

Ligand dependence of the synthetic approach and chiroptical properties of a magic cluster protected with a bicyclic chiral thiolate

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Electronic Supplementary Information

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1) Materials

Tetrachloroauric acid (Aldrich, 99.9+ %), sodium borohydride (Fluka, 96 %), (1*S*, 4*R*)- and (1*R*, 4*S*)-camphorsulfonic acid (98 %, 96 % ee), thionyl chloride (Fluka, 99 %), triphenylphosphine (Fluka, 98.5 %), *rac*-1-phenylethanol (Aldrich, 98 %), *R*-1-phenylethanol (Aldrich, 97 %, 94 % ee), *S*-1-phenylethanol (Aldrich, 97 %, 94 % ee), thiourea (Sigma-Aldrich, 99 %), thiolacetic acid (Alfa Aesar, 97 %), diisopropyl azodicarboxylate (Alfa Aesar, 94 %), lithium aluminium hydride (Aldrich, 95 %), 3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (Aldrich, > 98 %), diethyl ether (purum, ZBT/ Heidelberg), chloroform (VWR, 99.2 %), 1, 4-dioxane (VWR, 99.5 %), toluene (VWR, 99.5 %), ethyl acetate (ZBT, purum), cyclohexane (ZBT, purum), tetrahydrofuran (Sigma-Aldrich, 99.9 %), ethanol (Fluka, p.A.), chloroform-*d* (Aldrich, 99.96 atom % D), methylene chloride (Sigma-Aldrich, p.A.), methanol (VWR, 100 %), methylene chloride-*d*₂ (Aldrich, 99.96 atom % D), conc. hydrochloric acid (VWR), sodium chloride (J. T. Baker, 99.5 %), sodium bicarbonate (99.5 %, Grüssing), sodium sulfate (Grüssing, 99 %), potassium hydroxide (Grüssing, 85 %), Celite 545 (Carl Roth), silica gel 60 – 200 µm (Carl Roth, Karlsruhe), PTFE syringe filters 0.2 µm (Carl Roth), recovered cellulose filters 0.2 µm (Sartorius) and BioBeads S-X1 (BioRad) were used as received, if not mentioned otherwise. Nanopure water (≥ 18 MΩ) was used.

2) Characterization

NMR spectroscopy. NMR spectra were recorded on a *Bruker AC 300* or *DRX-500* spectrometer. The spectra (^1H) were calibrated to the signal of residual protons in the solvent (CDCl_3 , 7.26 ppm) or the center of the triplet signal (77.0 ppm) in ^{13}C spectra.¹

UV-Vis spectroscopy. UV-Vis spectra were measured on a *Varian Cary 50* spectrometer using 1 cm quartz cells. The signal of the blank solvent was used for reference. All spectra were recorded in methylene chloride and normalized at 300 nm (if not mentioned otherwise).

CD spectroscopy. CD spectra were recorded on a *JASCO J-815* spectrophotometer and either a 1 cm (organic compounds) or a 5 mm (gold nanoclusters) quartz cuvette was used. The signal of the blank solvent was subtracted from the spectra for baseline correction. Anisotropy factors $g = \theta[\text{mdeg}]/(32980 \cdot A)$ were calculated from the absorption spectra gained from the CD measurements. All spectra were measured in methylene chloride.

MALDI analysis. Mass spectra were obtained using a *Bruker Autoflex* mass spectrometer equipped with a nitrogen laser at near threshold laser fluence in positive linear mode. 3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was used as the matrix with 1:1000 analyte:matrix ratio. Two microliters of the analyte/matrix mixture were applied to the target and airdried.

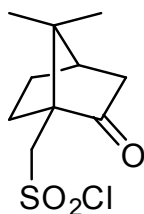
ESI spectra. Electrospray ionisation spectra were collected by using *Waters Synapt™ G2 Quan Tof High Definition* Mass Spectrometer in negative ion mode. The sample was dissolved in toluene and diluted 1:20 (v/v) ratio with acetonitrile. Then samples were electrosprayed by using stainless steel needle syringe. The Instrument parameters were maintained as follows: capillary voltage, -2.1 kV; detector voltage 1700 V; extraction cone voltage 1.0 V; sampling cone voltage 16.0 V; source Temperature 100 °C; desolvation

Temperature 150 °C. The mass spectra were collected in W optics mode for high mass accuracy. For simulation of the isotopic distribution pattern, the *Molecular Weight Calculator v6.46* was used.

IR spectroscopy. IR spectra were measured on a *Bruker Tensor 27* IR spectrometer. CaF₂ windows were used and the spectra were recorded in deuterated methylene chloride. The blank solvent was used as reference.

3) Synthesis of camphor-10-thiol²

Step 1 - Camphorsulfonic acid chloride



(1*S*, 4*R*)- or (1*R*, 4*S*)-Camphorsulfonic acid (10.000 g, 43.048 mmol) was placed in a round-bottomed flask with stopcock, reflux condenser, gas outlet and stirring bar. 3.5 equivalents of thionyl chloride (11.00 mL, 151.31 mmol) were added. The mixture was purged with argon for 5 min, stirred at room temperature for 10 min and then refluxed for 2 h. After cooling down to rt, excess thionyl chloride was removed in vacuo. 5 mL of toluene were added and removed in vacuo (two times). The product was dried in vacuo to give a yellow-white solid (10.420 g, 41.557 mmol, 96.54 %, Lit.: 97 %).²

¹H-NMR (CDCl₃, 300 MHz): δ = 0.928 (s, 3H, CH₃), 1.145 (s, 3H, CH₃), 1.443 - 1.528 (m, 1H, CH), 1.731 - 1.823 (m, 1H, CH), 1.962 - 2.024 (d, 1H, CH) 2.044 - 2.178 (m, 2H, CH₃), 2.395 - 2.520 (m, 2H, CH₃), 3.700 - 4.335 (dd, 2H, CH₃) ppm.

¹³C-NMR (CDCl₃, 75 MHz): δ = 19.7 (CH₃), 19.8 (CH₃), 25.3 (CH₂), 26.9 (CH₂), 42.3 (CH₂), 42.8 (CH), 48.2 (C_q), 59.7 (C_q), 64.3 (CH₂), 212.7 (C=O) ppm.

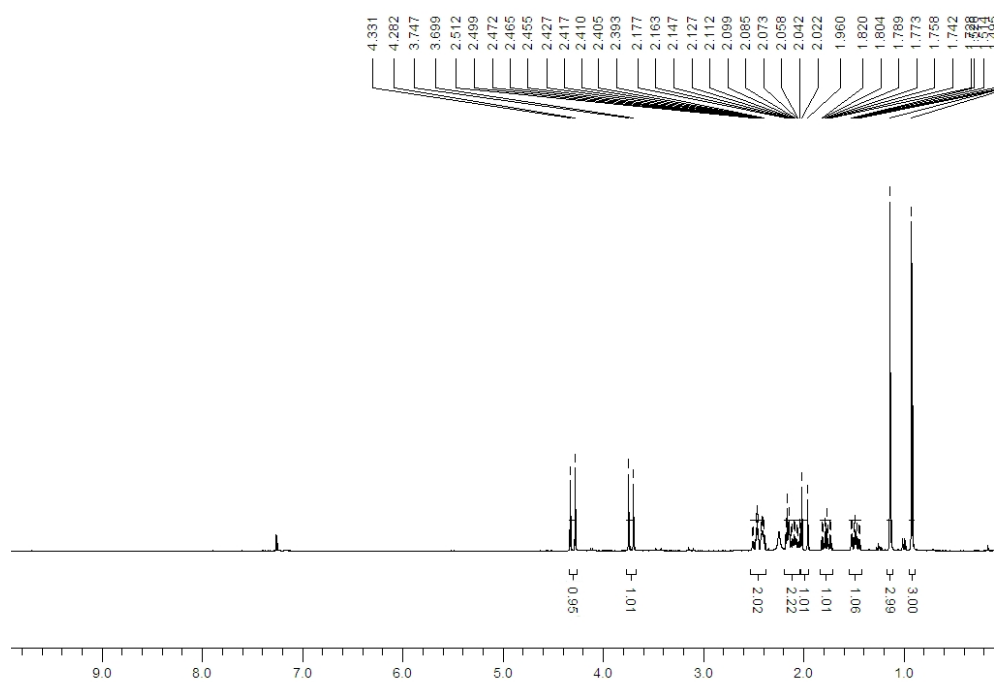


Figure S-1. ^1H -NMR spectrum (300 MHz, CDCl_3) of (1*R*, 4*S*)-camphorsulfonic acid chloride.

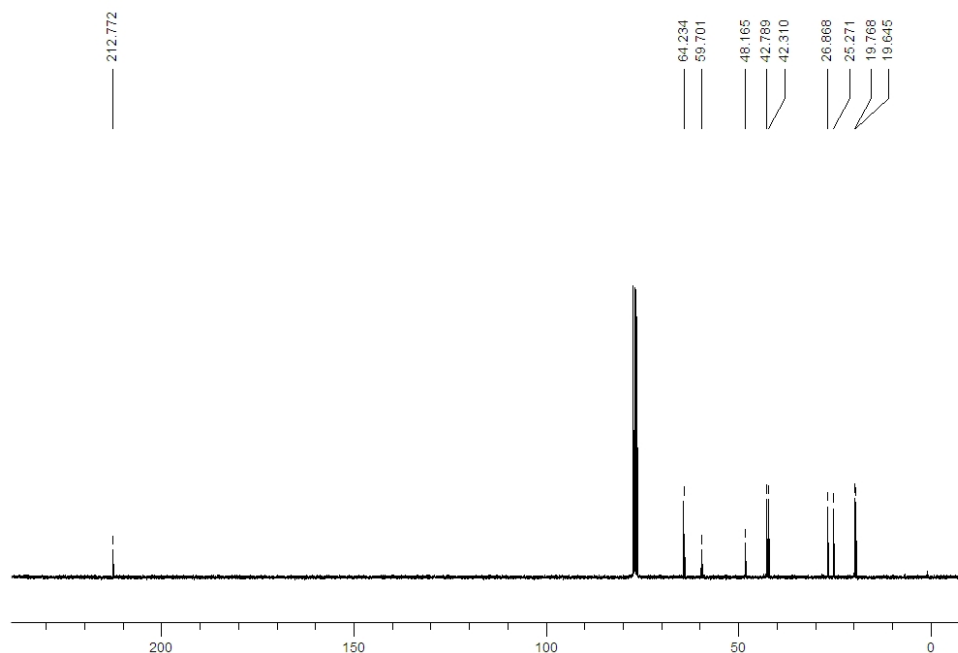


Figure S-2. ^{13}C -NMR spectrum (75 MHz, CDCl_3) of (1*R*, 4*S*)-camphorsulfonic acid chloride.

