Reversibly photoswitchable fluorescent diarylethenes resistant against photobleaching in aqueous solutions

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# equal contributions

Abbreviations

The following abbreviations are used in the text of *Supplementary Information*:
acetonitrile (MeCN), anti-parallel (ap), aqueous (aq.), argon (Ar), bis(pinacolato)diboron $(Bpin)_2$, bovine serum albumin (BSA), brine (saturated aq. NaCl), catalyst/catalysis (cat.), closed form (CF), concentrated (conc.), diarylethene (DAE), dichloromethane (DCM), dimethyl sulfoxide (DMSO), equivalent (equiv.), electrospray ionization (ESI), ethyl acetate (EtOAc), fluorescent diarylethene (f-DAE), high performance liquid chromatography (HPLC), high resolution mass-spectrometry (HR-MS), methanol (MeOH), NBS (*N*-bromosuccinimide), *N*-hydroxysuccinimide (NHS), *N,N*-diisopropylethylamine (DIEA), *N,N*-dimethylformamide (DMF), nitrogen (N_2), nuclear magnetic resonance (NMR), open form (OF), parallel (p), phosphate buffer saline (PBS), photostationary state (PSS), potassium acetate (KOAc), reversed phase (RP), room temperature (r.t.), saturated (sat.), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (Sphos), tetrahydrofurane (THF), thin layer chromatography (TLC), tricyclohexylphosphine (PCy_3), triethylamine (TEA), trifluoroacetic acid (TFA), ultraviolet (UV), visible (Vis), volume ratio of two solvents (v/v).

High performance liquid chromatography (HPLC)

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 and UV-indicator (F254). Flash chromatography was performed on Biotage Isolera 3.0 flash purification system using cartridges and solvent gradients indicated in the description of the

synthesis. Analytical HPLC was performed on a KNAUER Azura system with a photodiode array detector, a 20 µL injection loop, and a 150 × 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.

Nuclear magnetic resonance (NMR) spectroscopy

NMR Spectra (^{1}H, ^{13}C and ^{19}F) were recorded on an *Agilent 400MR DD2* spectrometer (400 MHz ^{1}H). 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), [d_7]DMF (^{1}H: 8.03 ppm, ^{13}C: 163.2 ppm). Multiplicities of the signals are described as follows: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, sept = septet, m = multiplet, 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).

SYNTHESIS

Starting materials

Aminotriesters (**A**) and (**B**) were purchased from Santa Cruz Biotechnology and Frontier Scientific, respectively. **1**-OMe[1], **Et-Ox-2I**[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.

[1] Roubinet, B.; Weber, M.; Shojaei, H.; Bates, M.; Bossi, M. L.; Belov, V. N.; Irie, M.; Hell, S. W. *J. Am. Chem. Soc.* **2017***, 139,* 6611–6620.

[2] Uno, K.; Niikura, H.; Morimoto, M.; Ishibashi, Y.; Miyasaka, H.; Irie, M.; *J. Am. Chem. Soc.* **2011**, *133*, 13558−13564.

Preparation of boronic esters

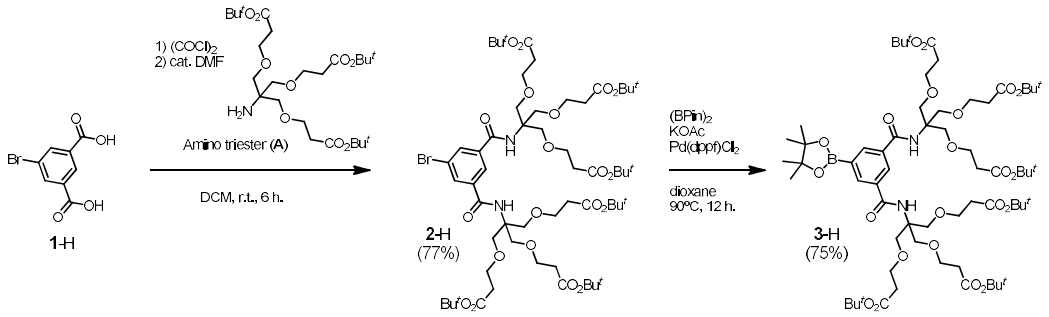
The synthetic routes leading to esters **3**-H, **3**-OMe, **5**-H, and **5**-OMe are given in Schemes S1a, S1b, S1c, and S1d, respectively.

General Procedure (GP 1) for the synthesis of esters 2-H, 2-OMe, 4-H, and 4-OMe.

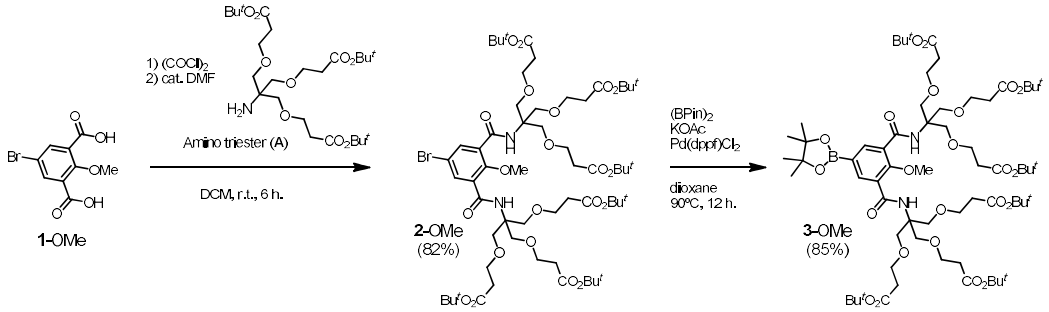
To a suspension of starting material (**1**-H or **1**-OMe) in DCM, oxalyl chroride was added at r.t. followed by DMF (several drops). After stirring for 1 h at r.t., DCM and DMF were removed in vacuum to give the corresponding acyl chloride as a colorless solid. It was suspended in DCM, to which another portion of DCM containing TEA and amino triester (**A** or **B**) was slowly added at r.t. The reaction solution was stirred at r.t. for 5 h under nitrogen. Then the solution was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The products were isolated by chromatography on regular silica gel with gradient elution of EtOAc in *n*-hexane to afford esters **2**-H, **2**-OMe, **4**-H, and **4**-OMe.

General Procedure (GP 2) for the synthesis of boronates 3-H, 3-OMe, 5-H, and 5-OMe.

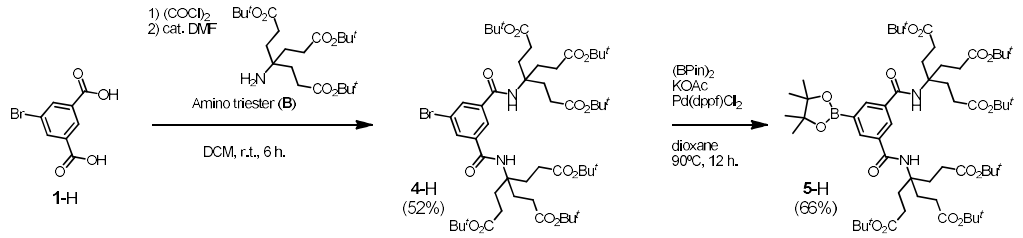
Into a flask flushed with N_2, one of the aryl bromides (**2**-H, **2**-OMe, **4**-H, and **4**-OMe) was added followed by $(Bpin)_2$, KOAc, and $Pd(dppf)Cl_2$. Then dry 1,4-dioxane (15 mL) was added under N_2. The reaction mixture was heated and stirred for 12 h at 90˚C. Upon cooling to r.t., sat. brine (100 mL) was added, the reaction mixture was extracted with DCM (2×100 mL), and the combined organic solutions were dried over anhydrous Na_2SO_4. After concentrating under reduced pressure, the crude material was subjected to chromatography on regular silica gel with gradient elution of EtOAc in *n*-hexane to afford one of the title compounds (**3**-H, **3**-OMe, **5**-H, and **5**-OMe).



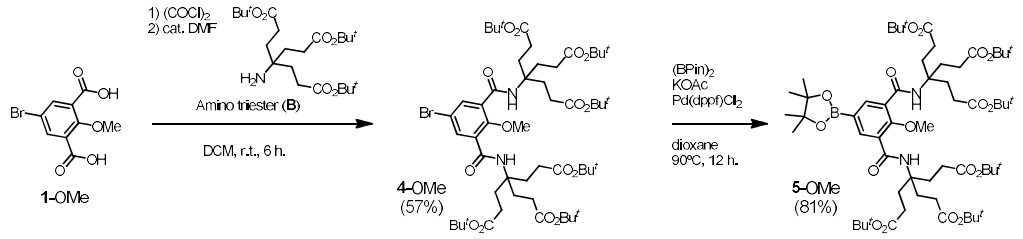
Scheme S1a. Synthesis of hexa-*tert*-butyl-carboxylated phenyl boronic ester **3**-H.



Scheme S1b. Synthesis of hexa-*tert*-butyl-carboxylated 4-methoxyphenyl boronic ester **3**-OMe.

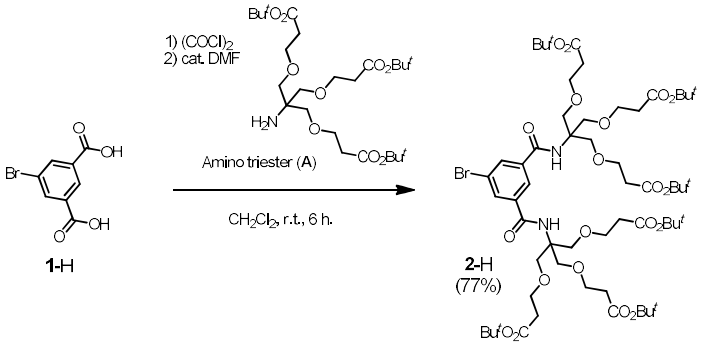


Scheme S1c. Synthesis of hexa-*tert*-butyl-carboxylated phenyl boronic ester **5**-H.



Scheme S1d. Synthesis of hexa-*tert*-butyl-carboxylated 4-methoxyphenyl boronic ester **5**-OMe.

Compound 2-H



Bromide **2**-H was synthesized according to **GP-1**.

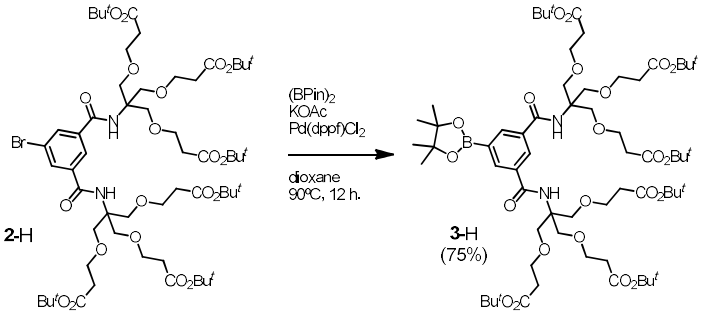
1-H (0.33 g, 1.4 mmol), DCM (12 mL), oxalyl chroride (0.70 g, 5.5 mmol, 4.1 equiv.) and DMF (5 drops) were used for the preparation of acyl chloride. The acyl chloride suspended in DCM (10 mL) was reacted with DCM (10 mL) containing TEA (1.0 mL, 7.2 mmol, 5.1 equiv.) and amine **A** (1.4 g, 2.8 mmol, 2.1 equiv.). Purification by chromatography on regular silica gel with gradient elution (*n*-hexane/EtOAc: 70/30 → 30/70) afforded **2**-H as pale yellow oil (1.27 g, 77% yield). R_f (*n*-hexane/EtOAc, 7/3, v/v) = 0.33.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.05 (t, J = 1.6 Hz, 1H), 8.02 (d, J = 1.6 Hz, 2H), 6.65 (s, 2H), 3.80 (s, 12H), 3.66 (t, J = 6.4 Hz, 12H), 2.44 (t, J = 6.4 Hz, 12H), 1.39 (s, 54H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) 170.8, 165.5, 137.3, 132.9, 124.7, 122.5, 80.4, 69.0, 67.0, 60.5, 36.1, 28.0.

ESI-MS: positive mode, *m/z* 1241.5586 $[M+Na, {}^{79}Br]^+$ (found), 1243.5567 $[M+Na, {}^{81}Br]^+$ (found), 1241.5554 (calculated for $C_{58}H_{95}BrN_2NaO_{20}^+$, $[M+Na, {}^{79}Br]^+$), 1243.5534 (calculated for $C_{58}H_{95}BrN_2NaO_{20}$, $[M+Na, {}^{81}Br]^+$).

Compound 3-H



Boronic ester **3**-H was synthesized according to **GP-2**.

2-H (1.0 g, 0.82 mmol), $(Bpin)_2$ (0.35 g, 1.4 mmol, 1.7 equiv.), KOAc (0.35 g, 3.6 mmol, 4.4 equiv.) and $Pd(dppf)Cl_2$ (0.12 g, 0.16 mmol, 0.2 equiv.) were combined in dry 1,4-dioxane (15 mL) and used in the reaction. Purification by chromatography with gradient elution (*n*-

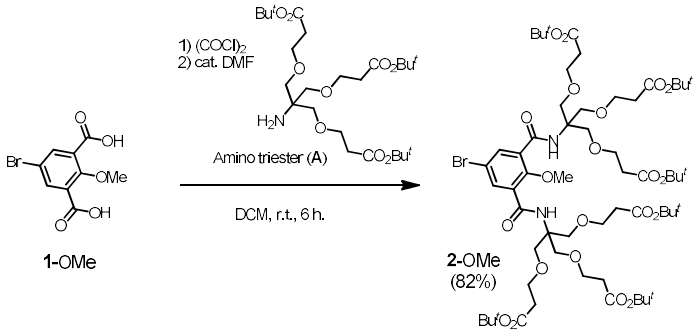
hexane/EtOAc: 80/20 → 20/80) afforded compound **3**-H as a yellow oil (0.78 g, 75% yield). R_f (*n*-hexane/EtOAc, 7/3, v/v) = 0.20.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.22 (s, 3H), 6.60 (s, 2H), 3.81 (s, 12H), 3.67 (t, J = 6.8 Hz, 12H), 2.45 (t, J = 6.8 Hz, 12H), 1.39 (s, 54H), 1.33 (s, 12H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 170.7, 166.7, 135.7, 135.0, 128.6, 84.2, 80.4, 69.1, 67.1, 60.2, 36.2, 28.0, 24.9.

ESI-MS: positive mode, *m/z* = 1289.7326 $[M+Na]^+$ (found), 1289.7301 (calculated for $C_{64}H_{107}BN_2NaO_{22}^+$, $[M+Na]^+$).

Compound 2-OMe



Bromide 2-OMe was synthesized according to **GP-1**.

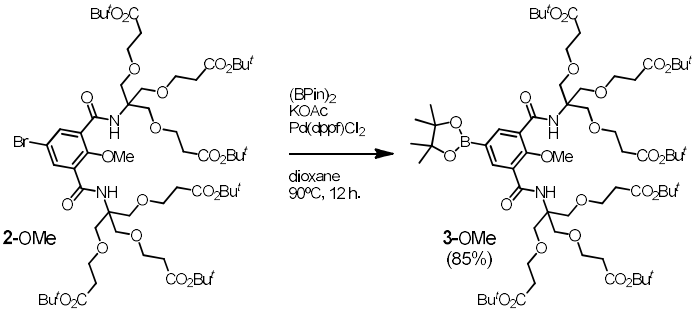
1-OMe (0.26 g, 0.95 mmol), DCM (10 mL), oxalyl chroride (0.48 g, 3.8 mmol, 4.0 equiv.), and DMF (5 drops) were used to generate acyl chloride. It was suspended in DCM (8 mL) and treated with DCM (8 mL) containing TEA (0.80 mL, 5.7 mmol, 6.0 equiv.) and compound **A** (1.0 g, 2.0 mmol, 2.1 equiv.). Separation by chromatography on regular silica gel with gradient elution (*n*-hexane/EtOAc: 80/20 → 30/70) afforded compound **2**-OMe as a pale yellow oil (0.97 g, 82% yield). R_f (*n*-hexane/EtOAc, 1/1, v/v) = 0.43.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.08 (s, 2H), 7.67 (s, 2H), 3.84 (s, 3H), 3.80 (s, 12H), 3.67 (t, J = 6.4 Hz, 12H), 2.44 (t, J = 6.4 Hz, 12H), 1.39 (s, 54H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) 170.6, 163.2, 155.0, 136.5, 130.5, 117.9, 80.4, 69.0, 67.1, 63.8, 60.2, 36.2, 28.0.

ESI-MS: positive mode, *m/z* 1249.5837 $[M+H, {}^{79}Br]^+$ (found), 1251.5807 $[M+H, {}^{81}Br]^+$ (found), 1249.5840 (calculated for $C_{59}H_{98}BrN_2O_{21}^+$, $[M+H, {}^{79}Br]^+$), 1251.5820 (calculated for $C_{59}H_{98}BrN_2O_{21}^+$, $[M+H, {}^{81}Br]^+$).

Compound 3-OMe



Boronate **3**-OMe was synthesized according to **GP-2**.

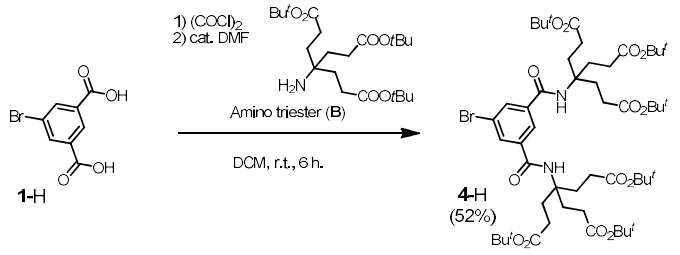
Bromide **2**-OMe (0.90 g, 0.72 mmol), $(Bpin)_2$ (0.28 g, 1.1 mmol, 1.5 equiv.), KOAc (0.21 g, 2.2 mmol, 3.0 equiv.) and $Pd(dppf)Cl_2$ (80 mg, 0.11 mmol, 0.15 equiv.) were combined in dry 1,4-dioxane (15 mL) and used in the reaction. Purification by chromatography with gradient elution (*n*-hexane/EtOAc: 80/20 → 40/60) afforded compound **3**-OMe as a pale yellow oil (0.79 g, 85% yield). R_f (*n*-hexane/EtOAc, 3/2, v/v) = 0.37.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.39 (s, 2H), 7.59 (s, 2H), 3.85 (s, 3H), 3.81 (s, 12H), 3.67 (t, J = 6.4 Hz, 12H), 2.44 (t, J = 6.4 Hz, 12H), 1.39 (s, 54H), 1.28 (s, 12H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 170.6, 164.8, 158.2, 140.5, 127.9, 83.9, 80.3, 74.9, 69.1, 67.1, 63.6, 60.1, 36.2, 28.0, 24.8.

ESI-MS: positive mode, *m/z* = 1297.7581 $[M+H]^+$ (found), 1297.7587 (calculated for $C_{65}H_{110}BN_2O_{23}^+$, $[M+H]^+$).

Compound 4-H



Bromide **4**-H was synthesized according to **GP-1**.

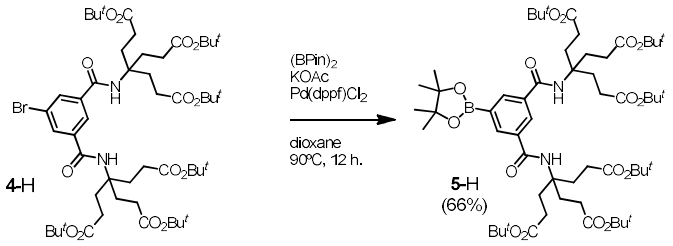
Acid **1**-H (0.50 g, 2.0 mmol), DCM (12 mL), oxalyl chroride (1.3 g, 10.2 mmol, 5.0 equiv.), and DMF (10 drops) were used for the generation of acyl chloride. The acyl chloride precursor was suspended in DCM (10 mL) and reacted with DCM (10 mL) containing TEA (1.0 mL, 7.2 mmol, 3.6 equiv.) and amine **B** (1.9 g, 4.6 mmol, 2.2 equiv.). Separation by chromatography on regular silica gel with gradient elution (*n*-hexane/EtOAc: 70/30 → 30/70) afforded **4**-H as white solid (1.1 g, 52% yield). R_f (*n*-hexane/EtOAc, 7/3, v/v) = 0.53.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.23 (t, J = 1.6 Hz, 1H), 8.09 (d, J = 1.6 Hz, 2H), 7.29 (s, 2H), 2.29 (t, J = 7.6 Hz, 12H), 2.11 (t, J = 7.6 Hz, 12H), 1.42 (s, 54H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) 173.1, 164.2, 137.0, 132.6, 124.3, 122.8, 80.9, 58.1, 30.2, 29.9, 28.1.

ESI-MS: positive mode, *m/z* 1061.4922 [M+Na, ^{79}Br]$^{+}$ (found), 1063.4924 [M+Na, ^{81}Br]$^{+}$ (found), 1061.4920 (calculated for $C_{52}H_{83}BrN_2NaO_{14}^{+}$, [M+Na, ^{79}Br]$^{+}$), 1063.4904 (calculated for $C_{52}H_{83}BrN_2NaO_{14}^{+}$, [M+Na, ^{81}Br]$^{+}$).

Compound 5-H



Boronate **5**-H was synthesized according to **GP-2**.

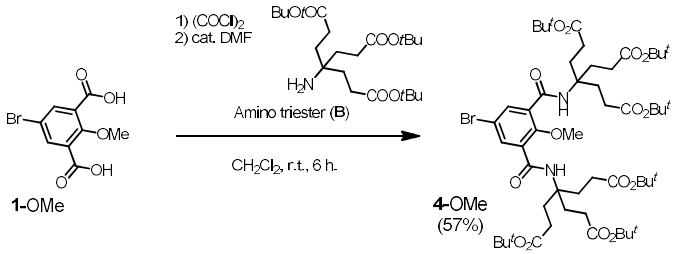
Ester **4**-H (1.05 g, 1.01 mmol, $(Bpin)_2$ (0.41 g, 1.6 mmol, 1.6 equiv.), KOAc (0.30 g, 3.0 mmol, 3.0 equiv.) and $Pd(dppf)Cl_2$ (0.15 g, 0.20 mmol, 0.2 equiv.) were combined in dry1,4-dioxane (15 mL) and used in the reaction. Separation by chromatography with gradient elution (*n*-hexane/EtOAc: 80/20 → 20/80) afforded compound **5**-H as a while solid (0.76 g, 66% yield). R_f (*n*-hexane/EtOAc, 7/3, v/v) = 0.47.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.37 (t, J = 1.6 Hz, 1H), 8.30 (d, J = 1.6 Hz, 2H), 6.74 (s, 2H), 2.32–2.23 (m, 12H), 2.16–2.07 (m, 12H), 1.42 (s, 54H), 1.36 (s, 12H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 172.8, 165.6, 135.5, 134.6, 128.5, 84.3, 80.7, 58.0, 29.8, 28.1, 24.9.

ESI-MS: positive mode, *m/z* = 1109.6686 [M+Na]$^{+}$ (found), 1109.6667 (calculated for $C_{58}H_{95}BN_2NaO_{16}^{+}$, [M+Na]$^{+}$).

Compound 4-OMe



Bromide 4-OMe was synthesized according to **GP-1**.

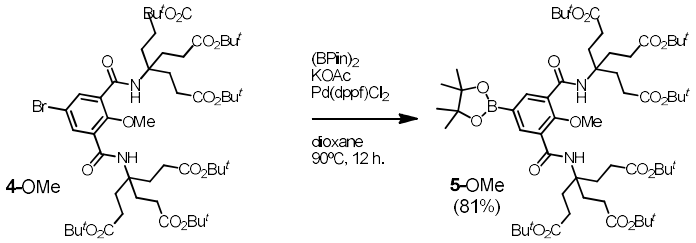
1-OMe (0.50 g, 1.8 mmol), DCM (10 mL), oxalyl chroride (1.2 g, 9.5 mmol, 5.2 equiv.), and DMF (5 drops) were used for generation of acyl chloride. Then it was suspended in DCM (8 mL) and reacted with DCM (8 mL) containing TEA (1.0 mL, 7.2 mmol, 4.0 equiv.) and amino-triester **B** (1.7 g, 4.1 mmol, 2.3 equiv.). Separation by chromatography on regular silica gel with gradient elution (*n*-hexane/EtOAc: 80/20 → 30/70) afforded compound **4**-OMe as a white solid (1.1 g, 57% yield). R_f (*n*-hexane/EtOAc, 7/3, v/v) = 0.43.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.03 (s, 2H), 7.09 (s, 2H), 3.93 (s, 3H), 2.30–2.22 (m, 12H), 2.12–2.04 (m, 12H), 1.42 (s, 54H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) 172.4, 162.9, 154.1, 136.1, 130.9, 118.2, 80.7, 64.2, 58.3, 29.8, 28.0.

ESI-MS: positive mode, *m/z* 1091.5017 [M+Na, ^{79}Br]$^+$ (found), 1093.5012 [M+Na, ^{81}Br]$^+$ (found), 1091.5026 (calculated for $C_{53}H_{85}BrN_2NaO_{15}^+$, [M+Na, ^{79}Br]$^+$), 1093.5006 (calculated for $C_{53}H_{85}BrN_2NaO_{15}^+$, [M+Na, ^{81}Br]$^+$).

Compound 5-OMe



Boronic ester **5**-OMe was prepared according to **GP-2**.

4-OMe (1.1 g, 1.0 mmol), $(Bpin)_2$ (0.42 g, 1.6 mmol, 1.6 equiv.), KOAc (0.30 g, 3.1 mmol, 3.0 equiv.) and $Pd(dppf)Cl_2$ (0.11 g, 0.15 mmol, 0.15 equiv.) were combined in 1,4-dioxane (15 mL) and used in the reaction. Separation by chromatography with gradient elution (*n*-hexane/EtOAc: 80/20 → 40/60) afforded the product **5**-OMe as a white solid (0.93 g, 81% yield). R_f (*n*-hexane/EtOAc, 7/3, v/v) = 0.37.

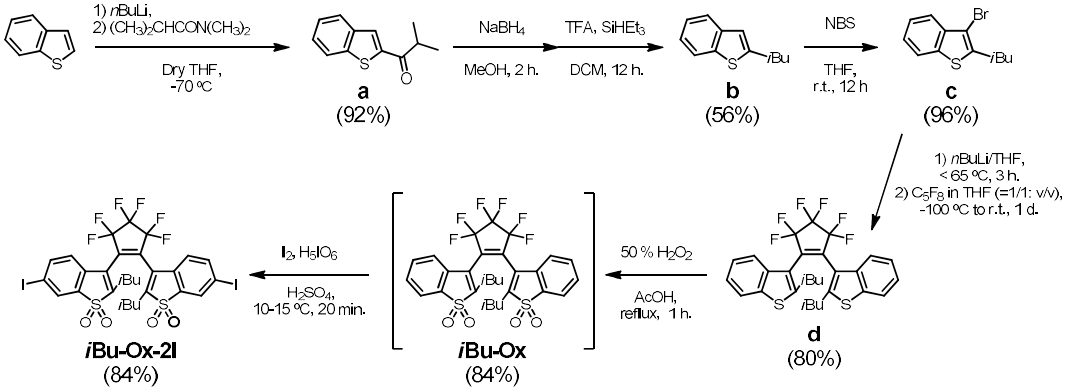
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.31 (s, 2H), 6.89 (s, 2H), 3.93 (s, 3H), 2.32–2.22 (m, 12H), 2.13–2.05 (m, 12H), 1.41 (s, 54H), 1.30 (s, 12H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) 172.4, 164.5, 157.3, 139.9, 128.5, 84.2, 80.6, 64.0, 58.1, 23.0, 29.8, 28.0, 24.8.

ESI-MS: positive mode, *m/z* = 1139.6782 $[M+Na]^+$ (found), 1139.6773 (calculated for $C_{59}H_{97}BN_2NaO_{17}^+$, $[M+Na]^+$).

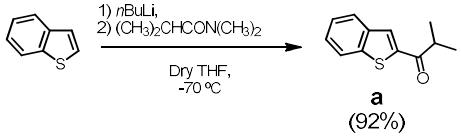
Preparation of diiodinated DAE sulfones

The synthesis of diiodinated DAE sulfones bearing *iso*-butyl groups at C-2 and C-2′ (***i*Bu-Ox-2I**) is given in Scheme S2. The corresponding diethyl analog (**Et-Ox-2I**) was prepared according to the published protocols (see footnote 2 on page 2).



Scheme S2. Preparation of ***i*Bu-Ox-2I**.

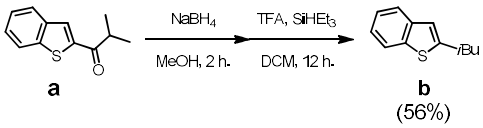
(Benzo[b]thiophen-2-yl)-(2-methylpropan)-1-one (a)



Benzothiophene (15 g, 0.11 mol) was dissolved in dry THF (100 mL) under N_2. The reaction solution was cooled to -70˚C. *n*BuLi (77 mL, 0.12 mmol, 1.1 equiv.) was slowly added with stirring over 1 h. The reaction solution was stirred for 2 h at -70˚C. *N,N*-dimethyl-isobutyramide (14 g, 0.12 mol, 1.1 equiv.) was added via syringe, and the reaction solution was gradually warmed-up to r.t. overnight. The reaction mixture was poured into sat. brine (250 mL) and extracted with ether (2×250 mL). The combined organic solutions were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was subjected to chromatography on regular silica gel with gradient elution (*n*-hexane/EtOAc: 100/0 → 90/10) to afford compound **a** as a colorless oil (21 g, 92% yield). R_f (*n*-hexane/EtOAc, 9/1, v/v) = 0.40. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.97 (s, 1H), 7.91–7.84 (m, 2H), 7.49–7.37 (m, 2H), 3.53 (sept, J = 6.8 Hz, 1H), 1.30 (d, J = 6.8 Hz, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) 198.9, 143.1, 142.5, 139.2, 128.6, 127.2, 125.8, 124.9, 122.9, 37.2, 19.4. All data are consistent with the previous report.[3]

2-Isobutylbenzo[b]thiophene (b)

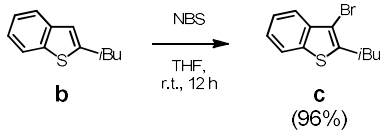


Compound **a** (21 g, 0.10 mmol) was dissolved in MeOH (200 mL) at r.t. The reaction mixture was cooled to 0 ˚C and $NaBH_4$ (4.2 g, 0.11 mmol, 1.1 equiv.) added in several portions. After stirring for 2 h, MeOH was removed under reduced pressure. Sat. brine (250 mL) was added to the residue, which was then extracted with EtOAc (2×250 mL). The combined organic solutions were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give a white solid. It was dissolved in DCM (100 mL) to which Et_3SiH (40 mL, 0.25 mol, 2.4 equiv.) and TFA (40 mL, 0.52 mol, 5.1 equiv.) were slowly added at 0 ˚C over 1 h. The reaction mixture was gradually warmed-up to r.t. and stirred for additional 12 h. The reaction mixture was added to sat. brine (250 mL) and extracted with *n*-hexane (2×250 mL). The combined organic solutions were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was subjected to chromatography on regular silica gel with gradient elution (*n*-hexane) to afford compound **b** as a colorless oil (11 g, 56% yield). R_f (*n*-hexane) = 0.30.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.82–7.76 (m, 1H), 7.72–7.67 (m, 1H), 7.37–7.24 (m, 2H), 7.03–6.99 (m, 1H), 2.79 (dd, J = 1.2, 7.2 Hz, 2H), 2.03 (sept, J = 6.8 Hz, 1H), 1.02 (d, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) 145.5, 140.2, 139.5, 124.0, 123.3, 122.6, 122.1, 121.3, 40.1, 30.3, 22.3. All data are consistent with the previous report.[4]

3-Bromo-2-isobutylbenzo[b]thiophene (c)



Compound **b** (11.2 g, 57.8 mmol) was dissolved in THF (200 mL) at r.t. NBS (11.5 g, 64.7 mmol, 1.1 equiv.) was added to reaction mixture in one portion at 0 ˚C. The reaction temperature was gradually warmed-up to r.t. and stirred for 12 h stirring. THF was removed under reduced pressure. 5 M NaOH aq. (200 mL) was added to the residue, and the mixture was

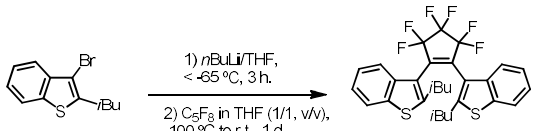
[3] Wang, C.-Y.; Ralph, G.; Derosa, J.; Biscoe, M. R. *Angew. Chem., Int. Ed*. **2017**, *56*, 856−860.
[4] Urban, S.; Beiring, B.; Ortega, N.; Paul, D.; Glorius, F. *J. Am. Chem. Soc.* **2012**, *134*, 15241−15244.

extracted with *n*-hexane (2×250 mL). The combined organic solutions were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was subjected to chromatography on regular silica gel; elution with *n*-hexane afforded compound **c** as a colorless oil (15.2 g, 95.6 % yield). R_f (*n*-hexane) = 0.30.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.80–7.71 (m, 2H), 7.47–7.39(m, 1H), 7.38–7.31(m, 1H), 2.86 (d, J = 7.2 Hz, 2H), 2.16–2.04 (m, 1H), 1.03 (d, J = 6.4 Hz, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) 139.8, 138.3, 137.3, 124.8, 124.7, 122.7, 122.2, 106.5, 38.8, 30.2, 22.3. All data are consistent with the previous report.[5]

3,3'-(Perfluorocyclopent-1-ene-1,2-diyl)bis(2-isobutylbenzo[b]thiophene) (d)



c **d** (80%)

Compound **c** (12.5 g, 56.5 mmol) was dissolved in THF (100 mL) under N_2. *n*-BuLi (1.6 M in *n*-hexane, 40 mL, 63.9 mmol, 1.1 equiv.) was added at temperature between -70 ˚C to -65 ˚C over 1 h. The reaction solution was stirred for 2 h at -70 ˚C. THF (6 mL) containing perfluorocyclopentene (6.0 g, 28.2 mmol, 0.50 equiv.) was slowly introduced over 1 h at temperature below -100 ˚C. Then the reaction mixture was slowly warmed-up to r.t. over 1 day. To the reaction mixture sat. aq. brine (250 mL) was added, and it was extracted with ether (2×250 mL). The combined organic solutions were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The solid residue was collected by filtration and washed with small amount of water and MeOH to give compound **d** as white solid (12.5 g, 80% yield). R_f (*n*-hexane) = 0.33.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.79–7.68 (m, 3.2 H, *ap/p*), 7.63–7.52 (m, 0.8 H, *p*), 7.42–7.37 (m, 1.6 H, *ap*), 7.35–7.29 (m, 1.6 H, *ap*), 7.21–7.11 (m, 0.8 H, *a*), 2.75–2.67 (m, 0.4 H, *p*), 2.64–2.57 (m, 0.4 H, *p*), 2.51–2.42 (m, 1.6 H, *ap*), 2.08–1.98 (m, 2 H, *ap/p*), 1.85–1.74 (m, 1.6 H, *ap*), 1.07 (d, J = 6.8 1.2 H, *p*), 0.95 (d, J = 6.8, 1.2 H, *p*), 0.77 (d, J = 6.8, 4.8 H, *ap*), 0.48 (d, J = 6.4, 4.8 H, *ap*).

