Supplementary Material (ESI) for Chemical Communications

Highly sensitive and selective turn-on fluorescent chemosensor for Ag^+ based on a coumarin-Se_2N chelating conjugate

Shanshan Huang, [a] Song He, [a] Yan Lu, *[a] Fangfang Wei, [a] Xianshun Zeng,*[a] and Liancheng Zhao [a,b]

[a] *Key Laboratory of Display Materials & Photoelectric Devices, Ministry of Education, School of Materials Science & Engineering, Tianjin University of Technology, Tianjin 300384, China..*
[b] *School of Materials Science and Engineering, Institute of Information Functional Materials& Devices, Harbin Institute of Technology, Harbin 150001, China.*

Materials and methods

1. Instruments

All solvents and reagents (analytical grade and spectroscopic grade) were obtained commercially and used as received unless otherwise mentioned. NMR spectra were recorded on a Bruker spectrometer at 400 (^{1}H NMR) MHz and 100 (^{13}C NMR) MHz. Chemical shifts (δ values) were reported in ppm down field from internal Me_4Si (^{1}H and ^{13}C NMR). EI mass spectra were recorded on a VG ZAB-HS mass spectrometer (VG, U. K.). Elemental analyses were performed on a Vanio-EL elemental analyzer (Analysensysteme GmbH, Germany). UV absorption spectra were recorded on a UV-3600 UV-VIS spectrophotometer (Shimadzu, Japan). Fluorescence measurements were performed using an F-4600 fluorescence spectrophotometer (Hitachi, Japan) equipped with a plotter unit and a quartz cell (1 cm × 1 cm). Melting points were recorded on a Boetius Block apparatus and are uncorrected.

2. Synthesis of SC1

Preparation of bis(2-phenylselenoethyl)amine 1

To a 250 reactor, was added 1,2-diphenyldiselenide (6.243 g, 20 mmol), sodium hydroxide (7.429 g, 0.19 mol) and ethanol (150 mL). The suspension was washed with nitrogen flow for 20 min, and then $NaBH_4$ (1.015 g, 27 mmol) was added in portion. After the addition of $NaBH_4$, the solution was stirred for 2 hours until the yellow color disappeared. Then bis(2-chloroethyl)amine (3.57g, 20 mmol) was added in portions.

The resulted solution was stirred at 80 ^{o}C for 5 h. The solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (50 mL) and water (100 mL). The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (30 mL ×2). The combined organic phase was dried over anhydrous Na_2SO_4. After removal of solvent, the residue was purified with column chromatography (SiO_2, petroleum ether/ethyl acetate, 1:1, v/v). The product was obtained as white powder in 95% yield; mp 54-55 ^{o}C; EI MS: m/z $[M-H]^+$ = 385.1, calcd 384.98; ^{1}H NMR($CDCl_3$, 400 MHz): 7.53 (d, 4H, *J* = 6.4 Hz), 7.28 (d, 6H, *J* = 5.6 Hz), 3.04 (d, 4H, *J* = 6.6 Hz), 2.89 (d, 4H, *J* = 6.4 Hz), 1.71 (s, 1H); ^{13}C NMR ($CDCl_3$, 400 MHz), 133.07, 129.71, 129.17, 127.12 48.57, 28.747; Anal. Calcd for $C_{16}H_{19}NSe_2$: C 50.14%, H 5.00%, N 3.65%; Found: C 50.39%, H 5.14%, N 3.68%.

