Supporting Information

Synthesis of N-heterocyclic carbene (NHC)-Au/Ag/Cu benzotriazolyl complexes and their catalytic activity in propargylamide cycloisomerization and carbonyl hydrosilylation reactions

Entzy Kaplanai,[a] Nikolaos V. Tzouras,*[a,b] Nikolaos Tsoureas,[a] Nestor Bracho Pozsoni,[b] Subhrajyoti Bhandary,[b] Kristof Van Hecke,[b] Steven P. Nolan,*[b] and Georgios C. Vougioukalakis*[a]

a. *Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis, 15771 Athens, Greece*
b. *Department of Chemistry and Centre of Sustainable Chemistry, Ghent University, Krijgslaan 281, S-3, 9000 Ghent, Belgium*

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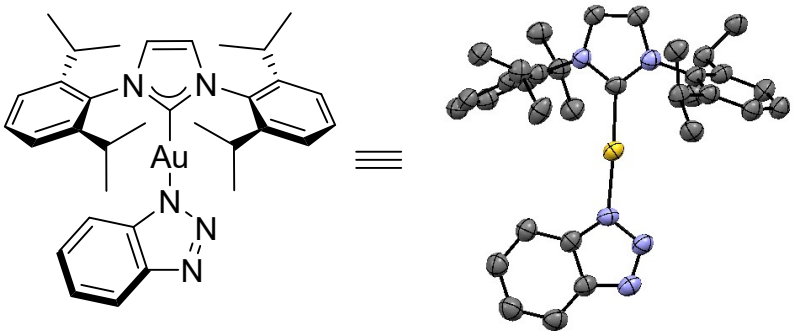
1. General considerations

The synthesis of all complexes, and the cycloisomerization reactions were carried out under air. The hydrosilylation reactions were carried out under an argon atmosphere using standard Schlenk techniques, and all the required chemicals were dried and then degassed under argon. Unless otherwise noted, all reactants and reagents were obtained from commercial suppliers and used as received. All [Au(NHC)Cl], [Ag(NHC)Cl], and [Cu(NHC)Cl] complexes were synthesized according to known procedures.[1–3] Purification of compounds by filtration or column chromatography was performed using silica gel 60 (230-400 mesh) purchased from Merck. Thin layer chromatography (TLC) was performed using aluminum sheets (0.2 mm) coated with

silica gel 60 with fluorescence indicator (silica gel 60 F254). The developed chromatograms were analyzed a by UV lamp (254 nm). ^{1}H and ^{13}C-{^{1}H}Nuclear Magnetic Resonance (NMR) spectra, including in Various Temperature (VT) experiments, were obtained with a Bruker Avance 400 MHz at 298K, using $CDCl_3$ or benzene-d_6 as solvent. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, td = triplet of doublets, q = quartet, m = multiplet, brs = broad singlet), coupling constant (Hz), and integration. The chlorinated solvents were neutralized, by filtration through dried basic alumina due to metal amido complexes sensitivity in traces of HCl. High resolution mass spectra (HRMS) were recorded on a QTOF maxis Impact (Bruker) spectrometer using ESI source. Single crystal X-ray diffraction measurements and analysis were performed both in National and Kapodistrian University of Athens and Ghent University and details are described in the corresponding section.

2. Synthesis and characterization of gold complex[4]

[N,N-bis(2,6-diisopropylphenyl)imidazol-2-ylidene](1H-benzotriazolyl)gold(I) [AuBTA(IPr)] (4a):



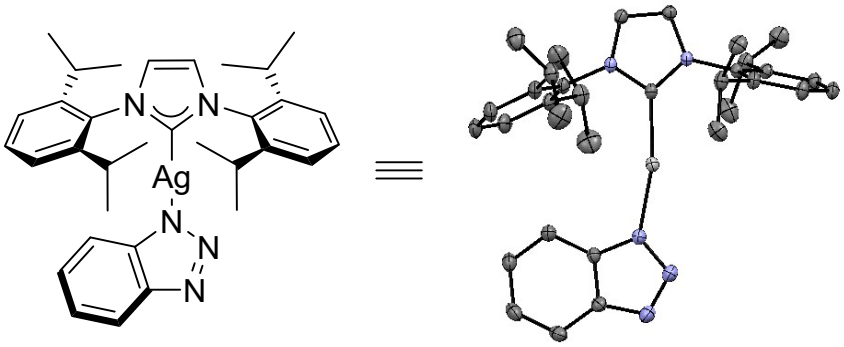
A 4 mL vial equipped with a septum cap and a stirring bar was charged with [Au(IPr)Cl] (200 mg, 0.32 mmol), 1H-benzotriazole (38.4 mg, 0.32 mmol, 1.0 equiv.), K_2CO_3 (132.7 mg, 0.96 mmol, 3.0 equiv.) and ethanol (1.0 mL). The reaction mixture was stirred at room temperature for 20 hours. After the reaction completed, the solvent was removed under vacuum and purification of the product was carried out by filtration of the mixture through a syringe filter, washed with THF, (4 mL) and through a basic alumina plug (ca. 2 cm) using an additional amount of THF (4 mL). Evaporation of the solvent, washing with pentane (3x3 mL), and drying under high vacuum afforded the product as a white powder in 98% yield (221 mg, 0.31 mmol). Crystals suitable for X-ray diffraction analysis were grown by vapor diffusion of hexane into a solution of the compound in $CDCl_3$ at 5 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.89 – 7.84 (m, 1H, $H_{Ar\text{-}BTA}$), 7.58 (t, *J* = 7.8 Hz, 2H, $H_{Ar(IPr)}$), 7.36 (d, *J* = 7.8 Hz, 4H, $H_{Ar(IPr)}$), 7.29 (s, 2H, NCH_{Imid}), 7.02 (m, 2H, $H_{Ar\text{-}BTA}$), 6.80 – 6.70 (m, 1H, $H_{Ar\text{-}BTA}$), 2.65 (sept, *J* = 6.8 Hz, 4H, C*H*$(CH_3)_2$), 1.37 (d, *J* = 6.9 Hz, 12H, CH(C*H*$_3)_2$), 1.27 (d, *J* = 6.9 Hz, 12H, CH(C*H*$_3)_2$).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) = 175.4 (C-Au), 145.9 (N*C*$_{Ar(IPr)}$), 145.0 ($C_{Ar\text{-}BTA}$), 142.9 ($C_{Ar\text{-}BTA}$), 134.1 ($C_{Ar\text{-}IPr}$), 131.1 ($CH_{Ar\text{-}IPr}$), 124.6 ($CH_{Ar\text{-}IPr}$), 123.7 (NCH_{Imid}), 123.5 ($CH_{Ar\text{-}BTA}$), 121.6 ($CH_{Ar\text{-}BTA}$), 118.5 ($CH_{Ar\text{-}BTA}$), 113.1 ($CH_{Ar\text{-}BTA}$), 29.1 (*C*H$(CH_3)_2$), 24.7 (CH(*C*H$_3)_2$), 24.2 (CH(*C*H$_3)_2$).

3. Synthesis and characterization of silver complexes

3.1 Synthesis of [*N*,*N*-bis(2,6-diisopropylphenyl)imidazol-2-ylidene](1H-benzotriazolyl)silver(I) [AgBTA(IPr)] (5a):



A 4 mL vial equipped with a septum cap and a stirring bar was charged with [Ag(IPr)Cl] (100 mg, 0.188 mmol), 1H-benzotriazole (22.4 mg, 0.188 mmol, 1.00 equiv.), K_2CO_3 (77.9 mg, 0.564 mmol, 3.0 equiv.) and ethanol (1.0 mL). The reaction mixture was stirred at room temperature for 20 hours. After the reaction completed, the solvent was removed under vacuum and purification of the product was carried out by filtration of the mixture through a syringe filter, wash with THF (4 mL), and through a basic alumina plug (ca. 2 cm) using an additional amount of THF (4 mL). Evaporation of the solvent, washing with pentane (3x3 mL), and drying under high vacuum afforded the product as a white powder in 93% yield (107 mg, 0.174 mmol).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.59 (t, *J* = 7.8 Hz, 2H, $H_{Ar(IPr)}$), 7.37 (d, *J* = 7.8 Hz, 4H, $H_{Ar(IPr)}$), 7.32 (br s, 2H, NCH_{Imid}), 7.22 (br s, 2H, $H_{Ar\text{-}BTA}$), 6.99 (m, 2H, $H_{Ar\text{-}BTA}$), 2.63 (sept, *J* = 6.8 Hz, 4H, C*H*$(CH_3)_2$), 1.29 (d, *J* = 6.9 Hz, 12H, CH(C*H*$_3)_2$), 1.26 (d, *J* = 6.9 Hz, 12H, CH(C*H*$_3)_2$).

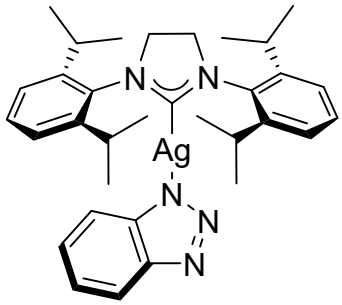
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) = 184.0 (dd, $J_{C\text{-}Ag}^{109}$ = 260.6, $J_{C\text{-}Ag}^{107}$ = 225.2 Hz, C-Ag), 145.9 ($C_{Ar(IPr)}$), 144.3 ($C_{Ar\text{-}BTA}$), 134.8 ($C_{Ar\text{-}IPr}$), 131.0 ($CH_{Ar\text{-}IPr}$), 124.7($CH_{Ar\text{-}IPr}$),

124.0 (d, $J_{C\text{-}Ag}$ = 7.3 Hz, NCH_{Imid}), 122.1 ($CH_{Ar\text{-}BTA}$), 115.8 (br, $CH_{Ar\text{-}BTA}$), 28.9 ($CH(CH_3)_2$), 24.9 ($CH(CH_3)_2$), 24.2 ($CH(CH_3)_2$).

^{1}H NMR (500 MHz, THF-d8): δ (ppm)= 7.77 (d, J = 1.8 Hz, 2H, NCH_{Imid}), 7.59 – 7.51 (t, *J* = 7.8 Hz, 2H, $H_{Ar(IPr)}$), 7.42 (d, *J = 7.8 Hz*, 4H, $H_{Ar(IPr)}$), 7.22 (bs, 2H, $H_{Ar\text{-}BTA}$), 6.87 – 6.80 (m, 2H, $H_{Ar\text{-}BTA}$), 2.72 (sept, *J = 6.9 Hz*, 4H, $CH(CH_3)_2$), 1.35 (d, *J = 6.9 Hz*, 12H, $CH(CH_3)_2$), 1.28 (d, *J = 6.9 Hz*, 12H, $CH(CH_3)_2$).

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{33}H_{41}AgN_5$: 614.2422, found: 614.2407

3.2 Synthesis of [N,N-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene](1H-benzotriazolyl)silver(I) [AgBTA(SIPr)] (5b):



A 4 mL scintillation vial equipped with a septum cap and a stirring bar was charged with [Ag(SIPr)Cl] (100 mg, 0.187 mmol), 1H-benzotriazole (22.3 mg, 0.187 mmol, 1.00 equiv.), K_2CO_3 (77.5 mg, 0.561 mmol, 3.0 equiv.) and ethanol (1.0 mL). The reaction mixture was stirred at room temperature for 20 hours. The solvent was removed under vacuum and purification of the product was carried out by filtration of the mixture through a syringe filter with THF (4 mL) and through a basic alumina plug (ca. 2 cm) using an additional amount of THF (4 mL). Evaporation of the solvent, washing with pentane (3x3 mL), and drying under high vacuum afforded the product as a white powder in 93% yield (107 mg, 0.174 mmol).

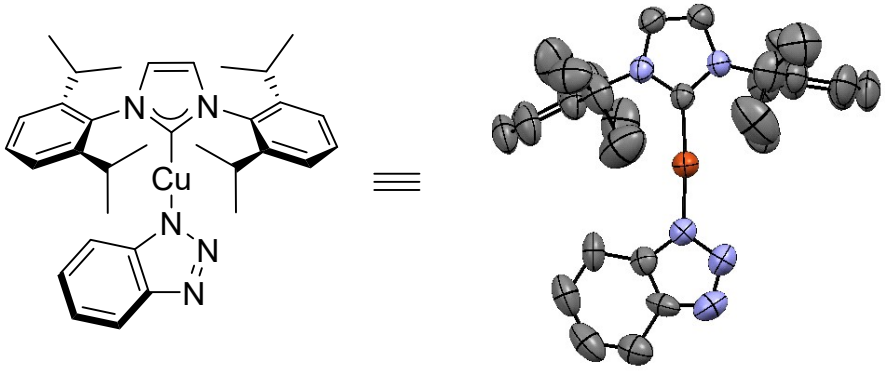
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm= 7.50 (t, *J* = 7.8 Hz, 2H, $H_{Ar(IPr)}$), 7.32 (d, *J* = 7.8 Hz, 4H, $H_{Ar(IPr)}$), 7.13 (bs, 2H, $H_{Ar\text{-}BTA}$), 6.97 (dt, *J* = 6.3, 3.4 Hz, 2H, $H_{Ar\text{-}BTA}$), 4.16 (s, 4H, NCH_{Imid}), 3.15 (sept, *J* = 6.8 Hz, 4H, $CH(CH_3)_2$), 1.38 (d, *J* = 6.9 Hz, 12H, $CH(CH_3)_2$), 1.35 (d, *J* = 6.8 Hz, 12H, $CH(CH_3)_2$).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm)= 207.5 (dd, $J_{C\text{-}Ag}^{109}$ = 245.2, $J_{C\text{-}Ag}^{107}$ = 206.8 Hz, C-Ag), 146.9 ($C_{Ar(IPr)}$), 144.2 ($C_{Ar\text{-}BTA}$), 134.7 ($C_{Ar\text{-}IPr}$), 130.3 ($CH_{Ar\text{-}IPr}$), 125.0 ($CH_{Ar\text{-}IPr}$), 122.0 ($CH_{Ar\text{-}BTA}$), 115.8 ($CH_{Ar\text{-}BTA}$), 54.1 (d, $J_{Ag\text{-}C}$ *= 8.4 Hz*, NCH_{Imid}), 29.1 ($CH(CH_3)_2$), 25.6 ($CH(CH_3)_2$), 24.1 ($CH(CH_3)_2$).

HRMS (MALDI-TOF): *m/z* $[M+H]^+$ calcd for $C_{33}H_{43}AgN_5$: 617.26, found: 617.66

4. Synthesis and characterization of copper complexes

4.1 Synthesis of [N,N-bis(2,6-diisopropylphenyl)imidazol-2-ylidene](1H benzotriazolyl)copper(I) [CuBTA(IPr)] (6a):



Procedure A: A 4 mL scintillation vial equipped with a septum cap and a stirring bar was charged with [Cu(IPr)Cl] (100 mg, 0.205 mmol), benzotriazole (24.4 mg, 0.205 mmol, 1.0 equiv.), K_2CO_3 (85.0 mg, 0.615 mmol, 3.0 equiv.) and ethanol (1.0 mL). The reaction mixture was stirred at room temperature for 20 hours. The solvent was removed under vacuum and purification of the product was carried out by filtration of the mixture through a syringe filter with THF (4 mL) and through a basic alumina plug (ca. 2 cm) using an additional amount of THF (4 mL). Evaporation of the solvent, washing with pentane (3x3 mL), and drying under high vacuum afforded the product as an off-white powder in 97% yield (113 mg, 0.198 mmol).

Procedure B (domino): A 4 mL scintillation vial equipped with a septum cap and a stirring bar was charged, under air, with 100 mg of IPr•HCl (0.235 mmol), 65 mg of K_2CO_3 (1.18 mmol, 5 equiv.), benzotriazole (28.0 mg, 0. 235 mmol, 1.0 equiv.) 23.3 mg of CuCl (0.235 mmol, 1 equiv.), and the solids were suspended in acetone (1.0 mL). The reaction mixture was stirred at 60 °C for 24 hours. The solvent was removed under vacuum and purification of the product was carried out by filtration of the mixture through a syringe filter with THF (4 mL) and through a basic alumina plug (ca. 2 cm) using an additional amount of THF (4 mL). Evaporation of the solvent, washing with with pentane (3x3 mL), and drying under high vacuum afforded the product as a white powder in 78% yield (105 mg, 0.184 mmol).

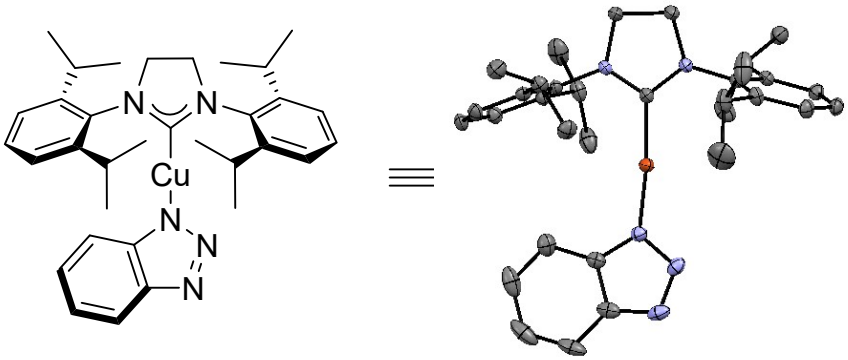
^{1}H NMR (400 MHz, CD_3CO): δ (ppm) = 8.32 (s, 2H, NCH_{Imid}), 8.05 (t, *J* = 7.7 Hz, 2H, $H_{Ar(IPr)}$), 7.92 (d, *J* = 7.7 Hz, 4H, $H_{Ar(IPr)}$), 7.62 (br s, 2H, $H_{Ar\text{-}BTA}$), 7.46 – 7.29 (m, 2H, $H_{Ar\text{-}BTA}$), 3.24 (sept, *J* = 6.6 Hz, 4H, $CH(CH_3)_2$), 1.79 (d, *J* = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.74 (d, *J* = 6.8 Hz, 12H, $CH(CH_3)_2$).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.58 (t, *J* = 7.8 Hz, 2H, $H_{Ar(IPr)}$), 7.37 (d, *J* = 7.8 Hz, 4H, $H_{Ar(IPr)}$), 7.25 (s, 2H, NCH_{Imid}), 6.96 (dd, *J* = 6.1, 3.0 Hz, 2H, $H_{Ar(BTA)}$), 2.66 (sept, *J* = 6.8 Hz, 4H, $CH(CH_3)_2$), 1.29 (d, *J* = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.27 (d, *J* = 7.2 Hz, 12H, $CH(CH_3)_2$), signals corresponding to 2H of the benzotriazolyl anion were too broad to be detected, however, they were detected in deuterated acetone (*vide supra*).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) = 180.5 (C-Cu), 145.9 ($C_{Ar(IPr)}$), 144.1 (C_{Ar^-BTA}), 134.6 (C_{Ar^-IPr}), 130.9 (CH_{Ar^-IPr}), 124.6 (CH_{Ar^-IPr}), 123.7 (NCH_{Imid}), 122.1 (CH_{Ar^-BTA}), 115.5 (br, CH_{Ar^-BTA}), 29.0 ($CH(CH_3)_2$), 25.1 ($CH(CH_3)_2$), 24.0 ($CH(CH_3)_2$).

HRMS (MALDI-TOF): *m/z* $[M+H]^+$ calcd for $C_{33}H_{41}CuN_5$: 570.26, found: 570.43.

