Electronic Supplementary Information (ESI)

Stereoselective synthesis and reaction of gold(I) (Z)-enethiolate

Kazunori Miyamoto,* Masaya Hirobe, Masanobu Uchiyama, and Masahito Ochiai

Graduate School of Pharmaceutical Sciences, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Advanced Elements Chemistry Research Team, RIKEN Center for Sustainable Resource Science, and Elements Chemistry Laboratory, RIKEN, 2-1 Hirosawa, Wako-shi, Saitama 351-0198, Japan

Graduate School of Pharmaceutical Sciences, University of Tokushima, 1-78 Shomachi, Tokushima 770-8505, Japan

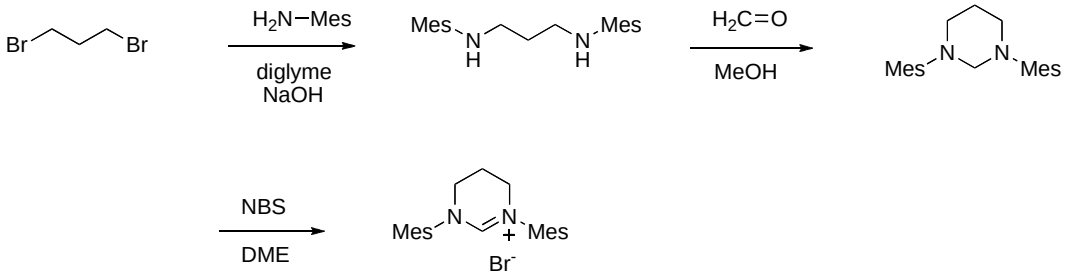
E-mail: kmiya@mol.f.u-tokyo.ac.jp

Table of Contents

1. Method

General Information. IR spectra were recorded on JASCO FT/IR-420 spectrometers. 1H NMR and ^{13}C NMR spectra were obtained on either a JEOL JNM-AL300, JNM-AL400, or Bruler AV400 spectrometers. Chemical shifts (d) are reported in parts per million (ppm) downfield from intermal Me_4Si. Mass spectra (MS) were obtained on either a Waters LCT Premier, or SHIMADZU Model GCMS-QP 505 spectrometer. Preparative thin layer chromatography (TLC) was carried out on precoated plates of silica gel (MERCK, silica gel F-254). Kiselgel 60 (MERCK, 230-400 mesh) was used for column chromatography. Melting points were determined with Yanaco micro melting points apparatus and are uncorrected.

Subsrate. (*Z*)-β-alkylvinylthioimidonium tetrafluoroborate **5** were prepared from corresponding (*E*)-β-alkylvinyl-λ^3-iodanes according to a literature method.[S1] AuCl-tetrahydrothiophene complex **6** was prepared by the reaction of tetrachloroauric acid and tetrahydrothiophene according to a literature method.[S2] 1,3-Dimesityl-3,4,5,6-tetrahydropyrimidin-1-ium bromide was prepared according to a literature method as shown below.[S3]



Synthesis of Gold Enethiolate 7. Gold (*Z*)-1-decenylthiolate (7a). To a stirred solution of gold(I) chloride-tetrahydrothiophene complex (**6**) (22.0 mg, 0.068 mmol) in THF (1.1 mL) was added (*Z*)-*S*-1-decenyl-*N,N*-(dimethyl)thiobenzimidonium tetrafluoroborate (**5a**) (26.9 mg, 0.068 mmol) and 5% aqueous solution of Na_2CO_3 (290 μL, 0.136 mmol) under argon, and the mixture was stirred for 4 h at room temperature. The reaction was added small portion of water and resulting yellow precipitate was collected by filtration, which was purified by repeated washing with methanol and then with ethyl acetate to give pure **7a** (22.4 mg, 90%) as a yellow amorphous. Mp 93-95℃ (decomposition); IR (Nujol) 2979, 2881, 2833, 1454, 1377, 721 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.74-6.03 (m, 1H), 5.83-5.50 (m, 1H), 2.54-2.10 (m, 2H), 1.50-1.19 (m, 12H), 0.89 (t, *J* = 6.6 Hz, 3H); HRMS (ESI, negative, THF:MeOH = 1:1) for monomer: calcd for $C_{10}H_{19}S$ [(M-Au)$^-$], 171.1207, found 171.1213; for dimer: calcd for $C_{20}H_{38}AuS_2$ [(M_2-Au)$^-$] 539.2081, found 539.2034; for trimer: calcd for $C_{30}H_{57}Au_2S_3$ [(3M-Au)$^-$] 907.2954, found

907.2971. Anal. Calcd for $C_{10}H_{19}AuS \cdot 1/4H_2O$: C, 32.22; H. 5.27. Found: C, 32.25; H, 5.10.

Gold (*Z*)-3-phenyl-1-propenylthiolate (7b): a yellow powder; mp 157-160 °C (decomposition); IR (neat) 3059, 3024, 1601, 1493, 1452, 1317, 1281, 1074, 1030, 750, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32-6.81 (m, 5H), 6.76-5.50 (m, 2H), 3.95-3.36 (m, 2H); HRMS (ESI, negative, $CHCl_3$:MeOH = 1:1) calcd for $C_{18}H_{18}S_2Au$ $[(2M-Au)^-]$ 495.0516, found 495.0514. Anal. Calcd for $C_9H_9AuS \cdot 1/2H_2O$: C, 30.43; H. 2.84. Found: C, 30.14; H, 2.60.

Synthesis of Gold Enethiolate-triphenylphosphine Complex 8a. To a stirred solution of gold (*Z*)-1-decenylthiolate (**7a**) (20.0 mg, 0.054 mmol) in dichloromethane (2.0 mL) was added triphenylphosphine (14.2 mg, 0.054 mmol) under argon, and the mixture was stirred for 30 min at room temperature. The reaction mixture was washed with water and the aqueous layer was extracted with dichloromethane four times. Combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under aspiratory vacuum to give (*Z*)-1-decenylthiolato(triphenylphosphine)gold (**8a**) (32.2 mg, 95%) as a colorless oil. IR (neat) 3053, 2924, 2850, 1587, 1479, 1435, 1346, 1309, 1182, 1101, 1028, 999, 746, 710, 692 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.59-7.39 (m, 15H), 6.62 (d, J = 9.1 Hz, 1H), 5.59 (dt, J = 9.1, 6.8 Hz, 1H), 2.44 (q, J = 6.8 Hz, 2H), 1.47-1.13 (m, 12H), 0.86 (t, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.2 (d, $^2J_{cp}$ = 13.7 Hz), 131.7, 131.6, (d, $^4J_{cp}$ = 2.5 Hz), 129.7 (d, $^1J_{cp}$ = 55.4 Hz), 129.1 (d, $^3J_{cp}$ = 11.2 Hz), 123.4, 31.9, 29.6(2C), 29.4, 29.3, 28.7, 22.7, 14.1; HRMS (ESI, positive) calcd for $C_{28}H_{34}AuNaSP$ $[(M+Na)^+]$ 653.1682, found 653.1686.