Preparation of the chemosensor SC1

To a 50 mL reactor, was added 7-hydroxy-4-methyl-2H-chromen-2-one (counnarin 4) (0.171 g, 1 mmol), bis(2-(phenylselenyl)ethyl)amine (0.424 g, 1.1 mmol), formaldehyde (37% , 100 *u*l , 1.23 mmol), glacial acetic acid (5 mL), THF (5 mL) and ethanol (5 mL). The reaction mixture was stirred for 72 h at room temperature. The solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate, 1:1, v/v). The product was obtained as light yellow powder in 58% yield; mp 85-86 ^{o}C; ESI MS: m/z $[M+H]^+$ = 574.03, calcd 574.03. ^{1}H NMR($CDCl_3$, 400 MHz): 6.81-7.45 (m, 12H), 6.82 (d, 1H, *J* = 7.6 Hz), 6.10 (s, 1H), 4.10 (S, 2H), 2.94-2.98 (m, 4H), 2.86-2.89 (m, 4H), 2.41 (s, 3H); ^{13}C NMR($CDCl_3$, 400 MHz), 162.13, 161.05, 153.30, 152.40, 152.5, 133.10, 129.26, 128.91, 127.42, 124.93, 113.57, 112.56, 110,91, 108.22, 53.50, 49.88, 23.68, 18.85. Anal. Calcd for $C_{27}H_{27}NO_3Se_2$: C 56.75%, H 4.76%, N 2.45%. Found: C 56.82%, H 4.85%, N 2.48%.

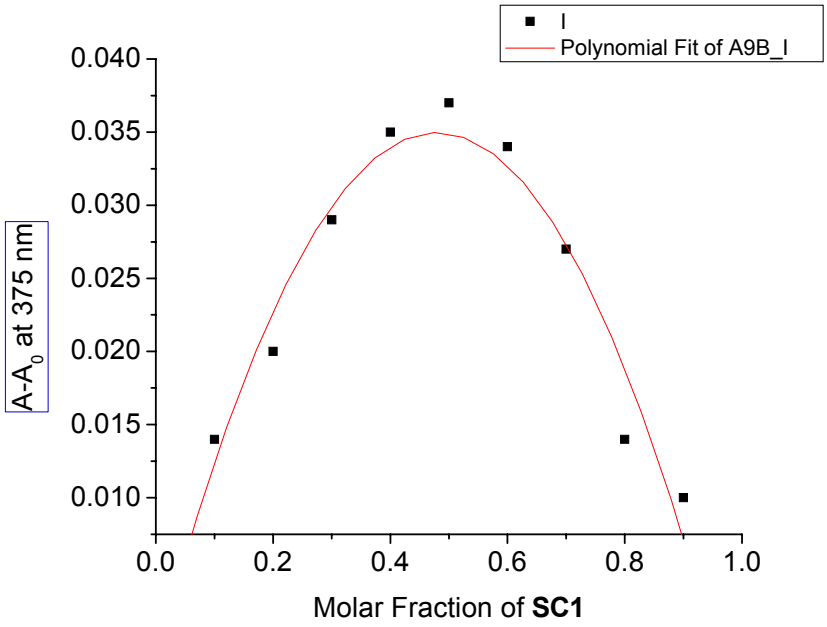

Figure S1. Job's plot of a 1:1 complex of **SC1** and Ag^{+} cation.

