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Supporting Information for:

Thianthrene-functionalized polynorbornenes as high-voltage materials for organic cathode-based dual-ion batteries

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Contents

1 Experimental section

1.1 Materials

Chemicals were obtained from commercial suppliers and used without further purification. Experiments with water- or oxygen-sensitive substances were carried out under an argon atmosphere using glassware dried by heating under vacuum and standard Schlenk-techniques. Anhydrous solvents were obtained from a solvent purification system (MB-SPS) by M-Braun. All other solvents were distilled prior to use.

1.2 Analytical methods

^{1}H and ^{13}C{^{1}H}NMR spectra were recorded on Bruker Avance dpx 400 and dmx 500 spectrometers at rt and referenced to the residual proton or carbon resonance of the deuterated solvent.[1] EI-MS spectra were recorded on a MAT 90 or a MAT 95 XL sector field device from Thermo Finnigan. Polymer molecular weights were determined using a GPC unit by Agilent Technologies. As eluent THF was used with a flow rate of 1 mL/min, and measurements were calibrated against polystyrene standards by PSS Polymer Standard Service GmbH. For thermal gravimetric analysis a TGA/STAA851 was used and for differential scanning calorimetry a DSC823^e, both by Mettler Toledo.

1.3 Synthetic procedures

2-Bromothianthrene (**2**)[2] and thianthrene-2-carbaldehyde (**3**)[3] were synthesized according to literature procedures.

*Thianthren-2-ylmethanol (**4**).* $NaBH_4$ (269 mg, 7.10 mmol) was added to a solution of thianthrene-2-carbaldehyde[3] (**3**, 3.48 g, 14.2 mmol) in a mixture of THF (50 mL) and H_2O (1.7 mL) at 0 °C. The resulting mixture was stirred at rt until TLC indicated completion of the reaction (1 h). H_2O (50 mL) was added, and the mixture was extracted with Et_2O. The organic extracts were washed with brine and dried ($MgSO_4$). Column chromatography (silica gel, cyclohexane/Et_2O: 5/1 to 2/1) afforded **4** (3.15 g, 90%) as a colorless solid. R_f 0.19 (cyclohexane/Et_2O: 2/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.43 (m, 4H), 7.26-7.19 (m, 3H), 4.64 (s, 2H), 1.83 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.9, 136.0, 135.6, 135.5, 134.7, 128.9, 128.8, 127.8, 127.2, 126.4, 64.5; MS (EI+): *m/z* 246.0 $[M]^+$, 229.0 $[M-OH]^+$, 216.0 $[M-CH_2O]^+$, 184.0 $[M-S-CH_2O]^+$; HRMS (EI+): *m/z* calcd for $C_{13}H_{10}OS_2$ 246.0173 $[M]^+$, found 246.0171; elemental analysis: calcd (%) for $C_{13}H_{10}OS_2$: C 63.38, H 4.09, S, 26.03; found: C 63.55; H 4.27; S 25.74.

*(1S,2R,4S)-Thianthren-2-ylmethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (**5**).* DCC (710 mg, 3.44 mmol) and 4-DMAP (87.0 mg, 712 µmol) were successively added to a suspension of *exo*-5-norbornene-2-carboxylic acid[4] (351 mg, 2.54 mmol). Thianthren-2-ylmethanol (**4**, 700 mg, 2.84 mmol) was added in a mixture of dry NEt_3 (0.44 mL, 3.16 mmol) and dry CH_2Cl_2 (5 mL) at -30 °C. The reaction mixture was vigorously stirred at 0 °C for 1 h and at rt for 6 d. 20 mL CH_2Cl_2 were added, and the solution was washed with 0.3 M HCl, H_2O, and brine and dried ($MgSO_4$). Column chromatography (silica gel, cyclohexane/CH_2Cl_2: 2/1) afforded **5** (554 mg, 59%) as a colorless, viscous oil. R_f 0.34 (cyclohexane/CH_2Cl_2: 2/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.44 (m, 4H), 7.26-7.22 (m, 3H), 6.14 (dd, J = 5.6, 2.9 Hz, 1H), 6.10 (dd, J = 5.6, 3.0 Hz, 1H), 5.09 (s, 2H), 3.06 (dddd, J = 2.2, 1.5, 0.8 Hz, 1H), 2.94-2.93 (m, 1H), 2.29-2.26 (m, 1H), 1.96-1.91 (m, 1H), 1.54-1.51 (m, 1H),

1.42-1.36 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 176.0, 138.2, 136.3, 136.0, 135.8, 135.6, 135.4, 135.4, 128.8, 128.8, 128.8, 128.4, 127.9, 127.8, 127.6, 65.4, 46.7, 46.5, 43.2, 41.8, 30.5; MS (EI+): *m/z* 366.1 $[M]^+$, 300.1 $[M-C_5H_6]^+$, 229.1 $[M-C_8H_9O_2]^+$; HRMS (EI+) *m/z* calcd for $C_{21}H_{18}O_2S_2$ 366.0748 $[M]^+$, found 366.0748; elemental analysis: calcd (%) for $C_{21}H_{18}O_2S_2$: C 68.82, H 4.95, S, 17.50; found: C 68.66; H 4.71; S 17.42.

*(1R,2S,3R,4S)-Bis(thianthren-2-ylmethyl) bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (**6**).* CMPI (592 mg, 2.28 mmol) and 4-DMAP (279 mg, 0.76 mmol) were successively added to a solution of thianthren-2-ylmethanol (**4**, 1.03 g, 4.18 mmol) and 5-norbornene-2,3-dicarboxylic anhydride (312 mg, 1.90 mmol) in a mixture of NEt_3 (0.32 mL, 2.28 mmol) and dry CH_2Cl_2 (15 mL) at 0 °C. The mixture was stirred at 0 °C for 1 h and at rt for 18 h. 15 mL CH_2Cl_2 were added, and the solution was washed with 0.3 M HCl, H_2O, and brine and dried ($MgSO_4$). Column chromatography (silica gel, cyclohexane/EtOAc: 10/1 to 5/1) afforded **6** (1.11 g, 91%) as a colorless, viscous oil. R_f 0.41 (cyclohexane/EtOAc: 5/1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47-7.41 (m, 4H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.37 (d, *J* = 1.8 Hz, 2H), 7.23-7.18 (m, 4H), 7.08 (dd, *J* = 8.0, 1.8 Hz, 2H), 6.25 (dd, *J* = 1.9, 1.9 Hz, 2H), 4.93 (d, *J* = 12.5 Hz, 2H), 4.83 (d, *J* = 12.5 Hz, 2H), 3.32-3.31 (m, 2H), 3.17 (q, *J* = 1.7 Hz, 2H), 1.48 (ddd, *J* = 8.7, 1.9 Hz, 1H), 1.31 (ddd, *J* = 8.8, 1.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.3, 135.9, 135.9, 135.6, 135.4, 135.3, 135.1, 128.8, 128.8, 128.8, 128.7, 127.9, 127.9, 127.8, 65.5, 48.9, 48.4, 46.5; MS (EI+): *m/z* 639.0 $[M]^+$, 638.0 $[M-H]^+$, 572.0 $[M-C_5H_7]^+$, 229.0 $[M-C_{22}H_{17}O_4S_2]^+$; HRMS (EI+): *m/z* calcd for $C_{35}H_{26}O_4S_4$ 638.0713 $[M]^+$, found 638.0716. The *endo*-configuration of **6** was determined by NOE spectroscopy.