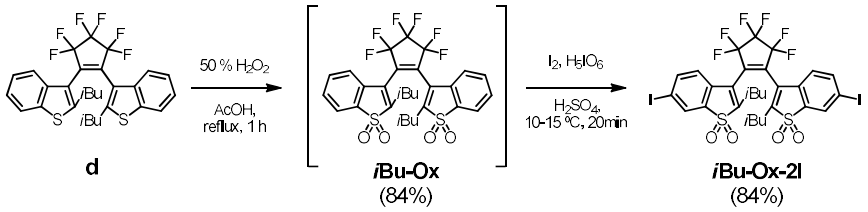
^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 148.5, 138.3, 138.0, 124.5, 124.3, 124.3, 124.3, 122.9, 122.9, 122.8, 122.8, 122.3, 122.2, 122.2, 121.8, 119.1, 39.1, 38.3, 30.6, 29.8, 23.1, 21.8, 21.5.

^{19}F-NMR (397 MHz, $CDCl_3$) δ (ppm) = -109.9 (m, 4 F), -119. (s, 2 F), 133.2 (m, 2 F), 130.4 (s, 2F).

[5] Lu, W. D.; Wu, M. J. *Tetrahedron* **2007**, *63*, 356−362.

ESI-MS: positive mode, m/z 552.1385 $[M]^+$ (found), 552.1380 (calculated for $C_{29}H_{26}F_6S_2$, $[M]^+$).

Diiodide ***i*Bu-Ox-2I**



Acetic acid (120 mL) containing compound **d** (3.0 g, 5.4 mmol) was heated to reflux (oil bath temperature 130 ˚C). 50% H_2O_2 (30 mL, 0.53 mol, 98 equiv.) was slowly added to the solution, and the mixture was refluxed for 2 h. After cooling to r.t., water (120 mL) was added to form a precipitate which was then filtered, washed with water and MeOH, and dried under vacuum to give ***i*Bu-Ox** as a white solid (2.8 g, 84% yield).

MS: positive mode, m/z = 639.1074 $[M+Na]^+$ (found), 639.1069 (calculated for $C_{29}H_{26}F_6NaO_4S_2^+$, $[M+Na]^+$)

***i*Bu-Ox** (2.8 g, 4.5 mmol) was fully dissolved in conc. H_2SO_4 (60 mL). I_2 (3.5 g, 13 mmol, 3.0 equiv.) and H_5IO_6 (1.5 g, 6.6 mmol, 1.5 equiv) were mixed and ground to a fine powder which was added to the reaction solution at 10 ˚C in one portion. The reaction solution was slowly warmed-up to 15˚C over 20 min., while monitoring the progress of reaction by TLC. The reaction solution was poured into ice (ca. 300 g), warmed-up to r.t. and extracted with ethyl acetate (2×250 mL). The combined organic solutions were washed with 1.0 M NaOH aq. (0.5 L), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. ***i*Bu-Ox-2I** was obtained by recrystallization of the residue (*n*-hexane /DCM, 9/1, v/v) as a pale yellow powder. (3.3 g, 84 % yield). R_f = 0.50 (*n*-hexane/EtOAc, 7/3, v/v).

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.08 (d, J = 1.2 Hz, 1.33 H, *ap*), 7.98 (d, J = 1.2 Hz, 0.67 H, *p*), 7.96 (dd, J = 8.0, 1.6 Hz, 1.33 H, *ap*), 7.73 (dd, J = 8.0, 1.6 Hz, 0.67 H, *p*), 6.99 (dd, J = 8.4, 1.6 Hz, 1.33 H, *ap*), 6.75 (dd, J = 8.0, 1.2 Hz, 0.67 H, *p*), 2.66 (dd, J = 14.4, 4.4 Hz, 0.67 H, *p*), 2.52–2.41 (m, J = 14.4, 4.4 Hz, 0.67 H, *p*), 2.31–2.21 (m, 1.33 H, *ap*), 2.14–2.05 (m, 2.0 H, *ap/p*), 2.01–1.93 (m, 1.33 H, *ap*), 1.06 (d, J = 6.8 Hz, 2.0 H, *p*), 0.96 (dd, J = 6.8, 1.6 Hz, 2.0 H, *p*), 0.86 (d, J = 6.4 Hz, 4.0 H, *ap*), 0.72 (d, J = 6.8 Hz, 4.0 H, *ap*).

^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 147.0, 146.9, 142.4, 142.2, 139.9, 137.0, 136.8, 131.3, 128.7, 128.6 (2×), 124.5, 124.3, 124.2, 123.5 (2×), 96.3, 96.3, 77.2, 35.5, 34.9, 26.0, 25.9, 23.8, 22.5, 21.8, 21.1 (2×).

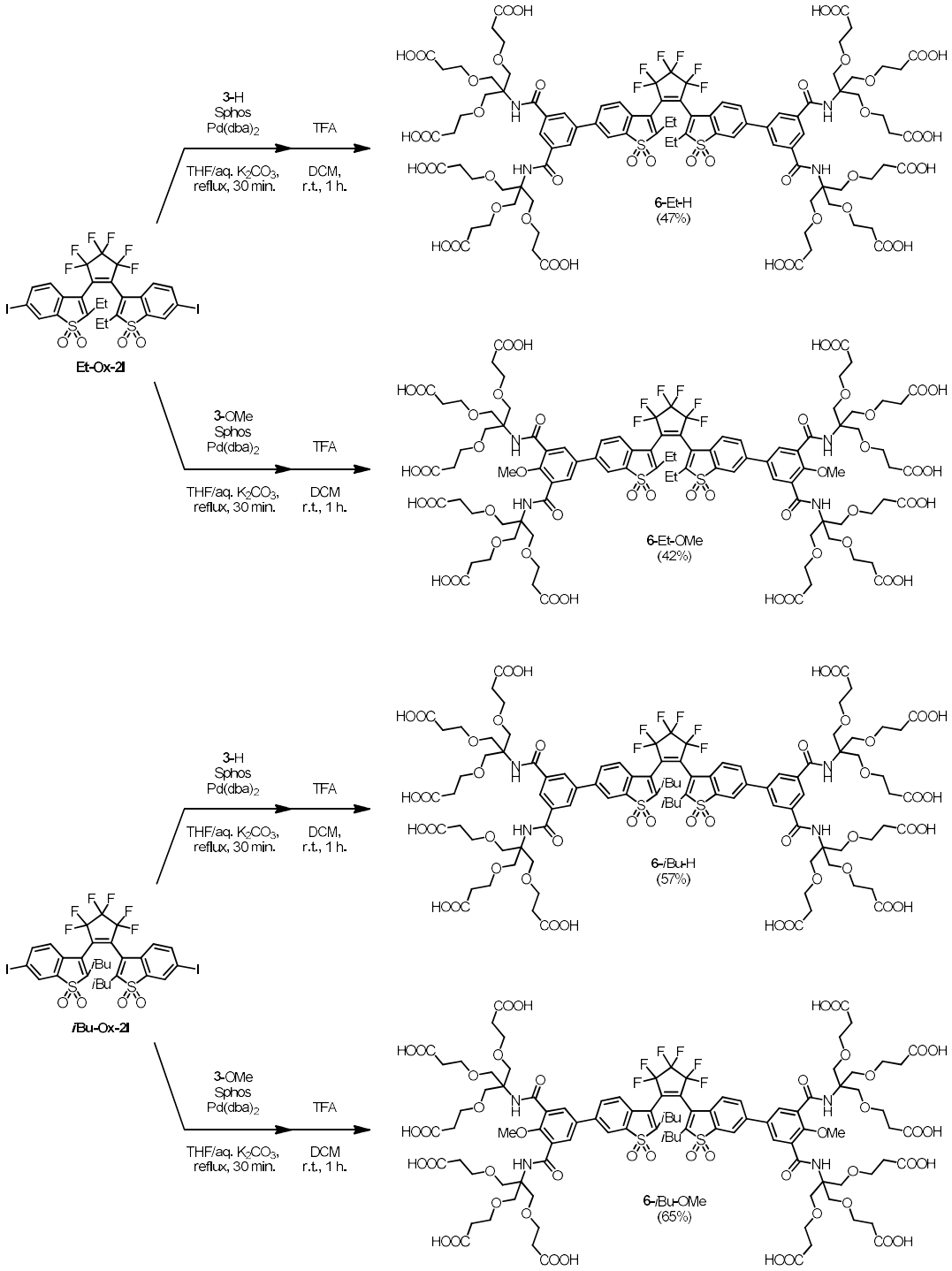
^{19}F-NMR (397 MHz, $CDCl_3$) δ (ppm) = -109.3 (m, 4 F), 132.9 (m, 2 F).

ESI-MS: negative mode, m/z 866.9038 $[M-H]^-$ (found), 866.9037 (calculated for $C_{29}H_{23}F_6I_2O_4S_2^-$, $[M-H]^-$).

Preparation of dodeca carboxylated diarylethenes

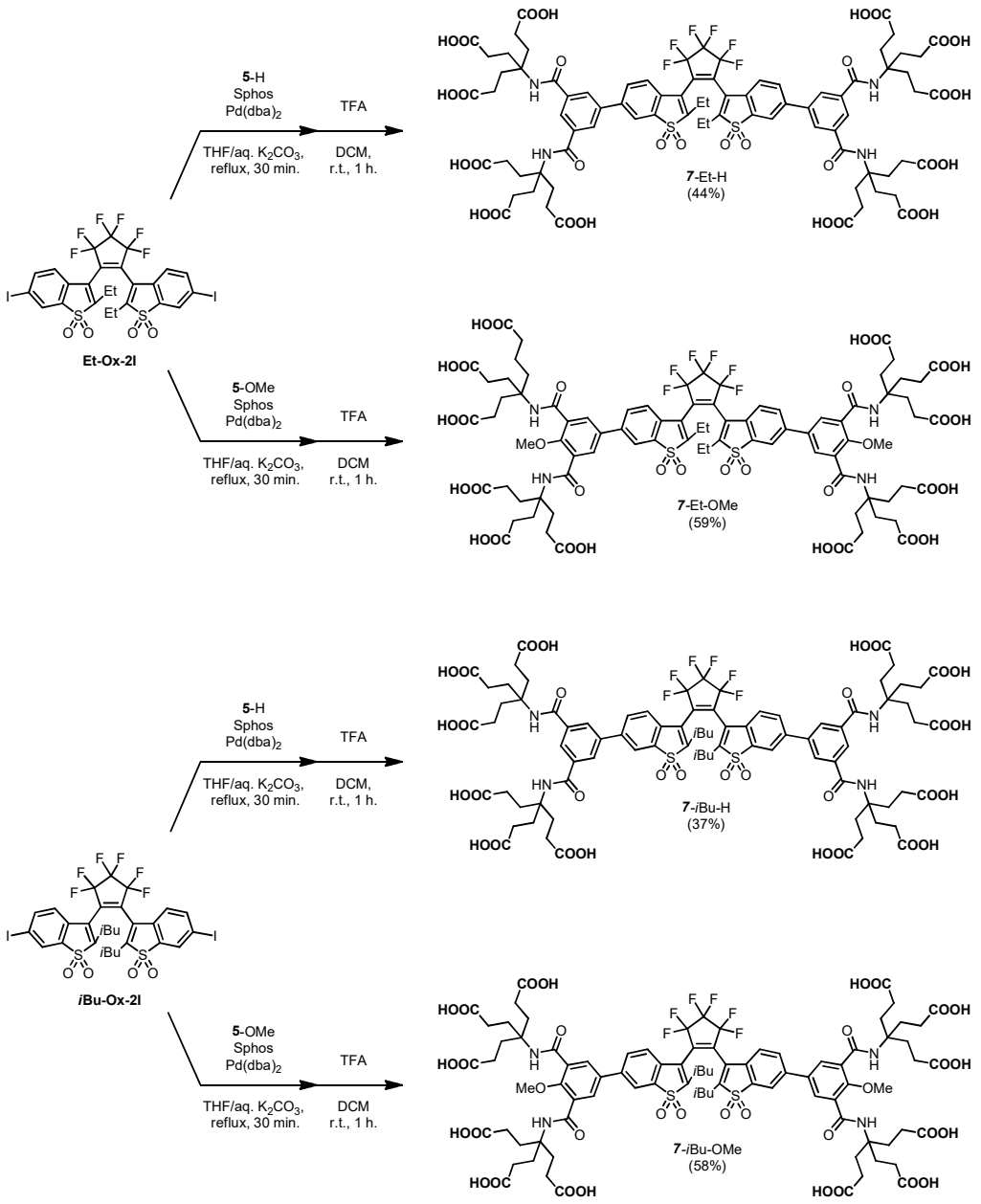
General Procedure 3 (GP 3) for the preparation of **6**-Et-H, **6**-Et-OMe, **6**-*i*Bu-H and **6**-*i*Bu-OMe (Scheme S3a), as well as **7**-Et-H, **7**-Et-OMe, **7**-*i*Bu-H and **7**-*i*Bu-OMe (Scheme S3b). Anhydrous THF containing corresponding diiodide (**Et-Ox-2I** or ***i*Bu-Ox-2I**) was diluted with water containing K_2CO_3. To the vigorously stirring solution, boronic ester, Sphos and $Pd(dba)_2$ were added sequentially under nitrogen . The reaction mixture was heated to reflux for 30 min. After cooling down to r.t., brine was added, and the reaction mixture was extracted with ethyl acetate (2×100 mL). The organic solutions were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The remaining dark solid was subjected to column chromatography with gradient elution of EtOAc in *n*-hexane (1/15→1/3, v/v). The isolated product was dissolved in a solution of DCM /TFA (10 mL/10 mL), which was then stirred at r.t. for 1 h. DCM and excess of TFA were removed under reduced pressure to give a yellow solid. 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) afforded dodeca-acids as solids.

The syntheses of **6**-Et-H, **6**-Et-OMe, **6**-*i*Bu-H, and **6**-*i*Bu-OMe are given in Scheme S3a.



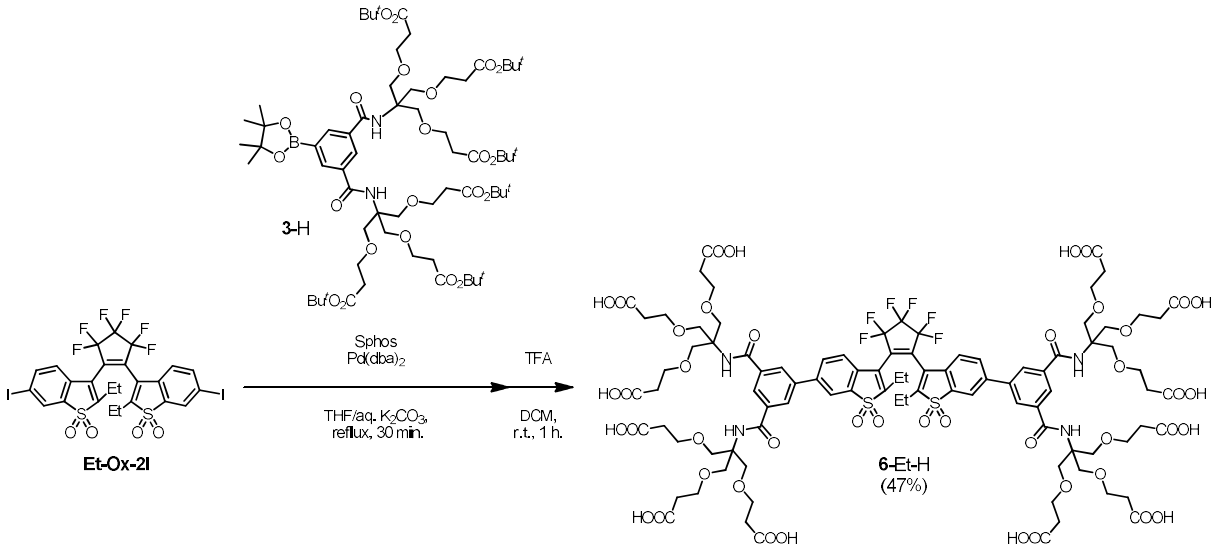
Scheme S3a. Synthesis of dodeca-acids **6**-Et-H, **6**-Et-OMe, **6**-*i*Bu-H, and **6**-*i*Bu-OMe.

The syntheses of **7**-Et-H, **7**-Et-OMe, **7**-*i*Bu-H, and **7**-*i*Bu-OMe are given in Scheme S3b.



Scheme S3b. Synthesis of dodeca-acids **7**-Et-H, **7**-Et-OMe, **7**-*i*Bu-H, and **7**-*i*Bu-OMe.

Dodeca-acid **6**-Et-H



Dodeca-acid **6**-Et-H was obtained according to **GP3**.

Anhydrous THF (10 mL), **Et-Ox-2I** (65 mg, 80 µmol), water (10 mL), K_2CO_3 (0.1 g), boronic ester **3**-H (0.25 g, 0.19 mmol, 2.4 equiv.), Sphos (8.0 mg, 19 µmol, 0.24 equiv.) and $Pd(dba)_2$ (10 mg, 18 µmol, 0.22 equiv.) were used in the reaction. Dodeca-acid **6**-Et-H was obtained as a yellow solid (82 mg, 47% yield).

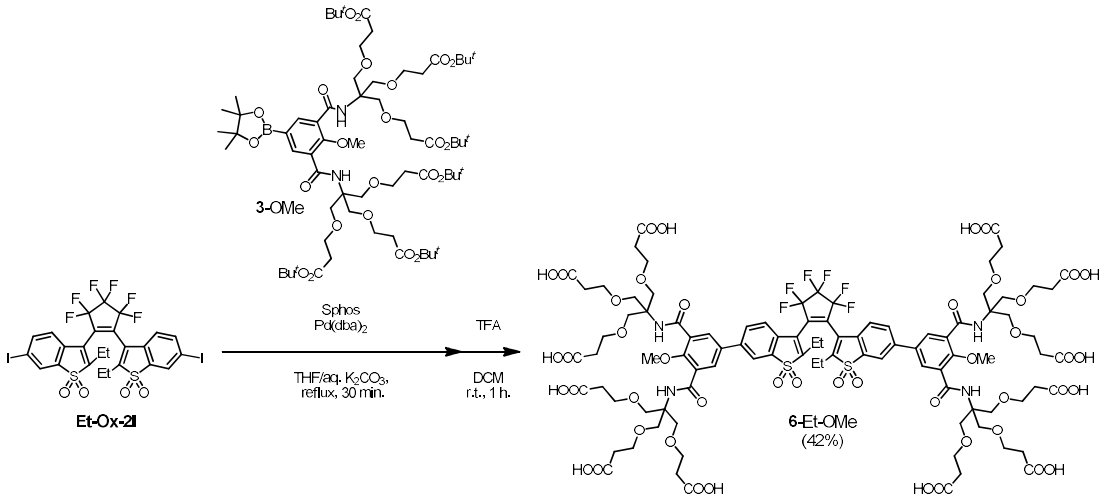
^{1}H-NMR (400 MHz, [d$_7$]DMF): δ (ppm) =12.4 (br, 12H, *ap/p*), 8.56 (d, J = 1.6 Hz, 1.5H, *ap*), 7.49 (d, J = 1.6 Hz, 0.5H, *p*), 8.43–8.39 (m, 3.0H, *ap*), 8.39–8.35 (m, 1.5H, *ap/p*), 8.33 (dd, J = 8.0, 1.6 Hz, 1.5H, *ap*), 8.29 (s, 1.5H, *ap*), 8.20 (dd, J = 8.0, 1.6 Hz, 0.5H, *p*), 7.97 (d, J = 8.0 Hz, 0.5H, *p*), 7.88 (d, J = 8.0 Hz, 1.5H, *ap*), 7.78 (s, 3.0H, *ap*), 7.71 (s, 1.0H, *p*), 3.87 (s, 18H, *ap*), 3.84 (s, 6H, *a*), 3.78–3.69 (m, 24H, *ap/p*), 2.88–2.76 (m, 3.0H, *a*), 2.67–2.60 (m, 1.0H, *ap*), 2.60–2.50 (m, 24.0H, *ap/a*), 1.43 (t, J = 7.6 Hz, 1.5H, *a*), 1.06 (t, J = 7.6 Hz, 4.5H, *ap*).

^{13}C-NMR (101 MHz, [d$_7$]DMF): δ (ppm) = 173.8 (2×), 167.6, 163.40 (2×), 150.2, 144.0, 143.8 (2×), 138.6, 137.9, 137.8, 137.5, 137.4, 134.7, 134.5, 129.6, 129.4, 128.4, 128.2, 125.7 (2×), 124.0 (2×), 122.3, 69.6, 68.3, 68.2, 62.2, 62.2, 35.8, 35.8, 20.2, 19.9, 12.8, 12.6.

^{19}F-NMR (397 MHz, [d$_7$]DMF) δ (ppm) = -109.5 (m, 4F, *p/ap*), -130.7 (m, 2F, *p/ap*).

ESI-MS: negative mode, *m/z* = 1081.7850 $[M-2H]^{2-}$ (found), 1081.7863, (calculated for $C_{93}H_{108}F_6N_4O_{44}S_2^{2-}$, $[M-2H]^{2-}$).

Dodeca-acid **6**-Et-OMe



Dodeca-acid **6**-Et-OMe was obtained according to **GP3**.

Anhydrous THF (10 mL), **Et-Ox-2I** (80 mg, 98 µmol), water (10 mL), K_2CO_3 (0.1 g), boronic ester **3**-OMe (0.28 g, 0.22 mmol, 2.2 equiv.), Sphos (10 mg, 25 µmol, 0.25 equiv.) and $Pd(dba)_2$ (11 mg, 20 µmol, 0.20 equiv.) were used in the reaction. Dodeca-acid **6**-Et-OMe was obtained as a yellow solid (92 mg, 42% yield).

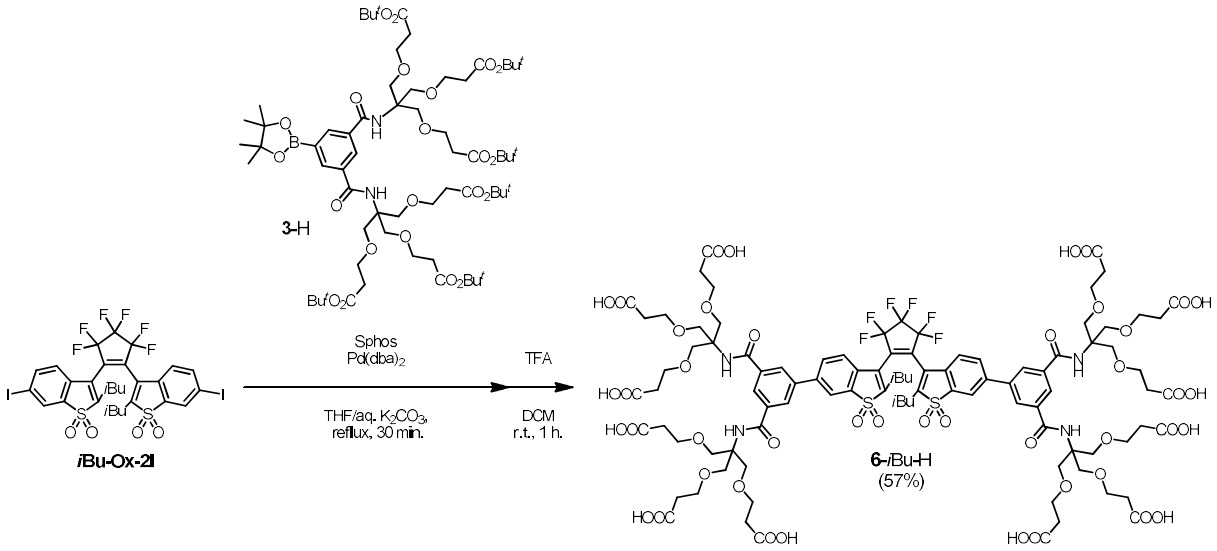
^{1}H-NMR (400 MHz, [d$_7$]DMF): δ (ppm) = 12.4 (br, 12H, *ap/p*), 8.49 (d, J = 1.2 Hz, 1.5H, *ap*), 7.42 (d, J = 1.2 Hz, 0.5H, *p*), 8.27–8.19 (m, 4.5H, *ap/p*), 8.15 (s, 1.0H, *p*), 8.09 (dd, J = 8.0, 1.2 Hz, 0.5H, *p*), 8.06 (s, 3.0H, *ap*), 8.00 (s, 1.0H, *p*), 7.93 (d, J = 8.0 Hz, 0.5H, *p*), 7.84 (d, J = 8.0 Hz, 1.5H, *ap*), 4.04 (s, 4.5H, *ap*), 3.99 (s, 1.5H, *p*), 3.88 (s, 18H, *ap*), 3.85 (s, 6H, *a*), 3.80–3.72 (m, 24H, *ap/p*), 2.87–2.76 (m, 3.0H, *ap*), 2.68–2.62 (m, 1.0H, *p*), 2.61–2.51 (m, 24.0H, *ap/a*), 1.10–1.02 (m, 1.5H, *a*), 1.06 (t, J = 7.6 Hz, 4.5H, *ap*).

^{13}C-NMR (101 MHz, [d$_7$]DMF): δ (ppm) = 172.8, 164.8, 164.7, 162.4, 156.4 (2×), 149.3, 149.1, 142.5, 142.3, 136.7, 136.5, 133.4, 133.2 (2×), 131.2, 131.1, 130.6, 130.5, 128.2, 128.0, 124.8, 123.1, 120.8, 69.0, 67.4, 63.6, 60.8, 60.7, 34.9, 19.2, 19.0, 11.8, 11.6.

^{19}F-NMR (397 MHz, [d$_7$]DMF) δ (ppm) = -109.6 (m, 4F, *p/ap*), -130.8 (s, 2F, *p/ap*).

ESI-MS: negative mode, *m/z* = 1111.7948 $[M-H2]^{2-}$ (found), 1111.7969 (calculated for $C_{95}H_{112}F_6N_4O_{46}S_2^{2-}$, $[M-2H]^{2-}$).

Dodeca-acid **6**-*i*Bu-H



Dodeca-acid **6**-*i*Bu-H was obtained according to **GP3**.

Anhydrous THF (10 mL), ***i*Bu-Ox-2I** (65 mg, 75 µmol), water (10 mL), K_2CO_3 (0.1 g), boronic ester **3**-H (0.25 g, 0.20 mmol, 2.6 equiv.), Sphos (8.0 mg, 19 µmol, 0.26 equiv.), and $Pd(dba)_2$ (10 mg, 18 µmol, 0.24 equiv.) were used in the reaction. Dodeca-acid **6**-*i*Bu-H was obtained as a yellow solid (95 mg, 57% yield).

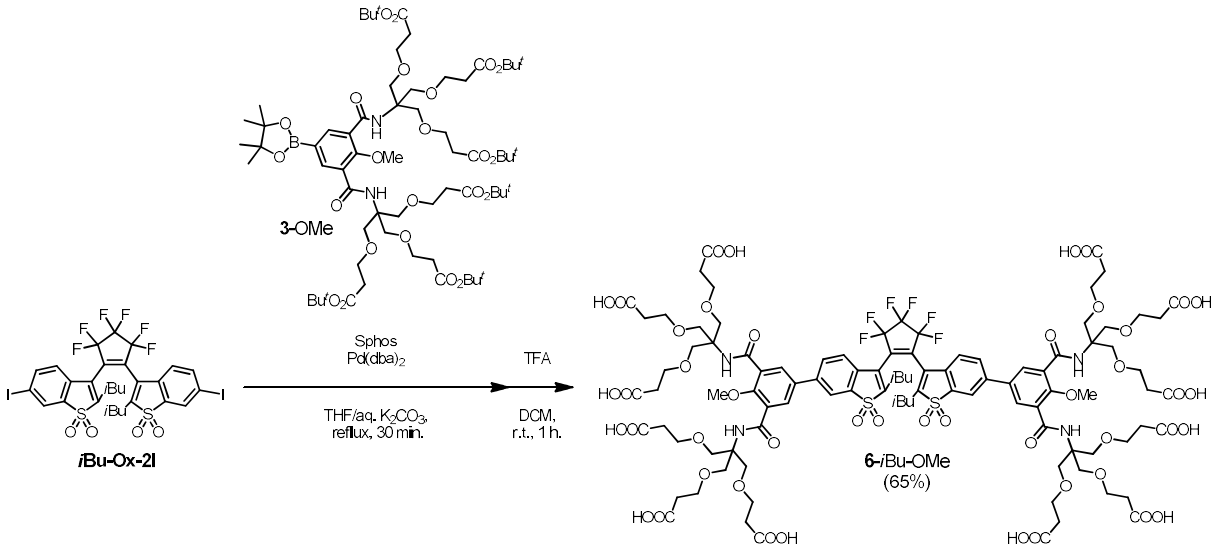
^{1}H-NMR (400 MHz, [d$_7$]DMF): δ (ppm) = 12.4 (br, 12H, *ap/p*), 8.57 (d, J = 1.6 Hz, 1.7H, *ap*), 8.46 (d, J = 1.6 Hz, 0.3H, *p*), 8.44–8.33 (m, 7.1H, *ap/p*), 8.27 (s, 0.6H, *p*), 8.09 (dd, J = 6.8, 1.6 Hz, 0.3H, *p*), 7.92–7.82 (m, 2.0H, *ap/p*), 7.77 (s, 3.4H, *ap*), 7.70 (s, 0.6H, *p*), 3.88 (s, 20.4H, *ap*), 3.84 (s, 3.6H, *p*), 3.77–3.69 (m, 24H, *ap/p*), 2.60– 2.52(m, 24H, *ap/p*), 2.48–2.17 (m, 6H, *ap/p*), 1.17 (d, J = 6.0 Hz, 0.9H, *a*), 1.05 (d, J = 5.6 Hz, 0.9H, *a*), 0.95 (d, J = 6.0 Hz, 5.1H, *ap*), 0.78 (d, J = 5.6 Hz, 5.1H, *ap*).

^{13}C-NMR (101 MHz, [d$_7$]DMF): δ (ppm) = 173.8 (2×) , 167.6, 163.4, 148.7, 144.3, 140.4, 138.9, 138. 6, 137.9, 137.7, 137.5, 137.2, 134.6, 129.7, 129.1, 128.3, 128.1, 126.4, 126.3, 125.8, 125.6, 122.4, 69.6, 68.3, 62.2, 62.2, 27.3, 27.1, 23.9, 22.7, 22.3, 21.8, 21.7.

^{19}F-NMR (397 MHz, [d$_7$]DMF) δ (ppm) = -109.1 (m, 4F, *p/ap*), -131.9 (s, 2F, *p/ap*).

ESI-MS: negative mode, *m/z* =1109.8161 $[M-H2]^{2-}$ (found), 1109.8176 (100.0%), (calculated for $C_{97}H_{116}F_6N_4O_{44}S_2^{2-}$, $[M-2H]^{2-}$).

Dodeca-acid **6**-*i*Bu-OMe



Dodeca-acid **6**-*i*Bu-OMe was obtained according to **GP3**.

Anhydrous THF (10 mL), ***i*Bu-Ox-2I** (65 mg, 75 µmol), water (10 mL), K_2CO_3 (0.1 g), boronic ester **3**-OMe (0.25 g, 0.19 mmol, 2.4 equiv.), Sphos (8.0 mg, 19 µmol, 0.24 equiv.), and $Pd(dba)_2$ (11 mg, 19 µmol, 0.24 equiv.) were used in the reaction. Dodeca-acid **6**-*i*Bu-OMe was obtained as a yellow solid (0.12 g, 65% yield).

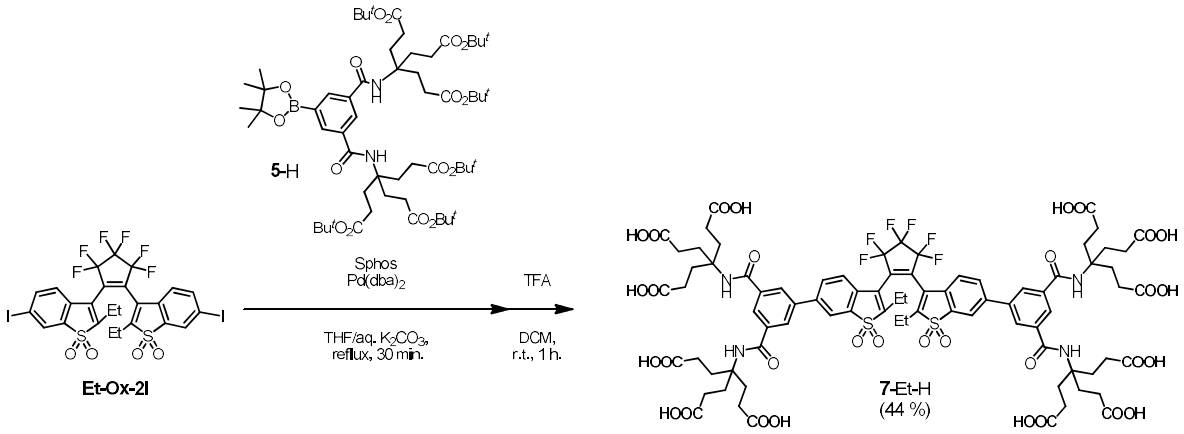
^{1}H-NMR (400 MHz, [d$_7$]DMF): δ (ppm) = 12.4 (br, 12H, *ap/p*),8.51 (d, J = 1.6 Hz, 1.7H, *ap*), 8.40 (d, J = 1.6 Hz, 0.3H, *p*), 8.30 (dd, J =8.0, 1.6 Hz, 1.7H, *ap/p*), 8.25 (s, 3.4H, *ap*), 8.13 (s, 0.6H, *p*), 8.10–8.04 (m, 3.7H, *ap/p*), 8.00 (s, 0.6H, *p*), 7.91–7.78 (m, 2.0H, *ap/p*), 4.04 (s, 5.1H, *ap*), 3.98 (s, 0.9H, *p*), 3.89 (s, 20.4H, *ap*), 3.85 (s, 3.6H, *p*), 3.81–3.73 (m, 24H, *ap/p*), 2.62–2.54 (m, 24H, *ap/p*), 2.49–2.2 (m, 6H, *ap/p*), 1.16 (d, J = 6.0 Hz, 0.9H, *a*), 1.04 (d, J = 5.2 Hz, 0.9H, *a*), 0.94 (d, J = 6.0 Hz, 5.1H, *ap*), 0.76 (d, J = 6.0 Hz, 5.1H, *ap*).

