Electronic Supplementary Material (ESI) for RSC Advances.

Chirality transfer through sulfur or selenium to chiral propellers

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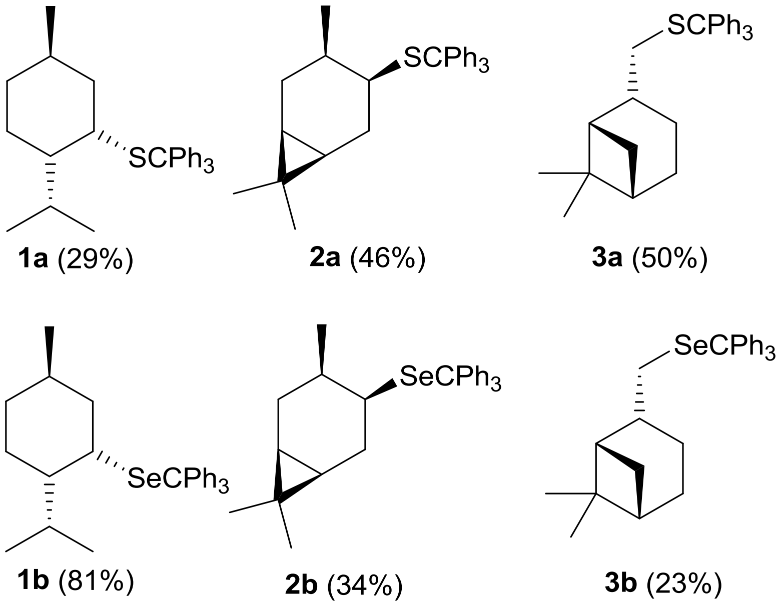

1a (29%) **2a** (46%) **3a** (50%)

1b (81%) **2b** (34%) **3b** (23%)

Figure 1. trityl sulfides **1a**, **2a**, **3a** and trityl selenides **1b**, **2b**, **3b**

EXPERIMENTAL

Melting points were measured with a Büchi Tottoli SPM-20 heating unit and are uncorrected. NMR spectra were recorded on Bruker Avance III/400 or Bruker Avance III/700. Chemical shifts are expressed in parts per million (ppm) relative to TMS. Optical rotations were measured in 10-mm cells with a polAAr 3000 polarimeter. TLC was conducted on precoated silica gel plates (Merck 60F254) and the spots were visualized under UV light. Column chromatography was carried out on column using Silica Gel 60 Merck (70–230 mesh). All reactions requiring anhydrous conditions were conducted in flame-dried apparatus.

1. General procedure for the synthesis of sulfur trityl derivatives

Trityl chloride (0.85g, 3.0mmol) was slowly added to the solution of thiol (3.0mmol) and pyridine (0.26g, 3.3mmol) in dry DCM (6ml). The mixture was stirred at room temperature for 24h, poured into water (100ml), and extracted with DCM (2 x 50ml). The combined organic layers were washed with water (2 x 50ml), dried over magnesium sulphate, and evaporated. The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate 98/2).

1.1. (+)-Neomenthyl trityl sulfide (1a)

Yield = 29%, oil; $[\alpha]_D^{20}$ = + 99.83 (c 3.0, $CHCl_3$); ^1H NMR (700 MHz, $CDCl_3$) σ = 0.36 (d, *J*=6.3 Hz, 3H, CH_3), 0.70-0.74 (m, 1H), 0.75 (d, *J*=7.0 Hz, 3H, CH_3), 0.81 (d, *J*=7.0 Hz, 3H, CH_3), 0.82-0.92 (m, 2H), 1.23-1.28 (m, 1H), 1.28-1.37 (m, 1H), 1.67-1.75 (m, 2H), 1.77-1.82 (m, 1H), 2.19-2.28 (m, 1H), 2.57 (d, *J*=2.8 Hz, 1H), 7.19-7.22 (m, 3H, arom.), 7.28 (t, *J*=7.7 Hz, 6H, arom.), 7.59-7.63 (m, 6H, arom.) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) σ = 20.39 (CH_3), 21.00 (CH_3), 21.62 (CH_3), 26.79 (CH_2), 26.88 (CH), 28.97 (CH), 35.36 (CH_2), 39.88 (CH_2), 45.64 (CH), 50.13 (CH), 66.50 (C), 126.17 (3 x CH), 127.43 (6 x CH), 129.51 (6 x CH), 145.42 (3 x C) ppm.

