Supporting Information

Bidentate (P^N) Au(III)-Azide Complexes: Synthesis and Reductive Elimination Studies

Urvashi and Nitin T. Patil*

Department of Chemistry, Indian Institute of Science Education and Research Bhopal, Bhauri, Bhopal 462 066, India
E-mail: npatil@iiserb.ac.in

1. General information:

1.1. Practical considerations:

All reactions were carried out in oven-dried vials or reaction vessels with magnetic stirring under nitrogen atmosphere, unless otherwise mentioned. Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringe cooled to ambient temperature in a desiccator. All the gold-catalyzed cross-coupling reactions were performed in 2.5 mL glass vials with a PTFE-lined cap, whereas all other reactions were performed in round-bottom flasks with rubber septa. All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on 0.25 mm precoated silica gel plates (60 F254). After elution, plate was visualized under UV at 254 nm for UV active materials. Further visualization was achieved by staining in I_2 and $KMnO_4$ solution and charring on a hot plate. Solvents were removed *in vacuo* and heated in a water bath at 35 °C. Silica gel finer than 200 mesh was used for flash column chromatography. Columns were packed as slurry of silica gel in pet ether and equilibrated with the appropriate solvent mixture prior to use. The compounds were loaded neat or as a concentrated solution using the appropriate solvent system. The elution was assisted by applying pressure with an air pump.

1.2. Instrumentation:

All ^{1}H NMR, ^{31}P NMR and ^{13}C NMR spectra were recorded in Bruker AVANCE III 400, 500 and 700 MHz NMR spectrometers at 25 °C unless specified otherwise using TMS as an internal standard or the solvent signals as secondary standards and the chemical shifts are shown in δ scales. Multiplicities of ^{1}H NMR signals are designated as s (singlet), br. s. (broad singlet), d (doublet), dd (doublet of doublet), ddd (doublet of doublet of doublet), t (triplet), q (quartet), m (multiplet) etc. HRMS (ESI) data were recorded on a Bruker Daltonics MicroTOF-Q-II spectrometer. Single crystal X-ray diffraction measurements were performed with Bruker D8 Venture Dual Source X-ray diffractometer and Bruker APEX-II CCD diffractometer.

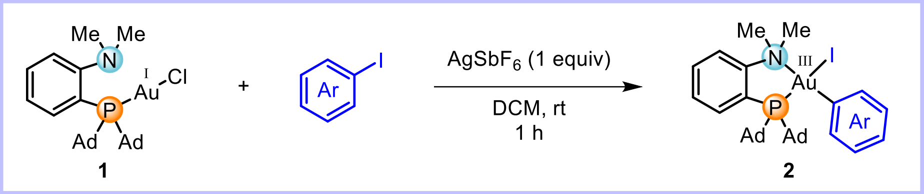
1.3. Materials:

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. THF was distilled from Na/benzophenone under an atmosphere of N_2. DMSO, MeCN, DCM, 1,4-dioxane and acetone were dried using standard protocol under N_2. Gold, silver salts and deuterated solvents were purchased from Sigma-Aldrich and stored under nitrogen atmosphere.

2. Synthesis of (P^N) Au(III)-azide complexes

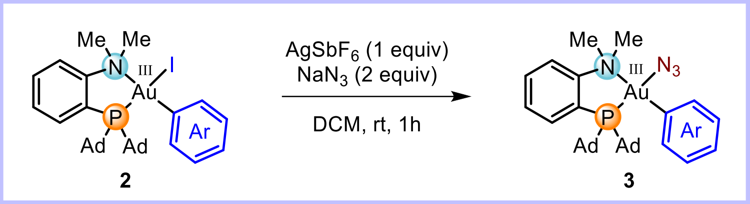
General Method:

Step 1: Oxidative addition of aryl iodides to gold(I) complexes



A reaction vial was charged with $AgSbF_6$ (1 equiv) in dichloromethane. Subsequently, aryl iodide (2 equiv) and gold(I) chloride complex (1 equiv) were added and the reaction mixture was stirred for 1 hour. After complete conversion, the reaction mixture was passed through a short pad of celite. The solvent was evaporated under reduced pressure and the residue was washed with benzene, diethyl ether and hexane twice. The Au(III) oxidative addition complexes **2** were dried under reduced pressure and high-vacuum and were directly subjected to the next step.

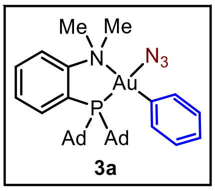
Step 2: Iodide abstraction followed by reaction with sodium azide



A reaction vial was charged with Au(III) oxidative addition complex **2** (1 equiv) in dichloromethane. Subsequently, $AgSbF_6$ (1 equiv) and NaN_3 (2 equiv) were added at room temperature and stirred for 1 hour. The reaction mixture was passed through a short pad of celite. Next, the solvent was evaporated under reduced pressure and the residue was washed with benzene, diethyl ether and hexane twice. The obtained solid was dried under reduced pressure and high-vacuum to furnish (P^N) Au(III)-azide complexes **3a-3i**.

Characterization data:

Au complex 3a:

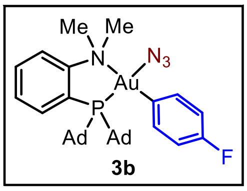


3a

White Solid, 95% yield; **^{1}H NMR (400 MHz, DICHLOROMETHANE-d$_2$)** δ = 7.98 - 7.87 (m, 3 H), 7.77 - 7.70 (m, 1 H), 7.59 (d, *J* = 7.9 Hz, 2 H), 7.44 (t, *J* = 7.5 Hz, 2 H), 7.33 - 7.27 (m, 1 H), 3.31 (s, 6 H), 2.24 (br. s., 6 H), 2.08 (br. s., 12 H), 1.81 - 1.71 (m, 12 H); **^{13}C NMR**

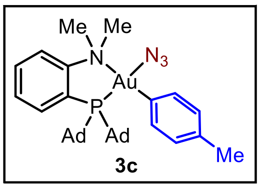
(176 MHz, DICHLOROMETHANE-d$_2$) δ = 158.8 (d, *J* = 7.6 Hz), 136.9, 136.6 (d, *J* = 2.5 Hz), 133.0, 132.4, 130.7 (d, *J* = 7.6 Hz), 128.5, 125.5 (d, *J* = 6.4 Hz), 120.1, 119.9, 53.1, 47.0 (d, *J* = 15.3 Hz), 40.9, 36.0, 29.0 (d, *J* = 10.2 Hz); **^{31}P NMR (202 MHz, DICHLOROMETHANE-d$_2$)** δ = 72.5. **HRMS (ESI)** calcd for $C_{34}H_{45}AuN_4P$ (M) 737.3042, found 737.3057.

