Supporting Information

Rhodamine F: A Novel Class of Fluorous Ponytailed Dyes for Bioconjugation

Dominik K. Kölmel,[a] Birgit Rudat,[a,b] Delia M. Braun,[a] Christin Bednarek,[a,c] Ute Schepers,[c] and Stefan Bräse*[a,c]

[a] Institute of Organic Chemistry, Karlsruhe Institute of Technology, Fritz-Haber-Weg 6, 76131 Karlsruhe (Germany)
[b] Light Technology Institute, Karlsruhe Institute of Technology, Engesserstraße 13, 76131 Karlsruhe (Germany)
[c] Institute of Toxicology and Genetics, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen (Germany)

General

UV/Vis absorption spectra were recorded by using a Varian Cary 300 scan UV/Vis spectrophotometer and fluorescence spectra were recorded by using a Varian Cary Eclipse fluorescence spectrophotometer. Closed quartz cuvettes with a 1 cm path length were used in all experiments. Fluorescence quantum yield measurements were performed on the previously mentioned fluorometer and UV/Vis instrument. The slit width was 5 nm for both excitation and emission. Relative quantum efficiencies were obtained by comparing the absorption values and the areas under the emission spectrum for the unknown substance with a standard. The following equation was used to calculate quantum yields:

$$\Phi_x = \Phi_s \times (F_x/F_s) \times (n_x/n_s)^2 \times (A_s/A_x)$$

Φ_s is the reported quantum yield of the standard, *F* is the integrated emission spectrum, *A* is the absorbance at the extinction wavelength, and *n* is the refractive index of the solvents used. The subscript *x* denotes unknown and *s* denotes standard. 5(6)-Carboxyfluorescein in 0.1 M aqueous NaOH (Φ_F = 0.95)[1] or rhodamine 101 in methanol (Φ_F = 0.99)[2] were used as standards. All reactions were carried out under stirring. Reactions under inert gas were carried out in flasks equipped with septa under argon (supplied by using a standard manifold with vacuum and argon lines). NMR spectra were recorded at 25 °C by using Bruker Avance 300 (300 (^{1}H) and 75 MHz (^{13}C)), Bruker AM 400 (400 (^{1}H), 100 (^{13}C) and 376.5 MHz (^{19}F)) and Bruker DRX 500 (500 (^{1}H) and 125 MHz (^{13}C)) spectrometer. All spectra are referenced to tetramethylsilane as the internal standard (δ = 0 ppm) by using the signals of the residual protons of $CHCl_3$ (7.26 ppm (^{1}H) or 77.0 ppm (^{13}C)) in $CDCl_3$, or CHD_2OD (3.31 ppm (^{1}H) or 49.1 ppm (^{13}C)) in CD_3OD. Multiplicities of signals are described as follows: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants (*J*) are given in Hz. Multiplicities in the ^{13}C NMR spectra were determined by DEPT (distortionless enhancement by polarization transfer) measurements. Perfluorinated carbon atoms were not

analyzed by ^{13}C NMR spectroscopy due to their weak and complex signals. Mass spectra (EI or FAB) were obtained by using a Finnigan MAT 90 spectrometer. High resolution mass spectra of molecules with molecular masses >1000 g/mol were obtained by using an Agilent 6230 TOF LC/MS. MALDI-TOF mass spectra from the peptoids were obtained by using a Bruker Biflex IV spectrometer with a pulsed ultraviolet nitrogen laser, 200 µJ at 337 nm and a time-of-flight mass analyzer with a 125 cm linear flight path. Reversed phase analytical HPLC was performed using Agilent Series 1100, equipped with a C18 PerfectSil Target (MZ Analytik, 3–5 µm, 4.0 × 250 mm). Reversed phase semi-preparative HPLC was performed using Agilent Series 1200, equipped with a C8 Zorbax 300SB-C8 column (Agilent, 5 µm, 9.4 × 250 mm). Flow rate: 1 mL/min; solvent A: 0.1% TFA in water; solvent B: 0.1% TFA in MeCN. Analytical TLC was performed on MERCK ready-to-use plates with silica gel 60 (F254). Column chromatography: MERCK silica gel 60, 0.04–0.063 mm. F-SPE was performed on SIGMA-ALDRICH Fluoro*Flash* SPE cartridges (2 g, 8 cm^3 tube). For microwave assisted peptoid synthesis the single mode CEM Discover microwave was used.

Experimental

N-Ethyl-*m*-methoxyaniline (**4**-Et)

The preparation and properties of compound **4**-Et have been reported in reference 3.

General method 1 for the preparation of *N*-acyl-*m*-methoxyanilines 5-R_{f6}-H, 5-R_{f6}-Et and 5-R_{f7}-H

m-Anisidine (**4**-H) or *N*-ethyl-*m*-anisidine (**4**-Et) (1 equiv.) and dry pyridine (1.2 equiv.) were dissolved in dry CH_2Cl_2. Perfluoroheptanoyl or perfluorooctanoyl chloride (1.2 equiv.) was then added dropwise with stirring. The mixture was stirred overnight at RT and then CH_2Cl_2 (10 mL) was added. The mixture was washed with water (5 mL), aqueous HCl (1 M, 5 mL), and saturated aqueous $NaHCO_3$ (5 mL). After drying over Na_2SO_4, the solvent was evaporated under reduced pressure und the crude product was purified by using column chromatography.

N-Perfluoroheptanoyl-*m*-methoxyaniline (**5**-R_{f6}-H)

After purification (chromatography with eluent cyclohexane/EtOAc 4:1) the title compound was obtained as colorless crystals from *m*-anisidine (**4**-H) (244 µL, 2.18 mmol) and perfluoroheptanoyl chloride (578 µL, 261 mmol) according to general method 1: yield 826 mg (81%).

R_f = 0.50 (cyclohexane/EtOAc 4:1); mp: 104 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 3.83 (s, 3H), 6.80 (dd, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 2.1 Hz, 1H), 7.04 (dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 1.5 Hz, 1H), 7.28–7.31 (m, 2H), 7.86 (bs, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.4 (CH_3), 106.1 (CH_{ar}), 112.4 (CH_{ar}), 112.4 (CH_{ar}), 130.1 (CH_{ar}), 136.2 (C_{ar}), 155.1 (t, ^2J(C,F) = 26 Hz, C), 160.3 (C_{ar}); ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –126.0 (m, CF_2), –122.7 (m, CF_2), –122.2 (m, CF_2), –121.6 (m, CF_2), –119.2 (tt, ^3J(F,F) = 12.8 Hz, ^4J(F,F) = 2.9 Hz, CF_2), –80.7 (tt, ^3J(F,F) = 9.8 Hz,

^4J(F,F) = 1.9 Hz, CF_3); EI MS: *m/z* (%): 469 (100) $[M]^+$, 450 (17) $[M–F]^+$, 319 (3) $[M–C_8H_8NO_2]^+$, 150 (69) $[M–C_6F_{13}]^+$, 122 (30) $[M–C_7F_{13}O]^+$, 107 (14) $[M–C_7HF_{13}NO]^+$, 77 (14) $[M–C_8H_3F_{13}NO_2]^+$, 69 (8) $[M–C_{13}H_8F_{10}NO_2]^+$; HRMS: *m/z* calcd for $C_{14}H_8F_{13}NO_2$: 469.0347; found: 469.0351 $[M]^+$.

N-Ethyl-*N*-perfluoroheptanoyl-*m*-methoxyaniline (**5**-R_{f6}-Et)

After purification (chromatography with eluent cyclohexane/EtOAc 8:1) the title compound was obtained as colorless oil from *N*-ethyl-*m*-anisidine (**4**-Et) (498 mg, 3.30 mmol) and perfluoroheptanoyl chloride (875 µL, 3.96 mmol) according to general method 1: yield 1.14 g (70%).

R_f = 0.33 (cyclohexane/EtOAc 8:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.20 (t, ^3J(H,H) = 7.2 Hz, 3H), 3.78 (q, ^3J(H,H) = 7.2 Hz, 2H), 3.82 (s, 3H), 6.72 (s, 1H), 6.78 (d, ^3J(H,H) = 7.8 Hz, 1H), 6.95 (dd, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 1.8 Hz, 1H), 7.33 (t, ^3J(H,H) = 8.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.1 (CH_3), 47.7 (CH_2), 55.5 (CH_3), 113.8 (CH_{ar}), 114.2 (CH_{ar}), 120.1 (CH_{ar}), 130.0 (CH_{ar}), 140.1 (C_{ar}), 157.1 (t, ^2J(C,F) = 22 Hz, C), 160.2 (C_{ar}); ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –126.0 (m, CF_2), –122.8 (m, CF_2), –120.8 (m, CF_2), –120.3 (m, CF_2), –108.9 (t, ^3J(F,F) = 13.0 Hz, CF_2), –80.8 (t, ^3J(F,F) = 9.8 Hz, CF_3); EI MS: *m/z* (%): 497 (70) $[M]^+$, 374 (80) $[M–C_7H_7O_2]^+$, 178 (32) $[M–C_6F_{13}]^+$, 150 (100) $[M–C_7F_{13}O]^+$, 107 (16) $[M–C_9H_5F_{13}NO]^+$, 77 (9) $[M–C_{10}H_7F_{13}NO_2]^+$, 69 (6) $[M–C_{15}H_{12}F_{10}NO_2]^+$; HRMS: *m/z* calcd for $C_{16}H_{12}F_{13}NO_2$: 497.0660; found: 497.0656 $[M]^+$.

N-Perfluorooctanoyl-*m*-methoxyaniline (**5**-R_{f7}-H)

After purification (chromatography with eluent cyclohexane/EtOAc 6:1) the title compound was obtained as white solid from *m*-anisidine (**4**-H) (323 µL, 2.89 mmol) and perfluorooctanoyl chloride (862 µL, 3.47 mmol) according to general method 1: yield 1.32 g (88%).

R_f = 0.40 (cyclohexane/EtOAc 6:1); mp: 117 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.83 (s, 3H), 6.80 (dd, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 2.2 Hz, 1H), 7.04 (dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 1.4 Hz, 1H), 7.27–7.32 (m, 2H), 7.89 (bs, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4 (CH_3), 106.2 (CH_{ar}), 112.4 (CH_{ar}), 112.5 (CH_{ar}), 130.1 (CH_{ar}), 136.2 (C_{ar}), 155.1 (t, ^2J(C,F) = 26 Hz, C), 160.4 (C_{ar}); ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –126.0 (m, CF_2), –122.6 (m, CF_2), –122.2 (m, CF_2), –121.9 (m, CF_2), –121.4 (m, CF_2), –119.2 (t, ^3J(F,F) = 12.8 Hz, CF_2), –80.7 (t, ^3J(F,F) = 10.2 Hz, CF_3); EI MS: *m/z* (%): 519 (100) $[M]^+$, 500 (10) $[M–F]^+$, 150 (14) $[M–C_7F_{15}]^+$; HRMS: *m/z* calcd for $C_{15}H_8F_{15}NO_2$: 519.0315; found: 519.0313 $[M]^+$; elemental analysis calcd (%) for $C_{15}H_8F_{15}NO_2$: C 34.70, H 1.55, N 2.70; found: C 34.47, H 1.33, N 2.46.

General method 2 for the reduction of amides 5-R_{f6}-H, 5-R_{f6}-Et, 5-R_{f7}-H and 8

A solution of BH_3 in THF (1 M) (2 equiv.) was added at RT to amide **5**-R_1-R_2 or **8** (1 equiv.) in dry THF (3 mL), and the mixture was heated at reflux overnight before being cooled to 0 °C. Excess BH_3 was carefully neutralized by adding MeOH (1 mL), and then aqueous NaOH (1 M, 10 mL) was added. After stirring at RT for 20 min, the mixture was diluted with diethyl ether (10 mL) and the organic layer was separated. The aqueous layer was extracted with diethyl ether (3 × 3 mL),

then the combined organic layers were washed with saturated aqueous $NaHCO_3$ (3 mL) and brine (3 mL), then dried and evaporated. The crude product was purified by using column chromatography.

N-(1*H*,1*H*-Perfluoroheptyl)-*m*-methoxyaniline (**6**-R_{f6}-H)

After purification (chromatography with eluent cyclohexane/EtOAc 6:1) the title compound was obtained as colorless oil from compound **5**-R_{f6}-H (811 mg, 1.73 mmol) according to general method 2: yield 479 mg (61%).

R_f = 0.23 (cyclohexane/EtOAc 6:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.78 (s, 3H), 3.87 (t, ^3J(H,F) = 14.6 Hz, 2H), 3.90 (bs, 1H, NH), 6.24 (t, ^4J(H,H) = 2.3 Hz, 1H), 6.30 (dd, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 2.3 Hz, 1H), 6.37 (dd, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 2.3 Hz, 1H), 7.12 (t, ^3J(H,H) = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.4 (t, ^2J(C,F) = 23 Hz, CH_2), 55.1 (CH_3), 99.6 (CH_{ar}), 104.1 (CH_{ar}), 106.1 (CH_{ar}), 130.2 (CH_{ar}), 147.8 (C_{ar}), 160.9 (C_{ar}); ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –126.1 (m, CF_2), –123.3 (m, CF_2), –122.8 (m, CF_2), –121.9 (m, CF_2), –118.1 (m, CF_2), –80.7 (tt, ^3J(F,F) = 9.8 Hz, ^4J(F,F) = 1.9 Hz, CF_3); EI MS: *m/z* (%): 455 (90) $[M]^+$, 436 (13) $[M–F]^+$, 185 (17) $[M–C_5HF_{11}]^+$, 136 (100) $[M–C_6F_{13}]^+$, 108 (24) $[M–C_7HF_{13}NO]^+$, 77 (14) $[M–C_8H_5F_{13}NO]^+$; HRMS: *m/z* calcd for $C_{14}H_{10}F_{13}NO$: 455.0555; found: 455.0557 $[M]^+$.

N-Ethyl-*N*-(1*H*,1*H*-perfluoroheptyl)-*m*-methoxyaniline (**6**-R_{f6}-Et)

After purification (chromatography with eluent cyclohexane/EtOAc 20:1) the title compound was obtained as white solid from compound **5**-R_{f6}-Et (1.06 g, 2.13 mmol) according to general method 2: yield 888 mg (91%).

R_f = 0.33 (cyclohexane/EtOAc 20:1); mp: 43 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.21 (t, ^3J(H,H) = 7.0 Hz, 3H), 3.49 (q, ^3J(H,H) = 7.0 Hz, 2H), 3.80 (s, 3H), 3.95 (t, ^3J(H,F) = 16.3 Hz, 2H), 6.33–6.34 (m, 1H), 6.36–6.41 (m, 2H), 7.17 (t, ^3J(H,H) = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.4 (CH_3), 46.3 (CH_2), 50.7 (t, ^2J(C,F) = 21 Hz, CH_2), 55.1 (CH_3), 99.9 (CH_{ar}), 102.6 (CH_{ar}), 106.0 (CH_{ar}), 130.0 (CH_{ar}), 148.9 (C_{ar}), 160.8 (C_{ar}); ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –126.1 (m, CF_2), –123.7 (m, CF_2), –122.8 (m, CF_2), –121.8 (m, CF_2), –116.6 (m, CF_2), –80.7 (t, ^3J(F,F) = 9.9 Hz, CF_3); EI MS: *m/z* (%): 483 (30) $[M]^+$, 468 (12) $[M–CH_3]^+$, 464 (10) $[M–F]^+$, 164 (100) $[M–C_6F_{13}]^+$, 77 (3) $[M–C_{10}H_9F_{13}NO]^+$; HRMS: *m/z* calcd for $C_{16}H_{14}F_{13}NO$: 483.0868; found: 483.0870 $[M]^+$; elemental analysis calcd (%) for $C_{16}H_{14}F_{13}NO$: C 39.76, H 2.92, N 2.90; found: C 39.55, H 2.91, N 2.72.

N-(1*H*,1*H*-Perfluorooctyl)-*m*-methoxyaniline (**6**-R_{f7}-H)

After purification (chromatography with eluent cyclohexane/EtOAc 20:1) the title compound was obtained as white solid from **5**-R_{f7}-H (1.73 g, 3.33 mmol) according to general method 2: yield 1.07 g (64%).

R_f = 0.20 (cyclohexane/EtOAc 20:1); mp: 53 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.78 (s, 3H), 3.80–3.93 (m, 3H), 6.24 (t, ^4J(H,H) = 2.2 Hz, 1H), 6.30 (dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 2.2 Hz,

1H), 6.37 (dd, ^{3}J(H,H) = 8.0 Hz, ^{4}J(H,H) = 2.2 Hz, 1H), 7.12 (t, ^{3}J(H,H) = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.4 (t, ^{2}J(C,F) = 23 Hz, CH_2), 55.2 (CH_3), 99.6 (CH_{ar}), 104.1 (CH_{ar}), 106.1 (CH_{ar}), 130.2 (CH_{ar}), 147.8 (C_{ar}), 160.9 (C_{ar}); ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –126.0 (m, CF_2), –123.3 (m, CF_2), –122.7 (m, CF_2), –122.0 (m, CF_2), –121.7 (m, CF_2), –118.1 (t, ^{3}J(F,F) = 12.5 Hz, CF_2), –80.7 (t, ^{3}J(F,F) = 10.1 Hz, CF_3); EI MS: *m/z* (%): 505 (92) $[M]^+$, 486 (73) $[M–F]^+$, 185 (16) $[M–C_6HF_{13}]^+$, 136 (100) $[M–C_7F_{15}]^+$, 77 (5) $[M–C_9H_5F_{15}NO]^+$; HRMS: *m/z* calcd for $C_{15}H_{10}F_{15}NO$: 505.0523; found: 505.0525 $[M]^+$; elemental analysis calcd (%) for $C_{15}H_{10}F_{15}NO$: C 35.66, H 2.00, N 2.77; found: C 35.56, H 1.81, N 2.59.

7-Hydroxy-1,2,3,4-tetrahydroquinoline (**9**)

The preparation and properties of compound **9** have been reported in reference 4.

N-(1*H*,1*H*-Perfluoroheptyl)-*m*-hydroxyaniline (**7**-R_{f6}-H)

Compound **6**-R_{f6}-H (316 mg, 964 µmol) was dissolved in glacial AcOH (400 µL), then 48% aqueous HBr (475 µL) was added and the mixture was heated at reflux for 6 h. After cooling, $CHCl_3$ (3 mL) was added and the solution was carefully neutralized to about pH 5-6 with aqueous NaOH (30%). The organic phase was separated and the aqueous phase was extracted with $CHCl_3$ (3 × 1.5 mL). The combined organic fractions were washed with saturated aqueous $NaHCO_3$ (4 mL), dried, and evaporated. The crude product was purified by using column chromatography (eluent cyclohexane/EtOAc 5:1) to give a white solid: yield 179 mg (58%).

R_f = 0.17 (cyclohexane/EtOAc 5:1); mp: 85 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.81–3.91 (m, 2H), 3.89 (bs, 1H, NH), 4.66 (bs, 1H, OH), 6.19 (t, ^{4}J(H,H) = 2.3 Hz, 1H), 6.26–6.29 (m, 2H), 7.06 (t, ^{3}J(H,H) = 8.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 44.3 (t, ^{2}J(C,F) = 23 Hz, CH_2), 100.1 (CH_{ar}), 106.1 (CH_{ar}), 106.1 (CH_{ar}), 130.4 (CH_{ar}), 148.0 (C_{ar}), 156.7 (C_{ar}); ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –126.1 (m, CF_2), –123.3 (m, CF_2), –122.8 (m, CF_2), –121.9 (m, CF_2), –118.1 (m, CF_2), –80.7 (tt, ^{3}J(F,F) = 10.2 Hz, ^{4}J(F,F) = 2.1 Hz, CF_3); EI MS: *m/z* (%): 441 (69) $[M]^+$, 422 (16) $[M–F]^+$, 122 (100) $[M–C_6F_{13}]^+$; HRMS: *m/z* calcd for $C_{13}H_8F_{13}NO$: 441.0398; found: 441.0396 $[M]^+$.

General method 3 for the demethylation of amines 6-R_{f6}-Et, 6-R_{f7}-H, 6-CH_2R_{f6}-H, 6-CH_2R_{f6}-Et and 6-$(CH_2)_2R_{f8}$-H

A solution of BBr_3 in CH_2Cl_2 (1 M) was added at RT to amine **6**-R_1-R_2 in dry CH_2Cl_2 (20 mL), and the mixture was stirred overnight at RT. Afterwards water (20 mL) was carefully added. The organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL) and brine (10 mL), then dried and evaporated. The crude product was purified by using column chromatography.

N-Ethyl-*N*-(1*H*,1*H*-perfluoroheptyl)-*m*-hydroxyaniline (**7**-R_{f6}-Et).

After purification (chromatography with eluent cyclohexane/EtOAc 5:1) the title compound was obtained as red solid from compound **6**-R_{f6}-Et (824 mg, 1.70 mmol) and 5 equiv. BBr_3 (8.50 mL, 8.50 mmol) according to general method 3: yield 592 mg (74%).

R_f = 0.38 (cyclohexane/EtOAc 5:1); mp: 42 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.20 (t, ^3J(H,H) = 7.0 Hz, 3H), 3.48 (q, ^3J(H,H) = 7.0 Hz, 2H), 3.94 (t, ^3J(H,F) = 16.3 Hz, 2H), 4.65 (bs, 1H, OH), 6.24–6.30 (m, 2H), 6.36 (d, ^3J(H,H) = 9.2 Hz, 1H), 7.07–7.13 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.4 (CH_3), 46.3 (CH_2), 50.6 (t, ^2J(C,F) = 20 Hz, CH_2), 100.2 (CH_{ar}), 104.9 (CH_{ar}), 105.8 (CH_{ar}), 130.2 (CH_{ar}), 149.2 (C_{ar}), 156.6 (C_{ar}); ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –126.1 (m, CF_2), –123.6 (m, CF_2), –122.8 (m, CF_2), –121.8 (m, CF_2), –116.7 (m, CF_2), –80.7 (t, ^3J(F,F) = 9.9 Hz, CF_3); EI MS: *m/z* (%): 469 (100) $[M]^+$, 454 (30) $[M–CH_3]^+$, 440 (16) $[M–C_2H_5]^+$, 150 (96) $[M–C_6F_{13}]^+$; HRMS: *m/z* calcd for $C_{15}H_{12}F_{13}NO$: 469.0711; found: 469.0710 $[M]^+$.

N-(1*H*,1*H*-Perfluorooctyl)-*m*-hydroxyaniline (**7**-R_{f7}-H)

After purification (chromatography with eluent cyclohexane/EtOAc 4:1) the title compound was obtained as white solid from compound **6**-R_{f7}-H (1.05 g, 2.09 mmol) and 5 equiv. BBr_3 (10.4 mL, 10.4 mmol) according to general method 3: yield 735 mg (71%).

R_f = 0.26 (cyclohexane/EtOAc 4:1); mp: 92 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.85 (t, ^3J(H,F) = 15.6 Hz, 2H), 3.89 (bs, 1H, NH), 4.72 (bs, 1H, OH), 6.19 (t, ^4J(H,H) = 2.3 Hz, 1H), 6.28 (d, ^3J(H,H) = 8.0 Hz, 1H), 6.28 (dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 4.9 Hz, 1H), 7.06 (t, ^3J(H,H) = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.3 (t, ^2J(C,F) = 24 Hz, CH_2), 100.2 (CH_{ar}), 106.1 (CH_{ar}), 130.4 (CH_{ar}), 148.0 (C_{ar}), 156.7 (C_{ar}); ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –126.1 (m, CF_2), –123.3 (m, CF_2), –122.7 (m, CF_2), –122.0 (m, CF_2), –121.7 (m, CF_2), –118.1 (m, CF_2), –80.7 (tt, ^3J(F,F) = 9.8 Hz, ^4J(F,F) = 2.0 Hz, CF_3); EI MS: *m/z* (%): 491 (100) $[M]^+$, 472 (22) $[M–F]^+$, 122 (76) $[M–C_7F_{15}]^+$; HRMS: *m/z* calcd for $C_{14}H_8F_{15}NO$: 491.0366; found: 491.0363 $[M]^+$.

N-(1*H*,1*H*,2*H*,2*H*-Perfluorooctyl)-*m*-hydroxyaniline (**7**-CH_2R_{f6}-H)

After purification (chromatography with eluent cyclohexane/EtOAc 2:3) the title compound was obtained as colorless oil from compound **6**-CH_2R_{f6}-H (1.45 g, 3.09 mmol) and 2.2 equiv. BBr_3 (6.80 mL, 6.80 mmol) according to general method 3: yield 860 mg (61%).

R_f = 0.80 (cyclohexane/EtOAc 2:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.38 (tt, ^3J(H,F) = 19.0 Hz, ^3J(H,H) = 7.1 Hz, 2H), 3.50 (t, ^3J(H,H) = 7.1 Hz, 2H), 3.79 (bs, 1H, NH), 4.64 (bs, 1H, OH), 6.10 (t, ^4J(H,H) = 2.1 Hz, 1H), 6.17–6.22 (m, 2H), 7.03 (t, ^3J(H,H) = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.6 (t, ^2J(C,F) = 22 Hz, CH_2), 35.8 (t, ^3J(C,F) = 5 Hz, CH_2), 99.6 (CH_{ar}), 105.2 (CH_{ar}), 105.9 (CH_{ar}), 130.5 (CH_{ar}), 148.5 (C_{ar}), 156.8 (C_{ar}); ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –126.1 (m, CF_2), –123.4 (m, CF_2), –122.8 (m, CF_2), –121.8 (m, CF_2), –113.8 (m, CF_2), –80.7 (t, ^3J(F,F) = 9.8 Hz, CF_3); EI MS: *m/z* (%): 455 (100) $[M]^+$, 436 (42) $[M–F]^+$, 122 (68) $[M–C_7H_2F_{13}]^+$; HRMS: *m/z* calcd for $C_{14}H_{10}F_{13}NO$: 455.0555; found: 455.0553 $[M]^+$.

N-Ethyl-*N*-(1*H*,1*H*,2*H*,2*H*-Perfluorooctyl)-*m*-hydroxyaniline (**7**-CH_2R_{f6}-Et)

The preparation and properties of compound **7**-CH_2R_{f6}-Et have been reported in reference 5.

N-(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-Perfluoroundecyl)-*m*-hydroxyaniline (**7**-$(CH_2)_2R_{f8}$-H)

After purification (chromatography with eluent cyclohexane/EtOAc 3:1) the title compound was obtained as white solid from compound **6**-$(CH_2)_2R_{f8}$-H (1.27 g, 2.18 mmol) and 2.2 equiv. BBr_3 (4.80 mL, 4.80 mmol) according to general method 3: yield 1.13 g (91%).

R_f = 0.29 (cyclohexane/EtOAc 3:1); mp: 67 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.93 (tt, ^3J(H,H) = 7.8 Hz, ^3J(H,H) = 7.0 Hz, 2H), 2.13–2.26 (m, 2H), 3.22 (t, ^3J(H,H) = 6.9 Hz, 2H), 3.77 (bs, 1H, NH), 4.58 (bs, 1H, OH), 6.11 (t, ^4J(H,H) = 2.3 Hz, 1H), 6.18–6.22 (m, 2H), 7.03 (t, ^3J(H,H) = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.6 (CH_2), 28.6 (t, ^2J(C,F) = 23 Hz, CH_2), 43.0 (CH_2), 99.6 (CH_{ar}), 104.7 (CH_{ar}), 105.9 (CH_{ar}), 130.3 (CH_{ar}), 149.4 (C_{ar}) 156.8 (C_{ar}); ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –126.1 (m, CF_2), –123.3 (m, CF_2), –122.7 (m, CF_2), –121.9 (m, 2 × CF_2), –121.7 (m, CF_2), –114.1 (t, ^3J(F,F) = 13 Hz, CF_2), –80.7 (t, ^3J(F,F) = 9.8 Hz, CF_3); EI MS: *m/z* (%): 569 (100) $[M]^+$, 550 (20) $[M–F]^+$, 122 (87) $[M–C_{10}H_4F_{17}]^+$; HRMS: *m/z* calcd for $C_{17}H_{12}F_{17}NO$: 569.0647; found: 569.0646 $[M]^+$; elemental analysis calcd (%) for $C_{17}H_{12}F_{17}NO$: C 35.87, H 2.12, N 2.46; found: C 35.57, H 1.88, N 2.35.

General method 4 for the preparation of rhodamine F dyes 1a–1f, 2 and 3

A solution of phenol **7**-R_1-R_2, **10** or **13** (2 equiv.) and phthalic anhydride (1.6 equiv.) in propionic acid (18 equiv.) was heated with *p*-toluenesulfonic acid monohydrate (0.15 equiv.) at 160 °C for 24 h. After cooling to RT MeOH (10 mL) and CH_2Cl_2 (10 mL) were added. The organic layer was washed with aqueous NaOH (0.3 M, 15 mL). Afterwards the aqueous layer was repeatedly extracted with CH_2Cl_2 until the organic layer remained colorless. Hydrochloric acid in MeOH (0.5 M, 2 mL) was added to the combined organic layers and afterwards the solvent was evaporated under reduced pressure. The crude product was purified by using column chromatography. After purification the product was converted into the hydrochloride by adding hydrochloric acid in MeOH (0.5 M, 2 mL).

Compound **1a**

After purification (chromatography with eluent cyclohexane/EtOAc 2:1) the title compound was obtained as orange solid from compound **7**-R_{f6}-H (120 mg, 272 µmol) according to general method 4: yield 35.2 mg (25%).

R_f = 0.18 (cyclohexane/EtOAc 2:1); mp: 192 °C; ^{1}H NMR (500 MHz, CD_3OD): δ = 3.78 (t, ^3J(H,F) = 15.6 Hz, 4H), 6.59 (dd, ^3J(H,H) = 8.8 Hz, ^4J(H,H) = 2.3 Hz, 2H), 6.69–6.71 (m, 4H), 7.24 (d, ^3J(H,H) = 7.4 Hz, 1H), 7.68 (td, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 0.9 Hz, 1H), 7.73 (td, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 1.2 Hz, 1H), 8.02 (d, ^3J(H,H) = 7.6 Hz, 1H); ^{13}C NMR (125 MHz, CD_3OD): δ = 44.3 (t, ^2J(C,F) = 24 Hz, CH_2), 99.1 (CH_{ar}), 111.2 (C_{ar}), 112.7 (CH_{ar}), 126.7 (CH_{ar}), 127.0 (CH_{ar}), 130.7 (CH_{ar}), 131.0 (CH_{ar}), 135.1 (CH_{ar}), 153.6 (C_{ar}), 153.6 (C_{ar}), 155.8 (C_{ar}),

172.2 (C_{ar}); ^{19}F NMR (376.5 MHz, CD_3OD): δ = –127.3 (m, 2 × CF_2), –124.2 (m, 2 × CF_2), –123.8 (m, 2 × CF_2), –122.9 (m, 2 × CF_2), –118.6 (m, 2 × CF_2), –82.4 (t, ^3J(F,F) = 9.9 Hz, 2 × CF_3); FAB MS: *m/z* (%): 995 (100) $[M]^+$, 951 (6) $[M–CO_2]^+$, 875 (2) $[M–C_2HF_5]^+$, 825 (1) $[M–C_3HF_7]^+$, 775 (2) $[M–C_4HF_9]^+$, 725 (6) $[M–C_5HF_{11}]^+$, 675 (6) $[M–C_6HF_{13}]^+$; HRMS: *m/z* calcd for $C_{34}H_{17}F_{26}N_2O_3$: 995.0824; found: 995.0816 $[M]^+$.

Compound **1b**

After purification (chromatography with eluent cyclohexane/EtOAc 3:1) the title compound was obtained as red solid from **7**-R_{f6}-Et (453 mg, 965 µmol) according to general method 4: yield 198 mg (38%).

R_f = 0.33 (cyclohexane/EtOAc 3:1); mp: 141 °C; ^{1}H NMR (500 MHz, CD_3OD): δ = 1.35 (t, ^3J(H,H) = 7.1 Hz, 6H), 3.87 (q, ^3J(H,H) = 7.1 Hz, 4H), 4.64 (t, ^3J(H,F) = 16.3 Hz, 4H), 7.23–7.26 (m, 4H), 7.34–7.36 (m, 2H), 7.47 (dd, ^3J(H,H) = 7.4 Hz, ^4J(H,H) = 0.9 Hz, 1H), 7.85 (td, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 1.3 Hz, 1H), 7.89 (td, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 1.4 Hz, 1H), 8.39 (dd, ^3J(H,H) = 7.8 Hz, ^4J(H,H) = 1.2 Hz, 1H); ^{13}C NMR (125 MHz, CD_3OD): δ = 12.0 (CH_3), 49.3 (CH_2), 50.8 (t, ^2J(C,F) = 21 Hz, CH_2), 99.5 (CH_{ar}), 116.5 (C_{ar}), 116.7 (CH_{ar}), 131.4 (CH_{ar}), 131.9 (CH_{ar}), 132.2 (C_{ar}), 132.7 (CH_{ar}), 132.8 (CH_{ar}), 134.1 (CH_{ar}), 134.9 (C_{ar}), 159.0 (C_{ar}), 159.6 (C_{ar}), 165.2 (C_{ar}), 168.1 (C); ^{19}F NMR (376.5 MHz, CD_3OD): δ = –127.2 (m, 2 × CF_2), –124.1 (m, 2 × CF_2), –123.8 (m, 2 × CF_2), –122.8 (m, 2 × CF_2), –116.4 (m, 2 × CF_2), –82.3 (t, ^{3}J(F,F) = 10.2 Hz, 2 × CF_3); FAB MS: *m/z* (%): 1051 (100) $[M]^+$, 931 (2) $[M–C_2HF_5]^+$, 781 (1) $[M–C_5HF_{11}]^+$, 732 (2) $[M–C_6HF_{13}]^+$, 717 (5) $[M–C_7H_3F_{13}]^+$; HRMS: *m/z* calcd for $C_{38}H_{25}F_{26}N_2O_3$: 1051.1445; found: 1051.1394 $[M]^+$.