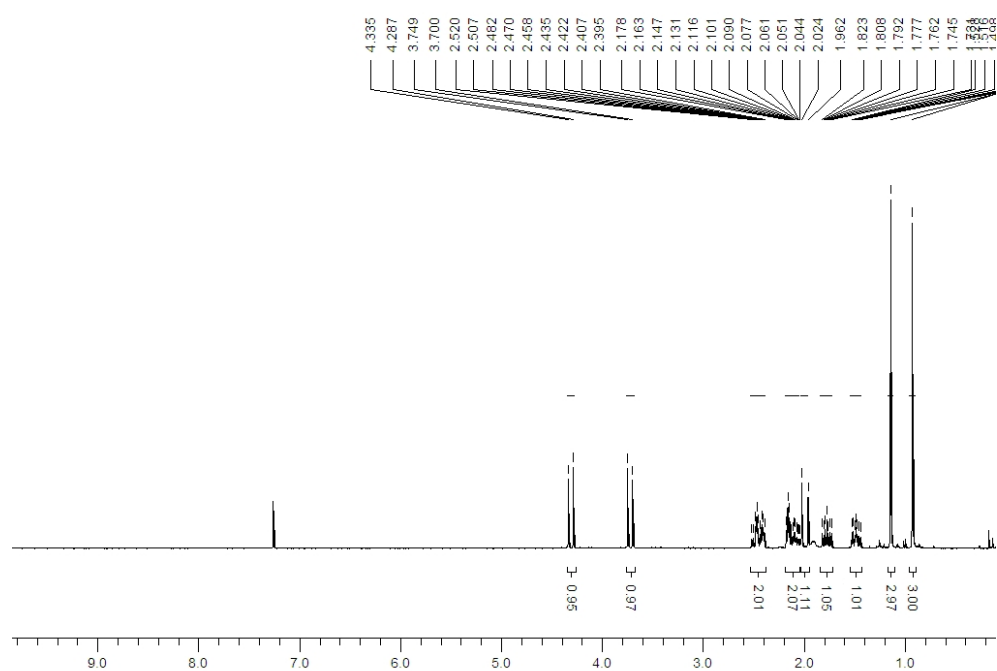


Figure S-3. ^1H -NMR spectrum (300 MHz, CDCl_3) of (1*S*, 4*R*)-camphorsulfonic acid chloride.

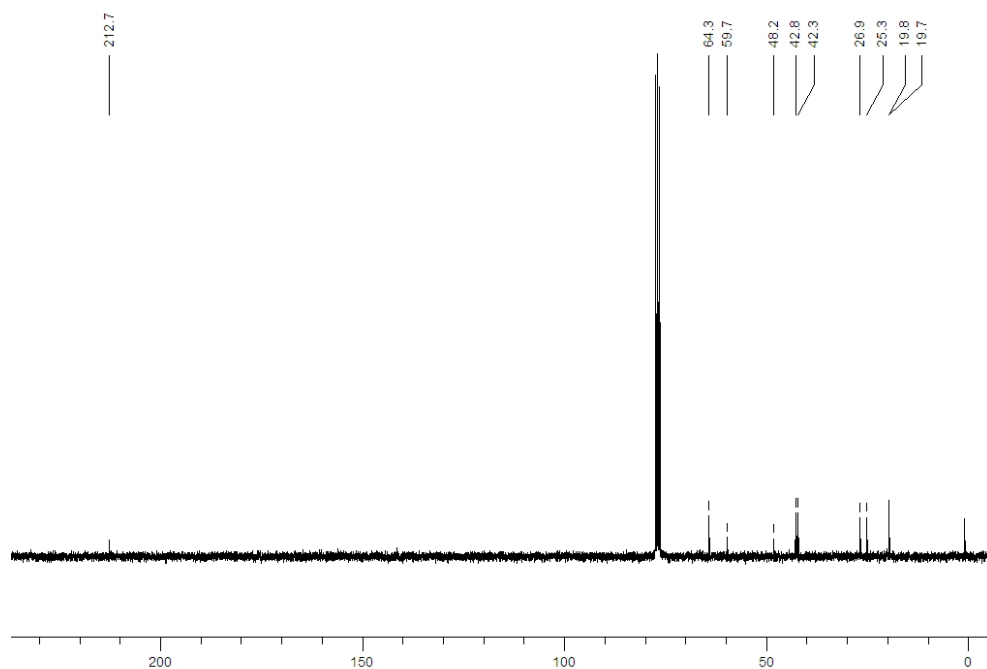
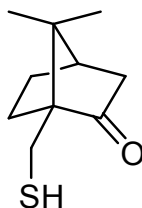


Figure S-4. ^{13}C -NMR spectrum (75 MHz, CDCl_3) of (1*S*, 4*R*)-camphorsulfonic acid chloride.

Step 2 - Camphorthiol



(1*S*, 4*R*)- or (1*R*, 4*S*)-Camphorsulfonic acid chloride (5.000 g, 19.941mmol) was placed in a round-bottomed flask with stopcock, reflux condenser and magnetic stirring bar. 3 equivalents of triphenylphosphine (15.691 g, 59.822mmol) and water/1,4-dioxane (10:40 mL) were added. The solution was refluxed for 2 h. After cooling down to room temperature, the reaction mixture was extracted with cyclohexane (3 times). The combined organic extracts were washed with water and dried over Na₂SO₄. The solvent was removed in vacuo to yield a white solid as crude product. Further purification was achieved by column chromatography (cyclohexane : ethyl acetate 40 : 1) over silica gel to give a white solid (2.221 g, 12.051 mmol, 60 %, Lit.: 88 %).²

¹H-NMR (CDCl₃, 300 MHz): δ = 0.907 (s, 3H, CH₃), 1.107 (s, 3H, CH₃), 1.359 - 2.094 (m, 7H), 2.318 - 2.404 (m, 2H), 2.835 - 2.904 (pq, 1H, SH, J = 6.8 Hz, J = 13.9 Hz) ppm.

¹³C-NMR (CDCl₃, 75 MHz): δ = 19.8 (CH₃), 20.3 (CH₃), 21.4 (CH₂), 26.6 (CH₂), 27.1 (CH₂), 43.3 (CH₂), 43.7 (CH), 47.8 (C_q), 60.4 (C_q), 217.9 (C=O) ppm.

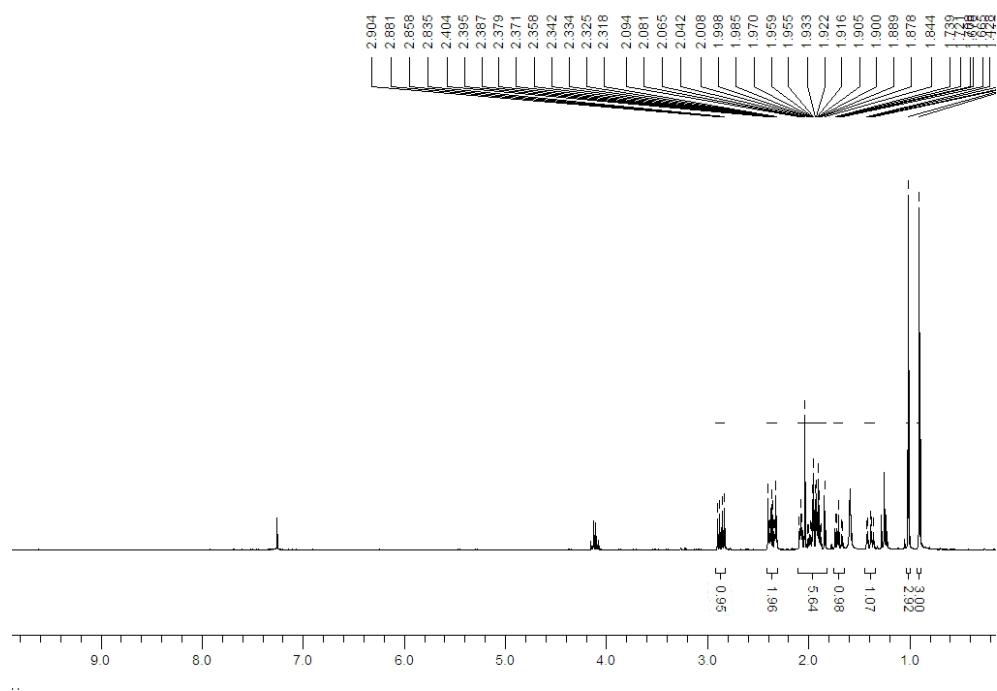


Figure S-5. ^1H -NMR spectrum (300 MHz, CDCl_3) of (1*R*, 4*S*)-camphorthiol.

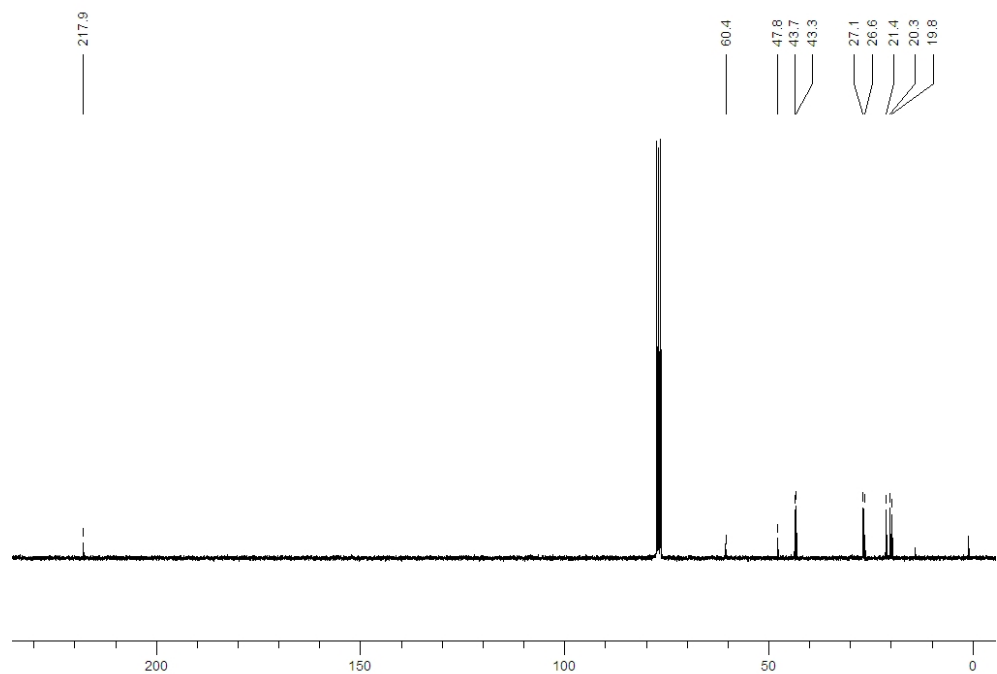


Figure S-6. ^{13}C -NMR spectrum (75 MHz, CDCl_3) of (1*R*, 4*S*)-camphorthiol.

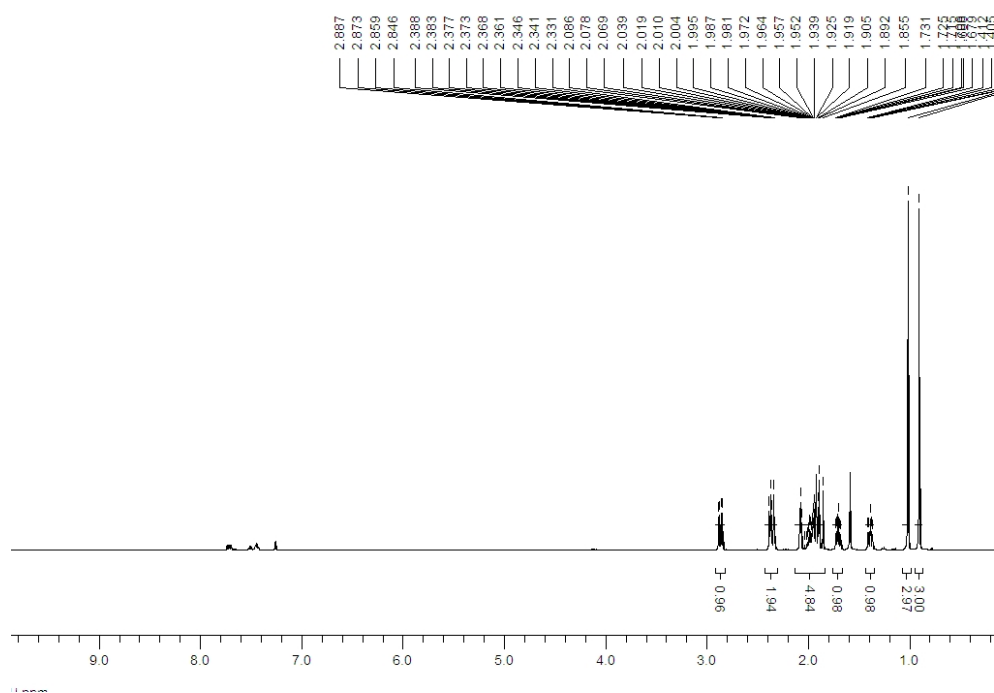


Figure S-7. ^1H -NMR spectrum (300 MHz, CDCl_3) of (1*S*, 4*R*)-camphorthiol.

