Electronic Supplementary Information

Towards novel liquid crystalline merocyanine dyes by tailoring donor units

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Contents

1) General Information

Techniques

All air sensitive reactions were carried out under nitrogen using standard Schlenk techniques. Column chromatography was performed using silica gel 60 (Fluka, mesh 40–63 mm). All chemicals used were commercially available and used without further purification, unless otherwise noted.

NMR spectroscopy

NMR spectra were recorded on Bruker Avance 700 (^{1}H, 700 MHz; ^{13}C, 176 MHz), Bruker Avance 500 (^{1}H, 500 MHz; ^{13}C, 126 MHz), Bruker Avance 400 (^{1}H, 400 MHz; ^{13}C, 101 MHz; ^{19}F, 376 MHz) and Bruker Avance 300 (^{1}H, 300 MHz; ^{13}C, 75 MHz). All NMR spectra were recorded at room temperature and the calibration was done on the residual solvent peaks. The evaluation was performed with the software MestReNova[1] from MESTRELAB RESEARCH.

IR spectroscopy

FT-IR spectra were recorded on a Bruker Vector 22 FT-IR spectrometer with MKII golden gate single recflection Diamant ATR system at room temperature.

Mass spectrometry

Mass spectra and high-resolution mass spectra were obtained by electrospray ionisation (ESI) using a MicroTOF-Q by Bruker Daltonics and by electron ionisation (EI) using a Variant MAT 711 by Finnigan.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) was performed using the instruments Mettler Toledo DSC822e or DSC25 from TA INSTRUMENTS. All experiments were performed in 40 µL aluminum pans from METTLER TOLEDO and TA INSTRUMENTS. The respective onset values were chosen as phase transition temperatures, which were calculated using the software STARe[2] from METTLER TOLEDO and TRIOS[3] from TA INSTRUMENTS.

Optical polarizing microscopy

Optical polarizing microscopy (POM) was performed with the polarizing microscope BX 50 of the company OLYMPUS. The microscope was equipped with an LTS 350 heating chamber and the TP93 temperature control unit from LINKAM SCIENTIFIC. A Color View camera and the software analySIS[4] from SOFT IMAGING SYSTEMS were used to digitize the textures. Temperature-dependent solid-state emission spectra were recorded on a NIKON 80i polarizing microscope equipped with a LINKAM LTS 420 heating chamber and a NIKON Intensilight C-

HFGI radiation source. Data acquisition was performed with a NIKON DSFI2 camera and a QE65000 photodetector from OCEAN OPTICS.

X-ray diffraction:

Temperature-dependent small- and wide-angle X-ray diffraction experiments were performed on a BRUKER AXS Nanostar C. As radiation source, a 1500 W X-ray tube, was used, which emitted characteristic X-ray radiation ($Cu_{K\alpha}$, $\lambda = 1.54056$ Å). X-ray diffraction images were obtained on a BRUKER HI-STAR or VÅNTEC 500 detector. Calibration was performed on the Diffraction image of a silver behenate sample at room temperature. The samples were placed in pith tubes (outer diameter: 0.7 mm; wall thickness: 0.01 mm) from the company HILGENBERG. If possible, the samples were pre-oriented via extrusion before filling. The data analysis was performed with the software SAXS[5] from BRUKER, Datasqueeze[6], OriginPro[7] from ORIGINLAB, and LCDiXray[8].

UV-Vis and fluorescence spectroscopy:

For UV/VIS and fluorescence measurements spectroscopic grade solvents were purchased from the manufacturer (ALFA AESAR and SIGMA ALDRICH) and used without further purification. The solutions were freshly prepared. Absorbance measurements were performed on a VARIAN Cary 100 spectrometer in a spectral range of 200-800 nm at room temperature. Emission measurements in solution were measured on a PERKIN ELMER LS 55 spectrometer. For direct measurements of quantum yields (solid and solution), a C9920-03 sphere from HAMAMATSU was used, which was equipped with a 150 W xenon lamp, a monochromator and a PMA-12 detector was used. Emission lifetimes (solid and solution) were measured on a setup equipped with a picosecond laser diode ($\lambda_{exc} = 375$ nm) from HORIBA and a C10910-25 streak camera from HAMAMATSU was equipped. Depending on the lifetime, a suitable integration window was chosen (between 10 ns and 1 ms). The obtained measurement data were analyzed using the software OriginPro[7] from ORIGINLAB. The reduced χ^2-value and the residual distribution served as signal quality. residual distribution.

2) General procedures

General procedure (GP1)

The respective secondary alcohol **18** (2.15 mmol, 1 equiv.) was dissolved in DMF (21 mL, 0.1 M) in adaptation to a patent specification[9] and ground potassium hydroxide (10.7 mmol, 5 equiv.) and the respective *n*-bromoalkane (4.29 mmol, 2 equiv.) were added. The reaction mixture was stirred for 48 h at room temperature. After the reaction was completed, CH_2Cl_2 and H_2O (30 mL each) were added and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (3×50 mL), and the combined organic phases were washed with 1 M

KOH solution (50 mL), dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with a solvent gradient of PE to EE shown for each derivative individually. The respective products **PipC(n)Br** were obtained as colorless solids.

General procedure (GP2)

Adapting a procedure of Wöhrle,[10] the *p*-bromophenol (17.3 mmol, 1 equiv.) was dissolved in acetonitrile (87 mL, 0.2 M) and potassium carbonate (86.7 mmol, 5 equiv.) as well as the respective *n*-bromoalkane (17.3 mmol, 1 equiv.) were added. The reaction mixture was stirred for 16 h under reflux. After cooling to room temperature, 1 M NaOH solution (100 mL) and *n*-pentane (100 mL) were added and the phases were separated. The aqueous phase and acetonitrile phase were combined and extracted with *n*-pentane (3×50 mL). The combined *n*-pentane phases were washed with 1 M NaOH solution (70 mL), dried over $MgSO_4$, and the solvent was removed under reduced pressure. The desired products **C(n)F(m)Br** and **C(n)Br** were obtained as colorless solids/oils.

General procedure (GP3)

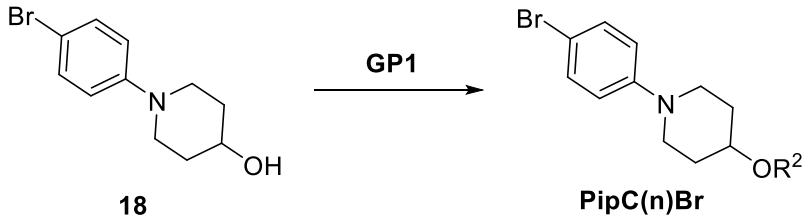
Adapting a procedure of Wu,[11] the respective donor building block **C(n)F(m)Br** or **PipC(n)Br** (707 µmol, 1.05 equiv.) was dissolved in abs. THF (6.7 mL, 0.1 M) at nitrogen atmosphere and the solution was cooled to –78 °C. Then, *n*-butyllithium (283 µL, 1.05 equiv.; 2.5 M in *n*-hexane) was added dropwise and the resulting mixture was stirred for 30 min at –78 °C. Subsequently, the respective vinylogous ester **O-k-OMe** (673 µmol, 1 equiv.) was dissolved in abs. THF (673 µL, 1 M) and added briskly to the reaction solution. The mixture was stirred for further 16 h at room temperature before the reaction was terminated by the addition of sat. NH_4Cl solution (2 mL). After that CH_2Cl_2 and H_2O (10 mL each) were added and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL), the combined organic phases were washed with sat. NaCl solution (20 mL), dried over $MgSO_4$, and the solvent was removed under reduced pressure. The respective crude product was purified by column chromatography on silica gel with a solvent gradient of PE to EE shown for each derivative individually, whereupon the respective products **O-k-C(n)F(m)** and **O-k-PipC(n)** were obtained as solids.

General procedure (GP4)[12]

The ketone **O-k-C(n)F(m)** or **O-k-PipC(n)** (172 µmol, 1 equiv.) was suspended/dissolved in toluene (1.7 mL, 0. 1 M) before adding the respective CH-acidic component (181 µmol, 1.05 equiv.), ammonium acetate (1.20 mmol, 7 equiv.) glacial acetic acid (2.41 mmol, 14 equiv.). The obtained suspension was heated for 12 h with a water separator under reflux. After cooling to room temperature, CH_2Cl_2 and H_2O (10 mL each) were added and the phases were

separated. The aqueous phase was extracted with CH_2Cl_2 (3×20 mL), the combined organic phases were washed with sat. NaCl solution (20 mL), dried over $MgSO_4$, and the solvent was then removed under reduced pressure. The respective crude product was purified by column chromatography on silica gel with a solvent gradient of PE to EE shown for each derivative individually and the desired product **Mal-k-PipC(n)** was obtained as a colored solid. The derivatives **Mal-k-C(n)F(m)** were afterwards recrystallized from PE (10 mL).

3) Synthesis of the *N*-donor building blocks (PipC(n)Br)



Scheme S3

***N*-(4-Bromophenyl)-4-(octyloxy)piperidine (PipC(8)Br):** According to GP1, yield: 522 mg, 1.42 mmol, 66 %, column chromatography on silica gel gradient PE : EE = 45 : 1 to 25 : 1 (R_f = 0.3). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.20–1.39 (m, 10H, 5×CH_2), 1.51–1.64 (m, 2H, OCH_2CH_2), 1.65–1.76 (m, 2H, 3-H), 1.91–2.04 (m, 2H, 3-H), 2.91 (ddd, *J* = 12.6 Hz, 9.3 Hz, 3.2 Hz, 2H, 2-H), 3.39–3.51 (m, 5H, 2-H, 4-H, OCH_2), 6.80 (d, *J* = 8.4 Hz, 2H, 6-H), 7.29–7.34 (m, 2H, 7-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.13 (CH_3), 22.69 (CH_3CH_2), 26.28 ($OCH_2CH_2CH_2$), 29.31, 29.48 (2×CH_2), 30.15 (OCH_2CH_2), 30.89 (C-3), 31.86 ($CH_3CH_2CH_2$), 47.16 (C-2), 68.10 (OCH_2), 74.29 (C-4), 111.22 (C-8), 118.00 (C-6), 131.82 (C-7), 150.41 (C-5) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2920 (m), 2851 (m), 1586 (w), 1566 (w), 1494 (m), 1466 (m), 1385 (w), 1365 (m), 1338 (w), 1311 (w), 1227 (m), 1183 (w), 1132 (m), 1109 (s), 999 (w), 959 (w), 914 (w), 825 (m), 817 (m), 748 (w), 723 (w), 710 (w), 665 (w), 536 (w), 516 (w), 420 (w) cm^{-1}. MS (ESI): *m*/*z* = 390.14 $[M+Na]^+$, 368.16 $[M+H]^+$, 290.25, 238.02. HRMS (ESI): calcd. for $[C_{19}H_{30}BrNO+H]^+$ 368.1584, found. 368.1578. M.p. (POM): 47 °C.

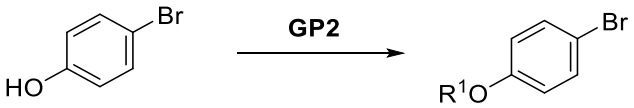
***N*-(4-Bromophenyl)-4-(decyloxy)piperidine (PipC(10)Br):** According to GP1, yield: 348 mg, 878 µmol, 41 %, column chromatography on silica gel gradient PE : EE = 50 : 1 to 30 : 1 (R_f = 0.2). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.20–1.39 (m, 14H, 7×CH_2), 1.53–1.62 (m, 2H, OCH_2CH_2), 1.65–1.75 (m, 2H, 3-H), 1.92–2.03 (m, 2H, 3-H), 2.91 (ddd, *J* = 12.6 Hz, 9.3 Hz, 3.2 Hz, 2H, 2-H), 3.39–3.51 (m, 5H, 2-H, 4-H, OCH_2), 6.80 (d, *J* = 8.4 Hz, 2H, 6-H), 7.29–7.34 (m, 2H, 7-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.15 (CH_3), 22.71 (CH_3CH_2), 26.27 ($OCH_2CH_2CH_2$), 29.35, 29.52, 29.61, 29.64 (4×CH_2), 30.15 (OCH_2CH_2), 30.89 (C-3), 31.93 ($CH_3CH_2CH_2$), 47.16 (C-2), 68.10 (OCH_2), 74.29 (C-4), 111.28

(C-8), 118.00 (C-6), 131.82 (C-7), 150.41 (C-5) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2951 (w), 2917 (s), 2849 (m), 1586 (w), 1566 (w), 1494 (m), 1466 (m), 1385 (w), 1365 (m), 1337 (w), 1303 (w), 1226 (m), 1182 (w), 1132 (w), 1108 (s), 1082 (m), 1040 (w), 1000 (w), 957 (w), 912 (w), 825 (m), 816 (m), 734 (w), 722 (w), 701 (w), 665 (w), 583 (w), 536 (w), 517 (w), 495 (w), 440 (w) cm^{-1}. MS (ESI): *m*/*z* = 396.19 $[M+H]^+$, 318.28, 238.02. HRMS (ESI): calcd. for $[C_{21}H_{34}BrNO+H]^+$ 396.1897, found. 368.1884. M.p. (POM): 54 °C.

***N*-(4-Bromophenyl)-4-(dodecyloxy)piperidine (PipC(12)Br):** According to GP1, yield: 214 mg, 504 µmol, 55 %, column chromatography on silica gel gradient PE : EE = 50 : 1 to 30 : 1 (R_f = 0.2). ^{1}H-NMR (700 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.0 Hz, 3H, CH_3), 1.22–1.37 (m, 18H, 9×CH_2), 1.57 (tt, *J* = 6.8 Hz, 7.0 Hz, 2H, OCH_2CH_2), 1.67–1.73 (m, 2H, 3-H), 1.93–2.00 (m, 2H, 3-H,), 2.88–2.94 (m, 2H, 2-H), 3.39–3.50 (m, 5H, 2-H, 4-H, OCH_2), 6.79 (d, *J* = 8.4 Hz, 2H, 6-H), 7.31 (d, *J* = 8.4 Hz, 2H, 7-H) ppm. ^{13}C-NMR (176 MHz, $CDCl_3$): δ = 14.15 (CH_3), 22.71 (CH_3CH_2), 26.27 ($OCH_2CH_2CH_2$), 29.38, 29.52, 29.64, 29.66, 29.69 (6×CH_2), 30.14 (OCH_2CH_2), 30.91 (C-3), 31.95 ($CH_3CH_2CH_2$), 47.14 (C-2), 68.10 (OCH_2), 74.30 (C-4), 111.28 (C-8), 117.98 (C-6), 131.82 (C-7), 150.43 (C-5) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2916 (s), 2849 (s), 1586 (w), 1567 (w), 1495 (m), 1466 (w), 1385 (w), 1365 (m), 1337 (w), 1303 (w), 1225 (m), 1182 (w), 1132 (m), 1108 (vs), 1040 (w), 1000 (w), 957 (w), 914 (w), 825 (m), 817 (m), 749 (w), 721 (w), 701 (w), 665 (m), 583 (w), 536 (w), 517 (w), 432 (w) cm^{-1}. MS (ESI): *m*/*z* = 424.22 $[M+H]^+$, 346.31, 240.02. HRMS (ESI): calcd. for $[C_{23}H_{38}BrNO+H]^+$ 424.2210, found: 424.2209. M.p. (POM): 63 °C.

***N*-(4-Bromophenyl)-4-(tetradecyloxy)piperidine (PipC(14)Br):** According to GP1, yield: 500 mg, 1.10 µmol, 51 %, column chromatography on silica gel gradient PE : EE = 55 : 1 to 35 : 1 (R_f = 0.3). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.22–1.38 (m, 22H, 11×CH_2), 1.53–1.60 (m, 2H, OCH_2CH_2), 1.65–1.75 (m, 2H, 3-H), 1.90–2.04 (m, 2H, 3-H), 2.91 (ddd, *J* = 12.5 Hz, 9.3 Hz, 3.2 Hz, 2H, 2-H), 3.39–3.51 (m, 5H, 2-H, 4-H, OCH_2), 6.80 (d, *J* = 8.4 Hz, 2H, 6-H), 7.29–7.34 (m, 2H, 7-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.16 (CH_3), 22.72 (CH_3CH_2), 26.27 ($OCH_2CH_2CH_2$), 29.39, 29.52, 29.65, 29.69, 29.71, 29.73 (8×CH_2), 30.15 (OCH_2CH_2), 30.89 (C-3), 31.95 ($CH_3CH_2CH_2$), 47.16 (C-2), 68.10 (OCH_2), 74.29 (C-4), 111.30 (C-8), 118.00 (C-6), 131.82 (C-7), 150.41 (C-5) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2951 (w), 2915 (s), 2849 (s), 1586 (w), 1566 (w), 1495 (m), 1467 (m), 1386 (w), 1365 (m), 1337 (w), 1304 (w), 1228 (m), 1182 (w), 1110 (s), 1040 (w), 999 (w), 957 (w), 914 (w), 825 (m), 817 (m), 720 (w), 665 (w), 536 (w), 517 (w) cm^{-1}. MS (ESI): *m*/*z* = 474.23 $[M+Na]^+$, 452.25 $[M+H]^+$, 374.34, 240.02. HRMS (ESI): calcd. for $[C_{25}H_{42}BrNO+H]^+$ 452.2523, found: 424.2511. M.p. (POM): 68 °C.

4) Synthesis of the *O*-donor building blocks (C(n)F(m)Br)



C(n)F(m)Br

Scheme S4

1-Bromo-4-(octyloxy)benzene (C(8)Br): According to GP2, yield: 3.24 g, 11.40 mmol, 98 %. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.7 Hz, 3H, CH_3), 1.22–1.40 (m, 8H, 4×CH_2), 1.39–1.49 (m, 2H, $OCH_2CH_2CH_2$), 1.71–1.82 (m, 2H, OCH_2CH_2), 3.91 (t, *J* = 6.6 Hz, 2H, OCH_2), 6.73–6.81 (m, 2H, 3-H), 7.32–7.40 (m, 2H, 2-H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 14.09 (CH_3), 22.65 (CH_3CH_2), 26.01 ($OCH_2CH_2CH_2$), 29.18, 29.22, 29.33 (3×CH_2), 31.81 ($CH_3CH_2CH_2$), 68.29 (OCH_2), 112.55 (C-1), 116.32 (C-3), 132.19 (C-2), 158.28 (C-4) ppm.

The spectroscopic data are in accordance to literature.[13]

1-Bromo-4-(decyloxy)benzene (C(10)Br): According to GP2, yield: 5.41 g, 17.30 mmol, 100 %. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.6 Hz, 3H, CH_3), 1.20–1.40 (m, 12H, 6×CH_2), 1.39–1.49 (m, 2H, $OCH_2CH_2CH_2$), 1.72–1.81 (m, 2H, OCH_2CH_2), 3.91 (t, *J* = 6.5 Hz, 2H, OCH_2), 6.75–6.80 (m, 2H, 3-H), 7.31–7.40 (m, 2H, 2-H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 14.11 (CH_3), 22.68 (CH_3CH_2), 26.00 ($OCH_2CH_2CH_2$), 29.18, 29.32, 29.37, 29.55, 29.57 (5×CH_2), 31.90 ($CH_3CH_2CH_2$), 68.29 (OCH_2), 112.55 (C-1), 116.32 (C-3), 132.19 (C-2), 158.28 (C-4) ppm.

The spectroscopic data are in accordance to literature.[10]

1-Bromo-4-(dodecyloxy)benzene (C(12)Br): According to GP2, yield: 10.50 g, 30.80 mmol, 97 %. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.7 Hz, 3H, CH_3), 1.22–1.40 (m, 16H, 8×CH_2), 1.40–1.49 (m, 2H, $OCH_2CH_2CH_2$), 1.71–1.82 (m, 2H, OCH_2CH_2), 3.91 (t, *J* = 6.6 Hz, 2H, OCH_2), 6.74–6.80 (m, 2H, 3-H), 7.32–7.40 (m, 2H, 2-H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 14.12 (CH_3), 22.70 (CH_3CH_2), 26.00 ($OCH_2CH_2CH_2$), 29.18, 29.35, 29.38, 29.57, 29.59, 29.64, 29.66 (7×CH_2), 31.93 ($CH_3CH_2CH_2$), 68.29 (OCH_2), 112.55 (C-1), 116.32 (C-3), 132.18 (C-2), 158.28 (C-4) ppm. M.p. (POM): 34 °C.

The spectroscopic data are in accordance to literature.[13]

1-Bromo-4-(tetradecyloxy)benzene (C(14)Br): According to GP2, yield: 9.10 g, 24.60 mmol, 95 %. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.7 Hz, 3H, CH_3), 1.22–1.40 (m, 20H, 10×CH_2), 1.38–1.50 (m, 2H, $OCH_2CH_2CH_2$), 1.71–1.82 (m, 2H, OCH_2CH_2), 3.91 (t, *J* = 6.6 Hz, 2H, OCH_2), 6.73–6.83 (m, 2H, 3-H), 7.31–7.42 (m, 2H, 2-H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 14.12 (CH_3), 22.70 (CH_3CH_2), 26.00 ($OCH_2CH_2CH_2$), 29.18, 29.37, 29.57, 29.60,

29.66, 29.68, 29.70 (9×CH_2), 31.94 ($CH_3CH_2CH_2$), 68.29 (OCH_2), 112.56 (C-1), 116.32 (C-3), 132.18 (C-2), 158.28 (C-4) ppm. M.p. (POM): 42 °C.

The spectroscopic data are in accordance to literature.[10]

1-Bromo-4-(5,5,6,6,7,7,8,8,8)-nonafluorooctyloxy)benzene (C(4)F(4)Br): According to GP2, yield: 2.31 g, 5.01 mmol, 92 %. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.73–1.92 (m, 4H, OCH_2CH_2, $OCH_2CH_2CH_2$), 2.09–2.23 (m, 2H, CF_2CH_2), 3.96 (t, *J* = 5.9 Hz, 2H, OCH_2), 6.74–6.80 (m, 2H, 3-H), 7.33–7.41 (m, 2H, 2-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 17.25 ($CF_2CH_2CH_2$), 28.62 (OCH_2CH_2), 30.56 (t, CF_2CH_2), 67.43 (OCH_2), 112.97 (C-1), 116.24 (C-3), 111–120 (m, CF_2, CF_3), 132.30 (C-2), 157.92 (C-4) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.03, -124.49, -114.63, -81.07 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2953 (w), 2929 (w), 2880 (w), 1591 (w), 1579 (w), 1489 (m), 1474 (w), 1438 (w), 1391 (w), 1355 (w), 1285 (w), 1218 (vs), 1171 (m), 1132 (s), 1072 (w), 1037 (w), 1003 (w), 958 (w), 928 (w), 879 (w), 849 (w), 822 (m), 735 (w), 717 (w), 640 (w), 598 (w), 531 (w), 506 (w), 418 (w) cm^{-1}. MS (EI): *m*/*z* = 446.0 $[M]^+$, 172.0 $[Educt]^+$. HRMS (EI): calcd. For $[C_{14}H_{12}BrF_9O]^+$ 445.9928, found 445.9933.

1-Bromo-4-(5,5,6,6,7,7,8,8,9,9,10,10,10)-tridecafluorodecyloxy)benzene (C(4)F(6)Br): According to GP2, yield: 2.91 g, 5.32 mmol, 97 %. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.75–1.93 (m, 4H, OCH_2CH_2, $OCH_2CH_2CH_2$), 2.16 (tt, *J* = 18.5 Hz, 7.6 Hz, 2H, CF_2CH_2), 3.96 (t, *J* = 5.8 Hz, 2H, OCH_2), 6.74–6.80 (m, 2H, 3-H), 7.34–7.41 (m, 2H, 2-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 17.27 ($CF_2CH_2CH_2$), 28.62 (OCH_2CH_2), 30.66 (t, CF_2CH_2), 67.43 (OCH_2), 112.97 (C-1), 116.24 (C-3), 109–120 (m, CF_2, CF_3), 132.30 (C-2), 157.92 (C-4) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.15, -123.54, -122.87, -121.90, -114.40, -80.84 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2948 (w), 2931 (w), 2881 (w), 1591 (w), 1579 (w), 1489 (m), 1474 (w), 1438 (w), 1391 (w), 1364 (w), 1285 (w), 1234 (vs), 1171 (s), 1142 (vs), 1122 (m), 1071 (m), 1036 (m), 1003 (w), 956 (w), 911 (w), 844 (w), 821 (m), 730 (m), 707 (m), 696 (m), 640 (m), 602 (w), 566 (w), 531 (w), 506 (w), 416 (w) cm^{-1}. MS (EI): *m*/*z* = 546.0 $[M]^+$, 172.0 $[Educt]^+$. HRMS (EI): calcd. for $[C_{16}H_{12}BrF_{13}O]^+$ 545.9864, found 545.9857.

1-Bromo-4-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,11,12,12,12)-heptadecafluorododecyloxy)-benzene (C(4)F(8)Br): According to GP2, yield: 2.91 g, 5.24 mmol, 95 %. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.78–1.92 (m, 4H, OCH_2CH_2, $OCH_2CH_2CH_2$), 2.09–2.23 (m, 2H, CF_2CH_2), 3.96 (t, *J* = 5.8 Hz, 2H, OCH_2), 6.74–6.80 (m, 2H, 3-H), 7.34–7.41 (m, 2H, 2-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 17.26 ($CF_2CH_2CH_2$), 28.62 (OCH_2CH_2), 30.66 (t, CF_2CH_2), 67.42 (OCH_2), 112.96 (C-1), 116.23 (C-3), 107–121 (m, CF_2, CF_3), 132.29 (C-2), 157.93 (C-4) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.15, -123.52, -122.75, -121.97, -121.92, -121.75, -114.43, -80.87 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2956 (w), 2927 (w), 2883 (w), 2854 (w), 1591 (w), 1489 (w), 1471 (w), 1439 (w), 1387 (w), 1371 (w), 1330 (w), 1285 (w), 1238 (s), 1202 (vs), 1143 (vs), 1115 (m), 1070 (w), 1034 (w), 1003 (w), 956 (w), 907 (m), 823 (m),

802 (w), 732 (s), 704 (m), 650 (m), 623 (w), 603 (w), 559 (w), 529 (w), 506 (w), 455 (w), 417 (w) cm^{-1}. MS (EI): *m*/*z* = 646.0 $[M]^+$, 172.0 $[Educt]^+$. HRMS (EI): calcd. for $[C_{18}H_{12}BrF_{17}O]^+$ 645.9800, found 645.9790. M.p. (POM): 58 °C.

1-Bromo-4-(7,7,8,8,9,9,10,10,10)-nonafluorodecyloxy)benzene (C(6)F(4)Br): According to GP2, yield: 2.45 g, 5.16 mmol, 95 %. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.41–1.56 (m, 4H, 2×CH_2), 1.60–1.69 (m, 2H, $CF_2CH_2CH_2$), 1.75–1.84 (m, 2H, OCH_2CH_2), 2.07 (tt, *J* = 18.7 Hz, 7.9 Hz, 2H, CF_2CH_2), 3.92 (t, *J* = 6.4 Hz, 2H, OCH_2), 6.73–6.80 (m, 2H, 3-H), 7.33–7.40 (m, 2H, 2-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 20.06 ($CF_2CH_2CH_2$), 25.74, 28.84 (2×CH_2), 28.93 (OCH_2CH_2), 30.71 (t, CF_2CH_2), 67.92 (OCH_2), 112.71 (C-1), 116.26 (C-3), 112–121 (m, CF_2, CF_3), 132.24 (C-2), 158.14 (C-4) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.04, -124.49, -114.57, -81.08 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2945 (w), 2865 (w), 1592 (w), 1578 (w), 1489 (m), 1472 (w), 1388 (w), 1355 (w), 1285 (w), 1217 (vs), 1169 (s), 1130 (vs), 1072 (w), 1046 (w), 1003 (m), 927 (w), 878 (m), 847 (w), 821 (s), 733 (m), 717 (m), 641 (w), 599 (w), 532 (w), 506 (w) cm^{-1}. MS (EI): *m*/*z* = 474.0 $[M]^+$, 171.9 $[Educt]^+$. HRMS (EI): calcd. for $[C_{16}H_{16}BrF_9O]^+$ 474.0241, found 474.0235.

1-Bromo-4-(7,7,8,8,9,9,10,10,11,11,12,12,12)-tridecafluorododecyloxy)benzene (C(6)F(6)Br): According to GP2, yield: 2.90 g, 5.04 mmol, 97 %. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.42–1.56 (m, 4H, 2×CH_2), 1.60–1.69 (m, 2H, $CF_2CH_2CH_2$), 1.76–1.83 (m, 2H, OCH_2CH_2), 2.07 (tt, *J* = 18.6 Hz, 7.8 Hz, 2H, CF_2CH_2), 3.92 (t, *J* = 6.3 Hz, 2H, OCH_2), 6.74–6.80 (m, 2H, 3-H), 7.33–7.40 (m, 2H, 2-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 20.08 ($CF_2CH_2CH_2$), 25.74, 28.84 (2×CH_2), 28.94 (OCH_2CH_2), 30.81 (t, CF_2CH_2), 67.92 (OCH_2), 112.71 (C-1), 116.25 (C-3), 107–121 (m, CF_2, CF_3), 132.24 (C-2), 158.15 (C-4) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.16, -123.56, -122.89, -121.94, -114.37, -80.86 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2946 (w), 2863 (w), 1591 (w), 1578 (w), 1489 (m), 1472 (w), 1438 (w), 1386 (w), 1365 (w), 1317 (w), 1285 (w), 1236 (vs), 1170 (s), 1143 (vs), 1122 (m), 1071 (w), 1048 (w), 1002 (w), 908 (m), 844 (w), 822 (m), 731 (vs), 707 (w), 696 (m), 650 (w), 602 (w), 567 (w), 532 (w), 505 (w), 469 (w) cm^{-1}. MS (EI): *m*/*z* = 574.0 $[M]^+$, 172.0 $[Educt]^+$. HRMS (EI): calcd. for $[C_{18}H_{16}BrF_{13}O]^+$ 574.0177, found: 574.0177. M.p. (POM): 42 °C.

1-Bromo-4-(7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14)-heptadecafluorotetra-decyloxy)benzene (C(6)F(8)Br): According to GP2, yield: 3.35 g, 4.96 mmol, 96 %. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.41–1.56 (m, 4H, 2×CH_2), 1.60–1.69 (m, 2H, $CF_2CH_2CH_2$), 1.79 (dt, *J* = 8.0 Hz, 6.3 Hz, 2H, OCH_2CH_2), 2.07 (tt, *J* = 18.8 Hz, 8.0 Hz, 2H, CF_2CH_2), 3.92 (t, *J* = 6.3 Hz, 2H, OCH_2), 6.74–6.80 (m, 2H, 3-H), 7.32–7.40 (m, 2H, 2-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 20.09 ($CF_2CH_2CH_2$), 25.74, 28.84 (2×CH_2), 28.93 (OCH_2CH_2), 30.81 (t, CF_2CH_2), 67.92 (OCH_2), 112.70 (C-1), 116.25 (C-3), 107–121 (m, CF_2, CF_3), 132.24 (C-2), 158.15 (C-4) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.12, -123.53, -122.73, -121.96, -

121.91, -121.73, -114.36, -80.84 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2947 (w), 1592 (w), 1489 (w), 1471 (w), 1285 (w), 1239 (m), 1204 (m), 1172 (w), 1147 (m), 1116 (w), 1072 (w), 1002 (w), 906 (s), 823 (w), 804 (w), 728 (vs), 651 (w), 602 (w), 558 (w), 530 (w), 507 (w) cm^{-1}. MS (EI): *m*/*z* = 674.0 $[M]^+$, 172.0 $[Educt]^+$. HRMS (EI): calcd. for $[C_{20}H_{16}BrF_{17}O]^+$ 674.0113, found: 674.0119. M.p. (POM): 70 °C.

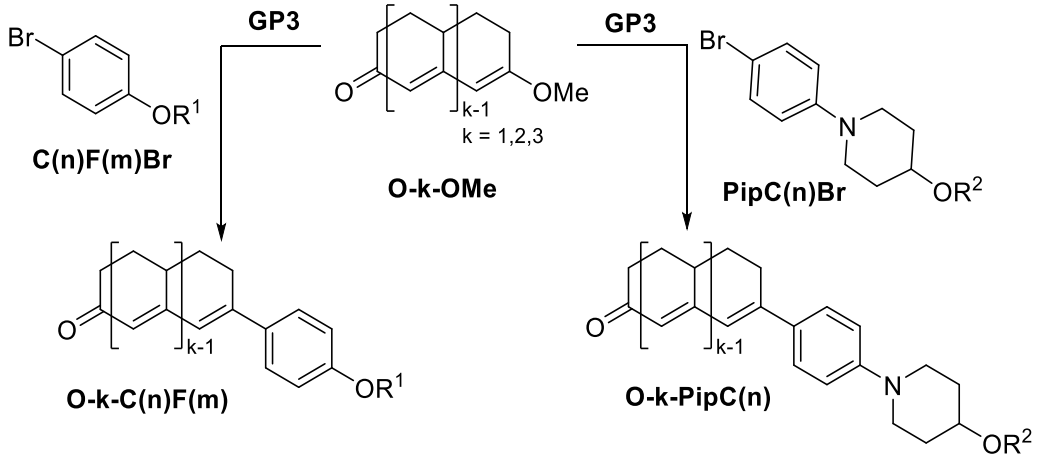
1-Bromo-4-(9,9,10,10,11,11,12,12,12)-nonafluorododecyloxy)benzene (C(8)F(4)Br): According to GP2, yield: 2.62 g, 5.21 mmol, 93 %. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.30–1.43 (m, 6H, 3×CH_2), 1.43–1.50 (m, 2H, $OCH_2CH_2CH_2$), 1.53–1.67 (m, 2H, $CF_2CH_2CH_2$), 1.73–1.82 (m, 2H, OCH_2CH_2), 1.98–2.13 (m, 2H, CF_2CH_2), 3.92 (t, *J* = 6.5 Hz, 2H, OCH_2), 6.73–6.81 (m, 2H, 3-H), 7.33–7.39 (m, 2H, 2-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 20.07 ($CF_2CH_2CH_2$), 25.94, 29.03, 29.11, 29.13, 29.15 (5×CH_2), 30.77 (t, CF_2CH_2), 68.14 (OCH_2), 112.61 (C-1), 116.28 (C-3), 117–121 (m, CF_2, CF_3), 132.21 (C-2), 158.23 (C-4) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.06, -124.52, -114.59, -81.11 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2933 (w), 2859 (w), 1591 (w), 1578 (w), 1489 (m), 1471 (w), 1438 (w), 1387 (w), 1355 (w), 1285 (w), 1217 (vs), 1169 (s), 1131 (vs), 1072 (w), 1049 (w), 1003 (m), 909 (w), 879 (m), 847 (w), 821 (m), 734 (w), 717 (m), 641 (w), 599 (w), 531 (w), 506 (w) cm^{-1}. MS (EI): *m*/*z* = 502.1 $[M]^+$, 172.0 $[Educt]^+$. HRMS (EI): calcd. for $[C_{18}H_{20}BrF_9O]^+$ 502.0554, found: 502.0551.

1-Bromo-4-(9,9,10,10,11,11,12,12,13,13,14,14,14)-tridecafluorotetradecyloxy)benzene (C(8)F(6)Br): According to GP2, yield: 3.05 g, 5.06 mmol, 92 %. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.32–1.43 (m, 6H, 3×CH_2), 1.43–1.50 (m, 2H, $OCH_2CH_2CH_2$), 1.56–1.67 (m, 2H, $CF_2CH_2CH_2$), 1.73–1.84 (m, 2H, OCH_2CH_2), 2.05 (tt, *J* = 18.8 Hz, 7.6 Hz, 2H, CF_2CH_2), 3.92 (t, *J* = 6.5 Hz, 2H, OCH_2), 6.72–6.80 (m, 2H, 3-H), 7.32–7.39 (m, 2H, 2-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 20.09 ($CF_2CH_2CH_2$), 25.94, 29.03, 29.11, 29.13, 29.15 (5×CH_2), 30.87 (t, CF_2CH_2), 68.14 (OCH_2), 112.61 (C-1), 116.28 (C-3), 107–121 (m, CF_2, CF_3), 132.21 (C-2), 158.23 (C-4) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.15, -123.56, -122.89, -121.94, -114.37, -80.84 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2937 (w), 2859 (w), 1591 (w), 1578 (w), 1489 (m), 1472 (w), 1365 (w), 1286 (w), 1236 (vs), 1170 (s), 1143 (vs), 1122 (w), 1071 (w), 1051 (w), 1025 (w), 1002 (w), 908 (w), 844 (w), 821 (m), 732 (s), 707 (w), 696 (w), 643 (w), 602 (w), 567 (w), 531 (w), 506 (w), 440 (w) cm^{-1}. MS (EI): *m*/*z* = 602.1 $[M]^+$, 172.0 $[Educt]^+$. HRMS (EI): calcd. for $[C_{20}H_{20}BrF_{13}O]^+$ 602.0490, found: 602.0488. M.p. (POM): 40 °C.

1-Bromo-4-(9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16)-heptadecafluorohexadecyloxy)benzene (C(8)F(8)Br): According to GP2, yield: 3.27 g, 4.65 mmol, 95 %. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.33–1.42 (m, 6H, 3×CH_2), 1.42–1.50 (m, 2H, $OCH_2CH_2CH_2$), 1.56–1.67 (m, 2H, $CF_2CH_2CH_2$), 1.69–1.82 (m, 2H, OCH_2CH_2), 2.05 (tt, *J* = 19.0 Hz, 8.2 Hz, 2H, CF_2CH_2), 3.92 (t, *J* = 6.5 Hz, 2H, OCH_2), 6.74–6.80 (m, 2H, 3-H), 7.33–7.39 (m, 2H, 2-

H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 20.09 ($CF_2CH_2CH_2$), 25.94, 29.03, 29.11, 29.13, 29.15 (5×CH_2), 30.87 (t, CF_2CH_2), 68.14 (OCH_2), 112.61 (C-1), 116.27 (C-3), 107–121 (m, CF_2, CF_3), 132.21 (C-2), 158.23 (C-4) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.13, -123.55, -122.74, -121.97, -121.92, -121.74, -114.37, -80.85 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2939 (w), 2860 (w), 1591 (w), 1489 (w), 1471 (w), 1285 (w), 1239 (s), 1206 (s), 1172 (w), 1147 (m), 1072 (w), 1026 (w), 1003 (w), 905 (vs), 823 (w), 728 (vs), 650 (m), 602 (w), 559 (w), 530 (w), 506 (w) cm^{-1}. MS (EI): *m*/*z* = 702.1 $[M]^+$, 172.0 $[Educt]^+$. HRMS (EI): calcd. for $[C_{22}H_{20}BrF_{17}O]^+$ 702.0430, found: 602.0426. M.p. (POM): 62 °C.

5) Synthesis of the chromophoric core (O-k-) with the respective donor units (-C(n)F(m) and -PipC(n))



Scheme S1

3-(4-(Octyloxy)phenyl)-cyclohex-2-enone (O-1-C(8)): According to GP3, yield: 322 mg, 1.07 mmol, 54 %, column chromatography on silica gel gradient PE : EE = 8 : 1 to 3 : 1 (R_f = 0.5). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.21–1.40 (m, 8H, 4×CH_2), 1.42–1.50 (m, 2H, $OCH_2CH_2CH_2$), 1.74–1.83 (m, 2H, OCH_2CH_2), 2.09–2.18 (m, 2H, 5-H), 2.43–2.49 (m, 2H, 6-H), 2.74 (dt, *J* = 6.1 Hz, 1.5 Hz, 2H, 4-H), 3.98 (t, *J* = 6.6 Hz, 2H, OCH_2), 6.39 (d, *J* = 1.5 Hz, 1H, 2-H), 6.88–6.94 (m, 2H, 3'-H), 7.47–7.54 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.12 (CH_3), 22.68 ($CH_3CH_2CH_2$), 22.80 (C-5), 26.02 ($OCH_2CH_2CH_2$), 27.86 (C-4), 29.18, 29.25 (2×CH_2), 29.35 (OCH_2CH_2), 31.82 (CH_3CH_2), 37.23 (C-6), 68.19 (OCH_2), 114.66 (C-3'), 123.57 (C-2), 127.62 (C-2'), 130.52 (C-1'), 159.22 (C-3), 160.88 (C-4'), 199.97 (C-1) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2924 (m), 2854 (w), 1660 (s), 1595 (s), 1568 (w), 1511 (s), 1468 (w), 1420 (w), 1366 (w), 1348 (w), 1325 (w), 1280 (m), 1242 (vs), 1181 (vs), 1135 (w), 1025 (w), 984 (w), 957 (w), 886 (w), 823 (m), 748 (w), 724 (w), 640 (w), 606 (w), 566 (w), 519 (w), 503 (w), 442 (w) cm^{-1}. MS (ESI): *m*/*z* = 323.20 $[M+Na]^+$, 301.21 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{20}H_{28}O_2+Na]^+$ 323.1982, found: 323.1966.

7-(4-(Octyloxy)phenyl)-4,4a,5,6-tetrahydronaphthalene-2(3*H*)-one (O-2-C(8)): According to GP3, yield: 473 mg, 1.34 mmol, 68 %, column chromatography on silica gel gradient PE : EE = 7 : 1 to 3 : 1 (R_f = 0.4). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 3H, CH_3), 1.18–1.41 (m, 8H, 4×CH_2), 1.42–1.49 (m, 2H, $OCH_2CH_2CH_2$), 1.55 (qd, *J* = 12.9 Hz, 4.9 Hz, 1H, 5-H), 1.70–1.82 (m, 3H, 4-H, OCH_2CH_2), 2.06–2.16 (m, 2H, 4-H, 5-H), 2.44 (ddd, *J* = 16.9 Hz, 14.5 Hz, 5.0 Hz, 1H, 3-H), 2.49–2.57 (m, 2H, 3-H, 4a-H), 2.61–2.71 (m, 1H, 6-H), 2.78 (ddd, *J* = 17.8 Hz, 4.9 Hz, 2.2 Hz, 1H, 6-H), 3.97 (t, *J* = 6.6 Hz, 2H, OCH_2), 5.87 (d, *J* = 2.7 Hz, 1H, 1-H), 6.59 (d, *J* = 2.2 Hz, 1H, 8-H), 6.87–6.93 (m, 2H, 3'-H), 7.44–7.49 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.13 (CH_3), 22.68 ($CH_3CH_2CH_2$), 26.04 ($OCH_2CH_2CH_2$), 28.25 (C-6), 29.23, 29.25 (2×CH_2), 29.37 (OCH_2CH_2), 29.78 (C-5), 30.14 (C-4), 31.83 (CH_3CH_2), 35.42 (C-4a), 37.95 (C-3), 68.15 (OCH_2), 114.54 (C-3'), 123.04 (C-8), 123.65 (C-1), 126.95 (C-2'), 131.84 (C-1'), 147.82 (C-7), 159.54 (C-8a), 159.90 (C-4'), 200.16 (C-2) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2923 (m), 2854 (m), 1652 (s), 1590 (s), 1576 (s), 1510 (s), 1468 (w), 1454 (w), 1422 (w), 1368 (w), 1348 (w), 1324 (w), 1282 (m), 1252 (s), 1180 (vs), 1143 (w), 1119 (w), 1023 (w), 1002 (w), 960 (w), 918 (w), 897 (w), 833 (m), 809 (w), 741 (w), 724 (w), 699 (w), 631 (w), 588 (w), 559 (w), 519 (w), 467 (w), 412 (w) cm^{-1}. MS (ESI): *m*/*z* = 375.23 $[M+Na]^+$, 353.25 $[M+H]^+$, 227.14, 205.16. HRMS (ESI): calcd. for $[C_{24}H_{32}O_2+H]^+$ 353.2475, found: 353.2460.

3-(4-(Decyloxy)phenyl)-cyclohex-2-enone (O-1-C(10)): According to GP3, yield: 248 mg, 755 µmol, 53 %, column chromatography on silica gel gradient PE : EE = 8 : 1 to 3 : 1 (R_f = 0.5). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 3H, CH_3), 1.19–1.40 (m, 12H, 6×CH_2), 1.39–1.51 (m, 2H, $OCH_2CH_2CH_2$), 1.74–1.83 (m, 2H, OCH_2CH_2), 2.09–2.17 (m, 2H, 5-H), 2.46 (dd, *J* = 7.4 Hz, 6.0 Hz, 2H, 6-H), 2.75 (dt, *J* = 6.1 Hz, 1.4 Hz, 2H, 4-H), 3.98 (t, *J* = 6.6 Hz, 2H, OCH_2), 6.39 (t, *J* = 1.4 Hz, 1H, 2-H), 6.89–6.93 (m, 2H, 3'-H), 7.48–7.52 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.14 (CH_3), 22.70 ($CH_3CH_2CH_2$), 22.80 (C-5), 26.02 ($OCH_2CH_2CH_2$), 27.86 (C-4), 29.17, 29.33, 29.39, 29.57, 29.58 (5×CH_2), 31.91 (CH_3CH_2), 37.22 (C-6), 68.19 (OCH_2), 114.66 (C-3'), 123.57 (C-2), 127.62 (C-2'), 130.52 (C-1'), 159.23 (C-3), 160.88 (C-4'), 199.98 (C-1) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2954 (m), 2933 (m), 2919 (vs), 2872 (m), 2852 (s), 1651 (vs), 1569 (m), 1509 (m), 1474 (m), 1464 (m), 1417 (m), 1395 (w), 1367 (w), 1351 (w), 1331 (w), 1314 (w), 1275 (s), 1260 (s), 1240 (vs), 1184 (s), 1144 (m), 1116 (w), 1050 (w), 1020 (m), 996 (w), 983 (w), 959 (w), 884 (w), 856 (w), 824 (m), 817 (m), 803 (w), 751 (w), 720 (w), 648 (w), 604 (w), 566 (w), 518 (w), 506 (w), 451 (w) cm^{-1}. MS (ESI): *m*/*z* = 679.47 $[2M+Na]^+$, 351.23 $[M+Na]^+$, 329.25 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{22}H_{32}O_2+H]^+$ 329.2475, found: 329.2474. M.p. (POM): 50 °C.

7-(4-(Decyloxy)phenyl)-4,4a,5,6-tetrahydronaphthalene-2(3*H*)-one (O-2-C(10)): According to GP3, yield: 1.13 g, 2.97 mmol, 53 %, column chromatography on silica gel gradient PE : EE

= 6 : 1 to 2 : 1 (R_f = 0.4). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.22–1.39 (m, 12H, 6×CH_2), 1.41–1.49 (m, 2H, $OCH_2CH_2CH_2$), 1.54 (qd, *J* = 12.8 Hz, 4.9 Hz, 1H, 5-H), 1.69–1.83 (m, 3H, 4-H, OCH_2CH_2), 2.05–2.17 (m, 2H, 4-H, 5-H), 2.44 (ddd, *J* = 16.9 Hz, 14.5 Hz, 5.0 Hz, 1H, 3-H), 2.49–2.57 (m, 2H, 3-H, 4a-H), 2.65 (dddd, *J* = 17.7 Hz, 12.3 Hz, 4.9 Hz, 2.3 Hz, 1H, 6-H), 2.78 (ddd, *J* = 17.8 Hz, 4.9 Hz, 2.3 Hz, 1H, 6-H), 3.97 (t, *J* = 6.6 Hz, 2H, OCH_2), 5.87 (d, *J* = 2.3 Hz, 1H, 1-H), 6.59 (d, *J* = 2.3 Hz, 1H, 8-H), 6.86–6.92 (m, 2H, 3'-H), 7.44–7.50 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.15 (CH_3), 22.70 ($CH_3CH_2CH_2$), 26.04 ($OCH_2CH_2CH_2$), 28.24 (C-6), 29.23, 29.34, 29.41, 29.58, 29.59, (5×CH_2) 29.78 (C-5), 30.14 (C-4), 31.92 (CH_3CH_2), 35.41 (C-4a), 37.96 (C-3), 68.14 (OCH_2), 114.54 (C-3'), 123.03 (C-8), 123.66 (C-1), 126.94 (C-2'), 131.83 (C-1'), 147.80 (C-7), 159.51 (C-8a), 159.90 (C-4'), 200.12 (C-2) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2921 (s), 2852 (m), 1652 (vs), 1590 (s), 1577 (s), 1510 (s), 1468 (m), 1453 (m), 1421 (w), 1367 (m), 1323 (m), 1281 (m), 1252 (s), 1182 (vs), 1143 (w), 1119 (w), 1022 (m), 1002 (m), 959 (w), 918 (w), 897 (w), 833 (m), 810 (w), 758 (w), 741 (w), 699 (w), 630 (w), 588 (w), 559 (w), 520 (w), 467 (w) cm^{-1}. MS (ESI): *m*/*z* = 783.53 $[2M+Na]^+$, 403.26 $[M+Na]^+$, 381.28 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{26}H_{36}O_2+H]^+$ 381.2788, found: 381.2785. M.p. (POM): 66 °C.

3-(4-(Dodecyloxy)phenyl)-cyclohex-2-enone (O-1-C(12)): According to GP3, yield: 274 mg, 768 µmol, 54 %, column chromatography on silica gel gradient PE : EE = 8 : 1 to 3 : 1 (R_f = 0.5). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.17–1.41 (m, 16H, 8×CH_2), 1.40–1.48 (m, 2H, $OCH_2CH_2CH_2$), 1.74–1.83 (m, 2H, OCH_2CH_2), 2.09–2.17 (m, 2H, 5-H), 2.46 (dd, *J* = 7.4 Hz, 6.0 Hz, 2H, 6-H), 2.74 (dt, *J* = 6.1 Hz, 1.5 Hz, 2H, 4-H), 3.98 (t, *J* = 6.5 Hz, 2H, OCH_2), 6.39 (d, *J* = 1.5 Hz, 1H, 2-H), 6.88–6.94 (m, 2H, 3'-H), 7.47–7.53 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.15 (CH_3), 22.71 ($CH_3CH_2CH_2$), 22.80 (C-5), 26.02 ($OCH_2CH_2CH_2$), 27.86 (C-4), 29.17, 29.37, 29.39, 29.58, 29.61, 29.65, 29.68 (7×CH_2), 31.94 (CH_3CH_2), 37.22 (C-6), 68.18 (OCH_2), 114.66 (C-3'), 123.57 (C-2), 127.62 (C-2'), 130.51 (C-1'), 159.21 (C-3), 160.88 (C-4'), 199.97 (C-1) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2954 (m), 2917 (vs), 2872 (m), 2851 (s), 1650 (vs), 1604 (s), 1569 (w), 1509 (m), 1474 (w), 1463 (w), 1417 (w), 1395 (w), 1367 (w), 1351 (w), 1331 (w), 1314 (w), 1276 (s), 1260 (s), 1240 (s), 1184 (s), 1145 (w), 1116 (w), 1026 (w), 1003 (w), 984 (w), 959 (w), 884 (w), 855 (w), 824 (m), 816 (m), 803 (w), 766 (w), 751 (w), 730 (w), 648 (w), 604 (w), 566 (w), 518 (w), 508 (w), 471 (w), 444 (w), 411 (w) cm^{-1}. MS (ESI): *m*/*z* = 735.53 $[2M+Na]^+$, 379.26 $[M+Na]^+$, 357.28 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{24}H_{36}O_2+H]^+$ 357.2788, found: 357.2789. M.p. (POM): 65 °C.

7-(4-(Dodecyloxy)phenyl)-4,4a,5,6-tetrahydronaphthalene-2(3*H*)-one (O-2-C(12)): According to GP3, yield: 1.32 g, 3.23 mmol, 58 %, column chromatography on silica gel gradient PE : EE = 8 : 1 to 2 : 1 (R_f = 0.5). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz,

3H, CH_3), 1.20–1.39 (m, 16H, 8×CH_2), 1.41–1.49 (m, 2H, $OCH_2CH_2CH_2$), 1.55 (qd, *J* = 12.9 Hz, 4.9 Hz, 1H, 5-H), 1.71–1.82 (m, 3H, 4-H, OCH_2CH_2), 2.05–2.19 (m, 2H, 4-H, 5-H), 2.44 (ddd, *J* = 16.9 Hz, 14.4 Hz, 5.0 Hz, 1H, 3-H), 2.49–2.58 (m, 2H, 3-H, 4a-H), 2.66 (dddd, *J* = 17.7 Hz, 12.3 Hz, 4.8 Hz, 2.4 Hz, 1H, 6-H), 2.78 (ddd, *J* = 17.9 Hz, 4.9 Hz, 2.1 Hz, 1H, 6-H), 3.98 (t, *J* = 6.6 Hz, 2H, OCH_2), 5.88 (s, 1H, 1-H), 6.59 (d, *J* = 2.2 Hz, 1H, 8-H), 6.86–6.93 (m, 2H, 3'-H), 7.44–7.51 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.13 (CH_3), 22.69 ($CH_3CH_2CH_2$), 26.02 ($OCH_2CH_2CH_2$), 28.23 (C-6), 29.21, 29.35, 29.39, 29.57, 29.60, 29.64, 29.66 (7×CH_2), 29.77 (C-5), 30.14 (C-4), 31.92 (CH_3CH_2), 35.40 (C-4a), 37.95 (C-3), 68.13 (OCH_2), 114.53 (C-3'), 123.04 (C-8), 123.66 (C-1), 126.92 (C-2'), 131.83 (C-1'), 147.76 (C-7), 159.45 (C-8a), 159.89 (C-4'), 200.07 (C-2) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2918 (vs), 2851 (s), 1652 (vs), 1594 (s), 1579 (s), 1510 (s), 1473 (m), 1420 (w), 1367 (m), 1326 (m), 1279 (m), 1254 (vs), 1182 (s), 1143 (w), 1117 (w), 1080 (w), 1026 (w), 1004 (w), 960 (w), 918 (w), 895 (w), 832 (m), 811 (w), 721 (w), 701 (w), 630 (w), 557 (w), 521 (w), 464 (w) cm^{-1}. MS (ESI): *m*/*z* = 431.29 $[M+Na]^+$. HRMS (ESI): calcd. for $[C_{28}H_{40}O_2+Na]^+$ 431.2921, found: 431.2924. M.p. (POM): 68 °C.

7-(4-(Dodecyloxy)phenyl)-4,4a,5,6,10,10a-hexahydroanthracene-2(3*H*)-one (O-3-C(12)): According to GP3, yield: 221 mg, 480 µmol, 44 %, column chromatography on silica gel gradient PE : EE = 8 : 1 to 4 : 1 (R_f = 0.3). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.18–1.39 (m, 17H, 10-H, 8×CH_2), 1.40–1.54 (m, 3H, 5-H, $OCH_2CH_2CH_2$), 1.68–1.82 (m, 3H, 4-H, OCH_2CH_2), 2.00 (ddd, *J* = 12.6 Hz, 4.3 Hz, 4.3 Hz, 1H, 10-H), 2.02–2.12 (m, 2H, 4-H, 5-H), 2.42 (ddd, *J* = 16.9 Hz, 14.4 Hz, 4.9 Hz, 1H, 3-H), 2.47–2.56 (m, 2H, 3-H, 10a-H), 2.56–2.65 (m, 2H, 4a-H, 6-H), 2.72 (ddd, *J* = 17.7 Hz, 4.9 Hz, 2.1 Hz, 1H, 6-H), 3.96 (t, *J* = 6.6 Hz, 2H, OCH_2), 5.81 (d, *J* = 2.2 Hz, 1H, 1-H), 6.11 (d, *J* = 2.3 Hz, 1H, 9-H), 6.58 (d, *J* = 2.1 Hz, 1H, 8-H), 6.85–6.91 (m, 2H, 3'-H), 7.42–7.46 (m, 2H, 2'-H), ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.15 (CH_3), 22.72 ($CH_3CH_2CH_2$), 26.05 ($OCH_2CH_2CH_2$), 27.97 (C-6), 29.25, 29.37, 29.41, 29.60, 29.62, 29.66, 29.68, 30.02, 30.31 (C-4, C-5, 7×CH_2), 31.94 (CH_3CH_2), 35.78 (C-10a), 36.04 (C-4a), 36.99 (C-10), 37.94 (C-3), 68.11 (OCH_2), 114.50 (C-3'), 122.72 (C-1), 123.39 (C-8), 124.32 (C-9), 126.55 (C-2'), 132.41 (C-1'), 144.00 (C-7), 149.66 (C-8a), 159.41 (C-4'), 160.07 (C-9a), 199.96 (C-2) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2918 (vs), 2850 (s), 1665 (s), 1607 (m), 1575 (s), 1511 (s), 1473 (w), 1430 (w), 1417 (w), 1375 (m), 1351 (w), 1325 (w), 1299 (w), 1275 (s), 1255 (s), 1199 (m), 1181 (s), 1120 (w), 1095 (w), 1049 (w), 1021 (w), 1003 (w), 912 (m), 875 (w), 834 (m), 820 (w), 767 (w), 731 (w), 666 (w), 638 (w), 612 (w), 557 (w), 528 (w), 475 (w), 436 (w) cm^{-1}. MS (ESI): *m*/*z* = 483.32 $[M+Na]^+$, 461.34 $[M+H]^+$, 257.19, 236.14. HRMS (ESI): calcd. for $[C_{32}H_{44}O_2+H]^+$ 461.3414, found: 461.3410. M.p. (POM): 127 °C.

3-(4-(Tetradecyloxy)phenyl)-cyclohex-2-enone (O-1-C(14)): According to GP3, yield: 277 mg, 720 µmol, 50 %, column chromatography on silica gel gradient PE : EE = 8 : 1 to 3 : 1 (R_f = 0.6). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.20–1.40 (m, 20H, 10×CH_2), 1.40–1.48 (m, 2H, $OCH_2CH_2CH_2$), 1.74–1.83 (m, 2H, OCH_2CH_2), 2.09–2.18 (m, 2H, 5-H), 2.46 (dd, *J* = 7.5 Hz, 6.0 Hz, 2H, 6-H), 2.75 (dt, *J* = 6.1 Hz, 1.5 Hz, 2H, 4-H), 3.98 (t, *J* = 6.6 Hz, 2H, OCH_2), 6.39 (d, *J* = 1.5 Hz, 1H, 2-H), 6.88–6.94 (m, 2H, 3'-H), 7.47–7.54 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.15 (CH_3), 22.72 ($CH_3CH_2CH_2$), 22.80 (C-5), 26.02 ($OCH_2CH_2CH_2$), 27.86 (C-4), 29.18, 29.39, 29.58, 29.61, 29.68, 29.70, 29.71 (9×CH_2), 31.95 (CH_3CH_2), 37.23 (C-6), 68.19 (OCH_2), 114.66 (C-3'), 123.57 (C-2), 127.62 (C-2'), 130.52 (C-1'), 159.21 (C-3), 160.88 (C-4'), 199.97 (C-1) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2955 (m), 2916 (vs), 2872 (m), 2850 (s), 1652 (s), 1603 (s), 1570 (w), 1509 (m), 1475 (m), 1462 (m), 1418 (w), 1394 (w), 1367 (w), 1351 (w), 1331 (w), 1314 (w), 1276 (m), 1260 (m), 1240 (s), 1184 (s), 1145 (w), 1116 (w), 1038 (w), 1024 (w), 983 (w), 959 (w), 908 (w), 884 (w), 855 (w), 825 (m), 816 (m), 730 (m), 648 (w), 604 (w), 566 (w), 518 (w), 506 (w), 477 (w), 454 (w), 443 (w), 417 (w) cm^{-1}. MS (ESI): *m*/*z* = 791.59 $[2M+Na]^+$, 407.29 $[M+Na]^+$, 385.31 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{26}H_{40}O_2+H]^+$ 385.3101, found: 385.3100. M.p. (POM): 73 °C.

7-(4-(Tetradecyloxy)phenyl)-4,4a,5,6-tetrahydronaphthalene-2(3*H*)-one (O-2-C(14)): According to GP3, yield: 463 mg, 1.06 mmol, 54 %, column chromatography on silica gel gradient PE : EE = 7 : 1 to 3 : 1 (R_f = 0.4). ^{1}H-NMR (700 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.1 Hz, 3H, CH_3), 1.22–1.38 (m, 20H, 10×CH_2), 1.42–1.48 (m, 2H, $OCH_2CH_2CH_2$), 1.55 (qd, *J* = 12.8 Hz, 4.8 Hz, 1H, 5-H), 1.72–1.81 (m, 3H, 4-H, OCH_2CH_2), 2.06–2.11 (m, 1H, 5-H), 2.11–2.16 (m, 1H, 4-H), 2.44 (ddd, *J* = 16.9 Hz, 14.7 Hz, 5.1 Hz, 1H, 3-H), 2.50–2.56 (m, 2H, 3-H, 4a-H), 2.66 (dddd, *J* = 17.6 Hz, 12.4 Hz, 4.9 Hz, 2.4 Hz, 1H, 6-H), 2.78 (ddd, *J* = 17.7 Hz, 4.8 Hz, 2.1 Hz, 1H, 6-H), 3.97 (t, *J* = 6.6 Hz, , 2H, OCH_2), 5.88 (d, *J* = 2.1 Hz, 1H, 1-H), 6.59 (d, *J* = 2.4 Hz, 1H, 8-H), 6.87–6.91 (m, 2H, 3'-H), 7.43–7.50 (m, 2H, 2'-H) ppm. ^{13}C-NMR (176 MHz, $CDCl_3$): δ = 14.14 (CH_3), 22.71 ($CH_3CH_2CH_2$), 26.03 ($OCH_2CH_2CH_2$), 28.24 (C-6), 29.22, 29.38, 29.40, 29.58, 29.61, 29.67, 29.69, 29.71 (9×CH_2), 29.78 (C-5), 30.14 (C-4), 31.94 (CH_3CH_2), 35.41 (C-4a), 37.96 (C-3), 68.14 (OCH_2), 114.54 (C-3'), 123.04 (C-8), 123.66 (C-1), 126.94 (C-2'), 131.83 (C-1'), 147.78 (C-7), 159.49 (C-8a), 159.90 (C-4'), 200.10 (C-2) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2917 (vs), 2850 (s), 1651 (s), 1594 (s), 1579 (s), 1511 (s), 1470 (m), 1421 (w), 1384 (w), 1367 (w), 1326 (w), 1300 (w), 1279 (m), 1255 (s), 1200 (m), 1184 (s), 1144 (w), 1117 (w), 1080 (w), 1039 (w), 1024 (w), 1005 (w), 960 (w), 919 (w), 893 (w), 831 (m), 811 (w), 741 (w), 720 (w), 701 (w), 631 (w), 587 (w), 556 (w), 520 (w), 467 (w) cm^{-1}. MS (ESI): *m*/*z* = 459.32 $[M+Na]^+$, 437.34 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{30}H_{44}O_2+H]^+$ 437.3414, found: 437.3400.

3-(4-(5,5,6,6,7,7,8,8,8-Nonafluoroctyloxy)phenyl)-cyclohex-2-enone (O-1-C(4)F(4)): According to GP3, yield: 187 mg, 404 µmol, 32 %, column chromatography on silica gel gradient PE : EE = 8 : 1 to 3 : 1 (R_f = 0.4). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.79–1.95 (m, 4H, OCH_2CH_2, $CF_2CH_2CH_2$), 2.10–2.24 (m, 4H, 5-H, CF_2CH_2), 2.43–2.50 (m, 2H, 6-H), 2.75 (ddd, *J* = 6.2 Hz, 6.1 Hz, 1.4 Hz, 2H, 4-H), 4.04 (t, *J* = 5.9 Hz, 2H, OCH_2), 6.39 (t, *J* = 1.4 Hz, 1H, 2-H), 6.88–6.95 (m, 2H, 3'-H), 7.48–7.55 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 17.27 ($CF_2CH_2CH_2$), 22.78 (C-5), 27.88 (C-4), 28.61 (OCH_2CH_2), 30.56 (t, CF_2CH_2), 37.21 (C-6), 67.33 (OCH_2), 114.61 (C-3'), 123.77 (C-2), 127.68 (C-2'), 130.96 (C-1'), 159.11 (C-3), 160.45 (C-4'), 199.97 (C-1) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.02, -124.48, -114.61, -81.05 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2949 (w), 2879 (w), 2248 (w), 1660 (m), 1597 (m), 1569 (w), 1512 (m), 1473 (w), 1421 (w), 1351 (w), 1327 (w), 1280 (m), 1219 (vs), 1132 (vs), 1072 (w), 1035 (w), 985 (w), 957 (w), 907 (m), 880 (m), 850 (w), 824 (m), 729 (s), 647 (m), 594 (w), 567 (w), 522 (w), 440 (w), 412 (w) cm^{-1}. MS (ESI): *m*/*z* = 485.11 $[M+Na]^+$, 463.13 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{20}H_{19}F_9O_2+H]^+$ 463.1314, found: 463.1316. M.p. (POM): 49 °C.

7-(4-(5,5,6,6,7,7,8,8,8-Nonafluoroctyloxy)phenyl)-4,4a,5,6-tetrahydronaphthalene-2(3*H*)-one (O-2-C(4)F(4)): According to GP3, yield: 225 mg, 437 µmol, 41 %, column chromatography on silica gel gradient PE : EE = 6 : 1 to 2 : 1 (R_f = 0.4). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.55 (dddd, *J* = 12.9 Hz, 12.9 Hz, 12.8 Hz, 4.9 Hz, 1H, 5-H), 1.70–1.94 (m, 5H, 4-H, OCH_2CH_2, $CF_2CH_2CH_2$), 2.06–2.24 (m, 4H, 4-H, 5-H, CF_2CH_2), 2.45 (ddd, *J* = 16.9 Hz, 14.5 Hz, 5.0 Hz, 1H, 3-H), 2.49–2.58 (m, 2H, 3-H, 4a-H), 2.66 (dddd, *J* = 17.7 Hz, 12.2 Hz, 4.9 Hz, 2.3 Hz, 1H, 6-H), 2.78 (ddd, *J* = 17.7 Hz, 4.9 Hz, 2.3 Hz, 1H, 6-H), 4.03 (t, *J* = 5.8 Hz, 2H, OCH_2), 5.88 (d, *J* = 2.3 Hz, 1H, 1-H), 6.59 (d, *J* = 2.3 Hz, 1H, 8-H), 6.86–6.93 (m, 2H, 3'-H), 7.45–7.52 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 17.28 ($CF_2CH_2CH_2$), 28.26 (C-6), 28.65 (OCH_2CH_2), 29.76 (C-5), 30.13 (C-4), 30.58 (t, CF_2CH_2), 35.40 (C-4a), 37.95 (C-3), 67.29 (OCH_2), 114.49 (C-3'), 123.26 (C-8), 123.77 (C-1), 127.02 (C-2'), 132.26 (C-1'), 147.67 (C-7), 159.43 (C-8a), 159.49 (C-4'), 200.15 (C-2) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.01, -124.47, -114.61, -81.05 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2932 (w), 2862 (w), 2251 (w), 1651 (m), 1592 (m), 1578 (m), 1512 (m), 1455 (w), 1422 (w), 1383 (w), 1368 (w), 1355 (w), 1326 (w), 1283 (w), 1218 (vs), 1182 (vs), 1073 (w), 1034 (w), 1003 (w), 956 (w), 908 (m), 879 (m), 850 (w), 834 (m), 810 (w), 730 (s), 645 (w), 591 (w), 557 (w), 520 (w), 471 (w), 413 (w) cm^{-1}. MS (ESI): *m*/*z* = 515.16 $[M+H]^+$, 459.17, 426.20. HRMS (ESI): calcd. for $[C_{24}H_{23}F_9O_2+H]^+$ 515.1627, found: 515.1626. M.p. (POM): 84 °C.

3-(4-(5,5,6,6,7,7,8,8,9,9,10,10,10-Tridecafluorodecyloxy)phenyl)-cyclohex-2-enone (O-1-C(4)F(6)): According to GP3, yield: 182 mg, 324 µmol, 31 %, column chromatography on silica gel gradient PE : EE = 8 : 1 to 3 : 1 (R_f = 0.3). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.79–1.94

(m, 4H, OCH_2CH_2, $CF_2CH_2CH_2$), 2.10–2.24 (m, 4H, 5-H, CF_2CH_2), 2.44–2.49 (m, 2H, 6-H), 2.75 (ddd, *J* = 6.1 Hz, 6.1 Hz, 1.5 Hz, 2H, 4-H), 4.04 (t, *J* = 5.9 Hz, 2H, OCH_2), 6.39 (t, *J* = 1.5 Hz, 1H, 2-H), 6.89–6.95 (m, 2H, 3'-H), 7.49–7.54 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 17.29 ($CF_2CH_2CH_2$), 22.78 (C-5), 27.88 (C-4), 28.62 (OCH_2CH_2), 30.66 (t, CF_2CH_2), 37.21 (C-6), 67.33 (OCH_2), 114.60 (C-3'), 123.78 (C-2), 127.68 (C-2'), 130.97 (C-1'), 159.10 (C-3), 160.45 (C-4'), 199.96 (C-1) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.13, -123.52, -122.86, -121.90, -114.39, -80.82 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2948 (w), 2878 (w), 2248 (w), 1660 (m), 1597 (m), 1569 (w), 1513 (m), 1474 (w), 1421 (w), 1365 (w), 1350 (w), 1318 (w), 1280 (w), 1234 (s), 1183 (vs), 1122 (m), 1073 (w), 1036 (w), 985 (w), 957 (w), 908 (m), 824 (m), 729 (s), 707 (m), 696 (m), 648 (m), 605 (w), 566 (w), 530 (w), 442 (w), 410 (w) cm^{-1}. MS (ESI): *m*/*z* = 585.10 $[M+Na]^+$, 563.12 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{22}H_{19}F_{13}O_2+H]^+$ 563.1250, found: 563.1241. M.p. (POM): 76 °C.

7-(4-(5,5,6,6,7,7,8,8,9,9,10,10,10-Tridecafluorodecyloxy)phenyl)-4,4a,5,6-tetrahydronaphthalene-2(3*H*)-one (O-2-C(4)F(6)): According to GP3, yield: 312 mg, 508 µmol, 50 %, column chromatography on silica gel gradient PE : EE = 6 : 1 to 2 : 1 (R_f = 0.3). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.55 (dddd, *J* = 12.9 Hz, 12.9 Hz, 12.8 Hz, 4.9 Hz, 1H, 5-H), 1.71–1.94 (m, 5H, 4-H, OCH_2CH_2, $CF_2CH_2CH_2$), 2.06–2.24 (m, 4H, 4-H, 5-H, CF_2CH_2), 2.45 (ddd, *J* = 17.0 Hz, 14.5 Hz, 5.0 Hz, 1H, 3-H), 2.49–2.58 (m, 2H, 3-H, 4a-H), 2.66 (dddd, *J* = 17.6 Hz, 12.4 Hz, 4.7 Hz, 2.2 Hz, 1H, 6-H), 2.78 (ddd, *J* = 17.6 Hz, 5.0 Hz, 2.2 Hz, 1H, 6-H), 4.03 (t, *J* = 5.8 Hz, 2H, OCH_2), 5.88 (s, 1H, 1-H), 6.59 (d, *J* = 2.2 Hz, 1H, 8-H), 6.86–6.93 (m, 2H, 3'-H), 7.46–7.52 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 17.30 ($CF_2CH_2CH_2$), 28.26 (C-6), 28.66 (OCH_2CH_2), 29.76 (C-5), 30.13 (C-4), 30.67 (t, CF_2CH_2), 35.40 (C-4a), 37.95 (C-3), 67.29 (OCH_2), 114.49 (C-3'), 123.26 (C-8), 123.77 (C-1), 127.02 (C-2'), 132.26 (C-1'), 147.68 (C-7), 159.44 (C-8a), 159.49 (C-4'), 200.14 (C-2) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.13, -123.51, -122.86, -121.90, -114.39, -80.81 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2938 (w), 2876 (w), 1650 (m), 1592 (m), 1579 (m), 1512 (m), 1476 (w), 1454 (w), 1422 (w), 1384 (w), 1366 (w), 1319 (w), 1283 (w), 1239 (s), 1184 (vs), 1122 (s), 1095 (w), 1069 (w), 1037 (m), 1004 (w), 957 (w), 909 (w), 831 (m), 810 (w), 789 (w), 731 (m), 695 (m), 647 (m), 629 (m), 567 (w), 521 (w), 496 (w), 472 (w), 435 (w), 410 (w) cm^{-1}. MS (ESI): *m*/*z* = 615.16 $[M+H]^+$, 559.16. HRMS (ESI): calcd. for $[C_{26}H_{23}F_{13}O_2+H]^+$ 615.1563, found: 615.1551. M.p. (POM): 135 °C.

3-(4-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluorododecyloxy)phenyl)-cyclohex-2-enone (O-1-C(4)F(8)): According to GP3, yield: 220 mg, 332 µmol, 32 %, column chromatography on silica gel gradient PE : EE = 10 : 1 to 3 : 1 (R_f = 0.3). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.79–1.95 (m, 4H, OCH_2CH_2, $CF_2CH_2CH_2$), 2.10–2.24 (m, 4H, 5-H, CF_2CH_2), 2.44–2.49 (m, 2H, 6-H), 2.75 (ddd, *J* = 6.2 Hz, 6.2 Hz, 1.5 Hz, 2H, 4-H),

4.04 (t, *J* = 5.9 Hz, 2H, OCH_2), 6.39 (t, *J* = 1.5 Hz, 1H, 2-H), 6.89–6.95 (m, 2H, 3'-H), 7.48–7.55 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 17.29 ($CF_2CH_2\mathit{C}H_2$), 22.78 (C-5), 27.88 (C-4), 28.62 ($OCH_2\mathit{C}H_2$), 30.67 (t, $CF_2\mathit{C}H_2$), 37.21 (C-6), 67.33 (OCH_2), 114.60 (C-3'), 123.78 (C-2), 127.68 (C-2'), 130.97 (C-1'), 159.09 (C-3), 160.45 (C-4'), 199.96 (C-1) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.10, -123.48, -122.70, -121.93, -121.87, -121.69, -114.37, -80.79 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2949 (w), 2877 (w), 1663 (m), 1599 (w), 1570 (w), 1513 (w), 1477 (w), 1420 (w), 1371 (w), 1331 (w), 1280 (w), 1239 (m), 1201 (s), 1146 (vs), 1117 (m), 1071 (w), 1037 (w), 1015 (w), 984 (w), 954 (w), 918 (w), 884 (w), 826 (w), 738 (w), 704 (w), 657 (m), 623 (w), 603 (w), 576 (w), 560 (w), 529 (w), 498 (w), 469 (w), 444 (w), 427 (w), 411 (w) cm^{-1}. MS (ESI): *m*/*z* = 685.10 $[M+Na]^+$, 663.12 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{24}H_{19}F_{17}O_2+H]^+$ 663.1186, found: 663.1180. M.p. (POM): 115 °C.

7-(4-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluordodecyloxy)phenyl)-4,4a,5,6-tetrahydronaphthalin-2(3*H*)-on (O-2-C(4)F(8)): According to GP3, yield: 374 mg, 523 µmol, 52 %, column chromatography on silica gel gradient PE : EE = 6 : 1 to 2 : 1 (R_f = 0.3). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.55 (dddd, *J* = 12.8 Hz, 12.8 Hz, 12.8 Hz, 4.9 Hz, 1H, 5-H), 1.69–1.94 (m, 5H, 4-H, $OCH_2C\mathit{H}_2$, $CF_2CH_2C\mathit{H}_2$), 2.05–2.24 (m, 4H, 4-H, 5-H, CF_2CH_2), 2.45 (ddd, *J* = 16.9 Hz, 14.5 Hz, 4.9 Hz, 1H, 3-H), 2.50–2.58 (m, 2H, 3-H, 4a-H), 2.67 (dddd, *J* = 17.7 Hz, 12.5 Hz, 4.9 Hz, 2.2 Hz, 1H, 6-H), 2.78 (ddd, *J* = 17.7 Hz, 4.9 Hz, 2.2 Hz, 1H, 6-H), 4.03 (t, *J* = 5.9 Hz, 2H, OCH_2), 5.88 (s, 1H, 1-H), 6.59 (d, *J* = 2.2 Hz, 1H, 8-H), 6.86–6.93 (m, 2H, 3'-H), 7.45–7.52 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 17.30 ($CF_2CH_2\mathit{C}H_2$), 28.26 (C-6), 28.66 ($OCH_2\mathit{C}H_2$), 29.76 (C-5), 30.13 (C-4), 30.68 (t, $CF_2\mathit{C}H_2$), 35.40 (C-4a), 37.95 (C-3), 67.29 (OCH_2), 114.49 (C-3'), 123.26 (C-8), 123.78 (C-1), 127.01 (C-2'), 132.27 (C-1'), 147.65 (C-7), 159.41 (C-8a), 159.49 (C-4'), 200.13 (C-2) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.08, -123.46, -122.68, -121.92, -121.87, -121.68, -114.36, -80.78 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2938 (w), 2876 (w), 2864 (w), 2246 (w), 1650 (m), 1593 (m), 1578 (m), 1512 (m), 1476 (w), 1455 (w), 1422 (w), 1369 (w), 1327 (w), 1283 (w), 1241 (s), 1201 (s), 1184 (s), 1145 (s), 1116 (m), 1072 (w), 1039 (w), 1005 (w), 953 (w), 906 (s), 833 (m), 809 (w), 727 (vs), 648 (m), 559 (w), 523 (w), 472 (w) cm^{-1}. MS (ESI): *m*/*z* = 737.13 $[M+Na]^+$, 715.15 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{28}H_{23}F_{17}O_2+H]^+$ 715.1499, found: 715.1491. M.p. (POM): 169 °C.

3-(4-(7,7,8,8,9,9,10,10,10-Nonafluorodecyloxy)phenyl)-cyclohex-2-enone (O-1-C(6)F(4)): According to GP3, yield: 150 mg, 306 µmol, 26 %, column chromatography on silica gel gradient PE : EE = 8 : 1 to 7 : 2 (R_f = 0.4). ^{1}H-NMR (700 MHz, $CDCl_3$): δ = 1.43–1.55 (m, 4H, 2×CH_2), 1.65 (tt, *J* = 8.0 Hz, 7.9 Hz, 2H, $CF_2CH_2C\mathit{H}_2$), 1.82 (tt, *J* = 6.6 Hz, 6.6 Hz, 2H, $OCH_2C\mathit{H}_2$), 2.02–2.17 (m, 4H, 5-H, CF_2CH_2), 2.46 (t, *J* = 6.6 Hz, 2H, 6-H), 2.75 (t, *J* = 6.2 Hz, 2H, 4-H), 4.00 (t, *J* = 6.4 Hz, 2H, OCH_2), 6.39 (s, 1H, 2-H), 6.91 (d, *J* = 8.5 Hz, 2H, 3'-H), 7.50

(d, *J* = 8.5 Hz, 2H, 2'-H) ppm. ^{13}C-NMR (176 MHz, $CDCl_3$): δ = 20.06 ($CF_2CH_2\mathit{C}H_2$), 22.79 (C-5), 25.75 ($OCH_2CH_2\mathit{C}H_2$), 27.86 (C-4), 28.83 ($CF_2CH_2CH2\mathit{C}H2$), 28.92 ($OCH_2\mathit{C}H_2$), 30.71 (t, $CF_2\mathit{C}H_2$), 37.21 (C-6), 67.84 (OCH_2), 108.48–119.90 (m, CF_2, CF_3), 114.63 (C-3'), 123.66 (C-2), 127.66 (C-2'), 130.71 (C-1'), 159.18 (C-3), 160.73 (C-4'), 199.98 (C-1) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.04, -124.49, -114.56, -81.07 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2946 (w), 2868 (w), 1656 (s), 1598 (m), 1569 (w), 1515 (w), 1469 (w), 1423 (w), 1356 (w), 1325 (w), 1281 (w), 1222 (vs), 1189 (s), 1133 (vs), 1043 (w), 1005 (w), 973 (w), 956 (w), 883 (w), 849 (w), 818 (w), 768 (w), 737 (w), 721 (w), 646 (w), 605 (w), 578 (w), 535 (w), 455 (w), 424 (w) cm^{-1}. MS (ESI): *m*/*z* = 513.14 $[M+Na]^+$, 491.16 $[M+H]^+$, 394.21. HRMS (ESI): calcd. for $[C_{22}H_{23}F_9O_2+H]^+$ 491.1627, found: 491.1628. M.p. (POM): 49 °C.

7-(4-(7,7,8,8,9,9,10,10,10-Nonafluorodecyloxy)phenyl)-4,4a,5,6-tetrahydronaphthalene-2(3*H*)-one (O-2-C(6)F(4)): According to GP3, yield: 324 mg, 597 µmol, 53 %, column chromatography on silica gel gradient PE : EE = 6 : 1 to 2 : 1 (R_f = 0.3). ^{1}H-NMR (700 MHz, $CDCl_3$): δ = 1.43–1.59 (m, 5H, 5-H, 2×CH_2), 1.65 (tt, *J* = 7.9 Hz, 7.8 Hz, 2H, $CF_2CH_2C\mathit{H}_2$), 1.71–1.85 (m, 3H, 4-H, $OCH_2C\mathit{H}_2$), 2.02–2.16 (m, 4H, 4-H, 5-H, CF_2CH_2), 2.44 (ddd, *J* = 16.7 Hz, 15.9 Hz, 4.9 Hz, 1H, 3-H), 2.50–2.56 (m, 2H, 3-H, 4a-H), 2.62–2.70 (m, 1H, 6-H), 2.78 (ddd, *J* = 17.8 Hz, 4.9 Hz, 2.0 Hz, 1H, 6-H), 3.99 (t, *J* = 6.3 Hz, 2H, OCH_2), 5.88 (s, 1H, 1-H), 6.59 (d, *J* = 2.4 Hz, 1H, 8-H), 6.89 (d, *J* = 8.5 Hz, 2H, 3'-H), 7.48 (d, *J* = 8.5 Hz, 2H, 2'-H) ppm. ^{13}C-NMR (176 MHz, $CDCl_3$): δ = 20.06 ($CF_2CH_2\mathit{C}H_2$), 25.76 ($OCH_2CH_2\mathit{C}H_2$), 28.24 (C-6), 28.84 ($CF_2CH_2CH2\mathit{C}H2$), 28.96 ($OCH_2\mathit{C}H_2$), 29.77 (C-5), 30.13 (C-4), 30.71 (t, $CF_2\mathit{C}H_2$), 35.41 (C-4a), 37.95 (C-3), 67.79 (OCH_2), 108.68–120.08 (m, CF_2, CF_3), 114.51 (C-3'), 123.14 (C-8), 123.72 (C-1), 126.98 (C-2'), 132.02 (C-1'), 147.74 (C-7), 159.47 (C-8a), 159.76 (C-4'), 200.13 (C-2) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.03, -124.48, -114.56, -81.07 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2942 (w), 2864 (w), 1655 (m), 1593 (m), 1512 (w), 1470 (w), 1455 (w), 1422 (w), 1356 (w), 1325 (w), 1284 (w), 1223 (vs), 1200 (s), 1187 (s), 1133 (s), 1047 (w), 1023 (w), 1004 (w), 898 (w), 880 (w), 834 (w), 810 (w), 733 (w), 719 (w), 632 (w), 592 (w), 557 (w), 520 (w), 467 (w), 428 (w), 411 (w) cm^{-1}. MS (ESI): *m*/*z* = 565.17 $[M+Na]^+$, 543.19 $[M+H]^+$, 394.21, 277.14, 204.11. HRMS (ESI): calcd. for $[C_{26}H_{27}F_9O_2+H]^+$ 543.1940, found: 543.1945. M.p. (POM): 97 °C.

3-(4-(7,7,8,8,9,9,10,10,11,11,12,12,12-Tridecafluorododecyloxy)phenyl)-cyclohex-2-enone (O-1-C(6)F(6)): According to GP3, yield: 171 mg, 290 µmol, 30 %, column chromatography on silica gel gradient PE : EE = 8 : 1 to 4 : 1 (R_f = 0.4). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.42–1.57 (m, 4H, 2×CH_2), 1.62–1.70 (m, 2H, $CF_2CH_2C\mathit{H}_2$), 1.77–1.86 (m, 2H, $OCH_2C\mathit{H}_2$), 2.00–2.18 (m, 4H, 5-H, CF_2CH_2), 2.43–2.50 (m, 2H, 6-H), 2.75 (ddd, *J* = 6.2 Hz, 6.1 Hz, 1.4 Hz, 2H, 4-H), 4.00 (t, *J* = 6.4 Hz, 2H, OCH_2), 6.39 (t, *J* = 1.4 Hz, 1H, 2-H), 6.88–6.94 (m, 2H, 3'-H), 7.48–7.54 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz,

$CDCl_3$): δ = 20.09 ($CF_2CH_2CH_2$), 22.79 (C-5), 25.75 ($OCH_2CH_2CH_2$), 27.86 (C-4), 28.83 ($CF_2CH_2CH2CH2$), 28.92 (OCH_2CH_2), 30.81 (t, CF_2CH_2), 37.21 (C-6), 67.83 (OCH_2), 114.62 (C-3'), 123.66 (C-2), 127.65 (C-2'), 130.70 (C-1'), 159.16 (C-3), 160.72 (C-4'), 199.97 (C-1) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.14, -123.54, -122.87, -121.92, -114.34, -80.82 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2945 (w), 2871 (w), 2249 (w), 1660 (m), 1597 (m), 1569 (w), 1512 (m), 1470 (w), 1421 (w), 1366 (w), 1350 (w), 1318 (w), 1280 (w), 1235 (vs), 1182 (vs), 1122 (m), 1047 (w), 984 (w), 957 (w), 908 (m), 825 (w), 812 (w), 729 (vs), 708 (m), 696 (m), 649 (m), 605 (w), 566 (w), 528 (w), 411 (w) cm^{-1}. MS (ESI): *m*/*z* = 591.16 $[M+H]^+$, 426.20, 389.29, 242.28. HRMS (ESI): calcd. for $[C_{24}H_{23}F_{13}O_2+H]^+$ 591.1563, found: 591.1565. M.p. (POM): 85 °C.

7-(4-(7,7,8,8,9,9,10,10,11,11,12,12,12-Tridecafluorododecyloxy)phenyl)-4,4a,5,6-tetra-hydronaphthalene-2(3*H*)-one (O-2-C(6)F(6)): According to GP3, yield: 439 mg, 683 µmol, 68 %, column chromatography on silica gel gradient PE : EE = 6 : 1 to 2 : 1 (R_f = 0.4). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.42–1.61 (m, 5H, 5-H, 2×CH_2), 1.61–1.69 (m, 2H, $CF_2CH_2CH_2$), 1.71–1.87 (m, 3H, 4-H, OCH_2CH_2), 2.00–2.18 (m, 4H, 4-H, 5-H, CF_2CH_2), 2.44 (ddd, *J* = 16.9 Hz, 14.4 Hz, 4.9 Hz, 1H, 3-H), 2.49–2.59 (m, 2H, 3-H, 4a-H), 2.66 (dddd, *J* = 17.6 Hz, 12.4 Hz, 4.9 Hz, 2.3 Hz, 1H, 6-H), 2.78 (ddd, *J* = 18.0 Hz, 4.9 Hz, 2.3 Hz, 1H, 6-H), 3.99 (t, *J* = 6.3 Hz, 2H, OCH_2), 5.88 (s, 1H, 1-H), 6.59 (d, *J* = 2.3 Hz, 1H, 8-H), 6.86–6.92 (m, 2H, 3'-H), 7.45–7.51 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 20.09 ($CF_2CH_2CH_2$), 25.77 ($OCH_2CH_2CH_2$), 28.25 (C-6), 28.85 ($CF_2CH_2CH2CH2$), 28.97 (OCH_2CH_2), 29.77 (C-5), 30.14 (C-4), 30.81 (t, CF_2CH_2), 35.41 (C-4a), 37.95 (C-3), 67.79 (OCH_2), 114.50 (C-3'), 123.14 (C-8), 123.72 (C-1), 126.97 (C-2'), 132.01 (C-1'), 147.73 (C-7), 159.47 (C-8a), 159.75 (C-4'), 200.12 (C-2) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.13, -123.53, -122.87, -121.91, -114.34, -80.81 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2944 (w), 2866 (w), 1650 (m), 1593 (m), 1579 (w), 1513 (w), 1476 (w), 1454 (w), 1422 (w), 1367 (w), 1322 (w), 1282 (w), 1244 (s), 1213 (s), 1202 (s), 1186 (vs), 1123 (w), 1048 (w), 1033 (w), 1004 (w), 975 (w), 909 (w), 830 (w), 810 (w), 730 (w), 698 (w), 647 (w), 569 (w), 530 (w), 468 (w) cm^{-1}.MS (ESI): *m*/*z* = 643.19 $[M+H]^+$,426.20. HRMS (ESI): calcd. for $[C_{28}H_{27}F_{13}O_2+H]^+$ 643.1876, found: 643.1872. M.p. (POM): 135 °C.

3-(4-(7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-Heptadecafluorotetra-decyloxy-)phenyl)-cyclohex-2-enone (O-1-C(6)F(8)): According to GP3, yield: 199 mg, 288 µmol, 36 %, column chromatography on silica gel gradient PE : EE = 8 : 1 to 4 : 1 (R_f = 0.4). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.42–1.56 (m, 4H, 2×CH_2), 1.60–1.70 (m, 2H, $CF_2CH_2CH_2$), 1.79–1.87 (m, 2H, OCH_2CH_2), 2.00–2.18 (m, 4H, 5-H, CF_2CH_2), 2.44–2.50 (m, 2H, 6-H), 2.75 (ddd, *J* = 6.2 Hz, 6.1 Hz, 1.5 Hz, 2H, 4-H), 4.00 (t, *J* = 6.4 Hz, 2H, OCH_2), 6.40 (t, *J* = 1.5 Hz, 1H, 2-H), 6.88–6.95 (m, 2H, 3'-H), 7.48–7.54 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz,

$CDCl_3$): δ = 20.09 ($CF_2CH_2CH_2$), 22.79 (C-5), 25.75 ($OCH_2CH_2CH_2$), 27.86 (C-4), 28.84 ($CF_2CH_2CH2CH2$), 28.92 (OCH_2CH_2), 30.82 (t, CF_2CH_2), 37.22 (C-6), 67.83 (OCH_2), 114.62 (C-3'), 123.67 (C-2), 127.65 (C-2'), 130.71 (C-1'), 159.15 (C-3), 160.72 (C-4'), 199.96 (C-1) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.08, -123.50, -122.69, -121.93, -121.88, -121.72, -114.32, -80.78 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2940 (w), 2868 (w), 2251 (w), 1661 (w), 1598 (w), 1569 (w), 1512 (w), 1471 (w), 1419 (w), 1370 (w), 1350 (w), 1330 (w), 1281 (w), 1238 (s), 1200 (vs), 1146 (vs), 1117 (m), 1045 (w), 1029 (w), 1002 (w), 973 (w), 955 (w), 908 (m), 886 (w), 825 (w), 730 (vs), 704 (w), 655 (m), 623 (w), 605 (w), 560 (w), 529 (w), 477 (w), 455 (w), 413 (w) cm^{-1}. MS (ESI): *m*/*z* = 713.13 $[M+Na]^+$, 691.15 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{26}H_{23}F_{17}O_2+H]^+$ 691.1499, found: 691.1495. M.p. (POM): 116 °C.

7-(4-(7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-Heptadecafluorotetradecyloxy)phenyl)-4,4a,5,6-tetrahydronaphthalene-2(3*H*)-one (O-2-C(6)F(8)): According to GP3, yield: 371 mg, 500 µmol, 74 %, column chromatography on silica gel gradient PE : EE = 6 : 1 to 2 : 1 (R_f = 0.4). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.41–1.58 (m, 5H, 5-H, 2×CH_2), 1.61–1.69 (m, 2H, $CF_2CH_2CH_2$), 1.70–1.86 (m, 3H, 4-H, OCH_2CH_2), 1.99–2.17 (m, 4H, 4-H, 5-H, CF_2CH_2), 2.44 (ddd, *J* = 17.0 Hz, 14.5 Hz, 4.9 Hz, 1H, 3-H), 2.49–2.58 (m, 2H, 3-H, 4a-H), 2.66 (dddd, *J* = 17.6 Hz, 12.3 Hz, 4.9 Hz, 2.3 Hz, 1H, 6-H), 2.78 (ddd, *J* = 17.9 Hz, 4.9 Hz, 2.3 Hz, 1H, 6-H), 3.99 (t, *J* = 6.4 Hz, 2H, OCH_2), 5.88 (d, *J* = 2.3 Hz, 1H, 1-H), 6.59 (d, *J* = 2.3 Hz, 1H, 8-H), 6.86–6.91 (m, 2H, 3'-H), 7.45–7.50 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 20.10 ($CF_2CH_2CH_2$), 25.77 ($OCH_2CH_2CH_2$), 28.24 (C-6), 28.85 ($CF_2CH_2CH2CH2$), 28.97 (OCH_2CH_2), 29.76 (C-5), 30.12 (C-4), 30.82 (t, CF_2CH_2), 35.41 (C-4a), 37.92 (C-3), 67.79 (OCH_2), 114.50 (C-3'), 123.12 (C-8), 123.67 (C-1), 126.98 (C-2'), 131.99 (C-1'), 147.81 (C-7), 159.60 (C-8a), 159.76 (C-4'), 200.26 (C-2) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.11, -123.51, -122.69, -121.94, -121.88, -121.70, -114.33, -80.80 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2940 (w), 2865 (w), 2252 (w), 1725 (w), 1650 (w), 1591 (w), 1512 (w), 1470 (w), 1369 (w), 1328 (w), 1239 (m), 1201 (s), 1182 (m), 1147 (m), 1117 (w), 1049 (w), 1024 (w), 906 (s), 833 (w), 728 (vs), 704 (w), 649 (w), 559 (w), 529 (w) cm^{-1}. MS (ESI): *m*/*z* = 765.16 $[M+Na]^+$, 743.18 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{30}H_{27}F_{17}O_2+H]^+$ 743.1812, found: 743.1814. M.p. (POM): 193 °C.