^{13}C-NMR (101 MHz, [d$_7$]DMF): δ (ppm) = 173.8 (2×) , 167.6, 163.4, 148.7, 144.3, 140.4, 138.9, 138. 6, 137.9, 137.7, 137.5, 137.2, 134.6, 129.7, 129.1, 128.3, 128.1, 126.4, 126.3, 125.8, 125.6, 122.4, 69.6, 68.3, 62.2, 62.2, 27.3, 27.1, 23.9, 22.7, 22.3, 21.8, 21.7.

^{19}F-NMR (397 MHz, [d$_7$]DMF) δ (ppm) = -109.1 (m, 4F, *p/ap*), -132.0 (s, 2F, *p/ap*).

ESI-MS: negative mode, *m/z* = 1139.8260 $[M\text{-}H2]^{2-}$ (found), 1139.8282 (calculated for $C_{99}H_{120}F_6N_4O_{46}S_2^{2-}$, $[M\text{-}2H]^{2-}$).

Dodeca-acid **7**-Et-H



Dodeca-acid **7**-Et-H was obtained according to **GP3**.

Anhydrous THF (10 mL), **Et-Ox-2I** (65 mg, 80 µmol), water (10 mL), K_2CO_3 (0.1 g), boronic ester **5**-H (0.21 g, 0.19 mmol, 2.4 equiv.), Sphos (8.0 mg, 19 µmol, 0.24 equiv.), and $Pd(dba)_2$ (11 mg, 19 µmol, 0.24 equiv.) were used in the reaction. Dodeca-acid **7**-Et-H was obtained as a yellow solid (63 mg, 44% yield).

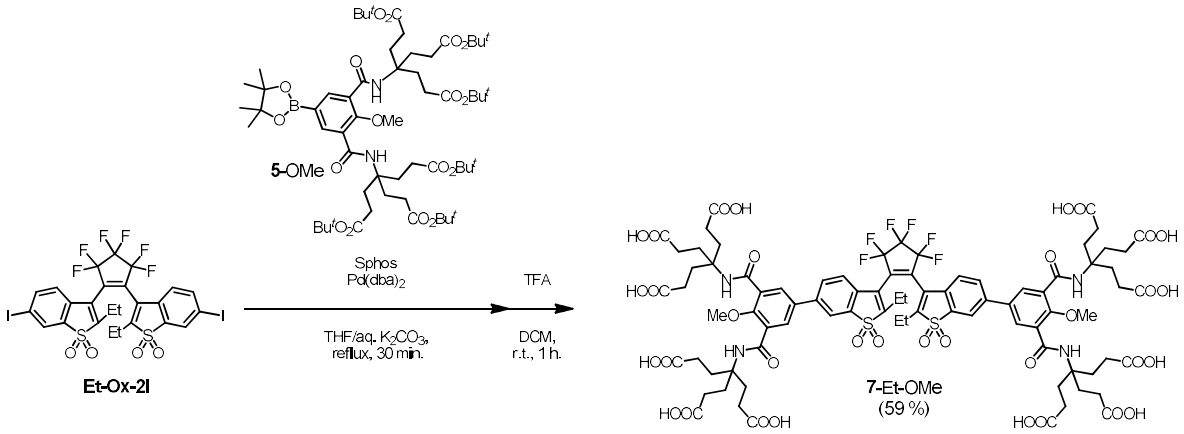
^{1}H-NMR (400 MHz, [d$_7$]DMF): δ (ppm) = 12.3 (br, 12H, *ap/p*), 8.59 (d, J = 1.6 Hz, 1.6H, *ap*), 8.56–8.52 (m, 4.8H, *ap/p*), 8.51 (d, J = 1.6 Hz, 0.4H, *p*), 8.47–8.44 (m, 0.4H, *p*), 8.41 (d, J = 1.6 Hz, 0.8H, *p*), 8.36 (dd, J = 8.0, 1.6 Hz, 1.6H, *ap*), 8.20 (dd, J = 8.0, 1.6 Hz, 0.4H, *p*), 8.06–8.03 (0.4H, overlapped with DMF peak, *p*), 7.95–7.87 (m, 4.8H, *ap*), 7.85 (s, 0.8H, *a*), 2.89–2.58 (m, 4.0H, *ap/p*), 1.42 (t, J = 7.6 Hz, 1.2H, *p*), 1.06 (t, J = 7.6 Hz, 4.8H, *ap*).

^{13}C-NMR (101 MHz, [d$_7$]DMF): δ (ppm) = 175.6 (2×), 166.9 (2×), 163.4, 150.3, 150.1, 144.1, 144.0, 138.7, 138.5, 137.8, 137.8, 137.5, 137.4, 134.6, 134.3, 129.7, 129.3, 129.2, 128.6, 128.5, 126.3, 125.8, 124.1, 124.0, 122.4, 122.3, 59.2, 29.4, 20.2, 19.9, 12.8, 12.6.

^{19}F-NMR (397 MHz, [d$_7$]DMF) δ (ppm) = -109.5 (m, 4F, *p/ap*), -130.6 (m, 2F, *p/ap*).

ESI-MS: negative mode, *m/z* = 901.2210 $[M-H2]^{2-}$ (found), 901.2212 (calculated for $C_{81}H_{84}F_6N_4O_{32}S_2^{2-}$, $[M-2H]^{2-}$).

Dodeca-acid **7**-Et-OMe



Dodeca-acid **7**-Et-OMe was obtained according to **GP3**.

Anhydrous THF (10 mL), **Et-Ox-2I** (60 mg, 74 µmol), water (10 mL), K_2CO_3 (0.1 g), boronic ester **5**-OMe (0.20 g, 0.18 mmol, 2.4 equiv.), Sphos (7.3 mg, 18 µmol, 0.24 equiv.), and $Pd(dba)_2$ (10 mg, 18 µmol, 0.24 equiv.) were used in the reaction. Dodeca-acid **7**-Et-OMe was obtained as a yellow solid (82 mg, 59% yield).

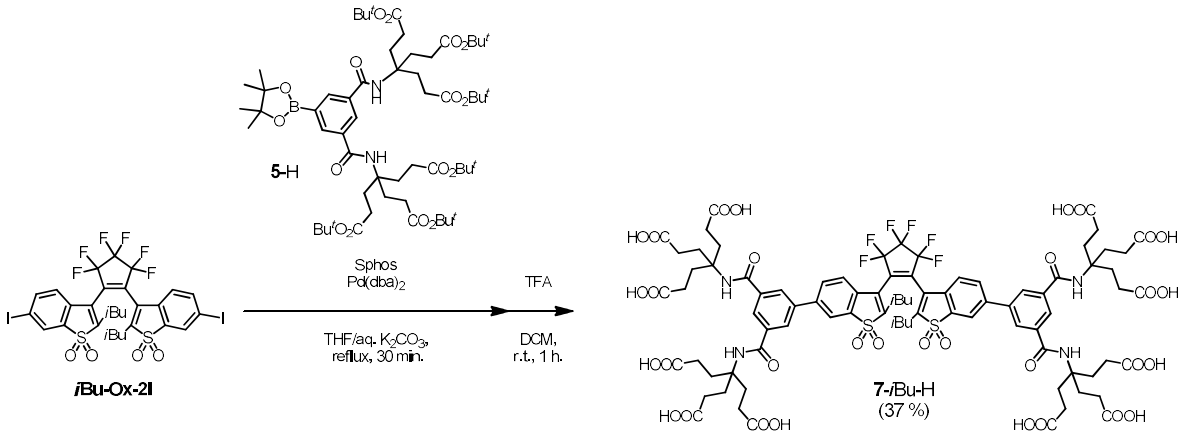
^{1}H-NMR (400 MHz, [d$_7$]DMF): δ (ppm) = 12.4 (br, 12H, *ap/p*), 8.56 (d, J = 1.2 Hz, 1.5H, *ap*), 8.47 (d, J = 1.2 Hz, 0.5H, *p*), 8.28 (dd, J = 8.0, 1.2 Hz, 1.5H, *ap*), 8.16–8.09 (m, 3.5H, *ap/p*), 8.05 (s, 1.0H, *p*), 7.97 (d, J = 8.0 Hz, 0.5H, *p*), 7.93 (s, 3.0H, *ap*), 7.90 (s, 1.0H, *p*), 7.86 (d, J = 8.0 Hz, 1.5H, *ap*), 4.07 (s, 4.5H, *ap*), 4.03 (s, 1.5H, *p*), 2.89–2.57 (m, 4H, *ap/p*, overlapped with DMF peaks), 2.55–2.40 (m, 24.0H, *ap/a*), 2.31–2.15 (m, 24.0H, *ap/a*),1.44 (t, J = 7.6 Hz, 1.5H, *a*), 1.06 (t, J = 7.6 Hz, 4.5H, *ap*).

^{13}C-NMR (101 MHz, [d$_7$]DMF): δ (ppm) = 175.6, 166.9 (2×), 163.4, 156.4 (2×), 150.1, 149.8, 143.4, 143.3, 137.6, 137.4, 133.9, 133.5 (2×), 133.4 (2×), 130.1 (2×), 129.0, 128.8, 125.8, 124.0 (2×), 121.9, 121.8, 116.5 (2×), 63.8 (2×), 59.1 (2×), 30.9, 29.4 (2×), 20.1, 19.9, 12.7, 12.5.

^{19}F-NMR (397 MHz, [d$_7$]DMF) δ (ppm) = -110.2 (m, 4F, *p/ap*), -131.3 (s, 2F, *p/ap*).

ESI-MS: positive mode, *m/z* =955.2268 $[M+2Na]^{2+}$ (found), 955.2283 (calculated for $C_{83}H_{90}F_6N_4Na_2O_{34}S_2^{2+}$, $[M+2Na]^{2+}$).

Dodeca-acid **7-*i*Bu-OMe**



Dodeca-acid **7-*i*Bu-H** was obtained according to **GP3**.

Anhydrous THF (10 mL ***i*Bu-Ox-2I** (70 mg, 81 µmol), water (10 mL), K_2CO_3 (0.1 g), boronic ester **5**-H (0.21 g, 0.19 mmol, 2.4 equiv.), Sphos (8.0 mg, 19 µmol, 0.24 equiv.) and $Pd(dba)_2$ (11 mg, 19 µmol, 0.24 equiv.) were used in the reaction. Dodeca-acid **7-**iBu-H was obtained as a yellow solid (55 mg, 37% yield). The closed ring-isomer was generated in aqueous acetonitrile by irradiation with UV-lamp (365 nm) followed by isolation with preparative HPLC. For the column specifications and flow rate, see the beginning of Supp. Inf. The analytical HPLC method is given below.

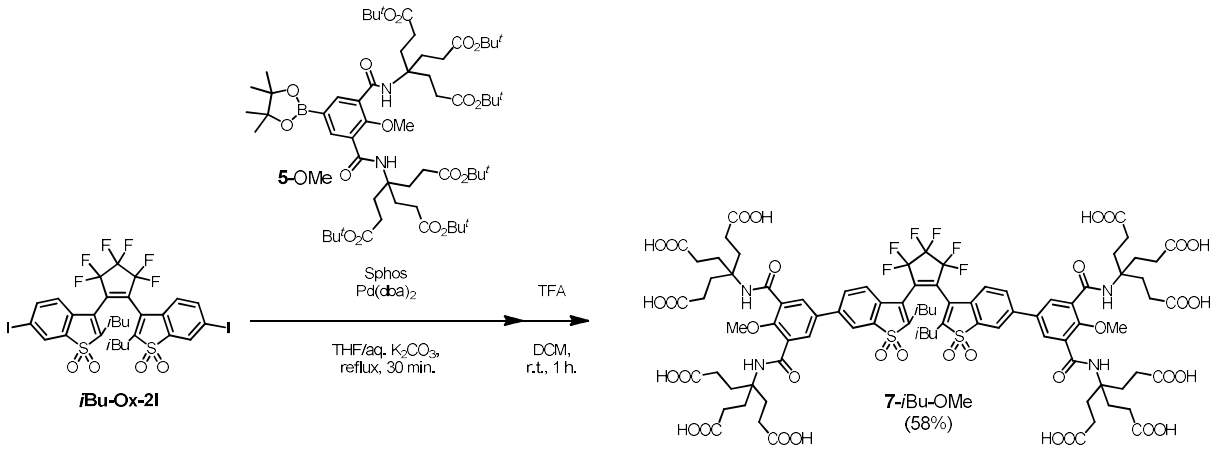
^{1}H-NMR (400 MHz, [d$_7$]DMF): δ (ppm) = 12.3 (br, 12H, *ap/p*), 8.60 (d, J = 1.2 Hz, 1.7H, *ap*), 8.57–8.50 (m, 5.1H, *ap*), 8.49 (d, J = 1.2 Hz, 0.3H, *a*), 8.46–8.44 (m, 0.3H, *a*), 8.44–8.38 (m, 2.3H, *ap/p*), 8.18 (dd, J = 8.0, 1.2 Hz, 0.3H, *p*), 7.95–7.86 (m, 5.4H, *ap/p*), 7.84 (s, 0.6H, *ap*), 2.58–2.08 (m, 54H, *ap/p*), 1.17 (d, J = 6.0 Hz, 0.9H, *a*), 1.04 (d, J = 4.8 Hz, 0.9H, *a*), 0.94 (d, J = 6.4 Hz, 5.1H, *ap*), 0.78 (d, J = 6.4 Hz, 5.1H, *ap*).

^{13}C-NMR (101 MHz, [d$_7$]DMF): δ (ppm) = 174.7 (2×), 166.1, 147.7, 143.5, 137.8, 137.5, 137.0, 136.9, 136.6, 133.6, 128.8, 128.7, 128.2, 127.7, 125.6, 125.4, 124.9, 124.7, 121. 5, 58.3, 28.5, 26.2, 21.9, 21.3.

^{19}F-NMR (397 MHz, [d$_7$]DMF) δ (ppm) = -109.2 (m, 4F, *p/ap*), -131.6 (s, 2F, *p/ap*).

ESI-MS: negative mode, *m/z* = 929.2523 $[M\text{-}H2]^{2-}$ (found), 929.2525 (calculated for $C_{85}H_{92}F_6N_4O_{32}S_2^{2-}$, $[M\text{-}2H]^{2-}$).

Dodeca-acid **7-*i*Bu-OMe**



Dodeca-acid **7-*i*Bu-OMe** was obtained according to **GP3**.

Anhydrous THF, ***i*Bu-Ox-2I** (60 mg, 69 µmol), water (10 mL), K_2CO_3 (0.1 g), boronic ester **5**-OMe (0.19 g, 0.17 mmol, 2.5 equiv.), Sphos (7.0 mg, 17 µmol, 0.25 equiv.), and $Pd(dba)_2$ (10 mg, 17 µmol, 0.25 equiv.) were used in the reaction. Dodeca-acid **7-*i*Bu-OMe** was obtained as a yellow solid (78 mg, 58% yield).

^{1}H-NMR (400 MHz, [d$_7$]DMF): δ (ppm) = 12.4 (br, 12H, *ap/p*), 8.55 (d, J = 1.2 Hz, 1.75H, *ap*), 8.44 (d, J = 1.2 Hz, 0.25H, *p*), 8.32 (dd, J = 8.0, 1.6 Hz, 1.75H, *ap*), 8.12–8.05 (m, 3.75H, *ap/p*), 8.00 (s, 0.5H, *p*), 7.94–7.81 (m, 6.0H, *ap/p*), 4.06 (s, 5.25H, *p*), 4.00 (s, 0.75H, *p*), 2.54–2.14 (m, 54H, *ap/p*), 1.16 (d, J = 6.0 Hz, 0.75H, *a*), 1.03 (d, J = 4.4 Hz, 0.75H, *a*), 0.93 (d, J = 6.0 Hz, 5.25H, *ap*), 0.75 (d, J = 6.0 Hz, 5.25H, *ap*).

^{13}C-NMR (101 MHz, [d$_7$]DMF): δ (ppm) = 174.6, 166.0, 155.5 (2×), 147.4, 142.8, 142.4, 136.7, 136.4, 132.9, 132.6 (2×), 132.5, 129.3, 129.1, 127.8, 125.5, 125.5, 125.4, 124.8, 124.6, 121.0, 120.9, 62.9 (2×), 58.2 (2×), 29.9, 28.5, 26.1, 23.0, 21.8 (2×), 21.4, 20.9.

^{19}F-NMR (397 MHz, [d$_7$]DMF) δ (ppm) = -109.0 (m, 4F, *p/ap*), -131.3 (s, 2F, *p/ap*).

ESI-MS: positive mode, *m/z* = 1944.5311 $[M+Na]^+$ (found), 1943.5301 (calculated for $C_{87}H_{98}F_6N_4NaO_{34}S_2^+$, $[M+Na]^+$).

HPLC conditions (Figures **21d** and **21e**); analytical column: Interchim Uptisphere Strategy C18-HQ, 10 µm, 250×4.6 mm, flow rate 1.2 mL/min. Solvent A: water + 0.1% TFA; solvent B: ACN + 0.1% TFA. 0-3 min: 30% B, 3–13 min: 30–100% B. UV-VIS detection with dioden array (see Figures **21d** and **21e** for details).

NMR spectra of **2**-H

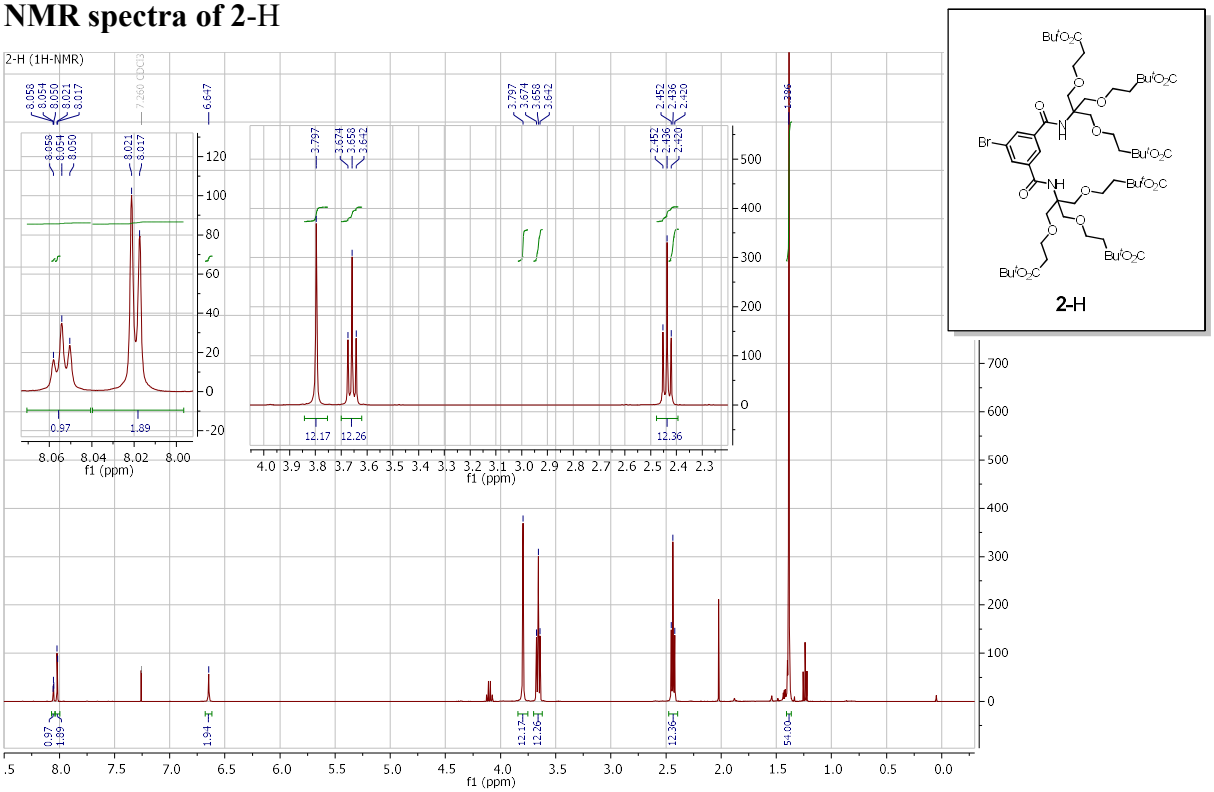


Figure S1a. ^{1}H-NMR (400 MHz) spectrum of **2**-H in $CDCl_3$

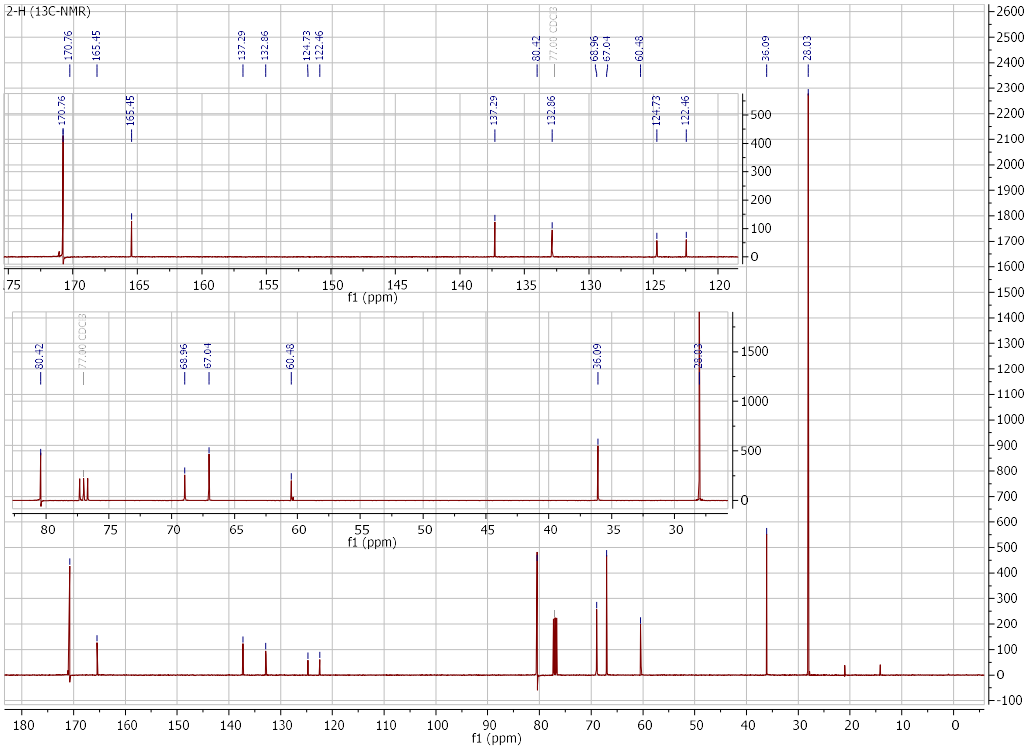
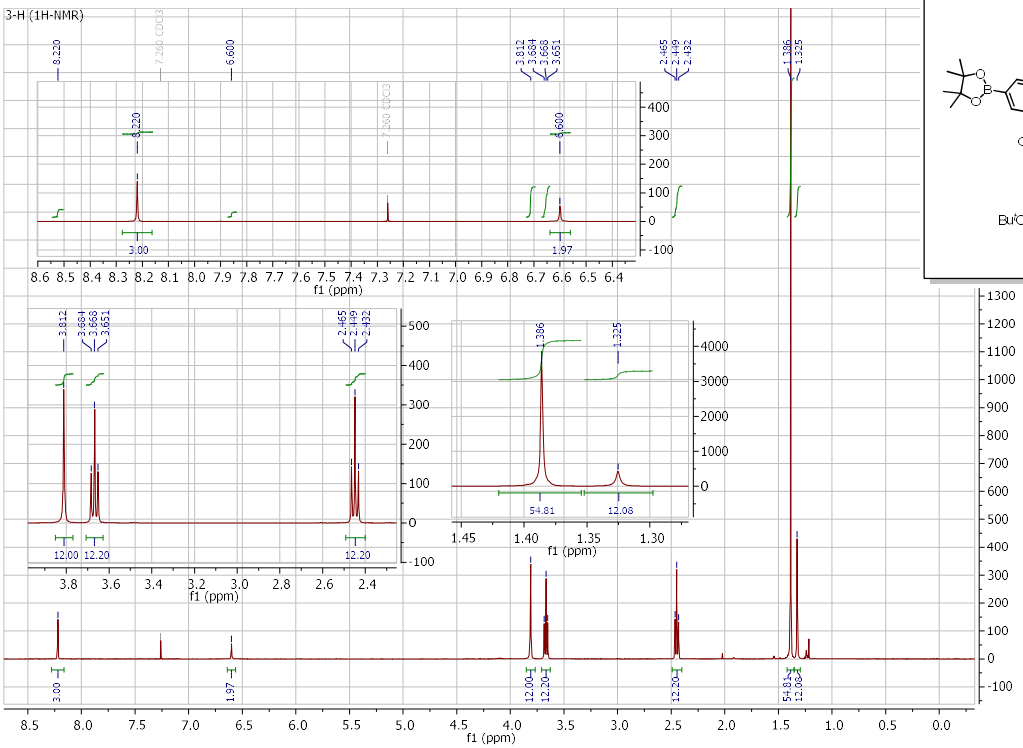


