Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Distance-dependent formation of electronic charge-transfer states in the ground states of anthracene and pyrene covalently linked to TEMPO free radical

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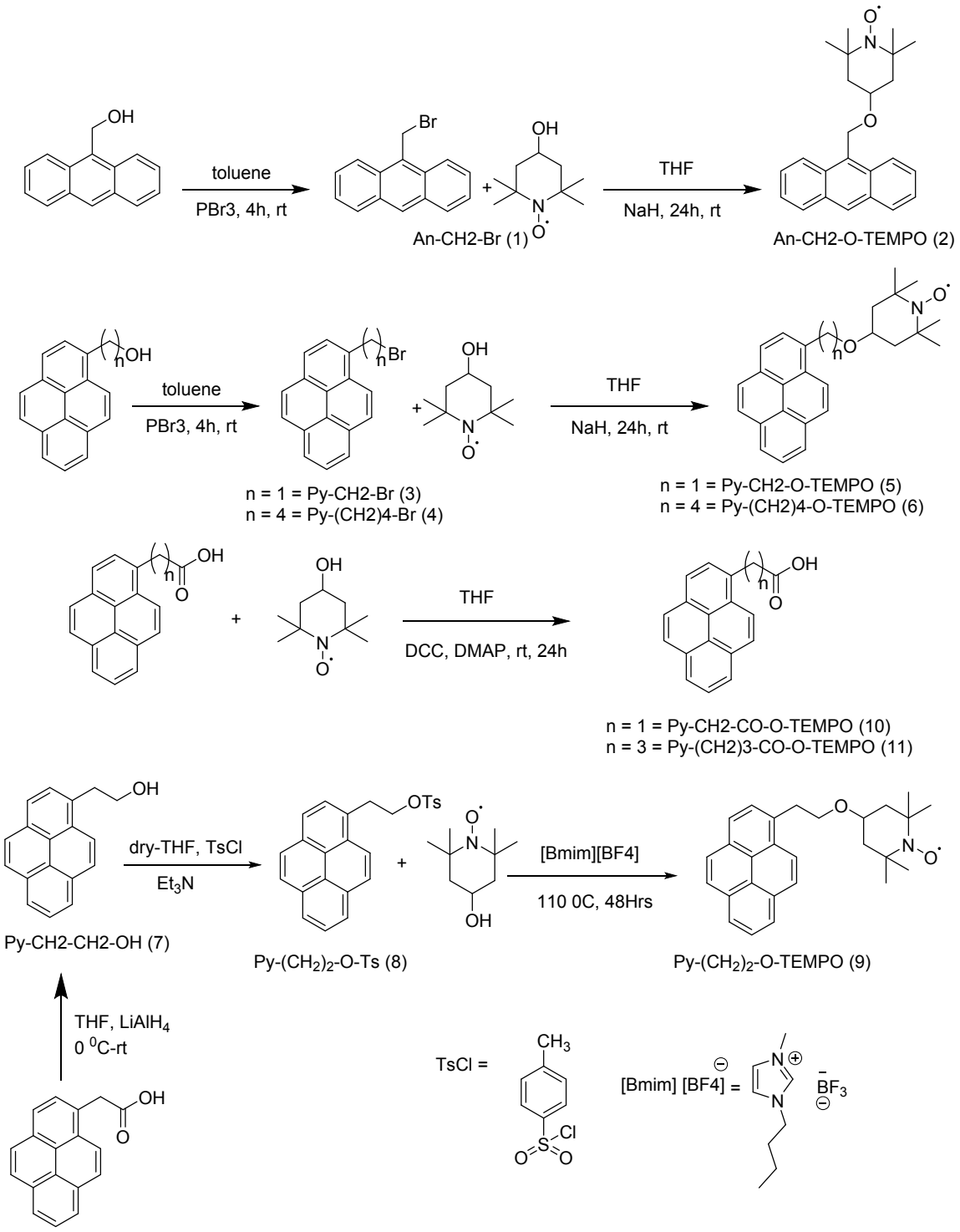
EXPERIMENTAL

All the molecules were synthesized according to the scheme given below. All reactions were carried out in dried glassware. The dry THF and toluene were prepared by Na-metal and benzophenone. Reactions were monitored by thin layer chromatography (TLC). The synthesized molecules were purified by column chromatography (standard 60-angstrom silica gel), and characterized by ^{1}H NMR spectroscopy in a Varian 600 MHz or a Bruker 500 MHz spectrometer, in $CDCl_3$ using TMS as an internal standard. TEMPO-linked molecules do not give any NMR signal because of the presence of the radical. Therefore, the nitroxyl group (-NO$^\bullet$) was reduced to a diamagnetic -NOH, using freshly distilled phenyl hydrazine. As a result, some NMR lines corresponding to phenyl hydrazine were present in their spectra. CD_3OD was used as a solvent in such cases, since in $CDCl_3$ we observed the formation of a suspension after the addition of phenyl hydrazine. Aromatic protons usually have long T_1 relaxation times (~10-15 s). So a delay of 60 s between successive acquisitions of the free induction decay signals was kept, which helped to acquire accurate intensities of the proton signals of the aromatic groups.



Scheme 1 Synthetic schemes of anthracene- and pyrene-TEMPO linked molecules.

Synthesis of An-CH_2-Br (1):

A solution of 9-anthracenemethanol (1 g, 4.8 mmol) in toluene (15 ml) was kept an ice bath and phosphorous tribromide (PBr_3) (0.55 ml, 5.7 mmol) was added to it with continuous stirring. The reaction mixture was warmed to room temperature and stirred for 4 h. After completion of the reaction, the reaction mixture was diluted with the aqueous solution of sodium carbonate. The organic compound was extracted by ethyl acetate (3×30 ml). The combined organic layer was washed with water (3 times) and finally washed with brine solution (one time). The organic layer was dried with sodium sulphate (Na_2SO_4). After filtration, the solvent was removed under reduced pressure. The product was purified by column chromatography, using 2% vol/vol of ethyl acetate in hexane as the eluent to give the product as a yellow solid (yield =1.1 g, 85%) (m. p. = 107 ºC). ^{1}H NMR δ in ppm ($CDCl_3$): 5.69 (s, 2H), 7.48-7.51 (t, 3H), 7.56-7.59 (s, 2H), 8.03-8.04 (d, 1H), 8.42-8.44 (d, 2H), 8.48 (s, 1H).

Synthesis of An-CH_2-O-TEMPO (2):

A solution of 4-hydroxy TEMPO (1.14 g, 6.6 mmol) in 20 ml of THF was added drop-wise to an ice-cold suspension of sodium hydride (NaH) (0.13 g, 5.6 mmol) in THF. The reaction mixture was stirred for 30 min. The molecule **1** (1 g, 3.7 mmol) was dissolved in THF and added in the reaction mixture. The reaction mixture was warmed to room temperature with stirring under N_2 atmosphere for 24 h. After completion of the reaction, the reaction mixture was diluted with water (50 ml) and the organic compound was extracted with ethyl acetate (3×40 ml). The combined organic layers were dried with anhydrous sodium sulphate (Na_2SO_4). The solvent was removed under reduced pressure. The product was purified by column chromatography using 5% vol/vol of ethyl acetate in hexane as an eluent, giving an orange solid of An-CH_2-O-TEMPO (yield = 1.2 g, 90%) (m. p. = 103 ºC). ^{1}H NMR δ in ppm (CD_3OD): 1.09 (s, 6H), 1.16 (s, 6H), 1.48-1.51 (d, 2H), 2.02-2.04 (d, 2H), 3.91-4.01 (m, 1H), 5.51 (s, 1H), 7.45-7.48 (t, 2H), 7.53-7.56 (t, 2H), 8.02-8.04 (d, 2H), 8.38-8.40 (d, 2H), 8.50 (s, 1H).

Synthesis of Py-CH_2-Br (3):

A solution of 1-pyrenemethanol (1gm, 4.3 mmol) in freshly distilled toluene (20 ml) was kept in an ice bath. Phosphorous tribromide (PBr_3) (0.5 ml, 5.1 mmol) added to this with continuous stirring. The reaction mixture was further stirred for 4 h. After completion of the

reaction, the reaction mixture was diluted with the aqueous solution of sodium carbonate (Na_2CO_3). The organic compound was extracted by ethyl acetate (3×40 ml), and the combined organic layer was washed with water (3 times), the finally with brine solution (one time). The organic layer was dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The product was purified by column chromatography using 2% vol/vol ethyl acetate in hexane as an eluent, giving the yellow solid product of Py-CH_2-Br (yield = 1.1 g, 87%) (m. p. = 130 ºC). ^{1}H NMR δ ($CDCl_3$): 4.74 (s, 2H), 8.08-8.12 (q, 2H), 8.20-8.23 (t, 2H), 8.27-8.31 (q, 3H), 8.38-8.40 (d, 1H), 8.99-9.00 (d, 1H).

Synthesis of Py-$(CH_2)_4$-Br (4):

A solution of 1-pyrenebutanol (1gm, 3.6 mmol) in freshly distilled toluene (25 ml) was kept in an ice bath and added PBr_3 (0.42 ml, 4.3 mmol) was added to it with continuous stirring. The solution was stirred for 4 h. After the completion of the reaction, the reaction mixture was diluted with the aqueous solution of Na_2CO_3. The organic compound was extracted by ethyl acetate (3×40 ml), and the combined organic layer was washed with water (3 times) and finally washed with brine solution (one time). The organic layer was dried with Na_2SO_4. The solvent was removed under reduced pressure. The product was purified by column chromatography using 2% vol/vol ethyl acetate in hexane as an eluent, giving a yellow solid product of Py-$(CH_2)_4$-Br (yield = 1.1 g, 89%) (m. p. = 125 ºC). ^{1}H NMR δ ($CDCl_3$): 2.02-2.04 (m, 4H), 3.37-3.39 (t, 2H), 3.46-3.48 (t, 2H), 7.85-7.87 (d, 1H), 7.79-7.99 (t, 1H), 8.02-8.03 (t, 2H), 8.11-8.12 (d, 2H), 8.15-8.17 (t, 2H), 8.26-8.28 (d, 1H).

