Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Ligand Engineering of Circularly Polarized Luminescence Inversion and Enhancement for Chiral Ag_6 Nanoclusters

Hui Chen, Xiangyang Zhang, Kuo Fu, Xuejuan Wang and Guofeng Liu*

School of Chemical Science and Engineering, Advanced Research Institute, Tongji University, Shanghai, 200092, P. R. China

E-mail: liuguofeng@tongji.edu.cn

1 Material.

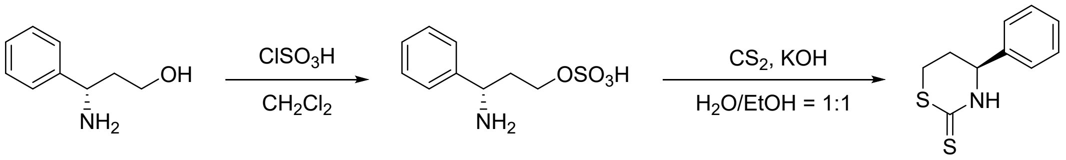
(S)-3-amino-3-phenylpropan-1-ol, (R)-3-amino-3-phenylpropan-1-ol, chlorosulphonic acid, carbon disulfide potassium hydroxide, triethylamine, (S)-3-aminobutan-1-ol, (R)-3-aminobutan-1-ol, 30% hydrogen peroxide and silver acetate were purchased from Shanghai Titan Scientific Co., Ltd. The organic solvents were purchased from Shanghai Titan Scientific Co., Ltd. without further purification.

2 Characterization

NMR spectra were recorded on a Bruker AVANCE III HD 400 MHz and 600 MHz Instrument at ambient temperature. Circular dichroism (CD) spectra were obtained using JASCO J-810 CD spectrometer with a bandwidth of 1.0 nm, scanning speed of 500 nm min^{-1}, and data integration time of 1 s. CD spectra of samples were recorded in the UV/Vis region (250–450 nm) using a 0.1 mm quartz cuvette. Fluorescence spectra were measured by F-4500 fluorescence spectrophotometer. CPL measurements were recorded on JASCO CPL-300 spectrometer, with the Ex and Em slit width of 3000 µm, scanning speed of 500 nm min^{-1}, and data integration time of 1 s. CPL spectra of samples were measured using a 0.1 mm quartz cuvette. The single crystal data were collected from a shock-cooled single crystal at 100(2) K on a Bruker D8 VENTURE dual wavelength Mo three-circle diffractometer with a microfocus sealed X-ray tube using a mirror optics as monochromator and a Bruker PHOTON II detector. The QY were measured using an Edinburgh FLS1000 equipped with a xenon lamp.

3 Synthesis

Synthesis of S-SPh



(*S*)-4-phenyl-1,3-thiazinane-2-thione

(S)-4-phenyl-1,3-thiazinane-2-thione (S-SPh).

Chlorosulphonic acid (1.0 mL, 14.5 mmol) was added dropwise to a solution of (S)-3-amino-3-phenylpropan-1-ol (2.0 mL, 13.8 mmol) in CH_2Cl_2 (20 mL) under a constant flow of N_2 at 0°C. The reaction mixture was stirred for 15 h at rt after which the solvent was removed in vacuo to afford a white solid. The white solid was triturated with MeOH and dried under reduced pressure to afford 2.32 g of (S)-3-amino-3-phenylpropyl hydrogen sulfate (10.0 mmol, 72%), which was pure enough by ^{1}H NMR and required no further purification. Then, CS_2 (0.72 mL, 12 mmol) was added dropwise to (S)-3-amino-3-phenylpropyl hydrogen sulfate (2.32 g, 10.0 mmol) under N_2 at rt. A solution of KOH (1.23 g, 22 mmol in 1:1 H_2O/EtOH 20 mL) was added dropwise to the reaction mixture at 0 °C. The resulting solution was then heated to reflux and stirred for 2 h, after which it was further stirred overnight at rt. Then, it was cooled with an ice-water bath. The white precipitate was filtered and rinsed with cold water. It was dissolved in CH_2Cl_2, and dried over anhydrous Na_2SO_4, and the solvent was removed in vacuo to obtain a white solid. The crude product was purified by recrystallization in CH_2Cl_2/hexane to obtain the (S)-4-phenyl-1,3-thiazinane-2-thione (S-SPh, 1.8 g, 62% for two steps).

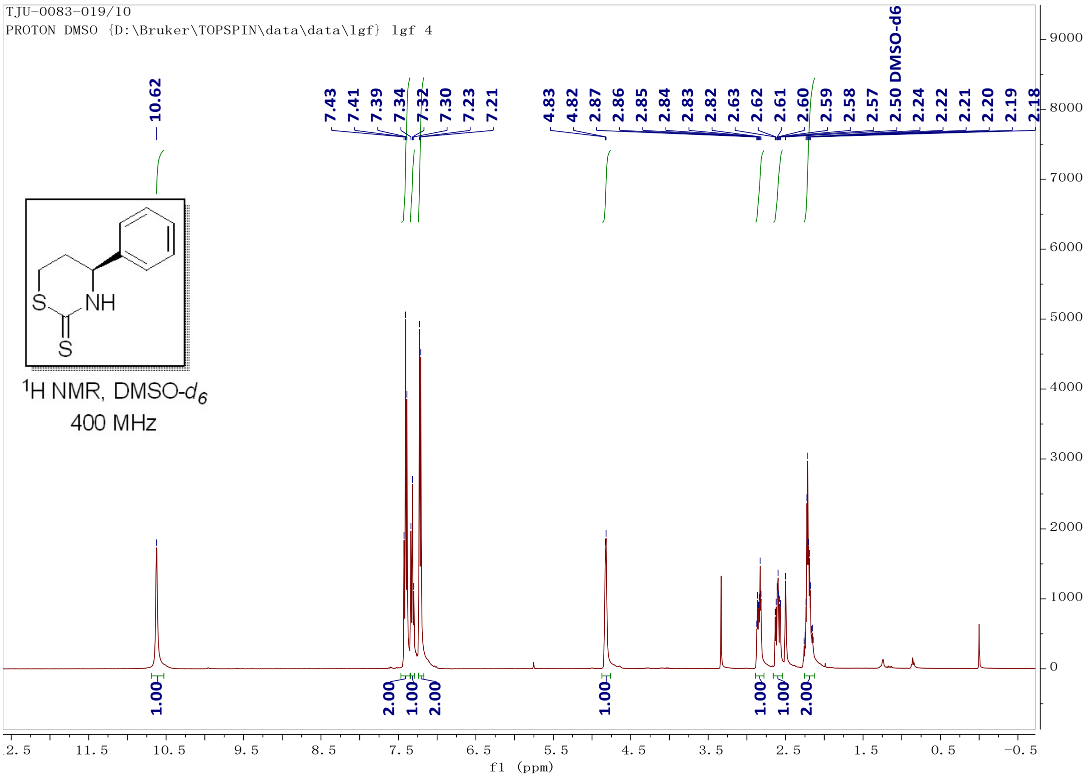
Physical State: white solid.

TLC: $R_f = 0.32$ (PE/EtOAc = 1:1).

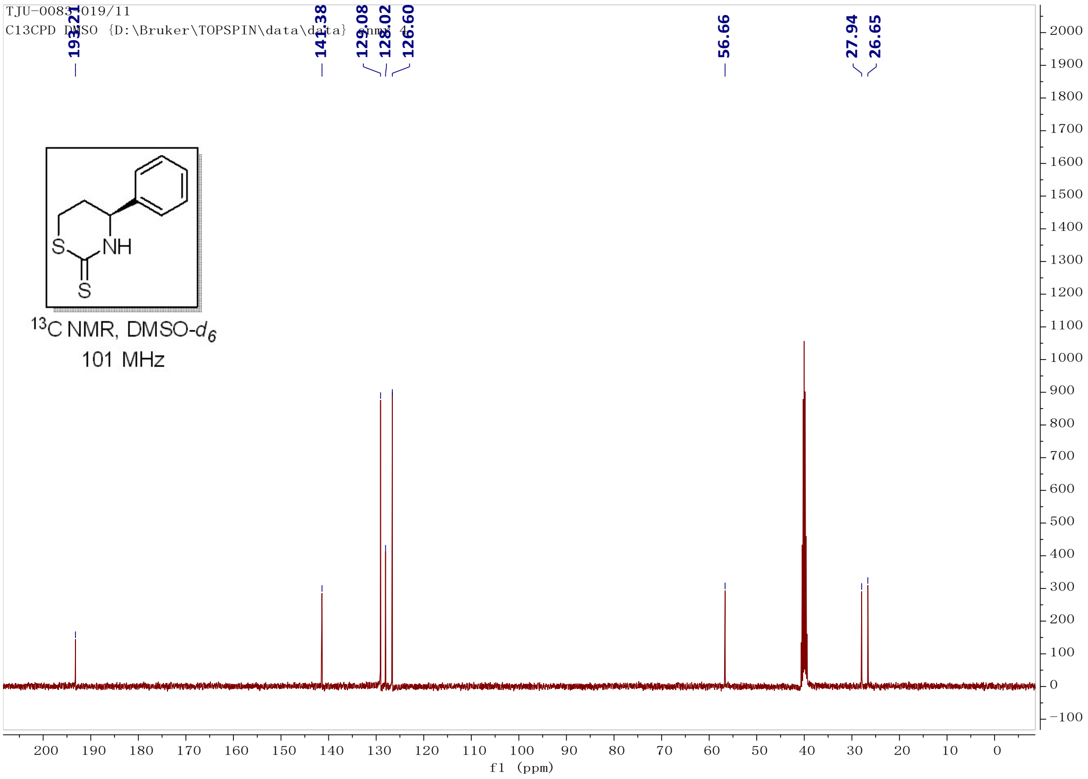
^{1}H NMR (400 MHz, DMSO-*d$_6$*) δ 10.62 (s, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 7.3 Hz, 2H), 4.82 (d, 1H), 2.89 – 2.78 (m, 1H), 2.66 – 2.54 (m, 1H), 2.26 – 2.12 (m, 2H).

^{13}C NMR (101 MHz, DMSO-*d$_6$*) δ 193.21, 141.38, 129.08, 128.02, 126.60, 56.66, 27.94, 26.65.

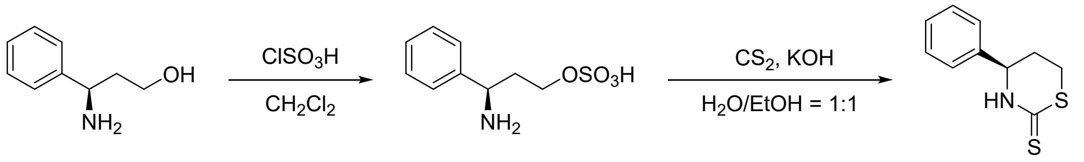
^{1}H spectra of S-SPh



^{13}C spectra of S-SPh



Synthesis of R-SPh



(*R*)-4-phenyl-1,3-thiazinane-2-thione

(R)-4-phenyl-1,3-thiazinane-2-thione (R-SPh).

Chlorosulphonic acid (0.5 mL, 7 mmol) was added dropwise to a solution of (R)-3-amino-3-phenylpropan-1-ol (1 g, 6.6 mmol) in CH_2Cl_2 (15 mL) under a constant flow of N_2 at 0°C. The reaction mixture was stirred for 15 h at RT after which the solvent was removed in vacuo to afford a white solid. The white solid was triturated with MeOH and dried under reduced pressure to afford 1.04 g of (R)-3-amino-3-phenylpropyl hydrogen sulfate (4.5 mmol, 68%), which was pure enough by ^1H NMR and required no further purification. Then, CS_2 (0.4 mL, 5.3 mmol) was added dropwise to (R)-3-amino-3-phenylpropyl hydrogen sulfate (1.04 g, 4.4 mmol) under N_2 at RT. A solution of KOH (560 mg, 10 mmol in 1:1 H_2O/EtOH 20 mL) was added dropwise to the reaction mixture at 0 °C. The resulting solution was then heated to reflux and stirred for 2 h, after which it was further stirred overnight at rt. Then, it was cooled with an ice-water bath. The white precipitate was filtered and rinsed with cold water. It was dissolved in CH_2Cl_2, and dried over anhydrous Na_2SO_4, and the solvent was removed in vacuo to obtain a white solid. The crude product was purified by recrystallization in CH_2Cl_2/hexane to obtain the (R)-4-phenyl-1,3-thiazinane-2-thione (R-SPh, 820 mg, 60% for two steps).