4.2 Synthesis of [N,N-bis(2,6-diisopropylphenyl) imidazolin-2-ylidene](1H benzotriazolyl)copper(I) [CuBTA(SIPr)] (6b):



A 4 mL vial equipped with a septum cap and a stirring bar was charged with [Cu(SIPr)Cl] (150 mg, 0.30 mmol), 1H-benzotriazole (36.5 mg, 0.30 mmol, 1.0 equiv.), K_2CO_3 (126.9 mg, 0.92 mmol, 3.0 equiv.) and ethanol (1.0 mL). The reaction mixture was stirred at room temperature for 20 hours. After the reaction completed, the solvent was removed under vacuum and purification of the product was carried out by filtration of the mixture through a syringe filter, washed with THF, (4 mL) and through a basic alumina plug (ca. 2 cm) using an additional amount of THF (4 mL). Evaporation of the solvent, washing with pentane (3x3 mL), and drying under high vacuum afforded the product as a white powder in 73% yield (126 mg, 0.22 mmol). Crystals suitable for X-ray diffraction analysis were grown by vapor diffusion of pentane into a solution of the compound in $CDCl_3$ at 5 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.50 (t, *J* = 7.8 Hz, 2H, $H_{Ar(IPr}$), 7.33 (d, *J* = 7.8 Hz, 4H, $H_{Ar(IPr)}$), 6.92 (dd, *J* = 5.6, 2.7 Hz, 2H, $H_{Ar(BTA)}$), 4.13 (s, 4H, NCH_{Imid}), 3.17 (sept, *J* = 7.0 Hz, 4H, $CH(CH_3)_2$), 1.38 (d, *J* = 6.9 Hz, 12H, $CH(CH_3)_2$), 1.35 (d, *J* = 6.8 Hz, 12H,

CH(CH_3)$_2$), signals corresponding to 2H of the benzotriazolyl anion were too broad to be detected.

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) = 203.4 (C-Cu), 146.9 ($C_{Ar(IPr)}$), 144.0 ($C_{Ar\text{-}BTA}$), 134.5 ($C_{Ar\text{-}IPr}$),, 130.2 ($CH_{Ar\text{-}IPr}$), 124.9 ($CH_{Ar\text{-}IPr}$), 122.0 ($CH_{Ar\text{-}BTA}$), 54.0 (NCH_{Imid}), 29.1 (CH(*C*H_3)$_2$), 25.7 (CH(*C*H_3)$_2$), 23.9 (CH(*C*H_3)$_2$).

HRMS (MALDI-TOF): *m/z* $[M+H]^+$ calcd for $C_{33}H_{43}CuN_5$: 573.28, found: 573.80.

5. Single crystal X-ray diffraction analysis

Data for **4a** were collected at 100 K, using a Rigaku Oxford Diffraction Supernova Dual Source (Cu at zero) diffractometer equipped with an Atlas CCD detector using ω scans and CuKα (λ = 1.54184 Å) radiation. The images were interpreted and integrated with the program CrysAlisPro [Rigaku Oxford Diffraction, (2020), CrysAlisPro Software system, version 1.171.41.93a, Rigaku Corporation, Oxford, UK]. Using Olex2 [O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, J. Appl. Crystallogr. 42 (2009) 339-341], the structure was solved by direct methods using the ShelXT structure solution program and refined by full-matrix least-squares on F^2 using the ShelXL program package [G.M. Sheldrick, Acta Crystallogr. Sect. A71 (2015) 3-8; G.M. Sheldrick, Acta Crystallogr. Sect. C71 (2015) 3-8]. Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode with isotropic temperature factors fixed at 1.2 times U(eq) of the parent atoms (1.5 times for methyl and hydroxyl groups). The hydrogen atoms of a solvent water molecule were located from a difference Fourier electron density map and were refined using O-H distance restraints (DFIX and DANG). Data for **5a**, **6a** and **6b** were collected using a Bruker D8-Venture dual source SC-XRD equipped with IμS Diamond Cu/Kα and Mo/Kα X-ray sources, a 4-circle kappa goniometer and Photon-III area detector, using ϕ and ω scans to fill the Ewald sphere. Data collection strategy, acquisition, integration and scaling were handled by the APEX4 software and packages within. Data for **5a** and **6b** were collected at 100K using Mo/Kα to a resolution of 0.70 Å and 0.73 Å respectively. In the case of **5a** a molecule of crystallization solvent ($CHCl_3$) was also present in the asymmetric unit, showing occupational disorder of its chlorine atoms over three positions. The disorder was modelled using the PART and SUMP commands and the occupancy of the chlorine atoms was refined freely and converged to *ca* 81:8:11. Furthermore, in this case the anisotropic displacement parameters of some of the chlorine atoms in the minor part had to constrained to their counterparts in the major part *via* the EADP command for the refinement to converge, while 1,3 SADI and DFIX distance restraints were used to restrain the bonds between C34 and the chlorine atoms in PART 3 to more realistic values. In the case of **6a**, the crystals were found to suffer invariably from thermal stress upon placing them in the cryostream at 100K causing immediate shattering of the crystals, and as such data were collected at 293K

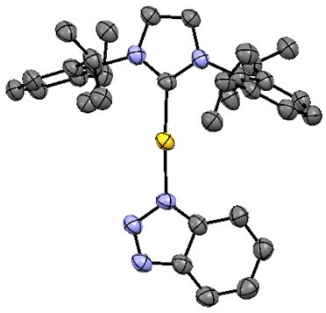
using Cu/Kα to a resolution of 0.81 Å. The data were collected, integrated and scaled as a non-merohedral two component twin (*ca* 89:11; 180˚ rotation through the 0 1 -1 direct-space direction); data solution and initial modelling were performed using the hkl4 file, while the final refinement was performed using the hkl5 file. The benzotriazole ligand and one of the isopropyls of the Dipp substituents were found to have occupational disorder which was modelled using the PART command and refined freely to converge to a ratio of *ca* 72:18 and 68:32 respectively. In the case of the disorder of the isopropyl atoms C22 and C22A were refined isotropically using the ISOR command; moreover, a SADI restraint was used to restrain the bond distance of C24 and C23 with the one of C23 and C22. In the case of the benzotriazole disorder the second part of the C6 ring was modelled as an ideal hexagon using the AFIX 66 constrain. In the case of **6b**, the model was refined as an inversion twin. Non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2 while H-atoms were added using the riding model with SHELXL default parameters. Structure solution (ShelXT, reference: Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8), modelling and refinement (ShelXL, reference: Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.) were achieved *via* their implementation into the Olex2-1.5 (reference: Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H.(2009), J. Appl. Cryst. 42, 339-341) software suite. Data collection, processing and final refinement details are given in the following table.

Compound	**4a**	**5a**	**6a**	**6b**
Colour, habit	Colourless/Plate	Colourless/Rod	Colourless/Plate	Colourless/Block
Size/mm	0.18x0.13x0.04	0.193x0.102x0.09	0.22x0.11x0.029	0.14x0.13x0.082
Empirical formula	$C_{33}H_{40}AuN_5.H_2O$	$C_{33}H_{40}AgN_5.CHCl_3$	$C_{33}H_{40}CuN_5$	$C_{33}H_{42}CuN_5$
FW	721.68	733.94	570.24	572.25
Crystal system	Triclinic	Orthorhombic	Triclinic	Orthorhombic
Space group	*P-1*	*Pbca*	*P-1*	*$Pna2_1$*
a/Å	8.1790(2)	21.405(2)	10.7992(4)	16.4504(11)
b/Å	9.1789(2)	14.1492(12)	12.5935(5)	12.4536(8)
c/Å	21.4433(4)	23.243(2)	12.9797(5)	15.0423(10)
α/°	86.470(2)	90	68.805(2)	90
β/°	79.752(2)	90	75.145(2)	90
γ/°	77.217(2)	90	82.058(2)	90
V/Å^3	1544.48(6)	7039.3(11)	1588.79(11)	3081.7(4)
Z	2	8	2	4
μ/mm^{-1}	9.202	0.831	1.174	0.738
T/K	100	100	293	100
θ min/max (˚)	4.191/73.877	1.935/30.543	4.994/72.222	2.051/29.151
Completeness to θ	98.6% to	99.8% to 30.543˚	98.8% to	99.8% to

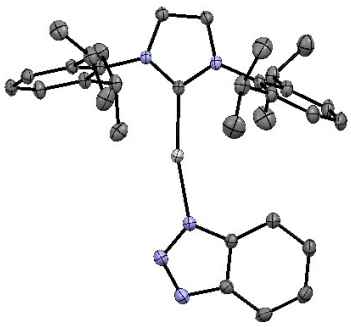
max (%)	73.877°		72.222°	29.151°
Reflections Total/ Independent	34591/6169	916707/9609	6191/5908	89547/7753
Parameters/restraints	375/3	429/7	416/13	361/1
R_{int}	0.0974	0.0523	N/A	0.0538
Final *R*1, *wR*2	0.0586, 0.1401	0.0249, 0.0676	0.0399, 0.1235	0.0249, 0.0647
Goof	1.088	1.095	1.048	1.017
Flack	-	-	-	0.011(9)
Largest peak, hole / e.Å^{-3}	3.592/-1.174	0.5/-0.4	0.2/-0.3	0.3/-0.2
ρ_{calc}/g cm^{-3}	1.552	1.385	1.192	1.233
CCDC Reference	2333564	2333769	2333767	2333768

5.1 Molecular structures of complexes 4a, 5a, 6a, 6b

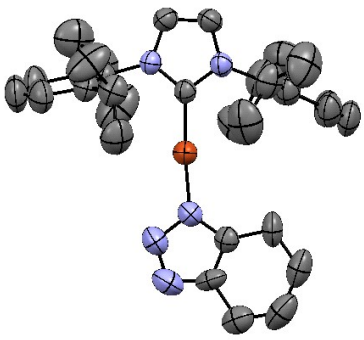
Suitable crystals for single crystal X-ray diffraction analysis were obtained in all cases by slow vapor diffusion of the antisolvent (hexane or pentane) into saturated solutions of the complexes (dichloromethane) at 4-5 °C as colorless blocks. CCDC 2333564, 2333769, 2333767, and 2333768 (**4a**, **5a**, **6a**, **6b**) respectively) contain the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.



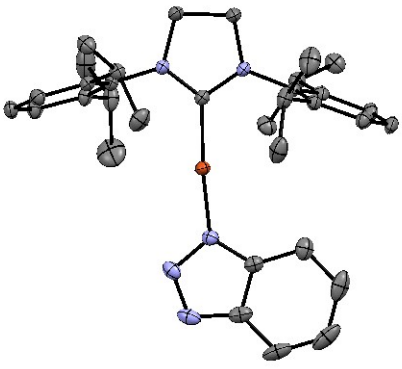
4a



5a



6a



6b

Figure S1: X-ray molecular structures of complexes **4a**, **5a**, **6a**, **6b** are presented, showing thermal displacement ellipsoids at the 50% probability level and hydrogen atoms omitted for clarity.

Selected structural data for these compounds may be found in Table S1. The highest values for M-N and M-C bond lengths as well as the maximum deviation from linear geometry is observed in the case of the silver complex **5a**.

Table S1: Selected bond lengths (Å) and angles (°) for each complex.

Complex	C_{NHC}-M (Å)	M-N (Å)	C_{NHC}-M-N(°)
4a	1.986(6)	2.009(5)	176.5(3)
5a	2.0586(13)	2.0753(11)	168.68(4)
6a	1.8698(15)	1.8568(14)	175.29(5)
6b	1.878	1.861	173.6

6. VT-NMR spectroscopy experiments on complex 5a

The choice of NMR solvent not only affected the resonances' broadness and chemical shifts, but also the number of observed species, as can be seen from the ^{1}H NMR spectra of complex **5a** in THF-d8 and $CDCl_3$ (Figure S2). This (solution) behavior can be rationalized by changes in ligation and/or conformation.

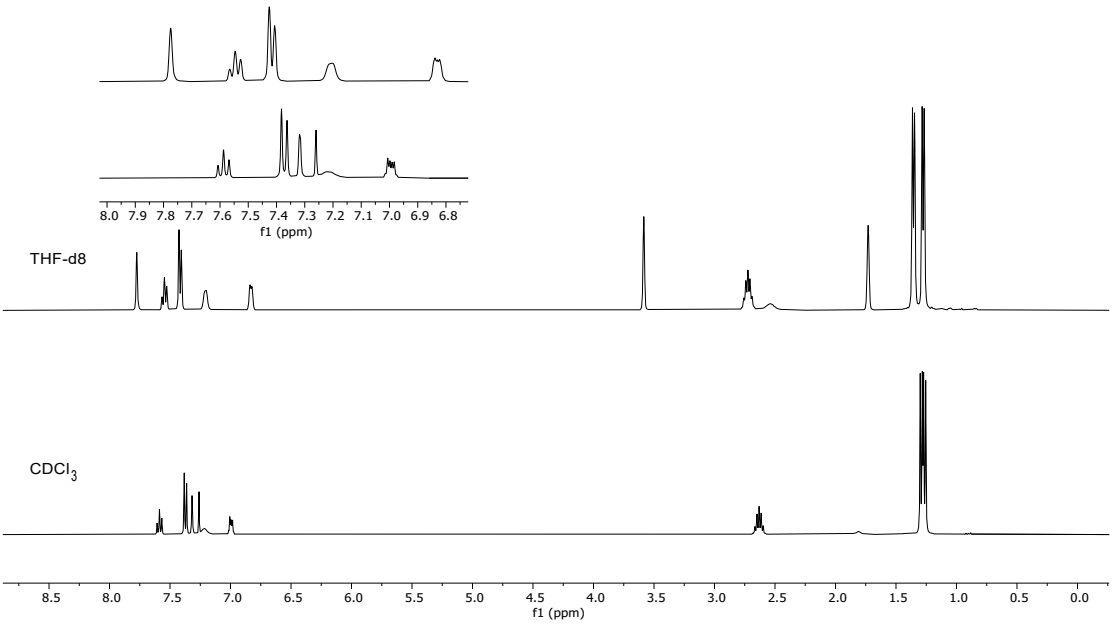
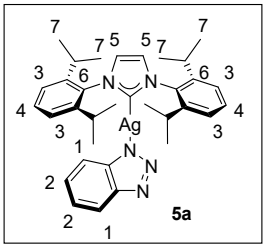


Figure S2: ^{1}H NMR spectra of complex **5a** (400 MHz, 25 °C) both in THF-d8 and $CDCl_3$.

The X-ray structure of **5a** revealed coordination of benzotriazole's nitrogen atom N1. On the other hand, as is shown in Figure S2, dissolving **5a** in THF-d8 resulted one broad signal assigned to the protons 1 of benzotriazole, suggesting, according to the literature, a rapid (on the NMR timescale) exchange between nitrogen atoms N1 and N2.[5] To examine if this is indeed taking place, we performed low/variable temperature NMR experiments, trying to decrease the exchange rate, that could lead to two signals instead of a broad one (Figure S3). All experiments were performed in THF-d8, to avoid freezing of the sample at very low temperatures. The sample was thus cooled to -50 ^{o}C in increments of 10 ^{o}C. However, at temperatures ranging between -50 and 45 ^{o}C, it was not possible to detect that exchange. Therefore, we assume that the only equilibrium taking place is that between N1 and N3 of the benzotriazole, which are equivalent, thus not affording distinct signals in the corresponding NMR spectra. As can be seen in Figure S3, upon gradually going from 25 to -50 ^{o}C, protons 1 are initially broadened, until they disappear completely at -20 ^{o}C. These changes are reversible, that is, when the sample returns to room temperature (25 ^{o}C) the spectrum is exactly the same as it was initially at 25 ^{o}C. When the temperature increases to 35 ^{o}C and 45 ^{o}C sharper benzotriazole signals are obtained, suggesting a quick exchange between N1 and N3 (on the NMR timescale). Moreover, the small amount of water contained in the freshly-opened THF-d8 ampule seems to interact with benzotriazole's N1, N2, and N3, through hydrogen bonds, as can be deduced from the gradual shift and sharpening of its signal.



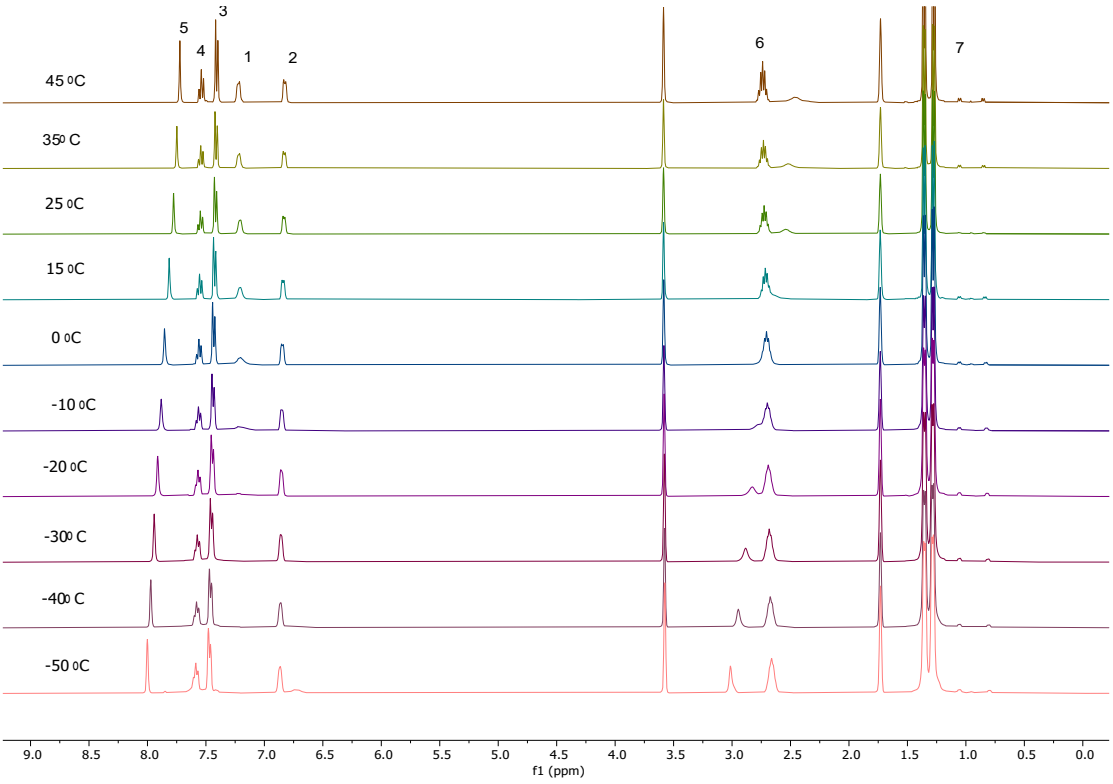


Figure S3: ^{1}H NMR spectra of complex **5a** (400 MHz) at different temperatures in THF-d8. The observed processes are reversible.

7. Synthesis of propargylic amides 7a-f

The synthesis of propargylic amides **7a-f** was performed according to our previously published procedure.[6]

8. General catalytic protocol for cycloisomerization

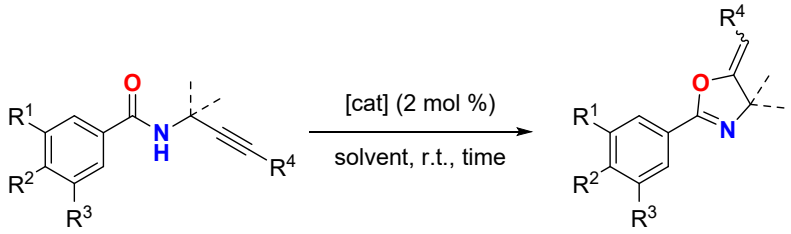
In a 4 mL vial equipped with a stirring bar were added the corresponding propargylic amide **7a-f** (79.6 mg, 0.5 mmol), the catalyst (**5a-b, 6a-b**) and 0.250 mL of solvent. The reaction mixture was stirred at room temperature for the required time. After the reaction was completed, a solution of 1,3,5-trimethoxybenzene in DCM (internal standard) was added. Then, the solvents were removed and the reaction yield was quantified by ^{1}H NMR in $CDCl_3$.

