Supporting Information

Alkyloxy modified pyrene fluorophores with tuneable photophysical and crystalline properties

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Synthetic procedures

General procedure for the synthesis of bromo compounds 2a-d

Compounds **2a-d** were synthesized using a modified literature procedure.[1]

5-Bromophenyl-1,2,3-triol **1a** (612 mg, 3 mmol) was dissolved in 20 mL dry DMF. 8 Eq. of the corresponding 1-bromoalkane and potassium carbonate (6.22 g, 45 mmol, 15 eq.) were added and the mixture was stirred at 60 °C for 24 h. After addition of water (100 mL) the resulting mixture was extracted with diethyl ether (3x 100 mL). The organic phase was dried over $MgSO_4$ and the resulting crude mixture was purified by column chromatography obtaining the products as light-yellow oils.

5-bromo-1,2,3-(tributoxy)benzene (**2a**): SiO_2, petroleum ether : dichoromethane 6 : 1 as a yellow oil, yield: 79 % (1.40 g, 2.36 mmol).
^{1}HNMR (400 MHz, $CHCl_3$): 6.80 (s, 2H, H-aromat), 3.93 (m, 6H, H-alkyl-OCH_2), 1.79-1.68 (m, 6H, H-alkyl-CH_2), 1.53-1.46 (m, 6H, H-alkyl-CH_2), 0.97 (m, 9H, H-alkyl-CH_3) ppm.

5-bromo-1,2,3-(trihexyloxy)benzene (**2b**): SiO_2, petroleum ether : dichoromethane 6 : 1 as a yellow oil, yield: 20 % (269 mg, 0.59 mmol).
^{1}HNMR (400 MHz, $CHCl_3$): 6.67 (s, 2H, H-aromat), 3.92 (m, 6H, H-alkyl-OCH_2), 1.82-1.68 (m, 6H, H-alkyl-CH_2), 1.48-1.43 (m, 6H, H-alkyl-CH_2), 1.34-1.30 (m, 12H, H-alkyl-CH_2), 0.97 (m, 9H, H-alkyl-CH_3) ppm.

5-bromo-1,2,3-tris(octyloxy)benzene (**2c**): SiO_2, petroleum ether : dichoromethane 6 : 1 as a yellow oil, yield: 93 % (1.50 g, 2.78 mmol).
^{1}HNMR (400 MHz, $CHCl_3$): 6.67 (s, 2H, H-aromat), 3.92 (m, 6H, H-alkyl-OCH_2), 1.89-1.76 (m, 6H, H-alkyl-CH_2), 1.43 (m, 6H, H-alkyl-CH_2), 1.28 (m, 24H, H-alkyl-CH_2), 0.88 (m, 9H, H-alkyl-CH_3) ppm.

5-bromo-1,2,3-tris(decyloxy)benzene (**2d**): SiO_2, petroleum ether : dichoromethane 10 : 1 as a yellow oil, yield: 53 % (992 mg, 1.59 mmol).
^{1}HNMR (400 MHz, $CHCl_3$): 6.68 (s, 2H, H-aromat), 3.91 (m, 6H, H-alkyl-OCH_2), 1.86-1.78 (m, 6H, H-alkyl-CH_2), 1.51-1.39 (m, 6H, H-alkyl-CH_2), 1.37-1.20 (m, 36H, H-alkyl-CH_2), 0.88 (m, 9H, H-alkyl-CH_3) ppm.

General procedure for the synthesis of trimethylsilyl acetylenes 3a-d

Compounds **3a-d** were synthesized using a modified literature procedure.[2]

The corresponding 5-bromo-1,2,3-tris(alkyloxy)benzene derivative (1 eq.) was dissolved in a mixture of dry toluene and triethylamine (1/1, v/v). Copper(I) iodide (40 Mol%), $Pd(PPh_3)_2Cl_2$ (10 Mol%), triphenylphosphine (0.8 eq.) and trimethylsilyl acetylene (TMSA, 4.6 eq.) were added and the resulting mixture was stirred at 80 °C for 20 h. After addition of water (100 mL) the resulting mixture was extracted with dichloromethane (3x 100 mL). The organic phase was dried over $MgSO_4$ and the resulting crude mixture was purified by column chromatography obtaining the products as light-yellow oils.

5-trimethylsilylethynyl-1,2,3-(tributoxy)benzene (**3a**): SiO_2, petroleum ether : dichloromethane 5 : 1 as a yellow oil, yield: 90 % (827 mg, 2.12 mmol).
^{1}HNMR (400 MHz, $CHCl_3$): 6.67 (s, 2H, H-aromat), 3.95 (m, 6H, H-alkyl-OCH_2), 1.79-1.68 (m, 6H, H-alkyl-CH_2), 1.51-1.43 (m, 6H, H-alkyl-CH_2), 0.97 (m, 9H, H-alkyl-CH_3), 0.24 (s, 9H, H-TMS) ppm.

5-trimethylsilylethynyl-1,2,3-(trihexyloxy)benzene (**3b**): SiO_2, petroleum ether : dichloromethane 6 : 1 as a yellow oil, yield: 95 % (265 mg, 0.56 mmol).
^{1}HNMR (400 MHz, $CHCl_3$): 6.66 (s, 2H, H-aromat), 3.95 (m, 6H, H-alkyl-OCH_2), 1.80-1.70 (m, 6H, H-alkyl-CH_2), 1.48-1.44 (m, 6H, H-alkyl-CH_2), 1.34-1.31 (m, 12H, H-alkyl-CH_2), 0.90 (m, 9H, H-alkyl-CH_3), 0.24 (s, 9H, H-TMS) ppm.

5-trimethylsilylethynyl-1,2,3-(tris(octyloxy))benzene (**3c**): SiO_2, petroleum ether : dichloromethane 5 : 1 as a yellow oil, yield: 96 % (1.50 g, 2.68 mmol).
^{1}HNMR (400 MHz, $CHCl_3$): 6.66 (s, 2H, H-aromat), 3.94 (m, 6H, H-alkyl-OCH_2), 1.80-1.70 (m, 6H, H-alkyl-CH_2), 1.44 (m, 6H, H-alkyl-CH_2), 1.28 (m, 24H, H-alkyl-CH_2), 0.88 (m, 9H, H-alkyl-CH_3), 0.24 (s, 9H, H-TMS) ppm.

5-trimethylsilylethynyl-1,2,3-(tris(decyloxy))benzene (**3d**): SiO_2, petroleum ether : dichloromethane 6 : 1 as a yellow oil, yield: 56 % (572 mg, 0.89 mmol).
^{1}HNMR (400 MHz, $CHCl_3$): 6.66 (s, 2H, H-aromat), 3.94 (m, 6H, H-alkyl-OCH_2), 1.83-1.67 (m, 6H, H-alkyl-CH_2), 1.49-1.40 (m, 6H, H-alkyl-CH_2), 1.35-1.20 (m, 36H, H-alkyl-CH_2), 0.88 (m, 9H, H-alkyl-CH_3), 0.24 (s, 9H, H-TMS) ppm.

General procedure for the synthesis of acetylenes 4a-d

The corresponding 5-trimethylsilylethynyl-1,2,3-tris(alkyloxy)benzene derivative (1 eq.) was dissolved in a mixture of dry THF and methanol (1/1, v/v). Potassium fluoride dihydrate (5 eq.) was added and the resulting mixture was stirred at rt for 24 h. After evaporation of the solvent the resulting crude mixture was purified by column chromatography obtaining the products as light-yellow oils.

5-ethynyl-1,2,3-(tributoxy)benzene (**4a**): SiO_2, petroleum ether : dichloromethane 5 : 1 as a yellow oil, yield: 82 % (554 mg, 1.74 mmol).
^{1}HNMR (400 MHz, $CHCl_3$): 6.69 (s, 2H, H-aromat), 3.96 (m, 6H, H-alkyl-OCH_2), 2.99 (s, 1H, H-acetylene), 1.80-1.76 (m, 6H, H-alkyl-CH_2), 1.56-1.43 (m, 6H, H-alkyl-CH_2), 0.97 (m, 9H, H-alkyl-CH_3) ppm.

5-ethynyl-1,2,3-(trihexyloxy)benzene (**4b**): SiO_2, petroleum ether : dichloromethane 4 : 1 as a yellow oil, yield: 98 % (195 mg, 0.50 mmol).
^{1}HNMR (400 MHz, $CHCl_3$): 6.69 (s, 2H, H-aromat), 3.96 (m, 6H, H-alkyl-OCH_2), 2.99 (s, 1H, H-acetylene), 1.81-1.73 (m, 6H, H-alkyl-CH_2), 1.48-1.44 (m, 6H, H-alkyl-CH_2), 1.35-1.30 (m, 12H, H-alkyl-CH_2), 0.90 (m, 9H, H-alkyl-CH_3) ppm. ^{1}HNMR spectrum corresponds to this published in the literature.[3]

5-ethynyl-1,2,3-(tris(octyloxy))benzene (**4c**): SiO_2, petroleum ether : dichloromethane 5 : 1 as a yellow oil, yield: 94 % (1.22 g, 2.51 mmol).
^{1}HNMR (400 MHz, $CHCl_3$): 6.69 (s, 2H, H-aromat), 3.94 (m, 6H, H-alkyl-OCH_2), 2.99 (s, 1H, H-acetylene),1.81-1.71 (m, 6H, H-alkyl-CH_2), 1.47-1.41 (m, 6H, H-alkyl-CH_2), 1.32-1.28 (m, 24H, H-alkyl-CH_2), 0.88 (m, 9H, H-alkyl-CH_3) ppm. ^{1}HNMR spectrum corresponds to this published in the literature.[4]

5-ethynyl-1,2,3-(tris(decyloxy))benzene (**4d**): SiO_2, petroleum ether : dichloromethane 4 : 1 as a yellow oil, yield: 47 % (235 mg, 0.42 mmol).
^{1}HNMR (400 MHz, $CHCl_3$): 6.66 (s, 2H, H-aromat), 3.95 (m, 6H, H-alkyl-OCH_2), 2.99 (s, 1H, H-acetylene),1.83-1.68 (m, 6H, H-alkyl-CH_2), 1.50-1.40 (m, 6H, H-alkyl-CH_2), 1.38-1.20 (m, 36H, H-alkyl-CH_2), 0.88 (m, 9H, H-alkyl-CH_3). ^{1}HNMR spectrum corresponds to this published in the literature.[5]

General procedure for the synthesis of bromo compounds 2e-h

Compounds **2e-h** were synthesized using a modified literature procedure.[2]

4-Bromophenol **1b** (2.60 g, 15 mmol) was dissolved in 40 mL dry DMSO. The corresponding 1-bromoalkane (14.25 mmol) and potassium hydroxide (6.22 g, 75 mmol, 5 eq.) were added and the mixture was stirred at 50 °C for 24 h. After addition of water (100 mL) the resulting mixture was extracted with diethyl ether (3x 100 mL). The organic phase was dried over $MgSO_4$ and the resulting crude mixture was purified by column chromatography obtaining the products as light-yellow oils.

1-bromo-4-butoxybenzene (**2e**): SiO_2, petroleum ether : dichloromethane 9 : 1 as a yellow oil, yield: 91 % (3.12 g, 13.66 mmol).
^{1}HNMR (400 MHz, $CHCl_3$): 7.36 (d, *J*=9.0 Hz, 2H, H-aromat), 6.77 (d, *J*=9.0 Hz, 2H, H-aromat), 3.92 (t, *J*=6.5 Hz, 2H, H-alkyl-OCH_2), 1.79-1.72 (m, 2H, H-alkyl-CH_2), 1.53-1.43 (m, 2H, H-alkyl-CH_2), 0.97 (t, *J*=7.4 Hz, 3H, H-alkyl-CH_3) ppm.

1-bromo-4-(hexyloxy)benzene (**2f**): SiO_2, petroleum ether : dichloromethane 6 : 1 as a yellow oil, yield: 90 % (3.44 g, 13.45 mmol).
^{1}HNMR (400 MHz, $CHCl_3$): 7.36 (d, *J*=9.0 Hz, 2H, H-aromat), 6.77 (d, *J*=9.0 Hz, 2H, H-aromat), 3.91 (t, *J*=6.5 Hz, 2H, H-alkyl-OCH_2), 1.80-1.73 (m, 2H, H-alkyl-CH_2), 1.46-1.43 (m, 2H, H-alkyl-CH_2), 1.35-1.31 (m, 4H, H-alkyl-CH_2), 0.90 (t, *J*=7.0 Hz, 3H, H-alkyl-CH_3) ppm.

1-bromo-4-(octyloxy)benzene (**2g**): SiO_2, petroleum ether : dichloromethane 15 : 1 as a yellow oil, yield: 84 % (3.60 g, 12.60 mmol).
^{1}HNMR (400 MHz, $CHCl_3$): 7.35 (d, *J*=9.0 Hz, 2H, H-aromat), 6.77 (d, *J*=9.0 Hz, 2H, H-aromat), 3.92 (t, *J*=6.5 Hz, 2H, H-alkyl-OCH_2), 1.79-1.71 (m, 2H, H-alkyl-CH_2), 1.46-1.41 (m, 2H, H-alkyl-CH_2), 1.37-1.29 (m, 8H, H-alkyl-CH_2), 0.90 (t, *J*=7.0 Hz, 3H, H-alkyl-CH_3) ppm.

1-bromo-4-(decyloxy)benzene (**2d**): SiO_2, petroleum ether : dichloromethane 30 : 1 as a yellow oil, yield: 91 % (4.28 g, 13.72 mmol).
^{1}HNMR (400 MHz, $CHCl_3$): 7.35 (d, *J*=9.0 Hz, 2H, H-aromat), 6.77 (d, *J*=9.0 Hz, 2H, H-aromat), 3.91 (t, *J*=6.6 Hz, 2H, H-alkyl-OCH_2), 1.78-1.74 (m, 2H, H-alkyl-CH_2), 1.45-1.42 (m, 2H, H-alkyl-CH_2), 1.30-1.27 (m, 12H, H-alkyl-CH_2), 0.88 (t, *J*=6.8 Hz, 3H, H-alkyl-CH_3) ppm.

General procedure for the synthesis of trimethylsilyl acetylenes 3e-h

Compounds **3e-h** were synthesized using a modified literature procedure.[2]

The corresponding 1-bromo-4-(alkyloxy)benzene derivative (1 eq.) was dissolved in a mixture of dry toluene and triethylamine (1/1, v/v). Copper(I) iodide (40 Mol%), $Pd(PPh_3)_2Cl_2$ (10 Mol%), triphenylphosphine (0.8 eq.) and trimethylsilyl acetylene (TMSA, 2 eq.) were added and the resulting mixture was stirred at 80 °C for 20 h. After addition of water (100 mL) the resulting mixture was extracted with dichloromethane (3x 100 mL). The organic phase was dried over $MgSO_4$ and the resulting crude mixture was purified by column chromatography obtaining the products as light-yellow oils.

1-trimethylsilylethynyl-4-butoxybenzene (**3e**): SiO_2, petroleum ether : dichloromethane 20 : 1 as a yellow oil, yield: 95 % (1.16 g, 4.73 mmol).
^{1}HNMR (400 MHz, $CHCl_3$): 7.35 (d, *J*=9.0 Hz, 2H, H-aromat), 6.77 (d, *J*=9.0 Hz, 2H, H-aromat), 3.91 (t, *J*=6.6 Hz, 2H, H-alkyl-OCH_2), 1.78-1.74 (m, 2H, H-alkyl-CH_2), 1.44-1.42 (m, 2H, H-alkyl-CH_2), 0.88 (t, *J*=7.4 Hz, 3H, H-alkyl-CH_3), 0.18 (s, 9H, H-TMS) ppm.

1-trimethylsilylethynyl-4-(hexyloxy)benzene (**3f**): SiO_2, petroleum ether : dichloromethane 6 : 1 as a yellow oil, yield: 92 % (1.26 g, 4.61 mmol).
^{1}HNMR (400 MHz, $CHCl_3$): 7.39 (d, *J*=8.9 Hz, 2H, H-aromat), 6.77 (d, *J*=8.9 Hz, 2H, H-aromat), 3.94 (t, *J*=6.6 Hz, 2H, H-alkyl-OCH_2), 1.79-1.75 (m, 2H, H-alkyl-CH_2), 1.46-1.43 (m, 2H, H-alkyl-CH_2), 1.35-1.32 (m, 4H, H-alkyl-CH_2), 0.90 (t, *J*=7.0 Hz, 3H, H-alkyl-CH_3), 0.23 (s, 9H, H-TMS) ppm.

1-trimethylsilylethynyl-4-(octyloxy)benzene (**3g**): SiO_2, petroleum ether : dichloromethane 20 : 1 as a yellow oil, yield: 86 % (1.28 g, 4.23 mmol).
^{1}HNMR (400 MHz, $CHCl_3$): 7.38 (d, *J*=9.0 Hz, 2H, H-aromat), 6.80 (d, *J*=9.0 Hz, 2H, H-aromat), 3.94 (t, *J*=6.6 Hz, 2H, H-alkyl-OCH_2), 1.78-1.74 (m, 2H, H-alkyl-CH_2), 1.46-1.42 (m, 2H, H-alkyl-CH_2), 1.32-1.24 (m, 8H, H-alkyl-CH_2), 0.88 (t, *J*=6.8 Hz, 3H, H-alkyl-CH_3), 0.23 (s, 9H, H-TMS) ppm.

1-trimethylsilylethynyl-4-(decyloxy)benzene (**2d**): SiO_2, petroleum ether : dichloromethane 30 : 1 as a yellow oil, yield: 55 % (906 mg, 2.74 mmol).
^{1}HNMR (400 MHz, $CHCl_3$): 7.35 (d, *J*=9.0 Hz, 2H, H-aromat), 6.77 (d, *J*=9.0 Hz, 2H, H-aromat), 3.91 (t, *J*=6.6 Hz, 2H, H-alkyl-OCH_2), 1.78-1.74 (m, 2H, H-alkyl-CH_2), 1.45-1.42 (m, 2H, H-alkyl-CH_2), 1.30-1.20 (m, 12H, H-alkyl-CH_2), 0.88 (t, *J*=6.8 Hz, 3H, H-alkyl-CH_3) 0.19 (s, 9H, H-TMS) ppm.

General procedure for the synthesis of acetylenes 4e-h

The corresponding 1-trimethylsilylethynyl-4-(alkyloxy)benzene derivative (1 eq.) was dissolved in a mixture of dry THF and methanol (1/1, v/v). Potassium fluoride dihydrate (5 eq.) was added and the resulting mixture was stirred at rt for 24 h. After evaporation of the solvent the resulting crude mixture was purified by column chromatography obtaining the products as light-yellow oils.

1-ethynyl-4-butoxybenzene (**4e**): SiO_2, petroleum ether : dichloromethane 10 : 1 as a yellow oil, yield: 69 % (360 mg, 2.07 mmol).
^{1}HNMR (400 MHz, $CHCl_3$): 7.41 (d, *J*=9.0 Hz, 2H, H-aromat), 6.83 (d, *J*=9.0 Hz, 2H, H-aromat), 3.96 (t, *J*=6.6 Hz, 2H, H-alkyl-OC*H*$_2$), 2.99 (s, 1H, H-acetylene), 1.80-1.73 (m, 2H, H-alkyl-C*H*$_2$), 1.50-1.43 (m, 2H, H-alkyl-C*H*$_2$), 0.97 (t, *J*=7.4 Hz, 3H, H-alkyl-C*H*$_3$) ppm. ^{1}HNMR spectrum corresponds to this published in the literature.[6]

1-ethynyl-4-(hexyloxy)benzene (**4f**): SiO_2, petroleum ether : dichloromethane 4 : 1 as a yellow oil, yield: 37 % (241 mg, 1.19 mmol).
^{1}HNMR (400 MHz, $CHCl_3$): 7.41 (d, *J*=8.9 Hz, 2H, H-aromat), 6.83 (d, *J*=8.9 Hz, 2H, H-aromat), 3.95 (t, *J*=6.6 Hz, 2H, H-alkyl-OC*H*$_2$), 2.99 (s, 1H, H-acetylene), 1.79-1.76 (m, 2H, H-alkyl-C*H*$_2$), 1.46-1.41 (m, 2H, H-alkyl-C*H*$_2$), 1.35-1.30 (m, 4H, H-alkyl-C*H*$_2$), 0.91 (t, *J*=7.0 Hz, 3H, H-alkyl-C*H*$_3$) ppm. ^{1}HNMR spectrum corresponds to this published in the literature.[7]

1-ethynyl-4-(octyloxy)benzene (**4g**): SiO_2, petroleum ether : dichloromethane 20 : 1 as a yellow oil, yield: 75 % (1.67 g, 7.26 mmol).
^{1}HNMR (400 MHz, $CHCl_3$): 7.41 (d, *J*=9.0 Hz, 2H, H-aromat), 6.83 (d, *J*=9.0 Hz, 2H, H-aromat), 3.95 (t, *J*=6.6 Hz, 2H, H-alkyl-OC*H*$_2$), 2.99 (s, 1H, H-acetylene), 1.79-1.75 (m, 2H, H-alkyl-C*H*$_2$), 1.45-1.42 (m, 2H, H-alkyl-C*H*$_2$), 1.34-1.28 (m, 8H, H-alkyl-C*H*$_2$), 0.89 (t, *J*=6.8 Hz, 3H, H-alkyl-C*H*$_3$) ppm. ^{1}HNMR spectrum corresponds to this published in the literature.[8]

1-ethynyl-4-(decyloxy)benzene (**6h**): SiO_2, petroleum ether : dichloromethane 30 : 1 as a yellow oil, yield: 95 % (732 mg, 2.84 mmol).
^{1}HNMR (400 MHz, $CHCl_3$): 7.41 (d, *J*=9.0 Hz, 2H, H-aromat), 6.83 (d, *J*=9.0 Hz, 2H, H-aromat), 3.95 (t, *J*=6.6 Hz, 2H, H-alkyl-OC*H*$_2$), 2.99 (s, 1H, H-acetylene), 1.79-1.75 (m, 2H, H-alkyl-C*H*$_2$), 1.44-1.42 (m, 2H, H-alkyl-C*H*$_2$), 1.30-1.27 (m, 12H, H-alkyl-C*H*$_2$), 0.88 (t, *J*=6.8 Hz, 3H, H-alkyl-C*H*$_3$) ppm. ^{1}HNMR spectrum corresponds to this published in the literature.[2]

General procedure for the synthesis of 4,5,9,10-tetrasubstituted pyrene derivatives 6a-h

2,7-*tert*-Butyl-4,5,9,10-tetrabromopyrene **5** (62 mg, 0.1 mmol) and the corresponding trialkoxy- (**4a-d**) or monoalkoxy phenylacetylenes (**4e-h**) (8 eq.) were dissolved in a mixture of dry DMF and triethylamine (4 mL, 1/1, v/v). Copper(I) iodide (10 Mol%), $Pd(PPh_3)_2Cl_2$ (5 Mol%) and triphenylphosphine (15 Mol%) were added and the resulting mixture was stirred at 100 °C for 48 h. After addition of diethyl ether (100 mL) the resulting mixture was washed with sat. NH_4Cl solution (1x 100 mL) and sat. NaCl solution (1x 100 mL). The organic phase was dried over $MgSO_4$ and the resulting crude mixture was purified by column chromatography obtaining the products as light-yellow oils.