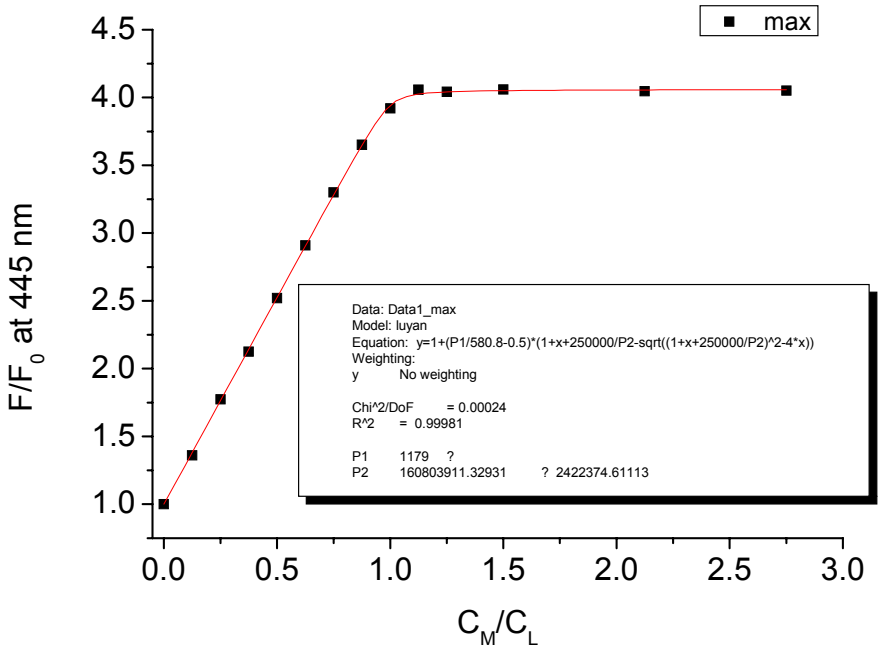

Figure S2. A nonlinear least-square analysis of a 1:1 complex of **SC1** and Ag^{+} cation. The nonlinear curve fitness based on 1:1 complex expression:[1]

$$F/F_0 = 1 + (F_{max}/2F_0 - 1/2)\{1 + C_M/C_L + 1/K_SC_L - [(1 + C_M/C_L + 1/K_SC_L)^2 - 4C_M/C_L]^{1/2}\}$$

where F and F_0 are the fluorescence intensity of **SC1** in the presence and absence of Ag^{+}, C_M and C_L are the concentrations of Ag^{+} and **SC1** (4 *u*M); K_S is the stability constant.

[1] (a) K. A. Connors, *Binding Constants*, *the Measurement of Molecular Complex Stability*; John Wiley & Sons: New York, 1987. (b) B. Valeur, *Molecular Fluorescence Principles and Applications*; Wiley-VCH Verlag GmbH: New York, 2001.

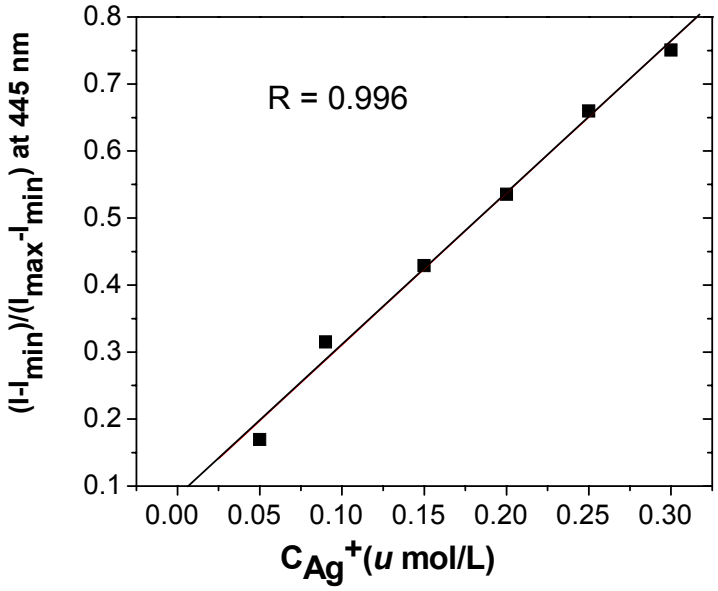

Figure S3. Emission (at 445 nm) of **SC1** at different concentrations of Ag^+ (0, 0.05, 0.075, 0.15, 0.2, 0.25, 0.30 *u*M) added, normalized between the minimum emission (0.0 *u*M Ag^+) and the emission at 0.3 *u*M Ag^+. The detection limit was determined to be 5.2×10^{-8} M.

