Supporting Information

For

Dinuclear Gold(I) Complexes Bearing Alkyl-Bridged bis(*N*-Heterocyclic Carbene) Ligands as Catalysts for Carboxylative Cyclization of Propargyl Amine: Synthesis, Structure, Kinetic and Mechanistic Comparison to the Mononuclear Complex [Au(IPr)Cl].

Tahani A. C. A. Bayrakdar,[†] Fady Nahra,[†,§] Jack V. Davis,[‡] Mohan M. Gamage,[‡] Burjor Captain*,[‡] Manuel Temprado*,[⊥] Marco Marazzi,[⊥] Marina Saab,[†] Kristof Van Hecke,[†] Dominic Ormerod,[§] Carl D. Hoff,*[,‡] and Steven P. Nolan*[,†]

[†]Department of Chemistry and Centre for Sustainable Chemistry, Ghent University, Building S3, Krijgslaan 281, 9000 Gent, Belgium.

§VITO (Flemish Institute for Technological Research), Separation and Conversion Technology, Boeretang 200, B-2400 Mol, Belgium.

‡Department of Chemistry, University of Miami, Coral Gables, Florida 33146, United States.

⊥Departamento de Química Analítica , Química Física e Ingeniería Química;, Instituto de Investigación Química "Andrés M. del Río" (IQAR), Universidad de Alcalá, Campus Universitario, 28805 Alcalá de Henares, Madrid, Spain.

Table of Contents

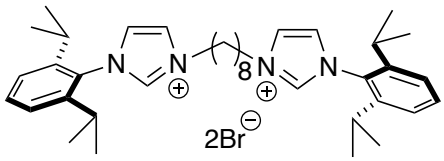
General information

All reactions were carried under air using technical grade solvents. All commercial substances were used without any further purification. N-Aryl imidazoles and N-(1-Adamantyl)-1*H*-imidazole were prepared according to literature procedures.[1] ^{1}H, and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on a bruker-500, 400 and 700 MHz spectrometer at ambient temperature in CD_2Cl_2, $CDCl_3$, C_6D_6 and DMSO. Chemical shifts are expressed in parts per million and they are referenced to residual solvent peaks ($CDCl_3$: δ_H= 7.26 ppm, δ_C= 77.16 ppm; CD_2Cl_2: δ_H= 5.32 ppm, δ_C= 53.84 ppm; C_6D_6 δ_H= 7.16ppm , δ_C= 128.06ppm; DMSO: δ_H= 2.50 ppm, δ_C= 39.52 ppm). Coupling constants, *J*, are given in hertz. Elemental analyses were performed at London Metropolitan University 166- 220 Holloway Road, London, N7 8DB. High resolution mass spectra (HRMS) were recorded in QTOF with an Agilent 6220A under electron spray ionization (ESI).

General procedure for the synthesis of the bis-imidazolium salts (L·2HX)

The salts were synthesized to a similar procedure reported in the literature.[2] A vial charged with stirring bar, imidazole (2 equiv.) and alkyl halide (1 equiv.) was heated to 140 °C for 24 hours. After 24 hours the reaction mixture changed to a block of brown solid. The reaction was cooled to room temperature then it was crushed out by adding diethyl ether while stirring it to obtain an off-white solid, which was then filtered, washed 3 times with diethyl ether and dried under vacuum.

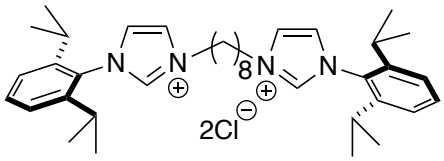
Preparation of 3,3'-(octane-1,8-diyl)bis(1-(2,6-diisopropylphenyl)-1*H*-imidazolium) bromide L^1·2HBr



This bis-imidazolium salt was prepared following the general procedure. 1-(2,6-diisopropylphenyl)-1*H*-imidazole (500 mg, 2 mmol) and 1,8 dibromo octane (300 mg, 1 mmol) were heated to 140 °C. An off-white solid was obtained. Yield: 779 mg (98%): **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 10.39 (s, 2H, NC*H*N), 8.49 (s, 2H, CH_{imid}), 7.49 (t, $J_{H\text{-}H}$ = 7.8 Hz, 2H, CH_{Ar}), 7.26 (d, $J_{H\text{-}H}$ = 7.9 Hz, 4H, CH_{Ar}), 7.15 (s, 2H, CH_{imid}), 4.77 (t, $J_{H\text{-}H}$ = 7.4 Hz, 4H, NCH_2CH$_2$), 2.24 (sept, $J_{H\text{-}H}$ = 6.8 Hz, 4H, C*H*$(CH_3)_2$), 2.10 (m, 4H, $CH_2CH_2CH_2$), 1.46 (m, 8H, $CH_2CH_2CH_2$), 1.19 (d, $J_{H\text{-}H}$=6.8 Hz, 12H, CH(CH_3)$_2$), 1.13 (d, $J_{H\text{-}H}$=6.8 Hz, 12H, CH(CH_3)$_2$). **^{13}C NMR** (101 MHz, $CDCl_3$): δ

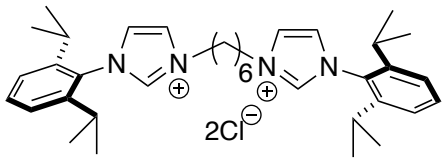
(ppm) = 145.4 (C_{Ar}), 138.1 (CH_{imid}), 131.8 (C_{Ar}), 130.4 (C_{Ar}), 124.7 (C_{imid}), 124.7 (C_{Ar}), 124.2 (C_{imid}), 50.1 (NCH_2), 30.1 (CH_2), 28.8 ($CH(CH_3)_2$), 27.6 (CH_2), 25.2 (CH_2), 24.6 ($CH(CH_3)_2$), 24.2 ($CH(CH_3)_2$).
HRMS (ESI) Calculated for $C_{38}H_{56}BrN_4^+$ (M^{2+}+Br^-) 647.36829; Found 647.3674.

Preparation of 3,3'-(octane-1,8-diyl)bis(1-(2,6-diisopropylphenyl)-1*H*-imidazolium chloride L^2·2HCl



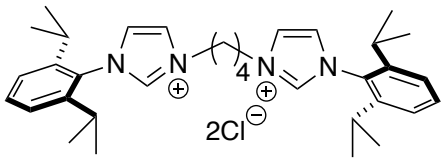
This bis-imidazolium salt was prepared following the general procedure. 1-(2,6-diisopropylphenyl)-1*H*-imidazole (500 mg, 2 mmol) and 1,8 dichloro octane (200 mg, 1 mmol) were heated to 140 °C. An off-white solid was obtained. Yield: 675 mg (96%): **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 10.65 (s, 2H, NC*H*N), 8.51 (s, 2H, CH_{imid}), 7.48(t, $J_{H\text{-}H}$ = 7.8 Hz, 2H,CH_{Ar}), 7.25 (d, $J_{H\text{-}H}$ = 7.8 Hz, 4H, CH_{Ar}), 7.13 (s, 2H, CH_{imid}), 4.74 (t, $J_{H\text{-}H}$ = 7.2 Hz, 4H, NCH_2CH_2), 2.25 (sept, $J_{H\text{-}H}$ = 6.8 Hz, 4H, $CH(CH_3)_2$), 2.09 (m, 4H, $CH_2CH_2CH_2$), 1.45 (m, 8H, $CH_2CH_2CH_2$), 1.18 (d, $J_{H\text{-}H}$=6.8 Hz, 12H, $CH(CH_3)_2$), 1.12 (d, $J_{H\text{-}H}$=6.8 Hz, 12H, $CH(CH_3)_2$). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 145.5 (C_{Ar}), 138.9 (CH_{imid}), 131.8 (C_{Ar}), 130.55 (C_{Ar}), 124.7 (C_{imid}), 124.7 (C_{Ar}), 124.2 (C_{imid}), 49.9 (NCH_2), 29.9 (CH_2), 28.8 ($CH(CH_3)_2$), 27.6 (CH_2), 25.2 (CH_2), 24.5 ($CH(CH_3)_2$), 24.2 ($CH(CH_3)_2$).
HRMS (ESI) Calculated for $C_{38}H_{56}ClN_4^+$ (M^{2+}+Cl^-) 603.41880; Found 603.4171.

Preparation of 3,3'-(hexane-1,6-diyl)bis(1-(2,6-diisopropylphenyl)-1*H*-imidazolium) chloride L^3·2HCl



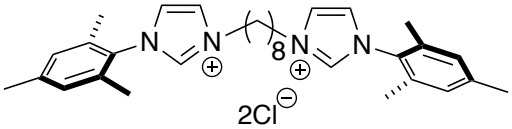
This bis-imidazolium salt was prepared following the general procedure. An off-white solid was obtained. Yield: 580 mg (93%): **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) = 10.64 (s, 2H, NC*H*N), 8.75 (s, 2H, CH_{imid}), 7.47 (t, $J_{H\text{-}H}$ = 7.8 Hz, 2H,CH_{Ar}), 7.25 (d, $J_{H\text{-}H}$ = 7.9 Hz, 4H, CH_{Ar}), 7.09 (s, 2H, CH_{imid}), 4.78 (t, $J_{H\text{-}H}$ = 7.0 Hz, 4H, NCH_2CH_2), i2.24 (sept, $J_{H\text{-}H}$ = 6.8 Hz, 4H, $CH(CH_3)_2$), 2.18 (m, 4H, $CH_2CH_2CH_2$), 1.58 (m, 4H, $CH_2CH_2CH_2$), 1.18 (d, $J_{H\text{-}H}$=6.8 Hz, 12H, $CH(CH_3)_2$), 1.13 (d, $J_{H\text{-}H}$=6.8 Hz, 12H, $CH(CH_3)_2$). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) = 145.44 (C_{Ar}), 138.69 (NCN), 131.77 (C_{Ar}), 130.54 (C_{Ar}), 124.66 (C_{Ar}) 124.54 (C_{imid}), 123.93 (C_{imid}), 49.65 (NCH_2), 29.53 (CH_2), 28.8 ($CH(CH_3)_2$), 24.5 ($CH(CH_3)_2$), 24.2 (CH_2), 24.2 ($CH(CH_3)_2$).
HRMS (ESI) Calculated for $C_{36}H_{52}ClN_4^+$ (M^{2+}+Cl^-) 575.38750; Found 575.3868.

Preparation of 3,3'-(butane-1,4-diyl)bis(1-(2,6-diisopropylphenyl)-1*H*-imidazolium) chloride L^4·2HCl



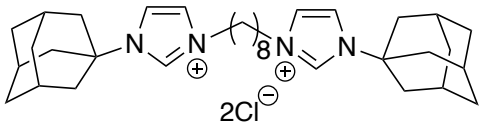
This bis-imidazolium salt was prepared following the general procedure. This bis-imidazolium salt was prepared following the general procedure. 1-(2,6-diisopropylphenyl)-1*H*-imidazole (500 mg, 2 mmol) and 1,4 dichloro butane (139 mg, 1 mmol) were heated to 140 °C. An off white solid was obtained. Yield: 600 mg (93%): **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 10.55 (s, 2H, NC*H*N), 8.92 (s, 2H, CH_{imid}), 7.48 (t, $J_{H\text{-}H}$ = 7.9 Hz, 2H,CH_{Ar}), 7.26 (d, $J_{H\text{-}H}$ = 7.9 Hz, 4H, CH_{Ar}), 7.09 (s, 2H, CH_{imid}), 4.99 (t, $J_{H\text{-}H}$ = 7.0 Hz, 4H, NCH_2CH_2), 2.35 (m, 4H, $CH_2CH_2CH_2$) 2.23 (sept, $J_{H\text{-}H}$ = 6.8 Hz, 4H, $CH(CH_3)_2$), 1.17 (d, $J_{H\text{-}H}$=6.8 Hz, 12H, $CH(CH_3)_2$), 1.12 (d, $J_{H\text{-}H}$=6.8 Hz, 12H, $CH(CH_3)_2$). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 145.4 (C_{Ar}), 138.5 (CH_{imid}), 131.8 (C_{Ar}), 130.4 (C_{Ar}), 124.8 (C_{imid}), 124.7 (C_{Ar}), 124.0 (C_{imid}), 48.7 (NCH_2), 28.8 ($CH(CH_3)_2$), 26.8 (CH_2), 24.5 ($CH(CH_3)_2$), 24.2 ($CH(CH_3)_2$).
HRMS (ESI) Calculated for $C_{34}H_{48}ClN_4^+$ (M^{2+}+Cl^-) 547.35620; Found 547.3562.

Preparation of 3,3'-(octane-1,8-diyl)bis(1-mesityl-1*H*-imidazolium) chloride L^5·2HCl



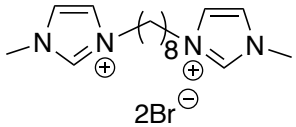
This bis-imidazolium salt was prepared following the general procedure. 1-(2,4,6-trimethylphenyl)-1*H*-imidazole (500 mg, 2 mmol) and 1,8 dichloro octane (245.8 mg, 1 mmol) were heated to 140 °C. An off white solid was obtained. Yield: 699 mg (91%) **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) = 10.64 (s, 2H, NC*H*N), 8.38 (s, 2H, CH_{imid}), 7.13 (s, 2H, CH_{imid}), 6.95 (s, 4H, CH_{Ar}), 4.69 (t, $J_{H\text{-}H}$ = 7.4 Hz, 4H, NC$H_2$$CH_2$), 2.30 (s, 6H, *para*-$CH_3$), 2.08 (m, 4H, CH_2C$H_2$$CH_2$), 2.02 (s, 12H, *ortho*-CH_3), 1.43 (m, 8H, CH_2CH_2C$H_2$$CH_2$). **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* (ppm) = 141.1 (*para*- C_{Ar}), 138.4 (NCN), 134.3 (*ortho*-C_{Ar}), 131.0 (*ipso*-C_{Ar}), 129.9 (CH_{Ar}), 123.9 (C_{imid}), 123.1 (C_{imid}), 49.9 (NCH_2), 29.8 (CH_2CH_2), 27.6 (CH_2), 25.3 (CH_2), 21.2 (*para*-CH_3), 17.7 (*ortho*-CH_3).
HRMS (ESI) Calculated for $C_{32}H_{44}ClN_4^+$ (M^{2+}+Cl^-) 519.32490; Found 519.3253.

Preparation of 3,3'-(octane-1,8-diyl)bis(1-((3*s*,5*s*,7*s*)-adamantan-1-yl)-1*H*-imidazolium) chloride L^6·2HCl



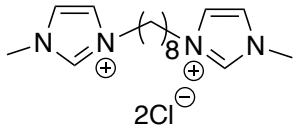
This bis-imidazolium salt was prepared following the general procedure. N-(1-Adamantyl)-1*H*-imidazole (500 mg, 2 mmol) and 1,8 dichloro octane (209.7 mg, 1 mmol) were heated to 140 °C. An off white solid was obtained. Yield: 700 mg (98%). **^{1}H NMR** (500 MHz, DMSO): *δ* (ppm) = 9.60 (s, 2H, NC*H*N), 8.09 (s, 2H, CH_{imid}), 7.92 (s, 2H, CH_{imid}), 4.18 (t, $J_{H\text{-}H}$ = 7.3 Hz, 4H, NC$H_2$$CH_2$), 2.21 (m, 6H, $CH_{adamantyl}$), 2.12 (m, 12H, $CH_{2\ adamantyl}$) 1.85-1.79 (m, 4H, CH_2C$H_2$$CH_2$), 1.71 (m, 12H, $CH_{2\ adamantyl}$) 1.29-1.23 (m, 8H, CH_2CH_2C$H_2$$CH_2$). **^{13}C NMR** (126 MHz, DMSO): *δ* (ppm) = 134.2 (NCN), 122.5 (C_{imid}), 119.3 (C_{imid}), 59.1 (N-$C_{adamantyl}$), 48.8 (N-CH_2), 41.6 ($CH_{2\ adamantyl}$), 34.8 ($CH_{2\ adamantyl}$), 29.2 (CH_2CH_2), 28.8 ($CH_{adamantyl}$), 28.1 (CH_2), 25.5(CH_2).
HRMS (ESI) Calculated for $C_{34}H_{52}ClN_4^+$ (M^{2+}+Cl^-) 551.38750; Found 551.3869.

Preparation of 3,3'-(octane-1,8-diyl)bis(1-methyl-1*H*-imidazolium) bromde L^7·2HBr



This bis-imidazolium salt was prepared following the general procedure with a modified work up. 1-methyl-1*H*-imidazole (250 mg, 3 mmol) and 1,8 dibromo octane (414 mg, 1.5 mmol) were heated to 140 °C, the obtained product was a very dense oil, a few drops of methanol was used followed by crushing with diethyl ether to obtain an off white solid. Yield: 590 mg (91%). **^{1}H NMR** (500 MHz, DMSO): *δ* (ppm) = 9.22 (s, 2H, NC*H*N), 7.81 (s, 2H, CH_{imid}), 7.73 (s, 2H, CH_{imid}), 4.16 (t, $J_{H\text{-}H}$ = 7.2 Hz, 4H, NC$H_2$$CH_2$), 3.86 (s, 6H, NC$H_3$), 1.80-1.74 (m, 4H, CH_2C$H_2$$CH_2$), 1.28-1.22 (m, 8H, CH_2CH_2C$H_2$$CH_2$). **^{13}C NMR** (126 MHz, DMSO): *δ* (ppm) = 136.5 (NCN), 123.6 (C_{imid}), 122.2 (C_{imid}), 48.7 (N-CH_2), 35.8 (CH_3), 29.3 (CH_2CH_2), 28.1 (CH_2), 25.4 (CH_2).
HRMS (ESI) Calculated for $C_{16}H_{28}BrN_4^+$ (M^{2+}+Br^-) 355.14919; Found 355.14983.

Preparation of 3,3'-(octane-1,8-diyl)bis(1-methyl-1*H*-imidazolium) bromide L^8·2HCl



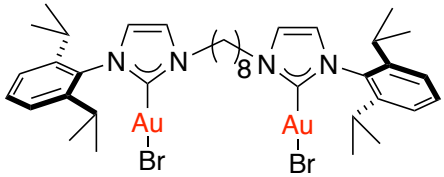
This bis-imidazolium salt was prepared following the general procedure with a modified work up. 1-methyl-1*H*-imidazole (250 mg, 3 mmol) and 1,8 dichloro octane (274 mg, 1.5 mmol) were heated to 140 °C, the obtained product was a very dense oil, a few drops of methanol was used followed by crushing with diethyl ether to obtain an off white solid. Yield: 470 mg (91%). **^{1}H**

NMR (500 MHz, DMSO): δ (ppm) = 9.41 (s, 2H, NC*H*N), 7.84 (s, 2H, CH_{imid}), 7.75 (s, 2H, CH_{imid}), 4.17 (t, J_{H-H} = 7.2 Hz, 4H, NC$H_2$$CH_2$), 3.87 (s, 6H, NC$H_3$), 1.80-1.75 (m, 4H, CH_2C$H_2$$CH_2$), 1.28-1.21 (m, 8H, CH_2CH_2C$H_2$$CH_2$). **^{13}C NMR** (126 MHz, DMSO): δ (ppm) = 136.6 (NCN), 123.6 (C_{imid}), 122.3 (C_{imid}), 48.6 (N-CH_2), 35.7 (CH_3), 29.3 (CH_2CH_2), 28.1 (CH_2), 25.4 (CH_2).
HRMS (ESI) Calculated for $C_{16}H_{28}ClN_4^+$ (M^{2+}+Cl^-) 311.19970; Found 311.19900.