Tri-substituted *n*-butyl derivative (**6a**): SiO_2, petroleum ether : dichloromethane 4 : 1 → 2 : 1 as a yellow solid, yield: 41 % (65 mg, 0.041 mmol).
M.P. (DSC): 181 °C.
^{1}HNMR (400 MHz, $CHCl_3$): 8.87 (s, 4H, H-aromat), 6.98 (s, 8H, H-aromat), 4.05-3.97 (m, 24H, H-alkyl-OC*H*$_2$), 1.85-1.75 (m, 24H, H-alkyl-C*H*$_2$), 1.68 (s, 18H, H-*tert*-butyl) 1.59-1.48 (m, 24H, H-alkyl-C*H*$_2$), 1.01-0.97 (m, 36H, H-alkyl-C*H*$_3$) ppm.
^{13}CNMR (100 MHz, $CHCl_3$): 153.4, 149.8, 139.8, 129.7, 124.1, 122.9, 121.3, 118.1, 110.5, 100.3, 86.8, 73.4, 69.1, 35.8, 32.5, 32.0, 31.6, 19.5, 19.4, 14.1, 14.0 ppm.
HRMS (MALDI): calculated for $C_{104}H_{138}O_{12}$: 1558.0222; found: 1580.1122.

Tri-substituted *n*-hexyl derivative (**6b**): SiO_2, petroleum ether : dichloromethane 4 : 1 → 2 : 1 as a yellow solid, yield: 42 % (79 mg, 0.042 mmol).
M.P. (DSC): 149 °C.
^{1}HNMR (400 MHz, $CHCl_3$): 8.87 (s, 4H, H-aromat), 6.98 (s, 8H, H-aromat), 4.04-3.94 (m, 24H, H-alkyl-OC*H*$_2$), 1.86-1.76 (m, 24H, H-alkyl-C*H*$_2$), 1.68 (s, 18H, H-*tert*-butyl) 1.54-1.46 (m, 24H, H-alkyl-C*H*$_2$), 1.38-1.34 (m, 48H, H-alkyl-C*H*$_2$) 0.95-0.90 (m, 36H, H-alkyl-C*H*$_3$) ppm.
^{13}CNMR (100 MHz, $CHCl_3$): 153.4, 149.8, 139.8, 129.8, 124.2, 122.9, 121.3, 118.1, 110.3, 100.3, 86.8, 73.8, 69.4, 35.8, 32.0, 31.9, 31.8, 30.5, 29.5, 26.0, 25.9, 22.9, 22.8, 14.3, 14.2 ppm.
HRMS (MALDI): calculated for $C_{128}H_{186}O_{12}$: 1916.3978; found: 1916.8178.

Tri-substituted *n*-octyl derivative (**6c**): SiO_2, petroleum ether : dichloromethane 6 : 1 → 3 : 1 as a yellow solid, yield: 35 % (78 mg, 0.035 mmol).
M.P. (DSC): 87 .°C
^{1}HNMR (400 MHz, $CHCl_3$): 8.88 (s, 4H, H-aromat), 6.98 (s, 8H, H-aromat), 4.05-3.97 (m, 24H, H-alkyl-OCH_2), 1.86-1.76 (m, 24H, H-alkyl-CH_2), 1.69 (s, 18H, H-*tert*-butyl) 1.52-1.46 (m, 24H, H-alkyl-CH_2), 1.35-1.27 (m, 96H, H-alkyl-CH_2) 0.91-0.89 (m, 36H, H-alkyl-CH_3) ppm.
^{13}CNMR (100 MHz, $CHCl_3$): 153.4, 149.8, 139.8, 129.8, 124.2, 122.9, 121.3, 118.1, 110.5, 100.3, 86.8, 73.8, 69.4, 35.8, 32.1, 32.0, 31.8, 30.5, 29.7, 29.6, 29.6, 29.5, 26.3, 26.3, 22.9, 22.8, 14.3, 14.3 ppm.
HRMS (MALDI): calculated for $C_{152}H_{234}O_{12}$: 2252.7734; found: 2253.4869.

Tri-substituted *n*-decyl derivative (**6d**): SiO_2, petroleum ether : dichloromethane 8 : 1 → 5 : 1 as a yellow solid, yield: 19 % (49 mg, 0.019 mmol).
M.P. (DSC): 78 °C.
^{1}HNMR (400 MHz, $CHCl_3$): 8.86 (s, 4H, H-aromat), 6.96 (s, 8H, H-aromat), 4.01-3.95 (m, 24H, H-alkyl-OCH_2), 1.83-1.76 (m, 24H, H-alkyl-CH_2), 1.67 (s, 18H, H-*tert*-butyl) 1.54-1.46 (m, 24H, H-alkyl-CH_2), 1.39-1.22 (m, 144H, H-alkyl-CH_2) 0.89-0.86 (m, 36H, H-alkyl-CH_3) ppm.
^{13}CNMR (100 MHz, $CHCl_3$): 153.4, 149.8, 139.8, 129.8, 124.2, 122.9, 121.3, 118.1, 110.5, 100.3, 86.8, 73.8, 69.4, 35.8, 32.1, 32.1, 32.0, 32.0, 30.5, 30.0, 29.9, 29.9, 29.8, 29.8, 29.7, 29.6, 29.6, 29.5, 29.4, 26.4, 26.3, 22.9, 22.9, 14.3, 14.3 ppm.
HRMS (MALDI): calculated for $C_{176}H_{282}O_{12}$: 2589.1490; found: 2590.1026.

Mono-substituted *n*-butyl derivative (**6e**): SiO_2, petroleum ether : dichloromethane 5 : 1 as a yellow solid, yield: 35 % (35 mg, 0.035 mmol).
M.P. (DSC): >330 °C.
^{1}HNMR (400 MHz, $CHCl_3$): 8.88 (s, 4H, H-aromat), 7.71 (d, *J*=8.8 Hz, 4H, H-aromat), 6.98 (d, *J*=8.8 Hz, 4H, H-aromat), 4.05 (t, *J*=6.5 Hz, 8H, H-alkyl-OCH_2), 1.86-1.79 (m, 8H, H-alkyl-CH_2), 1.68 (s, 18H, H-*tert*-butyl) 1.59-1.49 (m, 8H, H-alkyl-CH_2), 1.02 (t, *J*=7.4 Hz, 12H, H-alkyl-CH_3) ppm.
^{13}CNMR (100 MHz, $CHCl_3$): 159.7, 149.7, 133.4, 129.7, 124.0, 122.8, 121.2, 115.8, 115.0, 99.8, 86.9, 68.0, 35.8, 32.1, 31.4, 19.4, 14.0 ppm.
HRMS (MALDI): calculated for $C_{72}H_{74}O_4$: 1002.5587; found: 1002.4735.

Mono-substituted *n*-hexyl derivative (**6f**): SiO_2, petroleum ether : dichloromethane 8 : 1 → 4 : 1 as a yellow solid, yield: 27 % (30 mg, 0.027 mmol).
M.P. (DSC): 218 °C.
^{1}HNMR (400 MHz, $CHCl_3$): 8.88 (s, 4H, H-aromat), 7.71 (d, *J*=8.8 Hz, 4H, H-aromat), 6.98 (d, *J*=8.8 Hz, 4H, H-aromat), 4.03 (t, *J*=6.6 Hz, 8H, H-alkyl-OCH_2), 1.87-1.80 (m, 8H, H-alkyl-CH_2), 1.68 (s, 18H, H-*tert*-butyl) 1.52-1.47 (m, 8H, H-alkyl-CH_2), 1.40-1.35 (m, 16H), 0.94 (t, *J*=7.1 Hz, 12H, H-alkyl-CH_3) ppm.
^{13}CNMR (100 MHz, $CHCl_3$): 159.7, 149.7, 133.4, 129.7, 124.0, 122.8, 121.2, 115.8, 115.0, 99.8, 86.9, 68.3, 35.8, 32.1, 31.8, 29.4, 25.9, 22.8, 14.2 ppm.
HRMS (MALDI): calculated for $C_{80}H_{90}O_4$: 1114.6839; found: 1114.3510.

Mono-substituted *n*-octyl derivative (**6g**): SiO_2, petroleum ether : dichloromethane 5 : 1 as a yellow solid, yield: 33 % (40 mg, 0.033 mmol).
M.P. (DSC): 179 °C.
^{1}HNMR (400 MHz, $CHCl_3$): 8.89 (s, 4H, H-aromat), 7.71 (d, *J*=8.8 Hz, 4H, H-aromat), 6.97 (d, *J*=8.8 Hz, 4H, H-aromat), 4.02 (t, *J*=6.6 Hz, 8H, H-alkyl-OCH_2), 1.84-1.79 (m, 8H, H-alkyl-CH_2), 1.70 (s, 18H, H-*tert*-butyl) 1.51-1.45 (m, 8H, H-alkyl-CH_2), 1.37-1.29 (m, 32H), 0.92 (t, *J*=6.8 Hz, 12H, H-alkyl-CH_3) ppm.
^{13}CNMR (100 MHz, $CHCl_3$): 159.7, 149.6, 133.4, 129.7, 123.9, 122.8, 121.2, 115.8, 114.9, 99.8, 86.9, 68.3, 35.8, 32.1, 32.0, 29.9, 29.5, 29.4, 26.2, 22.8, 14.3 ppm.
HRMS (MALDI): calculated for $C_{88}H_{106}O_4$: 1226.8091; found: 1227.7895.

Mono-substituted *n*-decyl derivative (**6h**): SiO_2, petroleum ether : dichloromethane 5 : 1 as a yellow solid, yield: 21 % (28 mg, 0.021 mmol).
M.P. (DSC): 144 °C.
^{1}HNMR (400 MHz, $CHCl_3$): 8.89 (s, 4H, H-aromat), 7.71 (d, *J*=8.8 Hz, 4H, H-aromat), 6.98 (d, *J*=8.8 Hz, 4H, H-aromat), 4.03 (t, *J*=6.6 Hz, 8H, H-alkyl-OCH_2), 1.87-1.80 (m, 8H, H-alkyl-CH_2), 1.68 (s, 18H, H-*tert*-butyl) 1.52-1.46 (m, 8H, H-alkyl-CH_2), 1.38-1.29 (m, 48H), 0.90 (t, *J*=6.9 Hz, 12H, H-alkyl-CH_3) ppm.
^{13}CNMR (100 MHz, $CHCl_3$): 159.7, 149.7, 133.4, 129.7, 124.0, 122.8, 121.2, 115.8, 115.0, 99.8, 86.9, 68.3, 35.8, 32.1, 32.1, 29.8, 29.7, 29.6, 29.5, 29.4, 26.2, 22.9, 14.3 ppm.
HRMS (MALDI): calculated for $C_{96}H_{122}O_4$: 1339.9377; found: 1340.0189.

DSC diagrams

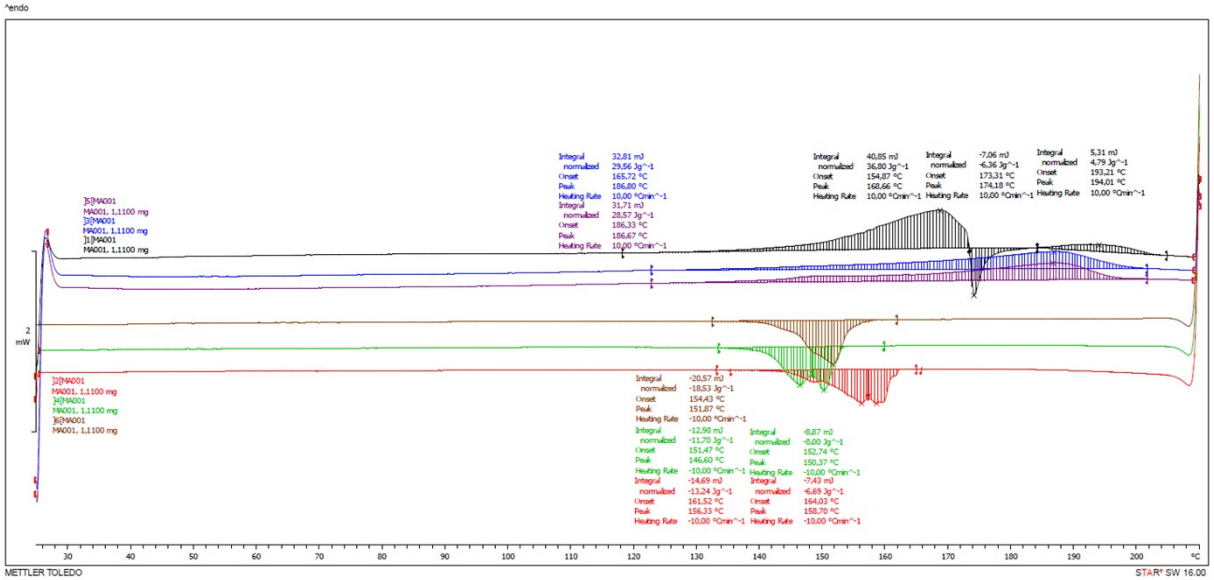

Figure 1. DSC heating and cooling cycles of 4,5,9,10-tetrasubstituted pyrene derivative **6a**. Measurements were performed with a heating/cooling speed of 10 °C/min.

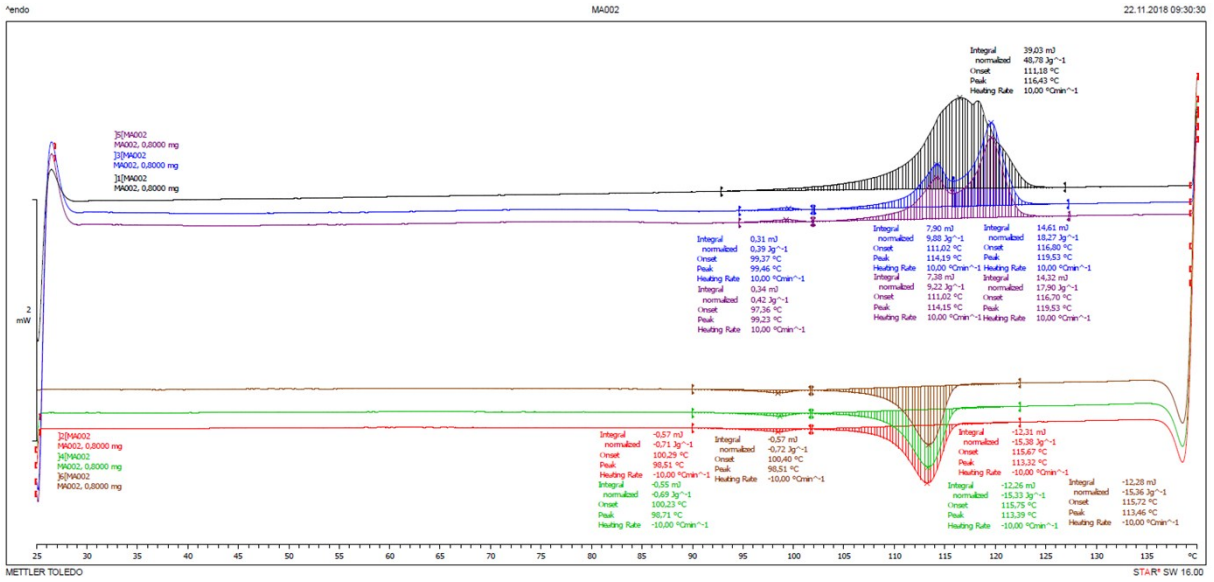

Figure 2. DSC heating and cooling cycles of 4,5,9,10-tetrasubstituted pyrene derivative **6b**. Measurements were performed with a heating/cooling speed of 10 °C/min.

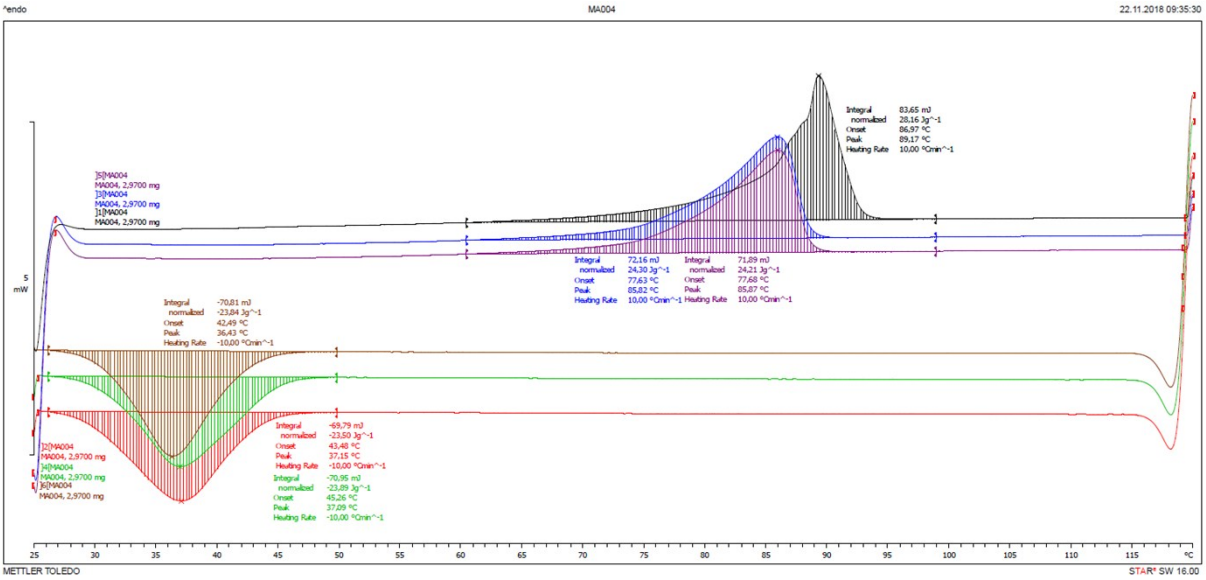

Figure 3. DSC heating and cooling cycles of 4,5,9,10-tetrasubstituted pyrene derivative **6c**. Measurements were performed with a heating/cooling speed of 10 °C/min.

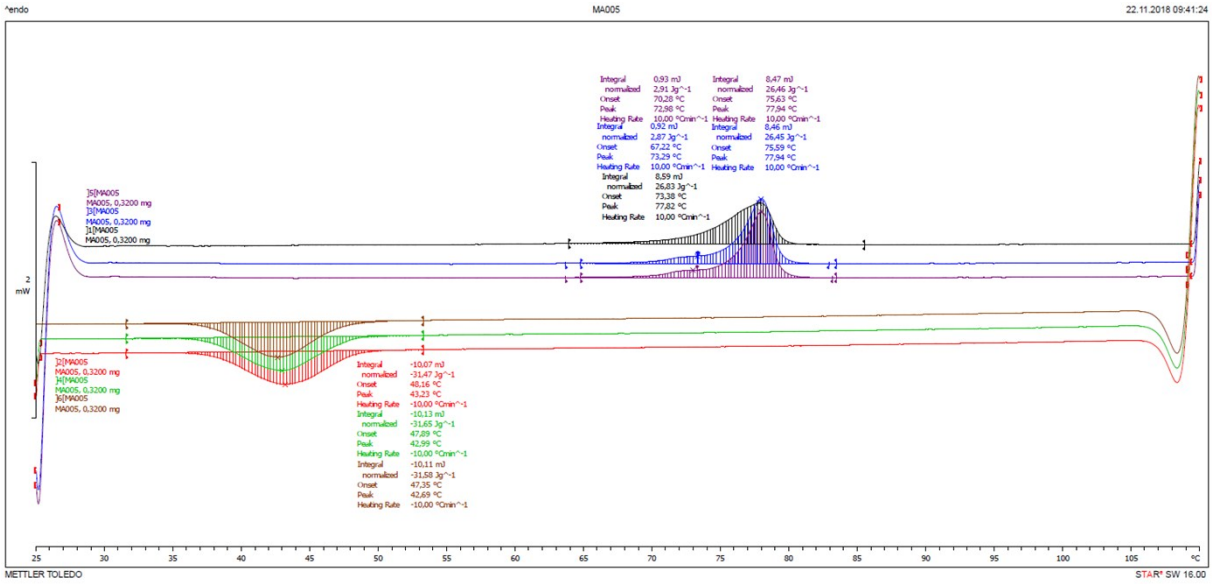

Figure 4. DSC heating and cooling cycles of 4,5,9,10-tetrasubstituted pyrene derivative **6d**. Measurements were performed with a heating/cooling speed of 10 °C/min.

