Supplementary Information

Functionalization and solubilization of polycyclic aromatic compounds by sulfoniumization

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1 General information

Unless otherwise stated, all reactions were performed under a positive atmosphere of nitrogen in oven-dried or flame-dried glassware. Prior to set-up of the reaction, glassware was evacuated and backfilled with nitrogen three times. Unless otherwise noted, all work-up and purification procedures were performed with reagent-grade solvents under air. The expression rt (room temperature) refers to 23–26 °C in this Supporting Information.

Chromatography and solvents: Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm). The developed chromatograms were analyzed by a UV lamp (254 or 365 nm) or stained with $KMnO_4$ solution. Flash column chromatography was performed with Biotage Isolera® equipped with Biotage SNAP Cartridge KP-Sil columns or KANTO Silica Gel 60N (spherical, neutral, 40-100 μm). Toluene, tetrahydrofuran (THF), and diethyl ether (Et_2O) for reactions were purified by passing through a solvent purification system (Glass Contour).

NMR and deuterated solvents: Unless otherwise noted, NMR spectra were recorded at room temperature on a JEOL ECS-600 (^{1}H 600 MHz, ^{13}C 150 MHz) spectrometer. Chemicals shifts (δ) are quoted in ppm downfield of tetramethylsilane. The residual solvent signals were used as references for ^{1}H and ^{13}C NMR spectra (relative to tetramethylsilane at 0.0 ppm, $CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; $C_2D_2Cl_4$: δ_H = 6.0 ppm, δ_C = 73.78 ppm; CD_2Cl_2: δ_H = 5.32 ppm, δ_C = 54.00 ppm). ^{19}F NMR spectra are not calibrated by an internal reference. The multiplicity of all signals was described with standard abbreviations as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, h = sextet, hept = heptet; m = multiplet, br = broad signal. All the NMR data were processed using Mestrenova 14 applying standard phase and baseline corrections. Coupling constants (J) are quoted in Hz. Crude yields were determined by ^{1}H NMR

using CH_2Br_2 as an internal standard. In ^{13}C NMR, peak overlaps are reported for the assigned peaks based on the extent of carbon signal overlap.

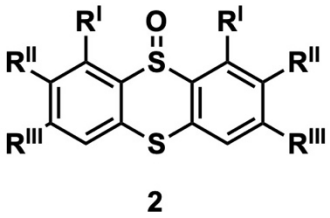
HRMS: High-resolution mass spectra (HRMS) were obtained by a Thermo Fisher Scientific Exactive (ESI-MS), a JEOL JMS-T100TD (Direct Analysis in Real Time, DART) or a Bruker ultrafleXtreme (MALDI-TOF MS).

Chemicals: Unless otherwise noted, all reactants or reagents including dry solvents were obtained from commercial suppliers and used as received. Thianthrene, TfOH, Tf_2O, 4,4'-thiodiphenol, 1-bromo-2-(2-(2-methoxyethoxy)ethoxy)ethane were purchased from Tokyo Chemical Industry Co., Ltd. (TCI). *p*-Tolyl sulfoxide (**9b**) was purchased from FUJIFILM Wako Pure Chemical Corporation. H_2SO_4 was purchased from KANTO CHEMICAL Co., Inc.

2 Experimental procedures and characterization data

2.1 Starting material synthesis

2.1.1 Synthesis of thianthrene oxide derivatives



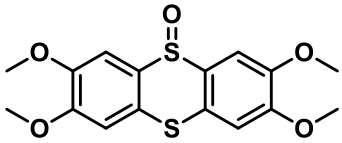
2

name	R^I	R^{II}	R^{III}
2a	H	H	H
2b	H	Me	Me
2c	H	OMe	OMe
2d	H	*p*-^{t}BuC$_6$H$_4$	*p*-^{t}BuC$_6$H$_4$
2e	TMS	H	H
2f	Si(Me)$_2$C$_{18}$H$_{37}$	H	H
2g	H	F	F

Scheme S1. Synthesized thianthrene oxide derivatives.

Thianthrene 5-oxide (**2a**) and 2,3,7,8-tetrafluorothianthrene 5-oxide (**2g**) were synthesized according to a procedure by Ritter and coworkers.[1] 2,3,7,8-Tetramethylthianthrene 5-oxide (**2b**) was synthesized according to a literature procedure.[2] 4,6-Bis(trimethylsilyl)thianthrene 5-oxide (**2e**) was synthesized according to a literature procedure.[3]

2,3,7,8-Tetramethoxythianthrene 5-oxide (**2c**)



2c was synthesized in three steps. According to literature procedures, 1,2-diiodo-4,5-dimethoxybenzene[4] and 2,3,7,8-tetramethoxythianthrene[5] were synthesized. Oxidation of 2,3,7,8-tetramethoxythianthrene (168 mg, 0.50 mmol, 1.0 equiv.) was performed according to Ritter's method.[1] Purification by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 30:70) afforded the title compound (146 mg, 0.41 mmol, 83%) as a yellow solid.

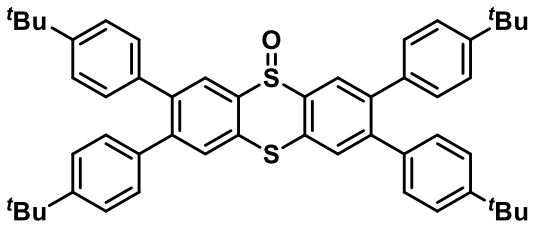
R_f (hexane/EtOAc = 30:70): 0.3.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (s, 3H), 7.10 (s, 2H), 3.97 (s, 6H), 3.91 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.3, 150.0, 133.4, 120.7, 111.9, 106.9, 56.5.

ESI-HRMS calcd for $C_{16}H_{16}O_5S_2Na$ $[M+Na]^+$: 375.0337; found: 375.0334.

2,3,7,8-Tetrakis[4-(*tert*-butyl)phenyl]thianthrene 5-oxide (**2d**)



2d was synthesized in three steps. First, 2,3,7,8-tetrabromothianthrene was synthesized according to a literature procedure.[6] Second, a J.-Young Schlenk tube was equipped with 2,3,7,8-tetrabromothianthrene (531.9 mg, 1.0 mmol, 1.0 equiv.), (4-(*tert*-butyl)phenyl)boronic acid (1.07 g, 6.0 mmol, 6.0 equiv.) and Na_2CO_3 (2.65 g, 25 mmol, 25 equiv.). Dist. H_2O (75 mL), toluene (125 mL) and EtOH (50 mL) were added and the mixture was purged with nitrogen for a prolonged time. $PdCl_2(PPh_3)_2$

(123 mg, 0.0175 mmol, 1.75 mol%) was added and the reaction mixture which was stirred under reflux for 72 h. After cooling to rt, the layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 100 mL). The organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. Flash column chromatography on silica gel (hexane/CH_2Cl_2 = 100:0 to 90:10) afforded 2,3,7,8-tetrakis(4-(*tert*-butyl)phenyl)thianthrene (633.1 mg, 0.85 mmol, 85%) as a colorless solid. Oxidation of 2,3,7,8-tetrakis(4-(*tert*-butyl)phenyl)thianthrene (590.4 mg, 0.79 mmol, 1.0 equiv.) was performed according to the Ritter's method.[1] Purification by flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 90:10) afforded the title compound (211.2 mg, 0.28 mmol, 35%) as a colorless solid.

R_f (hexane): 0.4.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (s, 2H), 7.70 (s, 2H), 7.26–7.20 (m, 8H), 7.08–7.05 (m, 8H), 1.29 (s, 36H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.4, 150.2, 142.7, 141.3, 139.8, 137.0, 136.8, 131.2, 129.5, 129.5, 127.2, 126.9, 125.1, 125.0, 34.6, 31.4.

MALDI-TOF MS calcd for $C_{52}H_{56}OS_2Na$ $[M+Na]^+$: 783.3665; found: 783.3661.

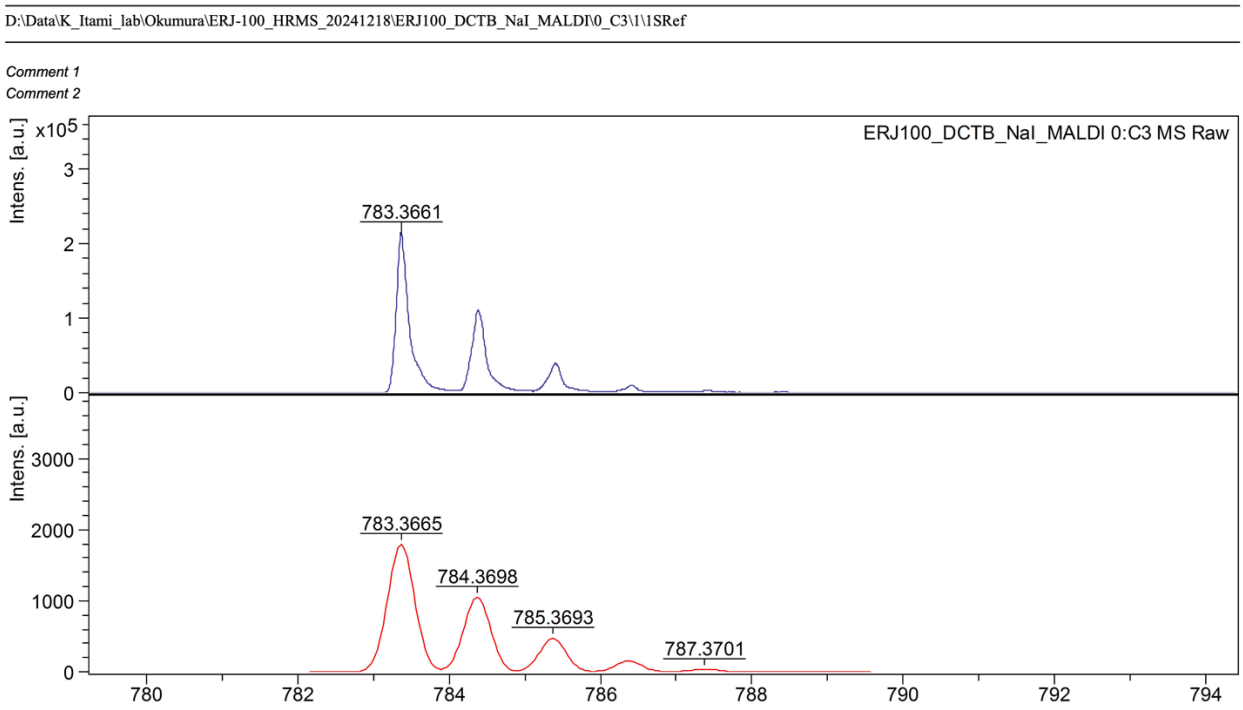
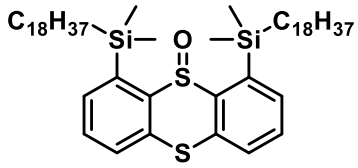


Figure S1. Observed and simulated MALDI-TOF MS spectra of **2d**.

4,6-Bis(dimethyl(octadecyl)silyl)thianthrene 5-oxide (**2f**)



According to a modified literature procedure[3] a J.-Young Schlenk tube was equipped with a PTFE-coated stirring bar, thianthrene oxide (1.0 g, 4.3 mmol, 1.0 equiv.) and THF (25 mL) under nitrogen and the solution was cooled to –78 °C, before freshly prepared LDA (10.8 mmol) in THF (6 mL) was added dropwise at the same temperature. After 3.5 h, the reaction mixture was allowed to warm up to rt. The reaction mixture was cooled to –30 °C after 1 h and chlorodimethyl(octadecyl)silane (4.60 g, 13.3 mmol, 3.1 equiv.) in THF (10 mL) was added. The vial containing chlorodimethyl(octadecyl)silane was further rinsed with THF (3 mL). The reaction mixture was stirred at the same temperature for 3 h before dist. H_2O and CH_2Cl_2 were added and the mixture was warmed up to rt. The layers were separated and the orgaic layer was washed with dist. H_2O (× 2) and brine (× 2). Flash column chromatography on silica gel (hexane/EtOAc = 100:0 to 92:8) afforded the title compound (486 mg, 0.57 mmol, 13%) as a colorless solid.

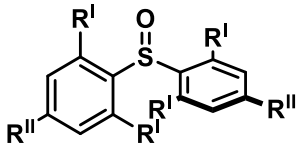
R_f (hexane/EtOAc = 95:5): 0.1.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, J = 7.6 Hz, 2H), 7.65–7.57 (m, 2H), 7.48–7.37 (m, 2H), 1.39–1.17 (m, 64H), 1.06–0.95 (m, 4H), 0.91–0.84 (m, 6H), 0.58 (s, 6H), 0.52 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.9, 141.5, 134.5, 134.0, 130.1, 129.5, 33.6, 32.1, 29.9 (6C), 29.8 (2C), 29.8, 29.7, 29.5, 29.5, 24.1, 22.8, 17.31, 14.3, –0.2, –0.3.

ESI-HRMS calcd for $C_{52}H_{92}OS_2Si_2Na$ $[M+Na]^+$: 875.6020; found: 875.6016.

2.1.2 Synthesis of diaryl sulfoxide derivatives



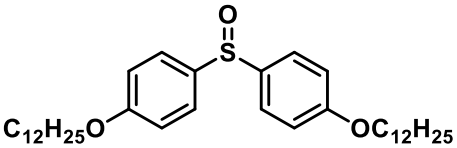
9

name	R^I	R^{II}
9a	Me	Me
9c	H	OMe
9d	H	$-OC_{12}H_{25}$
9e	H	$-(OCH_2CH_2)_3OMe$

Scheme S2. Synthesized diaryl sulfoxide derivatives.

2,2'-Sulfinylbis(1,3,5-trimethylbenzene) (**9a**) was synthesized according to a literature procedure.[7] 4,4'-Sulfinylbis(methoxybenzene) (**9c**) was synthesized according to a literature procedure.[8]

4,4'-Sulfinylbis((dodecyloxy)benzene) (**9d**)



9d was synthesized in two steps. 4,4'-Sulfinyldiphenol was prepared according to a literature procedure[9] and purified by washing the crystalline solid with CH_2Cl_2 after recrystallization from MeOH (minor amounts), hexane (minor amounts) and CH_2Cl_2. According to a modified literature procedure[10] a J.-Young Schlenk tube equipped with a PTFE-coated stirring bar was charged with 4,4'-sulfinyldiphenol (468.5 mg, 2.00 mmol, 1.00 equiv.), K_2CO_3 (624.7 mg, 4.52 mmol, 2.26 equiv.), TMEDA (15 μL, 0.10 mmol, 5 mol%) and DMSO (2.5 mL). Then, 1-bromododecane (1.00 mL, 4.2 mmol, 2.1 equiv.) was added and the resultant mixture was stirred at 90 °C for 18 h under nitrogen. Upon cooling to rt, the reaction mixture was diluted with EtOAc, washed with dist. H_2O (× 3), the organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. Flash column chromatography on silica gel (hexane/EtOAc = 75:25) afforded the title compound (800.9 mg, 1.40 mmol, 70%) as a colorless solid.

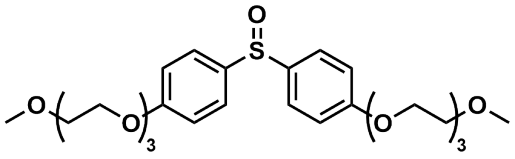
R_f (hexane/EtOAc = 80:20): 0.3.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, J = 8.9 Hz, 4H), 6.93 (d, J = 8.3 Hz, 4H), 3.94 (t, J = 6.5 Hz, 4H), 1.80–1.72 (m, 4H), 1.46–1.38 (m, 4H), 1.38–1.18 (m, 32H), 0.87 (t, J = 7.0 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.5, 136.8, 127.0, 115.3, 68.4, 32.0, 29.8, 29.7, 29.7, 29.7, 29.5 (2C), 29.2, 26.1, 22.8, 14.2.

ESI-MS calcd for $C_{36}H_{58}O_3SNa$ $[M+Na]^+$: 593.4004; observed 593.3999.

4,4'-Sulfinylbis((2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene) (**9e**)



9e was synthesized in two steps. 4,4'-Sulfinyldiphenol was prepared according to a literature procedure[9] and purified by washing the crystalline solid with CH_2Cl_2 after recrystallization from MeOH (minor amounts), hexane (minor amounts) and CH_2Cl_2. According to a modified literature procedure[10] a J.-Young Schlenk tube equipped with a PTFE-coated stirring bar was charged with 4,4'-sulfinyldiphenol (1.17 g, 5.0 mmol, 1.0 equiv.), K_2CO_3 (1.56 g, 11.3 mmol, 2.26 equiv.), TMEDA (37.5 μL, 0.25 mmol, 5 mol%) and DMSO (6.25 mL). Then, 1-bromo-2-(2-(2-methoxyethoxy)ethoxy)ethane (1.82 mL, 10.5 mmol, 2.1 equiv.), was added and the resultant mixture was stirred at 90 °C for 18 h under nitrogen. Upon cooling to rt, the reaction mixture was diluted with EtOAc, washed with dist. H_2O (× 3), the organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. Flash column chromatography on silica gel (EtOAc/MeOH = 95:5) afforded the title compound (1.98 g, 3.76 mmol, 75%) as a colorless oil.

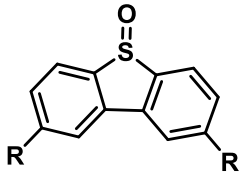
R_f (EtOAc/MeOH = 95:5): 0.3.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54–7.48 (m, 4H), 6.96 (d, J = 8.7 Hz, 4H), 4.16–4.09 (m, 4H), 3.87–3.82 (m, 4H), 3.71 (dd, J = 6.1, 3.5 Hz, 4H), 3.66 (dd, J = 5.9, 3.6 Hz, 4H), 3.63 (dd, J = 5.6, 3.6 Hz, 4H), 3.53 (dd, J = 5.5, 3.3 Hz, 4H), 3.36 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.1, 137.2, 127.0, 115.4, 72.0, 71.0, 70.8, 70.7, 69.6, 67.8, 59.2.

ESI-HRMS calcd for $C_{26}H_{38}O_9SNa$ $[M+Na]^+$: 549.2134; observed: 549.2129.

2.1.3 Synthesis of dibenzothiophene oxide derivatives



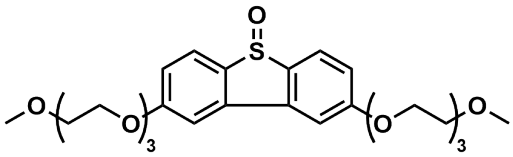
15

name	R
15a	H
15b	OMe
15c	$-(OCH_2CH_2)_3OMe$

Scheme S3. Synthesized dibenzothiophene oxide derivatives.

Dibenzothiophene oxide (**15a**) was synthesized according to a literature procedure.[11] 2,8-Dimethoxydibenzo[*b*,*d*]thiophene 5-oxide (**15b**) was synthesized from 2,8-dimethoxydibenzo[*b*,*d*]thiophene[12] according to a literature procedure.[11]

2,8-Bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)dibenzo[*b*,*d*]thiophene 5-oxide (**15c**)



15c was synthesized in three steps. First, 2,8-dihydroxydibenzo[*b*,*d*]thiophene was synthesized according to a literature procedure.[12] Second, 2,8-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)dibenzo[*b*,*d*]thiophene was synthesized according to a modified literature procedure.[10] A J.-Young Schlenk tube equipped with a PTFE-coated stirring bar was charged with 2,8-dihydroxydibenzo[*b*,*d*]thiophene (432.5 mg, 2.00 mmol, 1.00 equiv.), K_2CO_3 (624.7 mg, 4.52 mmol, 2.26 equiv.), TMEDA (15 μL, 0.10 mmol, 5 mol%) and DMSO

(2.5 mL). Then, 1-bromo-2-(2-(2-methoxyethoxy)ethoxy)ethane (0.73 mL, 4.20 mmol, 2.1 equiv.) was added and the resultant mixture was stirred at 90 °C for 18 h under nitrogen. Upon cooling to rt, the reaction mixture was diluted with EtOAc, washed with dist. H_2O (× 3), the organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. Flash column chromatography on silica gel (hexane/EtOAc = 66:33 – 0:100) afforded 2,8-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)dibenzo[*b*,*d*]thiophene (792.9 mg, 1.56 mmol, 78%) as a yellow solid. Third, following a modified literature procedure,[11] 2,8-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)dibenzo[*b*,*d*]thiophene (792.9 mg, 1.56 mmol, 1.0 equiv.) was dissolved in TFA (1.6 mL, 1 M) and the reaction mixture was cooled to 0°C. Aq. H_2O_2 (35%, 167*μ*L, 1.72 mmol, 1.1 equiv.) was added dropwise over 1 min and the reaction mixture was stirred for 1 h at 0 °C. The reaction mixture was poured into a mixture of ice / aq. Na_2CO_3 and CH_2Cl_2 was added. The layers were separated and the aq. layer was extracted with CH_2Cl_2 (× 2). The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. Flash column chromatography on silica gel (EtOAc/MeOH = 95:5) afforded the title compound (787.4 mg, 1.50 mml, 96%) as a colorless oil.

R_f (EtOAc/MeOH = 95:5): 0.2.

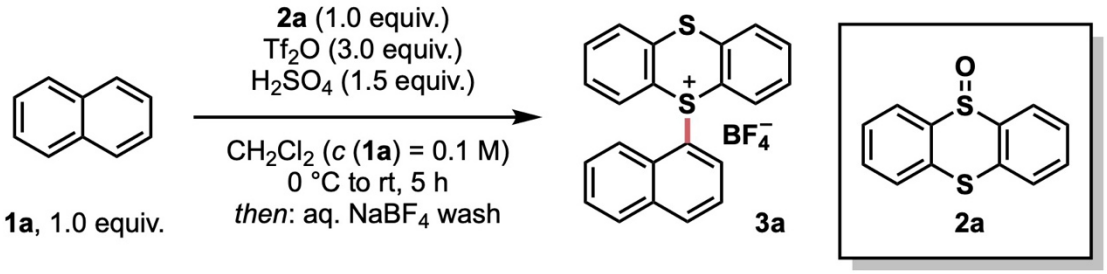
^{1}H NMR (600 MHz, CD_2Cl_2) *δ* 7.82 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 2.4 Hz, 2H), 7.02 (dd, *J* = 8.5, 2.4 Hz, 2H), 4.28–4.19 (m, 4H), 3.91–3.82 (m, 4H), 3.75–3.64 (m, 4H), 3.65–3.57 (m, 4H), 3.63–3.54 (m, 4H), 3.54–3.44 (m, 4H), 3.32 (s, 6H).

^{13}C NMR (151 MHz, CD_2Cl_2) *δ*162.8, 139.3, 138.6, 128.8, 116.1, 108.2, 72.2, 71.2, 70.9, 70.8, 69.8, 68.5, 59.0.

ESI-HRMS calcd for $C_{26}H_{36}O_9S$ $[M]^+$: 547.1978; found: 547.1976.

2.2 Thianthrenation of PAHs

2.2.1 Optimization studies for the thianthrenation of naphthalene



entry	*deviations of standard conditions*	*^{1}H NMR yield*	*scale*
1	none	77%	0.2 mmol
2	naphthalene (1.5 equiv.)	87%	0.2 mmol
3	TTO (1.5 equiv.)	quant.	0.2 mmol
4	1,2-dichloroethane (*c* = 0.1 M) instead of CH_2Cl_2	77%	0.2 mmol
5	CS_2 (*c* = 0.1 M) instead of CH_2Cl_2	50%	0.2 mmol
6	1,2-dichloroethane (*c* = 0.1 M) instead of CH_2Cl_2, 0 °C to 80 °C, 24 h	75%[a]	0.5 mmol
7	ball milling (30 Hz), neat, 30 min, rt	n.o.	0.2 mmol
8	$BF_3{\cdot}OEt_2$ (3.0 equiv.) instead of H_2SO_4	34	0.2 mmol
9	**CH_2Cl_2 (*c* = 0.025 M), 2a (1.5 equiv.)**	**quant. (78%[b])**	**0.5 mmol**
10	CH_2Cl_2 (*c* = 0.025 M), **2a** (1.5 equiv.), overnight reaction	(72%[b])	2.0 mmol

Scheme S4. Optimization studies on the formation of naphthalene thianthrenium salt **3a.**

[a]Isolated yield.

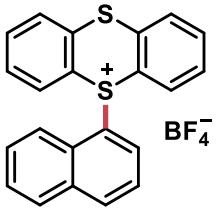
2.2.2 General procedure (GP-1) for the thianthrenation of PAHs

Thianthrene 5-oxide (1.5 equiv.) and the respective PAH (1.0 equiv.) were added to a 30-mL or 50-mL glass vial equipped with a PTFE-coated stirring bar under air. Dry CH_2Cl_2 (0.025 M) was added and the solution was cooled to 0 °C with an ice bath, before Tf_2O (3.0 equiv.) and conc. H_2SO_4 (1.5 equiv.) were added dropwise, respectively. The reaction mixture was allowed to

warm up to 26 °C and was stirred at the same temperature for 5 h. Upon completion, the reaction mixture was diluted with CH_2Cl_2, sat. aq. $NaHCO_3$ was added and the mixture was stirred for 1 min, before the layers were separated. The organic layer was washed with sat. aq. $NaBF_4$ (× 2 for small scale reactions / × 3 for large scale reactions), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Flash column chromatography on silica gel (hexane/CH_2Cl_2 = 100:0 to 0:100; then CH_2Cl_2/MeOH) afforded the thianthrenium salts as solids. For the indicated entries, after concentration upon column chromatography, the isolated compound was dissolved with minor amounts of CH_2Cl_2 and precipitated by the addition of Et_2O.

2.2.3 Synthesis of PAH thianthrenium salts

Mixture of 5-(Naphthalen-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate and 5-(Naphthalen-2-yl)-5*H*-thianthren-5-ium tetrafluoroborate (**3a, r.r. = 94:6**)



3a was synthesized according to **GP-1** using napthtalene (64.0 mg, 0.50 mmol, 1.0 equiv.) and thianthrene 5-oxide (174.2 mg, 0.75 mmol, 1.5 equiv.). Flash column chromatography on silica gel (hexane/CH_2Cl_2 = 100:0 to 0:100; then CH_2Cl_2/MeOH = 100:0 to 95:5), followed by concentration, addition of CH_2Cl_2 and precipitation by the addition of Et_2O afforded the title compound (192.4 mg, 0.39 mmol, 78%) as a mixture of regioisomers (r.r. 94:6) an off-white solid.

R_f (CH_2Cl_2/MeOH = 95:5): 0.2.

^{1}H NMR of naphthalen-1-yl isomer (396 MHz, $CDCl_3$) δ 8.63 (d, J = 8.5 Hz, 1H), 8.41 (dd, J = 8.0, 1.4 Hz, 2H), 8.02 (d, J = 8.2 Hz, 1H), 7.86 (d, J = 8.3 Hz, 1H), 7.80–7.65 (m, 5H), 7.60 (td, J = 7.6, 1.6 Hz, 2H), 7.55–7.47 (m, 1H), 7.41 (td, J = 8.0, 1.4 Hz, 1H), 7.24 (dd, J = 7.8, 1.2 Hz, 1H).

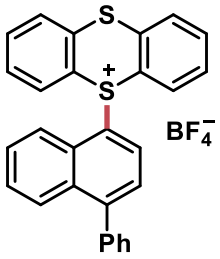
^{13}C NMR of naphthalen-1-yl isomer (151 MHz, $CDCl_3$) δ 137.0, 135.4, 134.9, 134.8, 134.3, 130.6, 130.3, 130.0, 129.9, 129.8, 129.4, 128.0, 125.1, 122.3, 117.2, 116.5.

^{19}F NMR of naphthalen-1-yl isomer (373 MHz, CD_2Cl_2) δ –151.78.

ESI-HRMS calcd for $C_{22}H_{15}S_2$ $[M–BF_4]^+$: 343.0615; found: 343.0609.

Note: 2D NMR studies for the regioselectivity determination are in line with the obtained crystal structure for the major regioisomer. Furthermore, the crystal structure of the minor regioisomer could be obtained (see Figures S5 and S6).

5-(4-Phenylnaphthalen-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate (**3b**)



3b was synthesized according to modified **GP-1** using 1-phenylnaphthalene (409 mg, 2.0 mmol, 1.0 equiv.) and thianthrene oxide (465 mg, 2.0 mmol, 1.0 equiv.). The organic layer was washed with sat. aq. $NaBF_4$ solution (× 3). Flash column chromatography on silica gel (hexane/CH_2Cl_2 = 100:0 to 0:100; then CH_2Cl_2/MeOH = 100:0 – 95:5), followed by concentration, addition of CH_2Cl_2 and precipitation by the addition of Et_2O afforded the title compound (855 mg, 1.69 mmol, 84%) as a colorless solid.

R_f (CH_2Cl_2/MeOH = 95:5): 0.2.

^{1}H NMR (600 MHz, $C_2D_2Cl_4$) δ 8.57 (d, J = 8.5 Hz, 1H), 8.29 (d, J = 8.0 Hz, 2H), 8.06 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 7.9 Hz, 2H), 7.92–7.86 (m, 1H), 7.83 (t, J = 7.6 Hz, 2H), 7.75 (t, J = 7.6 Hz, 2H), 7.66 (dd, J = 8.5, 7.1 Hz, 1H), 7.57–7.40 (m, 7H).

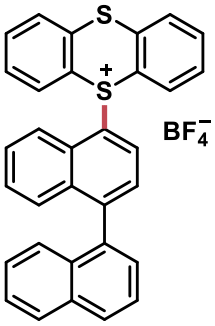
^{13}C NMR (151 MHz, $C_2D_2Cl_4$) δ 148.4, 137.7, 136.6, 134.7, 133.3, 133.2, 130.9, 130.4, 130.2, 129.9, 129.8, 129.5, 128.7, 128.6, 128.5, 128.3, 126.3, 122.0, 117.7, 114.5.

^{19}F NMR (376 MHz, CD_2Cl_2) δ –151.98.

ESI-HRMS calcd for $C_{28}H_{19}S_2$ $[M–BF_4]^+$: 419.0928; found: 419.0924.

Note: Regioselectivity was corroborated by crystal structure analysis (see Figure S7).

5-([1,1'-Binaphthalen]-4-yl)-5*H*-thianthren-5-ium tetrafluoroborate (**3c**)



3c was synthesized according to modified **GP-1** using 1,1'-binaphthalene (50.9 mg, 0.20 mmol, 1.0 equiv.) and thianthrene oxide (69.6 mg, 0.30 mmol, 1.0 equiv.). Flash column chromatography on silica gel (hexane/CH_2Cl_2 = 100:0 to 0:100, then CH_2Cl_2/MeOH = 100:0 to 92:8) afforded the title compound (68.3 mg, 0.12 mmol, 61%) as an off-white solid.

R_f (CH_2Cl_2/MeOH = 95:5): 0.2.

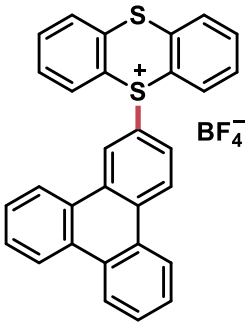
^{1}H NMR (396 MHz, $CDCl_3$) δ 8.71 (d, J = 8.6 Hz, 1H), 8.41 (ddd, J = 8.0, 3.8, 1.4 Hz, 2H), 7.76–7.50 (m, 9H), 7.34 (dd, J = 8.3, 7.0 Hz, 1H), 7.28–7.16 (m, 5H), 7.12 (dd, J = 7.1, 1.2 Hz, 1H), 7.05 (ddd, J = 8.2, 6.6, 1.3 Hz, 1H), 6.93 (d, J = 8.5 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 146.4, 137.5, 137.2, 135.8, 135.0, 134.1, 134.8, 134.8, 134.6, 133.5, 131.9, 130.8, 130.7, 130.6, 130.5, 130.1, 130.0, 129.3, 129.1, 128.6, 128.5, 128.2, 127.7, 127.0, 126.7, 126.4, 125.7, 125.3, 122.8, 117.7, 117.4, 116.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ –151.02.

ESI-HRMS calcd for $C_{32}H_{21}S_2$ $[M–BF_4]^+$: 469.1084; found 469.1083.

5-(Triphenylen-2-yl)-5*H*-thianthren-5-ium tetrafluoroborate (**3d**)



3d was synthesized according to **GP-1** using triphenylene (45.7 mg, 0.20 mmol, 1.0 equiv.) and thianthrene oxide (69.6 mg, 0.30 mmol, 1.5 equiv.). Flash column chromatography on silica gel (hexane/CH_2Cl_2 = 100:0 to 0:100; then CH_2Cl_2/MeOH = 100:0 to 97:3) afforded the title compound (67.5 mg, 0.12 mmol, 64%) as a colorless solid.

R_f (CH_2Cl_2/MeOH = 95:5): 0.3.

^{1}H NMR (600 MHz, $C_2D_2Cl_4$) δ 8.48 (dd, J = 11.3, 8.0 Hz, 4H), 8.44 (d, J = 9.0 Hz, 1H), 8.31 (d, J = 8.3 Hz, 1H), 8.23 (d, J = 2.2 Hz, 1H), 8.06 (d, J = 8.2 Hz, 1H), 7.85 (dt, J = 12.2, 4.4 Hz, 6H), 7.66 (dt, J = 10.7, 7.6 Hz, 2H), 7.60 (q, J = 6.8 Hz, 2H), 7.10 (dd, J = 8.9, 2.5 Hz, 1H).

^{13}C NMR (151 MHz, $C_2D_2Cl_4$) δ 136.3, 135.2, 134.5, 132.8, 130.9, 130.5, 130.3, 130.3, 129.9, 129.3, 128.9, 128.0, 127.9, 127.2, 127.0, 125.9, 124.0, 123.7, 123.5, 123.3, 123.3, 122.9, 121.3, 118.1.

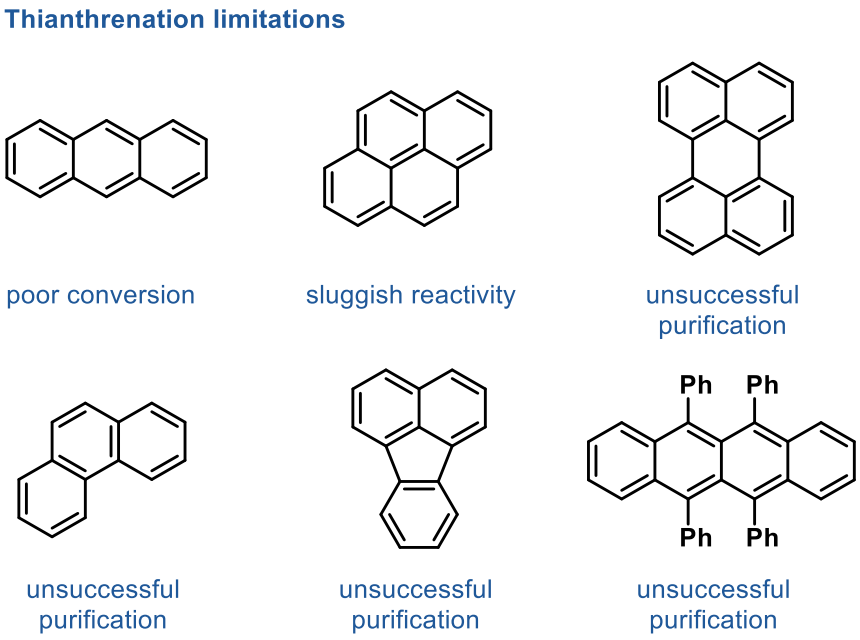
^{19}F NMR (373 MHz, $C_2D_2Cl_4$) δ –150.08.

ESI-HRMS calcd for $C_{30}H_{19}S_2$ $[M–BF_4]^+$: 443.0928; found: 443.0926.

Note: Regioisomer was determined by coupling constant of peak at 8.23 ppm (2.2 Hz) and COSY (no coupling with other protons).

2.2.4 Limitations

Moving to larger PAHs, the thianthrenation methodology using thianthrene oxide was found to be incompatible by either achieving product formation (anthracene) or adducts detected by ESI-HRMS appeared to have sluggish reactivity (pyrene) or have a more problematic isolation (perylene, phenanthrene fluoranthene, 5,6,11,12-tetraphenyltetracene), likely due to low solubility of products and the generation of side-products which could not been identified.



Scheme S5. Unsuccessfull PAHs fo the thianthrenation reaction.

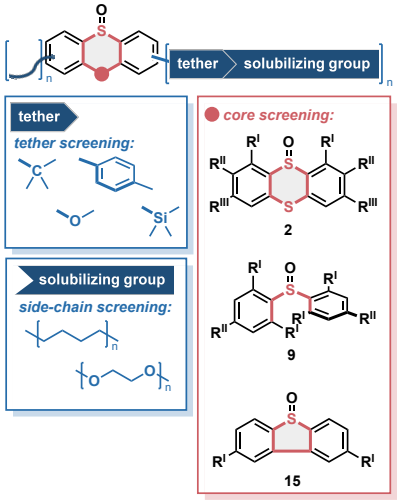
2.3 Sulfoniumization of PAHs

2.3.1 Screening of sulfoniumization reagents

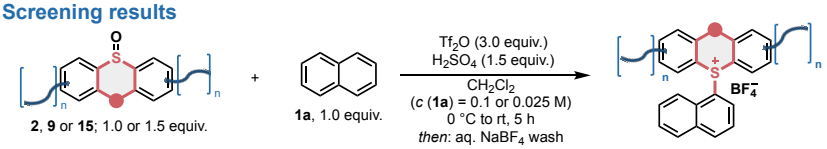
The sulfoxide (1.0 or 1.5 equiv.) and the naphthalene (1.0 equiv.) were added to a 30-mL or 50-mL glass vial equipped with a PTFE-coated stirring bar under air. Dry CH_2Cl_2 (0.025 M or 0.1 M with respect to naphthalene) was added and the solution was cooled to 0 °C with an ice bath, before Tf_2O (3.0 equiv.) and conc. H_2SO_4 (1.5 equiv.) were added dropwise, respectively. The reaction mixture was allowed to warm up to 26 °C and was stirred at the same temperature for 5 h. Upon completion, the reaction mixture was diluted with CH_2Cl_2, sat. aq. $NaHCO_3$ was added, and the mixture was stirred for 1 min, before the layers were separated. The organic layer was washed with sat. aq. $NaBF_4$ (× 2), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Crude ^1H NMR yield was determined by using CH_2Br_2 as an internal standard. If the

observed ^{1}H NMR yield was high, purification was attempted by flash column chromatography on silica gel (hexane/CH_2Cl_2 = 100:0 to 0:100; then CH_2Cl_2/MeOH) to afford thesulfonium salts.

A PAH sulfoniumization reagent design



B Screening results



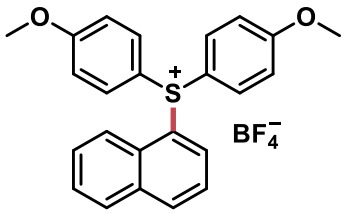
entry	reagent	R^I	R^{II}	R^{III}	sulfoxide	*c*	product	^{1}H NMR yield	purification
1	**2b**	H	Me	Me	1.0 equiv.	0.10 M	**4a**	75%	unsuccessful
2	**2c**	H	OMe	OMe	1.0 equiv.	0.10 M	**5a**	product n/o	–
3	**2d**	H	*p*-^{t}BuC$_6$H$_4$	*p*-^{t}BuC$_6$H$_4$	1.0 equiv.	0.025 M	**6a**	8%	–
4	**2e**	$SiMe_3$	H	H	1.5 equiv.	0.025 M	**7a**	98%	unsuccessful
5	**2f**	$SiMe_2C_{18}H_{37}$	H	H	1.5 equiv.	0.025 M	**8a**	95%	unsuccessful
6	**9a**	Me	Me	–	1.0 equiv.	0.10 M	**10a**	product n/o	–
7	**9b**	H	Me	–	1.0 equiv.	0.10 M	**11a**	quant.	unsuccessful
8	**9c**	H	OMe	–	1.0 equiv.	0.10 M	**12a**	quant.	97%
9	**9d**	H	$OC_{12}H_{25}$	–	1.0 equiv.	0.10 M	**13a**	84%	unsuccessful
10	**9e**	H	$O(CH_2CH_2O)_3Me$	–	1.0 equiv.	0.10 M	**14a**	–	93%
11	**15a**	H	–	–	1.0 equiv.	0.10 M	**16a**	26%	–
12	**15b**	OMe	–	–	1.0 equiv.	0.10 M	**17a**	product n/o	–
13	**15c**	$O(CH_2CH_2O)_3Me$	–	–	1.5 equiv.	0.025 M	**18a**	product n/o	–

Scheme S6. Sulfoniumization reagent screen.

*Note: "Unsuccessful" purification refers to the observation of byproducts after purification via column chromatography on silica gel. In most cases, CH_2Cl_2/MeOH mixtures were used, except for entry 9 (reagent **9d**), where hexane/EtOAc mixtures were employed. For entries 1, 4, and 7 (reagents **2b**, **2e**, and **9b**), precipitation with Et_2O from the isolated substances in CH_2Cl_2 was attempted; however, no improvement in product purity was observed. Additionally, for entry 4 (reagent **2e**), Gel Permeation Chromatography (GPC) using $CHCl_3$ was tested as an additional purification method after column chromatography and precipitation, but no significant enhancement in purity was achieved. While these results may, in part, stem from the lower selectivity of the reagents used, a correlation between purification success and the solubility of the obtained products cannot be excluded.*

2.3.2 Isolation of other PAH sulfonium salts

Bis(4-methoxyphenyl)(naphthalen-1-yl)sulfonium tetrafluoroborate (**12a**)



12a was synthesized according to modified **GP-1** using 4,4'-sulfinylbis(methoxybenzene) (52.5 mg, 0.2 mmol, 1.0 equiv.) and naphthalene (25.6 mg, 0.2 mmol, 1.0 equiv.). Flash column chromatography on silica gel (hexane/CH_2Cl_2 = 100:0 to 0:100; then CH_2Cl_2/MeOH = 100:0 to 95:5), followed by concentration, addition of CH_2Cl_2 and precipitation by the addition of Et_2O afforded the title compound (89.4 mg, 0.194 mmol, 97%) as a colorless solid.

R_f (CH_2Cl_2/MeOH = 95:5): 0.3.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, J = 8.2 Hz, 2H), 7.98 (d, J = 8.2 Hz, 1H), 7.69–7.56 (m, 7H), 7.44 (d, J = 7.3 Hz, 1H), 7.16–7.10 (m, 4H), 3.82 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.6, 135.0, 134.3, 133.3, 130.6, 129.9, 129.8, 129.6, 128.3, 126.3, 122.3, 121.8, 117.4, 112.6, 56.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ –152.06.

ESI-HRMS calcd for $C_{24}H_{21}O_2S$ $[M–BF_4]^+$: 373.1262; found: 373.1256.

2.3.3 General sulfoniumization procedures of PAHs with TEG-diaryl sulfoxide

General Procedure 2 (GP-2): for large PAHs

4,4'-Sulfinylbis((2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene) (1.0 equiv.) and the respective PAH (1.0 equiv.) were added to a flame-dried J.-Young Schlenk tube (50 mL) equipped with a PTFE-coated stirring bar under nitrogen. Dry 1,2-dichloroethane (0.0125 M with respect to the PAH) was added and the mixture was stirred at 85 °C until all solids were dissolved (typically

15–30 min). The reaction mixture was cooled to 26 °C, before Tf_2O (3.0 equiv.) and conc. H_2SO_4 (1.5 equiv.) were added dropwise under nitrogen, respectively. The reaction mixture was stirred at 26 °C for 5 h. Upon completion, the reaction mixture was diluted with CH_2Cl_2, sat. aq. $NaHCO_3$ was added, and the mixture was stirred for 1 min, before the layers were separated. The organic layer was washed with sat. aq. $NaBF_4$ (× 2), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Flash column chromatography on silica gel (hexane/CH_2Cl_2 = 100:0 to 0:100, then CH_2Cl_2/MeOH = 100:0 to 97:3) afforded the sulfonium salts as sticky oils.

Note 1: As separation of sat. aq. $NaBF_4$ with organic layer was poor, approx. 10 min should be allowed for separation.

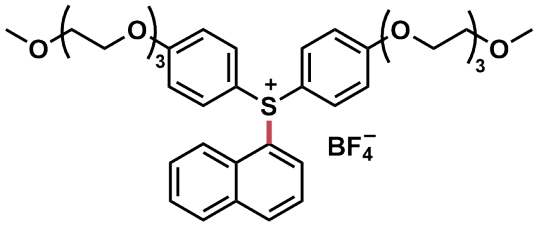
Note 2: With extending PAH size, longer column chromatography should be considered (up to 40 column volumes of CH_2Cl_2/MeOH = 97:3).

General Procedure 3 (GP-3): for medium-size PAHs

4,4'-Sulfinylbis((2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene) (1.0 equiv.) and the respective PAH (1.0 equiv.) were added to a glass vial (30 or 50 mL) equipped with a PTFE-coated stirring bar under air. Dry 1,2-dichloroethane (0.0125 M with respect to the PAH) was added and the mixture was stirred at 26 °C until all solids were dissolved. Then, Tf_2O (3.0 equiv.) and conc. H_2SO_4 (1.5 equiv.) were added dropwise under air, respectively. The reaction mixture was stirred at 26 °C for 5 h. Upon completion, the reaction mixture was diluted with CH_2Cl_2, sat. aq. $NaHCO_3$ was added, and the mixture was stirred for 1 min, before the layers were separated. The organic layer was washed with sat. aq. $NaBF_4$ (× 2), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Flash column chromatography on silica gel (hexane/CH_2Cl_2 = 100:0 to 0:100, then CH_2Cl_2/MeOH = 100:0 to 97:3) afforded the sulfonium salts as sticky oils.

2.3.4 Synthesis of PAH sulfonium salts using TEG-diaryl sulfoxide

Bis(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)(naphthalen-1-yl)sulfonium tetrafluoroborate (**14a**)



14a was prepared according to modified **GP-3** using 4,4'-sulfinylbis((2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene) (105.3 mg, 0.2 mmol, 1.0 equiv.), naphthalene (25.6 mg, 0.2 mmol, 1.0 equiv.) and CH_2Cl_2 (0.1 M with respect to the naphthalene) instead of 1,2-dichloroethane. Tf_2O (83.5 μL, 0.6 mmol, 3.0 equiv.) and H_2SO_4 (16 μL, 0.3 mmol, 1.5 equiv.) were added under ice-cooling and the reaction mixture was slowly allowed to warm up to 26 °C and stirred at the same temperature for 5 h. Upon completion, the reaction mixture was diluted with CH_2Cl_2, sat. aq. $NaHCO_3$ was added, and the mixture was stirred for 1 min, before the layers were separated. The organic layer was washed with sat. aq. $NaBF_4$ (× 2), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Flash column chromatography on silica gel (hexane/CH_2Cl_2 = 100:0 to 0:100; then CH_2Cl_2/MeOH = 100:0 – 97:3) afforded the title compound (134.8 mg, 0.186 mmol, 93%) as a colorless oil.

R_f (CH_2Cl_2/MeOH = 95:5): 0.2.

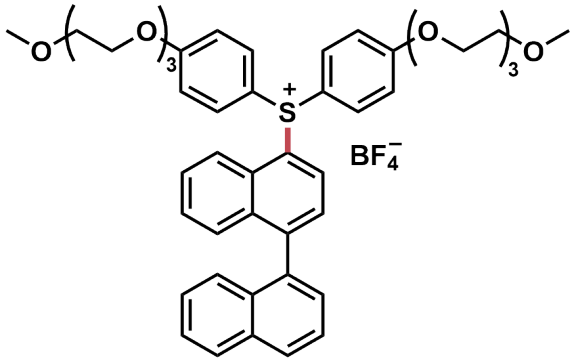
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16–8.09 (m, 2H), 7.98–7.93 (m, 1H), 7.65–7.60 (m, 2H), 7.60–7.56 (m, 5H), 7.36 (dd, J = 7.6, 1.0 Hz, 1H), 7.16–7.11 (m, 4H), 4.16–4.12 (m, 4H), 3.82–3.77 (m, 4H), 3.67–3.62 (m, 4H), 3.61–3.58 (m, 4H), 3.58–3.55 (m, 4H), 3.50–3.44 (m, 4H), 3.28 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.8, 135.0, 134.2, 133.1, 130.4, 129.8, 129.7, 129.4, 128.3, 126.1, 122.2, 121.6, 117.8, 112.5, 71.7, 70.6, 70.4, 70.4, 69.1, 68.2, 58.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ –152.16.

ESI-HRMS calcd for $C_{36}H_{45}O_8S$ $[M–BF_4]^+$: 637.2835; found: 637.2832.

[1,1'-Binaphthalen]-4-ylbis(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)sulfonium tetrafluoroborate (**14b**)



14b was prepared according to **GP-3** using 1,1'-binaphthalene (50.9 mg, 0.2 mmol, 1.0 equiv.). Flash column chromatography on silica gel (hexane/CH_2Cl_2 = 100:0 – 0:100; then CH_2Cl_2/MeOH = 100:0 to 97:3) afforded the title compound (131.7 mg, 0.155 mmol, 77%) as a yellow oil.

