Supporting Information

For

A Simple Access to Transition Metal Cyclopropenylidene Complexes

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General considerations

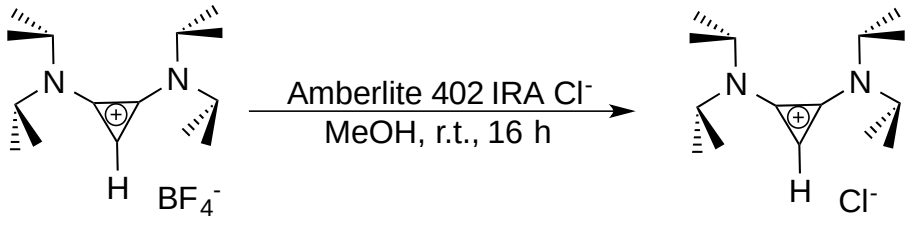
Syntheses of BAC complexes were performed under inert atmosphere using standard Schlenk and glovebox techniques. All other reactions (including catalysis) were carried out in air. Solvents were dispensed from a solvent purification system. All other reagents were used without further purification. Metal precursors such as $[Ir(\mu\text{-}Cl)(cod)]_2$, $[Rh(\mu\text{-}Cl)(CO)_2]_2$ and $[PdCl_2(NCPh)_2]$ were purchased from Alfa Aesar or Sigma-Aldrich and used as received. $[AuCl(SMe_2)]$[1] and [CuCl(SIMes)][2] were synthesised according to published procedures. Microwave-assisted reactions were carried out in a CEM Discover microwave. ^1H and $^{13}C\{^1H\}$ Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker AVANCE 400 Ultrashield spectrometer using the residual solvent peak as reference ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; CD_3CN, δ_H = 1.94 ppm, δ_C = 1.32; 118.26 ppm) at 298K. NMR spectra at 240K were recorded on a Bruker AVANCE 500 or Bruker AVANCE 300. SpectraGas chromatography (GC) analyses were performed on an Agilent 7890A apparatus equipped with a flame ionization detector and a (5%-Phenyl)-methylpolysiloxane column (30 m, 320 µm, film: 0.25 µm). Elemental analyses were carried out by the London Metropolitan University Service. Mass spectroscopy was performed by the EPSRC National Mass Spectrometry Service Centre at Swansea (UK) and by the molecular mass spectrometry facility (MMSF) at the University of California (San Diego, USA).

1. Synthesis of ligand precursors, complexes and azide substrates

1.1 Synthesis of 1·HCl

The cyclopropenium salt **1·HBF$_4$** was synthesised according to a published procedure and ^1H NMR spectra were found similar to reported data.[3]

Bis(diisopropylamino)cyclopropenium chloride, 1·HCl



1·HBF$_4$ **1·HCl**

A flask was charged with the cyclopropenium salt **1·HBF$_4$** (0.5 g, 1.5 mmol), Amberlite 402 IRA Cl^- (5 g) and methanol (50 mL). The reaction was stirred at room temperature for 16

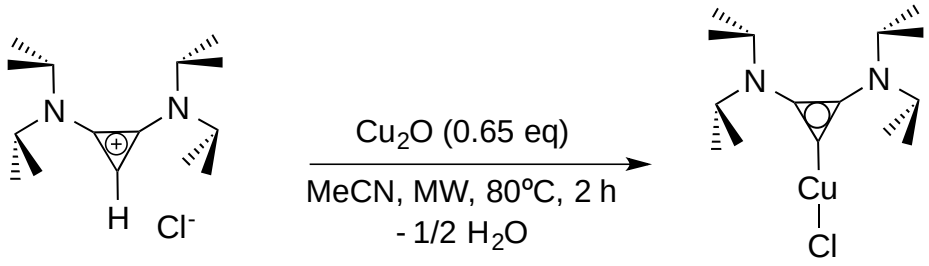
hours. The resin was removed by filtration and washed with dichloromethane (3x20 mL). The supernatant solution was concentrated *in vacuo* to 1 mL. Diethylether (30 mL) was added. **1·HCl** was collected by filtration and obtained as a colourless solid (0.391 g, 1.4 mmol, 93%).

^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 8.97 (s, 1H, CC*H*C); 4.02 (septet, 2H, ^{3}J(H,H) = 7.0 Hz, C*H*-CH_3), 3.91 (septet, 2H, ^{3}J(H,H) = 7.0 Hz, C*H*-CH_3), 1.46 (d, 12H, ^{3}J(H,H) = 7.0 Hz, CH_3-CH), 1.40 (d, 12H, ^{3}J(H,H) = 7.0 Hz, CH_3-CH).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K TMS): δ (ppm) = 133.6 (s, *C*-N), 102.0 (s, C*C*HC), 56.5 (s, *C*H-CH_3), 49.5 (s, *C*H-CH_3), 21.1 (s, *C*H_3-CH), 21.0 (s, *C*H_3-CH).

HRMS Calcd for $(C_{15}H_{29}N_2)^+$ 237.2325; Found 237.2322

1.2. Synthesis of [Cu(Cl)(BAC)], 2



1·HCl **2**

Reaction under MW heating. In a glovebox, a vial was charged with the cyclopropenium salt **1·HCl** (400 mg, 1.46 mmol), Cu_2O (136 mg, 0.95 mmol) and acetonitrile (10 mL). The reaction was heated for 2 hours at 80ºC in a microwave (200W). The reaction mixture was filtered through a pad on Celite and the volatiles were removed *in vacuo*. CH_2Cl_2 (1 mL) and Et_2O (10 mL) were added. The precipitate was collected by filtration and washed with Et_2O (2x10 mL). **2** was obtained as a pale yellow solid (452 mg, 1.34 mmol, 92%).

Reaction using conventional heating. In a glovebox, a Schlenk was charged with the cyclopropenium salt **1·HCl** (400 mg, 1.46 mmol), Cu_2O (136 mg, 0.95 mmol) and toluene (10 mL). The reaction was heated for 24 hours at 110ºC. The reaction mixture was filtered through a pad on Celite and the volatiles were removed *in vacuo*. CH_2Cl_2 (1 mL) and Et_2O (10 mL) were added. The precipitate was collected by filtration and washed with Et_2O (2x10 mL). **2** was obtained as a pale yellow solid (427 mg, 1.27 mmol, 87%).

^{1}H NMR (500 MHz, CD_3CN, 298K): δ (ppm) = 3.86 (br. s, 4H, C*H*-CH_3), 1.47 (br. s, 12H, CH_3-CH), 1.24 (br. s, 12H, CH_3-CH).

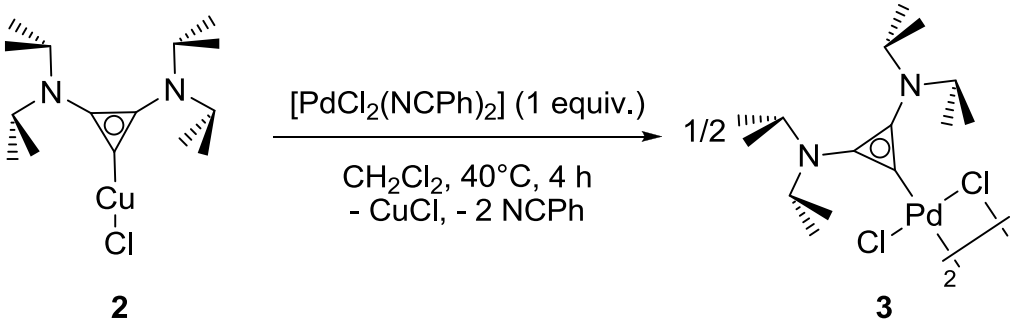
^{13}C-{^{1}H} NMR (125 MHz, CD_3CN, 298K): δ (ppm) = 148.4 (*C*-N), 139.3 ($C_{carbene}$), 56.7 (*C*H-CH_3), 48.8 (*C*H-CH_3), 21.8 (*C*H_3-CH), 21.0 (*C*H_3-CH).

^{1}H NMR (500 MHz, CD_3CN, 240K): δ (ppm) = 3.87-3.77 (m, 4H, C*H*-CH_3), 1.43 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, CH_3-CH), 1.20 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, CH_3-CH).

^{13}C-{^{1}H} NMR (125 MHz, CD_3CN, 240K): δ (ppm) = 147.4 (*C*-N), 137.5 ($C_{carbene}$), 56.7 (*C*HCH$_3$), 47.8 (*C*HCH$_3$), 21.3 (CH*C*H$_3$), 20.4 (CH*C*H$_3$).

Elemental Analysis Calcd (%) for $C_{15}H_{28}ClCuN_2$: C 53.72, H 8.41, N 8.35; found: C 53.62, H 8.30, N 8.26.

1.3. Synthesis of [Pd(μ-Cl)(Cl)(BAC)]$_2$, 3



2 **3**

In a glovebox, a vial was charged with complex **2** (50 mg, 0.150 mmol), [$PdCl_2(NCPh)_2$] (57.2 mg, 0.150 mmol) and dichloromethane (4 mL). The reaction was stirred during 4 hours at 40°C. The reaction mixture was filtered through Celite and the solution was concentrated *in vacuo* (1 mL). Hexane (10 mL) was added and the precipitate was collected by filtration, washed with hexane (3x10 mL) and dried *in vacuo*. The solid was redissolved in acetonitrile (5 mL) and filtered. The solvent was removed *in vacuo* to afford **3** as an orange solid (60 mg, 0.147 mmol, 98%).

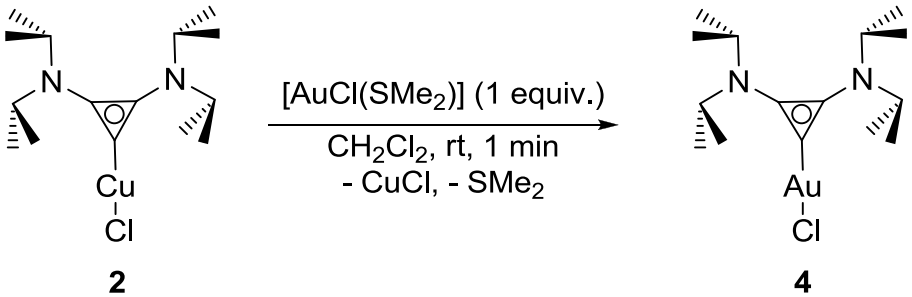
^{1}H NMR (500 MHz, CD_3CN, 240K): δ (ppm) = 3.86-3.76 (m, 4H, C*H*-CH$_3$), 1.62 (d, ^{3}J(H,H) = 6.8 Hz, C*H*$_3$-CH), 1.18 (d, ^{3}J(H,H) = 6.8 Hz, C*H*$_3$-CH).

^{13}C-{^{1}H} NMR (125 MHz, CD_3CN, 240K): δ (ppm) = 148.1 (s, *C*-N), 119.2 (s, $C_{carbene}$), 56.4 (s, *C*H-CH$_3$), 47.7 (s, *C*H-CH$_3$), 22.4 (s, *C*H$_3$-CH), 20.6 (s, *C*H$_3$-CH).

Elemental Analysis Calcd (%) for $C_{30}H_{56}Cl_4N_4Pd2$: C 43.55, H 6.82, N 6.77; found: C 43.47, H 6.93, N 6.68.

These data were found similar to those reported in the literature.[4]

1.4. Synthesis of [Au(Cl)(BAC)], 4



2 **4**

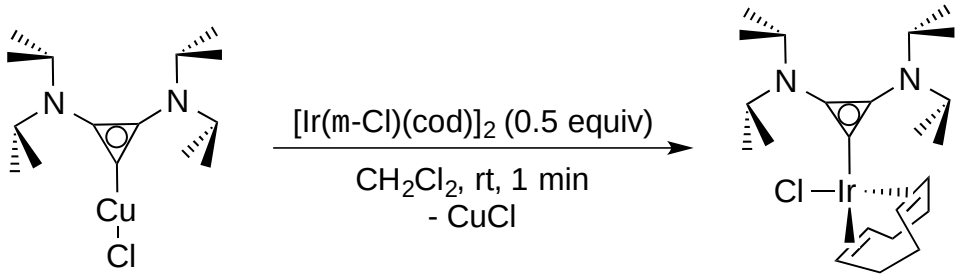
In a glovebox, a vial was charged with **2** (60 mg, 0.180 mmol), [AuCl(SMe_2)] (52.7 mg, 0.180 mmol) and dichloromethane (4 mL). The reaction mixture was stirred during 1 minute at room temperature, filtered through Celite and concentrated *in vacuo* (1 mL). Hexane (10 mL) was added. The precipitate was collected by filtration, washed with hexane (3x10 mL) and dried *in vacuo*. The solid was then redissolved in acetonitrile (5 mL) and the solution was filtered. Removal of the solvent *in vacuo* led to **4** as colourless solid (82 mg, 0.176 mmol, 98%).

^{1}H NMR (500 MHz, CD_3CN, 240K): δ (ppm) = 3.86 (septet, 2H, ^3J(H,H) = 6.8 Hz, C*H*-CH_3), 3.75 (septet, 2H, ^3J(H,H) = 6.8 Hz, C*H*-CH_3), 1.47 (d, ^3J(H,H) = 6.8 Hz, CH_3-CH), 1.21 (d, ^3J(H,H) = 6.8 Hz, CH_3-CH).

^{13}C-{^{1}H} NMR (125 MHz, CD_3CN, 240K): δ (ppm) = 144.6 (s, *C*-N), 130.7 (s, $C_{carbene}$), 56.9 (s, *C*H-CH_3), 47.8 (s, *C*H-CH_3), 21.5 (s, *C*H_3-CH), 20.3 (s, *C*H_3-CH).

Elemental Analysis Calcd (%) for $C_{15}H_{28}AuClN_2$: C 38.43, H 6.02, N 5.98; found: C 38.27, H 6.04, N 5.93.

1.5. Synthesis of [Ir(Cl)(BAC)(1,5-COD)], 5.



2 **5**

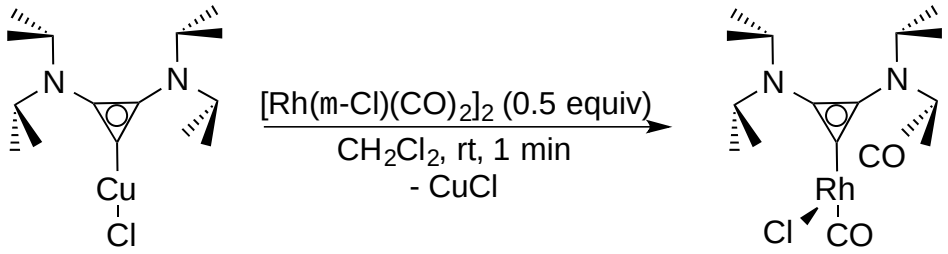
In a glovebox, a vial was charged with **2** (40 mg, 0.120 mmol), [Ir(μ□Cl)(cod)]$_2$ (40 mg, 0.060 mmol) and dichloromethane (4 mL). The reaction was stirred during 1 minute at room temperature. The reaction mixture was filtered through Celite and concentrated *in vacuo* (1 mL). Hexane (10 mL) was added and the precipitate was collected by filtration and washed with hexane (3x10 mL). The solid was redissolved in acetonitrile (5 mL) and the solution was filtered. Removal of the solvent *in vacuo* led to **5** which was obtained as a yellow solid (66 mg, 0.118 mmol, 98%).

^{1}H NMR (500 MHz, CD_3CN, 240K): δ (ppm) = 4.06-4.02 (m, 3H, 2H C*H*-CH_3 and 1H cod), 3.88-3.81 (m, 2H, C*H*-CH_3), 3.06-3.04 (m, 2H, cod), 2.11-2.08 (m, 4H, cod), 1.61-1.13 (m, 29H, CH_3-CH and cod).

^{13}C-{^{1}H} NMR (125 MHz, CD_3CN, 240K): δ (ppm) = 147.3 (s, $C_{carbene}$), 102.7 (s, *C*H cod), 102.5 (s, *C*-N), 78.8 (s, *C*H-CH_3), 52.5 (s, *C*H-CH_3), 33.3 (s, *C*H_2 cod), 29.9 (s, *C*H_2 cod), 21.5 (bs, *C*H_3-CH), 21.0 (s, *C*H_3-CH).

