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SUPPORTING INFORMATION

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Title: Bis-Sulfone- and Bis-Sulfoxide-Spirobifluorenes: Polar Acceptor Hosts with Tunable Solubilities for Blue-Phosphorescent Light-Emitting Devices
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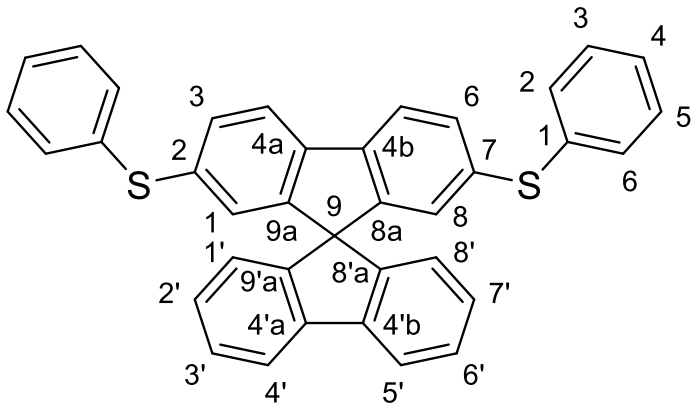
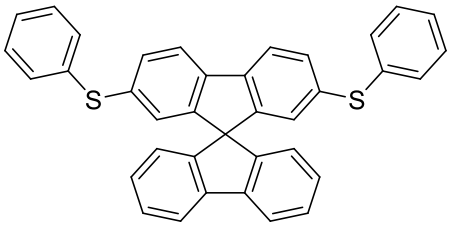
1. Additional synthetic details

Numbering system of the spirobifluorene compounds



1

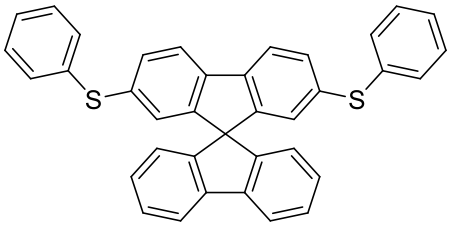
Synthesis of 2,7-bis(phenylthio)-9,9'-spirobifluorene (1): Method (b)



1

Thiophenol (0.1 mL, 108 mg, 0.969 mmol, 2.24 eq.) was added to a suspension of K_2CO_3 (74.1 mg, 0.531 mmol, 1.23 eq.) in dry *p*-xylene (1 mL) under an argon atmosphere at 0°C. After stirring for 2.5 h at room temperature, $Pd_2(dba)_3{\cdot}CHCl_3$ (87.7 mg, 84.7 μmol, 0.196 eq.), Xantphos (57.8 mg, 97.9 μmol, 0.226 eq.), 2,7-dibromo-9,9'-spirobifluorene (205 mg, 0.433 mmol, 1.00 eq.) and dry *p*-xylene (4 mL) were added to the suspension and the mixture was stirred for 21 h at 140°C. The solvent was distilled off and the residue was purified by column chromatography (SiO_2; cyclohexane:CH_2Cl_2 4:1). The solvent was removed under reduced pressure and the residue was dried under vacuum and recrystallized from cyclohexane to yield the product as colourless crystals. Yield: 130 mg, 0.25 mmol, 58 %. For analytical data of **1** see method (a) in the main text.

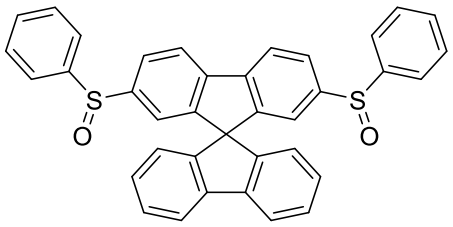
Synthesis of 2,7-bis(phenylthio)-9,9'-spirobifluorene (1): Method (c)



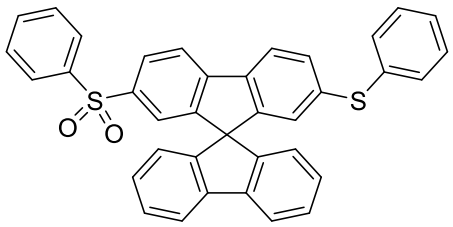
1

Magnesium (347 mg, 14.3 mmol, 2.08 eq.) was added to a dried flask and stirred for 10 min under an argon atmosphere before adding dry Et_2O (10 mL). 2-bromobiphenyl (1 mL) was added slowly until the reaction started, the remaining 2-bromobiphenyl (altogether 2.2 mL, 2.97 g, 12.5 mmol, 1.82 eq.) was then added dropwise during 20 min while cooling the reaction mixture with a water bath from time to time. The mixture was stirred at room temperature for another 5 min, until the reaction had stopped. Dry Et_2O (20 mL) was added to a dried flask charged with 2,7-bis(phenylthio)-9*H*-fluoren-9-one (**4,** 2.72 g, 6.86 mmol, 1.00 eq.) under an argon atmosphere (the synthesis of **4** is given below). Grignard reagent (1.56 M in Et_2O, 5.5 mL, 2.21 g, 8.58 mmol, 1.25 eq.) was added slowly during 10 min at 0°C. The reaction mixture was stirred for 30 min at room temperature, then heated to reflux for 1.25 h. After adding more Grignard reagent (1.5 mL, 0.602 g, 2.34 mmol, 0.341 eq.) and Et_2O (10 mL), the mixture was heated to reflux for another 1.5 h. Addition of more Grignard reagent (1.0 mL, 0.257 g, 1.56 mmol, 0.227 eq.) was followed by stirring overnight at room temperature, then heating to reflux again for 30 min. Ice water (120 mL) and conc. HCl (1 mL) solution were added to the suspension and the resulting solution was extracted with EtOAc (40 mL). The aqueous layer was extracted with CH_2Cl_2 (3x50 mL), the combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The resulting residue was suspended in AcOH (100 %, 12 mL) and heated. Conc. HCl solution (37 %, 0.47 mL, 0.556 g, 5.64 mmol, 0.822 eq.) was added to the dark red solution and the mixture was heated to reflux for 2 h and then cooled to room temperature. The precipitate was filtered, washed with hot acetic acid and H_2O, recrystallized from cyclohexane and dried under vacuum. The filtrate was concentrated under reduced pressure and the residue was again recrystallized from cyclohexane and dried under vacuum. From both recrystallizations, the product **1** was obtained as a slightly yellow powder. Yield: 2.91 g, 5.46 mmol, 80%. Analytical data are given in the main paper.

Synthesis of 2,7-bis(phenylsulfinyl)-9,9'-spirobifluorene (SPSX) and phenyl(2-(phenylsulfonyl)-9,9'-spirobifluorene-7-yl)sulfane (5): Oxidation with mCPBA



SPSX

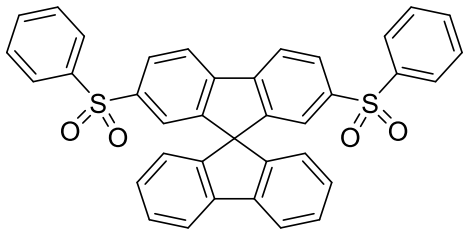


5

A solution of mCPBA (50 μL, 0.116 mmol, 2.03 eq.) in CH_2Cl_2 (1 mL) was added to a solution of bis(phenylthio)-9,9'-spirobifluorene (**1**, 30.5 mg, 57.3 μmol, 1.00 eq.) in CH_2Cl_2 (1 mL). The solution was stirred for 1 h at 0°C and then overnight at room temperature. Sat. $NaHCO_3$ solution and H_2O were added to the solution and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with sat. $NaHCO_3$ solution, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The two regioisomers were separated by column chromatography (SiO_2; cyclohexane:EtOAc 9:1 → 1:1), the solvent was removed under reduced pressure and both residues subsequently suspended in cyclohexane and the solvent again removed under reduced pressure. Drying under vacuum gave the two regioisomers as colourless powders. Yield: 15 mg, 27 μmol, 47 % 2,7-bis(phenylsulfinyl)-9,9'-spirobifluorene (**SPSX**) and 7.9 mg, 14 μmol, 24 % phenyl(2-(phenylsulfonyl)-9,9'-spirobifluorene-7-yl)sulfane (**5**). For analytical data of **SPSX** see method of oxidation using H_2O_2 in the main paper.