Compound **1c**

After purification (chromatography with eluent cyclohexane/EtOAc 2:1) the title compound was obtained as red solid from **7**-R_{f7}-H (500 mg, 1.02 mmol) according to general method 4: yield 110 mg (19%).

R_f = 0.17 (cyclohexane/EtOAc 2:1); mp: 229 °C; ^{1}H NMR (400 MHz, CD_3OD): δ = 4.38 (t, ^3J(H,F) = 15.6 Hz, 4H), 7.05 (d, ^3J(H,H) = 9.3 Hz, 2H), 7.16 (d, *4J*(H,H) = 1.9 Hz, 2H), 7.23 (d, ^3J(H,H) = 9.3 Hz, 2H), 7.45 (dd, ^3J(H,H) = 7.3 Hz, ^4J(H,H) = 1.4 Hz, 1H), 7.83 (td, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 1.4 Hz, 1H), 7.88 (td, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 1.5 Hz, 1H), 8.37 (dd, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 1.4 Hz, 1H); ^{13}C NMR was not obtained due to poor signal-to-noise ratio; ^{19}F NMR (376.5 MHz, CD_3OD): δ = –127.2 (m, 2 × CF_2), –123.9 (m, 2 × CF_2), –123.7 (m, 2 × CF_2), –123.0 (m, 2 × CF_2), –122.7 (m, 2 × CF_2), –118.1 (m, 2 × CF_2), –82.3 (t, ^3J(F,F) = 10.2 Hz, 2 × CF_3); FAB MS: *m/z* (%): 1095 (100) $[M]^+$, 875 (3) $[M–C_4HF_9]^+$, 775 (8) $[M–C_6HF_{13}]^+$, 725 (6) $[M–C_7HF_{15}]^+$; HRMS: *m/z* calcd for $C_{36}H_{17}F_{30}N_2O_3$: 1095.0755; found: 1095.0790 $[M]^+$.

Compound **1d**

After purification (chromatography with eluent cyclohexane/EtOAc 1:1 then EtOAc) the title compound was obtained as red solid from compound **7**-CH_2R_{f6}-H (678 mg, 1.49 mmol) according to general method 4: yield 115 mg (15%).

R_f = 0.12 (cyclohexane/EtOAc 1:1); mp: 253 °C; ^{1}H NMR (300 MHz, CD_3OD): δ = 2.63 (tt, ^3J(H,F) = 18.8 Hz, ^3J(H,H) = 6.8 Hz, 4H), 3.79 (t, ^3J(H,H) = 6.8 Hz, 4H), 6.89 (dd, ^3J(H,H) = 9.2 Hz, ^4J(H,H) = 2.2 Hz, 2H), 6.95 (d, ^4J(H,H) = 2.2 Hz, 2H), 7.12 (d, ^3J(H,H) = 9.2 Hz, 2H), 7.41 (dd, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.6 Hz, 1H), 7.75–7.87 (m, 2H), 8.34 (dd, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.6 Hz, 1H); ^{13}C NMR was not obtained due to poor signal-to-noise ratio; ^{19}F NMR (376.5 MHz, CD_3OD): δ = –127.3 (m, 2 × CF_2), –124.5 (m, 2 × CF_2), –123.8 (m, 2 × CF_2), –122.8 (m, 2 × CF_2), –115.1 (m, 2 × CF_2), –82.4 (t, ^3J(F,F) = 10.2 Hz, 2 × CF_3); FAB MS: *m/z* (%): 1023 (100) $[M]^+$; HRMS: *m/z* calcd for $C_{36}H_{21}F_{26}N_2O_3$: 1023.1132; found: 1023.1119 $[M]^+$.

Compound **1e**

After purification (chromatography with eluent cyclohexane/EtOAc 2:1 then EtOAc) the title compound was obtained as red solid from compound **7**-CH_2R_{f6}-Et (1.14 g, 2.36 mmol) according to general method 4: yield 112 mg (8.5%).

R_f = 0.19 (cyclohexane/EtOAc 2:1); mp: 92 °C; ^{1}H NMR (400 MHz, CD_3OD): δ = 1.33 (t, ^3J(H,H) = 7.0 Hz, 6H), 2.61–2.74 (m, 4H), 3.74 (q, ^3J(H,H) = 7.0 Hz, 4H), 4.02 (t, ^3J(H,H) = 7.0 Hz, 4H), 7.04–7.09 (m, 2H), 7.12 (dd, ^3J(H,H) = 9.4 Hz, ^4J(H,H) = 1.9 Hz, 2H), 7.25 (d, ^3J(H,H) = 9.4 Hz, 2H), 7.44 (d, ^3J(H,H) = 7.4 Hz, 1H), 7.82 (t, ^3J(H,H) = 7.7 Hz, 1H), 7.88 (t, ^3J(H,H) = 7.4 Hz, 1H), 8.37 (d, ^3J(H,H) = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ = 12.6 (CH_3), 29.5 (t, ^2J(C,F) = 21 Hz, CH_2), 44.0 (CH_2), 47.3 (CH_2), 97.8 (CH_{ar}), 115.6 (C_{ar}), 115.7 (CH_{ar}), 131.5 (CH_{ar}), 131.7 (CH_{ar}), 132.2 (C_{ar}), 132.7 (CH_{ar}), 132.9 (CH_{ar}), 134.0 (CH_{ar}), 135.2 (C_{ar}), 157.4 (C_{ar}), 159.6 (C_{ar}), 163.1 (C_{ar}), 168.1 (C); ^{19}F NMR (376.5 MHz, CD_3OD): δ = –127.3 (m, 2 × CF_2), –124.2 (m, 2 × CF_2), –123.8 (m, 2 × CF_2), –122.8 (m, 2 × CF_2), –115.0 (m, 2 × CF_2), –82.4 (t, ^3J(F,F) = 10.1 Hz, 2 × CF_3); FAB MS: *m/z* (%): 1079 (100) $[M]^+$; HRMS: *m/z* calcd for $C_{40}H_{29}F_{26}N_2O_3$: 1079.1758; found: 1079.1871 $[M]^+$.

Compound **1f**

After purification (chromatography with eluent EtOAc then MeOH/EtOAc 3:100) the title compound was obtained as red solid from compound **7**-$(CH_2)_2R_{f8}$-H (1.10 g, 1.94 mmol) according to general method 4: yield 125 mg (10%).

R_f = 0.35 (EtOAc); mp: 224 °C; ^{1}H NMR (400 MHz, CD_3OD): δ = 1.97–2.10 (m, 4H), 2.37 (tt, ^3J(H,F) = 18.5 Hz, ^3J(H,H) = 8.3 Hz, 4H), 3.52 (t, ^3J(H,H) = 6.9 Hz, 4H), 6.84–6.91 (m, 4H), 7.00–7.11 (m, 2H), 7.41 (d, ^3J(H,H) = 7.3 Hz, 1H), 7.78–7.90 (m, 2H), 8.34 (d, ^3J(H,H) = 7.7 Hz, 1H); ^{13}C NMR was not obtained due to poor signal-to-noise ratio; ^{19}F NMR (376.5 MHz, CD_3OD): δ = –127.2 (m, 2 × CF_2), –124.3 (m, 2 × CF_2), –123.7 (m, 2 × CF_2), –122.9 (m, 4 × CF_2),–122.6 (m, 2 × CF_2), –115.2 (m, 2 × CF_2), –82.3 (t, ^3J(F,F) = 10.1 Hz, 2 × CF_3); FAB MS:

m/z (%): 1251 (100) $[M]^+$; HRMS: *m/z* calcd for $C_{42}H_{25}F_{34}N_2O_3$: 1251.1317; found: 1251.1411 $[M]^+$.

Compound **2**

After purification (chromatography with eluent EtOAc) the title compound was obtained as purple solid from compound **10** (262 mg, 529 µmol) according to general method 4: yield 71.7 mg (24%).

R_f = 0.17 (EtOAc); mp: 153 °C; ^{1}H NMR (400 MHz, CD_3OD): δ = 1.92–2.02 (m, 4H), 2.63–2.81 (m, 8H), 3.62–3.97 (m, 4H), 4.00 (t, ^3J(H,H) = 7.0 Hz, 4H), 6.85 (s, 2H), 6.97 (s, 2H), 7.39 (d, ^3J(H,H) = 7.2 Hz, 1H), 7.79–7.82 (m, 1H), 7.84–7.88 (m, 1H), 8.34 (d, ^3J(H,H) = 8.6 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ = 21.9 (CH_2), 28.4 (t, ^2J(C,F) = 21 Hz, CH_2), 28.5 (CH_2), 45.3 (CH_2), 51.3 (CH_2), 96.3 (CH_{ar}), 115.6 (C_{ar}), 127.5 (C_{ar}), 129.2 (CH_{ar}), 131.5 (CH_{ar}), 132.2 (C_{ar}), 132.6 (CH_{ar}), 134.0 (CH_{ar}), 135.4 (C_{ar}), 155.1 (C_{ar}), 158.6 (C_{ar}), 160.5 (C_{ar}), 168.2 (C); ^{19}F NMR (376.5 MHz, CD_3OD): δ = –127.3 (m, 2 × CF_2), –124.2 (m, 2 × CF_2), –123.8 (m, 2 × CF_2), –122.8 (m, 2 × CF_2), –114.9 (t, ^3J(F,F) = 13 Hz, 2 × CF_2), –82.4 (t, ^3J(F,F) = 10.2 Hz, 2 × CF_3); FAB MS: *m/z* (%): 1103 (100) $[M]^+$; HRMS: *m/z* calcd for $C_{42}H_{29}F_{26}N_2O_3$: 1103.1758; found: 1103.1709 $[M]^+$.

Compound **3**

After purification (chromatography with eluent cyclohexane/EtOAc 3:2 then EtOAc) the title compound was obtained as purple solid from compound **13** (285 mg, 532 µmol) according to general method 4: yield 134 mg (41%).

R_f = 0.24 (cyclohexane/EtOAc 3:2); mp: 145 °C; ^{1}H NMR (400 MHz, CD_3OD): δ = 1.55 (s, 12H), 1.75 (s, 6H), 2.61–2.81 (m, 4H), 4.05 (t, ^3J(H,H) = 7.7 Hz, 4H), 5.60 (s, 2H), 6.83 (s, 2H), 6.84 (s, 2H), 7.47 (d, ^3J(H,H) = 7.3 Hz, 1H), 7.84 (t, ^3J(H,H) = 7.6 Hz, 1H), 7.90 (t, ^3J(H,H) = 7.1 Hz, 1H), 8.35 (dd, ^3J(H,H) = 7.7 Hz, ^4J(H,H) = 0.9 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ = 18.2 (CH_3), 29.3 (CH_3), 30.0 (t, ^2J(C,F) = 21 Hz, CH_2), 38.6 (CH_2), 62.1 (C), 96.7 (CH_{ar}), 116.0 (C_{ar}), 123.3 (CH_{ar}), 125.7 (C_{ar}), 126.5 (C_{ar}), 131.5 (CH_{ar}), 131.8 (CH_{ar}), 132.5 (CH_{ar}), 132.7 (C_{ar}), 134.1 (CH_{ar}), 134.4 (CH_{ar}), 134.7 (C_{ar}), 153.9 (C_{ar}), 159.7 (C_{ar}), 159.9 (C_{ar}), 168.4 (C); ^{19}F NMR (376.5 MHz, CD_3OD): δ = –127.3 (m, 2 × CF_2), –124.1 (m, 2 × CF_2), –123.9 (m, 2 × CF_2), –122.8 (m, 2 × CF_2), –115.2 (m, 2 × CF_2), –82.4 (t, ^{3}J(F,F) = 9.8 Hz, 2 × CF_3); FAB MS: *m/z* (%): 1183 (100) $[M]^+$, 1168 (28) $[M–CH_3]^+$; HRMS: *m/z* calcd for $C_{48}H_{37}F_{26}N_2O_3$: 1183.2384; found: 1183.2325 $[M]^+$.

N-(1*H*,1*H*,2*H*,2*H*-Perfluorooctyl)-*m*-methoxyaniline (**6**-CH_2R_{f6}-H)

The preparation and properties of compound **6**-CH_2R_{f6}-H have been reported in reference 5.

N-Ethyl-*N*-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-*m*-methoxyaniline (**6**-CH_2R_{f6}-Et)

The preparation and properties of compound **6**-CH_2R_{f6}-Et have been reported in reference 5.

N-(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-Perfluoroundecyl)-*m*-methoxyaniline (**6**-$(CH_2)_2R_{f8}$-H)

1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-Perfluoroundecyl iodide (1.82 g, 3.09 mmol) was added dropwise to *m*-anisidine (**4**-H) (1.73 mL, 15.4 mmol) at 90 °C. After complete addition, the mixture was stirred at 140 °C for 3 h. After cooling, diethyl ether (15 mL) was added, the organic layer was washed with aqueous NaOH (2 M, 15 mL), and the aqueous layer was extracted with diethyl ether (15 mL). Then, the organic layer was dried with sodium sulfate. The solvent was removed under reduced pressure. The crude product was purified by using column chromatography (eluent cyclohexane/EtOAc 5:1) to give a white solid: yield 1.34 g (74%).

R_f = 0.38 (cyclohexane/EtOAc 5:1); mp: 57 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.90–1.97 (m, 2H), 2.14–2.27 (m, 2H), 3.23 (t, ^3J(H,H) = 6.9 Hz, 2H), 3.78 (s, 3H), 6.18 (t, ^4J(H,H) = 2.2 Hz, 1H), 6.24 (dd, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 2.2 Hz, 1H), 6.31 (dd, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 2.2 Hz, 1H), 7.10 (t, ^3J(H,H) = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.6 (CH_2), 28.6 (t, ^2J(C,F) = 22 Hz, CH_2), 43.1 (CH_2), 55.1 (CH_3), 99.0 (CH_{ar}), 102.9 (CH_{ar}), 106.0 (CH_{ar}), 130.1 (CH_{ar}), 149.1 (C_{ar}), 160.9 (C_{ar}); ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –126.1 (m, CF_2), –123.4 (m, CF_2), –122.7 (m, CF_2), –121.9 (m, 2 × CF_2), –121.7 (m, CF_2), –114.1 (t, ^3J(F,F) = 14 Hz, CF_2), –80.7 (t, ^3J(F,F) = 10 Hz, CF_3); EI MS: *m/z* (%): 583 (88) $[M]^+$, 564 (53) $[M–F]^+$, 136 (100) $[M–C_{10}H_4F_{17}]^+$; HRMS: *m/z* calcd for $C_{18}H_{14}F_{17}NO$: 583.0804; found: 583.0802 $[M]^+$; elemental analysis calcd (%) for $C_{18}H_{14}F_{17}NO$: C 37.06, H 2.42, N 2.40; found: C 37.01, H 2.23, N 2.13.

7-Hydroxy-*N*-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,2,3,4-tetrahydroquinoline (**10**).

1*H*,1*H*,2*H*,2*H*-Perfluorooctyl iodide (823 µL, 3.35 mmol) was added dropwise to a solution of compound **9** (500 mg, 3.35 mmol) in DMF (1.8 mL) at 90 °C. After complete addition, the mixture was stirred at 140 °C for 2 h. After cooling, EtOAc (40 mL) and aqueous NaOH (2 M, 20 mL) were added. The organic layer was separated, washed with brine (10 mL) and the solvent was removed under reduced pressure. The crude product was purified by using column chromatography (eluent cyclohexane/EtOAc 9:1) to give a white solid: yield 592 mg (36%).

R_f = 0.18 (cyclohexane/EtOAc 9:1); mp: 82 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.92–1.98 (m, 2H), 2.37 (tt, ^3J(H,F) = 19.0 Hz, ^3J(H,H) = 7.6 Hz, 2H), 2.69 (t, ^3J(H,H) = 6.3 Hz, 2H), 3.27 (t, ^3J(H,H) = 5.6 Hz, 2H), 3.58–3.61 (m, 2H), 4.76 (bs, OH), 6.08 (d, ^4J(H,H) = 2.3 Hz, 1H), 6.11 (dd, ^3J(H,H) = 7.9 Hz, ^4J(H,H) = 2.3 Hz, 1H), 6.82 (d, ^3J(H,H) = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.3 (CH_2), 27.1 (CH_2), 27.2 (t, ^2J(C,F) = 22 Hz, CH_2), 43.1 (CH_2), 49.2 (CH_2), 97.4 (CH_{ar}), 103.1 (CH_{ar}), 115.4 (C_{ar}), 130.1 (CH_{ar}), 145.0 (C_{ar}), 155.1 (C_{ar}); ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –126.1 (m, CF_2), –123.3 (m, CF_2), –122.8 (m, CF_2), –121.8 (m, CF_2), –114.3 (t, ^3J(F,F) = 14.1 Hz, CF_2), –80.7 (t, ^3J(F,F) = 9.9 Hz, CF_3); EI MS: *m/z* (%): 495 (90) $[M]^+$, 476 (11) $[M–F]^+$, 162 (100) $[M–C_7H_2F_{13}]^+$; HRMS: *m/z* calcd for $C_{17}H_{14}F_{13}NO$: 495.0868; found: 495.0863 $[M]^+$.

7-Methoxy-2,2,4-trimethyl-1,2-dihydroquinoline (**11**)

The preparation and properties of compound **11** have been reported in reference 3.

7-Hydroxy-2,2,4-trimethyl-1,2-dihydroquinoline (**12**)

Compound **11** (2.34 g, 11.5 mmol) was dissolved in glacial AcOH (6.6 mL), then 48% aqueous HBr (7.9 mL) was added and the mixture was heated at reflux overnight. After cooling, $CHCl_3$ (3 mL) was added and the solution was carefully neutralized to about pH 5–6 with aqueous NaOH (30%). The organic phase was separated and the aqueous phase was extracted with $CHCl_3$ (3 × 20 mL). The combined organic fractions were washed with saturated aqueous $NaHCO_3$ (50 mL), dried, and evaporated. The crude product was purified by using column chromatography (eluent cyclohexane/EtOAc 4:1) to give a yellow solid: yield 1.12 g (51%). The obtained analytical data are identical to the published values.[6]

7-Hydroxy-2,2,4-trimethyl-N-(1H,1H,2H,2H-perfluorooctyl)-1,2-dihydroquinoline (**13**)

1*H*,1*H*,2*H*,2*H*-Perfluorooctyl iodide (463 µL, 1.88 mmol) was added dropwise to a solution of compound **12** (891 mg, 4.71 mmol) in DMF (2.5 mL) at 90 °C. After complete addition, the mixture was stirred at 140 °C for 3 h. After cooling, EtOAc (40 mL), aqueous NaOH (2 M, 20 mL) and brine (30 mL) were added. The organic layer was separated, washed with brine (20 mL) and the solvent was removed under reduced pressure. The crude product was purified by using column chromatography (eluent cyclohexane/EtOAc 10:1) to give a yellow oil: yield 302 mg (30%) Note: The product is not stabile and decomposes within hours.

R_f = 0.25 (cyclohexane/EtOAc 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (s, 6H), 1.94 (d, ^4J(H,H) = 1.1 Hz, 3H), 2.27–2.49 (m, 2H), 3.54–3.60 (m, 2H), 4.74 (bs, 1H, OH), 5.12 (d, ^4J(H,H) = 1.1 Hz, 1H), 5.98 (d, ^4J(H,H) = 2.2 Hz, 1H), 6.12 (dd, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 2.2 Hz, 1H), 6.94 (d, ^3J(H,H) = 8.1 Hz, 1H); ^{13}C NMR was not obtained due to decomposition of the product; ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –126.1 (m, CF_2), –123.3 (m, CF_2), –122.8 (m, CF_2), –121.8 (m, CF_2), –114.5 (m, CF_2), –80.7 (t, ^3J(F,F) = 9.8 Hz, CF_3); EI MS: *m/z* (%): 535 (44) $[M]^+$, 520 (100) $[M–CH_3]^+$, 501 (12) $[M–CH_3F]^+$, 420 (2) $[M–C_3H_3F_4]^+$, 188 (22) $[M–C_8H_4F_{13}]^+$, 173 (23) $[M–C_9H_7F_{13}]^+$; HRMS: *m/z* calcd for $C_{20}H_{18}F_{13}NO$: 535.1181; found: 535.1183 $[M]^+$.

General method 5 for the solid phase synthesis of rhodamine F labeled peptoids 14a–d, 15 and 16

Fmoc-protected Rink amide resin (0.67 mmol/g, 50 mg) was swollen in DMF (1 mL) for 1 h. Multiple washing steps using DMF were performed between each step as described below. Fmoc deprotection was completed by adding piperidine (20% in DMF, 1 mL) (3 × 5 min). Following, the monomer 2-((((9*H*-fluoren-9-yl)methoxy)carbonyl)(6-((*tert*-butoxycarbonyl)amino)-hexyl)amino)acetic acid was coupled to the resin. To achieve this, the monomer (50.2 mg, 101 µmol), diisopropylcarbodiimide (15.7 µL, 101 µmol) and 1-hydroxybenzotriazole hydrate (15.5 mg, 101 µmol) were dissolved in DMF *biograde* (1 mL) and added to the resin. The

reaction vessel was subjected to microwave irradiation to keep the constant temperature at 60 °C (max. 20 W) for 30 min while being stirred. The reaction solution was filtered and the resin was treated a second time with freshly prepared reaction solution under the same conditions as described above (double coupling). Afterwards, the resin was thoroughly washed with DMF (5 × 3 mL). This process of Fmoc deprotection and monomer coupling was repeated six times in total, so that a resin bound hexamer was obtained. Then another Fmoc deprotection step was carried out under the previously described conditions. Subsequently, rhodamine F **1b**, **1d–f**, **2** or **3** (0.5 equiv.), diisopropylcarbodiimide (15.7 µL, 101 µmol) and 1-hydroxybenzotriazole hydrate (15.5 mg, 101 µmol) dissolved in DMF *biograde* (1 mL) were added to the washed resin. The reaction vessel was shaken for 48 h at RT. Afterwards, the resin was thoroughly washed with DMF until the washing solution remained colorless. For the final cleavage the resin was incubated at RT overnight with TFA (95% in CH_2Cl_2, 1.5 mL). The solution was filtered and the resin was washed one more time with TFA (95% in CH_2Cl_2, 1.5 mL), followed by MeOH until the washing solution remained colorless. The crude product was lyophilized and purified using a Fluoro*Flash* column (2 g, 8 cm^3 tube).[7] To achieve this, a new cartridge was loaded with DMF (1 mL). Afterwards, MeOH/H_2O (60:40, 4 mL) was passed to condition the cartridge. The preconditioning solution was discarded. The crude product was dissolved in H_2O (250 µL) and loaded onto the cartridge. The cartridge was washed with MeOH/H_2O (60:40, 10 mL) to remove non-fluorous compounds. Then it was washed with hydrochloric acid in MeOH (0.1 M, 10 mL) to obtain the product. The purified product was isolated after removing the solvent under reduced pressure. If necessary the prepurified peptoid was purified again by semi-preparative HPLC.

2-((((9*H*-Fluoren-9-yl)methoxy)carbonyl)(6-((*tert*-butoxycarbonyl)-amino)hexyl)amino)acetic acid

The preparation and properties of the peptoid monomer have been reported in reference 8.

Compound **14a**

After F-SPE and HPLC purification the title compound was obtained as red solid from compound **1b** (18.3 mg, 16.8 µmol) according to general method 5: yield 0.42 mg (HPLC purity: 98%).

MALDI-TOF MS: *m/z*: 1987 $[M]^+$.

Compound **14b**

After F-SPE and HPLC purification the title compound was obtained as red solid from compound **1d** (17.8 mg, 16.8 µmol) according to general method 5: yield 1.69 mg (HPLC purity: 95%).

MALDI-TOF MS: *m/z*: 1959 $[M]^+$.

Compound **14c**

After F-SPE purification the title compound was obtained as dark red solid from compound **1e** (18.7 mg, 16.8 µmol) according to general method 5: yield 4.09 mg (HPLC purity: 96%).

MALDI-TOF MS: *m/z*: 2015 $[M]^+$.

Compound **14d**

After F-SPE and HPLC purification the title compound was obtained as red solid from compound **1f** (21.6 mg, 16.8 µmol) according to general method 5: yield 1.28 mg (HPLC purity: 96%).

MALDI-TOF MS: *m/z*: 2187 $[M]^+$.

Compound **15**

After F-SPE purification the title compound was obtained as dark red solid from compound **2** (19.1 mg, 16.8 µmol) according to general method 5: yield 5.33 mg (HPLC purity: 96%).

MALDI-TOF MS: *m/z*: 2040 $[M]^+$.

Compound **16**

After F-SPE and HPLC purification the title compound was obtained as violet solid from compound **3** (20.5 mg, 16.8 µmol) according to general method 5: yield 0.65 mg (HPLC purity: 93%).

MALDI-TOF MS: *m/z*: 2119 $[M]^+$.

Biological Methods

Cell culture techniques for mammalian cells

All procedures with mammalian cells were carried out under sterile conditions. 1×10^4 HeLa (human cervix carcinoma) cells were plated into each well of an 8-well µ-slide from IBIDI (Ibitreat), Germany, and cultured in 200 µL of Dulbecco's modified Eagle's medium, high glucose, (DMEM, Sigma Taufkirchen) supplemented with 10% fetal calf serum (FCS, PAA), and 1 u/mL Penicillin/Streptomycin at 37 °C, 5% CO_2.

Treatment of HeLa cells with the rhodamine F dye coupled peptoids

The peptoids were dissolved in bidistilled water to yield a 2 mM stock solution and were further diluted with 10% DMEM to yield the respective incubation media. The cells cultured as described above were incubated with the different peptoids at final concentrations of 0.1, 1, 5, 1, 20, 50 or 100 µM, respectively. Cellular uptake of the peptoids was measured by live-cell imaging after 24 and 48 h as fixation would alter the intracellular distribution as described for other polycationic species.

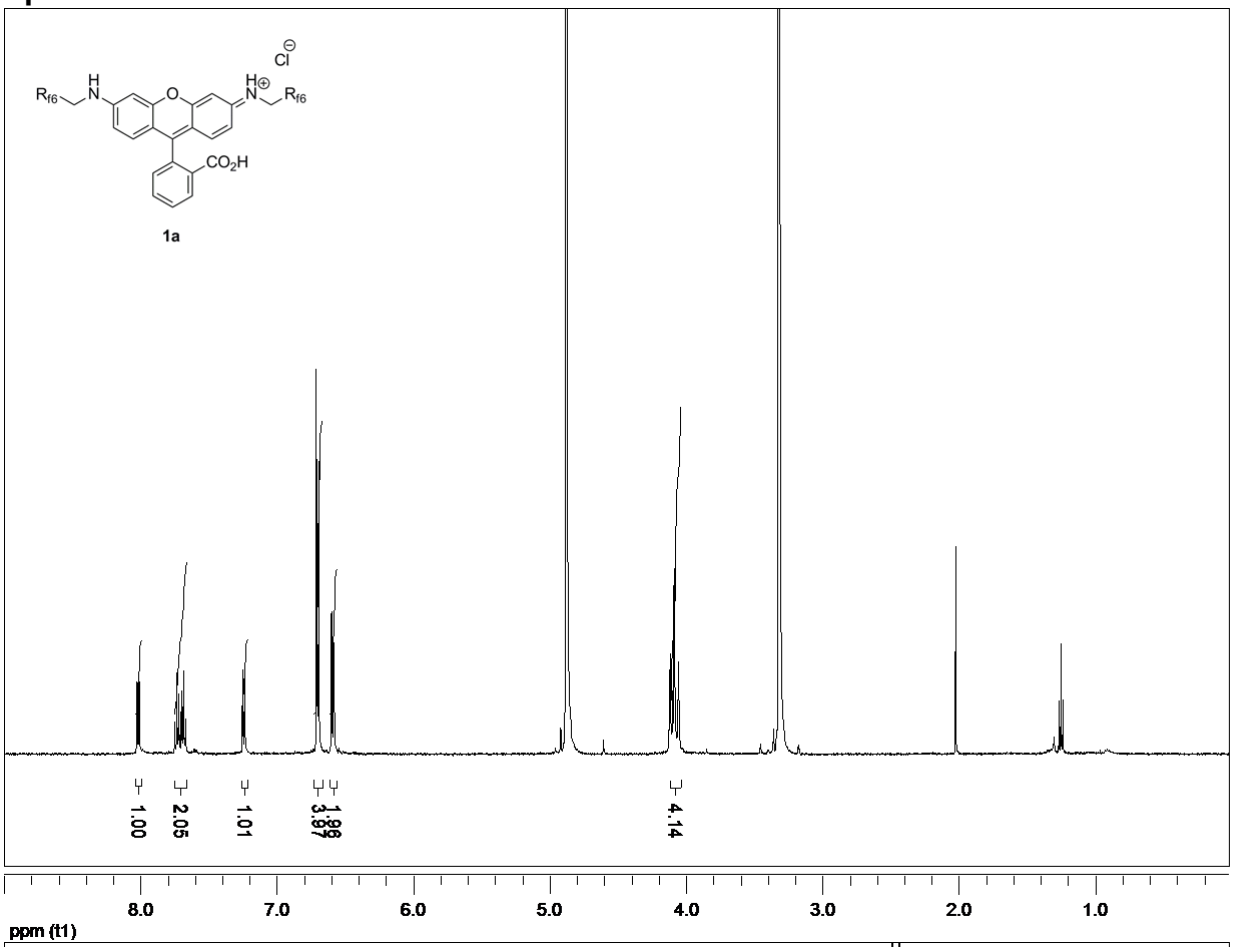
Subcellular Localization

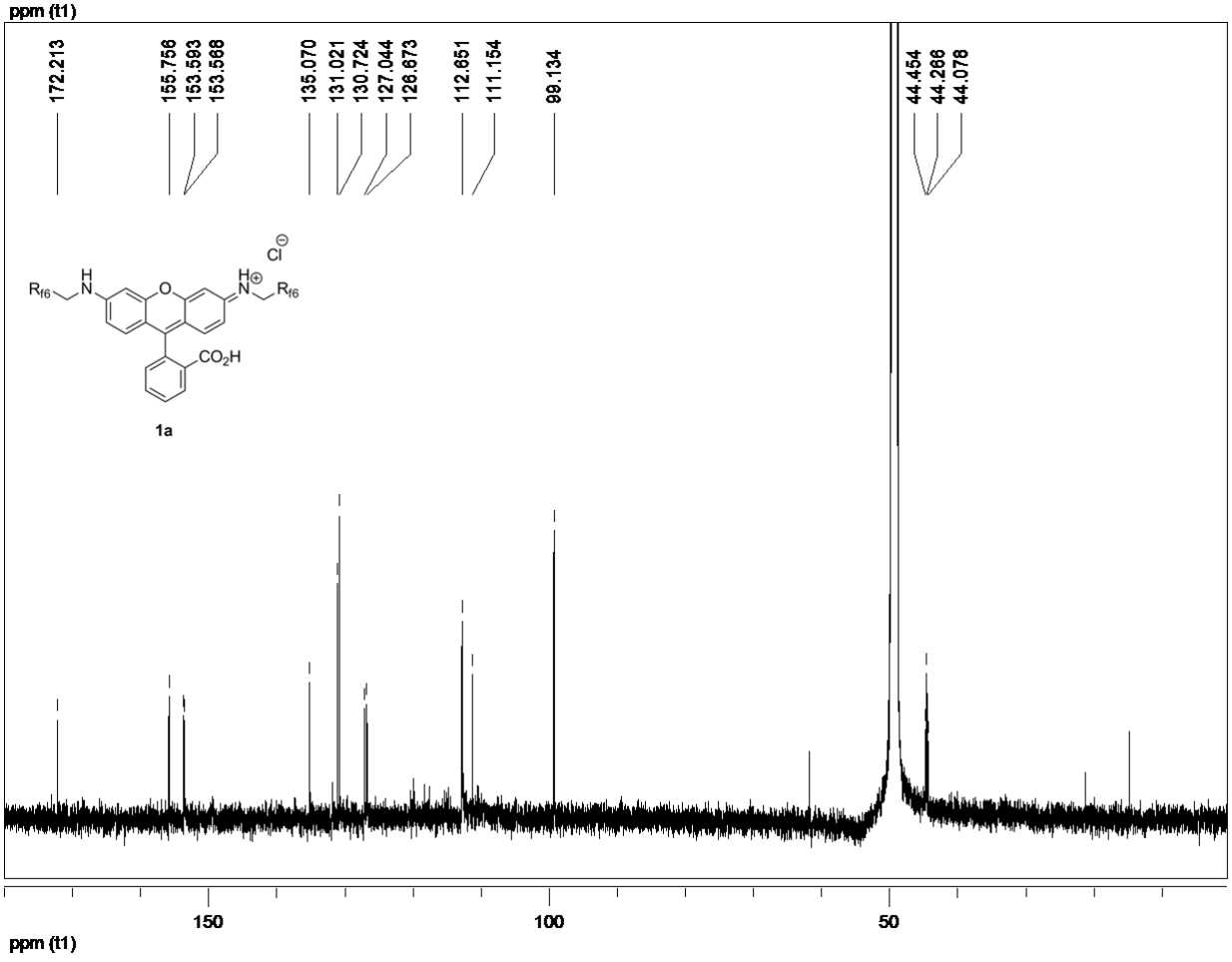
For the intracellular localization of the peptoids, the cells were co-incubated with fluorescent probes specific for different organelles (Molecular Probes, Karlsruhe). For mitochondria labeling the cells were treated with 100 nM MitoTracker® Green FM for 15 min, according to the manufacturer's manual, and washed three times with PBS. For the staining of the nuclei, the cells were eventually treated with Hoechst 33342 dye (2 µg/mL) after washing of the MitoTracker treated cells with PBS according to the manufacturer´s instructions. The cells were covered with DMEM and subjected to live confocal microscopy at 37 °C and 5% CO_2 atmosphere.