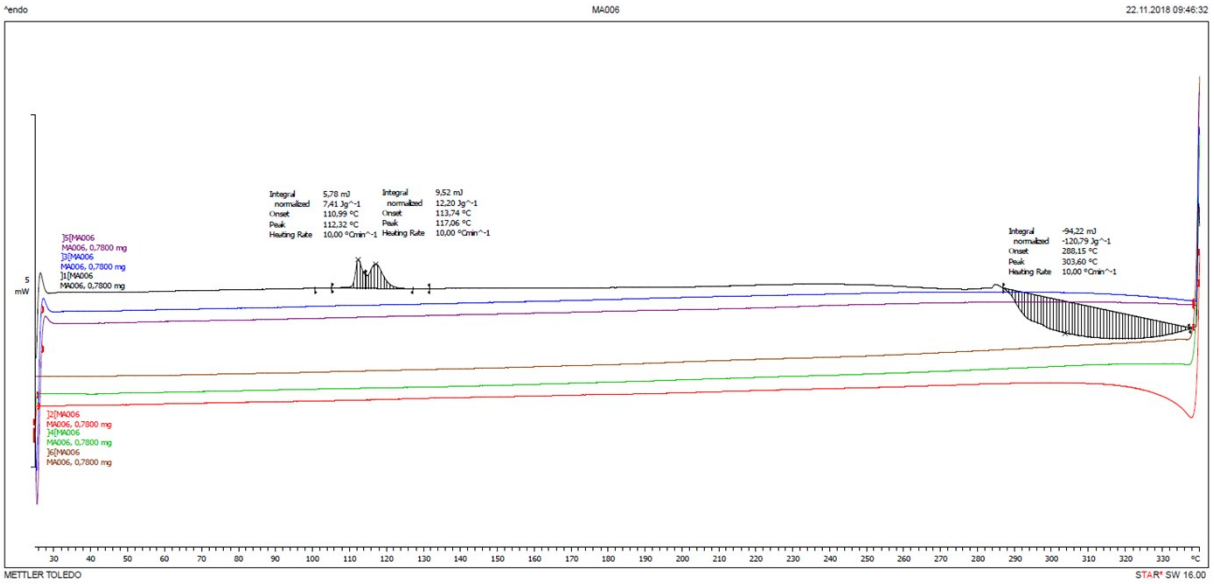

Figure 5. DSC heating and cooling cycles of 4,5,9,10-tetrasubstituted pyrene derivative **6e**. Measurements were performed with a heating/cooling speed of 10 °C/min.

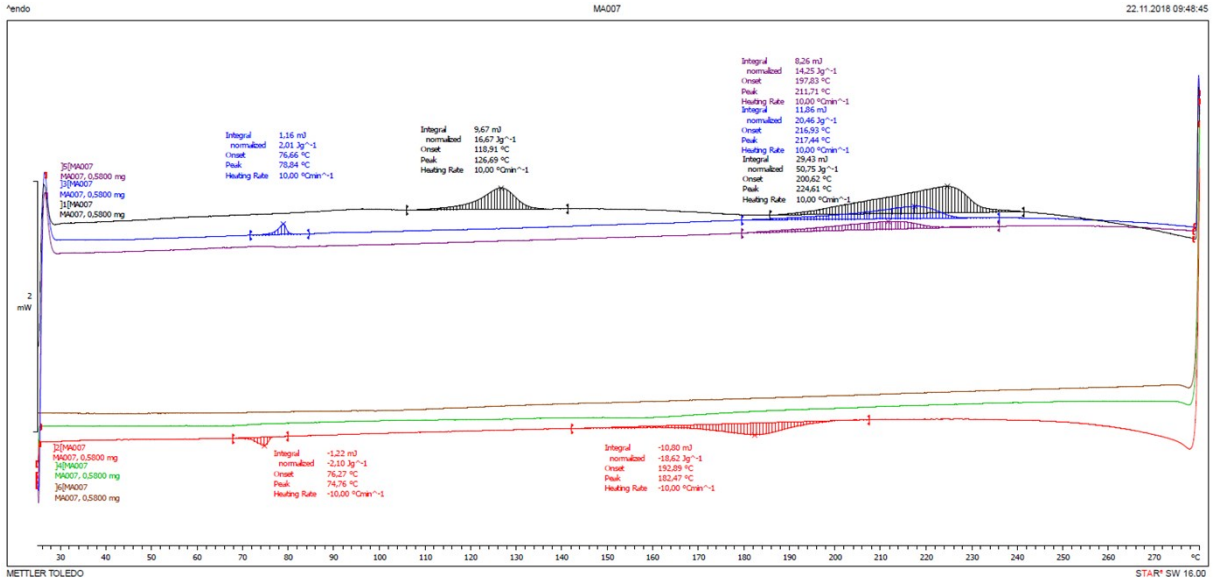

Figure 6. DSC heating and cooling cycles of 4,5,9,10-tetrasubstituted pyrene derivative **6f**. Measurements were performed with a heating/cooling speed of 10 °C/min.

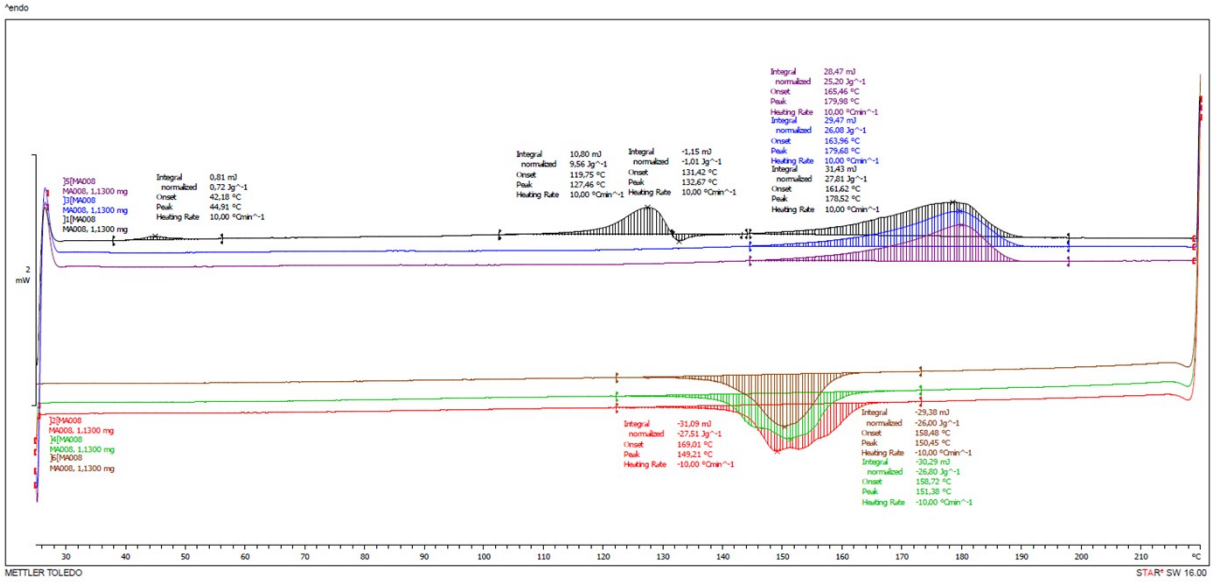

Figure 7. DSC heating and cooling cycles of 4,5,9,10-tetrasubstituted pyrene derivative **6g**. Measurements were performed with a heating/cooling speed of 10 °C/min.

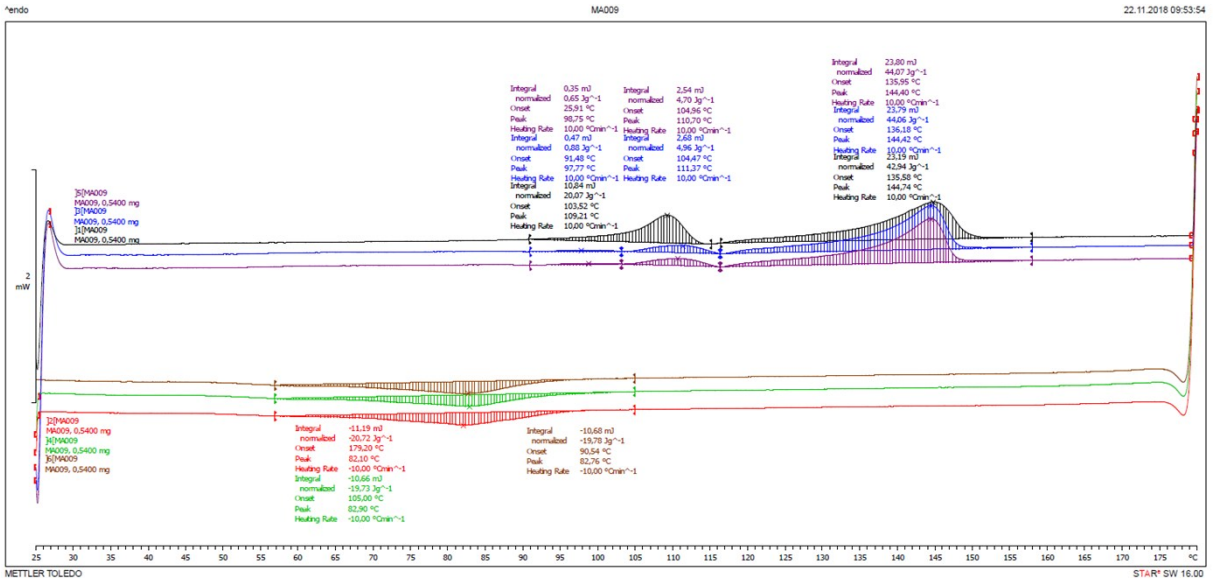

Figure 8. DSC heating and cooling cycles of 4,5,9,10-tetrasubstituted pyrene derivative **6h**. Measurements were performed with a heating/cooling speed of 10 °C/min.

[1]HNMR and [13]CNMR spectra of compounds 6a-h

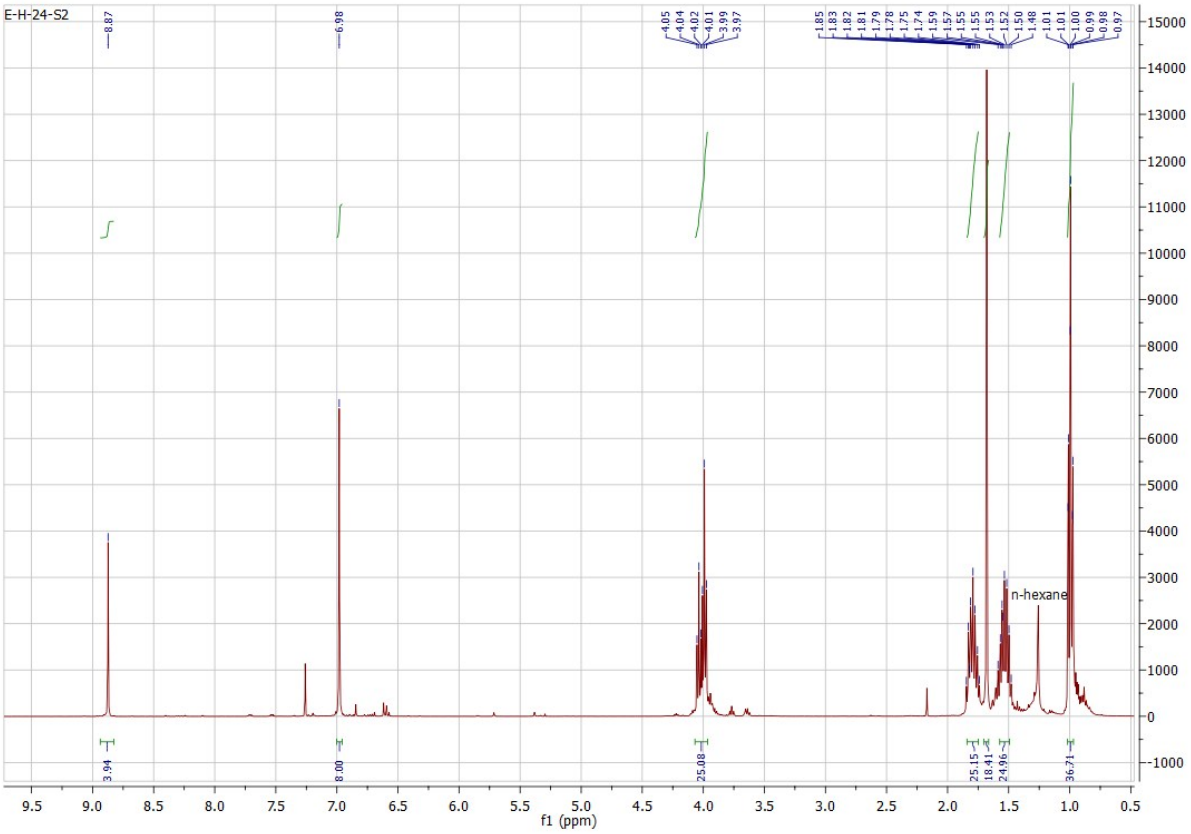

Figure 9. [1]HNMR spectrum of **6a** in $CDCl_3$.

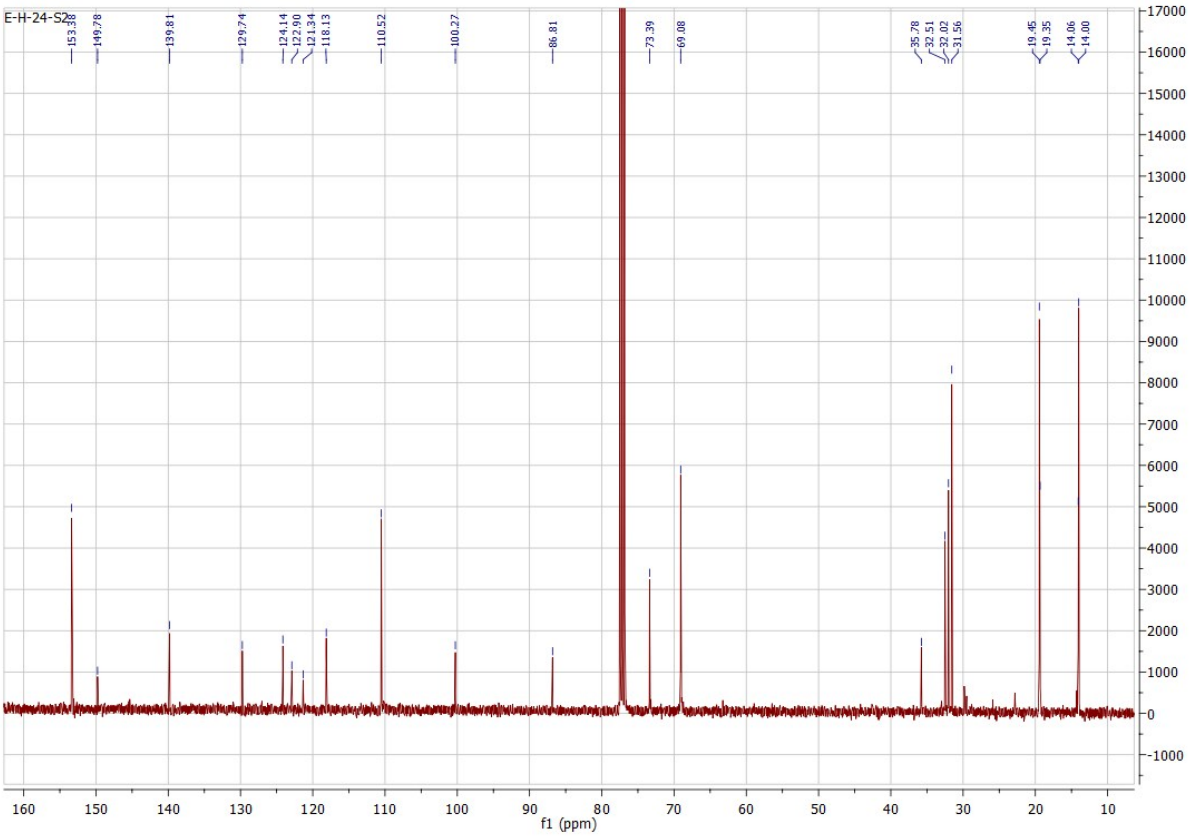

Figure 10. [13]CNMR spectrum of **6a** in $CDCl_3$.

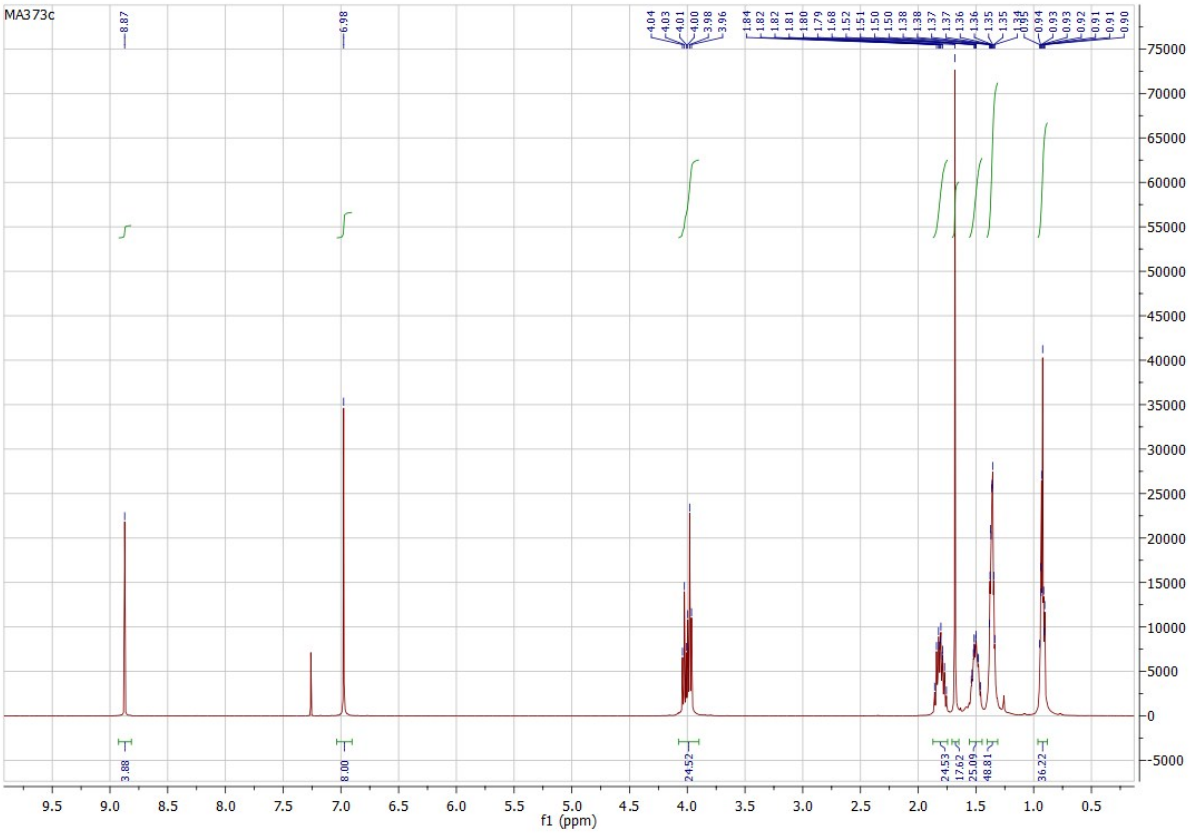

Figure 11. ^{1}HNMR spectrum of **6b** in $CDCl_3$.

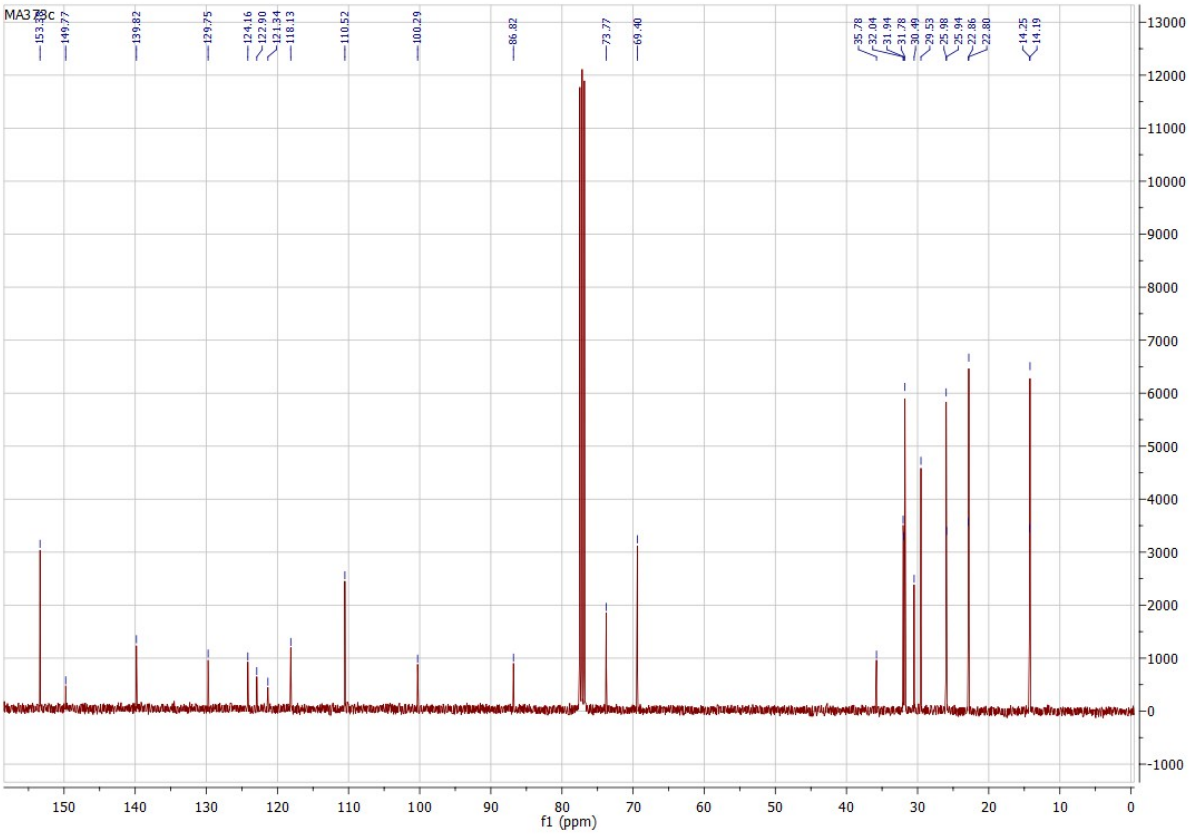

Figure 12. ^{13}CNMR spectrum of **6b** in $CDCl_3$.