Synthesis of Py-CH_2-O-TEMPO (5):

A solution of 4-hydroxy TEMPO (0.7 g, 4.0 mmol) in 15 ml of THF was added dropwise to the ice-cold suspension of NaH (0.12 g, 5.1 mmol) in THF (10 ml). The reaction mixture was stirred for further 30 min. Molecule **3** (1g, 3.4 mmol) was dissolved in THF (10 ml) and added to the reaction mixture. The reaction mixture was warmed to room temperature and was stirred under N_2 atmosphere for 24 h. After the completion of the reaction, the reaction mixture was diluted with water and extracted with ethyl acetate (3×50 ml). The combined organic layers were dried with anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure. The product was purified by column chromatography using 5% vol/vol ethyl acetate in hexane as an eluent, to give the product as an orange solid (yield = 1.2 g, 90%) (m. p. = 125 ºC). ^{1}H NMR δ (CD_3OD): 1.12 (s, 6H), 1.18 (s, 6H), 1.51-

1.56 (t, 2H), 2.04-2.07 (d, 2H), 3.92-3.96 (m, 1H), 5.24 (s, 2H), 8.00-8.07 (m, 4H), 8.16-8.23 (m, 4H), 8.38-8.39 (d, 1H).

Synthesis of Py-$(CH_2)_4$-O-TEMPO (6):

A solution of 4-hydroxy TEMPO (0.62 g, 3.6 mmol) was in 20 ml of THF was added drop-wise to an ice-cold suspension of NaH (0.11 g, 4.5 mmol) in THF (20 ml). The reaction mixture was stirred for further 30 min. Molecule **4** (1 g, 2.9 mmol) was dissolved in THF (10 ml) and added to the reaction mixture. The reaction mixture was warmed to room temperature and was stirred under N_2 atmosphere for 24 h. After completion of the reaction, the reaction mixture was diluted with 50 ml water and extracted with ethyl acetate (3×50 ml). The combined organic layers were dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure. The product was purified by column chromatography using 5% vol/vol of ethyl acetate in hexane as an eluent, to give the product as an orange solid (yield = 1.1 g, 87%) (m. p. = 130 ºC). ^{1}H NMR δ (CD_3OD): 1.12 (s, 6H), 1.18 (s, 6H), 1.29-1.33 (t, 2H), 1.69 (m, 2H), 1.79-1.81 (m, 2H), 1.91-1.95 (m, 2H), 3.37-3.40 (t, 2H), 3.48-3.50 (t, 2H), 4.58 (m, 1H), 7.73-7.75 (m, 1H), 7.89-7.97 (d, 2H), 7.98-8.03 (m, 2H), 8.05-8.13 (t, 2H), 8.12-8.18 (t, 2H), 8.33-8.35 (d, 1H).

Synthesis of Py-$(CH_2)_2$-OH (7):

A solution of 1-pyreneacetic acid (3g, 3.8 mmol) was added to a suspension of lithium aluminium hydride (0.22g, 5.7 mM) in dry THF at 0 ºC. The reaction mixture was stirred for 3 h at room temperature. The reaction was monitored by thin-layer chormatography. After completion of reaction, the reaction mixture was diluted by addition of water. The product was extracted by ethyl acetate (3×30 ml). The organic layers were combined and dried by anhydrous Na_2SO_4. The product was purified by column chromatography using 5 % vol/vol ethyl acetate in hexane as an eluent, to give the product as a yellow solid (yield = 2.4 g, 87%) (m. p. = 129 ºC). ^{1}H NMR δ (CD_2Cl_2): 3.61-6.36 (t, 2H), 4.06-4.07 (t, 2H), 7.94-8.01 (t, 1H), 8.02-8.04 (m, 2H), 8.047-8.09 (m, 4H), 8.15-8.19 (m, 1H).

Synthesis of Py-$(CH_2)_2$-OTs (8):

To a solution of the molecule **7** (1g, 4.06 mmol) in DCM, Et_3N (1.2 ml, 11.44 mmol) was added, followed by addition of *p*-toluenesulfonyl chloride (0.8g, 4.06 mmol). The reaction mixture was left over night at room temperature. The side product trietylamine hydrochloride

was produced in the reaction mixture. The solvent from the reaction mixture was evaporated under reduced pressure and the residue was dissolved in ethyl acetate. The solution was stirred with saturated sodium carbonate solution for one hour. The phases were separated and the organic layer was washed with dilute hydrochloric acid and water. The organic phase was dried by anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure, to give Py-$(CH_2)_2$-OTs as a while crystalline solid (yield = 1.4 g, 88%) (m. p. = 128 ºC). ^{1}H NMR δ (CD_2Cl_2): 2.33 (s, 1H), 3.06-3.08 (t, 2H), 4.27-4.29 (t, 2H), 7.12-7.14 (m, 2H), 7.20-7.21 (m, 2H), 7.43-7.46 (m, 2H), 7.47-7.51 (d, 1H), 7.55-7.57 (d, 2H), 7.70-7.72 (d, 2H), 7.79-7.08 (d, 1H).

Synthesis of Py-$(CH_2)_2$-OTEMPO (9):

A solution of 4-Hydroxy TEMPO (1.7g, 10 mmol) and molecule **8** (1g, 2.5 mmol) were added to a reaction vessel containing 2 ml of 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid ([Bmim] [BF4]). The resulting mixture was then heated at 110 °C for 48 h. The solution was then cooled to room temperature, diluted with water (30 ml) and extracted with ethyl acetate (3×50 ml). The combined organic layers were dried with anhydrous Na_2SO_4, filtered, concentrated and purified by column chromatography (0 to 10 % vol/vol of ethyl acetate in hexane, as an eluent, giving an orange solid product (yield = 0.4 g, 40%) (m. p. = 129 ºC). ^{1}H NMR δ (CD_3OD): 1.09 (s, 6H), 1.10 (s, 6H), 1.41-1.46 (t, 2H), 1.54-1.56 (t, 2H), 2.13-1.15 (t, 2H), 3.34-3.37 (t, 2H), 4.92-4.94 (m, 1H), 7.85-7.97 (m, 1H), 7.98-8.01 (m, 1H), 8.022-8.03 (m, 2H), 8.10-8.12 (m, 2H), 8.14-8.17 (m, 2H), 8.32-8.33 (d, 1H).

Synthesis of Py-CH_2-CO-O-TEMPO (10):

1-Pyreneacetic acid (1 g, 3.8 mmol), dicyclohexylcarbodiimide (DCC) (1.34 g, 6.5 mmol), (dimethy1amino) pyridine (DMAP) (0.47 g, 3.8 mmol), and 4-Hydroxy-TEMPO (0.80 g, 4.6 mmol) were dissolved in THF (30 ml). The reaction mixture was stirred for 24 h under N_2 atmosphere. The solid dicyclohexyl urea, formed during the reaction, was separated by filtration. The solid material remaining in the reaction vessel was further rinsed by ethyl acetate and filtered. The combined filtrate was washed with water (3×50 mL) and dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the product was purified by chromatography using 5% vol/vol ethyl acetate in hexane as an eluent, giving Py-CH_2-CO-O-TEMPO as an orange solid (yield = 1.3 g, 87%) (m. p. = 101 ºC). ^{1}H NMR δ (CD_3OD): 1.08 (s, 6H), 1.10 (s, 6H), 1.48-1.52 (t, 2H), 1.82-1.84 (t, 2H), 4.34 (s, 2H), 5.05-

5.08 (m, 1H), 7.92-7.93 (d, 1H), 7.98-8.00 (d, 1H), 8.01-8.05 (d, 2H), 8.13-8.15 (t, 2H), 8.15-8.20 (m, 2H), 8.23-8.25 (m, 1H).

Synthesis of Py-$(CH_2)_3$-CO-O-TEMPO (11):

1-Pyrenebutyric acid (1 g, 3.5 mmol) dicyclohexylcarbodiimide (DCC) (1.21 g, 5.9 mmol), (dimethy1amino)pyridine (DMAP) (0.42 g, 3.5 mmol), and 4-hydroxy-TEMPO (0.72 g, 4.1 mmol) were dissolved in THF (30 ml). The reaction mixture was stirred for 24 h under N_2 atmosphere. The solid dicyclohexyl urea, formed during the reaction, was separated by filtration. The solid material remaining in the reaction vessel was further rinsed by ethyl acetate and filtered. The combined filtrate was washed with water (3×50 mL) and dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the product was purified by chromatography using 5% vol/vol ethyl acetate in hexane as an eluent giving Py-$(CH_2)_3$-CO-O-TEMPO as an orange solid (yield = 1.2 g, 80%) (m. p. = 109 ºC). ^{1}H NMR δ (CD_3OD): 1.08 (s, 6H), 1.10 (s, 6H), 1.30-1.31 (d, 2H), 1.42-1.46 (t, 2H), 2.11-2.16 (m, 2H), 2.41-2.44 (t, 2H), 3.34-3.37 (m, 2H), 4.84 (m, 1H), 7.85-7.96 (t, 1H), 7.97-7.98 (d, 1H), 8.01-8.02 (d, 2H), 8.10-8.11 (t, 2H), 8.12-8.17 (m, 2H), 8.32-8.33 (d, 1H).