Figure S1b. ^{13}C-NMR (101 MHz) spectrum of **2**-H in $CDCl_3$

NMR spectra of **3**-H



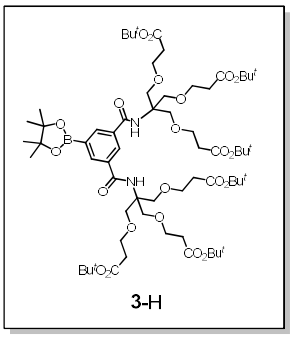


Figure S2a. ^{1}H-NMR (400 MHz) spectrum of **3**-H in $CDCl_3$

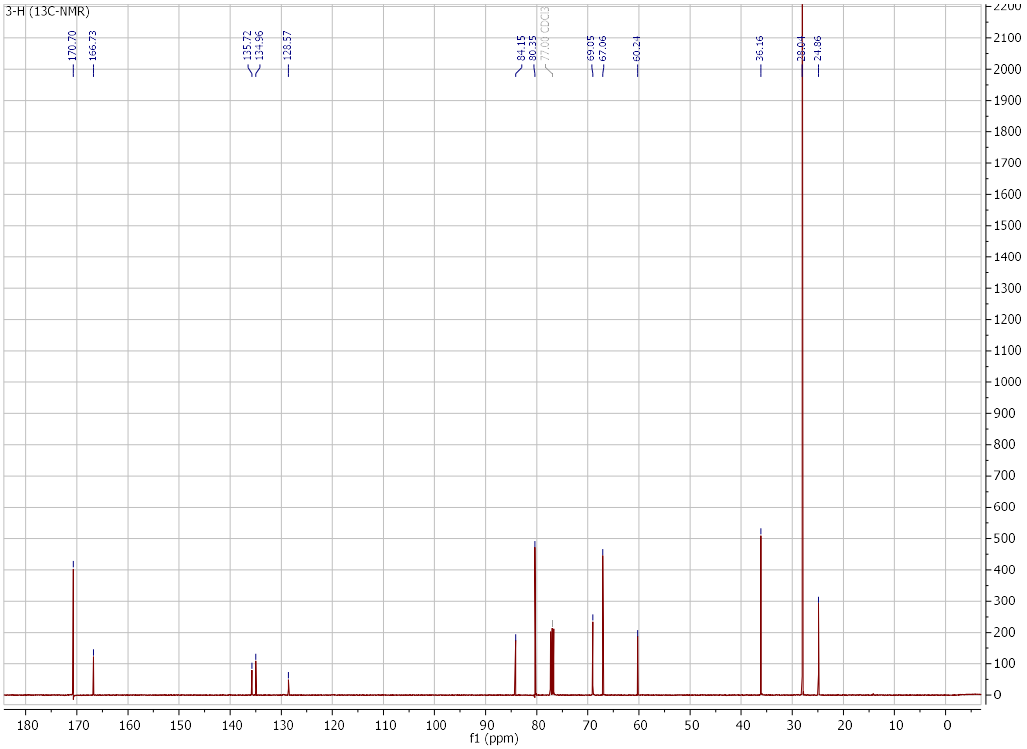


Figure S2b. ^{13}C-NMR (101 MHz) spectrum of **3**-H in $CDCl_3$

NMR spectra of **2**-OMe

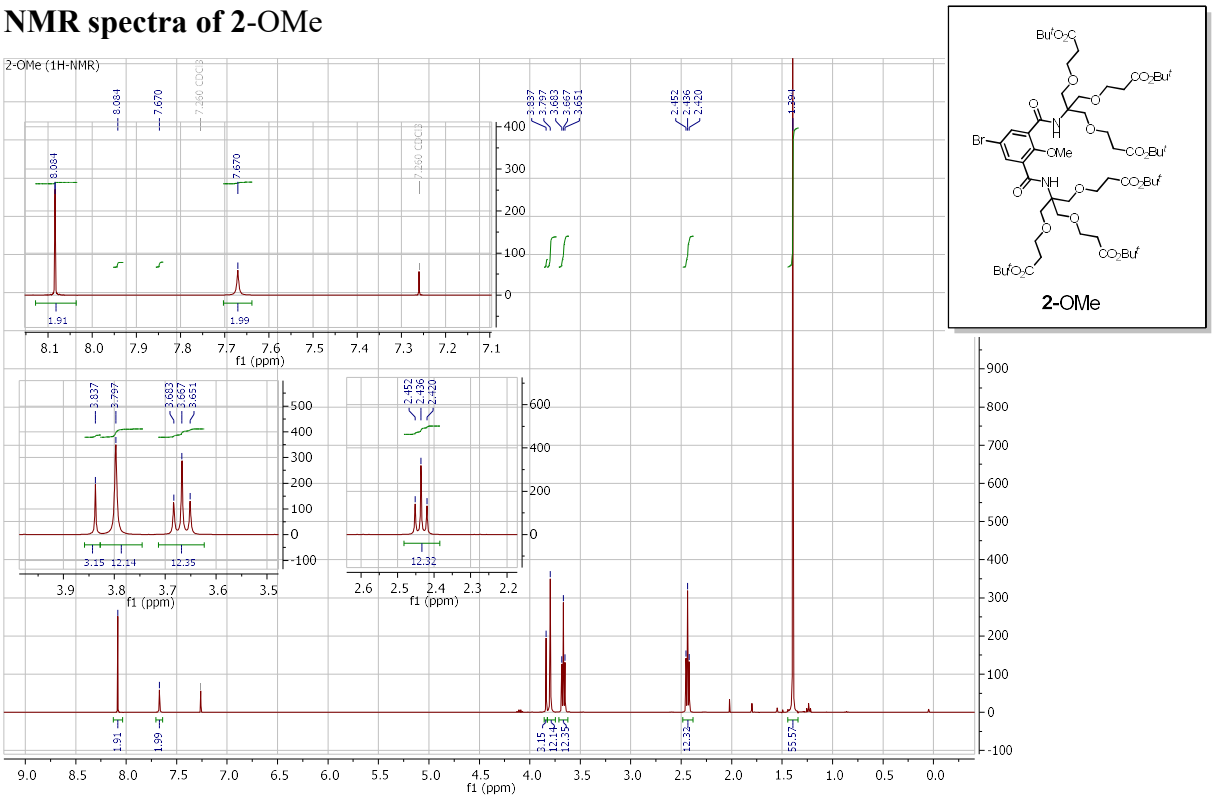


Figure S3a. ^{1}H-NMR (400 MHz) spectrum of **2**-OMe in $CDCl_3$

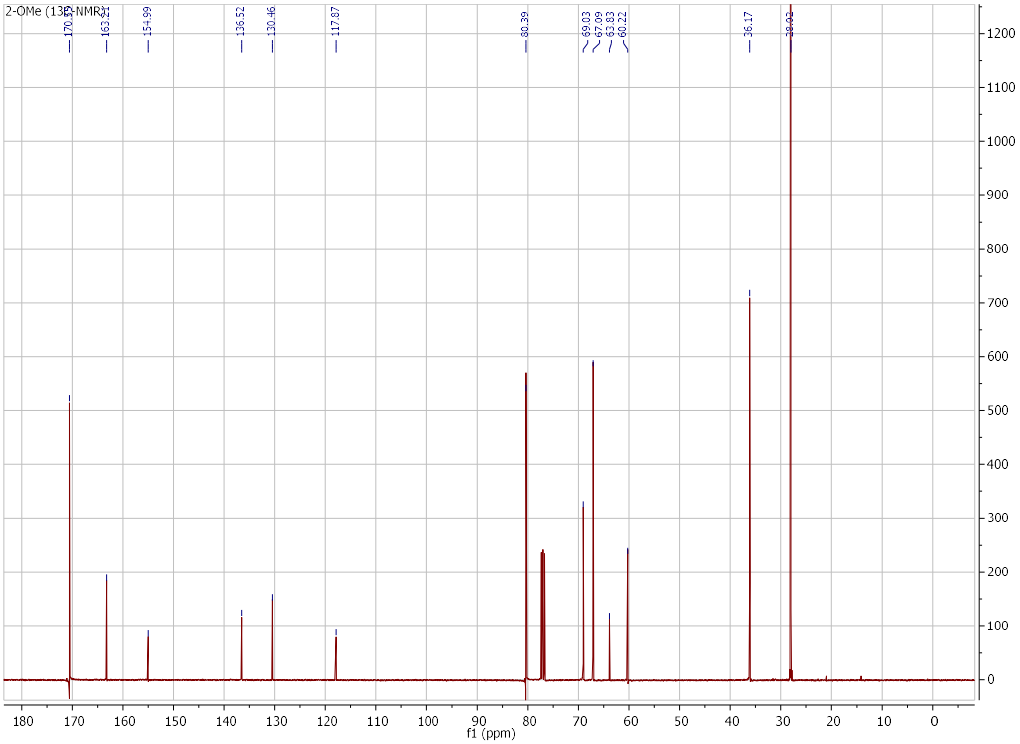


Figure S3b. ^{13}C-NMR (101 MHz) spectrum of **2**-OMe in $CDCl_3$

NMR spectra of **3**-OMe

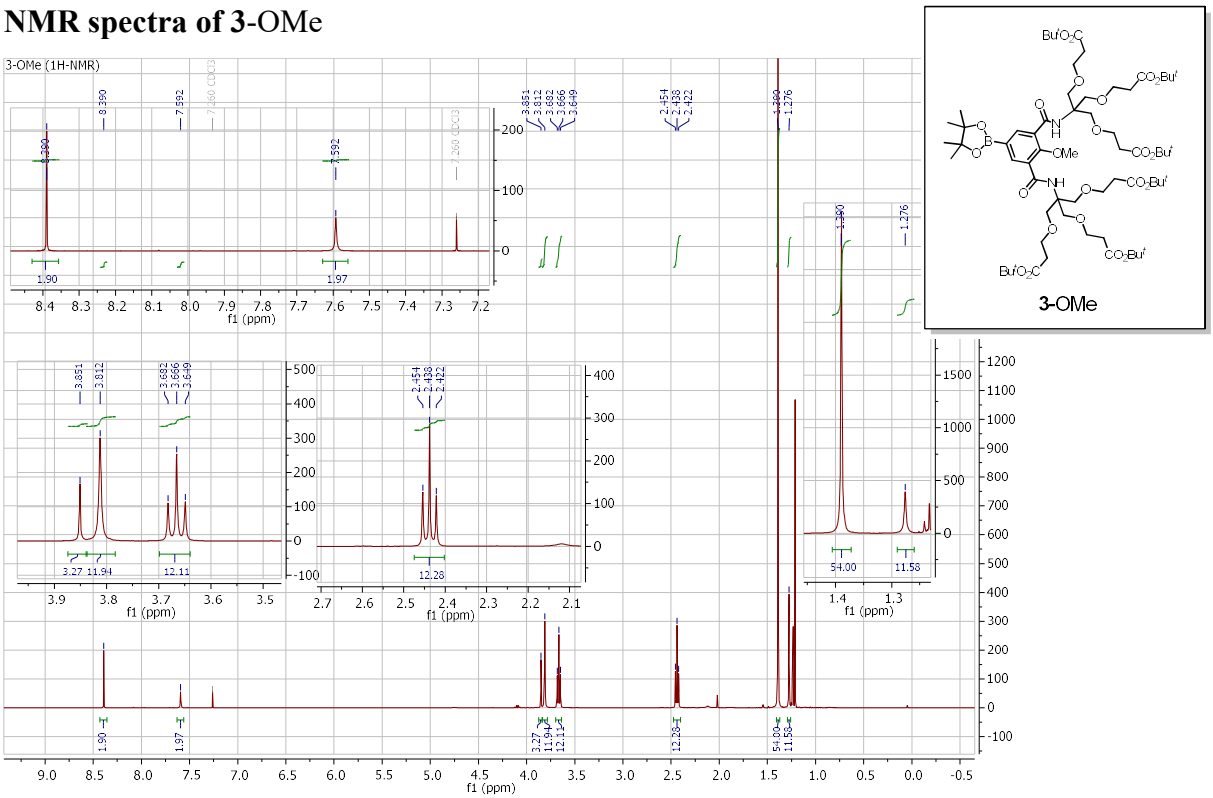


Figure S4a. ^{1}H-NMR (400 MHz) spectrum of **3**-OMe in $CDCl_3$

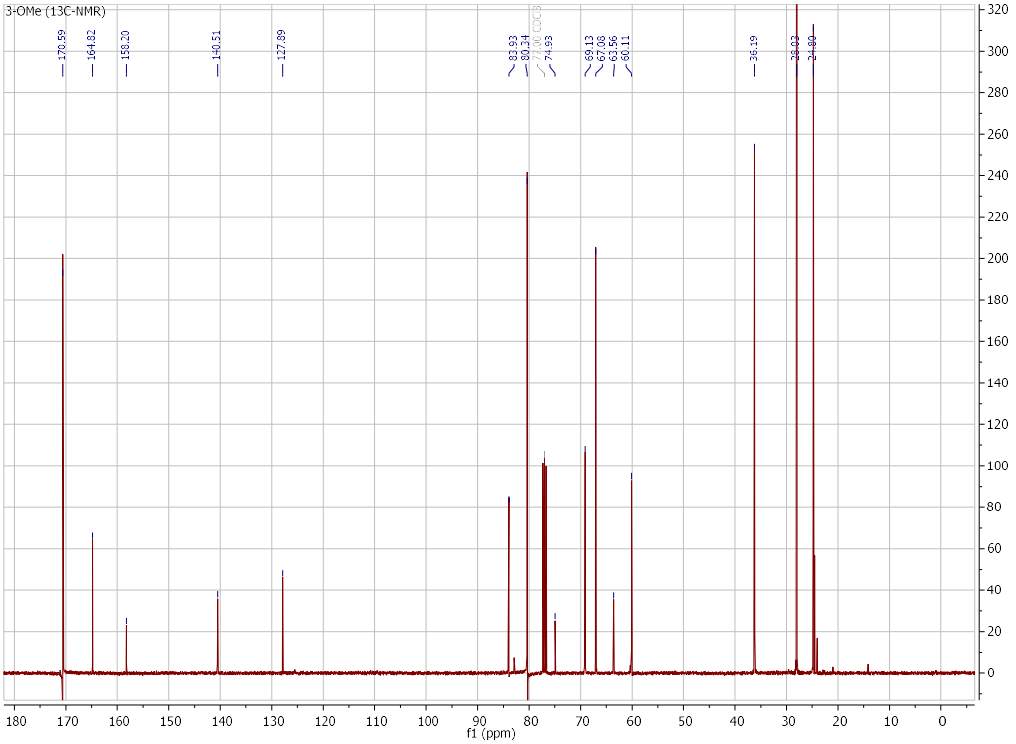
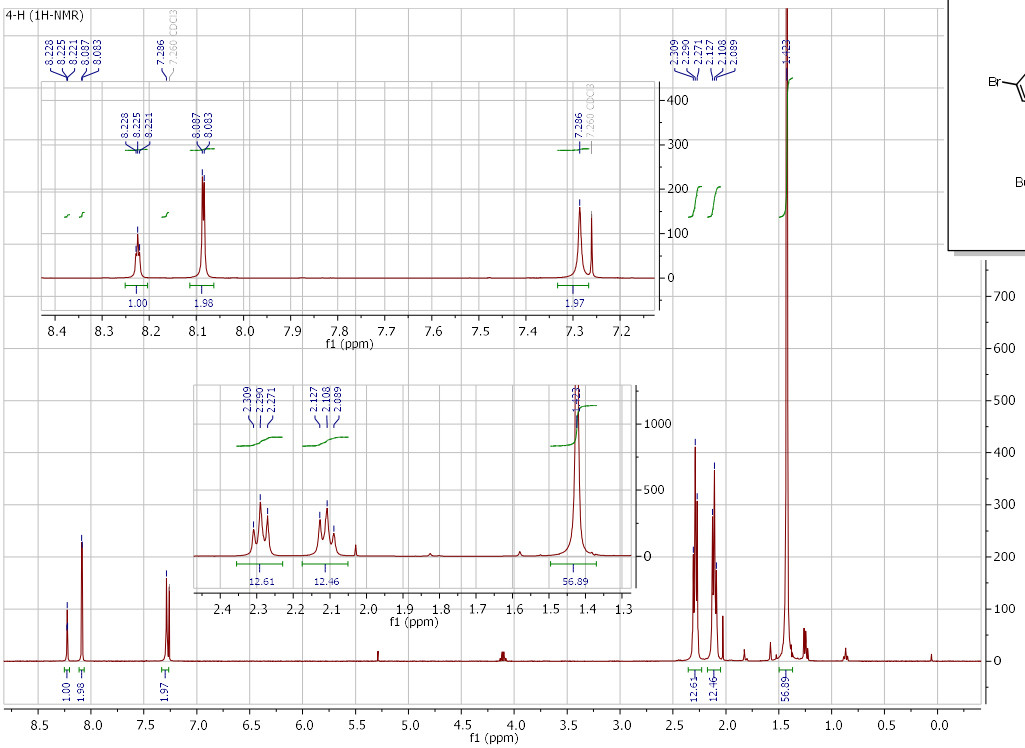


Figure S4b. ^{13}C-NMR (101 MHz) spectrum of **3**-OMe in $CDCl_3$

NMR spectra of 4-H



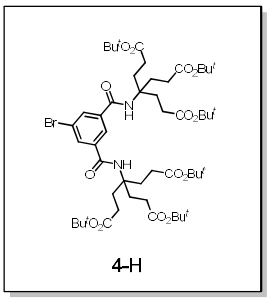


Figure S5a. ^{1}H-NMR (400 MHz) spectrum of **4**-H in $CDCl_3$

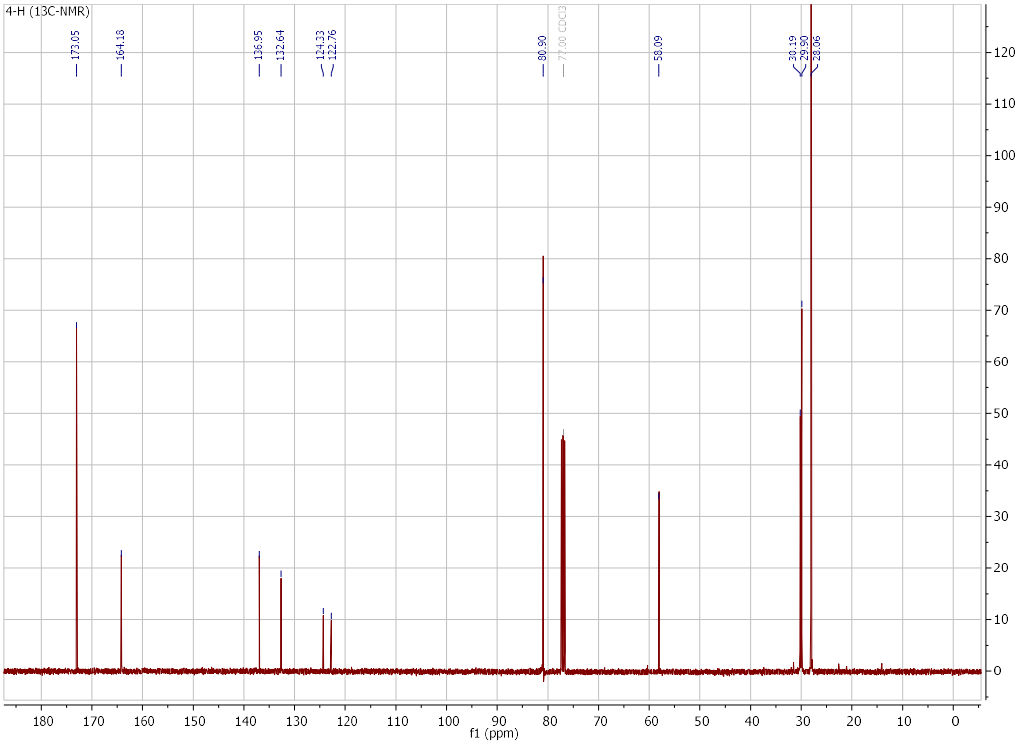


Figure S5b. ^{13}C-NMR (101 MHz) spectrum of **4**-H in $CDCl_3$

NMR spectra of **5**-H

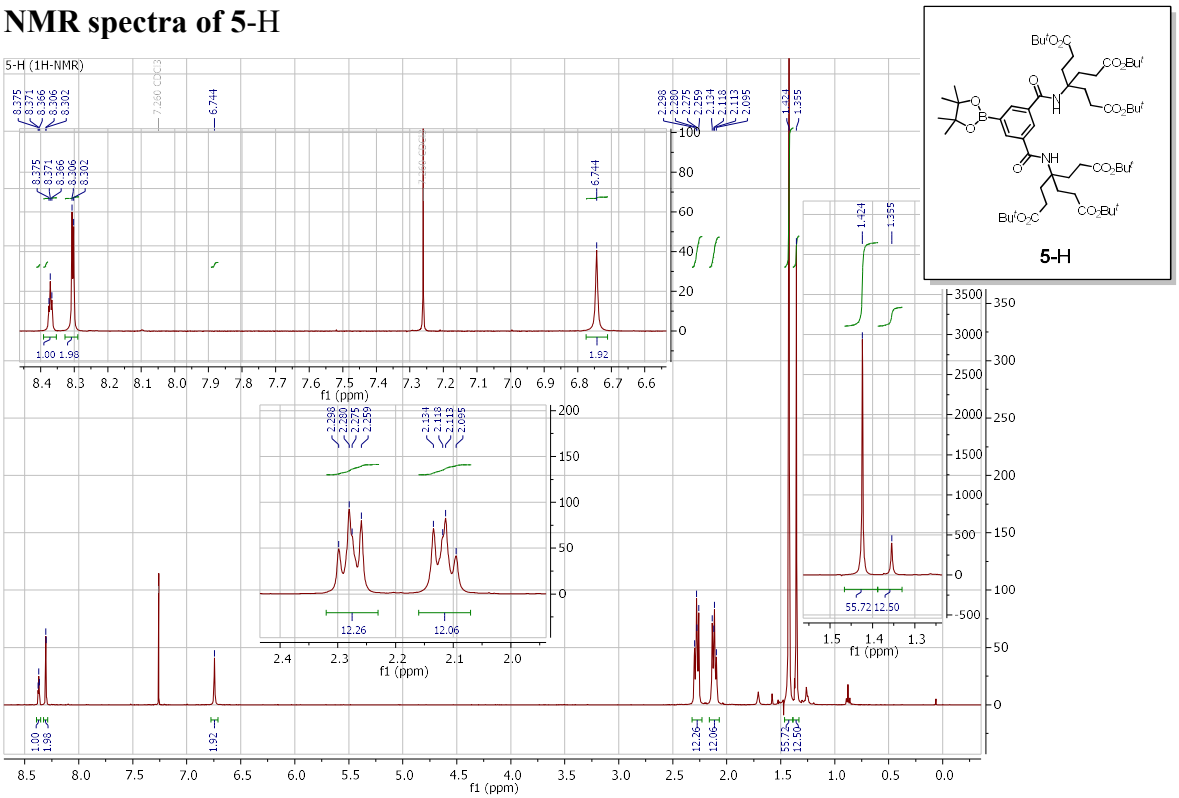


Figure S6a. ^{1}H-NMR (400 MHz) spectrum of **5**-H in $CDCl_3$

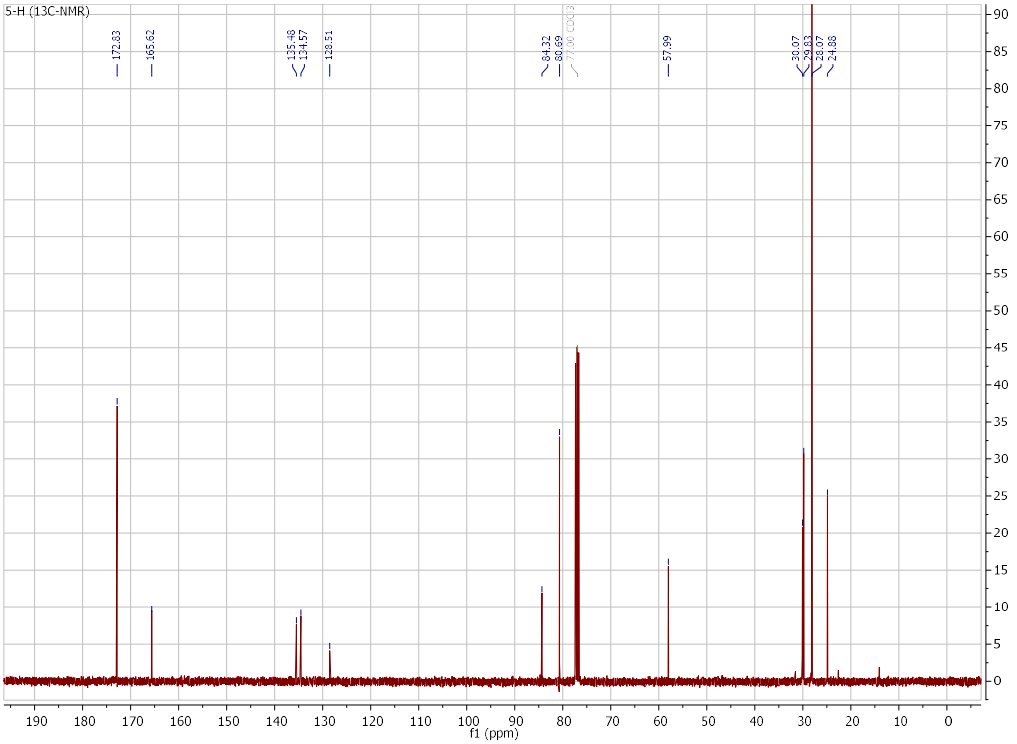
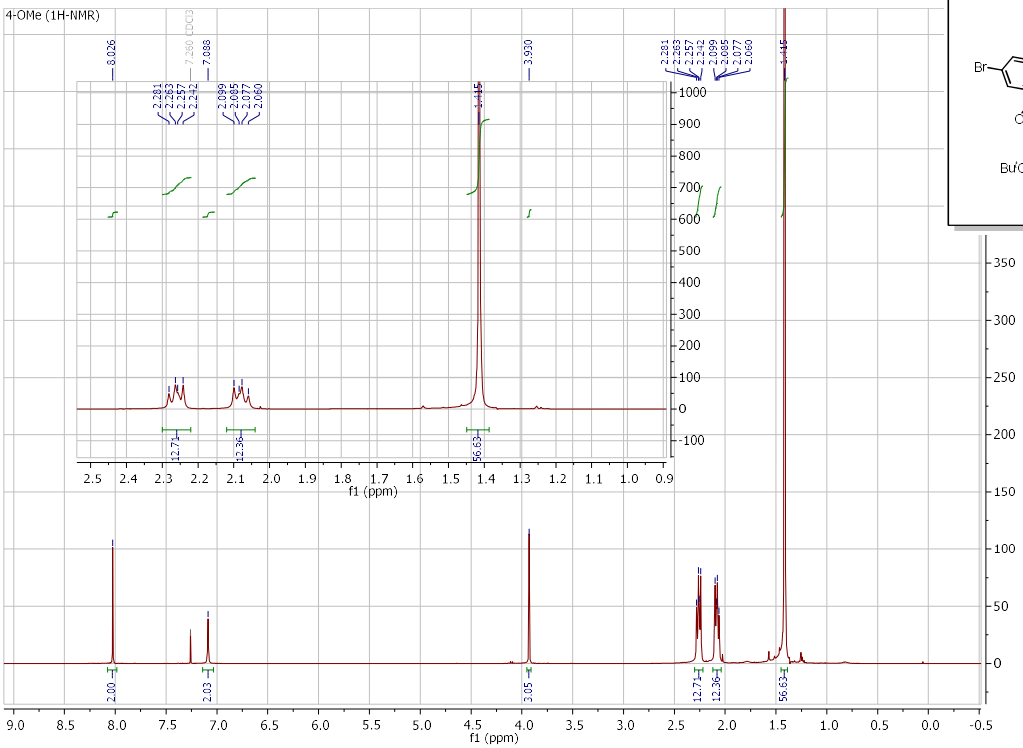


Figure S6b. ^{13}C-NMR (101 MHz) spectrum of **5**-H in $CDCl_3$

NMR spectra of 4-OMe



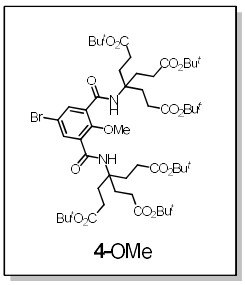


Figure S7a. ^{1}H-NMR (400 MHz) spectrum of **4**-OMe in $CDCl_3$

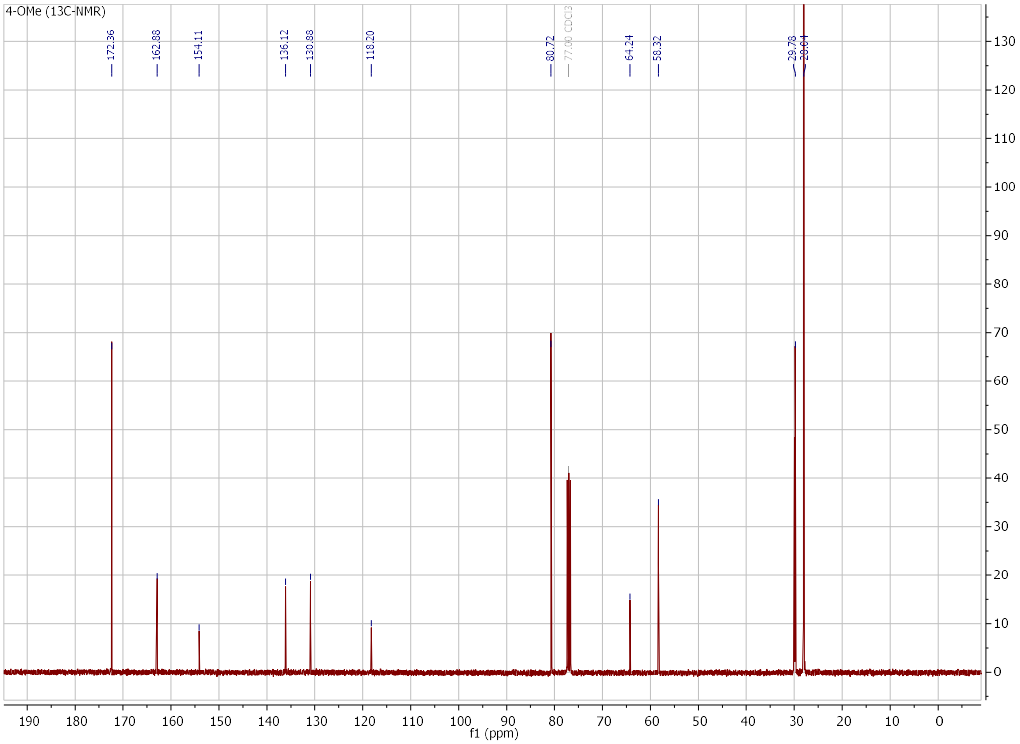


Figure S7b. ^{13}C-NMR (101 MHz) spectrum of **4**-OMe in $CDCl_3$

NMR spectra of **5**-OMe

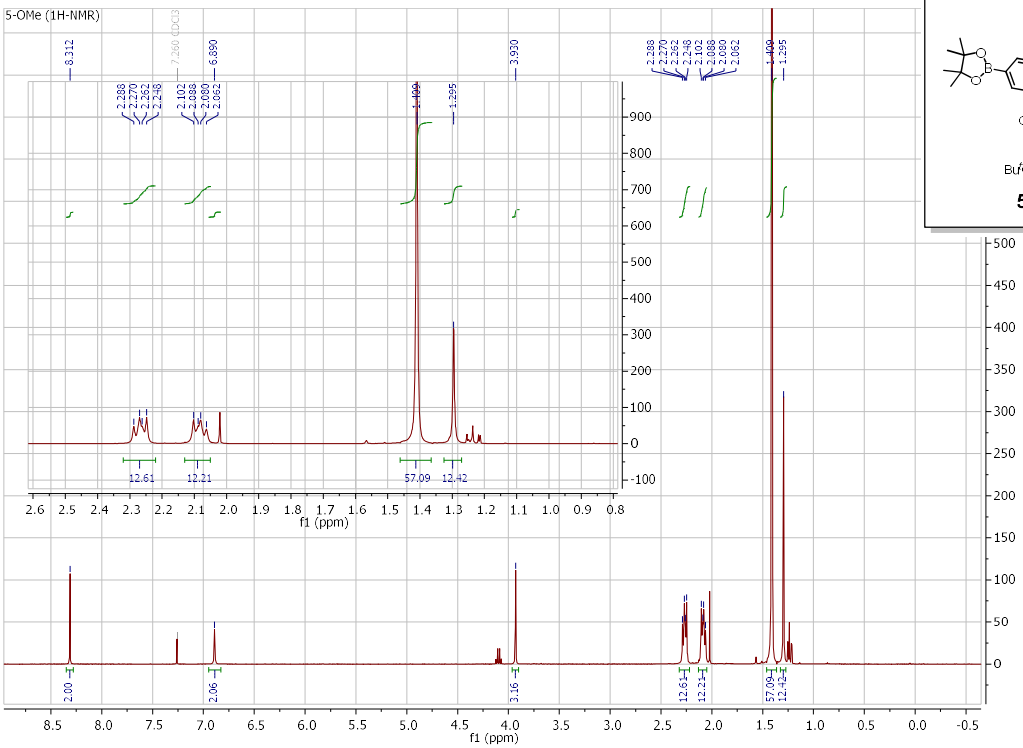


Figure S8a. ^{1}H-NMR (400 MHz) spectrum of **5**-OMe in $CDCl_3$

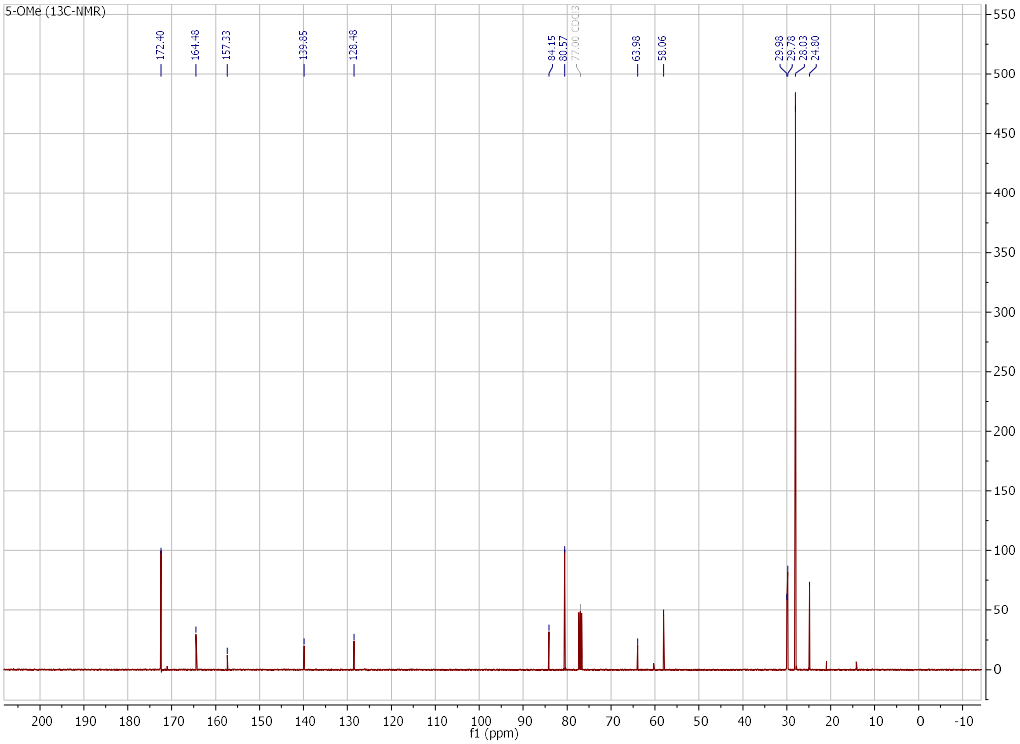


Figure S8b. ^{13}C-NMR (101 MHz) spectrum of **5**-OMe in $CDCl_3$

NMR spectra of compound a

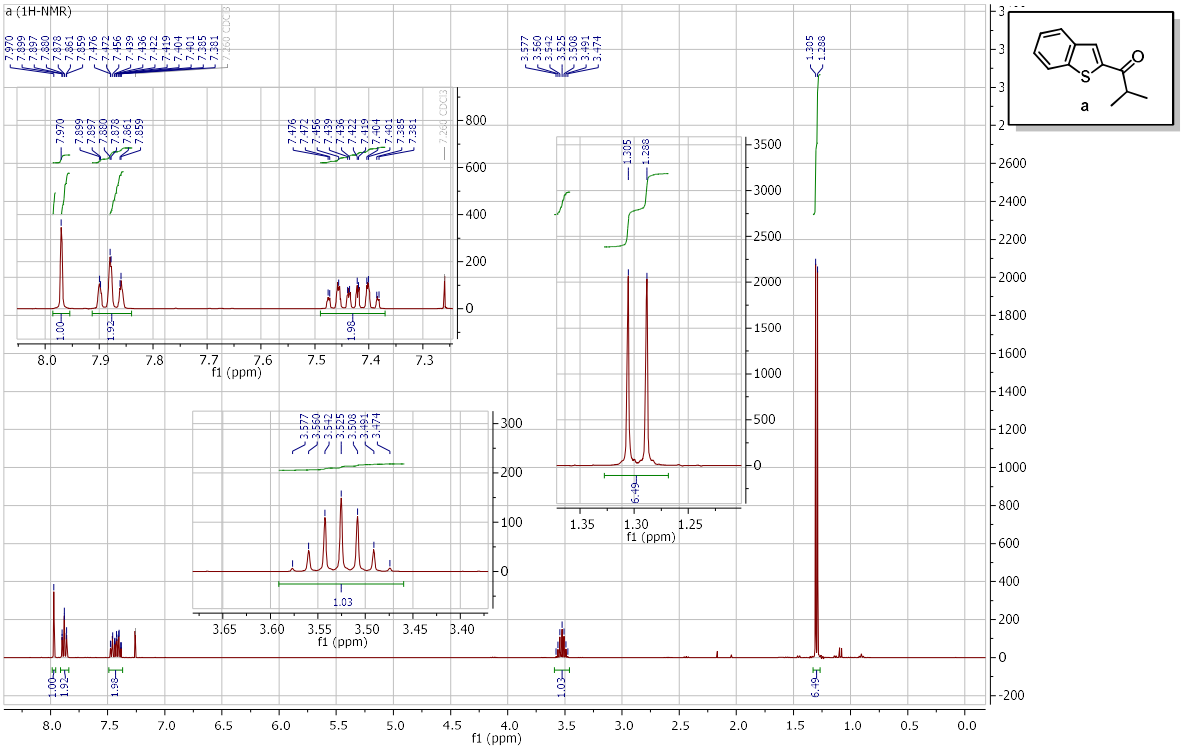


Figure S9a. ^{1}H-NMR (400 MHz) spectrum of **a** in $CDCl_3$

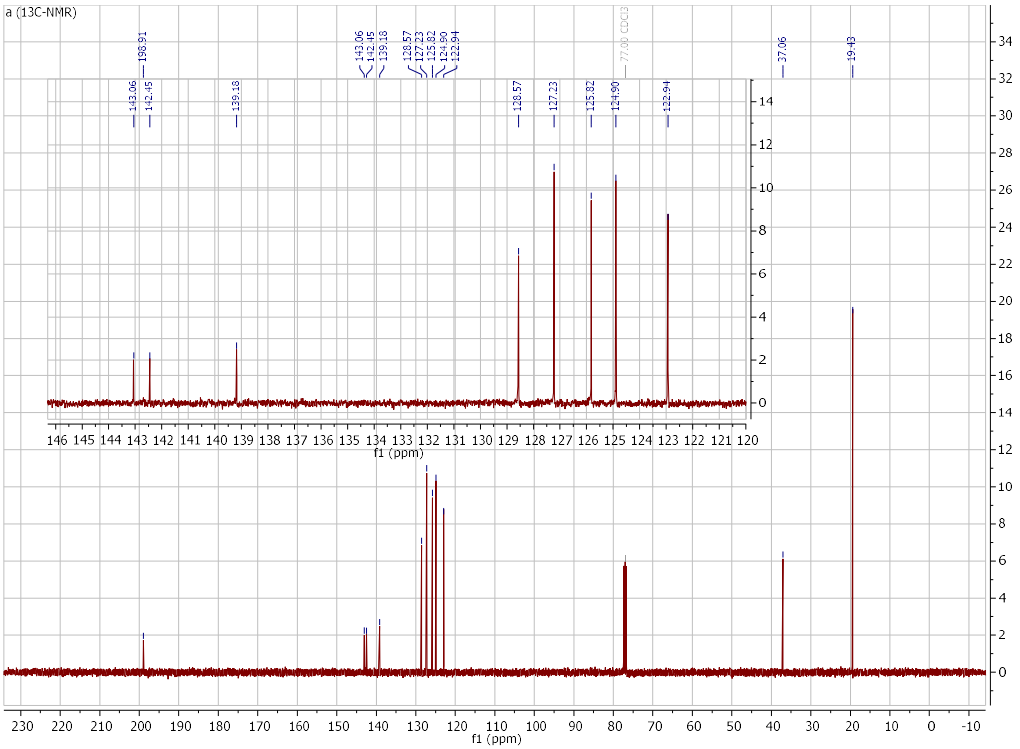


Figure S9b. ^{13}C-NMR (101 MHz) spectrum of **a** in $CDCl_3$

NMR spectra of compound b

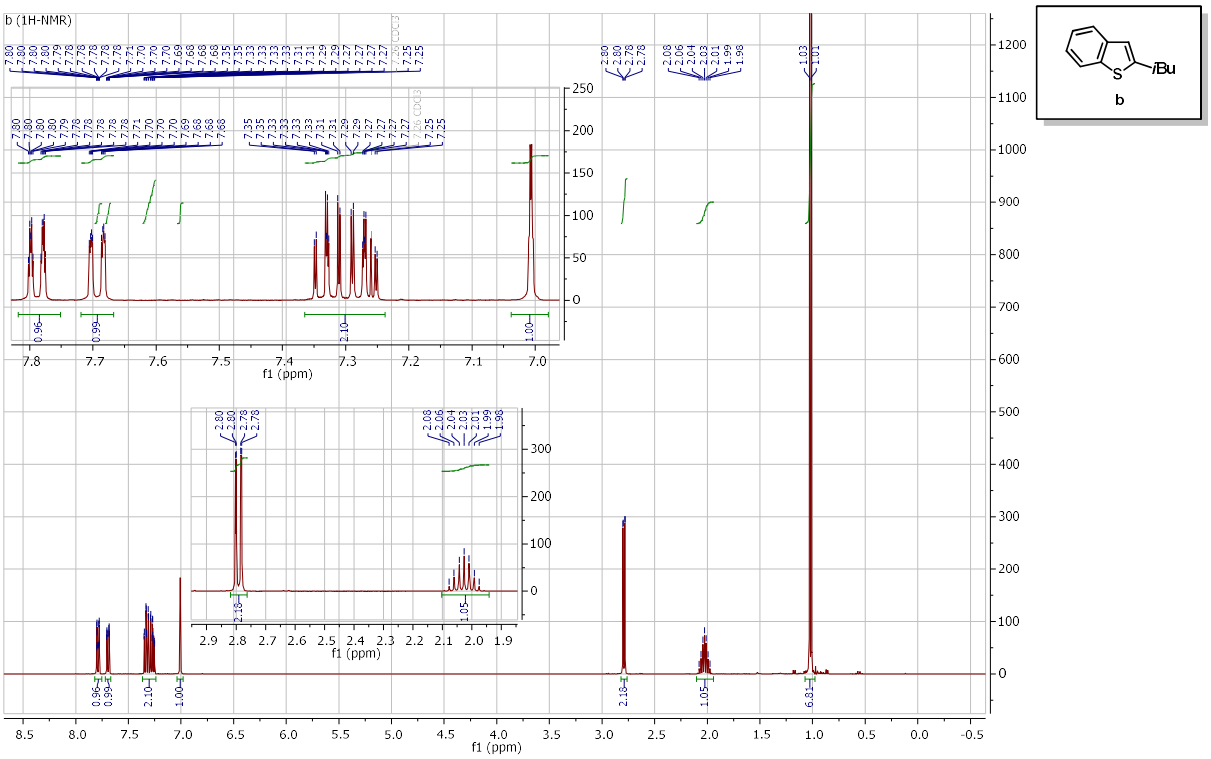


Figure S10a. ^{1}H-NMR (400 MHz) spectrum of **b** in $CDCl_3$

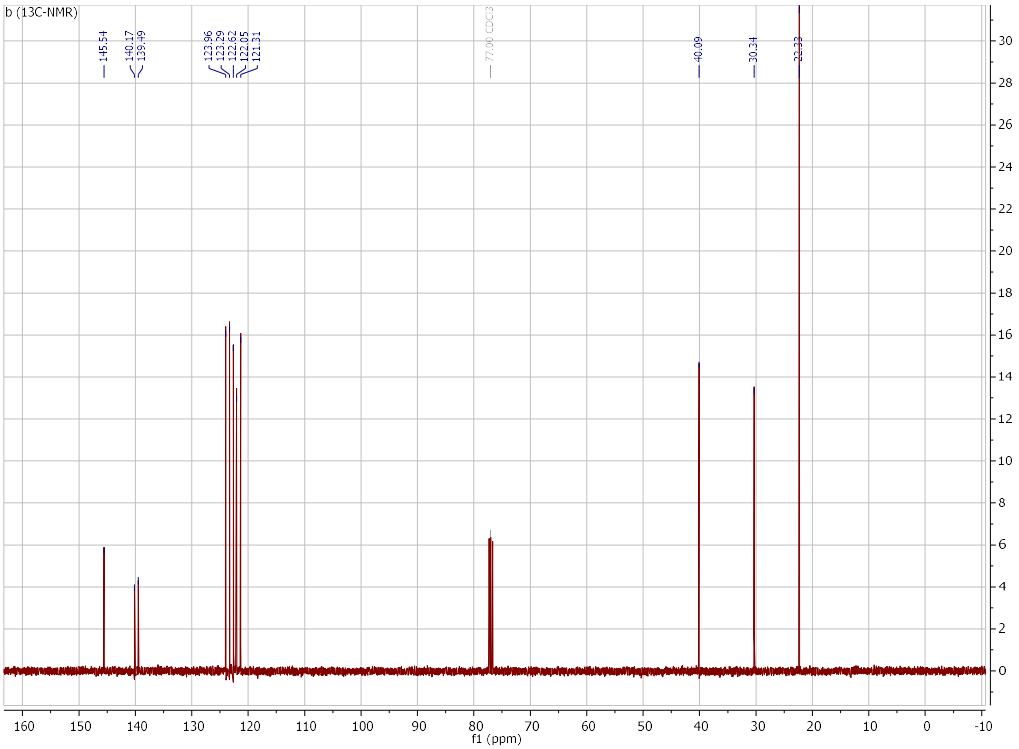
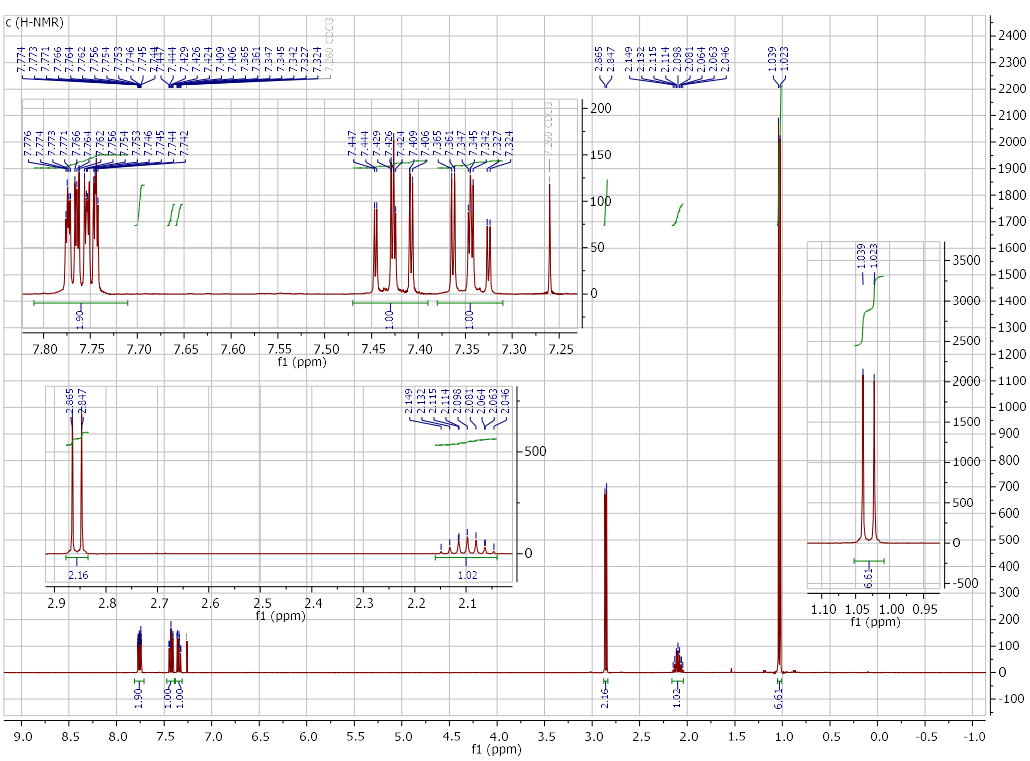