Elemental Analysis Calcd (%) for $C_{23}H_{40}ClIrN_2$: C 48.27, H 7.05, N 4.90; found: C 48.15, H 7.11, N 4.95.

1.6. Synthesis of complex [Rh(Cl)(BAC)(CO)$_2$], 6.



2 **6**

In a glovebox, a vial was charged with **2** (50 mg, 0.150 mmol), [Rh(μ-Cl)(CO)$_2$]$_2$ (29 mg, 0.075 mmol) and dichloromethane (4 mL). The reaction mixture was stirred during 1 minute at room temperature. The solution was filtered through Celite and concentrated *in vacuo* (1 mL). Hexane (10 mL) was added and the solid was collected by filtration and washed with hexane (3x10 mL). The product was redissolved in acetonitrile (5 mL) and the solution was filtered. The solvent was removed *in vacuo*, leading to **6** as a yellow solid (52 mg, 0.122 mmol, 81%).

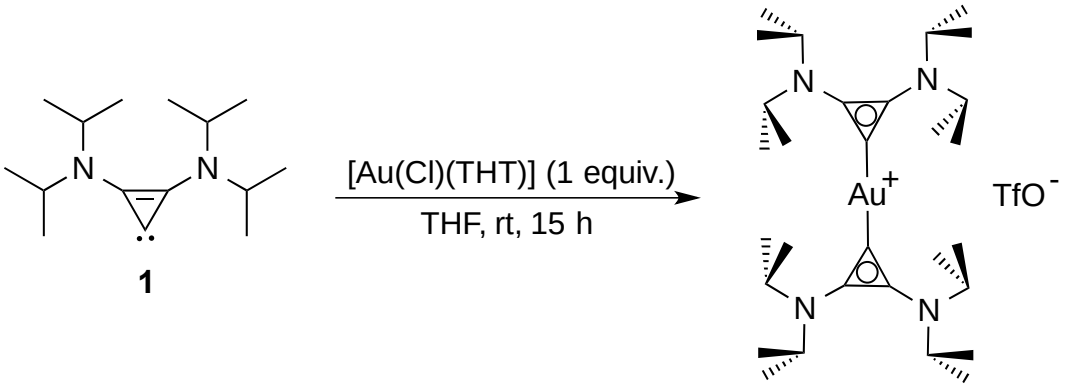
^{1}H NMR (500 MHz, CD$_3$CN, 240K): δ (ppm) = 3.88-3.80 (m, 4H, C*H*-CH$_3$), 1.50 (d, ^3J(H,H) = 6.7 Hz, C*H*$_3$-CH), 1.21 (d, ^3J(H,H) = 6.7 Hz, C*H*$_3$-CH).

^{13}C-{^{1}H} NMR (125 MHz, CD$_3$CN, 240K): δ (ppm) = 186.7 (d, ^1J(Rh,C) = 54.1 Hz, CO), 183.8 (d, ^1J(Rh,C) = 75.3 Hz, CO), 149.4 (s, *C*-N), 137.8 (d, ^1J(Rh,C) = 43.3 Hz, $C_{carbene}$), 56.5 (s, *C*H-CH$_3$), 47.8 (s, *C*H-CH$_3$), 22.3 (s, *C*H$_3$-CH), 20.6 (s, *C*H$_3$-CH).

Elemental Analysis Calcd (%) for $C_{17}H_{30}ClN_2O_2Rh$: C 47.18, H 6.99, N 6.47; found: C 47.22, H 7.14, N 6.51.

These data were found similar to those reported in the literature.[5]

1.7. Synthesis of $[Au(BAC)_2][OTf]$



A THF (10 mL) solution of carbene BAC **1**[6] (236 mg, 1.00 mmol) was added at -78°C to a suspension of [AuCl(THT)] (321 mg, 1.00 mmol) in THF (10 mL). The mixture was stirred at room temperature for 15 hours. After evaporation of the solvent and volatiles, the solid was washed with diethyl ether (3 x 20 mL). The white solid was added to a suspension of lithium trifluoromethanesulfonate (234 mg, 1.50 mmol) in dichloromethane (20 mL) and stirred at room temperature for 3 hours. After filtration through a pad of Celite, and evaporation of volatiles, the solid was washed with diethyl ether and dried under vacuum. The complex was isolated as a white powder (390 mg, 0.48 mmol, 48%) (based on [AuCl(THT)]).

Single crystals were obtained by vapor diffusion of diethyl ether into a saturated methylene chloride solution.

M.P.: 212 °C.

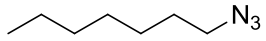
^{1}H NMR (300 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 3.78 (septet, 2H, ^{3}J(H,H) = 7.0 Hz, C*H*-CH_3), 3.68 (septet, 2 H, ^{3}J(H,H) = 7.0 Hz, C*H*-CH_3), 1.49 (d, 12H, ^{3}J(H,H) = 7.0 Hz, CH_3-CH), 1.26 (d, 12 H, ^{3}J(H,H) = 7.0 Hz, CH_3-CH).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K TMS): δ (ppm) = 149.42 (s, $C_{carbene}$), 145.77 (s, *C*-N), 56.25 (s, *C*H-CH_3), 48.31 (s, *C*H-CH_3), 21.53 (s, *C*H_3-CH), 21.18 (s, *C*H_3-CH).

HRMS Calcd. for $C_{30}H_{56}AuN_4^+$: 669.4165; found 669.4173.

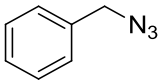
1.8. Synthesis of azide substrates.[7]

1-Azidoheptane



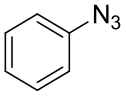
^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ = 3.26 (d, ^3J(H,H) = 7.05 Hz, 2H; CH_2CH$_2$N$_3$), 1.66-1.54 (m, 2H; CH_2CH$_2$N$_3$), 1.42-1.22 (m, 8H; CH_2CH_2CH_2CH_2CH$_3$), 0.89 (t, ^3J(H,H) = 6.7 Hz, 2H; CH$_2$CH_3).

Benzyl azide



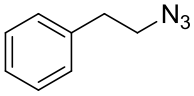
^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.27-7.44 (m, 5H, CH_{Ar}), 4.33 (s, 2H, CH_2).

Phenylazide



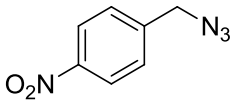
^{1}H NMR (400 MHz, DMSO, 298K): δ (ppm) = 7.41 (m, 2H, CH_{Ar}), 7.19 (m, 1H, CH_{Ar}), 7.11 (m, 2H, CH_{Ar}).

2-(Azidoethyl)benzene



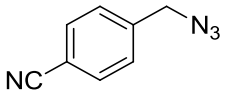
^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.35-7.19 (m, 5H, CH_{Ar}), 3.51 (t, ^3J(H,H) = 7.2 Hz, 2H, CH$_2$CH_2N$_3$), 2.90 (t, ^3J(H,H) = 7.2 Hz, 2H, CH_2CH$_2$N$_3$).

1-(azidomethyl)-4-nitrobenzene



^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 8.25 (d, ^3J(H,H) = 8.6 Hz, 2H, CH_{Ar}), 7.50 (d, ^3J(H,H) = 8.6 Hz, 2H, CH_{Ar}), 4.51 (s, 2H, CH_2N$_3$).

4-(Azidomethyl)benzonitrile

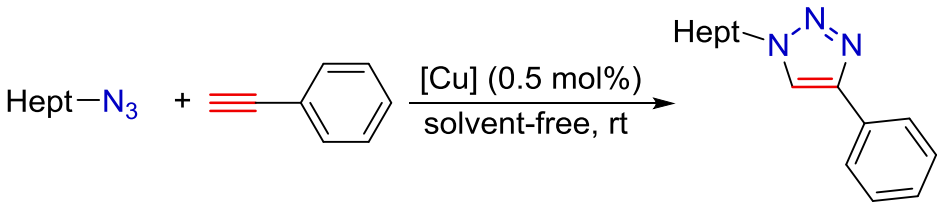


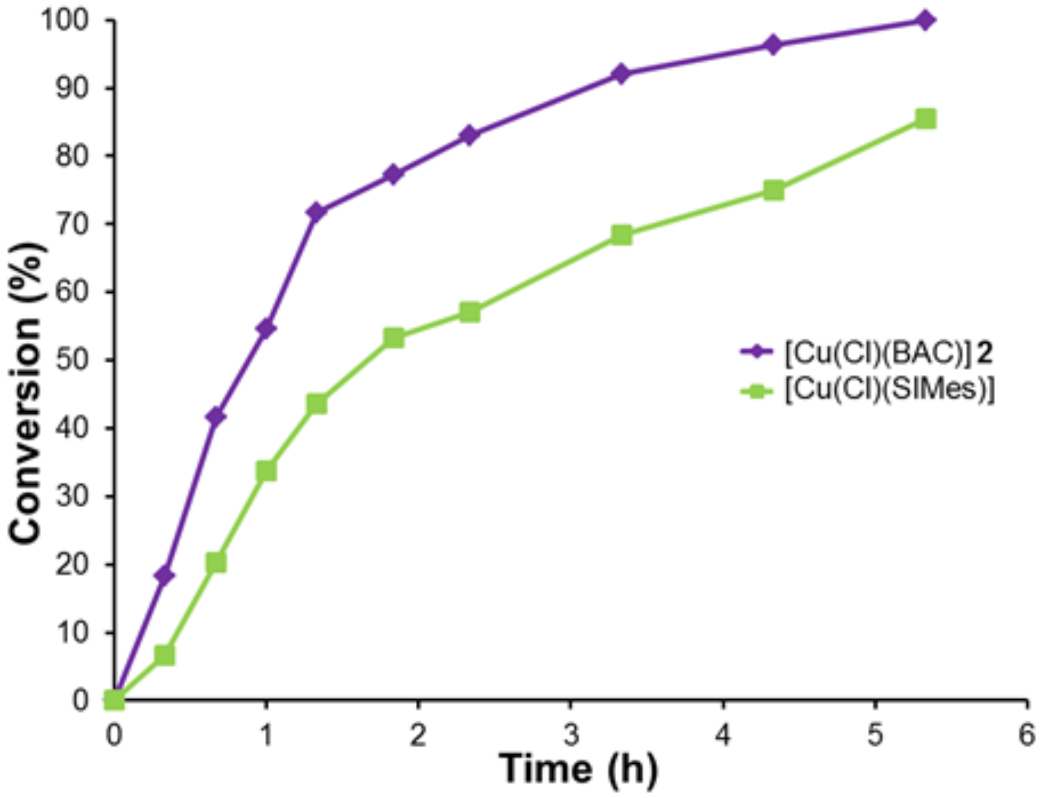
^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.68 (d, ^{3}J(H,H) = 8.5 Hz, 2H, CH_{Ar}), 7.44 (d, ^{3}J(H,H) = 8.5 Hz, 2H, CH_{Ar}), 4.45 (s, 2H, CH_2N_3).

2. Procedure for Catalysis

2.1 kinetic

A vial was charged with the azide (1.00 equiv., 1.00 mmol), alkyne (1.05 equiv., 1.10 mmol) and the appropriate catalyst (0.5 mol %). The reaction mixture was stirred at 25°C in neat conditions. An aliquot was taken at 20 minutes, 40 minutes, 60 minutes, 80 minutes, 110 minutes, 140 minutes, 200 minutes, 260 minutes, 320 minutes and then subjected to GC analysis to determine the conversion.



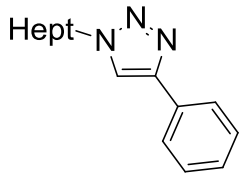


2.2 Catalysis

General procedure. A vial was charged with the azide (1.00 equiv., 1.00 mmol), alkyne (1.05 equiv., 1.10 mmol) and [Cu(Cl)BAC] (0.5 mol %). The reaction mixture was stirred at 25°C in neat conditions.

1-Heptyl-4-phenyl-1H-1,2,3-triazole[7]

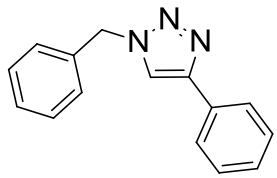
The general procedure yielded, 467 mg (96%) of the title compound as a colourless solid.



^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ = 7.85-7.82 (m, 2H, C*H*$_{Ar}$), 7.74 (s, 1H, NC*H*), 7.42 (t, ^3J(H,H) = 7.4 Hz, 2H, C*H*$_{Ar}$), 7.35-7.30 (m, 1H, C*H*$_{Ar}$), 4.39 (t, ^3J(H,H) = 7.1 Hz, 2H, NC*H*$_2$CH$_2$), 1.98-1.90 (m, 2H, NCH$_2$C*H*$_2$), 1.37-1.24 (m, 8H, C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.88 (t, ^3J(H,H) = 7.1 Hz, 3H, C*H*$_3$CH$_2$).

1-Benzyl-4-phenyl-1H-1,2,3-triazole[7]

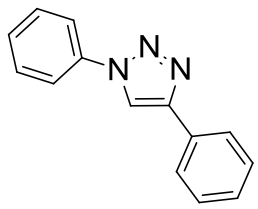
The general procedure yielded, 456 mg (97%) of the title compound as a colourless solid.



^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ= 7.80 (d, ^3J(H,H) = 7.3Hz, 2H, C*H*$_{Ar}$), 7.66 (s, 1H, C*H*), 7.42-7.36 (m, 5H, C*H*$_{Ar}$), 7.34-7.29 (m, 3H, C*H*$_{Ar}$), 5.58 (s, 2H, NC*H*$_2$).

1,4-Diphenyl-1H-1,2,3-triazole[7]

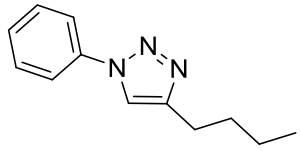
The general procedure yielded, 425 mg (96%) of the title compound as a yellow solid.



^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ = 8.20 (s, 1H, C*H*), 7.94-7.91 (m, 2H, C*H*$_{Ar}$), 7.83-7.79 (m, 2H, C*H*$_{Ar}$), 7.58-7.53 (m, 2H, C*H*$_{Ar}$), 7.49-7.45 (m, 3H, C*H*$_{Ar}$), 7.40-7.35 (m, 1H, C*H*$_{Ar}$).

4-butyl-1-phenyl-1H-1,2,3-triazole[8]

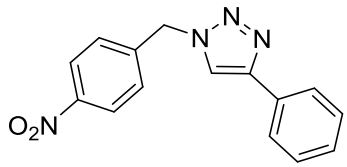
The general procedure yielded, 386 mg (96%) of the title compound as a yellow oil.



^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ = 7.74-7.70 (m, 3H, C*H* and CH_{Ar}), 7.51 (t, 2H, ^3J(H,H) = 7.8 Hz, CH_{Ar}),), 7.41 (t, 1H, ^3J(H,H) = 7.8 Hz, CH_{Ar}), 2.80 (t, ^3J(H,H) = 7.5 Hz, 2H, CH_2), 1.72 (quint, ^3J(H,H) = 7.5 Hz, 2H, CH_2), 1.43 (sextet, ^3J(H,H) = 7.5 Hz, 2H, CH_2), 0.96 (t, ^3J(H,H) = 7.5 Hz, 3H, CH_3).

1-(4-nitrobenzyl)-4-phenyl-1H-1,2,3-triazole[9]

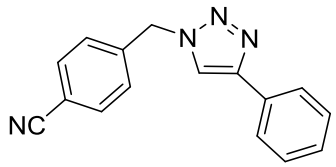
The general procedure yielded, 544 mg (97%) of the title compound as a yellow solid.



^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ= 8.24 (d, ^3J(H,H) = 8.2 Hz, 2H, CH_{Ar}), 7.81 (d, ^3J(H,H) = 8.2 Hz, 2H, CH_{Ar}), 7.75 (s, 1H, C*H*), 7.46-7.40 (m, 4H, CH_{Ar}), 7.37-7.32 (m, 1H, CH_{Ar}), 5.70 (s, 2H, NCH_2).