Au complex 3b:



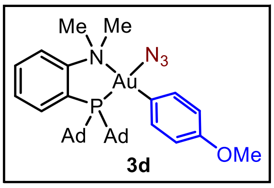
White Solid, 92% yield; **^{1}H NMR (400 MHz, DICHLOROMETHANE-d$_2$)** δ = 7.99 - 7.85 (m, 3 H), 7.78 - 7.69 (m, 1 H), 7.64 - 7.55 (m, 2 H), 7.24 (t, *J* = 8.3 Hz, 2 H), 3.32 (s, 6 H), 2.23 (br. s., 6 H), 2.10 (br. s., 6 H), 2.03 (br. s., 6 H), 1.80 - 1.72 (m, 12 H); **^{13}C NMR (176 MHz, DICHLOROMETHANE-d$_2$)** δ = 163.0 (d, *J* = 248 Hz), 158.8 (d, *J* = 7.6 Hz), 136.9 (d, *J* = 34.3 Hz), 134.0 (d, *J* = 6.4 Hz), 130.9 (d, *J* = 7.6 Hz), 129.5, 125.5 (d, *J* = 7.6 Hz), 120.0, 119.7, 119.2 (d, *J* = 21.6 Hz), 53.2, 47.1 (d, *J* = 14.0 Hz), 40.9, 36.0, 29.0 (d, *J* = 10.2 Hz); **^{31}P NMR (202 MHz, DICHLOROMETHANE-d$_2$)** δ = 73.8; **^{19}F NMR (377 MHz, DICHLOROMETHANE-d$_2$)** δ = -115.0. **HRMS (ESI)** calcd for $C_{34}H_{44}AuFN_4P$ (M) 755.2948, found 755.2964.

Au complex 3c:



White Solid, 90% yield; **^{1}H NMR (400 MHz, DICHLOROMETHANE-d$_2$)** δ = 7.99 - 7.85 (m, 3 H), 7.77 - 7.69 (m, 1 H), 7.48 - 7.40 (m, *J* = 7.8 Hz, 2 H), 7.30 - 7.22 (m, *J* = 7.8 Hz, 2 H), 3.30 (s, 6 H), 2.39 (s, 3 H), 2.24 (br. s., 6 H), 2.08 (br. s., 12 H), 1.82 - 1.69 (m, 12 H); **^{13}C NMR (176 MHz, DICHLOROMETHANE-d$_2$)** δ = 158.8 (d, *J* = 7.6 Hz), 138.6, 136.9 (d, *J* = 8.9 Hz), 133.0, 132.6, 132.4, 130.7 (d, *J* = 6.4 Hz), 125.5 (d, *J* = 6.4 Hz), 120.2, 120.0, 53.0, 46.9 (d, *J* = 15.3 Hz), 40.9, 36.0, 28.9 (d, *J* = 10.2 Hz), 20.9; **^{31}P NMR (202 MHz, DICHLOROMETHANE-d$_2$)** δ = 71.9. **HRMS (ESI)** calcd for $C_{35}H_{47}AuN_4P$ (M) 751.3198, found 751.3214.

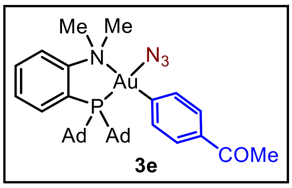
Au complex 3d:



3d

White Solid, 94% yield; **^{1}H NMR (400 MHz, DICHLOROMETHANE-d_2)** δ = 7.99 - 7.86 (m, 3 H), 7.78 - 7.68 (m, 1 H), 7.52 - 7.42 (m, J = 8.1 Hz, 2 H), 7.08 - 7.00 (m, J = 8.1 Hz, 2 H), 3.84 (s, 3 H), 3.30 (s, 6 H), 2.24 (br. s., 6 H), 2.09 (br. s., 12 H), 1.82 - 1.70 (m, 12 H); **^{13}C NMR (176 MHz, DICHLOROMETHANE-d_2)** δ = 160.0, 158.8 (d, J = 7.6 Hz), 136.9 (d, J = 5.1 Hz), 133.1, 130.7 (d, J = 6.4 Hz), 125.5 (d, J = 7.6 Hz), 124.8 (d, J = 3.8 Hz), 120.2, 120.0, 117.9, 55.9, 53.1, 46.9 (d, J = 15.3 Hz), 40.9, 36.0, 29.0 (d, J = 10.2 Hz); **^{31}P NMR (202 MHz, DICHLOROMETHANE-d_2)** δ = 72.1. **HRMS (ESI)** calcd for $C_{35}H_{47}AuN_4OP$ (M) 767.3148, found 767.3177.

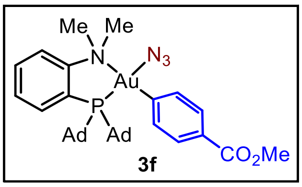
Au complex 3e:



3e

White Solid, 82% yield; **^{1}H NMR (400 MHz, DICHLOROMETHANE-d_2)** δ = 8.03 - 7.86 (m, 5 H), 7.76 (d, J = 7.9 Hz, 3 H), 3.34 (s, 6 H), 2.62 (s, 3 H), 2.24 (br. s., 6 H), 2.10 (br. s., 6 H), 2.04 (br. s., 6 H), 1.86 - 1.68 (m, 12 H); **^{13}C NMR (176 MHz, DICHLOROMETHANE-d_2)** δ = 197.6, 158.8 (d, J = 7.6 Hz), 142.9, 137.1 (d, J = 16.5 Hz), 136.8, 133.4, 131.4, 130.9 (d, J = 7.6 Hz), 125.6 (d, J = 6.4 Hz), 119.9, 119.6, 53.3, 47.2 (d, J = 14.0 Hz), 41.0, 35.9, 29.0 (d, J = 10.2 Hz), 27.0; **^{31}P NMR (202 MHz, DICHLOROMETHANE-d_2)** δ = 74.9. **HRMS (ESI)** calcd for $C_{36}H_{47}AuN_4OP$ (M) 779.3148, found 779.3173.

Au complex 3f:

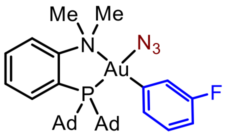


3f

White Solid, 88% yield; **^{1}H NMR (400 MHz, DICHLOROMETHANE-d_2)** δ = 8.07 (d, J = 8.3 Hz, 2 H), 8.00 - 7.87 (m, 3 H), 7.74 (d, J = 8.1 Hz, 3 H), 3.92 (s, 3 H), 3.33 (s, 6 H), 2.24 (br. s., 6 H), 2.10 (br. s., 6 H), 2.03 (br. s., 6 H), 1.83 - 1.69 (m, 12 H); **^{13}C NMR (176 MHz,**

DICHLOROMETHANE-d$_2$) δ = 166.6, 158.8 (d, *J* = 6.4 Hz), 142.7, 137.1, 136.8, 133.2, 132.6, 130.9 (d, *J* = 7.6 Hz), 130.6, 125.6 (d, *J* = 6.4 Hz), 119.8, 119.6, 53.3, 52.8, 47.2 (d, *J* = 14.0 Hz), 41.0, 35.9, 28.9 (d, *J* = 8.9 Hz); **^{31}P NMR (202 MHz, DICHLOROMETHANE-d$_2$)** δ = 74.8. **HRMS (ESI)** calcd for $C_{36}H_{47}AuN_4O_2P$ (M) 795.3097, found 795.3108.

