Electronic Supplementary Material (ESI) for Chemical Communications.
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Supporting Information

Multicolour Fluorescent "Sulfide - Sulfone" Diarylethenes with High Photo-Fatigue Resistance

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# equal contributions

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Abbreviations

acetonitrile (MeCN), anti-parallel (ap), aqueous (aq.), argon (Ar), closed form (CF), diarylethene (DAE), dichloromethane (DCM), equivalent (equiv.), electrospray ionization (ESI), ethyl acetate (EtOAc), high performance liquid chromatography (HPLC), high resolution mass-spectrometry (HR-MS), methanol (MeOH), *N,N*-dimethylformamide (DMF), nuclear magnetic resonance (NMR), open form (OF), parallel (p), photostationary state (PSS), potassium carbonate (K_2CO_3), reversed phase (RP), room temperature (r.t.), saturated (sat.), tetrahydrofurane (THF), thin layer chromatography (TLC), trifluoroacetic acid (TFA), UHP (Urea Hydrogen Peroxide), ultraviolet (UV), visible (Vis), volume ratio of two solvents (v/v).

High-performance liquid chromatography separations

Preparative HPLC was performed on puriFlash 4250 2X preparative HPLC/Flash hybrid system (Interchim) with a 2 mL injection loop, a 200-600 nm UV-Vis detector and an integrated ELSD detector. Preparative column: Interchim Uptisphere Strategy C18-HQ, 10 µm, 250×21.2 mm (US10C18HQ-250/212, Interchim), flow rate 20 mL/min, unless specified otherwise. Analytical TLC was performed on Merck Millipore ready-to-use plates with silica gel 60 (F254). Flash chromatography was performed on Biotage Isolera 3.0 flash purification system using cartridges and solvent gradients indicated below.

Analytical HPLC was performed on a KNAUER Azura system with a photodiode array detector, a 20 µL injection loop, and a 150 x 4 mm column (Knauer, Eurospher II 100-10 C18A with precolumn, Vertex Plus), at a flowrate of 1.2 mL/min with water/MeCN gradient; and both solvents containing 0.1% of TFA.

Synthesis. **Starting materials**

Compounds **a**[1] and compound **d**[2] were prepared according to published procedures. Other chemicals were purchased from TCI Deutschland (Tokyo Chemical Industry Co.) or Sigma-Aldrich and used without further purification.

Nuclear Magnetic Resonance (NMR)

NMR Spectra (^{1}H, ^{13}C and ^{19}F) were recorded on an *Agilent 400MR DD2* spectrometer. All ^{1}H- and ^{13}C-NMR spectra are referenced to the signals of the residual protons and ^{13}C in $CDCl_3$ (^{1}H: 7.26 ppm, ^{13}C: 77.00 ppm), Multiplicities of the signals are described as follows: s = singlet, d = doublet, t = triplet, q = quarltet, br = broad. Coupling constants (*J*) are given in Hz.

ESI and high resolution mass-spectrometry (ESI-MS)

ESI-MS were recorded on a Varian 500-MS spectrometer (Agilent). ESI-HRMS were recorded on a MICROTOF spectrometer (Bruker) equipped with an *Apollo* ion source and a direct injector as an LC-autosampler (Agilent RR 1200).

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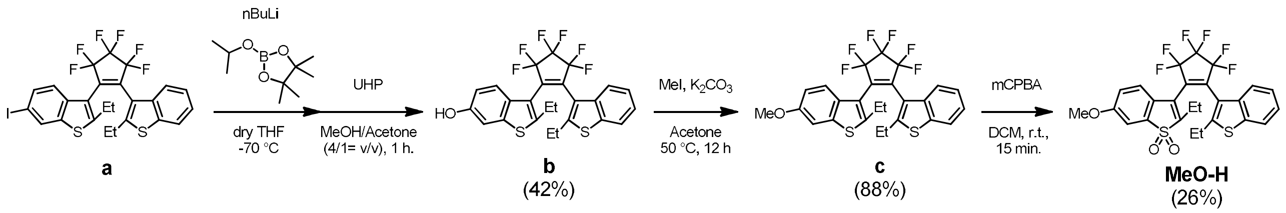
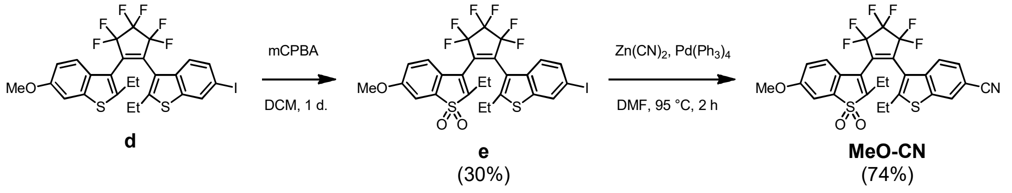
[1] L. Schleper, M. L. Bossi, V. N. Belov, S. W. Hell, *Beilstein J. Org. Chem.,* 2019**,** **15***,* 2344–2354.

[2] K. Uno, M. L. Bossi, T. Konen, V. N. Belov, M. Irie, S. W. Hell, *Adv. Opt. Mater*., 2019, **7**, 1801746–1801746.

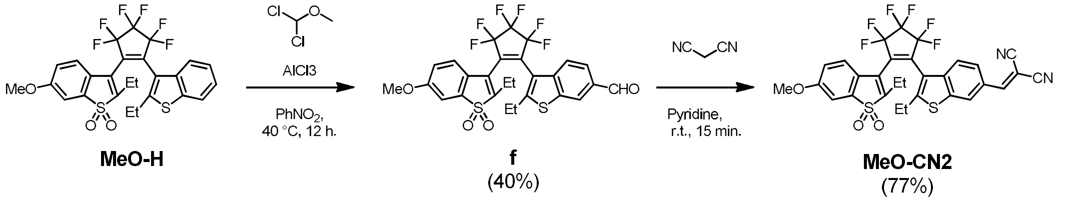
Preparation of MeO-H, MeO-CN and **MeO-CN2**



Scheme S1-a. Synthesis of **MeO-H**.

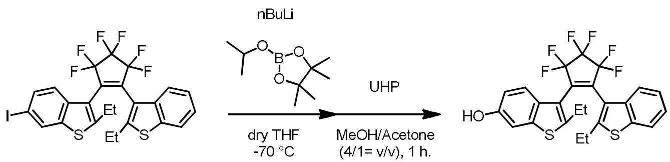


Scheme S1-b. Synthesis of **MeO-CN**.



Scheme S1-c. Synthesis of **MeO-CN2**.

Compound **b**



a

b
(42%)

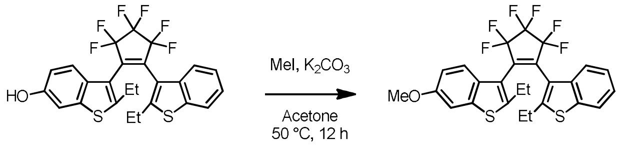
Compound **a** (3.2 g, 5.1 mmol) was dissolved in THF (12 ml) under N_2. *n*-BuLi (1.6 M in hexanes, 4.0 ml, 6.4 mmol, 1.25 eq.) was added at -70 ˚C with stirring, and the reaction solution was stirred for 30 min. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.5 g, 8.1 mmol, 1.6 eq.) was added, and the reaction mixture was warmed to r.t. over 1 h. Water (50 ml) was added to the reaction solution, and it was extracted with DCM (50 ml, twice). The organic phase was separated, dried over $MgSO_4$, and concentrated under reduced pressure to give a crude boronic ester intermediate which was oxidized without further purification. The crude boronic ester was dissolved in the mixture of MeOH/acetone (16 ml/4 ml) to which UHP (0.75 g, 0.80 mmol, 1.6 eq.) was added in several portions at room temperature. After stirring for 1 h at r.t., sat. aq. NaCl was added. The reaction mixture was extracted with DCM (50 ml). The organic phase was separated, dried over $MgSO_4$, and concentrated under reduced pressure. Column chromatography with gradient elution (hexane/ethyl acetate = 85/15→ 60/40) afforded compound **b** as a white solid (1.1 g, 42 %). R_f (n-hexane/EtOAc, 3/2, v/v) = 0.62.

ap:p = 7:3. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.76–7.69 (m, 0.7 H, *ap*), 7.69–7.65 (m, 0.7 H, *ap*), 7.65–7.35 (m, 1.0 H, *ap/p*), 7.58–7.54 (m, 0.3 H, *p*), 7.52 (dd, *J* = 8.8, 2.4 Hz, 0.7 H, *ap*), 7.44–7.35 (m, 0.3 H, *p*), 7.34–7.28 (m, 0.7 H, *ap*), 7.23–7.16 (m, 0.6 H, 2*p*), 7.14 (d, *J* = 2.4 Hz, 0.7 H, *ap*), 7.03 (d, *J* = 2.4 Hz, 0.3 H, *p*), 6.92 (dd, *J* = 8.8, 2.4 Hz, 0.7 H, *ap*), 6.70 (dd, *J* = 8.8, 2.4 Hz, 0.3 H, *p*), 5.14–4.45 (br, 1H, *ap/p*), 2.98–2.30 (m, 4.0 H, *ap/p*), 1.32–1.24 (m, 1.8H, 2*p*), 0.83 (t, *J* = 7.2, 2.1 H, *ap*), 0.74 (t, *J* = 7.2, 2.1 H, *ap*).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = ^{13}C NMR (101 MHz, cdcl3) δ 152.9, 152.8, 150.4, 150.0, 147.9, 139.6, 139.4, 138.4, 138.1, 138.0, 132.6, 132.3, 124.7, 124.4, 124.3, 123.0 (2×), 122.2 (2×), 122.02, 117.9, 117.6, 117.4, 114.4, 114.1, 107.7, 107.5, 23.2 (4×), 22.9, 22.8, 15.9 (2×), 15.4, 15.3.

^{19}F NMR (367 MHz, $CDCl_3$): δ (ppm) = -110.3 (m, 4.0 F, p/ap), -132.7 (m, 2.0 F, p/ap). ESI-MS: positive mode: m/z = 535.0595 $[M+Na]^+$ (found), 535.0595 (calculated for $C_{25}H_{18}F_6NaOS_2^+$, $[M+Na]^+$).

Compound **c**



b

c
(88%)

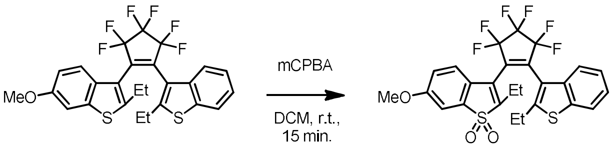
Compound **b** (1.1 g, 2.2 mmol) was dissolved in dry acetone (15 ml) under N_2. Finely ground K_2CO_3 (1.5 g, 10.7 mmol, 5.0 eq.) and MeI (1.5 g, 10.7 mmol, 5.0 eq.) were added to the solution. The reaction solution was heated to 50 ˚C and stirred for 5 h. Water (100 ml) was added, and the reaction mixture was extracted with DCM (50 ml, twice). The organic phase was collected, dried over $MgSO_4$, and concentrated under reduced pressure. The collected solid was washed with hexane to give compound **c** (1.0 g, 88 %) as a white solid.

ap:p = 7:3. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.76–7.70 (m, 0.7 H, *ap*), 7.70–7.65 (m, 0.7 H, *ap*), 7.65–7.59 (m, 0.3 H, *p*), 7.59–7.52 (m, 1.0 H, *ap/p*), 7.45 (dd, *J* = 8.8, 1.2 Hz, 0.3 H, *p*), 7.41–7.35 (m, 0.7 H, *ap*), 7.33–7.27 (m, 0.7 H, *ap*), 7.23–7.15 (m, 1.3 H, *ap/p*), 7.08 (d, *J* = 2.0 Hz, 0.3 H, *p*) 7.01 (dd, *J* = 8.8, 2.4 Hz, 0.7 H, *ap*), 6.80 (dd, *J* = 9.2, 2.4 Hz, 0.3 H, *p*), 3.85 (s, 2.1 H, *ap*), 3.77 (s, 0.9 H, *p*), 2.99–2.30 (m, 4.0 H, *ap/p*), 1.34–1.28 (m, 1.8H, *p*), 0.83 (t, *J* = 7.6, 2.1 H, *ap*), 0.75 (t, *J* = 7.2, 2.1 H, *ap*). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 157.2, 150.4, 145.0, 147.7, 147.1, 141.8, 139.6, 139.3, 138.4, 138.1, 137.9, 133.6, 133.3, 132.3, 132.0, 130.7, 130.1, 124.7, 124.4, 124.3, 122.8 (2×), 122.2, 122.1, 122.0, 118.1, 117.9, 117.6, 117.4, 114.5, 114.2, 104.8, 104.6, 55.6, 55.5, 23.3, 23.2, 23.2, 23.1, 22.9, 22.8, 16.0, 15.4, 15.3.

^{19}F NMR (367 MHz, $CDCl_3$): δ (ppm) = -110.4 (m, 4.0 F, p/ap), -132.7 (m, 2.0 F, p/ap).

ESI-MS: positive mode: m/z = 549.0740 $[M+Na]^+$ (found), 549.0752 (calculated for $C_{26}H_{20}F_6NaOS_2^+$, $[M+Na]^+$).

MeO-H



c

MeO-H
(26%)

Compound **c** (1.0 g, 1.9 mmol) was dissolved in DCM (20 ml), to which mCPBA (77%, 0.98 g, 4.4 mmol, 2.3 eq.) was added. The reaction solution was stirred for 15 min at r.t. The reaction solution was poured into water (30 ml) containing excess of sodium thiosulfate (10 g, 63 mmol, 33 eq), which was then stirred for 30 min at r.t. Water (50 ml) was added to the reaction solution, and it was extracted with DCM (50 ml, twice). The organic phase was separated, dried over $MgSO_4$, and concentrated under reduced pressure. Column chromatography with gradient elution (hexane/ethyl acetate = 90/10→ 75/25) afforded **MeO-H** as a white solid (0.28 g, 26 %). R_f (n-hexane/EtOAc, 3/1, v/v) = 0.48.

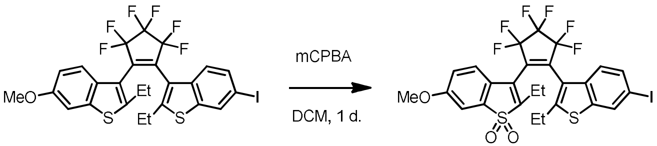
ap:p = 6:4. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.81–7.73 (m, 0.6 H, *ap*), 7.72–7.66 (m, 0.4 H, *p*), 7.58–7.50 (m, 1.0 H, *ap/p*), 7.43–7.21 (m, 3.4 H, *ap/p*), 7.10 (dd, *J* = 12.4, 2.4 Hz, 0.6 H, *ap*), 7.07–7.03 (m, 0.6 H, *ap*), 6.72 (dd, *J* = 8.4, 2.4 Hz, 0.4 H, *p*), 3.88 (s, 1.8 H, *ap*), 3.75 (s, 1.2 H, *p*), 2.84–2.16 (m, 4.0 H, *ap/p*), 1.40–1.31 (m, 2.4 H, *p*), 1.03 (t, *J* = 7.6, 1.8 H, *ap*), 0.73 (t, *J* = 7.6 Hz, 1.8 H, *ap*).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 161.8, 161.4, 151.5, 150.7, 145.8, 145.2, 138.3, 138.1, 137.9, 137.7, 137.4, 137.0, 131.1, 131.0, 125.1, 124. 8, 124.7, 124.7, 124.5, 124.4, 123.9, 122.5, 122.4, 122.2, 121.8, 121.7, 121.7, 121.6, 119.1, 118.6, 107.7, 107.5, 77.3, 56.1, 55.9, 31.6, 23.1, 22.7, 19.1, 18.5, 15.9, 15.6, 14.1, 12.1, 11.3.