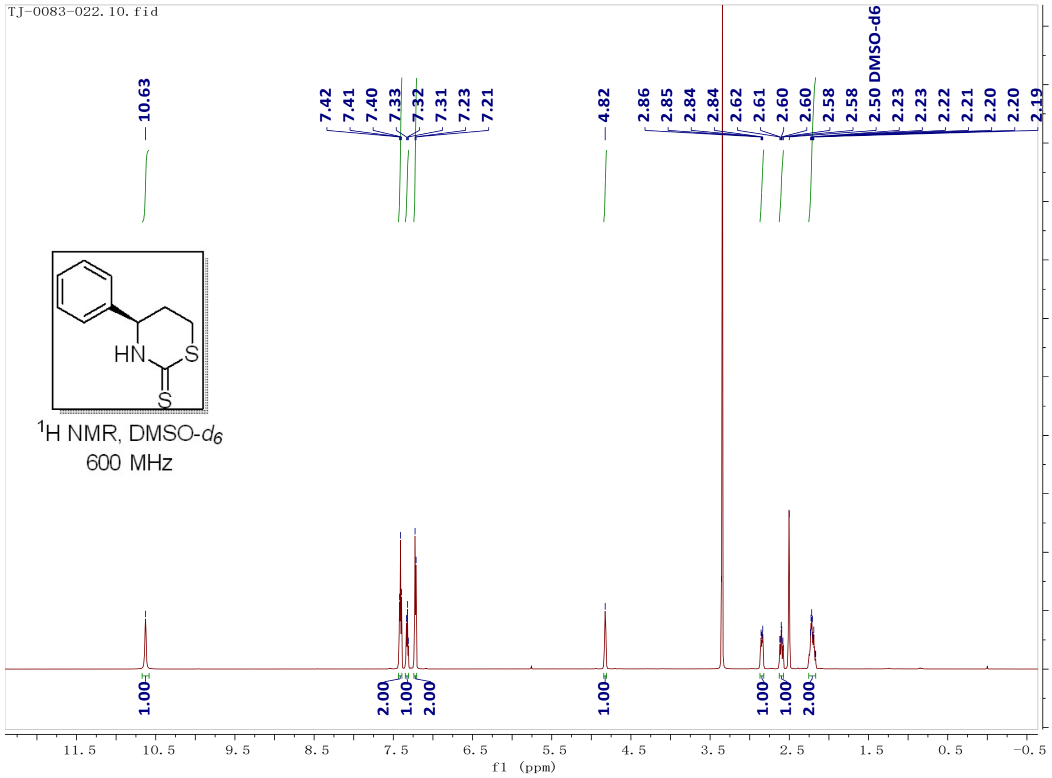
Physical State: white solid.

TLC: R_f = 0.32 (PE/EtOAc = 1:1).

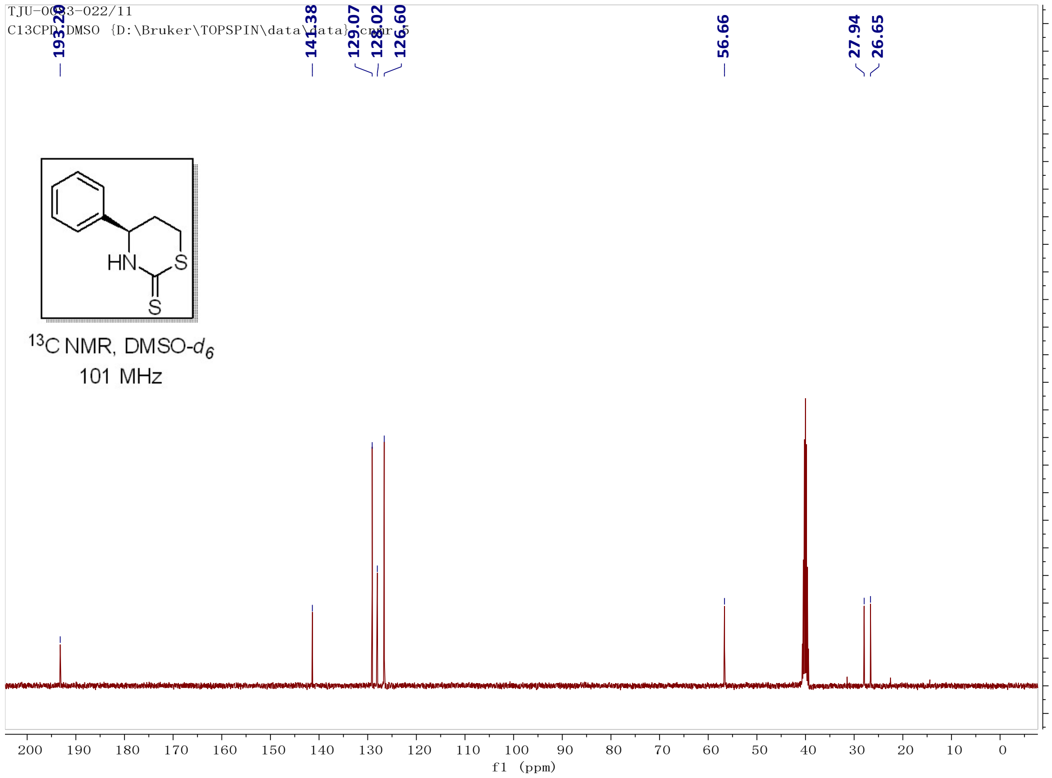
^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 10.63 (s, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 2H), 4.82 (s, 1H), 2.87 – 2.82 (m, 1H), 2.60 (td, *J* = 12.4, 11.5, 3.7 Hz, 1H), 2.25 – 2.17 (m, 2H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 193.20, 141.38, 129.07, 128.02, 126.60, 56.66, 27.94, 26.65.

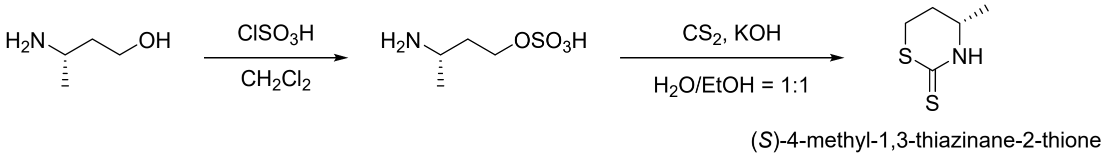
^{1}H spectra of R-SPh



^{13}C spectra of R-SPh



Synthesis of S-SMe



(S)-4-methyl-1,3-thiazinane-2-thione (S-SMe).

Chlorosulphonic acid (0.7 mL, 10.5 mmol) was added dropwise to a solution of (S)-3-aminobutan-1-ol (890 mg, 10 mmol) in CH_2Cl_2 (25 mL) under a constant flow of N_2 at 0°C. The reaction mixture was stirred for 15 h at RT after which the solvent was removed in vacuo to afford a white solid. The white solid was triturated with MeOH and dried under reduced pressure to afford 1.18 g of (S)-3-aminobutyl hydrogen sulfate (7 mmol, 70%), which was pure enough by ^1H NMR and required no further purification. Then, CS_2 (0.63 mL, 10.5 mmol) was added dropwise to (R)-3-aminobutyl hydrogen sulfate (1.18 g, 7 mmol) under N_2 at RT. A solution of KOH (840 mg, 15 mmol in 1:1 H_2O/EtOH 25 mL) was added dropwise to the reaction mixture at 0 °C. The resulting solution was then heated to reflux and stirred for 2 h, after which it was further stirred overnight at rt. Then, it was cooled with an ice-water bath. The white precipitate was filtered and rinsed with cold water. It was dissolved in CH_2Cl_2, and dried over anhydrous Na_2SO_4, and the solvent was removed in vacuo to obtain a white solid. The crude product was purified by recrystallization in CH_2Cl_2/hexane to obtain the (S)-4-methyl-1,3-thiazinane-2-thione (S-SMe, 970 mg, 66% for two steps).

TLC: $R_f = 0.40$ (PE/EtOAc = 1:1).

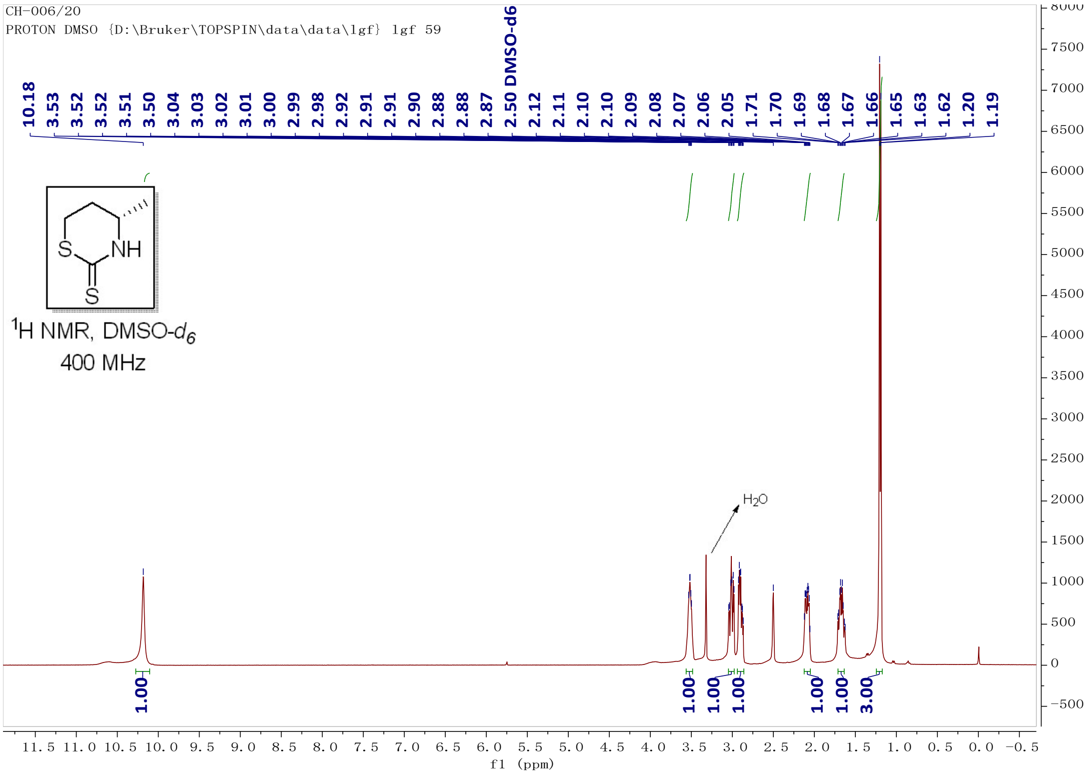
Physical State: white solid.

TLC: $R_f = 0.40$ (PE/EtOAc = 1:1).

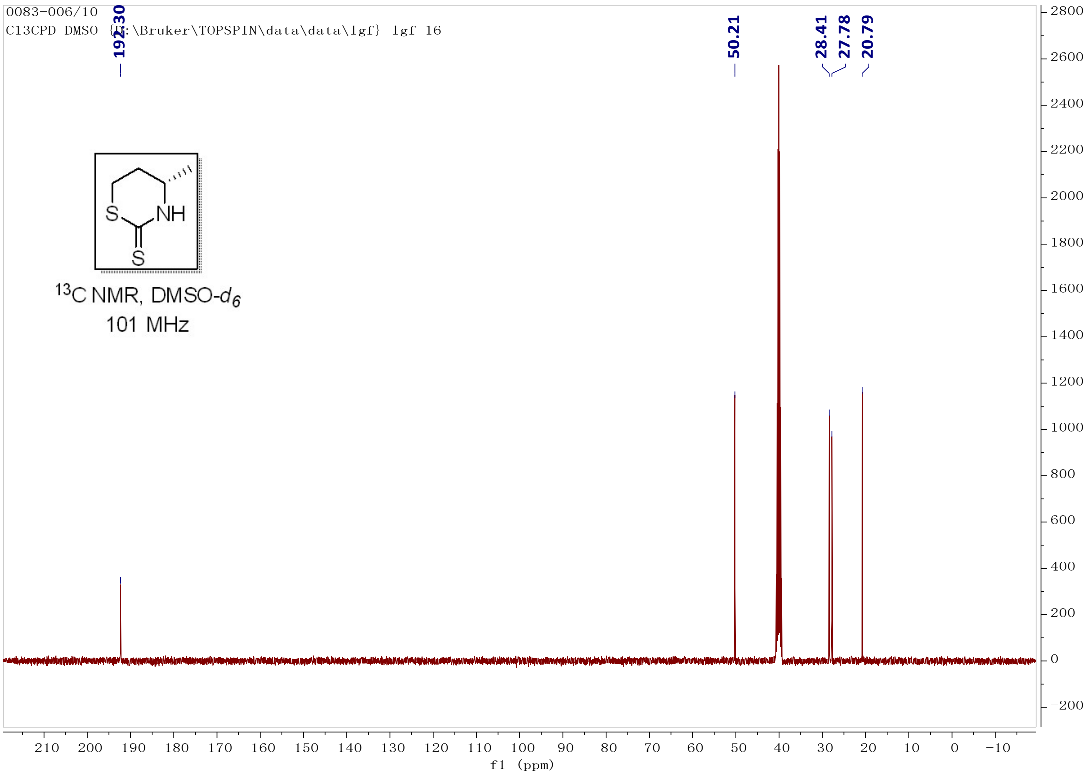
^{1}H NMR (400 MHz, DMSO-*d₆*) δ 10.18 (s, 1H), 3.56 – 3.48 (m, 1H), 3.01 (ddd, *J* = 13.3, 9.9, 3.7 Hz, 1H), 2.94 – 2.86 (m, 1H), 2.12 – 2.05 (m, 1H), 1.71 – 1.64 (m, 1H), 1.20 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-*d₆*) δ 192.30, 50.21, 28.41, 27.78, 20.79.

