 31.54, 28.90, 28.62, 22.67, 20.16, 14.15 ppm. MS (APCI) *m/z* 445 ([M + H]⁺, 100%), 477 ([M + Na]⁺, 85%). HRMS (EI⁺) C₃₄H₃₆. requires 444.2812 found 444.2826.

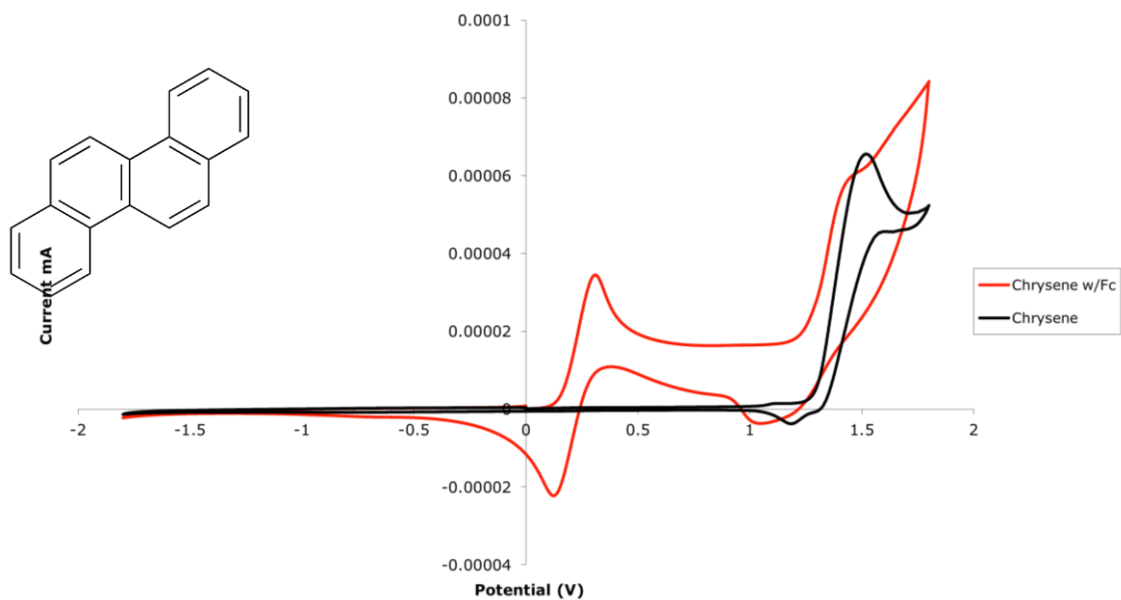
A major by-product of this reaction was (*E*)-hexadec-7-en-9-yne: ¹H NMR (400 MHz, CHLOROFORM-*d*) δ 5.95 (1H, dt, *J*=16, 6 Hz), 5.35 (1H, d, *J*=16 Hz), 2.18 (2H, m), 1.99 (2H, m), 1.10 - 1.50 (16H, m), 0.84 (6H, m).

Section 3 - UV/vis spectra of 4,10-chrysene derivatives

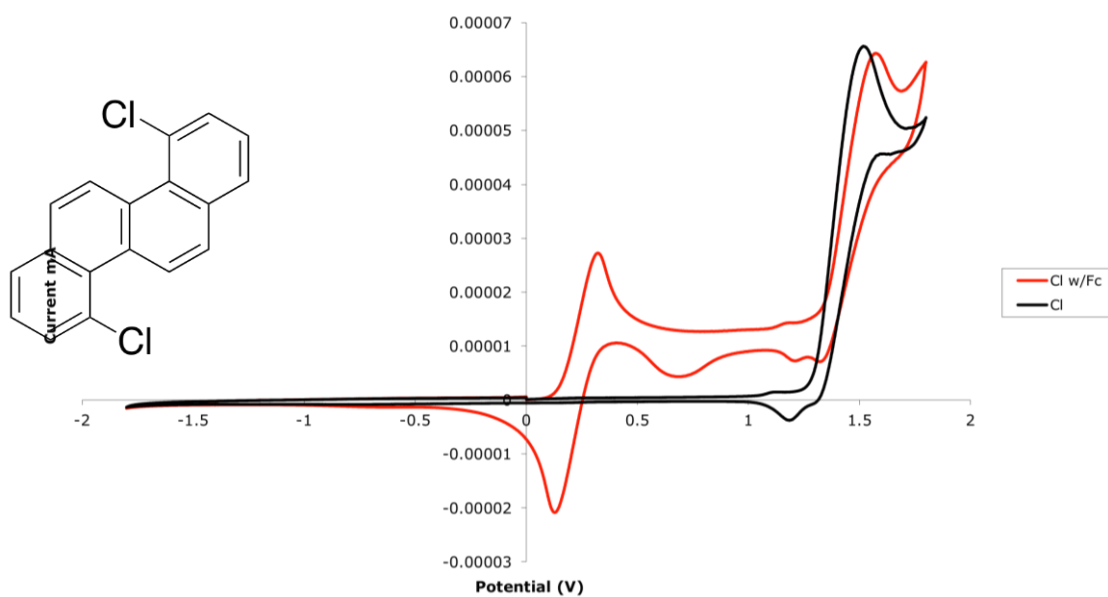


Section 4 - Cyclic voltammetry of 4,10-chrysene derivatives

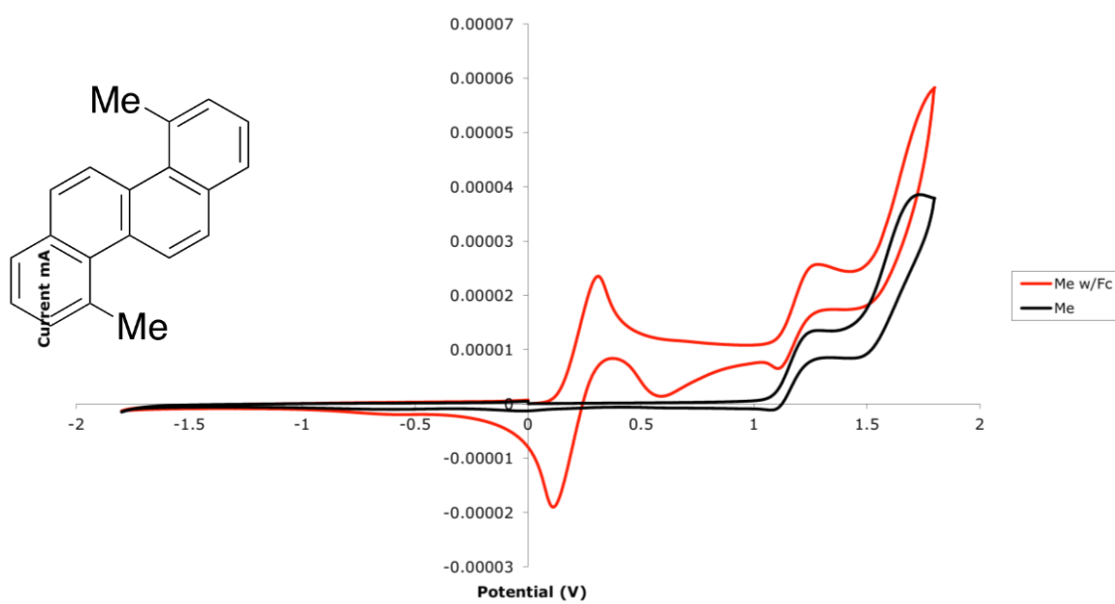
4.0 - Chrysene (24)



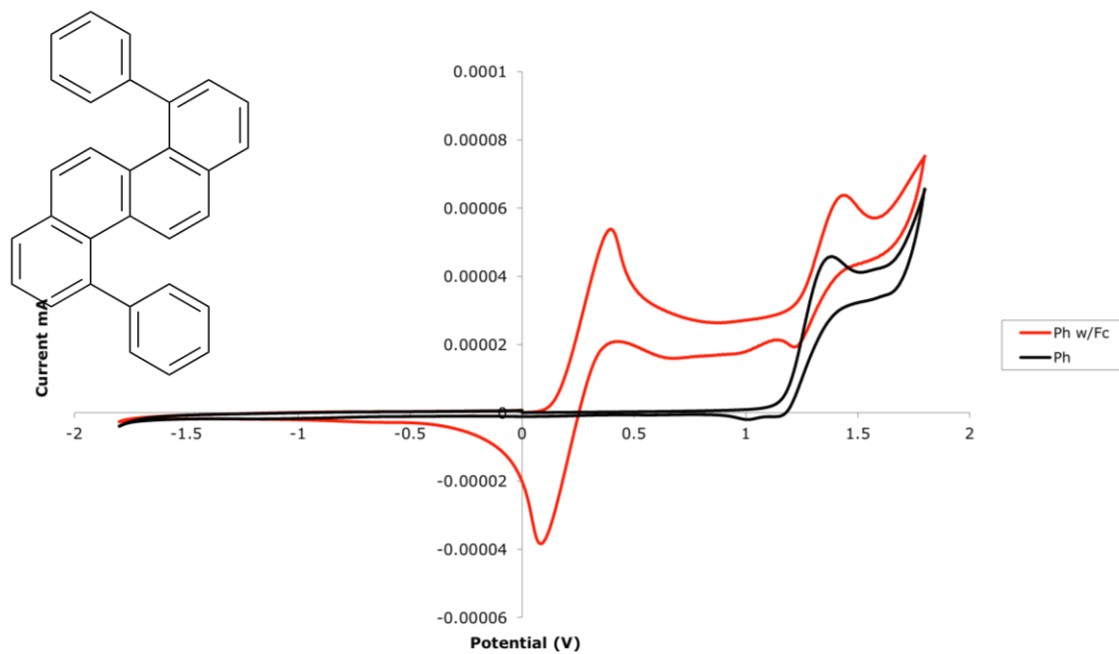
4.1 - 4,10-Dichlorochrysene (12)



