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SUPPORTING INFORMATION

Title: Synthesis of Polysubstituted Pyrenes with Tuned Spectroscopic Properties for Two-Point Attachment
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Ref. No.: O200600256

Experimental Section

General. ^{1}H (BRUKER AVANCE300, 300.18 MHz) and ^{13}C NMR (BRUKER AVANCE300 or BRUKER DRX500 instruments) spectra were collected in $CDCl_3$ and DMSO and calibrated using internal signals of remaining $CHCl_3$ (7.26, ^{1}H and 77.16 ^{13}C) or DMSO (2.52, ^{1}H and 39.52, ^{13}C).[1] Absorption spectra were collected on Perkin Elmer UV/Vis spectrometer Lambda 16 in CH_2Cl_2 (**2-7**, **9**) and H_2O (**8**). Fluorescence spectra were collected on Varian Cary Eclipse instrument. Modified pyrenes were analyzed by EI-MS (Micromass Autospec Q, Waters; at 70 eV ionization energy, positive ionization mode), either in high (HR) or low resolution (LR). Positive mode ESI-MS analysis was done on Applied Biosystems/Sciex QSTAR Pulsar (hybrid quadrupole TOF mass spectrometer) with the internal calibration using cesium iodide and reserpine. Calculated exact mass is mentioned as calcd in the experimental part.

All operations involving Pd-catalyzed couplings were carried out under argon. All starting reagents and solvents were obtained from Fluka, Aldrich or Acros. Compound **1** was obtained according to literature procedure.[2]

Compounds for fluorescence studies were purified by column chromatography or/and recrystallization from appropriate solvents.

Synthesis.

Pyrene-1,8-dicarboxylic acid dimethyl ester (2). A mixture of 0.725 g (2.5 mmol) of pyrene diacid **1**, CsF (1.139 g, 1.5 mmol) and MeI (1.0 mL) was stirred in DMF (25 ml) at rt overnight. After that the mixture was poured into water (75 mL). The precipitate formed was filtered off, washed with water and small amount of ethanol, and dried to give a yellow solid (0.720 g, 91%): ^{1}H NMR (DMSO-d^8) δ 4.08 (s, 6H, CH_3), 8.43 (s, 2H, pyrene), 8.50 (d, 2H, pyrene), 8.67 (d, 2H, pyrene), 9.23 (s, 2H, pyrene); LR EI-MS obsd 318, 287, 259, 228; calcd 318.0892 ($C_{20}H_{14}O_4$); HR ESI-TOF-MS obsd 319,0975, calcd 319.0970 ($C_{20}H_{15}O_4$); λ_{abs} (CH_2Cl_2) 231(sh), 245, 275 (sh), 286, 341(sh), 358, 375 nm; FC (CH_2Cl_2) 393, 414, 425, 438, 525 nm.

Note: use of Na_2CO_3 instead of CsF gave a similar result (89 % yield).

3-Nitro-pyrene-1,8-dicarboxylic acid dimethyl ester (3). A suspension of bis-methyl ester pyrene **2** (0.9540 g, 3.0 mmol) in acetic anhydride (5 mL) was treated with a nitric acid stock solution (2.0 mL, 1.5 eqv.) at 70 °C, and the resulting mixture was stirred for 3 h at 70 °C. Then it was cooled down and EtOH was added to precipitate the product. It was washed with EtOH and dried to give a crude material (0.8546 g). Two recrystallizations from and 110 mL respectively) followed to get yellow crystalls (0.6216 g, 57%): ^{1}H NMR ($CDCl_3$) δ 4.145 (s, 3H, CH_3), 4.152 benzene (140 (s, 3H, CH_3), 8.40 (m-'t', 2H), 8.75 ('d', 1H), 8.92 ('d', 1H), 9.29 (s, 1H), 9.47 (m, 2H); LR EI-MS obsd 363, 333, 318, 302, 287, 274; calcd 363.0743 ($C_{20}H_{13}NO_6$); HR ESI-TOF-MS obsd 364.0834, calcd 364.0821 ($C_{20}H_{14}NO_6$); λ_{abs} (CH_2Cl_2) 236, 289, 364(sh), 385, 405(sh) nm; FC (CH_2Cl_2) 410, 430, 465 nm.

Note: stock solution was prepared by solving 1.05 mL of HNO_3 in 10 mL of acetic anhydride

3,6-Dibromo-pyrene-1,8-dicarboxylic acid dimethyl ester (4). Dimethyl ester pyrene **1** (1.9239 g, 6.04 mmol) was disdissolved in nitrobenzene (30 mL) at 60 °C and the bromine stock solution (9 mL) was added. The mixture was reacted at 60 °C for 1 h to give a white precipitate. Then the reaction mixture was cooled down to rt and kept one more hour at rt to achieve a complete precipitation of bisbromo compound. The precipitate was filtered off, washed with ethanol (50 mL) and dried to give the product (2.3711 g, 83%): ^{1}H NMR ($CDCl_3$) δ 4.12 (s, 6H, CH_3), 8.69 (s, 2H), 8.93 (s, 2H), 9.31 (s, 2H); LR EI-MS obsd 476, 445, 432, 417, 399; calcd 473.9102 ($C_{20}H_{12}Br_2O_4$); HR EI-MS obsd 473.9118, calcd 473.9102 ($C_{20}H_{12}Br_2O_4$); λ_{abs} (CH_2Cl_2) 234(sh), 250, 282(sh), 293, 352(sh), 373, 400 nm; FC (CH_2Cl_2) 419, 442, 472 nm.

Note: 1) stock solution was prepared by solving of bromine (0.8 mL) in nitrobenzene (10 mL); 2) white precipitate formed upon 5-15 minutes of reaction, but anyway it was kept 1 h at reaction temperature.

3,6-Bis-(3-nitro-phenyl)-pyrene-1,8-dicarboxylic acid dimethyl ester (5). Bis-bromo pyrene **4** (0.0560 g, 0.12 mmol) was dissolved in DMF (10 mL) and THF (2 mL) at 100 °C. Boronic component (0.0584 g, 0.35 mmol), $Pd(PPh_3)_4$ (0.016 g, 13.8 μmol, 5.8 mol % of Br group) and K_2CO_3 (0.065 g, 0.470 mmol) were added and reaction mixture was stirred overnight at 100 ºC under argon. Resulting mixture was cooled down to rt, mixed with water and and extracted three times with $CHCl_3$ (3x25 mL). Organic extract was washed with $NaHCO_3$-water (6-7 times, 30-50 mL each time) and dried (Na_2SO_4). TLC ($CHCl_3$-MeOH, 100:3) showed a new product formation. Crystallization of product occurred upon reducing the solvent volume (1 mL). Prodcut was filtered off, recrystalized from $CHCl_3$-cyclohexane and dried to give a yellow solid (0.0460 g, 70%): ^{1}H NMR ($CDCl_3$) δ 4.14 (s, 6H, CH_3), 7.76 (m-'t', 2H, nitro-Ph), 7.96 (m-'dt', 2H, nitro-Ph), 8.13 (s, 2H, pyrene), 8.38 (m-'ddd', 2H, nitro-Ph), 8.50 (m-'t', 2H, nitro-Ph), 8.68 (s, 2H, pyrene), 9.46 (s, 2H, pyrene); LR EI-MS obsd 560; calcd 560.1220 ($C_{32}H_{20}N_2O_8$); HR EI- MS obsd 560.1215, calcd 560.1220 ($C_{32}H_{20}N_2O_8$); λ_{abs} (CH_2Cl_2) 248(sh), 283(sh), 295, 350(sh), 375, 396 nm; FC (CH_2Cl_2) very low fluorescence even at 10^{-6} M, intramolecular quenching occurs.

3,6-Di-pyridin-3-yl-pyrene-1,8-dicarboxylic acid dimethyl ester (6). Bis-bromo pyrene **4** (0.1683 g, 0.353 mmol) was solved in DMF (53 mL) and THF (7 mL) at 100 °C. Then boronic component (0.2178 g, 1.062 mmol, 1.5 eqv. per Br), $Pd(PPh_3)_4$ (0.041 g, 35.5 μmol, 5 mol % of Br group) and K_2CO_3 (0.192 g, 1.389 mmol) were added and the reaction mixture was stirred under argon at 100 ºC overnight. Then it was cooled down and extracted two times with $CHCl_3$ (2x70 mL), washed with $NaHCO_3$-water and dried (Na_2SO_4). TLC ($CHCl_3$-MeOH, 100:3) showed a new product formation. Precipitate formed upon a slow evaporation of solution at low pressure. Product was filtered and dried. Additional amount of product was obtained by adding of MeOH to the mother solution and evaporating of resulted mixture till precipitation started to occur. Both solid materials were combined (0.1140 g; 68%): ^{1}H NMR ($CDCl_3$) δ 4.13 (s, 6H, CH_3), 7.52 (m-'ddd', 2H, pyridine), 7.94 (m-'ddd', 2H, pyridine), 8.16 (s, 2H, pyrene), 8.66 (s, 2H, pyrene), 8.77 (m-'dd', 2H, pyridine), 8.88 (m-'dd', 2H, pyridine), 9.44 (s, 2H, pyrene); LR EI-MS obsd 472, 277;

calcd 472.1423 ($C_{30}H_{20}N_2O_4$); HR ESI-TOF-MS obsd 473.1501, calcd 473.1501 ($C_{30}H_{21}N_2O_4$); λ_{abs} (CH_2Cl_2) 248, 284(sh), 296, 378, 397 nm; FC (CH_2Cl_2) 425, 435, 454 nm.

3,6-Bis-[(triisopropylsilanyl)-ethynyl]-pyrene-1,8-dicarboxylic acid dimethyl ester (7). Bis-bromo pyrene **4** (0.2385 g, 0.50 mmol), $Pd(PPh_3)_2Cl_2$ (0.018 g, 25 µmol, 1 mol % of ethyne group) and CuI (2.38 mg, 12.5 µmol, 0.5 mol % of Pd) were loaded into the flask. Et_3N (3 mL) and THF (6 mL) were added and triisopropylsililacetylene (0.561 mL, ~2.5 mmol) was added in 5 minutes. The resulting mixture was stirred at 70 °C overnight. It was filtered, washed with ethylacetate, and solvents were evaporated. Crude product was purified by chromatography (SiO_2, 20 g, 1 cm column, $CHCl_3$-hexanes, 1:1, then $CHCl_3$) to give the desired compound as yellow needles (0.2699 g, 87%): ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 42H, TIPS), 4.12 (s, 6H, CH_3), 8.78 (s, 2H), 8.83 (s, 2H), 9.28 (s, 2H); LR EI-MS obsd 678; calcd 678.3561 ($C_{42}H_{54}O_4Si_2$); HR ESI-TOF-MS obsd 701.3440, calcd 701.3458 ($C_{42}H_{54}O_4NaSi_2$); λ_{abs} (CH_2Cl_2) 248, 293, 306, 380(sh), 400, 425 nm; FC (CH_2Cl_2) 443, 470, 480, 565 nm.

3,6-Bis-(1-methyl-pyridin-3-yl)-pyrene-1,8-dicarboxylic acid dimethyl ester, bis iodide (8): Bis-pyridine substituted pyrene **6** (15.6 mg, 0.033 mmol) was mixed with DMF (1 mL) and MeI (0.1 mL, excess) in a plastic tube. The resulting mixture was heated in a sealed tube for 2.5 h at 60 °C. It was cooled down, and acetone (2 mL) was added to induce the precipitation of methylated derivative. The precipitate was washed with acetone to take off the DMF (shaking-centrifugation, 2 times), filtered and dried to give product with an I^- as counterions, yellow solid (24.20 mg, 97 %): ^{1}H NMR (DMSO) δ 4.13 (s, 6H, O-CH_3), 4.50 (s, 6H, N-CH_3), 8.32 (s, 2H, pyrene), 8.38 (m-‘dd’, 2H, pyridinium), 8.82 (s, 2H, pyrene), 8.88 (’d’, 2H, pyridinium), 9.20 (’d’, 2H, pyridinium), 9.38 (s, 2H, pyrene), 9.49 (‘s’, 2H, pyridinium); LR EI-MS obsd 500, 486, 472; calcd 755.9982 ($C_{32}H_{26}I_2N_2O_4$) and (502.1893 ($C_{32}H_{26}N_2O_4$); HR ESI-TOF-MS obsd 502.1887, calcd (502.1893 ($C_{32}H_{26}N_2O_4$); λ_{abs} (H_2O) 291, 386 nm; FC (H_2O) 425, 525 nm.

Note: Use of acetonitril as a solvent with the same work up procedure gave a similar result.

3,6-Diethynyl-pyrene-1,8-dicarboxylic acid dimethyl ester (9). TBAF on SiO_2 (0.4 g; 1.1 mmol F^-/g) was added to the solution of bis-tips pyrene **7** (0.135 g, 0.20 mmol) in CH_2Cl_2-THF (7 mL, 50:1). The resulting mixture was stirred at rt for 20 min. It was filtered through the membrane filter (0.45 µm) and the silica was washed with an additional amount of CH_2Cl_2-THF (50:1, 15 mL). Hexane was added (20 mL) and the mixture of solvents was evaporated at reduced pressure. Product started to crystallize upon reduction of the solvent volume. Product was filtered off and dried (0.061 g, 84%): ^{1}H NMR ($CDCl_3$) δ 3.70 (s, 2H, ethyne), 4.12 (s, 6H, CH_3), 8.80 (s, 2H), 8.85 (s, 2H), 9.34 (s, 2H); LR EI-MS obsd 366, 335, 307, 276, 248; calcd 366.0892 ($C_{24}H_{14}O_4$); HR EI- MS obsd 366.0891, calcd 366.0892 ($C_{24}H_{14}O_4$); λ_{abs} (CH_2Cl_2) 248(sh), 283(sh), 295, 350(sh), 375, 396 nm; FC (CH_2Cl_2) 425, 451, 480, 570 nm.

Fluorescence.

Fluorescence spectra were recorded at a concentration range of $2\cdot10^{-6}$ – $2\cdot10^{-2}$ M in CH_2Cl_2. If 10^{-2} M concentration was not reachable, the saturated solution was used instead. The usual procedure consisted in preparation of pyrene stock solution ($2\cdot10^{-3}$ M and adjusting of required concentration; $2\cdot10^{-2}$ M or saturated solutions were prepared separately). Spectra were collected with a set of excitation and emission slit widths [5, 5; 2.5, 2.5; etc (ex; em respectively) which are mentioned in the brackets, see **S12 – S19**) and were not corrected and normalized. Whenever possible, spectra of compounds **2-9** were additionally collected in cyclohexane and CH_3CN. Because solubility of some compounds was limited in these solvents, and spectra collected in the available concentration range showed no significant differences compared to dichloromethane solutions, they are not presented here. Deoxygenating of solutions by Ar gave an increase of intensity (1.02 – 1.20 times) for diluted solutions (10^{-6} – 10^{-4} M) and almost no change were observed for more concentrated solutions. These data are not presented here for simplicity (for one representative example see Figure S9). Therefore spectra collected in CH_2Cl_2 were chosen to represent the picture of fluorescence properties of synthesized compounds (see figures **S12 – S19**).

