Electronic Supplementary Information

Chiral Properties of Tetrathiatriarylmethyl Spin Probes

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1.   General information

1.1   Chemistry

All reactions were carried out in flame-dried glassware under argon atmosphere and were monitored by thin layer chromatography (TLC) using aluminum sheets coated with silica gel 60 F254 (Merck). Anhydrous grade solvents were used for reactions and HPLC grade for purifications. All commercially available reagents were used as received without further purification. Preparative TLCs were done on plate 20 x 20 cm, silicagel 60 F254, 1 mm, (Merck). NMR spectra were recorded on a BRUKER Avance II (^{1}H: 300 MHz, ^{13}C: 75 MHz, ^{19}F 282 MHz) and a BRUKER Avance DPX (^{1}H: 500 MHz, ^{13}C: 125 MHz). Chemical shifts (δ) are reported in parts per million (ppm), referenced to NMR solvents: chloroform-d (δ ^{1}H=7.27 ppm, ^{13}C=77.2 ppm). The following abbreviations are used: s=singlet, d=doublet, t=triplet, m=multiplet. Coupling constants (J) are reported in Hertz (Hz). Infrared (IR) spectra are recorded using a Shimadzu spectrometer FTIR-8400S; products were analyzed as thin films deposited on a Se−Zn crystal by evaporation from the solvent. High resolution mass spectrometry (HRMS) analyses were performed at the University College London. Analytical HPLC was carried out on a Waters Alliance 2690 separations module equipped with a Waters 2998 PDA detector and a Gilson HPLC system (two Pumps 306, manometric module 805, dynamic mixer 811D, system interface 506C) equipped with a Jasco CD-2095 Plus chiral detector. Semi-preparative HPLC was carried out on a Waters 600 Pump equipped with a Waters 996 PDA detector. EPR spectrum was recorded on an X-Band BRUKER EMX spectrometer operating at ~9.46 GHz equipped with a ER4119HS resonator.

1.2   Computational methods

The bulk of the computations has been carried out using the Jaguar 7.5 pseudospectral program package.[1] All species have been fully optimized and the Cartesian coordinates are supplied in Section 8.

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[1] Jaguar, version 7.5, Schrödinger, LLC, New York, NY, 2008.

Geometry optimization was carried out using the well established UB3LYP hybrid density functional[2] as implemented in Jaguar with the standard split valence polarized 6-31G* basis.[3] Single point energy calculations were carried out at the UB3LYP-D level of theory (including an approximation correction for dispersion[4]) with the larger 6-311+G** basis, using ORCA package.[5]

In order to validate our chosen methodology, additional single energies have been evaluated for radical **1d** at several level of theory: UB3LYP/6-311+G**, UB3LYP-D/6-31G*, UB3LYP-D/6-31G**, RO-B3LYP-D/6-31G**, UBP86/6-31G** and LMP2/6-31G*. These results are reported in Section 8.1.

Vibrational frequencies were computed for all stationary points for radical **1d** at the UB3LYP/6-31G* level of theory and are used to include zero-point energy, thermal and entropic corrections to compute ideal gas free energies. The correct nature of stationary points was confirmed by checking the curvature and its eigenvectors: Ground state structures were found to be minima with zero imaginary frequency, while transition state structures were found to be first-order saddle points with a single imaginary frequency.

Solvation effects were estimated by performing additional single point energy calculations using the ORCA program package, at the UB3LYP-D/6-31G* level. These calculations were performed using the conductor-like screening model (COSMO) as implemented in ORCA,[6] using the parameters appropriate for ethyl acetate, the solvent used for racemization kinetics.

For the large reaction systems there are usually several local minima or saddle points corresponding to each intermediate or transition state. This is due to the possibility of multiple conformations. In particular, the non-planarity of the two five-member rings on each phenyl groups allows two different conformations for each ring. Test calculations showed that energy differences between the various accessible conformers[7] and energy barriers connecting them are much lower than barriers to enantiomerization. We have made a systematic attempt to locate all possible local saddle points, with the data presented referring to the lowest energy form.

[2] (a) A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648-5652. (b) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees D. J.; Pople, J. A. *J. Chem. Phys.* 1982, **77**, 3654.
[3] Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* 1972, **56**, 2257-2261.
[4] Grimme, S. *J. Comput. Chem.* 2006, **27**, 1787-1799.
[5] F. Neese, *ORCA, An Ab initio, DFT, and Semienpirical Electronic Structure Package*, version 2.7.0, Universität Boon, Germany, 2010.
[6] Sinnecker, S.; Rajendran, A.; Klamt, A.; Diedenhofen, M.; Neese, F. *J. Chem. Phys. A.* 2006, **110**, 2235-2245.
[7] In most cases, the more stable conformer is the one in which the five-member rings on each phenyl group are twisted in opposite directions so that the whole substituted phenyl group is in a chair-like conformation.

2.   NMR spectroscopy analysis of compound 2d with a chiral solvating agent

To a solution of 50 mg of trityl alcohol **2d** (containing 1.3 eq. of C_6H_6) in 0.6 mL of $CDCl_3$ was added 1,3,6,8 or 10 equivalents of (+)-2,2,2-trifluoro-1-(9-anthryl)ethanol (the Pirkle's alcohol)[8] as chiral solvating agent (CSA)[9] and ^1H,^{13}C and ^{19}F NMR spectra were recorded at 500 MHz, 125 MHz and 282 MHz, repectively.

[8] W. H. Pirkle, D. L. Sikkenga and M. S. Pavlin, *J. Org. Chem.*, 1977, **42**, 384-387.
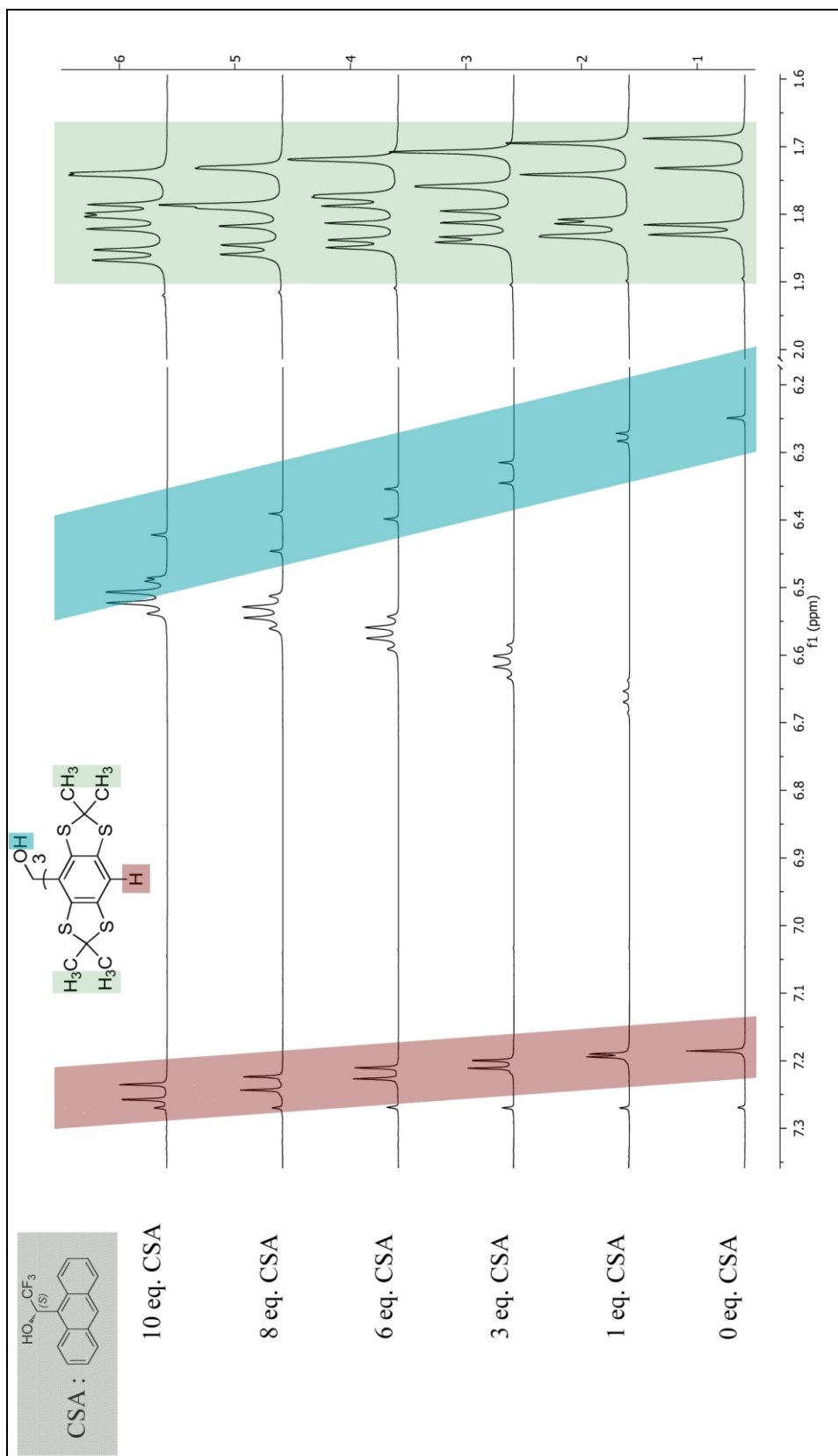[9] D. Parker, *Chem. Rev.*, 1991, **91**, 1441-1457.

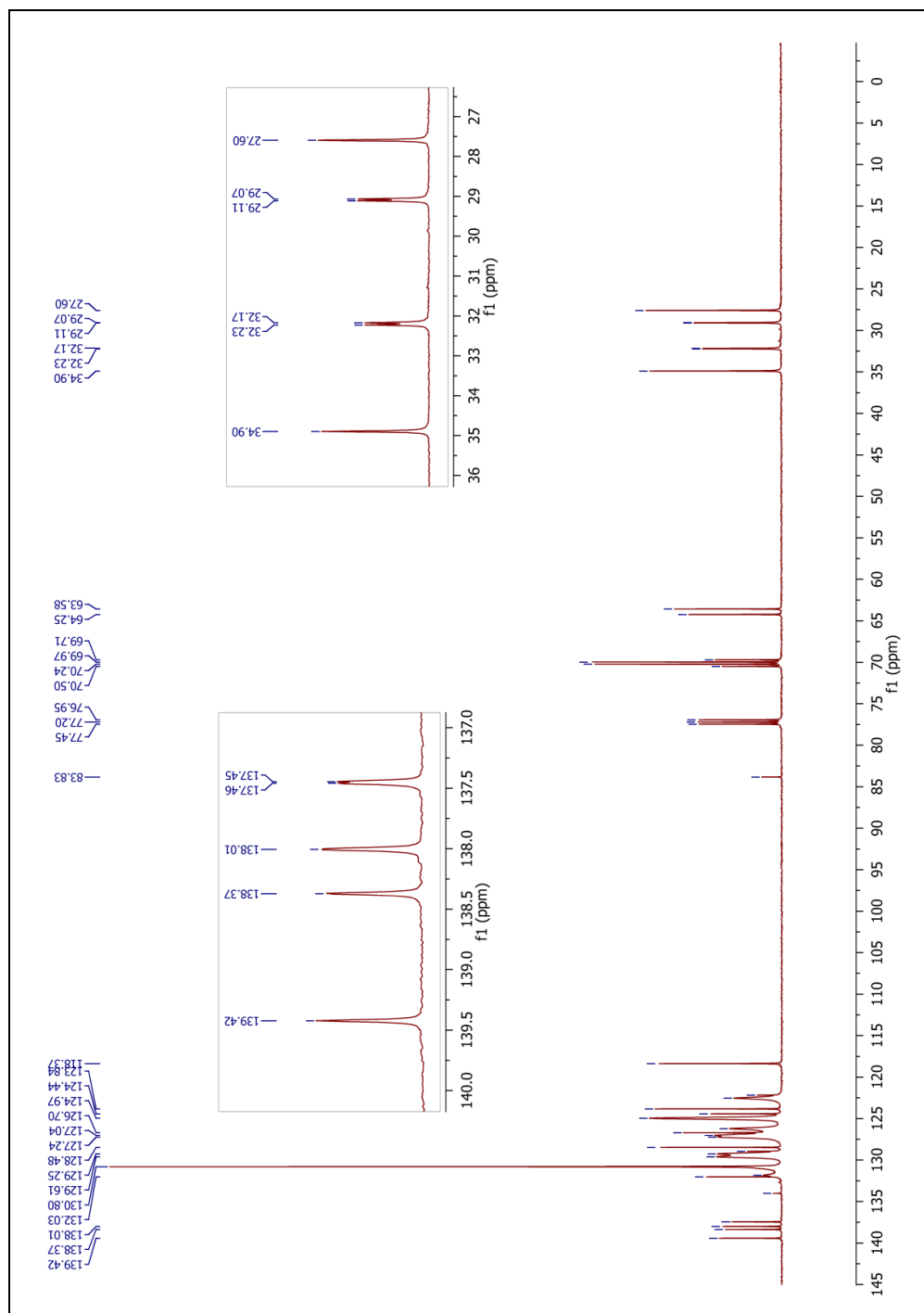Figure S1: Stacked ^{1}H NMR spectra at 500 MHz of **2d** with 0,1,3,6,8 and 10 equivalents of CSA

Figure S2: ^{13}C NMR spectrum at 125 MHz of **2d** with 10 equivalents of CSA.

N.B. No split of NMR resonances was observed in the ^{19}F spectra.