3-(4-(9,9,10,10,11,11,12,12,12-Nonafluorododecyloxy)phenyl)-cyclohex-2-enone (O-1-C(8)F(4)): According to GP3, yield: 180 mg, 347 µmol, 34 %, column chromatography on silica gel gradient PE : EE = 8 : 1 to 4 : 1 (R_f = 0.4). ^{1}H-NMR (700 MHz, $CDCl_3$): δ = 1.34–1.43 (m, 6H, 3×CH_2), 1.44–1.50 (m, 2H, $OCH_2CH_2CH_2$), 1.57–1.63 (m, 2H, $CF_2CH_2CH_2$), 1.76–1.83 (m, 2H, OCH_2CH_2), 2.05 (tt, *J* = 18.4 Hz, 8.1 Hz, 2H, CF_2CH_2), 2.13 (tt, *J* = 6.3 Hz, 6.0 Hz, 2H, 5-H), 2.44–2.49 (m, 2H, 6-H), 2.75 (t, *J* = 6.0 Hz, 2H, 4-H), 3.99 (t, *J* = 6.5 Hz, 2H, OCH_2), 6.39 (s, 1H, 2-H), 6.91 (d, *J* = 8.6 Hz, 2H, 3'-H), 7.51 (d, *J* = 8.6 Hz, 2H, 2'-H) ppm. ^{13}C-

NMR (176 MHz, $CDCl_3$): δ = 20.06 ($CF_2CH_2\mathit{C}H_2$), 22.79 (C-5), 25.94 ($OCH_2CH_2\mathit{C}H_2$), 27.86 (C-4), 29.02, 29.10, 29.12, 29.15 (4×CH_2), 30.76 (t, $CF_2\mathit{C}H_2$), 37.21 (C-6), 68.06 (OCH_2), 108.68–119.90 (m, CF_2, CF_3), 114.65 (C-3'), 123.62 (C-2), 127.64 (C-2'), 130.61 (C-1'), 159.20 (C-3), 160.83 (C-4'), 199.98 (C-1) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.04, -124.50, -114.57, -81.08 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2938 (w), 2861 (w), 2246 (w), 1655 (s), 1597 (w), 1569 (w), 1513 (w), 1471 (w), 1422 (w), 1351 (w), 1325 (w), 1281 (w), 1219 (vs), 1132 (vs), 1048 (w), 1026 (w), 957 (w), 907 (s), 881 (w), 848 (w), 822 (w), 723 (vs), 647 (w), 602 (w), 565 (w), 522 (w), 503 (w), 474 (w), 443 (w) cm^{-1}. MS (ESI): *m*/*z* = 541.17 $[M+Na]^+$, 519.19 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{24}H_{27}F_9O_2+H]^+$ 519.1940, found: 519.1943. M.p. (POM): 60 °C.

7-(4-(9,9,10,10,11,11,12,12,12-Nonafluorododecyloxy)phenyl)-4,4a,5,6-tetrahydronaphthalene-2(3*H*)-one (O-2-C(8)F(4)): According to GP3, yield: 288 mg, 505 µmol, 50 %, column chromatography on silica gel gradient PE : EE = 6 : 1 to 2 : 1 (R_f = 0.4). ^{1}H-NMR (700 MHz, $CDCl_3$): δ = 1.35–1.43 (m, 6H, 3×CH_2), 1.44–1.50 (m, 2H, $OCH_2CH_2C\mathit{H}_2$), 1.51–1.63 (m, 3H, 5-H, $CF_2CH_2C\mathit{H}_2$), 1.72–1.82 (m, 3H, 4-H, $OCH_2C\mathit{H}_2$), 2.00–2.16 (m, 4H, 4-H, 5-H, CF_2CH_2), 2.44 (ddd, *J* = 16.7 Hz, 14.6 Hz, 5.0 Hz, 1H, 3-H), 2.50–2.56 (m, 2H, 3-H, 4a-H), 2.63–2.70 (m, 1H, 6-H), 2.78 (ddd, *J* = 17.8 Hz, 5.0 Hz, 2.3 Hz, 1H, 6-H), 3.98 (t, *J* = 6.5 Hz, 2H, OCH_2), 5.88 (d, *J* = 2.3 Hz, 1H, 1-H), 6.59 (d, *J* = 2.3 Hz, 1H, 8-H), 6.89 (d, *J* = 8.5 Hz, 2H, 3'-H), 7.47 (d, *J* = 8.5 Hz, 2H, 2'-H) ppm. ^{13}C-NMR (176 MHz, $CDCl_3$): δ = 20.07 ($CF_2CH_2\mathit{C}H_2$), 25.96 ($OCH_2CH_2\mathit{C}H_2$), 28.24 (C-6), 29.02, 29.11, 29.15, 29.16 (4×CH_2), 29.77 (C-5), 30.14 (C-4), 30.76 (t, $CF_2\mathit{C}H_2$), 35.41 (C-4a), 37.95 (C-3), 68.01 (OCH_2), 108.69–119.96 (m, CF_2, CF_3), 114.53 (C-3'), 123.09 (C-8), 123.69 (C-1), 126.96 (C-2'), 131.92 (C-1'), 147.79 (C-7), 159.52 (C-8a), 159.86 (C-4'), 200.14 (C-2) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.04, -124.48, -114.56, -81.07 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2935 (w), 2860 (w), 2249 (w), 1650 (m), 1592 (m), 1578 (m), 1511 (m), 1470 (w), 1455 (w), 1422 (w), 1383 (w), 1368 (w), 1355 (w), 1327 (w), 1284 (w), 1233 (m), 1200 (m), 1182 (m), 1132 (m), 1022 (w), 1004 (w), 905 (s), 834 (w), 726 (vs), 647 (w), 590 (w), 558 (w), 521 (w), 465 (w), 411 (w) cm^{-1}. MS (ESI): *m*/*z* = 593.21 $[M+Na]^+$, 571.23 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{28}H_{31}F_9O_2+H]^+$ 571.2253, found: 571.2256. M.p. (POM): 98 °C.

3-(4-(9,9,10,10,11,11,12,12,13,13,14,14,14-Tridecafluorotetradecyloxy)phenyl)-cyclohex-2-enone (O-1-C(8)F(6)): According to GP3, yield: 199 mg, 322 µmol, 32 %, column chromatography on silica gel gradient PE : EE = 10 : 1 to 9 : 2 (R_f = 0.4). ^{1}H-NMR (700 MHz, $CDCl_3$): δ = 1.34–1.43 (m, 6H, 3×CH_2), 1.44–1.50 (m, 2H, $OCH_2CH_2C\mathit{H}_2$), 1.58–1.63 (m, 2H, $CF_2CH_2C\mathit{H}_2$), 1.80 (tt, *J* = 6.7 Hz, 6.5 Hz, 2H, $OCH_2C\mathit{H}_2$), 2.05 (tt, *J* = 18.4 Hz, 8.1 Hz, 2H, CF_2CH_2), 2.10–2.18 (m, 2H, 5-H), 2.46 (t, *J* = 6.7 Hz, 2H, 6-H), 2.75 (t, *J* = 6.1 Hz, 2H, 4-H), 3.99 (t, *J* = 6.5 Hz, 2H, OCH_2), 6.39 (s, 1H, 2-H), 6.91 (d, *J* = 8.6 Hz,

2H, 3'-H), 7.51 (d, *J* = 8.6 Hz, 2H, 2'-H) ppm. ^{13}C-NMR (176 MHz, $CDCl_3$): δ = 20.09 ($CF_2CH_2\mathit{C}H_2$), 22.79 (C-5), 25.94 ($OCH_2CH_2\mathit{C}H_2$), 27.86 (C-4), 29.03, 29.10, 29.12, 29.15 (4×CH_2), 30.86 (t, $CF_2\mathit{C}H_2$), 37.22 (C-6), 68.06 (OCH_2), 109.91–119.91 (m, CF_2, CF_3), 114.65 (C-3'), 123.63 (C-2), 127.63 (C-2'), 130.61 (C-1'), 159.19 (C-3), 160.83 (C-4'), 199.98 (C-1) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.13, -123.54, -122.87, -121.93, -114.35, -80.81 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2939 (w), 2860 (w), 2246 (w), 1658 (m), 1597 (m), 1568 (w), 1512 (m), 1470 (w), 1421 (w), 1366 (w), 1350 (w), 1318 (w), 1281 (w), 1236 (s), 1181 (s), 1143 (s), 1051 (w), 1024 (w), 985 (w), 957 (w), 908 (s), 824 (w), 728 (vs), 696 (m), 648 (m), 605 (w), 566 (w), 527 (w), 443 (w) cm^{-1}. MS (ESI): *m*/*z* = 641.17 $[M+Na]^+$, 619.19 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{26}H_{27}F_{13}O_2+H]^+$ 619.1876, found: 619.1878. M.p. (POM): 76 °C.

7-(4-(9,9,10,10,11,11,12,12,13,13,14,14,14-Tridecafluorotetradecyloxy)phenyl)-4,4a,5,6-tetrahydronaphthalene-2(3*H*)-one (O-2-C(8)F(6)): According to GP3, yield: 355 mg, 529 µmol, 52 %, column chromatography on silica gel gradient PE : EE = 7 : 1 to 3 : 1 (R_f = 0.4). ^{1}H-NMR (700 MHz, $CDCl_3$): δ = 1.34–1.43 (m, 6H, 3×CH_2), 1.44–1.50 (m, 2H, $OCH_2CH_2C\mathit{H}_2$), 1.51–1.64 (m, 3H, 5-H, $CF_2CH_2C\mathit{H}_2$), 1.71–1.83 (m, 3H, 4-H, $OCH_2C\mathit{H}_2$), 2.00–2.17 (m, 4H, 4-H, 5-H, CF_2CH_2), 2.45 (ddd, *J* = 16.7 Hz, 14.6 Hz, 5.0 Hz, 1H, 3-H), 2.50–2.56 (m, 2H, 3-H, 4a-H), 2.63–2.70 (m, 1H, 6-H), 2.78 (ddd, *J* = 17.8 Hz, 5.0 Hz, 2.1 Hz, 1H, 6-H), 3.98 (t, *J* = 6.4 Hz, 2H, OCH_2), 5.88 (s, 1H, 1-H), 6.59 (d, *J* = 2.4 Hz, 1H, 8-H), 6.89 (d, *J* = 8.5 Hz, 2H, 3'-H), 7.47 (d, *J* = 8.5 Hz, 2H, 2'-H) ppm. ^{13}C-NMR (176 MHz, $CDCl_3$): δ = 20.09 ($CF_2CH_2\mathit{C}H_2$), 25.96 ($OCH_2CH_2\mathit{C}H_2$), 28.24 (C-6), 29.03, 29.12, 29.15, 29.17 (4×CH_2), 29.77 (C-5), 30.14 (C-4), 30.86 (t, $CF_2\mathit{C}H_2$), 35.41 (C-4a), 37.95 (C-3), 68.01 (OCH_2), 110.09–119.92 (m, CF_2, CF_3), 114.53 (C-3'), 123.10 (C-8), 123.69 (C-1), 126.96 (C-2'), 131.92 (C-1'), 147.79 (C-7), 159.51 (C-8a), 159.86 (C-4'), 200.14 (C-2) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.13, -123.55, -122.86, -121.92, -114.34, -80.81 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2935 (w), 2861 (w), 2251 (w), 1650 (w), 1592 (w), 1578 (w), 1511 (w), 1470 (w), 1455 (w), 1367 (w), 1327 (w), 1283 (w), 1239 (m), 1200 (m), 1183 (m), 1144 (m), 1023 (w), 1004 (w), 905 (s), 834 (w), 811 (w), 726 (vs), 648 (w), 564 (w), 521 (w) cm^{-1}. MS (ESI): *m*/*z* = 671.22 $[M+H]^+$, 501.34, 351.23. HRMS (ESI): calcd. for $[C_{30}H_{31}F_{13}O_2+H]^+$ 671.2189, found: 671.2184. M.p. (POM): 131 °C.

3-(4-(9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-Heptadecafluorohexadecyloxy)phenyl)-cyclohex-2-enone (O-1-C(8)F(8)): According to GP3, yield: 182 mg, 253 µmol, 29 %, column chromatography on silica gel gradient PE : EE = 10 : 1 to 9 : 2 (R_f = 0.4). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.34–1.43 (m, 6H, 3×CH_2), 1.44–1.52 (m, 2H, $OCH_2CH_2C\mathit{H}_2$), 1.56–1.64 (m, 2H, $CF_2CH_2C\mathit{H}_2$), 1.75–1.83 (m, 2H, $OCH_2C\mathit{H}_2$), 1.98–2.18 (m, 4H, 5-H, CF_2CH_2), 2.42–2.50 (m, 2H, 6-H), 2.75 (td, *J* = 6.0 Hz, 1.5 Hz, 2H, 4-H), 3.99 (t, *J* = 6.5 Hz, 2H, OCH_2), 6.40 (t, *J* = 1.5 Hz, 1.5 Hz, 1H, 2-H), 6.88–6.94 (m, 2H, 3'-H), 7.48–

7.53 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 20.10 ($CF_2CH_2\mathit{C}H_2$), 22.79 (C-5), 25.95 ($OCH_2CH_2\mathit{C}H_2$), 27.86 (C-4), 29.03, 29.11, 29.12, 29.16 (4×CH_2), 30.87 (t, $CF_2\mathit{C}H_2$), 37.22 (C-6), 68.06 (OCH_2), 114.64 (C-3'), 123.62 (C-2), 127.63 (C-2'), 130.60 (C-1'), 159.19 (C-3), 160.82 (C-4'), 199.98 (C-1) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.07, -123.50, -122.68, -121.93, -121.88, -121.69, -114.32, -80.77 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2938 (w), 2859 (w), 2250 (w), 1655 (m), 1598 (m), 1568 (w), 1512 (m), 1470 (w), 1421 (w), 1367 (w), 1350 (w), 1329 (w), 1280 (w), 1239 (s), 1203 (s), 1181 (s), 1147 (s), 1118 (m), 1050 (w), 1026 (w), 985 (w), 957 (w), 907 (s), 824 (w), 729 (vs), 704 (m), 649 (m), 623 (w), 605 (w), 560 (w), 529 (w) cm^{-1}. MS (ESI): *m*/*z* = 719.18 $[M+H]^+$, 426.20. HRMS (ESI): calcd. for $[C_{28}H_{27}F_{17}O_2+H]^+$ 719.1812, found: 719.1815. M.p. (POM): 107 °C.

7-(4-(9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-Heptadecafluorohexadecyloxy)-phenyl)-4,4a,5,6-tetrahydronaphthalene-2(3*H*)-one (O-2-C(8)F(8)): According to GP3, yield: 350 mg, 454 µmol, 54 %, column chromatography on silica gel gradient PE : EE = 8 : 1 to 7 : 2 (R_f = 0.5). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.33–1.43 (m, 6H, 3×CH_2), 1.44–1.65 (m, 5H, 5-H, $OCH_2CH_2C\mathit{H}_2$, $CF_2CH_2C\mathit{H}_2$), 1.70–1.84 (m, 3H, 4-H, $OCH_2C\mathit{H}_2$), 1.98–2.19 (m, 4H, 4-H, 5-H, CF_2CH_2), 2.45 (ddd, *J* = 16.9 Hz, 14.5 Hz, 4.9 Hz, 1H, 3-H), 2.49–2.58 (m, 2H, 3-H, 4a-H), 2.66 (dddd, *J* = 17.8 Hz, 12.3 Hz, 4.9 Hz, 2.3 Hz, 1H, 6-H), 2.78 (ddd, *J* = 17.8 Hz, 4.9 Hz, 2.3 Hz, 1H, 6-H), 3.98 (t, *J* = 6.5 Hz, 2H, OCH_2), 5.88 (d, *J* = 2.3 Hz, 1H, 1-H), 6.59 (d, *J* = 2.3 Hz, 1H, 8-H), 6.85–6.93 (m, 2H, 3'-H), 7.44–7.51 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 20.10 ($CF_2CH_2\mathit{C}H_2$), 25.96 ($OCH_2CH_2\mathit{C}H_2$), 28.24 (C-6), 29.03, 29.12, 29.15, 21.16 (4×CH_2), 29.78 (C-5), 30.14 (C-4), 30.88 (t, $CF_2\mathit{C}H_2$), 35.42 (C-4a), 37.95 (C-3), 68.01 (OCH_2), 114.52 (C-3'), 123.09 (C-8), 123.69 (C-1), 126.96 (C-2'), 131.91 (C-1'), 147.78 (C-7), 159.50 (C-8a), 159.84 (C-4'), 200.14 (C-2) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.07, -123.49, -122.70, -121.92, -121.87, -121.71, -114.32, -80.77 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2938 (w), 2860 (w), 2245 (w), 1650 (w), 1593 (w), 1579 (w), 1512 (w), 1474 (w), 1454 (w), 1369 (w), 1328 (w), 1283 (w), 1243 (m), 1219 (m), 1201 (m), 1145 (m), 1117 (w), 1050 (w), 1028 (w), 1003 (w), 949 (w), 905 (s), 831 (w), 810 (w), 727 (vs), 648 (w), 606 (w), 560 (w), 527 (w), 470 (w), 429 (w) cm^{-1}. MS (ESI): *m*/*z* = 771.21 $[M+H]^+$, 426.20. HRMS (ESI): calcd. for $[C_{32}H_{31}F_{17}O_2+H]^+$ 771.2125, found: 771.2123. M.p. (POM): 162 °C.

3-(4-(4-Octyloxypiperidyl)phenyl)-cyclohex-2-enone (O-1-PipC(8)): According to GP3, yield: 87.0 mg, 227 µmol, 33 %, column chromatography on silica gel gradient PE : EE = 8 : 1 to 3 : 1 (R_f = 0.3). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.22–1.38 (m, 10H, 5×CH_2), 1.54–1.61 (m, 2H, $OCH_2C\mathit{H}_2$), 1.69 (dtd, *J* = 12.7 Hz, 8.7 Hz, 3.8 Hz, 2H, 2''-H), 1.91–2.02 (m, 2H, 2''-H), 2.07–2.17 (m, 2H, 5-H), 2.40–2.51 (m, 2H, 6-H), 2.74 (td, *J* = 6.2 Hz, 1.4 Hz, 2H, 4-H), 3.06 (ddd, *J* = 12.7 Hz, 9.2 Hz, 3.3 Hz, 2H, 1''-H), 3.41–3.53 (m, 3H, OCH_2, 3''-H), 3.58–3.69 (m, 2H, 1''-H), 6.41 (t, *J* = 1.4 Hz, 1H, 2-H), 6.85–6.93 (m, 2H, 3'-H), 7.44–

7.52 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.10 (CH_3), 22.66 ($CH_3CH_2CH_2$), 22.80 (C-5), 26.27 ($OCH_2CH_2CH_2$), 27.54 (C-4), 29.28, 29.46 (2×CH_2), 30.14 (OCH_2CH_2), 30.71 (C-2''), 31.85 (CH_3CH_2), 37.25 (C-6), 45.86 (C-1''), 68.13 (OCH_2), 74.24 (C-3''), 114.86 (C-3'), 122.25 (C-2), 127.44 (C-2'), 127.46 (C-1'), 152.30 (C-4'), 159.23 (C-3), 199.98 (C-1) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2924 (m), 2852 (m), 1653 (s), 1604 (m), 1586 (vs), 1550 (w), 1517 (s), 1463 (w), 1427 (w), 1388 (w), 1365 (m), 1348 (m), 1326 (m), 1246 (m), 1222 (s), 1204 (s), 1185 (vs), 1105 (s), 1045 (w), 1026 (w), 955 (m), 920 (w), 883 (w), 812 (m), 758 (w), 725 (w), 656 (w), 639 (w), 566 (w), 520 (w), 443 (w), 409 (w) cm^{-1}. MS (EI): *m*/*z* = 383.3 $[M]^+$. HRMS (EI): calcd. for $[C_{25}H_{37}NO_2]^+$ 383.2824, found: 383.2827. M.p. (POM): 62 °C.

7-(4-(4-Octyloxypiperidyl)phenyl)-4,4a,5,6-tetrahydronaphthalene-2(3*H*)-one (O-2-PipC(8)): According to GP3, yield: 98.0 mg, 225 µmol, 33 %, column chromatography on silica gel gradient PE : EE = 8 : 1 to 3 : 1 (R_f = 0.3). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 3H, CH_3), 1.23–1.38 (m, 10H, 5×CH_2), 1.49–1.61 (m, 3H, 5-H, OCH_2CH_2), 1.65–1.81 (m, 3H, 4-H, 2''-H), 1.94–2.01 (m, 2H, 2''-H), 2.05–2.16 (m, 2H, 4-H, 5-H), 2.44 (ddd, *J* = 16.9 Hz, 14.4 Hz, 4.9 Hz, 1H, 3-H), 2.48–2.57 (m, 2H, 3-H, 4a-H), 2.63 (dddd, *J* = 17.5 Hz, 12.5 Hz, 4.9 Hz, 2.3 Hz, 1H, 6-H), 2.80 (ddd, *J* = 17.7 Hz, 4.8 Hz, 2.3 Hz, 1H, 6-H), 3.02 (ddd, *J* = 12.7 Hz, 9.3 Hz, 3.2 Hz, 2H, 1''-H), 3.41–3.50 (m, 3H, OCH_2, 3''-H), 3.57–3.65 (m, 2H, 1''-H), 5.87 (d, *J* = 2.2 Hz, 1H, 1-H), 6.60 (d, *J* = 2.3 Hz, 1H, 8-H), 6.87–6.93 (m, 2H, 3'-H), 7.41–7.50 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.10 (CH_3), 22.66 (CH_3CH_2), 26.27 ($OCH_2CH_2CH_2$), 27.99 (C-6), 29.28, 29.46 (2×CH_2), 29.81 (C-5), 30.15 (OCH_2CH_2), 30.20 (C-4), 30.81 (C-2''), 31.85 ($CH_3CH_2CH_2$), 35.51 (C-4a), 37.95 (C-3), 46.26 (C-1''), 68.11 (OCH_2), 74.34 (C-3''), 115.23 (C-3'), 121.94 (C-8), 123.15 (C-1), 126.67 (C-2'), 129.26 (C-1'), 147.91 (C-7), 151.52 (C-4'), 159.85 (C-8a), 200.05 (C-2) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2923 (m), 2852 (m), 1646 (s), 1606 (w), 1573 (vs), 1516 (s), 1453 (w), 1427 (w), 1366 (m), 1325 (m), 1298 (w), 1254 (m), 1226 (m), 1196 (s), 1105 (vs), 1044 (w), 1023 (w), 1001 (w), 959 (w), 917 (w), 894 (w), 828 (m), 807 (m), 770 (w), 731 (w), 695 (w), 648 (w), 636 (w), 557 (w), 522 (w), 470 (w), 410 (w) cm^{-1}. MS (EI): *m*/*z* = 435.3 $[M]^+$. HRMS (EI): calcd. for $[C_{29}H_{41}NO_2]^+$ 435.3137, found: 435.3145. M.p. (POM): 83 °C.

3-(4-(4-Decyloxypiperidyl)phenyl)-cyclohex-2-enone (O-1-PipC(10)): According to GP3, yield: 91 mg, 221 µmol, 33 %, column chromatography on silica gel gradient PE : EE = 9 : 1 to 4 : 1 (R_f = 0.4). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.23–1.39 (m, 14H, 7×CH_2), 1.53–1.63 (m, 2H, OCH_2CH_2), 1.65–1.75 (m, 2H, 2''-H), 1.91–2.01 (m, 2H, 2''-H), 2.08–2.16 (m, 2H, 5-H), 2.41–2.49 (m, 2H, 6-H), 2.71–2.79 (m, 2H, 4-H), 3.06 (ddd, *J* = 12.7 Hz, 9.2 Hz, 3.3 Hz, 2H, 1''-H), 3.43–3.52 (m, 3H, OCH_2, 3''-H), 3.57–3.67 (m, 2H, 1''-H), 6.40 (t, *J* = 1.4 Hz, 1H, 2-H), 6.87–6.93 (m, 2H, 3'-H), 7.44–7.52 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.12 (CH_3), 22.69 (CH_3CH_2), 22.80 (C-5), 26.27 ($OCH_2CH_2CH_2$),

27.54 (C-4), 29.33, 29.50, 29.59, 29.62 (4×CH_2), 30.14 (OCH_2CH_2), 30.71 (C-2''), 31.91 ($CH_3CH_2CH_2$), 37.25 (C-6), 45.85 (C-1''), 68.13 (OCH_2), 74.23 (C-3''), 114.86 (C-3'), 122.24 (C-2), 127.44 (C-2', C-1'), 152.30 (C-4'), 159.24 (C-3), 199.97 (C-1) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2922 (s), 2852 (m), 1654 (m), 1604 (m), 1586 (s), 1549 (w), 1515 (s), 1463 (w), 1427 (w), 1388 (w), 1364 (m), 1347 (m), 1326 (m), 1245 (m), 1222 (s), 1204 (s), 1185 (vs), 1104 (vs), 1044 (w), 956 (w), 920 (w), 883 (w), 813 (m), 759 (w), 724 (w), 657 (w), 565 (w), 520 (w), 442 (w), 407 (w) cm^{-1}. MS (ESI): *m*/*z* = 434.30 $[M+Na]^+$, 412.32 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{27}H_{41}NO_2+H]^+$ 412.3210, found: 412.3210. M.p. (POM): 65 °C.

7-(4-(4-Decyloxypiperidyl)phenyl)-4,4a,5,6-tetrahydronaphthalene-2(3*H*)-one (O-2-PipC(10)): According to GP3, yield: 98.0 mg, 211 µmol, 29 %, column chromatography on silica gel gradient PE : EE = 8 : 1 to 4 : 1 (R_f = 0.3). ^{1}H-NMR (700 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.0 Hz, 3H, CH_3), 1.21–1.38 (m, 14H, 7×CH_2), 1.49–1.62 (m, 3H, 5-H, OCH_2CH_2), 1.62–1.81 (m, 3H, 4-H, 2''-H), 1.94–2.01 (m, 2H, 2''-H), 2.05–2.16 (m, 2H, 4-H, 5-H), 2.44 (ddd, *J* = 16.8 Hz, 14.6 Hz, 5.0 Hz, 1H, 3-H), 2.49–2.57 (m, 2H, 3-H, 4a-H), 2.63 (dddd, *J* = 17.5 Hz, 12.5 Hz, 4.9 Hz, 2.4 Hz, 1H, 6-H), 2.80 (ddd, *J* = 17.7 Hz, 4.7 Hz, 2.2 Hz, 1H, 6-H), 3.02 (ddd, *J* = 12.7 Hz, 9.3 Hz, 3.2 Hz, 2H, 1''-H), 3.43–3.50 (m, 3H, OCH_2, 3''-H), 3.55–3.63 (m, 2H, 1''-H), 5.87 (d, *J* = 2.2 Hz, 1H, 1-H), 6.60 (d, *J* = 2.4 Hz, 1H, 8-H), 6.87–6.93 (m, 2H, 3'-H), 7.42–7.48 (m, 2H, 2'-H) ppm. ^{13}C-NMR (176 MHz, $CDCl_3$): δ = 14.13 (CH_3), 22.69 (CH_3CH_2), 26.26 ($OCH_2CH_2CH_2$), 27.97 (C-6), 29.33, 29.50, 29.59, 29.62 (4×CH_2), 29.79 (C-5), 30.14 (OCH_2CH_2), 30.18 (C-4), 30.79 (C-2''), 31.91 ($CH_3CH_2CH_2$), 35.48 (C-4a), 37.95 (C-3), 46.26 (C-1''), 68.10 (OCH_2), 74.34 (C-3''), 115.23 (C-3'), 121.94 (C-8), 123.14 (C-1), 126.67 (C-2'), 129.25 (C-1'), 147.91 (C-7), 151.51 (C-4'), 159.88 (C-8a), 200.10 (C-2) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2922 (s), 2852 (m), 1649 (m), 1607 (w), 1582 (vs), 1517 (m), 1463 (w), 1454 (w), 1427 (w), 1366 (m), 1325 (m), 1298 (w), 1254 (m), 1226 (w), 1197 (s), 1183 (s), 1108 (s), 1023 (w), 1001 (w), 959 (w), 918 (w), 894 (w), 829 (w), 808 (w), 724 (w), 695 (w), 649 (w), 636 (w), 558 (w), 522 (w), 470 (w), 411 (w) cm^{-1}. MS (ESI): *m*/*z* = 486.33 $[M+Na]^+$, 464.35 $[M+H]^+$, 306.18, 226.95. HRMS (ESI): calcd. for $[C_{31}H_{45}NO_2+H]^+$ 464.3523, found: 464.3523. M.p. (POM): 95 °C.

3-(4-(4-Dodecyloxypiperidyl)phenyl)-cyclohex-2-enone (O-1-PipC(12)): According to GP3, yield: 123 mg, 280 µmol, 37 %, column chromatography on silica gel gradient PE : EE = 10 : 1 to 9 : 2 (R_f = 0.3). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 6.9 Hz, 3H, CH_3), 1.25–1.40 (m, 18H, 9×CH_2), 1.55–1.66 (m, 2H, OCH_2CH_2), 1.67–1.77 (m, 2H, 2''-H), 1.95–2.05 (m, 2H, 2''-H), 2.10–2.19 (m, 2H, 5-H), 2.45–2.51 (m, 2H, 6-H), 2.77 (t, *J* = 6.1 Hz, 2H, 4-H), 3.09 (ddd, *J* = 12.7 Hz, 9.2 Hz, 3.3 Hz, 2H, 1''-H), 3.46–3.56 (m, 3H, OCH_2, 3''-H), 3.61–3.70 (m, 2H, 1''-H), 6.43 (s, 1H, 2-H), 6.89–6.97 (m, 2H, 3'-H), 7.47–7.56 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.15 (CH_3), 22.72 (CH_3CH_2), 22.80 (C-5), 26.28 ($OCH_2CH_2CH_2$),

27.53 (C-4), 29.38, 29.52, 29.64, 29.66, 29.69 (6×CH_2), 30.14 (OCH_2CH_2), 30.71 (C-2''), 31.94 ($CH_3CH_2CH_2$), 37.26 (C-6), 45.86 (C-1''), 68.13 (OCH_2), 74.25 (C-3''), 114.86 (C-3'), 122.23 (C-2), 127.42 (C-1'), 127.45 (C-2'), 152.29 (C-4'), 159.24 (C-3), 200.02 (C-1) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2917 (vs), 2849 (s), 1645 (s), 1604 (m), 1586 (vs), 1550 (w), 1517 (m), 1465 (w), 1452 (w), 1428 (w), 1390 (w), 1364 (m), 1350 (m), 1326 (w), 1261 (w), 1248 (w), 1218 (m), 1187 (m), 1107 (vs), 1042 (w), 985 (w), 956 (w), 919 (w), 884 (w), 820 (m), 759 (w), 721 (w), 657 (w), 625 (w), 581 (w), 563 (w), 520 (w), 510 (w), 446 (w), 409 (w) cm^{-1}. MS (ESI): *m*/*z* = 462.33 $[M+Na]^+$, 440.35 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{29}H_{45}NO_2+Na]^+$ 462.3343, found: 462.3340. M.p. (POM): 69 °C.

7-(4-(4-Dodecyloxypiperidyl)phenyl)-4,4a,5,6-tetrahydronaphthalene-2(3*H*)-one (O-2-PipC(12)): According to GP3, yield: 118 mg, 240 µmol, 31 %, column chromatography on silica gel gradient PE : EE = 8 : 1 to 3 : 1 (R_f = 0.3). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.20–1.38 (m, 18H, 9×CH_2), 1.48–1.61 (m, 3H, 5-H, OCH_2CH_2), 1.65–1.81 (m, 3H, 4-H, 2''-H), 1.93–2.03 (m, 2H, 2''-H), 2.04–2.16 (m, 2H, 4-H, 5-H), 2.44 (ddd, *J* = 16.9 Hz, 14.4 Hz, 4.9 Hz, 1H, 3-H), 2.49–2.56 (m, 2H, 3-H, 4a-H), 2.63 (dddd, *J* = 17.7 Hz, 12.4 Hz, 4.9 Hz, 2.4 Hz, 1H, 6-H), 2.80 (ddd, *J* = 17.8 Hz, 4.9 Hz, 2.4 Hz, 1H, 6-H), 3.02 (ddd, *J* = 12.7 Hz, 9.4 Hz, 3.2 Hz, 2H, 1''-H), 3.42–3.50 (m, 3H, OCH_2, 3''-H), 3.55–3.64 (m, 2H, 1''-H), 5.86 (s, 1H, 1-H), 6.59 (d, *J* = 2.4 Hz, 1H, 8-H), 6.86–6.94 (m, 2H, 3'-H), 7.43–7.48 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.26 (CH_3), 22.83 (CH_3CH_2), 26.39 ($OCH_2CH_2CH_2$), 28.10 (C-6), 29.49, 29.63, 29.75, 29.77, 29.80 (6×CH_2), 29.91 (C-5), 30.26 (OCH_2CH_2), 30.30 (C-4), 30.92 (C-2''), 32.05 ($CH_3CH_2CH_2$), 35.60 (C-4a), 38.07 (C-3), 46.39 (C-1''), 68.22 (OCH_2), 74.47 (C-3''), 115.34 (C-3'), 122.05 (C-8), 123.25 (C-1), 126.79 (C-2'), 129.36 (C-1'), 148.05 (C-7), 151.62 (C-4'), 160.02 (C-8a), 200.24 (C-2) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2921 (s), 2851 (m), 1647 (m), 1606 (w), 1582 (vs), 1516 (m), 1463 (w), 1453 (w), 1427 (w), 1366 (m), 1325 (m), 1299 (w), 1254 (m), 1225 (m), 1197 (s), 1182 (s), 1107 (vs), 1043 (w), 1023 (w), 1001 (w), 959 (w), 918 (w), 895 (w), 828 (w), 808 (w), 732 (w), 695 (w), 648 (w), 636 (w), 557 (w), 522 (w), 470 (w) cm^{-1}. MS (ESI): *m*/*z* = 514.37 $[M+Na]^+$, 492.38 $[M+H]^+$, 306.18, 226.95. HRMS (ESI): calcd. for $[C_{33}H_{49}NO_2+H]^+$ 492.3836, found: 492.3843. M.p. (POM): 83 °C.

7-(4-(4-Dodecyloxypiperidyl)phenyl)-4,4a,5,6,10,10a-hexahydroanthracene-2(3*H*)-one (O-3-PipC(12)): According to GP3, yield: 149 mg, 274 µmol, 37 %, column chromatography on silica gel gradient PE : EE = 7 : 1 to 7 : 2 (R_f = 0.4). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.20–1.39 (m, 19H, 10-H, 9×CH_2), 1.47 (qd, *J* = 12.7 Hz, 4.8 Hz, 1H, 5-H), 1.54–1.62 (m, 2H, OCH_2CH_2), 1.65–1.80 (m, 3H, 4-H, 2''-H), 1.93–2.13 (m, 5H, 4-H, 5-H, 10-H, 2''-H), 2.42 (ddd, *J* = 17.0 Hz, 14.3 Hz, 4.9 Hz, 1H, 3-H), 2.48–2.65 (m, 4H, 3-H, 4a-H, 6-H, 10a-H), 2.74 (ddd, *J* = 17.7 Hz, 4.9 Hz, 2.1 Hz, 1H, 6-H), 2.99 (ddd, *J* = 12.6 Hz, 9.4 Hz,

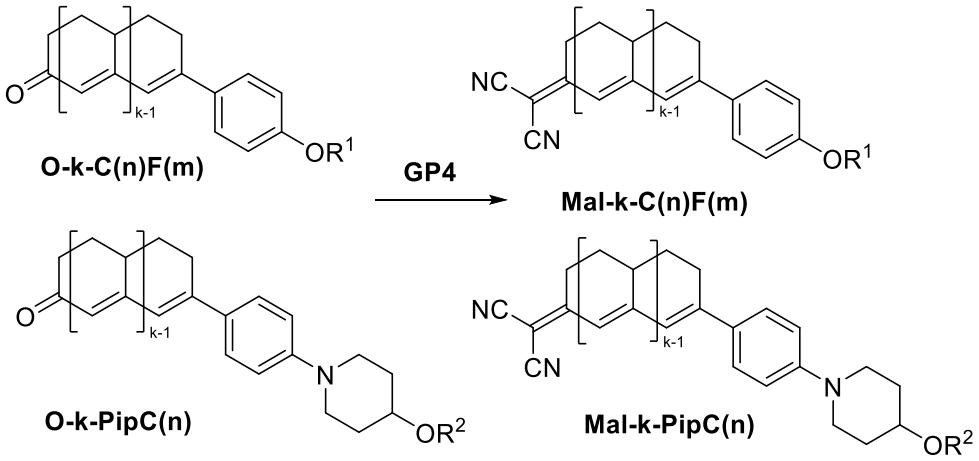
3.2 Hz, 2H, 1''-H), 3.41–3.49 (m, 3H, 3''-H, OCH_2), 3.58 (dt, *J* = 12.5 Hz, 4.6 Hz, 2H, 1''-H), 5.81 (d, *J* = 2.1 Hz, 1H, 1-H), 6.10 (d, *J* = 2.2 Hz, 1H, 9-H), 6.59 (d, *J* = 2.1 Hz, 1H, 8-H), 6.87–6.92 (m, 2H, 3'-H), 7.39–7.45 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.15 (CH_3), 22.72 ($CH_3CH_2CH_2$), 26.28 ($OCH_2CH_2CH_2$), 27.74 (C-6), 29.38, 29.52, 29.64, 29.66, 29.69, 30.05, 30.15, 30.34 (C-4, C-5, 7×CH_2), 30.87 (C-2''), 31.94 (CH_3CH_2), 35.86 (C-10a), 36.08 (C-4a), 37.04 (C-10), 37.95 (C-3), 46.49 (C-1''), 68.09 (OCH_2), 74.43 (C-3''), 115.44 (C-3'), 122.41 (C-8), 122.44 (C-1), 123.85 (C-9), 126.25 (C-2'), 130.04 (C-1'), 144.14 (C-7), 150.01 (C-8a), 151.10 (C-4'), 160.25 (C-9a), 199.92 (C-2) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2919 (vs), 2851 (s), 2233 (w), 1637 (vs), 1605 (m), 1566 (vs), 1517 (m), 1466 (m), 1451 (w), 1430 (w), 1366 (s), 1351 (w), 1326 (w), 1294 (w), 1253 (m), 1233 (w), 1212 (m), 1201 (m), 1180 (w), 1169 (w), 1152 (w), 1108 (vs), 1052 (w), 1008 (w), 950 (w), 926 (m), 906 (m), 853 (w), 817 (m), 793 (w), 731 (vs), 668 (w), 646 (w), 629 (w), 555 (w), 523 (w), 481 (w), 451 (w), 416 (w) cm^{-1}. MS (ESI): *m*/*z* = 544.41 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{37}H_{53}NO_2+H]^+$ 544.4149, found: 544.4133. M.p. (POM): 174 °C.

3-(4-(4-Tetradecyloxypiperidyl)phenyl)-cyclohex-2-enone (O-1-PipC(14)): According to GP3, yield: 77.2 mg, 165 µmol, 40 %, column chromatography on silica gel gradient PE : EE = 10 : 1 to 4 : 1 (R_f = 0.4). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.23–1.38 (m, 22H, 11×CH_2), 1.54–1.61 (m, 2H, OCH_2CH_2), 1.65–1.73 (m, 2H, 2''-H), 1.93–2.00 (m, 2H, 2''-H), 2.08–2.16 (m, 2H, 5-H), 2.43–2.47 (m, 2H, 6-H), 2.74 (td, *J* = 6.2 Hz, 1.4 Hz, 2H, 4-H), 3.06 (ddd, *J* = 12.7 Hz, 9.2 Hz, 3.3 Hz, 2H, 1''-H), 3.43–3.51 (m, 3H, OCH_2, 3''-H), 3.59–3.66 (m, 2H, 1''-H), 6.40 (d, *J* = 1.4 Hz, 1H, 2-H), 6.88–6.93 (m, 2H, 3'-H), 7.46–7.51 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.13 (CH_3), 22.70 (CH_3CH_2), 22.78 (C-5), 26.25 ($OCH_2CH_2CH_2$), 27.51 (C-4), 29.37, 29.50, 29.62, 29.66, 29.68, 29.70 (8×CH_2), 30.12 (OCH_2CH_2), 30.69 (C-2''), 31.93 ($CH_3CH_2CH_2$), 37.23 (C-6), 45.85 (C-1''), 68.12 (OCH_2), 74.24 (C-3''), 114.85 (C-3'), 122.20 (C-2), 127.41 (C-1'), 127.43 (C-2'), 152.27 (C-4'), 159.26 (C-3), 200.05 (C-1) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2916 (vs), 2849 (s), 1645 (s), 1604 (m), 1586 (s), 1519 (m), 1467 (w), 1429 (w), 1391 (w), 1365 (w), 1351 (w), 1328 (w), 1263 (w), 1247 (w), 1218 (m), 1189 (m), 1110 (vs), 1044 (w), 985 (w), 957 (w), 921 (w), 887 (w), 820 (m), 760 (w), 722 (w), 658 (w), 580 (w), 563 (w), 522 (w), 446 (w) cm^{-1}. MS (ESI): *m*/*z* = 490.36 $[M+Na]^+$, 468.38 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{31}H_{49}NO_2+H]^+$ 468.3836, found: 468.3832. M.p. (POM): 79 °C.

7-(4-(4-Tetradecyloxypiperidyl)phenyl)-4,4a,5,6-tetrahydronaphthalene-2(3*H*)-one (O-2-PipC(14)): According to GP3, yield: 74.1 mg, 143 µmol, 34 %, column chromatography on silica gel gradient PE : EE = 8 : 1 to 4 : 1 (R_f = 0.4). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.20–1.38 (m, 22H, 11×CH_2), 1.48–1.62 (m, 3H, 5-H, OCH_2CH_2), 1.62–1.81 (m, 3H, 4-H, 2''-H), 1.95–2.01 (m, 2H, 2''-H), 2.05–2.16 (m, 2H, 4-H, 5-H), 2.44 (ddd,

J = 16.9 Hz, 14.4 Hz, 4.9 Hz, 1H, 3-H), 2.49–2.57 (m, 2H, 3-H, 4a-H), 2.63 (dddd, *J* = 17.7 Hz, 12.5 Hz, 4.9 Hz, 2.3 Hz, 1H, 6-H), 2.80 (ddd, *J* = 17.8 Hz, 4.9 Hz, 2.3 Hz, 1H, 6-H), 3.02 (ddd, *J* = 12.6 Hz, 9.4 Hz, 3.3 Hz, 2H, 1''-H), 3.43–3.50 (m, 3H, OCH_2, 3''-H), 3.56–3.63 (m, 2H, 1''-H), 5.87 (s, 1H, 1-H), 6.60 (d, *J* = 2.3 Hz, 1H, 8-H), 6.88–6.92 (m, 2H, 3'-H), 7.43–7.48 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.14 (CH_3), 22.70 (CH_3CH_2), 26.25 ($OCH_2CH_2CH_2$), 27.96 (C-6), 29.37, 29.50, 29.62, 29.67, 29.69, 29.70 (8×CH_2), 29.78 (C-5), 30.13 (OCH_2CH_2), 30.17 (C-4), 30.79 (C-2''), 31.93 ($CH_3CH_2CH_2$), 35.47 (C-4a), 37.93 (C-3), 46.26 (C-1''), 68.09 (OCH_2), 74.35 (C-3''), 115.22 (C-3'), 121.92 (C-8), 123.12(C-1), 126.65 (C-2'), 129.23 (C-1'), 147.92 (C-7), 151.49 (C-4'), 159.90 (C-8a), 200.12 (C-2) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2918 (vs), 2850 (s), 1650 (s), 1578 (s), 1515 (m), 1465 (w), 1453 (w), 1427 (w), 1365 (m), 1327 (m), 1299 (w), 1255 (m), 1223 (m), 1198 (s), 1183 (s), 1110 (vs), 1042 (w), 1023 (w), 1002 (w), 958 (w), 918 (w), 896 (w), 831 (w), 809 (w), 723 (w), 694 (w), 649 (w), 636 (w), 559 (w), 523 (w), 469 (w) cm^{-1}. MS (ESI): *m/z* = 542.40 $[M+Na]^+$, 520.41 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{35}H_{53}NO_2+H]^+$ 520.4149, found: 520.4147. M.p. (POM): 98 °C.

6) Synthesis of Mal-k-C(n)F(m) and Mal-k-PipC(n)



Scheme S2

Synthesis of Mal-k-C(n)F(m)

1-(1,1-Dicyanomethylene)-3-(4-(octyloxy)phenyl)-cyclohex-2-ene (Mal-1-C(8)): According to GP4, yield: 150 mg, 430 µmol, 86 %, column chromatography on silica gel gradient PE : EE = 10 : 1 to 5 : 1 (R_f = 0.4). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.9 Hz, 3H, CH_3), 1.24–1.41 (m, 8H, 4×CH_2), 1.41–1.51 (m, 2H, $OCH_2CH_2CH_2$), 1.75–1.85 (m, 2H, OCH_2CH_2), 1.96–2.03 (m, 2H, 5-H), 2.75–2.84 (m, 4H, 4-H, 6-H), 4.00 (t, *J* = 6.5 Hz, 2H, OCH_2), 6.90–6.96 (m, 2H, 3'-H), 7.15 (t, *J* = 1.4 Hz, 1H, 2-H), 7.55–7.62 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.13 (CH_3), 21.65 (C-5), 22.68 ($CH_3CH_2CH_2$), 26.01 ($OCH_2CH_2CH_2$), 27.98 (C-4), 29.14, 29.23, 29.24, 29.35 (C-6, 3×CH_2), 31.82 (CH_3CH_2), 68.33

(OCH_2), 77.24 ($C(CN)_2$), 112.93, 113.66 (2×CN), 114.91 (C-3'), 118.81 (C-2), 128.15 (C-2'), 129.92 (C-1'), 157.64 (C-3), 161.76 (C-4'), 170.23 (C-1) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2923 (m), 2854 (m), 2218 (m), 1605 (w), 1579 (m), 1560 (s), 1529 (s), 1510 (m), 1468 (w), 1422 (w), 1374 (w), 1362 (w), 1336 (w), 1285 (m), 1247 (s), 1201 (m), 1178 (vs), 1147 (w), 1122 (w), 1023 (w), 996 (w), 965 (w), 881 (w), 859 (w), 826 (m), 724 (w), 637 (w), 612 (w), 566 (w), 544 (w), 466 (w), 443 (w), 416 (w) cm^{-1}. MS (ESI): *m*/*z* = 371.21 $[M+Na]^+$, 349.23 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{23}H_{28}N_2O+Na]^+$ 371.2094, found: 371.2079. M.p. (POM): 82 °C.

2-(1,1-Dicyanomethylene)-7-(4-(octyloxy)phenyl)-3,4,4a,5,6-pentahydronaphthalene (Mal-2-C(8)): According to GP4, yield: 62.0 mg, 155 µmol, 65 %, column chromatography on silica gel gradient PE : EE = 10 : 1 to 5 : 1 (R_f = 0.4). ^{1}H-NMR (700 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.9 Hz, 3H, CH_3), 1.25–1.38 (m, 8H, 4×CH_2), 1.43–1.48 (m, 2H, $OCH_2CH_2CH_2$), 1.48–1.59 (m, 2H, 4-H, 5-H), 1.77–1.82 (m, 2H, OCH_2CH_2), 2.08–2.13 (m, 2H, 4-H, 5-H), 2.45–2.53 (m, 1H, 4a-H), 2.55–2.63 (m, 1H, 3-H), 2.69 (dddd, *J* = 17.9 Hz, 12.5 Hz, 4.8 Hz, 2.3 Hz, 1H, 6-H), 2.86 (ddd, *J* = 18.0 Hz, 4.8 Hz, 2.1 Hz, 1H, 6-H), 3.07 (ddd, *J* = 17.4 Hz, 4.1 Hz, 2.3 Hz, 1H, 3-H), 3.99 (t, *J* = 6.6 Hz, 2H, OCH_2), 6.63 (d, *J* = 2.1 Hz, 1H, 1-H), 6.71 (d, *J* = 2.3 Hz, 1H, 8-H), 6.89–6.94 (m, 2H, 3'-H), 7.48–7.53 (m, 2H, 2'-H) ppm. ^{13}C-NMR (176 MHz, $CDCl_3$): δ = 14.12 (CH_3), 22.67 ($CH_3CH_2CH_2$), 26.03 ($OCH_2CH_2CH_2$), 28.17 (C-6), 28.69 (C-4), 29.19, 29.25, 29.36, 29.53 (C-5, 3×CH_2), 29.67 (C-3), 31.83 (CH_3CH_2), 35.68 (C-4a), 68.22 (OCH_2), 75.25 ($C(CN)_2$), 113.36, 114.07 (2×CN), 114.72 (C-3'), 120.32 (C-1), 122.95 (C-8), 127.22 (C-2'), 131.17 (C-1'), 151.06 (C-7), 158.67 (C-8a), 160.54 (C-4'), 170.03 (C-2) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2922 (m), 2853 (m), 2215 (s), 1605 (w), 1590 (w), 1549 (s), 1504 (vs), 1469 (m), 1453 (m), 1423 (w), 1394 (w), 1361 (w), 1339 (w), 1299 (w), 1278 (w), 1250 (m), 1200 (s), 1178 (vs), 1120 (w), 1062 (w), 1016 (w), 971 (w), 900 (w), 855 (w), 830 (m), 794 (w), 741 (w), 723 (w), 660 (w), 633 (w), 581 (w), 558 (w), 543 (w), 522 (w), 474 (w), 447 (w), 412 (w) cm^{-1}. MS (ESI): *m*/*z* = 423.24 $[M+Na]^+$, 401.26 $[M+H]^+$, 336.25 $[M–C(CN)_2]^+$. HRMS (ESI): calcd. for $[C_{27}H_{32}N_2O+H]^+$ 401.2587, found: 401.2557. M.p. (POM): 83 °C.

1-(1,1-Dicyanomethylene)-3-(4-(decyloxy)phenyl)-cyclohex-2-ene (Mal-1-C(10)): According to GP4, yield: 75.0 mg, 199 µmol, 82 %, column chromatography on silica gel gradient PE : EE = 12 : 1 to 6 : 1 (R_f = 0.4). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.0 Hz, 3H, CH_3), 1.21–1.39 (m, 12H, 6×CH_2), 1.41–1.49 (m, 2H, $OCH_2CH_2CH_2$), 1.75–1.84 (m, 2H, OCH_2CH_2), 1.96–2.06 (m, 2H, 5-H), 2.75–2.83 (m, 4H, 4-H, 6-H), 4.00 (t, *J* = 6.6 Hz, 2H, OCH_2), 6.90–6.96 (m, 2H, 3'-H), 7.15 (t, *J* = 1.4 Hz, 1H, 2-H), 7.55–7.62 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.15 (CH_3), 21.65 (C-5), 22.70 ($CH_3CH_2CH_2$), 26.00 ($OCH_2CH_2CH_2$), 27.98 (C-4), 29.13, 29.23, 29.33, 29.38, 29.57, 29.72 (C-6, 5×CH_2), 31.91 (CH_3CH_2), 68.33 (OCH_2), 77.23 ($C(CN)_2$), 112.93, 113.66 (2×CN), 114.91 (C-3'), 118.81 (C-2), 128.15 (C-2'), 129.92 (C-1'), 157.64 (C-3), 161.76 (C-4'), 170.24 (C-1) ppm. FT-IR (ATR):

$\tilde{\nu}$ = 2955 (w), 2918 (s), 2867 (w), 2851 (m), 2220 (m), 1607 (w), 1579 (vs), 1565 (s), 1530 (s), 1515 (m), 1470 (w), 1456 (w), 1427 (w), 1417 (w), 1407 (w), 1378 (w), 1361 (w), 1286 (w), 1269 (m), 1256 (s), 1188 (vs), 1125 (w), 1051 (w), 1019 (w), 994 (w), 980 (w), 964 (w), 872 (w), 860 (w), 830 (w), 739 (w), 721 (w), 639 (w), 612 (w), 546 (w), 468 (w), 444 (w), 421 (w) cm^{-1}. MS (ESI): *m*/*z* = 399.24 $[M+Na]^+$, 377.26 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{25}H_{32}N_2O+H]^+$ 377.2587, found: 377.2567. M.p. (POM): 94 °C.

2-(1,1-Dicyanomethylene)-7-(4-(decyloxy)phenyl)-3,4,4a,5,6-pentahydronaphthalene (Mal-2-C(10)): According to GP4, yield: 106 mg, 247 µmol, 91 %, column chromatography on silica gel gradient PE : EE = 10 : 1 to 6 : 1 (R_f = 0.4). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.22–1.39 (m, 12H, 6×CH_2), 1.42–1.59 (m, 4H, 4-H, 5-H, $OCH_2CH_2CH_2$), 1.74–1.82 (m, 2H, OCH_2CH_2), 2.07–2.14 (m, 2H, 4-H, 5-H), 2.44–2.52 (m, 1H, 4a-H), 2.57 (ddd, *J* = 17.4 Hz, 14.3 Hz, 4.8 Hz, 1H, 3-H), 2.63–2.73 (m, 1H, 6-H), 2.85 (ddd, *J* = 18.1 Hz, 4.8 Hz, 2.0 Hz, 1H, 6-H), 3.07 (ddd, *J* = 17.4 Hz, 4.1 Hz, 2.3 Hz, 1H, 3-H), 3.99 (t, *J* = 6.6 Hz, 2H, OCH_2), 6.62 (d, *J* = 2.0 Hz, 1H, 1-H), 6.70 (d, *J* = 2.3 Hz, 1H, 8-H), 6.88–6.94 (m, 2H, 3'-H), 7.47–7.53 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.15 (CH_3), 22.71 ($CH_3CH_2CH_2$), 26.03 ($OCH_2CH_2CH_2$), 28.17 (C-6), 28.69 (C-4), 29.20, 29.34, 29.40, 29.54, 29.58, 29.59 (C-5, 5×CH_2), 29.66 (C-3), 31.92 (CH_3CH_2), 35.68 (C-4a), 68.22 (OCH_2), 75.23 ($C(CN)_2$), 113.37, 114.08 (2×CN), 114.72 (C-3'), 120.32 (C-1), 122.94 (C-8), 127.23 (C-2'), 131.17 (C-1'), 151.08 (C-7), 158.69 (C-8a), 160.55 (C-4'), 170.05 (C-2) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2921 (m), 2852 (m), 2215 (s), 1605 (w), 1590 (w), 1550 (s), 1504 (vs), 1468 (m), 1453 (m), 1423 (m), 1394 (w), 1360 (w), 1339 (m), 1299 (m), 1249 (m), 1200 (s), 1177 (vs), 1120 (w), 1062 (w), 1015 (m), 963 (w), 899 (w), 873 (w), 856 (w), 830 (m), 795 (w), 741 (w), 722 (w), 659 (w), 633 (w), 582 (w), 558 (w), 543 (w), 521 (w), 475 (w), 446 (w), 415 (w) cm^{-1}. MS (ESI): *m*/*z* = 446.32 $[M+NH_4]^+$, 429.29 $[M+H]^+$, 242.28, 225.19. HRMS (ESI): calcd. for $[C_{29}H_{36}N_2O+H]^+$ 429.2900, found: 429.2903. M.p. (POM): 91 °C.

1-(1,1-Dicyanomethylene)-3-(4-(dodecyloxy)phenyl)-cyclohex-2-ene (Mal-1-C(12)): According to GP4, yield: 69.0 mg, 171 µmol, 87 %, column chromatography on silica gel gradient PE : EE = 12 : 1 to 6 : 1 (R_f = 0.4). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.18–1.39 (m, 16H, 8×CH_2), 1.41–1.49 (m, 2H, $OCH_2CH_2CH_2$), 1.75–1.84 (m, 2H, OCH_2CH_2), 1.96–2.05 (m, 2H, 5-H), 2.75–2.84 (m, 4H, 4-H, 6-H), 4.00 (t, *J* = 6.6 Hz, 2H, OCH_2), 6.90–6.96 (m, 2H, 3'-H), 7.15 (d, *J* = 1.4 Hz, 1H, 2-H), 7.55–7.62 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.15 (CH_3), 21.65 (C-5), 22.72 ($CH_3CH_2CH_2$), 26.00 ($OCH_2CH_2CH_2$), 27.98 (C-4), 29.13, 29.23, 29.37, 29.39, 29.58, 29.61, 29.66, 29.68 (C-6, 7×CH_2), 31.94 (CH_3CH_2), 68.33 (OCH_2), 77.24 ($C(CN)_2$), 112.92, 113.66 (2×CN), 114.91 (C-3'), 118.82 (C-2), 128.14 (C-2'), 129.92 (C-1'), 157.63 (C-3), 161.76 (C-4'), 170.23 (C-1) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2920 (s), 2851 (m), 2219 (m), 1607 (w), 1578 (vs), 1563 (s),

1529 (vs), 1514 (m), 1470 (w), 1417 (w), 1403 (w), 1377 (w), 1361 (w), 1337 (w), 1286 (m), 1269 (m), 1255 (vs), 1201 (w), 1186 (vs), 1123 (w), 1022 (w), 965 (w), 871 (w), 828 (m), 757 (w), 721 (w), 638 (w), 611 (w), 544 (w), 465 (w), 445 (w) cm^{-1}. MS (ESI): *m*/*z* = 422.32 $[M+NH_4]^+$, 405.29 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{27}H_{36}N_2O+H]^+$ 405.2900, found: 405.2898. M.p. (POM): 74 °C.

2-(1,1-Dicyanomethylene)-7-(4-(dodecyloxy)phenyl)-3,4,4a,5,6-pentahydronaphthalene (Mal-2-C(12)): According to GP4, yield: 99.0 mg, 209 µmol, 85 %, column chromatography on silica gel gradient PE : EE = 10 : 1 to 6 : 1 (R_f = 0.4). ^{1}H-NMR (700 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.0 Hz, 3H, CH_3), 1.22–1.38 (m, 16H, 8×CH_2), 1.42–1.48 (m, 2H, $OCH_2CH_2CH_2$), 1.48–1.59 (m, 2H, 4-H, 5-H), 1.76–1.82 (m, 2H, OCH_2CH_2), 2.08–2.13 (m, 2H, 4-H, 5-H), 2.45–2.51 (m, 1H, 4a-H), 2.58 (ddd, *J* = 18.1 Hz, 14.3 Hz, 4.8 Hz, 1H, 3-H), 2.65–2.72 (m, 1H, 6-H), 2.86 (ddd, *J* = 18.1 Hz, 4.8 Hz, 2.2 Hz, 1H, 6-H), 3.04–3.09 (m, 1H, 3-H), 3.99 (t, *J* = 6.5 Hz, 2H, OCH_2), 6.63 (d, *J* = 2.2 Hz, 1H, 1-H), 6.71 (d, *J* = 2.4 Hz, 1H, 8-H), 6.91 (d, *J* = 8.6 Hz, 2H, 3'-H), 7.50 (d, *J* = 8.6 Hz, 2H, 2'-H) ppm. ^{13}C-NMR (176 MHz, $CDCl_3$): δ = 14.13 (CH_3), 22.69 ($CH_3CH_2CH_2$), 26.00 ($OCH_2CH_2CH_2$), 28.14 (C-6), 28.67 (C-4), 29.17, 29.35, 29.37, 29.51, 29.57, 29.59, 29.63, 29.66, 29.70 (C-3, C-5, 7×CH_2), 31.92 (CH_3CH_2), 35.65 (C-4a), 68.19 (OCH_2), 75.22 ($C(CN)_2$), 113.33, 114.04 (2×CN), 114.70 (C-3'), 120.30 (C-1), 122.92 (C-8), 127.20 (C-2'), 131.14 (C-1'), 151.04 (C-7), 158.65 (C-8a), 160.53 (C-4'), 170.00 (C-2) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2918 (m), 2871 (w), 2849 (m), 2214 (m), 1604 (w), 1589 (w), 1549 (s), 1502 (vs), 1478 (m), 1467 (m), 1454 (m), 1423 (m), 1401 (m), 1362 (m), 1339 (m), 1303 (m), 1285 (m), 1264 (m), 1246 (m), 1204 (vs), 1121 (w), 1063 (w), 1013 (m), 963 (w), 915 (m), 871 (w), 833 (m), 795 (w), 726 (w), 661 (w), 633 (w), 581 (w), 556 (w), 542 (w), 520 (w), 509 (w), 489 (w), 469 (w), 448 (w) cm^{-1}. MS (ESI): *m*/*z* = 479.30 $[M+Na]^+$, 474.35 $[M+NH_4]^+$, 457.32 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{31}H_{40}N_2O+H]^+$ 457.3213, found: 457.3213. M.p. (POM): 88 °C.

2-(1,1-Dicyanomethylene)-7-(4-(dodecyloxy)phenyl)-4,4a,5,6,10,10a-hexahydroanthracene (Mal-3-C(12)): According to GP4, yield: 57.0 mg, 112 µmol, 75 %, column chromatography on silica gel gradient PE : EE = 10 : 1 to 6 : 1 (R_f = 0.4). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.20–1.39 (m, 17H, 10-H, 8×CH_2), 1.40–1.57 (m, 4H, 4-H, 5-H, $OCH_2CH_2CH_2$), 1.74–1.83 (m, 2H, OCH_2CH_2), 1.97–2.10 (m, 3H, 4-H, 5-H, 10-H), 2.50–2.59 (m, 3H, 3-H, 4a-H, 10a-H), 2.60–2.68 (m, 1H, 6-H), 2.78 (ddd, *J* = 17.9 Hz, 4.8 Hz, 2.1 Hz, 1H, 6-H), 3.00–3.07 (m, 1H, 3-H), 3.98 (t, *J* = 6.6 Hz, 2H, OCH_2), 6.18 (d, *J* = 2.2 Hz, 1H, 9-H), 6.55 (d, *J* = 2.0 Hz, 1H, 1-H), 6.64 (d, *J* = 2.1 Hz, 1H, 8-H), 6.87–6.92 (m, 2H, 3'-H), 7.44–7.49 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.16 (CH_3), 22.72 ($CH_3CH_2CH_2$), 26.04 ($OCH_2CH_2CH_2$), 28.02 (C-6), 28.81 (C-3), 29.23, 29.38, 29.41, 29.60, 29.62, 29.66, 29.69, 29.73, 29.89 (C-4, C-5, 7×CH_2), 31.94 (CH_3CH_2), 35.91 (C-10a),

36.33 (C-4a), 36.70 (C-10), 68.17 (OCH_2), 74.25 ($C(CN)_2$), 113.62 , 114.37 (2×CN), 114.60 (C-3'), 119.61 (C-1), 123.44 (C-8), 124.59 (C-9), 126.80 (C-2'), 131.93 (C-1'), 146.29 (C-7), 153.25 (C-8a), 159.18 (C-9a), 159.86 (C-4'), 169.61 (C-2) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2919 (s), 2851 (m), 2213 (s), 1606 (w), 1567 (w), 1534 (s) 1509 (vs), 1453 (s), 1423 (w), 1390 (m), 1360 (m), 1327 (m), 1290 (w), 1277 (w), 1248 (s), 1179 (vs), 1147 (w), 1119 (w), 1101 (w), 1053 (w), 1026 (m), 1011 (w), 975 (w), 907 (w), 830 (m), 804 (w), 745 (w), 722 (w), 630 (w), 561 (w), 524 (w), 495 (w), 412 (w) cm^{-1}. MS (ESI): *m*/*z* = 509.35 $[M+H]^+$, 305.20. HRMS (ESI): calcd. for $[C_{35}H_{44}N_2O+H]^+$ 509.3526, found: 509.3525. M.p. (POM): 122 °C.

1-(1,1-Dicyanomethylene)-3-(4-(tetradecyloxy)phenyl)-cyclohex-2-ene (Mal-1-C(14)): According to GP4, yield: 75.0 mg, 173 µmol, 67 %, column chromatography on silica gel gradient PE : EE = 12 : 1 to 6 : 1 (R_f = 0.5). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.21–1.40 (m, 20H, 10×CH_2), 1.41–1.49 (m, 2H, $OCH_2CH_2CH_2$), 1.75–1.84 (m, 2H, OCH_2CH_2), 1.96–2.05 (m, 2H, 5-H), 2.75–2.84 (m, 4H, 4-H, 6-H), 4.00 (t, *J* = 6.5 Hz, 2H, OCH_2), 6.90–6.96 (m, 2H, 3'-H), 7.15 (d, *J* = 1.4 Hz, 1H, 2-H), 7.55–7.62 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.15 (CH_3), 21.65 (C-5), 22.72 ($CH_3CH_2CH_2$), 26.00 ($OCH_2CH_2CH_2$), 27.98 (C-4), 29.14, 29.23, 29.39, 29.58, 29.61, 29.68, 29.70, 29.72 (C-6, 9×CH_2), 31.95 (CH_3CH_2), 68.33 (OCH_2), 77.24 ($C(CN)_2$), 112.92, 113.65 (2×CN), 114.91 (C-3'), 118.81 (C-2), 128.14 (C-2'), 129.92 (C-1'), 157.63 (C-3), 161.76 (C-4'), 170.23 (C-1) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2918 (vs), 2849 (s), 2219 (s), 1607 (w), 1578 (vs), 1563 (vs), 1528 (vs), 1514 (s), 1469 (s), 1426 (w), 1417 (w), 1402 (w), 1377 (w), 1361 (w), 1320 (w), 1285 (m), 1270 (s), 1255 (vs), 1201 (m), 1186 (vs), 1123 (w), 1036 (w), 1017 (m), 1006 (w), 964 (w), 908 (w), 870 (w), 826 (vs), 756 (w), 721 (w), 638 (w), 611 (w), 601 (w), 560 (w), 544 (w), 527 (w), 485 (w), 466 (w), 446 (w), 411 (w) cm^{-1}. MS (ESI): *m*/*z* = 455.30 $[M+Na]^+$, 450.35 $[M+NH_4]^+$, 433.32 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{29}H_{40}N_2O+Na]^+$ 455.3033, found: 455.3027. M.p. (POM): 84 °C.

2-(1,1-Dicyanomethylene)-7-(4-(tetradecyloxy)phenyl)-3,4,4a,5,6-pentahydro-naphthalene (Mal-2-C(14)): According to GP4, yield: 64.0 mg, 132 µmol, 72 %, column chromatography on silica gel gradient PE : EE = 12 : 1 to 6 : 1 (R_f = 0.5). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.19–1.39 (m, 20H, 10×CH_2), 1.41–1.49 (m, 2H, $OCH_2CH_2CH_2$), 1.49–1.61 (m, 2H, 4-H, 5-H), 1.74–1.87 (m, 2H, OCH_2CH_2), 2.08–2.14 (m, 2H, 4-H, 5-H), 2.45–2.53 (m, 1H, 4a-H), 2.58 (ddd, *J* = 17.5 Hz, 14.3 Hz, 4.8 Hz, 1H, 3-H), 2.64–2.73 (m, 1H, 6-H), 2.86 (ddd, *J* = 18.1 Hz, 4.8 Hz, 2.1 Hz, 1H, 6-H), 3.03–3.11 (m, 1H, 3-H), 3.99 (t, *J* = 6.6 Hz, 2H, OCH_2), 6.63 (d, *J* = 2.1 Hz, 1H, 1-H), 6.71 (d, *J* = 2.3 Hz, 1H, 8-H), 6.89–6.94 (m, 2H, 3'-H), 7.48–7.53 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.16 (CH_3), 22.72 ($CH_3CH_2CH_2$), 26.03 ($OCH_2CH_2CH_2$), 28.18 (C-6), 28.70 (C-4), 29.20, 29.39, 29.54, 29.59, 29.62, 29.68, 29.70, 29.72 (C-3, C-5, 9×CH_2), 31.95 (CH_3CH_2), 35.69 (C-

4a), 68.22 (OCH_2), 75.27 ($C(CN)_2$), 113.36, 114.07 (2×CN), 114.72 (C-3'), 120.34 (C-1), 122.96 (C-8), 127.22 (C-2'), 131.18 (C-1'), 151.06 (C-7), 158.66 (C-8a), 160.54 (C-4'), 170.03 (C-2) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2920 (vs), 2851 (s), 2216 (s), 1605 (w), 1590 (w), 1552 (vs), 1506 (vs), 1468 (m), 1454 (m), 1424 (w), 1395 (w), 1361 (w), 1339 (w), 1300 (m), 1250 (m), 1202 (vs), 1119 (w), 1016 (m), 901 (w), 831 (m), 794 (w), 723 (w), 660 (w), 633 (w), 582 (w), 558 (w), 522 (w), 473 (w) cm^{-1}. MS (ESI): *m/z* = 507.34 $[M+Na]^+$, 485.35 $[M+H]^+$, 336.25, 301.14. HRMS (ESI): calcd. for $[C_{33}H_{44}N_2O+H]^+$ 485.3526, found: 485.3530. M.p. (POM): 90 °C.

1-(1,1-Dicyanomethylene)-3-(4-(5,5,6,6,7,7,8,8,8-nonafluoroctyloxy)phenyl)-cyclohex-2-ene (Mal-1-C(4)F(4)): According to GP4, yield: 65.0 mg, 127 µmol, 65 %, column chromatography on silica gel gradient PE : EE = 12 : 1 to 5 : 1 (R_f = 0.5). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.80–1.88 (m, 2H, $CF_2CH_2CH_2$), 1.88–1.95 (m, 2H, OCH_2CH_2), 1.97–2.05 (m, 2H, 5-H), 2.17 (tt, *J* = 18.7 Hz, 7.6 Hz, 2H, CF_2CH_2), 2.75–2.84 (m, 4H, 4-H, 6-H), 4.06 (t, *J* = 5.9 Hz, 2H, OCH_2), 6.90–6.97 (m, 2H, 3'-H), 7.15 (t, *J* = 1.3 Hz, 1.3 Hz, 1H, 2-H), 7.56–7.63 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 17.26 ($CF_2CH_2CH_2$), 21.64 (C-5), 28.00 (C-4), 28.58 (OCH_2CH_2), 29.21 (C-6), 30.56 (t, CF_2CH_2), 67.47 (OCH_2), 77.48 ($C(CN)_2$), 112.87, 113.59 (2×CN), 114.85 (C-3'), 119.03 (C-2), 128.19 (C-2'), 130.37 (C-1'), 157.49 (C-3), 161.29 (C-4'), 170.19 (C-1) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.00, -124.47, -114.59, -81.04 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2951 (w), 2881 (w), 2221 (w), 1606 (w), 1581 (w), 1562 (m), 1532 (m), 1512 (w), 1473 (w), 1422 (w), 1358 (w), 1337 (w), 1287 (w), 1219 (s), 1202 (s), 1131 (s), 1070 (w), 1033 (w), 964 (w), 907 (m), 879 (m), 827 (m), 729 (vs), 648 (w), 599 (w), 543 (w), 466 (w), 444 (w), 413 (w) cm^{-1}. MS (ESI): *m/z* = 533.12 $[M+Na]^+$, 511.14 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{23}H_{19}F_9N_2O+Na]^+$ 533.1246, found: 533.1236. M.p. (POM): 78 °C.

2-(1,1-Dicyanomethylene)-7-(4-(5,5,6,6,7,7,8,8,8-nonafluoroctyloxy)phenyl)-3,4,4a,5,6-pentahydronaphthalene (Mal-2-C(4)F(4)): According to GP4, yield: 84.0 mg, 149 µmol, 75 %, column chromatography on silica gel gradient PE : EE = 10 : 1 to 5 : 1 (R_f = 0.4). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.45–1.61 (m, 2H, 4-H, 5-H), 1.79–1.87 (m, 2H, $CF_2CH_2CH_2$), 1.87–1.94 (m, 2H, OCH_2CH_2), 2.08–2.24 (m, 4H, 4-H, 5-H, CF_2CH_2), 2.44–2.53 (m, 1H, 4a-H), 2.58 (ddd, *J* = 17.5 Hz, 14.3 Hz, 4.9 Hz, 1H, 3-H), 2.69 (dddd, *J* = 19.1 Hz, 12.4 Hz, 4.9 Hz, 2.3 Hz, 1H, 6-H), 2.86 (ddd, *J* = 18.1 Hz, 4.9 Hz, 2.3 Hz, 1H, 6-H), 3.08 (ddd, *J* = 17.5 Hz, 4.1 Hz, 2.3 Hz, 1H, 3-H), 4.04 (t, *J* = 5.9 Hz, 2H, OCH_2), 6.63 (s, 1H, 1-H), 6.71 (d, *J* = 2.3 Hz, 1H, 8-H), 6.89–6.95 (m, 2H, 3'-H), 7.49–7.54 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 17.28 ($CF_2CH_2CH_2$), 28.18, 28.63, 28.67, 29.52, 29.66 (C-3, C-4, C-5, C-6, OCH_2CH_2), 30.57 (t, CF_2CH_2), 35.66 (C-4a), 67.36 (OCH_2), 75.42 ($C(CN)_2$), 113.33, 114.02 (2×CN), 114.66 (C-3'), 120.44 (C-1), 123.15 (C-8), 127.27 (C-2'), 131.60 (C-1'), 150.88

(C-7), 158.56 (C-8a), 160.10 (C-4'), 170.03 (C-2) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.00, -124.44, -114.60, -81.04 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2940 (w), 2869 (w), 2219 (w), 1605 (w), 1554 (m), 1507 (m), 1474 (w), 1455 (w), 1424 (w), 1395 (w), 1360 (w), 1340 (w), 1299 (w), 1234 (m), 1201 (m), 1179 (m), 1132 (m), 1070 (w), 1016 (w), 957 (w), 905 (s), 879 (w), 831 (w), 803 (w), 726 (vs), 649 (m), 581 (w), 529 (w), 475 (w), 413 (w) cm^{-1}. MS (ESI): *m*/*z* = 585.16 $[M+Na]^+$, 563.17 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{27}H_{23}F_9N_2O+H]^+$ 563.1739, found: 563.1726. M.p. (POM): 63 °C.

1-(1,1-Dicyanomethylene)-3-(4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl-oxy)phenyl)-cyclohex-2-ene (Mal-1-C(4)F(6)): According to GP4, yield: 81.0 mg, 133 µmol, 74 %, column chromatography on silica gel gradient PE : EE = 12 : 1 to 5 : 1 (R_f = 0.5). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.80–1.88 (m, 2H, $CF_2CH_2CH_2$), 1.88–1.96 (m, 2H, OCH_2CH_2), 2.01 (tt, *J* = 6.2 Hz, 6.1 Hz, 2H, 5-H), 2.10–2.25 (m, 2H, CF_2CH_2), 2.76–2.84 (m, 4H, 4-H, 6-H), 4.06 (t, *J* = 5.9 Hz, 2H, OCH_2), 6.90–6.97 (m, 2H, 3'-H), 7.15 (d, *J* = 1.5 Hz, 1H, 2-H), 7.56–7.63 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): *δ* = 17.28 ($CF_2CH_2CH_2$), 21.64 (C-5), 28.00 (C-4), 28.59 (OCH_2CH_2), 29.21 (C-6), 30.65 (t, CF_2CH_2), 67.47 (OCH_2), 77.49 ($C(CN)_2$), 112.87, 113.58 (2×CN), 114.85 (C-3'), 119.03 (C-2), 128.18 (C-2'), 130.37 (C-1'), 157.49 (C-3), 161.29 (C-4'), 170.18 (C-1) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.10, -123.51, -122.85, -121.89, -114.36, -80.81 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2954 (w), 2877 (w), 2221 (w), 1606 (w), 1581 (w), 1562 (m), 1532 (m), 1512 (w), 1473 (w), 1423 (w), 1363 (w), 1337 (w), 1286 (w), 1237 (s), 1200 (s), 1143 (s), 1122 (m), 1072 (w), 1035 (w), 964 (w), 908 (m), 827 (m), 811 (w), 729 (vs), 708 (m), 696 (m), 650 (m), 607 (w), 566 (w), 543 (w), 467 (w), 444 (w), 411 (w) cm^{-1}. MS (ESI): *m*/*z* = 633.12 $[M+Na]^+$, 611.13 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{25}H_{19}F_{13}N_2O+Na]^+$ 633.1182, found: 633.1177. M.p. (POM): 91 °C.

2-(1,1-Dicyanomethylene)-7-(4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl-oxy)phenyl)-3,4,4a,5,6-pentahydronaphthalene (Mal-2-C(4)F(6)): According to GP4, yield: 101 mg, 152 µmol, 81 %, column chromatography on silica gel gradient PE : EE = 10 : 1 to 5 : 1 (R_f = 0.4). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.45–1.61 (m, 2H, 4-H, 5-H), 1.79–1.87 (m, 2H, $CF_2CH_2CH_2$), 1.87–1.95 (m, 2H, OCH_2CH_2), 2.08–2.24 (m, 4H, 4-H, 5-H, CF_2CH_2), 2.44–2.54 (m, 1H, 4a-H), 2.58 (ddd, *J* = 17.6 Hz, 14.2 Hz, 4.9 Hz, 1H, 3-H), 2.69 (dddd, *J* = 19.4 Hz, 12.5 Hz, 4.9 Hz, 2.3 Hz, 1H, 6-H), 2.86 (ddd, *J* = 18.2 Hz, 4.9 Hz, 2.3 Hz, 1H, 6-H), 3.08 (ddd, *J* = 17.5 Hz, 4.2 Hz, 2.3 Hz, 1H, 3-H), 4.04 (t, *J* = 5.9 Hz, 2H, OCH_2), 6.64 (s, 1H, 1-H), 6.71 (d, *J* = 2.3 Hz, 1H, 8-H), 6.89–6.95 (m, 2H, 3'-H), 7.49–7.54 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): *δ* = 17.30 ($CF_2CH_2CH_2$), 28.18, 28.64, 28.68, 29.52, 29.66 (C-3, C-4, C-5, C-6, OCH_2CH_2), 30.66 (t, CF_2CH_2), 35.67 (C-4a), 67.36 (OCH_2), 75.43 ($C(CN)_2$), 113.32, 114.02 (2×CN), 114.66 (C-3'), 120.44 (C-1), 123.15 (C-8), 127.27 (C-2'), 131.61 (C-1'), 150.87 (C-7), 158.55 (C-8a), 160.10 (C-4'), 170.03 (C-2) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -

126.10, -123.50, -122.83, -121.89, -114.36, -80.80 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2930 (w), 2866 (w), 2217 (m), 1605 (w), 1554 (m), 1507 (m), 1475 (w), 1454 (w), 1423 (w), 1396 (w), 1362 (w), 1340 (w), 1299 (w), 1235 (m), 1200 (s), 1180 (s), 1143 (s), 1122 (m), 1070 (w), 1037 (w), 1016 (w), 955 (w), 907 (m), 831 (w), 811 (w), 729 (m), 707 (m), 696 (m), 649 (m), 633 (w), 605 (w), 565 (w), 533 (w), 474 (w), 446 (w), 430 (w) cm^{-1}. MS (ESI): *m*/*z* = 680.19 $[M+NH_4]^+$, 663.17 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{29}H_{23}F_{13}N_2O+H]^+$ 663.1676, found: 663.1665. M.p. (POM): 134 °C.

1-(1,1-Dicyanomethylene)-3-(4-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluoro-dodecyloxy)phenyl)-cyclohex-2-ene (Mal-1-C(4)F(8)): According to GP4, yield: 59.0 mg, 83.1 µmol, 68 %, column chromatography on silica gel gradient PE : EE = 12 : 1 to 5 : 1 (R_f = 0.5). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.76–1.96 (m, 4H, $CF_2CH_2CH_2$, OCH_2CH_2), 1.97–2.06 (m, 2H, 5-H), 2.09–2.26 (m, 2H, CF_2CH_2), 2.74–2.85 (m, 4H, 4-H, 6-H), 4.06 (t, *J* = 5.8 Hz, 2H, OCH_2), 6.89–6.98 (m, 2H, 3'-H), 7.15 (d, *J* = 1.6 Hz, 1H, 2-H), 7.55–7.63 (m, 2H, 2'-H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 17.29 ($CF_2CH_2CH_2$), 21.63 (C-5), 28.00 (C-4), 28.59 (OCH_2CH_2), 29.20 (C-6), 30.67 (t, CF_2CH_2), 67.47 (OCH_2), 77.54 ($C(CN)_2$), 112.83, 113.54 (2×CN), 114.85 (C-3'), 119.04 (C-2), 128.16 (C-2'), 130.39 (C-1'), 157.43 (C-3), 161.29 (C-4'), 170.11 (C-1) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.07, -123.47, -122.68, -121.91, -121.86, -121.70, -114.36, -80.77 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2928 (w), 2853 (w), 2220 (w), 1596 (w), 1563 (w), 1533 (w), 1512 (w), 1494 (w), 1466 (w), 1422 (w), 1366 (w), 1349 (w), 1329 (w), 1282 (w), 1239 (s), 1202 (vs), 1147 (s), 1116 (m), 1073 (w), 1038 (w), 957 (w), 908 (m), 886 (w), 826 (w), 730 (vs), 704 (m), 649 (m), 623 (w), 605 (w), 559 (w), 529 (w), 466 (w), 439 (w), 411 (w) cm^{-1}. MS (ESI): *m*/*z* = 733.11 $[M+Na]^+$, 703.12. HRMS (ESI): calcd. for $[C_{27}H_{19}F_{17}N_2O+Na]^+$ 733.1118, found: 733.1107. M.p. (POM): 119 °C.

2-(1,1-Dicyanomethylene)-7-(4-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluoro-dodecyloxy)phenyl)-3,4,4a,5,6-pentahydronaphthalene (Mal-2-C(4)F(8)): According to GP4, yield: 100 mg, 131 µmol, 74 %, column chromatography on silica gel gradient PE : EE = 10 : 1 to 5 : 1 (R_f = 0.4). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.46–1.61 (m, 2H, 4-H, 5-H), 1.79–1.87 (m, 2H, $CF_2CH_2CH_2$), 1.87–1.95 (m, 2H, OCH_2CH_2), 2.08–2.24 (m, 4H, 4-H, 5-H, CF_2CH_2), 2.45–2.53 (m, 1H, 4a-H), 2.58 (ddd, *J* = 17.5 Hz, 14.3 Hz, 4.9 Hz, 1H, 3-H), 2.69 (dddd, *J* = 19.2 Hz, 12.4 Hz, 4.9 Hz, 2.3 Hz, 1H, 6-H), 2.86 (ddd, *J* = 18.2 Hz, 4.9 Hz, 2.3 Hz, 1H, 6-H), 3.08 (ddd, *J* = 17.6 Hz, 4.3 Hz, 2.3 Hz, 1H, 3-H), 4.04 (t, *J* = 5.9 Hz, 2H, OCH_2), 6.64 (s, 1H, 1-H), 6.71 (d, *J* = 2.3 Hz, 1H, 8-H), 6.89–6.95 (m, 2H, 3'-H), 7.49–7.54 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$) δ = 17.30 ($CF_2CH_2CH_2$), 28.18, 28.64, 28.68, 29.52, 29.66 (C-3, C-4, C-5, C-6, OCH_2CH_2), 30.67 (t, CF_2CH_2), 35.67 (C-4a), 67.36 (OCH_2), 75.44 ($C(CN)_2$), 113.32, 114.02 (2×CN), 114.66 (C-3'), 120.45 (C-1), 123.15 (C-8), 127.27 (C-2'), 131.61 (C-1'), 150.86 (C-7), 158.54 (C-8a), 160.10 (C-4'), 170.02 (C-2) ppm. ^{19}F-

NMR (376 MHz, $CDCl_3$): δ = -126.07, -123.46, -122.68, -121.91, -121.86, -121.67, -114.36, -80.77 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2947 (w), 2892 (w), 2217 (w), 1605 (w), 1555 (m), 1508 (m), 1477 (w), 1454 (w), 1424 (w), 1396 (w), 1363 (w), 1340 (w), 1300 (w), 1238 (m), 1199 (s), 1145 (s), 1116 (m), 1063 (w), 1035 (w), 1013 (w), 955 (w), 908 (m), 872 (w), 830 (w), 793 (w), 732 (m), 703 (w), 651 (m), 558 (w), 529 (w), 480 (w), 413 (w) cm^{-1}. MS (ESI): *m*/*z* = 780.19 $[M+NH_4]^+$, 763.16 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{31}H_{23}F_{17}N_2O+H]^+$ 763.1612, found: 763.1597. M.p. (POM): 182 °C.

1-(1,1-Dicyanomethylene)-3-(4-(7,7,8,8,9,9,10,10,10-nonafluorodecyloxy)phenyl)-cyclohex-2-ene (Mal-1-C(6)F(4)): According to GP4, yield: 62.0 mg, 115 µmol, 71 %, column chromatography on silica gel gradient PE : EE = 12 : 1 to 5 : 1 (R_f = 0.5). ^{1}H-NMR (700 MHz, $CDCl_3$): δ = 1.45–1.51 (m, 2H, $CF_2CH_2CH_2CH_2$), 1.51–1.56 (m, 2H, $OCH_2CH_2CH_2$), 1.61–1.69 (m, 2H, $CF_2CH_2CH_2$), 1.80–1.86 (m, 2H, OCH_2CH_2), 2.01 (tt, *J* = 6.5 Hz, 6.1 Hz, 2H, 5-H), 2.08 (tt, *J* = 17.4 Hz, 7.5 Hz, 2H, CF_2CH_2), 2.78 (t, *J* = 6.1 Hz, 2H, 4-H), 2.81 (t, *J* = 6.5 Hz, 2H, 6-H), 4.02 (t, *J* = 6.4 Hz, 2H, OCH_2), 6.91–6.95 (m, 2H, 3'-H), 7.15 (s, 1H, 2-H), 7.57–7.61 (m, 2H, 2'-H) ppm. ^{13}C-NMR (176 MHz, $CDCl_3$): δ = 20.07 ($CF_2CH_2CH_2$), 21.64 (C-5), 25.73 ($OCH_2CH_2CH_2$), 27.98 (C-4), 28.83, 28.88 (2×CH_2), 29.21 (C-6), 30.71 (t, CF_2CH_2), 67.98 (OCH_2), 77.35 ($C(CN)_2$), 108.68–119.91 (m, CF_2, CF_3), 112.91, 113.62 (2×CN), 114.88 (C-3'), 118.91 (C-2), 128.17 (C-2'), 130.11 (C-1'), 157.58 (C-3), 161.59 (C-4'), 170.22 (C-1) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.02, -124.45, -114.55, -81.06 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2946 (w), 2870 (w), 2219 (m), 1605 (w), 1580 (m), 1561 (m), 1531 (m), 1512 (m), 1471 (w), 1423 (w), 1358 (w), 1337 (w), 1287 (m), 1221 (vs), 1201 (vs), 1131 (vs), 1049 (w), 1020 (w), 982 (w), 911 (w), 879 (m), 847 (w), 827 (m), 733 (m), 718 (m), 638 (w), 613 (w), 543 (w), 489 (w), 464 (w), 443 (w), 413 (w) cm^{-1}. MS (ESI): *m*/*z* = 561.15 $[M+Na]^+$, 556.20 $[M+NH_4]^+$, 539.17 $[M+H]^+$, 509.17. HRMS (ESI): calcd. for $[C_{25}H_{23}F_9N_2O+H]^+$ 539.1739, found: 539.1738. M.p. (POM): 94 °C.

2-(1,1-Dicyanomethylene)-7-(4-(7,7,8,8,9,9,10,10,10-nonafluorodecyloxy)phenyl)-3,4,4a,5,6-pentahydronaphthalene (Mal-2-C(6)F(4)): According to GP4, yield: 89.0 mg, 151 µmol, 82 %, column chromatography on silica gel gradient PE : EE = 10 : 1 to 5 : 1 (R_f = 0.4). ^{1}H-NMR (700 MHz, $CDCl_3$): δ = 1.43–1.61 (m, 6H, 4-H, 5-H, $OCH_2CH_2CH_2$, CF_2CH_2-CH_2CH_2), 1.63–1.69 (m, 2H, $CF_2CH_2CH_2$), 1.82 (tt, *J* = 6.8 Hz, 6.7 Hz, 2H, OCH_2CH_2), 2.03–2.13 (m, 4H, 4-H, 5-H, CF_2CH_2), 2.46–2.52 (m, 1H, 4a-H), 2.58 (ddd, *J* = 18.0 Hz, 14.2 Hz, 4.8 Hz, 1H, 3-H), 2.66–2.72 (m, 1H, 6-H), 2.86 (ddd, *J* = 18.1 Hz, 4.8 Hz, 2.3 Hz, 1H, 6-H), 3.05–3.10 (m, 1H, 3-H), 4.01 (t, *J* = 6.4 Hz, 2H, OCH_2), 6.63 (s, 1H, 1-H), 6.71 (d, *J* = 2.3 Hz, 1H, 8-H), 6.89–6.93 (m, 2H, 3'-H), 7.49–7.53 (m, 2H, 2'-H) ppm. ^{13}C-NMR (176 MHz, $CDCl_3$): δ = 20.07 ($CF_2CH_2CH_2$), 25.75 ($OCH_2CH_2CH_2$), 28.17 (C-6), 28.68 (C-4), 28.83, 28.94 (2×CH_2), 29.53 (C-3), 29.66 (C-5), 30.71 (t, CF_2CH_2), 35.67 (C-4a), 67.87 (OCH_2), 75.33

(C(CN)$_2$), 108.68–119.90 (m, CF_2, CF_3), 113.35, 114.05 (2×CN), 114.69 (C-3'), 120.38 (C-1), 123.04 (C-8), 127.25 (C-2'), 131.36 (C-1'), 150.98 (C-7), 158.62 (C-8a), 160.39 (C-4'), 170.04 (C-2) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.02, -124.47, -114.55, -81.05 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2940 (w), 2864 (w), 2221 (m), 1605 (w), 1554 (s), 1507 (s), 1471 (w), 1454 (w), 1424 (w), 1395 (w), 1360 (w), 1340 (w), 1300 (w), 1221 (s), 1201 (vs), 1179 (vs), 1131 (s), 1045 (w), 1015 (m), 906 (s), 878 (m), 831 (m), 728 (vs), 648 (w), 633 (w), 581 (w), 557 (w), 530 (w), 474 (w), 446 (w), 412 (w) cm^{-1}. MS (ESI): *m*/*z* = 629.23, 613.26 $[M+Na]^+$, 608.23 $[M+NH_4]^+$, 591.21 $[M+H]^+$, 509.21, 493.23. HRMS (ESI): calcd. for $[C_{29}H_{27}F_9N_2O+H]^+$ 591.2052, found: 591.2054. M.p. (POM): 99 °C.

1-(1,1-Dicyanomethylene)-3-(4-(7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluorododecyl-oxy)phenyl)-cyclohex-2-ene (Mal-1-C(6)F(6)): According to GP4, yield: 66.0 mg, 103 µmol, 76 %, column chromatography on silica gel gradient PE : EE = 12 : 1 to 5 : 1 (R_f = 0.5). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.43–1.60 (m, 4H, $CF_2CH_2CH_2CH_2$, $OCH_2CH_2CH_2$), 1.61–1.70 (m, 2H, $CF_2CH_2CH_2$), 1.79–1.88 (m, 2H, OCH_2CH_2), 1.95–2.15 (m, 4H, 5-H, CF_2CH_2), 2.75–2.84 (m, 4H, 4-H, 6-H), 4.02 (t, *J* = 6.4 Hz, 2H, OCH_2), 6.90–6.96 (m, 2H, 3'-H), 7.15 (d, *J* = 1.4 Hz, 1H, 2-H), 7.56–7.62 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 20.10 ($CF_2CH_2CH_2$), 21.64 (C-5), 25.74 ($OCH_2CH_2CH_2$), 27.98 (C-4), 28.84, 28.89 (2×CH_2), 29.22 (C-6), 30.81 (t, CF_2CH_2), 67.97 (OCH_2), 77.35 (C(CN)$_2$), 112.90, 113.61 (2×CN), 114.87 (C-3'), 118.91 (C-2), 128.16 (C-2'), 130.10 (C-1'), 157.56 (C-3), 161.58 (C-4'), 170.20 (C-1) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.12, -123.52, -122.85, -121.91, -114.32, -80.80 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2947 (w), 2873 (w), 2222 (w), 1735 (w), 1606 (w), 1581 (w), 1562 (w), 1533 (w), 1512 (w), 1470 (w), 1422 (w), 1362 (w), 1337 (w), 1286 (w), 1239 (m), 1202 (m), 1181 (m), 1144 (w), 1052 (w), 905 (s), 828 (w), 811 (w), 725 (vs), 649 (m), 566 (w), 544 (w), 469 (w), 413 (w) cm^{-1}. MS (ESI): *m*/*z* = 639.17 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{27}H_{23}F_{13}N_2O+H]^+$ 639.1676, found: 639.1675. M.p. (POM): 96 °C.