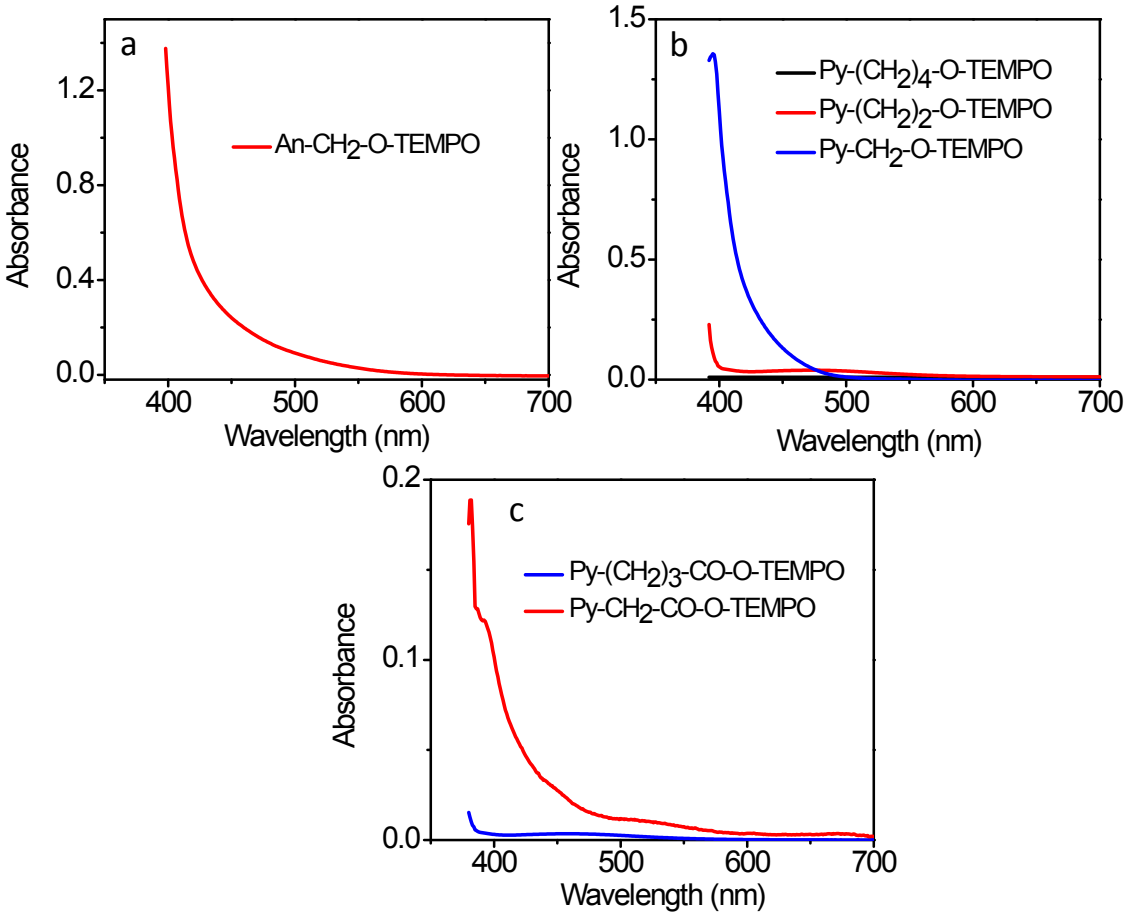


Fig. S1 Partial absorption spectra of the CT states of (a) An-CH_2-O-TEMPO (b) Py-CH_2-O-TEMPO and (c) Py-CH_2-CO-O-TEMPO. Conc: 10 mM in acetonitrile. The spectra were obtained by numerically subtracting the spectrum of a linked molecule from that of the corresponding "unlinked system", recorded under identical conditions. At wavelengths below ~375 nm, the absorbance is too high, and the spectra showed saturation. So no meaningful subtraction could be achieved, resulting in the appearance of partial bands shown here.

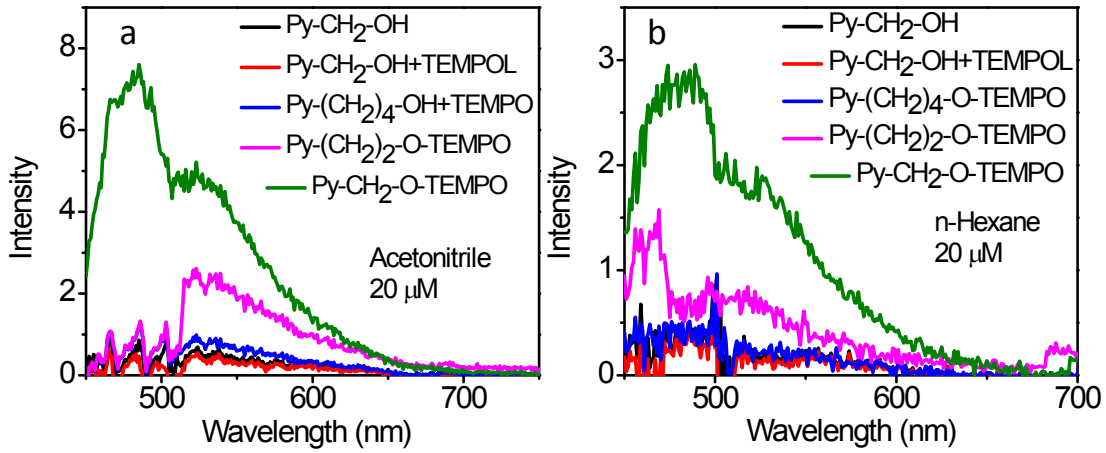


Fig. S2 Fluorescence emissions spectra of Py-CH_2-OH, Py-CH_2-OH+TEMPOL, Py-$(CH_2)_4$-O-TEMPO, Py-$(CH_2)_2$-O-TEMPO and Py-CH_2-O-TEMPO at λ_{ex} = 450 nm (a) in acetonitrile (a) and *n*-hexane (b), after subtraction of Raman lines. Concentration: 20 μM.

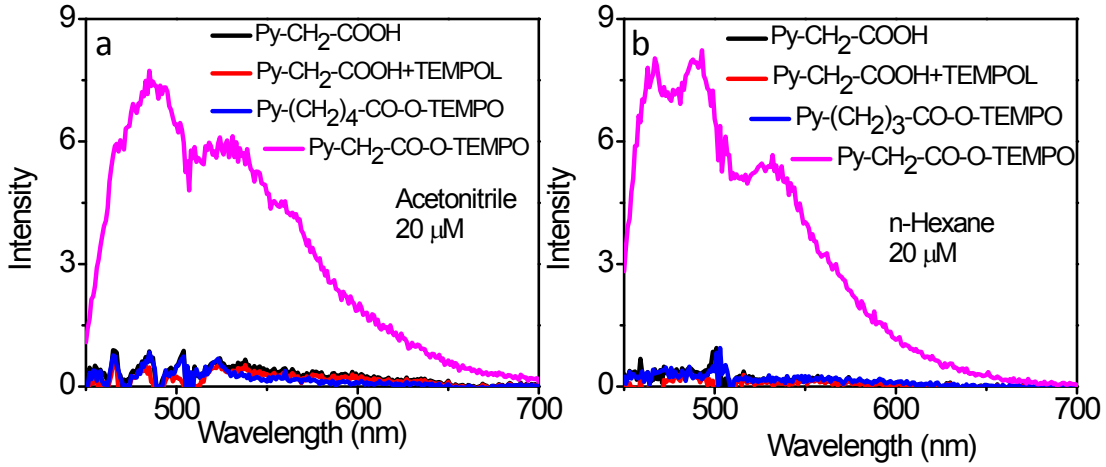


Fig. S3 Fluorescence emissions spectra of Py-CH_2-COOH, Py-CH_2-COOH+TEMPOL, Py-$(CH_2)_3$-CO-O-TEMPO and Py-CH_2-CO-O-TEMPO, recorded at λ_{ex} = 450 nm, in acetonitrile (a) and *n*-hexane (b), after subtraction of Raman lines. Concentration: 20 μM.

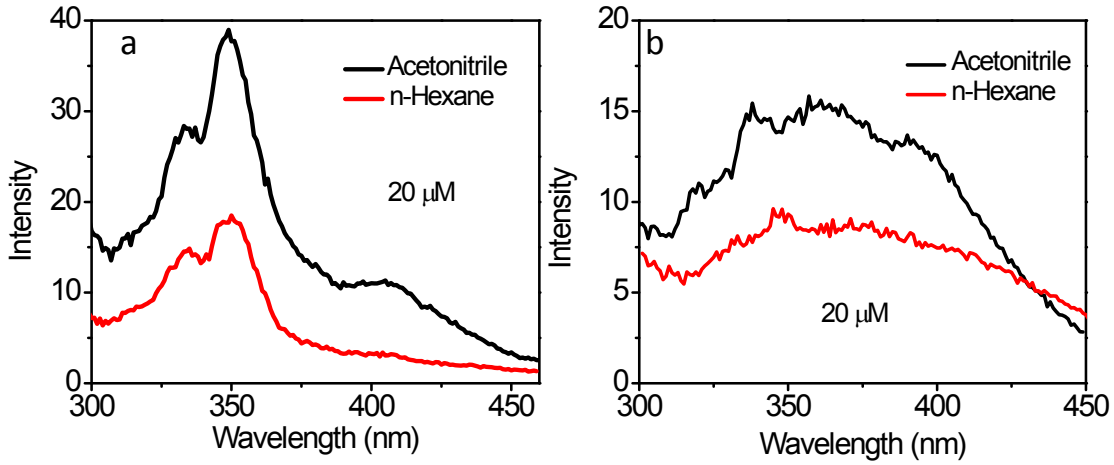


Fig. S4 Fluorescence excitation spectra of Py-CH_2-O-TEMPO (a) and Py-CH_2-CO-O-TEMPO (b), in *n*-hexane and in acetonitrile, recorded at λ_{em} = 450 nm. Concentration: 20 μM.