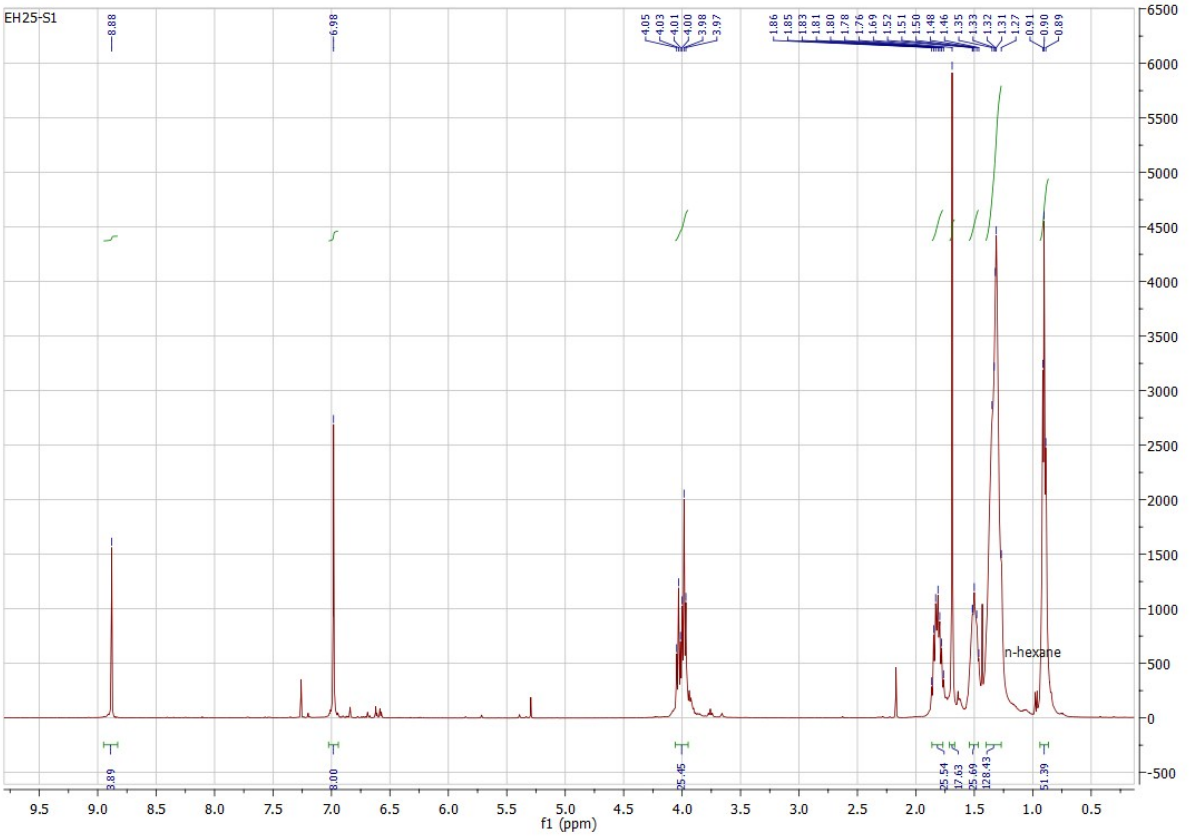

Figure 13. ^{1}HNMR spectrum of **6c** in $CDCl_3$.

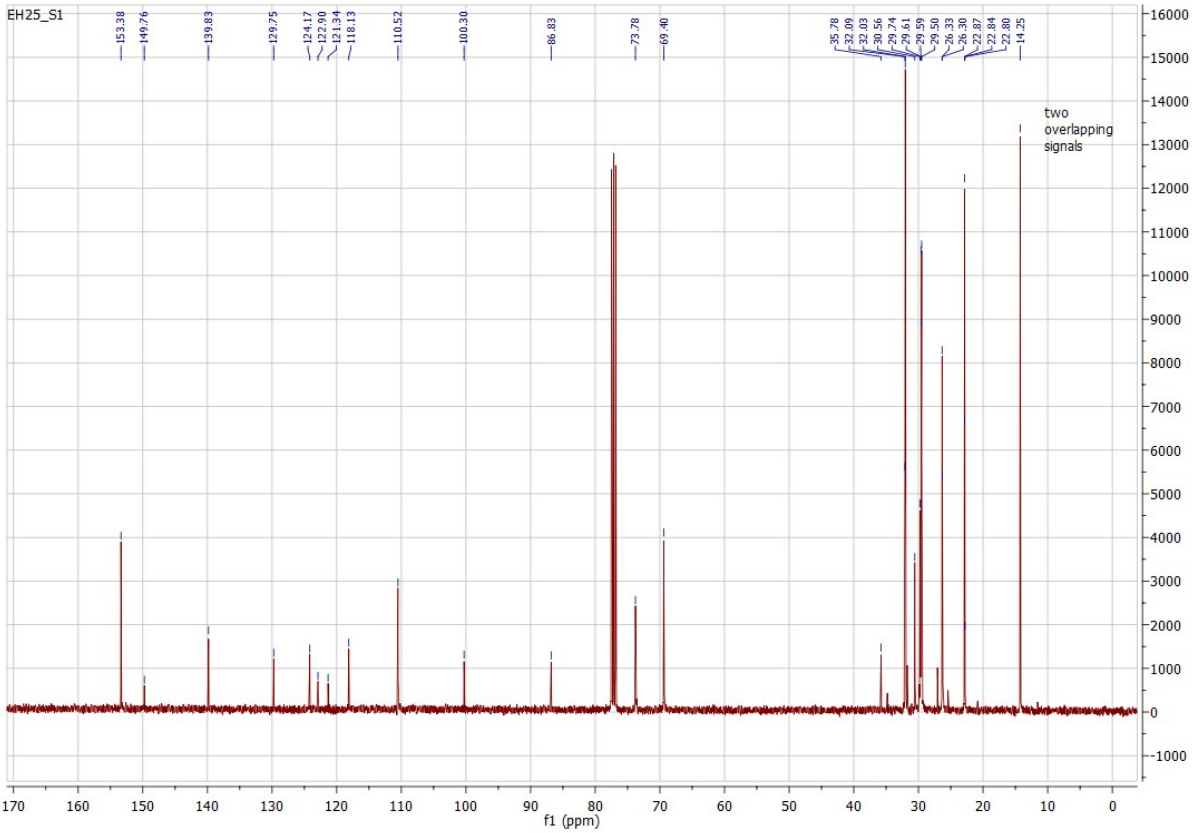

Figure 14. ^{13}CNMR spectrum of **6c** in $CDCl_3$.

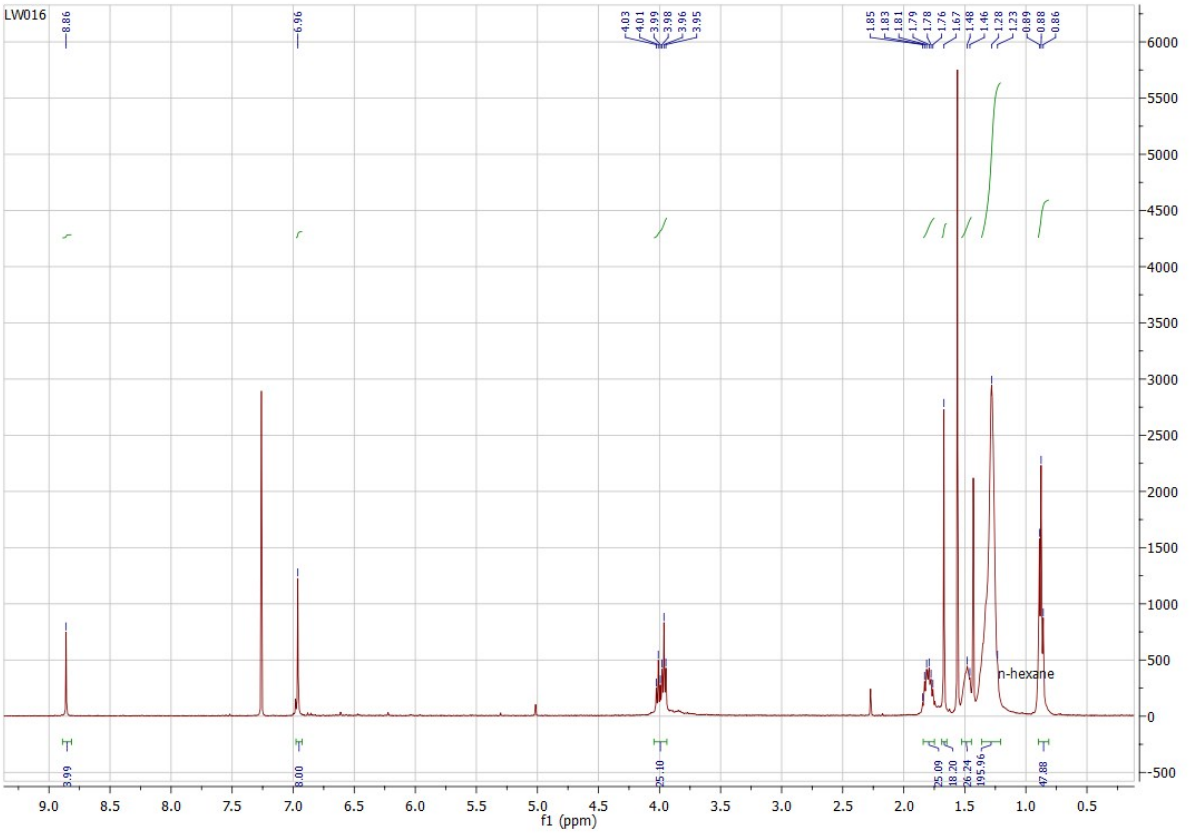

Figure 15. ^{1}HNMR spectrum of **6d** in $CDCl_3$.

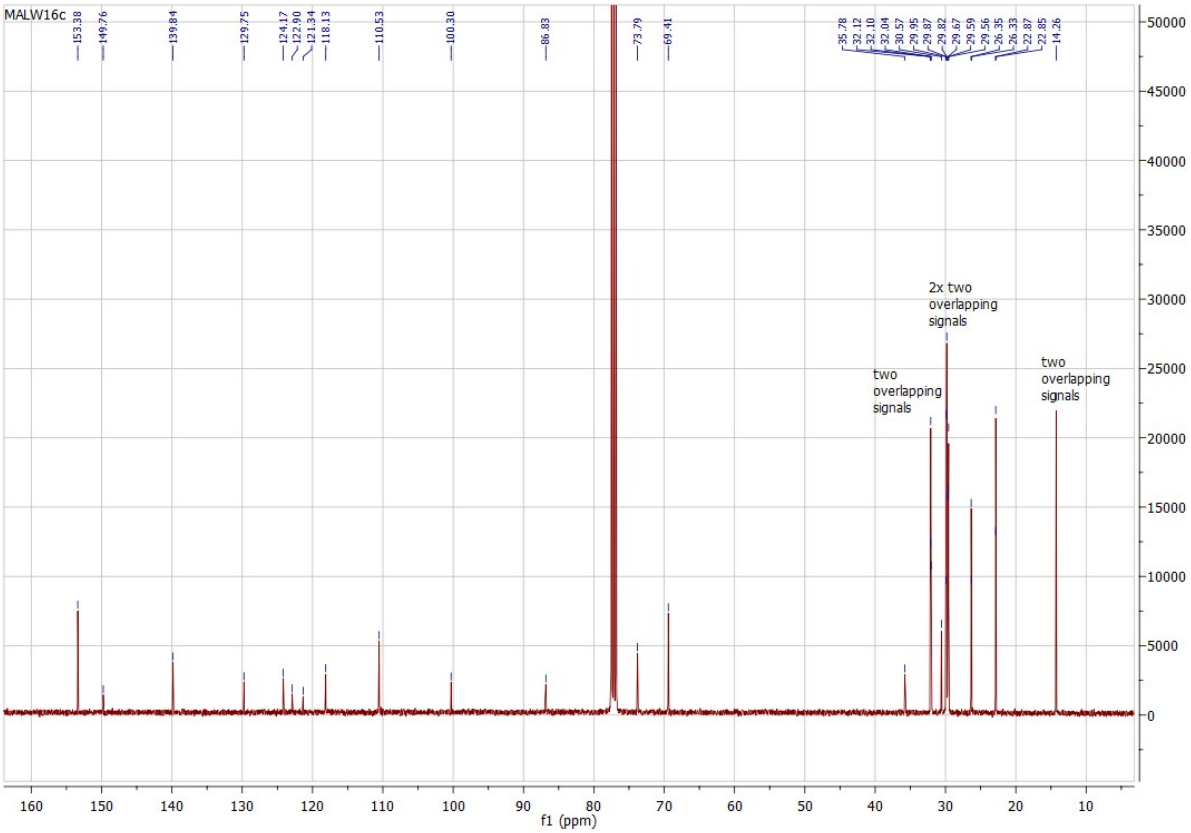

Figure 16. ^{1}HNMR spectrum of **6d** in $CDCl_3$.

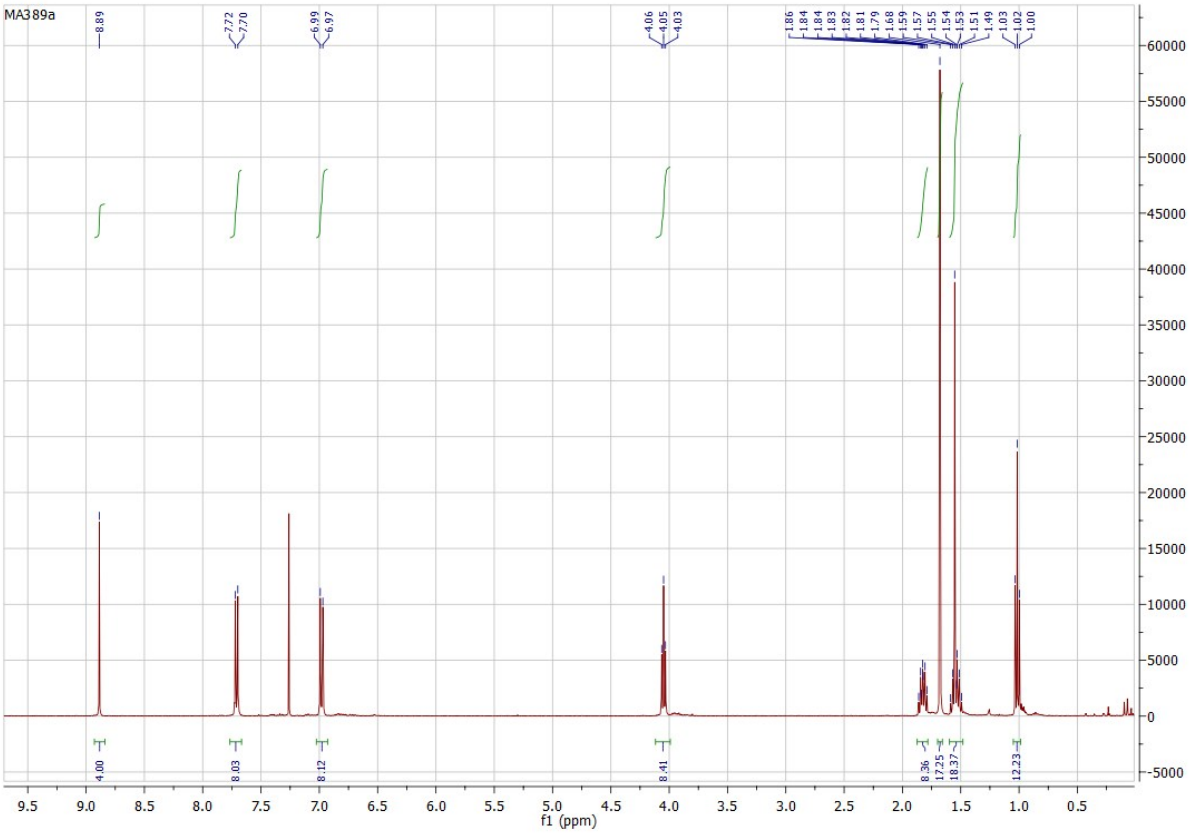

Figure 17. ^{1}HNMR spectrum of **6e** in $CDCl_3$.

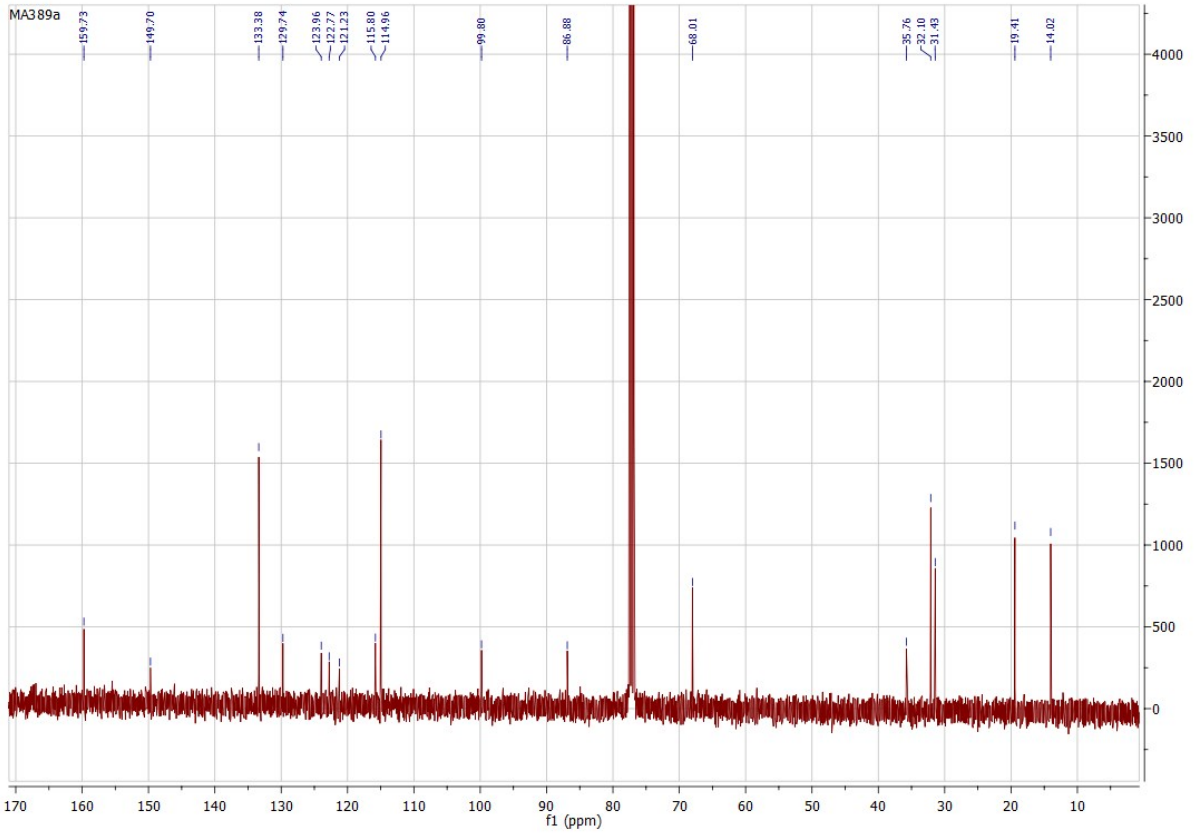

Figure 18. ^{13}CNMR spectrum of **6e** in $CDCl_3$.

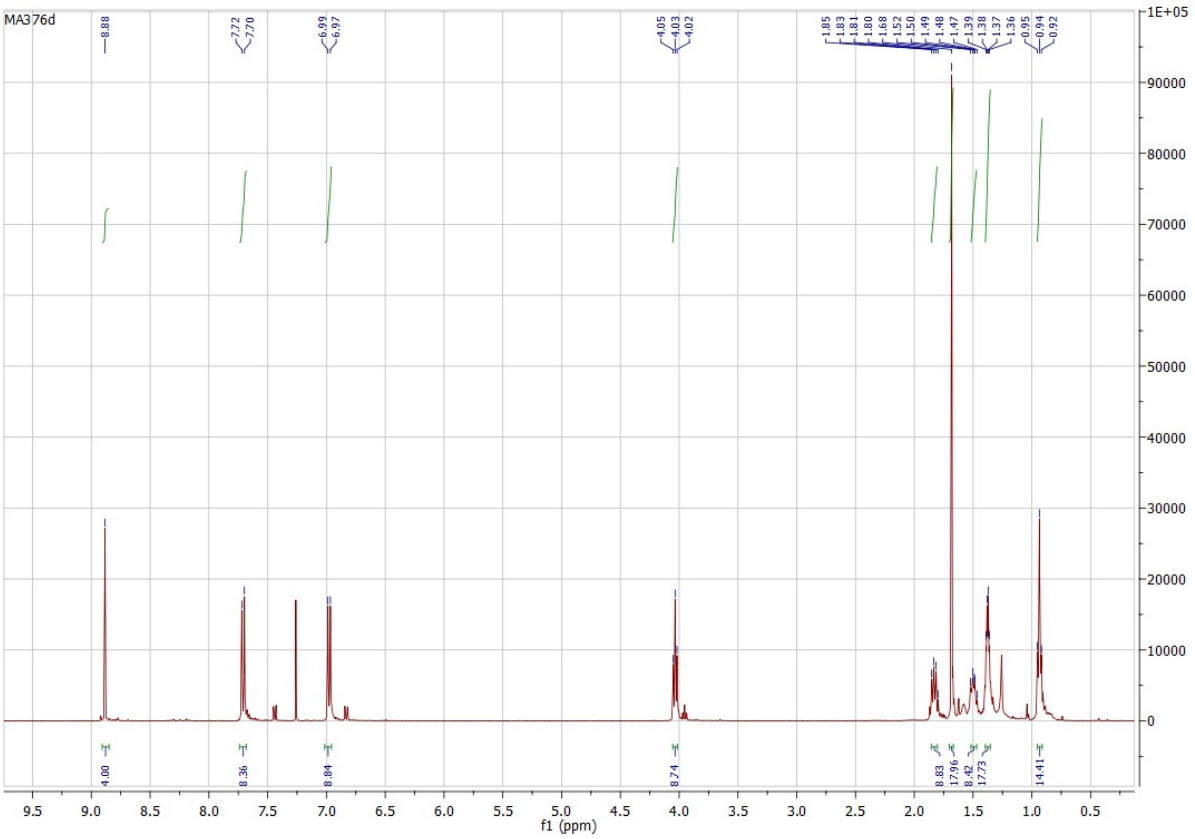

Figure 19. ^{1}HNMR spectrum of **6f** in $CDCl_3$.