8.1 Optimization reactions for the cyclization of propargylic amides 9a-d

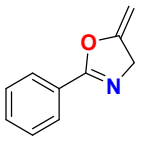
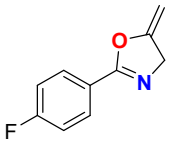
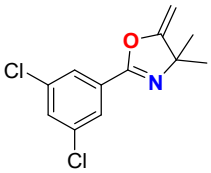
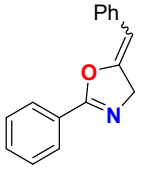
All the reaction of Table S2 were performed according to general catalytic protocol for cycloisomerization (Section 6). In all cases of Table S2, the nonaromatic 5-exo-dig products (**8b-d**, **8f**) were obtained only in HFIP on times varying from 1 to 16 hours. Furthermore, no product formation was observed in the presence of catalyst **2a** and **2b**, enhancing the necessity of the 1H-Benzotriazole moiety in our catalysts. Finally,

propargyl amide **7f** remained unreactive under our reaction conditions and no product was obtained even under heating.

Table S2: Summary of varying catalyst, solvent and time for the intramolecular cyclization of propargylic amides **7b-d** and **7f**.

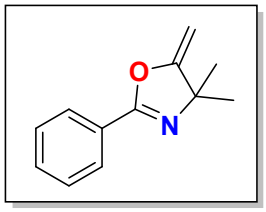


7b-d, 7f **8b-d, 8f**

entry[a]	substituents	[cat]	solvent	time	product	Yield[b]
1	R^1=R^2=R^3=R^4=H	**5a**	DCE	1h	 **8b**	N.R.
2		**5a**	HFIP	1h		36%
3		**5a**	HFIP	16h		67%
4		**5b**	HFIP	16h		96%
5		**6a/6b**	HFIP	16h		N.R.
6		**2a/3a**	HFIP	16h		N.R.
7	R^1= R^3=R^4=H R^2=F	**5a**	DCE	16h	 **8c**	N.R.
8		**5a**	HFIP	16h		90%
9		**5b**	HFIP	16h		83%
10		**6a**	HFIP	16h		16%
11		**6b**	HFIP	16h		5%
12		**2a/2b**	HFIP	16h		N.R.
13	R^1= R^3= Cl R^4=R^2=H	**5a**	DCE	16h	 **8d**	30
14		**5a**	HFIP	16h		>99%
15		**5a**	HFIP	1h		>99%
16		**5b**	HFIP	1h		90%
17		**6a/6b**	HFIP	1h		>99%
18		**2a/2b**	HFIP	1h		N.R.
19	R^1= R^3= R^2=H R^4=Ph	**5a**	HFIP	16h	 **8f**	N.R.
20[c]		**5a**	HFIP	16h		N.R.
21		**5a**	DCE	16h		N.R.

[a] Reaction conditions: 0.5 mmol of **9a-d**, 0.01 mmol (2 mol%) catalyst, 0.250 mL of solvent, 25 °C, time, under. [b] the reaction yields were determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [c] the reaction was heated at 50 ^{0}C in an oil bath.

8.2 Synthesis of 4,4-dimethyl-5-methylene-2-phenyl-4,5-dihydrooxazole (8a)



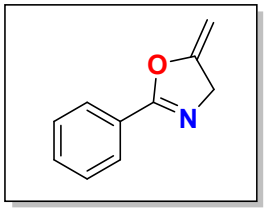
In a 4 mL vial equipped with a stirring bar were added propargylic amide **7a** (94.0 mg, 0.5 mmol), catalyst **5a** (6.2 mg, 2 mol%) and 0.250 mL of DCE. The reaction mixture was stirred at room temperature for 1 hour and then, the solvent was removed under vacuum. A total of 15 mL of pentane were used to precipitate the Ag complex and filter the mixture through a silica gel plug (ca. 2 cm). The solvent was removed again and the desired product **8a** was isolated as a white of solid in 97% yield (91.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.99 (d, J = 7.6 Hz, 2H, CH_{Ar}), 7.49 (m, 1H, CH_{Ar}), 7.42 (m, 2H, CH_{Ar}), 4.74 (d, J = 2.9 Hz, 1H, CH), 4.24 (d, J = 2.8 Hz, 1H, CH), 1.45 (s, 6H, CH_3).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) = 168.0, 159.9, 131.7, 128.5, 128.2, 127.0, 82.4, 69.1, 29.8.

Analytical data obtained are in agreement with the literature.

8.3 Synthesis of 2-phenyl-5-methylene-4,5-dihydrooxazole (8b)



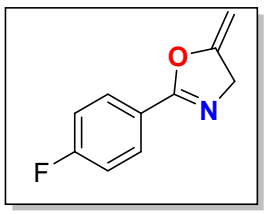
In a 4 mL vial equipped with a stirring bar were added propargylic amide **7b** (80.0 mg, 0.5 mmol), catalyst **5a** (6.2 mg, 2 mol%) and 0.250 mL of HFIP. The reaction mixture was stirred at room temperature for 16 hours and then, the solvent was removed under vacuum. The reaction mixture was further purified by column chromatography (cyclohexane/EtOAc= 5/1) and the desired product **8b** was isolated as a colorless oil in 67% yield (54.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.97 (d, J = 7.1 Hz, 2H, CH_{Ar}), 7.54 (m, 1H, CH_{Ar}), 7.45 (m, 2H, CH_{Ar}), 4.87 (q, J = 3.1 Hz, 1H, CH), 4.63 (d, J = 3.1 Hz, 2H, CH_2), 4.42 (q, J = 2.8 Hz, 1H, CH).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) = 164.7, 158.2, 132.3, 128.7, 128.2, 126.2, 84.5, 57.1.

Analytical data obtained are in agreement with the literature.[7]

8.4 Synthesis of 2-(4-fluorophenyl)-5-methylene-4,5-dihydrooxazole (8c)



In a 4 mL vial equipped with a stirring bar were added propargylic amide **7c** (88.6 mg, 0.5 mmol), catalyst **5a** (6.2 mg, 2 mol%) and 0.250 mL of HFIP. The reaction mixture was stirred at room temperature for 16 hours and then, the solvent was removed under vacuum. A total of 15 mL of pentane were used

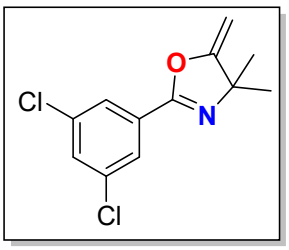
to precipitate the Ag complex and filter the mixture through a silica gel plug (ca. 2 cm). The solvent was removed again and the desired product **8c** was isolated as a white solid in 90% yield (78.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.95 (m, 2H, CH_{Ar}), 7.11 (t, J = 8.4 Hz, 2H, CH_{Ar}), 4.83 (m, 1H, CH), 4.59 (d, J = 3.3 Hz, 2H, CH_2), 4.39 (m, 2H, CH).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) = 166.4, 163.9, 163.3, 158.5, 130.5, 130.4, 116.0, 115.9, 115.7, 84.3, 57.5.

Analytical data obtained are in agreement with the literature.[6,8]

8.5 Synthesis of 2-(3,5-dichlorophenyl)-4,4-dimethyl-5-methylene-4,5-dihydrooxazole (8d)



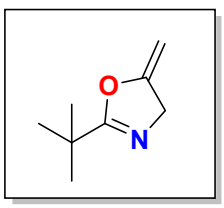
In a 4 mL vial equipped with a stirring bar were added propargylic amide **7d** (128.1 mg, 0.5 mmol), catalyst **5a** (6.2 mg, 2 mol%) and 0.250 mL of HFIP. The reaction mixture was stirred at room temperature for 1 hour and then, the solvent was removed under vacuum. A total of 15 mL of pentane were used to precipitate the Ag complex and filter the mixture through a silica gel plug (ca. 2 cm). The solvent was removed again and the desired product **8d** was isolated as a colorless oil in 99% yield (128.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.86 (m, 2H, CH_{Ar}), 7.46 (m, 1H, CH_{Ar}), 4.75 (d, J = 3.1 Hz, 1H, CH), 4.27 (d, J = 3.1 Hz, 1H, CH), 1.43 (s, 6H, CH_3).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) = 167.4, 157.8, 135.4, 131.5, 129.9, 126.5, 83.3, 69.5, 29.7.

Analytical data obtained are in agreement with the literature.[6]

8.6 Synthesis of 2-(tert-butyl)-5-methylene-4,5-dihydrooxazole (8e)



In a 4 mL vial equipped with a stirring bar were added propargylic amide **7b** (70.0 mg, 0.5 mmol), catalyst **5a** (6.2 mg, 2 mol%) and 0.250 mL of HFIP. The reaction mixture was stirred at room temperature for 16 hours and then, the solvent was removed under vacuum. The reaction was monitored by ^{1}H NMR spectroscopy and the yield determined by integration and comparison with the internal standard.

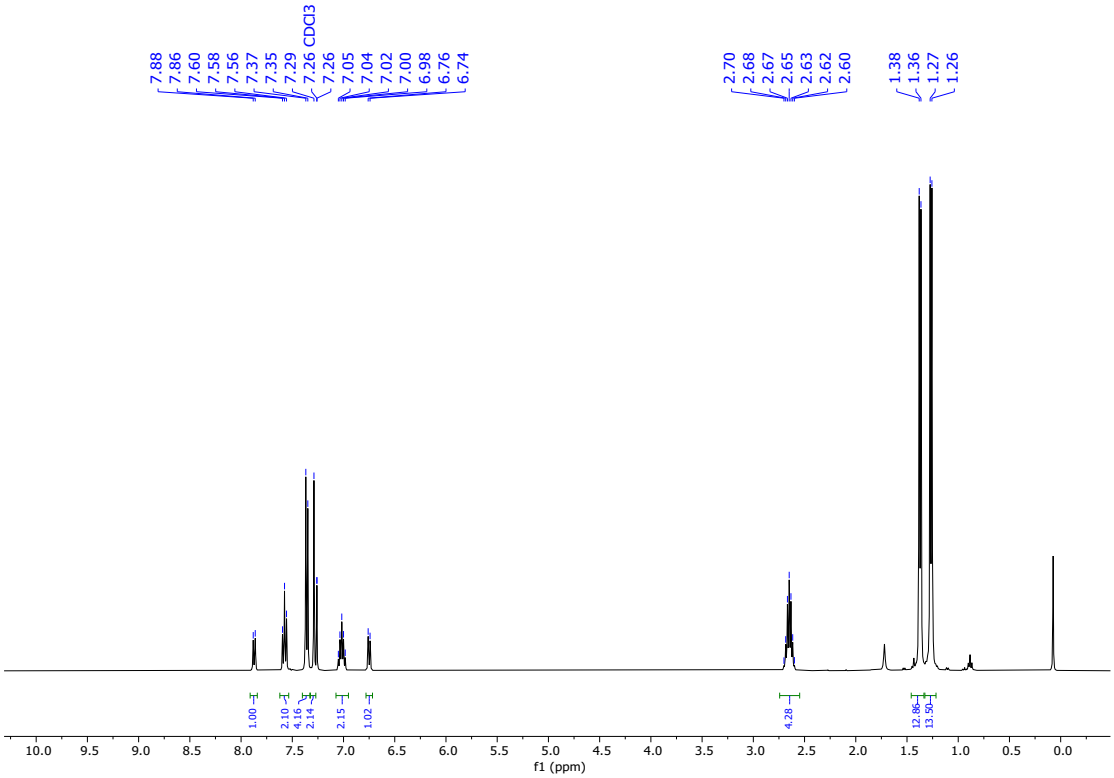
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.73 (m, 1H, CH), 4.39 – 4.26 (m, 3H, CH and CH_2), 1.25 (s, 9H, $(CH_3)_3$).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) = 175.4, 158.4, 83.8, 56.3, 33.5, 27.1.

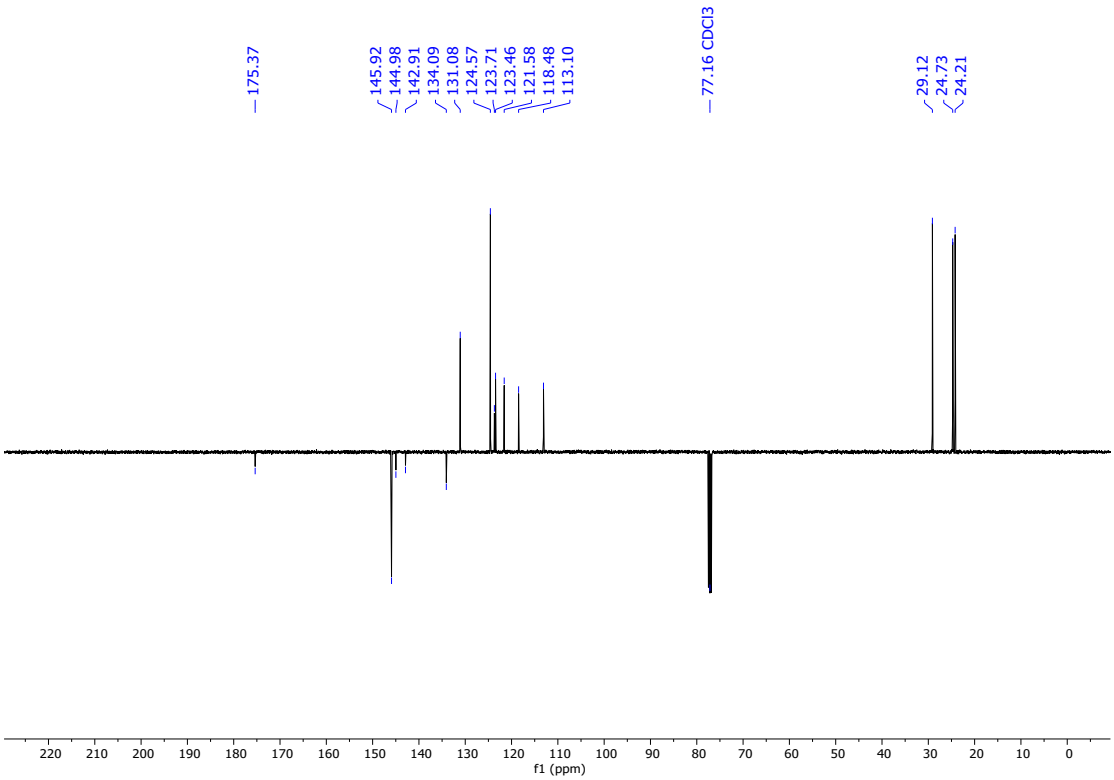
Analytical data obtained are in agreement with the literature.[6,8]

9. Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of complexes 4a, 5a,b and 6a,b and compounds 8a-e

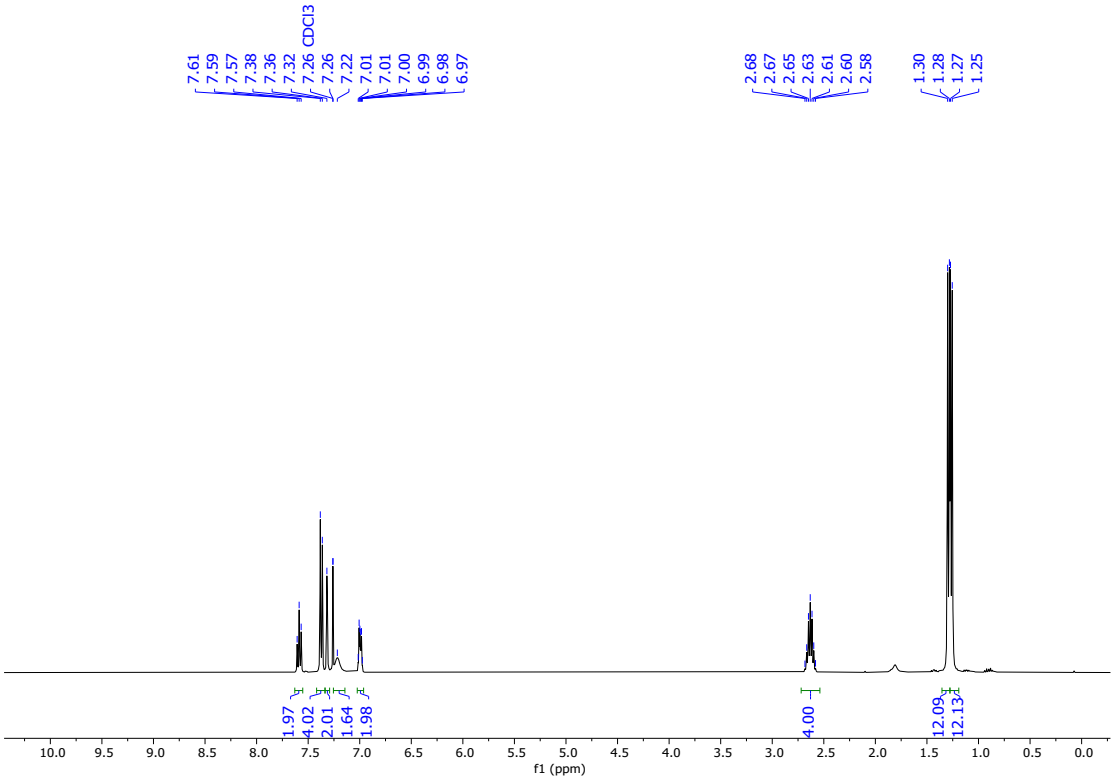
^{1}H NMR (400 MHz, $CDCl_3$) of 4a:



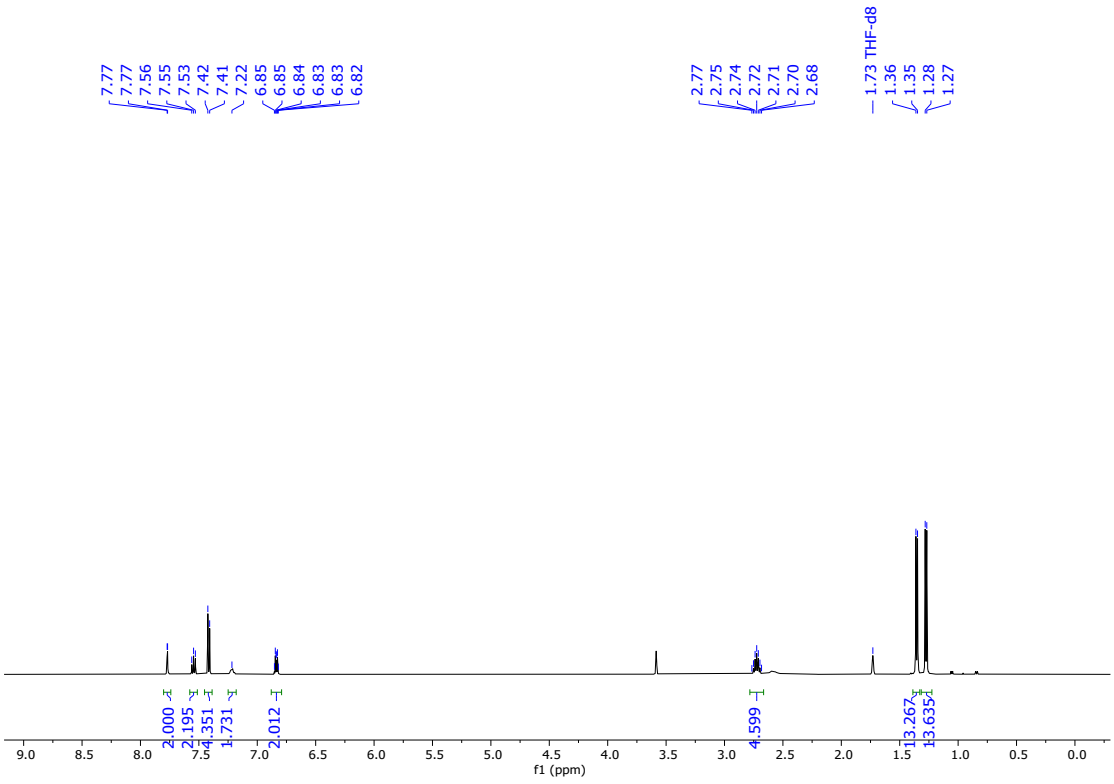
$^{13}C\{^{1}H\}$, DEPT-Q NMR (101 MHz, $CDCl_3$) of 4a:



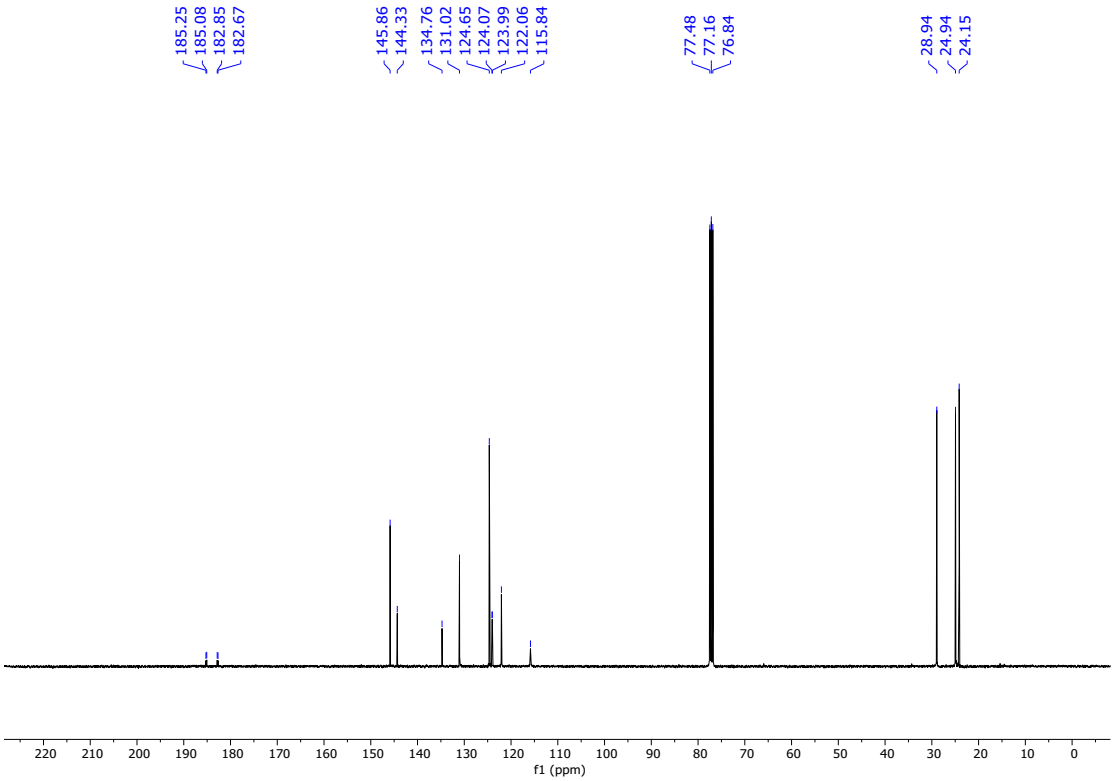
^{1}H NMR (400 MHz, $CDCl_3$) of 5a:



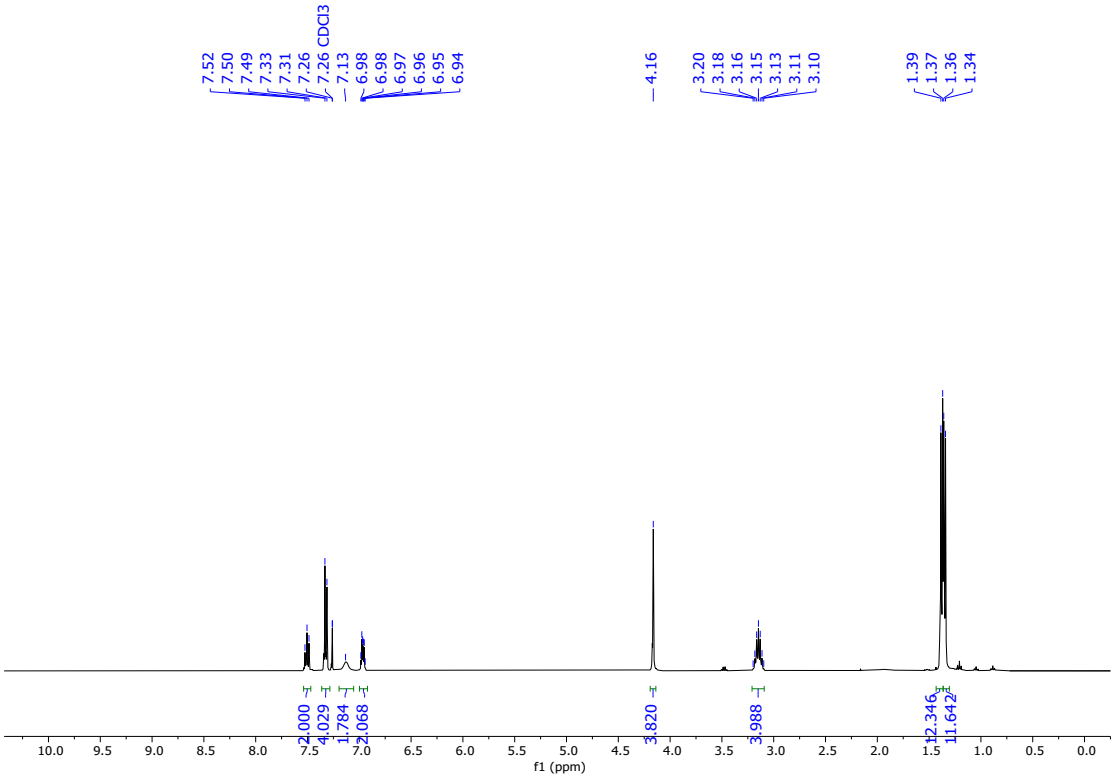
^{1}H NMR (500 MHz, THF-d8) of 5a:



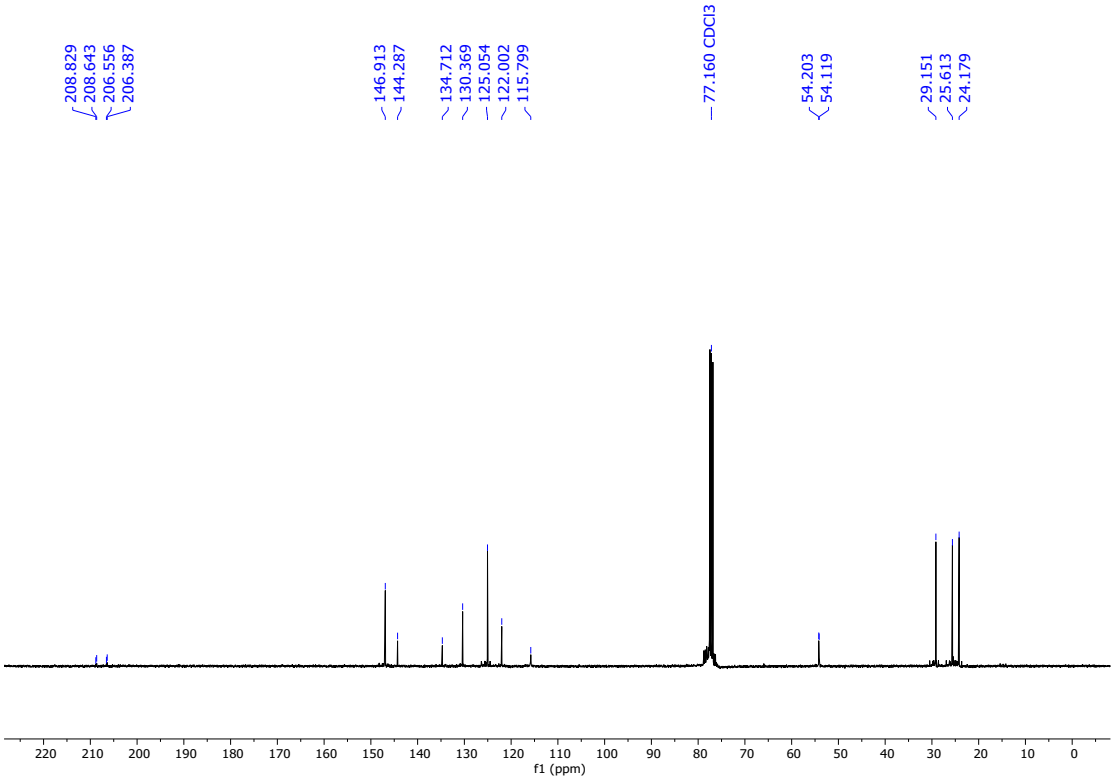
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of 5a:



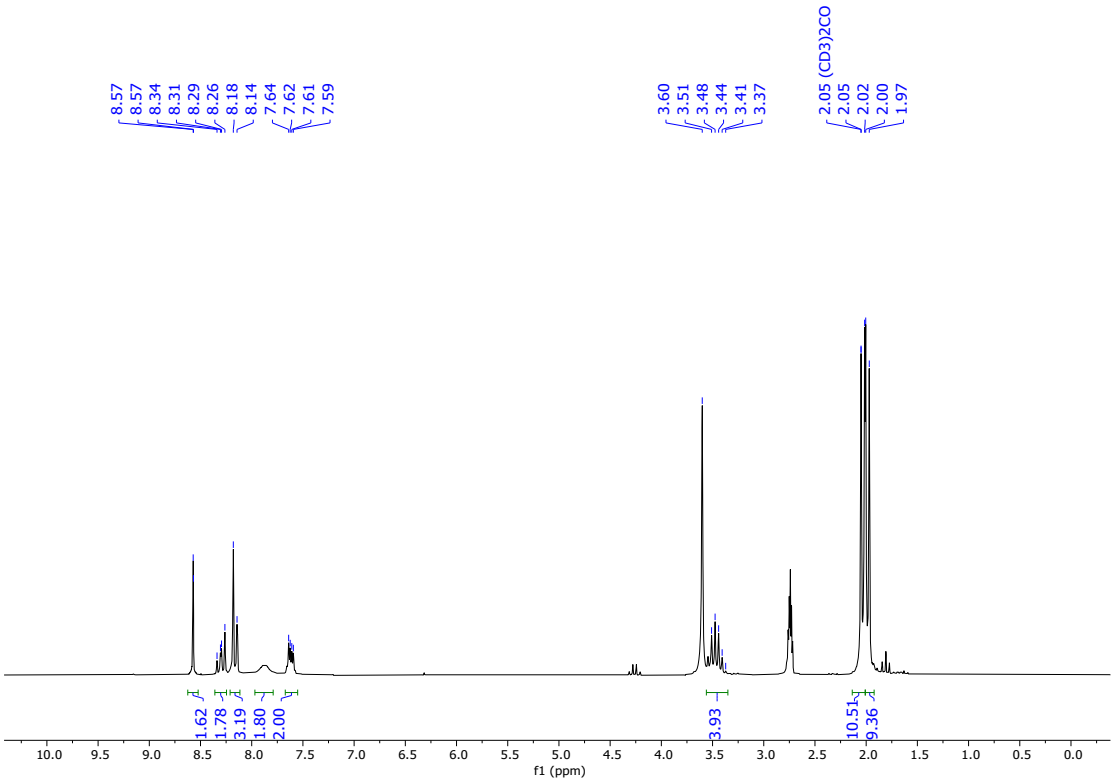
^{1}H NMR (400 MHz, $CDCl_3$) of 5b:



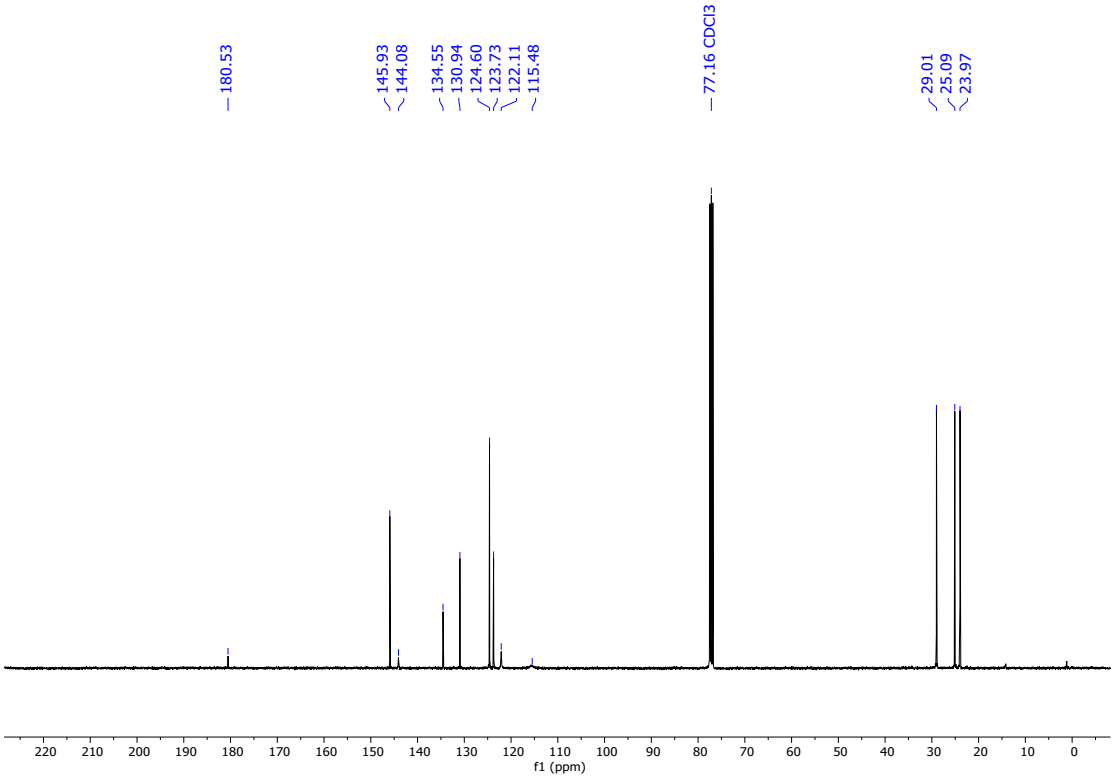
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 5b:



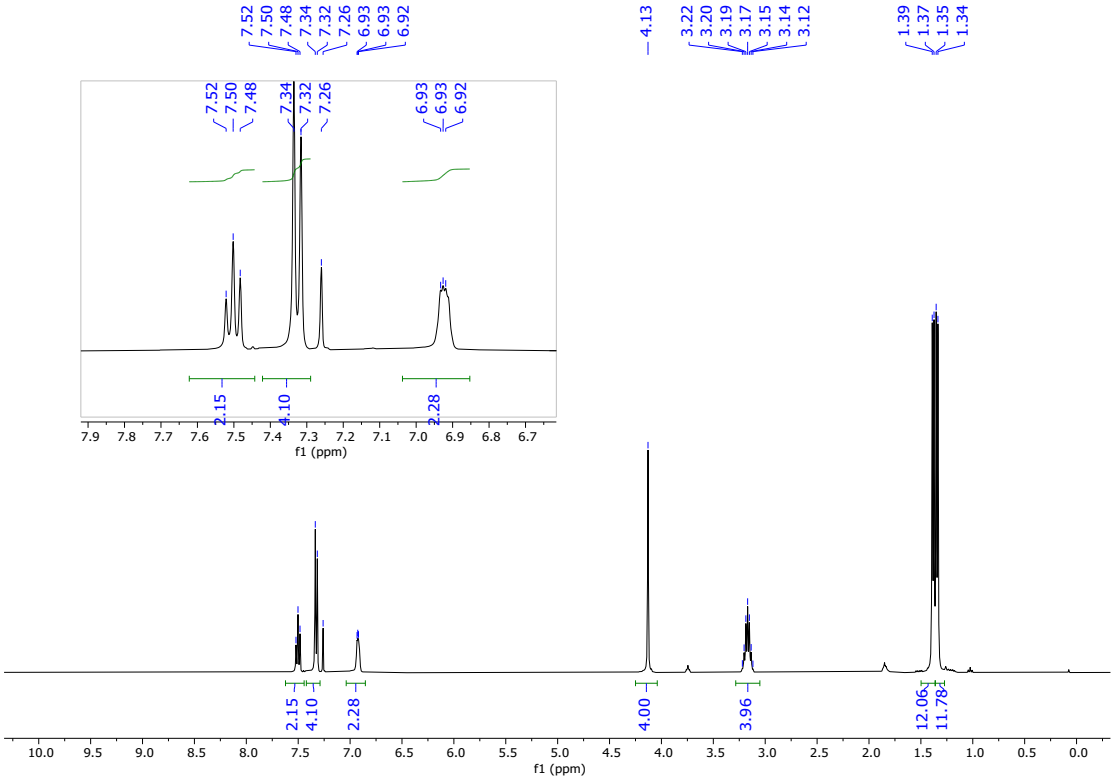
^{1}H NMR (200 MHz, acetone-d6) of 6a:



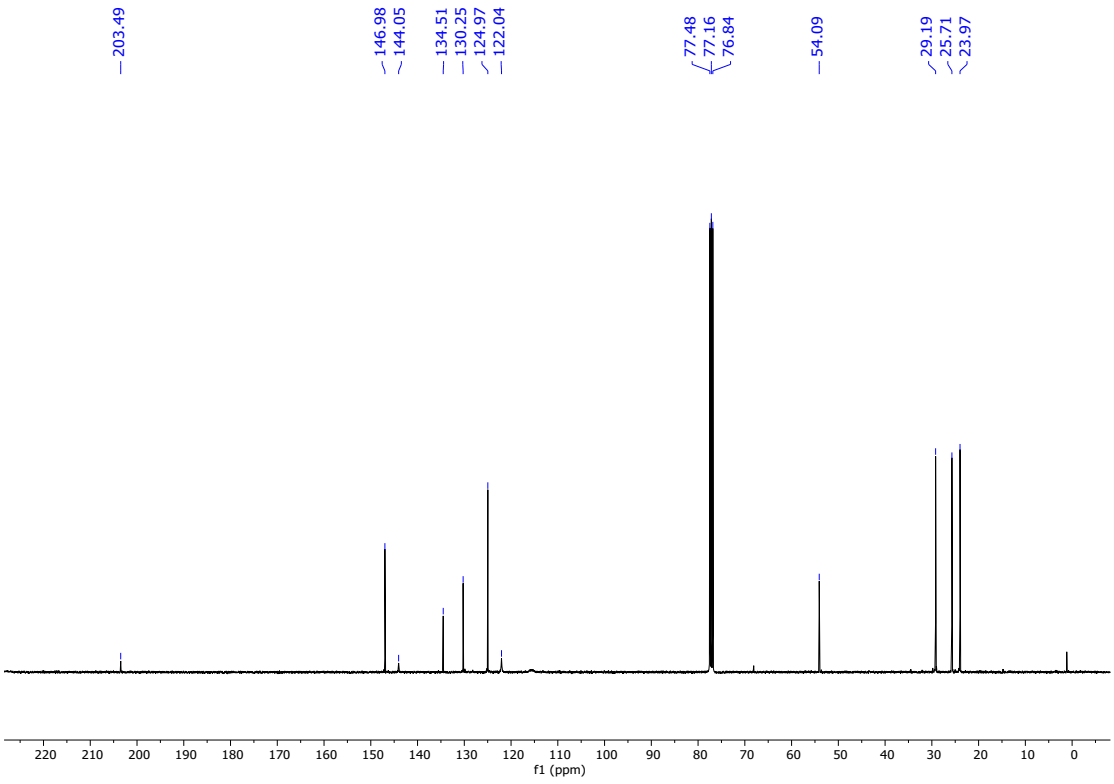
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 6a:



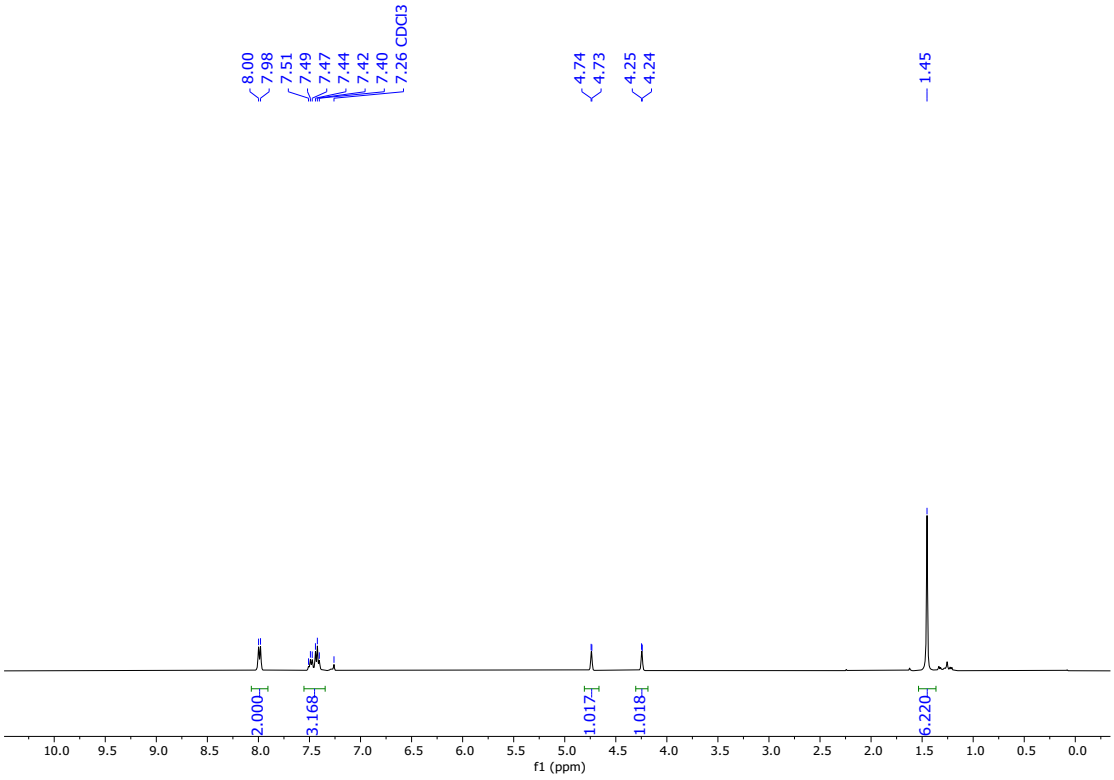
^{1}H NMR (400 MHz, $CDCl_3$) of 6b:



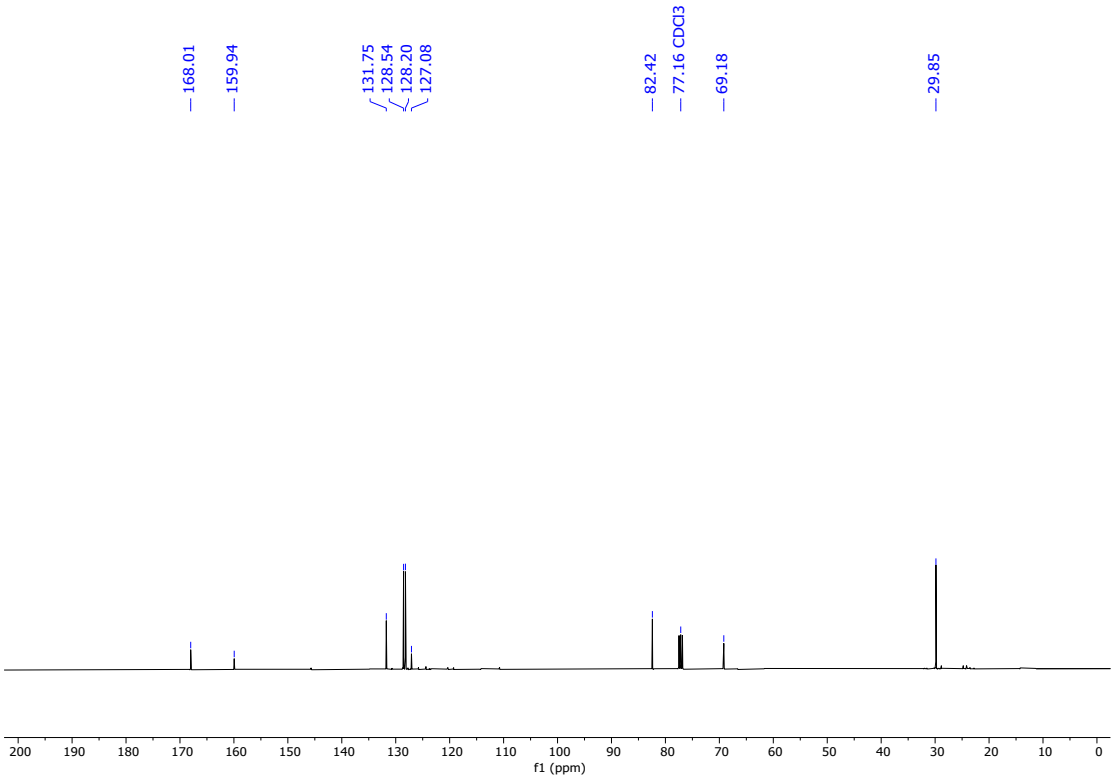
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 6b:



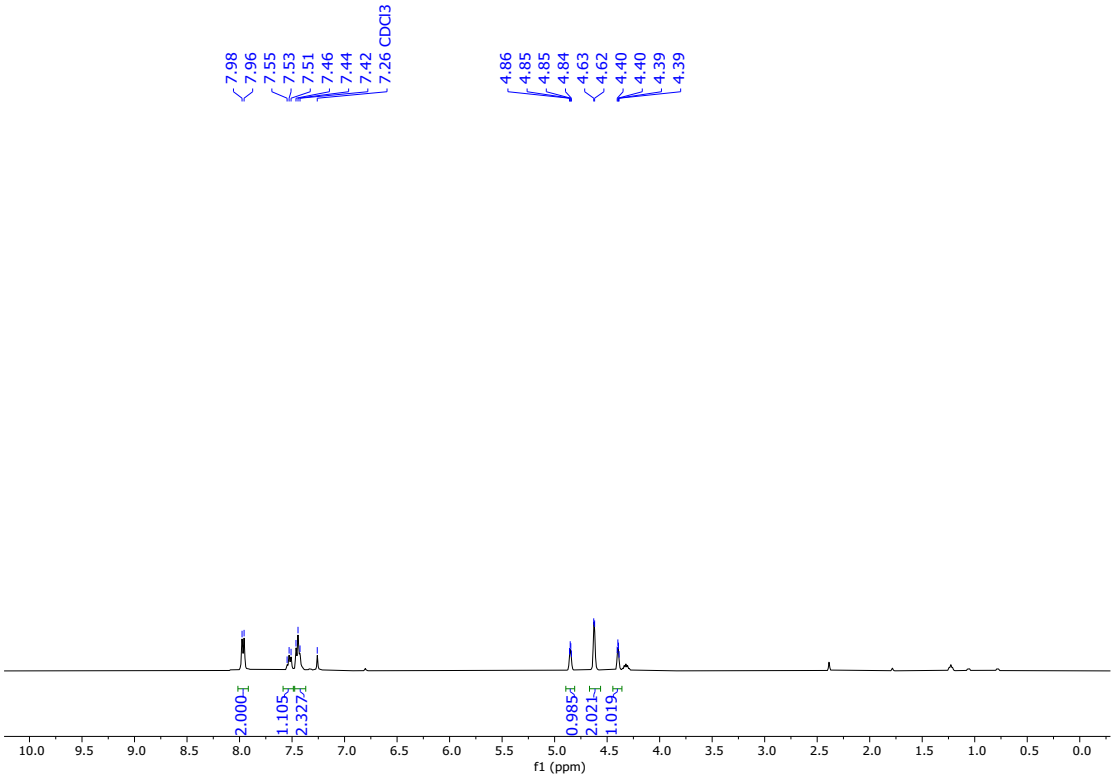
^{1}H NMR (400 MHz, $CDCl_3$) of 8a:



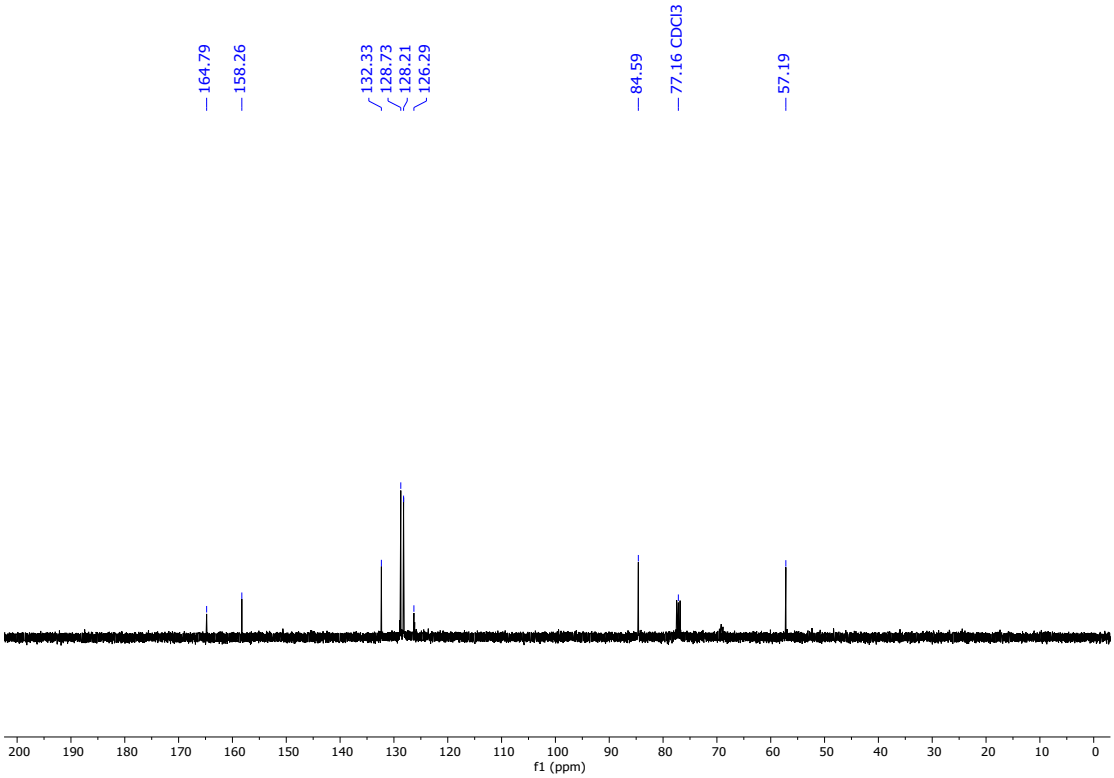
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 8a:



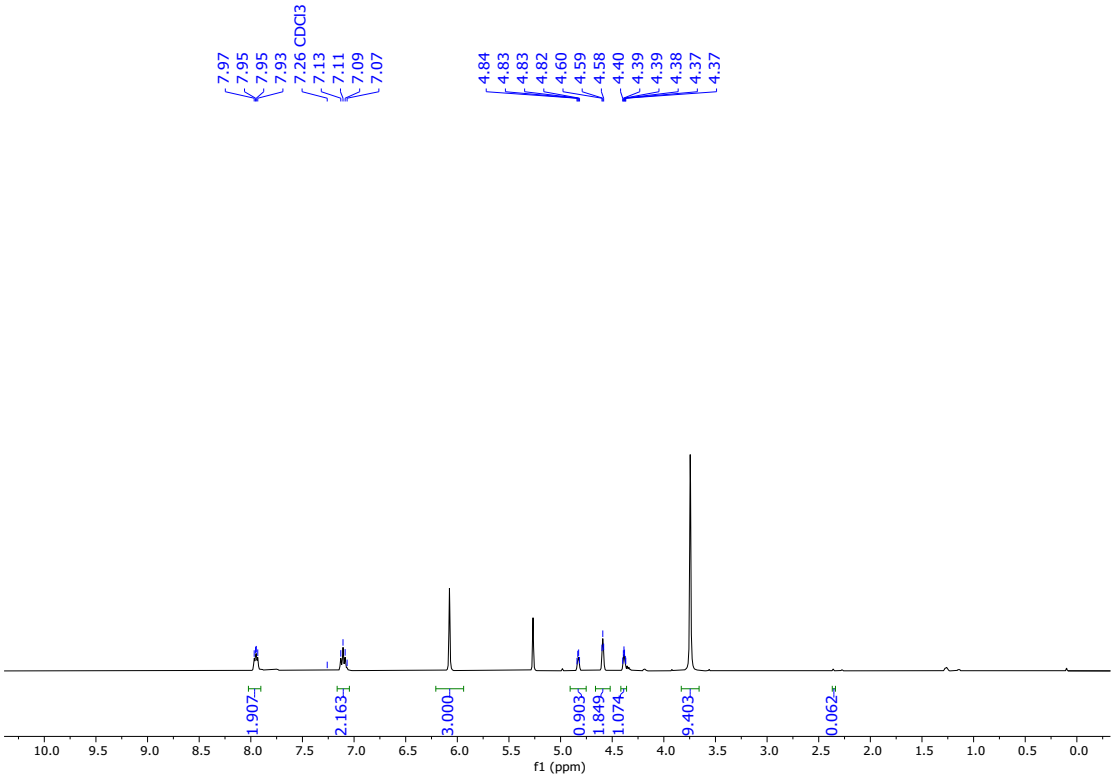
^{1}H NMR (400 MHz, $CDCl_3$) of 8b:



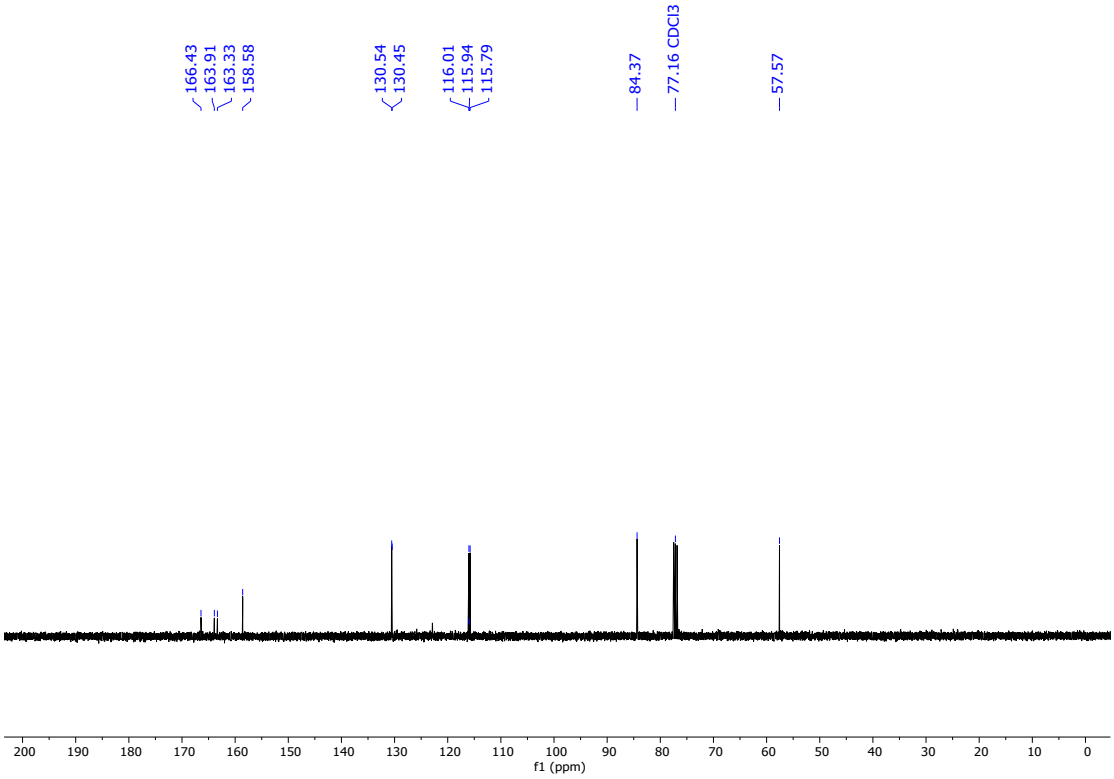
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 8b:



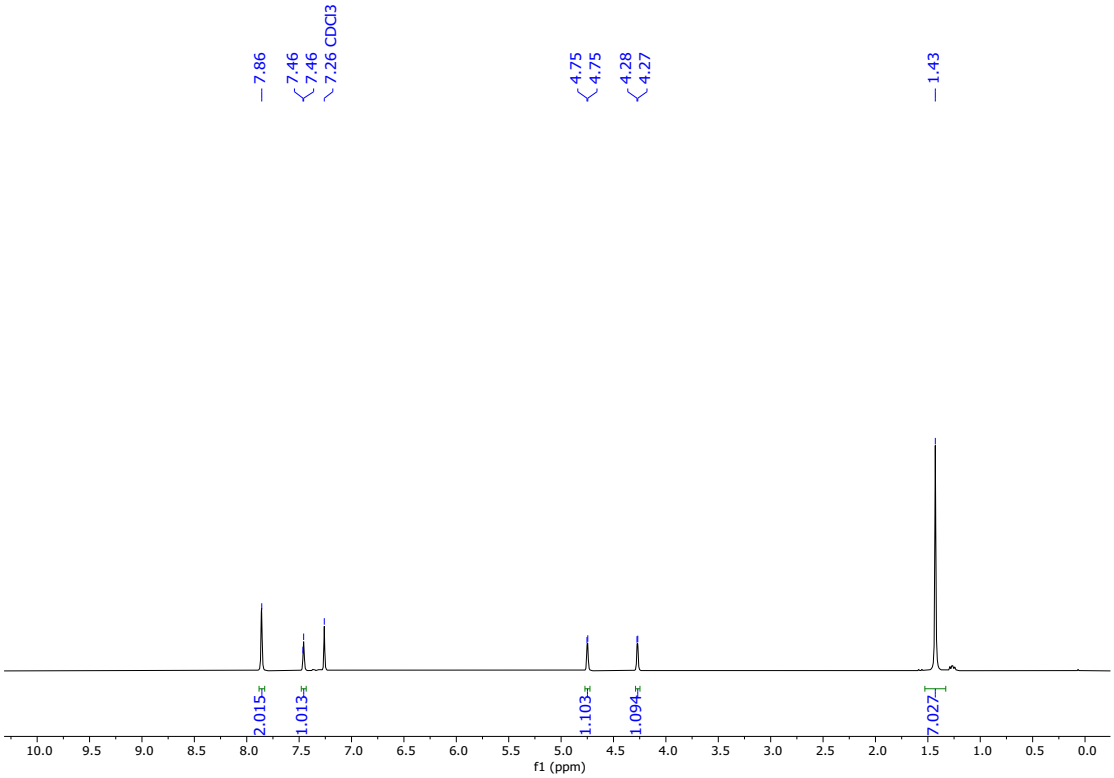
^{1}H NMR (400 MHz, $CDCl_3$) of 8c:



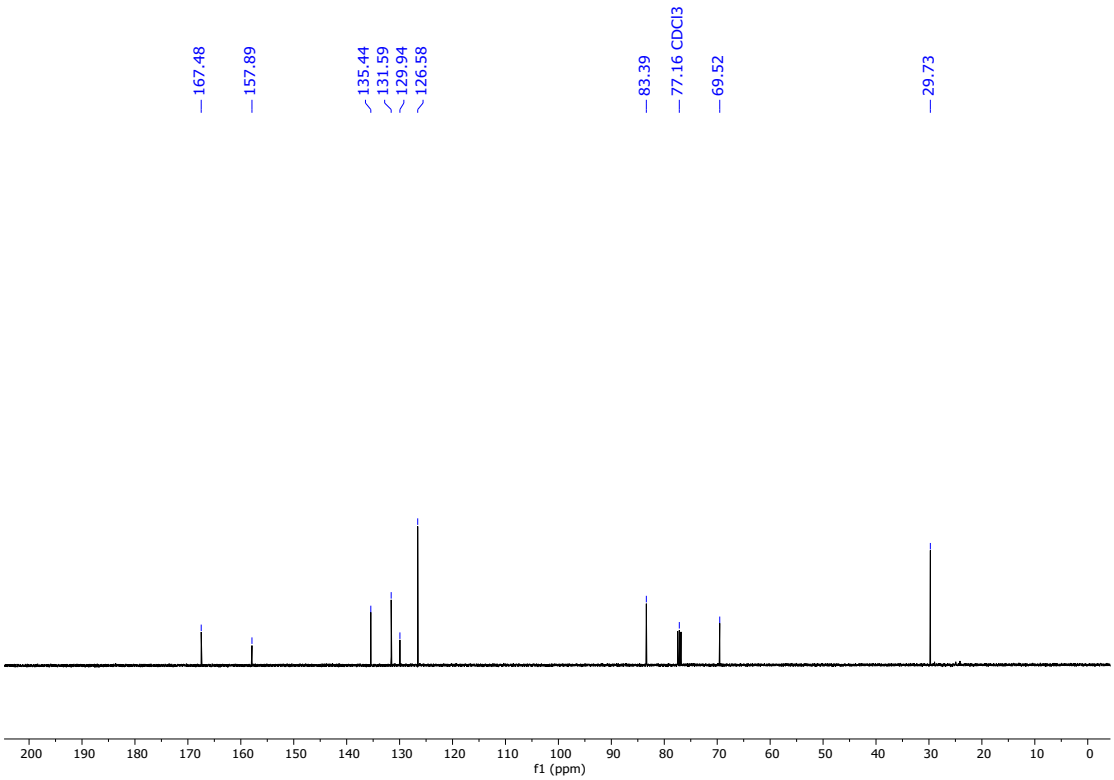
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 8c:



^{1}H NMR (400 MHz, $CDCl_3$) of 8d:



$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 8d:



10. General procedure for the hydrosilylation of carbonyl compounds

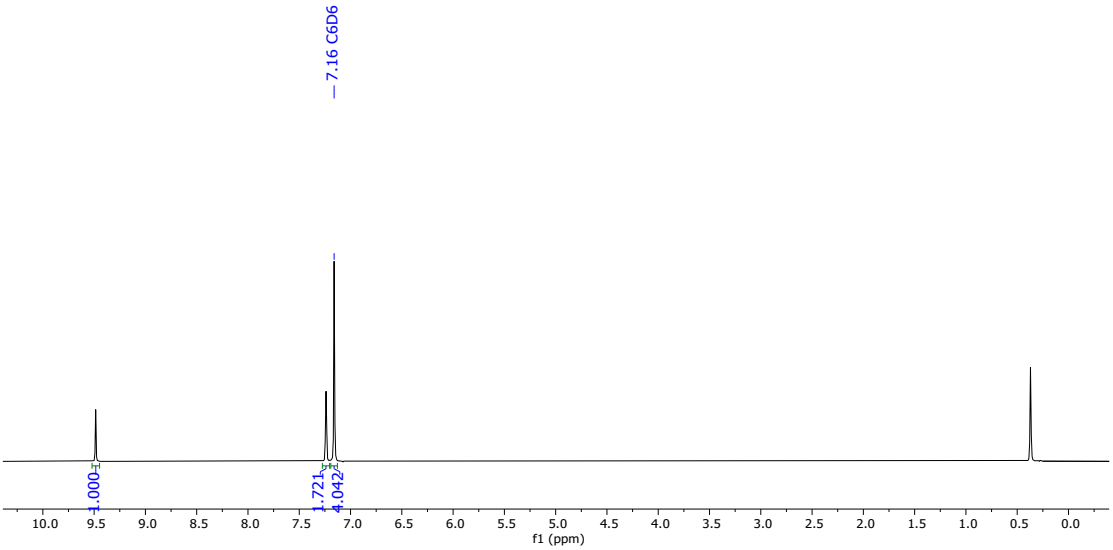
In a 4 mL screw capped, flame dried vial, equipped with a stirring bar, were added the corresponding carbonyl compounds (0.5 mmol), Ph_2SiH_2 (1.5 mmol), the catalyst (2 mol%) and 0.250 mL of benzene-d_6, under an atmosphere of argon. The reaction mixture was stirred at room temperature for the required time. Then, 1,3,5-trimethoxybenzene (0.5 mmol) was added and the reaction stirred for another 2 minutes. The reaction mixture was moved in amber J. Young NMR tube and the reaction yield was quantified by ^{1}H NMR spectroscopy.

10.1 Typical quenching reaction for the hydrosilylations

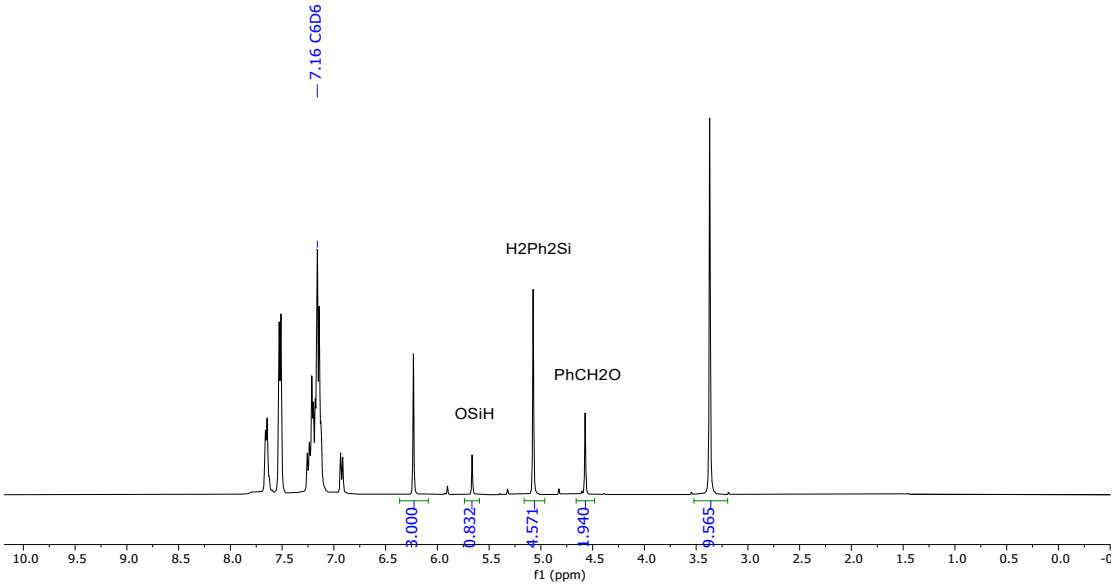
In a 4 mL screw capped, flame dried vial, equipped with a stirring bar, were added the corresponding carbonyl compounds (0.5 mmol), Ph_2SiH_2 (1.5 mmol), the catalyst (2 mol%) and 0.250 mL of benzene-d_6, under an argon atmosphere. The reaction mixture was stirred at room temperature for the required time and then, was cooled to 0 ^{o}C with an ice bath. Continuously, a solution of TBAF (1.1 equiv., 1M solution in THF) was added dropwise and the reaction was left stirred at room temperature. The completion of the reaction was monitored by TLC. Then, in the reaction was added water and the product was extracted with DCM many times. The combined organic phases were dried over anhydrous Na_2SO_4, filtered and evaporated in vacuo. The crude mixture was quantified by ^{1}H NMR in $CDCl_3$, using 1,3,5-trimethoxybenzene (0.5 mmol) as internal standard.

10.2 ^{1}H NMR spectra of hydrosilylation of 4-bromobenzaldehyde

- ^{1}H NMR spectra of 4-Bromobenzaldehyde before addition of Ph_2SiH_2 and catalyst **5a**



- ^{1}H NMR spectra of the reaction mixture after 2 hours
- Conversion: 100%, Yield: 95%



- ^{1}H NMR spectra of the reaction mixture after quench

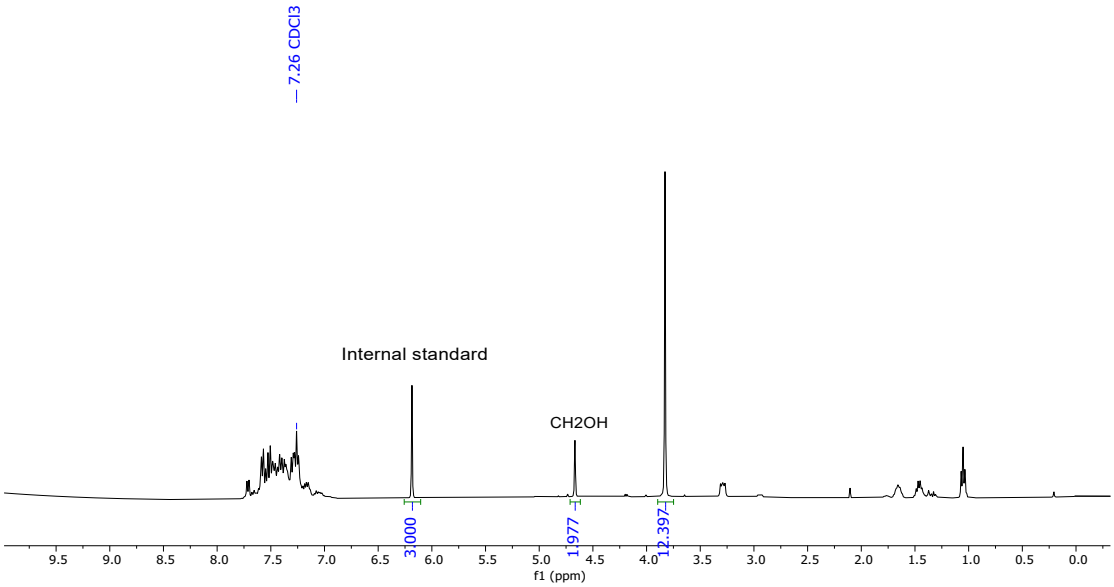


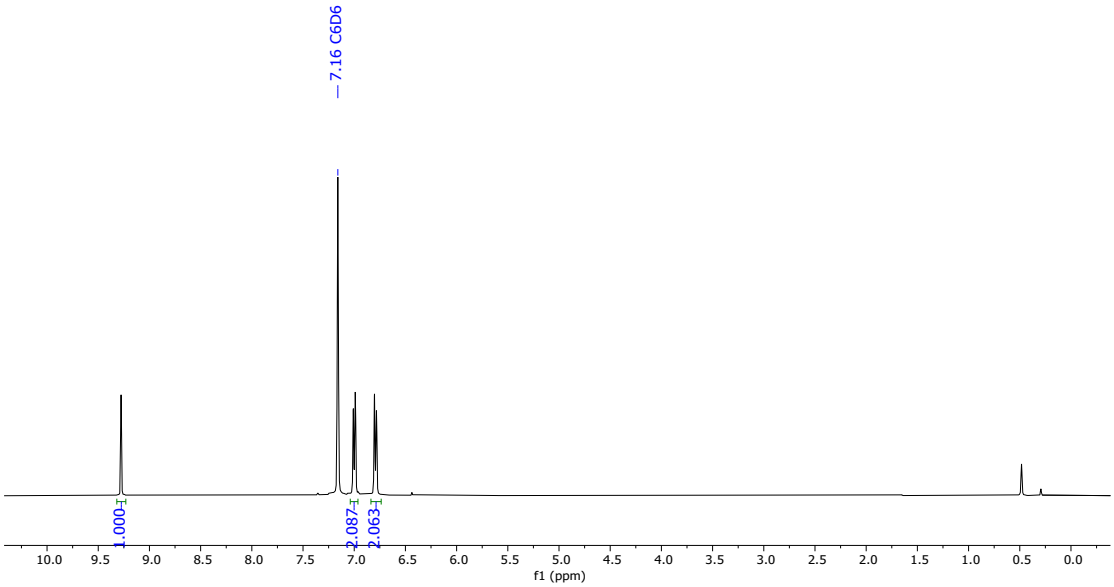
Figure S4: A) ^{1}H NMR of 4-Bromobenzaldehyde in C_6D_6. B) ^{1}H NMR in overlay of catalytic hydrosilylation of 4-Bromobenzaldehyde with Ph_2SiH_2 using **5a** (2 mol%) in C_6D_6. C) ^{1}H NMR of 4-Bromobenzyl alcohol, mixture of products resulting from the quench of **10a** with TBAF, in $CDCl_3$.

^{1}H NMR (400 MHz, $CDCl_3$) of **11a**: δ 7.48 (d, J = 8.4 Hz, 2H, CH_{Ar}), 7.23 (d, J = 8.0 Hz, 2H, CH_{Ar}), 4.64 (s, 2H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) of **11a**: δ 139.8, 131.7, 128.7, 121.5, 64.6.

10.3 ^{1}H NMR spectra of hydrosilylation of 4-cyanobenzaldehyde

- ^{1}H NMR spectra of 4-Cyanobenzaldehyde before addition of Ph_2SiH_2 and catalyst **5a**



- ^{1}H NMR spectra of the reaction mixture after 2 hours
- Conversion: 100%, Yield: 75%

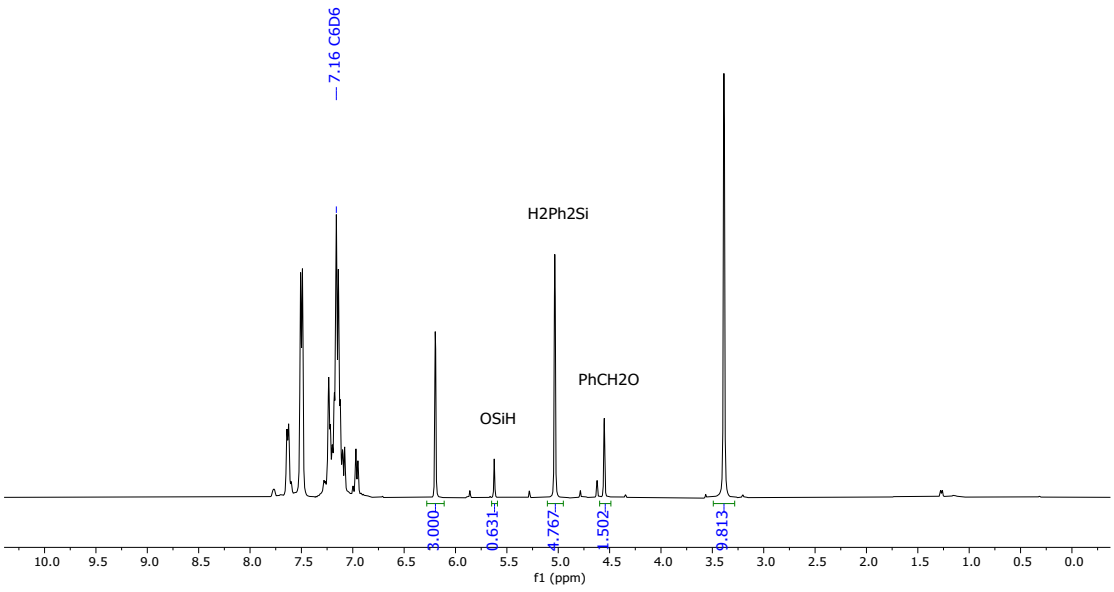
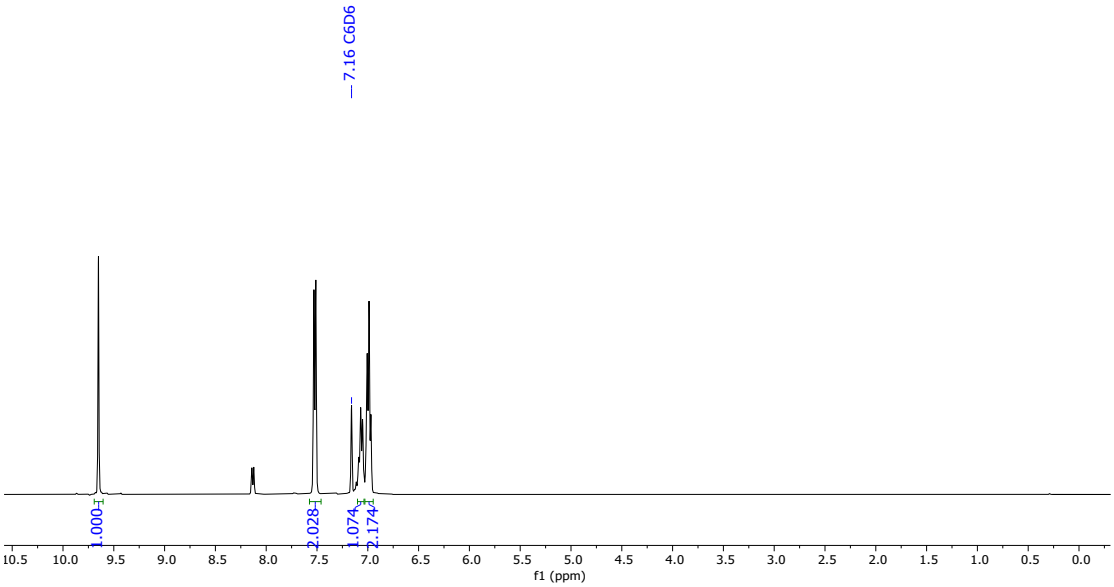


Figure S5: A) ^{1}H NMR of 4-Cyanobenzaldehyde C_6D_6. B) ^{1}H NMR in overlay of catalytic hydrosilylation of 4-Cyanobenzaldehyde with Ph_2SiH_2 using **5a** (2 mol%) in C_6D_6.