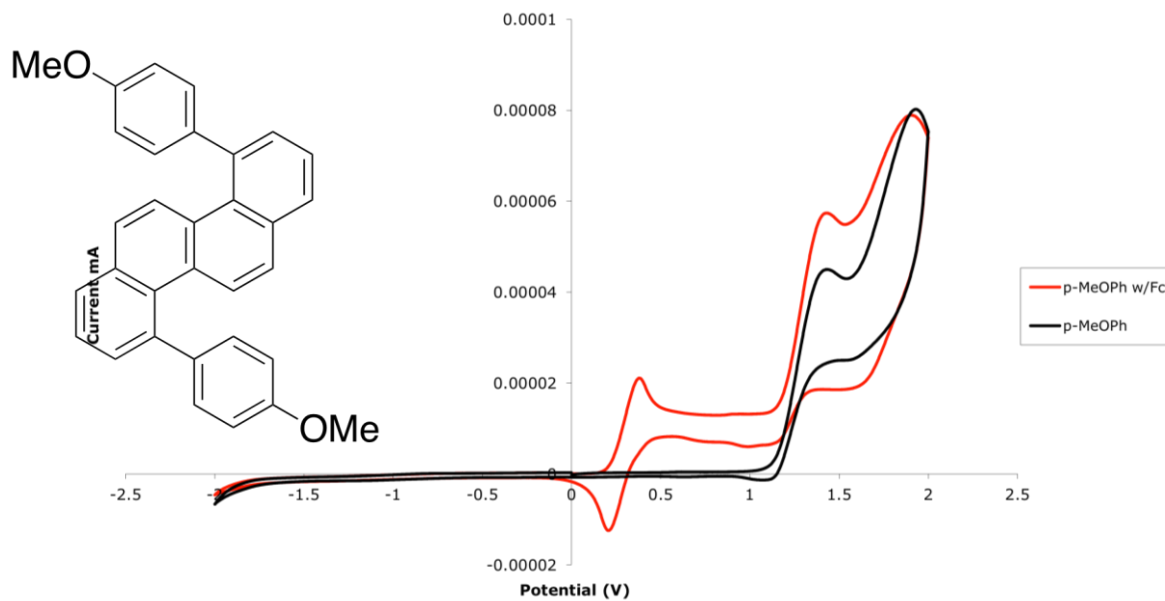
4.2 - 4,10-Dimethylchrysene (15)



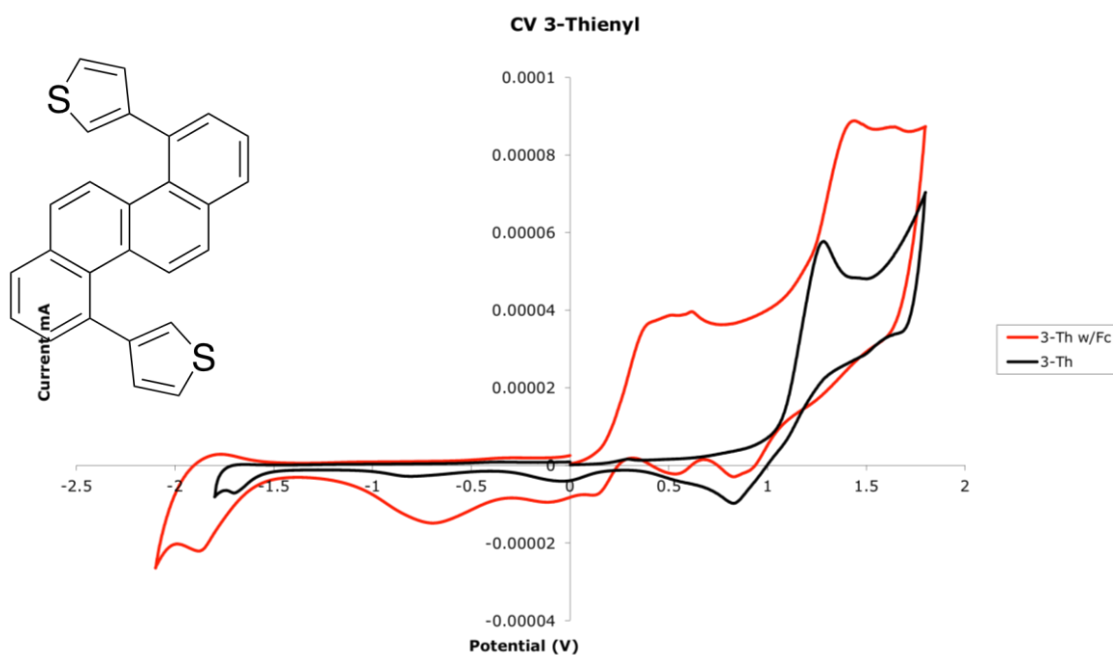
4.3 - 4,10-Diphenylchrysene (16)



4.4 - 4,10-Bis(4-methoxyphenyl)chrysene (17)

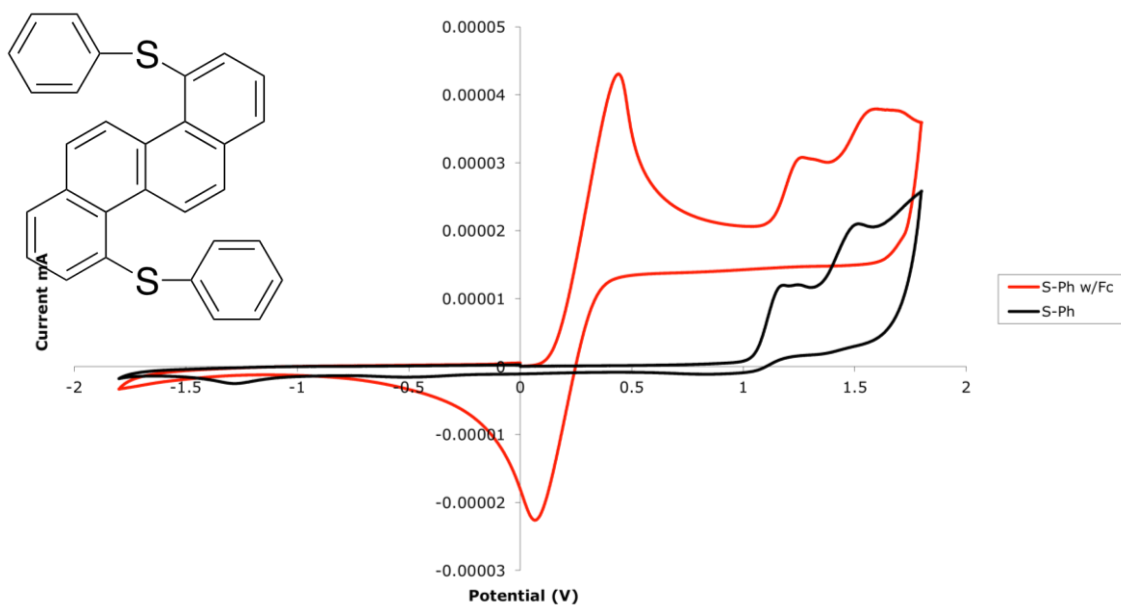


4.5 - 4,10-Bis(3-thienyl)chrysene (19)

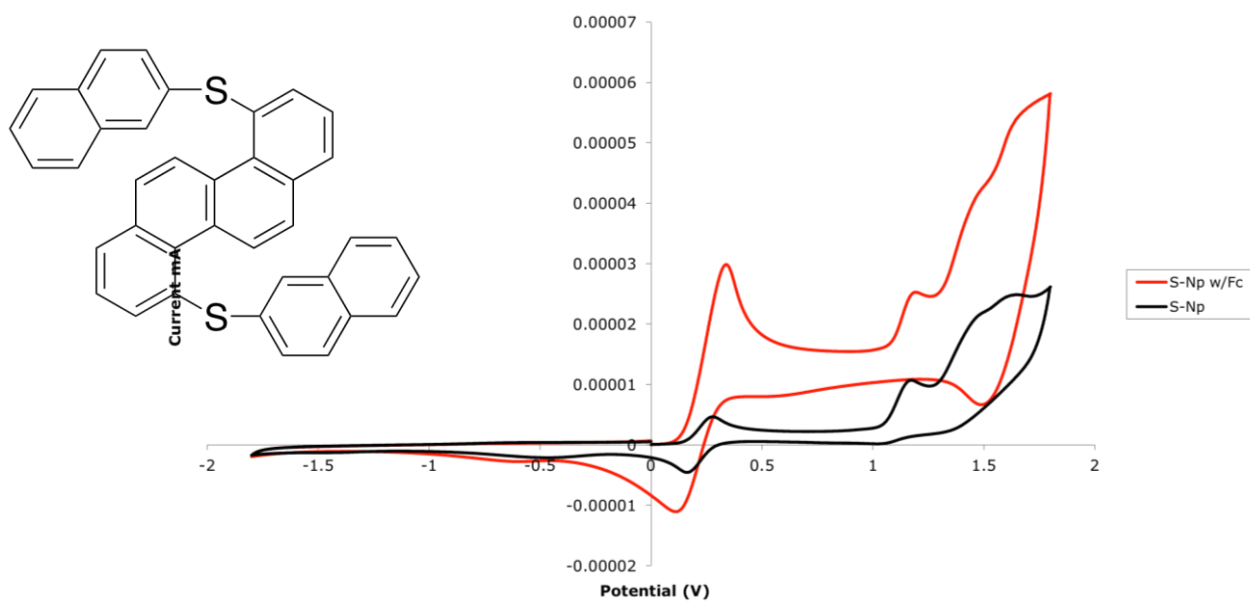


** 4,10-bis(3-thienyl)chrysene underwent reaction upon voltammetry, leaving a polymeric film on the working electrode.*

4.6 - 4,10-Bis(phenylthio)chrysene (20)