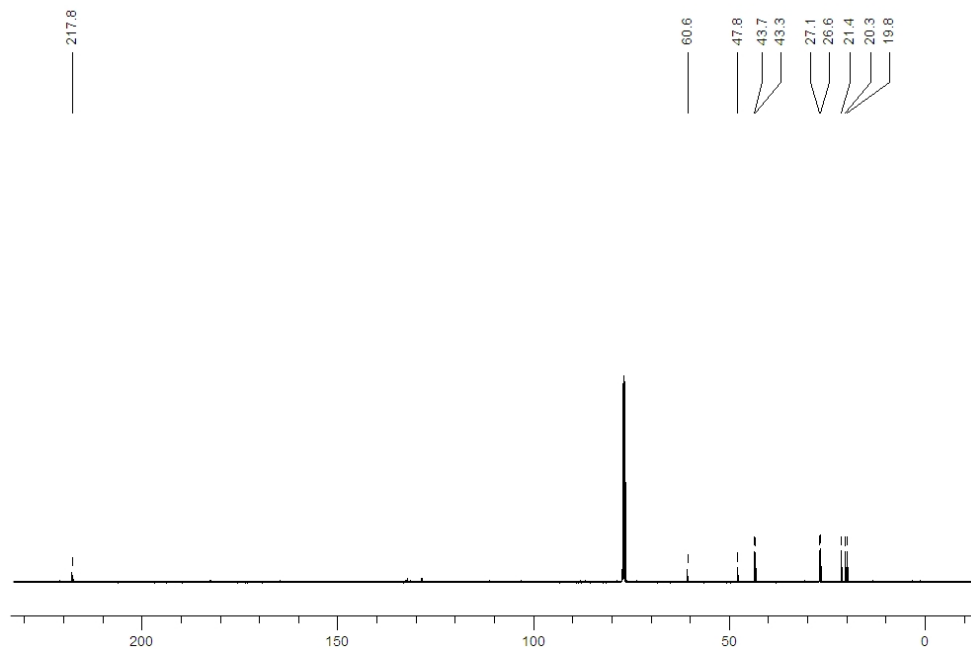
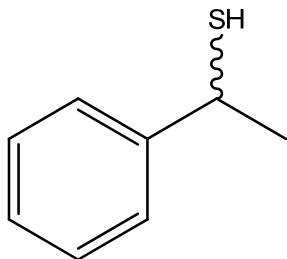


Figure S-8. ^{13}C -NMR spectrum (75 MHz, CDCl_3) of (1*S*, 4*R*)-camphorthiol.

4) Synthesis of *rac*-1-phenylethanethiol³



rac-1-Phenylethanol (10 mL, 82.5 mmol) was dissolved in 60 mL of conc. hydrochloric acid and purged with argon for 1 h. Thiourea (9.500 g, 118.2 mmol) was added and the solution was purged with argon for another 30 min. The reaction mixture was heated to reflux for 18 h under inert gas atmosphere. After that, the system was allowed to cool down to room temperature. A 6 M aqueous potassium hydroxide solution was added up to pH 10. The resulting suspension was heated to a gentle reflux for 3 h under inert gas atmosphere. After cooling down to room temperature, the suspension was acidified with conc. hydrochloric acid (pH 3) and extracted with diethyl ether (three times 50 mL each). The combined organic extracts were dried over sodium sulfate and the solvent was removed *in vacuo* to yield a yellow crude product. The crude product was purified via column chromatography (cyclohexane: ethyl acetate 7:1) and the solvent was removed *in vacuo* to yield 7.338 g (64.16 % on the basis of *rac*-1-phenylethanol) of a colourless liquid.

¹H-NMR (CDCl₃, 500 MHz): δ = 1.56 (d, 3H, -CH₃), 1.88 (d, 1H, -SH), 4.13 (m, 1H, -CH), 7.11-7.27 (m, 5H, -CH_{Ar}) ppm.

¹³C-NMR (CDCl₃, 125 MHz): δ = 26.0 (s, -CH₃), 38.6 (s, -CH), 126.3 (s, -CH_{Ar}), 127.0 (s, -CH_{Ar}), 128.5 (s, -CH_{Ar}), 145.8 (s, -C_{ipso}) ppm.

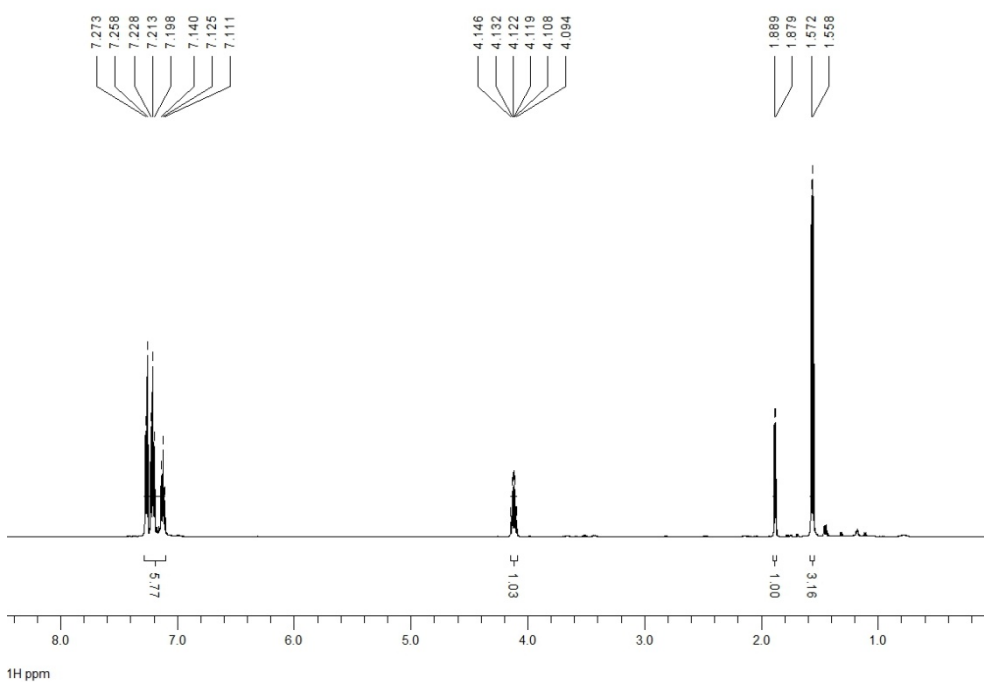


Figure S-9. ^1H -NMR spectrum (CDCl_3 , 500 MHz) of *rac*-1-phenylethanethiol.

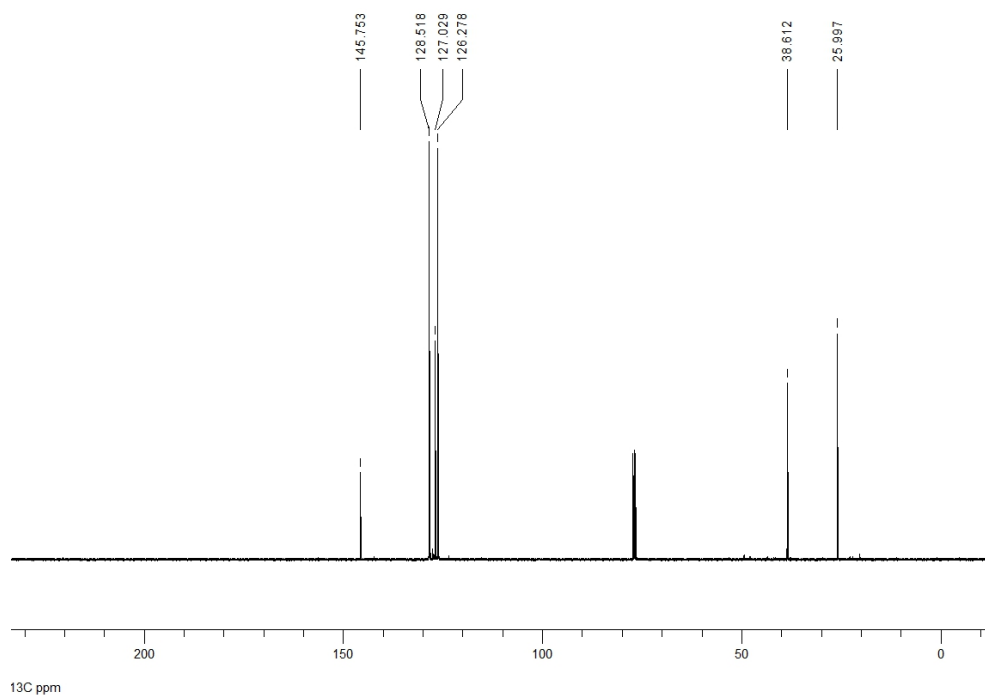
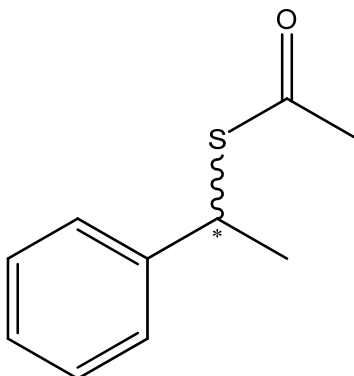


Figure S-10. ^{13}C -NMR spectrum (CDCl_3 , 125 MHz) of *rac*-1-phenylethanethiol.

5) Synthesis of *R*- and *S*-1-phenylethylthioacetate⁴



Triphenylphosphine (8.6086 g, 32.8 mmol) was dissolved in tetrahydrofuran (40 mL) at 0 °C and DIAD (6.45 mL, 31 mmol) was added dropwise. The solution was stirred under argon at 0 °C for 30 min and a white slurry formed. A mixture of *S*- or *R*-1-phenylethanol (2 mL, 16.2 mmol, note the inversion of absolute configuration!), respectively, and thiolacetic acid (2.35 mL, 29 mmol) in THF (20 mL) was added dropwise within 10 min, and the slurry became greenish-black. The reaction mixture was stirred under argon at 0 °C for 1 h and additional 2 h at 25 °C. The reaction mixture was washed with a saturated solution of NaHCO₃, concentrated to a quarter of its original volume and diluted with pentane to produce a white precipitate, which was filtered over Celite 545 (pH > 8.5). The filtrate was concentrated in vacuo, filtered over a pad of silica gel which was washed with pentane, dried over Na₂SO₄ and again concentrated to afford an orange oil. Further purification was achieved by column chromatography (cy : DCM 1:1, followed by cy : ethyl acetate 9:1) to give the product as a colourless oil (38 %). ¹H-NMR (CDCl₃, 300 MHz): δ = 1.588 (d, 3H, CH-CH₃, ³J = 7.2 Hz), 2.229 (s, 3H, CO-CH₃), 4.674 (dd, 1H, -CH, ³J = 7.2 Hz), 7.138 – 7.287 (m, 5H, -CH_{Ar}) ppm. ¹³C-NMR (CDCl₃, 75 MHz): δ = 22.2 (s, CH-CH₃), 30.4 (s, CO-CH₃), 42.9 (s, -CH), 127.2 (s, -CH_{ortho}), 127.3 (s, -CH_{para}), 128.6 (s, -CH_{meta}), 142.6 (s, -C_{ipso}), 195.0 (s, CO) ppm.