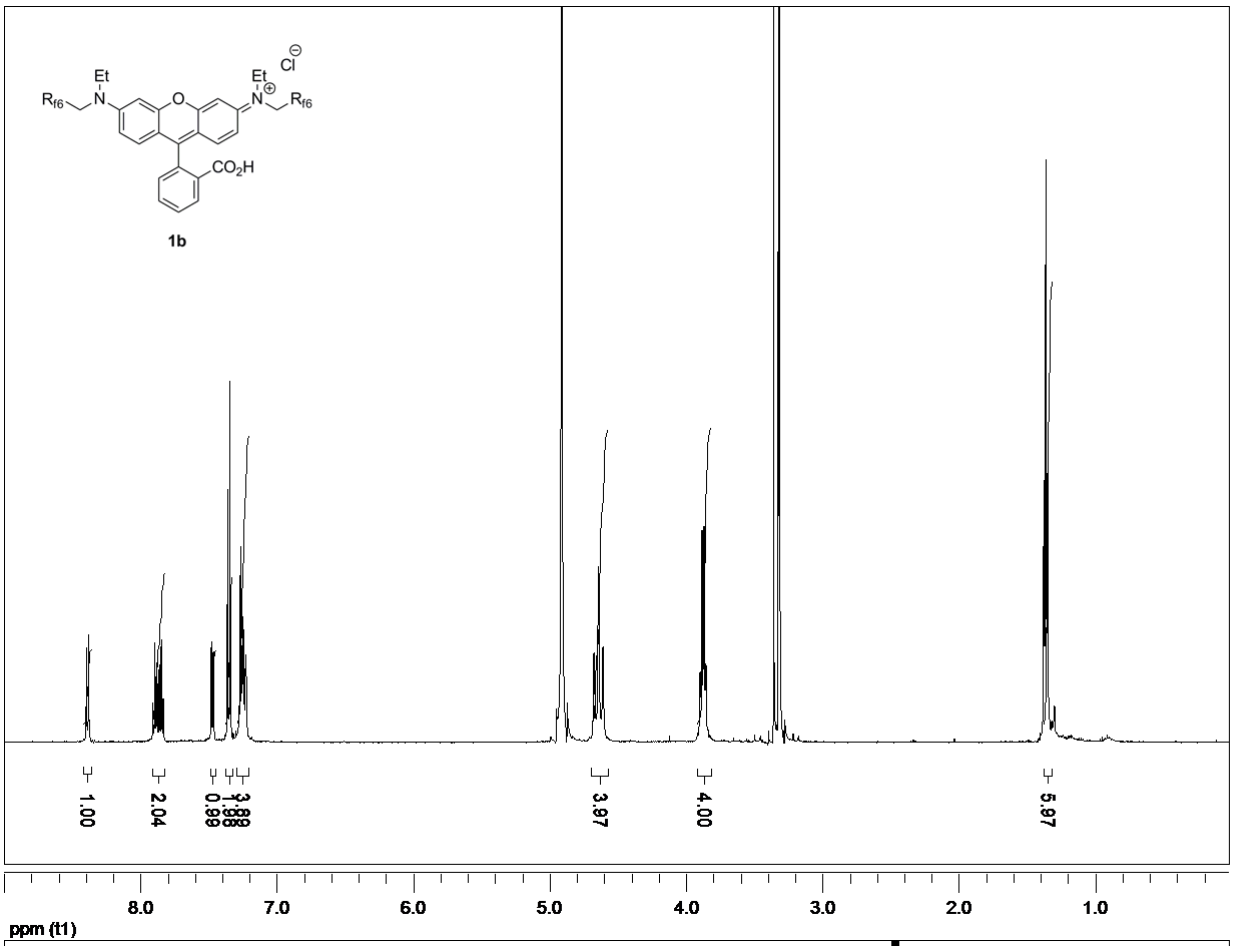
Live imaging by confocal microscopy

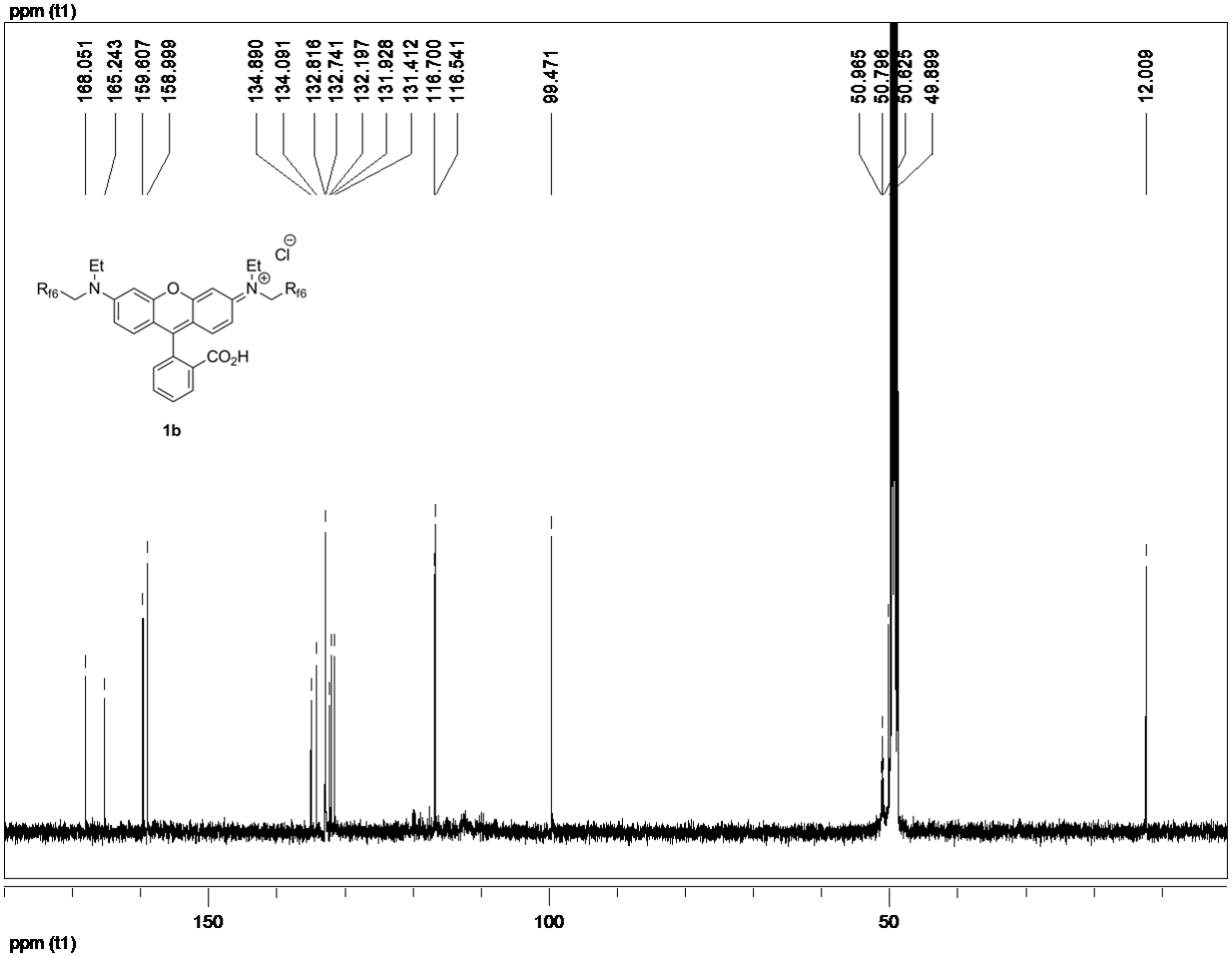
Simultaneous visualization of the colocalization of the peptoids and mitochondria and nuclei was achieved by confocal microscopy using Leica TCS-SP5 II, equipped with a DMI6000 microscope. MitoTracker® Green FM was excited using the 488 nm line of an argon ion laser, the nuclei were excited with a UV laser at 364 nm, the peptoids were excited at 514 nm using an argon laser (**14a**), 561 nm using a DPSS laser(**15**) and 594 nm using a HeNe laser (**16**). The objective was a HCX PL APO CS 63.0x1.2 Water UV. The exposure was set to minimize oversaturated pixels in the final images. Fluorescence emission was measured at 400–461 nm (for Hoechst 33342), 503–538 nm (for MitoTracker® Green FM), 522–600 nm (for **14a**), 567–646 nm (for **15**), and 600–650 nm (for **16**) using a simultaneous detection of the MitoTracker® Green FM and the respective peptoid. Image acquisition was conducted at a lateral resolution of 1024 × 1024 pixels and 8 bit depth using LAS-AF 2.0.2.4647 acquisition software.

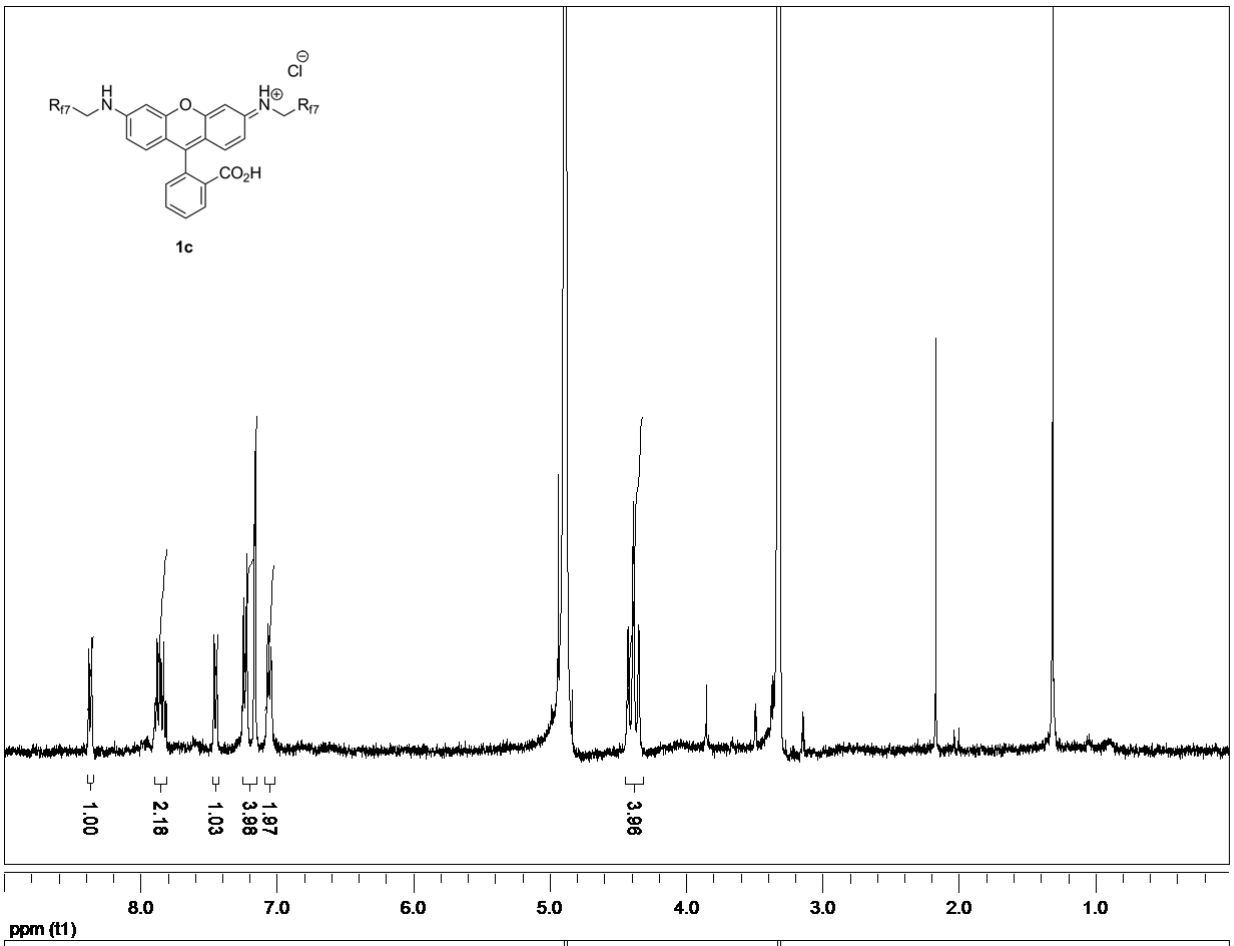
Spectral Data

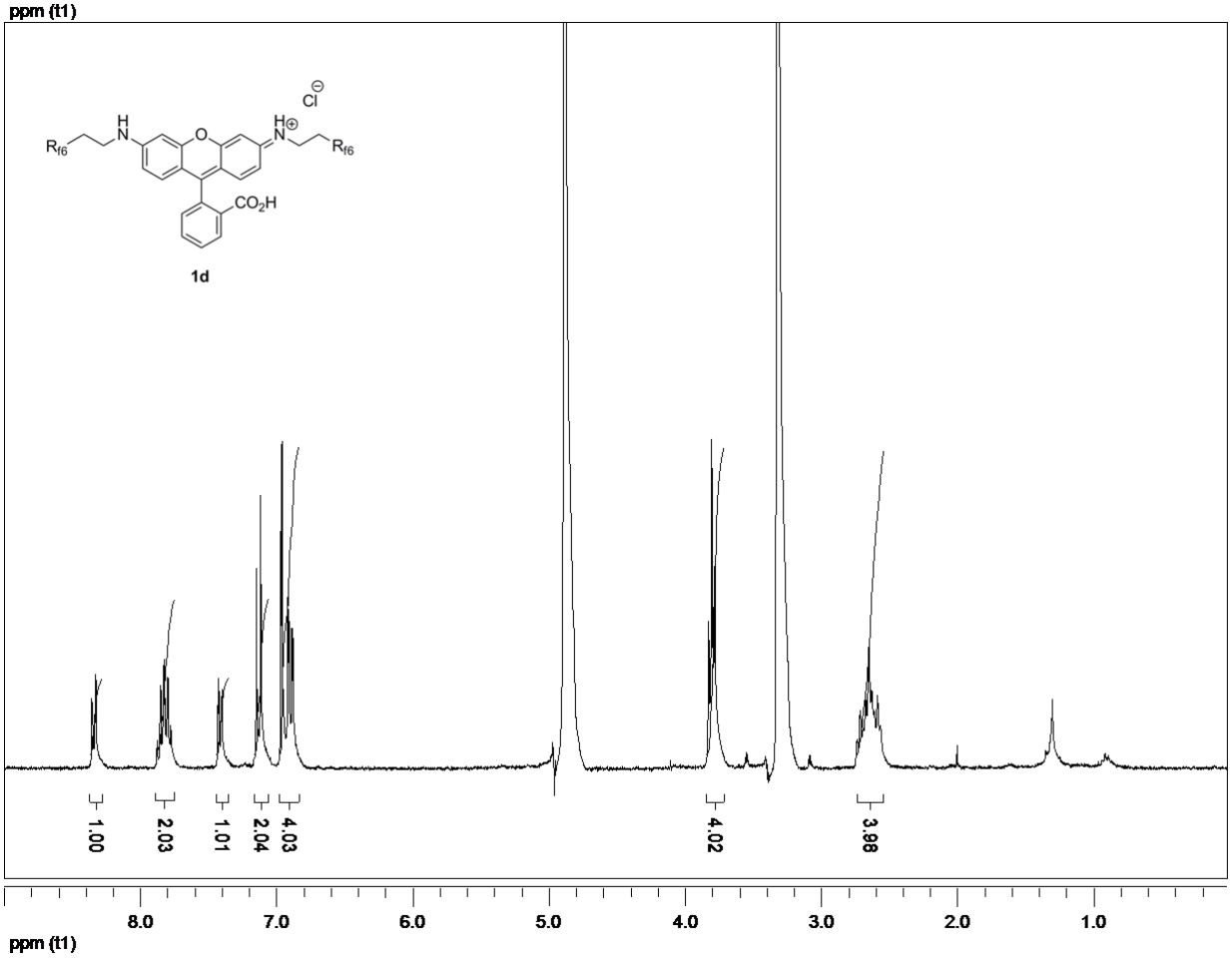


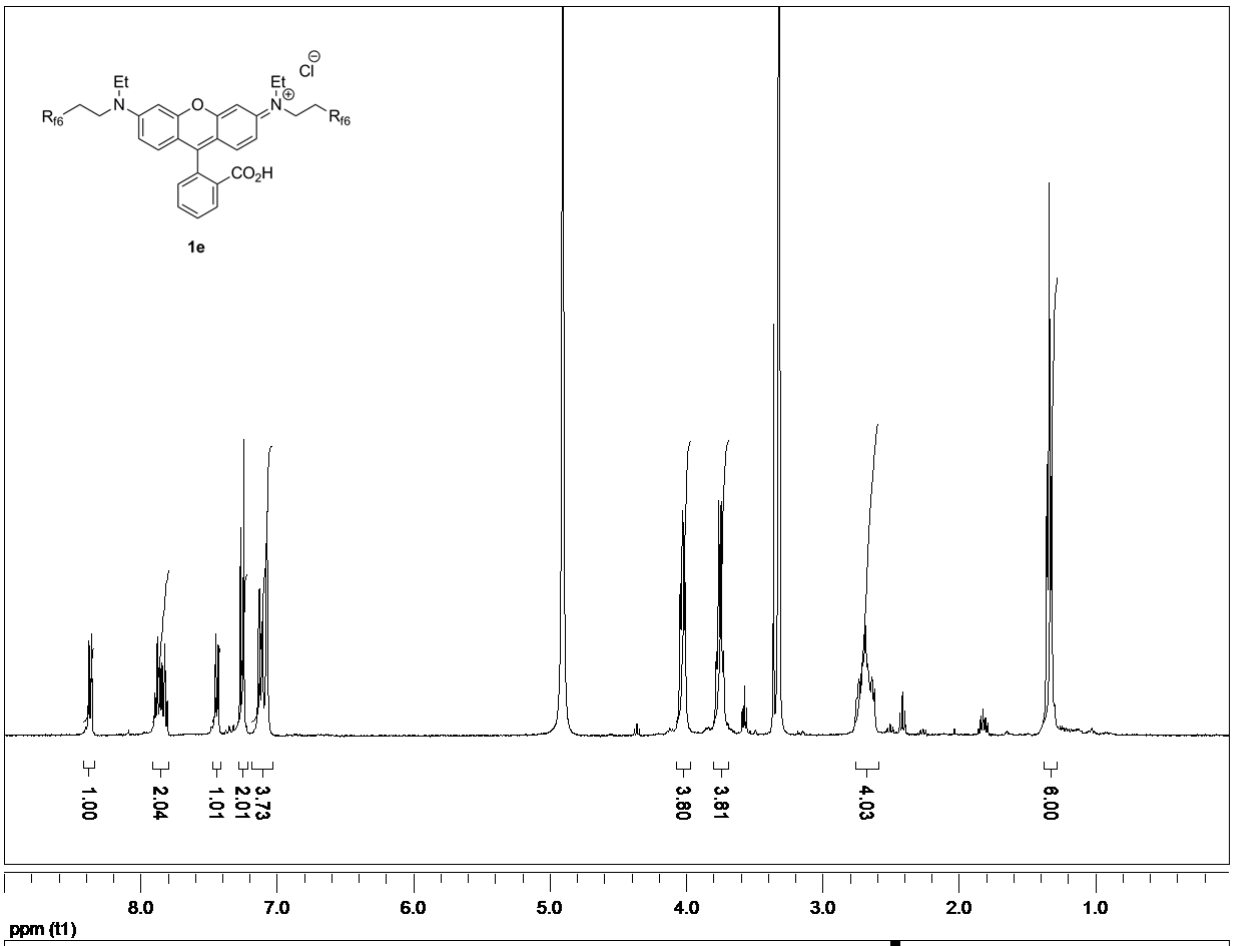


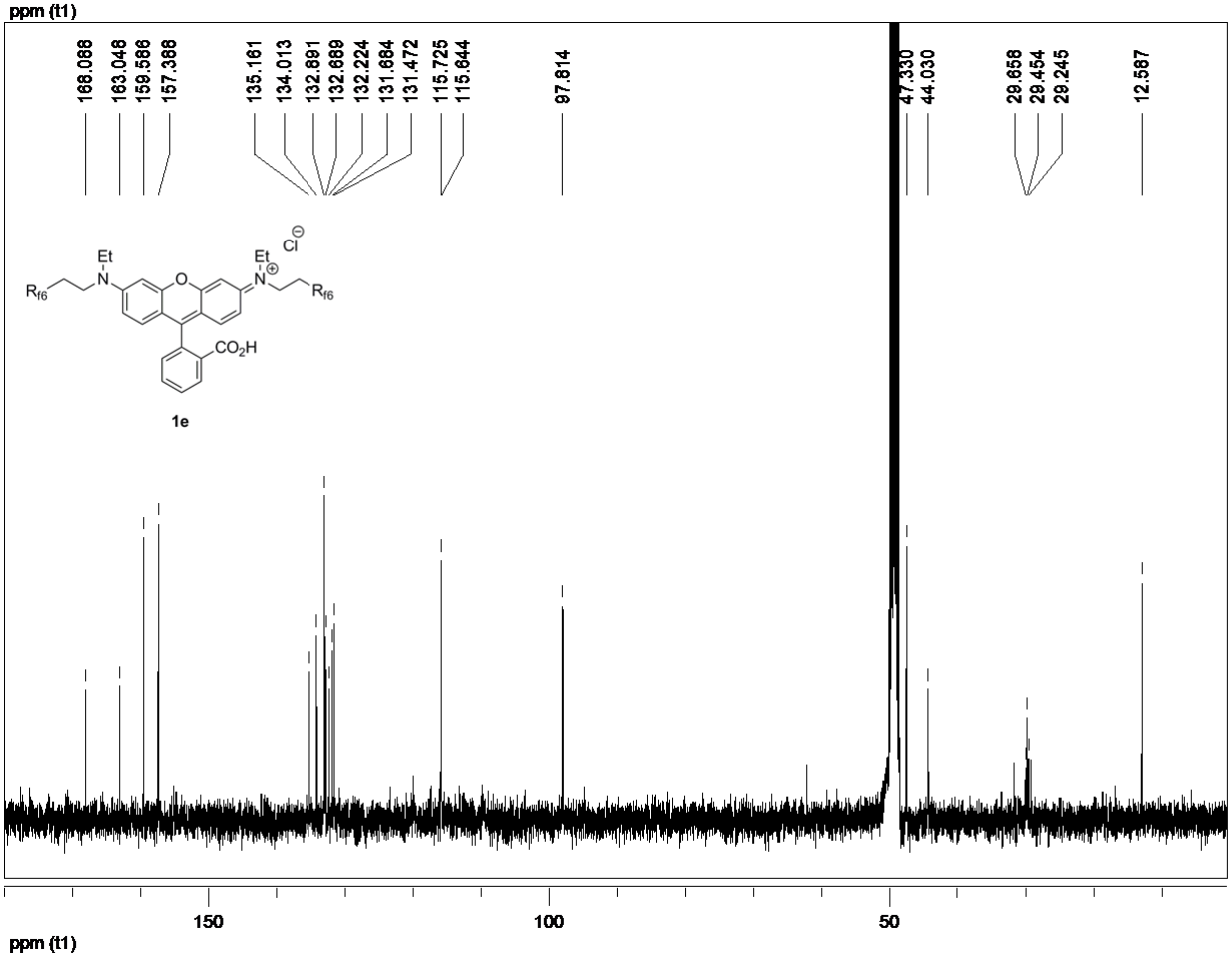


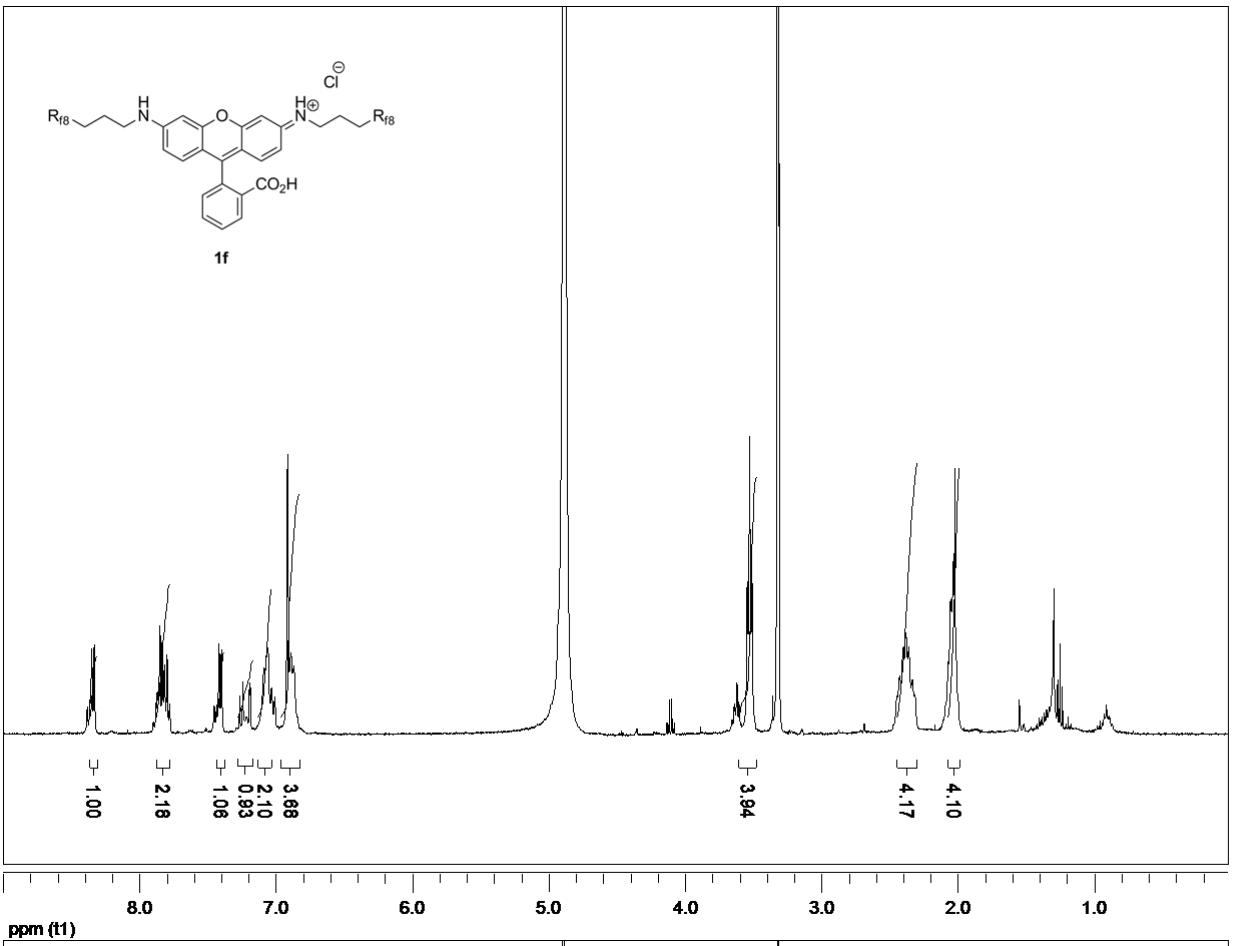












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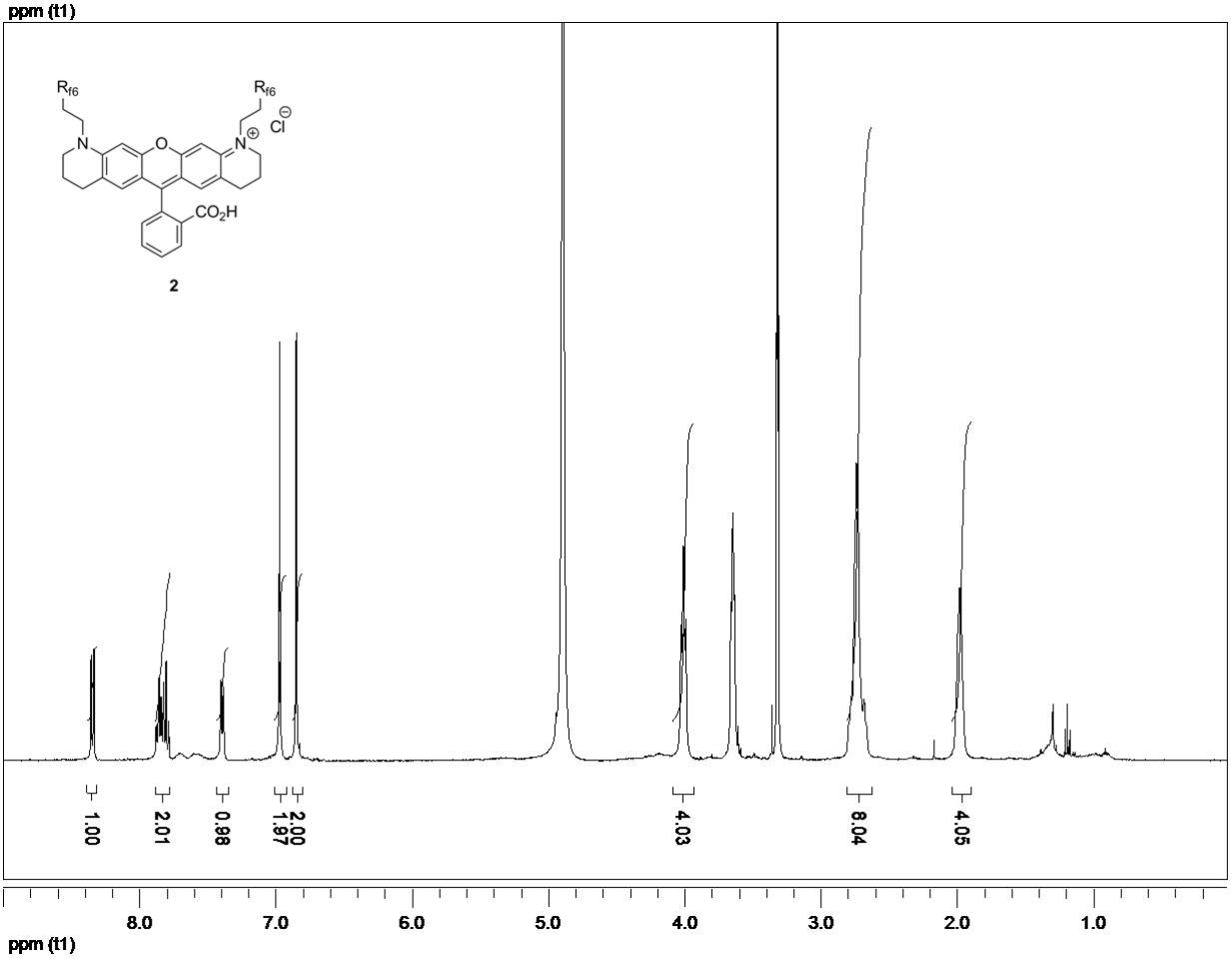