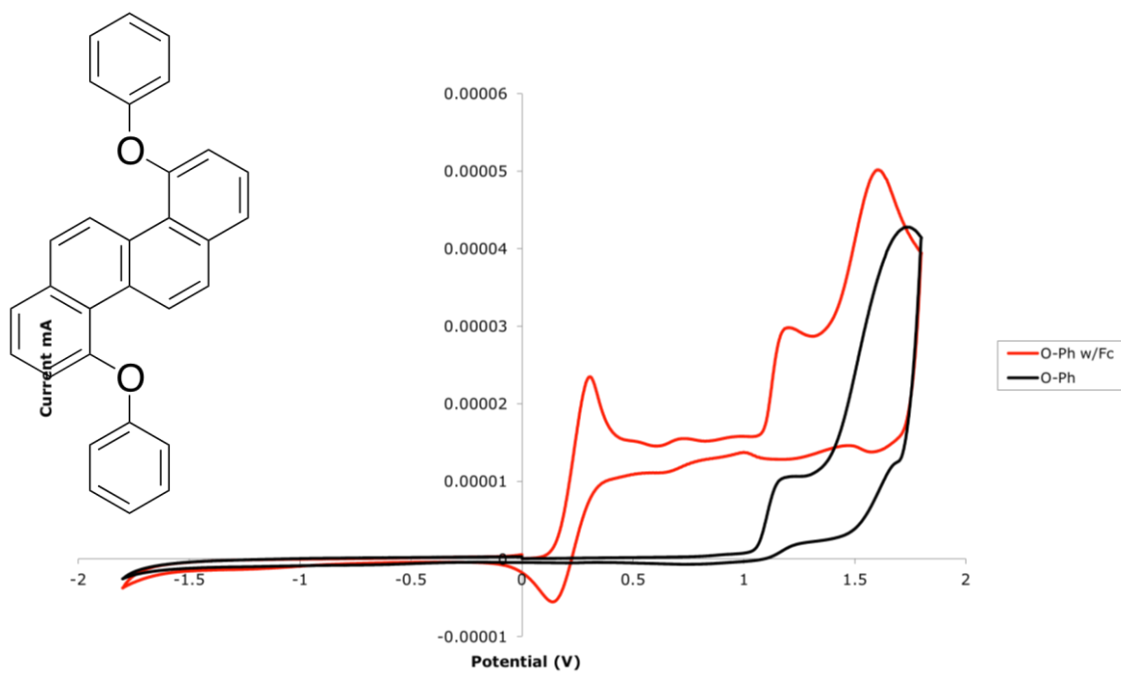


4.7 - 4,10-Bis(2-naphthylthio)chrysene (21)

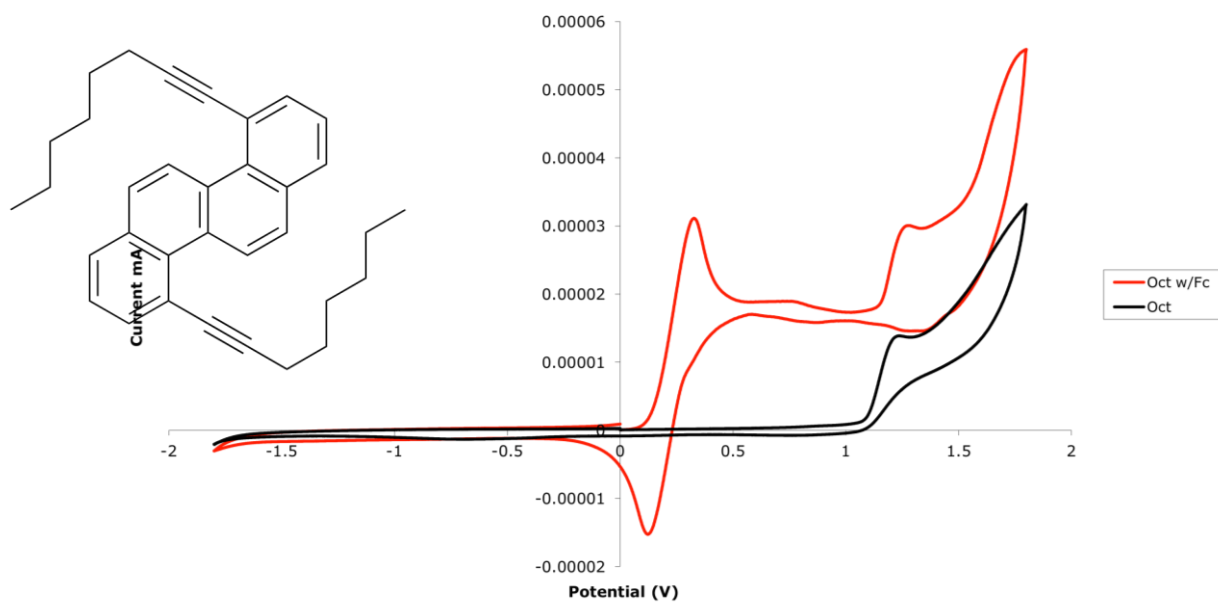


* Oxidation peak at 0.2 V for naphthyl thioether due to ferrocene.

4.8 - 4,10-Bis(phenyloxy)chrysene (22)



4.9 - 4,10-Bis(oct-1-yn-yl)chrysene (23)



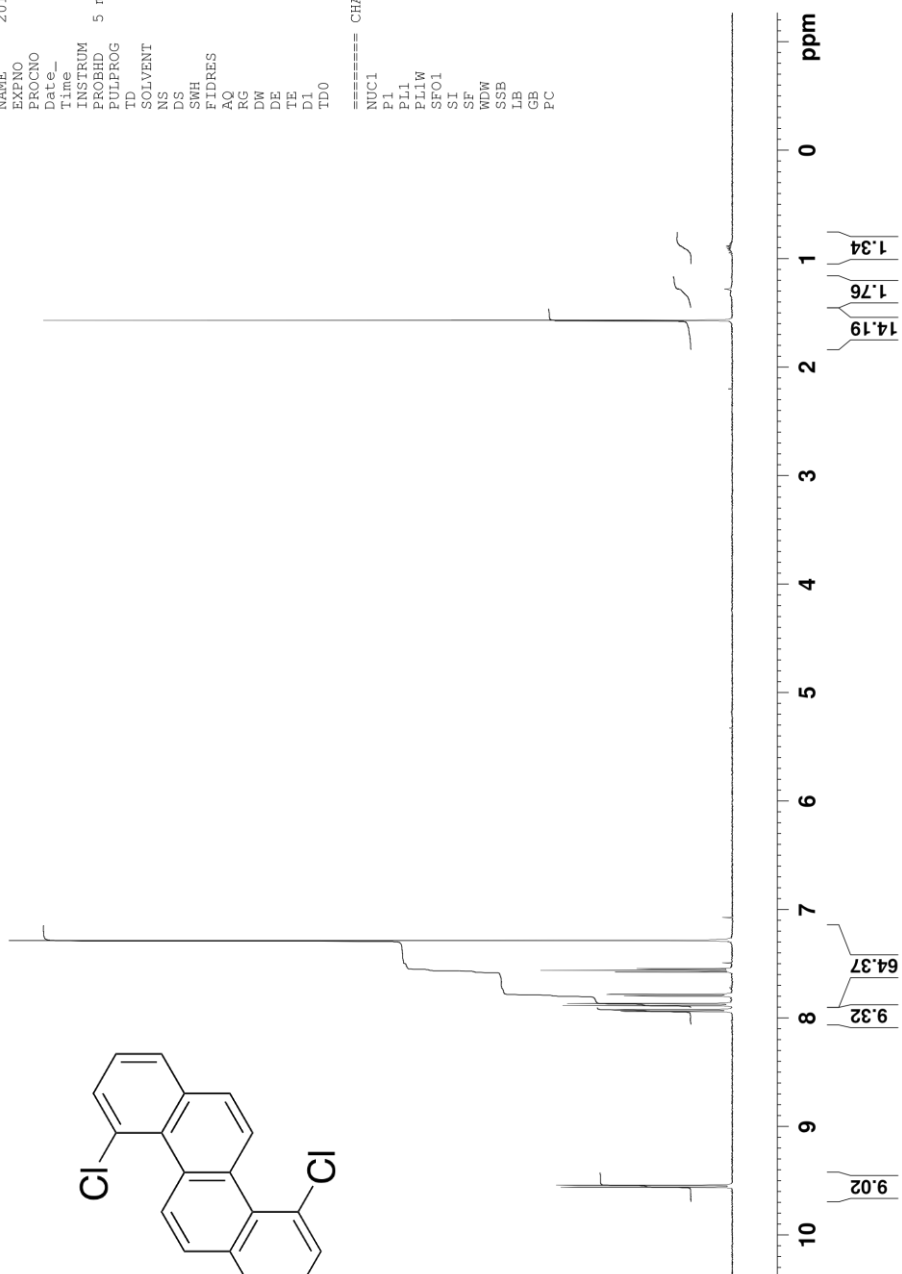
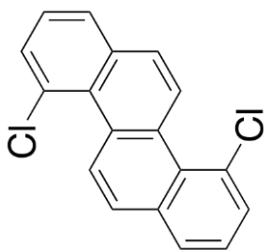
5 - NMR spectra for 4,10-chrysenes derivatives