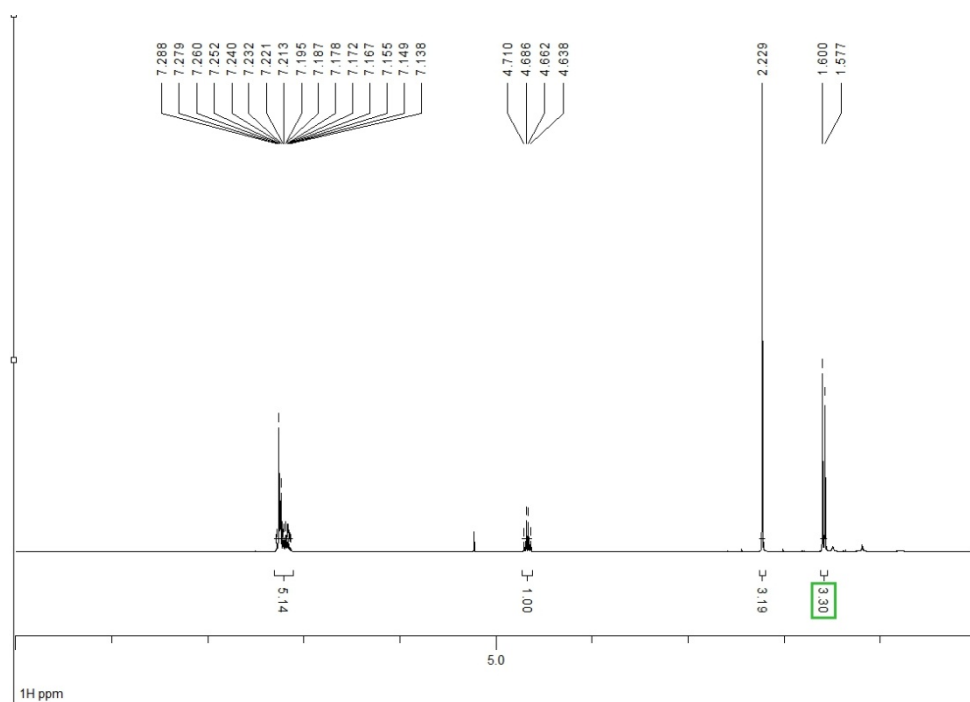


Figure S-11. ¹H-NMR spectrum (300 MHz, CDCl₃) of *R*-1-phenylethylethanethioate.

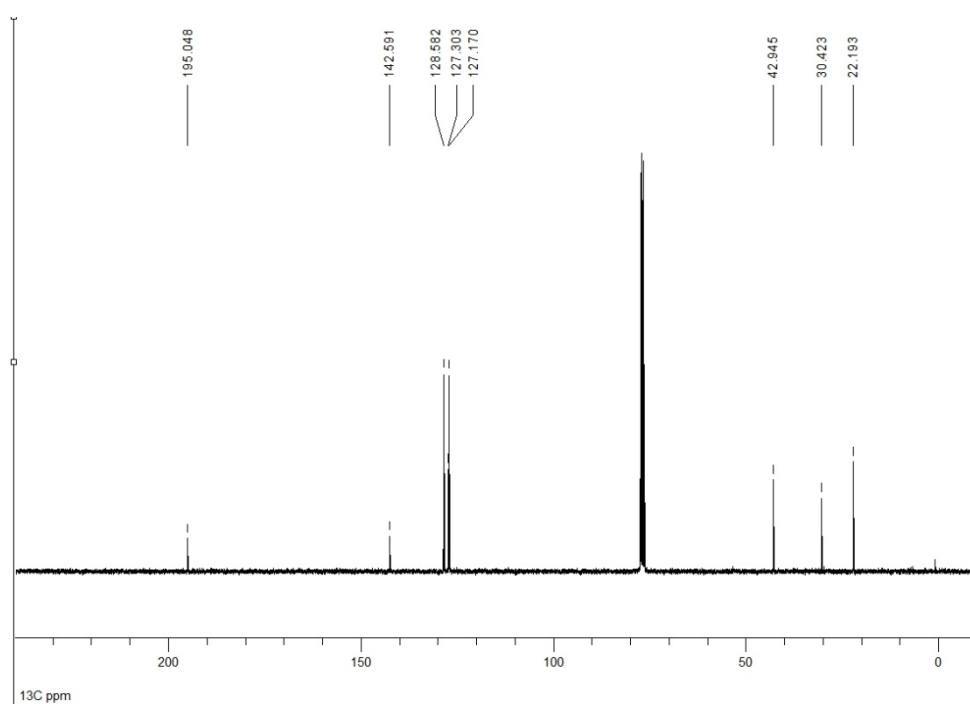


Figure S-12. ¹³C-NMR spectrum (75 MHz, CDCl₃) of *R*-1-phenylethylethanethioate.

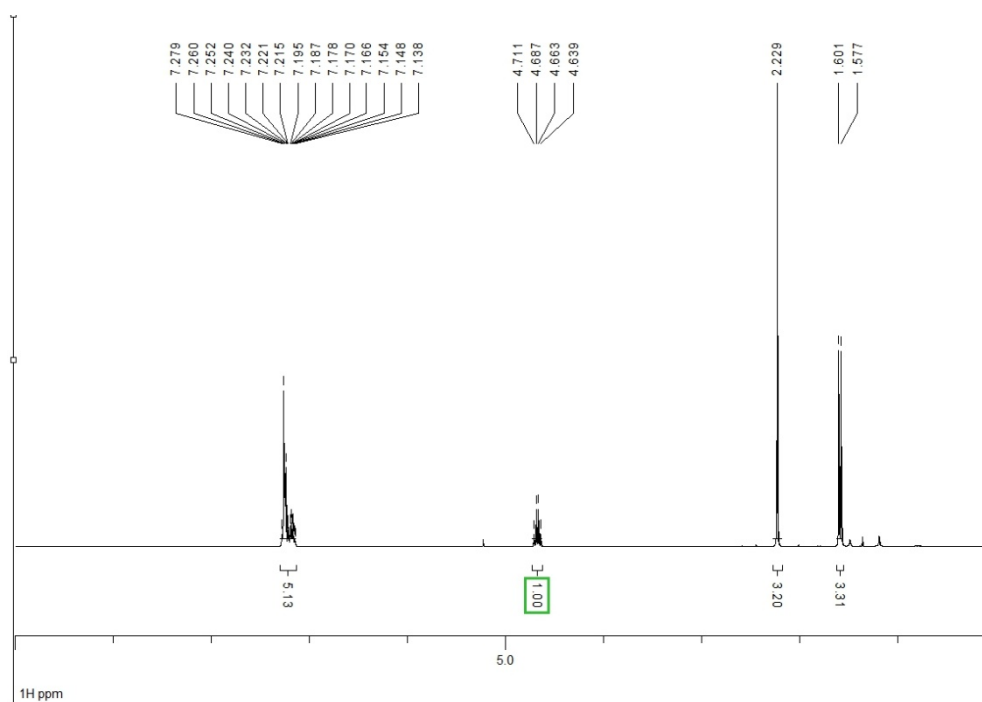


Figure S-13. ¹H-NMR spectrum (300 MHz, CDCl₃) of *S*-1-phenylethylethanethioate.

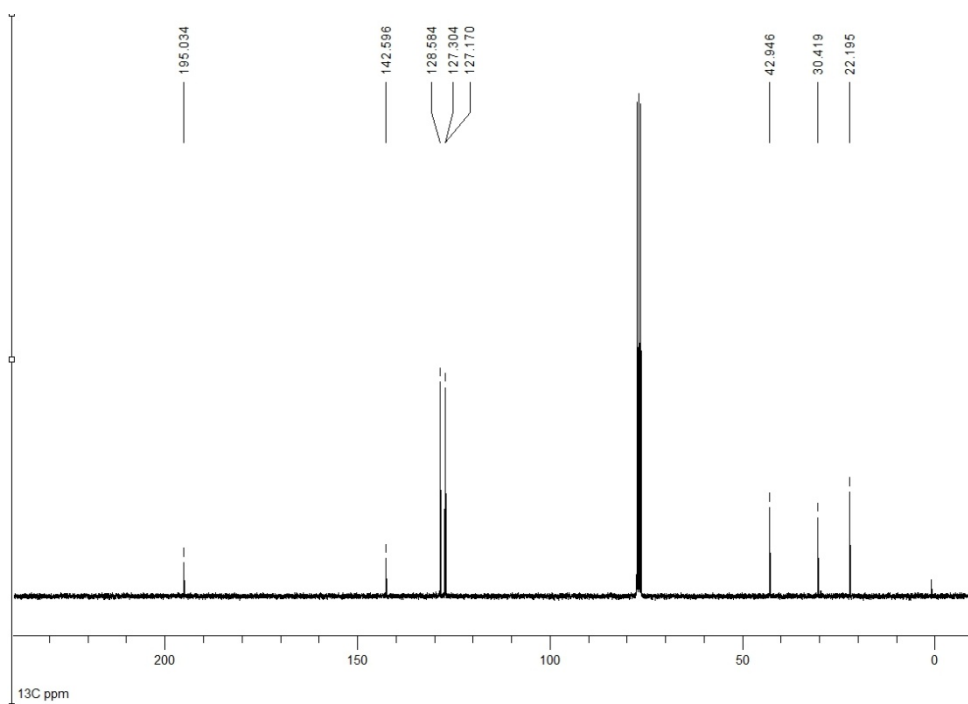
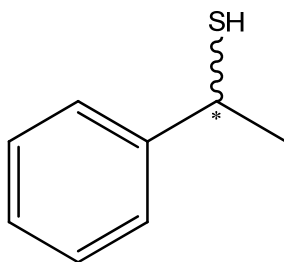


Figure S-14. ¹³C-NMR spectrum (75 MHz, CDCl₃) of *S*-1-phenylethylethanethioate.

6) Synthesis of *R*- and *S*-1-phenylethanethiol⁴



Lithium aluminum hydride (445 mg, 11.9 mmol) was dissolved in tetrahydrofuran (3 mL) at 0 °C and purged with argon for 10 min. A solution of the respective 1-phenylethylethanoate (770 mg, 4.3 mmol) in THF (5 mL) was added dropwise. The resulting mixture was stirred for 20 min at 0 °C and an additional 1 h at room temperature. After recooling to 0 °C, 3N hydrochloric acid was added until the entire solid dissolved. The biphasic mixture was dissolved with diethyl ether and water. The organic phase is separated and washed with brine, dried over Na₂SO₄ and concentrated to give the product as a colourless oil (540 mg, 90 %).
¹H-NMR (CDCl₃, 300 MHz): δ = 1.613 (d, 3 H, -CH₃), 1.930 (d, 1 H, -SH), 4.173 (m, 1H, -CH), 7.142 – 7.330 (m, 5H, -CH_{Ar}) ppm.