Figure S10b. ^{13}C-NMR (101 MHz) spectrum of **b** in $CDCl_3$

NMR spectra of compound c



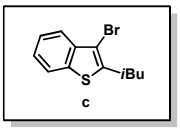


Figure S11a. ^{1}H-NMR (400 MHz) spectrum of **c** in $CDCl_3$

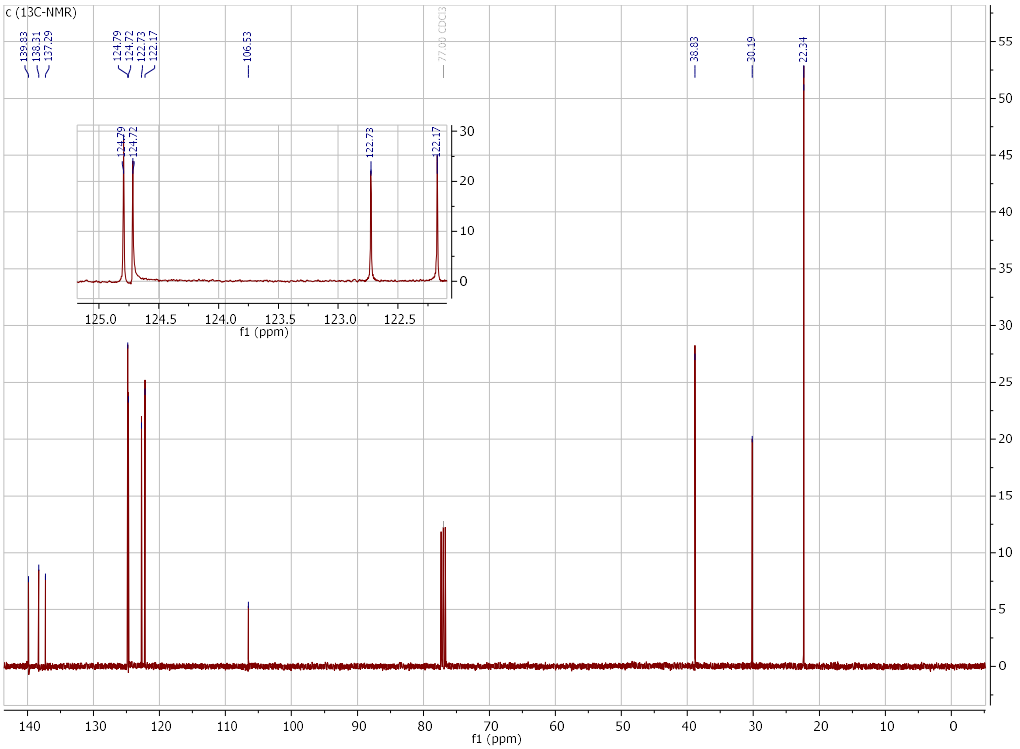


Figure S11b. ^{13}C-NMR (101 MHz) spectrum of **c** in $CDCl_3$

NMR spectra of compound d

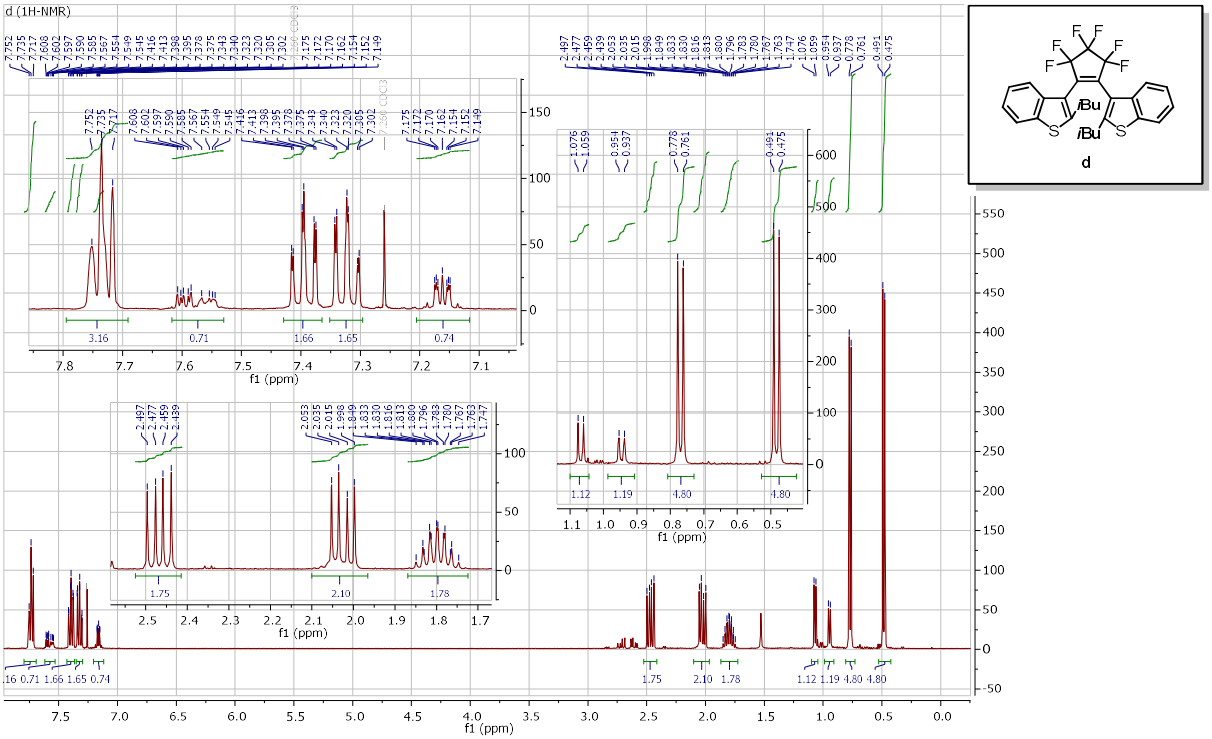


Figure S12a. ^{1}H-NMR (400 MHz) spectrum of **d** in $CDCl_3$

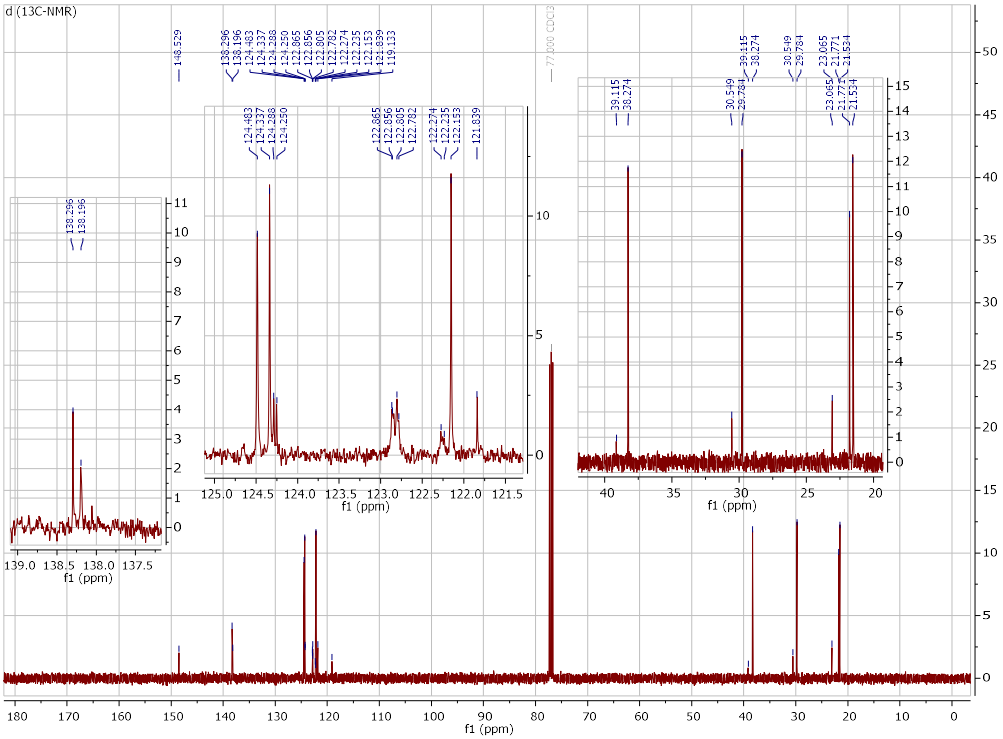


Figure S12b. ^{13}C-NMR (101 MHz) spectrum of **d** in $CDCl_3$

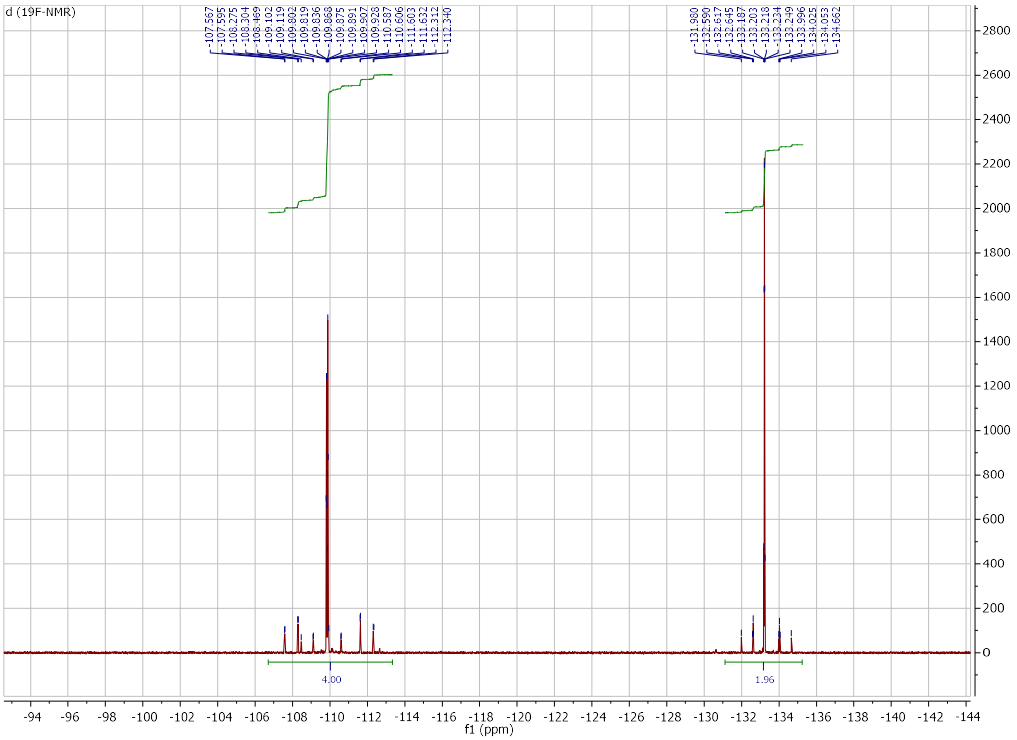


Figure S12c. ^{19}F-NMR (397 MHz) spectrum of **d** in $CDCl_3$

NMR spectra of *i*Bu-Ox-2I

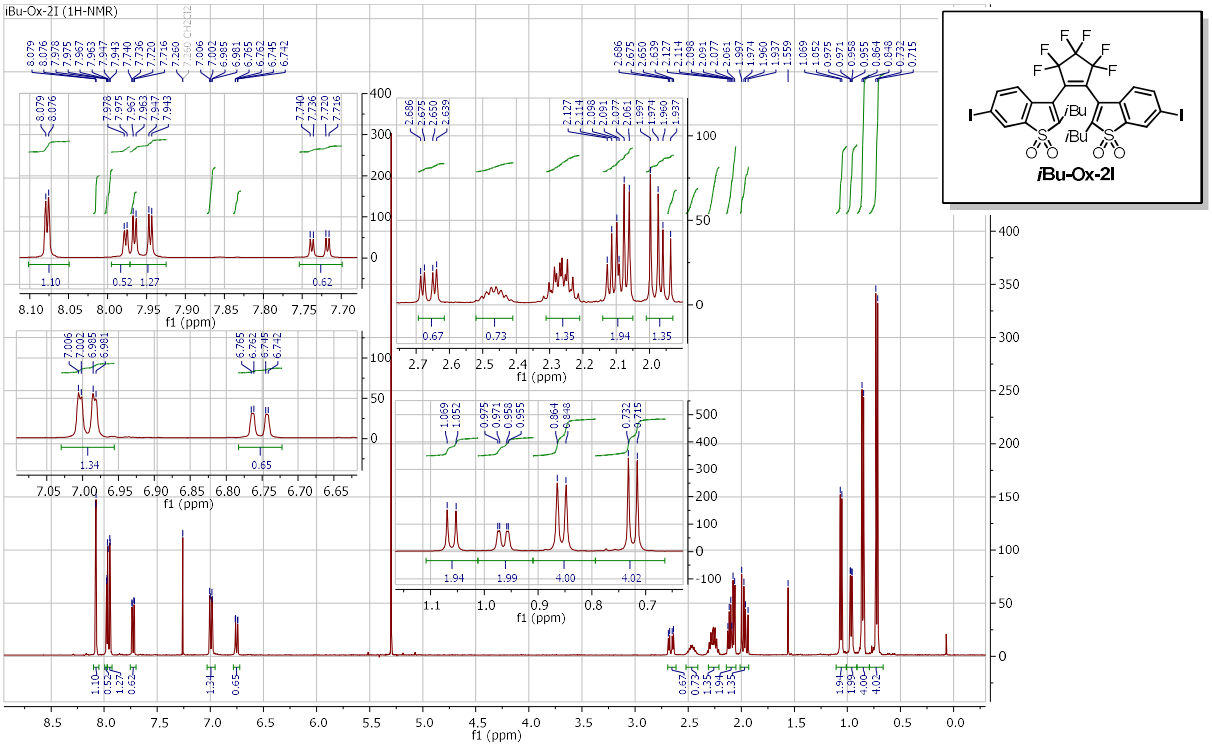


Figure S13a. ^{1}H-NMR (400 MHz) spectrum of ***i*Bu-Ox-2I** in $CDCl_3$

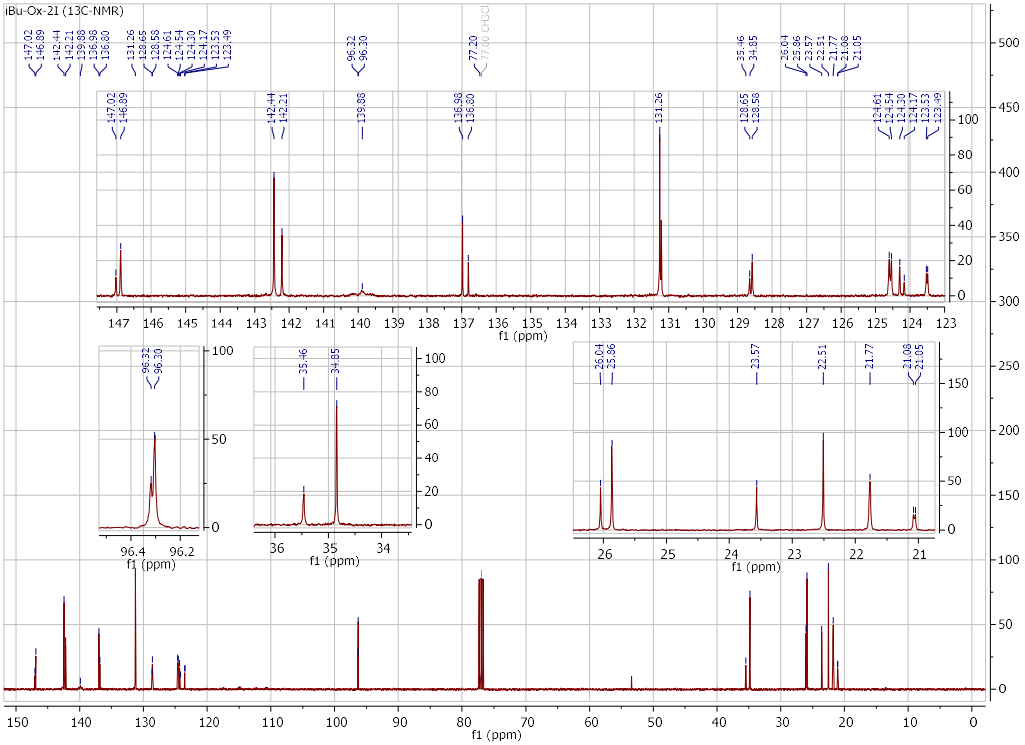


Figure S13b. ^{13}C-NMR (101 MHz) spectrum of ***i*Bu-Ox-2I** in $CDCl_3$

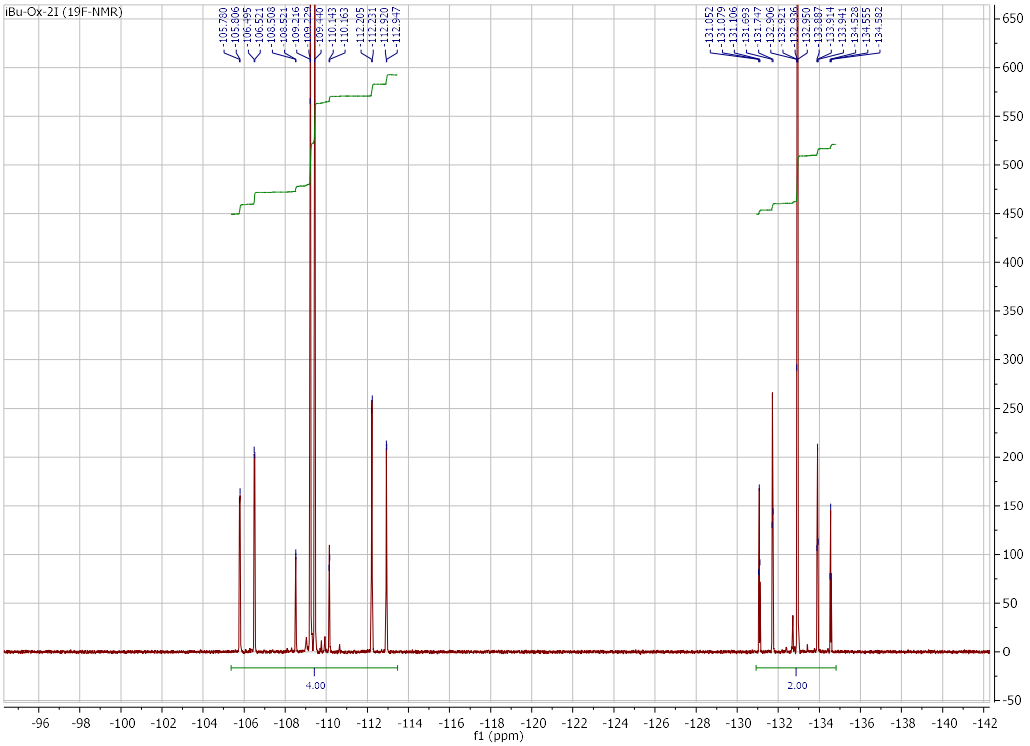


Figure S13c. ^{19}F-NMR (397 MHz) spectrum of ***i*Bu-Ox-2I** in $CDCl_3$

NMR spectra of **6**-Et-H

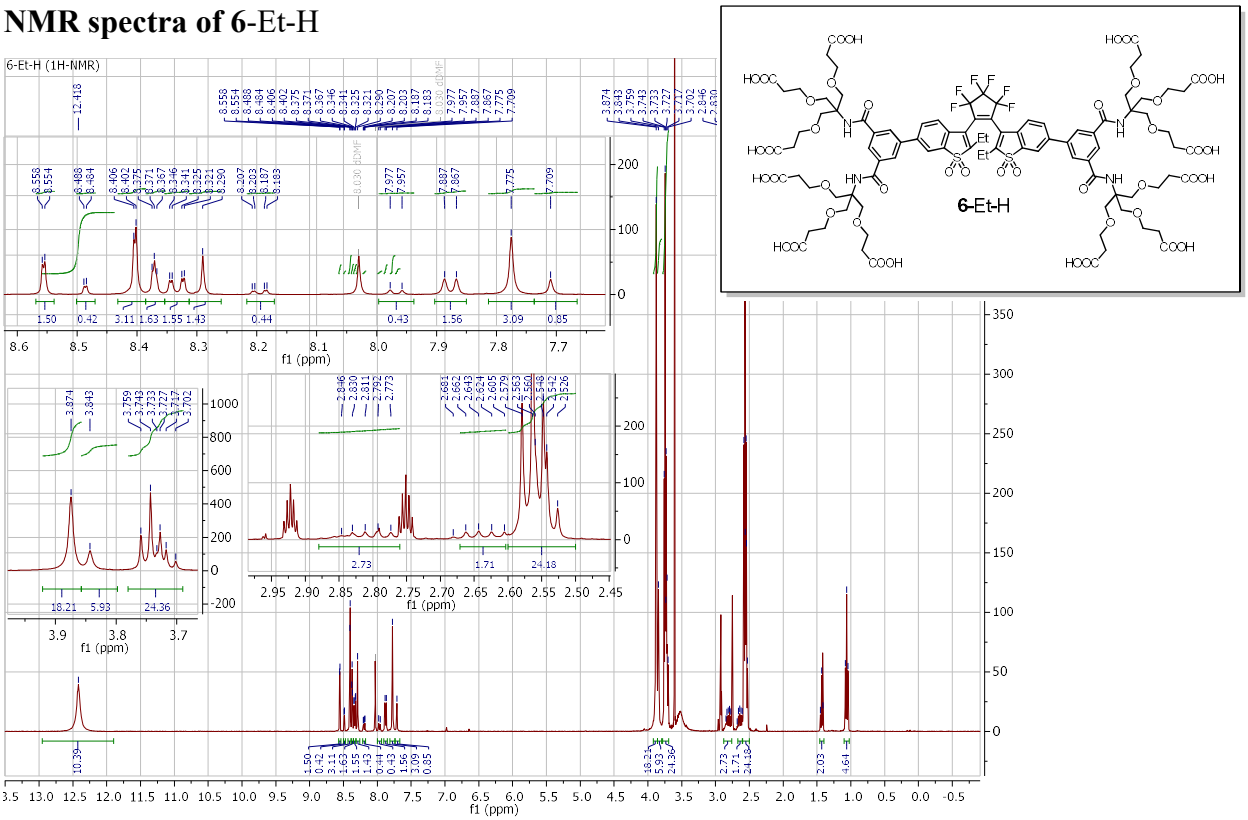


Figure S14a. ^{1}H-NMR (400 MHz) spectrum of **6**-Et-H in [d_7]DMF

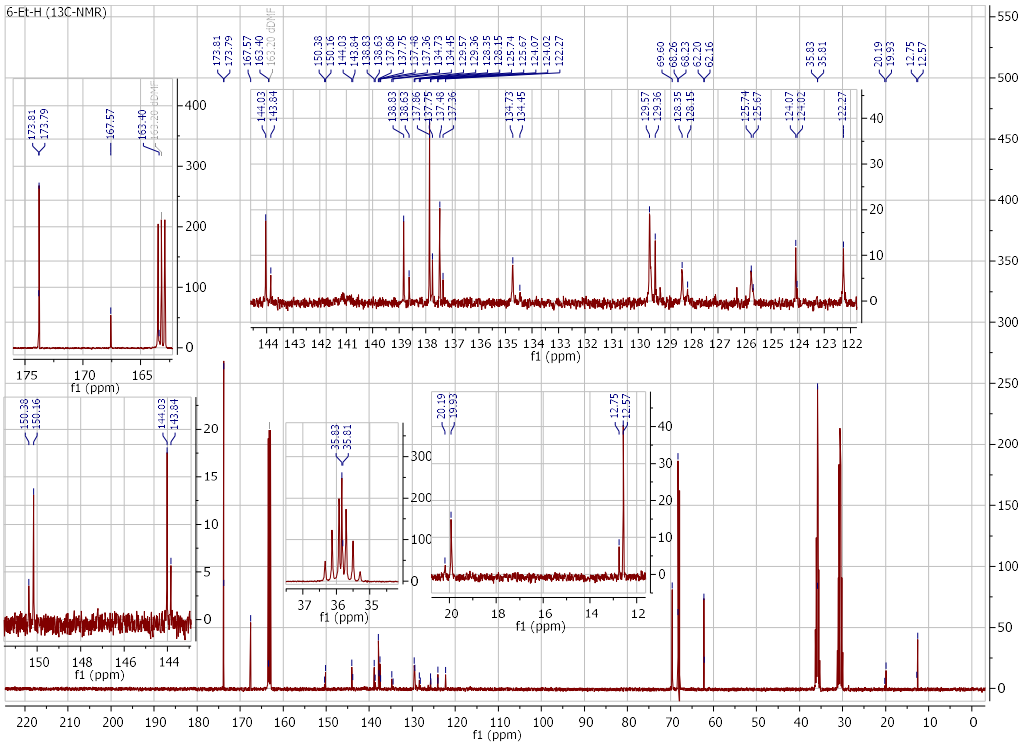


Figure S14b. ^{13}C-NMR (101 MHz) spectrum of **6**-Et-H in [d_7]DMF

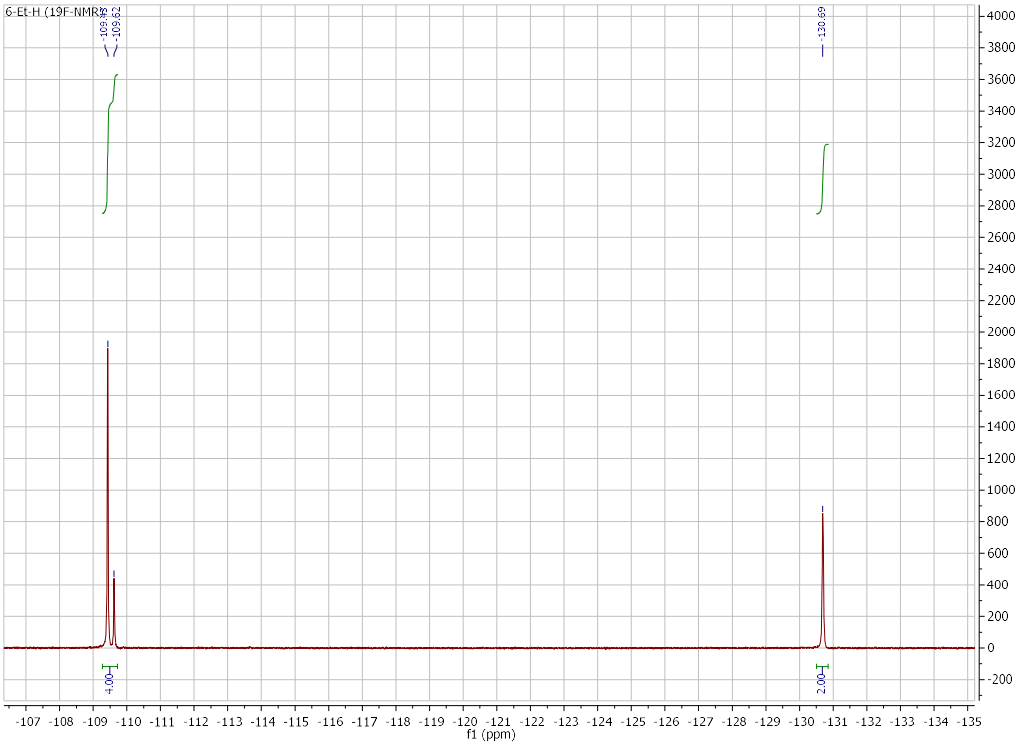


Figure S14c. ^{19}F-NMR (397 MHz) spectrum of **6**-Et-H in [d_7]DMF

NMR spectra of **6**-Et-OMe

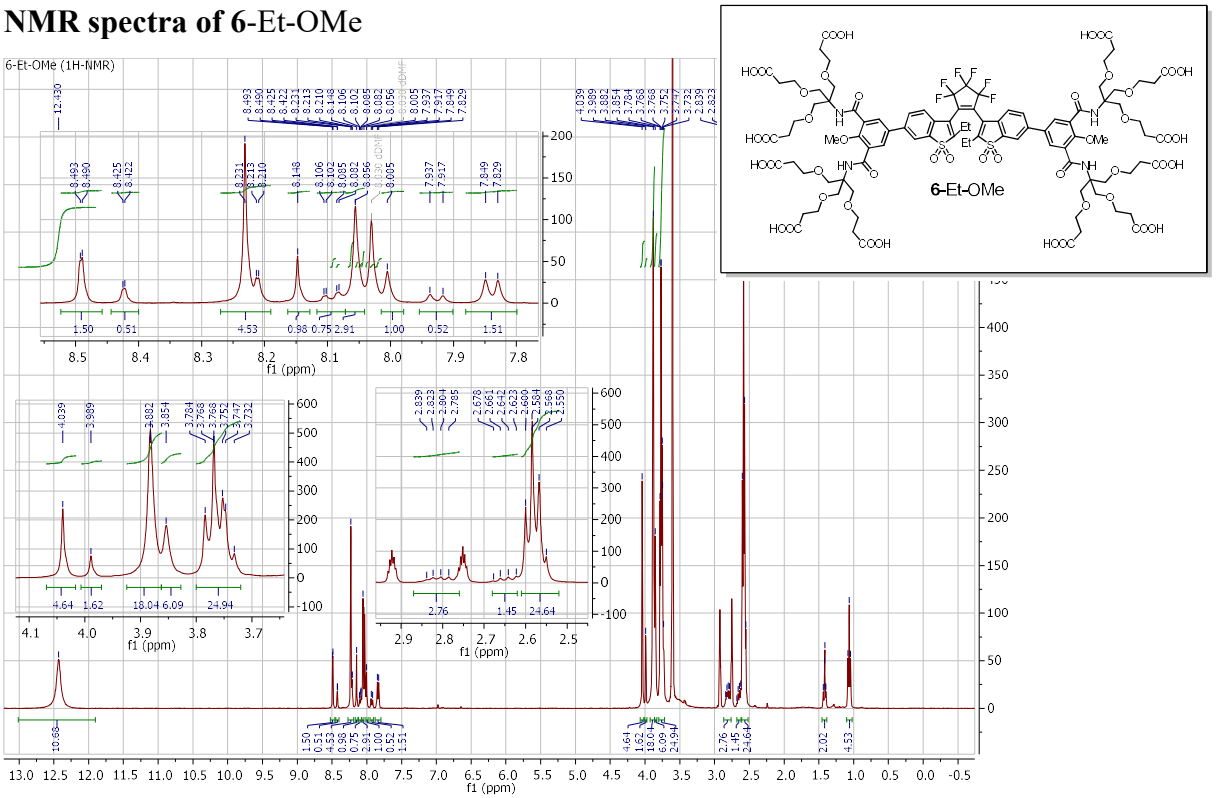


Figure S15a. ^{1}H-NMR (400 MHz) spectrum of **6**-Et-OMe in [d$_7$]DMF

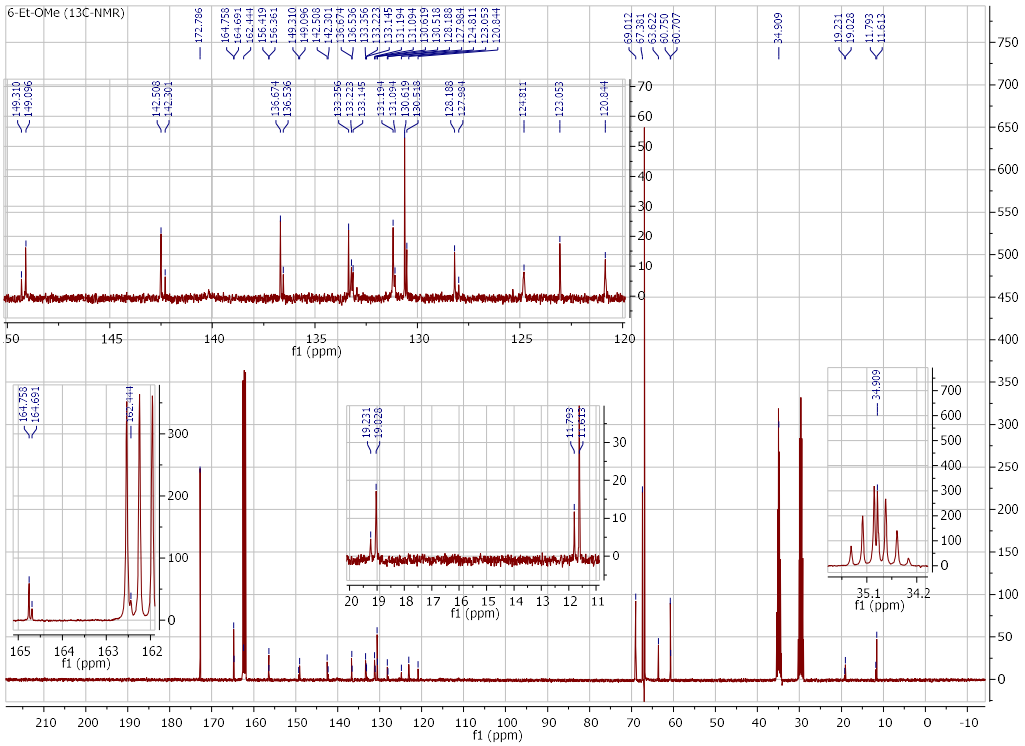


Figure S15b. ^{13}C-NMR (101 MHz) spectrum of **6**-Et-OMe in [d$_7$]DMF

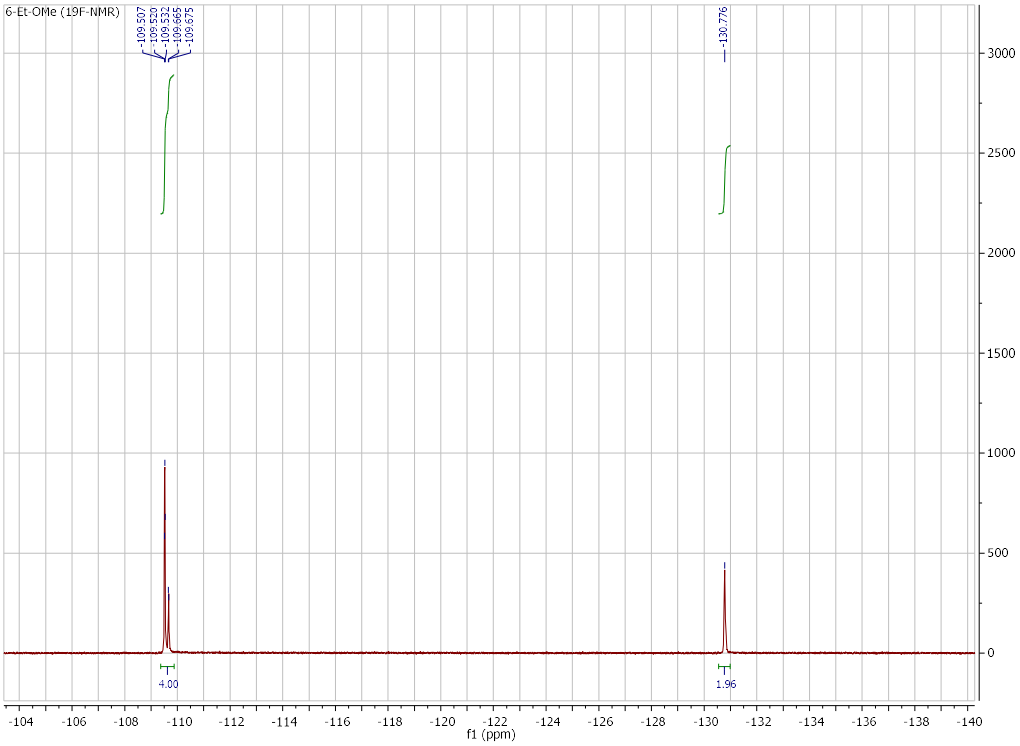


Figure S15c. ^{19}F-NMR (397 MHz) spectrum of **6**-Et-OMe in [d_7]DMF

NMR spectra of 6-*i*Bu-H

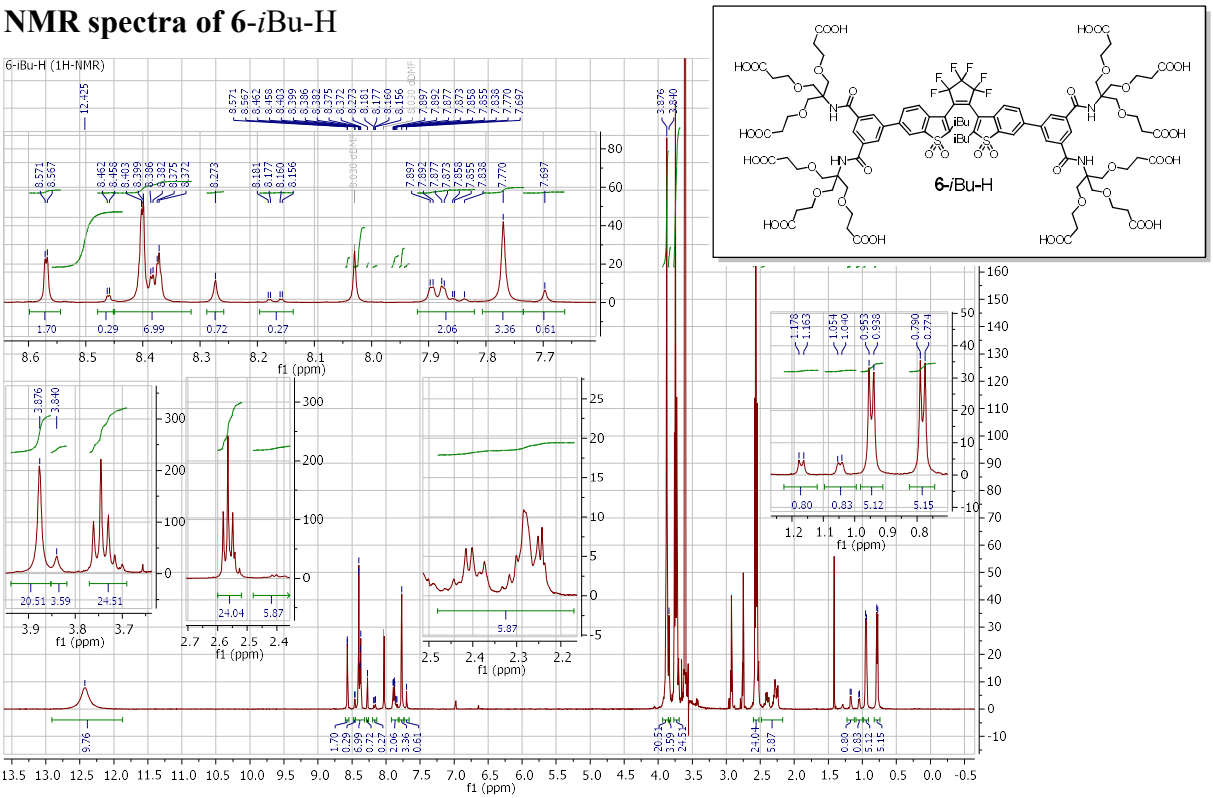


Figure S16a. ^{1}H-NMR (400 MHz) spectrum of **6-*i*Bu-H** in [d_7]DMF

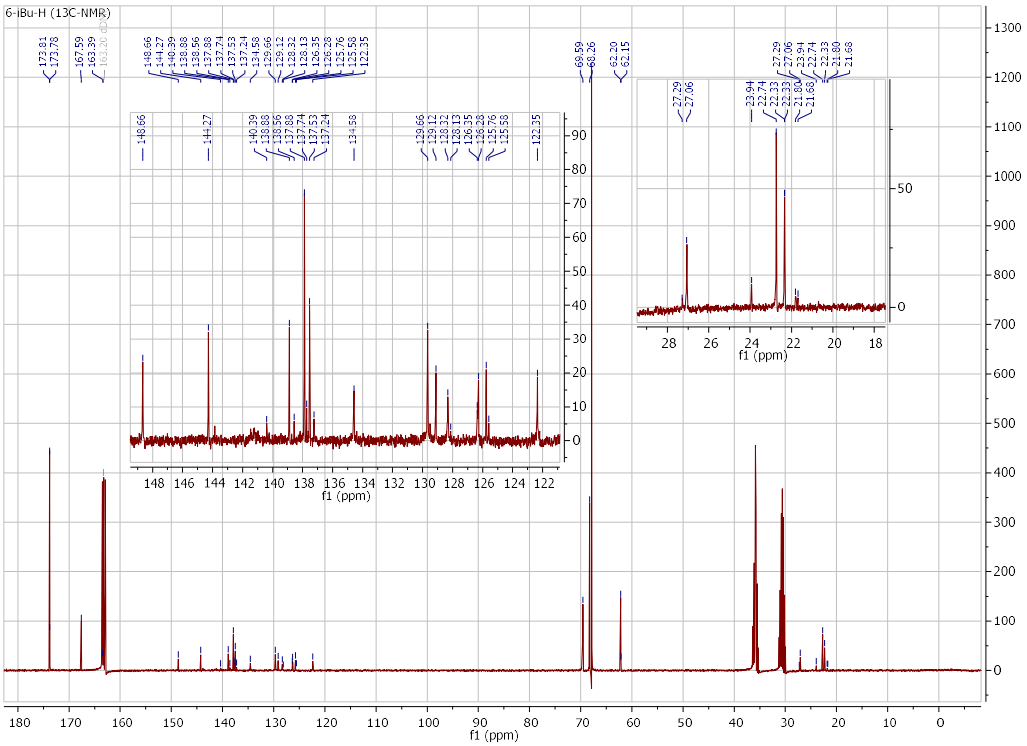


Figure S16b. ^{13}C-NMR (101 MHz) spectrum of **6-*i*Bu-H** in [d_7]DMF

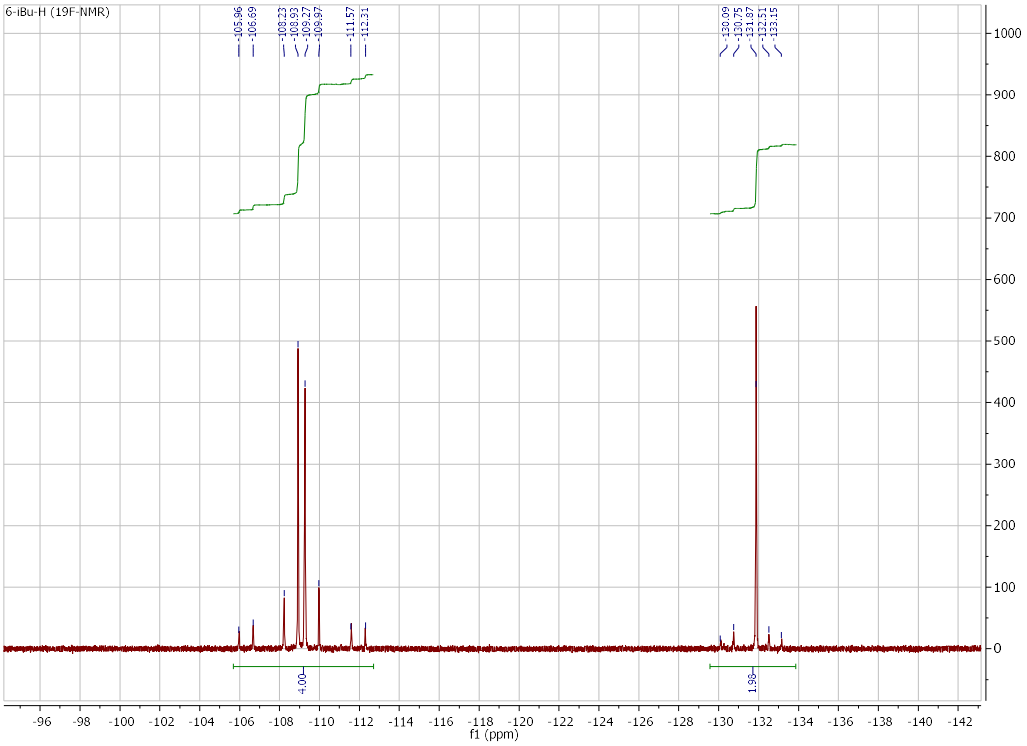


Figure S16c. ^{19}F-NMR (397 MHz) spectrum of **6**-*i*Bu-H in [d_7]DMF

NMR spectra of 6-*i*Bu-OMe

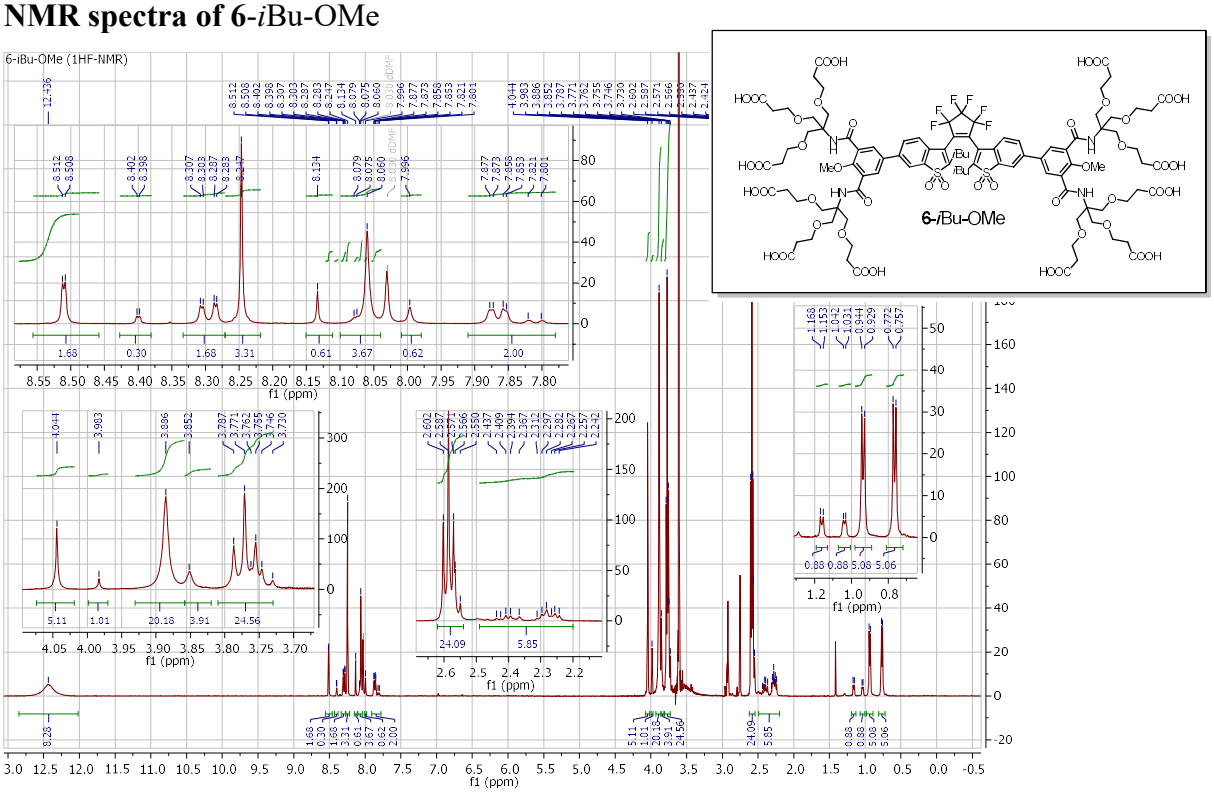


Figure S17a. ^{1}H-NMR (400 MHz) spectrum of **6**-*i*Bu-OMe in [d$_7$]DMF

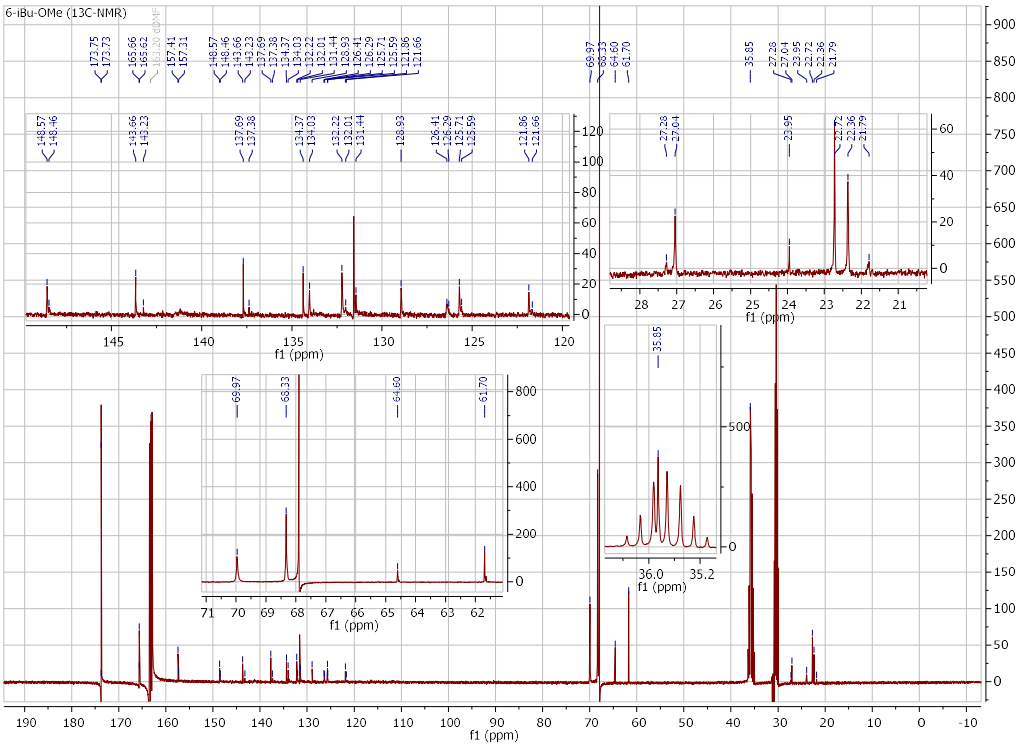


Figure S17b. ^{13}C-NMR (101 MHz) spectrum of **6**-*i*Bu-OMe in [d$_7$]DMF

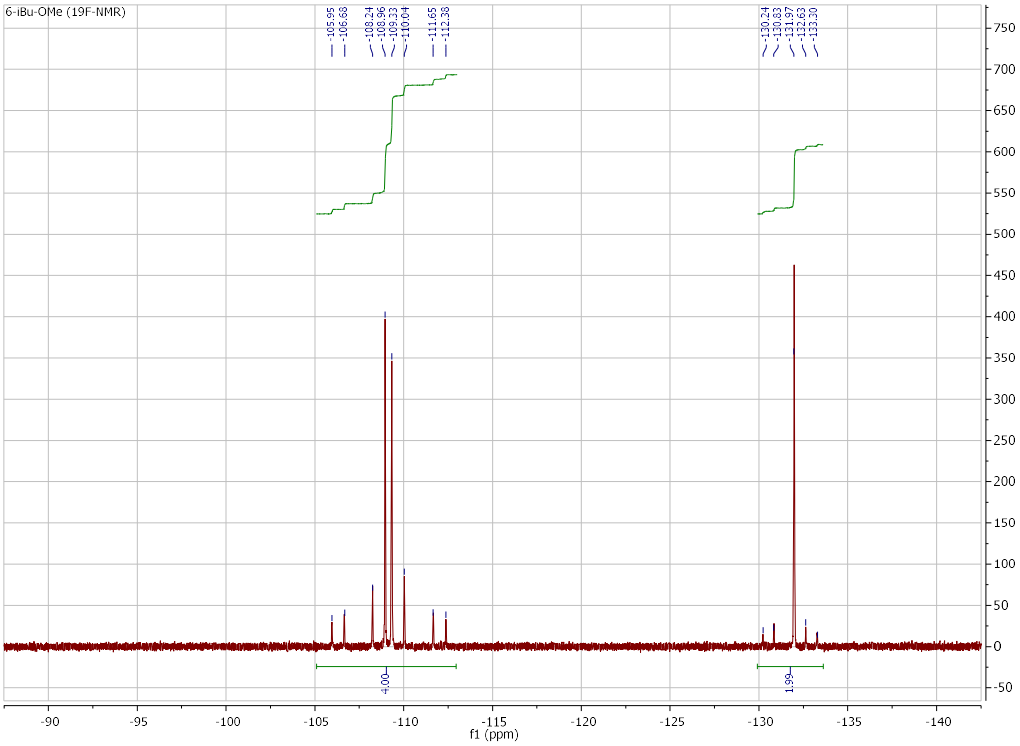


Figure S17c. ^{19}F-NMR (397 MHz) spectrum of **6-*i*Bu-OMe** in [d_7]DMF

NMR spectra of 7-Et-H

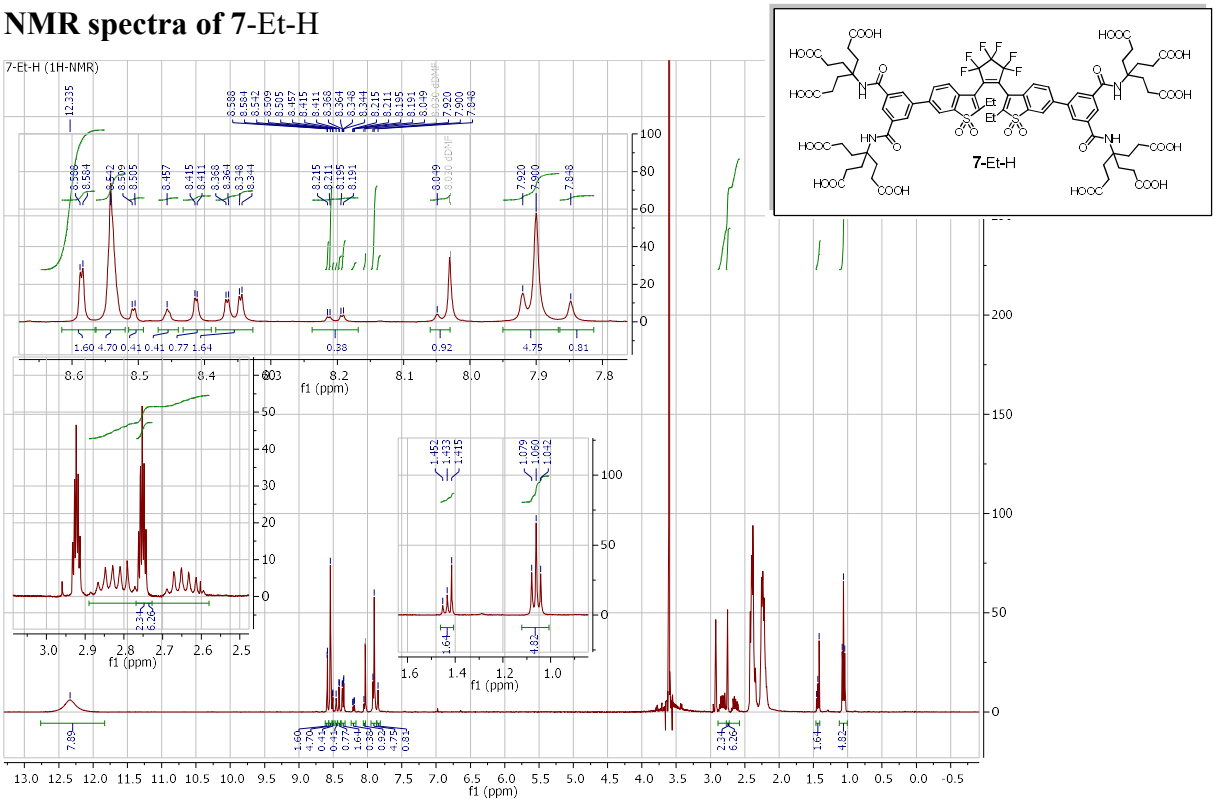


Figure S18a. ^{1}H-NMR (400 MHz) spectrum of **7**-Et-H in [d_7]DMF

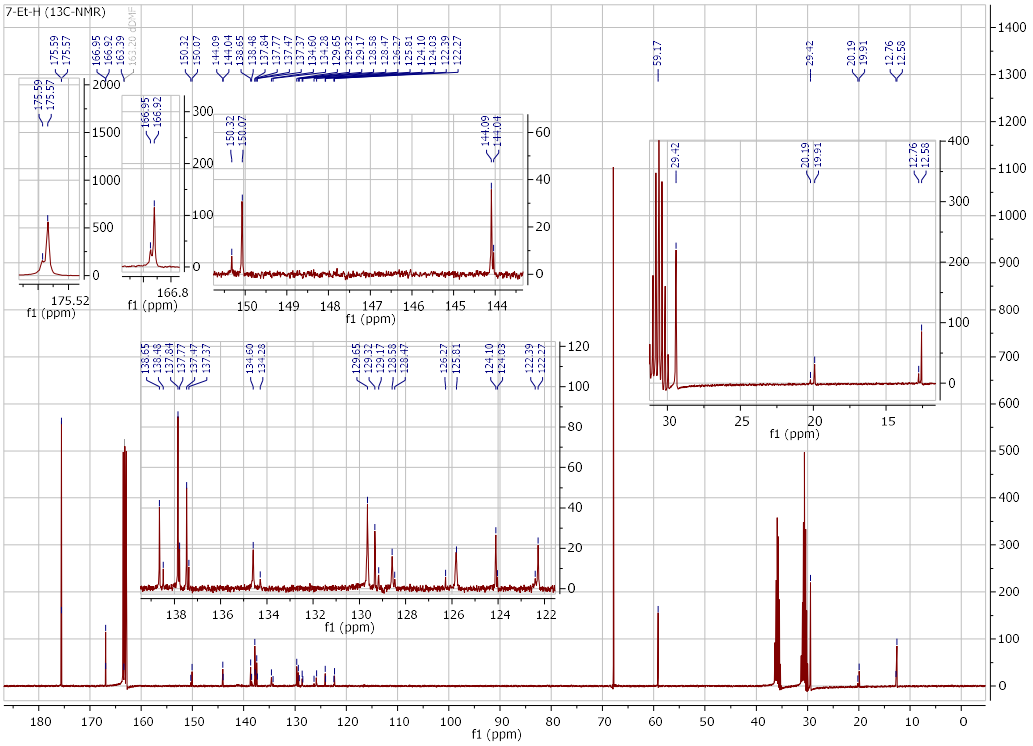


Figure S18b. ^{13}C-NMR (101 MHz) spectrum of **7**-Et-H in [d_7]DMF

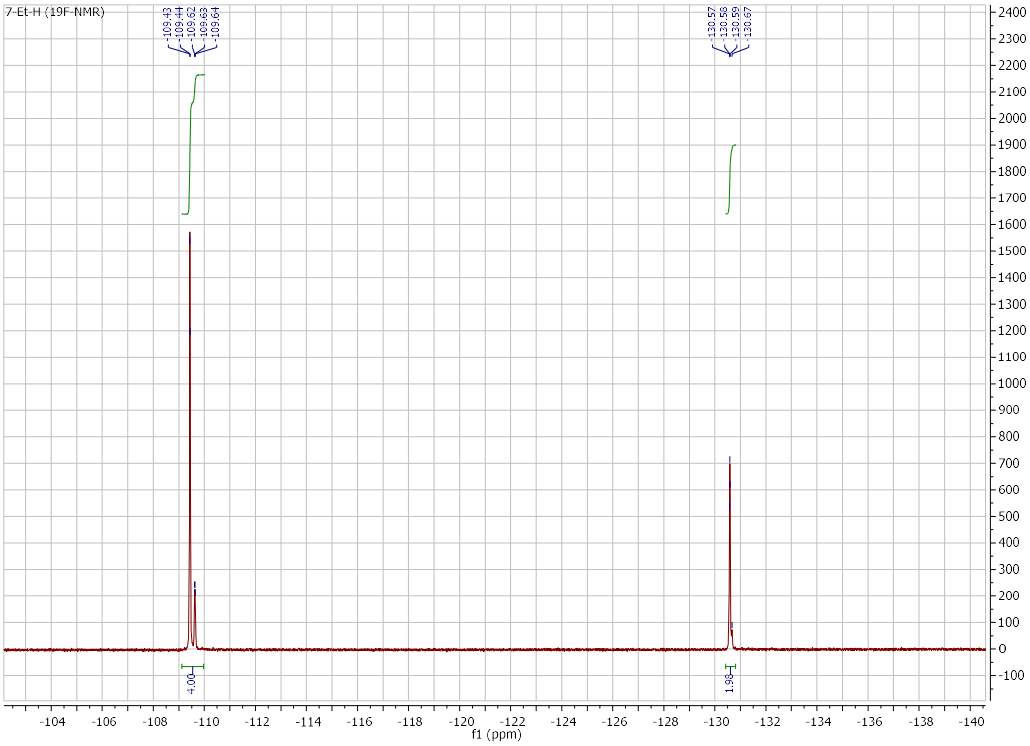


Figure S18c. ^{19}F-NMR (397 MHz) spectrum of **7**-Et-H in [d_7]DMF

NMR spectra of 7-Et-OMe

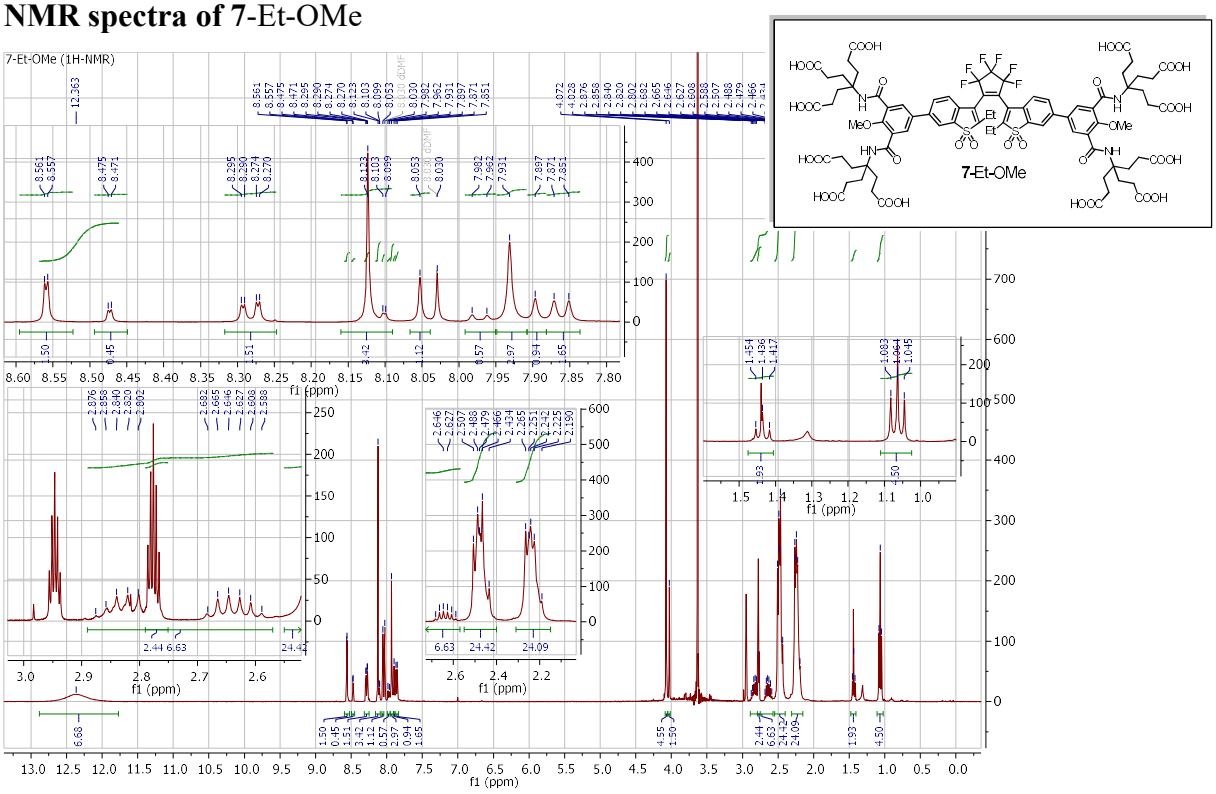


Figure S19a. ^{1}H-NMR (400 MHz) spectrum of **7**-Et-OMe in [d_7]DMF

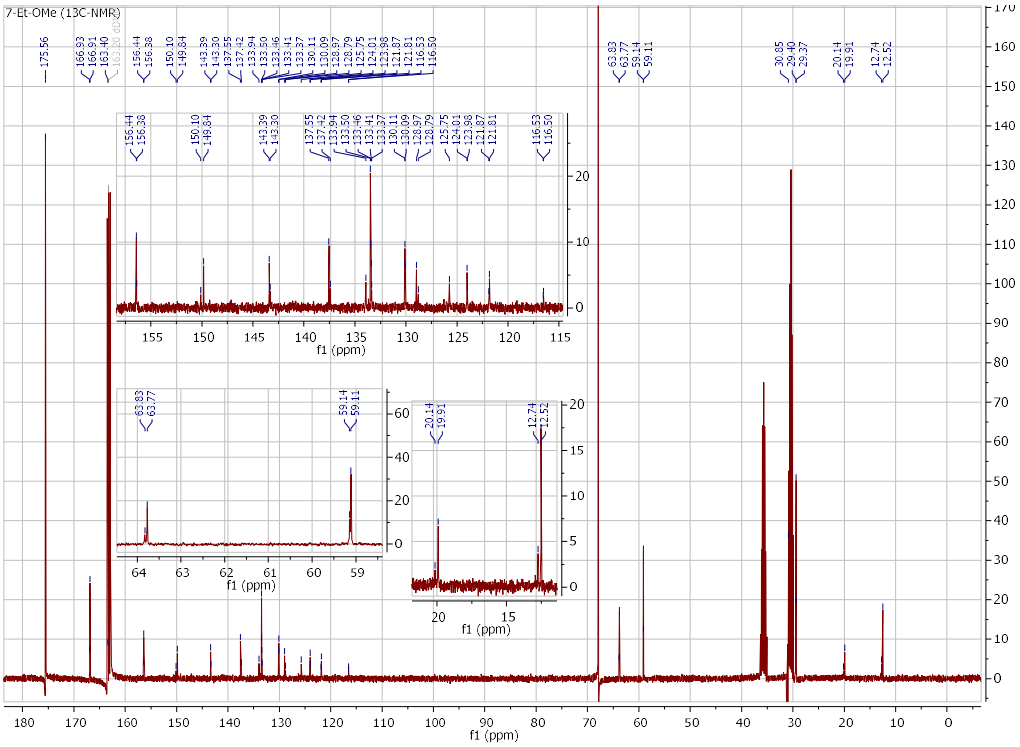