Synthesis of Gold Enethiolate-NHC Complex 9a. To a stirred solution of 1,3-diisopropylimidazolium chloride (7.5 mg, 0.04 mmol) in THF (2 mL) was added 1.63 M butyllithium (29 μl, 0.047 mmol) in hexane at -78 °C under argon, and the mixture was gradually warmed to room temperature for 3.5 h. The resulting NHC solution was then cooled to -30 °C and gold (*Z*)-1-decenylthiolate (**7a**) (10.2 mg, 0.028 mmol) was added in one portion. The mixture was gradually warmed to room temperature and stirred for 5 h. After addition of water, the mixture was extracted with diethyl ether four times. Combined organic phase was dried over Na_2SO_4, filtered, and concentrated under an aspiratory vacuum to give an oil, which was washed several times with hexane by decantaion at room temperature to give (*Z*)-1-decenylthiolato(1,3-diisopropylimidazol-2-ylidene)gold (**9a**) (18.6 mg, 89 %) as a colorless oil. IR (neat) 2972, 2924, 2852, 1462, 1431, 1415, 1394, 1371, 1211 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 2H), 6.60 (d, J = 8.5 Hz, 1H),

5.54 (dt, J = 8.5, 6.6 Hz, 1H), 5.07 (sept, J = 6.6 Hz, 2H), 2.43 (q, J = 6.6 Hz, 2H), 1.51-1.17 (m, 12H), 1.46 (d, J = 6.6 Hz, 12H), 0.87 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.2, 130.8, 124.9, 116.5, 53.2, 32.0, 29.7, 29.6, 29.5, 29.4, 28.4, 23.4, 22.7, 14.1; HRMS (ESI, positive) calcd for $C_{19}H_{35}AuN_2NaS$ [$(M+Na)^+$] 543.2084, found 543.2082.

Synthesis of Gold Enethiolate-NHC Complex 10a. To a stirred solution of 1,3-bis[1,3,5-(trimethyl)phenyl]-3,4,5,6-tetrahydropyrimidin-1-ium bromide (25.7 mg, 0.064 mmol) and gold (*Z*)-1-decenylthiolate (**7a**) (10.7 mg, 0.029 mmol) in THF (2 mL) was added 0.26 M lithium *tert*-butoxide (267 μl, 0.069 mmol) in THF at room temperature under argon, and the mixture was warmed to 45 °C and stirred at the temperature for 14 h. After addition of water, the mixture was extracted with hexane four times. Combined organic phase was dried over Na_2SO_4, filtered, and concentrated under an aspiratory vacuum to give an oil, which was washed several times with hexane by decantaion at room temperature to give (*Z*)-1-decenylthiolato{1,3-bis[1,3,5-(trimethyl)phenyl]-3,4,5,6-tetrahydropyrimidin-2-ylidene}gold (**10a**) (19.4 mg, 97 %) as colorless oil. Recrystallization from ethyl acetate-hexane at 4 °C yielded pure complex **10a** as colorless prisms. mp 136-138 °C; IR (neat) 2922, 2852, 1608, 1520, 1479, 1402, 1375, 1344, 1308, 1207, 1032, 852, 754 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (s, 4H), 5.48 (dt, J = 9.2 1.5 Hz, 1H), 5.11 (dt, J = 9.2, 7.0 Hz, 1H), 3.40 (t, J = 6.2 Hz, 4H), 2.32 (t, J = 6.2 Hz, 2H), 2.27 (s, 12H), 2.25 (s, 6H), 2.07 (q, J = 7.0 Hz, 2H), 1.29-1.15 (m, 12H), 0.85 (t, J = 7.0 Hz, 3H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.8, 141.8, 138.0, 134.8, 129.6, 129.0, 125.8, 45.2, 31.9, 29.6, 29.6, 29.3, 27.8, 22.7, 21.1, 21.0, 18.0, 14.1; HRMS (ESI, positive) calcd for $C_{32}H_{47}AuN_2NaS$ [$(M+Na)^+$] 711.3023, found 711.2952. Anal. Calcd for $C_{32}H_{47}AuN_2S•1/4H_2O$: C, 55.43; H. 6.91; N, 4.04. Found: C, 55.22; H, 6.94; N, 4.02.

General Procedure for Alkylation of Gold (Z)-Enethiolates. A Typical Example (Table 1, entry 6). To a stirred solution of (*Z*)-1-decenylthiolato{1,3-bis[1,3,5-(trimethyl)phenyl] -3,4,5,6-tetrahydropyrimidin-2-ylidene}gold (**10a**) (14.6 mg, 0.021 mmol) in dichloromethane (2.0 mL) was added TEMPO (0.3 mg, 0.0021 mmol) and iodomethane (30.1 mg, 0.21 mmol) under argon, and the mixture was stirred at room temperature for 30 min. The reaction mixture was washed with water and the aqueous layer was extracted with dichloromethane four times. Combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under aspiratory vacuum to give an oil, which was purified by silica gel column chromatography using

hexane to give (Z)-1-decenyl methyl sulfide (**11a**) (3.7 mg, 95%) as a colorless oil. The *Z*:*E* ratio was determined by ^{1}H NMR of a crude oil. (Z)-**11a**:[S4,S5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (d, *J* = 9.1 Hz, 1H), 5.53 (dt, *J* = 9.1, 7.3 Hz, 1H), 2.27 (s, 3H), 2.11 (q, *J* = 7.3 Hz, 2H), 1.44-1.28 (m, 4H), 0.91 (t, *J* = 7.3 Hz, 3H).

(Z)-1-decenyl ethyl sulfide (**11b**) (Table 1, Entry 7):[S4,S6] a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 (d, *J* = 9.1 Hz, 1H), 5.57 (dt, *J* = 9.1, 6.9 Hz, 1H), 2.67 (q, *J* = 6.9 Hz, 2H), 2.11 (q, *J* = 6.9 Hz, 2H), 1.44-1.20 (m, 15H), 0.88 (t, *J* = 6.9 Hz, 3H).

(Z)-1-decenyl isopropyl sulfide (**11c**) (Entry 9):[S4] a colorless oil; IR (neat) 2958, 2924, 2854, 1607, 1462, 1243, 770 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.98 (d, *J* = 9.4 Hz, 1H), 5.58 (dt, *J* = 9.4, 7.0 Hz, 1H), 3.05 (sept, *J* = 6.6 Hz, 1H), 2.11 (dt, *J* = 7.0, 6.8 Hz, 2H), 1.42-1.21 (m, 12H), 1.31 (d, *J* = 6.6 Hz, 6H), 0.87 (t, *J* = 6.6 Hz, 3H).

(*Z*)-1-Decenyl allyl sulfide (11d) (Entry 12):[S4] a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (d, *J* = 9.1 Hz, 1H), 5.84 (ddt, *J* = 17.6, 10.6, 7.3 Hz, 1H), 5.58 (dt, *J* = 9.1, 6.9 Hz, 1H), 5.16 (d, *J* = 17.6 Hz, 1H), 5.11 (d, *J* = 10.6 Hz, 1H), 3.28 (d, *J* = 7.3 Hz, 2H), 2.11 (q, *J* = 6.9 Hz, 2H), 1.43-1.18 (m, 12H), 0.88 (t, *J* = 6.5 Hz, 3H).

(*Z*)-1-Decenyl benzyl sulfide (11e) (Entry 13):[S4] a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.28 (m, 5H), 5.89 (d, *J* = 9.2 Hz, 1H), 5.55 (dt, *J* = 9.2, 7.0 Hz, 1H), 3.86 (s, 2H), 2.09 (q, *J* = 7.0 Hz, 2H), 1.39-1.16 (m, 12H), 0.88 (t, *J* = 6.6 Hz, 3H).

(*Z*)-1-Decenyl phenacyl sulfide (11f) (Entry 14):[S4] a colorless oil; IR (neat) 3060, 2925, 2854, 1680, 1599, 1579, 1448, 1277, 1014, 688 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.3 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.3 Hz, 2H), 5.97 (d, *J* = 9.1 Hz, 1H), 5.65 (dt, *J* = 9.1, 6.9 Hz, 1H), 3.95 (s, 2H), 2.07 (q, *J* = 6.9 Hz, 2H), 1.37-1.14 (m, 12H), 0.87 (t, *J* = 6.9 Hz, 3H).