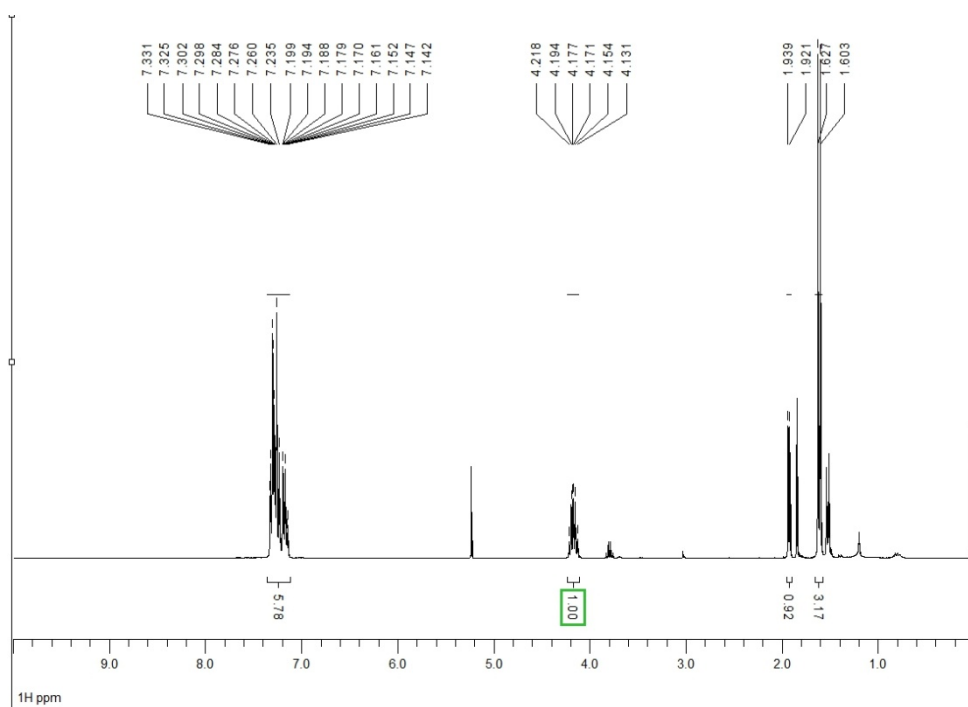


Figure S-15. ¹H-NMR spectrum (300 MHz, CDCl₃) of *R*-1-phenylethanethiol.

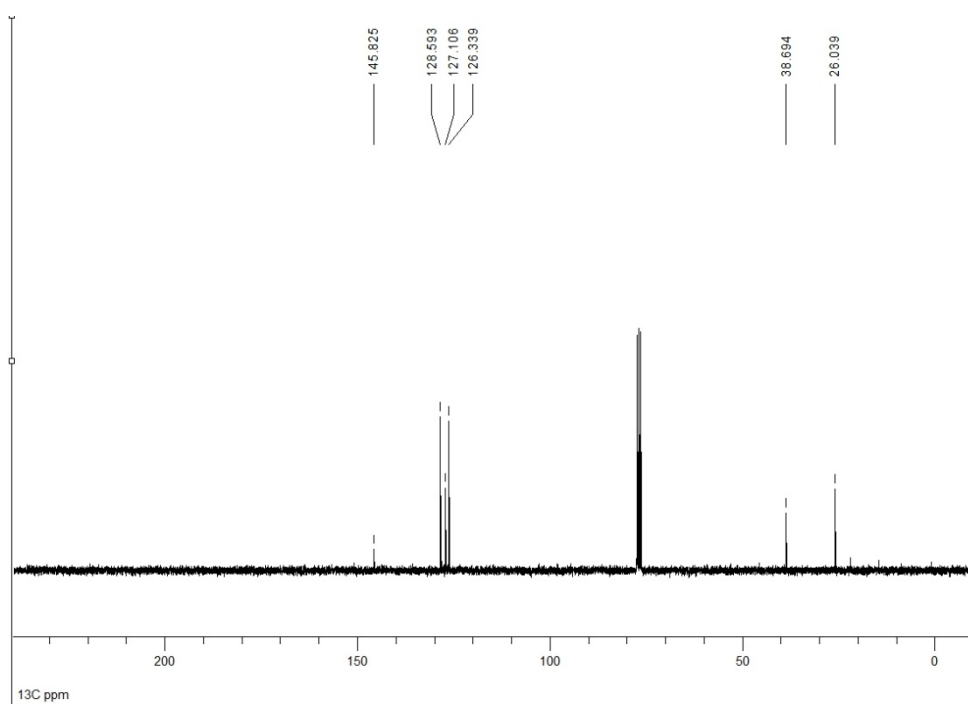


Figure S-16. ¹³C-NMR spectrum (75 MHz, CDCl₃) of *R*-1-phenylethanethiol.

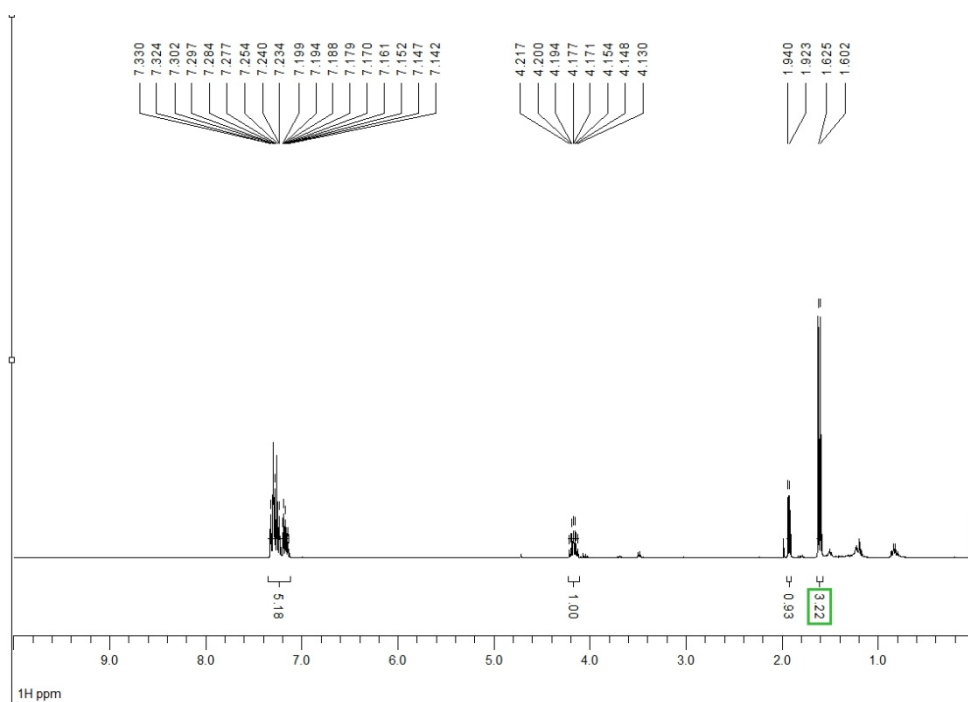


Figure S-17. ¹H-NMR spectrum (300 MHz, CDCl₃) of *S*-1-phenylethanethiol.

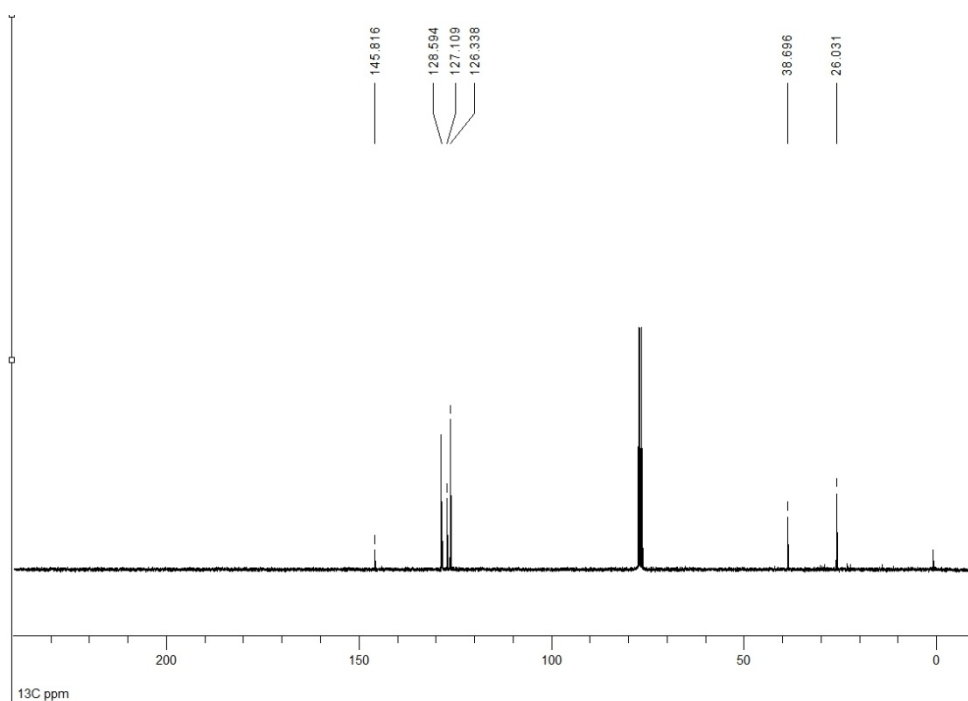


Figure S-18. ¹³C-NMR spectrum (75 MHz, CDCl₃) of *S*-1-phenylethanethiol.

7) CD spectra of the free ligands

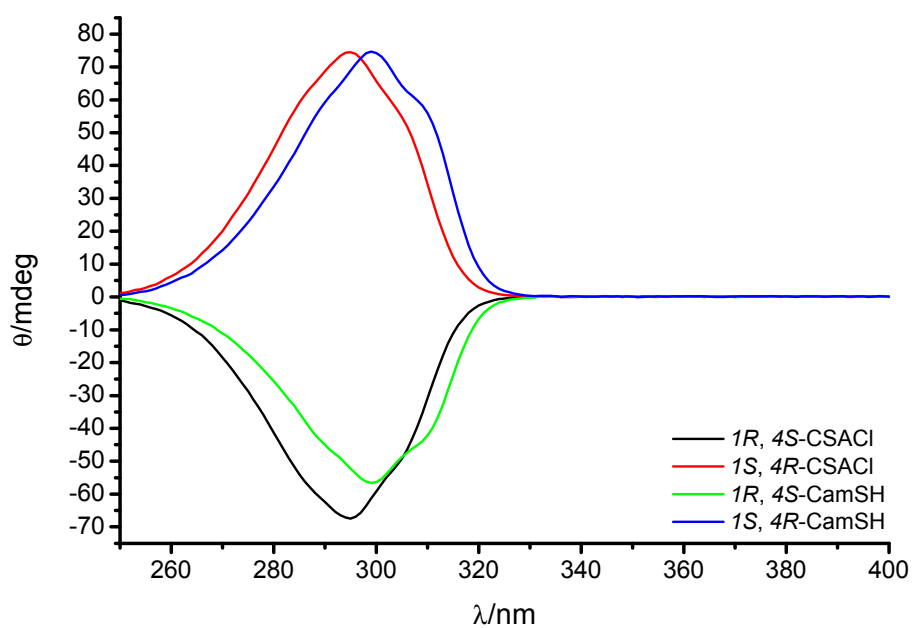


Figure S-19. CD spectra of camphorsulphonic acid chloride and camphorthiol.