Figure S19b. ^{13}C-NMR (101 MHz) spectrum of **7**-Et-OMe in [d_7]DMF

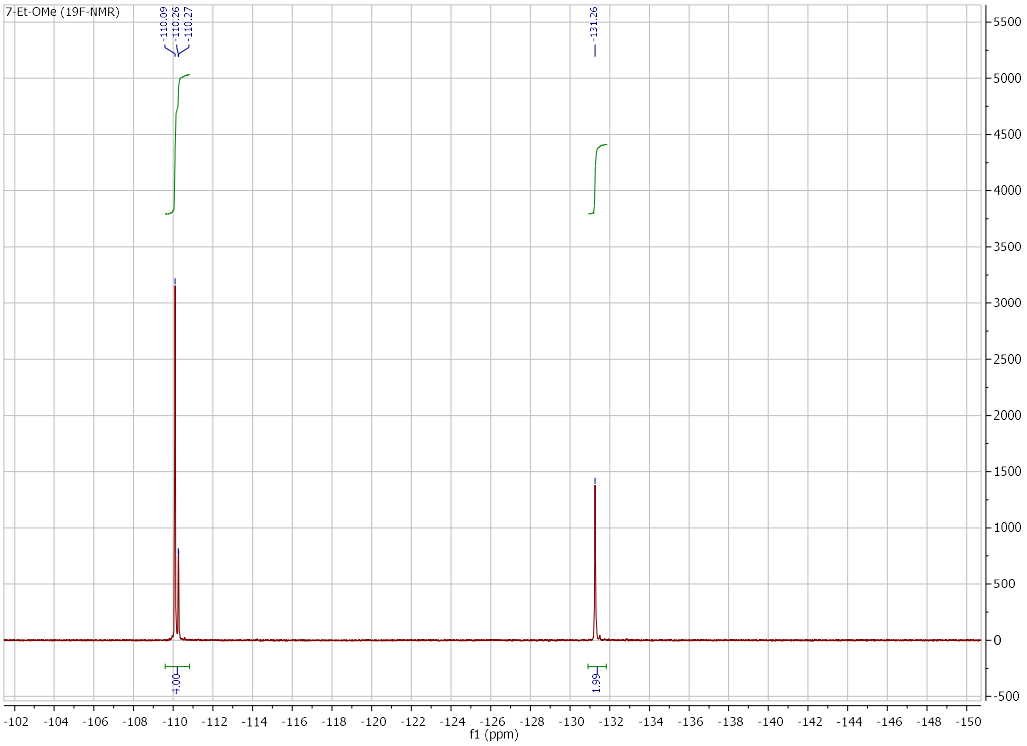


Figure S19c. ^{19}F-NMR (397 MHz) spectrum of **7**-Et-OMe in [d_7]DMF

NMR spectra of 7-*i*Bu-H

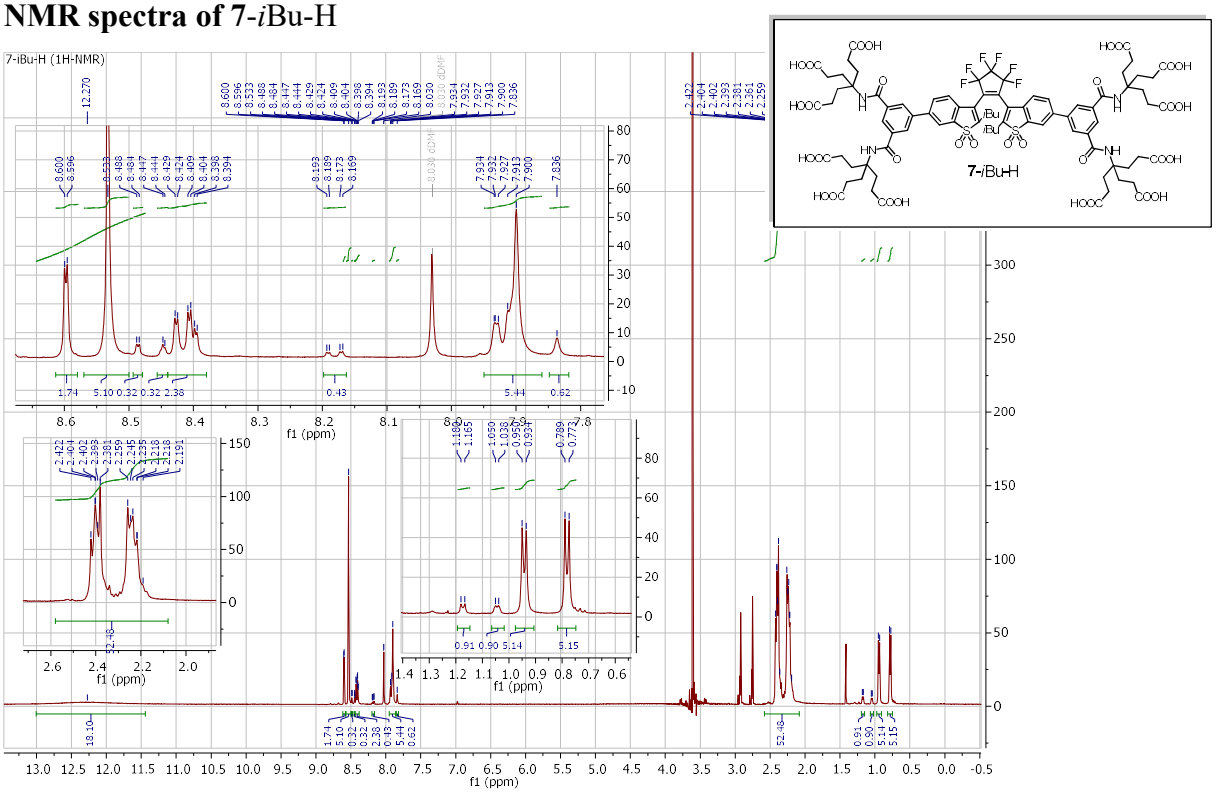


Figure S20a. ^{1}H-NMR (400 MHz) spectrum of **7**-*i*Bu-H in [d_7]DMF

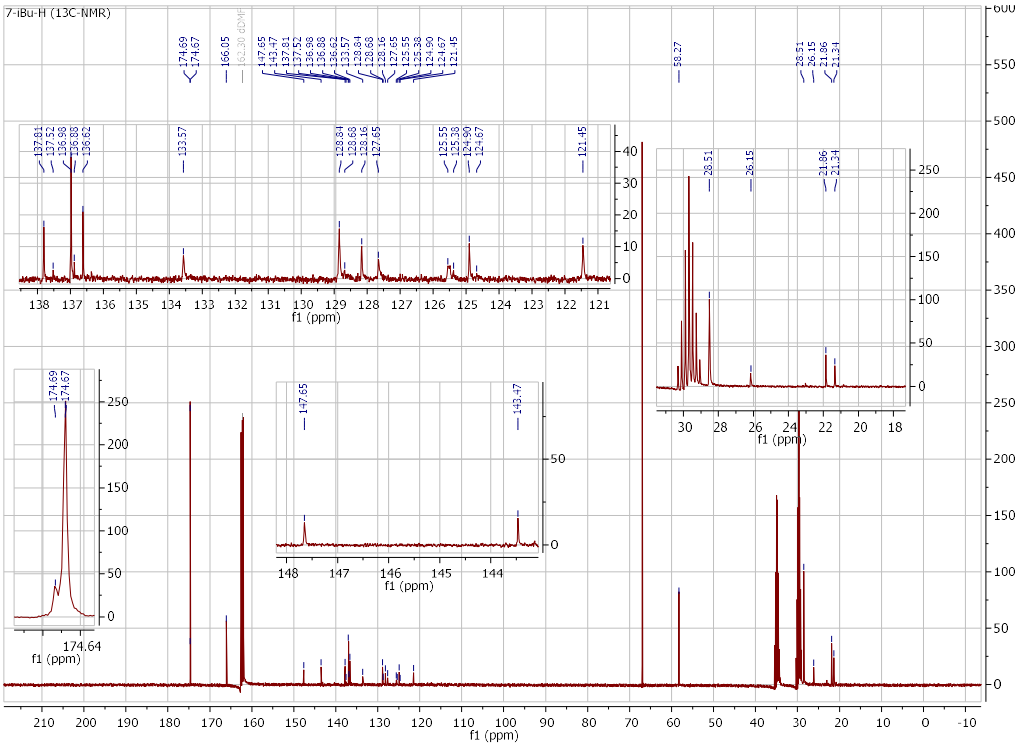


Figure S20b. ^{13}C-NMR (101 MHz) spectrum of **7**-*i*Bu-H in [d_7]DMF

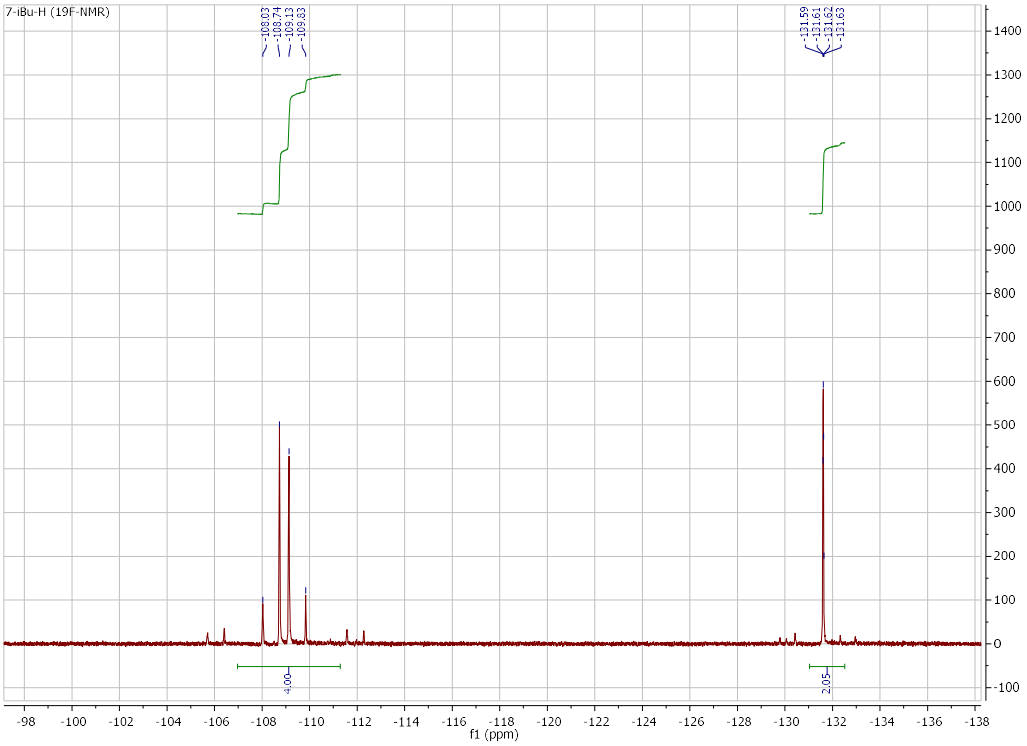


Figure S20c. ^{19}F-NMR (397 MHz) spectrum of **7-*i*Bu-H** in [d_7]DMF

NMR spectra of 7-*i*Bu-OMe

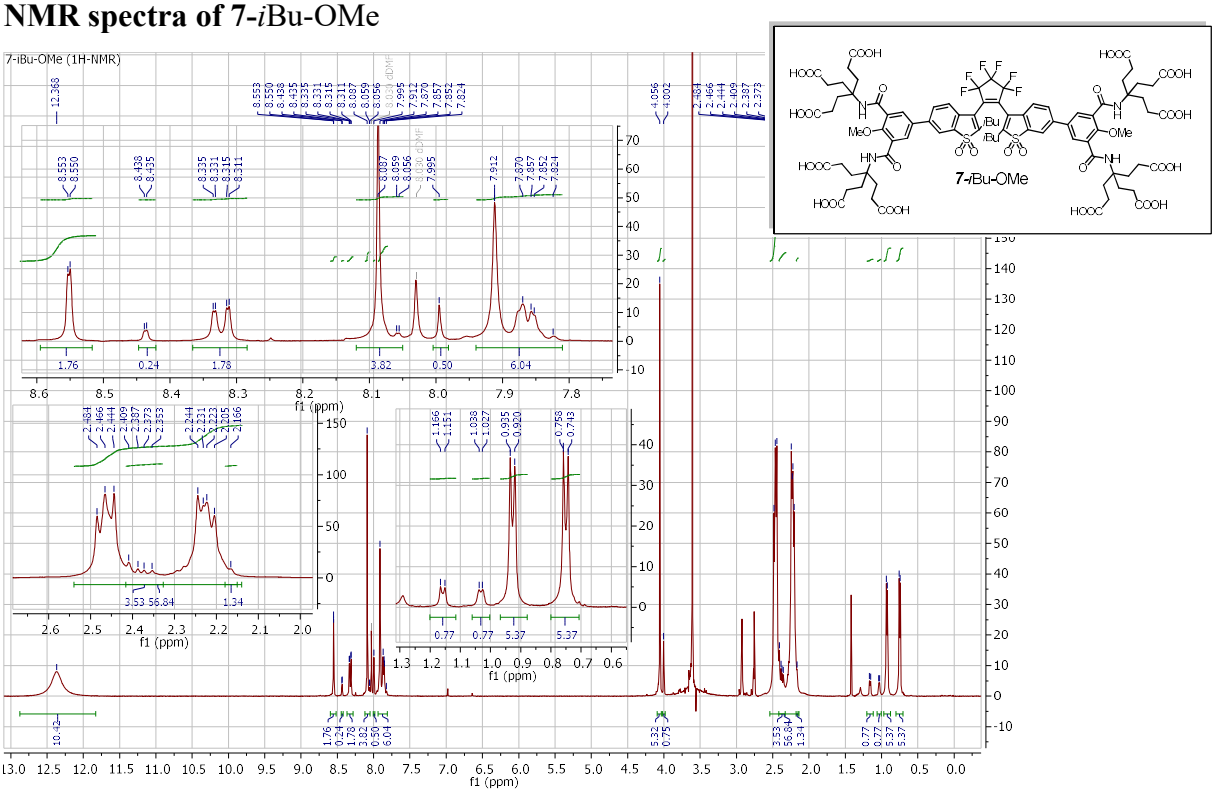


Figure S21a. ^{1}H-NMR (400 MHz) spectrum of **7**-*i*Bu-OMe in [d$_7$]DMF

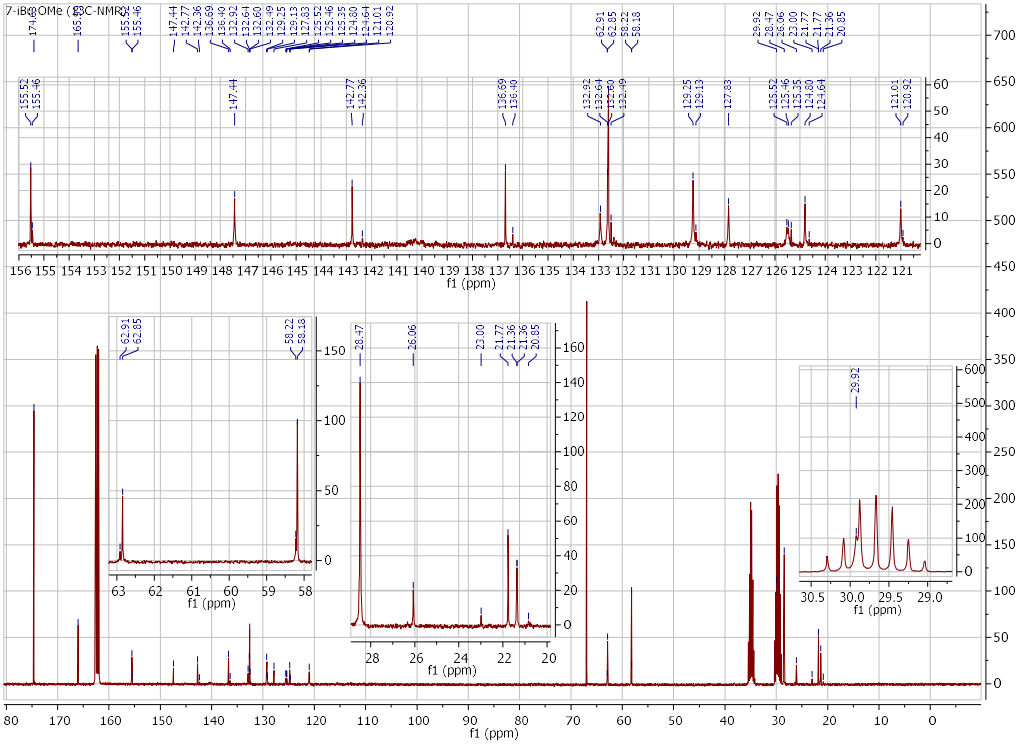


Figure S21b. ^{13}C-NMR (101 MHz) spectrum of **7**-*i*Bu-OMe in [d$_7$]DMF

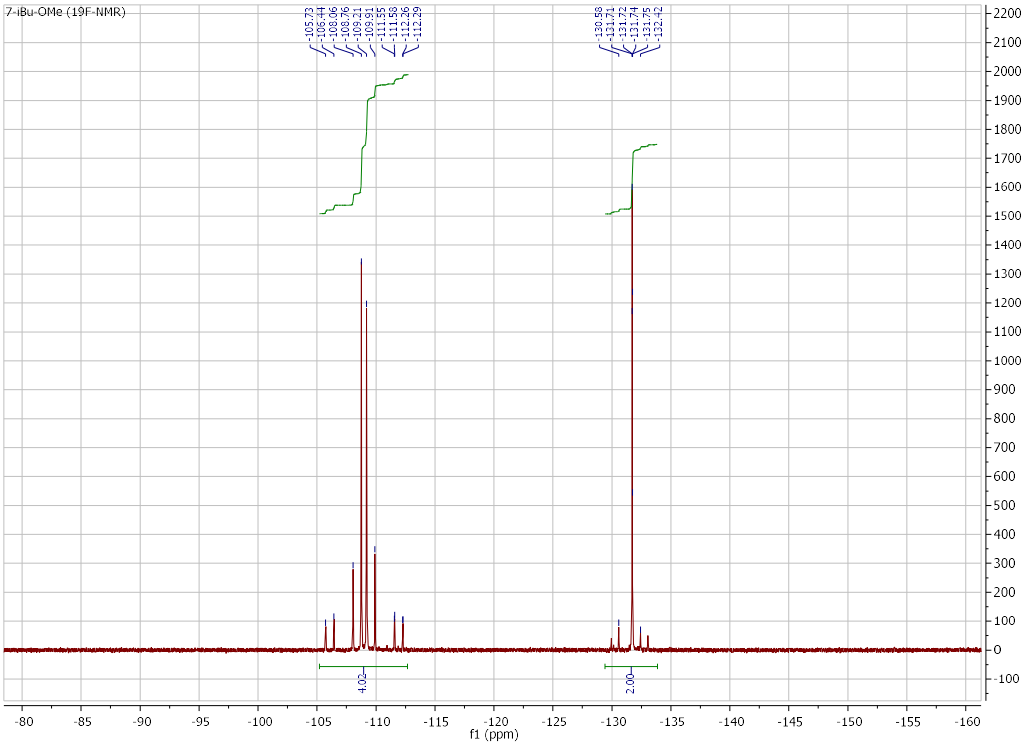


Figure S21c. ^{19}F-NMR (397 MHz) spectrum of **7**-*i*Bu-OMe in [d$_7$]DMF

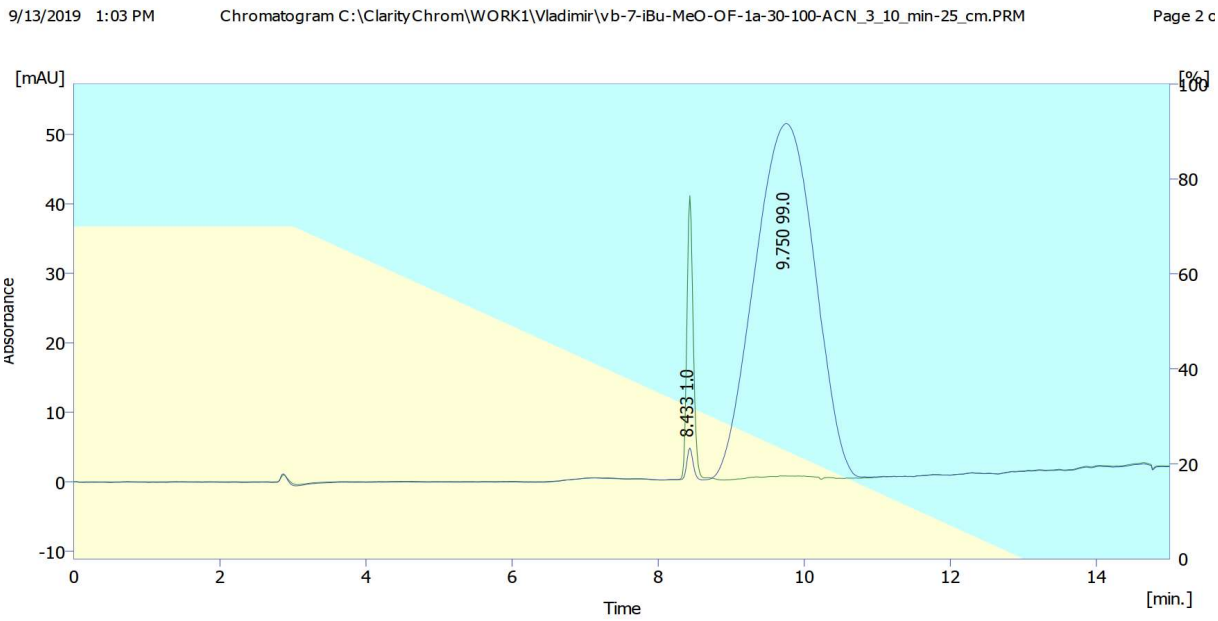


Figure S21d. HPLC trace of the open-ring isomer of **7**-*i*Bu-OMe. Blue curve: detection at 370 nm (isosbestic point); green curve: detection at 465 nm (closed-ring isomer).

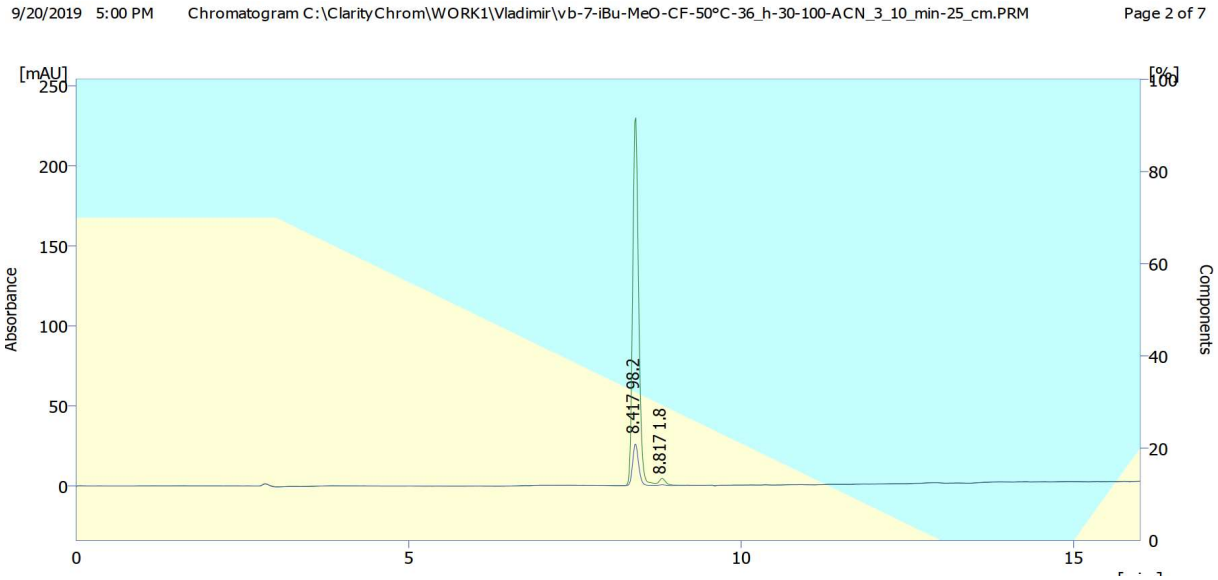


Figure S21e. HPLC trace of the closed-ring isomer of **7**-*i*Bu-OMe *after heating at 50 °C in aqueous acetonitrile for 36 h*. Blue curve: detection at 370 nm (isosbestic point); green curve: detection at 465 nm (closed-ring isomer).

PHOTOSWITCHING AND PHOTODECOMPOSITION

Photoswitching conditions

Irradiation experiments were performed in a home-made setup described previously.[6] It contained two high power light emitting diodes (LED; Thorlabs, M365L2 and M470L3) as irradiation sources, and a fiber-coupled diode array spectrometer (Ocean Optics, Flame-S UV-Vis configuration). For absorption measurements, a fiber-coupled halogen/deuterium light source (Ocean Optics, DH-2000-BAL) was used at 180 degrees. The sample was placed into a quartz cuvette for fluorescence (Hellma Analytics, 119F-10-40), in a peltier-based temperature-controlled cuvette holder, with four optical ports and magnetic stirring (Quantum Northwestern, Luma 40). A set of lenses and circular apertures was used to ensure the irradiation beams are collimated and have a diameter of around 6 mm at the sample. The collimation of the optical fibers at the sample holder was achieved by the use of dedicated achromatic lenses (Ocean Optics, 74-UV).

Absorption and emission of the sample were probed after each irradiation step, with the shutters of the irradiation sources closed. For fluorescence excitation, the irradiation source (470 nm) was switched on for ca. 10 microseconds. This pulse is much shorter than irradiation times (they are on the order of seconds). It was confirmed for all compounds that the excitation dose did not produce an observable change in the state of the photochromic system. Solutions in acetonitrile or aqueous buffer (concentrations 1-5 μM) were applied for switching experiments and calculations of the isomerization quantum yields. For irradiation experiments combined with HPLC measurements (i.e. distribution of photoproducts and calculation of the conversion degree in the PSS), higher concentrations of up to 15 μM were used in acetonitrile.