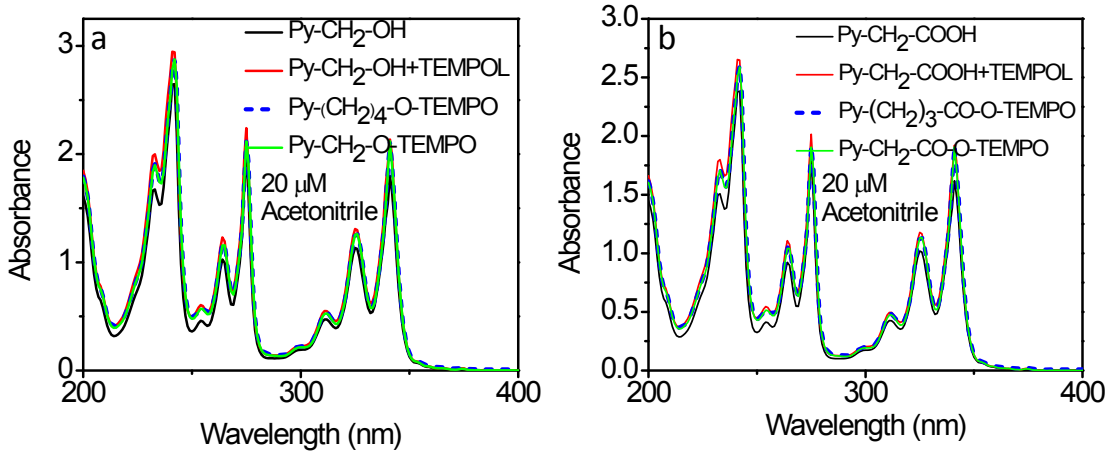


Fig. S5 Absorption spectra of Py-CH_2-OH, Py-CH_2-OH+TEMPOL (1:1), Py-$(CH_2)_4$-O-TEMPO, Py-CH_2-O-TEMPO (a), and Py-CH_2-OOH and Py-CH_2-COOH+TEMPOL (1:1), Py-$(CH_2)_3$-O-TEMPOL and Py-CH_2-CO-O-TEMPOL (b) in acetonitrile. Concentration: 20 μM.

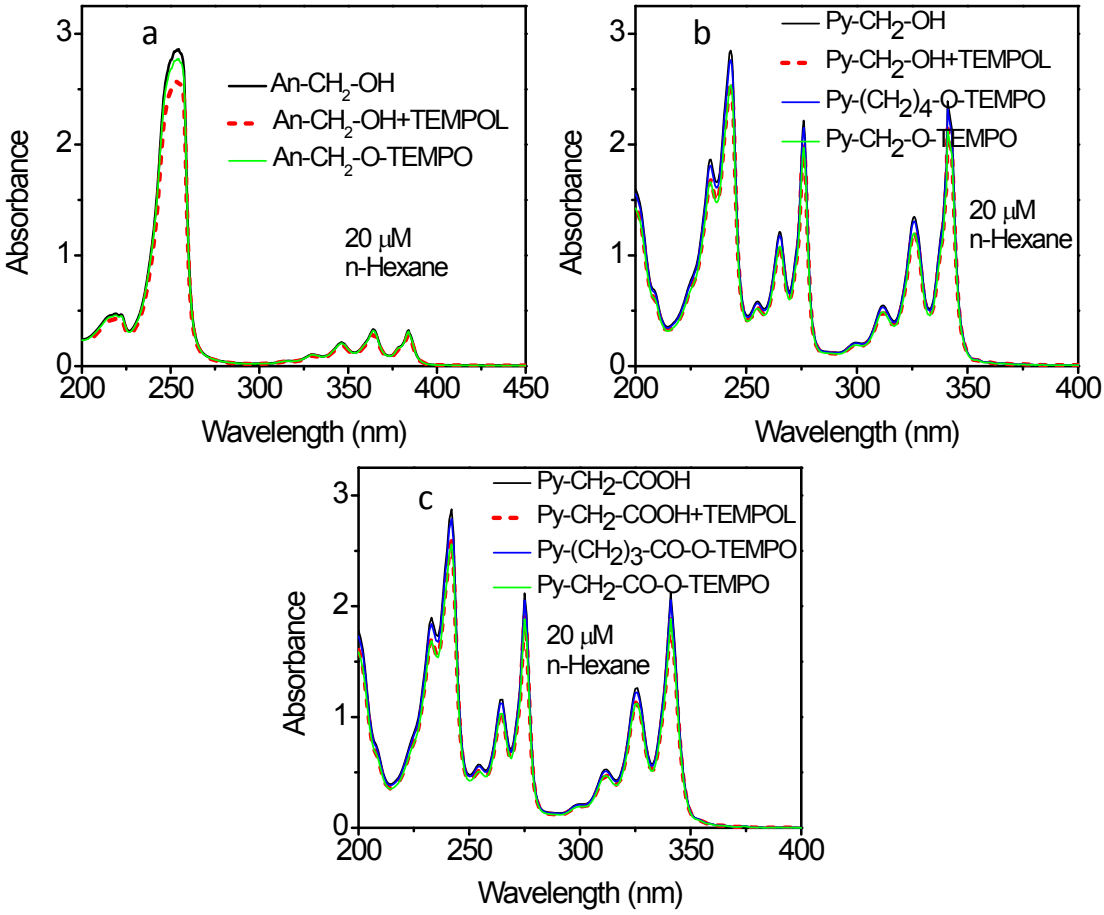


Fig. S6 Absorption spectra of An-CH_2-OH, An-CH_2-OH+TEMPOL (1:1) and An-CH_2-O-TEMPO (a), Py-CH_2-OH, Py-CH_2-OH+TEMPOL (1:1), Py-$(CH_2)_4$-O-TEMPO, Py-CH_2-O-TEMPO (b), Py-CH_2-OOH and Py-CH_2-COOH+TEMPOL (1:1), Py-$(CH_2)_3$-O-TEMPO and Py-CH_2-CO-O-TEMPO (c) in *n*-hexane. Concentration: 20 μM.

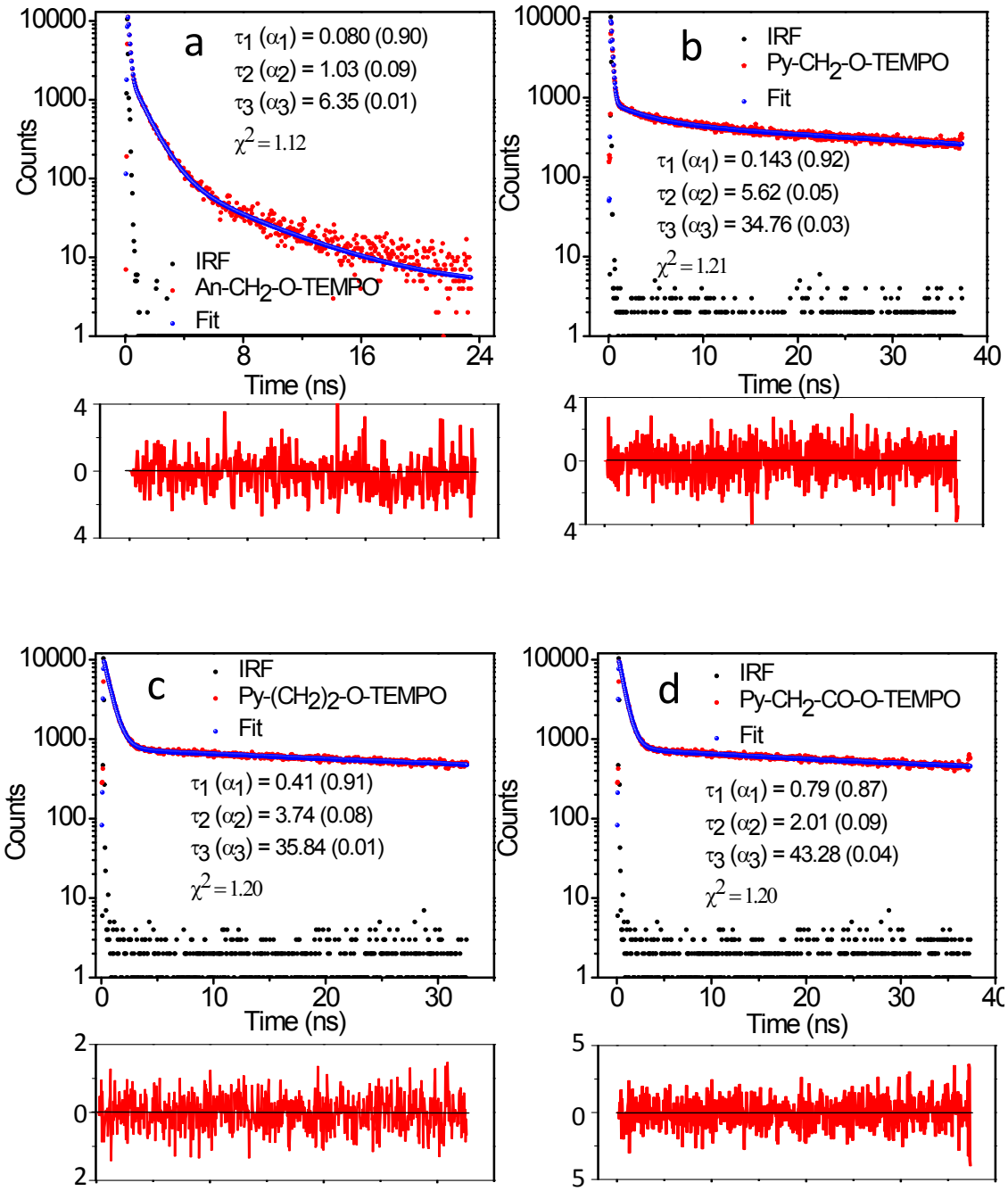


Fig. S7 Representative time-resolved fluorescence signals and their fits to a sum of multiexponentials. Plots of weighted residuals are shown below each panel. An-CH_2-O-TEMPO (a), Py-CH_2-O-TEMPO (b), Py-$(CH_2)_2$-O-TEMPO (c) and Py-CH_2-CO-O-TEMPO (d) in nitrogen-saturated *n*-hexane at room temperature. Concentration: 20 μM.