*2-((1S,4S)-Bicyclo[2.2.1]hept-5-en-2-yl)thianthrene (**7**).* 2-Bromothianthrene (**2**, 1.20 g, 4.06 mmol),[2] freshly distilled norbornadiene (1.67 mL, 16.3 mmol), $PdCl_2(PPh_3)_2$ (144 mg, 0.16 mmol), and formic acid (0.48 mL, 8.13 mmol) were dissolved in a mixture of NEt_3 (1.80 mL, 12.2 mmol) and DMF (1.9 mL) and degassed by purging with argon for 15 min. The resulting mixture was stirred at 80 °C for 6 h and cooled to rt. Toluene (10 mL) and HCl (10wt% in H_2O) were added, and the organic layer was separated. The aq. layer was extracted with toluene. The combined organic extracts were washed with H_2O and brine and dried ($MgSO_4$). Column chromatography (silica gel, cyclohexane) followed by two successive Kugelrohr distillation steps and another column chromatography step (silica gel, cyclohexane) afforded **7** (724 mg, 58%) as a colorless solid. R_f 0.41 (cyclohexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.46 (m, 2H), 7.41-7.40 (m, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.25-7.21 (m, 2H), 7.15 (ddd, *J* = 8.1, 2.0, 0.7 Hz, 1H), 6.24 (dd, *J* = 5.7, 3.1 Hz, 1H), 6.17 (dd, *J* = 5.7, 2.9 Hz, 1H), 2.98-2.95 (m, 1H), 2.89-2.86 (m, 1H), 2.69-2.65 (m, 1H), 1.71-1.66 (m, 1H), 1.65-1.60 (m, 1H), 1.54-1.51 (m, 1H), 1.45-1.42 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.5, 137.6, 137.2, 136.0, 135.9, 135.6, 132.2, 128.9, 128.8, 128.6, 127.9, 127.7, 127.7, 127.4, 48.3, 45.9, 43.5, 42.4, 33.9; MS (EI+): *m/z* 308.1 $[M]^+$, 242.0 $[M-C_5H_6]^+$; HRMS (EI+): *m/z* calcd for $C_{19}H_{16}S_2$ 308.0693 $[M]^+$, found 308.0693.

*Synthesis of **P1** by ROMP.* A degassed solution of (1*S*,2*R*,4*S*)-thianthren-2-ylmethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (**5**, 728 mg, 1.99 mmol) in 4.6 mL CH_2Cl_2 was rapidly added to a stirred and degassed solution of **G3** (4.4 mg, 5.0 µmol) in 2.4 mL CH_2Cl_2. The resulting solution was stirred at rt for 21 h. Ethylvinylether (1.5 mL) was added, and the solution was stirred at rt for 2 h. The polymer was precipitated into methanol and isolated by filtration. The polymer was purified by twofold dissolution in $CHCl_3$ and precipitation from MeOH. **P1** (627 mg, 86%) was isolated as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (br s, 4H), 7.17-7.06 (m, 3H), 5.35-5.16 (m, 2H), 5.01-4.93 (m, 2H), 3.07-2.96 (m, 1H), 2.67-2.51

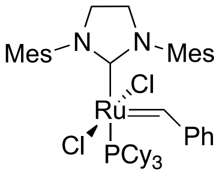
(m, 2H), 2.06-1.91 (m, 2H), 1.59 (br s, 1H), 1.11-0.98 (m, 1H); GPC (eluent THF, polystyrene standard): M_n 2.04 × 10^5, M_w/M_n 1.35; DSC (10 °C/min, N_2): T_g 83 °C; TGA (10 °C/min, N_2): $T_{d10\%}$ 382 °C.

*Synthesis of **P2** by ROMP.* A degassed solution of (1R,2S,3R,4S)-bis(thianthren-2-ylmethyl) bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (**6**, 1.19 g, 1.87 mmol) in 3.8 mL CH_2Cl_2 was rapidly added to a stirred and degassed solution of **G3** (8.3 mg, 9.34 µmol) in 2.4 mL CH_2Cl_2. The resulting solution was stirred at rt for 23 h. Ethylvinylether (2 mL) was added, and the solution was concentrated *in vacuo*. The residue was dissolved in $CHCl_3$, and the polymer was precipitated into methanol and isolated by filtration. This procedure was repeated once, yielding **P2** (861 mg, 72%) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (br s), 7.22 (br s), 7.11 (br s), 7.01 (br s), 6.89 (br s), 5.48 (br s), 5.32 (br s), 4.92 (br s), 4.73 (br s), 3.10 (br s), 3.01 (br s), 2.88 (br s), 2.53 (br s), 1.72 (br s); GPC (eluent THF, polystyrene standard): M_n 1.10 × 10^5, M_w/M_n 1.23; DSC (10 °C/min, N_2): T_g 112 °C; TGA (10 °C/min, N_2): $T_{d10\%}$ 372 °C.

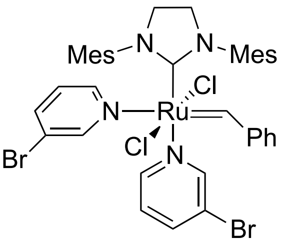
*Synthesis of **P3** by ROMP.* A degassed solution of **G3** (1.1 mg, 1.26 µmol) in 0.33 mL CH_2Cl_2 was rapidly added to a stirred and degassed solution of (2-((1*S*,4*S*)-bicyclo[2.2.1]hept-5-en-2-yl)thianthrene (**7**, 38.9 mg, 0.126 mmol) in 0.5 mL CH_2Cl_2. The resulting solution was stirred at rt for 2 h. Ethylvinylether (0.4 mL) was added, and the solution was concentrated *in vacuo*. The residue was dissolved in $CHCl_3$, and the solution was filtered through a short pad of Al_2O_3. The solution was concentrated *in vacuo* to a small volume, and the polymer was precipitated into methanol and isolated by filtration, yielding **P3** (26 mg, 67%) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (br s), 7.36 (br s), 7.18 (br s), 6.99 (br s), 5.13 (br s), 2.68 (br s), 2.58 (br s), 2.44 (br s), 2.04 (br s), 1.86 (br s), 1.19 (br s); GPC (eluent THF, polystyrene standard): M_n 2.94 × 10^4, M_w/M_n 1.63; DSC (10 °C/min, N_2): T_g 130 °C; TGA (10 °C/min, N_2): $T_{d10\%}$ 417 °C.