Photodecomposition experiments

Compounds **1a** (Figure S22), **1b** (Figures S23, S27-S29), **1c** (Figures S25, S30), **6**-Et-H (Figure S24), and **6**-Et-OMe (Figure S26) were switched 20 full on/off cycles in MeCN (~10 μM). Solutions were irradiated with 365 nm and 470 nm light, until the photostationary states (PSS) were reached. An aliquot was analysed by HPLC at the first PPS (365 nm). After 20 cycles, the sample was irradiated again to the PSS (365 nm), and an aliquot was analysed by HPLC. For compounds **1b** and **1c**, multiple peaks were observed already in the first PSS (365 nm). To identify the CF of the starting compound, a duplicate (fresh) sample was irradiated, until 40%

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

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conversion was observed ([CF]/C_0 ≈ 0,5) and analysed by HPLC. In both cases, only one peak (of the closed form) was observed at the indicated retention time (orange arrows in Figures S23 and S25). (LC)MS measurements and the optical spectra (diode array detection) confirm that the photoproduct is indeed the CF of the starting compound. The absorption and emission of the photoproducts formed from compounds **1b** and **1c** are very similar to the spectra of the initial DAEs **1b** and **1c**. This observation is confirmed by comparison of the absorption and emission spectra of compound **1b** recorded in the first and the last cycle of 20 cycles in PSS (365 nm) (Figures S23 and S27). Practically no difference can be observed, though initially one peak of the CF of compound **1b** had been present, and after 20 cycles a mixture of compounds with the spectra undistinguishable from the spectra of the initial CF has been formed (Figures S23C and S23F, respectively; Figure 27). HPLC and LC-MS traces were recorded for the photoconverted DAE **1b** in the closed form (Figures S28-S29). They show relatively well resolved peaks with increasing retention times (lower polarity) and the mass-difference of 30 Da (for M+H): 1349 (starting material) - 1319 - 1289 - 1259 – (1230).

In the case of compound **1c** (Figure S30), a small blue shift of the absorption and emission maxima is observed. Probably, only one (minor) photoproduct features a blue shift.

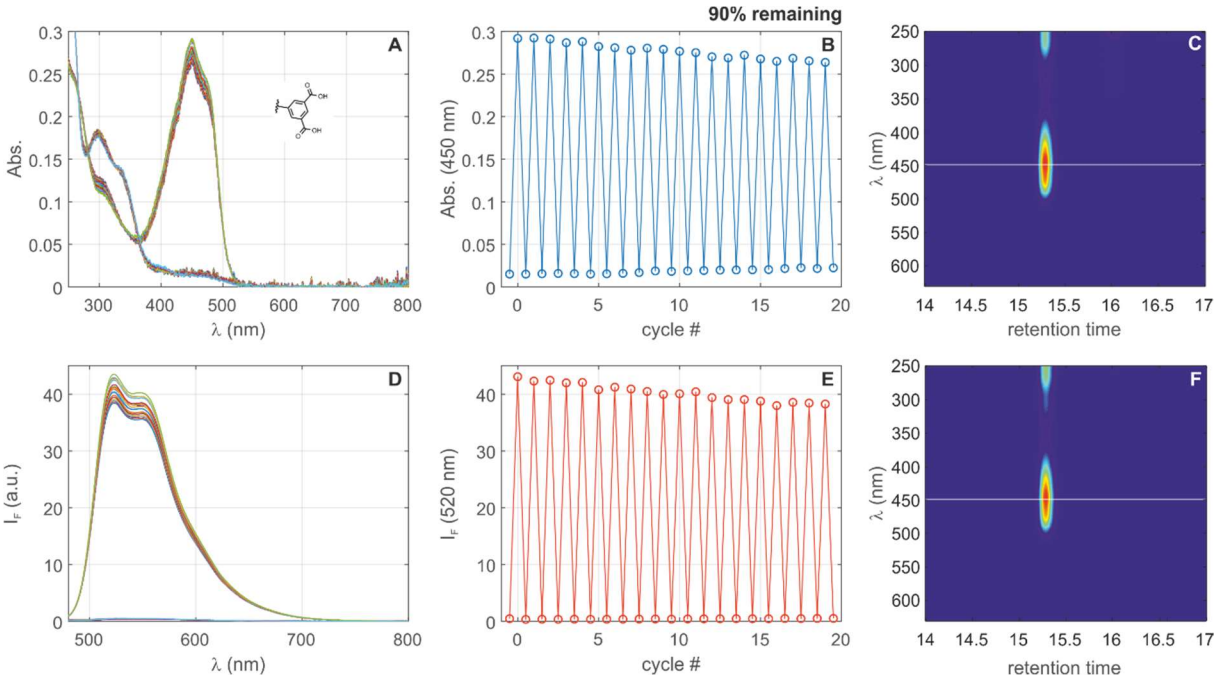


Figure S22. Photoswitching of compound **1a** in MeCN. Absorption (A) and emission (D) spectra; absoprtion (B) and emission (E) at the corresponding maxima of the CF; HPLC 2D-maps of a selected area at the first PSS-365 nm (C) and after 20 cycles (F).

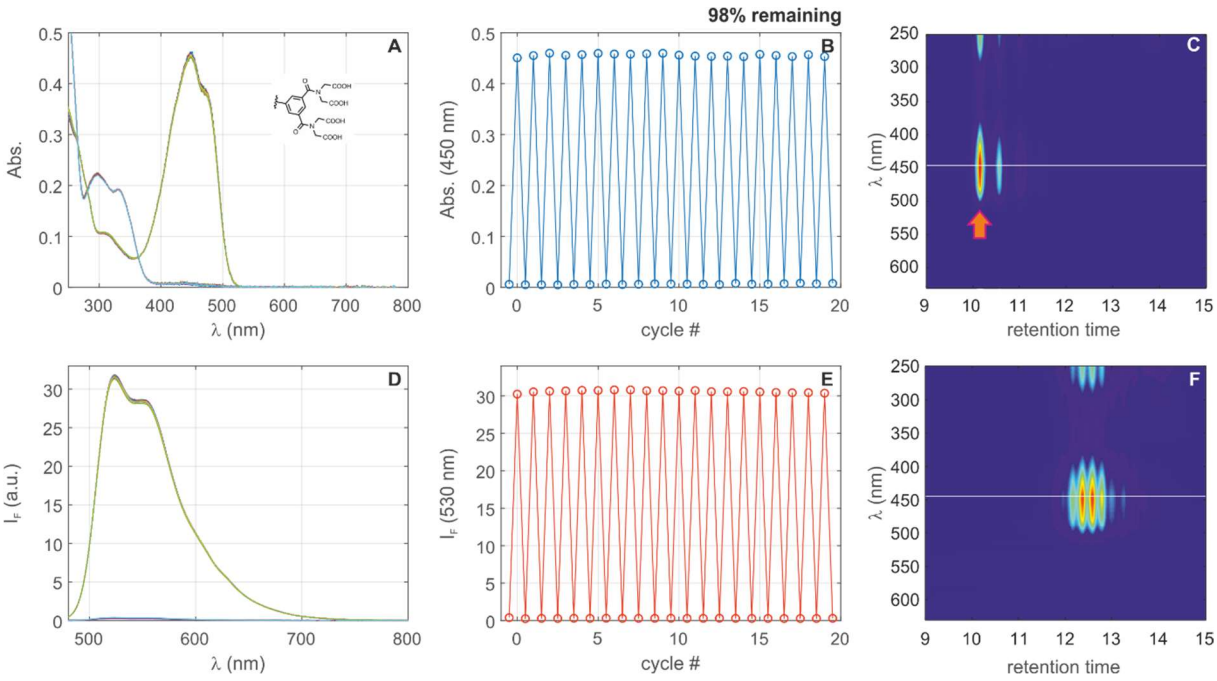


Figure S23. Photoswitching of compound **1b** in MeCN. Absorption (A) and emission (D) spectra; absoprtion (B) and emission (E) at the corresponding maximum of the CF; HPLC 2D-maps of a selected area at the first PSS-365 nm (C) and after 20 cycles (F). The orange arrow in (C) indicates the retention time of the initial CF.