Absorption spectra for quantum yield determination were collected using a Varian Cary 100 Bio UV-Vis spectrophotometer with a temperature controller at 20 ºC. Fluorescence spectra were collected on Varian Cary Eclipse fluorescence instrument with a temperature controller at 20 ºC. The fluorescence quantum yields were determined via comparative method using well characterazed standarts.[3] Pyrene derivatives samples were prepared in 1 cm pathlength quartz cells with absorbance < 0.05 at the wavelength of excitation in order to achieve uniform illumination across the sample and with absorbance < 0.1 at all wavelengths in the emission scan in order to avoid the inner-filter effect.[3] The fluorescence quantum yields were measured in cyclohexane using antracene (Antracene OEKANAL, Riedel-deHaen) and diphenylanthracene (9,10-Diphenylanthracene OEKANAL, Riedel-deHaen). $\Phi_f = 0.90$ for diphenylantracene and $\Phi_f = 0.36$ for anthracene in cyclohexane were used as standarts.[3b,3c]

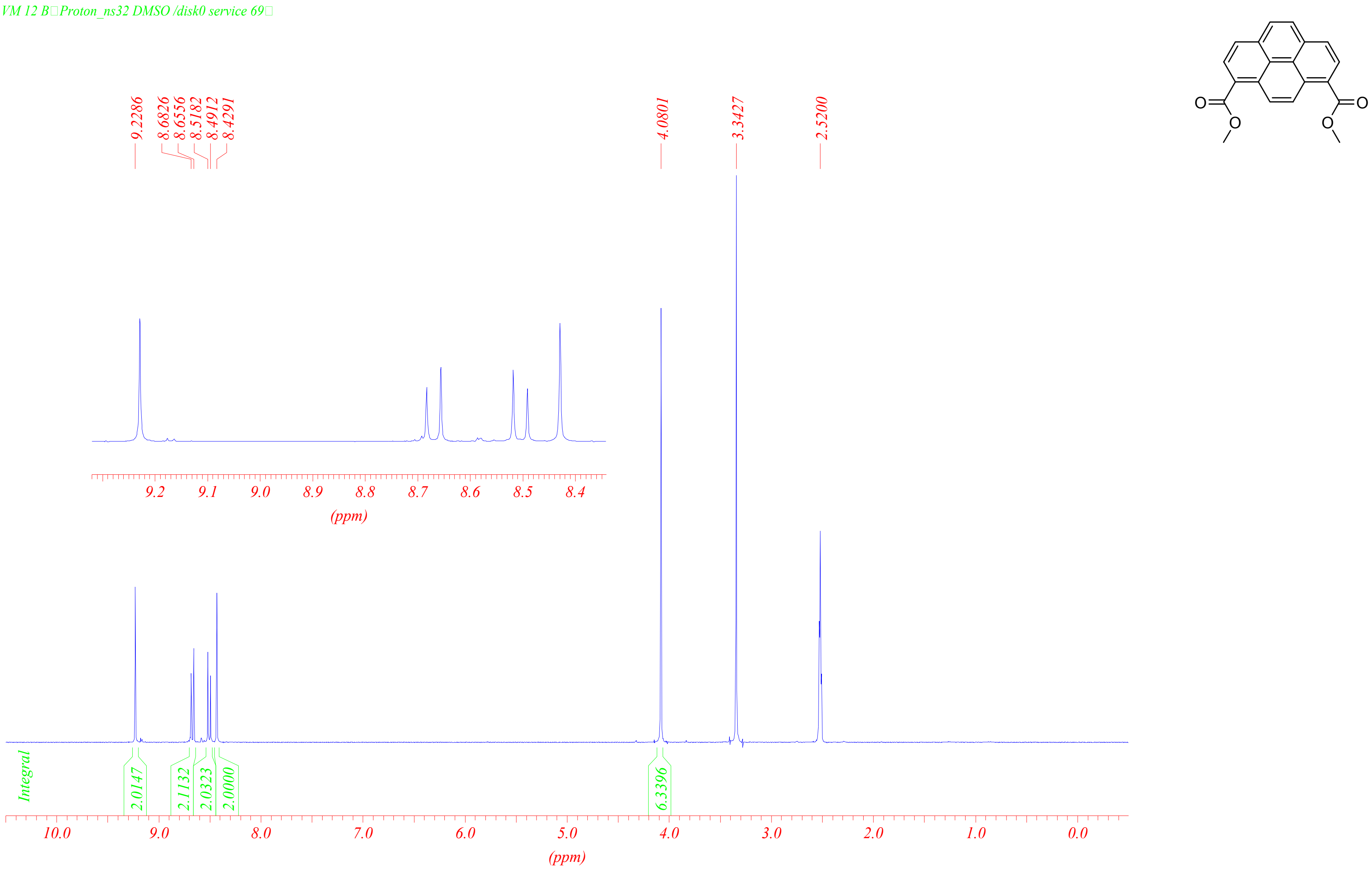


Figure S1. NMR of bis-ester pyrene **2** in DMSO.

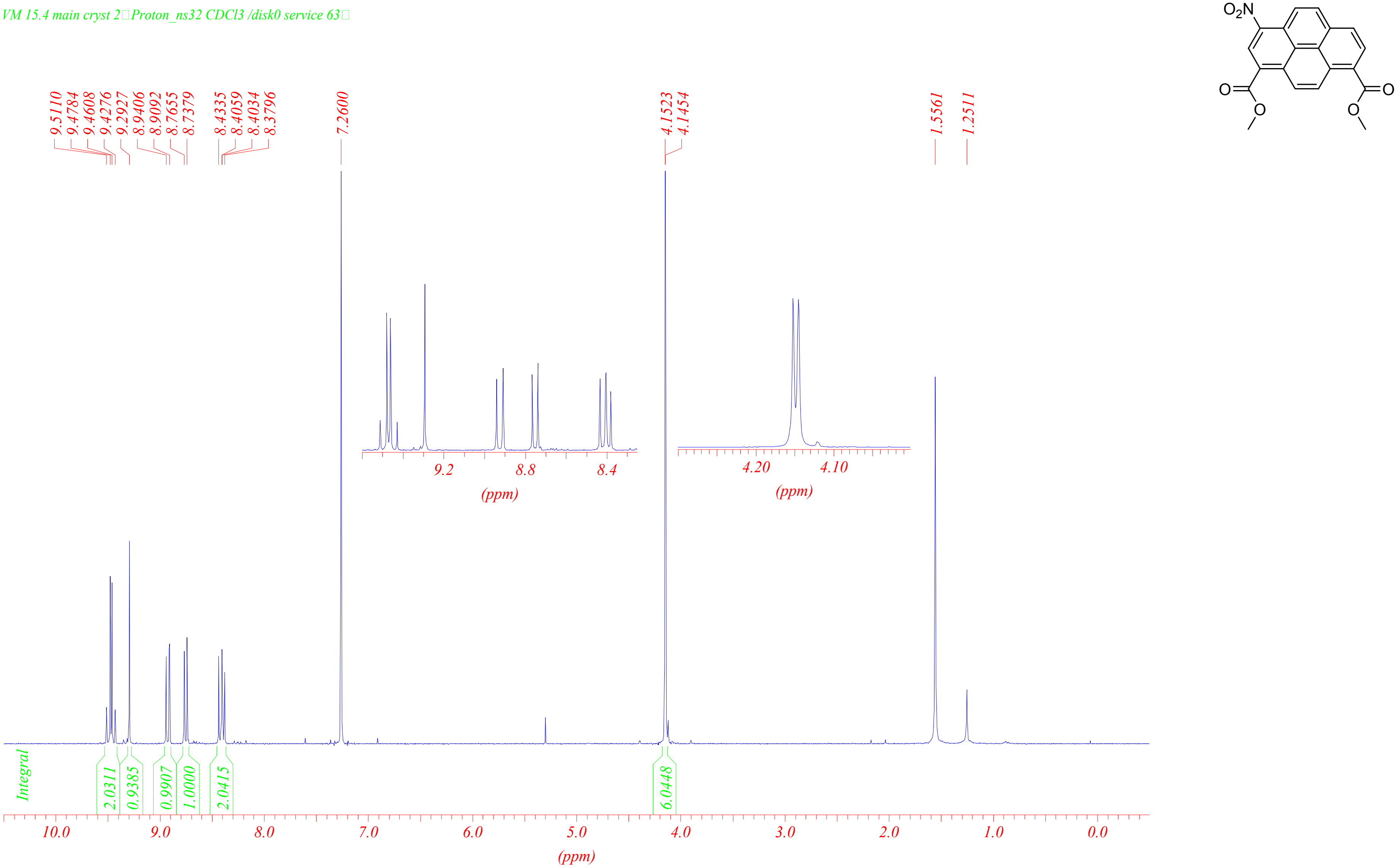


Figure S2. NMR of mononitropyrene **3** in $CDCl_3$.

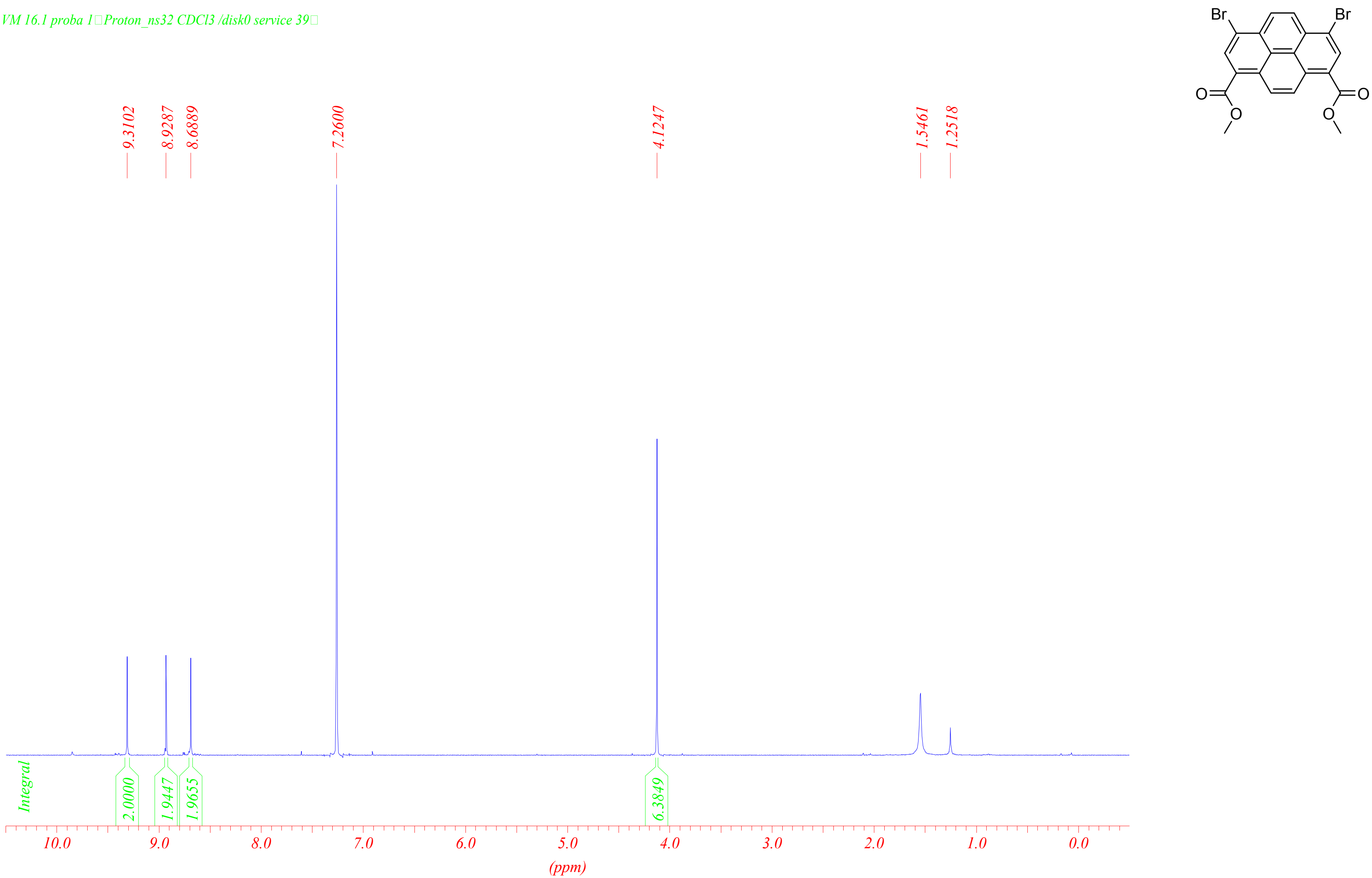


Figure S3. NMR of bis-bromo pyrene **4** in $CDCl_3$.

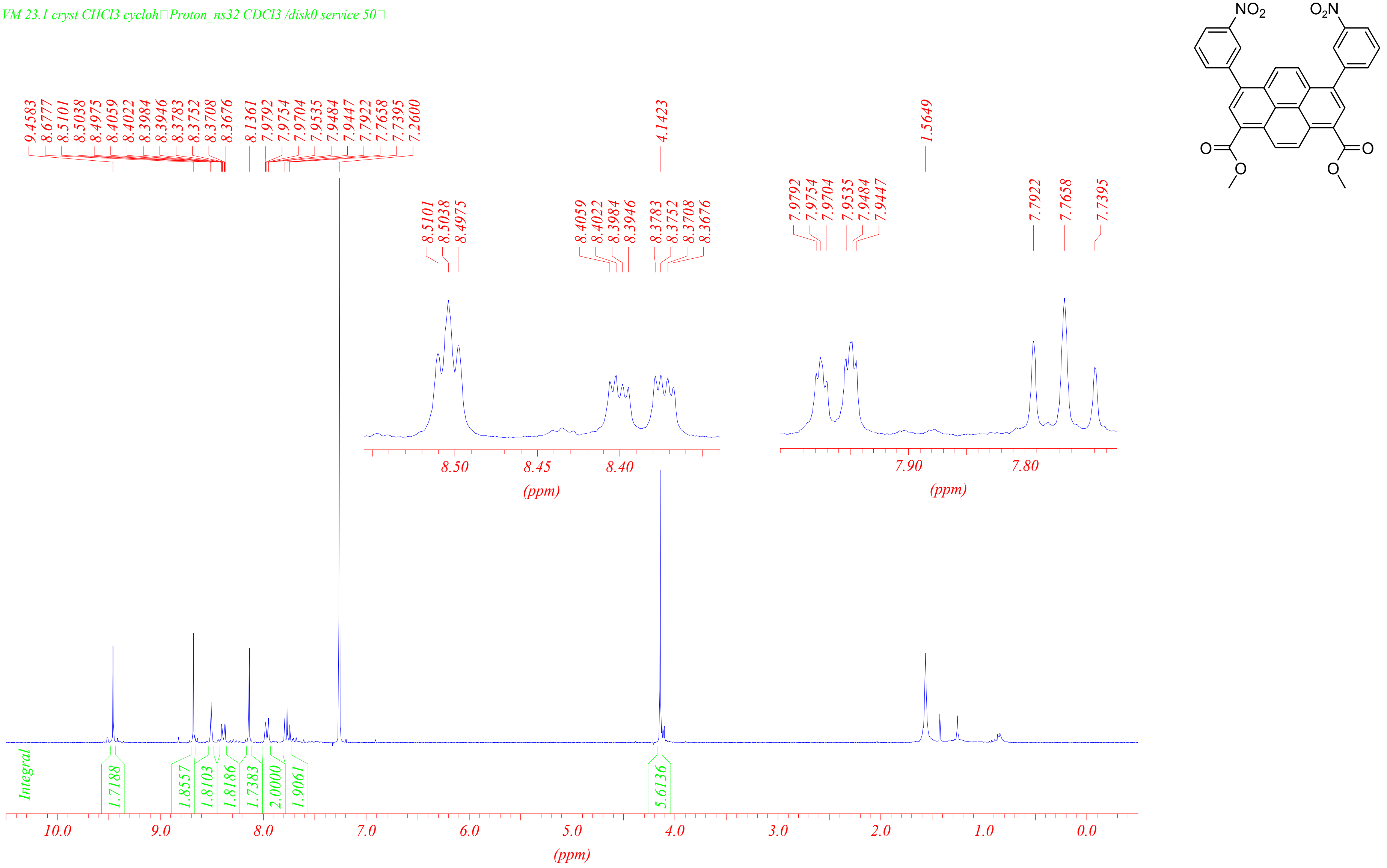


Figure S4. NMR of bis-nitrophenyl pyrene **5** in $CDCl_3$.