Bis((*Z*)-1-decenylthio)methane (**13**):[S4] a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.06 (d, *J* = 9.1 Hz, 2H), 5.69 (dt, *J* = 9.1, 6.9 Hz, 2H), 3.87 (s, 2H), 2.12 (q, *J* = 6.9 Hz, 4H), 1.44-1.17 (m, 24H), 0.88 (t, *J* = 6.6 Hz, 6H).

Nucleophilic Substitution of 2,4-dinitrohalobenzene with Gold (Z)-Enethiolates. A Typical Example (Scheme 6, Reaction of 10a with 14b). To a stirred solution of (*Z*)-1-decenylthiolato{1,3-bis[1,3,5-(trimethyl)phenyl]-3,4,5,6-tetrahydropyrimidin-2-ylidene}gold (**10a**) (13.4 mg, 0.019 mmol) in THF (2.0 mL) was added TEMPO (0.3 mg, 0.002 mmol) and 2,4-dinitro-1-bromobenzene (4.8 mg, 0.019 mmol) under argon, and the mixture was stirred at room temperature for 24 h. The reaction mixture was washed with water and the aqueous layer was extracted with dichloromethane four times. Combined organic phase was dried over

anhydrous Na_2SO_4, filtered, and concentrated under aspiratory vacuum to give a yellow oil, which was purified by preparative TLC (hexane:diethyl ether = 6:4) to give (*Z*)-1-decenyl 2,4-dinitrophenyl sulfide (**15**) (5.6 mg, 88%) as yellow oil. The *Z*:*E* ratio was determined by ^{1}H NMR of a crude oil. (*Z*)-**15**:[S4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (d, *J* = 2.6 Hz, 1H), 8.34 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 6.45 (dt, *J* = 9.1, 6.9 Hz, 1H), 6.19 (d, *J* = 9.1 Hz, 1H), 2.39 (q, *J* = 6.9 Hz, 2H), 1.51-1.41 (m, 2H), 1.38-1.17 (m, 10H), 0.87 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.4, 144.7, 143.9, 143.4, 127.7, 126.0, 120.7, 116.3, 30.9, 28.4, 28.3(2C), 27.9, 21.7, 13.2.

(***E*)-1-Decenyl 2,4-dinitrophenyl sulfide** (**15**): yellow oil: IR (neat) 3105, 2925, 2854, 1595, 1523, 1456, 1340, 1304, 1051, 962, 918, 833, 735 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (d, *J* = 1.8 Hz, 1H), 8.34 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.65 (d, *J* = 7.7 Hz, 1H), 6.46 (dt, *J* = 14.7, 7.4 Hz, 1H), 6.14 (dt, *J* = 14.7, 1.5 Hz, 1H), 2.33 (dq, *J* = 7.4, 1.5 Hz, 2H), 1.56-1.18 (m, 12H), 0.90 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.5, 147.4, 144.3, 144.2, 128.3, 126.9, 121.6, 116.5, 33.5, 31.9, 29.3, 29.2(2C), 28.5, 22.7, 14.1 ; MS *m/z* (relative intensity) 338 (M^+, 73 %), 239 (35), 183 (100), 137 (51), 83 (51); HRMS calcd for $C_{16}H_{22}O_4N_2S$ (M^+) 338.1300, found 338.1310.

Michael Addition of Gold (Z)-Enethiolate to Cycloalkenone. A Typical Example (Scheme 8, Reaction of 7a with 15b). To a stirred solution of gold (*Z*)-1-decenylthiolate (**7a**) (17.2 mg, 0.047 mmol) was added triphenylphosphine (24.7 mg, 0.094 mmol) in dichloromethane (3.5 mL) under argon, and stirred at room temperature for 10 min. After addition of lithium iodide (37.6 mg, 0.28 mmol) to the resulting (*Z*)-gold thiolate-PPh_3 complex solution, 2-cyclohexen-1-one (4.5 mg, 0.047 mmol) was added and stirred at room temperature for 24 h. The reaction mixture was washed with water and the aqueous layer was extracted with dichloromethane four times. Combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under aspiratory vacuum to give an yellow solid, which was purified by column chromatography (dichloromethane-ethyl acetate 9:1) to give 3-[(*Z*)-1-decenylthio]cyclohexanone (**16b**) (9.6 mg, 76%) as a colorless oil;[S4] IR (neat) 2925, 2854, 1715, 1457, 1313, 1220 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (d, *J* = 9.2 Hz, 1H), 5.68 (dt, *J* = 9.2, 7.0 Hz, 1H), 3.21-3.11 (m, 1H), 2.73 (dd, *J* = 14.6, 3.6 Hz, 1H), 2.46-2.25 (m, 3H), 2.22-2.03 (m, 4H), 1.83-1.65 (m, 2H), 1.43-1.18 (m, 12H), 0.88 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.6, 132.8, 121.2, 48.2, 44.7, 40.9, 31.9, 31.6, 29.4, 29.3, 29.2(2C), 28.9, 24.1, 22.7, 14.1.

3-[(*Z*)-1-Decenylthio]cyclopentanone (**16a**): a colorless oil; IR (neat) 2925, 2854, 1747, 1608,

1457, 1403, 1274, 1248, 1157 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.94 (d, *J* = 9.2 Hz, 1H), 5.71 (dt, *J* = 7.0, 9.2 Hz, 1H), 3.61 (quint, *J* = 7.3 Hz, 1H), 2.62 (dd, *J* = 18.3, 7.3 Hz, 1H), 2.54-2.19 (m, 3H), 2.19-1.98 (m, 4H), 1.44-1.19 (m, 12H), 0.88 (t, *J* = 6.6 Hz, 3H); MS *m/z* (relative intensity) 254 (12%, M^+), 191 (8), 171 (9), 96 (42), 82 (100): HRMS calcd for $C_{15}H_{26}OS$ (M^+) 254.1704, found 254.1718.

3-[(*Z*)-1-Decenylthio]cycloheptanone (**16c**): a colorless oil; IR (neat) 2925, 2854, 1703, 1608, 1456, 1346, 1284, 1192, 935, 889, 723 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.93 (d, *J* = 9.2 Hz, 1H), 5.69 (t, *J* = 9.2, 7.3 Hz, 1H), 3.11 (tt, *J* = 9.2, 2.9 Hz, 1H), 2.87-2.73 (m, 2H), 2.61-2.44 (m, 2H), 2.20-2.07 (m, 3H), 2.03-1.63 (m, 4H), 1.60-1.49 (m, 1H), 1.42-1.20 (m, 12H), 0.88 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.6, 132.8, 122.0, 50.2, 44.0, 43.1, 37.4, 31.9, 29.4, 29.3, 29.2, 29.2, 29.0, 28.1, 23.9, 22.7, 14.1; MS *m/z* (relative intensity): 282 (13 %, M^+), 171 (26), 138 (30), 111 (43), 96 (25), 83 (100), 81 (60): HRMS calcd for $C_{17}H_{30}OS$ (M^+) 282.2017, found 282.2057.