4-((4-phenyl-1H-1,2,3-triazol-1-yl)methyl)benzonitrile[10]

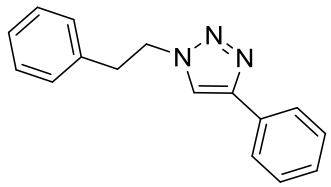
The general procedure yielded, 500 mg (96%) of the title compound as a colourless solid.



^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ= 7.81 (d, ^3J(H,H) = 8.0 Hz, 2H, CH_{Ar}), 7.73 (s, 1H, C*H*), 7.67 (d, ^3J(H,H) = 8.0 Hz, 2H, CH_{Ar}), 7.44-7.32 (m, 5H, CH_{Ar}), 5.65 (s, 2H, NCH_2).

1-phenethyl-4-phenyl-1H-1,2,3-triazole[9]

The general procedure yielded, 424 mg (85%) of the title compound as a colourless solid.

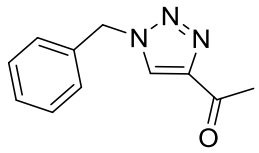


^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ = 7.76 (d, ^3J(H,H) = 7.7 Hz, 2H, CH_{Ar}), 7.46 (s, 1H, N-C*H*), 7.41 (t, ^3J(H,H) = 7.7 Hz, 2H, CH_{Ar}), 7.34-7.26 (m, 4H, CH_{Ar}), 7.14 (d,

^{3}J(H,H) = 7.7 Hz, 2H, CH_{Ar}), 4.64 (t, ^{3}J(H,H) = 7.5 Hz, 2H, CH_2), 3.26 (t, ^{3}J(H,H) = 7.5 Hz, 2H, CH_2).

1-(1-benzyl-1H-1,2,3-triazol-4-yl)ethan-1-one[11]

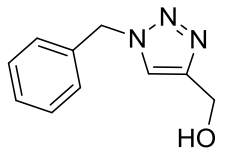
The general procedure yielded, 390 mg (97%) of the title compound as a brownish solid.



^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ= 7.94 (s, 1H, C*H*), 7.41-7.37 (m, 3H, CH_{Ar}), 7.30-7.27 (m, 2H, CH_{Ar}), 5.56 (s, 2H, NCH_2), 2.67 (s, 3H, CH_3).

(1-benzyl-1H-1,2,3-triazol-4-yl)methanol[9]

The general procedure yielded, 363 mg (96%) of the title compound as a yellowish solid.

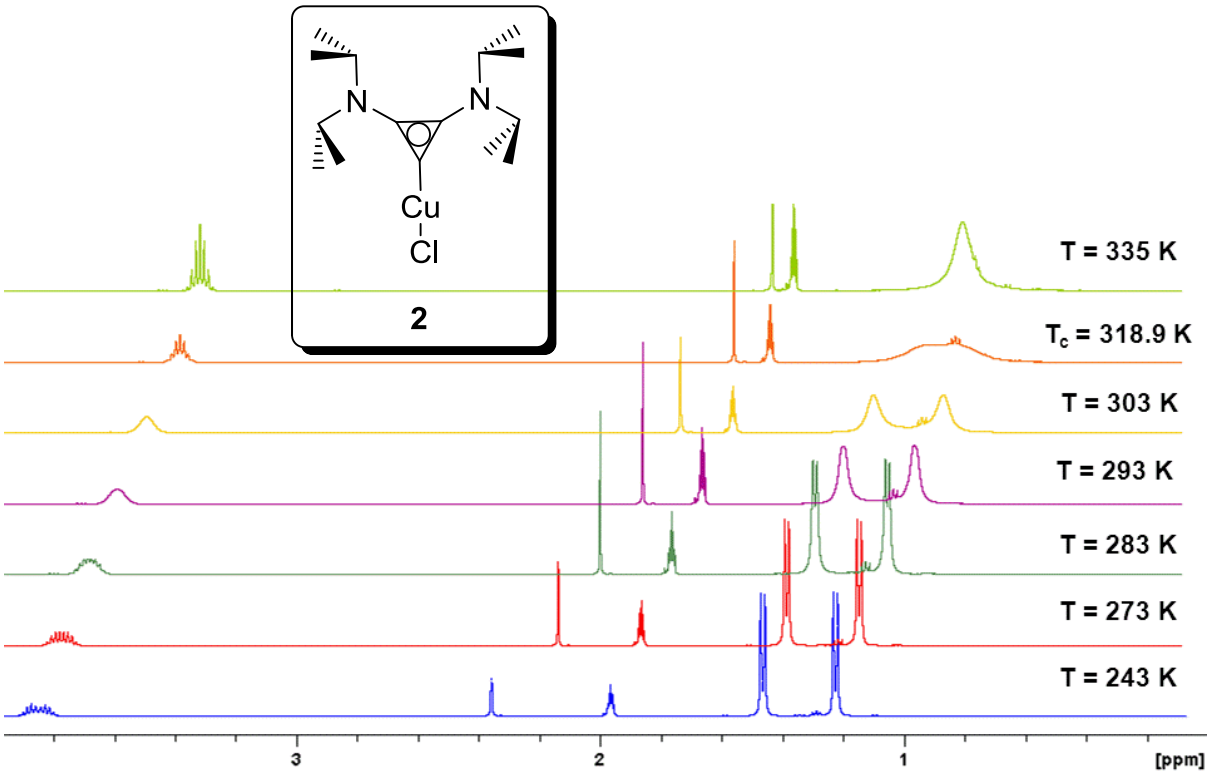


^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ= 7.46 (s, 1H, C*H*), 7.39-7.33 (m, 3H, CH_{Ar}), 7.27-7.24 (m, 2H, CH_{Ar}), 5.49 (s, 2H, NCH_2), 4.74 (broad s, 2H, CH_2), 3.22 (broad s, 1H, O*H*).

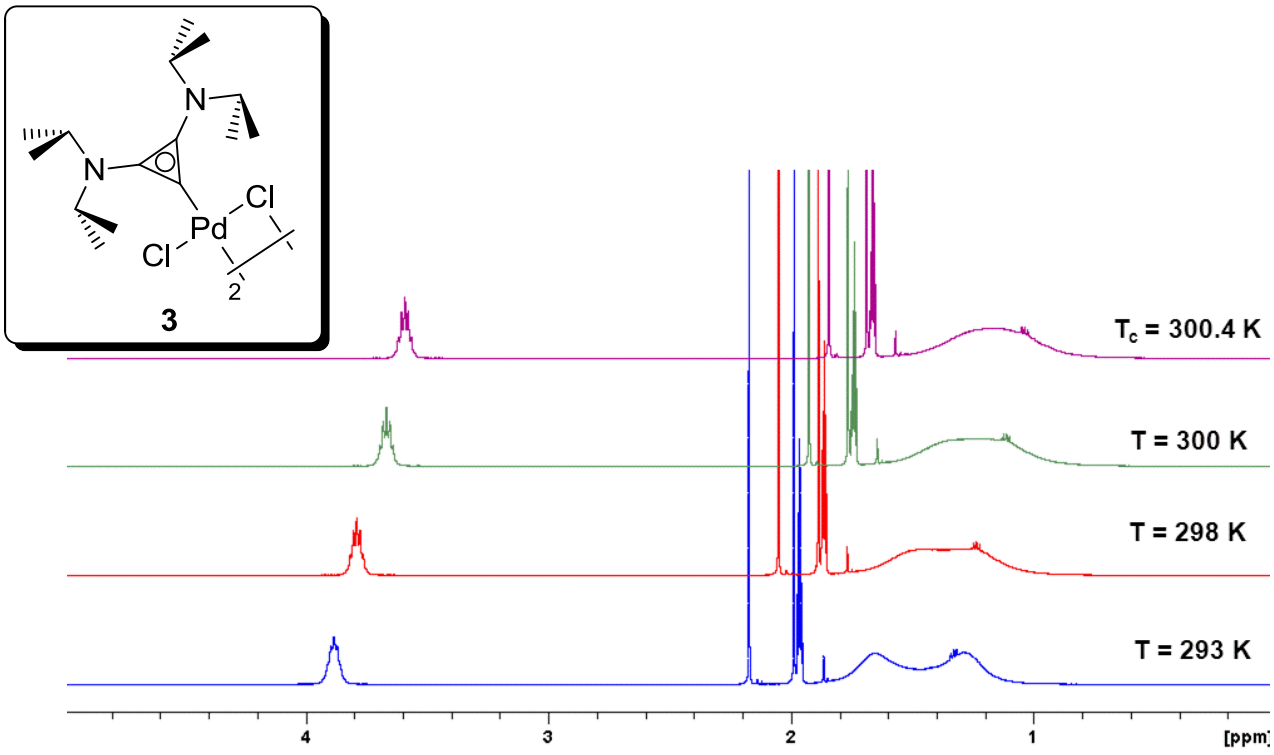
3. NMR Experiments

3.1. VT studies

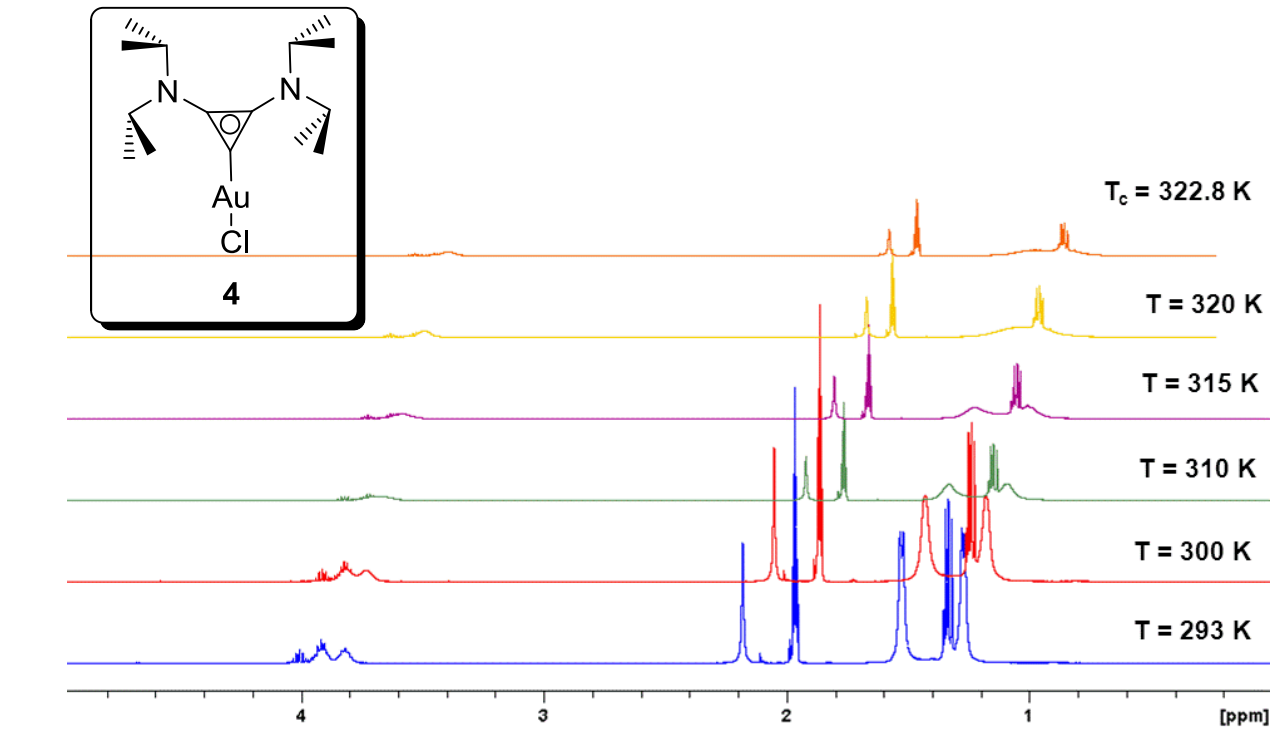
VT NMR of complex **2** (500 MHz, CD_3CN)



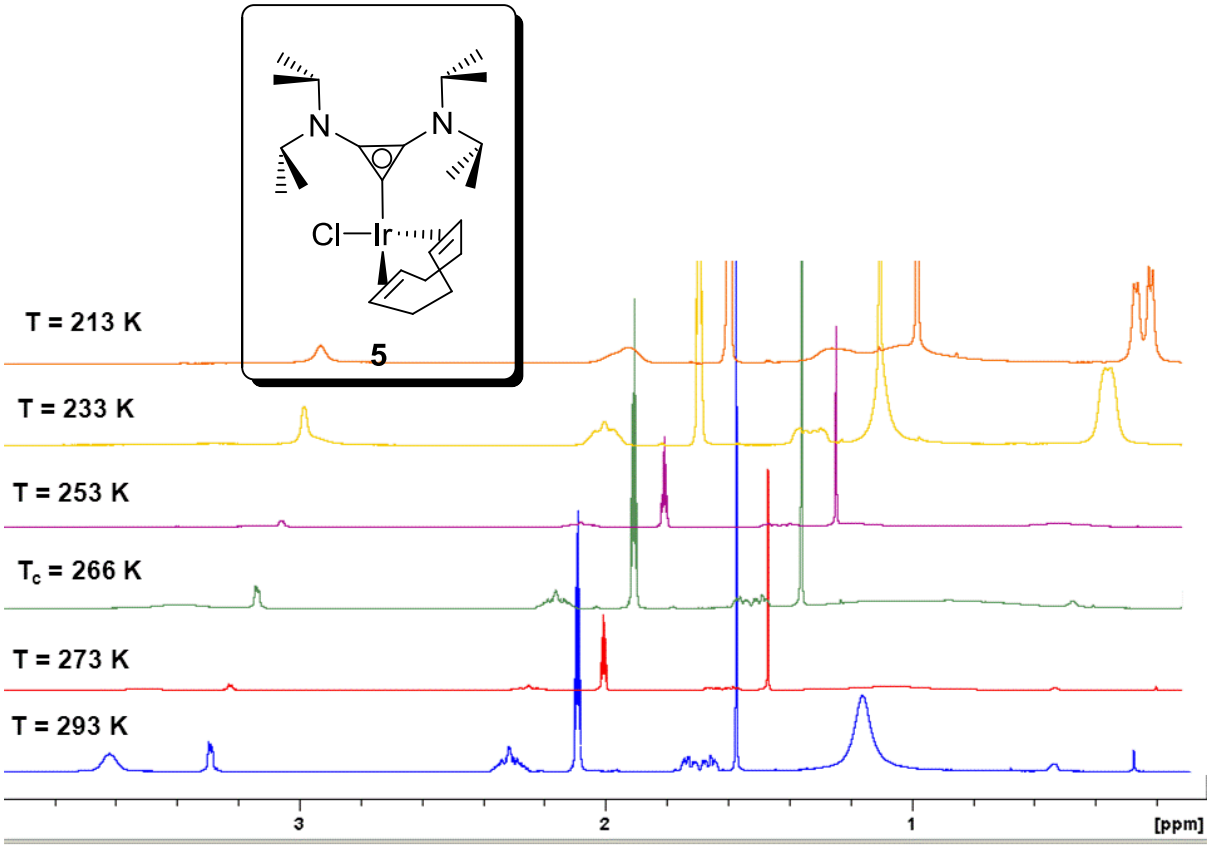
VT NMR of complex **3** (500 MHz, CD_3CN)