3.   Syntheses and characterizations of compounds 3a and 3b

Synthesis of tris(8-(S)-α-methylbenzylaminocarbonyl-2,2,6,6-tetramethylbenzo[1,2-d;4,5-d']bis[1,3]dithiol-4-yl)methanol **3a**
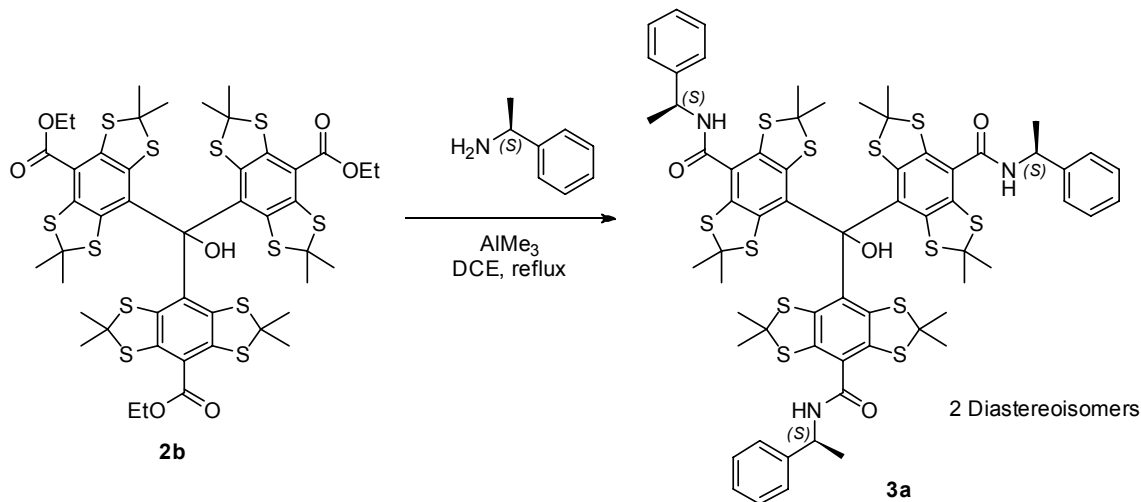
To a solution of (S)-(−)-α-methylbenzylamine (117 μL, 0.908 mmol, 20 eq.) in dichloroethane (DCE) (1 mL) was added AlMe$_3$ 2M in toluene (0.454 mL, 0.908 mmol, 20 eq). The solution was stirred for 10 min and trityl alcohol **2b** (50 mg, 0.045 mmol, 1 eq.) in DCE (1 mL) was then added. The orange solution was stirred 1 h at room temperature and refluxed for 19 h. After cooling the solution to room temperature KH$_2$PO$_4$ sat. (2 mL) was carefully added. The mixture was diluted with dichloromethane (DCM) (3 mL) and the organic layer was separated. The aqueous layer was extracted with DCM (3x3 mL). The combined organic layers were dried over MgSO$_4$, filtered and the solvent was removed under reduced pressure. The crude mixture was purified by preparative TLC with EtOAc 5% in DCM to provide 25 mg (42%) of the title compound **3a** as an orange solid. R$_f$: 0.35 DCM/EtOAc (95:5) UV (254,366 nm). ^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 1.63-1.80 (several signals, 45H), 5.25-5.36 (m, 3H), 6.47-6.57 (m, 4H, OH+NH), 7.28-7.47 (m, 15H). ^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm): 21.9+22.0, 27.8+28.1, 29.2+29.2, 32.1, 34.5+34.6, 50.1+50.2, 62.4+62.5, 63.0+63.1, 84.2+84.2, 126.6+126.7, 126.9+127.1, 127.7+127.7, 128.9+128.9, 132.7, 137.3+137.4, 137.5+137.7, 139.8+139.9, 140.8+140.8, 142.7+142.8, 166.1. HRMS (TOF MS ES+) *m/z* : [M+H]$^+$ calcd for C$_{64}$H$_{68}$N$_3$O$_4$S$_{12}$: 1326.1858, found: 1326.1954. ATR-IR (ν$_{MAX}$/cm^{-1}): 3331, 2960, 2924, 1655, 1522, 1495, 1452, 1230.
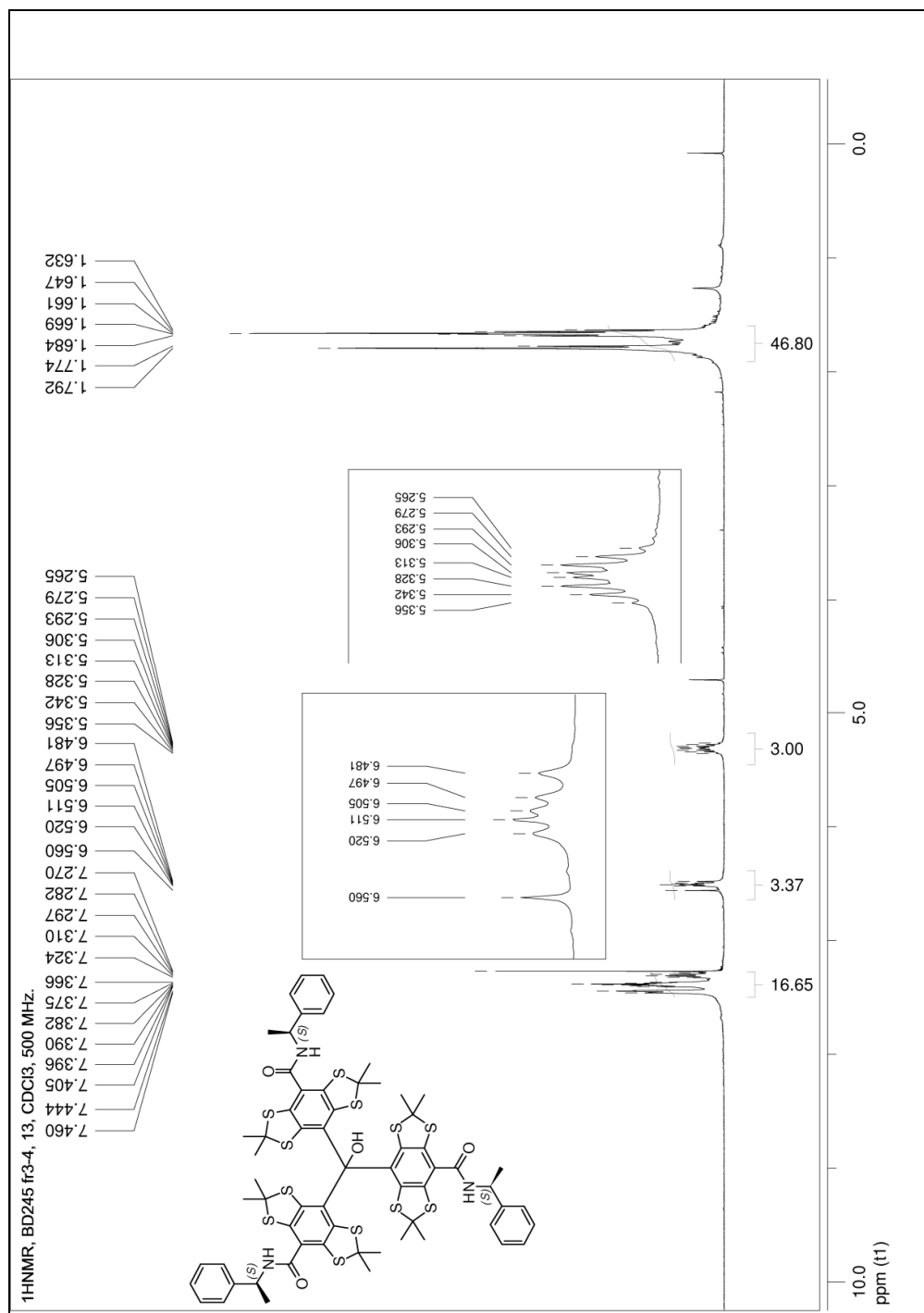
Figure S3: ^{1}H NMR spectrum (at 500 MHz) of compound **3a**

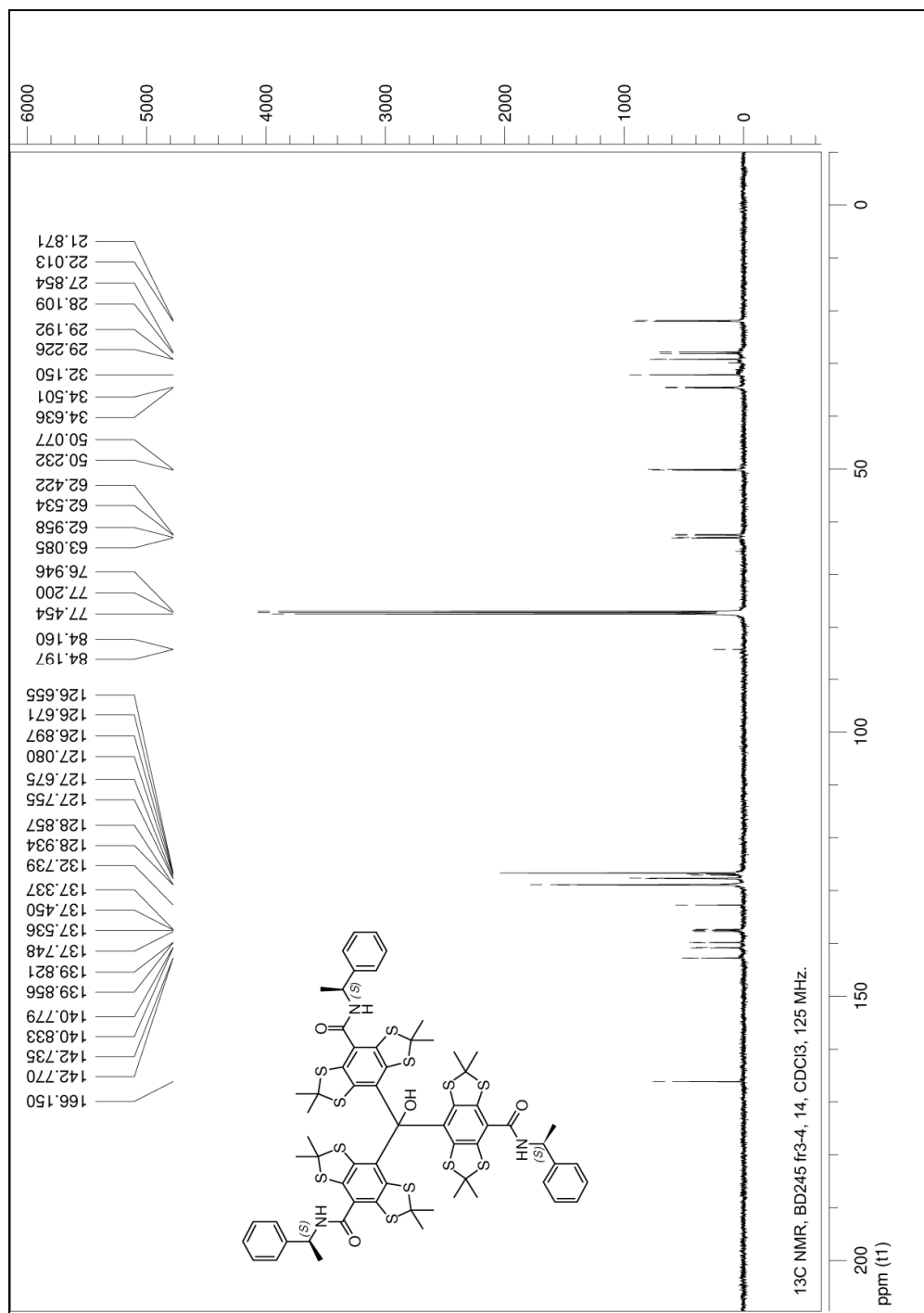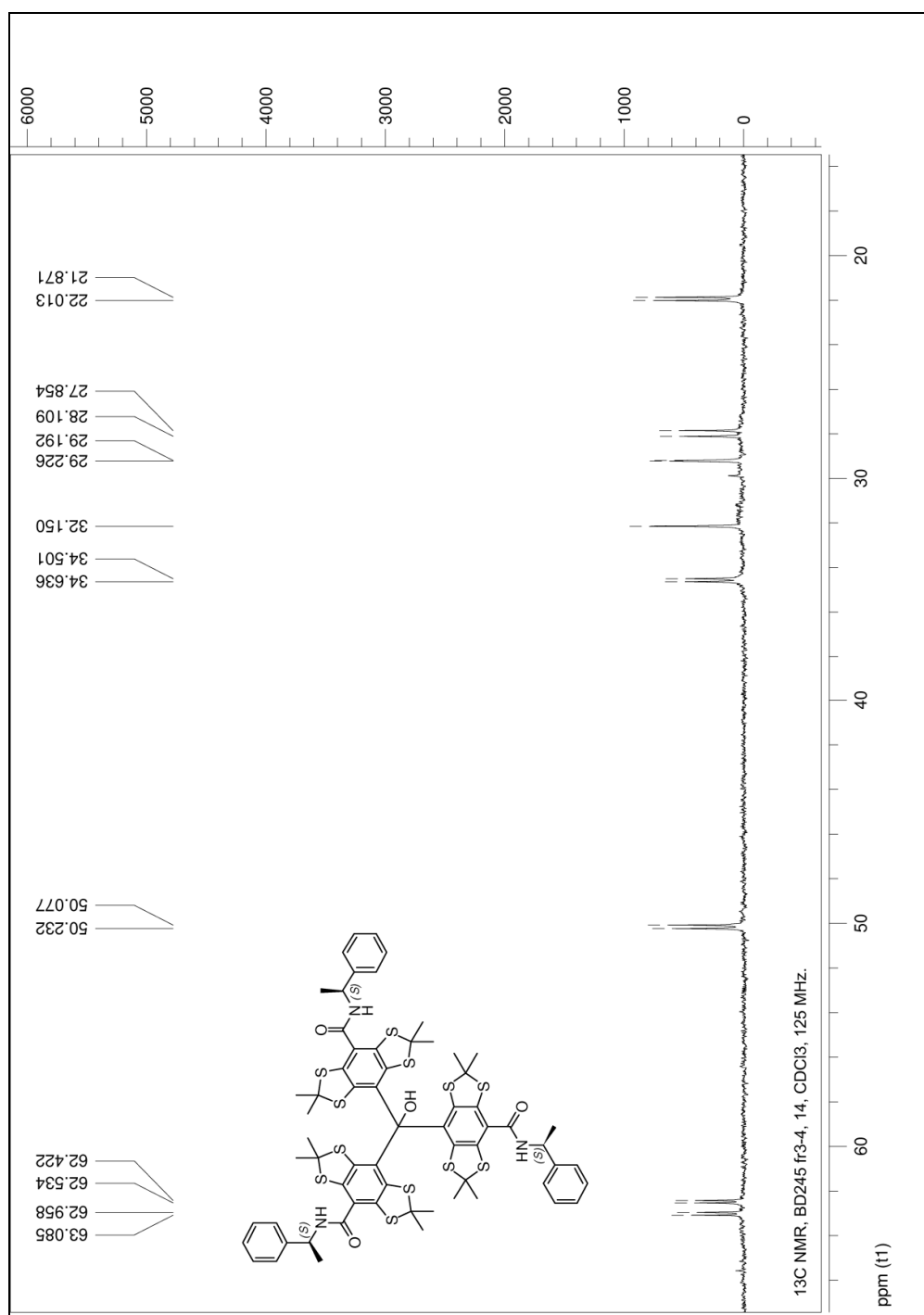Figure S4 a: ^{13}C NMR spectrum (at 125 MHz) of compound **3a**