1.4 ROMP of monomers 5, 6 and 7

Table S1. Ring Opening Metathesis Polymerizations of Monomers **5**, **6**, and **7** using Catalysts **G2** and **G3**.[a]



G2



G3

Entry	Monomer (M)	Polymer	Catalyst (C)	[M]/[C]	$M_{\mathrm{n,theo}}$ [kDa]	$M_{\mathrm{n,obs}}$ [kDa][b]	PDI[b]	Yield [%]
1	**5**	**P1**	**G2**	40	14.8	38.0	1.89	74
2	**5**	**P1**	**G3**	67	24.7	48.5	1.22	60
3[c]	**5**	**P1**	**G3**	400	146	204	1.35	86
4	**6**	**P2**	**G3**	100	63.9	35.9	1.18	35
5[c]	**6**	**P2**	**G3**	200	128	110	1.23	72
6[c]	**6**	**P2**	**G3**	432	276	180	1.23	71
7	**7**	**P3**	**G2**	35	10.8	7.36	2.17	63
8	**7**	**P3**	**G3**	100	30.8	29.4	1.63	67

[a]Polymerizations in CH_2Cl_2 at rt; [b]estimated by GPC in THF against polystyrene standard; [c]performed on a large scale (1.2-2.0 mmol).

1.5 Preparation of composite electrodes

Cell assembly and electrode preparation were performed in a dry room with < 0.02% water content. Composite electrodes were prepared by dispersing polymer, hard carbon or carbon black Super P Li (Imerys), and polyvinylidene fluoride (PVdF) binder (Kynar Flex, Arkema) in NMP with an Ultra-Turrax® T25 digital by IKA at 5000 rpm for 1 h. The resulting suspension was cast on etched alumina foil (30 µm, Schlenk) using a doctor blade (200 µm wet film thickness). Electrodes with 12 mm diameter were cut out and dried in a vacuum oven (BÜCHI B-585) at 80 °C and 10^{-5} mbar for 48 h.

1.6 Electrochemical measurements

Cyclic voltammograms (CVs) in solution were measured inside a glovebox using a PGSTAT128N by Metrohm Autolab. As working, counter, and reference electrode a glassy carbon disc electrode (2 mm diameter), a platinum rod, and a $Ag/AgNO_3$ electrode containing a silver wire immersed in an inner chamber filled with 0.1 M $AgNO_3$ and 0.1 M *n*-Bu_4NPF_6 were used, respectively. The ferrocene/ferrocenium redox couple was used as internal reference. Composite electrodes were tested in Swagelok® type T-cells with a three-electrode setup. Lithium foil (500 µm, Rockwood Lithium) was used as counter and reference electrode, and Freudenberg polypropylene separators (FS2190) were employed soaked with 120 µL of 1 M $LiPF_6$ in EC/DMC (1:1). CVs were measured at 20 °C using a Biologic VMP3 potentiostat. Each measurement was preceded by an open circuit potential step of 6 h to ensure sufficient wetting of the electrodes and separator. Galvanostatic investigations were performed on a MACCOR® 4000 series battery cycler at 20 °C in an environmental chamber. A rest step of 12 h was applied before starting the constant current cycling experiment.

1.7 Rate capability measurements of the P1 composite electrode

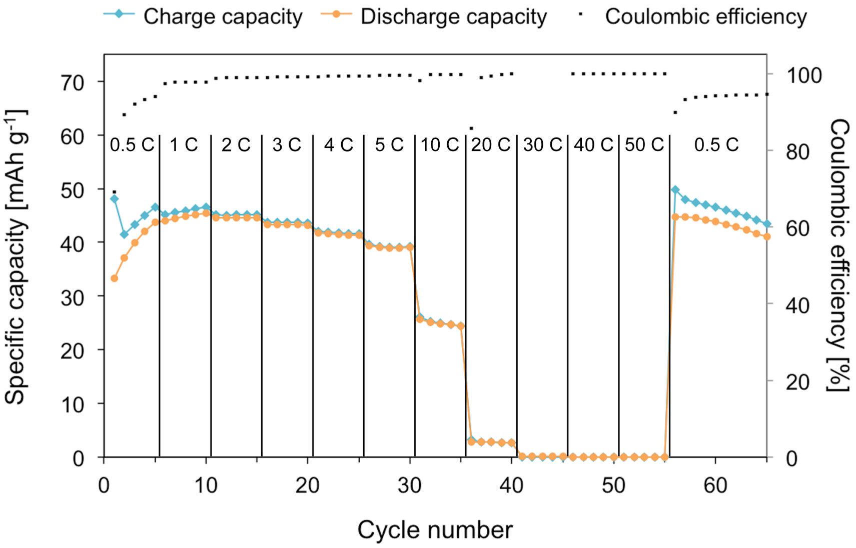


Figure 1. Constant current cycling data of a P1 composite electrode at different C rates (P1/Super P Li/PVdF (50:47:3 wt%), EC/DMC (1:1), 1 M $LiPF_6$, Li counter/reference electrode, potential range 3.3-4.4 V vs. Li/Li^+).