2-(1,1-Dicyanomethylene)-7-(4-(7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluorododecyl-oxy)phenyl)-3,4,4a,5,6-pentahydronaphthalene (Mal-2-C(6)F(6)): According to GP4, yield: 122 mg, 177 µmol, 71 %, column chromatography on silica gel gradient PE : EE = 10 : 1 to 5 : 1 (R_f = 0.4). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.44–1.60 (m, 6H, 4-H, 5-H, $OCH_2CH_2CH_2$, $CF_2CH_2CH_2CH_2$), 1.61–1.70 (m, 2H, $CF_2CH_2CH_2$), 1.78–1.86 (m, 2H, OCH_2CH_2), 2.01–2.15 (m, 4H, 4-H, 5-H, CF_2CH_2), 2.45–2.53 (m, 1H, 4a-H), 2.58 (ddd, *J* = 17.6 Hz, 14.2 Hz, 4.8 Hz, 1H, 3-H), 2.64–2.73 (m, 1H, 6-H), 2.86 (ddd, *J* = 18.1 Hz, 4.8 Hz, 2.2 Hz, 1H, 6-H), 3.08 (ddd, *J* = 17.5 Hz, 4.2 Hz, 2.2 Hz, 1H, 3-H), 4.01 (t, *J* = 6.4 Hz, 2H, OCH_2), 6.63 (d, *J* = 2.2 Hz, 1H, 1-H), 6.71 (d, *J* = 2.2 Hz, 1H, 8-H), 6.89–6.95 (m, 2H, 3'-H), 7.48–7.54 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 20.10 ($CF_2CH_2CH_2$), 25.76 ($OCH_2CH_2CH_2$), 28.17 (C-6), 28.68 (C-4), 28.84, 28.94 (2×CH_2), 29.53 (C-3), 29.66 (C-5), 30.81 (t, CF_2CH_2), 35.67 (C-4a), 67.86

(OCH_2), 75.33 ($C(CN)_2$), 113.34, 114.04 (2×CN), 114.68 (C-3'), 120.38 (C-1), 123.04 (C-8), 127.24 (C-2'), 131.35 (C-1'), 150.97 (C-7), 158.61 (C-8a), 160.38 (C-4'), 170.03 (C-2) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.12, -123.52, -122.86, -121.91, -114.32, -80.80 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2940 (w), 2862 (w), 2217 (m), 1739 (w), 1605 (w), 1556 (m), 1508 (m), 1472 (w), 1454 (w), 1424 (w), 1395 (w), 1362 (w), 1340 (w), 1300 (w), 1236 (s), 1201 (vs), 1144 (s), 1122 (m), 1048 (w), 1016 (w), 902 (w), 831 (w), 812 (w), 732 (w), 708 (w), 697 (w), 654 (w), 633 (w), 566 (w), 532 (w), 449 (w), 415 (w) cm^{-1}. MS (ESI): *m*/*z* = 691.20 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{31}H_{27}F_{13}N_2O+H]^+$ 691.1989, found: 691.1987. M.p. (POM): 138 °C.

1-(1,1-Dicyanomethylene)-3-(4-(7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptadeca-fluorotetradecyloxy)phenyl)-cyclohex-2-ene (Mal-1-C(6)F(8)): According to GP4, yield: 86.0 mg, 116 µmol, 80 %, column chromatography on silica gel gradient PE : EE = 12 : 1 to 5 : 1 (R_f = 0.5). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.41–1.58 (m, 4H, $CF_2CH_2CH_2CH_2$, $OCH_2CH_2CH_2$), 1.61–1.72 (m, 2H, $CF_2CH_2CH_2$), 1.77–1.88 (m, 2H, OCH_2CH_2), 1.97–2.16 (m, 4H, 5-H, CF_2CH_2), 2.75–2.84 (m, 4H, 4-H, 6-H), 4.02 (t, *J* = 6.3 Hz, 2H, OCH_2), 6.90–6.96 (m, 2H, 3'-H), 7.15 (d, *J* = 1.4 Hz, 1H, 2-H), 7.56–7.62 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 20.10 ($CF_2CH_2CH_2$), 21.64 (C-5), 25.74 ($OCH_2CH_2CH_2$), 27.98 (C-4), 28.84, 28.89 (2×CH_2), 29.21 (C-6), 30.82 (t, CF_2CH_2), 67.97 (OCH_2), 77.36 ($C(CN)_2$), 112.90, 113.61 (2×CN), 114.86 (C-3'), 118.91 (C-2), 128.16 (C-2'), 130.10 (C-1'), 157.55 (C-3), 161.58 (C-4'), 170.20 (C-1) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.08, -123.49, -122.69, -121.92, -121.87, -121.69, -114.31, -80.78 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2948 (w), 2859 (w), 2221 (w), 1606 (w), 1578 (w), 1563 (w), 1531 (w), 1514 (w), 1472 (w), 1377 (w), 1287 (w), 1243 (m), 1203 (m), 1183 (m), 1149 (w), 1049 (w), 1030 (w), 997 (w), 903 (vs), 828 (w), 724 (vs), 650 (m), 558 (w), 542 (w) cm^{-1}. MS (ESI): *m*/*z* = 761.14 $[M+Na]^+$, 756.19 $[M+NH_4]^+$, 739.16 $[M+H]^+$, 709.16. HRMS (ESI): calcd. for $[C_{29}H_{23}F_{17}N_2O+Na]^+$ 761.1431, found: 761.1427. M.p. (POM): 136 °C.

2-(1,1-Dicyanomethylene)-7-(4-(7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptadeca-fluorotetradecyloxy)phenyl)-3,4,4a,5,6-pentahydronaphthalene (Mal-2-C(6)F(8)): According to GP4, yield: 76.0 mg, 96.1 µmol, 86 %, column chromatography on silica gel gradient PE : EE = 10 : 1 to 5 : 1 (R_f = 0.5). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.43–1.60 (m, 6H, 4-H, 5-H, $OCH_2CH_2CH_2$, $CF_2CH_2CH_2CH_2$), 1.61–1.70 (m, 2H, $CF_2CH_2CH_2$), 1.78–1.87 (m, 2H, OCH_2CH_2), 1.98–2.16 (m, 4H, 4-H, 5-H, CF_2CH_2), 2.45–2.53 (m, 1H, 4a-H), 2.58 (ddd, *J* = 18.0 Hz, 14.2 Hz, 4.8 Hz, 1H, 3-H), 2.65–2.73 (m, 1H, 6-H), 2.86 (ddd, *J* = 18.2 Hz, 4.8 Hz, 2.2 Hz, 1H, 6-H), 3.04–3.11 (m, 1H, 3-H), 4.01 (t, *J* = 6.4 Hz, 2H, OCH_2), 6.63 (d, *J* = 2.2 Hz, 1H, 1-H), 6.71 (d, *J* = 2.2 Hz, 1H, 8-H), 6.89–6.94 (m, 2H, 3'-H), 7.48–7.53 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 20.10 ($CF_2CH_2CH_2$), 25.76 ($OCH_2CH_2CH_2$), 28.17 (C-6), 28.68 (C-4), 28.85, 28.94 (2×CH_2), 29.53 (C-3), 29.66 (C-5), 30.82 (t, CF_2CH_2), 35.68 (C-4a),

67.86 (OCH_2), 75.35 ($C(CN)_2$), 113.34, 114.04 (2×CN), 114.68 (C-3'), 120.39 (C-1), 123.04 (C-8), 127.24 (C-2'), 131.36 (C-1'), 150.96 (C-7), 158.60 (C-8a), 160.37 (C-4'), 170.03 (C-2) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.06, -123.48, -122.68, -121.91, -121.86, -121.71, -114.30, -80.76 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2926 (w), 2855 (w), 2217 (w), 1737 (w), 1605 (w), 1555 (m), 1508 (m), 1470 (w), 1454 (w), 1424 (w), 1369 (w), 1339 (w), 1300 (w), 1238 (s), 1200 (vs), 1146 (vs), 1117 (m), 1047 (w), 1015 (w), 980 (w), 909 (w), 871 (w), 830 (m), 793 (w), 734 (m), 704 (m), 655 (m), 605 (w), 559 (m), 530 (m), 442 (w) cm^{-1}. MS (ESI): *m*/*z* = 808.22 $[M+NH_4]^+$, 791.19 $[M+H]^+$, 541.17, 519.19. HRMS (ESI): calcd. for $[C_{33}H_{27}F_{17}N_2O+H]^+$ 791.1925, found: 791.1922. M.p. (POM): 173 °C.

1-(1,1-Dicyanomethylene)-3-(4-(9,9,10,10,11,11,12,12,12-nonafluorododecyl-oxy)phenyl)-cyclohex-2-ene (Mal-1-C(8)F(4)): According to GP4, yield: 79.0 mg, 139 µmol, 87 %, column chromatography on silica gel gradient PE : EE = 12 : 1 to 5 : 1 (R_f = 0.5). ^{1}H-NMR (700 MHz, $CDCl_3$): δ = 1.34–1.44 (m, 6H, 3×CH_2), 1.48 (tt, *J* = 7.3 Hz, 6.9 Hz, 2H, $OCH_2CH_2CH_2$), 1.58–1.64 (m, 2H, $CF_2CH_2CH_2$), 1.77–1.84 (m, 2H, OCH_2CH_2), 1.98–2.10 (m, 4H, 5-H, CF_2CH_2), 2.78 (t, *J* = 6.2 Hz, 2H, 4-H), 2.81 (t, *J* = 6.5 Hz, 2H, 6-H), 4.01 (t, *J* = 6.5 Hz, 2H, OCH_2), 6.91–6.95 (m, 2H, 3'-H), 7.15 (s, 1H, 2-H), 7.57–7.61 (m, 2H, 2'-H) ppm. ^{13}C-NMR (176 MHz, $CDCl_3$): δ = 20.07 ($CF_2CH_2CH_2$), 21.64 (C-5), 25.92 ($OCH_2CH_2CH_2$), 27.97 (C-4), 29.02, 29.08, 29.10, 29.14 (4×CH_2), 29.21 (C-6), 30.76 (t, CF_2CH_2), 68.20 (OCH_2), 77.30 ($C(CN)_2$), 112.92, 113.64 (2×CN), 114.90 (C-3'), 118.86 (C-2), 128.15 (C-2'), 130.01 (C-1'), 157.61 (C-3), 161.70 (C-4'), 170.22 (C-1) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.04, -124.47, -114.56, -81.07 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2923 (w), 2857 (w), 2219 (m), 1740 (w), 1607 (w), 1578 (m), 1563 (m), 1529 (m), 1514 (m), 1471 (w), 1426 (w), 1417 (w), 1404 (w), 1377 (w), 1358 (w), 1319 (w), 1287 (m), 1241 (s), 1218 (s), 1130 (vs), 1050 (m), 1020 (m), 994 (m), 964 (w), 909 (w), 871 (w), 845 (m), 827 (s), 767 (w), 756 (w), 717 (s), 690 (w), 638 (w), 611 (w), 600 (w), 543 (w), 530 (w), 486 (w), 464 (w), 442 (w) cm^{-1}. MS (ESI): *m*/*z* = 589.19 $[M+Na]^+$, 584.23, 567.21 $[M+H]^+$, 537.21. HRMS (ESI): calcd. for $[C_{27}H_{27}F_9N_2O+H]^+$ 567.2052, found: 567.2051. M.p. (POM): 83 °C.

2-(1,1-Dicyanomethylene)-7-(4-(9,9,10,10,11,11,12,12,12-nonafluorododecyloxy)-phenyl)-3,4,4a,5,6-pentahydronaphthalene (Mal-2-C(8)F(4)): According to GP4, yield: 91.0 mg, 147 µmol, 84 %, column chromatography on silica gel gradient PE : EE = 10 : 1 to 5 : 1 (R_f = 0.5). ^{1}H-NMR (700 MHz, $CDCl_3$): δ = 1.33–1.43 (m, 6H, 3×CH_2), 1.44–1.64 (m, 6H, 4-H, 5-H, 2×CH_2), 1.76–1.83 (m, 2H, OCH_2CH_2), 1.99–2.13 (m, 4H, 4-H, 5-H, CF_2CH_2), 2.45–2.52 (m, 1H, 4a-H), 2.58 (ddd, *J* = 18.1 Hz, 14.2 Hz, 4.8 Hz, 1H, 3-H), 2.64–2.72 (m, 1H, 6-H), 2.82–2.88 (m, 1H, 6-H), 3.04–3.10 (m, 1H, 3-H), 3.99 (t, *J* = 6.5 Hz, 2H, OCH_2), 6.62 (d, *J* = 2.2 Hz, 1H, 1-H), 6.71 (d, *J* = 2.2 Hz, 1H, 8-H), 6.89–6.93 (m, 2H, 3'-H), 7.48–7.52 (m, 2H, 2'-H) ppm. ^{13}C-NMR (176 MHz, $CDCl_3$): δ = 20.06 ($CF_2CH_2CH_2$), 25.94 ($OCH_2CH_2CH_2$), 28.16

(C-6), 28.67 (C-4), 29.01, 29.10, 29.13, 29.14 (4×CH_2), 29.52 (C-5), 29.66 (C-3), 30.76 (t, CF_2CH_2), 35.67 (C-4a), 68.09 (OCH_2), 75.20 ($C(CN)_2$), 113.37, 114.08 (2×CN), 114.71 (C-3'), 120.34 (C-1), 122.99 (C-8), 127.24 (C-2'), 131.25 (C-1'), 151.08 (C-7), 158.74 (C-8a), 160.49 (C-4'), 170.11 (C-2) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.03, -124.46, -114.55, -81.05 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2935 (w), 2860 (w), 2217 (m), 1737 (w), 1639 (w), 1606 (w), 1553 (s), 1507 (s), 1470 (w), 1454 (w), 1426 (w), 1395 (w), 1360 (w), 1340 (w), 1300 (w), 1232 (s), 1201 (vs), 1131 (s), 1015 (m), 901 (w), 878 (w), 832 (m), 802 (w), 735 (w), 718 (w), 660 (w), 633 (w), 582 (w), 558 (w), 525 (w), 471 (w), 436 (w), 413 (w) cm^{-1}. MS (ESI): *m*/*z* = 641.22 $[M+Na]^+$, 636.26, 619.24 $[M+H]^+$, 571.23. HRMS (ESI): calcd. for $[C_{31}H_{31}F_9N_2O+H]^+$ 619.2365, found: 619.2362. M.p. (POM): 108 °C.

1-(1,1-Dicyanomethylene)-3-(4-(9,9,10,10,11,11,12,12,13,13,14,14,14-tridecafluorotetradecyloxy)phenyl)-cyclohex-2-ene (Mal-1-C(8)F(6)): According to GP4, yield: 82.0 mg, 123 µmol, 72 %, column chromatography on silica gel gradient PE : EE = 12 : 1 to 5 : 1 (R_f = 0.5). ^{1}H-NMR (700 MHz, $CDCl_3$): δ = 1.35–1.43 (m, 6H, 3×CH_2), 1.45–1.51 (m, 2H, $OCH_2CH_2CH_2$), 1.58–1.65 (m, 2H, $CF_2CH_2CH_2$), 1.78–1.84 (m, 2H, OCH_2CH_2), 1.98–2.11 (m, 4H, 5-H, CF_2CH_2), 2.78 (t, *J* = 6.1 Hz, 2H, 4-H), 2.81 (t, *J* = 6.5 Hz, 2H, 6-H), 4.01 (t, *J* = 6.5 Hz, 2H, OCH_2), 6.91–6.95 (m, 2H, 3'-H), 7.15 (s, 1H, 2-H), 7.57–7.61 (m, 2H, 2'-H) ppm. ^{13}C-NMR (176 MHz, $CDCl_3$): δ = 20.09 ($CF_2CH_2CH_2$), 21.64 (C-5), 25.93 ($OCH_2CH_2CH_2$), 27.98 (C-4), 29.03, 29.08, 29.10, 29.15 (4×CH_2), 29.22 (C-6), 30.86 (t, CF_2CH_2), 68.20 (OCH_2), 77.31 ($C(CN)_2$), 112.91, 113.63 (2×CN), 114.90 (C-3'), 118.87 (C-2), 128.15 (C-2'), 130.01 (C-1'), 157.59 (C-3), 161.69 (C-4'), 170.21 (C-1) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.12, -123.53, -122.87, -121.92, -114.33, -80.80 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2938 (w), 2859 (w), 2221 (w), 1606 (w), 1580 (w), 1562 (w), 1532 (w), 1512 (w), 1470 (w), 1422 (w), 1363 (w), 1337 (w), 1286 (w), 1240 (m), 1201 (m), 1182 (m), 1144 (w), 1122 (w), 1052 (w), 1023 (w), 965 (w), 905 (vs), 828 (w), 726 (vs), 649 (m), 612 (w), 566 (w), 543 (w), 414 (w) cm^{-1}. MS (ESI): *m*/*z* = 689.18 $[M+Na]^+$, 684.23, 667.20 $[M+H]^+$, 637.20. HRMS (ESI): calcd. for $[C_{29}H_{27}F_{13}N_2O+H]^+$ 667.1989, found: 667.1989. M.p. (POM): 97 °C.

2-(1,1-Dicyanomethylene)-7-(4-(9,9,10,10,11,11,12,12,13,13,14,14,14-tridecafluorotetradecyloxy)phenyl)-3,4,4a,5,6-pentahydronaphthalene (Mal-2-C(8)F(6)): According to GP4, yield: 122 mg, 170 µmol, 80 %, column chromatography on silica gel gradient PE : EE = 10 : 1 to 5 : 1 (R_f = 0.4). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.32–1.68 (m, 12H, 5×CH_2, 4-H, 5-H), 1.73–1.89 (m, 2H, OCH_2CH_2), 1.93–2.19 (m, 4H, 4-H, 5-H, CF_2CH_2), 2.42–2.76 (m, 3H, 4a-H, 3-H, 6-H), 2.80–2.93 (m, 1H, 6-H), 3.03–3.15 (m, 1H, 3-H), 4.00 (t, *J* = 6.5 Hz, 2H, OCH_2), 6.63 (s, 1H, 1-H), 6.71 (d, *J* = 2.3 Hz, 1H, 8-H), 6.87–6.96 (m, 2H, 3'-H), 7.46–7.55 (m, 2H, 2'-H) ppm. ^{13}C-NMR (176 MHz, $CDCl_3$): δ = 20.09 ($CF_2CH_2CH_2$), 25.95 ($OCH_2CH_2CH_2$), 28.16 (C-6), 28.68 (C-4), 29.03, 29.11, 29.14, 29.15 (4×CH_2), 29.53 (C-5), 29.66 (C-3), 30.86 (t,

CF_2CH_2), 35.68 (C-4a), 68.09 (OCH_2), 75.29 ($C(CN)_2$), 113.35, 114.06 (2×CN), 114.71 (C-3'), 120.36 (C-1), 123.00 (C-8), 127.23 (C-2'), 131.26 (C-1'), 151.03 (C-7), 158.65 (C-8a), 160.49 (C-4'), 170.05 (C-2) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.12, -123.53, -122.86, -121.92, -114.33, -80.80 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2934 (w), 2860 (w), 2218 (m), 1736 (w), 1650 (w), 1591 (w), 1554 (m), 1508 (m), 1470 (w), 1454 (w), 1424 (w), 1395 (w), 1362 (w), 1340 (w), 1300 (w), 1236 (s), 1200 (vs), 1179 (vs), 1143 (m), 1122 (m), 1062 (w), 1016 (w), 907 (s), 831 (w), 811 (w), 729 (vs), 696 (m), 649 (m), 633 (w), 565 (w), 528 (w), 473 (w), 436 (w), 412 (w) cm^{-1}. MS (ESI): *m*/*z* = 736.26, 719.23 $[M+H]^+$, 693.20, 671.22. HRMS (ESI): calcd. for $[C_{33}H_{31}F_{13}N_2O+H]^+$ 719.2302, found: 719.2302. M.p. (POM): 137 °C.

1-(1,1-Dicyanomethylene)-3-(4-(9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-heptadecafluorohexadecyloxy)phenyl)cyclohex-2-ene (Mal-1-C(8)F(8)): According to GP4, yield: 89.0 mg, 116 µmol, 83 %, column chromatography on silica gel gradient PE : EE = 12 : 1 to 5 : 1 (R_f = 0.5). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.34–1.44 (m, 6H, 3×CH_2), 1.44–1.52 (m, 2H, $OCH_2CH_2CH_2$), 1.53–1.66 (m, 2H, $CF_2CH_2CH_2$), 1.75–1.85 (m, 2H, OCH_2CH_2), 1.96–2.13 (m, 4H, 5-H, CF_2CH_2), 2.75–2.84 (m, 4H, 4-H, 6-H), 4.01 (t, *J* = 6.5 Hz, 2H, OCH_2), 6.89–6.96 (m, 2H, 3'-H), 7.15 (d, *J* = 1.4 Hz, 1H, 2-H), 7.55–7.62 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 20.10 ($CF_2CH_2CH_2$), 21.64 (C-5), 25.93 ($OCH_2CH_2CH_2$), 27.98 (C-4), 29.03, 29.08, 29.11, 29.16 (4×CH_2), 29.22 (C-6), 30.87 (t, CF_2CH_2), 68.20 (OCH_2), 77.22^i ($C(CN)_2$), 112.91, 113.63 (2×CN), 114.89 (C-3'), 118.86 (C-2), 128.14 (C-2'), 130.00 (C-1'), 157.58 (C-3), 161.68 (C-4'), 170.21 (C-1) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.07, -123.50, -122.69, -121.93, -121.87, -121.70, -114.32, -80.77 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2928 (w), 2221 (w), 1580 (w), 1562 (w), 1531 (w), 1512 (w), 1471 (w), 1374 (w), 1243 (m), 1204 (m), 1182 (m), 1150 (w), 1023 (w), 904 (vs), 828 (w), 726 (vs), 650 (m), 542 (w) cm^{-1}. MS (ESI): *m*/*z* = 784.22, 767.19 $[M+H]^+$, 737.19. HRMS (ESI): calcd. for $[C_{31}H_{27}F_{17}N_2O+H]^+$ 767.1925, found: 767.1921. M.p. (POM): 133 °C.

2-(1,1-Dicyanomethylene)-7-(4-(9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-heptadecafluorohexadecyloxy)phenyl)-3,4,4a,5,6-pentahydronaphthalene (Mal-2-C(8)F(8)): 131 mg, 160 µmol, 88 %, column chromatography on silica gel gradient PE : EE = 10 : 1 to 5 : 1 (R_f = 0.4). ^{1}H-NMR (700 MHz, $CDCl_3$): δ = 1.34–1.43 (m, 6H, 3×CH_2), 1.45–1.64 (m, 6H, 4-H, 5-H, 2×CH_2), 1.77–1.83 (m, 2H, OCH_2CH_2), 2.00–2.13 (m, 4H, 4-H, 5-H, CF_2CH_2), 2.46–2.52 (m, 1H, 4a-H), 2.58 (ddd, *J* = 18.1 Hz, 14.2 Hz, 4.8 Hz, 1H, 3-H), 2.65–2.72 (m, 1H, 6-H), 2.85 (ddd, *J* = 18.1 Hz, 4.8 Hz, 2.3 Hz, 1H, 6-H), 3.05–3.10 (m, 1H, 3-H), 3.99 (t, *J* = 6.5 Hz, 2H, OCH_2), 6.63 (d, *J* = 2.1 Hz, 1H, 1-H), 6.71 (d, *J* = 2.3 Hz, 1H, 8-H), 6.91 (d, *J* = 8.6 Hz, 2H, 3'-H), 7.51 (d, *J* = 8.6 Hz, 2H, 2'-H) ppm. ^{13}C-NMR (176 MHz, $CDCl_3$): δ = 20.10 ($CF_2CH_2CH_2$), 25.95 ($OCH_2CH_2CH_2$), 28.16 (C-6), 28.68 (C-4), 29.03, 29.11, 29.14, 29.16 (4×CH_2), 29.53 (C-5), 29.66 (C-3), 30.87 (t, CF_2CH_2), 35.68 (C-4a), 68.09 (OCH_2), 75.30 ($C(CN)_2$), 108.52–119.93

(m, CF_2, CF_3), 113.35, 114.05 (2×CN), 114.71 (C-3'), 120.36 (C-1), 123.00 (C-8), 127.23 (C-2'), 131.26 (C-1'), 151.02 (C-7), 158.65 (C-8a), 160.49 (C-4'), 170.05 (C-2) ppm. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -126.05, -123.49, -122.67, -121.91, -121.87, -121.72, -114.29, -80.75 ppm. FT-IR (ATR): $\tilde{\nu}$ = 2933 (w), 2860 (w), 2219 (w), 1638 (w), 1555 (w), 1508 (m), 1469 (w), 1424 (w), 1395 (w), 1370 (w), 1340 (w), 1299 (w), 1239 (m), 1201 (s), 1180 (s), 1148 (m), 1016 (w), 907 (s), 832 (w), 792 (w), 764 (w), 728 (vs), 649 (m), 558 (w), 528 (w), 440 (w) cm^{-1}. MS (ESI): *m*/*z* = 841.20 $[M+Na]^+$, 819.22 $[M+H]^+$, 793.20, 771.21, 606.30. HRMS (ESI): calcd. for $[C_{35}H_{31}F_{17}N_2O+H]^+$ 819.2238, found: 819.2239. M.p. (POM): 112 °C.

Synthesis of Mal-k-PipC(n)

1-(1,1-Dicyanomethylene)-3-(4-(4-octyloxypiperidyl)phenyl)-cyclohex-2-ene (Mal-1-PipC(8)): According to GP4, yield: 68.0 mg, 158 µmol, 92 %, column chromatography on silica gel gradient PE : EE = 10 : 1 to 5 : 1 (R_f = 0.3). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.0 Hz, 3H, CH_3), 1.19–1.40 (m, 10H, 5×CH_2), 1.54–1.62 (m, 2H, OCH_2CH_2), 1.64–1.74 (m, 2H, 2''-H), 1.92–2.02 (m, 4H, 2''-H, 5-H), 2.74–2.81 (m, 4H, 4-H, 6-H), 3.14 (ddd, *J* = 12.7 Hz, 8.9 Hz, 3.4 Hz, 2H, 1''-H), 3.44–3.55 (m, 3H, 3''-H, OCH_2), 3.67 (ddd, *J* = 12.9 Hz, 6.7 Hz, 3.9 Hz, 2H, 1''-H), 6.89 (d, *J* = 8.6 Hz, 2H, 3'-H), 7.15 (d, *J* = 1.3 Hz, 1H, 2-H), 7.54–7.60 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.13 (CH_3), 21.66 (C-5), 22.68 ($CH_3CH_2CH_2$), 26.28 ($OCH_2CH_2CH_2$), 27.57 (C-4), 29.25, 29.30, 29.47 (C-6, 2×CH_2), 30.13 (OCH_2CH_2), 30.60 (C-2''), 31.86 (CH_3CH_2), 45.29 (C-1''), 68.20 (OCH_2), 74.01 (C-3''), 75.27 ($C(CN)_2$), 113.43, 114.18 (2×CN), 114.35 (C-3'), 117.15 (C-2), 126.20 (C-1'), 128.18 (C-2'), 152.77 (C-4'), 157.62 (C-3), 170.22 (C-1) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2923 (m), 2852 (m), 2214 (s), 1606 (m), 1563 (s), 1519 (vs), 1462 (m), 1433 (m), 1390 (w), 1360 (s), 1334 (m), 1305 (m), 1275 (w), 1255 (w), 1228 (m), 1182 (vs), 1148 (w), 1104 (s), 1052 (w), 1024 (w), 990 (w), 964 (w), 921 (w), 875 (w), 857 (w), 816 (m), 776 (w), 726 (w), 679 (w), 638 (w), 601 (w), 543 (w), 467 (w), 410 (w) cm^{-1}. MS (ESI): *m*/*z* = 454.28 $[M+Na]^+$, 432.30 $[M+H]^+$, 302.16 $[M-OC_8H_{17}]^+$. HRMS (ESI): calcd. for $[C_{28}H_{37}N_3O+H]^+$ 432.3009, found: 432.3004. M.p. (POM): 84 °C.

2-(1,1-Dicyanomethylene)-7-(4-(4-octyloxypiperidyl)phenyl)-3,4,4a,5,6-pentahydro-naphthalene (Mal-2-PipC(8)): According to GP4, yield: 71.0 mg, 147 µmol, 88 %, column chromatography on silica gel gradient PE : EE = 10 : 1 to 5 : 1 (R_f = 0.3). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.7 Hz, 3H, CH_3), 1.20–1.41 (m, 10H, 5×CH_2), 1.44–1.63 (m, 4H, 4-H, 5-H, OCH_2CH_2), 1.69 (dtd, *J* = 12.7 Hz, 8.7 Hz, 3.7 Hz, 2H, 2''-H), 1.91–2.03 (m, 2H, 2''-H), 2.03–2.14 (m, 2H, 4-H, 5-H), 2.40–2.52 (m, 1H, 4a-H), 2.52–2.70 (m, 2H, 3-H, 6-H), 2.88 (ddd, *J* = 18.1 Hz, 5.0 Hz, 2.2 Hz, 1H, 6-H), 3.02–3.11 (m, 3H, 3-H, 1''-H), 3.44–3.52 (m, 3H, 3''-H, OCH_2), 3.64 (dt, *J* = 11.4 Hz, 4.4 Hz, 4.4 Hz, 2H, 1''-H), 6.60 (s, 1H, 1-H),

6.71 (d, *J* = 2.2 Hz, 1H, 8-H), 6.90 (d, *J* = 8.6 Hz, 2H, 3'-H), 7.48 (d, *J* = 8.6 Hz, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.08 (CH_3), 22.63 (CH_3CH_2), 26.22 ($OCH_2CH_2CH_2$), 27.81 (C-6), 28.69 (C-5), 29.25, 29.42, 29.49, 29.60 (C-3, C-4, 2×CH_2), 30.09 (OCH_2CH_2), 30.66 (C-2''), 31.80 ($CH_3CH_2CH_2$), 35.71 (C-4a), 45.77 (C-1''), 68.09 (OCH_2), 74.07 ($C(CN)_2$), 74.17 (C-3''), 113.61, 114.32 (2×CN), 114.81 (C-3'), 119.67 (C-1), 121.60 (C-8), 127.04 (C-2'), 128.02 (C-1'), 151.32 (C-7), 151.84 (C-4'), 159.12 (C-8a), 169.91 (C-2) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2924 (m), 2853 (m), 2214 (s), 1605 (w), 1582 (w), 1544 (vs), 1502 (vs), 1453 (m), 1429 (m), 1389 (m), 1361 (m), 1340 (m), 1321 (w), 1298 (w), 1275 (w), 1233 (w), 1192 (vs), 1151 (w), 1106 (s), 1017 (w), 961 (w), 898 (w), 823 (w), 799 (w), 724 (w), 665 (w), 636 (w), 524 (w), 439 (w), 409 (w) cm^{-1}. MS (ESI): *m*/*z* = 524.32, 506.31 $[M+Na]^+$, 484.33 $[M+H]^+$, 354.20 $[M–OC_8H_{17}]^+$. HRMS (ESI): calcd. for $[C_{32}H_{41}N_3O+H]^+$ 484.3322, found: 484.3321. M.p. (POM): 132 °C.

1-(1,1-Dicyanomethylene)-3-(4-(4-decyloxypiperidyl)phenyl)-cyclohex-2-ene (Mal-1-PipC(10)): According to GP4, yield: 55.0 mg, 120 µmol, 75 %, column chromatography on silica gel gradient PE : EE = 10 : 1 to 5 : 1 (R_f = 0.3). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.20–1.39 (m, 14H, 7×CH_2), 1.54–1.62 (m, 2H, OCH_2CH_2), 1.69 (dddd, *J* = 12.6 Hz, 8.6 Hz, 8.4 Hz, 3.6 Hz, 2H, 2''-H), 1.94–2.02 (m, 4H, 2''-H, 5-H), 2.74–2.81 (m, 4H, 4-H, 6-H), 3.15 (ddd, *J* = 12.7 Hz, 8.9 Hz, 3.4 Hz, 2H, 1''-H), 3.44–3.55 (m, 3H, 3''-H, OCH_2), 3.67 (ddd, *J* = 12.9 Hz, 6.7 Hz, 3.4 Hz, 2H, 1''-H), 6.89 (d, *J* = 8.5 Hz, 2H, 3'-H), 7.15 (s, 1H, 2-H), 7.54–7.60 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.15 (CH_3), 21.66 (C-5), 22.71 ($CH_3CH_2CH_2$), 26.27 ($OCH_2CH_2CH_2$), 27.58 (C-4), 29.25, 29.34, 29.51, 29.60, 29.64 (C-6, 4×CH_2), 30.13 (OCH_2CH_2), 30.60 (C-2''), 31.92 (CH_3CH_2), 45.29 (C-1''), 68.20 (OCH_2), 74.00 (C-3''), 75.28 ($C(CN)_2$), 113.43, 114.18 (2×CN), 114.35 (C-3'), 117.16 (C-2), 126.21 (C-1'), 128.18 (C-2'), 152.77 (C-4'), 157.61 (C-3), 170.21 (C-1) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2922 (m), 2851 (m), 2214 (m), 1606 (m), 1563 (s), 1521 (vs), 1462 (m), 1433 (m), 1390 (w), 1360 (s), 1333 (m), 1305 (m), 1275 (w), 1257 (w), 1228 (m), 1191 (vs), 1148 (w), 1103 (s), 1025 (m), 964 (w), 921 (w), 875 (w), 857 (w), 816 (m), 777 (w), 725 (w), 677 (w), 638 (w), 601 (w), 543 (w), 467 (w), 408 (w) cm^{-1}. MS (ESI): *m*/*z* = 482.31 $[M+Na]^+$, 460.33 $[M+H]^+$, 298.13. HRMS (ESI): calcd. for $[C_{30}H_{41}N_3O+H]^+$ 460.3322, found: 460.3321. M.p. (POM): 81 °C.

2-(1,1-Dicyanomethylene)-7-(4-(4-decyloxypiperidyl)phenyl)-3,4,4a,5,6-pentahydro-naphthalene (Mal-2-PipC(10)): According to GP4, yield: 57.0 mg, 111 µmol, 77 %, column chromatography on silica gel gradient PE : EE = 10 : 1 to 5 : 1 (R_f = 0.3). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.20–1.38 (m, 14H, 7×CH_2), 1.45–1.63 (m, 4H, 4-H, 5-H, OCH_2CH_2), 1.69 (dtd, *J* = 12.7 Hz, 8.7 Hz, 3.9 Hz, 2H, 2''-H), 1.93–2.02 (m, 2H, 2''-H), 2.04–2.14 (m, 2H, 4-H, 5-H), 2.42–2.51 (m, 1H, 4a-H), 2.56 (ddd, *J* = 18.0 Hz,

14.2 Hz, 4.9 Hz, 1H, 3-H), 2.61–2.69 (m, 1H, 6-H), 2.88 (ddd, *J* = 18.1 Hz, 4.9 Hz, 2.2 Hz, 1H, 6-H), 3.01–3.13 (m, 3H, 1''-H, 3-H), 3.44–3.53 (m, 3H, 3''-H, OCH_2), 3.63 (ddd, *J* = 12.5 Hz, 6.2 Hz, 3.9 Hz, 2H, 1''-H), 6.61 (d, *J* = 2.0 Hz, 1H, 1-H), 6.71 (d, *J* = 2.2 Hz, 1H, 8-H), 6.87–6.93 (m, 2H, 3'-H), 7.45–7.52 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.12 (CH_3), 22.69 (CH_3CH_2), 26.26 ($OCH_2CH_2CH_2$), 27.86 (C-6), 28.74 (C-5), 29.33, 29.50, 29.54, 29.58, 29.62, 29.65 (C-3, C-4, 4×CH_2), 30.13 (OCH_2CH_2), 30.71 (C-2''), 31.90 ($CH_3CH_2CH_2$), 35.76 (C-4a), 45.80 (C-1''), 68.14 (OCH_2), 74.15 ($C(CN)_2$), 74.20 (C-3''), 113.63, 114.34 (2×CN), 114.85 (C-3'), 119.71 (C-1), 121.64 (C-8), 127.07 (C-2'), 128.08 (C-1'), 151.35 (C-7), 151.89 (C-4'), 159.14 (C-8a), 169.92 (C-2) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2924 (s), 2853 (m), 2214 (s), 1605 (w), 1582 (w), 1547 (vs), 1464 (w), 1453 (w), 1429 (w), 1390 (w), 1361 (m), 1340 (w), 1321 (w), 1298 (w), 1275 (w), 1233 (w), 1195 (vs), 1108 (s), 1017 (w), 962 (w), 898 (w), 823 (w), 798 (w), 724 (w), 665 (w), 634 (w), 544 (w), 524 (w), 484 (w) cm^{-1}. MS (ESI): *m*/*z* = 534.34 $[M+Na]^+$, 512.36 $[M+H]^+$, 354.20 $[M–OC_{10}H_{21}]^+$. HRMS (ESI): calcd. for $[C_{34}H_{45}N_3O+H]^+$ 512.3635, found: 512.3631. M.p. (POM): 97 °C.

1-(1,1-Dicyanomethylene)-3-(4-(4-dodecyloxypiperidyl)phenyl)-cyclohex-2-ene (Mal-1-PipC(12)): According to GP4, yield: 60.0 mg, 123 µmol, 87 %, column chromatography on silica gel gradient PE : EE = 10 : 1 to 5 : 1 (R_f = 0.4). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.20–1.37 (m, 18H, 9×CH_2), 1.54–1.61 (m, 2H, OCH_2CH_2), 1.69 (dtd, *J* = 12.6 Hz, 8.5 Hz, 3.9 Hz, 2H, 2''-H), 1.92–2.01 (m, 4H, 2''-H, 5-H), 2.74–2.81 (m, 4H, 4-H, 6-H), 3.14 (ddd, *J* = 12.7 Hz, 9.0 Hz, 3.9 Hz, 2H, 1''-H), 3.43–3.54 (m, 3H, , 3''-H, OCH_2), 3.67 (ddd, *J* = 12.9 Hz, 6.6 Hz, 3.9 Hz, 2H, 1''-H), 6.84–6.92 (m, 2H, 3'-H), 7.14 (d, *J* = 1.3 Hz, 1H, 2-H), 7.54–7.60 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.17 (CH_3), 21.66 (C-5), 22.73 ($CH_3CH_2CH_2$), 26.28 ($OCH_2CH_2CH_2$), 27.57 (C-4), 29.25, 29.39, 29.52, 29.65, 29.67, 29.70 (C-6, 6×CH_2), 30.14 (OCH_2CH_2), 30.61 (C-2''), 31.95 (CH_3CH_2), 45.29 (C-1''), 68.20 (OCH_2), 74.02 (C-3''), 75.23 ($C(CN)_2$), 113.46, 114.21 (2×CN), 114.34 (C-3'), 117.13 (C-2), 126.18 (C-1'), 128.19 (C-2'), 152.77 (C-4'), 157.63 (C-3), 170.24 (C-1) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2921 (m), 2851 (m), 2215 (m), 1606 (m), 1565 (s), 1521 (vs), 1462 (m), 1433 (m), 1390 (w), 1360 (m), 1334 (m), 1305 (w), 1275 (w), 1256 (w), 1228 (m), 1192 (vs), 1148 (w), 1105 (s), 1025 (w), 990 (w), 964 (w), 921 (w), 875 (w), 857 (w), 816 (m), 776 (w), 725 (w), 675 (w), 638 (w), 601 (w), 543 (w), 466 (w), 409 (w) cm^{-1}. MS (ESI): *m*/*z* = 510.34 $[M+Na]^+$, 488.36 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{32}H_{45}N_3O+H]^+$ 488.3635, found: 488.3623. M.p. (POM): 74 °C.

2-(1,1-Dicyanomethylene)-7-(4-(4-dodecyloxypiperidyl)phenyl)-3,4,4a,5,6-pentahydro-naphthalene (Mal-2-PipC(12)): According to GP4, yield: 50.0 mg, 92.6 µmol, 91 %, column chromatography on silica gel gradient PE : EE = 10 : 1 to 5 : 1 (R_f = 0.3). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.22–1.38 (m, 18H, 9×CH_2), 1.45–

1.62 (m, 4H, 4-H, 5-H, OCH_2CH_2), 1.69 (dtd, *J* = 12.7 Hz, 8.8 Hz, 3.9 Hz, 2H, 2''-H), 1.97 (ddd, *J* = 13.1 Hz, 6.4 Hz, 3.4 Hz, 2H, 2''-H), 2.05–2.12 (m, 2H, 4-H, 5-H), 2.43–2.51 (m, 1H, 4a-H), 2.56 (ddd, *J* = 18.0 Hz, 14.2 Hz, 4.9 Hz, 1H, 3-H), 2.65 (dddd, *J* = 18.2 Hz, 12.9 Hz, 4.9 Hz, 2.2 Hz, 1H, 6-H), 2.88 (ddd, *J* = 18.0 Hz, 4.9 Hz, 2.2 Hz, 1H, 6-H), 3.01–3.12 (m, 3H, 1''-H, 3-H), 3.42–3.53 (m, 3H, 3''-H, OCH_2), 3.64 (ddd, *J* = 12.9 Hz, 6.4 Hz, 3.9 Hz, 2H, 1''-H), 6.60 (d, *J* = 2.0 Hz, 1H, 1-H), 6.71 (d, *J* = 2.2 Hz, 1H, 8-H), 6.86–6.94 (m, 2H, 3'-H), 7.44–7.51 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.16 (CH_3), 22.72 (CH_3CH_2), 26.28 ($OCH_2CH_2CH_2$), 27.87 (C-6), 28.74 (C-5), 29.38, 29.52, 29.55, 29.65, 29.66, 29.70 (C-3, C-4, 6×CH_2), 30.15 (OCH_2CH_2), 30.72 (C-2''), 31.95 ($CH_3CH_2CH_2$), 35.76 (C-4a), 45.82 (C-1''), 68.15 (OCH_2), 74.13 ($C(CN)_2$), 74.23 (C-3''), 113.67, 114.38 (2×CN), 114.87 (C-3'), 119.72 (C-1), 121.65 (C-8), 127.09 (C-2'), 128.08 (C-1'), 151.38 (C-7), 151.90 (C-4'), 159.18 (C-8a), 169.97 (C-2) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2921 (s), 2851 (s), 2213 (s), 1604 (w), 1582 (w), 1544 (vs), 1502 (vs), 1464 (m), 1453 (m), 1429 (w), 1389 (m), 1361 (m), 1340 (m), 1321 (w), 1298 (w), 1275 (w), 1233 (w), 1192 (vs), 1107 (s), 1017 (w), 961 (w), 898 (w), 823 (w), 799 (w), 725 (w), 666 (w), 636 (w), 543 (w), 524 (w), 483 (w), 410 (w) cm^{-1}. MS (ESI): *m*/*z* = 562.38 $[M+Na]^+$, 540.40 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{36}H_{49}N_3O+H]^+$ 540.3948, found: 540.3958. M.p. (POM): 94 °C.

2-(1,1-Dicyanomethylene)-7-(4-(4-dodecyloxypiperidyl)phenyl)-4,4a,5,6,10,10a-hexahydroanthracene (Mal-3-PipC(12)): According to GP4, yield: 50 mg, 84.5 µmol, 77 %, column chromatography on silica gel gradient PE : EE = 12 : 1 to 5 : 1 (R_f = 0.3). ^{1}H-NMR (700 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.0 Hz, 3H, CH_3), 1.20–1.38 (m, 19H, 10-H, 9×CH_2), 1.45–1.53 (m, 2H, 4-H, 5-H), 1.54–1.62 (m, 2H, OCH_2CH_2), 1.69 (dtd, *J* = 12.8 Hz, 8.9 Hz, 3.7 Hz, 2H, 2''-H), 1.94–2.02 (m, 3H, 4-H, 5-H, 10-H), 2.05 (td, *J* = 11.4 Hz, 10.5 Hz, 5.6 Hz, 2H, 2''-H), 2.50–2.67 (m, 4H, 3-H, 4a-H, 6-H, 10a-H), 2.80 (dd, *J* = 17.6 Hz, 4.5 Hz, 1H, 6-H), 3.00–3.06 (m, 3H, 1''-H, 3-H), 3.44–3.49 (m, 3H, 3''-H, OCH_2), 3.61 (dt, *J* = 11.4 Hz, 4.9 Hz, 2H, 1''-H), 6.16 (s, 1H, 9-H), 6.53 (s, 1H, 1-H), 6.64 (s, 1H, 8-H), 6.90 (d, *J* = 8.5 Hz, 2H, 3'-H), 7.45 (d, *J* = 8.5 Hz, 2H, 2'-H) ppm. ^{13}C-NMR (176 MHz, $CDCl_3$): δ = 14.15 (CH_3), 22.71 ($CH_3CH_2CH_2$), 26.27 ($OCH_2CH_2CH_2$), 27.75 (C-6), 28.84 (C-3), 29.38, 29.52, 29.59, 29.64, 29.66, 29.69, 29.90, 30.15 (C-4, C-5, 7×CH_2), 30.79 (C-2''), 31.94 (CH_3CH_2), 36.00 (C-10a), 36.36 (C-4a), 36.74 (C-10), 46.19 (C-1''), 68.12 (OCH_2), 73.59 ($C(CN)_2$), 74.34 (C-3''), 113.80, 114.56 (2×CN), 115.20 (C-3'), 119.25 (C-1), 122.37 (C-8), 124.11 (C-9), 126.58 (C-2'), 129.24 (C-1'), 146.59 (C-7), 151.42 (C-4'), 153.81 (C-8a), 159.43 (C-9a), 169.55 (C-2) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2918 (s), 2849 (s), 2219 (m), 1736 (w), 1604 (m), 1577 (w), 1566 (w), 1532 (s), 1517 (vs), 1465 (m), 1449 (m), 1428 (w), 1386 (m), 1361 (m), 1336 (m), 1301 (w), 1235 (m), 1209 (m), 1180 (vs), 1107 (vs), 1040 (w), 1025 (w), 1011 (w), 958 (w), 919 (w), 908 (w), 893 (s), 829 (m), 807 (w), 770 (w), 730 (w), 651 (w), 636 (w), 564 (w), 527 (w), 494 (w), 478 (w), 429 (w) cm^{-1}. MS (ESI): *m*/*z* = 680.48, 663.45, 592.43 $[M+H]^+$, 548.50,

475.41, 419.35, 279.10. HRMS (ESI): calcd. for $[C_{40}H_{53}N_3O+H]^+$ 592.4261, found: 592.4254. M.p. (POM): 133 °C.

1-(1,1-Dicyanomethylene)-3-(4-(4-tetradecyloxypiperidyl)phenyl)-cyclohex-2-en (Mal-1-PipC(14)): According to GP4, yield: 58.0 mg, 112 µmol, 91 %, column chromatography on silica gel gradient PE : EE = 10 : 1 to 5 : 1 (R_f = 0.5). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.20–1.39 (m, 22H, 11×CH_2), 1.54–1.62 (m, 2H, OCH_2CH_2), 1.70 (dtd, *J* = 12.1 Hz, 8.5 Hz, 3.9 Hz, 2H, 2''-H), 1.92–2.02 (m, 4H, 2''-H, 5-H), 2.74–2.81 (m, 4H, 4-H, 6-H), 3.15 (ddd, *J* = 12.7 Hz, 8.9 Hz, 3.9 Hz, 2H, 1''-H), 3.44–3.55 (m, 3H, 3''-H, OCH_2), 3.67 (ddd, *J* = 12.8 Hz, 6.8 Hz, 3.9 Hz, 2H, 1''-H), 6.89 (d, *J* = 8.5 Hz, 2H, 3'-H), 7.15 (d, *J* = 1.3 Hz, 1H, 2-H), 7.54–7.60 (m, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.10 (CH_3), 21.61 (C-5), 22.67 ($CH_3CH_2CH_2$), 26.22 ($OCH_2CH_2CH_2$), 27.53 (C-4), 29.20, 29.34, 29.46, 29.59, 29.63, 29.65, 29.67 (C-6, 8×CH_2), 30.08 (OCH_2CH_2), 30.55 (C-2''), 31.90 (CH_3CH_2), 45.25 (C-1''), 68.16 (OCH_2), 73.95 (C-3''), 75.24 ($C(CN)_2$), 113.37, 114.13 (2×CN), 114.31 (C-3'), 117.11 (C-2), 126.18 (C-1'), 128.13 (C-2'), 152.72 (C-4'), 157.55 (C-3), 170.16 (C-1) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2922 (m), 2851 (m), 2215 (m), 1606 (m), 1566 (m), 1524 (vs), 1462 (w), 1433 (w), 1390 (w), 1361 (m), 1334 (w), 1305 (w), 1259 (m), 1228 (w), 1193 (vs), 1090 (s), 1020 (vs), 964 (w), 917 (w), 873 (w), 798 (vs), 727 (w), 637 (w), 600 (w), 542 (w), 465 (w), 445 (w), 408 (w) cm^{-1}. MS (ESI): *m*/*z* = 538.38 $[M+Na]^+$, 516.39 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{34}H_{49}N_3O+H]^+$ 516.3948, found: 516.3948. M.p. (POM): 80 °C.

2-(1,1-Dicyanomethylene)-7-(4-(4-tetradecyloxypiperidyl)phenyl)-3,4,4a,5,6-pentahydro-naphthalene (Mal-2-PipC(14)): According to GP4, yield: 50.0 mg, 88.1 µmol, 85 %, column chromatography on silica gel gradient PE : EE = 10 : 1 to 5 : 1 (R_f = 0.4). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.20–1.39 (m, 22H, 11×CH_2), 1.45–1.62 (m, 4H, 4-H, 5-H, OCH_2CH_2), 1.64–1.76 (m, 2H, 2''-H), 1.93–2.03 (m, 2H, 2''-H), 2.06–2.12 (m, 2H, 4-H, 5-H), 2.42–2.52 (m, 1H, 4a-H), 2.52–2.70 (m, 2H, 3-H, 6-H), 2.88 (ddd, *J* = 18.1 Hz, 4.9 Hz, 2.2 Hz, 1H, 6-H), 3.02–3.12 (m, 3H, 1''-H, 3-H), 3.44–3.50 (m, 3H, 3''-H, OCH_2), 3.64 (ddd, *J* = 12.7 Hz, 6.5 Hz, 3.9 Hz, 2H, 1''-H), 6.61 (d, *J* = 1.9 Hz, 1H, 1-H), 6.72 (d, *J* = 2.2 Hz, 1H, 8-H), 6.90 (d, *J* = 8.8 Hz, 2H, 3'-H), 7.49 (d, *J* = 8.8 Hz, 2H, 2'-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.16 (CH_3), 22.72 (CH_3CH_2), 26.28 ($OCH_2CH_2CH_2$), 27.87 (C-6), 28.74 (C-5), 29.39, 29.52, 29.54, 29.64, 29.69, 29.71, 29.72 (C-3, C-4, 8×CH_2), 30.14 (OCH_2CH_2), 30.71 (C-2''), 31.95 ($CH_3CH_2CH_2$), 35.76 (C-4a), 45.84 (C-1''), 68.16 (OCH_2), 74.16 ($C(CN)_2$), 74.22 (C-3''), 113.65, 114.37 (2×CN), 114.88 (C-3'), 119.75 (C-1), 121.67 (C-8), 127.09 (C-2'), 128.10 (C-1'), 151.36 (C-7), 151.89 (C-4'), 159.16 (C-8a), 169.97 (C-2) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2921 (s), 2851 (m), 2214 (m), 1605 (w), 1583 (w), 1546 (vs), 1502 (vs), 1464 (m), 1453 (m), 1428 (w), 1389 (w), 1361 (m), 1340 (m), 1321 (w), 1298 (w), 1275 (w), 1261 (w), 1235 (w), 1195 (vs), 1107 (s), 1016 (w), 961 (w), 908 (m), 875 (w),

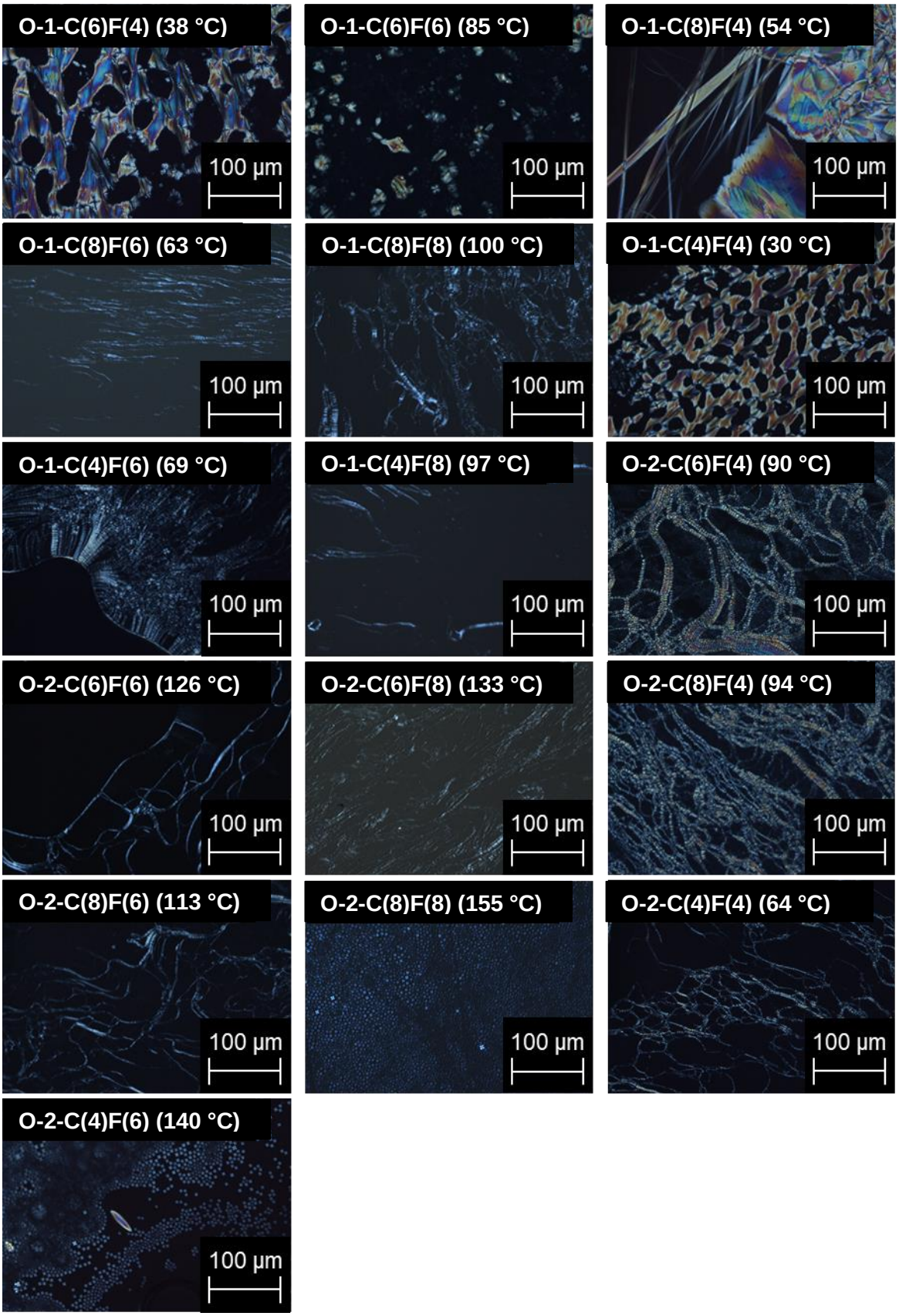
822 (w), 799 (w), 731 (m), 666 (w), 638 (w), 603 (w), 544 (w), 524 (w), 484 (w), 408 (w) cm^{-1}. MS (ESI): *m*/*z* = 590.41 $[M+Na]^+$, 568.43 $[M+H]^+$. HRMS (ESI): calcd. for $[C_{38}H_{53}N_3O+H]^+$ 568.4261, found: 568.4264. M.p. (POM): 96 °C.

7) DSC data of the merocyanines derivatives

Table S1 Transition temperatures T (in °C) and -enthalpies ΔH (in kJ·mol^{-1}) of the liquid crystalline merocyanines. Values were taken from the 2nd cooling curve (at 10 K·min^{-1}). Cr – crystalline; G – glassy,; I – isotropic liquid.

Comp.	Cr / G	T	ΔH	SmE	T	ΔH	SmA	T	ΔH	I
O-1-C(4)F(4)	●	32		–			–			●
O-1-C(4)F(6)	●	18	7.1	–			●	78	2.0	●
O-1-C(4)F(8)	●	70	26.3	–			●	115	2.8	●
O-1-C(6)F(4)	●	23	16.5	–			●	38	0.8	●
O-1-C(6)F(6)	●	56	26.2	–			●	84	2.3	●
O-1-C(6)F(8)	●	80	33.9	–			●	115	2.3	●
O-1-C(8)F(4)	●	43	28.0	–			–			●
O-1-C(8)F(6)	●	58	28.9	–			●	73	2.2	●
O-1-C(8)F(8)	●	82	36.8	–			●	105	2.3	●
O-2-C(4)F(4)	●	40		–			●	89		●
O-2-C(4)F(6)	●	12	11.0	–			●	136	2.9	●
O-2-C(4)F(8)	●	53	12.4	–			●	170	2.9	●
O-2-C(6)F(4)	●	27	17.2	–			●	99	1.8	●
O-2-C(6)F(6)	G	27		–			●	136	2.1	●
O-2-C(6)F(8)	●	73		–			●	193		●
O-2-C(8)F(4)	●	52	28.9	–			●	100	2.2	●
O-2-C(8)F(6)	●	68	34.5	–			●	129	2.6	●
O-2-C(8)F(8)	●	80	33.4	–			●	158	3.1	●
Mal-1-C(4)F(4)	●	46		–			–			●
Mal-1-C(4)F(6)	●	44		–			●	88	1.9	●
Mal-1-C(4)F(8)	●	33	9.0	–			●	116	2.0	●
Mal-1-C(6)F(4)	●	23	27.5	–			●	33	1.3	●
Mal-1-C(6)F(6)	●	50	19.0	–			●	92	1.9	●
Mal-1-C(6)F(8)	●	79	51.9	–			●	134	2.6	●
Mal-1-C(8)F(4)	●	32	19.2	–			●	44	1.9	●
Mal-1-C(8)F(6)	●	80	45.9	–			●	93	2.1	●
Mal-1-C(8)F(8)	●	90	55.4	–			●	130	2.3	●
Mal-2-C(4)F(4)	–			–			●	58	0.5	●
Mal-2-C(4)F(6)	●	45		–			●	132	1.8	●
Mal-2-C(4)F(8)	G	50		–			●	180	2.7	●
Mal-2-C(6)F(4)	●	80	1.2	–			–			●
Mal-2-C(6)F(6)	–			–			●	134	1.2	●
Mal-2-C(6)F(8)	●	100		–			●	175		●
Mal-2-C(8)F(4)	●	37	9.3	–			●	87	1.6	●
Mal-2-C(8)F(6)	●	30	10.8	–			●	136	2.3	●
Mal-2-C(8)F(8)	●	44	8.2	–			●	118		●
O-2-PipC(8)	●	28		–			●	86	1.4	●
O-2-PipC(10)	●	10	8.0	–			●	93	2.2	●
O-2-PipC(12)	●	6	10.8	–			●	77		●
O-2-PipC(14)	●	30	15.3	–			●	97	2.9	●
O-3-PipC(12)	●	109	0.8	●	150	12.6	●	168	2.7	●

8) Polarizing optical microscopy (POM)



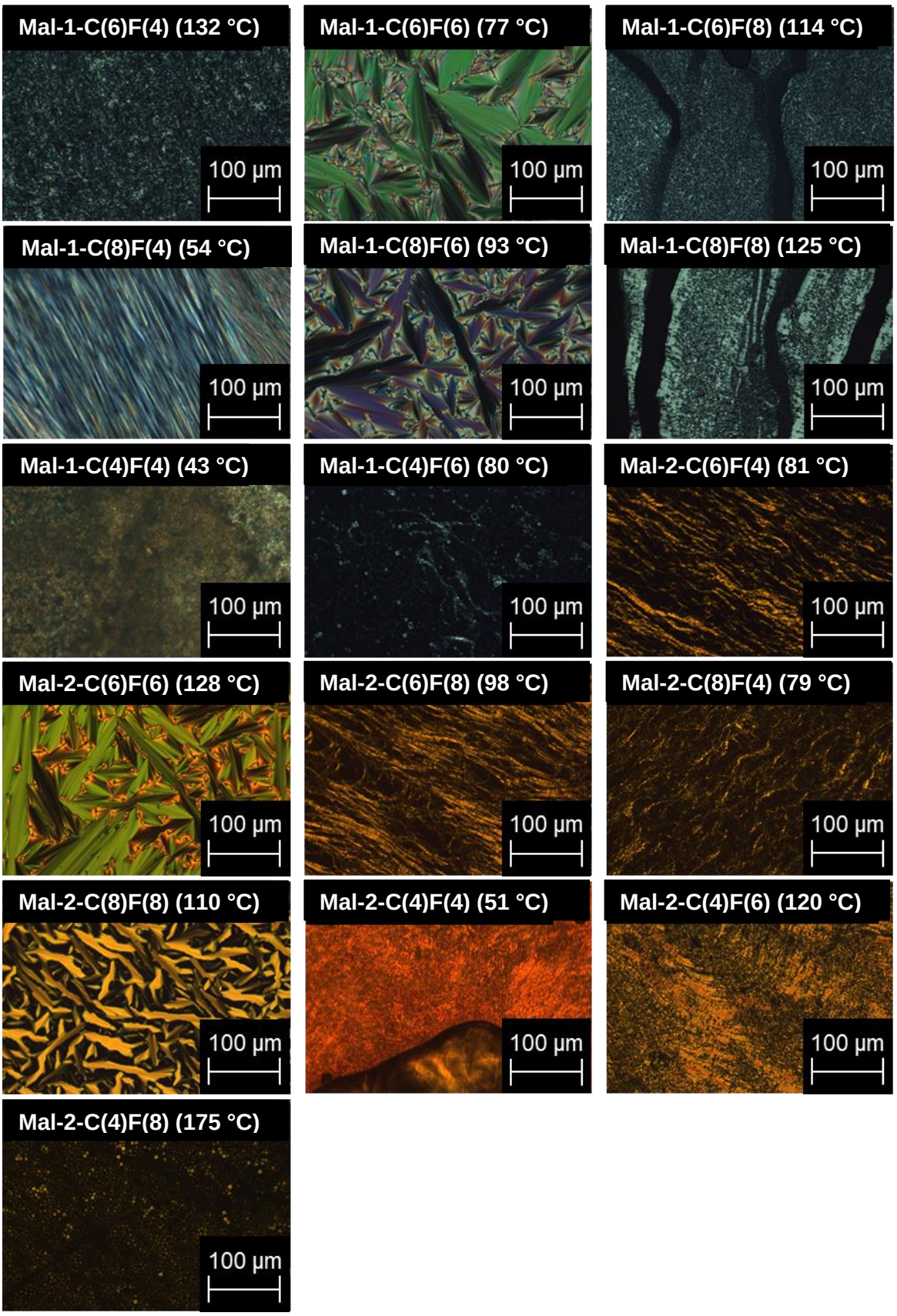
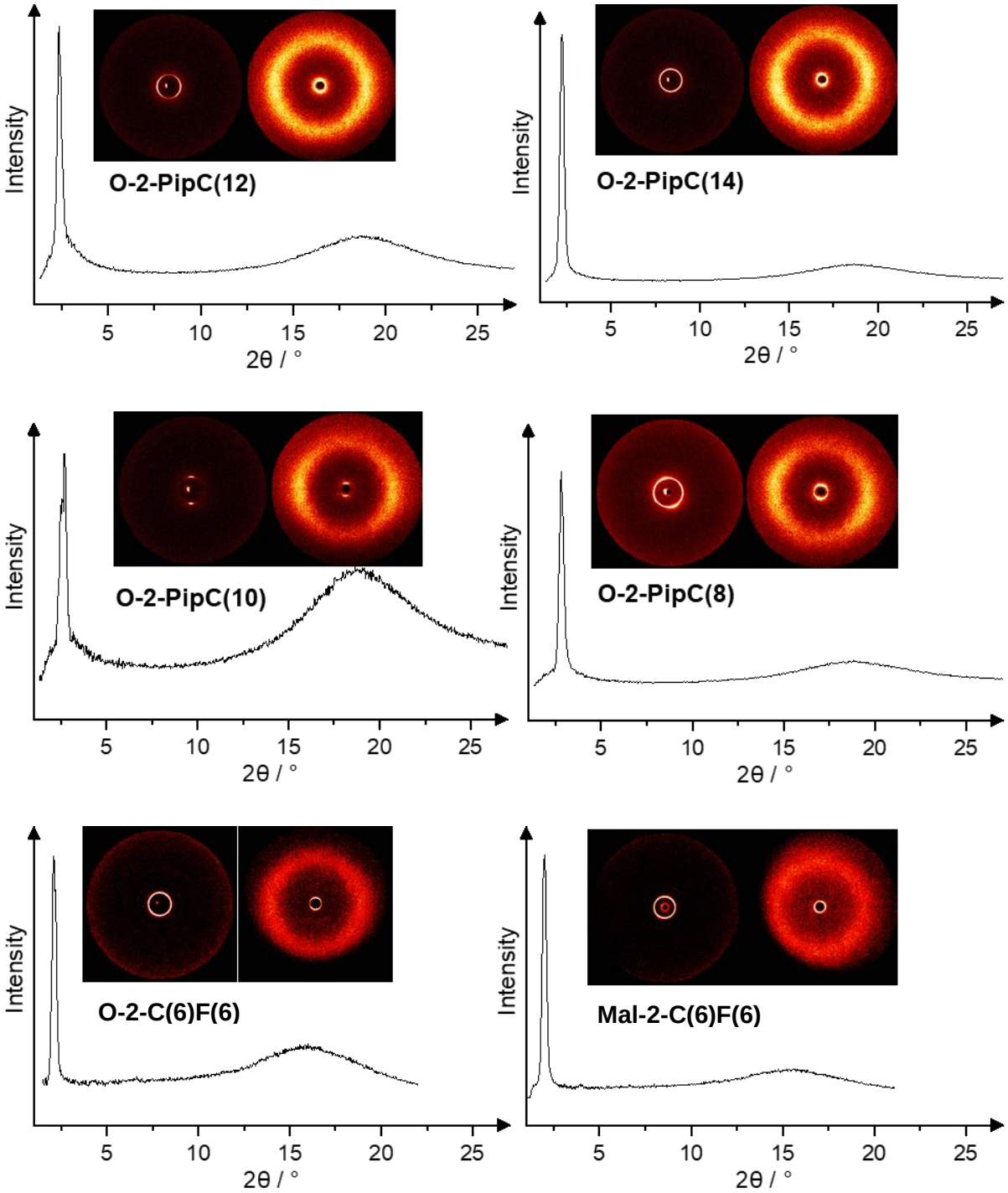
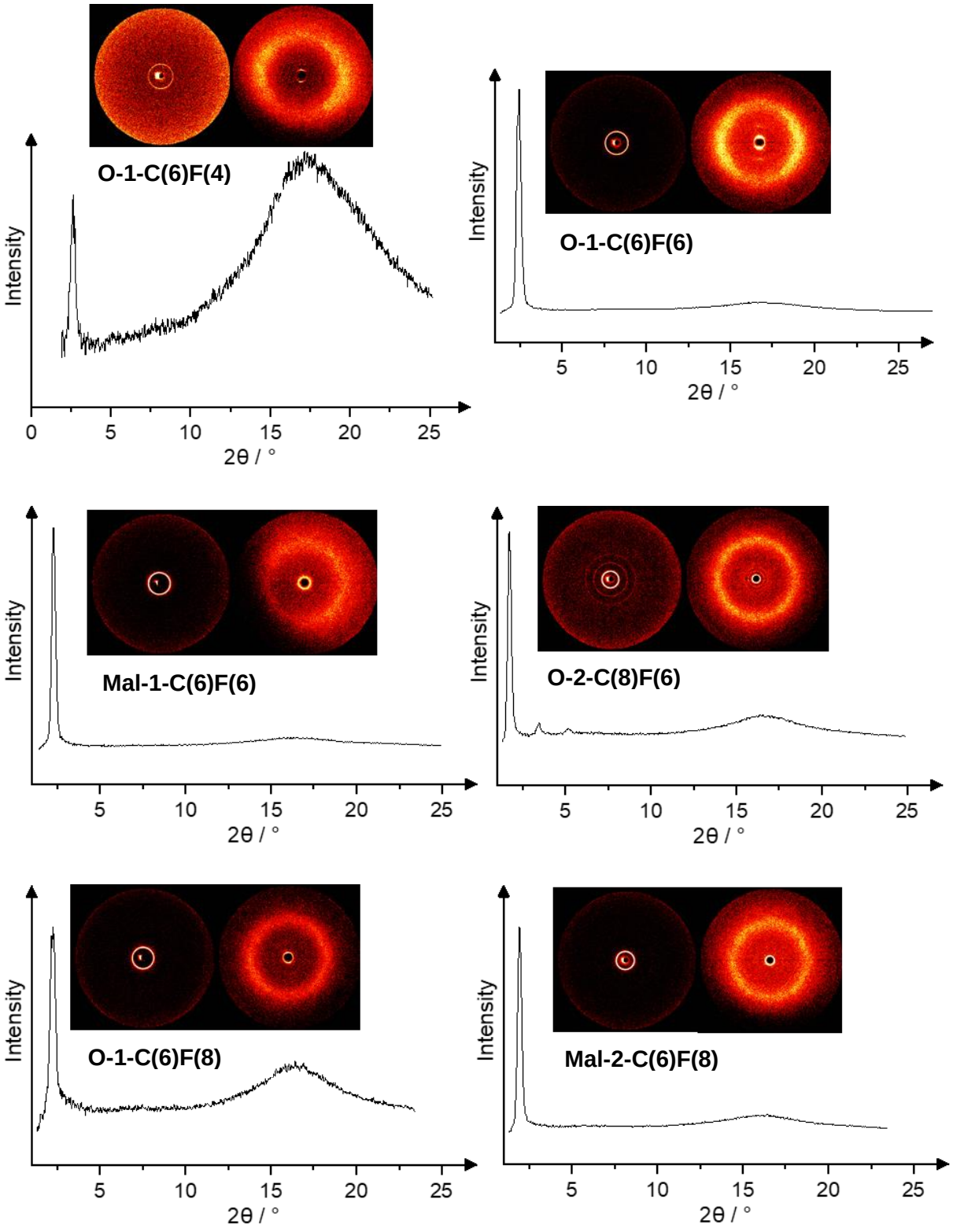
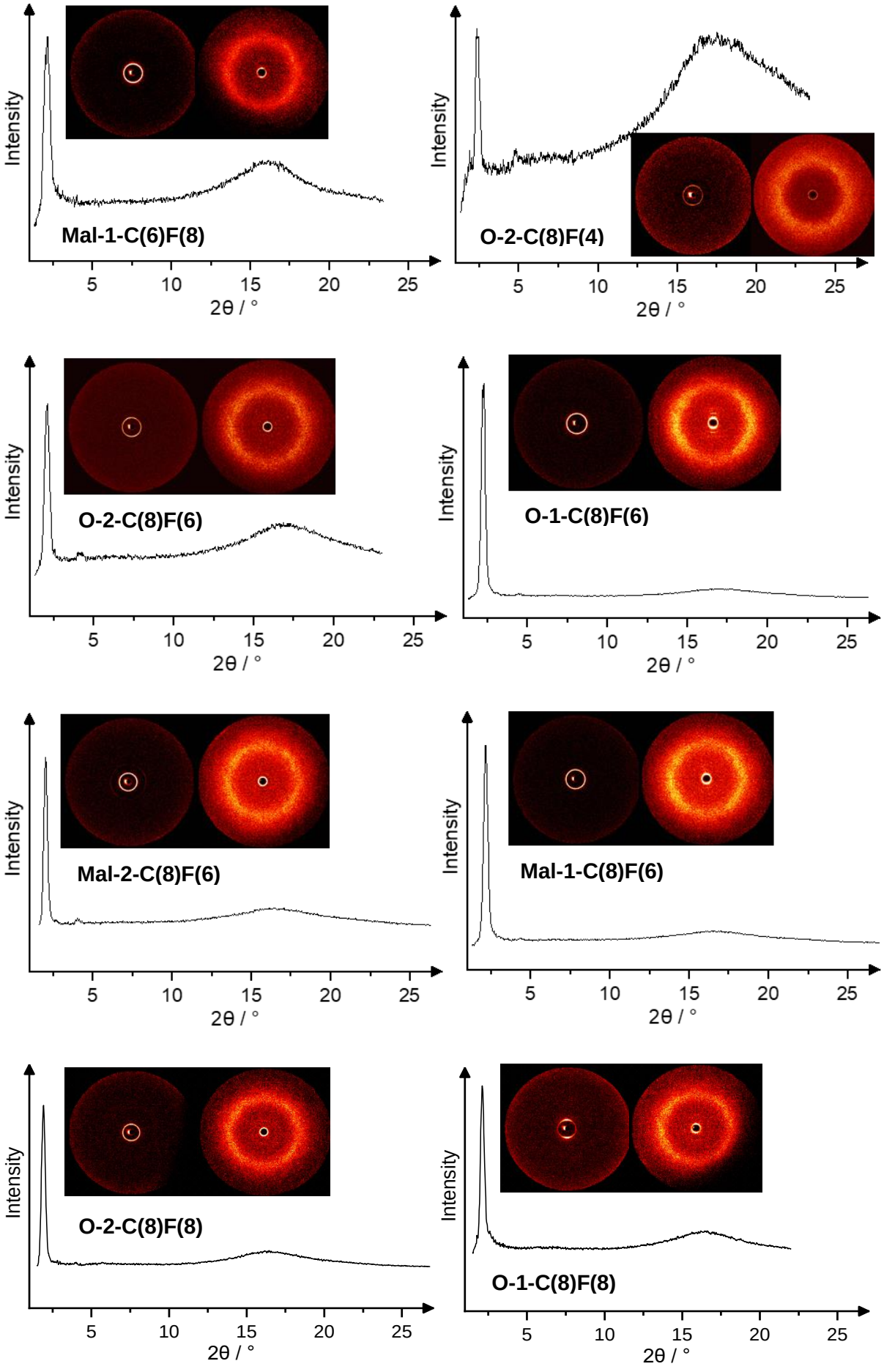


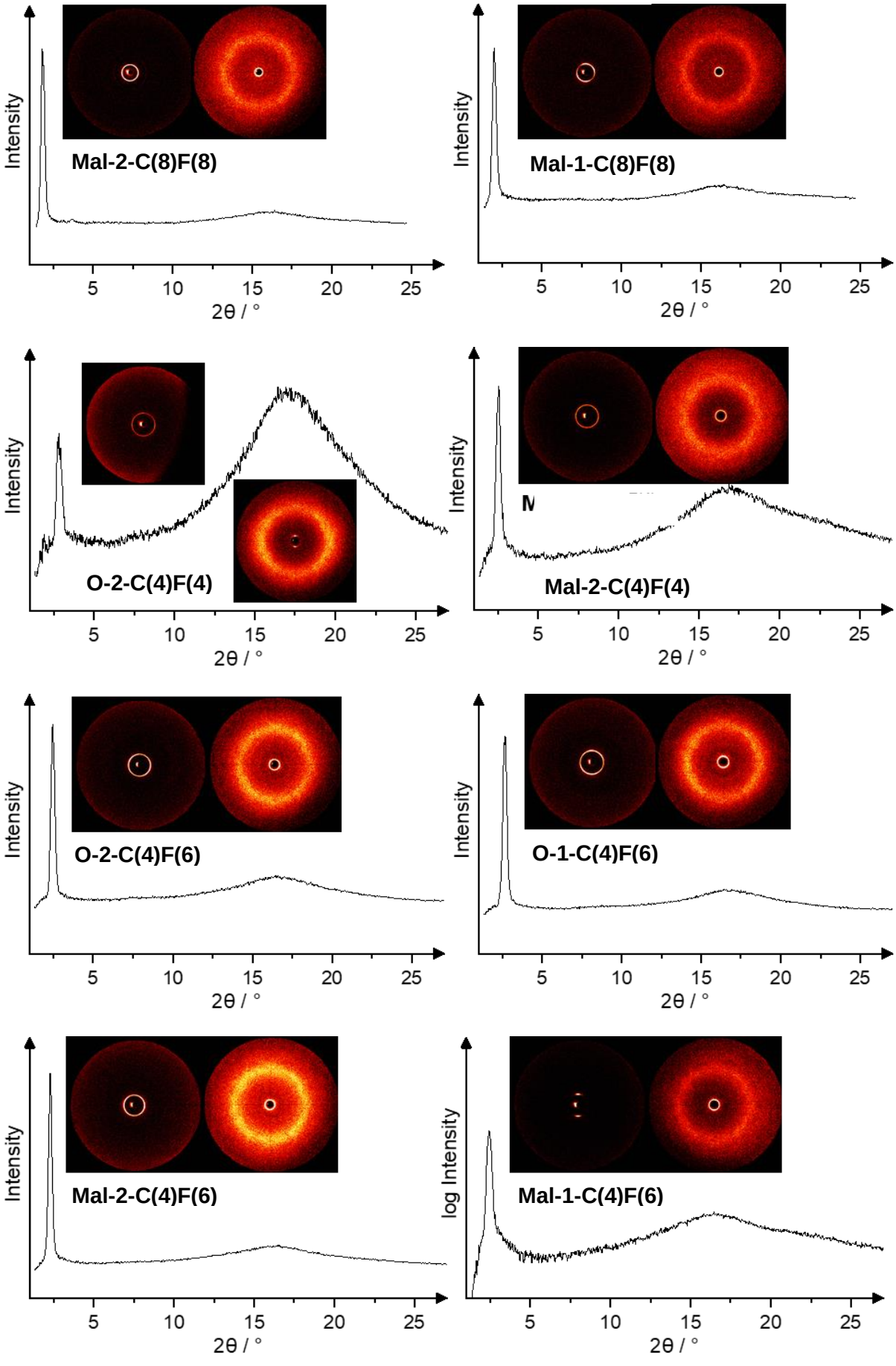
Figure S1 POM-textures of the liquid crystalline merocyanines at given temperatures.

9) X-ray diffraction




O-1-C(6)F(4)
Intensity
0
5
10
15
20
25
2θ / °
O-1-C(6)F(6)
Intensity
5
10
15
20
25
2θ / °
Mal-1-C(6)F(6)
Intensity
5
10
15
20
25
2θ / °
O-2-C(8)F(6)
Intensity
5
10
15
20
25
2θ / °
O-1-C(6)F(8)
Intensity
5
10
15
20
25
2θ / °
Mal-2-C(6)F(8)
Intensity
5
10
15
20
25
2θ / °


Intensity
Mal-1-C(6)F(8)
O-2-C(8)F(4)
O-2-C(8)F(6)
O-1-C(8)F(6)
Mal-2-C(8)F(6)
Mal-1-C(8)F(6)
O-2-C(8)F(8)
O-1-C(8)F(8)
5
10
15
20
25
2θ / °


Intensity
Mal-2-C(8)F(8)
2θ / °
Intensity
Mal-1-C(8)F(8)
2θ / °
Intensity
O-2-C(4)F(4)
2θ / °
Intensity
Mal-2-C(4)F(4)
2θ / °
Intensity
O-2-C(4)F(6)
2θ / °
Intensity
O-1-C(4)F(6)
2θ / °
Intensity
Mal-2-C(4)F(6)
2θ / °
log Intensity
Mal-1-C(4)F(6)
2θ / °

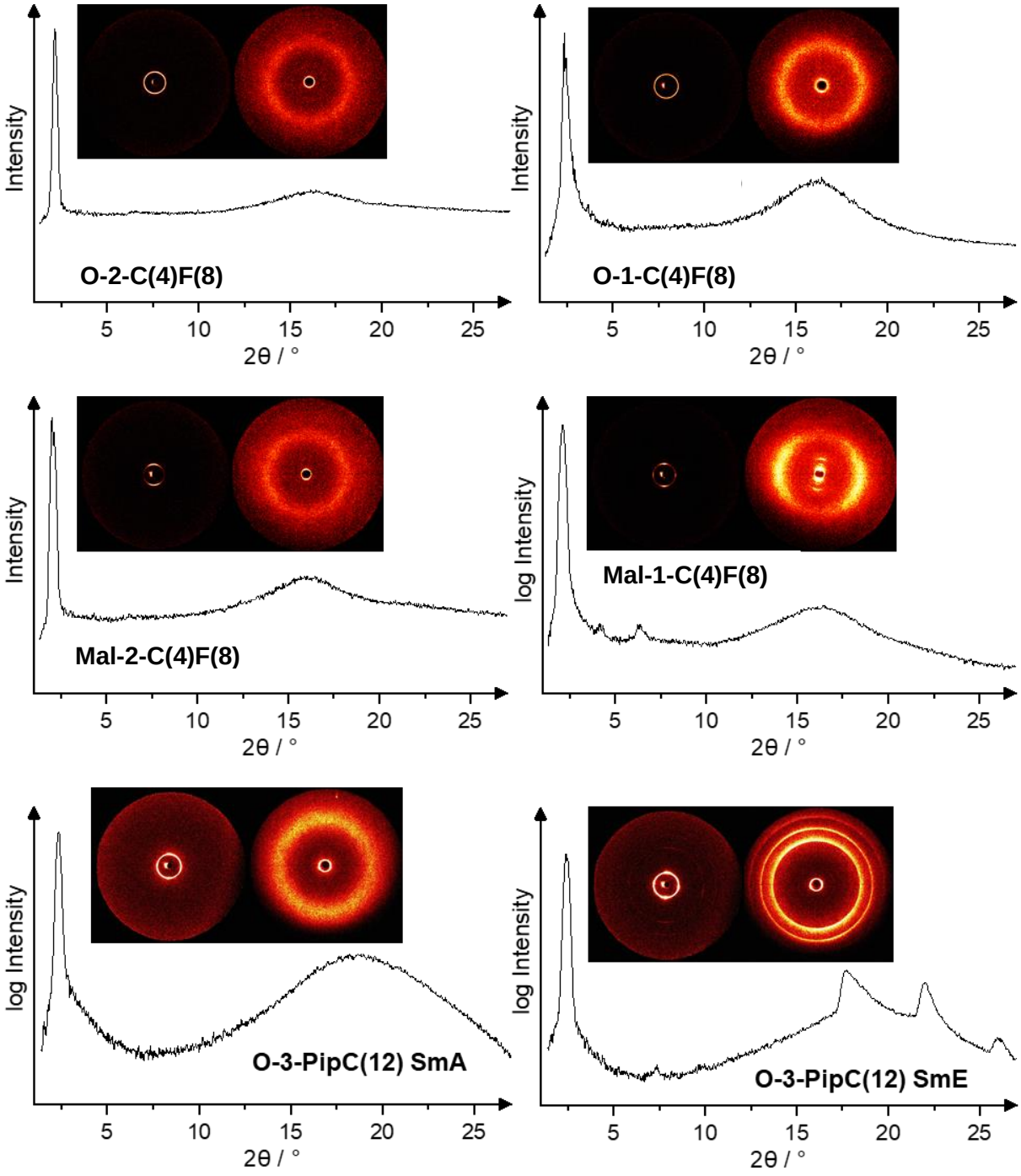


Figure S2 XRD results of the liquid crystalline merocyanines.

Table S2 Summary of the XRD results of the liquid crystalline merocyanines in relation to the layer spacings *d* and the calculated molecule lengths L_M.

Verb.	*d* / Å	L_M / Å	Verb.	*d* / Å	L_M / Å
O-1-C(4)F(6)	32.9 (001)	22.7	**Mal-1-C(8)F(6)**	40.3 (001) 20.0 (002)	28.6
O-1-C(4)F(8)	37.5 (001) 18.7 (002) 12.4 (003)	25.3	**Mal-1-C(8)F(8)**	43.7 (001) 14.6 (003)	31.2
O-1-C(6)F(6)	35.9 (001)	25.3	**Mal-2-C(4)F(4)**	34.6 (001)	22.9
O-1-C(6)F(8)	39.0 (001)	25.3	**Mal-2-C(4)F(6)**	37.8 (001)	25.4
O-1-C(8)F(6)	38.9 (001) 19.4 (002)	27.8	**Mal-2-C(4)F(8)**	42.8 (001)	27.9
O-1-C(8)F(8)	41.4 (001)	30.4	**Mal-2-C(6)F(4)**	36.6 (001) 18.0 (002)	25.3
O-2-C(4)F(4)	30.6 (001)	21.9	**Mal-2-C(6)F(6)**	41.8 (001) 20.8 (002)	27.9
O-2-C(4)F(6)	35.2 (001)	24.5	**Mal-2-C(6)F(8)**	45.9 (001) 23.0 (002) 15.2 (003)	27.9
O-2-C(4)F(8)	41.1 (001) 20.6 (002) 13.6 (003)	27.0	**Mal-2-C(8)F(4)**	39.4 (001) 19.3 (002)	27.6
O-2-C(6)F(4)	33.4 (001)	24.4	**Mal-2-C(8)F(6)**	43.7 (001) 21.8 (002)	30.2
O-2-C(6)F(6)	39.6 (001) 19.6 (002)	27.0	**Mal-2-C(8)F(8)**	47.7 (001) 23.8 (002)	32.6
O-2-C(6)F(8)	49.9 (001) 24.9 (002) 16.6 (003)	26.4	**O-2-PipC(8)**	30.5 (001)	24.2
O-2-C(8)F(4)	36.2 (001) 18.0 (002)	26.9	**O-2-PipC(10)**	34.0 (001)	26.7
O-2-C(8)F(6)	41.3 (001) 20.6 (002)	29.4	**O-2-PipC(12)**	36.6 (001)	28.7
O-2-C(8)F(8)	45.4 (001) 22.9 (002) 15.1 (003)	32.0	**O-2-PipC(14)**	38.8 (001)	31.1
Mal-1-C(4)F(6)	35.8 (001)	23.7	**O-3-PipC(12) (SmA)**	37.4 (001)	29.9
Mal-1-C(4)F(8)	39.4 (001)	26.2	**O-3-PipC(12) (SmE)**	36.1 (001) 12.0 (003) 9.0 (004) 4.9 (110) 4.0 (200) 3.4 (210)	29.9
Mal-1-C(6)F(6)	38.3 (001) 19.2 (002)	25.6			
Mal-1-C(6)F(8)	41.3 (001)	26.2			

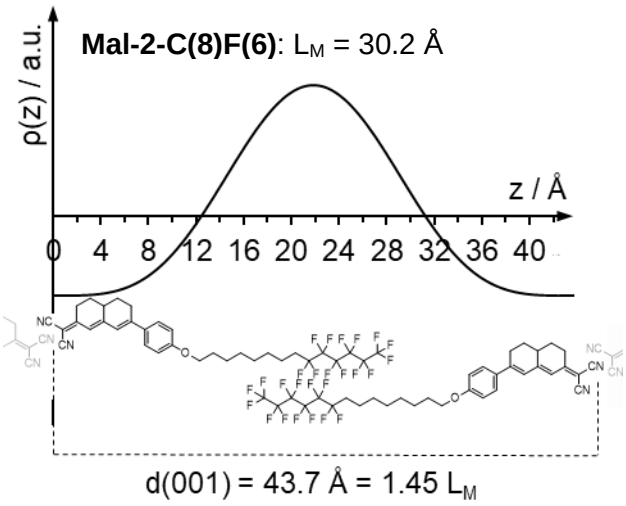


Figure S3 Deviation from the mean electron density ρ(z) along the z-axis for **Mal-2-C(8)F(6)**.

10) Absorption and emission

Table S3 Summary of the solution absorption and emission measurements of the merocyanines.

Compound	Solvent	$\lambda_{max, Abs.}$ / nm	ε / L·mol^{-1}·cm^{-1}	$\lambda_{max, Ems.}$ / nm
Mal-1-C(12)	Chloroform	388	43446	488
	Acetone	381	23552	–
	DMSO	390	49878	–
	Dichlormethane	386	63295	490
Mal-1-C(6)F(6)	Chloroform	388	29448	–
Mal-2-C(12)	Chloroform	427	64858	540
	Acetone	422	42629	–
	DMSO	435	22658	–
	Dichlormethane	427	57365	544
Mal-2-C(8)F(4)	Chloroform	427	53194	540
	Acetone	422	35038	–
Mal-2-C(6)F(6)	Chloroform	427	54835	538
	Acetone	421	71564	–
Mal-2-C(4)F(8)	Chloroform	427	56091	536
Mal-3-C(12)	Chloroform	465	189116	547
	Acetone	457	73982	–
	DMSO	472	65402	–
	Dichlormethane	465	49228	605
Mal-1-PipC(8)	Chloroform	458	54233	–
Mal-1-PipC(10)	Chloroform	458	33088	–
Mal-1-PipC(12)	Chloroform	458	52070	547
	Acetone	453	42542	–
	DMSO	470	31855	–
	Dichlormethane	458	52777	554
Mal-1-PipC(14)	Chloroform	458	17559	–
Mal-2-PipC(8)	Chloroform	481	37176	–
Mal-2-PipC(10)	Chloroform	482	93062	–
Mal-2-PipC(12)	Chloroform	481	44960	612
	Acetone	478	123122	632
	DMSO	498	42154	643

	Dichlormethane	481	50767	621
Mal-2-PipC(14)	Chloroform	482	57981	–
O-3-PipC(12)	Chloroform	408	11968	570
	Acetone	400	14831	572
	DMSO	413	20002	593
Mal-3-PipC(12)	Chloroform	505	20853	550
	Acetone	499	75905	–
	DMSO	522	45047	–
	Dichlormethane	503	50968	676

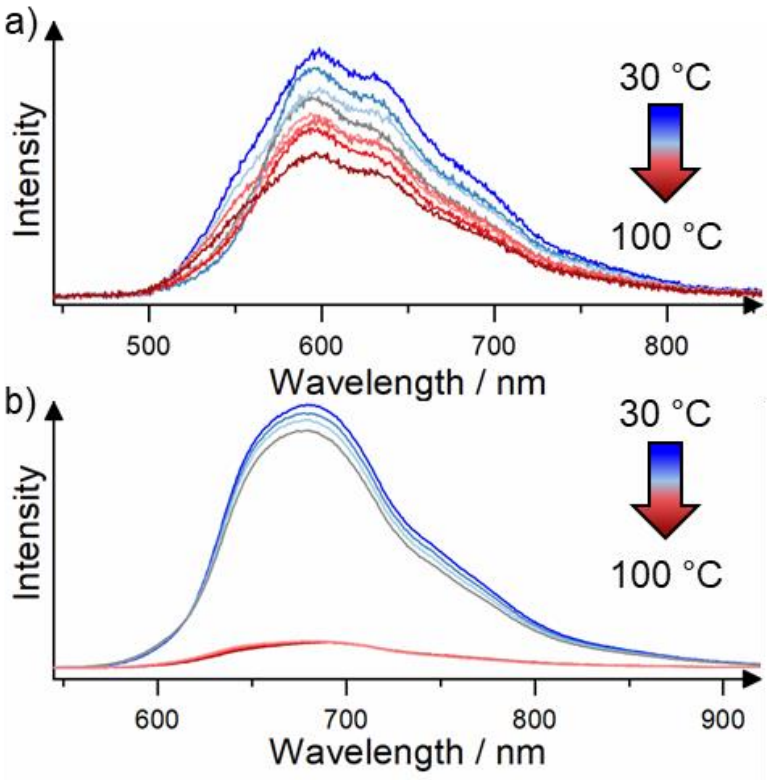


Figure S4 Temperature dependent emission spectra of merocyanines **Mal-2-C(12)** (a) and **Mal-2-PipC(12)** (b) in the solid state at given wavelengths (λ_{Exc} = 350 – 380 nm).

11) Theoretical details

General procedure

Molecular geometries for the electronic ground state (S0) and the first exited singlet state (S1) were optimized with the DL-FIND[14] optimization library in ChemShell.[15,16] The program package ORCA 5.0.1[17] was used for the electronic structure calculations. Geometry optimization and subsequent frequency calculations were performed with density functional theory (DFT) or time-dependent density functional theory (TD-DFT), the PBE0-functional,[18,19] Grimme´s empirical dispersion correction with Becke-Johnson damping scheme D3(BJ),[20,21] and the def2-TZVPP basis set.[22] To account for solvent effects, a conductor-like polarizable continuum model CPCM,[23] modeling CH_2Cl_2, was used in all calculations. The optimized structures were confirmed to be local minima by analytical (S0) or numerical (S1) frequency analysis.

Theoretical results

The geometric changes of the merocyanines were descripted by a single effective coordinate *Q*. This is the mean difference between C-C single and C=C double bond length in the polymethine chain.[24] In Figure S5 values for the bond lengths of the polymethine chain for S0 and S1 were summarized for **Mal-1-C(12)**. Figure S6 does the same for **Mal-2-PipC(12)**. Calculated values for *Q* are listed in Table S4.

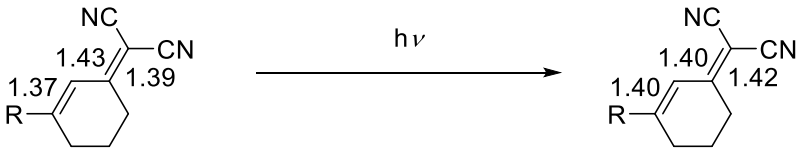


Figure S5 C-C single and C=C double bond length in the polymethine chain for S0 (left) and S1 (right) states for **Mal-1-C(12)**. Distances are given in Å.

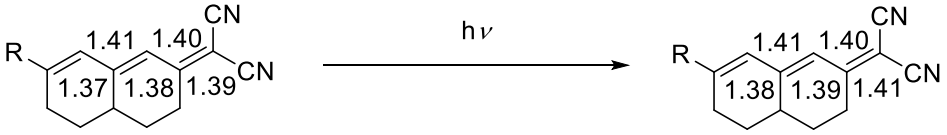


Figure S6 Figure 1: C-C single and C=C double bond length in the polymethine chain for S0 (left) and S1 (right) states for **Mal-2-PipC(12)**. Distances are given in Å.

Table S4 Geometric parameters Q for **Mal-1-C(12)** and **Mal-2-PipC(12)**.