Job Plot. Equimolar solutions (0.17 M) of (*Z*)-gold thiolate **7a** and triphenylphosphine were prepared and mixed in various amount. ^{13}C NMR spectra of the mixture were recorded at room temperature, and the complexation induced chemical shifts of an *ipso* carbon of triphenylphosphine were analyzed by the method developed by Newcomb and co-workers.[S7]

^{13}C NMR Titration. A solution of triphenylphosphine (0.178 M) in $CDCl_3$ was prepared. Nine NMR tunes were each filled with the solution and with an adequate amount of (*Z*)-gold thiolate **7a** (0-2.2 equiv). ^{13}C NMR spectra of the mixtures were recorded at room temperature. The curve-fittings of the chemical shift data of an *ipso* carbon of triphenylphosphine were carried out by a nonlinear least-squares method (Marquardt–Levenberg Algorithm) according to the reported equation[S8] with use of SigmaPlot (Jandel Scientific, San Rafael, CA).

2. ESI-MS spectrum observed for gold (Z)-enethiolate 7a

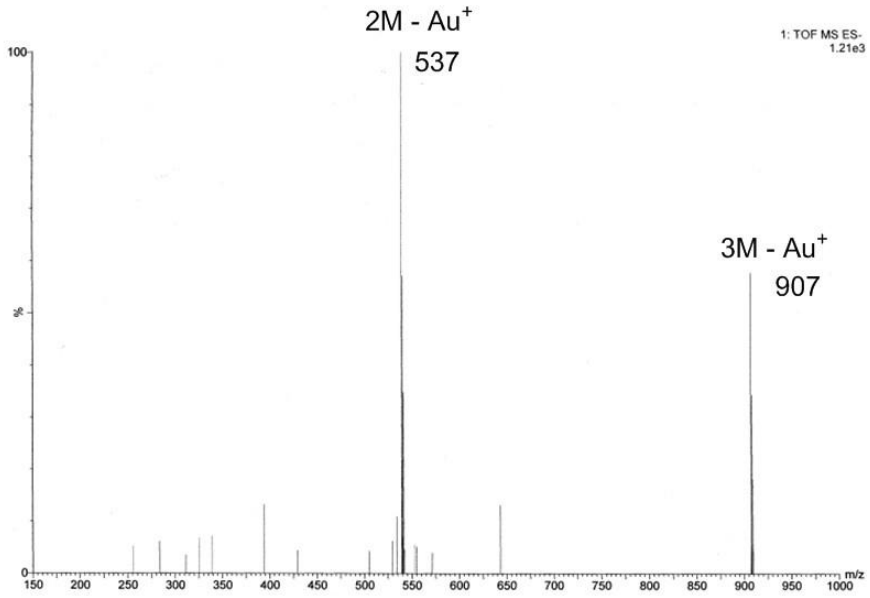


Figure S1. ESI-MS spectrum observed for gold (Z)-enethiolate **7a** in CH_2Cl_2-MeOH (1:1). No monomeric gold enethiolate **7a** species $[M\text{-}Au]^+$ was detected under the conditions.

3. Job plot for complexation of gole (Z)-enethiolate 7a with triphenylphosphine

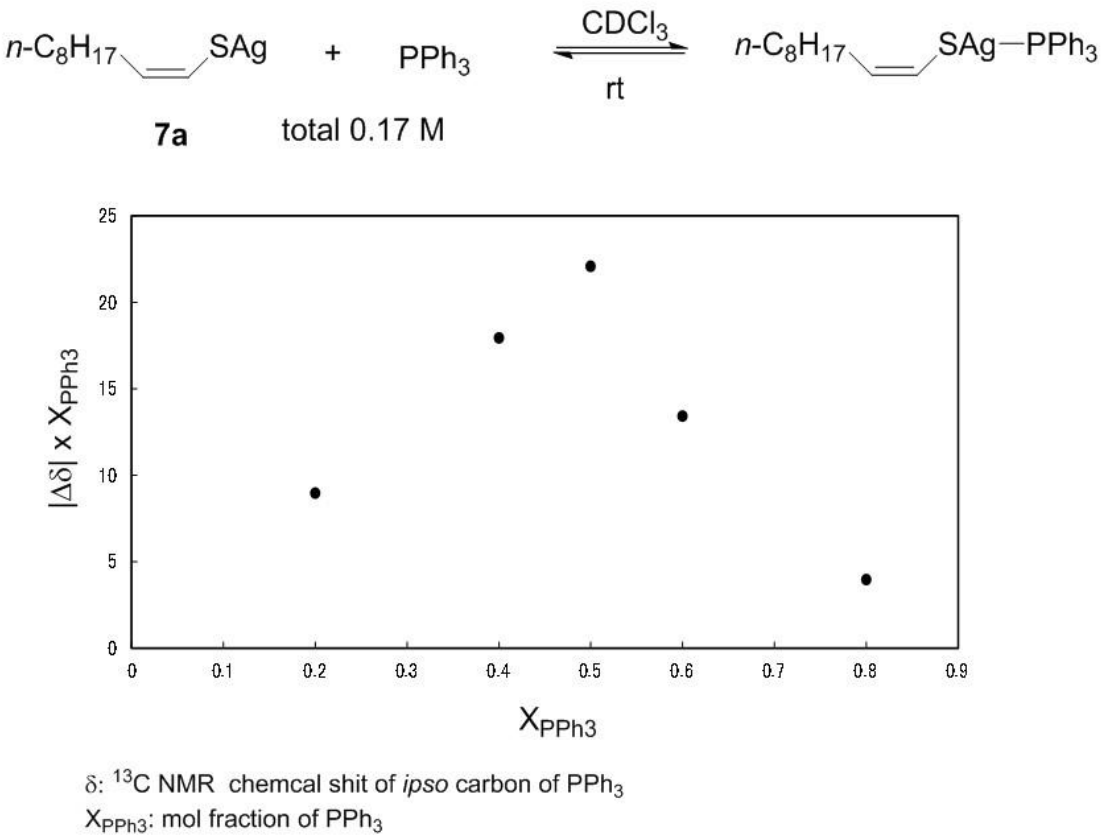


Figure S2. Job plot for complexation between gole (Z)-enethiolate **7a** and triphenylphosphine in $CDCl_3$ at rt.

4. Observed ^{13}C NMR chemical shifts of PPh_3 (0.178 M) when titrated with 7a in $CDCl_3$ at rt

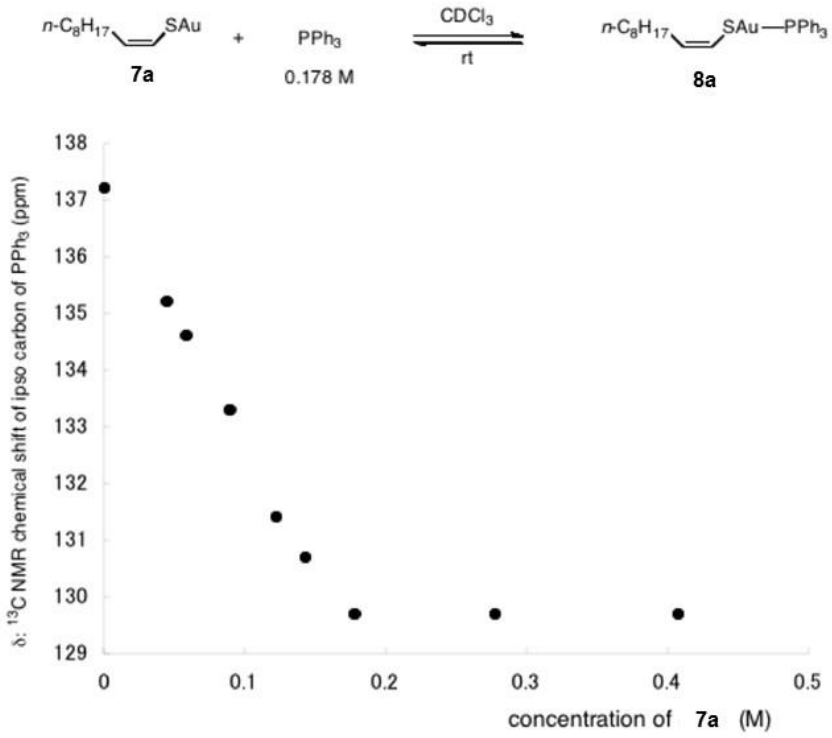


Figure S3. Observed ^{13}C NMR chemical shifts of PPh_3 (0.178 M) when titrated with **7a** in $CDCl_3$ at rt.