General procedure for the synthesis of the dinuclear gold(I) Complexes [Au_2X_2(L)] (1-8)

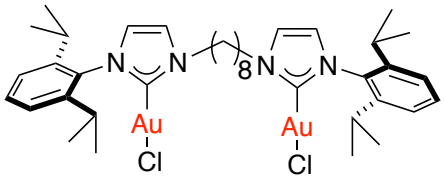
A vial was charged, under air, with the corresponding L·2HX (1 equiv.), [Au(DMS)Cl] (2 equiv.), and acetone (0.2 M) the vial was closed in a needle-pierced cap, the mixture was stirred initially at 30 °C for 10 minutes. Afterwards, K_2CO_3 (4 equiv.) was added to the reaction mixture and the vial was sealed and stirred for 40 minutes-3 hours at 60 °C. After this time, the mixture was filtered through a pad of silica and the silica was washed with dichloromethane. The solvent was then concentrated and pentane was added to precipitate the complex, affording an off-white solid which was washed with further portions of pentane and dried under vacuum.

Synthesis of 1



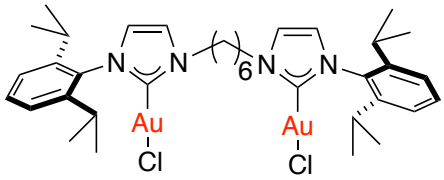
This complex was prepared following the general procedure. A mixture of L[1]·2HBr (1 g, 1.37 mmol), [Au(DMS)Cl] (808 mg, 2.75 mmol) in acetone (7 ml) was stirred initially for 10 minutes in a vial pierced with a needle, K_2CO_3 (758 mg, 5.49 mmol) was then added to the reaction mixture and stirred for 2 hrs at 60 °C. An off white solid was obtained. Yield: 1.05 g (70%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.46 (t, J_{H-H} = 7.8 Hz, 2H,CH_{Ar}), 7.25 (d, J_{H-H} = 7.8 Hz, 4H, CH_{Ar}), 7.24 (s, 2H, CH_{imid}), 6.93 (s, 2H, CH_{imid}), 4.33 (t, J_{H-H} = 7.2 Hz, 4H, NC$H_2$$CH_2$), 2.39 (sept, J_{H-H} = 6.8 Hz, 4H, C*H*$(CH_3)_2$), 1.99-1.95 (m, 4H, CH_2C$H_2$$CH_2$), 1.44-1.40 (m, 8H, CH_2C$H_2$$CH_2$), 1.28 (d, J_{H-H}=6.8 Hz, 12H, CH(CH_3)$_2$), 1.12 (d, J_{H-H}=6.9 Hz, 12H, CH(CH_3)$_2$). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 176.2 (C-Au), 145.9 (C_{Ar}), 134.3 (C_{Ar}), 130.7 (C_{Ar}), 124.3 (C_{Ar}), 123.5 (C_{imid}), 120.4 (C_{imid}), 51.1 (NCH_2CH_2), 30.9 (CH_2), 28.6 (CH_2), 28.5 (*C*H$(CH_3)_2$), 25.9 (CH_2), 24.5 (CH(*C*H_3)$_2$), 24.4 (CH(*C*H_3)$_2$). Anal. Calcd. for $C_{38}H_{54}Au_2Br_2N_4$: C 40.73; N 4.86; H 5.00. Found: C 40.57; N 4.95; H 4.66

Synthesis of 2



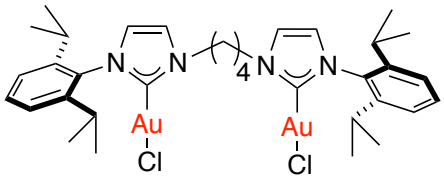
This complex was prepared following the general procedure. A mixture of L[2]·2HCl (1 g, 1.56 mmol), [Au(DMS)Cl] (920 mg, 3.13 mmol) in acetone (8 ml) was stirred initially for 10 minutes in a vial pierced with a needle, K_2CO_3 (864 mg, 6.25 mmol) was then added to the reaction mixture and stirred for 35 minutes at 60 °C. An off white solid was obtained. Yield: 1.36 g (84%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.45 (t, J_{H-H} = 7.8 Hz, 2H,CH_{Ar}), 7.25 (s, 2H, CH_{imid}), 7.24 (d, J_{H-H} = 7.7 Hz, 4H, CH_{Ar}), 6.92 (s, 2H, CH_{imid}), 4.32 (t, J_{H-H} = 7.2 Hz, 4H, NC$H_2$$CH_2$), 2.38 (sept, J_{H-H} = 6.8 Hz, 4H, C*H*$(CH_3)_2$), 2.00-1.93 (m, 4H, CH_2C$H_2$$CH_2$), 1.44-1.40 (m, 8H, CH_2C$H_2$$CH_2$), 1.28 (d, J_{H-H}=6.8 Hz, 12H, CH(CH_3)$_2$), 1.11 (d, J_{H-H}=6.9 Hz, 12H, CH(CH_3)$_2$). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 172.7 (C-Au), 145.9 (C_{Ar}), 134.3 (C_{Ar}), 130.7 (C_{Ar}), 124.4 (C_{Ar}), 123.6 (C_{imid}), 120.5 (C_{imid}), 51.2 (NCH_2CH_2), 30.9 (CH_2), 28.7 (CH_2), 28.5 (*C*H$(CH_3)_2$), 25.9 (CH_2), 24.5 (CH(*C*H_3)$_2$), 24.4 (CH(*C*H_3)$_2$). Anal. Calcd. for $C_{38}H_{54}Au_2Cl_2N_4$: C 44.24; N 5.43; H 5.28. Found: C 44.06; N 5.57; H 5.24.

Synthesis of 3



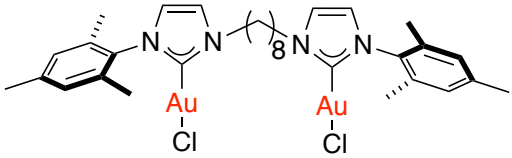
This complex was prepared following the general procedure. A mixture of L^3·2HCl (500 mg, 0.817 mmol), [Au(DMS)Cl] (481 mg, 1.63 mmol) in acetone (3.6 ml) was stirred initially for 10 minutes in a vial pierced with a needle, K_2CO_3 (450 mg, 3.26 mmol) was then added to the reaction mixture and stirred for 50 minutes at 60 °C. An off white solid was obtained. Yield: 580 mg (70%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.46 (t, $J_{H\text{-}H}$ = 7.8 Hz, 2H, CH_{Ar}), 7.35 (s, 2H, CH_{imid}), 7.24 (d, $J_{H\text{-}H}$ = 7.8 Hz, 4H, CH_{Ar}), 6.92 (s, 2H, CH_{imid}), 4.36 (t, $J_{H\text{-}H}$ = 7.1 Hz, 4H, NCH_2CH_2), 2.37 (sept, $J_{H\text{-}H}$ = 6.8 Hz, 4H, $CH(CH_3)_2$), 1.99-1.96 (m, 4H, $CH_2CH_2CH_2$), 1.55-1.53 (m, 4H, $CH_2CH_2CH_2$), 1.27 (d, $J_{H\text{-}H}$=6.9 Hz, 12H, $CH(CH_3)_2$), 1.12 (d, $J_{H\text{-}H}$=6.9 Hz, 12H, $CH(CH_3)_2$). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 172.5 (C-Au), 145.8 (C_{Ar}), 134.3 (C_{Ar}), 130.7 (C_{Ar}), 124.3 (C_{Ar}), 123.7 (C_{imid}), 120.8 (C_{imid}), 50.6 (NCH_2CH_2), 31.0 (CH_2) 28.5 ($CH(CH_3)_2$), 24.9 (CH_2), 24.5 ($CH(CH_3)_2$), 24.5 ($CH(CH_3)_2$). Anal. Calcd. for $C_{36}H_{50}Au_2Cl_2N_4$: C 43.08; N 5.58; H 5.02. Found: C 42.97; N 5.48; H 4.96.

Synthesis of 4



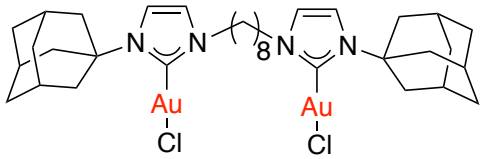
This complex was prepared following the general procedure. A mixture of L^4·2HCl (163 mg, 0.27 mmol), [Au(DMS)Cl] (164 mg, 0.56 mmol) in acetone (1.2 ml) was stirred initially for 10 minutes in a vial pierced with a needle, K_2CO_3 (154 mg, 1.11 mmol) was then added to the reaction mixture and stirred for 35 minutes at 60 °C. For this complex the workup was modified; the complex was filtered through a pad of silica using DCM as eluent, then DCM was concentrated and diethyl ether was added, affording off-white solid which was washed with further portions of diethyl ether and dried under vacuum. An off white solid was obtained. Yield: 136 mg (50%). **^{1}H NMR** (700 MHz, CD_2Cl_2): δ (ppm) = 7.53 (t, $J_{H\text{-}H}$ = 7.7 Hz, 2H,CH_{Ar}), 7.40 (s, 2H, CH_{imid}), 7.31 (d, $J_{H\text{-}H}$ = 7.7 Hz, 4H, CH_{Ar}), 7.02 (s, 2H, CH_{imid}), 4.43 (t, $J_{H\text{-}H}$ = 6.7 Hz, 4H, NCH_2), 2.38 (sept, $J_{H\text{-}H}$ = 6.8 Hz, 4H, $CH(CH_3)_2$), 2.13-2.08 (m, 4H, CH_2CH_2), 1.27 (d, $J_{H\text{-}H}$=6.7 Hz, 12H, $CH(CH_3)_2$), 1.13 (d, $J_{H\text{-}H}$=6.7 Hz, 12H, $CH(CH_3)_2$). **^{13}C NMR** (175 MHz, CD_2Cl_2): δ (ppm) = 173.2 (C-Au), 146.4 (C_{Ar}), 134.8 (C_{Ar}), 131.1 (C_{Ar}), 124.8 (C_{Ar}), 123.7 (C_{imid}), 121.2 (C_{imid}), 50.9 (NCH_2), 29.0 ($CH(CH_3)_2$), 28.2 (CH_2), 24.6 ($CH(CH_3)_2$), 24.6 ($CH(CH_3)_2$). Anal. Calcd. for $C_{34}H_{46}Au_2Cl_2N_4$: C 41.86; N 5.74; H 4.75. Found: C 42.04; N 5.70; H 4.52.

Synthesis of 5



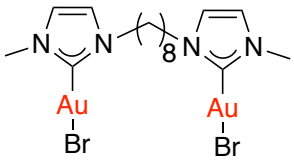
This complex was prepared following the general procedure. A mixture of L^5·2HCl (500 mg, 0.89 mmol), [Au(DMS)Cl] (530 mg, 1.8 mmol) in acetone (9 ml) was stirred initially for 10 minutes in a vial pierced with a needle, K_2CO_3 (485mg, 3.6 mmol) was then added to the reaction mixture and stirred for 1 hr at 60 °C. An off white solid was obtained. Yield: 655 mg (77%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) = 7.22 (s, 2H, CH_{imid}), 6.94 (s, 4H, CH_{Ar}), 6.87 (s, 2H, CH_{imid}), 4.29 (t, $J_{H\text{-}H}$ = 7.2 Hz, 4H, NCH_2CH_2), 2.32 (s, 6H, *para*-CH_3), 2.00 (s, 12H, *ortho*-CH_3) 1.98-1.91 (m, 4H, $CH_2CH_2CH_2$), 1.41 (m, 8H, $CH_2CH_2CH_2CH_2$). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) = 171.7 (C-Au) 139.7 (*para*- C_{Ar}), 135.0 (*ipso*-C_{Ar}), 135.0 (*ortho*-C_{Ar}), 129.5 (CH_{Ar}), 122.3 (C_{imid}), 120.7 (C_{imid}), 51.3 (NCH_2), 30.9 (CH_2), 28.6 (CH_2), 25.1(CH_2), 21.2 (*para*-CH_3), 17.9 (*ortho*-CH_3). Anal. Calcd. for $C_{34}H_{46}Au_2Cl_2N_4$: C 40.56; N 5.91; H 4.47. Found: C 40.59; N 6.01; H 4.28.

Synthesis of 6



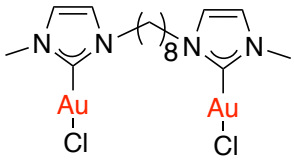
This complex was prepared following the general procedure. A mixture of L^6·2HCl (200 mg, 0.34 mmol), [Au(DMS)Cl] (190 mg, 0.68 mmol) in acetone (2 ml) was stirred initially for 10 minutes in a vial pierced with a needle, K_2CO_3 (188 mg, 1.3 mmol) was then added to the reaction mixture and stirred for 1 hr at 60 °C. For this complex the workup was modified; the complex was filtered through a pad of silica using DCM as eluent, then DCM was concentrated and diethyl ether was added, affording off white solid which was washed with further portions of diethyl ether and dried under vacuum. (It should be noted that just with this complex, it is important to wash with diethyl ether in order to get rid of some impurities that might cause complex decomposition). An off white solid was obtained. Yield: 233 mg (70%). **^{1}H NMR** (500 MHz, DMSO): δ (ppm) = 7.50 (s, 2H, CH_{imid}), 7.49 (s, 2H, CH_{imid}), 4.16 (t, $J_{H\text{-}H}$ = 7.1 Hz, 4H, NCH_2CH_2), 2.44 (m, 12H, CH_2), 2.20 (m, 6H, $CH_{adamantyl}$) 1.86-1.75 (m, 4H, $CH_2CH_2CH_2$), 1.70 (m, 12H, $CH_{2\ adamantyl}$) 1.29 (m, 8H, $CH_2CH_2CH_2CH_2$). **^{13}C NMR** (126 MHz, DMSO): δ (ppm) = 166.2 (C-Au), 119.8 (C_{imid}), 118.7 (C_{imid}), 58.3 (N-$C_{adamantyl}$), 51.9 (N-CH_2), 43.5 ($CH_{2\ adamantyl}$), 35.2 ($CH_{adamantyl}$), 30.3 (CH_2), 29.3 ($CH_{2\ adamantyl}$) 28.2 (CH_2), 25.5 (CH_2). Anal. Calcd. for $C_{34}H_{50}Au_2Cl_2N_4$: C 41.69; N 5.72; H 5.14. Found: C 41.73; N 5.78; H 5.09.

Synthesis of 7



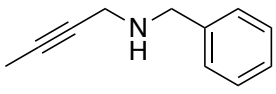
This complex was prepared following the general procedure. A mixture of L^7·2HBr (500 g, 1.15 mmol), [Au(DMS)Cl] (675 mg, 2.30 mmol) in acetone (6 ml) was stirred initially for 10 minutes in a vial pierced with a needle, K_2CO_3 (636 mg, 4.60 mmol) was then added to the reaction mixture and stirred for 1 hr at 60 °C. A light brown solid was obtained. Yield: 570 mg (60%) **^{1}H NMR** (500 MHz, DMSO): δ (ppm) = 7.48 (s, 2H, CH_{imid}), 7.43 (s, 2H, CH_{imid}), 4.09 (t, $J_{H\text{-}H}$ = 7.0 Hz 4H, NCH_2CH_2), 3.74 (s, 6H, NCH_3), 1.83-1.74 (m, 4H, $CH_2CH_2CH_2$), 1.30-1.23 (m, 8H, $CH_2CH_2CH_2CH_2$). **^{13}C NMR** (126 MHz, DMSO): δ (ppm) = 171.7 (C-Au), 122.7 (C_{imid}), 121.3 (C_{imid}), 50.0 (N-CH_2), 37.6 (CH_3), 30.3 (CH_2CH_2), 28.2 (CH_2CH_2), 25.4 (CH_2CH_2). Anal. Calcd. for $C_{16}H_{26}Au_2Br_2N_4$: C 23.21; N 6.77; H 3.16. Found: C 23.13; N 6.59; H 3.08.

Synthesis of 8



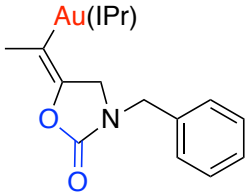
This complex was prepared following the general procedure. A mixture of L^8·2HCl (100 mg, 0.29mmol), [Au(DMS)Cl] (163 mg, 0.58 mmol) in acetone (1.5 ml) was stirred initially for 10 minutes in a vial pierced with a needle, K_2CO_3 (159mg, 1.15 mmol) was then added to the reaction mixture and stirred for 1 hr at 60 °C. A light brown solid was obtained. Yield: 164 mg (77%). **^{1}H NMR** (500 MHz, DMSO): δ (ppm) = 7.47 (s, 2H, CH_{imid}), 7.42 (s, 2H, CH_{imid}), 4.08 (t, $J_{H\text{-}H}$ = 7.1 Hz, 4H, NCH_2CH_2), 3.74 (s, 6H, NCH_3), 1.82-1.73 (m, 4H, $CH_2CH_2CH_2$), 1.30-1.24 (m, 8H, $CH_2CH_2CH_2CH_2$). **^{13}C NMR** (126 MHz, DMSO): δ (ppm) = 168.4 (C-Au), 122.7 (C_{imid}), 121.4(C_{imid}), 50.1 (N-CH_2), 37.6 (CH_3), 30.3 (CH_2CH_2), 28.2 (CH_2CH_2), 25.5 (CH_2CH_2). Anal. Calcd. for $C_{16}H_{26}Au_2Br_2N_4$: C 26.00; N 7.58; H 3.55. Found: C 26.06; N 7.49; H 3.41.