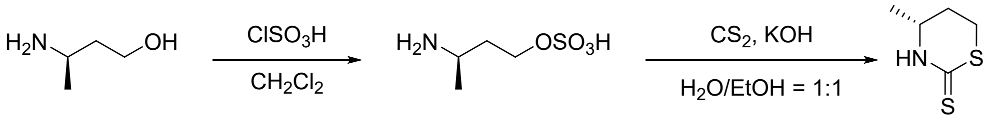
^{1}H spectra of S-SMe



^{13}C spectra of S-SMe



Synthesis of R-SMe



(*R*)-4-methyl-1,3-thiazinane-2-thione

(R)-4-methyl-1,3-thiazinane-2-thione (R-SMe).

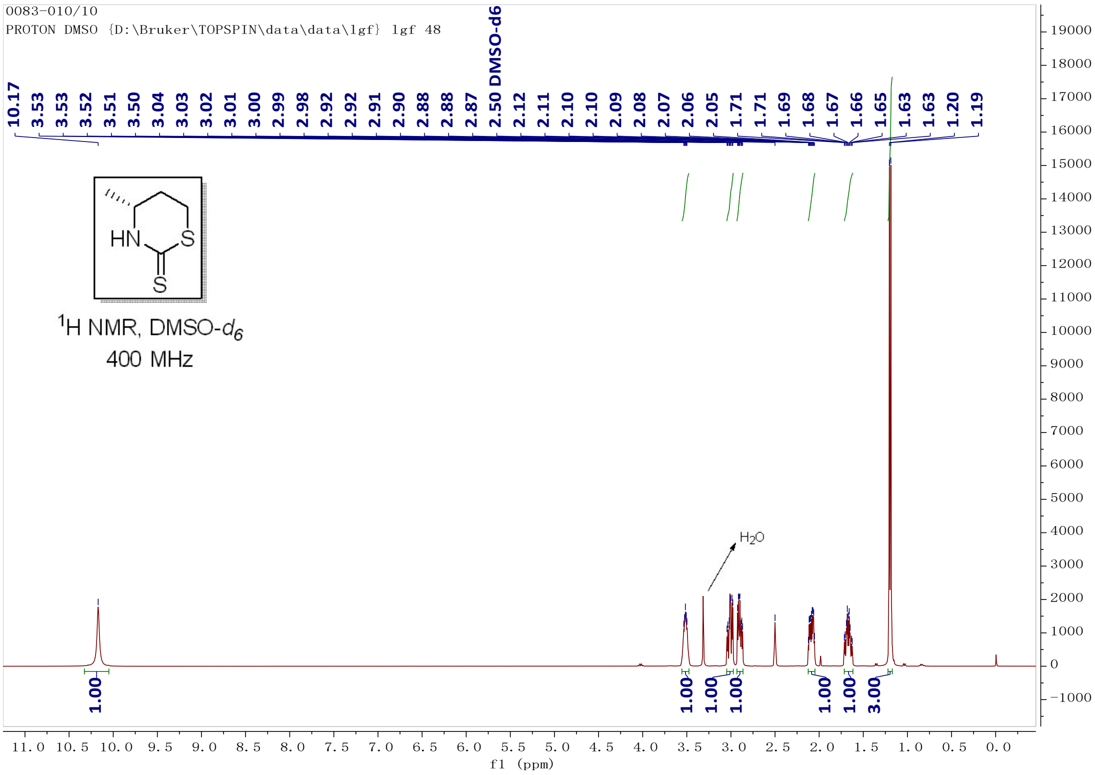
Chlorosulphonic acid (2.1 mL, 31.5 mmol) was added dropwise to a solution of (R)-3-aminobutan-1-ol (2.67 g, 30 mmol) in CH_2Cl_2 (100 mL) under a constant flow of N_2 at 0°C. The reaction mixture was stirred for 15 h at RT after which the solvent was removed in vacuo to afford a white solid. The white solid was triturated with MeOH and dried under reduced pressure to afford 3.8 g of (R)-3-aminobutyl hydrogen sulfate (22.5 mmol, 75%), which was pure enough by ^{1}H NMR and required no further purification.Then, CS_2 (1.63 mL, 27 mmol) was added dropwise to (R)-3-aminobutyl hydrogen sulfate (3.8 g, 22.5 mmol) under N_2 at RT. A solution of KOH (2.8 g, 50 mmol in 1:1 H_2O/EtOH 100 mL) was added dropwise to the reaction mixture at 0 °C. The resulting solution was then heated to reflux and stirred for 2 h, after which it was further stirred overnight at rt. Then, it was cooled with an ice-water bath. The white precipitate was filtered and rinsed with cold water. It was dissolved in CH_2Cl_2, and dried over anhydrous Na_2SO_4, and the solvent was removed in vacuo to obtain a white solid. The crude product was purified by recrystallization in CH_2Cl_2/hexane to obtain the (R)-4-methyl-1,3-thiazinane-2-thione (R-SMe, 3.17 g, 72% for two steps).

TLC: R_f = 0.40 (PE/EtOAc = 1:1).

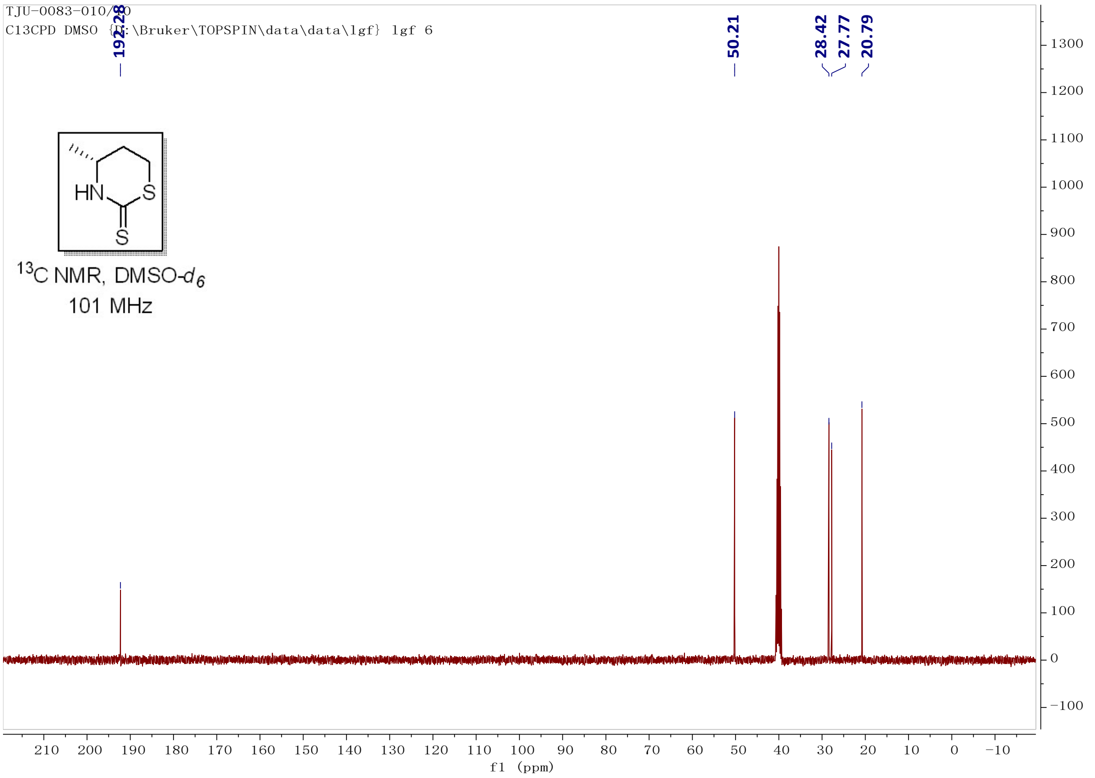
^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.17 (s, 1H), 3.56 – 3.48 (m, 1H), 3.01 (ddd, *J* = 13.1, 9.9, 3.7 Hz, 1H), 2.93 – 2.86 (m, 1H), 2.12 – 2.05 (m, 1H), 1.72 – 1.62 (m, 1H), 1.20 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 192.28, 50.21, 28.42, 27.77, 20.79.

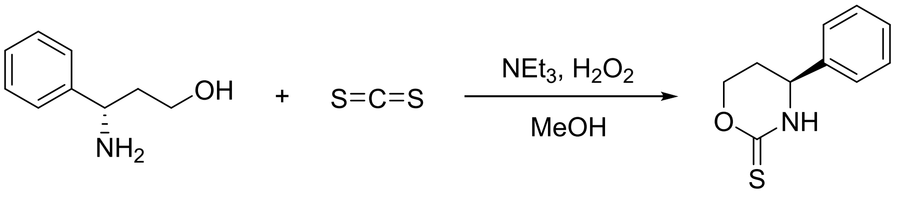
^1H spectra of R-SMe



^{13}C spectra of R-SMe



Synthesis of S-OPh



(*S*)-4-phenyl-1,3-oxazinane-2-thione

***(S)-4-phenyl-1,3-oxazinane-2-thione* (*S-OPh*).**

The triethylamine (0.92 mL, 6.6 mmol) was added to a solution of (S)-3-amino-3-phenylpropan-1-ol (1.0 g, 6.6 mmol) in methanol (20 mL) at 0°C, while carbon disulfide (0.4 mL, 6.6 mmol) is added dropwise. Then the solution is stirred at room temperature for 30 min. Hydrogen peroxide (30%, 0.43 mL, 8 mmol) is then added and stirred for 2 h. The methanol was removed by reduced pressure and the resulting mixture was diluted with CH_2Cl_2 (100 mL) and then was washed with H_2O (2×50 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and then concentrated to dryness under vacuum. The crude product was purified by recrystallization in CH_2Cl_2/hexane to obtain the (S)-4-phenyl-1,3-oxazinane-2-thione (S-OPh, 1.04 g, 82%).

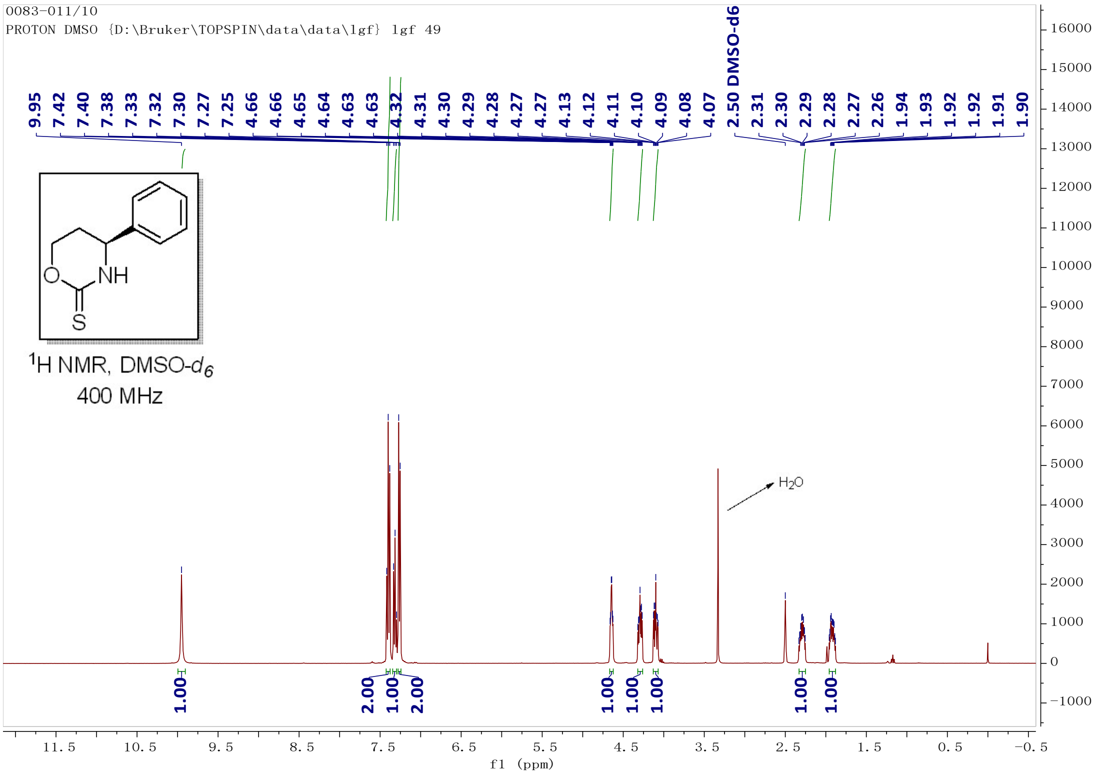
Physical State: white solid.