Analytical data of phenyl(2-(phenylsulfonyl)-9,9'-spirobifluorene-7-yl)sulfane (**5**): ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm = 7.91 – 7.86 (m, 5H), 7.78 – 7.76 (m, 2H), 7.54 (dd, ^3J (H,H) = 8.1 Hz, ^4J (H,H) = 1.6 Hz, 1H), 7.50 (tt, ^3J (H,H) = 7.4 Hz, ^4J (H,H) = 1.3 Hz, 1H), 7.47 – 7.45 (m, 2H), 7.44 – 7.35 (m, 8H), 7.16 (d, ^4J (H,H) = 1.5 Hz, 1H), 7.11 – 7.06 (m, 2H), 6.56 (t, ^3J (H,H) = 7.8 Hz, 2H). IR (solid): $\tilde{\nu}$ /cm^{-1} = 2911 (w), 2849 (w), 1445 (m), 1405 (w), 1314 (m), 1307 (m), 1172 (w), 1146 (s), 1096 (m), 1086 (s), 1070 (w), 1041 (m), 1003 (m), 907 (m), 821 (w), 809 (w), 766 (s), 749 (s), 734 (s), 720 (s), 717 (s), 686 (s), 672 (m), 664 (w), 649 (m). MS (MALDI-TOF, without matrix): m/z = 565.4 $[M+H]^+$ (base peak, calcd. 564.1).

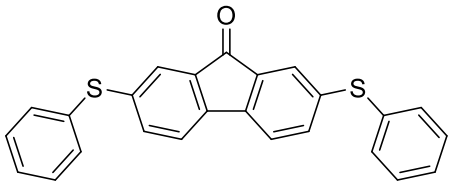
Synthesis of 2,7-bis(phenylsulfonyl)-9,9'-spirobifluorene (SPSO1): Oxidation at room temperature.



SPSO1

2 mL of a 0.89 M H_2O_2 (1.80 mmol, 8.00 eq.) solution in AcOH (100 %) were added to a solution of 2,7-bis(phenylthio)-9,9'-spirobifluorene (**1,** 121 mg, 0.227 mmol, 1.00 eq.) in $CHCl_3$ (2 mL) at 0°C. The solution was stirred for 21 h at room temperature, poured onto H_2O and extracted with CH_2Cl_2. The combined organic layers were washed with H_2O until no peroxide was present any more, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO_2; cyclohexane:EtOAc 1:1) to yield **SPSO1** as a colourless powder. Yield: 0.10 g, 0.18 mmol, 77 %. For analytical data of **SPSO1** see the oxidation at elevated temperature described in the main paper.

Synthesis of 2,7-bis(phenylthio)-9*H*-fluoren-9-one (4)



4

A dried flask was charged with 2,7-dibromo-9*H*-fluoren-9-one (**7,** 6.12 g, 18.1 mmol, 1.00 eq.), K_2CO_3 (5.52 g, 39.9 mmol, 2.21 eq.), thiophenol (3.9 mL, 4.20 g, 38.2 mmol, 2.11 eq.) and dry DMF (60 mL) under an inert atmosphere. After heating the reaction mixture to 130°C for 5 h, additional DMF (40 mL) and thiophenol (1.00 mL, 1.08 g, 9.78 mmol, 0.540 eq.) were added. The mixture was heated to 130°C for another 2 h, additional thiophenol (0.5 mL, 0.539 g, 4.89 mmol, 0.27 eq.) was added and the mixture was stirred overnight at room temperature and then heated again to 140°C for 3 h. After cooling to room temperature, the reaction mixture was poured into 700 mL ice water. The orange suspension was extracted four times with 400 mL *t*-BME. The combined organic layers were washed with H_2O (100 mL) and brine (150 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure. The brown-orange residue was recrystallized from a mixture of cyclohexane and EtOAc (5:2). The solvent was decanted and the residue was washed with cold cyclohexane and dried under vacuum. The decanted solution was concentrated under reduced pressure and the resulting residue was again recrystallised from a mixture of cyclohexane and EtOAc (10:1). Yield: 3.9 g, 9.9 mmol, 55 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.52 (m, 2H), 7.43 – 7.29 (m, 14H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)**:** δ/ppm = 192.65 (C=O), 142.37, 138.70, 136.05, 135.04, 134.18, 132.27, 129.67, 128.14, 126.09, 120.95. MS (EI, 70 eV)**:** *m*/*z* (%) = 396.1 $[M]^+$ (100, calcd. 396.1). The analytical data were consistent with the literature data.[1]

Reference:

1. F.-M. Hsu, C.-H. Chien, Y.-J. Hsieh, C.-H. Wu, C.-F. Shu, S.-W. Liu, C.-T. Chen, *J. Mater. Chem.* **2009**, *19*, 8002–8008.

2. Theoretical calculations

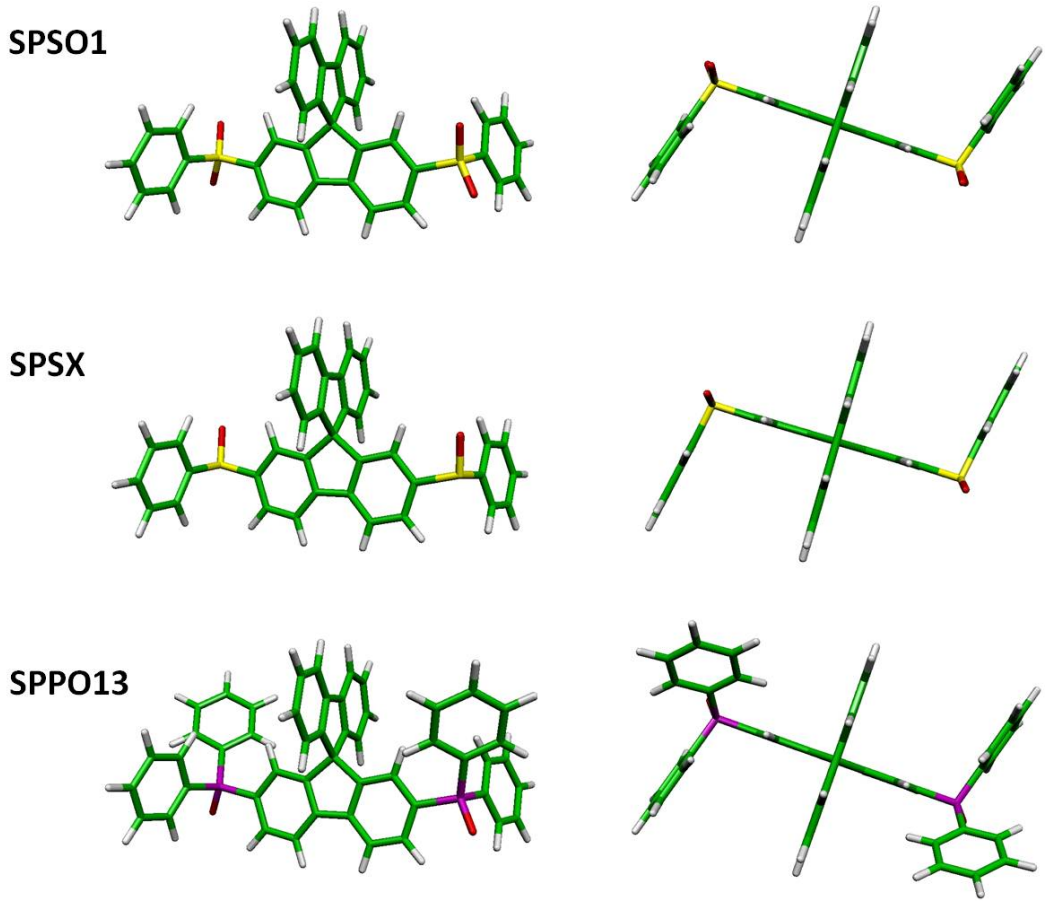


Figure S1. Front (left) and top (right) views of the B3LYP/6-31G** minimum-energy optimized structures of **SPSO1**, **SPSX**, and **SPPO13**. Atom colors: C = green, S = yellow, P = purple, O = red, H = white.