Synthesis of N-benzylbut-2-yn-1-amine PPA 10



In a 500 ml round bottomed flask equipped with a stirring bar, benzylamine (210 mmol) and 150 ml of Et_2O were added together. The mixture was cooled to 0 °C, then 1-Bromo-2-butyne (35 mmol) was added dropwise. The mixture was then allowed to stir at room temperature overnight. After that, the reaction mixture was quenched with 250 ml H_2O and extracted with diethyl ether (3x 150 ml). The organic phase was combined and washed with saturated solution of $NaHCO_3$ (1x200 ml) and with brine (1x200 ml). The solvent was removed *in vacuo* to yield a crude oil which was purified by column chromatography with silica gel using 3:7 (ethyl acetate/hexane) to yield a light yellow oil. Yield: 4.2 g (75%). Spectroscopic data is in accordance with the literature. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.35-7.22 (m, 5H, CH_{Ar}), 3.84 (s, 2H, CH_2N), 3.37 (q, $^5J_{H\text{-}H}$= 2.3 Hz, 2H, CH_2N), 1.83 (t, $^5J_{H\text{-}H}$=2.4 Hz, 3H, $CH_3C{\equiv}C$). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 139.9 (C_{Ar}), 128.5 (C_{Ar}), 128.5 (C_{Ar}), 127.2 (C_{Ar}), 79.3 ($CH_2C{\equiv}CCH_3$), 77.3 ($CH_3C{\equiv}CCH_2$), 52.7 (CH_2), 38.0 (CH_2), 3.7 (CH_3).
Spectroscopic data are in accordance with the literature.[3]

Synthesis of IKa complex

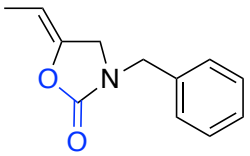


[Au(IPr)(OH)] (301 mg, 0.5 mmol) and N-benzylbut-2-yn-1-amine (79.6 mg, 0.5 mmol) were stirred together in THF (7 mL) under CO_2 atmosphere (balloon of CO_2) at 40 °C for 20 hours. The solvent was then concentrated and diethyl ether was added to precipitate the complex, affording an off-white solid which was washed with further portions of diethyl ether and dried under vacuum. Yield: 370 mg (90%). **^{1}H NMR** (400 MHz, C_6D_6): 7.13-7.11 (m, 5H, CH_{Ar}), 7.0-6.94 (m, 6H, CH_{Ar}), 6.31 (s, 2H, CH_{imid}), 4.16 (s, 2H, $NCH_2C_6H_5$), 3.34(s, 2H, CCH_2N), 2.57-2.50 (sept, $J_{H\text{-}H}$ = 6.8 Hz, 4H, $CH(CH_3)_2$), 2.09 (s, 3H, CH_3), 1.32 (d, $J_{H\text{-}H}$=6.8 Hz, 12H, $CH(CH_3)_2$), 1.06 (d, $J_{H\text{-}H}$=6.8 Hz, 12H, $CH(CH_3)_2$). δ (ppm) = **^{13}C NMR** (101 MHz, C_6D_6): δ (ppm) = 197.9 (NCN),158.1 (C=O), 145.9 (C_{Ar}), 140.9 (C-O), 137.8 (C_{Ar}), 134.9 (C_{Ar}), 131.8 (C_{Ar}), 130.5 (C_{Ar}), 128.7 (C_{Ar}), 127.2 (C_{Ar}), 124.1 (C_{imid}), 122.5 (C-Au), 48.5 (CH_2), 47.7 (CH_2), 28.9 ($CH(CH_3)_2$), 24.6 ($CH(CH_3)_2$), 23.9 ($CH(CH_3)_2$), 20.1 (CH_3). Anal. Calcd. for $C_{39}H_{48}AuN_3O_2$: C 59.46; N 5.33; H 6.14. Found: C 59.48; N 5.56; H 6.15.

General procedure for the carboxylative cyclization of *N*-benzylbut-2-yn-1-amine 11 (for the screening reactions of table 2 and 3)

The solvent was purged for a few minutes with CO_2 before use. To a vial charged with the catalyst and a stirring bar under CO_2 atmosphere (balloon of CO_2), N-benzylbut-2-yn-1-amine (0.5 mmol) in solvent (0.4 ml) was added. The reaction was allowed to stir for 15 hours under CO_2 atmosphere at the designated temperature. The resulting mixture was evaporated, and the yield was determined by ^{1}HNMR using 1,3,5 trimethoxybenzene as internal standard.

3-benzyl-5-vinyloxazolidin-2-one 11



^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.31-7.19 (m, 5H, CH_{Ar}), 4.51-4.45 (qt, $^3J_{H\text{-}H}$ = 6.9 Hz, $^4J_{H\text{-}H}$ = 2.2 Hz, 1H, CH_3CH), 4.39 (s, 2H, $NCH_2C_6H_5$), 3.90-3.88 (dq, $^4J_{H\text{-}H}$ = 2.2 Hz, $^5J_{H\text{-}H}$ = 2.2 Hz, 2H, CCH_2N), 1.61-1.59 (dt, $^3J_{H\text{-}H}$ = 6.9 Hz, $^5J_{H\text{-}H}$ = 2.3 Hz, 3H, CH_3CH).). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 156.2 (C=O), 141.8 (C-O), 135.3 (C_{Ar}), 129.1 (C_{Ar}), 128.3 (C_{Ar}), 97.7 (CH=C), 48.0 (CH_2), 47.2 (CH_2), 10.1 (CH_3).
Spectroscopic data is in accordance with the literature.[3]

Kinetic Studies of Carboxylative cyclization of PPA 10

In a typical kinetic study, a solution containing 42.5 mg **PPA 10** in 5 mL of EtOH that had been dried and stored on molecular sieves was prepared and loaded into a Hamilton gas tight syringe in the glove box. The reactor was loaded under a CO_2 atmosphere with an inner glass tube containing 22.3 mg when using **[Au(IPr)(Cl)] 9** and 18.6 mg when using the linker catalyst **2** providing 0.0072M concentration of gold in the solution. The reactor was purged and under a flow of CO_2 the 5 ml solution of **PPA 10** was added without dissolution of the catalyst. The reactor was stirred for approximately 30 minutes under CO_2. During that time IR spectra were taken until the carbamic acid/carbamate equilibrium process for **PPA 10** was complete. IR data were collected by transfer and return of an aliquot of the solution under constant CO_2 pressure to a Harrick medium pressure FTIR cell with CaF_2 windows through stainless steel and heavy wall Teflon tubing. The catalytic reaction was initiated by shaking the tube vigorously and mixing the catalyst with the already equilibrated solution of the carbamic acid and carbamate salt of **PPA 10**.

FTIR data for carbamic acid (CA)/carbamate salt (CS) Prior to addition of catalyst

Prior to each catalytic run the equilibrated stock solution of PPA **10** under 2 atm CO_2 in EtOH at 21 °C was collected. The ratio of the broad bands assigned to the **CA** and **CS** were observed to change. The relative concentration shifted to favor the **CA** at lower total concentration of PPA **10** and the **CS** at higher total concentration of PPA **10** as shown in the Figure S1 below.

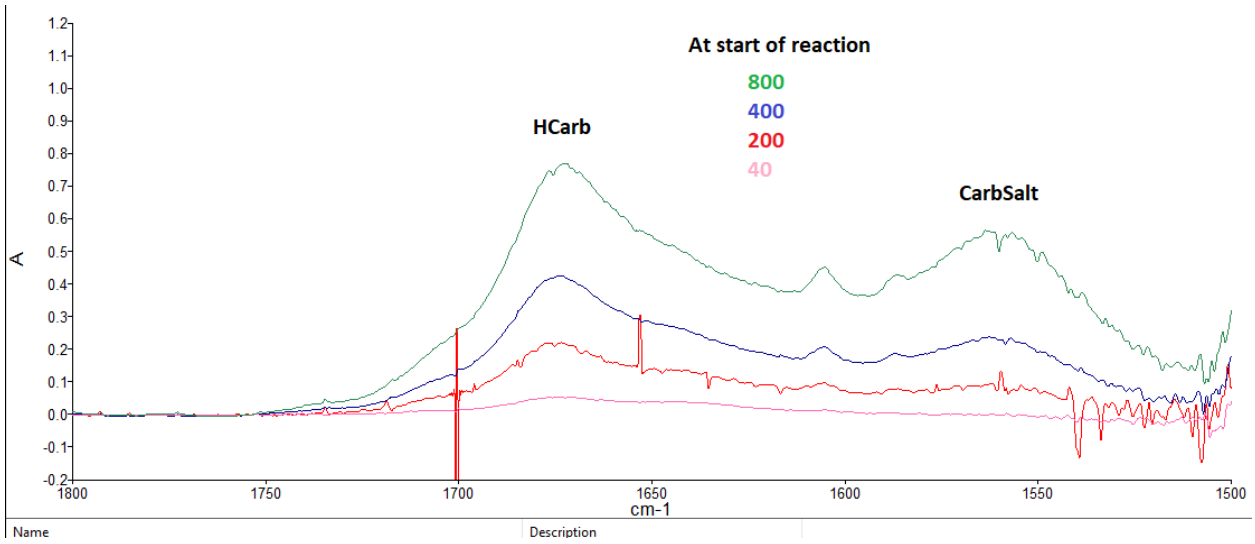


Figure S1. Infrared spectra at various concentrations of PPA in 5 ml EtOH under CO_2 pressure 2 atm absolute. The band near 1667 cm^{-1} is $HOOCNR_1R_2$ ($R1 = CH_2C_6H_5$, $R_2 = CH_2\text{-}C{\equiv}C\text{-}CH_3$) = HCarb and the band near 1560 cm^{-1} is assigned to[PPAH(+)]{(-) $OOCNR_1R_2$ = CarbSalt.

Table of rate constants and slopes for initial rates of reaction

A table of Initial Rate Constants as a Function of Catalyst and PPA **10** Concentration determined during the first 450 minutes of reaction. The slopes in the table below were used to measure the initial rate of reaction and are summarized for both the Linker **2** and [Au(IPr)(Cl)] **9** in the table below and represented in the main text in Figure 2. The correlation coefficients of the lines were all > 0.997.

Catalyst	**Linker 2**				**[Au(IPr)(Cl)] 9**			
[PPA 10] (M)	0.05	0.25	0.5	1	0.05	0.25	0.5	1
Slope (M/L.min)	2.2E-05	0.00017	0.00029	0.00042	2.8E-05	0.00013	0.00018	0.00023
Intercept (M/L)	5.7E-05	-0.0008	0.00142	0.00185	-0.0005	0.00036	0.00031	0.00147
R^2	0.997	0.998	0.9982	0.9997	0.997	0.9995	0.9983	0.997

Table S1. Data of Figure 2 for initial rate of the reaction in M/L.min for **2** and **9**.

Detection and Quantitative Determination of IKa

Reaction data followed by FTIR were computer subtracted from standard stock solutions using an iterative approach. The derived spectral data for **IKa** of solutions 0.0072M per Au catalyst and 0.05M in PPA **10** are shown in Figure S2.

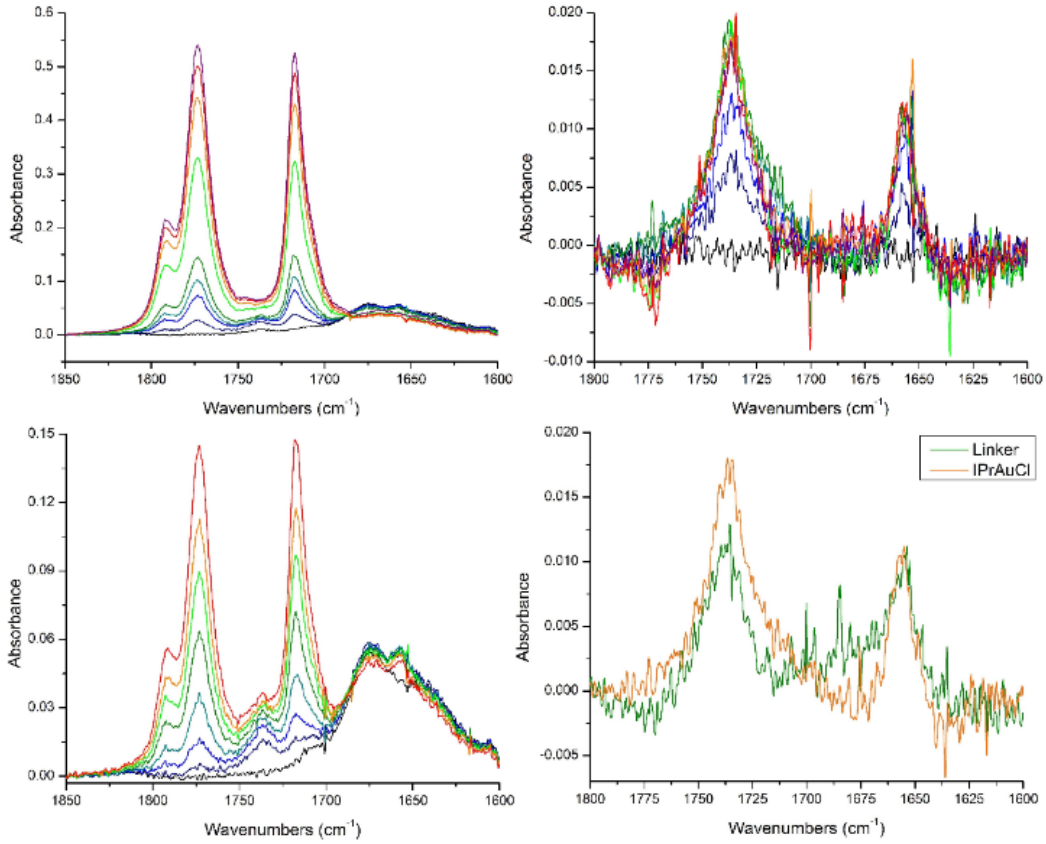


Figure S2. Representative FTIR data for Au catalyzed carbonylation of PPA, not all acquired data are shown for clarity. *Top left*: Data for reaction of **9** over first week showing growth of product at 1792(sh), 1773(s) and 1717(s) cm^{-1} and a broad band near 1674 cm^{-1} due to PPA carbamate. *Bottom left*: Data for first 463 min in which careful examination reveals growth of small intermediate bands as shoulders on the main bands. *Top Right:* Iterative computer subtraction removes product and reactant bands showing isolated intermediate bands at 1736 cm^{-1} and 1656 cm^{-1} assigned to IKa and Au-$OOCNR_1R_2$ as described in the text. *Bottom Right:* View of the intermediate bands for **9** (orange) and ½ **2** (green) allowing comparison after at ≈ 50 minutes reaction time and showing a higher level of the band near 1736 cm^{-1}assigned to IKa for the monomeric complex.

Due to the variable rates of concentration as a function of initial PPA the relative ratio of bands assigned to the **IKa** derivatives of **2** and **9** were also compared at 0.25M concentration as shown in Figure S3.

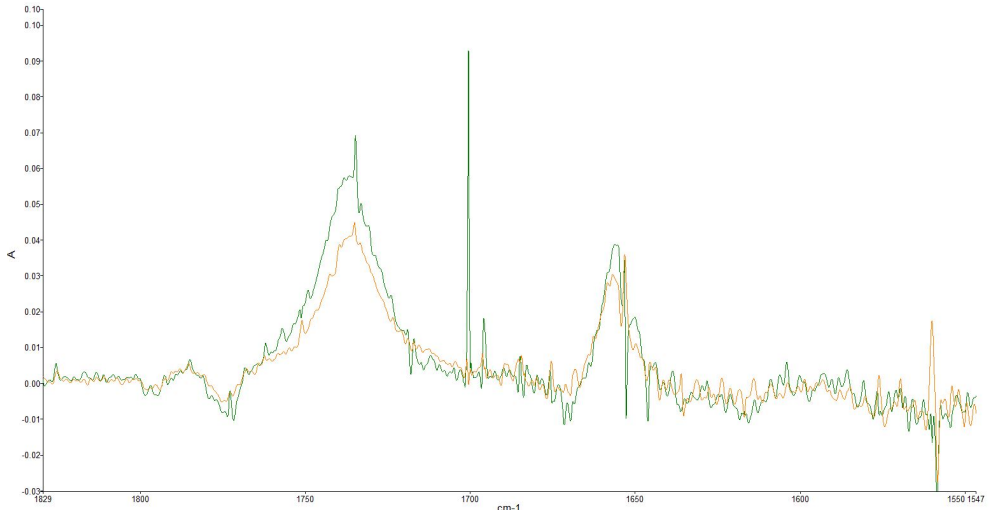


Figure S3. Comparison of computer subtracted levels of the **IKa** derivatives of **2** (green spectrum) and **9** (orange spectrum). The spike near 1700 cm^{-1} is due to noise that was in the background spectrum and is of a real peak. At the higher PPA **10** concentration there appears to be a higher level of the **IKa** derivative assuming a similar extinction coefficient. The two peaks overlap and also agree with an authentic spectrum of the **IKa** complex of **9** which was prepared as described in a different section of ESI.

Estimation of Turnover Frequency (TOF)

Data from the plot of turnover frequency versus PPA **10** shown in the main text (Figure 4) were assumed to fit obey an exponential approach to a final limiting value of the maximum attainable turnover frequency under experimental conditions of the form ln{TF} = – ln {TFmax-TF} [PPA **10**]. The optimal fit data were chosen based on best linear fit as shown in the Figure S4 below. In spite of the excellent correlation coefficients the estimated data is considered to be reliable within assigned error limits: For complex **2** to TOF_{max} = 0.06 ± 0.02 min^{-1} for **2** and 0.0335 ± 0.01 for **9.**

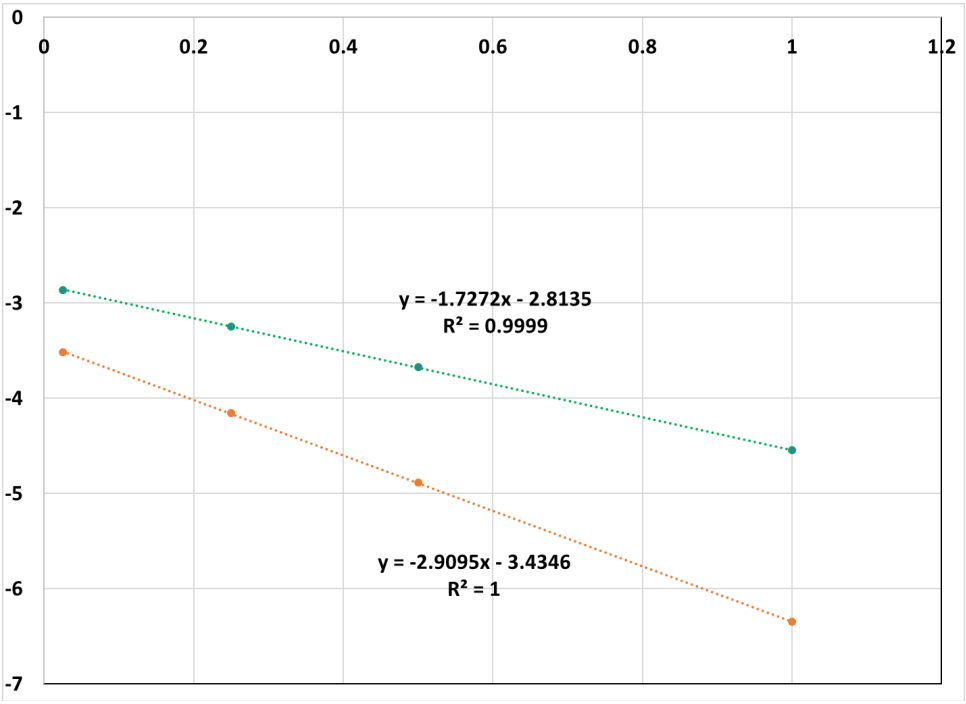


Figure S4. Best linear fit for **2** (top line in green) corresponded to TOF_{max} = 0.06 min^{-1} and for **9** (bottom line in orange) TOF_{max} = 0.0335 min^{-1}.