2 NMR spectra

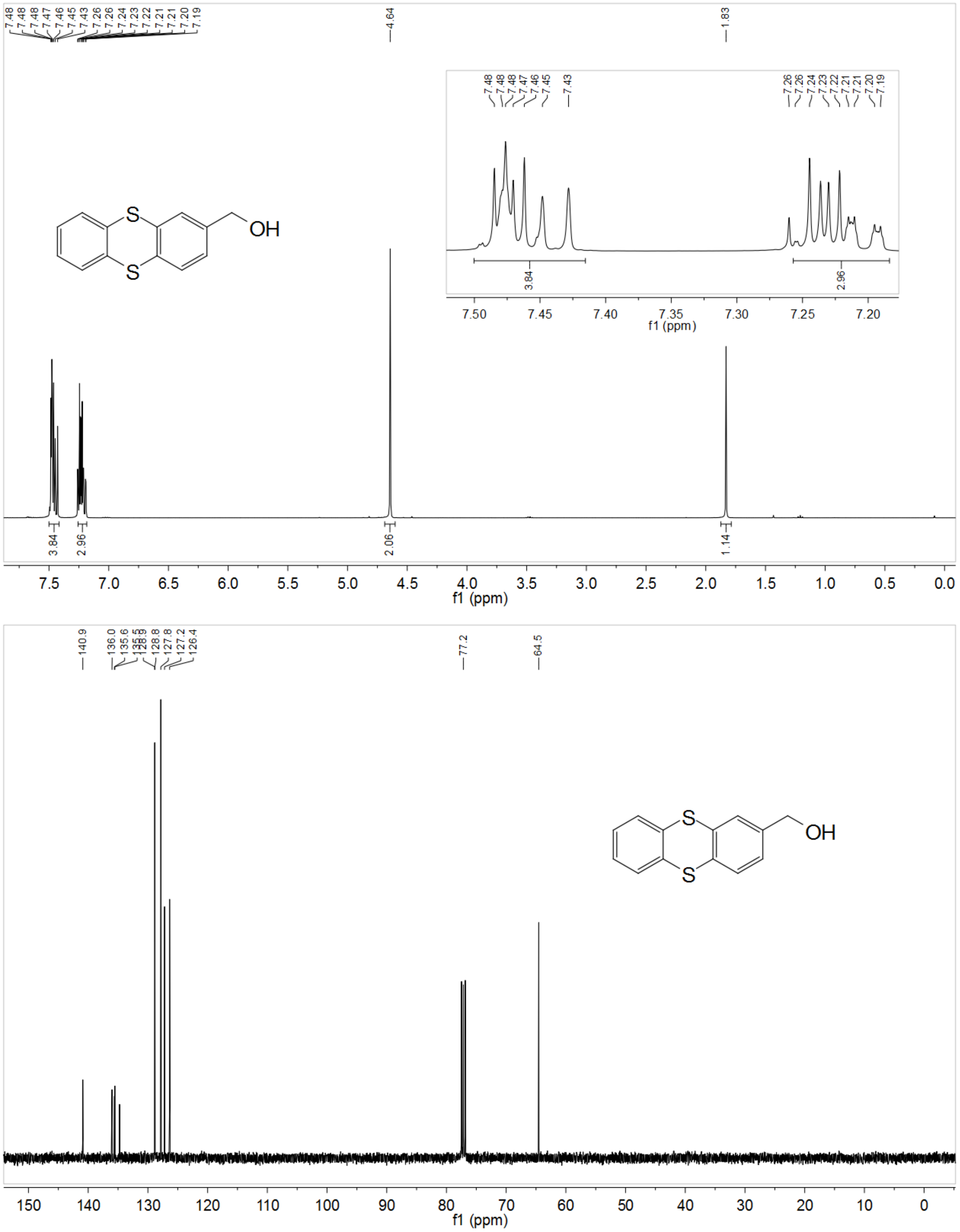


Figure S1: 400 MHz ^{1}H NMR and 101 MHz ^{13}C{H} NMR spectrum of thianthren-2-ylmethanol (**4**) in $CDCl_3$.

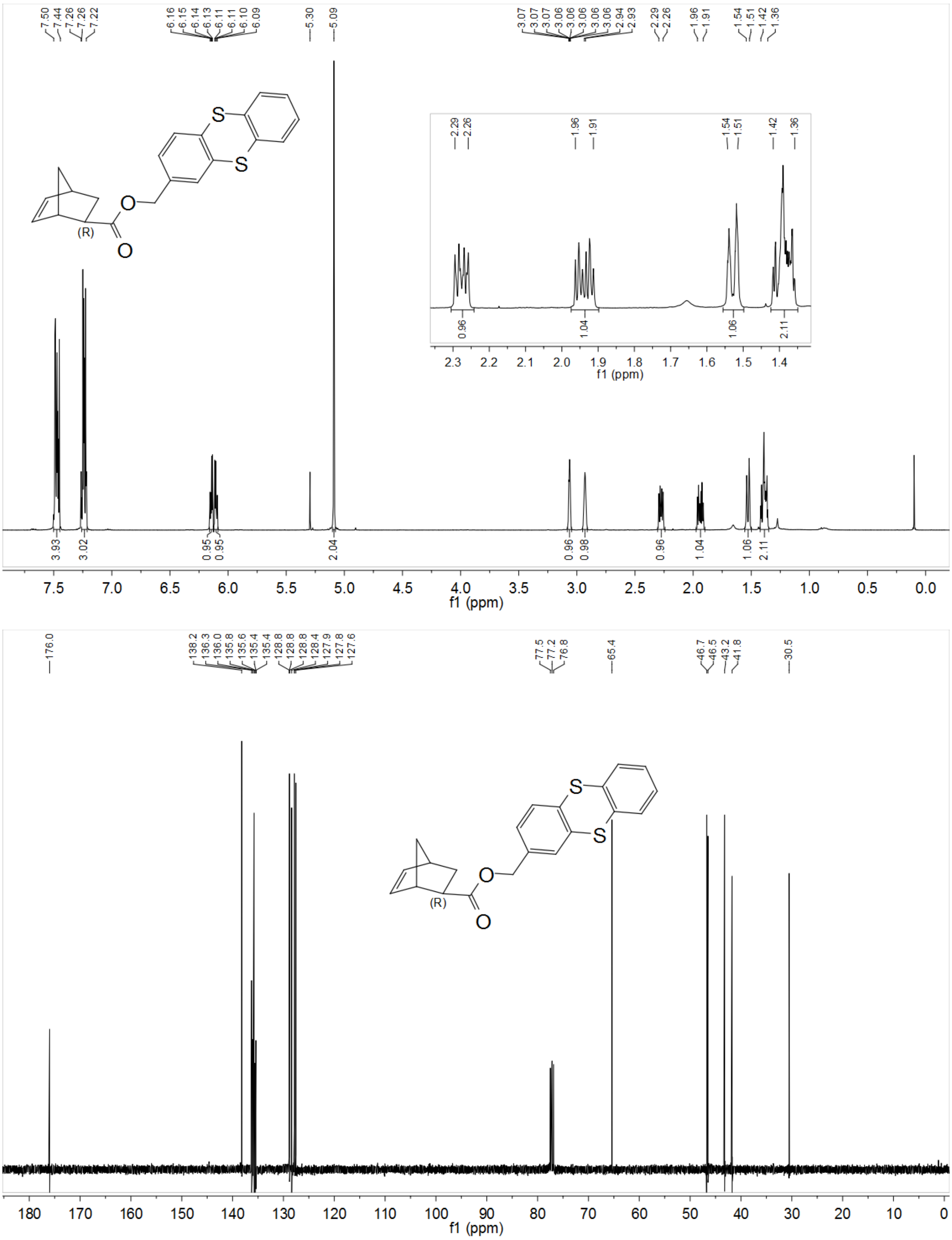


Figure S2: 400 MHz ^{1}H NMR and 101 MHz ^{13}C{H} NMR spectrum of (1S,2R,4S)-thianthren-2-ylmethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (**5**) in $CDCl_3$.