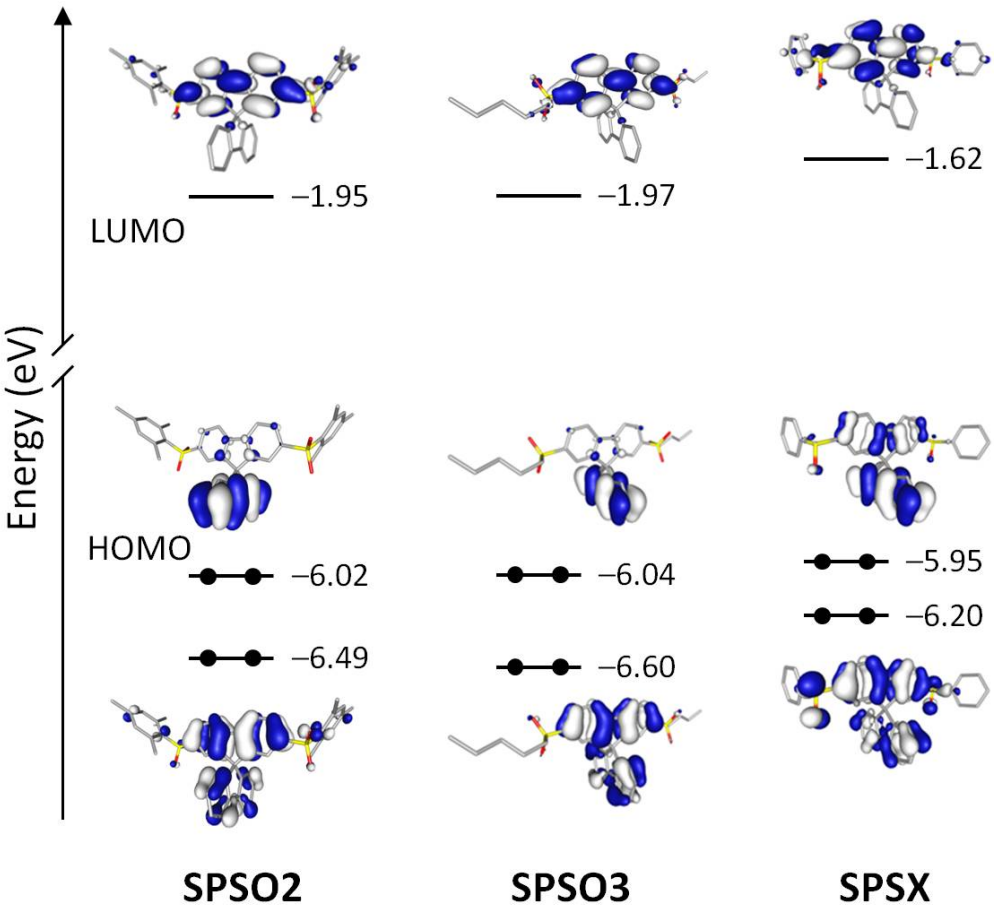


Figure S2. Schematic representation showing the isovalue contours (±0.03 a.u.) and energies calculated for the frontier molecular orbitals of **SPSO2**, **SPSO3**, and **SPSX**. Hydrogen atoms are omitted.

Table S1. Lowest singlet excited states calculated at the TD-DFT B3LYP/6-31G** level in acetonitrile for compounds **SPSO1–3** and **SPSX**. Vertical excitation energies (*E*), oscillator strengths (*f*), and dominant monoexcitations with contributions (within parentheses in %) greater than 18%.

	Excited state	*E* (eV/nm)	*f*	Monoexcitations[a]
SPSO1	S_1	3.39 / 366	0.05	H → L (98)
	S_2	3.90 / 318	0.78	H–1 → L (98)
	S_4	4.26 / 291	0.29	H–3 → L (82)
	S_5	4.35 / 285	0.22	H → L+3 (54) H → L+2 (25) H–3 → L (18)
	S_6	4.40 / 282	0.50	H → L+2 (63) H → L+3 (29)
SPSO2	S_1	3.50 / 355	0.06	H → L (98)
	S_2	3.98 / 311	0.83	H–1 → L (98)
	S_5	4.39 / 283	0.16	H–2 → L (67) H → L+3 (19)
	S_7	4.39 / 283	0.47	H → L+1 (90)
	S_8	4.41 / 281	0.25	H–4 → L (61) H–2 → L (23)
SPSO3	S_1	3.49 / 355	0.03	H → L (98)
	S_2	4.06 / 305	0.53	H–1 → L (98)
	S_5	4.40 / 282	0.51	H → L+1 (92)
	S_6	4.47 / 278	0.64	H–3 → L (77)
	S_8	4.62 / 268	0.11	H–4 → L (82)
SPSX	S_1	3.74 / 332	0.27	H → L (98)
	S_2	4.00 / 310	0.67	H–1 → L (98)
	S_4	4.34 / 284	0.36	H → L+1 (90)
	S_7	4.55 / 273	0.18	H–1 → L+2 (35) H–4 → L (30) H → L+2 (19)

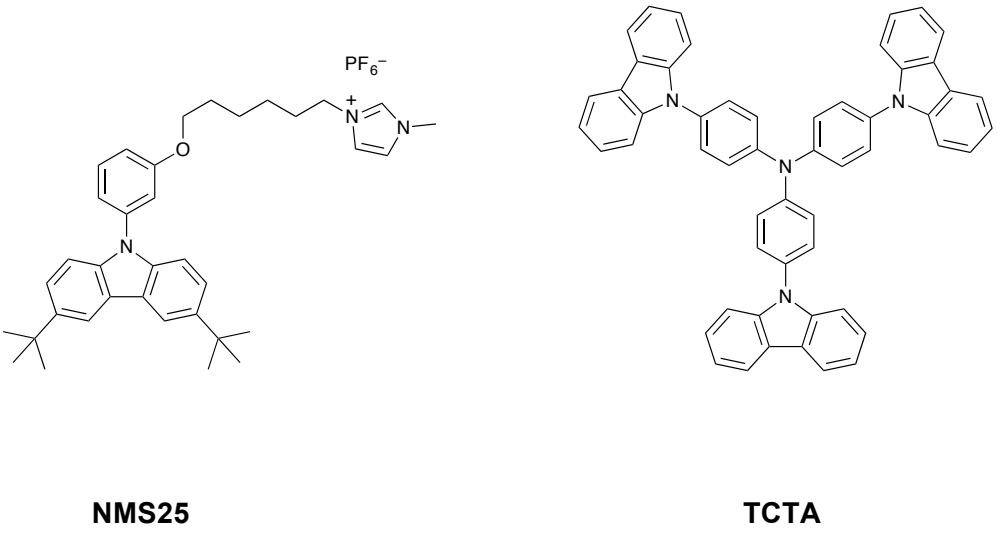
[a] H and L denote HOMO and LUMO, respectively.

Table S2. Lowest triplet excited states calculated at the TD-DFT B3LYP/6-31G** level in acetonitrile for compounds **SP**, **SPSO1–3**, **SPSX**, **SPPO13**, and **FIrpic**.[a] Vertical excitation energies (*E*) and dominant monoexcitations with contributions (within parentheses in %) greater than 18%.