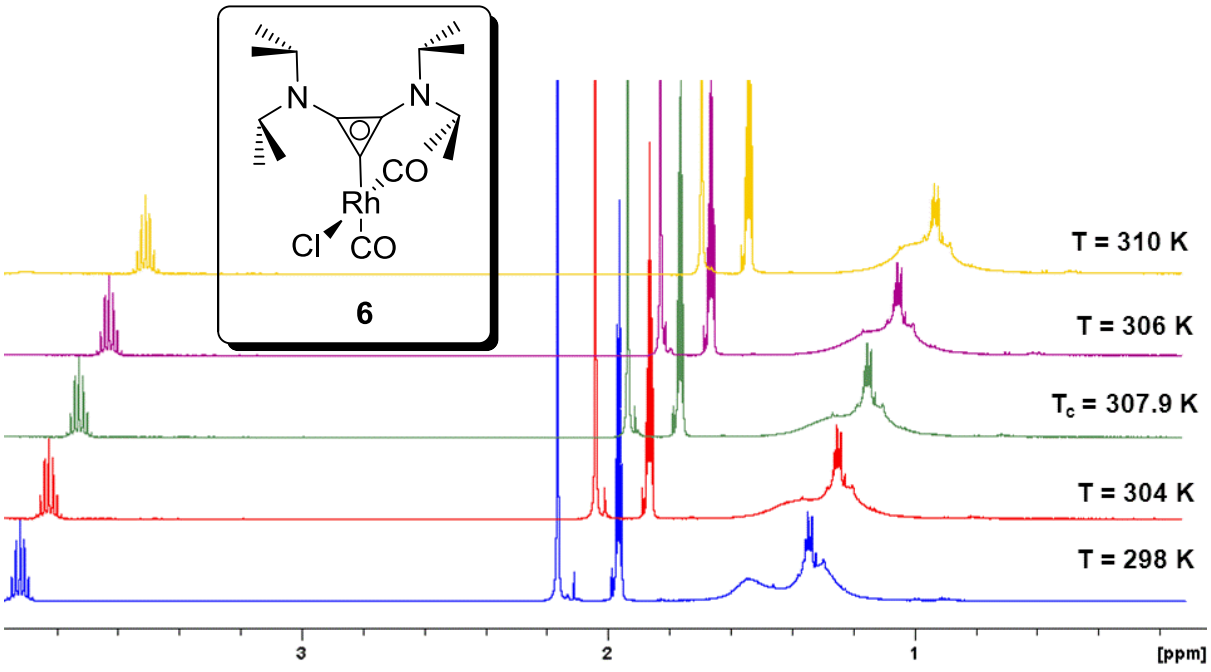
VT NMR of complex **4** (500 MHz, CD_3CN)



VT NMR of complex **5** (500 MHz, toluene-d8)

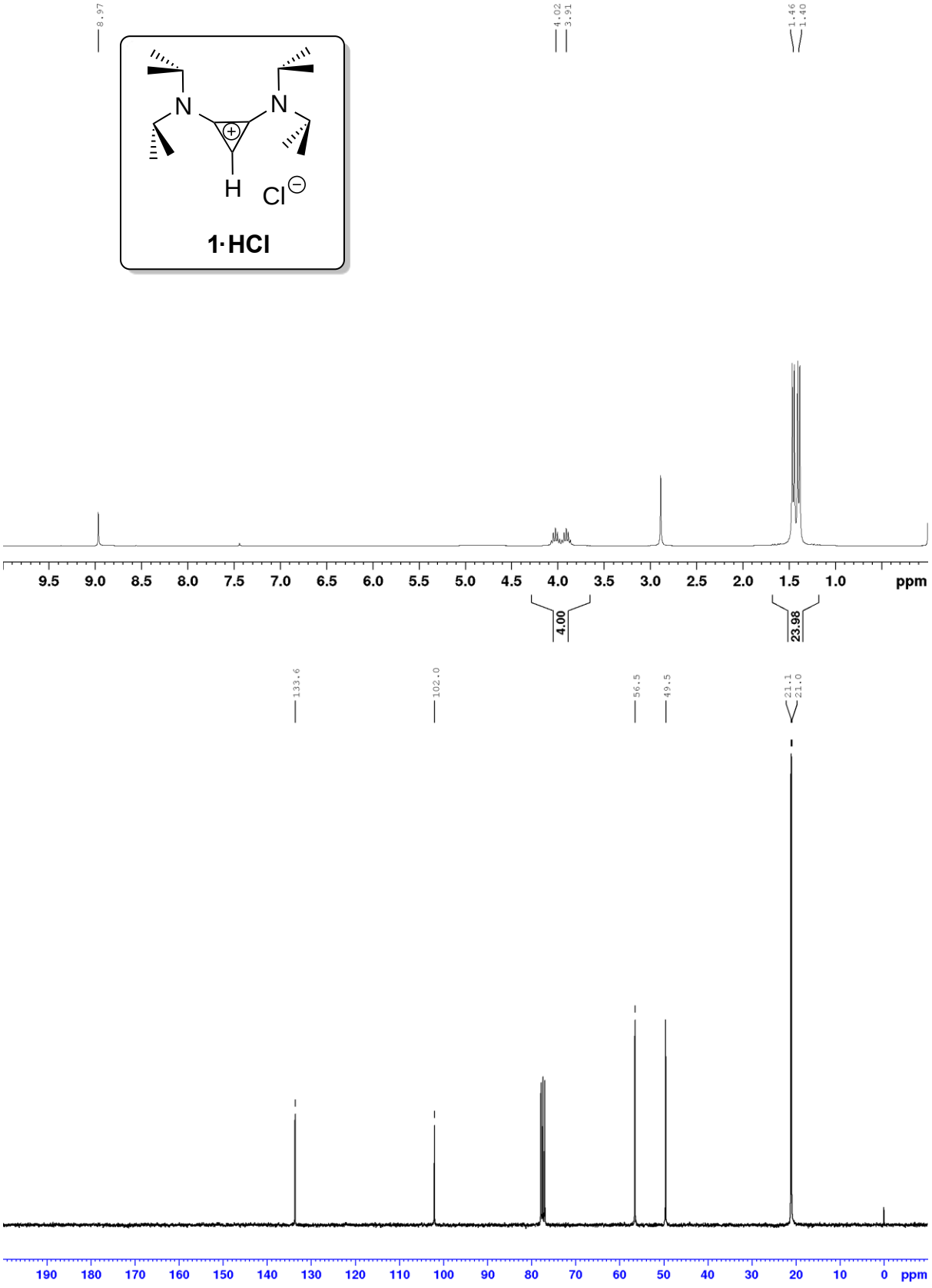


VT NMR of complex **6** (500 MHz, CD_3CN)

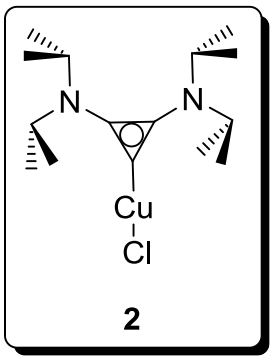


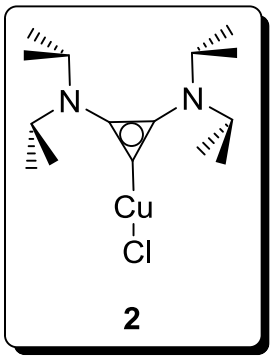
3.2. ^{1}H and ^{13}C-{^{1}H} NMR spectra

^{1}H and ^{13}C-{^{1}H} NMR of 1·HCl at 298K (500 MHz, $CDCl_3$, TMS):

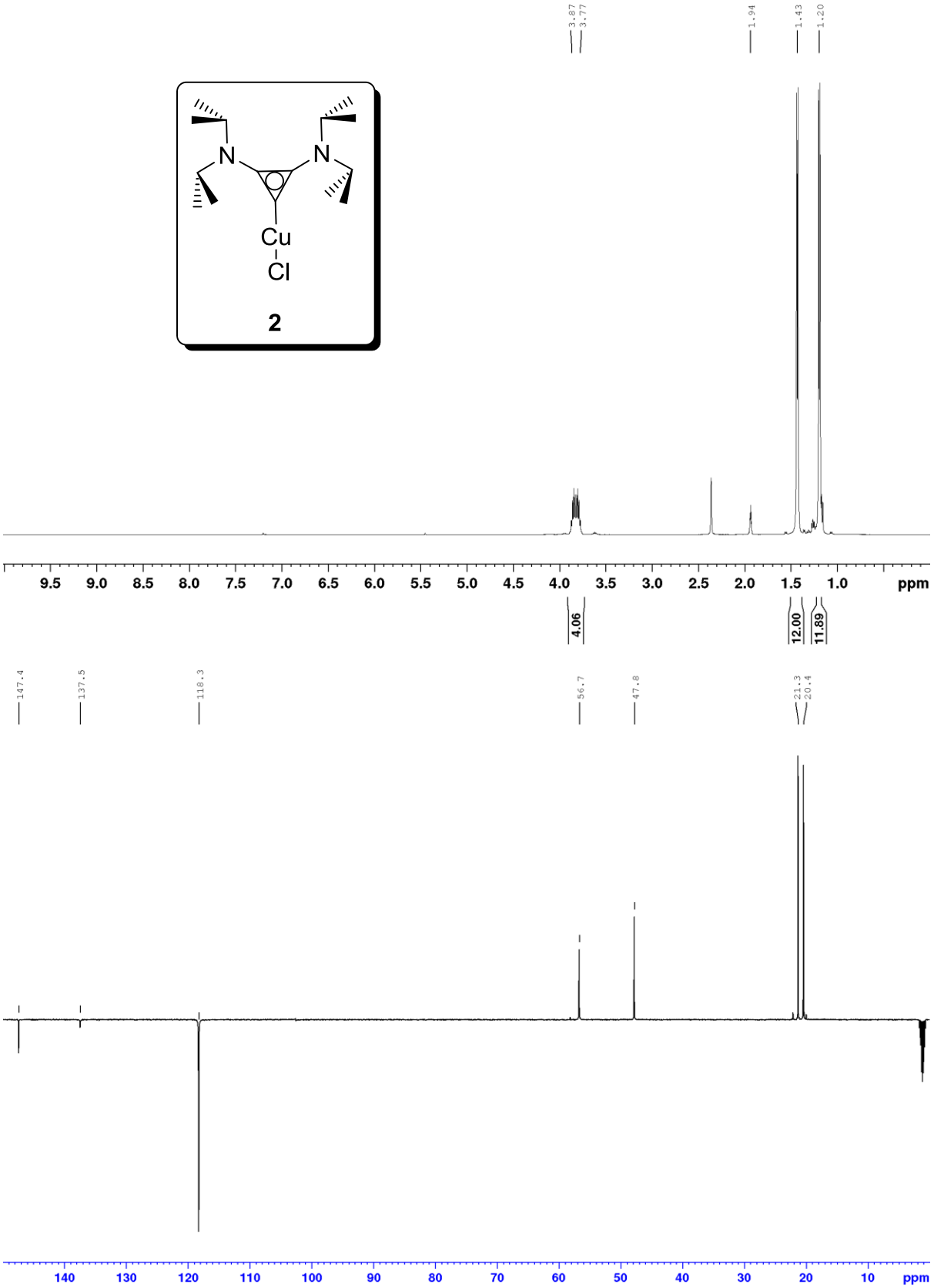


^{1}H and (135DEPT)-^{13}C-{^{1}H} NMR of 2 at 298K (500 MHz, CD_3CN):

