Electronic Supplementary Information

"Snorkelling" *vs* "Diving" in Mixed Micelles Probed by Means of a Molecular Bathymeter

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1. Experimental Section

Materials and solvents. (*S*)-Naproxen (NPX), glycine methyl ester hydrochloride, β-alanine methyl ester hydrochloride, methyl 4-aminobutyrate hydrochloride, cholesterol (Ch), egg lecithin from fresh egg yolk (L), *N*-(3-dimethylaminopropyl)-*N′*-ethylcarbodiimide (EDC), *N*,*N*-diisopropyl-*N*-ethylamine (DIEA), 4-pyrrolidylpyridine (4-Pr-Py), N-methylmorpholine N-oxide, osmium tetroxide, 1-Hydroxybenzotriazole hydrate (HOBt·H_2O), potassium bromide, sulfuric acid, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), benzyl bromide, O-(benzotriazol-1-yl)-*N,N,N′,N′*-tetramethyluronium tetrafluoroborate (TBTU) 2-methoxy-6-vinylnaphthalene, 1-(6-methoxy-2-naphthyl)ethanol, lithocholic acid (LA), KOH and NaCl were purchased from Sigma–Aldrich. Sodium cholate (NaCA) was provided by Across Organics.

Chemicals purchased from commercial sources were used as received.

Milli-Q® water from Merck (Millipore) was used for sample preparation. Dichloromethane and methanol (HPLC grade) were from Scharlab. Melting points were recorded using a Stuart™ melting point apparatus SMP3AC/DC input 110 V and were not corrected. The ^{1}H and ^{13}C NMR spectra were measured by means of a Bruker (Rheinstetten, Germany) 300 MHz instrument; $CDCl_3$ and CD_3OD were used as solvents, and the signal corresponding to the solvent in each case was taken as the reference: $CDCl_3$ ($\delta = 7.26$ for ^{1}H NMR, $\delta = 77.2$ for ^{13}C NMR) and CD_3OD ($\delta = 3.31$ for ^{1}H NMR, $\delta = 49.0$ for ^{13}C NMR); coupling constants are given in Hz.

UPLC−MS/MS analysis for determination of exact mass. Liquid chromatography was performed on an ACQUITY UPLC system (Waters Corp.) with a conditioned autosampler at 10 °C. The separation was carried out on an ACQUITY UPLC BEH C18 column (50 mm × 2.1 mm i.d., 1.7 μm). The column temperature was maintained at 40 °C. The ESI source was operated in positive ionization mode with the capillary voltage at 1.9 kV. The temperature of the source and desolvation was set at 80 and 400 °C, respectively. The cone and desolvation gas flows were 20 and 800 L h^{-1}, respectively. All data were collected in centroid mode. Leucine-enkephalin was used as the lock mass generating an $[M + H]^+$ ion (m/z 556.2771) at a concentration of 250 pg/mL and flow rate of 50 μL/min to ensure accuracy during the MS analysis.

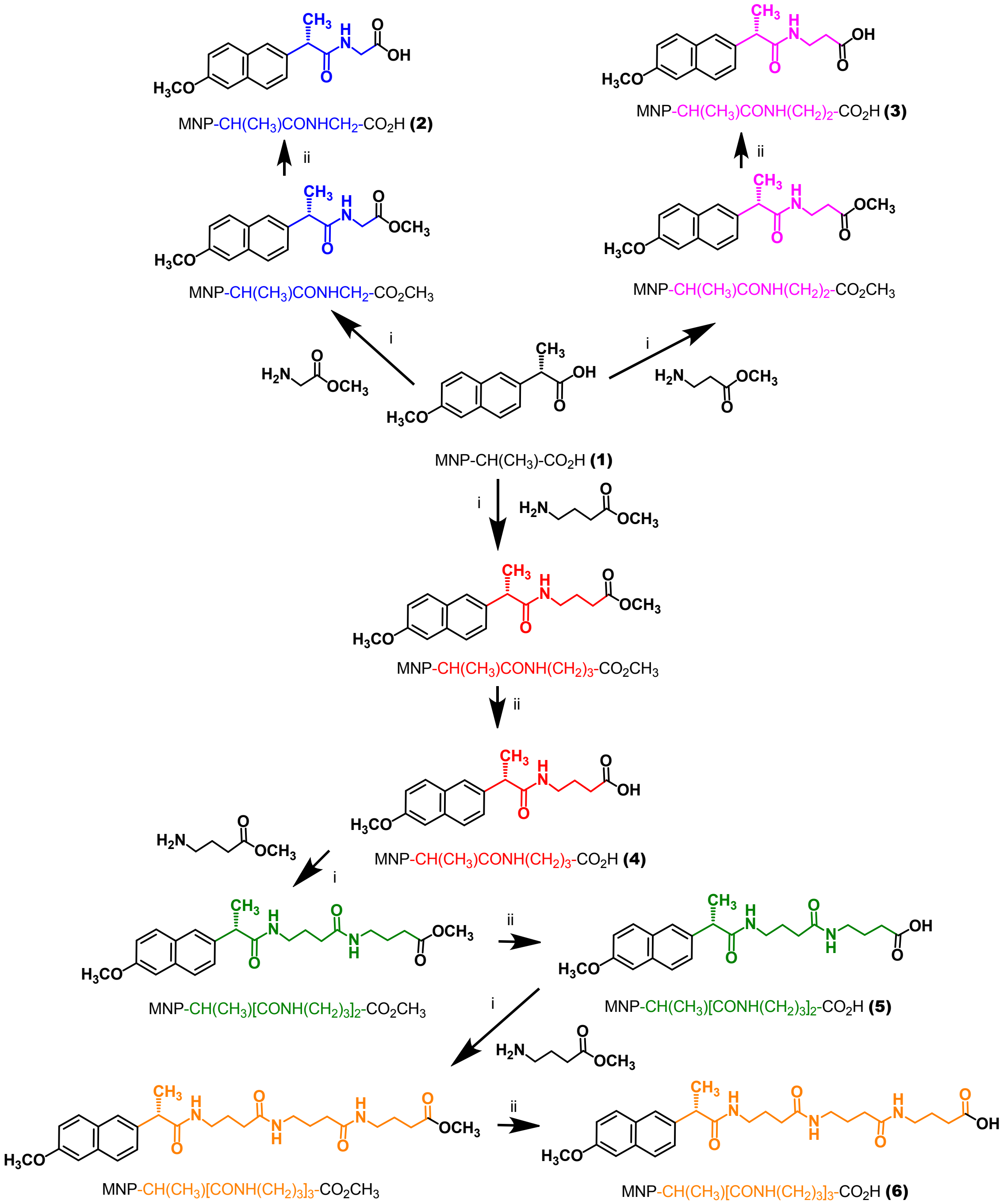
Preparation of mixed micelles (MM). To a solution of L (35.6 μmol) and NaCA (77.6 μmol) in CH_3OH (400 μL), Ch (10.8 μmol) in CH_2Cl_2 (200 μL) was added followed by a methanolic solution of the corresponding photoactive probe (0.054 μmol in 54.8 μL CH_3OH). Then, it was diluted with CH_3OH to reach a total volume of 10 mL. The final solution was concentrated using a rotary evaporation for thirty minutes at 50 ºC, and for further thirty minutes at room temperature using an oil pump. The obtained dry film was rehydrated with 2.74 mL of 0.2 M aqueous NaCl to form a clear MM solution.

Steady-state monochromatic irradiation. A Microbeam system (model L-201) including a Xe lamp (150 W) equipped with a monochromator (model 101) was employed for this purpose. The excitation wavelength was fixed at 330 nm and the samples were irradiated for 60 min.

Photophysical instrumentation. Steady-state fluorescence experiments were performed on a Photon Technology International (PTI, Germany) LPS-220B spectrofluorometer, equipped with a 75 W Xe lamp and a monochromator in the region of 200-700 nm. Time-resolved fluorescence measurements were carried out either with a Time Master fluorescence lifetime spectrometer TM 2/2003 from PTI, equipped with a hydrogen/nitrogen flash lamp as the excitation source or with an EasyLife V (OBB), apparatus equipped with a diode LED (λ_{exc} = 295 nm) excitation source; the residual excitation signal was filtered in emission by using a cut-off filter (50% transmission at 310 nm).

Photophysical experiments. Emission measurements were performed upon excitation of the probe (2 x 10^{-5} M) at 290 nm (steady-state measurements) or 295 nm (time-resolved experiments) under aerobic conditions at room temperature using 10 x 10 mm^2 quartz cells of 4 mL capacity. The kinetic traces were fitted to monoexponential decay functions.

2. Synthesis and Characterization of Probes 2-6



Scheme 1. Synthesis of probes **2-6**: (i) EDC, DIEA, 4-Pr-Py, CH_2Cl_2, N_2, rt; (ii) KOH, CH_3OH, rt.

2.1. Synthesis of MNP-$CH(CH_3)CONHCH_2$-CO_2H (2)

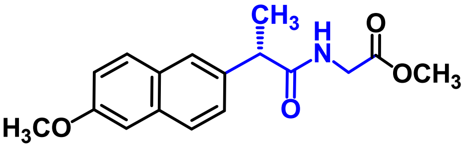
To a solution of (*S*)-NPX (500 mg, 2.17 mmol, 1 eq) in anhydrous CH_2Cl_2 (10 mL), EDC (423 µL, 2.40 mmol, 1.1 eq) was added, and the reaction mixture was cooled to 0 °C. Then, a solution of glycine methyl ester hydrochloride (354 mg, 2.82 mmol, 1.3 eq) in anhydrous CH_2Cl_2 (10 mL), containing DIEA (532 µL, 3.25 mmol, 1.5 eq) and 4-Pr-Py (160 mg, 1.08 mmol, 0.5 eq) was added dropwise under inert atmosphere, and the reaction mixture was stirred overnight at rt. Afterwards, the mixture was poured into water and extracted with CH_2Cl_2 (x3). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. Purification by column chromatography (ethyl acetate / n-hexane, 30:70), gave the ester MNP-$CH(CH_3)CONHCH_2$-CO_2CH_3 (395 mg, 60%).

The obtained methyl ester (136.9 mg, 0.45 mmol) was dissolved in MeOH (5 mL), treated with a solution of KOH in MeOH (1 M, 4.5 mL) and stirred overnight at room temperature. Then, the solvent was evaporated, and the mixture redissolved in H_2O (5 mL), acidified with 1 M HCl, extracted with AcOEt (x2) and purified by column chromatography (AcOEt / n-hexane / AcOH, 60 : 40 : 1) to give **2** (120 mg, 92%); mp: 96-99 ºC.

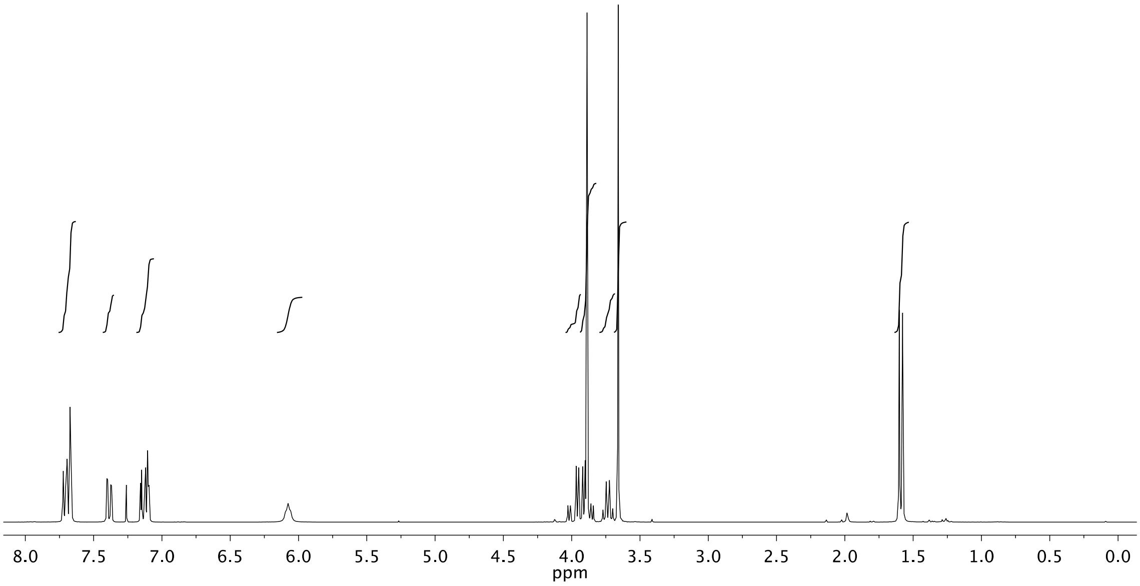
MNP-$CH(CH_3)CONHCH_2$-CO_2CH_3. ^1H NMR (300 MHz, $CDCl_3$): δ 1.59 (d, J = 7.2 Hz, 3H, CH_3), 3.66 (s, 3H, OCH_3), 3.73 (q, J = 7.2 Hz, 1H, CH), 3.88 (dd, J = 18.3 and 5.1 Hz, 1H, CHAHB), 3.89 (s, 3H, CO_2CH_3), 3.99 (dd, J = 18.3 and 5.7 Hz, 1H, CH_AH_B), 6.08 (br s, 1H, NH), 7.09-7.16 (m, 2H, Ar-H), 7.39 (m, 1H, Ar-H), 7.65-7.74 (m, 3H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.5 (CH_3), 41.3 (CH_2), 46.7 (CH), 52.2 (CH_3), 55.3 (CH_3), 105.7 (CH), 119.2 (CH), 126.2 (CH), 126.3 (CH), 127.5CH), 129.0 (C), 129.3 (CH), 133.8 (C), 136.1 (C), 157.7 (C), 170.4 (CO), 174.6 (CO). Exact mass: m/z found 302.1396, calculated for $C_{17}H_{20}NO_4$ (MH^+) 302.1392.

MNP-$CH(CH_3)CONHCH_2$-CO_2H (2). ^1H NMR (300 MHz, CD_3OD): δ 1.52 (d, *J* = 7.2 Hz, 3H, CH_3), 3.81 (d, *J* = 17.7 Hz, 1H, CHAHB), 3.82 (s, 3H, OCH_3) 3.83 (m, 1H, CH), 3.94 (d, *J* = 17.7 Hz, 1H, CH_AH_B), 7.07 (m, 1H, Ar-H), 7.13 (br d, *J* = 2.4 Hz, 1H, Ar-H), 7.42 (m, 1H, Ar-H), 7.63-7.72 (m, 3H, Ar-H); ^{13}C NMR (75 MHz, CD_3OD): δ 18.8 (CH_3), 41.9 (CH_2), 47.2 (CH), 55.6 (CH_3), 106.5 (CH), 119.8 (CH), 126.9 (CH), 127.2 (CH), 128.0 (CH), 130.2 (CH), 130.3 (C), 135.1 (C), 137.7 (C), 158.9 (C), 172.9 (CO), 177.6 (CO). Exact mass: m/z found 288.1224, calculated for $C_{16}H_{18}NO_4$ (MH^+) 288.1236.