^{19}F NMR (367 MHz, $CDCl_3$): δ (ppm) = -110.1 (m, 4.0 F, p/ap), -132.6 (m, 2.0 F, p/ap).

ESI-MS: positive mode: m/z = 581.0656 $[M+Na]^+$ (found), 581.0650 (calculated for $C_{26}H_{20}F_6NaO_3S_2^+$, $[M+Na]^+$).

Compound **e**



d

e
(30%)

Compound **d** (0.30 g, 0.57 mmol) was dissolved in DCM (15 ml), to which mCPBA (77%, 0.39 g, 2.3 mmol, 4.0 eq.) was added. The reaction solution was stirred for 24 h. at r.t. The reaction solution was poured into water (30 mL) containing excess of sodium thiosulfate (5 g, 32 mmol, 55 eq.), which was then stirred for 30 min at r.t. Water (50 ml) was added to the reaction solution, and it was extracted with DCM (50 ml, twice). The organic phase was separated, dried over $MgSO_4$, and concentrated under reduced pressure. Column chromatography with gradient elution (hexane/ethyl acetate = 95/5→ 50/50) afforded compound **e** as a white solid (95 mg, 30 %). R_f (n-hexane/EtOAc, 4/1, v/v) = 0.40.

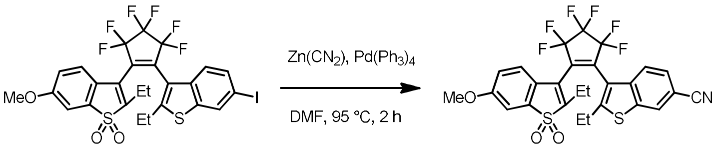
ap:p = 6:4. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.11 (d, *J* = 1.6 Hz, 0.6 H, *ap*), 8.04 (d, *J* = 1.6 Hz, 0.4 H, *p*), 7.68 (dd, *J* = 8.4, 1.6 Hz, 0.6 H, *ap*), 7.58 (dd, *J* = 8.8, 1.6 Hz, 0.4 H, *p*), 7.32–7.20 (m, 2.2 H, *ap/p*), 7.14 (d, *J* = 2.4 Hz, 0.4 H, *p*), 7.07 (dd, *J* = 8.4, 2.4 Hz, 0.6 H, *ap*), 6.99 (d, *J* = 8.8 Hz, 0.4 H, *p*), 6.76 (dd, *J* = 8.4, 2.4 Hz, 0.4 H, *p*), 3.88 (s, 1.8 H, *ap*), 3.79 (s, 1.2 H, *p*), 2.84–2.13 (m, 4.0 H, *ap/p*), 1.39–1.31 (m, 2.4 H, *p*), 1.02 (t, *J* = 7.6 Hz 1.8 H, *ap*), 0.80 (t, *J* = 7.2 Hz, 1.8 H, *ap*).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 161.6, 161.5, 152.1, 151.3, 145.8, 145.3, 140.1, 140.0, 137.4, 137.1, 137.0, 136.9, 134.0, 133.6, 131.0 (2), 124.8, 124.6, 124.4, 124.3, 123.6, 122.9, 122.0, 121.5, 119.1, 118.7, 116.6, 116.5, 107.7, 107.7, 89.3(2×), 56.1, 56.0, 23.0, 19.1, 18.5, 15.8, 15.5, 12.1, 11.5.

^{19}F NMR (367 MHz, $CDCl_3$): δ (ppm) = -110.1 (m, 4.0 F, p/ap), -132.5 (m, 2.0 F, p/ap).

ESI-MS: positive mode: m/z = 706.9615 $[M+Na]^+$ (found), 706.9617 (calculated for $C_{26}H_{19}F_6INaO_3S_2^+$, $[M+Na]^+$).

MeO-CN



e

MeO-CN
(74%)

Compound **e** (75 mg, 0.11 mmol), Pd(PPh$_3$)$_4$ (50 mg, 44 μmol, 0.4 eq.), and Zn(CN)$_2$ (25 mg, 0.22 mmol, 2.0 eq.) were dissolved in dry DMF (1 ml) under N$_2$ atmosphere. The reaction mixture was heated to 95 ˚C for 2 h. DMF was removed under vacuum at 80 ˚C. After cooling to r.t., aq. NaCl (20 ml) was added and the reaction mixture was extracted with DCM (20 ml, twice). The organic phase was collected, dried over MgSO$_4$, and concentrated under reduced pressure. The resulting crude material was subjected to chromatography (DCM/Hexane, 80/20→40/60) to give **MeO-CN** as white solid (47 mg, 74%). R$_f$ (n-hexane/EtOAc, 4/1, v/v) = 0.20.

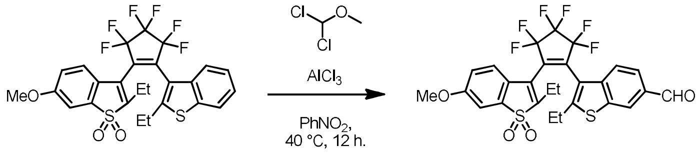
ap:p = 6:4. ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 8.11 (s, 0.6 H, *ap*), 8.03 (s, 0.4 H, *p*), 7.67–7.50 (m, 2.0 H, *ap/p*), 7.28–7.19 (m, 2.0 H, *ap/p*),, 7.32–7.20 (m, 1.2 H, *ap*), 7.13 (d, *J* = 2.4 Hz, 0.4 H, *p*), 7.08 (dd, *J* = 8.4, 2.4 Hz, 0.6 H, *ap*), 6.99 (d, *J* = 8.4 Hz, 0.4 H, *p*), 6.76 (dd, *J* = 8.8, 2.4 Hz, 0.4 H, *p*), 3.88 (s, 1.8 H, *ap*), 3.79 (s, 1.2 H, *p*), 2.90–2.11 (m, 4.0 H, *ap/p*), 1.42–1.33 (m, 2.4 H, *p*), 1.07 (t, *J* = 7.6 Hz 1.8 H, *ap*), 0.78 (t, *J* = 7.6 Hz, 1.8 H, *ap*).

^{13}C NMR (101 MHz, CDCl$_3$): δ (ppm) = 161.8, 161.7, 156.6, 156.0, 145.8, 145.5, 140.7, 140.5, 138.2, 138.1, 137.4, 137.1, 127.8, 127.5, 127.2, 127.1, 124.5, 124.4, 124.3, 124.2 (2×), 123.5, 122.3 (2×), 122.3, 121.8, 121.3, 119.2, 118.6, 118.5 (2×), 117.0, 116.9, 115.4, 115.3, 108.4, 108.2, 107.9, 107.8, 56.1, 56.0, 23.4, 22.6, 19.2, 18.6, 15.8, 15.4, 12.1, 11.5.

^{19}F NMR (367 MHz, CDCl$_3$): δ (ppm) = -110.1 (m, 4.0 F, p/ap), -132.4 (m, 2.0 F, p/ap).

ESI-MS: positive mode: m/z = 606.0605 [M+Na]$^+$ (found), 606.0603 (calculated for $C_{27}H_{19}F_6NNaO_3S_2^+$, [M+Na]$^+$).

Compound **f**



MeO-H

f
(40%)

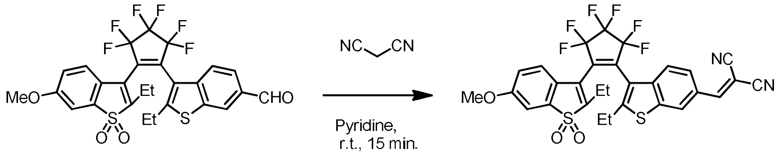
MeO-H (0.26 g, 0.47 mmol) was dissolved in nitrobenzene (1.5 ml). To the reaction solution was added 1,1-dichloromethyl methyl ether (80 mg, 0.70 mmol, 1.5 eq.) and aluminium chloride (93 mg, 0.7 mmol, 1.5 eq.). The reaction solution was stirred for 12 h at 40 ˚C. Water (50 ml) was added, and the reaction mixture was extracted with DCM (50 ml, twice). The organic phase was collected, dried over MgSO$_4$, and concentrated under reduced pressure. Column chromatography with gradient elution (hexane/ethyl acetate = 80/20→ 50/50) afforded compound **f** as a white solid (110 mg, 40%). R$_f$ (n-hexane/EtOAc, 3/1, v/v) = 0.2.

ap:p = 6:4.^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 10.09 (s, 0.6 H, *ap*), 10.03 (s, 0.4 H, *p*), 8.30 (d, *J* = 0.8 Hz, 0.6 H, *ap*), 8.22 (d, *J* = 0.8 Hz, 0.4 H, *p*), 7.92 (dd, *J* = 8.4, 1.6 Hz, 0.6 H, *ap*), 7.81 (dd, *J* = 8.4, 1.2 Hz, 0.4 H, *ap*), 7.70–7.58 (m, 1 H, *ap/p*), 7.26–7.10 (m, 1.2 H, *ap*), 7.12 (d, *J* = 2.4 Hz, 0.4 H, *p*), 7.08 (dd, *J* = 8.4, 2.4 Hz, 0.6 H, *ap*), 7.04 (d, *J* = 8.4 Hz, 0.4 H, *p*), 6.76 (dd, *J* = 8.4, 2.8 Hz, 0.4 H, *ap*), 3.88 (s, 1.8 H, *ap*), 3.76 (s, 1.2 H, *p*), 2.91–2.13 (m, 4.0 H, *ap/p*), 1.42–1.33 (m, 2.4 H, *p*), 1.08 (t, *J* = 7.6 Hz 1.8 H, *ap*), 0.77 (t, *J* = 7.6 Hz, 1.8 H, *ap*). ^{13}C NMR (101 MHz, CDCl$_3$): δ (ppm) = 191.1 (2×), 161.7, 161.6, 156.9, 156.3, 145.9, 145.4, 142.3, 142.0, 138.4, 138.3, 137.4, 137.0, 133.0 (2×), 125.8, 125.6, 125.3, 124.7, 124.5, 124.3 (2×), 123.7, 123.3, 123.2, 122.2, 122.1, 121.9, 121.4, 119.1, 118.6, 117.1, 117.0, 107.8 (2×), 56.1, 56.0, 23.5, 19.1, 18.6, 15.8, 15.5, 12.1, 11.4.

^{19}F NMR (367 MHz, CDCl$_3$): δ (ppm) = -110.1 (m, 4.0 F, p/ap), -132.4 (m, 2.0 F, p/ap).

ESI-MS: positive mode: m/z = 609.0602 [M+Na]$^+$ (found), 609.0599 (calculated for $C_{27}H_{20}F_6NaO_4S_2^+$, [M+Na]$^+$).

MeO-CN2



f

MeO-CN2
(77%)

Compound **f** (30 mg, 51 μmol) was dissolved in pyridine(1.0 ml). To the reaction solution was added malonodinitrile (6.8 mg, 0.10 mmol, 2.0 eq.). The reaction solution was stirred for 15 min. at r.t. Pyridine was removed under reduced pressure. The resulting crude product was subjected to column chromatography with gradient elution (hexane/ethyl acetate = 95/5→ 50/50) to afforded crude **MeO-CN2**. Further purification by reversed phase column chromatography (0.1% aq. TFA/MeCN, gradient from 7/3 to 3/7 followed by lyophilization (solvent: distilled water/1,4-dioxane, 1/9, v/v) gave **MeO-CN2** as a pale yellow solid (25 mg, 77%). R_f (n-hexane/EtOAc, 4/1, v/v) = 0.16.

ap:p = 6:4. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.34 (s, 0.6 H, *ap*), 8.22 (s, 0.4 H, *p*), 8.30 (dd, *J* = 8.8, 1.6 Hz, 0.6 H, *ap*), 7.89 (dd, *J* = 8.8, 1.6 Hz, 0.4 H, *p*), 7.86 (s, 0.6 H, *ap*), 7.81 (s, 0.4 H, *p*), 7.70–7.60 (m, 1 H, *ap/p*), 7.30–7.21 (m, 1.2 H, *ap*), 7.14 (d, *J* = 2.4 Hz, 0.4 H, *p*), 7.09 (dd, *J* = 8.4, 2.4 Hz, 0.6 H, *ap*), 7.05 (d, *J* = 8.4 Hz, 0.4 H, *p*), 6.81 (dd, *J* = 8.4, 2.4 Hz, 0.4 H, *ap*), 3.89 (s, 1.8 H, *ap*), 3.78 (s, 1.2 H, *p*), 2.94–2.16 (m, 4.0 H, *ap/p*), 1.45–1.34 (m, 2.4 H, *p*), 1.11 (t, *J* = 7.6 Hz 1.8 H, *ap*), 0.82 (t, *J* = 7.6 Hz, 1.8 H, *ap*). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 161.7, 161.6, 158.8, 158.7, 158.1, 157.6, 145.8, 145.5, 142.1, 141.8, 138.8, 138.7, 137.3, 137.0, 127.3, 127.3, 126. 5, 126.0, 125.9, 124.4 (2×), 124.2 (2×), 123.6, 122.5 (2×), 121.3, 119.1, 118.5, 117.2, 117.2, 113. 7, 113.6, 112.7, 108.0, 107.8, 82.4, 82.4, 56.1, 56.0, 30.2, 23.6, 19.1, 18.6, 15.7, 15.4, 12.1, 11.5.

^{19}F NMR (367 MHz, $CDCl_3$): δ (ppm) = -110.1 (m, 4.0 F, p/ap), -132.3 (m, 2.0 F, p/ap).

ESI-MS: positive mode: m/z = 657.0699 $[M+Na]^+$ (found), 657.0712 (calculated for $C_{30}H_{20}F_6N_2NaO_3S_2^+$, $[M+Na]^+$).