Structural Determination of the Product (CCDC No. 1977714)

Single crystals of **11** suitable for diffraction analysis were grown by slow evaporation of a chloroform/hexane solvent mixture at room temperature. The data crystals for **11** was mounted onto the end of a thin glass fiber using Paratone-N for data collection at 100 K under N_2. X-ray intensity data were measured by using a Bruker SMART APEX2 CCD-based diffractometer using Mo Kα radiation (λ = 0.71073 Å)[4]. The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm[4]. Corrections for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS. The structure was solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares on F^2, by using the SHELXTL software package.[5-6] Crystal data, data collection parameters, and results of the analyses are listed in Table 1. Compound **11** crystallized in the monolinic crystal system. The systematic absences in the intensity data identified the unique space group $P2_1/c$. With Z = 8, there are two formula -equivalents of the molecule present in the asymmetric crystal unit. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms during the least squares refinements.

Table S2. Crystallographic Data for Compounds **11**.

	11
Empirical formula	$C_{12}H_{13}NO_2$
Formula weight	202.23
Crystal system	Monoclinic
Lattice parameters	
a (Å)	12.0413(5)
b (Å)	5.7999(2)
c (Å)	30.2883(13)
β (deg)	97.5637(6)
V (Å^3)	2096.88(14)
Space group	$P2_1/c$ (# 14)
Z value	8
ρ_{calc} (g / cm^3)	1.288
μ (Mo Kα) (mm^{-1})	0.088
Temperature (K)	100
$2\Theta_{max}$ (°)	54.0
No. Obs. (I > 2σ(I))	4115
No. Parameters	273
Goodness of fit	1.048
Max. shift in cycle	0.000
Residuals*:R1; wR2	0.0394; 0.0935
Absorption Correction, Max/min	Multi-scan 0.7461/0.6887
Largest peak in Final Diff. Map (e$^-$ / Å^3)	0.544

*$R1 = \Sigma_{hkl}(||F_{obs}| - |F_{calc}||)/\Sigma_{hkl}|F_{obs}|$; $wR2 = [\Sigma_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\Sigma_{hkl}wF_{obs}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$; $GOF = [\Sigma_{hkl}w(|F_{obs}| - |F_{calc}|)^2/(n_{data} - n_{vari})]^{1/2}$.

Following one of the catalytic reaction studies by filtration, concentration, and storage in the freezer yielded single crystals that were analyzed by X-ray analysis (Figure S5).

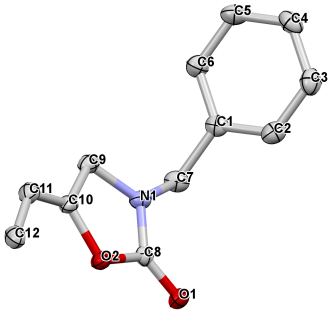


Figure S5. An ORTEP of the molecular structure of (**11)** showing 50 % thermal ellipsoid probability. Selected bond distances (in Å) and angles (in °) are as follows: O1 – C8 = 1.2072(15), O2 – C8 = 1.3832(14), O2 – C10 = 1.4021(14), N1 – C8 = 1.3434(16), N1 – C9 = 1.4494(16), N1 – C7 = 1.4588(16), C11 – C12 = 1.496(2), C8 – O2 – C10 = 108.80(9), C8 – N1 – C9 = 112.64(10), N1 – C7 – C1 = 111.38(10), C10 – C11 – C12 = 124.58(12), O1 – C8 – O2 = 121.35(11), C11 – C10 – C9 = 130.53(12).

Computational Details

Electronic structure calculations were carried out using the PBE0 functional,[7] the D3 version of Grimme's dispersion with Becke-Johnson damping (D3(BJ))[8] and using the Def2-TZVP basis set[9] along with the corresponding ECP for Au.[10] All stationary points were optimized in methanol solution with the polarizable continuum model (PCM) using the integral equation formalism.[11] Optimizations were performed without any symmetry restrictions by computing analytical energy gradients. The obtained stationary points were characterized by performing energy second derivatives, confirming them as minima by the absence of negative eigenvalues of the Hessian matrix of the energy. To determine *H*(298K) and *G*(298K) values, computed electronic energies were corrected for zero-point energy, thermal energy and entropic effects estimated from the normal mode analysis. Final Gibbs energy values referenced to the c = 1 mol/L standard state in methanol solution were obtained by adding 0.003019 hartrees (1.89 kcal/mol) to the computed Gibbs energy data referenced to the p = 1 atm ideal gas standard state. All calculations were performed with the Gaussian 16 suite of programs.[12]

Optimized structures of complexes [Au(NHC)(OC(=O)N(CH_3)CH_2C≡CCH_3)] and [Au^+(IPr)(η^2-C(CH_3)≡CCH_2N(CH_3)CO_2^-)] are shown for both NHC = IPr and IMe in figures S6-S9. The optimized structure of **Int2^{IPr}** is in reasonably good agreement with that computed in a previous theoretical study[13] although the current structure presents a slightly stronger interaction, and consequently shorter distances, between the Au center and both the NHC-carbene and alkyne ligands. Likewise, the geometrical parameters of the optimized structure of the carbamate species [Au(IPr)(OC(=O)N(CH_3)CH_2C≡CCH_3)], **Int1^{IPr}**, are comparable to those for the published structure of the related carbamate [Au(PPh_3)(O_2CNEt_2)] product.[14]

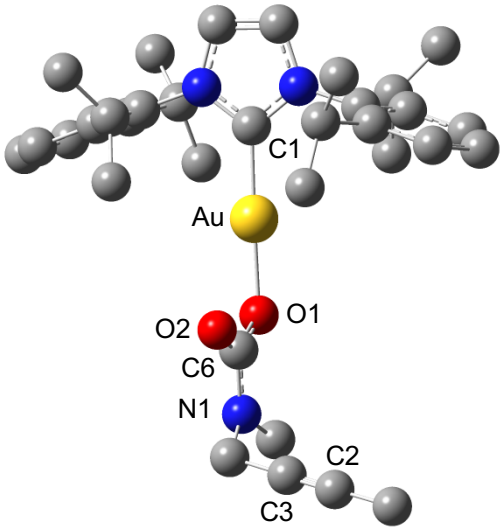


Figure S6. Optimized Structure of [Au(IPr)(OC(=O)N(CH_3)CH_2C≡CCH_3)], **Int1^{IPr}**. Hydrogen atoms omitted for clarity. Selected lengths (Å) and angles (°): Au–C1 1.964; Au–O1 2.040; Au–O2 3.088; O1–C6 1.297; O2–C6 1.234; C6–N1 1.378; C2–C3 1.204; C1–Au–O1 177.5.

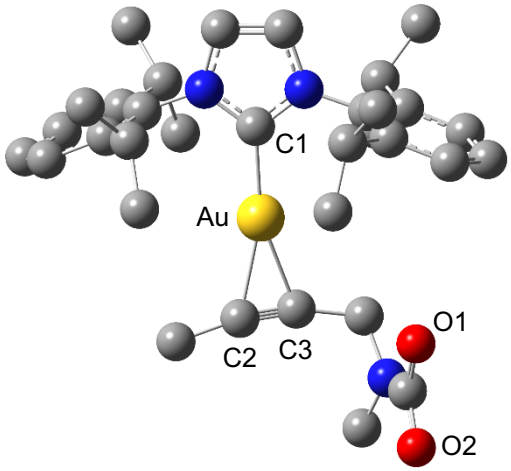


Figure S7. Optimized Structure of [Au^+(IPr)(η^2-C(CH_3)≡CCH_2N(CH_3)CO_2^-)], **Int2^{IPr}**. Hydrogen atoms omitted for clarity. Selected lengths (Å) and angles (°): Au–C1 2.007 (2-038); Au–C2 2.223 (2.306); Au–C3 2.178 (2.246); Au–O1 4.595 (5.119); Au–O2 6.050 (6.429); C2–C3 1.231 (1.237); C1–Au–C2 166.7 (164.1); C1–Au–C3 160.8 (164.4). Between parentheses previous computed values reported for this complex.[10]

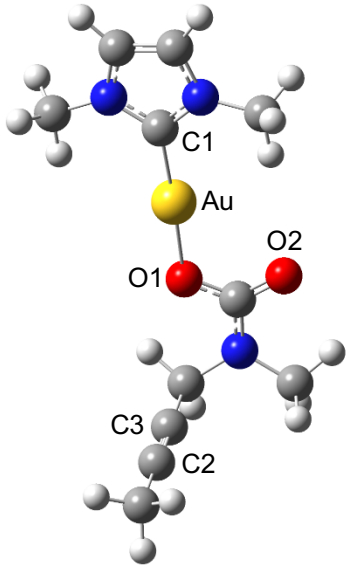


Figure S8. Optimized Structure of [Au(IMe)(OC(=O)N(CH_3)CH_2C≡CCH_3)], **Int1**. Selected lengths (Å) and angles (°): Au–C1 1.972; Au–O1 2.041; Au–O2 3.089; C2–C3 1.204; C1–Au–O1 177.5.

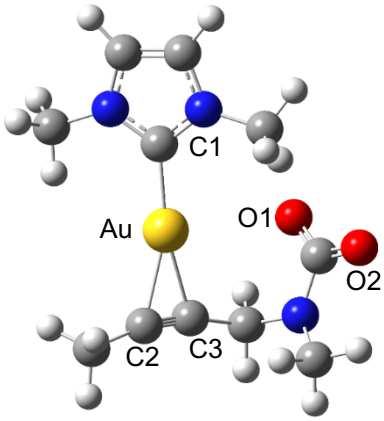


Figure S9. Optimized Structure of [Au^{+}(IMe)(η^2-C(CH_3)≡$CCH_2N(CH_3)CO_2^-$)], **Int2**. Selected lengths (Å) and angles (°): Au–C1 2.018; Au–C2 2.212; Au–C3 2.193; Au–O1 3.130; Au–O2 4.309; C2–C3 1.231; C1–Au–C2 160.0; C1–Au–C3 167.6.

As it can be seen in Figures S6 and S8, the computed structural parameters of **Int1** and **Int1^{IPr}** are in perfect agreement. Likewise, the optimized structures of the alkyne complexes (**Int2** and **Int2^{IPr}**) are similar. Moreover, the thermodynamic parameters for the isomerization process shown in reaction 1, where the carbamate bound complex is converted into the less thermodynamically favorable alkyne bound complex, are not dependent on the NHC used in the calculations (ΔG^0(298K) = 10.2 and 10.3 kcal/mol when NHC = IMe and IPr respectively).

$$[Au(NHC)(OC(=O)N(CH_3)CH_2C{\equiv}CCH_3)] \longrightarrow [Au^{+}(NHC)(\eta^2\text{-}C(CH_3){\equiv}CCH_2N(CH_3)CO_2^-)] \quad (1)$$

Accordingly, the mechanism of **IKa** formation from the reaction of [Au(NHC)Cl] with the carbamate salt and the thermodynamics of **IKa** protonation described in the main text were performed using the simpler truncated model with NHC = IMe. Figures S10 and S11 show the optimized structures of the two transition states computed in the current work. Table S2 collects the energies, enthalpies and Gibbs energies of all species studied computationally.

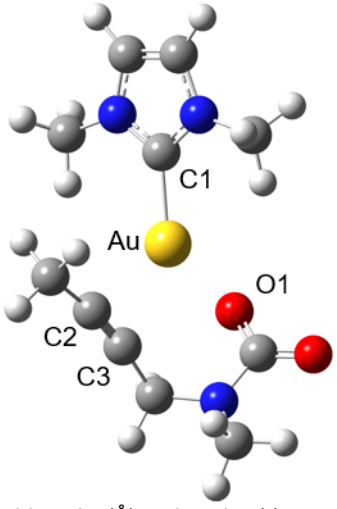


Figure S10. Optimized Structure of **TS1.** Selected lengths (Å) and angles (°): Au–C1 2.000; Au–C2 2.471; Au–C3 2.468; Au–O1 2.290; Au–O2 3.947; C2–C3 1.218; C1–Au–C2 118.9; C1–Au–C3 147.3; C1–Au–O1 136.4.

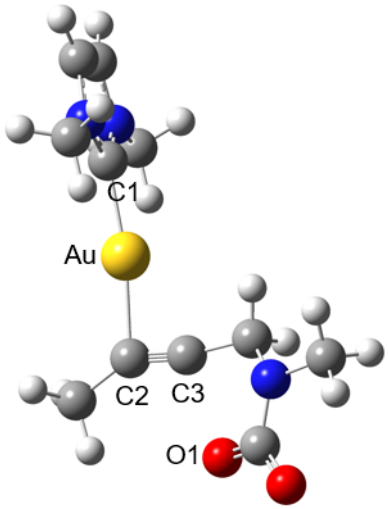


Figure S11. Optimized Structure of **TS1.** Selected lengths (Å) and angles (°): Au–C1 2.018; Au–C2 2.121; Au–C3 2.464; C3–O1 2.281; C2–C3 1.243; C1–Au–C2 171.6; C1–Au–C3 158.1.

Table S3. Computed electronic energy (E_0), enthalpy (H_{298}) and Gibbs energy values (G_{298}) at 298.15 K in methanol solution for all computed species. All values in hartrees.

Species	E_0	H_{298}	G_{298}[a]
Int1^{IPr}	−1733.29097	−1732.53814	−1732.66640
Int2^{IPr}	−1733.27881	−1732.52673	−1732.64712
[Au(IMe)Cl]	−900,51509	−900.37242	−900.41990
Int1	−878.71810	−878.43184	−878.50735
TS1	−878.69445	−878.41007	−878.48021
Int2	−878.70681	−878.42121	−878.49116
TS2	−878.69379	−878.40967	−878.48091
IKa	−878.74687	−878.45997	−878.52990
$CH_3C{\equiv}CCH_2(CH_3)NH$	−250.42347	−250.28393	−250.32288
$CH_3C{\equiv}CCH_2(CH_3)NC(=O)OH$	−438.90903	−438.75152	−438.79883
$[CH_3C{\equiv}CCH_2(CH_3)NH_2^+\cdots Cl^-]$	−711.13483	−710.97847	−711.02442
$[CH_3C{\equiv}CCH_2(CH_3)NH_2^+\cdots {}^-OC(=O)N(CH_3)CH_2C{\equiv}CCH_3]$	−689.354450	−689.055862	−689.12366
N-methylbut-2-yn-1-amine	−438.954584	−438.796671	−438.83875

[a] Values corrected by adding 0.003019 hartrees (1.89 kcal/mol) to change computed Gibbs energy data from the p = 1 atm ideal gas standard state to the c = 1 mol/L standard state in solution phase.

Estimation of Carbamate complex [Au(IPr)O(O=C)NR$_1$R$_2$] starting concentrations from Computational Data

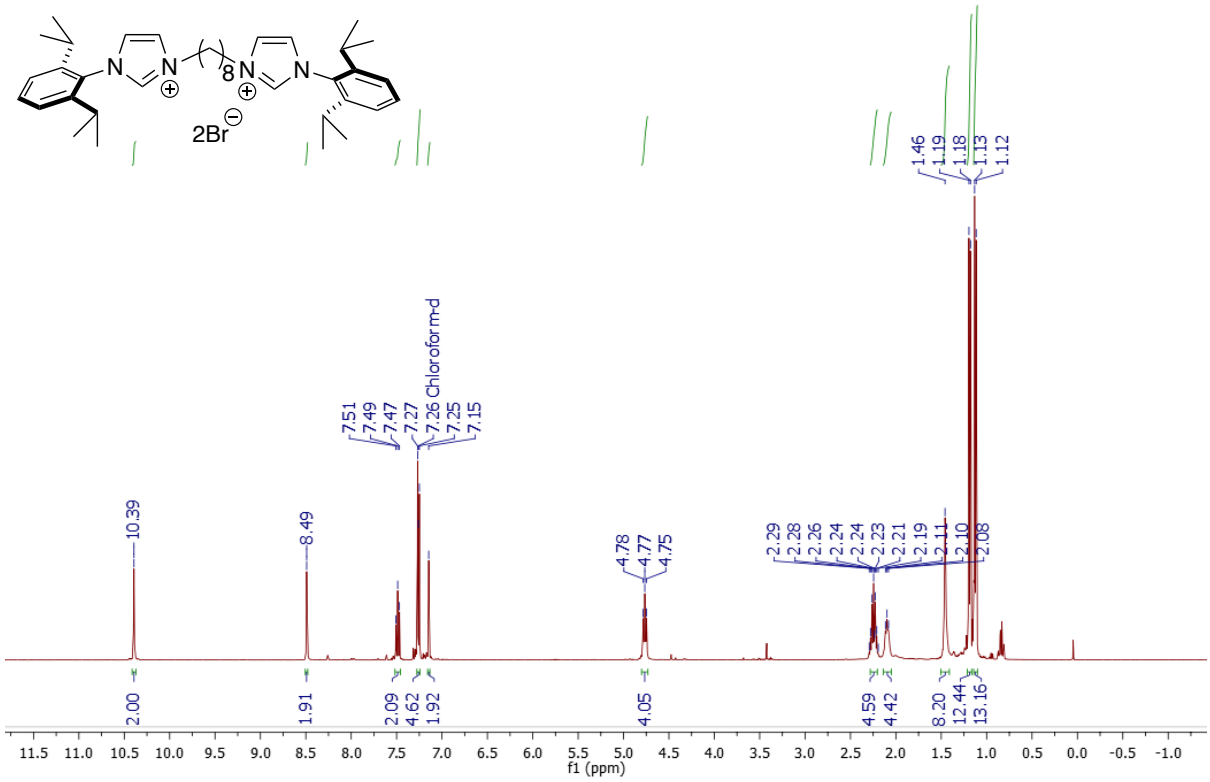
The computed ΔG^o for production of the [Au(IPr)O(O=C)NR$_1$R$_2$] complex from **9** and **CS** was computed as + 7.4 kcal/mol with an error assigned error limit of ± 3 kcal/mol. This value, as well as values at +6.4 and +5.4 kcal/mol were used to calculate the value of Keq for these reactions all of which are unfavorable. Under actual reaction concentrations of typically 0.072 M in **9** and the stated concentrations of **10** given below in the table below, it was concluded that in spite of an unfavorable Keq, under operating reaction conditions, equilibrium concentrations on the order of a few mole percent are predicted to be thermally accessible.

