

Supporting Information

**Gold(I) “Click” 1,2,3-Triazolyldenes:
Synthesis, Self-Assembly and Catalysis.**

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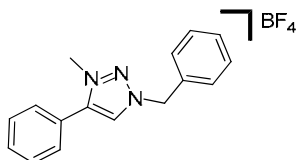
1. Experimental

1.1 General

Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. Petrol refers to the fraction of petroleum ether boiling in the range 40–60 °C. All melting points were determined using a Sanyo Gallenkamp apparatus and are uncorrected. ¹H and ¹³C NMR spectra were recorded on either a 400 MHz Varian 400 MR, Varian 500 MHz VNMRS, or Bruker AV 400 spectrometer at 298 K. Chemical shifts are reported in parts per million and referenced to residual solvent. Coupling constants (*J*) are reported in Hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: m = multiplet, t = triplet, d = doublet, s = singlet, br = broad. IR spectra were recorded on a Bruker ALPHA FT-IR spectrometer with an attached ALPHA-P measurement module or Perkin-Elmer Spectrum 100 FT-IR Universal ATR Sampling Accessory. Microanalyses were performed at the Campbell Microanalytical Laboratory at the University of Otago. Electrospray ionization mass spectra (ESI-MS) were collected on a Bruker micrOTOF-Q spectrometer. Mass spectra of organic compounds were obtained at the EPSRC National Mass Spectrometry Service Centre in Swansea. The ligands 1-benzyl-4-phenyl-1*H*-1,2,3-triazole **1** and 4,4'-benzene-1,3-diylbis(1-benzyl-1*H*-1,2,3-triazole) **6** were prepared as described previously.¹

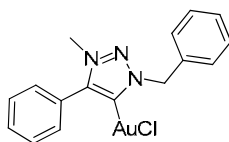
1.2 Synthetic Procedures

1.2.1 Synthesis of **2**



1 (250 mg, 1.06 mmol) and Meerwein's salt, $[(\text{CH}_3)_3\text{O}]\text{BF}_4$ (204 mg, 1.38 mmol) were stirred under nitrogen in dry dichloromethane (100 mL) for 2 days. 10 drops of methanol were added and the solvent was removed under reduced pressure to give a yellow oil. Crystallisation from chloroform/diethyl ether gave **2** as a white solid (280 mg, 78%). Mp: 114-116 °C; NMR (400 MHz, CDCl_3): ^1H δ 8.51 (s, 1H, triazole C-H), 7.57-7.45 (m, 7H, Ar-H), 7.40-7.38 (m, 3H, Ar-H), 5.71 (s, 2H, CH_2), 4.19 (s, 3H, CH_3); ^{13}C δ 143.57, 131.95, 131.40, 130.03, 129.88, 129.75, 129.57, 129.52, 128.38, 122.02, 57.64, 38.60 ppm; IR (ATR): ν 1582, 1493, 1454, 1350, 1322, 1306, 1284, 1213, 1161, 1332 (br), 854, 821, 801, 763, 741, 708, 692, 670, 652, 617, 584, 541, 520, 467 cm^{-1} ; HR-ESIMS (CH_3CN): m/z 250.134 ($[\text{M}]^+$, calculate for $\text{C}_{16}\text{H}_{16}\text{N}_3$ 250.134); Anal. calcd for $\text{C}_{16}\text{H}_{16}\text{N}_3\text{BF}_4$: C 57.00, H 4.78, N 12.46. Found: C 56.90, H 4.73, N 12.63%

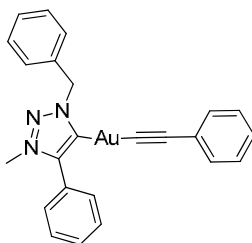
1.2.2 Synthesis of **3**



To a solution of **2** (50 mg, 0.15 mmol) in acetonitrile/dichloromethane (1:1, 10 mL) was added Ag_2O (17 mg, 0.08 mmol) and NMe_4Cl (16 mg, 0.15 mmol) and the suspension solution stirred for 18 hr in a foil-covered flask. To the yellow solution was added $\text{Au}(\text{SMe}_2)\text{Cl}$ (44 mg, 0.15 mmol) and the

solution stirred for a further 2 hr. The AgCl was removed by filtration through a small plug of celite and bright yellow solution was evaporated to dryness. Crystallisation from dichloromethane/pentane gave **2** as yellow crystals (58 mg, 82%); Mp: 105 °C (decomp); NMR (400 MHz, CDCl₃): ¹H δ 7.63 (m, 4H, Ar-H), 7.51 (m, 3H, Ar-H), 7.39 (m, 3H, Ar-H), 5.68 (s, 2H, CH₂), 4.07 (s, 3H, CH₃); ¹³C δ 158.06, 147.30, 133.70, 130.52, 129.63, 129.39, 129.31, 129.28, 129.18, 126.18, 59.29, 37.96 ppm; IR (ATR): ν 1480, 1454, 1322, 1159, 1074, 1020, 979, 922, 832, 769, 746, 696, 649, 579, 541, 458 cm⁻¹; HR-ESIMS (DCM/MeOH): *m/z* 504.052 ([M+Na]⁺, calc for C₁₆H₁₅N₃AuClNa 504.051); Anal. calcd for C₁₆H₁₅N₃AuCl•CH₂Cl₂: C 36.03, H 3.02, N 7.42; Found C 36.80, H 3.11, N 8.23%

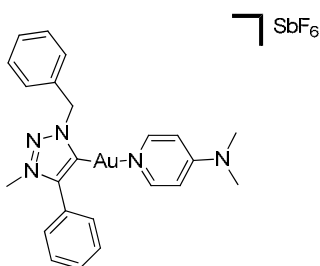
1.2.3 Synthesis of **4**



KOBu^t (23 mg, 0.21 mmol) was added to a solution of phenylacetylene (21 mg, 0.21 mmol) in methanol (4 mL) and the solution was stirred for 20 min, during which time the solid dissolved and the solution became yellow. **3** (50 mg, 0.10 mmol) was added in 1 portion and the solution stirred overnight causing the precipitation of a white solid. This was isolated by filtration and washed with water, methanol and diethyl ether to give **4** as an off white solid (14 mg, 25 %). Mp: 128 °C (decomp); NMR (400 MHz, CDCl₃): ¹H δ 7.67-7.62 (m, 4H, Ar-H), 7.51 (m, 5 H, Ar-H), 7.39 (m, 3H, Ar-H), 7.20 (m, 2H, Ar-H), 7.14 (m, 1H, Ar-H), 5.77 (s, 2H, CH₂), 4.04 (s, 3H, CH₃); ¹³C δ 174.15, 148.61, 134.11, 132.48, 130.31, 129.76, 129.30, 129.29, 129.24, 129.12, 128.79, 127.87, 126.61, 126.20, 126.06, 104.99, 59.19, 37.69 ppm; IR (ATR): ν 2107, 1594, 1484, 1453, 1438, 1323, 1209, 1165, 1069, 1022, 920, 842, 761, 742, 694, 597, 557, 529, 509, 479, 460, 410 cm⁻¹; HR-ESIMS (CH₃CN): *m/z* 570.118 ([M+Na]⁺, calc for

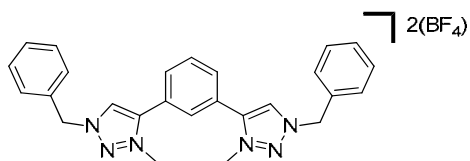
$C_{24}H_{20}N_3AuNa$ 570.122); Anal. calcd for $C_{24}H_{20}N_3Au$: C 52.66, H 3.68, N 7.68; Found C 52.17, H 3.65, N 7.65%

1.2.4 Synthesis of **5**



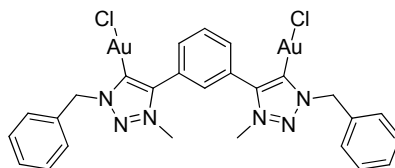
3 (50 mg, 0.10 mmol), 4-dimethylaminopyridine (13 mg, 0.1 mmol) and AgSbF₆ (36 mg, 0.1 mmol) were stirred in acetone (6 mL) in a foil-covered flask for 1 hr. The AgCl was removed by filtration through celite and the light yellow solution evaporated to dryness. Crystallisation from acetonitrile/diethyl ether gave 56 mg (67 %) of **5**. Mp: 158 °C (decomp); NMR (500 MHz, CDCl₃): ¹H δ 7.85 (d, *J* = 5.5 Hz, 2H, α-DMAP), 7.64 (m, 2H, Ar-H), 7.56-7.51(m, 5H, Ar-H), 7.43-7.41 (m, 3H, Ar-H), 6.60 (d, *J* = 5.5 Hz, 2H, β-DMAP), 5.73 (s, 2H, CH₂), 4.15 (s, 3H, triazole CH₃), 3.09 (s, 6H, DMAP CH₃); ¹³C 155.31, 152.31, 149.99, 148.33, 134.04, 130.77, 129.76, 129.42, 129.42, 129.28, 129.03, 126.16, 107.76, 59.28, 39.56, 38.09 ppm; IR (ATR): ν 1621, 1548, 1486, 1442, 1396, 1333, 1316, 1224, 1173, 1075, 1026, 832, 813, 764, 742, 711, 694, 678, 653, 628, 588, 560, 526 cm⁻¹. HR-ESIMS (CH₃CN): *m/z* 568.175 ([M]⁺, calc for C₂₃H₂₅N₅Au 568.177); Anal. calcd for C₂₃H₂₅N₅AuSbF₆: C 34.35, H 3.13, N 8.71. Found: C 34.15, H 3.03, N 8.76%

1.2.5 Synthesis of **7**



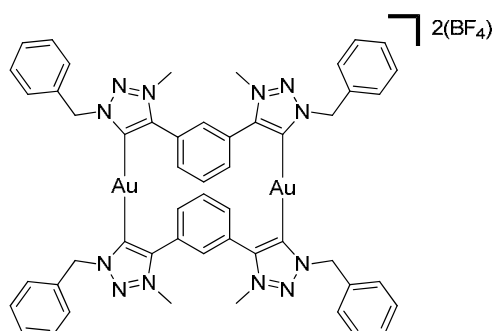
6 (500 mg, 1.27 mmol) and Meerwein's salt, $[(\text{CH}_3)_3\text{O}]\text{BF}_4$ (490 mg, 3.31 mmol) were stirred in dichloromethane (100 mL) under a nitrogen environment for 3 days. The reaction was quenched by the addition of 10 drops of methanol and the volatiles removed under vacuum to leave a white solid. This was further purified by column chromatography (SiO_2 gel, 95:5 dichloromethane/methanol) to give **7** as a yellow oil, which solidified on standing in an acetone/diethyl ether solvent mixture (530 mg, 70 %). Mp: 145-147 °C; NMR (400 MHz, d_6 -acetone): ^1H δ 9.09 (s, 2H, triazole C-H), 8.23 (m, 1H, Ar-H), 8.08 (dd, $J = 7.9, 1.7$ Hz, 2H, Ar-H), 7.92 (t, $J = 7.9$ Hz, 1H, Ar-H), 7.65-7.61 (m, 4H, Ar-H), 7.49 (m, 6H, Ar-H), 6.01 (s, 4H, CH_2), 4.46 (s, 6H, CH_3); ^{13}C δ 143.20, 133.47, 133.39, 131.69, 131.51, 130.42, 130.23, 130.20, 130.10, 125.09, 58.02, 39.59 ppm; IR (ATR): ν 1573, 1457, 1353, 1316, 1166, 1150, 1034 (br), 968, 907, 852, 838, 826, 806, 765, 726, 702, 693, 682, 648, 579, 519, 502, 467, 458 cm^{-1} ; HR-ESIMS (CH_3CN): m/z 509.224 ($[\text{M}-\text{BF}_4]^+$, calc for $\text{C}_{26}\text{H}_{26}\text{N}_6\text{BF}_4$ 509.225); Anal. calcd for $\text{C}_{26}\text{H}_{26}\text{N}_6\text{B}_2\text{F}_8$: C 52.38, H 4.40, N 14.10. Found: C 52.72, H 4.52, N 14.00%