NMR spectra of compound b

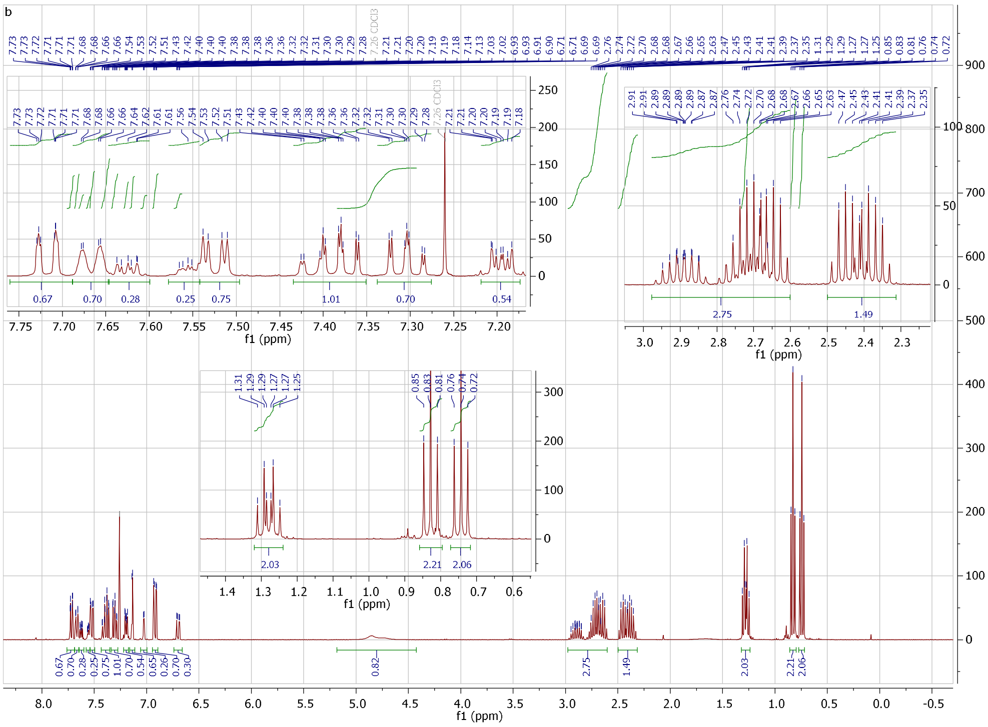


Figure S1-a. ^{1}H-NMR (400 MHz) spectrum of **b** in $CDCl_3$

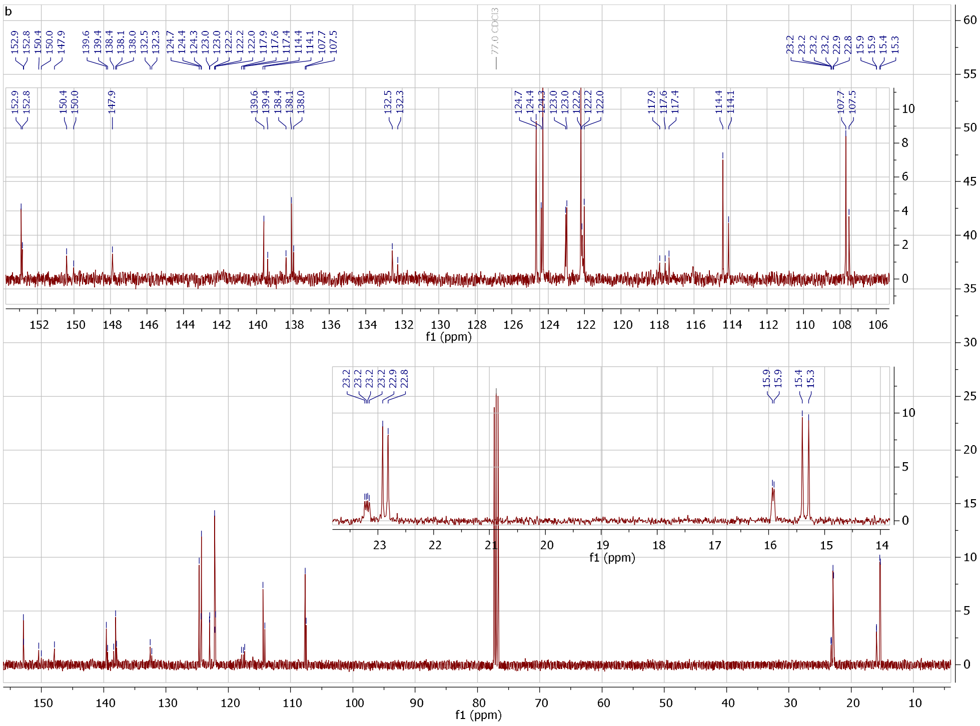


Figure S1-b. ^{13}C-NMR (101 MHz) spectrum of **b** in CDCl$_3$

Figure S1-c. ^{19}F-NMR (367 MHz) spectrum of **b** in CDCl$_3$

NMR spectra of compound c

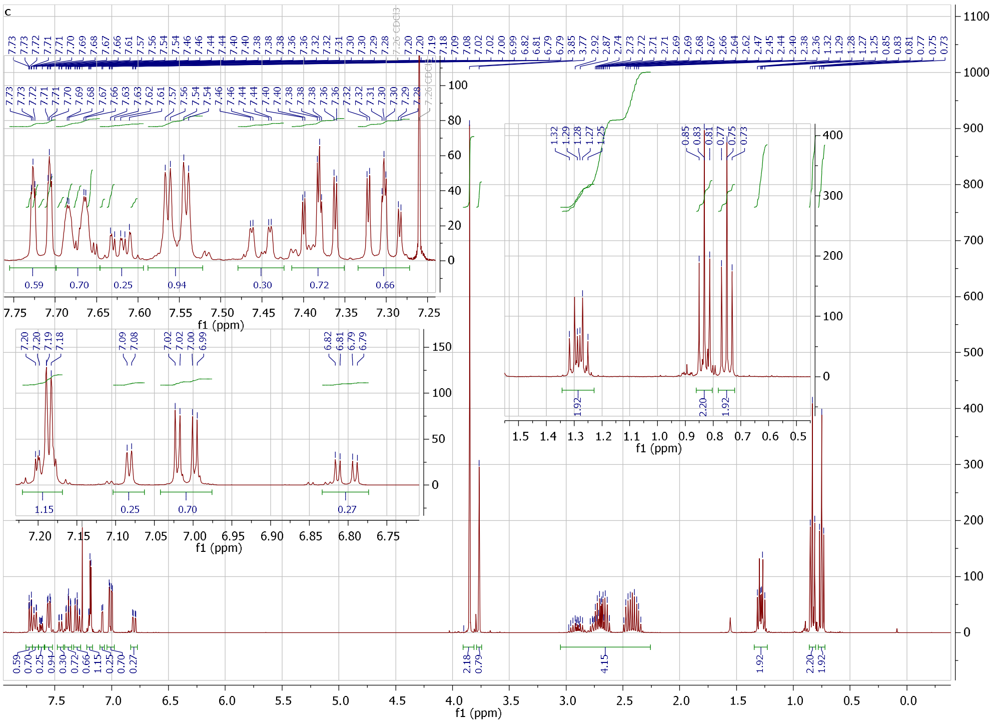


Figure S2-a. ^{1}H-NMR (400 MHz) spectrum of **c** in $CDCl_3$

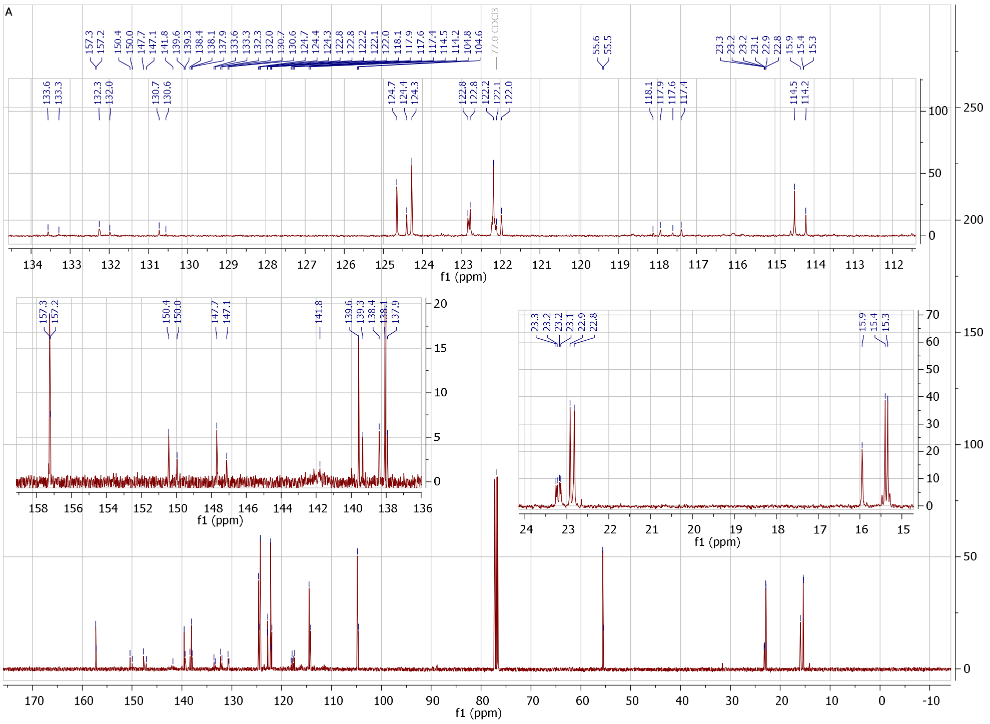


Figure S2-b. ^{13}C-NMR (101 MHz) spectrum of **c** in CDCl$_3$

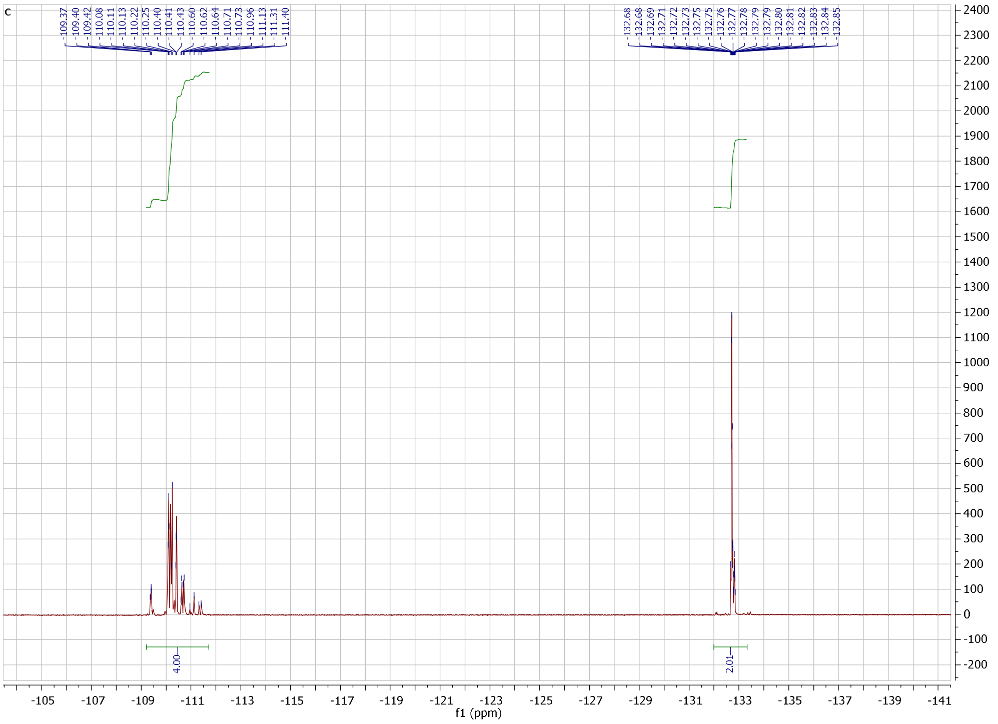


Figure S2-c. ^{19}F-NMR (367 MHz) spectrum of **c** in CDCl$_3$

NMR spectra of compound MeO-H

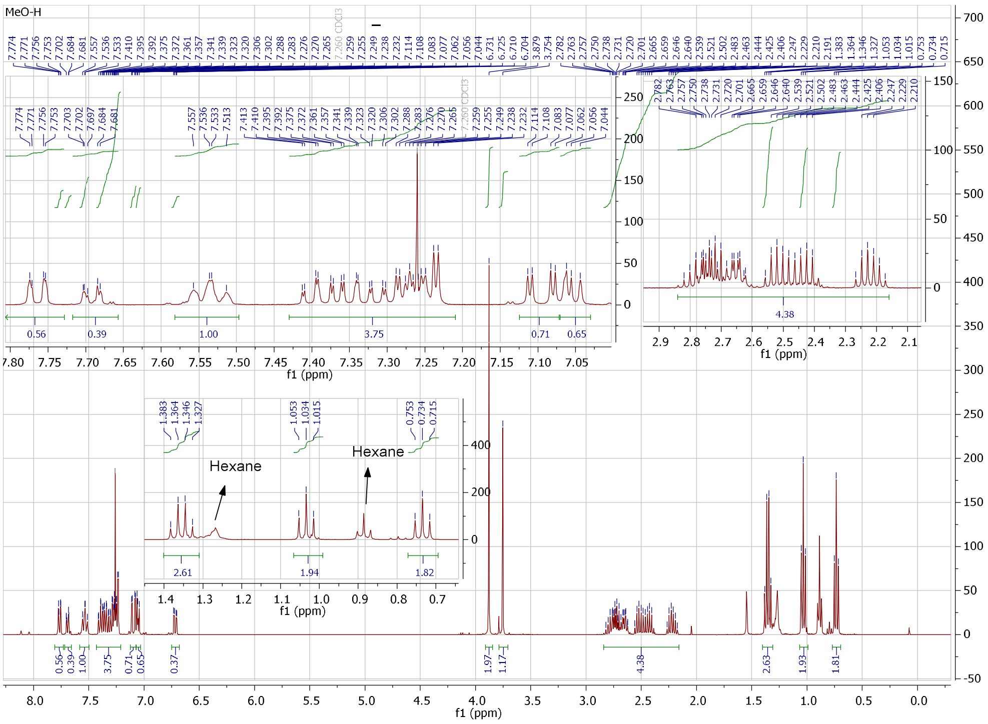


Figure S3-a. ^{1}H-NMR (400 MHz) spectrum of **MeO-H** in CDCl$_3$

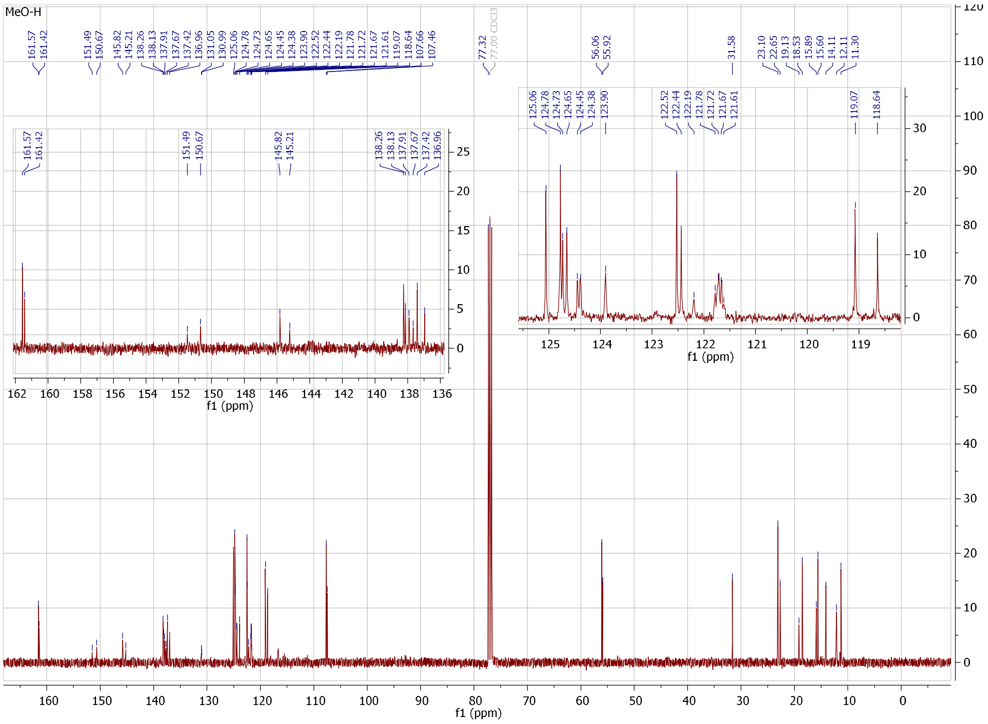


Figure S3-b. ^{13}C-NMR (101 MHz) spectrum of **MeO-H** in CDCl₃

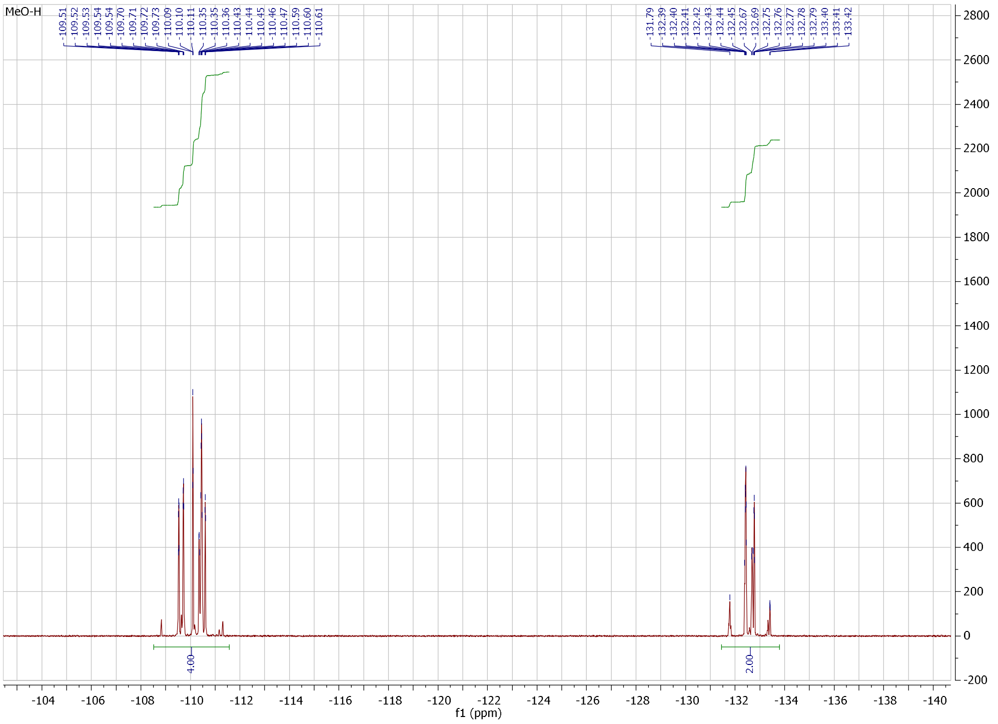


Figure S3-c. ^{19}F-NMR (367 MHz) spectrum of **MeO-H** in CDCl₃

NMR spectra of compound e

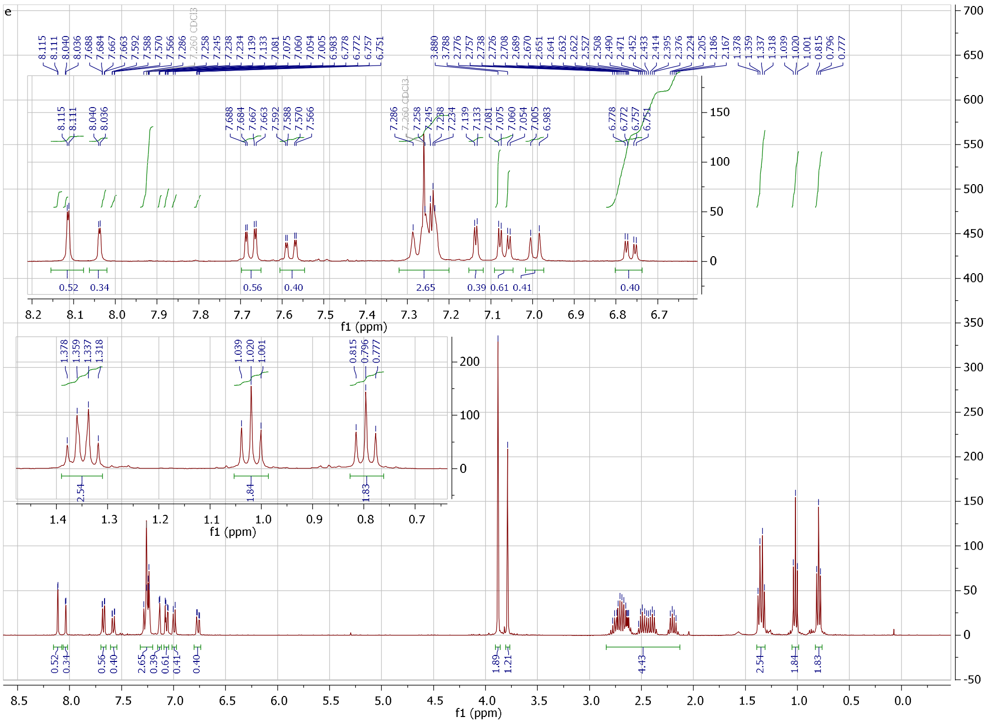


Figure S4-a. ^{1}H-NMR (400 MHz) spectrum of compound **e** in $CDCl_3$

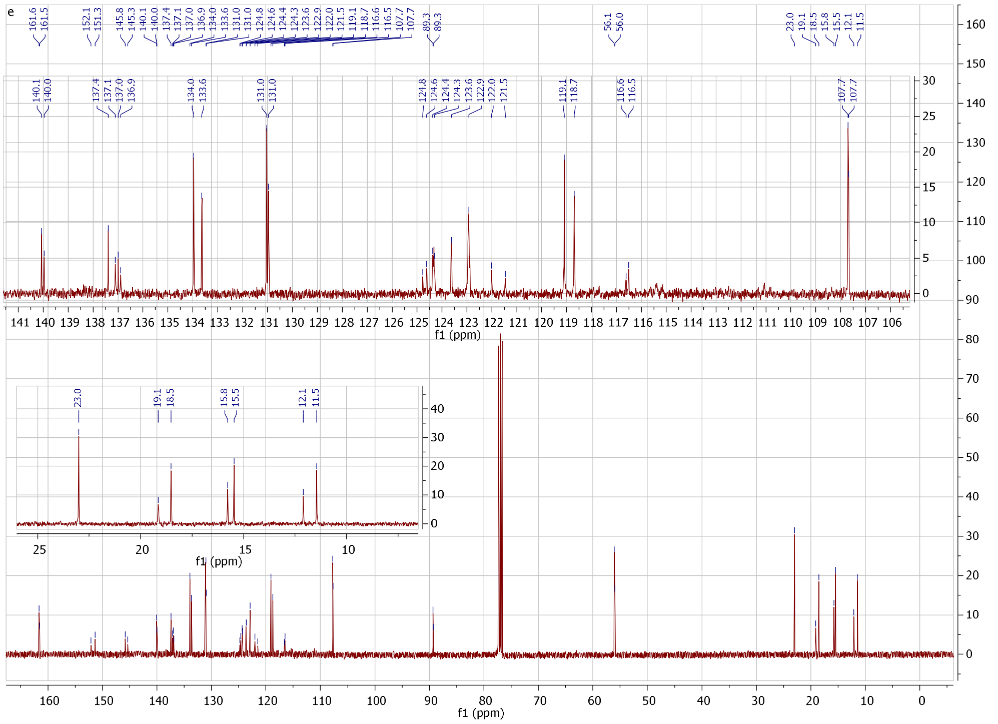


Figure S4-b. ^{13}C-NMR (101 MHz) spectrum of compound **e** in CDCl$_3$

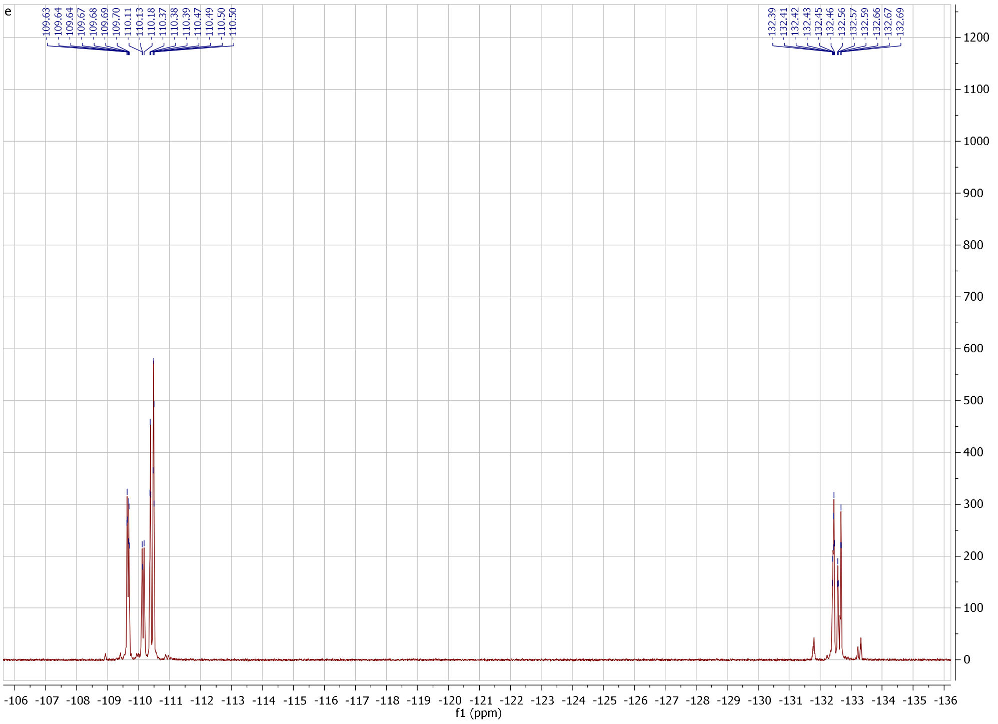


Figure S4-c. ^{19}F-NMR (367 MHz) spectrum of compound **e** in CDCl$_3$

NMR spectra of compound MeO-CN

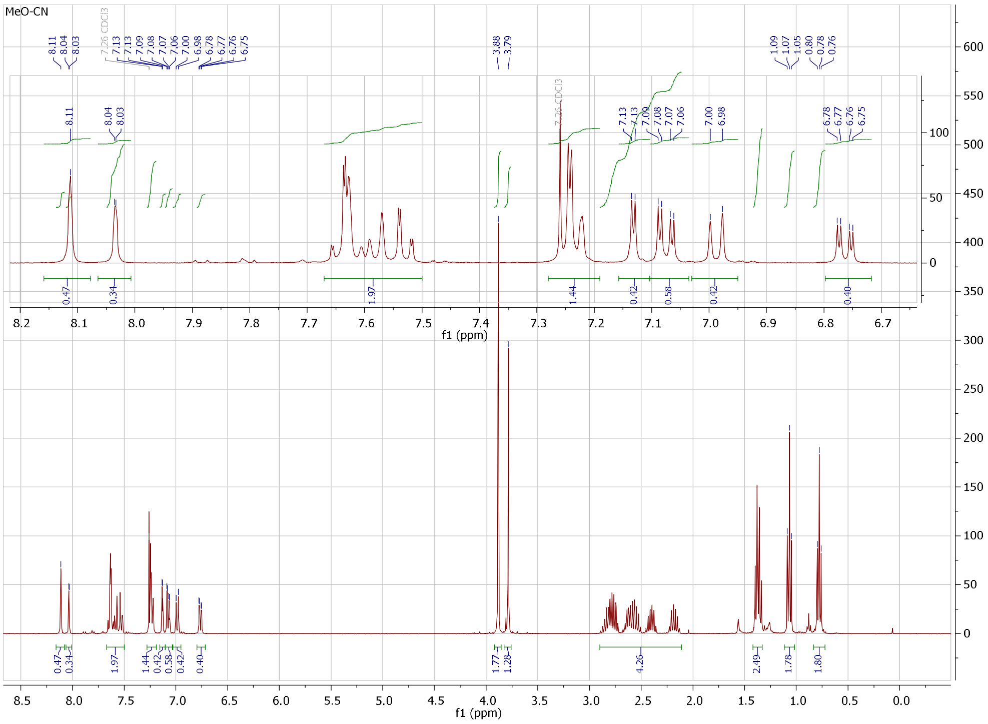


Figure S5-a. ^{1}H-NMR (400 MHz) spectrum of **MeO-CN** in $CDCl_3$

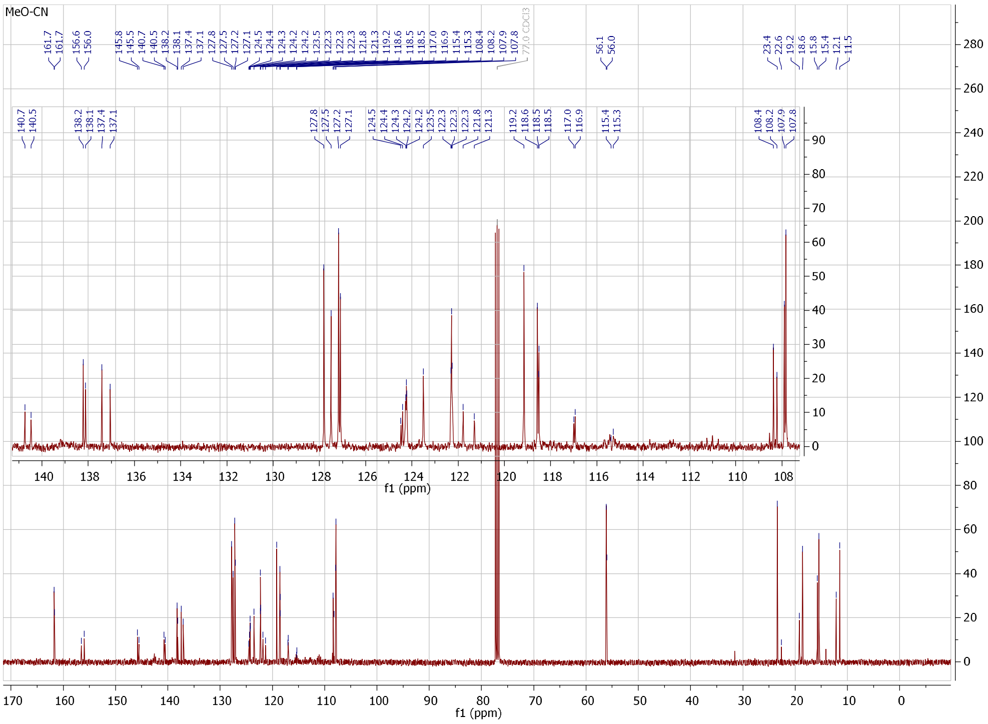


Figure S5-b. ^{13}C-NMR (101 MHz) spectrum of **MeO-CN** in CDCl$_3$

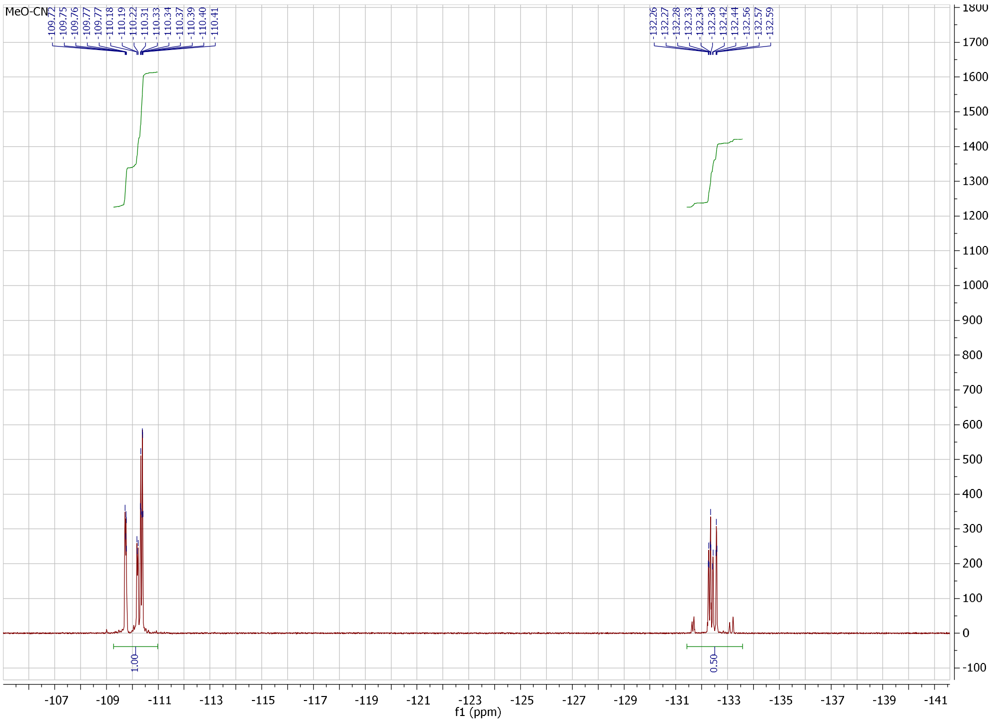


Figure S5-c. ^{19}F-NMR (367 MHz) spectrum of **MeO-CN** in CDCl$_3$

NMR spectra of compound f