1.2. (–)-Caranyl trityl sulfide (2a)

Yield = 46%, oil; $[\alpha]_D^{20}$ = - 49.13 (c 2.5, $CHCl_3$); ^1H NMR (700 MHz, $CDCl_3$) σ = 0.25-0.32 (m, 2H), 0.79-0.82 (m, 2H), 0.89 (s, 3H, CH_3), 0.91 (s, 3H, CH_3), 0.98 (d, *J*=7.0 Hz, 3H, CH_3), 1.02-1.05 (m, 1H), 1.82-1.89 (m, 1H), 1.92-1.98 (m, 1H), 2.40-2.44 (m, 1H), 7.22-7.25 (m, 3H, arom.), 7.29-7.33 (m, 6H, arom.), 7.57-7.59 (m, 6H, arom.) ppm; ^{13}C NMR (176 MHz, CDCl3) σ = 15.52 (CH_3), 17.45 (C), 18.19 (CH), 18.81 (CH_3), 24.06 (CH_2), 24.67 (CH), 26.87(CH_2), 28.39 (CH_3), 29.16 (CH), 45.19 (CH), 67.27 (C), 126.44 (3 x CH), 127.78 (6 x CH), 129.77 (6 x CH), 145.52 (3 x C) ppm.

1.3. (–)-Myrtanyl trityl sulfide (3a)

Yield = 50%, oil; $[\alpha]_D^{20}$ = - 40.25 (c 2.8, $CHCl_3$); ^1H NMR (700 MHz, $CDCl_3$) σ = 0.75 (s, 3H, CH_3), 0.82 (d, *J*=9.8 Hz, 1H), 0.87-0.92 (m, 1H), 1.14 (s, 3H, CH_3), 1.30-1.38 (m, 1H), 1.78-1.81 (m, 1H), 1.82-1.90 (m, 2H, CH_2), 1.96-1.98 (m, 1H), 2.04-2.10 (m, 1H), 2.18 (dd, *J*=7.7 Hz, *J*=11.2 Hz, 1H), 2.29 (dd, *J*=7.7 Hz, *J*=11.2 Hz, 1H) 2.29-2.32 (m, 1H), 7.22-7.24 (m, 3H, arom.), 7.29-7.33 (m, 6H, arom.), 7.44-7.46 (m, 6H, arom.) ppm; ^{13}C NMR (176 MHz, $CDCl_3$) σ = 22.21 (CH_2), 22.78 (CH_3), 26.19 (CH_2), 27.94 (CH_3), 33.36 (CH_2), 38.94 (CH_2), 40.33 (CH), 41.23 (CH), 45.51 (CH), 66.30 (C), 126.48 (3 x CH), 127.78 (6 x CH), 129.65 (6 x CH), 145.12 (C) ppm.

2. General procedure for the synthesis of selenyl trityl derivatives

Selenol (2.3 mmol) in dry DCM (10ml) was carefully added to the suspension of sodium hydride (0.06g, 2.5mmol) in dry DCM (5ml) under argon atmosphere. After stirring for 10 min the mixture was cooled to 0 °C and trityl chloride (0.64g, 2.3mmol) in dry DCM (10ml) was added. The mixture was stirred at room temperature for 1h, poured into water (100ml) and extracted with DCM (3 x 50ml). The combined organic layers were dried over magnesium sulphate, and evaporated. The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate 99/1).

2.1. (+)-Neomenthyl trityl selenide (1b)

Yield 81%, mp = 137-139 ^{o}C (from methanol); $[\alpha]_{D}^{20}$= - 199.00 (c 3.01, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) σ = 0.54 (d, *J*=6.3 Hz, 3H, CH_3), 0.79-1.02 (m, 9H), 1.16-1.21 (m, 1H), 1.36 (d, *J*=13.3 Hz, 1H), 1.64-1.69 (m, 1H), 1.79 (t, *J*=14.7 Hz, 2H, CH_2), 2.25-2.33 (m, 1H), 2.59 (s, 1H), 7.19 (t, *J*=7.0 Hz, 3H, arom.), 7.25-7.29 (m, 6H, arom.), 7.57 (d, *J*=7.7 Hz, 6H, arom.) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) σ = 20.63 (CH_3), 21.09 (CH_3), 21.69 (CH_3), 27.88 (CH), 28.20 (CH_2), 30.34 (CH), 35.28 (CH_2), 40.41 (CH_2), 47.62 (CH), 50.57 (CH), 64.50 (C), 126.15 (3 x CH), 127.56 (6 x CH), 129.89 (6 x CH), 145.76 (3 x C) ppm; ^{77}Se NMR (76 MHz, $CDCl_3$) σ = 474.04 ppm.