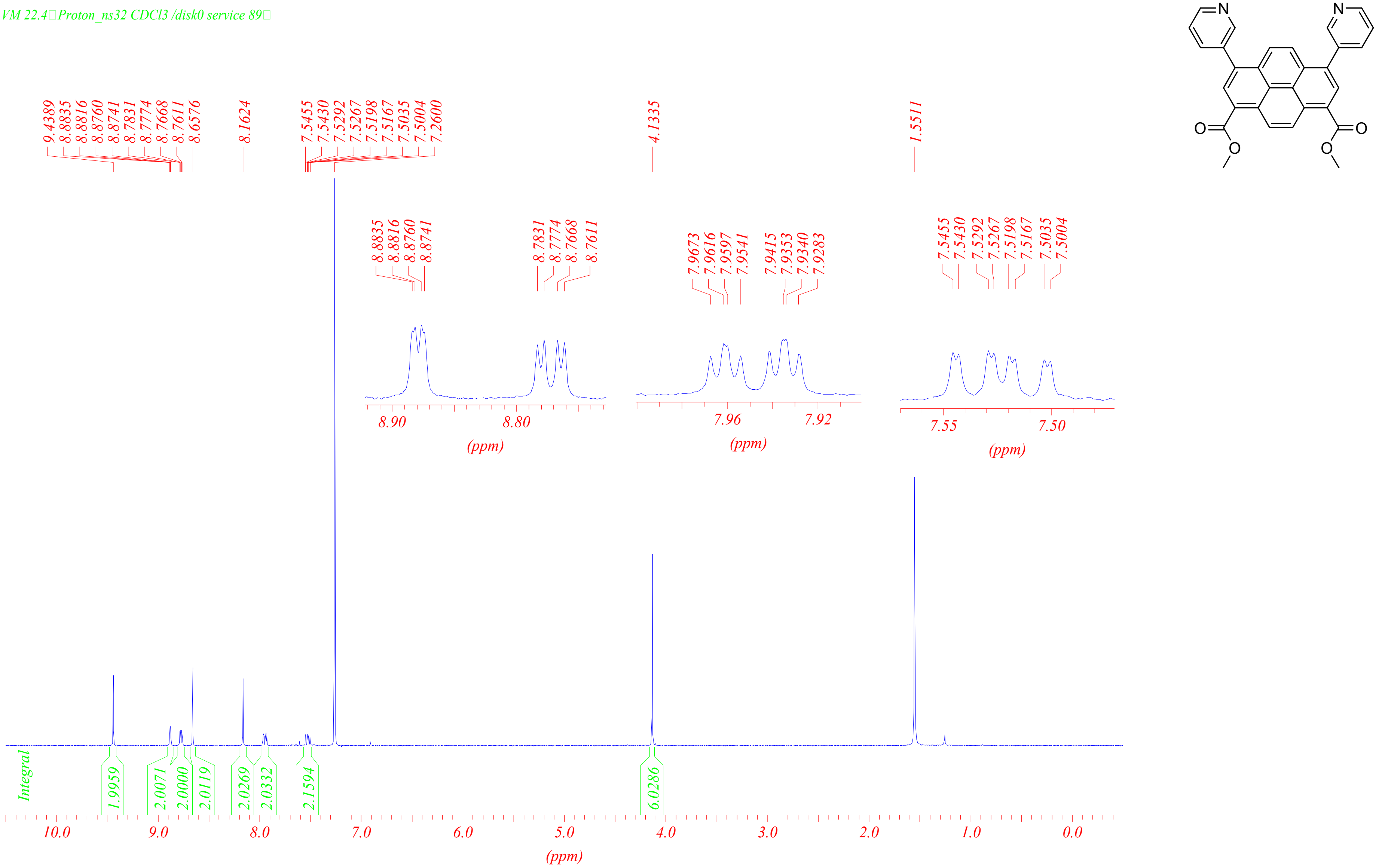


Figure S5. NMR of bis-pyridine pyrene **6** in $CDCl_3$.

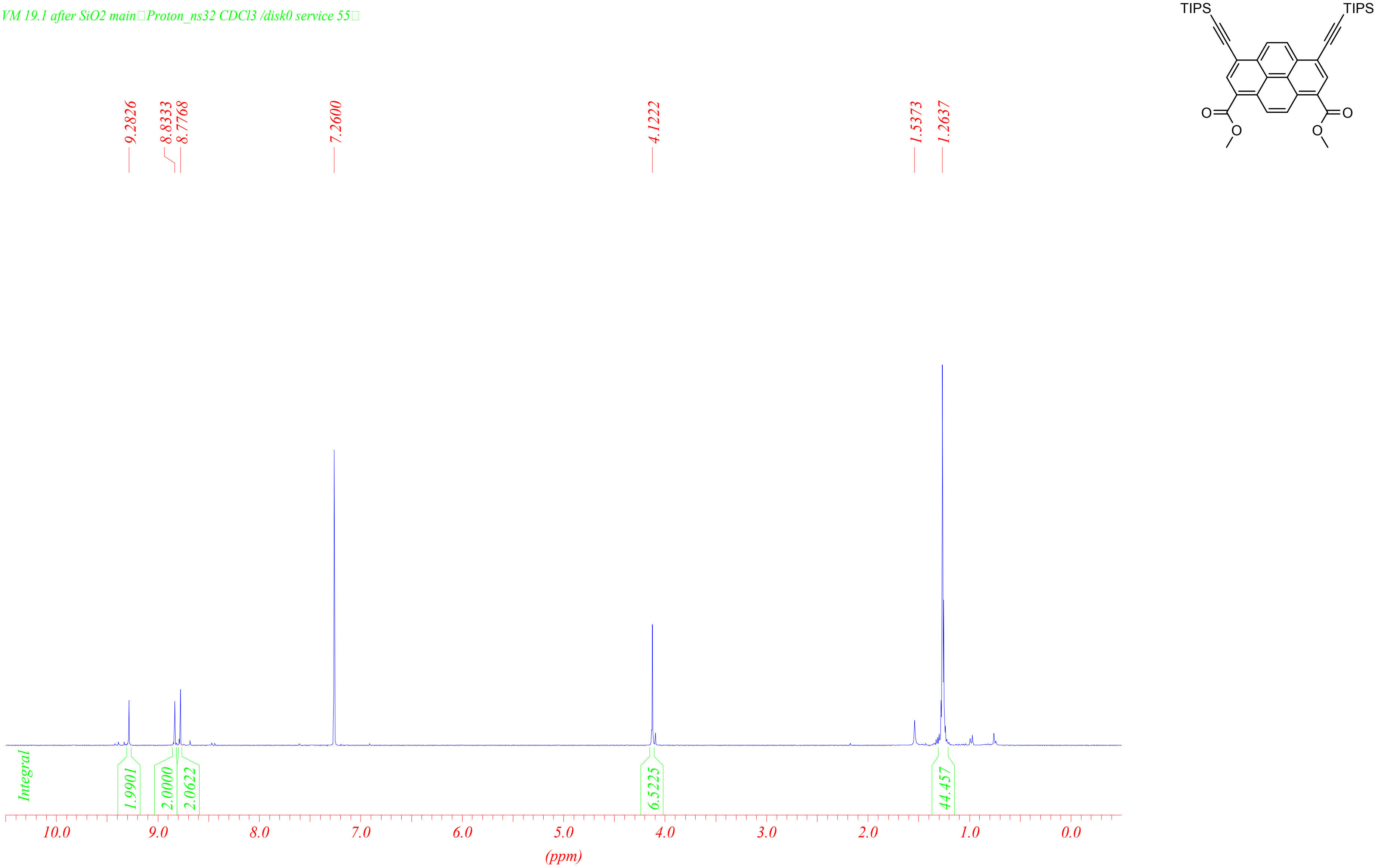


Figure S6. NMR of bis-ethynetips pyrene **7** in $CDCl_3$.

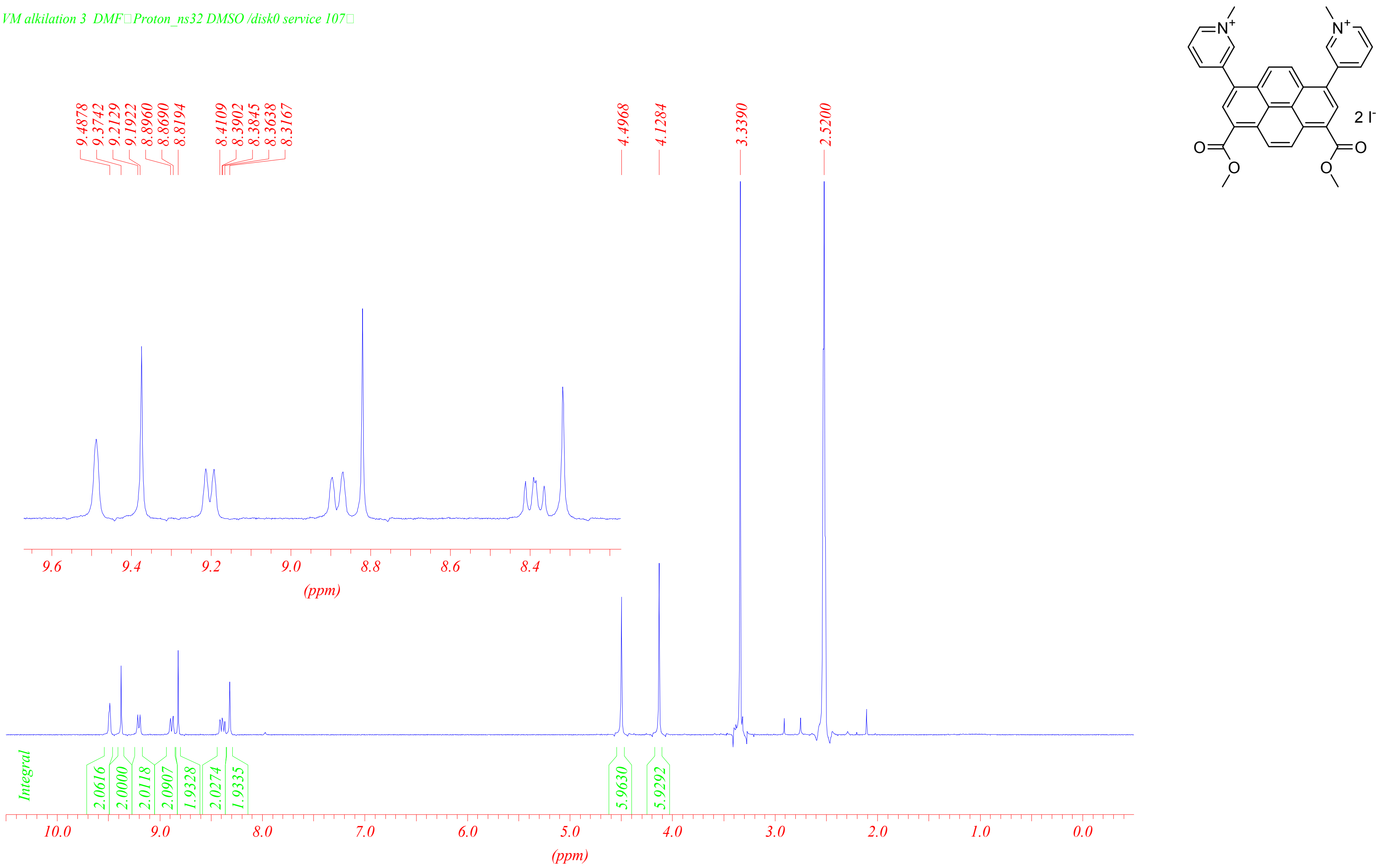
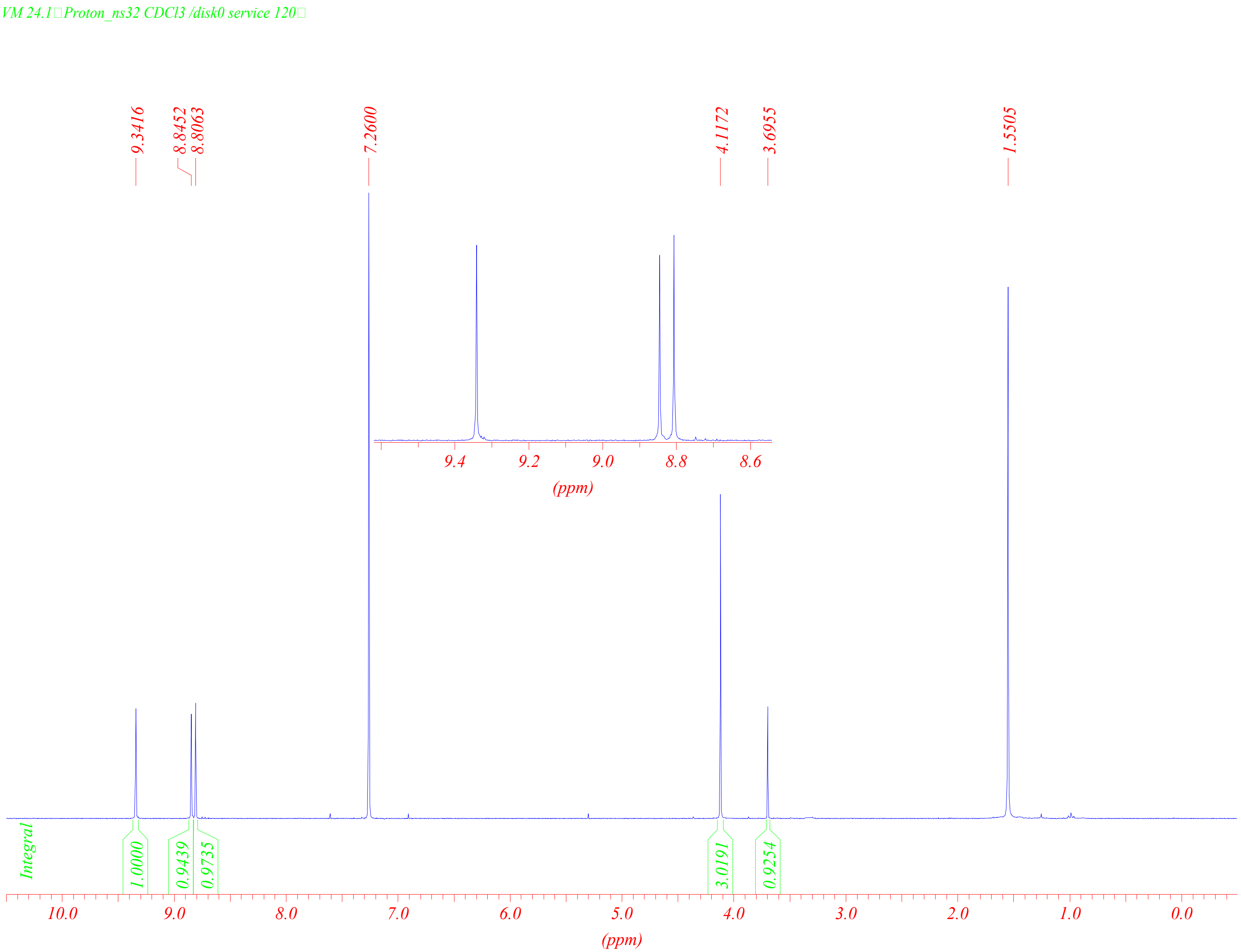


Figure S7. NMR of bis-pyridinium pyrene **8** in DMSO.