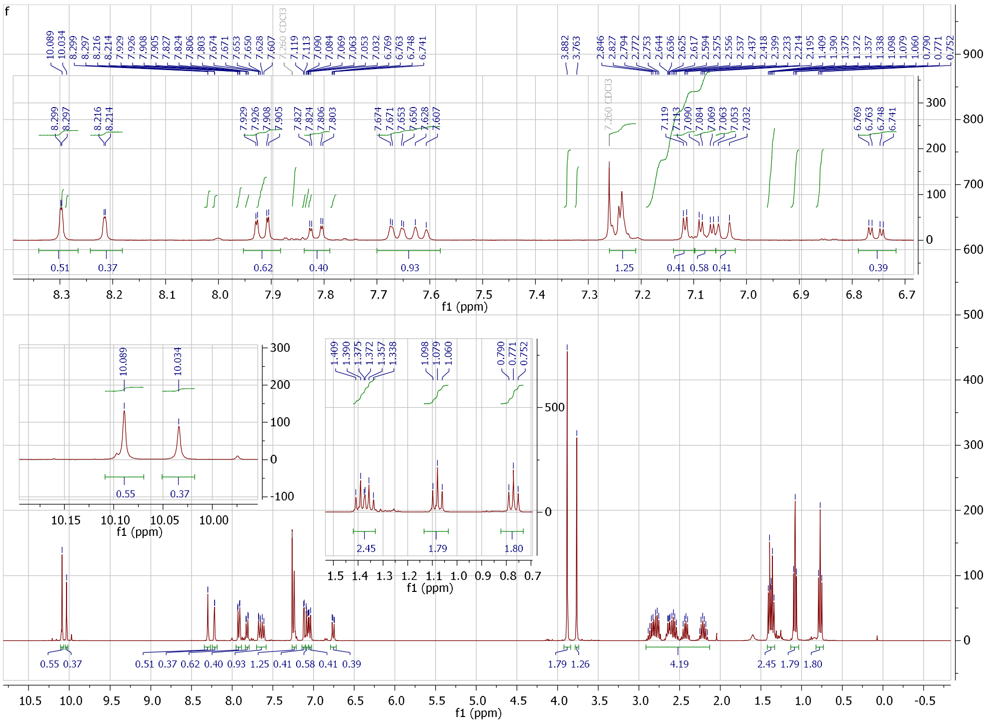


Figure S6-a. ^{1}H-NMR (400 MHz) spectrum of compound **f** in $CDCl_3$

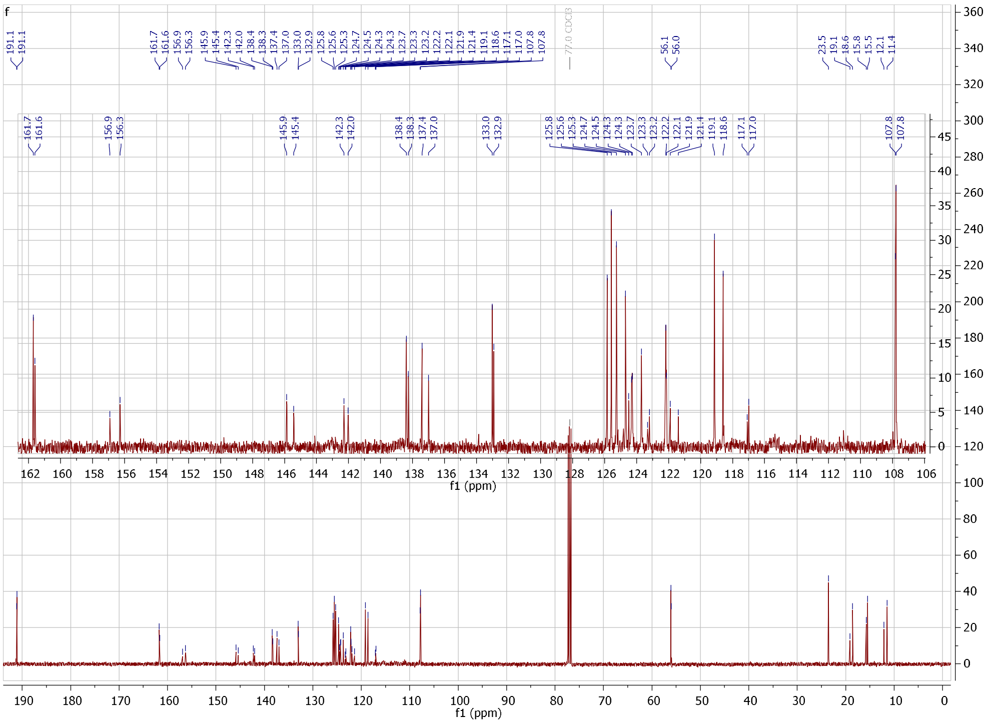


Figure S6-b. ^{13}C-NMR (101 MHz) spectrum of compound **f** in CDCl$_3$

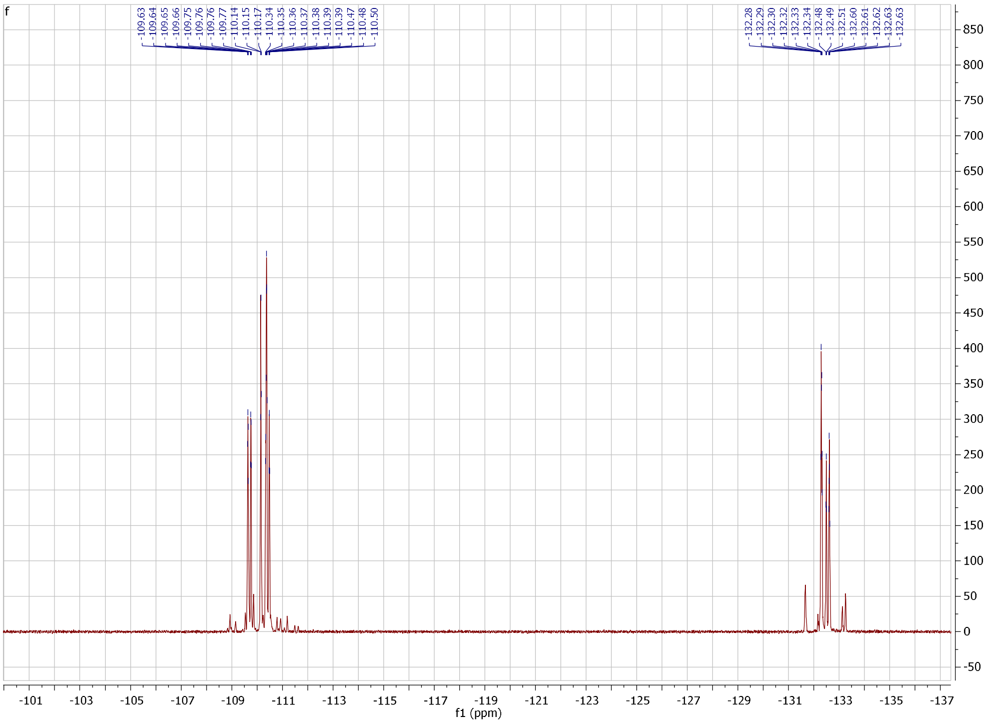


Figure S6-c. ^{19}F-NMR (367 MHz) spectrum of compound **f** in CDCl$_3$

NMR spectra of compound MeO-CN2

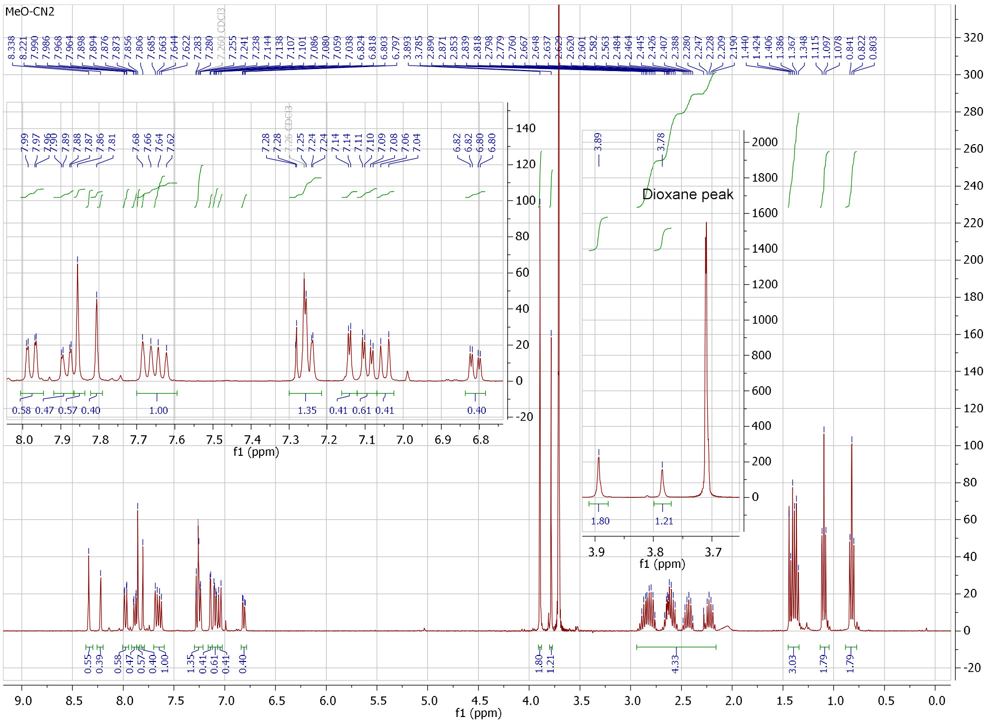


Figure S7-a. ^{1}H-NMR (400 MHz) spectrum of **MeO-CN2** in CDCl$_3$

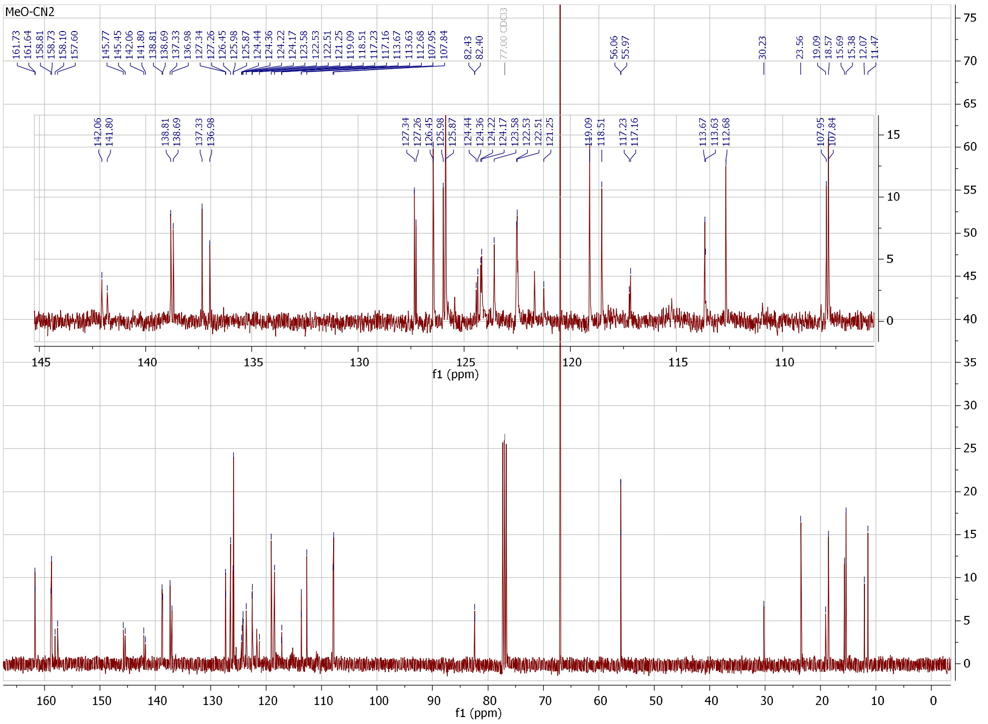


Figure S7-b. ^{13}C-NMR (101 MHz) spectrum of **MeO-CN2** in CDCl$_3$

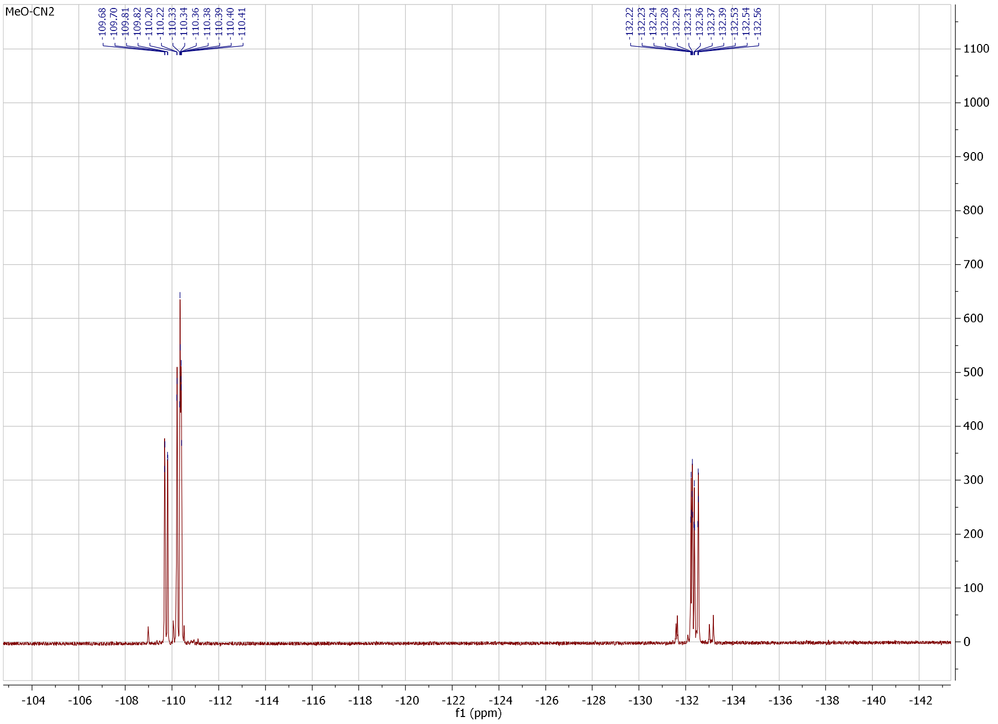


Figure S7-c. ^{19}F-NMR (367 MHz) spectrum of **MeO-CN2** in CDCl$_3$

UV-Vis Absorption and emission spectra

Absorption spectra (Figure S8) were recorded in a Cary 5000 UV-Vis-NIR spectrometer (Agilent Technologies), and emission spectra (Figure S9) in a Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies), in 3 mL quartz cuvettes with magnetic stirring (model 119F-10-40, Hellma Analytics). The spectra of the OFs were obtained from non-irradiated solutions (ca. 10 μM). The samples were irradiated with 365 nm light, in a custom-built setup [2]. At the photo-stationary state, samples were immediately transferred in the dark to the spectrometers, and absorption and emission were recorder again. The conversion was estimated from the modulation of the emission of the OF, at a wavelength were the CF has negligible emission. Attempts to calculate the conversion from HPLC measurements of irradiated solutions yielded systematically lower values, probably due to the changes produced by the illumination source in the diode array detector, as a result of the high isomerization quantum yields. In addition, the emission of the CF in acetonitrile and toluene solutions (Figure S10), and the modulation of the signal between the two photostationary states (under irradiation with UV and visible light), were assessed by excitation with 540 nm light. At this wavelength, we could be sure that only the CF absorbs because the absorption cut-off of the OF is quite far away (ca. at 400-420 nm), and thus the emission pattern correspond exclusively to the CF, independent from the conversion achieved at each state.

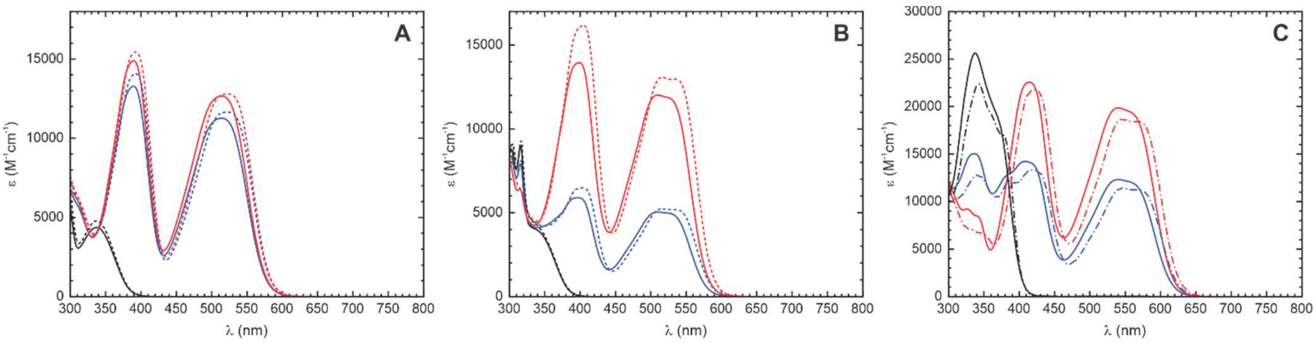


Figure S8. Absorption coefficients of compounds (A) **MeO-H**, (B) **MeO-CN**, and (C) **MeO-CN2**, in acetonitrile (full lines) and in toluene (dashed lines). The spectra of the OFs (black lines) were measured with the non-irradiated solutions, and that of the CFs (red lines) were calculated from the spectra measured at the photo-stationary state (blue lines, scaled by the total concentration)and the conversion degrees.

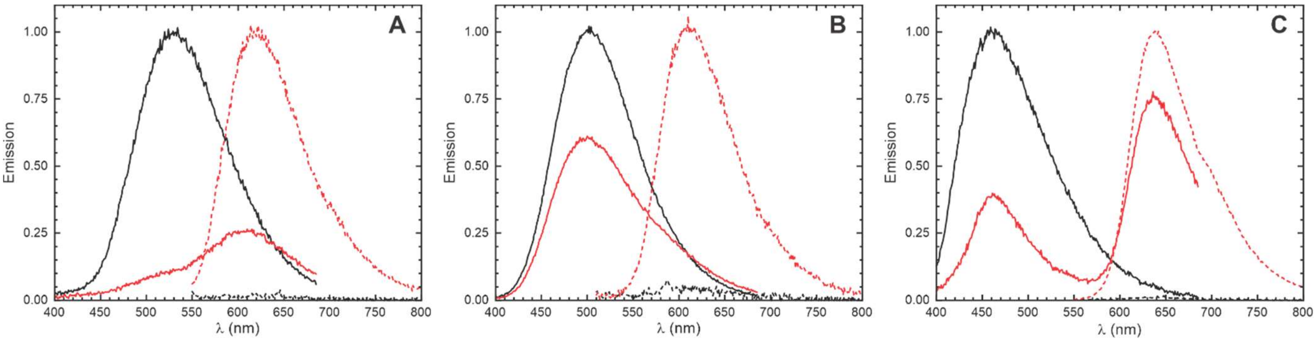


Figure S9. Emission modulation of compounds (A) **MeO-H**, (B) **MeO-CN** and (C) **MeO-CN2** in acetonitrile. Black lines: emission of solutions containing only OFs (non-irradiated solutions). Red lines: emission of solutions irradiated to the photo-stationary states. Samples were excited at 355 nm (full lines), and at 500 nm (B) or 540 nm (A, C) (dashed lines).

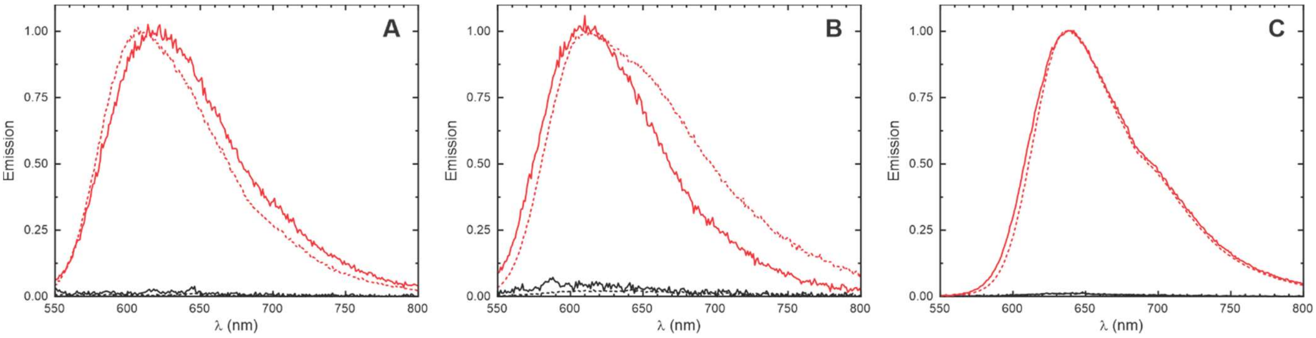


Figure S10. Emission modulation of the CFs (excitation at 540 nm) of compounds **MeO-H** (A), **MeO-CN** (B) and **MeO-CN2** (C) from the photostationary states under irradiation with UV (black lines) and with visible light (redlines), in acetonitrile solutions (full lines) and in toluene solutions (dashed lines). The emission was normalized to the corresponding maxima in the photostationary state under irradiation with UV light.

Photochromism