1.2.6 Synthesis of **8**



A suspension of **7** (100 mg, 0.17 mmol), Ag₂O (39 mg, 0.17 mmol) and NMe₄Cl (37 mg, 0.34 mmol) were stirred in acetonitrile/dichloromethane (1:1, 10 mL) in a foil-covered flask for 18 hrs. The solvent was removed under reduced pressure and the white residue re-suspended in dichloromethane (10 mL). Au(SMe₂)Cl (99 mg, 0.34 mmol) was added and the suspension stirred for a further 18 hrs. The solution was filtered through Celite to remove AgCl and the addition of diethyl ether to the filtrate resulted in the precipitation of a white solid. This was isolated by filtration and washed with diethyl ether to produce **8** as a white solid (106 mg, 71%). Mp >200 °C; NMR (400 MHz, CDCl₃): ¹H δ 7.94 (m, 1H, Ar-H), 7.75-7.73 (m, 2H, Ar-H), 7.68-7.60 (m, 5H, Ar-H), 7.43-7.38 (m, 6H, Ar-H), 5.69 (s, 4H, CH₂), 4.25 (s, 6H, CH₃); ¹³C δ 158.30, 146.02, 133.44, 131.14, 130.82, 130.27, 129.54, 129.28, 129.27, 127.50, 59.36, 38.71 ppm; IR (ATR): ν 1495, 1476, 1455, 1434, 1314, 1285, 1152, 1071, 950, 915, 854, 807, 760, 730, 706, 694, 650, 579, 464 cm⁻¹; HR-ESIMS (CH₂Cl₂/CH₃CN): *m/z* 849.109 ([M-Cl]⁺, calc for C₂₆H₂₄N₆Au₂Cl 849.108); Anal. calcd for C₂₆H₂₄N₆Cl₂Au₂: C 35.27, H 2.73, N 9.49. Found: C 35.35, H 2.69, N 9.26%

1.2.7 Synthesis of **9**



A suspension of **7** (20 mg, 0.03 mmol), Ag₂O (8 mg, 0.03 mmol) and NMe₄Cl (7 mg, 0.07 mmol) were stirred in acetonitrile/dichloromethane (1:1, 10 mL) in a foil-covered flask for 18 hrs. The solvent was removed under reduced pressure and the white residue re-suspended in dichloromethane (10 mL). **8** (30 mg, 0.03 mmol) was added and the suspension stirred for a further 18 hrs. The solution was filtered through celite and reduced in volume. Vapour diffusion of diethyl ether into the dichloromethane solution afforded a pale yellow solid that was isolated by filtration (36 mg, 75%). Mp 169 °C: IR (ATR): ν 3029, 1496, 1454, 1318, 1159, 1051 (br), 857, 804, 702, 658, 578, 520, 459 cm⁻¹; HR-ESIMS (CH₃CN/CH₃OH); 617.174 ([M-2BF₄]²⁺, calc for C₅₂H₄₈N₁₂Au₂ 617.172), 1269.310 ([M-2BF₄+Cl]⁺, calc for C₅₂H₄₈N₁₂AuCl 1269.314), 1321.348 ([M-BF₄]⁺, calc for C₅₂H₄₈N₁₂Au₂BF₄ 1321.349); Anal. calcd for C₅₂H₄₈N₁₂Au₂B₂F₈•4H₂O: C 42.18, H 3.81, N 11.35. Found: C 42.05, H 3.25, N 11.13%

2. X-ray Crystallography

2.1 General

X-Ray quality crystals of **2'** (X = PF₆) were grown by the slow diffusion of *n*-hexane into a solution of **2** (X = BF₄) and excess NH₄PF₆ in CHCl₃. Crystals of **3** were grown by diffusion of *n*-pentane into a dichloromethane solution. The slow evaporation of an *n*-pentane/dichloromethane solution of **4** produced long needles of **4** and the vapour diffusion of diethyl ether into a dichloromethane solution of **5** produced yellow crystals. All crystallisations were carried out at room temperature in the absence of light.

2.2 Data Collection and Refinement

X-Ray data for **2'**, **3**, **4** and **5** were recorded using a Bruker APEX II CCD diffractometer using Mo-K α radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied by semi-empirical methods (SADABS²). The structures were solved by SIR-97³. In all cases, the heavy metal was initially located, followed by all other non-hydrogen atoms by a series of difference maps. Weighted full-matrix least-squares refinement on F^2 was carried out using SHELXL-97⁴ with all non-hydrogen atoms being refined anisotropically. The hydrogen atoms were included in calculated positions and were refined as riding atoms with individual (or group, if appropriate) isotropic displacement parameters. All ORTEP⁴ diagrams have been drawn with 50% probability ellipsoids, with the exception of **5** (30% probability ellipsoids). Crystal data and collection parameters are given in Table S1.

Table S1: Crystal and Structural Refinement Details for **2'**, **3** and **5**

| | 2' | 3 | 4 | 5 |
|-----------------------------------------------------|-------------------------------------------------------------------|-------------------------------------------------------------------|-------------------------------------------------------------------|--------------------------------------------------------------------|
| CCDC Depository | 782313 | 782314 | 782316 | 782315 |
| Empirical formula | C ₁₆ H ₁₆ N ₃ F ₆ P | C ₁₆ H ₁₅ N ₃ AuCl | C ₂₄ H ₂₉ N ₃ Au | C ₂₃ H ₂₅ N ₅ AuF ₆ Sb |
| Formula weight | 395.29 | 481.73 | 547.40 | 804.20 |
| <i>T</i> (K) | 89(2) | 90(2) | 93(2) | 91(2) |
| Crystal system | Monoclinic | Orthorhombic | Orthorhombic | Triclinic |
| Space group | <i>P</i> 2 ₁ / <i>n</i> | <i>P</i> 2 ₁ 2 ₁ 2 ₁ | <i>Pna</i> 2 ₁ | <i>P</i> -1 |
| <i>a</i> (Å) | 6.3316(6) | 7.6316(10) | 14.9399(15) | 10.8541(15) |
| <i>b</i> (Å) | 15.3693(13) | 7.8947(9) | 19.6839(17) | 10.8554(14) |
| <i>c</i> (Å) | 17.6088(16) | 25.267(4) | 6.9061(7) | 11.2188(14) |
| α (°) | 90 | 90 | 90 | 101.367(7) |
| β (°) | 99.548(4) | 90 | 90 | 92.615(7) |
| γ (°) | 90 | 90 | 90 | 102.371(8) |
| <i>V</i> (Å ³) | 1689.8(3) | 1522.3(3) | 2030.9(3) | 1260.5(3) |
| <i>Z</i> | 4 | 4 | 4 | 2 |
| ρ_{calc} (mg mm ⁻³) | 1.554 | 2.102 | 1.790 | 2.119 |
| μ (mm ⁻¹) | 0.230 | 9.835 | 7.257 | 6.951 |
| Crystal size (mm) | 0.40 × 0.26 × 0.07 | 0.31 × 0.24 × 0.07 | 0.58 × 0.3 × 0.08 | 0.42 × 0.21 × 0.14 |
| Colour, habit | colourless, plate | yellow, rhomb | colourless, needle | colourless, block |
| Reflections collected | 21123 | 28911 | 12320 | 14555 |
| Independent reflections (<i>R</i> _{int}) | 3454 (0.1120) | 3141 (0.0462) | 3418 (0.0472) | 4677 (0.0589) |
| Data/restraints/parameters | 3454/0/237 | 3141/0/191 | 3418/1/254 | 4677/0/328 |
| Goodness of fit | 1.052 | 1.046 | 0.970 | 1.063 |
| Final <i>R</i> indexes [<i>I</i> > 2σ(<i>I</i>)] | <i>R</i> ₁ = 0.0514 <i>wR</i> ₂ = 0.1269 | <i>R</i> ₁ = 0.0175 <i>wR</i> ₂ = 0.0378 | <i>R</i> ₁ = 0.0265 <i>wR</i> ₂ = 0.0443 | <i>R</i> ₁ = 0.0378 <i>wR</i> ₂ = 0.0896 |
| Final <i>R</i> indexes (all data) | <i>R</i> ₁ = 0.0675 <i>wR</i> ₂ = 0.1390 | <i>R</i> ₁ = 0.0196 <i>wR</i> ₂ = 0.0385 | <i>R</i> ₁ = 0.0397 <i>wR</i> ₂ = 0.0473 | <i>R</i> ₁ = 0.0429 <i>wR</i> ₂ = 0.0927 |
| Largest diff. peak/hole | 0.344 and -0.582 | 0.761 and -0.707 | 0.632 and -0.844 | 1.686 and -1.819 |
| Flack <i>x</i> parameter | - | -0.021(7) | 0.004(10) | - |

2.3 Molecular Diagrams and Selected Bond Lengths/Angles

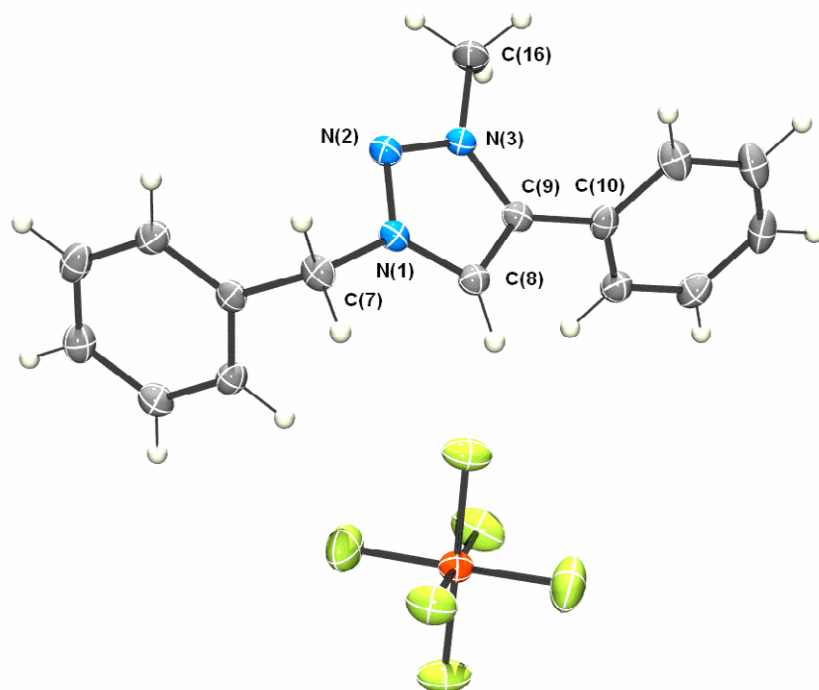


Figure S1: ORTEP diagram of the molecular structure of **2'**. Thermal ellipsoids are shown drawn at the 50% probability level. Selected bond lengths (Å) for **2'**: N(1)-N(2) 1.313(3), N(2)-N(3) 1.319(3), N(3)-C(9) 1.364(2), C(9)-C(8) 1.367(3), C(8)-N(1) 1.350(2), N(3)-C(16) 1.469(3).