TLC: R_f = 0.38 (PE/EtOAc = 1:1).

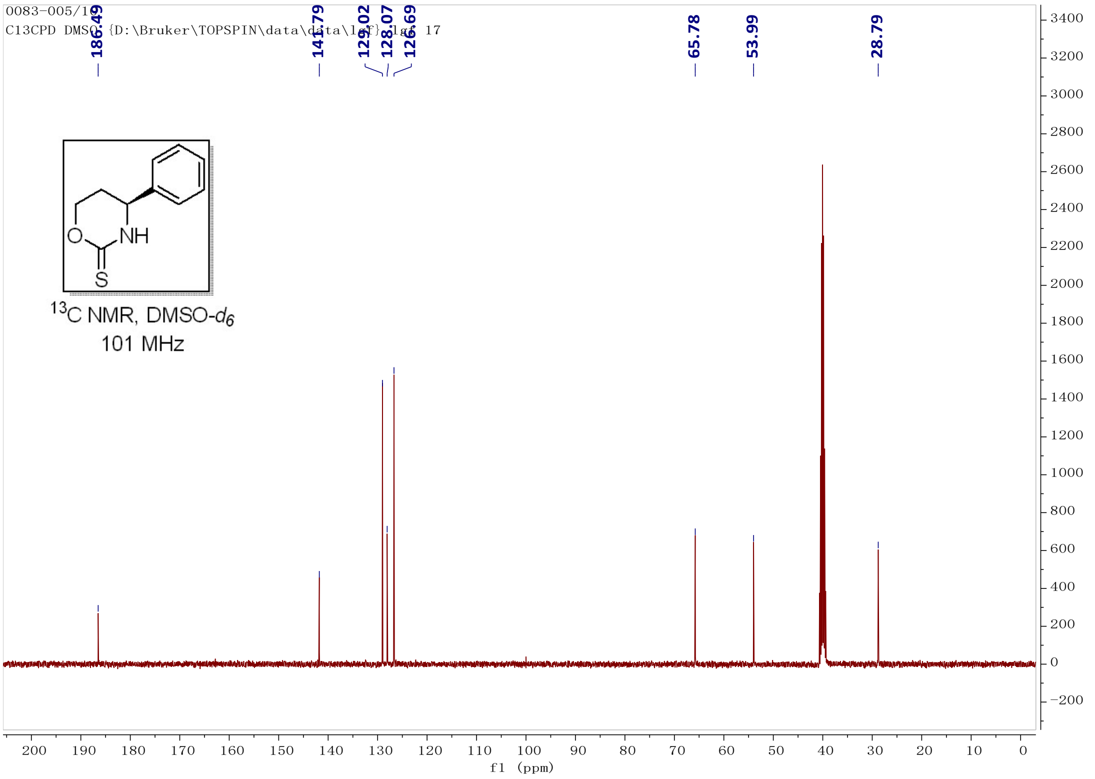
^{1}H NMR (400 MHz, DMSO-*d$_6$*) δ 9.95 (s, 1H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.26 (d, *J* = 7.3 Hz, 2H), 4.64 (td, *J* = 5.8, 2.5 Hz, 1H), 4.32 – 4.26 (m, 1H), 4.13 – 4.07 (m, 1H), 2.33 – 2.25 (m, 1H), 1.96 – 1.88 (m, 1H).

^{13}C NMR (101 MHz, DMSO-*d$_6$*) δ 186.49, 141.79, 129.02, 128.07, 126.69, 65.78, 53.99, 28.79.

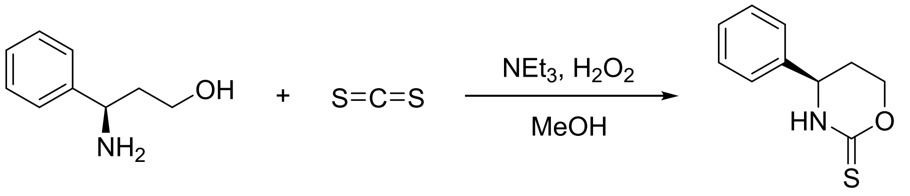
^{1}H spectra of S-OPh



^{13}C spectra of S-OPh



Synthesis of R-OPh



(*R*)-4-phenyl-1,3-oxazinane-2-thione

(R)-4-phenyl-1,3-oxazinane-2-thione (R-OPh).

The triethylamine (0.56 mL, 4 mmol) was added to a solution of (R)-3-amino-3-phenylpropan-1-ol (605 mg, 4 mmol) in methanol (10 mL) at 0°C, while carbon disulfide (0.24 mL, 4 mmol) is added dropwise. Then the solution is stirred at room temperature for 30 min. Hydrogen peroxide (30%, 0.26 mL, 8 mmol) is then added and stirred for 2 h. The methanol was removed by reduced pressure and the resulting mixture was diluted with CH_2Cl_2 (100 mL) and then was washed with H_2O (2×50 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and then concentrated to dryness under vacuum. The crude product was purified by recrystallization in CH_2Cl_2/hexane to obtain the (R)-4-phenyl-1,3-oxazinane-2-thione (R-OPh, 586 mg, 76%).

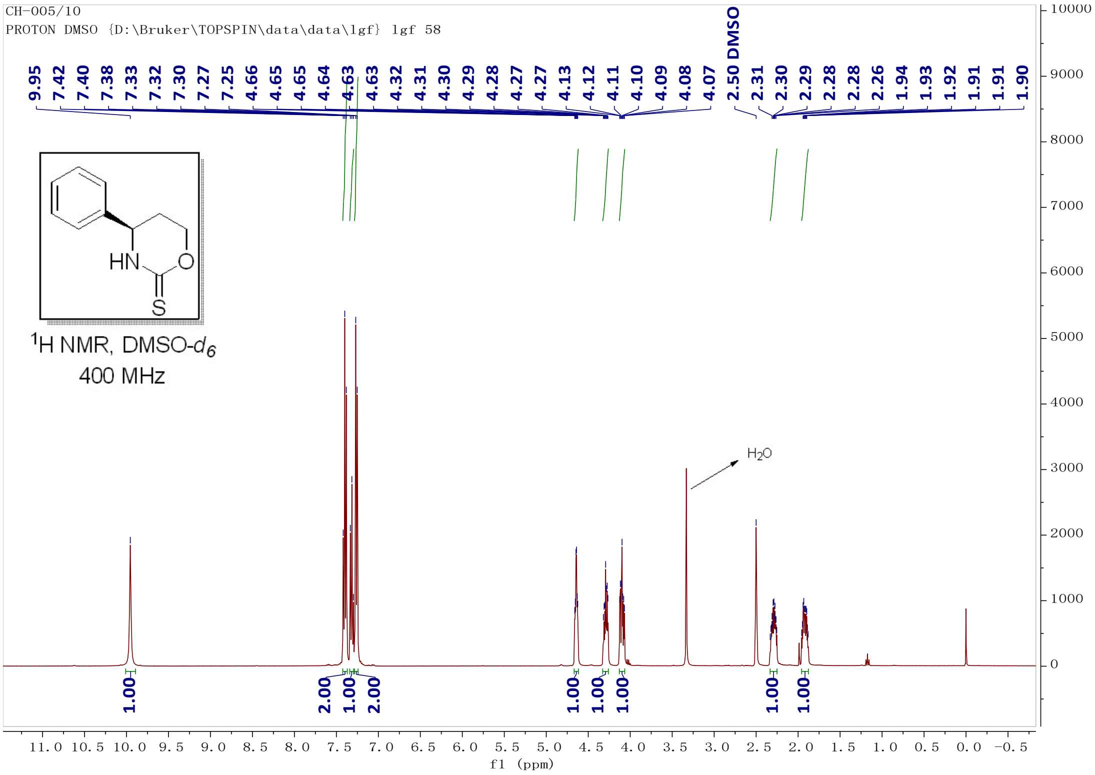
Physical State: white solid.

TLC: R_f = 0.38 (PE/EtOAc = 1:1).

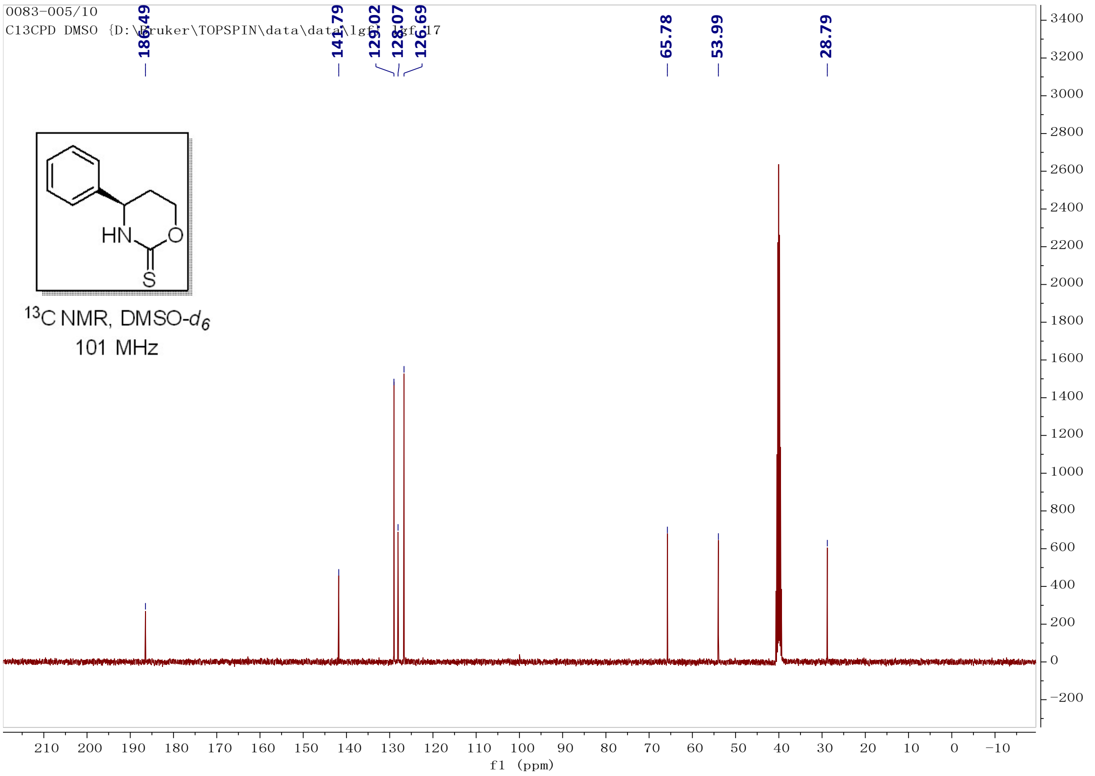
^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.95 (s, 1H), 7.40 (t, J = 7.4 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 7.26 (d, J = 7.1 Hz, 2H), 4.64 (td, J = 5.8, 2.5 Hz, 1H), 4.33 – 4.26 (m, 1H), 4.13 – 4.07 (m, 1H), 2.33 – 2.25 (m, 1H), 1.96 – 1.88 (m, 1H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 186.49, 141.79, 129.02, 128.07, 126.69, 65.78, 53.99, 28.79.

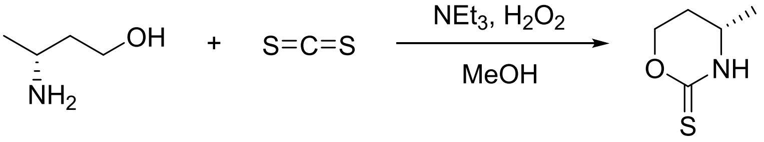
^{1}H spectra of R-OPh



^{13}C spectra of R-OPh



Synthesis of S-OMe



(*S*)-4-methyl-1,3-oxazinane-2-thione

(S)-4-methyl-1,3-oxazinane-2-thione (S-OMe)

The triethylamine (1.8 mL, 13 mmol) was added to a solution of (S)-3-aminobutan-1-ol (1.16 g, 13 mmol) in methanol (30 mL) at 0°C, while carbon disulfide (0.78 mL, 13 mmol) is added dropwise. Then the solution is stirred at room temperature for 30 min. Hydrogen peroxide (30%, 0.85 mL, 26 mmol) is then added and stirred for 2 h. The methanol was removed by reduced pressure and the resulting mixture was diluted with CH_2Cl_2 (100 mL) and then was washed with H_2O (2×50 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and then concentrated to dryness under vacuum. The crude product was purified by recrystallization in CH_2Cl_2/hexane to obtain the (S)-4-methyl-1,3-oxazinane-2-thione (S-OMe, 936 mg, 55%).