Table of computed mole fraction of [Au(IPr)O(O=C)NR$_1$R$_2$] as a function of and at the computed free energy (+7.4 kcal/mol) as well as two others (+6.4 and +5.4 kcal/mol) which remain within expected limits showing that the mole fractions ranging from 0.00562 (lowest) to 0.1247) (highest) would be expected to accumulate by replacement of chloride by **CS.**

Table S4. Estimated Mole Fraction at 298 K for the Reaction: **9** + **CA** ⇄ [Au(IPr)O(O=C)NR_1R_2] + **CS**

		Gibbs energy ΔG^o (Kcal/Mol)		
		7.4	6.4	5.4
Mass of PPA (mg)	Concentration of PPA (M/L)	Mol fraction	Mol fraction	Mol fraction
800	1.04	0.02489	0.05636	0.1247
400	0.52	0.01767	0.04019	0.08991
200	0.259	0.0125	0.02853	0.06434
43	0.052	0.00562	0.01289	0.02936

NMR Spectra


8
2Br
1.46
1.19
1.18
1.13
1.12
7.51
7.49
7.47
7.27
7.26 Chloroform-d
7.25
7.15
10.39
8.49
4.78
4.77
4.75
2.29
2.28
2.26
2.24
2.24
2.23
2.21
2.19
2.11
2.10
2.08
2.00
1.91
2.09
4.62
1.92
4.05
4.59
4.42
8.20
12.44
13.16
f1 (ppm)

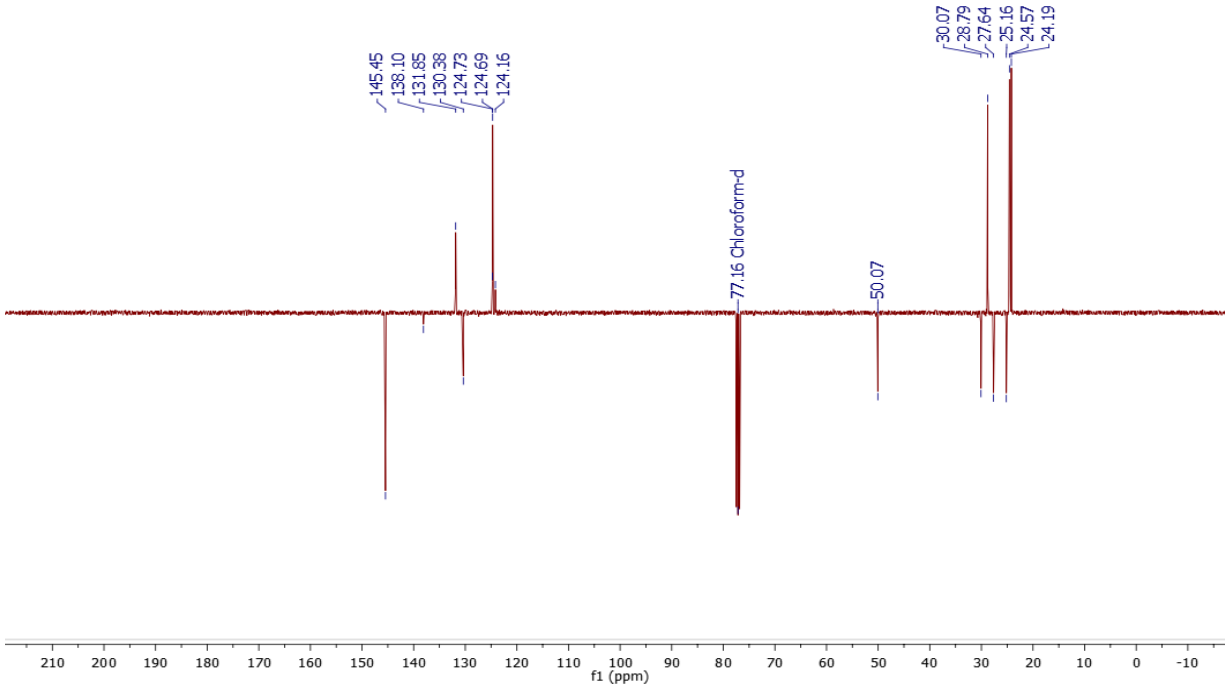


Figure S12. ^{1}H and ^{13}C {1H} APT NMR of **L^{1}·2HBr** ($CDCl_3$).

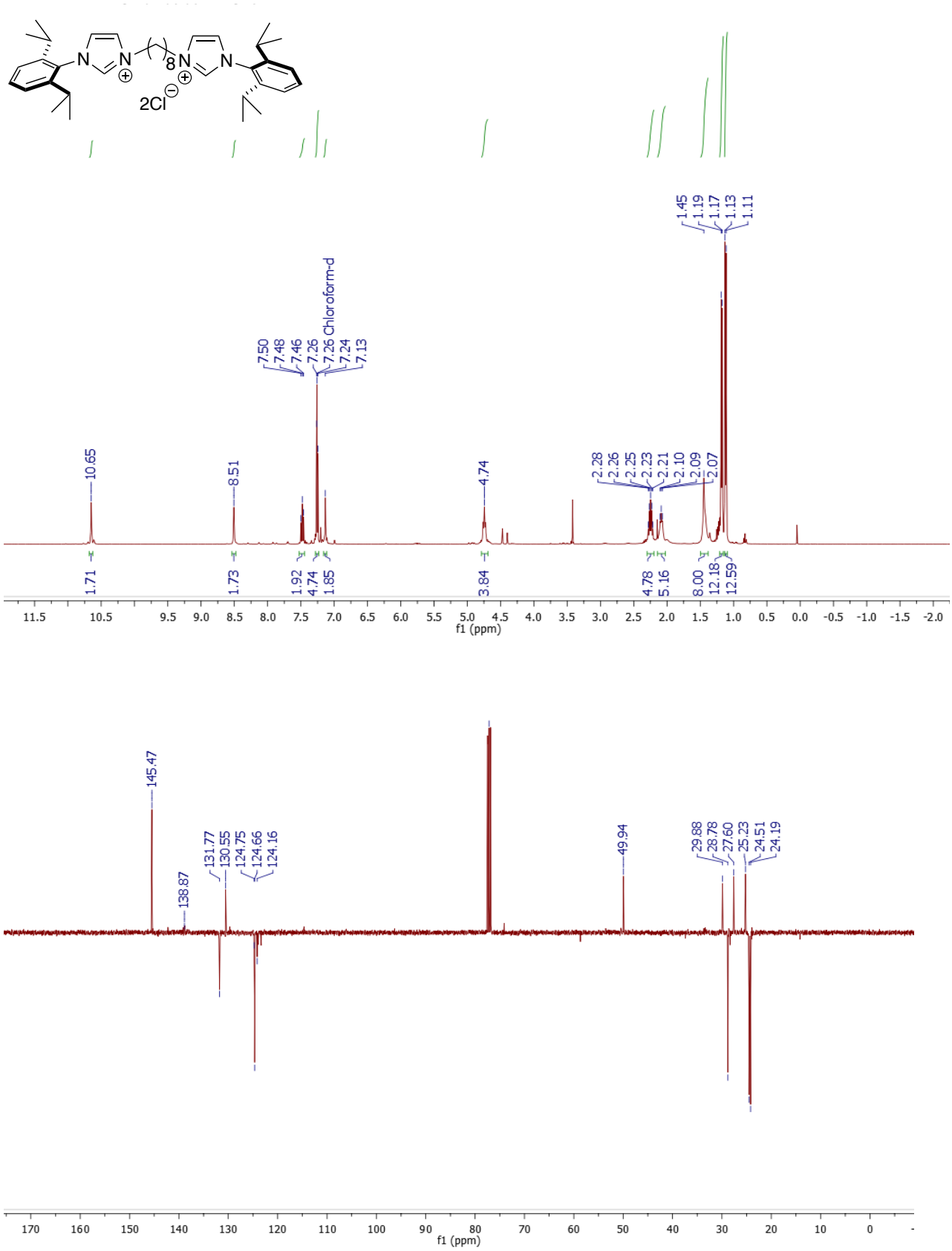


Figure S13. ^{1}H and ^{13}C {1H} APT NMR of **L^{2}·2HCl** ($CDCl_3$)

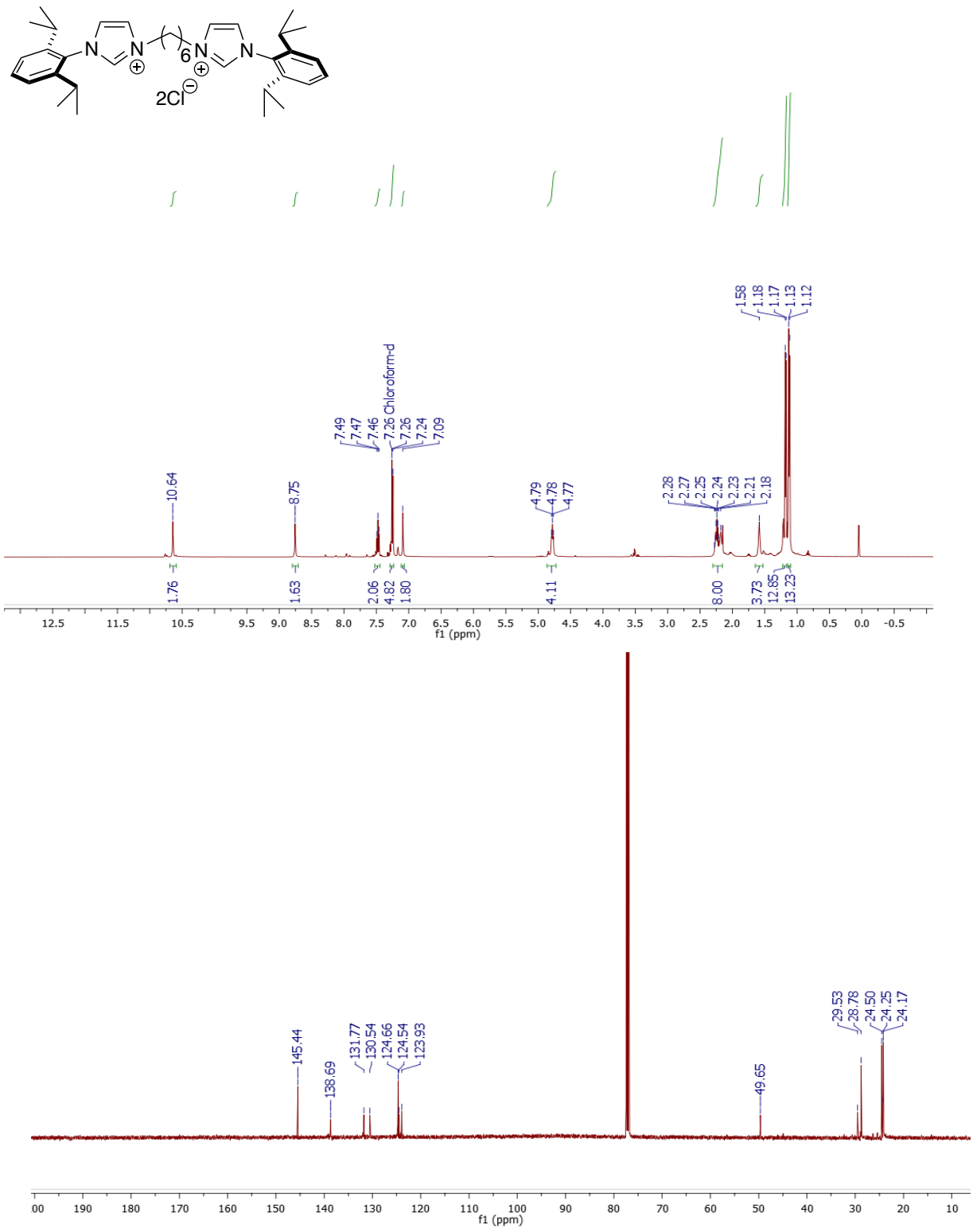


Figure S14. ^{1}H and ^{13}C {1H} NMR of **L^{3}·2HCl** ($CDCl_3$).

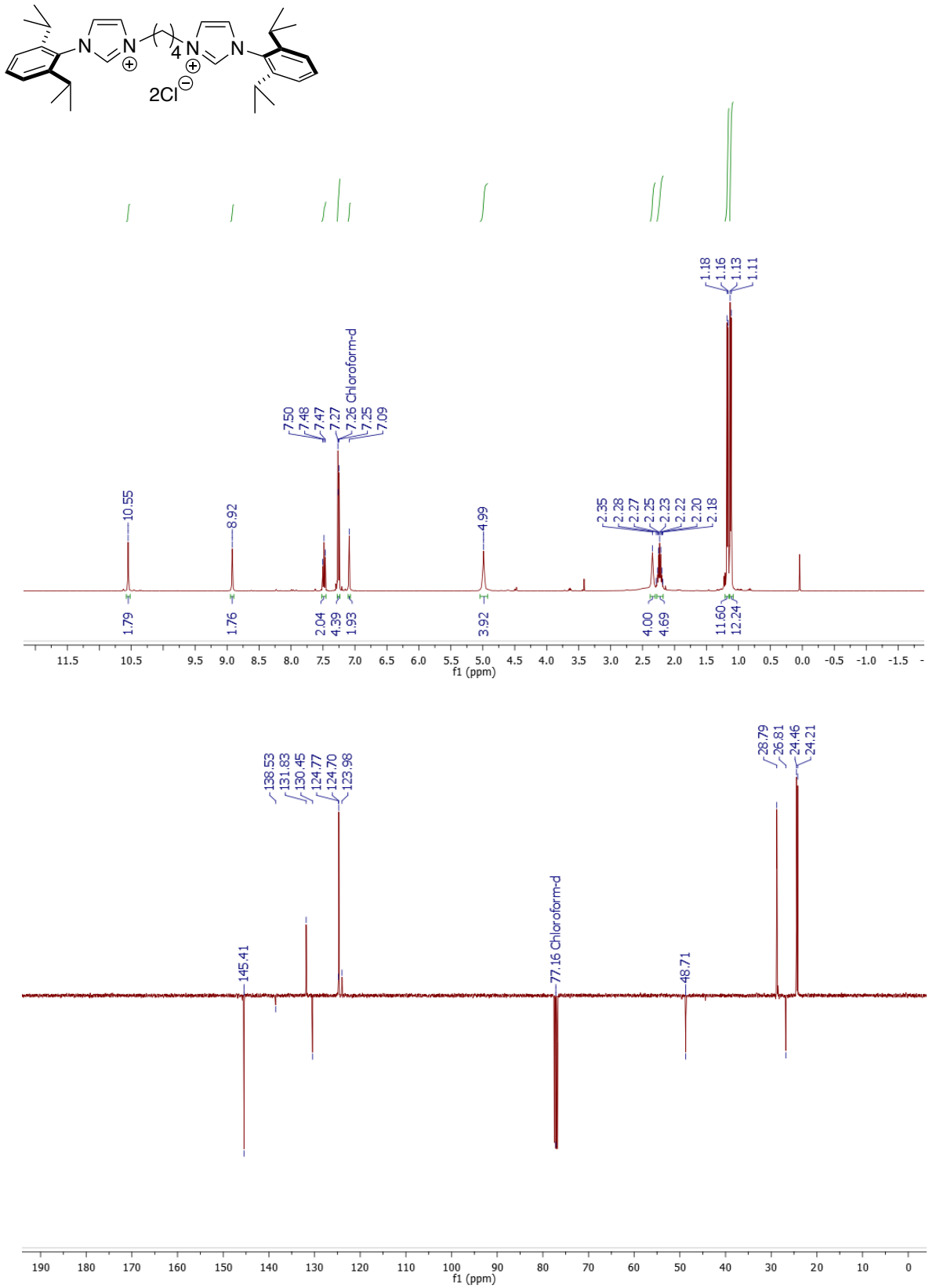


Figure S15. ^{1}H and ^{13}C {1H} APT NMR of **L^4·2HCl** ($CDCl_3$).

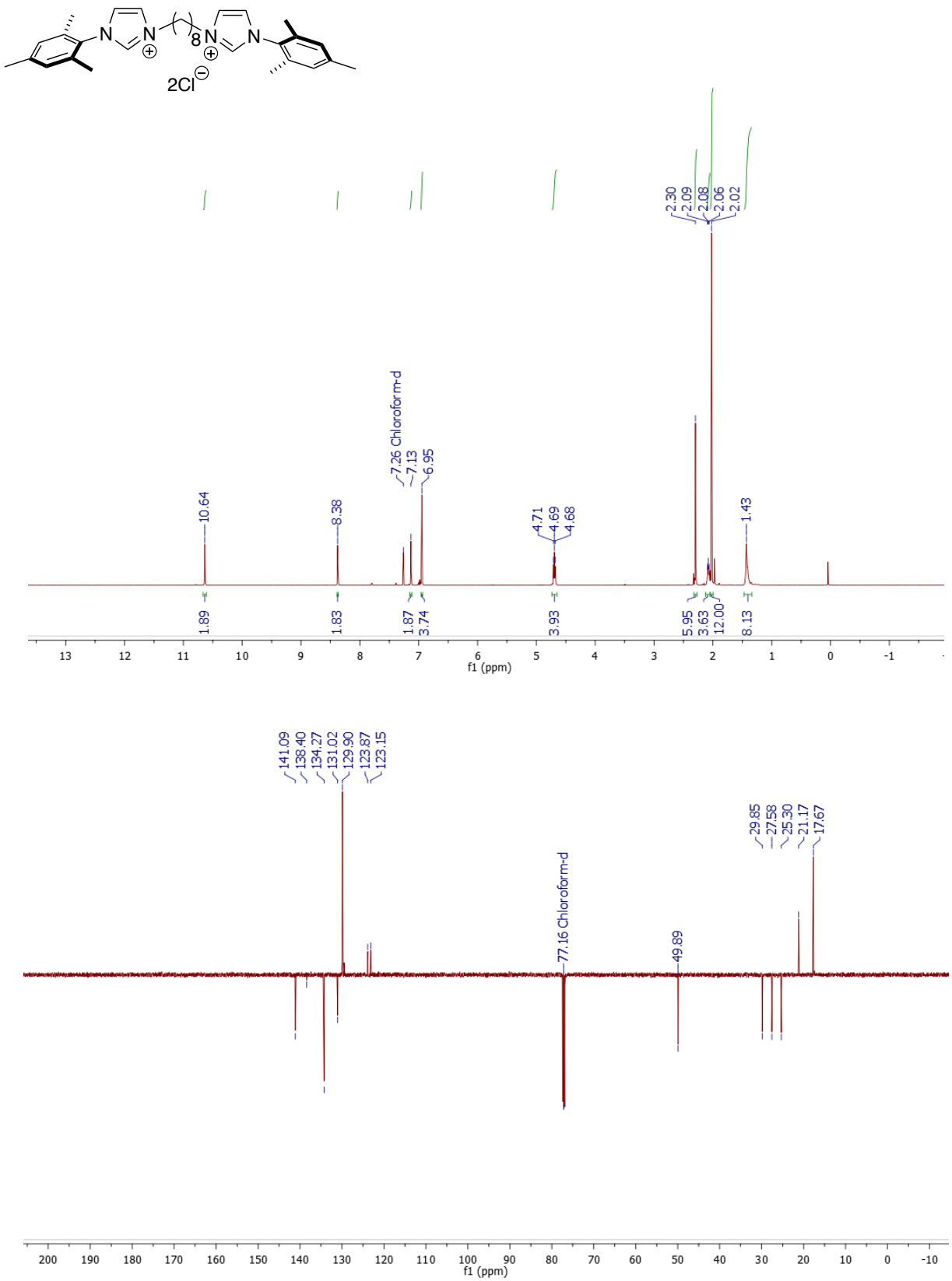


Figure S16. ^{1}H and ^{13}C {1H} APT NMR of **L^{5}·2HCl** ($CDCl_3$).