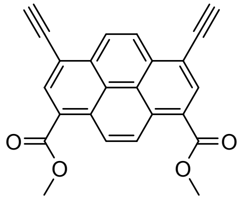
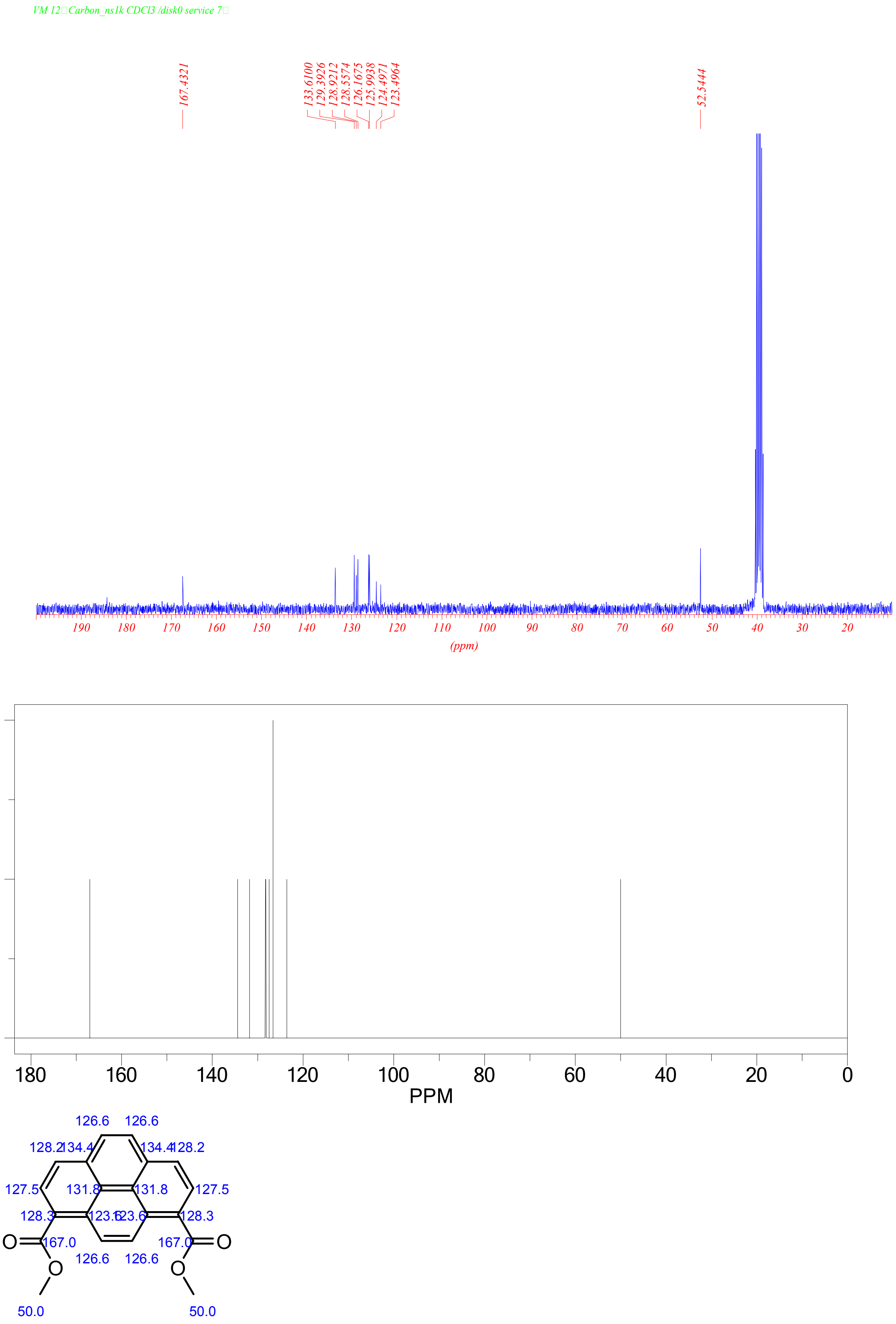


Figure S8. NMR of bis-ethyne pyrene **9** in $CDCl_3$.

Figure S9. ^{13}C NMR of bis-ester pyrene **2** in DMSO.



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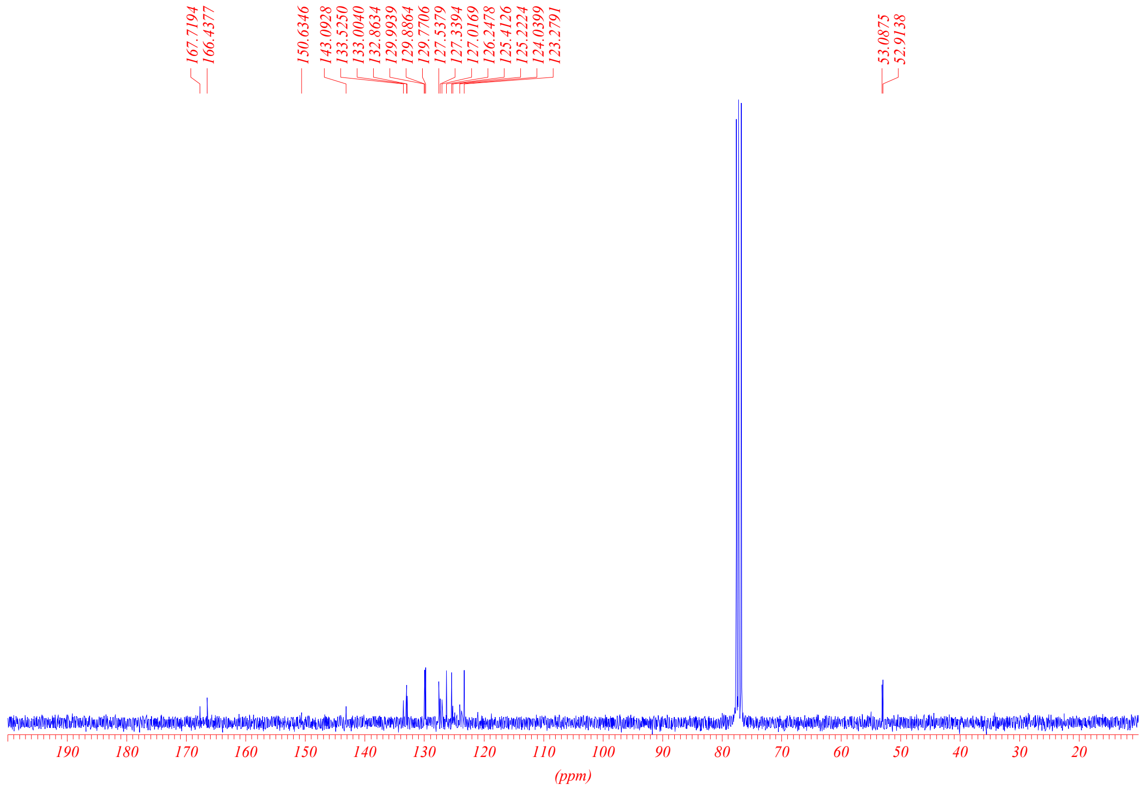
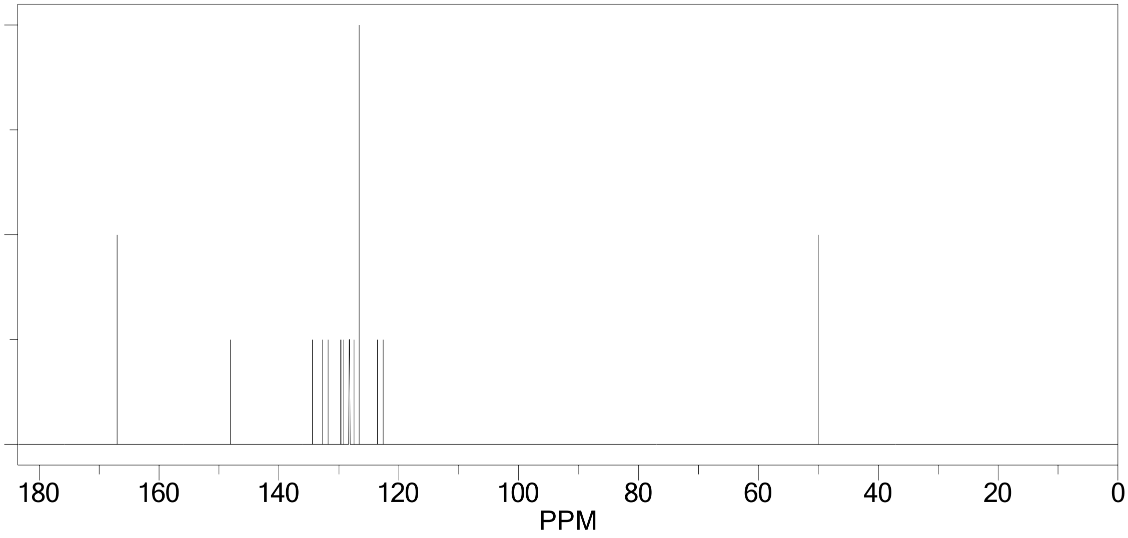




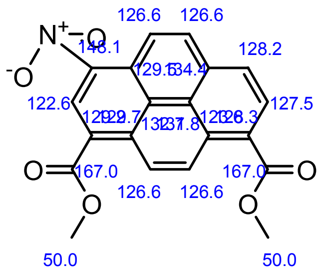
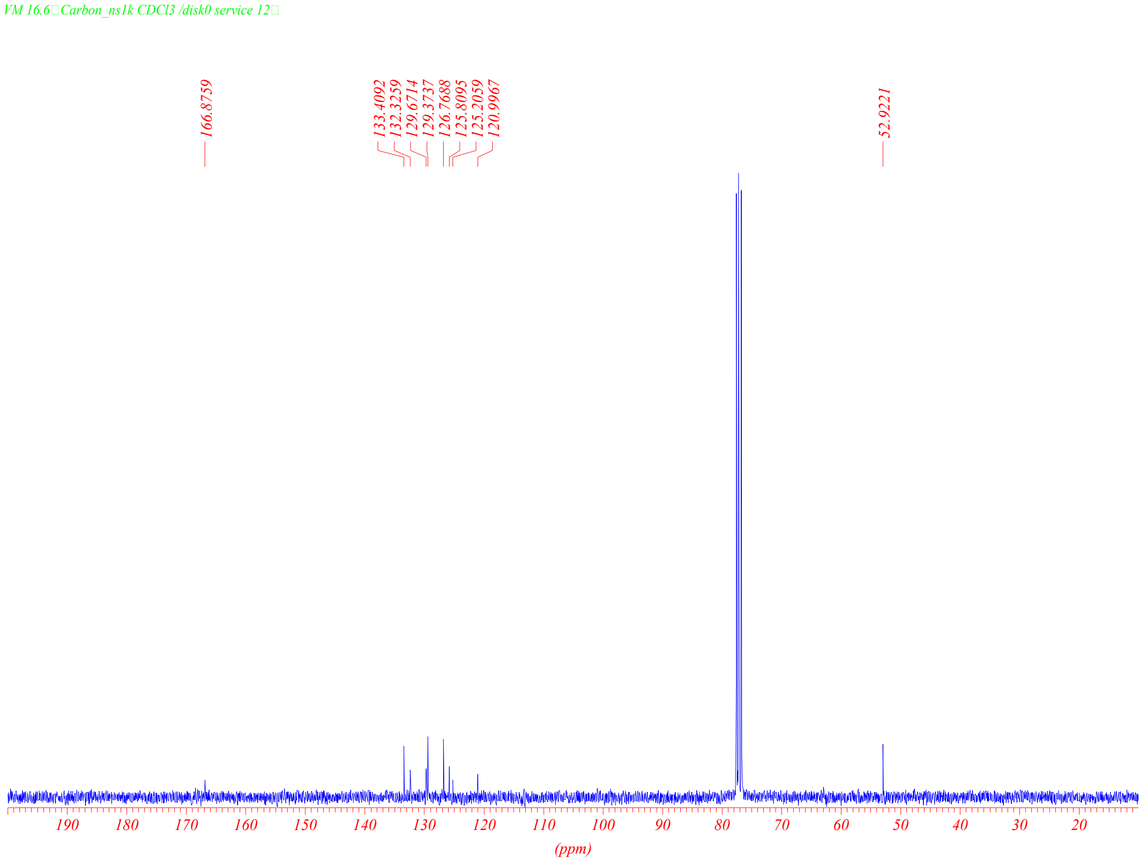
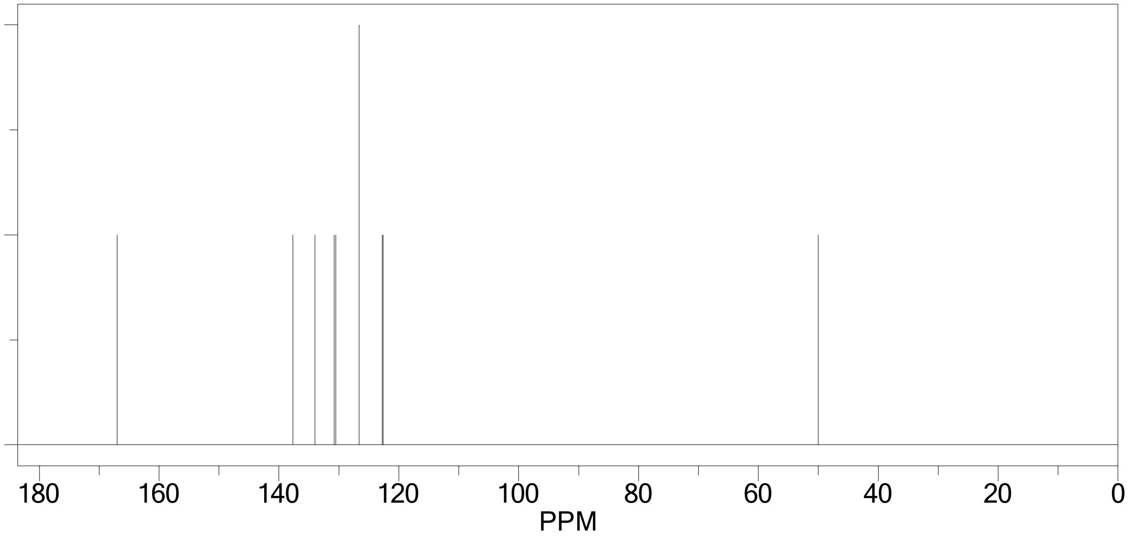
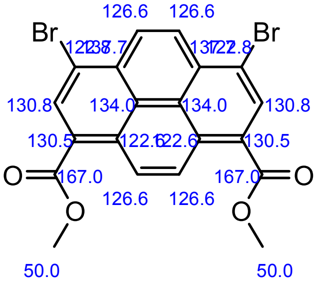


Figure S11. ^{13}C NMR of bis-bromo pyrene **4** in CDCl$_3$.