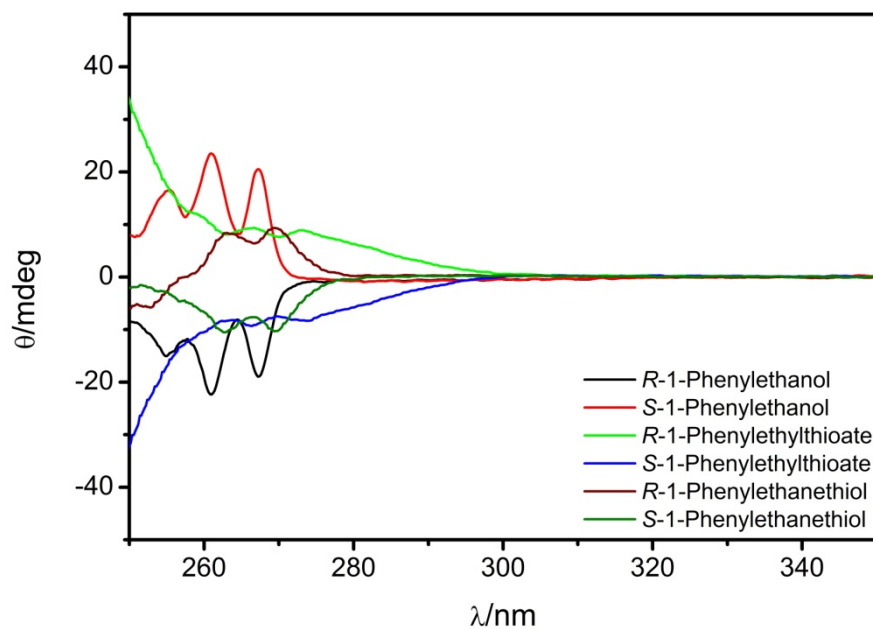


Figure S-20. CD spectra of 1-phenylethanol, 1-phenylethylthioate and 1-phenylethylthiol.

8) Synthesis and Size Selection of Cams-protected clusters^{5,6}

Synthesis of Au₂₅(CamS)₁₈. In a typical reaction, HAuCl₄*3H₂O (110 mg, 0.279 mmol) was dissolved in tetrahydrofuran (20 mL) and slowly stirred at 0 °C. A four-fold molar excess of the enantiopure thiol (220 mg, 1.194 mmol) was added and the solution was slowly stirred (250 rpm) for 30 min to form a brown solution. A freshly prepared solution of sodium borohydride (115 mg, 3.040 mmol) in cold MilliQ[®] water (10 mL) was added and the reaction mixture was vigorously stirred (1400 rpm) for 72 h. Over the course of the reaction time, the reaction mixture was allowed to warm up to room temperature.

The reaction was stopped by separation of insoluble byproducts over a PTFE syringe membrane and removal of the solvent in vacuo. Water residues were removed by addition of a water/methanol mixture and filtration over a recovered cellulose membrane.

Size Exclusion Chromatography of Au₂₅(CamS)₁₈. For SEC, the solvent (THF) was dried over sodium sulfate and purged with argon. 50 g of *BioBeads* were suspended in about 300 mL of THF and stirred over night under argon atmosphere. The swollen stationary phase was given on a column (2 cm in diameter) to give a column height of about 100 cm. The packed column was washed with about 5 times the column volume. The raw material was given on the column and chromatographed at an elution speed of ca 0.7 mL/min.

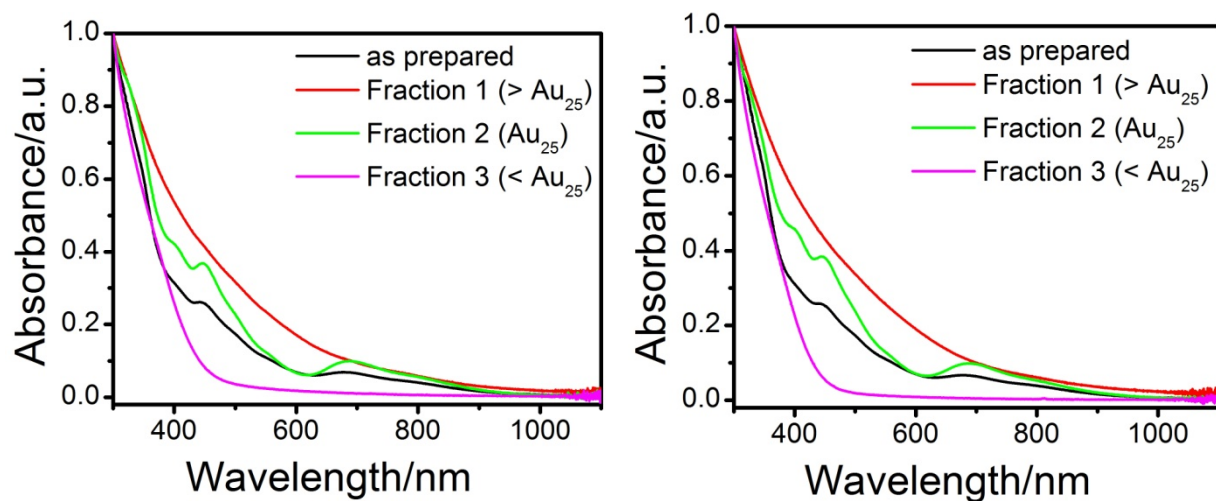


Figure S-21. left: UV-Vis spectra of 1*R*, 4*S*-CamS-protected clusters before (black) and after SEC (red, green, magenta). Right: UV-Vis spectra of 1*S*, 4*R*-CamS-protected clusters before (black) and after SEC (red, green, magenta).

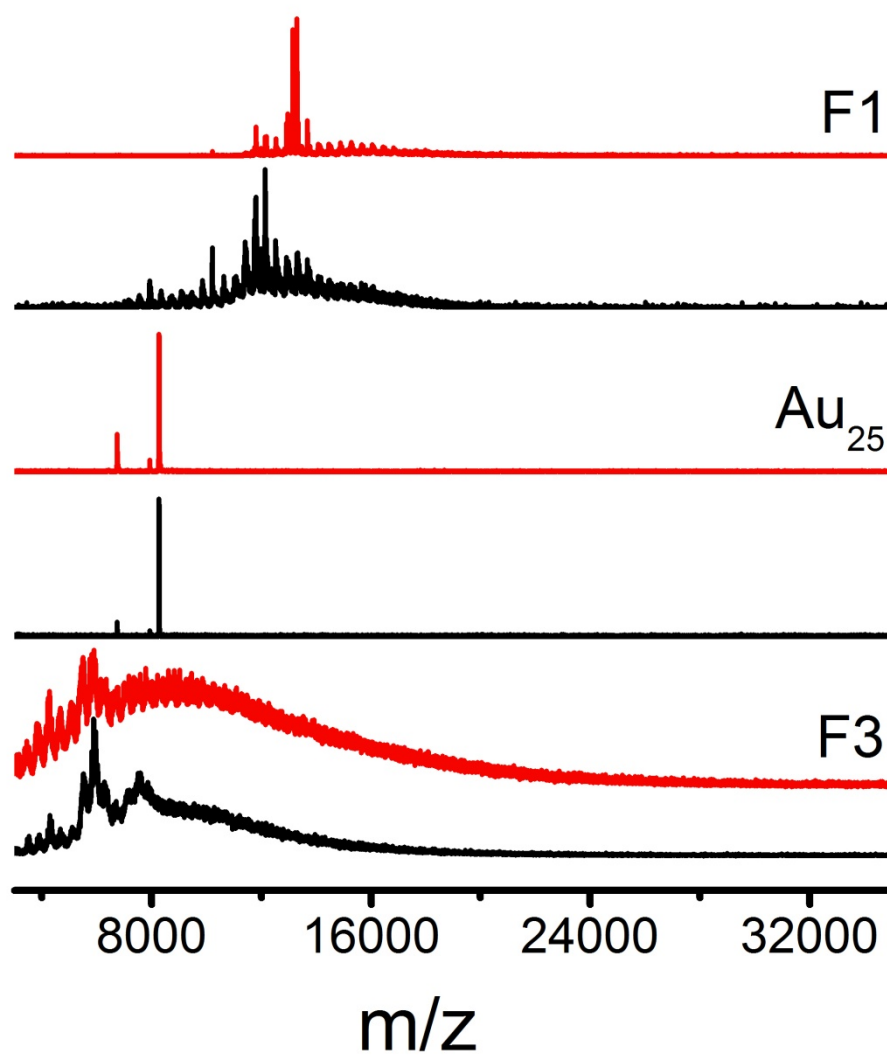


Figure S-22. MALDI mass spectra of camphorthiolate-protected gold clusters. Top: Fraction **1**, heavier than Au_{25} ; middle: fraction **2** (Au_{25}); bottom: fraction **3**, presumably $Au_{18}(SR)_{13}$. Black: 1*S*, 4*R*-CamS; Red: 1*R*, 4*S*-CamS.

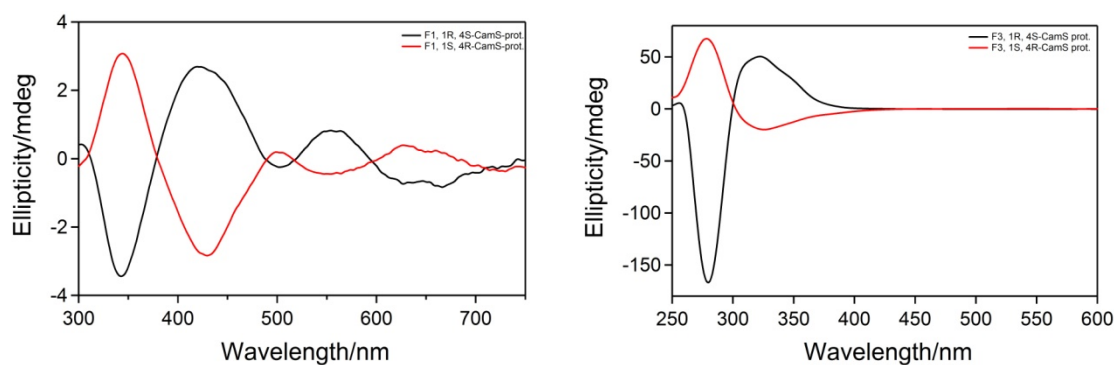


Figure S-23. CD spectra of $\text{Au}_m(\text{CamS})_n$ after SEC. Left: Fraction 1; Right: Fraction 3. Black: 1R, 4S-CamS; red: 1S, 4R-CamS. The spectra of $\text{Au}_{25}(\text{CamS})_{18}$ are shown in the manuscript.