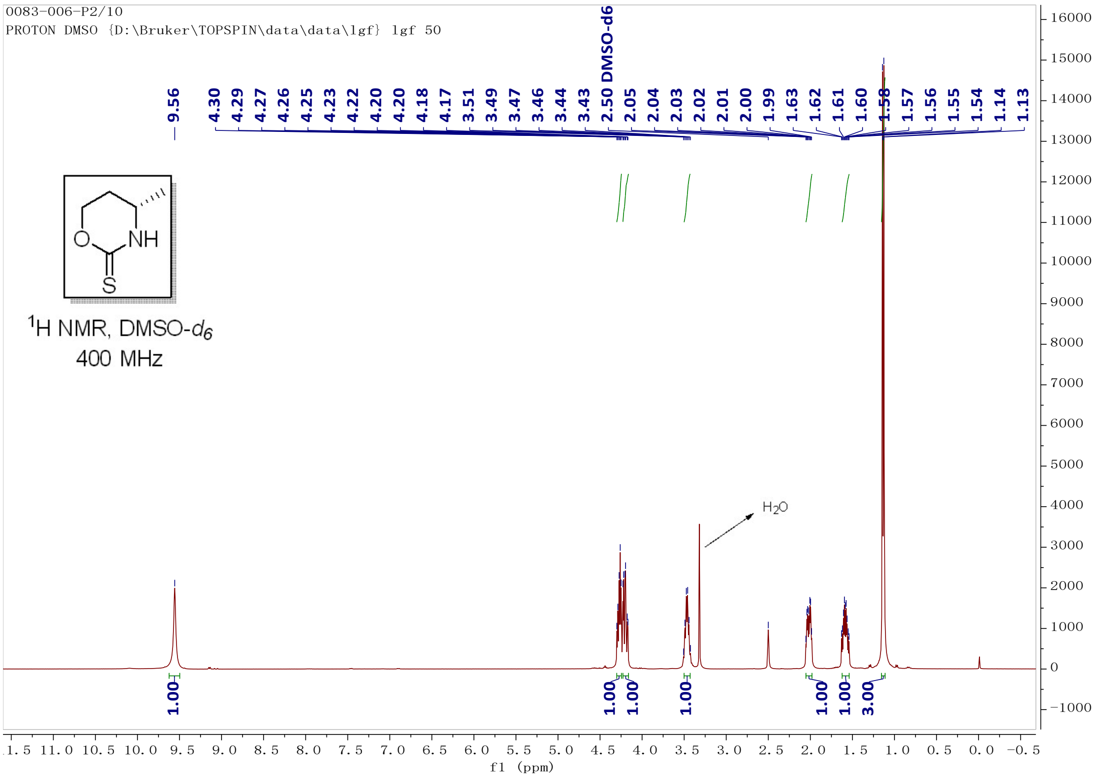
Physical State: white solid.

TLC: R_f = 0.30 (PE/EtOAc = 1:1).

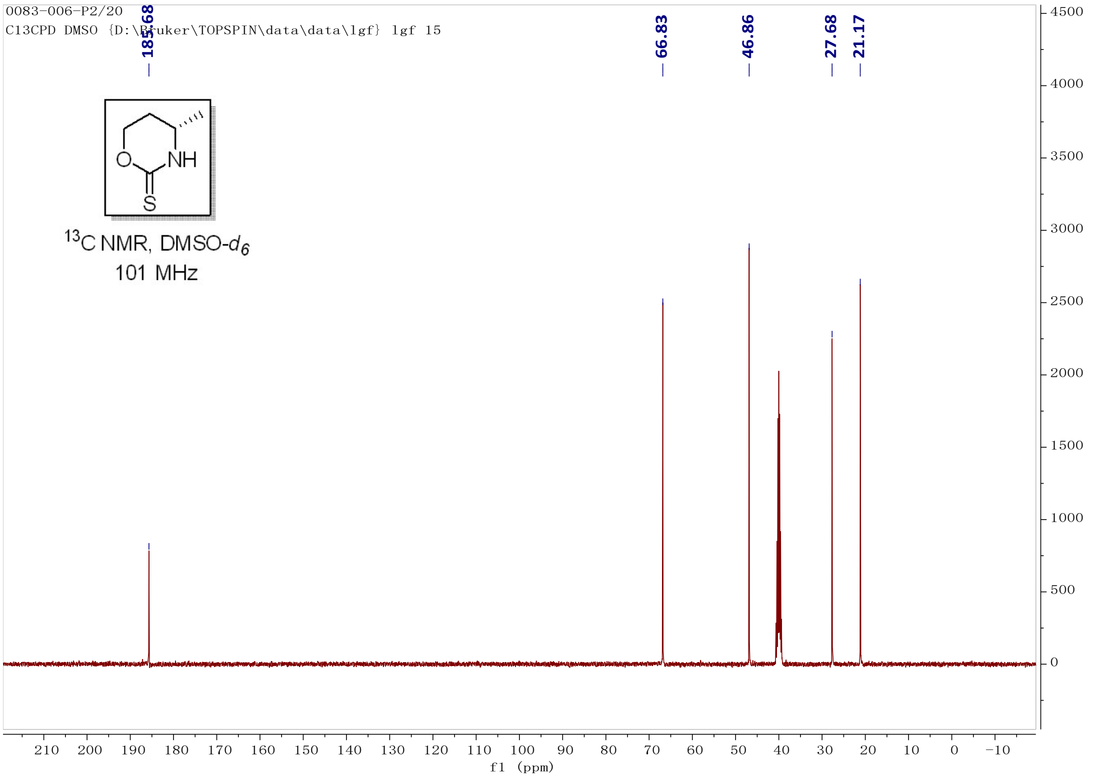
^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.56 (s, 1H), 4.30 – 4.25 (m, 1H), 4.20 (td, *J* = 11.2, 10.2, 3.2 Hz, 1H), 3.47 (q, *J* = 6.5 Hz, 1H), 2.05 – 1.98 (m, 1H), 1.62 – 1.54 (m, 1H), 1.13 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 185.68, 66.83, 46.86, 27.68, 21.17.

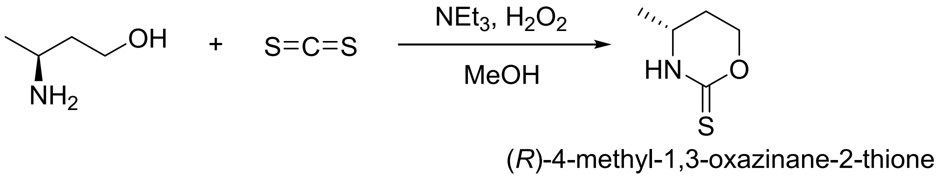
^{1}H spectra of S-OMe



^{13}C spectra of S-OMe



Synthesis of R-OMe



(R)-4-methyl-1,3-thiazinane-2-thione (R-OMe).

The triethylamine (1.8 mL, 13 mmol) was added to a solution of (R)-3-aminobutan-1-ol (1.16 g, 13 mmol) in methanol (30 mL) at 0ºC, while carbon disulfide (0.78 mL, 13 mmol) is added dropwise. Then the solution is stirred at room temperature for 30 min. Hydrogen peroxide (30%, 0.85 mL, 26 mmol) is then added and stirred for 2 h. The methanol was removed by reduced pressure and the resulting mixture was diluted with CH_2Cl_2 (100 mL) and then was washed with H_2O (2×50 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and then concentrated to dryness under vacuum. The crude product was purified by recrystallization in CH_2Cl_2/hexane to obtain the (R)-4-methyl-1,3-oxazinane-2-thione (R-OMe, 1.02 g, 60%).

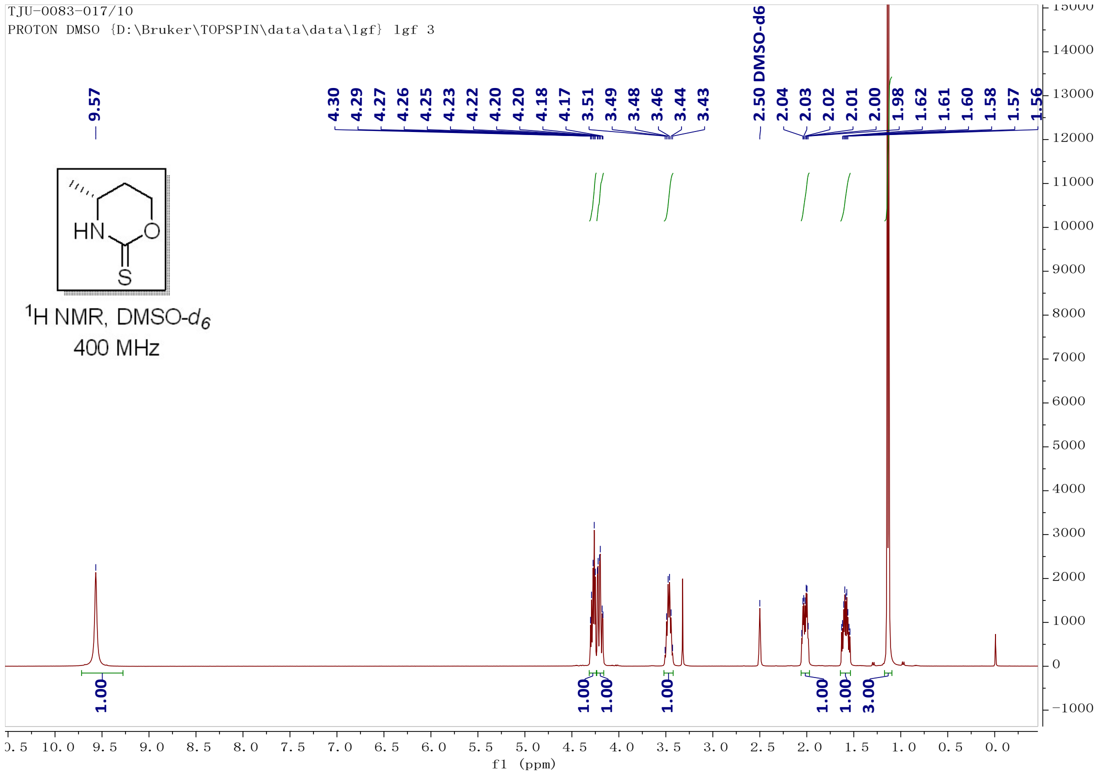
Physical State: white solid.

TLC: R_f = 0.30 (PE/EtOAc = 1:1).

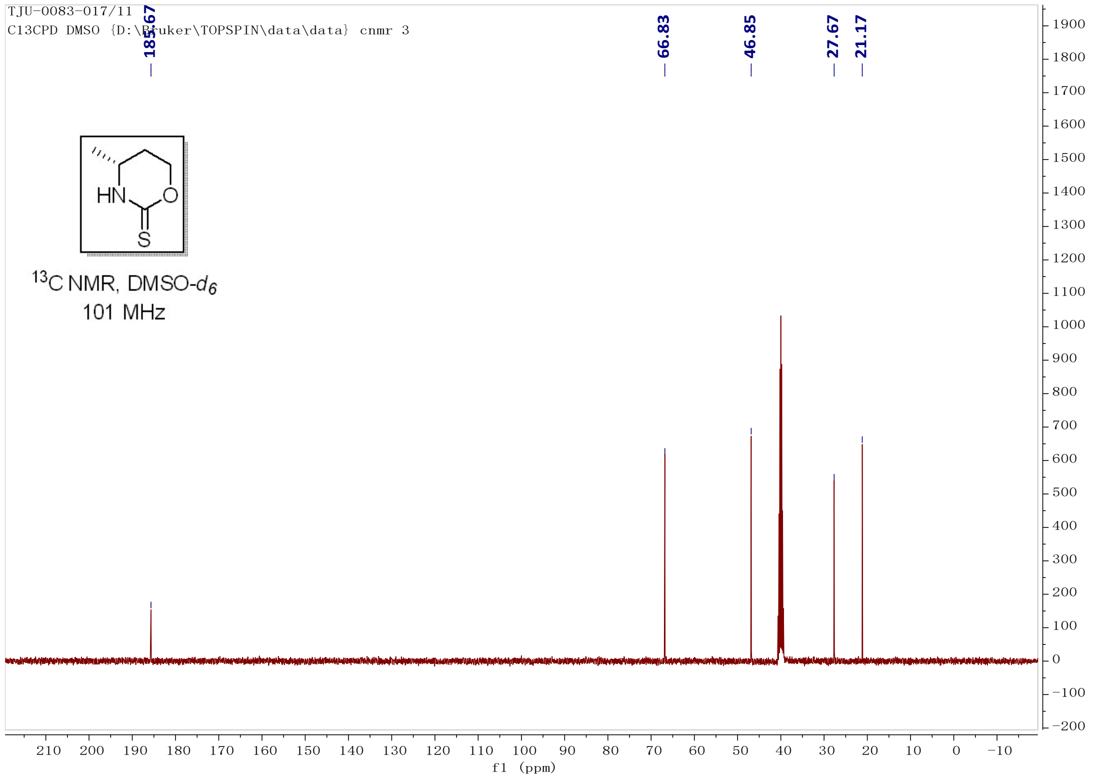
^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.57 (s, 1H), 4.31 – 4.24 (m, 1H), 4.20 (td, *J* = 11.2, 10.3, 3.2 Hz, 1H), 3.52 – 3.42 (m, 1H), 2.06 – 1.97 (m, 1H), 1.58 (dtd, *J* = 13.5, 9.0, 4.0 Hz, 1H), 1.14 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 185.67, 66.83, 46.85, 27.67, 21.17.