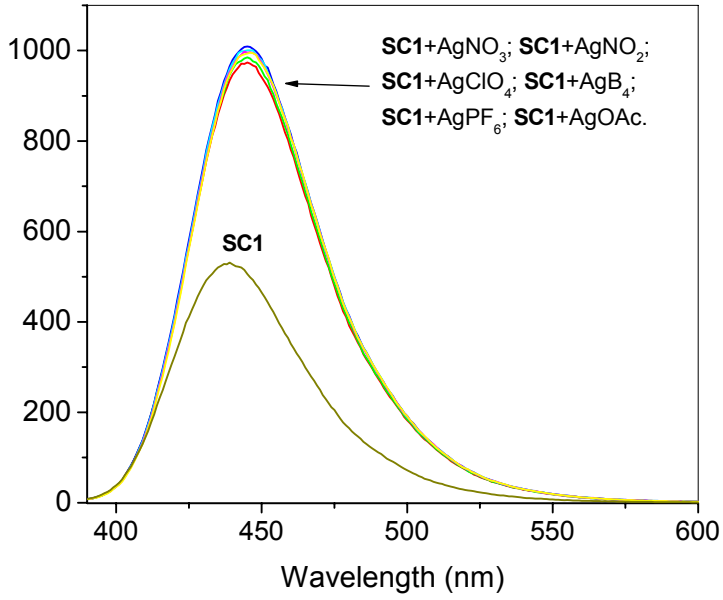

Figure S4. The emission spectra of **SC1** with Ag^+ salts with different counteranions (ClO_4^-, NO_2^-, PF_6^-, AcO^- and BF_4^-).

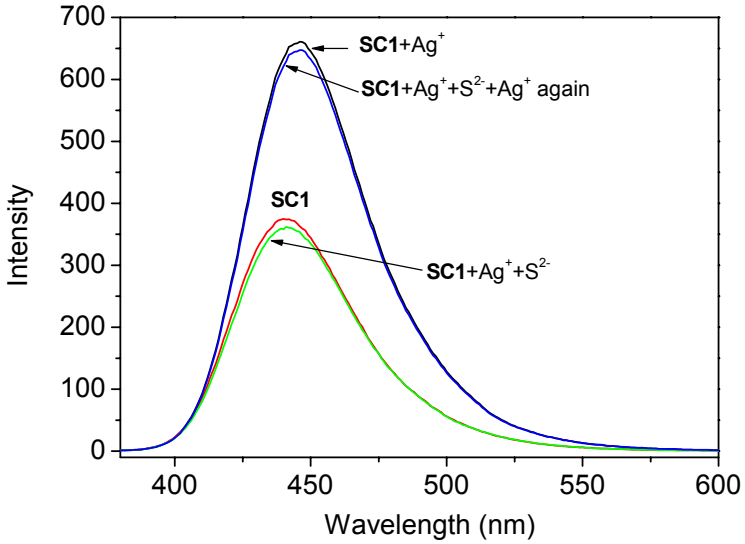

Figure S5. Fluorescence spectra of **SC1**(5 μM) upon the addition of 0.4 equivalent of $AgNO_3$ in ethanol/H_2O (1:1, v/v). Na_2S (0.2 equiv) was added to **SC1**+Ag^+ mixture to show the reversible binding nature of Ag^+ with **SC1.**

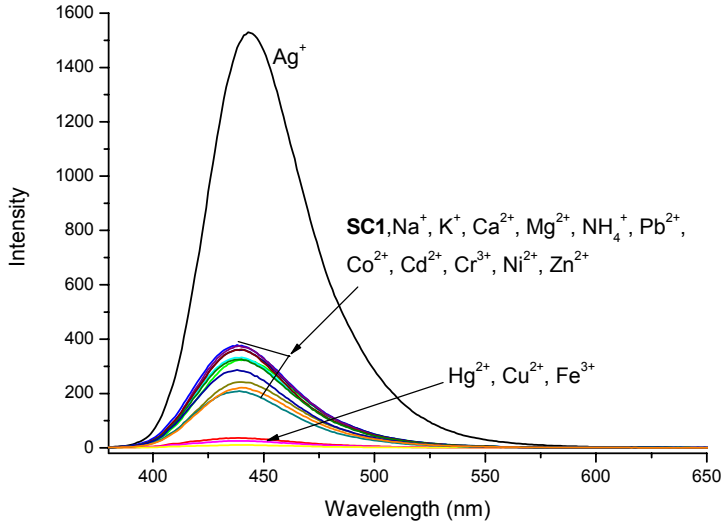

Figure S6. Fluorescence spectra of **SC1**(4.6 μM) upon the addition of the nitrate salts (50.0 equiv) of Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Pb^{2+}, Hg^{2+}, Co^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}, Cr^{3+} Fe^{3+}, and 2.0 equiv of Ag^+ in ethanol/H_2O (1:1, v/v).