	Excited state	*E* (eV/nm)	Monoexcitations[b]
SP	T_1	3.05 / 406	H → L+1 (42) H–1 → L+1 (34)
	T_2	3.05 / 406	H → L (42) H–1 → L (34)
	T_3	3.89 / 318	H → L+4 (18)
SPSO1	T_1	2.86 / 433	H–1 → L (56)
	T_2	3.05 / 406	H → L+2 (56) H → L+3 (20)
	T_3	3.40 / 364	H → L (79)
SPSO2	T_1	2.88 / 431	H–1 → L (56)
	T_2	3.05 / 407	H → L+1 (74)
	T_3	3.52 / 353	H → L (77)
SPSO3	T_1	2.92 / 424	H–1 → L (52) H–3 → L (18)
	T_2	3.05 / 406	H → L+1 (77)
	T_3	3.50 / 355	H → L (79)
SPSX	T_1	2.90 / 428	H–1 → L (46) H → L (29)
	T_2	3.05 / 406	H → L+1 (63)
	T_5	3.76 / 330	H → L (61) H–1 → L (22)
SPPO13	T_1	2.90 / 428	H–1 → L (58) H → L (18)
	T_2	3.05 / 406	H → L+1 (70)
	T_3	3.65 / 340	H → L (70)
FIrpic	T_1	2.83 / 438	H → L+1 (42) H → L (20)
	T_2	2.87 / 431	H → L+2 (25)
	T_5	3.15 / 393	H → L (58) H → L+1 (37)

[a] Calculations for **FIrpic** were performed at the B3LYP/(6-31G**+LANL2DZ) level. [b] H and L denote HOMO and LUMO, respectively.

3. Device testing



NMS25 **TCTA**

Scheme S1. Chemical structures of hole-transporting hosts

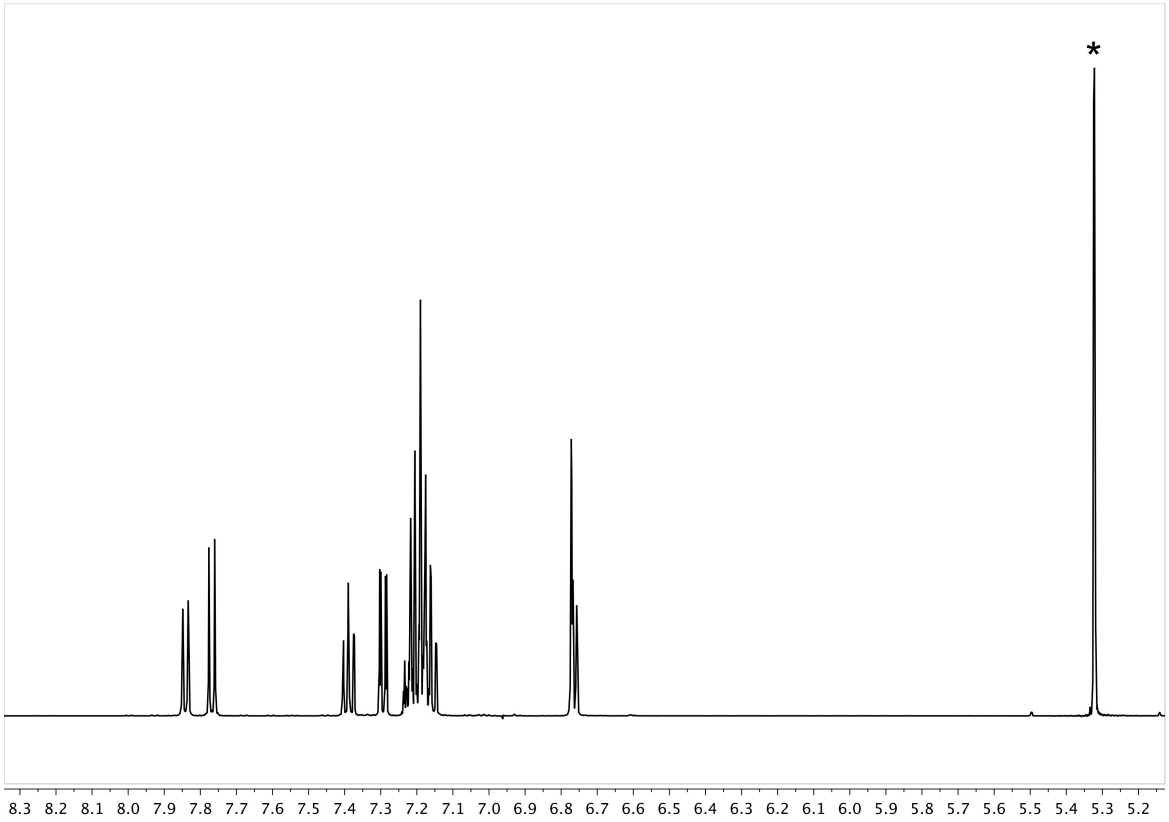
Table S3. Solubility tests for the sulfone-host series at room temperature

Acceptor-Host	**Anisole**	**MeCN**	**THP**	**HFP**
SPSO1	very soluble	insoluble	partially soluble	partially soluble
SPSO2	very soluble	insolible or soluble (with 20% MeTHF added)	very soluble	very soluble
SPSO3	very soluble	partially soluble or very soluble (with 20% MeTHF added)	soluble	soluble

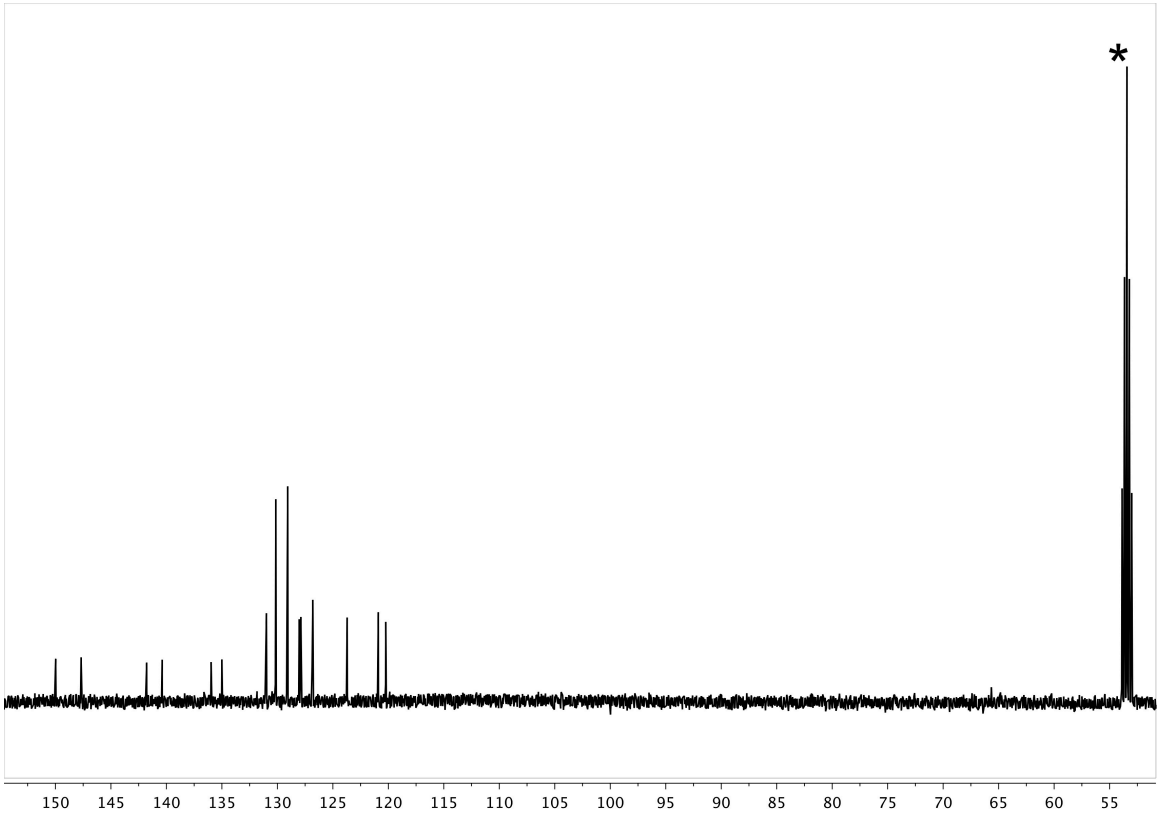
THP = Tetrahydropyran, HFP = 1,1,1,3,3,3-Hexafluoro-2-propanol