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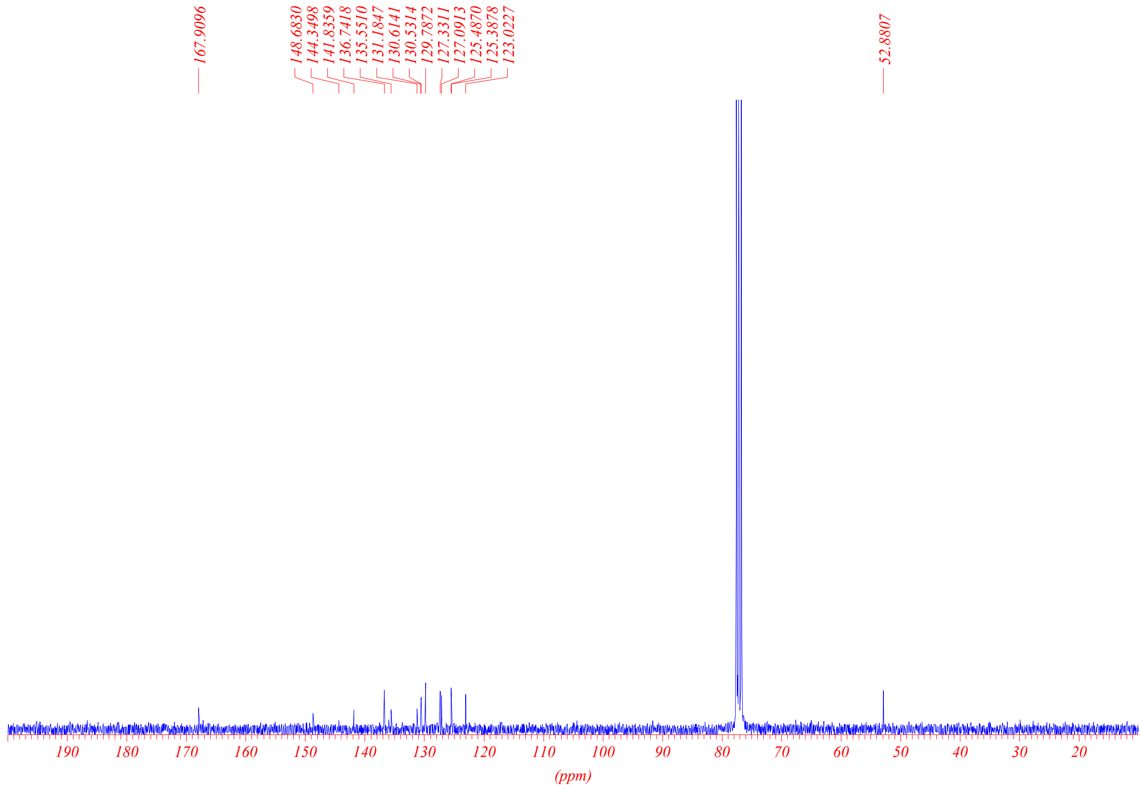

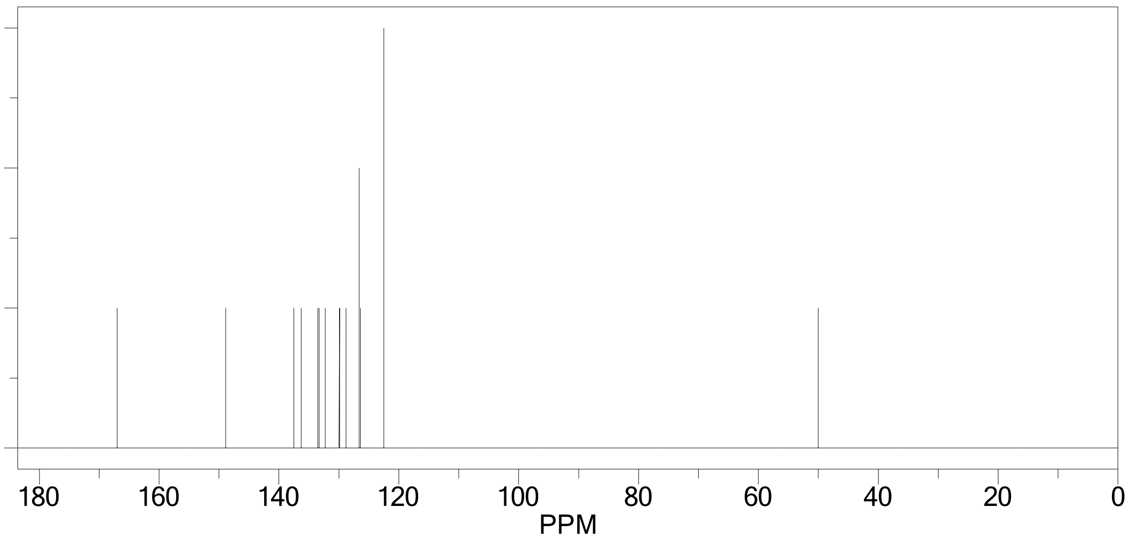

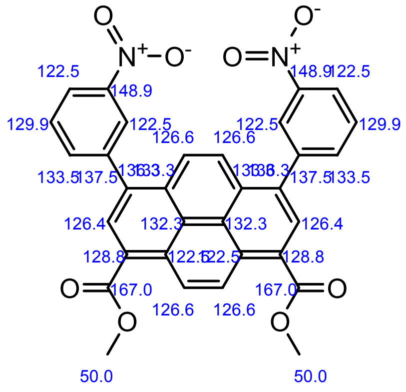

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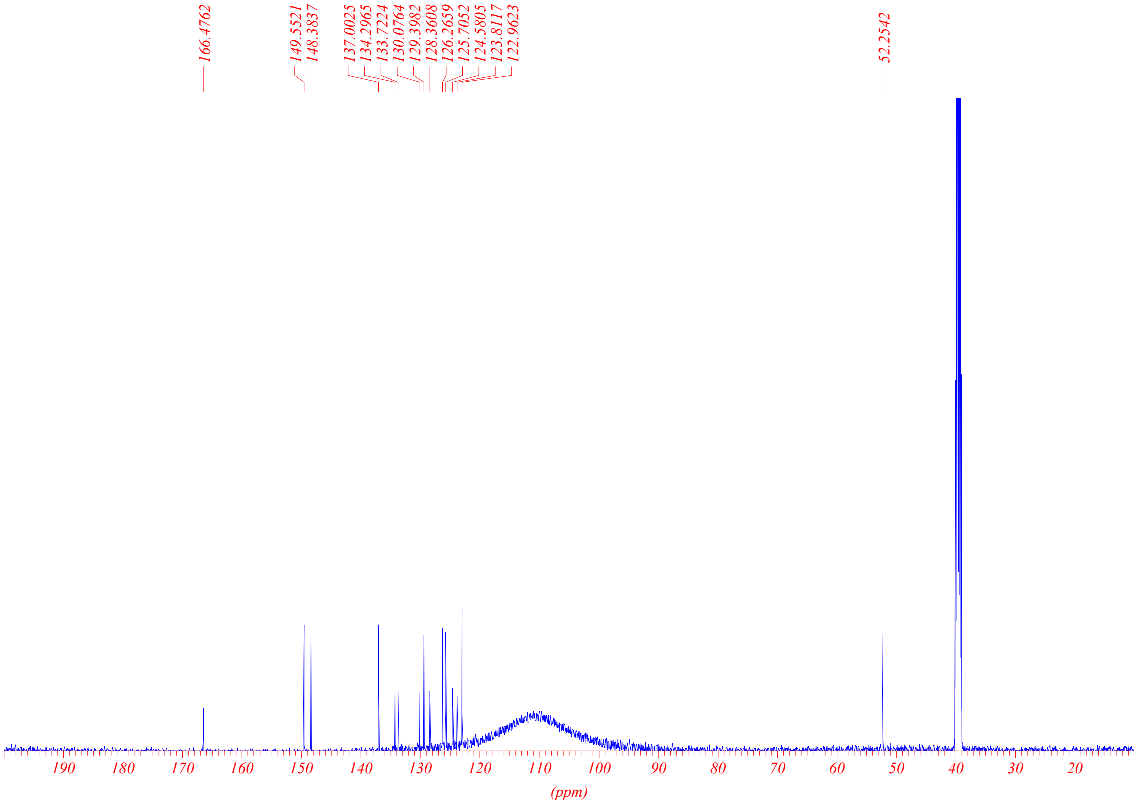

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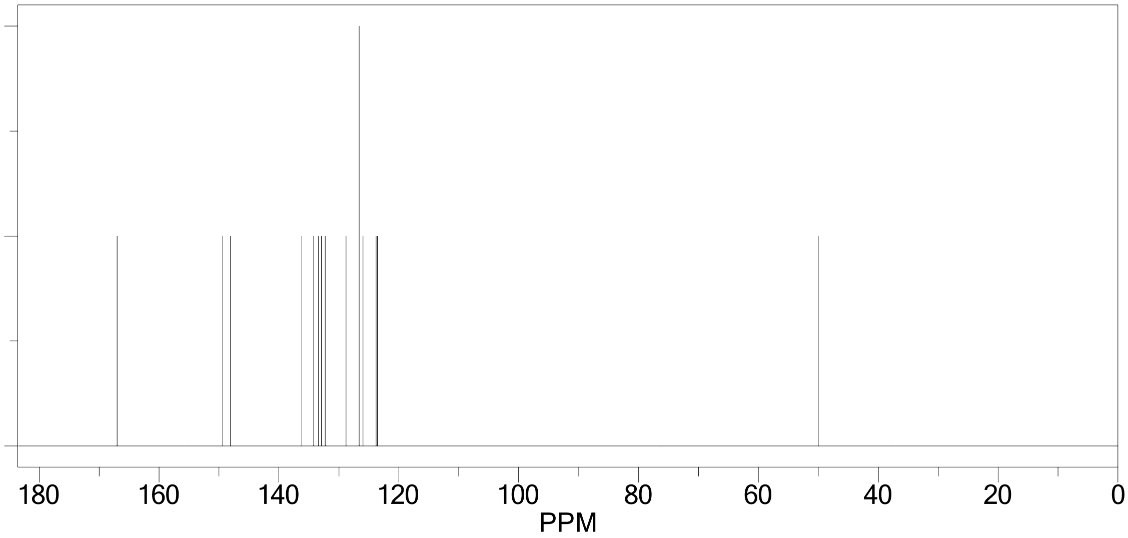

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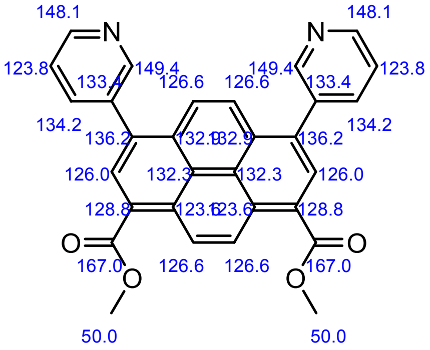

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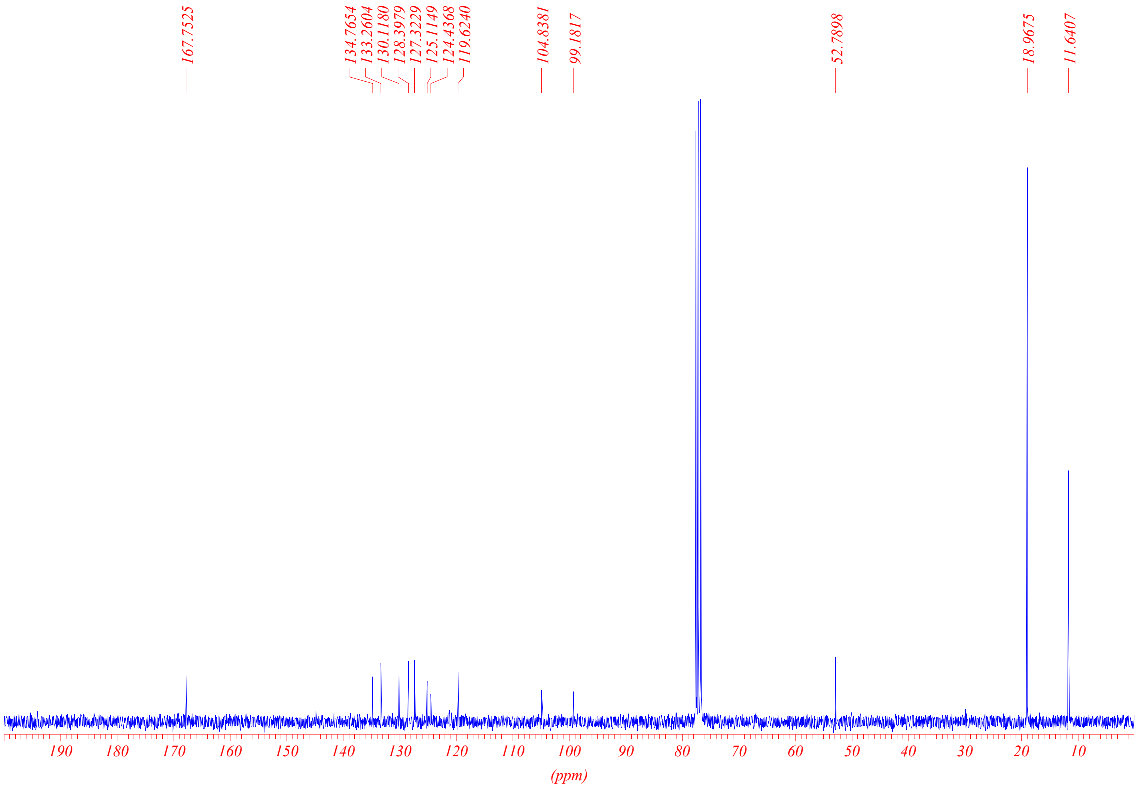