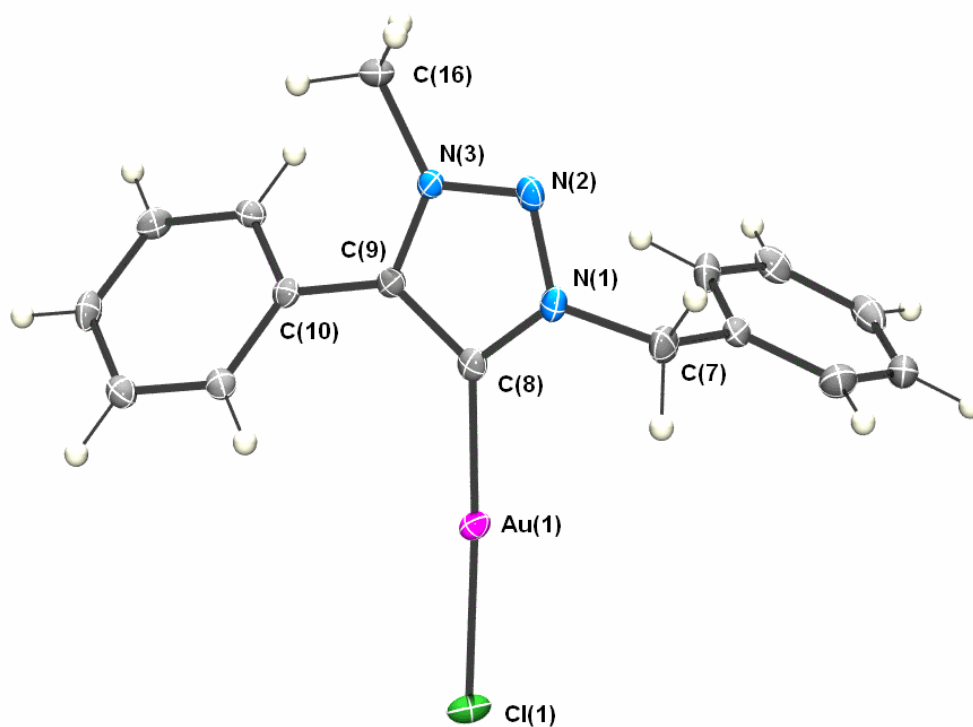


Figure S2: ORTEP diagram of the molecular structure of **3**. Thermal ellipsoids are shown drawn at the 50% probability level. Selected bond lengths (Å) and angles (°) for **3**: Au(1)-Cl(1) 2.2940(10), C(8)-Au(1) 1.982(4), C(8)-N(1) 1.363(5), N(1)-N(2) 1.326(4), N(2)-N(3) 1.315(4), N(3)-C(9) 1.361(5), C(9)-C(8) 1.402(5), N(3)-C(16) 1.467(5); C(8)-Au(1)-Cl(1) 177.18(12).

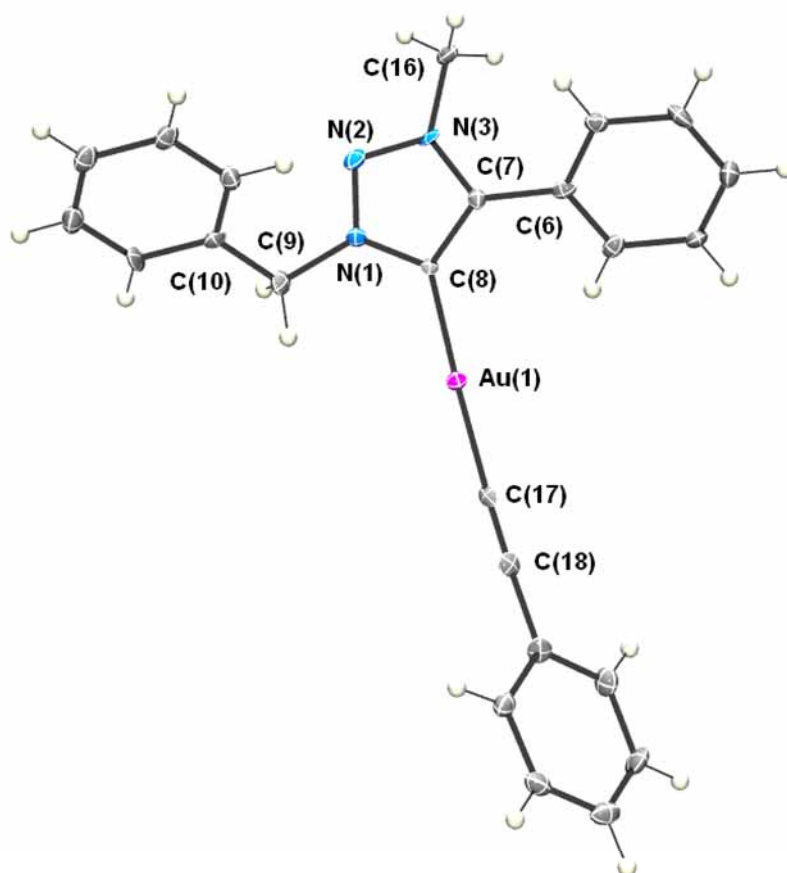


Figure S3: ORTEP diagram of the molecular structure of **4**. Thermal ellipsoids are shown drawn at the 50% probability level. Selected bond lengths (Å) and angles (°) for **4**: Au(1)-C(17) 2.011(6), Au(1)-C(8) 2.020(5), C(17)-C(18) 1.171(7), N(1)-N(2) 1.351(6), N(2)-N(3) 1.315(6), N(3)-C(7) 1.363(7), C(7)-C(8) 1.378(7), C(8)-N(1) 1.363(7), N(3)-C(16) 1.463(6); C(8)-Au(1)-C(17) 177.7(3), C(17)-C(18)-C(19) 177.2(10).

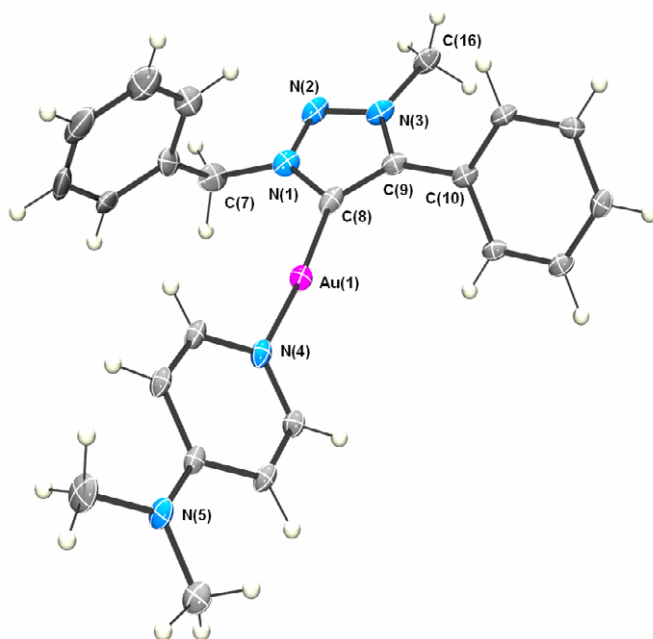


Figure S4: ORTEP diagram of the molecular structure of **5**, with SbF_6^- removed for clarity. Thermal ellipsoids are shown drawn at the 30% probability level. Selected bond lengths (\AA) and angles ($^\circ$) for **5**: Au(1)-N(4) 2.055(6), Au(1)-C(8) 1.962(8), N(1)-N(2) 1.319(9), N(2)-N(3) 1.318(8), N(3)-C(9) 1.338(8), C(9)-C(8) 1.393(10), C(8)-N(1) 1.381(9), N(3)-C(16) 1.478(9); C(8)-Au(1)-N(4) 173.6(2).

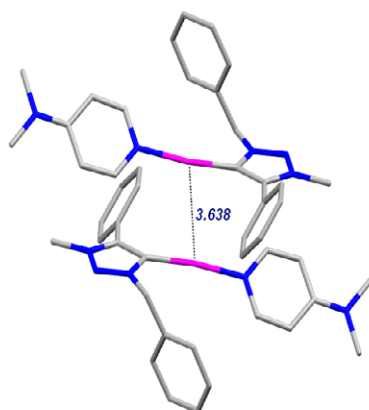


Figure S5: Molecular packing diagram of **5** (SbF_6^- removed for clarity), showing dimer stabilised by weak Au---Au interactions (Au-Au distance 3.6381(6) \AA).

3. Catalysis

3.1 Gold(I)-Catalysed Carbene Transfer Reactions from Ethyl diazoacetate (EDA) (**10 R = H**) with:

3.1.1 Alcohols and phenol (Table 1, Entries 1-5)

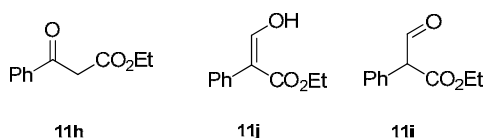
Alcohol or phenol (3 equivalents, 0.38 mmol) was added to a solution of complex **3** (3 mg, 6×10^{-6} mol) and AgSbF₆ (2 mg, 6×10^{-6} mol) in CDCl₃ (0.7 mL). The resulting mixture was allowed to stir for 15 min before EDA (**10 R = H**) (14 mg, 0.13 mmol) was added in one portion. The mixture was allowed to stir for 3.5 to 18 h at 20 °C while reaction progress was monitored by TLC. After filtration through a plug of cotton wool, 1,3,5-trimethoxybenzene (7 mg, 0.04 mmol, 1/3 equiv.) was added to the mixture as internal standard. ¹H-NMR yields were obtained by analysis of the crude reaction mixture with internal standard. Products **11a-e** were identified through comparison with literature NMR data.⁵

3.1.2 Aniline (Table 1, Entry 6)

Aniline (3 equivalents, 35 mg, 34 μ L, 0.38 mmol) was added to a solution of complex **3** (3 mg, 6×10^{-6} mol) and AgSbF₆ (2 mg, 6×10^{-6} mol) in CDCl₃ (0.7 mL). The resulting mixture was allowed to stir for 15 min before EDA (**10 R = H**) (14 mg, 0.13 mmol) was added in one portion. The mixture was allowed to stir for 70 h at 40 °C. After filtration through a plug of cotton wool, 1,3,5-trimethoxybenzene (7 mg, 0.04 mmol, 1/3 equiv.) was added to the mixture as internal standard. ¹H-NMR yields were obtained by analysis of the crude reaction mixture with internal standard. Product **11f** was identified through comparison with literature NMR data.⁶

3.1.3 Benzaldehyde (Table 1, Entry 8)

Benzaldehyde (3 equivalents, 39 mg, 38 μ L, 0.38 mmol) was added to a solution of complex **3** (3 mg, 6×10^{-6} mol) and AgSbF_6 (2 mg, 6×10^{-6} mol) in CDCl_3 (0.7 mL). The resulting mixture was allowed to stir for 15 min before EDA (**10 R = H**) (15 mg, 0.13 mmol) was added in one portion. The mixture was allowed to stir for 1 h at 20 $^\circ\text{C}$. 1,3,5-Trimethoxybenzene (7 mg, 0.04 mmol, 1/3 equiv.) was added to the mixture as internal standard. The mixture was filtered through a plug of cotton wool and $^1\text{H-NMR}$ yields were obtained by analysis of the crude reaction mixture with internal standard. Product mixture **11h-j** was identified through comparison with pure commercial samples and literature NMR data.⁷