Figure S4 b: ^{13}C NMR spectrum (at 125 MHz) of compound **3a** (enlargement)
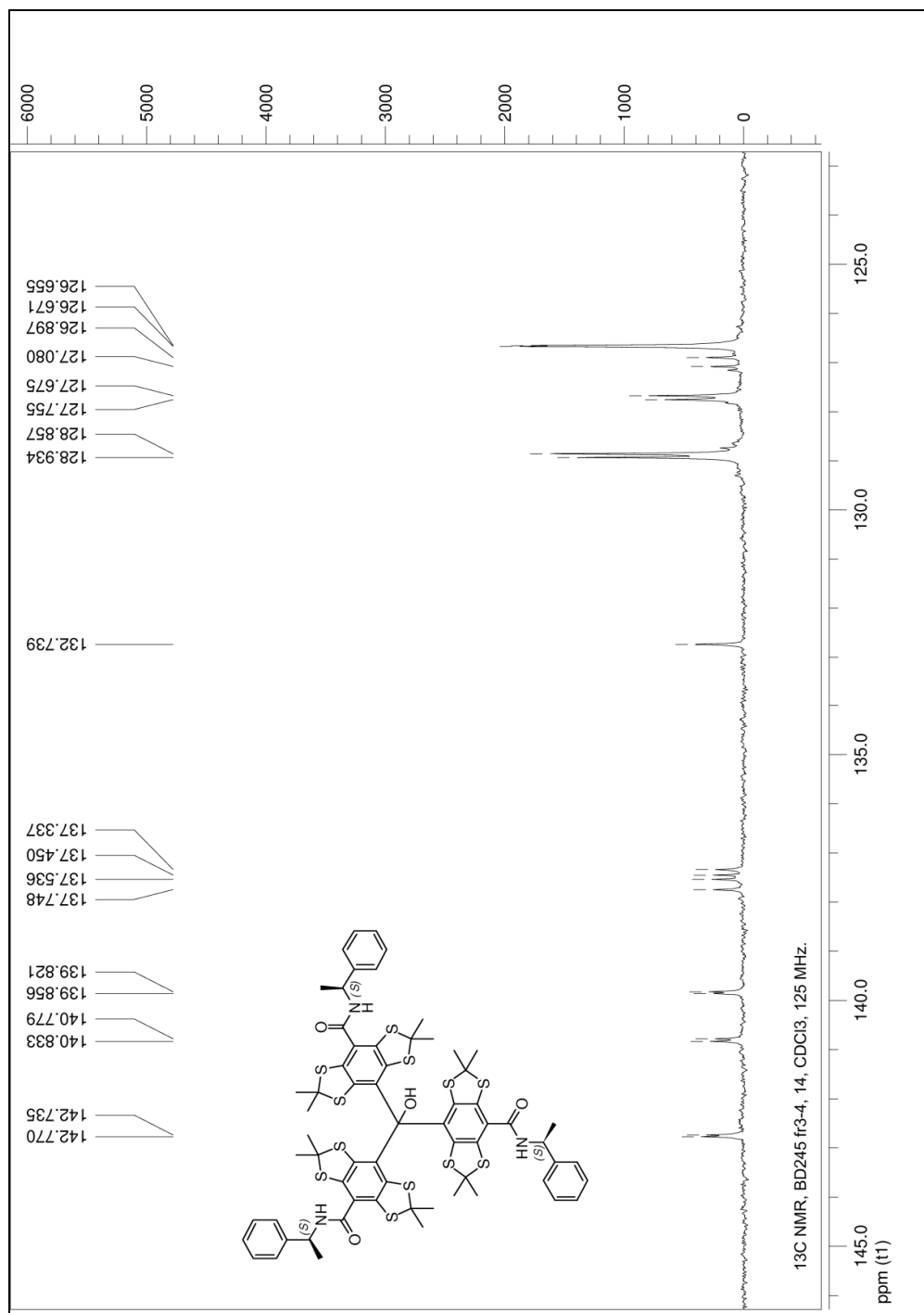
Figure S4 c: ^{13}C NMR spectrum (at 125 MHz) of compound **3a** (enlargement)
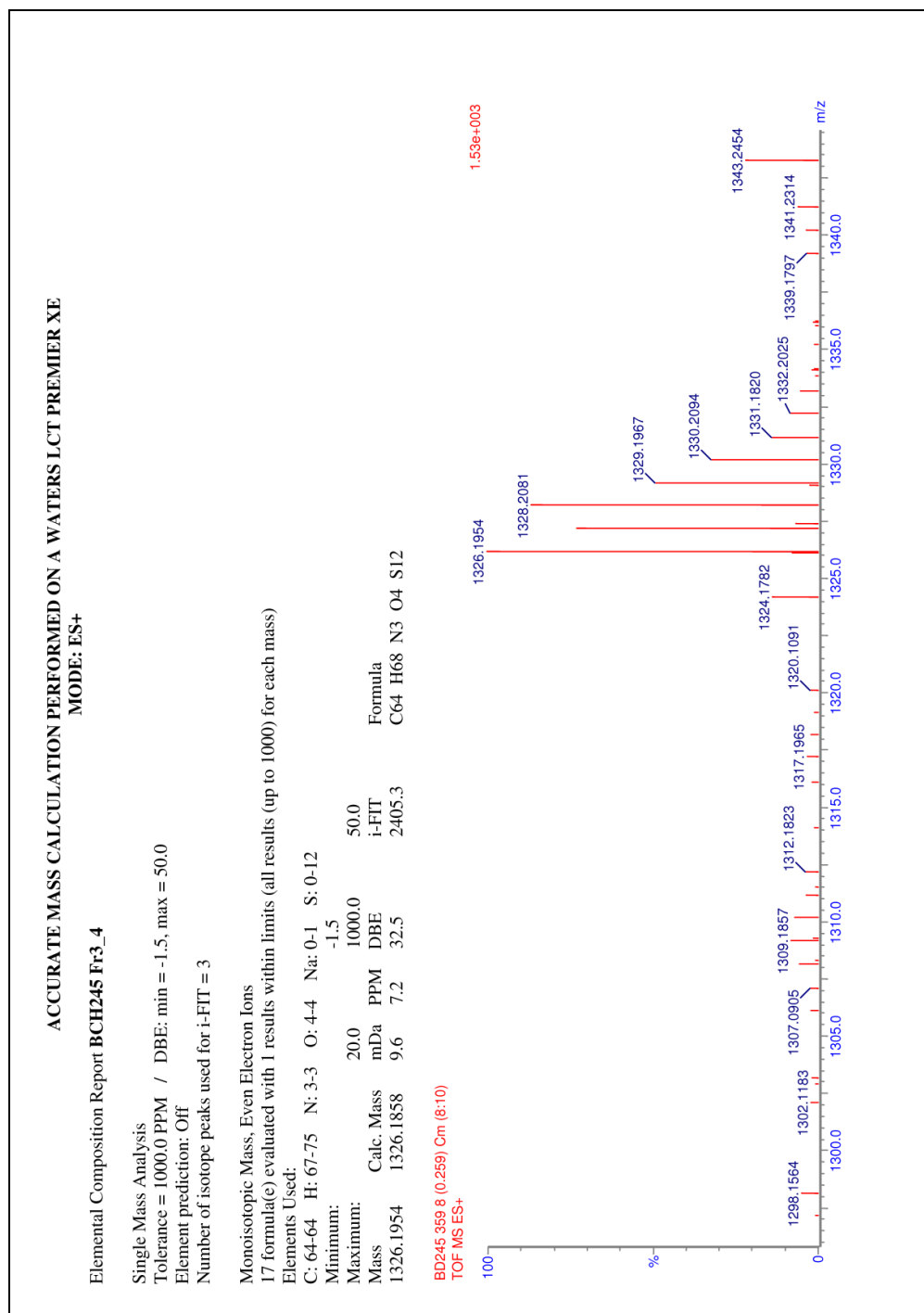
Figure S5: HRMS of compound **3a**

Synthesis of tris(8-benzylaminocarbonyl-2,2,6,6-tetramethylbenzo[1,2-d;4,5-d']bis[1,3]dithiol-4-yl)methanol **3b**
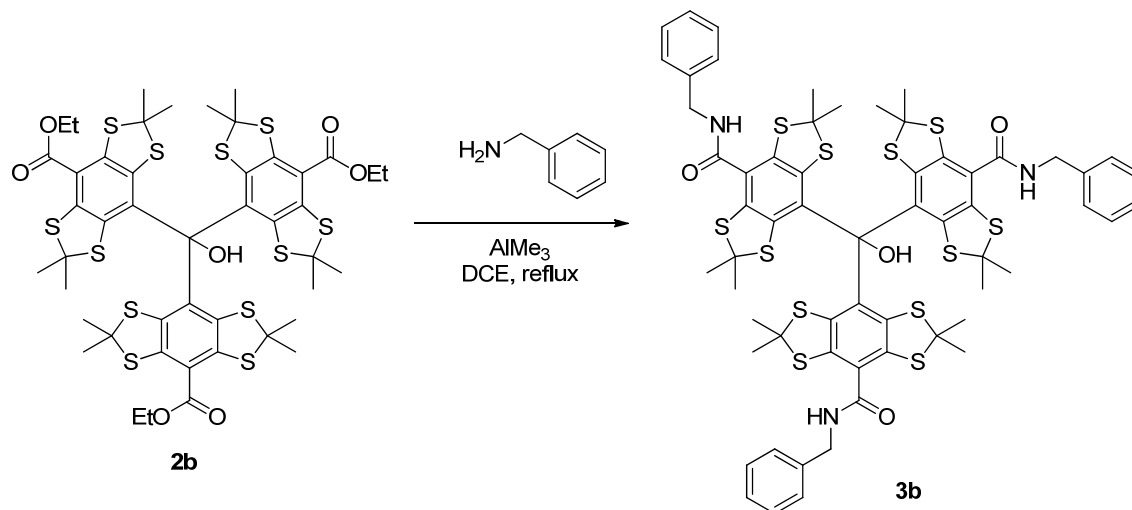
To a solution of benzylamine (49 µL, 0.454 mmol, 10 eq.) in DCE (1 mL) was added AlMe$_3$ 2M in toluene (0.227 mL, 0.454 mmol, 10 eq). The solution was stirred for 10 min and trityl alcohol **2b** (50 mg, 0.045 mmol, 1 eq.) in DCE (1 mL) was then added. The orange solution was stirred for 1 h at room temperature and refluxed for 16h30. After cooling the solution to room temperature, KH$_2$PO$_4$ sat. (2 mL) was added carefully. The mixture was diluted with DCM (3 mL) and the organic layer was separated. The aqueous layer was extracted with DCM (3x3 mL). The combined organic layers were dried over Na$_2$SO$_4$, filtered and the solvent was removed under reduced pressure. The crude mixture was purified by preparative TLC with MeOH 4% in DCM to provide 32 mg (55%) of the title compound **3b** as an orange solid. R$_f$: 0.10 DCM/MeOH (99 :1); 0.34 DCM/MeOH (98:2); 0.51 DCM/MeOH(96:4) UV (254,366 nm). ^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 1.66 (s, 9H), 1.68 (s, 9H), 1.78 (s, 18H), 4.67 (d, J=5.7 Hz, 6H), 6.55 (s, 1H, OH), 6.60 (t, J=5.6 Hz, 3H, NH), 7.30-7.50 (m, 15H). ^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm) : 27.9, 29.1, 32.1, 34.6, 44.4, 62.5, 63.0, 84.1, 126.8, 127.8, 128.2, 128.9, 132.8, 137.3, 137.6, 137.8, 139.9, 140.8, 167.0. HRMS (TOF MS ES+) m/z : [M-OH]$^+$ calcd for C$_{61}$H$_{60}$N$_3$O$_3$S$_{12}$: 1266.1278, found: 1265.7814, [M+H]$^+$: calcd for C$_{61}$H$_{62}$N$_3$O$_4$S$_{12}$: 1284.1389, found: 1283.7803, [M+Na]$^+$: calcd for C$_{61}$H$_{61}$N$_3$NaO$_4$S$_{12}$: 1306.1208, found: 1305.7568. ATR-IR (ν$_{MAX}$/cm^{-1}): 3342, 2959, 2920, 1651, 1526, 1497, 1452, 1229, 910.
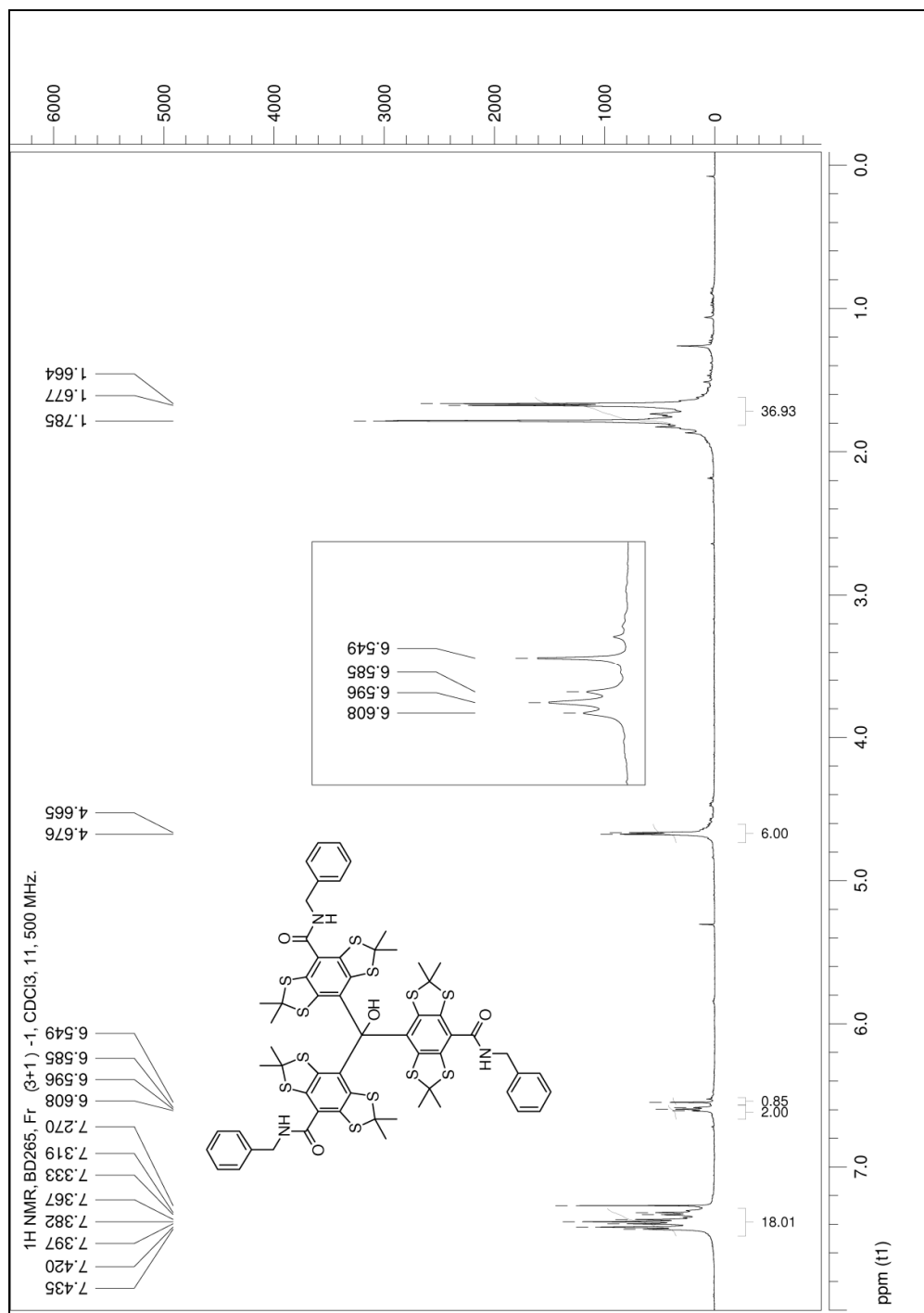
Figure S6: ^{1}H NMR spectrum (at 500 MHz) of compound **3b**
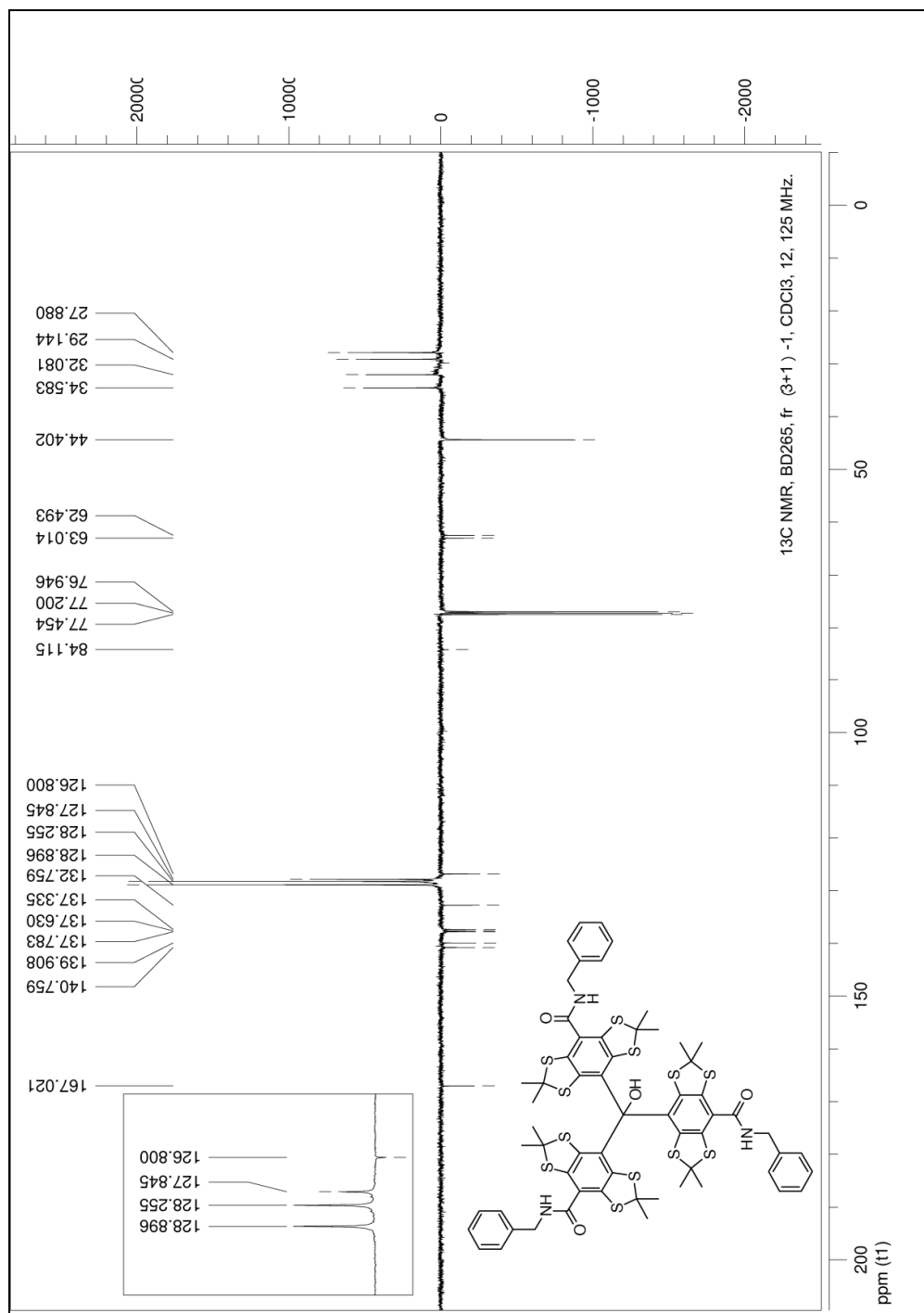
Figure S7: ^{13}C NMR (spectrum at 125 MHz) of compound **3b**