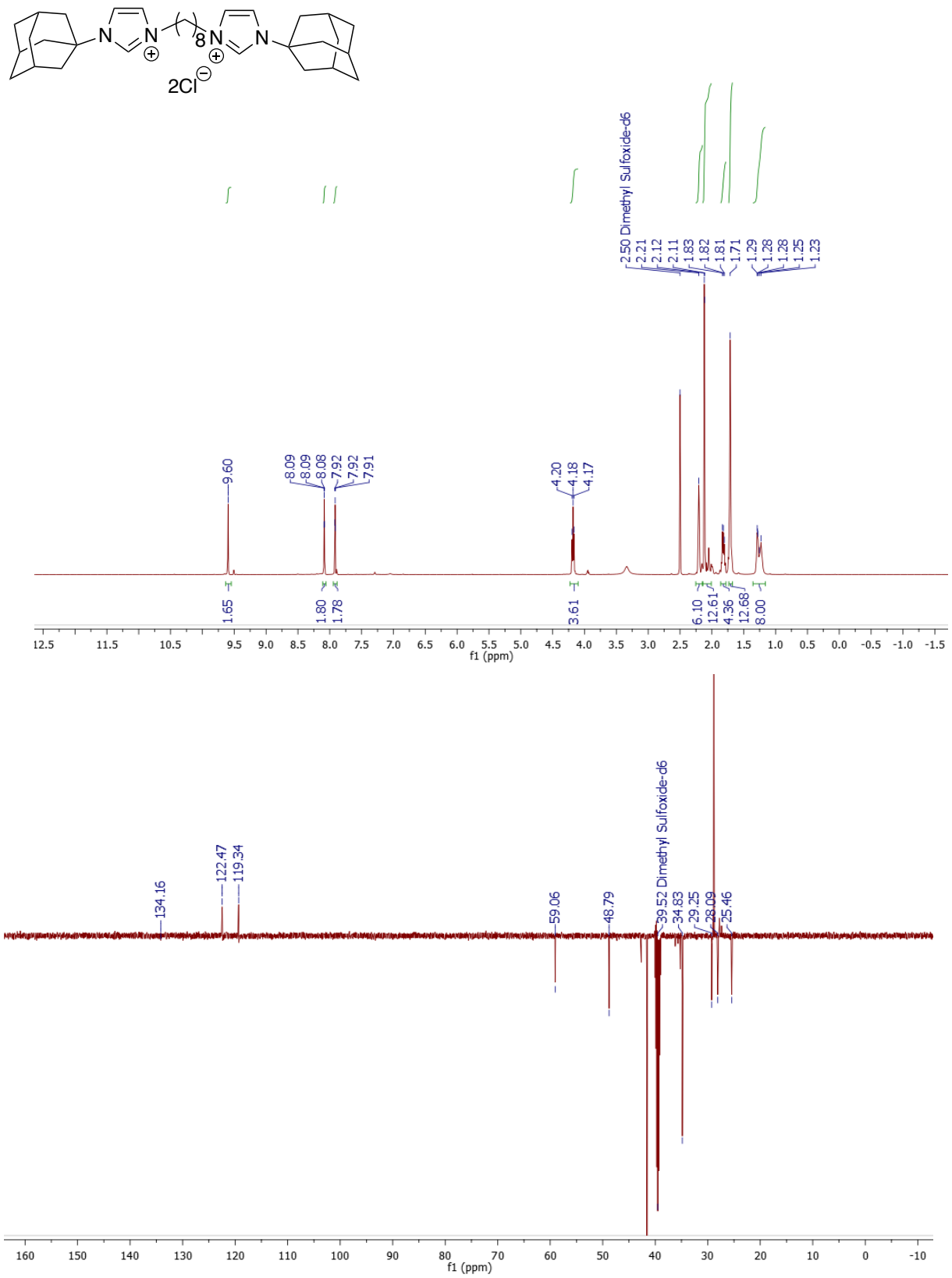


Figure S17. ^{1}H and ^{13}C {1H} APT NMR of **L^{6}·2HCl** (DMSO).

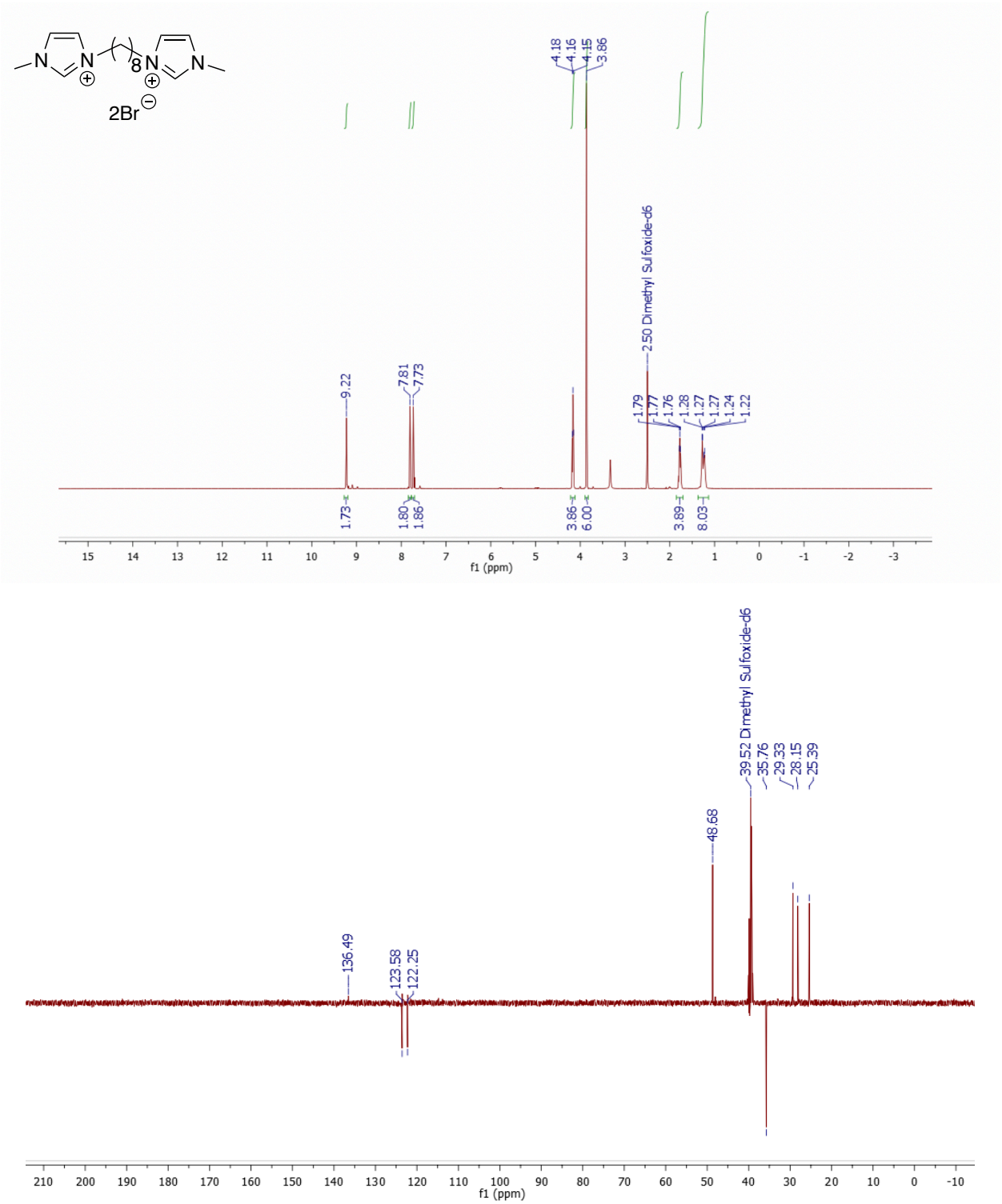


Figure S18. ^{1}H and ^{13}C {1H} APT NMR of **L^{7}·2HBr** (DMSO).

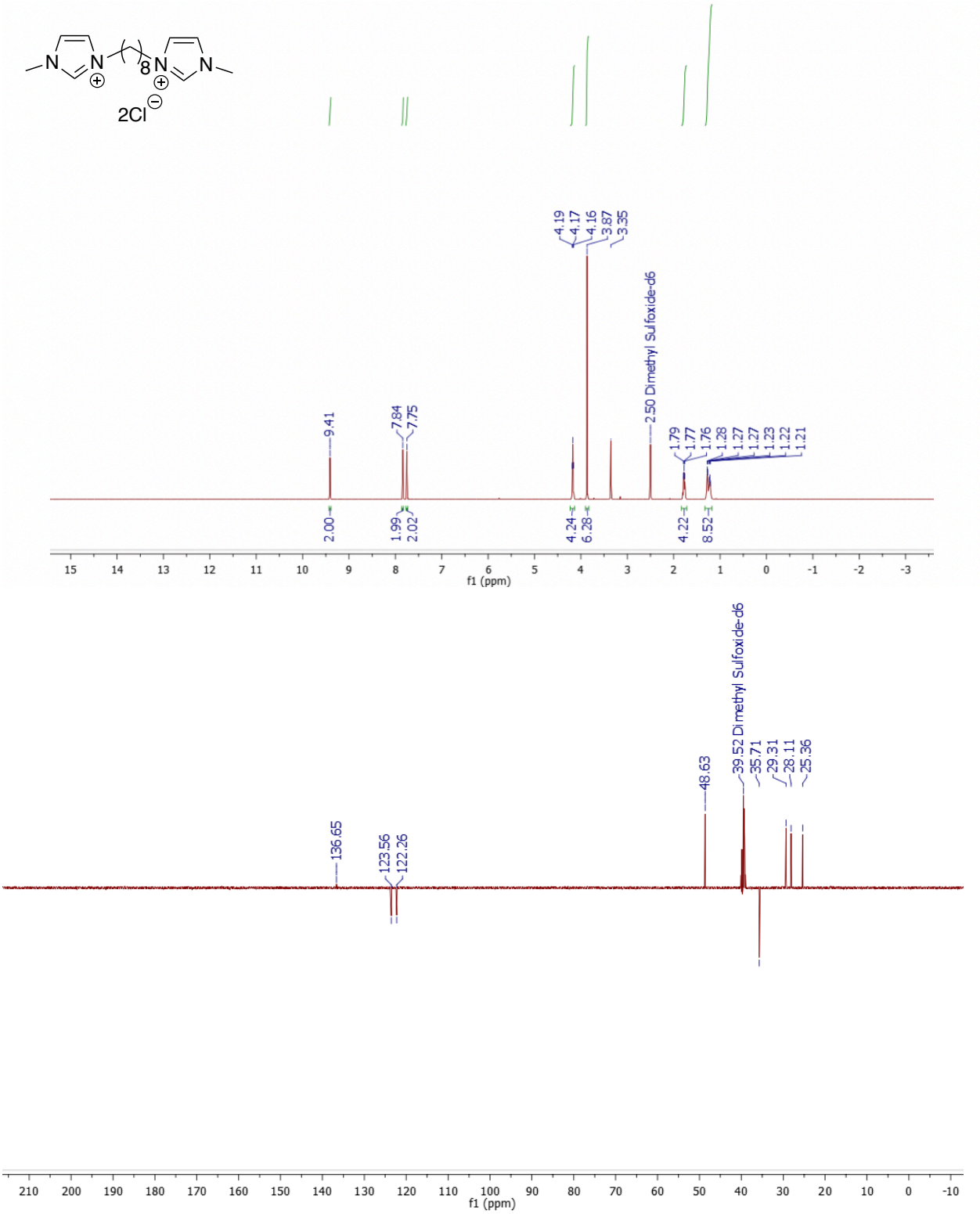


Figure S19. ^{1}H and ^{13}C {1H} APT NMR of **L^{8}·2HCl** (DMSO).

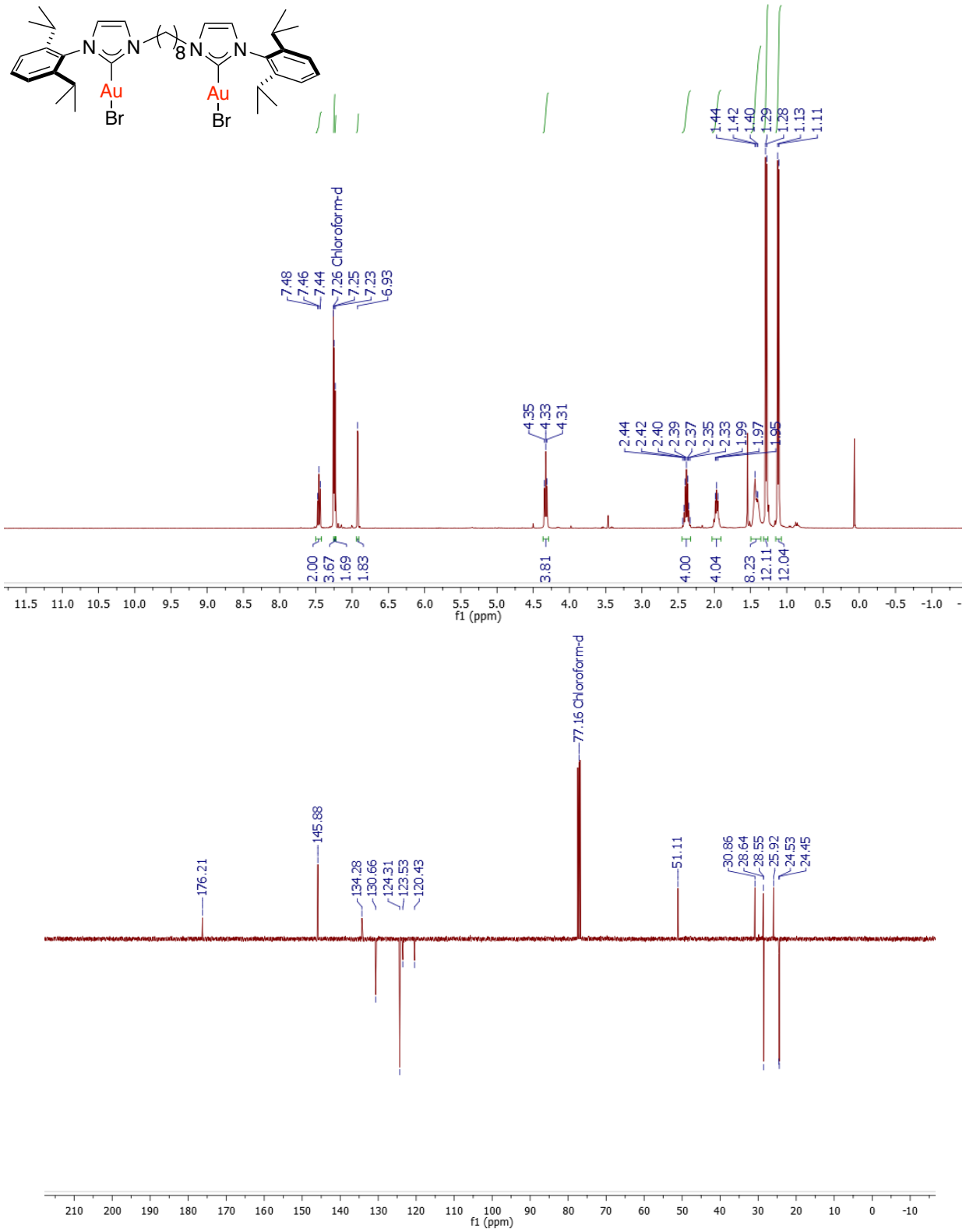


Figure S20. ^{1}H and ^{13}C {1H} APT NMR of **1** ($CDCl_3$).

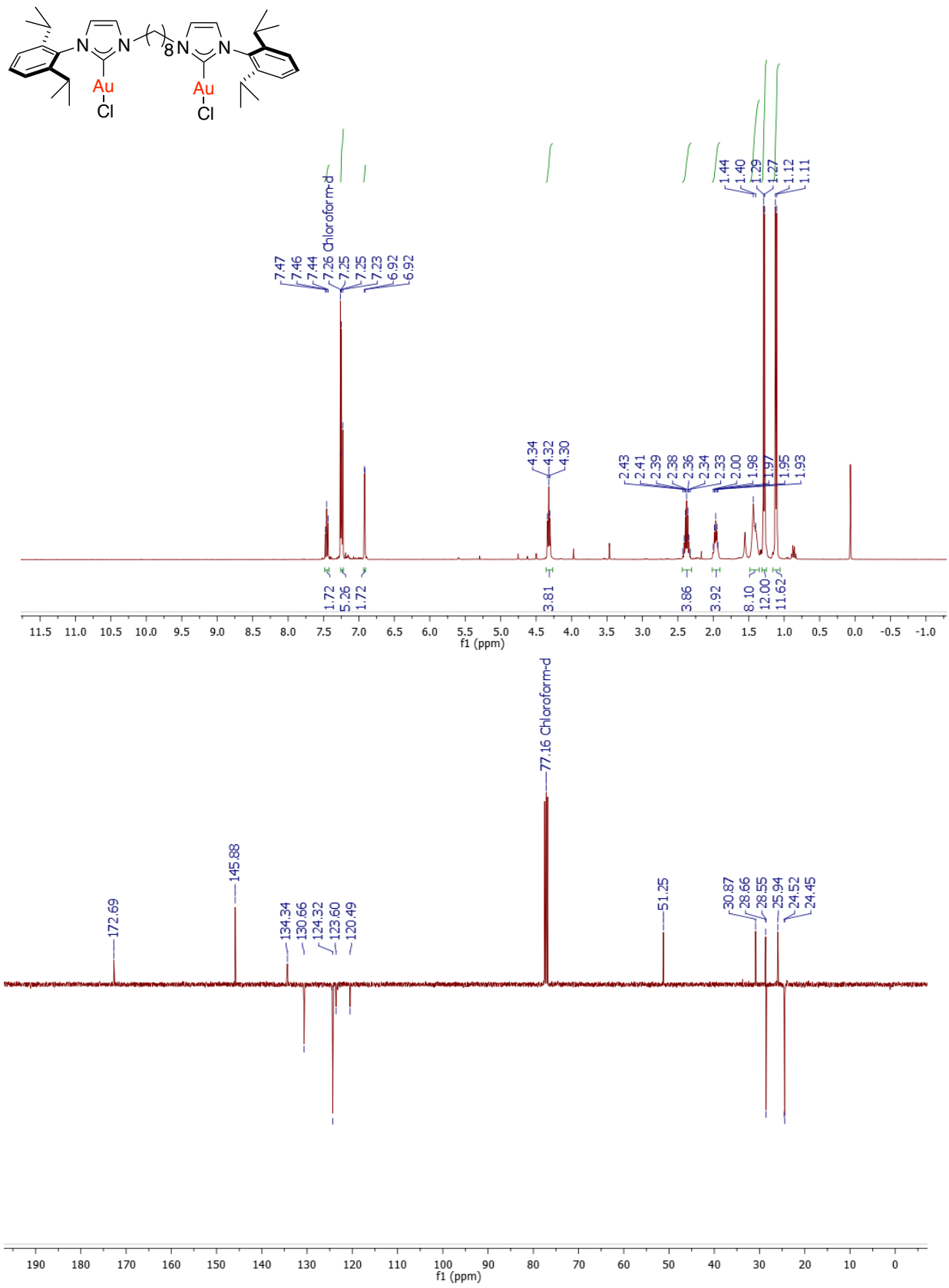


Figure S21. ^{1}H and ^{13}C {1H} APT NMR of **2** ($CDCl_3$).