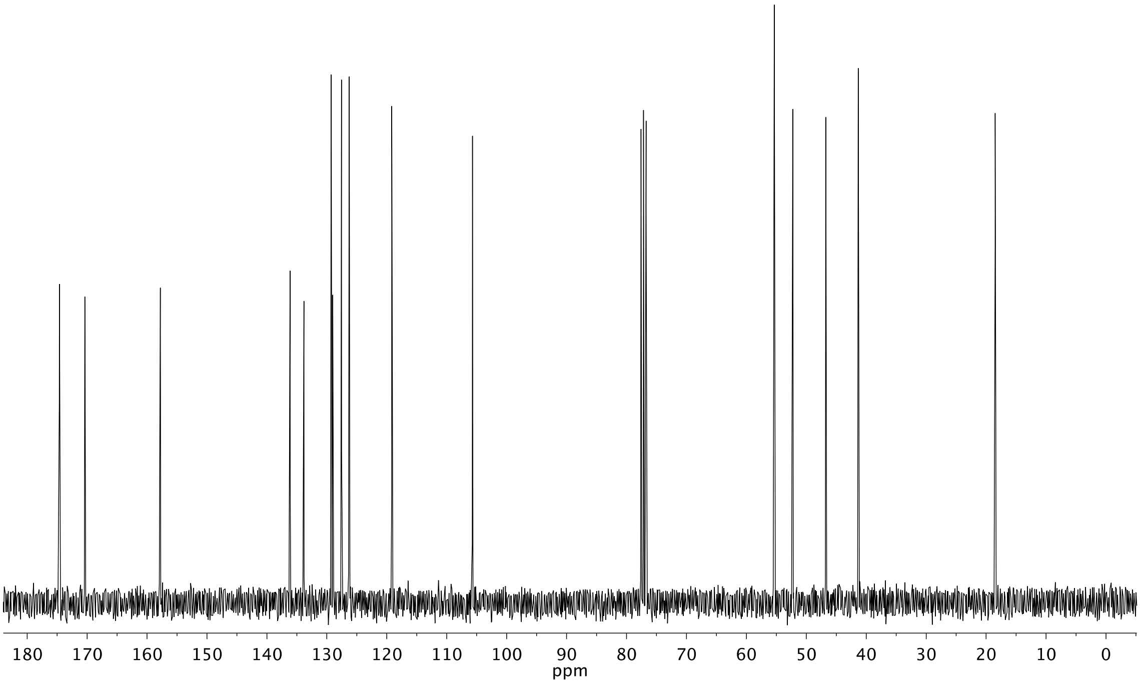
2.2. ^{1}H and ^{13}C NMR spectra of MNP-CH(CH$_3$)CONHCH$_2$-CO$_2$CH$_3$



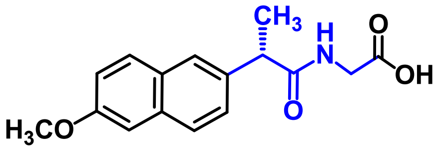
^{1}H NMR (CDCl$_3$, 300 MHz)



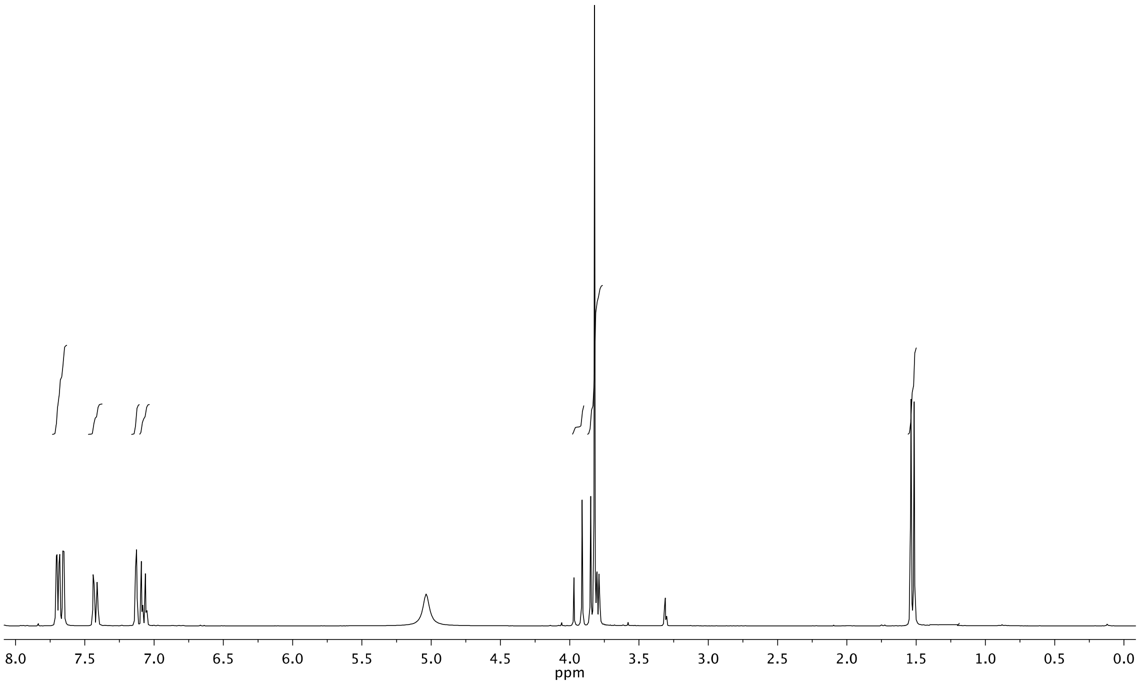
^{13}C NMR (CDCl$_3$, 75 MHz)



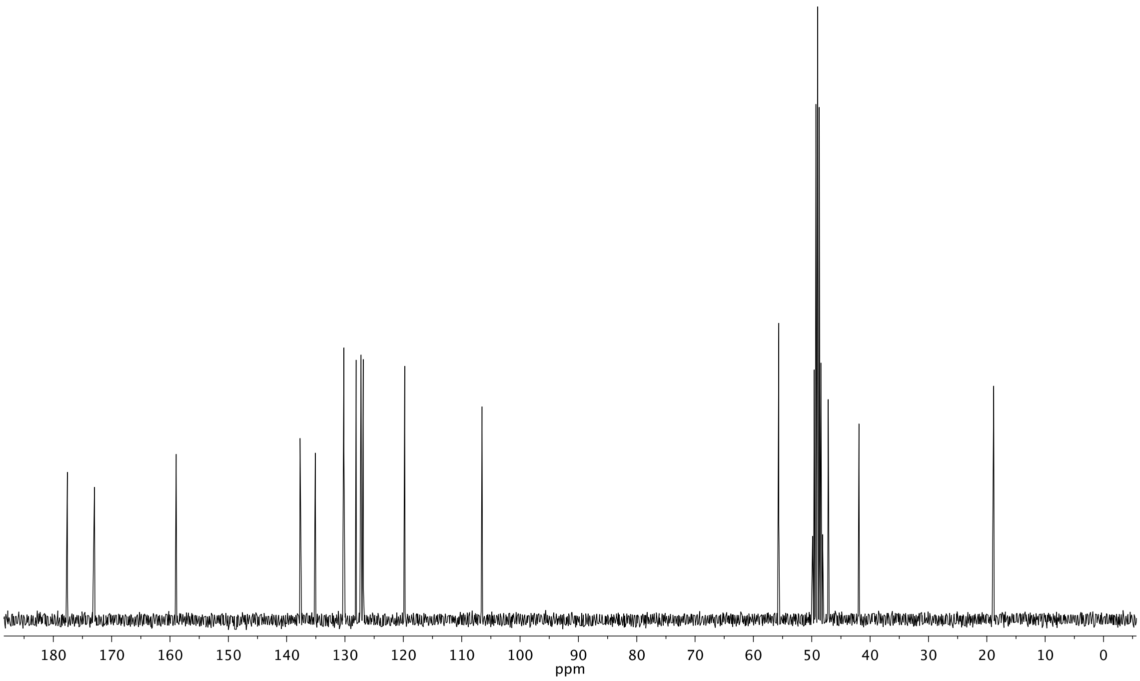
2.3. ^{1}H and ^{13}C NMR spectra of MNP-$CH(CH_3)CONHCH_2$-CO_2H (2)



^{1}H NMR (CD_3OD, 300 MHz)



^{13}C NMR (CD_3OD, 75 MHz)



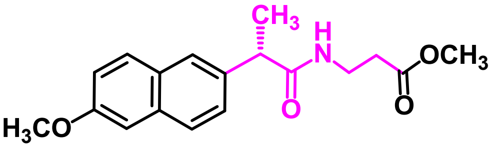
2.4. Synthesis of MNP-$CH(CH_3)CONH(CH_2)_2$-CO_2H (3)

The corresponding **3** methyl ester was prepared following the same experimental procedure described above in detail for the methyl ester of **2**. Briefly, starting from (*S*)-NPX (250 mg, 1.08 mmol, 1 eq) and using β-alanine methyl ester hydrochloride (180 mg, 1.30 mmol, 1.2 eq) as spacer, the ester MNP-$CH(CH_3)CONH(CH_2)_2$-CO_2CH_3 was obtained in 35% yield (120 mg) after purification by column chromatography (ethyl acetate / n-hexane, 30 : 70). Then, the ester was saponified as described in detail for the preparation of **2**. Thus, after purification by column chromatography (AcOEt / n-hexane / AcOH, 60 : 40 : 1), **3** was obtained in 75% yield.

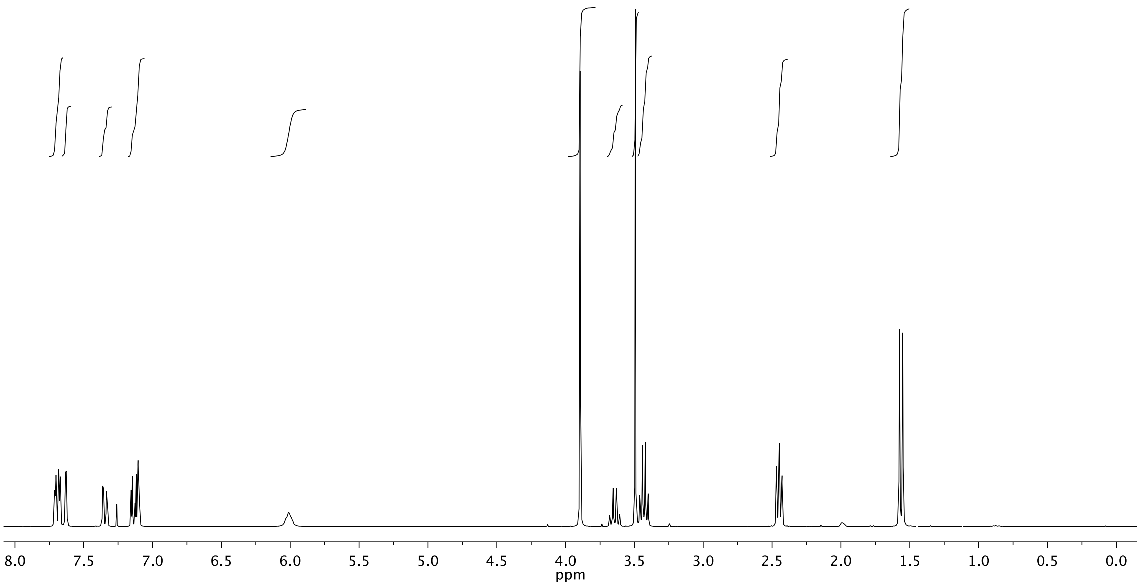
MNP-$CH(CH_3)CONH(CH_2)_2$-CO_2CH_3. ^1H NMR (300 MHz, $CDCl_3$): δ 1.56 (d, *J* = 7.2 Hz, 3H, CH_3), 2.45 (t, *J* = 6.3 Hz, 2H, CH_2), 3.43 (q, *J* = 6.0 Hz, 2H, CH_2), 3.49 (s, 3H, OCH_3), 3.64 (q, *J* = 7.2 Hz, 1H, CH), 3.89 (s, 3H, CO_2CH_3), 6.01 (*br* s, 1H, NH), 7.07-7.17 (m, 2H, Ar-H), 7.35 (m, 1H, Ar-H), 7.63 (*br* s, 1H, Ar-H), 7.68-7.70 (m, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.5 (CH_3), 33.8 (CH_2), 35.1 (CH_2), 47.0 (CH), 51.7 (CH_3), 55.4 (CH_3), 105.7 (CH), 119.1 (CH), 126.1 (CH), 126.2 (CH), 127.5 (CH), 129.0 (C), 129.3 (CH), 133.8 (C), 136.5 (C), 157.7 (C), 172.8 (CO), 174.4 (CO).

MNP-$CH(CH_3)CONH(CH_2)_2$-CO_2H (3). ^1H NMR (300 MHz, CD_3OD): δ 1.50 (d, *J* = 7.2 Hz, 3H, CH_3), 2.46 (t, *J* = 6.6 Hz, 2H, CH_2), 3.40 (*br* t, *J* = 6.9 Hz, 2H, CH_2), 3.73 (q, *J* = 6.9 Hz, 1H, CH), 3.85 (s, 3H, OCH_3), 7.08 (m, 1H, Ar-H), 7.15 (*br* s, 1H, Ar-H), 7.40 (m, 1H, Ar-H), 7.65-7.71 (m, 3H, Ar-H); ^{13}C NMR (75 MHz, CD_3OD): δ 18.8 (CH_3), 34.5 (CH_2), 36.5 (CH_2), 47.3 (CH), 55.7 (CH_3), 106.5 (CH), 119.8 (CH), 126.7 (CH), 127.1 (CH), 128.1 (CH), 130.1 (CH), 130.3 (C), 135.1 (C), 137.8 (C), 159.0 (C), 175.2 (CO), 177.3 (CO). Exact mass: *m/z* found 302.1381, calculated for $C_{17}H_{20}NO_4$ (MH^+) 302.1392.

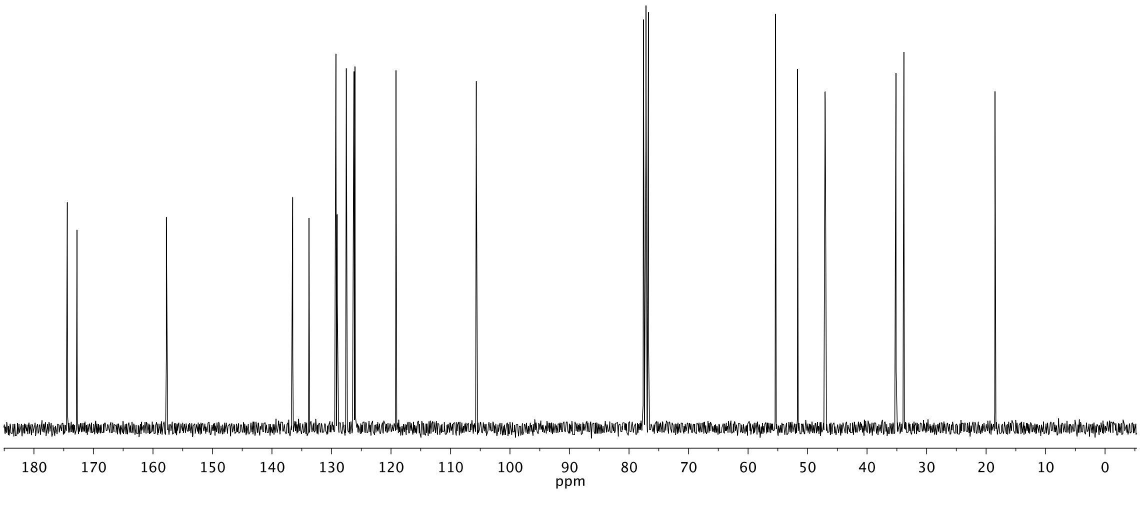
2.5. ^{1}H and ^{13}C NMR spectra of MNP-$CH(CH_3)CONH(CH_2)_2$-CO_2CH_3



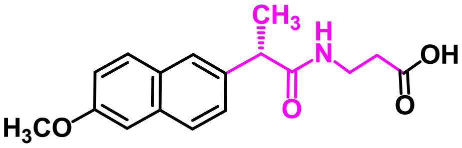
^{1}H NMR ($CDCl_3$, 300 MHz)



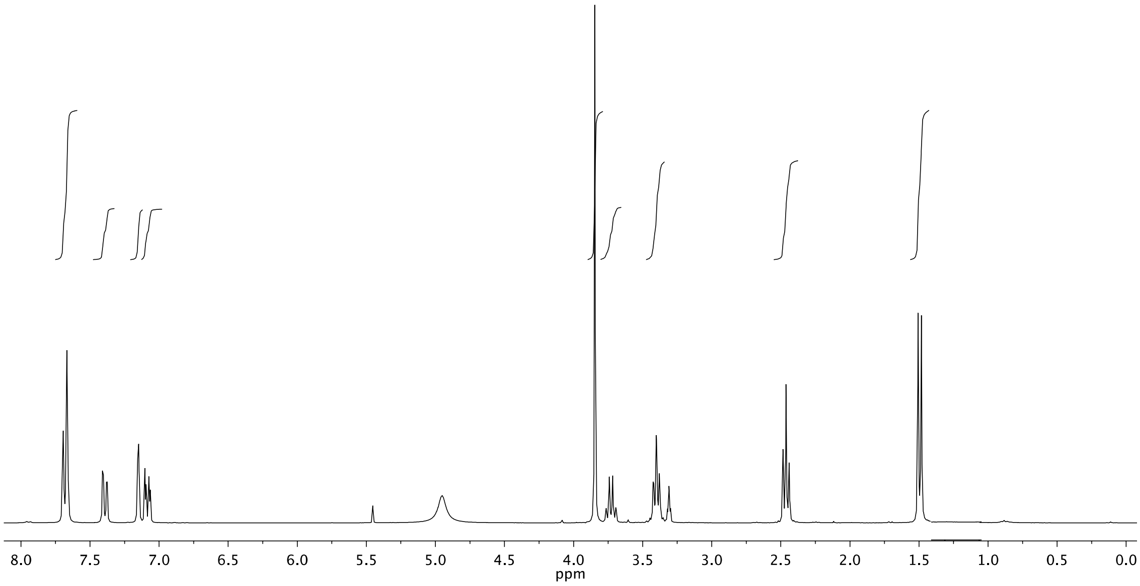
^{13}C NMR ($CDCl_3$, 75 MHz)