2.2. (–)-Caranyl trityl selenide (2b)

Yield = 34%, oil; $[\alpha]_{D}^{20}$= - 24.95 (c 3.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) σ = 0.27-0.32 (m, 2H), 0.77-0.88 (m, 1H), 0.90 (s, 3H, CH_3), 0.93 (s, 3H, CH_3), 0.97 (d, *J*=6.8 Hz, 2H), 1.00-1.09 (m, 2H), 1.35-1.43 (m, 1H), 1.92-1.97 (m, 2H), 2.49-2.51 (m, 1H), 7.19-7.24 (m, 3H, arom.), 7.28-7.35 (m, 6H, arom.), 7.51-7.53 (m, 6H, arom.) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) σ = 15.51 (CH_3), 17.31 (C), 18.37 (CH), 20.29 (CH_3), 24.67 (CH), 24.69 (CH_2), 26.69 (CH_2), 28.29 (CH_3), 29.49 (CH), 45.26 (CH), 64.76 (C), 126.28 (3 x CH), 127.67 (6 x CH), 130.09 (6 x CH), 145.83 (3 x C) ppm; ^{77}Se NMR (76 MHz, $CDCl_3$) σ = 551.30 ppm.

2.3. (–)-Myrtanyl trityl selenide (3b)

Yield = 23%, oil; $[\alpha]_{D}^{20}$= - 28.60 (c 0.93, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) σ = 0.80 (d, *J*=9.6 Hz, 1H), 0.81 (s, CH_3, 3H), 1.14 (s, 3H, CH_3), 1.32-1.35 (m, 1H), 1.75-1.89 (m, 5H), 2.08-2.11 (m, 1H), 2.25-2.31 (m, 1H), 2.34 (dd, *J*=8.0 Hz, *J*=10.8 Hz, 1H), 2.45-2.50 (dd, *J*=7.6 Hz, *J*=10.8 Hz, 1H), 7.19-7.24 (m, 3H, arom.), 7.27-7.30 (m, 6H, arom.), 7.35-7.36 (m, 6H, arom.) ppm; ^{13}C MNR (100 MHz, $CDCl_3$) σ = 22.76 (CH_2), 22.80 (CH_3), 26.08 (CH_2), 27.87 (CH_3), 33.33 (CH_2), 35.76 (CH_2), 40.84 (CH), 41.13 (CH), 46.32 (CH), 64.03 (C), 126.37 (3 x CH), 127.69 (6 x CH), 129.97 (6 x CH), 145.79 (3 x C) ppm; ^{77}Se NMR (76 MHz, $CDCl_3$) σ = 492.63 ppm.