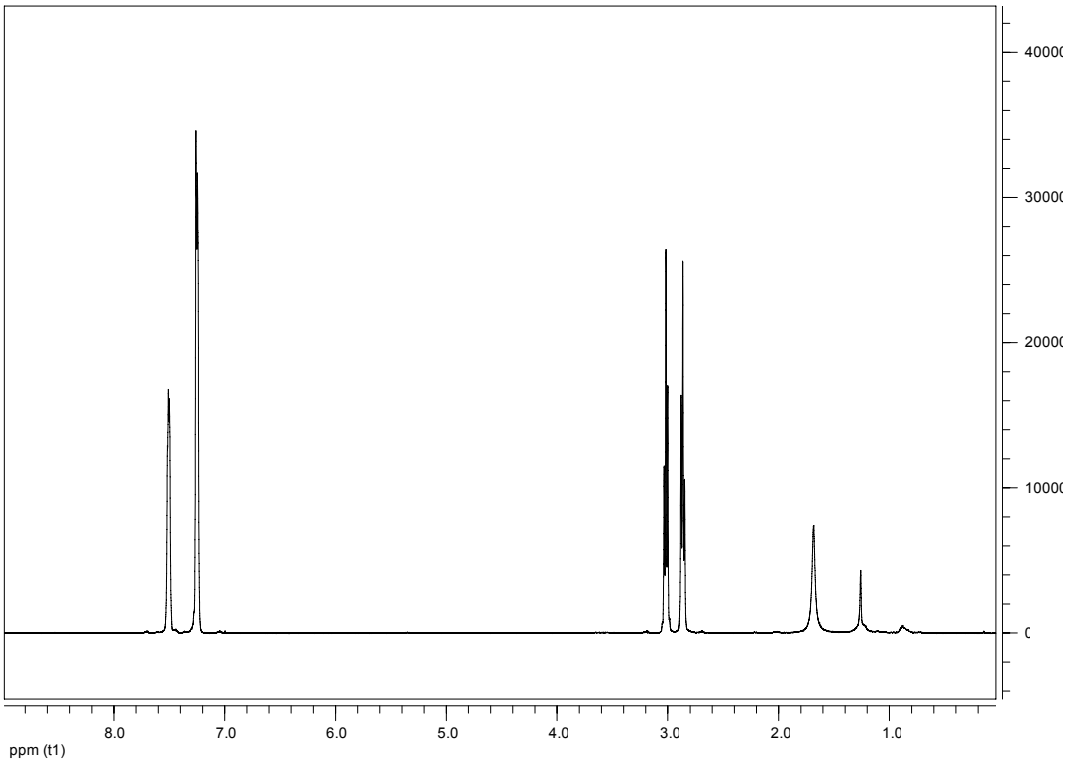

Figure S7. ^{1}H NMR of compound **1** (400 MHz, $CDCl_3$).