R_f (CH_2Cl_2/MeOH = 95:5): 0.2.

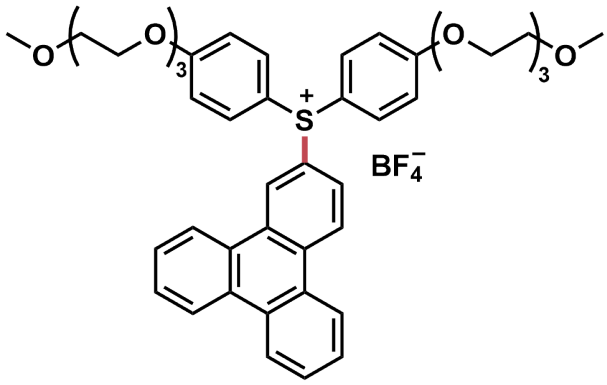
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (d, J = 8.6 Hz, 1H), 8.02 (d, J = 8.2 Hz, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.81 (d, J = 8.9 Hz, 2H), 7.77 (d, J = 8.9 Hz, 2H), 7.72–7.67 (m, 2H), 7.66–7.54 (m, 3H), 7.54–7.42 (m, 3H), 7.41–7.24 (m, 6H), 4.29–4.20 (m, 4H), 3.92–3.86 (m, 4H), 3.79–3.72 (m, 4H), 3.72–3.67 (m, 4H), 3.67–3.64 (m, 4H), 3.61–3.53 (m, 4H), 3.38 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.0, 163.9, 146.0, 135.7, 133.9, 133.4 (2C), 133.2, 131.9, 130.0, 129.9, 129.7, 129.1, 128.4, 128.3, 128.3, 128.0, 127.8, 126.7, 126.3, 125.7, 125.3, 122.6, 121.3, 118.0, 118.0, 112.8, 112.4, 71.8, 70.7, 70.5, 70.4, 69.1, 68.3, 59.0.

^{19}F NMR (471 MHz, $CDCl_3$) δ –152.08.

ESI-HRMS calcd for $C_{46}H_{51}O_8S$ $[M–BF_4]^+$: 763.3305, found: 763.3301.

Bis(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)(triphenylen-2-yl)sulfonium tetrafluoroborate (**14c**)



14c was prepared according to **GP-3** using triphenylene (45.7 mg, 0.2 mmol, 1.0 equiv.). Flash column chromatography on silica gel (hexane/CH_2Cl_2 = 100:0 to 0:100; then CH_2Cl_2/MeOH = 100:0 to 97:3) afforded the title compound (141.7 mg, 0.172 mmol, 86%) as a yellow oil.

R_f (CH_2Cl_2/MeOH = 95:5): 0.2.

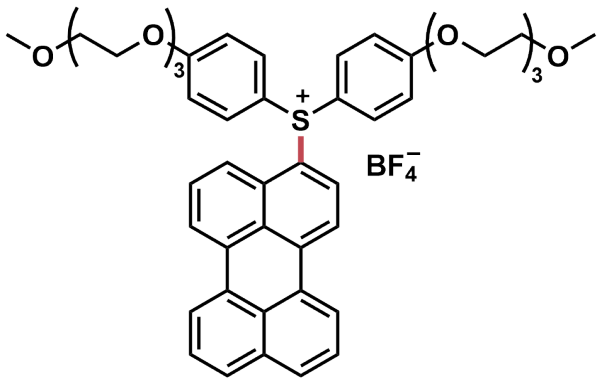
^{1}H NMR (396 MHz, $CDCl_3$) δ 8.81 (d, J = 2.3 Hz, 1H), 8.60 (d, J = 9.1 Hz, 1H), 8.32–8.24 (m, 4H), 7.70–7.63 (m, 4H), 7.59 (dd, J = 8.9, 2.1 Hz, 1H), 7.56–7.41 (m, 4H), 7.15–7.09 (m, 4H), 4.16–4.04 (m, 4H), 3.83–3.74 (m, 4H), 3.66–3.56 (m, 12H), 3.51–3.44 (m, 4H), 3.29 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 133.4, 132.9, 131.1, 130.6, 129.9, 129.2, 128.7, 128.0, 127.7, 127.5, 127.4, 126.8 (2C), 126.0, 123.9 (2C), 123.5, 123.2, 123.1, 117.6, 114.8, 71.8, 70.7, 70.5, 70.4, 69.1, 68.2, 58.9.

^{19}F NMR (373 MHz, $CDCl_3$) δ –151.15.

ESI-HRMS calcd for $C_{44}H_{49}O_8S$ $[M–BF_4]^+$: 737.3148; found 737.3140.

Bis(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)(perylen-3-yl)sulfonium tetrafluoroborate (**14d**)



14d was prepared according to the procedures as noted below using perylene (1.0 equiv.). Flash column chromatography on silica gel (hexane/CH_2Cl_2 = 100:0 to 0:100, then CH_2Cl_2/MeOH = 100:0 to 97:3) afforded the title compound (isolated yield noted below) as a red sticky oil, which appears fluorescent yellow in dilution.

Isolated yield according to GP-3 [0.2 mmol scale]: 76.5 mg, 0.087 mmol, 44%.

Isolated yield according to GP-2 [0.2 mmol scale]: 91.2 mg, 0.107 mmol, 54%.

Isolated yield according to GP-2 [0.5 mmol scale]: 206.3 mg, 0.243 mmol, 49%.

R_f (CH_2Cl_2/MeOH = 95:5): 0.3.

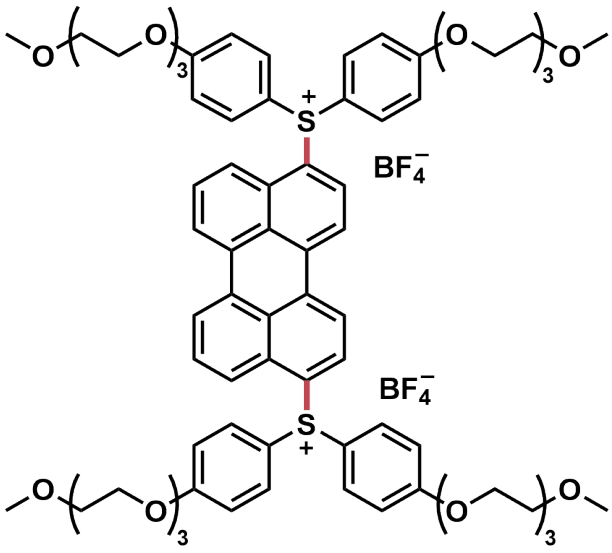
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, J = 8.2 Hz, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.82 (d, J = 7.6 Hz, 1H), 7.77 (dd, J = 14.1, 7.9 Hz, 2H), 7.68 (d, J = 8.9 Hz, 4H), 7.53 (d, J = 8.2 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.27–7.20 (m, 3H), 7.18 (d, J = 9.0 Hz, 5H), 4.17 (dd, J = 6.2, 3.4 Hz, 4H), 3.85–3.80 (m, 4H), 3.69–3.66 (m, 4H), 3.63 (d, J = 4.9 Hz, 4H), 3.61–3.57 (m, 4H), 3.52–3.48 (m, 4H), 3.32 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.9, 137.6, 133.9, 133.3, 132.3, 131.4, 130.8, 130.6, 129.6, 129.2, 129.2, 129.0, 128.2, 127.5, 126.8, 126.6, 123.1, 121.9, 121.4, 121.2, 119.9, 118.6, 117.9, 113.2, 71.9, 70.8, 70.6, 70.6, 69.2, 68.3, 59.1.

^{19}F NMR (471 MHz, $CDCl_3$) δ –151.70.

ESI-HRMS calcd for $C_{46}H_{49}O_8S$ $[M–BF_4]^+$: 761.3148; found: 761.3137.

Perylene-3,10-diylbis(bis(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)sulfonium) ditetrafluoroborate (14d')



Perylene-bis-sulfonium salt **14d'** was prepared according to a modified general procedure **GP-3** using 4,4'-sulfinylbis((2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene) (322.5 mg, 0.61 mmol, 3.0 equiv.) and perylene (51.4 mg, 0.20 mmol, 1.0 equiv.). Tf_2O (0.30 mL, 1.8 mmol, 9.0 equiv.) and conc. H_2SO_4 (0.050 mL, 0.94 mmol, 4.6 equiv.) were added dropwise under air, respectively. The reaction mixture was stirred at rt for 5 h. Upon completion, the reaction mixture was diluted with CH_2Cl_2, and sat. aq. $NaHCO_3$ was added to the mixture, which was further stirred for 1 min. Then, the organic layer was separated and washed with sat. $NaBF_4$ aq. (2×), dried over $NaBF_4$, filtered and concentrated in vacuo. Flash column chromatography on silica gel (eluent: hexane/CH_2Cl_2 = 100:0 to 0:100; then CH_2Cl_2/MeOH = 100:0 to 95:5 to 90:10) afforded the title compound (100.4 mg, 0.20 mmol, 34%) as a red sticky oil.

R_f (CH_2Cl_2/MeOH = 90:10): 0.0 – 0.2 (broad).

<u>Note 1:</u> When the anion exchanging between TfO^- and BF_4^- with $NaBF_4$ is not completed by above procedure, further washing with sat. aq. $NaBF_4$ is required.

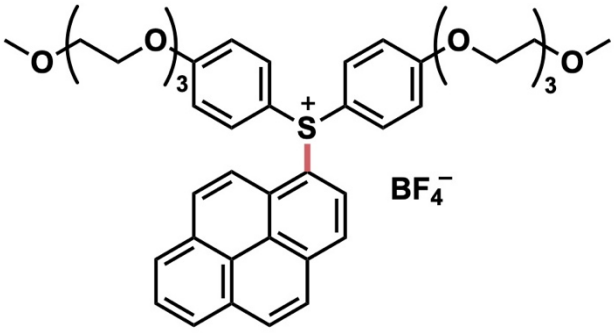
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, J = 8.2 Hz, 2H), 8.04 (d, J = 8.2 Hz, 2H), 7.76–7.72 (m, 10H), 7.47 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.9 Hz, 8H), 6.99 (t, J = 7.9 Hz, 2H), 4.23 (t, J = 4.5 Hz, 8H), 3.88 (t, J = 4.5 Hz, 8H), 3.73–3.72 (m, 8H), 3.68–3.66 (m, 8H), 3.65–3.63 (m, 8H), 3.54–3.53 (m, 8H), 3.36 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.0, 135.0, 133.4, 131.5, 130.3, 129.3 (2C), 128.0, 124.3, 124.2, 122.3, 120.8, 117.9, 113.4, 71.9, 70.9, 70.7, 70.60, 69.3, 68.4, 59.1.

^{19}F NMR (373 MHz, $CDCl_3$) –150.90.

ESI-HRMS calcd for $C_{72}H_{86}O_{16}S_2$ $[M–(BF_4)_2]^{2+}$: 635.2673; found: 635.2676.

Bis(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)(pyren-1-yl)sulfonium tetrafluoroborate (**14e**)



14e was prepared according to **GP-3** using pyrene (40.5 mg, 0.2 mmol, 1.0 equiv.). Flash column chromatography on silica gel (hexane/CH_2Cl_2 = 100:0 to 0:100; then CH_2Cl_2/MeOH = 100:0 to 97:3) afforded the title compound (119.2 mg, 0.149 mmol, 75%) as a yellow oil.

R_f (CH_2Cl_2/MeOH = 95:5): 0.2.

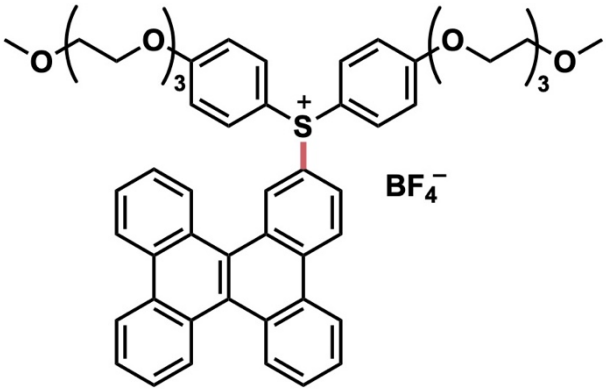
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.43 (d, J = 9.1 Hz, 1H), 8.25–8.16 (m, 3H), 8.16–8.08 (m, 2H), 8.00 (t, J = 7.7 Hz, 1H), 7.94 (d, J = 8.9 Hz, 1H), 7.77 (d, J = 8.3 Hz, 1H), 7.63 (d, J = 9.1 Hz, 4H), 7.14 (d, J = 8.9 Hz, 4H), 4.17–4.10 (m, 4H), 3.79 (t, J = 4.5 Hz, 4H), 3.65 (t, J = 4.7 Hz, 4H), 3.62–3.59 (m, 4H), 3.59–3.55 (m, 4H), 3.50–3.45 (m, 4H), 3.29 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.9, 135.4, 133.3, 132.5, 131.8, 131.2, 131.1, 130.4, 128.2, 128.2, 127.8, 127.1, 126.3, 125.4, 123.6, 120.7, 118.0, 116.3, 113.9 (2C), 72.0, 70.9, 70.9, 70.7, 70.7, 70.5, 69.4, 68.4, 59.2.

^{19}F NMR (471 MHz, $CDCl_3$) δ –152.31.

ESI-HRMS calcd for $C_{42}H_{47}O_8S$ $[M–BF_4]^+$: 711.2992, observed 711.2987.

Dibenzo[*g*,*p*]chrysen-3-ylbis(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)sulfonium tetrafluoroborate (**14f**)



14f was prepared according to **GP-2** using dibenzo[*g*,*p*]chrysene (32.8 mg, 0.1 mmol, 1.0 equiv.). Flash column chromatography on silica gel (hexane/CH_2Cl_2 = 100:0 to 0:100; then CH_2Cl_2/MeOH = 100:0 to 97:3) afforded the title compound (62.5 mg, 0.067 mmol, 67%) as a colorless oil.

R_f (CH_2Cl_2/MeOH = 95:5): 0.1.

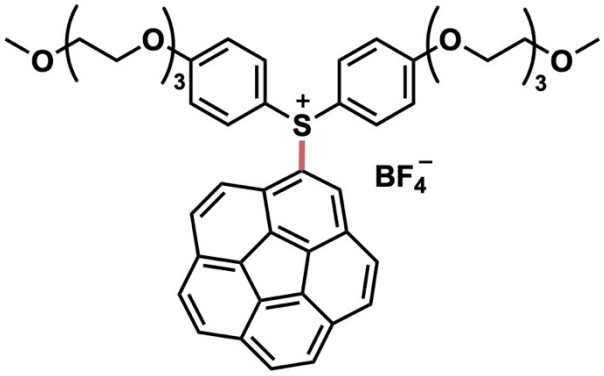
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.96 (d, J = 2.3 Hz, 1H), 8.69 (d, J = 8.9 Hz, 1H), 8.59 (t, J = 7.6 Hz, 2H), 8.53 (d, J = 8.2 Hz, 1H), 8.47 (dd, J = 8.3, 5.2 Hz, 2H), 8.35 (d, J = 8.0 Hz, 1H), 7.67–7.50 (m, 11H), 7.15 (d, J = 8.9 Hz, 4H), 4.16 (dd, J = 6.0, 3.7 Hz, 4H), 3.82 (t, J = 4.7 Hz, 4H), 3.68 (q, J = 3.6, 2.8 Hz, 4H), 3.64 (t, J = 4.6 Hz, 4H), 3.62–3.60 (m, 3H), 3.53–3.49 (m, 4H), 3.33 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ163.8, 135.5, 133.1, 132.3, 132.0, 131.9, 131.6, 130.9, 130.5, 129.6, 129.2, 129.2, 129.0, 128.5, 128.4, 128.4, 128.0, 127.9, 127.4, 127.0, 126.7, 125.9, 125.3, 124.1, 123.8, 122.8, 117.8, 114.8, 72.0, 70.9, 70.6, 70.6, 69.3, 68.4, 59.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ –151.38.

ESI-HRMS calcd for $C_{52}H_{53}O_8S$ $[M–BF_4]^+$: 837.3461; found: 837.3454.

Dibenzo[*ghi*,*mno*]fluoranthen-2-ylbis(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)sulfonium tetrafluoroborate (**14g**)



14g was prepared according to **GP-2** using dibenzo[*ghi*,*mno*]fluoranthene (50.6 mg, 0.2 mmol, 1.0 equiv.). Flash column chromatography on silica gel (hexane/CH_2Cl_2 = 100:0 to 0:100; then CH_2Cl_2/MeOH = 100:0 to 97:3) afforded the title compound (113.6 mg, 0.134 mmol, 67%) as a yellow oil.

R_f (CH_2Cl_2/MeOH = 95:5): 0.1.

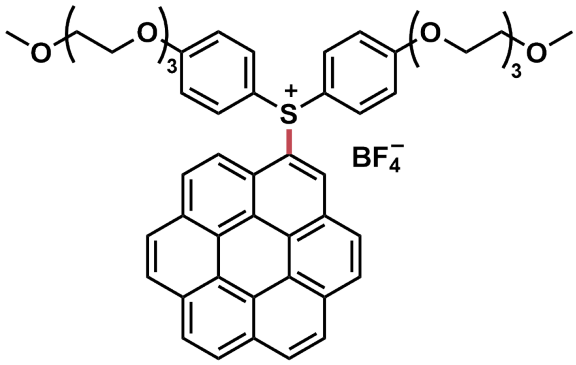
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84–7.75 (m, 5H), 7.72–7.65 (m, 6H), 7.65–7.55 (m, 2H), 7.26–7.17 (m, 4H), 4.19 (dd, J = 5.6, 3.5 Hz, 4H), 3.87–3.79 (m, 4H), 3.68 (dd, J = 6.0, 3.4 Hz, 4H), 3.63 (dd, J = 5.9, 3.4 Hz, 4H), 3.64–3.56 (m, 4H), 3.54–3.46 (m, 4H), 3.32 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.0, 137.2, 135.7, 135.6, 134.8, 134.4, 133.5, 132.6, 132.1, 131.3, 131.1, 129.8, 129.4, 129.2, 129.0, 128.8, 128.7, 127.7, 127.3, 127.1, 126.9, 122.9, 122.7, 118.0, 113.7, 71.8, 70.7, 70.5, 70.5, 69.2, 68.3, 59.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ –151.41.

ESI-HRMS calcd for $C_{46}H_{47}O_8S$ $[M–BF_4]^+$: 758.2992, found 759.2985.

Coronen-1-ylbis(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)sulfonium tetrafluoroborate (**14h**)



14h was prepared according to **GP-2** using coronene (scale noted below, 1.0 equiv.). Flash column chromatography on silica gel (hexane/CH_2Cl_2 = 100:0 to 0:100, then CH_2Cl_2/MeOH = 100:0 to 97:3) afforded the title compound (isolated yield noted below) as a dark yellow sticky oil.

Isolated yield according to GP-2 [0.2 mmol scale]: 101.8 mg, 0.114 mmol, 57%.

Isolated yield according to GP-2 [0.5 mmol scale]: 357.7 mg, 0.399 mmol, 80%.

R_f (CH_2Cl_2/MeOH = 95:5): 0.1.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (d, J = 8.2 Hz, 1H), 8.14 (s, 1H), 8.09 (d, J = 8.3 Hz, 1H), 7.93 (d, J = 8.8 Hz, 4H), 7.85 (d, J = 8.2 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.58 (d, J = 8.1 Hz, 1H), 7.47 (d, J = 8.1 Hz, 1H), 7.40 (d, J = 8.1 Hz, 1H), 7.33 (d, J = 8.2 Hz, 1H), 7.28 (d, J = 9.2 Hz, 5H), 7.22 (d, J = 8.1 Hz, 1H), 4.28–4.18 (m, 4H), 3.85 (t, J = 4.6 Hz, 4H), 3.69 (dd, J = 5.9, 3.5 Hz, 4H), 3.63 (dd, J = 5.8, 3.7 Hz, 4H), 3.63–3.52 (m, 4H), 3.54–3.43 (m, 4H), 3.31 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.9, 133.8, 131.0, 128.4, 128.4, 127.1, 126.8, 126.7, 126.6, 126.5, 126.4, 126.0, 125.8, 125.6, 124.9, 124.6, 124.6, 124.5, 122.8, 121.7, 121.0, 118.6, 118.3, 118.3, 118.3, 118.0 (2C), 117.8, 114.0, 71.9, 70.8, 70.6, 70.5, 69.3, 68.4, 59.0.

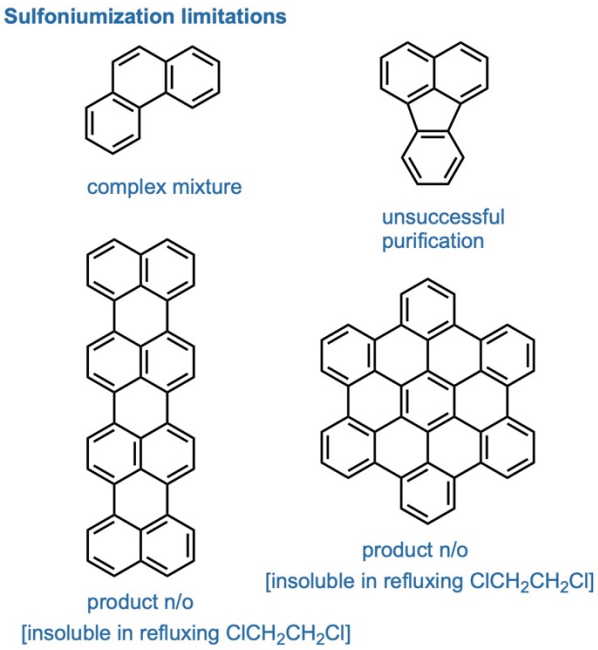
^{19}F NMR –150.32.

ESI-HRMS calcd for $C_{50}H_{49}O_8S$ $[M–BF_4]^+$: 809.3148; found 809.3132.

Note: The increase in yield in scaled up experiments may be partially due to more facile workup on a larger scale.

2.3.5 Limitations

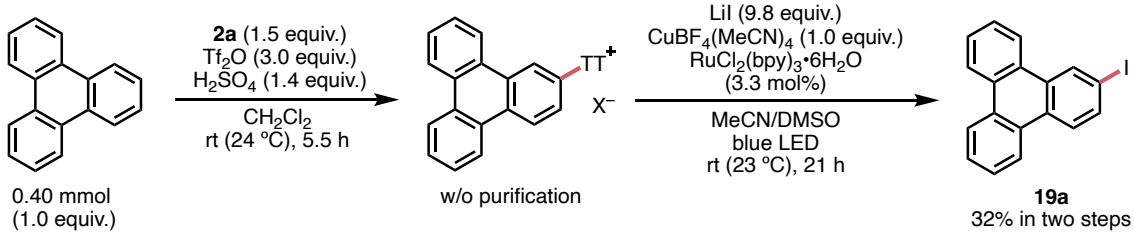
Similar as in the thianthrenation protocol, phenanthrene delivered a complex reaction mixture using TEG-diaryl sulfoxide **9e**, while the fluoranthene adduct could not be sufficiently purified. No product formation was observed for very large PAHs such as quaterrylene or hexabenzocoronene, likely due to their low solubility in refluxing 1,2-dichloroethane.



Scheme S7. Unsuccessful PAHs for the sulfoniumization using TEG-diaryl sulfoxide **9e**.

2.4 Postfunctionalizations of PAH sulfonium salts

2.4.1 Thianthrenation of triphenylene and and iodination



Thianthrene 5-oxide (**2a**) (141.1 mg, 0.61 mmol, 1.5 equiv.) and triphenylene (91.4 mg, 0.40 mmol, 1.0 equiv.) were added to a 25-mL test tube equipped with a PTFE-coated stirring bar under air. Dry CH_2Cl_2 (8 mL) was added before Tf_2O (0.25 mL, 1.2 mmol, 3.0 equiv.) and conc. H_2SO_4 (0.040 mL, 0.56 mmol, 1.4 equiv.) were added dropwise, respectively. The reaction mixture was stirred at rt (24 °C) for 5.5 h. Upon completion of thianthrenation, CH_2Cl_2 and sat. aq. $NaHCO_3$ were added and the mixture was stirred for 1 min. Then, organic layer was separated, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude triphenylene-thianthrenium salt was used for the next reaction without further purification.

Under an ambient atmosphere, a 25-mL test tube equipped with a PTFE-coated stirring bar was charged with $RuCl_2(bpy)_3{\cdot}6H_2O$ (10.0 mg, 0.013 mmol, 3.3 mol%), LiI (527.1 mg, 3.9 mmol, 9.8 equiv.), $CuBF_4(MeCN)_4$ (126.7 mg, 0.40 mmol, 1.0 equiv.), and the crude thianthrenium salt (maximum 0.040 mmol, 1.0 equiv.) in MeCN (8 mL). The mixture was degassed by bubbling with N_2 and the test tube was capped with a plastic cap and a PTFE-coated septum. The test tube was irradiated with blue LEDs (456 nm, 40 W × 2) at rt (23 °C) for 21 h. The reaction mixture was passed through a short pad of silica gel, and the solvent was removed under reduced pressure. The residue was purified by preparative thin-layer column chromatography (pTLC) (hexane) and GPC (eluent: $CHCl_3$). The product was dried in vacuo to afford 45.7 mg (0.13 mmol, 32 %) of 2-iodotriphenylene (**19a**) as a colorless solid.

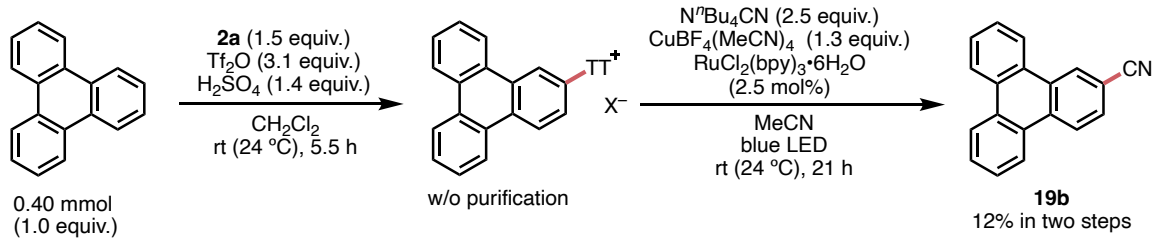
R_f (hexane): 0.3.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.98 (d, J = 1.7 Hz, 1H), 8.65 (d, J = 7.6 Hz, 2H), 8.61–8.56 (m, 2H), 8.37 (d, J = 8.6 Hz, 1H), 7.93 (dd, J = 8.6, 1.7 Hz, 1H), 7.70–7.65 (m, 4H).

^{13}C NMR (600 MHz, $CDCl_3$) δ 135.8, 132.5, 131.8, 130.0, 129.8, 129.2, 129.1, 128.4, 127.9, 127.7, 127.5, 127.4, 125.1, 123.4, 123.4f, 123.4, 123.1, 93.4.

DART-HRMS calcd for $C_{18}H_{12}I$ $[M+H]^+$: 354.9984; found: 354.9969.

2.4.2 Thianthrenation of triphenylene and cyanation



Using the similar procedure in the synthesis of **19a**, the crude triphenylene-thianthrenium salt was prepared by the reaction of thianthrene 5-oxide (**2a**) (139.3 mg, 0.60 mmol, 1.5 equiv.) and triphenylene (91.5 mg, 0.40 mmol, 1.0 equiv.).

Under an ambient atmosphere, a 25-mL test tube equipped with a PTFE-coated stirring bar was charged with N^{n}Bu$_4$CN (265.2 mg, 0.99 mmol, 2.5 equiv.), $RuCl_2(bpy)_3{\cdot}6H_2O$ (6.6 mg, 0.0088 mmol, 2.5 mol%) and $CuBF_4(MeCN)_4$ (157.9 mg, 0.50 mmol, 1.3 equiv.). The test tube capped with a plastic cap and a PTFE-coated septum and filled with N_2. The crude thianthrenium salt (maximum 0.40 mmol, 1.0 equiv.) in MeCN (8 mL) was added by a syringe and the test tube was irradiated with blue LEDs (456 nm, 40 W × 2) at rt (24 °C) for 21 h. The reaction mixture was passed through a short pad of silica gel, and the solvent was removed under reduced pressure. The residue was purified by pTLC (eluent: hexane/EtOAc = 9:1) and GPC (eluent: $CHCl_3$). The product was dried in vacuo to afford 12.6 mg (0.050 mmol, 12%) of 2-cyanotriphenylene (**19b**) as a white solid.

Note: As N^nBu_4CN is hygroscopic, N^nBu_4CN was dried in vacuo after added to the test tube.

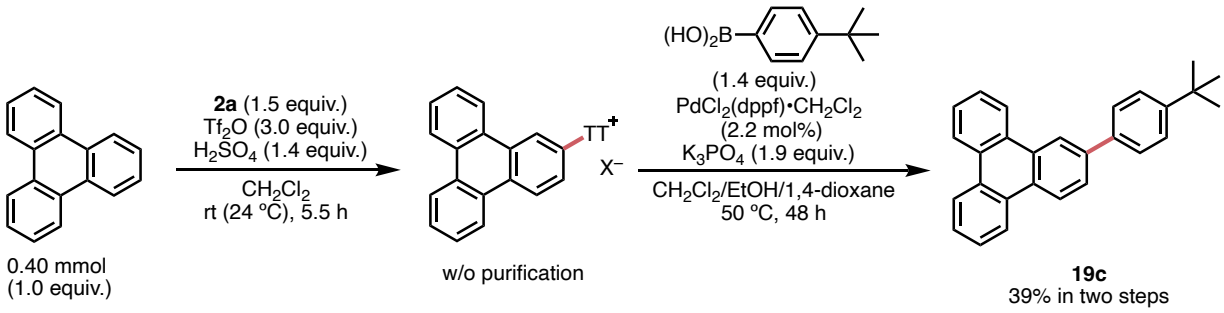
R_f (hexane/EtOAc = 90:10): 0.3.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.72 (d, J = 8.2 Hz, 1H), 8.69–8.67 (m, 2H), 8.64 (d, J = 8.2 Hz, 1H), 8.58 (d, J = 7.6 Hz, 1H), 7.86 (dd, J = 8.2, 1.4 Hz, 1H), 7.77–7.70 (m, 4H).

^{13}C NMR (600 MHz, $CDCl_3$) δ 133.1, 131.0, 130.3, 130.1, 129.1, 129.1, 128.6, 128.5, 128.4, 128.0, 127.9, 124.5, 124.1, 123.7, 123.7, 123.4, 119.5, 110.7.

DART-HRMS calcd for $C_{19}H_{11}N$ $[M]^+$: 253.0892; found: 253.0895.

2.4.3 Thianthrenation of triphenylene and Suzuki–Miyaura coupling



Using a similar procedure as for the synthesis of **19a**, the crude triphenylene-thianthrenium salt was prepared by the reaction of thianthrene 5-oxide (**2a**) (140.4 mg, 0.60 mmol, 1.5 equiv.) and triphenylene (92.3 mg, 0.40 mmol, 1.0 equiv.).

Under an ambient atmosphere, a 25-mL test tube equipped with a PTFE-coated stirring bar was charged with 4-*tert*-butylphenylboronic acid (97.5 mg, 0.55 mmol, 1.4 equiv.), $PdCl_2(dppf)\cdot CH_2Cl_2$ (6.6 mg, 9.0 μmol, 2.2 mol%), K_3PO_4 (167 mg, 0.79 mmol, 1.9 equiv.), the crude of thianthrenium salt (maximum 0.40 mmol, 1.0 equiv.) in CH_2Cl_2 (8 mL), 1,4-dioxane (0.8 mL) and EtOH (0.8 mL). The mixture was degassed by bubbling with N_2 and the test tube was capped with a plastic cap and a PTFE-coated septum. The mixture was stirred at 50 °C for 48

h, and then passed through a short pad of silica gel. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel (hexane) and GPC ($CHCl_3$). The product was dried in vacuo to afford 57.3 mg (0.16 mmol, 39 % in two steps) of 2-(4-*tert*-butylphenyl)triphenylene (**19c**) as a colorless solid.

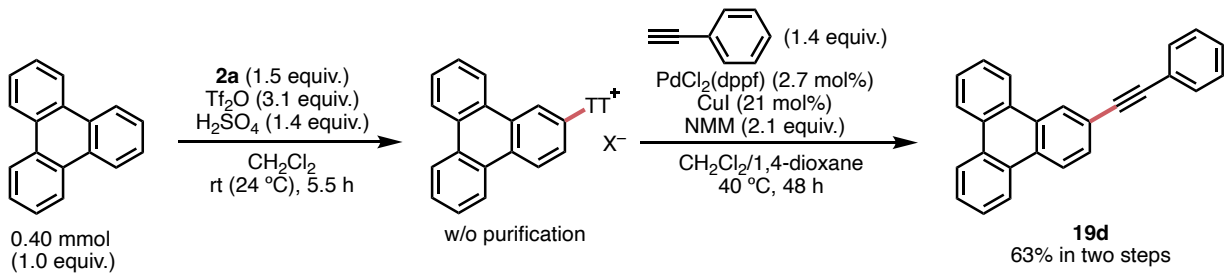
R_f (hexane/EtOAc = 95:5): 0.4.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.86 (d, J = 1.4 Hz, 1H), 8.75–8.74 (m, 1H), 8.71 (d, J = 8.6 Hz, 1H), 8.69–8.67 (m, 3H), 7.91 (dd, J = 8.4, 1.5 Hz, 1H), 7.76 (d, J = 8.2 Hz, 2H), 7.70–7.67 (m, 4H), 7.57 (d, J = 7.9 Hz, 2H), 1.41 (s, 9H).

^{13}C NMR (600 MHz, $CDCl_3$) δ 150.7, 139.9, 138.4, 130.2, 130.2, 130.0, 129.9, 129.8, 128.8, 127.4, 127.4 (2C), 127.3, 127.2, 126.4, 126.0, 124.0, 123.5, 123.5, 123.4 (2C), 121.7, 34.8, 31.6.

DART-HRMS calcd for $C_{28}H_{25}$ $[M+H]^+$: 361.1956; found: 361.1968.

2.4.4 Thianthrenation of triphenylene and Sonogashira–Hagihara coupling



Using the similar procedure in the synthesis of **19a**, the crude triphenylene-thianthrenium salt was prepared by the reaction of thianthrene 5-oxide (**2a**) (139.9 mg, 0.60 mmol, 1.5 equiv.) and triphenylene (90.6 mg, 0.40 mmol, 1.0 equiv.).

Under an ambient atmosphere, a 25-mL test tube equipped with a PTFE-coated stirring bar was charged with CuI (16.1 mg, 0.085 mmol, 21 mol%), $PdCl_2$(dppf)·CH_2Cl_2 (7.8 mg, 9.6 μmol, 2.4

mol%), ethynylbenzene (0.060 mL, 0.55 mmol, 1.4 equiv.), *N*-methylmorphine (NMM) (0.092 mL, 0.83 mmol, 2.1 equiv.) and the crude of thianthrenium salt (maximum 0.40 mmol, 1.0 equiv.) in CH_2Cl_2 (8 mL) and 1,4-dioxane (1.6 mL). The mixture was degassed by bubbling with N_2 and the test tube was capped with a plastic cap and a PTFE-coated septum. The mixture was stirred at 40 °C for 48 h, and then passed through a short pad of silica gel. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel (eluent: hexane). The product was dried in vacuo to afford 82.6 mg (0.25 mmol, 63 % in two steps) of 2-(2-phenylethynyl)triphenylene (**19d**) as a colorless solid.

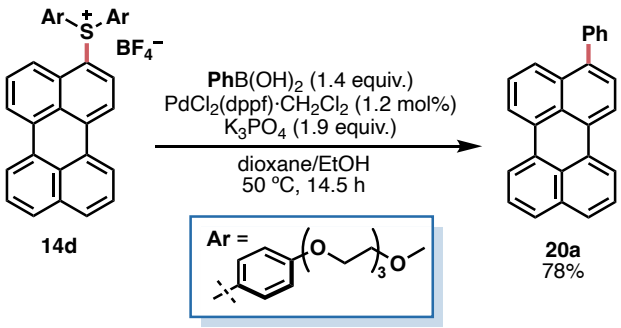
R_f (hexane/EtOAc = 95:5): 0.4.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.69–8.62 (m, 5H), 7.80 (dd, J = 8.2, 1.4 Hz, 1H), 7.70–7.66 (m, 4H), 7.64 (dd, J = 8.2, 1.4 Hz, 2H), 7.42–7.37 (m, 3H).

^{13}C NMR (600 MHz, $CDCl_3$) δ 131.8, 130.1, 130.1, 130.0, 129.8, 129.6, 129.4, 129.2, 128.6, 128.5, 127.7, 127.7, 127.5, 127.4, 126.9, 123.6, 123.5, 123.5, 123.4, 123.4 (2C), 122.0, 90.3, 90.0.

DART-HRMS calcd for $C_{26}H_{17}$ $[M+H]^+$: 329.1330; found: 329.1331.

2.4.5 Suzuki–Miyaura coupling of perylene mono-sulfonium salt



Under an ambient atmosphere, a 7-mL test tube equipped with a PTFE-coated stirring bar was charged with sulfonium salt **14d** (83.5 mg, 0.098 mmol, 1.0 equiv.), phenylboronic acid (16.8

mg, 0.14 mmol, 1.4 equiv.), K_3PO_4 (39.6 mg, 0.19 mmol, 1.9 equiv.), $PdCl_2(dppf)\cdot CH_2Cl_2$ (1.0 mg, 1.2 μmol, 1.2 mol%), 1,4-dioxane (0.4 mL), and EtOH (0.4 mL). The mixture was degassed by bubbling with N_2 and the test tube was capped with a plastic cap and a PTFE-coated septum. The mixture was stirred at 50 °C for 14.5 h, and then passed through a short pad of silica gel, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: CH_2Cl_2) to afford 25.3 mg (0.077 mmol, 78 %) of 3-phenylperylene (**20a**) as a yellow solid.

R_f (hexane/EtOAc = 95:5): 0.4.

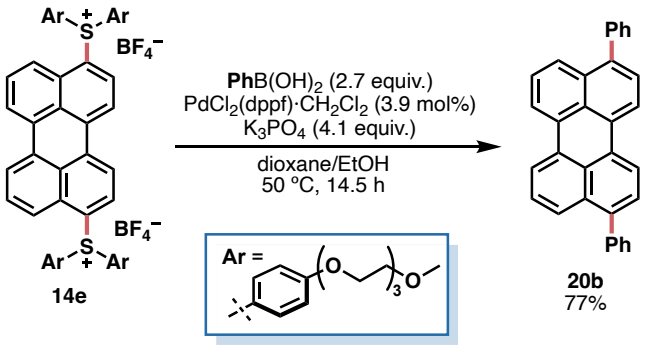
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25–8.21 (m, 4H), 7.77 (d, J = 8.2 Hz, 1H), 7.70 (d, J = 8.2 Hz, 2H), 7.54–7.48 (m, 6H), 7.46–7.42 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.9, 140.1, 134.9, 133.1, 131.6, 131.6, 131.4, 130.8, 130.1 (2C), 129.2, 128.8, 128.5 (2C), 128.0, 127.9, 127.9, 127.5, 126.8 (2C), 126.7, 126.3, 120.5 (2C), 120.3, 120.1.

DART-HRMS calcd for $C_{26}H_{17}$ $[M+H]^+$: 329.1330; found: 329.1335.

Note: All multiple carbon counts have been accounted for in the ^{13}C NMR.

2.4.6 Suzuki-Miyaura coupling of perylene bis-sulfonium salt and Scholl reaction



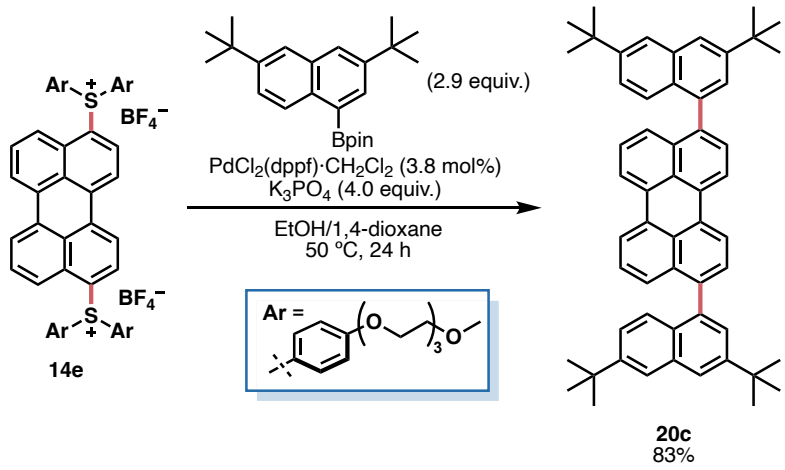
Under an ambient atmosphere, a 7-mL test tube equipped with a PTFE-coated stirring bar was charged with sulfonium salt **14e** (141.2 mg, 0.098 mmol, 1.0 equiv.), phenylboronic acid (32.1 mg, 0.26 mmol, 2.7 equiv.), K_3PO_4 (84.8 mg, 0.40 mmol, 4.1 equiv.), $PdCl_2(dppf)\cdot CH_2Cl_2$ (3.1 mg, 3.8 μmol, 3.9 mol%), 1,4-dioxane (0.4 mL), and EtOH (0.4 mL). The mixture was degassed by bubbling with N_2, and the test tube was capped with a plastic cap and a PTFE-coated septum. The mixture was stirred at 50 °C for 14.5 h, and then passed through a short pad of silica gel. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel (eluent: CH_2Cl_2). The product was dried in vacuo to afford 30.5 mg (0.75 mmol, 77 %) of 3,10-diphenylperylene (**20b**) as a yellow solid.

R_f (hexane/EtOAc = 95:5): 0.4.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (d, J = 7.6 Hz, 2H), 8.26 (d, J = 6.2 Hz, 2H), 7.78 (d, J = 8.2 Hz, 2H), 7.55–7.51 (m, 8H), 7.47–7.44 (m, 6H).

^{13}C NMR (600 MHz, $CDCl_3$) δ 140.9, 140.1, 133.0, 131.6, 131.0, 130.1, 129.1, 128.5, 128.0, 127.5, 126.7, 126.2, 120.4, 120.2.

DART-HRMS calcd for $C_{32}H_{21}$ $[M+H]^+$: 405.1643; found: 405.1647.



Under an ambient atmosphere, a 7-mL test tube equipped with a PTFE-coated stirring bar was charged with sulfonium salt **14e** (70.3 mg, 0.049 mmol, 1.0 equiv.), phenylboronic acid (51.1 mg, 0.14 mmol, 2.9 equiv.), K_3PO_4 (41.6 mg, 0.20 mmol, 4.0 equiv.), $PdCl_2(dppf)\cdot CH_2Cl_2$ (1.5 mg, 1.8 μmol, 3.8 mol%), 1,4-dioxane (0.2 mL), and EtOH (0.2 mL). The mixture was degassed by bubbling with N_2, and the test tube was capped with a plastic cap and a PTFE-coated septum The mixture was stirred at 50 °C for 24 h. The reaction mixture was passed through a short pad of silica, and the solvent was removed under reduced pressure. The residue was purified by pTLC (eluent: hexane). The product was dried in vacuo to afford 29.4 mg (0.040 mmol, 83 %) of 3,10-bis(3,6-di(*tert*-butyl)naphthyl)perylene (**20c**) as a yellow solid.

R_f (hexane/EtOAc = 95:5): 0.5.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (dd, J = 7.9, 1.7 Hz, 2H), 8.29–8.28 (m, 2H), 7.88 (d, J = 7.6 Hz, 4H), 7.59 (d, J = 2.1 Hz, 2H), 7.53 (d, J = 7.6 Hz, 2H), 7.43 (dd, J = 8.9, 5.5 Hz, 2H), 7.39 (dd, J = 8.9, 2.1 Hz, 2H), 7.37–7.35 (m, 4H), 1.48 (s, 9H), 1.47 (s, 9H), 1.42 (s, 9H), 1.41 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.7, 148.3, 139.0, 137.7, 134.3, 133.7, 131.6, 131.1, 129.3, 128.9, 126.9, 126.7, 126.4, 125.9, 125.9, 124.6, 123.4, 123.2, 120.3, 120.1, 35.1, 34.9, 31.5, 31.4.

MALDI-TOF MS calcd for $C_{56}H_{56}^{\bullet+}$ $[M]^{\bullet+}$: 728.4377; found: 728.4381.

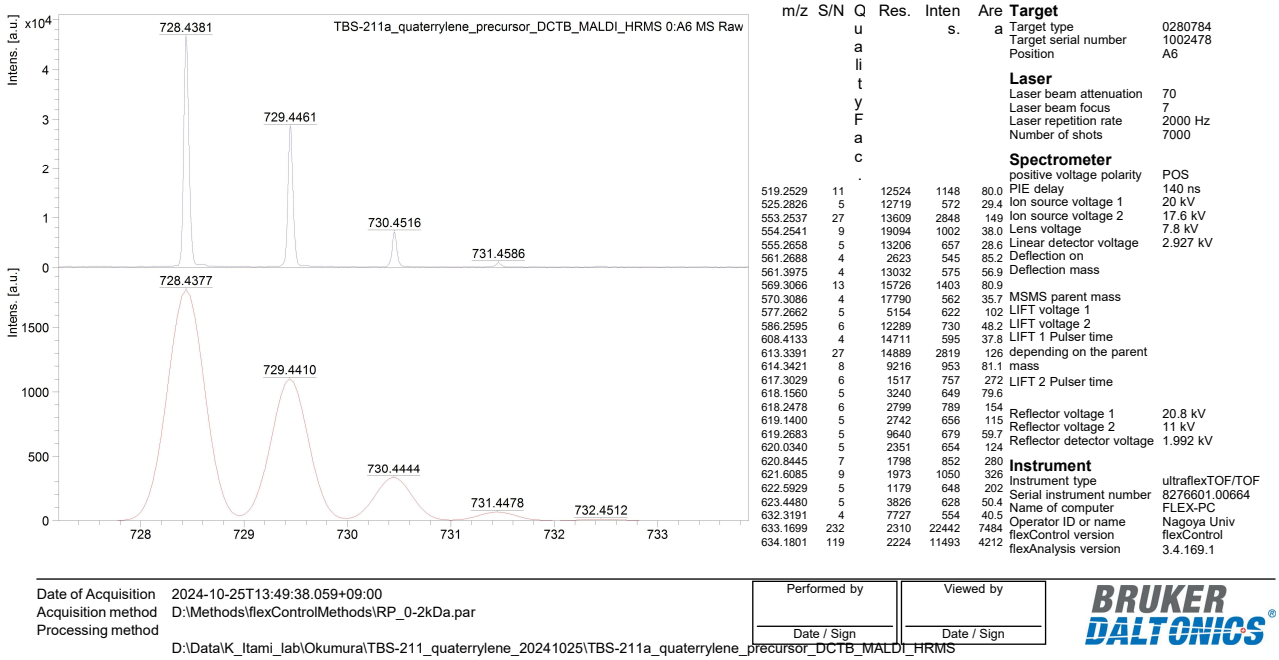
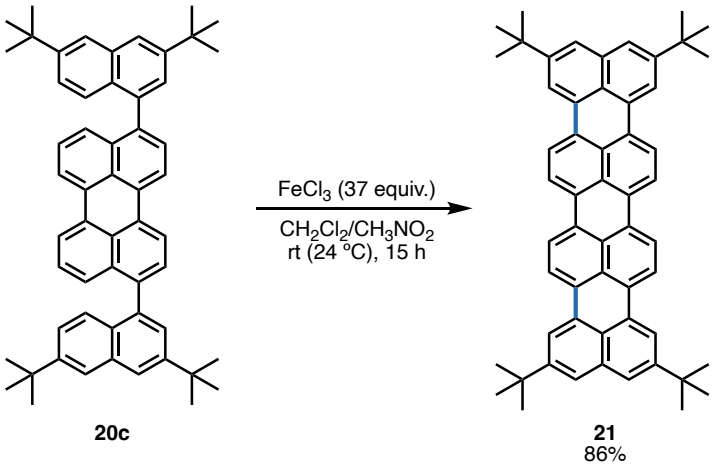


Figure S2. Observed and simulated MALDI-TOF MS spectra of **20c**.



20c **21** 86%

A flame-dried 100-mL two-neck round-bottom flask equipped with a PTFE-coated stir bar was charged with **20c** (27.0 mg, 0.037 mmol, 1.0 equiv.) and CH_2Cl_2 (24 mL) under nitrogen. The mixture was degassed by bubbling with N_2, and the flask was sealed with rubber-septa. Then a solution of $FeCl_3$ (181.3 mg, 1.4 mmol, 37 equiv.) in CH_3NO_2 (0.6 mL) was added dropwise by a syringe. The mixture was stirred at rt (24 °C) for 15 h, and the reaction was quenched by adding excess of methanol. The dark blue precipitate was collected by a membrane filter and washed by methanol. The dark blue solid was transferred to a vial and washed with hexane to remove soluble a red fluorescence component. This hexane-washing is repeated until the red solvent color became transparent. Finally, the solid was dried in vacuo to afford 23.2 mg (0.32 mmol, 86%) of 2,5,12,15-tetrakis(*tert*-butyl)quinterrylene (**21**) as a dark blue solid.