5.0 - 4,10-Dichlorochrysenes



2010-11-09-paq-9
NAME
EXPNO 10
PROCNO 1
Date_ 20101109
Time 11.38
INSTRUM spect
PROBHD 5 mm TXI LH/D-
PULPROG zg30b
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 912
DW 48.400 usec
DE 13.38 usec
TE 293.8 K
D1 1.00000000 sec
TD0 1
===== CHANNEL f1 =====
NUC1 1H
P1 8.20 usec
PL1 3.25 dB
PL1W 12.12272263 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

ML017
mPROTON CDCl3 /opt/bruk500data/2010/Nov paq 9



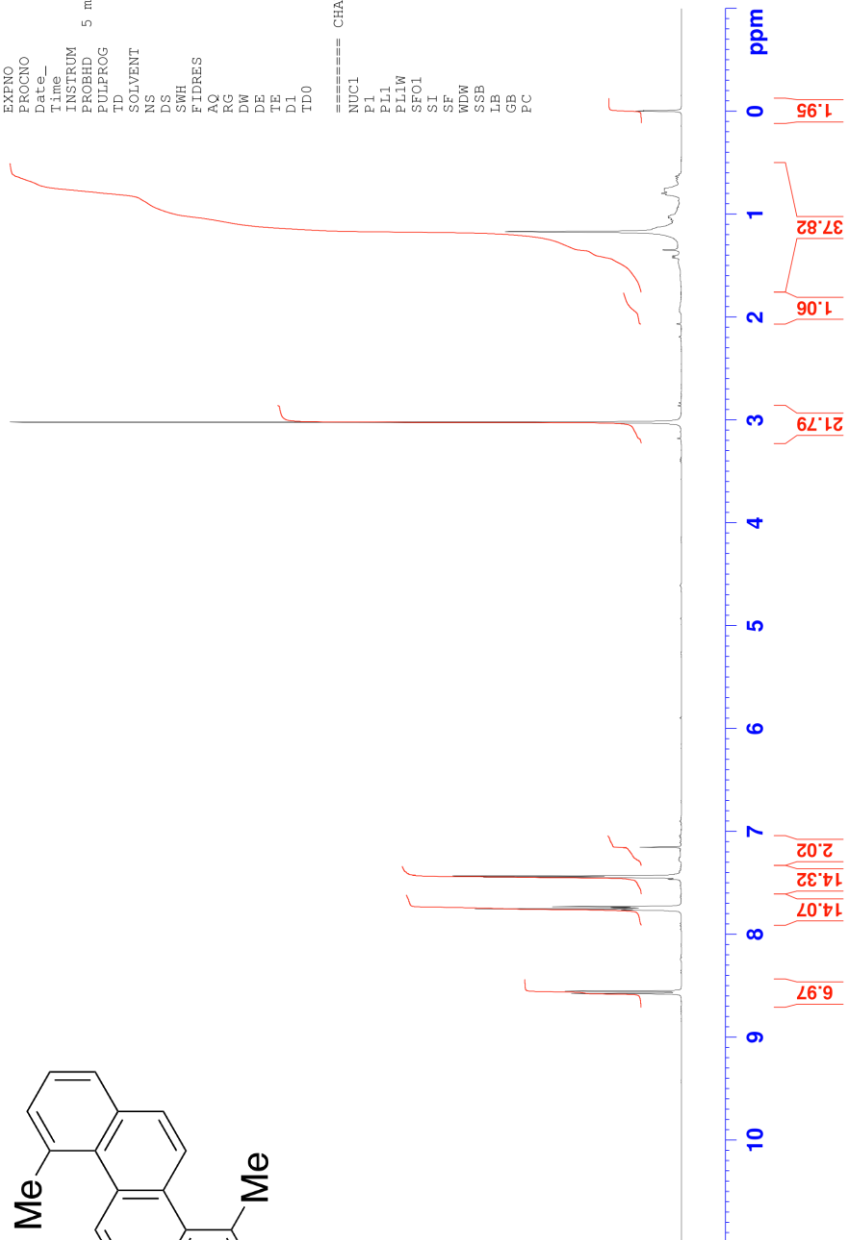
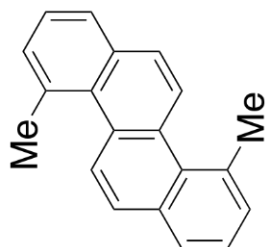
5.1 - 4,10-Dimethylchrysenene

ML076 full data
mPROTON CDCI3 {e:\bruk400data\2011\Aug} paq 43



NAME 2011-08-25-paq-43
EXPNO 10
PROCNO 1
Date_ 20110825
Time 11.48
INSTRUM AV400
PROBHD 5 mm FAPBO BB-
PULPROG zg30b
TD 65536
SOLVENT CDCI3
NS 16
DS 0
SWH 8264.463 Hz
FIDRES 0.126106 Hz
AQ 3.9649780 sec
RG 161
DW 60.500 usec
DE 9.40 usec
TE 292.2 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 10.00 usec
PL1 0.00 dB
PL12 17.83863891 W
SFO1 400.1320710 MHz
SI 32768
SF 400.1300593 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



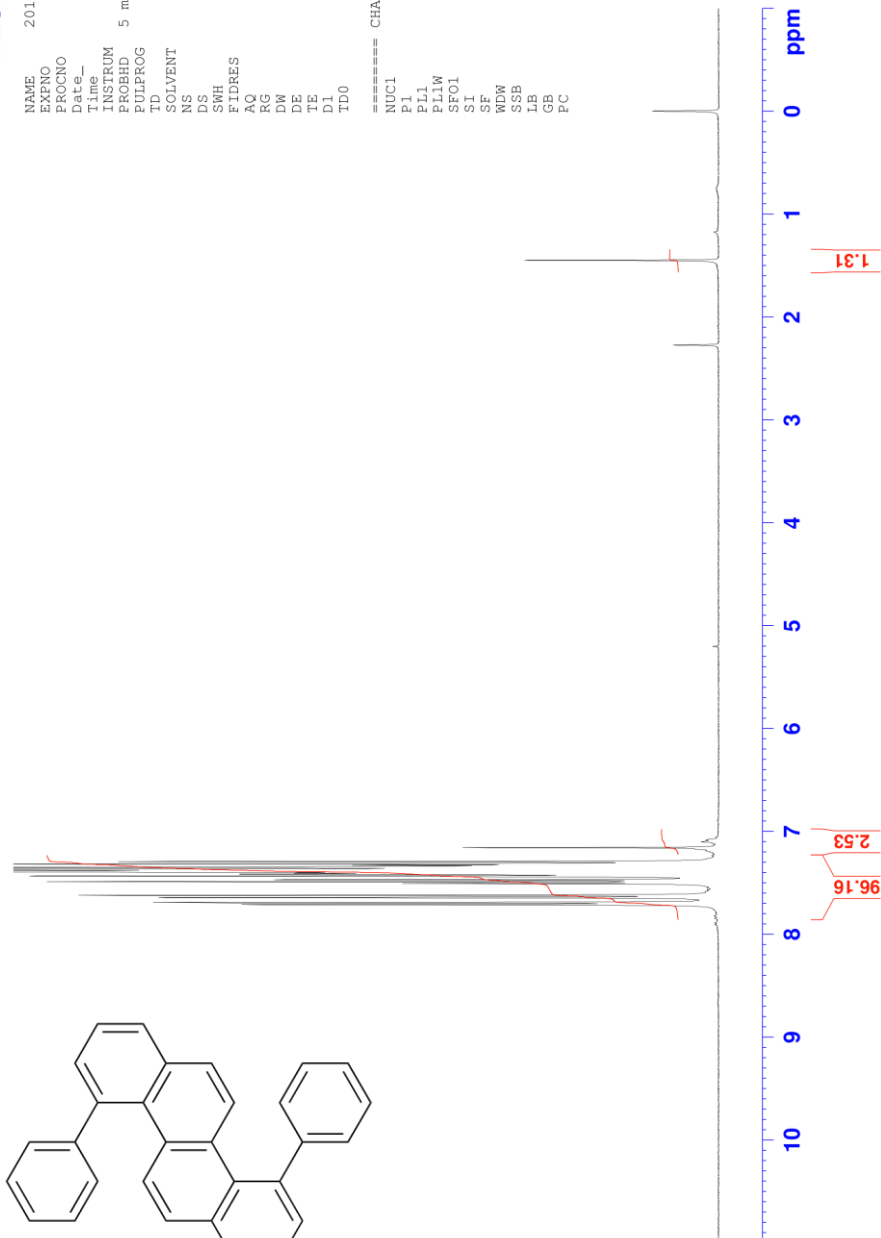
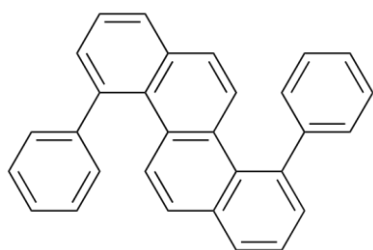
5.2 - 4,10-Diphenylchrysenes