Acetonitrile solutions were irradiated in a home-made setup [2], with UV (365 nm) and visible (505 nm) light. Samples were continuously stirred at 20 °C with a Peltier-based temperature control (Luma 40, Quantum Northwest, Inc.). Absorption spectra were recorded at certain intervals (ca. 0.1-0.5 s); the control experiments verified that the lamp of the diode array absorption spectrometer did not induce any photo-isomerization reactions. Isomerization quantum yields were calculated from numerical fits of the transients obtained at the absorption maxima of the corresponding CFs. A full irradiation cycle is shown for compounds **MeO-H**, **MeO-CN** and **MeO-CN2** in Figures S11, S12 and S13, respectively.

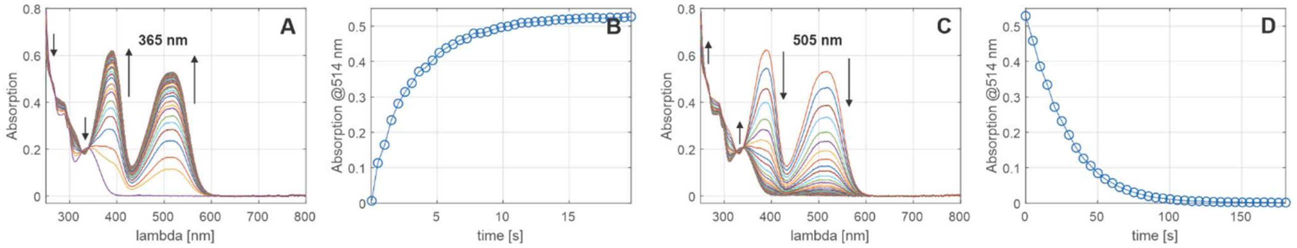


Figure S11. Absorption changes of a solution of **MeO-H** in acetonitrile, under irradiation with 365 nm light (A, B) and 505 nm light (C, D). Emission spectra were not recorded.

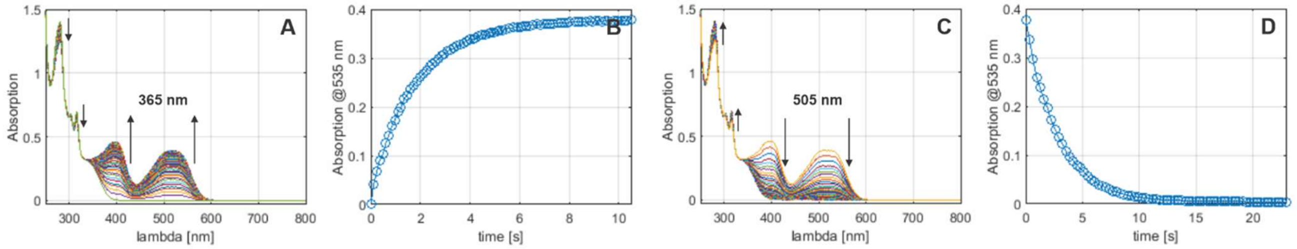


Figure S12. Absorption changes of a solution of **MeO-CN** in acetonitrile, under irradiation with 365 nm light (A, B) and 505 nm light (C, D). Emission spectra were not recorded.

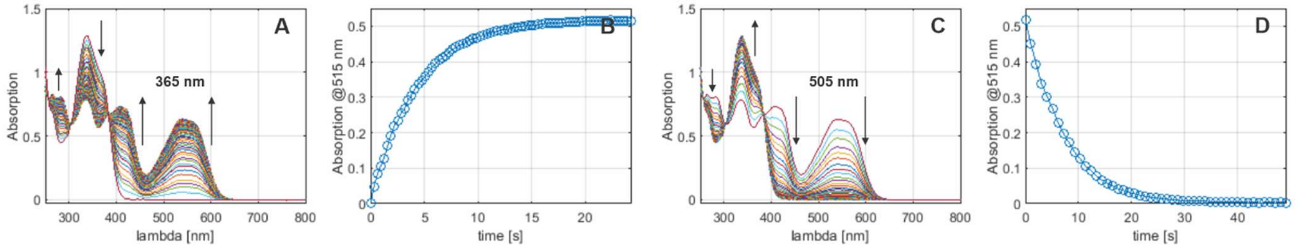


Figure S13. Absorption changes of a solution of **MeO-CN2** in acetonitrile, under irradiation with 365 nm light (A, B) and 505 nm light (C, D). Emission spectra were not recorded.

The same experiments were repeated, but recording the absorption and the emission spectra (ex = 365 nm) after each irradiation interval (Figures S14-S16). Excitation intensities were as low as possible. However, due to high values of the cyclization quantum yields, the excitation light induced partial isomerization and prevented the full conversion to the OF in the photo-stationary state under visible irradiation.