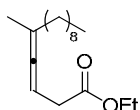


3.2 Gold(I)-catalysed Reaction of Methyl 2-diazo-2-phenylacetate (MPDA) (**10 R = Ph**) with Ethanol (Table 1, Entry 7)

Ethanol (17 mg, 21 μ L, 0.38 mmol) was added to a solution of complex **3** (3 mg, 6×10^{-6} mol) and AgSbF_6 (2 mg, 6×10^{-6} mol) in CDCl_3 (0.7 mL). The resulting mixture was allowed to stir for 15 min before MPDA (**10, R = Ph**) (23 mg, 0.13 mmol) was added in one portion. The mixture was allowed to stir for 6 d at 20 $^\circ\text{C}$. TLC analysis showed that the reaction did not go to completion even after 6 days. After filtration through a plug of cotton wool, 1,3,5-trimethoxybenzene (7 mg, 0.04 mmol, 1/3 equiv.) was added to the mixture as internal standard. $^1\text{H-NMR}$ yields were obtained by analysis of the crude reaction mixture with internal standard. Product **11g** was identified through comparison with literature NMR data.⁸

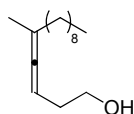
3.3 Intramolecular Hydroalkoxylation of allene **12** catalysed by complex **3**/AgSbF₆

3.3.1 Preparation of the precursor ethyl 5-methyl-3,4-tetradecadienoate **SI-1** (following general procedure by Ma and co-workers⁹)



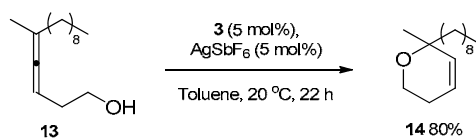
3-Methyldodecyn-3-ol (4.5 g, 5.3 mL, 22 mmol), triethyl orthoacetate (13 g, 15 mL, 78 mmol) and propionic acid (0.5 mL) were added under nitrogen to a dried three-neck flask and the mixture was allowed to stir at 145 °C for 1 h, before a second portion of propionic acid (0.5 mL) was added and the mixture was left refluxing at 145 °C with a Dean-Stark trap to remove the resulting ethanol. After 24 h, as monitored by TLC, the starting material was completely consumed and the mixture was cooled to room temperature, concentrated and the residue purified by flash column chromatography (eluent: hexane/diethyl ether = 10/1) to afford ethyl 5-methyl-3,4-tetradecadienoate, **SI-1**, (3.1 g, 11 mmol, 48%) as yellowish oil. NMR (400 MHz, CDCl₃): ¹H δ 5.15-5.11 (m, 1H, C=CH), 4.13 (q, *J* = 7.1 Hz, 2H, OCH₂), 2.95 (d, *J* = 7.1 Hz, 2H, CH₂CO₂Et), 1.91 (dt, *J* = 2.9, 7.2 Hz, 2H, CH₂C=C), 1.66 (d, *J* = 2.9 Hz, 3H, CH₃), 1.27-1.23 (m, 17H, 7 CH₂, CH₃), 0.87 (t, *J* = 6.9 Hz, 3H, CH₃); ¹³C δ 171.8 (C=O), 100.7 (2C), 83.2 (CH), 60.4 (OCH₂), 35.4 (CH₂), 33.8 (CH₂), 31.8 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 27.3 (CH₂), 22.6 (CH₂), 18.8 (CH₃), 14.1 (CH₃), 13.9 (CH₃); IR (ATR): ν 2924, 2854, 1970, 1738, 1464, 1318, 1254, 1153 cm⁻¹; HRMS: exact mass calculated for C₁₇H₃₀O₂ requires *m/z* [M]⁺: 266.2240, found 266.2239.

3.3.2 Synthesis of Allene **12**



Ethyl 5-methyl-3,4-tetradecadienoate, **SI-1**, (2.0 g, 7.5 mmol) was added dropwise to a stirred suspension of LiAlH_4 (1.3 g, 34 mmol) in dry THF at 0 °C and the mixture was allowed to warm to room temperature overnight. Then the reaction was quenched by successive addition of water (1.8 mL), 15% NaOH (1.8 mL) and water (1.8 mL) at 0 °C. The resulting white suspension was filtered through Celite, eluted with THF (50 mL), extracted with sat. NaHCO_3 solution (50 mL), water (50 mL) and THF (50 mL) and the combined organic layers were then dried over MgSO_4 and concentrated. The crude product was finally purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10/1) to afford 5-methyl-3,4-tetradecadien-1-ol, **13**, (1.1 g, 5.0 mmol, 66%) as a colourless oil. NMR (400 MHz, CDCl_3): ^1H δ 5.05-5.00 (m, 1H, $\text{C}=\underline{\text{C}}\text{H}$), 3.70 (t, 2H, $J = 6.2$ Hz, OCH_2), 2.24 (dt, 2H, $J = 6.2, 6.2$ Hz, $\underline{\text{C}}\text{H}_2\text{CH}=\text{C}$), 1.95 (dt, 2H, $J = 2.8, 7.4$ Hz, $\underline{\text{C}}\text{H}_2\text{C}=\text{C}=\text{C}$), 1.70 (d, 3H, $J = 2.8$ Hz, CH_3), 1.66 (br s, 1H, OH), 1.47-1.28 (m, 14H, 7 CH_2), 0.90 (t, 3H, $J = 6.9$ Hz, CH_3); ^{13}C δ 100.2 (2C), 86.2 (CH), 62.2 (OCH_2), 40.0 (CH_2), 32.6 (CH_2), 31.9 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 29.3 (CH_2), 27.6 (CH_2), 22.7 (CH_2), 19.2 (CH_3), 14.1 (CH_3); IR (ATR): ν 3340 (br), 2923, 2853, 1966, 1717, 1465, 1370, 1047 cm^{-1} ; HRMS: exact mass calculated for $\text{C}_{15}\text{H}_{28}\text{O}$ requires m/z $[\text{M}+\text{H}]^+$: 225.2213, found 225.2215.

3.3.3 Gold(I)-catalysed Hydroalkoxylation of **12**



Complex **3** (5.0 mg, 0.01 mmol) and AgSbF_6 (3.5 mg, 0.01 mmol) were added to a stirred solution of **12** (45 mg, 0.20 mmol) in dry toluene (3 mL) under nitrogen. The mixture was allowed to stir at 20 °C and the reaction was monitored by TLC. After 1 d the mixture was filtered through a plug of silica, the solvent was removed *in vacuo* and the resulting crude product was purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 50/1) to afford 2-methyl-2-nonyl-5,6-dihydro-2H-pyran, **13**, (36 mg, 0.16 mmol, 80%) as a colourless oil. NMR (400 MHz, CDCl_3): ^1H δ 5.81-5.77 (m, 1H, CHC_q), 5.59 (dt, 1H, $J = 2.0, 10.3$ Hz, $\text{CH}=\text{CHC}_q$), 3.81-3.77 (m, 2H, OCH_2), 2.17-2.08 (m, 1H, $\text{C}_{\text{ring}}\text{H}_2$), 2.01-1.93 (m, 1H, $\text{C}_{\text{ring}}\text{H}_2$), 1.53-1.22 (m, 19H, 8 CH_2 , CH_3), 0.90 (t, 3H, $J = 6.9$ Hz, CH_3); ^{13}C δ 134.5 (C), 123.2 (C), 73.7 (C), 59.2 (OCH_2), 40.9 (CH_2), 31.9 (CH_2), 30.2 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 25.1 (CH_2), 25.0 (CH_3), 23.6 (CH_2), 22.7 (CH_2), 14.1 (CH_3); IR (ATR): ν 3029, 2922, 2854, 1653, 1466, 1364, 1211, 1081, 720 cm^{-1} ; HRMS: exact mass calculated for $\text{C}_{15}\text{H}_{28}\text{O}$ requires m/z $[\text{M}]^+$: 224.2135, found 224.2136.

3.4 Gold(I)-catalysed reactions of enyne **14**

3.4.1 Cycloisomerisation

To a solution of enyne **14**¹⁰ (60 mg, 0.25 mmol) in dichloromethane (2.5 mL) was added complex **3** (6 mg, 0.01 mmol) followed by AgSbF_6 (3 mg, 0.01 mmol). The mixture was stirred at 23 °C for 15 minutes until all of the starting material was consumed (monitored by TLC) and then filtered through a plug of silica. After removal of the volatiles *in vacuo*, the crude mixture was purified by flash column chromatography (eluent: hexane/diethyl ether = 8/3) to give a mixture of the two isomers **15** and **16**

(together 25 mg, 0.11 mmol, 42%) in a 2:1 ratio. Spectroscopic analyses were in agreement with those previously reported in literature.¹¹

3.4.2 Methoxycyclisation

To a solution of enyne **14** (60 mg, 0.25 mmol) in 1:1 dichloromethane (1.25 mL) and ethanol (1.25 mL) was added first the precatalyst **3** (6 mg, 0.01 mmol) followed by AgSbF₆ (3 mg, 0.01 mmol). The mixture was allowed to stir at 23 °C with the reaction was monitored by TLC. After 20 h the starting material was completely consumed and the mixture was filtered through a plug of silica. After removal of the volatiles the resulting crude material was purified by flash column chromatography (eluent: hexane/diethyl ether = 8/3) to give compound **17** (66 mg, 0.24 mmol, 98%). Spectroscopic analyses were in agreement with those previously reported in literature.¹¹