ML075 full data
mPROTON CDCI3 {e:\bruk400data\2011\Aug\} paq 42



NAME 2011-08-25-paq-42
EXPNO 10
PROCNO 1
Date_ 20110825
Time_ 11.44
INSTRUM AV400
PROBHD 5 mm PABBO BB-
PULPROG zg30b
TD 65536
SOLVENT CDCI3
NS 16
DS 0
SWH 8264.463 Hz
FIDRES 0.126106 Hz
AQ 3.9649780 sec
RG 228
DW 60.500 usec
DE 9.40 usec
TE 292.2 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 10.00 usec
PL1 -3.60 dB
PL1W 17.83863831 W
SF01 400.1324710 MHz
SI 32768
SF 400.1300505 MHz
EM
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



5.3 - 4,10-Bis(4-methoxyphenyl)chrysene

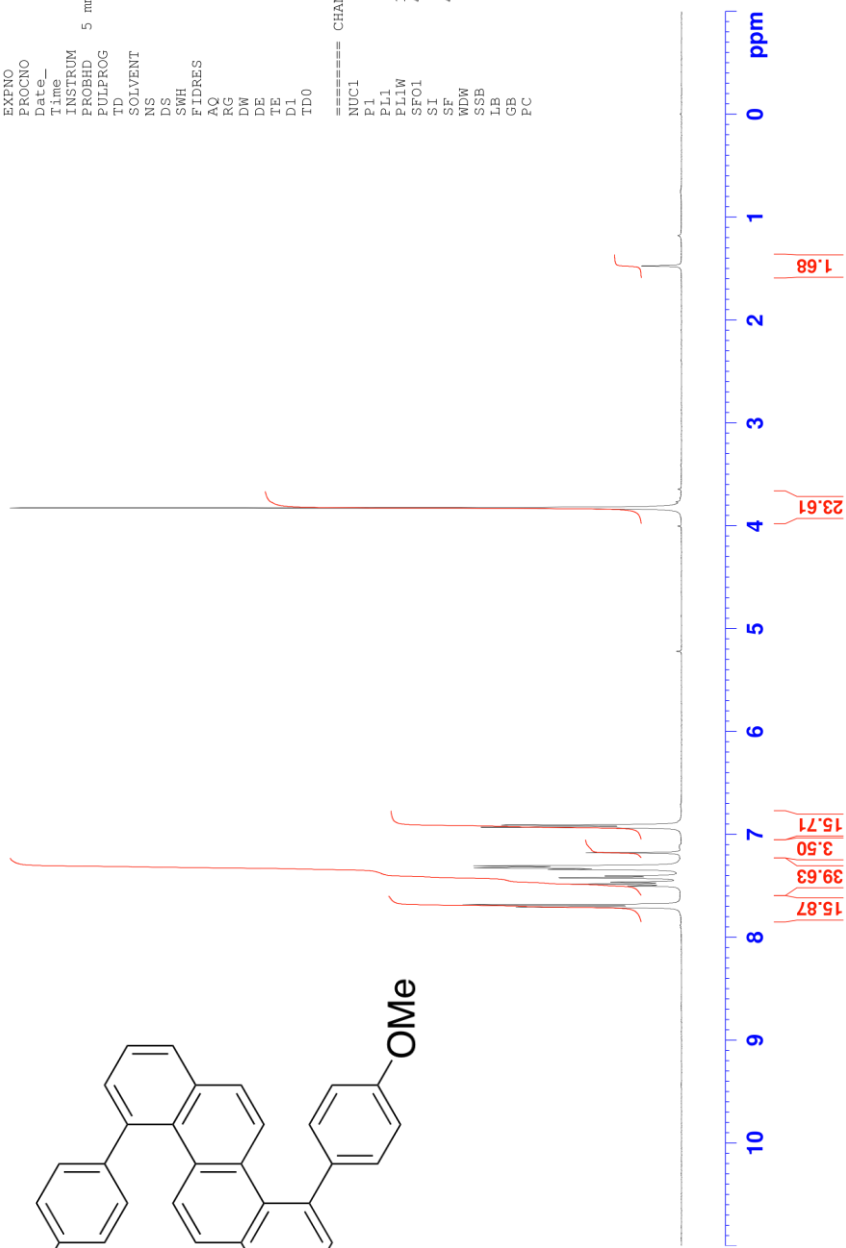
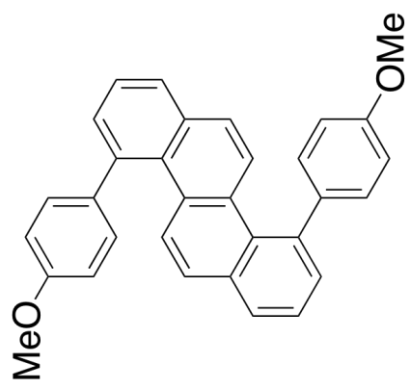
ML082 full data
 mPROTON CDCl3 {e:\bruk400data\2011\Aug\} paq 44



```

NAME      2011-08-25-paq-44
EXPNO    10
PROCNO   1
Date_    20110825
Time     11.52
INSTRUM  AV400
PROBHD   5 mm PABBO BB-
PULPROG  zg30b
TD       65536
SOLVENT  CDCl3
NS       16
DS       0
SWH      8264.463 Hz
FIDRES   0.126106 Hz
AQ       3.9649780 sec
RG       362
DW       60.500 usec
DE       9.40 usec
TE       292.2 K
D1       1.00000000 sec
TD0      1

===== CHANNEL f1 =====
NUC1     1H
P1       10.00 usec
PL1      -3.60 dB
PL1W     17.83863831 W
SF01     400.1324710 MHz
SI       32768
SF       400.1300425 MHz
EM
WDW      EM
SSB      0
LB       0.30 Hz
GB       0
PC       1.00
  
```



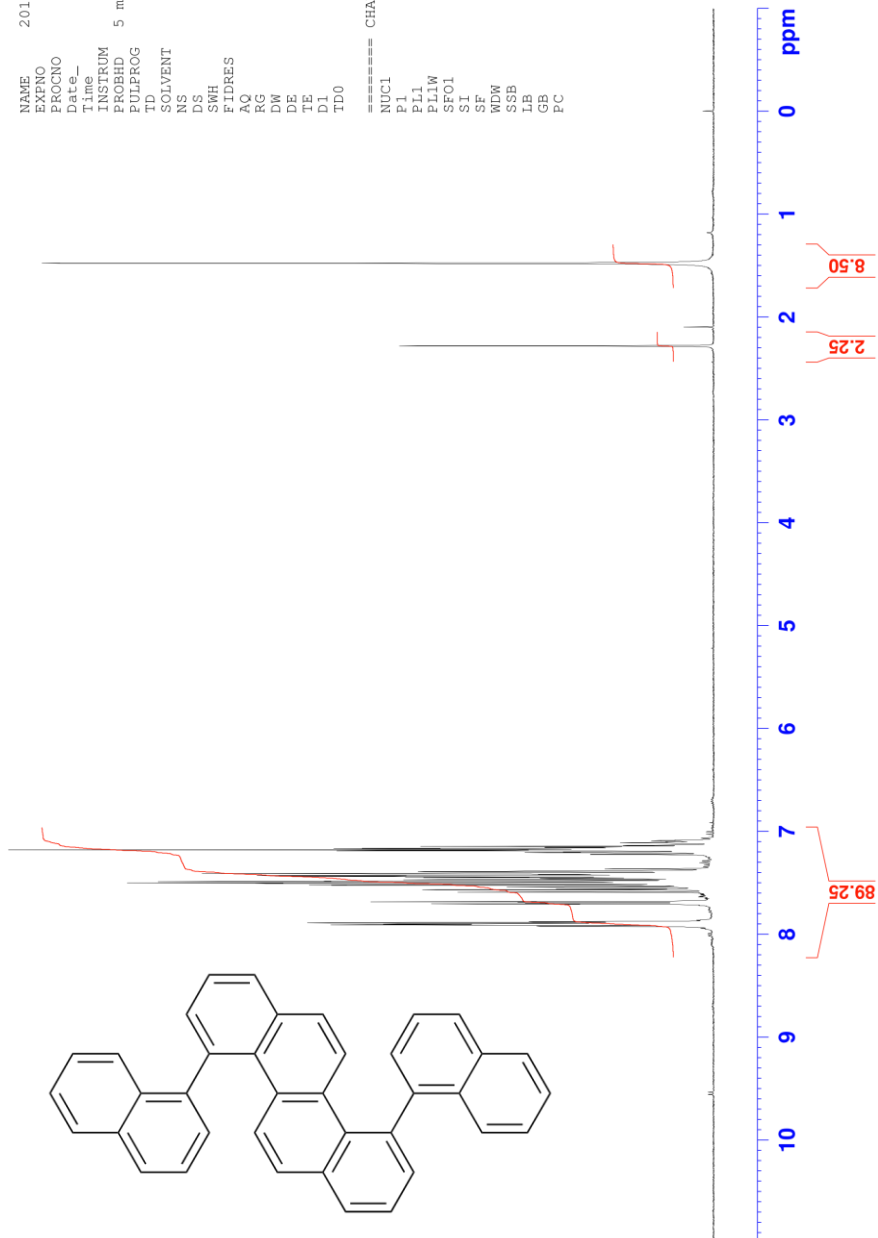
5.4 - 4,10-Bis(1-naphthyl)chrysene

ML055 fin
mPROTONnight CDCI3 {e:\bruk400data\2011\Feb} paq 22



NAME 2011-02-24-paq-22
EXPNO 10
PROCNO 1
Date_ 20110226
Time_ 8.45
INSTRUM AV400
PROBHD 5 mm PABBO BB-
PULPROG zg30b
TD 65536
SOLVENT CDCI3
NS 16
DS 0
SWH 8264.463 Hz
FIDRES 0.126106 Hz
AQ 3.9649780 sec
RG 456
DW 60.500 usec
DE 9.40 usec
TE 293.0 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 10.00 usec
PL1 -3.60 dB
PL1W 17.83863831 W
SF01 400.1324710 MHz
SI 32768
SF 400.1300415 MHz
EM
WDW 0
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