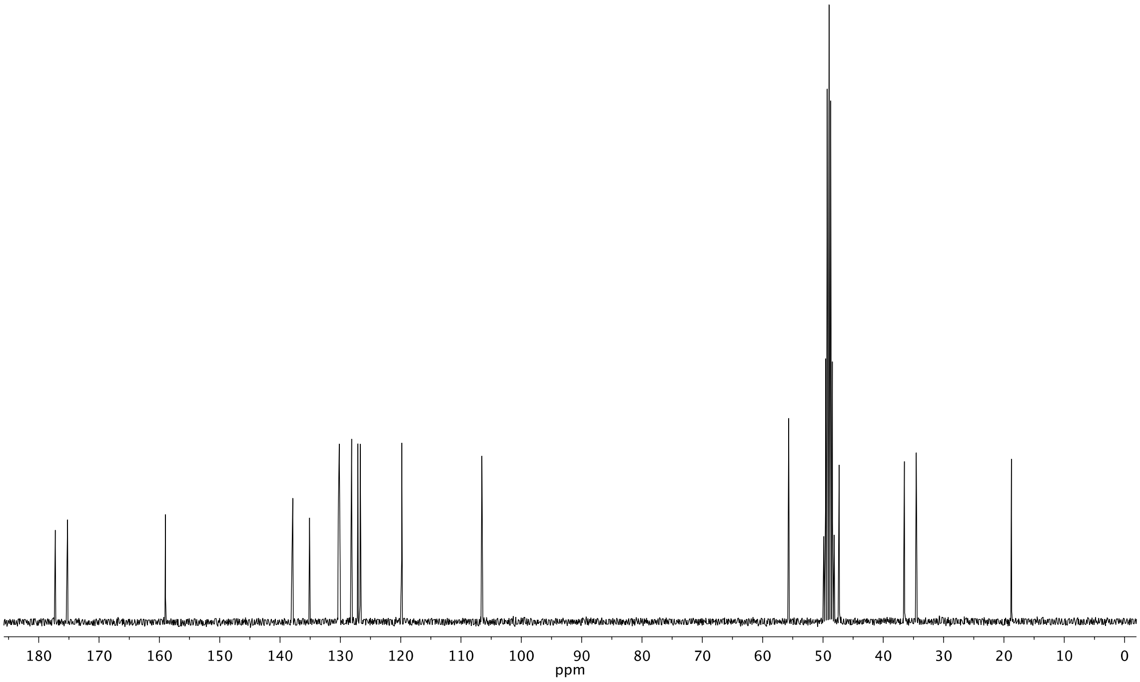
2.6. ^{1}H and ^{13}C NMR spectra of MNP-CH(CH$_3$)CONH(CH$_2$)$_2$-CO$_2$H (3)



^{1}H NMR (CD$_3$OD, 300 MHz)



^{13}C NMR (CD$_3$OD, 75 MHz)



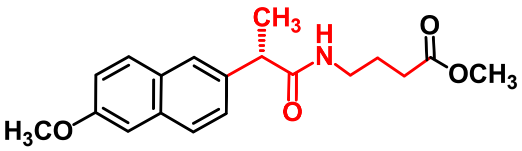
2.7. Synthesis of MNP-$CH(CH_3)CONH(CH_2)_3$-CO_2H (4)

The corresponding methyl ester of **4** was prepared following the same experimental procedure described above in detail for the methyl ester of **2**. Briefly, starting from (*S*)-NPX (1 g, 4.32 mmol, 1 eq) and using methyl 4-aminobutyrate hydrochloride (0.8 g, 5.20 mmol, 1.2 eq) as spacer, the ester MNP-$CH(CH_3)CONH(CH_2)_3$-CO_2CH_3 was obtained in 58% yield (840 mg) after purification by column chromatography (ethyl acetate / n-hexane, 30 : 70). Then, the ester was saponified following the preparation described in detail for **2**. Thus, after purification of the crude by column chromatography (AcOEt / n-hexane / AcOH, 60 : 40 : 1) **4** was obtained in 92% yield; mp: 138-140 ºC.

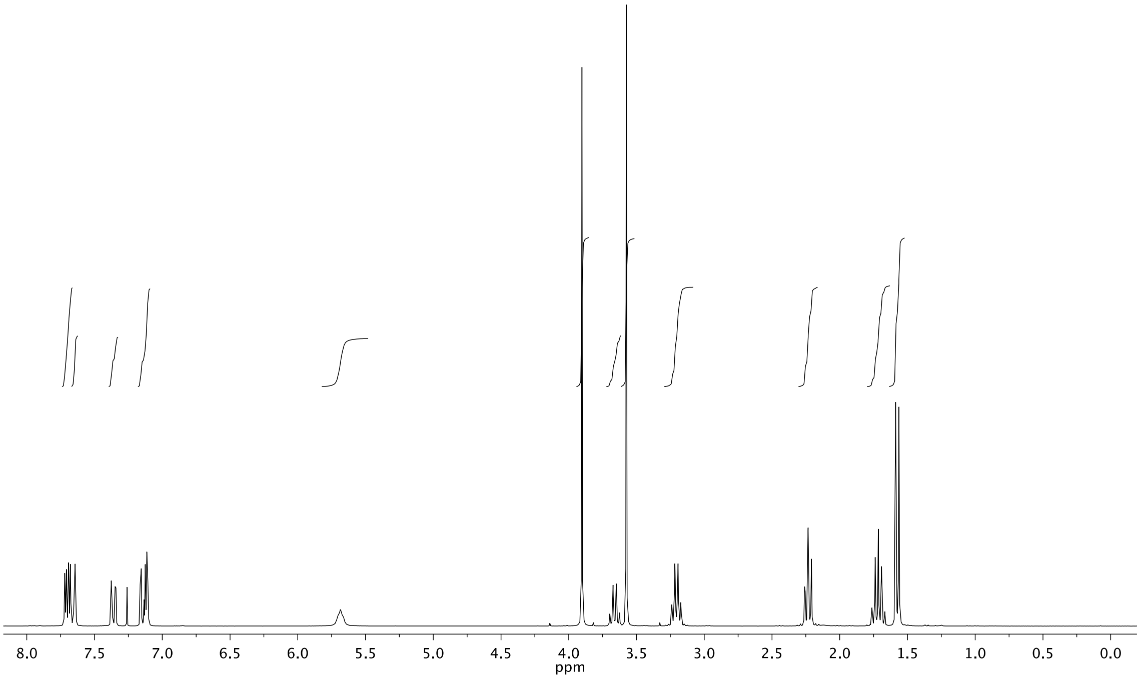
MNP-$CH(CH_3)CONH(CH_2)_3$-CO_2CH_3. ^1H NMR (300 MHz, $CDCl_3$): δ 1.56 (d, J = 7.2 Hz, 3H, CH_3), 1.71 (quint, J = 6.9 Hz, 2H, CH_2), 2.23 (t, J = 7.5 Hz, 2H, CH_2), 3.20 (q, J = 7.2 Hz, 2H, CH_2), 3.58 (s, 3H, OCH_3), 3.66 (q, J = 7.2 Hz, 1H, CH), 3.90 (s, 3H, CO_2CH_3), 5.69 (*br* s, 1H, NH), 7.09-7.17 (m, 2H, Ar-H), 7.36 (m, 1H, Ar-H), 7.65 (*br* s, 1H, Ar-H), 7.68-7.72 (m, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.6 (CH_3), 24.6 (CH_2), 31.4 (CH_2), 39.1 (CH_2), 47.1 (CH), 51.7 (CH_3), 55.4 (CH_3), 105.7 (CH), 119.2 (CH), 126.2 (CH), 126.3 (CH), 127.6 (CH), 129.0 (C), 129.3 (CH), 133.8 (C), 136.6 (C), 157.8 (C), 173.7 (CO), 174.5 (CO). Exact mass: *m/z* found 330.1704, calculated for $C_{19}H_{24}NO_4$ (MH^+) 330.1705.

MNP-$CH(CH_3)CONH(CH_2)_3$-CO_2H (4). ^1H NMR (300 MHz, CD_3OD): δ 1.51 (d, J = 7.2 Hz, 3H, CH_3), 1.74 (quint, J = 7.2 Hz, 2H, CH_2), 2.24 (t, J = 7.5 Hz, 2H, CH_2), 3.20 (t, J = 6.9 Hz, 2H, CH_2), 3.74 (q, J = 7.2 Hz, 1H, CH), 3.89 (s, 3H, OCH_3), 7.10 (m, 1H, Ar-H), 7.19 (*br* s, 1H, Ar-H), 7.41 (*br* d, J = 8.4 Hz, 1H, Ar-H), 7.66-7.73 (m, 3H, Ar-H); ^{13}C NMR (75 MHz, CD_3OD): δ 18.8 (CH_3), 25.7 (CH_2), 32.1 (CH_2), 39.8 (CH_2), 47.5 (CH), 55.7 (CH_3), 106.6 (CH), 119.8 (CH), 126.7 (CH), 127.1 (CH), 128.1 (CH), 130.2 (CH), 130.4 (C), 135.2 (C), 138.1 (C), 159.0 (C), 176.9 (CO), 177.3 (CO). Exact mass: *m/z* found 316.1545, calculated for $C_{18}H_{22}NO_4$ (MH^+) 316.1549.

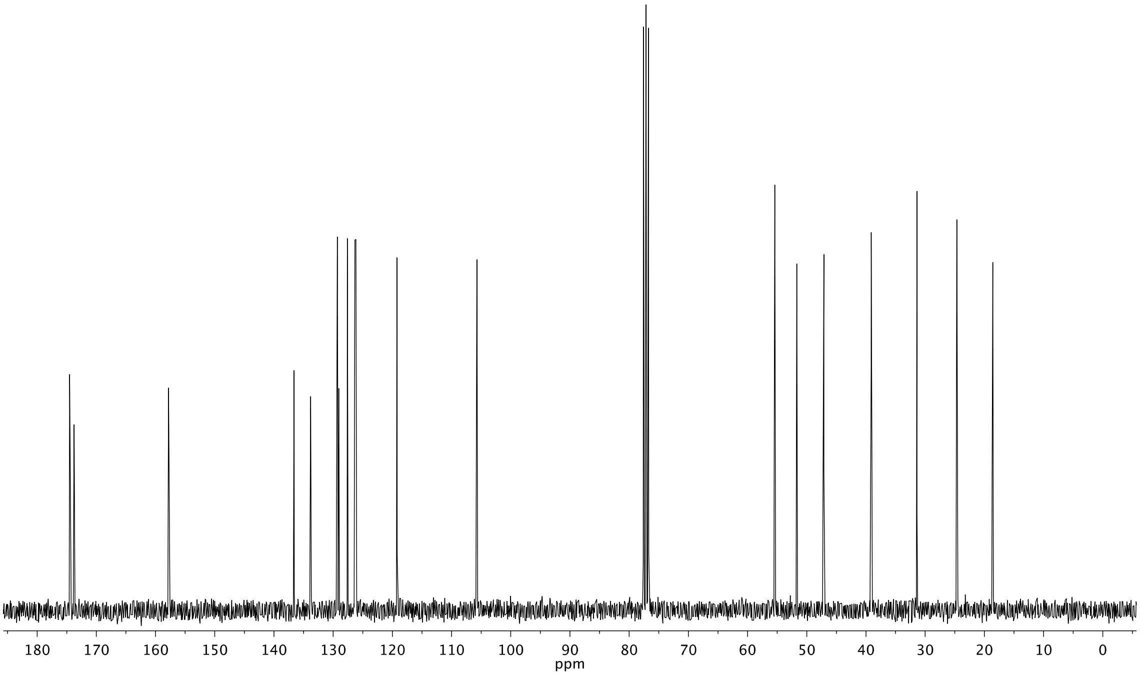
2.8. ^{1}H and ^{13}C NMR spectra of MNP-$CH(CH_3)CONH(CH_2)_3$-CO_2CH_3



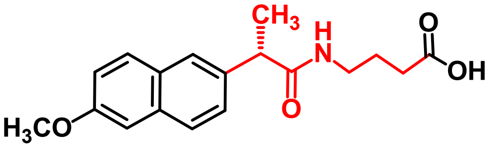
^{1}H NMR ($CDCl_3$, 300 MHz)



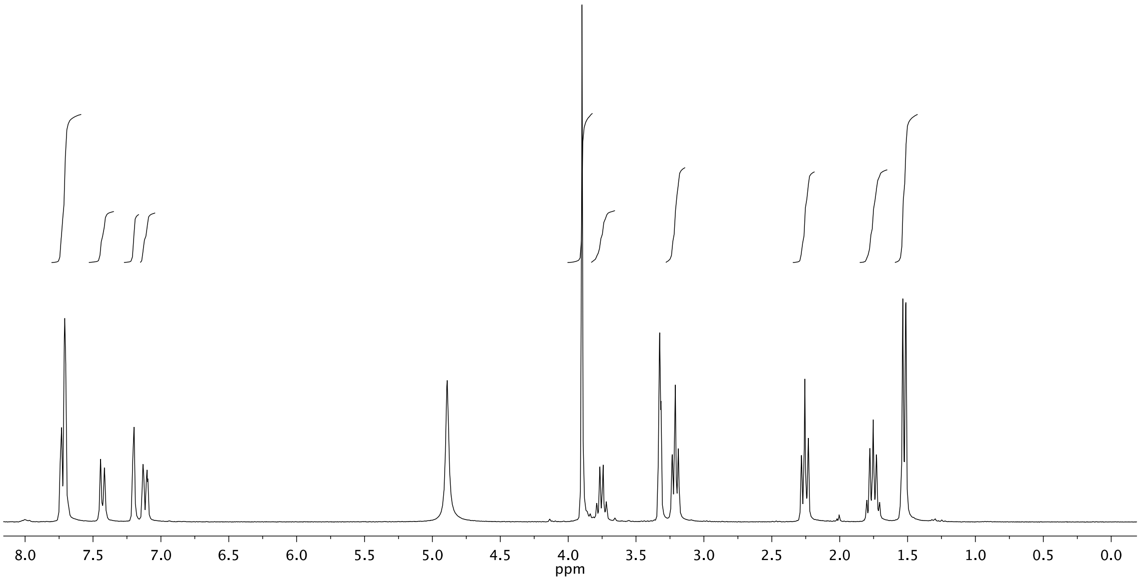
^{13}C NMR ($CDCl_3$, 75 MHz)



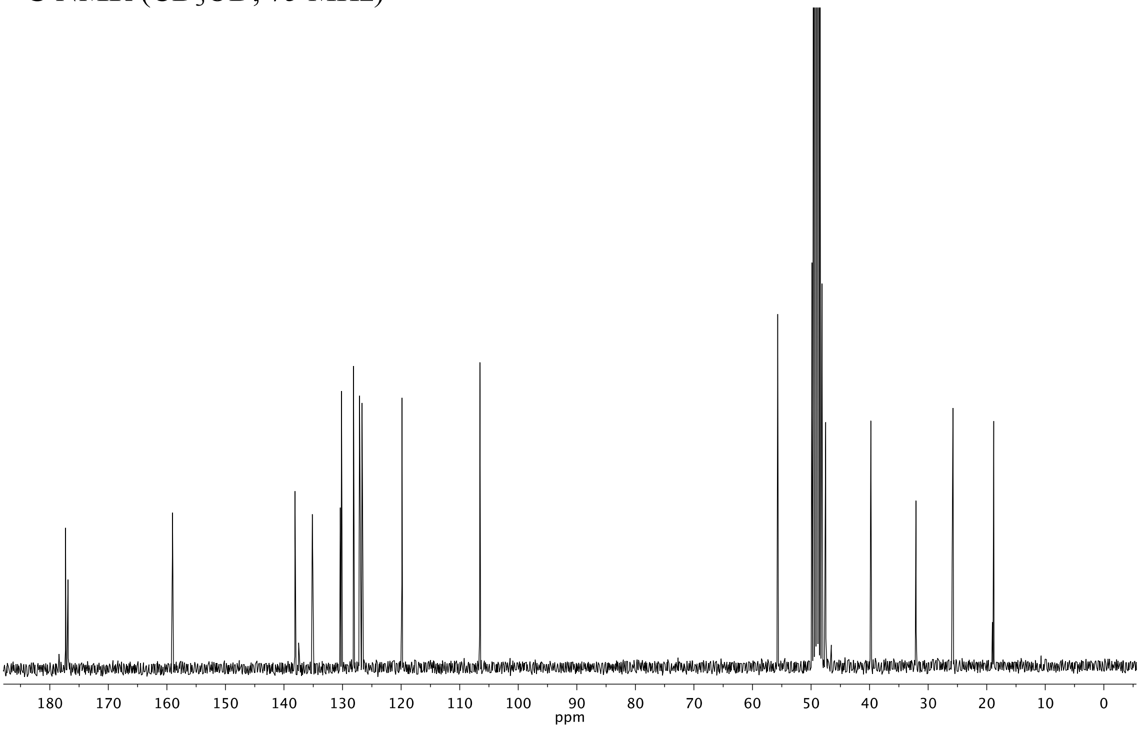
2.9. ^{1}H and ^{13}C NMR spectra of MNP-$CH(CH_3)CONH(CH_2)_3$-CO_2H (4)



^{1}H NMR (CD_3OD, 300 MHz)



^{13}C NMR (CD_3OD, 75 MHz)



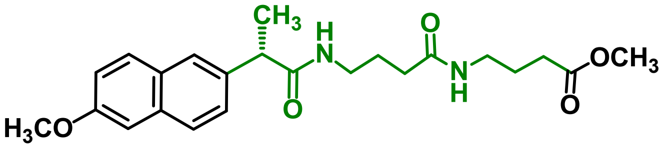
2.10. Synthesis of MNP-$CH(CH_3)[CONH(CH_2)_3]_2$-CO_2H (5)

The corresponding methyl ester of **5** was prepared following the same experimental procedure described above in detail for the methyl ester of **2**. Briefly, starting from **4** (740 mg, 2.35 mmol, 1 eq) and using methyl 4-aminobutyrate hydrochloride (433 mg, 2.82 mmol, 1.2 eq) as spacer, the ester MNP-$CH(CH_3)[CONH(CH_2)_3]_2$-CO_2CH_3 was obtained in 50% yield (500 mg), after purification by column chromatography (ethyl acetate / n-hexane, 50 : 50). Then, the ester was saponified following the preparation described in detail for **2**. Thus, after purification by column chromatography (AcOEt / n-hexane / AcOH, 80 : 20 : 1), **5** was obtained in 85% yield; mp: 100-102 ºC.