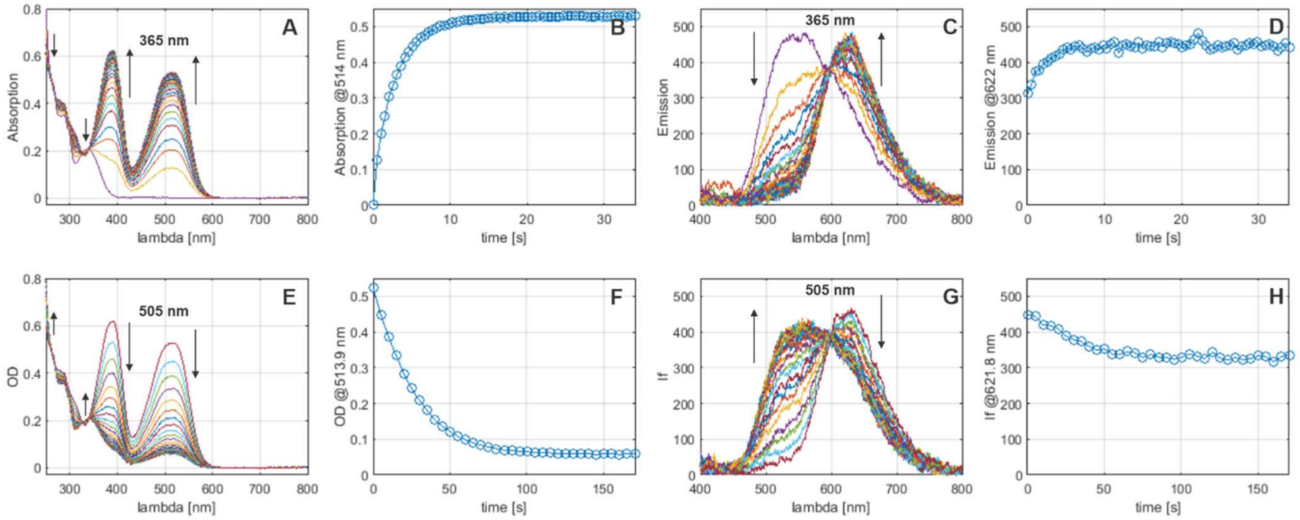


Figure S14. Absorption (A-B, E-F) and emission (C-D, G-H) changes of **MeO-H** dissolved in acetonitrile under irradiation with 365 nm light (A-D) and 505 nm light (E-H). Emission spectra were recorded after each step, using a short excitation pulse of 365 nm.

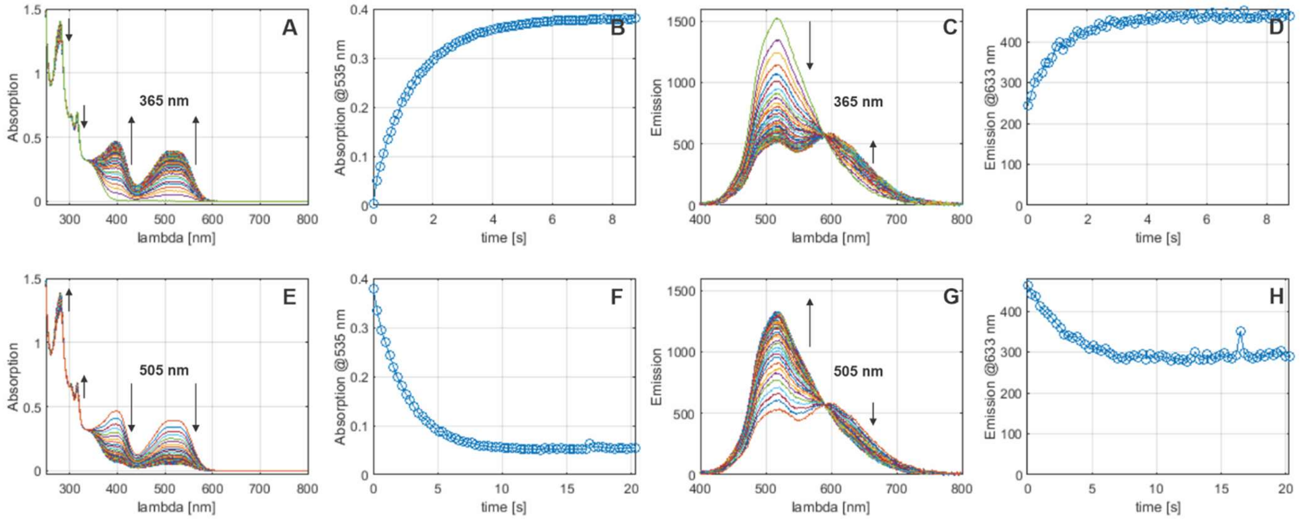


Figure S15. Absorption (A-B, E-F) and emission (C-D, G-H) changes of a **MeO-CN** dissolved in acetonitrile under irradiation with 365 nm light (A-D) and 505 nm light (E-H). Emission spectra were recorded after each step, using a short excitation pulse of 365 nm.

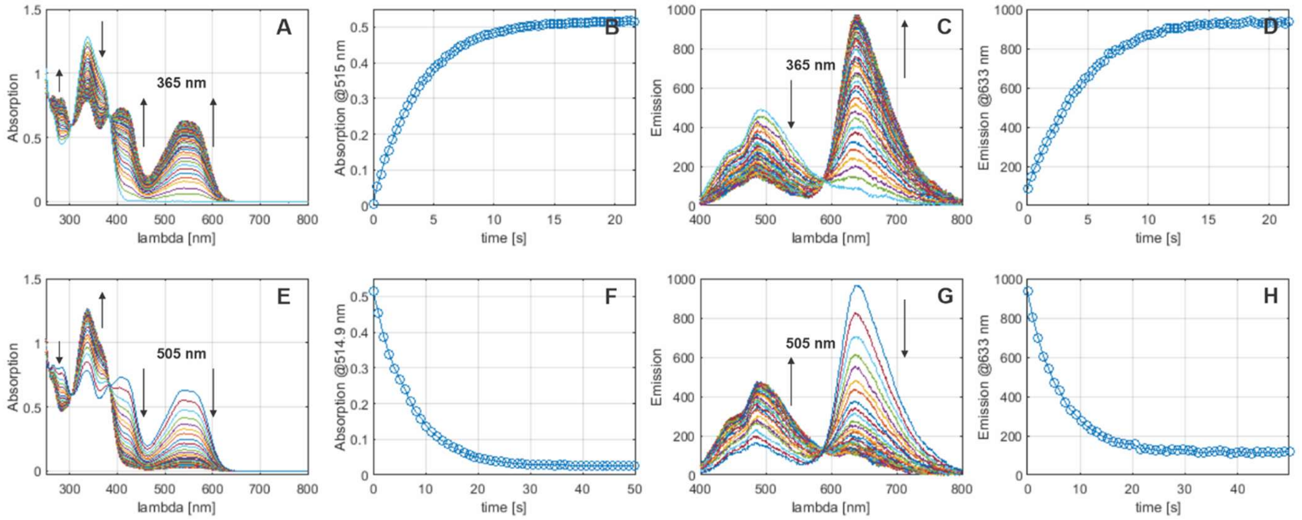


Figure S16. Absorption (A-B, E-F) and emission (C-D, G-H) changes of **MeO-CN2** dissolved in acetonitrile under irradiation with 365 nm light (A-D) and 505 nm light (E-H). Emission spectra were recorded after each step, using a short excitation pulse of 365 nm.

Reversible Photoswitching of Absorption and Emission Signals

Acetonitrile solutions of three dyes (**MeO-H**, **MeO-CN**, and **MeO-CN2**) were submitted to successive switching cycles, by alternating irradiation with UV and visible light (Figures S17-S19). The duration of each step was determined from the results of the separate experiments, as the time required to achive the corresponding photo-stationary state. Absorption and emission (ex = 365 nm) spectra were recorded after each semi-cycle. In addition to the absorption changes, where the state of the system was assessed from monitoring the absorption modulation in the visible range (close to the maximum of the CF), the alternation of the emission signal was also monitored. The binary state of the system may be determined from measuring the fluorescence intensities at the emission maxima of both isomers, or from the ratio of these intensities, as exemplified in Figures S17-S19. Similar results were obtained in toluene solutions (Figures S20-22), where the emission quantum yields are higher than in acetonitrile.

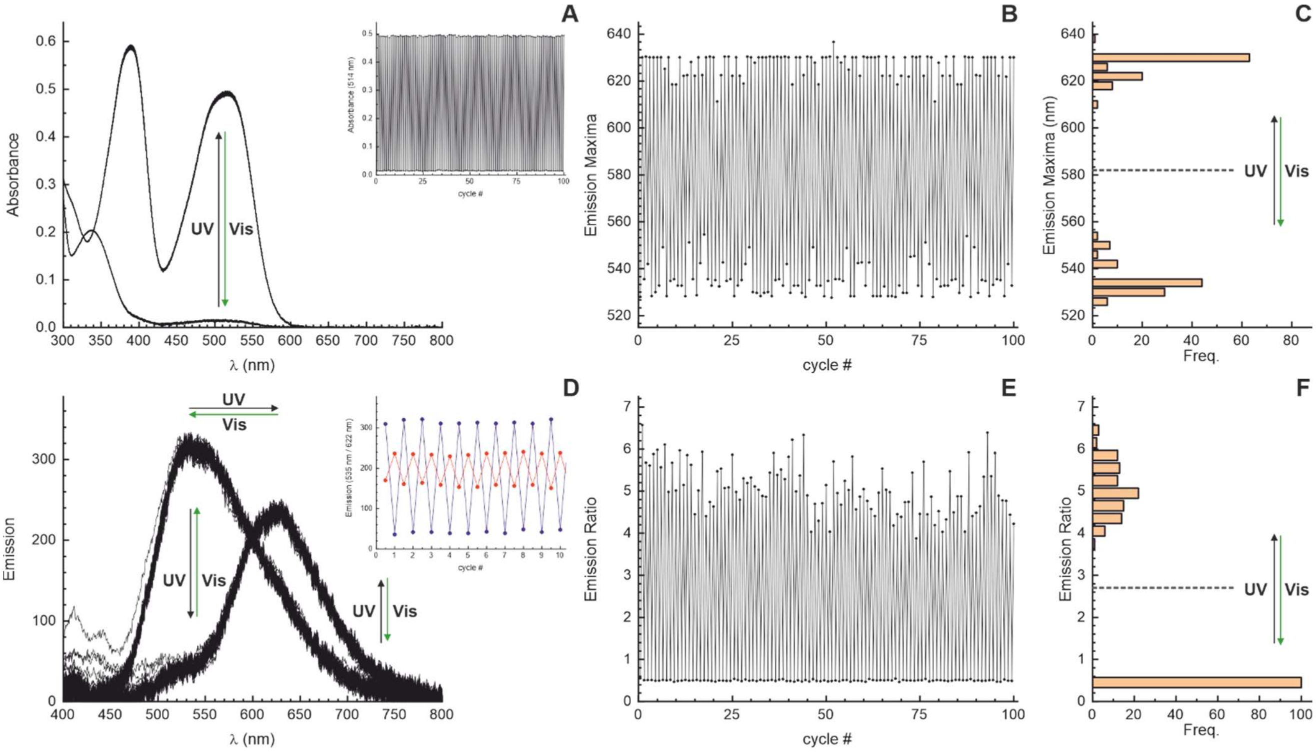


Figure S17. Absorption (A) and emission (D) spectra of compound **MeO-H** in acetonitrile switched with 365 nm (UV) and 515 nm (Vis) light. The insets show the intensity at the absorption maximum of the CF and at the emission maxima of the OF and the CF, respectively. Emission maxima (B) and the corresponding frequency counts (C). Ratio of the emission intensities at the maxima of each isomer (E), and the corresponding histogram (F). All plots were derived from the first 100 cycles, except the lower inset in (D) which was plotted for the first 10 cycles.

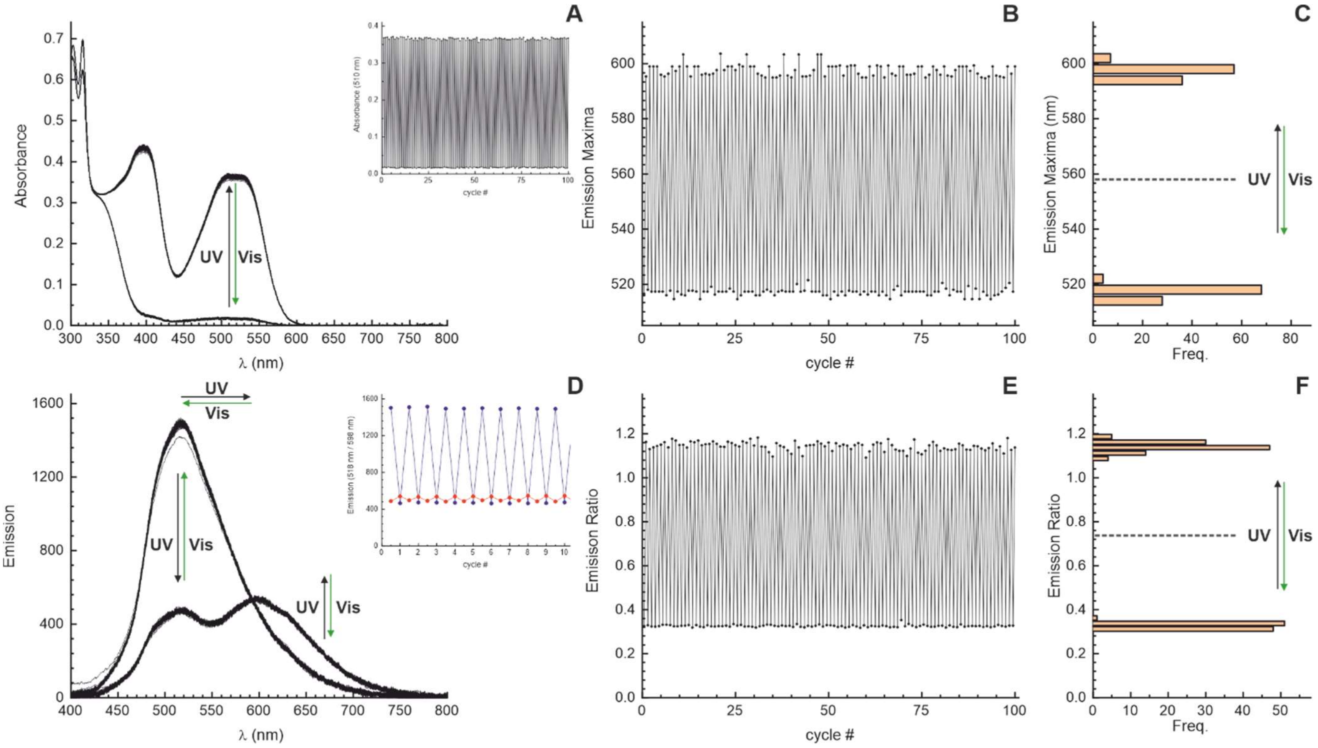


Figure S18. Absorption (A) and emission (D) spectra of compound **MeO-CN** in acetonitrile acquired in the course of switching with 365 nm (UV) and 515 nm (Vis) light. The insets shows the intensity at the absorption maximum of the CF and at the emission maxima of the OF and the CF, respectively. Emission maxima (B) and the corresponding frequency count (C). Ratio of the emission intensities at the maxima of each isomer (E), and the corresponding histogram (F). All plots were derived from the first 100 cycles, except the lower inset in (D) which was plotted for the first 10 cycles.