Thursday, September 23, 2010

ACCURATE MASS PERFORMED ON A WATERS LCT PREMIER XE

MODE: ES+

Elemental Composition Report **BD265**

Single Mass Analysis
Tolerance = 300.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
2 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 61-61 H: 5-500 N: 3-3 O: 4-4 Na: 0-1 S: 12-12

Minimum:				-1.5	
Maximum:		20.0	300.0	50.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
1305.7568	1306.1208	-364.0	-278.8	32.5	C61 H61 N3 O4 Na S12

Figure S8: HRMS of compound **3b**

4.   Resolution of trityl alcohol 2b by CSP HPLC

The two enantiomers of **2b** were separated on a semipreparative CHIRALPAK® IB column 10x250 mm 5µm equipped with a precolumn CHIRALPAK® IB 10x20 mm 5µm. The conditions of resolution were as follows: flow rate: 4.7 mL/min; eluent: *i*-hex 93%/EtOAc 4%/MeOH 3% (premixed); UV detection: 274 nm; injection volume: 50 µL; column temperature: ambient; sample: 5.5 mg/mL of EtOAc. Fraction 1 corresponding to the first peak, was collected in a flask cooled at -78°C from the beginning of the upward slope to the half-height of the downward slope as depicted in Figure S9. Fraction 2 corresponding to the second peak, was collected in a flask cooled at -78°C starting from the half-height of the upward slope to the end of the downward slope (Figure S9).
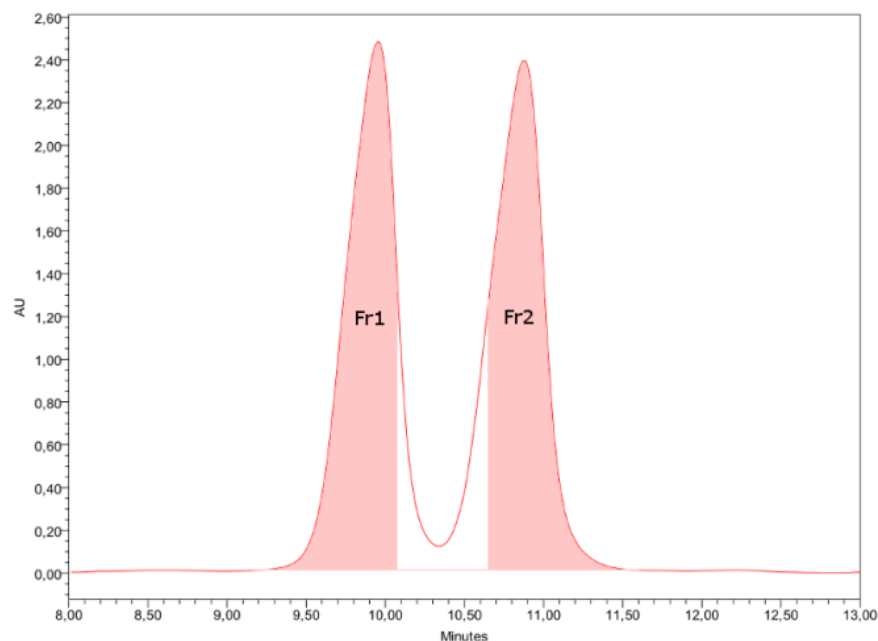
Figure S9

In the optimized final procedure, 50 µL of the racemate were injected every 8 min without stopping the run (Figure S10). About 1.5 mg of each enantiomers was recovered.
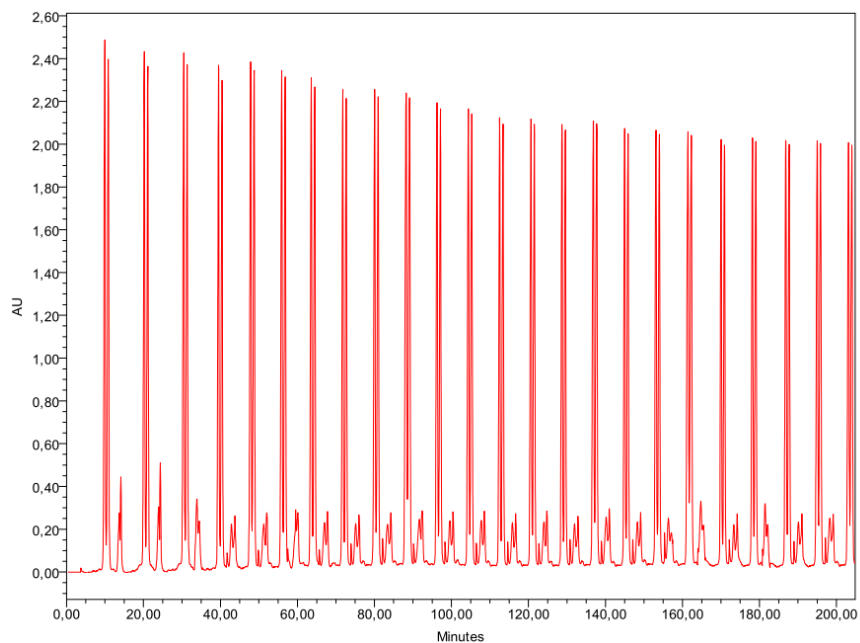
Figure S10

The enantiomeric purity of the two enantiomers **2b** was controlled by analytical CSP HPLC (Figure S11) on a CHIRALPAK® IB column 4.6x250 mm 5µm equipped with a precolumn CHIRALPAK® IB 4.6x20 mm 5µm. The conditions were as follows; flow rate: 1 mL/min; eluent: *i*-hex 93%/EtOAc 4%/MeOH 3% (premixed); UV detection: 274 nm; injection volume: 20 µL; column temperature: 25°C; sample: Fr1 and Fr2 directly from the semipreparative CSP HPLC. The enantiomeric excess was 100% for both fraction 1 and fraction 2.
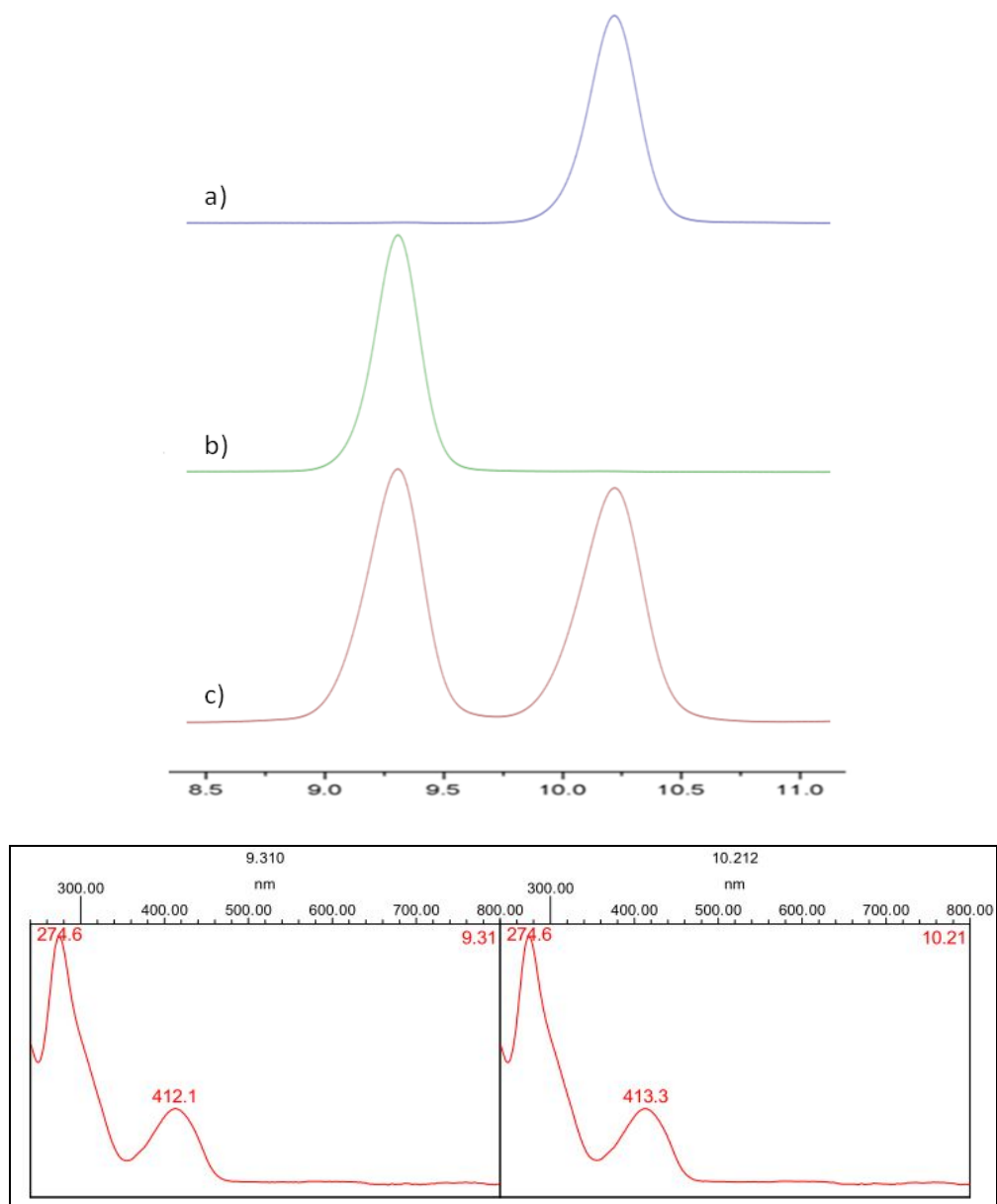
Figure S11. Stacked analytical chromatograms and UV spectra of the two fractions collected from the semipreparative CSP HPLC and racemate. a) Fraction 2; ee=100%, Rt=10.21 min b) Fraction 1; ee=100%, Rt=9.31 min c) racemate.