4. NMR spectra of compounds:

Compound **1**

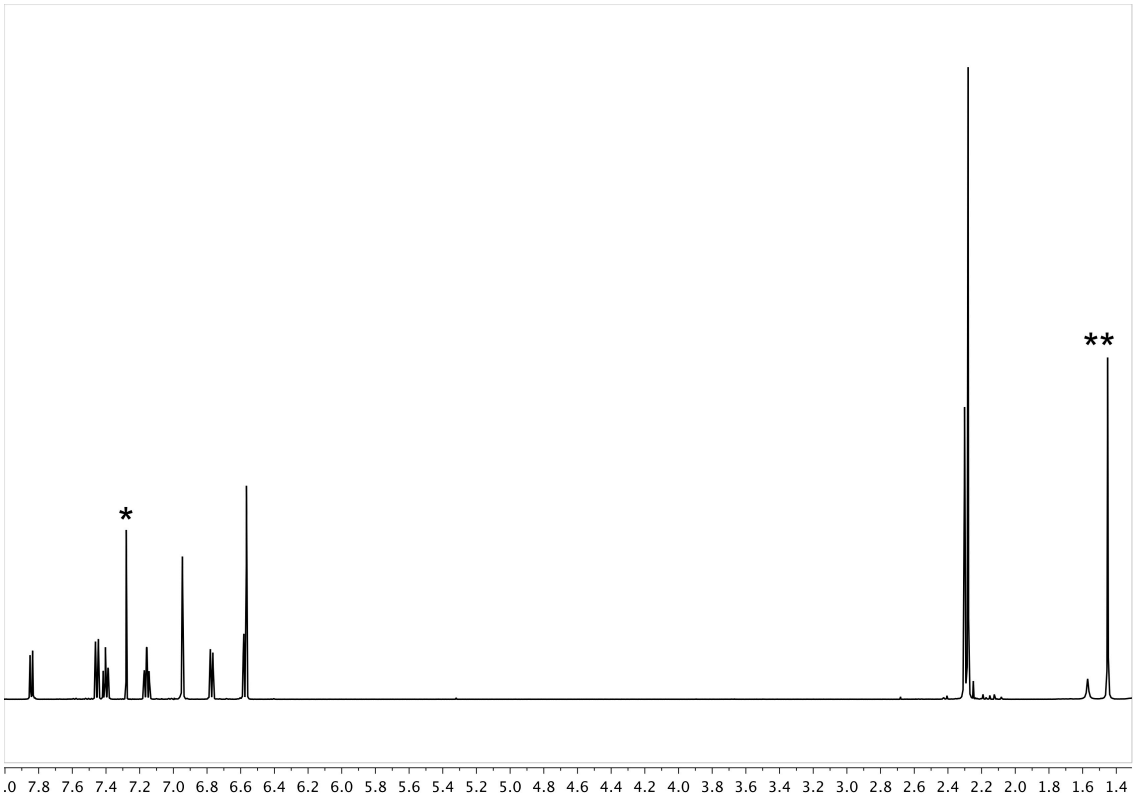


500 MHz ^{1}H NMR spectrum of intermediate **1** in CD_2Cl_2. * = residual $CHDCl_2$.

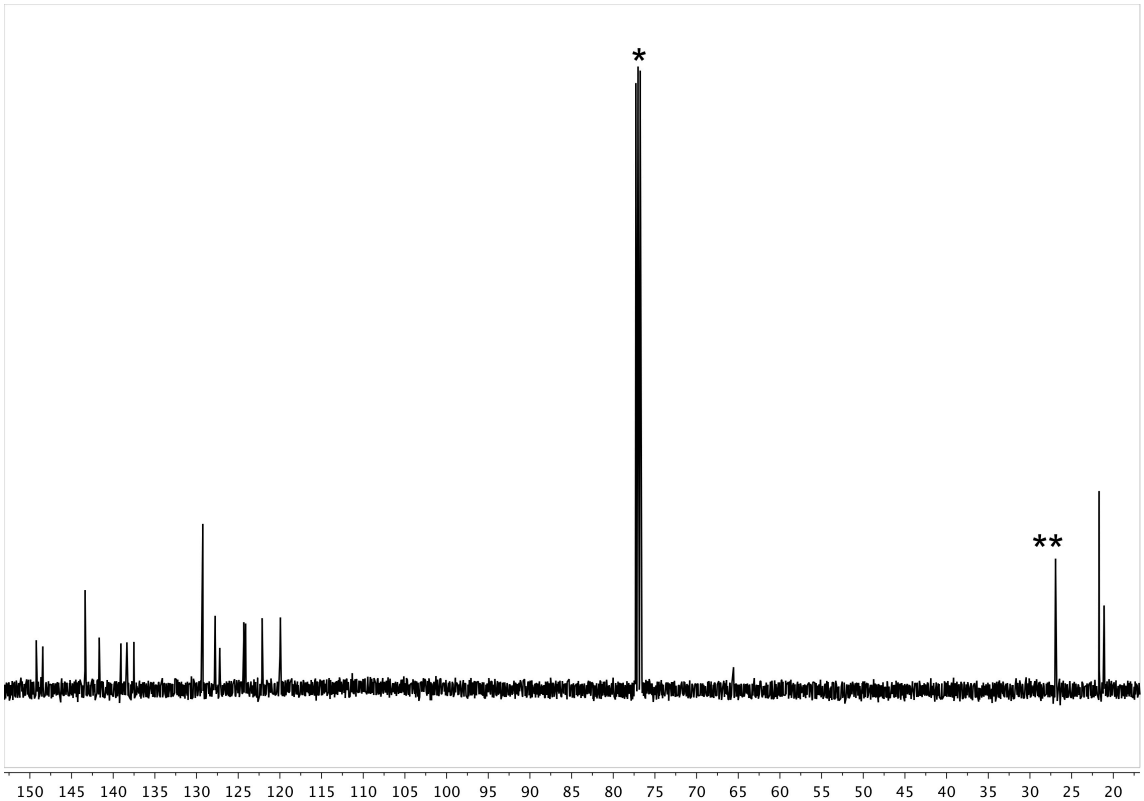


126 MHz ^{13}C NMR spectrum of intermediate **1** in CD_2Cl_2. *= CD_2Cl_2.

Compound **2**

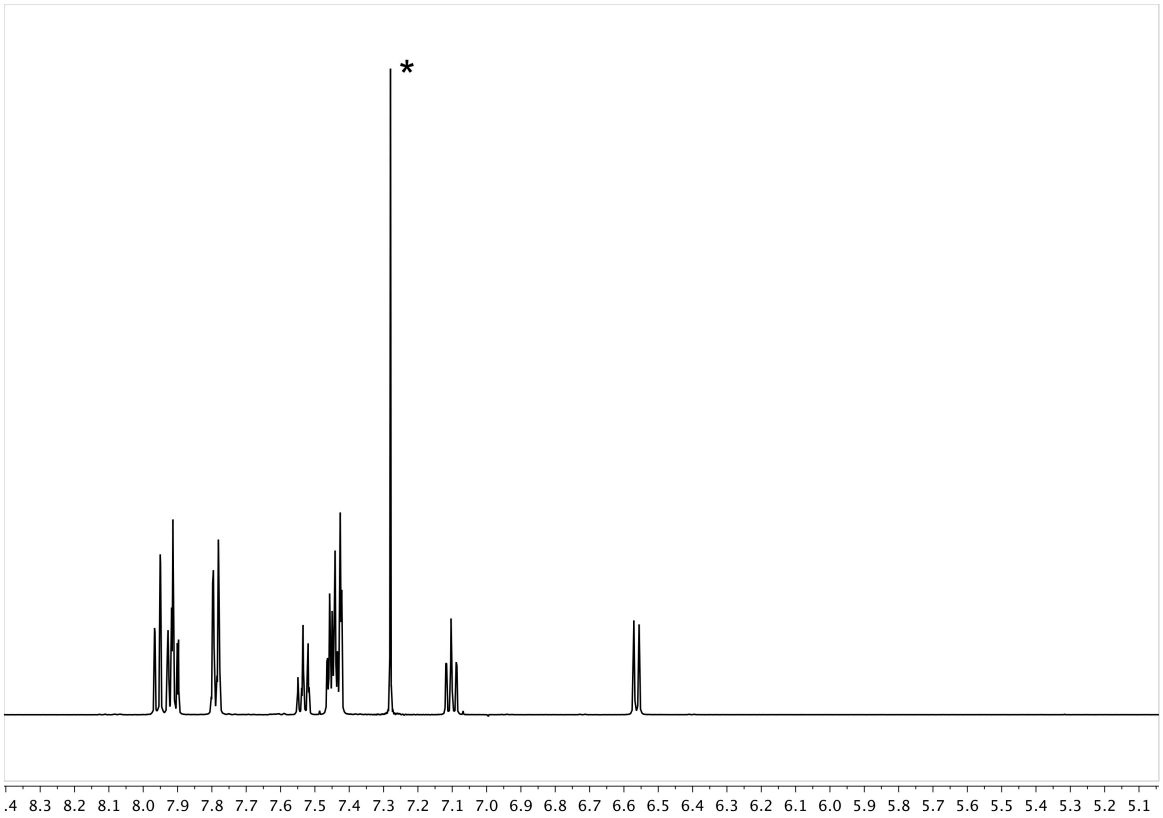