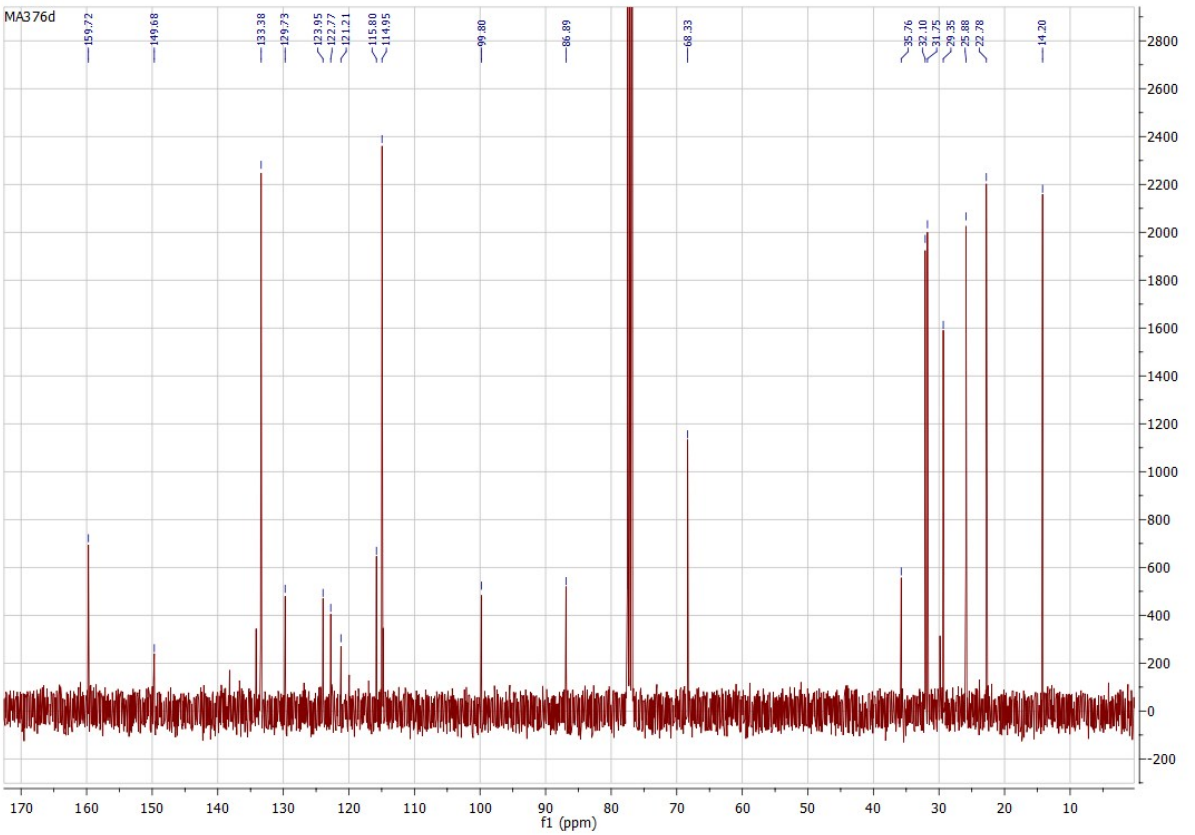

Figure 20. ^{13}CNMR spectrum of **6f** in $CDCl_3$.

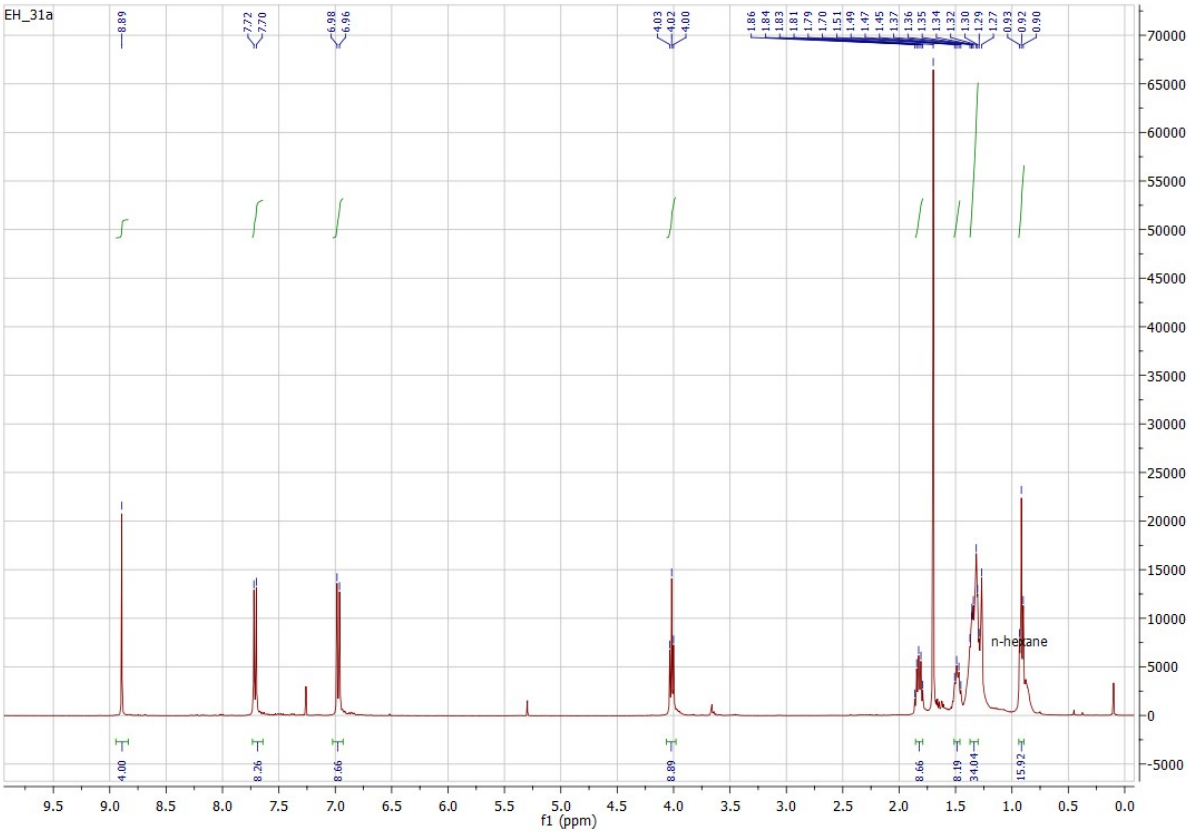

Figure 21. [1]HNMR spectrum of **6g** in $CDCl_3$.

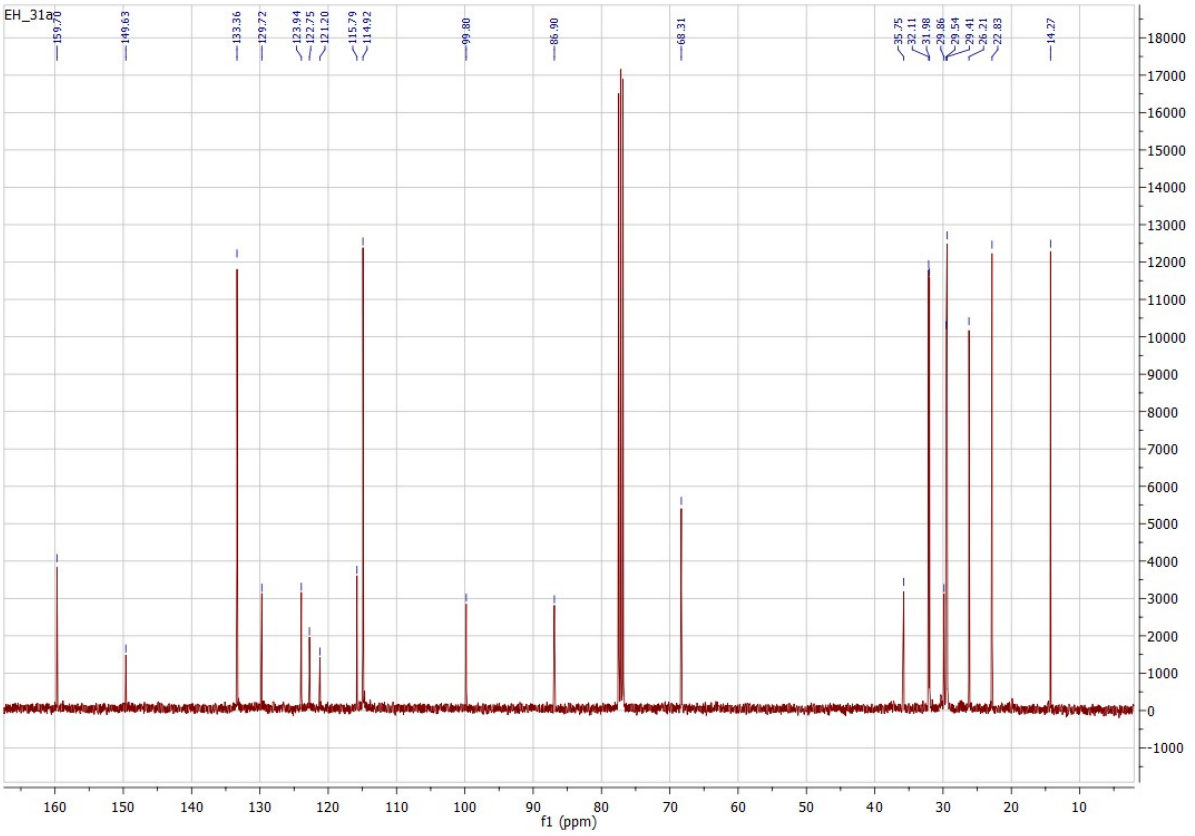

Figure 22. [13]CNMR spectrum of **6g** in $CDCl_3$.

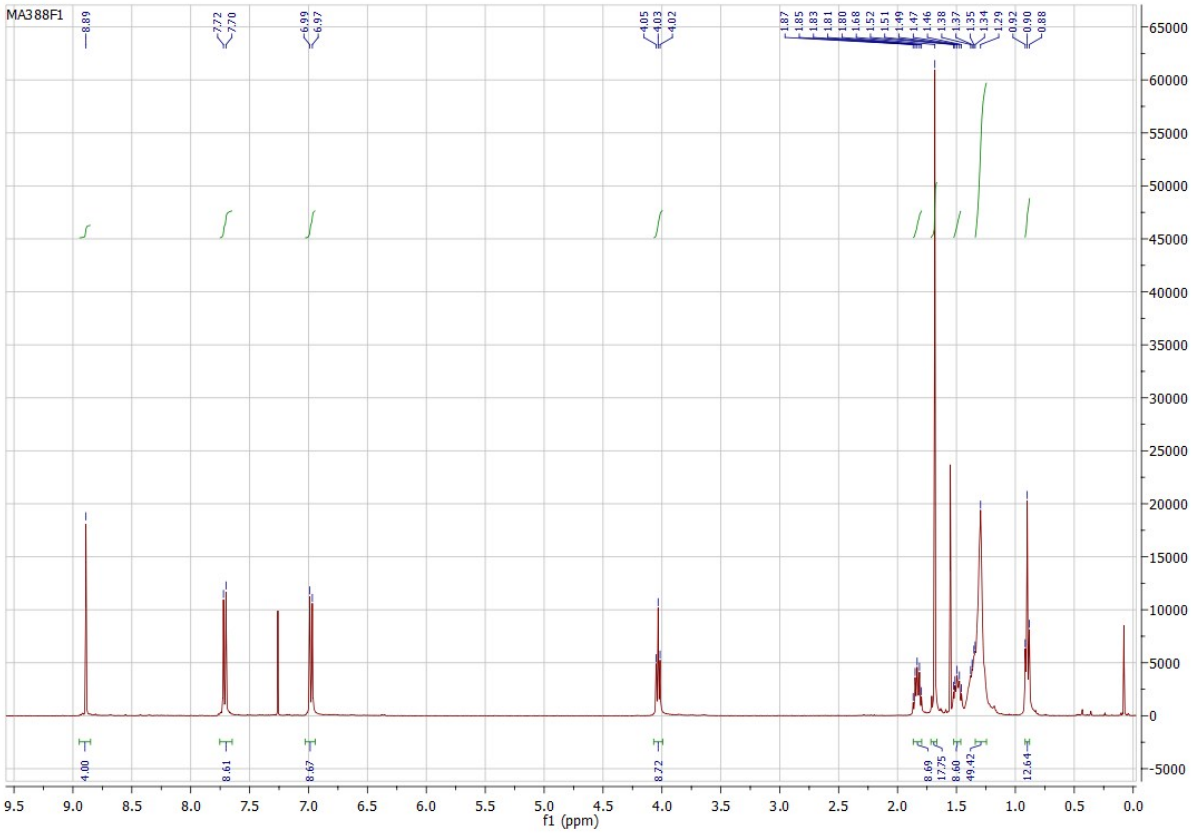

Figure 23. ^{1}HNMR spectrum of **6h** in $CDCl_3$.

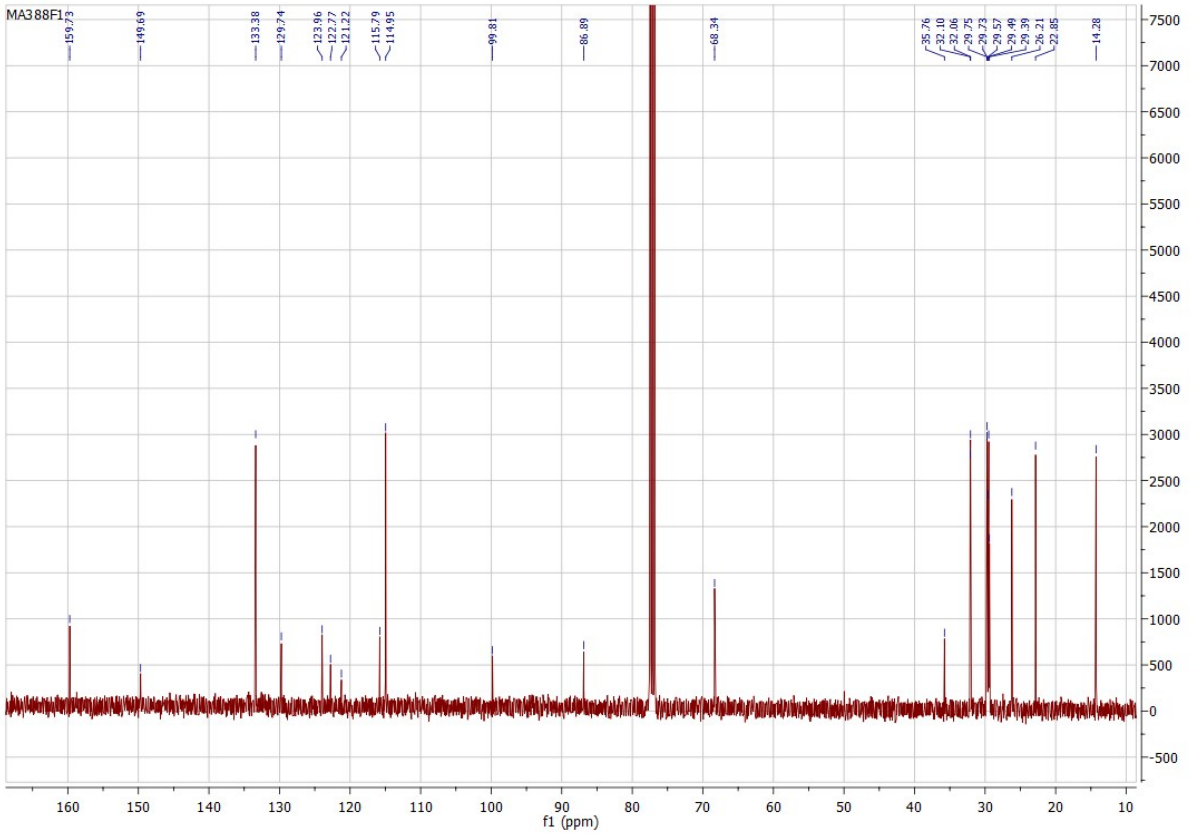

Figure 23. ^{13}CNMR spectrum of **6h** in $CDCl_3$.

Crystallographic analysis of pyrene 6e

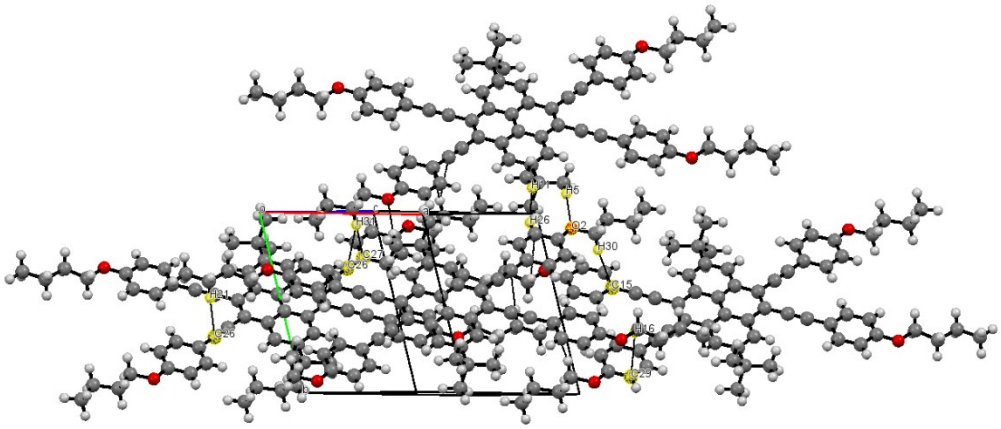

Figure 24. Partial intermolecular landscape of **6e**. Lines between the yellow highlighted atoms represent short intermolecular contacts below the sum of the van der Waals radii of the respective atoms.

Crystallographic analysis of pyrene 6h

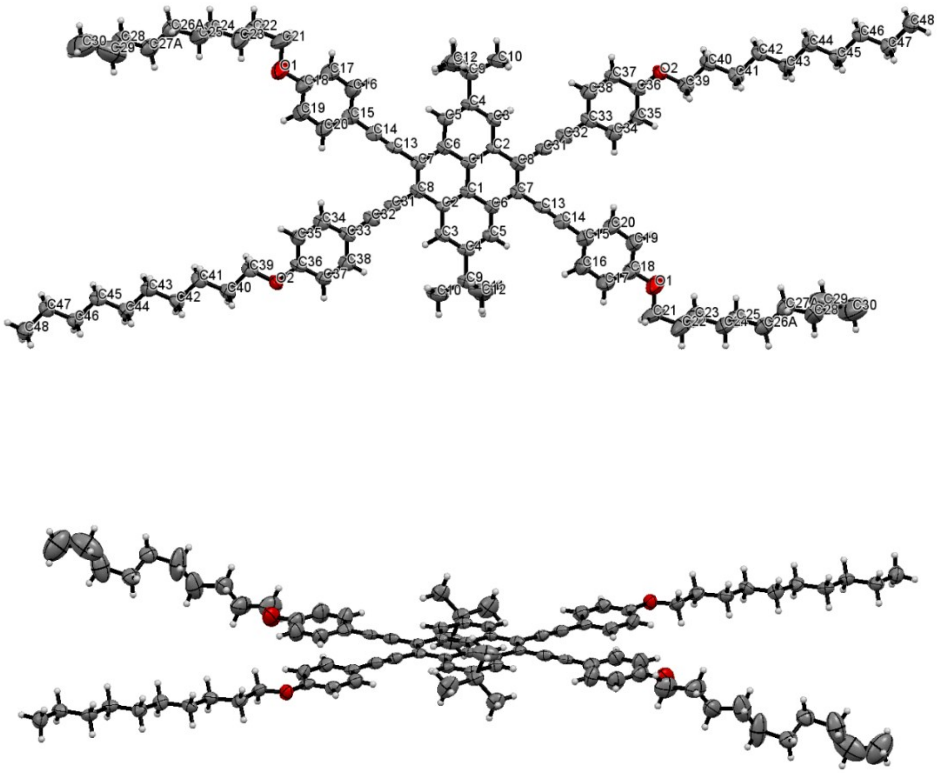

Figure 25. X-ray single structure of **6h** (*top*) top view and (*bottom*) side view. Twist angle between the pyrene core of and the C(15)-C(20) ring is 3.9°. Twist angle between the pyrene core of and the C(33)-C(38) phenyl ring is 4.9°. Acetylene carbon atoms are slightly distorted with twist angles of 2.8° for the C(25)-C(26) bond and 12.5° for the C(13)-C(14) bond, respectively. Twist angles between the methoxy groups and the corresponding phenyl rings are 2.8 (O(1)) and 0.5 (O(2)).