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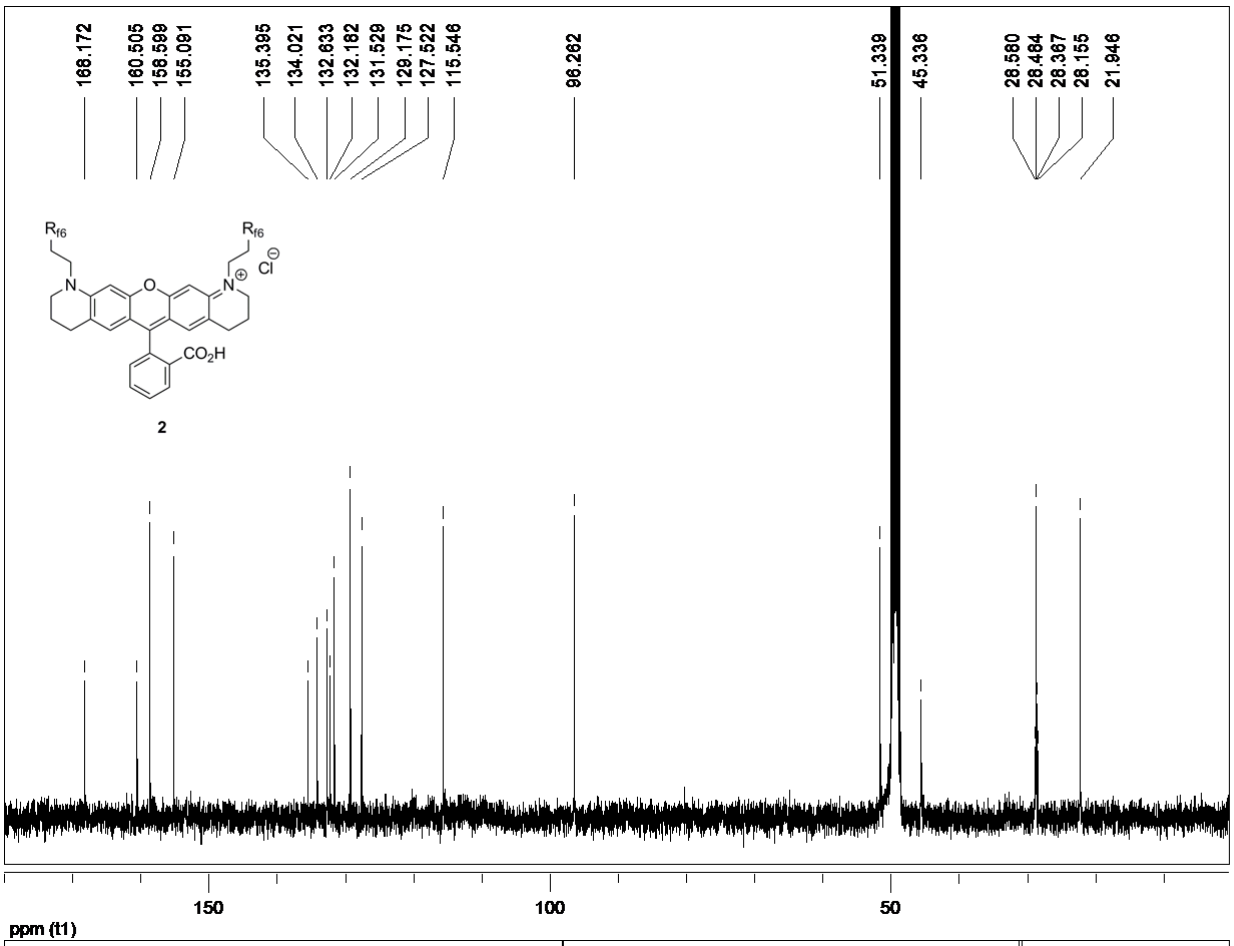
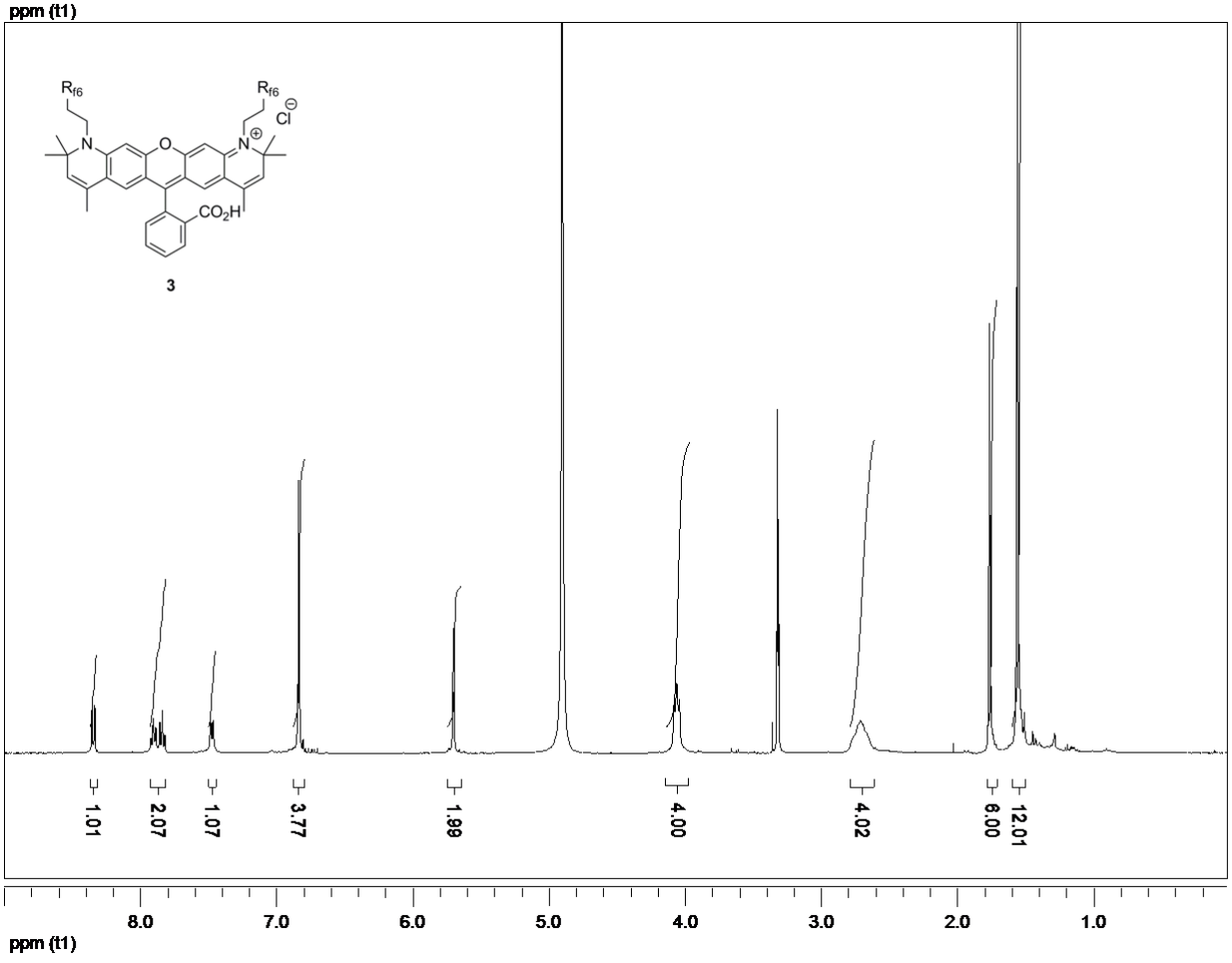
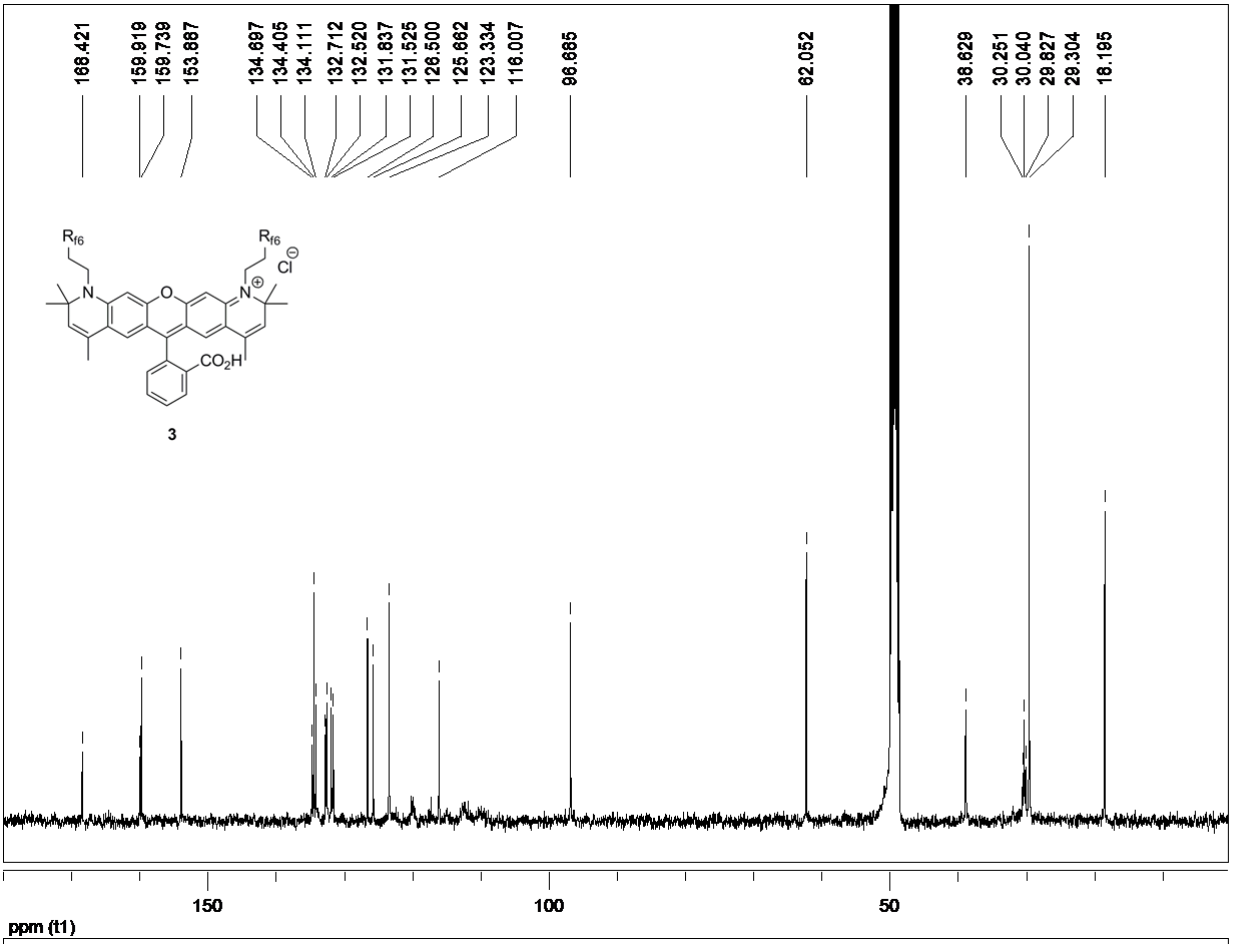
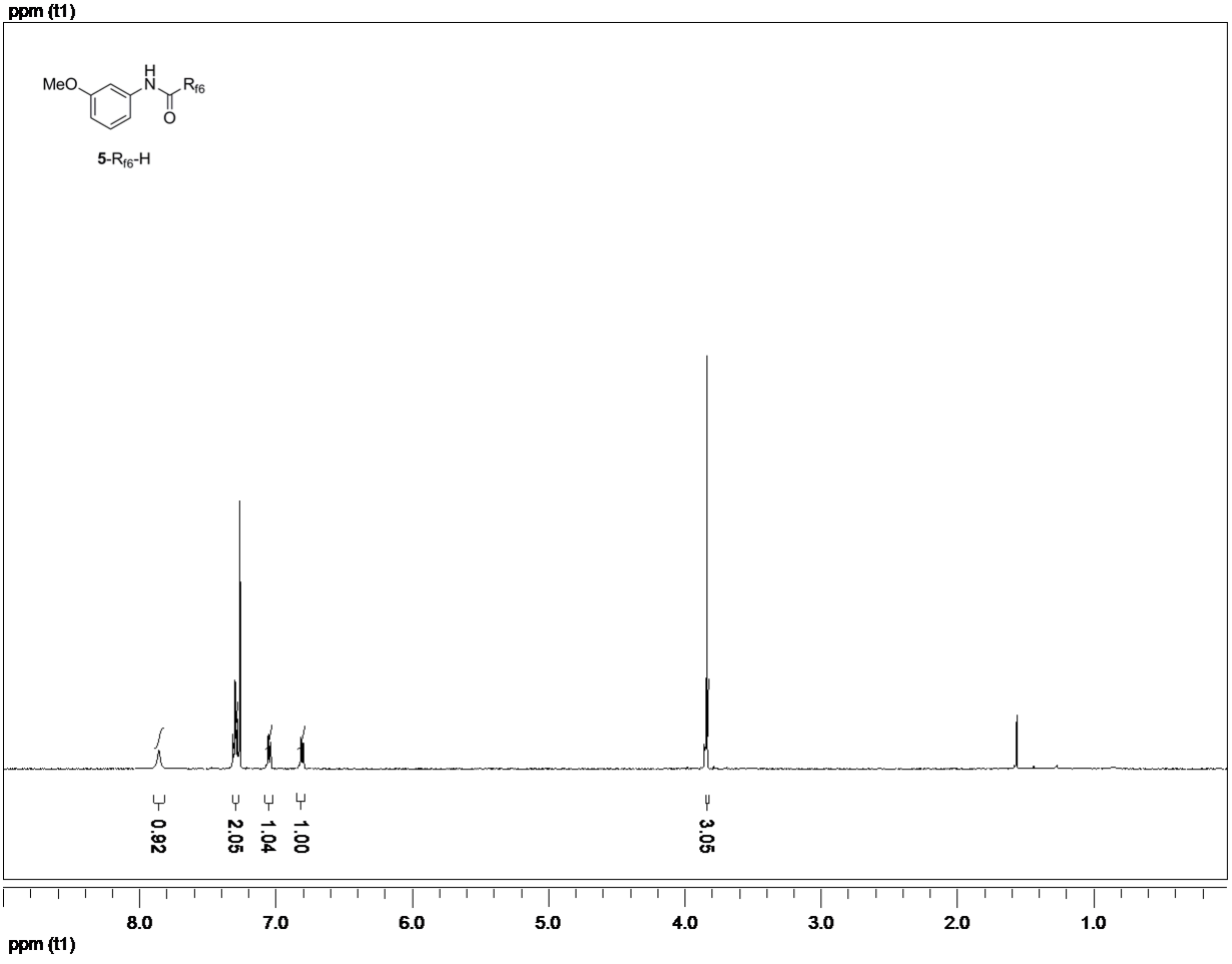
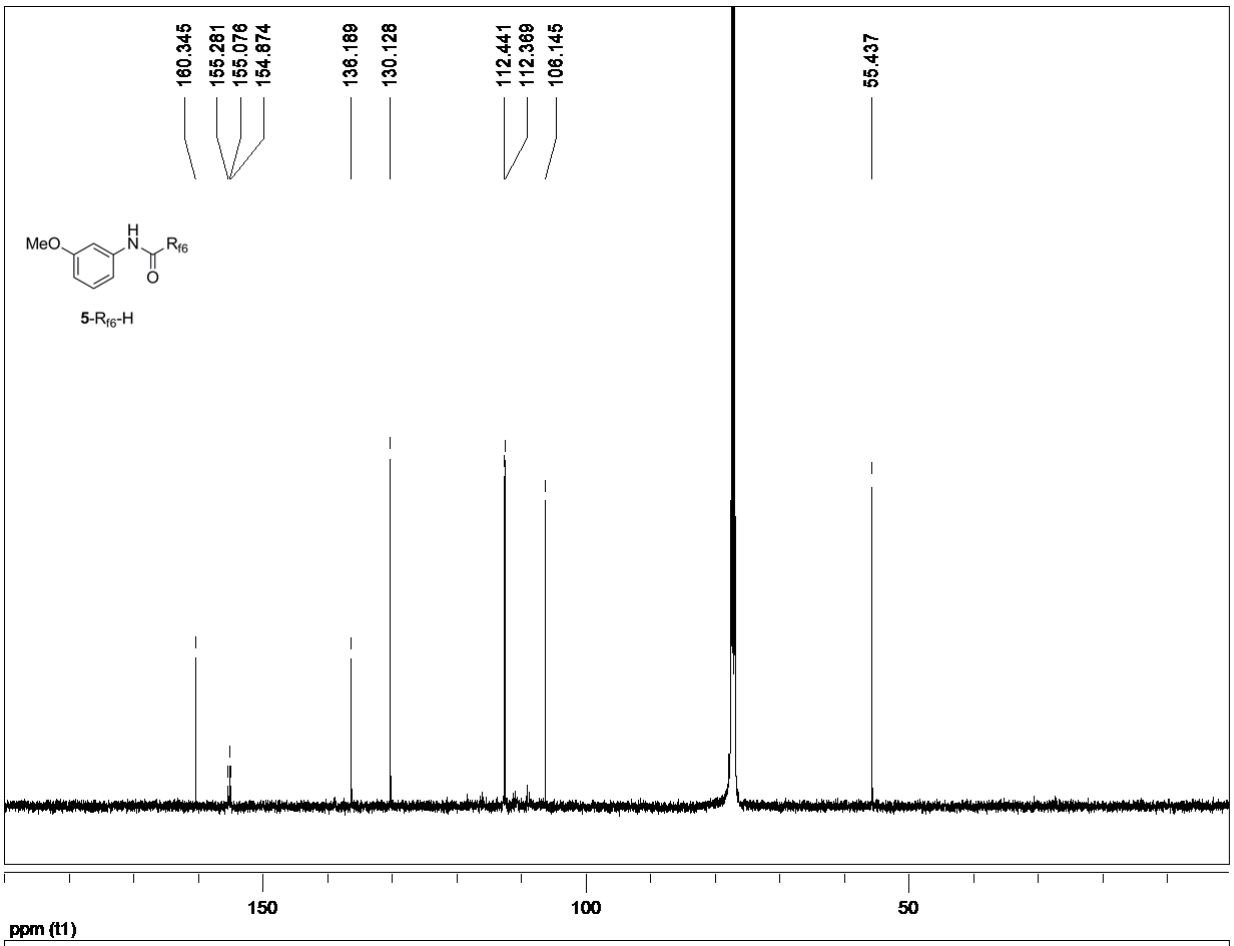
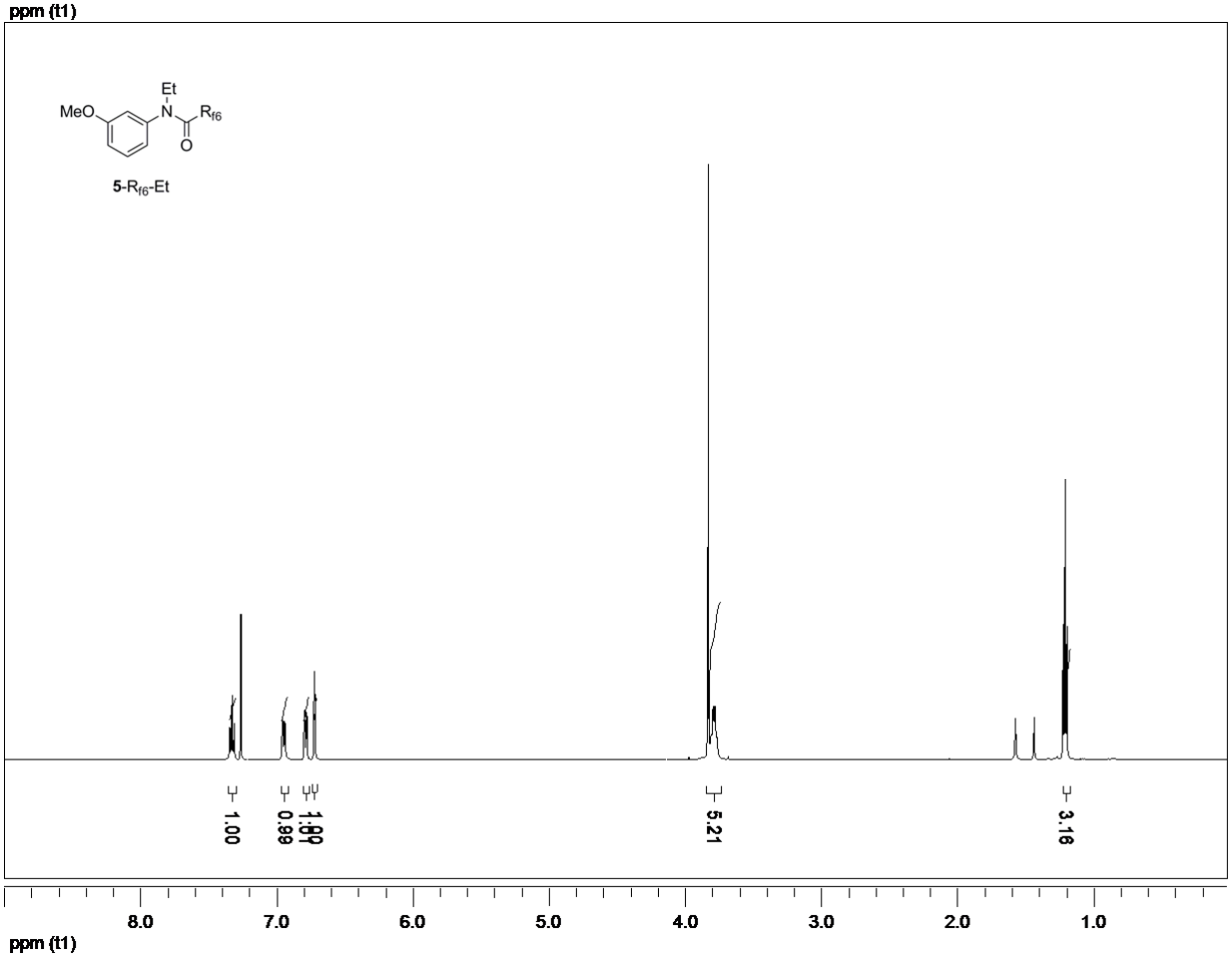