^1H spectra of R-OMe



^{13}C spectra of R-OMe



4 X-ray crystal structure data

Table S1. X-ray crystal structure of R-AgSMe

Identification code	2342767
Empirical formula	$C_{30}H_{48}Ag_6N_6S_{12}$
Formula weight	1524.68
Temperature	100 K
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	15.4231(12)
b/Å	16.7198(13)
c/Å	17.9114(14)
α/°	90
β/°	90
γ/°	90
Z	4
Volume/Å^3	4618.8(6)
ρ_{calc}g/cm^3	2.193
μ/mm^{-1}	3.069
F(000)	2976.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.332 to 52.714
Index ranges	$-19 \leq h \leq 19$, $-20 \leq k \leq 20$, $-22 \leq l \leq 22$
Reflections collected	58533
Independent reflections	9363 [R_{int} = 0.0301, R_{sigma} = 0.0181]
Data/restraints/parameters	9363/0/493
Goodness-of-fit on F^2	1.152
Final R indexes [I>=2σ (I)]	R_1 = 0.0295, wR_2 = 0.0799
Final R indexes [all data]	R_1 = 0.0295, wR_2 = 0.0799
Largest diff. peak/hole / e Å^{-3}	2.61/-1.50
Flack parameter	0.096(4)

Table S2. X-ray crystal structure of S-AgSMe

Identification code	2342766
Empirical formula	$C_{30}H_{48}Ag_6N_6S_{12}$
Formula weight	1524.68
Temperature	100 K
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	15.4401(4)
b/Å	16.7151(4)
c/Å	17.8546(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4607.96(19)
Z	4
ρ_{calc}g/cm^3	2.198
μ/mm^{-1}	3.076
F(000)	2976.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.174 to 54.24
Index ranges	-19 ≤ h ≤ 19, -20 ≤ k ≤ 20, -22 ≤ l ≤ 22
Reflections collected	58928
Independent reflections	10156 [Rint = 0.0392, Rsigma = 0.0272]
Data/restraints/parameters	10156/0/493
Goodness-of-fit on F^2	1.102
Final R indexes [I>=2σ (I)]	R_1 = 0.0203, wR_2 = 0.0386
Final R indexes [all data]	R_1 = 0.0224, wR_2 = 0.0393
Largest diff. peak/hole / e Å^{-3}	0.59/-0.45
Flack parameter	-0.024(11)

Table S3. X-ray crystal structure of R-AgOMe

Identification code	2342764
Empirical formula	$C_{31}H_{50}Ag_6Cl_2N_6O_6S_6$
Formula weight	1513.25
Temperature	100 K
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	12.2559(8)
b/Å	19.1800(12)
c/Å	20.0247(14)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4707.2(5)
Z	4
ρ_{calc}g/cm^3	2.135
μ/mm^{-1}	2.873
F(000)	2952.0
Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.94 to 54.986
Index ranges	-15 ≤ h ≤ 15, -23 ≤ k ≤ 24, -25 ≤ l ≤ 25
Reflections collected	57878
Independent reflections	10652 [Rint = 0.0394, Rsigma = 0.0268]
Data/restraints/parameters	10652/12/521
Goodness-of-fit on F^2	1.150
Final R indexes [I>=2σ (I)]	R_1 = 0.0230, wR_2 = 0.0573
Final R indexes [all data]	R_1 = 0.0231, wR_2 = 0.0574
Largest diff. peak/hole / e Å^{-3}	0.75/-1.28
Flack parameter	0.18(2)

Table S4. X-ray crystal structure of S-AgOMe

Identification code	2342765
Empirical formula	$C_{30}H_{44}Ag_6N_6O_6S_6$
Formula weight	1424.29
Temperature	100 K
Crystal system	trigonal
Space group	R-3
a/Å	35.3936(6)
b/Å	35.3936(6)
c/Å	11.7131(3)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	12707.3(4)
Z	9
ρ_{calc}g/cm^3	1.675
μ/mm^{-1}	2.297
F(000)	6228.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.92 to 50.08
Index ranges	$-42 \le h \le 42$, $-42 \le k \le 40$, $-13 \le l \le 13$
Reflections collected	90046
Independent reflections	4999 [R_{int} = 0.0997, R_{sigma} = 0.0308]
Data/restraints/parameters	4999/0/245
Goodness-of-fit on F^2	1.153
Final R indexes [I>=2σ (I)]	R_1 = 0.0899, wR_2 = 0.2375
Final R indexes [all data]	R_1 = 0.1049, wR_2 = 0.2479
Largest diff. peak/hole / e Å^{-3}	3.34/-1.56

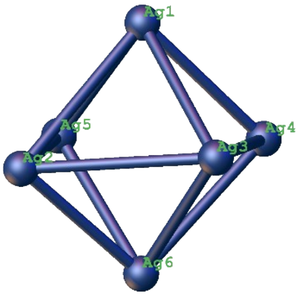
Table S5. X-ray crystal structure of R-AgOPh

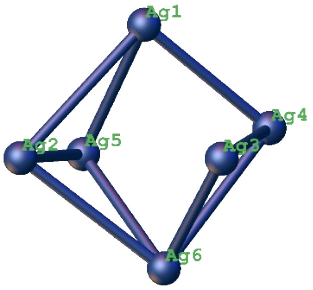
Identification code	2342768
Empirical formula	$C_{60}H_{60}Ag_6N_6O_6S_6$
Formula weight	1800.72
Temperature	100 K
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	29.2719(16)
b/Å	12.2808(8)
c/Å	19.1727(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	6892.2(7)
Z	4
ρ_{calc}g/cm^3	1.735
μ/mm^{-1}	1.903
F(000)	3552.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.938 to 52.816
Index ranges	$-36 \le h \le 36$, $-15 \le k \le 15$, $-23 \le l \le 23$
Reflections collected	82797
Independent reflections	14133 [Rint = 0.1251, Rsigma = 0.0816]
Data/restraints/parameters	14133/841/746
Goodness-of-fit on F^2	1.244
Final R indexes [I>=2σ (I)]	R_1 = 0.1520, wR_2 = 0.3351
Final R indexes [all data]	R_1 = 0.1718, wR_2 = 0.3497
Largest diff. peak/hole / e Å^{-3}	3.04/-2.68
Flack parameter	0.08(2)

Table S6. X-ray crystal structure of S-AgSPh

Identification code	2351225
Empirical formula	$C_{60}H_{60}Ag_6N_6S_{12}$
Formula weight	1897.08
Temperature	100 K
Crystal system	tetragonal
Space group	$P4_1$
a/Å	16.0961(8)
b/Å	16.0961(8)
c/Å	50.412(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	13060.9(16)
Z	8
ρ_{calc}g/cm^3	1.930
μ/mm^{-1}	2.192
F(000)	7488.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.656 to 54.984
Index ranges	$-20 \le h \le 20$, $-19 \le k \le 20$, $-65 \le l \le 65$
Reflections collected	125624
Independent reflections	29645 [Rint = 0.0552, Rsigma = 0.0434]
Data/restraints/parameters	29645/2203/1514
Goodness-of-fit on F^2	1.137
Final R indexes [I>=2σ (I)]	R_1 = 0.0586, wR_2 = 0.1580
Final R indexes [all data]	R_1 = 0.0589, wR_2 = 0.1582
Largest diff. peak/hole / e Å^{-3}	3.26/-1.51
Flack parameter	0.34(4)

Table S7. The distance of silver atoms in the core of R-AgOMe and R-AgOPh





	R-AgOMe	R-AgOPh
Ag_1-Ag_2	3.2899 Å	3.307 Å
Ag_1-Ag_3	3.0675 Å	-
Ag_1-Ag_4	3.0014 Å	2.990 Å
Ag_1-Ag_5	2.9981 Å	3.089 Å
Ag_2-Ag_3	3.3170 Å	-
Ag_2-Ag_5	2.9811 Å	2.939 Å
Ag_2-Ag_6	2.9389 Å	3.243 Å
Ag_3-Ag_4	2.9674 Å	3.182 Å
Ag_3-Ag_6	3.0554 Å	2.872 Å
Ag_4-Ag_6	3.1252 Å	3.277 Å
Ag_4-Ag_5	-	-
Ag_5-Ag_6	3.0918 Å	3.180
Volume-core	123.51 Å^3	124.80 Å^3

Table S8. The distance between R-AgSMe, R-AgOMe and adjacent cluster

	R-AgSMe	R-AgOMe
Nc1…Nc2	11.70 Å	11.74 Å
Nc1…Nc3	11.37 Å	12.26 Å
Nc1…Nc4	11.75 Å	12.38 Å
Nc1…Nc5	11.93 Å	11.73 Å
Nc1…Nc6	12.13 Å	11.73 Å
Nc1…Nc7	11.38 Å	12.25 Å
Nc1…Nc8	11.93 Å	13.89 Å
Nc1…Nc9	11.38 Å	11.74 Å
Nc1…Nc10	12.38 Å	13.89 Å
Nc1…Nc11	11.70 Å	13.89 Å
Nc1…Nc12	12.13 Å	13.89 Å
Nc1…Nc13	11.37 Å	11.74 Å
Nc1…Nc14	-	11.05 Å
Nc1…Nc15	-	11.05 Å

5 Additional experimental data and figures

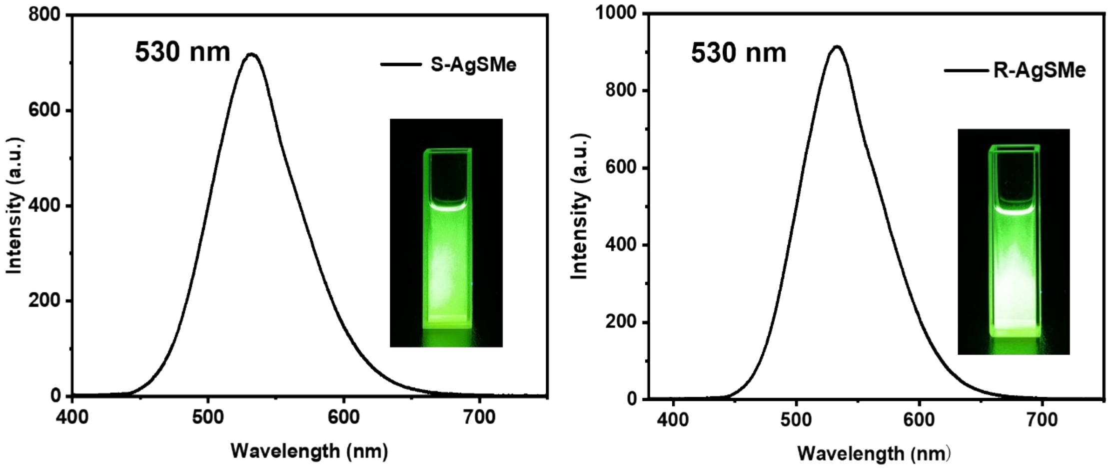


Fig.S1. The photoluminescence (PL) spectra of S/R-AgSMe in EtOH suspension.

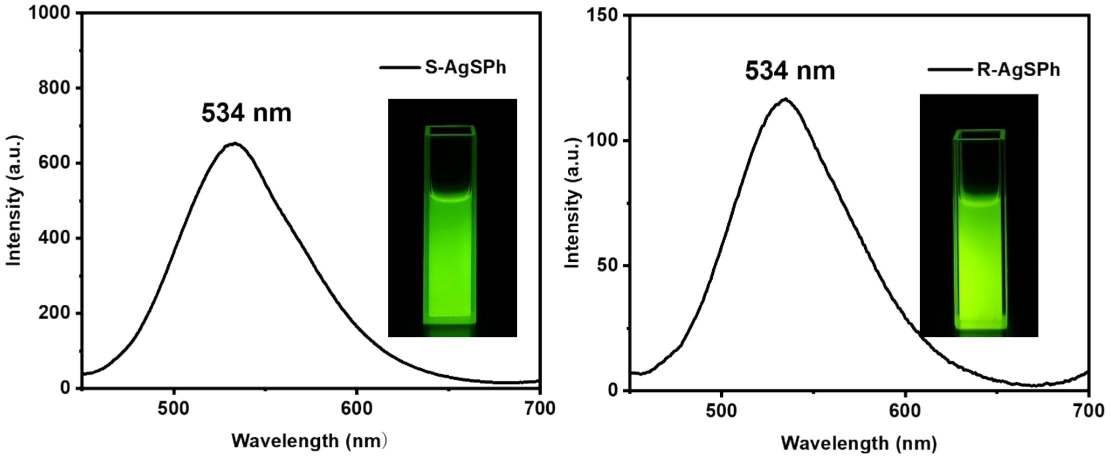


Fig.S2. The PL spectra of S/R-AgSPh in EtOH suspension.