5.　Conversion of optically pure trityl alcohols 2b into radicals 1b

Approximately 0.25 mg of one pure enantiomer of **2b** (Fr1 or Fr2) was dissolved in 1 mL of trifluoroacetic acid (TFA) at 0°C. After 1h30 at 0°C, TFA was removed under reduced pressure and the resulting trityl radical was dissolved in 1.5 mL of EtOAc and the optical purity was controlled by analytical CSP HPLC on a CHIRALPAK® IB column 4.6x250 mm 5µm equipped with a precolumn CHIRALPAK® IB 4.6x20 mm 5µm. The conditions were as follows: flow rate: 1 mL/min; eluent: *i*-hex 93%/EtOAc 4%/MeOH 3% (premixed); UV detection: 485 nm; injection volume: 10 µL; column temperature: 25°C. The enantiomeric excess of the two enantiomers of trityl radical **1b** were 94% and 91% for Fraction 1 and fraction 2, respectively.
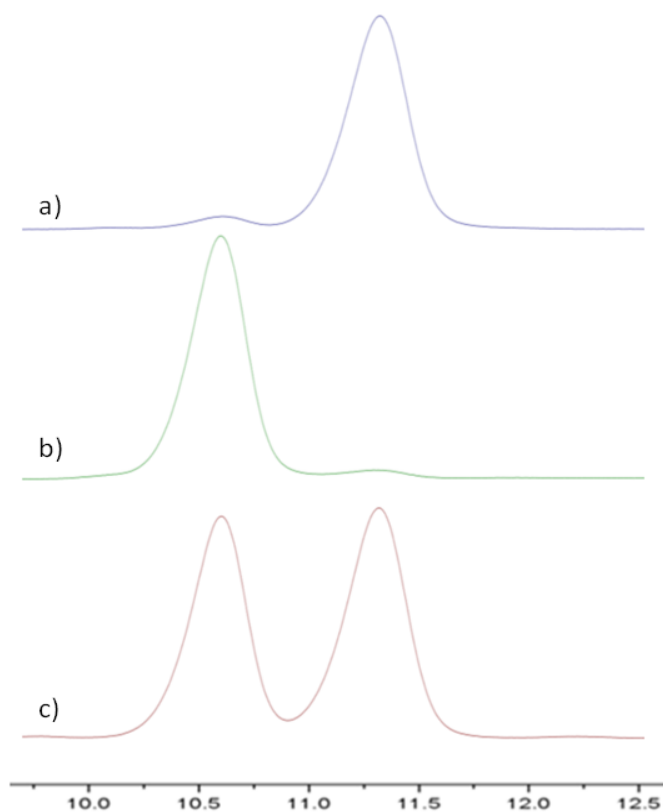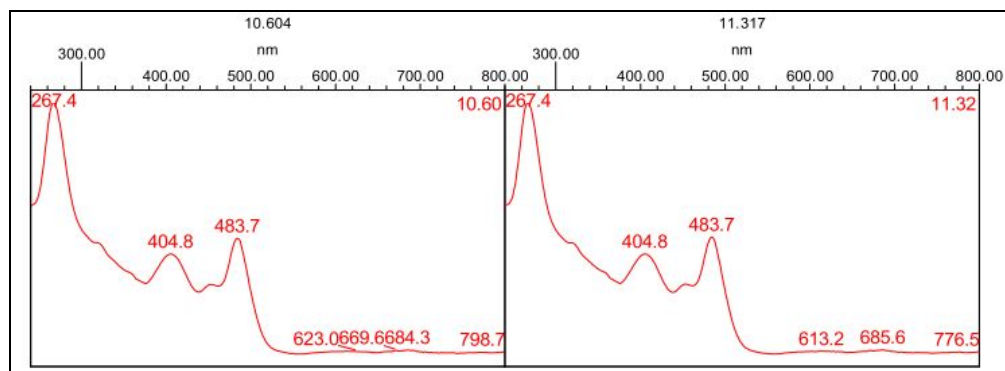
Figure S12: Stacked analytical chromatograms and UV spectra of the highly optically enriched enantiomers of trityl radical **1b** and racemate. a) Fraction 2 of trityl alcohol treated with TFA; ee=91%, Rt=11.32 min, b) Fraction 1 of trityl alcohol treated with TFA; ee=94%, Rt=10.60 min, c) trityl alcohol racemate treated with TFA.

6. Kinetics of racemization for trityl radical 1b

The irreversible racemization processes follow a first-order kinetic[10] and thus, the racemization of enantiomers **1b** (Figure S13) has been treated according the following relation:

$$ee = ee_0 e^{-k_{rac} t}$$

Where, ee is the enantiomeric excess

ee_0 is the initial enantiomeric excess

k_{rac} is the rate constant of the racemization

t is the time

k_{rac} was determined by a nonlinear modeling using SAS JMP® 7.0 software.

The relation between the rate constant of racemization (k_{rac}) and enantiomerization (k_{enant}) is:

$$k_{rac} = 2 k_{enant}$$

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[10] C. Wolf, in *Dynamic Stereochemistry of Chiral Compounds,* RSC Publishing, Cambridge, UK, 2008, ch. 3, pp. 29-36.

The half-lifes of racemization and enantiomerization are given by:

$$t_{1/2_{rac}} = \frac{\ln 2}{k_{rac}} = \frac{\ln 2}{2k_{enant}} \quad \text{and} \quad t_{1/2_{enant}} = \frac{\ln 2}{k_{enant}}$$
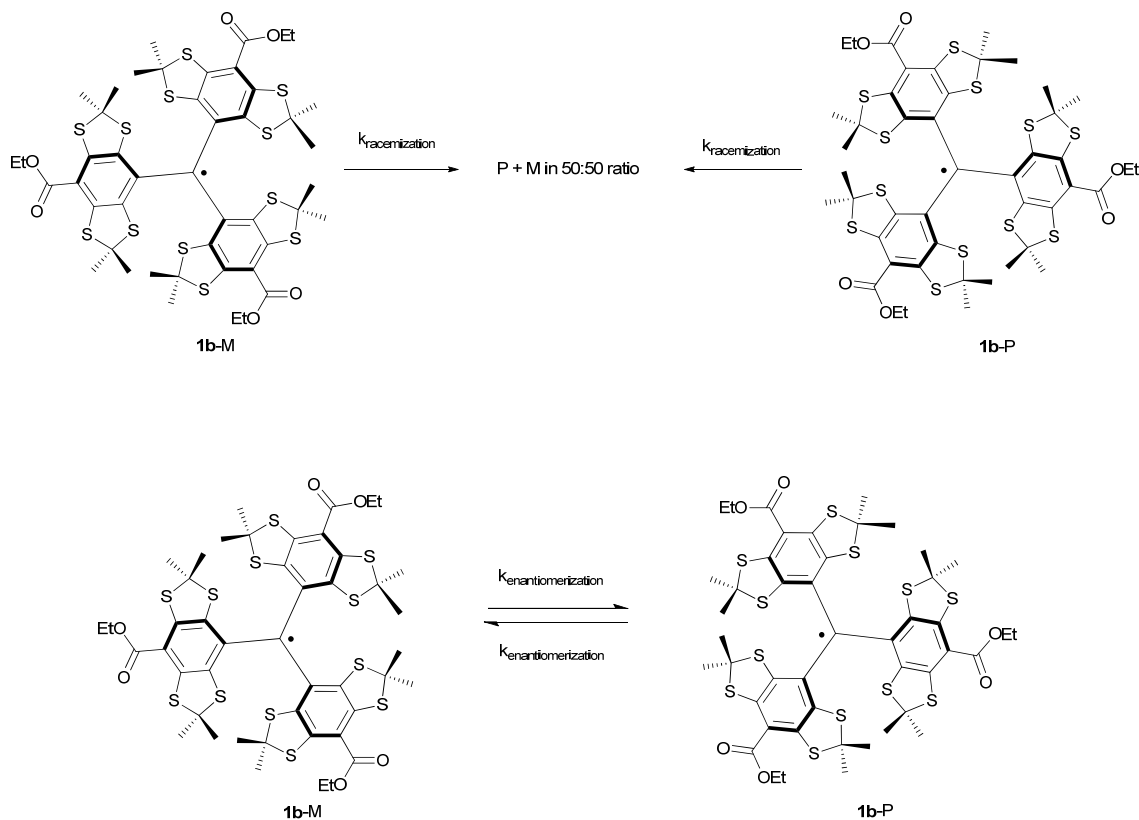
Figure S13

The racemization of trityl radical **1b** in EtOAc at 25°C, 35°C and 40°C was followed by analytical CSP HPLC on a CHIRALPAK® IB column 4.6x250 mm 5µm equipped with a precolumn CHIRALPAK® IB 4.6x20 mm 5µm.

Approximately 0.25 mg of one pure enantiomer of **2b** (Fr1 or Fr2) was dissolved in 1 mL of TFA at 0°C. After 1h30 at 0°C, TFA was removed under reduced pressure and the resulting trityl radical was dissolved in an HPLC vial (VWR™ 1.5 mL, 32 x 11.6 mm) with 1.5 mL of EtOAc at 25°C, 35°C or 40°C. The vial was then put inside the HPLC oven where the sample temperature was controlled to 25°C, 35°C or 40°C. Chromatograms were recorded periodically over the time, the enantiomeric excess was obtained by integration of the two

enantiomers at 485 nm. The first chromatogram was considered to be t=0. When necessary, the vial was topped-up with solvent at 25°C, 35°C or 40°C. The conditions were as follows: flow rate: 1 mL/min; eluent: *i*-hex 93%/EtOAc 4%/MeOH 3% (premixed); UV detection: 485 nm; injection volume: 10 µL; column temperature: 25°C.

Fr1 40°C		Fr2 40°C		Fr2 35°C		Fr2 25°C	
time (min)	ee (%)	time (min)	ee (%)	time (min)	ee (%)	time (min)	ee (%)
0	93.82	0	91.38	0	93.92	0	91.14
169	90.48	169	88.56	104	92.46	108	90.98
338	87.54	338	86.04	238	90.34	428	89.14
537	84.5	537	82.98	566	87.16	868	86.92
796	80.16	796	79.66	760	85.36	1521	84.48
1116	76.68	1115	75.5	918	84.04	2353	81.52
1675	70.04	2433	61.94	1373	79.74	3097	79.14
2440	61.7	3198	54.76	2158	73.72	3846	77.26
3205	53.76	3963	48.38	2782	69.26	4616	75.9
3970	46.9	4728	42.6	3553	64.38	5369	74.02
4736	41.42	5494	37.82	4325	59.24	6123	71.88
5501	36.24	6269	33.62	5096	55.24	6503	71.52
6277	32.12	7035	29.76	5868	51.28	7271	69.56
7042	28.3	7800	26.72	6640	47.96	8025	68.28
7808	24.8	8267	23.8	7412	44.62	8779	66.76
8275	23	9891	19.16	8183	41.46	9532	65.26
9898	18.14	11300	14.52	8859	39.16	9711	65.16
11307	13.32	18389	4.68	9630	36.6	10464	63.38
18396	4.22	/	/	9829	36	11218	62.5
/	/	/	/	12809	26.88	11971	60.4
/	/	/	/	16774	18.82	12646	58.68
/	/	/	/	19953	12.38	13400	57.3
/	/	/	/	22887	8.76	14152	55.94
/	/	/	/	26835	5.76	14906	54.24
/	/	/	/	/	/	15660	53.12
/	/	/	/	/	/	16413	51.26
/	/	/	/	/	/	16594	50.78

Table S1

Fr1 40°C
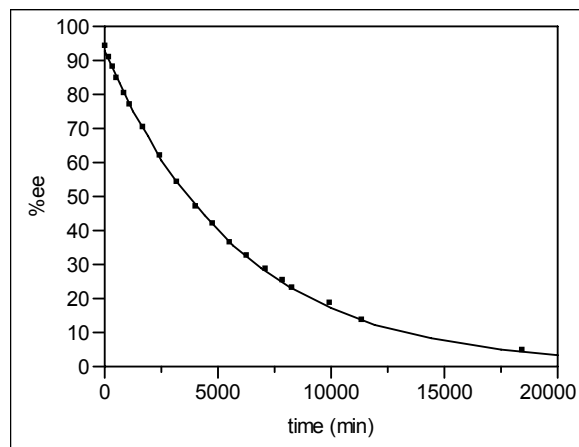
Figure S14

Parameter	Estimate	ApproxStdErr	Lower CL	Upper CL
ee0	92.849821397	0.20392574	92.4195222	93.280662
krac	0.0001696465	8.7453e-7	0.0001678	0.0001715

Fr2 40°C
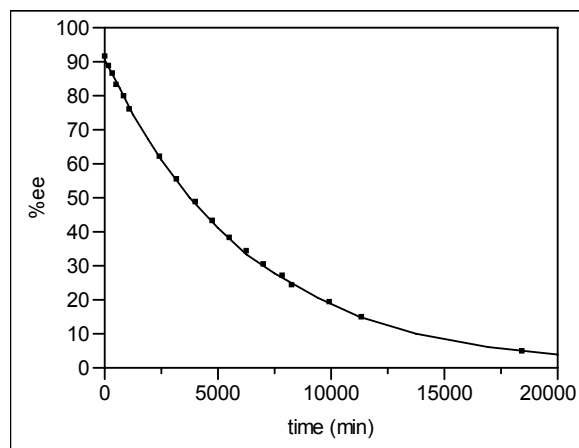
Figure S15

Parameter	Estimate	ApproxStdErr	Lower CL	Upper CL
ee0	90.806728653	0.16624645	90.4545031	91.1592601
krac	0.0001592682	6.78006e-7	0.00015784	0.00016071

Fr2 35°C
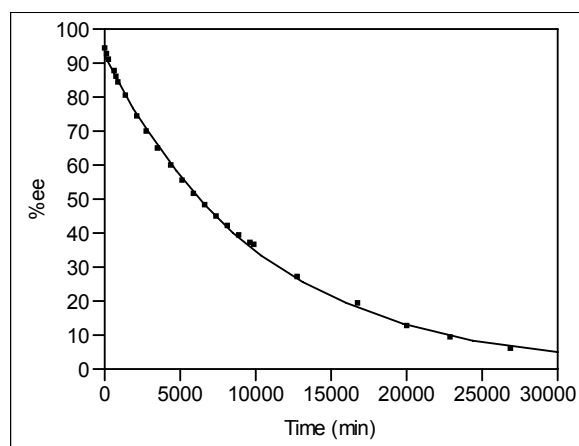
Figure S16

Parameter	Estimate	ApproxStdErr	Lower CL	Upper CL
ee0	92.271367902	0.31723797	91.6137091	92.930463
krac	0.0000985793	8.6452e-7	9.67939e-5	0.00010039

Fr2 25°C
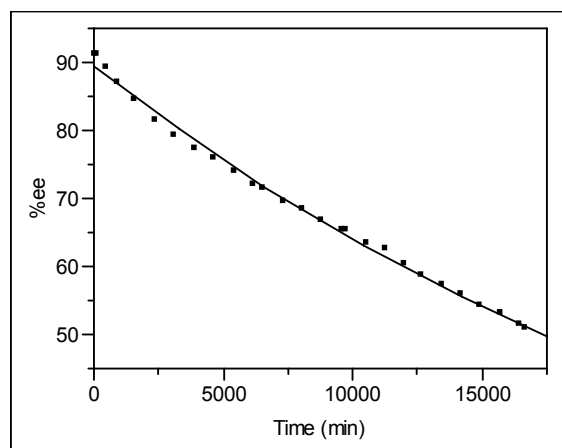
Figure S17

Parameter	Estimate	ApproxStdErr	Lower CL	Upper CL
ee0	89.503665787	0.32548101	88.8331384	90.1754959
krac	0.0000336519	4.5625e-7	3.27113e-5	3.45946e-5

6.1 Summary of k_{rac} found at 25°C, 35°C and 40°C

	T (°C)	T (K)	k (min⁻¹)	k_{min} (min⁻¹)	k_{max} (min⁻¹)	k (sec⁻¹)	k_{min} (sec⁻¹)	k_{max} (sec⁻¹)
Fr1	40	313.15	0.00016965	0.0001678	0.0001715	2.8274E-06	2.7967E-06	2.8583E-06
Fr2	40	313.15	0.00015927	0.00015784	0.00016071	2.6545E-06	2.6307E-06	2.6785E-06
Fr2	35	308.15	9.8579E-05	9.6794E-05	0.00010039	1.643E-06	1.6132E-06	1.6732E-06
Fr2	25	298.15	3.3652E-05	3.2711E-05	3.4595E-05	5.6087E-07	5.4519E-07	5.7658E-07