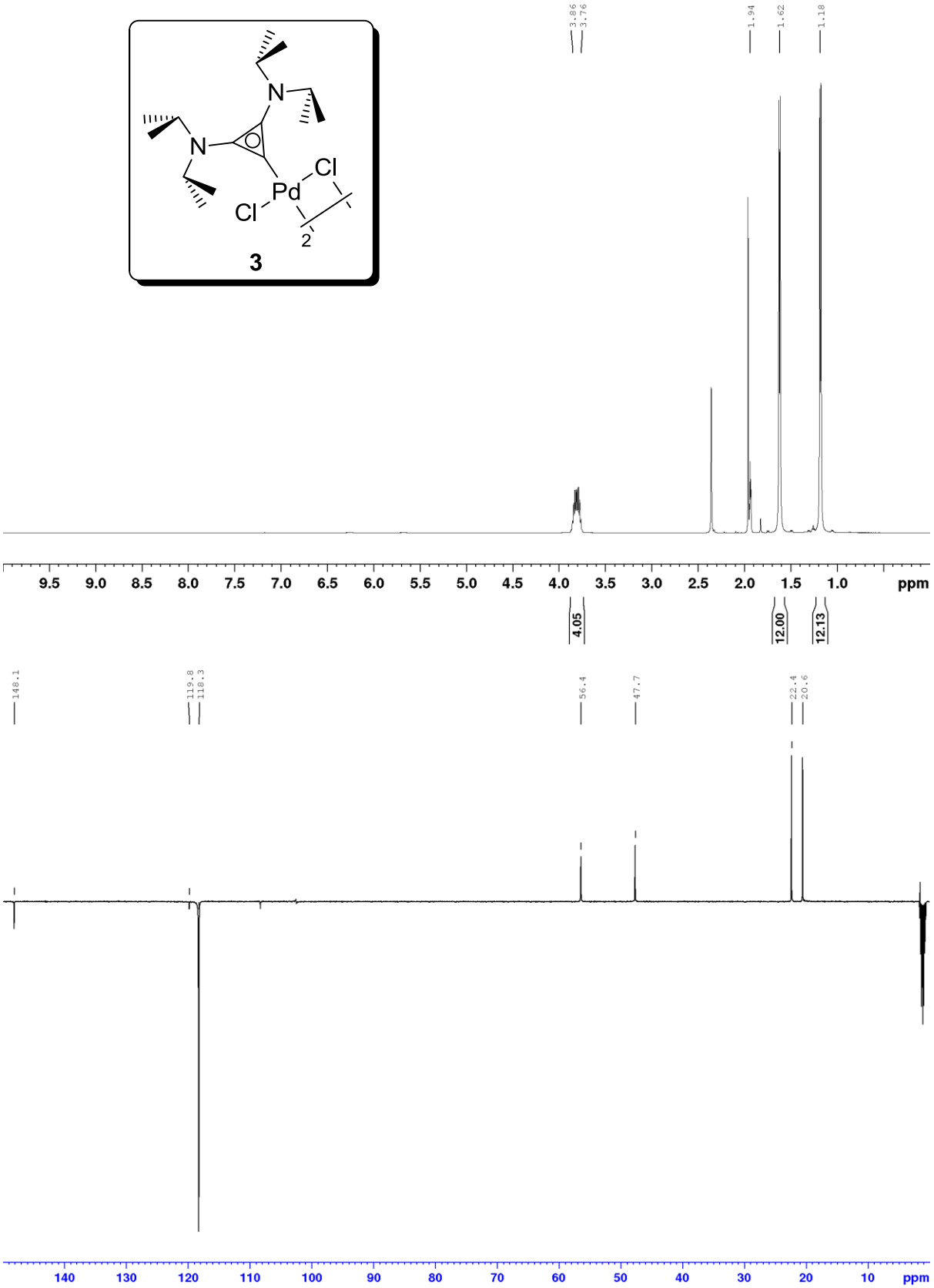




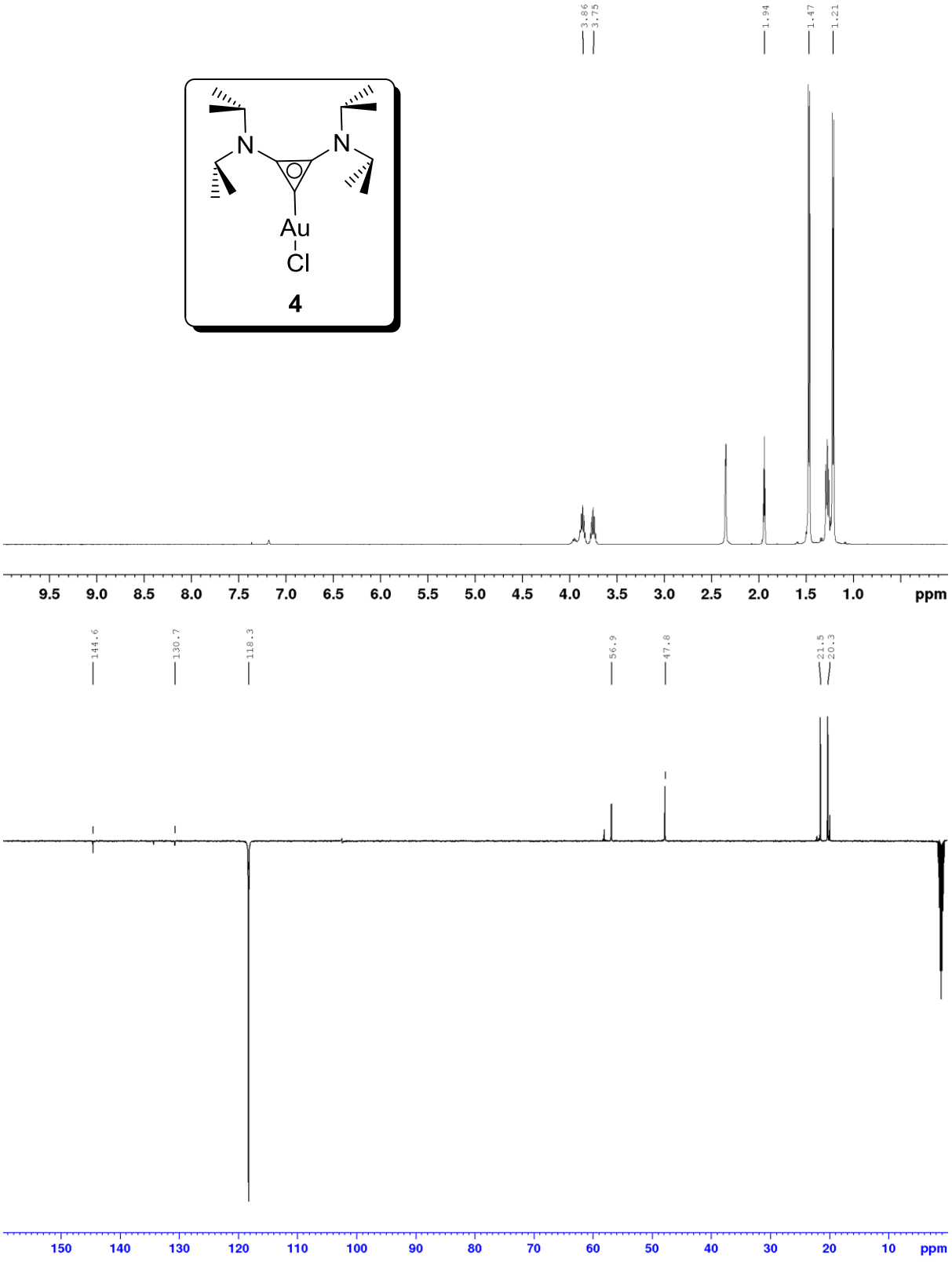
^{1}H and (135DEPT)-^{13}C-{^{1}H} NMR of 2 at 240K (500 MHz, CD_3CN):



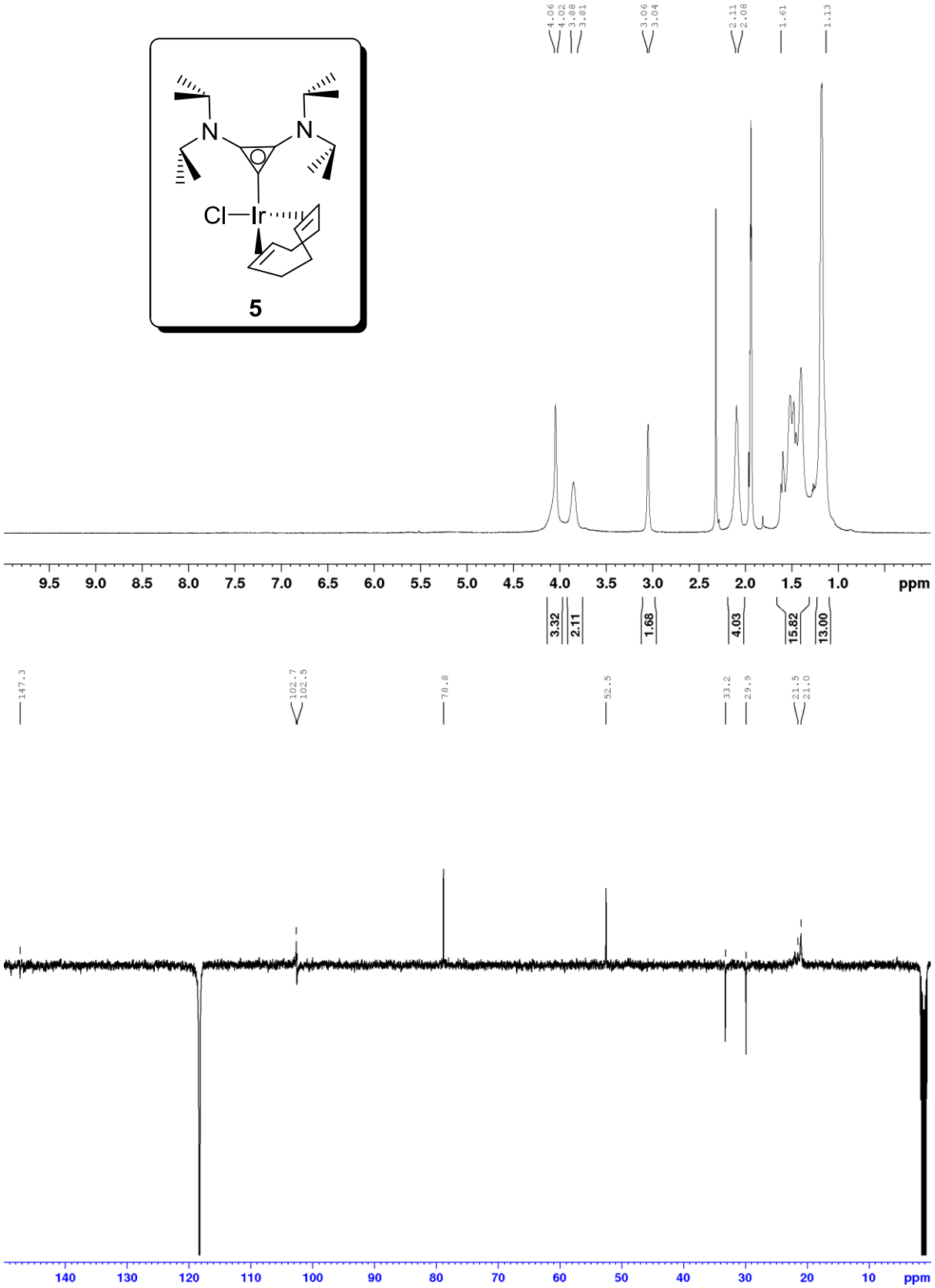
^{1}H and (135DEPT)-^{13}C-{^{1}H} NMR of 3 at 240K (500 MHz, CD_3CN):



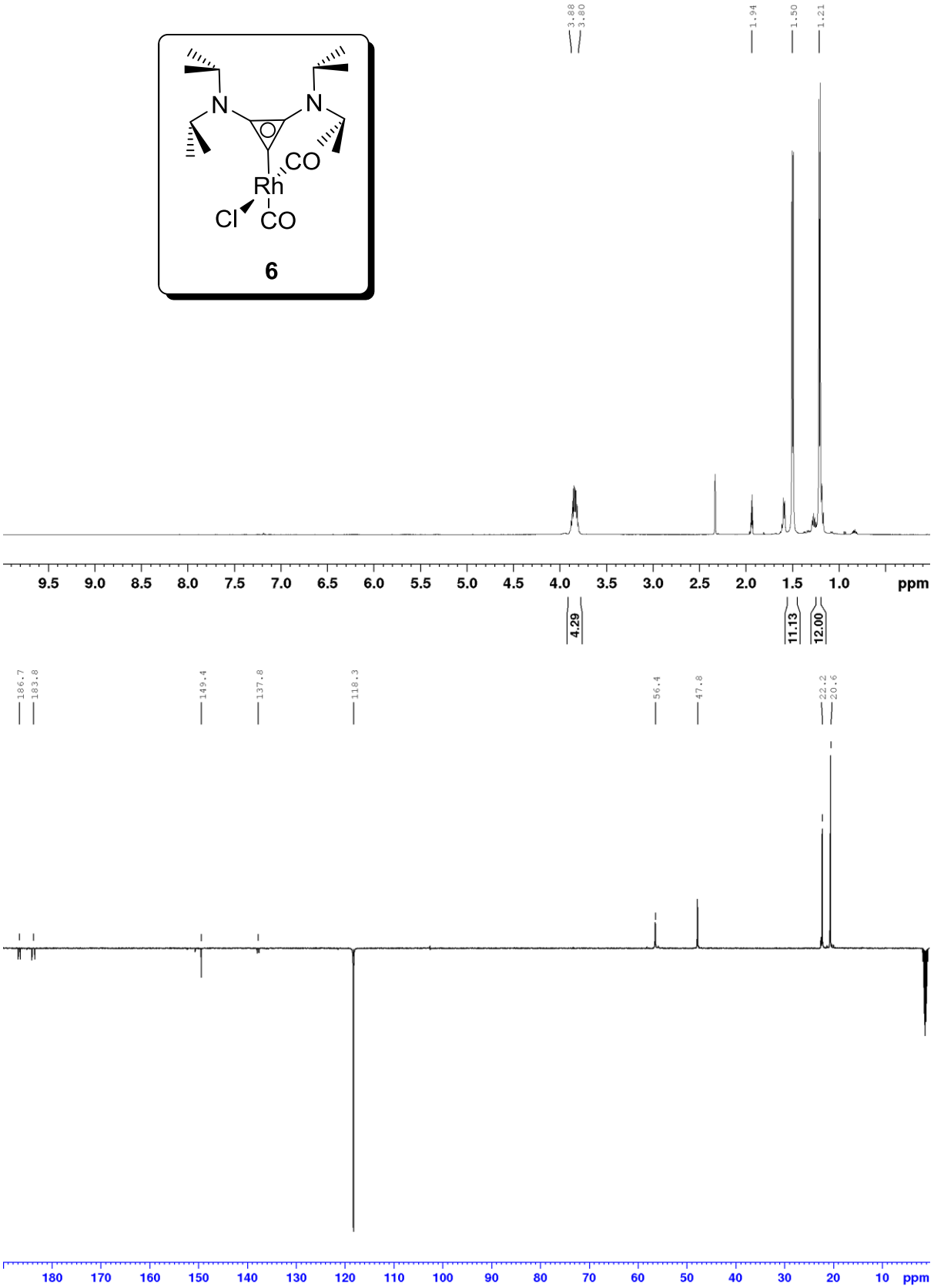
^{1}H and (135DEPT)-^{13}C-{^{1}H} NMR of 4 at 240K (500 MHz, CD_3CN):



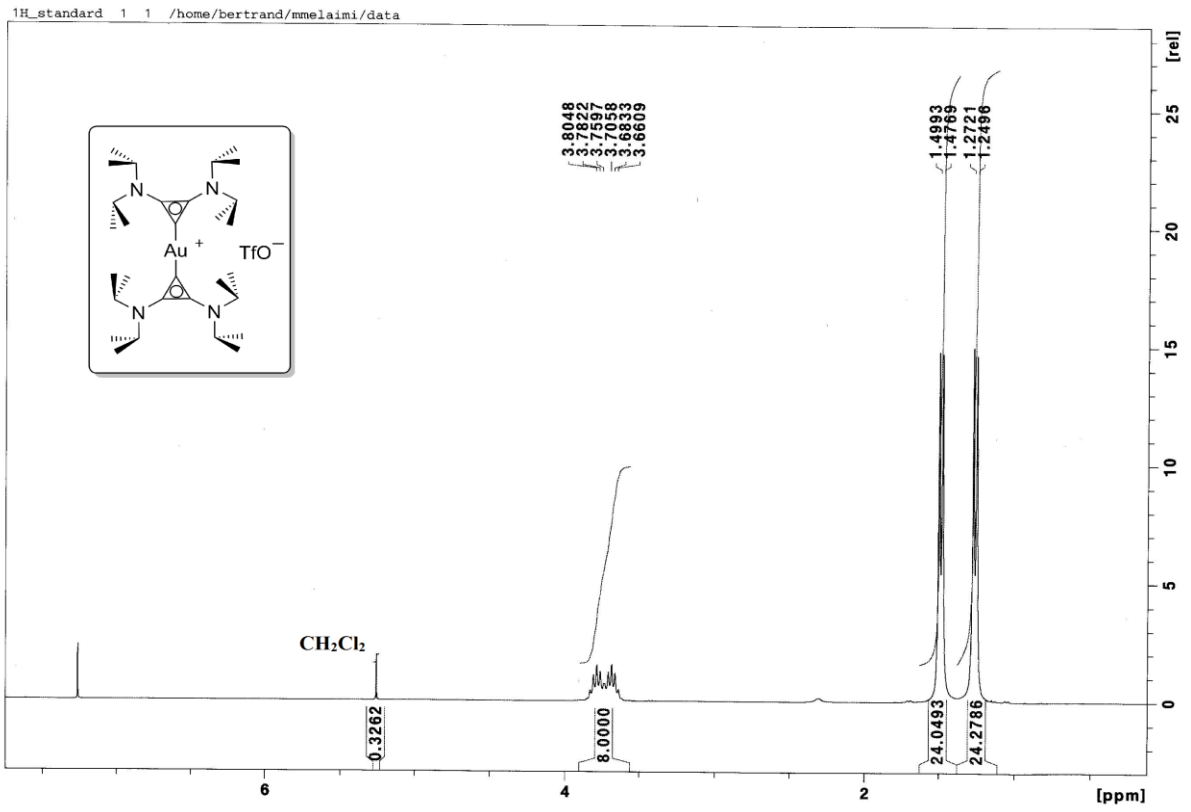
^{1}H and (135DEPT)-^{13}C-{^{1}H} NMR of 5 at 2408K (500 MHz, CD_3CN):