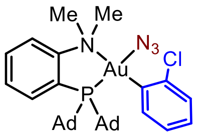
Au complex 3g:



3g

White Solid, 93% yield; **^{1}H NMR (400 MHz, DICHLOROMETHANE-d$_2$)** δ = 8.01 - 7.86 (m, 3 H), 7.79 - 7.71 (m, 1 H), 7.52 - 7.34 (m, 3 H), 7.05 (t, *J* = 7.9 Hz, 1 H), 3.33 (s, 6 H), 2.24 (br. s., 6 H), 2.10 (br. s., 6 H), 2.05 (br. s., 6 H), 1.77 (br. s., 12 H); **^{13}C NMR (176 MHz, DICHLOROMETHANE-d$_2$)** δ = 164.0 (d, *J* = 253.0 Hz), 158.8 (d, *J* = 6.4 Hz), 137.1 (d, *J* = 2.5 Hz), 136.9, 136.4 (dd, *J* = 2.5 Hz), 133.2 (d, *J* = 7.6 Hz), 130.9 (d, *J* = 7.6 Hz), 128.9 (d, *J* = 2.5 Hz), 125.5 (d, *J* = 7.6 Hz), 120.4 (d, *J* = 22.9 Hz), 119.9, 119.6, 115.4 (d, *J* = 20.3 Hz), 53.3, 47.3 (d, *J* = 16.5 Hz), 41.0 (d, *J* = 24.2 Hz), 36.0, 29.0 (dd, *J* = 6.4 Hz); **^{31}P NMR (202 MHz, DICHLOROMETHANE-d$_2$)** δ = 74.5. **^{19}F NMR (377 MHz, DICHLOROMETHANE-d$_2$)** δ = -108.8. **HRMS (ESI)** calcd for $C_{34}H_{44}AuN_4FP$ (M) 755.2948, found 755.2930.

Au complex 3h:

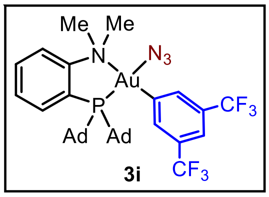


3h

White Solid, 85% yield; **^{1}H NMR (400 MHz, DICHLOROMETHANE-d$_2$)** δ = 8.01 - 7.90 (m, 3 H), 7.79 - 7.72 (m, 1 H), 7.67 (d, *J* = 7.8 Hz, 1 H), 7.55 (d, *J* = 7.8 Hz, 1 H), 7.43 - 7.37 (m, 1 H), 7.36 - 7.29 (m, 1 H), 3.34 (s, 3 H), 3.38 (s, 3 H), 2.34 (d, *J* = 6.4 Hz, 3 H), 2.19 (br. s., 9 H), 2.01 (br. s., 3 H), 1.94 (br. s., 3 H), 1.86 - 1.67 (m, 12 H); **^{13}C NMR (176 MHz, DICHLOROMETHANE-d$_2$)** δ = 158.8 (d, *J* = 7.6 Hz), 137.1, 136.5, 135.5 (d, *J* = 2.5 Hz), 134.9, 134.5, 133.3, 131.2 (d, *J* = 7.6 Hz), 130.2, 129.7, 125.5 (d, *J* = 6.4 Hz), 120.2 (d, *J* = 44.5 Hz), 53.5, 53.1, 47.1 (d, *J* = 15.3 Hz), 46.8 (d, *J* = 14.0 Hz), 41.3, 39.6, 36.0, 35.7, 29.0

(dd, *J* = 10.2 Hz); ^{31}**P NMR (202 MHz, DICHLOROMETHANE-d$_2$)** δ = 77.9. **HRMS (ESI)** calcd for $C_{34}H_{44}AuClN_4P$ (M) 771.2652, found 771.2644.

Au complex 3i:

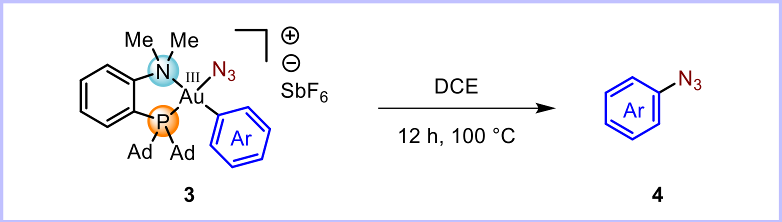


3i

White Solid, 81% yield, ^{1}**H NMR (400 MHz, DICHLOROMETHANE-d$_2$)** δ = 8.16 (s, 2 H), 8.03 - 7.94 (m, 2 H), 7.93 - 7.85 (m, 2 H), 7.78 (d, *J* = 6.7 Hz, 1 H), 3.39 (s, 6 H), 2.23 (br. s., 6 H), 2.10 (br. s., 6 H), 1.99 (br. s., 6 H), 1.77 (d, *J* = 13.2 Hz, 9 H), 1.84 - 1.70 (m, 3 H); ^{13}**C NMR (176 MHz, DICHLOROMETHANE-d$_2$)** δ = 158.9 (d, *J* = 7.6 Hz), 137.4 (d, *J* = 2.5 Hz), 137.3 (d, *J* = 2.5 Hz), 136.9, 134.2 - 133.6 (q, *J* = 34.3 Hz), 134.0, 131.3 (d, *J* = 7.6 Hz), 125.7, 125.6 (d, *J* = 7.6 Hz), 124.1, 122.6, 122.4 (t, *J* = 3.8 Hz), 121.0, 119.2, 119.0, 53.8, 47.7, 47.6, 41.2, 35.8, 28.9, 28.9 (d, *J* = 10.2 Hz); ^{31}**P NMR (202 MHz, DICHLOROMETHANE-d$_2$)** δ = 78.2; ^{19}**F NMR (377 MHz, DICHLOROMETHANE-d$_2$)** δ = -63.2. **HRMS (ESI)** calcd for $C_{36}H_{43}AuF_6N_4P$ (M) 873.2790, found 873.2788.

3. Reductive elimination studies from Au(III)-azide complexes

3.1. Reductive elimination from Au(III)-azide complex under thermal conditions:



An oven dried vial was charged with Au(III)-azide complex **3** (0.4 mmol, 1 equiv) in dichloroethane. The reaction mixture was heated at 100 ºC and stirred for 12 hour. The formation of the C(sp^2)-N_3 cross-coupled product **4** was indicated by TLC analysis and the product was further isolated and characterized by ^{1}H NMR spectroscopy.

azidobenzene (4a):[1]

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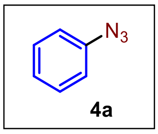
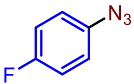
[1] 1) A. S. Kumar, M. A. Reddy, M. Knorn, O. Reiser, B. Sreedhar, *Eur. J. Org. Chem.*, 2013, 4674–4680.



4a

Colorless oil, 96% yield, ***R**_f* = 0.90 (petroleum ether); **^{1}H NMR (400 MHz, CHLOROFORM-d)** δ = 7.37 (t, *J* = 7.4 Hz, 2 H), 7.16 (t, *J* = 7.4 Hz, 1 H), 7.05 (d, *J* = 7.8 Hz, 2 H).

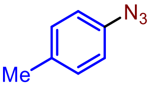
1-azido-4-fluorobenzene (4b):[1]



4b

Yellow oil, 92% yield, R_f = 0.90 (petroleum ether); **^{1}H NMR (500 MHz, DICHLOROMETHANE-d$_2$)** δ = 7.08 - 7.05 (m, 2 H), 7.01 - 6.98 (m, 2 H). **^{19}F NMR (500 MHz, DICHLOROMETHANE-d$_2$)** δ = -118.54.

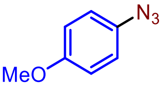
1-azido-4-methylbenzene (4c):[2]



4c

Yellow oil, 95% yield, R_f = 0.90 (petroleum ether); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.17 (d, *J* = 8.4 Hz, 2 H), 6.94 (d, *J* = 8.3 Hz, 2 H), 2.35 (s, 3 H).