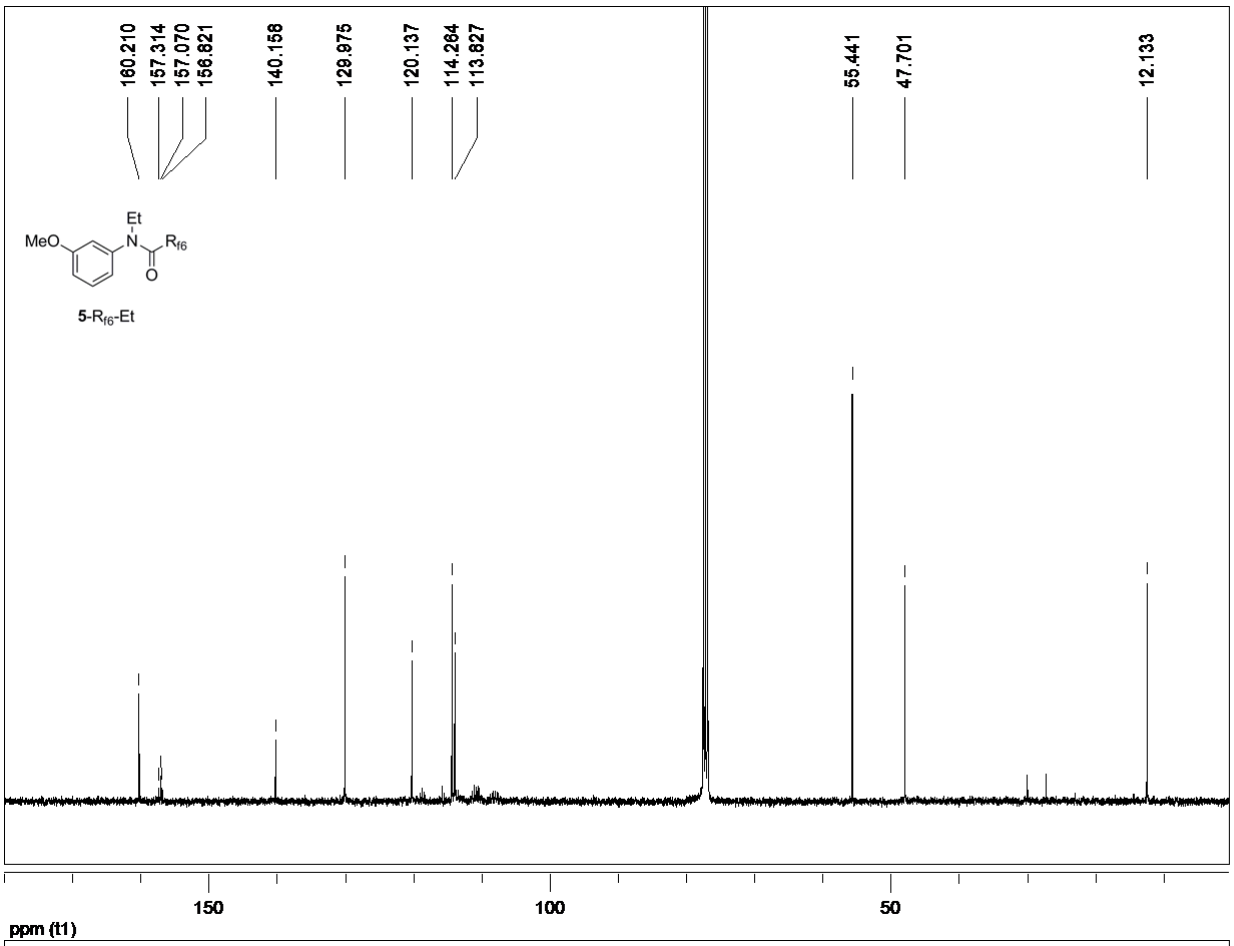


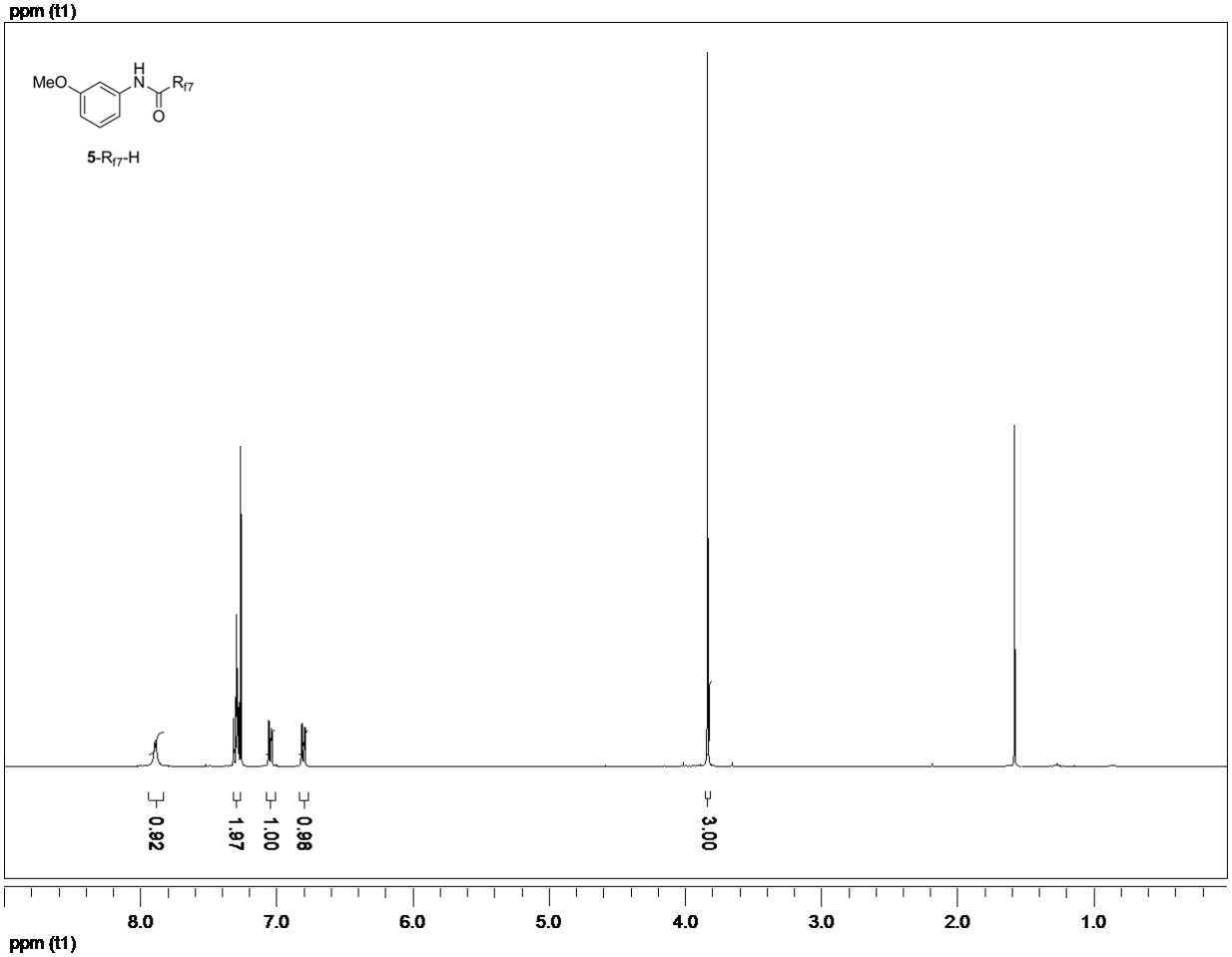


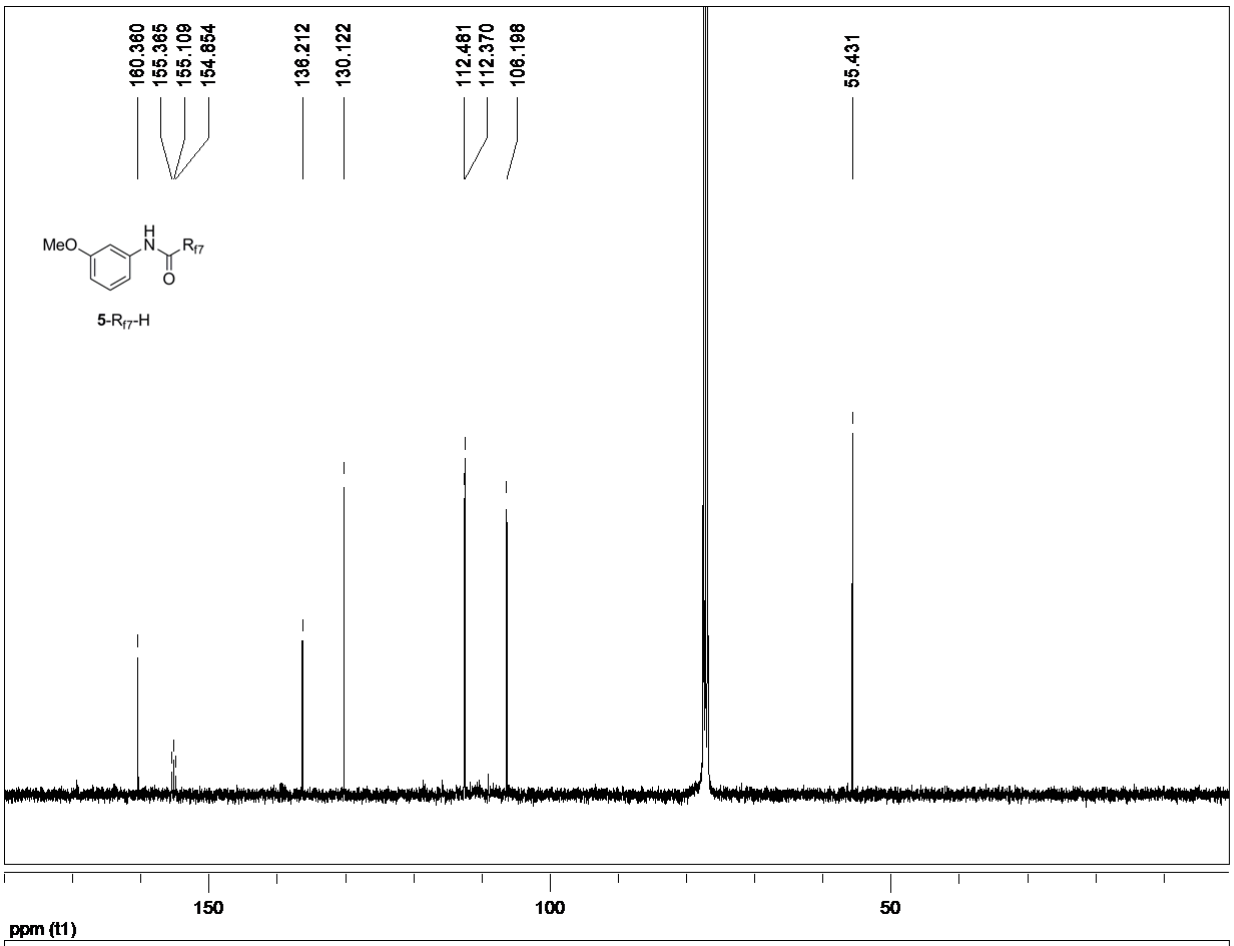


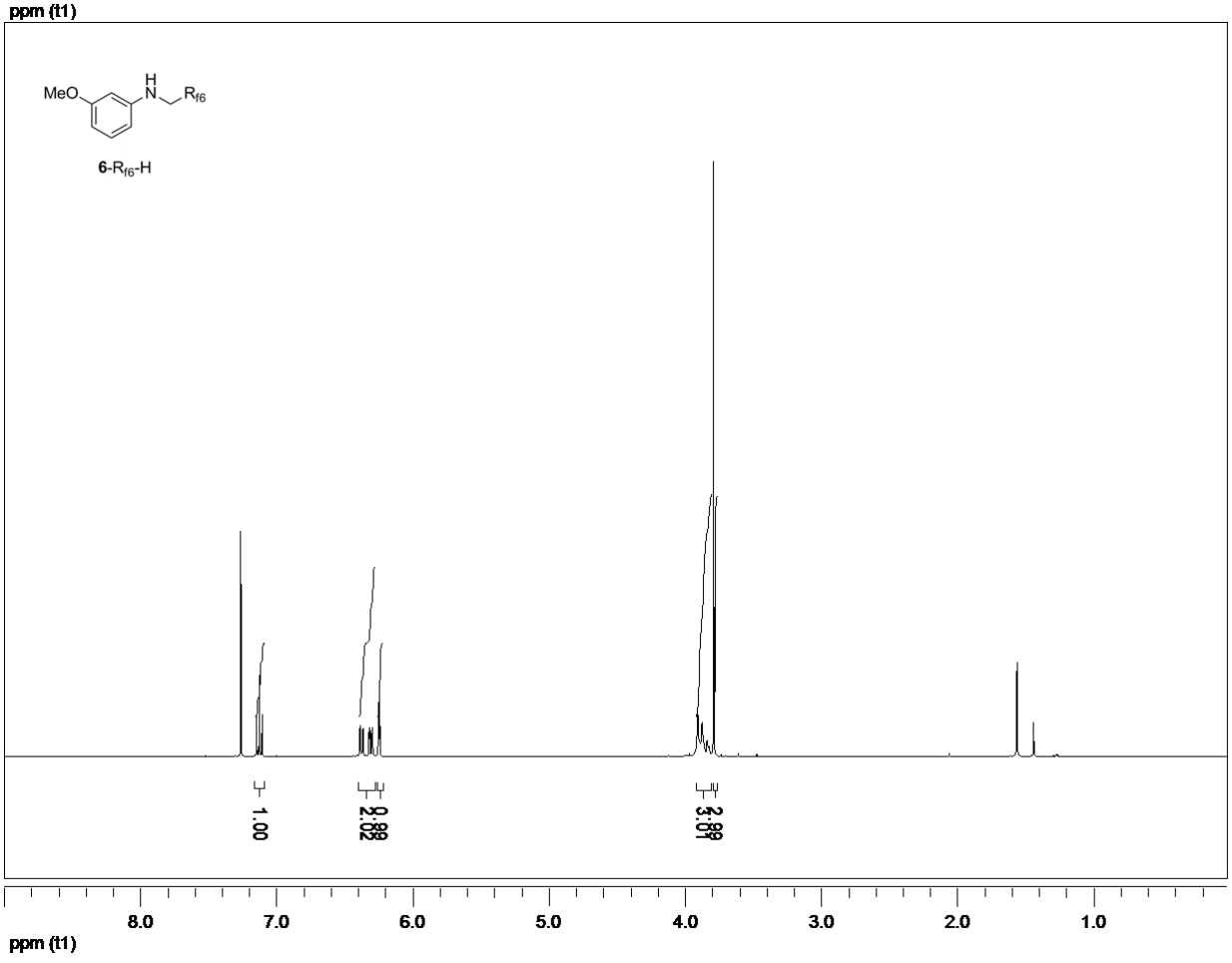


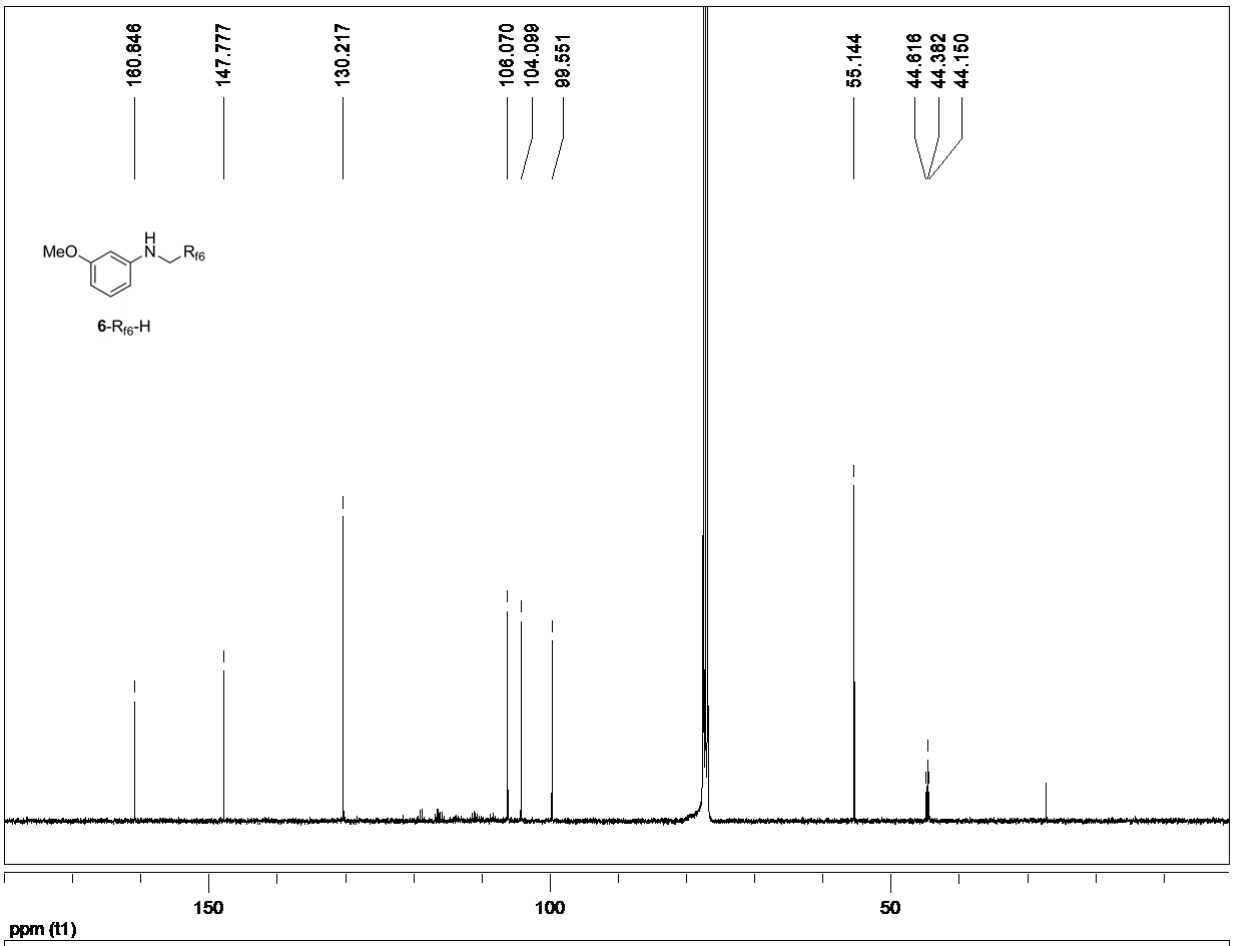


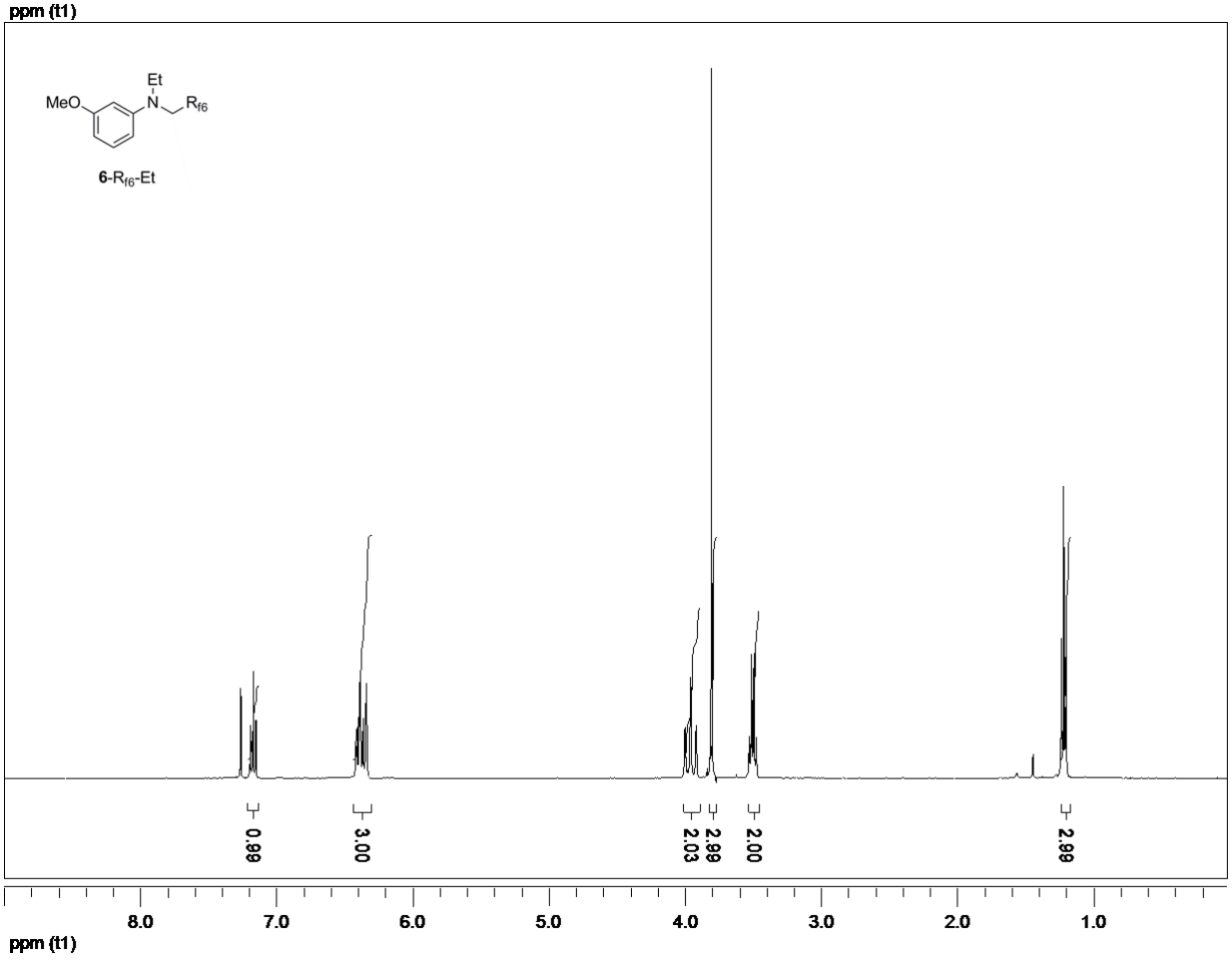


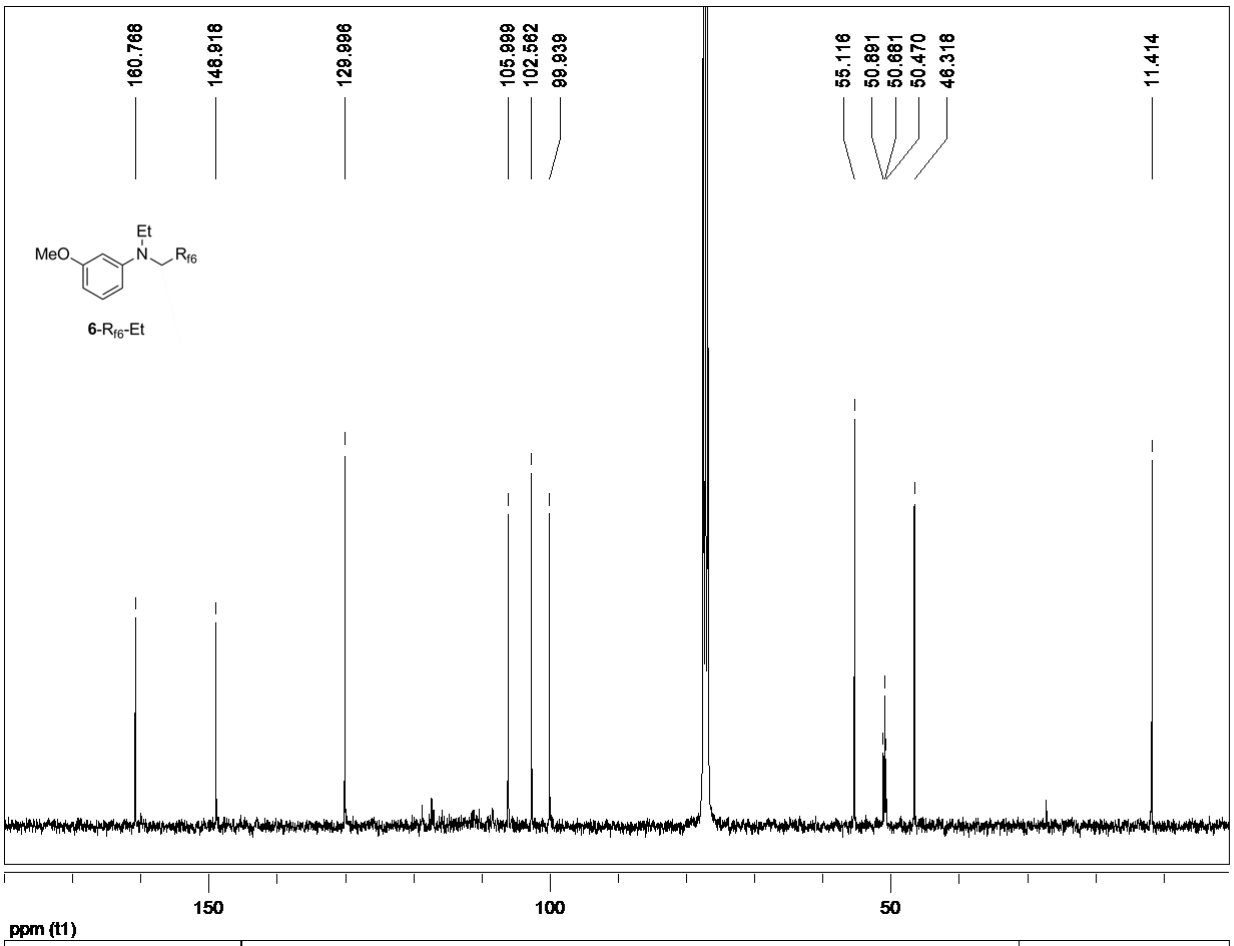


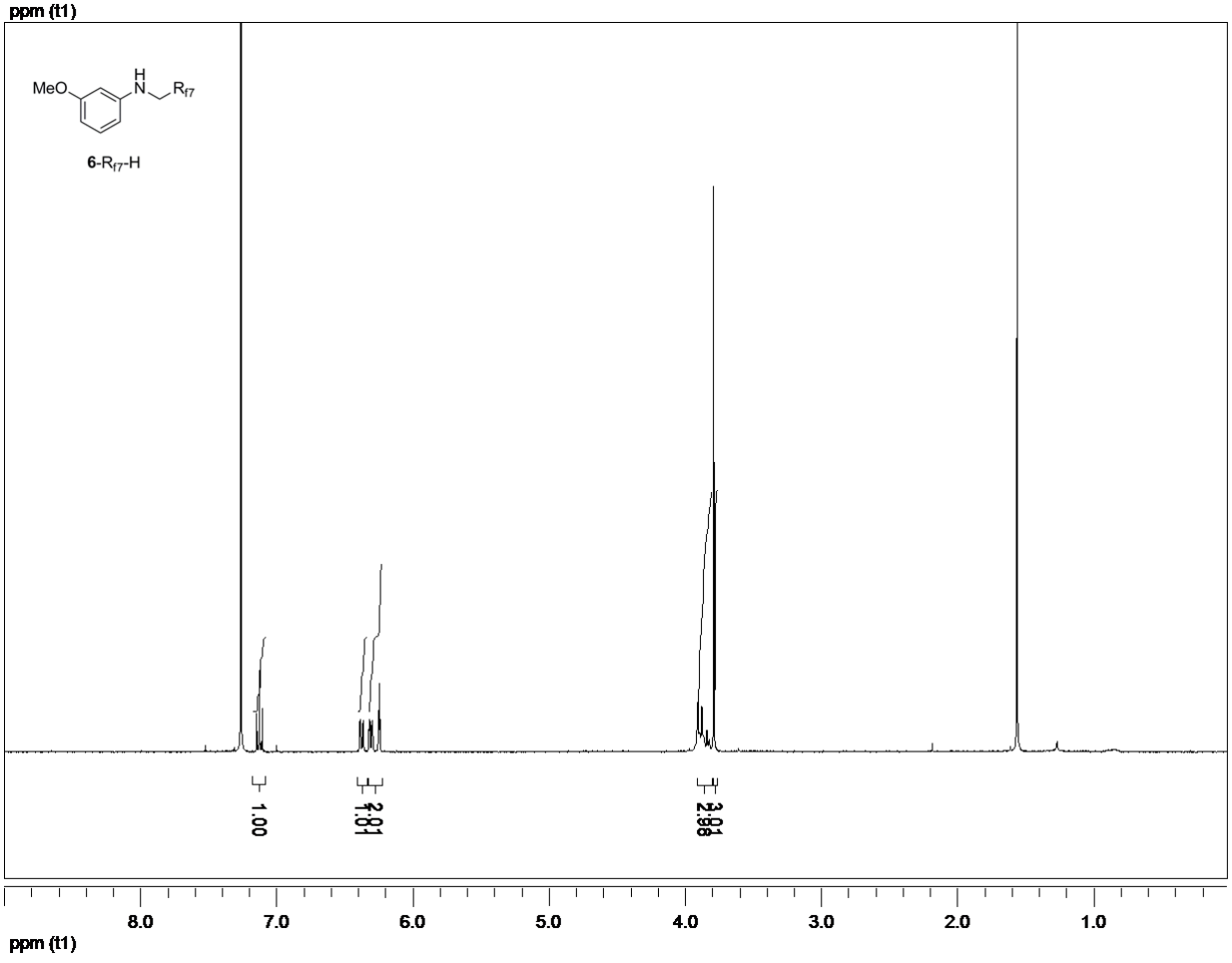


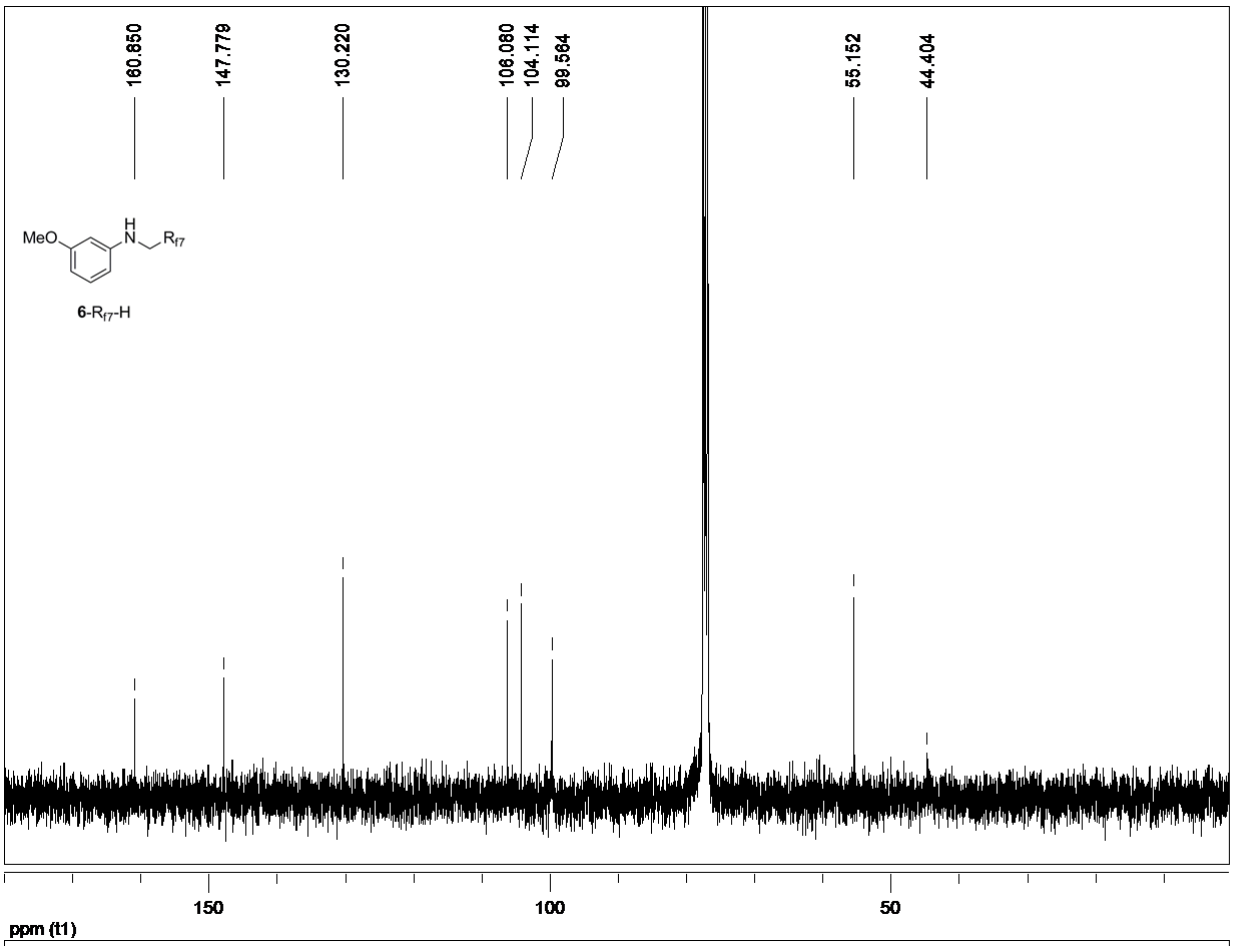


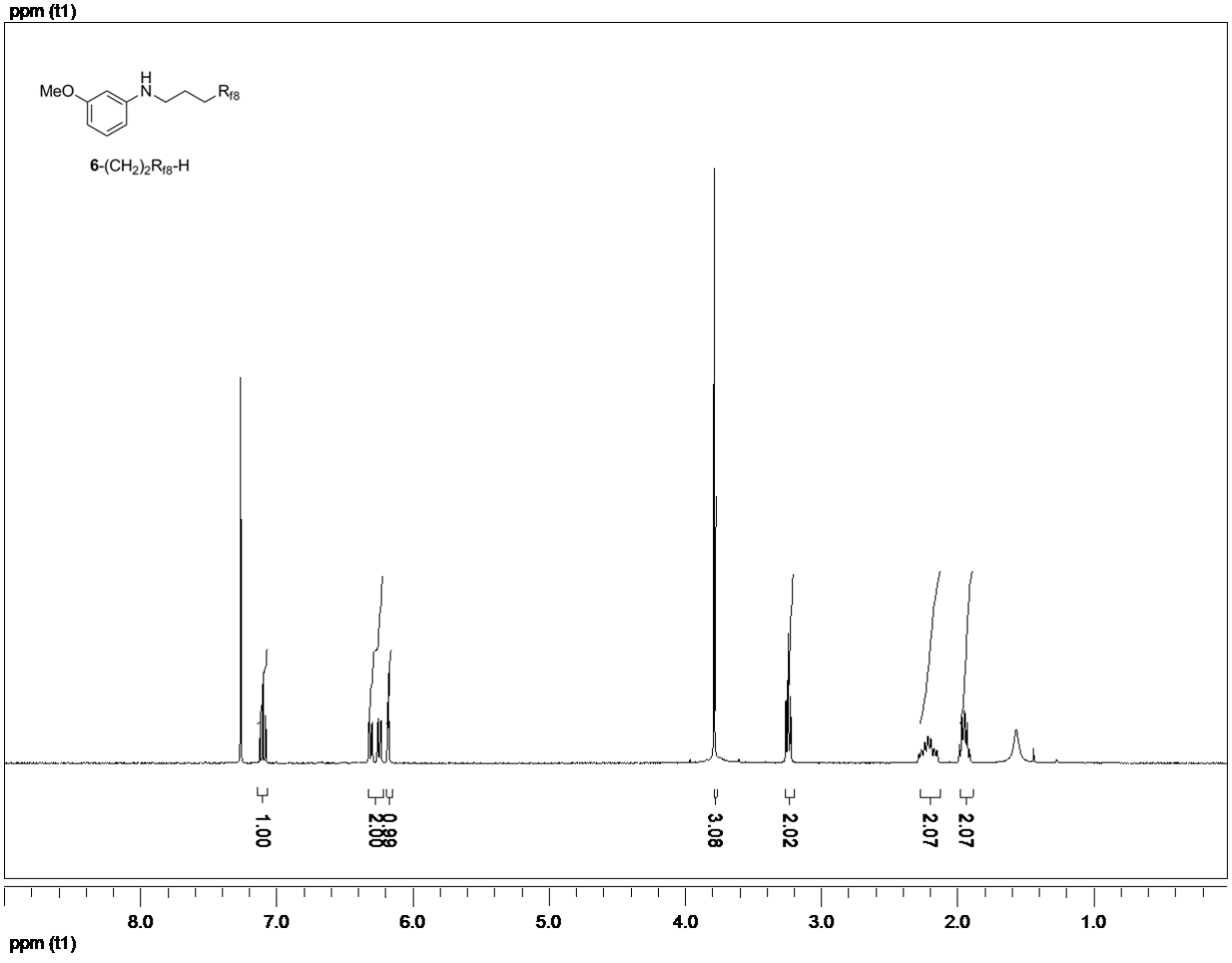


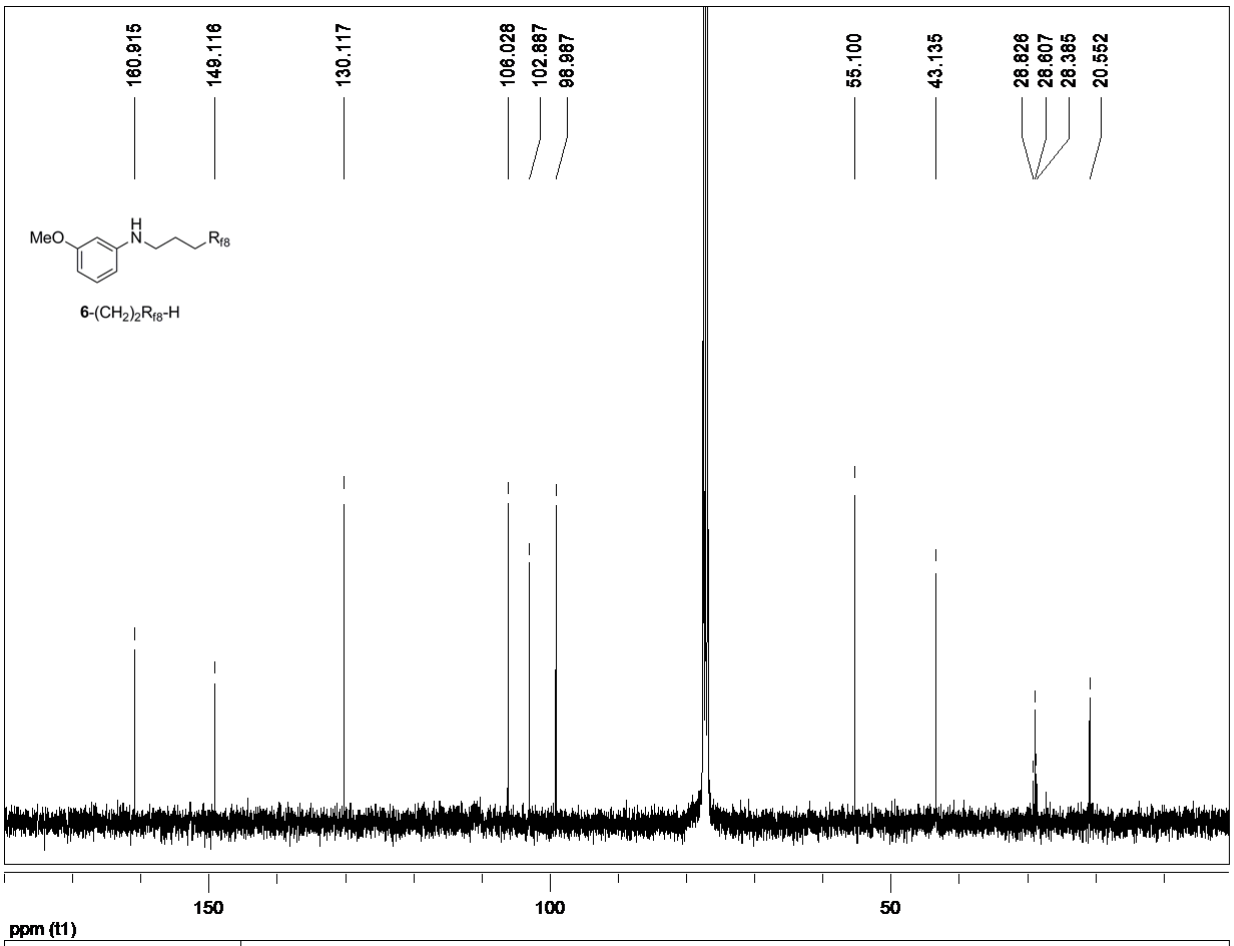


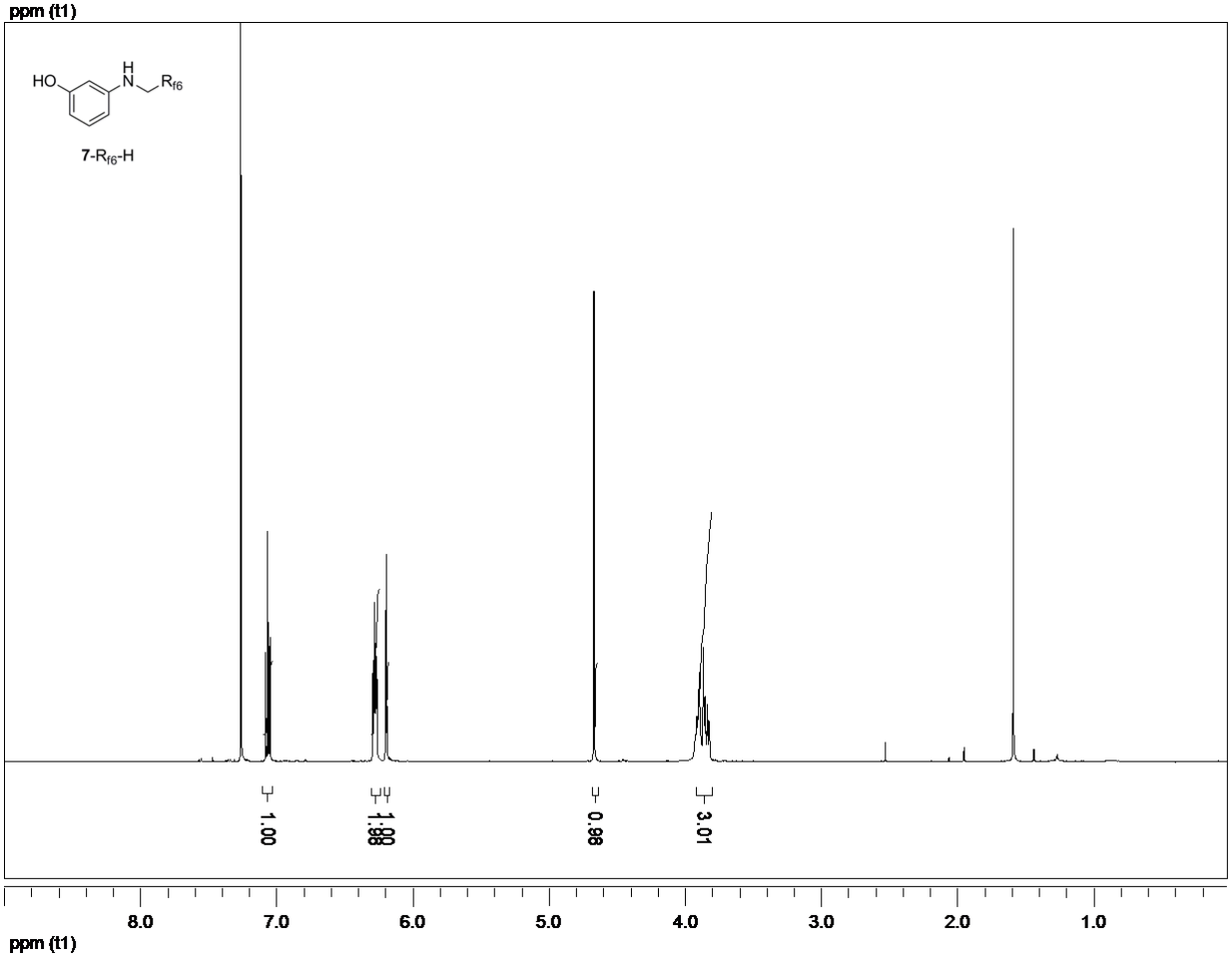


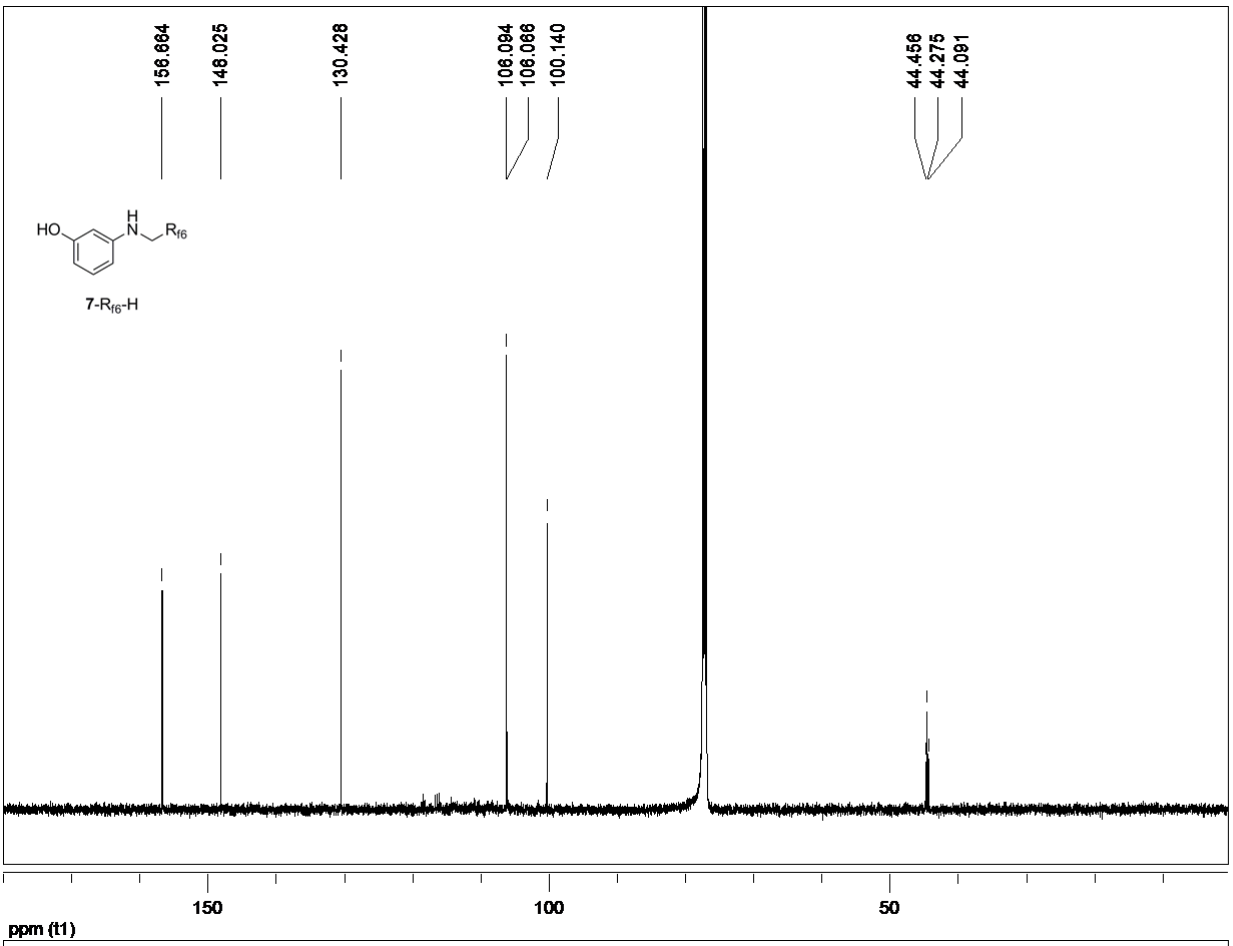


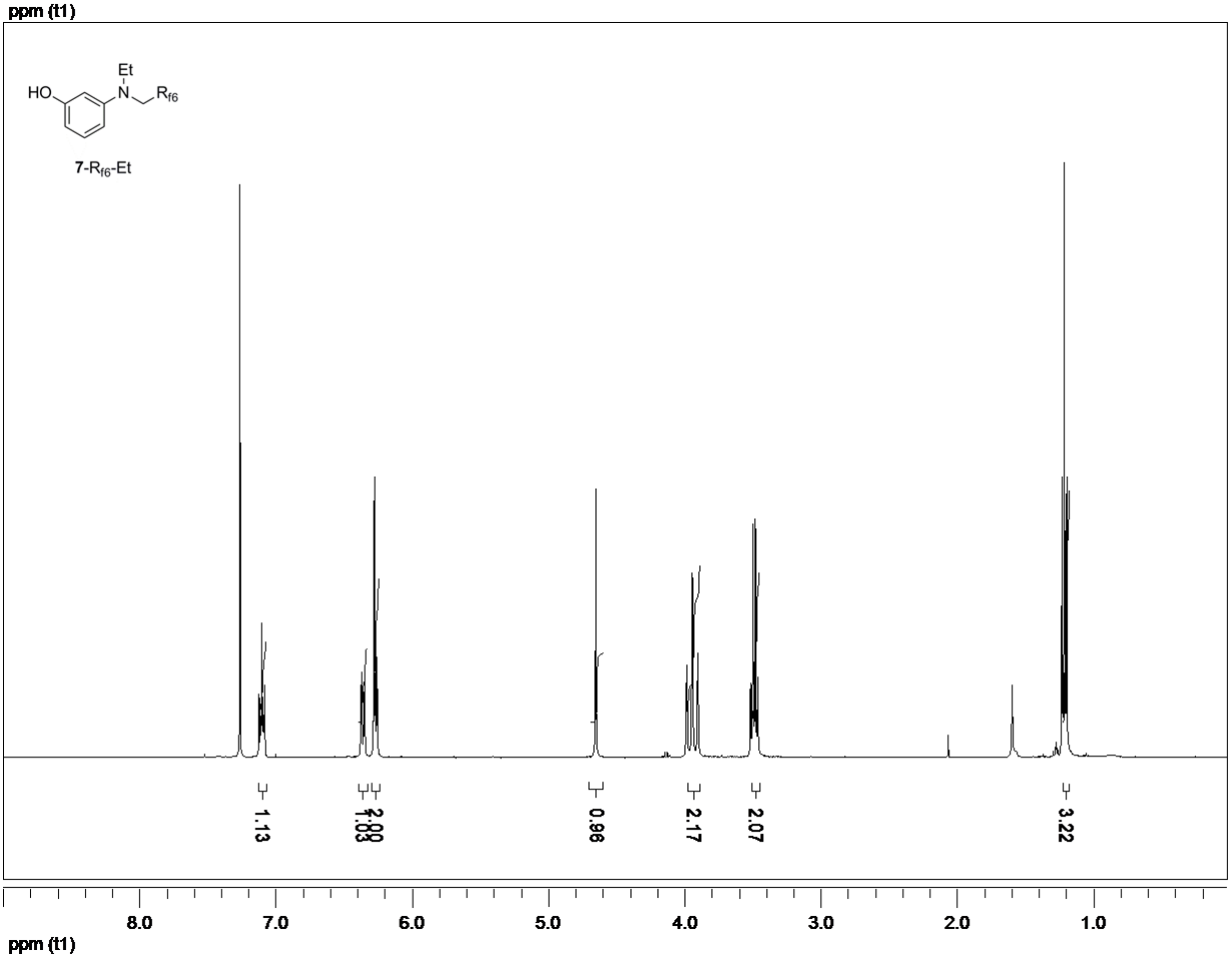


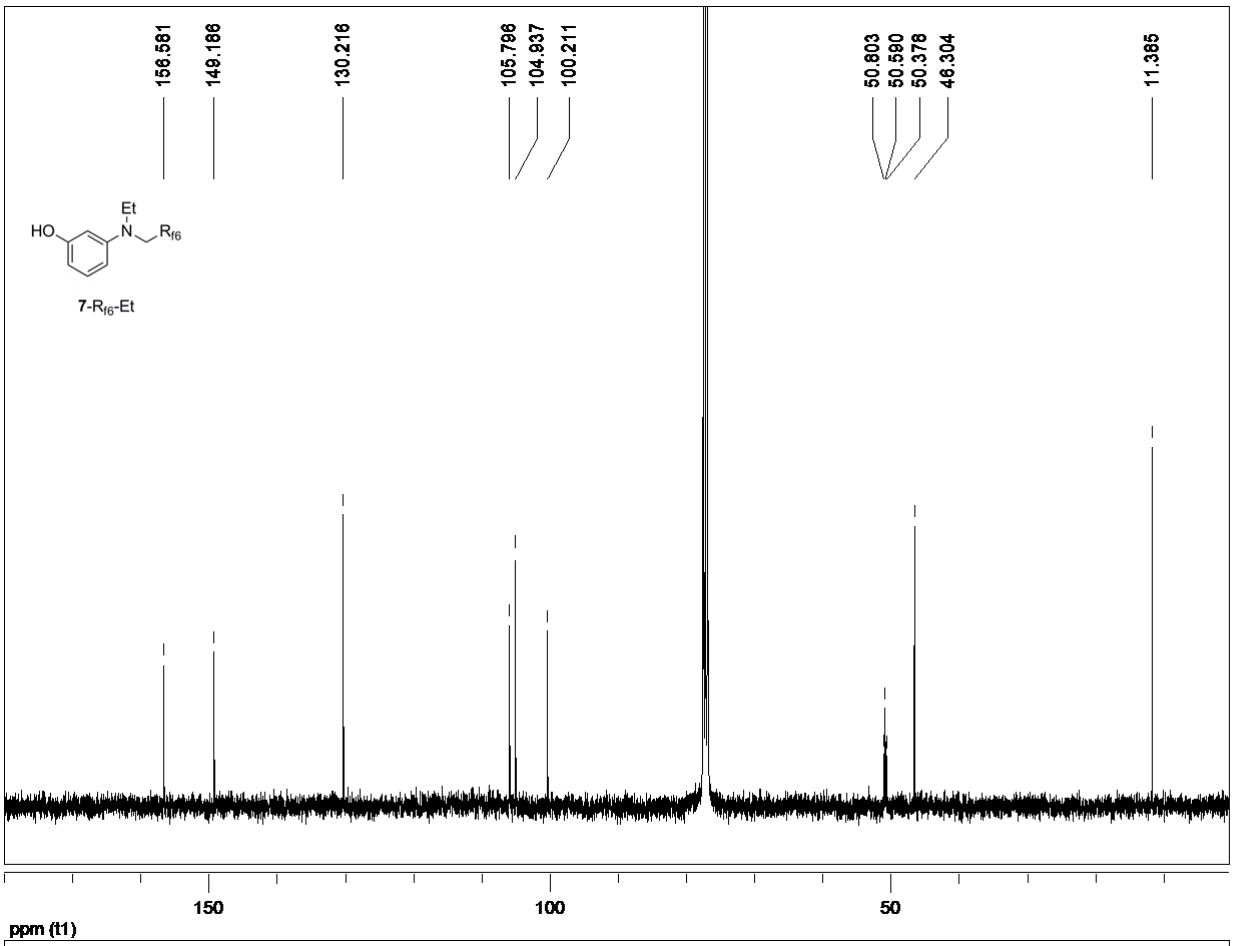


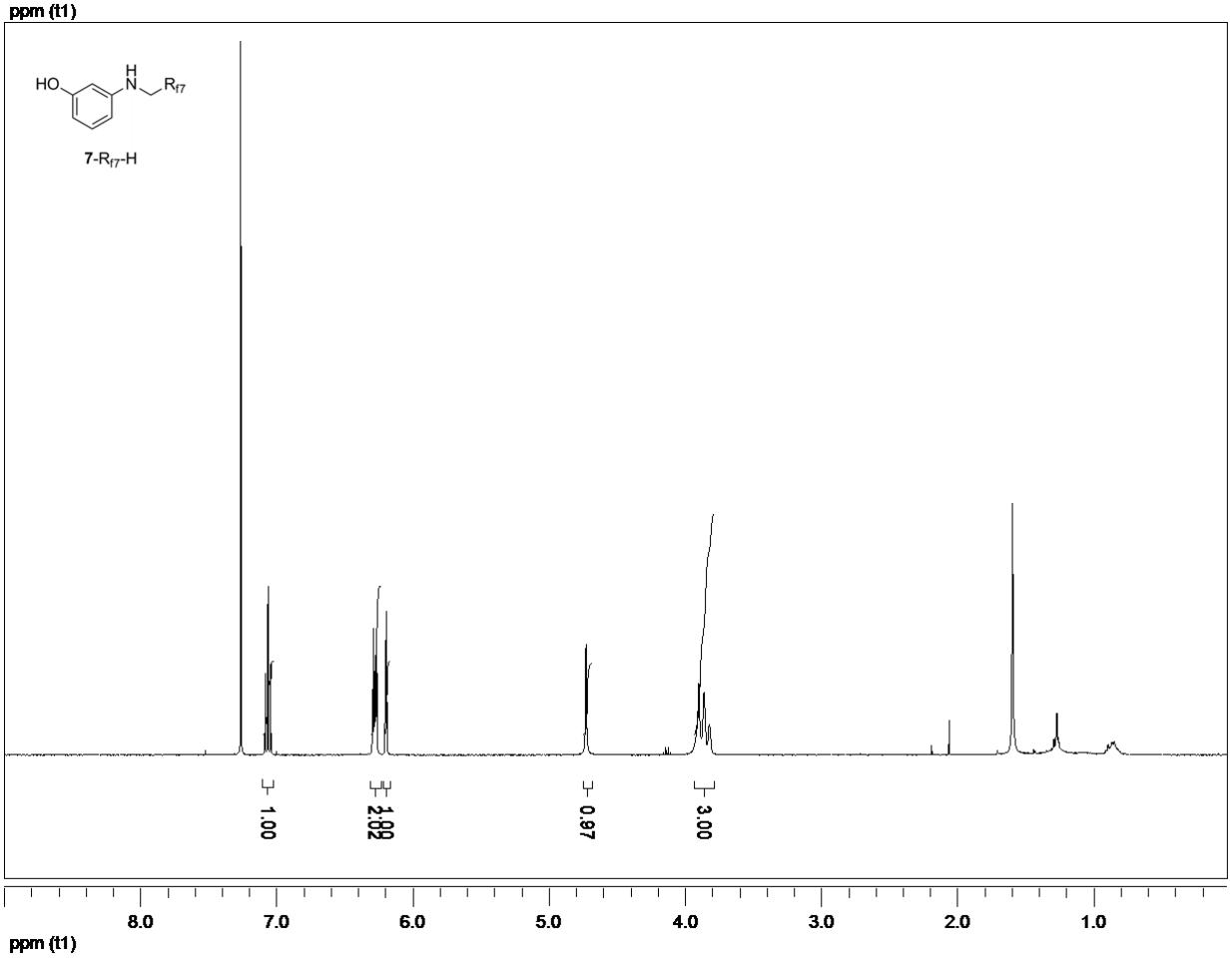


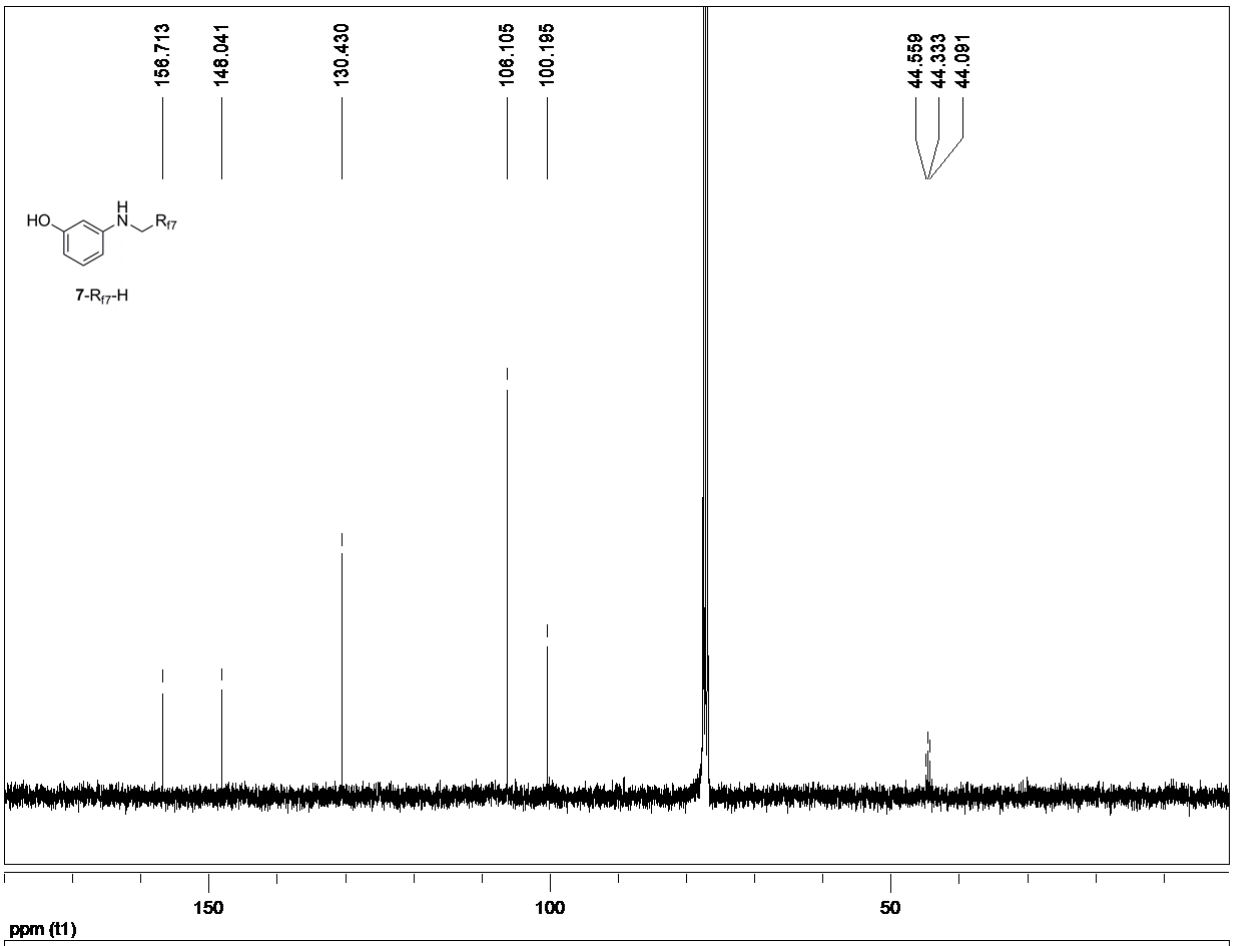


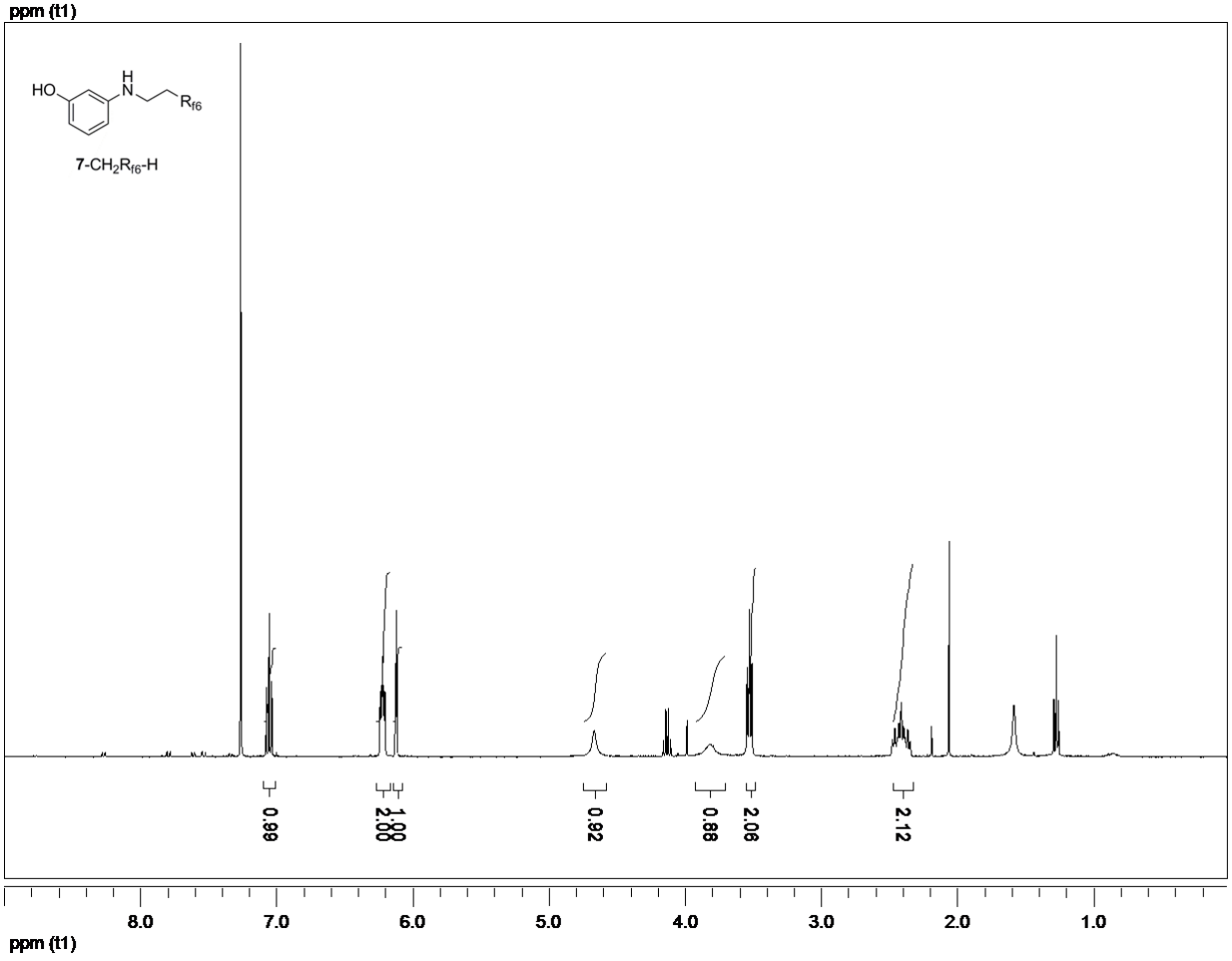


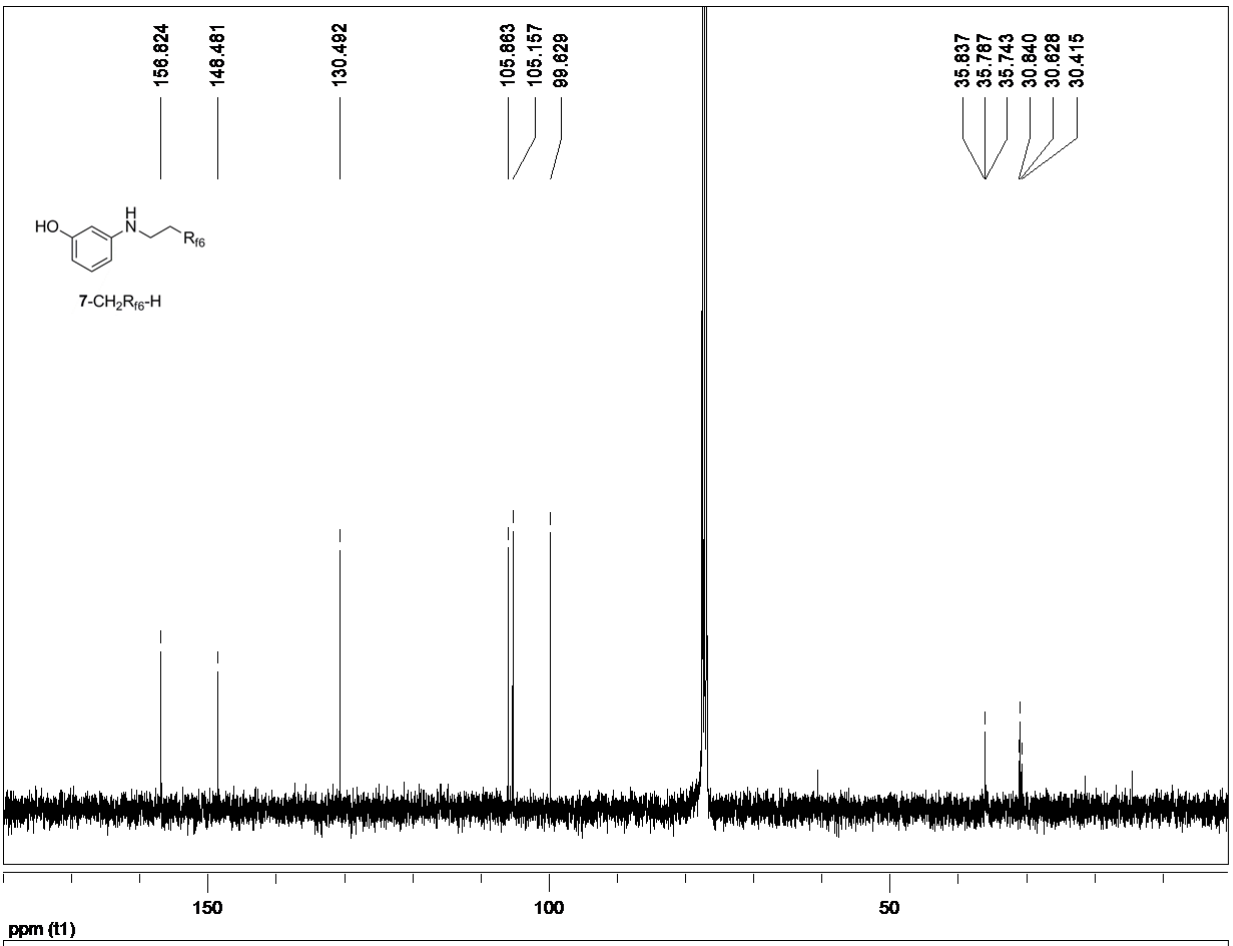


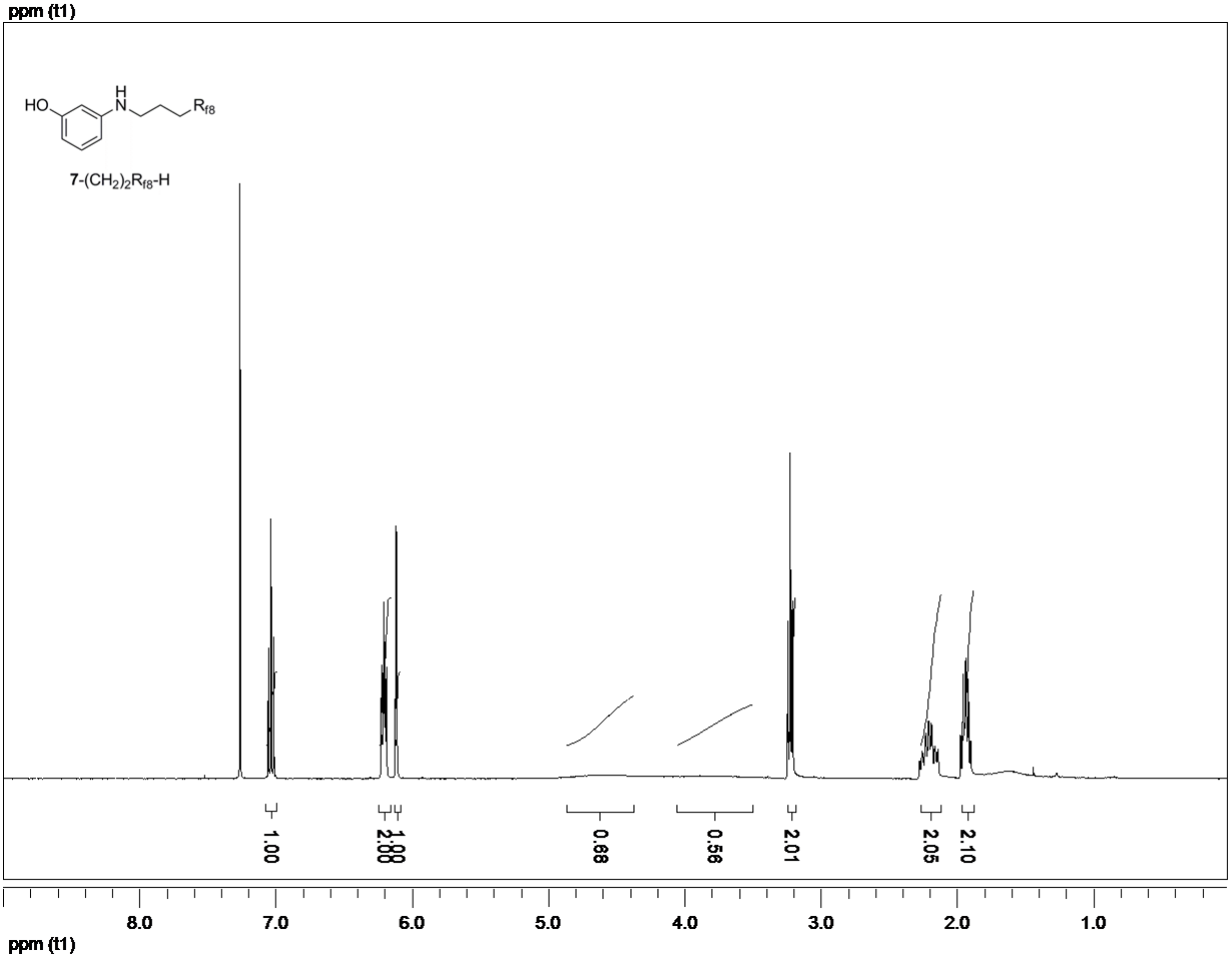


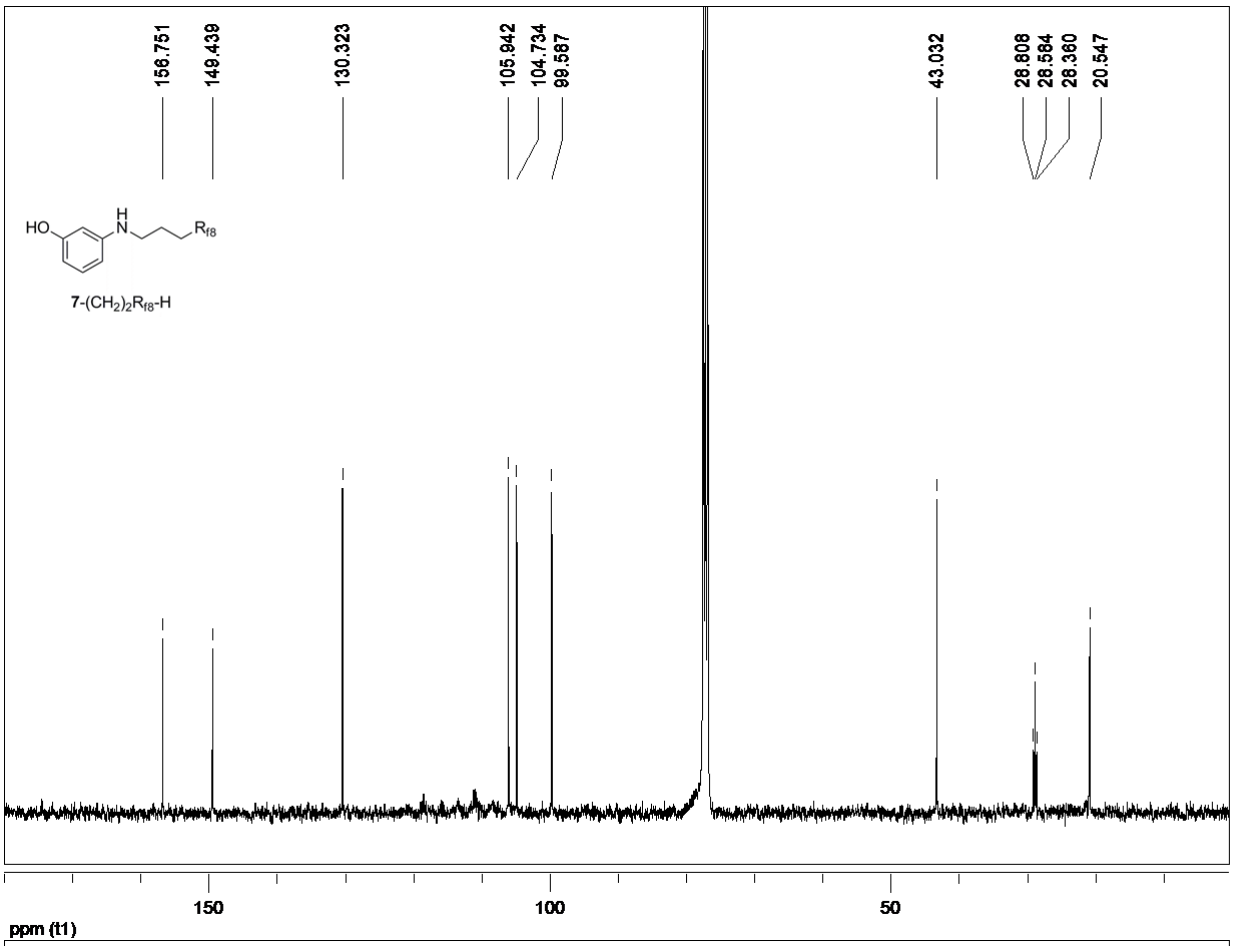


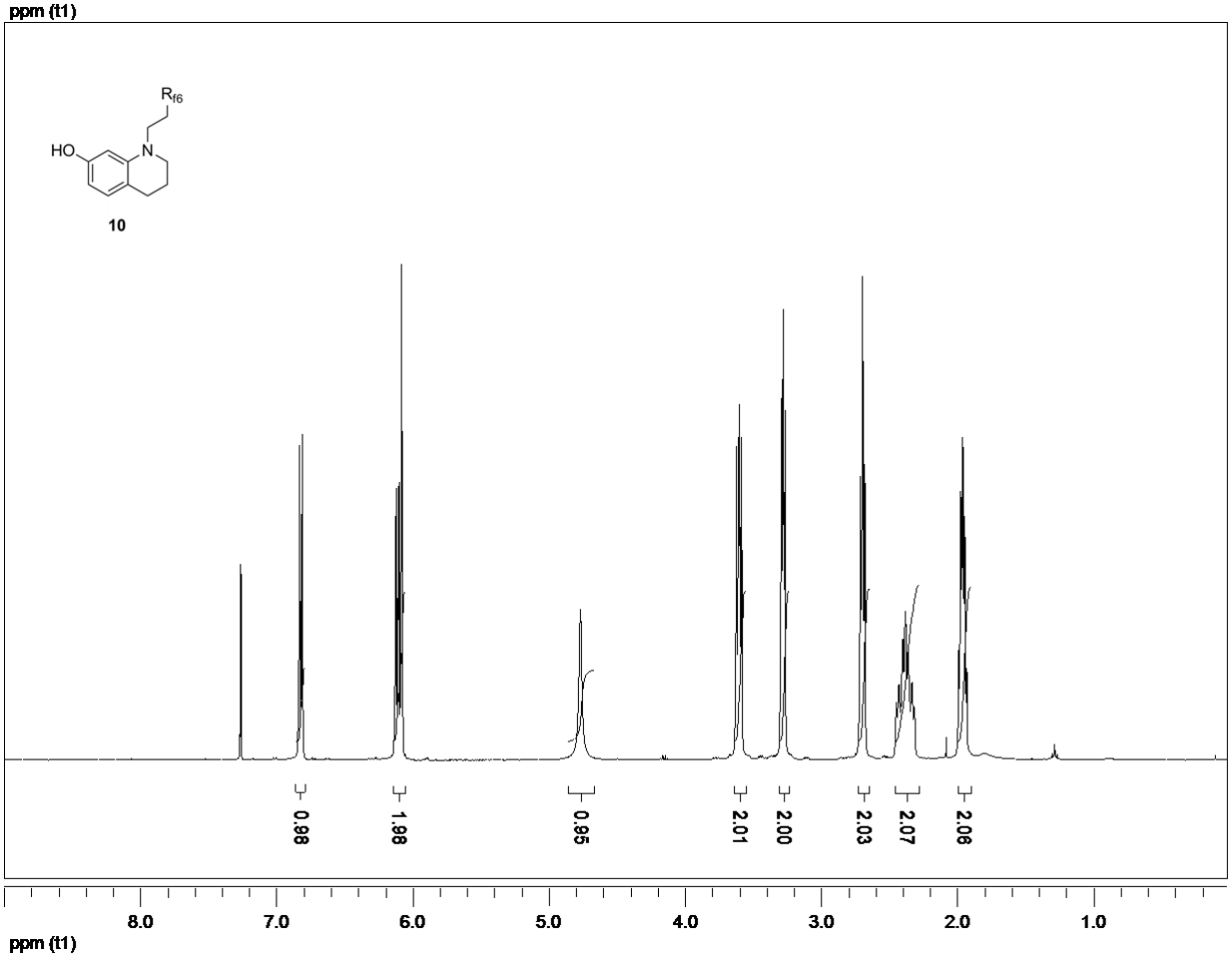


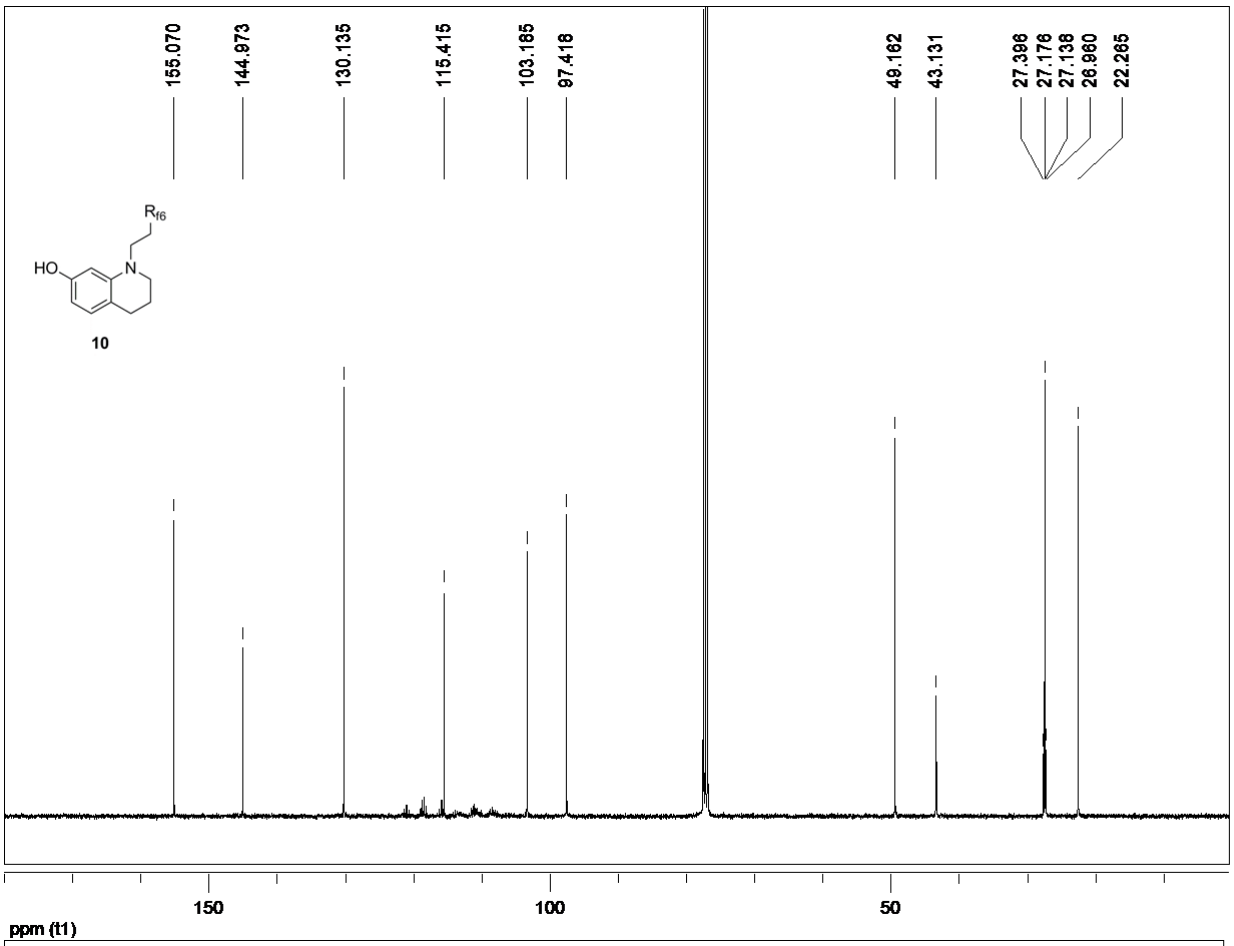


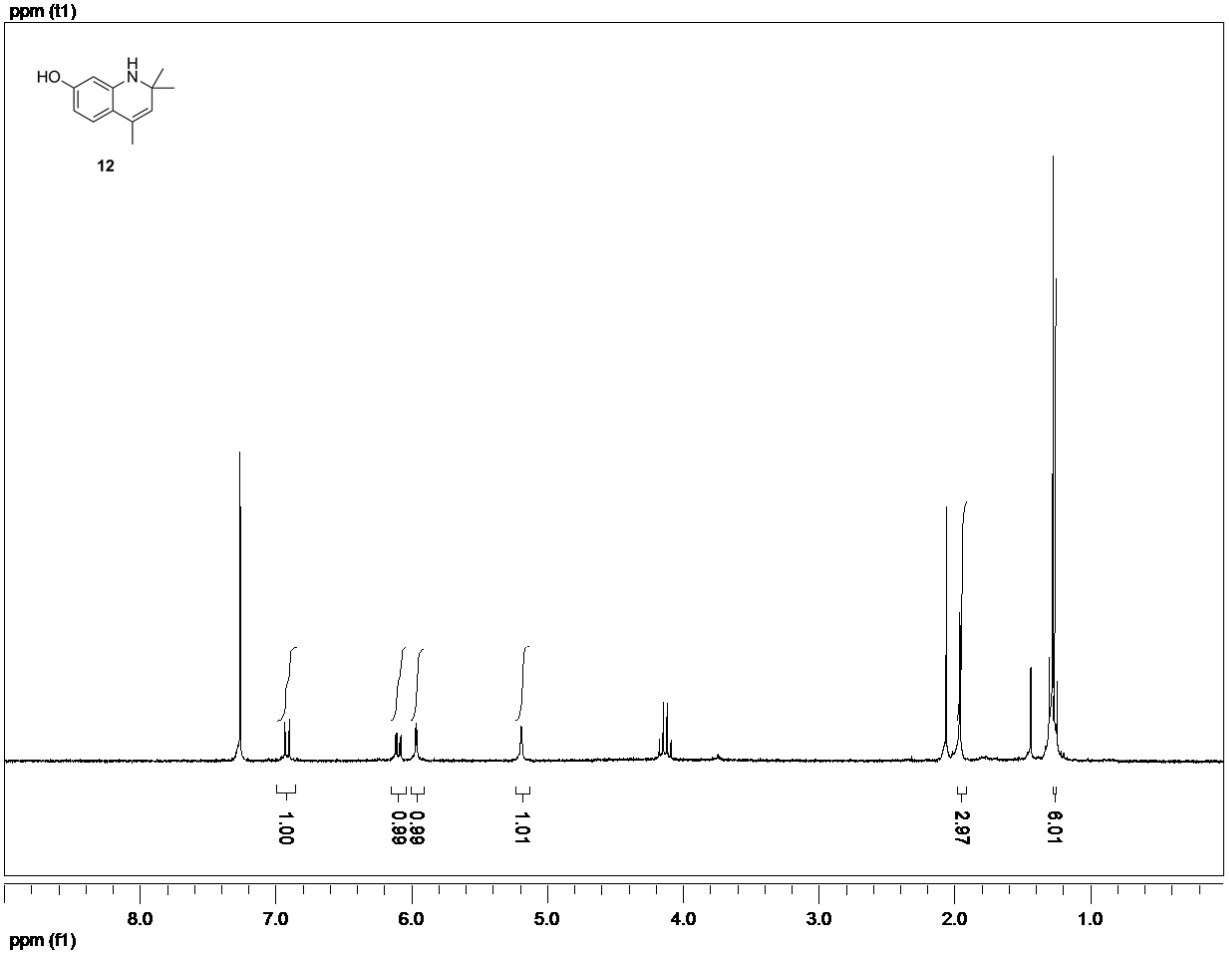


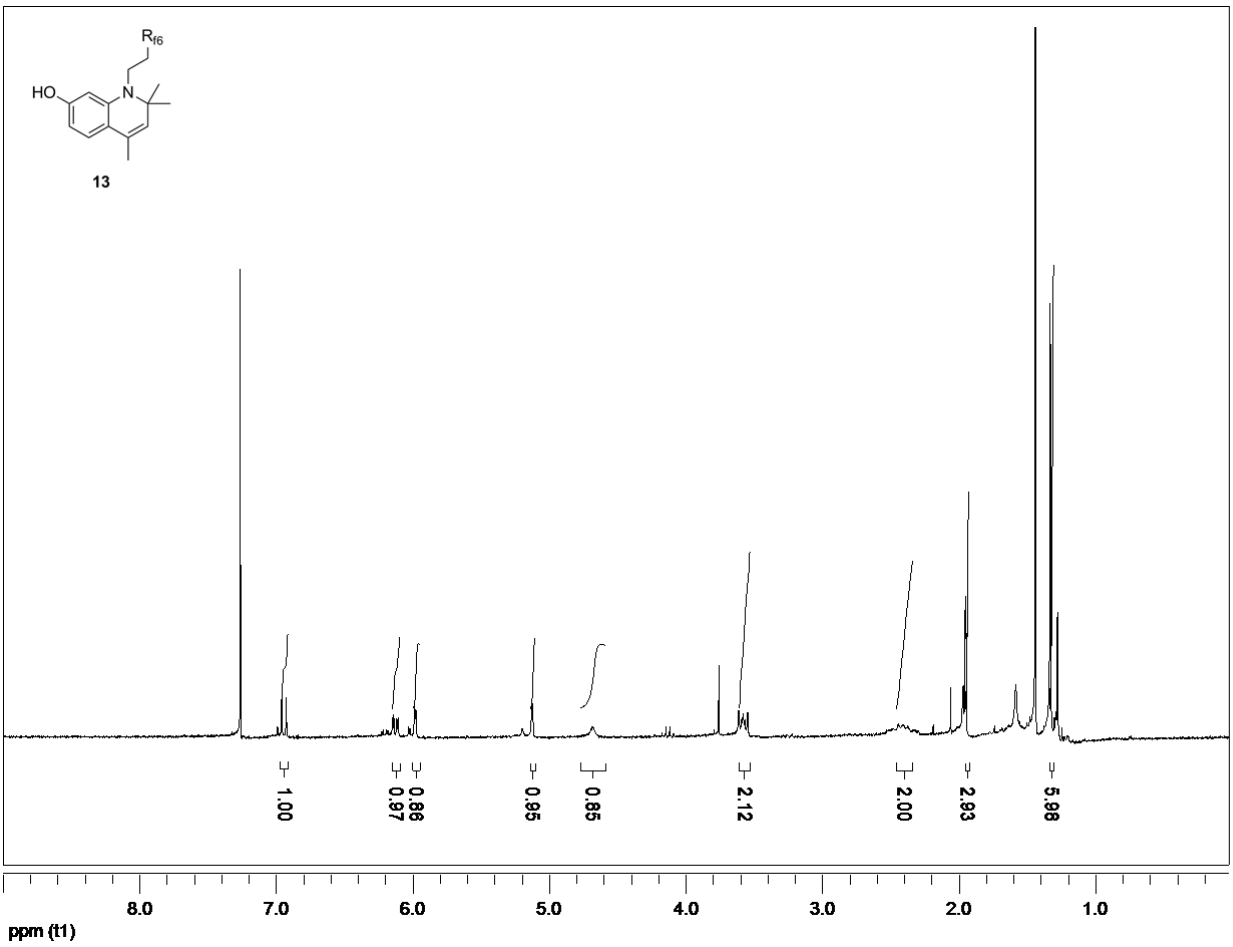




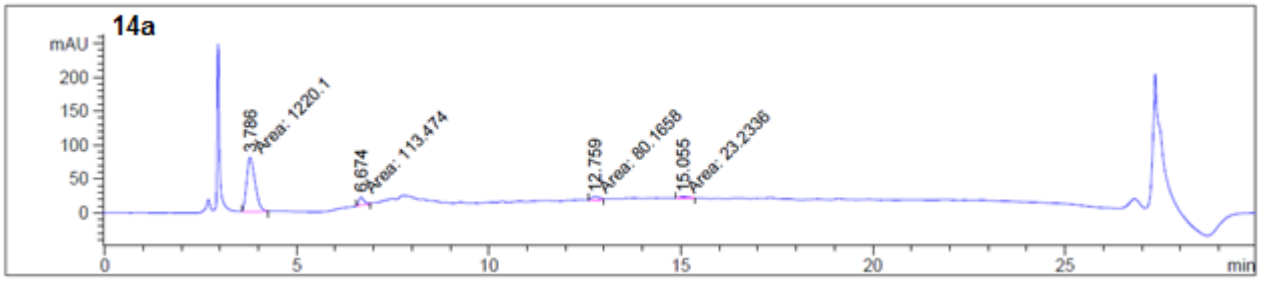






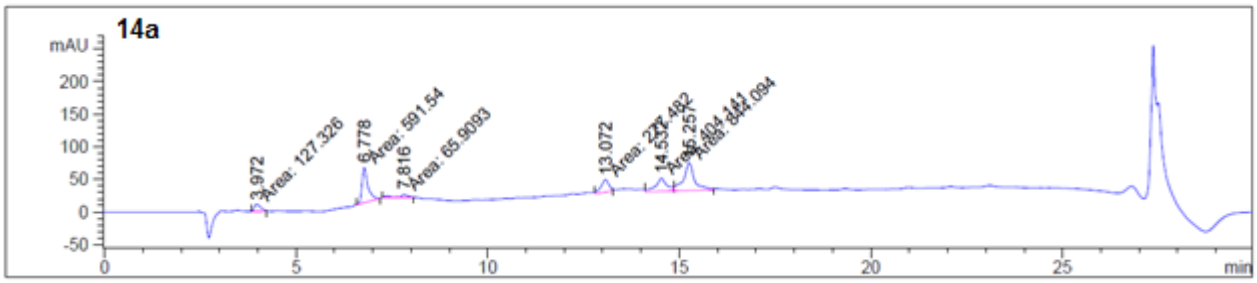


Supporting Figures



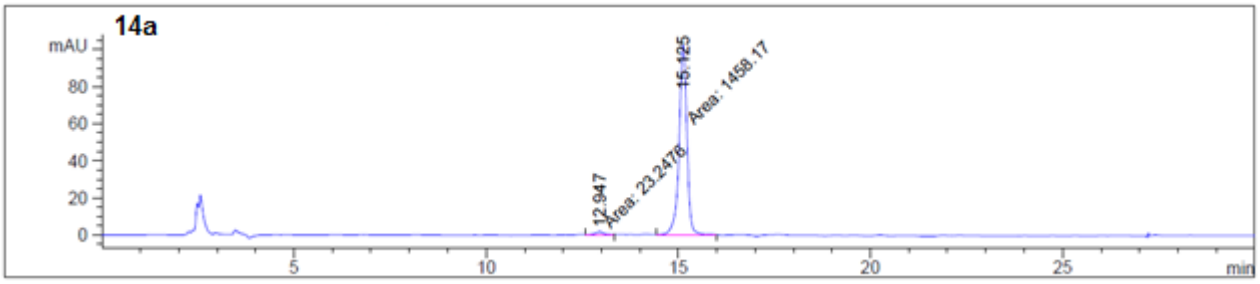
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.786	MM	0.2539	1220.09692	80.10103	84.9076
2	6.674	MM	0.1560	113.47441	12.12167	7.8968
3	12.759	MM	0.2501	80.16581	5.34303	5.5788