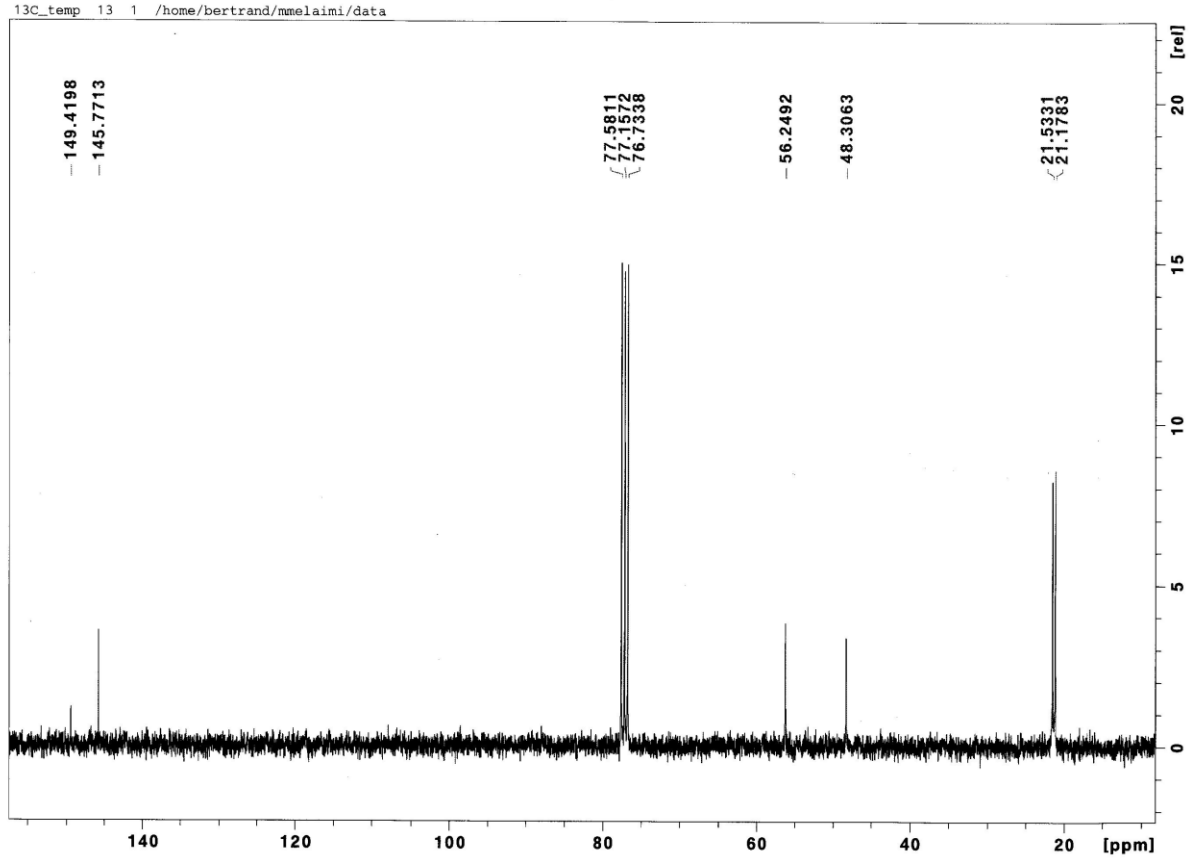


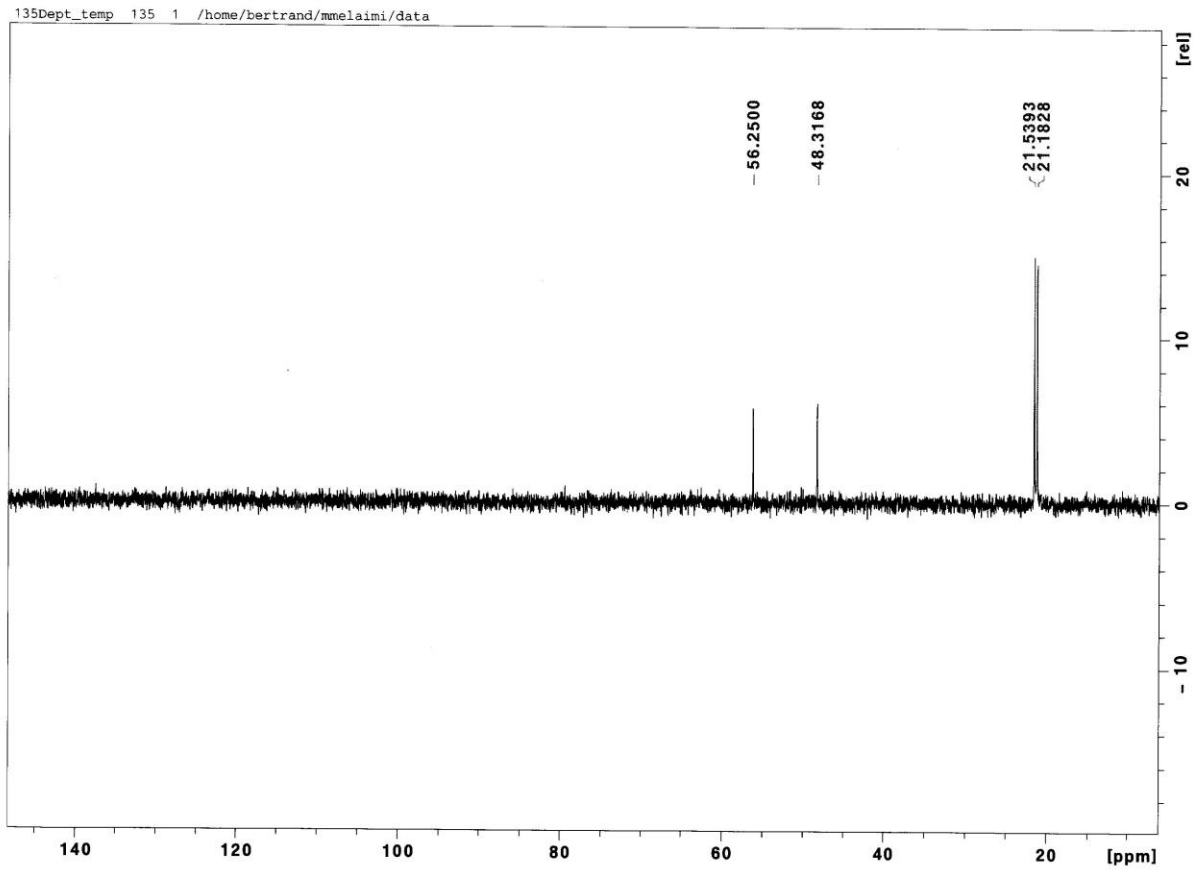
^{1}H and (135DEPT)-^{13}C-{^{1}H} NMR of 6 at 240K (500 MHz, CD_3CN):



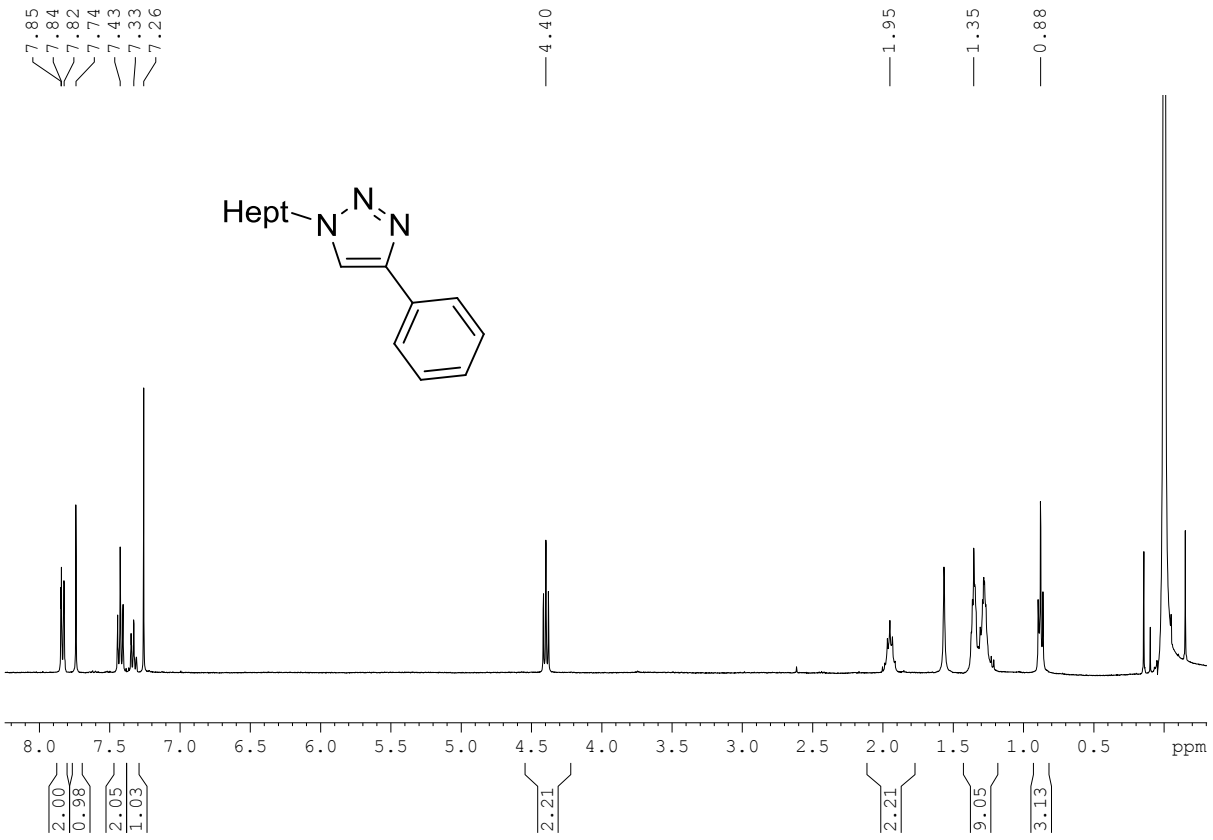
^{1}H and (135DEPT)-^{13}C-{^{1}H} NMR of [Au(BAC)$_2$]$^{+}$OTf^{-} at 298K (300 MHz, CD_2Cl_2):



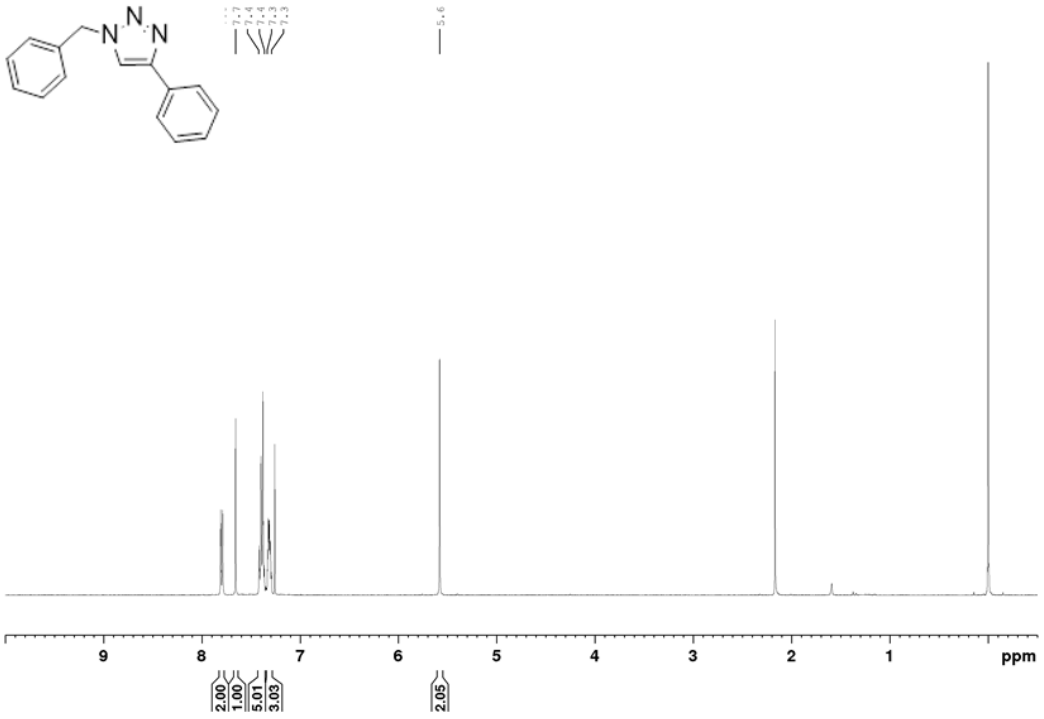




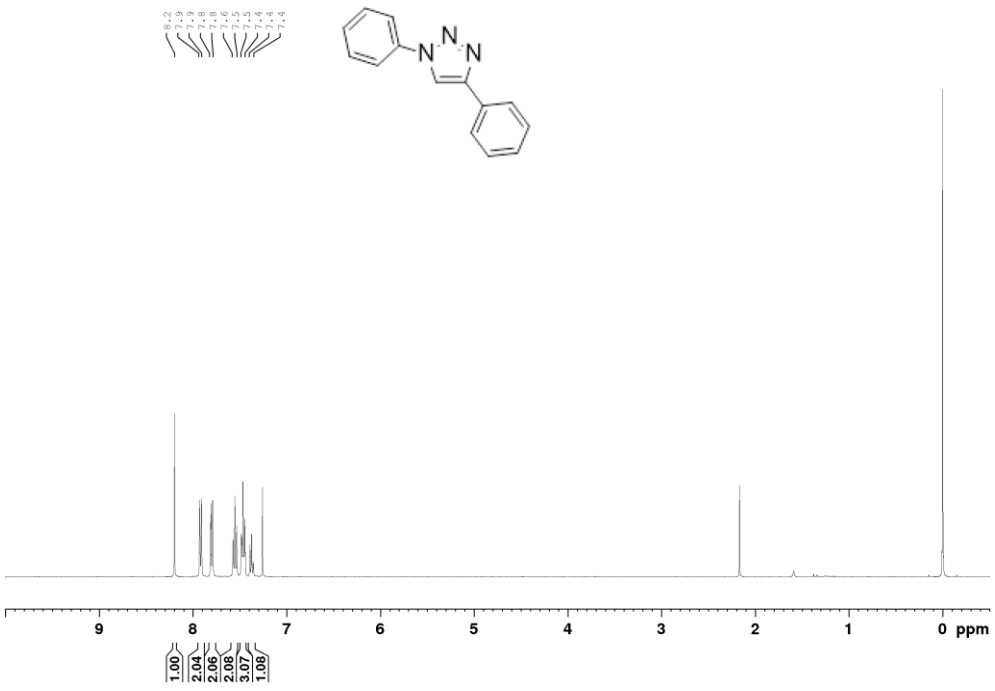
^{1}H NMR at 298K of 1-heptyl-4-phenyl-1H-1,2,3-triazole (400 MHz, $CDCl_3$, TMS)



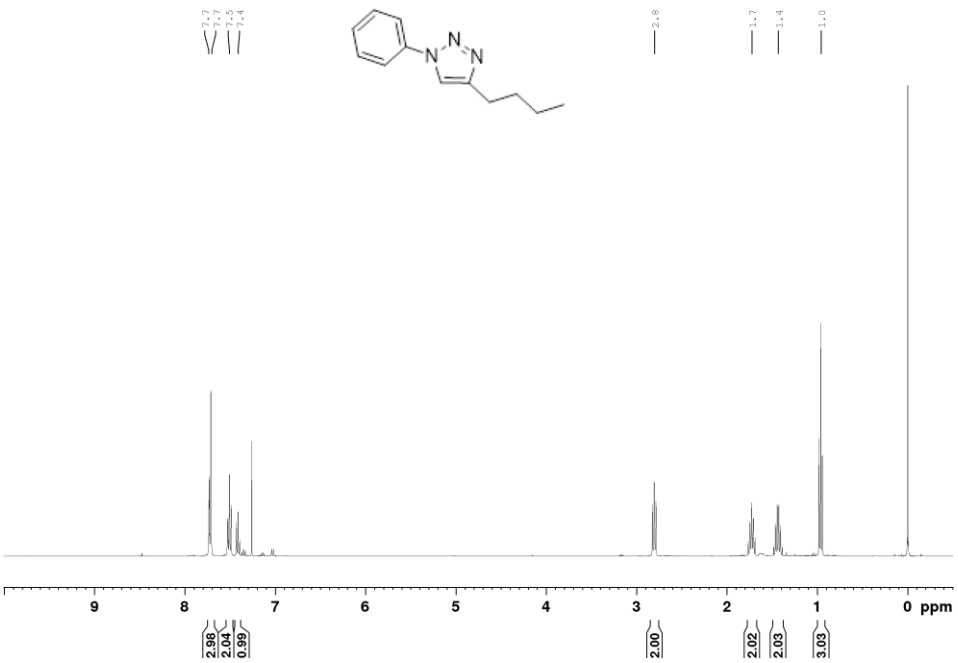
^{1}H NMR at 298K of 1-benzyl-4-phenyl-1H-1,2,3-triazole (400 MHz, $CDCl_3$, TMS)



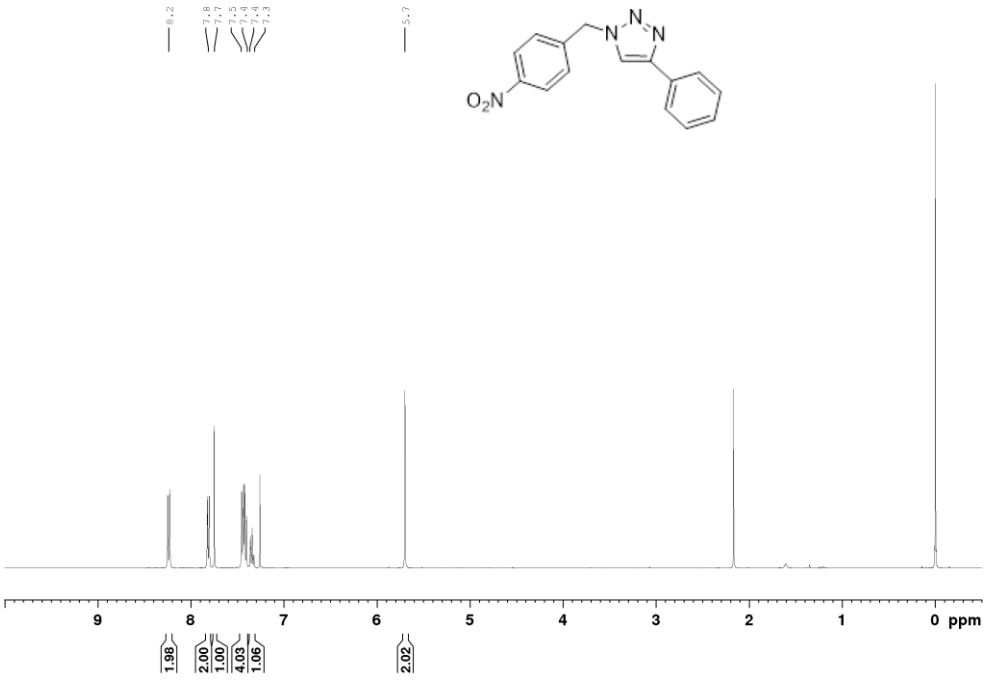
^{1}H NMR at 298K of 1,4-diphenyl-1H-1,2,3-triazole (400 MHz, $CDCl_3$, TMS)