500 MHz ^{1}H NMR spectrum of intermediate **2** in $CDCl_3$; * = residual $CHCl_3$; ** = residual cyclohexane from column chromatography.

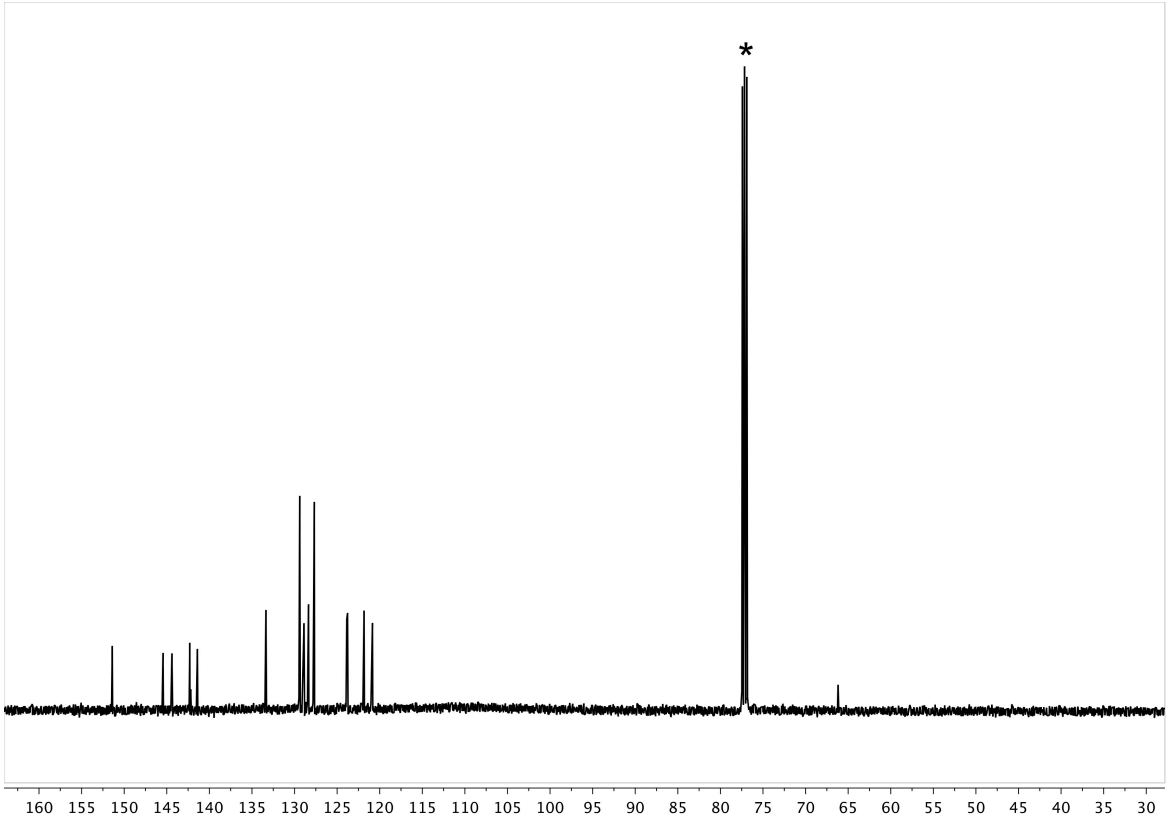


126 MHz ^{13}C NMR spectrum of intermediate **2** in $CDCl_3$. *= $CDCl_3$; ** = residual cyclohexane from column chromatography.