Compound	Electronic State	*Q* / pm
Mal-1-C(12)	S0	5.0
	S1	-1.0
Mal-2-PipC(12)	S0	3.0
	S1	1.2

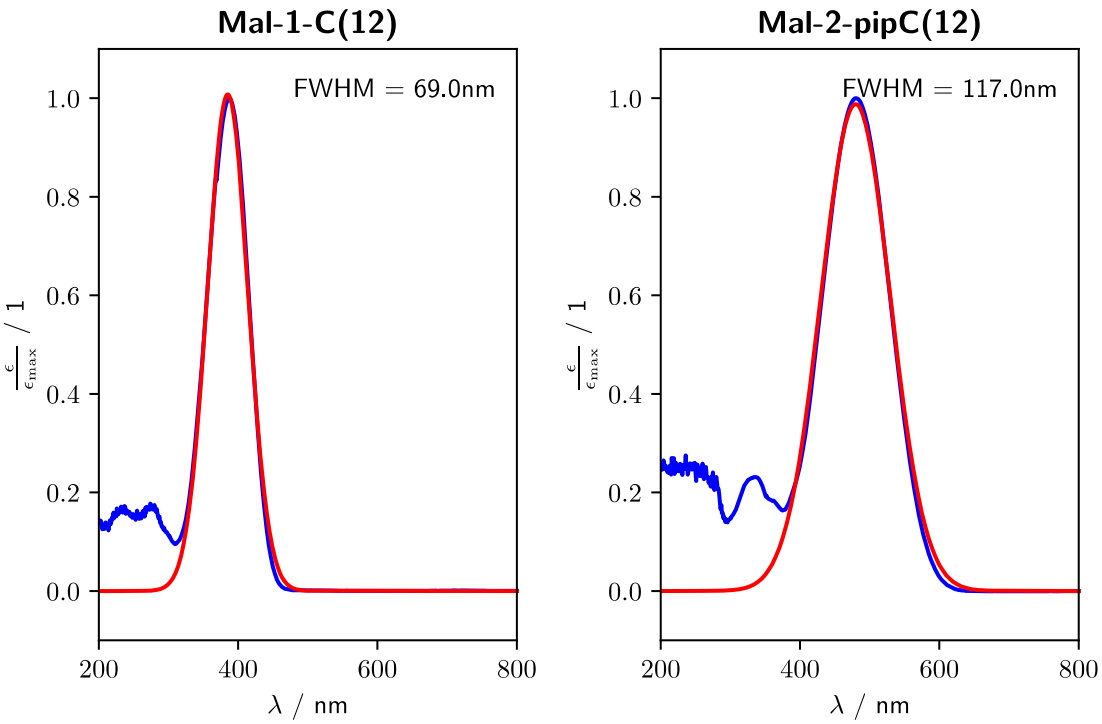


Figure S7 Experimental absorption spectra for **Mal-1-C(12)** (left) and **Mal-2-PipC(12)** (right).

The S0-S1- absorption bands have been fitted with a gaussian function of the type.

$$\frac{\epsilon}{\epsilon_{\max}} = a \cdot \frac{1}{\sqrt{2\pi}\,\frac{FWHM}{2\sqrt{2\log 2}}} \exp\left(-\frac{(\lambda-\mu)^2}{2\left(\frac{FWHM}{2\sqrt{2\log 2}}\right)}\right)$$

Cartesian Coordinates in Ang

Mal-1-C(12) S0 state:

66

C 3.778117 -0.204474 1.392442
C 5.180933 -0.057304 1.273146
C 3.147951 0.556953 2.407470
N 2.628628 1.172588 3.234215
N 6.323374 0.072720 1.171242
C 3.062591 -1.025028 0.545719
C 3.768347 -1.774292 -0.535800
C 1.651308 -1.125272 0.651500
H 4.777269 -2.039721 -0.216795
H 3.882941 -1.089396 -1.385435
C 2.982903 -2.995030 -0.972580
C 0.895317 -1.850019 -0.219804
H 1.165096 -0.538708 1.420572
H 2.972316 -3.730711 -0.163519
H 3.470410 -3.461372 -1.829460
C 1.556649 -2.616751 -1.323305
H 0.972538 -3.507785 -1.557188
H 1.546910 -1.993956 -2.227800
C -0.556576 -1.864163 -0.129243
C -1.228746 -1.562659 1.061032
C -1.338365 -2.175263 -1.251469
H -0.665635 -1.358702 1.963046
C -2.607051 -1.552468 1.136253
C -2.713234 -2.144058 -1.196790
H -0.862721 -2.411521 -2.194457
C -3.366188 -1.826186 -0.004043
H -3.309574 -2.356970 -2.075099
H -3.082659 -1.336461 2.082441

O -4.707192 -1.830655 -0.049694

C -5.452097 -1.241551 1.018670

C -5.252158 0.256346 1.118964

H -5.207133 -1.739995 1.960838

H -6.487776 -1.477661 0.773554

H -5.926924 0.622885 1.899279

C -5.505050 0.996331 -0.184448

H -4.240602 0.466370 1.470365

H -6.552384 0.870294 -0.477560

H -4.912105 0.536914 -0.979424

C -5.177342 2.483604 -0.107634

H -5.384687 2.936094 -1.083206

C -3.739988 2.804820 0.292577

H -5.856217 2.965731 0.604066

H -3.561803 2.491056 1.326642

H -3.614436 3.892824 0.289828

C -2.673819 2.188263 -0.599842

H -2.771275 1.097553 -0.608629

C -1.264692 2.552697 -0.163624

H -2.831617 2.516899 -1.634339

H -1.093126 2.177277 0.852666

H -1.178326 3.644267 -0.101440

C -0.178337 2.022489 -1.084291

H -0.220607 0.927385 -1.108885

C 1.213839 2.470738 -0.673654

H -0.377623 2.359953 -2.108438

H 1.420193 2.126849 0.346484

H 1.237409 3.566507 -0.633825

C 2.318189 1.986577 -1.596885

H 2.345927 0.890705 -1.589758

C 3.684911 2.535734 -1.220530

H 2.084712 2.275924 -2.628607

H 3.891441 2.296254 -0.172304

H 3.653402 3.629185 -1.277733

C 4.809993 2.011392 -2.095106

H 5.773007 2.440153 -1.810212

H 4.634289 2.252399 -3.146885

H 4.896400 0.925115 -2.015226

Mal-1-C(12) S1 state:

66

C 3.805948 -0.204900 1.423044

C 5.192559 -0.033700 1.295867

C 3.173786 0.505836 2.454009

N 2.621088 1.082562 3.296052

N 6.338002 0.110781 1.173108

C 3.080050 -1.057319 0.546300

C 3.812900 -1.805400 -0.517727

C 1.694798 -1.184140 0.662494

H 4.784391 -2.133980 -0.139457

H 4.028996 -1.120532 -1.347795

C 3.005427 -2.988263 -1.020416

C 0.905926 -1.893374 -0.254784

H 1.210155 -0.638690 1.463204

H 2.956074 -3.750023 -0.236694

H 3.502352 -3.440184 -1.879757

C 1.590654 -2.572975 -1.396839

H 1.022513 -3.447860 -1.717656

H 1.626843 -1.893132 -2.260819

C -0.518044 -1.894094 -0.147169

C -1.197249 -1.488270 1.037314

C -1.330328 -2.295650 -1.242702

H -0.628399 -1.214225 1.915414

C -2.565585 -1.458892 1.120003

C -2.694349 -2.256882 -1.172874

H -0.865425 -2.614115 -2.165642

C -3.340059 -1.822463 0.003071

H -3.306738 -2.539992 -2.019844

H -3.033863 -1.158797 2.046416

O -4.664294 -1.800443 -0.051018

C -5.438242 -1.233237 1.014428

C -5.278090 0.270102 1.116824

H -5.177796 -1.728827 1.953311

H -6.461424 -1.502450 0.755104

H -5.973986 0.610207 1.890371

C -5.530132 1.014843 -0.183774

H -4.277894 0.502003 1.484881

H -6.577376 0.894192 -0.477874

H -4.937439 0.561227 -0.982451

C -5.197618 2.500508 -0.092294

H -5.405998 2.962936 -1.062558

C -3.758556 2.815672 0.307509

H -5.874577 2.976890 0.625063

H -3.579619 2.502817 1.341820

H -3.630338 3.903190 0.305351

C -2.694588 2.196626 -0.586031

H -2.781930 1.104953 -0.578017

C -1.284911 2.578432 -0.167697

H -2.865478 2.506892 -1.624027

H -1.110110 2.239861 0.860843

H -1.200755 3.671568 -0.143609

C -0.198634 2.018649 -1.070899

H -0.243625 0.923303 -1.063245

C 1.193947 2.475338 -0.670874

H -0.395896 2.324908 -2.105290

H 1.399056 2.156908 0.358131

H 1.217374 3.571862 -0.657354

C 2.300709 1.968323 -1.579419

H 2.326217 0.872637 -1.547360

C 3.668056 2.519116 -1.207456

H 2.072914 2.237592 -2.617932

H 3.875171 2.281508 -0.158567

H 3.638300 3.612626 -1.269110

C 4.792345 1.989371 -2.080311

H 5.756418 2.416466 -1.796391

H 4.618416 2.226003 -3.133430

H 4.876322 0.903318 -1.995961

Mal-2-PipC(12) S0 state:

89

C -5.361847 -0.874606 -1.452325

C -6.736423 -0.922251 -1.133594

C -5.025760 -0.339768 -2.716486

N -4.739880 0.098264 -3.746942

N -7.862473 -0.964720 -0.875365

C -4.388459 -1.324410 -0.567887

C -4.793981 -1.819822 0.784169

C -3.024690 -1.299083 -0.903057

H -5.791444 -2.260116 0.742524

H -4.871721 -0.944631 1.441835

C -3.785414 -2.798976 1.353704

H -3.799689 -3.722149 0.765270

H -4.060191 -3.062121 2.377025

C -2.382421 -2.220110 1.328246

C -2.036390 -1.715128 -0.039874

H -2.734410 -0.925082 -1.879302

C -0.676413 -1.640446 -0.425872

C -1.329781 -3.203818 1.802639

H -2.356295 -1.344924 1.995893

H -1.380650 -4.103417 1.180070
H -1.545757 -3.509786 2.828479
C 0.064428 -2.613037 1.720287
C 0.366152 -2.021564 0.373870
H 0.799790 -3.380347 1.964174
H 0.183698 -1.825263 2.475692
H -0.483043 -1.214966 -1.403059
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C 2.802368 -2.090165 0.877552
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C 4.114776 -1.832925 0.559981
N 5.758092 -0.953831 -0.965998
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H 6.104168 -0.445152 1.013930
C 7.426134 0.693762 -0.230858
H 7.393277 -1.409711 0.296135
H 5.570896 -0.937568 -3.047309
H 7.197852 -0.855838 -2.424429
C 6.170638 1.041195 -2.350832
H 7.795364 1.136466 0.695350
C 6.525860 1.656240 -0.997984
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Mal-2-PipC(12) S1 state:

89

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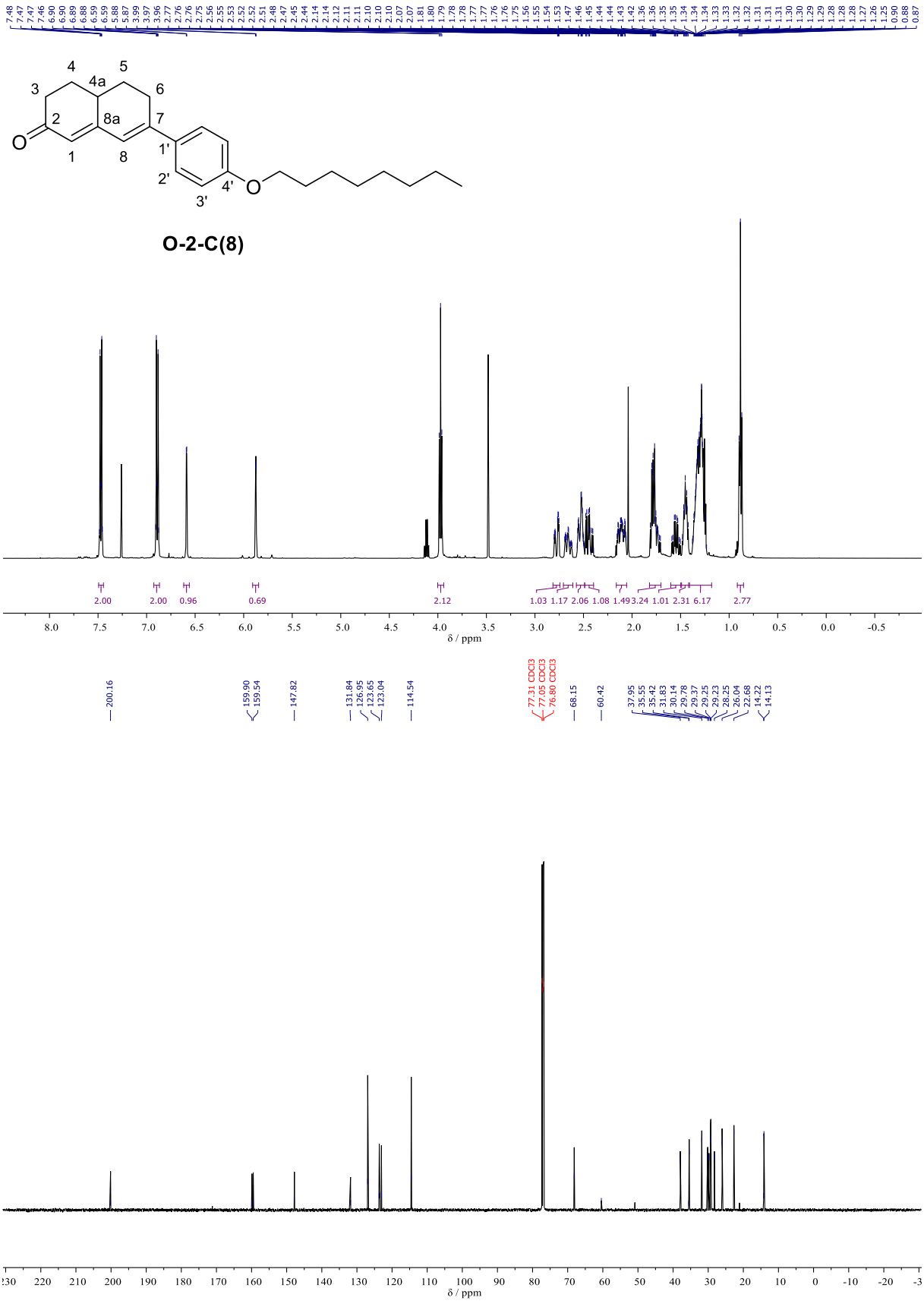
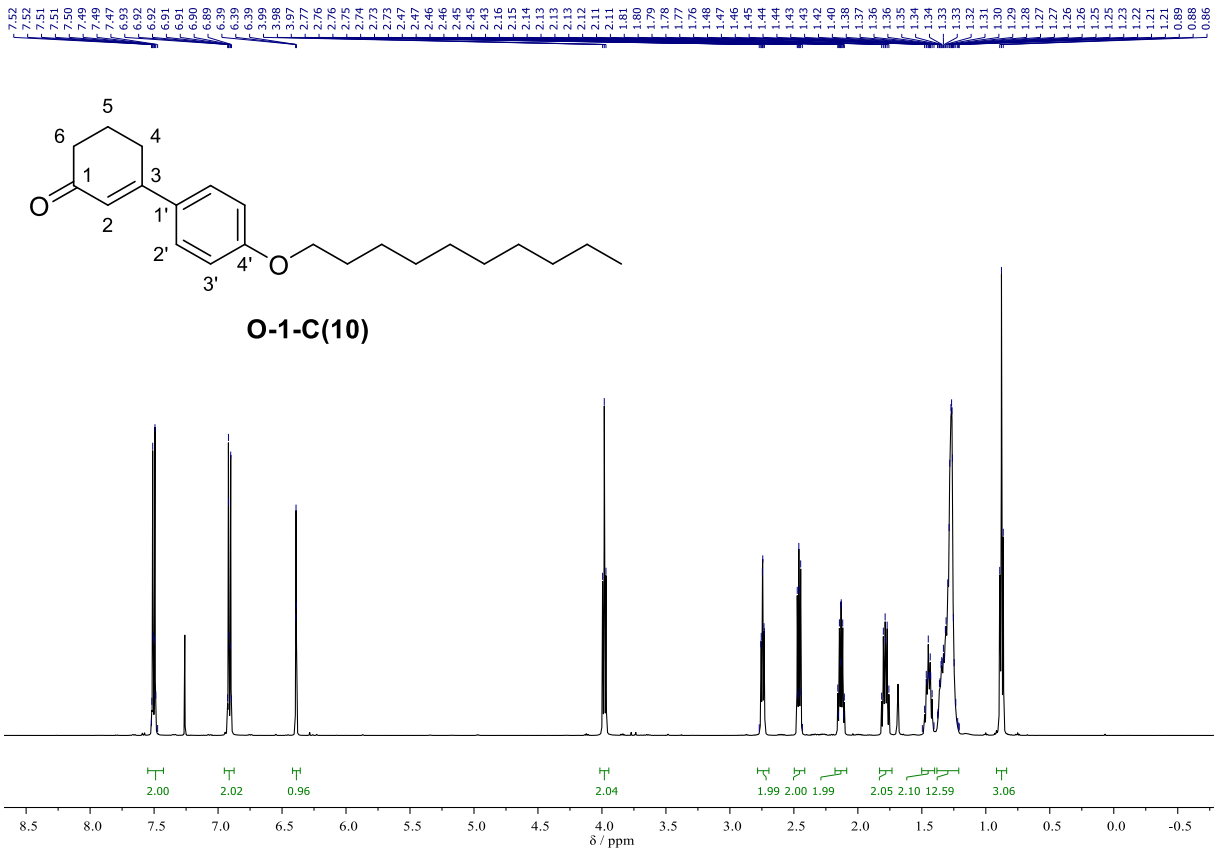
13) NMR (^{1}H and ^{13}C)

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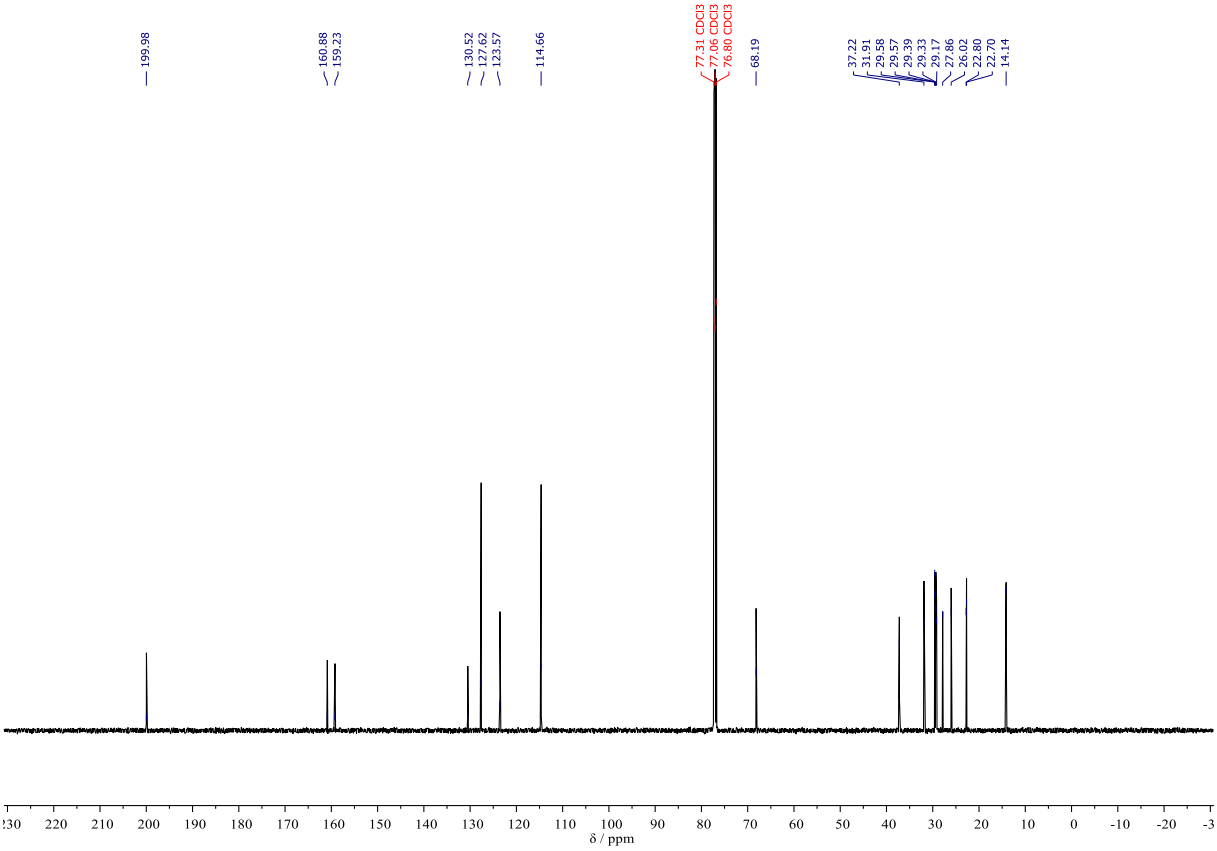
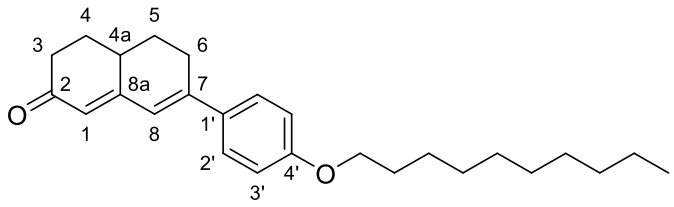

δ / ppm


4
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8a
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O
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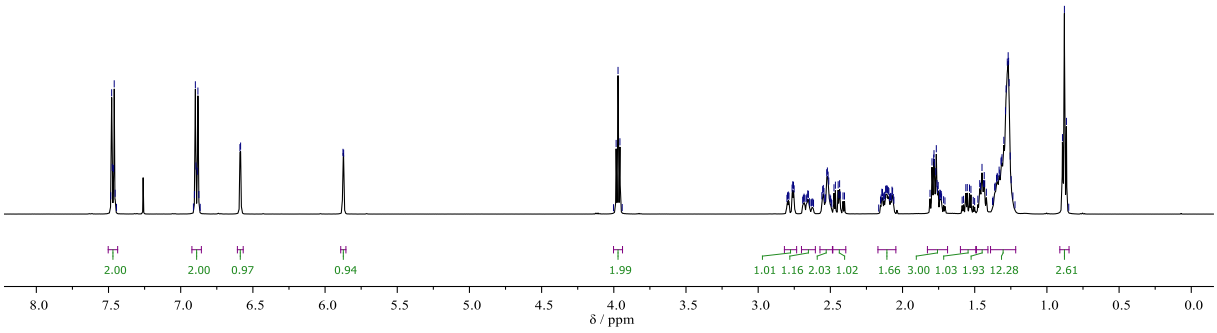
8
1'
2'
4'
O
3'

O-2-C(10)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1.99
1.01 1.16 2.03 1.02
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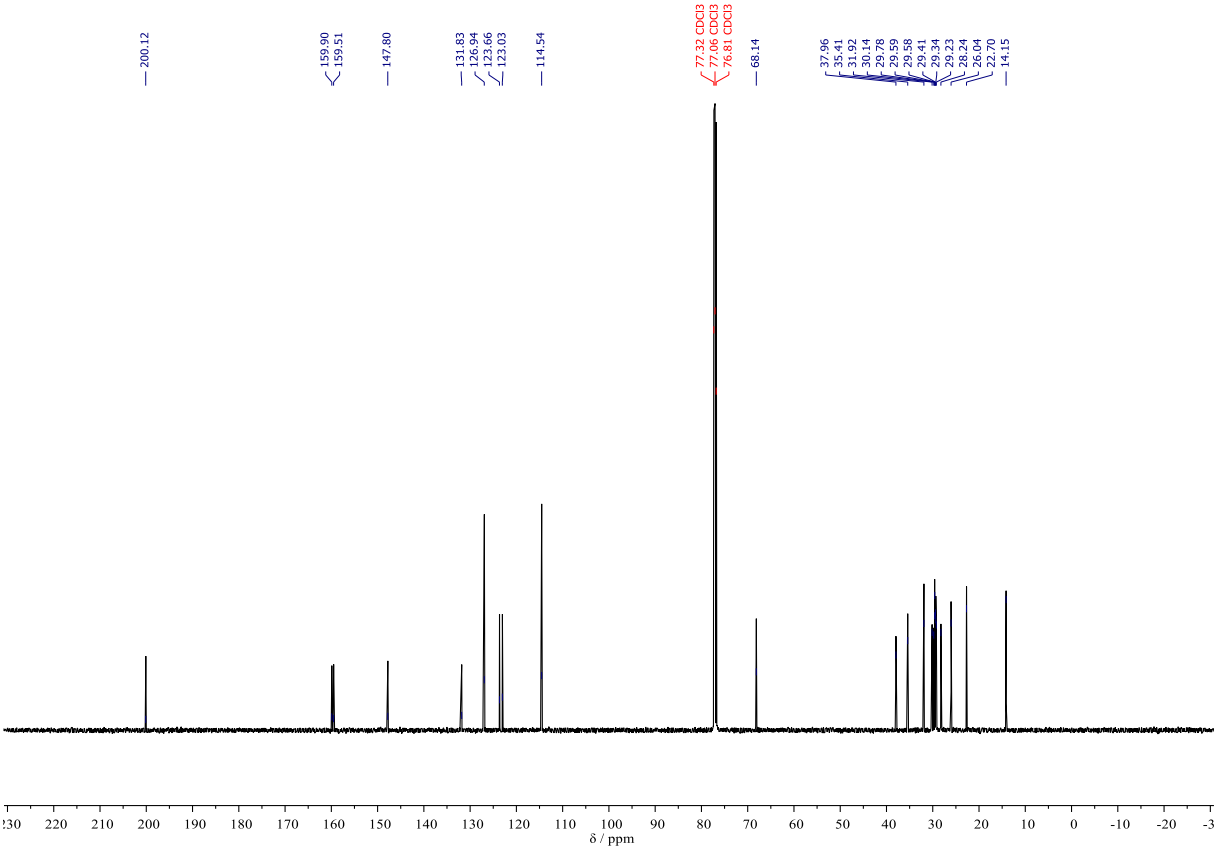
3.00 1.03 1.93 12.28
2.61
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm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126.94
123.66
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77.32 CDCl3
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68.14
37.96
35.41
31.92
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29.59
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29.34
29.23
28.24
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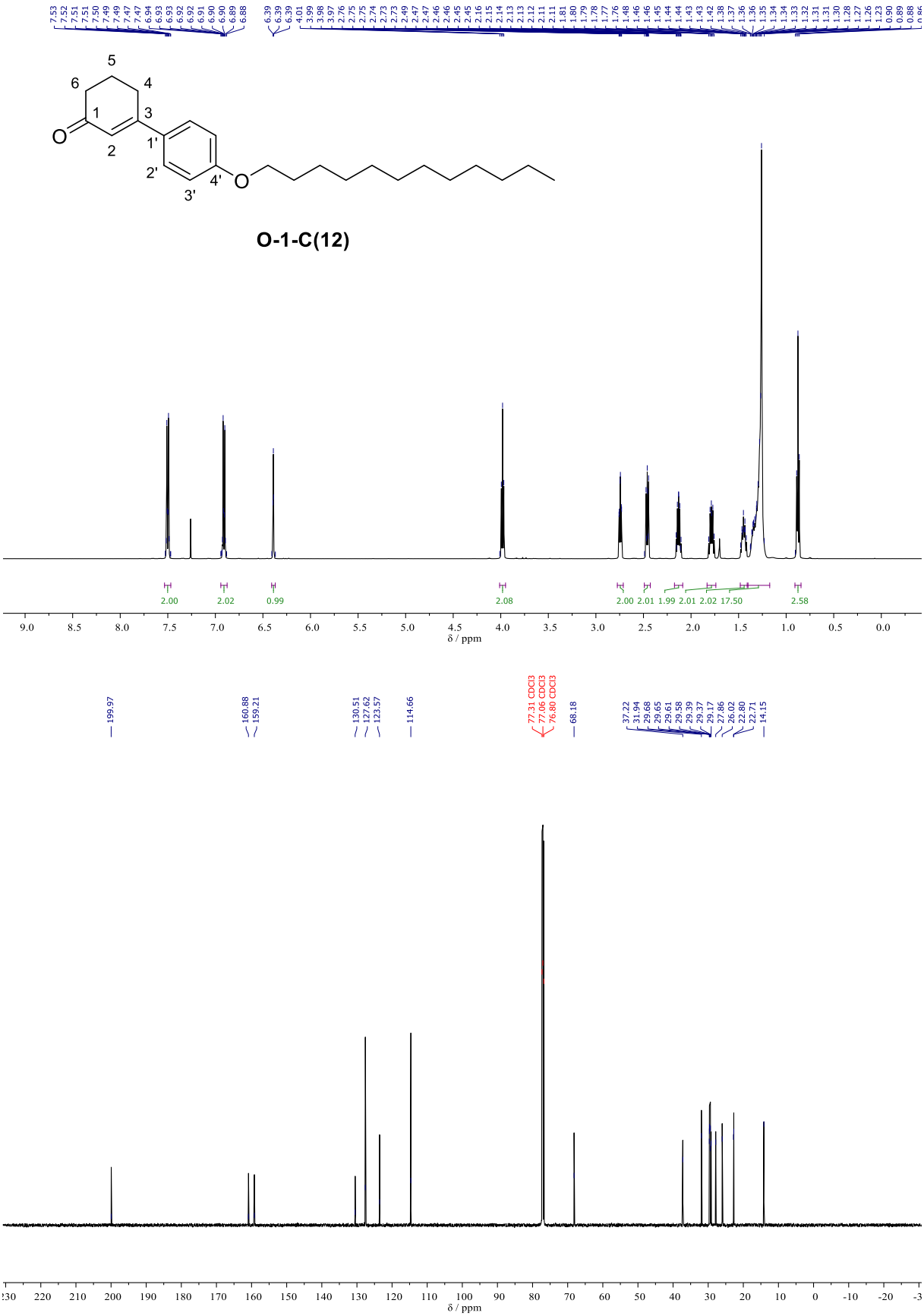
22.70
14.15
δ / ppm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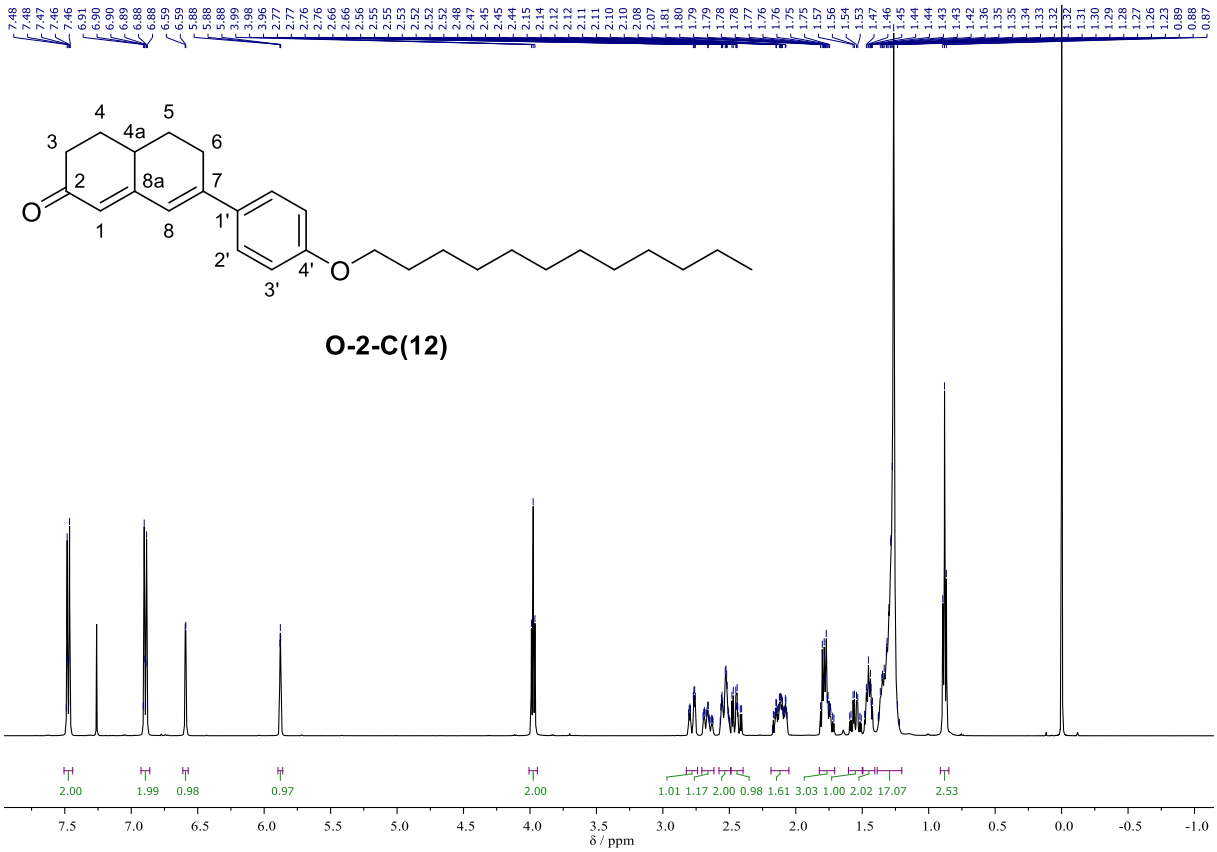
δ / ppm
δ / ppm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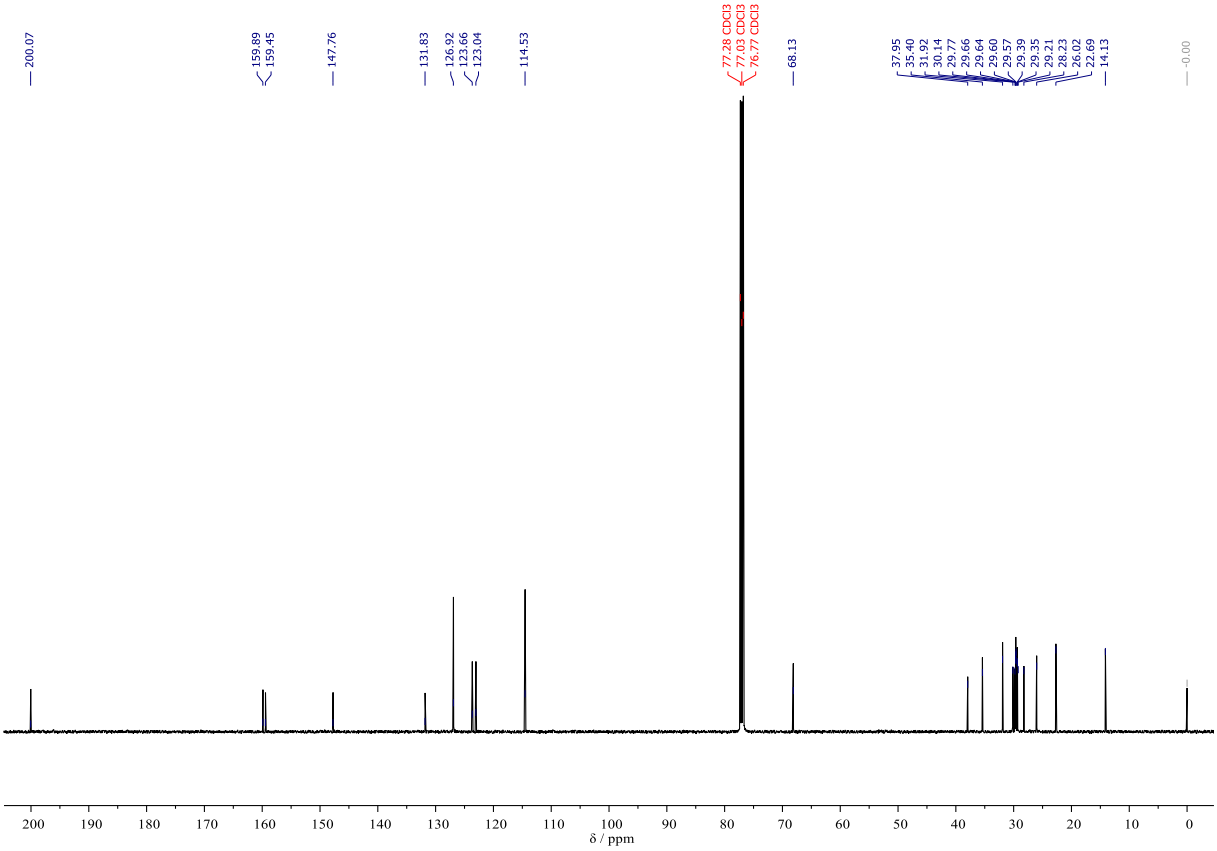
δ / ppm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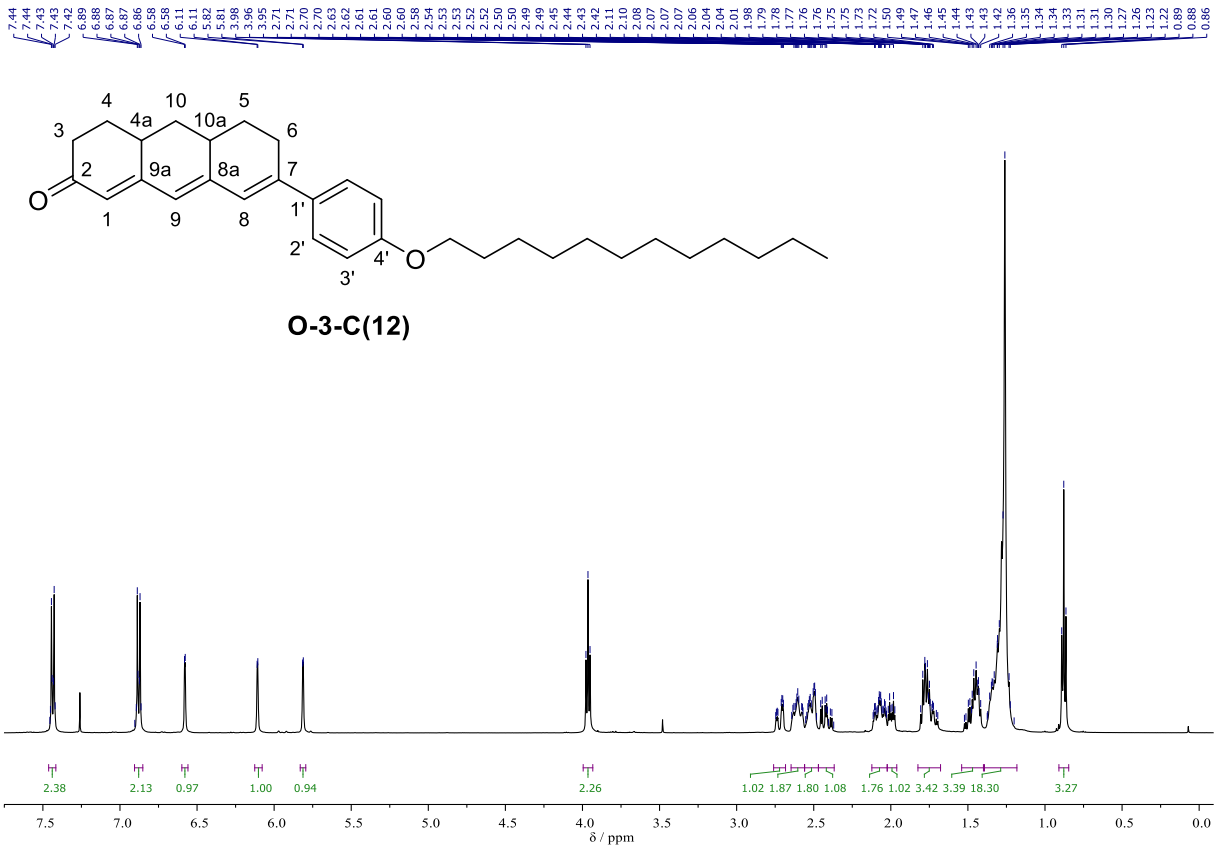

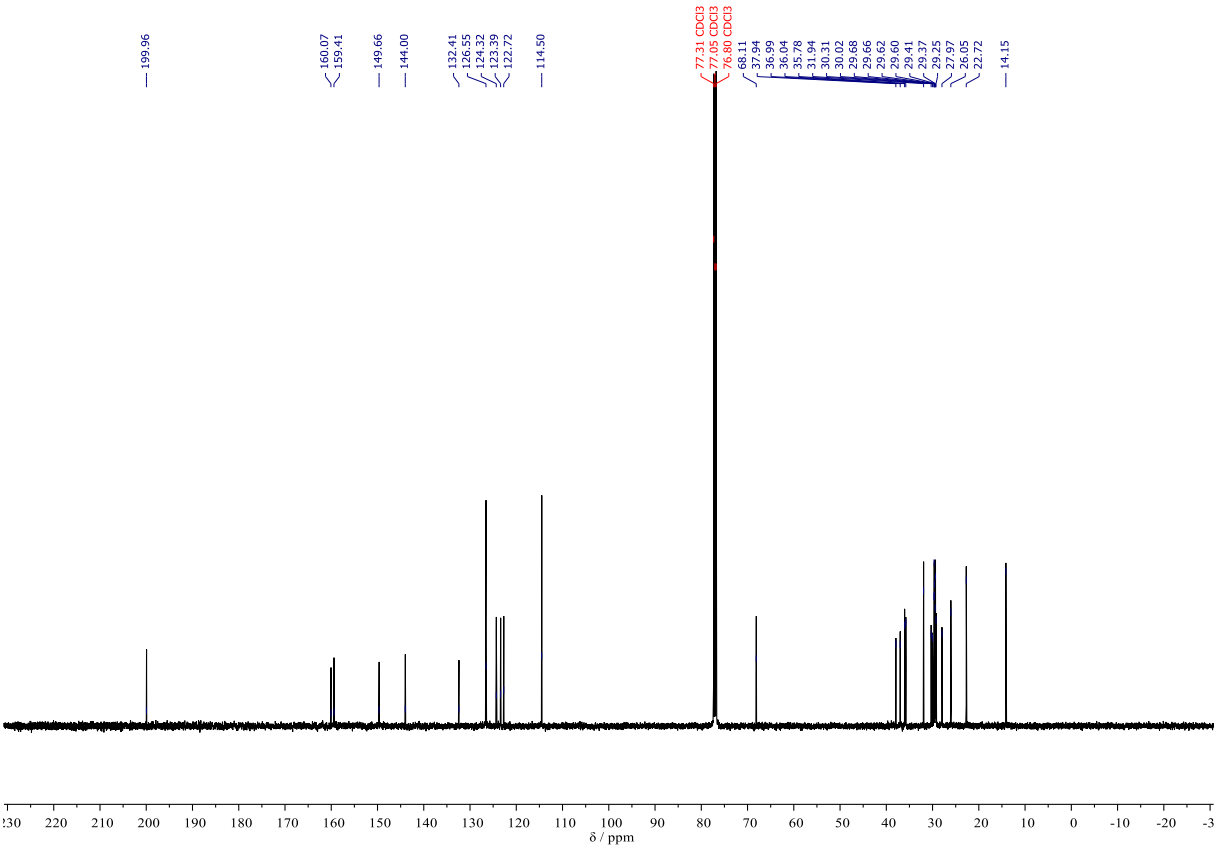

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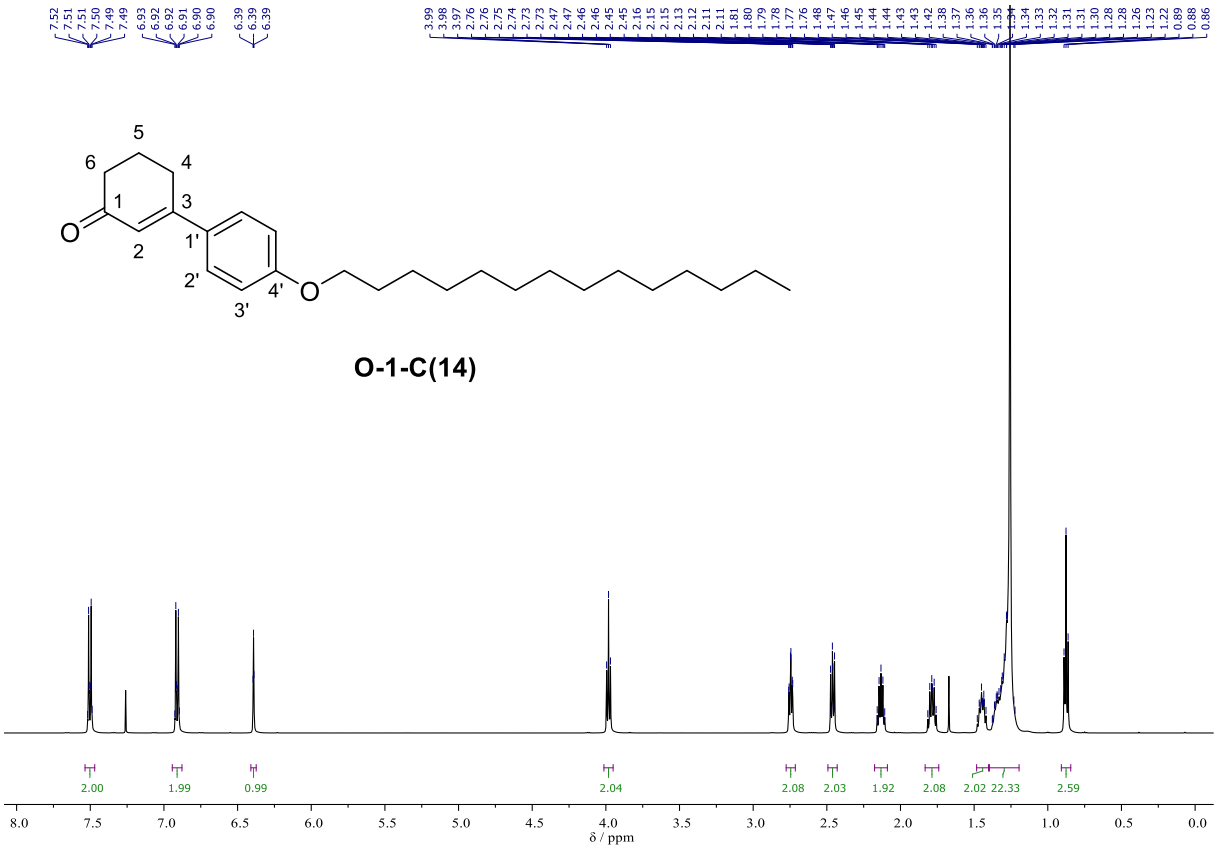
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1.34
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1.33
1.32
1.31
1.31
1.30
1.28
1.28
1.26
1.23
1.22
0.89
0.88
0.86
5
6
4
1
3
O
2
1'
2'
4'
O
3'
O-1-C(14)
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1.99
0.99
2.04
2.08
2.03
1.92
2.08
2.02
22.33
2.59
8.0
7.5
7.0
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6.0
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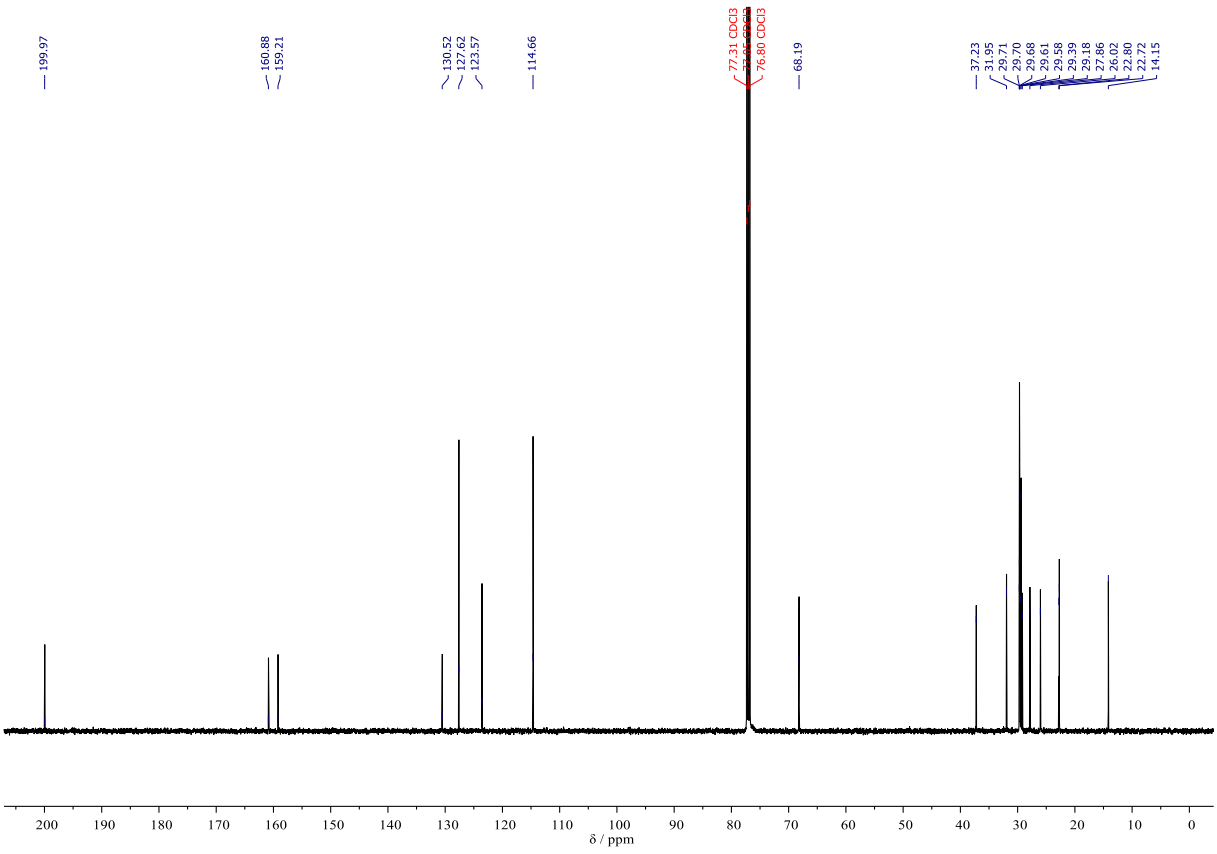
δ / ppm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68.19
37.23
31.95
29.71
29.70
29.68
29.61
29.58
29.39
29.18
27.86
26.02
22.80
22.72
14.15
200
190
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140
130
120
110
100
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80
70
60
50
40
30
20
10
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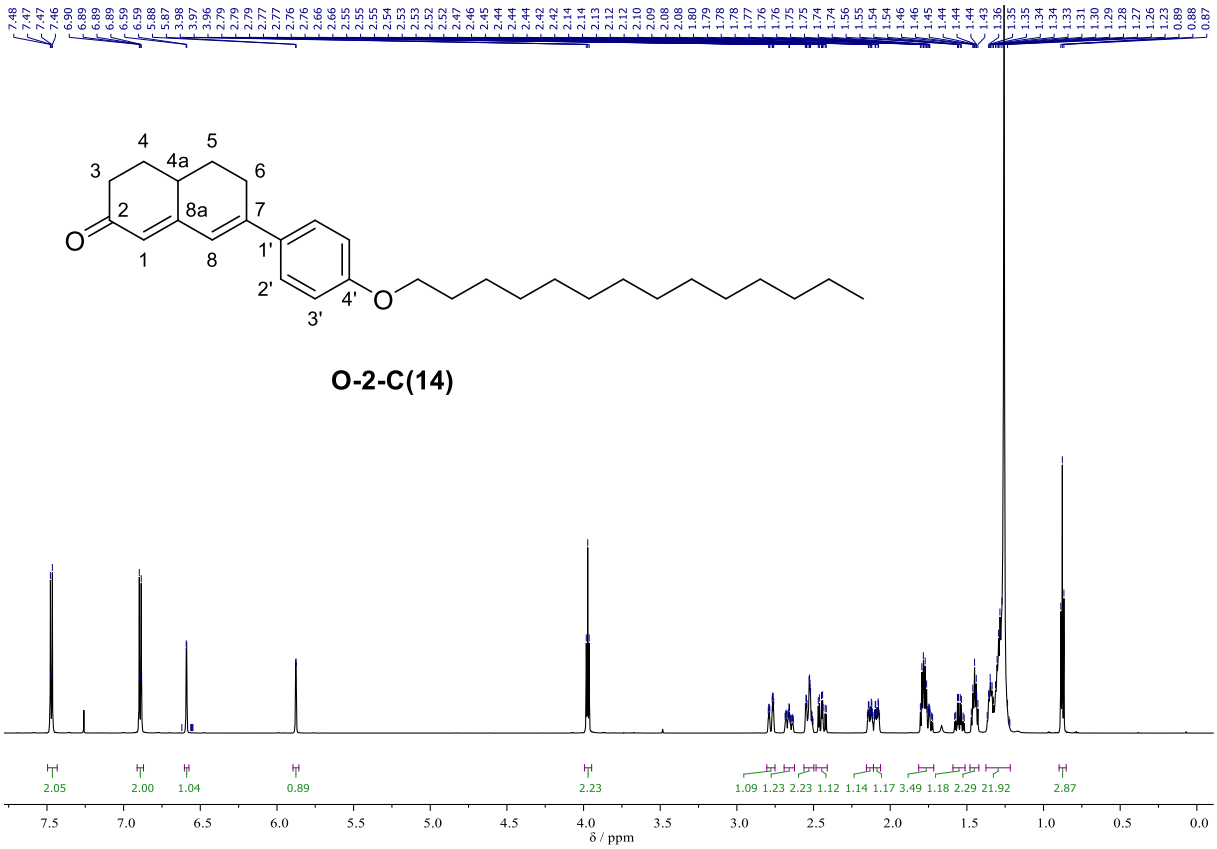
δ / ppm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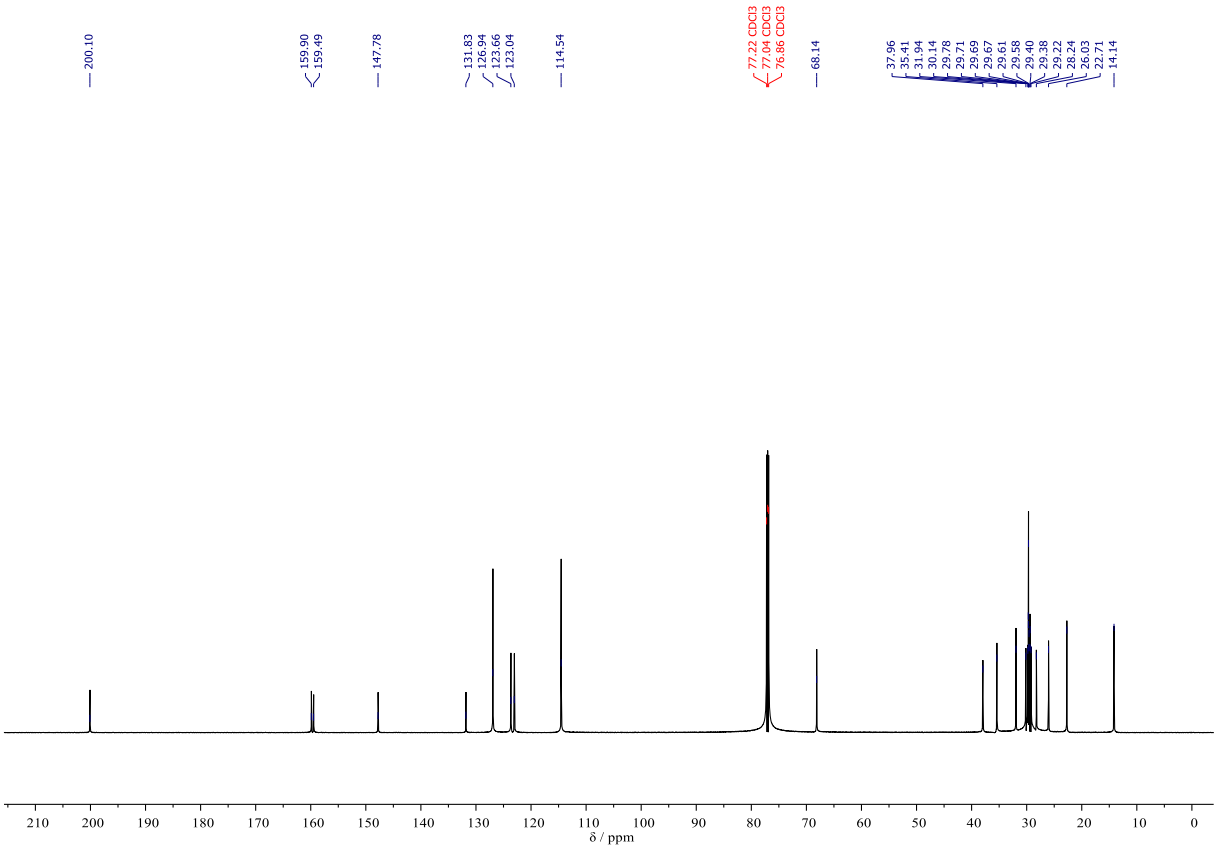

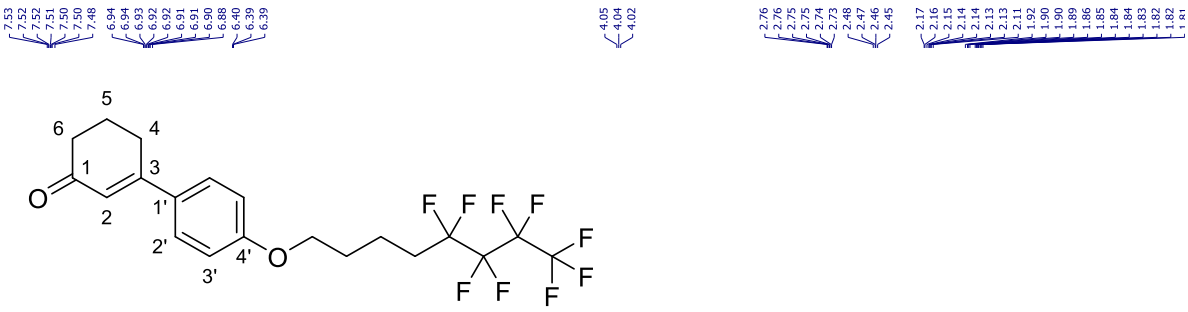
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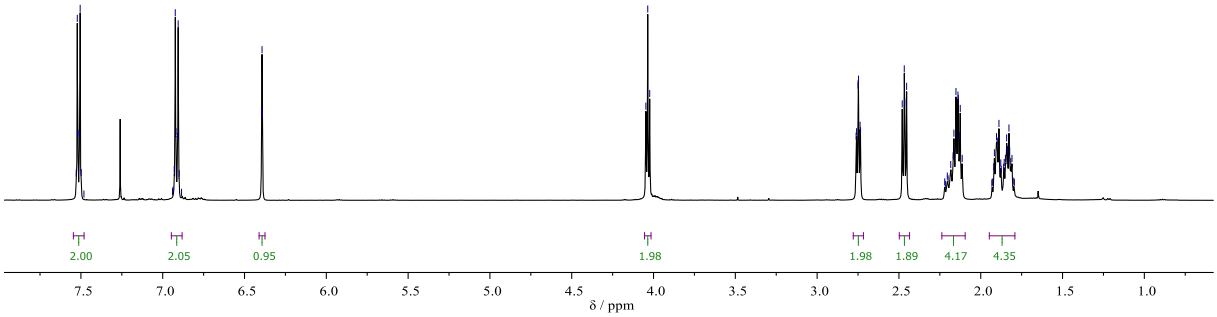
4.05 4.04 4.02
2.76 2.76 2.75 2.75 2.74 2.73 2.48 2.47 2.46 2.45
2.17 2.16 2.15 2.14 2.14 2.13 2.13 2.11 1.92 1.90 1.90 1.89 1.86 1.85 1.84 1.84 1.83 1.82 1.82

5
6
4
1
3
O
2
1'
2'
4'
O
3'
F F F F
F
F F F

O-1-C(4)F(4)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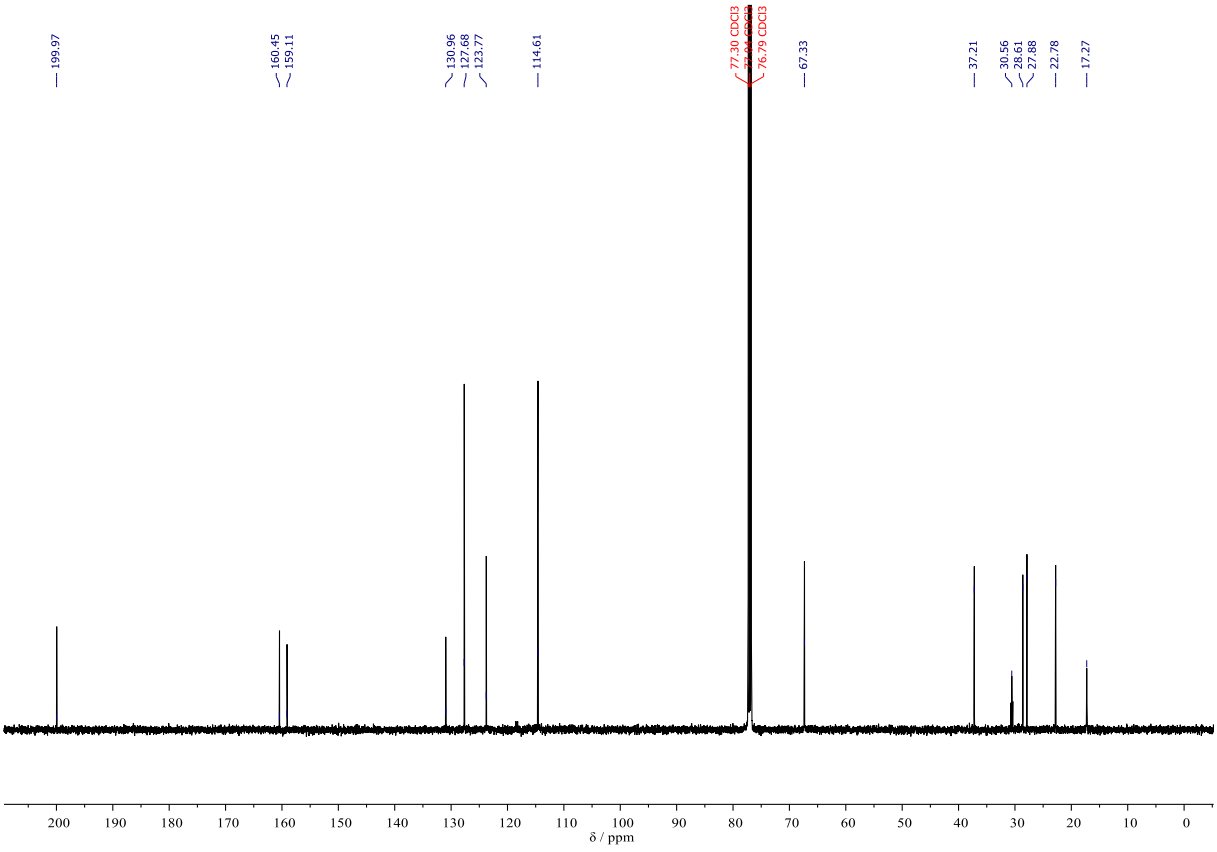
δ / ppm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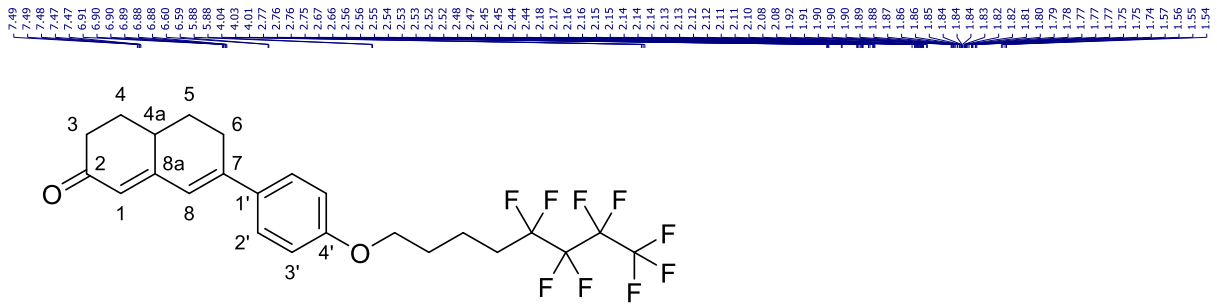
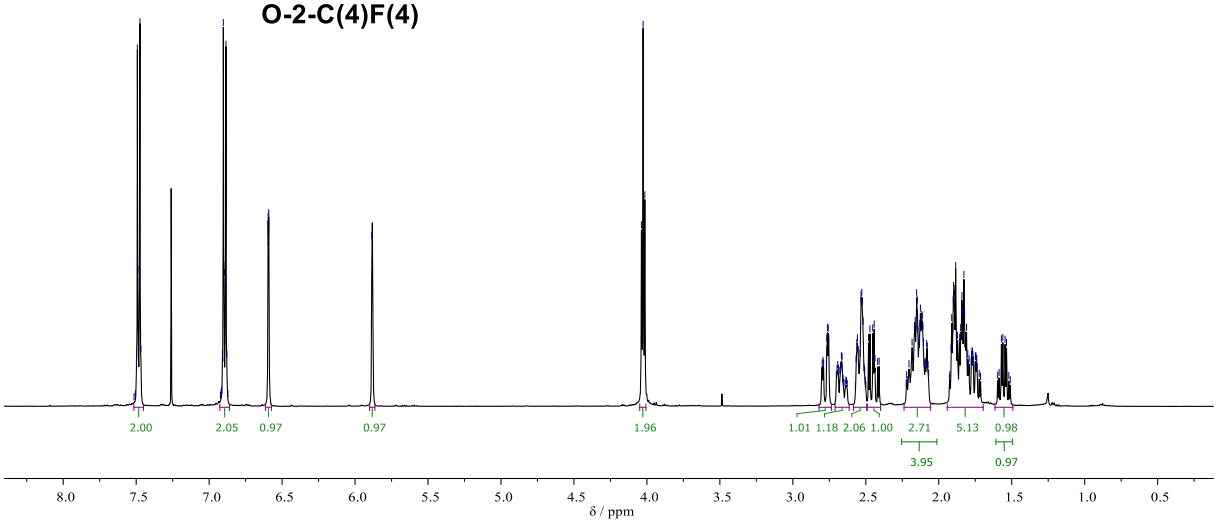
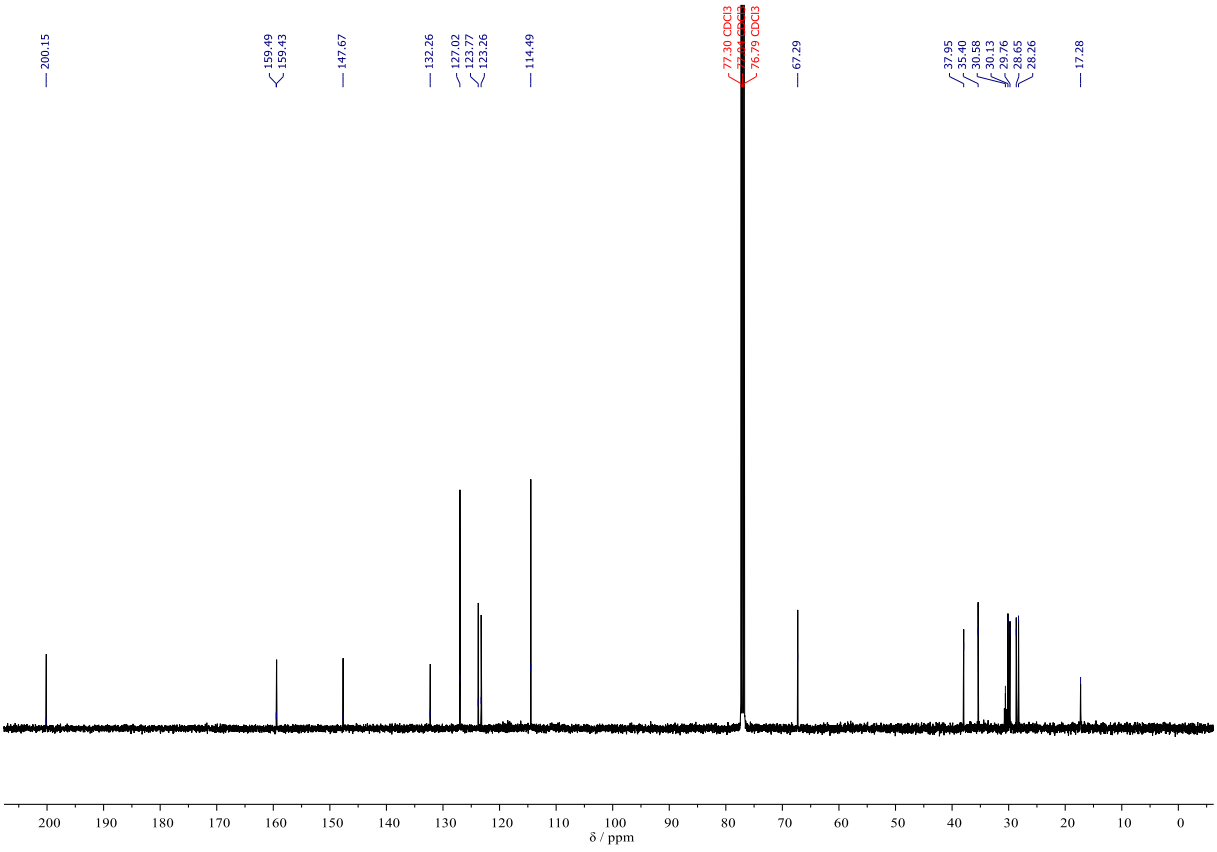
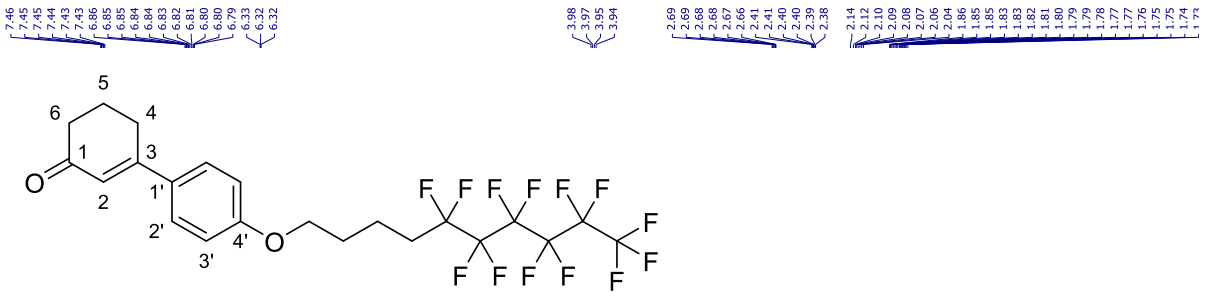
δ / ppm



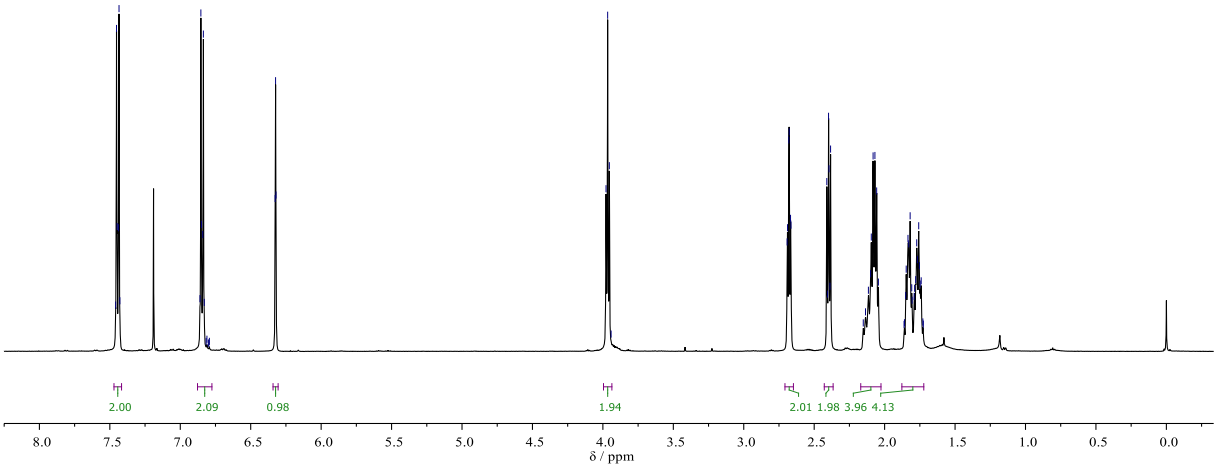
O-2-C(4)F(4)

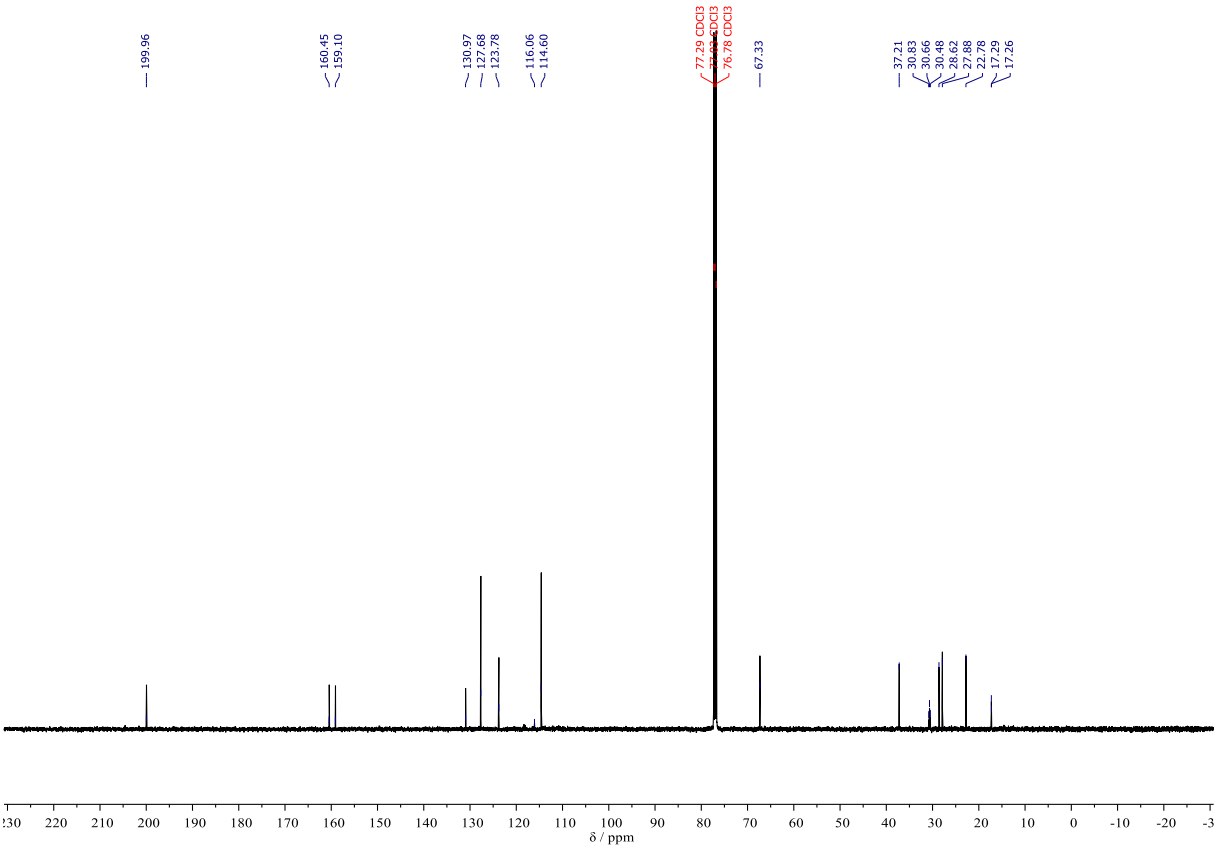

2.00
2.05
0.97
0.97
1.96
1.01
1.18
2.06
1.00
2.71
5.13
0.98
3.95
0.97
δ / ppm

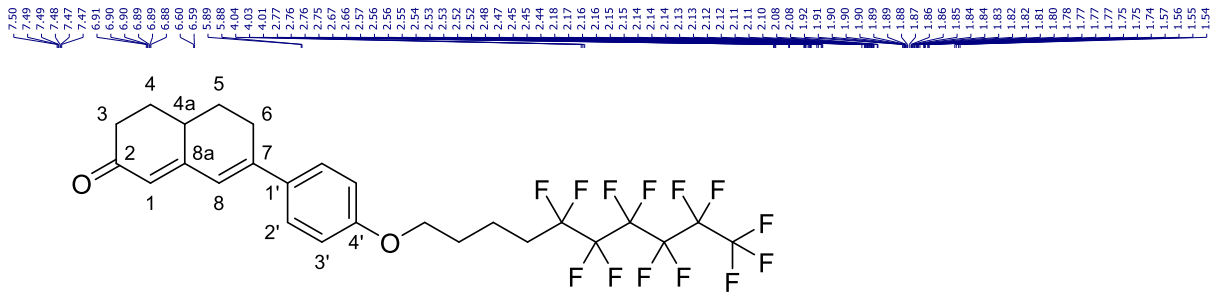

200.15
159.49
159.43
147.67
132.26
127.02
123.77
123.26
114.49
77.30 CDCl3
76.79 CDCl3
67.29
37.95
35.40
30.58
30.13
29.76
28.65
28.26
17.28
δ / ppm



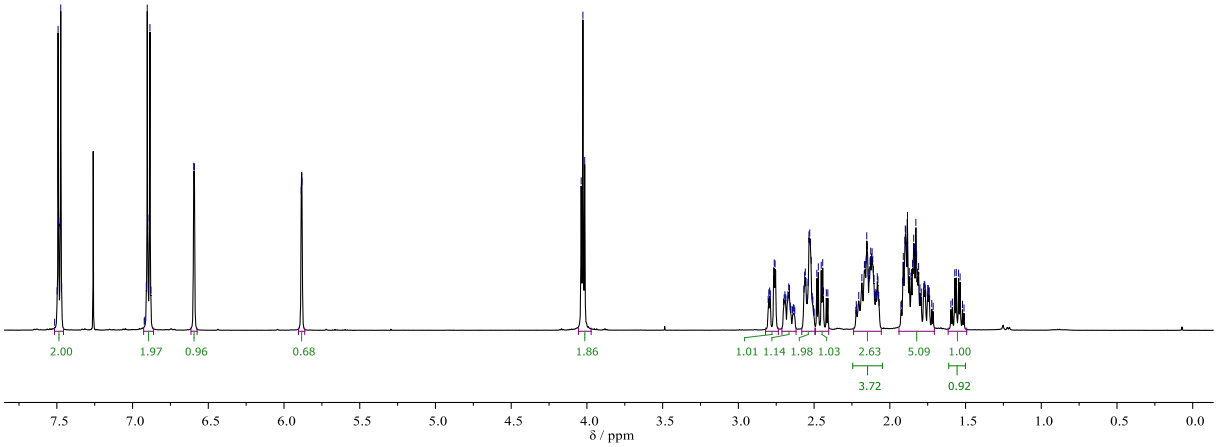
O-1-C(4)F(6)

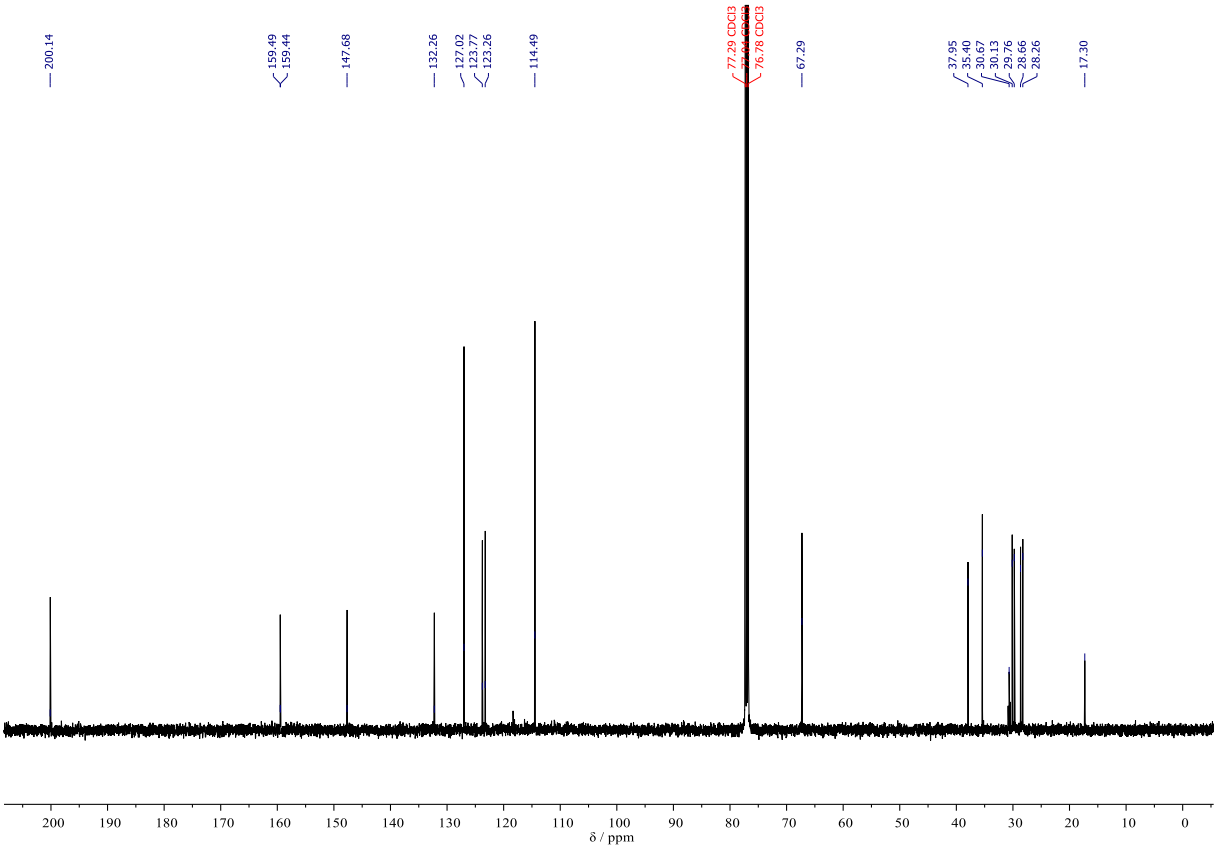

2.00
2.09
0.98
1.94
2.01 1.98 3.96 4.13
δ / ppm

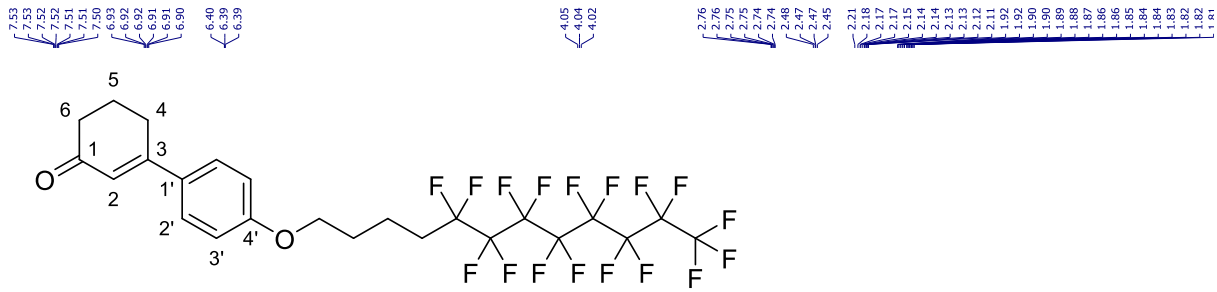

199.96
160.45
159.10
130.97
127.68
123.78
116.06
114.60
77.29 CDCl3
76.78 CDCl3
67.33
37.21
30.83
30.66
30.48
28.62
27.88
22.78
17.29
17.26
δ / ppm



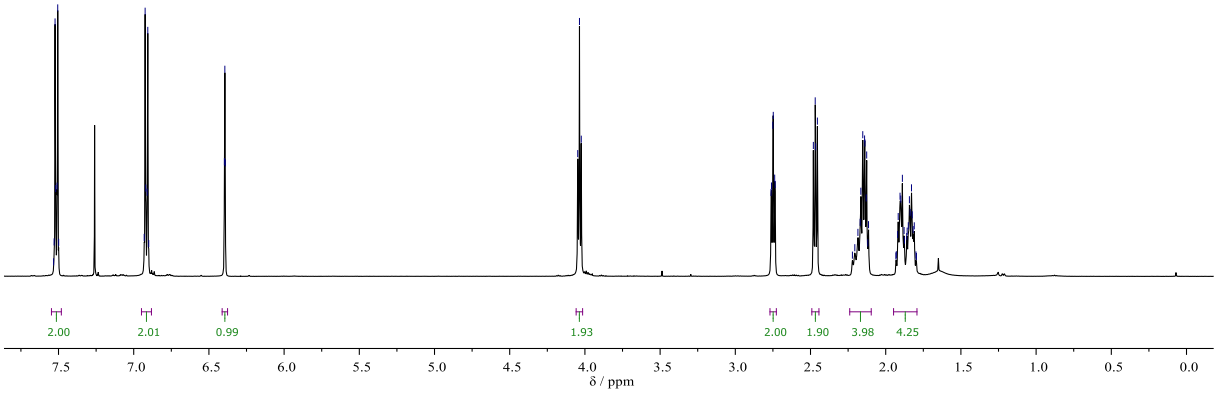
O-2-C(4)F(6)

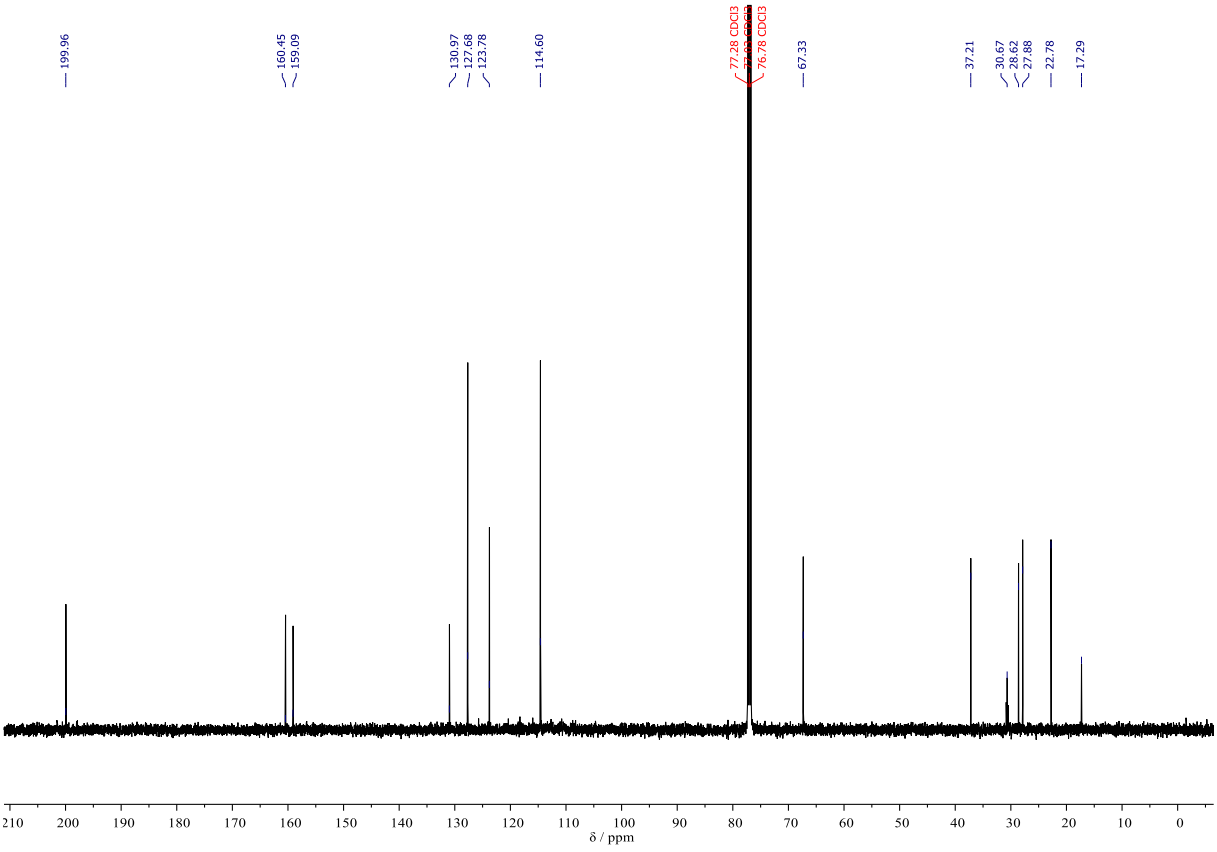


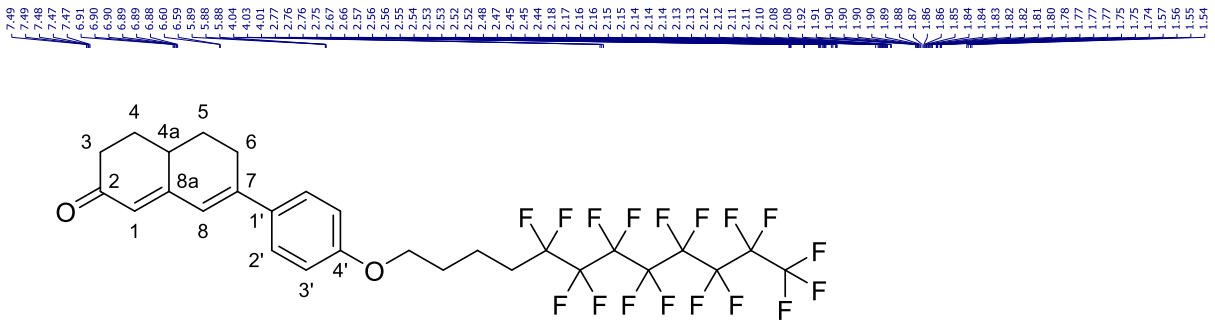



7.53
7.53
7.52
7.52
7.51
7.51
7.50
6.93
6.92
6.92
6.91
6.91
6.90
6.40
6.39
6.39
4.05
4.04
4.02
2.76
2.76
2.75
2.75
2.74
2.74
2.48
2.47
2.47
2.45
2.21
2.18
2.17
2.17
2.15
2.14
2.14
2.13
2.13
2.12
2.11
1.92
1.92
1.90
1.90
1.88
1.88
1.87
1.86
1.86
1.85
1.84
1.84
1.83
1.82
1.82
5
6
4
1
3
O
2
1'
2'
4'
3'
O
F F F F F F F F
F
F
F F F F F F F

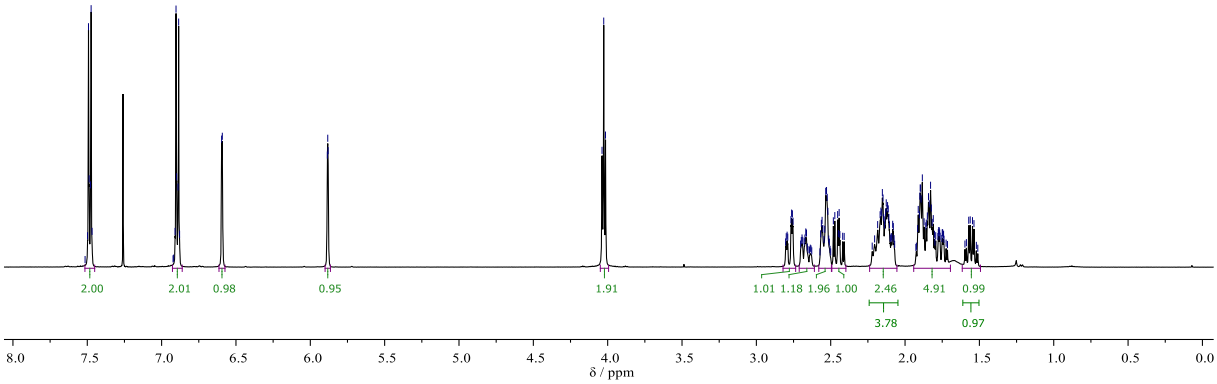
O-1-C(4)F(8)

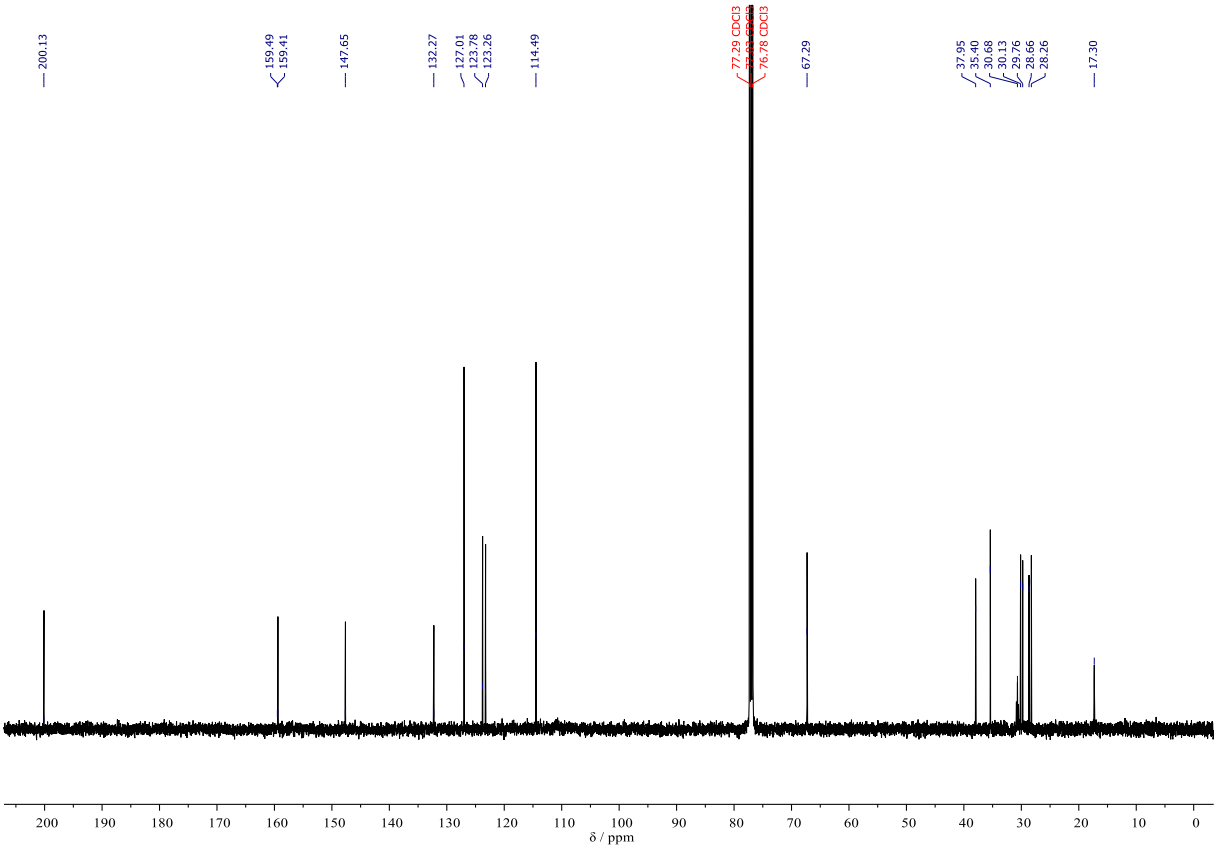

2.00
2.01
0.99
1.93
2.00
1.90
3.98
4.25
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm

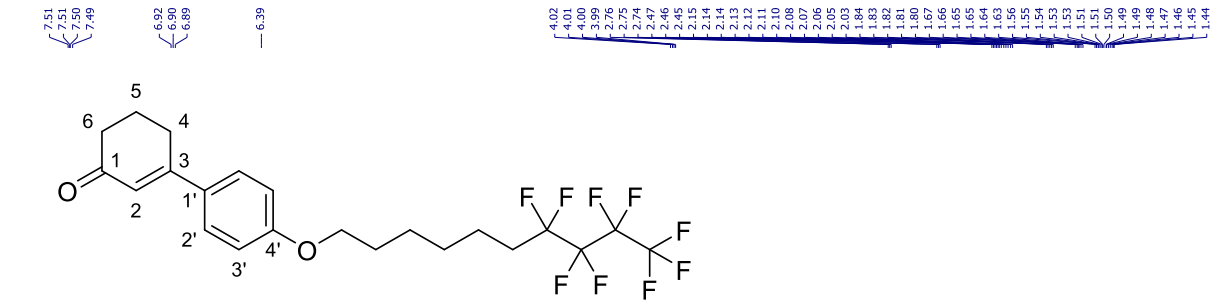

199.96
160.45
159.09
130.97
127.68
123.78
114.60
77.28 CDCl3
77.03 CDCl3
76.78 CDCl3
67.33
37.21
30.67
28.62
27.88
22.78
17.29
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ / ppm



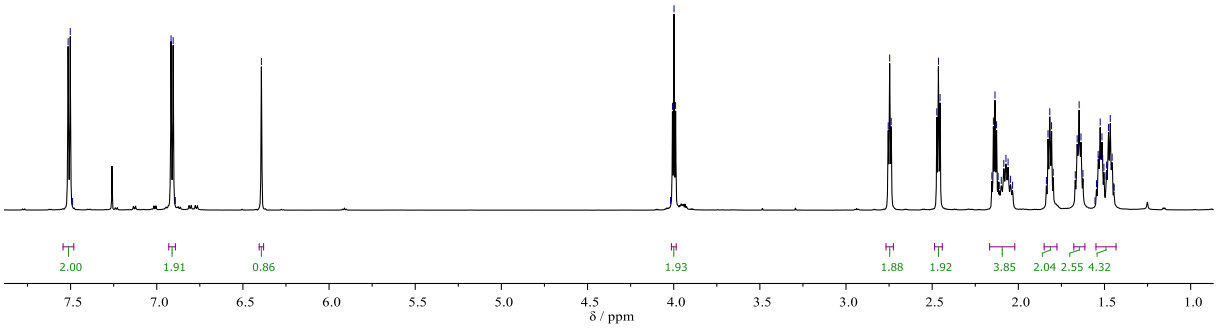
O-2-C(4)F(8)

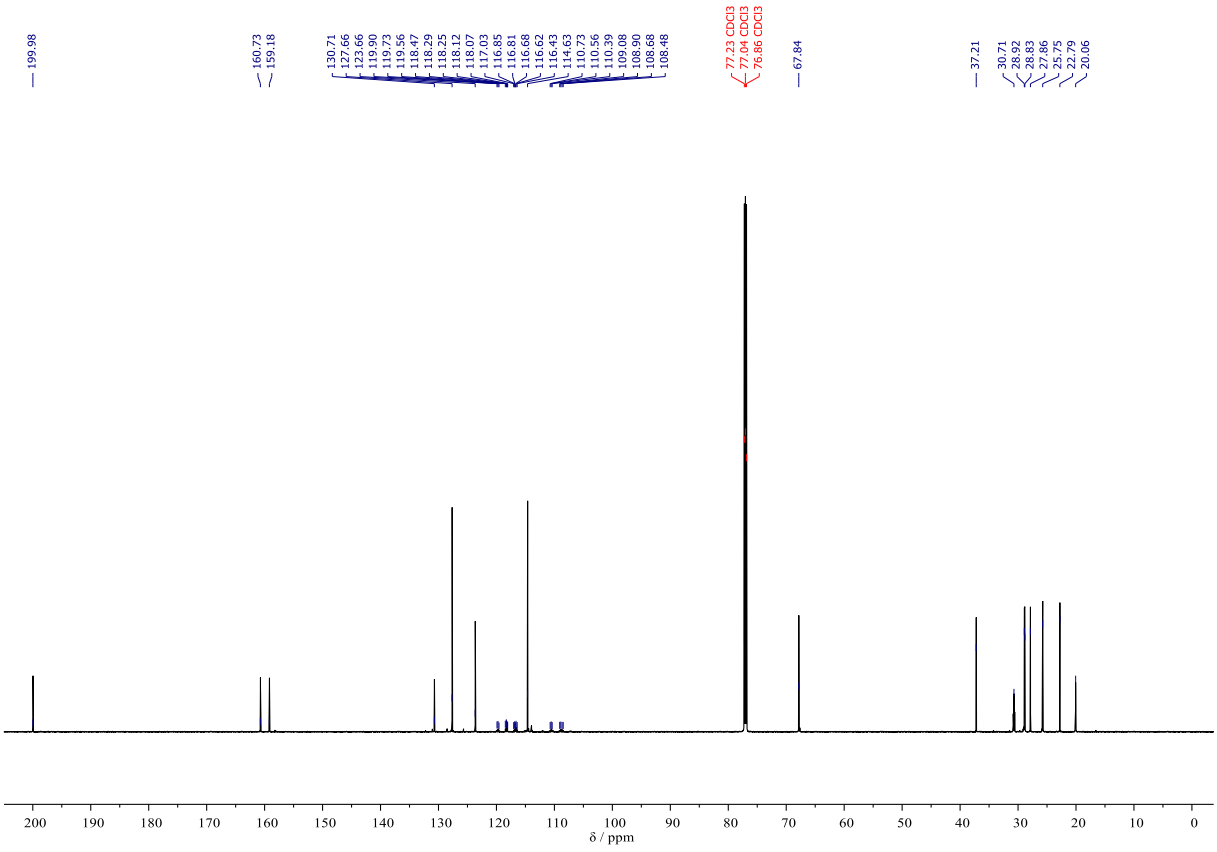

2.00
2.01
0.98
0.95
1.91
1.01 1.18 1.96 1.00
2.46
4.91
0.99
3.78
0.97
δ / ppm

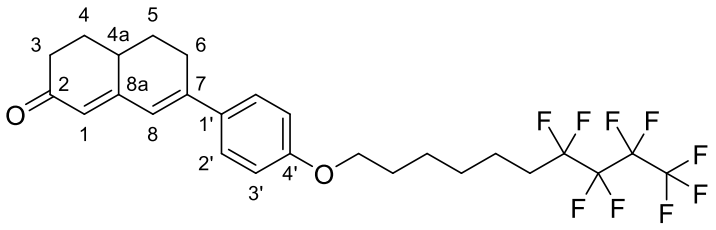

200.13
159.49
159.41
147.65
132.27
127.01
123.78
123.26
114.49
77.29 CDCl3
76.78 CDCl3
67.29
37.95
35.40
30.68
30.13
29.76
28.66
28.26
17.30
δ / ppm


7.51
7.51
7.50
7.49
6.92
6.90
6.89
6.39
4.02
4.01
4.00
3.99
2.76
2.75
2.74
2.47
2.46
2.45
2.15
2.14
2.14
2.13
2.12
2.11
2.10
2.08
2.07
2.06
2.05
2.03
1.84
1.83
1.82
1.81
1.80
1.67
1.66
1.65
1.65
1.64
1.63
1.56
1.55
1.54
1.53
1.53
1.51
1.51
1.50
1.49
1.49
1.48
1.47
1.46
1.45
1.44
O
F
F
F
F
F
F
F
F
F

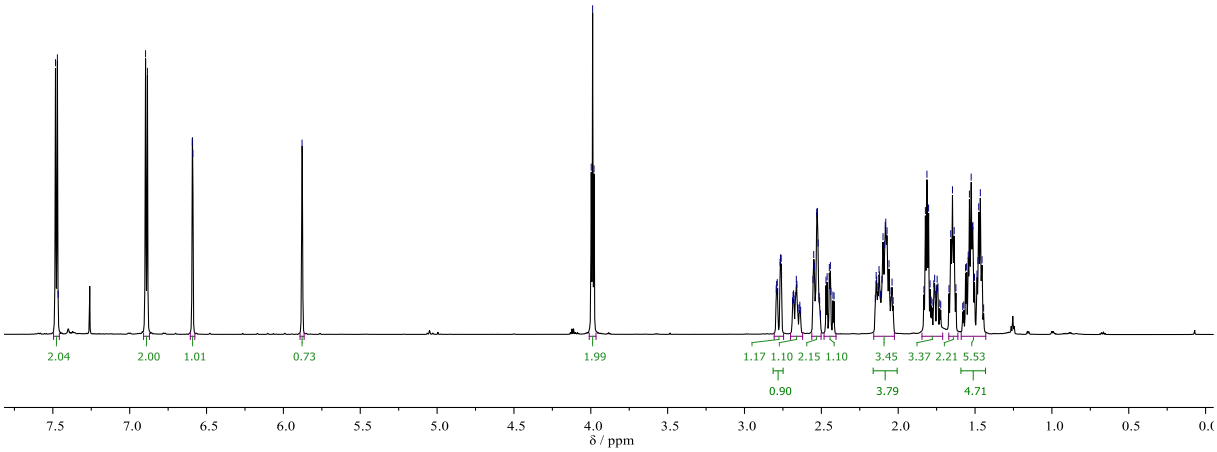
O-1-C(6)F(4)

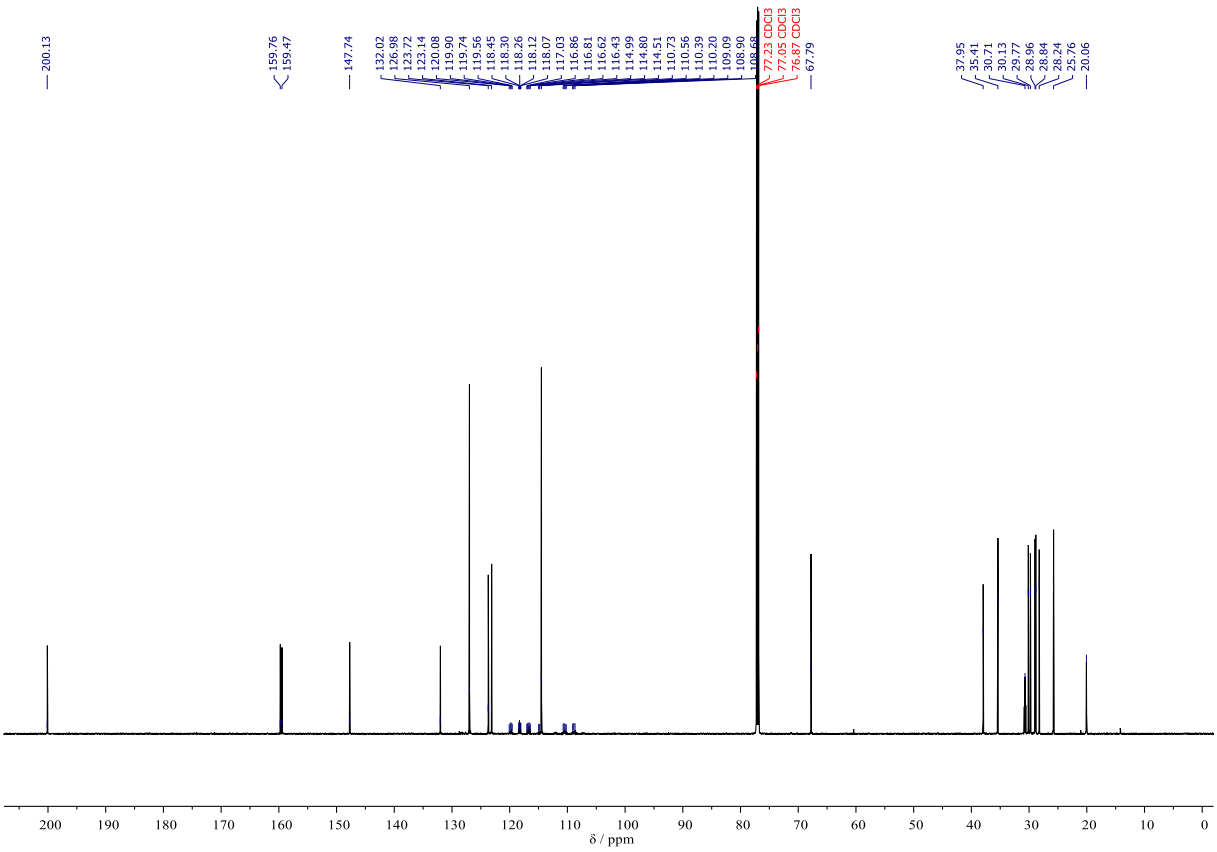

2.00
1.91
0.86
1.93
1.88
1.92
3.85
2.04
2.55
4.32
δ / ppm

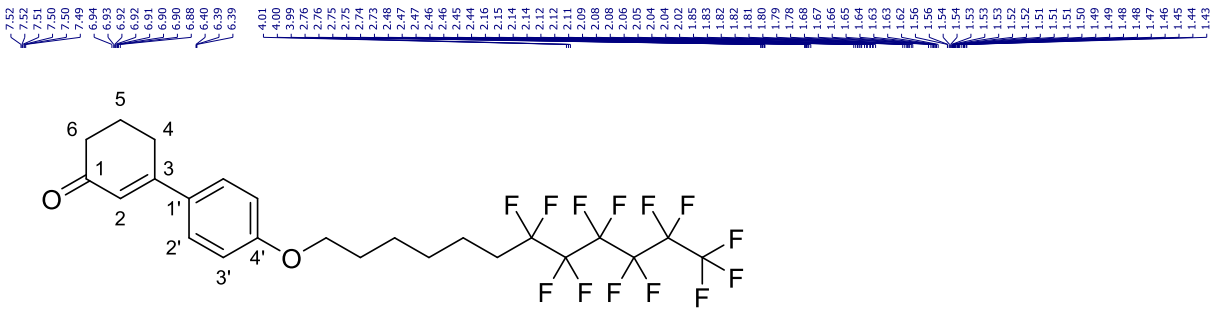

199.98
160.73
159.18
130.71
127.66
123.66
119.90
119.73
119.56
118.47
118.29
118.25
118.12
118.07
117.03
116.85
116.81
116.68
116.62
116.43
114.63
110.73
110.56
110.39
109.08
108.90
108.68
108.48
77.23 CDCl3
77.04 CDCl3
76.86 CDCl3
67.84
37.21
30.71
28.92
28.83
27.86
25.75
22.79
20.06
δ / ppm


4
5
4a
3
6
2
8a
7
O
1
8
1'
2'
4'
3'
O
F F F F
F
F F F
F

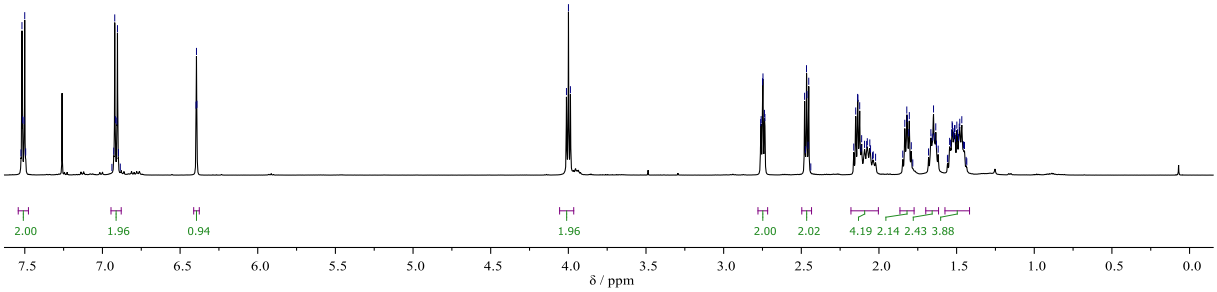
O-2-C(6)F(4)

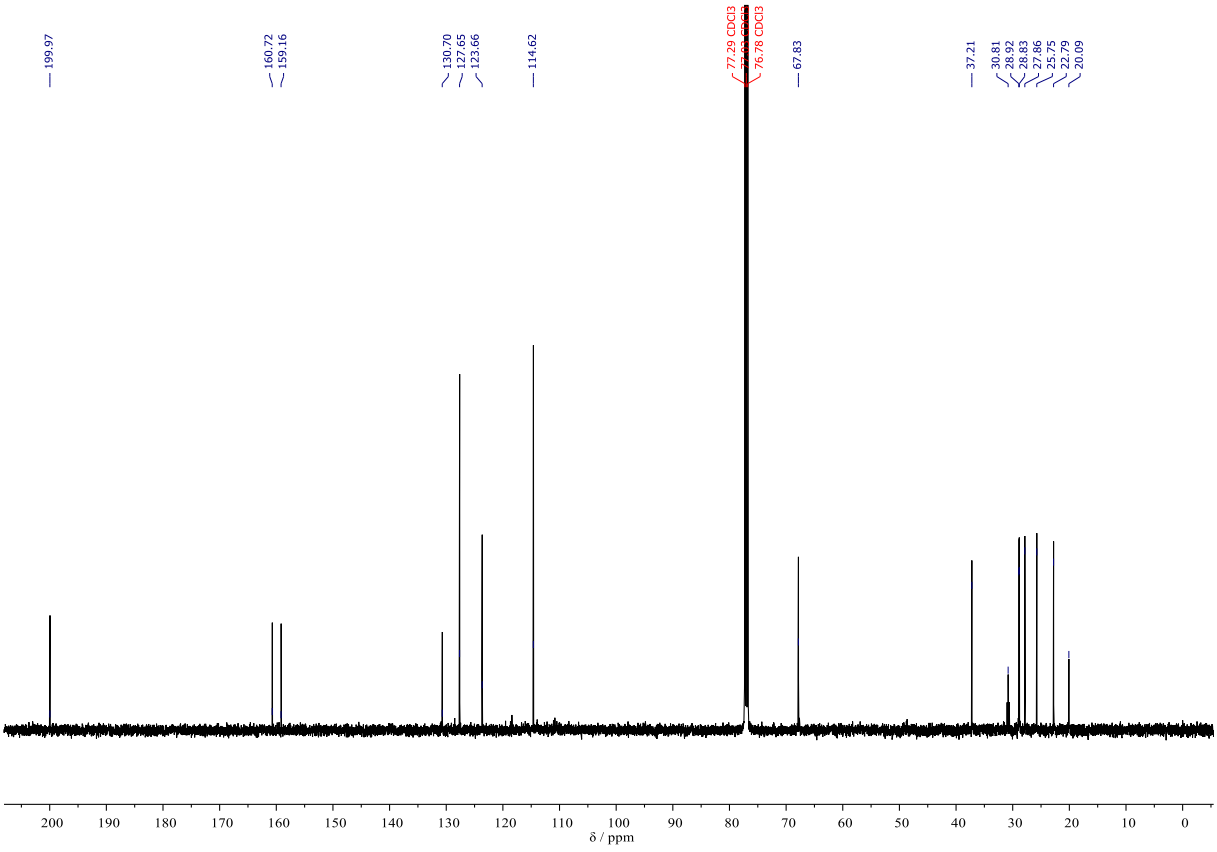

2.04
2.00
1.01
0.73
1.99
1.17 1.10 2.15 1.10
0.90
3.45 3.37 2.21 5.53
3.79
4.71
δ / ppm

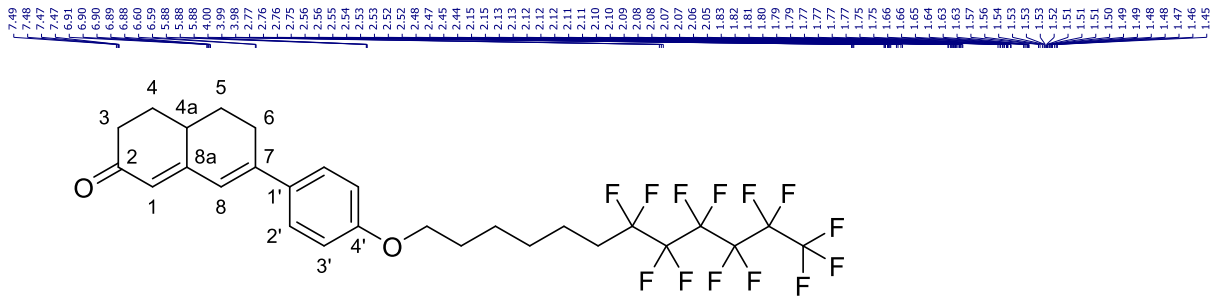

200.13
159.76
159.47
147.74
132.02
126.98
123.72
123.14
120.08
119.90
119.74
119.56
118.45
118.30
118.26
118.12
118.07
117.03
116.86
116.81
116.62
116.43
114.99
114.80
114.51
110.73
110.56
110.39
110.20
109.09
108.90
77.23 CDCl3
77.05 CDCl3
76.87 CDCl3
67.79
37.95
35.41
30.71
30.13
29.77
28.96
28.84
28.24
25.76
20.06
δ / ppm



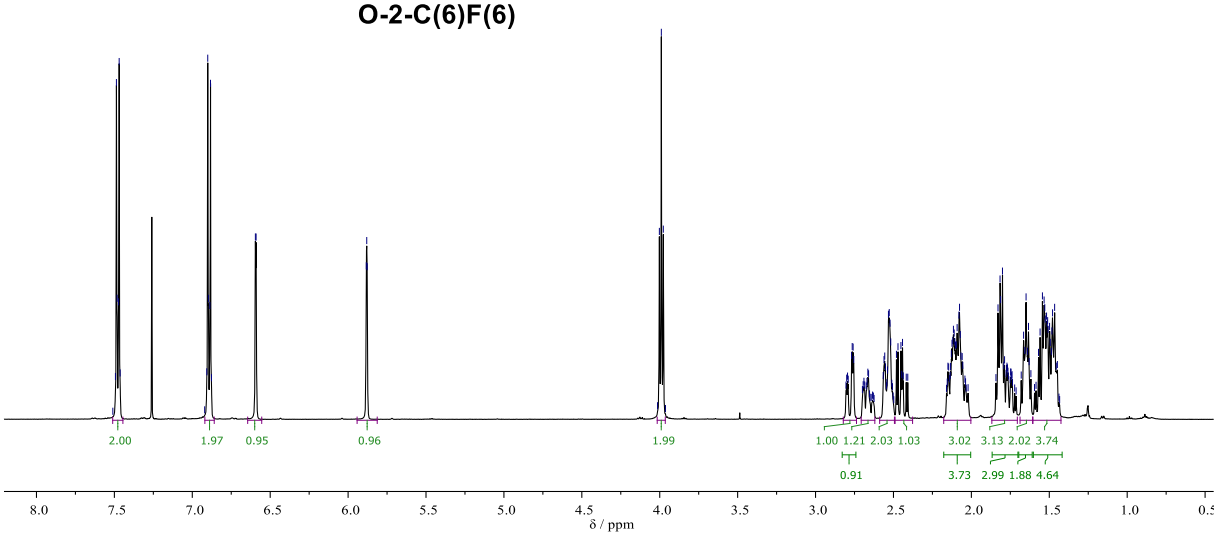
O-1-C(6)F(6)

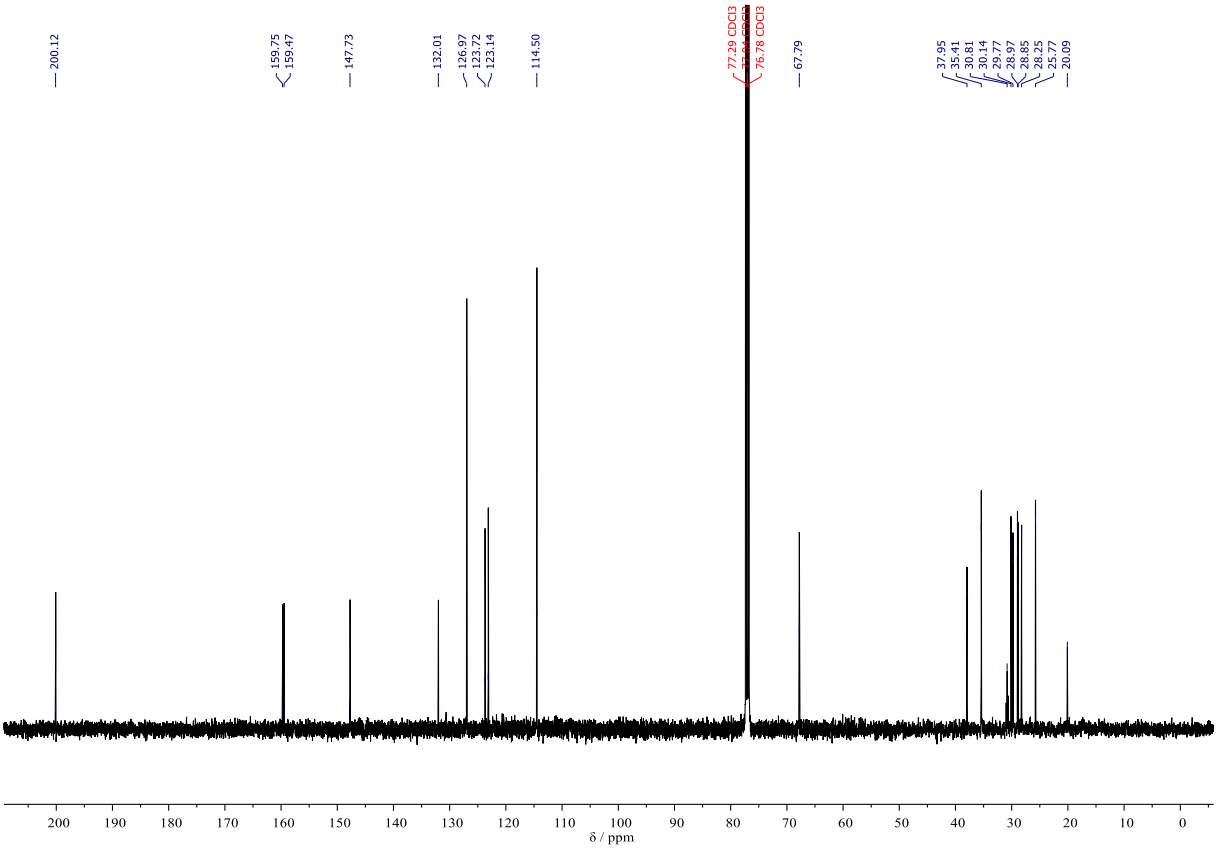

2.00
1.96
0.94
1.96
2.00
2.02
4.19 2.14 2.43 3.88
δ / ppm

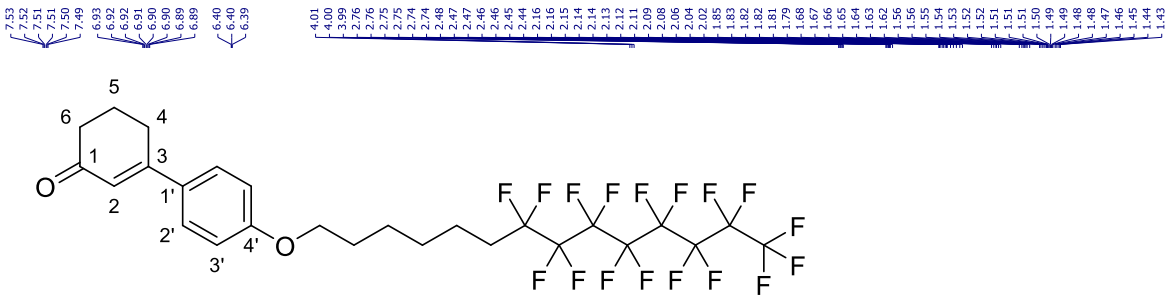

199.97
160.72
159.16
130.70
127.65
123.66
114.62
77.29 CDCl3
76.78 CDCl3
67.83
37.21
30.81
28.92
28.83
27.86
25.75
22.79
20.09
δ / ppm


4
5
4a
3
6
2
8a
7
O
1
8
1'
2'
4'
3'
O
F F F F F F
F
F
F F F F F

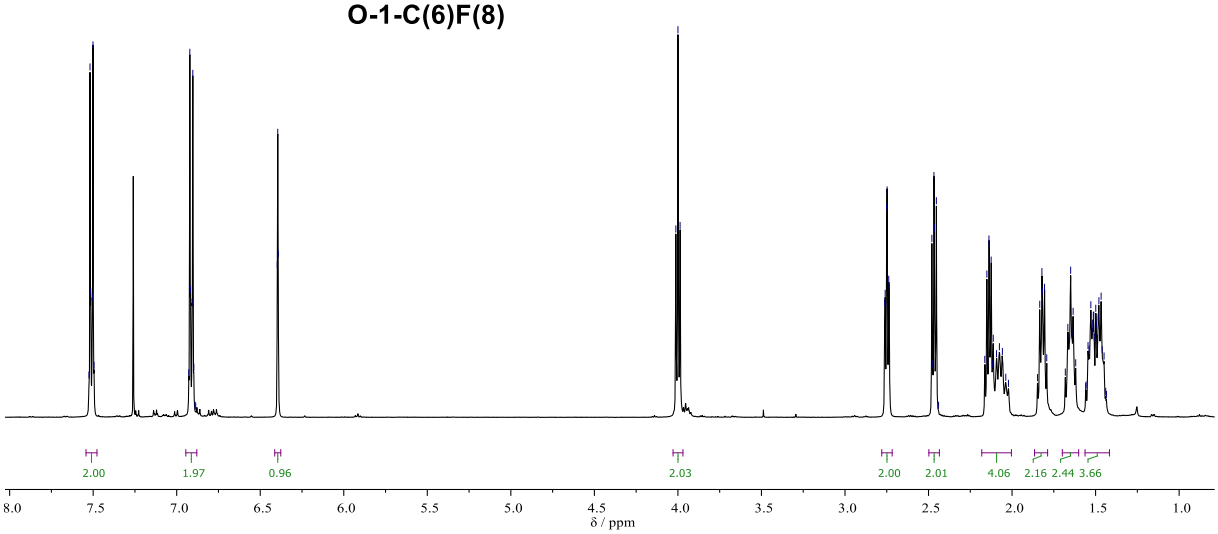
O-2-C(6)F(6)

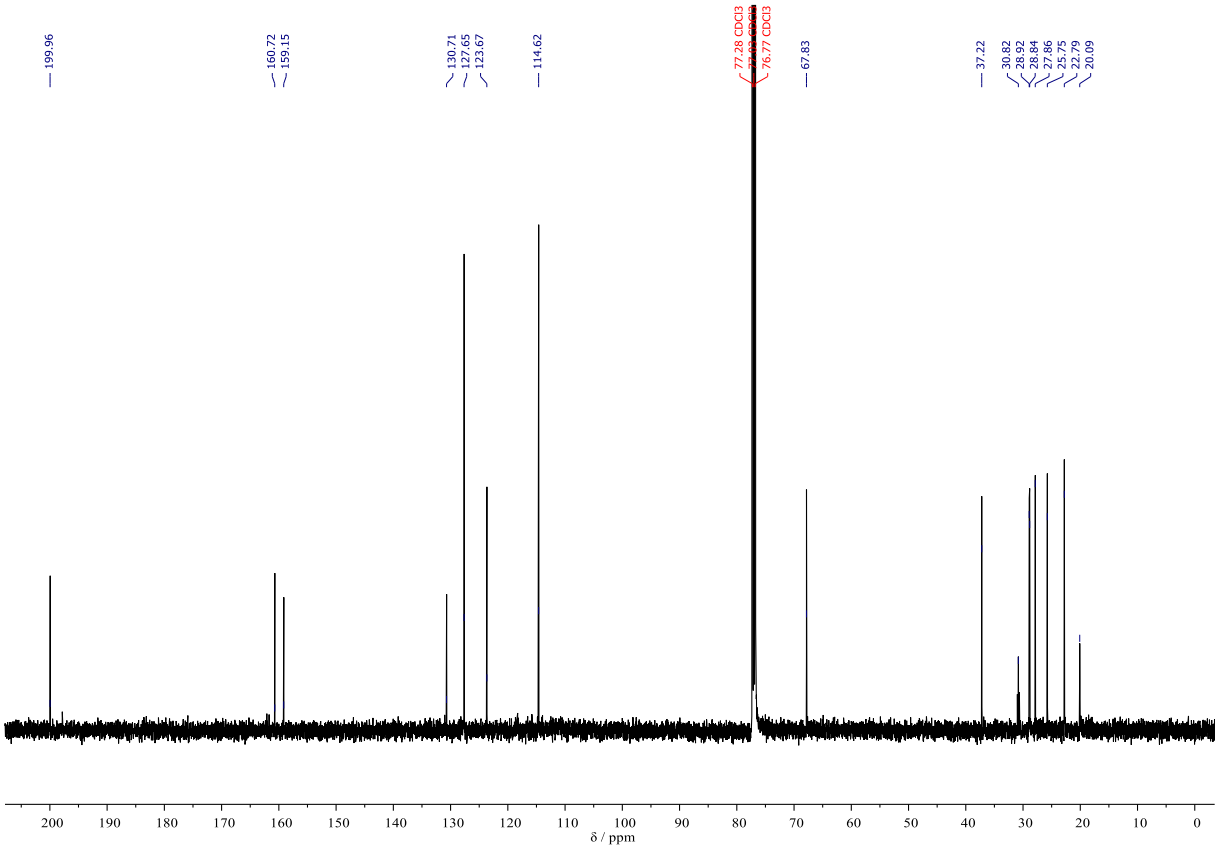

2.00
1.97
0.95
0.96
1.99
1.00 1.21 2.03 1.03
0.91
3.02 3.13 2.02 3.74
3.73 2.99 1.88 4.64
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
δ / ppm

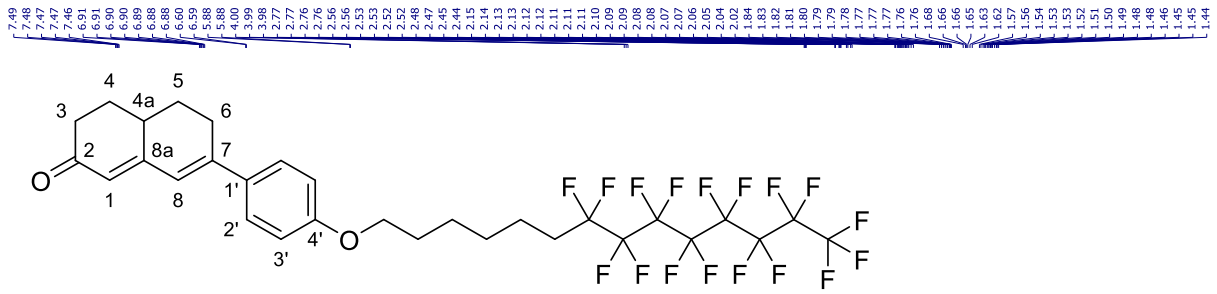

200.12
159.75
159.47
147.73
132.01
126.97
123.72
123.14
114.50
77.29 CDCl3
76.78 CDCl3
67.79
37.95
35.41
30.81
30.14
29.77
28.97
28.85
28.25
25.77
20.09
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ / ppm


7.53 7.52 7.51 7.51 7.50 7.49 6.93 6.92 6.92 6.91 6.90 6.90 6.89 6.89 6.40 6.40 6.39
4.01 4.00 3.99 2.76 2.75 2.75 2.74 2.74 2.48 2.47 2.47 2.46 2.46 2.45 2.44 2.16 2.16 2.15 2.14 2.14 2.13 2.12 2.11 2.09 2.08 2.06 2.04 2.02 1.85 1.83 1.82 1.81 1.79 1.68 1.67 1.66 1.65 1.64 1.63 1.62 1.56 1.56 1.55 1.54 1.53 1.52 1.52 1.51 1.51 1.51 1.50 1.49 1.49 1.48 1.48 1.47 1.46 1.45 1.44 1.43
O
1
2
3
4
5
6
1'
2'
3'
4'
O
F F F F F F F F F F F F F F F F F

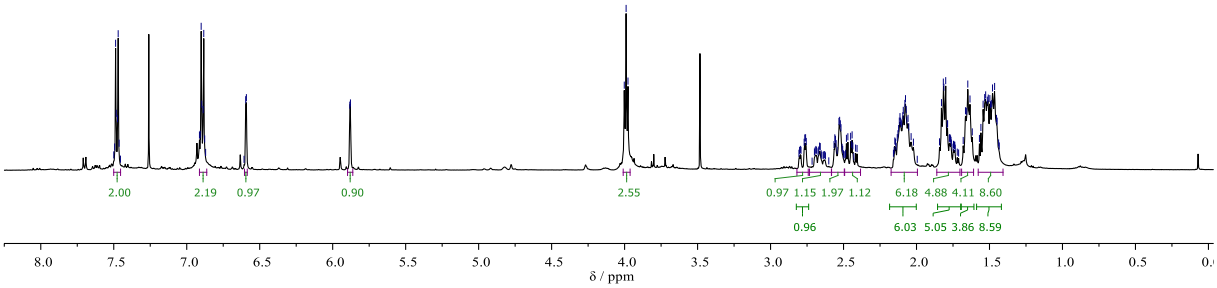
O-1-C(6)F(8)

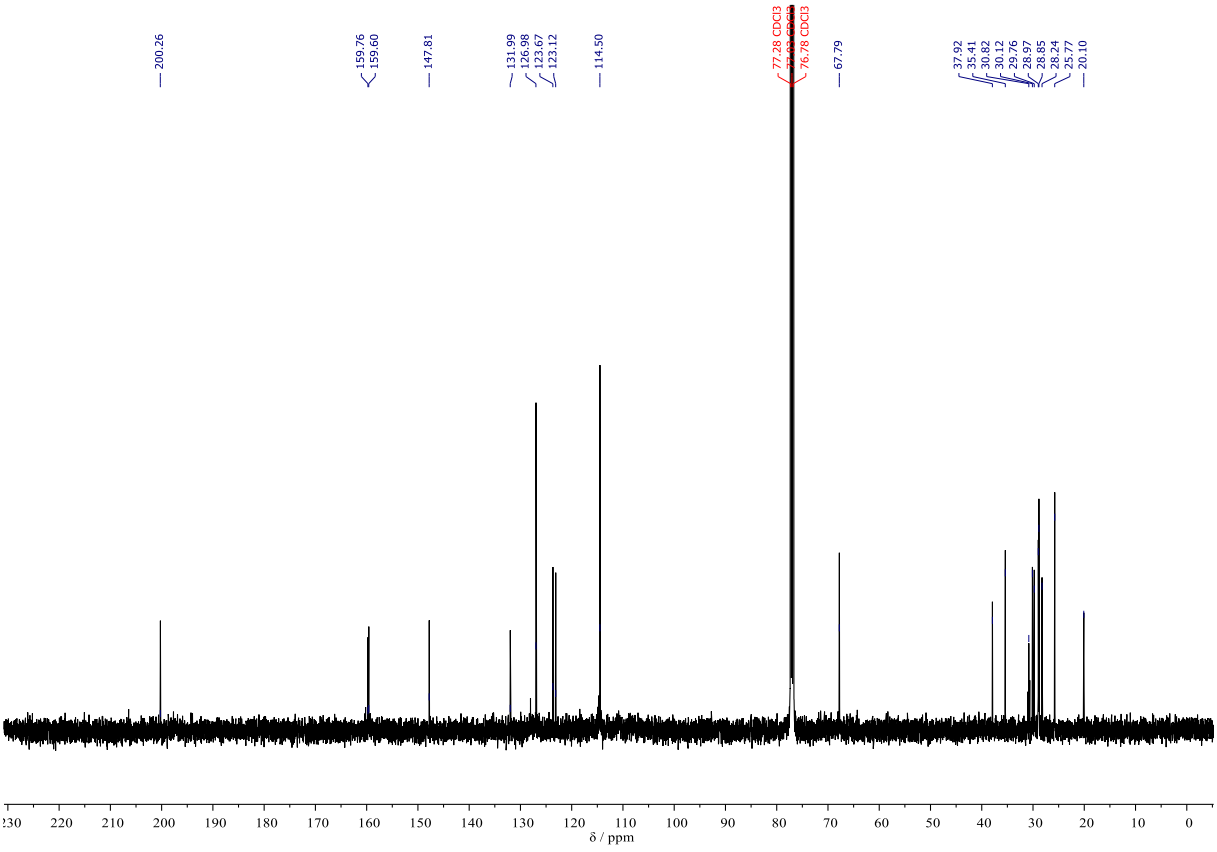

2.00 1.97 0.96 2.03 2.00 2.01 4.06 2.16 2.44 3.66
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
δ / ppm

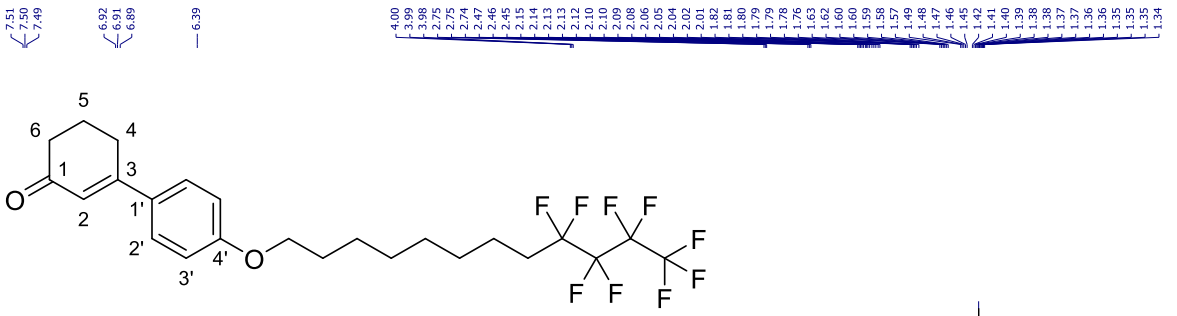

199.96
160.72 159.15
130.71 127.65 123.67
114.62
77.28 CDCl3 76.77 CDCl3
67.83
37.22
30.82 28.92 28.84 27.86 25.75 22.79 20.09
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ / ppm



O-2-C(6)F(8)

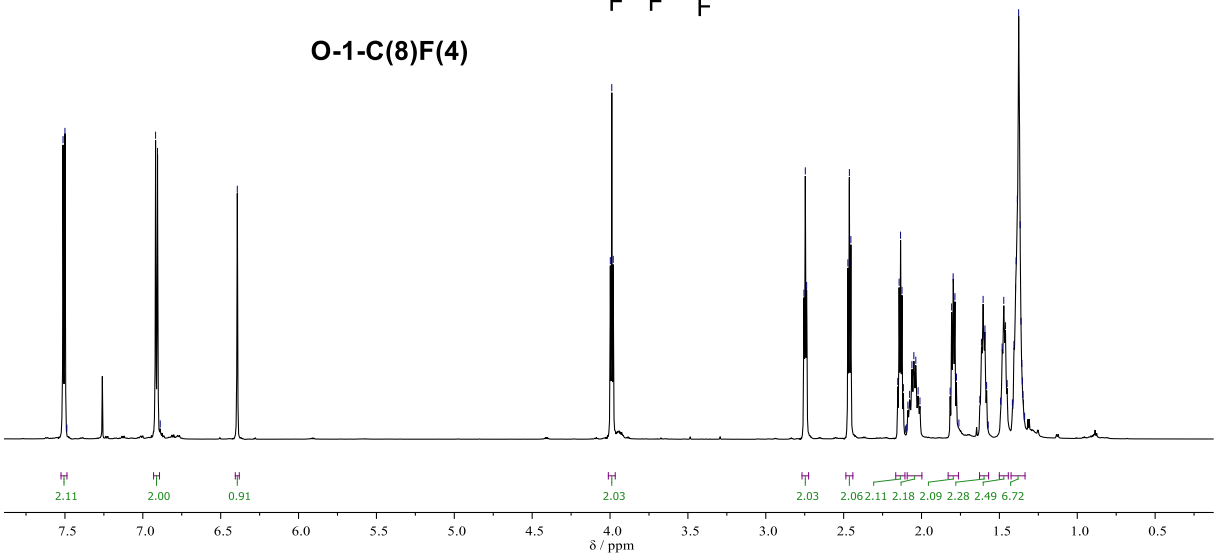

2.00
2.19
0.97
0.90
2.55
0.97 1.15 1.97 1.12
6.18 4.88 4.11 8.60
0.96
6.03 5.05 3.86 8.59
δ / ppm

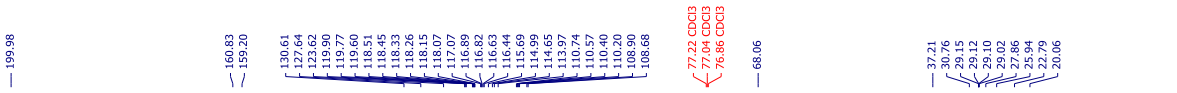

200.26
159.76
159.60
147.81
131.99
126.98
123.67
123.12
114.50
77.28 CDCl3
76.78 CDCl3
67.79
37.92
35.41
30.82
30.12
29.76
28.97
28.85
28.24
25.77
20.10
δ / ppm

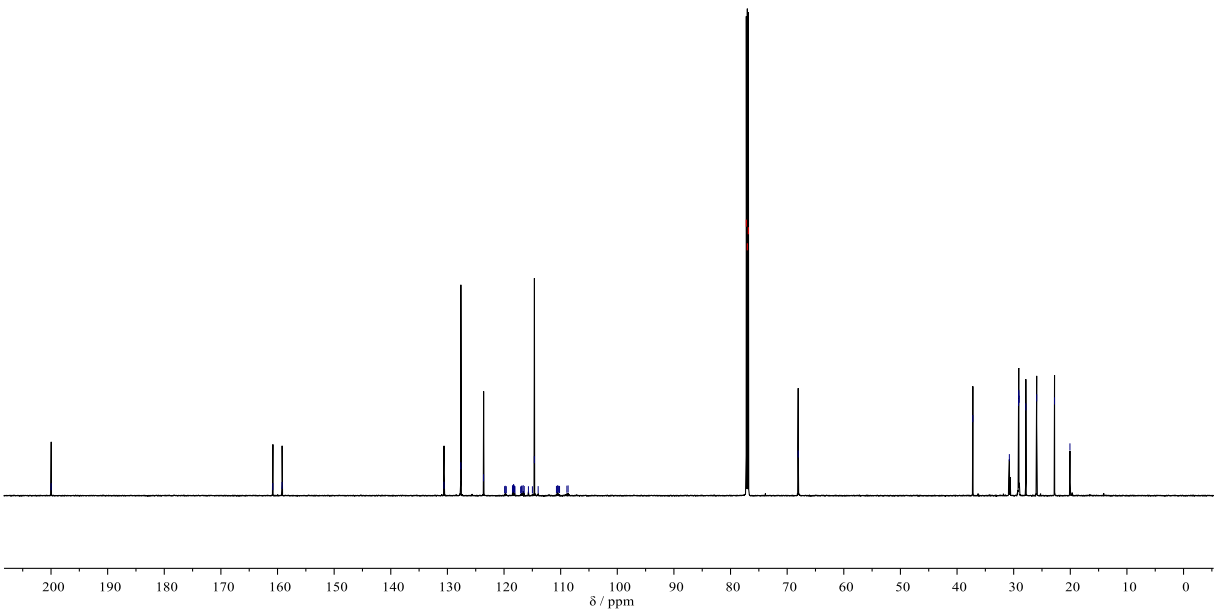

7.51
7.50
7.49
6.92
6.91
6.89
6.39
4.00
3.99
3.98
2.75
2.74
2.47
2.46
2.45
2.15
2.14
2.13
2.12
2.10
2.09
2.08
2.06
2.05
2.04
2.02
2.01
1.82
1.81
1.80
1.79
1.78
1.76
1.63
1.62
1.60
1.59
1.58
1.57
1.49
1.48
1.47
1.46
1.45
1.42
1.41
1.40
1.39
1.38
1.37
1.36
1.35
1.35
1.34

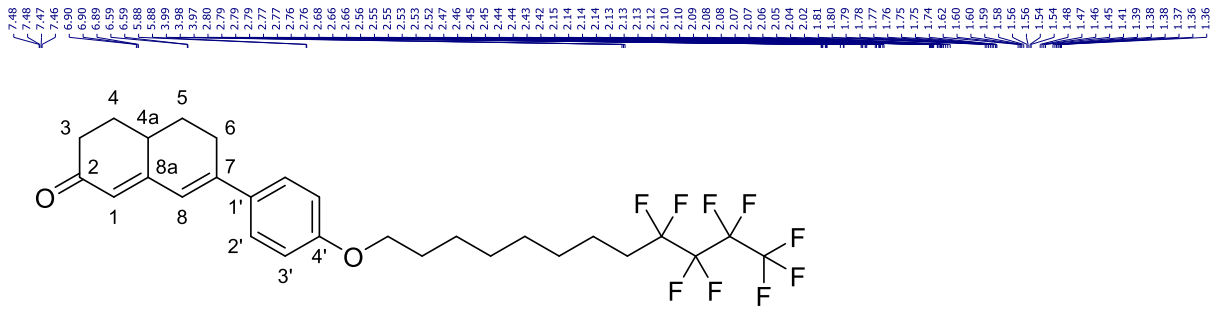
5
6
4
1
3
O
2
1'
2'
4'
O
3'
F
F
F
F
F
F
F
F
F

O-1-C(8)F(4)

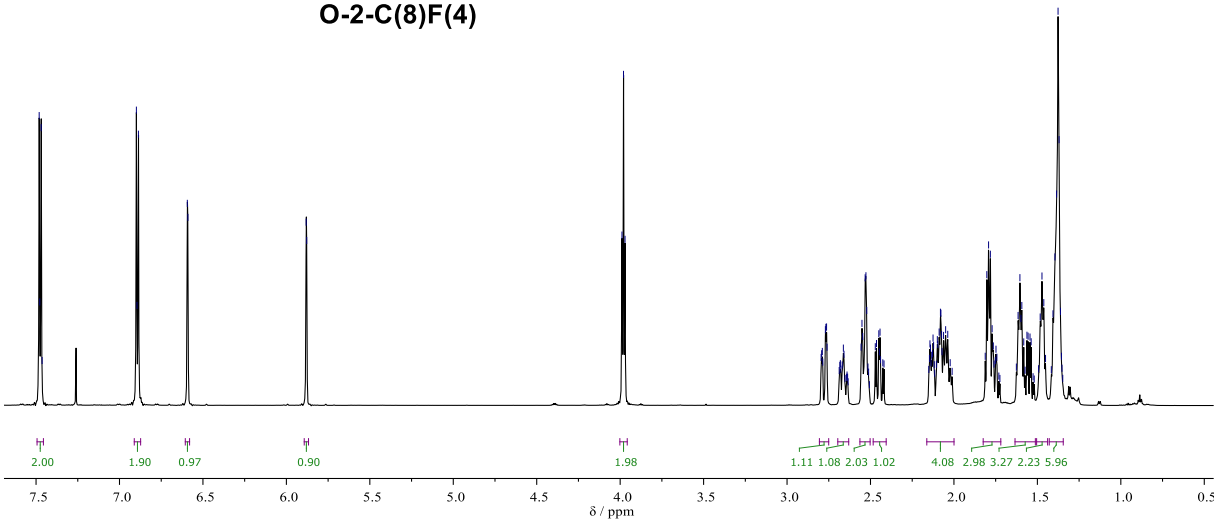

2.11
2.00
0.91
2.03
2.03
2.06
2.11
2.18
2.09
2.28
2.49
6.72
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
δ / ppm

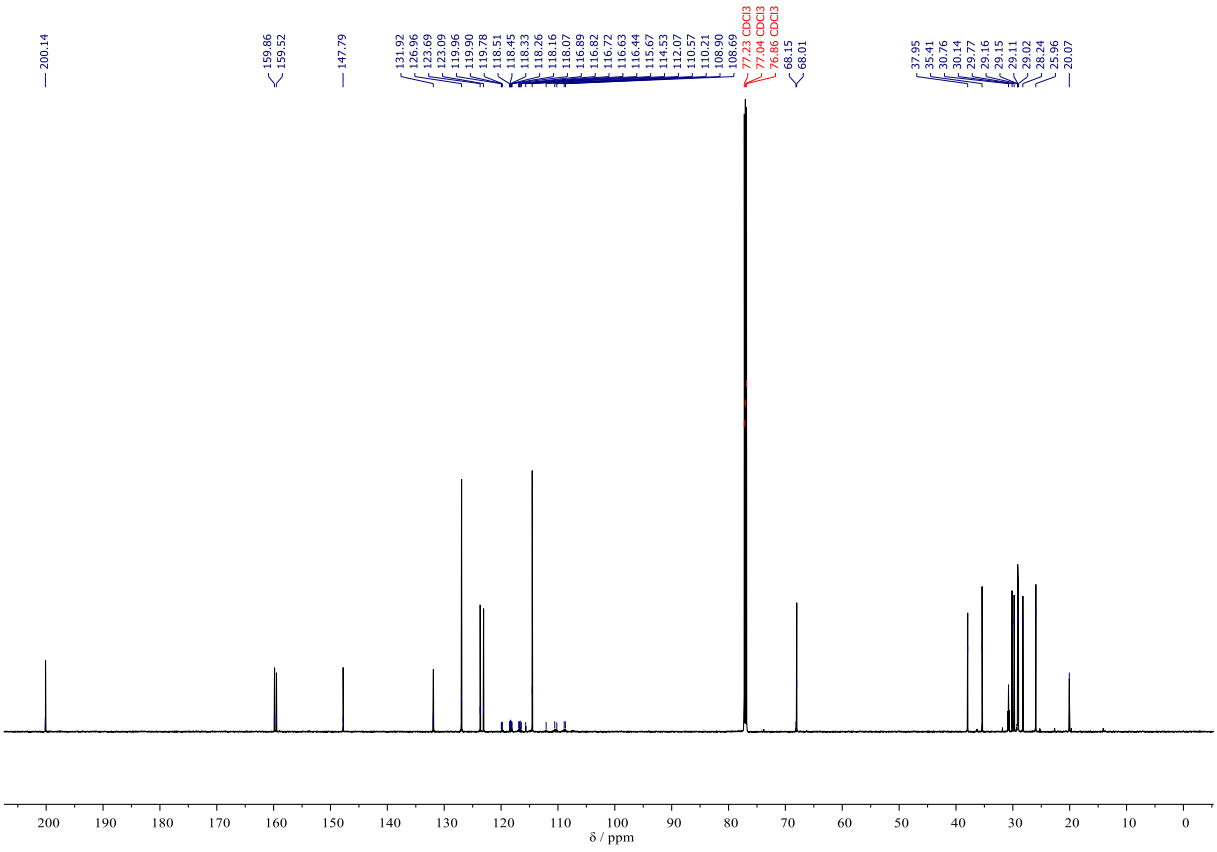

199.98
160.83
159.20
130.61
127.64
123.62
119.90
119.77
119.60
118.51
118.45
118.33
118.26
118.15
118.07
117.07
116.89
116.82
116.63
116.44
115.69
114.99
114.65
113.97
110.74
110.57
110.40
110.20
108.90
108.68
77.22 CDCl3
77.04 CDCl3
76.86 CDCl3
68.06
37.21
30.76
29.15
29.12
29.10
29.02
27.86
25.94
22.79
20.06

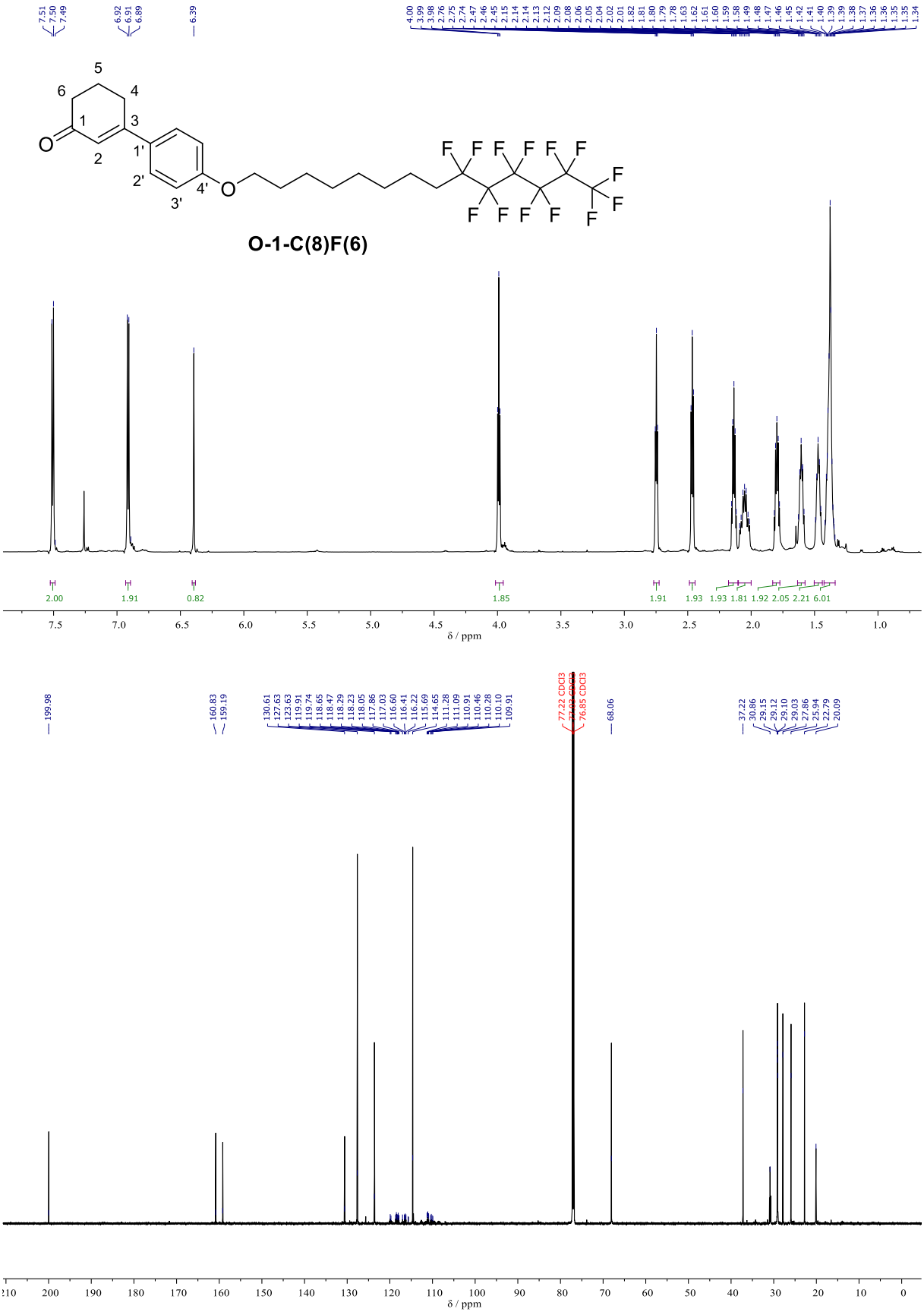

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ / ppm

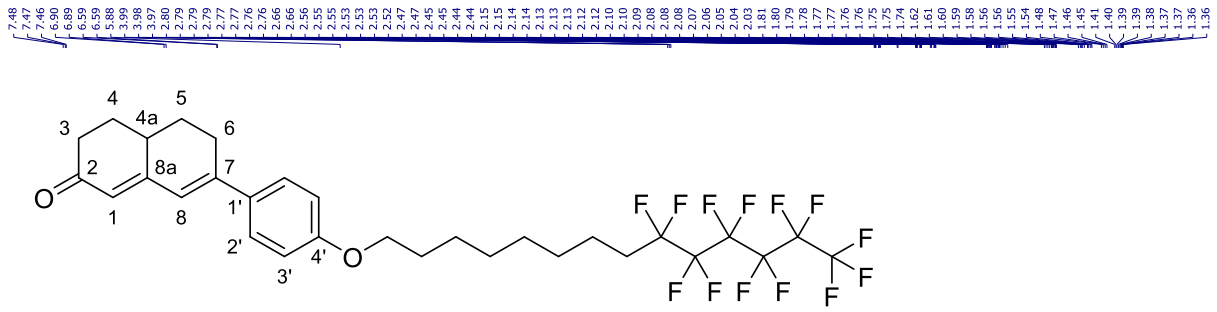


O-2-C(8)F(4)

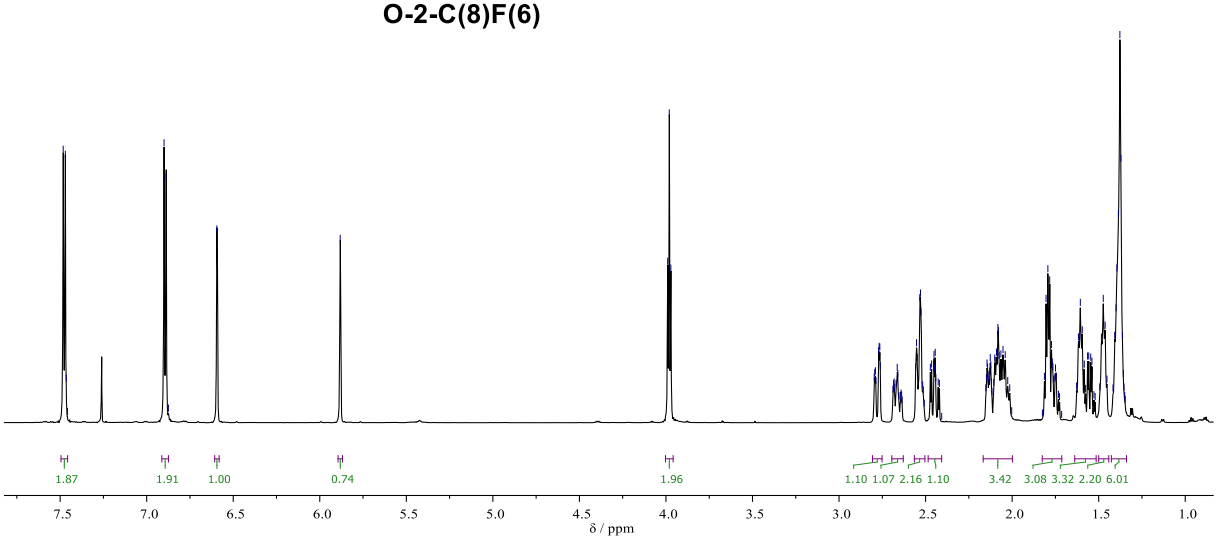

2.00
1.90
0.97
0.90
1.98
1.11 1.08 2.03 1.02
4.08 2.98 3.27 2.23 5.96
δ / ppm

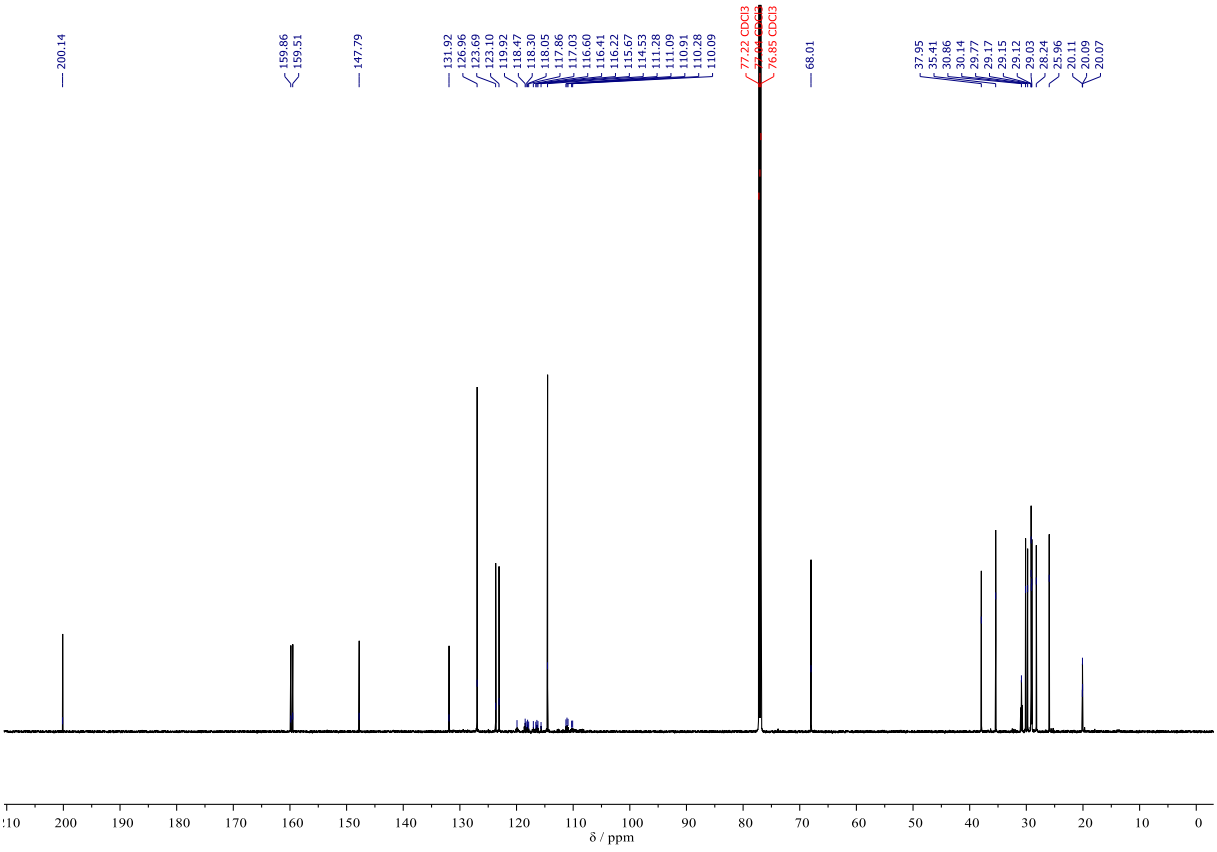

δ / ppm

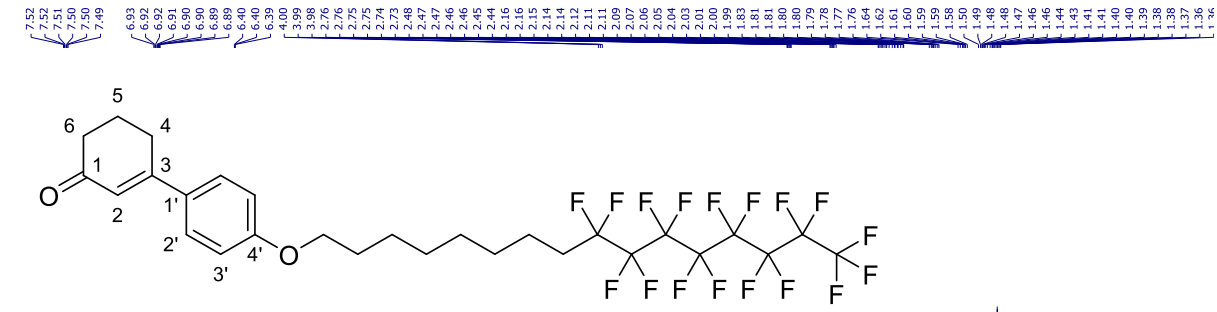

7.51
7.50
7.49
6.92
6.91
6.89
6.39
4.00
3.99
3.98
2.76
2.75
2.74
2.47
2.46
2.45
2.15
2.14
2.14
2.13
2.12
2.09
2.08
2.06
2.05
2.04
2.02
2.01
1.82
1.81
1.80
1.79
1.78
1.63
1.62
1.61
1.60
1.59
1.58
1.49
1.48
1.47
1.46
1.45
1.42
1.41
1.40
1.39
1.39
1.38
1.37
1.36
1.36
1.35
1.35
1.34
O-1-C(8)F(6)
2.00
1.91
0.82
1.85
1.91
1.93
1.93 1.81 1.92 2.05 2.21 6.01
δ / ppm
199.98
160.83
159.19
130.61
127.63
123.63
119.91
119.74
118.65
118.47
118.29
118.23
118.05
117.86
117.03
116.60
116.41
116.22
115.69
114.65
111.28
111.09
110.91
110.46
110.28
110.10
109.91
77.22 CDCl3
76.85 CDCl3
68.06
37.22
30.86
29.15
29.12
29.10
29.03
27.86
25.94
22.79
20.09
δ / ppm

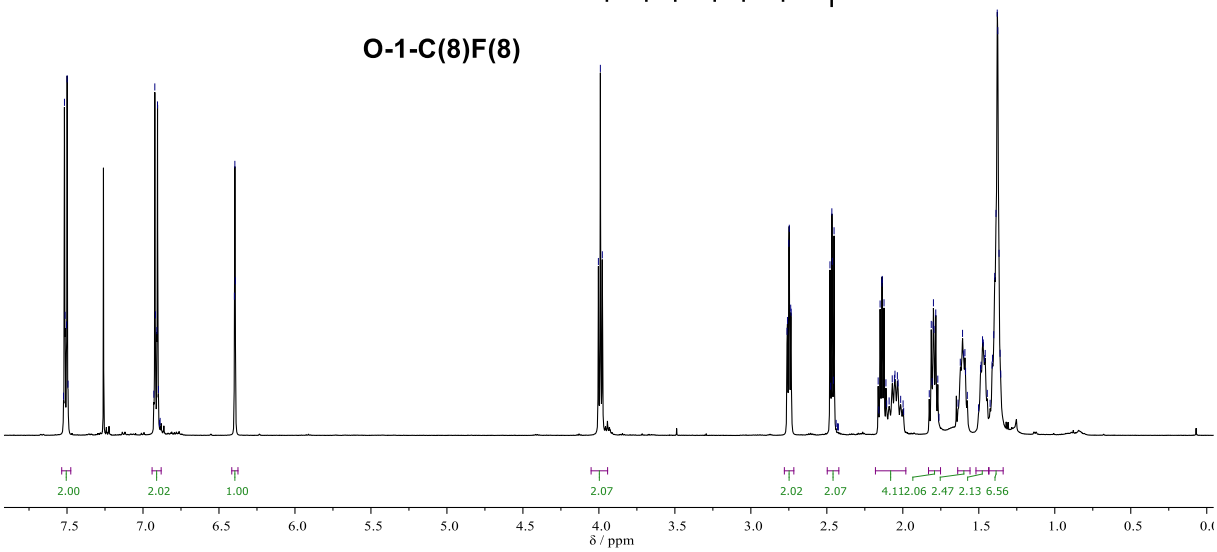


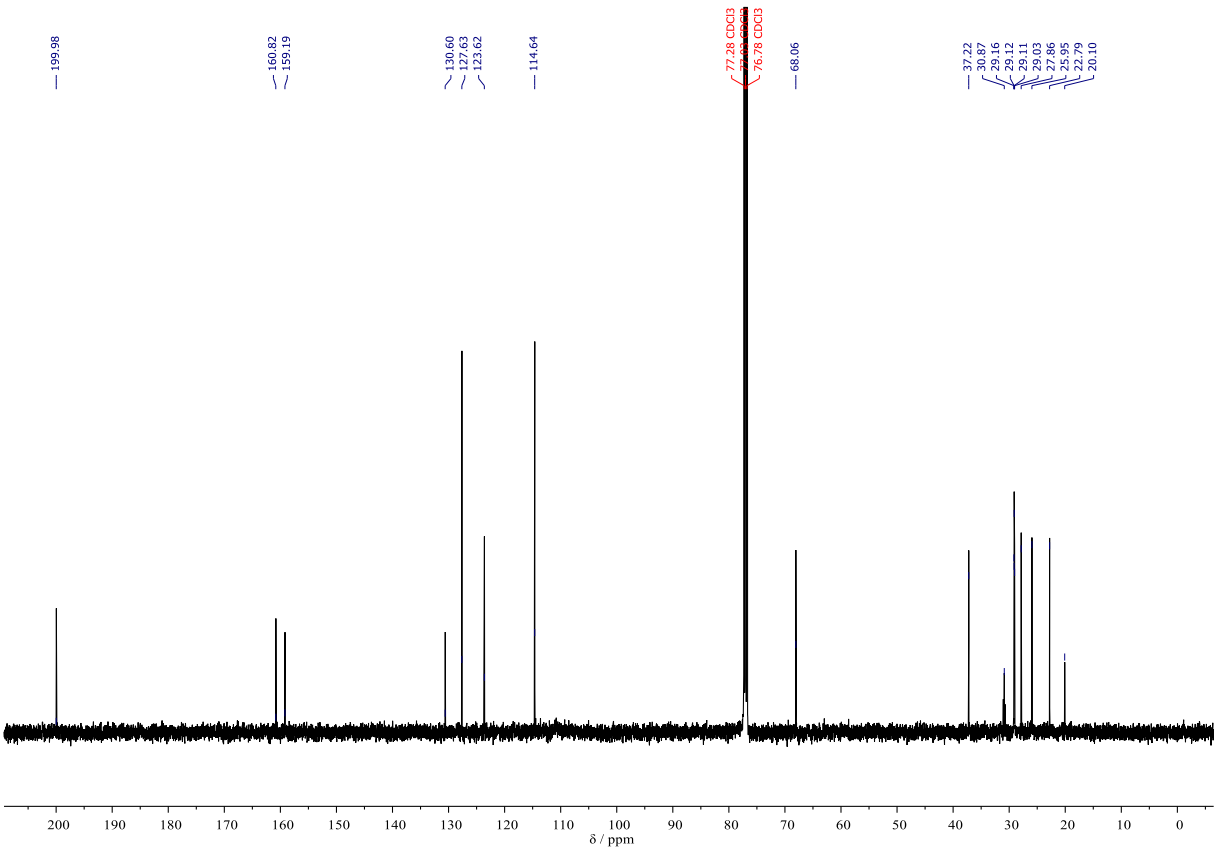
O-2-C(8)F(6)

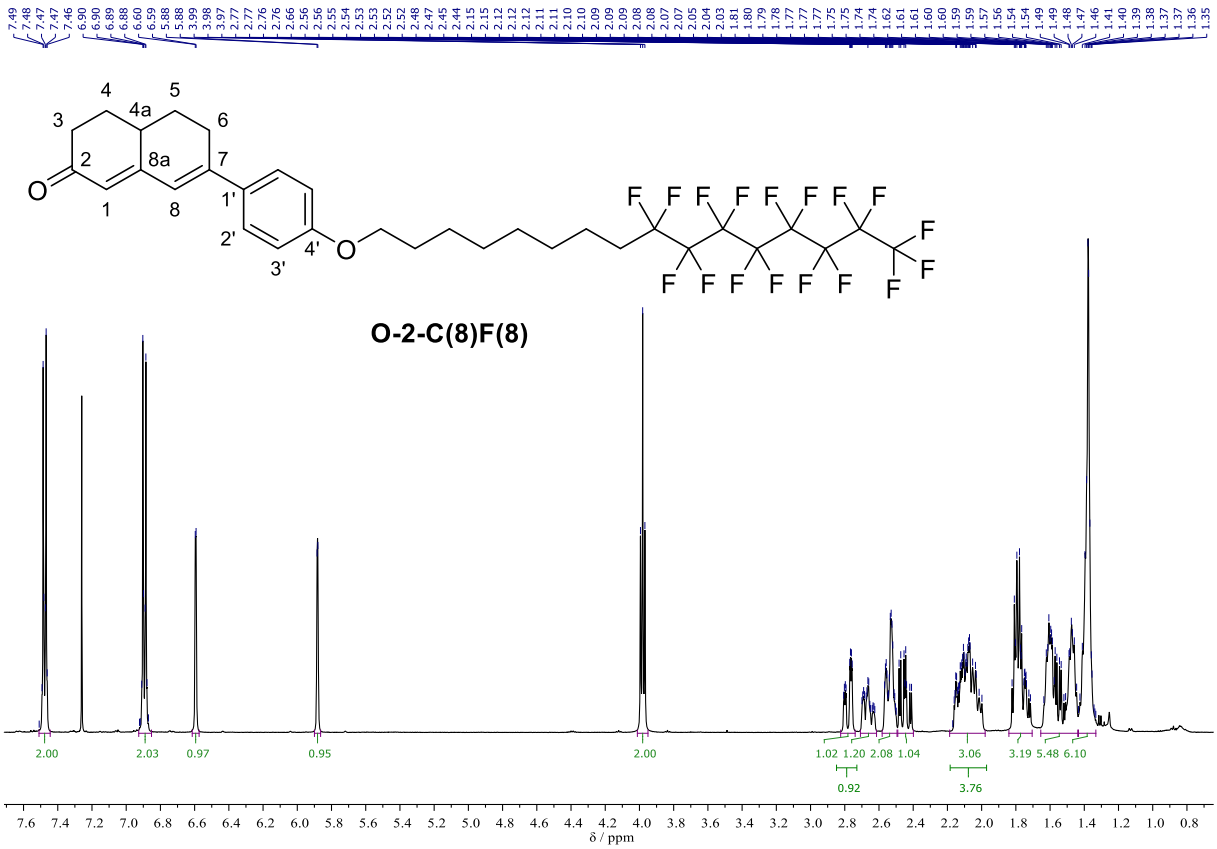

1.87
1.91
1.00
0.74
1.96
1.10 1.07 2.16 1.10
3.42
3.08 3.32 2.20 6.01
δ / ppm

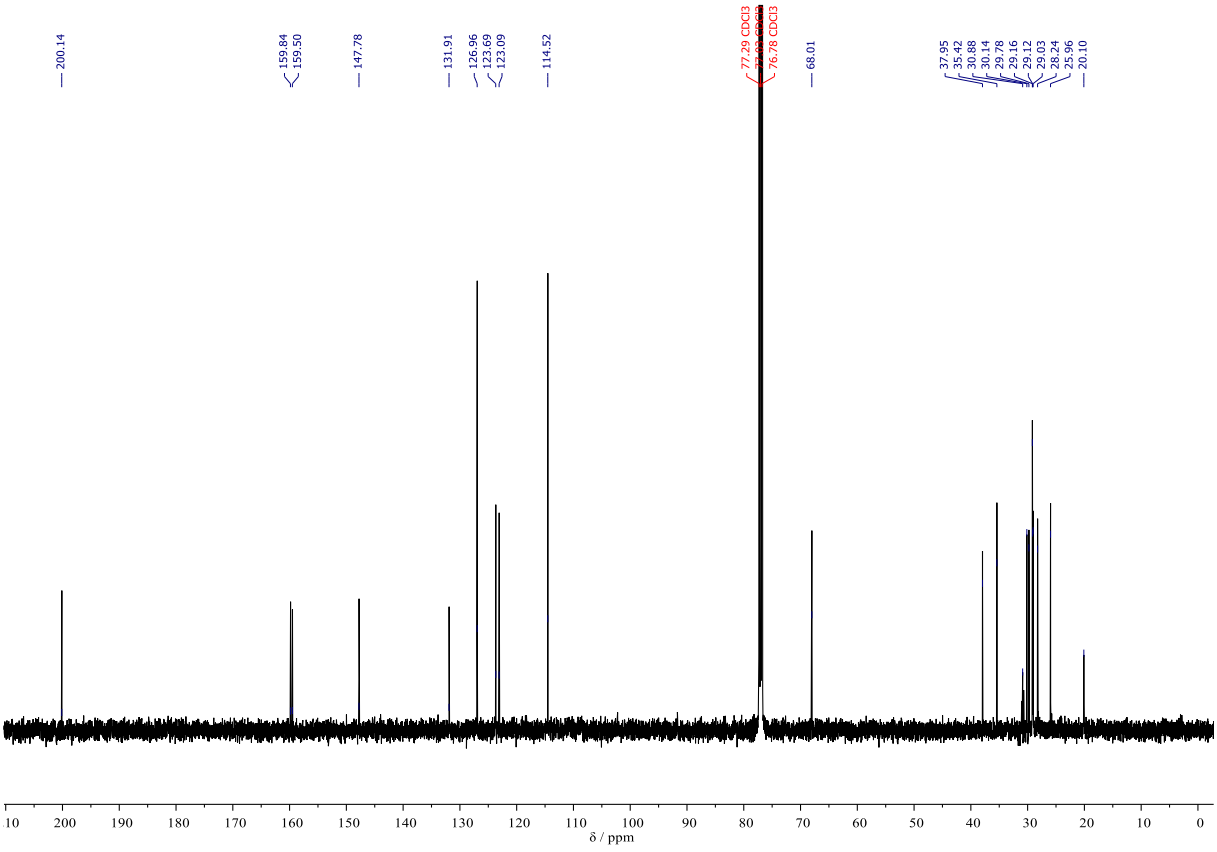

200.14
159.86
159.51
147.79
131.92
126.96
123.69
123.10
119.92
118.47
118.30
118.05
117.86
117.03
116.60
116.41
116.22
115.67
114.53
111.28
111.09
110.91
110.28
110.09
77.22 CDCl3
76.85 CDCl3
68.01
37.95
35.41
30.86
30.14
29.77
29.17
29.15
29.12
29.03
28.24
25.96
20.11
20.09
20.07
δ / ppm

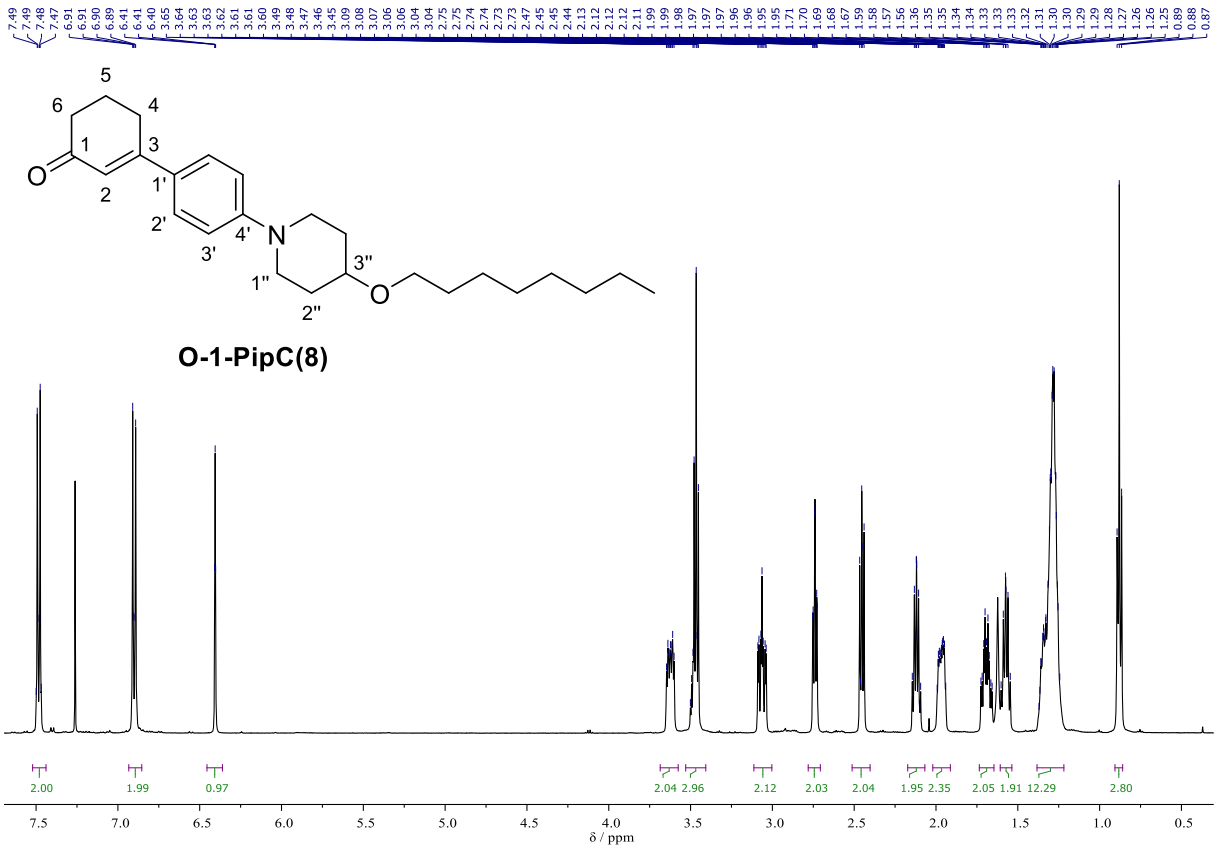


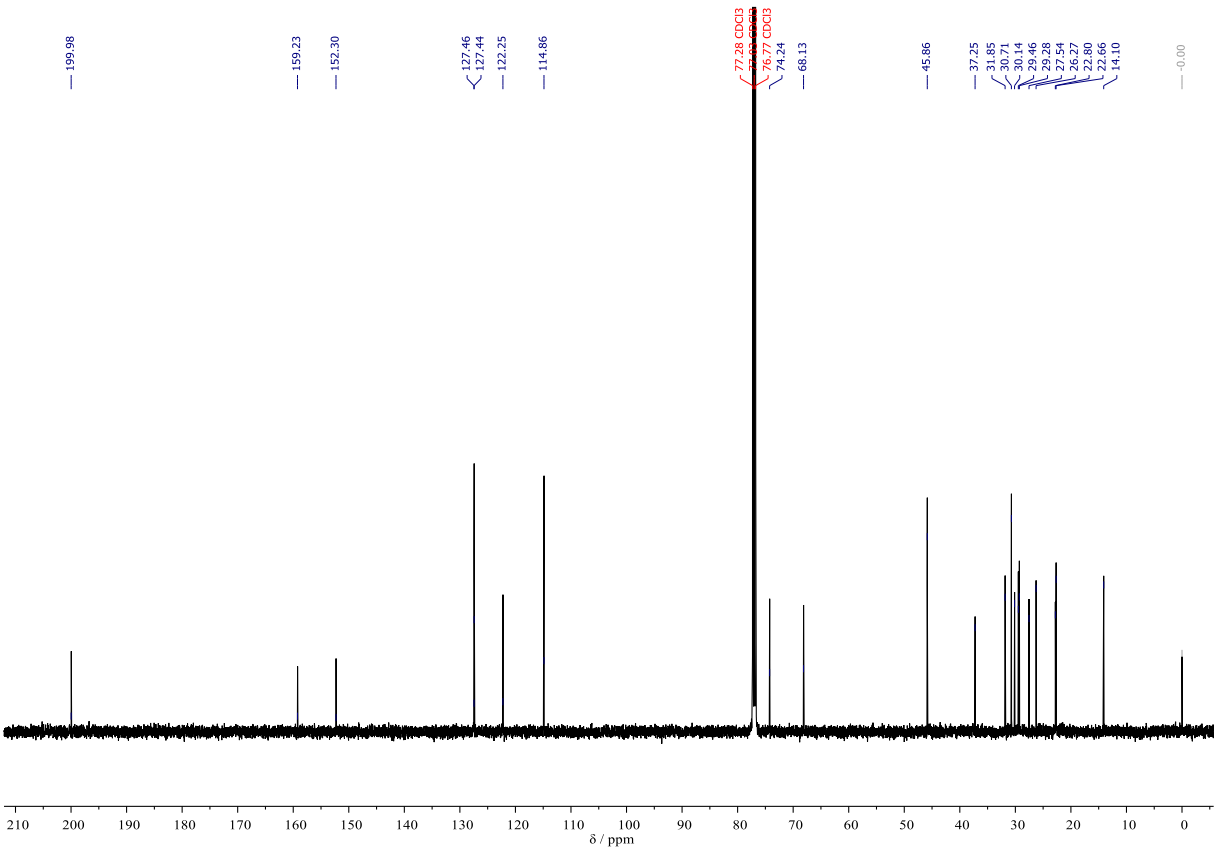

O-1-C(8)F(8)
2.00
2.02
1.00
2.07
2.02
2.07
4.11
2.06
2.47
2.13
6.56
δ / ppm

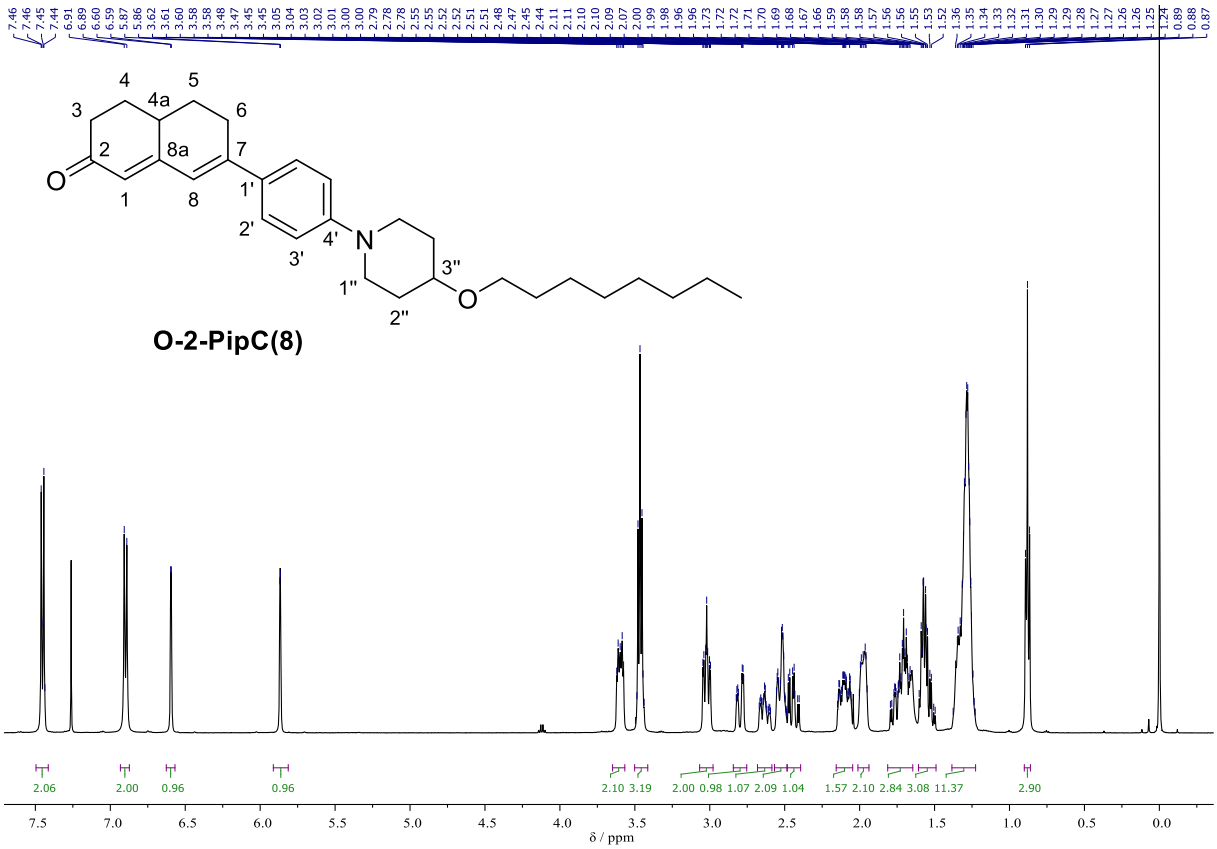

199.98
160.82
159.19
130.60
127.63
123.62
114.64
77.28 CDCl3
76.78 CDCl3
68.06
37.22
30.87
29.16
29.12
29.11
29.03
27.86
25.95
22.79
20.10
δ / ppm

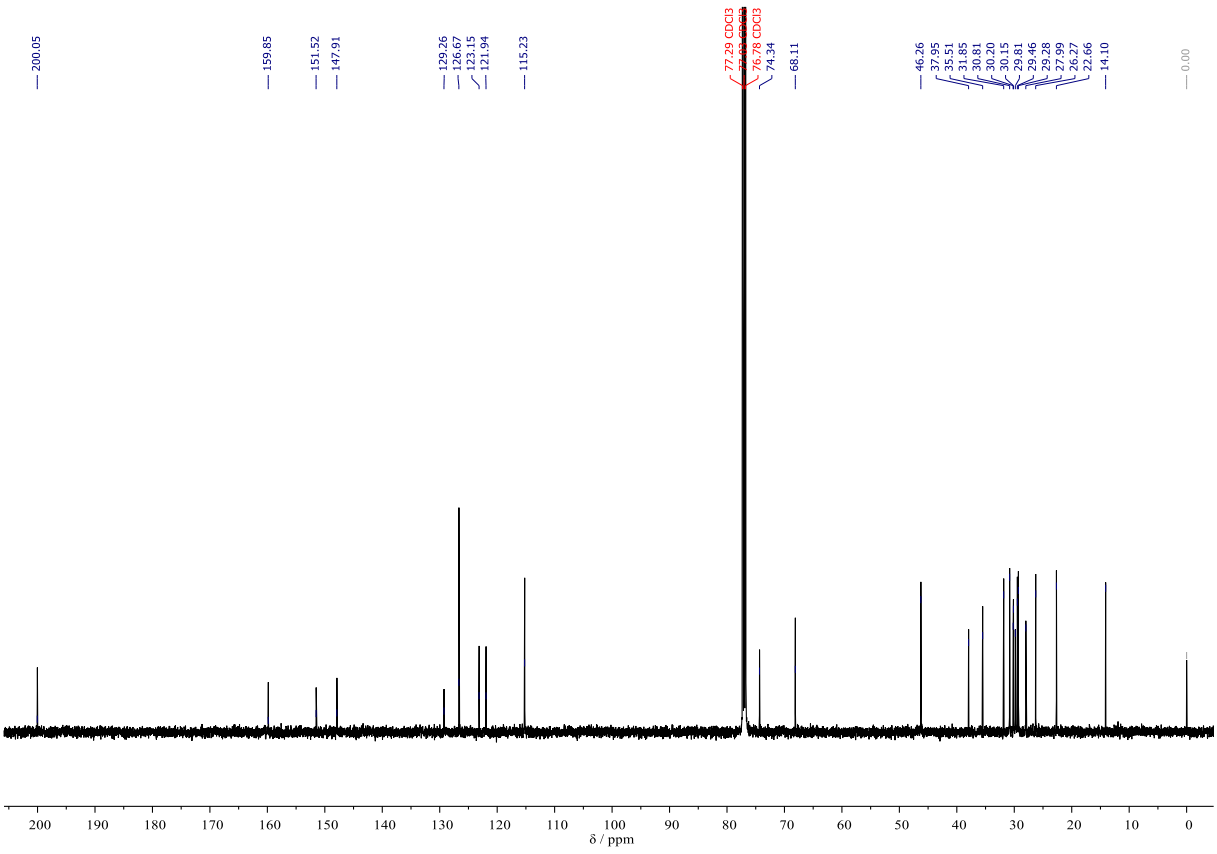

O-2-C(8)F(8)
2.00
2.03
0.97
0.95
2.00
1.02 1.20 2.08 1.04
0.92
3.06
3.76
3.19 5.48 6.10
δ / ppm