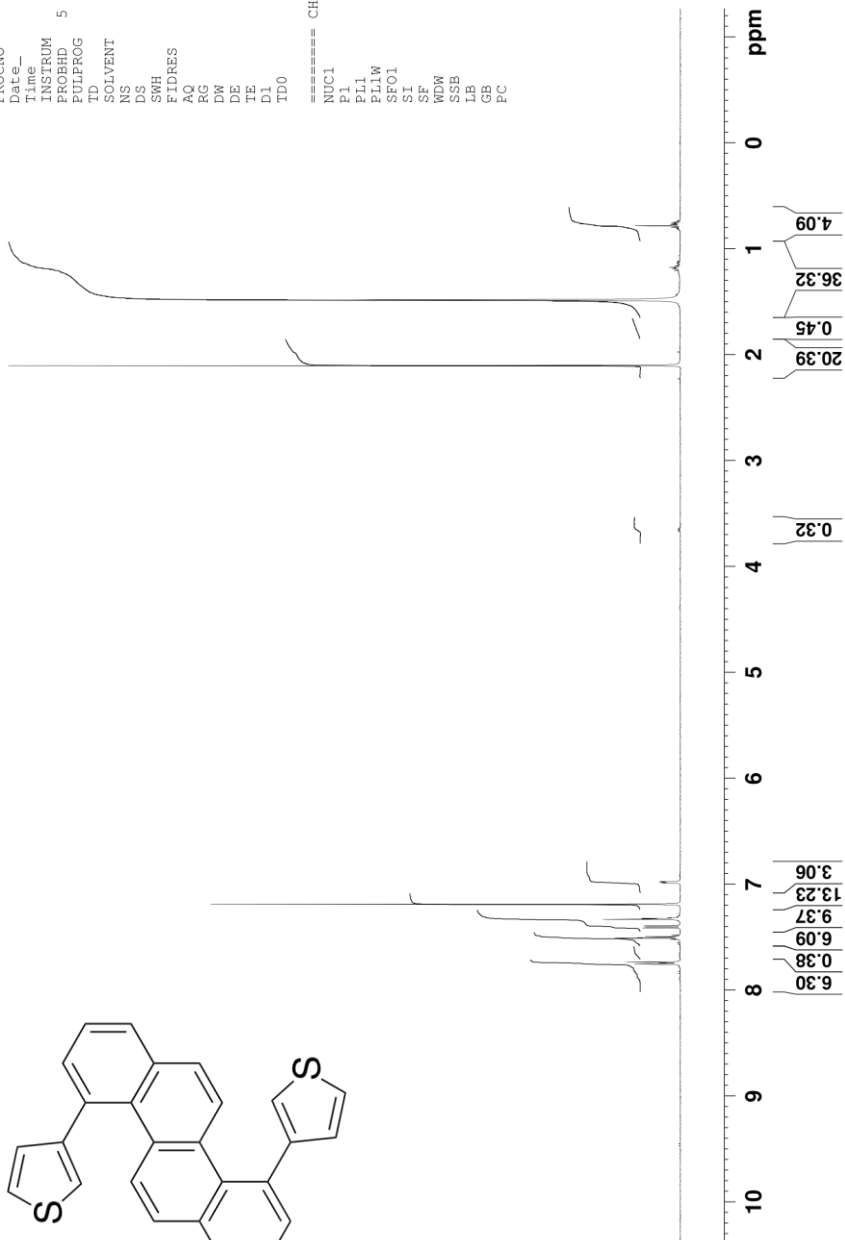
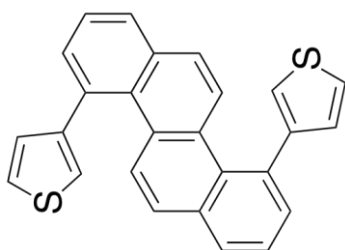


5.5 - 4,10-Bis(3-thienyl)chrysene



NAME 2011-02-23-paq-14
 EXPNO 10
 PROCNO 1
 Date_ 20110223
 Time_ 10.29
 INSTRUM spect
 PROBHD 5 mm TXI 1H/D-
 PULPROG zg30b
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 0
 SWH 10330.578 Hz
 FIDRES 0.157632 Hz
 AQ 3.1719923 sec
 RG 724
 DW 48.400 usec
 DE 13.38 usec
 TE 294.8 K
 D1 1.00000000 sec
 TD0 1
 ===== CHANNEL f1 =====
 NUC1 1H
 P1 8.20 usec
 PL1 3.25 dB
 PL1W 12.12272263 W
 SFO1 500.1330885 MHz
 SI 32768
 SF 500.1300475 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

ML054 20h
 mPROTON CDCI3 /opt/bruk500data/2011/Feb paq 14



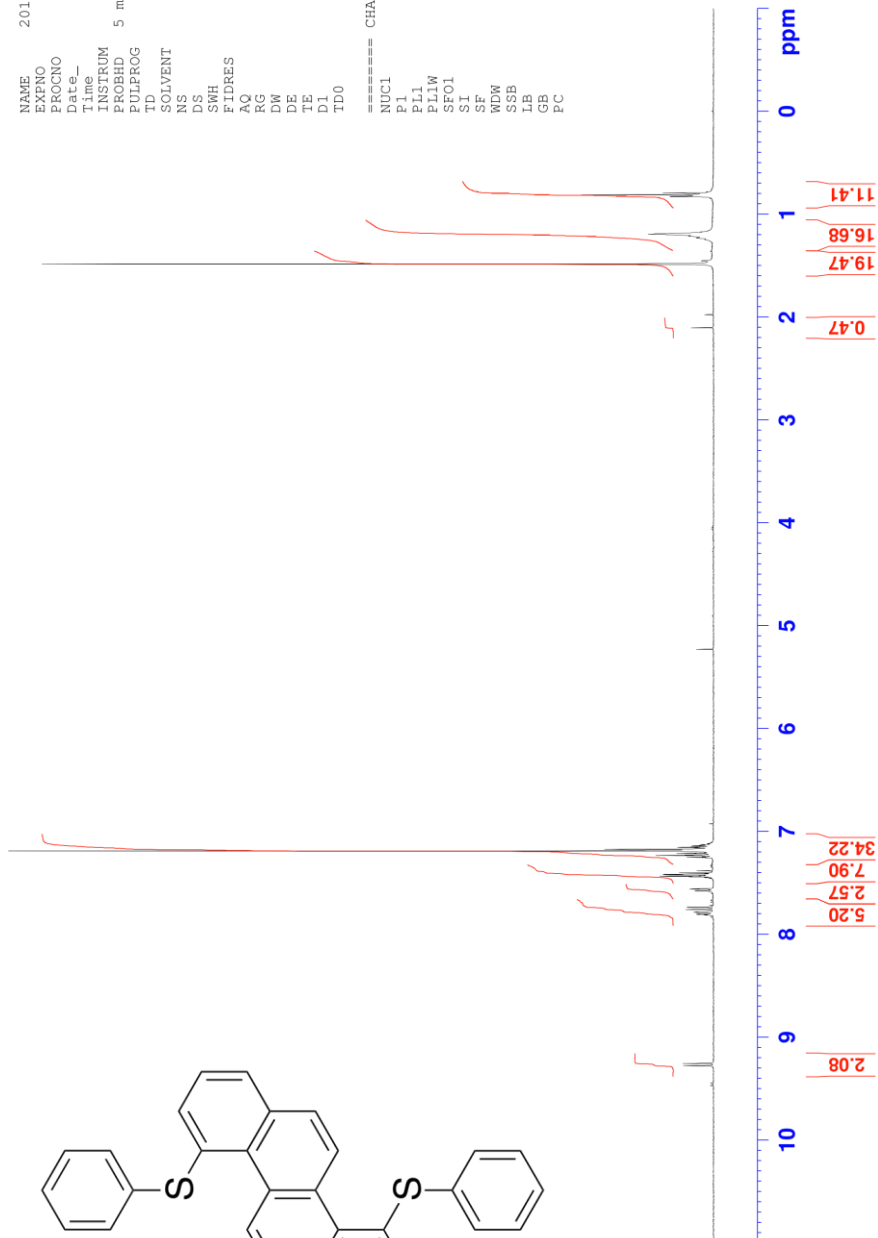
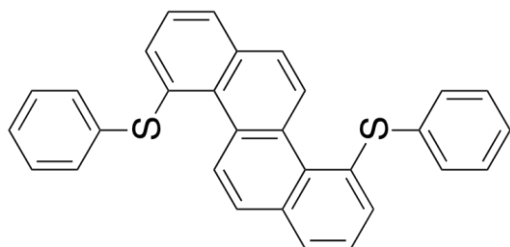
5.6 - 4,10-Bis(phenylthio)chrysenes

PAQ-ML170 col
 mPROTON CDCI3 {e:\bruk400data\2012\Apr} paq 38



```

NAME 2012-04-30-paq-38
EXPNO 10
PROCNO 1
Date_ 20120430
Time 17.03
INSTRUM AV400
PROBHD 5 mm FAPBO BB-
PULPROG zg30b
TD 65536
SOLVENT CDCI3
NS 16
DS 0
SWH 8264.463 Hz
FIDRES 0.126106 Hz
AQ 3.9649780 sec
RG 406
DW 60.500 usec
DE 9.40 usec
TE 293.8 K
D1 1.00000000 sec
TD0 1
===== CHANNEL f1 =====
NUC1 1H
P1 10.00 usec
PL1 0.00 dB
PL12 17.83863891 W
SFOL 400.1320710 MHz
SI 32768
SF 400.1300372 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
  