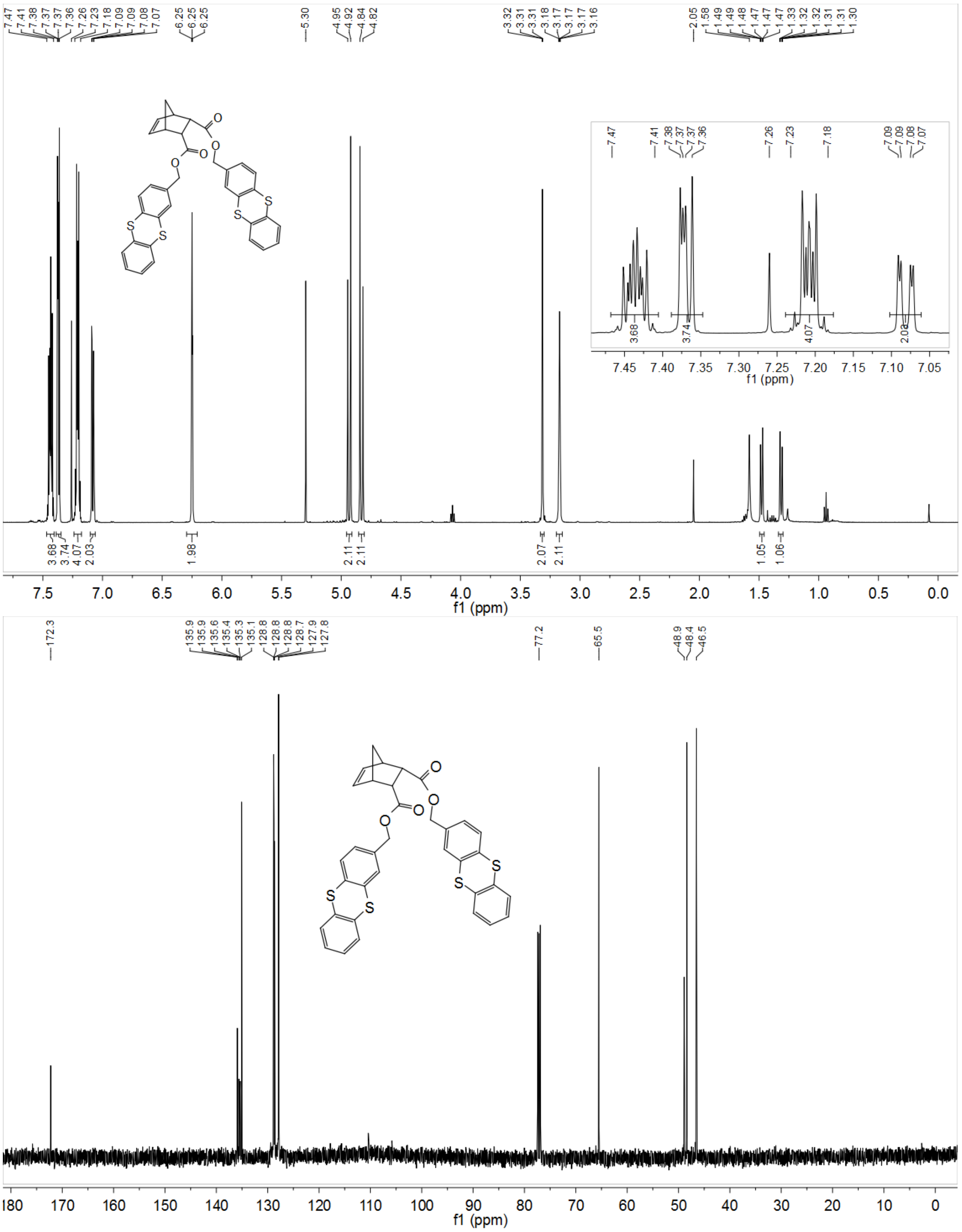


Figure S3: 500 MHz ^{1}H NMR and 126 MHz ^{13}C{H} NMR spectrum of (1R,2S,3R,4S)-bis(thianthren-2-ylmethyl) bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (**6**) in $CDCl_3$.

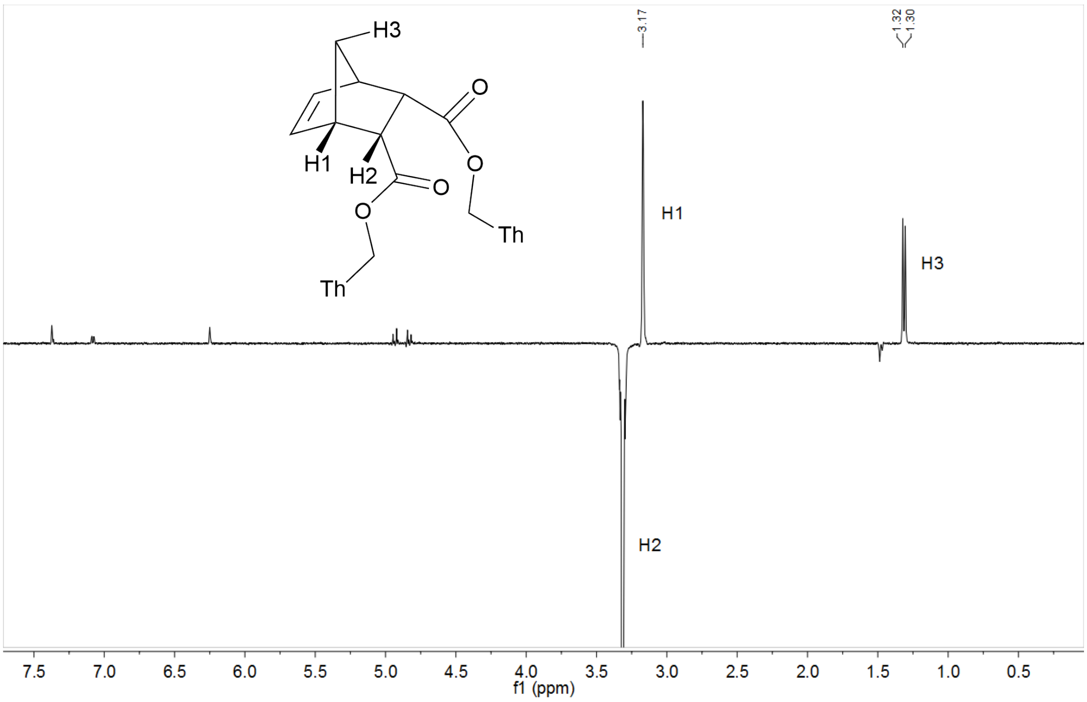


Figure S4: 500 MHz NOE difference ^1H NMR spectrum of (1R,2S,3R,4S)-bis(thianthren-2-ylmethyl) bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (**6**) in $CDCl_3$ (irradiation at H2 (3.31 ppm)).

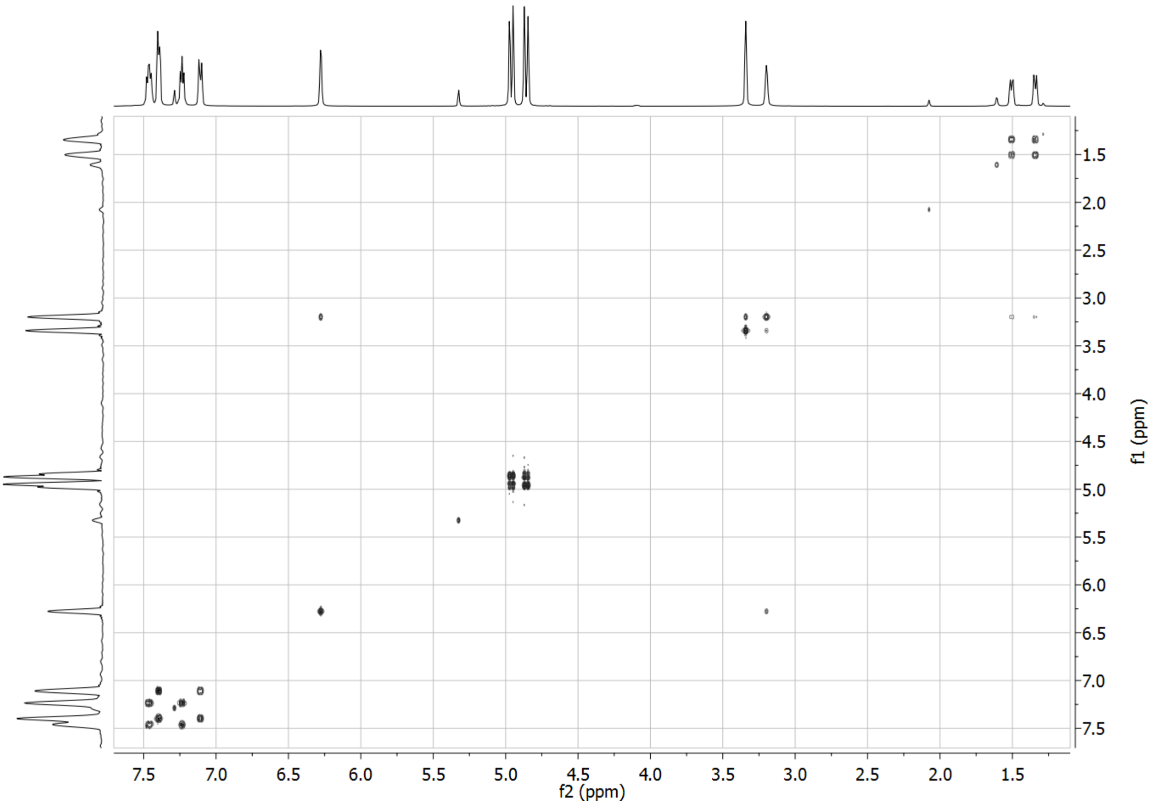


Figure S5: HH COSY spectrum of (1R,2S,3R,4S)-bis(thianthren-2-ylmethyl) bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (**6**) in $CDCl_3$.