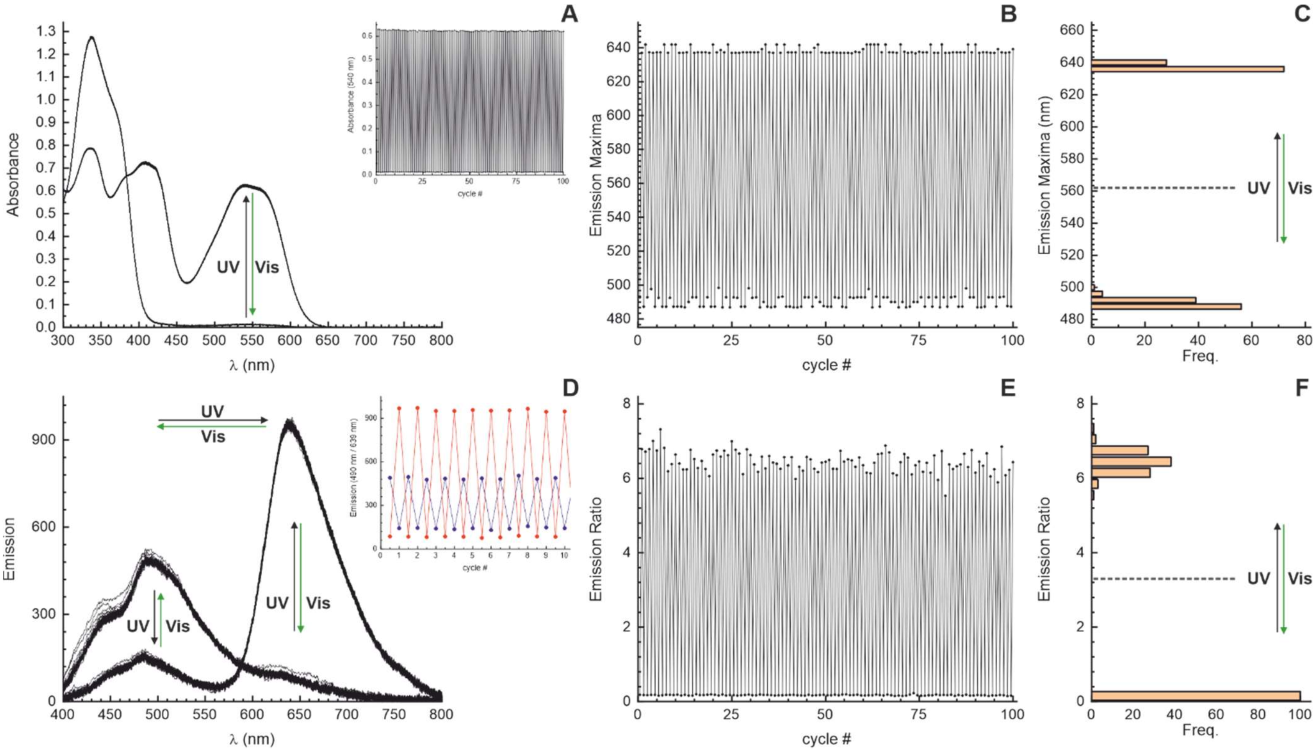


Figure S19.

Absorption (A) and emission (D) spectra of compound **MeO-CN2** in acetonitrile obtained in the course of switching with 365 nm (UV) and 515 nm (Vis) light. The insets shows the intensity at the absorption maximum of the CF and at the emission maxima of the OF and the CF, respectively. Emission maxima (B) and the corresponding frequency count (C). Ratio of the emission intensities at the maxima of each isomer (E) and the corresponding histogram (F). All plots were derived from the first 100 cycles, except the lower inset in (D) which was plotted for the first 10 cycles.

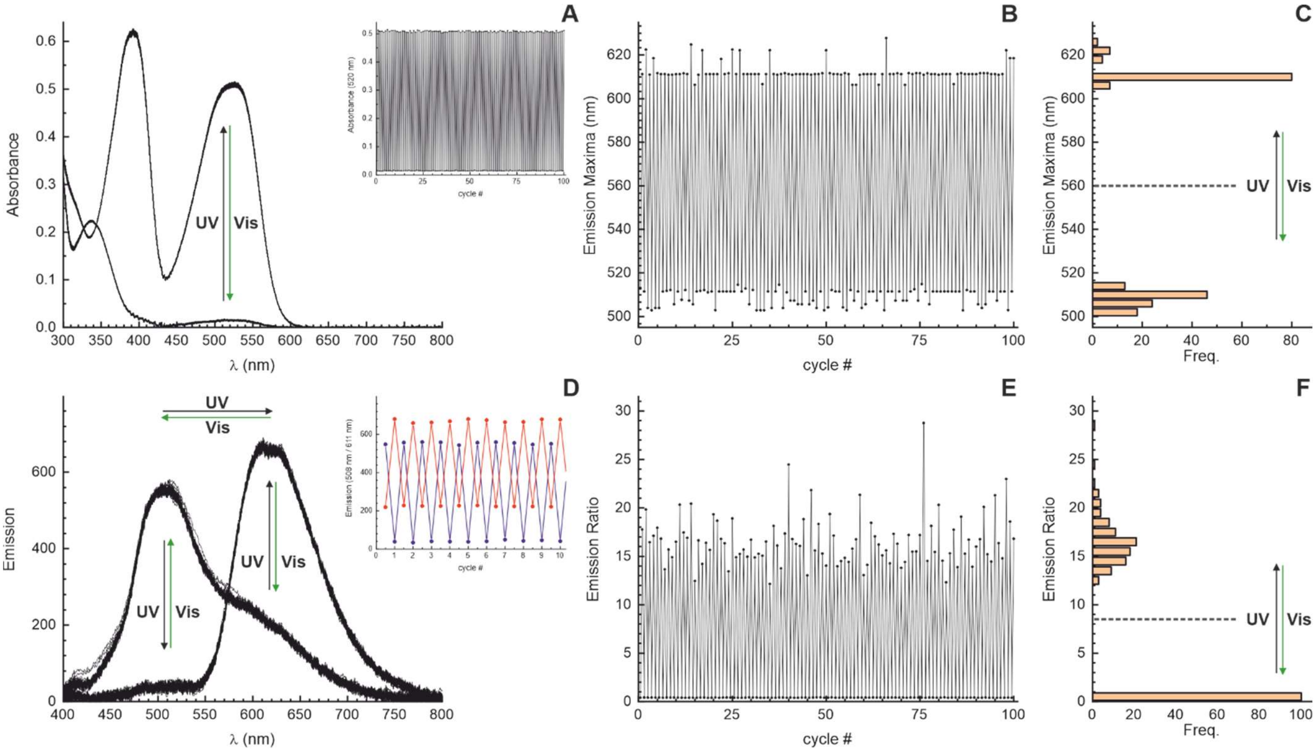


Figure S20. Absorption (A) and emission (D) switching of compound **MeO-H** in toluene irradiated with 365 nm (UV) and 515 nm (Vis) light. The insets show the intensity at the absorption maximum of the CF and at the emission maxima of the OF and the CF, respectively. Emission maxima (B), and the corresponding frequency count (C). Ratio of the emission signals at the maxima of each isomer (E) and the corresponding histogram (F). All plots were derived from the first 100 cycles, except the inset in (D) which was plotted for the first 10 cycles.

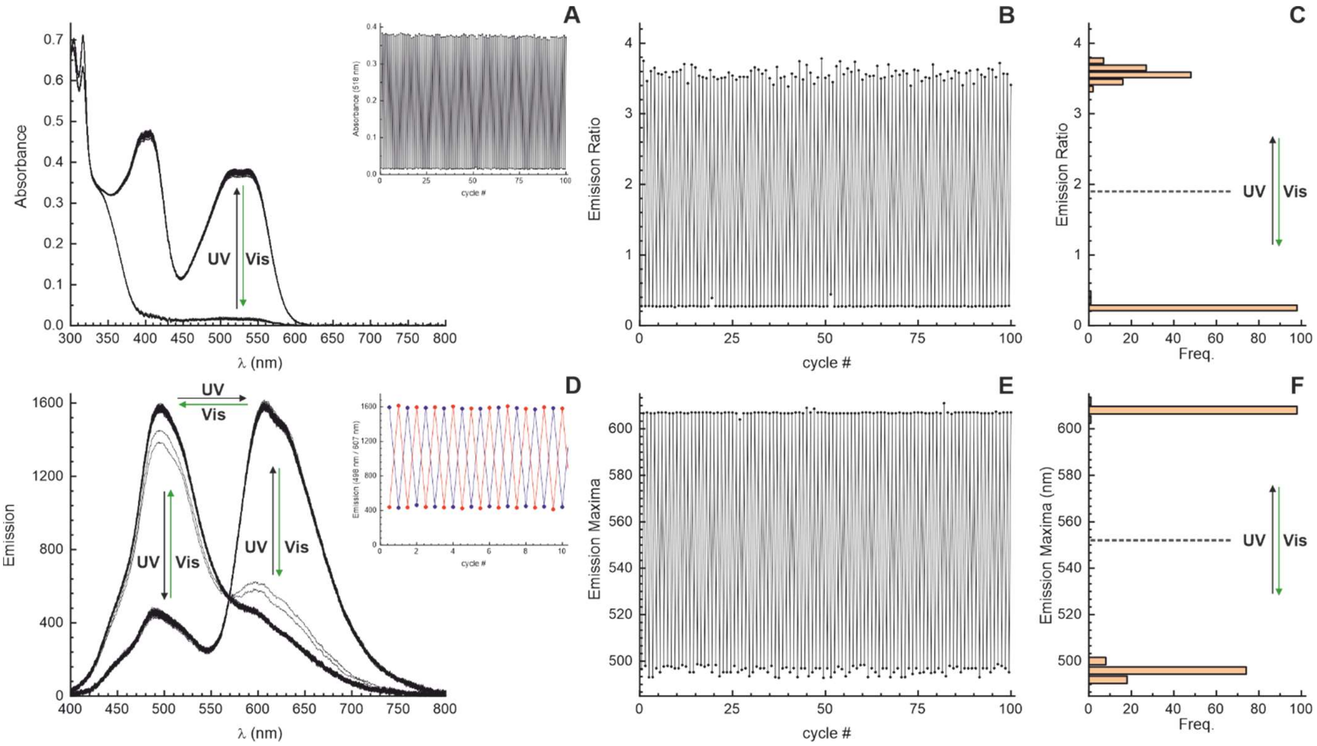


Figure S21. Absorption (A) and emission (D) switching of compound **MeO-CN** in toluene irradiated with 365 nm (UV) and 515 nm (Vis) light. The insets shows the intensity at the absorption maximum of the CF, and at the emission maxima of the OF and the CF, respectively. Emission maxima, (B) and the corresponding frequency count (C). Ratio of the emission at the maxima of each isomer (E) and the corresponding histogram (F). All plots were derived from the first 100 cycles, except the inset in (D) which was plotted for the first 10 cycles.

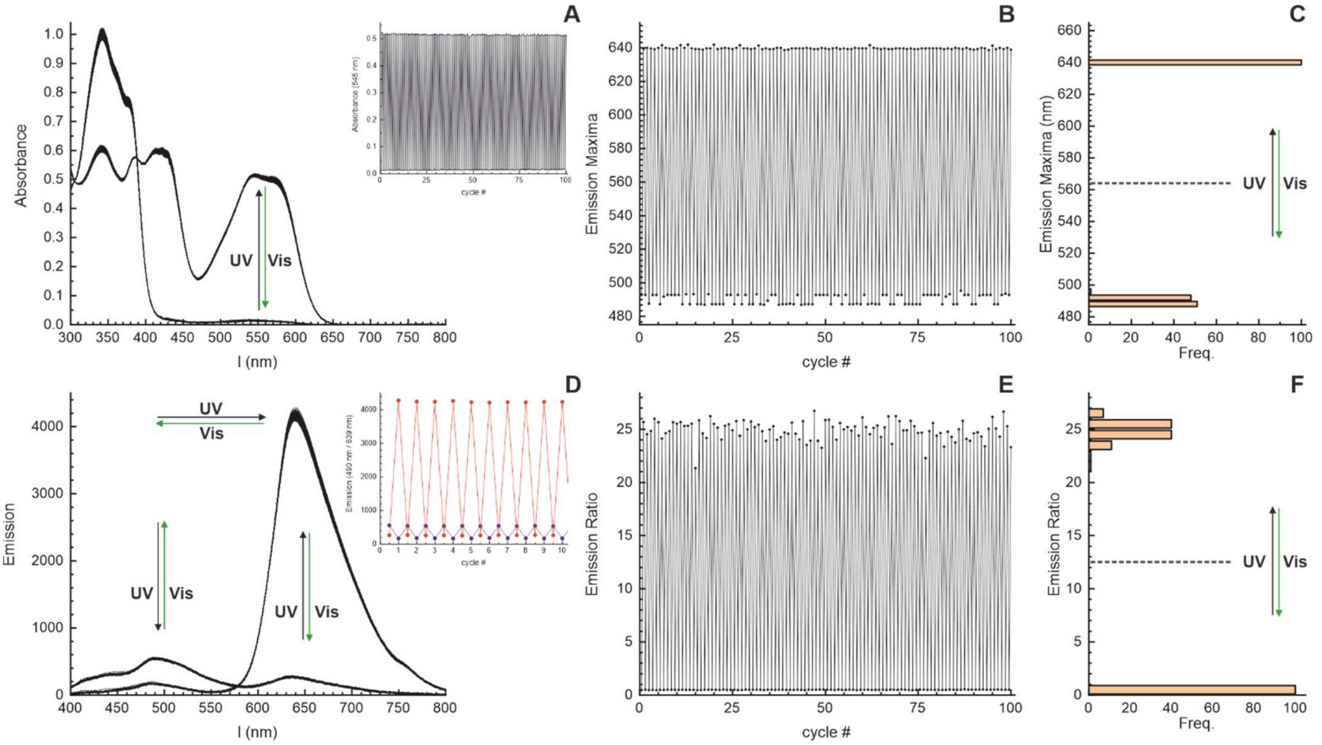


Figure S22. Absorption (A) and emission (D) switching of compound **MeO-CN2** in toluene irradiated with 365 nm (UV) and 515 nm (Vis) light. The insets shows the intensity at the absorption maximum of the CF, and at the emission maxima of the OF and the CF, respectively. Emission maxima (B), and the corresponding frequency count (C). Ratio of the emission at the maxima of each isomer (E) and the corresponding histogram (F). All plots were obrained from the first 100 cycles, except the inset in (D) which was plotted for the first 10 cycles.

References

1) Schleper, L.; Bossi, M. L.; Belov, V. N.; Hell, S. W. *Beilstein J. Org. Chem.* **2019**, *15*, 2344–2354.

2) Uno, K.; Bossi, M. L.; Konen, T.; Belov, V. N.; Irie, M.; Hell, S. W. *Adv. Opt. Mater.* **2019**, *7*, 1801746.