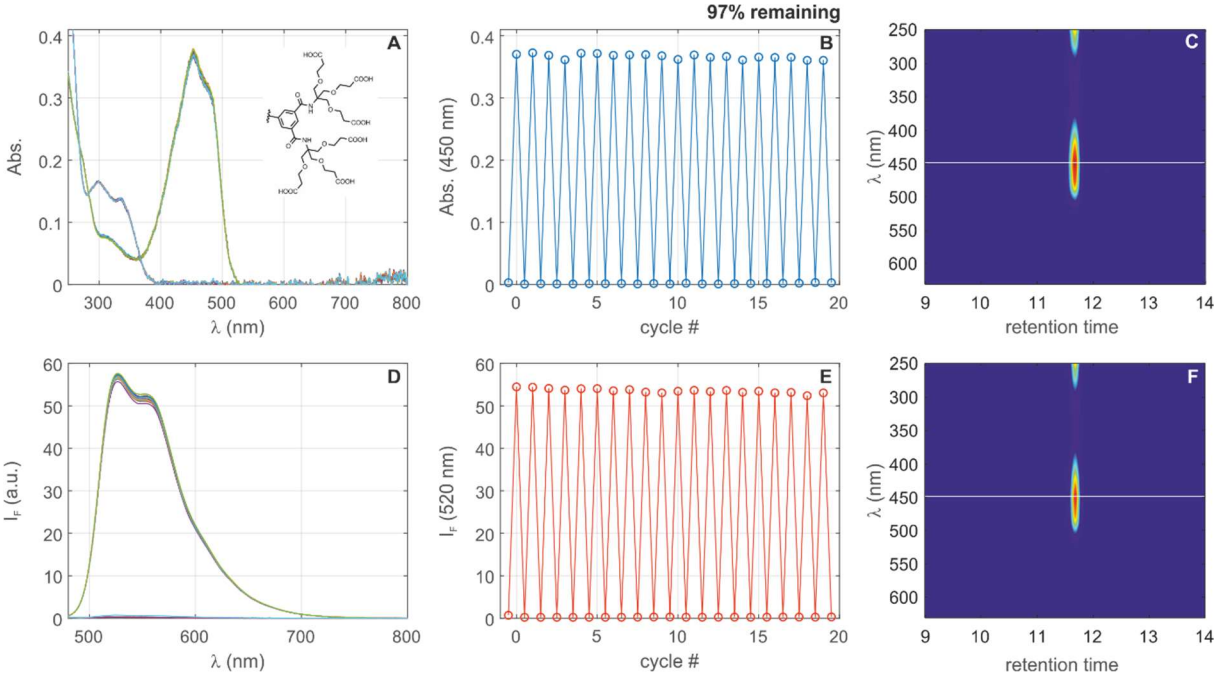


Figure S24. Photoswitching of compound **6**-Et-H in MeCN. Absorption (A) and emission (D) spectra; absoprtion (B) and emission (E) at the corresponding maxima of the CF; HPLC 2D-maps of a selected area at the first PSS-365nm (C) and after 20 cycles (F). The orange arrow in (C) indicates the retention time of the initial CF.

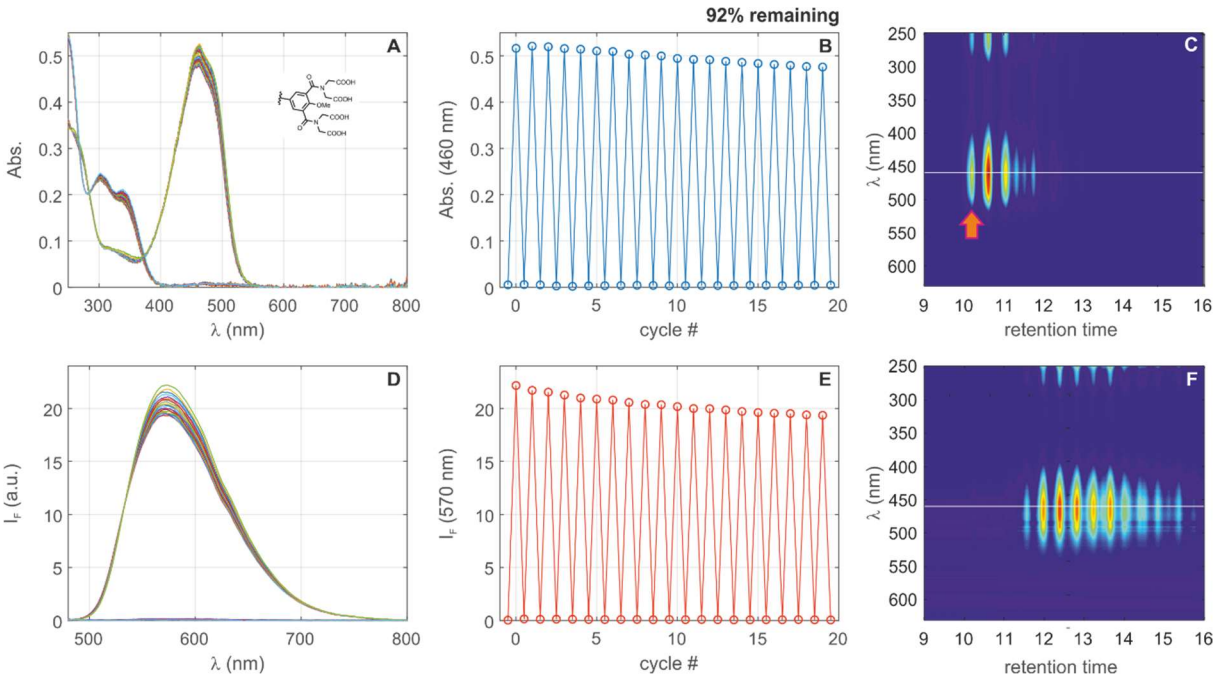


Figure S25. Photoswitching of compound **1c** in MeCN. Absorption (A) and emission (D) spectra; absoprtion (C) and emission (E) at the corresponding maxima of the CF; HPLC 2D-maps of a selected area at the first PSS-365 nm (C) and after 20 cycles (F). The orange arrow in (C) indicates the retention time of the initial CF.

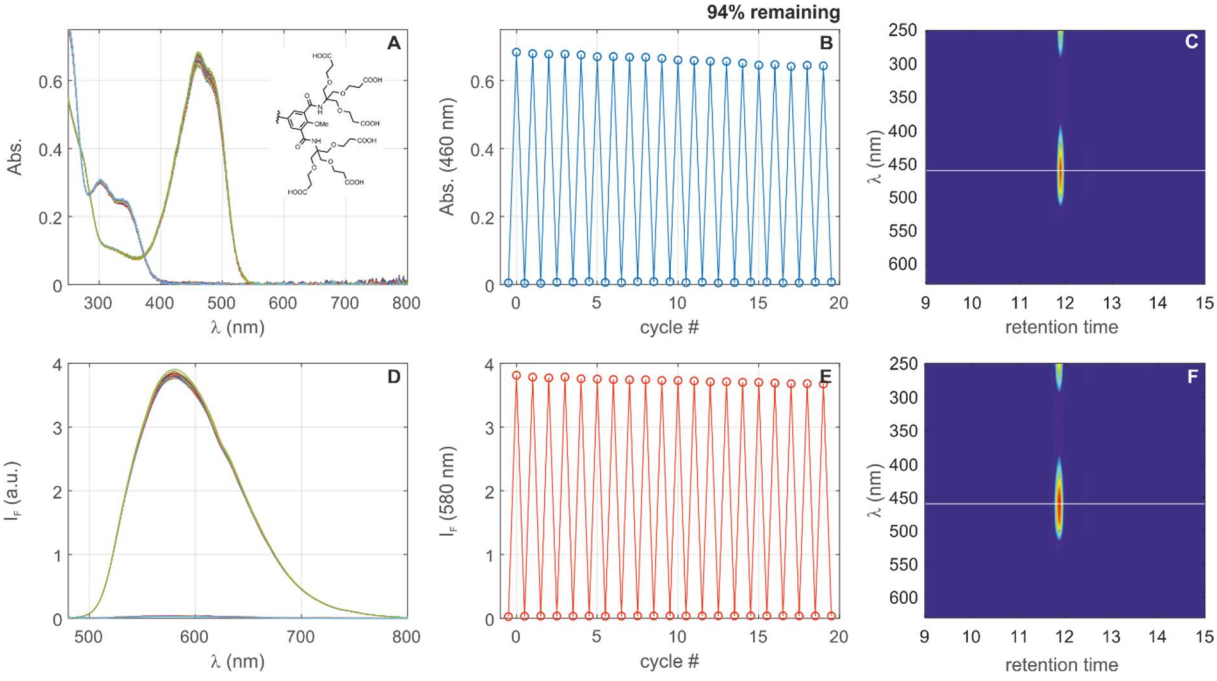


Figure S26. Photoswitching of compound **6**-Et-OMe in MeCN. Absorption (A) and emission (D) spectra; Absoprtion (B) and emission (E) at the corresponding maxima of the CF; HPLC 2D-maps of a selected area at the first PSS-365 nm (C) and after 20 cycles (F).

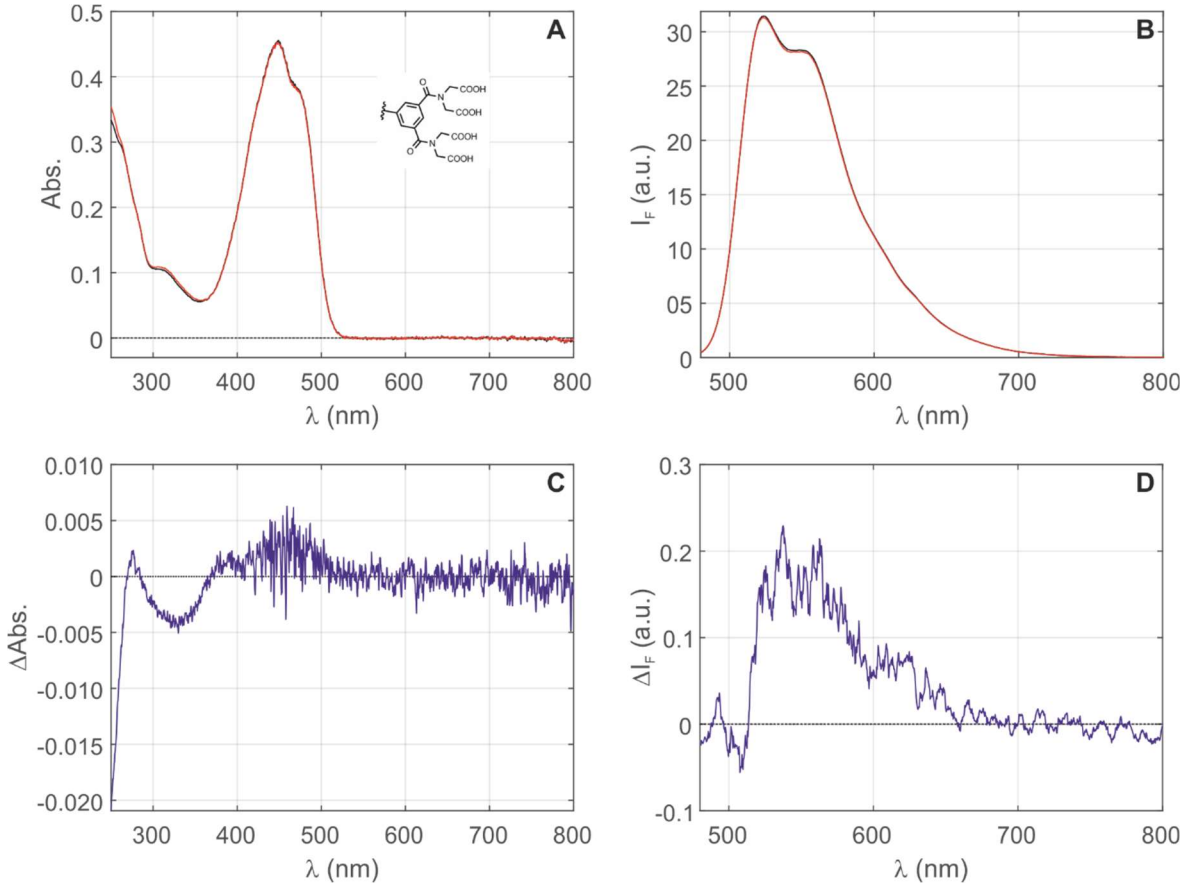


Figure S27. Absorption (A) and emission (B) spectra of compound **1b** in MeCN at the first PSS-365 nm (black lines) and after 20 cycles (red lines). The corresponding differences are plotted in (C) and (D).

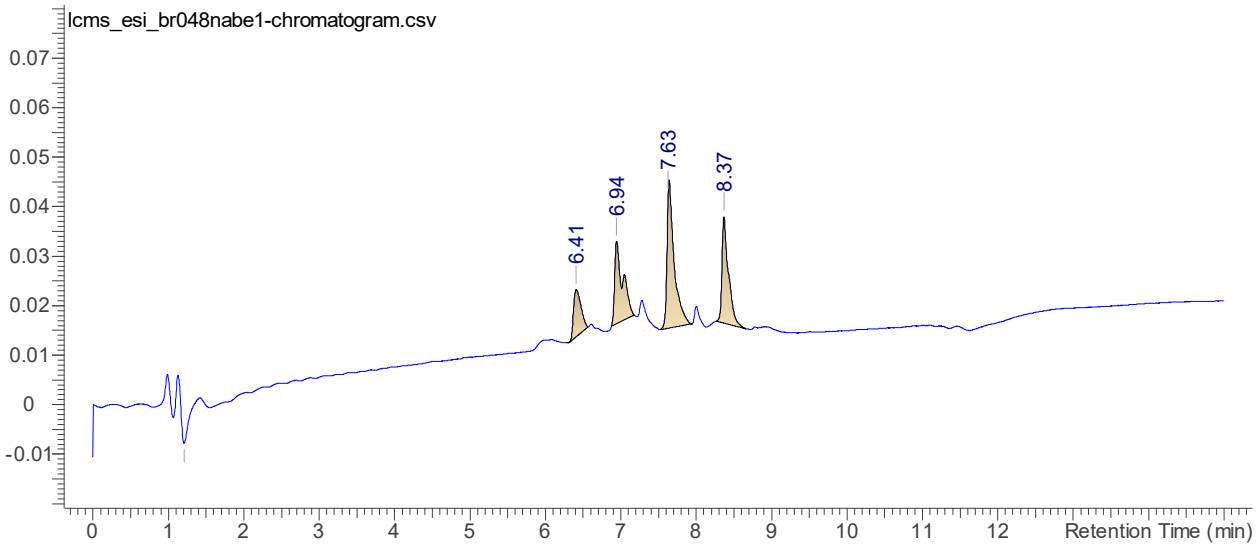
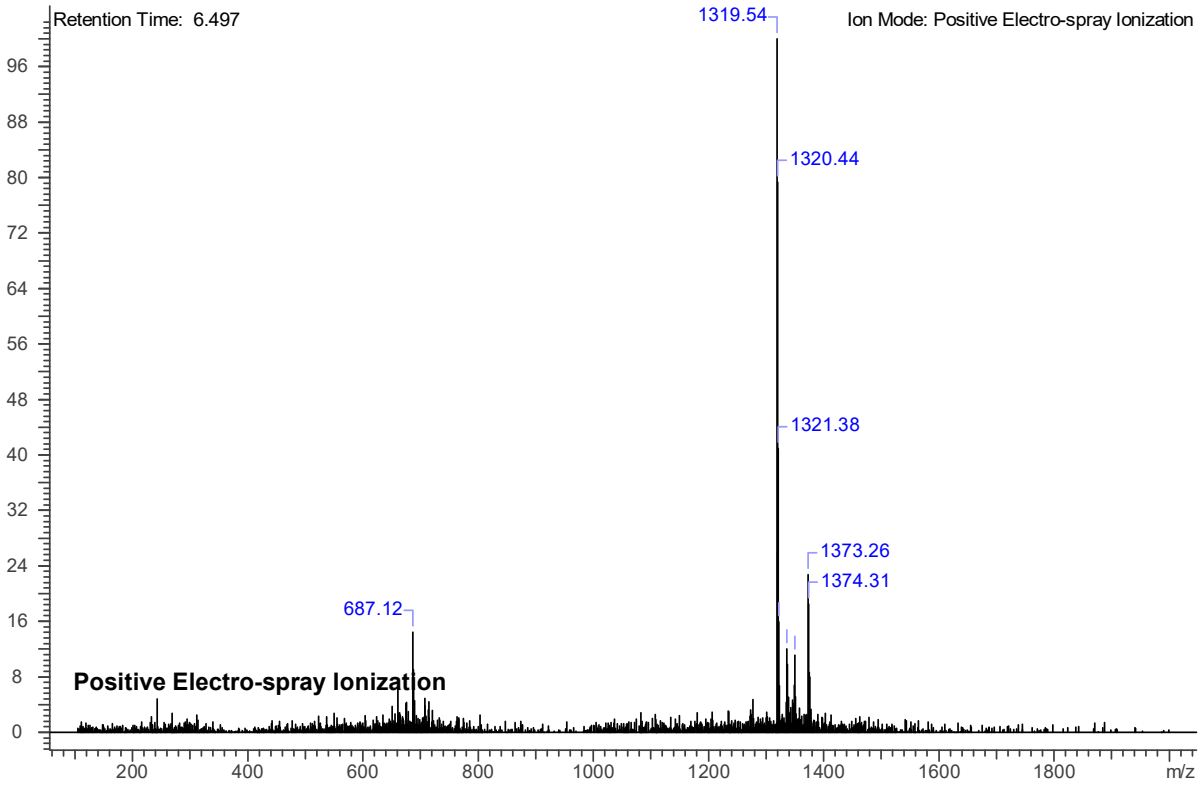
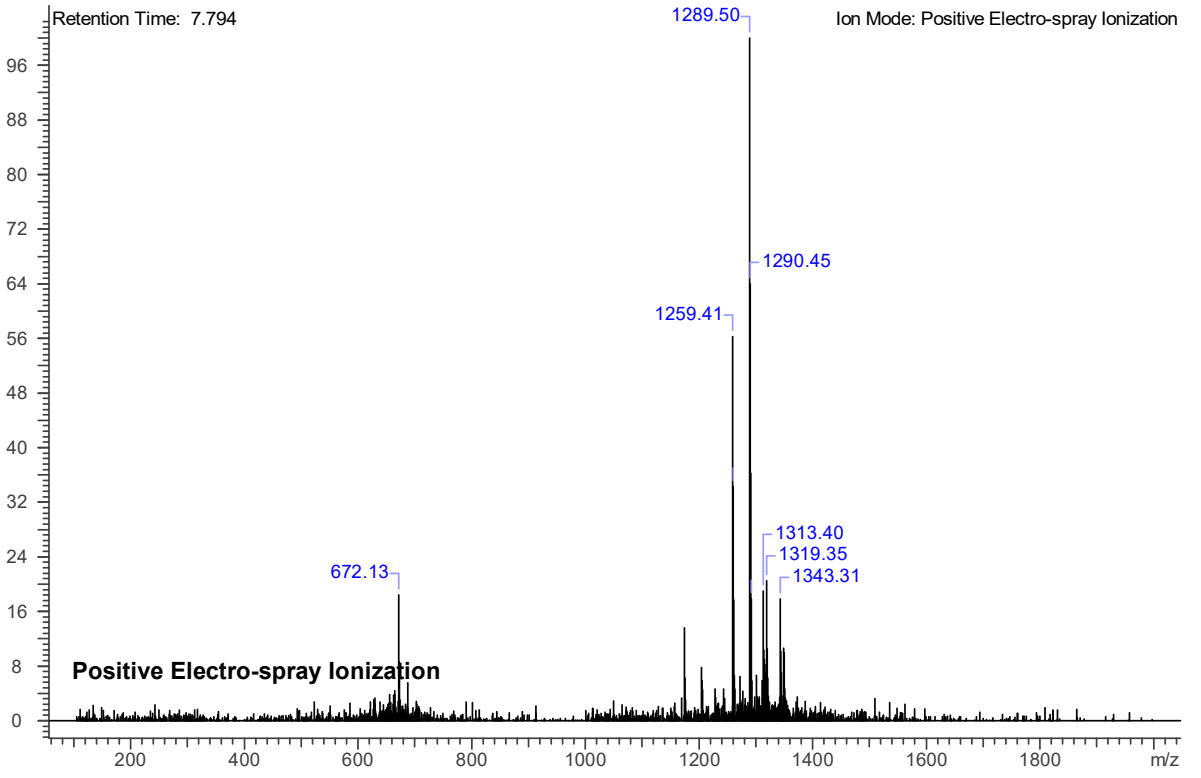
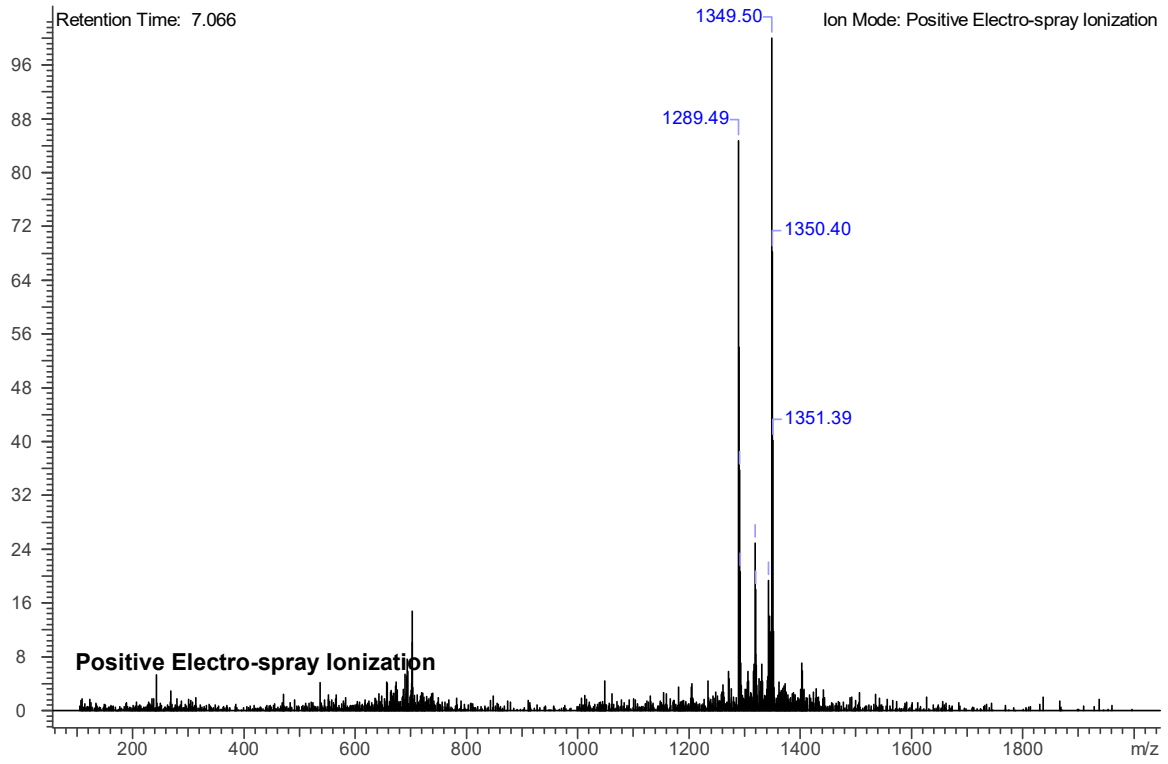


Figure S28. LC-MS trace of the photoconverted compound **1b** (closed form; detection at 450 nm) in MeCN shows well-resolved peaks with very similar absorption spectra. MS data for four peaks is given in Figure S29.


Retention Time: 6.497
Ion Mode: Positive Electro-spray Ionization
1319.54
1320.44
1321.38
1373.26
1374.31
687.12
Positive Electro-spray Ionization
m/z


Retention Time: 7.794
Ion Mode: Positive Electro-spray Ionization
1289.50
1290.45
1259.41
1313.40
1319.35
1343.31
672.13
Positive Electro-spray Ionization
m/z


Retention Time: 7.066
Ion Mode: Positive Electro-spray Ionization
1349.50
1289.49
1350.40
1351.39
Positive Electro-spray Ionization
96
88
80
72
64
56
48
40
32
24
16
8
0
200
400
600
800
1000
1200
1400
1600
1800
m/z

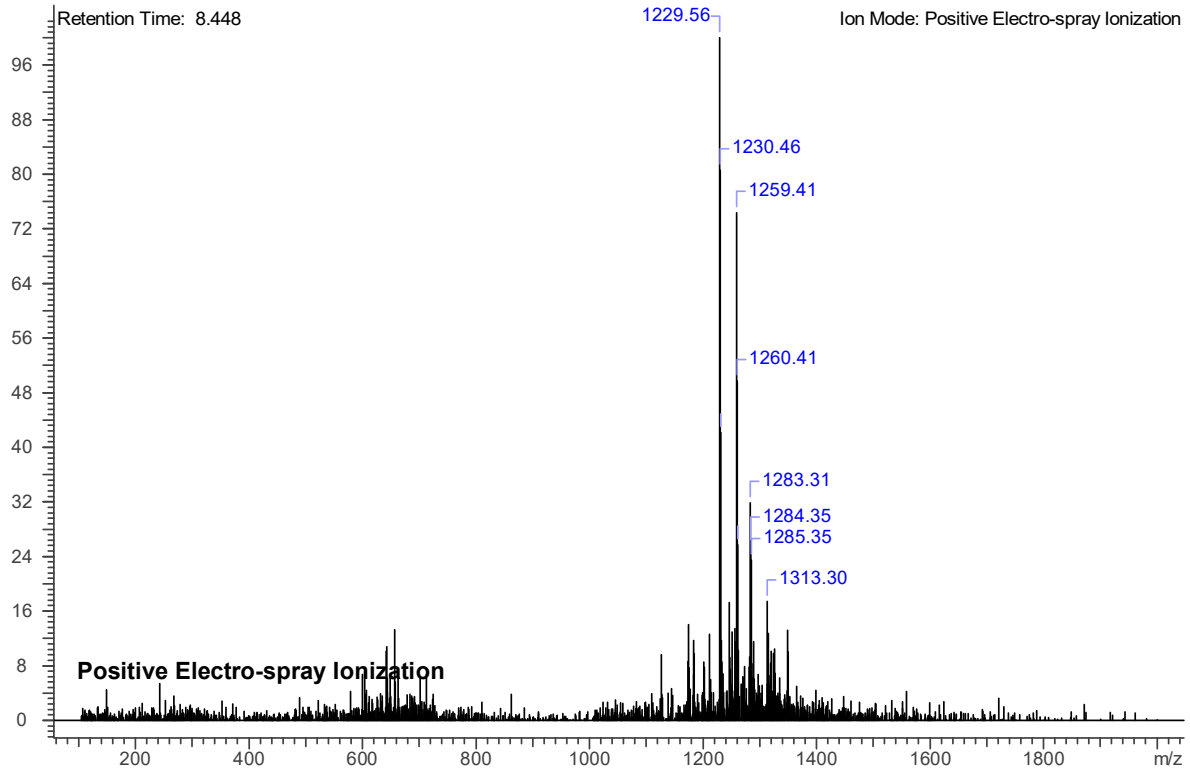

Retention Time: 8.448
Ion Mode: Positive Electro-spray Ionization
1229.56
1230.46
1259.41
1260.41
1283.31
1284.35
1285.35
1313.30
Positive Electro-spray Ionization
96
88
80
72
64
56
48
40
32
24
16
8
0
200
400
600
800
1000
1200
1400
1600
1800
m/z

Figure S29. MS spectra (positive mode) for the peaks detected in Figure S28. The mass difference of 30 Da (for M+H) is observed: 1349 (starting material **1b**) - 1319 - 1289 - 1259 - 1230, while the polarity of the photoproducts is decreasing in this series.

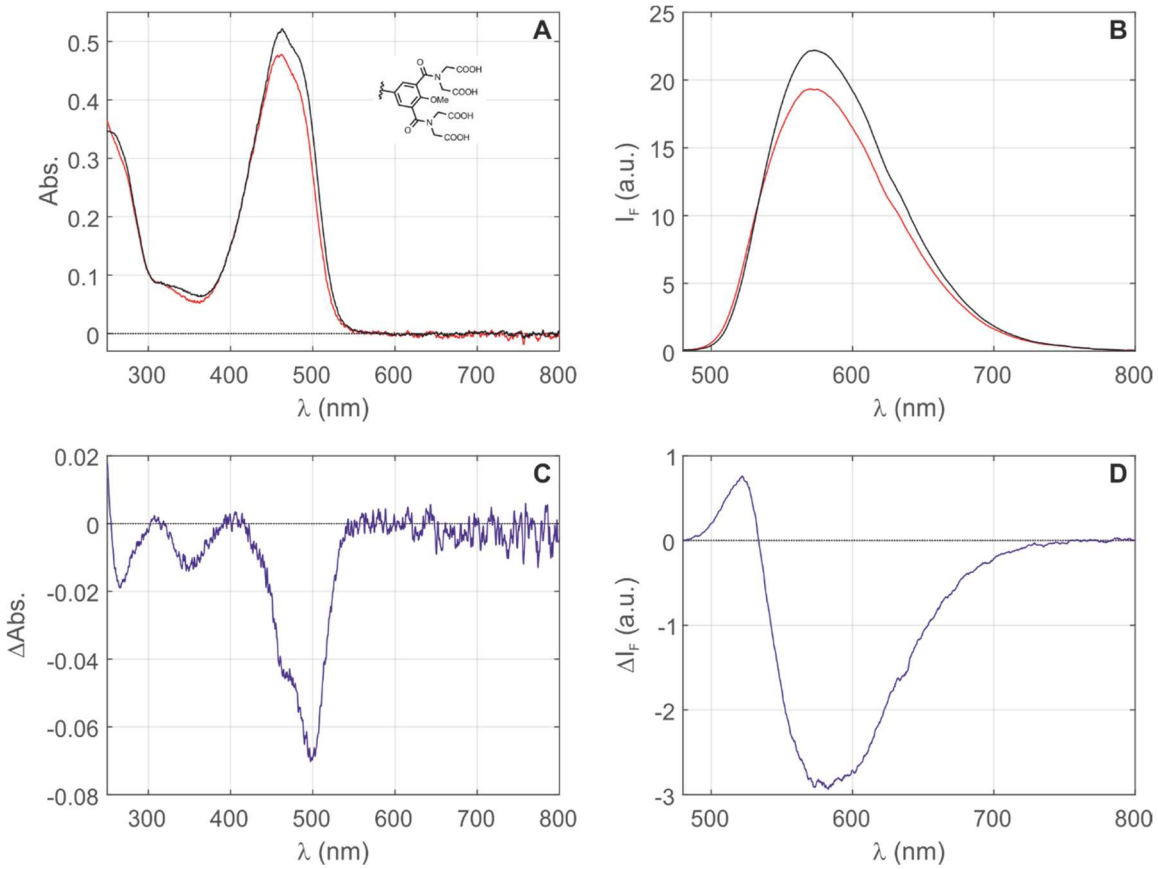


Figure S30. Absorption (A) and emission (B) spectra of compound **1c** in MeCN at the first PSS-365nm (black lines) and after 20 cycles (red lines). The corresponding differences are plotted in C and D.

ABSORPTION AND EMISSION SPECTRA

Normalized absorption spectra of the OF and the CF of all DAEs were recorder in aqueous phosphate buffer (100 mM, pH = 7,4) and are given in Figure S31. Compounds with methoxy residues (**6**-Et-OMe, **6**-*i*Bu-OMe, **7**-Et-OMe, and **7**-*i*Bu-OMe) in phenyl groups (dotted lines) feature small red-shifts in the absorption bands and larger red-shifts in the emission bands compared to corresponding non-substituted compounds (**6**-Et-H, **6**-*i*Bu-H, **7**-Et-H, and **7**-*i*Bu-H). The absorption spectra of the CFs was calculated from the spectrum of the photostationary state (365 nm), with the conversion value and the spectrum of the OF. The emission of the CF was measured from mixtures of the OF and the CF, at low conversion (absorption of the CF at the maximum < 0,1), with excitation at 470 nm.

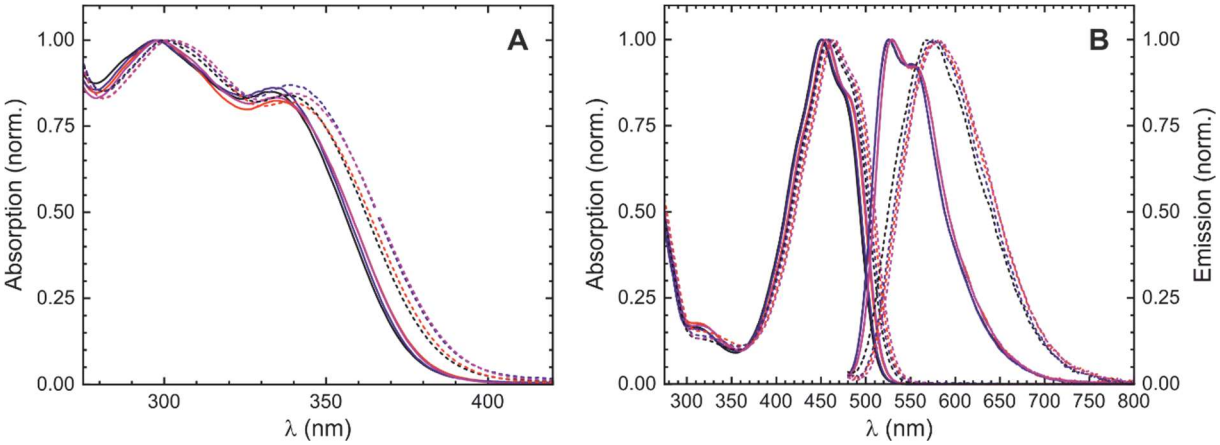


Figure S31. (A) Absorption of the OFs; (B) Absorption and emission of the CFs. All measurements performed in phosphate buffer solutions (100 mM, pH = 7,4); concentration in the range ca. 2-5 μM. Solid lines – compounds without methoxy substituents in phenyl groups (**6**-Et-H, **6**-*i*Bu-H, **7**-Et-H, and **7**-*i*Bu-H); dotted lines – compounds with methoxy residues in phenyl groups (**6**-Et-OMe, **6**-*i*Bu-OMe, **7**-Et-OMe, and **7**-*i*Bu-OMe).