```

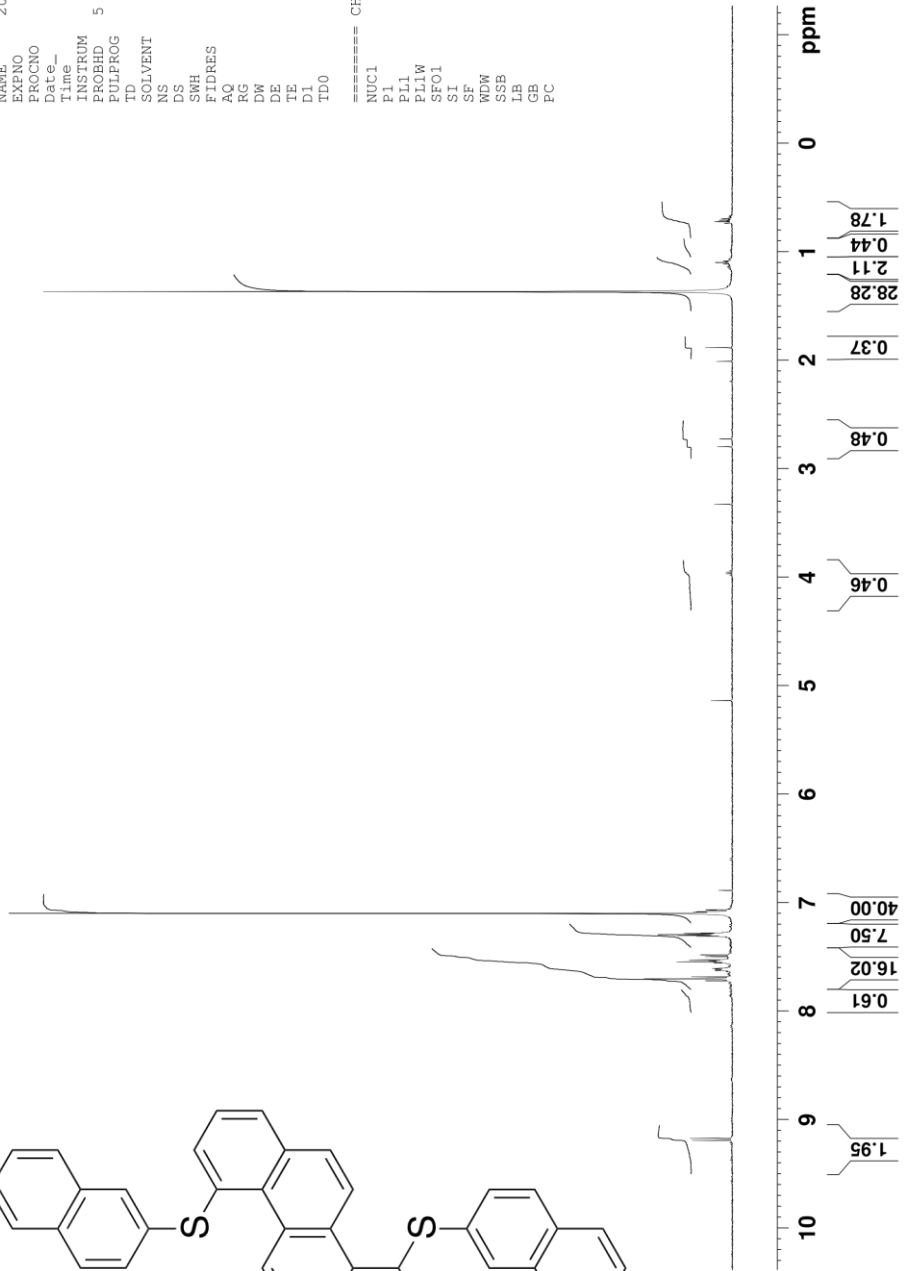
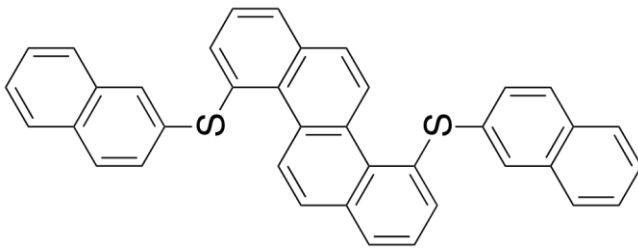


5.7 - 4,10-Bis(2-naphthylthio)chryse



2012-05-04-paq-10
 NAME
 EXENO 10
 PROCNO 1
 Date_ 20120504
 Time 10.40
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 FULLPROG zg30b
 ID 65536
 SOLVENT CDCl3
 NS 16
 DS 0
 SWH 10330.578 Hz
 FIDRES 0.157632 Hz
 AQ 3.1719923 sec
 RG 406
 DW 48.400 usec
 DE 13.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 TD0 1
 ===== CHANNEL f1 =====
 NUC1 LH
 P1 10.00 usec
 PL1 -0.10 dB
 PL1W 26.21803665 W
 SF01 500.1330885 MHz
 SI 32768
 SF 500.1330929 MHz
 EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

PAQ-ML173 recryst
 mPROTON CDCl3 /opt/bruk500data/2012/May paq 10



5.8 - 4,10-Bis(phenyloxy)chrysene

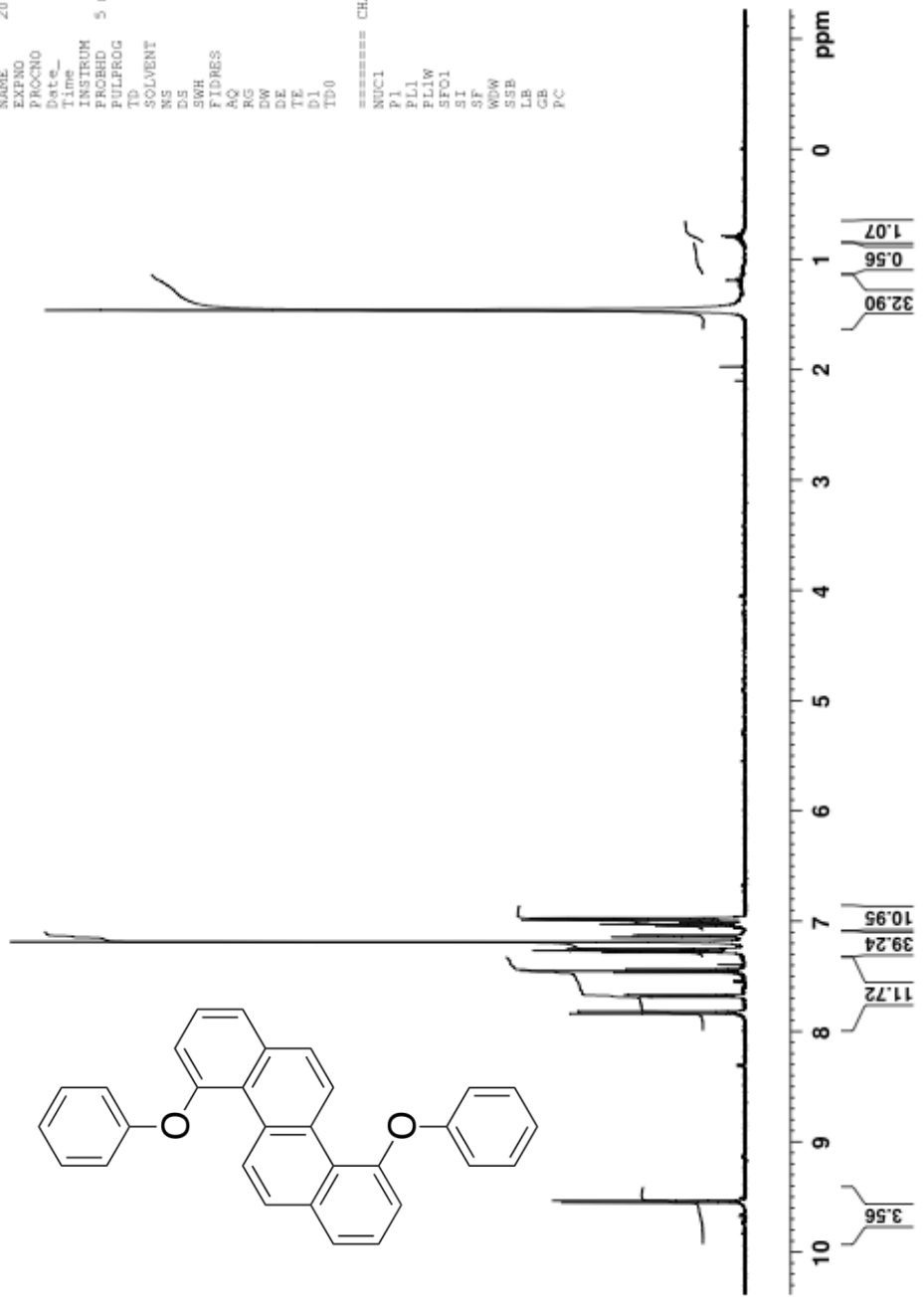


PAQ-ML138 OPh
mPROTON CDC13 /opt/bruk500data/2012/Nov paq 41

```

NAME      2012-11-20-paq-41
EXPNO     10
PROCNO    1
Date_     20121120
Time      16.05
INSTRUM   spect
PROBHD    5 mm F4BBO BB-
PULPROG   zgpg30
TD         65536
SOLVENT   CDC13
NS         16
DS         0
SWH        10330.578 Hz
FIDRES     0.157632 Hz
AQ         3.171923 sec
RG         362
DW         48.400 usec
DE         13.00 usec
TE         298.0 K
D1         1.00000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1      1H
P1         10.00 usec
PL         -0.10 dB
PL1        26.21803665 W
PL12       500.1330885 MHz
SFO1       500.1330885 MHz
SI         32768
SF         500.1300490 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
    
```