Table S2

6.2 Determination of $t_{1/2}$ enantiomerization and $t_{1/2}$ racemization

				Racemization				
	T(°C)	T(K)	k (min⁻¹)	k_{min} (min⁻¹)	k_{max} (min⁻¹)	$t_{1/2}$ (min)	$t_{1/2max}$ (min)	$t_{1/2min}$ (min)
Fr1	40	313.15	0.00016965	0.0001678	0.0001715	4086	4131	4042
Fr2	40	313.15	0.00015927	0.00015784	0.00016071	4352	4391	4313
Fr2	35	308.15	9.8579E-05	9.6794E-05	0.00010039	7031	7161	6905
Fr2	25	298.15	3.3652E-05	3.2711E-05	3.4595E-05	20598	21190	20036

				Enantiomerization				
	T(°C)	T(K)	k (min⁻¹)	k_{min} (min⁻¹)	k_{max} (min⁻¹)	$t_{1/2}$ (min)	$t_{1/2max}$ (min)	$t_{1/2min}$ (min)
Fr1	40	313.15	8.4823E-05	0.0000839	0.00008575	8172	8262	8083
Fr2	40	313.15	7.9634E-05	0.00007892	8.0355E-05	8704	8783	8626
Fr2	35	308.15	4.929E-05	4.8397E-05	5.0195E-05	14063	14322	13809
Fr2	25	298.15	1.6826E-05	1.6356E-05	1.7297E-05	41195	42380	40073

Table S3

6.3 Determination of $\Delta G^{\ddagger}$ according to the Eyring equation

$$k = \frac{k_B T}{h} e^{\frac{-\Delta G^{\ddagger}}{RT}}$$

Where, k is the rate constant

k_B is the Boltzman's constant

T is the temperature

h is the Planck's constant

R is the ideal gas constant

	T (°C)	T (K)	$\Delta G^{\ddagger}$ (kJ mol⁻¹)*	$\Delta G^{\ddagger}_{max}$ (kJ mol⁻¹)*	$\Delta G^{\ddagger}_{min}$ (kJ mol⁻¹)*	$\Delta G^{\ddagger}$ (kcal mol⁻¹)	$\Delta G^{\ddagger}_{max}$ (kcal mol⁻¹)	$\Delta G^{\ddagger}_{min}$ (kcal mol⁻¹)
Fr1	40	313.15	110.0844	110.112885	110.05611	26.31	26.32	26.30
Fr2	40	313.15	110.24875	110.272194	110.22528	26.35	26.36	26.34
Fr2	35	308.15	109.67623	109.72306	109.6296	26.21	26.22	26.20
Fr2	25	298.15	108.69947	108.76975	108.63099	25.98	26.00	25.96

*Calculated by http://www-jmg.ch.cam.ac.uk/tools/magnus/eyring.html

Table S4

7   Complete enantiomerization pathways for radical 1d

The four potential pathways for enantiomerization of **1d** (the Kurland's flip mechanisms) are depicted in figure S18.
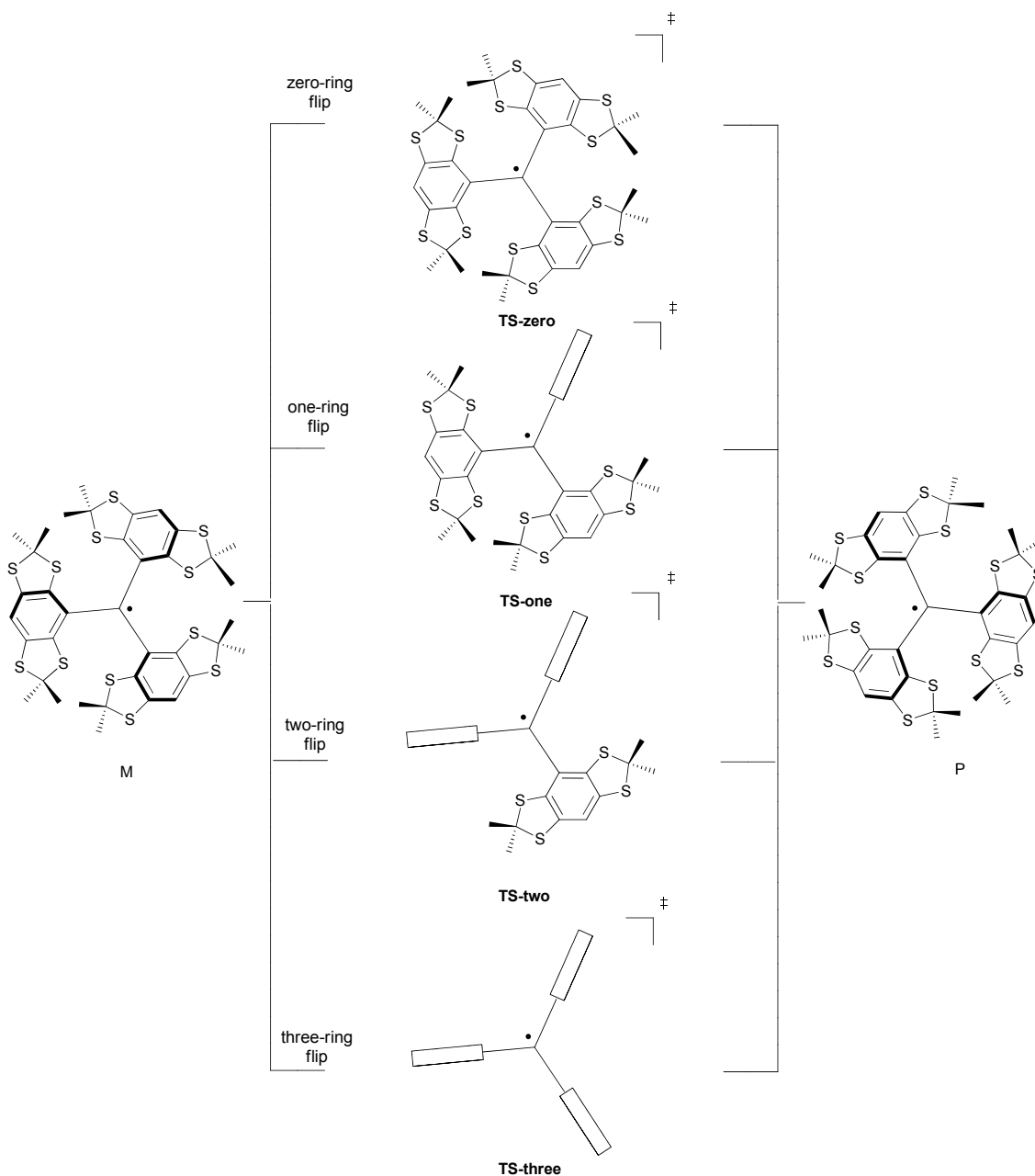
Figure S18: The four potential pathways for enantiomerization on trityl radical **1d**.

8   Computed optimized geometries and energies

8.1   Single point calculations

Energy barriers ($\Delta E^{\ddagger}$) for isomerization of radical **1d** computed at different levels of theory (energies in kcal mol^{-1})

Mechanism	TS-two	TS-three
UB3LYP/6-31G*	28.9	72.0
UB3LYP/6-311+G**	27.2	72.3
UB3LYP-D/6-31G*	25.7	74.2
UB3LYP-D/6-31G**	25.6	74.4
UB3LYP-D/6-311+G**	25.6	74.8
RO-B3LYP-D/6-31G**	26.0	74.5
UBP86/6-31G**	25.5	76.6
LMP2/6-31G*	23.1	59.7

Table S5

Obtained UB3LYP and UB3LYP-D energies indicate that dispersion effects have a rather limited influence on the energy barrier to isomerization.

Obtained energies varying the basis set reveal no significant basis set effects.

The low variation in energy barriers observed with the various methods supports the appropriateness of the chosen methodology to describe the studied system.

Obtained RO-B3LYP-D energies and $<S^2>$ values (always within 3% of the expected s(s+1) values) indicate that spin contamination is negligible in our calculations.

8.2 Radical 1d
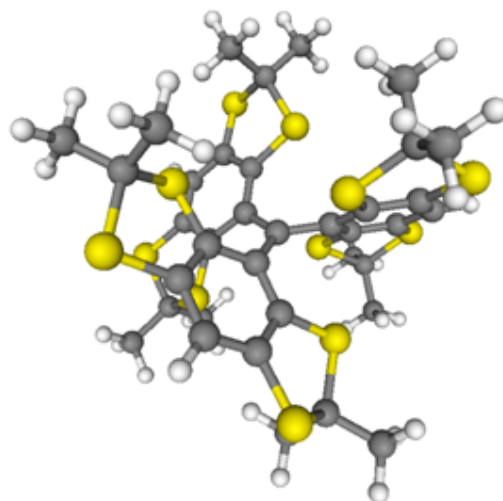
Figure S19: Optimized structure of **1d** (UB3LYP/6-31G*)

E(UB3LYP-D/6-31G*) = -6210.110014
E(UB3LYP-D/6-31G*(AcOEt)) = -6210.128250
E(UB3LYP-D/6-31G**) = -6210.163852
E(UB3LYP-D/6-311+G**) = -6210.163824
E(RO-B3LYP-D/6-31G**) = -6210.161620
E(UB3LYP/6-31G*) = -6211.704131
E(UB3LYP/6-311+G*) = -6212.3669944
E(UBP86/6-31G**)=-6211.864957
E(LMP2/6-31G*)= -6200.030085

```
C    -2.707000  -2.541000  -0.856000
C    -3.744000  -2.158000  -0.007000
C    -3.561000  -1.069000   0.843000
C    -2.353000  -0.354000   0.849000
C    -1.275000  -0.730000  -0.004000
C    -1.485000  -1.851000  -0.859000
C    -0.002000   0.005000  -0.001000
S    -2.847000  -3.938000  -1.944000
S    -0.275000  -2.470000  -2.007000
S    -4.842000  -0.497000   1.932000
S    -2.289000   1.001000   2.001000
C    -3.684000   0.399000   3.074000
C    -1.487000  -3.387000  -3.081000
C     1.270000  -0.732000   0.006000
C     1.476000  -1.854000   0.860000
C     2.697000  -2.545000   0.862000
C     3.738000  -2.162000   0.019000
C     3.559000  -1.073000  -0.831000
C     2.352000  -0.357000  -0.842000
```

C	-0.001000	1.474000	-0.004000
C	-0.869000	2.217000	-0.855000
C	-0.854000	3.621000	-0.853000
C	0.000000	4.326000	-0.008000
C	0.853000	3.622000	0.840000
C	0.867000	2.219000	0.846000
S	4.848000	-0.499000	-1.912000
S	2.295000	0.999000	-1.994000
C	3.698000	0.401000	-3.058000
S	2.831000	-3.944000	1.949000
S	0.261000	-2.474000	2.004000
C	1.466000	-3.394000	3.081000
S	2.013000	1.486000	1.994000
S	1.994000	4.446000	1.925000
S	-2.017000	1.482000	-2.001000
S	-1.995000	4.442000	-1.940000
C	-2.199000	2.989000	-3.077000
H	4.678000	-2.707000	0.024000
H	0.000000	5.412000	-0.009000
C	2.196000	2.995000	3.065000
H	-4.684000	-2.702000	-0.008000
C	3.607000	3.012000	3.661000
H	3.746000	3.909000	4.275000
H	3.752000	2.141000	4.311000
H	4.370000	2.997000	2.879000
C	-1.124000	3.004000	-4.169000
H	-1.235000	2.126000	-4.816000
H	-1.221000	3.908000	-4.781000
H	-0.122000	2.984000	-3.733000
C	-3.611000	3.006000	-3.671000
H	-3.757000	2.135000	-4.320000
H	-4.373000	2.994000	-2.889000
H	-3.749000	3.903000	-4.287000
C	-4.403000	1.609000	3.677000
H	-5.248000	1.277000	4.292000
H	-3.721000	2.167000	4.329000
H	-4.774000	2.281000	2.900000
C	-0.792000	-4.617000	-3.672000
H	-1.497000	-5.188000	-4.287000
H	0.036000	-4.307000	-4.321000
H	-0.399000	-5.269000	-2.888000
C	-2.039000	-2.468000	-4.176000
H	-1.223000	-2.123000	-4.823000
H	-2.770000	-3.009000	-4.789000
H	-2.528000	-1.591000	-3.743000
C	4.421000	1.613000	-3.652000
H	5.271000	1.284000	-4.261000
H	3.743000	2.173000	-4.306000
H	4.787000	2.282000	-2.869000
C	3.181000	-0.541000	-4.151000
H	2.663000	-1.400000	-3.717000
H	2.479000	-0.010000	-4.804000
H	4.017000	-0.909000	-4.759000
C	0.768000	-4.625000	3.666000
H	1.470000	-5.199000	4.282000
H	-0.062000	-4.317000	4.312000
H	0.377000	-5.274000	2.878000

```
C   -3.160000  -0.547000   4.160000
H   -2.453000  -0.017000   4.810000
H   -3.991000  -0.917000   4.772000
H   -2.644000  -1.404000   3.719000
C    2.014000  -2.479000   4.181000
H    1.196000  -2.134000   4.825000
H    2.741000  -3.022000   4.797000
H    2.507000  -1.602000   3.754000
C    1.121000   3.014000   4.157000
H    1.219000   3.919000   4.768000
H    0.118000   2.994000   3.722000
H    1.231000   2.137000   4.807000
```

8.3   TS-two for enantiomerization of radical 1d
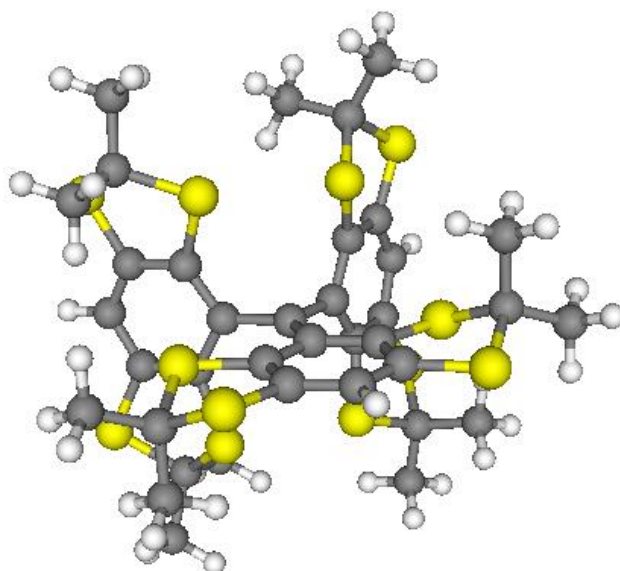
Figure S20: Optimized two-ring flip TS for radical **1d** (UB3LYP/6-31G*)