4. Selected NMR Spectra and Stacked Plots

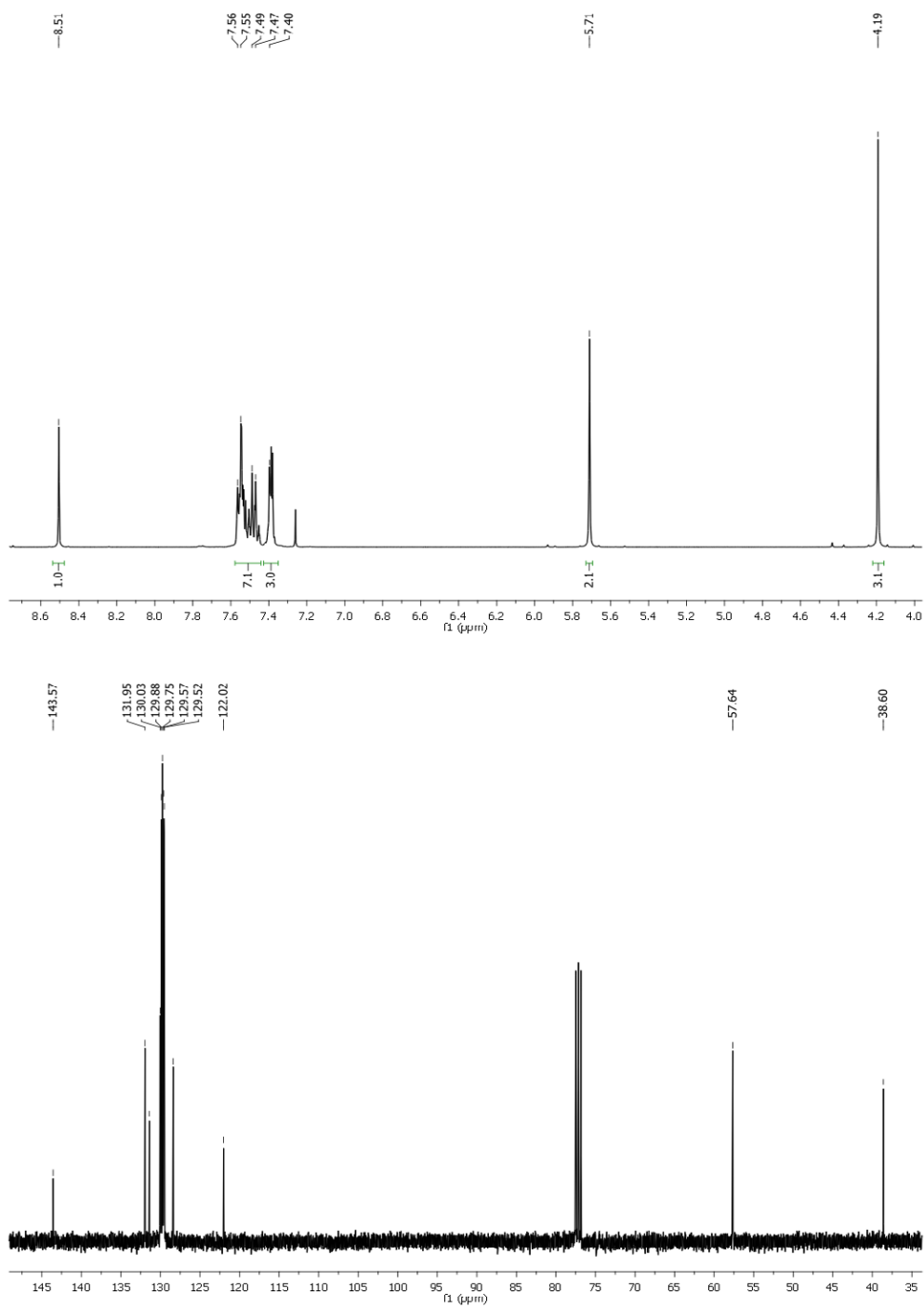


Figure S6: ^1H (top) and ^{13}C (bottom) NMR spectra (CDCl_3) of 2'