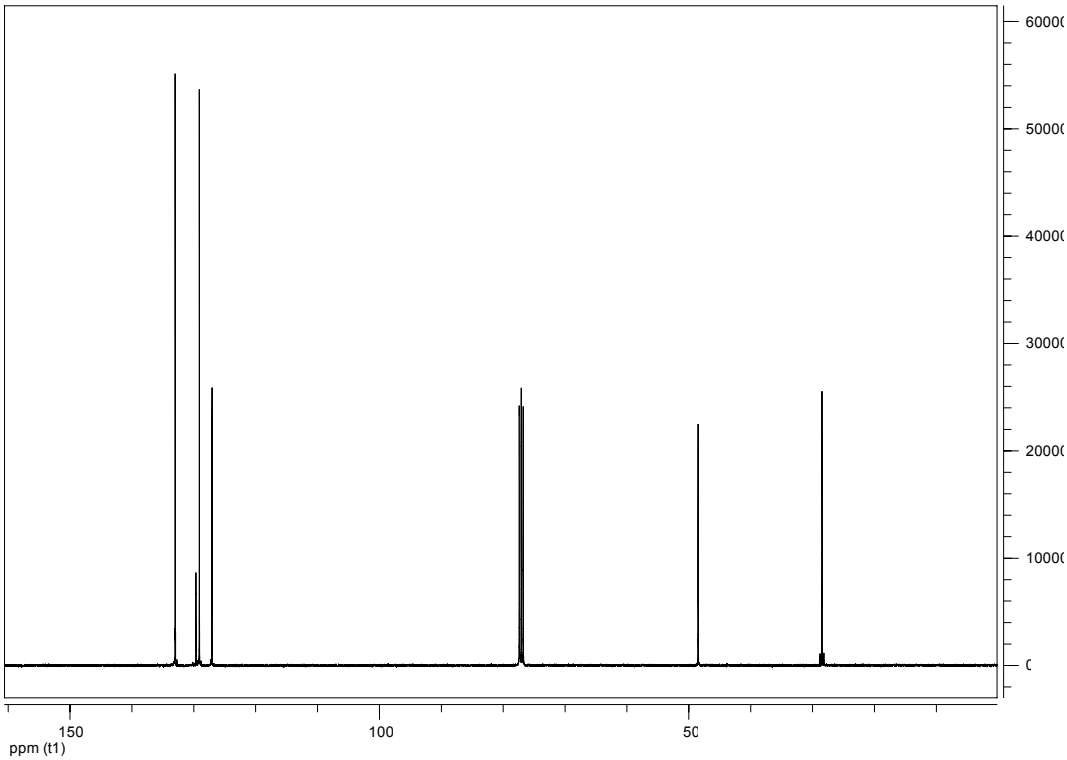

Figure S8. ^{13}C NMR of compound **1** (100 MHz, $CDCl_3$).