E(UB3LYP-D/6-31G*) = -6210.069052
E(UB3LYP-D/6-31G*(AcOEt)) = -6210.085014
E(UB3LYP-D/6-31G**) = -6210.122962
E(UB3LYP-D/6-311+G**) = -6210.122962
E(RO-B3LYP-D/6-31G**) = 26.032059
E(UB3LYP/6-31G*) = -6211.658027
E(UB3LYP/6-311+G*) = -6212.323687
E(UBP86/6-31G**)= -6211.824249
E(LMP2/6-31G*)= -6199.993303

```
C   -3.027944  -2.346631  -0.335212
C   -4.098806  -1.500581  -0.601845
C   -3.866751  -0.132112  -0.685341
C   -2.583318   0.409379  -0.520088
```

```
C   -1.439658  -0.434732  -0.230298
C   -1.729493  -1.853263  -0.139632
C   -0.115496   0.095952  -0.046069
S   -3.270551  -4.106285  -0.294831
S   -0.533874  -3.140029   0.175354
S   -5.221722   0.987189  -0.945866
S   -2.552166   2.188028  -0.659747
C   -4.157252   2.360617  -1.575137
C   -1.750374  -4.438682   0.702131
C    1.109355  -0.762899   0.246561
C    1.493589  -1.040180   1.585520
C    2.731350  -1.626830   1.899863
C    3.615690  -1.996142   0.893965
C    3.210899  -1.857892  -0.428410
C    1.970295  -1.272878  -0.764565
C    0.222421   1.580250  -0.124576
C    0.615037   2.167631  -1.356703
C    1.152538   3.464187  -1.426971
C    1.283198   4.239707  -0.281659
C    0.786418   3.741019   0.916734
C    0.240542   2.441749   1.007188
S    4.225328  -2.439574  -1.767255
S    1.588417  -1.376120  -2.510365
C    2.781408  -2.756507  -2.881913
S    3.040398  -2.025336   3.601260
S    0.373181  -0.956795   2.960918
C    1.684957  -0.944179   4.274472
S   -0.501624   2.094364   2.598558
S    0.786457   4.728251   2.394959
S    0.212023   1.475018  -2.941558
S    1.493565   4.123401  -3.038781
C    1.439803   2.479106  -3.906253
H    4.571684  -2.451784   1.132783
H    1.695986   5.242517  -0.332382
C   -0.693039   3.874574   3.109037
H   -5.097740  -1.901017  -0.741413
C   -0.632357   3.949118   4.637804
H   -0.711601   4.991823   4.966850
H   -1.473595   3.400223   5.076648
H    0.301194   3.530823   5.023042
C    2.831830   1.841615  -3.912327
H    2.800185   0.864247  -4.404945
H    3.532058   2.490243  -4.452333
H    3.207081   1.694500  -2.896741
C    0.905208   2.675790  -5.327901
H    0.840215   1.709948  -5.841885
H   -0.083572   3.141186  -5.323702
H    1.590320   3.310121  -5.902109
C   -3.935097   2.231789  -3.085640
H   -4.891886   2.318431  -3.614528
H   -3.262736   3.023364  -3.436106
H   -3.485493   1.267694  -3.337152
C   -2.044459  -4.328091   2.201749
H   -2.775510  -5.089931   2.498122
H   -1.123764  -4.476716   2.777694
H   -2.447460  -3.343583   2.453160
C   -1.182081  -5.813879   0.338894
```

```
H   -0.254128  -5.996107   0.893145
H   -1.892991  -6.600181   0.617901
H   -0.974575  -5.890927  -0.731388
C    3.229871  -2.629114  -4.341005
H    3.958436  -3.412530  -4.580234
H    2.373238  -2.759516  -5.012357
H    3.686346  -1.655349  -4.536748
C    2.164064  -4.130182  -2.606507
H    1.846408  -4.220274  -1.565275
H    1.284957  -4.279699  -3.244336
H    2.893969  -4.920178  -2.820524
C    1.114469  -1.581184   5.545002
H    1.888190  -1.631355   6.319786
H    0.294207  -0.968703   5.936528
H    0.742051  -2.590911   5.355108
C   -4.782885   3.710438  -1.210615
H   -4.132497   4.528488  -1.541230
H   -5.746067   3.828285  -1.720440
H   -4.942117   3.799676  -0.133051
C    2.221113   0.464359   4.544062
H    1.421514   1.109576   4.922507
H    3.023739   0.416945   5.289826
H    2.618695   0.920173   3.634092
C   -1.991632   4.482646   2.572472
H   -2.068726   5.533370   2.876926
H   -2.032617   4.430551   1.482141
H   -2.853737   3.935407   2.971654
```

8.4   TS-three for enantiomerization of radical 1d
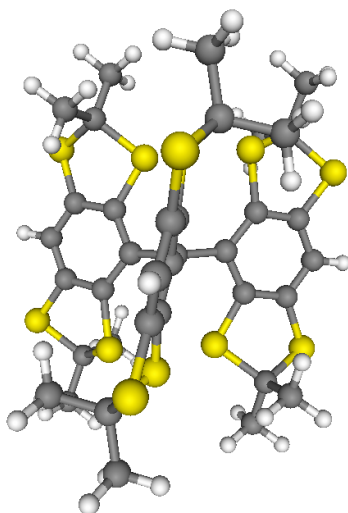
Figure S21: Optimized three-ring flip TS for radical **1d** (UB3LYP/6-31G*)

E(UB3LYP-D/6-31G*) = -6209.991736

E(UB3LYP-D/6-31G*(AcOEt)) = -6210.006901

E(UB3LYP-D/6-31G**) = -6210.045749

E(UB3LYP-D/6-311+G**) = -6210.044629

E(RO-B3LYP-D/6-31G**) = -6210.042829

E(UB3LYP/6-31G*) = -6211.589339

E(UB3LYP/6-311+G*) = -6212.251843

E(UBP86/6-31G**)= -6211.742808

E(LMP2/6-31G*)= -6199.934930

```
C    -2.833000  -2.229000  -1.701000
C    -3.748000  -2.358000  -0.673000
C    -3.464000  -1.738000   0.531000
C    -2.291000  -0.969000   0.716000
C    -1.308000  -0.823000  -0.315000
C    -1.628000  -1.513000  -1.525000
C     0.020000  -0.041000  -0.162000
S    -3.121000  -3.027000  -3.259000
S    -0.558000  -1.683000  -2.937000
S    -4.618000  -1.871000   1.872000
S    -2.318000  -0.146000   2.301000
C    -3.371000  -1.399000   3.153000
C    -1.911000  -1.962000  -4.169000
C     1.188000  -0.713000   0.651000
C     1.367000  -0.841000   2.083000
C     2.447000  -1.601000   2.611000
C     3.334000  -2.308000   1.818000
```

```
C     3.207000   -2.194000    0.451000
C     2.194000   -1.388000   -0.109000
C     0.106000    1.389000   -0.820000
C     0.416000    1.801000   -2.177000
C     0.366000    3.177000   -2.539000
C    -0.022000    4.178000   -1.665000
C    -0.345000    3.820000   -0.375000
C    -0.256000    2.474000    0.035000
S     4.364000   -2.982000   -0.640000
S     2.378000   -1.252000   -1.864000
C     3.244000   -2.867000   -2.114000
S     2.694000   -1.673000    4.371000
S     0.441000   -0.128000    3.465000
C     1.847000   -0.064000    4.653000
S    -0.625000    2.290000    1.757000
S    -0.842000    5.033000    0.820000
S     0.875000    0.839000   -3.645000
S     0.759000    3.672000   -4.200000
C     1.784000    2.183000   -4.526000
H     4.125000   -2.903000    2.265000
H    -0.067000    5.212000   -1.992000
C    -1.702000    3.793000    1.893000
H    -4.662000   -2.928000   -0.805000
C    -1.695000    4.270000    3.346000
H    -2.281000    5.191000    3.441000
H    -2.160000    3.516000    3.991000
H    -0.679000    4.460000    3.701000
C     3.213000    2.360000   -4.003000
H     3.786000    1.438000   -4.157000
H     3.713000    3.178000   -4.535000
H     3.218000    2.588000   -2.934000
C     1.772000    1.853000   -6.022000
H     2.327000    0.927000   -6.209000
H     0.752000    1.735000   -6.399000
H     2.264000    2.653000   -6.587000
C    -4.074000   -0.715000    4.329000
H    -4.761000   -1.416000    4.817000
H    -3.337000   -0.401000    5.077000
H    -4.642000    0.160000    4.002000
C    -1.335000   -2.736000   -5.357000
H    -2.130000   -2.969000   -6.075000
H    -0.589000   -2.125000   -5.878000
H    -0.867000   -3.671000   -5.038000
C    -2.569000   -0.651000   -4.612000
H    -1.831000   -0.003000   -5.097000
H    -3.379000   -0.862000   -5.320000
H    -2.989000   -0.111000   -3.760000
C     4.075000   -2.779000   -3.395000
H     4.652000   -3.700000   -3.534000
H     3.414000   -2.668000   -4.262000
H     4.766000   -1.932000   -3.367000
C     2.275000   -4.052000   -2.146000
H     1.689000   -4.110000   -1.225000
H     1.579000   -3.954000   -2.986000
H     2.838000   -4.986000   -2.256000
C     1.265000   -0.018000    6.069000
H     2.073000   -0.041000    6.809000
```

```
H     0.708000   0.915000   6.217000
H     0.594000  -0.861000   6.255000
C    -2.569000  -2.622000   3.609000
H    -1.789000  -2.320000   4.316000
H    -3.233000  -3.346000   4.097000
H    -2.086000  -3.116000   2.762000
C     2.785000   1.119000   4.395000
H     2.239000   2.062000   4.509000
H     3.618000   1.106000   5.108000
H     3.198000   1.085000   3.383000
C    -3.123000   3.527000   1.389000
H    -3.724000   4.440000   1.467000
H    -3.120000   3.204000   0.345000
H    -3.595000   2.739000   1.987000
```

8.5   Radical 1c
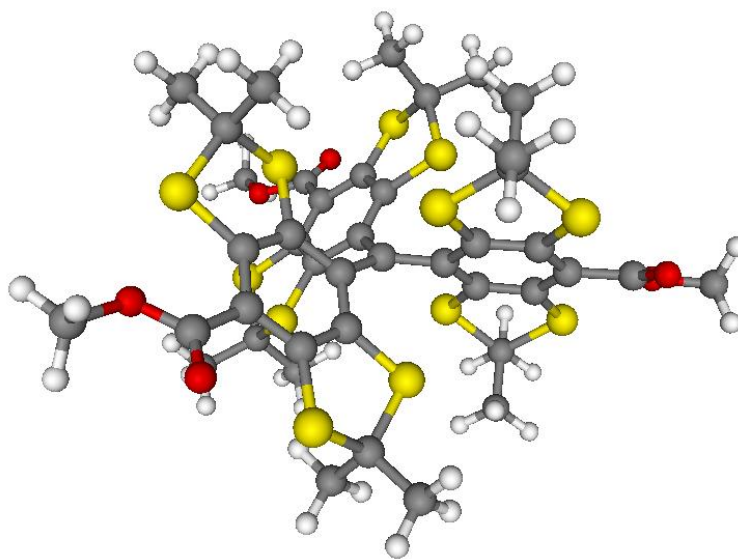
Figure S22: Optimized structure of radical **1c** (UB3LYP/6-31G*)

E(UB3LYP-D/6-31G**) = -6893.470095
E(UB3LYP-D/6-311+G**) = -6893.470095
E(UB3LYP/6-31G*) = -6895.321938

```
C   -2.653269  -2.570665  -0.870652
C   -3.712506  -2.217920  -0.005392
C   -3.557728  -1.108993   0.854462
C   -2.363028  -0.370105   0.859496
C   -1.274877  -0.726786   0.016111
C   -1.453479  -1.843063  -0.850826
C   -0.008767   0.020601   0.033764
```

```
S   -2.729308  -3.912275  -2.042197
S   -0.201474  -2.385140  -1.993766
S   -4.833581  -0.561226   1.965456
S   -2.307326   0.998365   1.990643
C   -3.699723   0.415336   3.061396
C   -1.362468  -3.281104  -3.120621
C    1.266187  -0.711624   0.037006
C    1.463669  -1.841580   0.881450
C    2.670741  -2.557353   0.876922
C    3.719346  -2.177180   0.009617
C    3.546410  -1.053553  -0.827119
C    2.343852  -0.328070  -0.808461
C   -0.013443   1.490508   0.030745
C   -0.872720   2.223563  -0.833143
C   -0.851577   3.627620  -0.858362
C    0.016076   4.347136  -0.008559
C    0.856629   3.637484   0.878014
C    0.848030   2.233902   0.887867
S    4.805307  -0.472558  -1.941442
S    2.262581   1.056418  -1.918728
C    3.644462   0.497306  -3.014836
S    2.770219  -3.921070   2.020797
S    0.226648  -2.418539   2.023158
C    1.405326  -3.325680   3.122343
S    1.952263   1.462384   2.050929
S    1.962414   4.416951   2.038753
S   -2.011017   1.449380  -1.956205
S   -1.967565   4.417139  -1.995948
C   -2.212629   2.919185  -3.062183
C    2.120119   2.942191   3.148987
C    3.517915   2.942509   3.777501
H    3.648719   3.832587   4.404109
H    3.643108   2.064843   4.422291
H    4.299165   2.931877   3.013568
C   -1.177499   2.887321  -4.193066
H   -1.321488   1.994764  -4.813903
H   -1.284555   3.776125  -4.826753
H   -0.159960   2.866634  -3.793750
C   -3.642864   2.935159  -3.613902
H   -3.820516   2.050713  -4.236933
H   -4.381048   2.951859  -2.808323
H   -3.791578   3.818700  -4.245719
C   -4.460505   1.633843   3.597371
H   -5.310610   1.306995   4.207713
H   -3.807968   2.238765   4.237876
H   -4.833530   2.260500   2.783623
C   -0.631240  -4.475660  -3.743204
H   -1.314157  -5.041209  -4.387991
H    0.199026  -4.127154  -4.368430
H   -0.236185  -5.145714  -2.975637
C   -1.913113  -2.338076  -4.197096
H   -1.094360  -1.955026  -4.818022
H   -2.621333  -2.873399  -4.841231
H   -2.429123  -1.485852  -3.746863
C    4.381210   1.728837  -3.553640
H    5.225154   1.417286  -4.180197
H    3.710632   2.330170  -4.178705
```

```
H    4.759569   2.353967 -2.741173
C    3.107139  -0.375917 -4.155229
H    2.576327  -1.248528 -3.764940
H    2.411730   0.199386 -4.778312
H    3.934902  -0.725241 -4.784307
C    0.689748  -4.539311  3.725974
H    1.382369  -5.111004  4.354778
H   -0.139311  -4.211116  4.363661
H    0.295462  -5.197649  2.947966
C   -3.169992  -0.459844  4.203825
H   -2.491646   0.119097  4.842172
H   -4.003432  -0.823783  4.816979
H   -2.622679  -1.323079  3.815655
C    1.954250  -2.399367  4.213759
H    1.136146  -2.037275  4.847857
H    2.672327  -2.940384  4.842052
H    2.458529  -1.533152  3.777103
C    1.022999   2.951821  4.220085
H    1.114204   3.848137  4.845667
H    0.029028   2.945990  3.764826
H    1.112760   2.066193  4.860592
C   -0.022626   5.828651 -0.081306
O    1.103863   6.409792  0.377069
O   -0.957525   6.467716 -0.529621
C   -5.005044  -2.945408  0.030760
O   -4.914731  -4.204863 -0.442114
O   -6.043574  -2.476674  0.461168
C    5.018844  -2.890790 -0.053570
O    4.940531  -4.166547  0.374778
O    6.051677  -2.397955 -0.470029
C   -6.144459  -4.947489 -0.481952
H   -5.885542  -5.911347 -0.920130
H   -6.541978  -5.074607  0.528048
H   -6.884984  -4.428250 -1.095351
C    1.108392   7.847005  0.379652
H    2.068448   8.132055  0.809731
H    1.011962   8.226756 -0.640518
H    0.282615   8.230714  0.983921
C    6.177337  -4.898046  0.388405
H    5.928159  -5.878881  0.793225
H    6.575044  -4.986277 -0.625638
H    6.913227  -4.392943  1.018983
```