R_f (hexane/EtOAc = 95:5): 0.4.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.46–8.22 (m, 12H), 7.67 (br s, 4H), 1.51 (s, 36H).

MALDI-TOF MS calcd $C_{56}H_{52}^{\bullet+}$ $[M]^{\bullet+}$: 724.4064; found: 724.4072.

*Note: Due to poor solubility of **21**, no ^{13}C NMR spectrum with sufficient quality could be obtained. A similar difficulty in the NMR measument of **21** was previously reported by Koch and Müllen.[13] Absorption spectrum of **21** were identical to those reported in the literature (Figure S3).[13]*

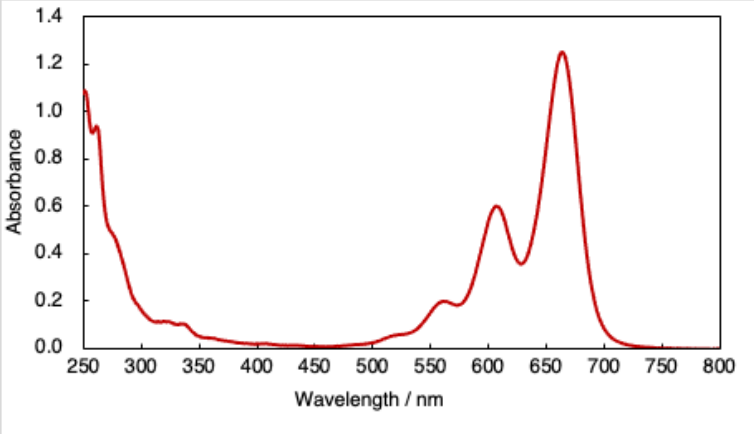


Figure S3. Absorption spectrum of **21** in 1,4-dioxane.

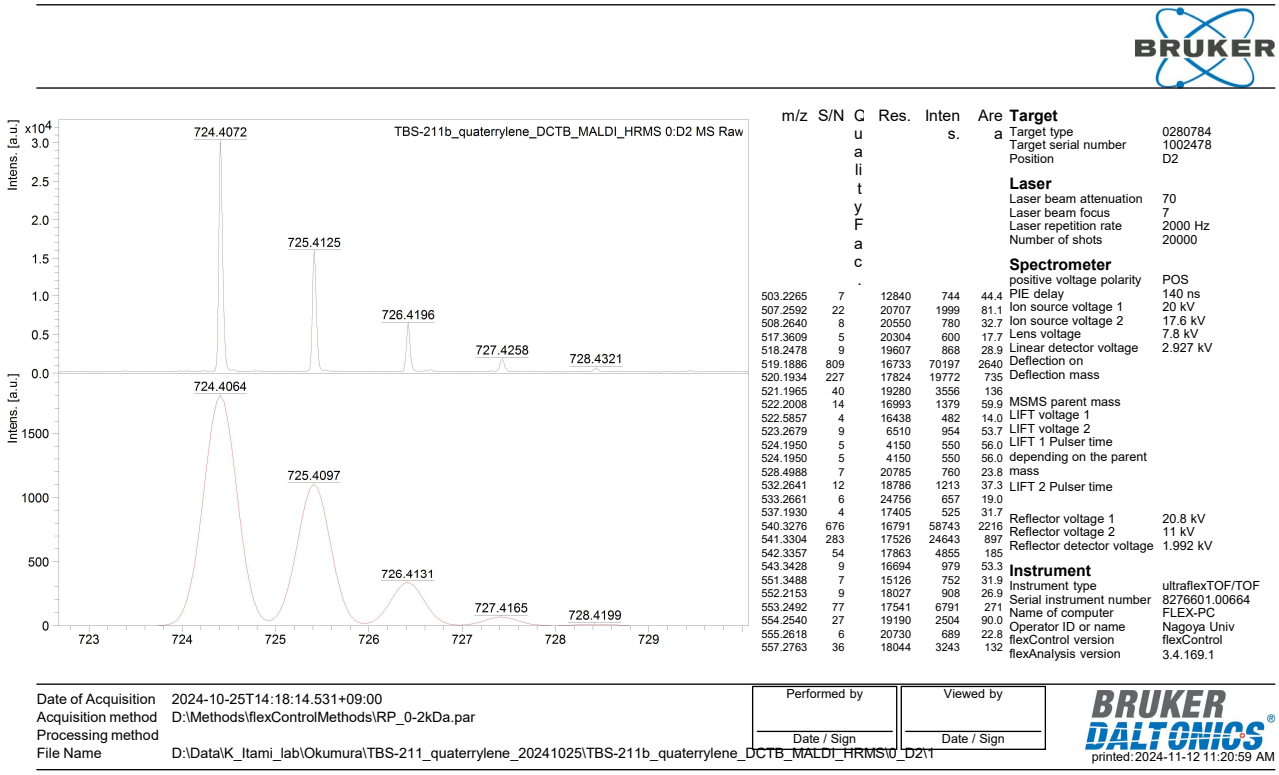


Figure S4. Observed and simulated MALDI-TOF MS spectra of **21**.

2.5 Crystallographic data

Deposition numbers 2408570 (for **3a**-major), 2408571 (for **3a**-minor), 2408572 (for **3b**), and 2397243 (for **21**) contain the supplementary crystallographic data for this manuscript. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service. Regioisomeric mixture of **3a** was recrystallized from CH_2Cl_2/pentane by slow vapor deposition method and the different specimens were analyzed. **3b** was recrystallized from CH_2Cl_2/pentane by slow vapor deposition method, and **21** was recrystallized from $CHCl_3$/hexane by slow vapor deposition method.

X-Ray diffraction analysis of 3a-major, **3a-minor and 3b:** Data sets were collected with a Bruker D8 Venture Photon III Diffractometer. Programs used: data collection: *APEX4* Version 2021.4-0[14] (Bruker AXS Inc., **2021**); cell refinement: *SAINT* Version 8.40B (Bruker AXS Inc., **2021**); data reduction: *SAINT* Version 8.40B (Bruker AXS Inc., **2021**); absorption correction, *SADABS* Version 2016/2 (Bruker AXS Inc., **2021**); structure solution *SHELXT*-Version 2018-3;[15] structure refinement *SHELXL*- Version 2018-3[16] and graphics, *XP*[17] (Version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA, **1998**). *R*-values are given for observed reflections, and wR^2 values are given for all reflections.

X-ray crystal structure analysis of 3a-major: A colorless, prism-like specimen of $C_{22}H_{15}BF_4S_2$, approximate dimensions 0.053 mm × 0.069 mm × 0.087 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Mo ImS (MoKα, λ = 0.71073 Å) and a MX mirror monochromator. A total of 962 frames were collected. The total exposure time was 4.28 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 35379 reflections to a maximum θ angle of 26.74° (0.79 Å resolution), of which 3939 were independent (average redundancy 8.982, completeness = 99.3%, R_{int} = 5.60%, R_{sig} = 2.81%) and 3359 (85.28%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a}$ = 10.6757(6) Å, $\underline{b}$ = 15.4534(7) Å, $\underline{c}$ = 11.9779(7) Å, β = 109.437(2)°, volume = 1863.44(17) Å^3, are based upon the refinement of the XYZ-centroids of 9889 reflections above 20 σ(I) with 4.434° < 2θ < 53.47°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.944. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9720 and 0.9830. The structure was solved and refined using the Bruker SHELXTL Software

Package, using the space group $P2_1/n$, with $Z = 4$ for the formula unit, $C_{22}H_{15}BF_4S_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 262 variables converged at R_1 = 3.25%, for the observed data and wR_2 = 8.74% for all data. The goodness-of-fit was 1.013. The largest peak in the final difference electron density synthesis was 0.321 $e^-/Å^3$ and the largest hole was –0.235 $e^-/Å^3$ with an RMS deviation of 0.051 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.534 g/cm^3 and F(000), 880 e^-. **CCDC Nr.: 2408570**.

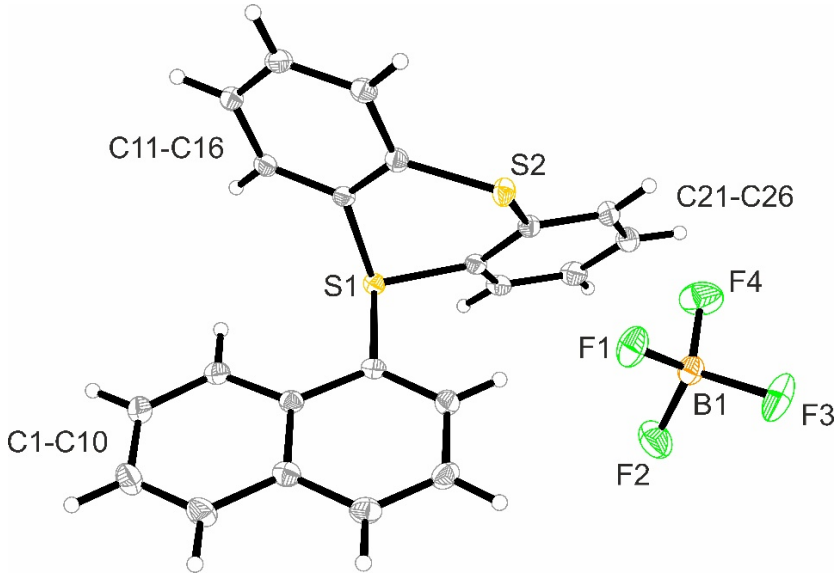


Figure S5: Crystal structure of compound **3a-major** (**CCDC Nr.: 2408570**). Thermal ellipsoids are shown at 50% probability.

X-ray crystal structure analysis of 3a-minor: A colorless, prism-like specimen of $C_{23}H_{17}BCl_2F_4S_2$, approximate dimensions 0.076 mm × 0.118 mm × 0.167 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Mo ImS (MoKα, λ = 0.71073 Å) and a MX mirror monochromator. A total of 1689 frames were collected. The total exposure time was 4.53 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic

unit cell yielded a total of 24570 reflections to a maximum θ angle of 25.35° (0.83 Å resolution), of which 3975 were independent (average redundancy 6.181, completeness = 97.6%, R_{int} = 3.82%, R_{sig} = 2.32%) and 3623 (91.14%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a}$ = 10.3623(3) Å, $\underline{b}$ = 10.7490(3) Å, $\underline{c}$ = 11.4494(3) Å, α = 65.1580(10)°, β = 86.1400(10)°, γ = 73.8820(10)°, volume = 1110.01(5) Å^3, are based upon the refinement of the XYZ-centroids of 9978 reflections above 20 σ(I) with 5.834° < 2θ < 53.45°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.942. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9180 and 0.9610. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 2 for the formula unit, $C_{23}H_{17}BCl_2F_4S_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 363 variables converged at R_1 = 4.24%, for the observed data and wR_2 = 12.18% for all data. The goodness-of-fit was 1.054. The largest peak in the final difference electron density synthesis was 0.530 e$^-$/Å^3 and the largest hole was –0.478 e$^-$/Å^3 with an RMS deviation of 0.057 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.541 g/cm^3 and F(000), 524 e$^-$. **CCDC Nr.: 2408571**.

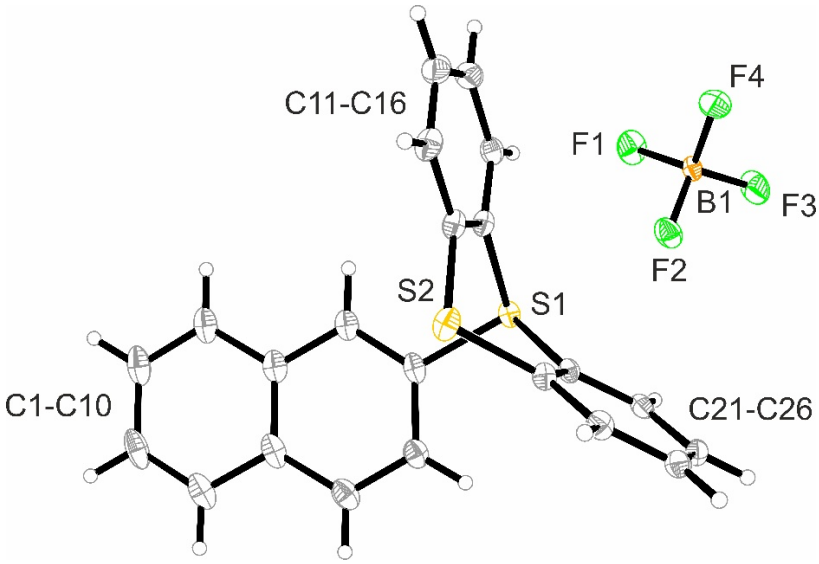


Figure S6: Crystal structure of compound **3a-minor** (**CCDC Nr.: 2408571**). Thermal ellipsoids are shown at 30% probability.

X-ray crystal structure analysis of 3b: A colorless, plate-like specimen of $C_{28}H_{19}BF_4S_2$, approximate dimensions 0.045 mm × 0.108 mm × 0.146 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Mo ImS (MoKα, λ = 0.71073 Å) and a MX mirror monochromator. A total of 1777 frames were collected. The total exposure time was 11.91 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 54106 reflections to a maximum θ angle of 26.73° (0.79 Å resolution), of which 5311 were independent (average redundancy 10.188, completeness = 99.6%, R_{int} = 3.57%, R_{sig} = 1.73%) and 4840 (91.13%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a}$ = 15.1406(8) Å, $\underline{b}$ = 10.3948(5) Å, $\underline{c}$ = 32.4934(17) Å, β = 100.849(2)°, volume = 5022.5(4) Å^3, are based upon the refinement of the XYZ-centroids of 9941 reflections above 20 σ(I) with 4.781° < 2θ < 54.97°. Data were corrected for absorption effects using the multi-scan

method (SADABS). The ratio of minimum to maximum apparent transmission was 0.955. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9640 and 0.9890. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *C*2/*c*, with $Z = 8$ for the formula unit, $C_{28}H_{19}BF_4S_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 362 variables converged at $R_1 = 3.37\%$, for the observed data and w$R_2 = 8.85\%$ for all data. The goodness-of-fit was 1.038. The largest peak in the final difference electron density synthesis was 0.373 $e^-/Å^3$ and the largest hole was –0.307 $e^-/Å^3$ with an RMS deviation of 0.046 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.339 g/cm^3 and *F*(000), 2080 e^-. **CCDC Nr.: 2408572**.

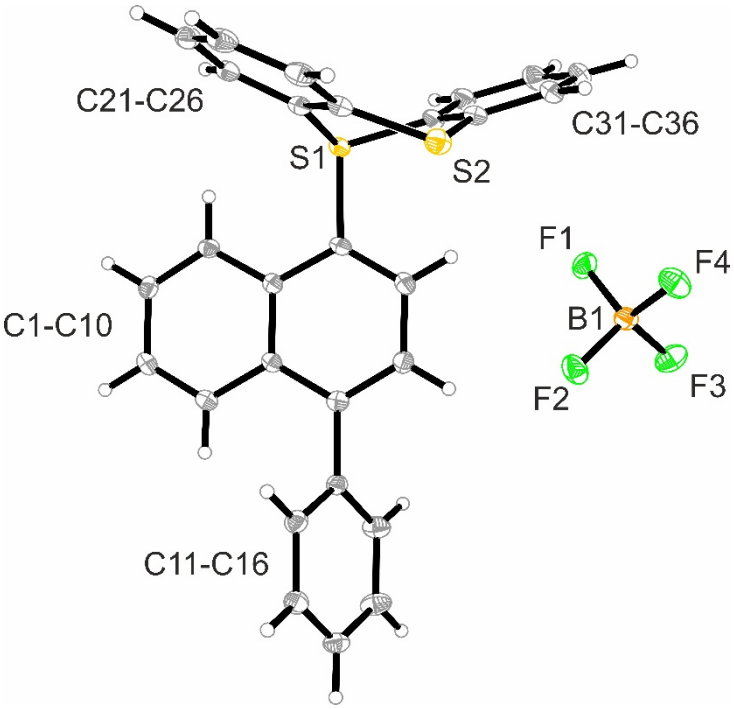


Figure S7: Crystal structure of compound **3b** (**CCDC Nr.: 2408572**). Thermal ellipsoids are shown at 50% probability.

X-ray crystal structure analysis of 21 (**CCDC Nr.: 2397243**)**:** Crystal data details and intensity data collection parameter summary for **21** is listed in Table S1. A suitable crystal was mounted with mineral oil on a MiTeGen MicroMounts and transferred to the goniometer of the kappa goniometer of a RIGAKU XtaLAB Synergy-S system with 1.2 kW MicroMax-007HF microfocus rotating anode (Graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and PILATUS200K hybrid photon-counting detector. The cell parameters were determined and refined, and the raw frame data were integrated using CrysAlis^{Pro} (Agilent Technologies, 2010). The structures were solved by direct methods with (SHELXT)[15] and refined by full-matrix least-squares techniques against $F2$ (SHELXL-2018/3)[16] by using Olex2 software package.[18] The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions. Visualization was performed with Mercury[19] 3.8 using ORTEP style.

Table S1. Crystallographic data and structure refinement details of **21** (**CCDC Nr.: 2397243**).

formula	$C_{29}H_{27}Cl_3$ (**21** + $CHCl_3$)	V (Å^3)	2409.6(4)
fw	963.71	Z	2
T (K)	123(2)	ρ_{calc} (g cm^{-3})	1.328
λ (Å)	0.71073	μ (mm^{-1})	0.396
crystal system	*monoclinic*	F(000)	1008.0
space group	$P2_1/c$	Crystal size (mm^3)	0.25 × 0.15 × 0.03
a (Å)	20.8136(18)	2 θ range (°)	3.808–59.654
b (Å)	6.0124(4)	reflections collected	21448
c (Å)	21.4653(18)	independent reflections / R_{int}	5652 / 0.0582
α (°)	90	GOF on F^2	1.075
β (°)	116.226(10)	R_1, wR_2 [$I \geq 2\sigma(I)$]	0.0735, 0.2135
γ (°)	90	R_1, wR_2 (all data)	0.1094, 0.2358

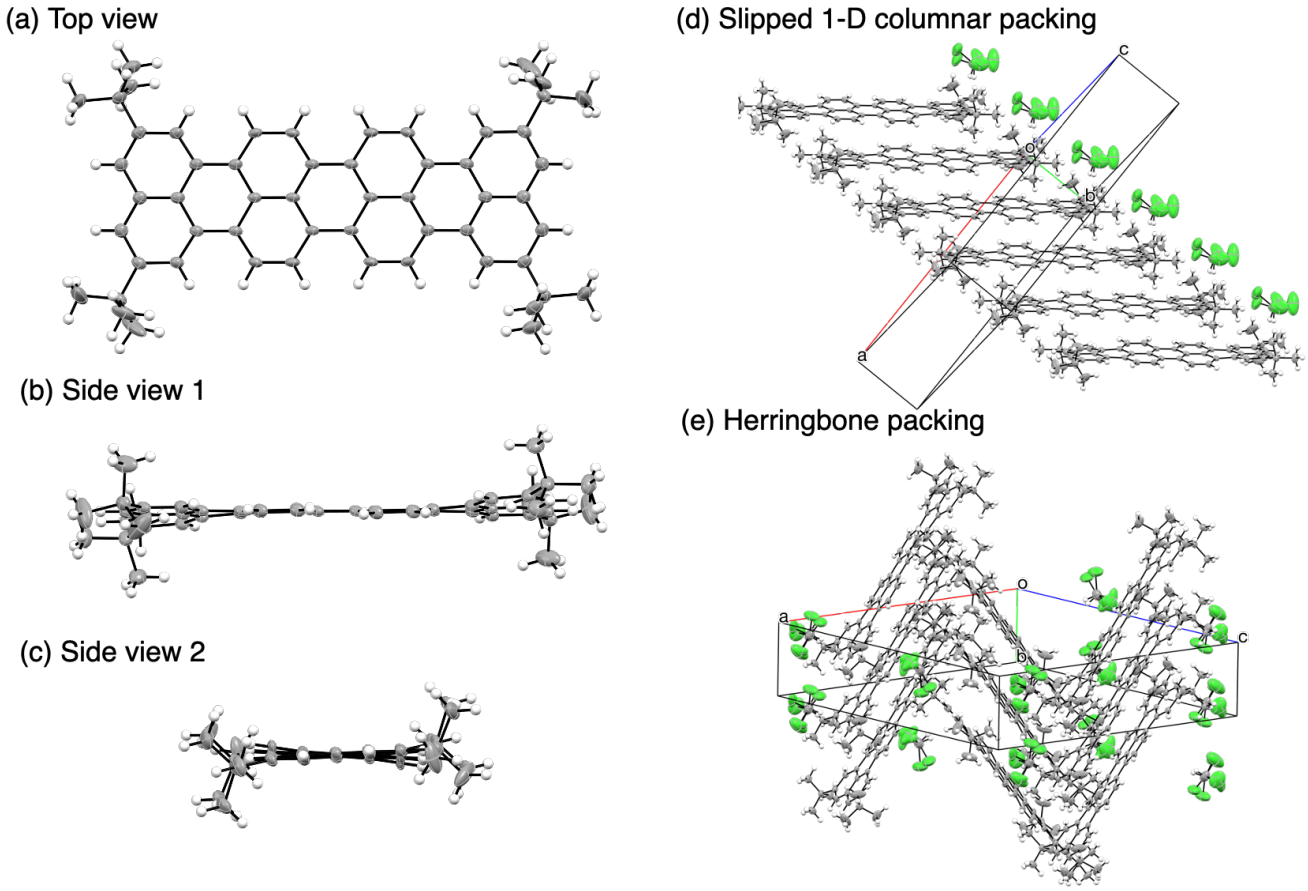


Figure S8. ORTEP drawing of **21** (**CCDC: 2397243**) with 50% thermal ellipticity. Counteranion and solvent are omitted for clarity.

2.6 Photochemical properties

UV-Vis absorption spectra of **14d** (c = 1.46 × 10^{-5} M), **14d′** (c = 1.71 × 10^{-5} M), **perylene** (c = 1.31 × 10^{-5} M) in CH_2Cl_2 and **14d** in H_2O were recorded in a 1.0 × 1.0 cm square quartz cell on a SHIMADZU UV-3600 spectrophotometer with a resolution of 0.5 nm. Emission spectra of **14d, 14d′** and perylene in CH_2Cl_2 or H_2O were measured in degassed spectral grade CH_2Cl_2 or H_2O in a 1.0 × 1.0 cm square quartz cell with a SHIMADZU RF-6000 spectrofluorophotometer with a resolution of 0.2 nm upon excitation at 400 nm (for **14d** in CH_2Cl_2), 450 nm (for **14d** in H_2O), 400 nm (for **14d′** in CH_2Cl_2) and 400 nm (for perylene in CH_2Cl_2), respectively.

3 Biological studies

HeLa cells (ATCC, 0.5 × 10^5 cells) were seeded on glass area of 35-mm glass-bottom dishes (Matsunami) and incubated in high glucose Dulbecco's Modified Eagle Medium (DMEM, Sigma-Aldrich) with 10% fetal bovine serum (FBS, Sigma F7524, Lot: BCBV4600) and 1% Antibiotic-Antimycotic (Anti-Anti, Sigma-Aldrich) under a humidified atmosphere of 5% CO_2 in air at 37 °C for 1 day. Accoding to general procedure, the cell was stained by a mitocondorial marker (MitoBright LT Red, Dojindo). Subsequently, the medium was replaced with a DMEM solution (1.0 mL) of **14d** (1 mM in DMSO, 1 μL) without 10% FBS and 1% Anti-Anti and incubated under a humidified atmosphere of 5% CO_2 in air at 37 °C. After 30 min incubation, the medium was replaced with fresh DMEM, followed by cell imaging with a confocal laser scanning microscope equipped with a 63 × oil immersion objective lens (Carl Zeiss LSM900). The compounds were excited at 488 nm and detected with a window of 490–700 nm, and the mitochondorial marker were excited at 557 nm and detected with a window of 560–700 nm.

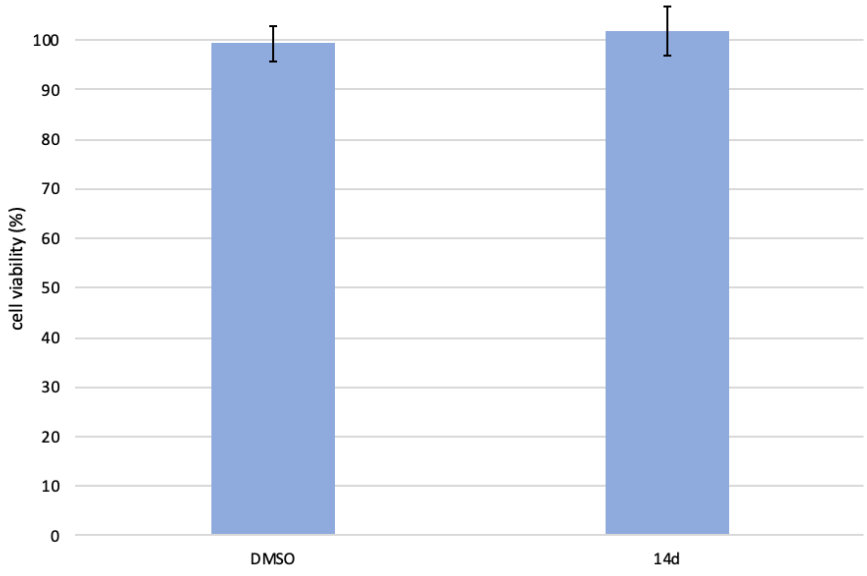


Figure S9. Cytotoxicity test. According to general procedure of MTT assay kit (#10009365 MTT Cell Proliferation Assay Kit, Cayman Chemical Company), **14d** was incubated for 24 h. Values are presented as mean ± SE (n = 3).

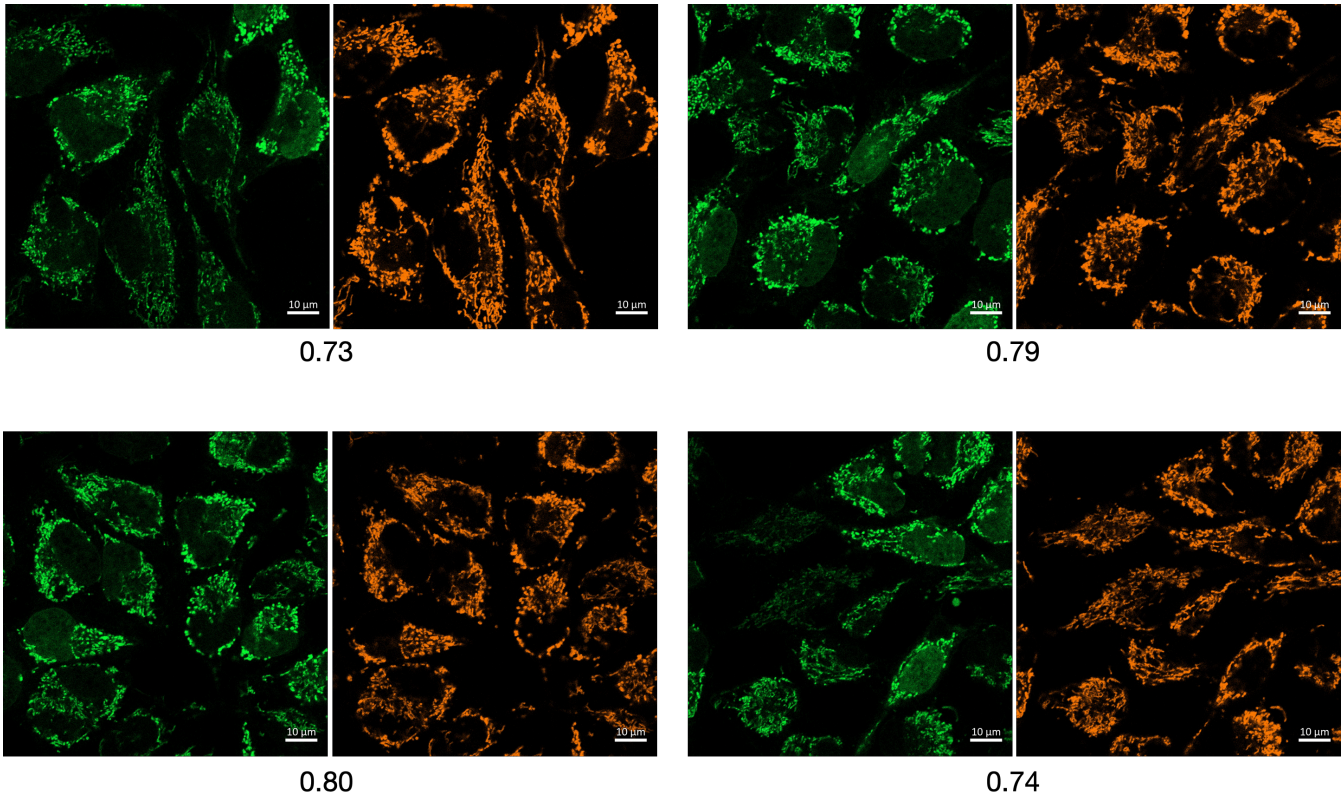


Figure S10. Calculation of Pearson's correlation coefficient by Coloc 2 program in Fiji.

4 Computational studies

For simplification of DFT calculation, **14d-OMe** and **14d′-OMe** were chosen as model compounds for **14d** and **14d′** (Figure S9). Geometry optimizations and frequency calculations of **14d-OMe**, **14d′-OMe** and perylene were performed with the Gaussian 16 program[20] at the B3LYP[21]/6-31G(d,p) level of theory at 298.15 K and 1 atm. Solvent effects by CH_2Cl_2 with a dielectric constant of 8.93 was incorporated using the self-consistent reaction field with conductor-like polarizable continuum model (CPCM).[22] Frequency analysis was performed to verify all stationary points as local minima (with no imaginary frequency) or transition states (with one imaginary frequency). Time-dependant DFT (TD-DFT) calculations with the solvation model based on density (SMD)[23] of optimized **14d**, **14d′** and perylene were also performed at the B3LYP/6-31+G(d,p) level of theory. Corrections to Gibbs free energy were

obtained from the same method as geometry optimization at 298.15 K with the Gaussian 16 programs. Visualization of the results was performed by use of GaussView 6.1 software.[24]

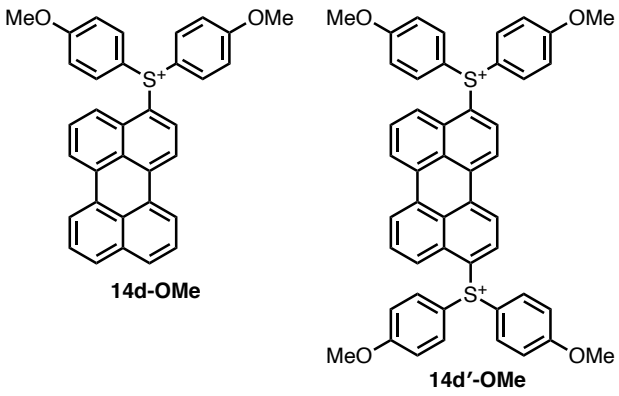


Figure S11. Structures of **14d-OMe** and **14d′-OMe** as model compounds for **14d** and **14d′**.

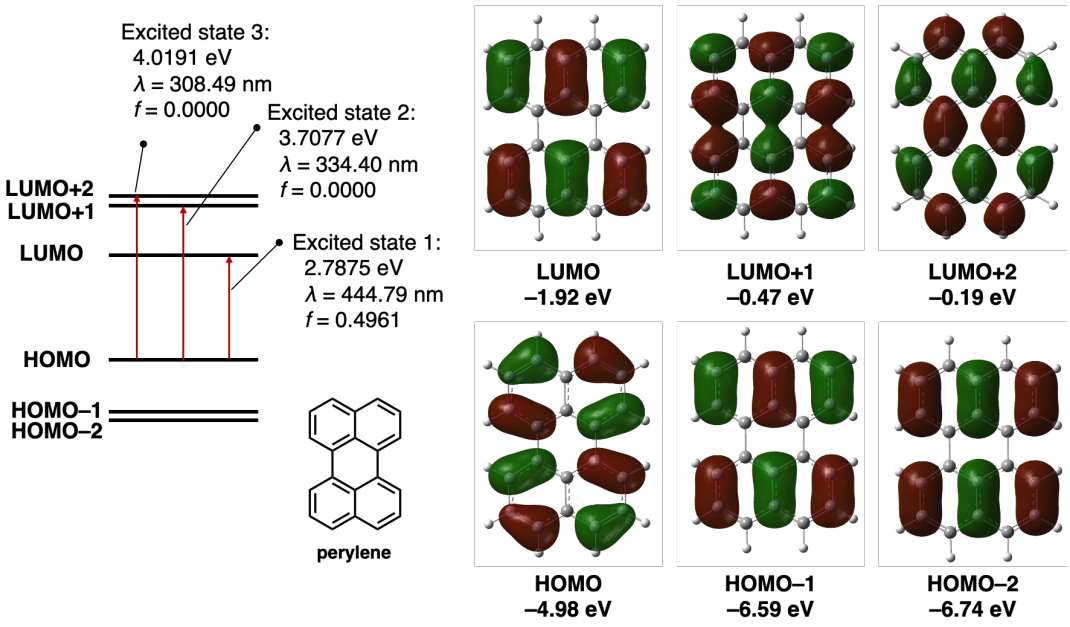


Figure S12. Pictrical frontier molecular orbitals of perylene calculated at B3LYP/6-31G(d,p)/SMD(CH_2Cl_2)// B3LYP/6-31G(d,p)/CPCM(CH_2Cl_2).

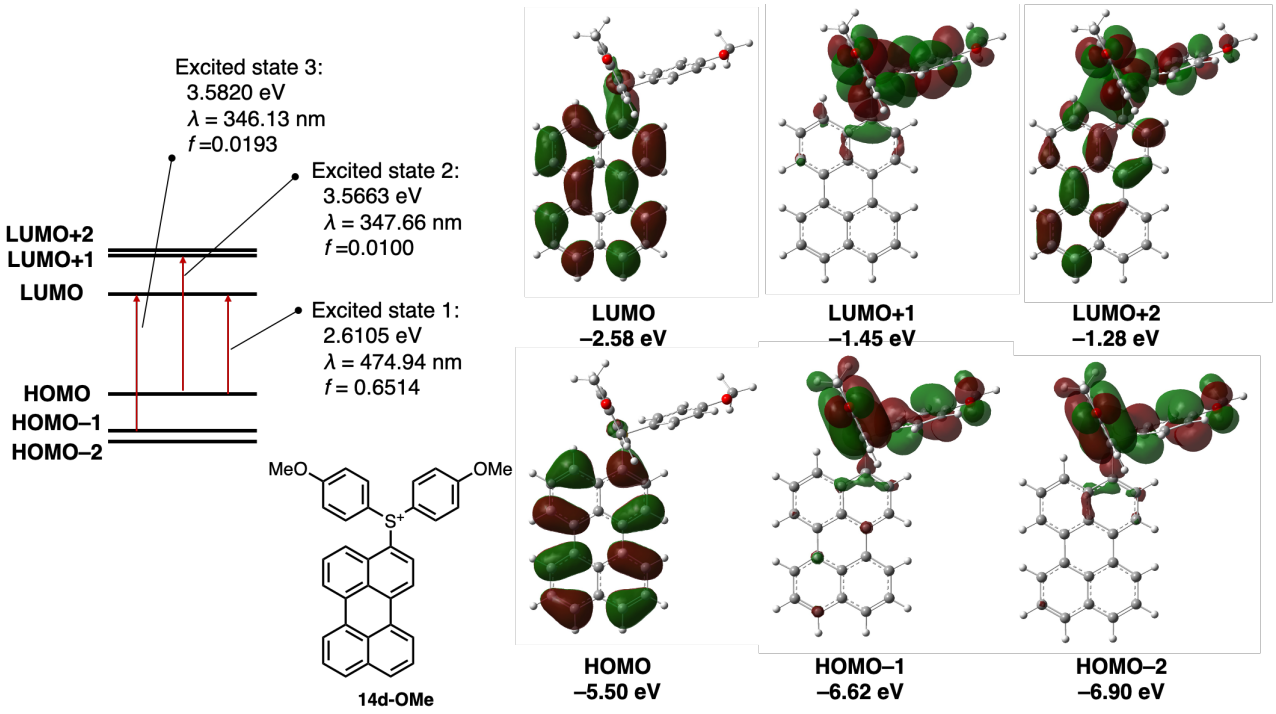


Figure S13. Pictrical frontier molecular orbitals of **14d′ -OMe** calculated at B3LYP/6-31G(d,p)/SMD(CH_2Cl_2)// B3LYP/6-31G(d,p)/CPCM(CH_2Cl_2).

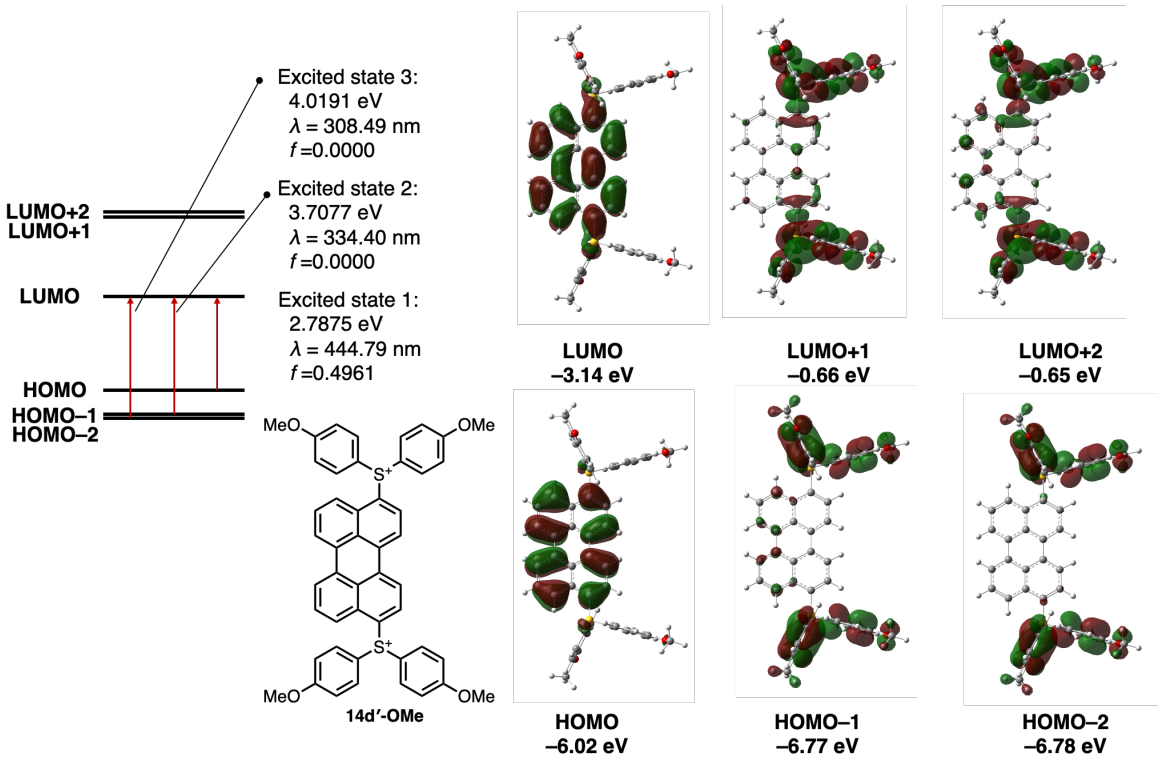


Figure S14. Pictrical frontier molecular orbitals of **14d′-OMe** calculated at B3LYP/6-31G(d,p)/SMD(CH_2Cl_2)// B3LYP/6-31G(d,p)/CPCM(CH_2Cl_2).

Table S2. Uncorrected and thermal-corrected (298.15 K, 1 atm) energies (Hartree) of stationary points calculated at the B3LYP/6-31G(d,p)/CPCM(CH_2Cl_2) level of theory.

Structure	*E*	*ZPEC*	*TCE*	*TCF*	*H*	*G*
14d-OMe	-1859.189659	0.493087	0.524030	0.428818	-1858.665629	-1858.760841
14d′-OMe	-2948.939864	0.732122	0.780111	0.643692	-2948.159753	-2948.296172
perylene	-769.430299	0.253916	0.266944	0.216250	-769.163356	-769.214049

E: electronic energy; ZPEC: zeropoint energy correction; TCE: thermal correction to enthalpy; TEF: thermal correction to free energy; *H* (enthalpy) = *E* + *TCE*: sum of electronic energy and thermal correction to enthalpy; *G* (free energy) = *E* + *TCF*: sum of electronic energy and thermal correction to free energy.

Table S3. Cartesian coordinates of optimized structures at the B3LYP/6-31G(d,p)/CPCM(CH_2Cl_2) level of theory.

14d-OMe

C	-2.8487350	-0.5863570	-2.5594710	S	-0.0814210	2.5524450	-1.0856670
C	-2.8355290	-1.9182260	-2.1214950	C	-1.3499740	3.3778370	-0.1198160
C	-1.9295010	-2.3636830	-1.1636160	C	1.4864330	3.2705990	-0.5984100
C	-0.9835410	-1.4303050	-0.6222360	C	2.4934260	3.2618120	-1.5680890
C	-1.0102060	-0.0619450	-1.0719680	C	3.7399290	3.8094630	-1.2776320
C	-1.9598840	0.3314170	-2.0462690	C	3.9704110	4.3819180	-0.0160100
C	-0.0148730	-1.8456370	0.3520540	C	2.9404550	4.4027940	0.9444340
C	0.8812280	-0.9037680	0.8516410	C	1.7025020	3.8510020	0.6597670
C	0.8615130	0.4323900	0.4345870	C	-1.9741110	4.4737620	-0.7214560
C	-0.0646350	0.8448080	-0.4990220	C	-2.9672290	5.1676180	-0.0351310
C	0.0131590	-3.2499170	0.7980000	C	-3.3429010	4.7506290	1.2523700
C	-0.9440790	-4.1723710	0.2679340	C	-2.7170620	3.6341320	1.8396790
C	-0.9252700	-5.5353940	0.7139700	C	-1.7245360	2.9467930	1.1606330
C	0.0438580	-5.9476970	1.6635180	O	5.1352930	4.9432340	0.3682420
C	0.9620530	-5.0485740	2.1575530	O	-4.2942210	5.3450840	2.0021680
C	0.9437720	-3.7103080	1.7267670	C	6.2322870	4.9612060	-0.5522700
C	-1.9189190	-3.7630890	-0.6952060	C	-4.9815010	6.4844150	1.4729930
C	-2.8314630	-4.7058810	-1.1611770	H	-3.5691600	-0.2796460	-3.3107630
C	-2.8127230	-6.0411840	-0.7188540	H	-3.5551560	-2.6011140	-2.5546480
C	-1.8760060	-6.4542450	0.2010040	H	-1.9918050	1.3553390	-2.4006950

H	1.6245210	-1.1822580	1.5865300	H	-1.6925600	4.7918070	-1.7201250
H	1.5840360	1.1256060	0.8481380	H	-3.4425130	6.0155660	-0.5109070
H	0.0483330	-6.9828360	1.9920370	H	-3.0297140	3.3227250	2.8300990
H	1.7051660	-5.3637210	2.8828520	H	-1.2575920	2.0810630	1.6163680
H	1.6842200	-3.0382620	2.1427140	H	7.0509160	5.4483830	-0.0241120
H	-3.5878200	-4.4258490	-1.8840110	H	5.9837520	5.5346790	-1.4510500
H	-3.5439880	-6.7406820	-1.1110350	H	6.5294620	3.9451500	-0.8313630
H	-1.8517450	-7.4831300	0.5474830	H	-5.6861010	6.7878240	2.2462810
H	2.3141970	2.8308180	-2.5476950	H	-5.5283360	6.2265270	0.5602970
H	4.5118750	3.7940800	-2.0359430	H	-4.2862070	7.3050870	1.2688880
H	3.1353640	4.8609040	1.9076270				
H	0.9143580	3.8834590	1.4032140				