Table X1. NATURAL POPULATIONS: Natural atomic orbital occupancies on sulfur atom

```
   NAO  Atom  No  lang   Type(AO)    Occupancy      Energy
 ---------------------------------------------------------
   295    S   30  S      Cor( 1S)     2.00000     -87.68626
   296    S   30  S      Cor( 2S)     1.99946      -8.79986
   297    S   30  S      Val( 3S)     1.68161      -0.70676
   298    S   30  S      Ryd( 4S)     0.00461       1.00685
   299    S   30  S      Ryd( 5S)     0.00001      14.06031
   300    S   30  S      Ryd( 6S)     0.00000     182.68265
   301    S   30  px     Cor( 2p)     1.99988      -5.87156
   302    S   30  px     Val( 3p)     0.89619      -0.13957
   303    S   30  px     Ryd( 4p)     0.00465       0.83838
   304    S   30  px     Ryd( 5p)     0.00015       2.56111
   305    S   30  px     Ryd( 6p)     0.00000      16.74413
   306    S   30  py     Cor( 2p)     1.99997      -5.86387
   307    S   30  py     Val( 3p)     1.89676      -0.22085
   308    S   30  py     Ryd( 4p)     0.00461       0.64485
   309    S   30  py     Ryd( 5p)     0.00011       2.32687
   310    S   30  py     Ryd( 6p)     0.00000      16.82928
   311    S   30  pz     Cor( 2p)     1.99991      -5.86902
   312    S   30  pz     Val( 3p)     1.32865      -0.18850
   313    S   30  pz     Ryd( 4p)     0.00191       0.39130
   314    S   30  pz     Ryd( 5p)     0.00014       2.49061
   315    S   30  pz     Ryd( 6p)     0.00000      16.73898
   316    S   30  dxy    Ryd( 3d)     0.00118       1.12932
   317    S   30  dxz    Ryd( 3d)     0.00625       1.33749
   318    S   30  dyz    Ryd( 3d)     0.00130       1.04503
   319    S   30  dx2y2  Ryd( 3d)     0.00290       1.22194
   320    S   30  dz2    Ryd( 3d)     0.00175       1.09093

Natural Electron Configuration of sulfur atom:  [core]3S( 1.68)3p( 4.12)3d( 0.01)4p( 0.01)
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Table X2. Occupancy of natural orbitals (NBOs) located on sulfur atom (except core NBOs)

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       (Occupancy)   Bond orbital/ Coefficients/ Hybrids
 ---------------------------------------------------------------------------------
    13. (1.97232) BD ( 1) C  10 - S  30
                ( 51.28%)   0.7161* C  10 s( 18.71%)p 4.34( 81.16%)d 0.01(  0.14%)
                                                0.0002  0.4322 -0.0176 -0.0007  0.6794
                                               -0.0078 -0.0071 -0.0706 -0.0053  0.0019
                                               -0.5872  0.0054  0.0057 -0.0050 -0.0312
                                                0.0047  0.0176  0.0050
                ( 48.72%)   0.6980* S  30 s( 16.90%)p 4.89( 82.63%)d 0.03(  0.47%)
                                                0.0000  0.0003  0.4095  0.0365  0.0006
                                                0.0000 -0.0001 -0.6328  0.0436  0.0048
                                                0.0005  0.0000  0.1185  0.0011 -0.0015
                                               -0.0001  0.0002  0.6401 -0.0131  0.0049
                                                0.0000 -0.0110 -0.0582  0.0127  0.0247
                                                0.0213
    31. (1.94403) BD ( 1) S  30 - C  31
                ( 46.76%)   0.6838* S  30 s( 14.79%)p 5.73( 84.78%)d 0.03(  0.43%)
                                                0.0000  0.0005  0.3829  0.0353 -0.0009
                                                0.0000  0.0003  0.7663 -0.0405 -0.0054
                                               -0.0005  0.0000  0.0706  0.0010 -0.0002
                                               -0.0002  0.0002  0.5039 -0.0001  0.0048
                                               -0.0007  0.0086  0.0545  0.0048  0.0349
                                               -0.0006
                ( 53.24%)   0.7297* C  31 s( 15.88%)p 5.29( 84.02%)d 0.01(  0.10%)
                                                0.0000  0.3972 -0.0322 -0.0003 -0.8308
                                                0.0300  0.0044 -0.0275  0.0003 -0.0003
                                               -0.3850  0.0067  0.0027  0.0032  0.0217
                                                0.0016  0.0212 -0.0059
   111. (1.97559) LP ( 1) S  30          s( 68.54%)p 0.46( 31.45%)d 0.00(  0.01%)
                                                0.0000 -0.0003  0.8277 -0.0162  0.0000
                                                0.0000 -0.0001 -0.0414 -0.0020  0.0000
                                               -0.0001  0.0000 -0.0910 -0.0011  0.0018
                                                0.0000 -0.0001 -0.5518  0.0015 -0.0015
                                                0.0003  0.0002  0.0012 -0.0037 -0.0074
                                               -0.0071
   112. (1.91543) LP ( 2) S  30          s(  0.00%)p 1.00( 99.98%)d 0.00(  0.02%)
                                                0.0000 -0.0001  0.0005  0.0027 -0.0005
                                                0.0000  0.0001 -0.0178 -0.0005  0.0004
                                               -0.0003  0.0000 -0.9856 -0.0298  0.0002
                                               -0.0006  0.0000  0.1647  0.0070  0.0021
                                               -0.0002 -0.0011  0.0007 -0.0122  0.0004
                                                0.0038
```