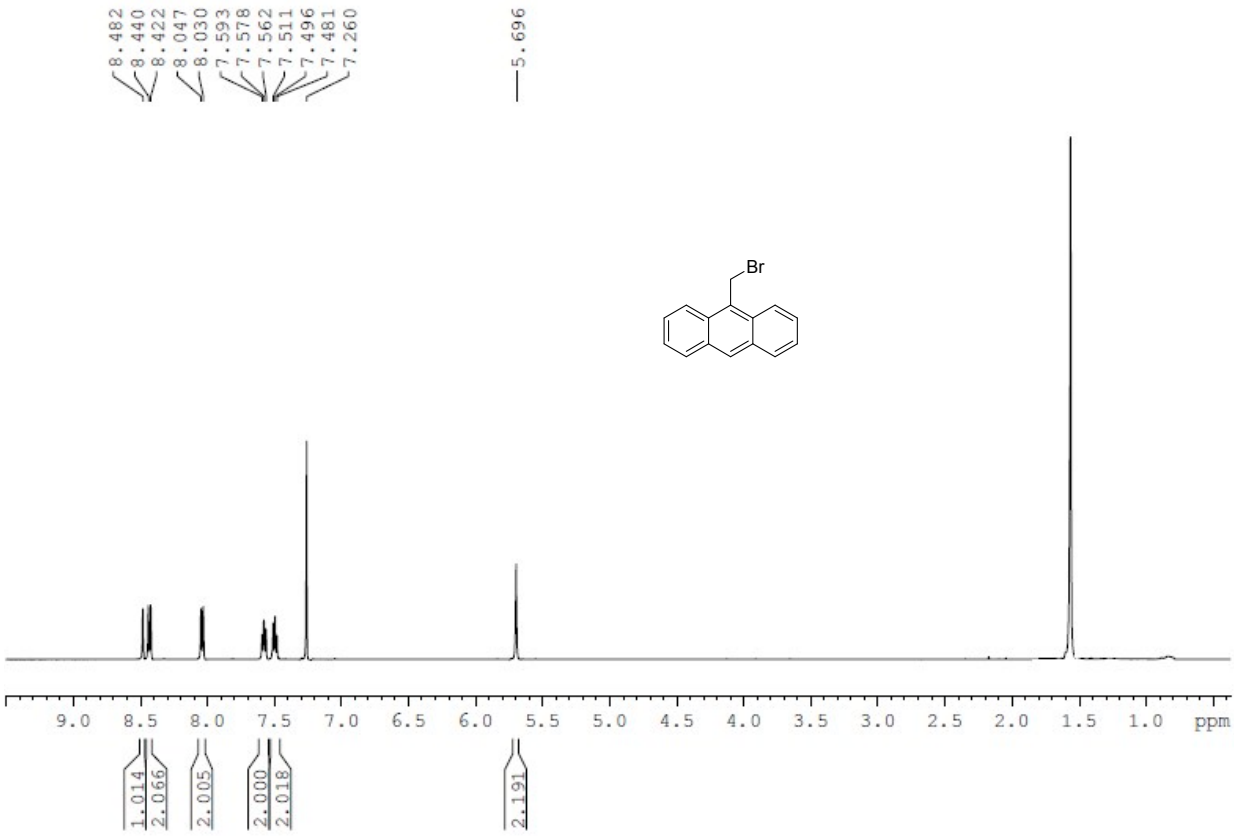


Fig. S8 600 MHz ^{1}H NMR spectrum of An-CH_2-Br (**1**) in $CDCl_3$.

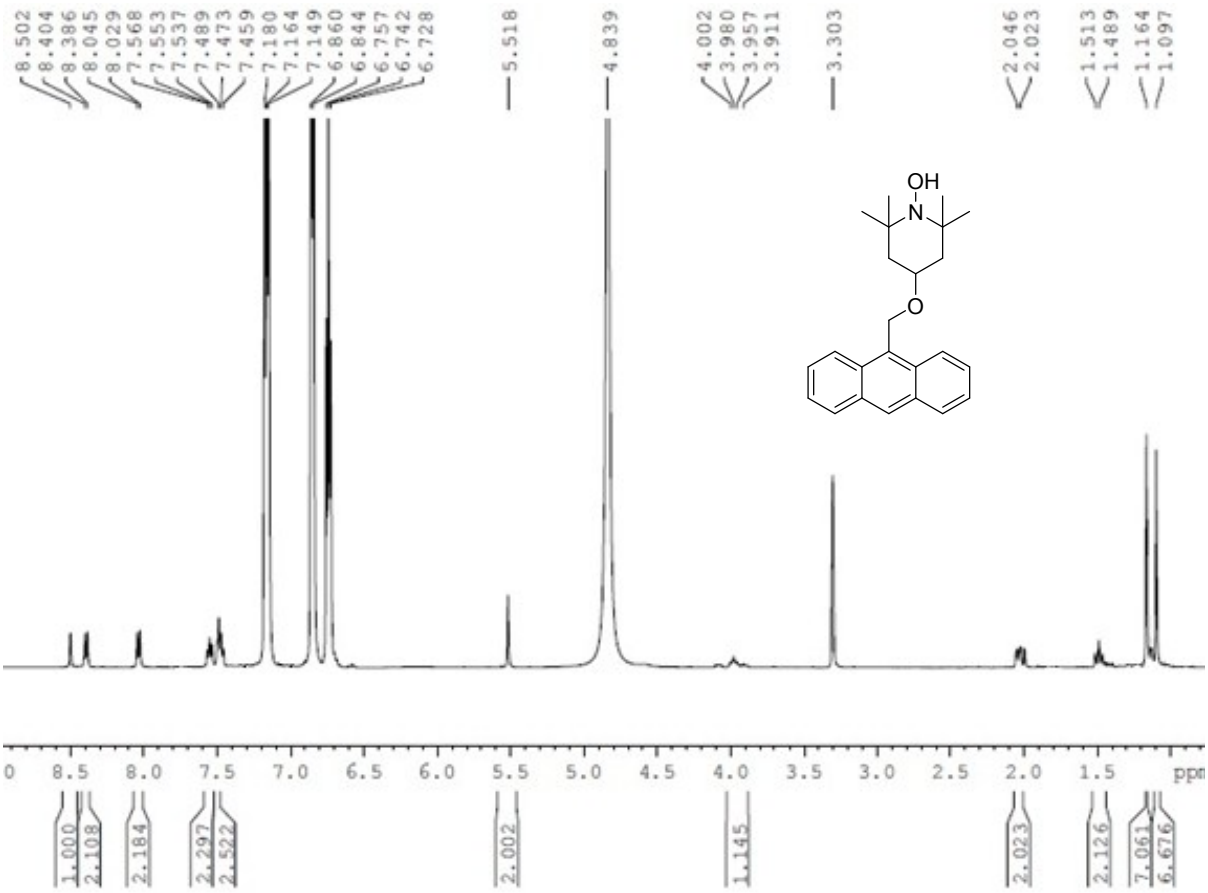


Fig. S9 600 MHz ^{1}H NMR spectrum of An-CH_2-O-TEMPOH after reduction of An-CH_2-O-TEMPO (**2**) by phenyl hydrazine in CD_3OD.