14d′ -OMe

S	-0.6410410	5.2736890	-0.9930120	C	-0.9437940	6.0870580	0.5761470
S	-0.6428190	-5.2747410	0.9919130	C	1.0276020	5.6917980	-1.4880040
O	4.8112360	6.7160070	-2.7788180	C	1.2662630	5.7288880	-2.8653010
O	-1.6897150	8.0655960	4.1201710	C	2.5316530	6.0621970	-3.3396860
O	4.8036130	-6.7184600	2.7942680	C	3.5550530	6.3743820	-2.4295160
O	-1.6740660	-8.0610480	-4.1278930	C	3.2952900	6.3514570	-1.0448760
C	-4.3139280	2.7963710	-0.6538550	C	2.0393190	6.0129660	-0.5708670
C	-4.3137420	1.4226600	-0.3680440	C	-1.5988790	7.3203150	0.5161220
C	-3.1311010	0.7195790	-0.1649110	C	-1.8624540	8.0211490	1.6896820
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C	-1.8943790	2.8321730	-0.5481680	C	-0.8334830	6.2248580	2.9724770
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C	-1.8871060	-1.4203010	0.2702210	C	3.2936190	-6.3514240	1.0556570
C	-1.8953320	-2.8332950	0.5445130	C	3.5485780	-6.3765460	2.4411540
C	-0.6351020	-3.5024180	0.6180630	C	2.5219500	-6.0661030	3.3482780
C	0.5547990	-2.8274630	0.4637100	C	1.2581290	-5.7323370	2.8700510
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C	-4.3145440	-1.4246620	0.3557210	C	-1.4672340	-7.4729140	-2.9325280
C	-4.3152670	-2.7984250	0.6412810	C	-1.8547400	-8.0194110	-1.6979330
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H	-5.2697350	0.9178970	-0.3161520	H	-2.3969200	9.6098240	5.2129760
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H	1.5043870	-3.3431930	0.5369780	H	4.0967940	-6.6068800	0.3736490
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H	-5.2705300	-0.9202570	0.3003480	H	0.4633010	-5.5046370	3.5728500
H	-5.2596020	-3.3099780	0.7939140	H	-0.0707670	-4.5592730	-1.8531160
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H	-2.3685620	8.9758480	1.6309500	H	-2.3772630	-9.6042300	-5.2247510
H	-0.5551800	5.8177120	3.9380550	H	-3.3416950	-9.2712410	-3.7613270
H	-0.0782680	4.5615910	1.8545730	H	-1.7545310	-10.0911160	-3.6253650

perylene

C	-2.4238010	2.8865130	0.0000000	C	1.2332960	-3.5766850	0.0000000
C	-2.4292490	1.4793470	0.0000000	C	2.4238010	-2.8865130	0.0000000
C	-1.2506580	0.7385680	0.0000000	C	2.4292490	-1.4793470	0.0000000
C	0.0000000	1.4394920	0.0000000	C	1.2506580	-0.7385680	0.0000000
C	0.0000000	2.8752990	0.0000000	H	-3.3687310	3.4212660	0.0000000
C	-1.2332960	3.5766850	0.0000000	H	-3.3895620	0.9778030	0.0000000
C	1.2506580	0.7385680	0.0000000	H	-1.2189710	4.6628320	0.0000000
C	2.4292490	1.4793470	0.0000000	H	3.3895620	0.9778030	0.0000000
C	2.4238010	2.8865130	0.0000000	H	3.3687310	3.4212660	0.0000000
C	1.2332960	3.5766850	0.0000000	H	1.2189710	4.6628320	0.0000000
C	-1.2506580	-0.7385680	0.0000000	H	-3.3895620	-0.9778030	0.0000000
C	-2.4292490	-1.4793470	0.0000000	H	-3.3687310	-3.4212660	0.0000000
C	-2.4238010	-2.8865130	0.0000000	H	-1.2189710	-4.6628320	0.0000000
C	-1.2332960	-3.5766850	0.0000000	H	1.2189710	-4.6628320	0.0000000
C	0.0000000	-2.8752990	0.0000000	H	3.3687310	-3.4212660	0.0000000
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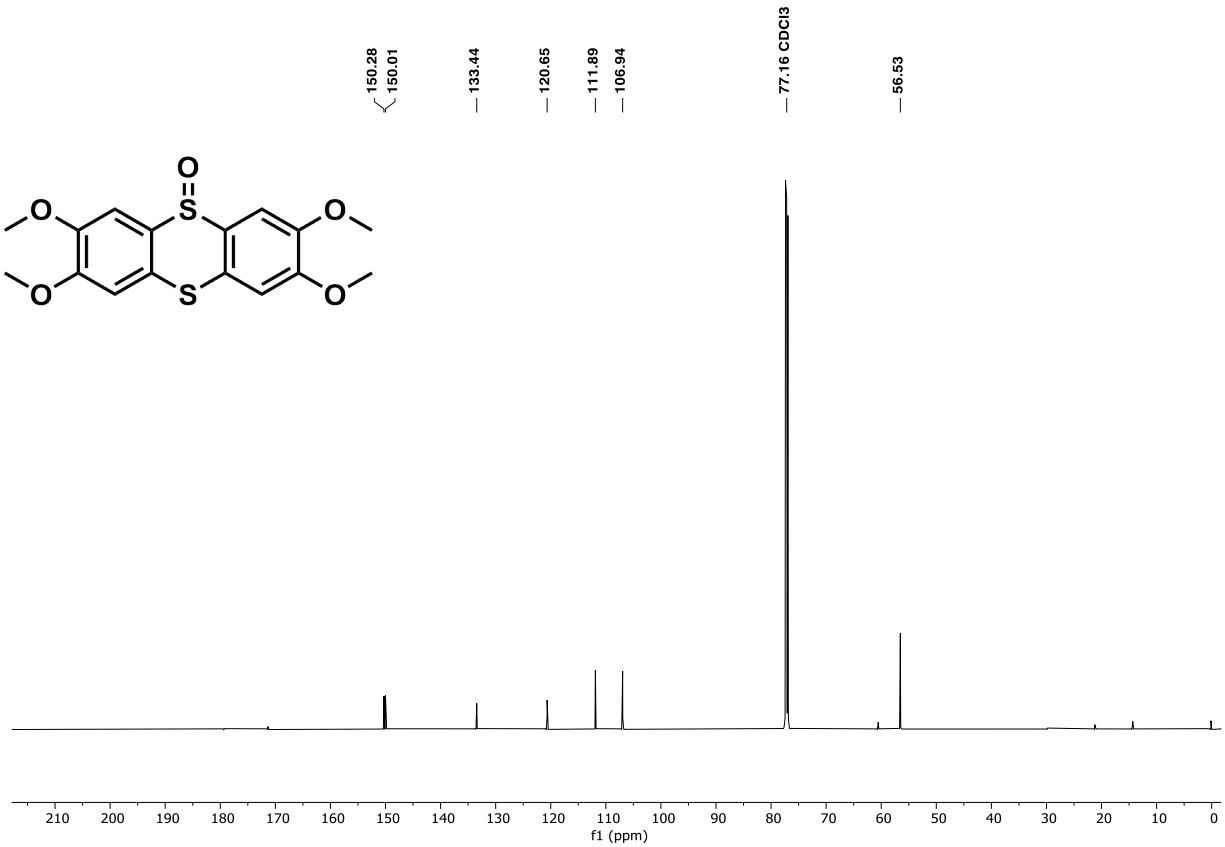
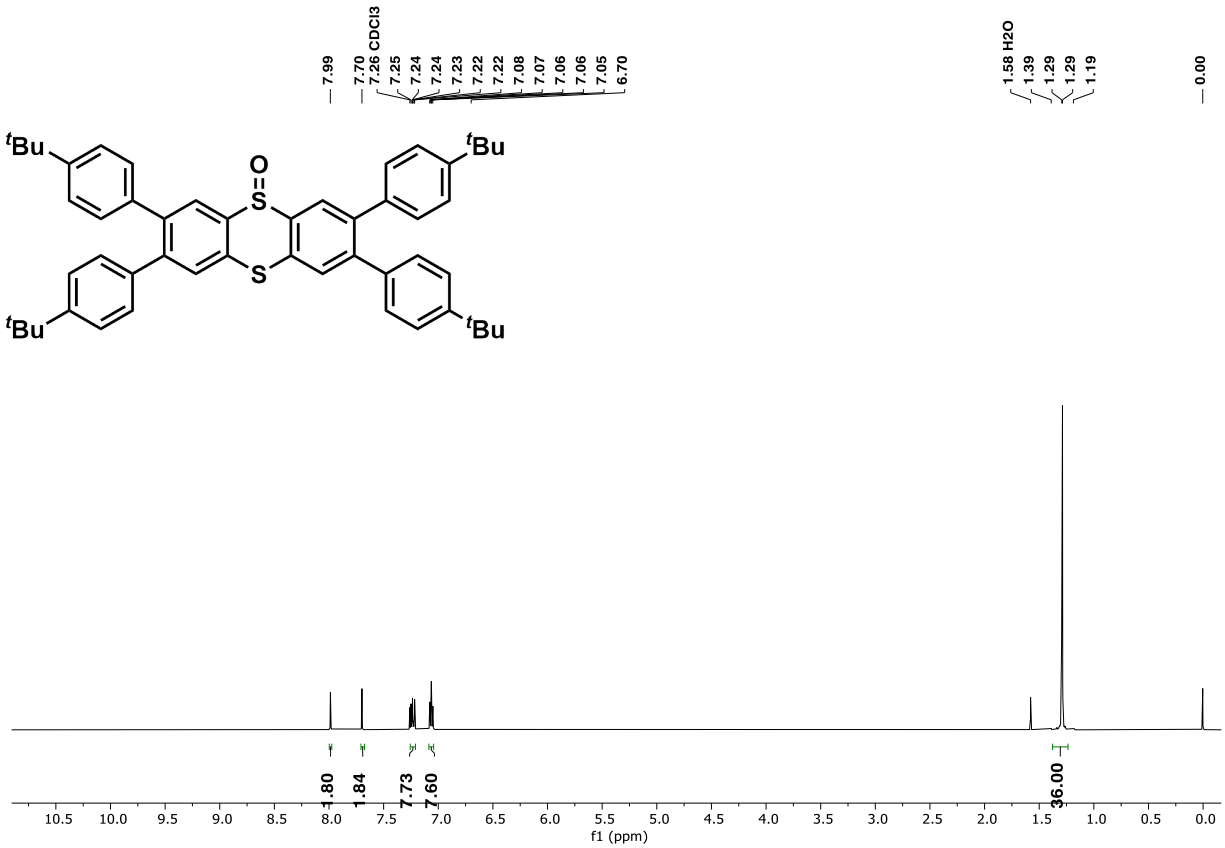
5 NMR spectra

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7.25
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7.06
7.06
7.05
6.70
1.58 H2O
1.39
1.29
1.29
1.19
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tBu
O
S
S
tBu
tBu
tBu
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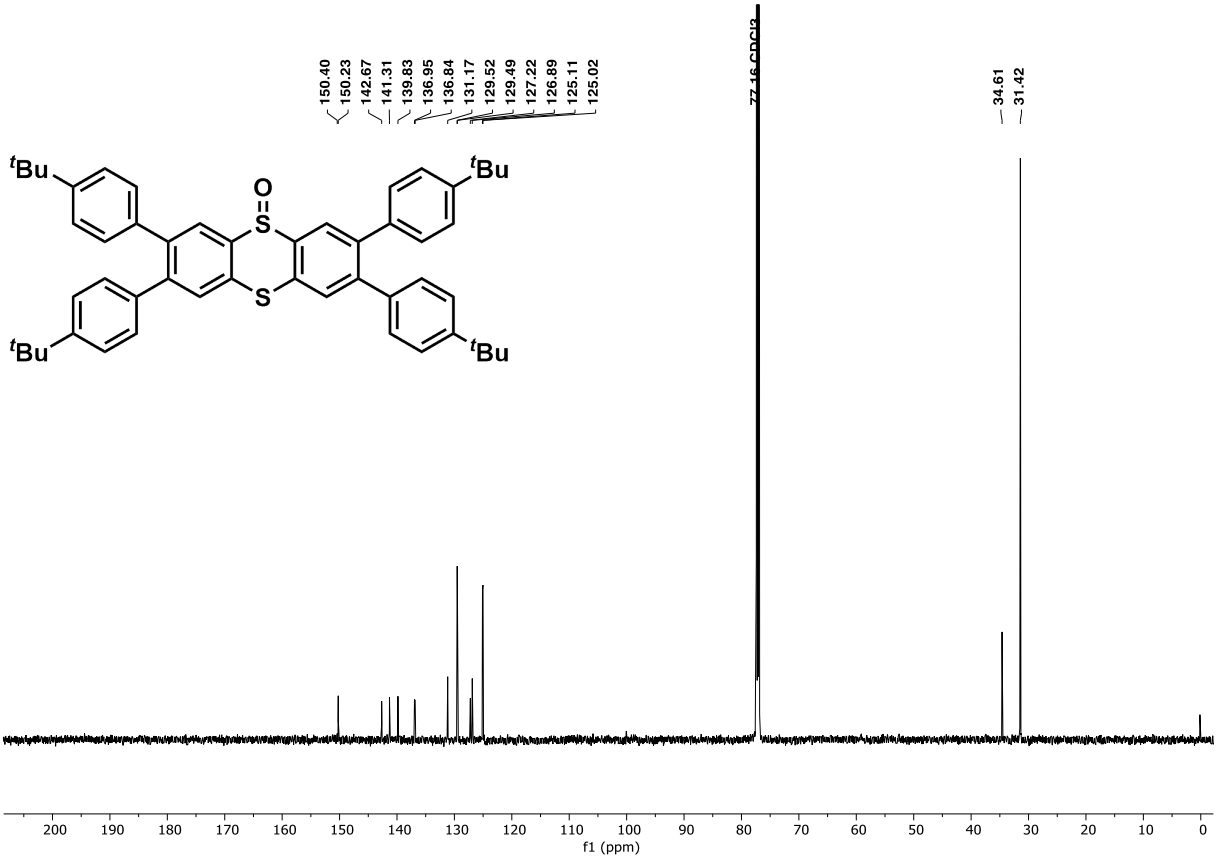
36.00
f1 (ppm)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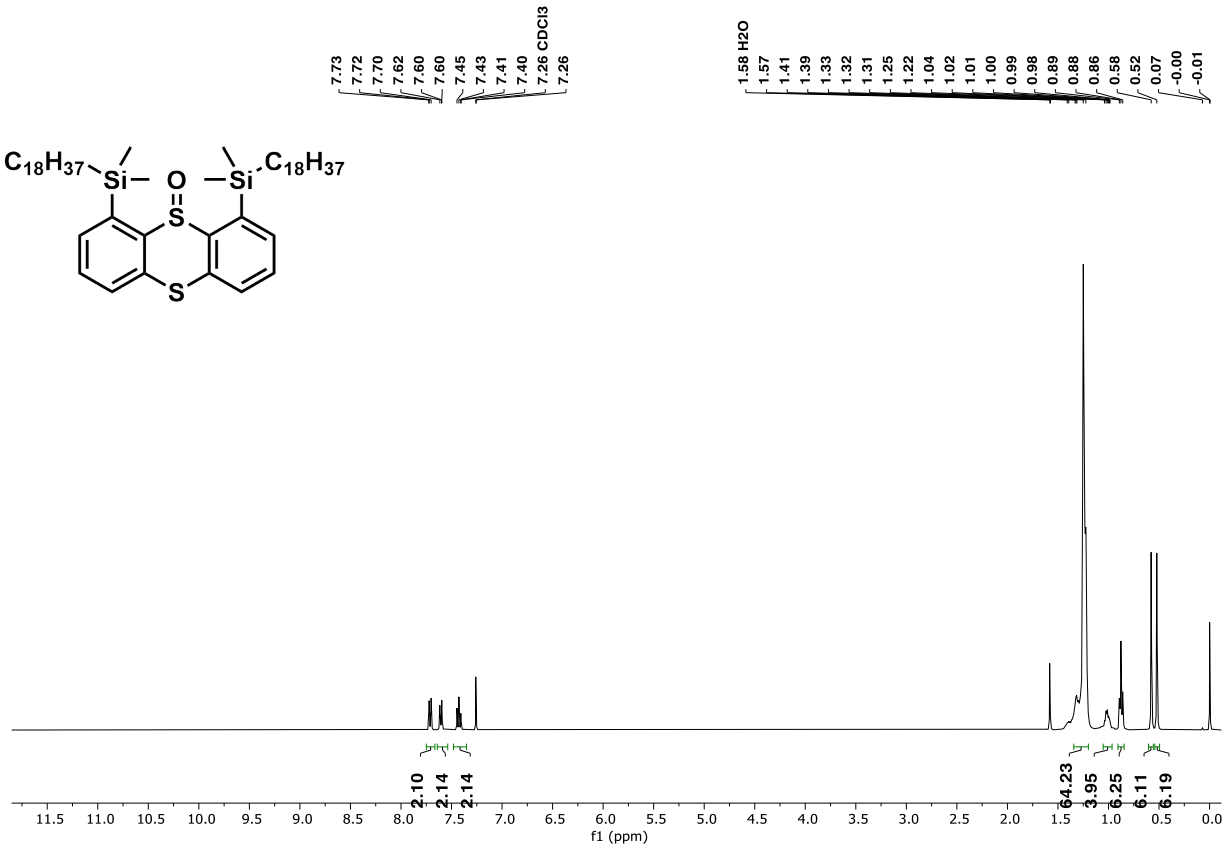
S
S
tBu
tBu
tBu
f1 (ppm)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1.58 H2O
1.57
1.41
1.39
1.33
1.32
1.31
1.25
1.22
1.04
1.02
1.01
1.00
0.99
0.98
0.89
0.88
0.86
0.58
0.52
0.07
-0.00
-0.01
C18H37
Si
O
Si
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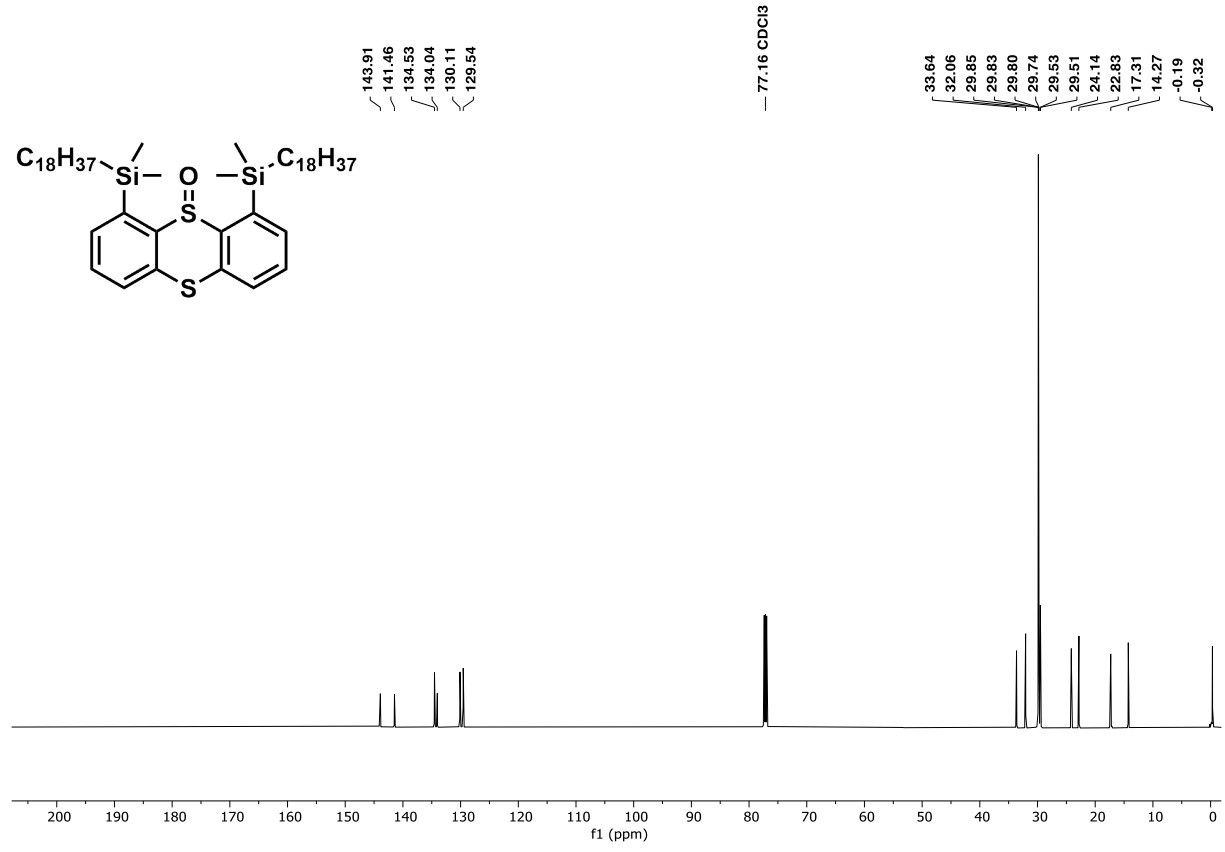
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29.74
29.53
29.51
24.14
22.83
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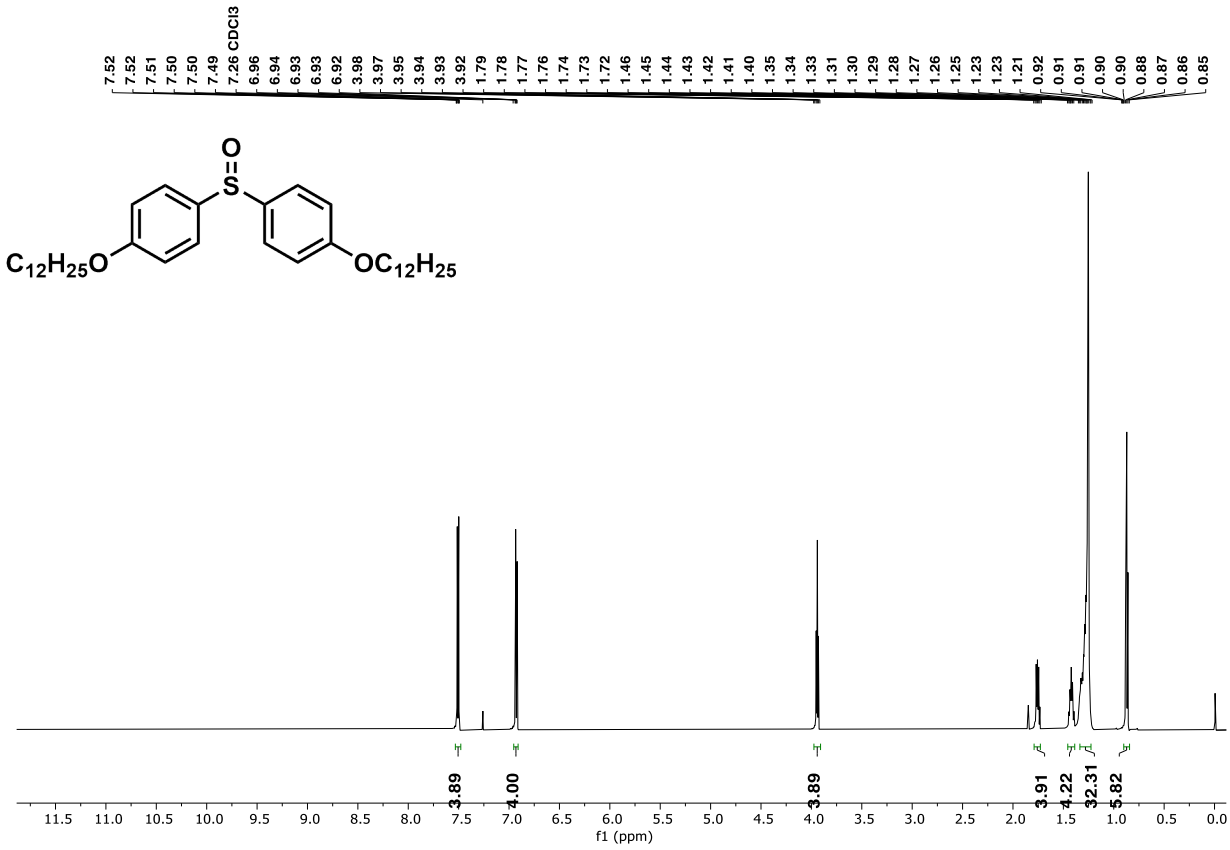
Si
O
Si
C18H37
S
S
f1 (ppm)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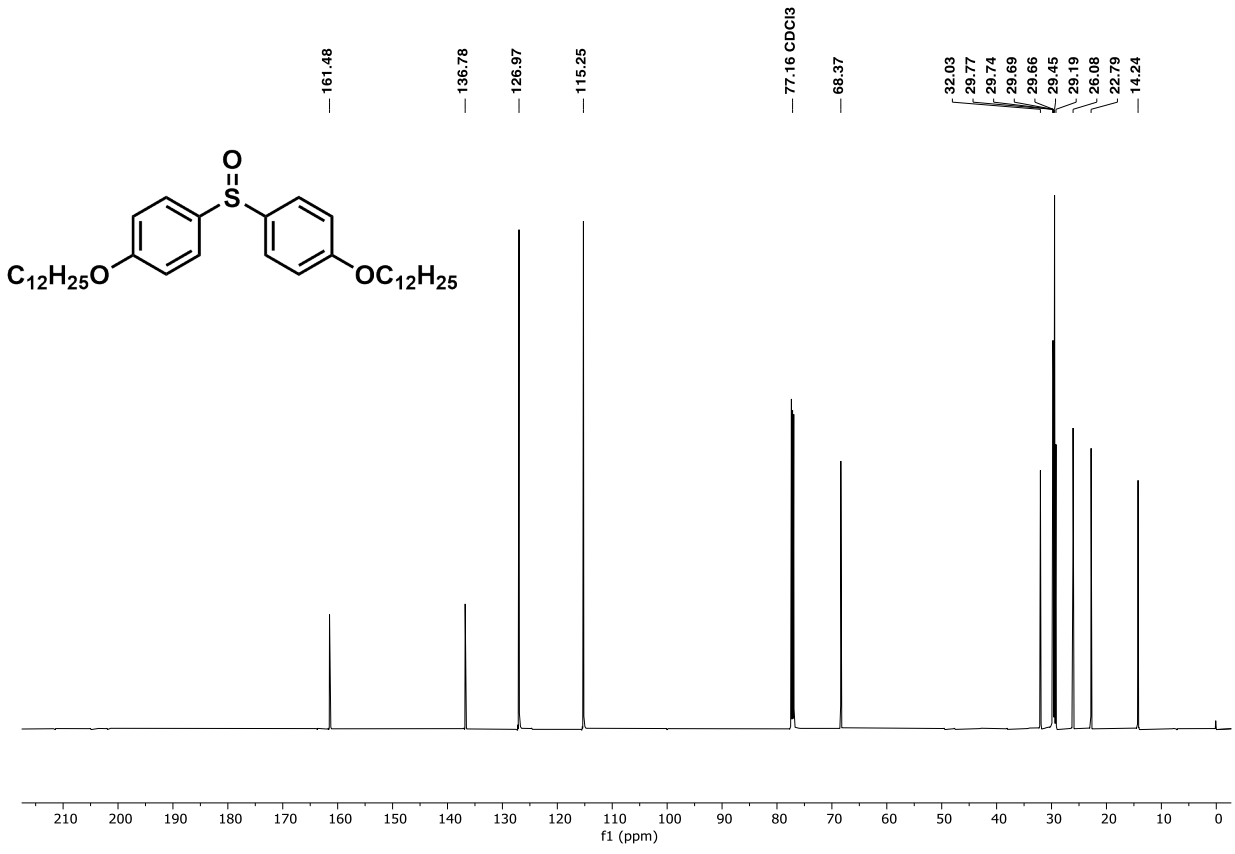
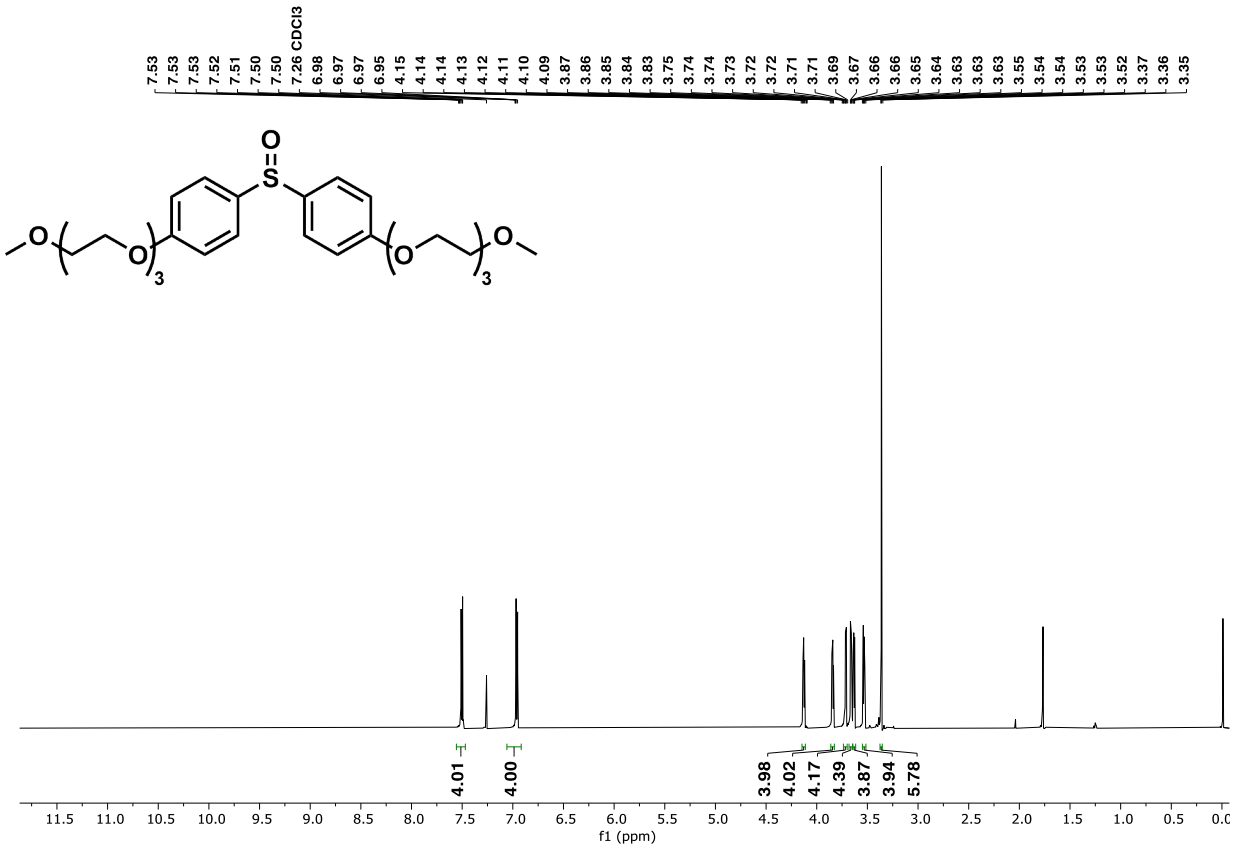
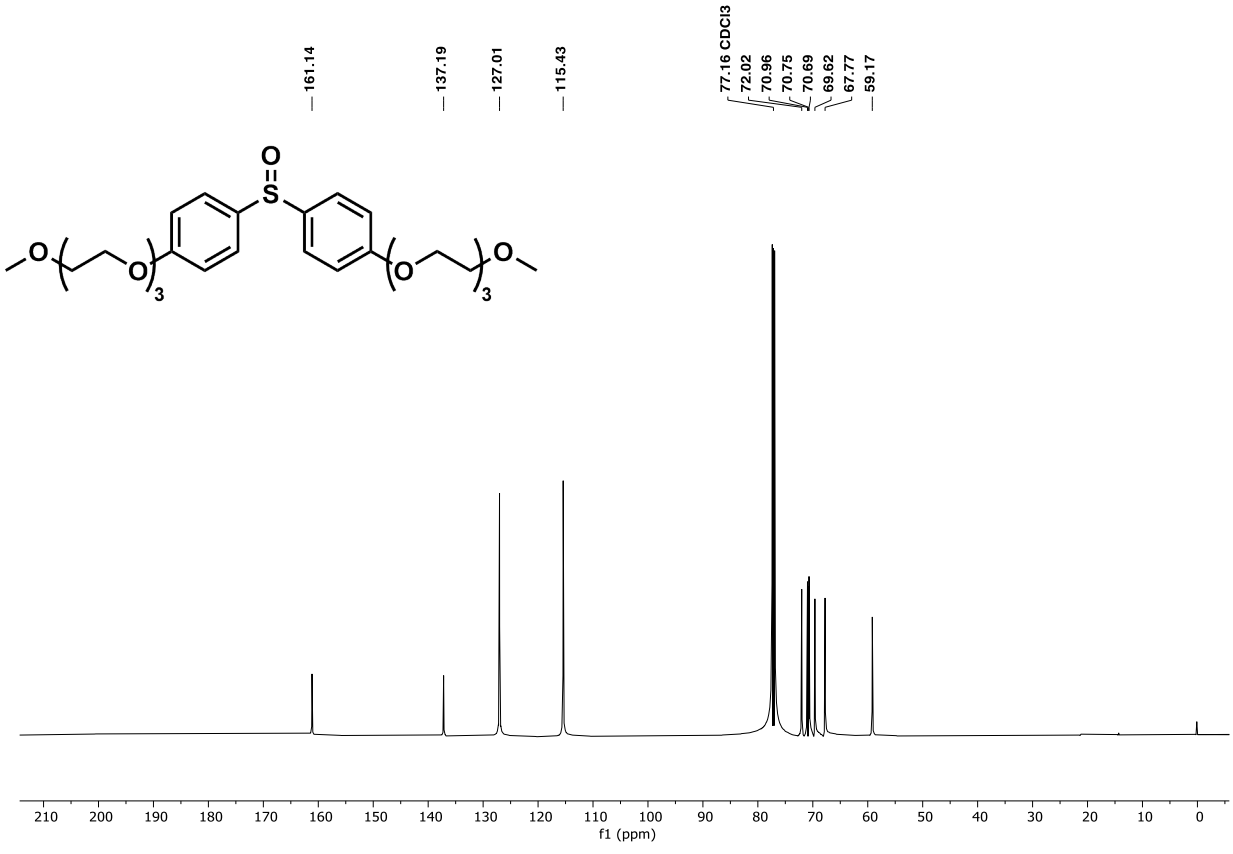
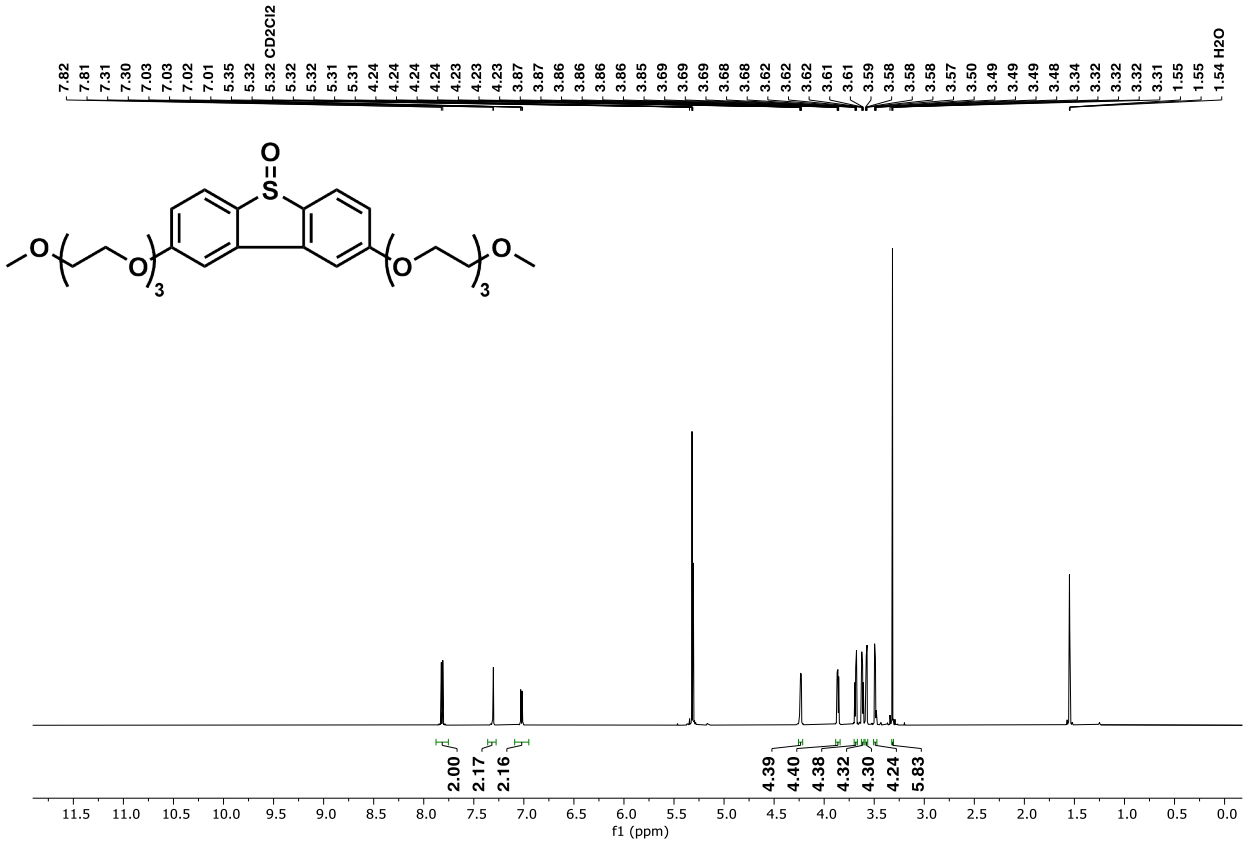
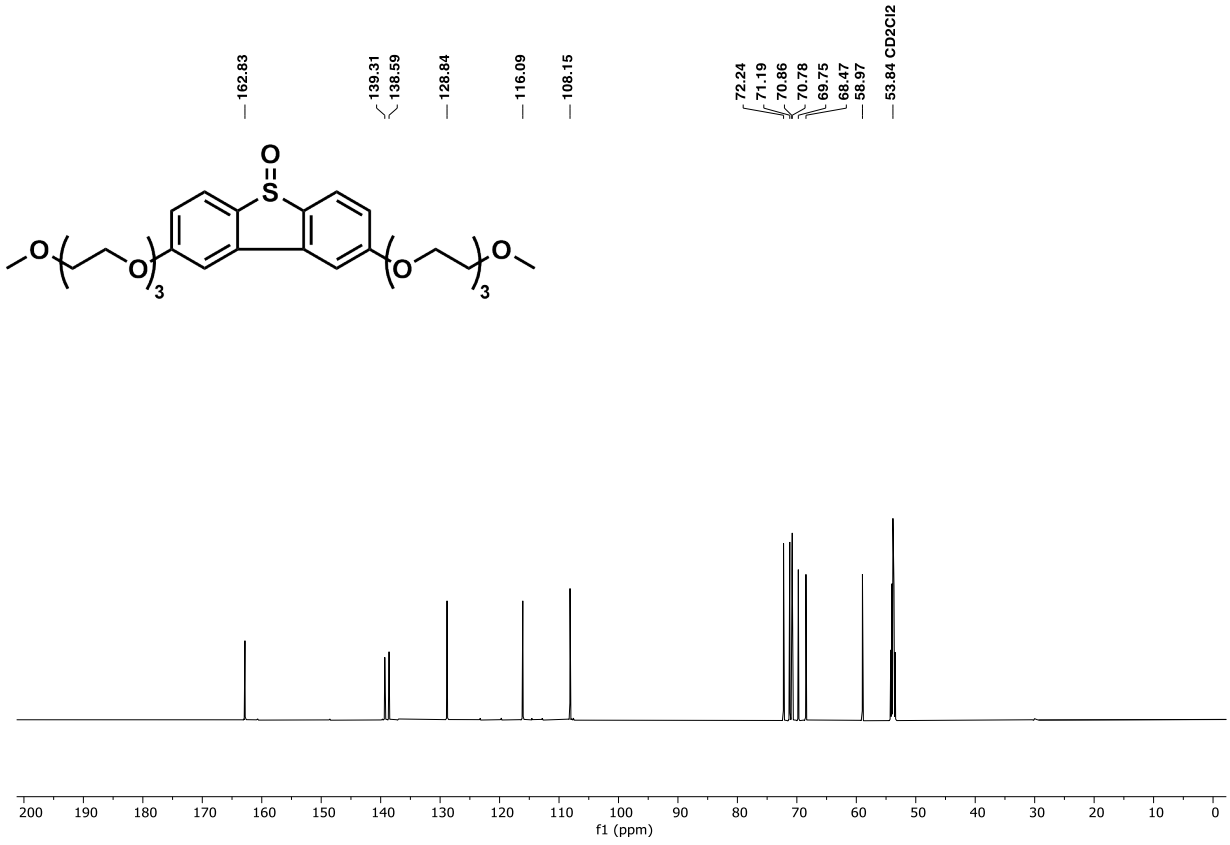
O
S
C12H25O
OC12H25
3.89 4.00 3.89 3.91 4.22 32.31 5.82
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

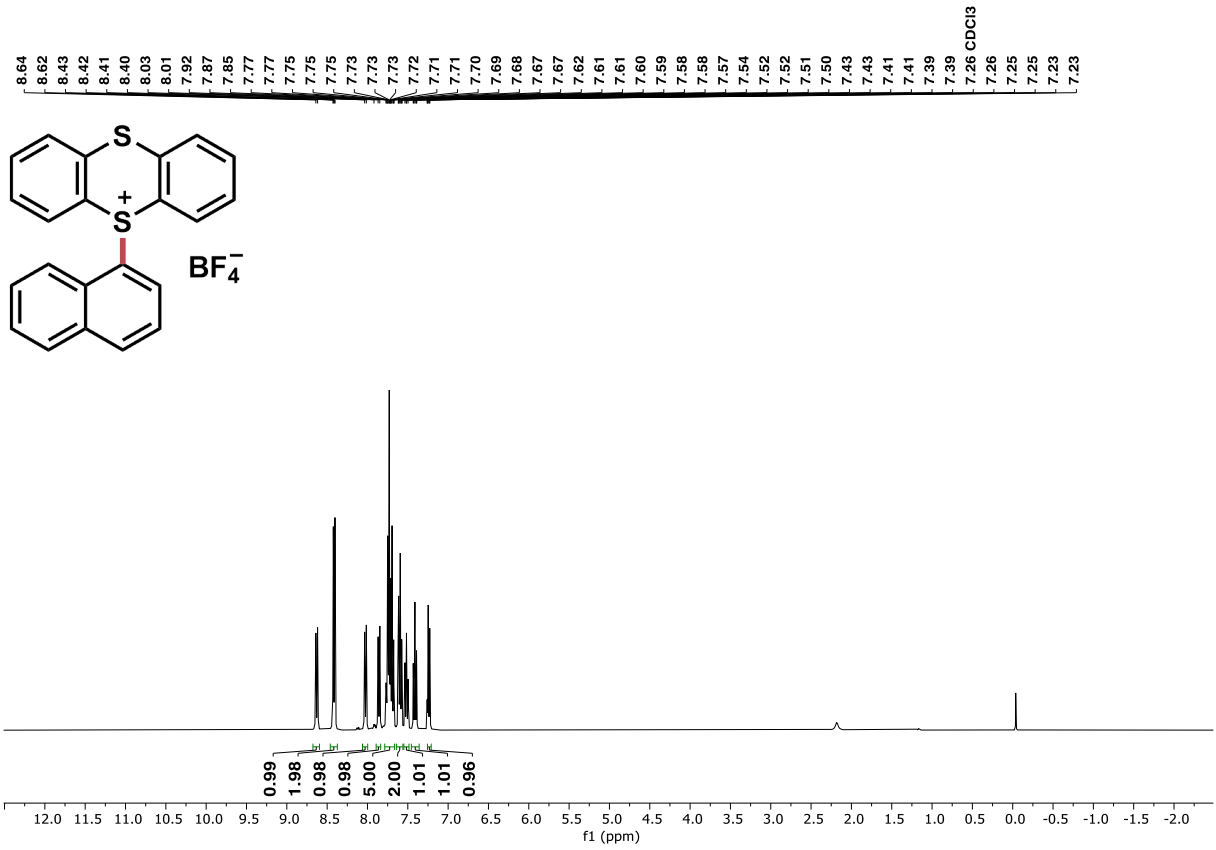

161.48 136.78 126.97 115.25 77.16 CDCl3 68.37 32.03 29.77 29.74 29.69 29.66 29.45 29.19 26.08 22.79 14.24
O
S
C12H25O
OC12H25
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

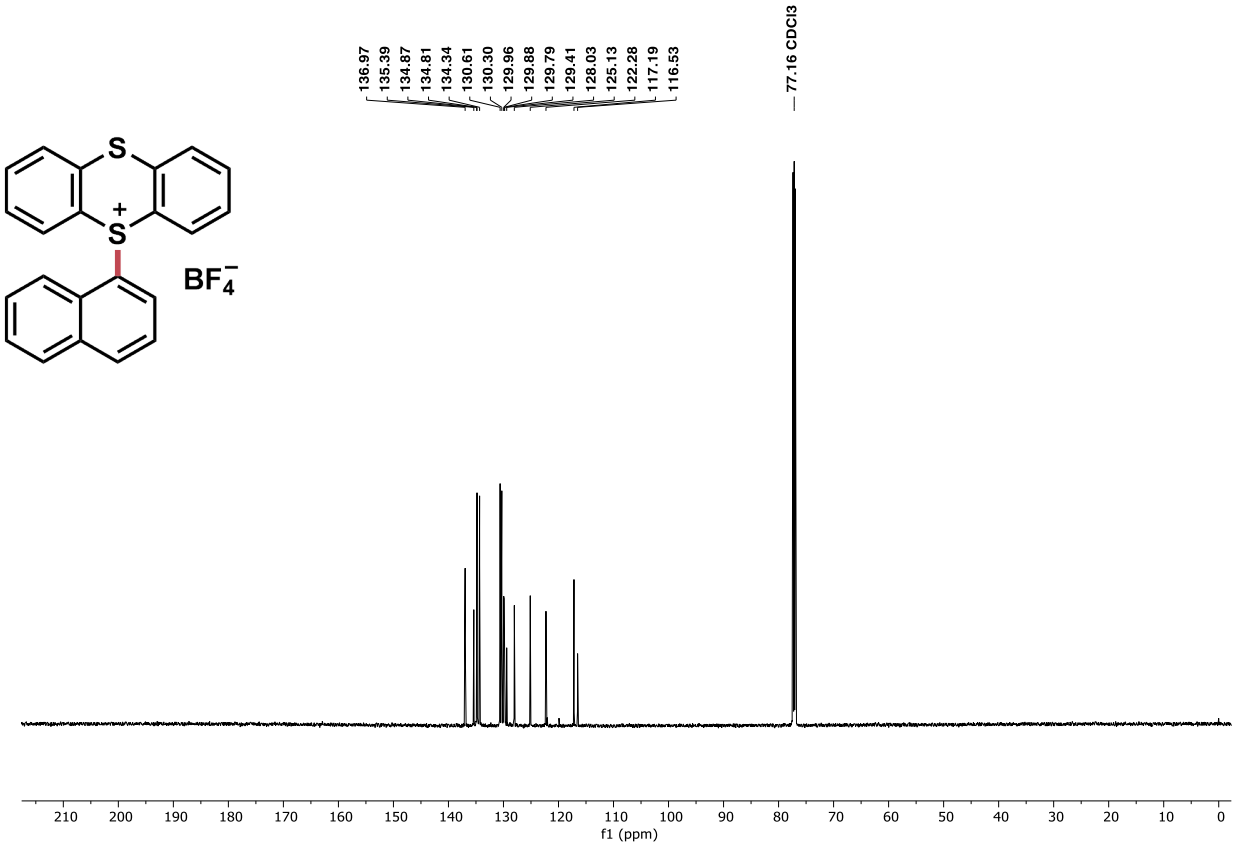

7.53 7.53 7.53 7.52 7.51 7.50 7.50 7.26 CDCl3 6.98 6.97 6.97 6.95 4.15 4.14 4.14 4.13 4.12 4.11 4.10 4.09 3.87 3.86 3.85 3.84 3.83 3.75 3.74 3.74 3.73 3.72 3.72 3.71 3.71 3.69 3.67 3.66 3.66 3.65 3.64 3.63 3.63 3.63 3.55 3.54 3.54 3.53 3.53 3.52 3.37 3.36 3.35
O
S
O
3
O
3
4.01
4.00
3.98
4.02
4.17
4.39
3.87
3.94
5.78
f1 (ppm)

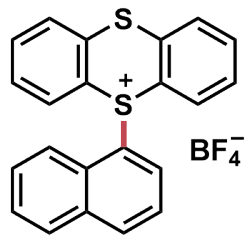

161.14
137.19
127.01
115.43
77.16 CDCl3
72.02
70.96
70.75
70.69
69.62
67.77
59.17
O
S
O
3
O
3
f1 (ppm)


7.82 7.81 7.31 7.30 7.03 7.03 7.02 7.01 5.35 5.32 5.32 CD2Cl2 5.32 5.32 5.31 5.31 4.24 4.24 4.24 4.24 4.23 4.23 4.23 3.87 3.87 3.86 3.86 3.86 3.86 3.85 3.69 3.69 3.69 3.68 3.68 3.62 3.62 3.62 3.61 3.61 3.59 3.58 3.58 3.58 3.57 3.50 3.49 3.49 3.49 3.48 3.34 3.32 3.32 3.32 3.31 1.55 1.55 1.54 H2O
2.00 2.17 2.16 4.39 4.40 4.38 4.32 4.30 4.24 5.83
f1 (ppm)

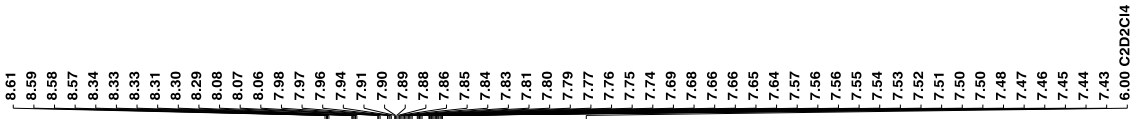

162.83 139.31 138.59 128.84 116.09 108.15 72.24 71.19 70.86 70.78 69.75 68.47 58.97 53.84 CD2Cl2
f1 (ppm)

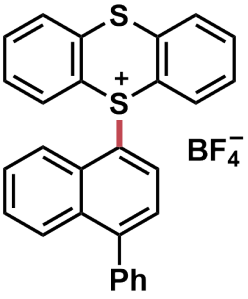

8.64 8.62 8.43 8.42 8.41 8.40 8.03 8.01 7.92 7.87 7.85 7.77 7.77 7.75 7.75 7.75 7.73 7.73 7.73 7.72 7.71 7.71 7.70 7.69 7.68 7.67 7.67 7.62 7.61 7.61 7.60 7.59 7.58 7.58 7.57 7.54 7.52 7.52 7.51 7.50 7.43 7.43 7.41 7.41 7.39 7.39 7.26 CDCl3 7.26 7.25 7.25 7.23 7.23
S
+
S
BF4−
0.99 1.98 0.98 0.98 5.00 2.00 1.01 1.01 0.96
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)


136.97 135.39 134.87 134.81 134.34 130.61 130.30 129.96 129.88 129.79 129.41 128.03 125.13 122.28 117.19 116.53
77.16 CDCl3
S
+
S
BF4−
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