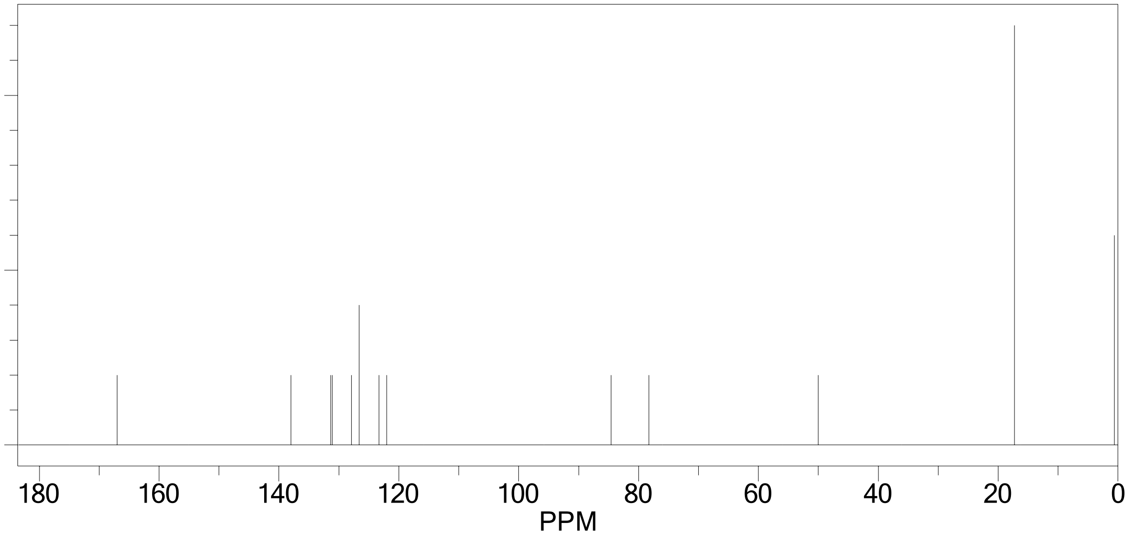

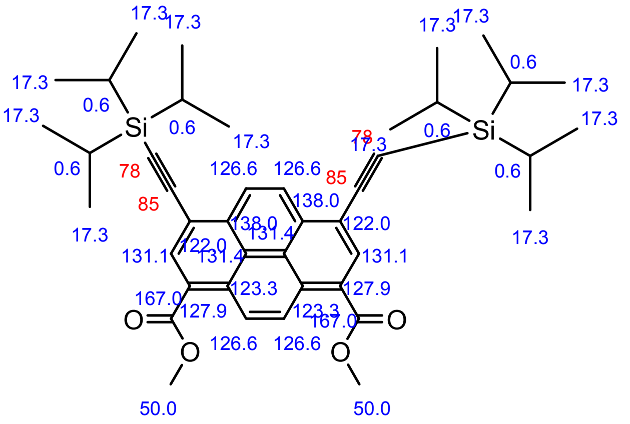

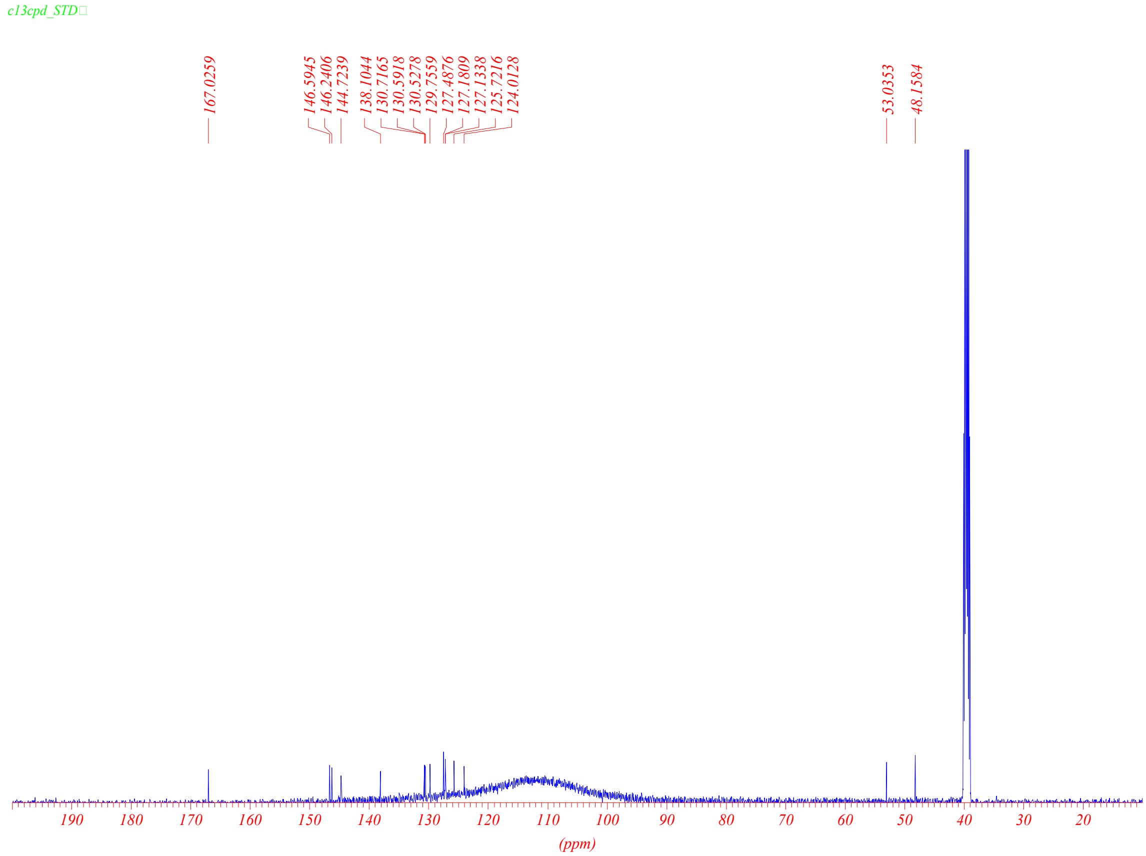
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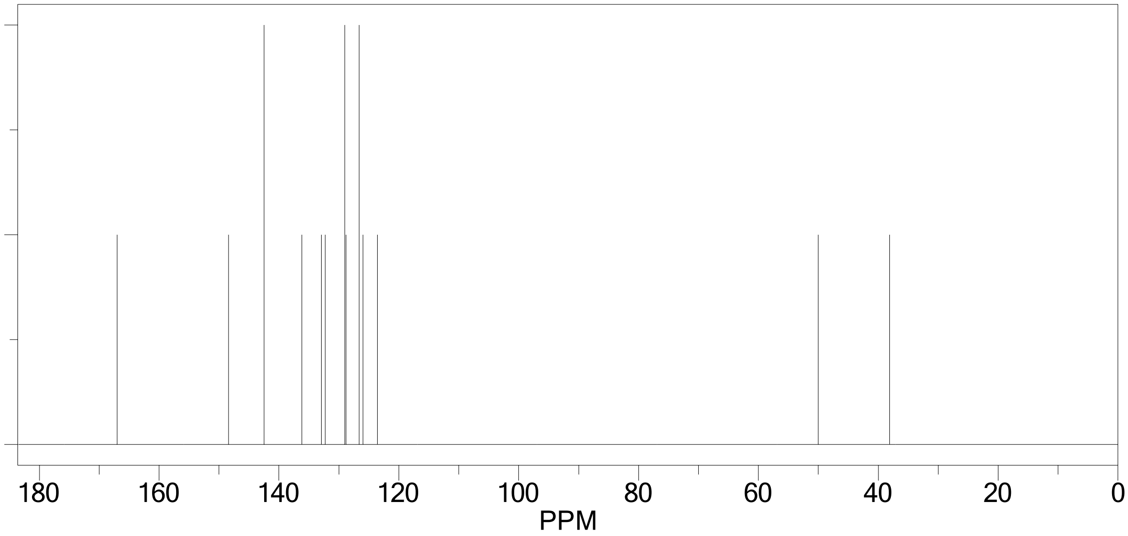
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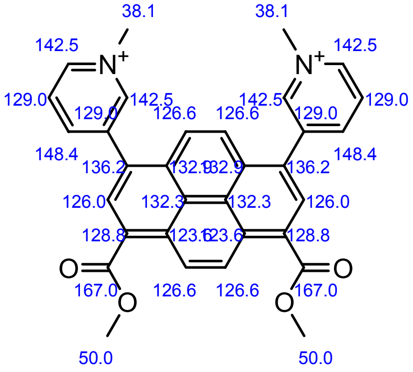
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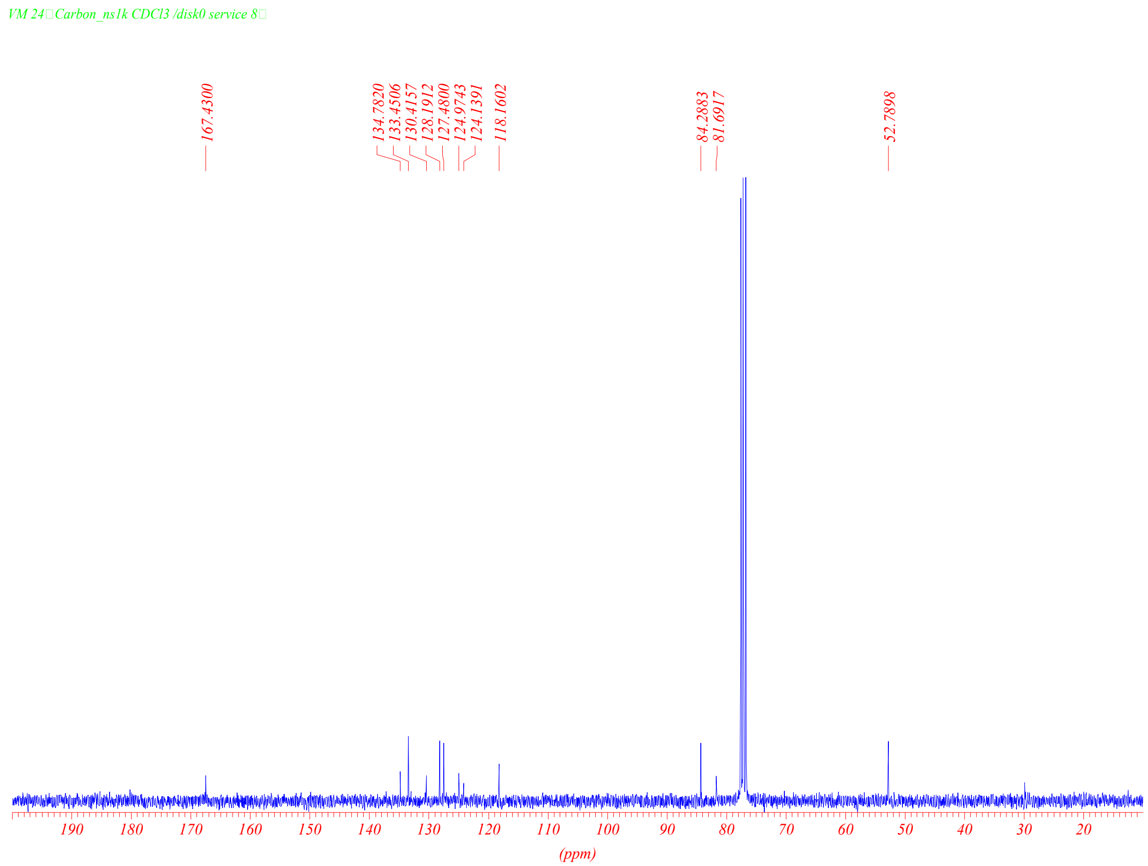
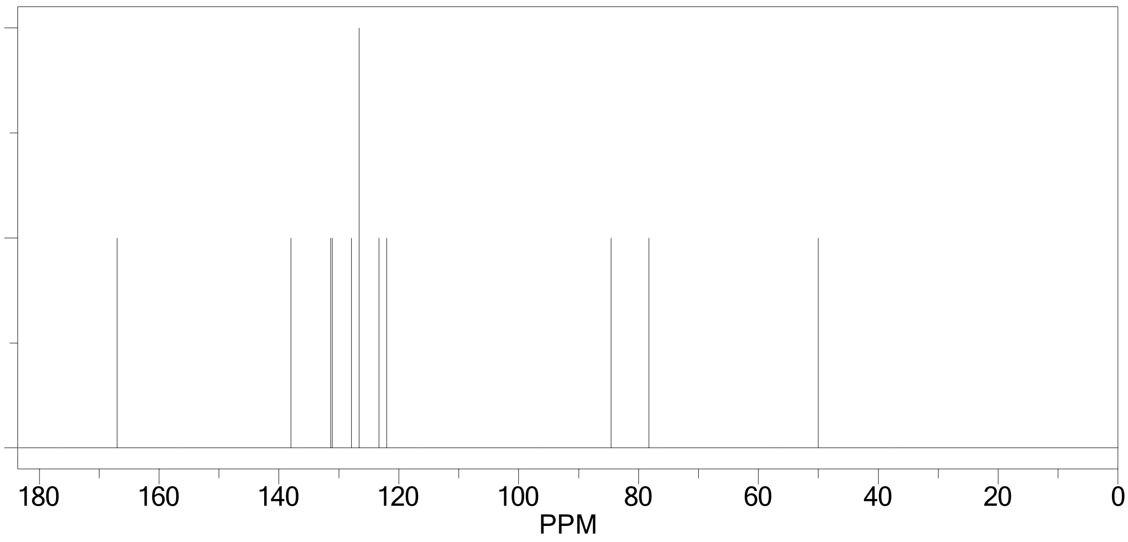
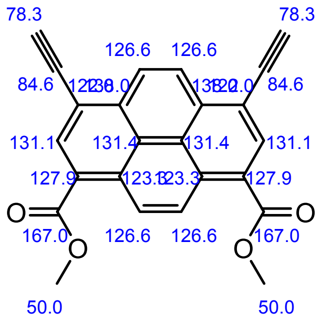
38.1
142.5
142.5
N+
N+
129.0
142.5
142.5
129.0
129.0
129.0
126.6
126.6
148.4
148.4
136.2
132.9
132.9
136.2
126.0
132.3
132.3
126.0
128.8
123.6
123.6
128.8
O
O
167.0
126.6
126.6
167.0
O
O
50.0
50.0


VM 24 Carbon_ns1k CDCl3 /disk0 service 8
167.4300
134.7820
133.4506
130.4157
128.1912
127.4800
124.9743
124.1391
118.1602
84.2883
81.6917
52.7898
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
(ppm)


180
160
140
120
100
80
60
40
20
0
PPM


78.3
78.3
126.6
126.6
84.6
122.0
138.0
138.0
122.0
84.6
131.1
131.4
131.4
131.1
127.9
123.3
123.3
127.9
O
O
167.0
126.6
126.6
167.0
O
O
50.0
50.0