10.4 ^{1}H NMR spectra of hydrosilylation of benzaldehyde

- ^{1}H NMR spectra of Benzaldehyde before addition of Ph_2SiH_2 and catalyst **5a**



- ^{1}H NMR spectra of the reaction mixture after 2 hours
- Conversion: 100%, Yield: >99%

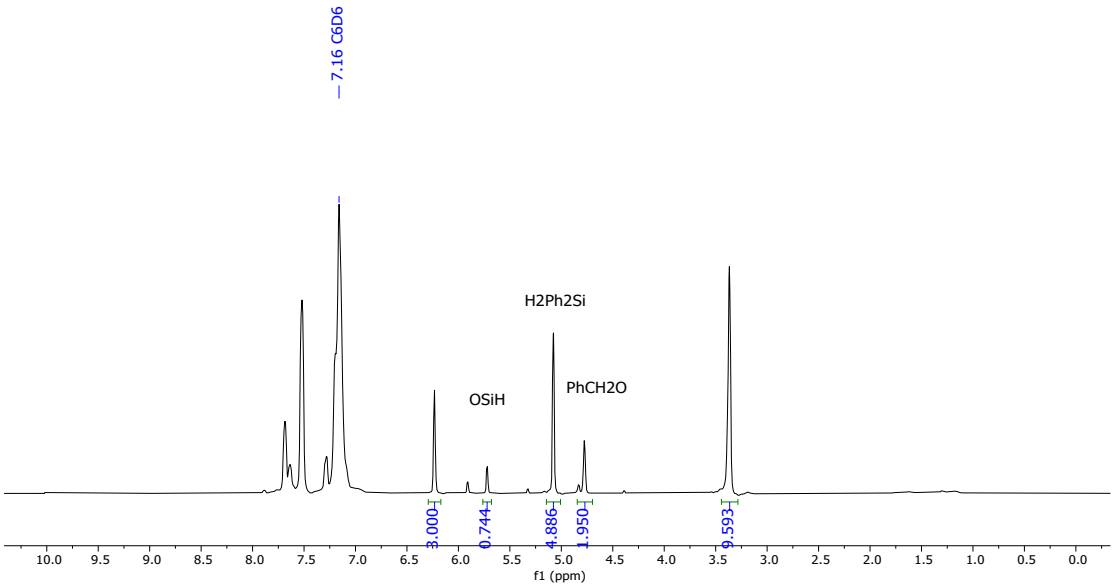
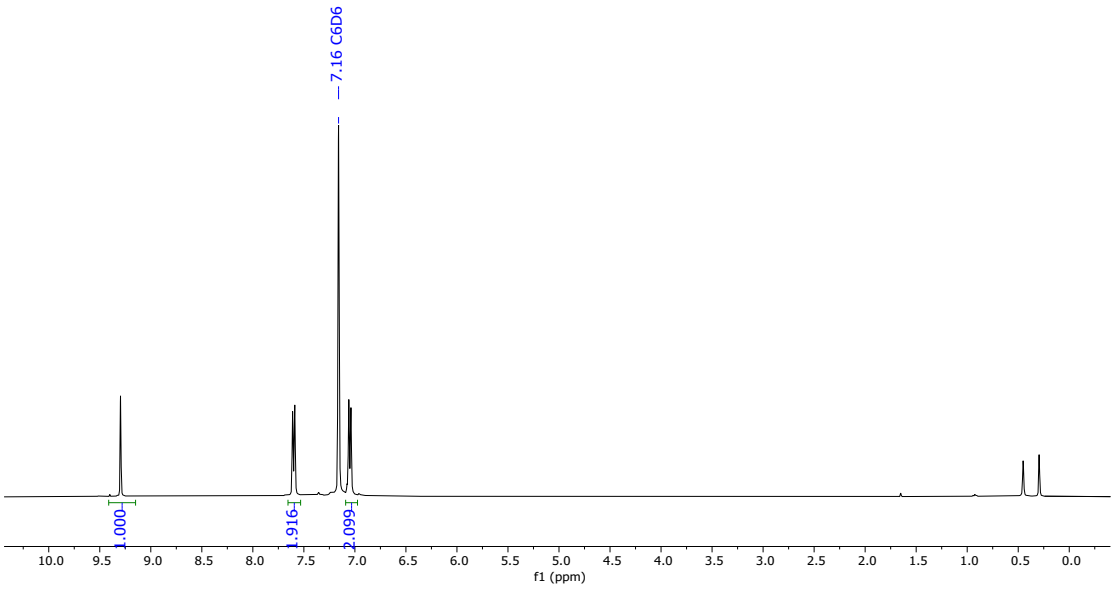


Figure S6: A) ^{1}H NMR of Benzaldehyde C_6D_6. B) ^{1}H NMR in overlay of catalytic hydrosilylation of Benzaldehyde with Ph_2SiH_2 using **5a** (2 mol%) in C_6D_6.

10.5 ^{1}H NMR spectra of hydrosilylation of 4-nitrobenzaldehyde

- ^{1}H NMR spectra of 4-Nitrobenzaldehyde before addition of Ph_2SiH_2 and catalyst **5a**



- ^{1}H NMR spectra of the reaction mixture after 2 hours
- Conversion: 100%, Yield: 75%

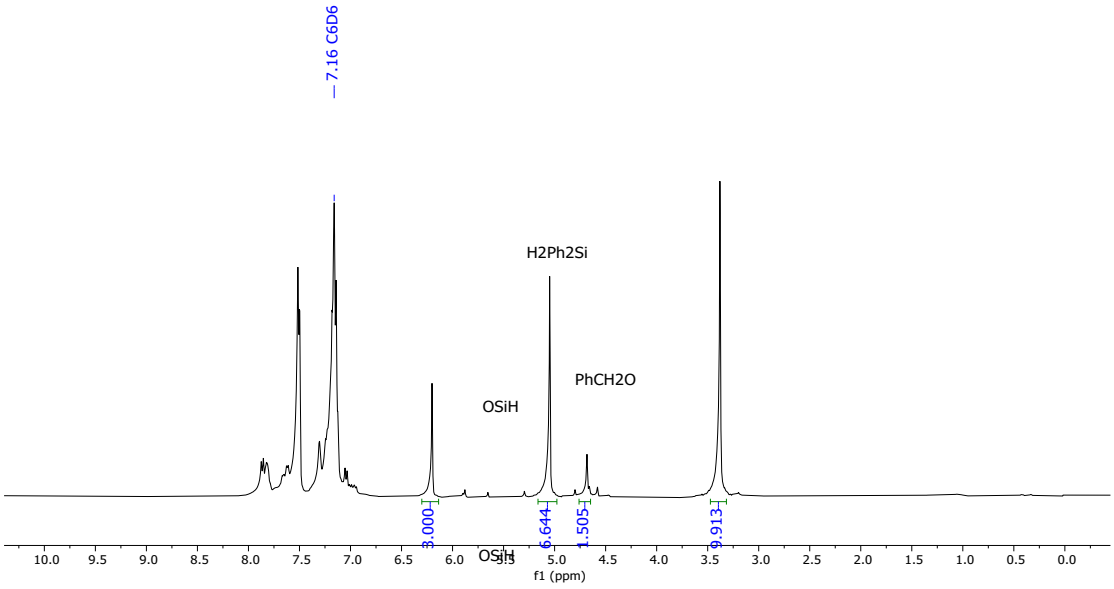
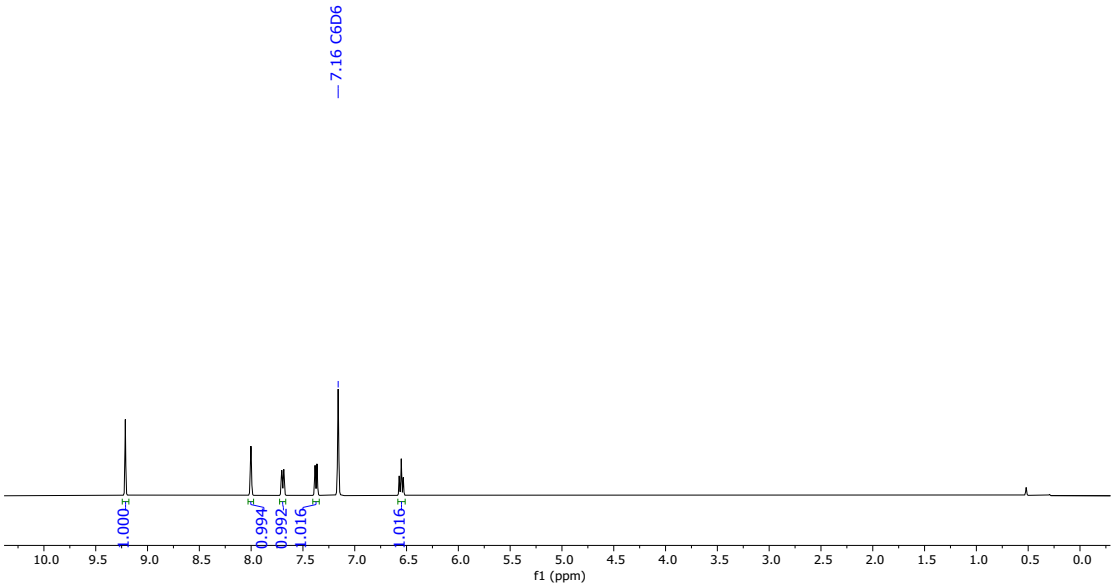


Figure S7: A) ^{1}H NMR of 4-Nitrobenzaldehyde C_6D_6. B) ^{1}H NMR in overlay of catalytic hydrosilylation of 4-Nitrobenzaldehyde with Ph_2SiH_2 using **5a** (2 mol%) in C_6D_6.

10.6 ^{1}H NMR spectra of hydrosilylation of 3-nitrobenzaldehyde

- ^{1}H NMR spectra of 4-Nitrobenzaldehyde before addition of Ph_2SiH_2 and catalyst **5a**



- ^{1}H NMR spectra of the reaction mixture after 2 hours
- Conversion: 100%, Yield: 46%

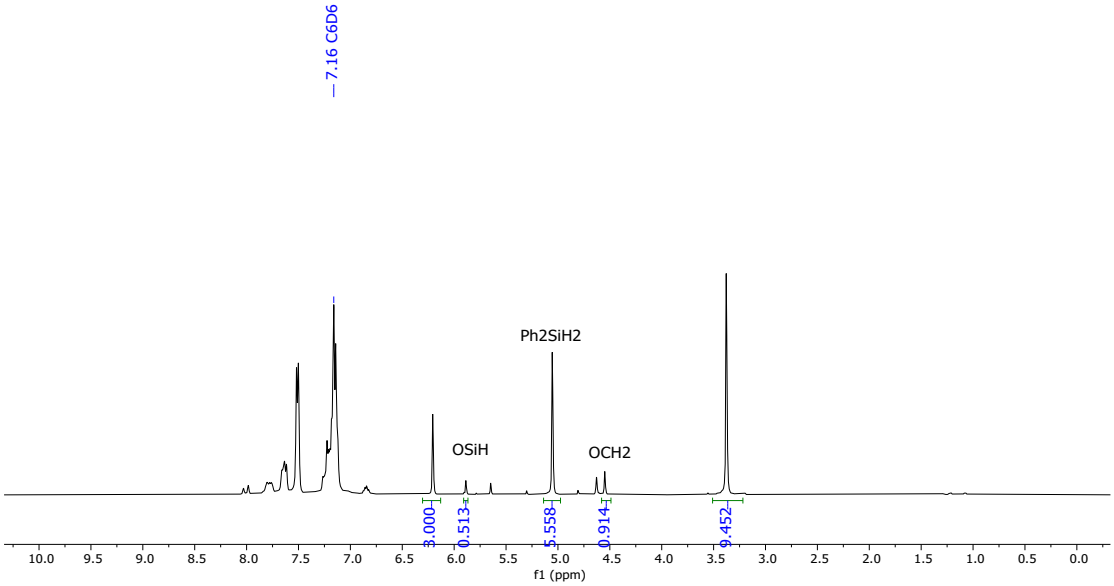
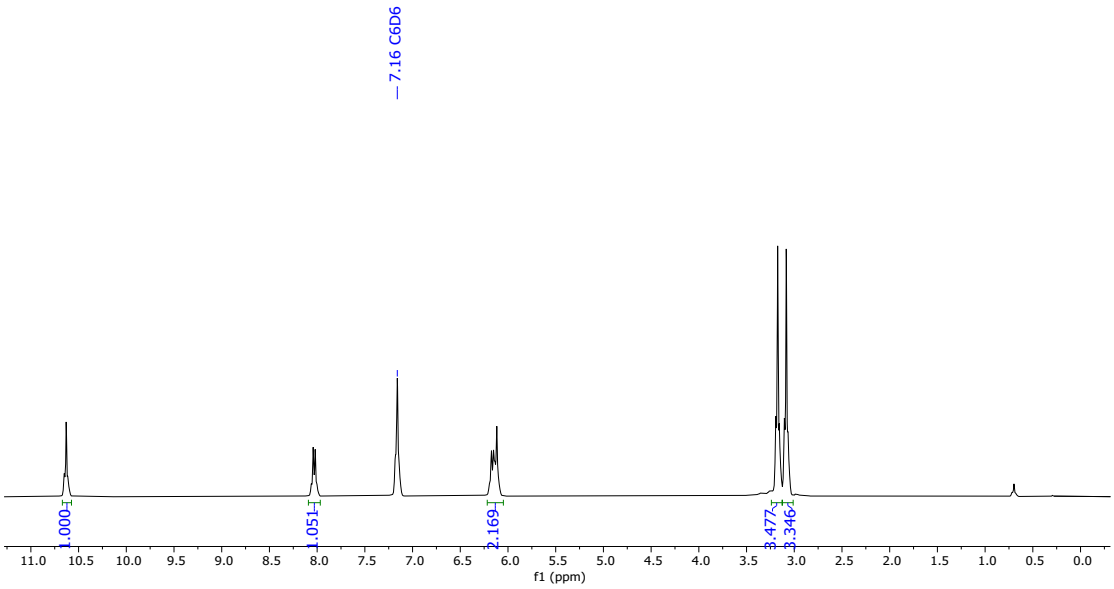


Figure S8: A) ^{1}H NMR of 3-Nitrobenzaldehyde C_6D_6. B) ^{1}H NMR in overlay of catalytic hydrosilylation of 3-Nitrobenzaldehyde with Ph_2SiH_2 using **5a** (2 mol%) in C_6D_6.

10.7 ^{1}H NMR spectra of hydrosilylation of 2,4-dimethoxybenzaldehyde

- ^{1}H NMR spectra of 2,4-Dimethoxybenzaldehyde before addition of Ph_2SiH_2 and catalyst **5a**



- ^{1}H NMR spectra of the reaction mixture after 2 hours
- Conversion: 100%, Yield: >99%

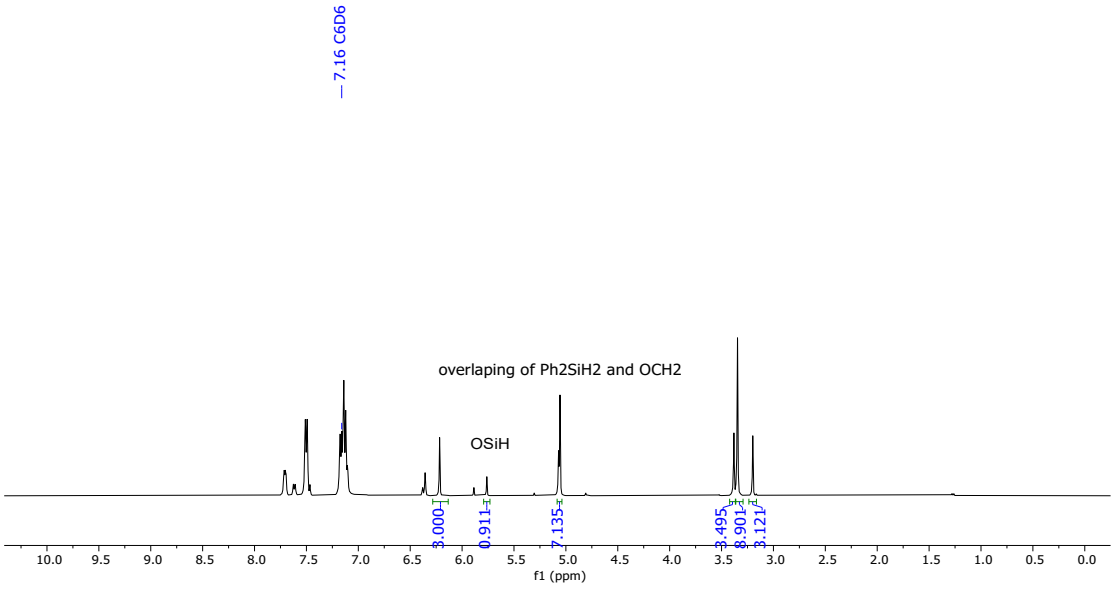
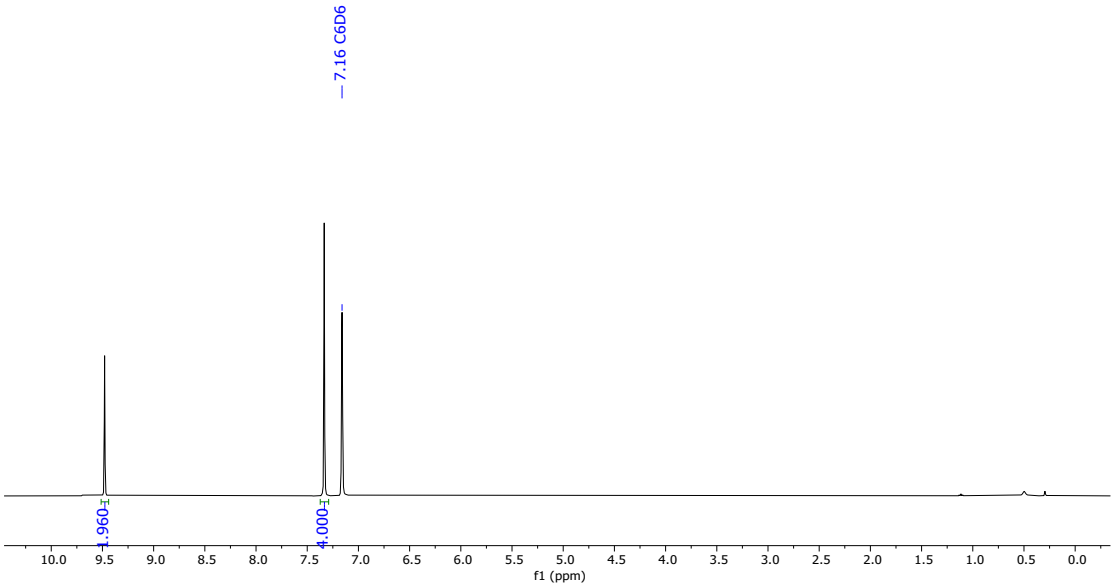


Figure S9: A) ^{1}H NMR of 2,4-Dimethoxybenzaldehyde C_6D_6. B) ^{1}H NMR in overlay of catalytic hydrosilylation of 2,4-Dimethoxybenzaldehyde with Ph_2SiH_2 using **5a** (2 mol%) in C_6D_6.