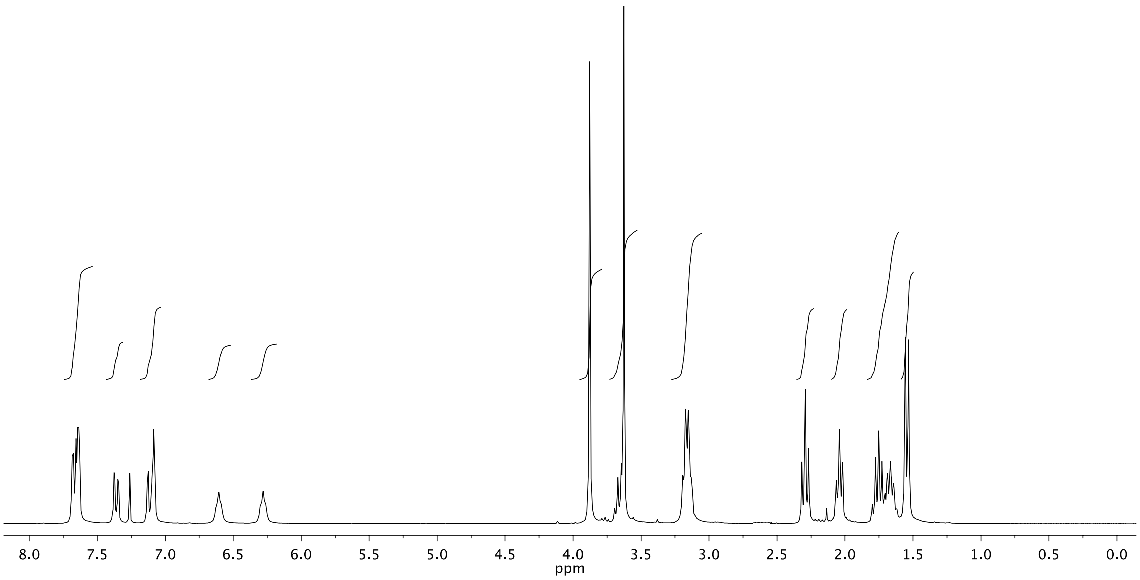
MNP-$CH(CH_3)[CONH(CH_2)_3]_2$-CO_2CH_3. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.54 (d, J = 7.2 Hz, 3H, CH_3), 1.60-1.83 (m, 4H, 2 x CH_2), 2.04 (t, J = 6.9 Hz, 2H, CH_2), 2.29 (t, J = 7.2 Hz, 2H, CH_2), 3.10-3.24 (m, 4H, 2 x CH_2), 3.63 (s, 3H, OCH_3), 3.66 (m, 1H, CH), 3.88 (s, 3H, CO_2CH_3), 6.28 (*br* s, 1H, NH), 6.60 (*br* s, 1H, NH), 7.05-7.15 (m, 2H, Ar-H), 7.36 (m, 1H, Ar-H), 7.60-7.72 (m, 3H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.5 (CH_3), 24.7 (CH_2), 25.6 (CH_2), 31.5 (CH_2), 33.6 (CH_2), 38.9 (CH_2), 39.0 (CH_2), 47.0 (CH), 51.7 (CH_3), 55.4 (CH_3), 105.7 (CH), 119.1 (CH), 126.0 (CH), 126.3 (CH), 127.4 (CH), 129.0 (C), 129.2 (CH), 133.7 (C), 136.6 (C), 157.7 (C), 172.8 (CO), 173.8 (CO), 175.1 (CO). Exact mass: *m/z* found 415.2216, calculated for $C_{23}H_{31}N_2O_5$ (MH^+) 415.2233.

MNP-$CH(CH_3)[CONH(CH_2)_3]_2$-CO_2H (5). ^{1}H NMR (300 MHz, CD_3OD): δ 1.50 (d, J = 6.9 Hz, 3H, CH_3), 1.72 (m, 4H, 2 x CH_2), 2.11 (t, J = 7.5 Hz, 2H, CH_2), 2.21-2.30 (m, 2H, CH_2), 3.10-3.24 (m, 4H, 2 x CH_2), 3.73 (q, J = 6.9 Hz, 1H, CH), 3.85 (s, 3H, OCH_3), 7.09 (m, 1H, Ar-H), 7.16 (*br* s, 1H, Ar-H), 7.41 (m, 1H, Ar-H), 7.65-7.73 (m, 3H, Ar-H); ^{13}C NMR (75 MHz, CD_3OD): δ 18.8 (CH_3), 25.7 (CH_2), 26.4 (CH_2), 32.2 (CH_2), 34.2 (CH_2), 39.7 (CH_2), 39.9 (CH_2), 47.5 (CH), 55.7 (CH_3), 106.5 (CH), 119.9 (CH), 126.7 (CH), 127.1 (CH), 128.1 (CH), 130.2 (CH), 130.3 (C), 135.1 (C), 138.1 (C), 159.0 (C), 175.4 (CO), 176.8 (CO), 177.2 (CO). Exact mass: *m/z* found 401.2065, calculated for $C_{22}H_{29}N_2O_4$ (MH^+) 401.2076.

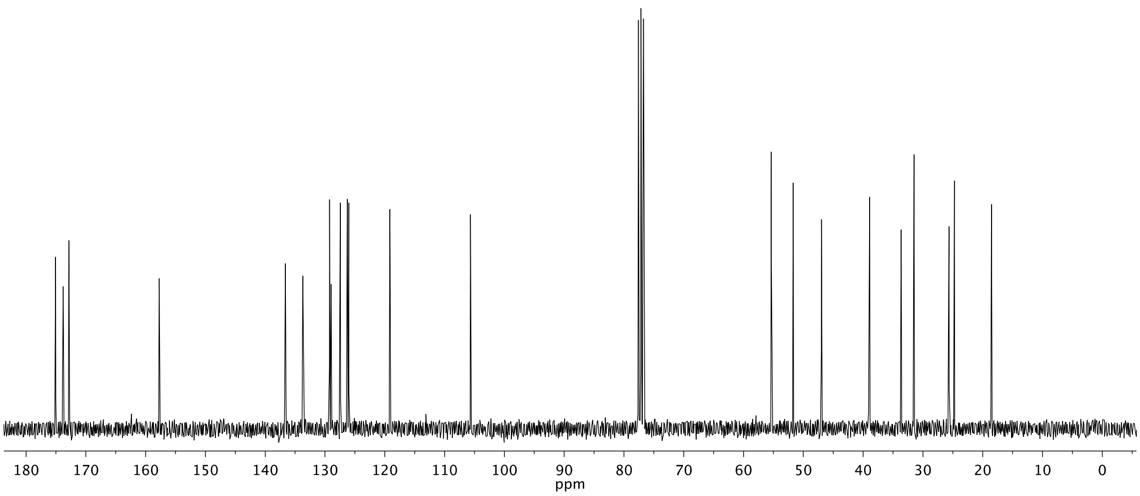
2.11. ^{1}H and ^{13}C NMR spectra of MNP-CH(CH$_3$)[CONH(CH$_2$)$_3$]$_2$-CO$_2$CH$_3$



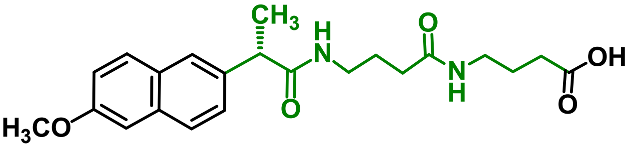
^{1}H NMR (CDCl$_3$, 300 MHz)



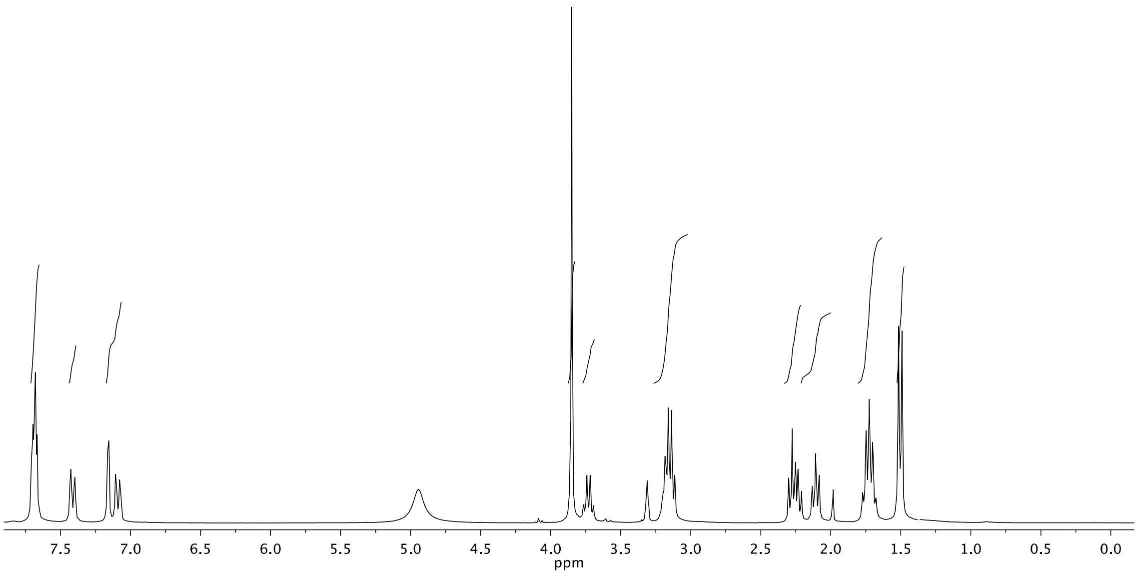
^{13}C NMR (CDCl$_3$, 75 MHz)



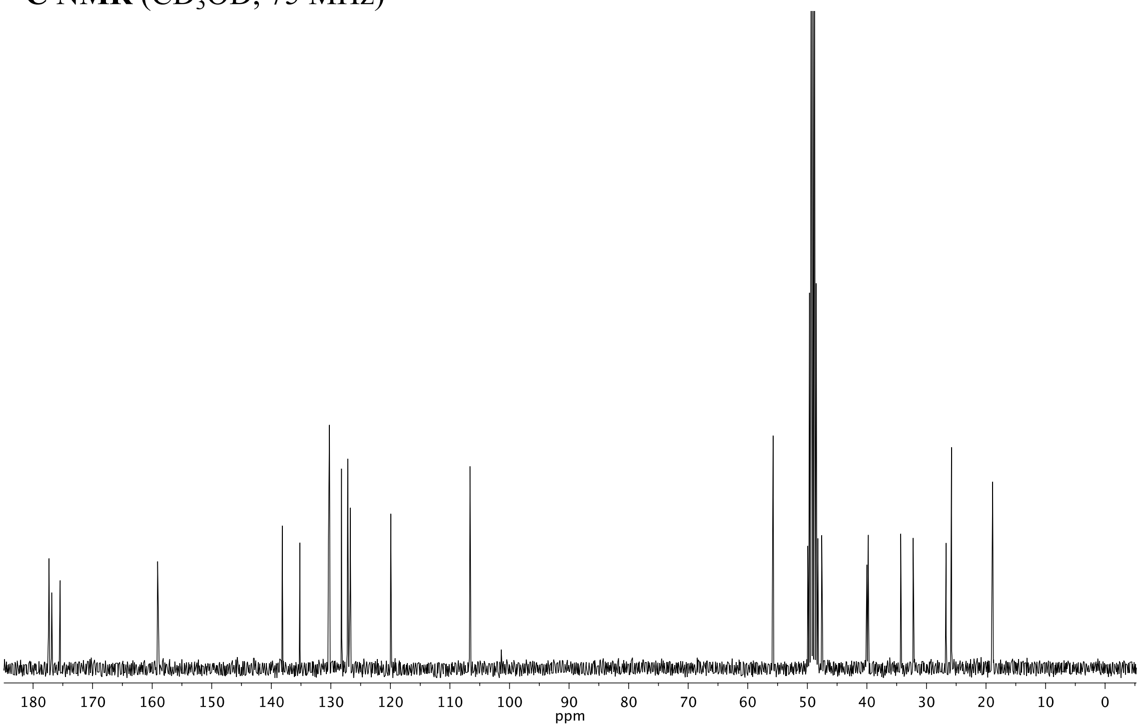
2.12. ^{1}H and ^{13}C NMR spectra of MNP-CH(CH$_3$)[CONH(CH$_2$)$_3$]$_2$-CO$_2$H (5)



^{1}H NMR (CD$_3$OD, 300 MHz)



^{13}C NMR (CD$_3$OD, 75 MHz)



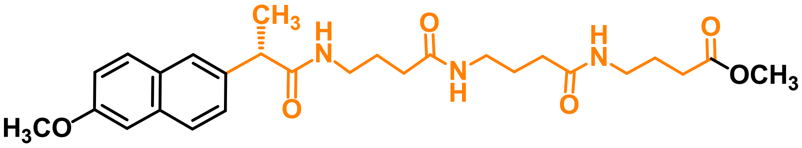
2.13. Synthesis of MNP-CH(CH$_3$)[CONH(CH$_2$)$_3$]$_3$-CO$_2$H (6)

The corresponding methyl ester of **6** was prepared following the same experimental procedure described above in detail for the methyl ester of **2**. Briefly, starting from **5** (400 mg, 1.00 mmol, 1 eq) and using methyl 4-aminobutyrate hydrochloride (186 mg, 1.20 mmol, 1.2 eq) as spacer, the ester MNP-CH(CH$_3$)[CONH(CH$_2$)$_3$]$_3$-CO$_2$CH$_3$ was obtained in 30% yield (148 mg), after purification by column chromatography (ethyl acetate / n-hexane, 60 : 40). Then, the ester was saponified following the preparation described in detail for **2**. Thus, after purification by column chromatography (AcOEt / MeOH / AcOH, 95 : 5 : 1), **6** was obtained in 78% yield.

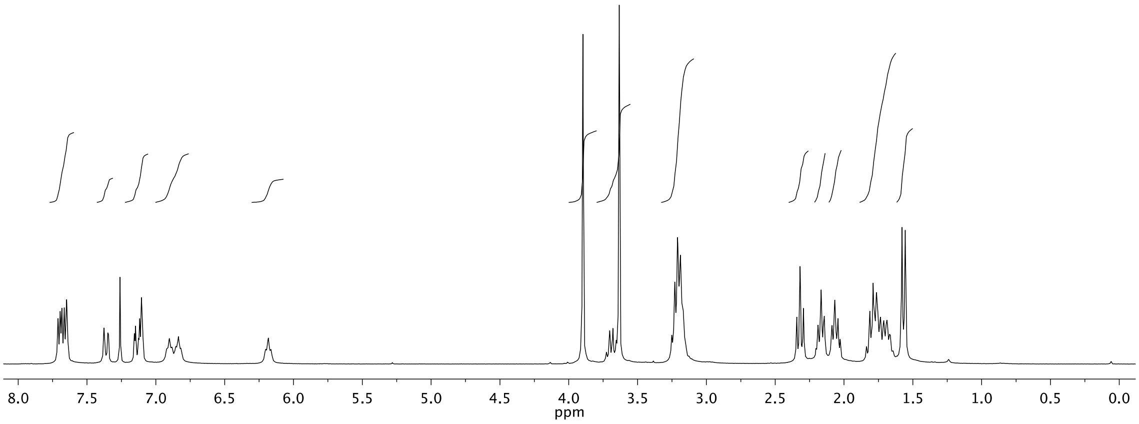
MNP-CH(CH$_3$)[CONH(CH$_2$)$_3$]$_3$-CO$_2$CH$_3$. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.57 (d, *J* = 7.2 Hz, 3H, CH$_3$), 1.64-1.84 (m, 6H, 3 x CH$_2$), 2.06 (m, 2H, CH$_2$), 2.17 (m, 2H, CH$_2$), 2.32 (t, *J* = 7.5 Hz, 2H, CH$_2$), 3.13-3.26 (m, 6H, 3 x CH$_2$), 3.63 (s, 3H, OCH$_3$), 3.69 (m, 1H, CH), 3.90 (s, 3H, CO$_2$CH$_3$), 6.18 (*br* s, 1H, NH), 6.84 (*br* s, 1H, NH), 6.90 (*br* s, 1H, NH), 7.07-7.17 (m, 2H, Ar-H), 7.36 (m, 1H, Ar-H), 7.63-7.72 (m, 3H, Ar-H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 18.5 (CH$_3$), 24.8 (CH$_2$), 25.8 (CH$_2$), 25.9 (CH$_2$), 31.6 (CH$_2$), 33.5 (CH$_2$), 33.8 (CH$_2$), 38.8 (CH$_2$), 38.9 (CH$_2$), 39.0 (CH$_2$), 47.0 (CH), 51.7 (CH$_3$), 55.5 (CH$_3$), 105.7 (CH), 119.3 (CH), 126.1 (CH), 126.2 (CH), 127.6 (CH), 129.0 (C), 129.3 (CH), 133.8 (C), 136.4 (C), 157.9 (C), 173.1 (2 x CO), 173.8 (CO), 175.5 (CO). Exact mass: *m/z* found 500.2749, calculated for $C_{27}H_{38}N_3O_6$ (MH$^+$) 500.2761.