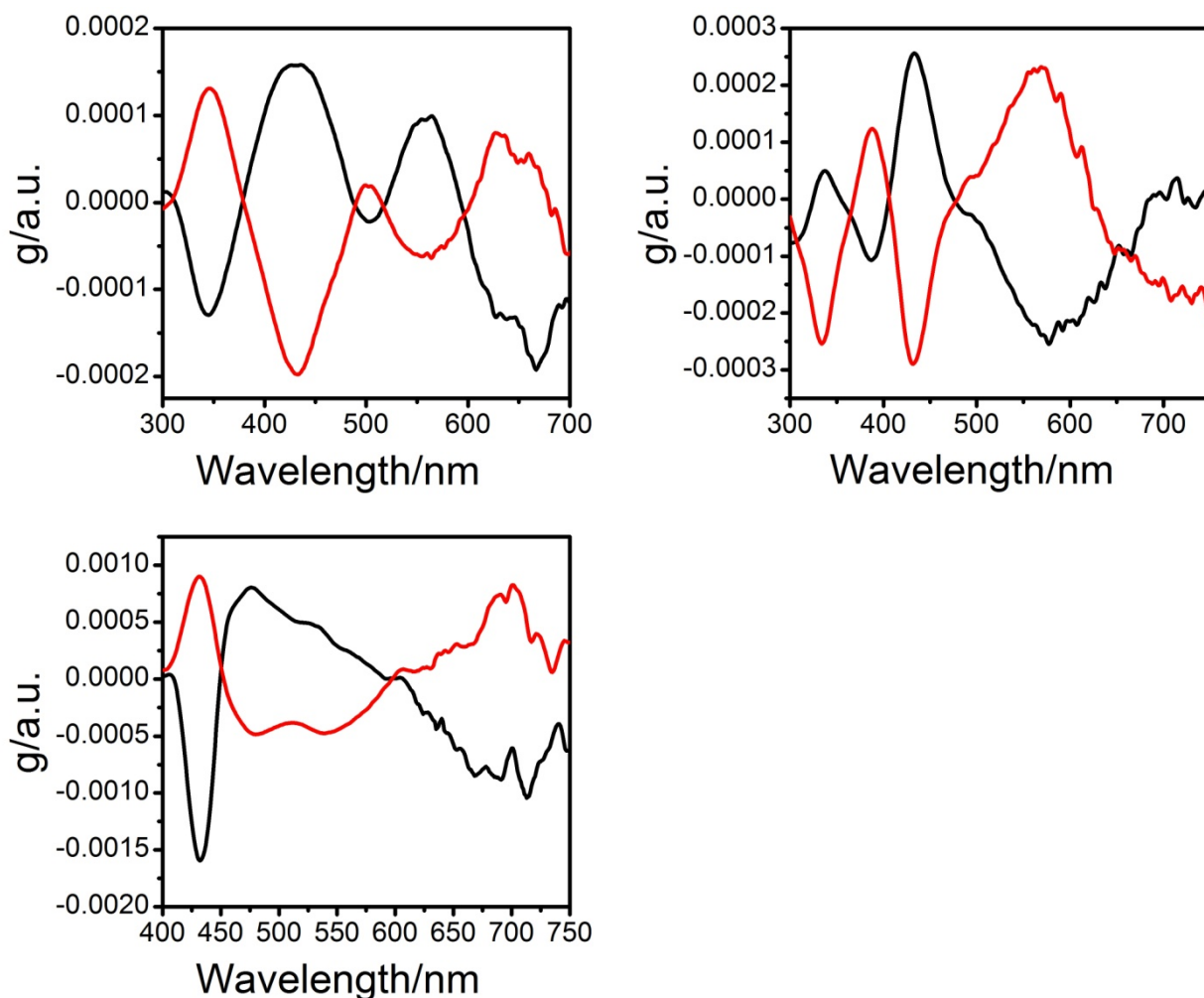


Figure S-24. Anisotropy factors of $\text{Au}_n(\text{CamS})_m$. Top left: Fraction 1, top right: Au_{25} ; bottom left: Fraction 3. Black: 1R, 4S-CamS; red: 1S, 4R-CamS.

9) Synthesis of 1-PET-protected clusters⁵

Synthesis of the nanoclusters. 130 mg (0.330 mmol) of tetrahydrochloric acid trihydrate were dissolved in 20 mL of tetrahydrofuran and the solution was cooled to 0 °C. 170 µL (1.278 mmol) of the respective 1-phenylethanethiol (racemic or enantiopure) were added and the solution was slowly (250 rpm) stirred at 0 °C for 30 min. 137 mg (36.226 mmol) of sodium borohydride were dissolved in 5 mL of ice-cooled water and added all at once. The stirring speed was increased to 1250 rpm and the reaction was allowed to warm up to room temperature over the course of 3 h. For aging of the resulting dark brown clusters, the solution was stirred for another 60 h. After that, the solution was filtered over a PTFE syringe filter (0.2 µm) and the solvent was removed by rotary evaporation. Residual water was washed away by the addition of ethanol and filtration (recovered cellulose, 0.2 µm) of the resulting suspension. The filtrate was collected, redissolved in THF or methylene chloride, concentrated and precipitated from ethanol. Overall, five cycles of precipitation/filtration and redissolving were performed. The clusters were eventually dissolved in methylene chloride and passed through a PTFE syringe filter to remove insoluble material. Clusters were stored dry and under inert gas, protected from light.

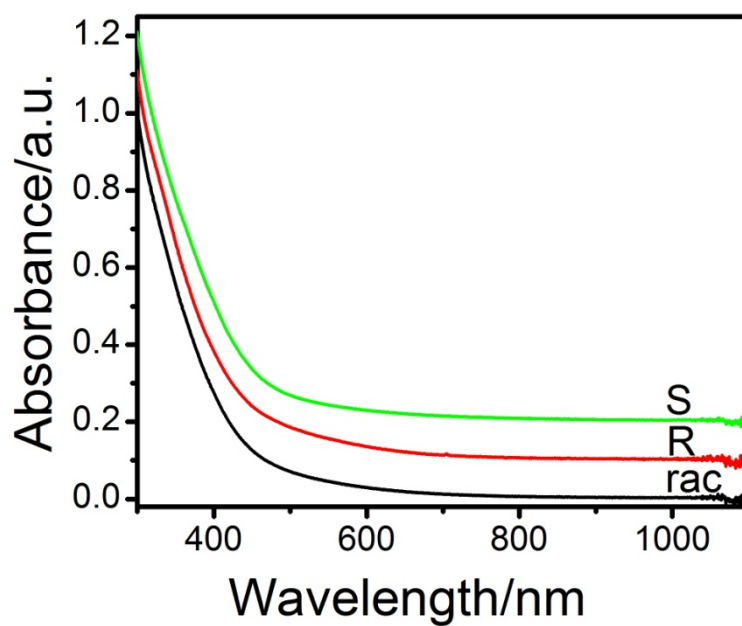


Figure S-25. UV-Vis spectra of *rac*-1-PET-, *R*-1-PET and *S*-1-Pet-protected gold clusters.

The spectra are offset vertically for clarity.

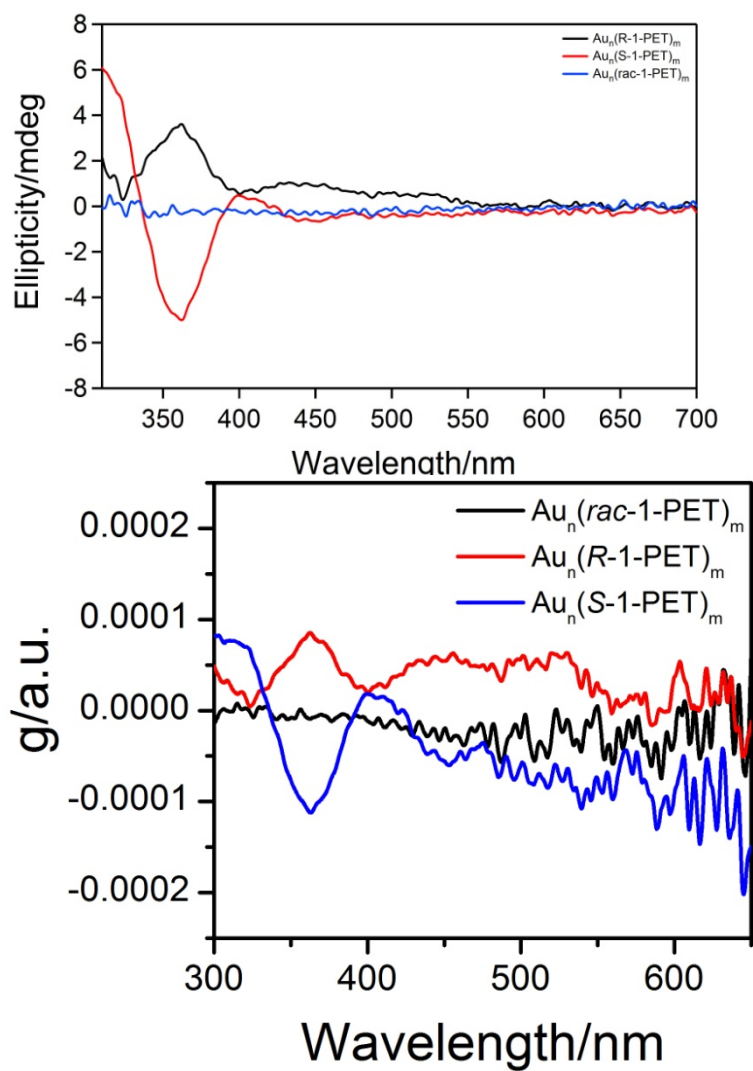


Figure S-26. top: CD spectra of 1-PET-protected Au clusters. Bottom: corresponding anisotropy factors. Black: *R*-1-PET; red. *S*-1-PET; blue: *rac*-1-PET.

10) A closer look to the MALDI spectra of 1-PET-protected clusters

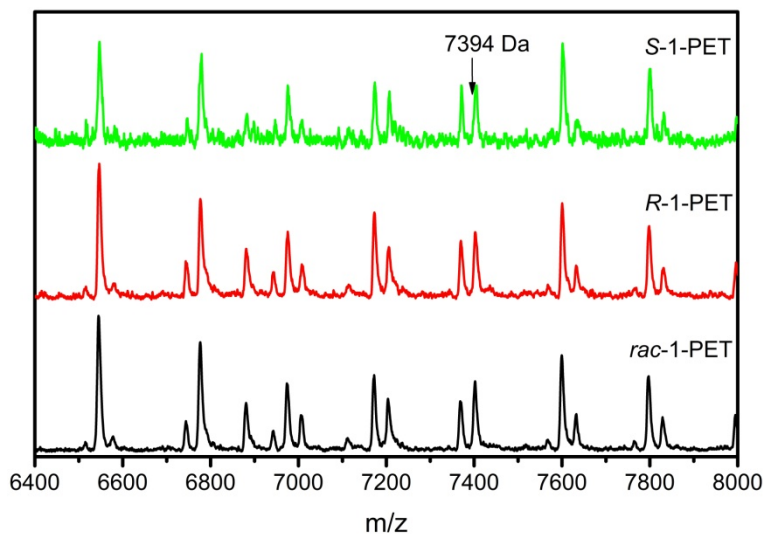


Figure S-27. MALDI mass spectra of 1-PET-protected clusters in the mass range of 6,400 – 8,000 Da. The expected position of $\text{Au}_{25}(\text{1-PET})_{18}$ (calcd: 7394 da) is marked by an arrow. Two signals at 7401 and 7371 Da are neighbouring the expected Au_{25} species. This may be due to a drift in the mass spectrometer but this is unlikely as the peaks are highly reproducible (spectra were not measured the same day).

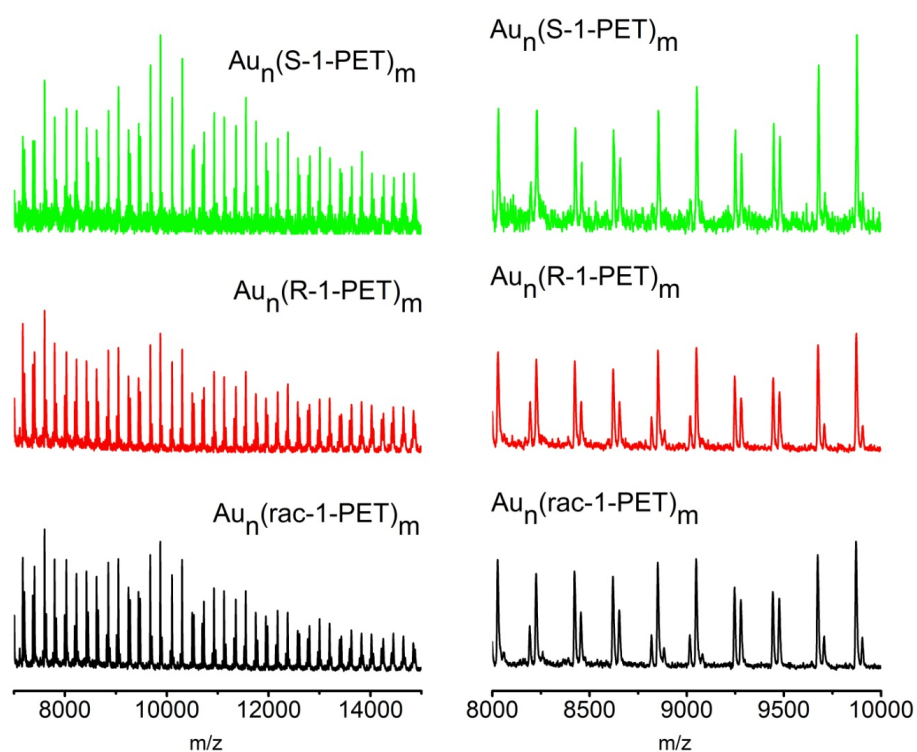


Figure S-28. MALDI mass spectra of 1-PET-protected clusters in the mass range of 7,000 – 15,000 Da (left) and 8,000 – 10,000 Da (right). The spectra are highly reproducible between the different reaction batches and do not depend on the enantiomeric purity of the used ligand.