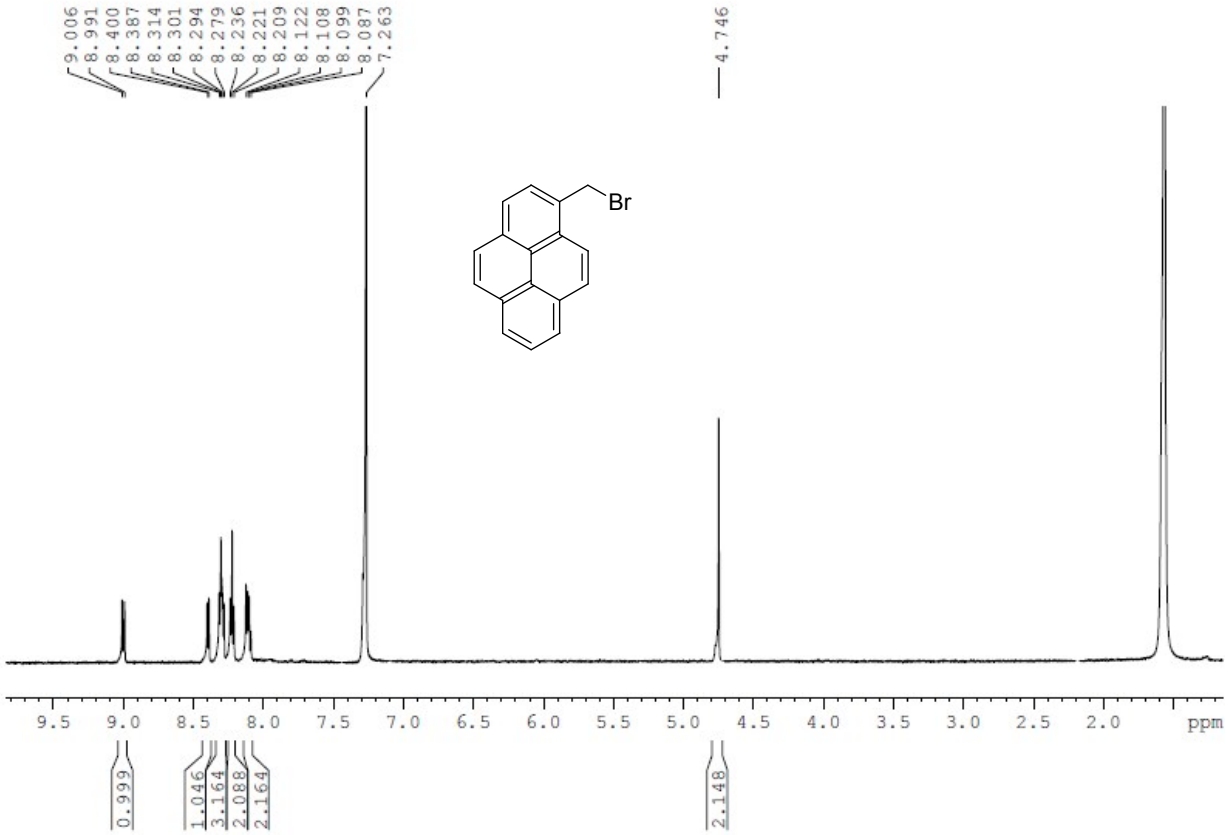


Fig. S10 600 MHz ^{1}H NMR spectrum of Py-CH_2-Br (**3**) in $CDCl_3$.

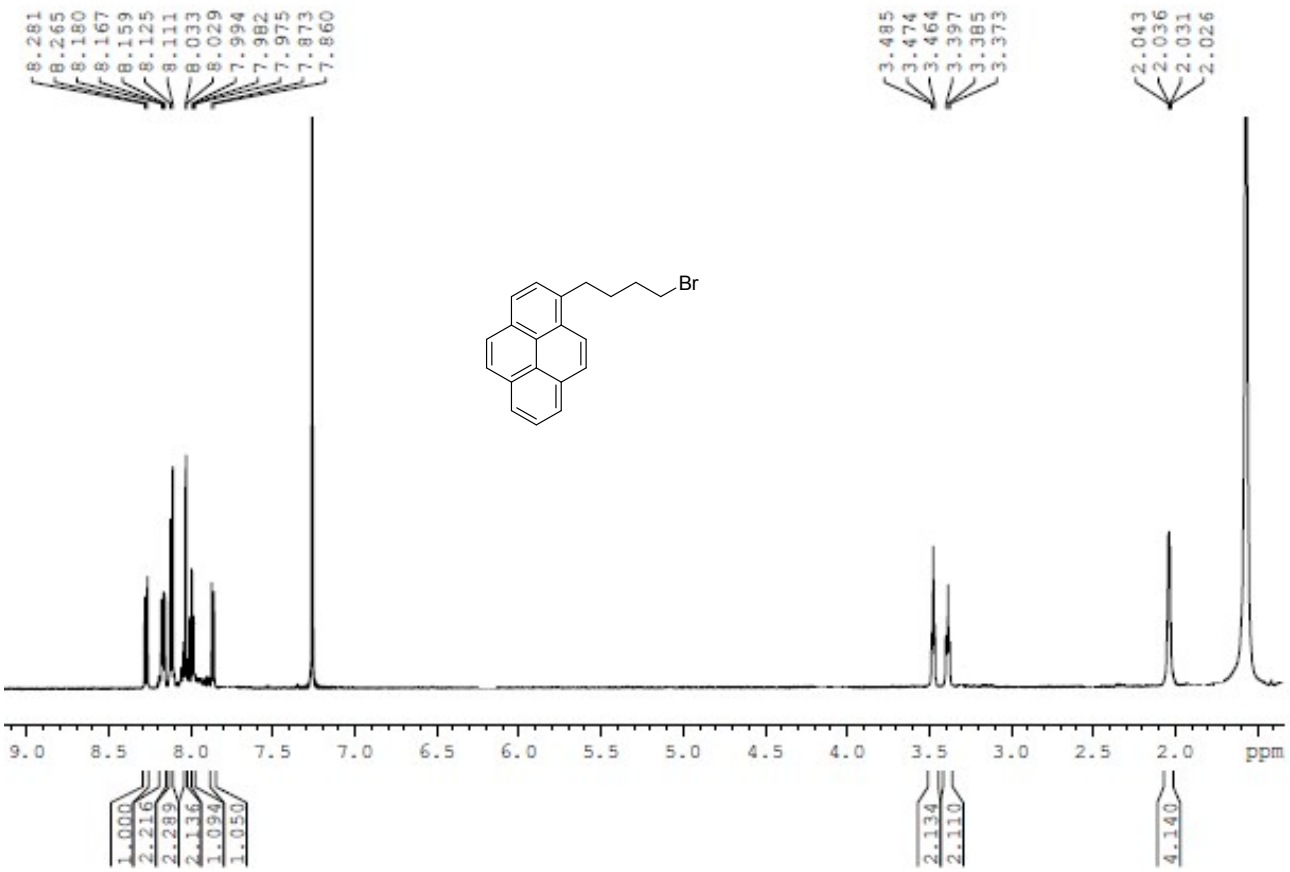


Fig. S11 600 MHz ^{1}H NMR spectrum of Py-$(CH_2)_4$-Br (**4**) in $CDCl_3$.

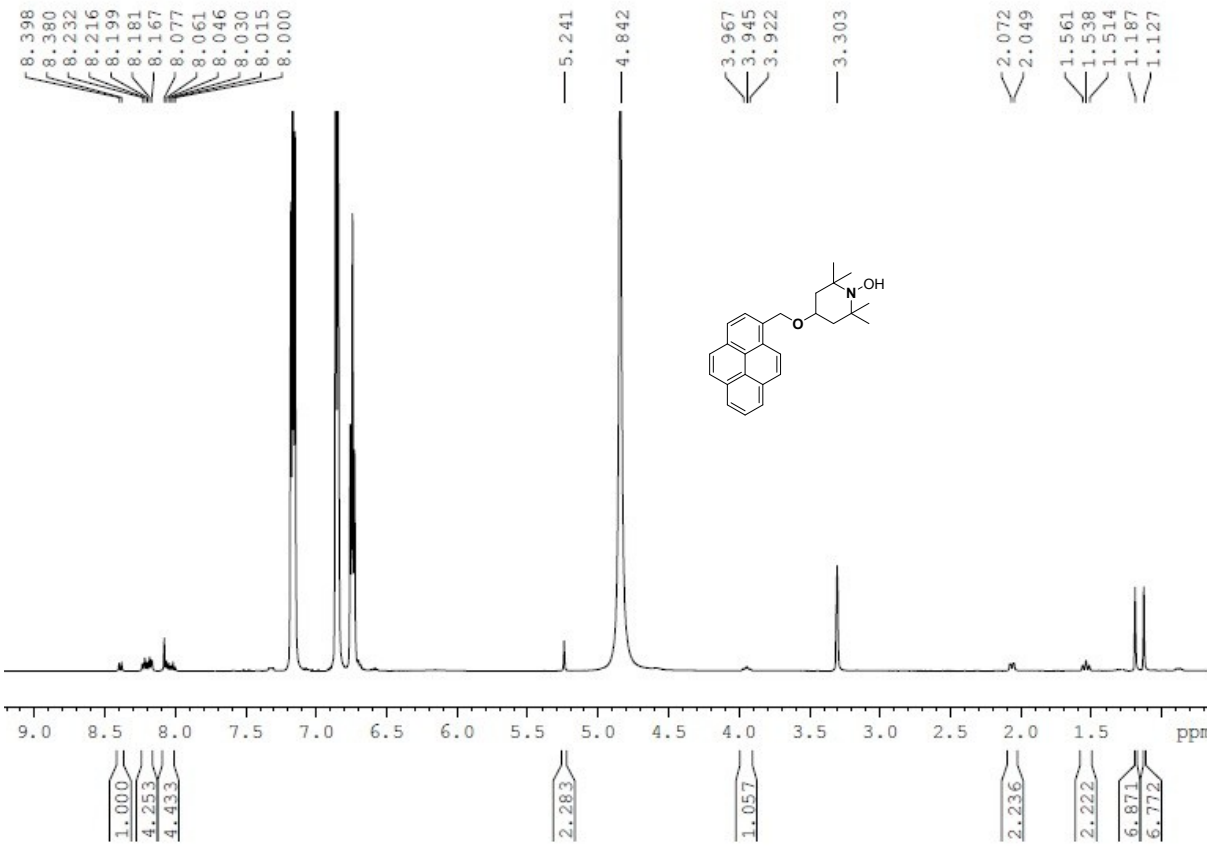


Fig. S12 600 MHz ^{1}H NMR spectrum of Py-CH_2-O-TEMPOH after reduction of Py-CH_2-O-TEMPO (**5**) by phenyl hydrazine in CD_3OD.