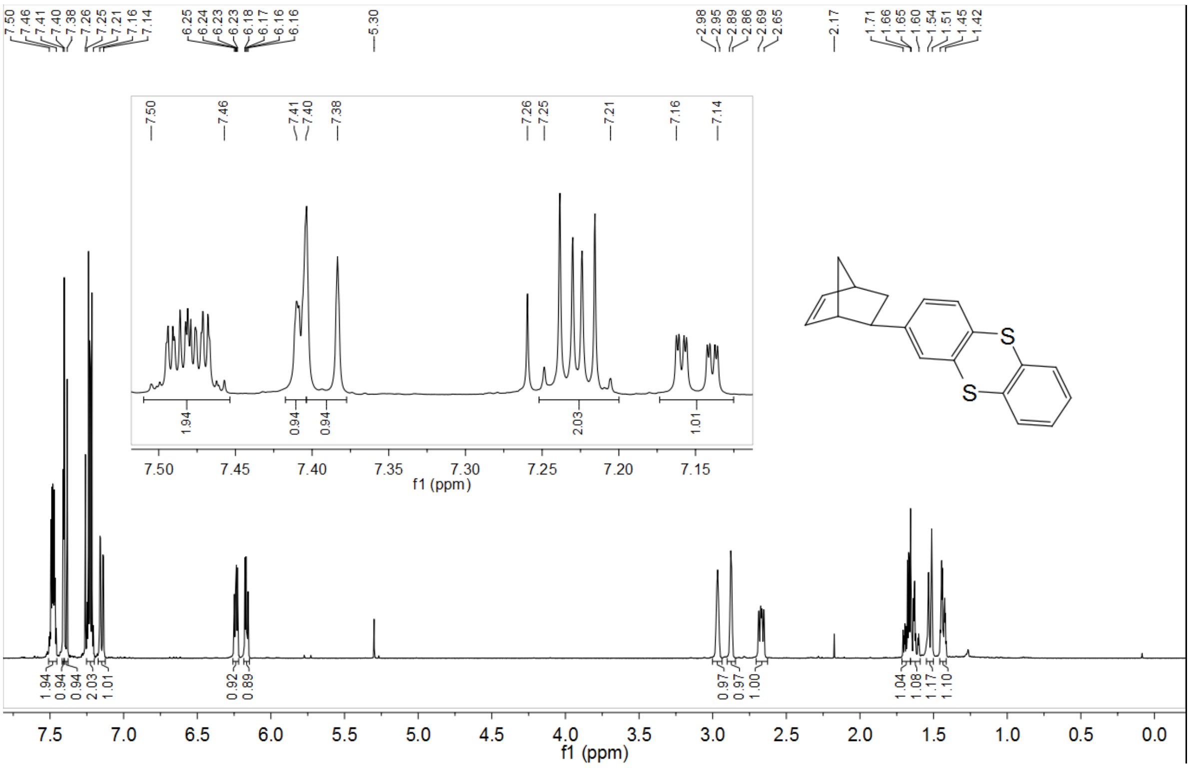


Figure S6: 400 MHz ^{1}H NMR spectrum of 2-((1S,4S)-bicyclo[2.2.1]hept-5-en-2-yl)thianthrene (**7**) in $CDCl_3$.

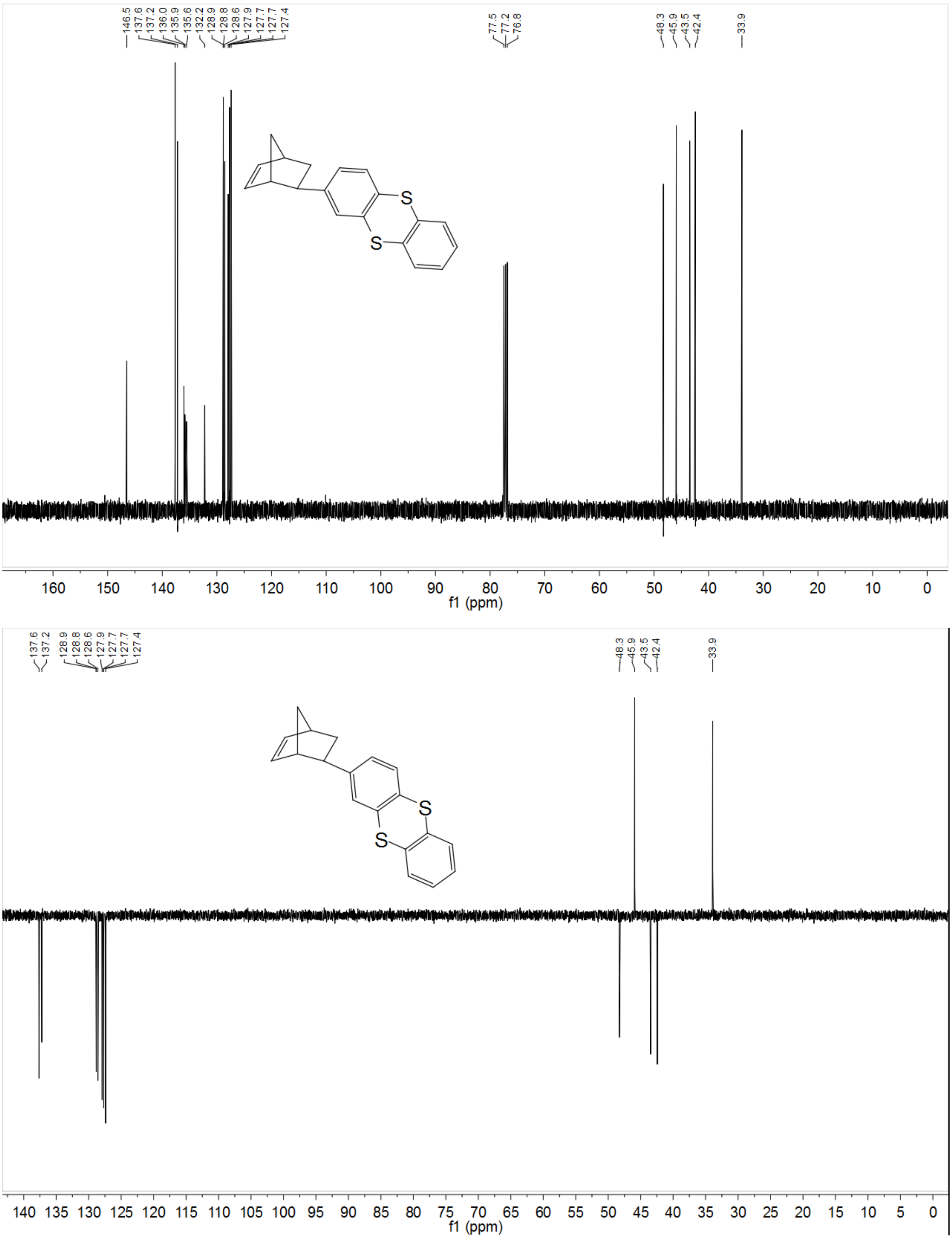


Figure S7: 101 MHz $^{13}C\{H\}$ NMR and DEPT-135 spectrum of 2-((1S,4S)-bicyclo[2.2.1]hept-5-en-2-yl)thianthrene (**7**) in $CDCl_3$.