5. Isomerization of 8a in $CDCl_3$ at 23 °C in the dark.

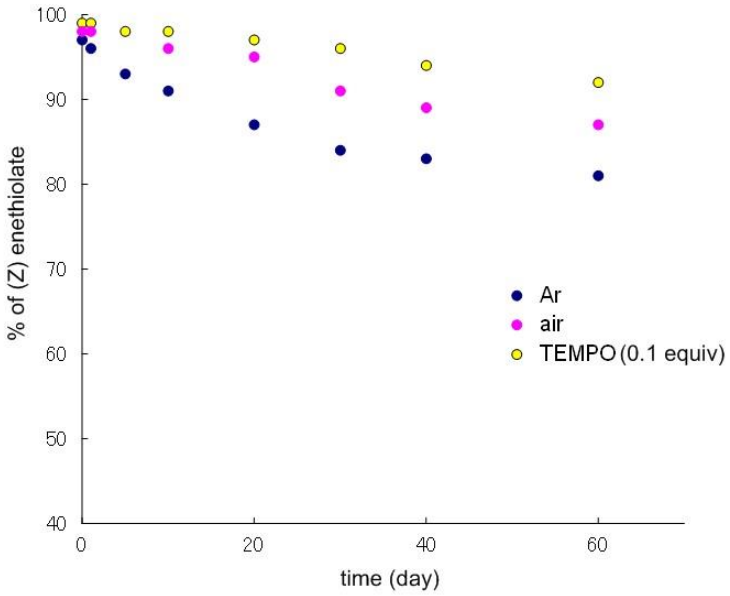


Figure S4. Effect of additives on the configurational stability of gold (Z)-enethiolate-PPh_3 complex **8a** in $CDCl_3$ (0.01 M) at 23 °C in the dark. The filled blue circle means under argon. The filled pink circle means under air. The filled yellow circle means in the presence of TEMPO (0.1 equiv) under Ar.

References

S1 M. Ochiai, S. Yamamoto, S. K. Sato, *Chem. Commun*. **1999***,* 1363.

S2 R. Uson, A. Laguna, *Organomet. Synth*. **1986,** *3*, 324.

S3 M. Mayr, K. Wurst, K. K.-H. Ongania, M. Buchmeiser, *Chem. Eur. J.* **2004**, *10*, 1256.

S4 M. Ochiai, M. Hirobe, K. Miyamoto, *J. Am. Chem. Soc.* **2006**, *128*, 9046.

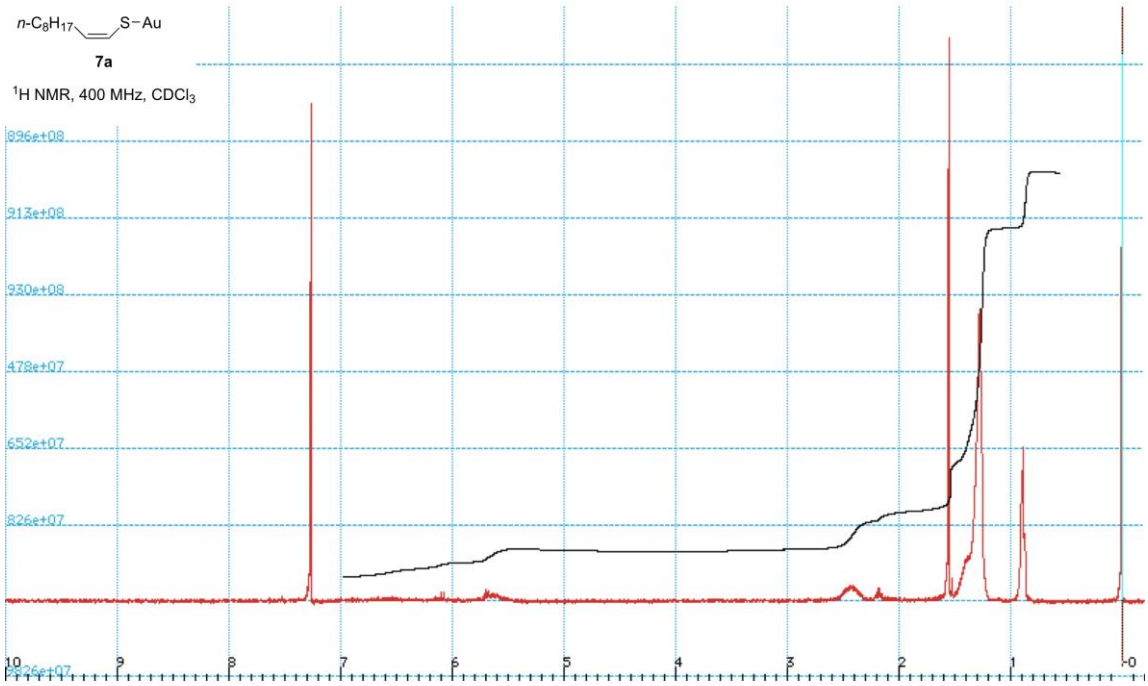
S5 K. Oshima, K, Shimoji, H. Takahashi, H. Yamamoto, H. Nozaki, *J. Am. Chem. Soc.* **1973**, *95*, 2694.

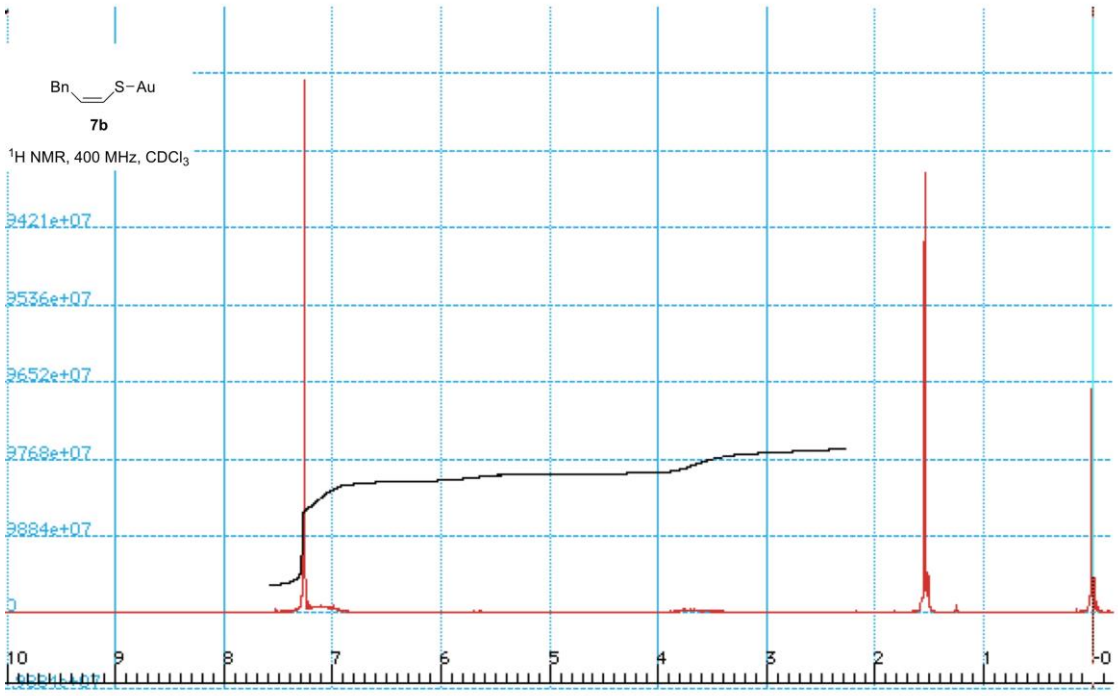
S6 M. A. Khan, *J. Chem. Res. Synopses*, **1991**, 163.