Table X3. Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis – selected data for interactions of NBOs located on sulfur atom

```
     Threshold for printing:   0.50 kcal/mol
                                                                            E(2)  E(j)-E(i) F(i,j)
         Donor NBO (i)                     Acceptor NBO (j)               kcal/mol   a.u.    a.u.
===================================================================================================
   9. BD (   1) C   7 - H   9       /689. BD*(   1) C  10 - S  30            6.33    0.63    0.057
  12. BD (   1) C  10 - C  12       /338. RY*(   1) S  30                    0.56    1.39    0.025
  12. BD (   1) C  10 - C  12       /707. BD*(   1) S  30 - C  31            0.97    0.70    0.023
  34. BD (   1) C  31 - C  34       /689. BD*(   1) C  10 - S  30            0.80    0.77    0.022
  35. BD (   1) C  32 - C  35       /707. BD*(   1) S  30 - C  31            0.70    0.80    0.021
  36. BD (   2) C  32 - C  35       /707. BD*(   1) S  30 - C  31            5.07    0.36    0.041
  38. BD (   1) C  33 - C  45       /707. BD*(   1) S  30 - C  31            2.03    0.80    0.036
  39. BD (   2) C  33 - C  45       /707. BD*(   1) S  30 - C  31            2.21    0.36    0.027
  43. BD (   2) C  34 - C  44       /707. BD*(   1) S  30 - C  31            2.13    0.36    0.027

  92. CR (   1) C  31               /707. BD*(   1) S  30 - C  31            0.76   10.22    0.080