MNP-CH(CH$_3$)[CONH(CH$_2$)$_3$]$_3$-CO$_2$H (6). ^{1}H NMR (300 MHz, CD$_3$OD): δ 1.51 (d, *J* = 7.2 Hz, 3H, CH$_3$), 1.66-1.80 (m, 6H, 3 x CH$_2$), 2.06-2.33 (m, 6H, 3 x CH$_2$), 3.10-3.22 (m, 6H, 3 x CH$_2$), 3.74 (q, *J* = 6.9 Hz, 1H, CH), 3.87 (s, 3H, OCH$_3$), 7.10 (m, 1H, Ar-H), 7.18 (*br* s, 1H, Ar-H), 7.42 (m, 1H, Ar-H), 7.65-7.75 (m, 3H, Ar-H); ^{13}C NMR (75 MHz, CD$_3$OD): δ 18.8 (CH$_3$), 25.8 (CH$_2$), 26.7 (2 x CH$_2$), 32.4 (CH$_2$), 34.2 (CH$_2$), 34.3 (CH$_2$), 39.8 (CH$_2$), 39.9 (CH$_2$), 40.0 (CH$_2$), 47.5 (CH), 55.7 (CH$_3$), 106.6 (CH), 119.9 (CH), 126.7 (CH), 127.1 (CH), 128.1 (CH), 130.1 (CH), 130.4 (C), 135.2 (C), 138.1 (C), 159.1 (C), 175.4 (CO), 175.5 (CO), 177.1 (CO), 177.3 (CO). Exact mass: *m/z* found 486.2603, calculated for $C_{26}H_{36}N_3O_6$ (MH$^+$) 486.2604.

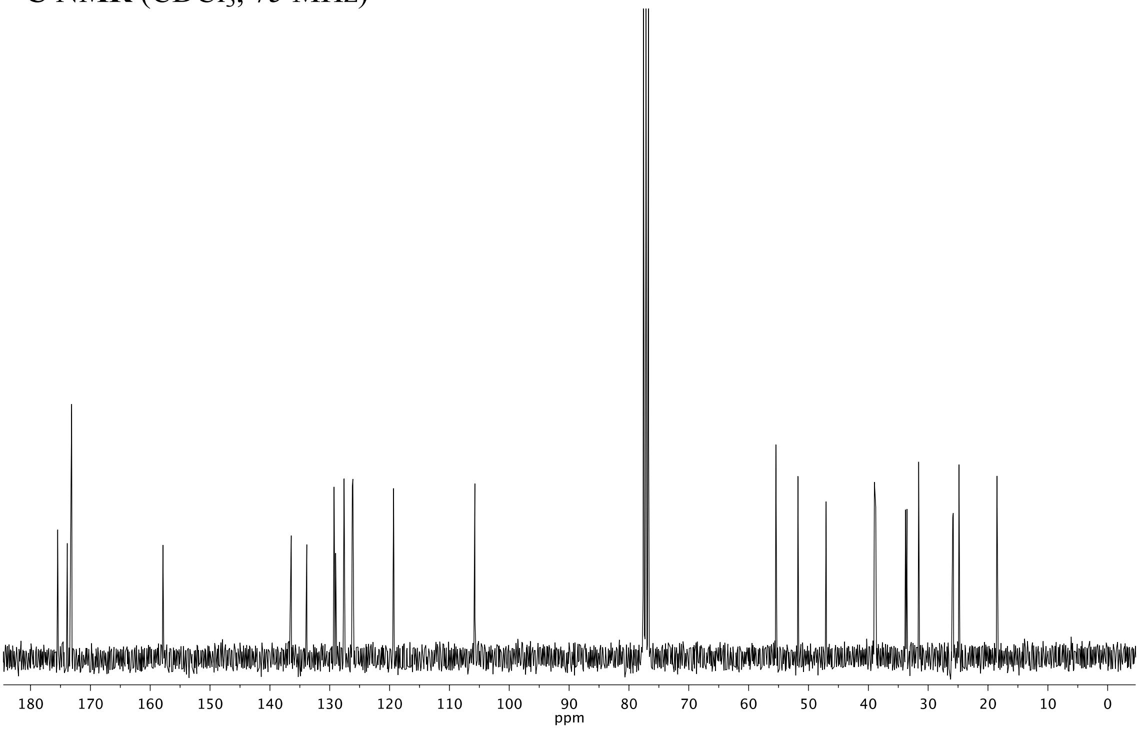
2.14. ^{1}H and ^{13}C NMR spectra of MNP-CH(CH$_3$)[CONH(CH$_2$)$_3$]$_3$-CO$_2$CH$_3$



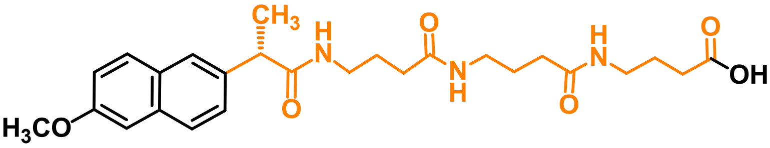
^{1}H NMR (CDCl$_3$, 300 MHz)



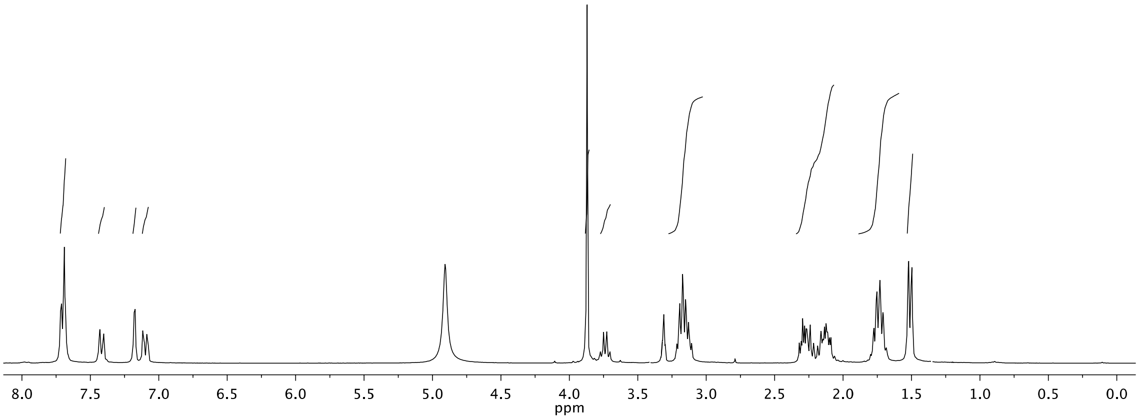
^{13}C NMR (CDCl$_3$, 75 MHz)



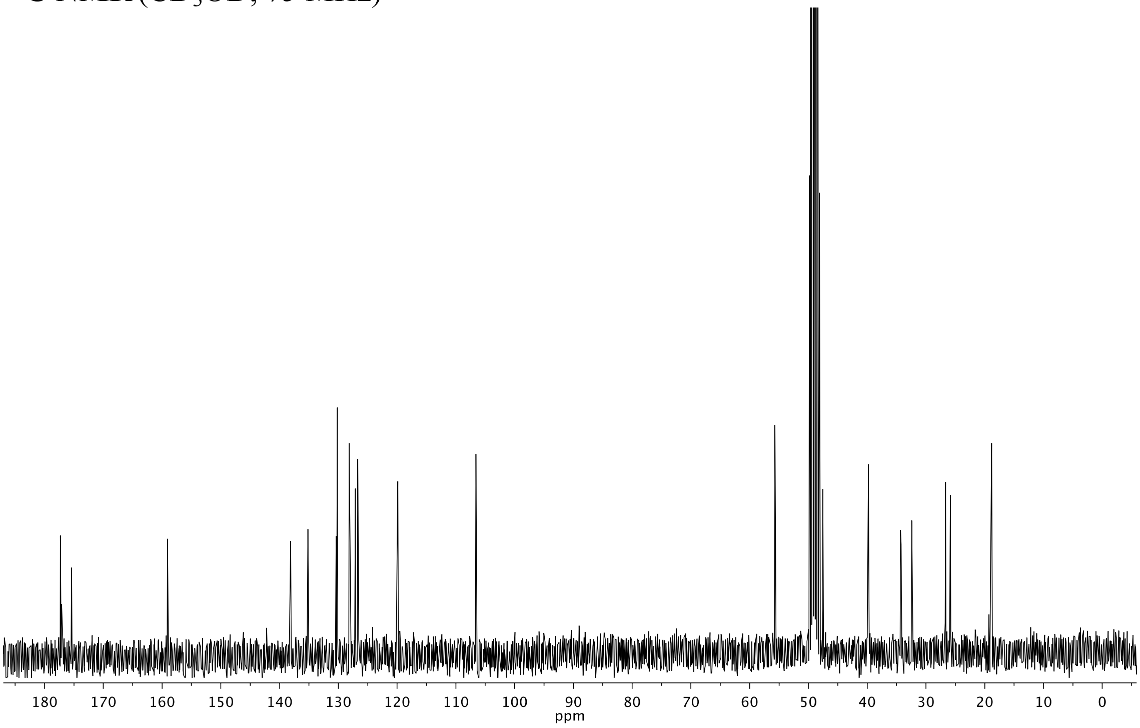
2.15. ^{1}H and ^{13}C NMR spectra of MNP-$CH(CH_3)[CONH(CH_2)_3]_3$-CO_2H (6)



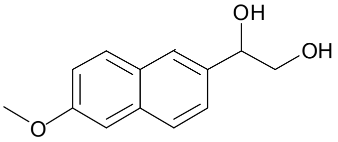
^{1}H NMR (CD_3OD, 300 MHz)



^{13}C NMR (CD_3OD, 75 MHz)



3. Characterization of MNP derivatives 9-13



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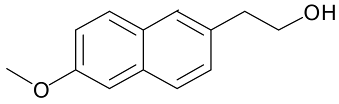

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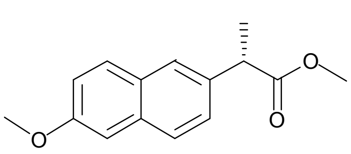

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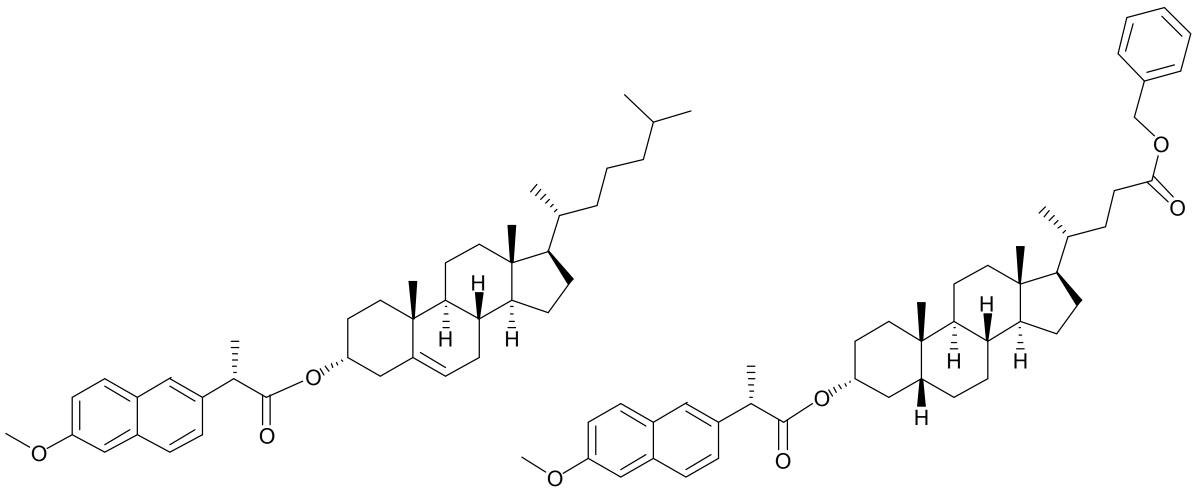

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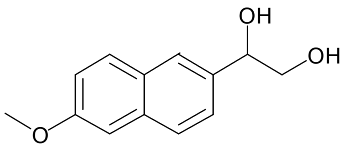
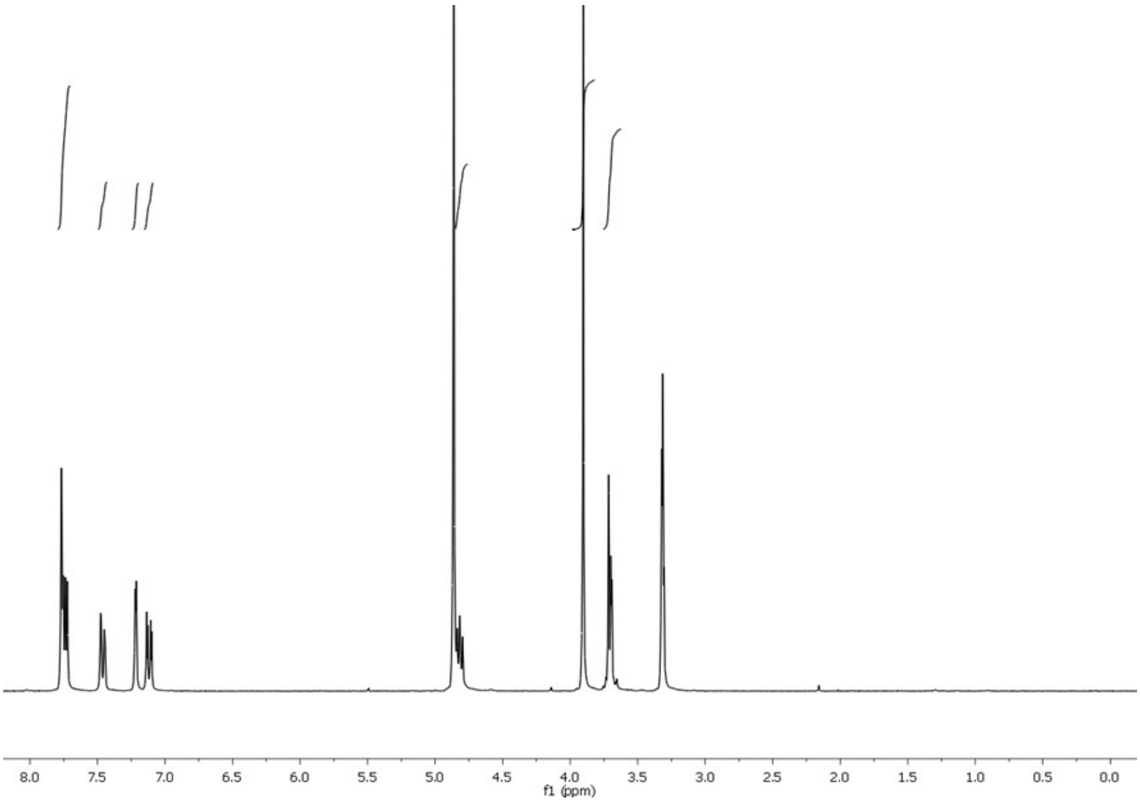
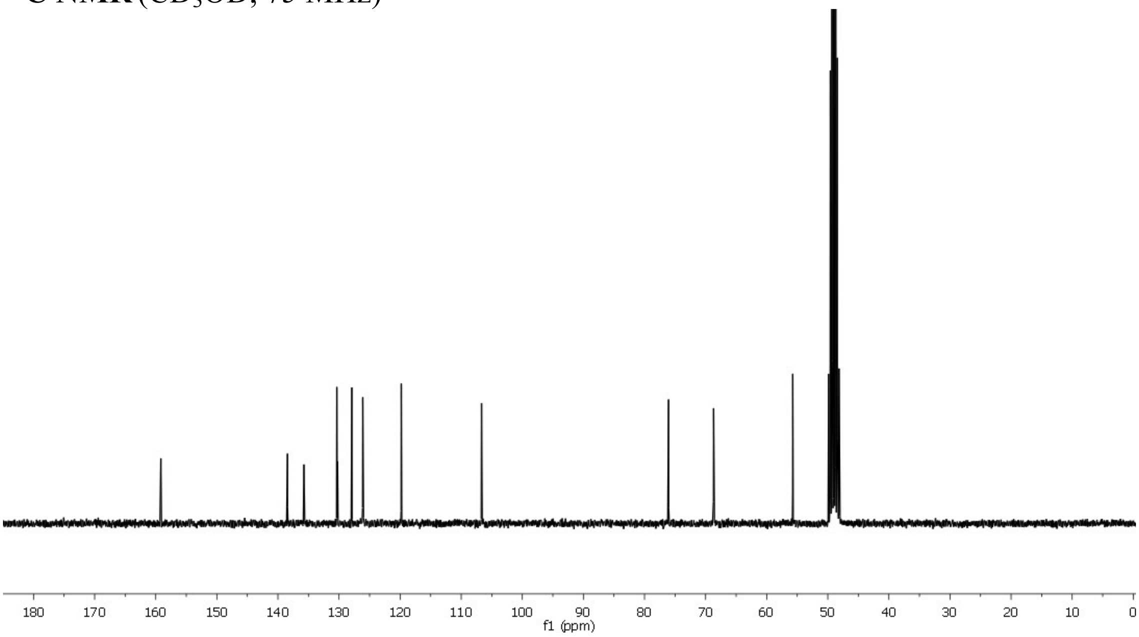
3.1. ^{1}H and ^{13}C NMR spectra of 9