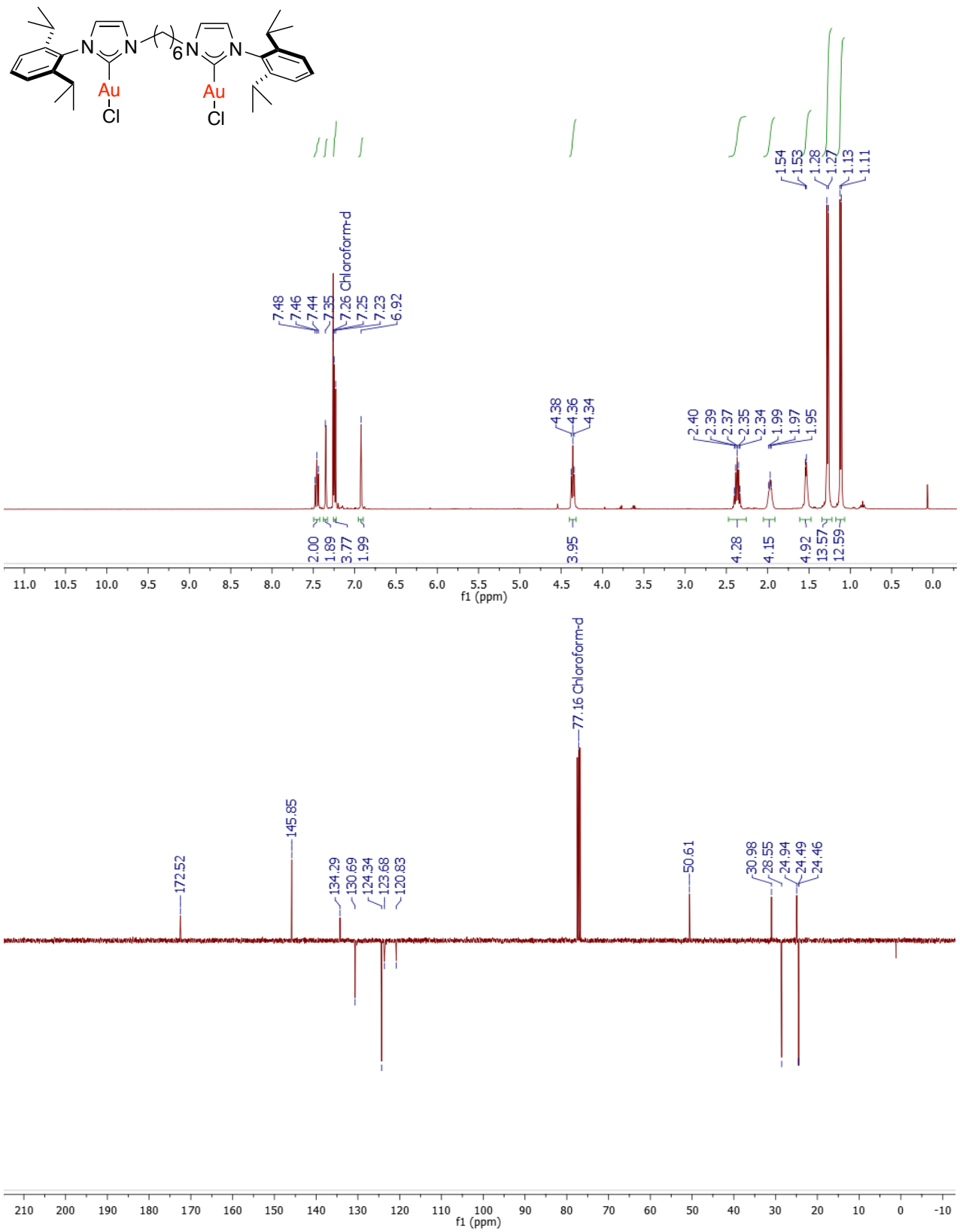


Figure S22. ^{1}H and ^{13}C {1H} APT NMR of **3** ($CDCl_3$)**.**

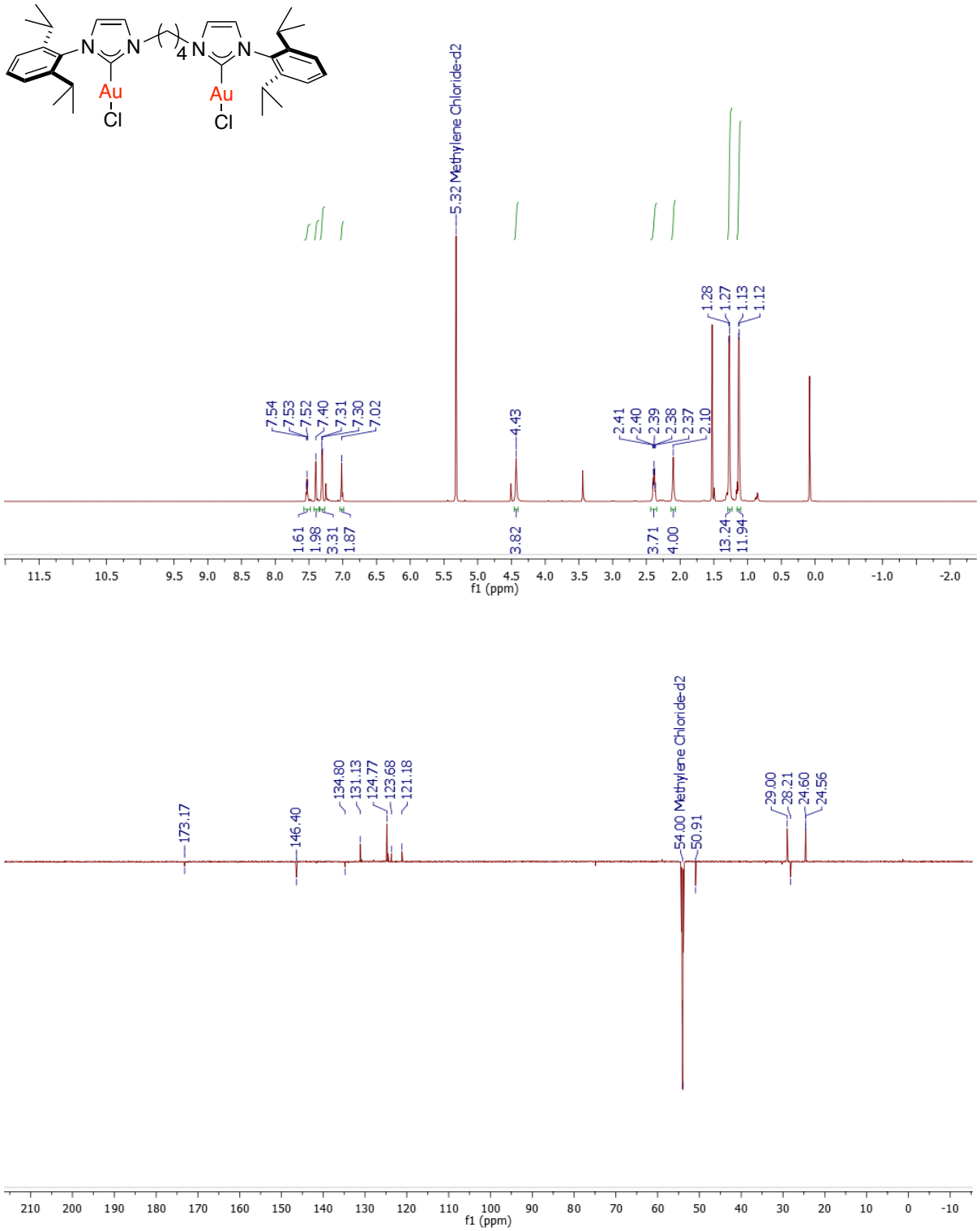


Figure S23. ^{1}H and ^{13}C {1H} APT NMR of **4** (CD_2Cl_2).

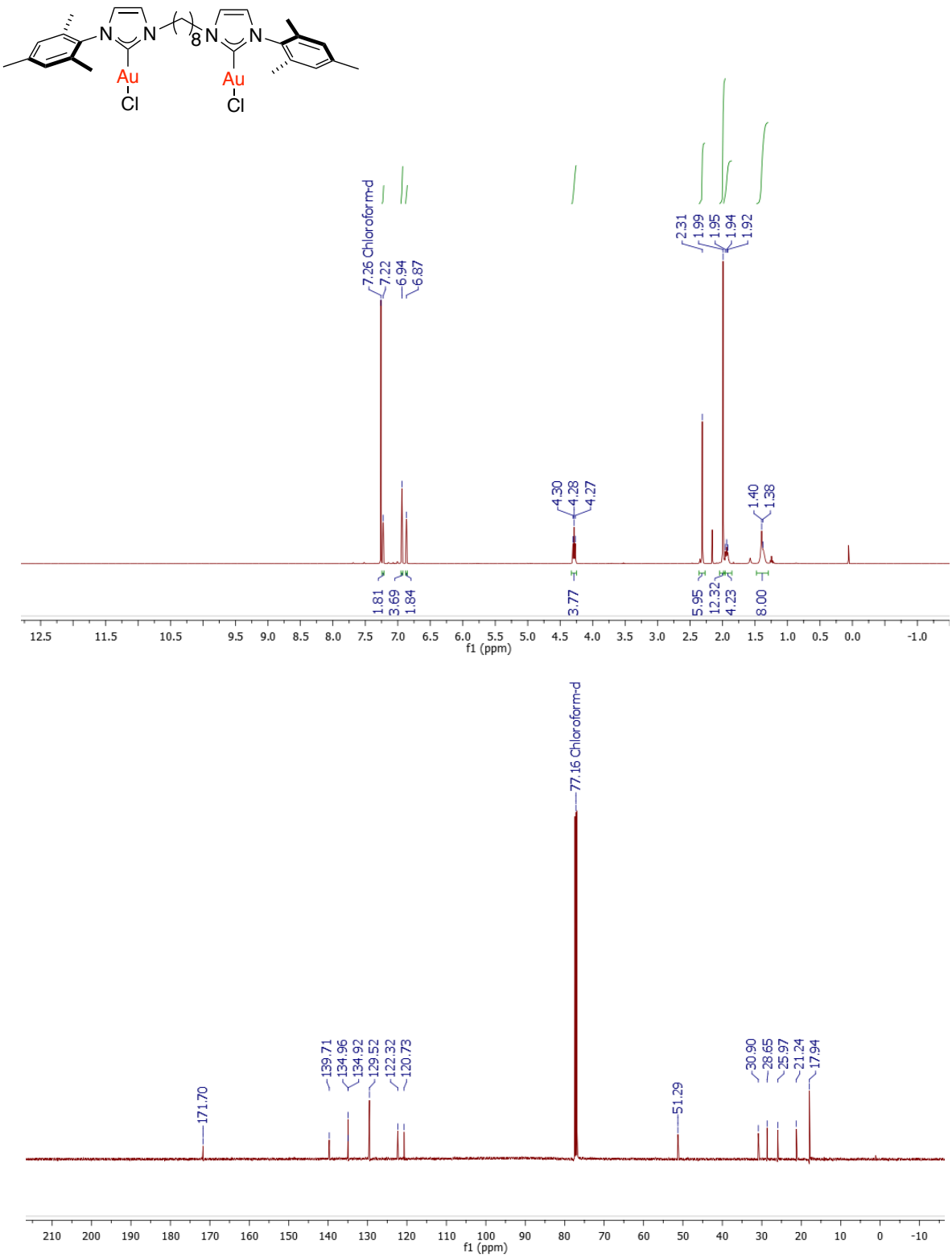


Figure S24. ^{1}H and ^{13}C {1H} NMR of **5** ($CDCl_3$).

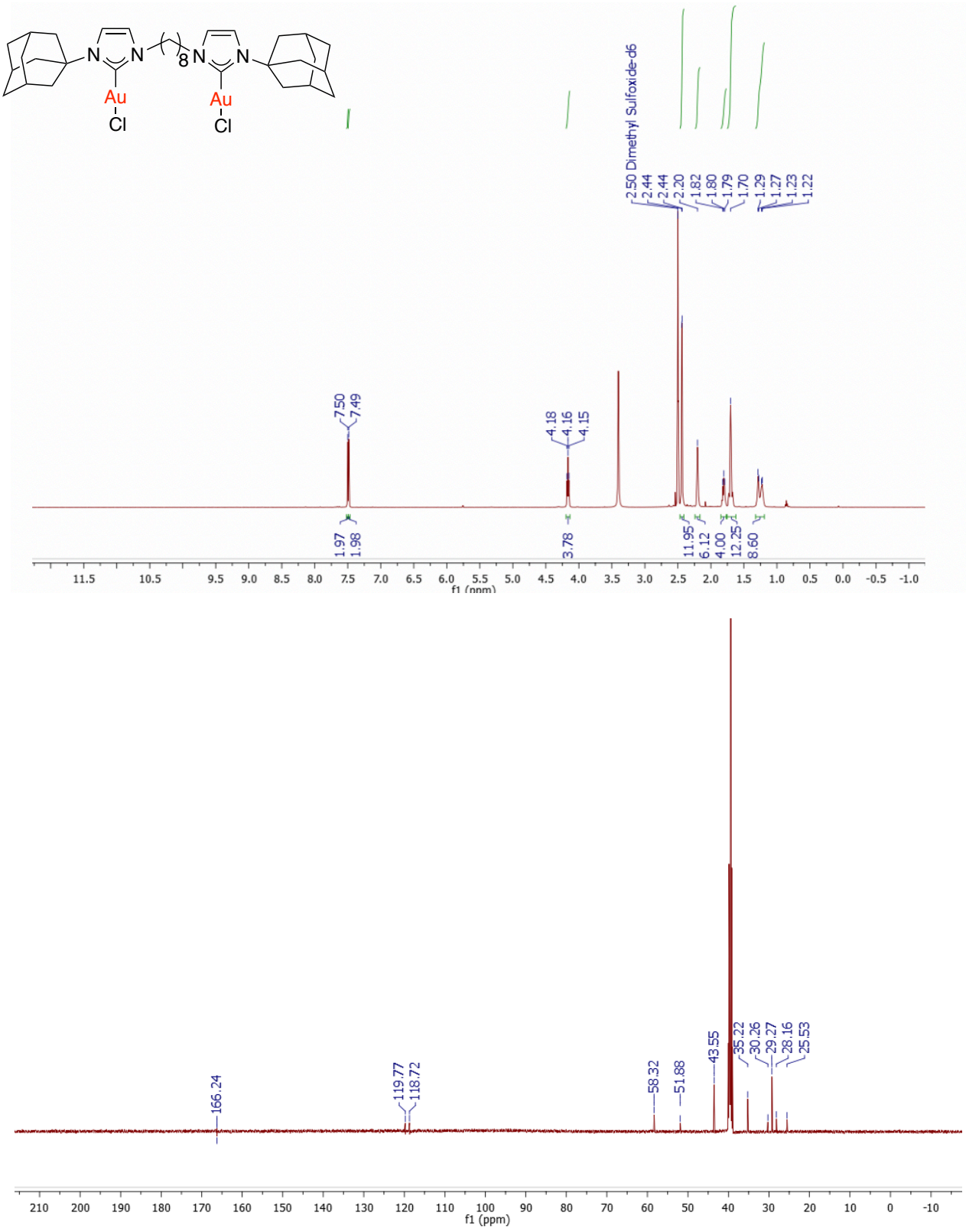


Figure S25. ^{1}H and ^{13}C {1H} NMR of **6** (DMSO).

^{1}H and ^{13}C {1H} APT NMR of 7 (DMSO)

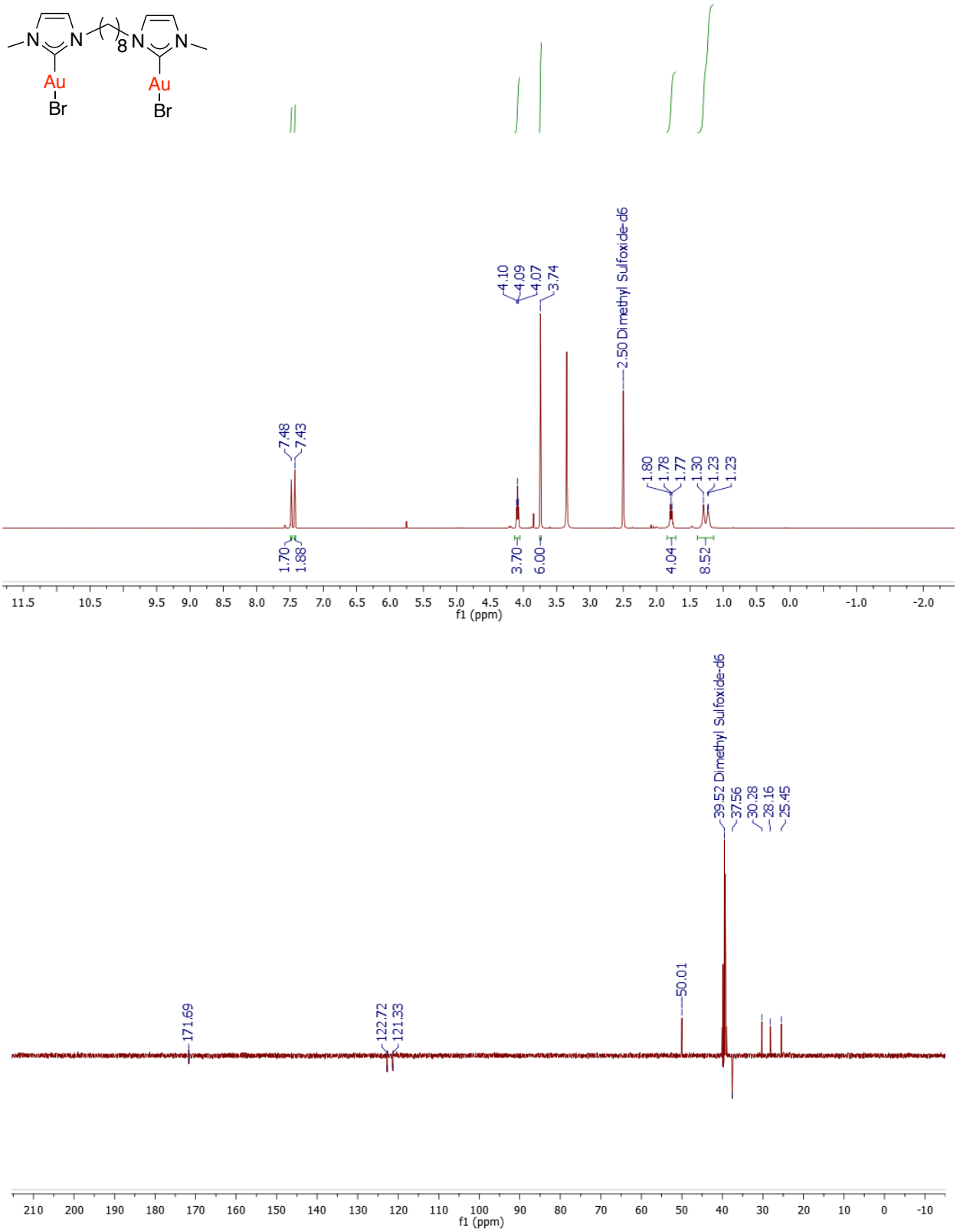


Figure S26. ^{1}H and ^{13}C {1H} APT NMR of **7** (DMSO).