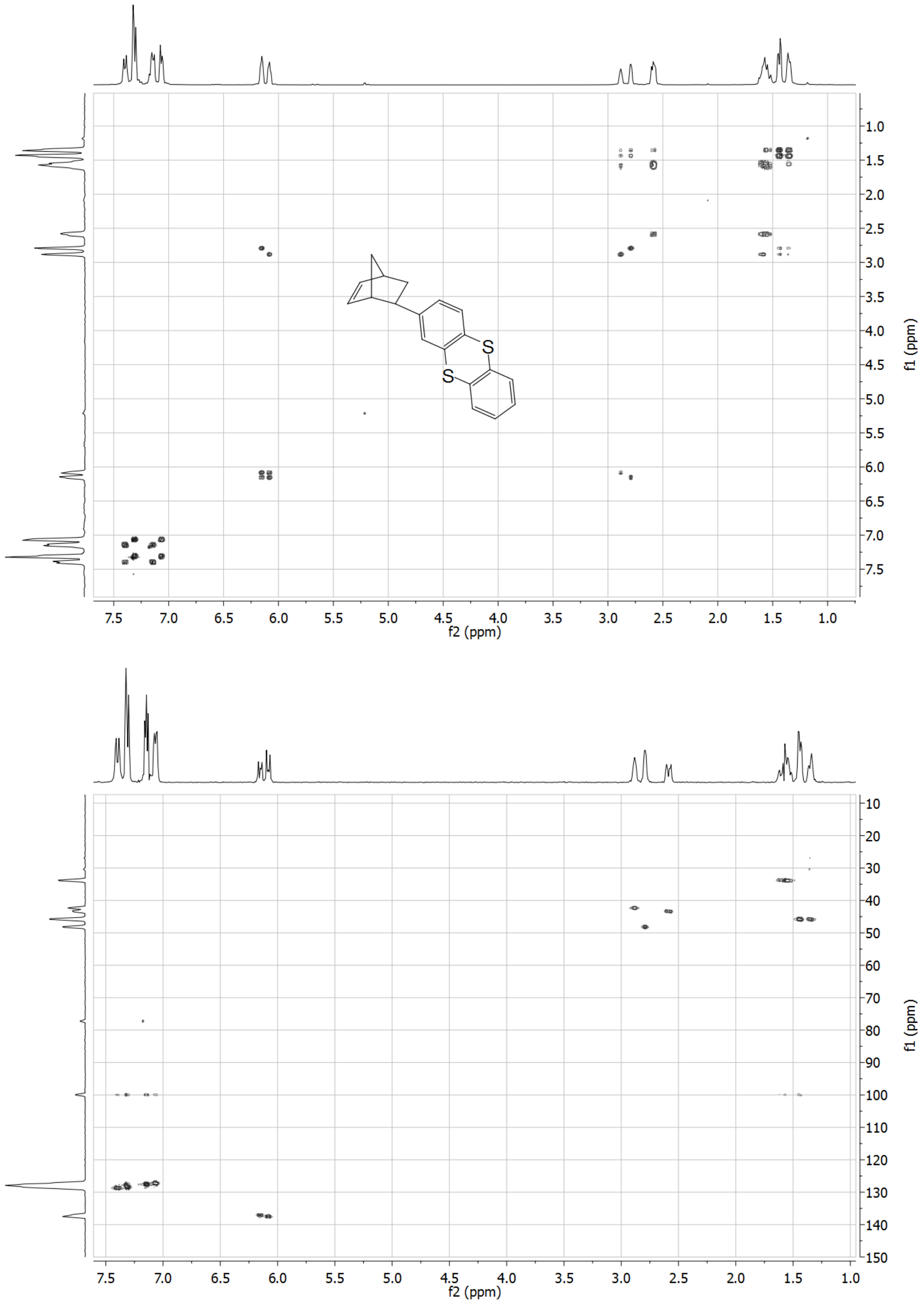


Figure S8: HH-COSY and HMQC spectrum of 2-((1S,4S)-bicyclo[2.2.1]hept-5-en-2-yl)thianthrene (**7**) in $CDCl_3$.

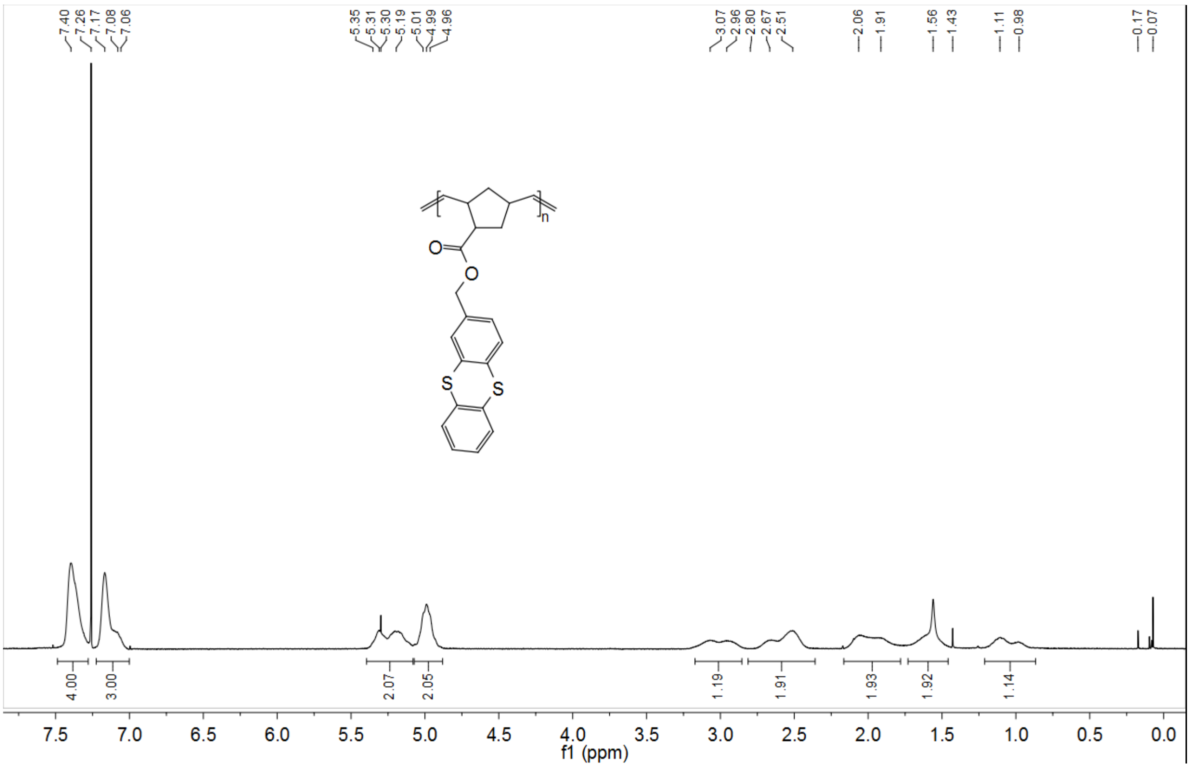


Figure S9: 400 MHz ^{1}H NMR spectrum of **P1** in $CDCl_3$.