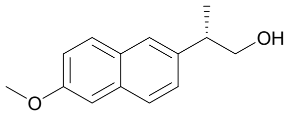
^{1}H NMR (CD$_3$OD, 300 MHz)



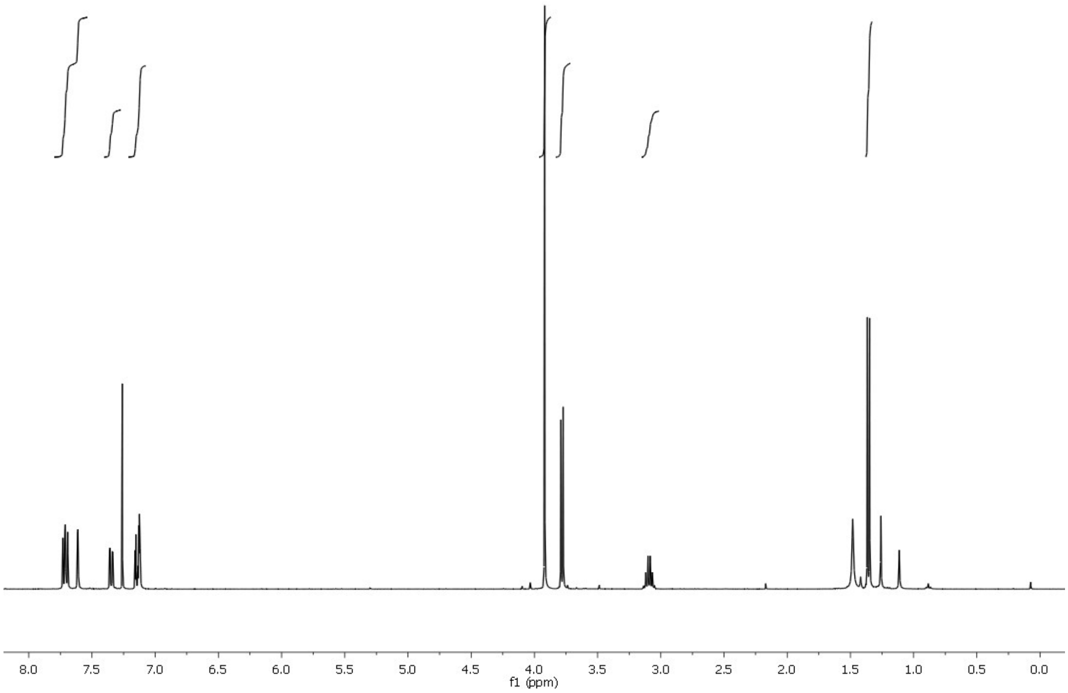
^{13}C NMR (CD$_3$OD, 75 MHz)



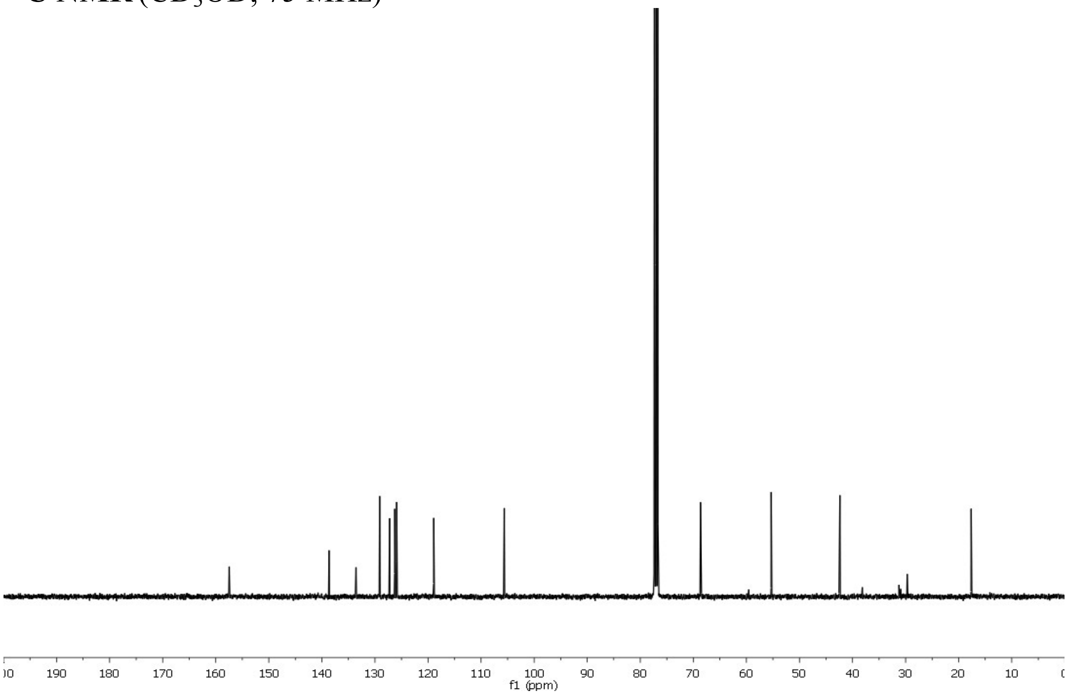
3.2. ^{1}H and ^{13}C NMR spectra of 10



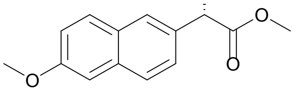
^{1}H NMR (CD$_3$OD, 300 MHz)



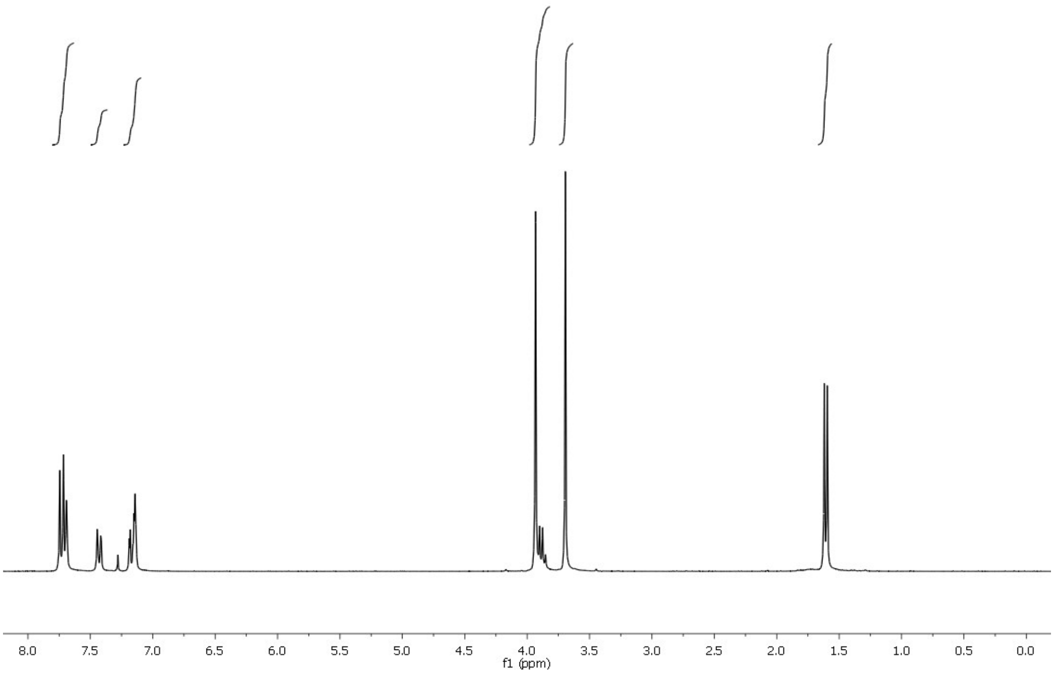
^{13}C NMR (CD$_3$OD, 75 MHz)



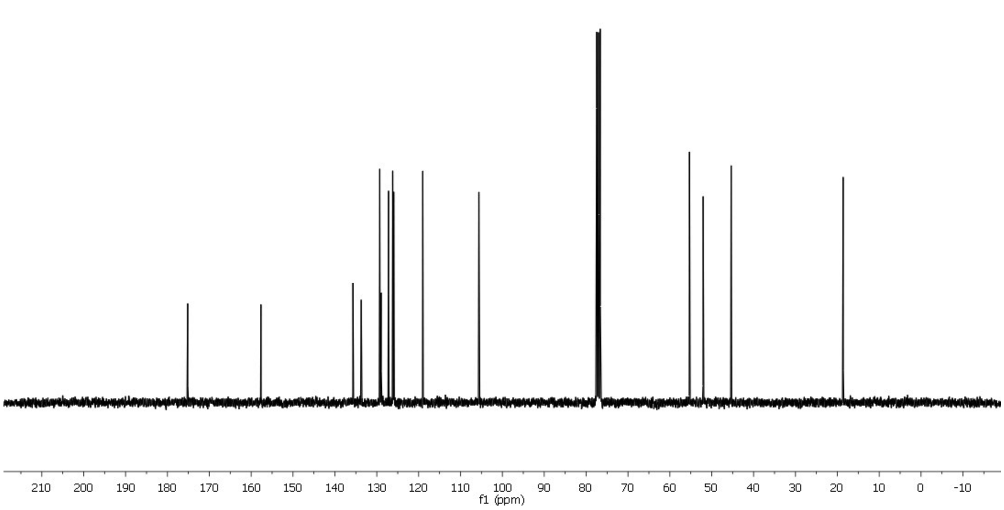
3.5. ^{1}H and ^{13}C NMR spectra of 11



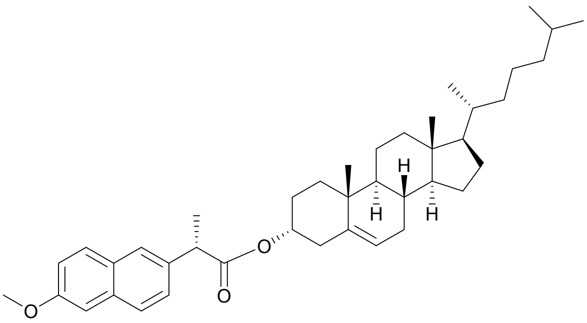
^{1}H NMR (CDCl$_3$, 300 MHz)



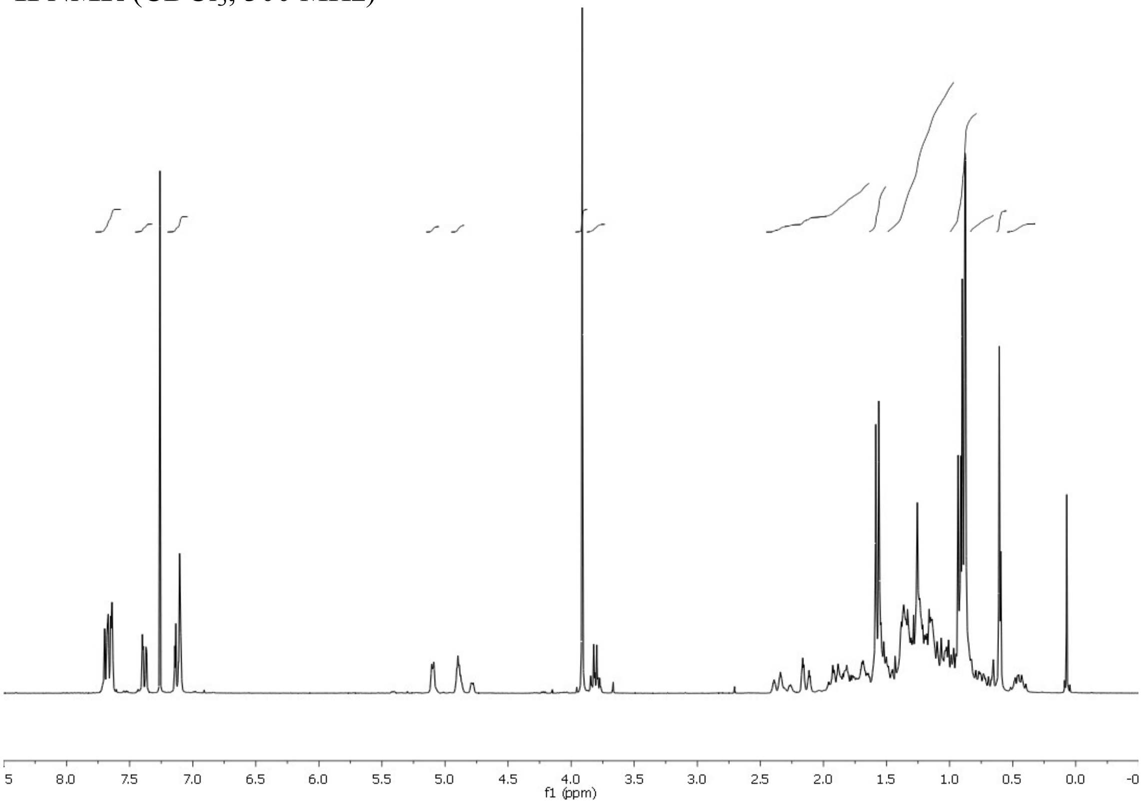
^{13}C NMR (CDCl$_3$, 75 MHz)



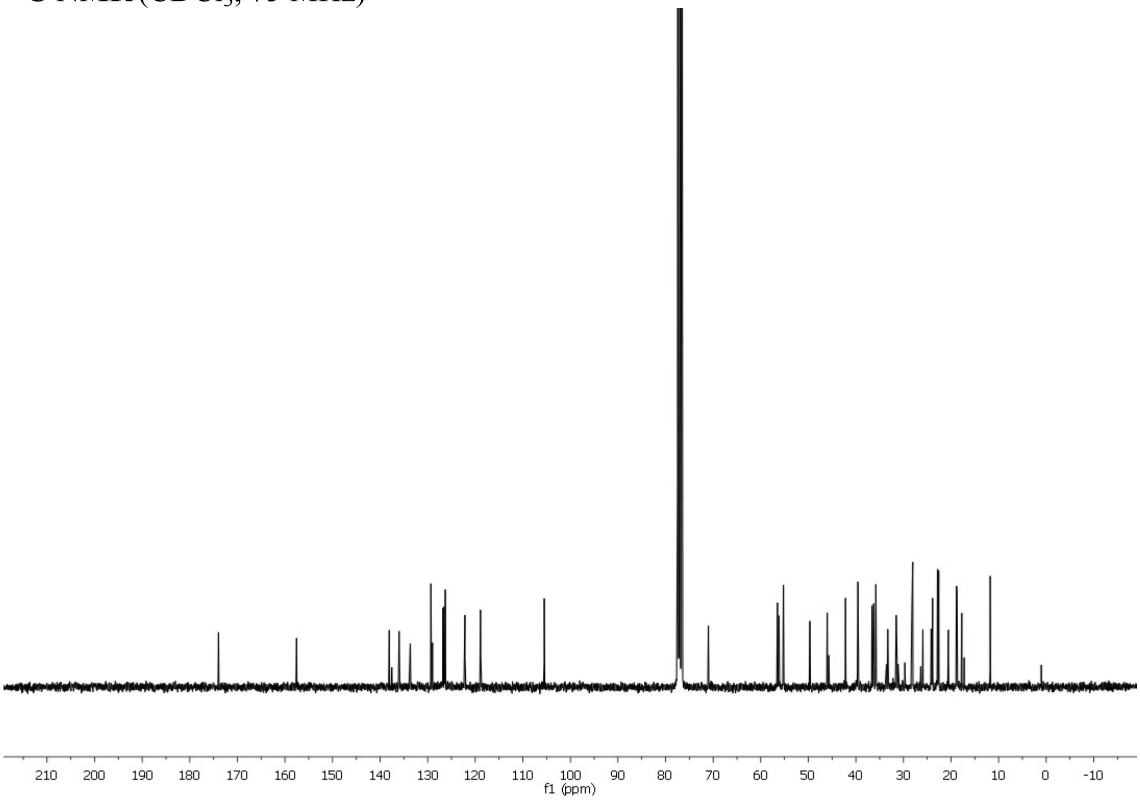
3.6. ^{1}H and ^{13}C NMR spectra of 12



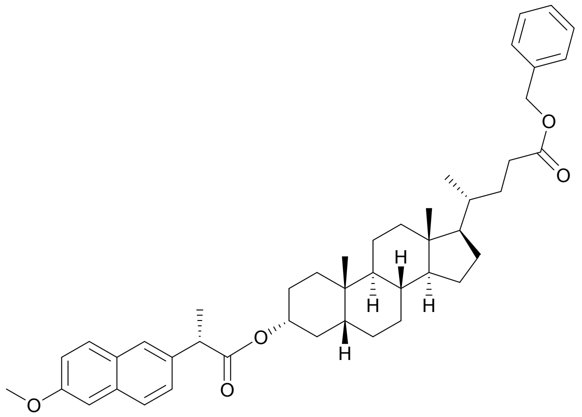
^{1}H NMR (CDCl$_3$, 300 MHz)