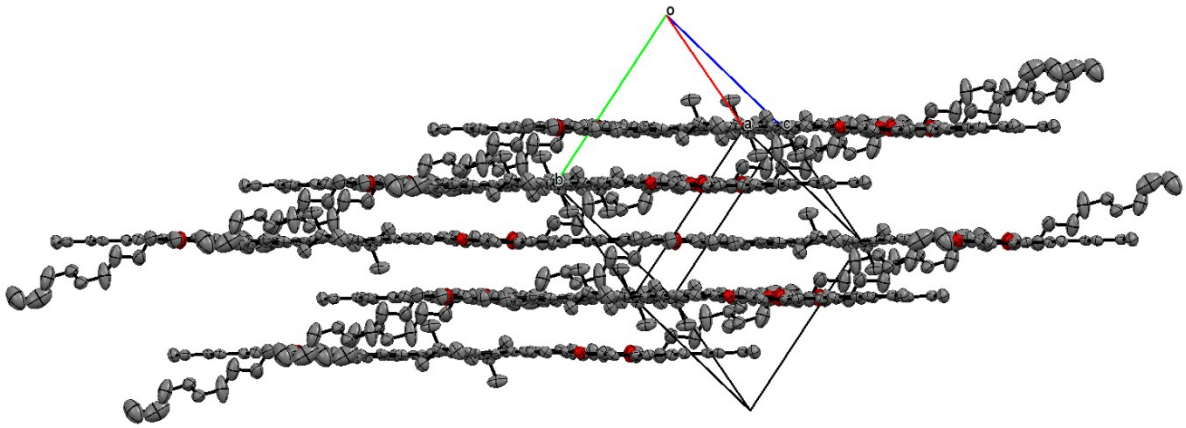

Figure 26. Molecular packing of **6h**. Individual layers possess a distance of 3.3 Å.

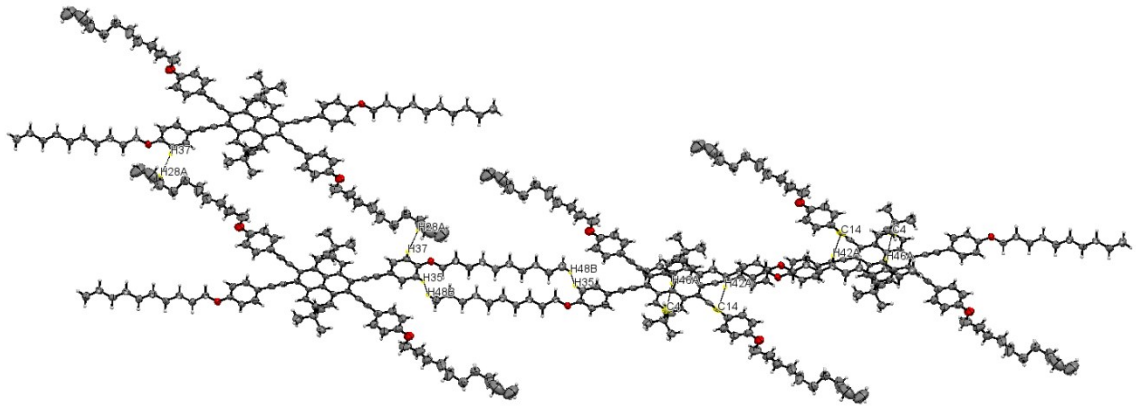

Figure 27. Partial intermolecular landscape of **6h**. Lines between the yellow highlighted atoms represent short intermolecular contacts below the sum of the van der Waals radii of the respective atoms.

Crystallographic data of pyrene 6e

Table 1. Crystal data and structure refinement for **6e**.

Identification code	sh4089	
Empirical formula	C72 H74 O4	
Formula weight	1003.31	
Temperature	122(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.4191(5) Å	a= 87.451(2)°.
	b = 11.0485(5) Å	b= 81.0290(10)°.
	c = 13.1357(5) Å	g = 75.138(2)°.
Volume	1443.64(11) $Å^3$	
Z	1	
Density (calculated)	1.154 Mg/m^3	
Absorption coefficient	0.070 mm^{-1}	
F(000)	538	
Crystal size	0.494 x 0.255 x 0.090 mm^3	
Theta range for data collection	1.907 to 30.764°.	
Index ranges	-14<=h<=14, -15<=k<=15, -18<=l<=18	
Reflections collected	77583	
Independent reflections	8961 [R(int) = 0.0779]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.7117	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8961 / 0 / 491	
Goodness-of-fit on F^2	1.004	
Final R indices [I>2sigma(I)]	R1 = 0.0493, wR2 = 0.1139	
R indices (all data)	R1 = 0.0993, wR2 = 0.1407	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.445 and -0.279 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **6e**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	270(1)	5469(1)	-277(1)	14(1)
C(2)	-329(1)	6111(1)	-1109(1)	15(1)
C(3)	233(1)	7016(1)	-1650(1)	17(1)
C(4)	1379(1)	7298(1)	-1402(1)	17(1)
C(5)	1950(1)	6669(1)	-578(1)	17(1)
C(6)	1419(1)	5764(1)	-10(1)	14(1)
C(7)	2028(1)	5105(1)	839(1)	15(1)
C(8)	1494(1)	4205(1)	1385(1)	15(1)
C(9)	1979(1)	8264(1)	-2043(1)	22(1)
C(10)	3363(2)	8265(2)	-1795(1)	30(1)
C(11)	1041(2)	9572(2)	-1835(1)	33(1)
C(12)	2145(2)	7953(2)	-3192(1)	28(1)
C(13)	3193(1)	5396(1)	1103(1)	17(1)
C(14)	4173(1)	5661(1)	1297(1)	18(1)
C(15)	5334(1)	5955(1)	1577(1)	17(1)
C(16)	5846(1)	5413(1)	2456(1)	20(1)
C(17)	6962(1)	5681(1)	2756(1)	20(1)
C(18)	7583(1)	6507(1)	2173(1)	18(1)
C(19)	7089(1)	7052(1)	1288(1)	20(1)
C(20)	5981(1)	6780(1)	992(1)	19(1)
O(1)	8674(1)	6840(1)	2404(1)	24(1)
C(21)	9248(1)	6254(1)	3281(1)	22(1)
C(22)	10435(1)	6769(2)	3373(1)	25(1)
C(23)	11135(2)	6190(2)	4275(1)	28(1)
C(24)	12421(2)	6583(2)	4297(2)	42(1)
C(25)	2062(1)	3592(1)	2250(1)	17(1)
C(26)	2470(1)	3092(1)	3008(1)	19(1)
C(27)	2960(1)	2512(1)	3914(1)	18(1)
C(28)	2360(1)	1645(1)	4483(1)	20(1)
C(29)	2845(1)	1086(1)	5353(1)	21(1)
C(30)	3941(1)	1370(1)	5683(1)	18(1)
C(31)	4538(1)	2235(1)	5131(1)	22(1)
C(32)	4045(1)	2798(1)	4259(1)	23(1)
O(2)	4347(1)	766(1)	6541(1)	21(1)

C(33)	5480(1)	1030(1)	6903(1)	19(1)
C(34)	5749(1)	241(1)	7844(1)	20(1)
C(35)	6969(2)	411(2)	8266(1)	29(1)
C(36)	7220(2)	-378(2)	9223(1)	34(1)

Table 3. Bond lengths [Å] and angles [°] for **6e**.

C(1)-C(2)	1.4151(16)
C(1)-C(6)	1.4155(16)
C(1)-C(1)#1	1.423(2)
C(2)-C(3)	1.3993(17)
C(2)-C(8)#1	1.4462(16)
C(3)-C(4)	1.3958(17)
C(3)-H(1)	1.006(17)
C(4)-C(5)	1.3898(17)
C(4)-C(9)	1.5281(17)
C(5)-C(6)	1.3963(17)
C(5)-H(2)	0.982(16)
C(6)-C(7)	1.4448(17)
C(7)-C(8)	1.3818(17)
C(7)-C(13)	1.4280(17)
C(8)-C(25)	1.4278(17)
C(8)-C(2)#1	1.4462(16)
C(9)-C(10)	1.527(2)
C(9)-C(11)	1.532(2)
C(9)-C(12)	1.537(2)
C(10)-H(4)	1.009(19)
C(10)-H(3)	1.000(17)
C(10)-H(5)	1.020(18)
C(11)-H(7)	0.998(17)
C(11)-H(6)	1.021(19)
C(11)-H(8)	1.033(19)
C(12)-H(10)	1.017(18)
C(12)-H(9)	1.03(2)
C(12)-H(11)	1.008(17)
C(13)-C(14)	1.1976(17)
C(14)-C(15)	1.4337(17)
C(15)-C(16)	1.3938(18)
C(15)-C(20)	1.4027(18)
C(16)-C(17)	1.3882(18)
C(16)-H(12)	1.025(16)
C(17)-C(18)	1.3870(19)
C(17)-H(13)	0.968(16)
C(18)-O(1)	1.3605(15)

C(18)-C(19)	1.3939(18)
C(19)-C(20)	1.3790(18)
C(19)-H(14)	0.986(16)
C(20)-H(15)	0.994(16)
O(1)-C(21)	1.4335(16)
C(21)-C(22)	1.5097(19)
C(21)-H(16)	0.995(15)
C(21)-H(17)	1.000(15)
C(22)-C(23)	1.519(2)
C(22)-H(18)	0.985(17)
C(22)-H(19)	1.006(17)
C(23)-C(24)	1.515(2)
C(23)-H(20)	1.015(17)
C(23)-H(21)	0.987(18)
C(24)-H(24)	0.98(2)
C(24)-H(23)	1.01(2)
C(24)-H(22)	0.99(2)
C(25)-C(26)	1.1993(18)
C(26)-C(27)	1.4293(17)
C(27)-C(32)	1.3927(18)
C(27)-C(28)	1.4011(18)
C(28)-C(29)	1.3779(18)
C(28)-H(25)	0.989(17)
C(29)-C(30)	1.3922(18)
C(29)-H(26)	0.980(17)
C(30)-O(2)	1.3538(15)
C(30)-C(31)	1.3890(18)
C(31)-C(32)	1.3861(18)
C(31)-H(27)	0.958(18)
C(32)-H(28)	1.011(17)
O(2)-C(33)	1.4377(15)
C(33)-C(34)	1.5018(18)
C(33)-H(29)	1.003(16)
C(33)-H(30)	0.997(16)
C(34)-C(35)	1.519(2)
C(34)-H(32)	0.991(16)
C(34)-H(31)	1.004(16)
C(35)-C(36)	1.516(2)
C(35)-H(33)	1.004(19)

C(35)-H(34)	1.023(19)
C(36)-H(35)	0.957(19)
C(36)-H(36)	1.01(2)
C(36)-H(37)	1.01(2)

C(2)-C(1)-C(6)	119.16(11)
C(2)-C(1)-C(1)#1	120.30(13)
C(6)-C(1)-C(1)#1	120.54(13)
C(3)-C(2)-C(1)	119.18(11)
C(3)-C(2)-C(8)#1	121.90(11)
C(1)-C(2)-C(8)#1	118.92(11)
C(4)-C(3)-C(2)	121.99(11)
C(4)-C(3)-H(1)	119.7(9)
C(2)-C(3)-H(1)	118.3(9)
C(5)-C(4)-C(3)	118.22(11)
C(5)-C(4)-C(9)	121.95(11)
C(3)-C(4)-C(9)	119.83(11)
C(4)-C(5)-C(6)	121.85(11)
C(4)-C(5)-H(2)	120.3(9)
C(6)-C(5)-H(2)	117.8(9)
C(5)-C(6)-C(1)	119.59(11)
C(5)-C(6)-C(7)	121.48(11)
C(1)-C(6)-C(7)	118.92(11)
C(8)-C(7)-C(13)	120.51(11)
C(8)-C(7)-C(6)	120.56(11)
C(13)-C(7)-C(6)	118.93(11)
C(7)-C(8)-C(25)	120.48(11)
C(7)-C(8)-C(2)#1	120.75(11)
C(25)-C(8)-C(2)#1	118.75(11)
C(10)-C(9)-C(4)	112.24(11)
C(10)-C(9)-C(11)	108.70(13)
C(4)-C(9)-C(11)	109.44(12)
C(10)-C(9)-C(12)	107.50(12)
C(4)-C(9)-C(12)	109.28(11)
C(11)-C(9)-C(12)	109.64(12)
C(9)-C(10)-H(4)	112.4(10)
C(9)-C(10)-H(3)	111.8(10)
H(4)-C(10)-H(3)	106.5(14)
C(9)-C(10)-H(5)	106.5(10)

H(4)-C(10)-H(5)	108.5(14)
H(3)-C(10)-H(5)	111.1(13)
C(9)-C(11)-H(7)	111.3(10)
C(9)-C(11)-H(6)	110.6(10)
H(7)-C(11)-H(6)	105.5(14)
C(9)-C(11)-H(8)	110.0(10)
H(7)-C(11)-H(8)	109.1(14)
H(6)-C(11)-H(8)	110.3(15)
C(9)-C(12)-H(10)	112.3(10)
C(9)-C(12)-H(9)	109.6(10)
H(10)-C(12)-H(9)	110.3(14)
C(9)-C(12)-H(11)	109.3(9)
H(10)-C(12)-H(11)	107.8(13)
H(9)-C(12)-H(11)	107.4(14)
C(14)-C(13)-C(7)	177.99(14)
C(13)-C(14)-C(15)	177.30(14)
C(16)-C(15)-C(20)	118.33(11)
C(16)-C(15)-C(14)	119.68(12)
C(20)-C(15)-C(14)	121.99(12)
C(17)-C(16)-C(15)	121.39(12)
C(17)-C(16)-H(12)	118.9(9)
C(15)-C(16)-H(12)	119.7(9)
C(18)-C(17)-C(16)	119.47(12)
C(18)-C(17)-H(13)	121.0(10)
C(16)-C(17)-H(13)	119.5(10)
O(1)-C(18)-C(17)	124.13(12)
O(1)-C(18)-C(19)	115.97(12)
C(17)-C(18)-C(19)	119.91(12)
C(20)-C(19)-C(18)	120.39(12)
C(20)-C(19)-H(14)	122.2(9)
C(18)-C(19)-H(14)	117.3(9)
C(19)-C(20)-C(15)	120.52(12)
C(19)-C(20)-H(15)	118.4(9)
C(15)-C(20)-H(15)	121.0(9)
C(18)-O(1)-C(21)	117.58(11)
O(1)-C(21)-C(22)	107.57(12)
O(1)-C(21)-H(16)	109.7(8)
C(22)-C(21)-H(16)	111.2(8)
O(1)-C(21)-H(17)	109.2(8)

C(22)-C(21)-H(17)	110.0(8)
H(16)-C(21)-H(17)	109.1(12)
C(21)-C(22)-C(23)	111.88(13)
C(21)-C(22)-H(18)	107.9(9)
C(23)-C(22)-H(18)	110.6(9)
C(21)-C(22)-H(19)	108.7(9)
C(23)-C(22)-H(19)	111.0(9)
H(18)-C(22)-H(19)	106.5(13)
C(24)-C(23)-C(22)	112.18(15)
C(24)-C(23)-H(20)	111.3(9)
C(22)-C(23)-H(20)	110.2(9)
C(24)-C(23)-H(21)	109.3(10)
C(22)-C(23)-H(21)	108.4(10)
H(20)-C(23)-H(21)	105.1(14)
C(23)-C(24)-H(24)	108.8(12)
C(23)-C(24)-H(23)	111.8(12)
H(24)-C(24)-H(23)	107.1(16)
C(23)-C(24)-H(22)	110.2(11)
H(24)-C(24)-H(22)	108.6(17)
H(23)-C(24)-H(22)	110.2(16)
C(26)-C(25)-C(8)	176.39(14)
C(25)-C(26)-C(27)	179.18(14)
C(32)-C(27)-C(28)	118.16(12)
C(32)-C(27)-C(26)	120.76(12)
C(28)-C(27)-C(26)	121.07(12)
C(29)-C(28)-C(27)	120.59(12)
C(29)-C(28)-H(25)	121.4(10)
C(27)-C(28)-H(25)	118.0(10)
C(28)-C(29)-C(30)	120.70(13)
C(28)-C(29)-H(26)	120.3(10)
C(30)-C(29)-H(26)	119.0(10)
O(2)-C(30)-C(31)	124.40(12)
O(2)-C(30)-C(29)	116.24(12)
C(31)-C(30)-C(29)	119.36(12)
C(32)-C(31)-C(30)	119.79(12)
C(32)-C(31)-H(27)	119.6(11)
C(30)-C(31)-H(27)	120.6(11)
C(31)-C(32)-C(27)	121.39(13)
C(31)-C(32)-H(28)	118.3(9)

C(27)-C(32)-H(28)	120.3(9)
C(30)-O(2)-C(33)	117.87(10)
O(2)-C(33)-C(34)	108.01(11)
O(2)-C(33)-H(29)	109.8(9)
C(34)-C(33)-H(29)	111.0(9)
O(2)-C(33)-H(30)	110.4(9)
C(34)-C(33)-H(30)	111.0(9)
H(29)-C(33)-H(30)	106.7(12)
C(33)-C(34)-C(35)	112.28(12)
C(33)-C(34)-H(32)	108.1(9)
C(35)-C(34)-H(32)	109.7(9)
C(33)-C(34)-H(31)	108.8(9)
C(35)-C(34)-H(31)	110.3(9)
H(32)-C(34)-H(31)	107.6(13)
C(36)-C(35)-C(34)	111.79(14)
C(36)-C(35)-H(33)	109.9(10)
C(34)-C(35)-H(33)	107.9(10)
C(36)-C(35)-H(34)	110.2(10)
C(34)-C(35)-H(34)	109.4(10)
H(33)-C(35)-H(34)	107.5(15)
C(35)-C(36)-H(35)	110.0(11)
C(35)-C(36)-H(36)	110.0(12)
H(35)-C(36)-H(36)	106.6(17)
C(35)-C(36)-H(37)	114.3(12)
H(35)-C(36)-H(37)	107.9(16)
H(36)-C(36)-H(37)	107.8(16)

Symmetry transformations used to generate equivalent atoms:

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

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **6e**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	14(1)	16(1)	12(1)	1(1)	-3(1)	-4(1)
C(2)	14(1)	17(1)	13(1)	1(1)	-4(1)	-4(1)
C(3)	18(1)	19(1)	15(1)	4(1)	-5(1)	-6(1)
C(4)	18(1)	18(1)	16(1)	2(1)	-3(1)	-7(1)
C(5)	17(1)	20(1)	17(1)	2(1)	-5(1)	-8(1)
C(6)	14(1)	17(1)	13(1)	1(1)	-4(1)	-5(1)
C(7)	15(1)	18(1)	13(1)	0(1)	-4(1)	-5(1)
C(8)	15(1)	17(1)	13(1)	1(1)	-5(1)	-4(1)
C(9)	24(1)	22(1)	22(1)	6(1)	-6(1)	-12(1)
C(10)	29(1)	36(1)	33(1)	12(1)	-10(1)	-21(1)
C(11)	36(1)	22(1)	40(1)	8(1)	-3(1)	-11(1)
C(12)	32(1)	33(1)	21(1)	9(1)	-4(1)	-16(1)
C(13)	18(1)	19(1)	15(1)	2(1)	-5(1)	-5(1)
C(14)	18(1)	20(1)	18(1)	0(1)	-6(1)	-4(1)
C(15)	14(1)	19(1)	20(1)	-2(1)	-6(1)	-4(1)
C(16)	18(1)	19(1)	24(1)	3(1)	-7(1)	-7(1)
C(17)	19(1)	21(1)	22(1)	3(1)	-9(1)	-6(1)
C(18)	14(1)	21(1)	22(1)	-4(1)	-6(1)	-5(1)
C(19)	18(1)	22(1)	19(1)	1(1)	-2(1)	-8(1)
C(20)	18(1)	22(1)	18(1)	0(1)	-5(1)	-5(1)
O(1)	19(1)	30(1)	27(1)	2(1)	-10(1)	-12(1)
C(21)	17(1)	27(1)	22(1)	-2(1)	-9(1)	-4(1)
C(22)	18(1)	34(1)	27(1)	-6(1)	-6(1)	-10(1)
C(23)	21(1)	38(1)	29(1)	-7(1)	-10(1)	-8(1)
C(24)	25(1)	71(1)	35(1)	-9(1)	-11(1)	-17(1)
C(25)	17(1)	19(1)	16(1)	0(1)	-4(1)	-5(1)
C(26)	19(1)	21(1)	18(1)	1(1)	-6(1)	-5(1)
C(27)	20(1)	19(1)	14(1)	2(1)	-6(1)	-2(1)
C(28)	21(1)	21(1)	21(1)	2(1)	-10(1)	-7(1)
C(29)	24(1)	20(1)	21(1)	6(1)	-8(1)	-9(1)
C(30)	20(1)	18(1)	14(1)	2(1)	-6(1)	-2(1)
C(31)	20(1)	29(1)	19(1)	6(1)	-9(1)	-11(1)
C(32)	22(1)	29(1)	19(1)	9(1)	-7(1)	-11(1)
O(2)	25(1)	24(1)	18(1)	8(1)	-11(1)	-9(1)

C(33)	20(1)	22(1)	18(1)	3(1)	-8(1)	-6(1)
C(34)	22(1)	22(1)	17(1)	4(1)	-7(1)	-3(1)
C(35)	26(1)	40(1)	24(1)	6(1)	-13(1)	-8(1)
C(36)	32(1)	48(1)	21(1)	2(1)	-14(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **6e**.

	x	y	z	U(eq)
H(2)	2760(16)	6841(15)	-386(12)	28(4)
H(1)	-220(16)	7483(15)	-2225(13)	31(4)
H(12)	5397(15)	4798(15)	2890(12)	23(4)
H(14)	7592(16)	7592(15)	872(12)	27(4)
H(4)	4014(18)	7413(18)	-1880(14)	40(5)
H(7)	1429(17)	10229(16)	-2217(13)	33(4)
H(3)	3317(16)	8526(16)	-1068(14)	31(4)
H(5)	3719(17)	8868(17)	-2305(14)	35(5)
H(6)	924(18)	9793(17)	-1074(15)	40(5)
H(16)	8563(15)	6435(14)	3910(12)	18(4)
H(17)	9551(15)	5329(15)	3172(11)	20(4)
H(18)	10107(16)	7683(16)	3454(12)	28(4)
H(13)	7279(16)	5310(15)	3382(13)	28(4)
H(15)	5670(16)	7164(15)	346(13)	28(4)
H(20)	10499(17)	6397(15)	4948(13)	28(4)
H(21)	11345(17)	5270(17)	4217(13)	33(5)
H(29)	6280(16)	838(14)	6348(12)	25(4)
H(32)	4943(16)	479(15)	8376(12)	24(4)
H(30)	5293(15)	1937(15)	7062(11)	22(4)
H(31)	5875(16)	-661(16)	7667(12)	26(4)
H(33)	7767(19)	164(17)	7711(14)	43(5)
H(25)	1584(17)	1449(16)	4241(13)	33(5)
H(34)	6837(18)	1337(18)	8423(14)	41(5)
H(10)	1247(18)	8049(16)	-3442(13)	37(5)
H(9)	2737(19)	7055(19)	-3326(14)	46(5)
H(8)	121(19)	9613(17)	-2053(14)	44(5)
H(11)	2620(16)	8539(16)	-3611(13)	31(4)
H(19)	11073(17)	6620(15)	2706(13)	31(4)
H(24)	13020(20)	6330(20)	3653(17)	57(6)
H(23)	12910(20)	6158(19)	4876(16)	54(6)
H(22)	12224(19)	7510(20)	4362(15)	48(6)
H(27)	5266(18)	2471(17)	5364(14)	41(5)
H(26)	2429(17)	474(16)	5744(13)	34(5)

H(28)	4503(16)	3419(16)	3867(13)	30(4)
H(35)	6460(19)	-142(17)	9752(14)	39(5)
H(36)	7330(20)	-1290(20)	9068(16)	62(6)
H(37)	8040(20)	-310(20)	9515(16)	60(6)

Crystallographic data of pyrene 6h

Table 6. Crystal data and structure refinement for **6h**.