 712. BD*(   2) C  32 - C  35       /707. BD*(   1) S  30 - C  31            7.18    0.08    0.046
 715. BD*(   2) C  33 - C  45       /707. BD*(   1) S  30 - C  31            2.19    0.08    0.026
 719. BD*(   2) C  34 - C  44       /707. BD*(   1) S  30 - C  31            1.78    0.07    0.023


  13. BD (   1) C  10 - S  30       /159. RY*(   1) C   7                    0.58    1.49    0.026
  13. BD (   1) C  10 - S  30       /161. RY*(   3) C   7                    0.71    1.49    0.029
  13. BD (   1) C  10 - S  30       /200. RY*(   1) C  12                    0.69    1.44    0.028
  13. BD (   1) C  10 - S  30       /202. RY*(   3) C  12                    0.54    1.43    0.025
  13. BD (   1) C  10 - S  30       /357. RY*(   3) C  31                    0.59    1.39    0.026
  13. BD (   1) C  10 - S  30       /685. BD*(   1) C   7 - H   9            2.17    0.98    0.041
  13. BD (   1) C  10 - S  30       /690. BD*(   1) C  12 - H  13            2.32    0.99    0.043
  13. BD (   1) C  10 - S  30       /710. BD*(   1) C  31 - C  34            0.78    0.95    0.024
  31. BD (   1) S  30 - C  31       /370. RY*(   3) C  32                    1.17    1.27    0.035
  31. BD (   1) S  30 - C  31       /382. RY*(   2) C  33                    0.54    1.73    0.028
  31. BD (   1) S  30 - C  31       /383. RY*(   3) C  33                    0.59    1.32    0.025