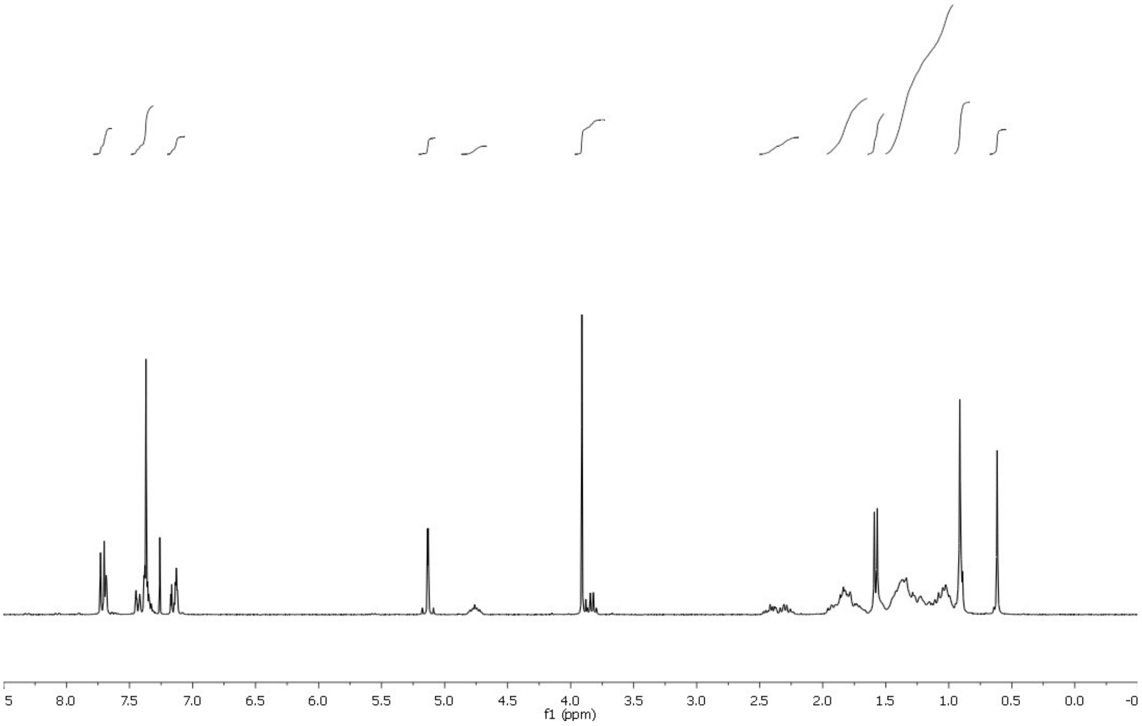
^{13}C NMR (CDCl$_3$, 75 MHz)



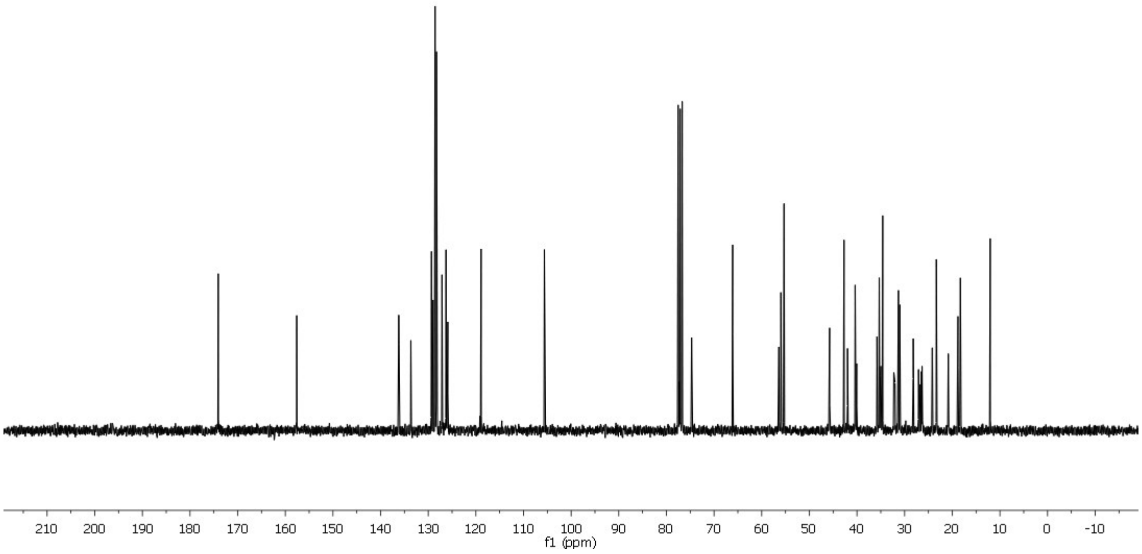
3.7. ^{1}H and ^{13}C NMR spectra of 13



^{1}H NMR (CDCl$_3$, 300 MHz)



^{13}C NMR (CDCl$_3$, 75 MHz)



4. Steady-state fluorescence quenching by iodide of probes 1-6

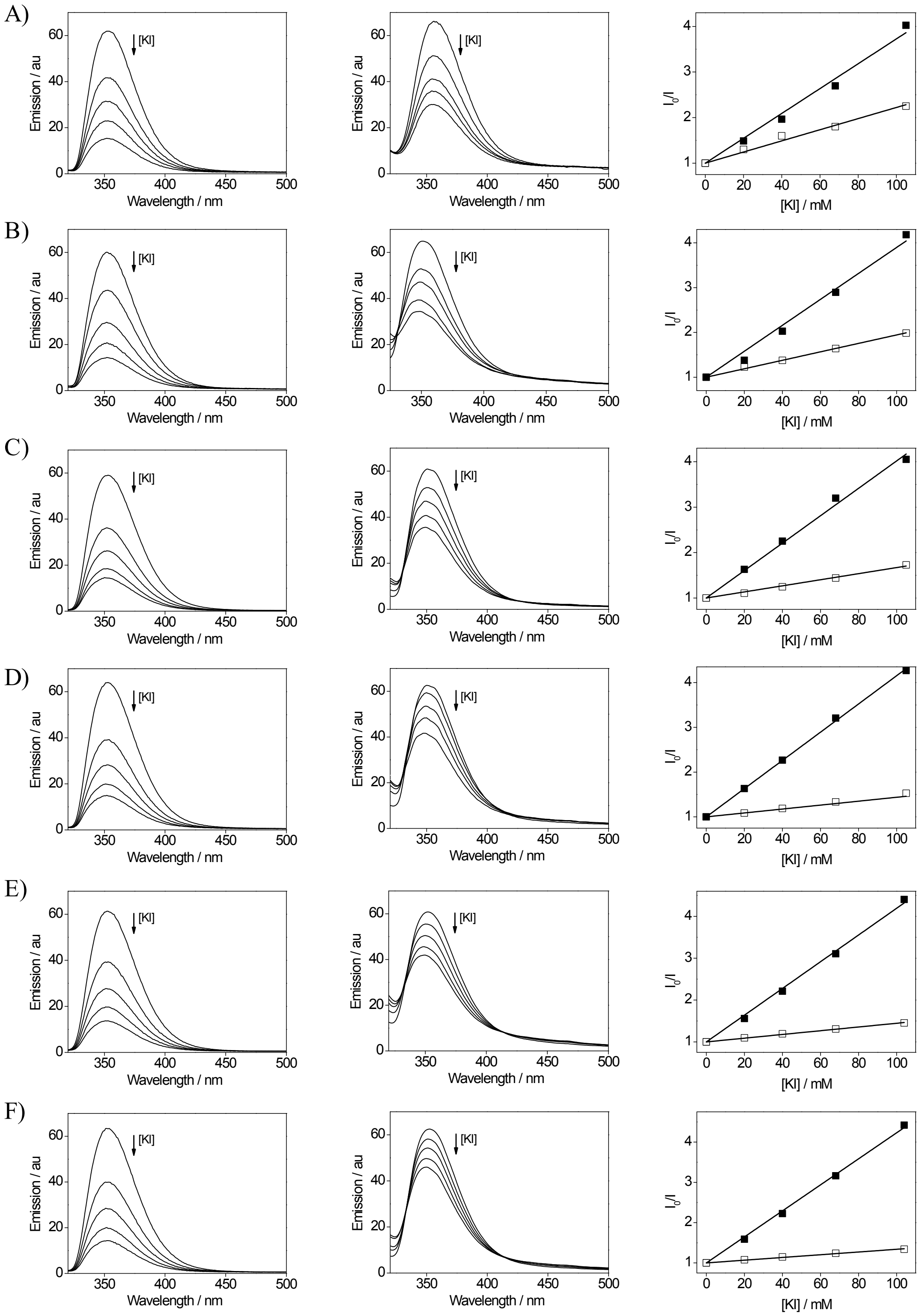


Figure S1. Emission spectra (λ_{exc} = 290 nm) upon addition of increasing amounts of KI (0-104 mM) of A) MNP-CH(CH_3)-CO_2H (**1**), B) MNP-CH(CH_3)CONHCH_2-CO_2H (**2**), C) MNP-CH(CH_3)CONH(CH_2)$_2$-CO_2H (**3**), D) MNP-CH(CH_3)CONH(CH_2)$_3$-CO_2H (**4**), E) MNP-CH(CH_3)[CONH(CH_2)$_3$]$_2$-CO_2H (**5**) and F) MNP-CH(CH_3)[CONH(CH_2)$_3$]$_3$-CO_2H (**6**) in aqueous NaCl 0.2 M (left column) and in MM (middle column). Corresponding Stern-Volmer plots in solution (○) and in MM (◉) (right column).

5. Time-resolved fluorescence quenching by iodide of probes 1-6

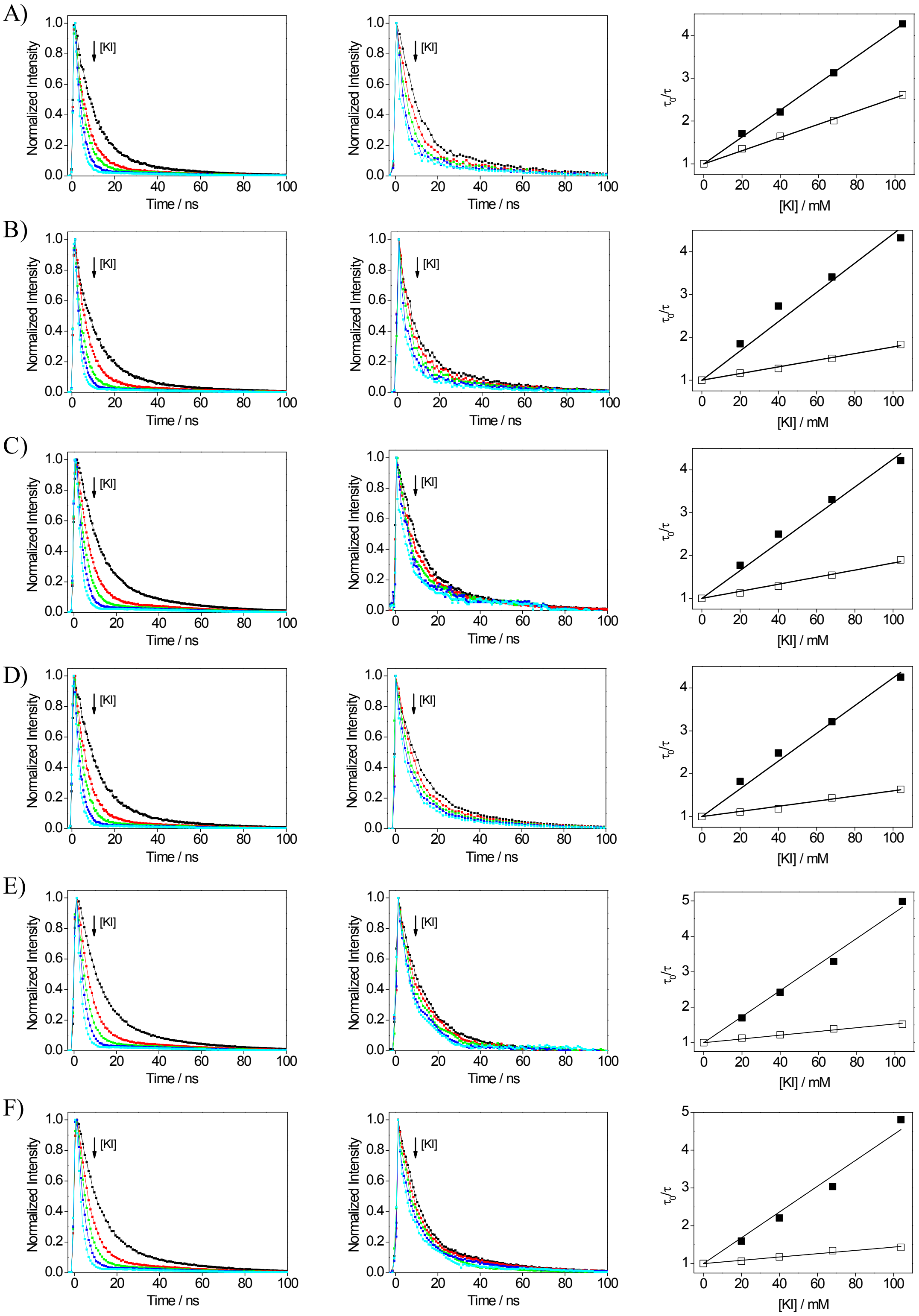


Figure S2. Changes in the emission decay traces (λ_{exc} = 295 nm) upon addition of increasing amounts of KI (0-104 mM) of A) MNP-$CH(CH_3)$-CO_2H (**1**), B) MNP-$CH(CH_3)CONHCH_2$-CO_2H (**2**), C) MNP-$CH(CH_3)CONH(CH_2)_2$-CO_2H (**3**), D) MNP-$CH(CH_3)CONH(CH_2)_3$-CO_2H (**4**), E) MNP-$CH(CH_3)[CONH(CH_2)_3]_2$-CO_2H (**5**) and F) MNP-$CH(CH_3)[CONH(CH_2)_3]_3$-CO_2H (**6**) in aqueous NaCl 0.2 M (left column) and in MM (middle column). Corresponding Stern-Volmer plots in solution (**○**) and in MM (**⊙**) (right column).

6. Determined rate constants for iodide fluorescence quenching of 1-6 in solution.[a,b]

NMP probe	k_q x 10^{-9} / $M^{-1}s^{-1}$ in Solution
1	3.07 ± 0.03 (2.90 ± 0.06)
2	3.00 ± 0.10 (3.10 ± 0.20)
3	2.90 ± 0.10 (2.90 ± 0.01)
4	2.87 ± 0.05 (3.10 ± 0.10)
5	3.16 ± 0.10 (3.00 ± 0.05)
6	3.09 ± 0.10 (3.17 ± 0.10)

[a] Each rate constant is the average of three independent runs; [b] Values obtained from steady-state measurements are given in parentheses.

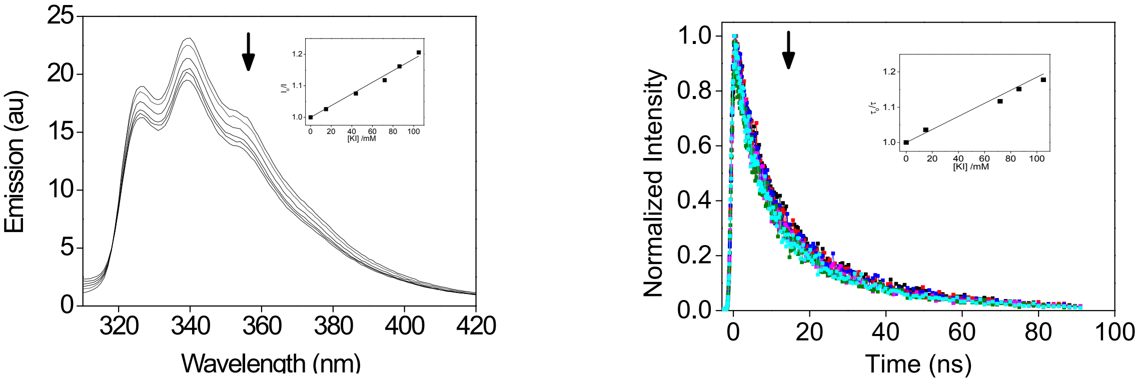
7. Steady-state rate constants for iodide fluorescence quenching of 1-6 in MM.[a]

NMP probe	k_q x 10^{-9} / $M^{-1}s^{-1}$ in MM
1	1.33 ± 0.01
2	0.78 ± 0.04
3	0.57 ± 0.02
4	0.41 ± 0.03
5	0.34 ± 0.01
6	0.28 ± 0.01

[a] Each rate constant is the average of three independent runs.