Compound **SPSO1**

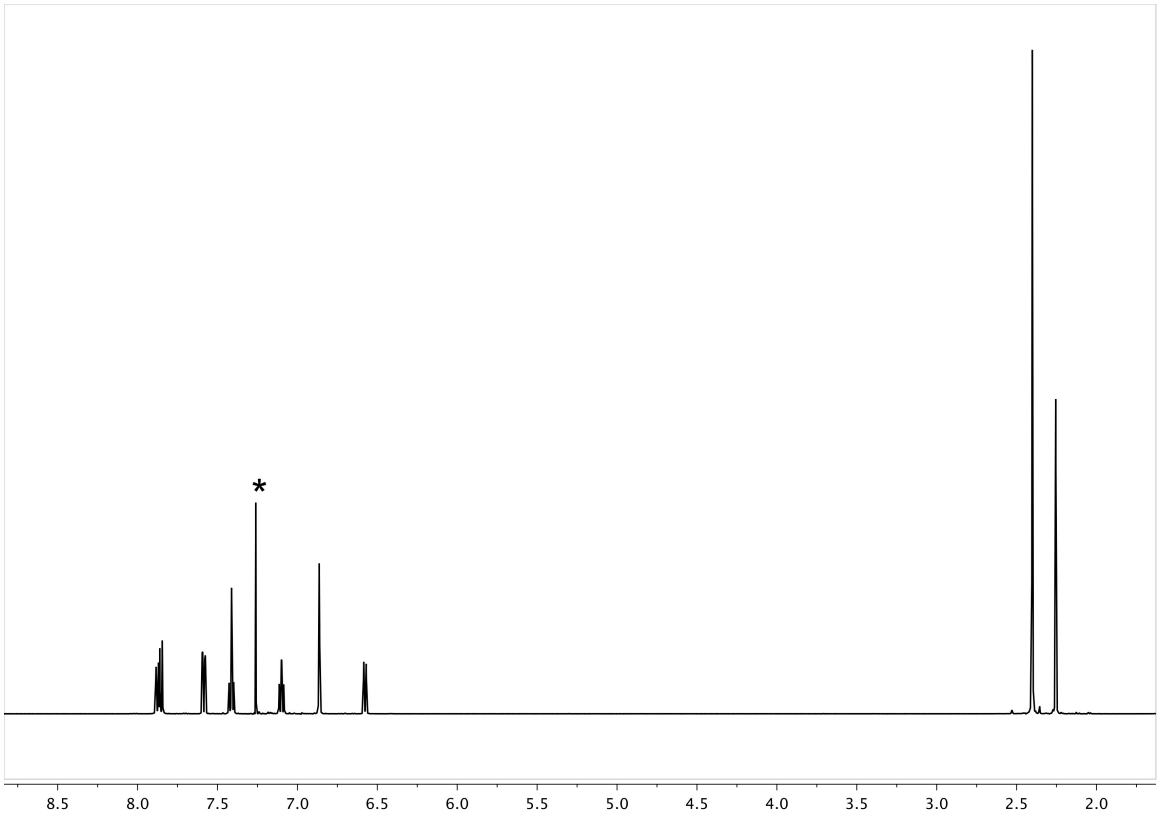


500 MHz ^{1}H NMR spectrum of **SPSO1** in $CDCl_3$; * = residual $CHCl_3$.

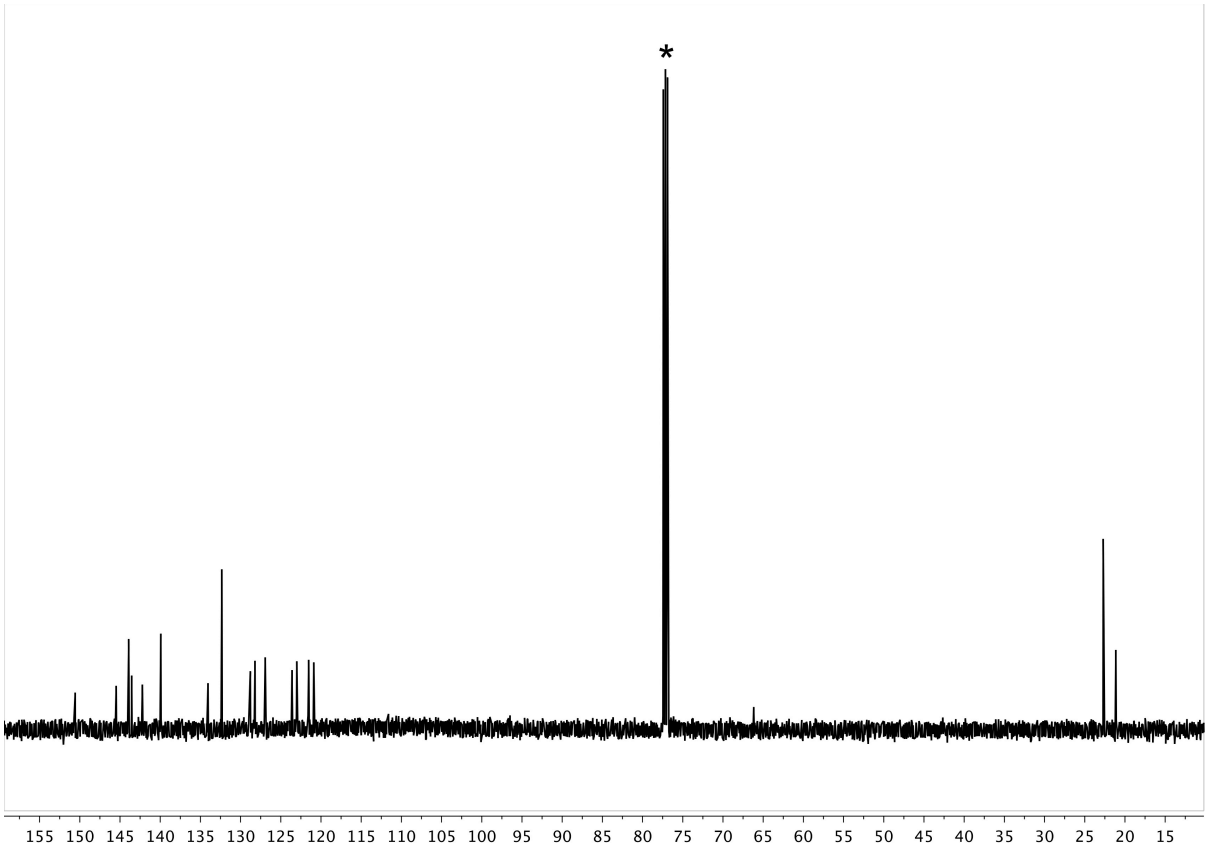


126 MHz ^{13}C NMR spectrum of **SPSO1** in $CDCl_3$; *= $CDCl_3$.

Compound **SPSO2**

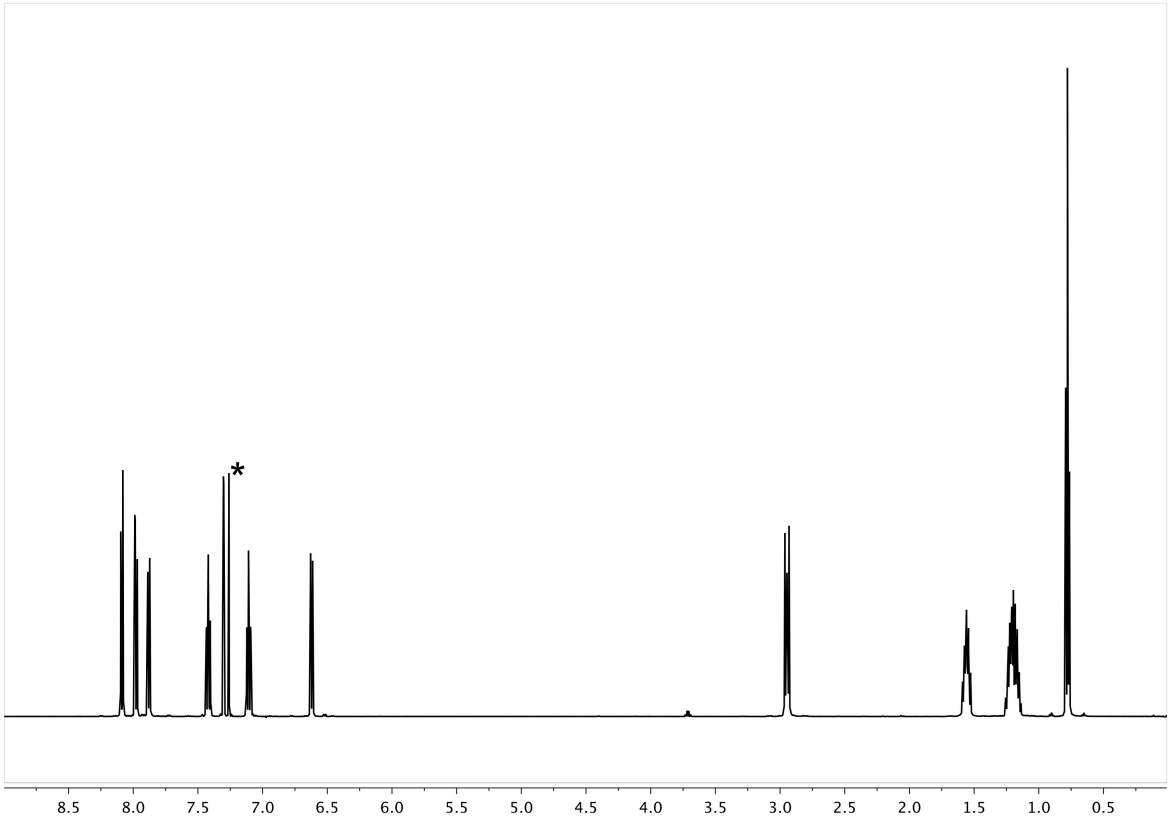


500 MHz ^{1}H NMR spectrum of **SPSO2** in $CDCl_3$; * = residual $CHCl_3$.

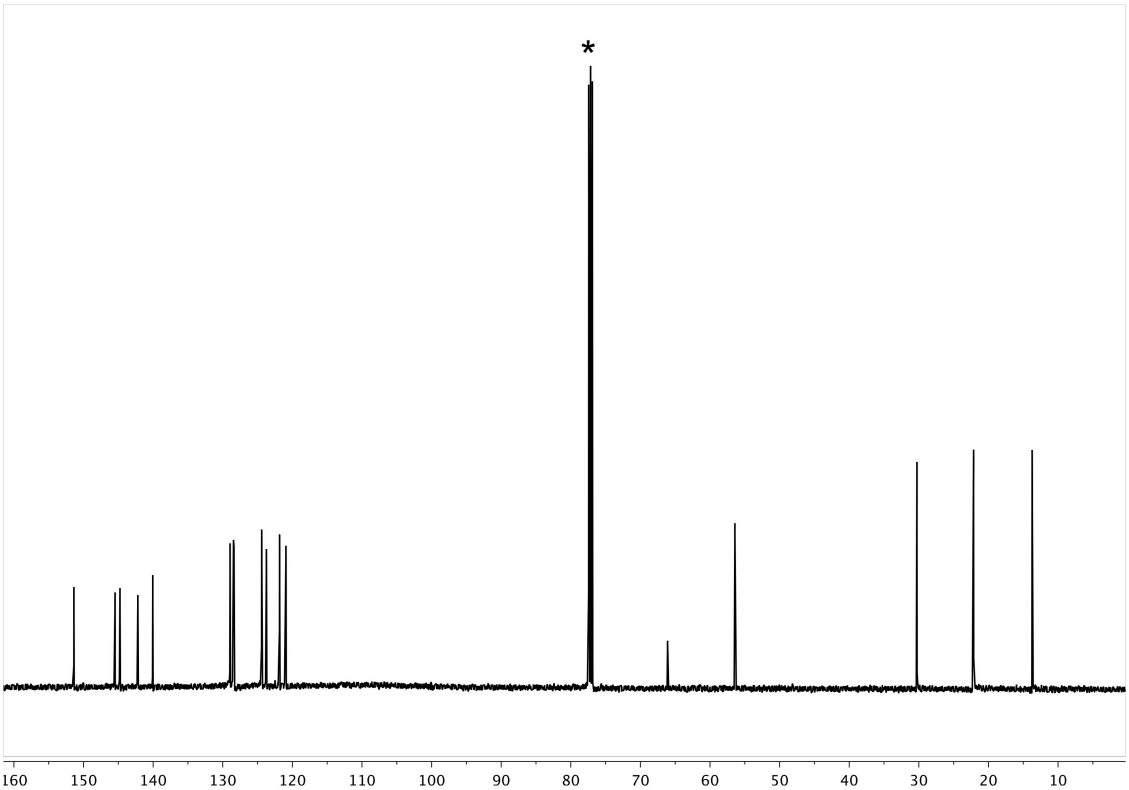


126 MHz ^{13}C NMR spectrum of **SPSO2** in $CDCl_3$; *= $CDCl_3$.