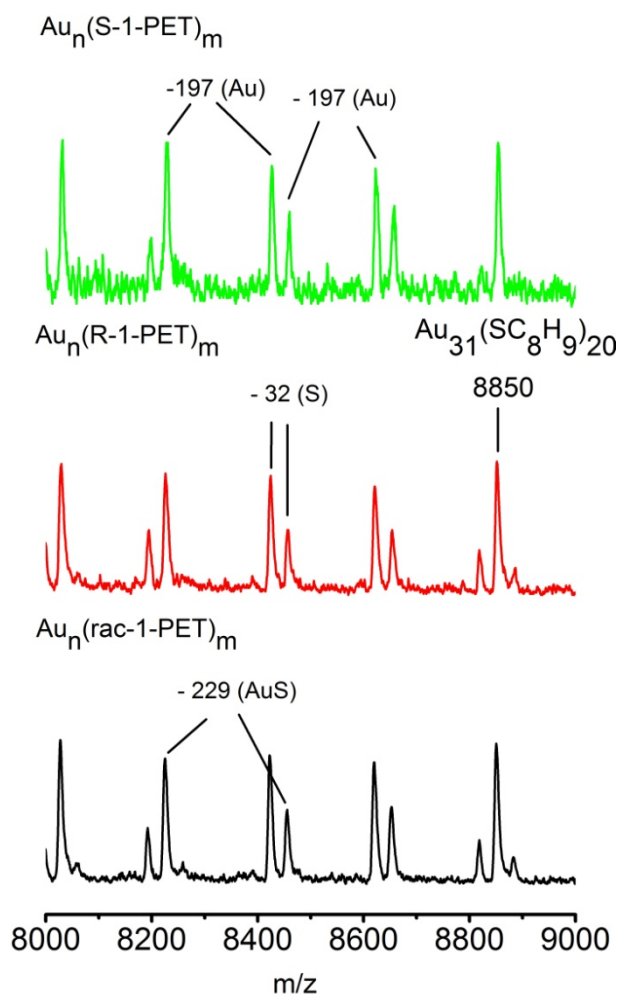


Figure S-29. MALDI mass spectrum of 1-PET-protected clusters in the mass range of 8,000 – 9,000 Da. The 229 Da distance between peaks is assigned to a difference of AuS (the loss of the organic backbone must have occurred earlier; thus, the signals are fragments of a parent cluster). The 32 Da difference in a signal ‘doublet’ corresponds to loss of a sulfur atom. The signal at 8850 can be assigned to intact $\text{Au}_{31}(\text{1-PET})_{20}$.

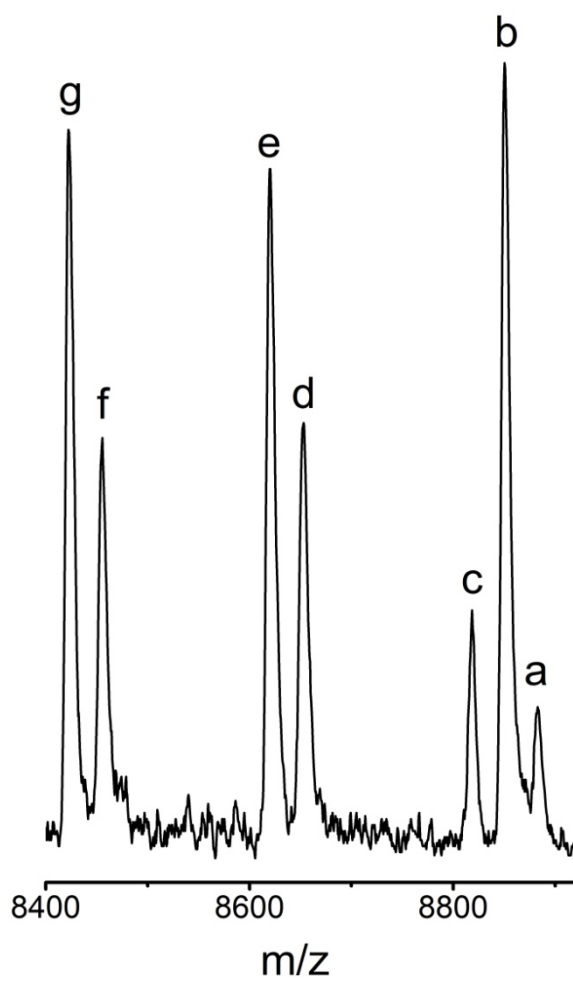


Figure S-30. Zoom in to the MALDI mass spectrum of $\text{Au}_n(\text{rac-1-PET})_m$ (8,400 – 8,920 Da).

Table S-1. Masses for the peaks assigned in Figure S-30 and their relationships (subtraction of masses in row by masses in column).

Peak (m/z)	a (8883)	b (8850)	c (8818)	d (8652)	e (8620)	f (8455)	g (8423)
a (8883)		-33 (S)	- 65 (S ₂)	- 231 (AuS)	-263 (AuS ₂)	-428	-460
b (8850)		Au ₃₁ (SC ₈ H ₉) ₂₀	-32 (S)	-198 (Au)	-230	-395	-427
c (8818)				-166	-198 (Au)	-363	-395
d (8652)				Au ₃₀ (SC ₈ H ₉) ₂₀	-32 (S)	-197 (Au)	-229 (AuS)
e (8620)						-165	-197 (Au)
f (8455)						Au ₂₉ (SC ₈ H ₉) ₂₀	-32 (S)

A closer look to mass differences in the assigned peaks in Table S-1 reveals the following:

Peak **b** is assigned to be the cluster Au₃₁(SC₈H₉)₂₀; either an intact cluster or a fragment of a different parent cluster. As the mass difference of 32 Da in peak **c** is assigned to loss of a single sulphur atom, the fragment **c** cannot stem from peak **b**. Similar argumentation holds true for peak **d** (-198 Da (loss of one Au atom)). The other peaks (**e** – **g**) similarly differ on masses of 32, 197 and 229 Da, respectively, corresponding to loss of S, Au and AuS, respectively.

In conclusion, different fragmentation patterns overlay; hence it is difficult to identify meaningful species (parent clusters) in the cluster mixture. Interestingly, no peaks for loss of the organic backbone (C₈H₉, 105 Da or SC₈H₉, 137 Da) are found.

11) IR spectrum of camphorthiol-protected clusters

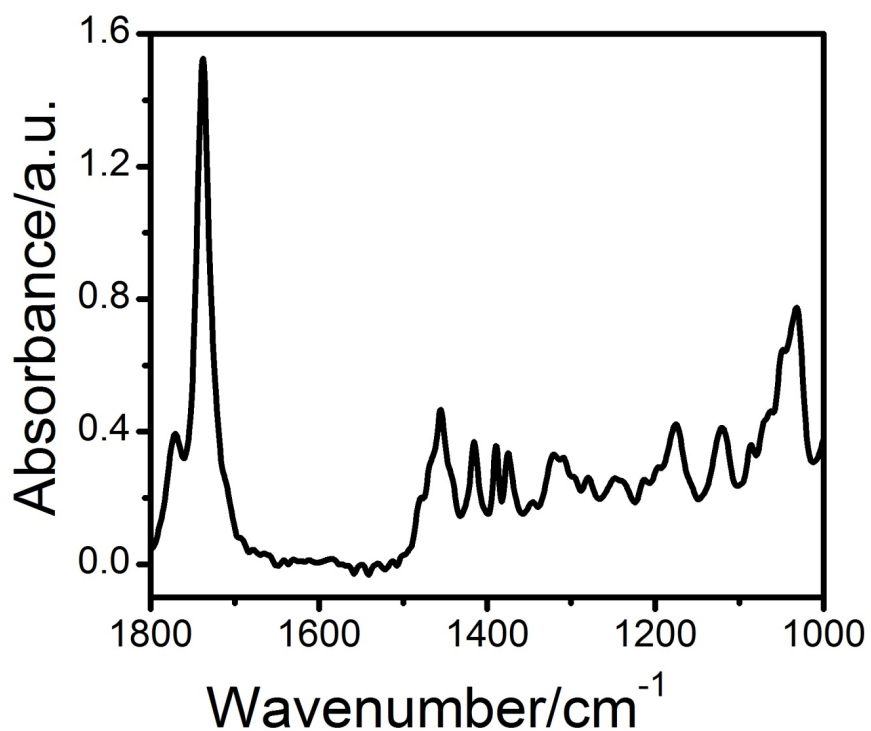


Figure S-31. IR-spectrum (CD_2Cl_2 solution) of 1*S*, 4*R*-CamS-protected clusters (prior to size-separation). The transition of the keto-group in the ligand is clearly visible (1740 cm^{-1}), indicating that it is not reduced upon NaBH_4 treatment during synthesis of the clusters.

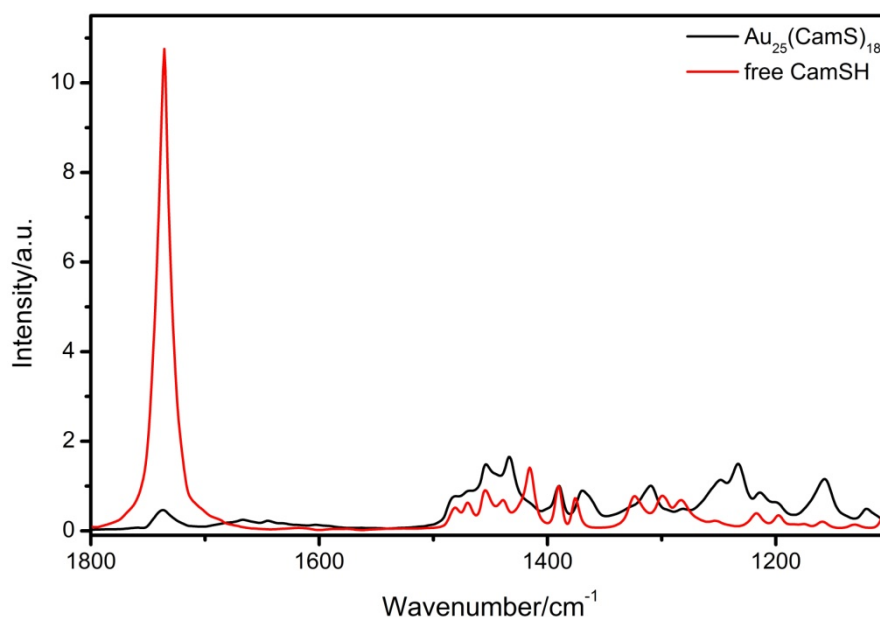


Figure S-32. IR-spectra (CD_2Cl_2 solution) of $\text{Au}_{25}(\text{Cams})_{18}$ and free camphorhiol. The spectra are normalised to the band at 1390 cm^{-1} for comparison. The intensity of the carbonyl band at 1740 cm^{-1} decreases by factor 20. This, in combination with the mass spectra, strongly suggests nearly complete reduction of the keto group (in Au_{25}).

¹ Sigma-Aldrich, NMR-solvents – Unsurpassed Quality for Peak Performance, **2009**.

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