8. Steady-state and time-resolved fluorescence quenching by iodide of probes 7-13 in MM

7



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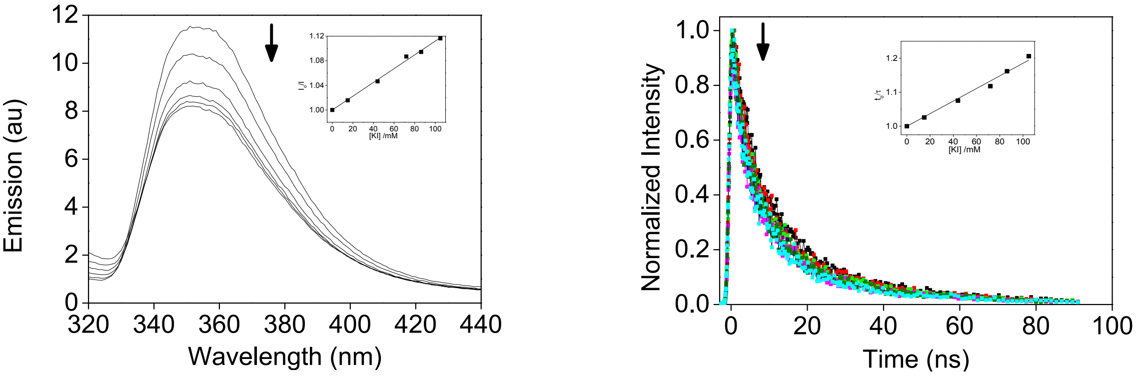

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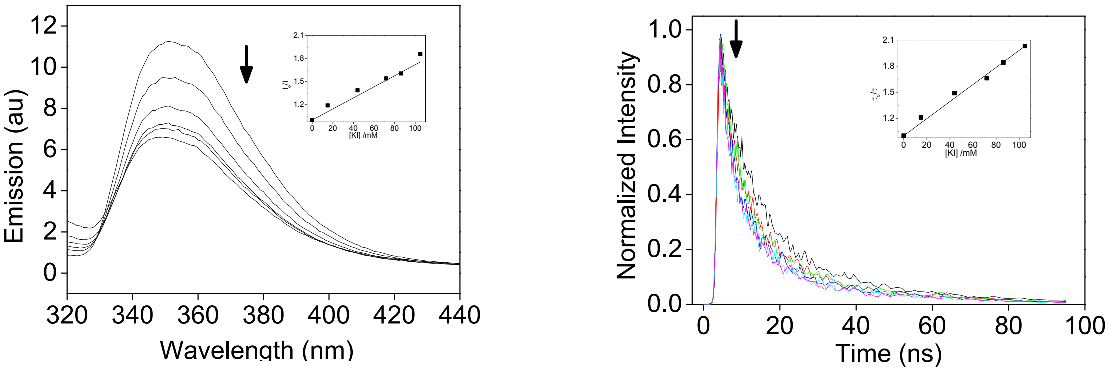

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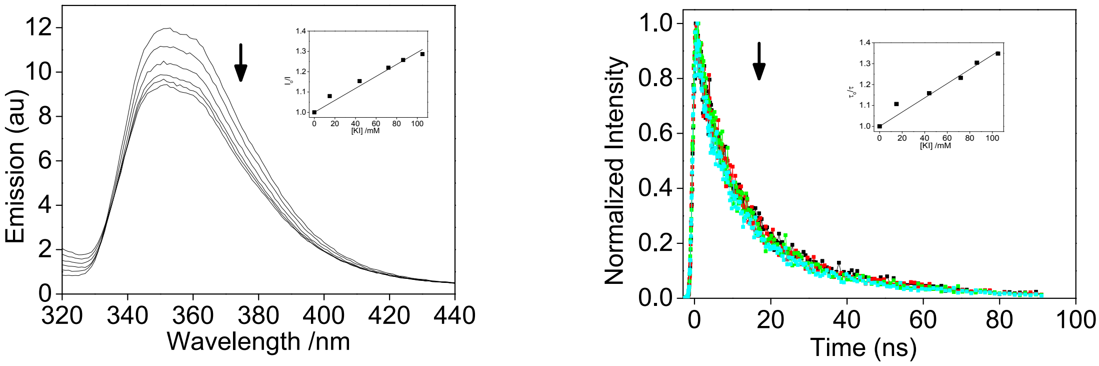


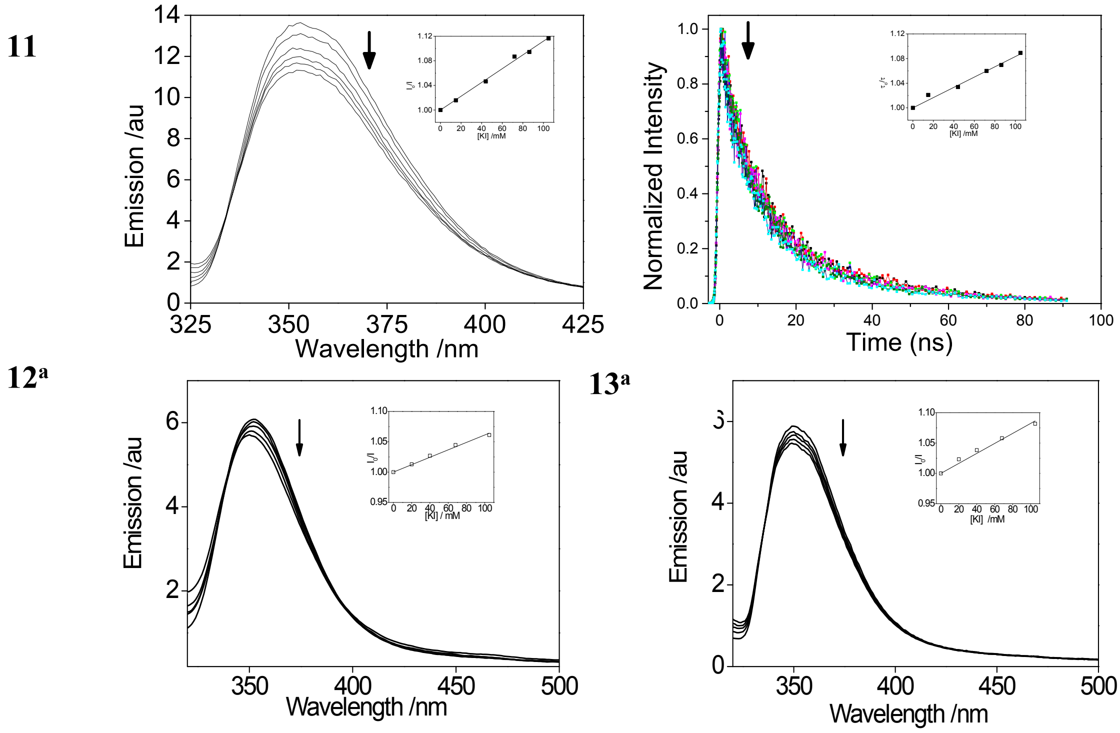


Figure S3. Emission spectra (λ_{exc} = 290 nm, left column) and changes in the emission decay traces (λ_{exc} = 295 nm,right column) upon addition of increasing amounts of KI (0-104 mM) to **7-13** encapsulated in MM. Inset: Corresponding Stern-Volmer plots.[a] Only results from steady state experiments are shown for compounds **12** and **13**.

9. Thermodynamic estimation of the photo-redox process

The thermodynamic feasibility of the photo-redox process was evaluated according to the Rehm-Weller equation:[1]

$$\Delta G\ (kcal\ mol^{-1}) = 23.06\left[E\left(I^{\cdot}/I^{-}\right) - E\left(MNP/MNP^{\cdot -}\right)\right] - E_S^{*}(MNP)$$

The values for the reduction potentials were taken from the literature: the $E\left(I^{\cdot}/I^{-}\right)$ as +1.33 V *vs* SCE in water or +1.23 V in CH_3CN,[2] while the $E\left(MNP/MNP^{\cdot -}\right)$ was taken as -2.60 V *vs* SCE in DMF.[3] The singlet energy of MNP derivatives was estimated as the corresponding for MNP, as 85 kcal mol^{-1}.[4] Applying the Rehm-Weller equation with these data resulted in a nearly thermoneutral photoinduced electron transfer.

10. Monochromatic irradiation of 1, 4 and 5 in the presence of iodide

A typical experiment was performed as follows:

KI (67 µL, 3.22 mM) was added to 2 mL of freshly prepared and rehydrated MM containing **1**, **4** or **5** (final [KI] in cuvette 104 mM). The cuvette was irradiated with a monochromatic lamp (330 nm) for 40 minutes and the evolution of triiodide was monitored by UV-visible spectrophotometry.

A blank with the same concentration of KI added to freshly prepared MM without any photoactive probe was irradiated under the same conditions.

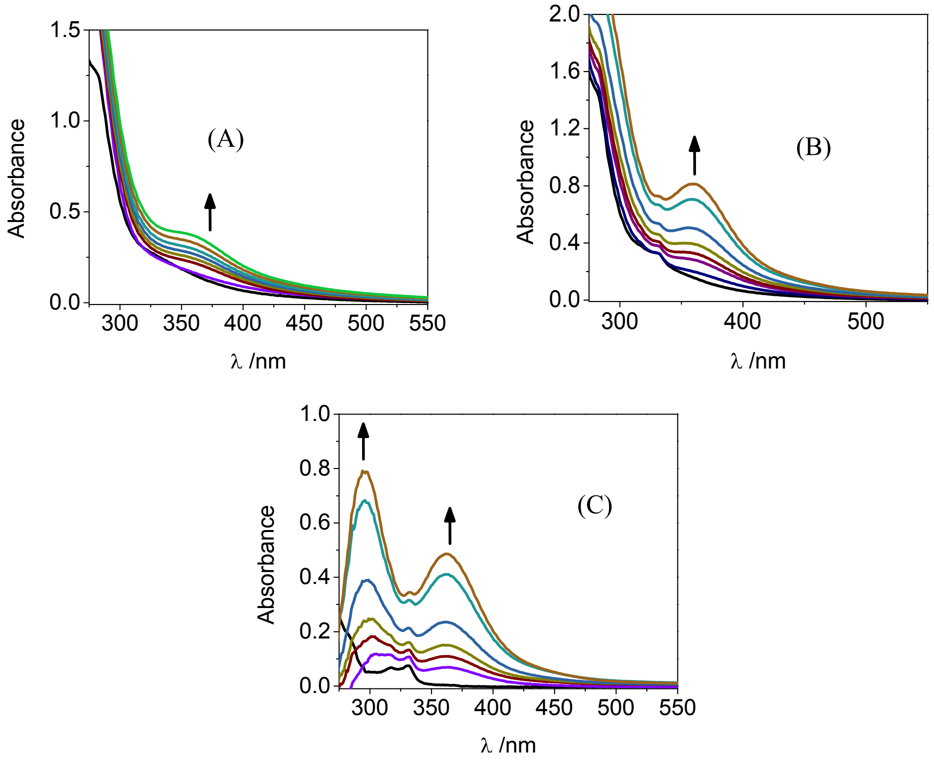


Figure S4. UV-vis spectra recorded at different reaction times (0 to 40 minutes) in the presence of KI (104 mM) for (A) blank MM and (B) **4** within MM. Graph C is mathematically obtained by substracting A from B for each corresponding time trace, to avoid dispersion due to the irradiation of the blank MM.

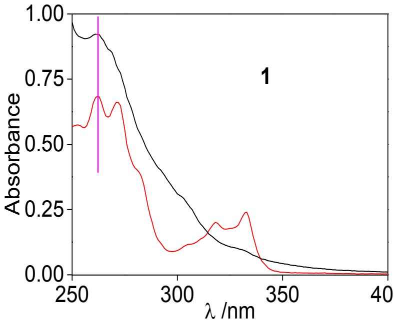
11. Partition coefficient experiments

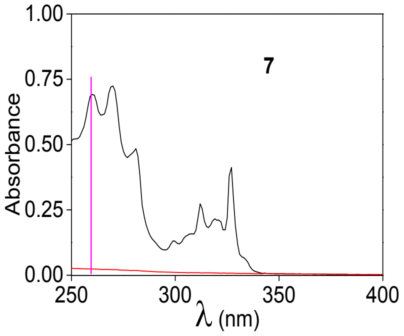
The solubility of the MNP derivatives (**1, 7, 8** and **10-13**) was assessed from the mixture pentane/water.

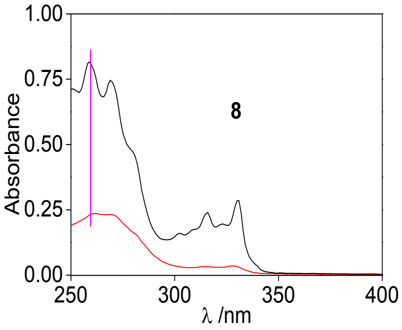
In a typical experiment a well-known amount of each probe (**1, 7, 8** and **10-13**) was weighted to achieve a concentration of 0.152 mM in pentane (solution P). This solution P was stirred for 24 h before the UV was registered.

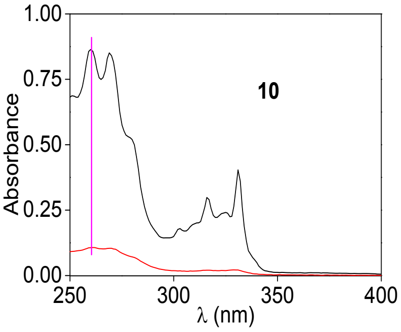
Then 25 mL of solution P were mixed with 25 mL of water and stirred for further 2 h.

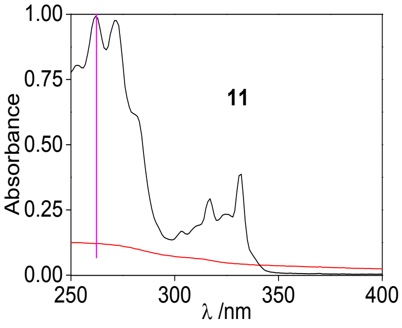
Then the two phases were separated and the corresponding UV spectra for both were recorded.

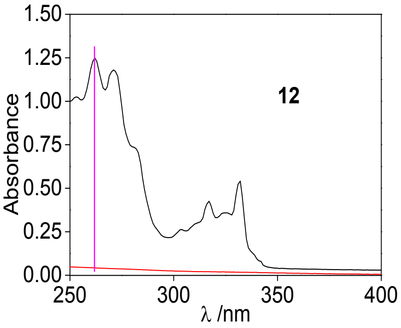












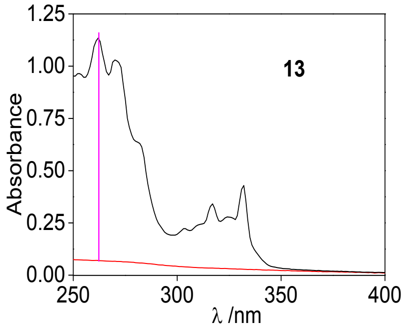


Figure S5. UV-vis spectra recorded for the compounds **1**, **7, 8, 10-13** extracted from the pentane (black curve) or from the aqueous phase (red curve).

12. TLC

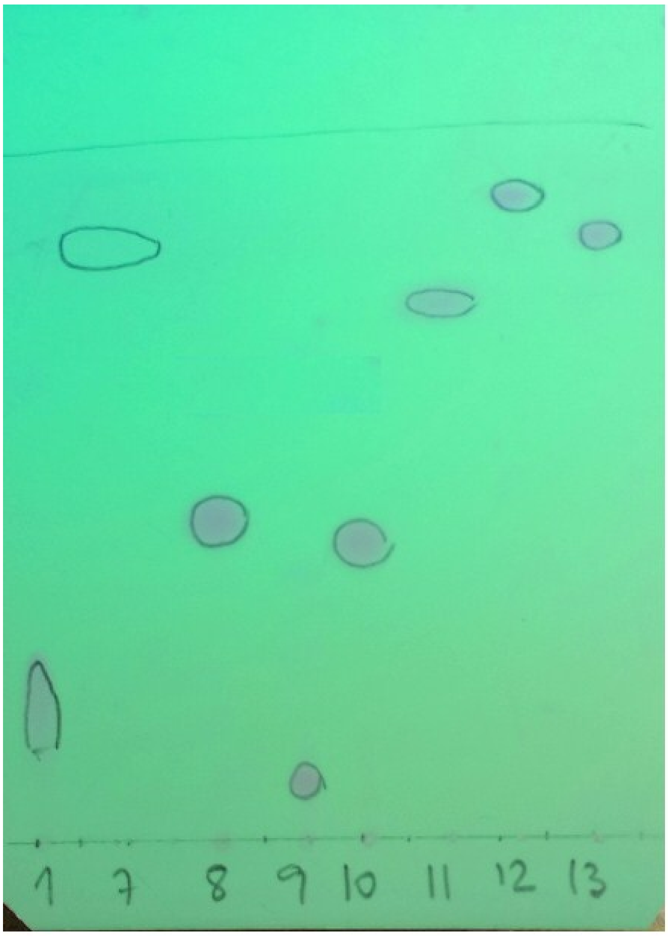


Figure S6. TLC of compounds **1, 7-13**. Mobile phase: hexane / ethyl acetate (1 : 0.6).

13. References

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