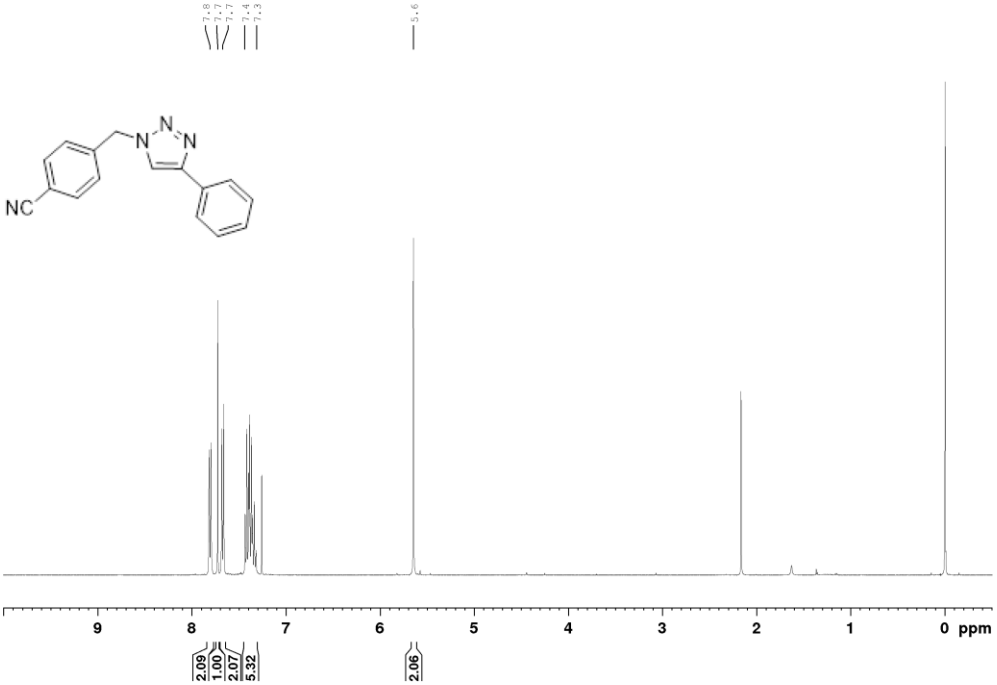
^{1}H NMR at 298K of 4-butyl-1-phenyl-1H-1,2,3-triazole (400 MHz, $CDCl_3$, TMS)



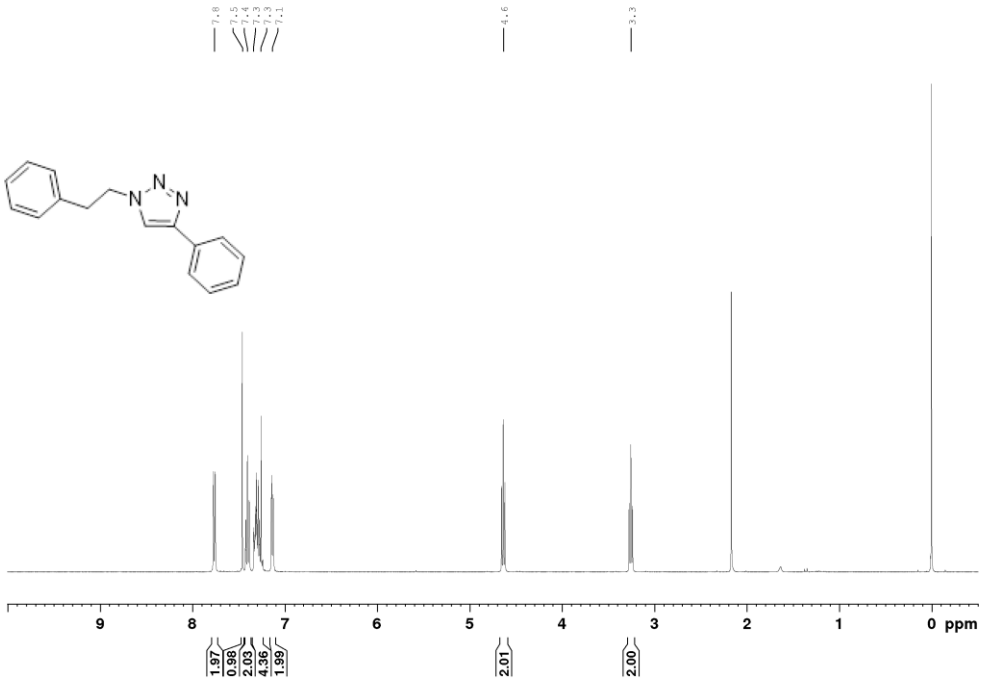
^{1}H NMR at 298K of 1-(4-nitrobenzyl)-4-phenyl-1H-1,2,3-triazole (400 MHz, $CDCl_3$, TMS)



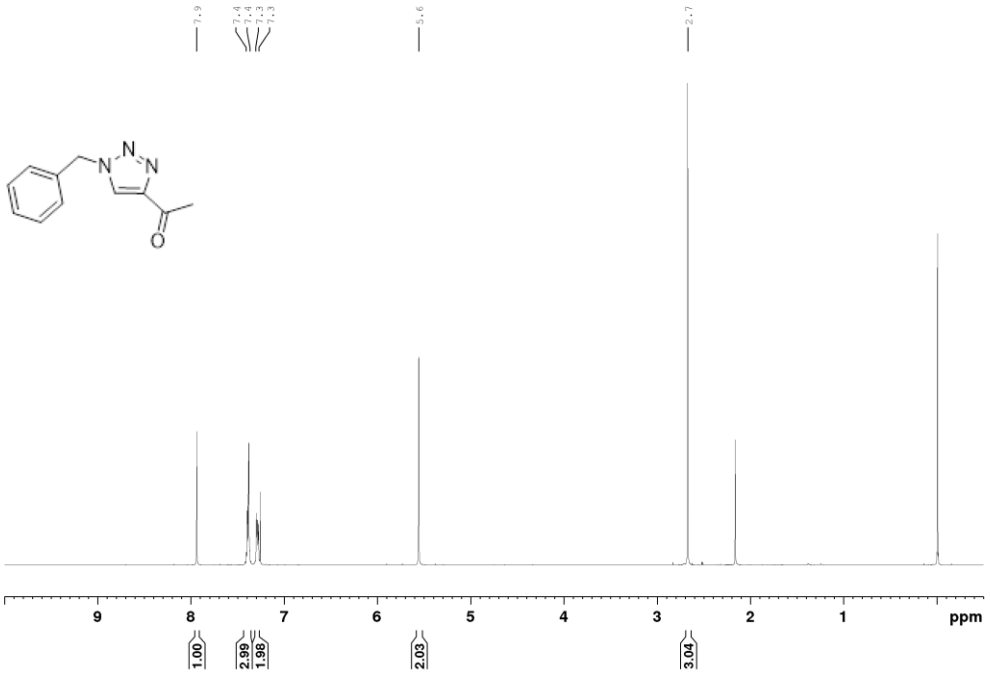
^{1}H NMR at 298K of 4-((4-phenyl-1H-1,2,3-triazol-1-yl)methyl)benzonitrile (400 MHz, $CDCl_3$, TMS)



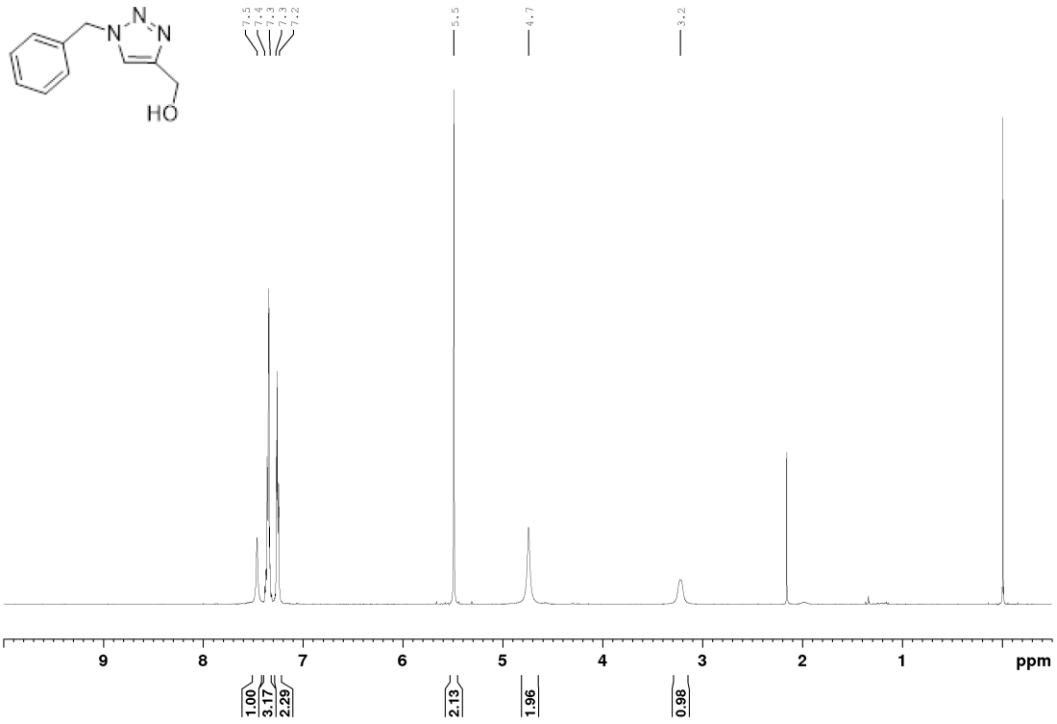
^{1}H NMR at 298K of 1-phenethyl-4-phenyl-1H-1,2,3-triazole (400 MHz, $CDCl_3$, TMS)



^{1}H NMR at 298K of 1-(1-benzyl-1H-1,2,3-triazol-4-yl)ethan-1-one (400 MHz, $CDCl_3$, TMS)



^{1}H NMR at 298K of (1-benzyl-1H-1,2,3-triazol-4-yl)methanol (400 MHz, $CDCl_3$, TMS)



4. % V_{Bur} and 3D mapping

%V_{Bur} of BAC in [Cu(Cl)(BAC)], 2

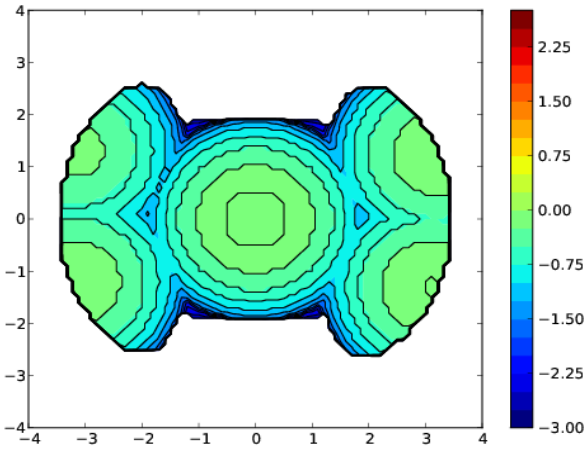
V Free	V Buried	V Total	V Exact
122.8	56.7	179.5	179.6

%V_Free	**%V_Bur**	% Tot/Ex
68.4	**31.6**	100.0

xy	V_f	V_b	V_t	%V_f	**%V_b**
--	30.6	14.3	44.9	68.2	**31.85**
-+	31.2	13.7	44.9	69.6	**30.43**
++	30.7	14.2	44.9	68.3	**31.66**
+-	30.3	14.5	44.9	67.6	**32.36**

xy	--+	-++	+++	+-+	--	-+-	++-	+--
%V_b	0.0	0.0	0.0	0.0	62.4	59.6	62.0	63.4

Steric Map



$\%V_{Bur}$ of IPr in [Cu(Cl)(IPr)]

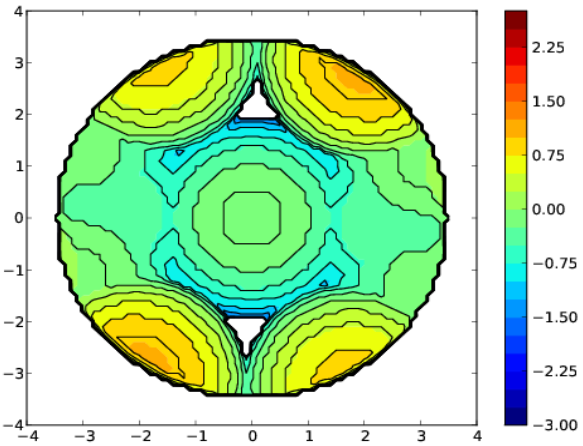
V Free	V Buried	V Total	V Exact
90.6	89.0	179.5	179.6

%V_Free	**%V_Bur**	% Tot/Ex
50.4	**49.6**	100.0

xy	V_f	V_b	V_t	%V_f	**%V_b**
--	22.1	22.8	44.9	49.3	**50.74**
-+	23.2	21.7	44.9	51.6	**48.37**
++	22.1	22.8	44.9	49.3	**50.74**
+-	23.2	21.7	44.9	51.6	**48.36**

xy	--+	-++	+++	+-+	--	-+-	++-	+--
%V_b	10.5	6.6	10.5	6.6	89.3	88.4	89.3	88.3

Steric Map



%V_{Bur} IMes in [Cu(Cl)(IMes)]

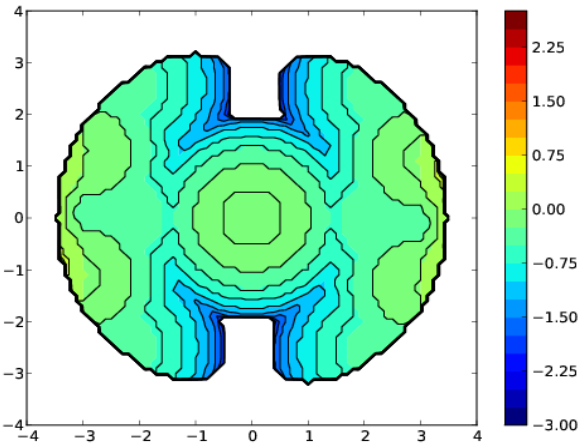
V Free	V Buried	V Total	V Exact
111.2	68.3	179.5	179.6

%V_Free	**%V_Bur**	% Tot/Ex
62.0	**38.0**	100.0

xy	V_f	V_b	V_t	%V_f	**%V_b**
--	27.8	17.1	44.9	61.9	**38.14**
-+	27.8	17.0	44.9	62.1	**37.94**
++	27.7	17.1	44.9	61.9	**38.15**
+-	27.8	17.0	44.9	62.1	**37.94**

xy	--+	-++	+++	+-+	--	-+-	++-	+--
%V_b	0.3	0.2	0.3	0.2	74.4	74.1	74.4	74.1

Steric Map



$\%V_{Bur}$ ICy in [Cu(Cl)(ICy)]