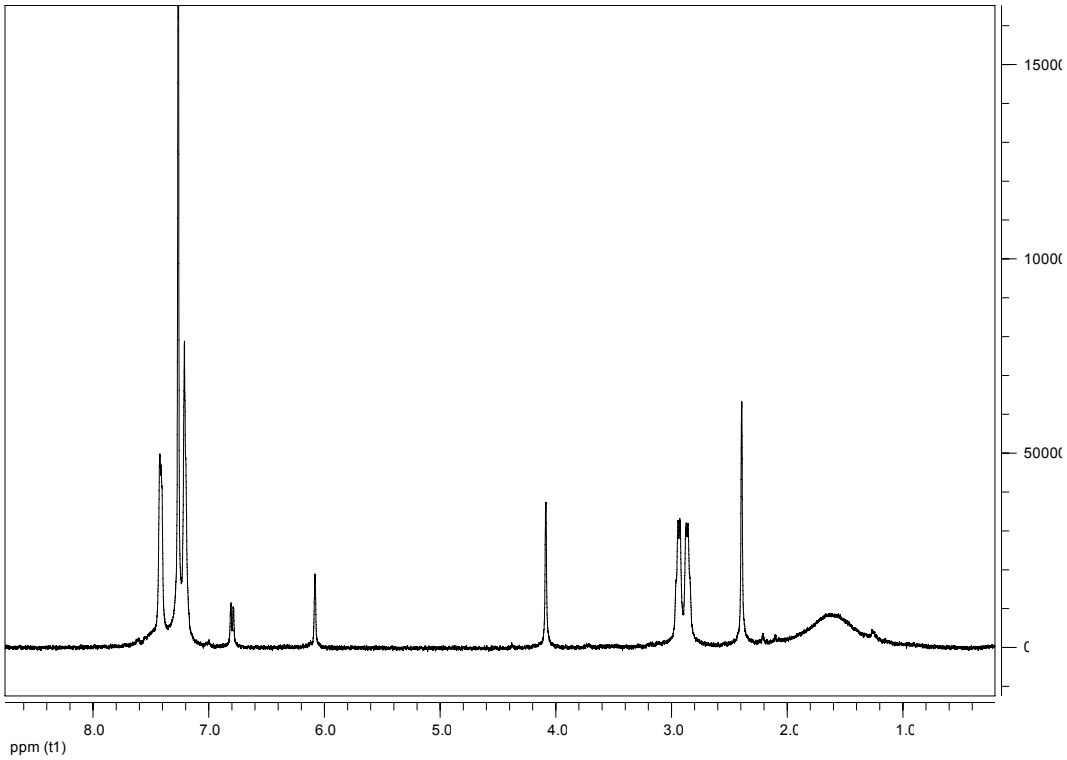

Figure S9. ^{1}H NMR of compound **SC1** (400 MHz, $CDCl_3$).

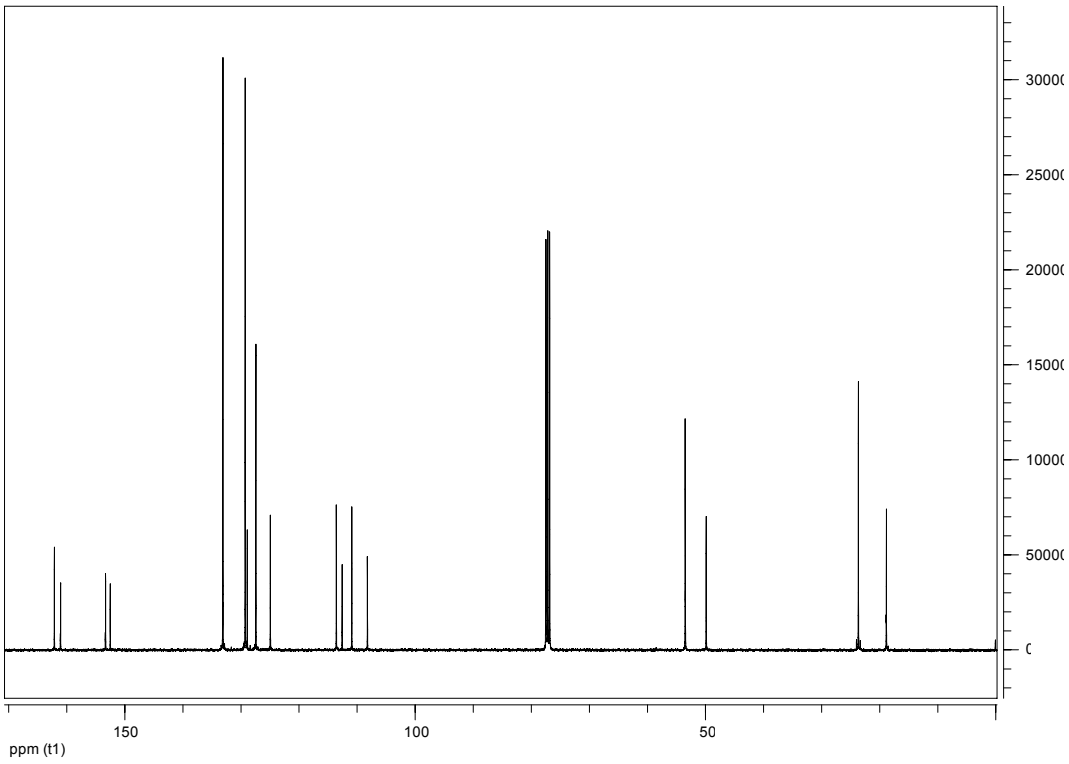

Figure S10. ^{13}C NMR of compound **SC1** (100 MHz, $CDCl_3$).