1-azido-4-methoxybenzene (4d):[2]



4d

Yellow oil, 93% yield, R_f = 0.80 (petroleum ether); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 6.97 (d, *J* = 9.1 Hz, 2 H), 6.90 (d, *J* = 9.0 Hz, 2 H), 3.81 (s, 3 H).

1-(4-azidophenyl)ethan-1-one (4e):[2]

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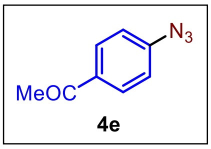
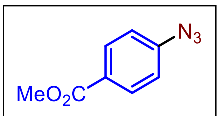
2) Y. Li, L.-X. Gao, F.-S. Han, *Chem. Eur. J.*, 2010, **16**, 7969 – 7972.



4e

White Solid, 95% yield, ***R**$_f$* = 0.80 (petroleum ether); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.95 (d, *J* = 8.8 Hz, 2 H), 7.07 (d, *J* = 8.8 Hz, 2 H), 2.57 (s, 3 H).

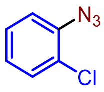
1-(4-azidophenyl)ethan-1-one (4f):[3]



4f

White Solid, 91% yield, ***R**$_f$* = 0.80 (petroleum ether); **^{1}H NMR (400 MHz, CHLOROFORM-d)** δ = 8.03 (d, *J* = 8.6 Hz, 2 H), 7.06 (d, *J* = 8.6 Hz, 2 H), 3.91 (s, 3 H).

1-azido-2-chlorobenzene (4h):[4]



4h

Yellow oil, 90% yield, ***R**$_f$* = 0.90 (petroleum ether); **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.39 (dd, *J* = 1.4, 8.0 Hz, 1 H), 7.33 - 7.28 (m, 1 H), 7.19 (dd, *J* = 1.4, 8.0 Hz, 1 H), 7.12 - 7.06 (m, 1 H).

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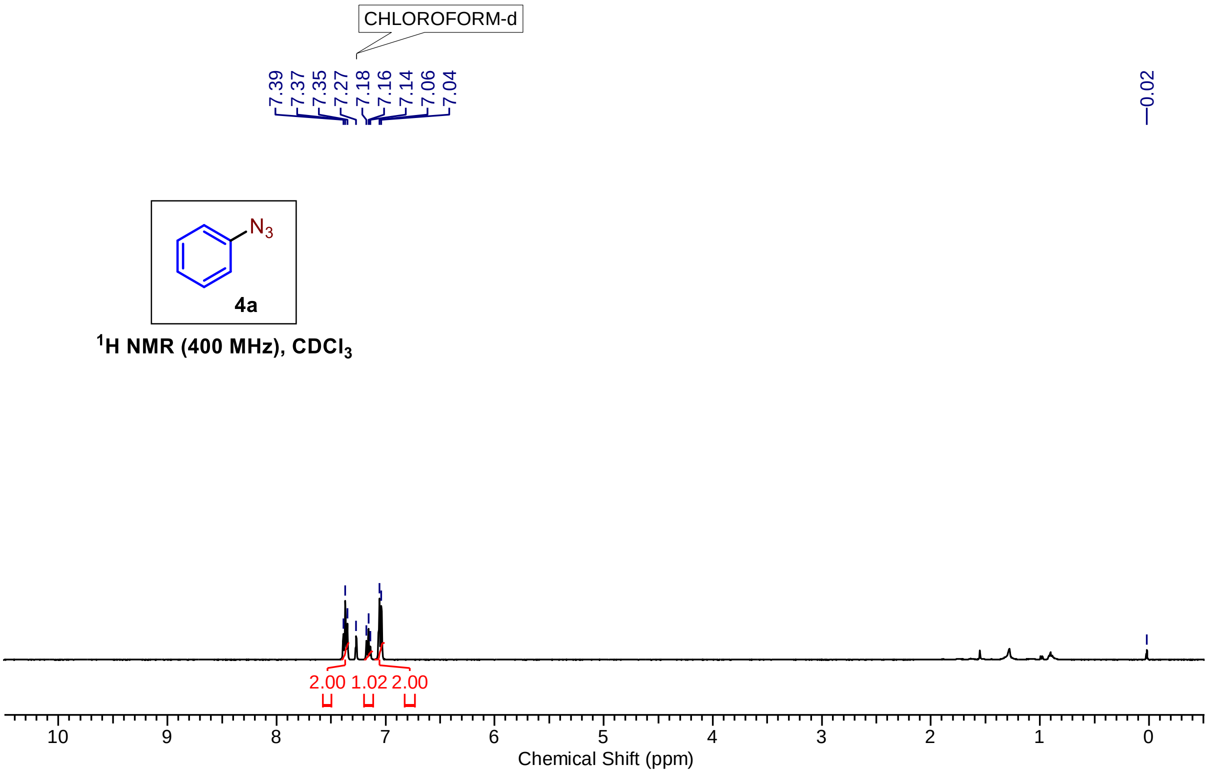
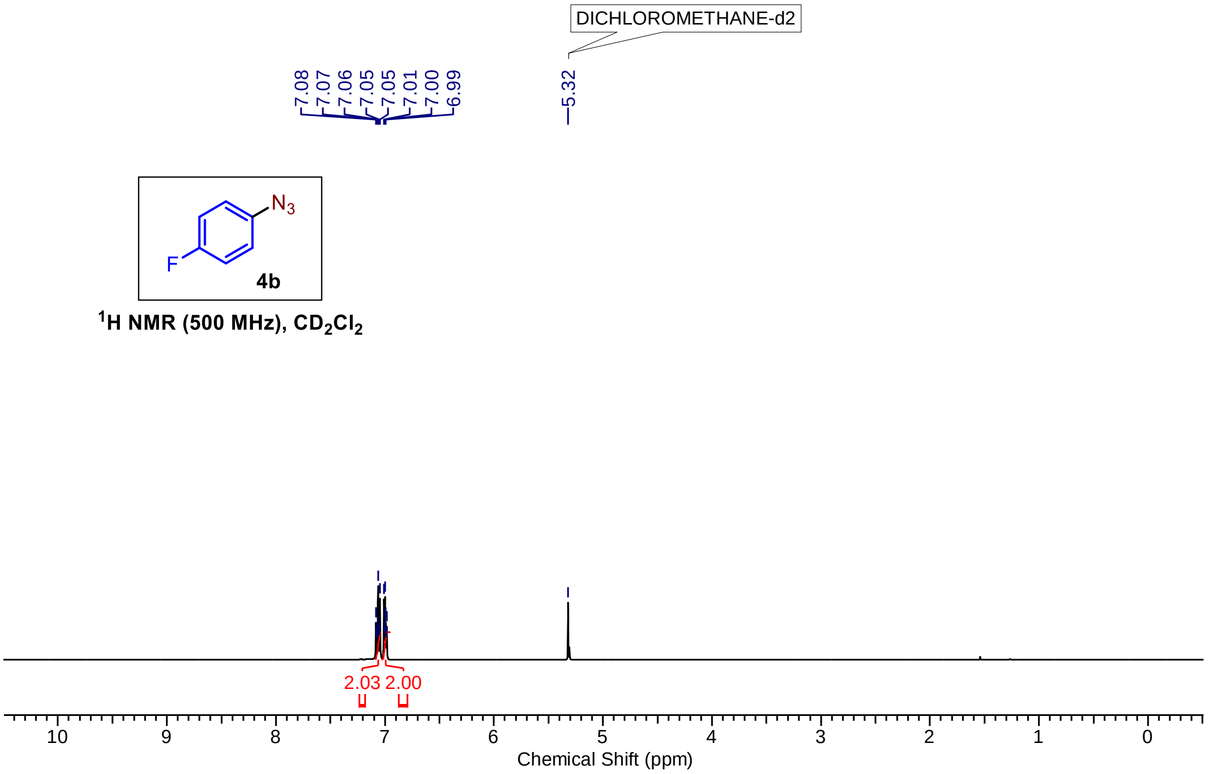
[3] W. Song, N. Zheng, M. Li, J. He, J. Li, K. Dong, K. Ullah, Y. Zheng, *Adv. Synth. Catal.*, 2019, **361**, 469–475.
[4] H. Zheng, R. McDonald, D. G. Hall, *Chem. Eur. J.*, 2010, **16**, 5454–5460.