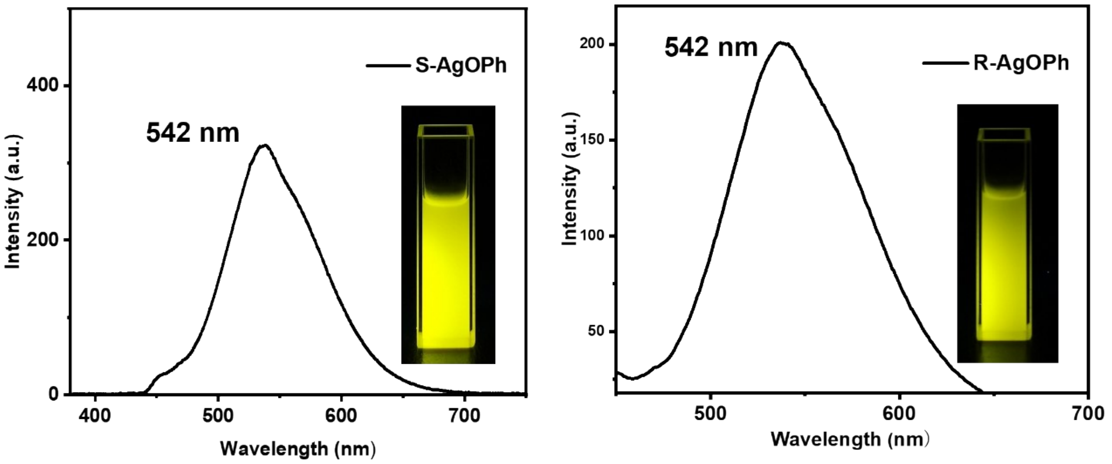


Fig.S3. The photoluminescence spectra of S/R-AgOPh in EtOH suspension.

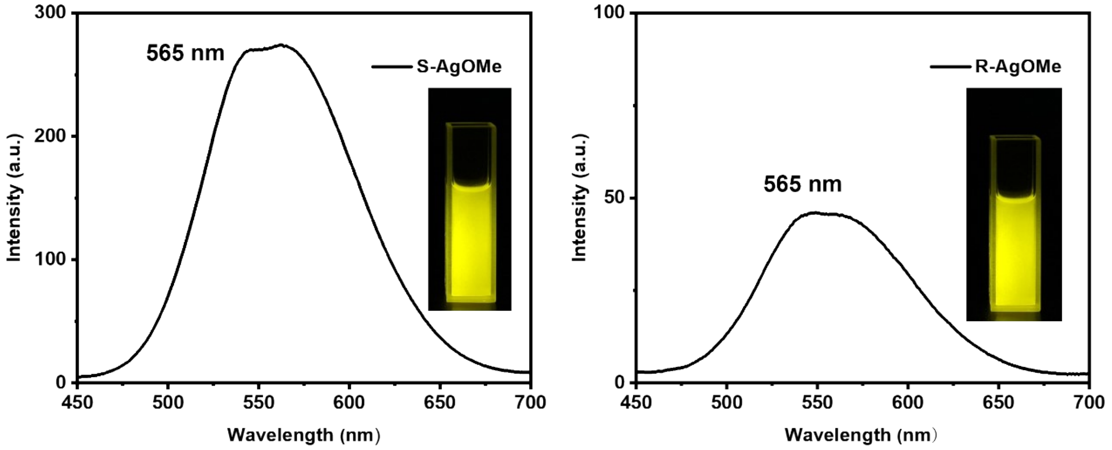
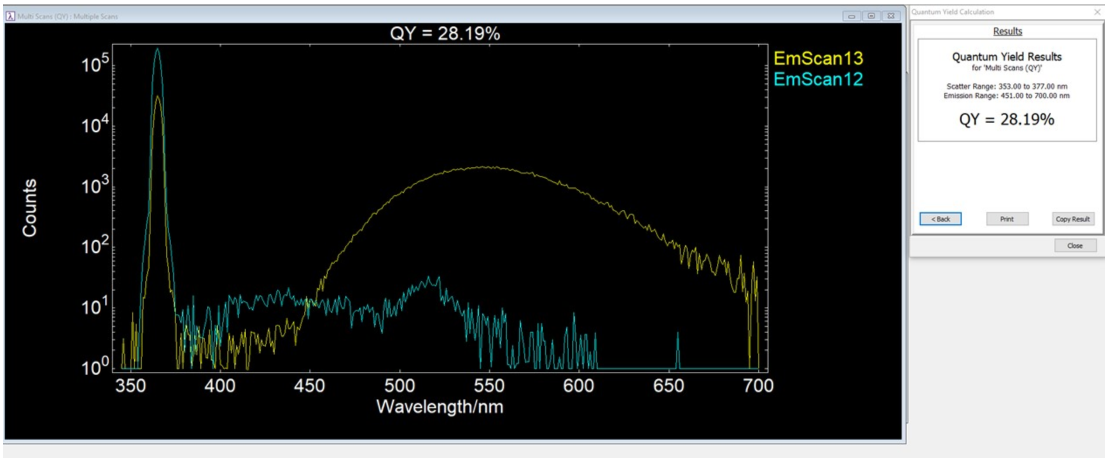


Fig.S4. The photoluminescence spectra of S/R-AgOMe in EtOH suspension.



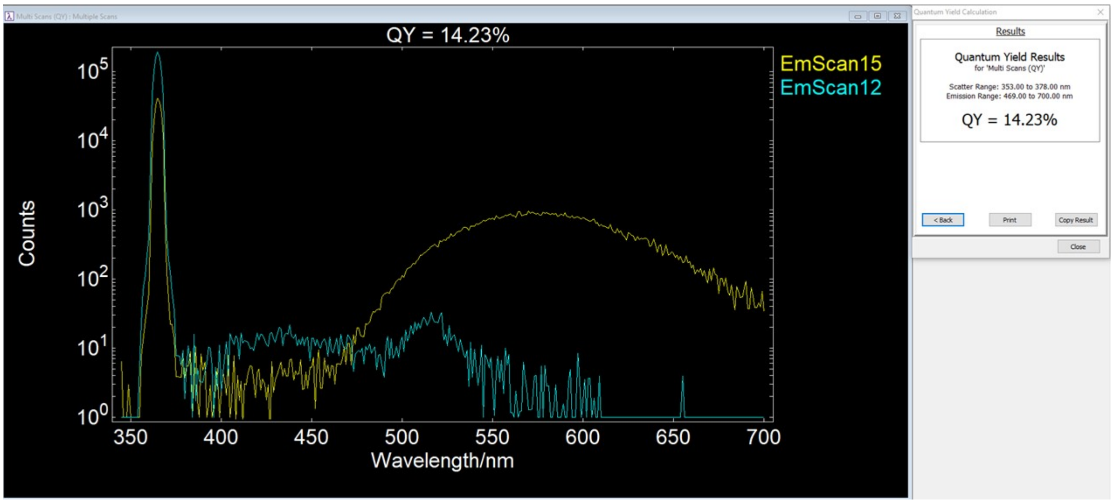
Results

Quantum Yield Results
for 'Multi Scans (QY)'

Scatter Range: 353.00 to 377.00 nm
Emission Range: 451.00 to 700.00 nm

QY = 28.19%

Fig.S5. The quantum yield of R-AgSMe in the solid state.



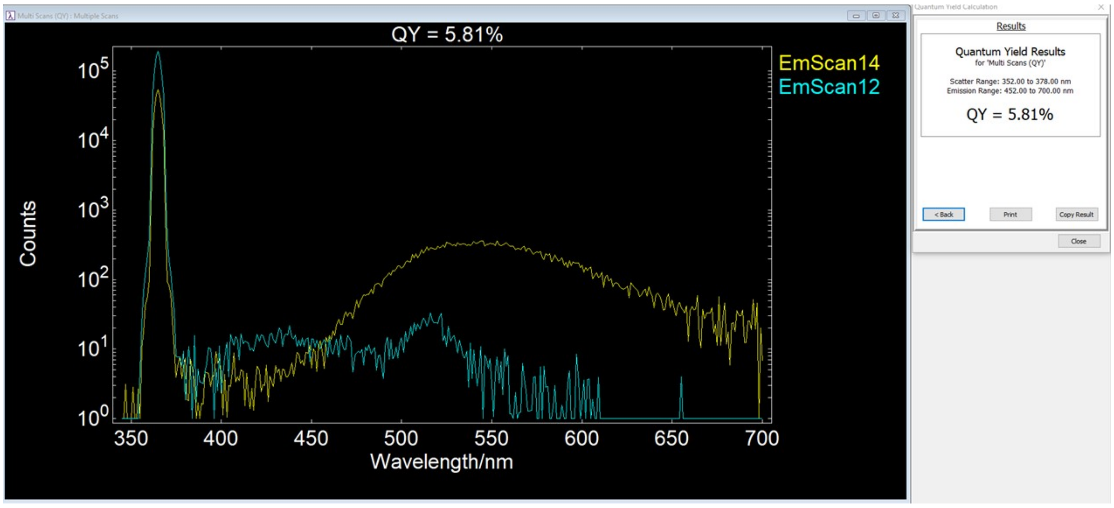
Results

Quantum Yield Results
for 'Multi Scans (QY)'

Scatter Range: 353.00 to 378.00 nm
Emission Range: 469.00 to 700.00 nm

QY = 14.23%

Fig.S6. The quantum yield of R-AgOMe in the solid state.



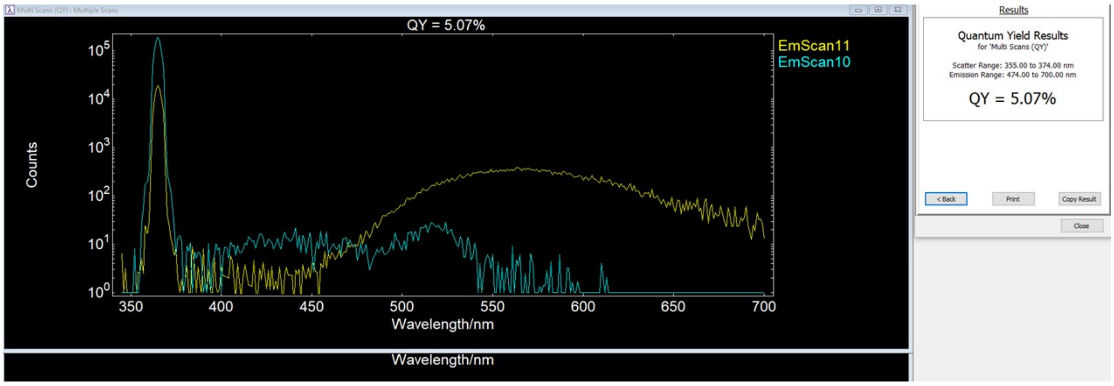
Results

Quantum Yield Results
for 'Multi Scans (QY)'

Scatter Range: 352.00 to 378.00 nm
Emission Range: 452.00 to 700.00 nm

QY = 5.81%

Fig.S7. The quantum yield of R-AgSPh in the solid state.



Quantum Yield Results
for 'Multi Scans (QY)'

Scatter Range: 355.00 to 374.00 nm
Emission Range: 474.00 to 700.00 nm

QY = 5.07%

Fig.S8. The quantum yield of R-AgOPh in the solid state.

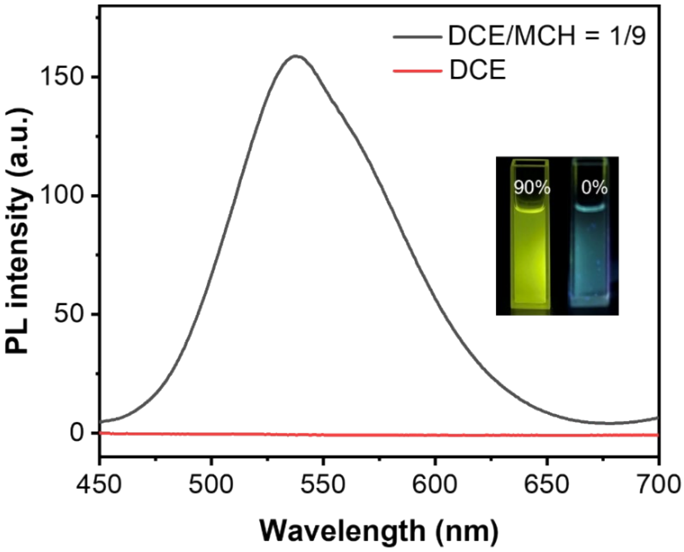
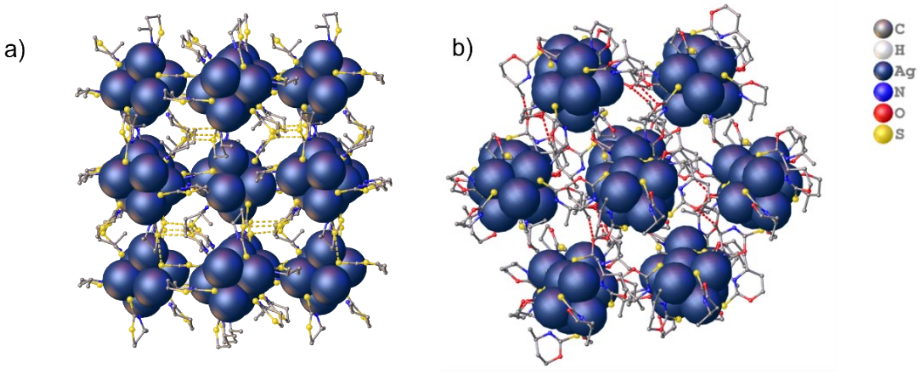


Fig.S9. a) PL spectra of R-AgSMe in a mixed solvent of DCE (1,2-Dichloroethane) and MCH (methylcyclohexane) at 1×10^{-4} mol/L.