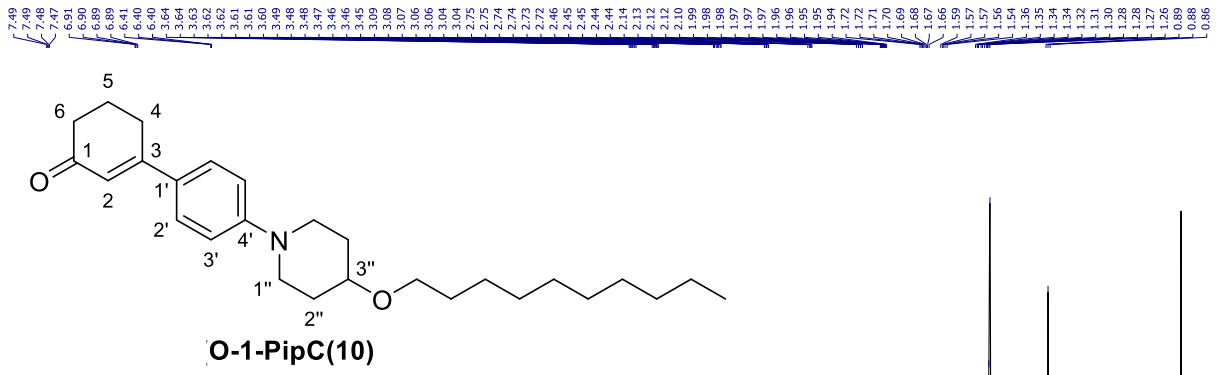

200.14
159.84
159.50
147.78
131.91
126.96
123.69
123.09
114.52
77.29 CDCl3
76.78 CDCl3
68.01
37.95
35.42
30.88
30.14
29.78
29.16
29.12
29.03
28.24
25.96
20.10
δ / ppm


O-1-PipC(8)
δ / ppm


δ / ppm


O-2-PipC(8)

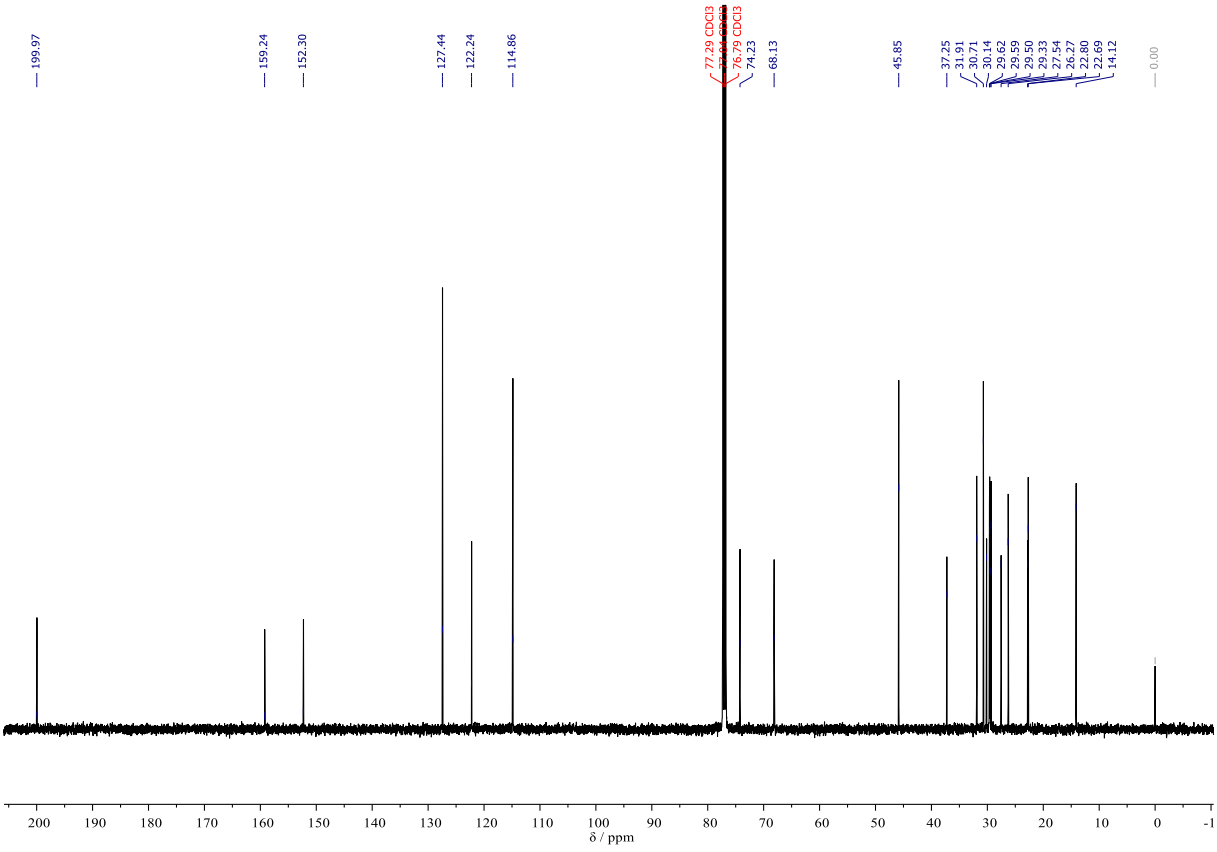


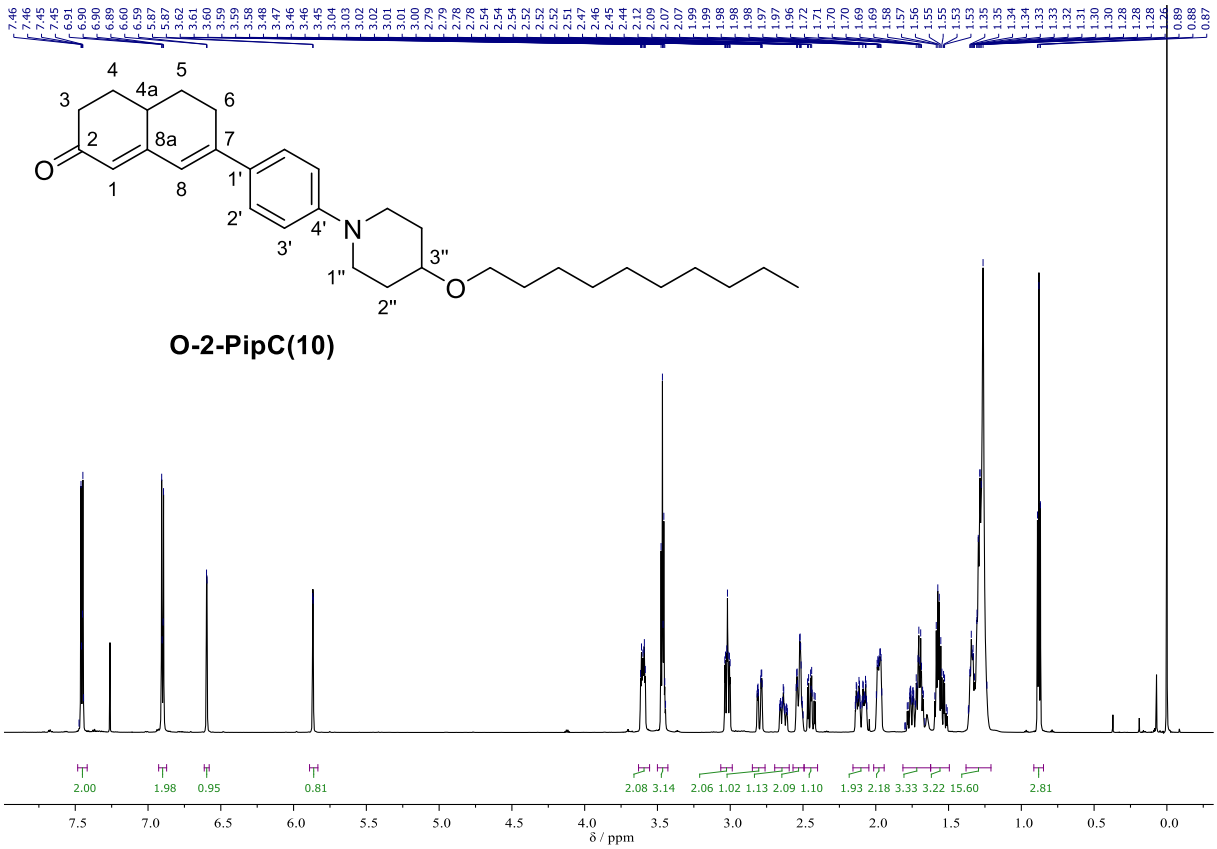


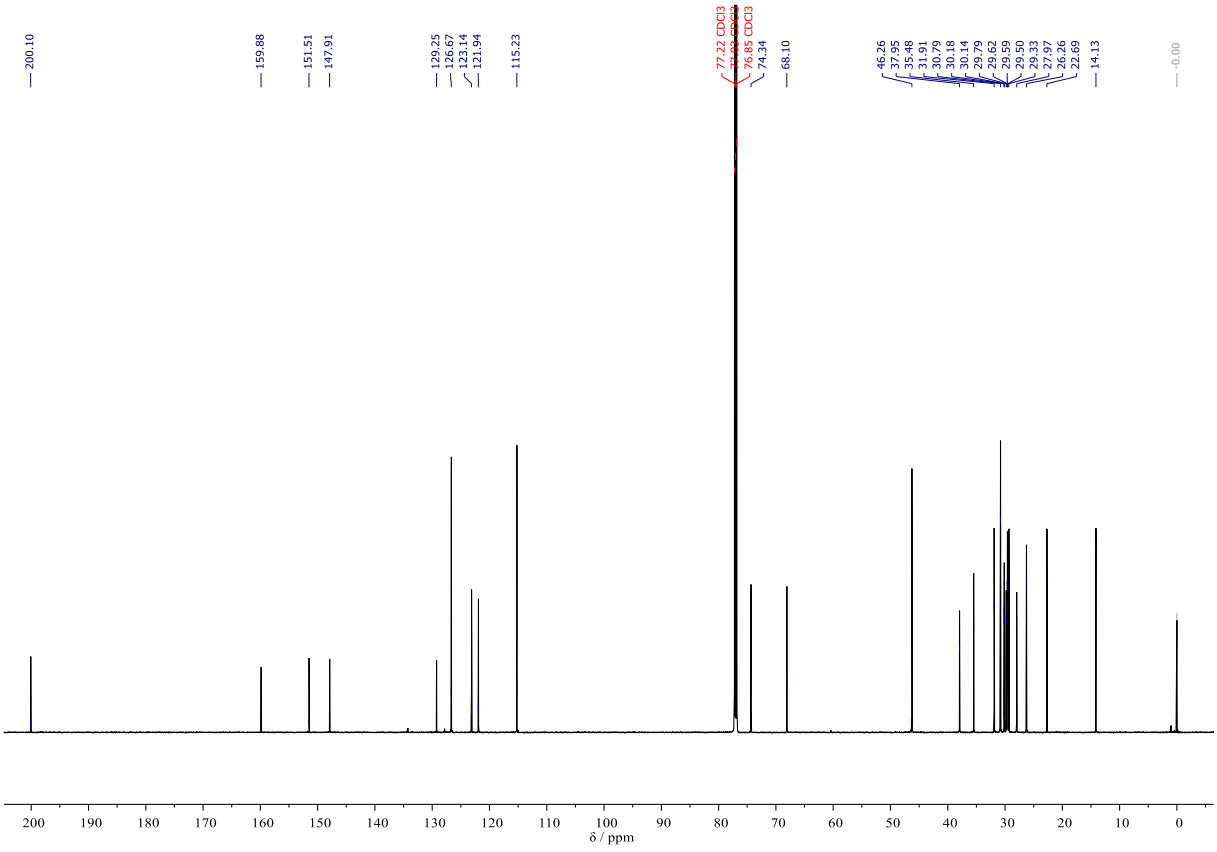
5
6
4
1
3
O
2
1'
2'
4'
N
3'
3"
1"
2"
O

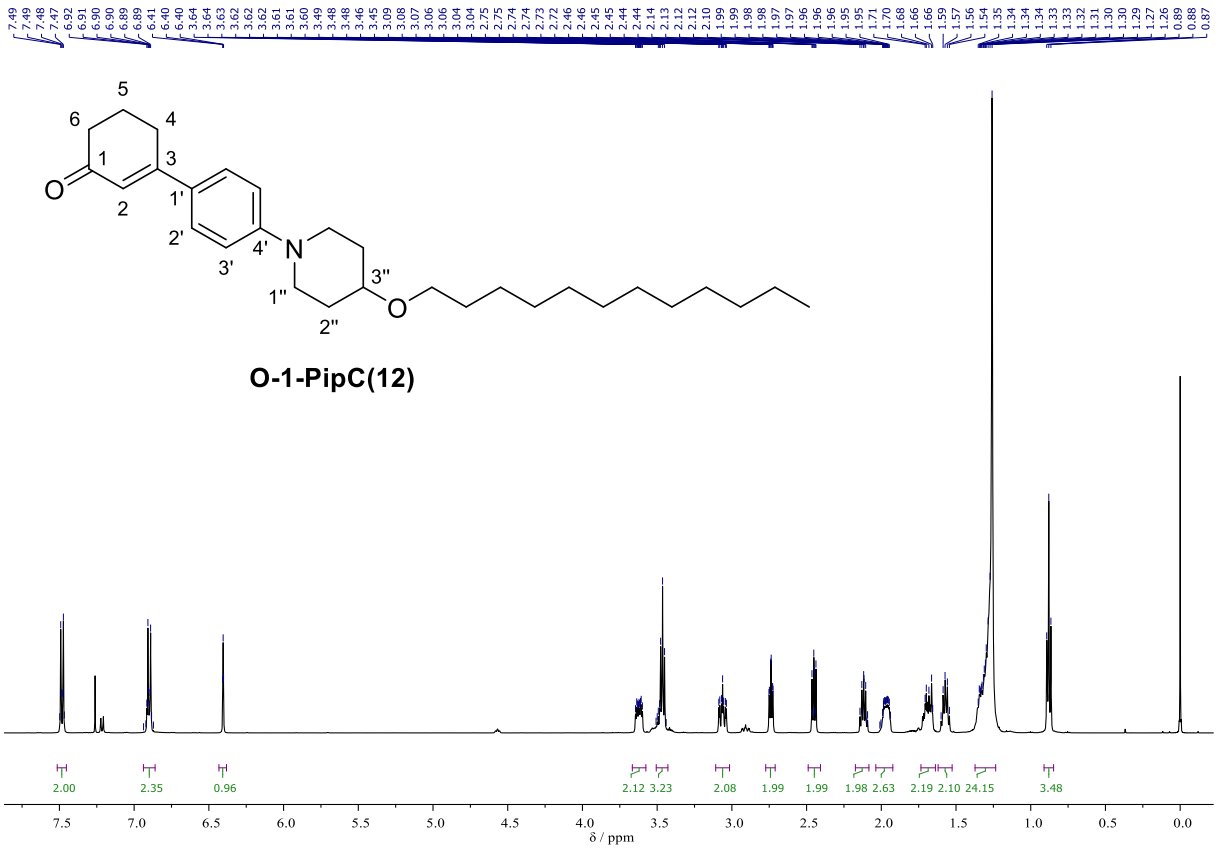
O-1-PipC(10)

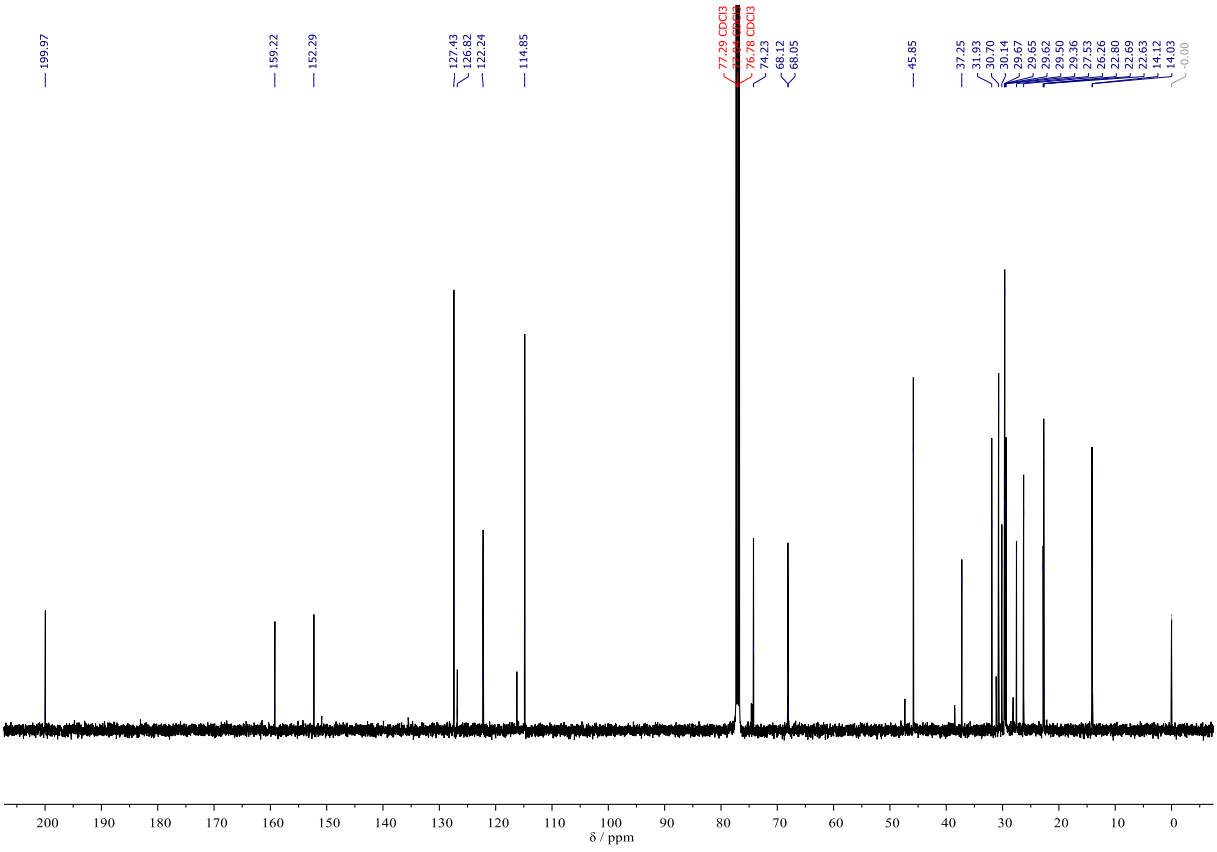
2.00
2.06
0.99
2.01
3.08
2.02
1.96
1.97
1.99
2.17
2.21
2.15
16.27
2.86
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm

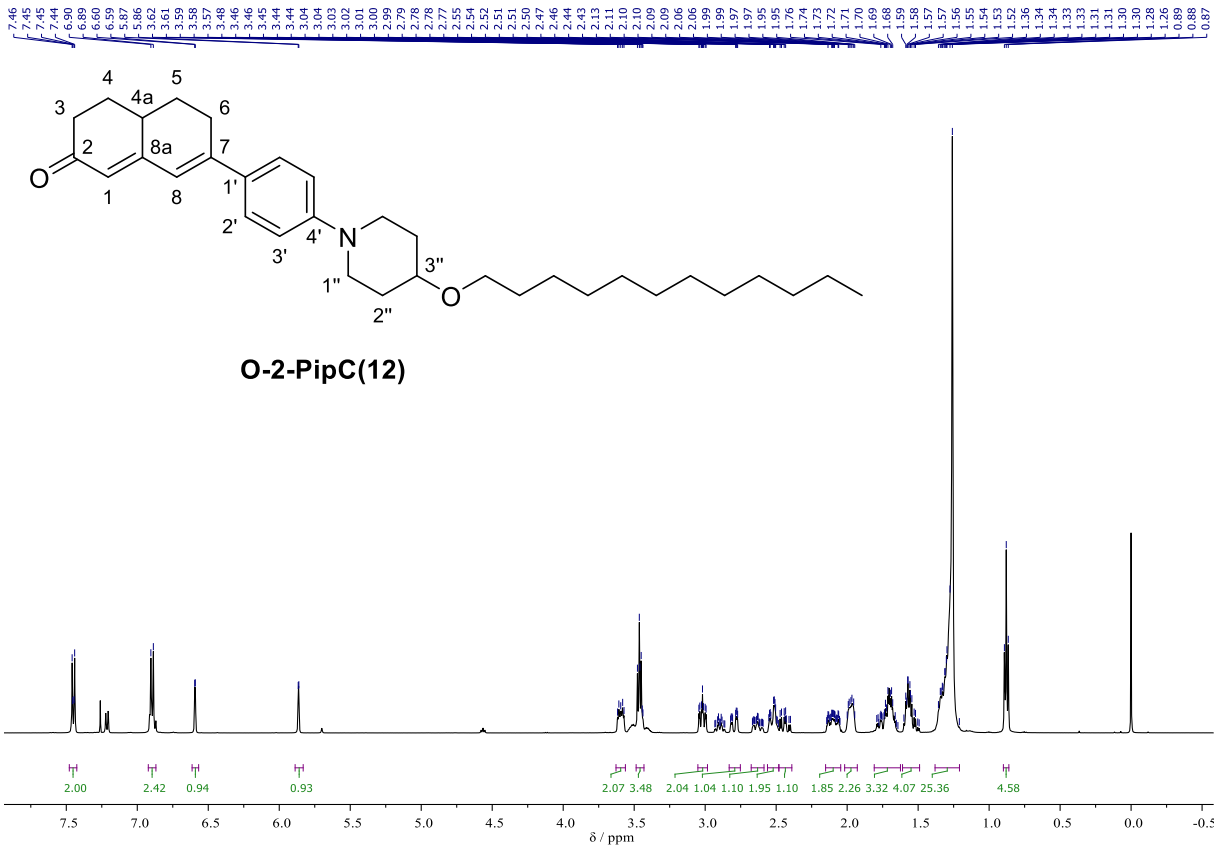

199.97
159.24
152.30
127.44
122.24
114.86
77.29 CDCl3
76.79 CDCl3
74.23
68.13
45.85
37.25
31.91
30.71
30.14
29.62
29.59
29.50
29.33
27.54
26.27
22.80
22.69
14.12
0.00
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
δ / ppm

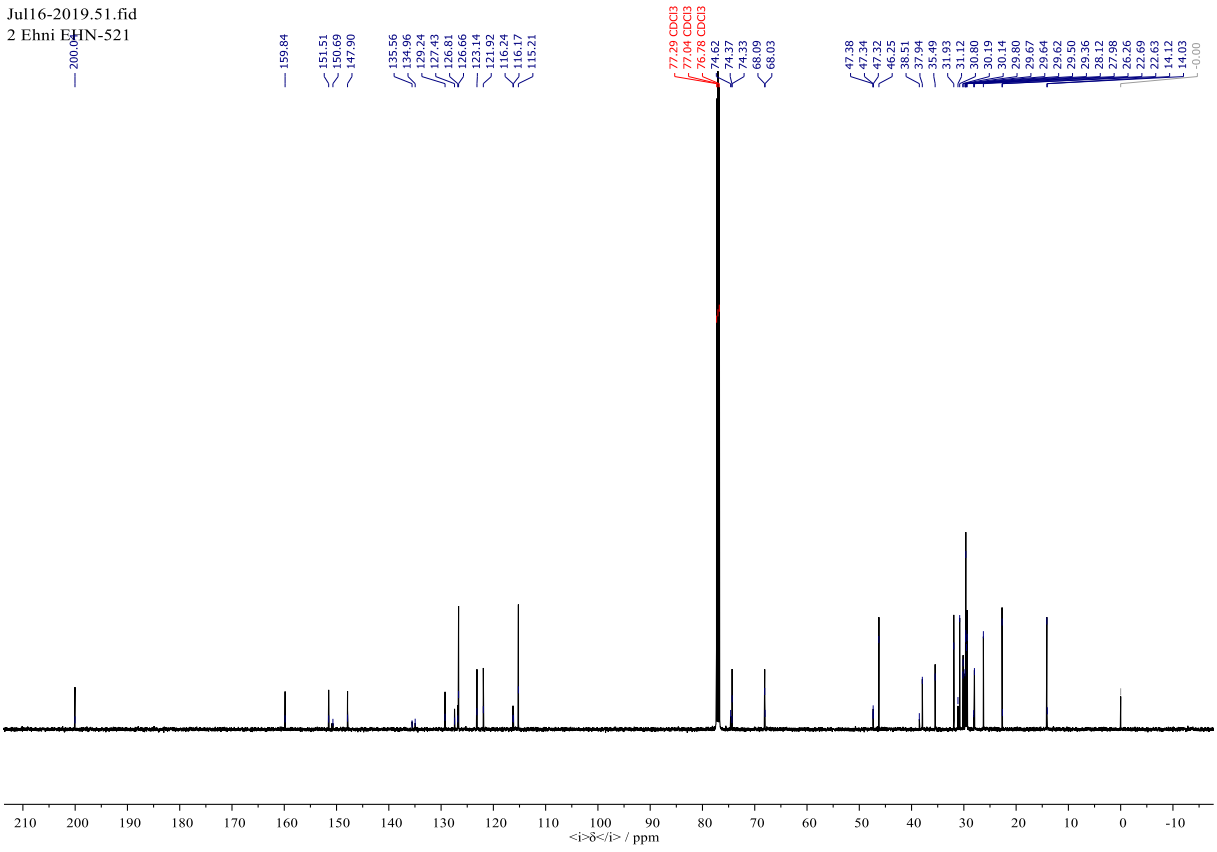

O-2-PipC(10)
δ / ppm

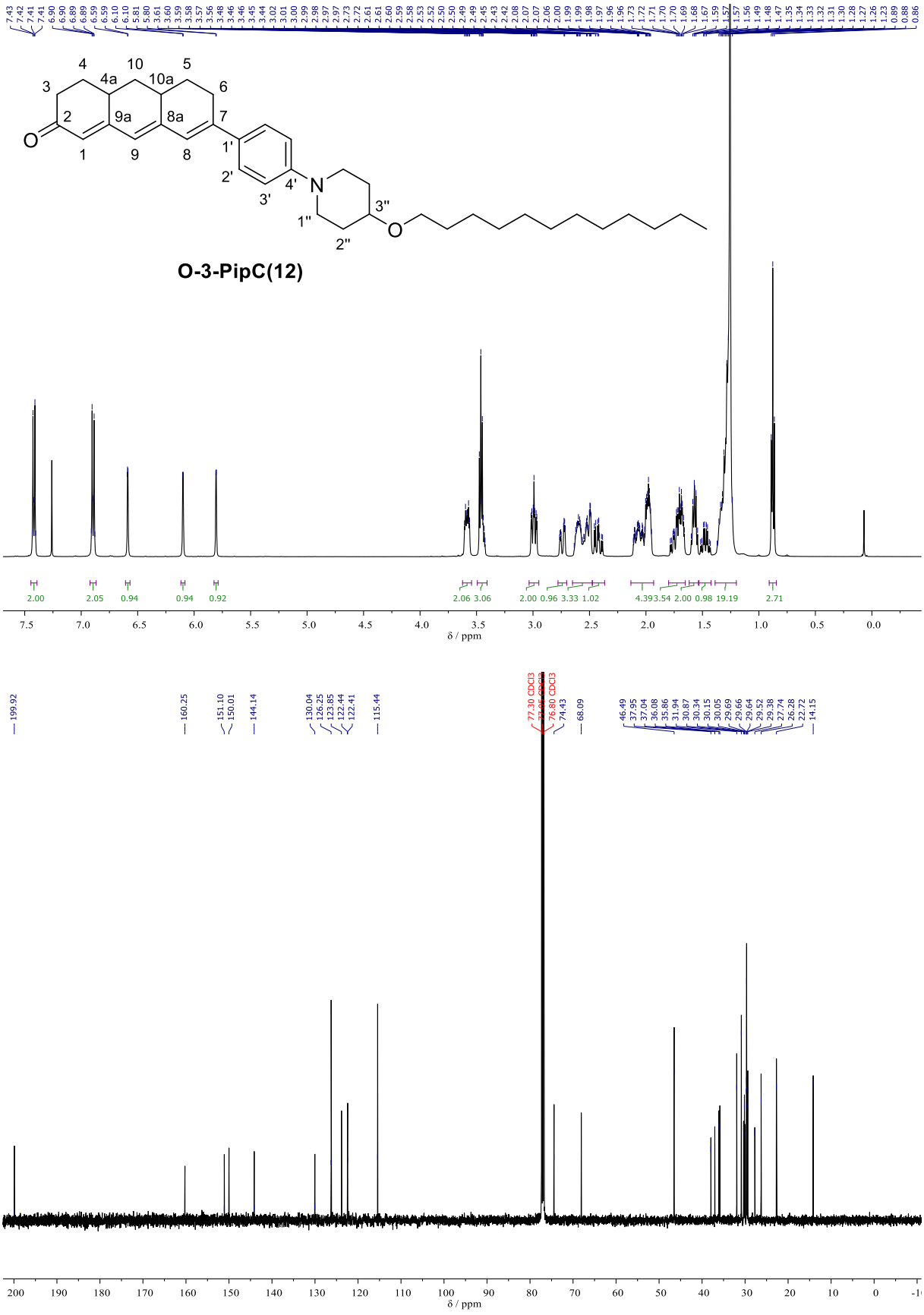

δ / ppm

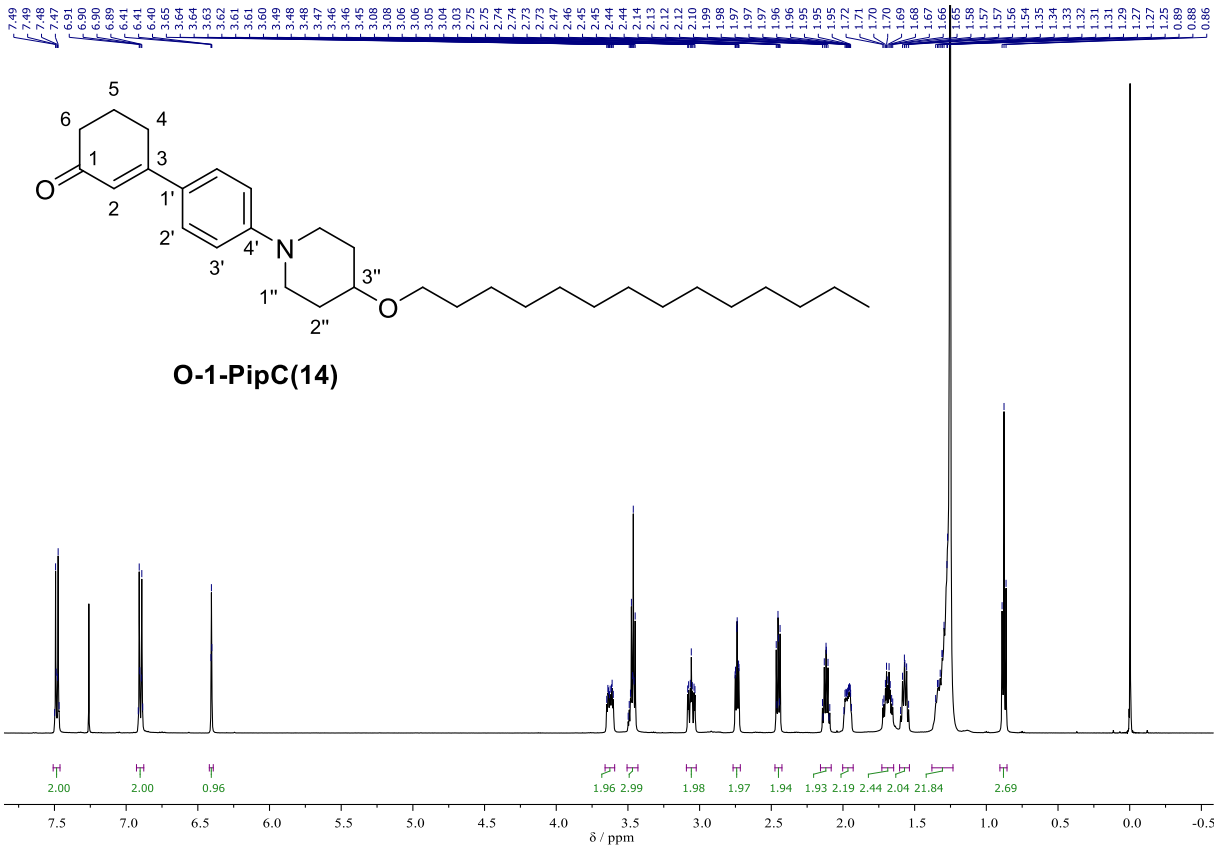

O-1-PipC(12)
δ / ppm

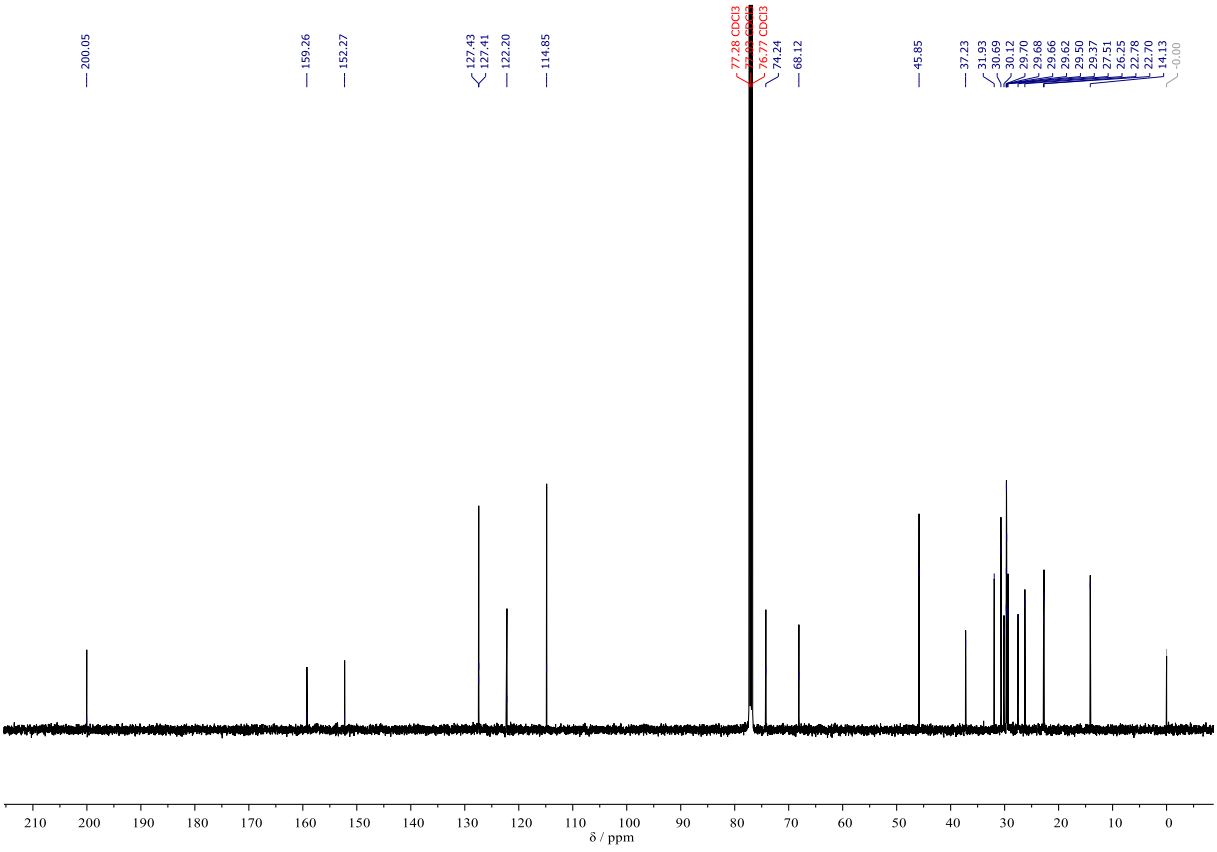

δ / ppm

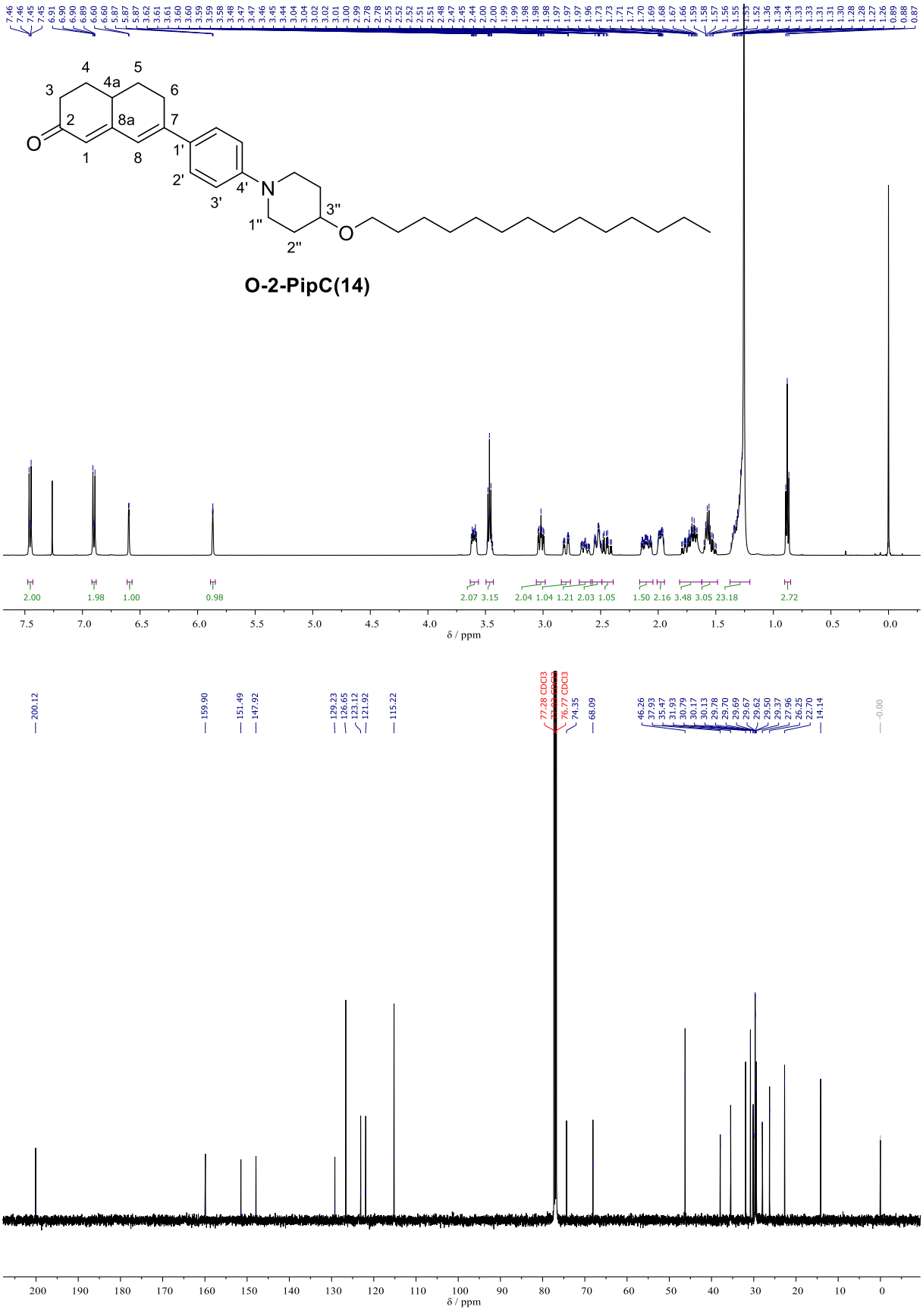

O-2-PipC(12)
δ / ppm


Jul16-2019.51.fid
2 Ehni EHN-521
δ / ppm


O-3-PipC(12)
δ / ppm
δ / ppm


O-1-PipC(14)
δ / ppm

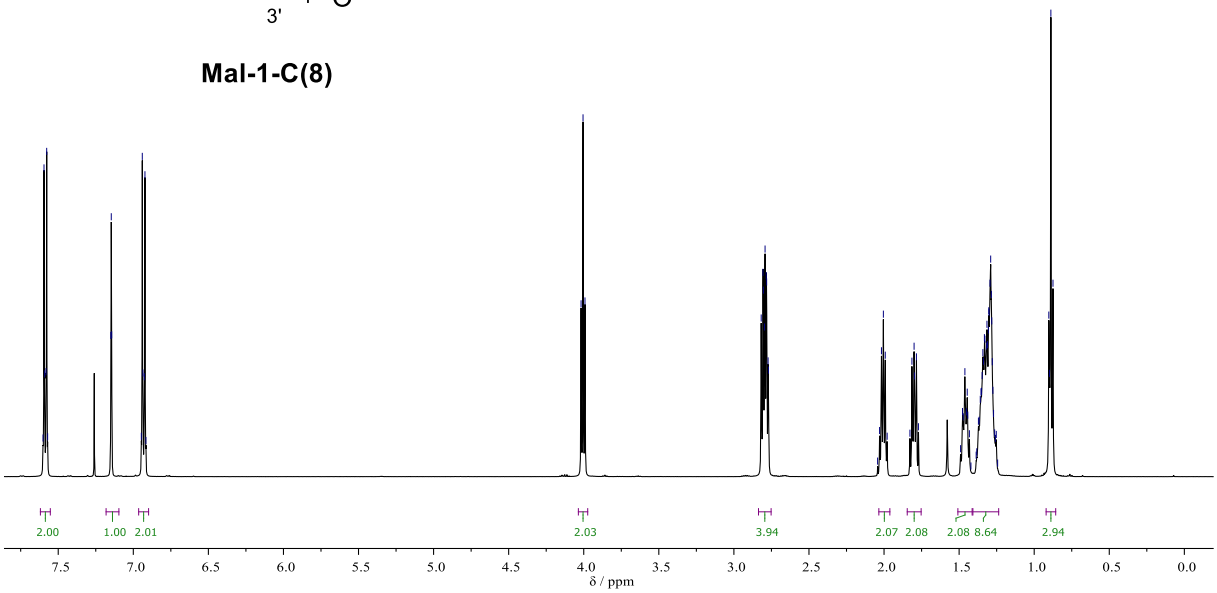

δ / ppm

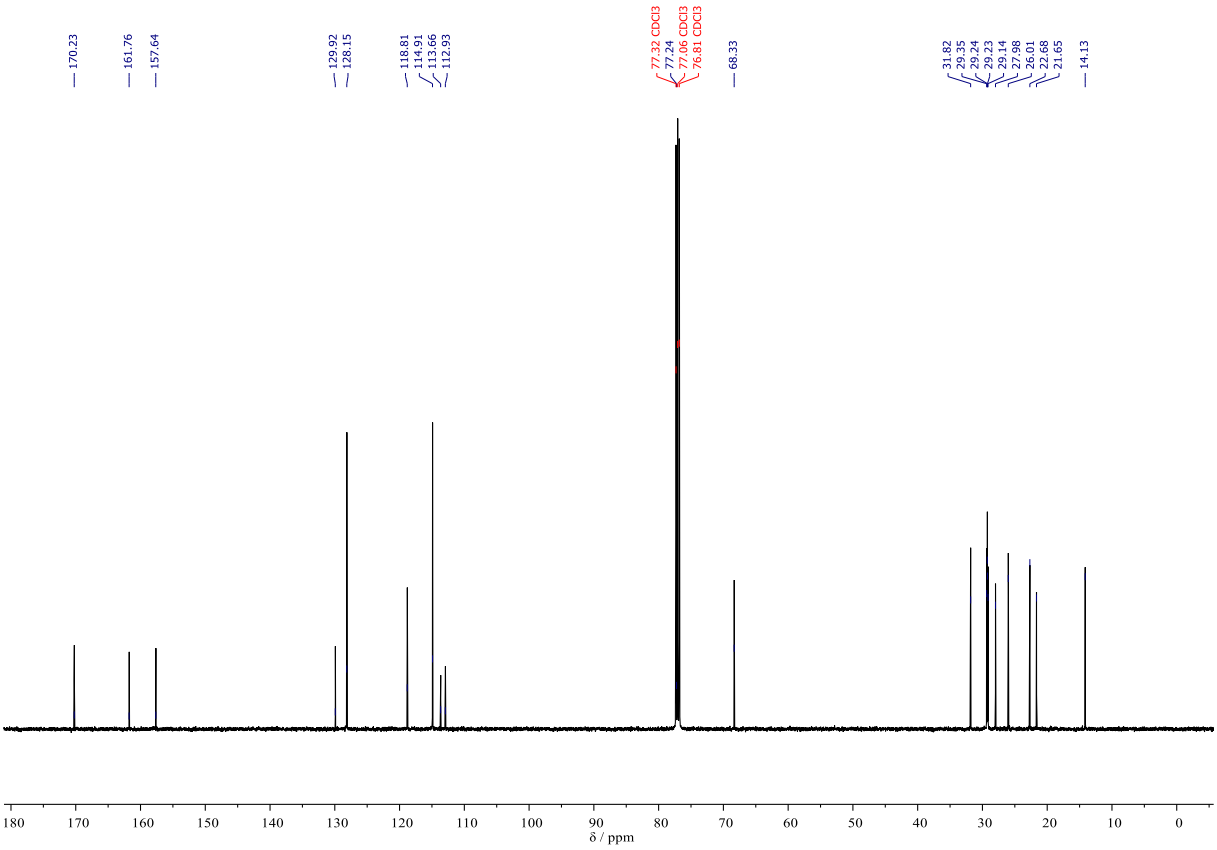

O-2-PipC(14)
δ / ppm
δ / ppm

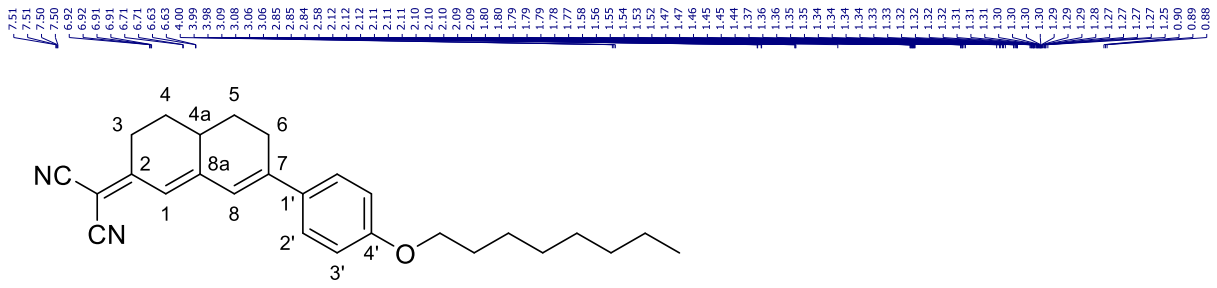

7.59
7.59
7.58
7.58
7.57
7.15
7.15
6.94
6.94
6.94
6.93
6.92
6.92
4.02
4.00
3.99
2.82
2.81
2.80
2.80
2.79
2.78
2.78
2.77
2.77
2.04
2.03
2.02
2.00
1.99
1.98
1.83
1.81
1.80
1.80
1.78
1.77
1.49
1.48
1.47
1.46
1.45
1.45
1.44
1.43
1.42
1.39
1.38
1.37
1.37
1.36
1.35
1.35
1.34
1.34
1.33
1.33
1.32
1.31
1.31
1.31
1.30
1.30
1.29
1.29
1.29
1.28
1.28
1.28
1.27
1.26
1.26
1.25
1.24
0.90
0.90
0.89
0.87

5
6
4
1
3
NC
2
1'
CN
2'
4'
O
3'

MaI-1-C(8)

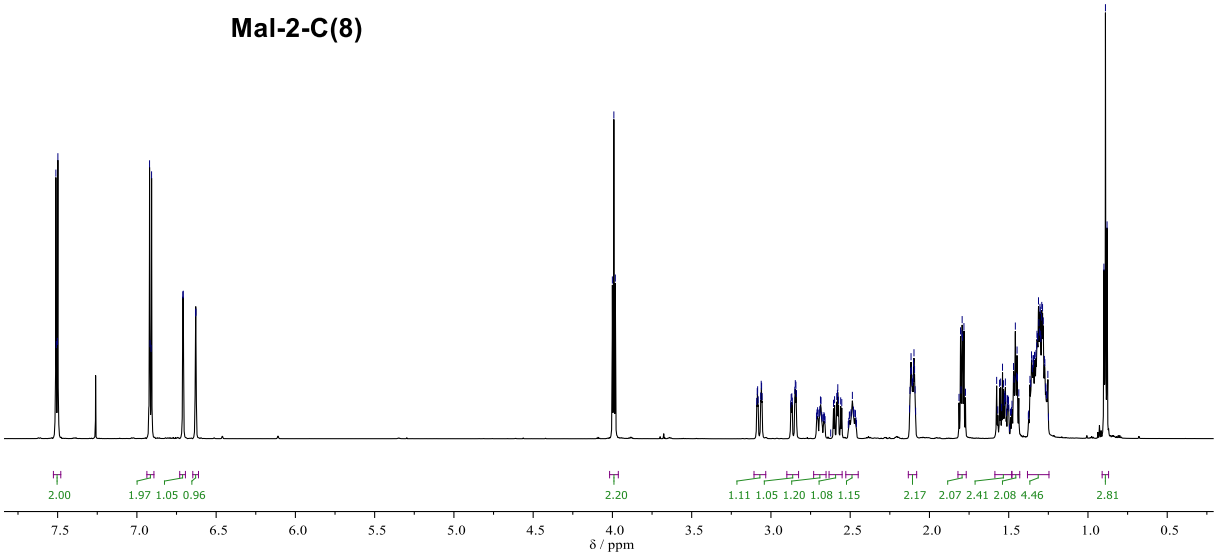

2.00
1.00
2.01
2.03
3.94
2.07
2.08
2.08
8.64
2.94
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm

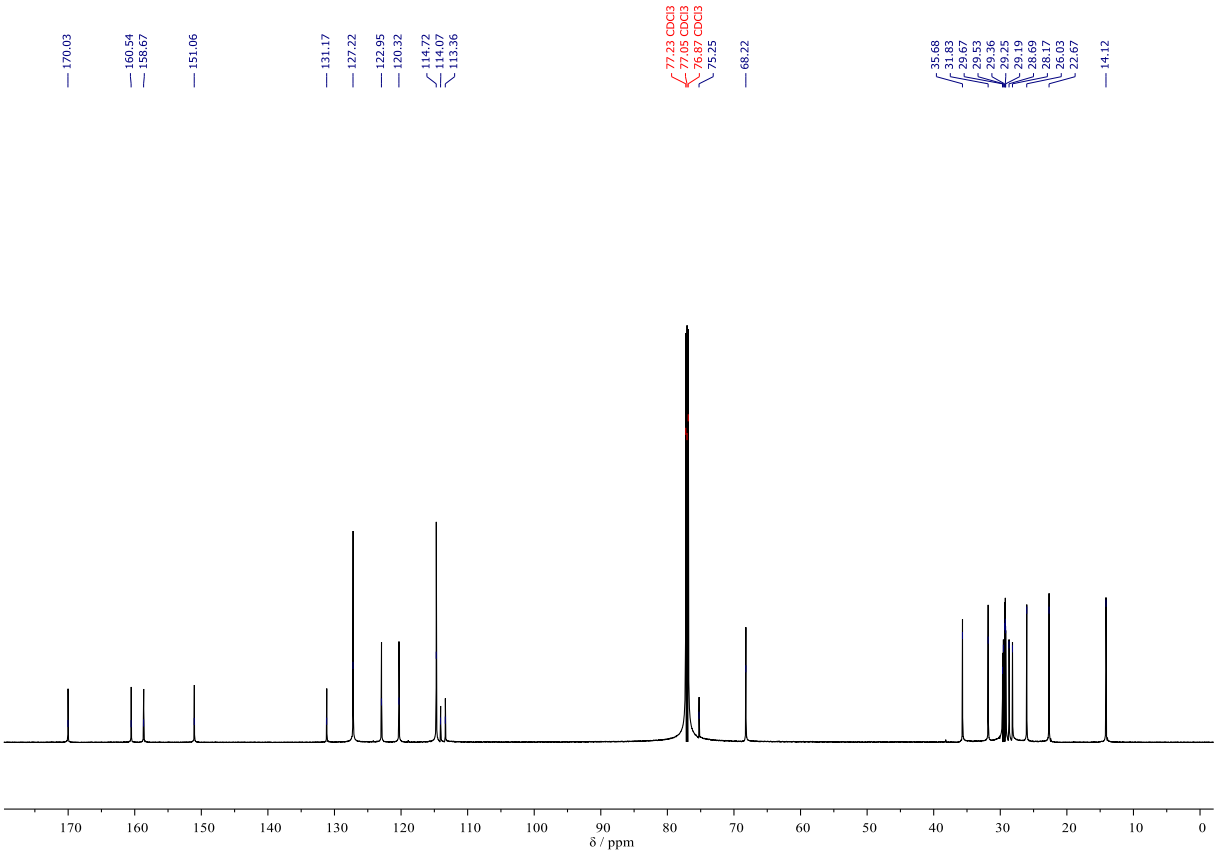

170.23
161.76
157.64
129.92
128.15
118.81
114.91
113.66
112.93
77.32 CDCl3
77.24
77.06 CDCl3
76.81 CDCl3
68.33
31.82
29.35
29.24
29.23
29.14
27.98
26.01
22.68
21.65
14.13
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ / ppm



4
5
4a
3
6
2
8a
7
NC
1'
1
8
CN
2'
4'
O
3'

MaI-2-C(8)

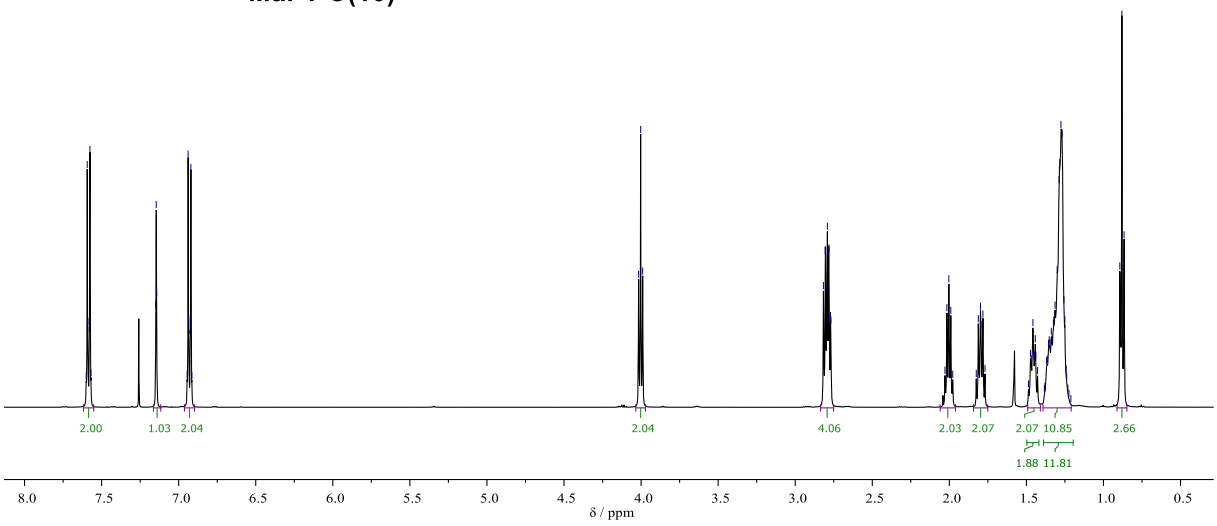

2.00
1.97 1.05 0.96
2.20
1.11 1.05 1.20 1.08 1.15
2.17
2.07 2.41 2.08 4.46
2.81
δ / ppm

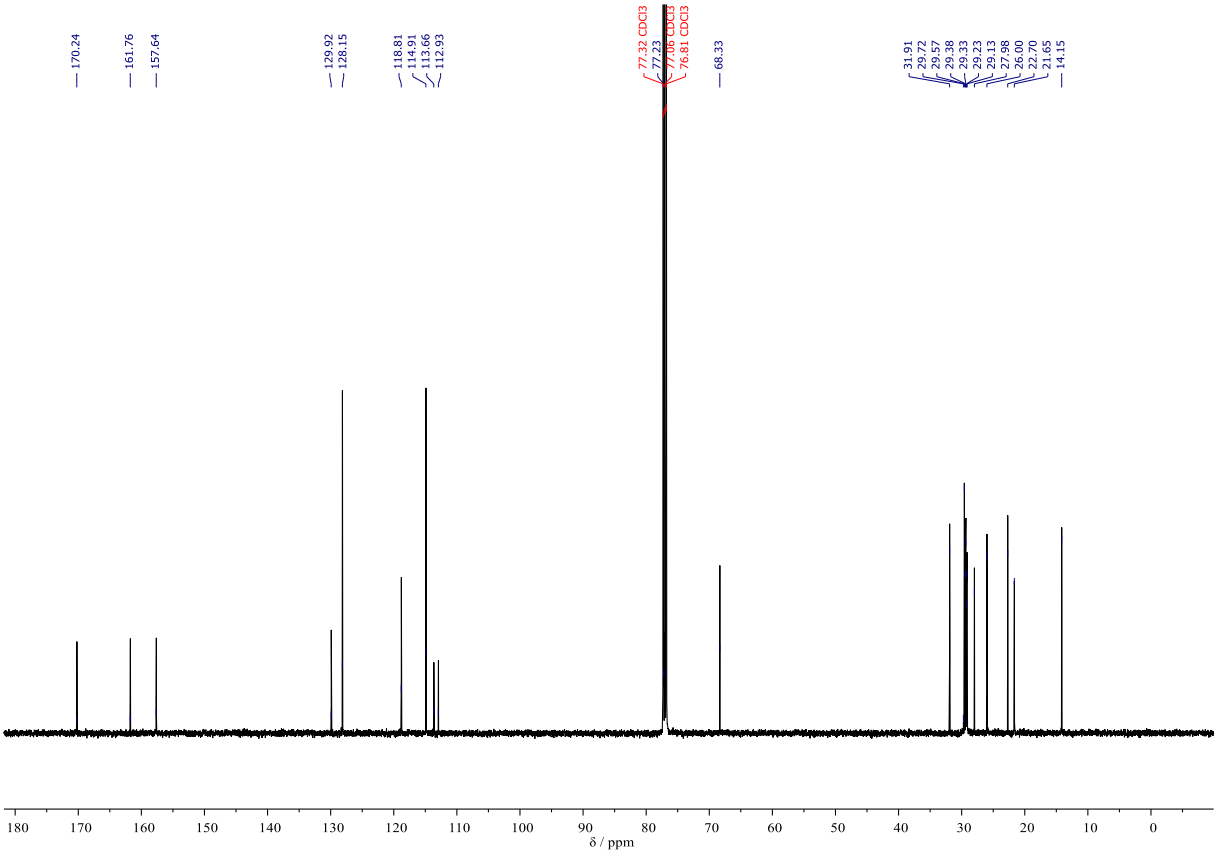

170.03
160.54
158.67
151.06
131.17
127.22
122.95
120.32
114.72
114.07
113.36
77.23 CDCl3
77.05 CDCl3
76.87 CDCl3
75.25
68.22
35.68
31.83
29.67
29.53
29.36
29.15
29.19
28.69
28.17
26.03
22.67
14.12
δ / ppm

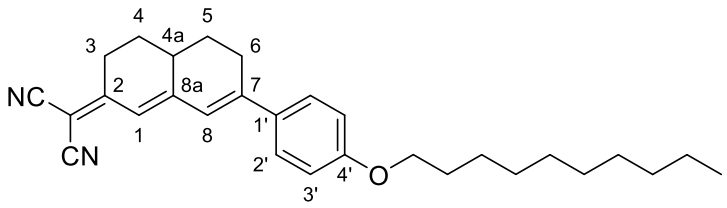

7.60
7.59
7.59
7.58
7.58
7.57
7.15
7.15
7.14
6.94
6.93
6.93
6.92
6.91
4.02
4.00
3.99
2.82
2.81
2.80
2.80
2.79
2.78
2.78
2.77
2.77
2.03
2.02
2.00
1.99
1.98
1.83
1.81
1.80
1.79
1.78
1.77
1.49
1.47
1.47
1.46
1.45
1.44
1.44
1.43
1.38
1.38
1.37
1.36
1.36
1.35
1.35
1.34
1.33
1.32
1.32
1.31
1.30
1.29
1.29
1.28
1.28
1.27
1.26
1.25
1.24
1.24
1.23
1.22
1.21
0.89
0.88
0.87

5
6
4
1
3
NC
2
1'
CN
2'
4'
O
3'

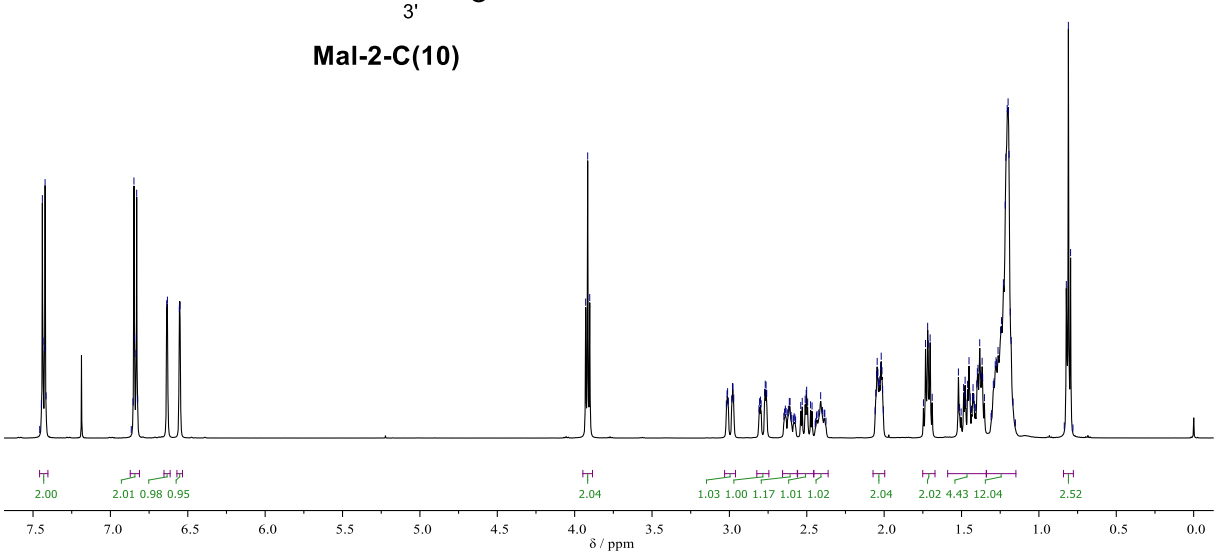
Mal-1-C(10)

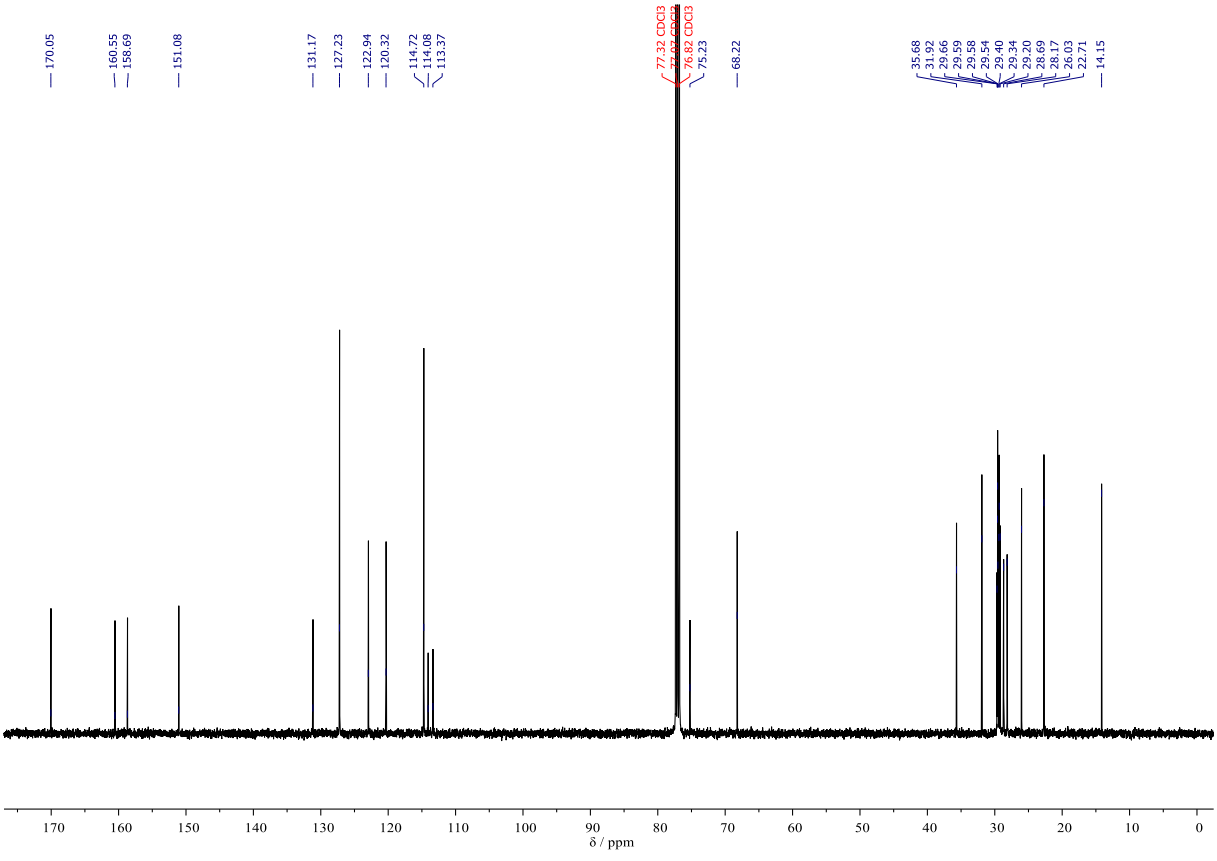

2.00
1.03
2.04
2.04
4.06
2.03
2.07
2.07
10.85
2.66
1.88
11.81
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
δ / ppm

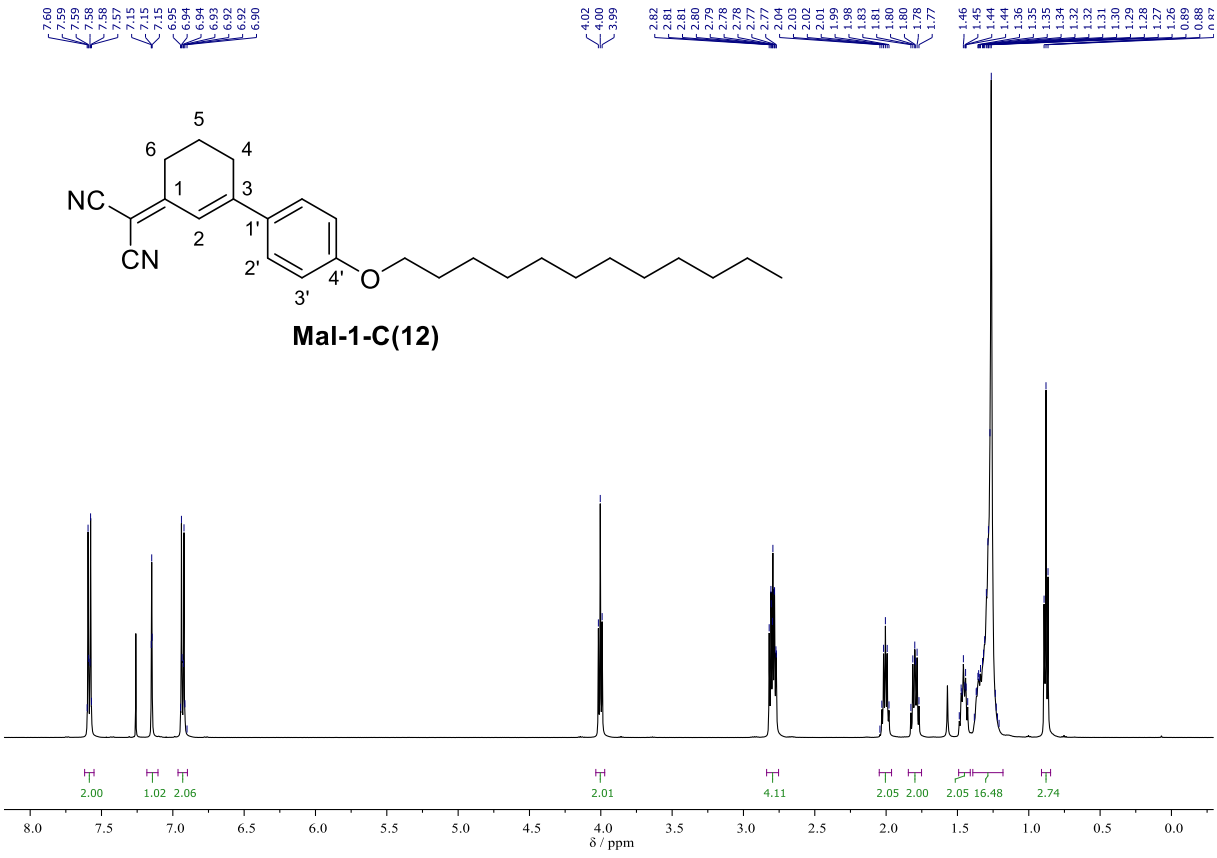

170.24
161.76
157.64
129.92
128.15
118.81
114.91
113.66
112.93
77.32 CDCl3
77.23
77.06 CDCl3
76.81 CDCl3
68.33
31.91
29.72
29.57
29.38
29.33
29.23
29.13
28.98
26.00
22.70
21.65
14.15
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ / ppm

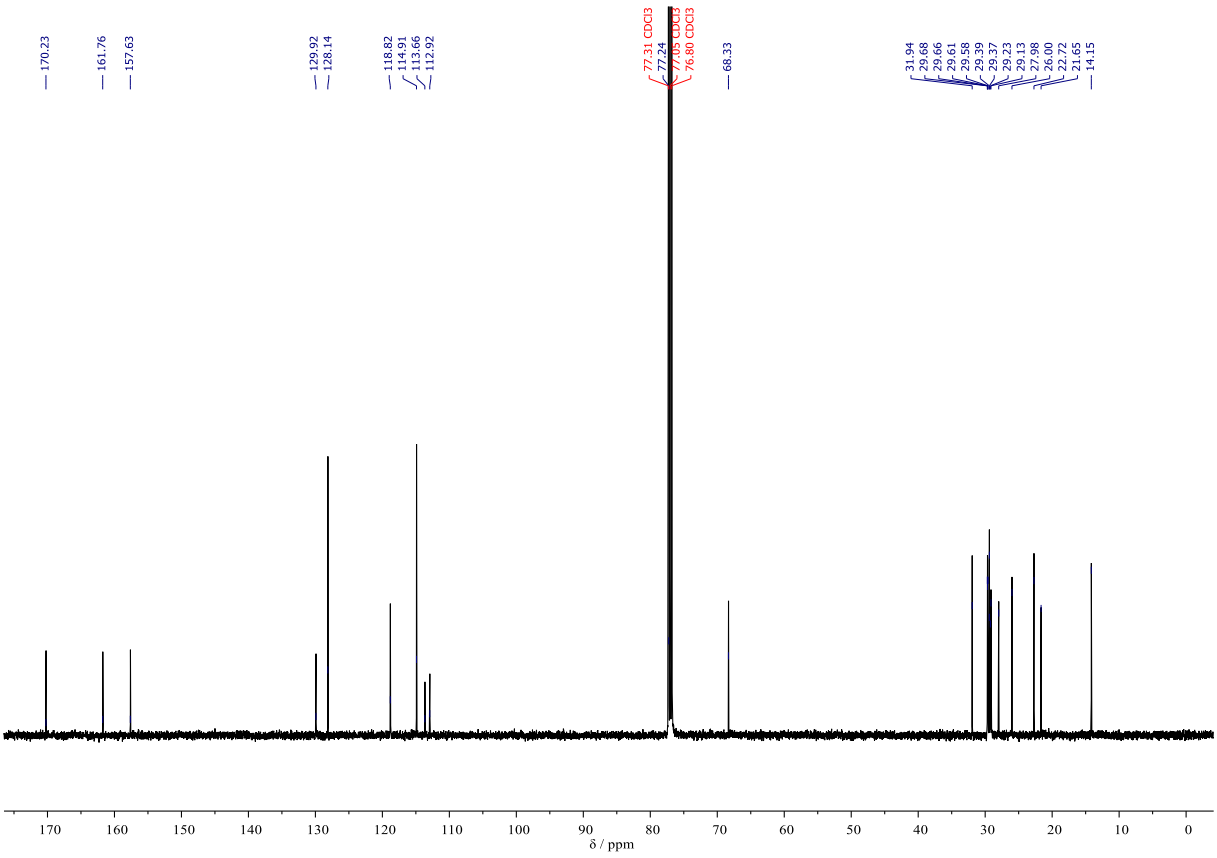

4
5
4a
3
6
2
8a
7
NC
1
8
1'
CN
2'
4'
O
3'

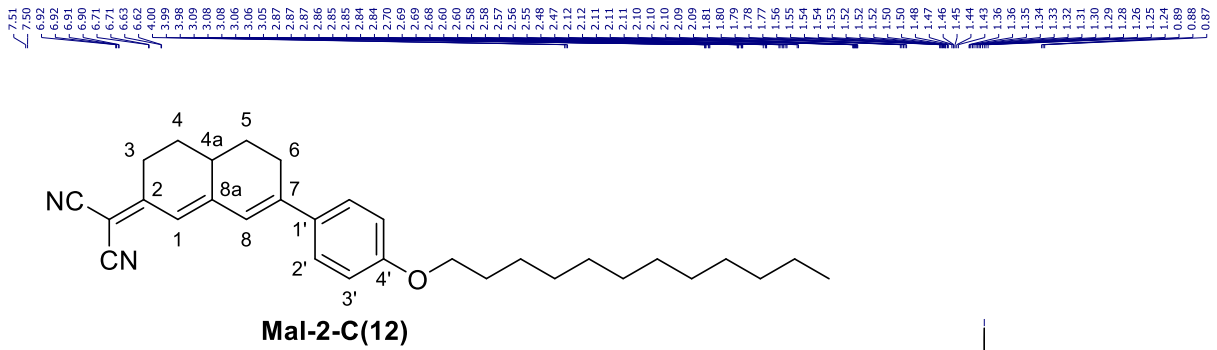
Mal-2-C(10)

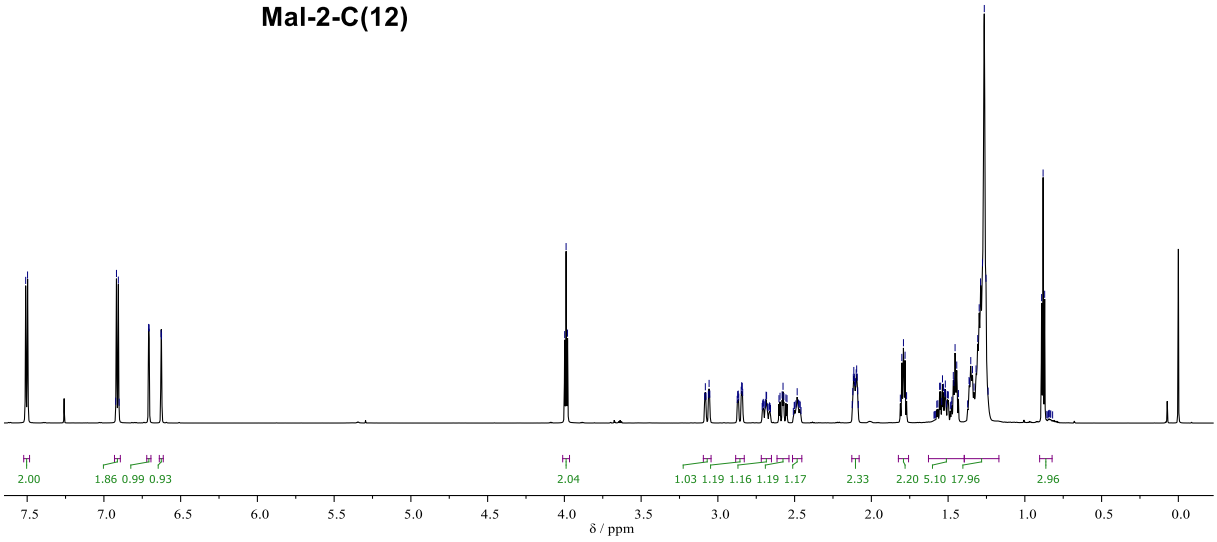

2.00
2.01 0.98 0.95
2.04
1.03 1.00 1.17 1.01 1.02
2.04
2.02 4.43 12.04
2.52
δ / ppm

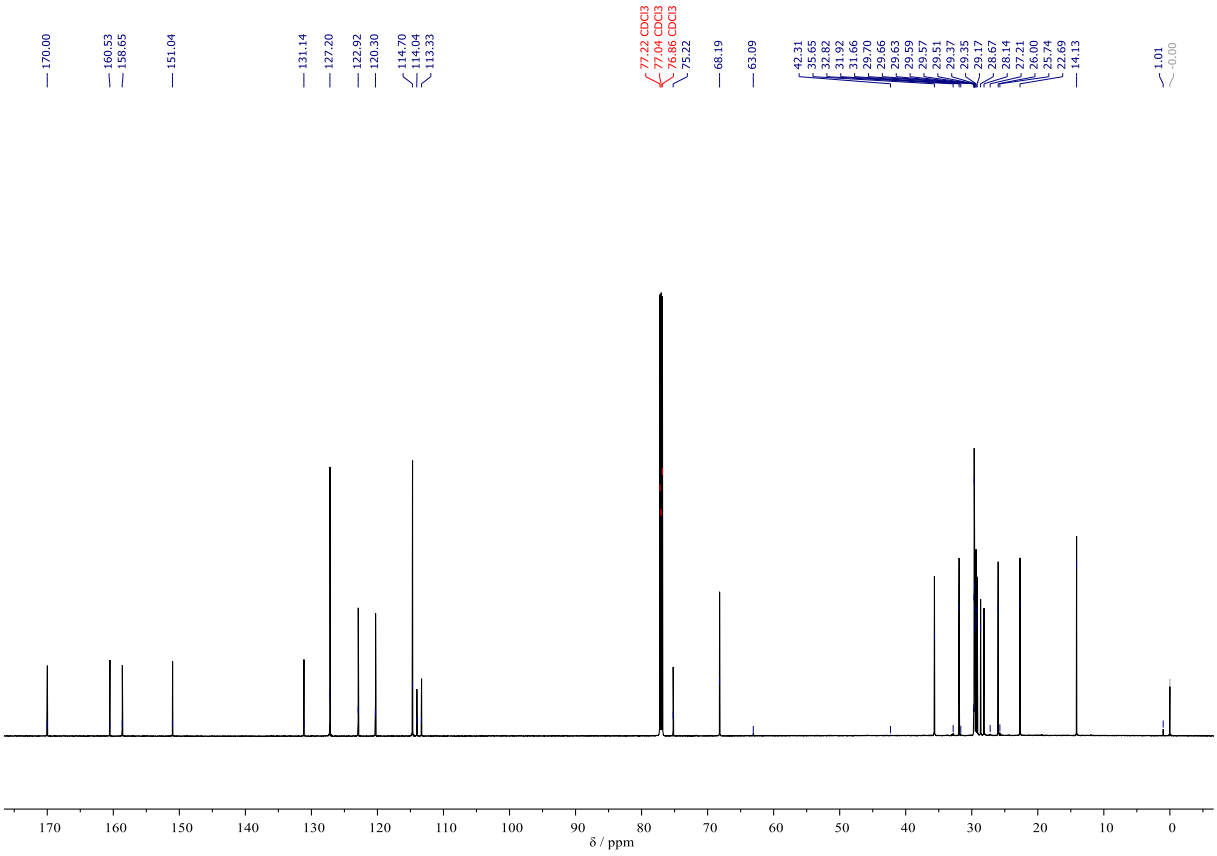

170.05
160.55
158.69
151.08
131.17
127.23
122.94
120.32
114.72
114.08
113.37
77.32 CDCl3
76.82 CDCl3
75.23
68.22
35.68
31.92
29.66
29.59
29.58
29.54
29.40
29.34
29.20
28.69
28.17
26.03
22.71
14.15
δ / ppm

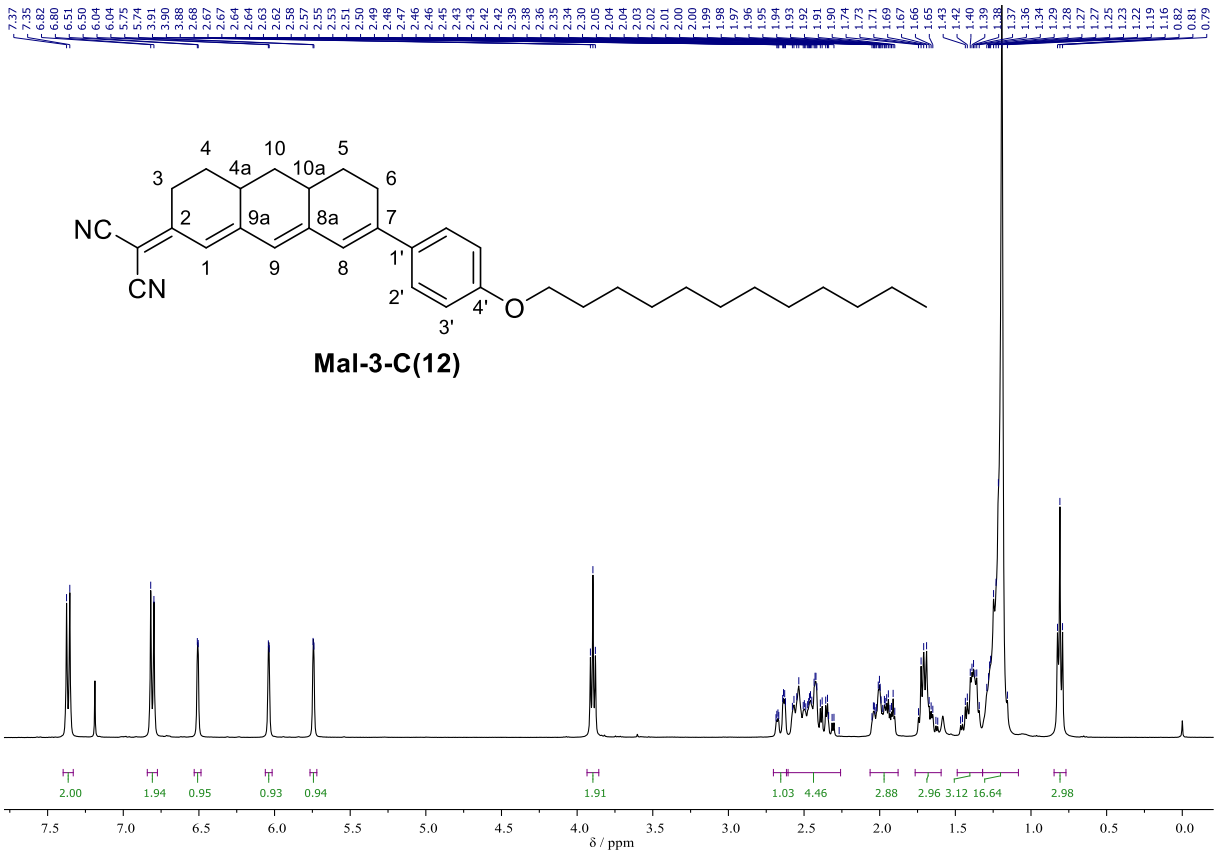

NC
CN
O
Mal-1-C(12)
δ / ppm

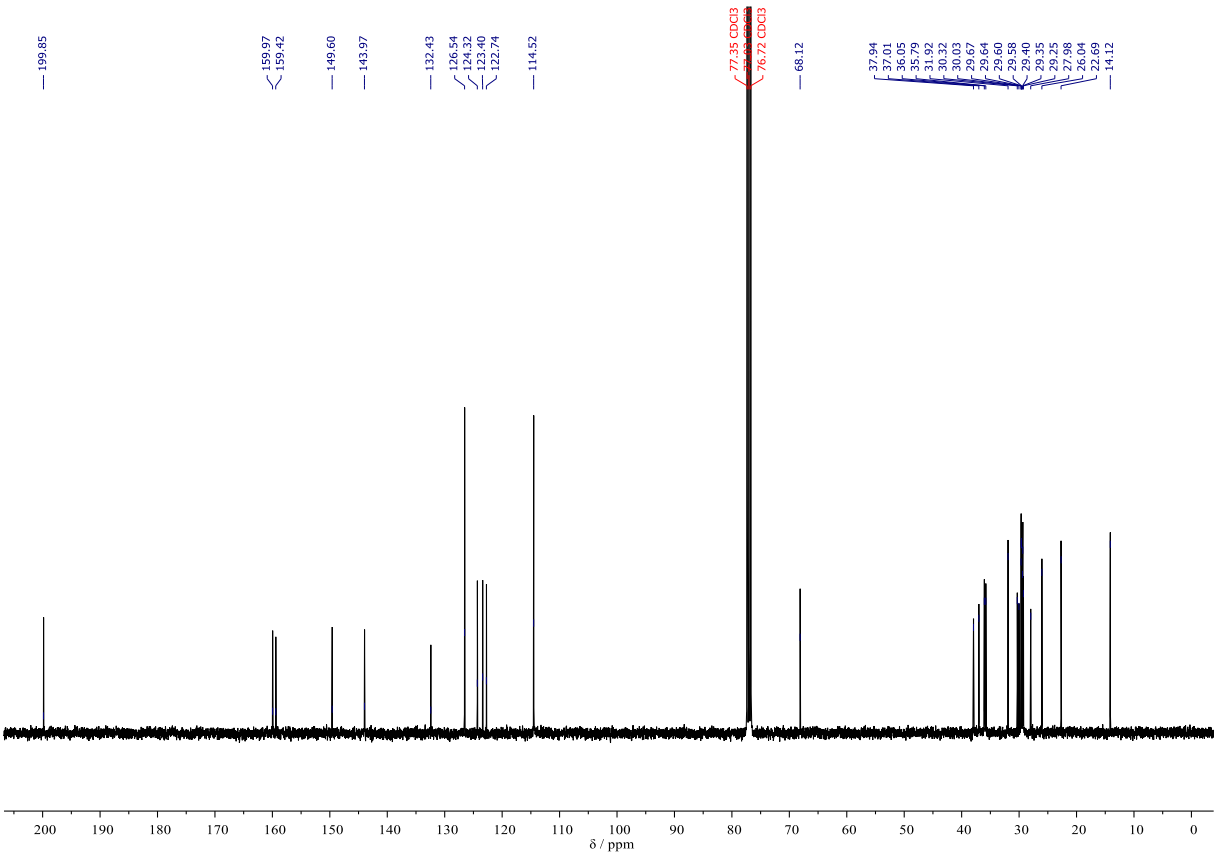

δ / ppm

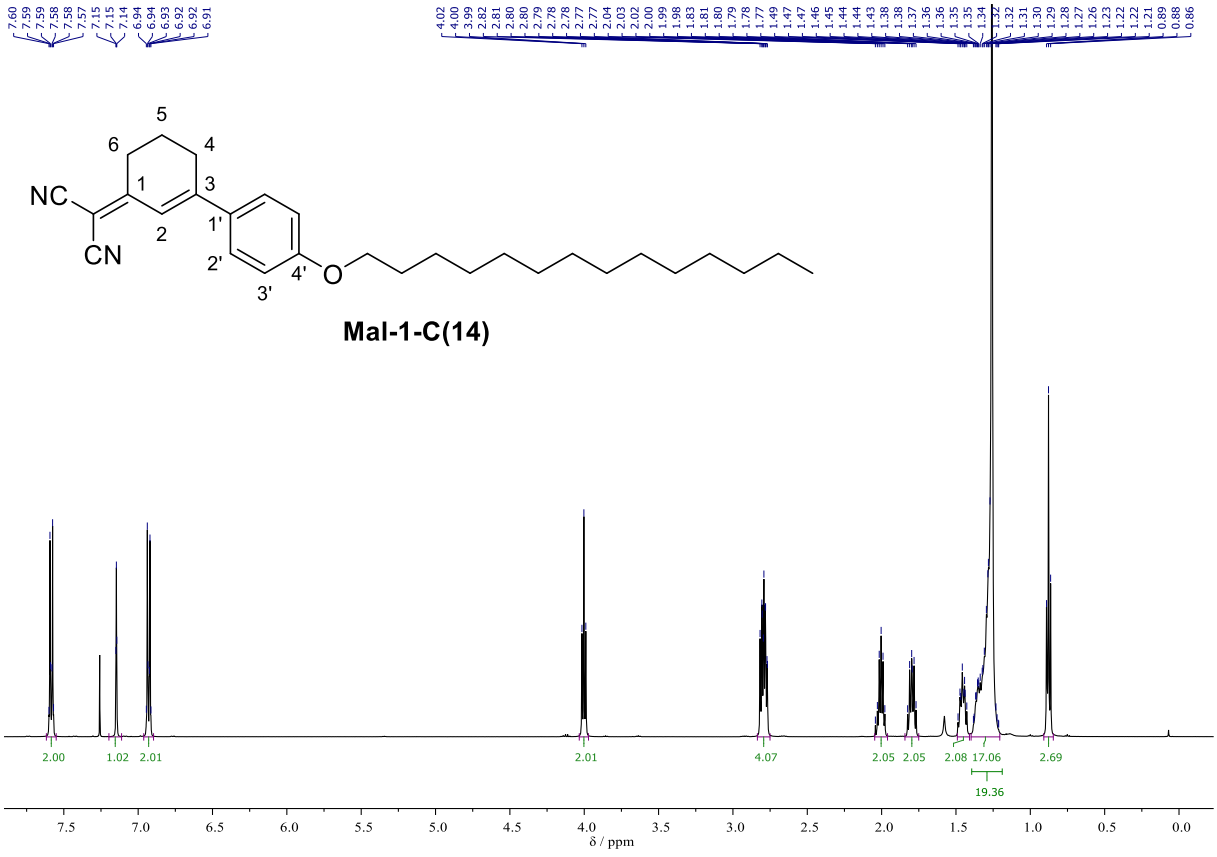

NC
CN
O
Mal-2-C(12)

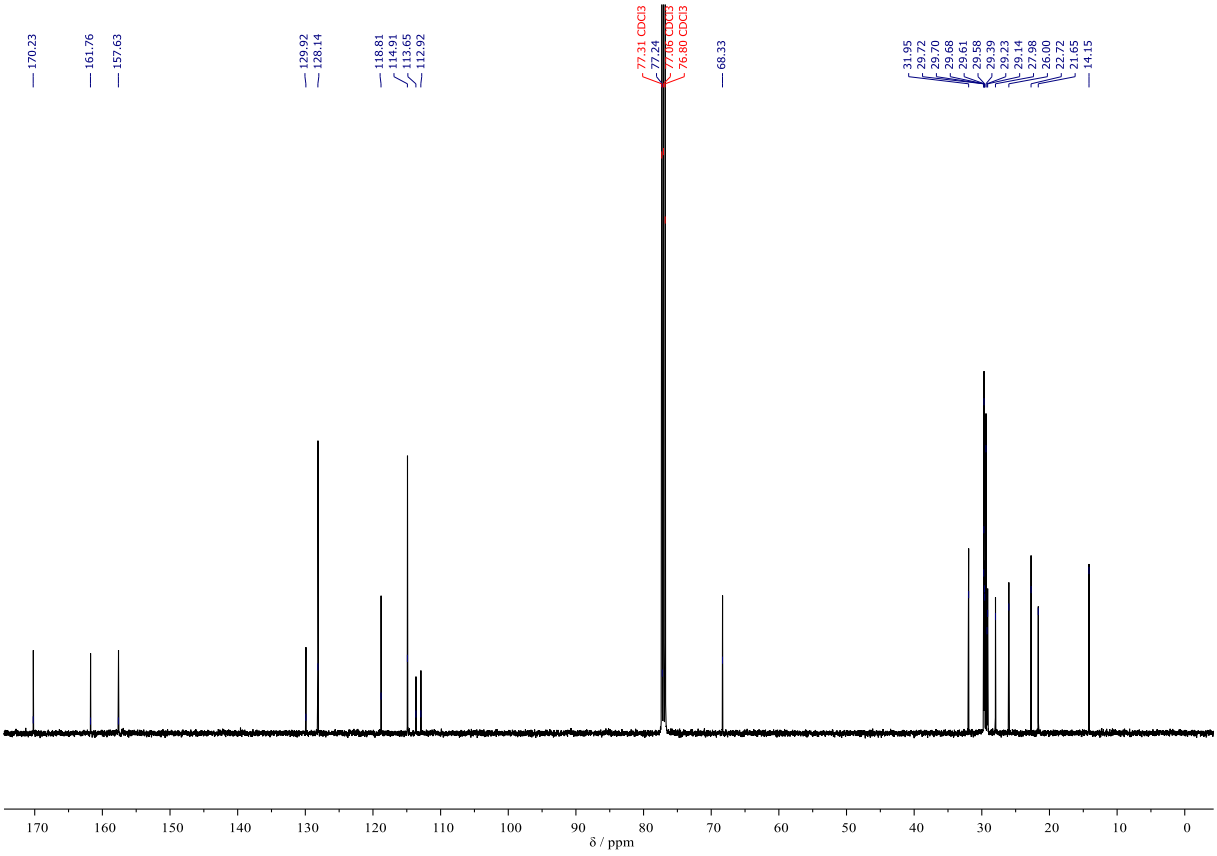

2.00
1.86 0.99 0.93
2.04
1.03 1.19 1.16 1.19 1.17
2.33
2.20 5.10 17.96
2.96
δ / ppm