4	15.055	MM	0.2327	23.23360	1.66426	1.6168

Fig. SI-1 HPLC trace of crude peptoid **14a** after cleavage from solid supports. Signals were detected at 218 nm. Retention time of **14a**: 15.1 min.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.972	MM	0.1938	127.32559	10.95095	5.5108
2	6.778	MM	0.1829	591.53961	53.91122	25.6023
3	7.816	MM	0.2301	65.90932	4.77481	2.8526
4	13.072	MM	0.2408	277.48199	19.20371	12.0097
5	14.532	MF	0.3401	404.14127	19.80792	17.4916
6	15.257	FM	0.3315	844.09375	42.43276	36.5331

Fig. SI-2 HPLC trace of peptoid **14a** after F-SPE. Signals were detected at 218 nm. Retention time of **14a**: 15.3 min.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.947	MM	0.2548	23.24762	1.52070	1.5693
2	15.125	FM	0.2373	1458.16736	102.40260	98.4307

Fig. SI-3 HPLC trace of peptoid **14a** after HPLC purification. Signals were detected at 218 nm. Retention time of **14a**: 15.1 min.

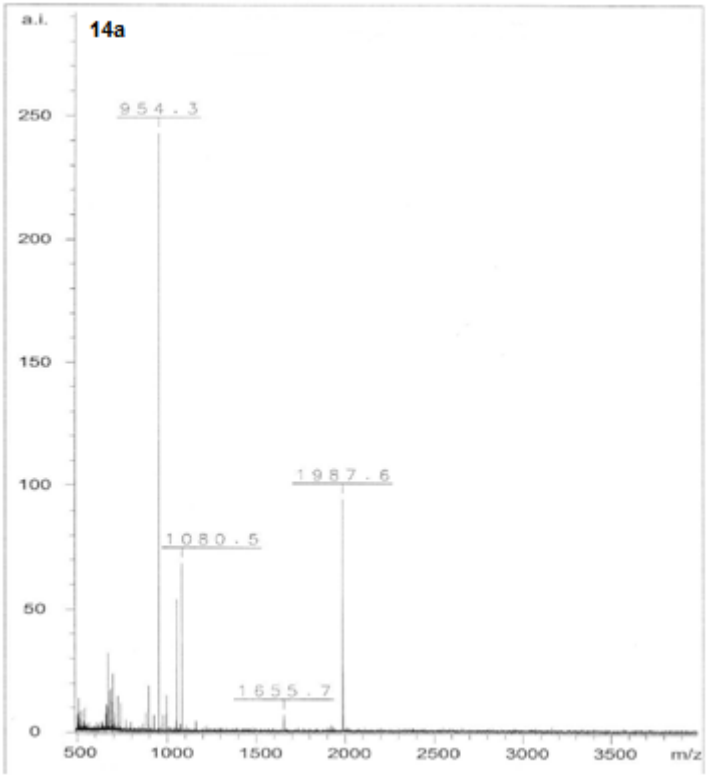


Fig. SI-4 MALDI-TOF-mass spectrum of crude peptoid **14a** after cleavage from solid supports.

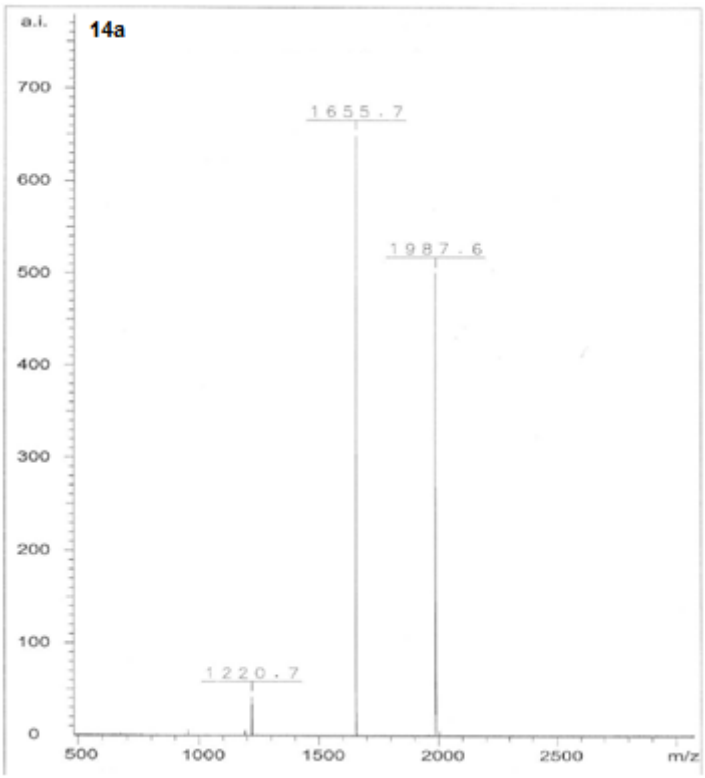


Fig. SI-5 MALDI-TOF-mass spectrum of peptoid **14a** after F-SPE.

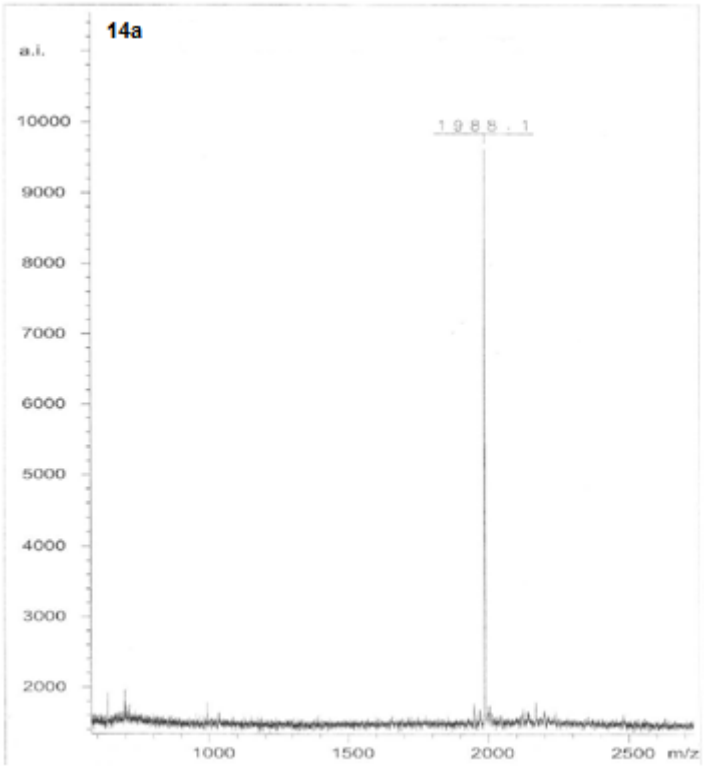
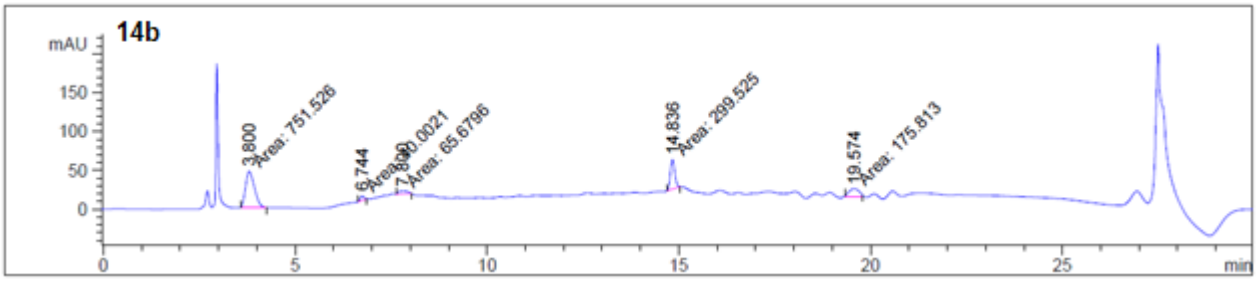
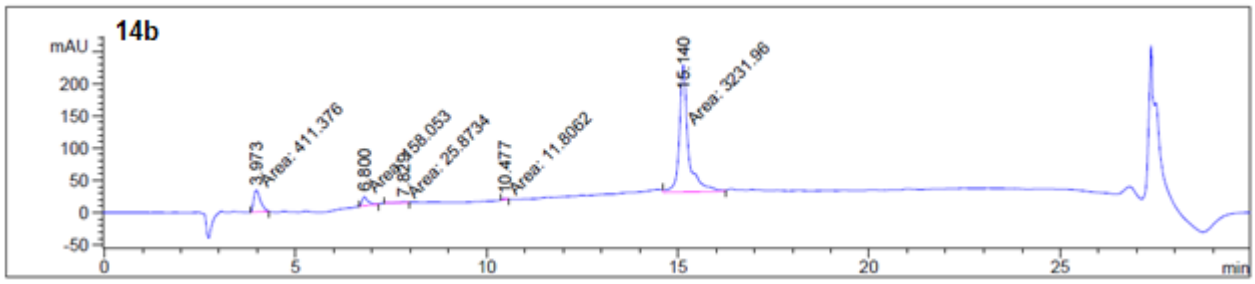


Fig. SI-6 MALDI-TOF-mass spectrum of peptoid **14a** after HPLC purification.



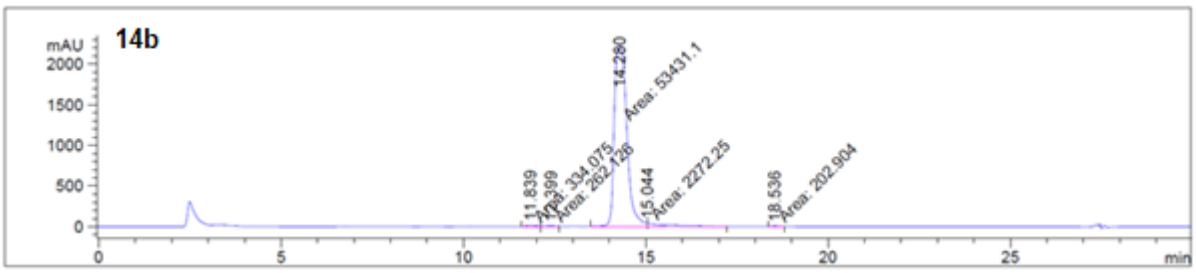