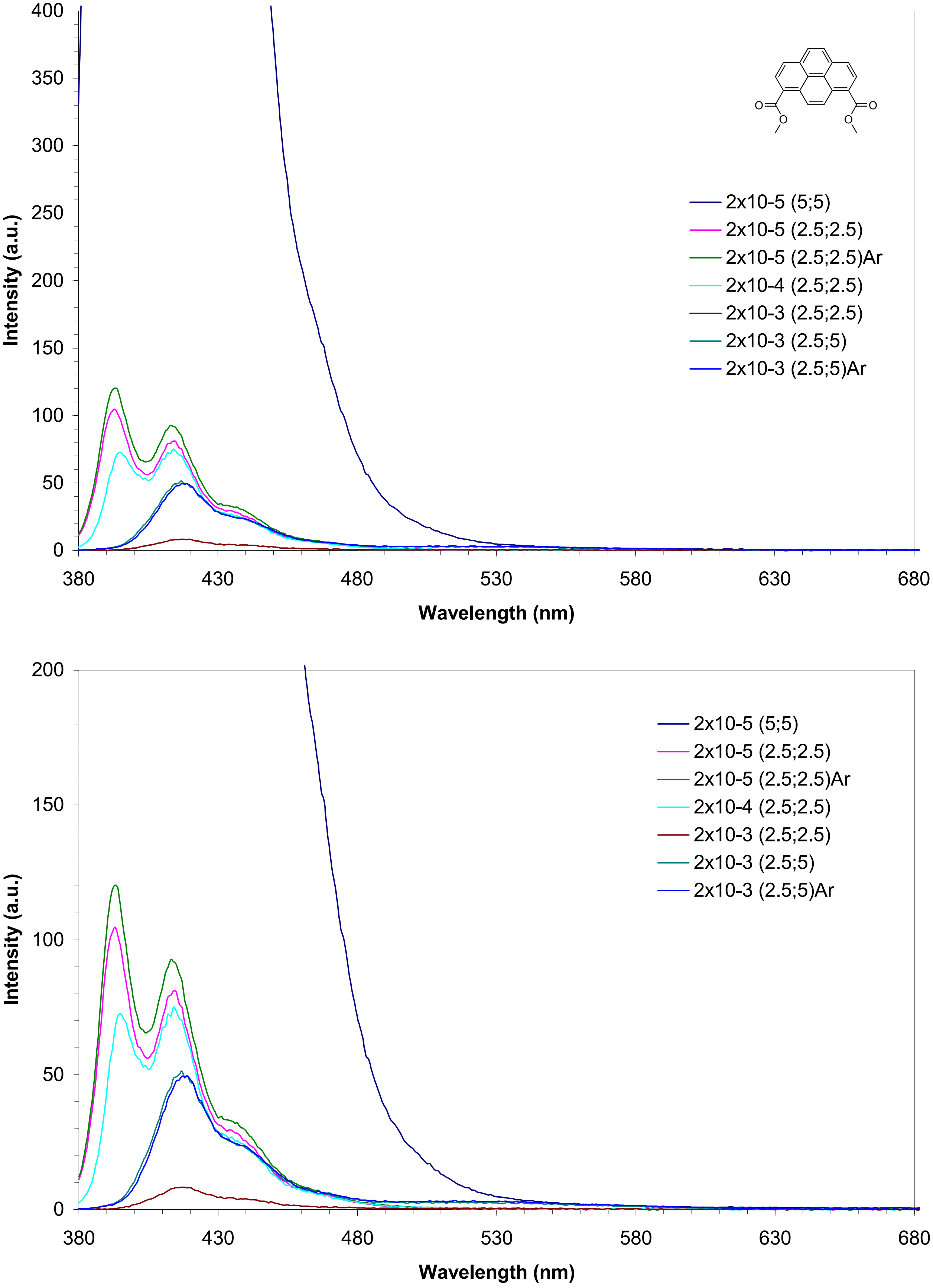


Figure S17. Fluorescence of bis-ester pyrene **2** in CH_2Cl_2.
$I_{[Ar]}/I_{[air]}$ = 120.33 : 104.70 = 1.15 (at 393 nm) and $I_{[air]}/I_{[Ar]}$ = 91.96 : 81.15 = 1.13 (at 414 nm) for $2\cdot10^{-5}$ M, see entries 2 and 3; and the difference is negligible (0.97-0.99) for $2\cdot10^{-3}$ M solutions (entries 6 and 7).

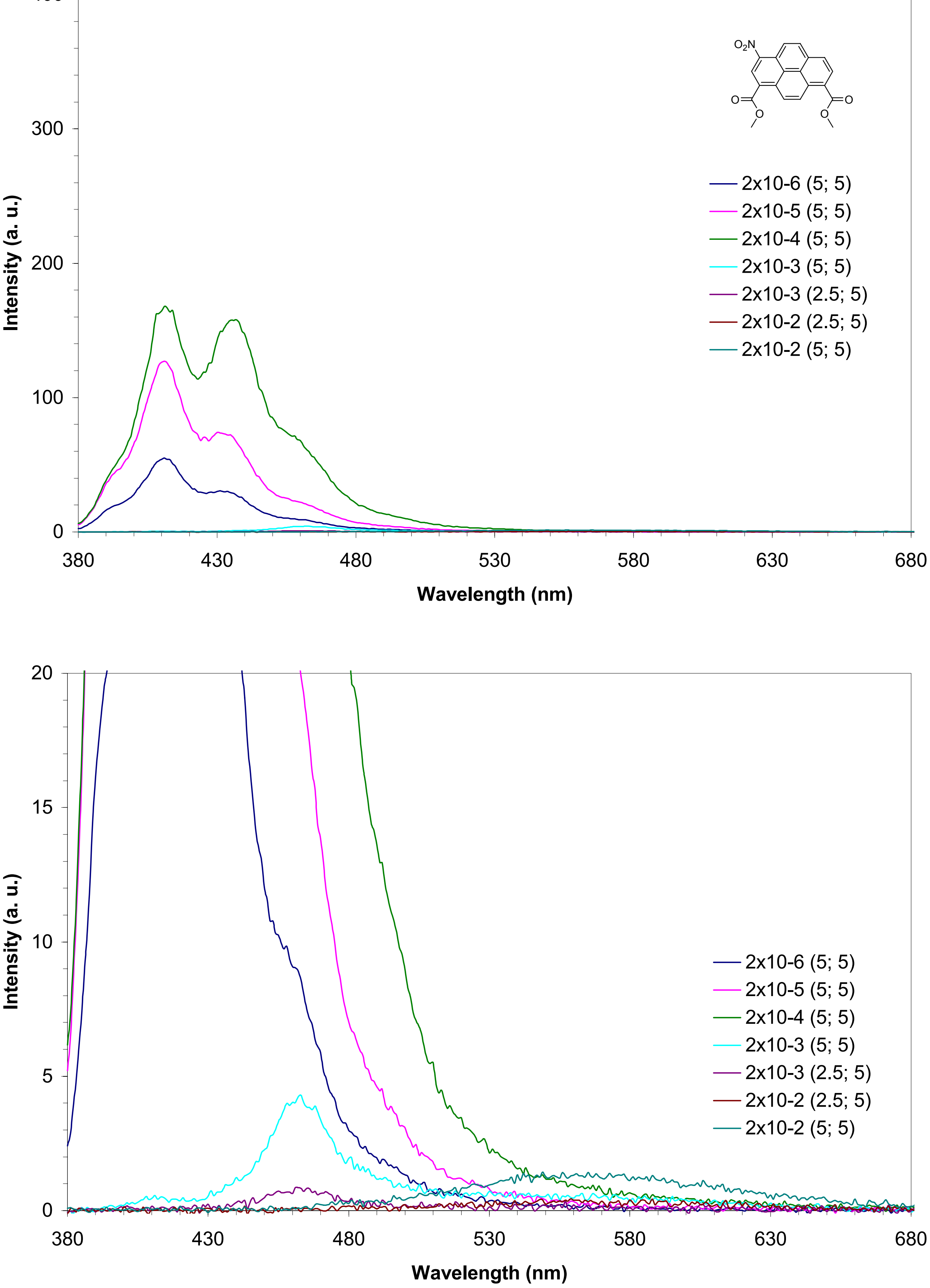


Figure S18. Fluorescence of mononitropyrene **3** in CH_2Cl_2.

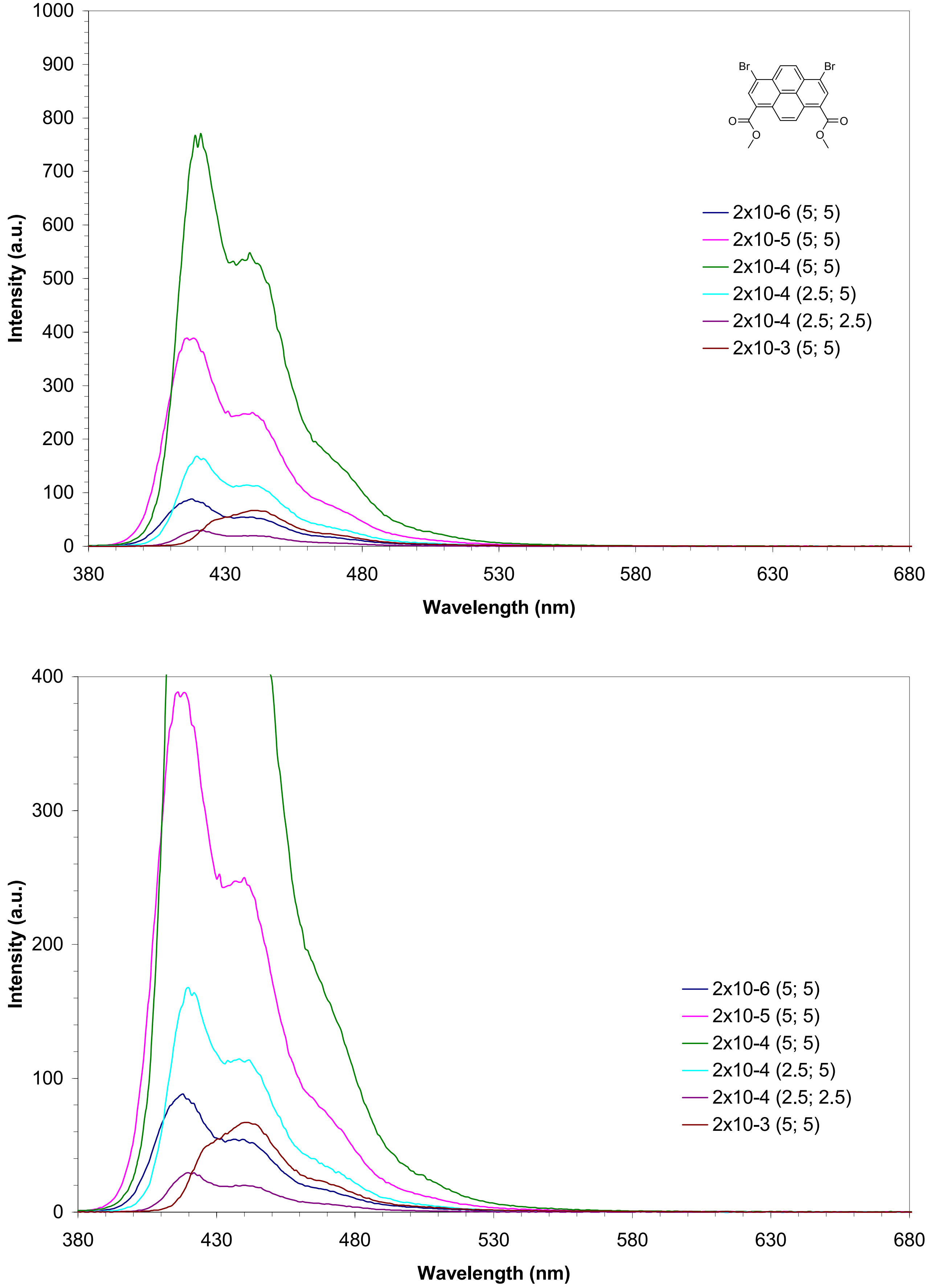


Figure S19. Fluorescence of bis-bromo pyrene **4** in CH_2Cl_2.

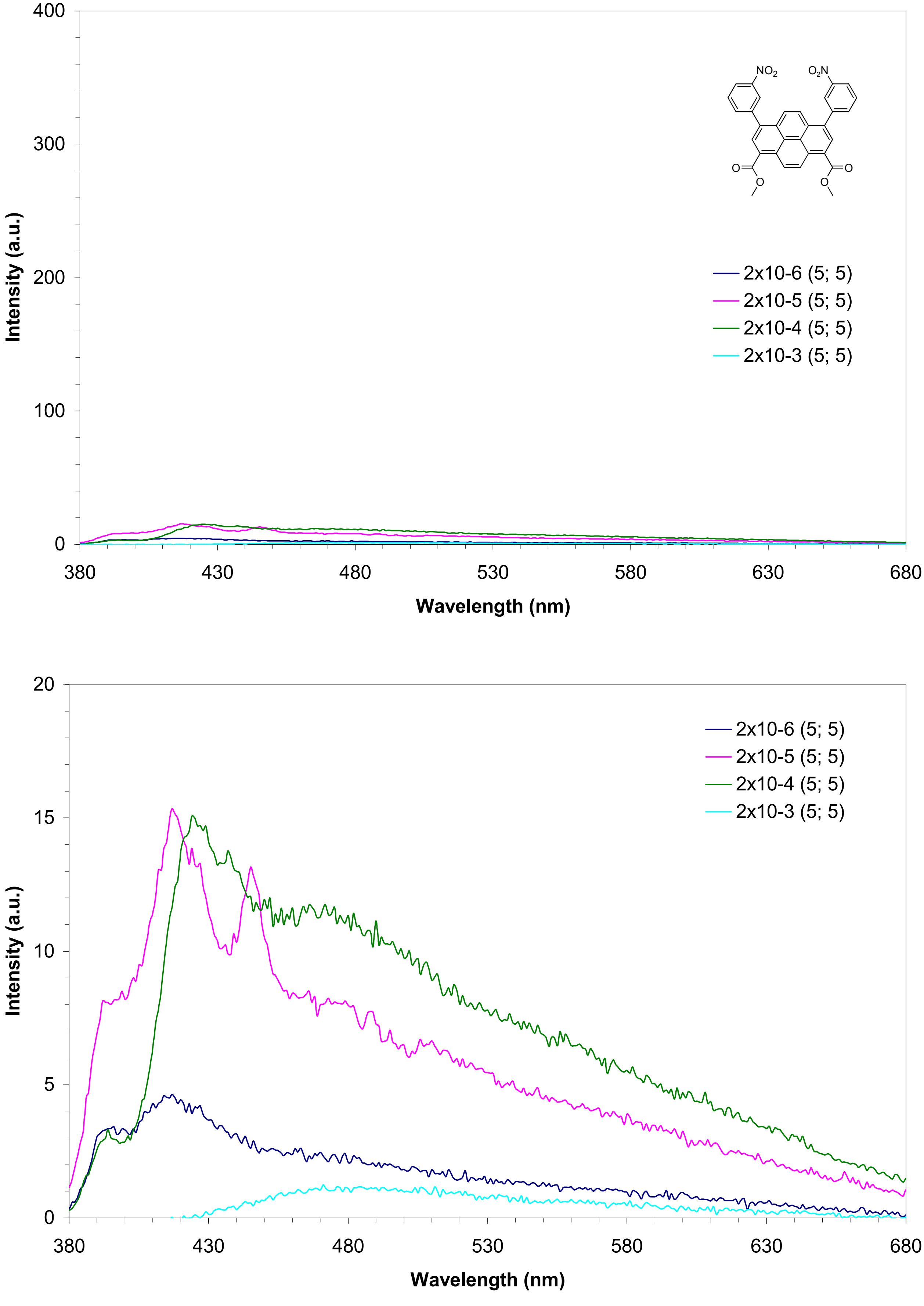


Figure S20. Fluorescence of bis-nitrophenyl pyrene **5** in CH_2Cl_2.