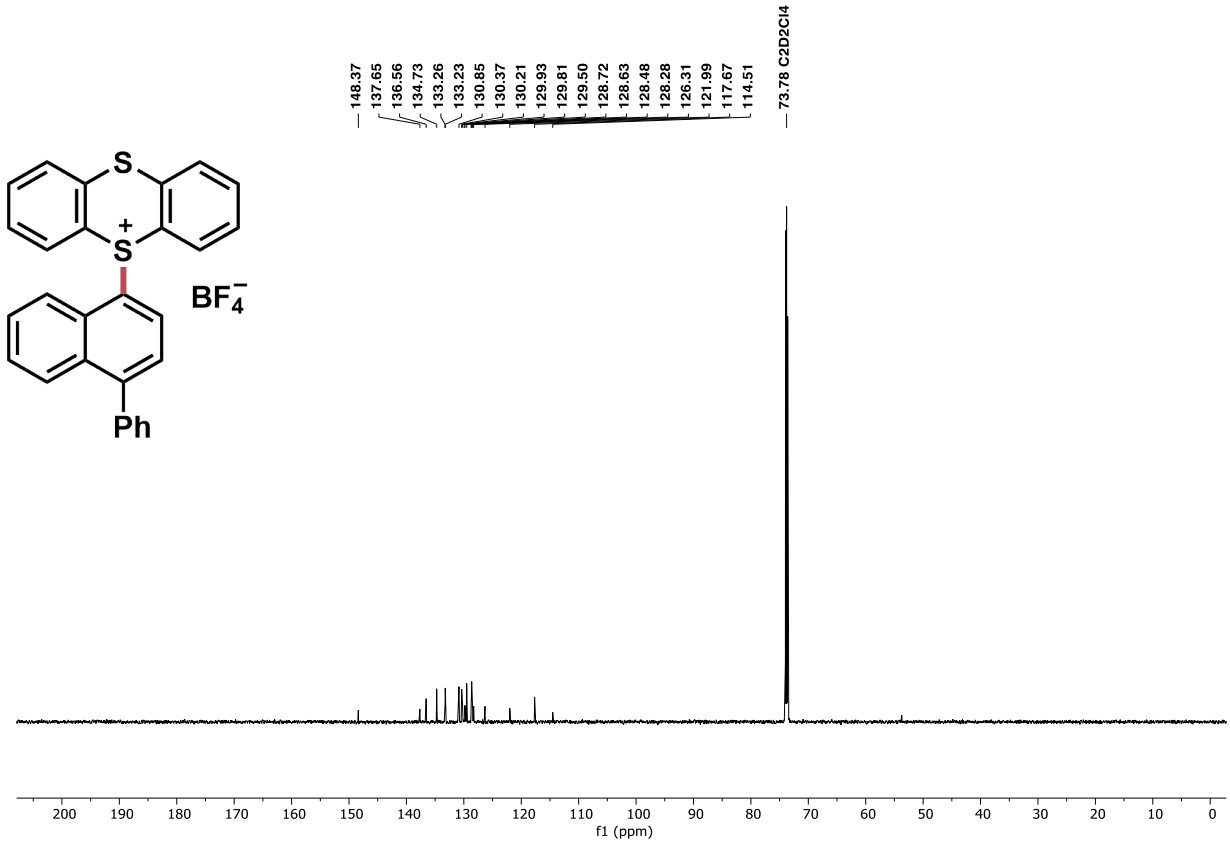

S
+
S
BF4−

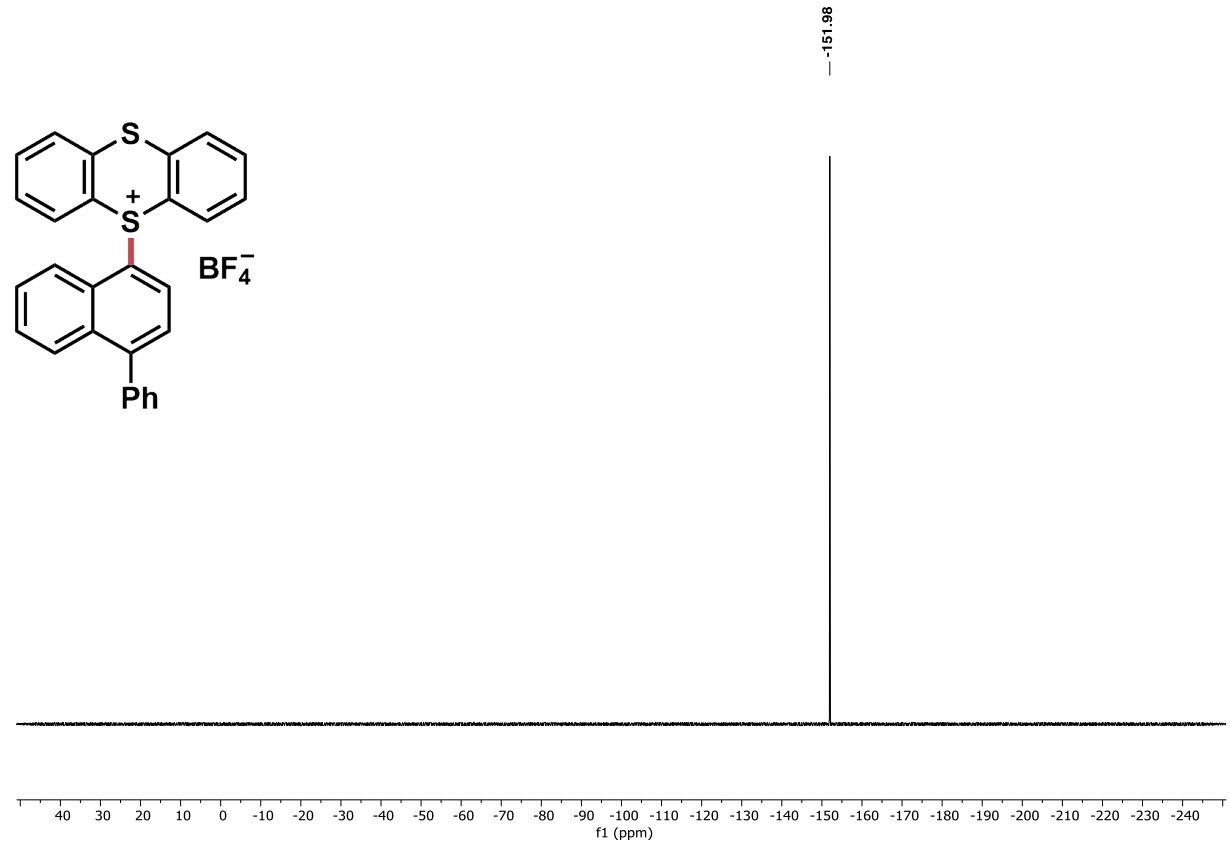
-151.78
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

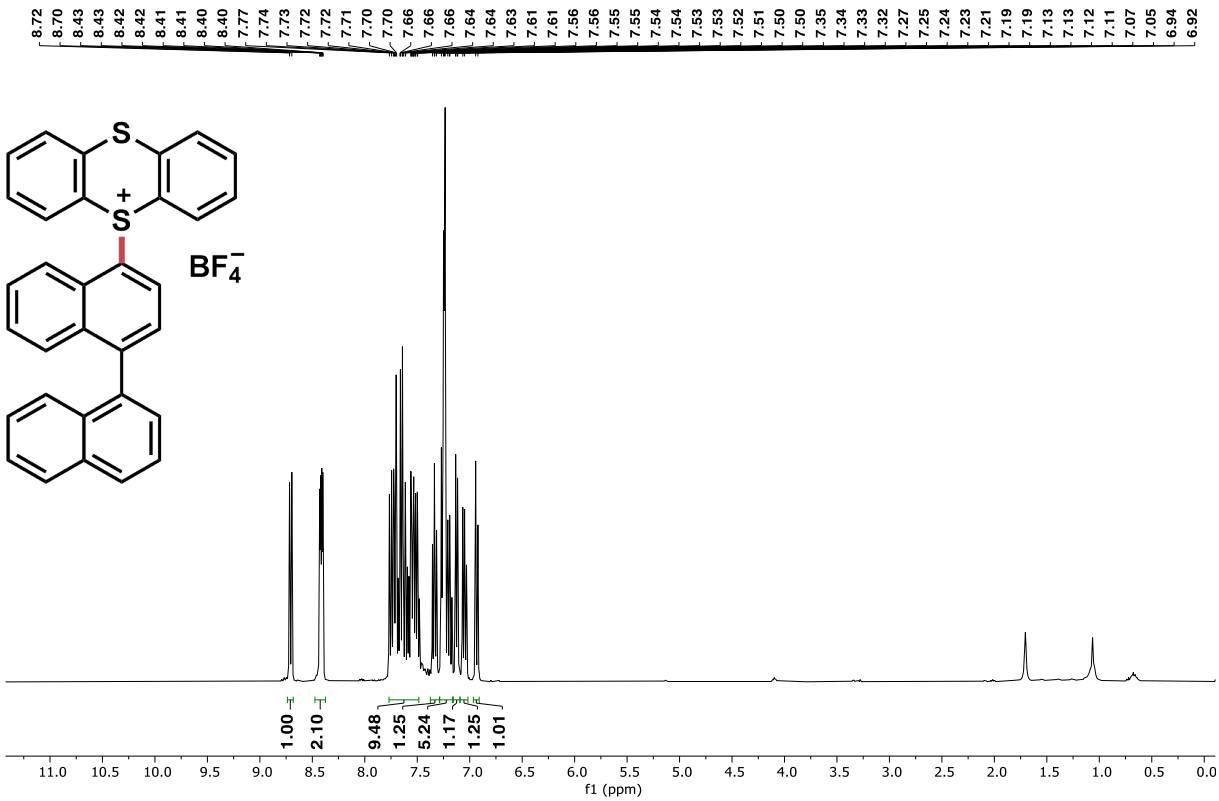

8.61
8.59
8.58
8.57
8.34
8.33
8.33
8.31
8.30
8.29
8.08
8.07
8.06
7.98
7.97
7.96
7.94
7.91
7.90
7.89
7.88
7.86
7.85
7.84
7.83
7.81
7.80
7.79
7.77
7.76
7.75
7.74
7.69
7.68
7.66
7.66
7.65
7.64
7.57
7.56
7.56
7.55
7.54
7.53
7.52
7.51
7.50
7.50
7.48
7.47
7.46
7.45
7.44
7.43
6.00 C2D2Cl4

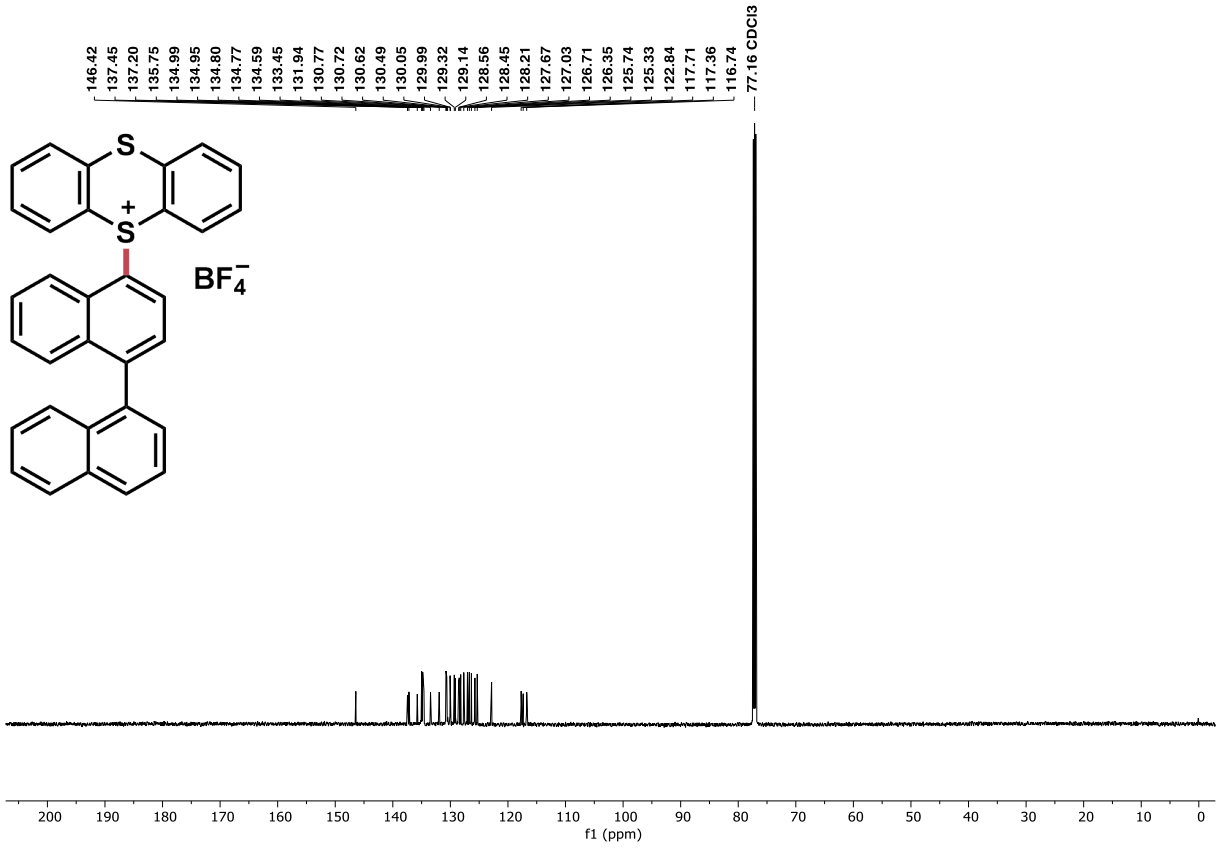

S
+
S
BF4−
Ph

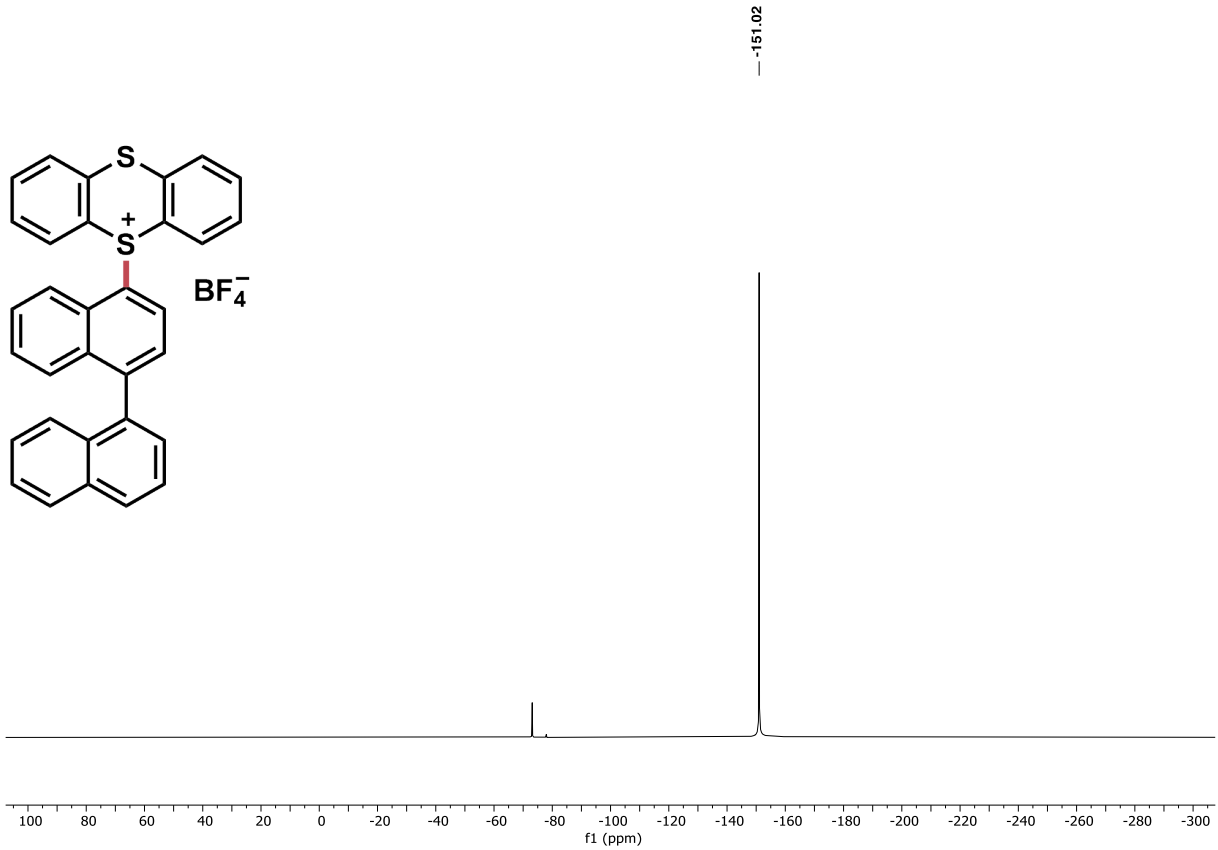
0.96
1.92
0.94
1.91
1.00
1.96
1.98
1.00
6.80
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

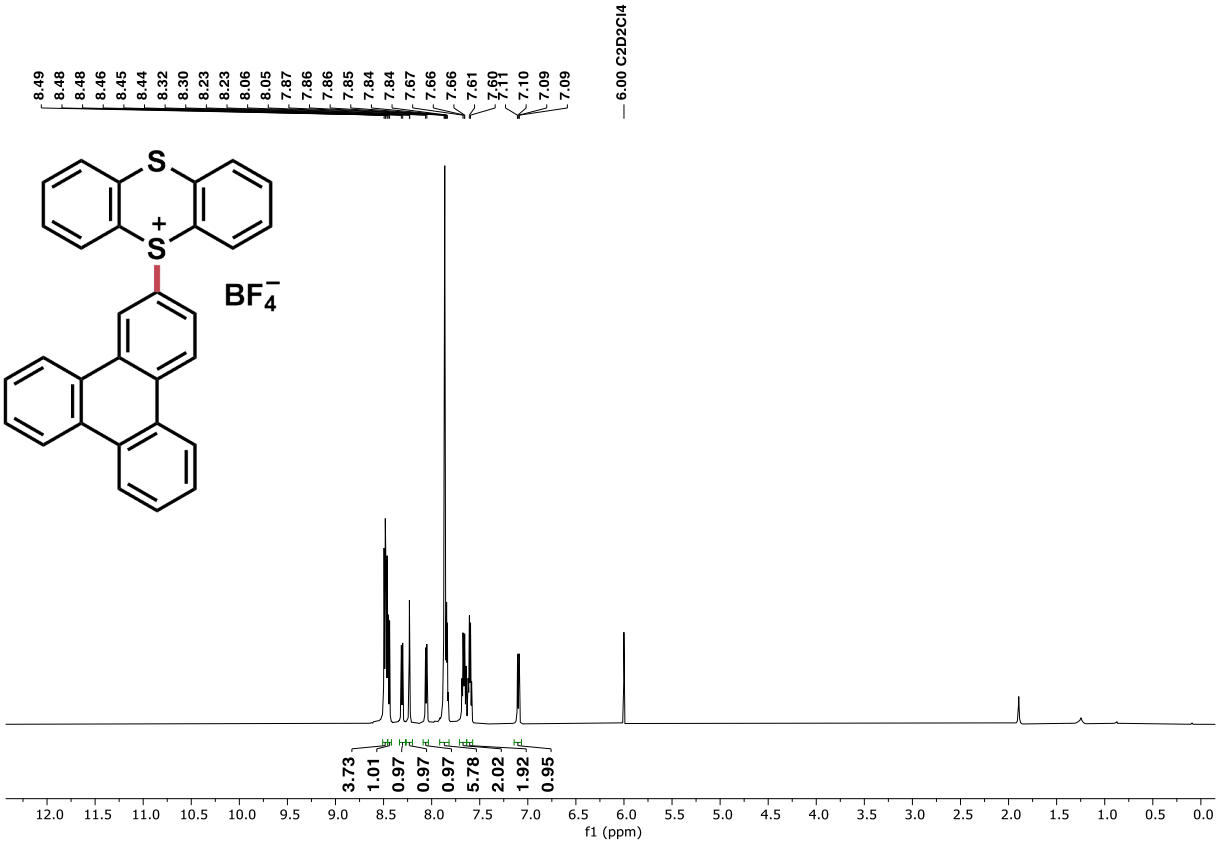

148.37
137.65
136.56
134.73
133.26
133.23
130.85
130.37
130.21
129.93
129.81
129.50
128.72
128.63
128.48
128.28
126.31
121.99
117.67
114.51
73.78 C2D2Cl4
S
+
S
BF4−
Ph
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

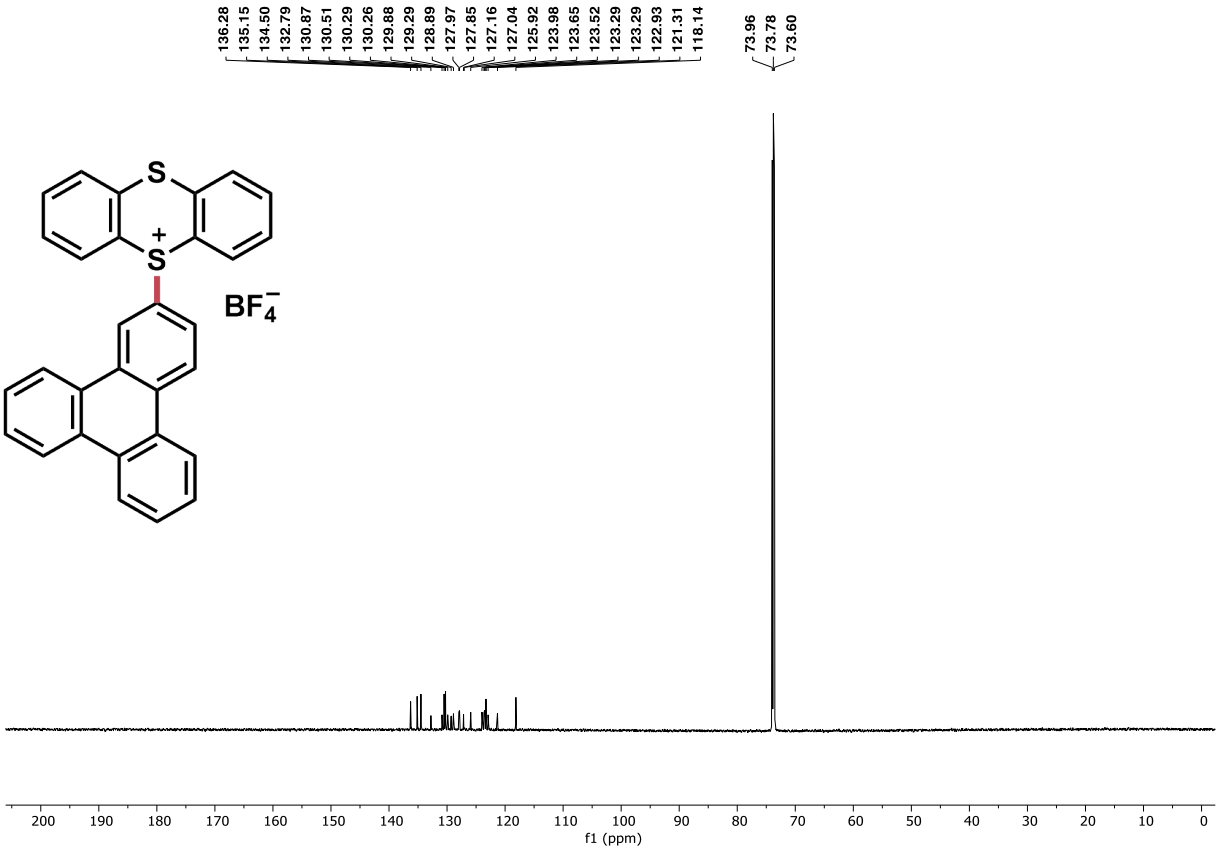

-151.98
S
+
S
BF4−
Ph
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

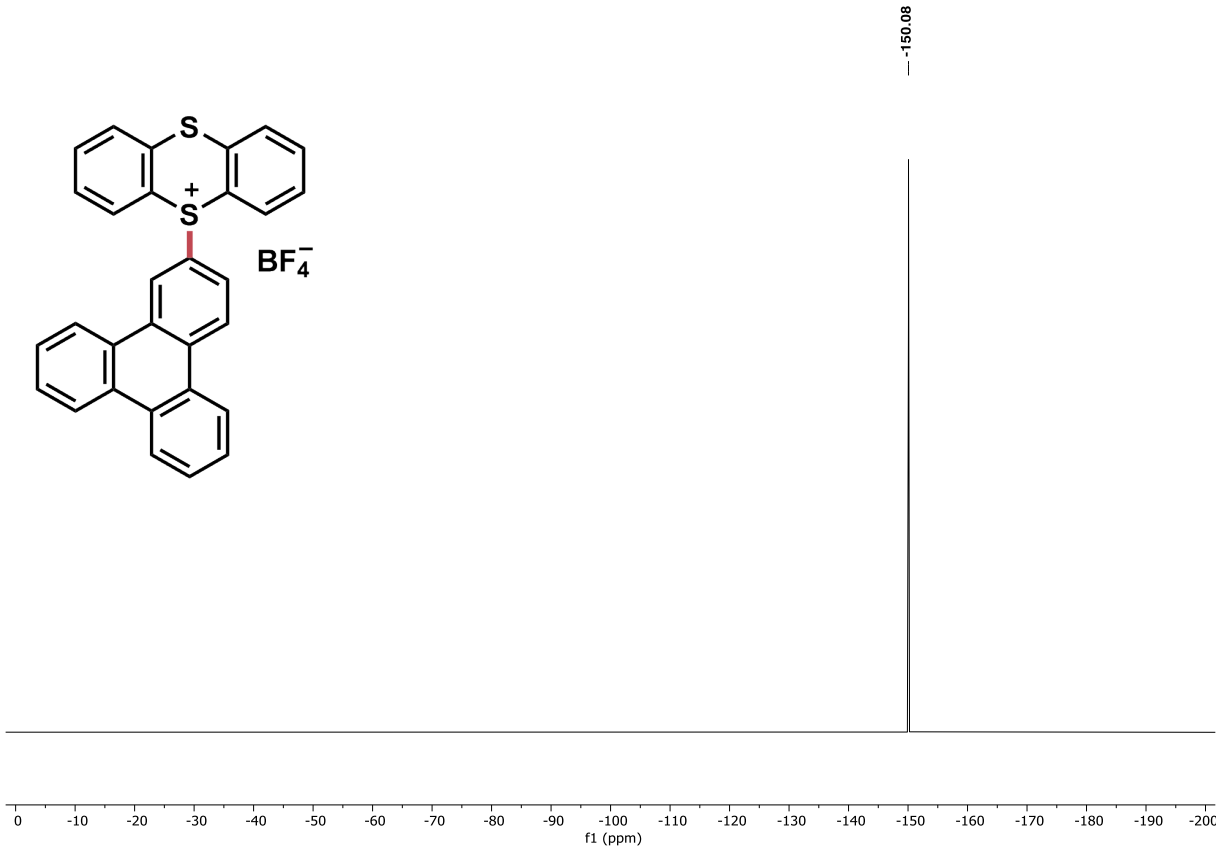

8.72 8.70 8.43 8.43 8.42 8.42 8.42 8.41 8.41 8.40 8.40 8.40 7.77 7.74 7.73 7.72 7.72 7.71 7.70 7.70 7.70 7.66 7.66 7.66 7.64 7.64 7.63 7.61 7.61 7.56 7.56 7.55 7.55 7.54 7.54 7.53 7.53 7.52 7.51 7.50 7.50 7.35 7.34 7.33 7.32 7.27 7.25 7.24 7.23 7.21 7.19 7.19 7.13 7.13 7.12 7.11 7.07 7.05 6.94 6.92
S
+
S
BF4−
1.00 2.10 9.48 1.25 5.24 1.17 1.25 1.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


146.42 137.45 137.20 135.75 134.99 134.95 134.80 134.77 134.59 133.45 131.94 130.77 130.72 130.62 130.49 130.05 129.99 129.32 129.14 128.56 128.45 128.21 127.67 127.03 126.71 126.35 125.74 125.33 122.84 117.71 117.36 116.74 77.16 CDCl3
S
+
S
BF4−
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-151.02
S
+
S
BF4−
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)


8.49 8.48 8.48 8.46 8.45 8.44 8.32 8.30 8.23 8.23 8.06 8.05 7.87 7.86 7.86 7.85 7.84 7.84 7.67 7.66 7.66 7.61 7.60 7.11 7.10 7.09 7.09
6.00 C2D2Cl4
S
+
S
BF4−
3.73 1.01 0.97 0.97 0.97 5.78 2.02 1.92 0.95
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


136.28
135.15
134.50
132.79
130.87
130.51
130.29
130.26
129.88
129.29
128.89
127.97
127.85
127.16
127.04
125.92
123.98
123.65
123.52
123.29
123.29
122.93
121.31
118.14
73.96
73.78
73.60
S
+
S
BF4−
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-150.08
S
+
S
BF4−
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
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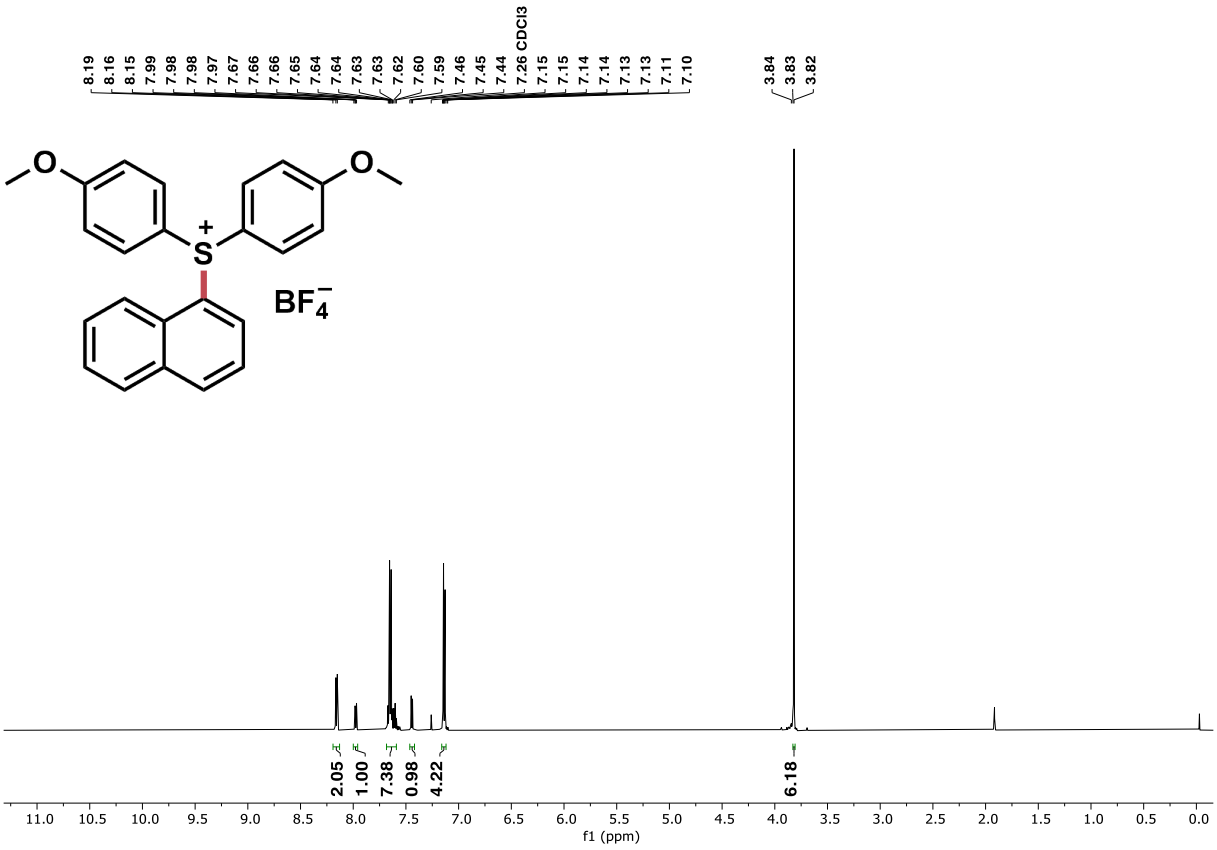
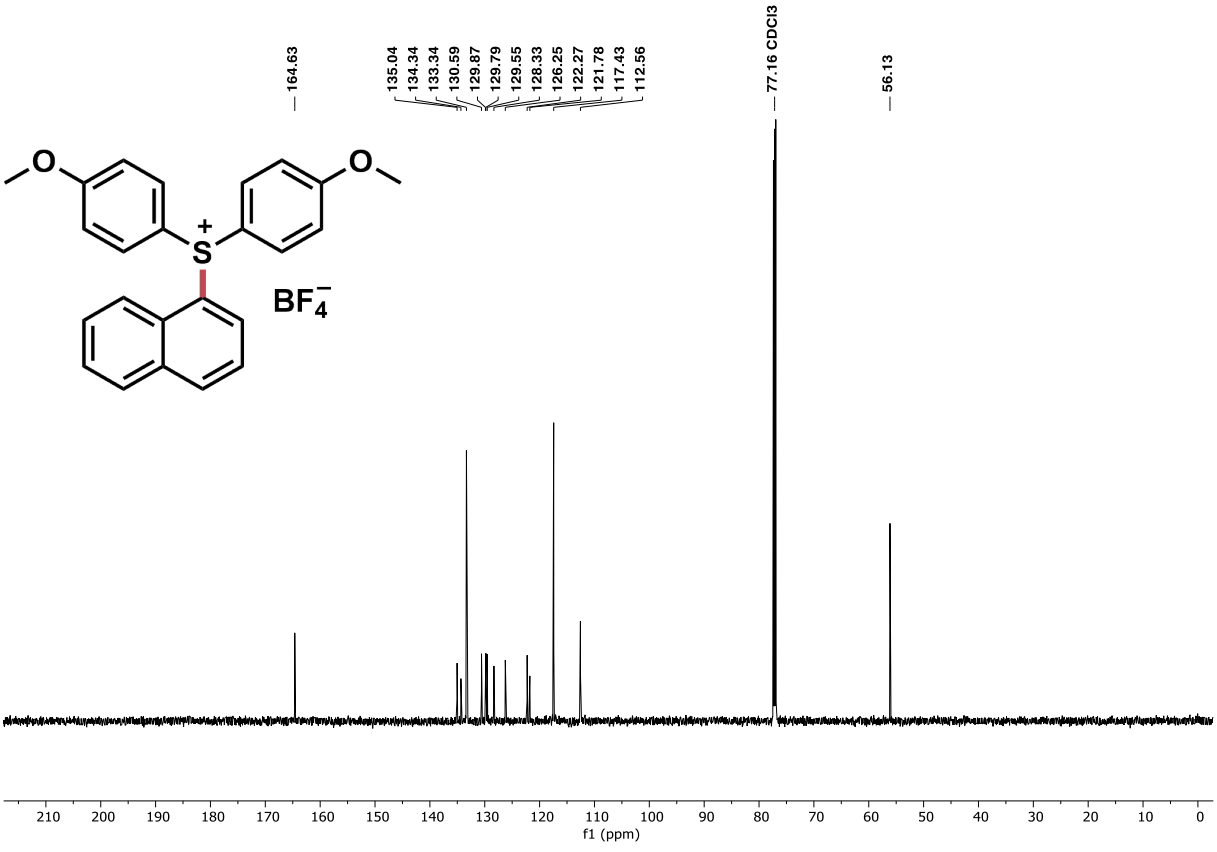
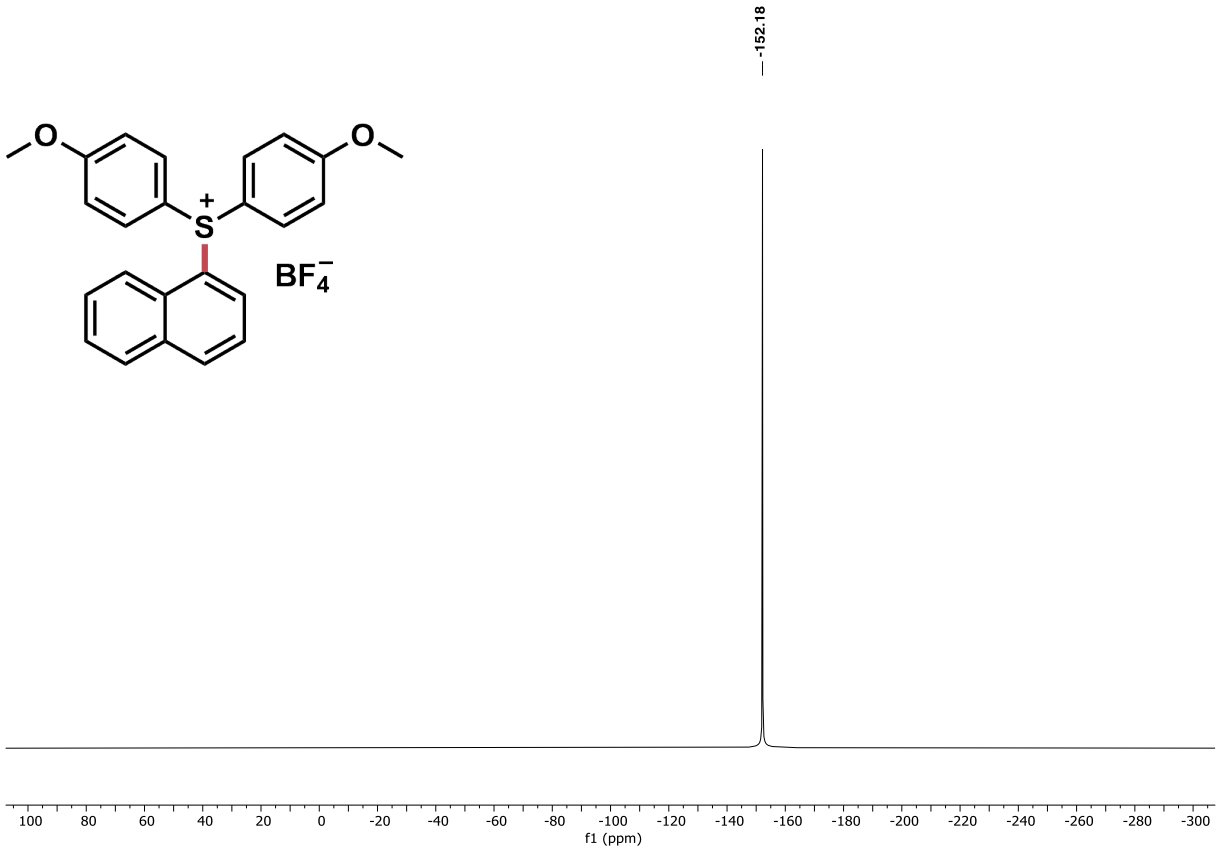
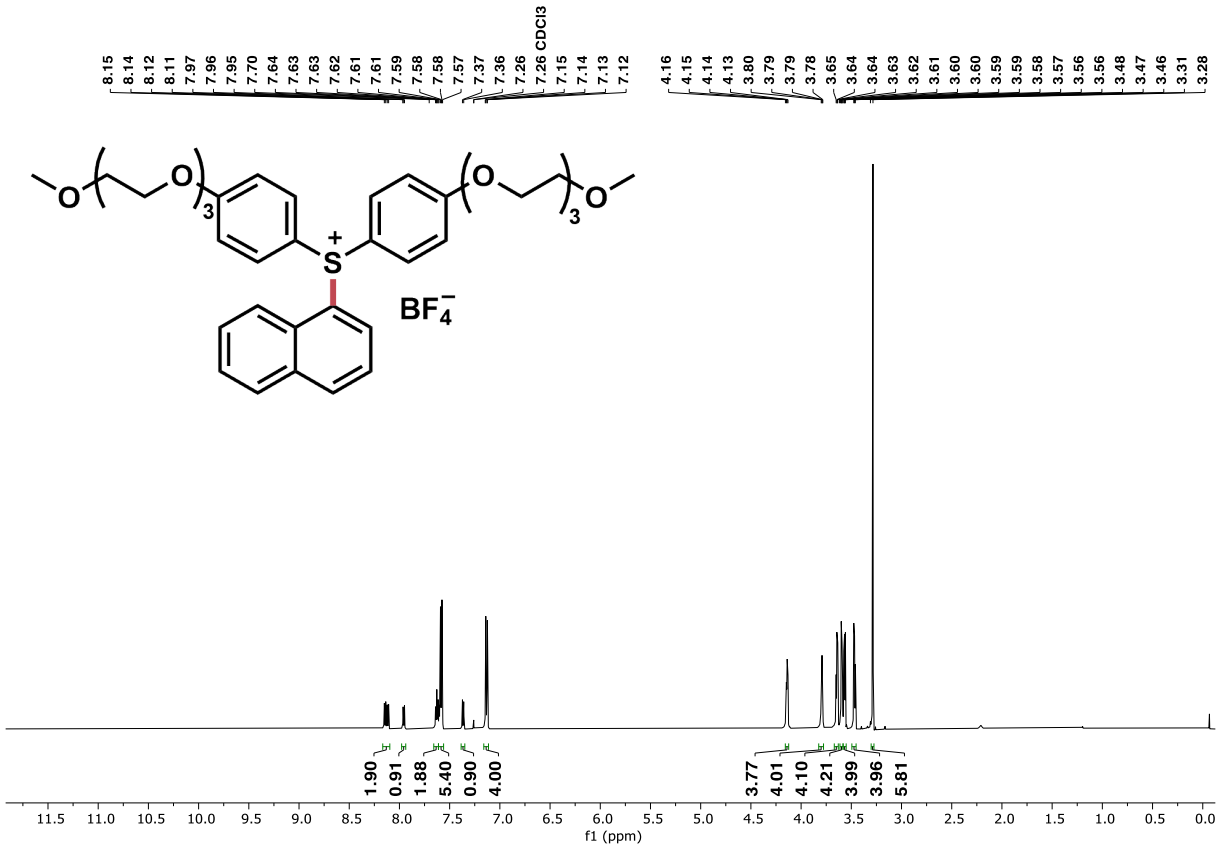
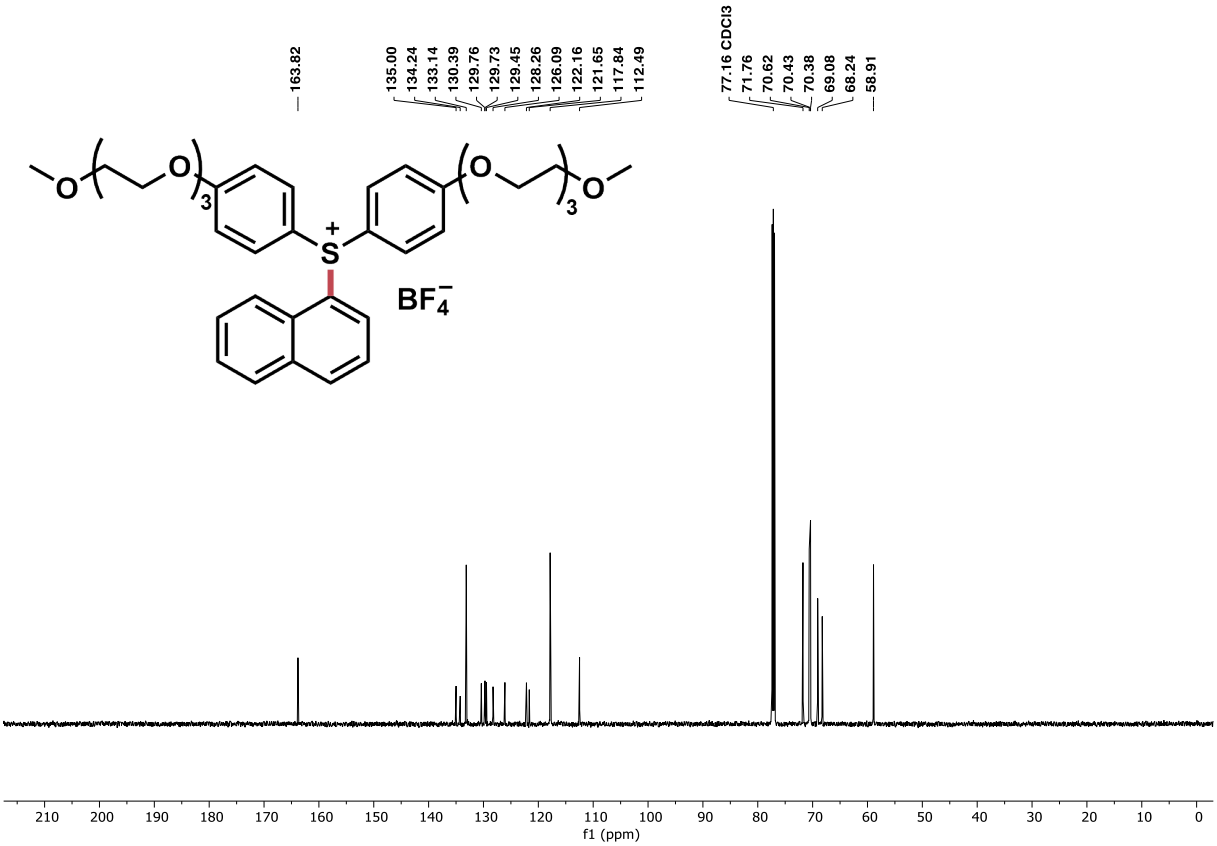
-150
-160
-170
-180
-190
-200
f1 (ppm)

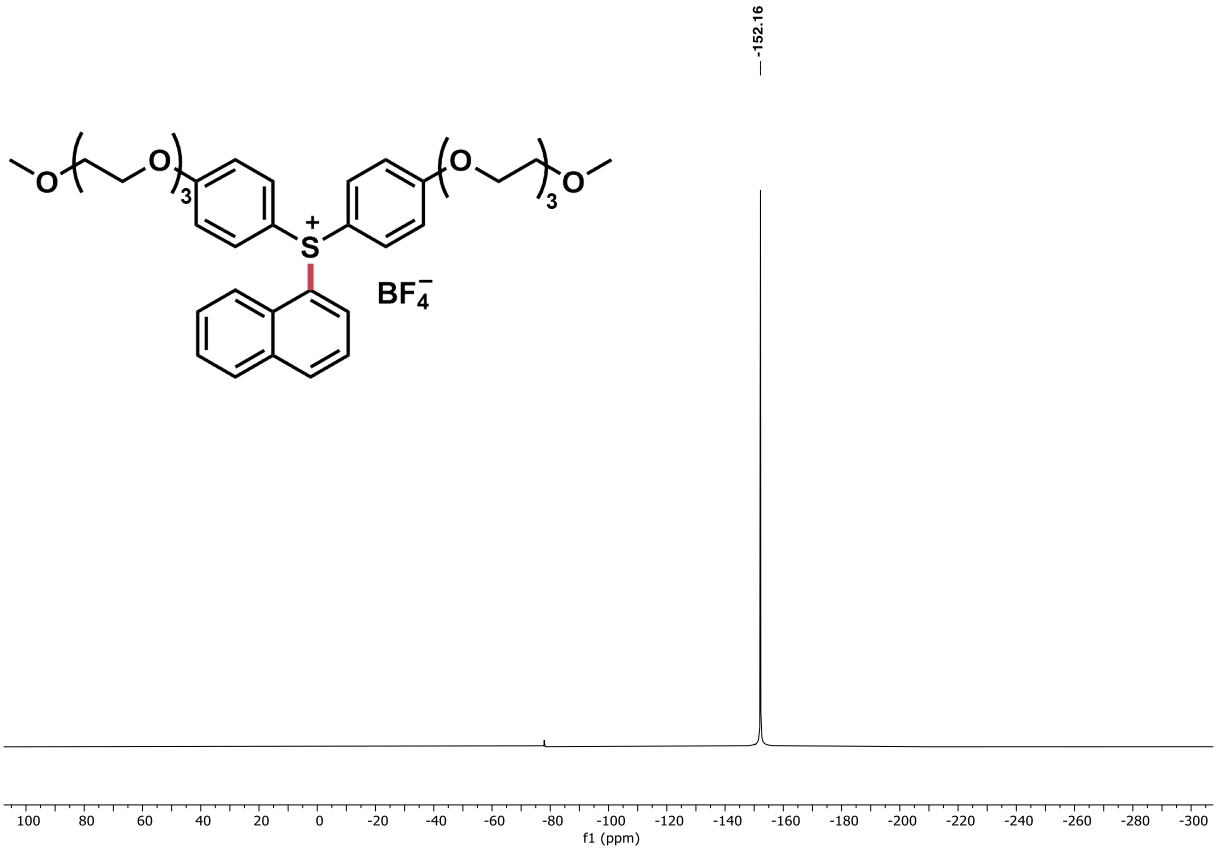

8.19
8.16
8.15
7.99
7.98
7.98
7.97
7.67
7.66
7.66
7.65
7.64
7.64
7.63
7.63
7.62
7.60
7.59
7.46
7.45
7.44
7.26 CDCl3
7.15
7.15
7.14
7.14
7.13
7.13
7.11
7.10
3.84
3.83
3.82
O
O
S
+
BF4−
2.05
1.00
7.38
0.98
4.22
6.18
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

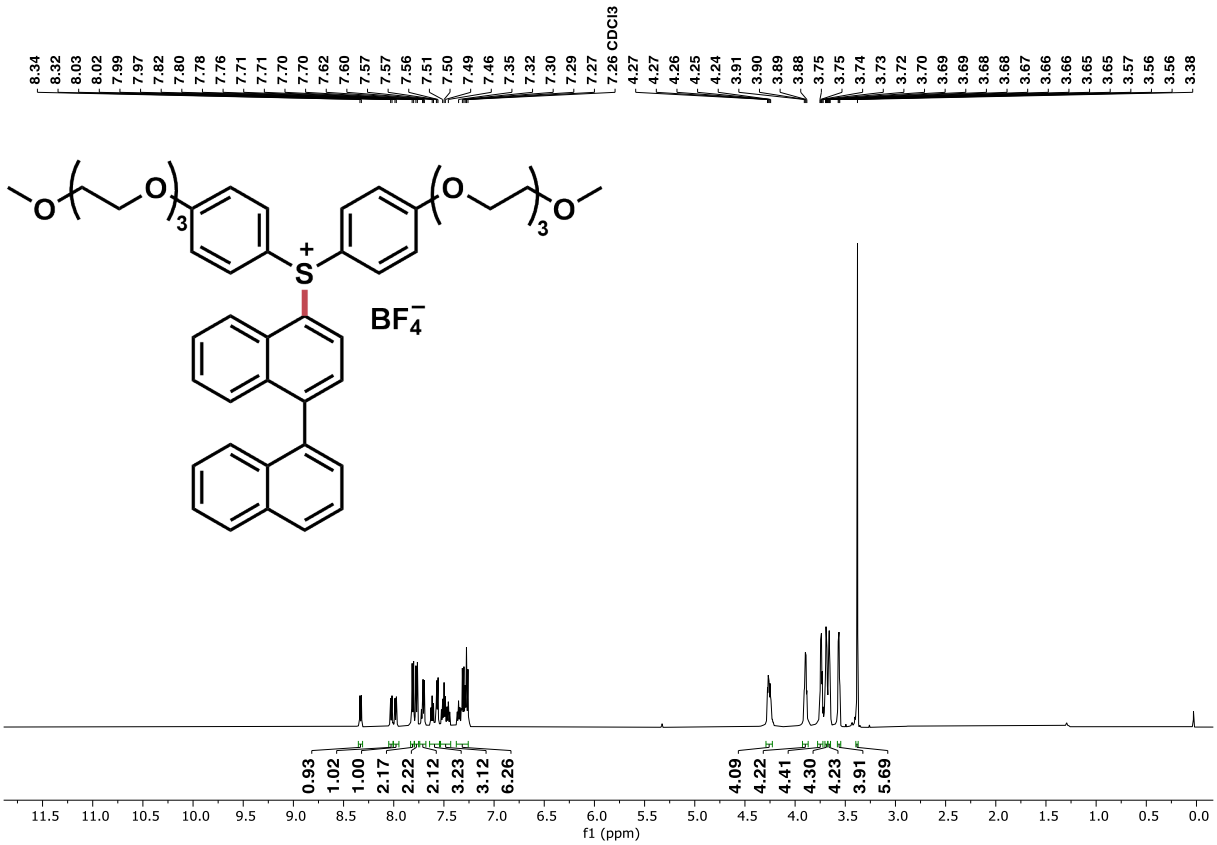

164.63
135.04
134.34
133.34
130.59
129.87
129.79
129.55
128.33
126.25
122.27
121.78
117.43
112.56
77.16 CDCl3
56.13
O
O
S
+
BF4−
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