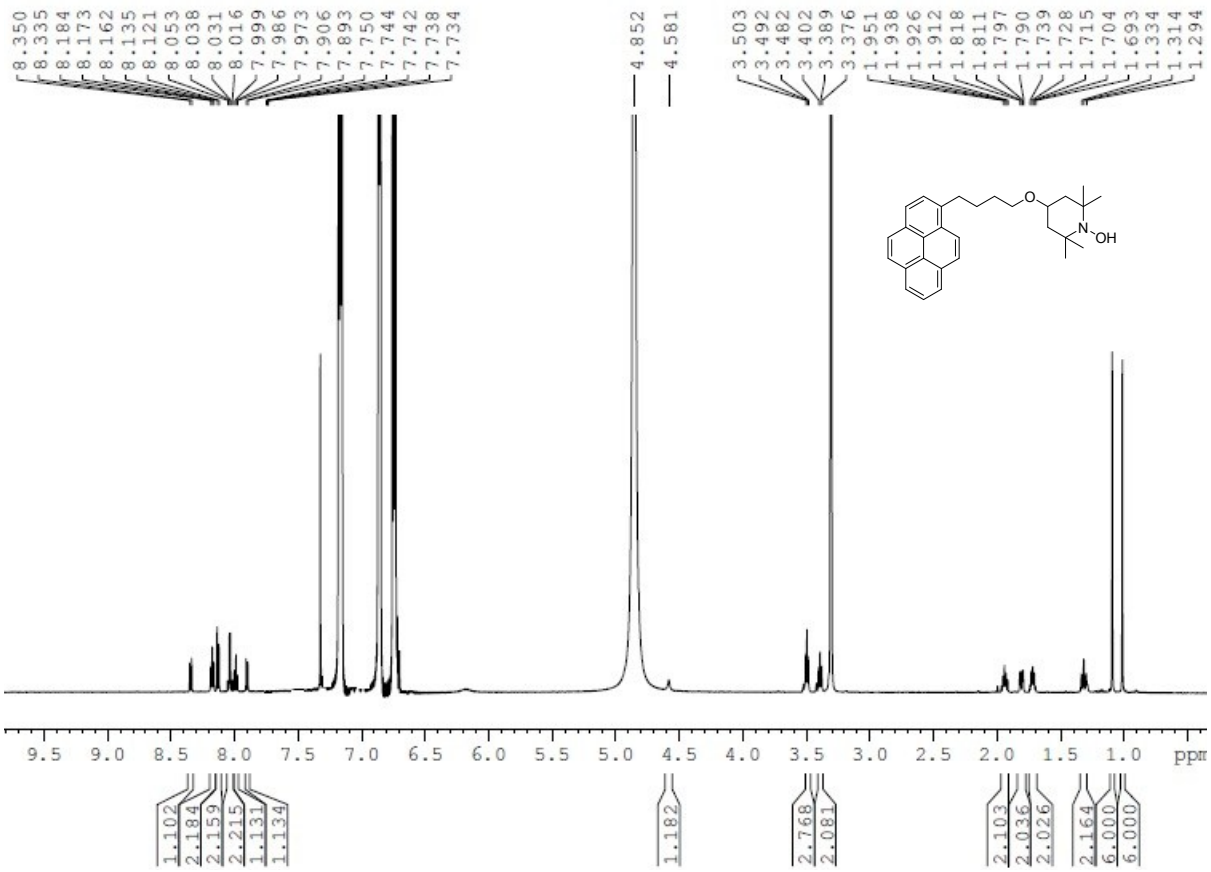


Fig. S13 600 MHz ^{1}H NMR spectrum of Py-$(CH_2)_4$-O-TEMPOH after reduction of Py-$(CH_2)_4$-O-TEMPO (**6**) by phenyl hydrazine in CD_3OD.

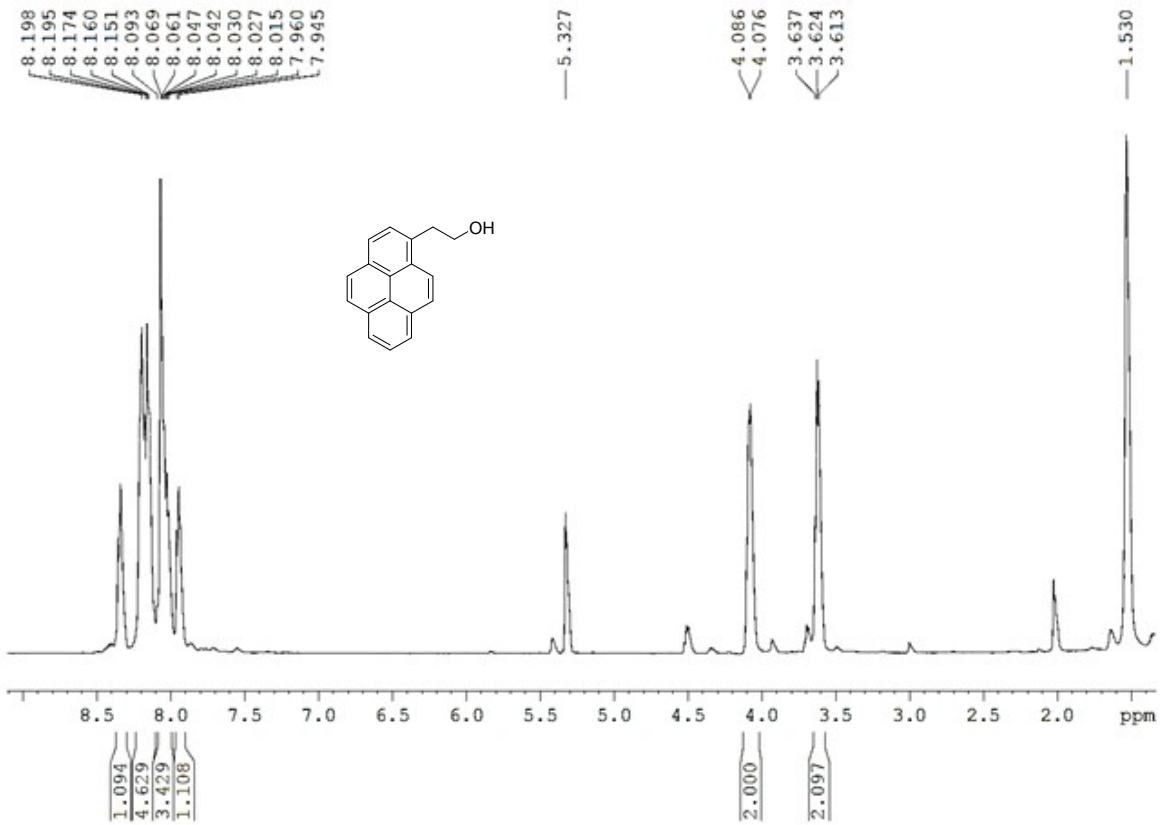


Fig. S14 500 MHz ^{1}H NMR spectrum of Py-$(CH_2)_2$-OH (**7**) in CD_2Cl_2.

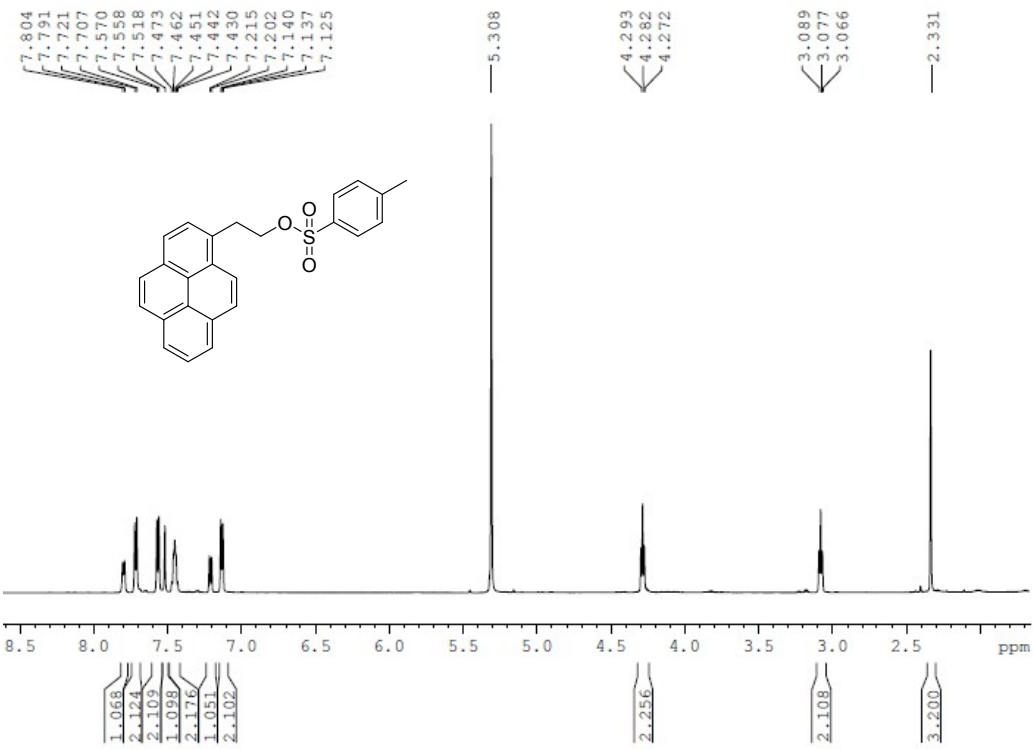


Fig. S15 600 MHz ^{1}H NMR spectrum of Py-$(CH_2)_2$-OTs (**8**) in CD_2Cl_2.