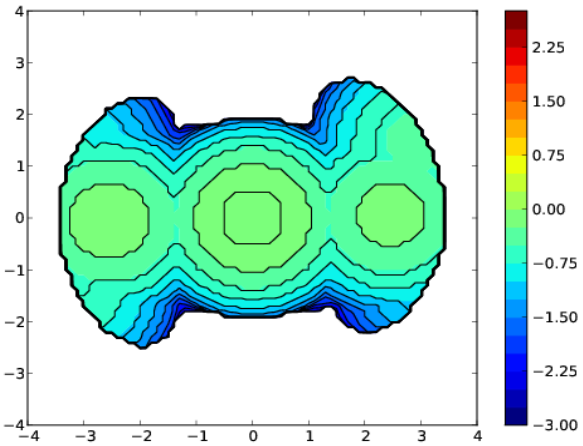
V Free	V Buried	V Total	V Exact
124.8	54.7	179.5	179.6

%V_Free	**%V_Bur**	% Tot/Ex
69.5	**30.5**	100.0

xy	V_f	V_b	V_t	%V_f	**%V_b**
--	30.9	14.0	44.9	68.9	**31.15**
-+	31.7	13.1	44.9	70.7	**29.28**
++	30.1	14.8	44.9	67.1	**32.88**
+-	32.1	12.8	44.9	71.5	**28.52**

xy	--+	-++	+++	+-+	--	-+-	++-	+--
%V_b	0.0	0.0	0.0	0.0	61.0	57.3	64.4	55.8

Steric Map



%V_{Bur} of BAC in [Pd(μ-Cl)(Cl)(BAC)]$_2$, 3

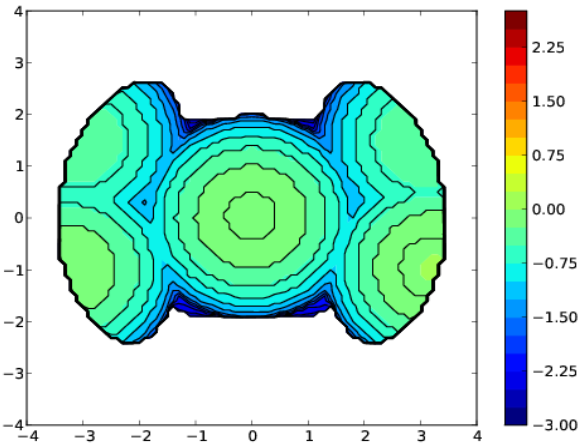
V Free	V Buried	V Total	V Exact
124.1	55.4	179.5	179.6

%V_Free	%V_Bur	% Tot/Ex
69.1	**30.9**	100.0

xy	V_f	V_b	V_t	%V_f	%V_b
−−	31.0	13.9	44.9	69.1	**30.87**
−+	31.3	13.5	44.9	69.8	**30.17**
++	30.9	14.0	44.9	68.8	**31.18**
+−	30.8	14.0	44.9	68.7	**31.27**

xy	--+	-++	+++	+-+	--	-+-	++-	+--
%V_b	0.0	0.0	0.0	0.1	60.4	59.1	61.1	61.2

Steric Map



$\%V_{Bur}$ of BAC in [Au(Cl)(BAC)], 4

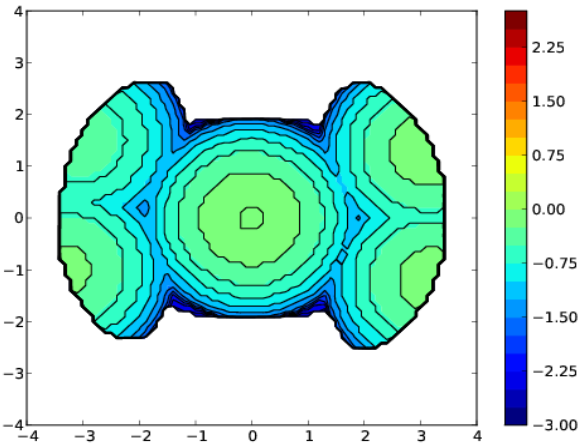
V Free	V Buried	V Total	V Exact
125.9	53.7	179.5	179.6

%V_Free	%V_Bur	% Tot/Ex
70.1	**29.9**	100.0

xy	V_f	V_b	V_t	%V_f	%V_b
−−	31.8	13.1	44.9	70.8	**29.17**
−+	31.7	13.2	44.9	70.6	**29.41**
++	30.9	14.0	44.9	68.9	**31.10**
+−	31.5	13.4	44.9	70.2	**29.83**

xy	−−+	−++	+++	+−+	−−	−+−	++−	+−−
%V_b	0.0	0.0	0.0	0.0	57.1	57.6	60.9	58.4

Steric Map



$\%V_{Bur}$ of BAC in [Ir(Cl)(BAC)(1,5-COD)], 5

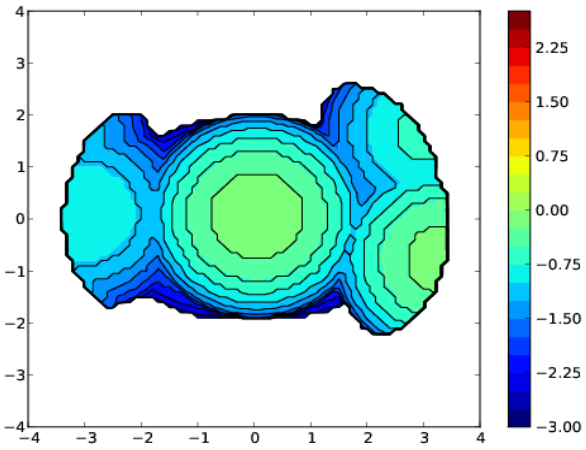
V Free	V Buried	V Total	V Exact
133.8	45.7	179.5	179.6

%V_Free	**%V_Bur**	% Tot/Ex
74.5	**25.5**	100.0

xy	V_f	V_b	V_t	%V_f	**%V_b**
--	34.9	10.0	44.9	77.7	**22.27**
-+	34.2	10.7	44.9	76.2	**23.78**
++	32.2	12.7	44.9	71.8	**28.20**
+-	32.5	12.4	44.9	72.3	**27.66**

xy	--+	-++	+++	+-+	--	-+-	++-	+--
%V_b	0.0	0.0	0.0	0.0	43.6	46.6	55.2	54.2

Steric Map



5. Determination of $\Delta G^{\neq}$

The rate constant at the coalescence point for two site exchange with equal site populations:

$$k_c = \frac{\pi \Delta \vartheta}{\sqrt{2}} \; [s^{-1}]$$

Eyring equation

Free activation energy at the coalescence point

$$\Delta G^{\neq} = RT_c \left(23.759 - \ln \frac{k_c}{T_c} \right) \; [J.mol^{-1}]$$

With R = 8.32

T_c = coalescence temperature

Data for copper complex **2**:

Δν (at 240K) = 118.6 Hz

T_c = 318.9±2.0 K

$k_c = 2.63 \times 10^2 \; s^{-1}$

$\Delta G^{\neq} = 6.35 \times 10^4 \; J.mol^{-1}$

$\Delta G^{\neq}$ = 15.18±0.10 kcal.mol^{-1}

Data for palladium complex **3**:

Δν (at 240K) = 219.9 Hz

T_c = 300.4±2.0 K

$k_c = 4.88 \times 10^2 \; s^{-1}$

$\Delta G^{\neq} = 5.82 \times 10^4 \; J.mol^{-1}$

$\Delta G^{\neq}$ = 13.90±0.09 kcal.mol^{-1}

Data for gold complex **4**:

$\Delta\nu$ (at 240K) = 126.8 Hz

T_c = 322.8±2.0 K

$k_c = 2.82 \times 10^2\ s^{-1}$

$\Delta G^{\neq} = 6.42 \times 10^4\ J.mol^{-1}$

$\Delta G^{\neq}$ = 15.33±0.10 kcal.mol^{-1}

Data for iridium complex **5**:

$\Delta\nu$ (at 223K) = 376.6 Hz

T_c = 266.0±2.0 K

$k_c = 8.37 \times 10^2\ s^{-1}$

$\Delta G^{\neq} = 5.00 \times 10^4\ J.mol^{-1}$

$\Delta G^{\neq}$ = 11.96±0.09 kcal.mol^{-1}

Data for rhodium complex **6**:

$\Delta\nu$ (at 240K) = 144.9 Hz

T_c = 307.9±2.0 K

$k_c = 3.22 \times 10^2\ s^{-1}$

$\Delta G^{\neq} = 6.08 \times 10^4\ J.mol^{-1}$

$\Delta G^{\neq}$ = 14.53±0.08 kcal.mol^{-1}

6. Crystallographic data for complexes 2-5, and $[Au(BAC)_2]^+OTf^-$.

Complex	2	3
CCDC number	CCDC 1012888	CCDC 1012889
Emperical formula	$C_{15}H_{28}ClCuN_2$	$C_{30.5}H_{57}Cl_5N_4Pd_2$
Formula Weight	335.40 g.mol^{-1}	869.88 g.mol^{-1}
Crystal color, Habit	colourless, needle	yellow, platelet
Temperature (K)	173.15	173.15
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$ (#14)	P-1 (#2)
Unit cell dim.	0.240 X 0.020 X 0.020 mm	0.210 X 0.060 X 0.020 mm
Lattice type	Primitive	Primitive
Lattice parameter a,b,c (Å)	a = 6.043(3) Å b = 18.944(7) Å c = 15.635(6) Å	a = 8.6743(10) Å b = 15.1390(18) Å c = 15.947(2) Å
α,β,γ (°)	β = 100.450(11) ^{o}	α = 86.794(7) ^{o} β = 85.946(7) ^{o} γ = 80.765(6) ^{o}
Volume (Å)^3	V = 1760.3(11) Å^3	V = 2059.8(4) Å^3
Z	4	2
Density calculated	1.265 g/cm^3	1.402 g/cm^3
Absorption coefficient (cm^{-1})	13.831 cm^{-1}	12.212 cm^{-1}
F(000)	712.00	890.00
Diffractometer	Mercury70	XtaLAB P200
Radiation	MoKα (λ = 0.71075 Å)	MoKα (λ = 0.71075 Å) multi-layer mirror monochromated
Voltage, Current	50kV, 16mA	45kV, 66mA
Theta range for data collection (°)	$2\theta_{max}$ = 50.7^o	$2\theta_{max}$ = 50.8^o
Reflexions collected	Total: 11039 Unique: 3196 (R_{int} = 0.0688)	Total: 33898 Unique: 7540 (R_{int} = 0.0609)
Correction	Lorentz-polarization Absorption (trans. factors: 0.638 - 0.973)	Lorentz-polarization Absorption (trans. factors: 0.755 - 0.976)
Structure solution	Direct Methods (SHELX97)	Patterson Methods (SHELXS2013)

Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Anomalous dispersion	All non-hydrogen atoms	All non-hydrogen atoms
No. Observations (all reflections)	3196	7540
No. variables	180	396
Reflection/parameter ratio	17.76	19.04
Goodness-of-fit on F^2	1.119	1.008
Final R indices [I>2sigma(I)]	0.0763	0.0444
R indices (all data)	0.2005	0.1218
Maximum peak in Final Diff Map ($e.Å^{-3}$)	1.84 $e^-/Å^3$	1.14 $e^-/Å^3$
Minimum peak in Final Diff Map ($e.Å^{-3}$)	-0.56 $e^-/Å^3$	-0.97 $e^-/Å^3$
Max shift/error in final cycle	0.000	0.001

Complex	**4**	**5**
CCDC number	CCDC 1012890	CCDC 1012887
Emperical formula	$C_{15}H_{28}AuClN_2$	$C_{23}H_{40}ClIrN_2$
Formula Weight	468.82 $g.mol^{-1}$	572.26 $g.mol^{-1}$
Crystal color, Habit	colourless, prism	yellow, chip
Temperature (K)	173.15	173.15
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$ (#14)	$P2_1/n$ (#14)
Unit cell dim.	0.150 X 0.150 X 0.150 mm	0.060 X 0.030 X 0.020 mm
Lattice type	Primitive	Primitive
Lattice parameter a,b,c (Å)	a = 11.3202(7) Å b = 12.8913(10) Å c = 12.5373(10) Å	a = 11.8497(10) Å b = 12.2144(9) Å c = 16.7180(14) Å
α,β,γ (°)	β = 90.2151(19) º	β = 91.591(2) º
Volume $(Å)^3$	V = 1829.6(2) $Å^3$	V = 2418.8(3) $Å^3$
Z	4	4
Density calculated	1.702 g/cm^3	1.571 g/cm^3
Absorption coefficient (cm^{-1})	82.063 cm^{-1}	56.555 cm^{-1}
F(000)	912.00	1144.00
Diffractometer	XtaLAB P200	XtaLAB P200
Radiation	MoKα (λ = 0.71075 Å) multi-layer mirror monochromated	MoKα (λ = 0.71075 Å) multi-layer mirror monochromated
Voltage, Current	45kV, 66mA	45kV, 66mA
Theta range for data collection (°)	$2\theta_{max}$ = 50.8º	$2\theta_{max}$ = 50.8º
Reflexions collected	Total: 21959 Unique: 3368 (R_{int} = 0.0313)	Total: 28943 Unique: 4451 (R_{int} = 0.0284)
Correction	Lorentz-polarization Absorption (trans. factors: 0.223 - 0.292)	Lorentz-polarization Absorption (trans. factors: 0.794 - 0.893)
Structure solution	Patterson Methods	Direct Methods

	(SHELXS2013)	(SHELXS2013)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Anomalous dispersion	All non-hydrogen atoms	All non-hydrogen atoms
No. Observations (all reflections)	3368	4451
No. variables	180	252
Reflection/parameter ratio	18.71	17.66
Goodness-of-fit on F^2	1.072	1.045
Final R indices [I>2sigma(I)]	0.0134	0.0139
R indices (all data)	0.0343	0.0367
Maximum peak in Final Diff Map ($e.Å^{-3}$)	0.31 $e^-/Å^3$	0.60 $e^-/Å^3$
Minimum peak in Final Diff Map ($e.Å^{-3}$)	-0.68 $e^-/Å^3$	-0.46 $e^-/Å^3$
Max shift/error in final cycle	0.003	0.006

Complex	**$[Au(BAC)_2]^+OTf^-$**
CCDC number	CCDC 1020907
Emperical formula	$C_{31}H_{56}AuF_3N_4O_3S$
Formula Weight	818.82g.mol^{-1}
Crystal color, Habit	colourless, plate
Temperature (K)	173.15
Crystal system	monoclinic
Space group	$P2_1/c$ (#14)
Unit cell dim.	0.105 X 0.083 X 0.032 mm
Lattice type	Primitive
Lattice parameter a,b,c (Å)	a = 13.2941(6) Å b = 9.5096(5) Å c = 14.5324(7) Å
α,β,γ (°)	β = 93.610(2) ^{o}
Volume $(Å)^3$	V = 1833.56(15) $Å^3$
Z	2
Density calculated	1.483 g/cm^3
Absorption coefficient (cm^{-1})	4.118 cm^{-1}
F(000)	832.00
Diffractometer	
Radiation	MoKα (λ = 0.71075 Å)
Voltage, Current	
Theta range for data collection (°)	$2\theta_{max}$ = 52.834^o

Reflexions collected	Total: 12626 Unique: 3719 (R_{int} = 0.0509)
Correction	MULTI-SCAN (trans. factors: 0.670 - 0.877)
Structure solution	Direct Methods (SHELX97)
Refinement method	Full-matrix least-squares on F^2
Anomalous dispersion	All non-hydrogen atoms
No. Observations (all reflections)	3719
No. variables	204
Reflection/parameter ratio	18.23
Goodness-of-fit on F^2	1.201
Final R indices [I>2sigma(I)]	0.0377
R indices (all data)	0.0441
Maximum peak in Final Diff Map ($e.Å^{-3}$)	0.90 $e^-/Å^3$
Minimum peak in Final Diff Map ($e.Å^{-3}$)	-1.24 $e^-/Å^3$
Max shift/error in final cycle	0.000

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