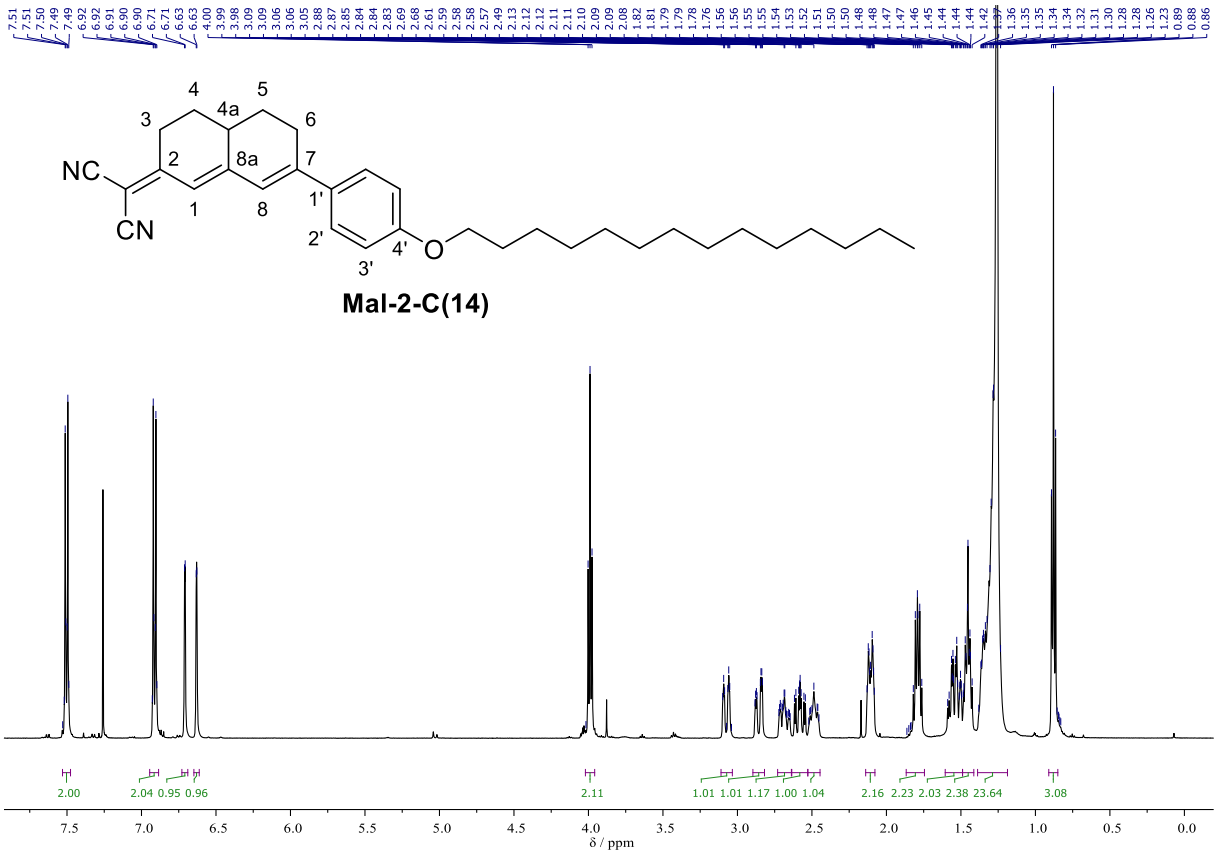

δ / ppm

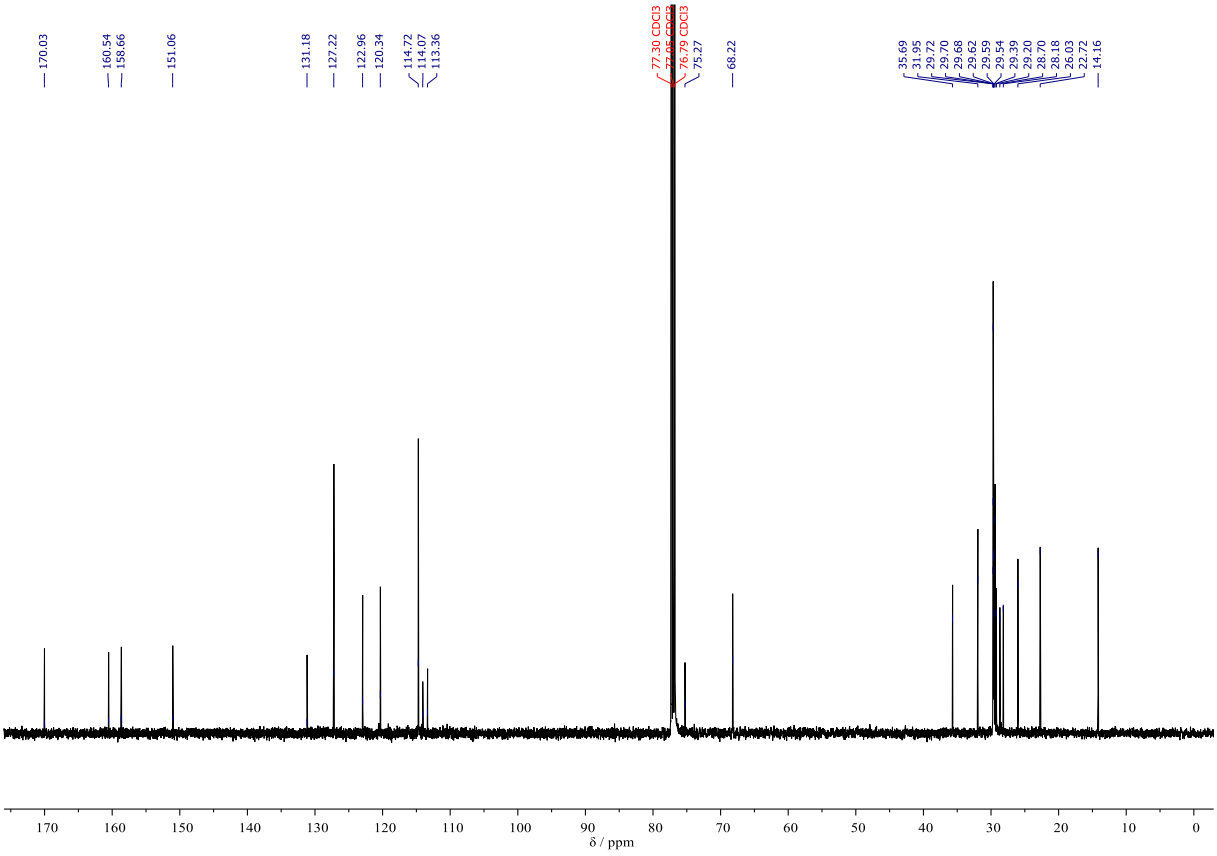

NC
CN
O
Mal-3-C(12)
δ / ppm

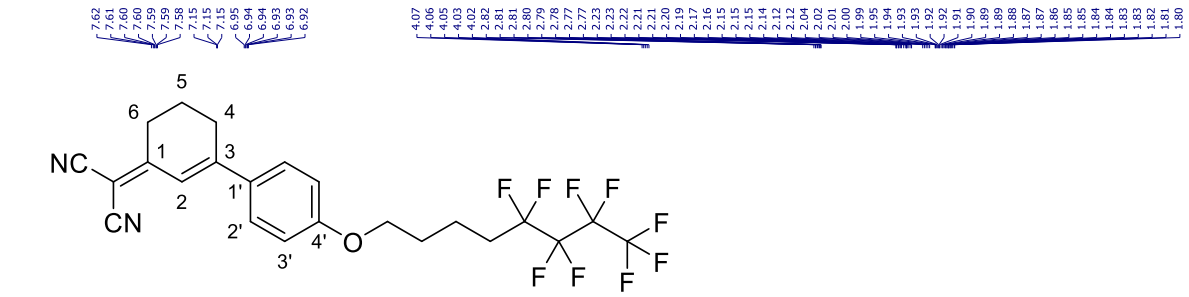

δ / ppm


NC
CN
O
Mal-1-C(14)
δ / ppm


δ / ppm

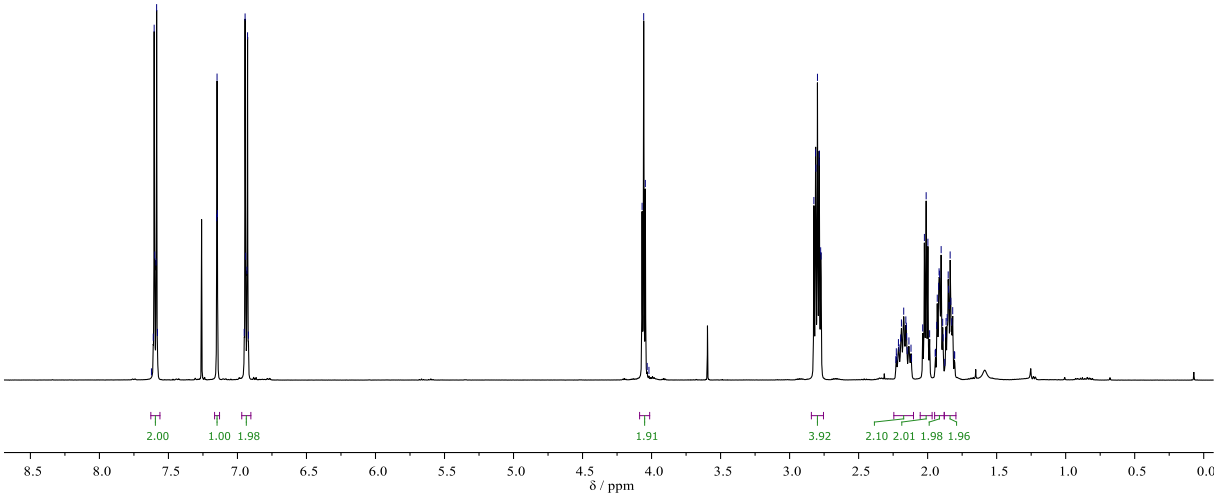

NC
CN
O
Mal-2-C(14)
δ / ppm

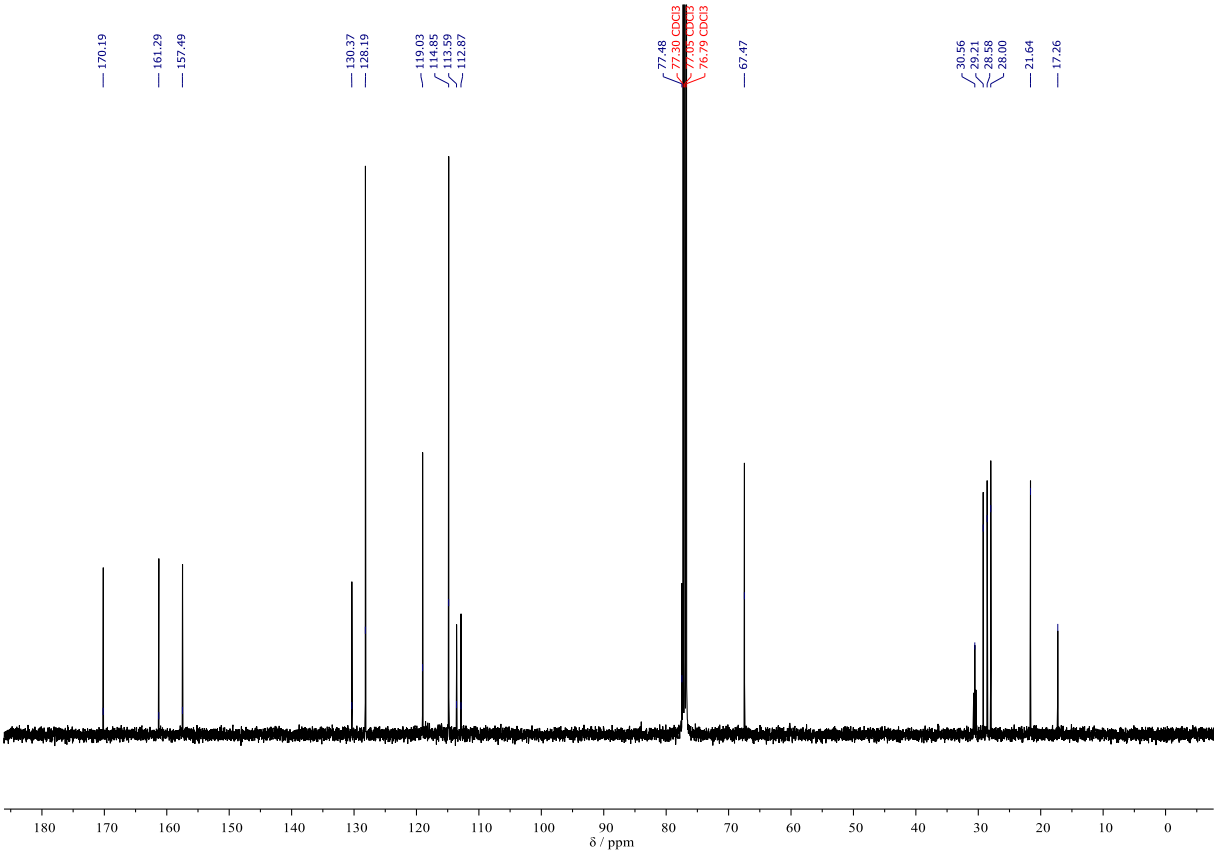

δ / ppm

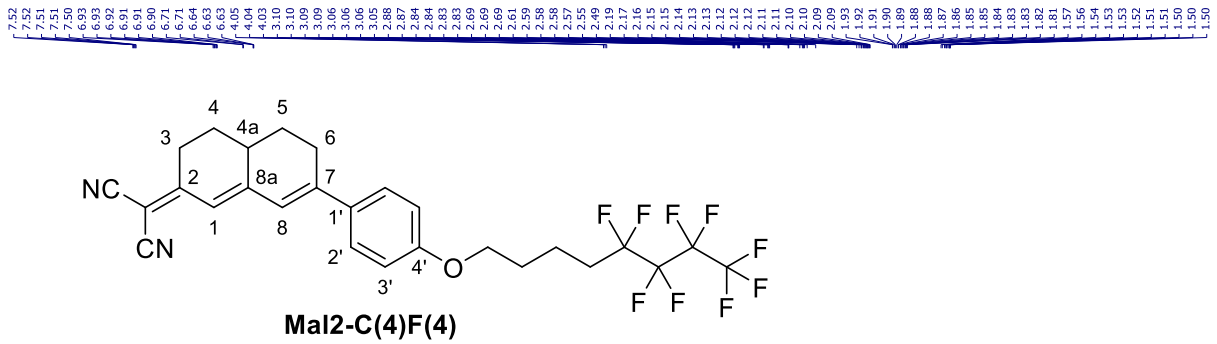

7.62
7.61
7.60
7.60
7.59
7.59
7.58
7.15
7.15
7.15
6.95
6.94
6.94
6.93
6.93
6.92
4.07
4.06
4.05
4.03
4.02
2.82
2.81
2.81
2.80
2.79
2.78
2.77
2.77
2.23
2.22
2.21
2.21
2.20
2.19
2.17
2.16
2.15
2.15
2.14
2.12
2.12
2.04
2.02
2.01
2.00
1.99
1.95
1.94
1.93
1.93
1.92
1.92
1.91
1.90
1.89
1.89
1.88
1.87
1.87
1.86
1.85
1.85
1.84
1.84
1.83
1.83
1.82
1.81
1.80

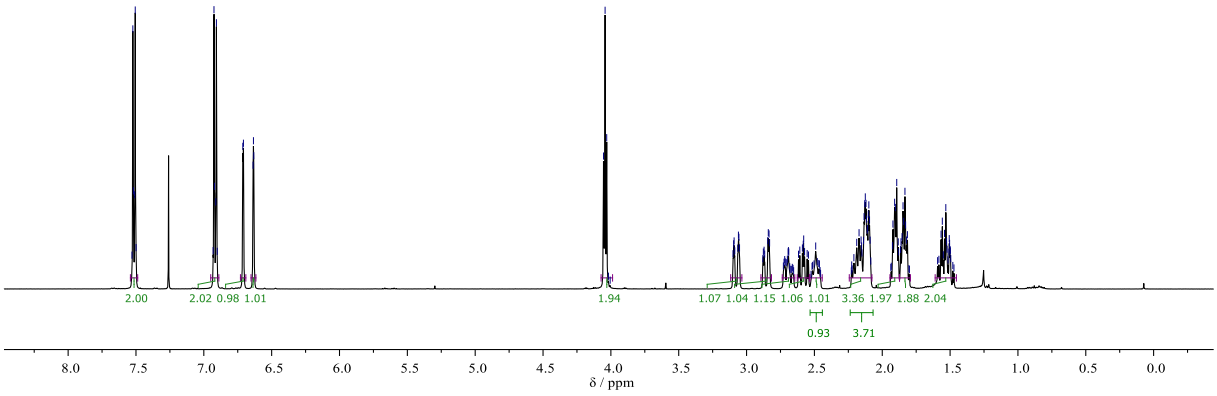
5
6
4
1
3
NC
2
1'
CN
2'
4'
O
3'
F
F
F
F
F
F
F
F
F

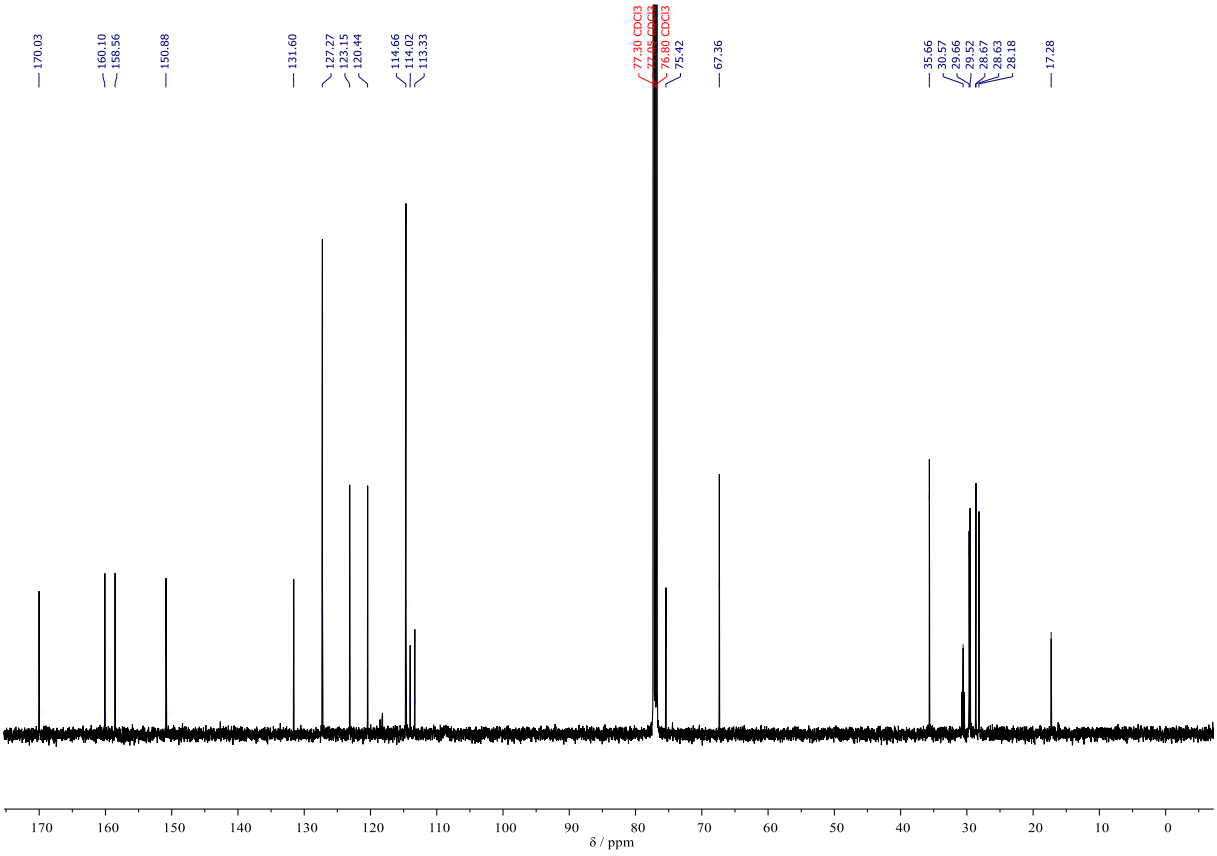
MaI-1-C(4)F(4)

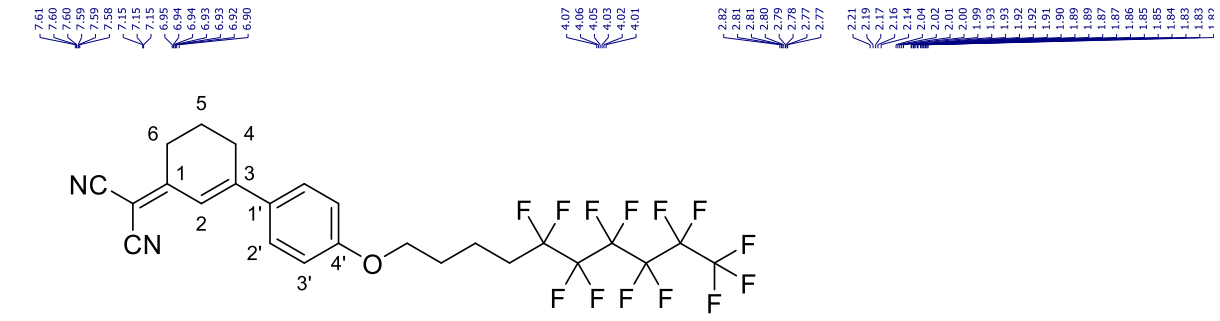

2.00
1.00
1.98
1.91
3.92
2.10
2.01
1.98
1.96
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm


170.19
161.29
157.49
130.37
128.19
119.03
114.85
113.59
112.87
77.48
77.30 CDCl3
77.05 CDCl3
76.79 CDCl3
67.47
30.56
29.21
28.58
28.00
21.64
17.26
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ / ppm


NC
CN
O
F
Mal2-C(4)F(4)

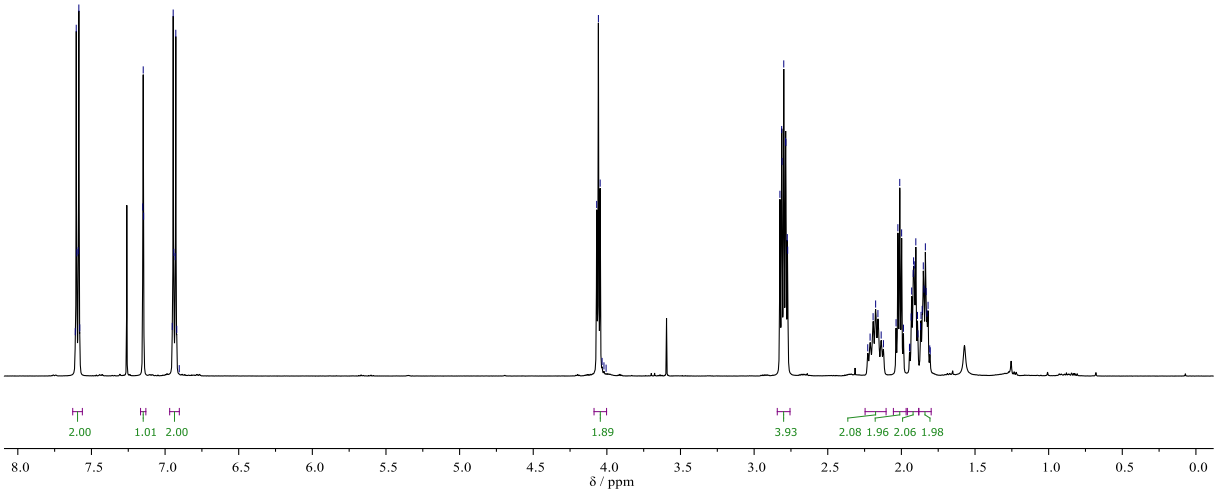

2.00
2.02 0.98 1.01
1.94
1.07 1.04 1.15 1.06 1.01 3.36 1.97 1.88 2.04
0.93
3.71
δ / ppm

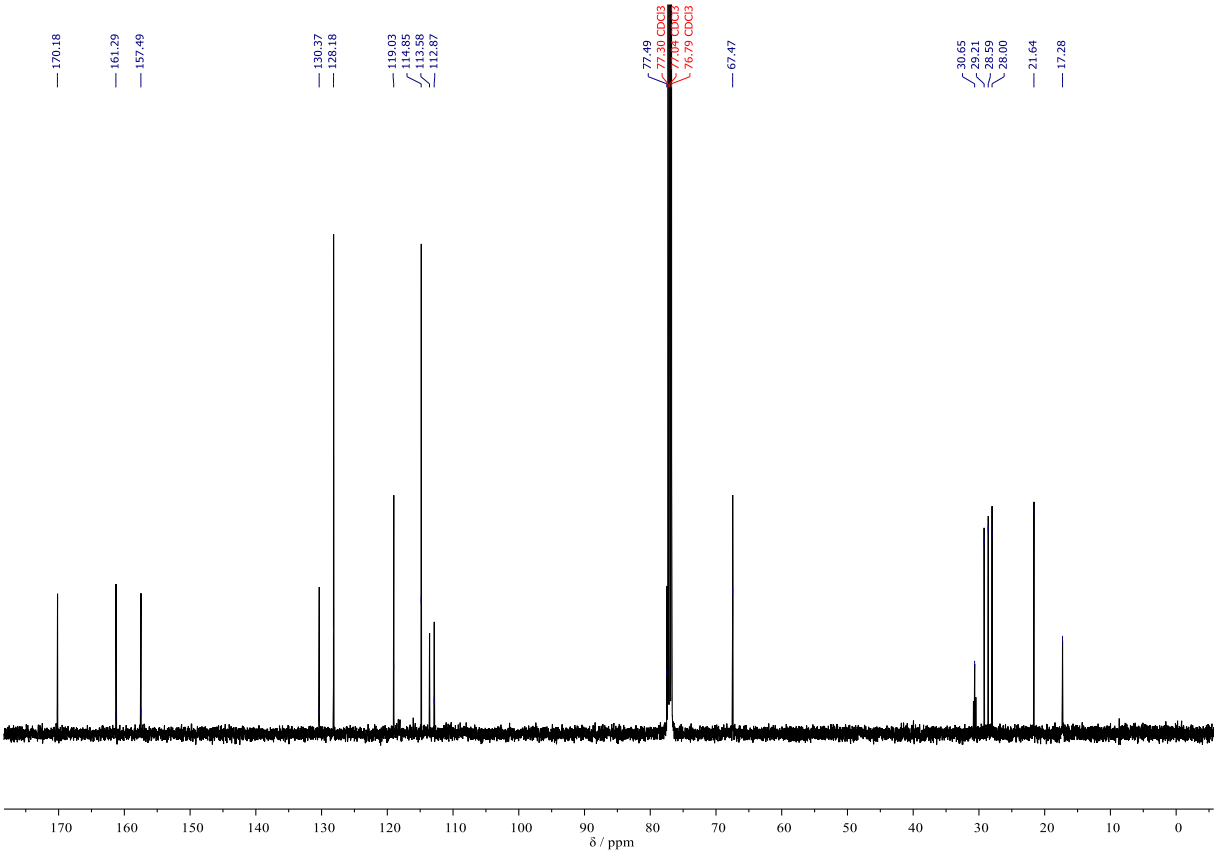

170.03
160.10
158.56
150.88
131.60
127.27
123.15
120.44
114.66
114.02
113.33
77.30 CDCl3
77.05 CDCl3
76.80 CDCl3
75.42
67.36
35.66
30.57
29.66
29.52
28.67
28.63
28.18
17.28
δ / ppm

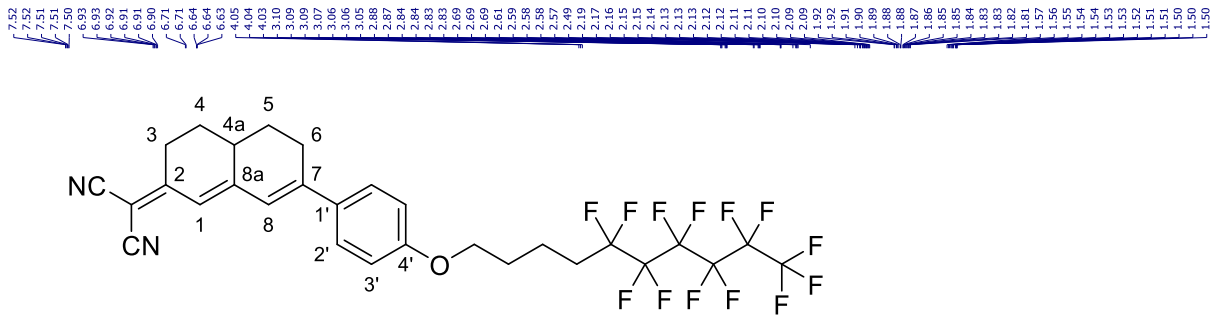

7.61
7.60
7.60
7.59
7.59
7.58
7.15
7.15
7.15
6.95
6.94
6.94
6.93
6.93
6.92
6.90
4.07
4.06
4.05
4.03
4.02
4.01
2.82
2.81
2.81
2.80
2.79
2.78
2.77
2.77
2.21
2.19
2.17
2.16
2.14
2.04
2.02
2.01
2.00
1.99
1.93
1.93
1.92
1.92
1.91
1.90
1.89
1.89
1.87
1.87
1.86
1.85
1.85
1.84
1.83
1.83

5
6
4
1
3
NC
CN
2
1'
2'
4'
O
3'
F
F
F
F
F
F
F
F
F
F
F
F
F

MaI-1-C(4)F(6)

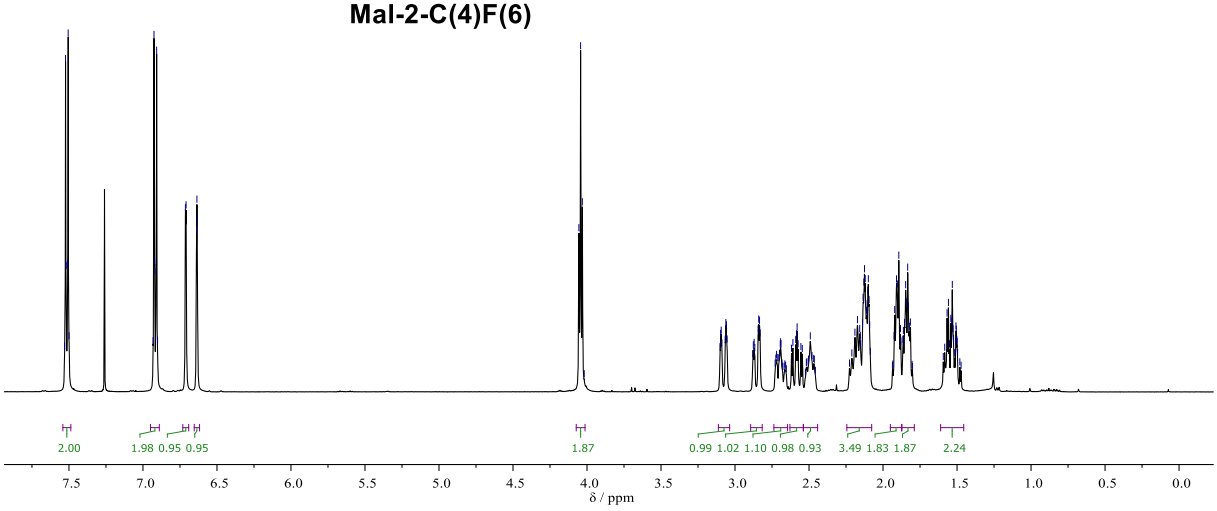

2.00
1.01
2.00
1.89
3.93
2.08
1.96
2.06
1.98
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm

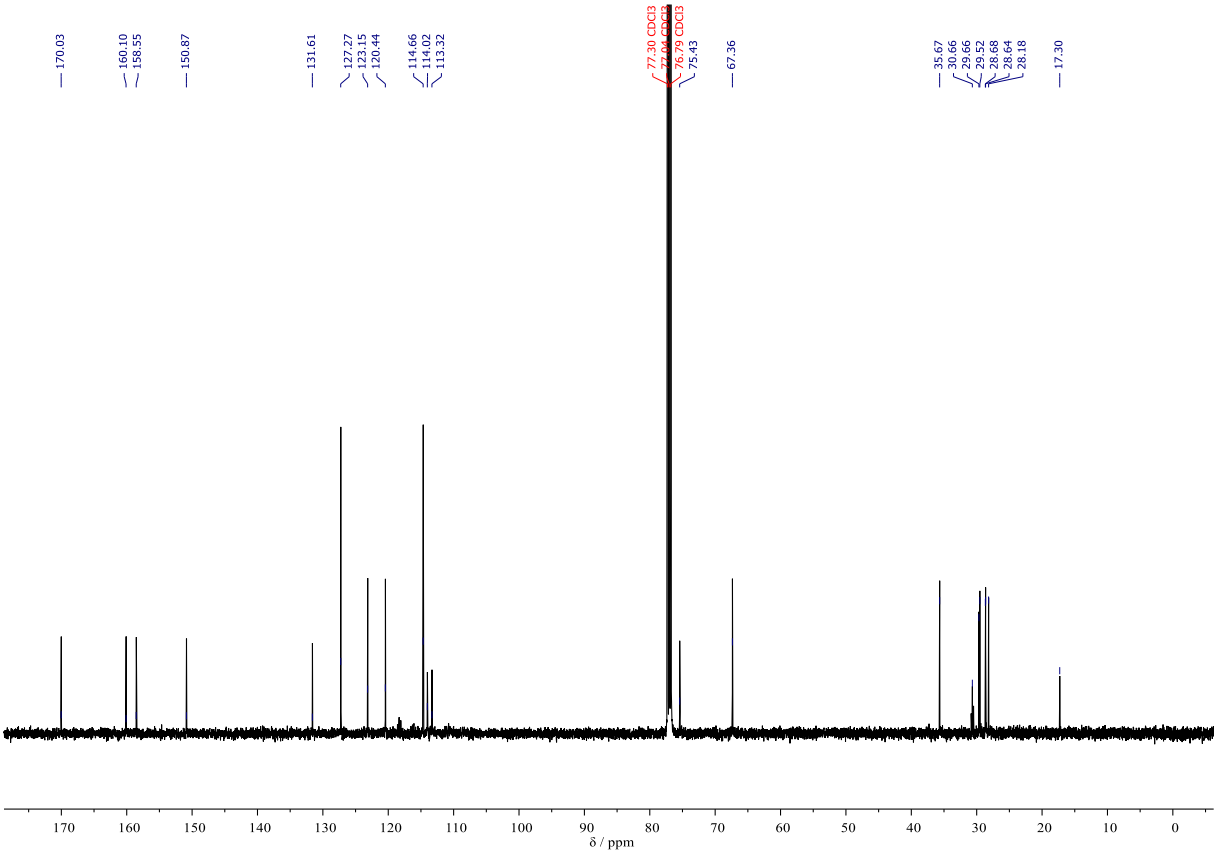

170.18
161.29
157.49
130.37
128.18
119.03
114.85
113.58
112.87
77.49
77.30 CDCl3
77.04 CDCl3
76.79 CDCl3
67.47
30.65
29.21
28.59
28.00
21.64
17.28
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ / ppm

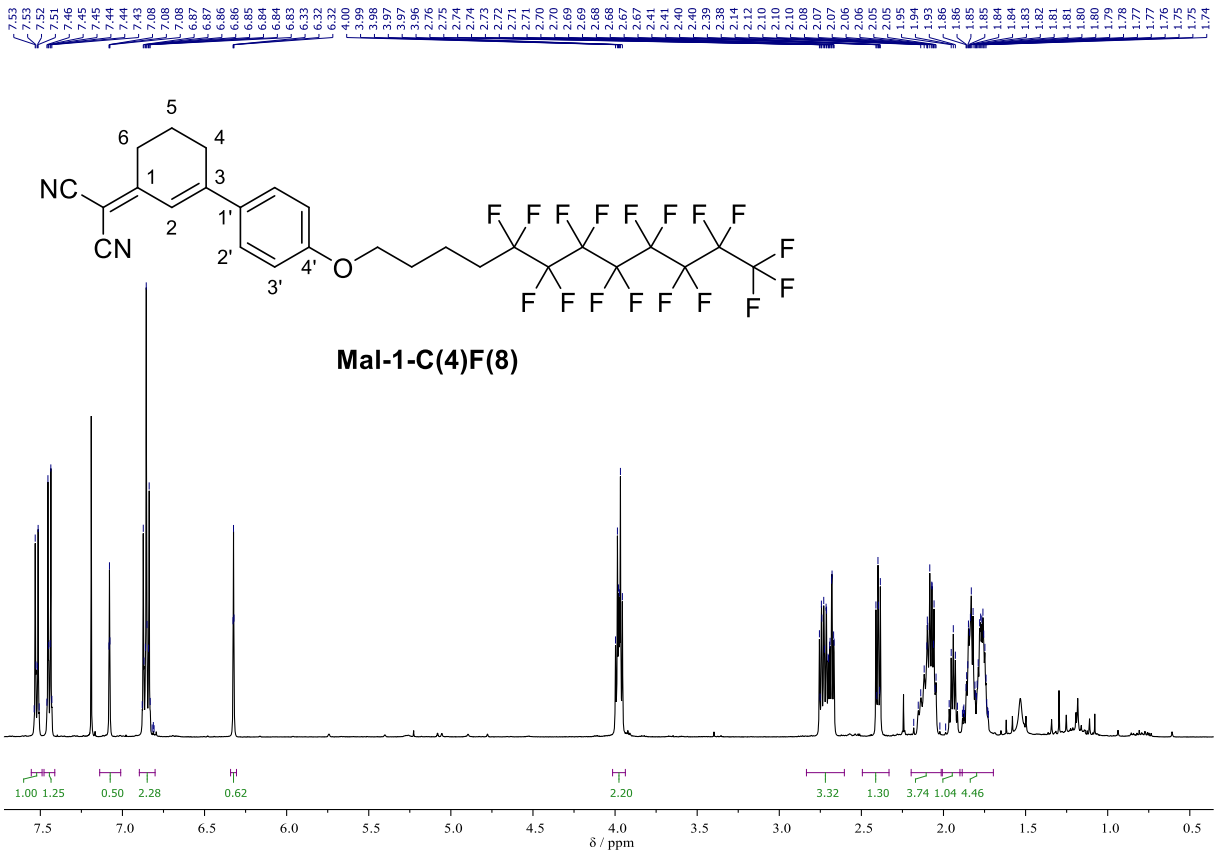


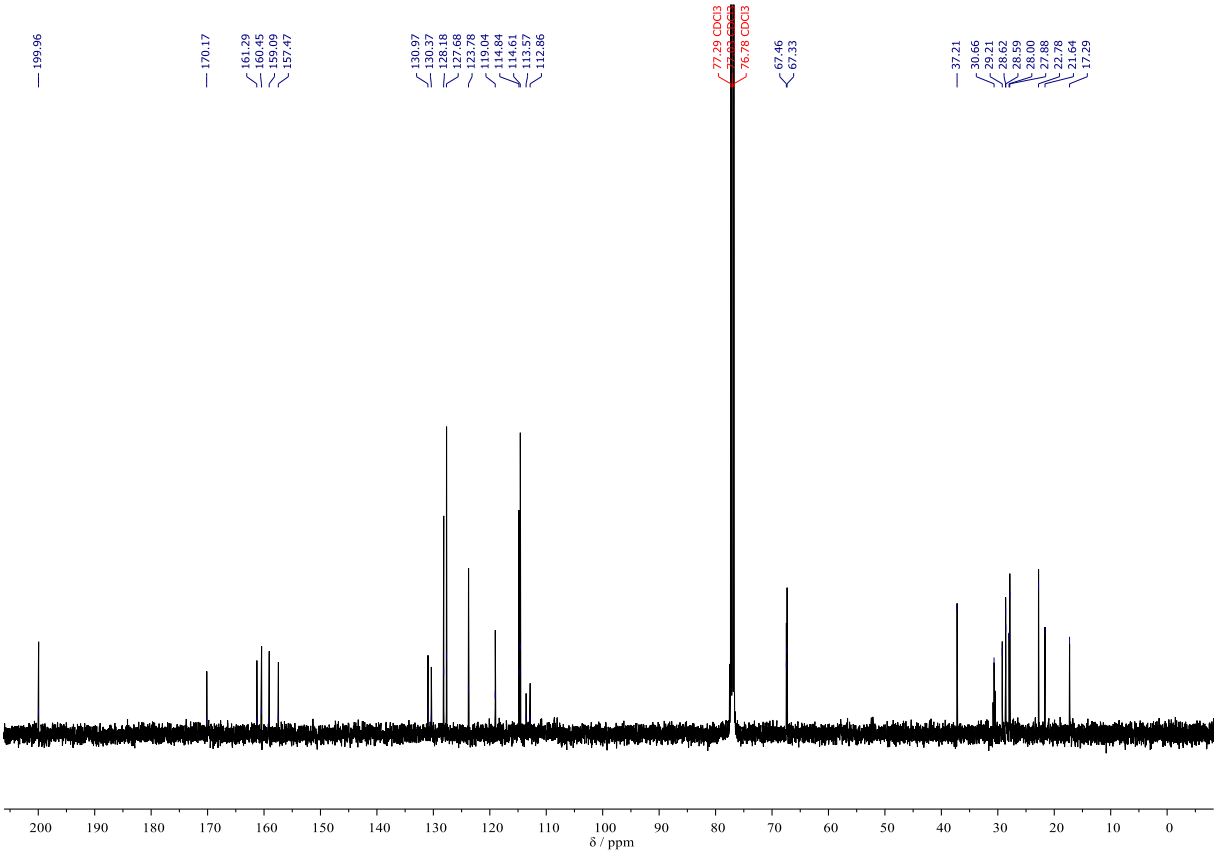
4
5
4a
3
6
2
8a
7
NC
1
8
1'
CN
2'
4'
O
3'
F F F F F F
F
F F F F F
F

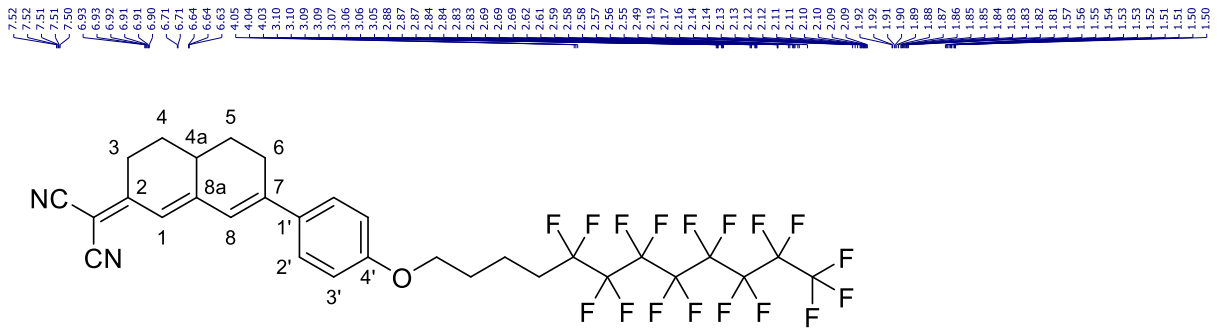
Mal-2-C(4)F(6)

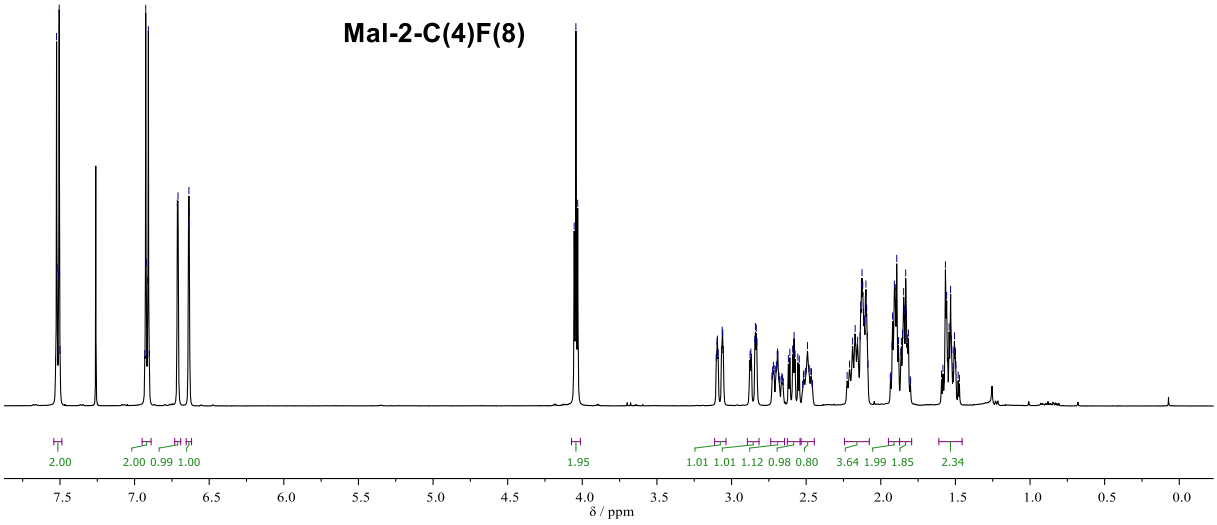

2.00
1.98 0.95 0.95
1.87
0.99 1.02 1.10 0.98 0.93
3.49 1.83 1.87
2.24
δ / ppm

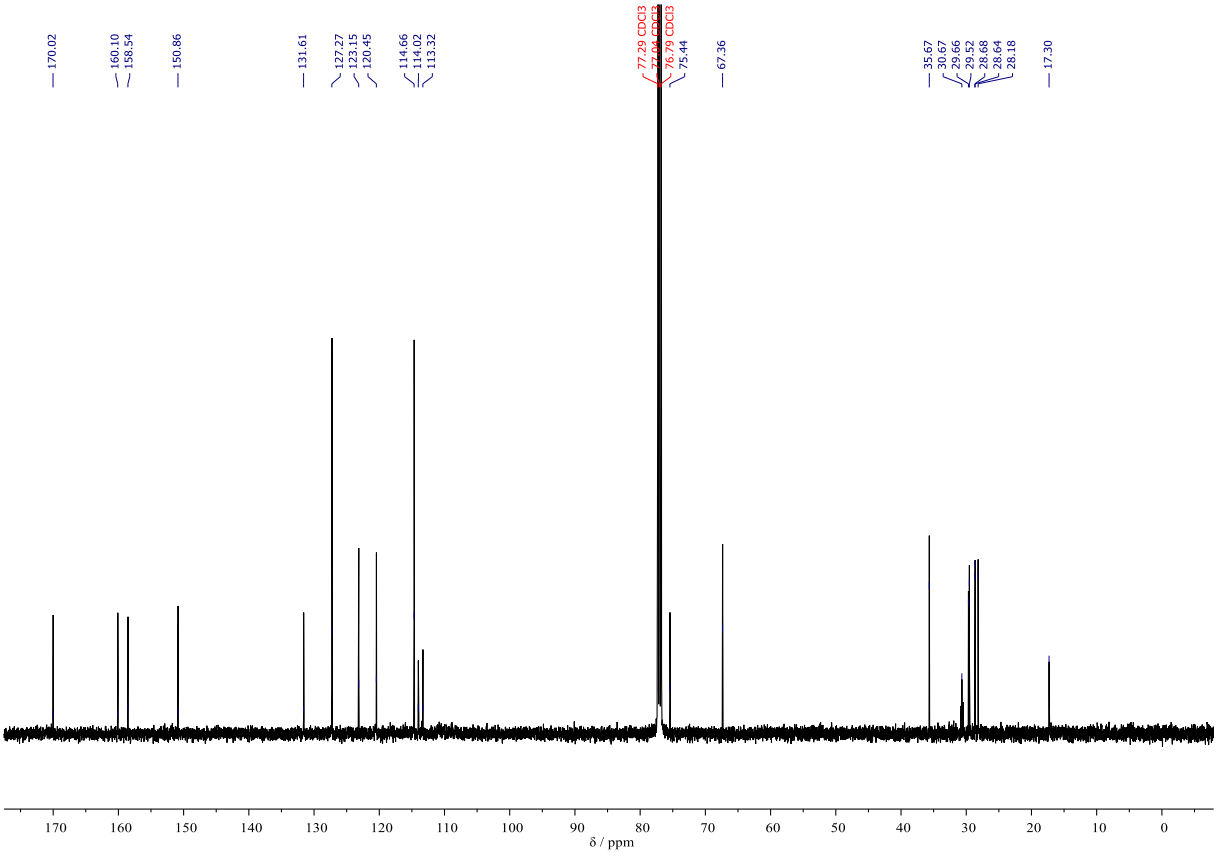

170.03
160.10
158.55
150.87
131.61
127.27
123.15
120.44
114.66
114.02
113.32
77.30 CDCl3
77.04 CDCl3
76.79 CDCl3
75.43
67.36
35.67
30.66
29.66
29.52
28.68
28.64
28.18
17.30
δ / ppm

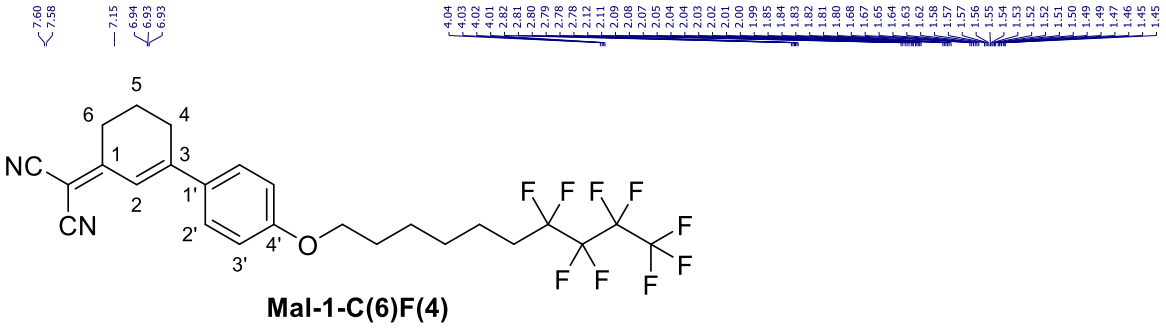

NC
CN
O
F
Mal-1-C(4)F(8)
1.00 1.25
0.50
2.28
0.62
2.20
3.32
1.30
3.74 1.04 4.46
δ / ppm


199.96
170.17
161.29
160.45
159.09
157.47
130.97
130.37
128.18
127.68
123.78
119.04
114.84
114.61
113.57
112.86
77.29 CDCl3
76.78 CDCl3
67.46
67.33
37.21
30.66
29.21
28.62
28.59
28.00
27.88
22.78
21.64
17.29
δ / ppm

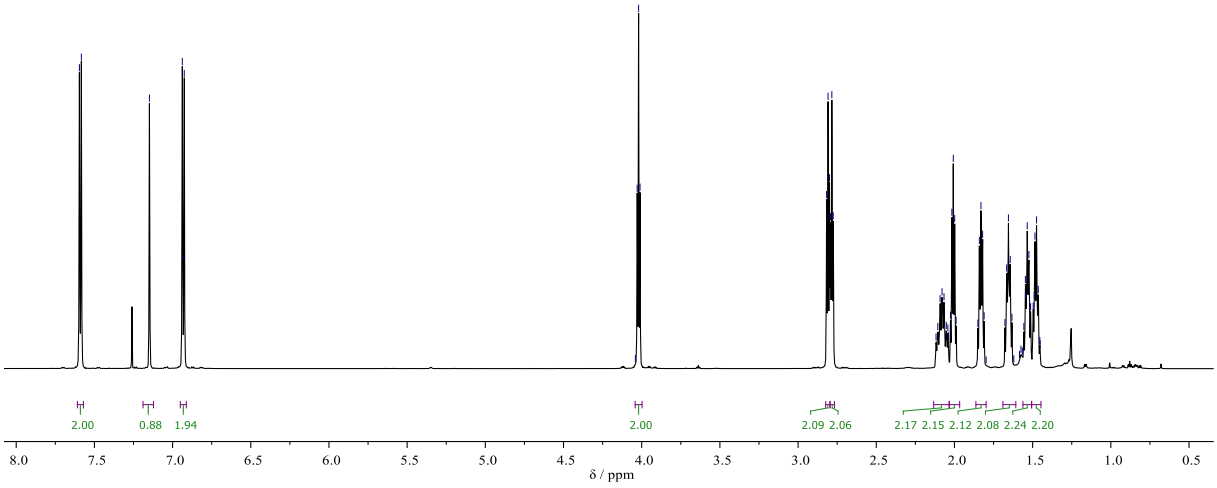

NC
CN
O
F
4
5
4a
3
6
2
8a
7
1
8
1'
2'
3'
4'

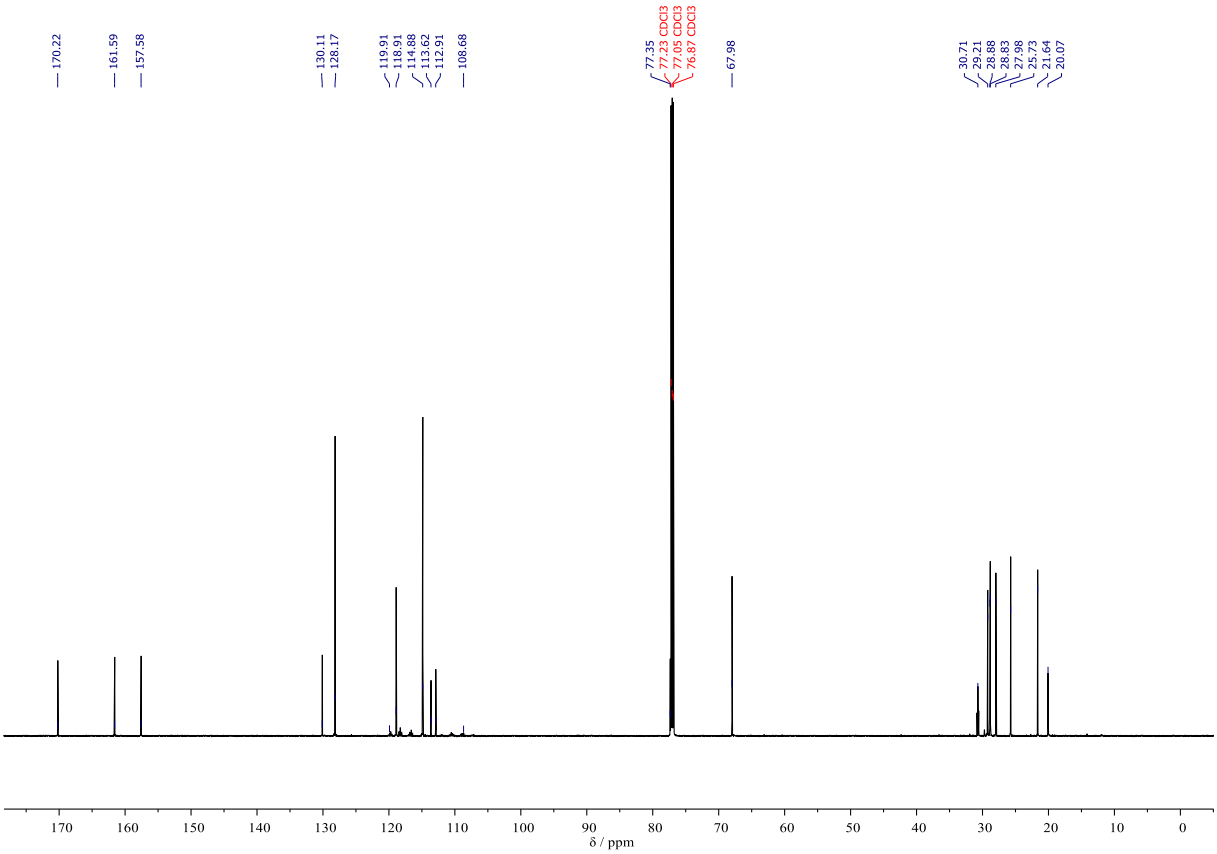

MaI-2-C(4)F(8)
2.00
2.00 0.99 1.00
1.95
1.01 1.01 1.12 0.98 0.80
3.64 1.99 1.85
2.34
δ / ppm

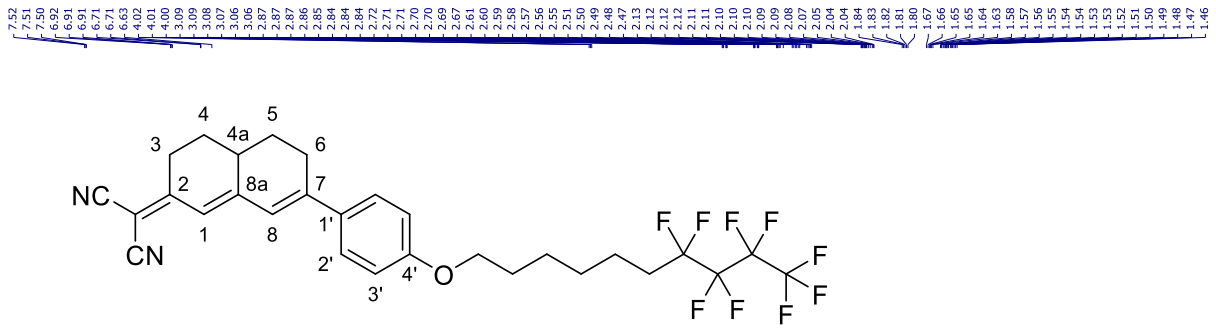

170.02
160.10
158.54
150.86
131.61
127.27
123.15
120.45
114.66
114.02
113.32
77.29 CDCl3
77.04 CDCl3
76.79 CDCl3
75.44
67.36
35.67
30.67
29.66
29.52
28.68
28.64
28.18
17.30
δ / ppm


7.60
7.58
7.15
6.94
6.93
6.93
4.04
4.03
4.02
4.01
2.82
2.81
2.80
2.79
2.78
2.78
2.12
2.11
2.09
2.08
2.07
2.05
2.04
2.04
2.03
2.02
2.01
2.00
1.99
1.85
1.84
1.83
1.82
1.81
1.80
1.68
1.67
1.65
1.64
1.63
1.62
1.58
1.57
1.57
1.56
1.55
1.54
1.53
1.52
1.52
1.51
1.50
1.49
1.49
1.47
1.46
1.45
1.45
5
6
4
1
3
NC
2
1'
CN
2'
4'
O
3'
F
F
F
F
F
F
F
F
F

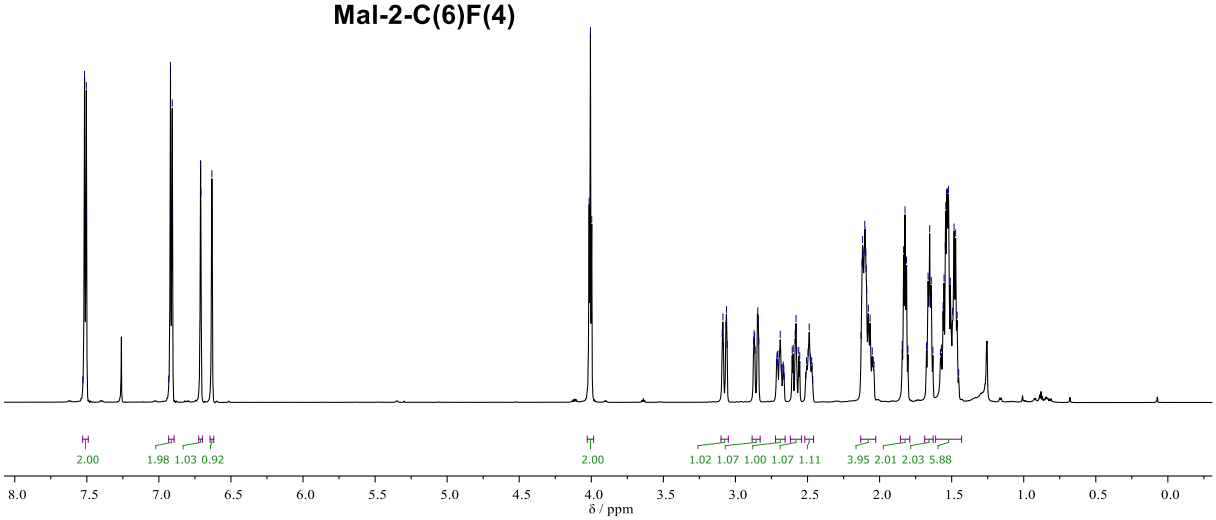
MaI-1-C(6)F(4)

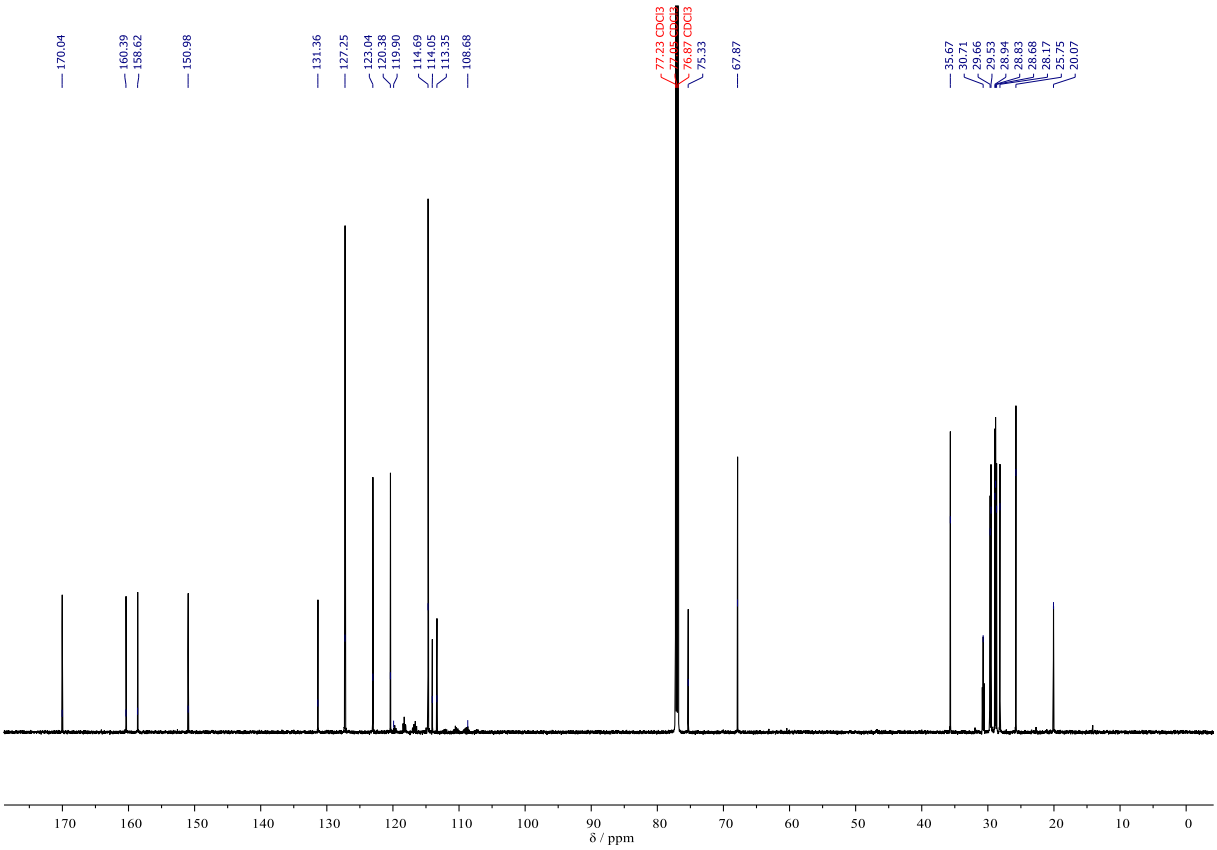

2.00
0.88
1.94
2.00
2.09 2.06
2.17 2.15 2.12 2.08 2.24 2.20
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
δ / ppm


170.22
161.59
157.58
130.11
128.17
119.91
118.91
114.88
113.62
112.91
108.68
77.35
77.23 CDCl3
77.05 CDCl3
76.87 CDCl3
67.98
30.71
29.21
28.88
29.83
25.98
25.73
21.64
20.07
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ / ppm


4
5
4a
3
6
2
8a
7
NC
1
8
1'
CN
2'
4'
O
3'
F
F
F
F
F
F
F
F
F

Mal-2-C(6)F(4)


2.00
1.98 1.03 0.92
2.00
1.02 1.07 1.00 1.07 1.11
3.95 2.01 2.03 5.88
δ / ppm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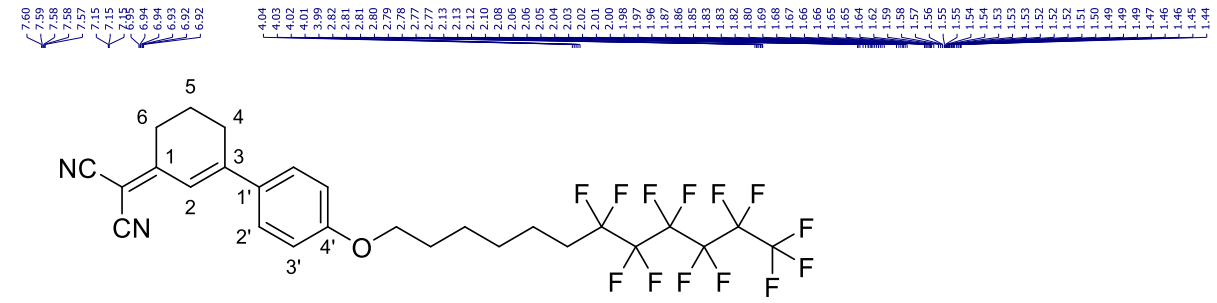
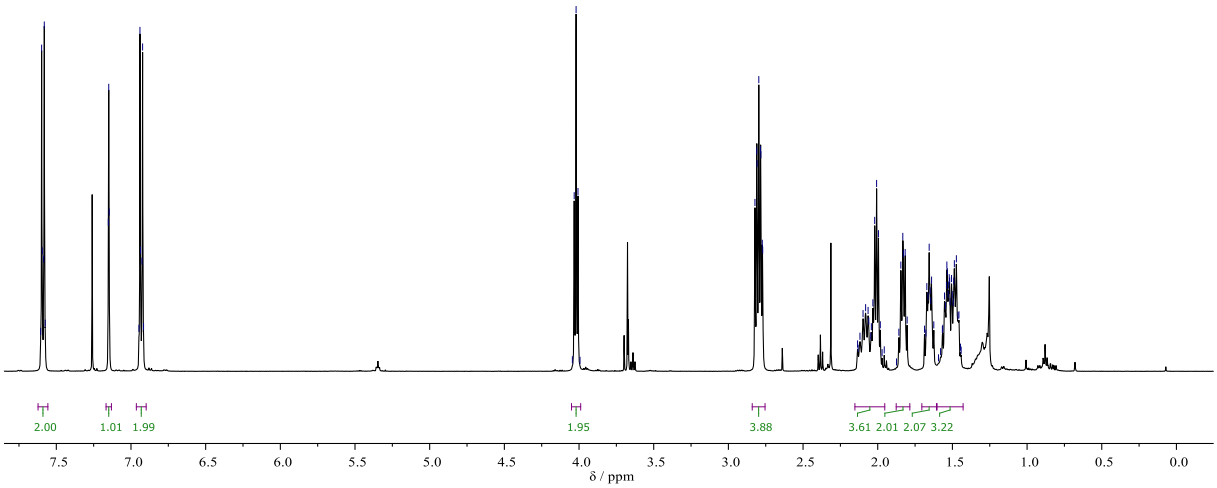
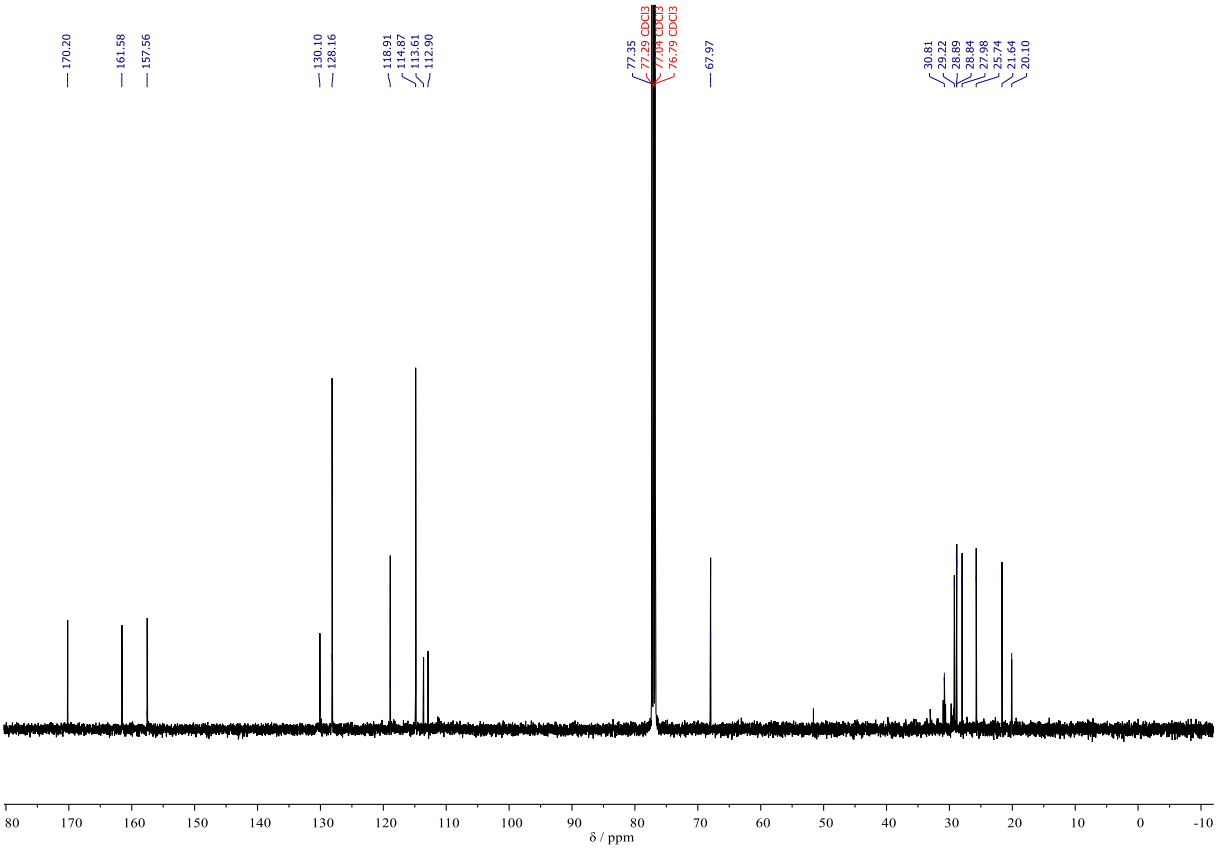
150.98
131.36
127.25
123.04
120.38
119.90
114.69
114.05
113.35
108.68
77.23 CDCl3
76.87 CDCl3
75.33
67.87
35.67
30.71
29.66
29.53
28.94
28.83
28.68
28.17
25.75
20.07
δ / ppm


NC
CN
O
F

MaI-1-C(6)F(6)


2.00
1.01
1.99
1.95
3.88
3.61 2.01 2.07 3.22
δ / ppm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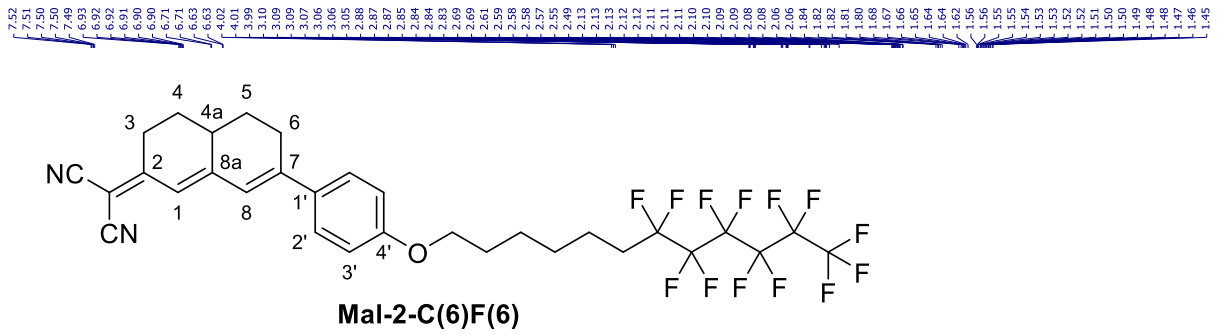
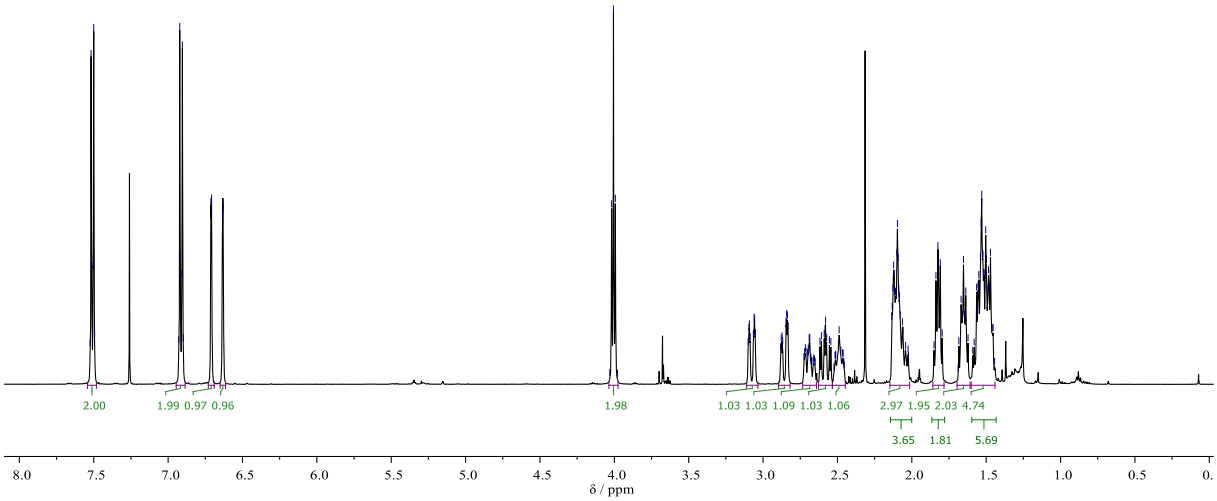
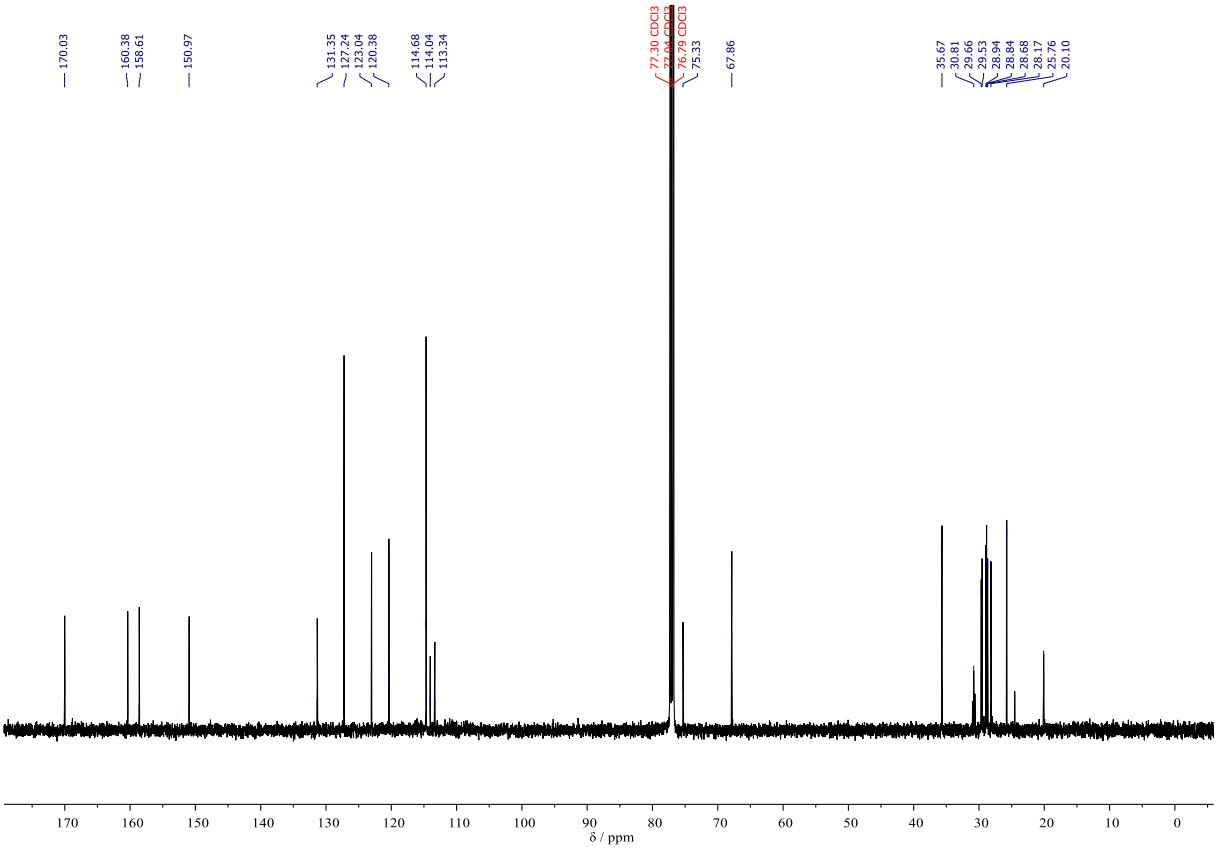
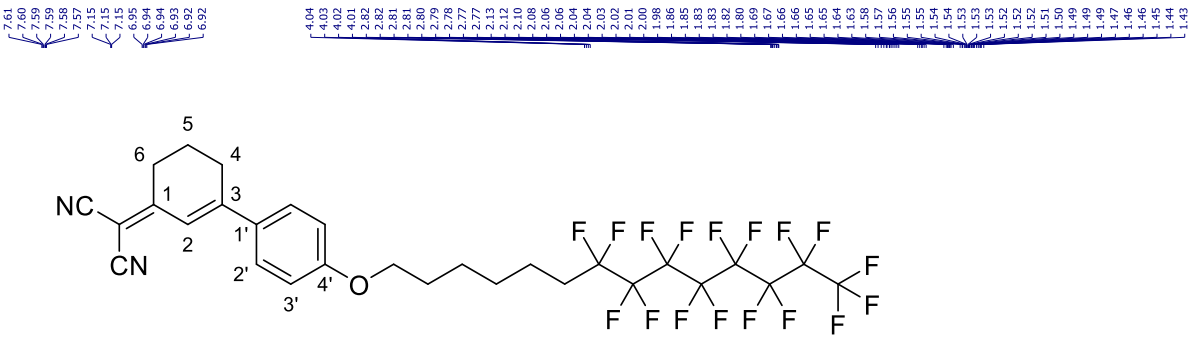
161.58
157.56
130.10
128.16
118.91
114.87
113.61
112.90
77.35
77.29 CDCl3
77.04 CDCl3
76.79 CDCl3
67.97
30.81
29.22
28.89
28.84
27.98
25.74
21.64
20.10
δ / ppm


NC
CN
O
F
4
5
4a
3
6
2
8a
7
1
8
1'
2'
4'
3'

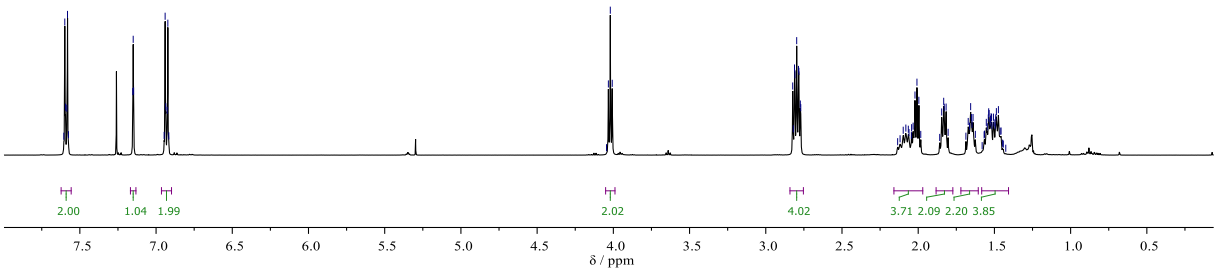
MaI-2-C(6)F(6)


2.00
1.99 0.97 0.96
1.98
1.03 1.03 1.09 1.03 1.06
2.97 1.95 2.03 4.74
3.65 1.81 5.69
δ / ppm


170.03
160.38
158.61
150.97
131.35
127.24
123.04
120.38
114.68
114.04
113.34
77.30 CDCl3
77.04 CDCl3
76.79 CDCl3
75.33
67.86
35.67
30.81
29.66
29.53
28.94
28.84
28.68
28.17
25.76
20.10
δ / ppm


NC
CN
O
F

Mal-1-C(6)F(8)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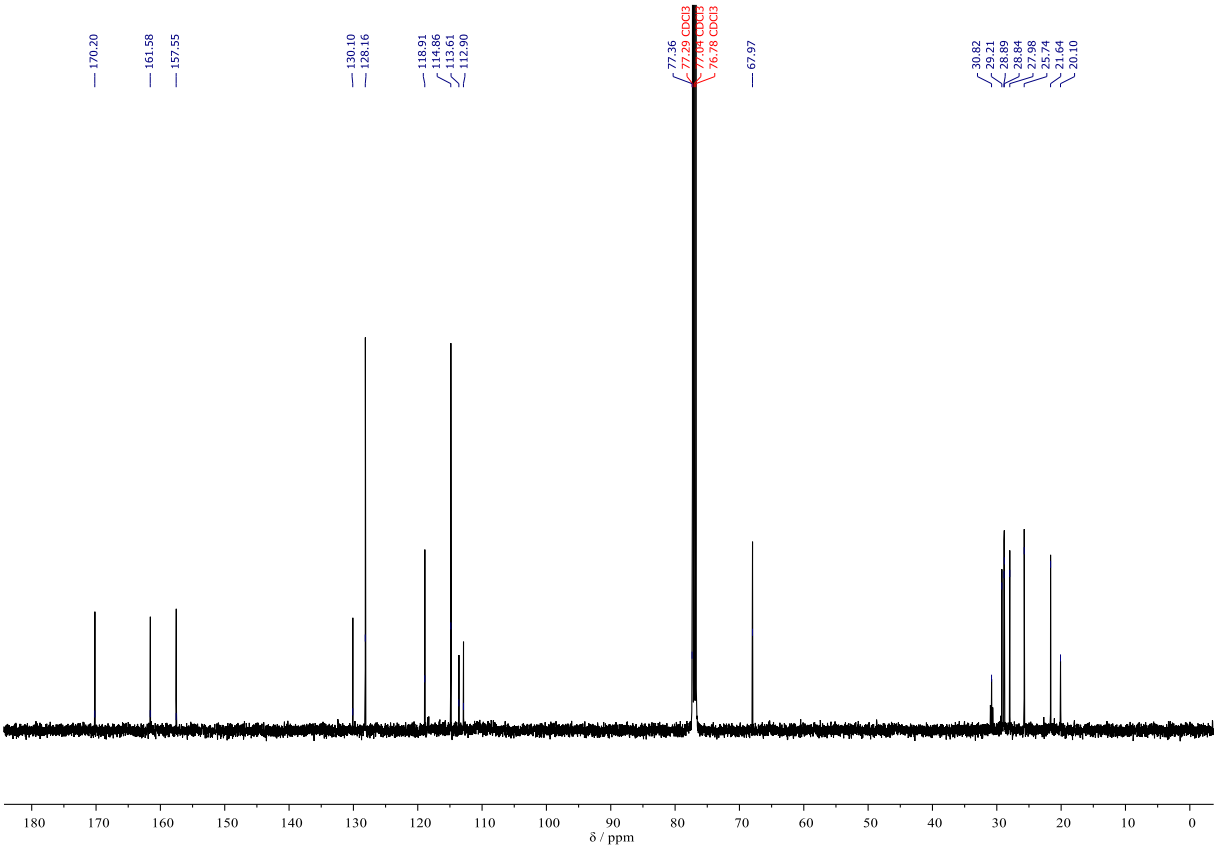
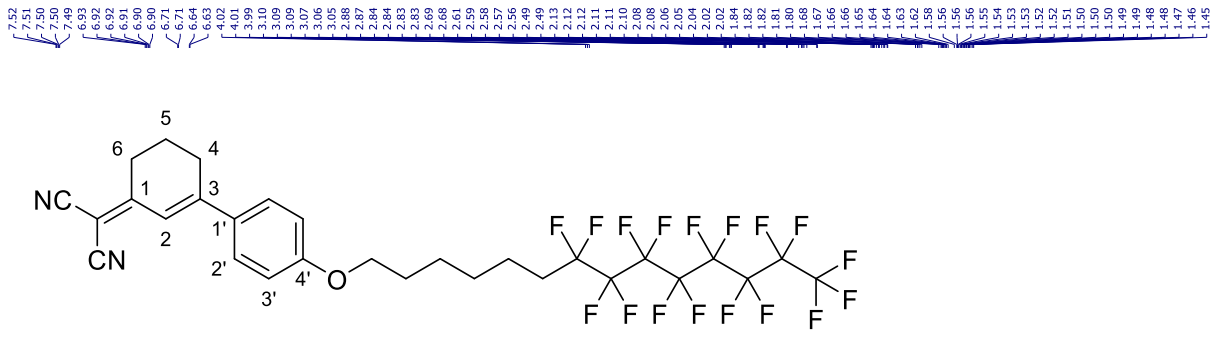
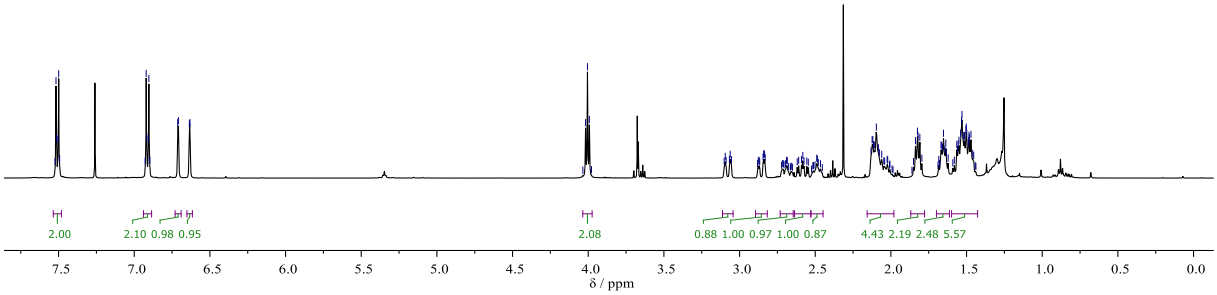
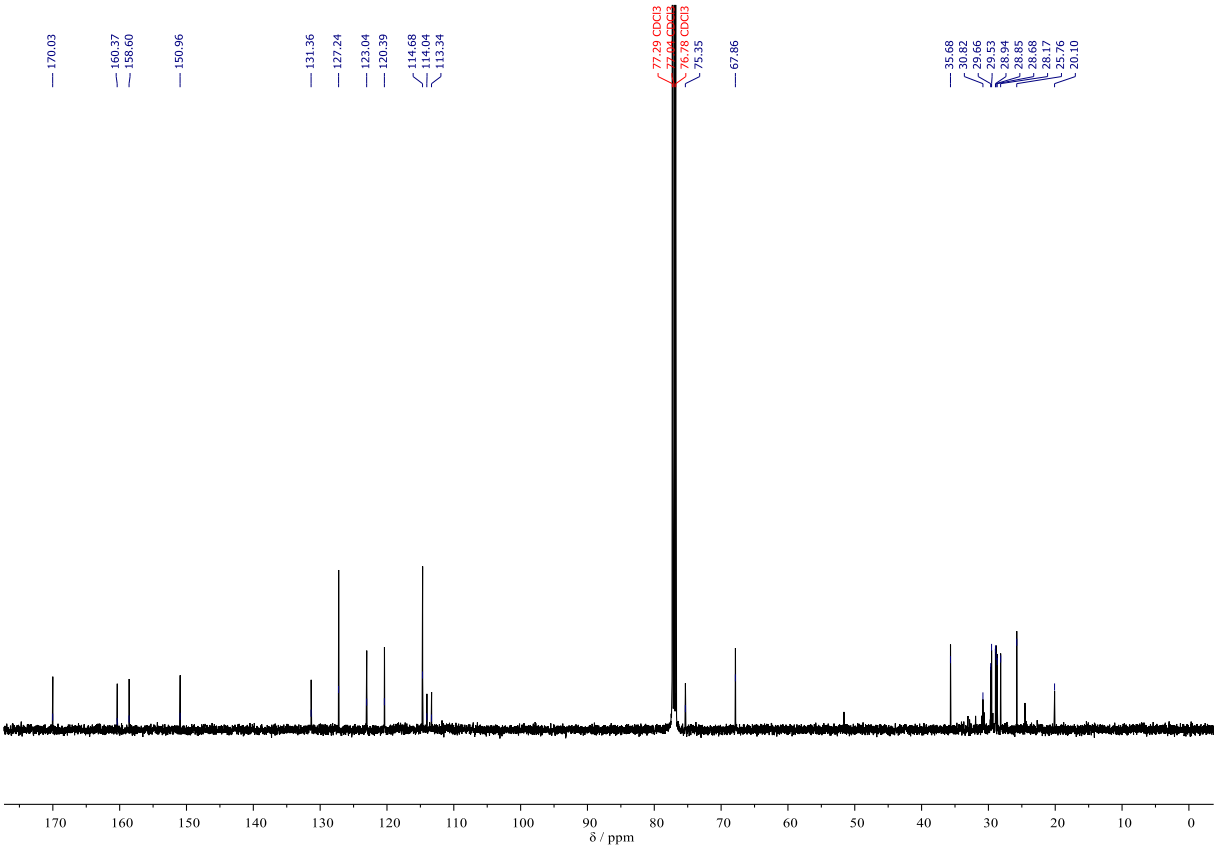
1.04
1.99
2.02
4.02
3.71
2.09
2.20
3.85
δ / ppm

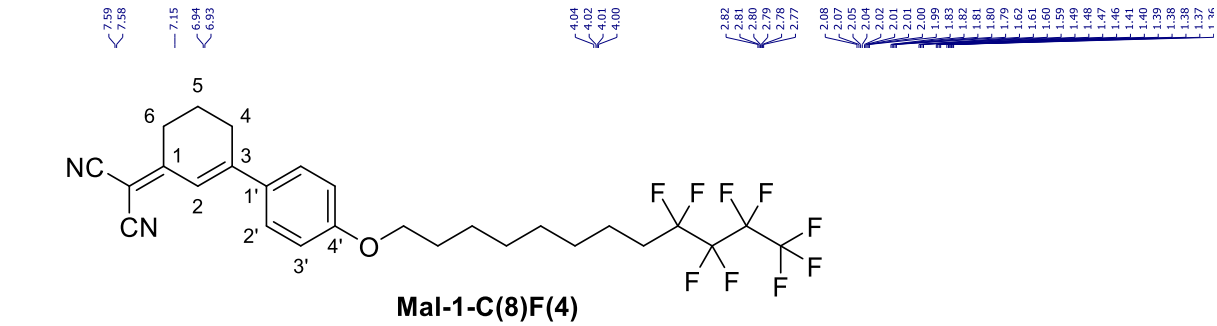

170.20
161.58
157.55
130.10
128.16
118.91
114.86
113.61
112.90
77.36
77.29 CDCl3
77.04 CDCl3
76.78 CDCl3
67.97
30.82
29.21
28.85
28.84
27.98
25.74
21.64
20.10
δ / ppm