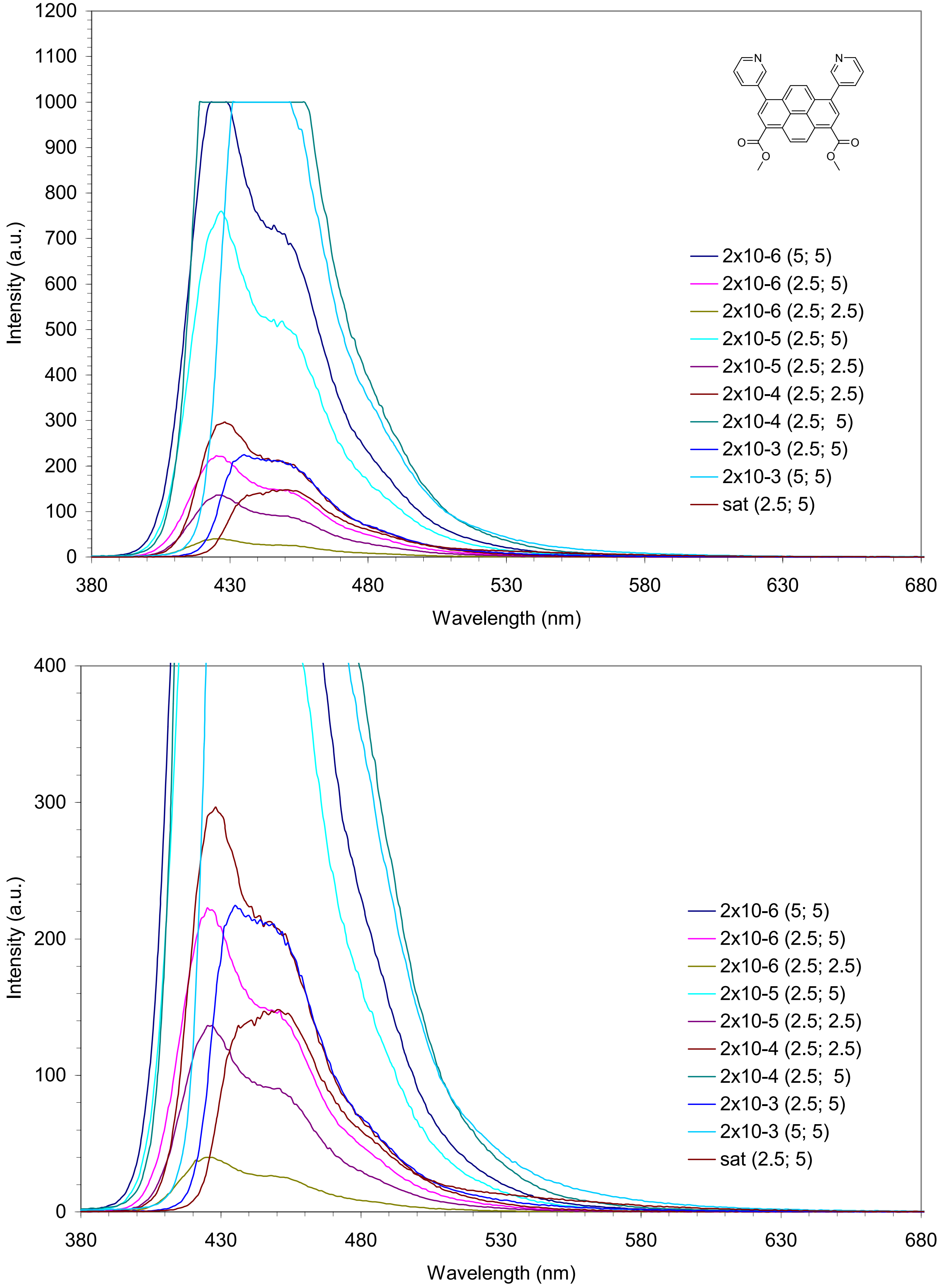


Figure S21. Fluorescence of bis-pyridine pyrene **6** in CH_2Cl_2.

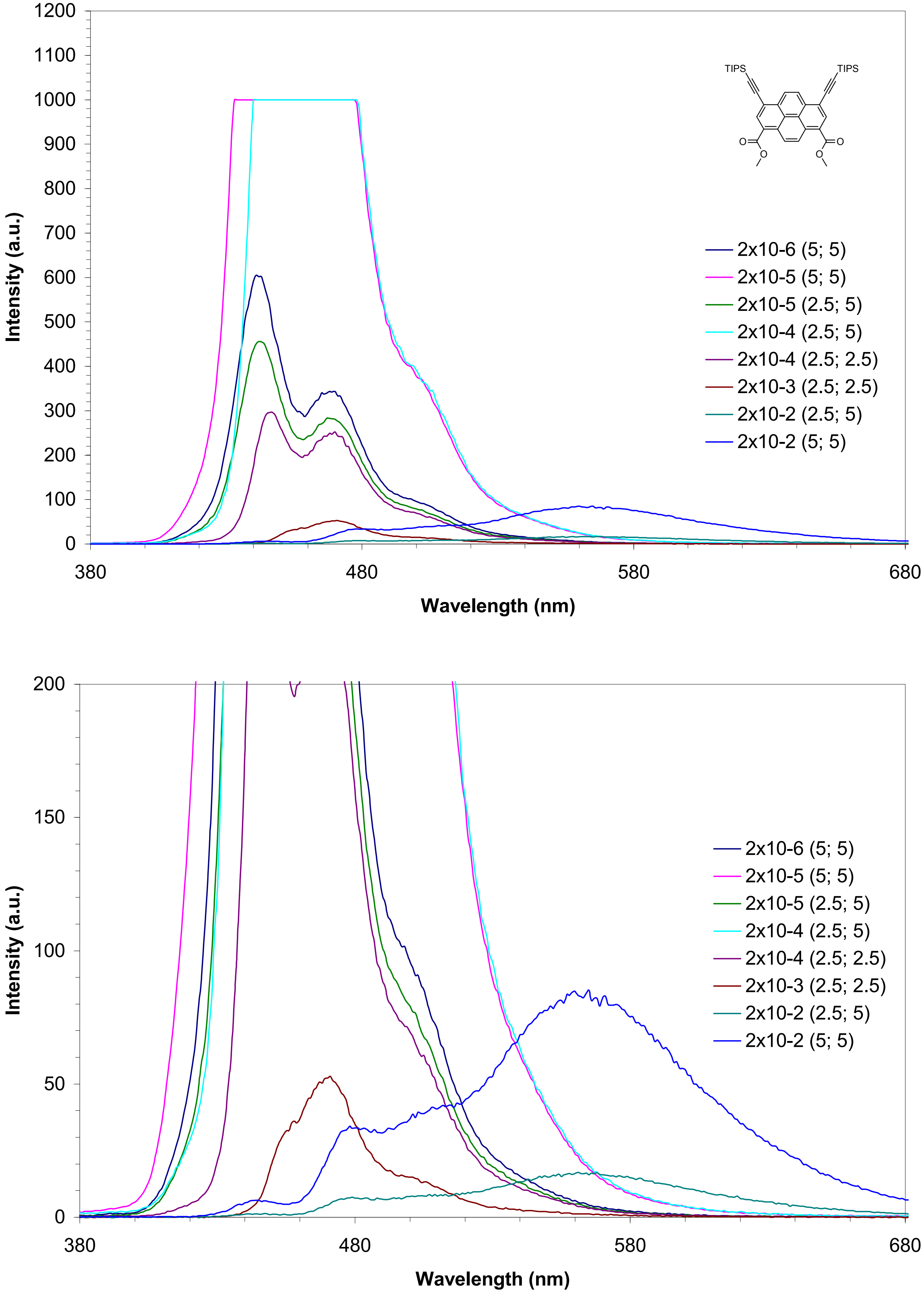


Figure S22. Fluorescence of bis-tips pyrene **7** in CH_2Cl_2.

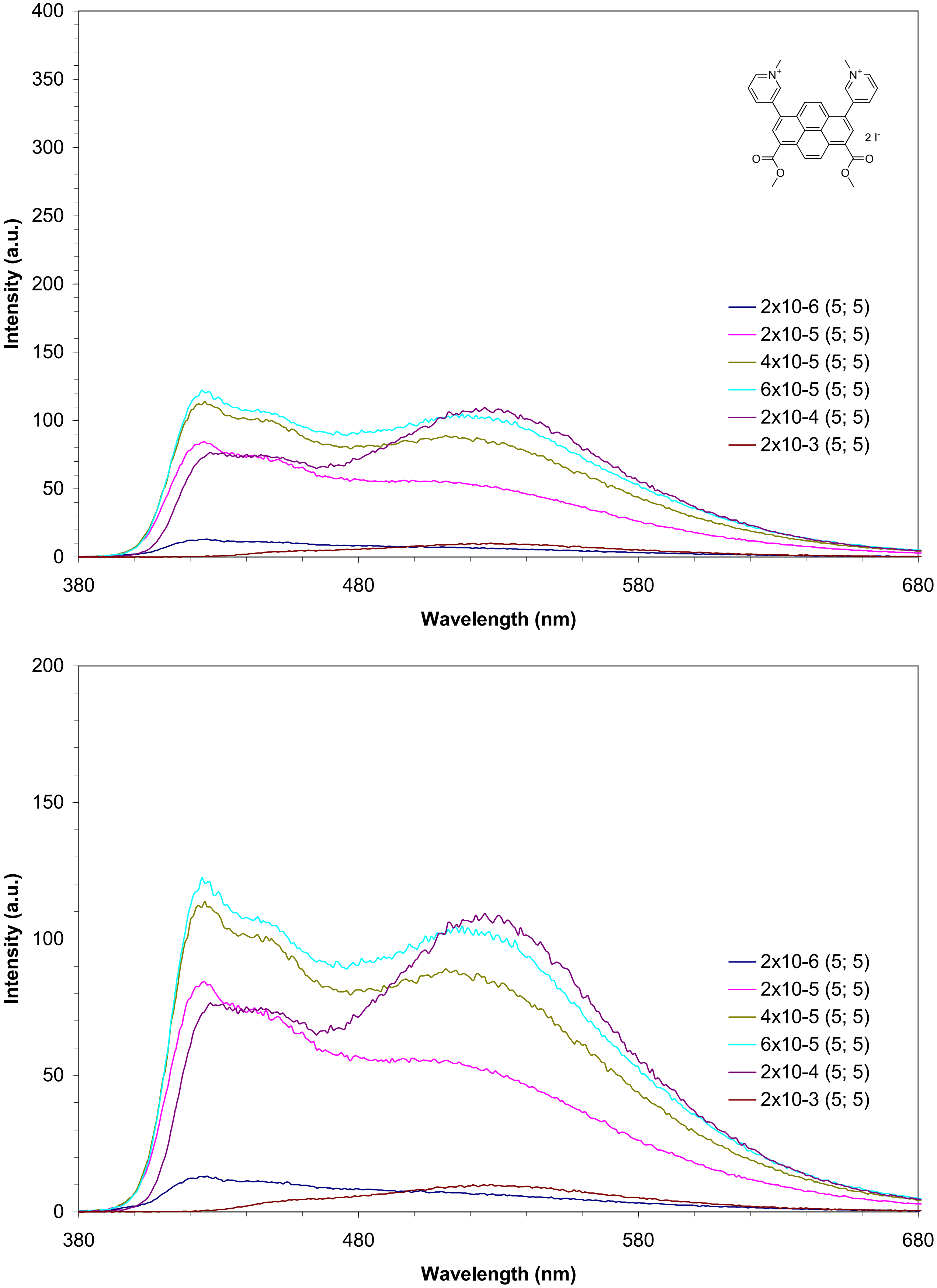


Figure S23. Fluorescence of bis-pyridinium pyrene **8** in H_2O.

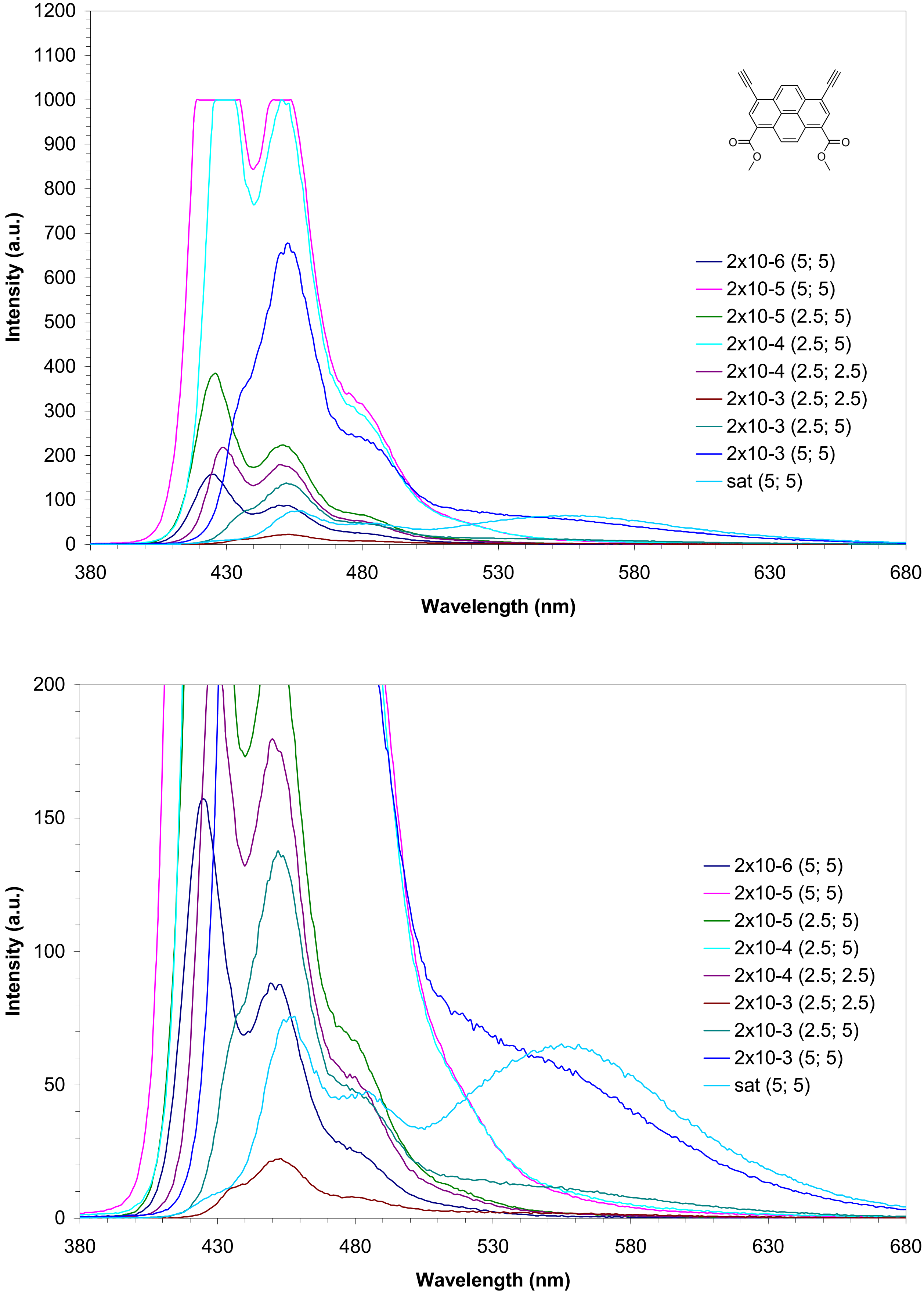


Figure S24. Fluorescence spectra of bis-ethyne pyrene **9** in CH_2Cl_2.

1) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512-7515.
2) Vollmann, H.; Becker, H.; Corell, M.; Streeck, H.; Langbein, G. *Justus Liebigs Ann. Chem*. **1937**, *531*, 1-159.
3) a) Demas, J. N. and G. A. Crosby (The measurement of photoluminescence quantum yields. A review.) *J. Phys. Chem.* **1971**, *75*, 991-1024; b) www.juhoriba.co.uk (A Guide to Recording a Fluorescence Quantum Yields); c) http://www.photochemcad.com (database of spectroscopic data).