Compound **SPSO3**

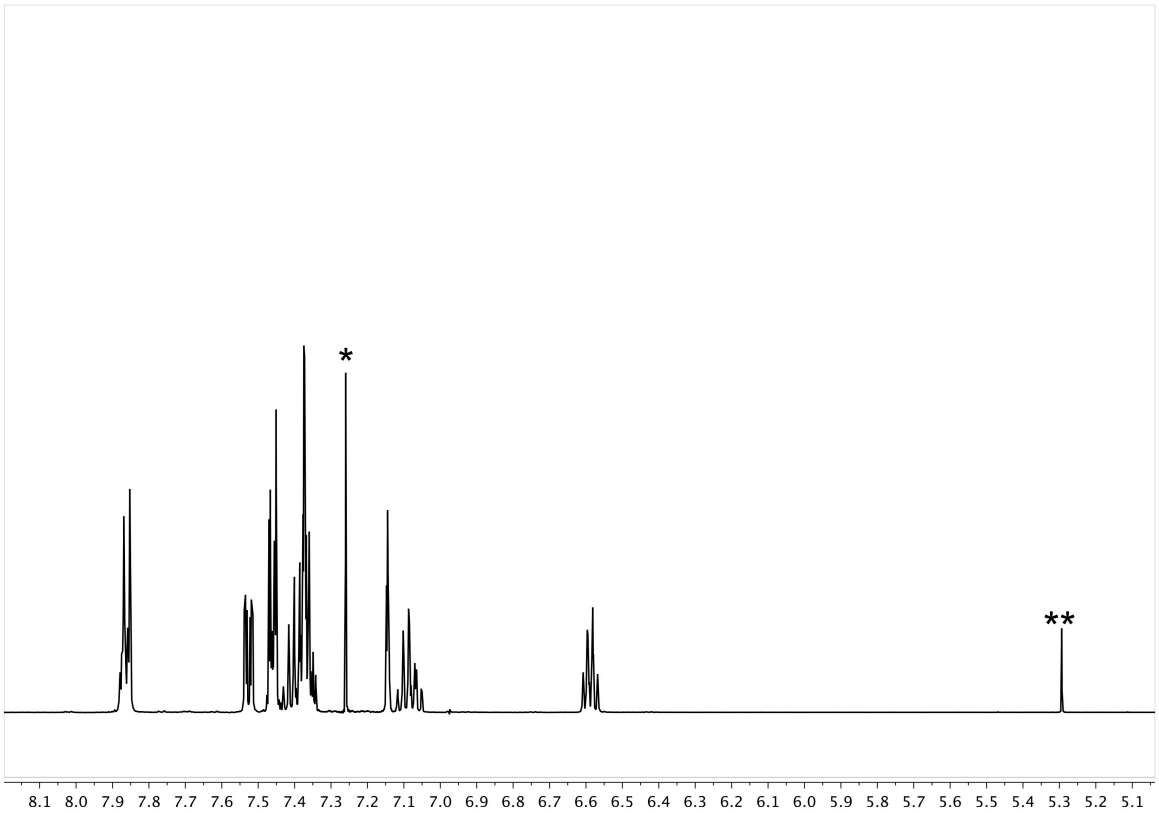


500 MHz ^{1}H NMR spectrum of **SPSO3** in $CDCl_3$; * = residual $CHCl_3$.

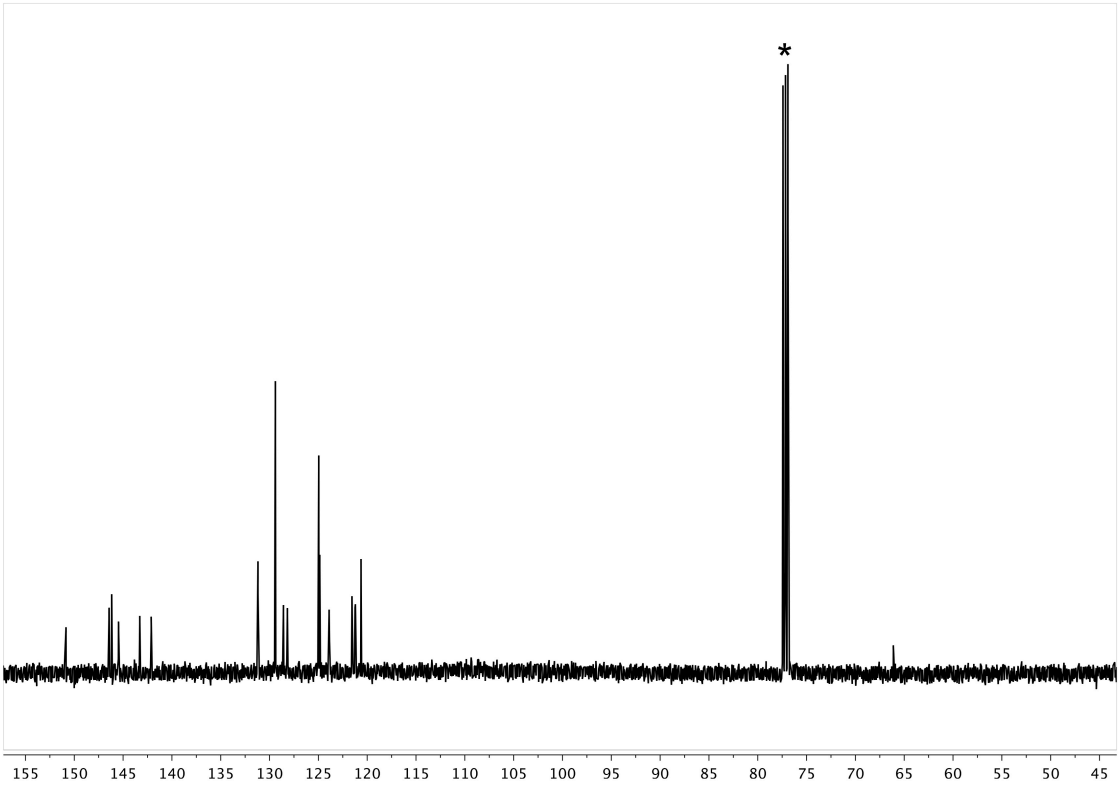


126 MHz ^{13}C NMR spectrum of **SPSO3** in $CDCl_3$; *= $CDCl_3$.

Compound **SPSX**



500 MHz ^{1}H NMR spectrum of **SPSX** in $CDCl_3$; * = residual $CHCl_3$; ** = trace of CH_2Cl_2.



126 MHz ^{13}C NMR spectrum of **SPSX** in $CDCl_3$; *= $CDCl_3$.