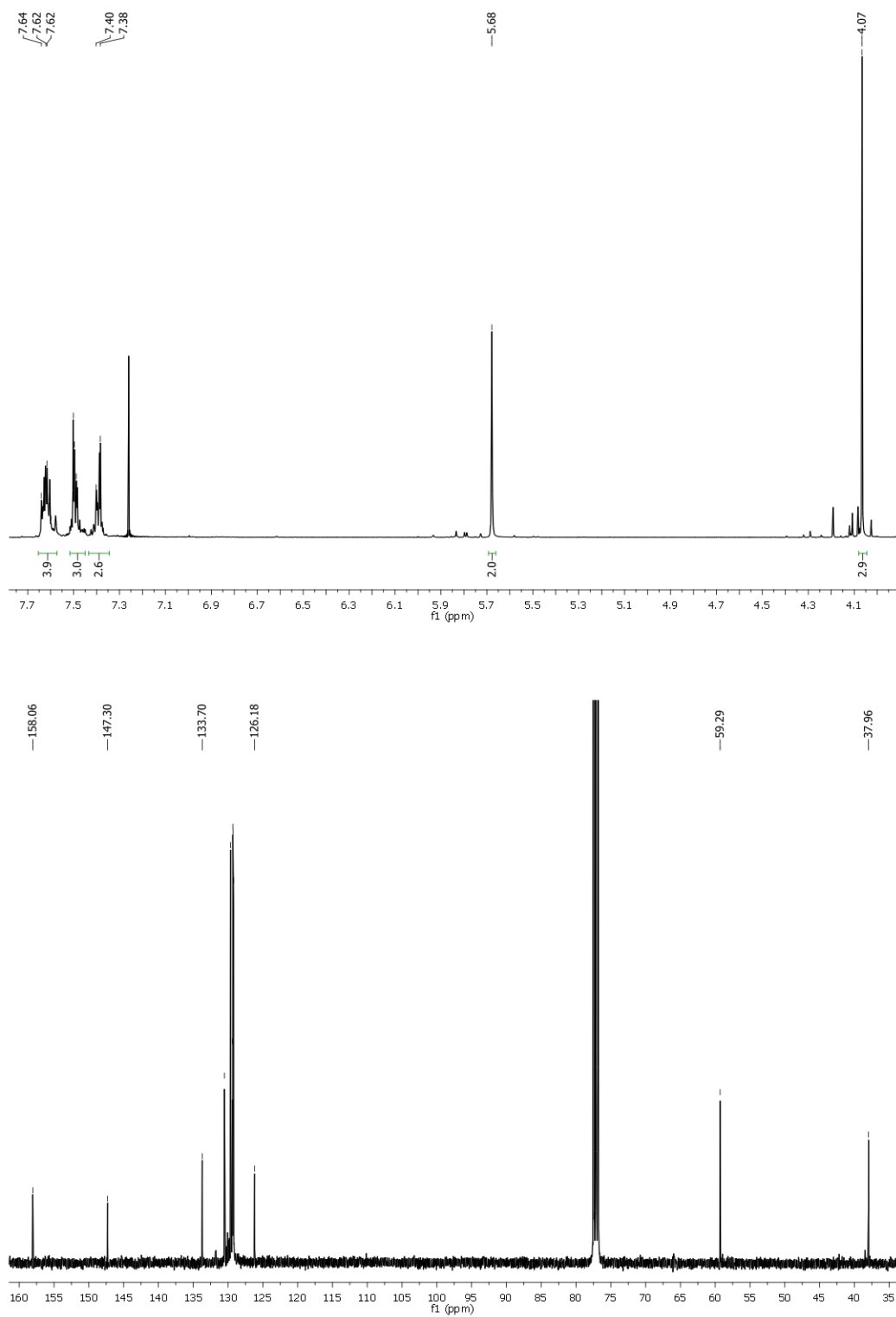


Figure S7: ¹H (top) and ¹³C (bottom) NMR spectra (CDCl₃) of **3**

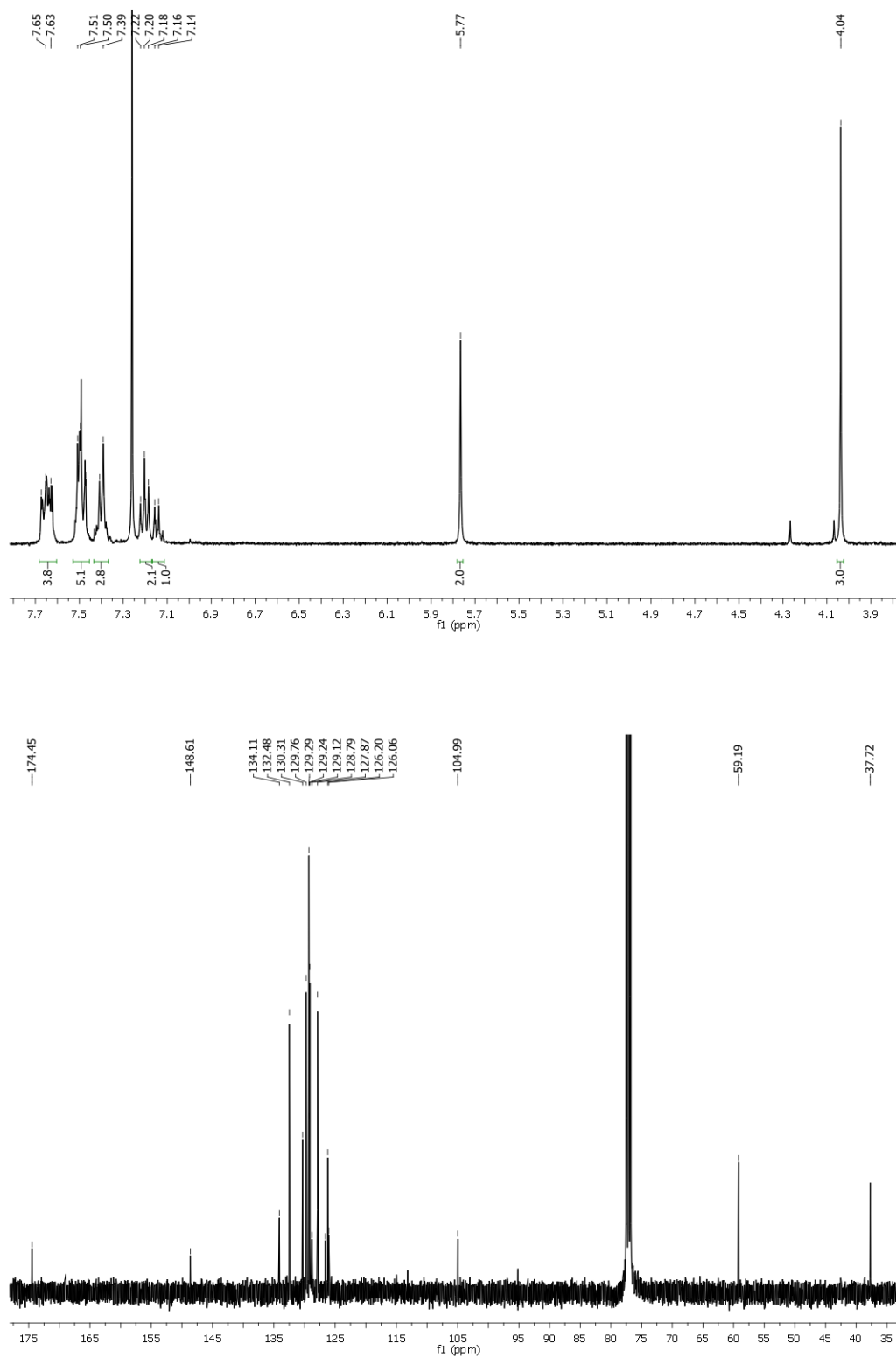


Figure S8: ^1H (top) and ^{13}C (bottom) NMR spectra (CDCl_3) of 4

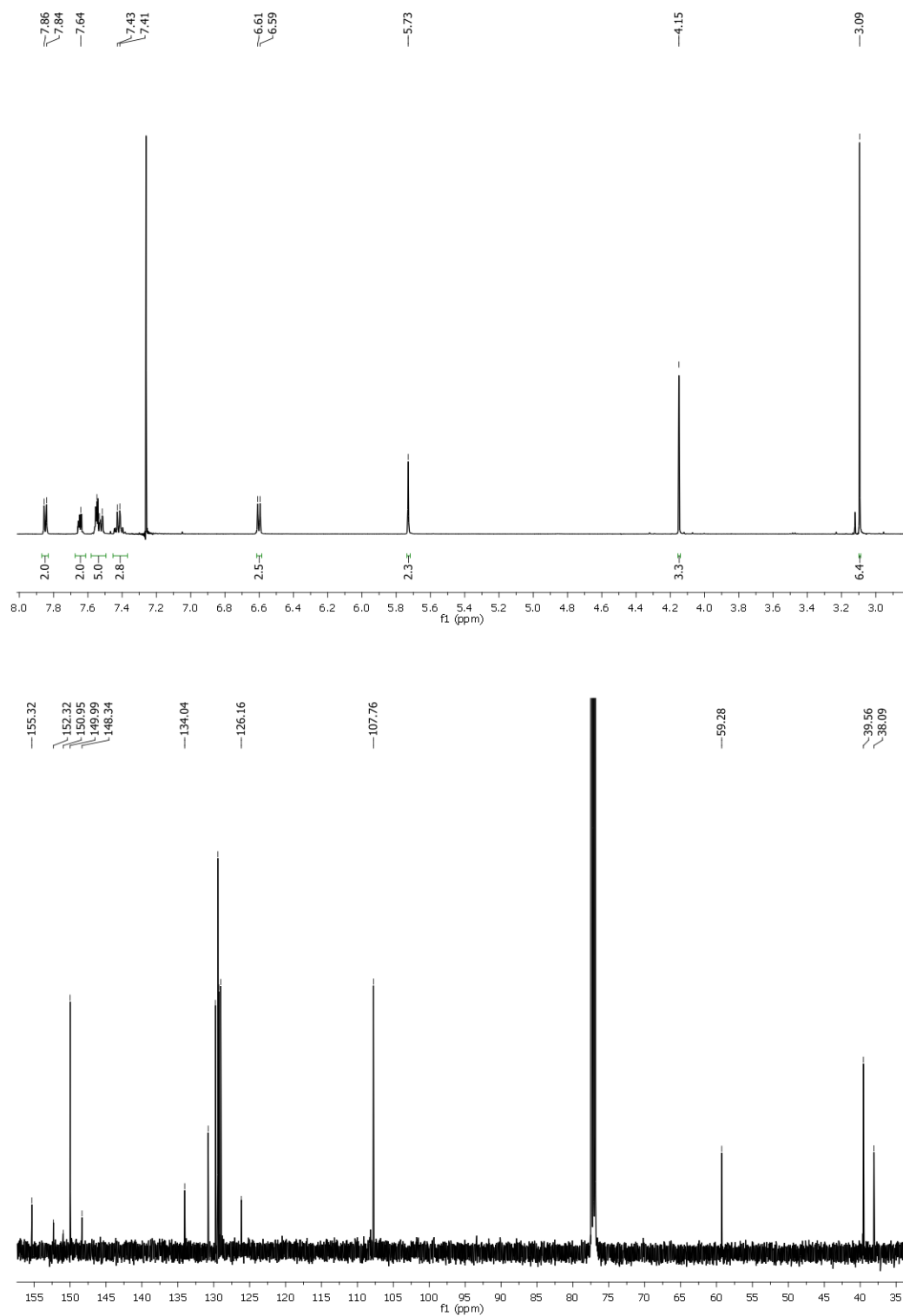


Figure S9: ^1H (top) and ^{13}C (bottom) NMR spectra (CDCl_3) of **5**

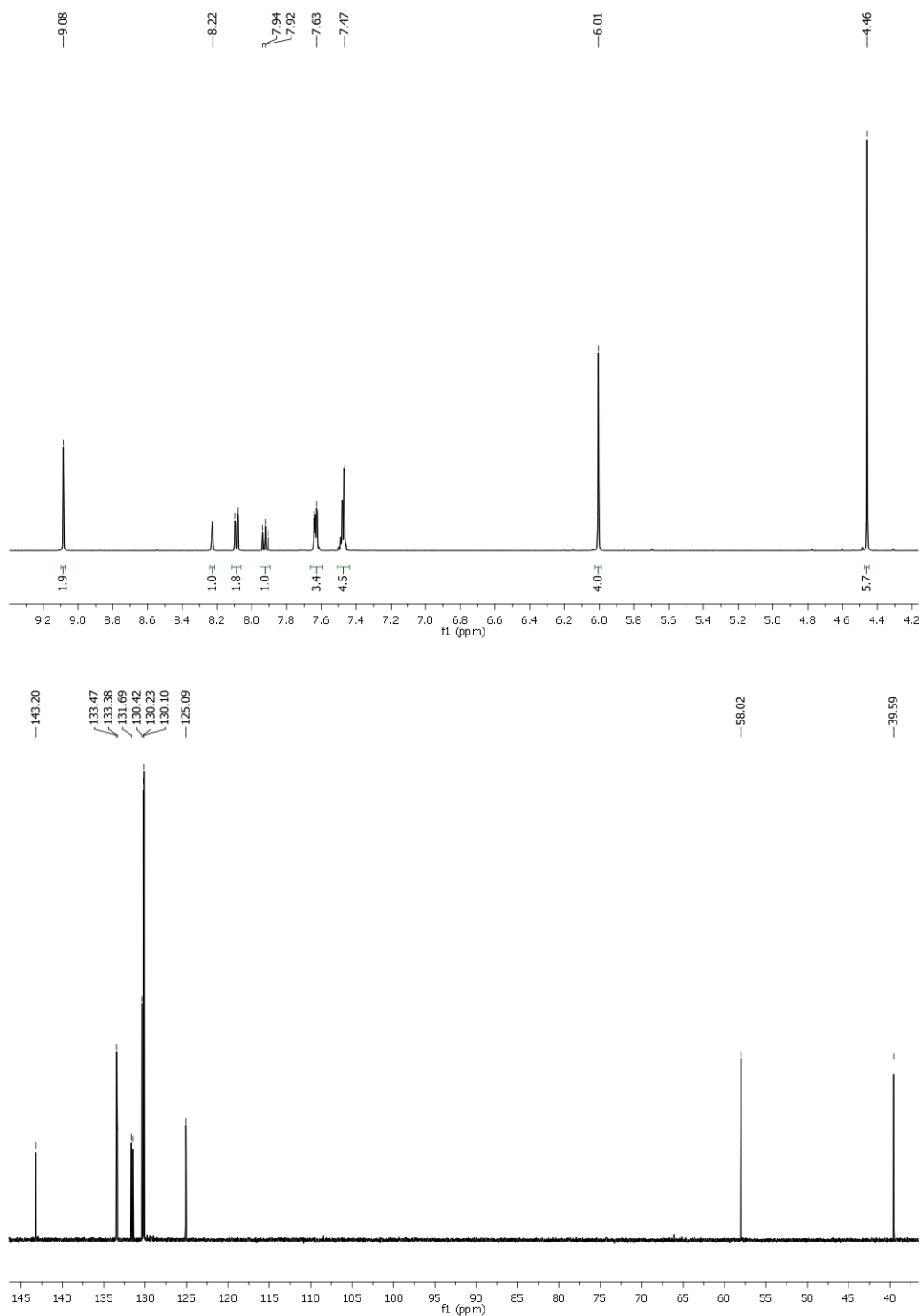


Figure S10: ^1H (top) and ^{13}C (bottom) NMR spectra (CDCl_3) of 7

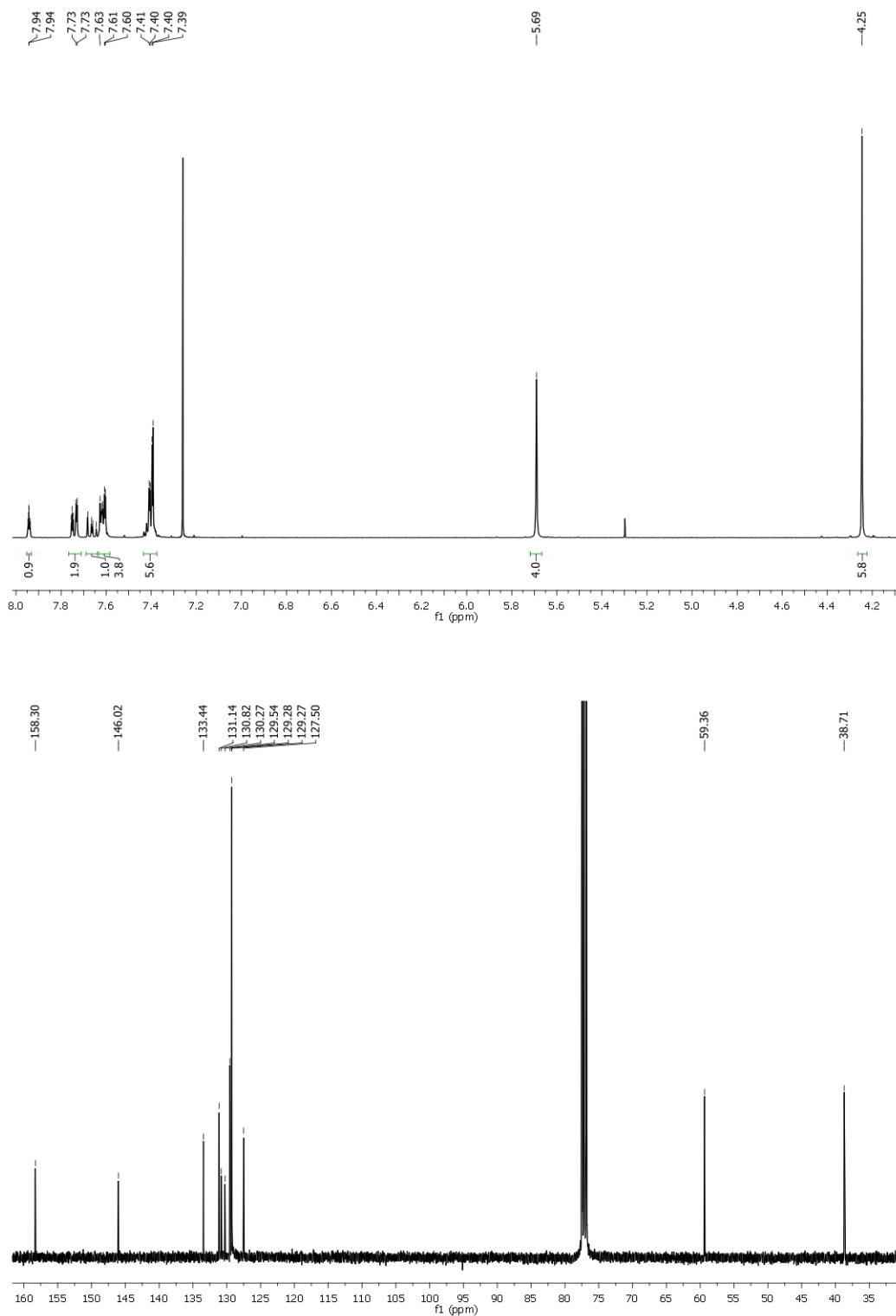


Figure S11: ^1H (top) and ^{13}C (bottom) NMR spectra (CDCl_3) of **8**

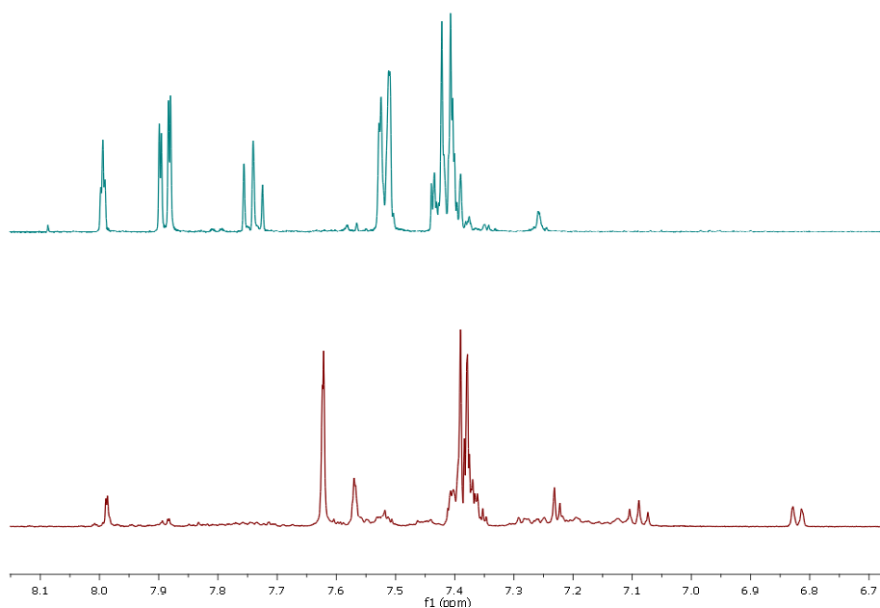


Figure S12: Stacked ¹H NMR (CD₃CN, 500 MHz) spectra the aromatic region of **8** (top) and **9** (bottom). An upfield shift of protons due to face to face π - π stacking can clearly be seen (refer to molecular model, Figure S17). The increased number of signals in **9** is presumably due to hindered rotation which comes about upon formation of the metallomacrocyclic.