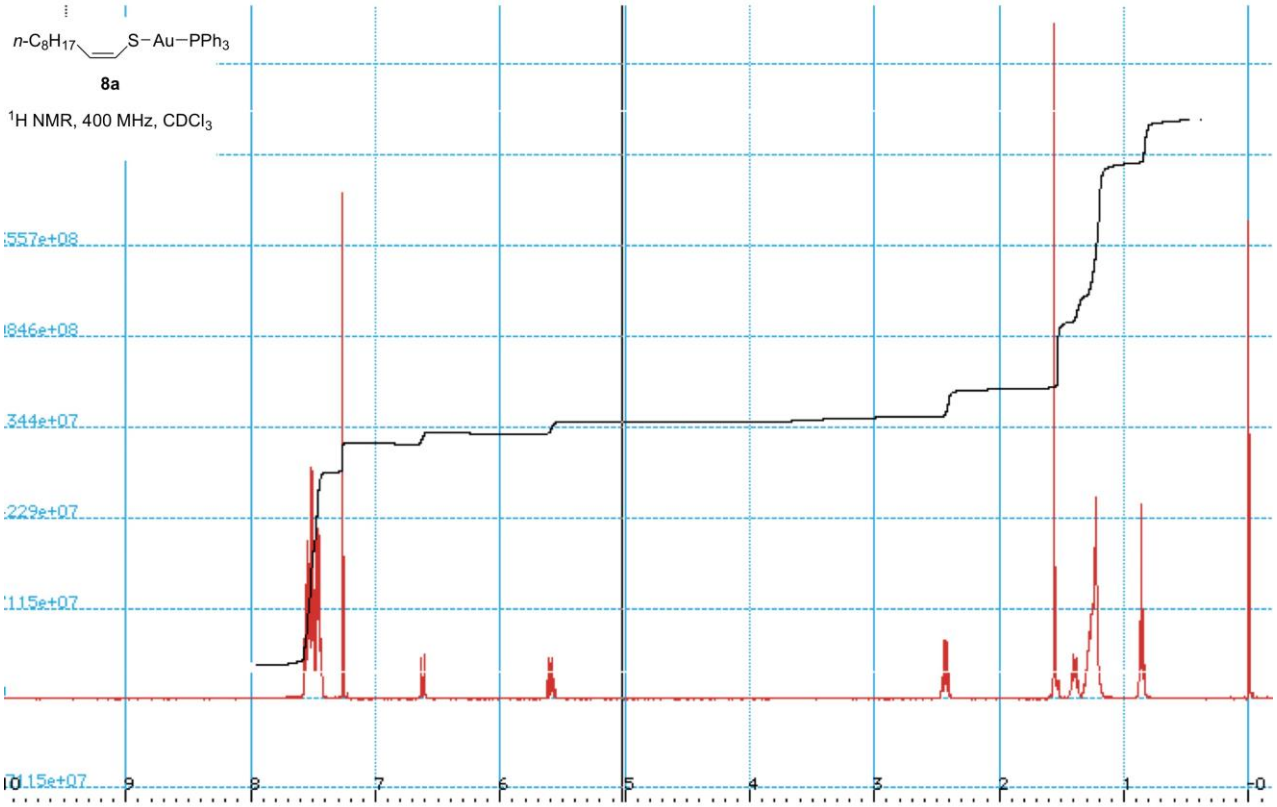
S7 M. T. Blanda, J. T. Horner, M. Newcomb, *J. Org. Chem.* **1989**, *54*, 4626.

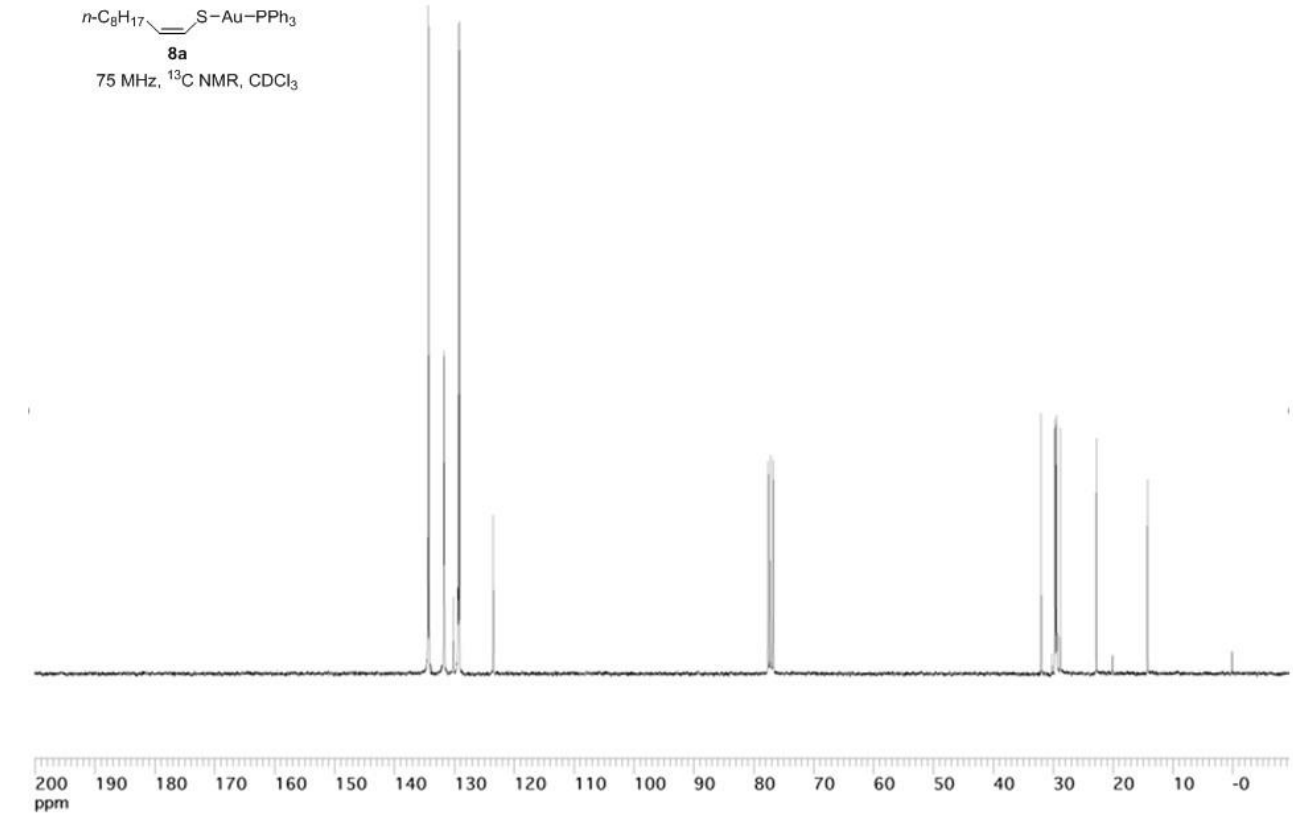
S8 N. Funasaki, S. Ishikawa, S, Neya, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 719.