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.800	MM	0.2673	751.52551	46.85045	56.3978
2	6.744	MM	0.1159	40.00211	5.75281	3.0019
3	7.800	MM	0.2872	65.67959	3.81150	4.9289
4	14.836	MM	0.1306	299.52475	38.21313	22.4777
5	19.574	MM	0.2964	175.81268	9.88701	13.1938

Fig. SI-7 HPLC trace of crude peptoid **14b** after cleavage from solid supports. Signals were detected at 218 nm. Retention time of **14b**: 14.8 min.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.973	MM	0.2028	411.37564	33.80816	10.7155
2	6.800	MM	0.1856	158.05258	14.19111	4.1170
3	7.829	MM	0.2153	25.87337	2.00319	0.6739
4	10.477	MM	0.1293	11.80624	1.52187	0.3075
5	15.140	MM	0.2741	3231.95728	196.54265	84.1861

Fig. SI-8 HPLC trace of peptoid **14b** after F-SPE. Signals were detected at 218 nm. Retention time of **14b**: 15.1 min.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.839	MF	0.3504	334.07455	15.88804	0.5913
2	12.399	FM	0.4005	262.12619	10.90803	0.4639
3	14.280	MF	0.3989	5.34311e4	2232.55713	94.5642
4	15.044	FM	0.8258	2272.24976	45.86146	4.0215
5	18.536	MM	0.3349	202.90395	10.09696	0.3591

Fig. SI-9 HPLC trace of peptoid **14b** after HPLC purification. Signals were detected at 218 nm. Retention time of **14b**: 14.3 min.

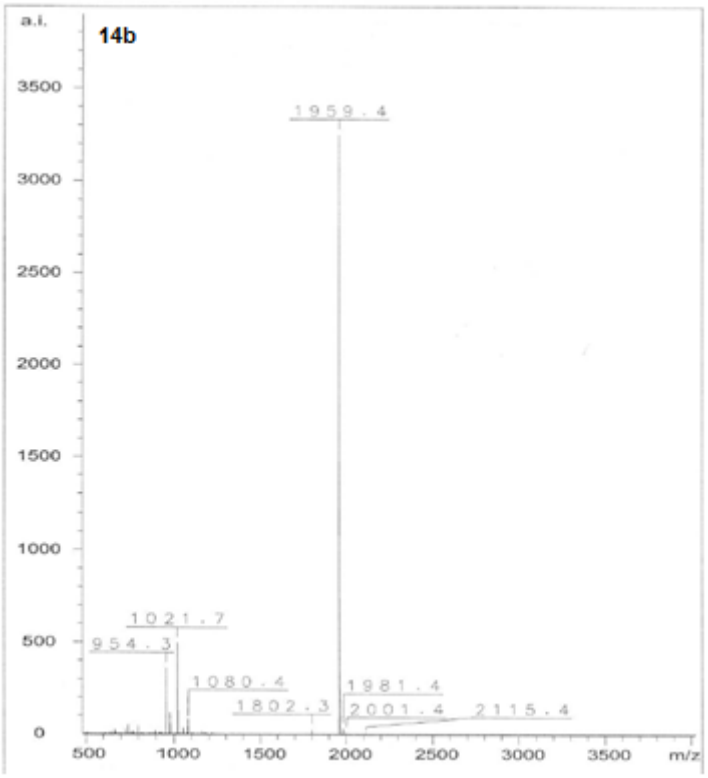


Fig.SI-10 MALDI-TOF-mass spectrum of crude peptoid **14b** after cleavage from solid supports.

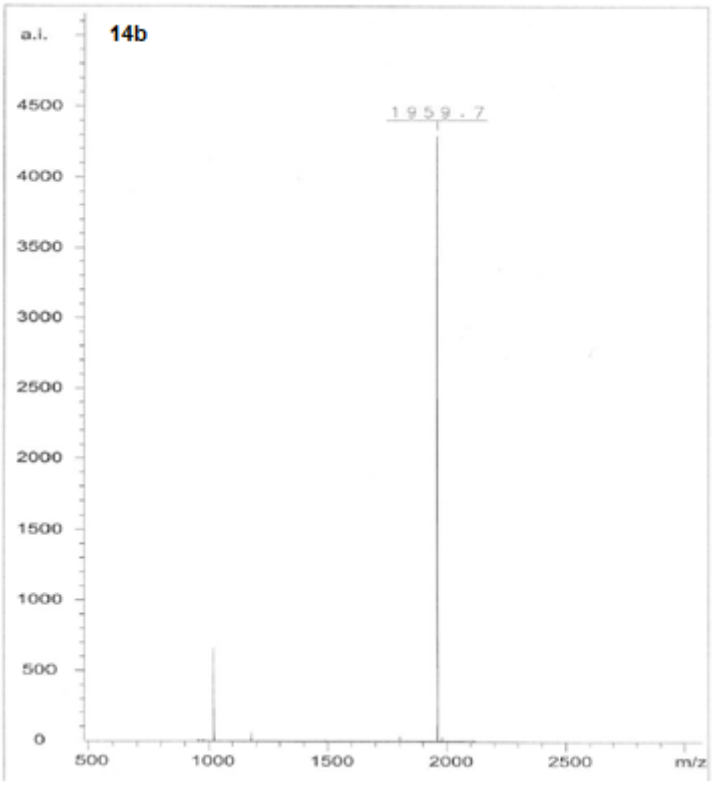


Fig. SI-11 MALDI-TOF-mass spectrum of peptoid **14b** after F-SPE.