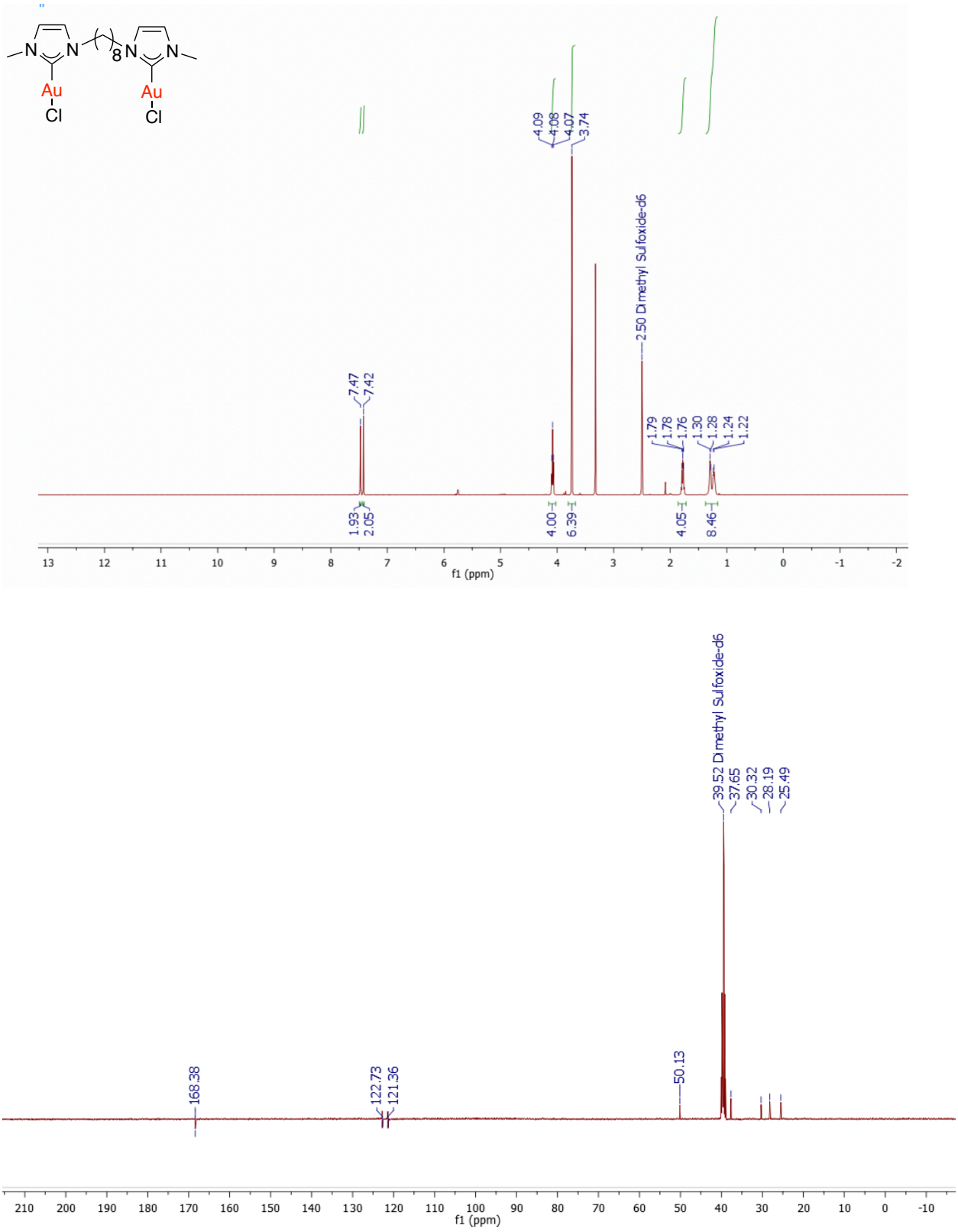


Figure S27. ^{1}H and ^{13}C {1H} APT NMR of **8** (DMSO).

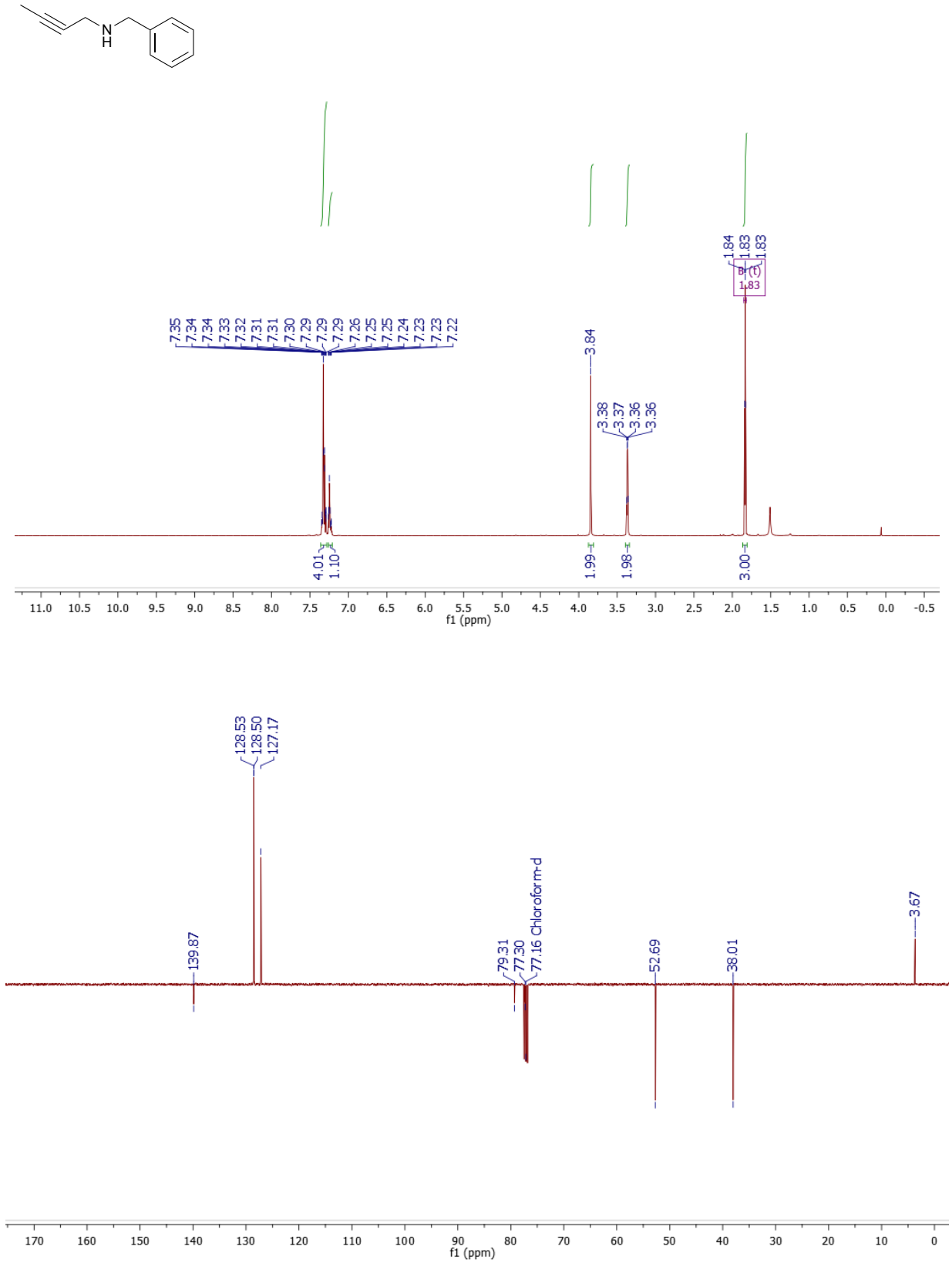


Figure S28. ^{1}H and ^{13}C {1H} APT NMR of **10** ($CDCl_3$).

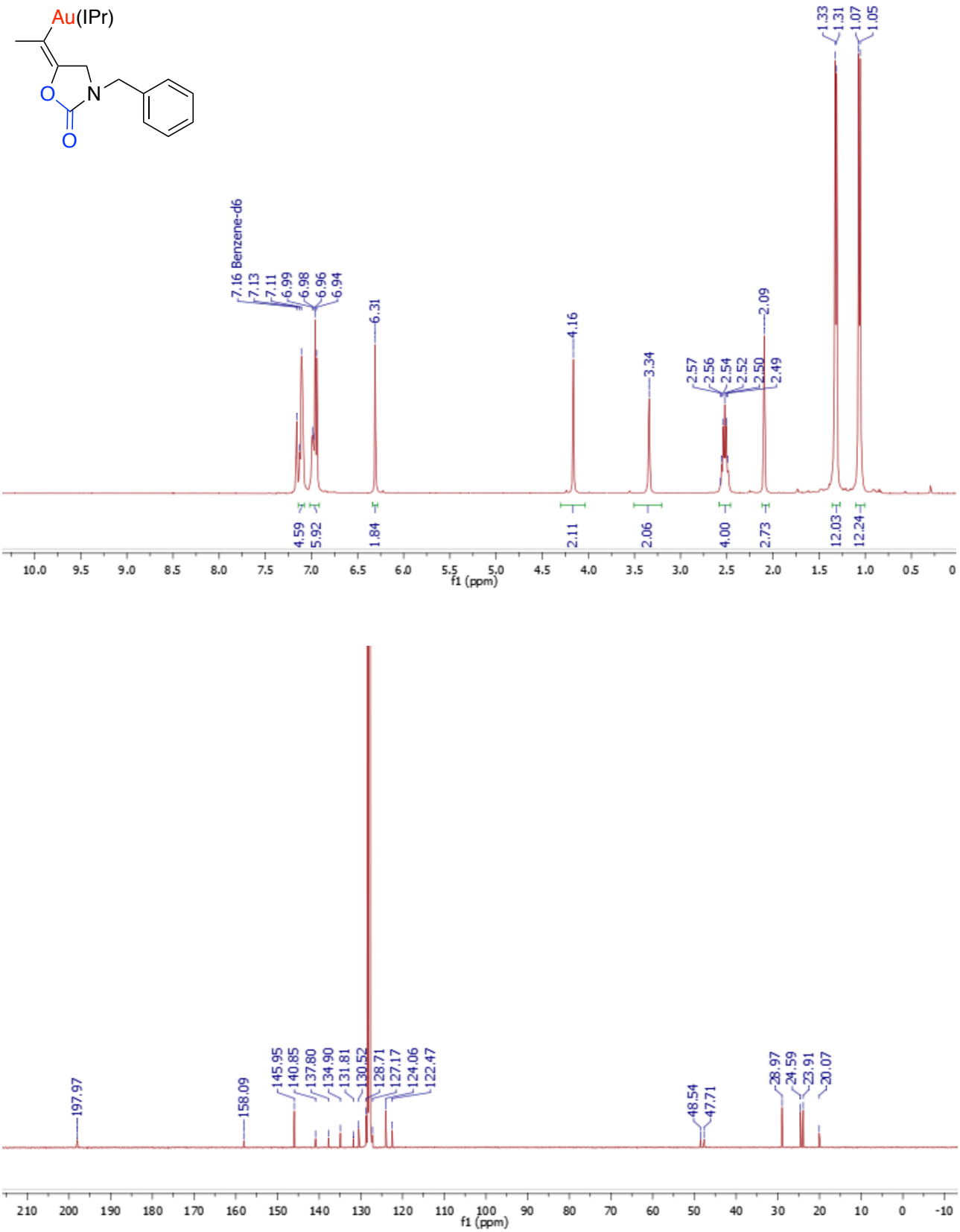


Figure S29. ^{1}H and ^{13}C {1H} NMR of **IKa** complex (C_6D_6).

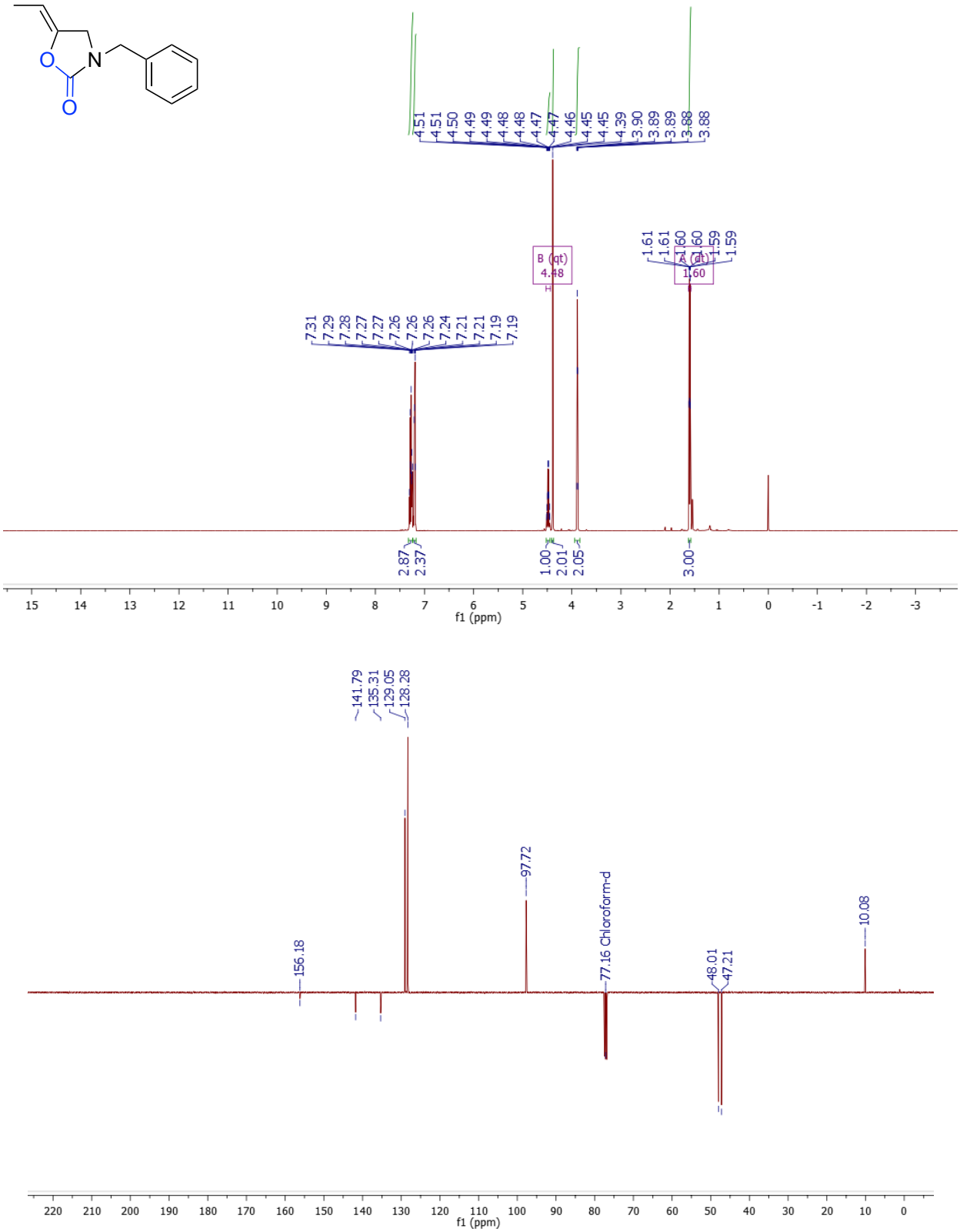


Figure S30. ^{1}H and ^{13}C {1H} APT NMR of **11** ($CDCl_3$).

References

1. (a) Zhang, H.; Liu, J.; Chen, J.; Zhao, J.; Zhao, Y.; Li, L., A Modified Procedure for the Synthesis of 1-Arylimidazoles. *Synthesis* **2003,**2661-2666; (b) Brill, M.; Collado, A.; Cordes, D. B.; Slawin, A. M. Z.; Vogt, M.; Grützmacher, H.; Nolan, S. P., Synthesis and Characterization of Gold(I) Complexes of Dibenzotropylidene-Functionalized NHC Ligands (Trop-NHCs). *Organometallics* **2014,** *34*, 263-274.
2. Cao, C.; Zhuang, Y.; Zhao, J.; Liu, H.; Geng, P.; Pang, G.; Shi, Y., Green Synthesis of Alkane Bridged Bisimidazolium Salts Under Solvent-Free Conditions. *Synth. Commun.* **2012,** *42*, 380-387.
3. Hase, S.; Kayaki, Y.; Ikariya, T., NHC–Gold(I) Complexes as Effective Catalysts for the Carboxylative Cyclization of Propargylamines with Carbon Dioxide. *Organometallics* **2013,** *32*, 5285-5288.
4. Apex2 Version 2.2-0 and SAINT+ Version 7.46A; Bruker Analytical X-ray System, Inc., Madison, Wisconsin, USA, 2007.
5. G. M. Sheldrick , *Acta. Crystallogr.* **2015**, *C71*, 3-8.
6. G. M. Sheldrick. SHELXTL Version 6.1; Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2000.
7. C. Adamo, V. Barone, Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* 1999**, *110***, 6158-6170.
8. S. Grimme, S. Ehrlich, L. Goerigk, Effect of the damping function in dispersion corrected density functional theory. *J. Comp. Chem.* 2011, **32**, 1456-1465.
9. Weigend, F.; Ahlrichs, R., Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* 2005, **7**, 3297-3305.
10. D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuß, Energy-adjusted ab initio pseudopotentials for the second and third row transition elements. *Theor. Chim. Acta* 1990, **77**, 123-141.
11. a) S. Miertuš, E. Scrocco, J. Tomasi, Electrostatic interaction of a solute with a continuum. A direct utilization of ab initio molecular potentials for the prevision of solvent effects. *Chem. Phys*. 1981, **55**, 117-129; b) J. Tomasi, B. Mennucci, R. Cammi, Quantum Mechanical Continuum Solvation Models. *Chem. Rev*. 2005, **105**, 2999-3094; c) G. Scalmani, M. J. Frisch, Continuous surface charge polarizable continuum models of solvation. I. General formalism. *J. Chem. Phys.* 2010, **132**, 114110.
12. Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
13. S. Hase, Y. Kayaki, T. Ikariya, Mechanistic Aspects of the Carboxylative Cyclization of Propargylamines and Carbon Dioxide Catalyzed by Gold(I)Complexes Bearing an N-Heterocyclic Carbene Ligand, *ACS Catal.* 2015, **5**, 5135−5140.
14. R. Alessio, D. Belli Dell'Amico, F. Calderazzo, U. Englert, A. Guarini, L. Labella, P. Strasser. N,N-Dialkylcarbamato Complexes of the d^{10} Cations of Copper, Silver, and Gold *Helv. Chim. Acta*, 1998, **81**, 219-230.