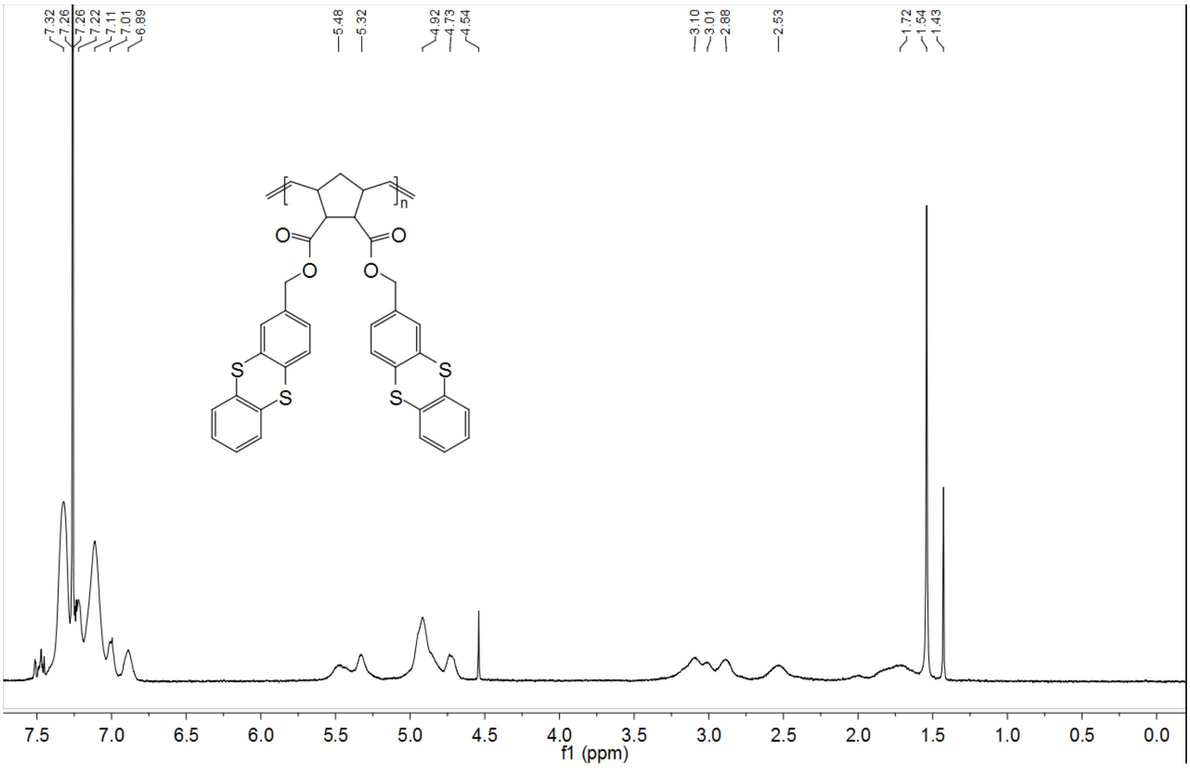


Figure S10: 400 MHz ^{1}H NMR spectrum of **P2** in $CDCl_3$.

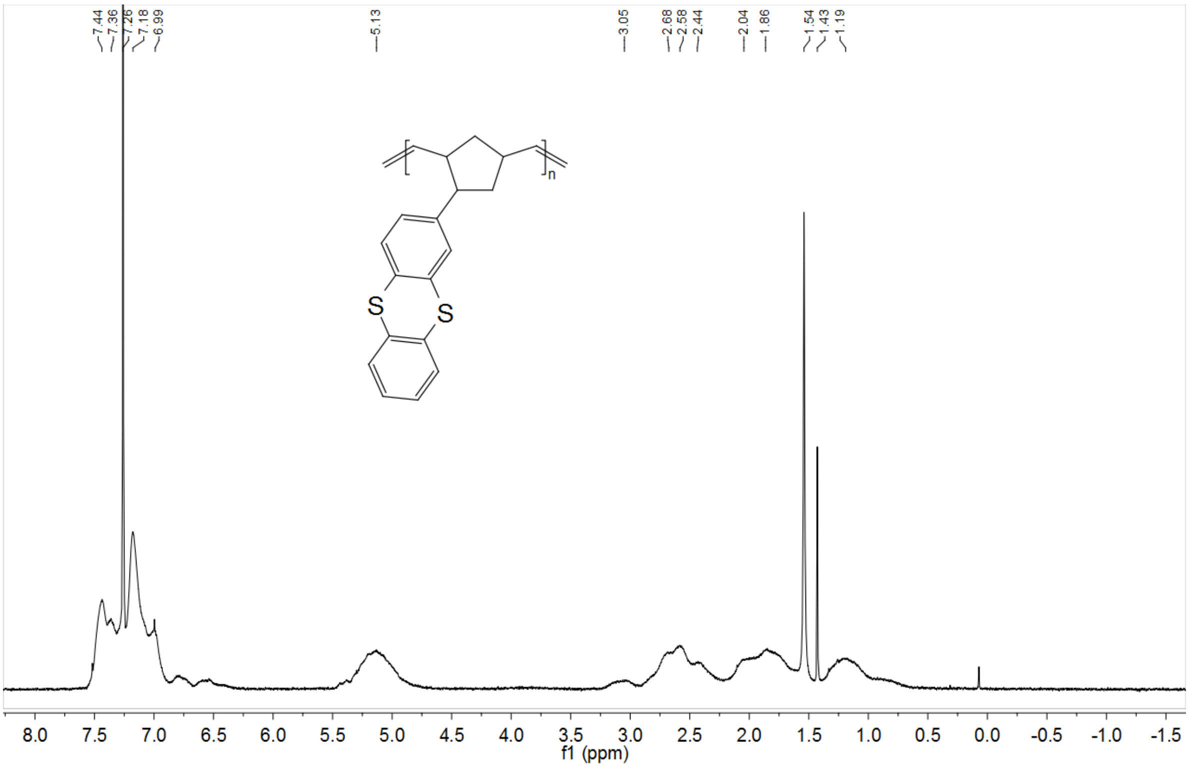


Figure S11: 400 MHz ^{1}H NMR spectrum of **P3** in $CDCl_3$.

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