R-AgSMe

R-AgOMe

Fig.S10. a) The stacking of R-AgSMe cluster in the single crystal driven by S···S interaction, b) The stacking of R-AgOMe cluster in the single crystal driven by C···O interaction.

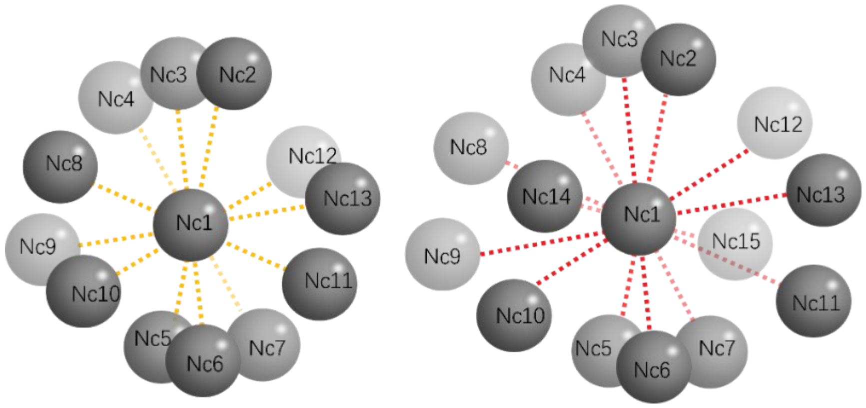


Fig.S11. The left is a schematic diagram of the distance between R-AgSMe and adjacent cluster. The right is a schematic diagram of the distance between R-AgOMe and adjacent cluster. Nc: Nanocluster.

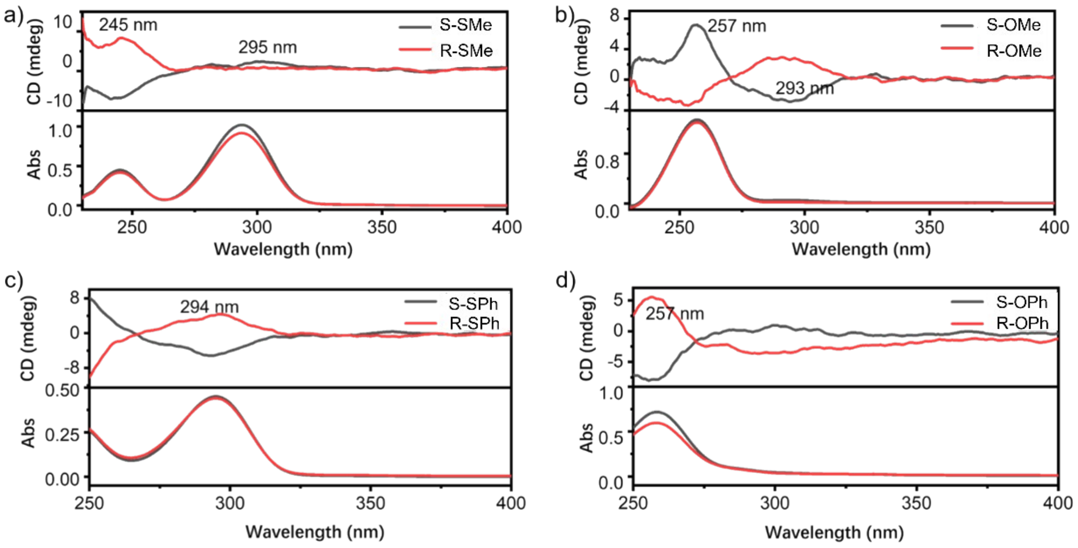


Fig.S12. CD spectra of a) S/R-SMe, b) S/R-OMe, c) S/R-SPh, and d) S/R-OPh in DCM solution. The concentration of ligands was fixed at 1.0×10^{-3} mol/L.

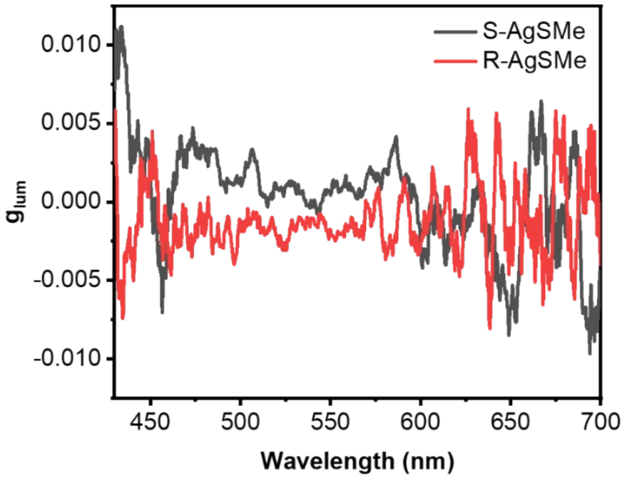


Fig.S13. The g_{lum} values of S/R-AgSMe.

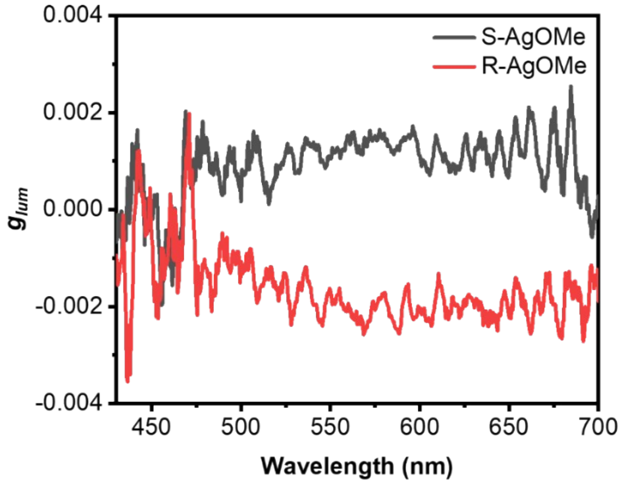


Fig.S14. The g_{lum} values of S/R-AgOMe.

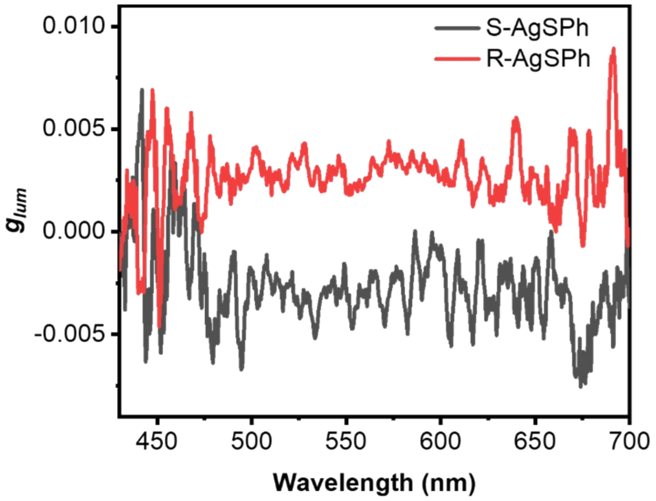


Fig.S15. The g_{lum} values of S/R-AgSPh.

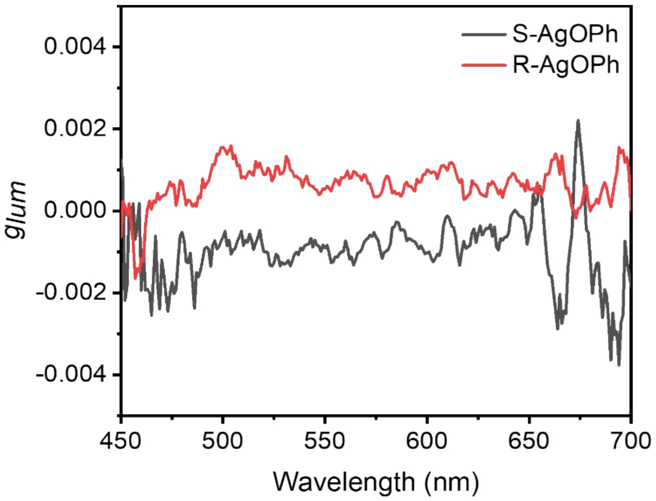


Fig.S16. The g_{lum} values of S/R-AgOPh.

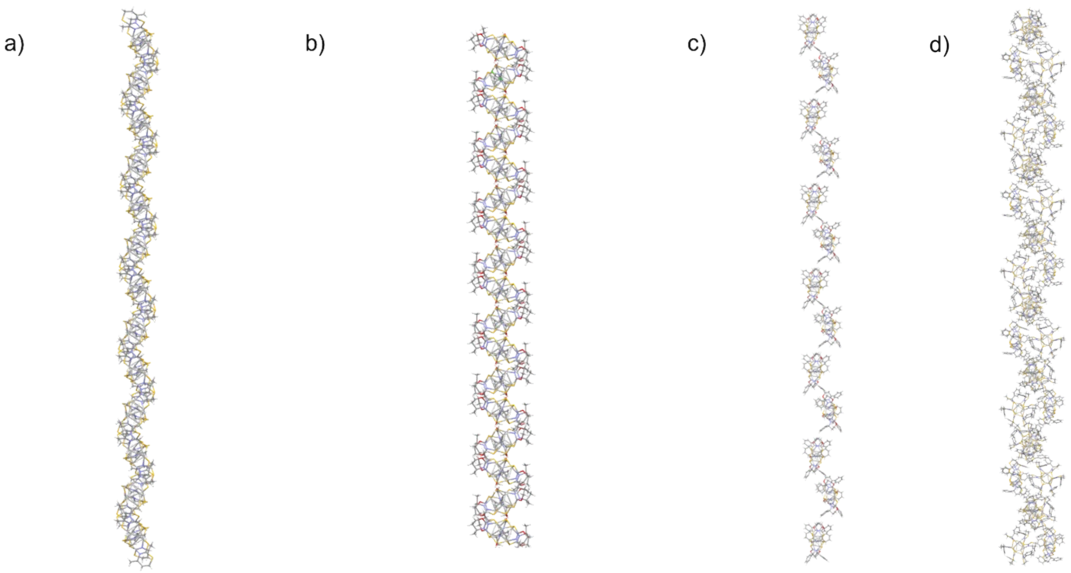


Fig.S17. a) C-H···S interaction driven right-handed (P) helical stacking R-AgSMe cluster in the single crystal structure, b) H-C···H interaction driven right-handed (P) helical stacking R-AgOMe cluster in the single crystal structure, and c) C-H···π interaction driven left-handed (M) helical stacking R-AgOPh cluster in the single crystal structure. d) The left-handed (M) helical stacking of S-AgSPh cluster driven by H-C···S, H-C···S and C-H···π interactions in the single crystal structure.

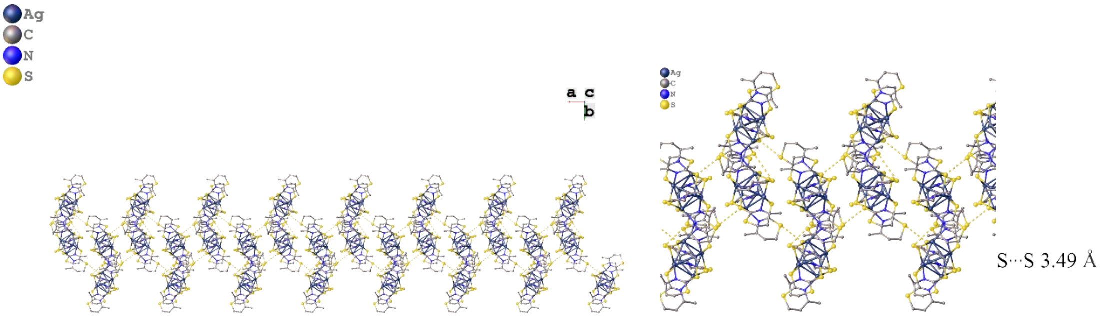


Fig.S18. The stacking model of R-AgSMe chains driven by S···S interaction.