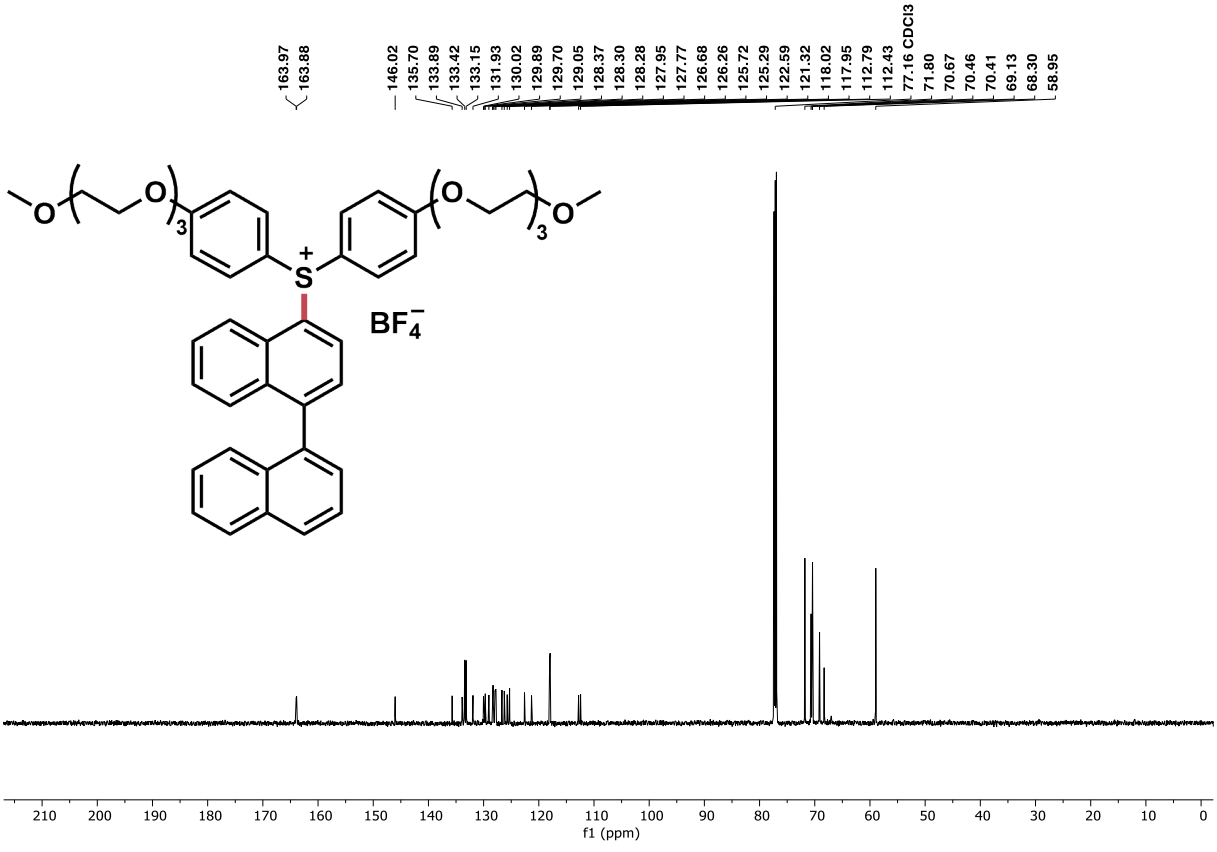

-152.18
f1 (ppm)

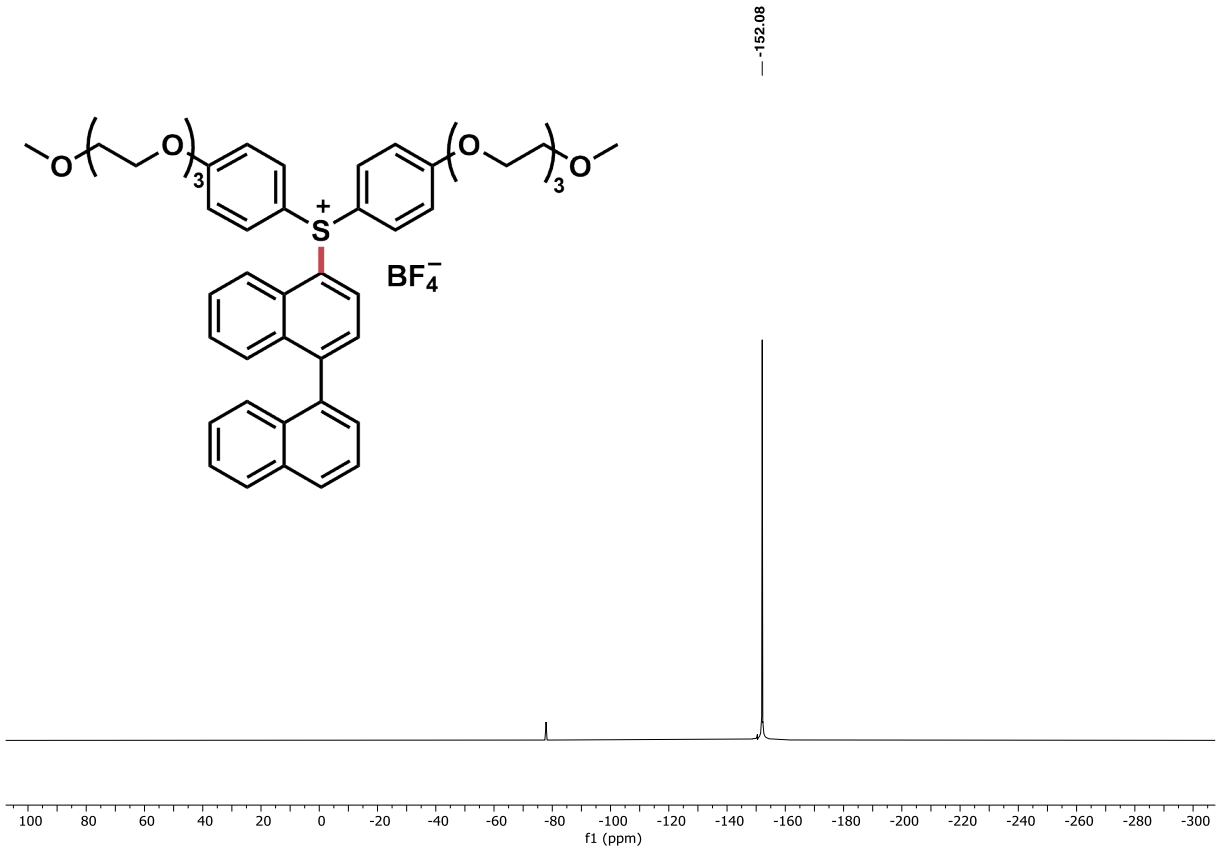

CDCl3
1.90
0.91
1.88
5.40
0.90
4.00
3.77
4.01
4.10
4.21
3.99
3.96
5.81
f1 (ppm)

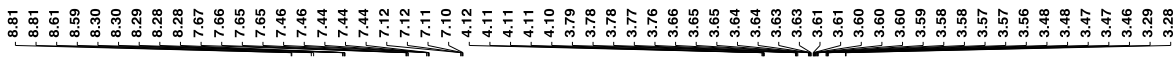

163.82
135.00
134.24
133.14
130.39
129.76
129.73
129.45
128.26
126.09
122.16
121.65
117.84
112.49
77.16 CDCl3
71.76
70.62
70.43
70.38
69.08
68.24
58.91
BF4−
f1 (ppm)

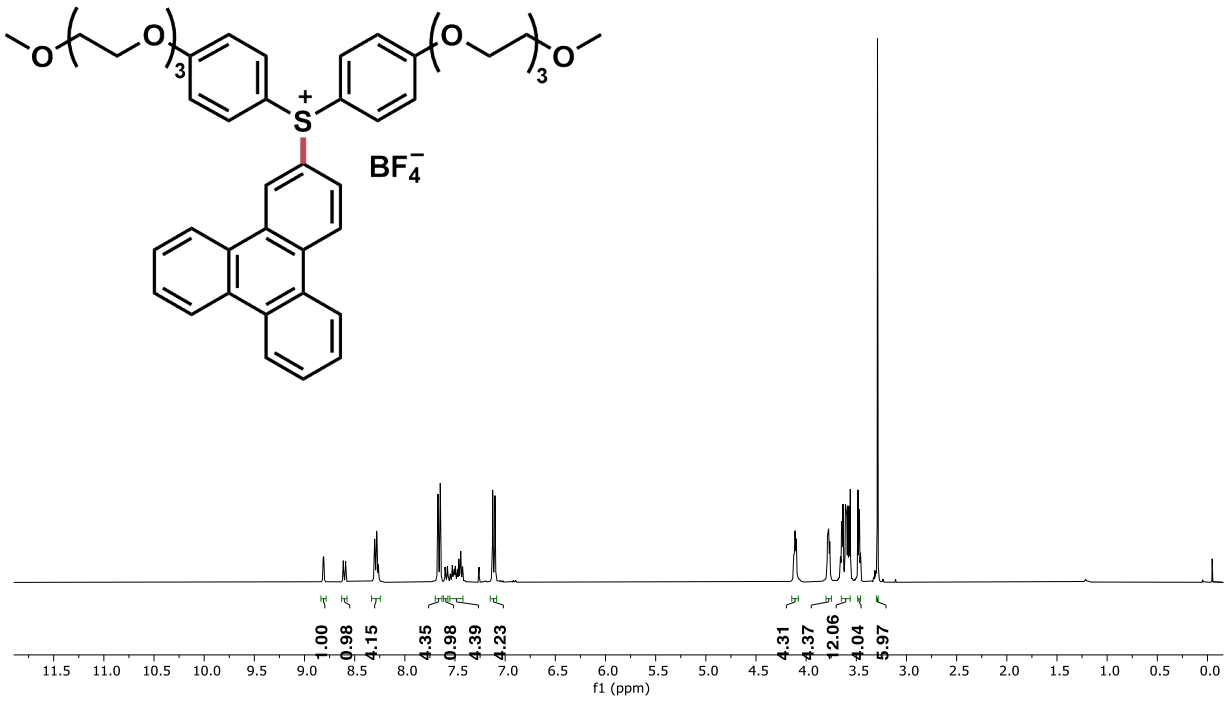

-152.16
BF4−
f1 (ppm)

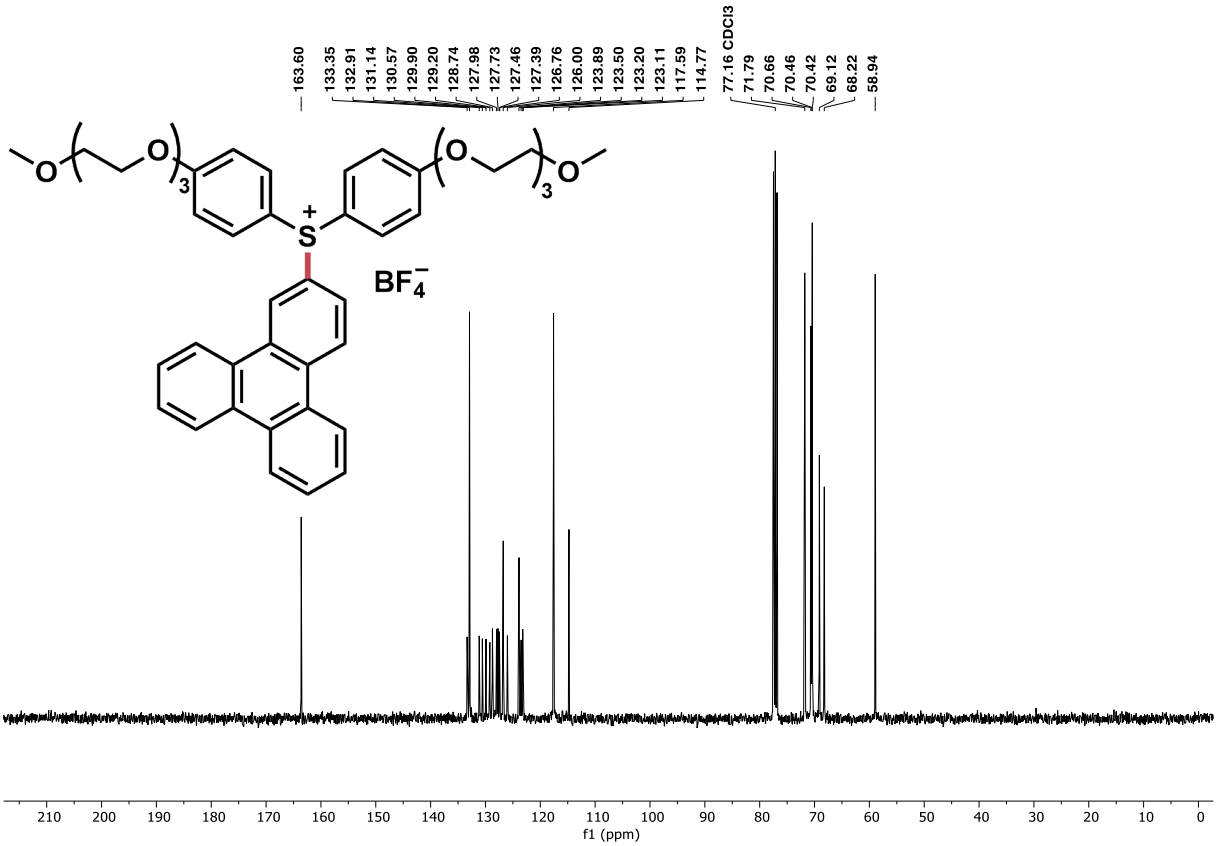

8.34 8.32 8.03 8.02 7.99 7.97 7.82 7.80 7.78 7.76 7.71 7.71 7.70 7.70 7.62 7.60 7.57 7.57 7.56 7.51 7.50 7.49 7.46 7.35 7.32 7.30 7.29 7.27 7.26 CDCl3
4.27 4.27 4.26 4.25 4.24 3.91 3.90 3.89 3.88 3.75 3.75 3.74 3.73 3.72 3.70 3.69 3.69 3.68 3.68 3.67 3.66 3.66 3.65 3.57 3.56 3.56 3.38
BF4−
0.93 1.02 1.00 2.17 2.22 2.12 3.23 3.12 6.26
4.09 4.22 4.41 4.30 4.23 3.91 5.69
f1 (ppm)

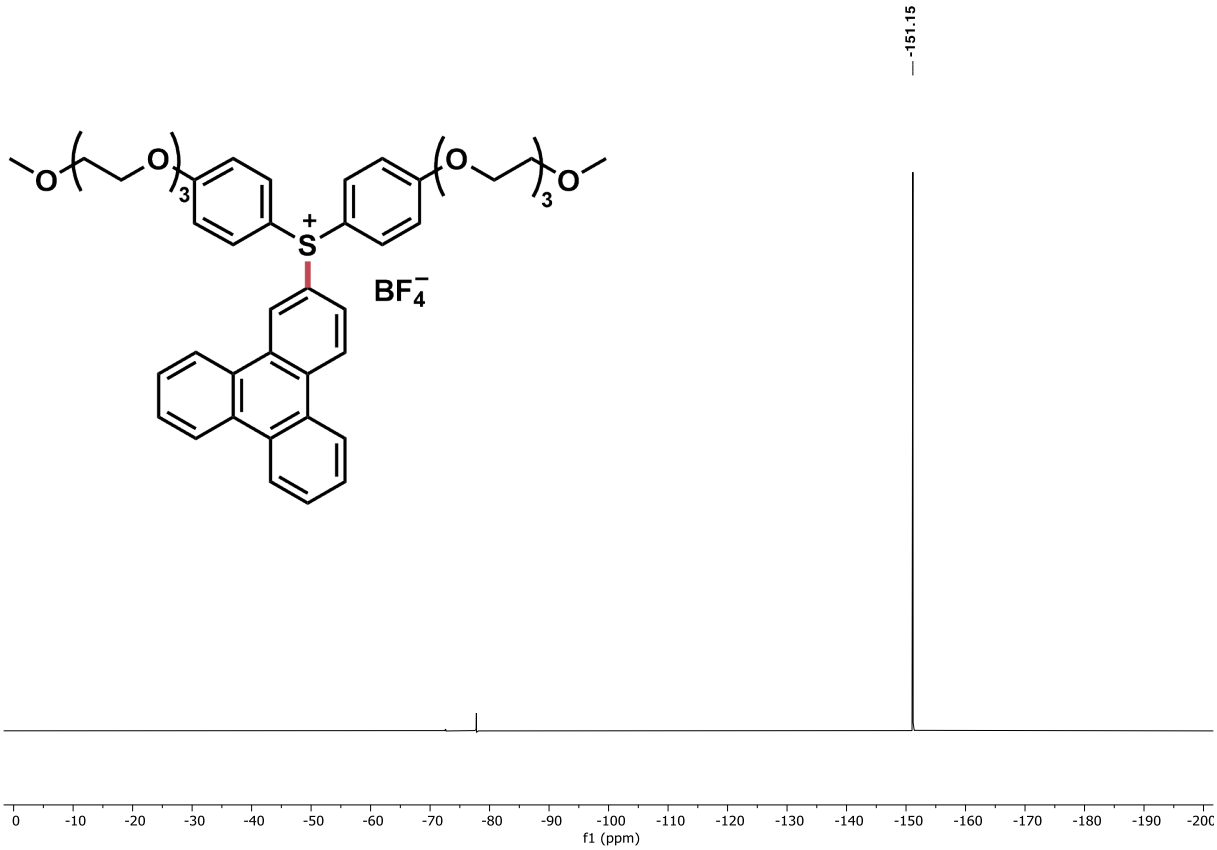

163.97 163.88
146.02 135.70 133.89 133.42 133.15 131.93 130.02 129.89 129.70 129.05 128.37 128.30 128.28 127.95 127.77 126.68 126.26 125.72 125.29 122.59 121.32 118.02 117.95 112.79 112.43 77.16 CDCl3 71.80 70.67 70.46 70.41 69.13 68.30 58.95
BF4−
f1 (ppm)


-152.08
BF4−
f1 (ppm)


8.81 8.81 8.61 8.59 8.30 8.30 8.29 8.28 8.28 7.67 7.66 7.65 7.65 7.46 7.46 7.44 7.44 7.44 7.12 7.12 7.11 7.10 4.12 4.11 4.11 4.11 4.10 3.79 3.78 3.78 3.77 3.76 3.66 3.65 3.65 3.64 3.64 3.63 3.63 3.61 3.61 3.60 3.60 3.60 3.59 3.58 3.58 3.57 3.57 3.56 3.48 3.48 3.47 3.47 3.46 3.29 3.28


BF4−
1.00 0.98 4.15 4.35 0.98 4.39 4.23 4.31 4.37 12.06 4.04 5.97
f1 (ppm)


163.60
133.35
132.91
131.14
130.57
129.90
129.20
128.74
127.98
127.73
127.46
127.39
126.76
126.00
123.89
123.50
123.20
123.11
117.59
114.77
77.16 CDCl3
71.79
70.66
70.46
70.42
69.12
68.22
58.94
BF4−
f1 (ppm)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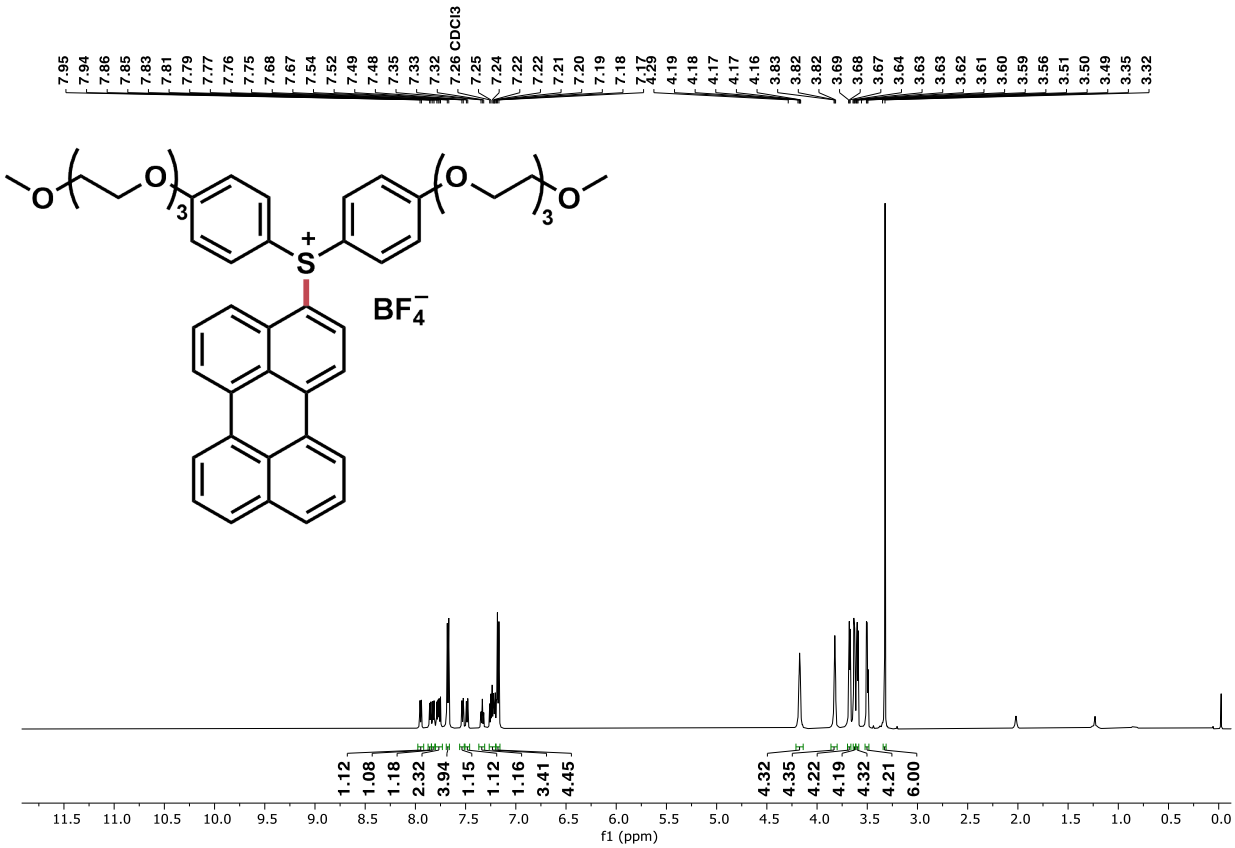
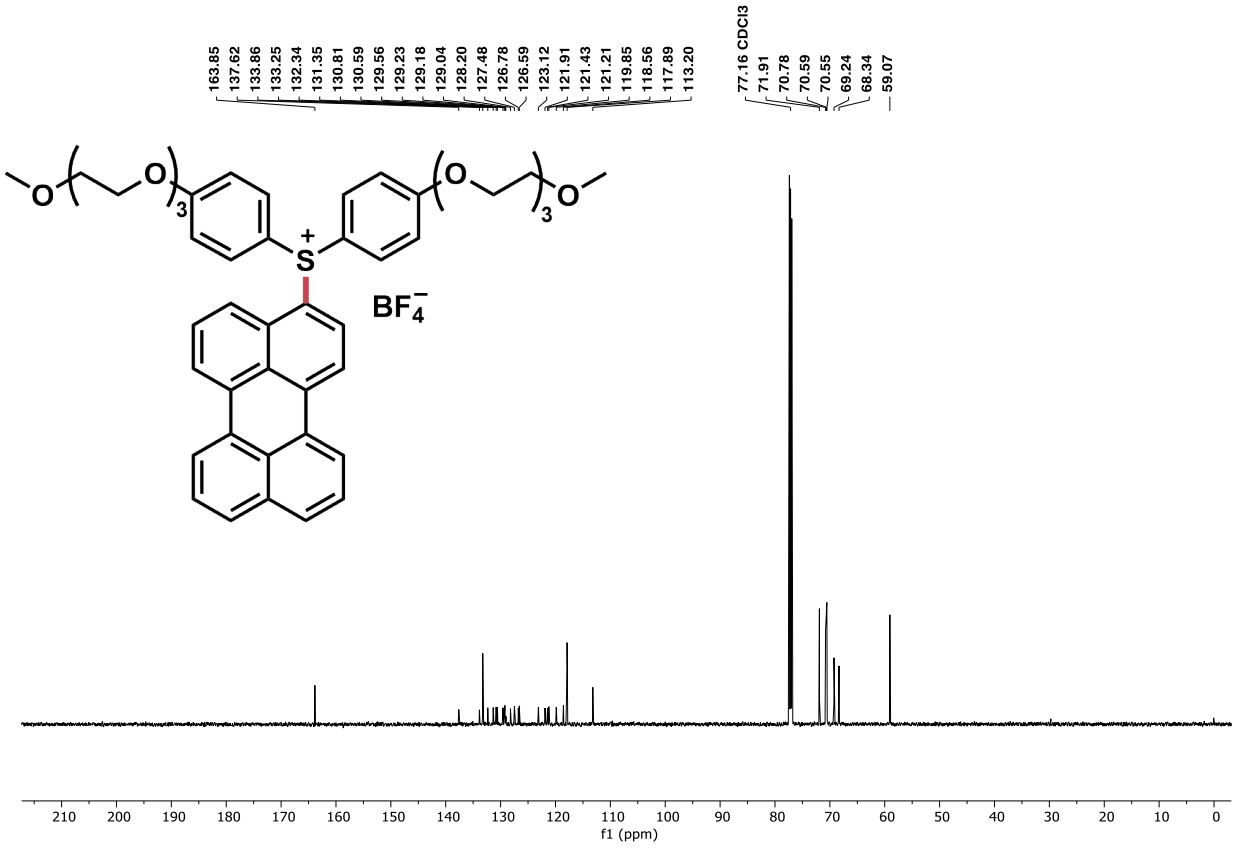
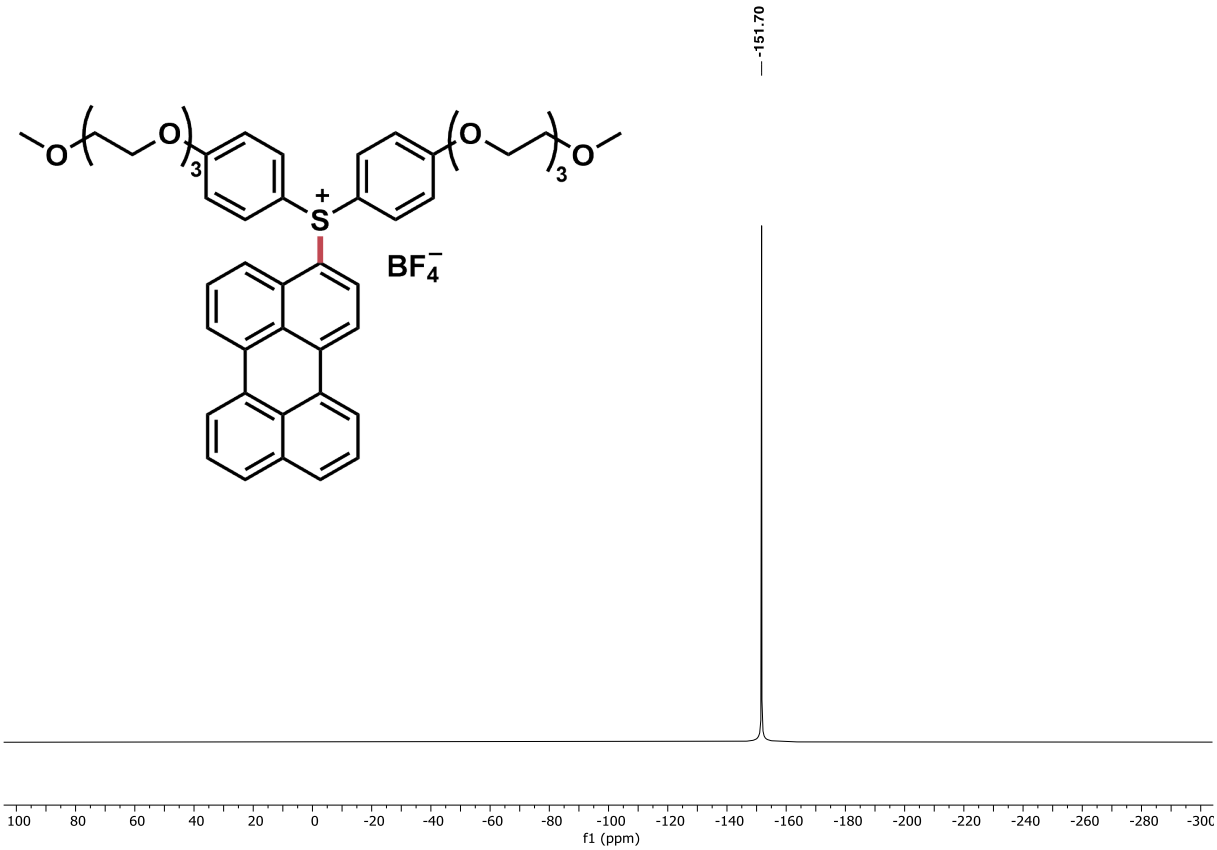
BF4−
f1 (ppm)


7.95 7.94 7.86 7.85 7.83 7.81 7.79 7.77 7.76 7.75 7.68 7.67 7.54 7.52 7.49 7.48 7.35 7.33 7.32 7.26 CDCl3 7.25 7.24 7.22 7.22 7.21 7.20 7.19 7.18 7.17 4.29 4.19 4.18 4.17 4.17 4.16 3.83 3.82 3.82 3.69 3.68 3.67 3.64 3.63 3.63 3.62 3.61 3.60 3.59 3.56 3.51 3.50 3.49 3.35 3.32
BF4−
1.12 1.08 1.18 2.32 3.94 1.15 1.12 1.16 3.41 4.45
4.32 4.35 4.22 4.19 4.32 4.21 6.00
f1 (ppm)


163.85 137.62 133.86 133.25 132.34 131.35 130.81 130.59 129.56 129.23 129.18 129.04 128.20 127.48 126.78 126.59 123.12 121.91 121.43 121.21 119.85 118.56 117.89 113.20
77.16 CDCl3 71.91 70.78 70.59 70.55 69.24 68.34 59.07
BF4−
f1 (ppm)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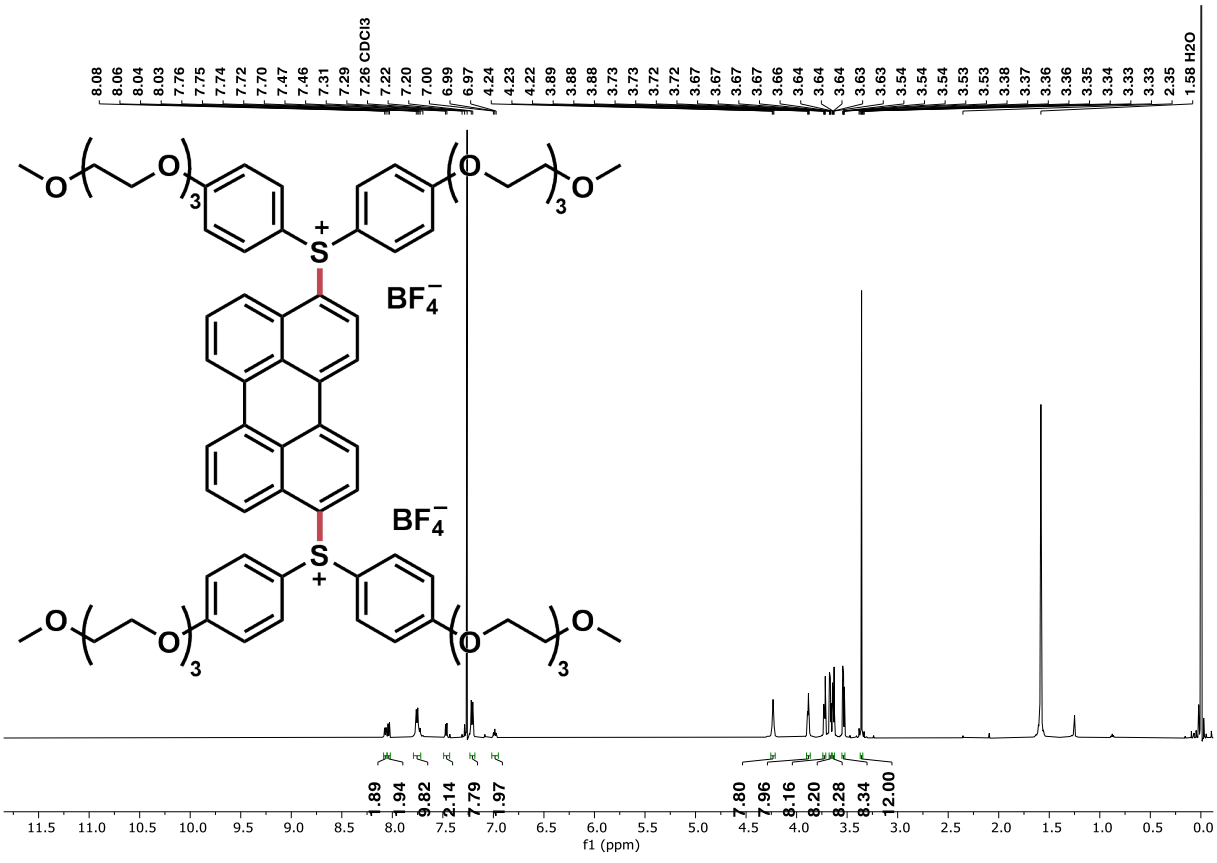
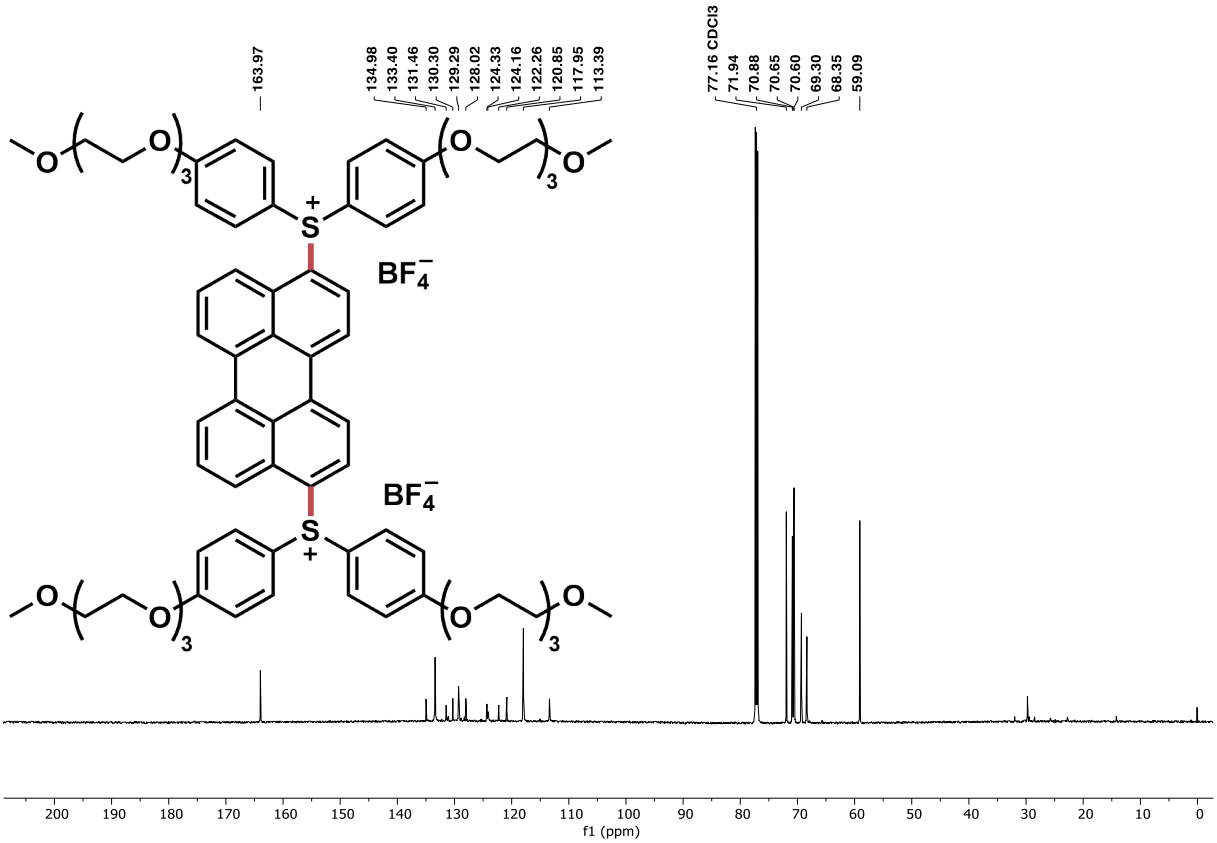
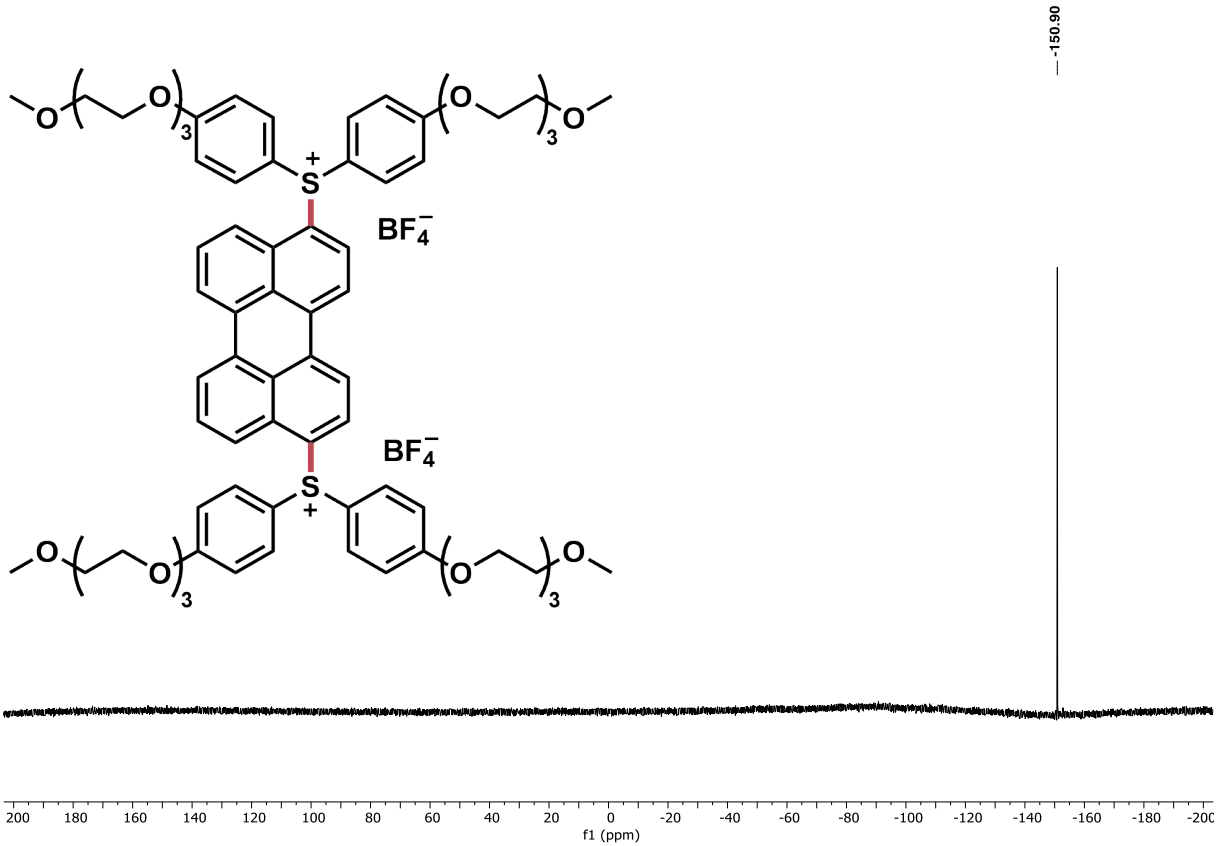
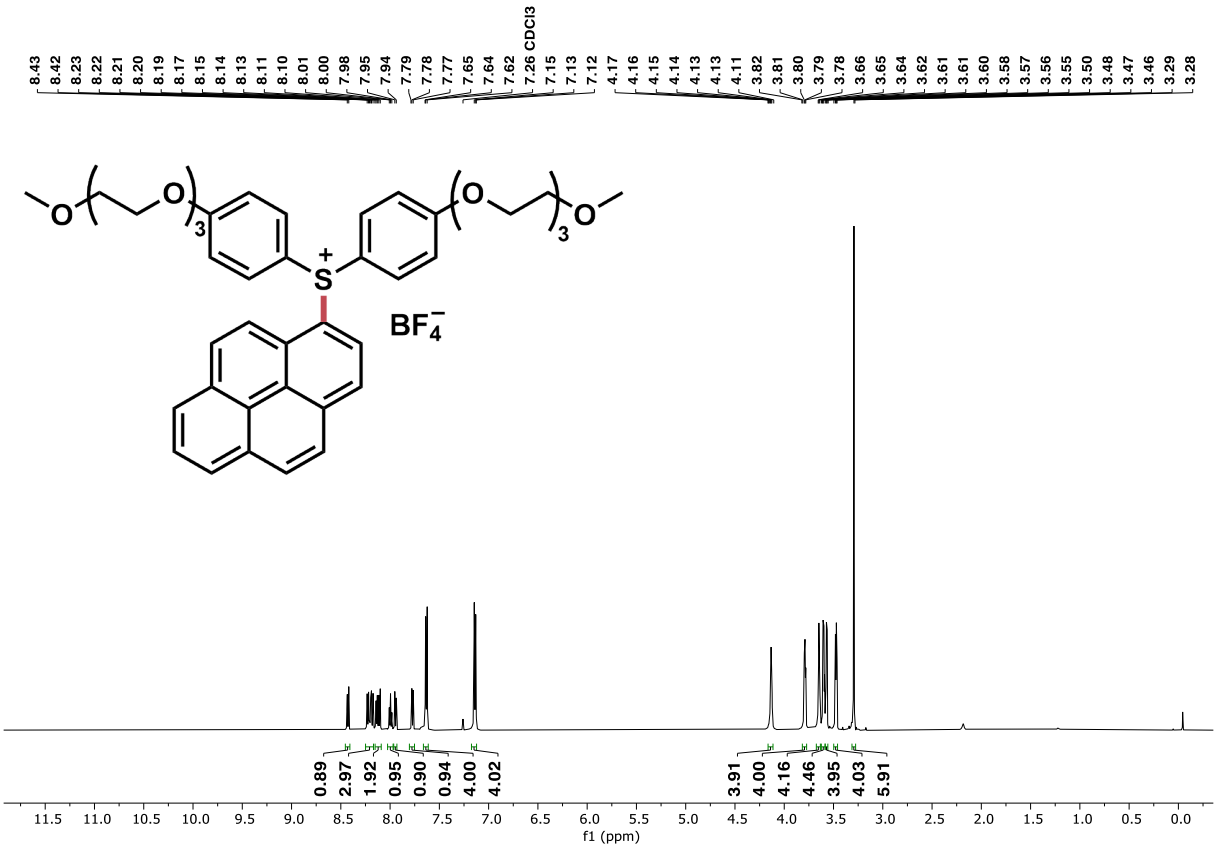
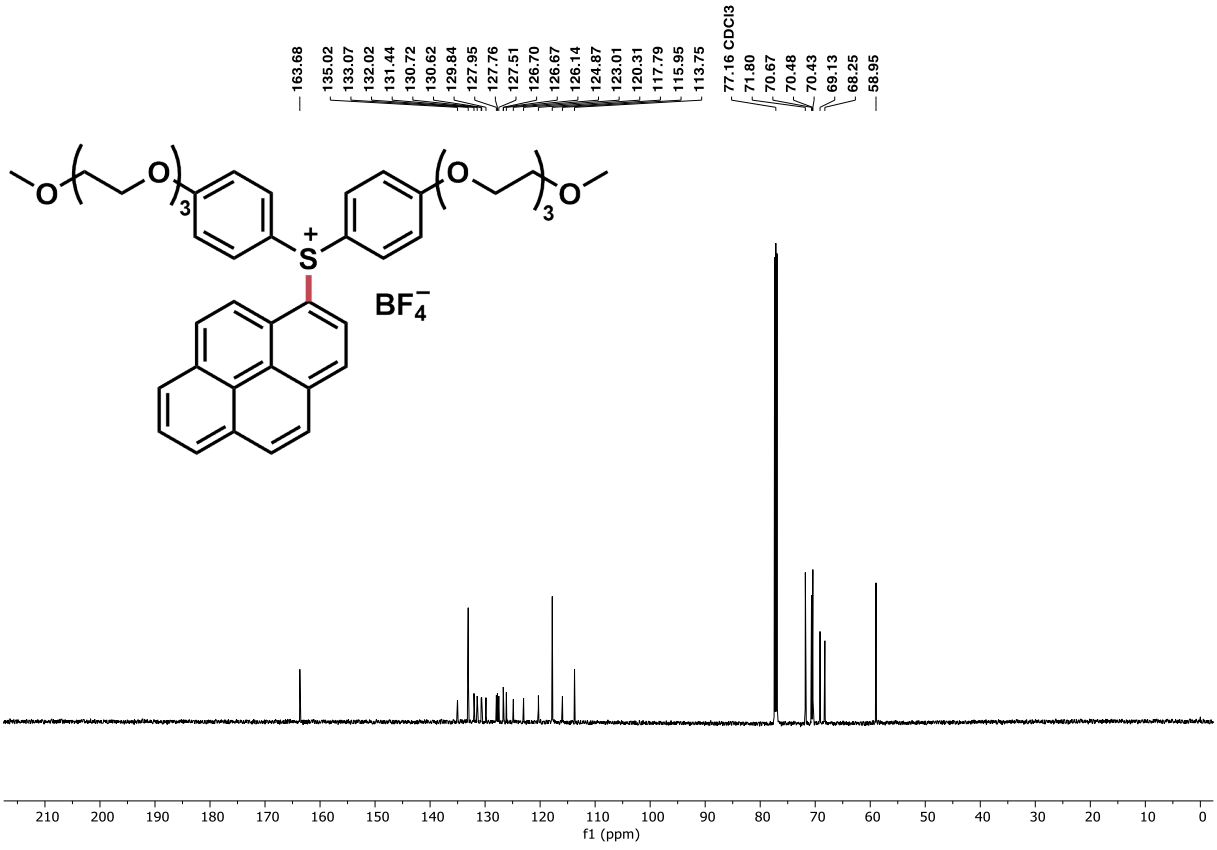
f1 (ppm)