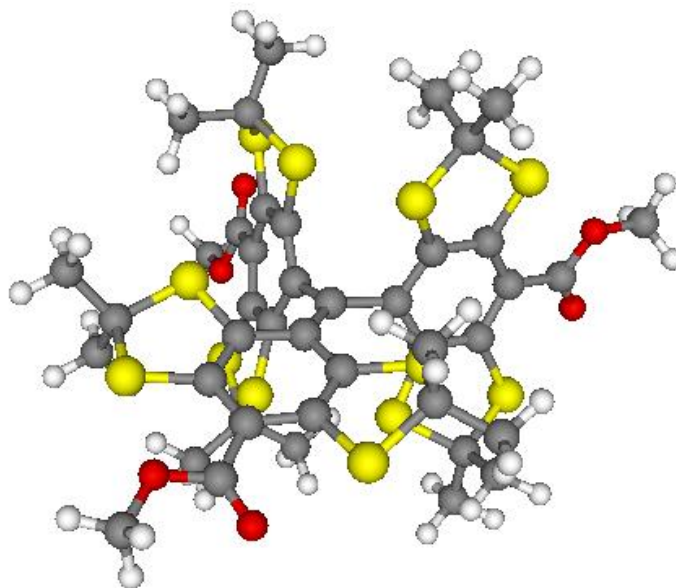## 8.6   TS-two for enantiomerization of radical 1c

Figure S23: Optimized two-ring flip TS for radical **1c** (UB3LYP/6-31G*)

E(UB3LYP-D/6-31G*) = -6893.364650
E(UB3LYP-D/6-311+G**) = -6893.425740
E(UB3LYP/6-31G*) = -6895.273954

C	-2.752104	-2.455410	-1.015654
C	-3.765012	-1.617933	-1.544459
C	-3.697707	-0.230956	-1.273456
C	-2.591482	0.309687	-0.603559
C	-1.437982	-0.495429	-0.242567
C	-1.642043	-1.927040	-0.348465
C	-0.189259	0.077302	0.147754
S	-2.854902	-4.233490	-1.121343
S	-0.535378	-3.139941	0.331263
S	-5.033957	0.885732	-1.649784
S	-2.768082	1.995681	-0.084701
C	-4.182701	2.459614	-1.177682
C	-1.756775	-4.525129	0.336860
C	1.050523	-0.734848	0.511424
C	1.400566	-0.958556	1.869816
C	2.673335	-1.424657	2.250547
C	3.640650	-1.711440	1.262691
C	3.234803	-1.700002	-0.087615
C	1.957566	-1.225202	-0.459311
C	0.171962	1.539596	-0.078539
C	0.405887	2.016991	-1.396328
C	1.022833	3.258967	-1.640837
C	1.389556	4.087313	-0.557437
C	0.942638	3.729637	0.732456
C	0.341680	2.476205	0.966322

```
S     4.278546   -2.274671   -1.410654
S     1.607195   -1.326767   -2.201784
C     2.858834   -2.645672   -2.539209
S     2.907587   -1.735901    3.985970
S     0.168300   -1.000262    3.151314
C     1.346939   -0.919145    4.573458
S    -0.243131    2.220786    2.629103
S     1.093804    4.810733    2.139610
S    -0.319317    1.236731   -2.820538
S     1.194647    3.738123   -3.344839
C     0.665562    2.129203   -4.105129
C    -0.300069    4.018458    3.064013
C    -0.054008    4.176804    4.568842
H    -0.049823    5.239664    4.837774
H    -0.857641    3.696684    5.139737
H     0.901799    3.738884    4.867233
C     1.903929    1.344629   -4.549544
H     1.608698    0.398500   -5.018116
H     2.468515    1.933925   -5.282581
H     2.556931    1.118202   -3.705111
C    -0.254815    2.423008   -5.298568
H    -0.592663    1.485051   -5.755131
H    -1.129688    3.003585   -4.996509
H     0.290499    2.985152   -6.065669
C    -3.695646    3.200351   -2.428919
H    -4.549027    3.440032   -3.075559
H    -3.199850    4.137072   -2.147000
H    -2.985147    2.593085   -2.993166
C    -2.564383   -4.525604    1.641387
H    -3.298326   -5.340484    1.628744
H    -1.897921   -4.665741    2.500923
H    -3.100168   -3.581664    1.774707
C    -1.007712   -5.848860    0.149041
H    -0.332328   -6.028018    0.993793
H    -1.721416   -6.680373    0.115879
H    -0.425254   -5.851768   -0.775706
C     3.332512   -2.516431   -3.991513
H     4.102681   -3.267649   -4.201922
H     2.499291   -2.698700   -4.680405
H     3.747441   -1.525460   -4.192734
C     2.291050   -4.042808   -2.267940
H     1.949711   -4.138359   -1.234746
H     1.437496   -4.238818   -2.927652
H     3.062082   -4.800239   -2.453447
C     0.766671   -1.746328    5.729317
H     1.467451   -1.759014    6.572244
H    -0.166828   -1.294023    6.084571
H     0.565569   -2.776075    5.424116
C    -5.156537    3.329550   -0.368231
H    -4.665971    4.259901   -0.057928
H    -6.019981    3.602630   -0.986310
H    -5.514451    2.806349    0.521490
C     1.653898    0.509417    5.030511
H     0.744478    0.994827    5.402406
H     2.391157    0.481840    5.842311
H     2.053589    1.115291    4.215758
C    -1.640369    4.643625    2.657606
```

H	-1.648638	5.710843	2.910644
H	-1.812452	4.543061	1.582694
H	-2.465140	4.150777	3.185909
C	-4.820286	-2.255696	-2.365280
O	-5.893545	-1.465919	-2.573598
O	-4.747638	-3.388041	-2.813615
C	2.147632	5.354153	-0.691172
O	2.357940	5.726634	-1.968607
O	2.557121	6.007334	0.253357
C	5.047384	-2.086254	1.553734
O	5.273478	-2.359977	2.853673
O	5.926181	-2.143329	0.710667
C	-6.942589	-2.030159	-3.376195
H	-7.708424	-1.256486	-3.435153
H	-6.568486	-2.282853	-4.371491
H	-7.338263	-2.932357	-2.902890
C	6.626596	-2.700620	3.196754
H	6.613823	-2.886232	4.270883
H	6.943244	-3.593500	2.651946
H	7.300353	-1.875129	2.953558
C	3.107266	6.938041	-2.154928
H	3.164822	7.078067	-3.234511
H	2.595567	7.779230	-1.680622
H	4.106304	6.837314	-1.723262

9. Circular dichroism spectra of radical 1b

The CD spectra of the two enantiomers **1b** were recorded by stopped-flow spectrometry on a CHIRALPAK® IB column 4.6x250 mm 5µm equipped with a precolumn CHIRALPAK® IB 4.6x20 mm 5µm. The conditions were as follows: flow rate: 1 mL/min; eluent: *i*-hex 93%/EtOAc 4%/MeOH 3% (premixed); UV and CD detection: 267 nm. The flow was stopped at the maximum of the CD signal for each enantiomer and the circular dichroism spectra were recorded from 220 to 440 nm with a Jasco CD-2095 Plus chiral HPLC detector. As expected for two enantiomers, the two spectra are mirror images.
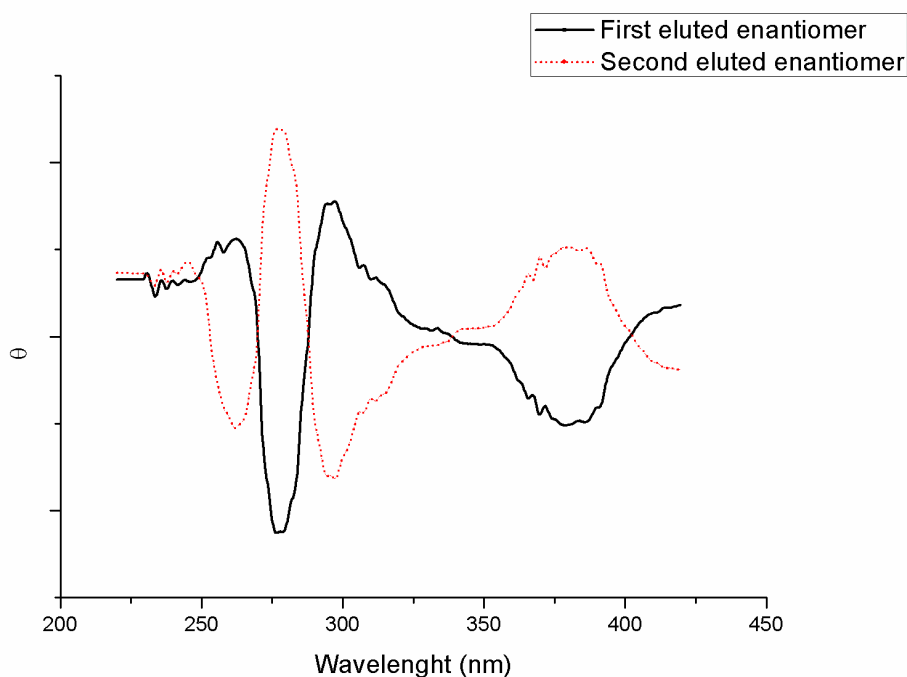

Figure S24: CD spectra of enantiomers **1b**.

10.   Conversion of alcohol 2b to radical 1b with neat TFA

Tetrathiatriarylmethyl radical **1b** has been synthesized from the corresponding alcohol **2b** by treatment with neat trifluoroacetic acid (TFA). This unclassical but straightforward method is widely used for quantitative conversion of a tetrathiatriarylmethyl alcohol into radical.[11] However, the mechanistic aspects of this transformation remain unknown.

5.5 mg of **2b** was dissolved in 2 mL of neat TFA and stirred for 2h. TFA was then removed under reduced pressure and the dark green residue dissolved in 1 mL of EtOAc, the EPR spectrum was then recorded and the quantitative conversion was check by RP HPLC.
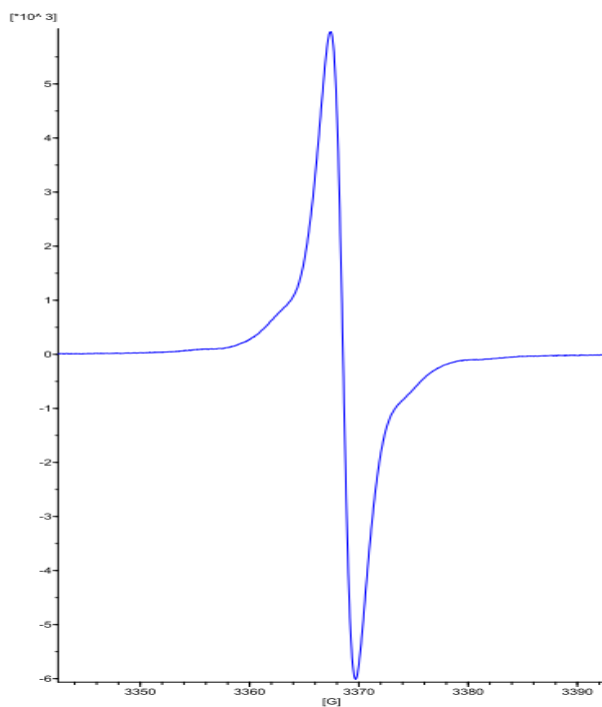

Figure S25: X-Band EPR spectrum of radical **1b** in EtOAc. The acquisition settings were; sweep width: 50 G, center field: 3367.5 G, resolution: 1024 pts, power: 1.269 mW, modulation frequency: 10 kHz, modulation amplitude: 0.25 G, conversion time: 20.48 ms, time constant: 20.48ms.

---

[11] (a) I. Dhimitruka, M. Velayutham, A. A. Bobko, V. V. Khramtsov, F. A. Villamena, C. M. Hadad and J. L. Zweier, *Bioorg. Med. Chem. Lett.*, 2007, **17**, 6801-6805. (b) A. A. Bobko, I. Dhimitruka, J. L. Zweier and V. V. Khramtsov, *J. Am. Chem. Soc.*, 2007, **129**, 7240-7241.(c) I. Dhimitruka, A. A. Bobko, C. M. Hadad, J. L. Zweier and V. V. Khramtsov, *J. Am. Chem. Soc.*, 2008, **130**, 10780-10787. (d) Y. Liu, F. A. Villamena, J. Sun, Y. Xu, I. Dhimitruka and J. L. Zweier, *J. Org. Chem.*, 2008, **73**, 1490-1497. (e) A. A. Bobko, I. Dhimitruka, T. D. Eubank, C. B. Marsh, J. L. Zweier and V. V. Khramtsov, *Free Radical Biol. Med.*, 2009, **47**, 654-658.
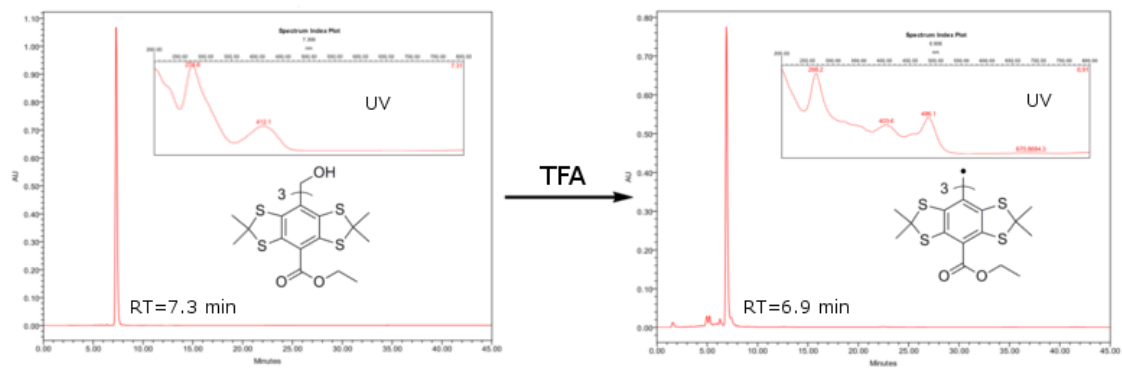
Figure S26: RP HPLC Chromatograms of **2b** and **1b**. The conditions were as follows: Column Symmetry C18 (4.6 x 250 mm) 5 μm, ACN100%, 1mL/min, 25°C, 254 nm.