  31. BD (   1) S  30 - C  31       /395. RY*(   2) C  34                    1.27    1.64    0.041
  31. BD (   1) S  30 - C  31       /688. BD*(   1) C  10 - C  12            1.15    0.91    0.029
  31. BD (   1) S  30 - C  31       /711. BD*(   1) C  32 - C  35            0.83    1.11    0.027
  31. BD (   1) S  30 - C  31       /712. BD*(   2) C  32 - C  35            4.04    0.57    0.046
  31. BD (   1) S  30 - C  31       /714. BD*(   1) C  33 - C  45            2.79    1.11    0.050
  31. BD (   1) S  30 - C  31       /715. BD*(   2) C  33 - C  45            1.19    0.57    0.025
  31. BD (   1) S  30 - C  31       /718. BD*(   1) C  34 - C  44            3.10    1.11    0.053
  31. BD (   1) S  30 - C  31       /719. BD*(   2) C  34 - C  44            1.55    0.57    0.029

  88. CR (   2) S  30               /183. RY*(   2) C  10                    0.83    9.75    0.080
  88. CR (   2) S  30               /355. RY*(   1) C  31                    0.93    9.78    0.085


 111. LP (   1) S  30               /355. RY*(   1) C  31                    1.52    1.60    0.044
 111. LP (   1) S  30               /686. BD*(   1) C   7 - C  10            0.90    1.01    0.027
 111. LP (   1) S  30               /687. BD*(   1) C  10 - H  11            0.67    1.08    0.024
 111. LP (   1) S  30               /708. BD*(   1) C  31 - C  32            1.23    1.01    0.032
 111. LP (   1) S  30               /709. BD*(   1) C  31 - C  33            0.81    1.00    0.026