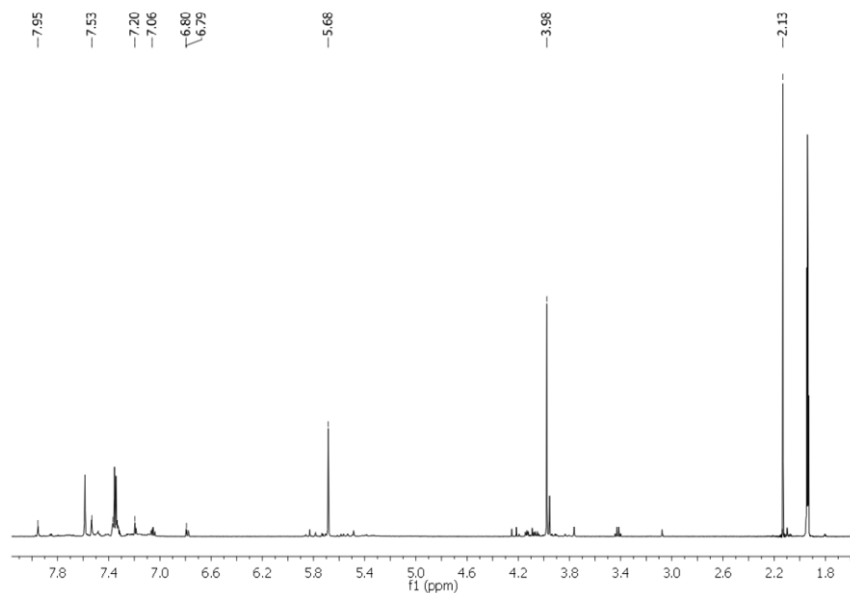


Figure S13: ¹H NMR (CD₃CN, 500 MHz) spectrum of **9** showing presence of water.