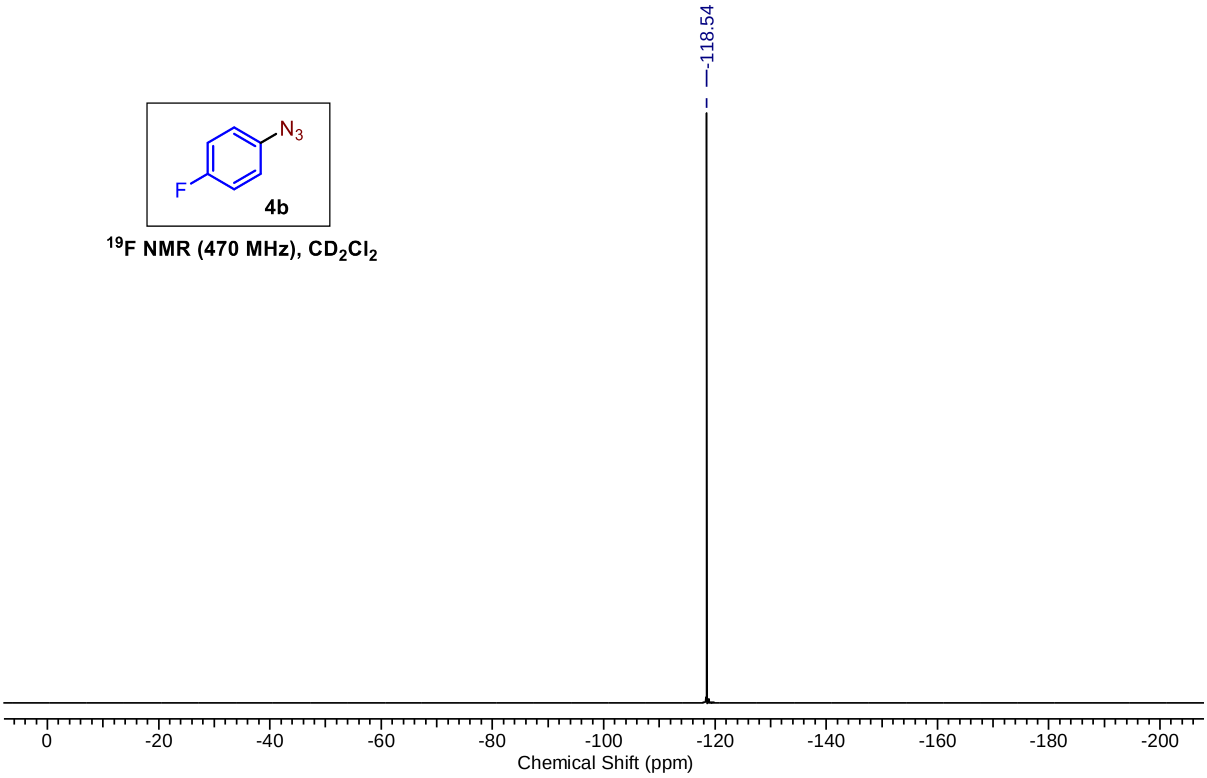
4a

^{1}H NMR (400 MHz), CDCl$_3$

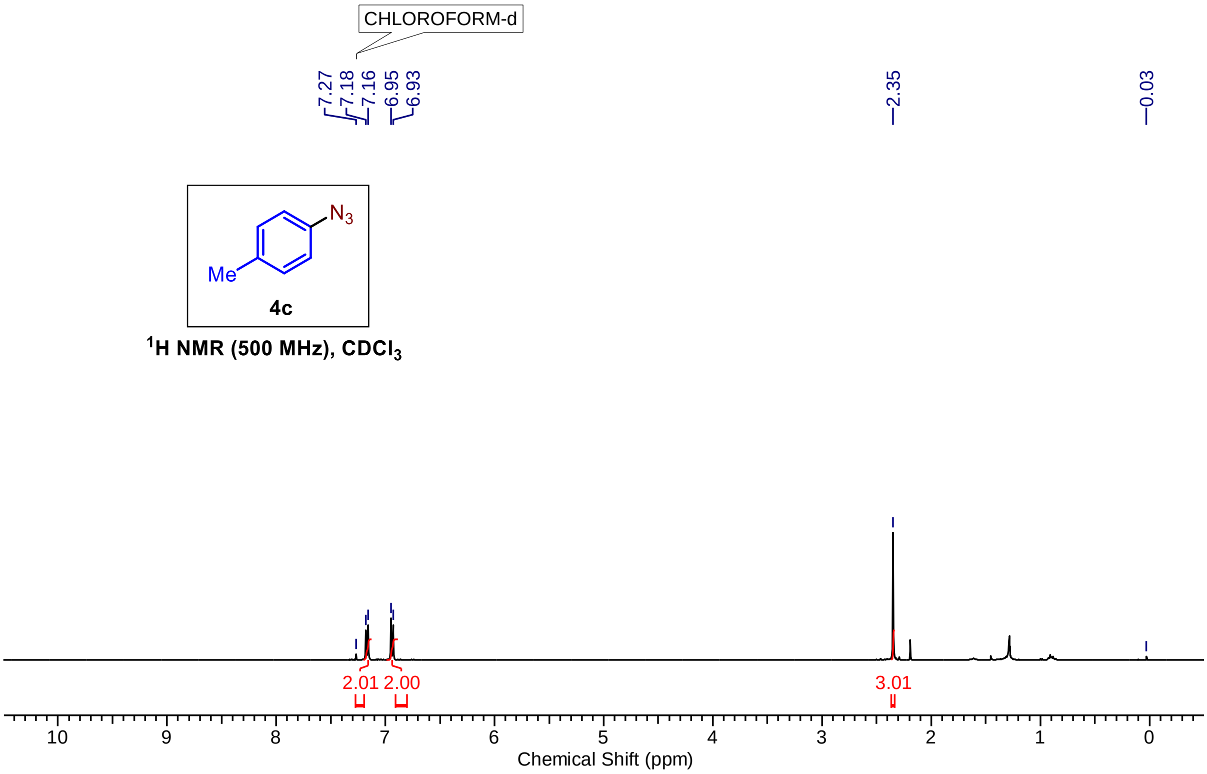


4b

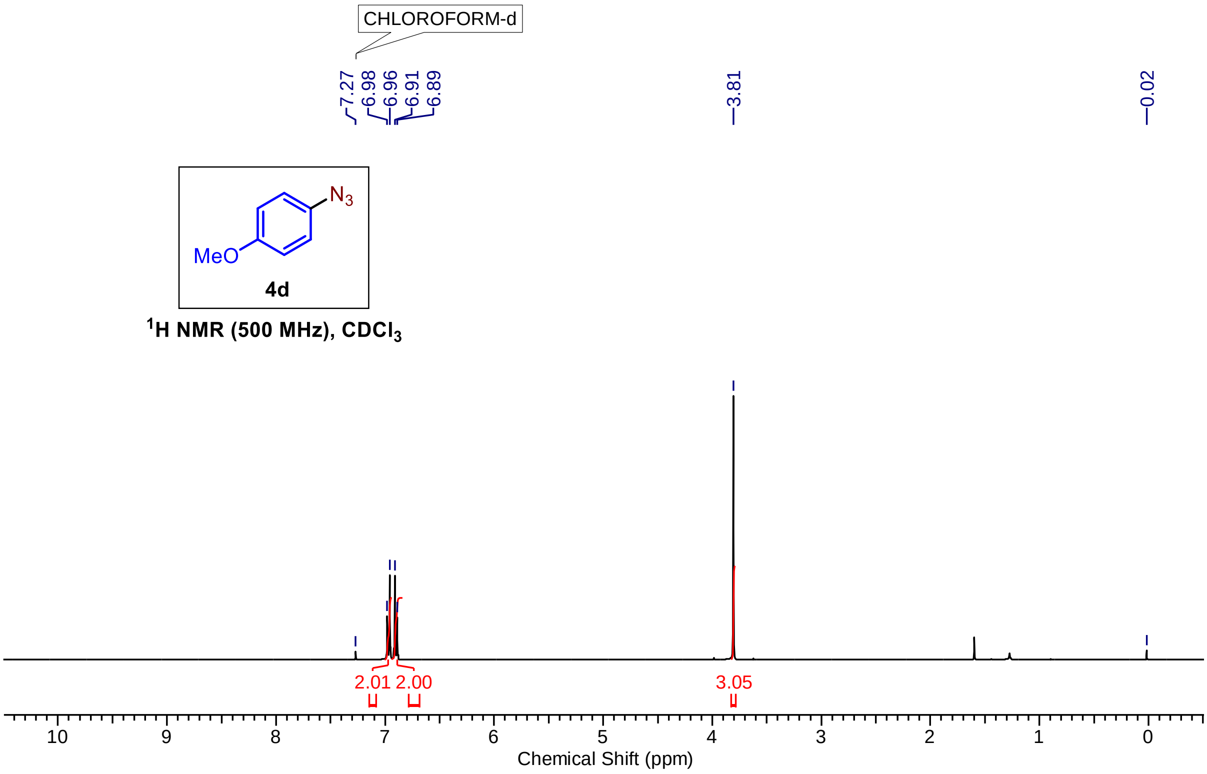
^{1}H NMR (500 MHz), CD$_2$Cl$_2$



-118.54
N3
F
4b
19F NMR (470 MHz), CD2Cl2