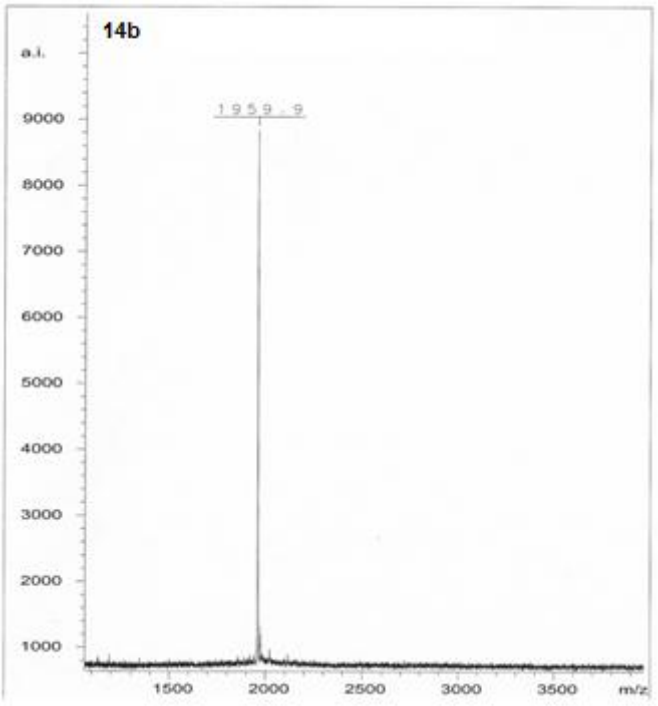
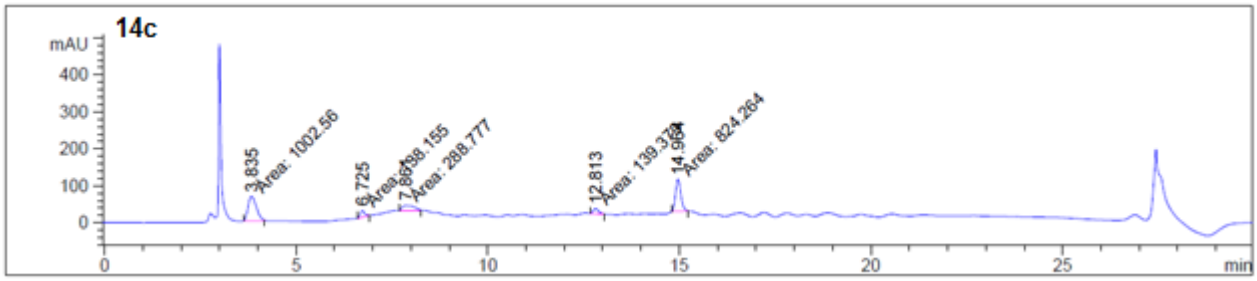
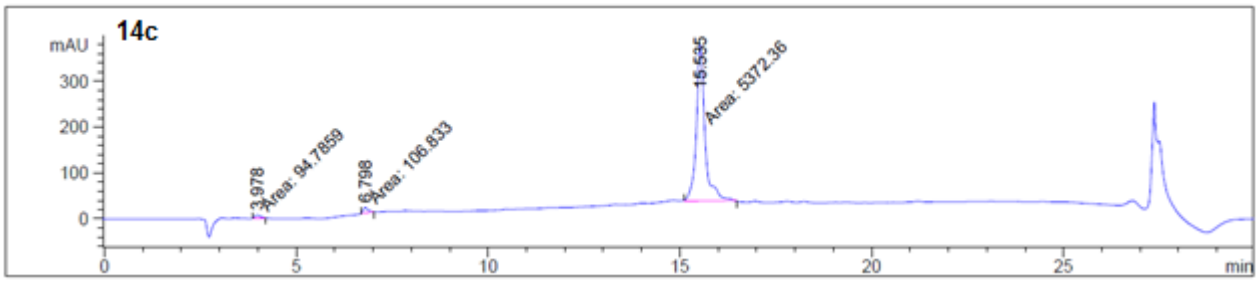


Fig. SI-12 MALDI-TOF-mass spectrum of peptoid **14b** after HPLC purification.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.835	MM	0.2507	1002.56232	66.65386	41.8932
2	6.725	MM	0.1285	138.15538	17.91528	5.7730
3	7.861	MM	0.3765	288.77679	12.78418	12.0669
4	12.813	MM	0.1671	139.37930	13.90369	5.8241
5	14.964	MM	0.1579	824.26379	86.99781	34.4428

Fig.SI-13 HPLC trace of crude peptoid **14c** after cleavage from solid supports. Signals were detected at 218 nm. Retention time of **14c**: 15.0 min.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.978	MM	0.2026	94.78590	7.79790	1.7005
2	6.798	MM	0.1480	106.83344	12.02846	1.9166
3	15.535	MM	0.2634	5372.35693	339.94412	96.3828

Fig. SI-14 HPLC trace of peptoid **14c** after F-SPE. Signals were detected at 218 nm. Retention time of **14c**: 15.5 min.

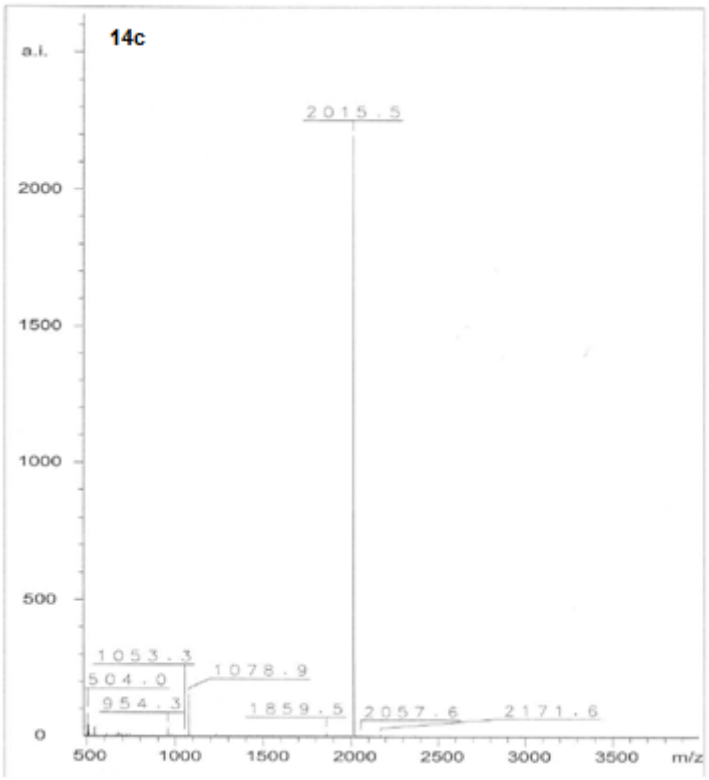


Fig. SI-15 MALDI-TOF-mass spectrum of crude peptoid **14c** after cleavage from solid supports.

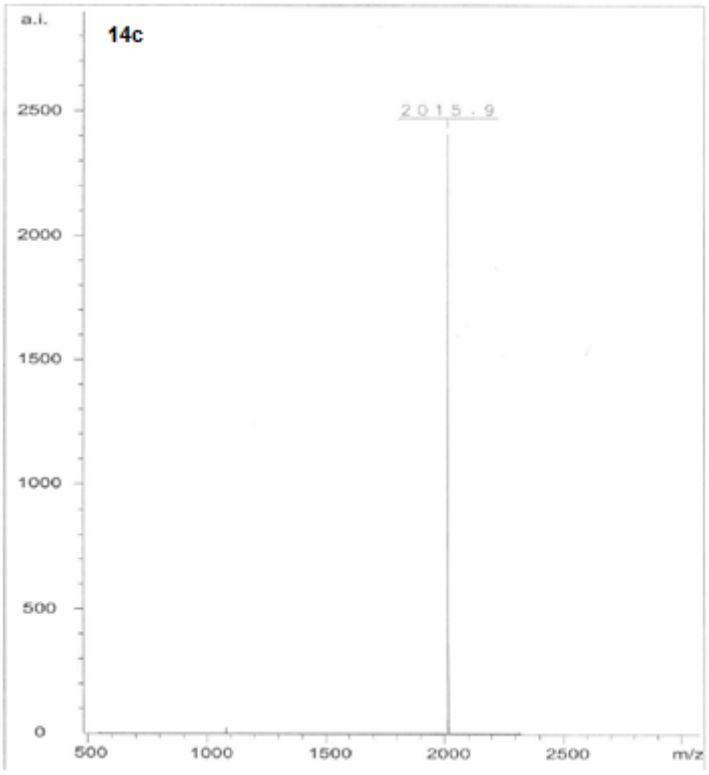
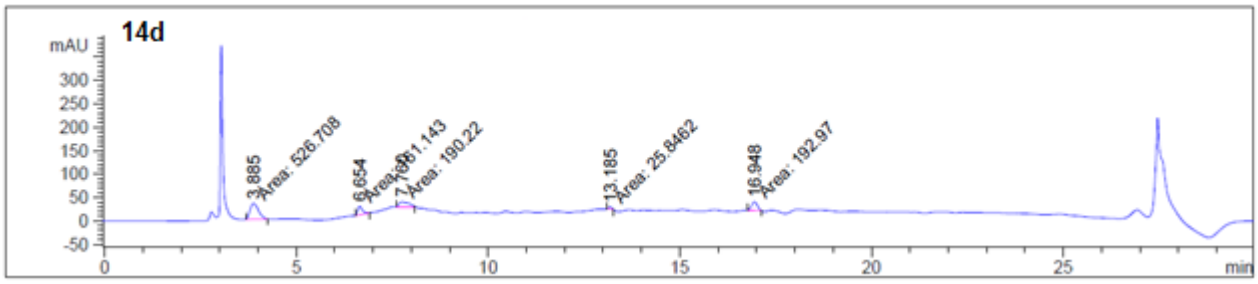
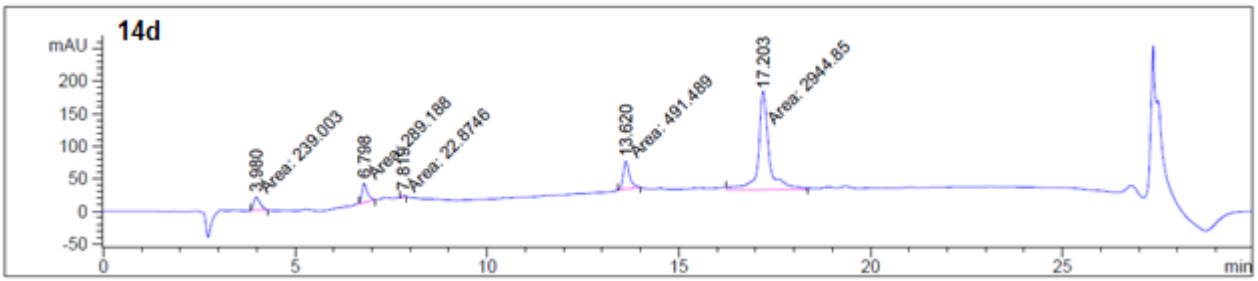


Fig. SI-16 MALDI-TOF-mass spectrum of peptoid **14c** after F-SPE.



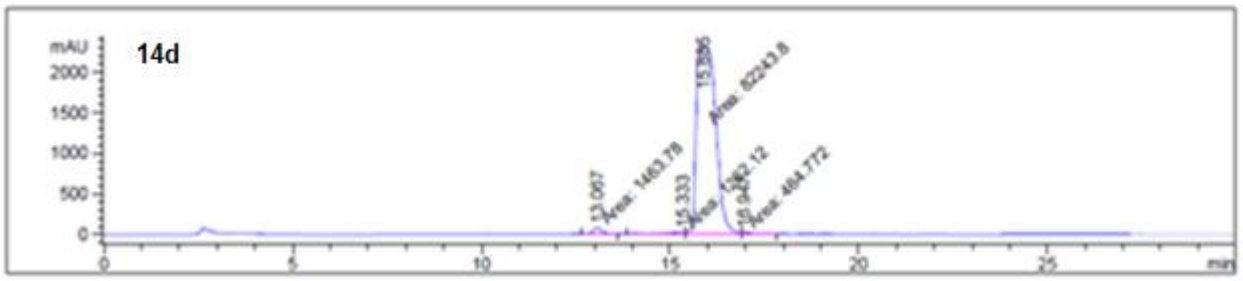
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.885	MM	0.2569	526.70795	34.17724	48.0184
2	6.654	MM	0.1418	161.14264	18.94631	14.6909
3	7.760	MM	0.3147	190.22009	10.07407	17.3418
4	13.185	MM	0.0885	25.84616	4.86742	2.3563
5	16.948	MM	0.1764	192.96996	18.22906	17.5925

Fig. SI-17 HPLC trace of crude peptoid **14d** after cleavage from solid supports. Signals were detected at 218 nm. Retention time of **14d**: 16.9 min.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.980	MM	0.1974	239.00316	20.17522	5.9939
2	6.798	MM	0.1628	289.18753	29.60132	7.2525
3	7.819	MM	0.1141	22.87457	3.34063	0.5737
4	13.620	MM	0.1934	491.48935	42.34525	12.3260
5	17.203	MM	0.3238	2944.85205	151.56383	73.8538

Fig. SI-18 HPLC trace of peptoid **14d** after F-SPE. Signals were detected at 218 nm. Retention time of **14d**: 17.2 min.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.067	MM	0.3037	1463.78418	80.34235	1.7133
2	15.333	MF	0.7924	1262.11865	26.54576	1.4773
3	15.885	MF	0.5931	8.22438e4	2311.19531	96.2654
4	16.947	FM	0.3365	464.77191	23.02280	0.5440

Fig. SI-19 HPLC trace of peptoid **14d** after HPLC purification. Signals were detected at 218 nm. Retention time of **14d**: 15.9 min.

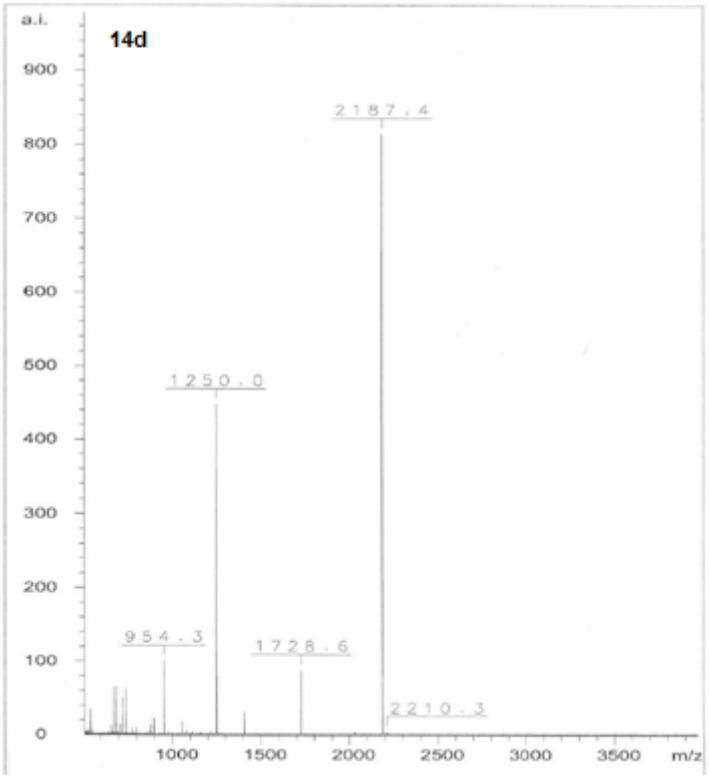


Fig. SI-20 MALDI-TOF-mass spectrum of crude peptoid **14d** after cleavage from solid supports.

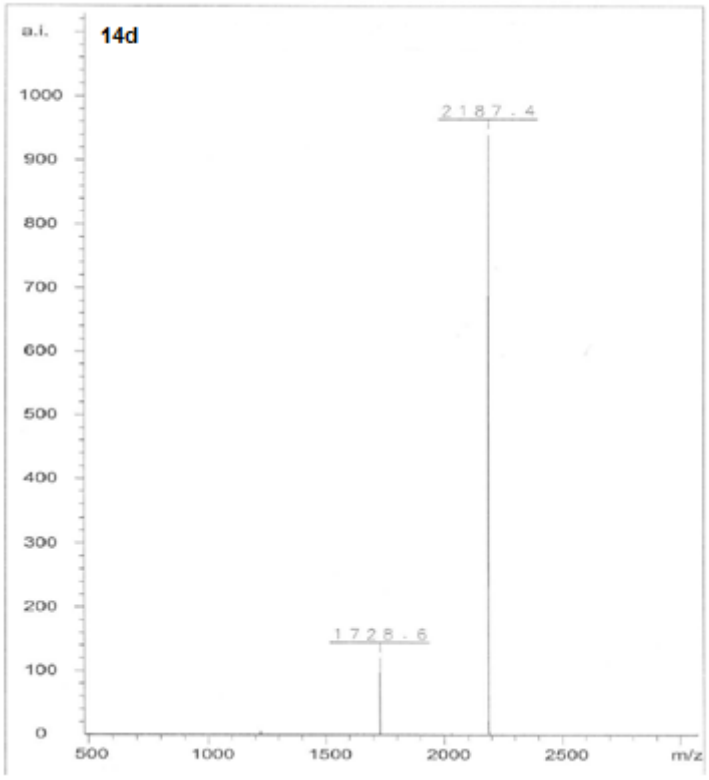


Fig. SI-21 MALDI-TOF-mass spectrum of peptoid **14d** after F-SPE.

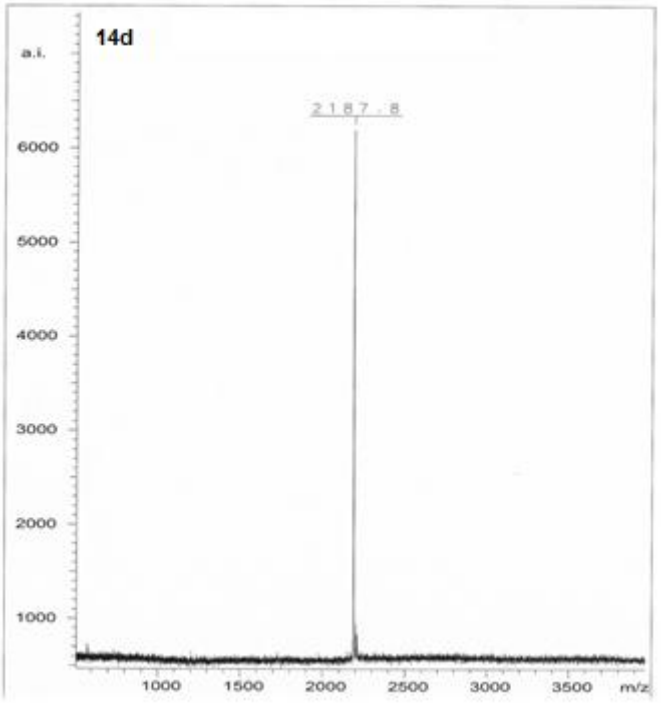
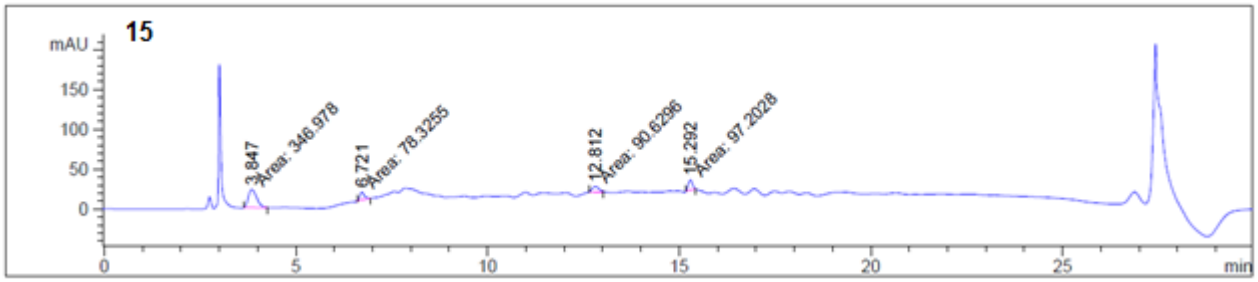
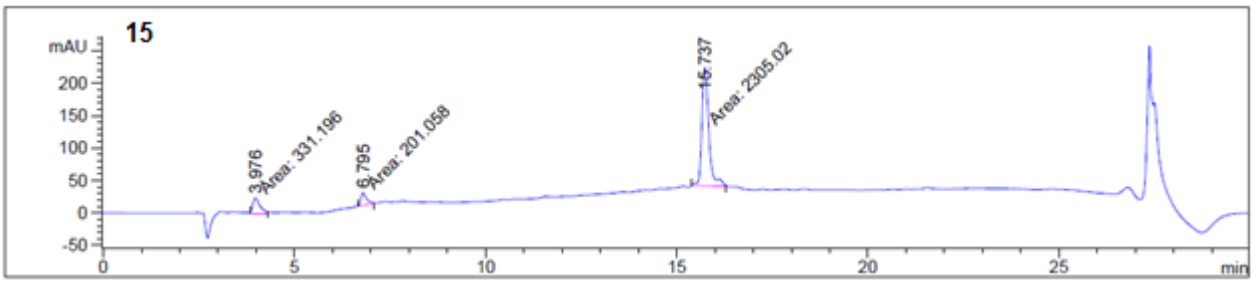


Fig. SI-22 MALDI-TOF-mass spectrum of peptoid **14d** after HPLC purification.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.847	MM	0.2533	346.97784	22.82984	56.5907
2	6.721	MM	0.1343	78.32552	9.72364	12.7746
3	12.812	MM	0.2079	90.62957	7.26388	14.7813
4	15.292	MM	0.1240	97.20277	13.06693	15.8534

Fig. SI-23 HPLC trace of crude peptoid **15** after cleavage from solid supports. Signals were detected at 218 nm. Retention time of **15**: 15.3 min.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.976	MM	0.2290	331.19601	24.10313	11.6730
2	6.795	MM	0.1714	201.05818	19.55532	7.0863
3	15.737	MM	0.2108	2305.01733	182.26642	81.2406

Fig. SI-24 HPLC trace of peptoid **15** after F-SPE. Signals were detected at 218 nm. Retention time of **15**: 15.7 min.

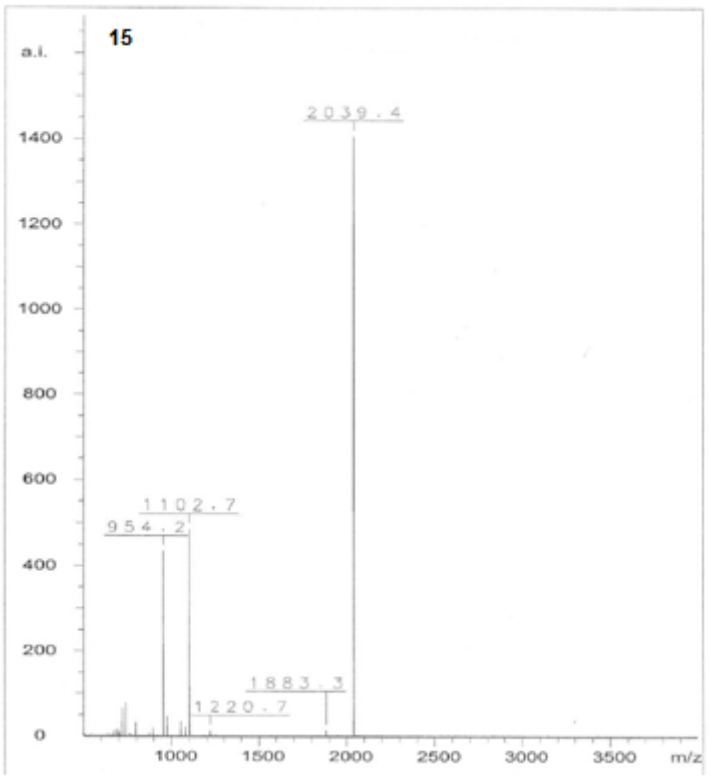


Fig. SI-25 MALDI-TOF-mass spectrum of crude peptoid **15** after cleavage from solid supports.

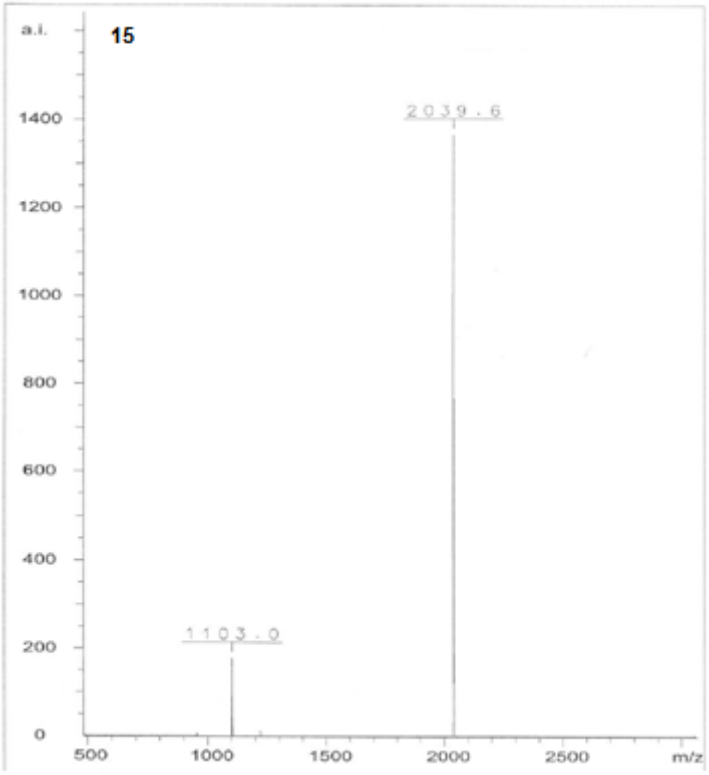
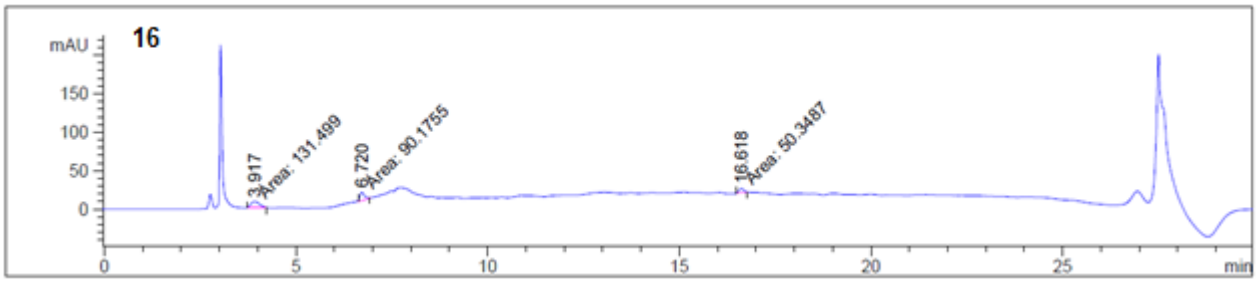
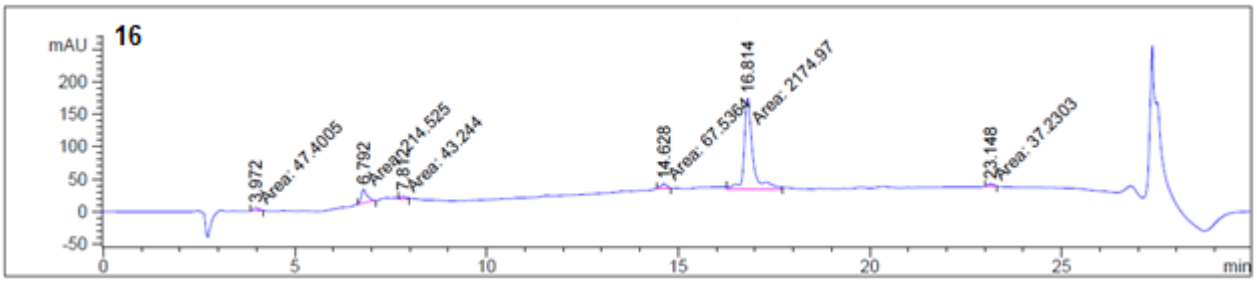


Fig. SI-26 MALDI-TOF-mass spectrum of peptoid **15** after F-SPE.



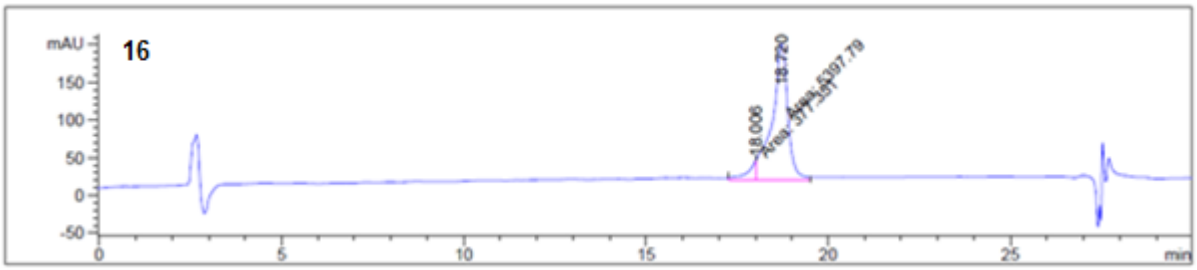
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.917	MM	0.2659	131.49907	8.24378	48.3411
2	6.720	MM	0.1382	90.17547	10.87820	33.1499
3	16.618	MM	0.1498	50.34874	5.60265	18.5090

Fig. SI-27 HPLC trace of crude peptoid **16** after cleavage from solid supports. Signals were detected at 218 nm. Retention time of **16**: 16.6 min.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.972	MM	0.1663	47.40054	4.75113	1.8337
2	6.792	MM	0.1710	214.52496	20.91212	8.2991
3	7.812	MM	0.1739	43.24400	4.14454	1.6729
4	14.628	MM	0.1691	67.53642	6.65542	2.6127
5	16.814	MM	0.2590	2174.96729	139.98576	84.1411
6	23.148	MM	0.1714	37.23030	3.61972	1.4403

Fig. SI-28 HPLC trace of peptoid **16** after F-SPE. Signals were detected at 218 nm. Retention time of **16**: 16.8 min.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.006	MF	0.2529	377.35107	24.86360	6.5341
2	18.720	FM	0.4989	5397.78564	180.33830	93.4659

Fig. SI-29 HPLC trace of peptoid **16** after HPLC purification. Signals were detected at 218 nm. Retention time of **16**: 18.7 min.

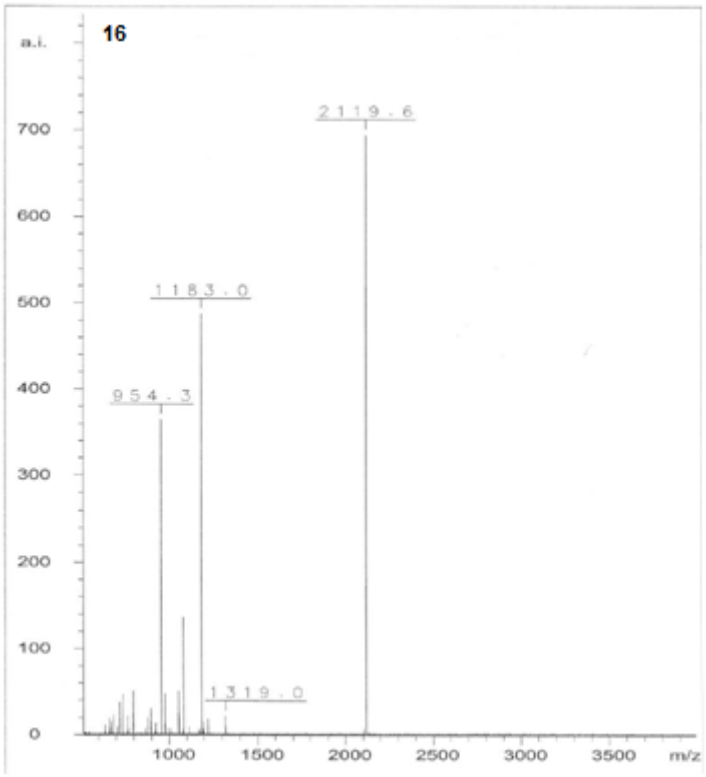


Fig. SI-30. MALDI-TOF-mass spectrum of crude peptoid **16** after cleavage from solid supports.

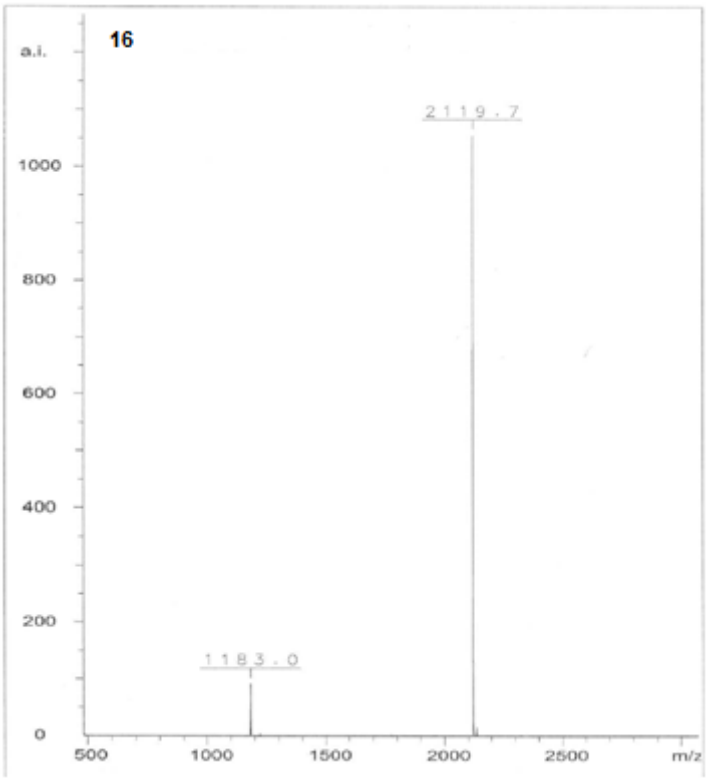


Fig. SI-31 MALDI-TOF-mass spectrum of peptoid **16** after F-SPE.

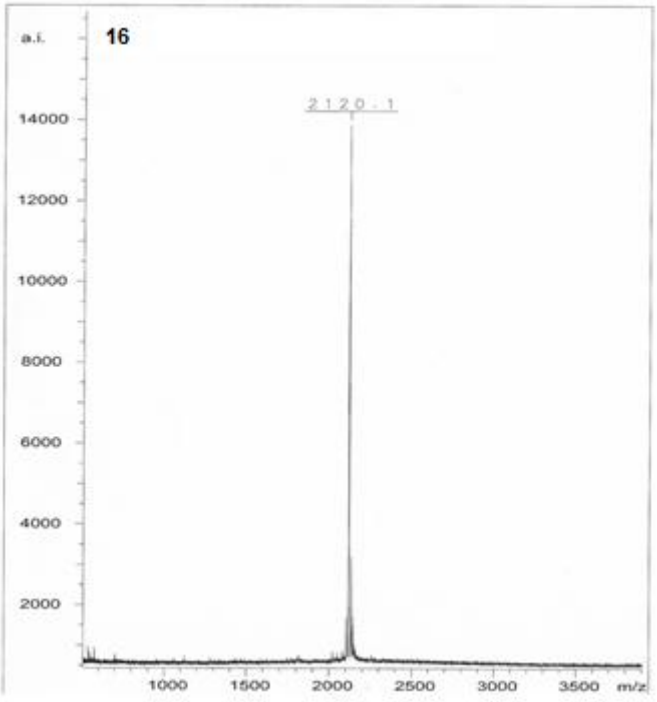


Fig. SI-32 MALDI-TOF-mass spectrum of peptoid **16** after HPLC purification.

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