10.8 ^{1}H NMR spectra of hydrosilylation of terephthalaldehyde

- ^{1}H NMR spectra of Terephthalaldehyde before addition of Ph_2SiH_2 and catalyst **5a**



- ^{1}H NMR spectra of the reaction mixture after 2 hours
- Conversion: 100%, Yield: 82%

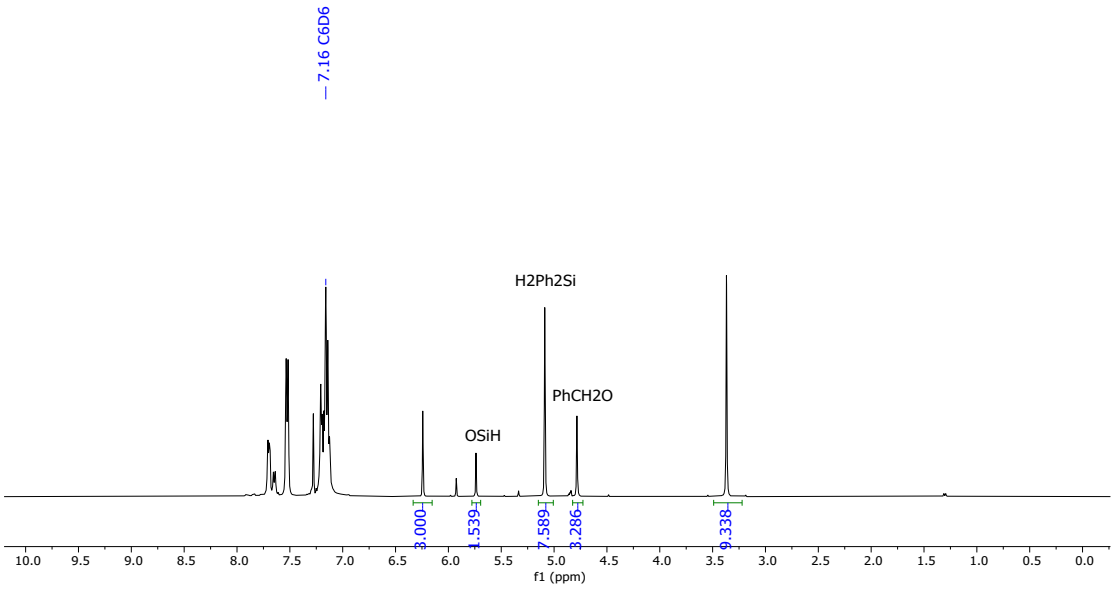
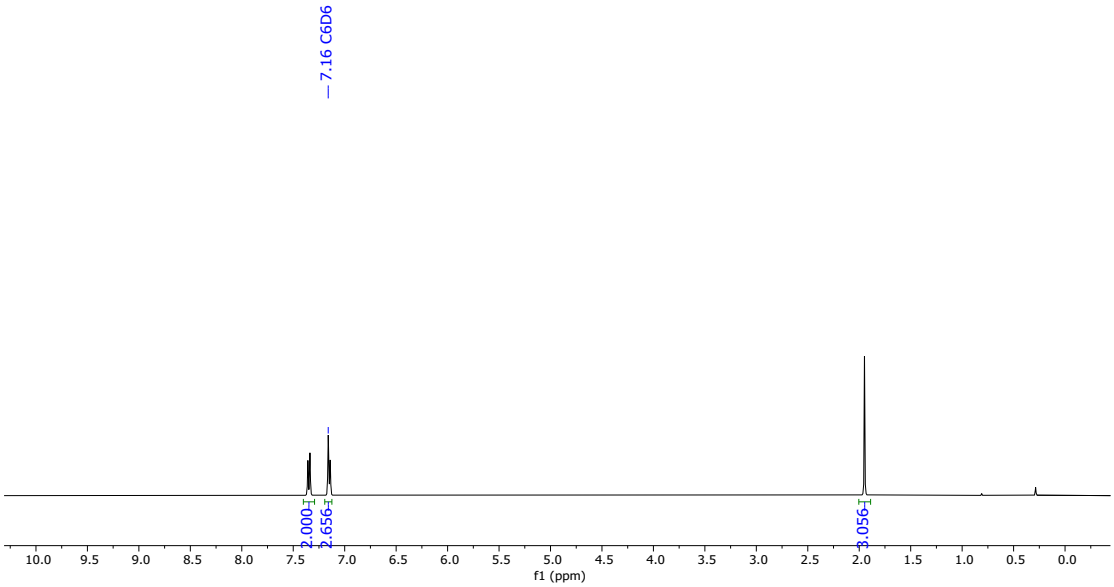


Figure S10: A) ^{1}H NMR of Terephthalaldehyde in C_6D_6. B) ^{1}H NMR in overlay of catalytic hydrosilylation of Terephthalaldehyde Ph_2SiH_2 using **5a** (2 mol%) in C_6D_6.

10.9 ^{1}H NMR spectra of hydrosilylation of 4-bromoacetophenone

- ^{1}H NMR spectra of 4-Bromoacetophenone before addition of Ph_2SiH_2 and catalyst **5a**



- ^{1}H NMR spectra of the reaction mixture after 2 hours
- Conversion: <20%

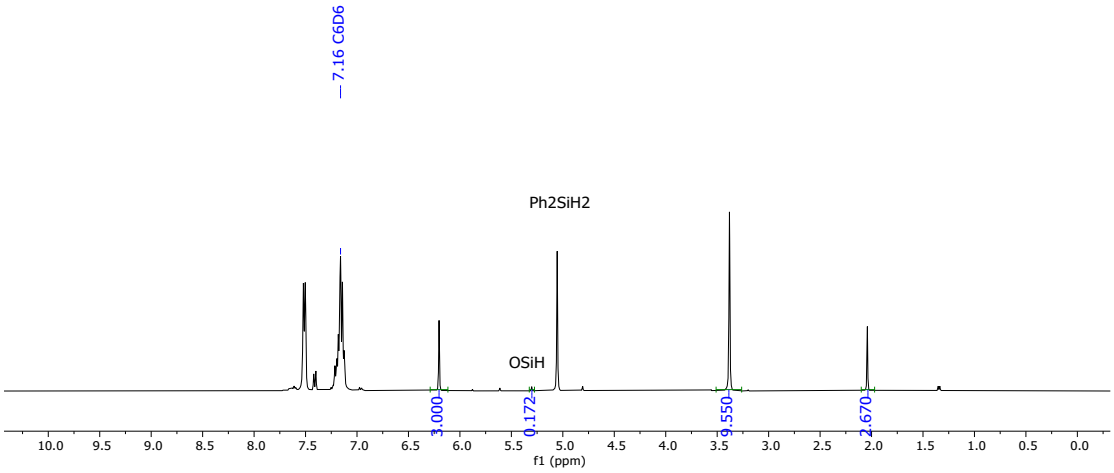
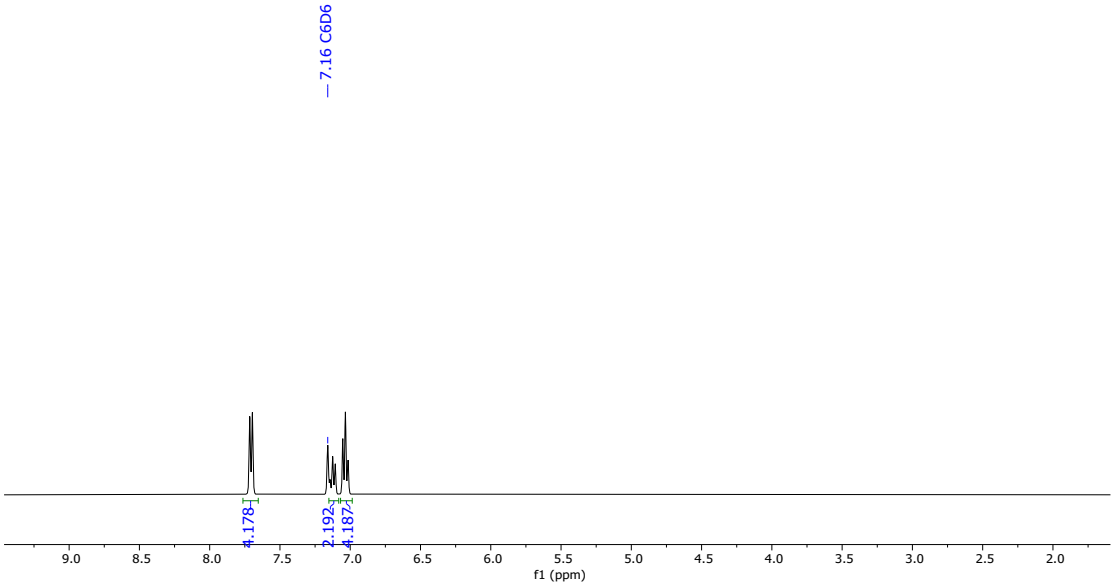


Figure S11: A) ^{1}H NMR of 4-Bromoacetophenone in C_6D_6. B) ^{1}H NMR in overlay of catalytic hydrosilylation of 4-Bromoacetophenone Ph_2SiH_2 using **5a** (2 mol%) in C_6D_6.

10.10 ^{1}H NMR spectra of hydrosilylation of benzophenone

- ^{1}H NMR spectra of Benzophenone before addition of Ph_2SiH_2 and catalyst **5a**



- ^{1}H NMR spectra of the reaction mixture after 2 hours
- Conversion: <15%

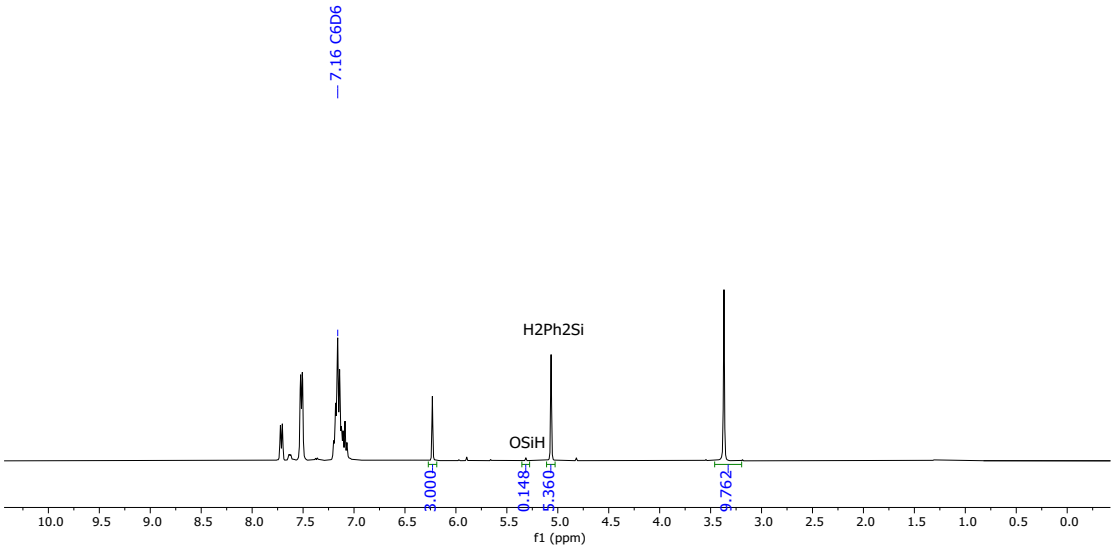
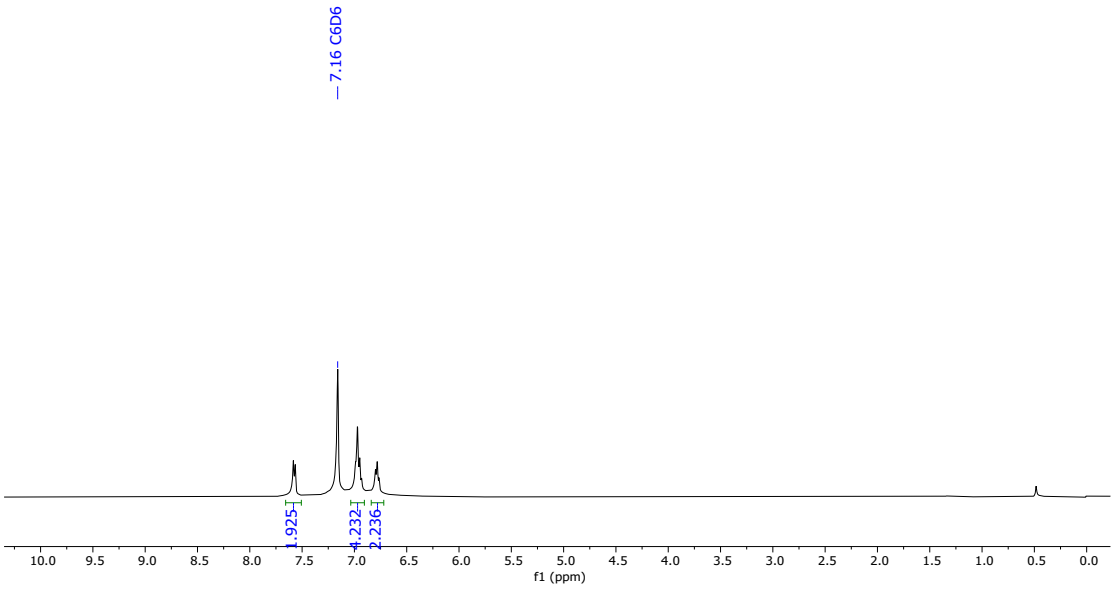


Figure S12: A) ^{1}H NMR of Benzophenone in C_6D_6. B) ^{1}H NMR in overlay of catalytic hydrosilylation of Benzophenone Ph_2SiH_2 using **5a** (2 mol%) in C_6D_6.

10.11 ^{1}H NMR spectra of hydrosilylation of 9-fluorenone

- ^{1}H NMR spectra of Benzophenone before addition of Ph_2SiH_2 and catalyst **5a**



- ^{1}H NMR spectra of the reaction mixture after 2 hours
- Conversion: 100%, Yield: >99%

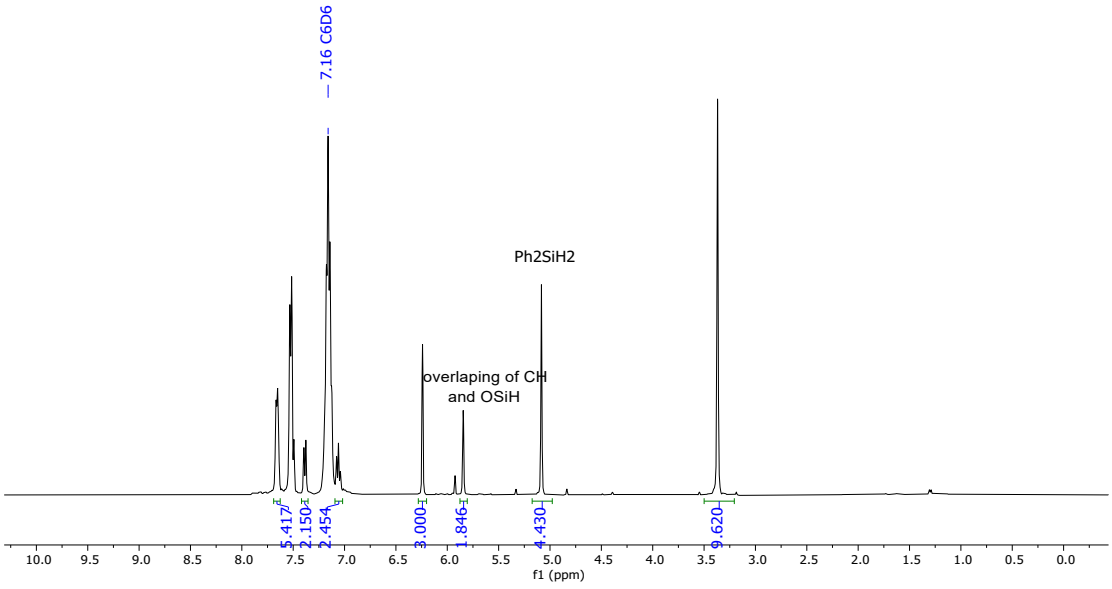
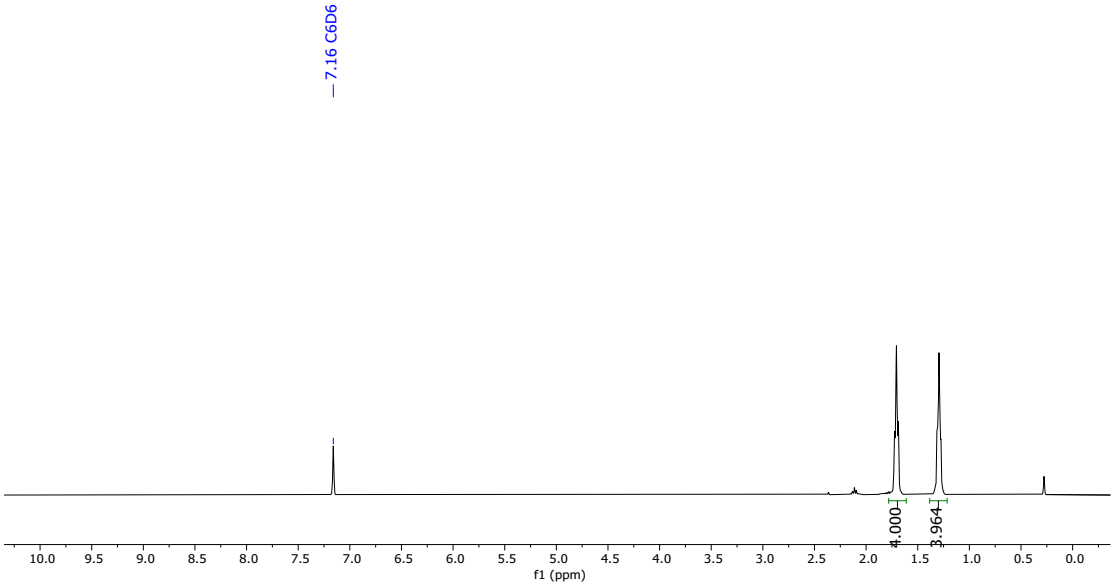


Figure S13: A) ^{1}H NMR of 9-Fluorenone C_6D_6. B) ^{1}H NMR in overlay of catalytic hydrosilylation of 9-Fluorenone with Ph_2SiH_2 using **5a** (2 mol%) in C_6D_6.

10.12 ^{1}H NMR spectra of hydrosilylation of cyclopentanone

- ^{1}H NMR spectra of Cyclopentanone before addition of Ph_2SiH_2 and catalyst **5a**



- ^{1}H NMR spectra of the reaction mixture after 2 hours
- Conversion: <5%

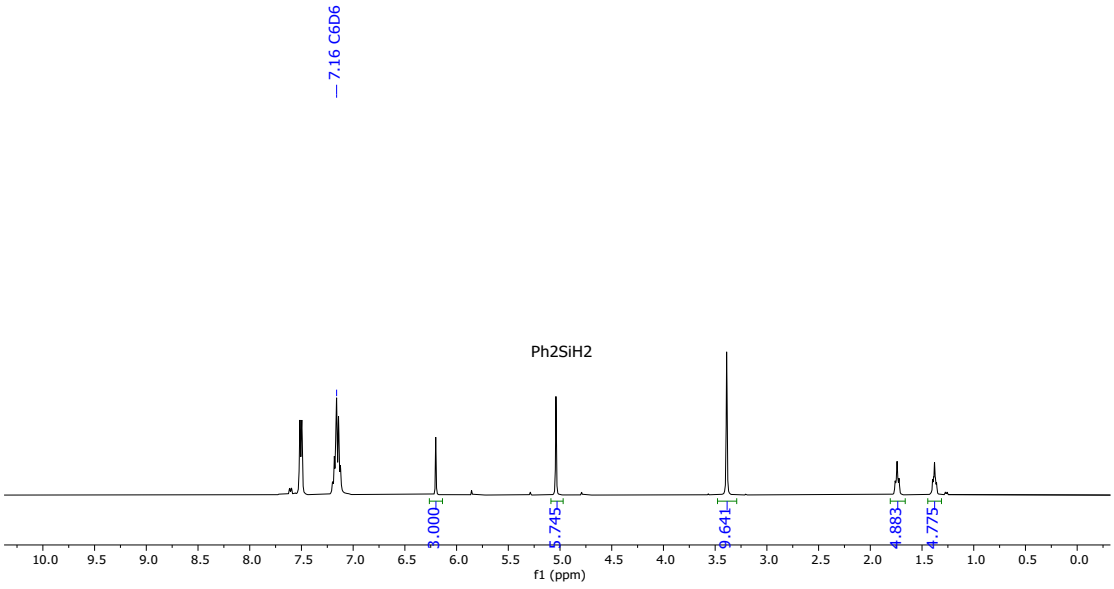


Figure S14: A) ^{1}H NMR of Cyclopentanone C_6D_6. B) ^{1}H NMR in overlay of catalytic hydrosilylation of Cyclopentanone with Ph_2SiH_2 using **5a** (2 mol%) in C_6D_6.

11. References

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