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)

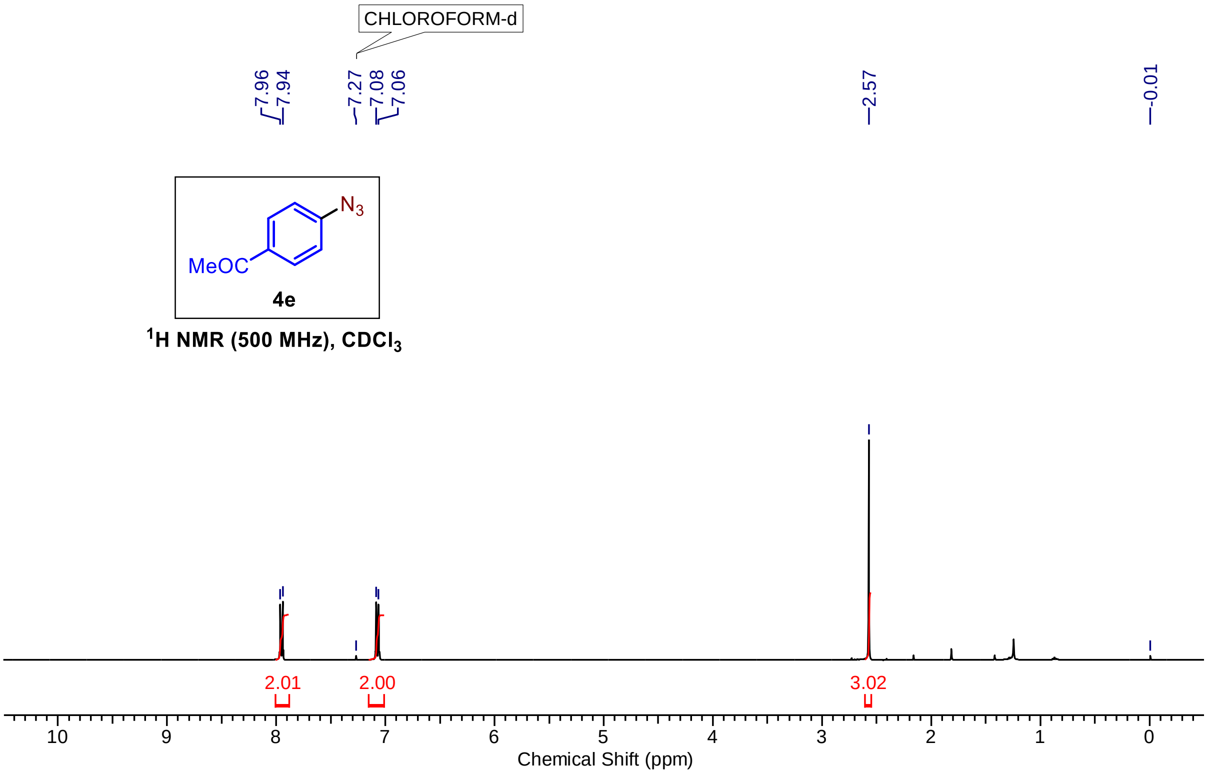


CHLOROFORM-d
7.27
7.18
7.16
6.95
6.93
2.35
0.03
N3
Me
4c
1H NMR (500 MHz), CDCl3
2.01
2.00
3.01
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)