Identification code	sh4092	
Empirical formula	C48 H60 O2	
Formula weight	1339.94	
Temperature	122(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.701(3) Å	a= 76.316(9)°.
	b = 12.944(4) Å	b= 80.633(8)°.
	c = 17.212(5) Å	g = 74.795(9)°.
Volume	2014.7(11) $Å^3$	
Z	2	
Density (calculated)	1.103 Mg/m^3	
Absorption coefficient	0.065 mm^{-1}	
F(000)	728	
Crystal size	0.696 x 0.322 x 0.028 mm^3	
Theta range for data collection	1.225 to 26.722°.	
Index ranges	-12<=h<=12, -16<=k<=15, -20<=l<=21	
Reflections collected	16558	
Independent reflections	8277 [R(int) = 0.1055]	
Completeness to theta = 25.242°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7454 and 0.6433	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8277 / 57 / 476	
Goodness-of-fit on F^2	0.860	
Final R indices [I>2sigma(I)]	R1 = 0.0699, wR2 = 0.1197	
R indices (all data)	R1 = 0.2736, wR2 = 0.1838	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.323 and -0.371 $e.Å^{-3}$	

Table 7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **6h**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	15289(4)	74(3)	4586(2)	20(1)
C(2)	16575(4)	-646(3)	4339(2)	18(1)
C(3)	17107(4)	-506(3)	3527(2)	23(1)
C(4)	16414(4)	315(3)	2950(2)	22(1)
C(5)	15167(4)	1031(3)	3204(2)	24(1)
C(6)	14591(4)	929(3)	4011(2)	20(1)
C(7)	13267(4)	1669(3)	4267(2)	21(1)
C(8)	12726(4)	1527(3)	5068(2)	21(1)
C(9)	16906(5)	400(3)	2048(2)	30(1)
C(10)	18388(5)	-339(3)	1883(2)	48(1)
C(11)	15817(5)	54(4)	1665(2)	49(1)
C(12)	16953(4)	1581(3)	1633(2)	36(1)
C(13)	12580(4)	2538(3)	3679(2)	24(1)
C(14)	12035(5)	3254(3)	3152(2)	25(1)
C(15)	11398(5)	4103(3)	2526(2)	29(1)
C(16)	12075(5)	4242(3)	1754(2)	40(1)
C(17)	11447(5)	5051(4)	1144(3)	44(1)
C(18)	10134(5)	5739(4)	1311(3)	38(1)
O(1)	9424(3)	6565(2)	748(2)	50(1)
C(19)	9451(5)	5627(4)	2087(3)	41(1)
C(20)	10066(5)	4811(3)	2691(2)	36(1)
C(21)	10048(5)	6670(4)	-77(2)	54(2)
C(22)	9040(5)	7592(4)	-571(3)	54(2)
C(23)	8896(5)	8694(4)	-372(3)	50(1)
C(24)	7824(5)	9622(4)	-816(3)	61(2)
C(25)	7776(6)	10731(4)	-665(3)	74(2)
C(26A)	6986(8)	11900(6)	-1047(5)	40(2)
C(27A)	5395(8)	12017(6)	-670(5)	40(2)
C(26B)	6282(8)	11427(6)	-966(5)	42(2)
C(27B)	6091(8)	12574(6)	-767(5)	42(2)
C(28)	4584(6)	13232(5)	-1033(3)	72(2)
C(29)	4534(7)	14248(6)	-751(3)	94(2)
C(30)	3478(7)	15204(4)	-1115(3)	95(2)
C(31)	11432(5)	2273(3)	5318(2)	23(1)

C(32)	10366(5)	2867(3)	5553(2)	26(1)
C(33)	9060(4)	3559(3)	5846(2)	24(1)
C(34)	8306(5)	4460(3)	5336(2)	30(1)
C(35)	7019(4)	5097(3)	5619(2)	30(1)
C(36)	6469(5)	4852(3)	6417(2)	23(1)
O(2)	5199(3)	5427(2)	6741(2)	28(1)
C(37)	7222(4)	3985(3)	6932(2)	26(1)
C(38)	8489(4)	3343(3)	6650(2)	31(1)
C(39)	4346(4)	6281(3)	6208(2)	28(1)
C(40)	2992(4)	6795(3)	6690(2)	28(1)
C(41)	2056(4)	7737(3)	6172(2)	29(1)
C(42)	736(4)	8346(3)	6637(2)	27(1)
C(43)	-159(4)	9318(3)	6116(2)	30(1)
C(44)	-1466(4)	9943(3)	6578(2)	29(1)
C(45)	-2358(4)	10919(3)	6055(2)	27(1)
C(46)	-3704(4)	11505(3)	6520(2)	27(1)
C(47)	-4594(4)	12504(3)	6015(2)	30(1)
C(48)	-5921(4)	13071(3)	6503(2)	37(1)

Table 8. Bond lengths [Å] and angles [°] for **6h**.

C(1)-C(6)	1.404(5)
C(1)-C(2)	1.418(5)
C(1)-C(1)#1	1.430(6)
C(2)-C(3)	1.395(4)
C(2)-C(8)#1	1.439(5)
C(3)-C(4)	1.382(5)
C(3)-H(3)	0.9500
C(4)-C(5)	1.395(5)
C(4)-C(9)	1.534(5)
C(5)-C(6)	1.399(4)
C(5)-H(5)	0.9500
C(6)-C(7)	1.460(5)
C(7)-C(8)	1.380(5)
C(7)-C(13)	1.422(5)
C(8)-C(2)#1	1.439(5)
C(8)-C(31)	1.441(5)
C(9)-C(10)	1.529(5)
C(9)-C(12)	1.536(5)
C(9)-C(11)	1.537(5)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(14)	1.209(5)
C(14)-C(15)	1.432(6)
C(15)-C(16)	1.377(5)
C(15)-C(20)	1.404(5)
C(16)-C(17)	1.386(5)
C(16)-H(16)	0.9500
C(17)-C(18)	1.381(6)
C(17)-H(17)	0.9500
C(18)-O(1)	1.378(5)

C(18)-C(19)	1.383(5)
O(1)-C(21)	1.439(4)
C(19)-C(20)	1.379(5)
C(19)-H(19)	0.9500
C(20)-H(20)	0.9500
C(21)-C(22)	1.510(6)
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
C(22)-C(23)	1.511(5)
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
C(23)-C(24)	1.510(5)
C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900
C(24)-C(25)	1.506(6)
C(24)-H(24A)	0.9900
C(24)-H(24B)	0.9900
C(25)-C(26A)	1.547(6)
C(25)-C(26B)	1.587(6)
C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900
C(25)-H(25C)	0.9900
C(25)-H(25D)	0.9900
C(26A)-C(27A)	1.557(7)
C(26A)-H(26A)	0.9900
C(26A)-H(26B)	0.9900
C(27A)-C(28)	1.590(6)
C(27A)-H(27A)	0.9900
C(27A)-H(27B)	0.9900
C(26B)-C(27B)	1.559(7)
C(26B)-H(26C)	0.9900
C(26B)-H(26D)	0.9900
C(27B)-C(28)	1.566(6)
C(27B)-H(27C)	0.9900
C(27B)-H(27D)	0.9900
C(28)-C(29)	1.493(7)
C(28)-H(28A)	0.9900
C(28)-H(28B)	0.9900
C(28)-H(28C)	0.9900

C(28)-H(28D)	0.9900
C(29)-C(30)	1.467(7)
C(29)-H(29A)	0.9900
C(29)-H(29B)	0.9900
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800
C(31)-C(32)	1.191(5)
C(32)-C(33)	1.440(5)
C(33)-C(34)	1.394(5)
C(33)-C(38)	1.396(5)
C(34)-C(35)	1.389(5)
C(34)-H(34)	0.9500
C(35)-C(36)	1.385(5)
C(35)-H(35)	0.9500
C(36)-O(2)	1.369(4)
C(36)-C(37)	1.374(5)
O(2)-C(39)	1.427(4)
C(37)-C(38)	1.378(5)
C(37)-H(37)	0.9500
C(38)-H(38)	0.9500
C(39)-C(40)	1.518(5)
C(39)-H(39A)	0.9900
C(39)-H(39B)	0.9900
C(40)-C(41)	1.508(5)
C(40)-H(40A)	0.9900
C(40)-H(40B)	0.9900
C(41)-C(42)	1.528(5)
C(41)-H(41A)	0.9900
C(41)-H(41B)	0.9900
C(42)-C(43)	1.512(5)
C(42)-H(42A)	0.9900
C(42)-H(42B)	0.9900
C(43)-C(44)	1.527(5)
C(43)-H(43A)	0.9900
C(43)-H(43B)	0.9900
C(44)-C(45)	1.516(5)
C(44)-H(44A)	0.9900
C(44)-H(44B)	0.9900

C(45)-C(46)	1.533(5)
C(45)-H(45A)	0.9900
C(45)-H(45B)	0.9900
C(46)-C(47)	1.517(5)
C(46)-H(46A)	0.9900
C(46)-H(46B)	0.9900
C(47)-C(48)	1.531(5)
C(47)-H(47A)	0.9900
C(47)-H(47B)	0.9900
C(48)-H(48A)	0.9800
C(48)-H(48B)	0.9800
C(48)-H(48C)	0.9800

C(6)-C(1)-C(2)	119.3(3)
C(6)-C(1)-C(1)#1	120.5(5)
C(2)-C(1)-C(1)#1	120.2(5)
C(3)-C(2)-C(1)	119.5(4)
C(3)-C(2)-C(8)#1	121.6(4)
C(1)-C(2)-C(8)#1	118.9(3)
C(4)-C(3)-C(2)	122.0(4)
C(4)-C(3)-H(3)	119.0
C(2)-C(3)-H(3)	119.0
C(3)-C(4)-C(5)	117.9(4)
C(3)-C(4)-C(9)	122.1(4)
C(5)-C(4)-C(9)	119.7(4)
C(4)-C(5)-C(6)	122.4(4)
C(4)-C(5)-H(5)	118.8
C(6)-C(5)-H(5)	118.8
C(5)-C(6)-C(1)	118.9(4)
C(5)-C(6)-C(7)	121.9(4)
C(1)-C(6)-C(7)	119.2(3)
C(8)-C(7)-C(13)	121.6(4)
C(8)-C(7)-C(6)	119.9(4)
C(13)-C(7)-C(6)	118.5(4)
C(7)-C(8)-C(2)#1	121.3(4)
C(7)-C(8)-C(31)	119.5(4)
C(2)#1-C(8)-C(31)	119.1(3)
C(10)-C(9)-C(4)	112.6(4)
C(10)-C(9)-C(12)	108.3(3)

C(4)-C(9)-C(12)	111.0(3)
C(10)-C(9)-C(11)	108.2(3)
C(4)-C(9)-C(11)	108.4(3)
C(12)-C(9)-C(11)	108.1(4)
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(9)-C(11)-H(11A)	109.5
C(9)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(9)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(9)-C(12)-H(12A)	109.5
C(9)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(9)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(14)-C(13)-C(7)	177.1(5)
C(13)-C(14)-C(15)	179.6(5)
C(16)-C(15)-C(20)	118.7(4)
C(16)-C(15)-C(14)	120.9(4)
C(20)-C(15)-C(14)	120.4(4)
C(15)-C(16)-C(17)	120.9(5)
C(15)-C(16)-H(16)	119.5
C(17)-C(16)-H(16)	119.5
C(18)-C(17)-C(16)	119.9(4)
C(18)-C(17)-H(17)	120.0
C(16)-C(17)-H(17)	120.0
O(1)-C(18)-C(17)	124.2(4)
O(1)-C(18)-C(19)	115.8(5)
C(17)-C(18)-C(19)	120.0(4)
C(18)-O(1)-C(21)	117.8(4)
C(20)-C(19)-C(18)	120.1(5)
C(20)-C(19)-H(19)	120.0

C(18)-C(19)-H(19)	120.0
C(19)-C(20)-C(15)	120.4(4)
C(19)-C(20)-H(20)	119.8
C(15)-C(20)-H(20)	119.8
O(1)-C(21)-C(22)	107.3(4)
O(1)-C(21)-H(21A)	110.3
C(22)-C(21)-H(21A)	110.3
O(1)-C(21)-H(21B)	110.3
C(22)-C(21)-H(21B)	110.3
H(21A)-C(21)-H(21B)	108.5
C(21)-C(22)-C(23)	113.5(4)
C(21)-C(22)-H(22A)	108.9
C(23)-C(22)-H(22A)	108.9
C(21)-C(22)-H(22B)	108.9
C(23)-C(22)-H(22B)	108.9
H(22A)-C(22)-H(22B)	107.7
C(24)-C(23)-C(22)	115.0(4)
C(24)-C(23)-H(23A)	108.5
C(22)-C(23)-H(23A)	108.5
C(24)-C(23)-H(23B)	108.5
C(22)-C(23)-H(23B)	108.5
H(23A)-C(23)-H(23B)	107.5
C(25)-C(24)-C(23)	114.6(4)
C(25)-C(24)-H(24A)	108.6
C(23)-C(24)-H(24A)	108.6
C(25)-C(24)-H(24B)	108.6
C(23)-C(24)-H(24B)	108.6
H(24A)-C(24)-H(24B)	107.6
C(24)-C(25)-C(26A)	132.4(6)
C(24)-C(25)-C(26B)	101.9(5)
C(24)-C(25)-H(25A)	104.1
C(26A)-C(25)-H(25A)	104.1
C(24)-C(25)-H(25B)	104.1
C(26A)-C(25)-H(25B)	104.1
H(25A)-C(25)-H(25B)	105.5
C(24)-C(25)-H(25C)	111.4
C(26B)-C(25)-H(25C)	111.4
C(24)-C(25)-H(25D)	111.4
C(26B)-C(25)-H(25D)	111.4

H(25C)-C(25)-H(25D)	109.3
C(25)-C(26A)-C(27A)	105.3(6)
C(25)-C(26A)-H(26A)	110.7
C(27A)-C(26A)-H(26A)	110.7
C(25)-C(26A)-H(26B)	110.7
C(27A)-C(26A)-H(26B)	110.7
H(26A)-C(26A)-H(26B)	108.8
C(26A)-C(27A)-C(28)	105.8(6)
C(26A)-C(27A)-H(27A)	110.6
C(28)-C(27A)-H(27A)	110.6
C(26A)-C(27A)-H(27B)	110.6
C(28)-C(27A)-H(27B)	110.6
H(27A)-C(27A)-H(27B)	108.7
C(27B)-C(26B)-C(25)	105.1(6)
C(27B)-C(26B)-H(26C)	110.7
C(25)-C(26B)-H(26C)	110.7
C(27B)-C(26B)-H(26D)	110.7
C(25)-C(26B)-H(26D)	110.7
H(26C)-C(26B)-H(26D)	108.8
C(26B)-C(27B)-C(28)	104.5(6)
C(26B)-C(27B)-H(27C)	110.9
C(28)-C(27B)-H(27C)	110.9
C(26B)-C(27B)-H(27D)	110.9
C(28)-C(27B)-H(27D)	110.9
H(27C)-C(27B)-H(27D)	108.9
C(29)-C(28)-C(27B)	97.3(5)
C(29)-C(28)-C(27A)	127.4(6)
C(29)-C(28)-H(28A)	105.5
C(27A)-C(28)-H(28A)	105.5
C(29)-C(28)-H(28B)	105.5
C(27A)-C(28)-H(28B)	105.5
H(28A)-C(28)-H(28B)	106.0
C(29)-C(28)-H(28C)	112.3
C(27B)-C(28)-H(28C)	112.3
C(29)-C(28)-H(28D)	112.3
C(27B)-C(28)-H(28D)	112.3
H(28C)-C(28)-H(28D)	109.9
C(30)-C(29)-C(28)	113.5(5)
C(30)-C(29)-H(29A)	108.9

C(28)-C(29)-H(29A)	108.9
C(30)-C(29)-H(29B)	108.9
C(28)-C(29)-H(29B)	108.9
H(29A)-C(29)-H(29B)	107.7
C(29)-C(30)-H(30A)	109.5
C(29)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
C(29)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
C(32)-C(31)-C(8)	177.6(5)
C(31)-C(32)-C(33)	178.4(4)
C(34)-C(33)-C(38)	117.5(4)
C(34)-C(33)-C(32)	121.3(4)
C(38)-C(33)-C(32)	121.2(4)
C(35)-C(34)-C(33)	120.7(4)
C(35)-C(34)-H(34)	119.6
C(33)-C(34)-H(34)	119.6
C(36)-C(35)-C(34)	120.4(4)
C(36)-C(35)-H(35)	119.8
C(34)-C(35)-H(35)	119.8
O(2)-C(36)-C(37)	116.5(4)
O(2)-C(36)-C(35)	124.0(4)
C(37)-C(36)-C(35)	119.5(4)
C(36)-O(2)-C(39)	117.6(3)
C(36)-C(37)-C(38)	120.2(4)
C(36)-C(37)-H(37)	119.9
C(38)-C(37)-H(37)	119.9
C(37)-C(38)-C(33)	121.6(4)
C(37)-C(38)-H(38)	119.2
C(33)-C(38)-H(38)	119.2
O(2)-C(39)-C(40)	108.6(3)
O(2)-C(39)-H(39A)	110.0
C(40)-C(39)-H(39A)	110.0
O(2)-C(39)-H(39B)	110.0
C(40)-C(39)-H(39B)	110.0
H(39A)-C(39)-H(39B)	108.3
C(41)-C(40)-C(39)	111.9(3)
C(41)-C(40)-H(40A)	109.2

C(39)-C(40)-H(40A)	109.2
C(41)-C(40)-H(40B)	109.2
C(39)-C(40)-H(40B)	109.2
H(40A)-C(40)-H(40B)	107.9
C(40)-C(41)-C(42)	114.2(3)
C(40)-C(41)-H(41A)	108.7
C(42)-C(41)-H(41A)	108.7
C(40)-C(41)-H(41B)	108.7
C(42)-C(41)-H(41B)	108.7
H(41A)-C(41)-H(41B)	107.6
C(43)-C(42)-C(41)	113.7(3)
C(43)-C(42)-H(42A)	108.8
C(41)-C(42)-H(42A)	108.8
C(43)-C(42)-H(42B)	108.8
C(41)-C(42)-H(42B)	108.8
H(42A)-C(42)-H(42B)	107.7
C(42)-C(43)-C(44)	114.1(3)
C(42)-C(43)-H(43A)	108.7
C(44)-C(43)-H(43A)	108.7
C(42)-C(43)-H(43B)	108.7
C(44)-C(43)-H(43B)	108.7
H(43A)-C(43)-H(43B)	107.6
C(45)-C(44)-C(43)	113.9(3)
C(45)-C(44)-H(44A)	108.8
C(43)-C(44)-H(44A)	108.8
C(45)-C(44)-H(44B)	108.8
C(43)-C(44)-H(44B)	108.8
H(44A)-C(44)-H(44B)	107.7
C(44)-C(45)-C(46)	113.3(3)
C(44)-C(45)-H(45A)	108.9
C(46)-C(45)-H(45A)	108.9
C(44)-C(45)-H(45B)	108.9
C(46)-C(45)-H(45B)	108.9
H(45A)-C(45)-H(45B)	107.7
C(47)-C(46)-C(45)	114.4(3)
C(47)-C(46)-H(46A)	108.7
C(45)-C(46)-H(46A)	108.7
C(47)-C(46)-H(46B)	108.7
C(45)-C(46)-H(46B)	108.7

H(46A)-C(46)-H(46B)	107.6
C(46)-C(47)-C(48)	112.8(3)
C(46)-C(47)-H(47A)	109.0
C(48)-C(47)-H(47A)	109.0
C(46)-C(47)-H(47B)	109.0
C(48)-C(47)-H(47B)	109.0
H(47A)-C(47)-H(47B)	107.8
C(47)-C(48)-H(48A)	109.5
C(47)-C(48)-H(48B)	109.5
H(48A)-C(48)-H(48B)	109.5
C(47)-C(48)-H(48C)	109.5
H(48A)-C(48)-H(48C)	109.5
H(48B)-C(48)-H(48C)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+3,-y,-z+1