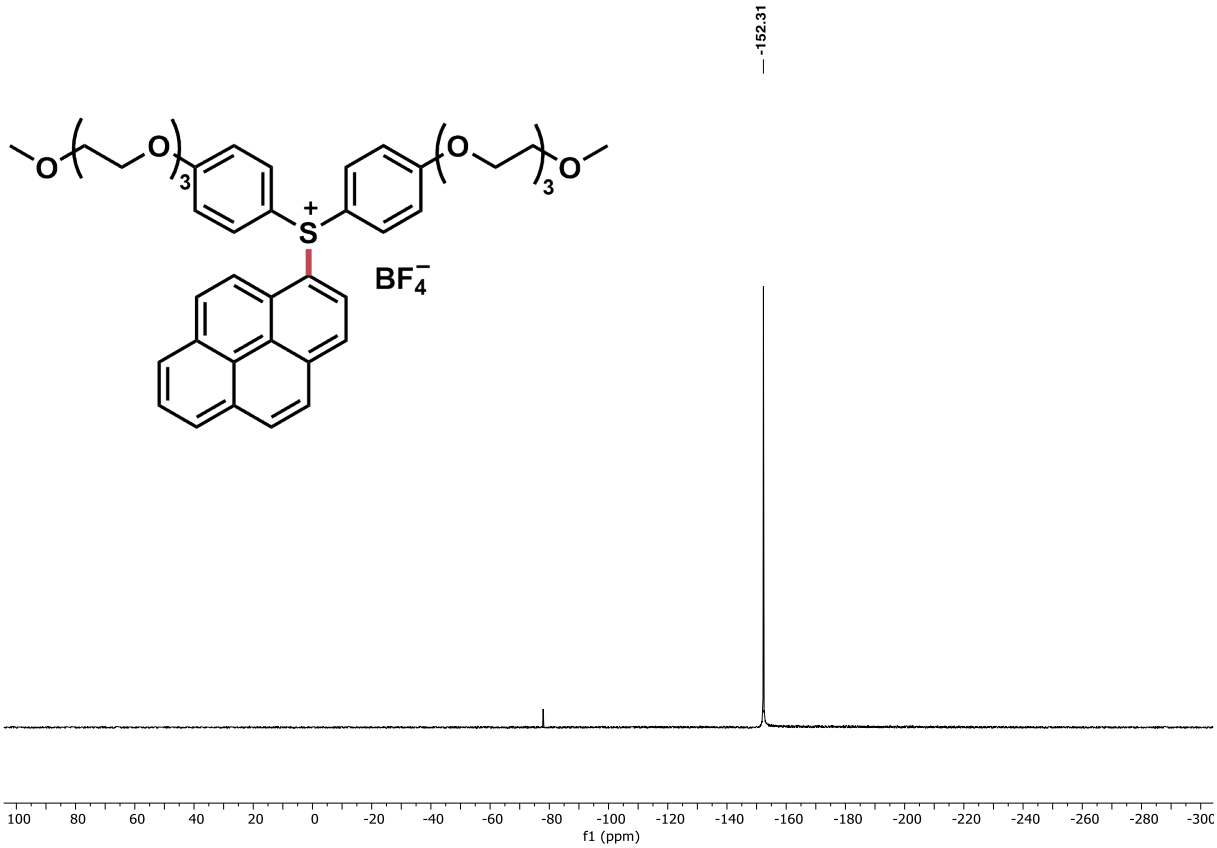

8.08 8.06 8.04 8.03 7.76 7.75 7.74 7.72 7.70 7.47 7.46 7.31 7.29 7.26 CDCl3 7.22 7.20 7.00 6.99 6.97 4.24 4.23 4.22 3.89 3.88 3.88 3.73 3.73 3.72 3.72 3.67 3.67 3.67 3.67 3.66 3.64 3.64 3.64 3.63 3.63 3.54 3.54 3.54 3.53 3.53 3.38 3.37 3.36 3.36 3.35 3.34 3.33 3.33 2.35 1.58 H2O
BF4−
BF4−
1.89 1.94 9.82 2.14 7.79 7.97 7.80 7.96 8.16 8.20 8.28 8.34 12.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

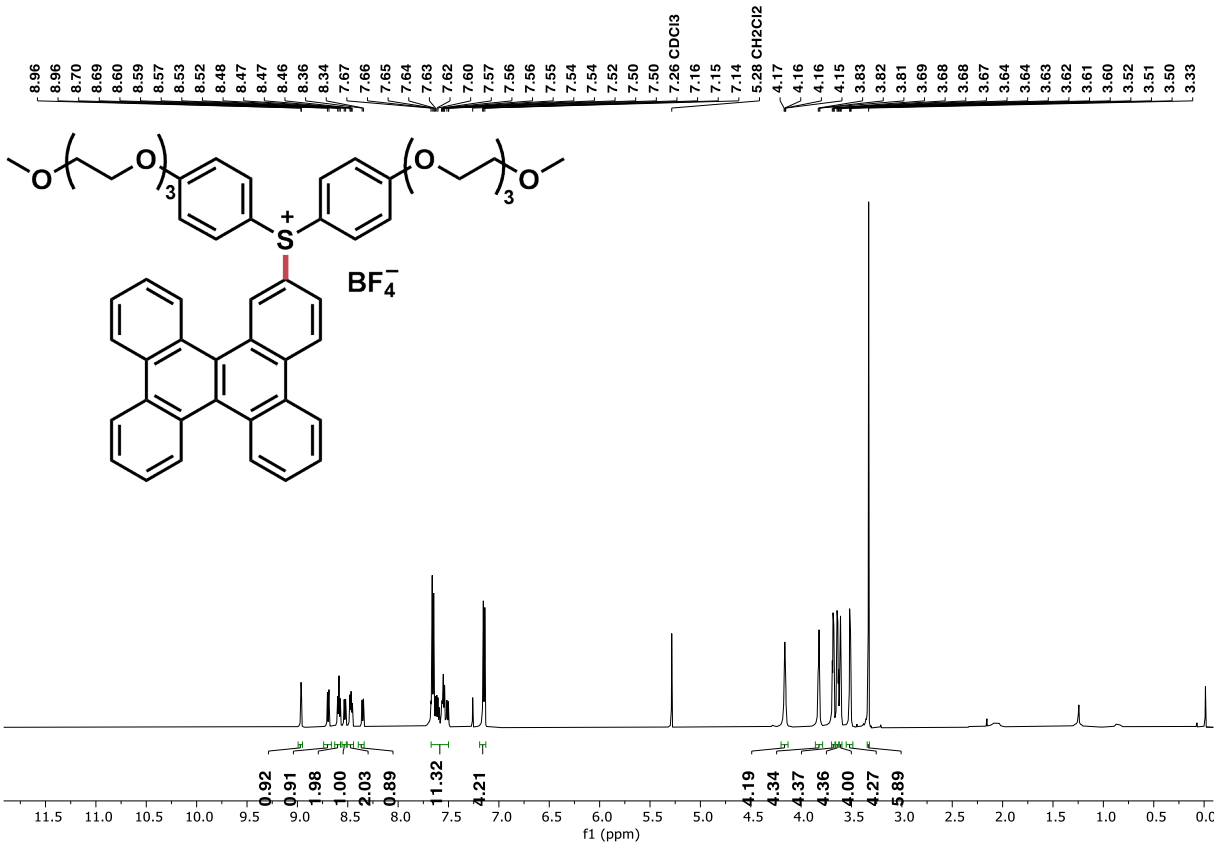

163.97
134.98
133.40
131.46
130.30
129.29
128.02
124.33
124.16
122.26
120.85
117.95
113.39
77.16 CDCl3
71.94
70.88
70.65
70.60
69.30
68.35
59.09
BF4−
BF4−
f1 (ppm)

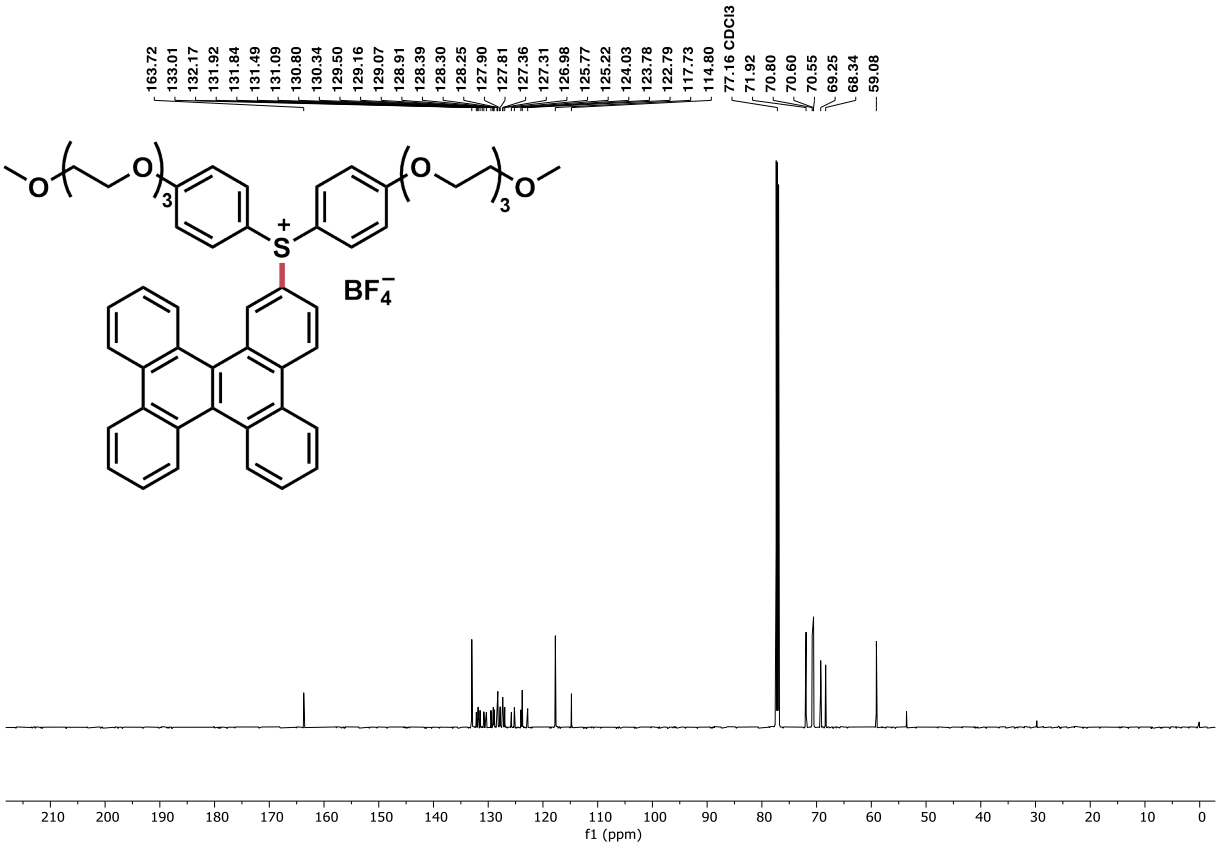

-150.90
BF4−
BF4−
f1 (ppm)


8.43 8.42 8.23 8.22 8.21 8.20 8.19 8.17 8.15 8.14 8.13 8.11 8.10 8.01 8.00 7.98 7.95 7.94 7.79 7.78 7.77 7.65 7.64 7.62 7.26 CDCl3 7.15 7.13 7.12 4.17 4.16 4.15 4.14 4.13 4.11 3.82 3.81 3.80 3.79 3.78 3.66 3.65 3.64 3.62 3.61 3.61 3.60 3.58 3.57 3.56 3.55 3.50 3.48 3.47 3.46 3.29 3.28
BF4−
0.89 2.97 1.92 0.95 0.90 0.94 4.00 4.02 3.91 4.00 4.16 4.46 3.95 4.03 5.91
f1 (ppm)


163.68 135.02 133.07 132.02 131.44 130.72 130.62 129.84 127.95 127.76 127.51 126.70 126.67 126.14 124.87 123.01 120.31 117.79 115.95 113.75 77.16 CDCl3 71.80 70.67 70.48 70.43 69.13 68.25 58.95
BF4−
f1 (ppm)


-152.31
BF4−
f1 (ppm)


7.26 CDCl3
5.28 CH2Cl2
BF4−
0.92
0.91
1.98
1.00
2.03
0.89
11.32
4.21
4.19
4.34
4.37
4.36
4.00
4.27
5.89
f1 (ppm)


163.72
133.01
132.17
131.92
131.84
131.49
131.09
130.80
130.34
129.50
129.16
129.07
128.91
128.39
128.30
128.25
127.90
127.81
127.36
127.31
126.98
125.77
125.22
124.03
123.78
122.79
117.73
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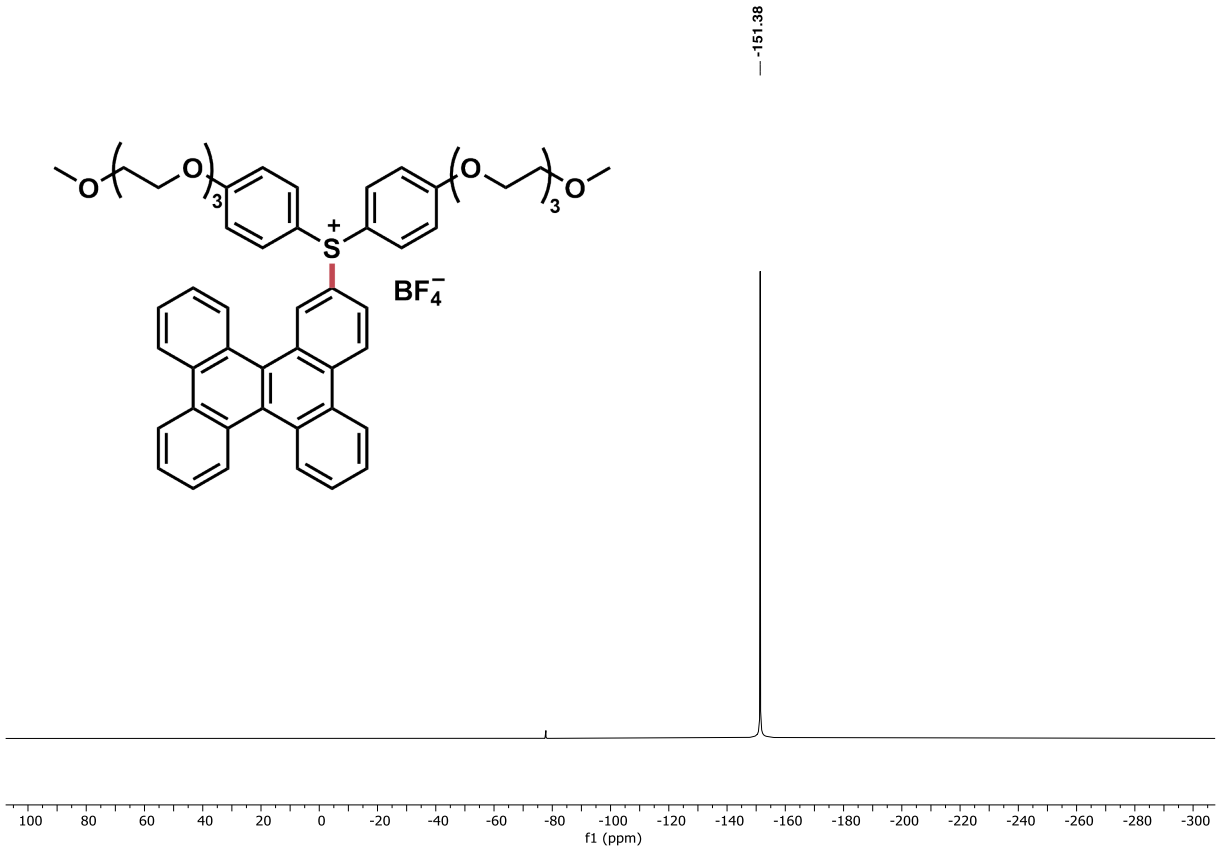
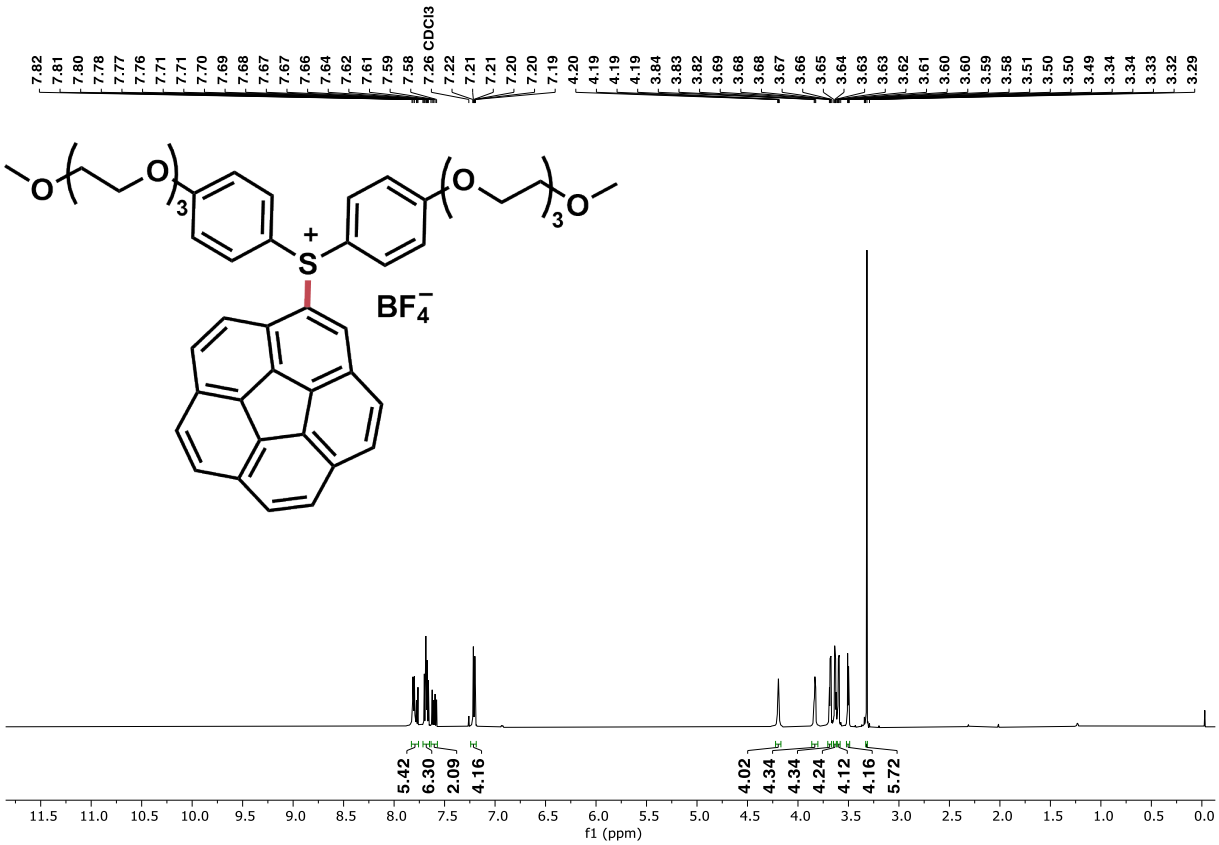
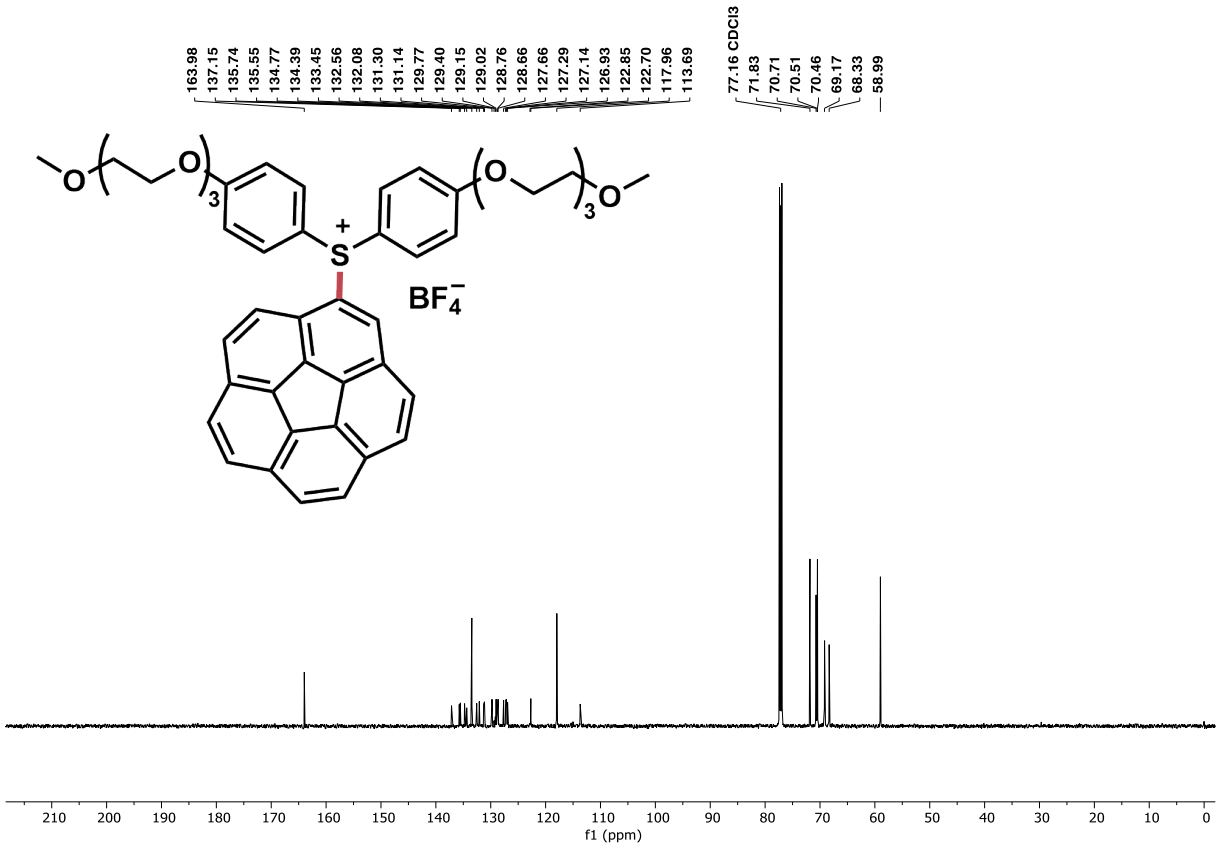
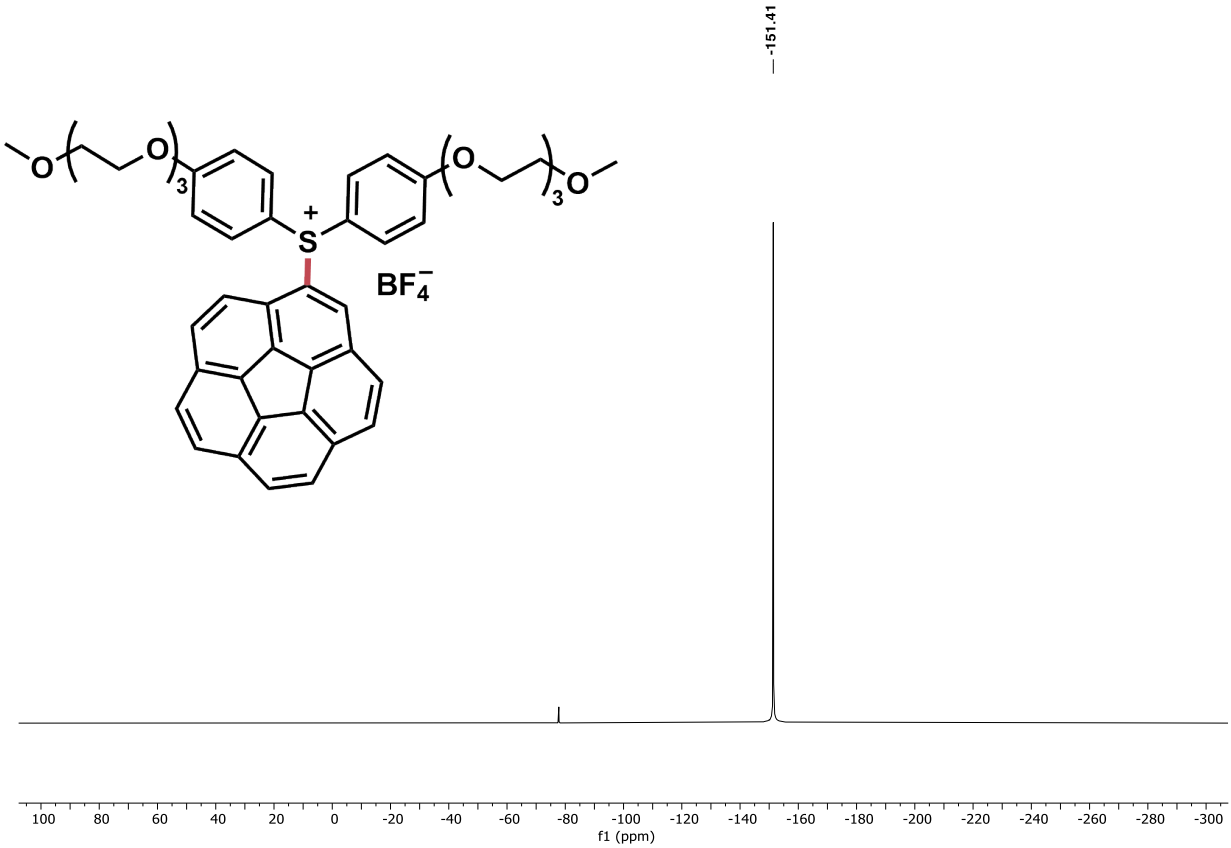
69.25
68.34
59.08
BF4−
f1 (ppm)


-151.38
BF4−
f1 (ppm)


7.82 7.81 7.80 7.78 7.77 7.76 7.71 7.71 7.70 7.69 7.68 7.67 7.67 7.66 7.64 7.62 7.61 7.59 7.58 7.26 CDCl3 7.22 7.21 7.21 7.20 7.20 7.19 4.20 4.19 4.19 4.19 3.84 3.83 3.82 3.69 3.68 3.68 3.67 3.66 3.65 3.64 3.63 3.63 3.62 3.61 3.60 3.60 3.59 3.58 3.51 3.50 3.50 3.49 3.34 3.34 3.33 3.32 3.29
O
3
O
S
+
BF4−
O
3
O
5.42 6.30 2.09 4.16 4.02 4.34 4.34 4.24 4.12 4.16 5.72
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


163.98 137.15 135.74 135.55 134.77 134.39 133.45 132.56 132.08 131.30 131.14 129.77 129.40 129.15 129.02 128.76 128.66 127.66 127.29 127.14 126.93 122.85 122.70 117.96 113.69
77.16 CDCl3 71.83 70.71 70.51 70.46 69.17 68.33 58.99
O
3
O
S
+
BF4−
O
3
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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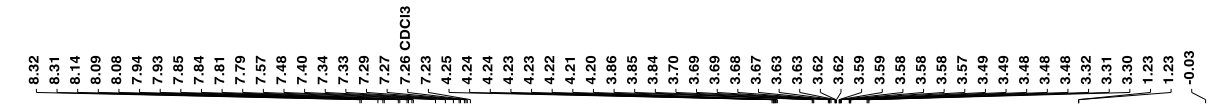
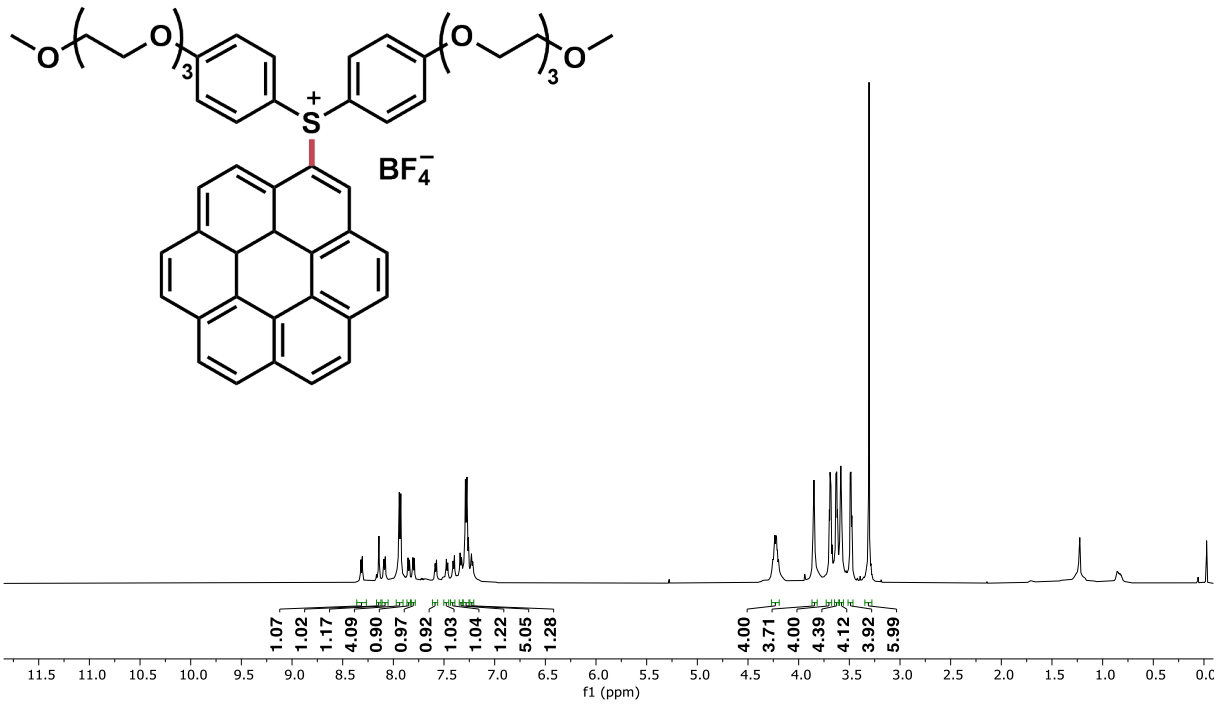
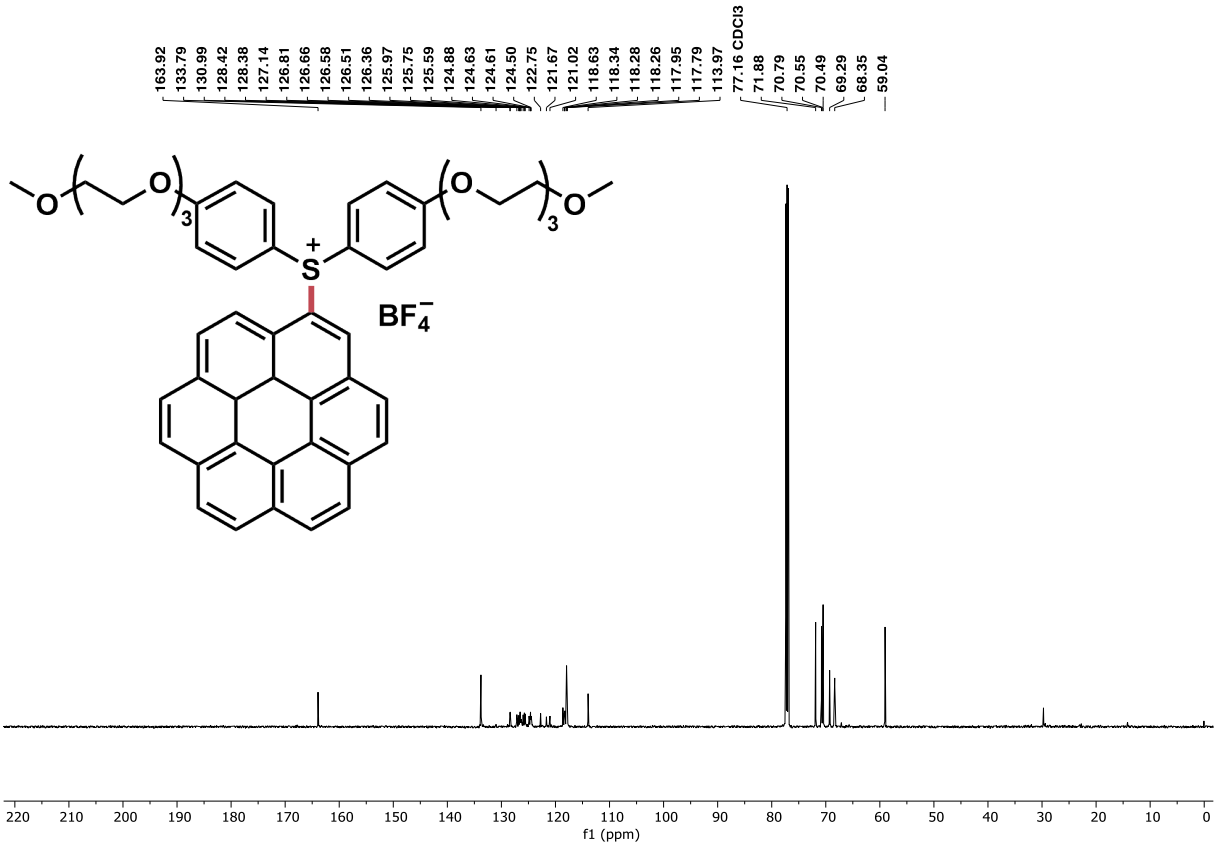
BF4−
f1 (ppm)


CDCl3


BF4−
1.07
1.02
1.17
4.09
0.90
0.97
0.92
1.03
1.04
1.22
5.05
1.28
4.00
3.71
4.00
4.39
4.12
3.92
5.99
f1 (ppm)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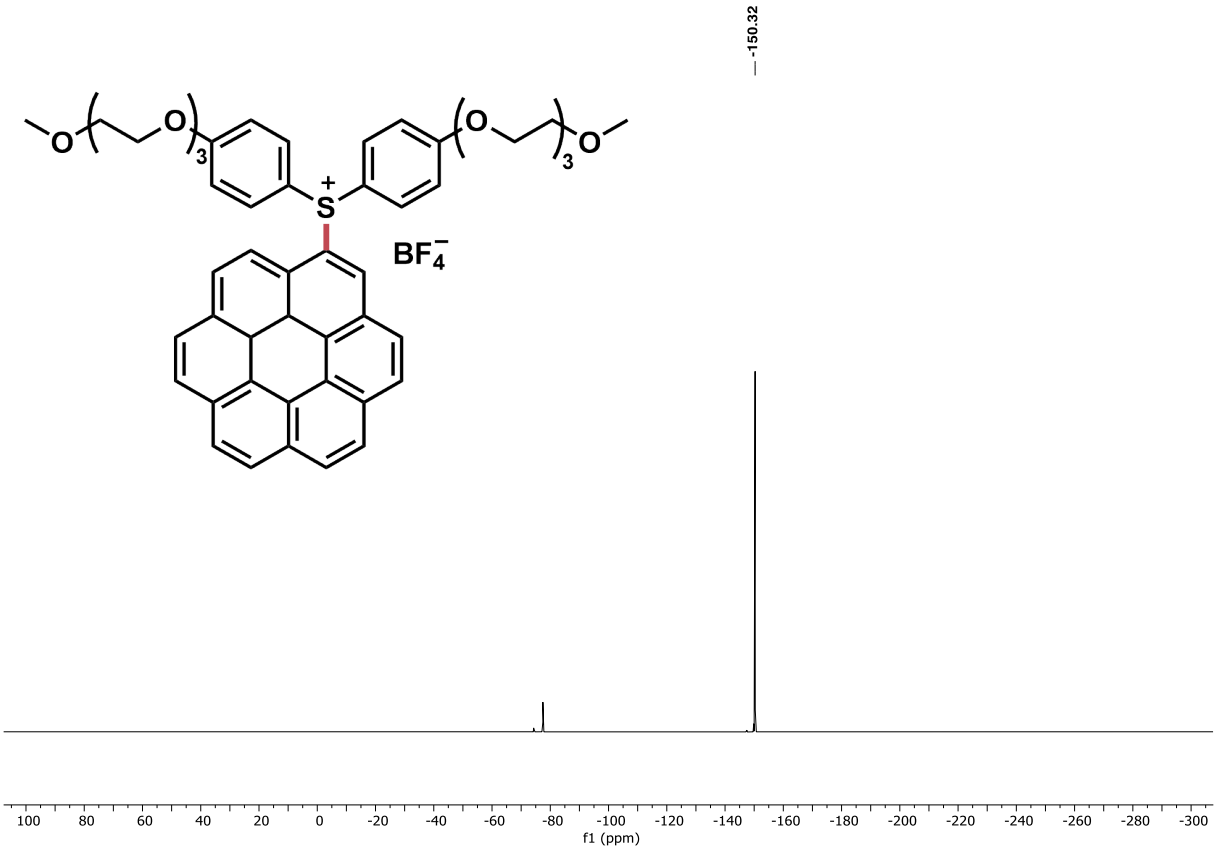
127.14
126.81
126.66
126.58
126.51
126.36
125.97
125.75
125.59
124.88
124.63
124.61
124.50
122.75
121.67
121.02
118.63
118.34
118.28
118.26
117.95
117.79
113.97
77.16 CDCl3
71.88
70.79
70.55
70.49
69.29
68.35
59.04
BF4−
f1 (ppm)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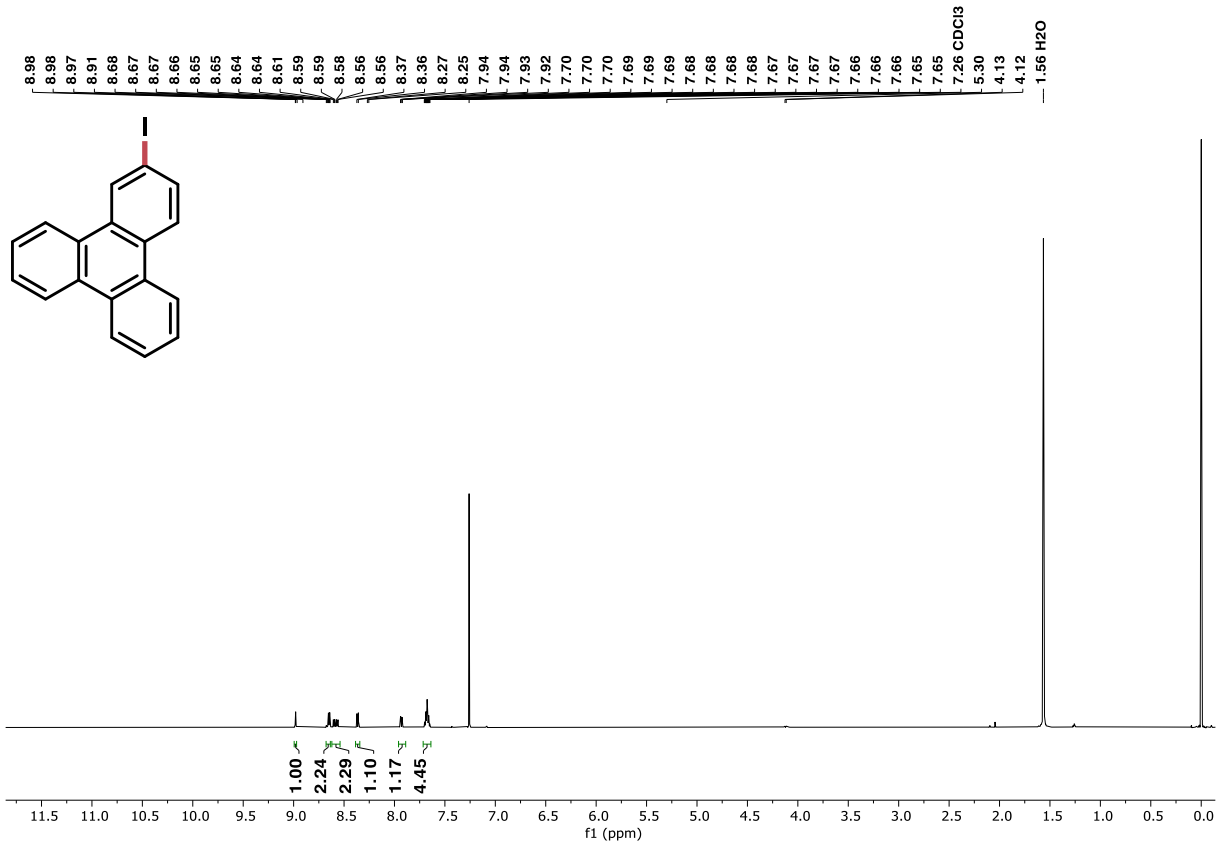
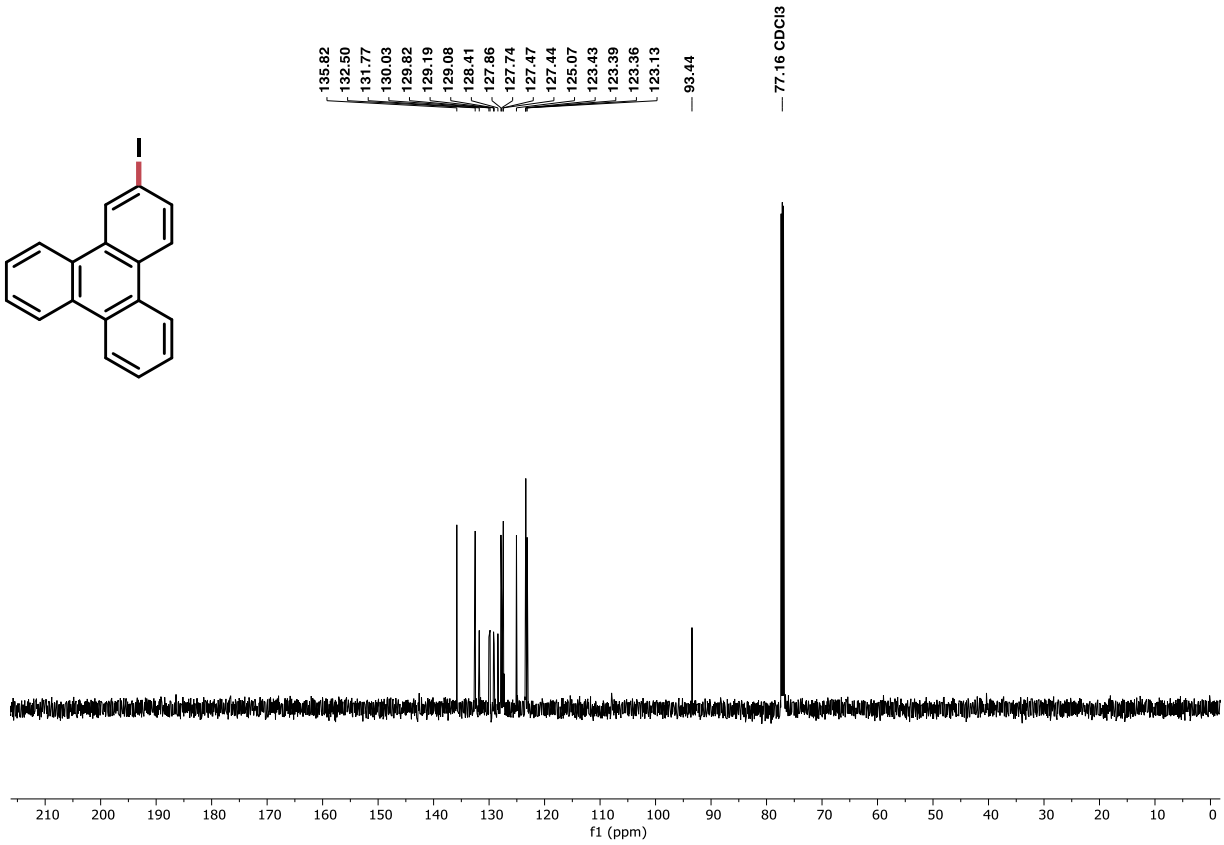
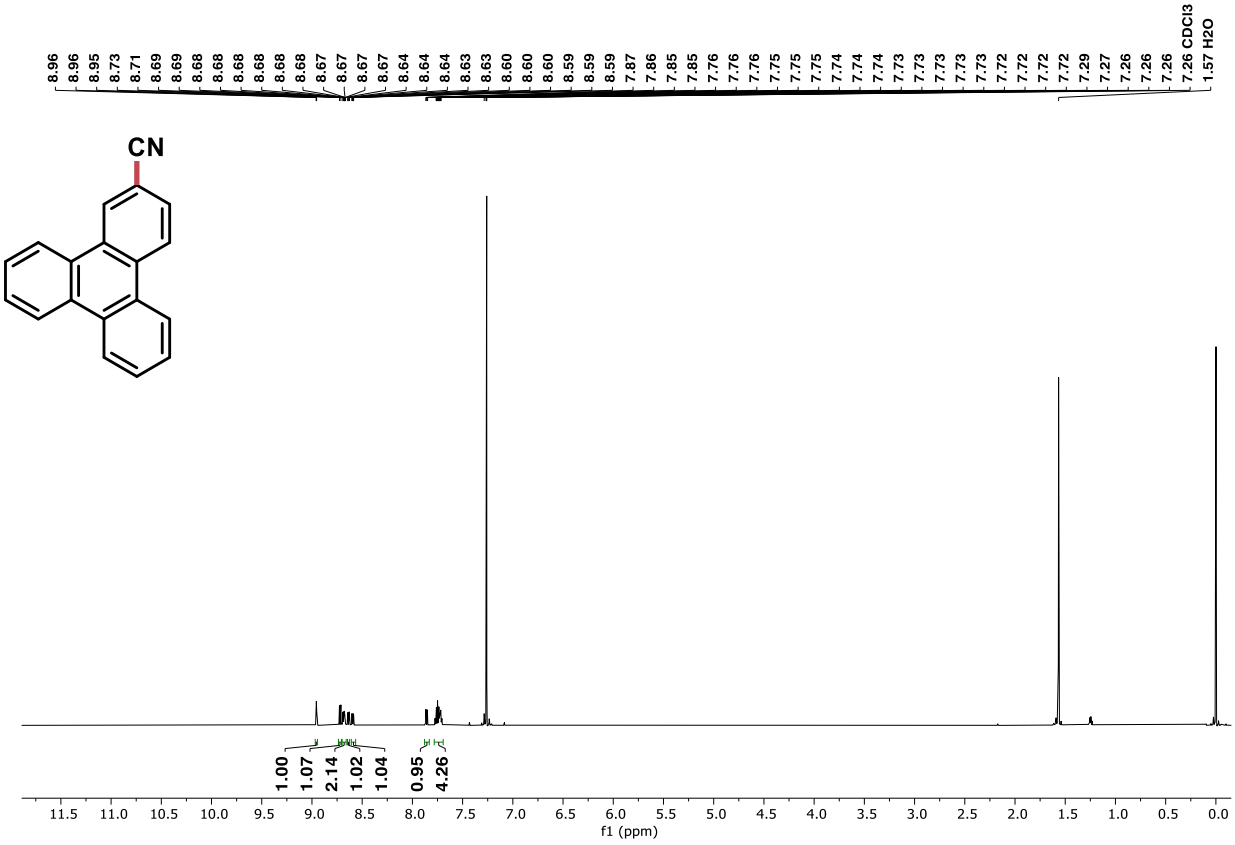
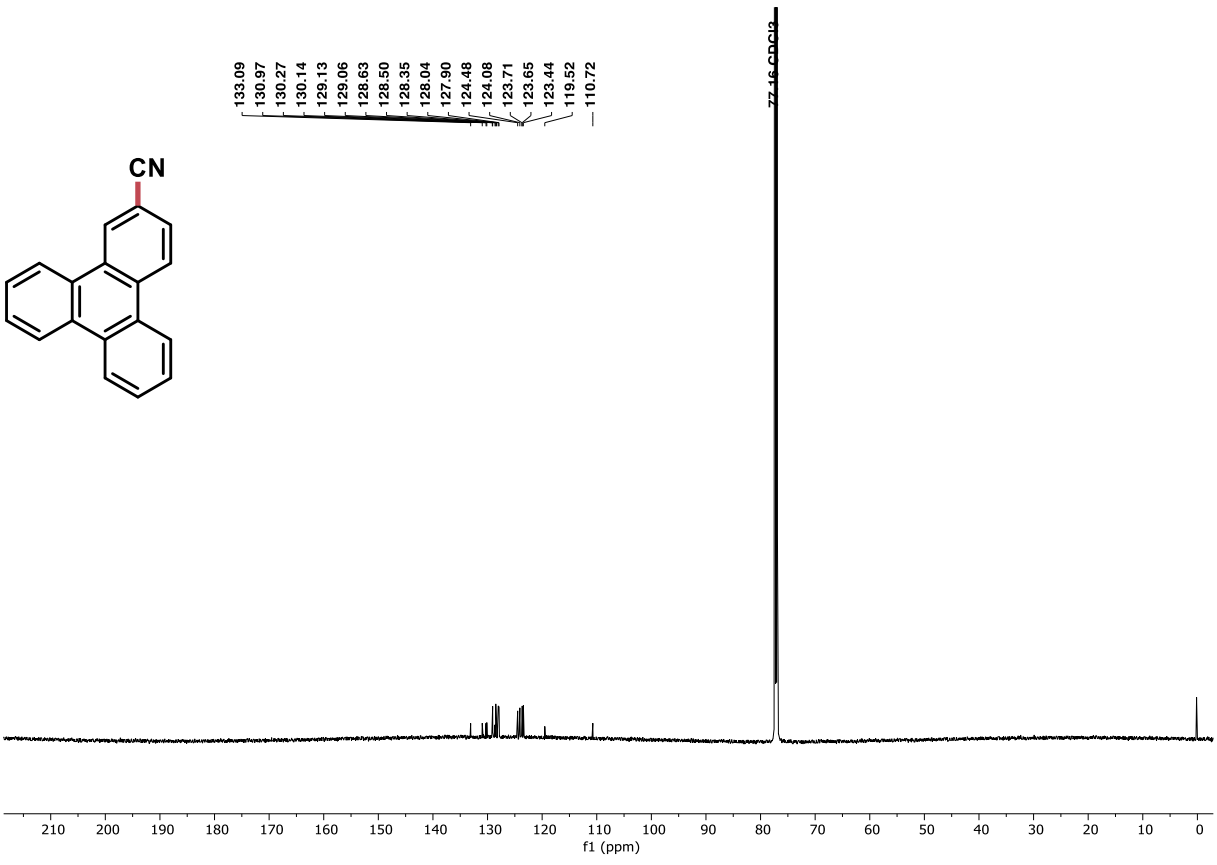
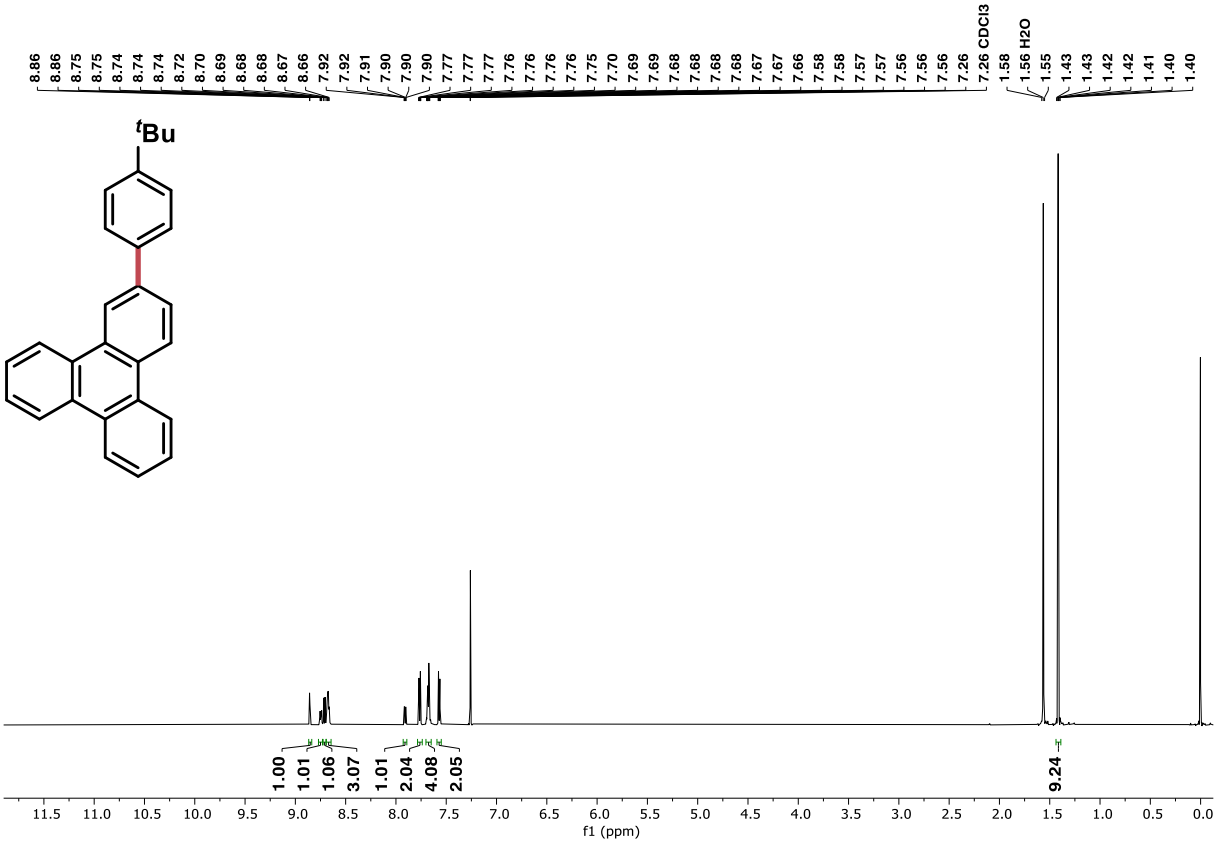
BF4−
f1 (ppm)