5.9 - 4,10-Bis(Oct-1-yn-1-yl)chrysene

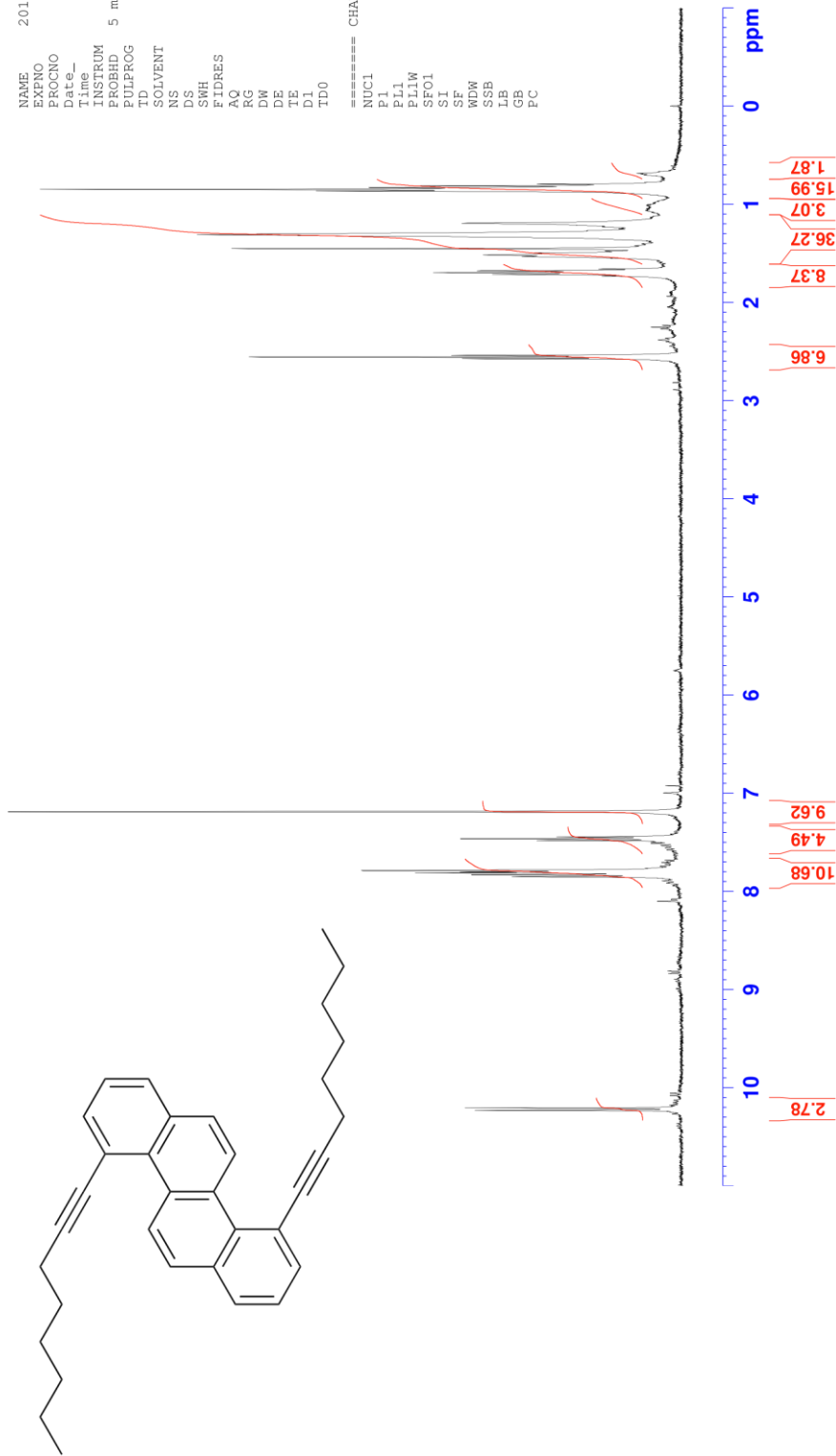
PAQ-ML187 frac 3
 mPROTON CDCI3 {e:\bruk400data\2012\Jun} paq 17



```

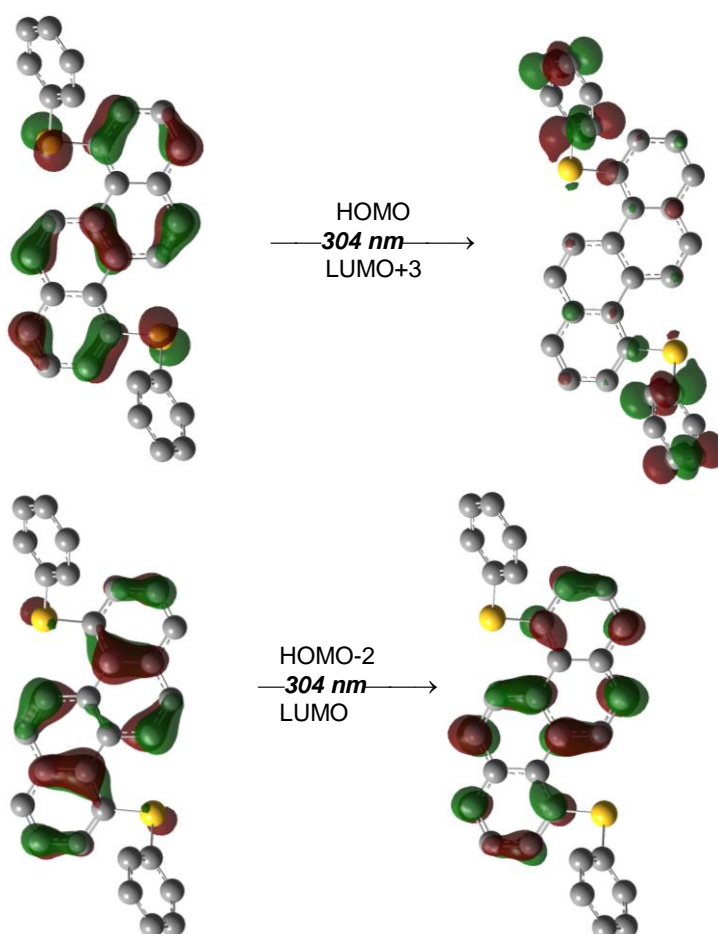
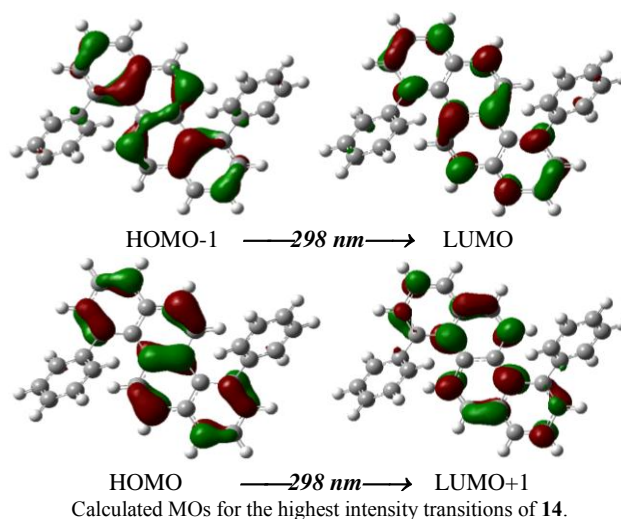
NAME      2012-06-18-paq-17
EXPNO    10
PROCNO   1
Date_    20120618
Time     15.07
INSTRUM  AV400
PROBHD   5 mm FAPBO BB-
PULPROG  zg30b
TD       65536
SOLVENT  CDCI3
NS       16
DS       0
SWH      8264.463 Hz
FIDRES   0.126106 Hz
AQ       3.9649780 sec
RG       322
DW       60.500 usec
DE       9.40 usec
TE       294.2 K
D1       1.00000000 sec
TD0      1

===== CHANNEL f1 =====
NUC1     1H
P1       10.00 usec
PL1      0.00 dB
PL12     17.83863891 W
SFO1     400.1320710 MHz
SI       32768
SF       400.1300385 MHz
WDW      EM
SSB      0
LB       0.30 Hz
GB       0
PC       1.00
  
```



6 - MO Calculations

Each substituted chrysene was fully optimised at the B3LYP/6-31G(d,p) level using the Gaussian09 suite of programs. Using these geometries, the UV/Vis absorption spectra were obtained using time-dependent DFT with the B3LYP functional and the larger 6-311G(d,p) basis set. The MOs of 4,10-diphenylchrysene **14** that correspond to the most intense transition in the calculated electronic spectrum. It can be seen that there is very little contribution from the peripheral phenyl groups in these MOs. This can be attributed to the orthogonal conformation the molecule prefers; it suggests that there is no significant delocalisation from the core to the periphery. In contrast, the MOs associated with the most intense transitions of 4,10-bis(phenylthio)chrysene **18** indicate that there is significant contribution to these MOs from the S-substituent. The appearance of an additional absorption in the UV/vis trace of **18** - a "shoulder" at 310 nm may be indicative of this mode of transition.



Calculated MOs for the highest intensity transitions of **18**.