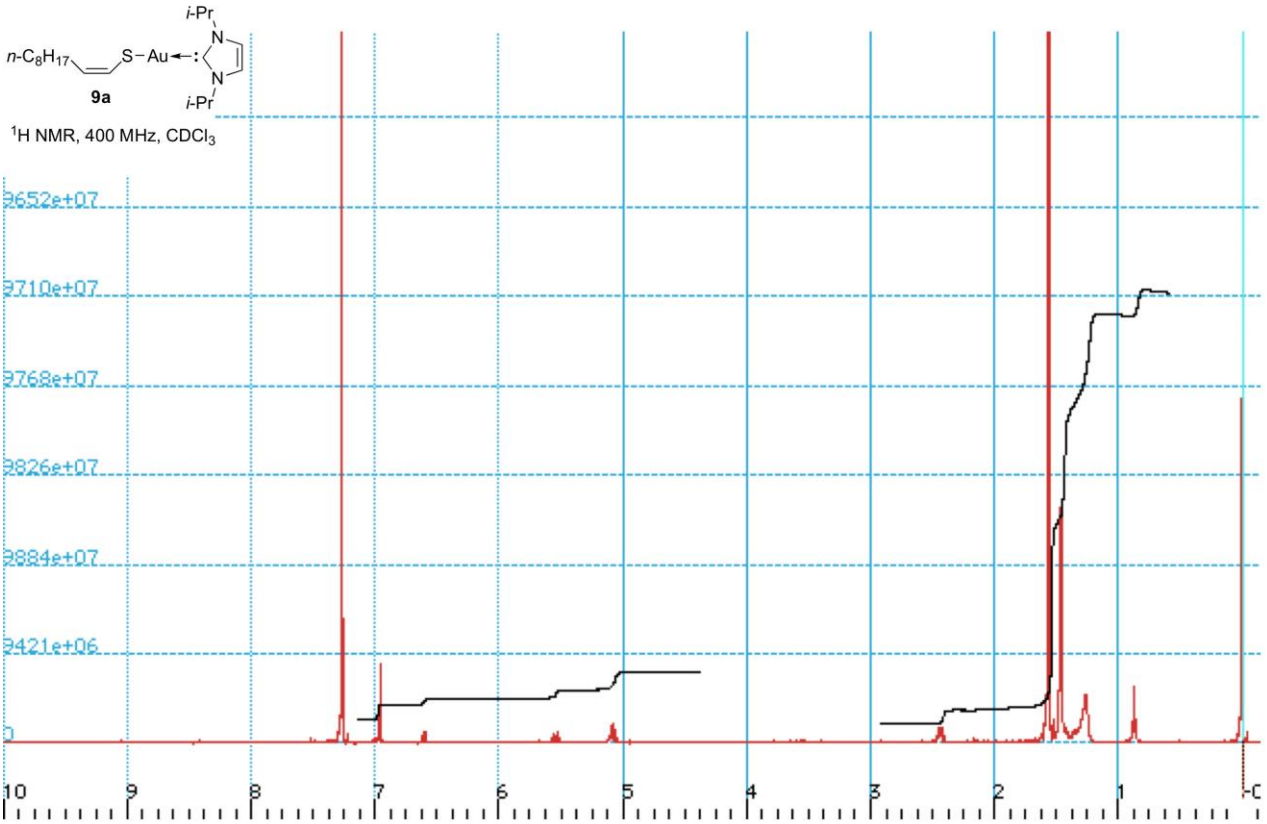
6. Spectra

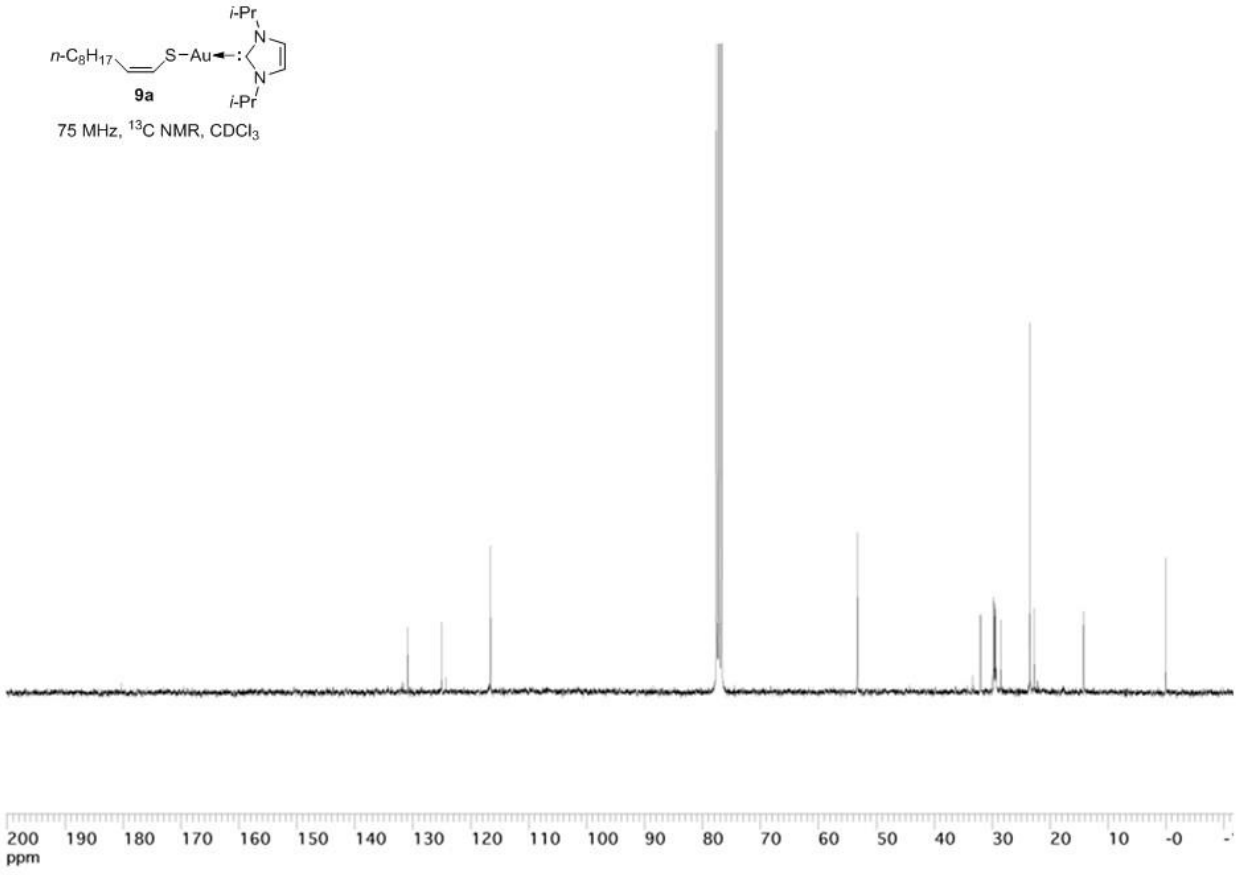

n-C8H17
S−Au
7a
1H NMR, 400 MHz, CDCl3
896e+08
913e+08
930e+08
478e+07
652e+07
826e+07
10
9
8
7
6
5
4
3
2
1
0