Table 9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **6h**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	19(3)	24(3)	20(2)	-9(2)	3(2)	-12(2)
C(2)	16(3)	22(2)	17(2)	-6(2)	4(2)	-10(2)
C(3)	21(3)	22(3)	27(3)	-9(2)	6(2)	-8(2)
C(4)	27(3)	25(3)	20(2)	-10(2)	6(2)	-15(2)
C(5)	26(3)	25(3)	23(2)	-8(2)	2(2)	-10(2)
C(6)	19(3)	21(2)	23(2)	-9(2)	-1(2)	-10(2)
C(7)	22(3)	18(2)	25(2)	-5(2)	1(2)	-11(2)
C(8)	22(3)	22(2)	25(2)	-11(2)	1(2)	-11(2)
C(9)	34(3)	29(3)	27(2)	-11(2)	8(2)	-11(2)
C(10)	61(4)	44(3)	30(3)	-8(2)	16(3)	-10(3)
C(11)	58(4)	76(4)	27(3)	-19(2)	7(2)	-40(3)
C(12)	40(3)	38(3)	26(2)	-4(2)	6(2)	-11(3)
C(13)	23(3)	29(3)	22(2)	-10(2)	8(2)	-14(2)
C(14)	22(3)	30(3)	28(3)	-5(2)	-1(2)	-17(2)
C(15)	34(3)	29(3)	30(3)	-7(2)	-5(2)	-14(3)
C(16)	47(4)	31(3)	36(3)	-1(2)	-5(3)	-1(3)
C(17)	44(4)	42(3)	36(3)	4(3)	4(3)	-9(3)
C(18)	44(4)	34(3)	35(3)	3(3)	-9(3)	-14(3)
O(1)	44(2)	52(2)	43(2)	14(2)	-8(2)	-12(2)
C(19)	39(3)	41(3)	36(3)	4(2)	-3(3)	-5(3)
C(20)	35(3)	35(3)	32(3)	4(2)	-2(2)	-11(3)
C(21)	69(4)	63(4)	27(3)	9(3)	-8(3)	-26(3)
C(22)	66(4)	53(4)	45(3)	15(3)	-22(3)	-28(3)
C(23)	46(4)	48(3)	50(3)	10(3)	-12(3)	-16(3)
C(24)	49(4)	75(4)	35(3)	11(3)	-1(3)	4(4)
C(25)	83(5)	65(4)	35(3)	6(3)	7(3)	27(4)
C(26A)	44(5)	42(5)	36(3)	-6(3)	-10(3)	-14(4)
C(27A)	42(5)	44(5)	38(3)	-7(3)	-10(3)	-13(4)
C(26B)	46(5)	42(5)	37(3)	-5(3)	-7(3)	-10(4)
C(27B)	45(5)	44(5)	37(3)	-7(3)	-9(3)	-11(4)
C(28)	59(4)	97(5)	41(3)	-11(3)	-10(3)	16(4)
C(29)	68(5)	157(8)	70(5)	-49(5)	10(4)	-37(5)
C(30)	147(7)	68(5)	60(4)	1(3)	-8(4)	-20(5)
C(31)	28(3)	22(3)	20(2)	-6(2)	6(2)	-12(2)

C(32)	26(3)	24(3)	32(3)	-10(2)	6(2)	-12(2)
C(33)	24(3)	21(2)	31(2)	-12(2)	8(2)	-12(2)
C(34)	34(3)	25(3)	32(3)	-6(2)	2(2)	-11(2)
C(35)	34(3)	20(3)	31(3)	-3(2)	2(2)	-3(2)
C(36)	28(3)	19(3)	25(2)	-10(2)	8(2)	-11(2)
O(2)	24(2)	26(2)	31(2)	-5(1)	4(2)	-2(2)
C(37)	28(3)	27(3)	23(2)	-6(2)	6(2)	-9(2)
C(38)	32(3)	28(3)	32(3)	-6(2)	1(2)	-9(2)
C(39)	29(3)	21(3)	32(3)	-4(2)	4(2)	-10(2)
C(40)	31(3)	23(3)	32(3)	-9(2)	4(2)	-8(2)
C(41)	25(3)	29(3)	34(3)	-7(2)	1(2)	-12(2)
C(42)	20(3)	33(3)	30(2)	-8(2)	1(2)	-9(2)
C(43)	32(3)	30(3)	28(2)	-8(2)	-1(2)	-8(2)
C(44)	30(3)	26(3)	31(3)	-8(2)	-2(2)	-7(2)
C(45)	29(3)	28(3)	28(2)	-6(2)	1(2)	-14(2)
C(46)	28(3)	27(3)	27(2)	-3(2)	1(2)	-13(2)
C(47)	27(3)	31(3)	35(3)	-8(2)	-2(2)	-11(2)
C(48)	36(3)	32(3)	40(3)	-6(2)	-4(2)	-3(3)

Table 10. Below we give a chart which explain the information given in the following figure.

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
1	2	3	4	5	6	7	8	9	10

1) Structure Determinant color, as provided in Figure 3 in the manuscript.
2) The number of pairs, N, in the graphics window with that energy.
3) Symmetry operator joining the two molecules in the pair.
4) Distance between centers of mass of both molecules.
5) Level of theory at which the electron density is computed: B3LYP/6-31G(d,p) here.
6) Electrostatic contribution (kJ/mol).
7) Polarization contribution (kJ/mol).
8) Dispersion contribution (kJ/mol).
9) Repulsion contribution (kJ/mol).
10) Total energy (kJ/mol): This is the *sum of scaled components* (using the scale factors appropriate to the model as given below), but the *separate components are not scaled*.

Energy model	k_ele	K_pol	K_dis	K_rep
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.019	0.651	0.901	0.811

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	2	x, y, z	17.02	B3LYP/6-31G(d,p)	-1.1	-0.7	-17.0	1.4	-15.7
	2	x, y, z	17.99	B3LYP/6-31G(d,p)	-30.5	-9.6	-144.1	73.3	-107.7
	2	x, y, z	16.78	B3LYP/6-31G(d,p)	-10.0	-2.6	-53.2	32.2	-33.7
	2	x, y, z	30.35	B3LYP/6-31G(d,p)	-0.3	-0.2	-6.9	2.6	-4.6
	2	x, y, z	10.42	B3LYP/6-31G(d,p)	-20.5	-15.5	-225.3	106.7	-147.5
	2	x, y, z	26.31	B3LYP/6-31G(d,p)	0.6	-1.2	-37.9	11.9	-24.7
	2	x, y, z	19.34	B3LYP/6-31G(d,p)	-8.1	-4.7	-85.7	41.4	-55.0
	2	x, y, z	11.05	B3LYP/6-31G(d,p)	2.0	-1.0	-12.3	0.1	-9.6

Emission spectra of compound 6b-h in different solvents

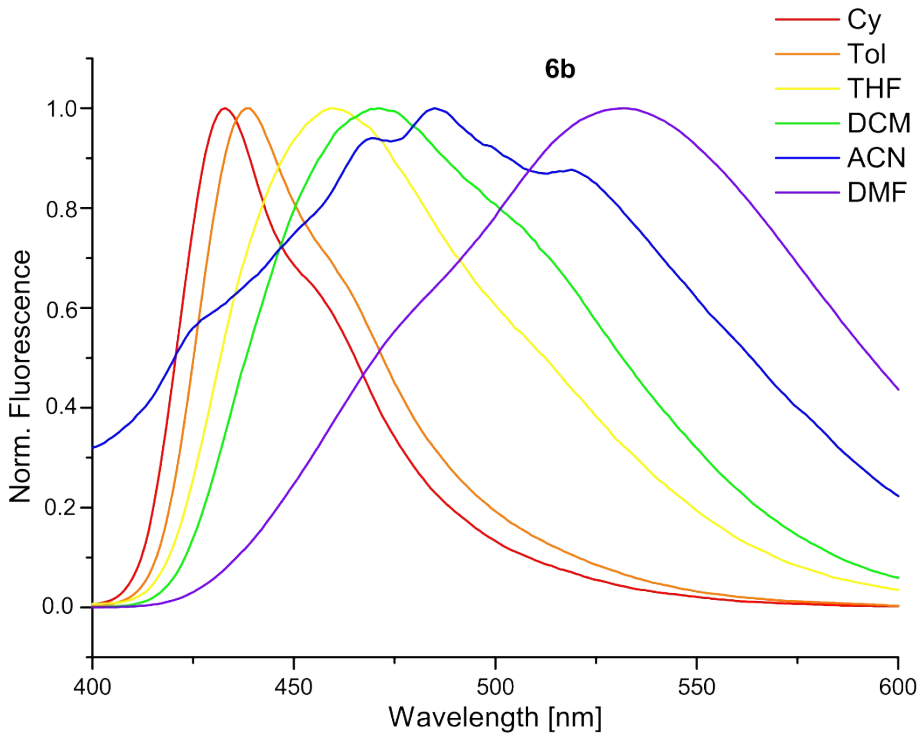

Diagram 1. Normalized fluorescence spectra of substituted pyrene derivative **6b** in different solvents at a concentration of 10^{-5} M excited at a wavelength of 340 nm.

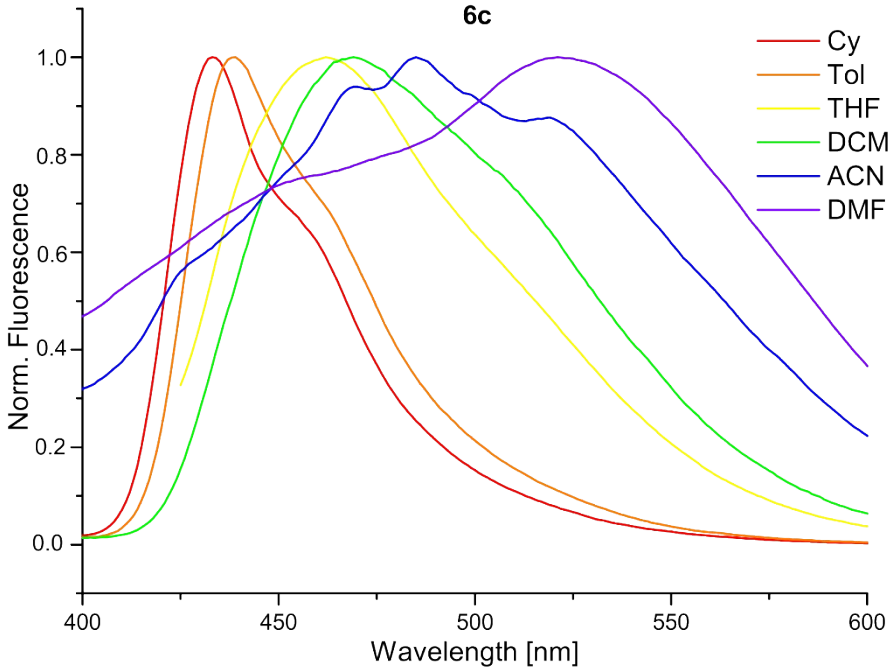

Diagram 2. Normalized fluorescence spectra of substituted pyrene derivative **6c** in different solvents at a concentration of 10^{-5} M excited at a wavelength of 340 nm.

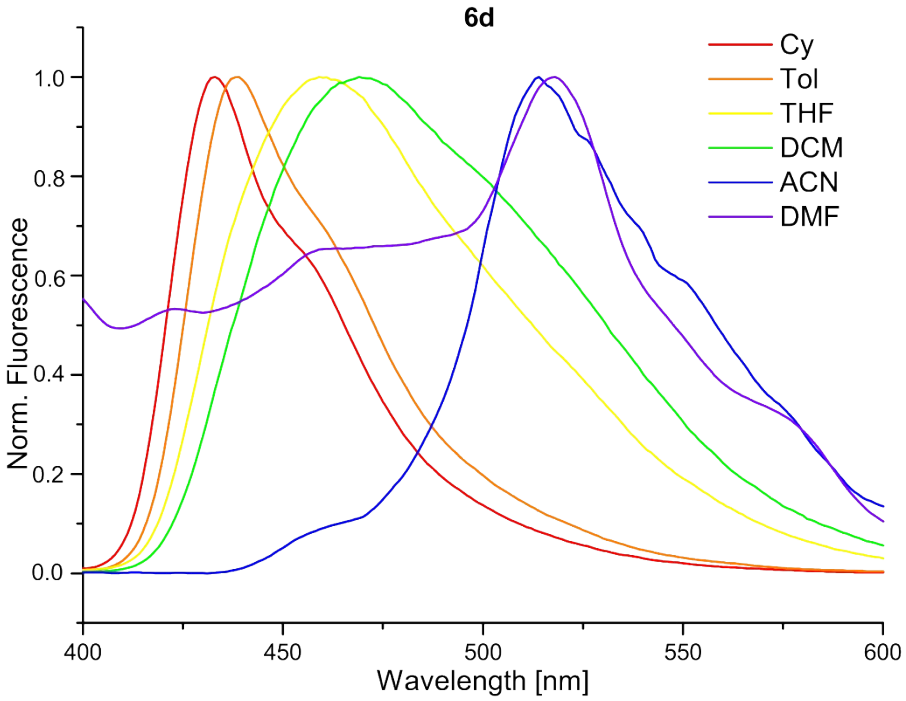

Diagram 3. Normalized fluorescence spectra of substituted pyrene derivative **6d** in different solvents at a concentration of 10^{-5} M excited at a wavelength of 340 nm.

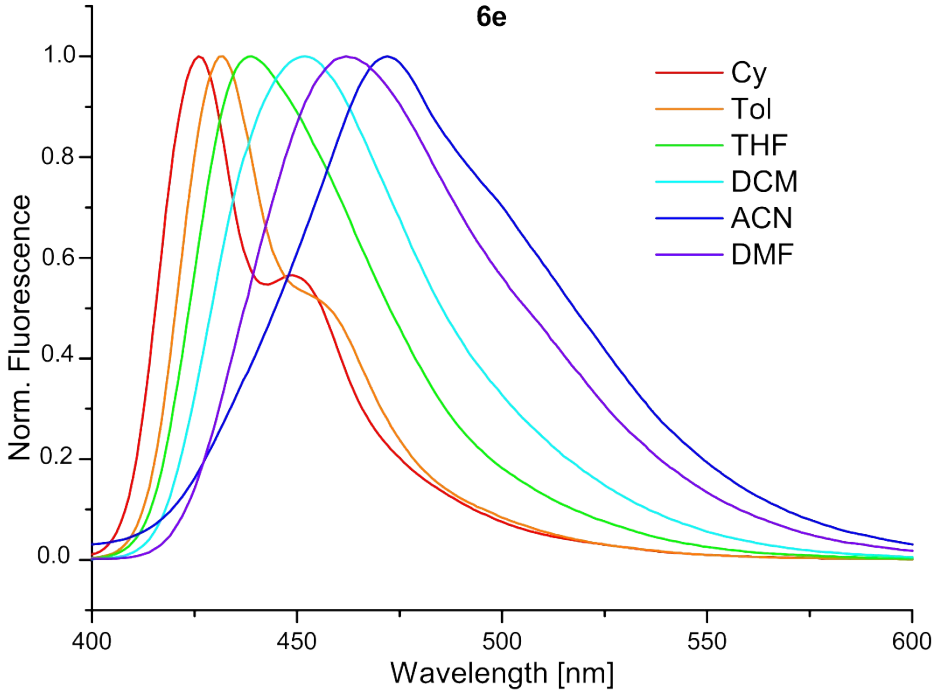

Diagram 4. Normalized fluorescence spectra of substituted pyrene derivative **6e** in different solvents at a concentration of 10^{-5} M excited at a wavelength of 340 nm.

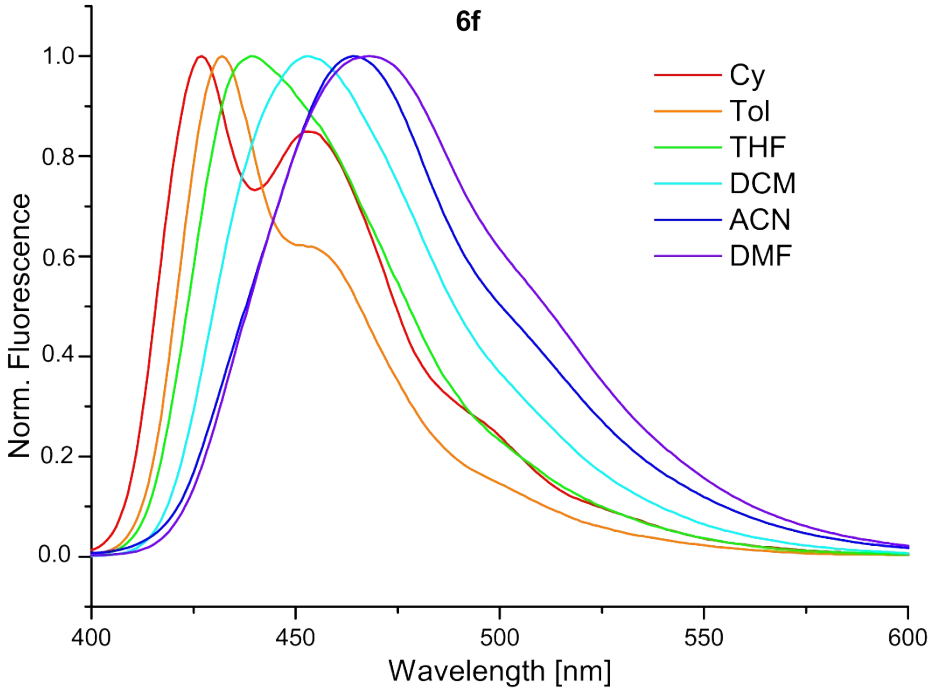

Diagram 5. Normalized fluorescence spectra of substituted pyrene derivative **6f** in different solvents at a concentration of 10^{-5} M excited at a wavelength of 340 nm.

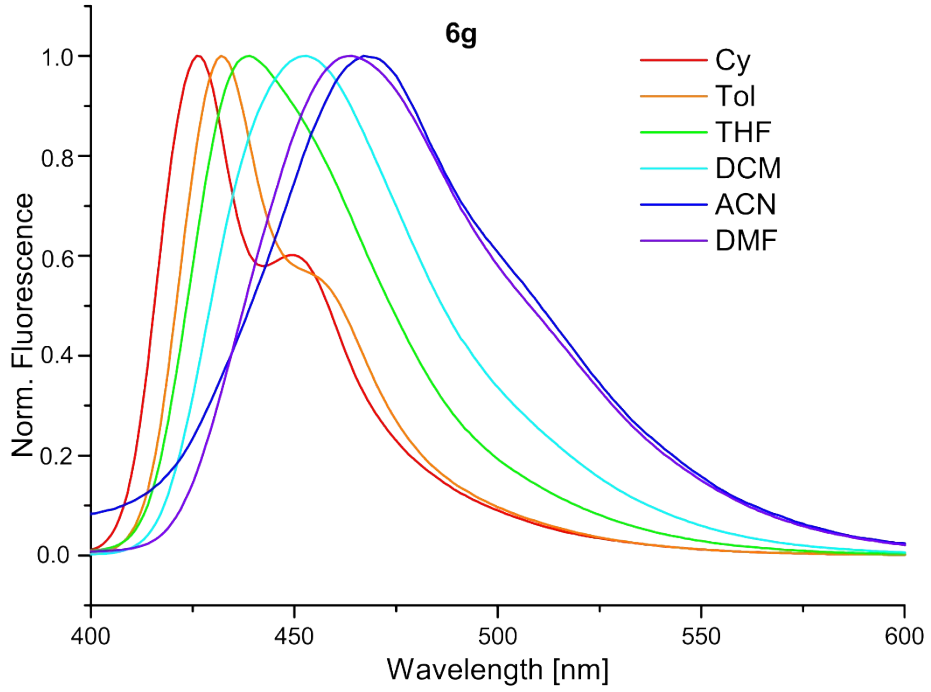

Diagram 6. Normalized fluorescence spectra of substituted pyrene derivative **6g** in different solvents at a concentration of 10^{-5} M excited at a wavelength of 340 nm.

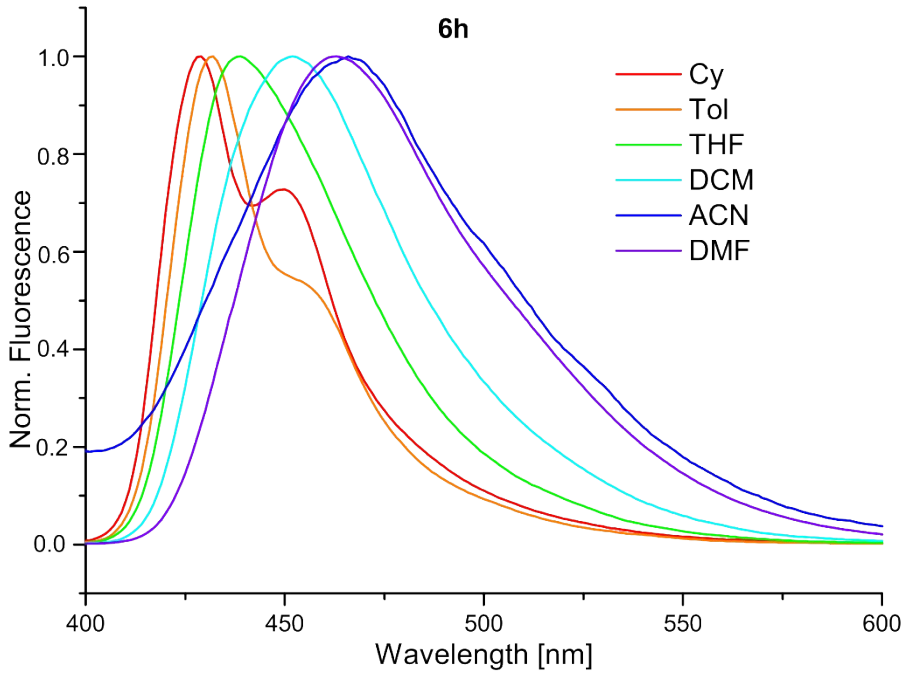

Diagram 7. Normalized fluorescence spectra of substituted pyrene derivative **6h** in different solvents at a concentration of 10^{-5} M excited at a wavelength of 340 nm.

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