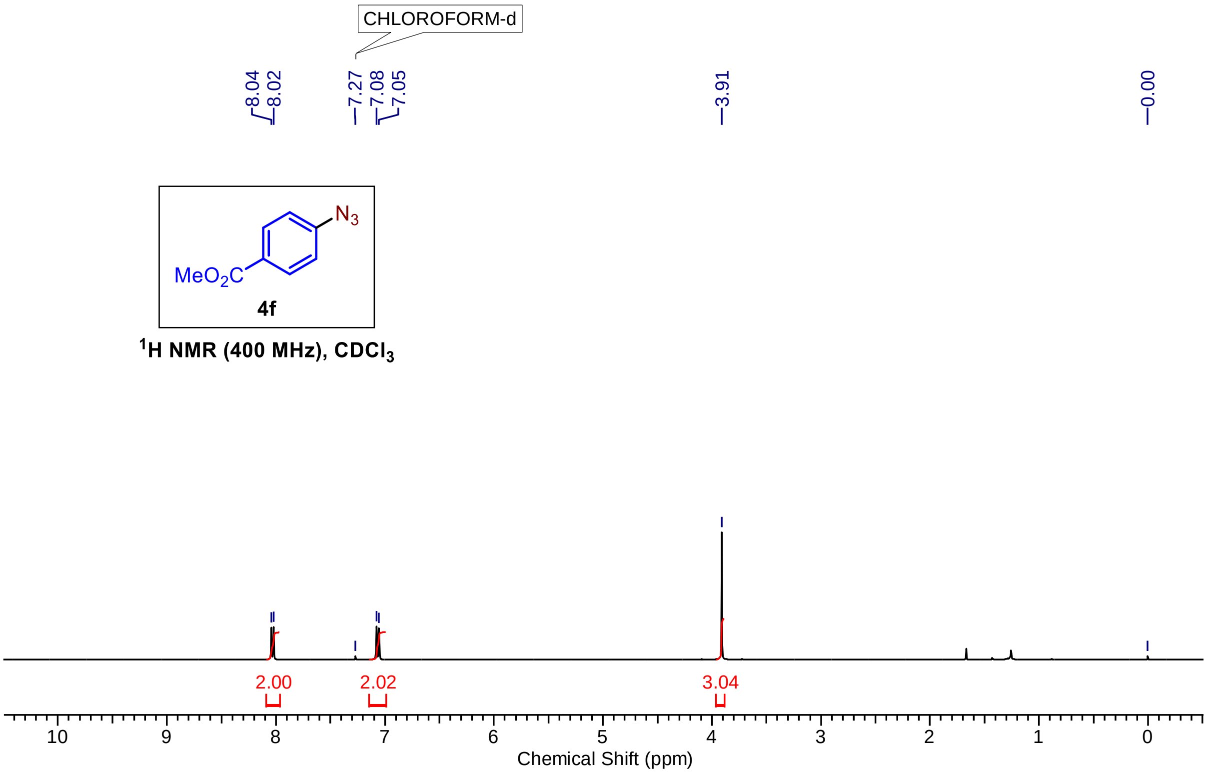
4d

^{1}H NMR (500 MHz), CDCl$_3$



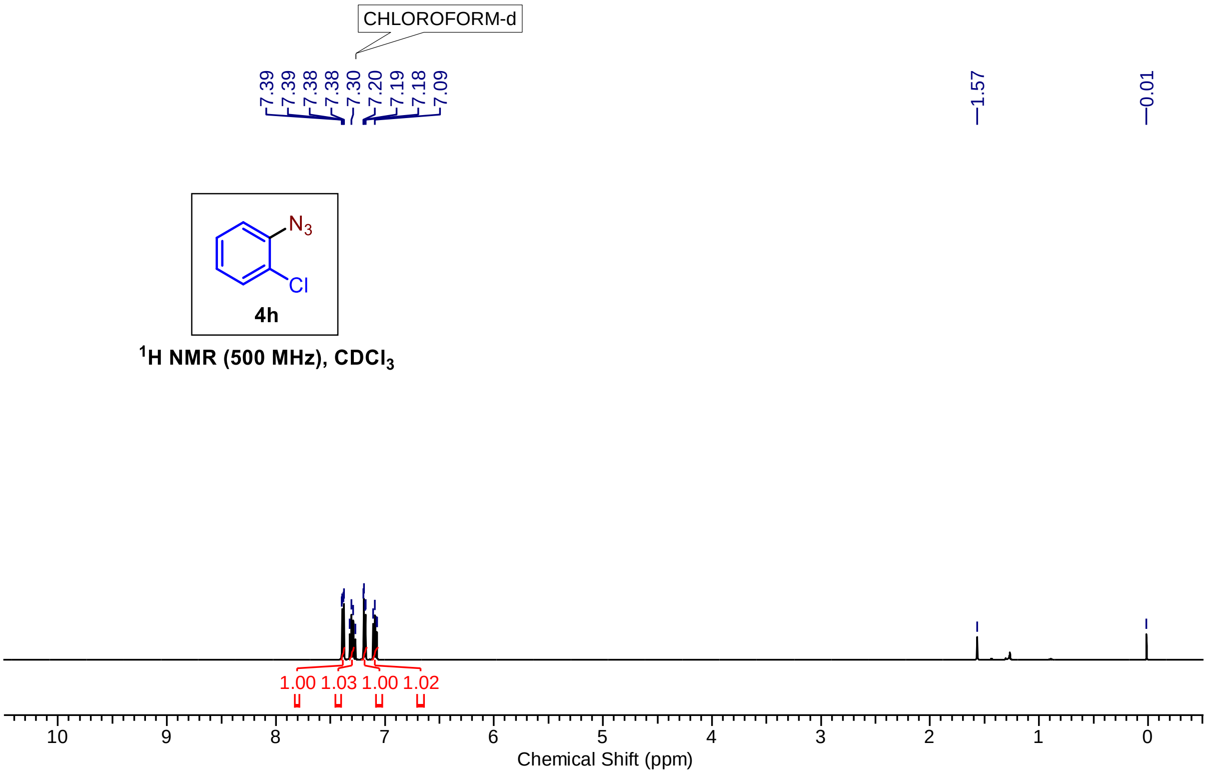
4e

^{1}H NMR (500 MHz), CDCl$_3$



4f

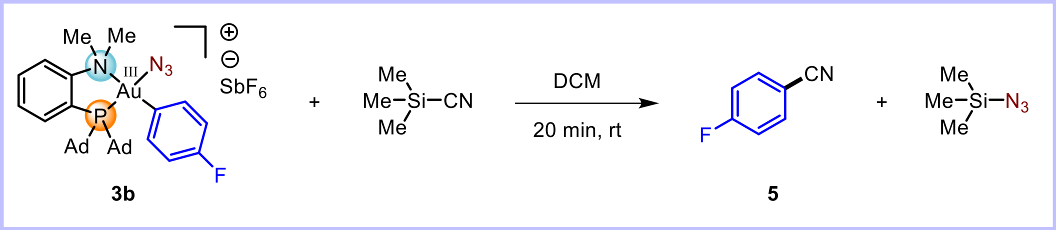
^{1}H NMR (400 MHz), CDCl$_3$



4h

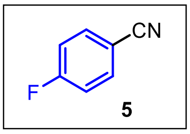
^{1}H NMR (500 MHz), CDCl$_3$

3.2. Reaction of Au(III)-azide complex with TMSCN:

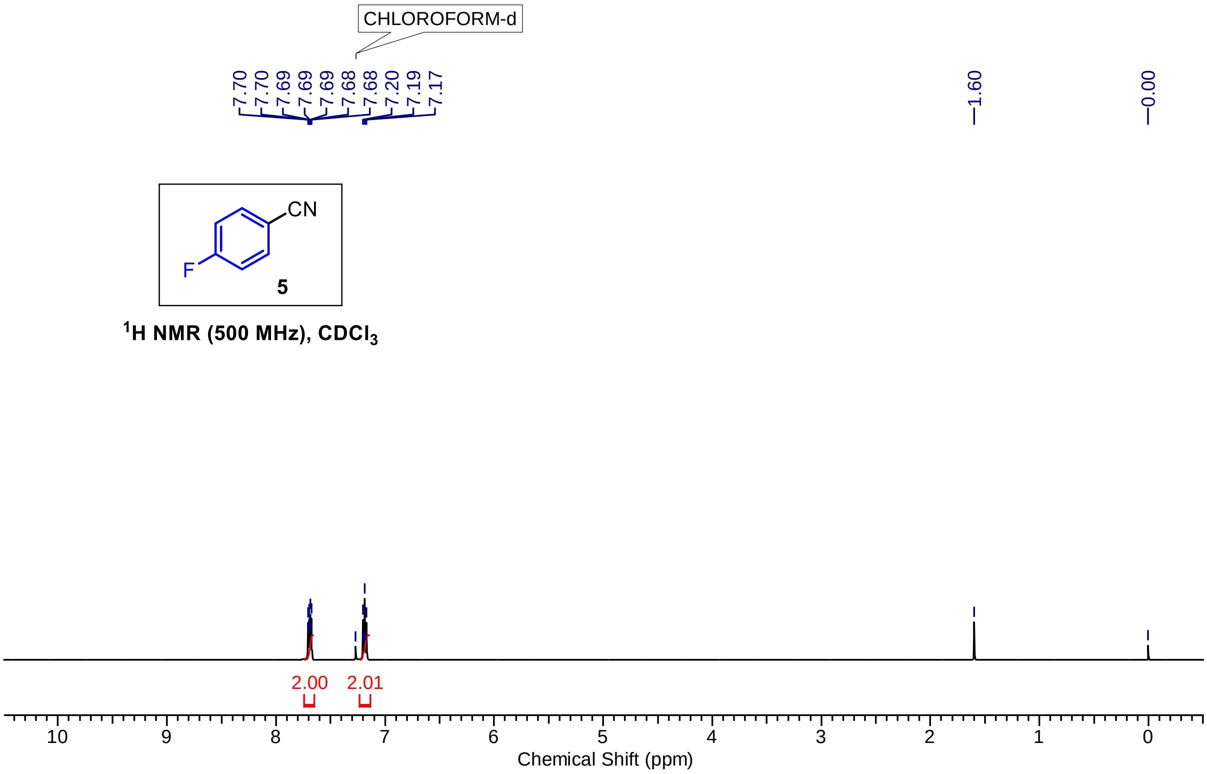


An oven dried vial was charged with Au(III) azide complex **3b** (0.2 mmol, 1 equiv) in dichloromethane. Trimethylsilyl cyanide (1 mmol, 5 equiv) was added, and the reaction mixture was stirred for 20 minutes at room temperature. The formation of 4-fluorobenzonitrile **5** was indicated by TLC analysis and the product was further isolated and characterized by ^{1}H NMR spectroscopy.

4-fluorobenzonitrile (5):[5]



99% yield, **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.70 - 7.68 (m, 2 H), 7.20 - 7.17 (m, 2 H). **^{19}F NMR (470 MHz, CHLOROFORM-d)** δ = -102.4.