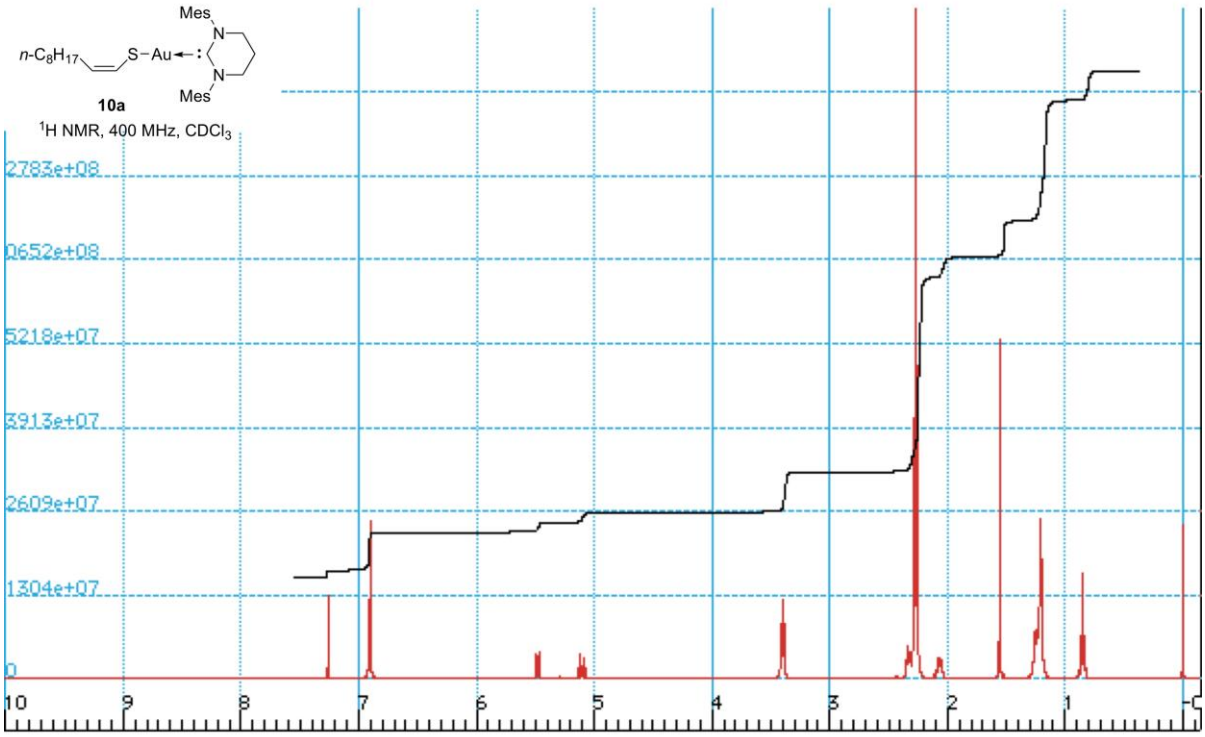

Bn
S−Au
7b
1H NMR, 400 MHz, CDCl3
9421e+07
9536e+07
9652e+07
9768e+07
9884e+07
0
10
9
8
7
6
5
4
3
2
1
0

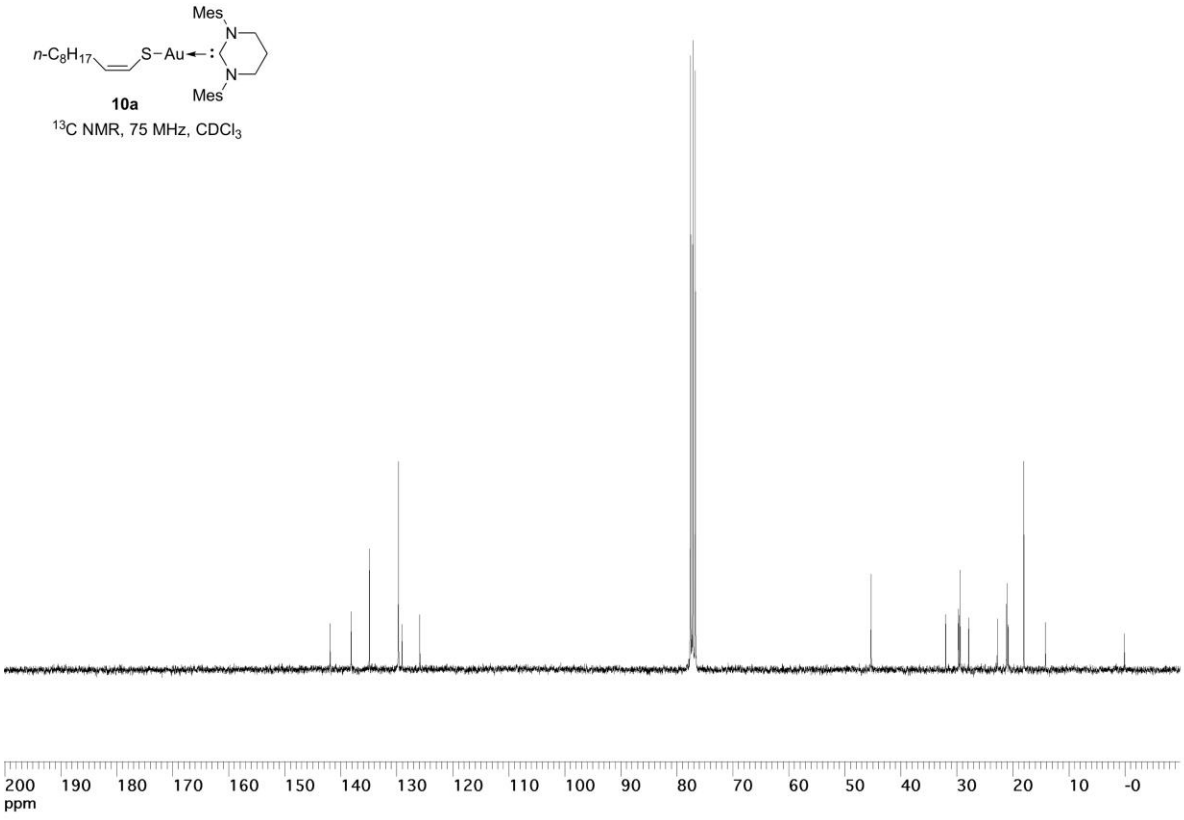

n-C8H17
S−Au−PPh3
8a
1H NMR, 400 MHz, CDCl3
557e+08
846e+08
344e+07
229e+07
115e+07
0.15e+07
9
8
7
6
5
4
3
2
1
-0


n-C8H17
S−Au−PPh3
8a
75 MHz, 13C NMR, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
-0
ppm


i-Pr
n-C8H17
S–Au
i-Pr
9a
1H NMR, 400 MHz, CDCl3
9652e+07
9710e+07
9768e+07
9826e+07
9884e+07
9421e+06
10
9
8
7
6
5
4
3
2
1


i-Pr
n-C8H17
S–Au
i-Pr
9a
75 MHz, 13C NMR, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
-0
ppm


Mes
N
n-C8H17
S–Au
N
Mes
10a
1H NMR, 400 MHz, CDCl3
2783e+08
0652e+08
5218e+07
3913e+07
2609e+07
1304e+07
0
10
9
8
7
6
5
4
3
2
1


Mes
N
n-C8H17
S–Au
N
Mes
10a
13C NMR, 75 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
-0
ppm