 112. LP (   2) S  30               /685. BD*(   1) C   7 - H   9            0.75    0.63    0.020
 112. LP (   2) S  30               /686. BD*(   1) C   7 - C  10            4.69    0.61    0.049
 112. LP (   2) S  30               /687. BD*(   1) C  10 - H  11            2.31    0.69    0.036
 112. LP (   2) S  30               /688. BD*(   1) C  10 - C  12            0.55    0.60    0.016
 112. LP (   2) S  30               /708. BD*(   1) C  31 - C  32            2.16    0.62    0.033
 112. LP (   2) S  30               /709. BD*(   1) C  31 - C  33            3.86    0.61    0.044
 112. LP (   2) S  30               /712. BD*(   2) C  32 - C  35            0.75    0.26    0.013
 112. LP (   2) S  30               /733. BD*(   1) C  40 - H  55            0.62    0.69    0.019
 112. LP (   2) S  30               /752. BD*(   1) C  49 - H  64            0.53    0.69    0.017
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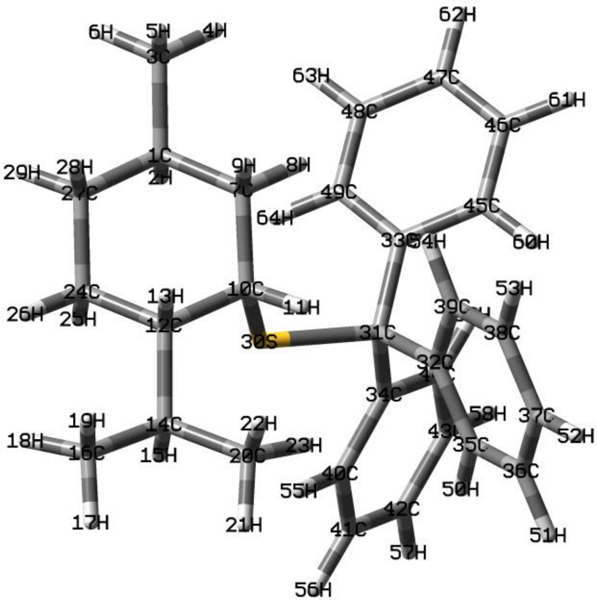
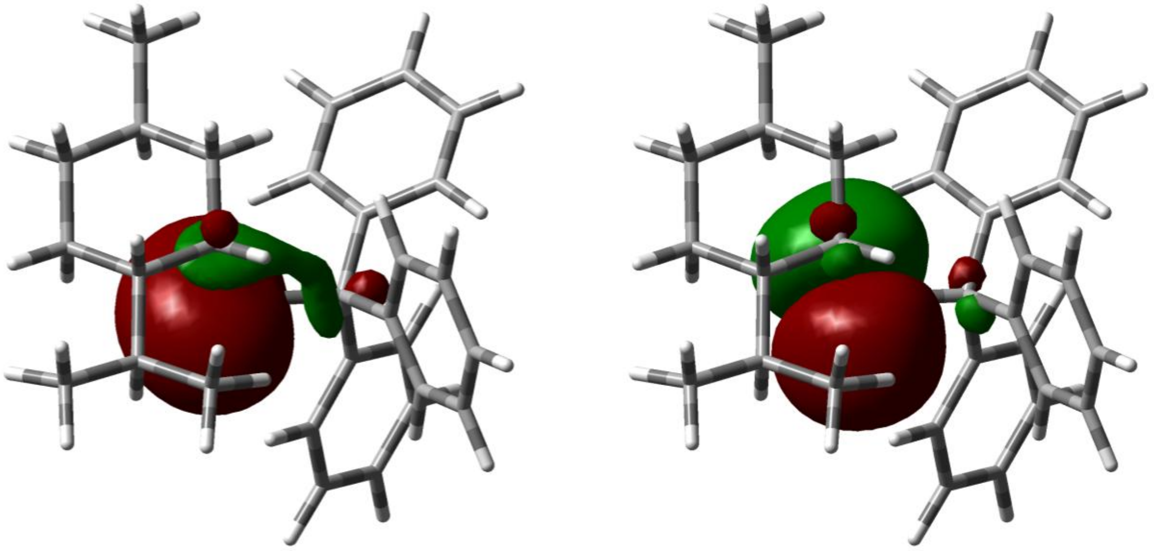


Figure X1. Atom numbering in the structure of conf 1 of **1.**



a/ b/

Figure X2. Lone pairs orbitals a/ lower in energy *s*-type, b/ highest occupied NBO of *p*-type

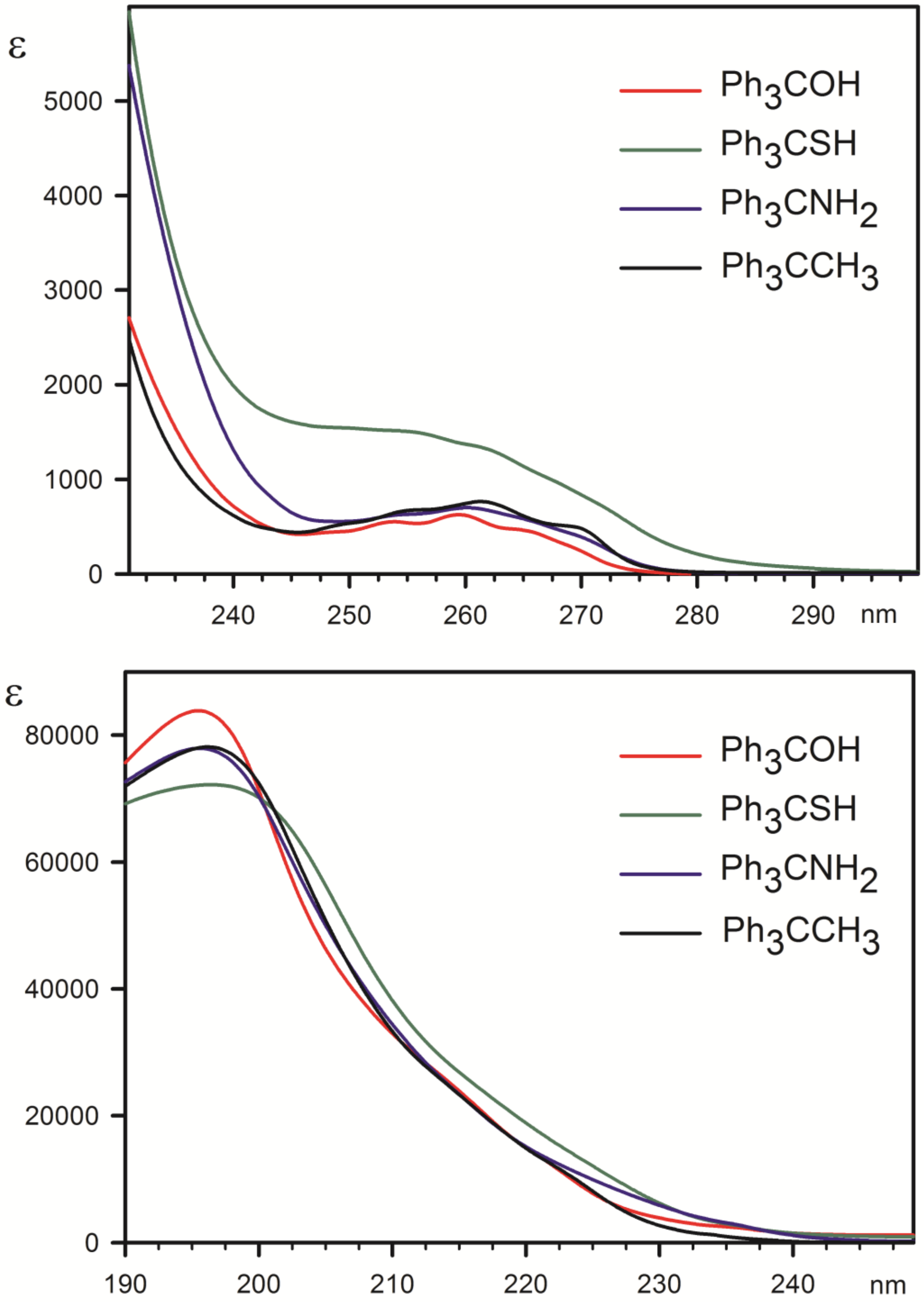


Figure X3. UV spectra of trityl derivatives in acetonitrile

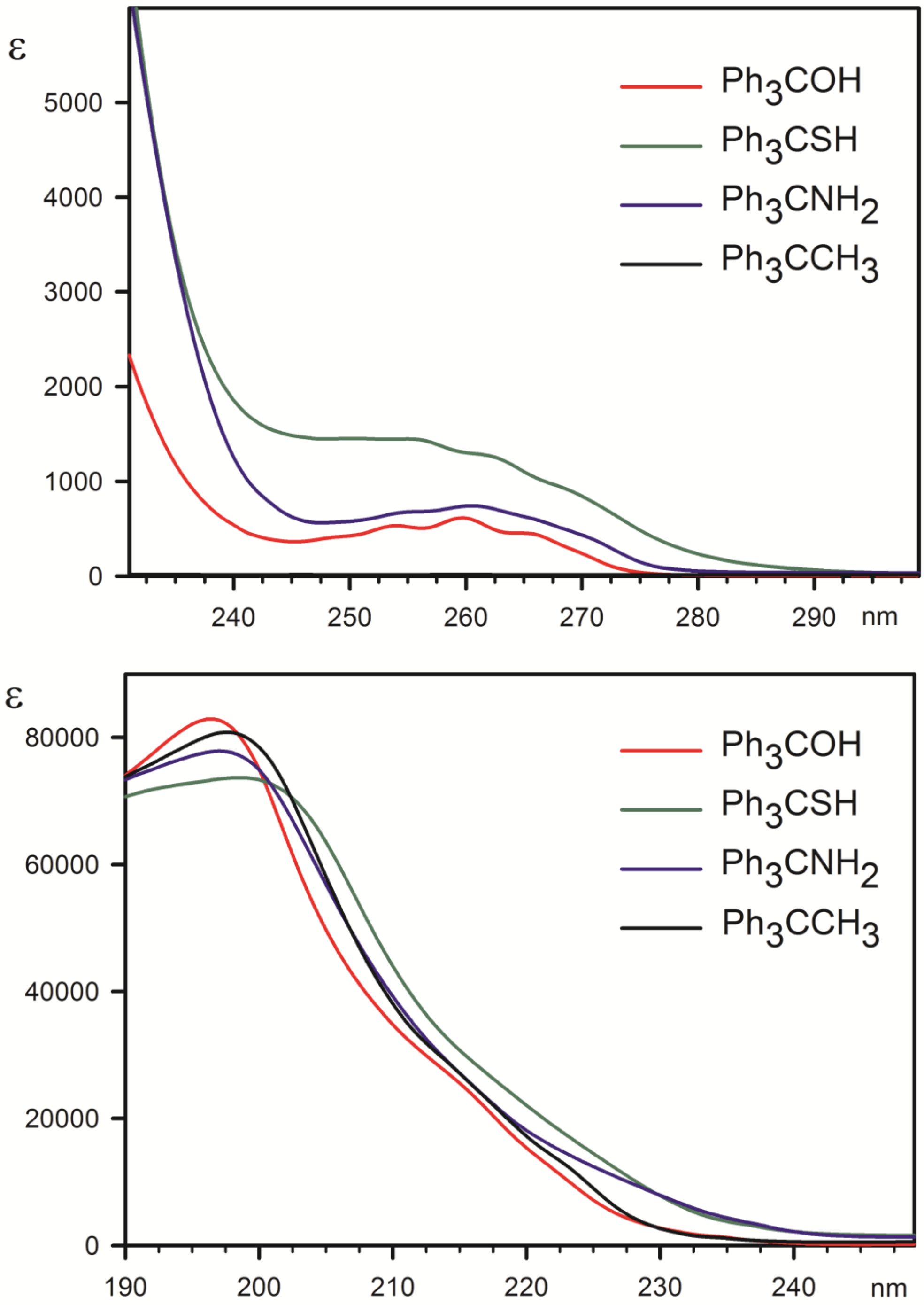


Figure X4. UV spectra of trityl derivatives in cyclohexane