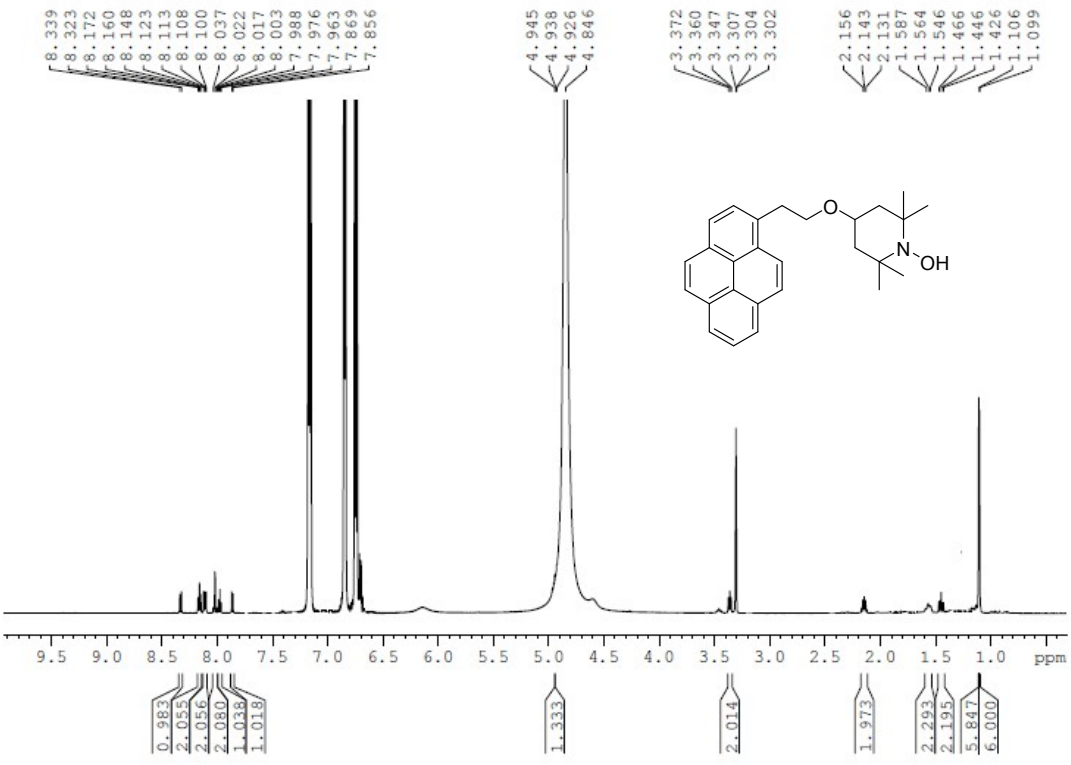


Fig. S16 600 MHz ^{1}H NMR spectrum of Py-$(CH_2)_2$-O-TEMPOH after reduction of Py-$(CH_2)_2$-O-TEMPO (**9**) by phenyl hydrazine in CD_3OD.

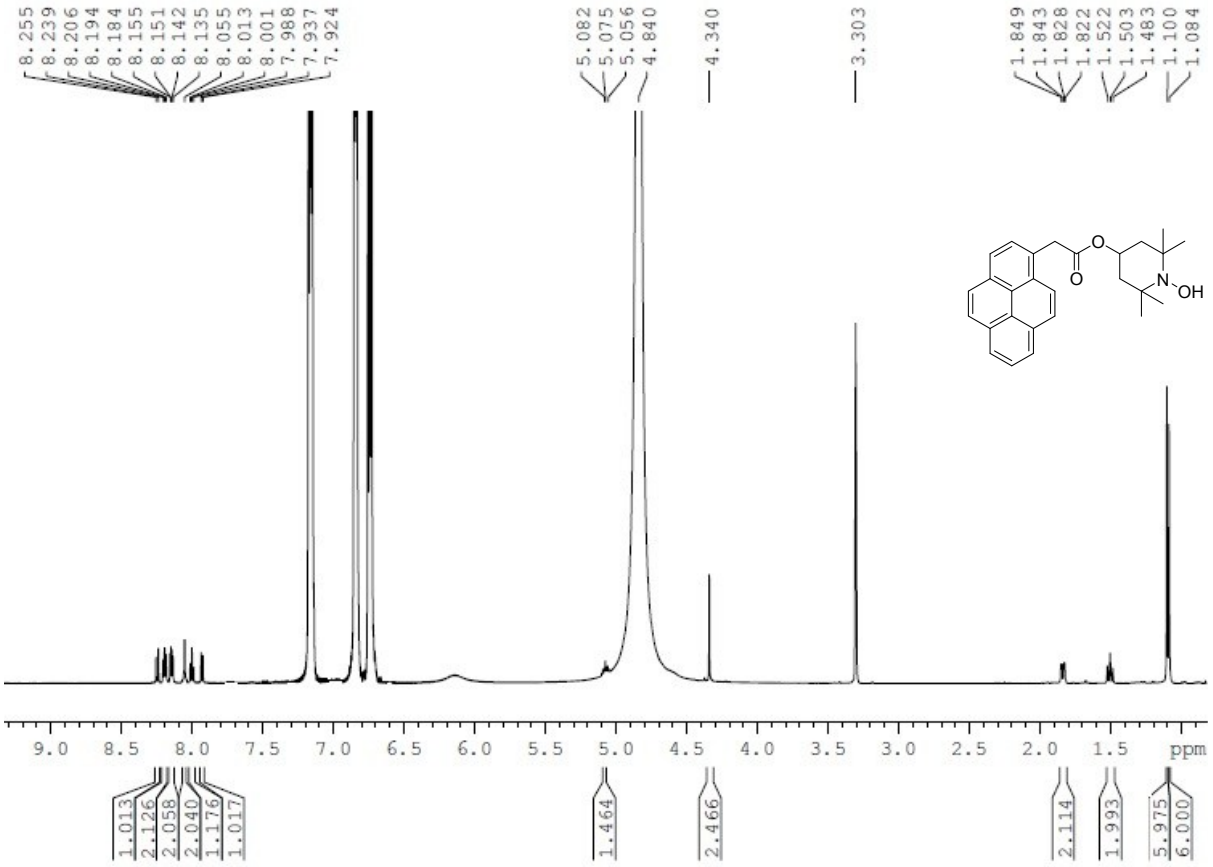


Fig. S17 600 MHz ^{1}H NMR) spectrum of Py-CH_2-CO-O-TEMPOH after reduction of Py-CH_2-CO-O-TEMPO (**10**) by phenyl hydrazine in CD_3OD.

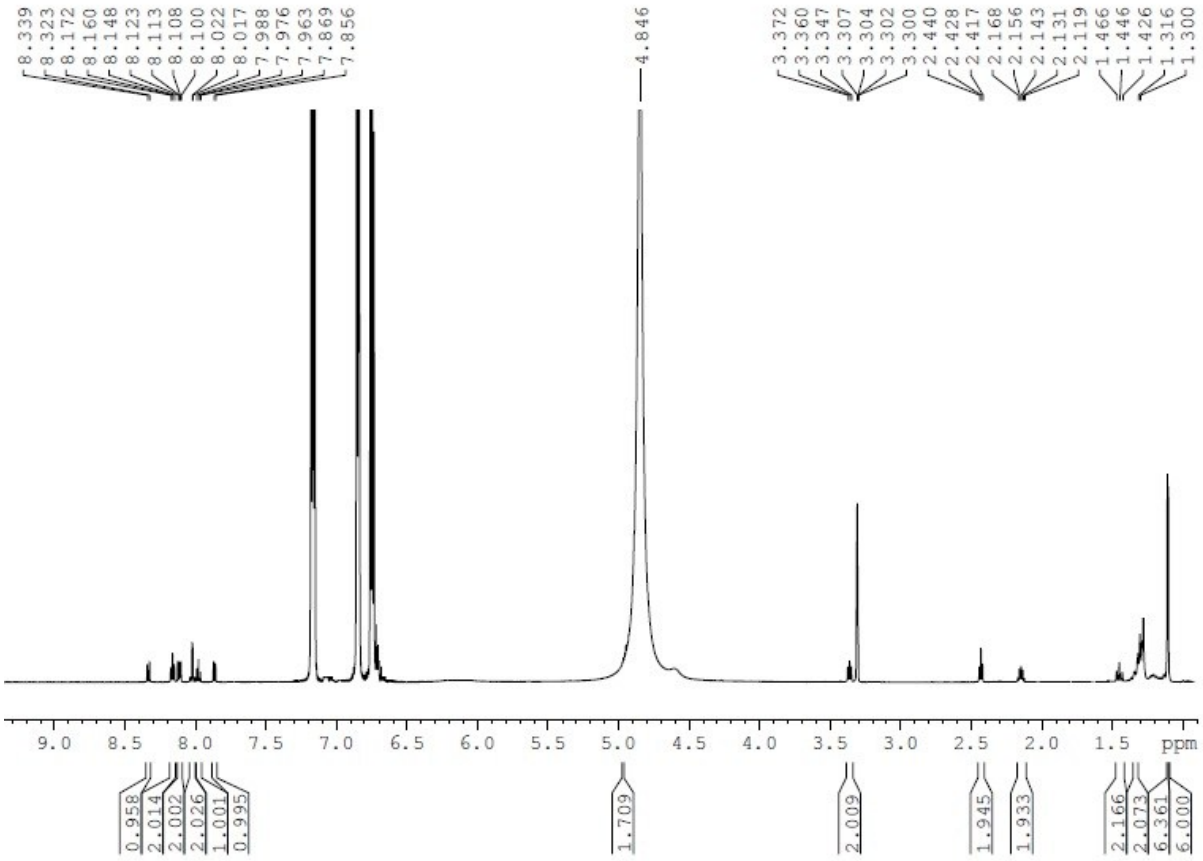


Fig. S18 600 MHz ^{1}H NMR spectrum of Py-$(CH_2)_3$-CO-O-TEMPOH after reduction of Py-$(CH_2)_3$-CO-O-TEMPO (**11**) by phenyl hydrazine in CD_3OD.