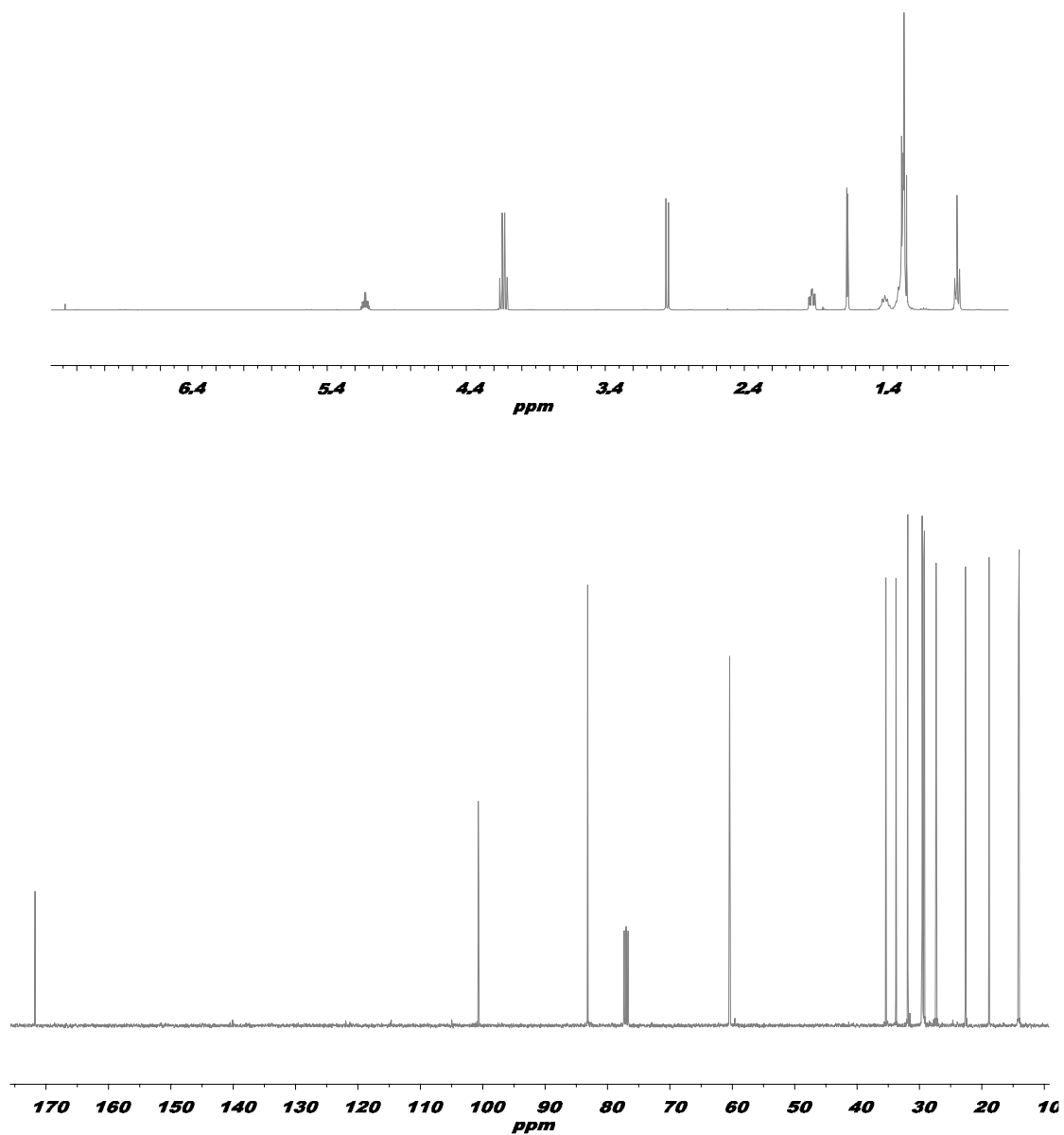


Figure S14: ^1H (top) and ^{13}C (bottom) NMR spectra (CDCl_3) of SI-1

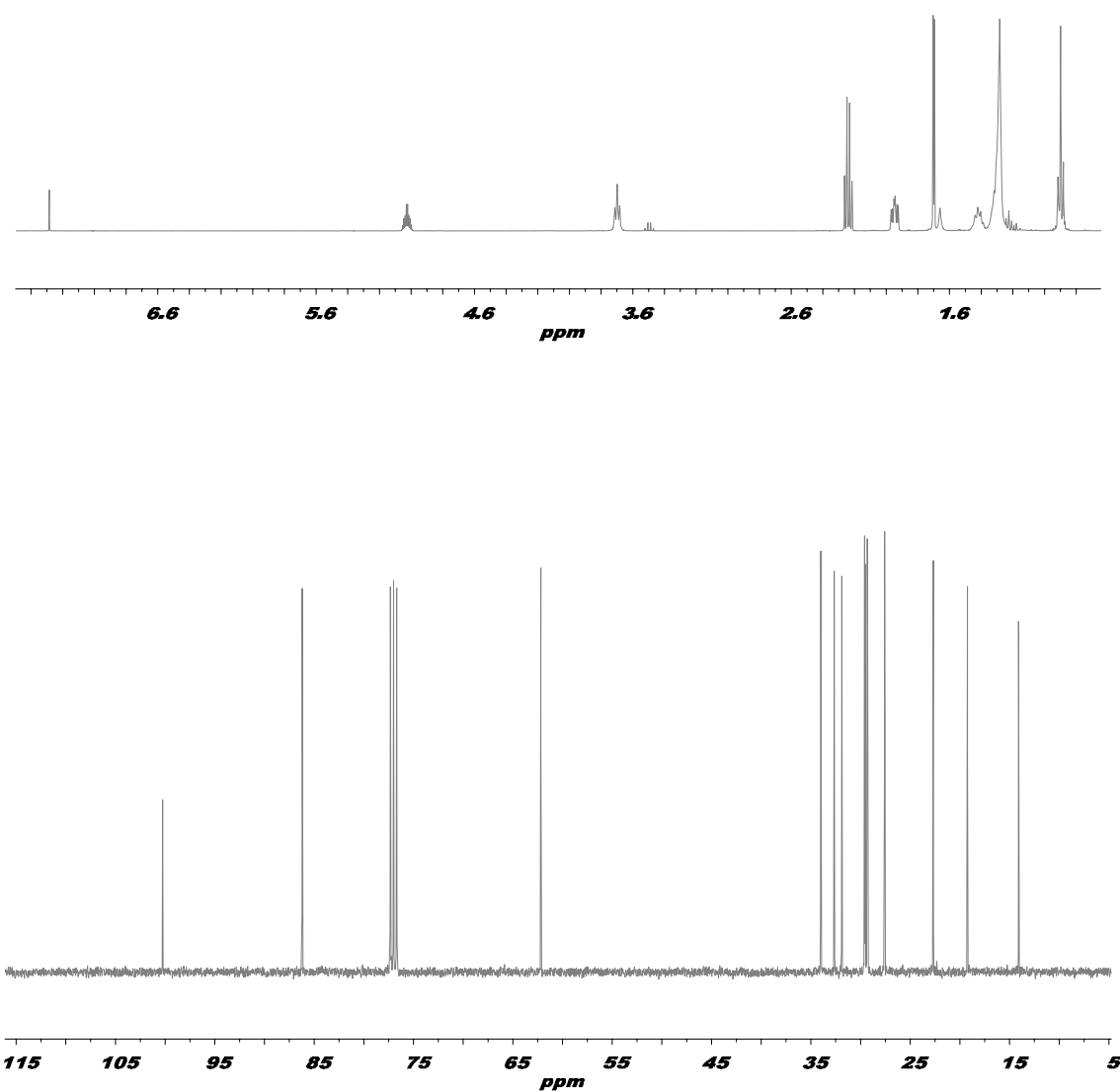


Figure S15: ^1H (top) and ^{13}C (bottom) NMR spectra (CDCl_3) of **13**

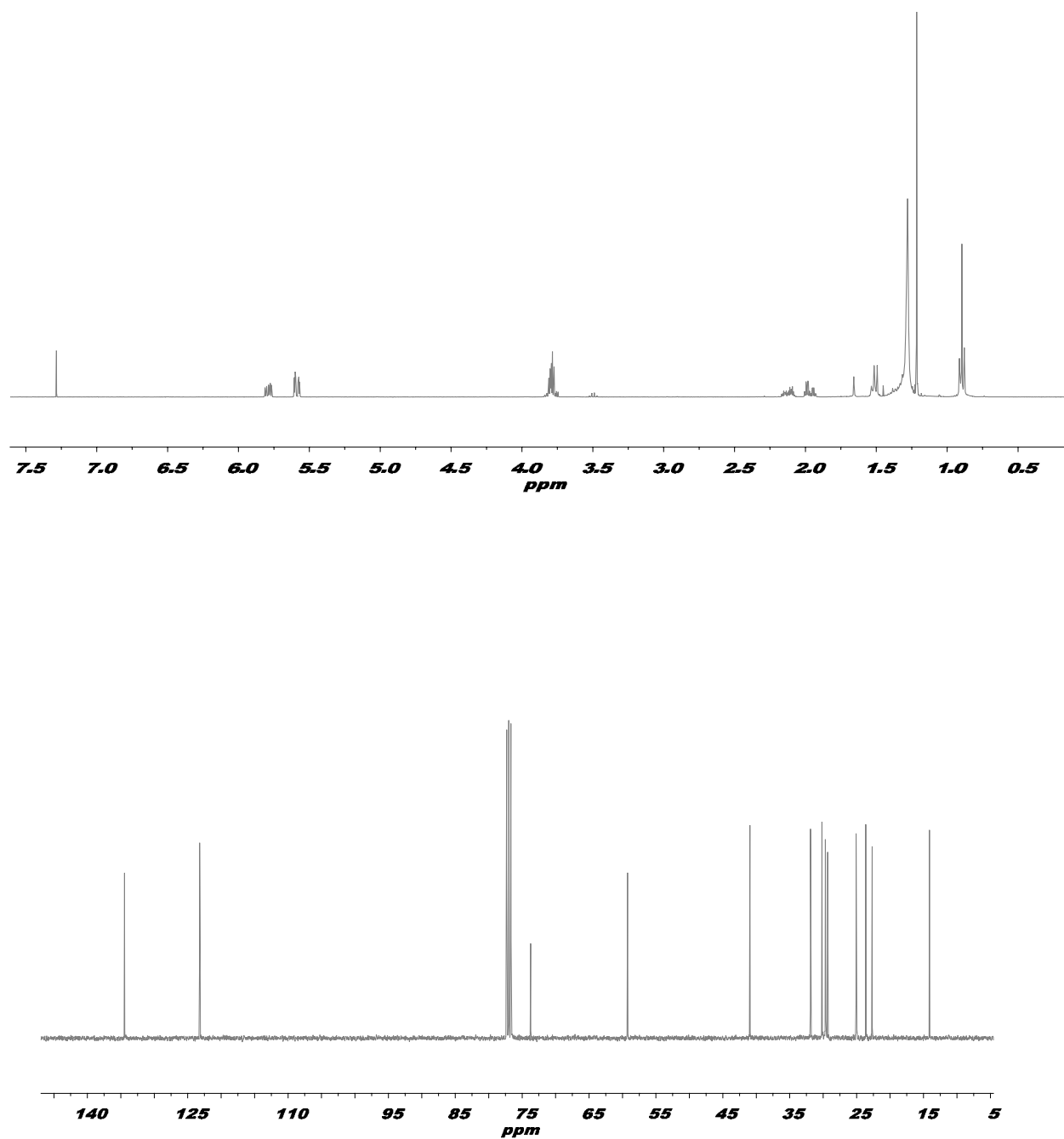


Figure S16: ^1H (top) and ^{13}C (bottom) NMR spectra (CDCl_3) of **14**

5. Selected HR-ESI Mass spectra

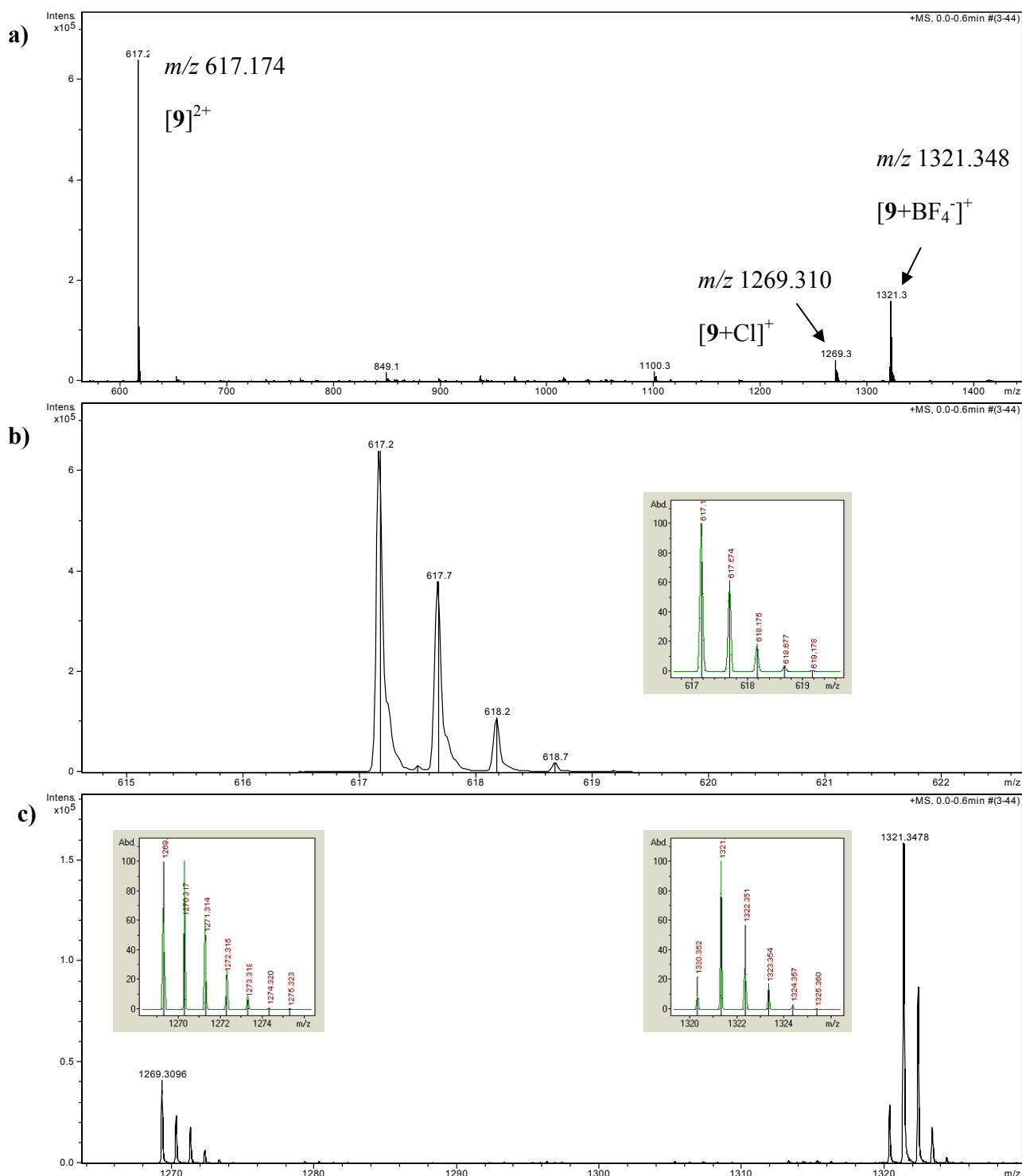


Figure S17: a) Full positive ion HR-ESI Mass Spectrum of **9** (CH₃CN/CH₃OH) with expansions of peaks at b) m/z 617.174 and c) 1269.310 and 1321.348 (insets show calculated isotope patterns).

6. SPARTAN Molecular Models of **9**

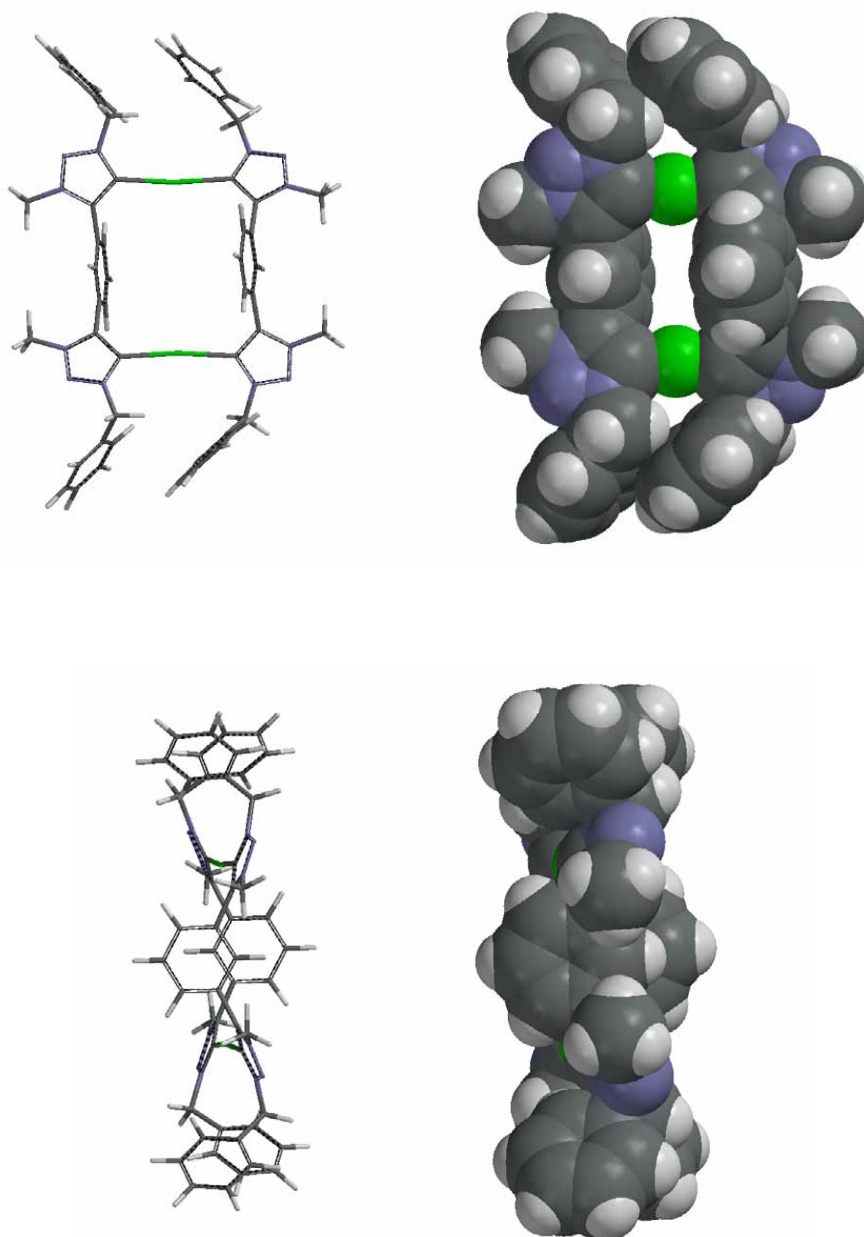


Figure S18. Space Filling (CPK, left) and tube (right) molecular models (MMFF) of the metallomacrocyclic **9**. (Spartan '06 Essential Edition for Windows, Wavefunction, Irvine, CA). Colour scheme: Green = Au, blue = N, grey = C.

7. References

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