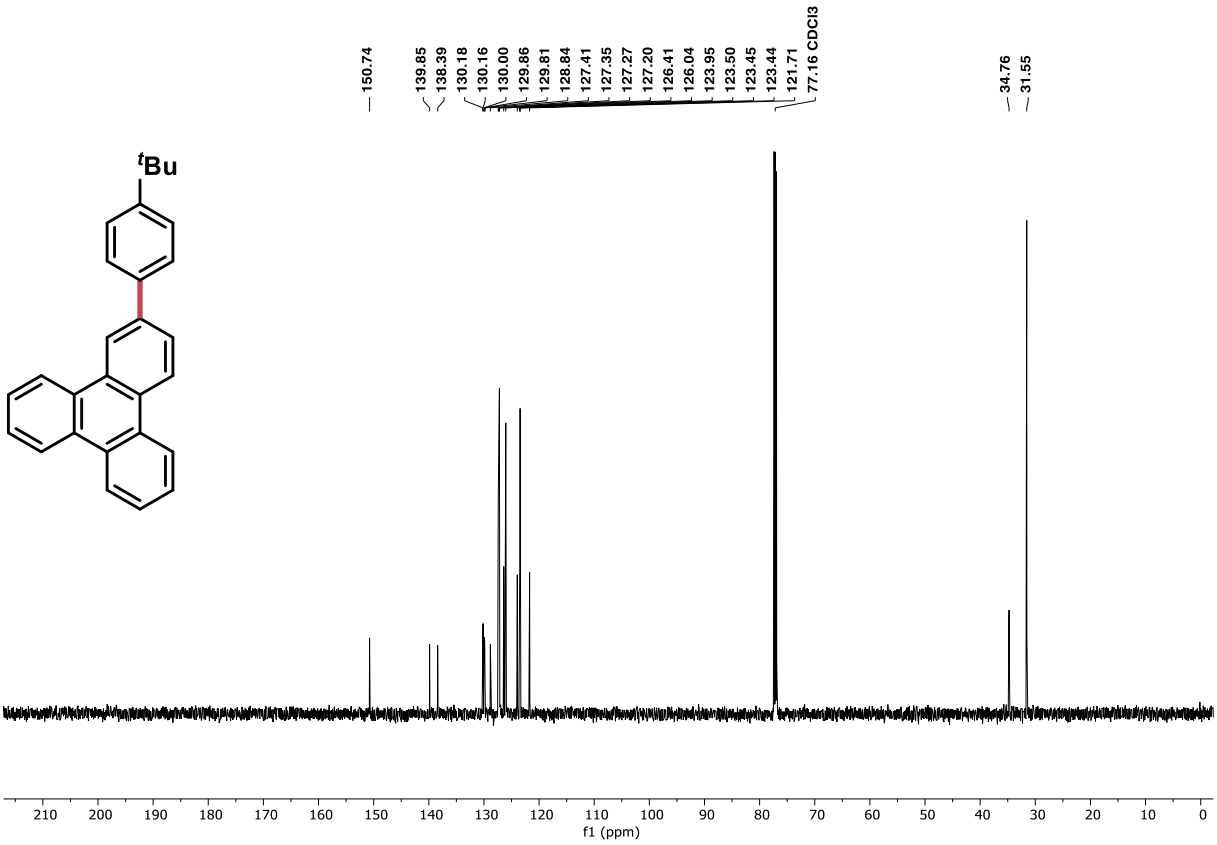

8.98 8.98 8.97 8.91 8.68 8.67 8.67 8.66 8.65 8.65 8.64 8.64 8.61 8.59 8.59 8.58 8.56 8.56 8.37 8.36 8.27 8.25 7.94 7.94 7.93 7.92 7.70 7.70 7.70 7.69 7.69 7.69 7.68 7.68 7.68 7.68 7.67 7.67 7.67 7.67 7.66 7.66 7.66 7.65 7.65 7.26 CDCl3 5.30 4.13 4.12 1.56 H2O
1.00 2.24 2.29 1.10 1.17 4.45
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


135.82 132.50 131.77 130.03 129.82 129.19 129.08 128.41 127.86 127.74 127.47 127.44 125.07 123.43 123.39 123.36 123.13 93.44 77.16 CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.96 8.96 8.95 8.73 8.71 8.69 8.69 8.68 8.68 8.68 8.68 8.68 8.68 8.67 8.67 8.67 8.67 8.64 8.64 8.64 8.63 8.63 8.60 8.60 8.60 8.59 8.59 8.59 7.87 7.86 7.85 7.85 7.76 7.76 7.76 7.75 7.75 7.75 7.74 7.74 7.74 7.73 7.73 7.73 7.73 7.72 7.72 7.72 7.72 7.29 7.27 7.26 7.26 7.26 7.26 CDCl3 1.57 H2O
CN
1.00 1.07 2.14 1.02 1.04 0.95 4.26
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


133.09 130.97 130.27 130.14 129.13 129.06 128.63 128.50 128.35 128.04 127.90 124.48 124.08 123.71 123.65 123.44 119.52 110.72
77.16 CDCl3
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.86 8.86 8.75 8.75 8.74 8.74 8.74 8.74 8.72 8.70 8.69 8.68 8.68 8.67 8.66 7.92 7.92 7.91 7.90 7.90 7.90 7.77 7.77 7.77 7.76 7.76 7.76 7.76 7.76 7.75 7.70 7.69 7.69 7.68 7.68 7.68 7.68 7.67 7.67 7.66 7.58 7.58 7.57 7.57 7.56 7.56 7.56 7.56 7.26 CDCl3 1.58 1.56 H2O 1.55 1.43 1.43 1.42 1.42 1.41 1.40 1.40
tBu
1.00 1.01 1.06 3.07 1.01 2.04 4.08 2.05 9.24
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


150.74 139.85 138.39 130.18 130.16 130.00 129.86 129.81 128.84 127.41 127.35 127.27 127.20 126.41 126.04 123.95 123.50 123.45 123.44 121.71 77.16 CDCl3 34.76 31.55
tBu
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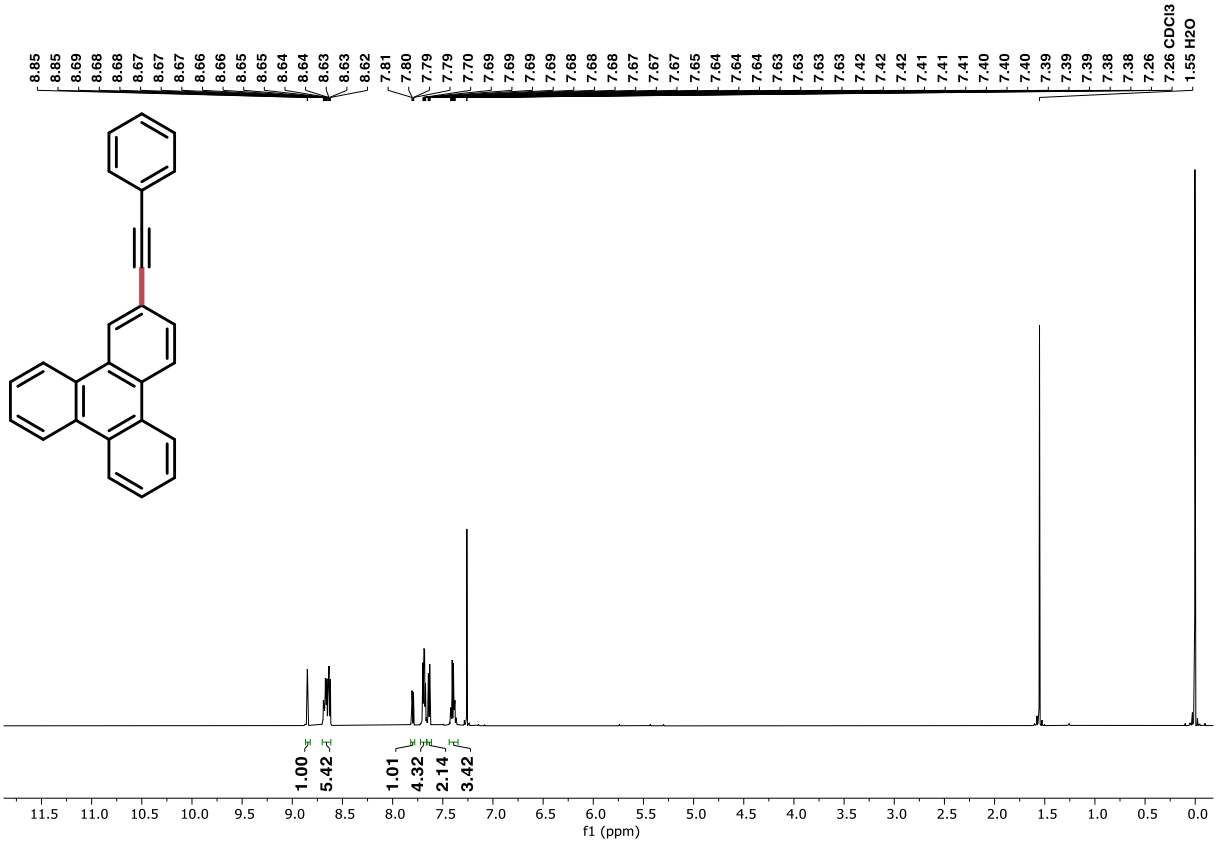
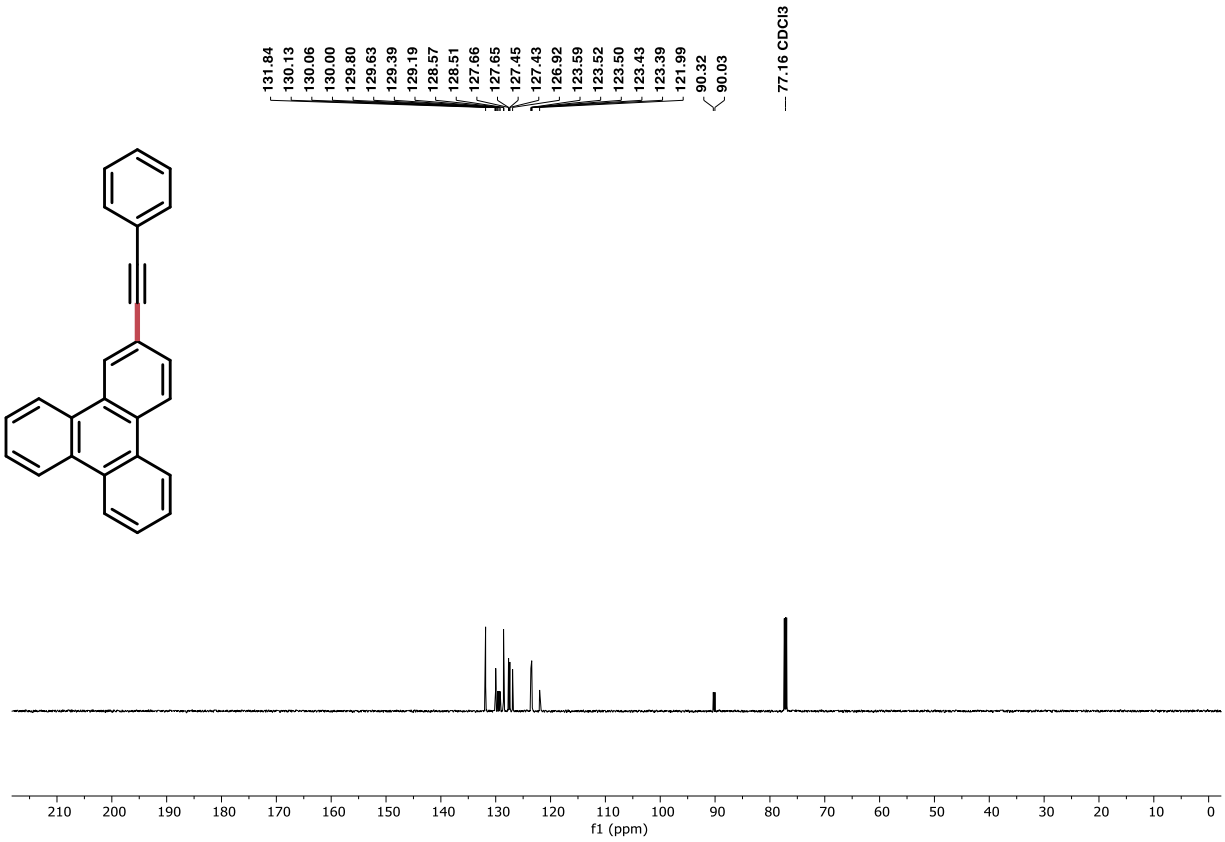
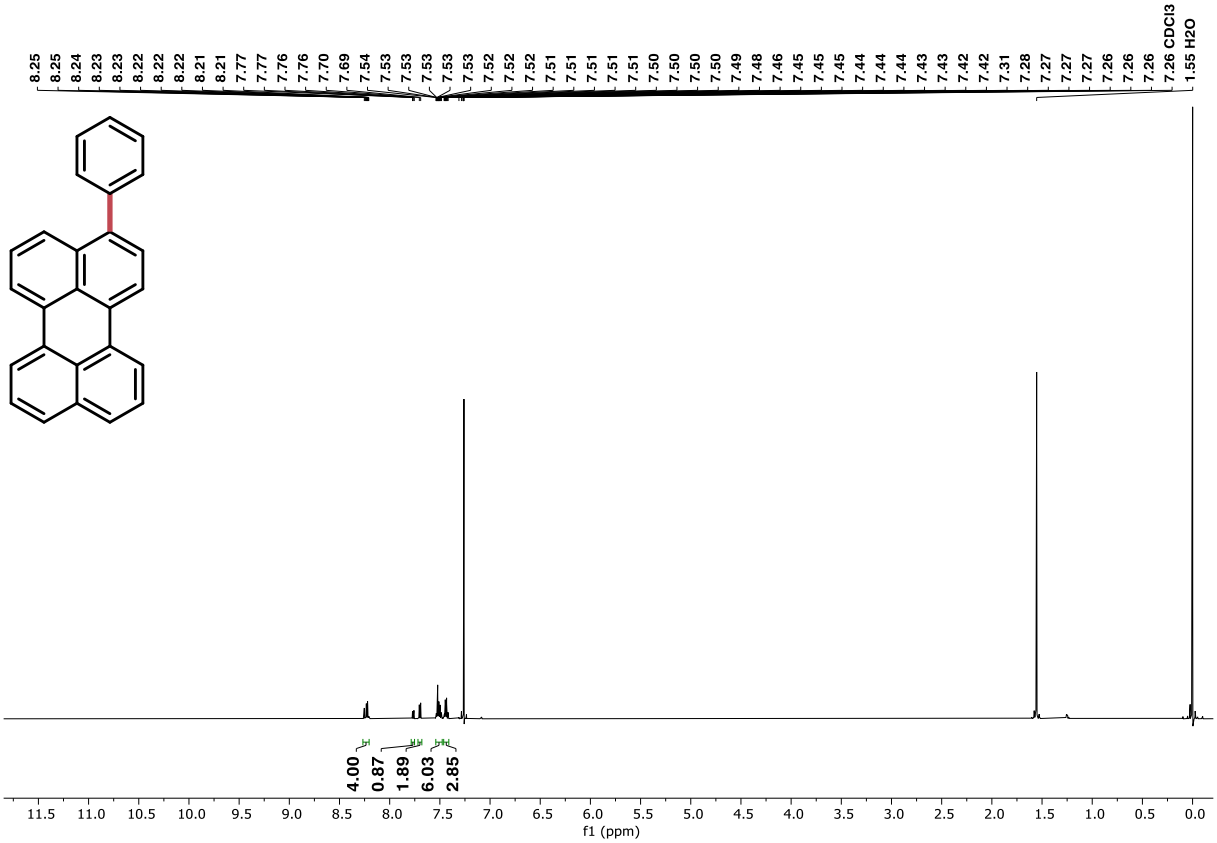
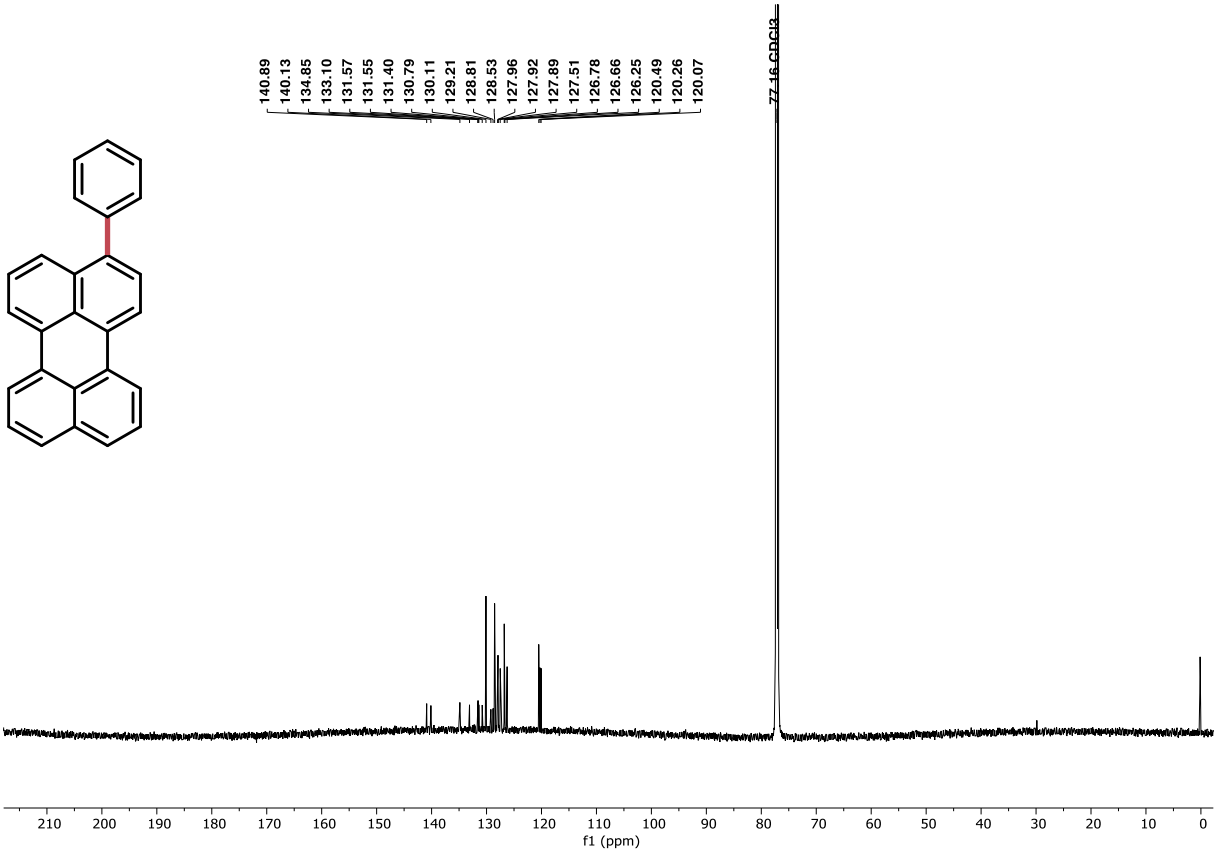
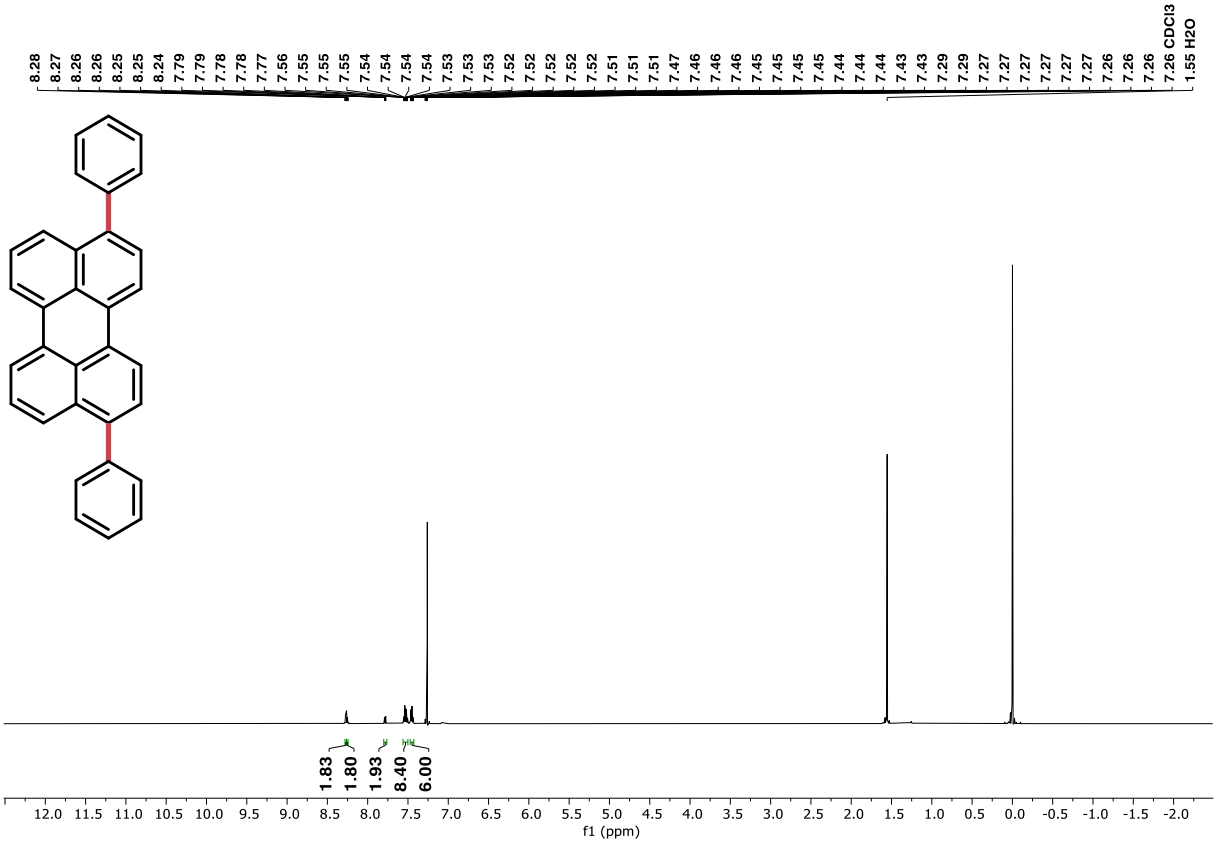
f1 (ppm)

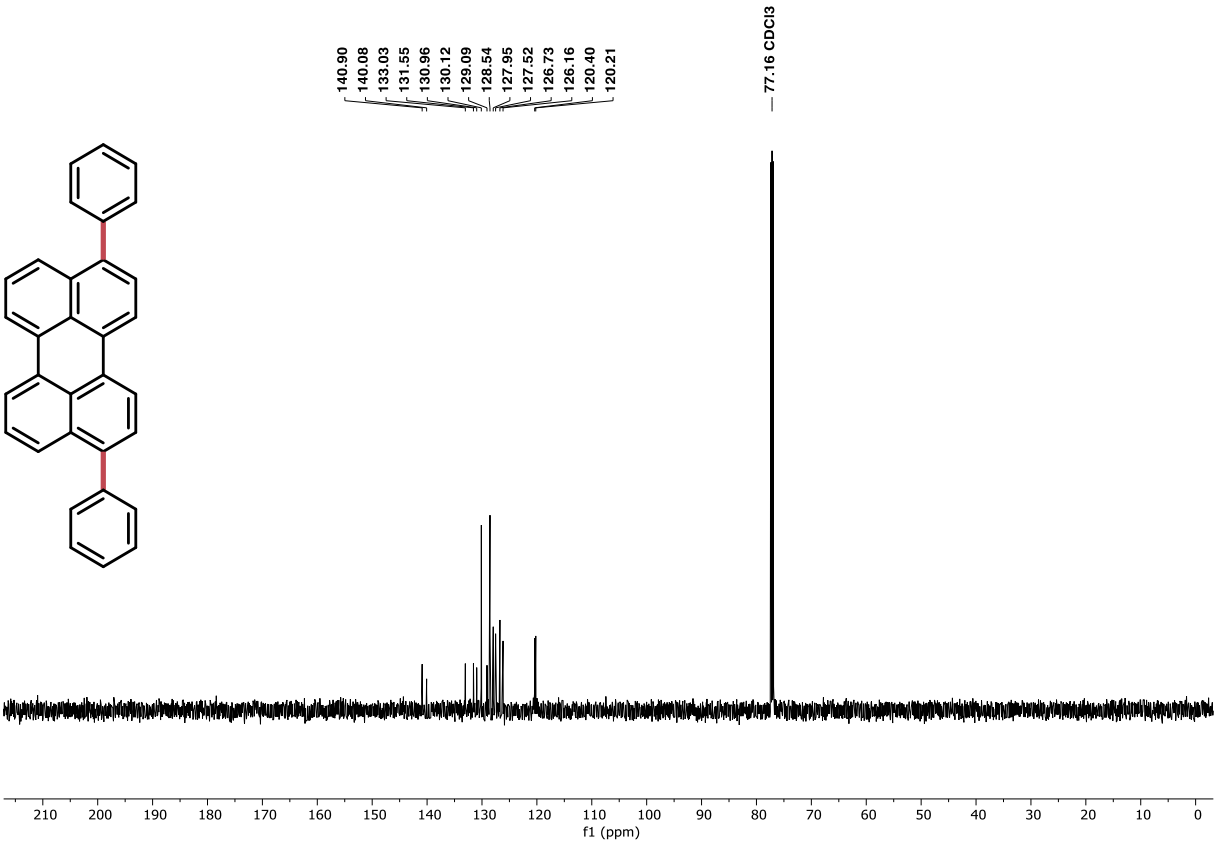

8.85 8.85 8.69 8.68 8.68 8.67 8.67 8.67 8.66 8.66 8.65 8.65 8.64 8.64 8.63 8.63 8.62
7.81 7.80 7.79 7.79 7.70 7.69 7.69 7.69 7.69 7.68 7.68 7.68 7.67 7.67 7.67 7.65 7.64 7.64 7.64 7.63 7.63 7.63 7.63 7.42 7.42 7.41 7.41 7.40 7.40 7.40 7.39 7.39 7.39 7.38 7.38
7.26 CDCl3
1.55 H2O
1.00
5.42
1.01
4.32
2.14
3.42
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

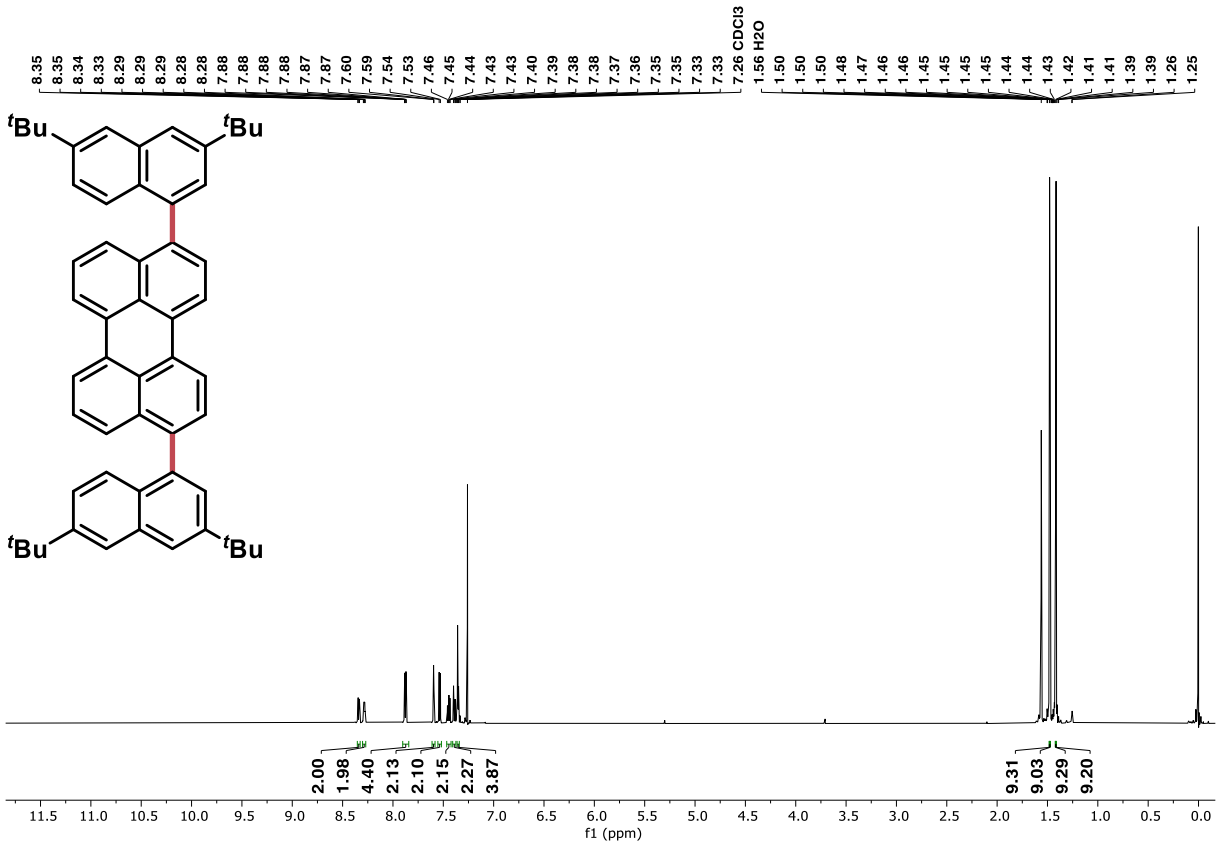

131.84 130.13 130.06 130.00 129.80 129.63 129.39 129.19 128.57 128.51 127.66 127.65 127.45 127.43 126.92 123.59 123.52 123.50 123.43 123.39 121.99 90.32 90.03
77.16 CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.25 8.25 8.24 8.23 8.23 8.22 8.22 8.22 8.21 8.21 7.77 7.77 7.76 7.76 7.70 7.69 7.54 7.53 7.53 7.53 7.53 7.52 7.52 7.52 7.51 7.51 7.51 7.51 7.50 7.50 7.50 7.50 7.49 7.48 7.46 7.45 7.45 7.44 7.44 7.44 7.43 7.43 7.42 7.42 7.31 7.28 7.27 7.27 7.27 7.26 7.26 7.26 7.26 CDCl3 1.55 H2O
4.00 0.87 1.89 6.03 2.85
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


140.89 140.13 134.85 133.10 131.57 131.55 131.40 130.79 130.11 129.21 128.81 128.53 127.96 127.92 127.89 127.51 126.78 126.66 126.25 120.49 120.26 120.07
77.16 CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.28 8.27 8.26 8.26 8.25 8.25 8.24 7.79 7.79 7.78 7.78 7.77 7.56 7.55 7.55 7.54 7.54 7.54 7.54 7.53 7.53 7.52 7.52 7.52 7.52 7.51 7.51 7.51 7.47 7.46 7.46 7.46 7.45 7.45 7.45 7.45 7.44 7.44 7.44 7.43 7.43 7.29 7.27 7.27 7.27 7.27 7.27 7.27 7.26 7.26 7.26 7.26 CDCl3 1.55 H2O
1.83 1.80 1.93 8.40 6.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)


140.90 140.08 133.03 131.55 130.96 130.12 129.09 128.54 127.95 127.52 126.73 126.16 120.40 120.21
77.16 CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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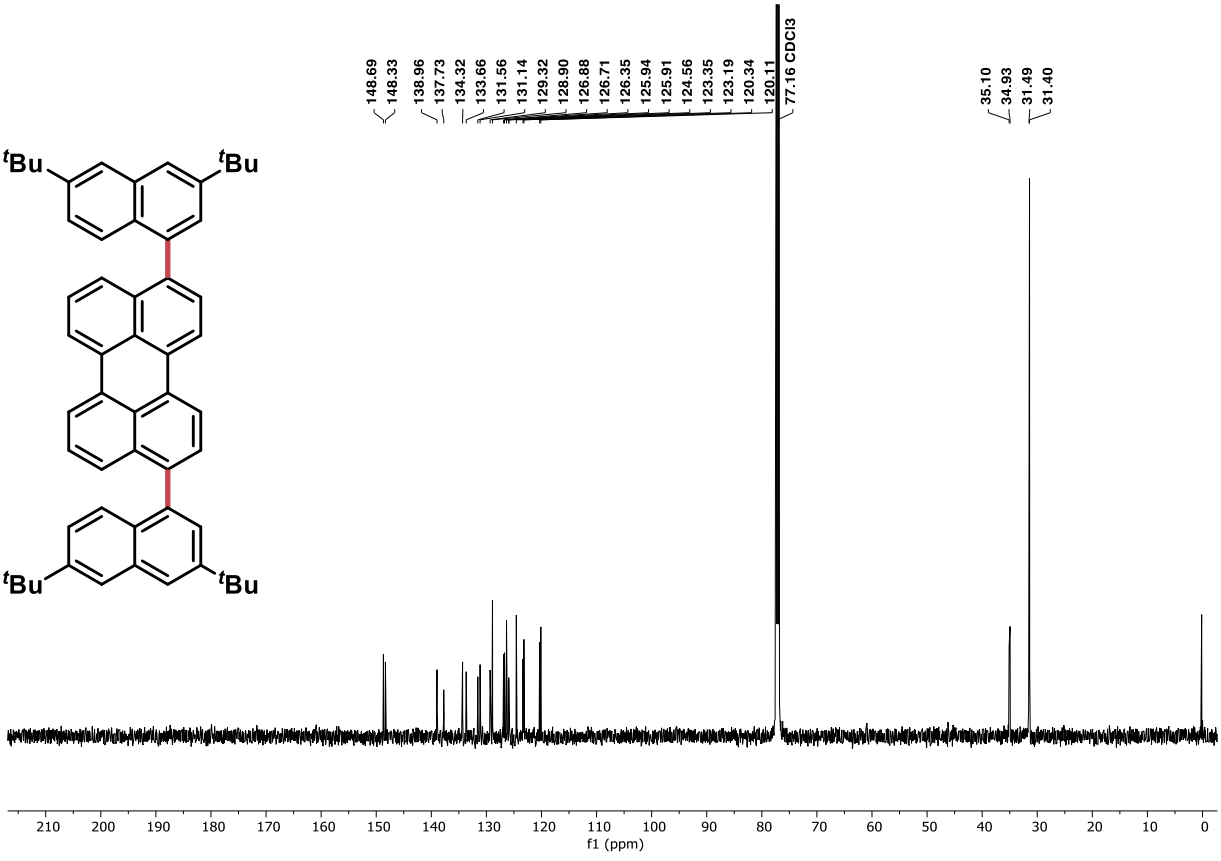
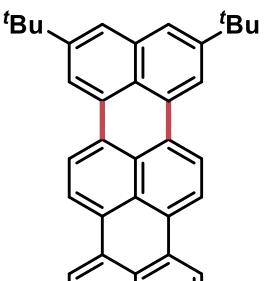
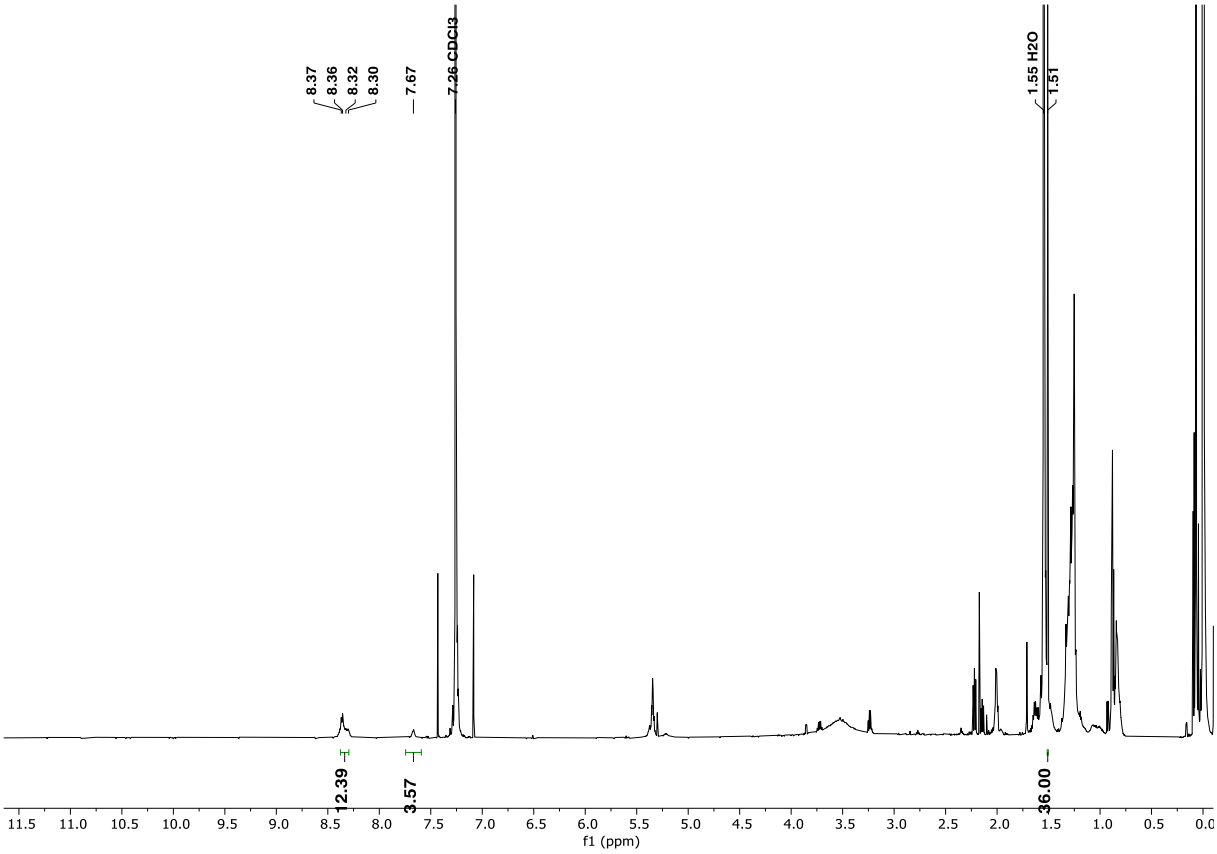
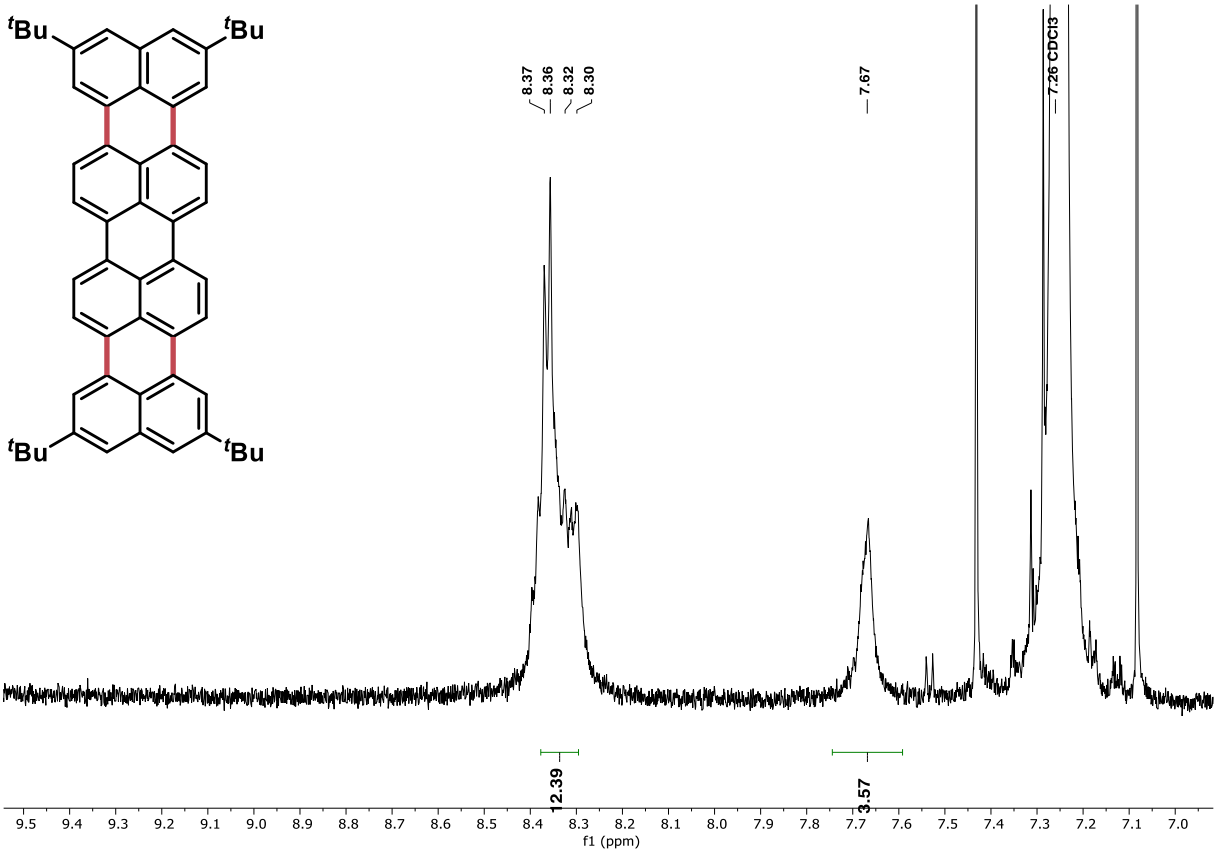
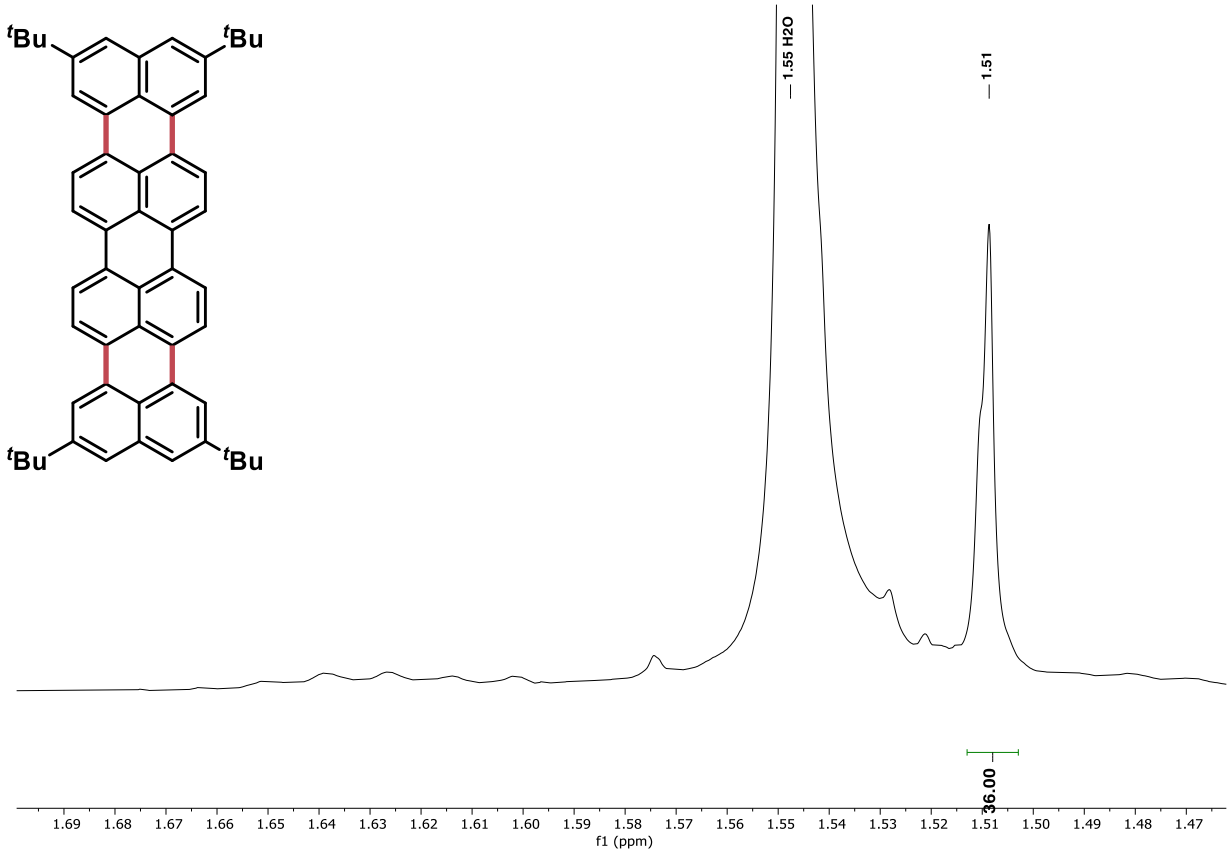
tBu tBu tBu tBu
2.00 1.98 4.40 2.13 2.10 2.15 2.27 3.87 9.31 9.03 9.29 9.20
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


148.69 148.33 138.96 137.73 134.32 133.66 131.56 131.14 129.32 128.90 126.88 126.71 126.35 125.94 125.91 124.56 123.35 123.19 120.34 120.11 77.16 CDCl3
35.10 34.93 31.49 31.40
tBu tBu tBu tBu
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


tBu tBu


8.37
8.36
8.32
8.30
7.67
7.26 CDCl3
1.55 H2O
1.51
12.39
3.57
36.00
f1 (ppm)


tBu
tBu
tBu
tBu
8.37
8.36
8.32
8.30
7.67
7.26 CDCl3
12.39
3.57
f1 (ppm)


tBu
tBu
tBu
tBu
1.55 H2O
1.51
36.00
1.69 1.68 1.67 1.66 1.65 1.64 1.63 1.62 1.61 1.60 1.59 1.58 1.57 1.56 1.55 1.54 1.53 1.52 1.51 1.50 1.49 1.48 1.47
f1 (ppm)

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