NC
CN
O
F

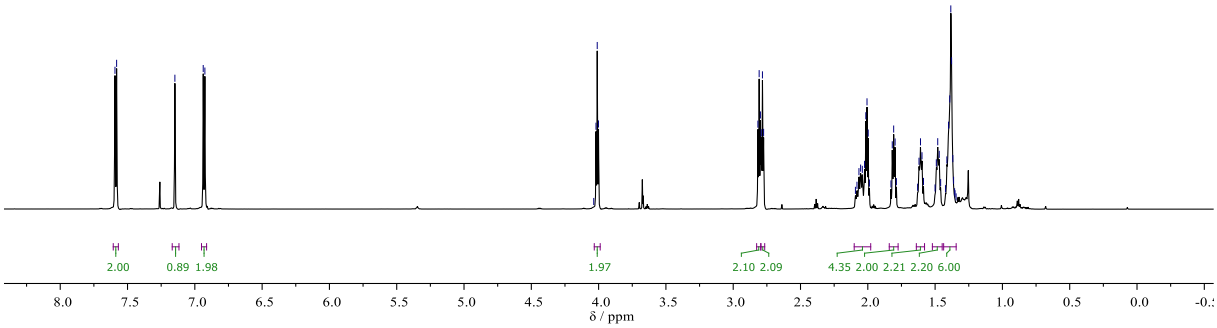
MaI-2-C(6)F(8)

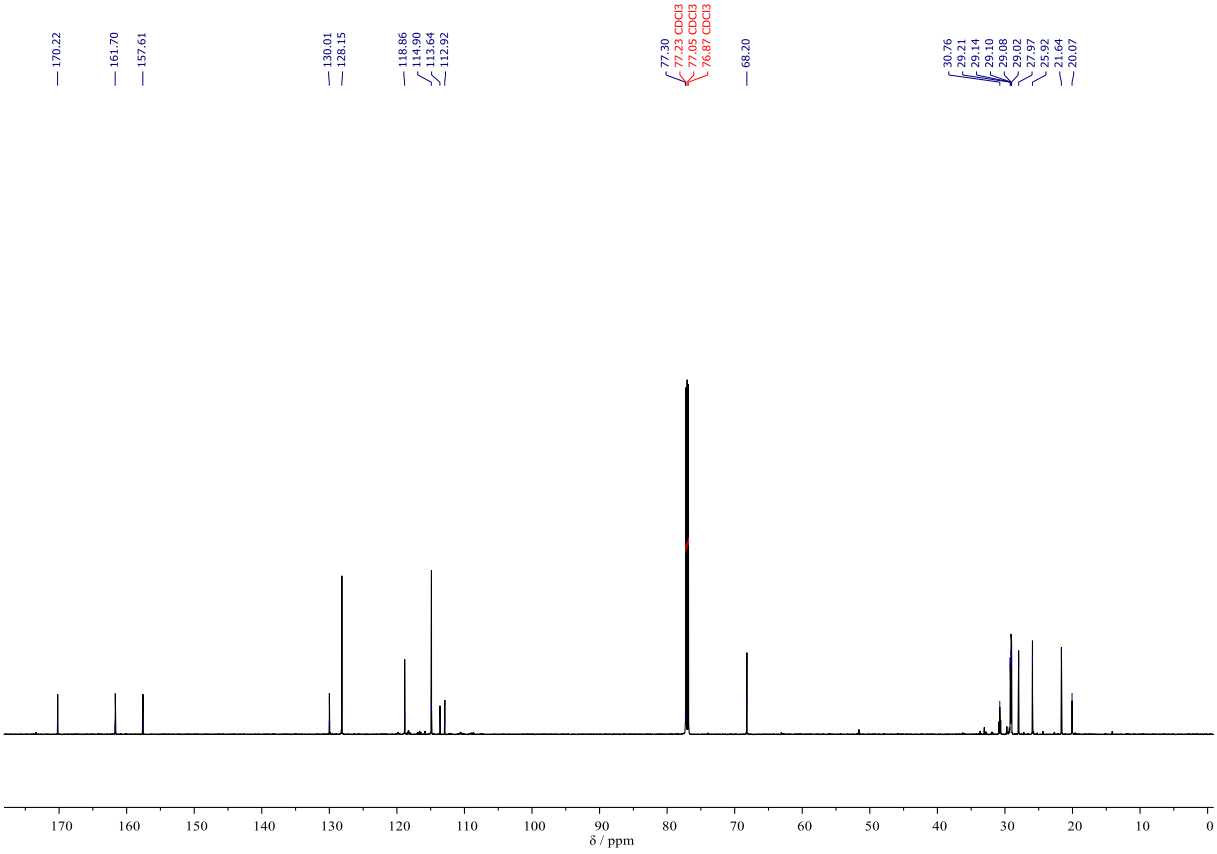

2.00
2.10 0.98 0.95
2.08
0.88 1.00 0.97 1.00 0.87
4.43 2.19 2.48 5.57
δ / ppm

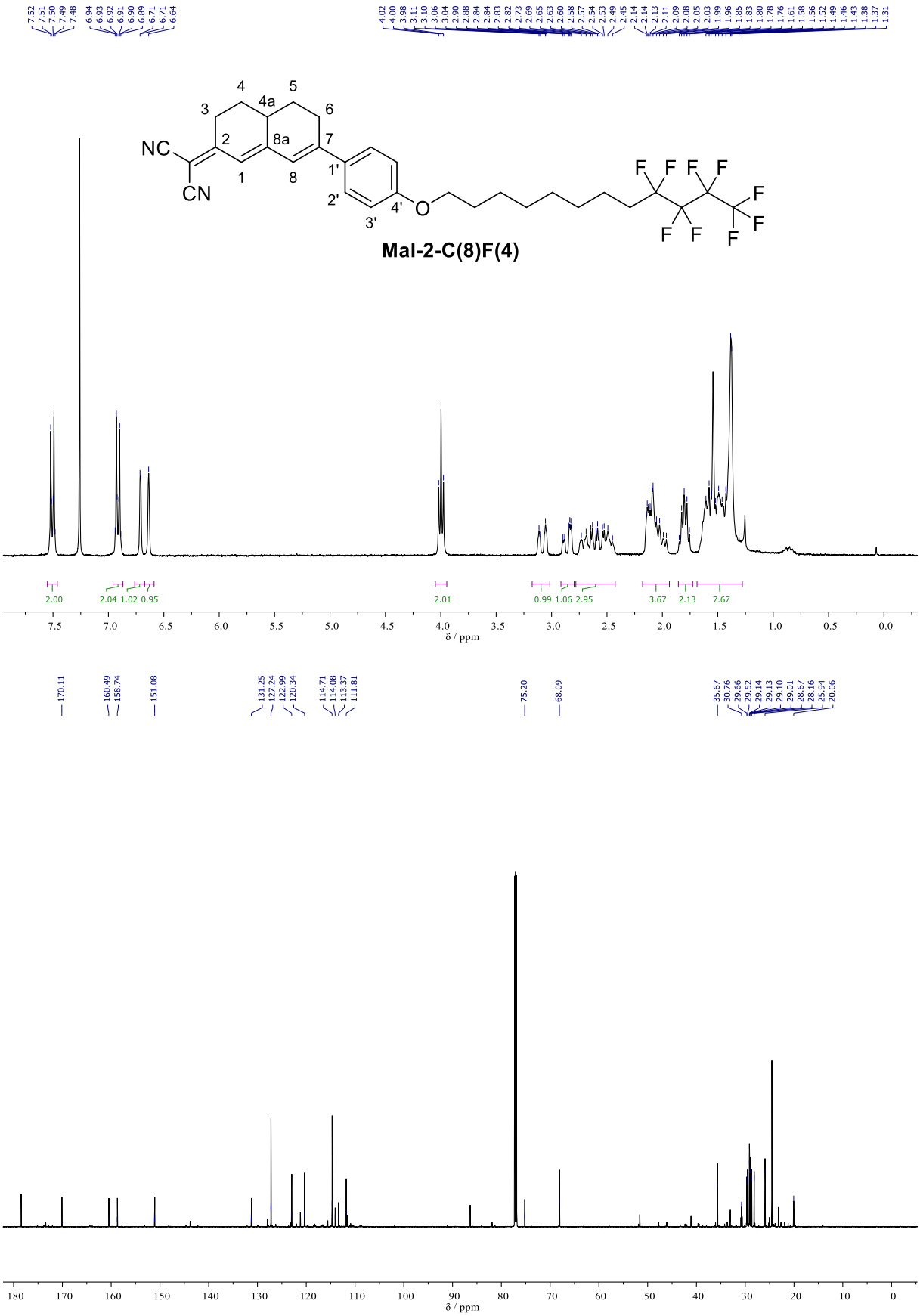

170.03
160.37
158.60
150.96
131.36
127.24
123.04
120.39
114.68
114.04
113.34
77.29 CDCl3
76.78 CDCl3
75.35
67.86
35.68
30.82
29.66
29.53
28.94
28.85
28.68
28.17
25.76
20.10
δ / ppm

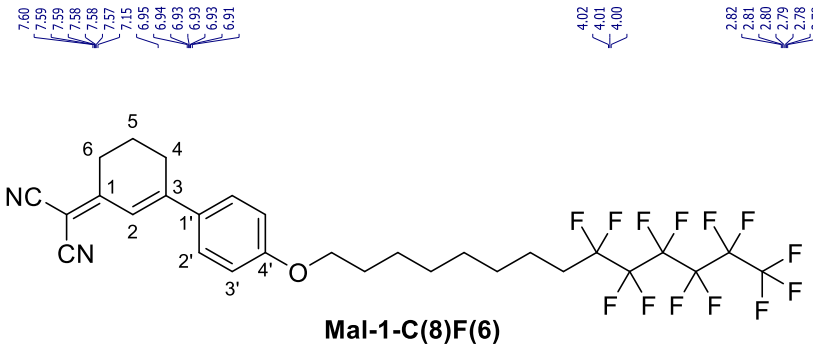

7.59
7.58
7.15
6.94
6.93
4.04
4.02
4.01
4.00
2.82
2.81
2.80
2.79
2.78
2.77
2.08
2.07
2.05
2.04
2.02
2.01
2.01
2.00
1.99
1.83
1.82
1.81
1.80
1.79
1.62
1.61
1.60
1.59
1.49
1.48
1.47
1.46
1.41
1.40
1.39
1.38
1.38
1.37
5
6
4
1
3
NC
2
1'
CN
2'
4'
O
3'
F
F
F
F
F
F
F
F
F

MaI-1-C(8)F(4)

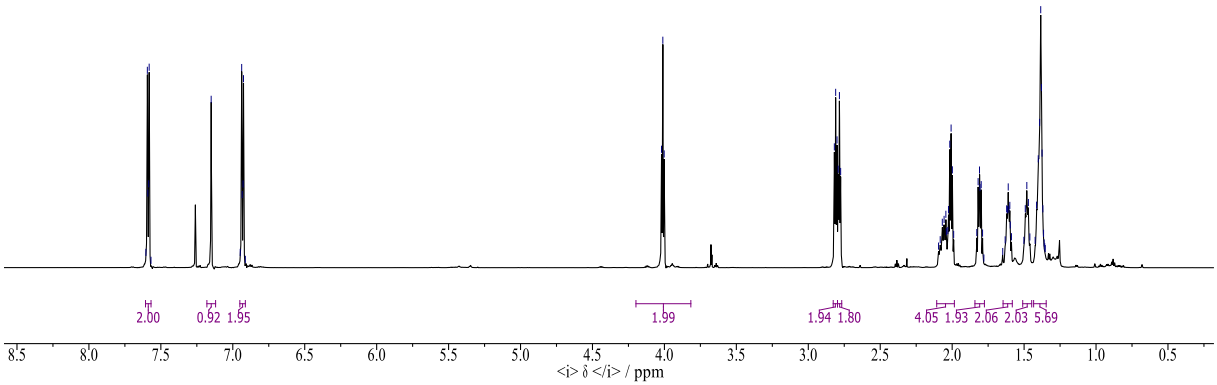

2.00
0.89
1.98
1.97
2.10
2.09
4.35
2.00
2.21
2.20
6.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ / ppm

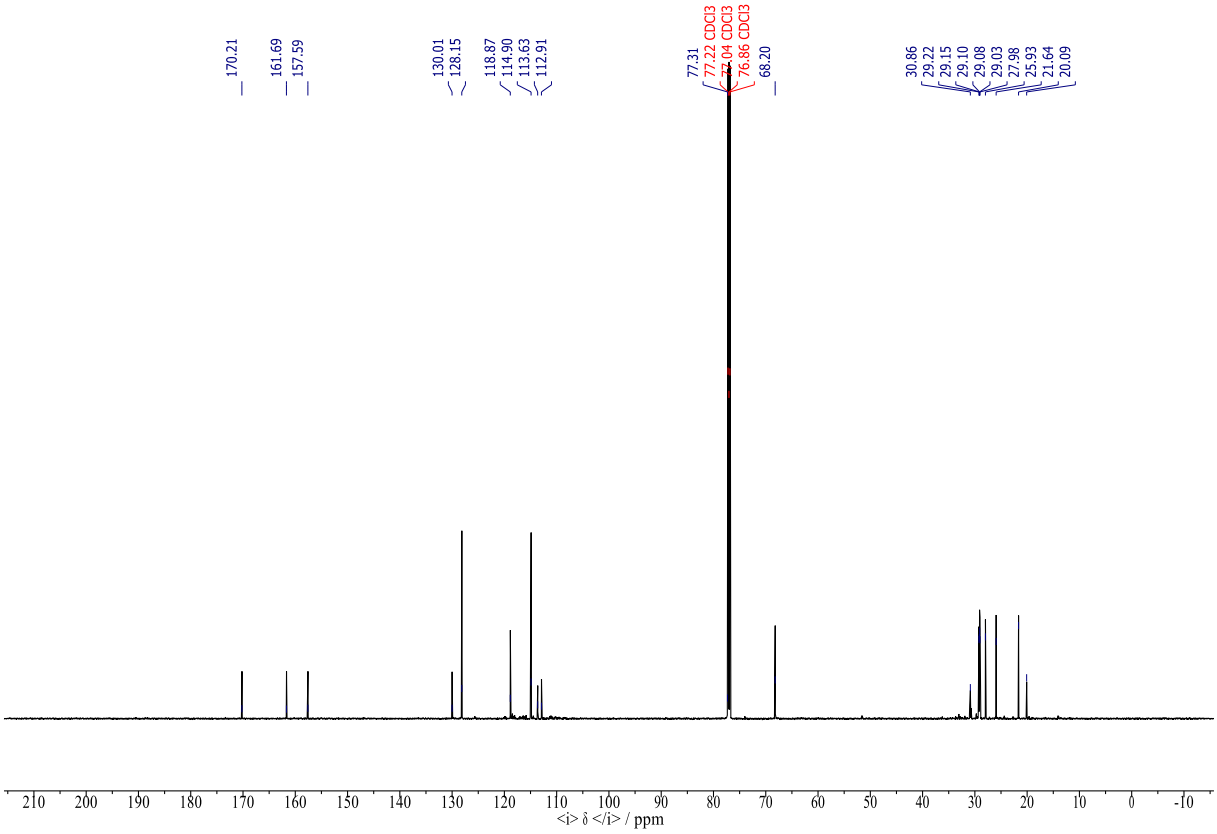

170.22
161.70
157.61
130.01
128.15
118.86
114.90
113.64
112.92
77.30
77.23 CDCl3
77.05 CDCl3
76.87 CDCl3
68.20
30.76
29.21
29.14
29.10
29.08
29.02
27.97
25.92
21.64
20.07
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ / ppm

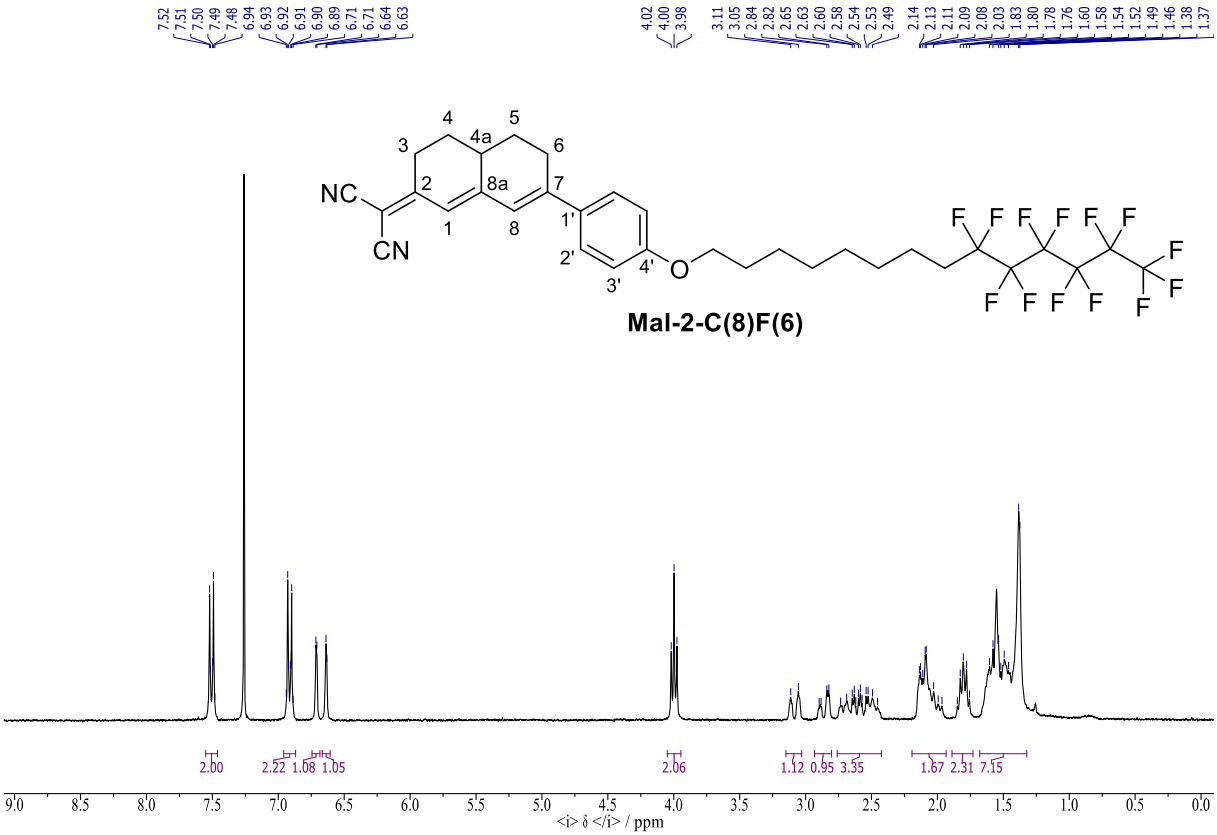

7.52 7.51 7.50 7.49 7.48 6.94 6.93 6.92 6.91 6.90 6.89 6.71 6.71 6.64
4.02 4.00 3.98 3.11 3.10 3.06 3.04 2.90 2.88 2.84 2.84 2.83 2.82 2.73 2.69 2.65 2.63 2.60 2.58 2.57 2.54 2.53 2.49 2.45 2.14 2.14 2.13 2.11 2.09 2.08 2.05 2.03 1.99 1.96 1.85 1.83 1.80 1.78 1.76 1.61 1.58 1.56 1.52 1.49 1.46 1.43 1.38 1.37 1.31
NC
CN
O
F
Mal-2-C(8)F(4)
2.00 2.04 1.02 0.95 2.01 0.99 1.06 2.95 3.67 2.13 7.67
δ / ppm
170.11 160.49 158.74 151.08 131.25 127.24 122.99 120.34 114.71 114.08 113.37 111.81 75.20 68.09 35.67 30.76 29.66 29.52 29.14 29.13 29.10 29.01 28.67 28.16 25.94 20.06
δ / ppm

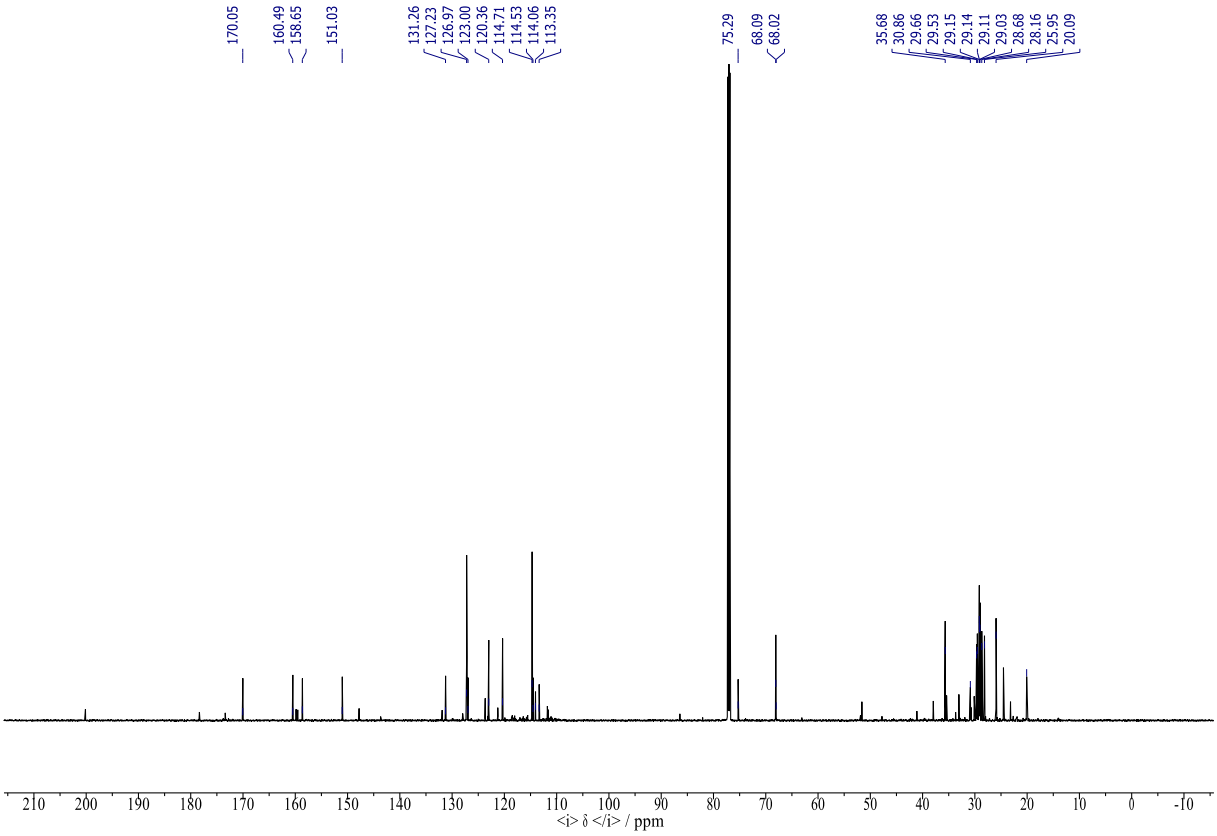

NC
CN
O
F

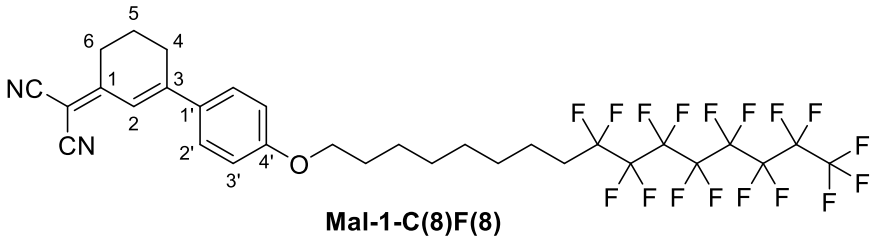
MaI-1-C(8)F(6)


2.00
0.92
1.95
1.99
1.94
1.80
4.05
1.93
2.06
2.03
5.69
 δ / ppm

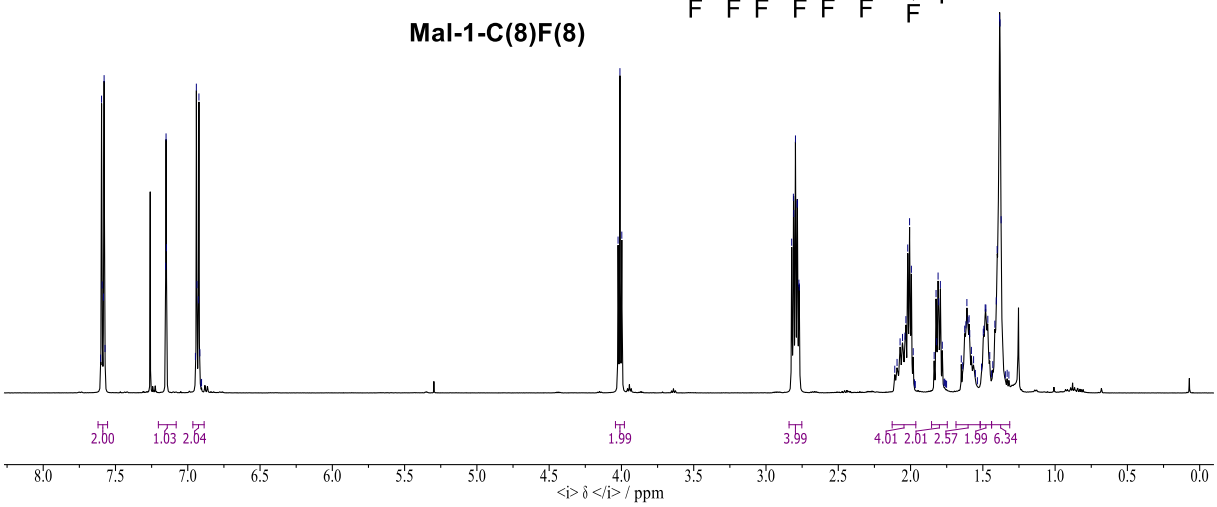

170.21
161.69
157.59
130.01
128.15
118.87
114.90
113.63
112.91
77.31
77.22 CDCl3
77.04 CDCl3
76.86 CDCl3
68.20
30.86
29.22
29.15
29.10
29.08
29.03
27.98
25.93
21.64
20.09
 δ / ppm

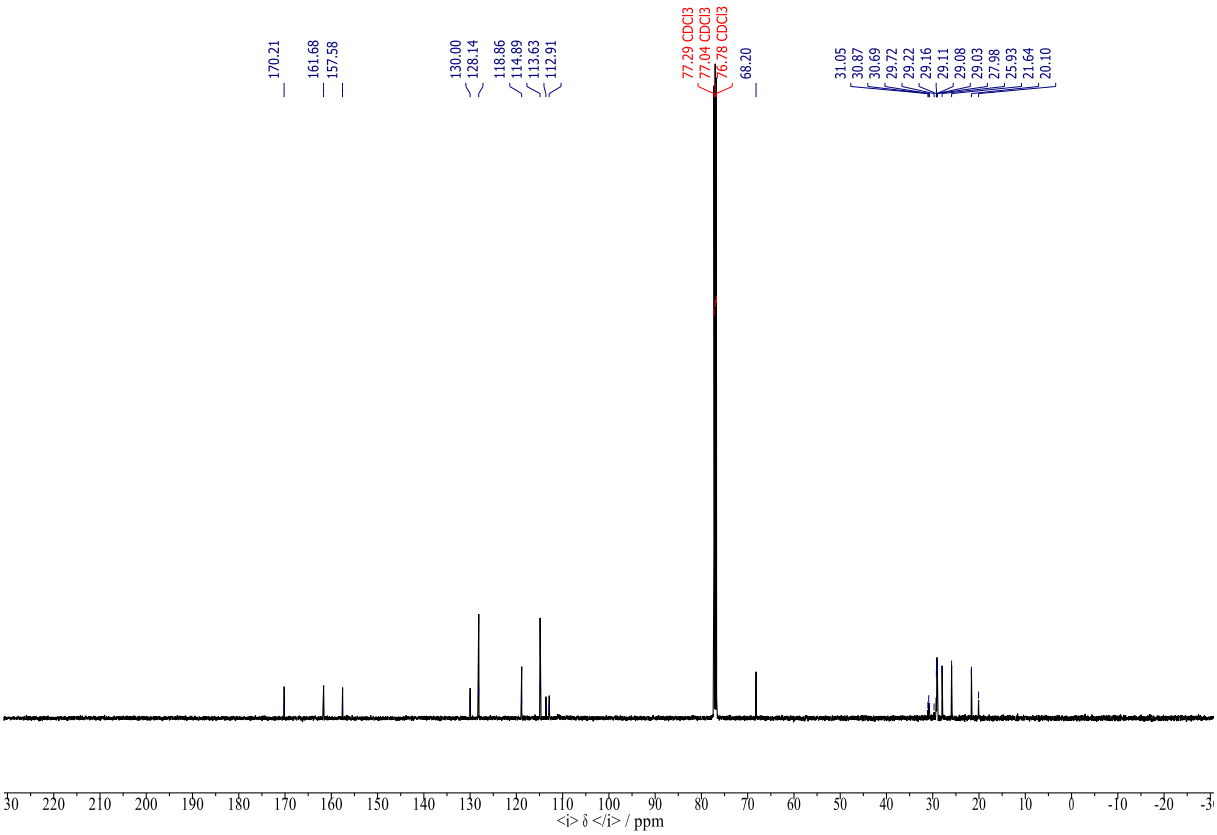

7.52 7.51 7.50 7.49 7.48 6.94 6.93 6.92 6.91 6.90 6.89 6.71 6.71 6.64 6.63
4.02 4.00 3.98 3.11 3.05 2.84 2.82 2.65 2.63 2.60 2.58 2.54 2.53 2.49 2.14 2.13 2.11 2.09 2.08 2.03 1.83 1.80 1.78 1.76 1.60 1.58 1.54 1.52 1.49 1.46 1.38 1.37
NC
CN
O
F
Mal-2-C(8)F(6)
2.00 2.22 1.08 1.05 2.06 1.12 0.95 3.35 1.67 2.31 7.15
 δ / ppm

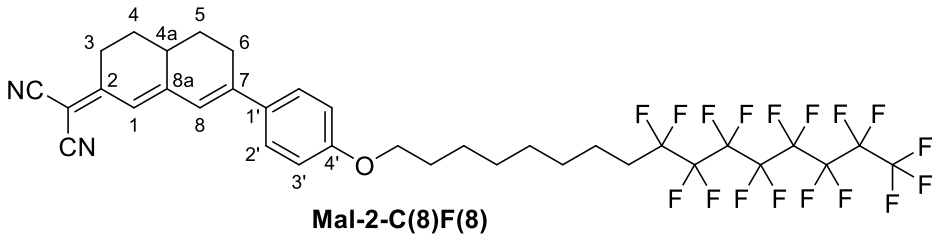

170.05 160.49 158.65 151.03 131.26 127.23 126.97 123.00 120.36 114.71 114.53 114.06 113.35 75.29 68.09 68.02 35.68 30.86 29.66 29.53 29.15 29.14 29.11 29.03 28.68 28.16 25.95 20.09
 δ / ppm


NC
CN
O
F F F F F F F F
F F F F F F F F
F F

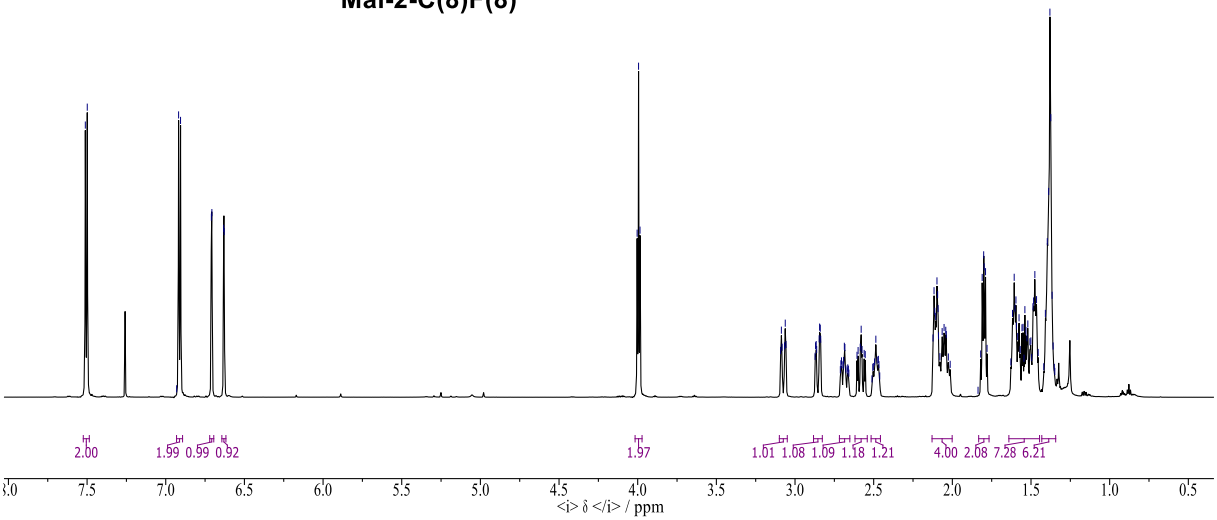
Mal-1-C(8)F(8)

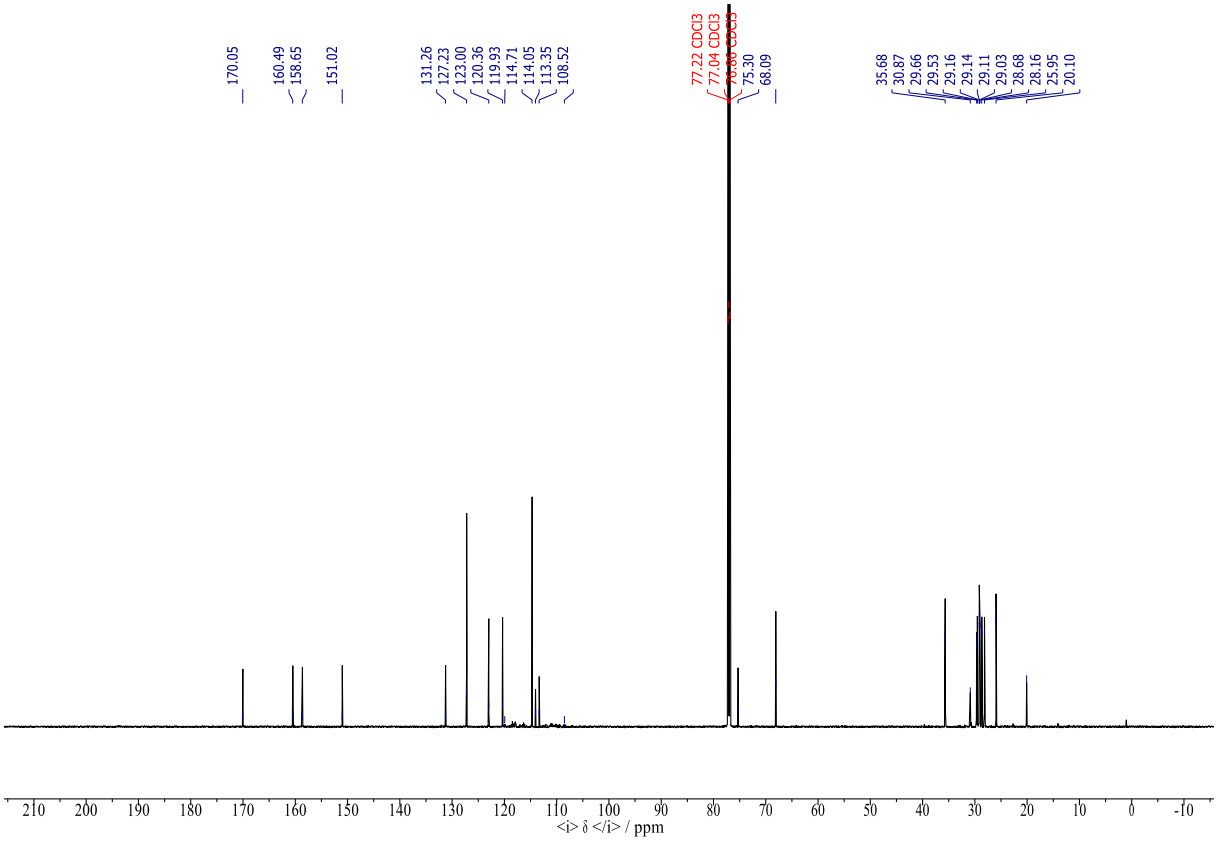

2.00
1.03
2.04
1.99
3.99
4.01
2.01
2.57
1.99
6.34
 δ / ppm

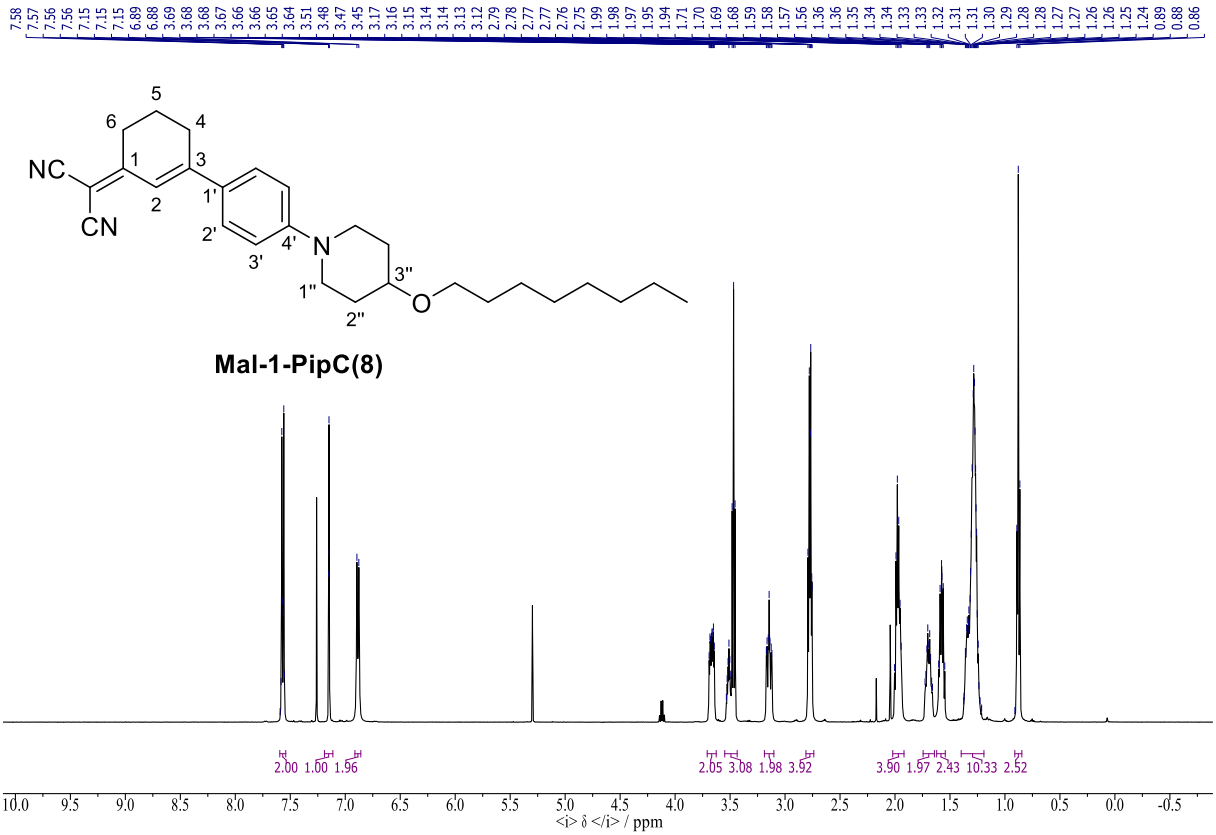

170.21
161.68
157.58
130.00
128.14
118.86
114.89
113.63
112.91
77.29 CDCl3
77.04 CDCl3
76.78 CDCl3
68.20
31.05
30.87
30.69
29.72
29.22
29.16
29.11
29.08
29.03
27.98
25.93
21.64
20.10
 δ / ppm

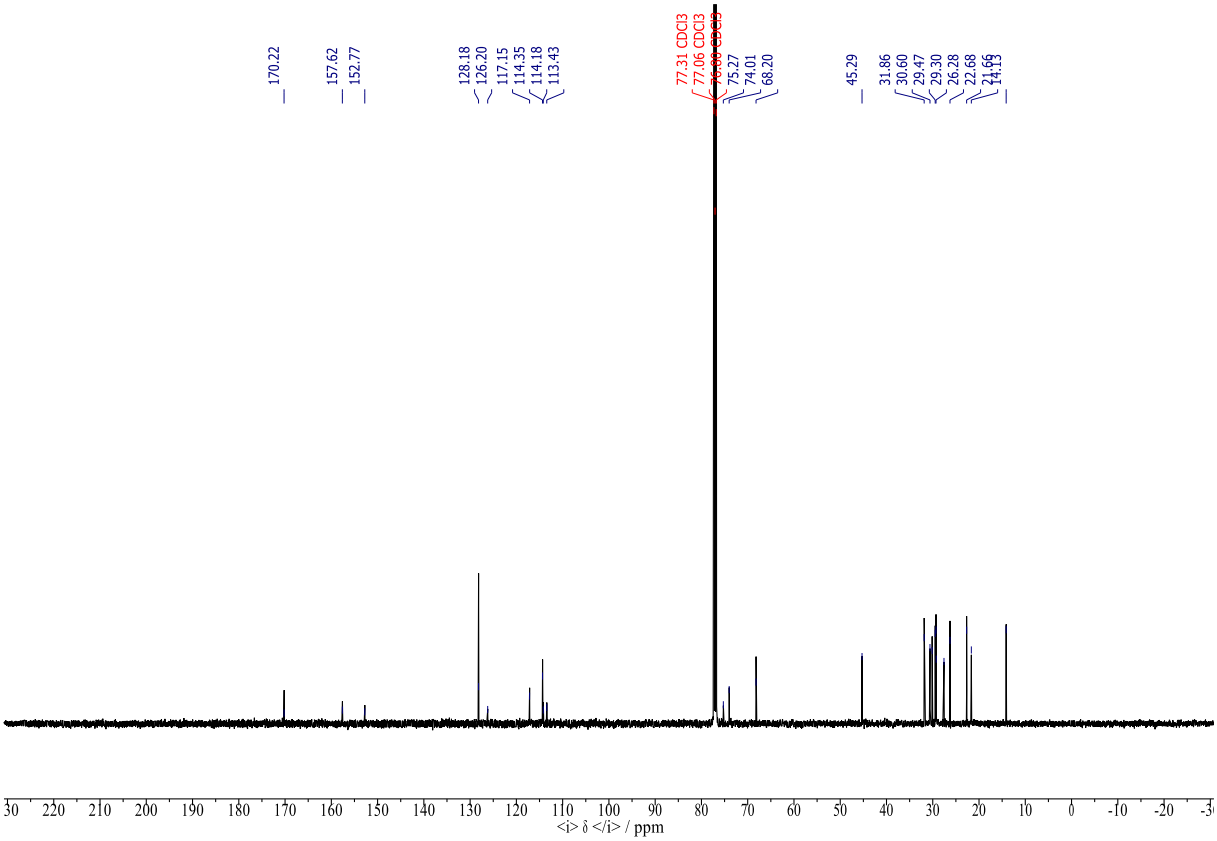

4
5
4a
3
6
2
8a
7
NC
1
8
1'
CN
2'
4'
O
3'
F F F F F F F F
F
F
F F F F F F F F

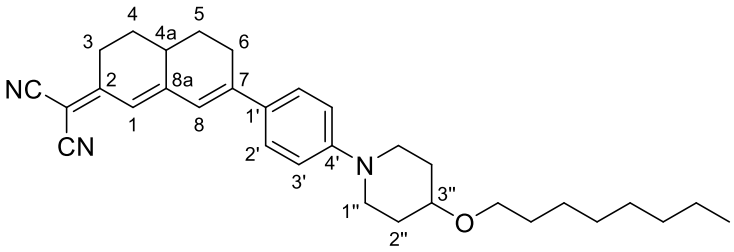
MaI-2-C(8)F(8)


2.00
1.99
0.99
0.92
1.97
1.01
1.08
1.09
1.18
1.21
4.00
2.08
7.28
6.21
 δ / ppm

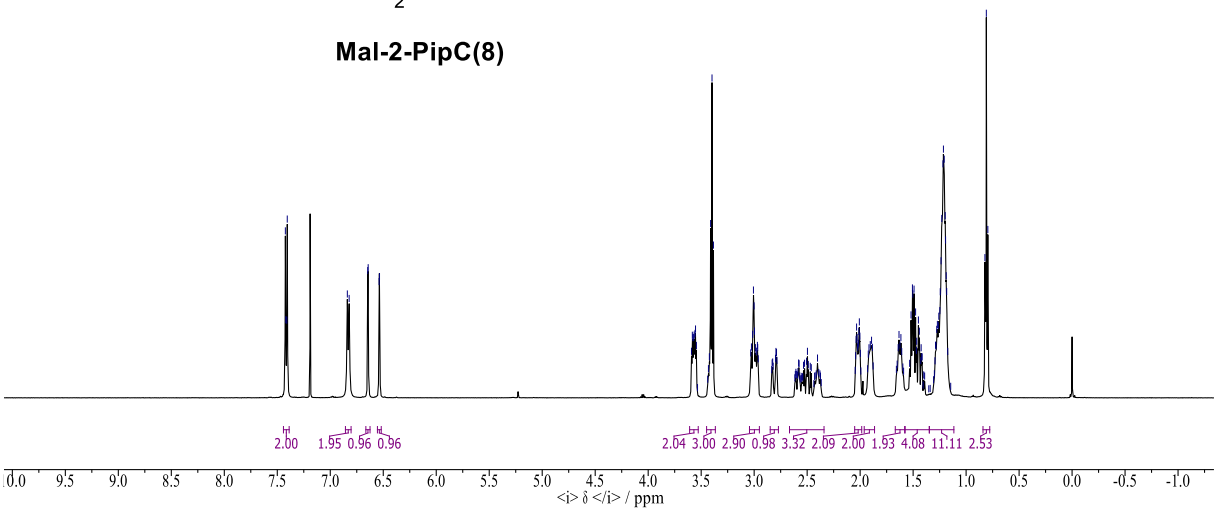

170.05
160.49
158.65
151.02
131.26
127.23
123.00
120.36
119.93
114.71
114.05
113.35
108.52
77.22 CDCl3
77.04 CDCl3
76.86 CDCl3
75.30
68.09
35.68
30.87
29.66
29.53
29.16
29.14
29.11
29.03
28.68
28.16
25.95
20.10
 δ / ppm

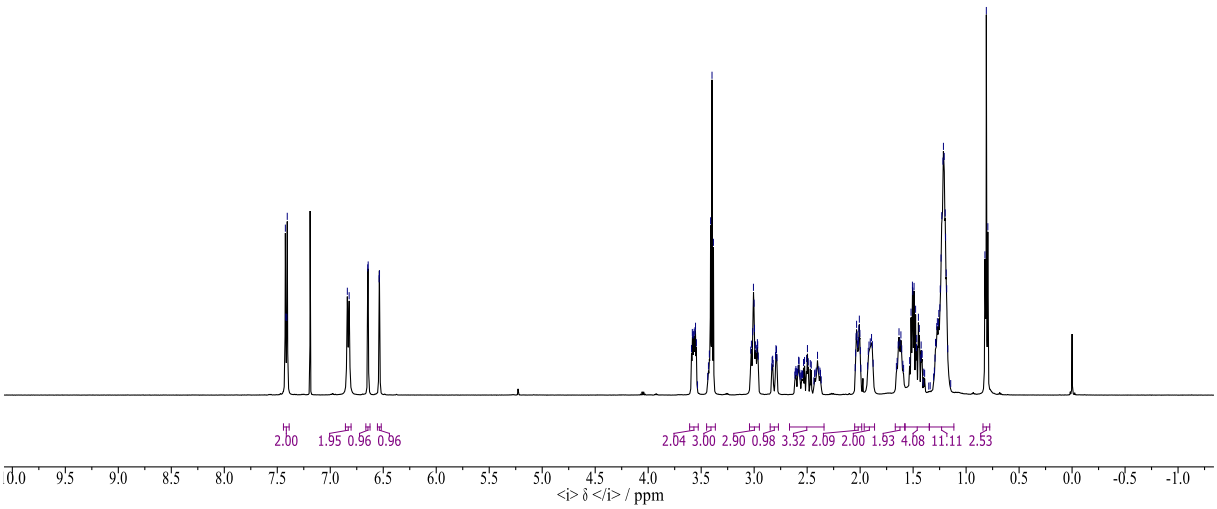

NC
CN
Mal-1-PipC(8)
2.00 1.00 1.96
2.05 3.08 1.98 3.92
3.90 1.97 2.43 10.33 2.52
 δ / ppm

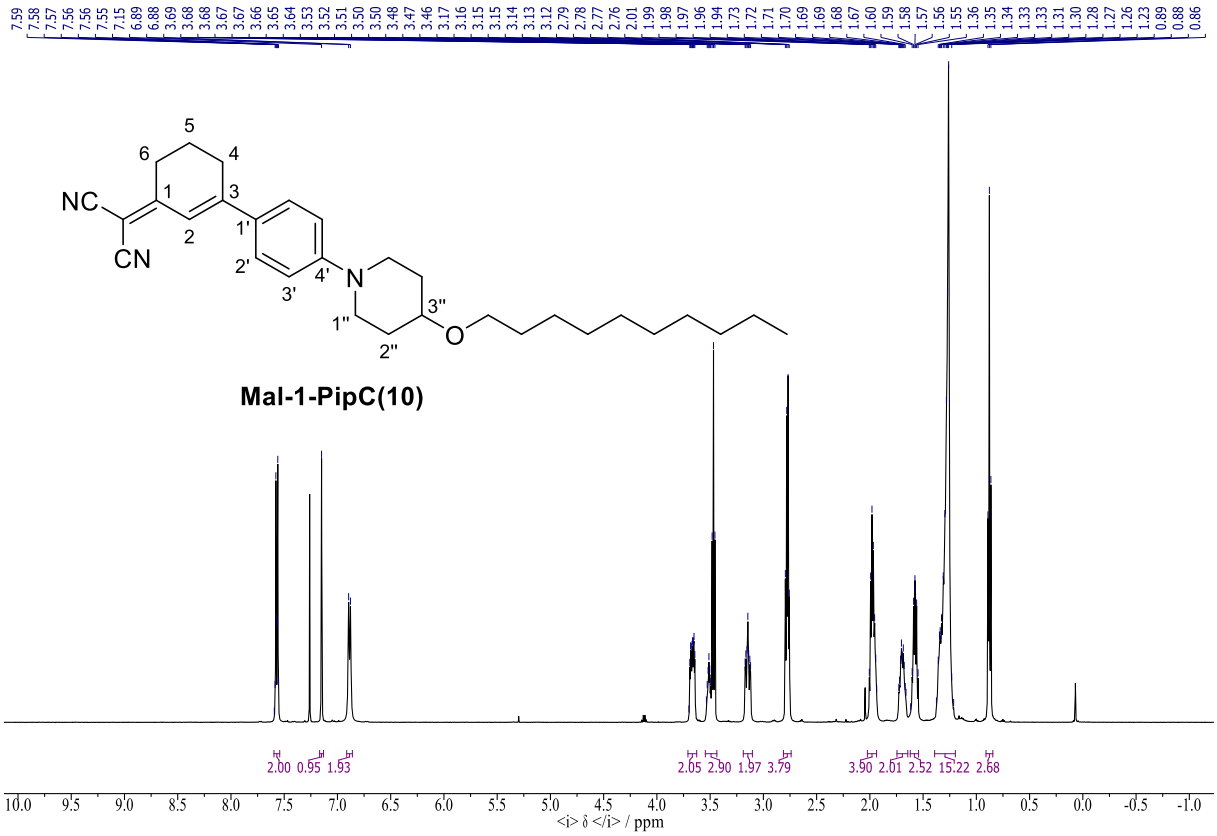

170.22
157.62
152.77
128.18
126.20
117.15
114.35
114.18
113.43
77.31 CDCl3
77.06 CDCl3
75.27
74.01
68.20
45.29
31.86
30.60
29.47
29.30
26.28
22.68
21.66
14.13
 δ / ppm

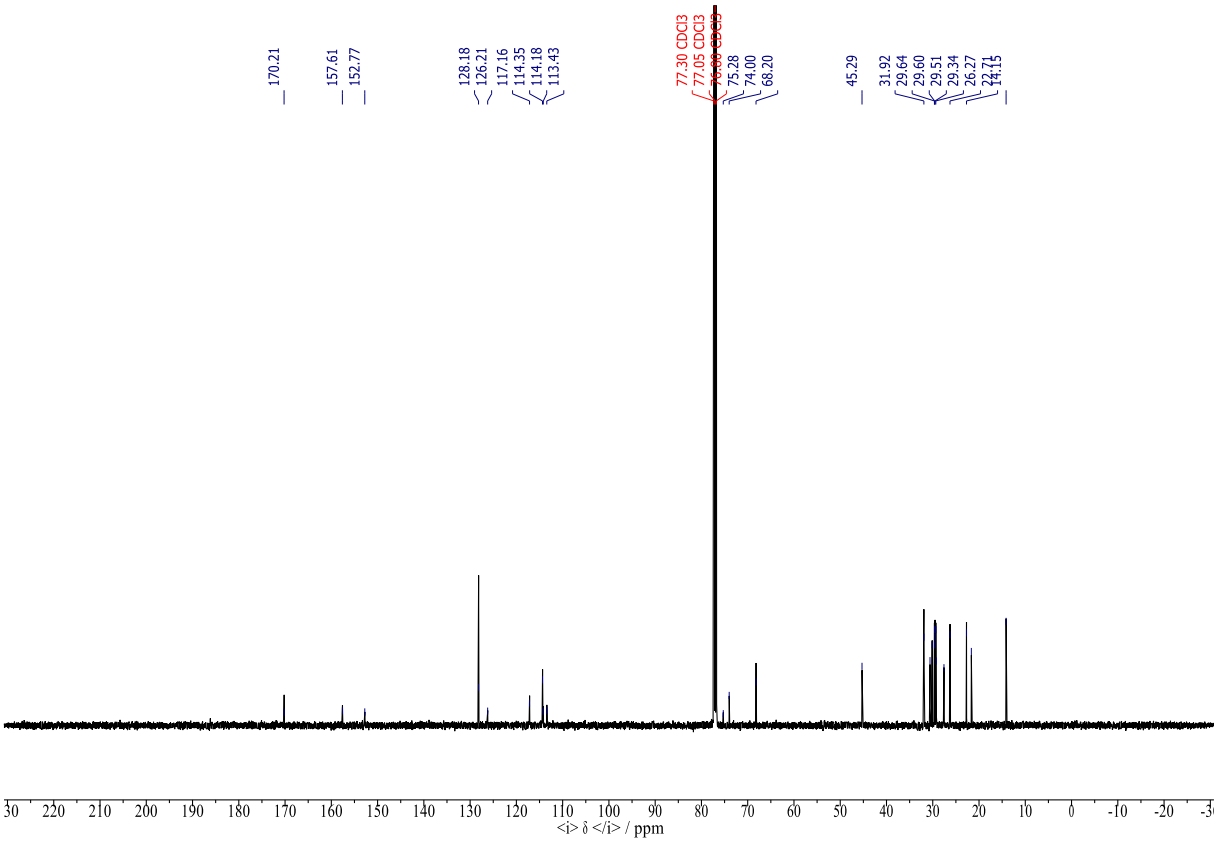

4
5
4a
3
6
2
8a
7
NC
1
8
1'
CN
2'
4'
N
3'
3"
1"
2"
O

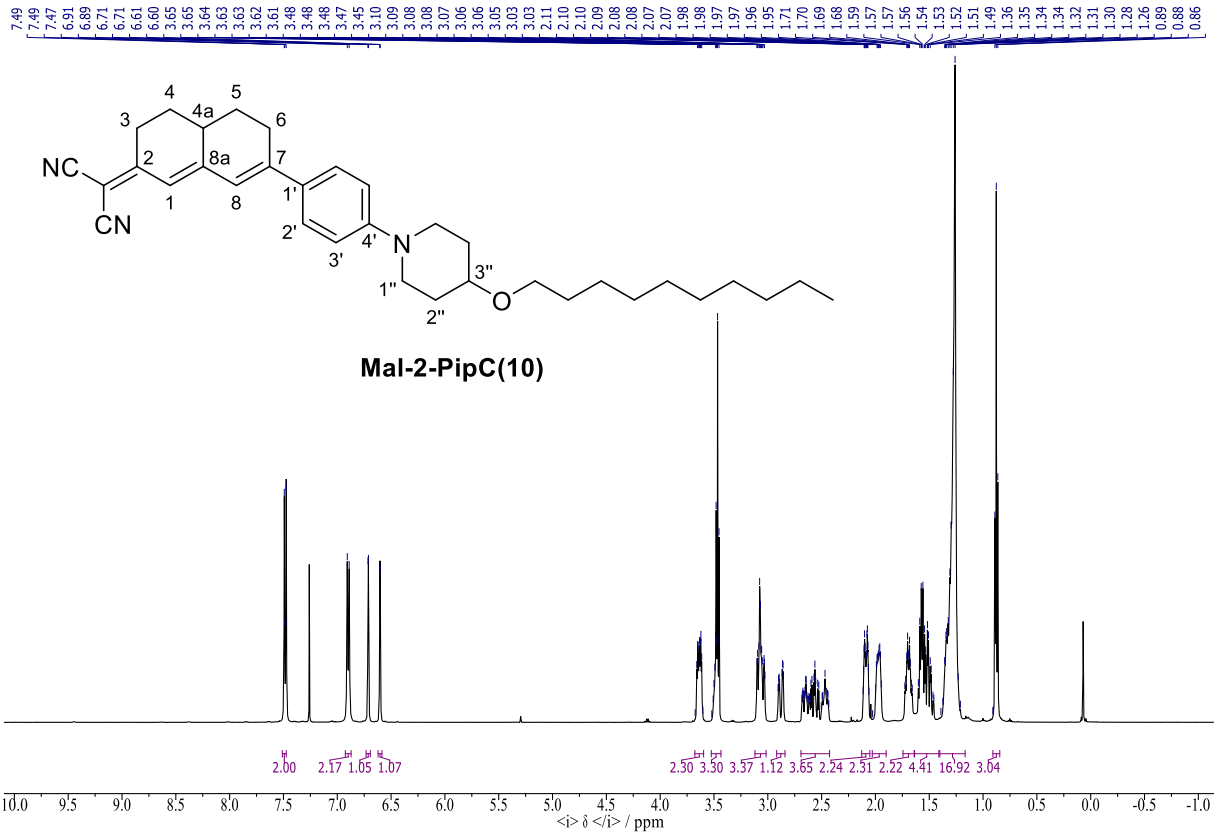
Mal-2-PipC(8)

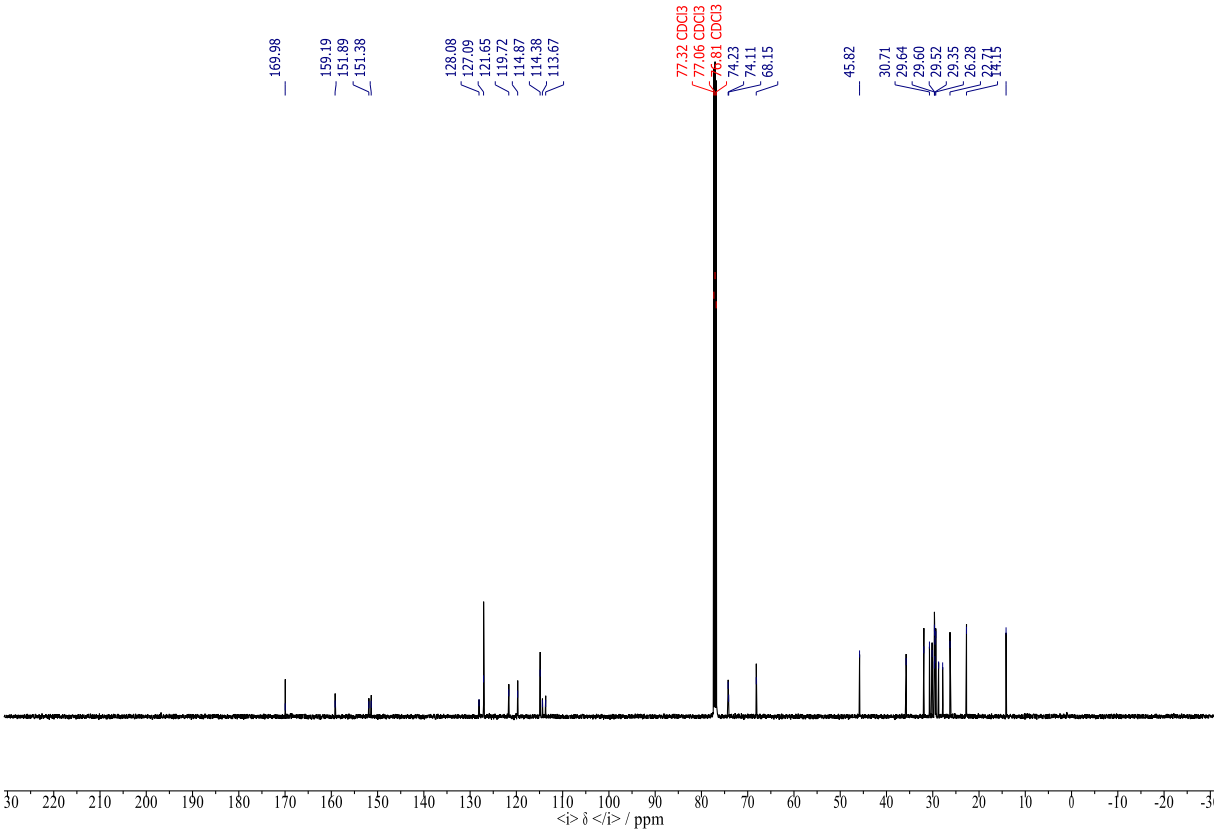

2.00
1.95
0.96
0.96
2.04
3.00
2.90
0.98
3.32
2.09
2.00
1.93
4.08
11.11
2.53
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
 δ / ppm

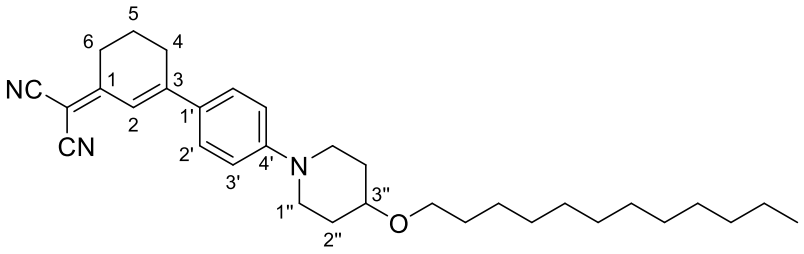

2.00
1.95
0.96
0.96
2.04
3.00
2.90
0.98
3.32
2.09
2.00
1.93
4.08
11.11
2.53
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
 δ / ppm


7.59 7.58 7.57 7.56 7.56 7.55 7.15 6.89 6.88 3.69 3.68 3.68 3.67 3.67 3.66 3.65 3.64 3.53 3.52 3.51 3.50 3.50 3.48 3.47 3.46 3.17 3.16 3.15 3.15 3.14 3.13 3.12 2.79 2.78 2.77 2.76 2.01 1.99 1.98 1.97 1.96 1.94 1.73 1.72 1.71 1.70 1.69 1.69 1.68 1.67 1.60 1.59 1.58 1.57 1.56 1.55 1.36 1.35 1.34 1.33 1.33 1.31 1.30 1.28 1.27 1.26 1.23 0.89 0.88 0.86
NC
CN
Mal-1-PipC(10)
2.00 0.95 1.93
2.05 2.90 1.97 3.79
3.90 2.01 2.52 15.22 2.68
 δ / ppm


170.21
157.61
152.77
128.18
126.21
117.16
114.35
114.18
113.43
77.30 CDCl3
77.05 CDCl3
75.28
74.00
68.20
45.29
31.92
29.64
29.60
29.51
29.34
26.27
22.71
14.15
 δ / ppm

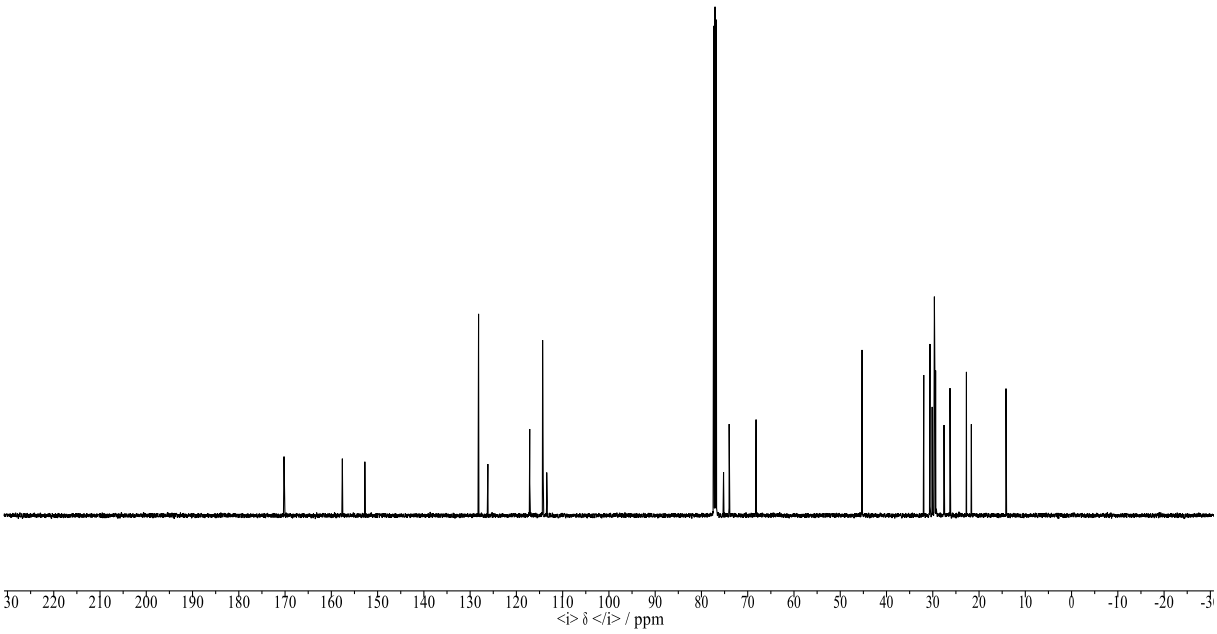

NC
CN
Mal-2-PipC(10)
 δ / ppm

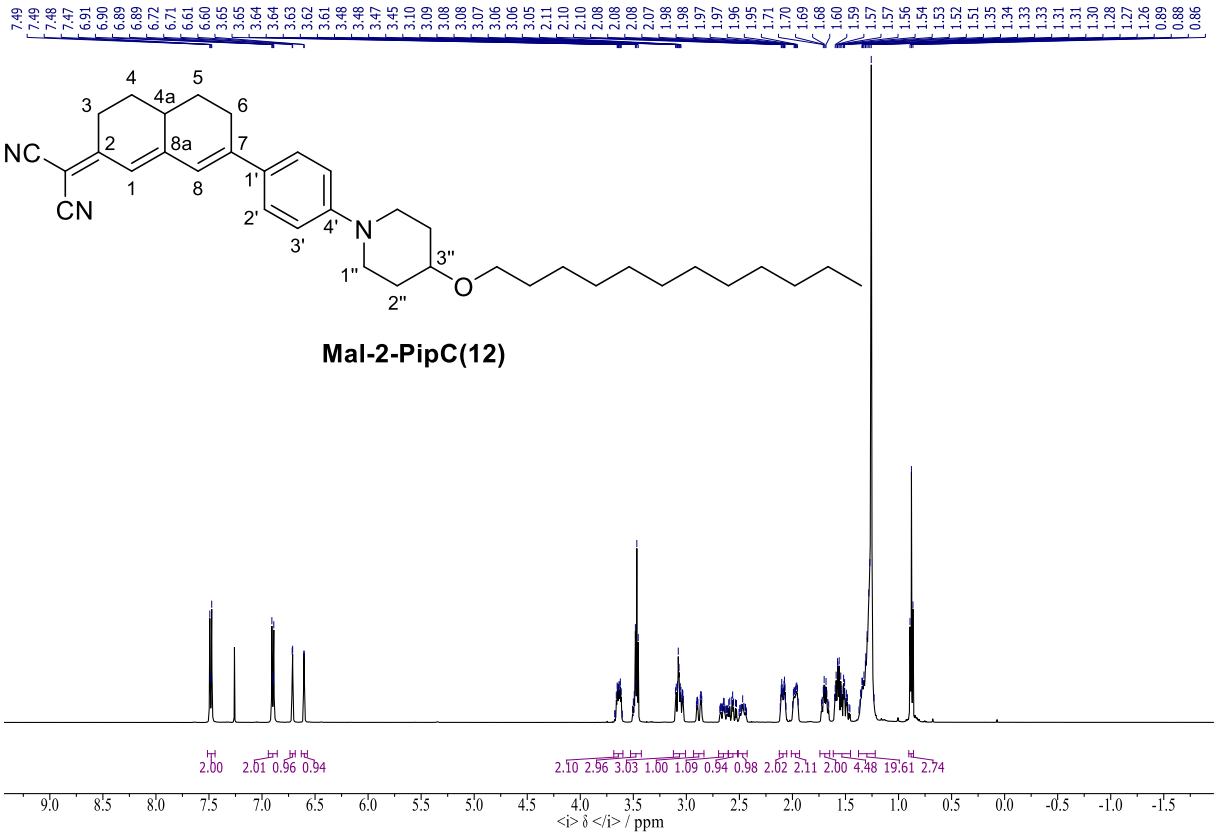

77.32 CDCl3
77.06 CDCl3
76.81 CDCl3
 δ / ppm

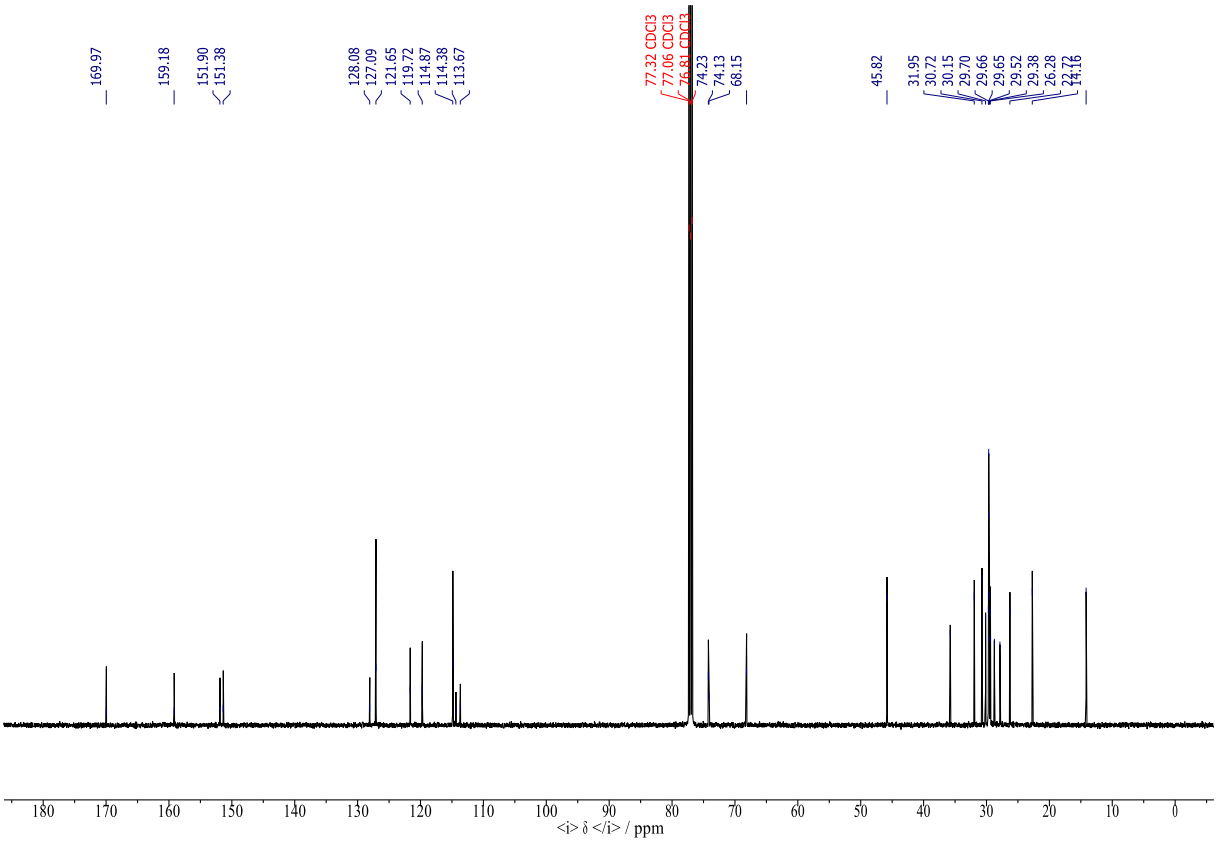

5
6
4
1
3
NC
2
1'
CN
2'
4'
N
3'
3"
1"
O
2"

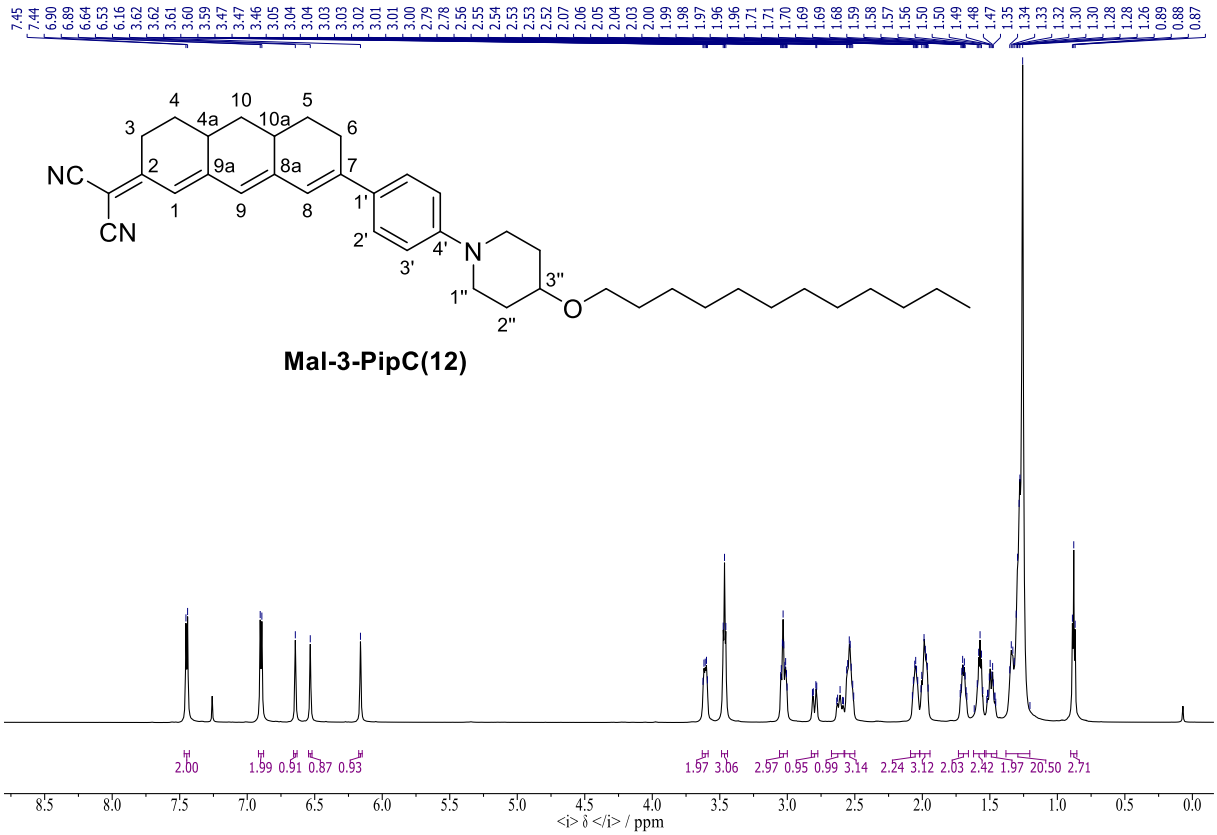
MaI-1-PipC(12)

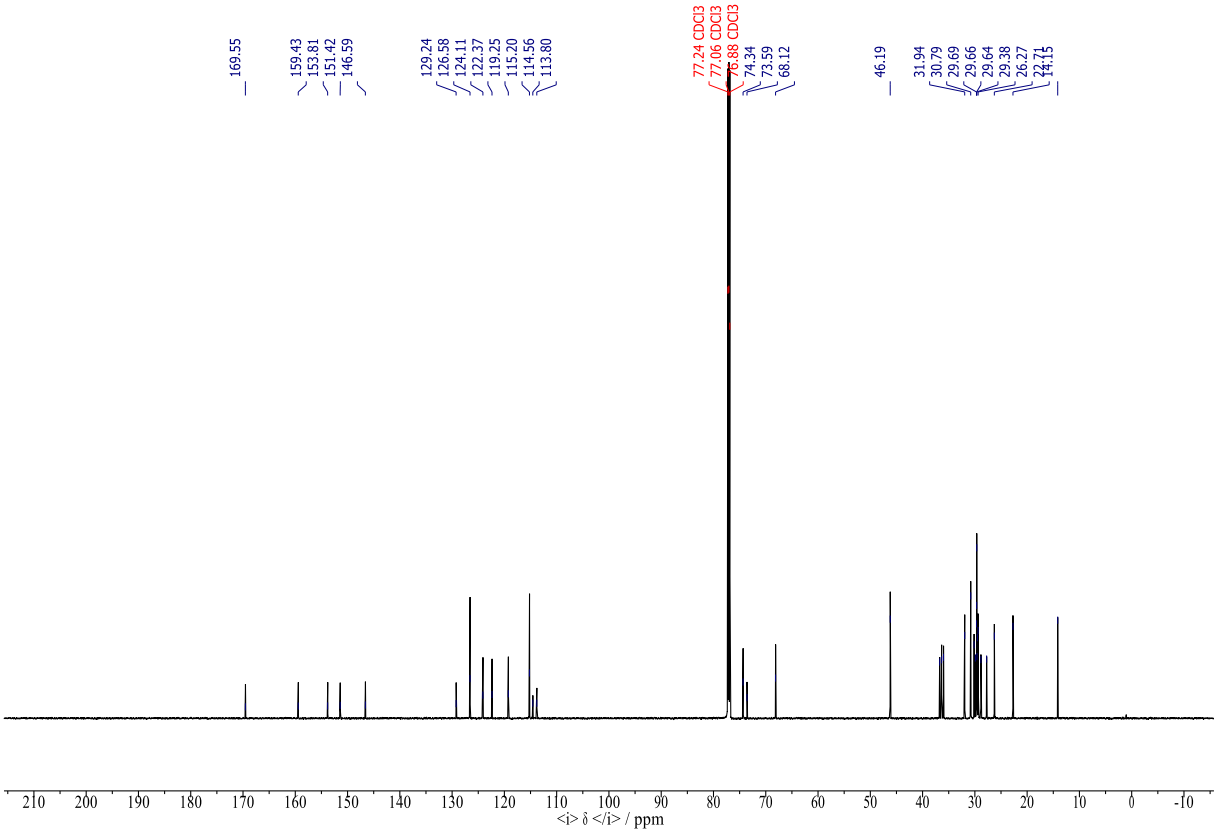
2.00 1.00 1.94
2.03 3.09 2.07 3.93
4.07 2.02 2.32 18.97 2.74
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
 δ / ppm

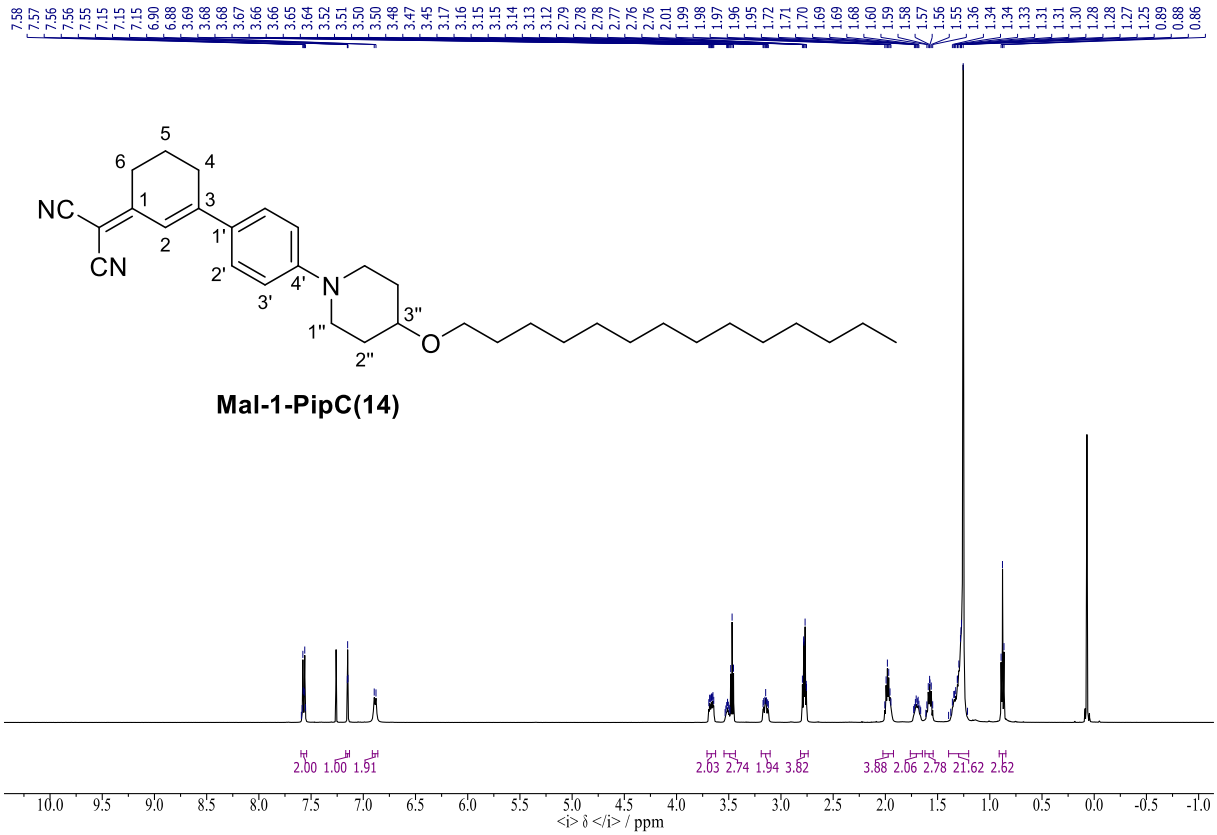

30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
 δ / ppm

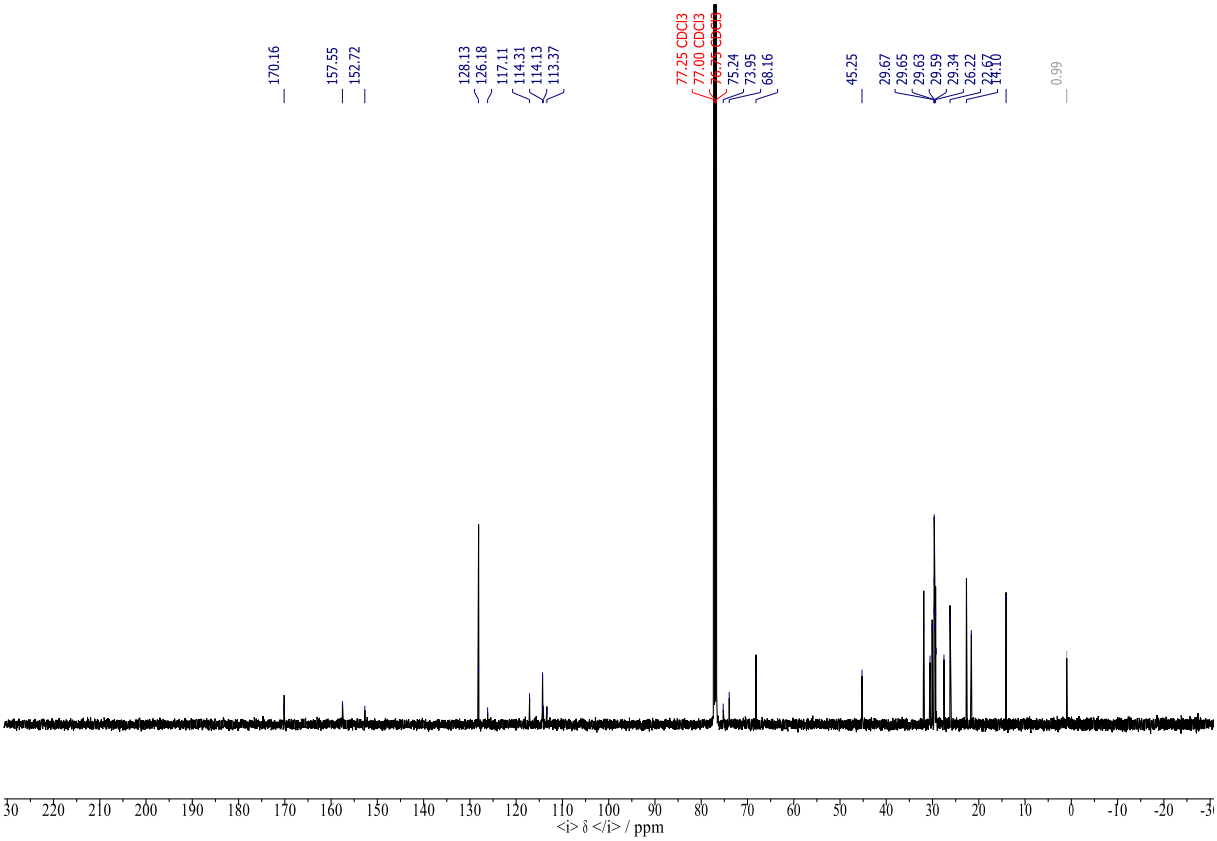

NC
CN
N
O
Mal-2-PipC(12)
 δ / ppm

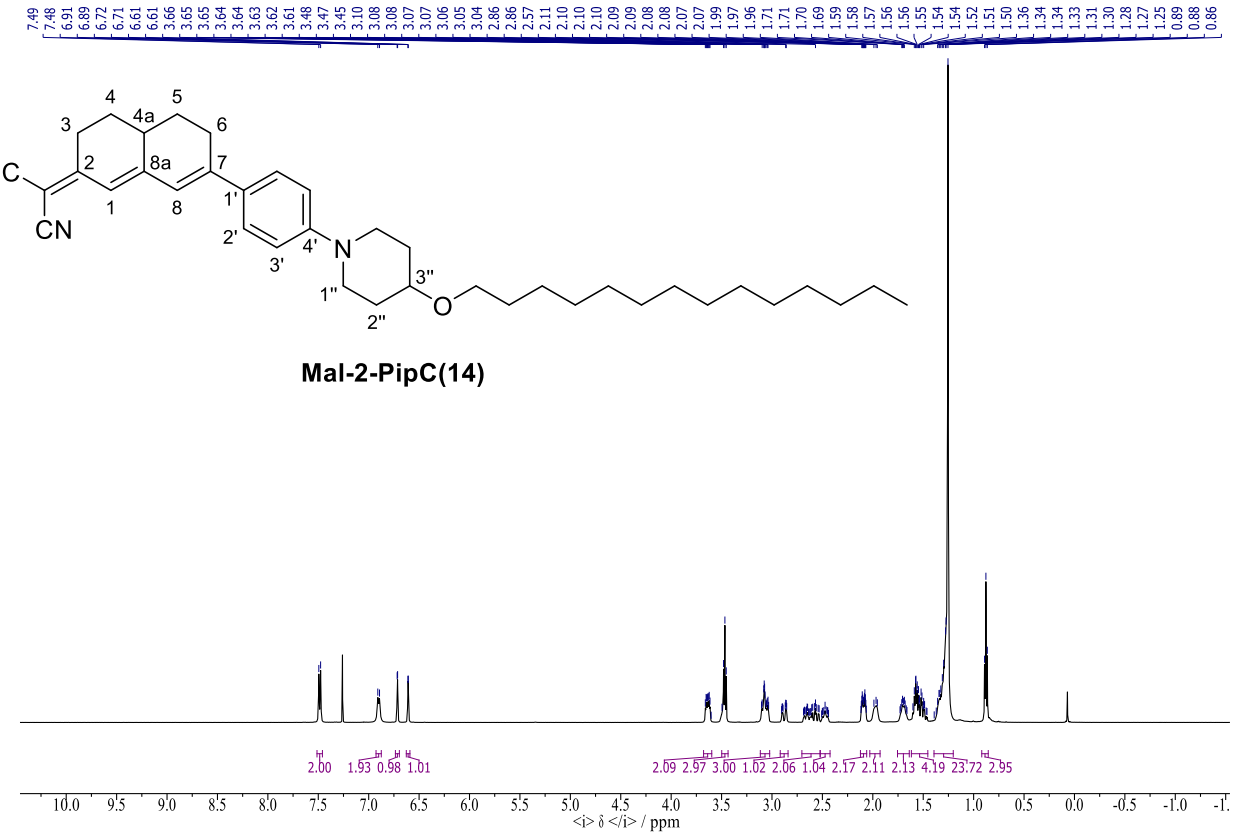

77.32 CDCl3
77.06 CDCl3
76.81 CDCl3
 δ / ppm

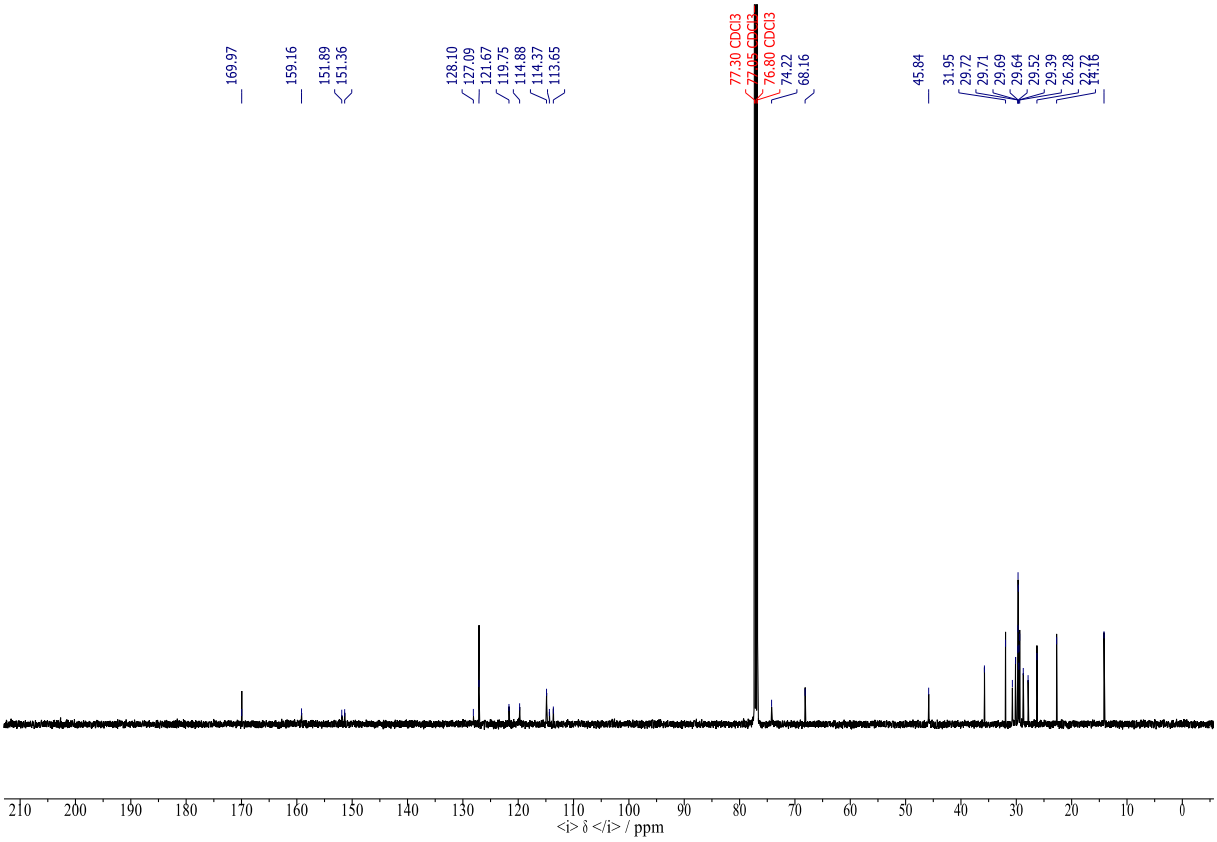

NC
CN
N
O
Mal-3-PipC(12)
 δ / ppm


77.24 CDCl3
77.06 CDCl3
76.88 CDCl3
 δ / ppm


NC
CN
N
O
Mal-1-PipC(14)
2.00 1.00 1.91
2.03 2.74 1.94 3.82
3.88 2.06 2.78 21.62 2.62
 δ / ppm


170.16
157.55
152.72
128.13
126.18
117.11
114.31
114.13
113.37
77.25 CDCl3
77.00 CDCl3
75.24
73.95
68.16
45.25
29.67
29.65
29.63
29.59
29.34
26.22
22.67
14.10
0.99
 δ / ppm


NC
CN
Mal-2-PipC(14)
2.00 1.93 0.98 1.01
2.09 2.97 3.00 1.02 2.06 1.04 2.17 2.11 2.13 4.19 23.72 2.95
 δ / ppm


169.97
159.16
151.89
151.36
128.10
127.09
121.67
119.75
114.88
114.37
113.65
77.30 CDCl3
77.05 CDCl3
76.80 CDCl3
74.22
68.16
45.84
31.95
29.72
29.71
29.69
29.64
29.52
29.39
26.28
22.72
14.16
 δ / ppm

i