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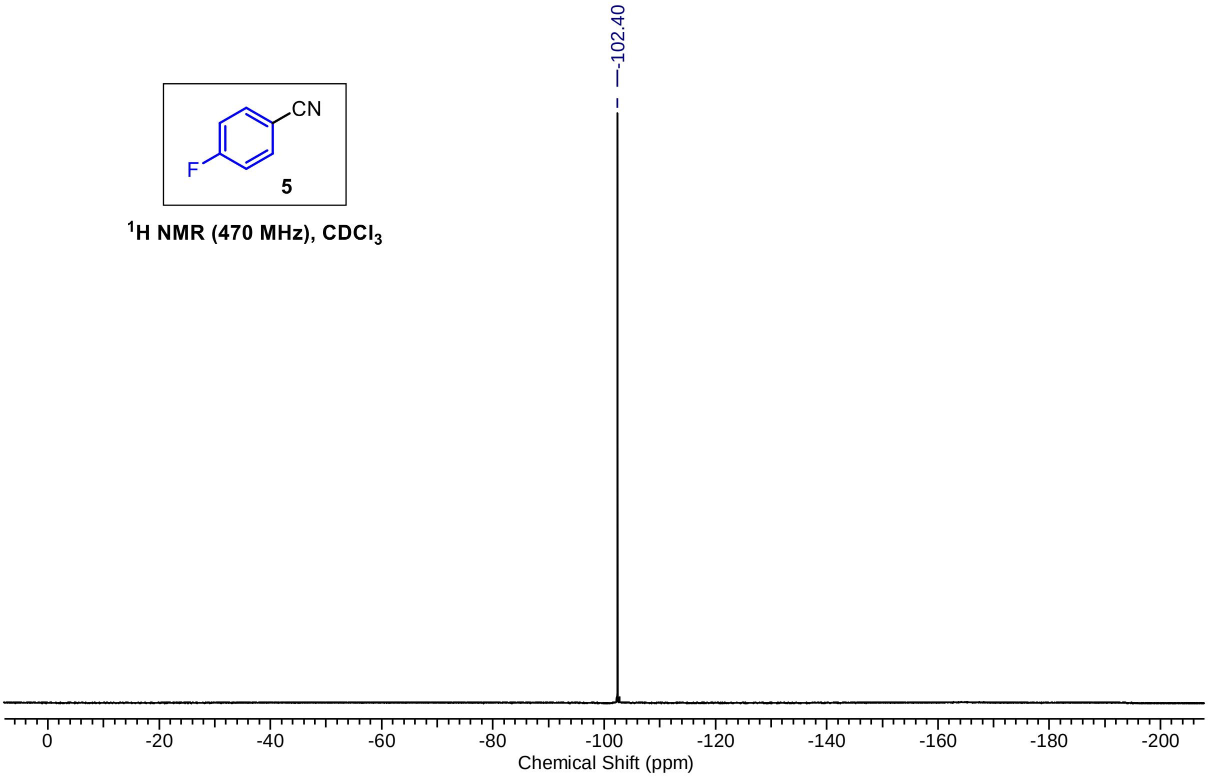
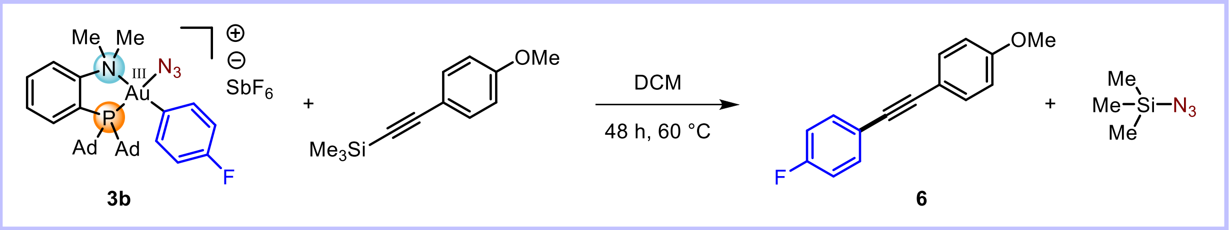
[5] R. Gerber, M. Oberholzer, C. M. Frech, *Chem. Eur. J.*, 2012, **18**, 2978–2986.

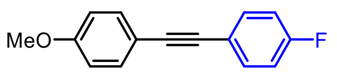


3.3. Reaction of Au(III)-azide complex with TMS-alkyne:



An oven dried vial was charged with Au(III)-azide complex **3b** (0.2 mmol, 1 equiv) in dichloromethane. Trimethylsilyl alkyne (1 mmol, 5 equiv) was added, and the reaction mixture was stirred for 48 hours at 60 ºC. The formation of the C(sp^2)-C(sp) cross-coupled product **6** was indicated by TLC analysis and the product was further isolated and characterized by ^{1}H NMR spectroscopy.

1-fluoro-4-((4-methoxyphenyl)ethynyl)benzene (6):[6]



6

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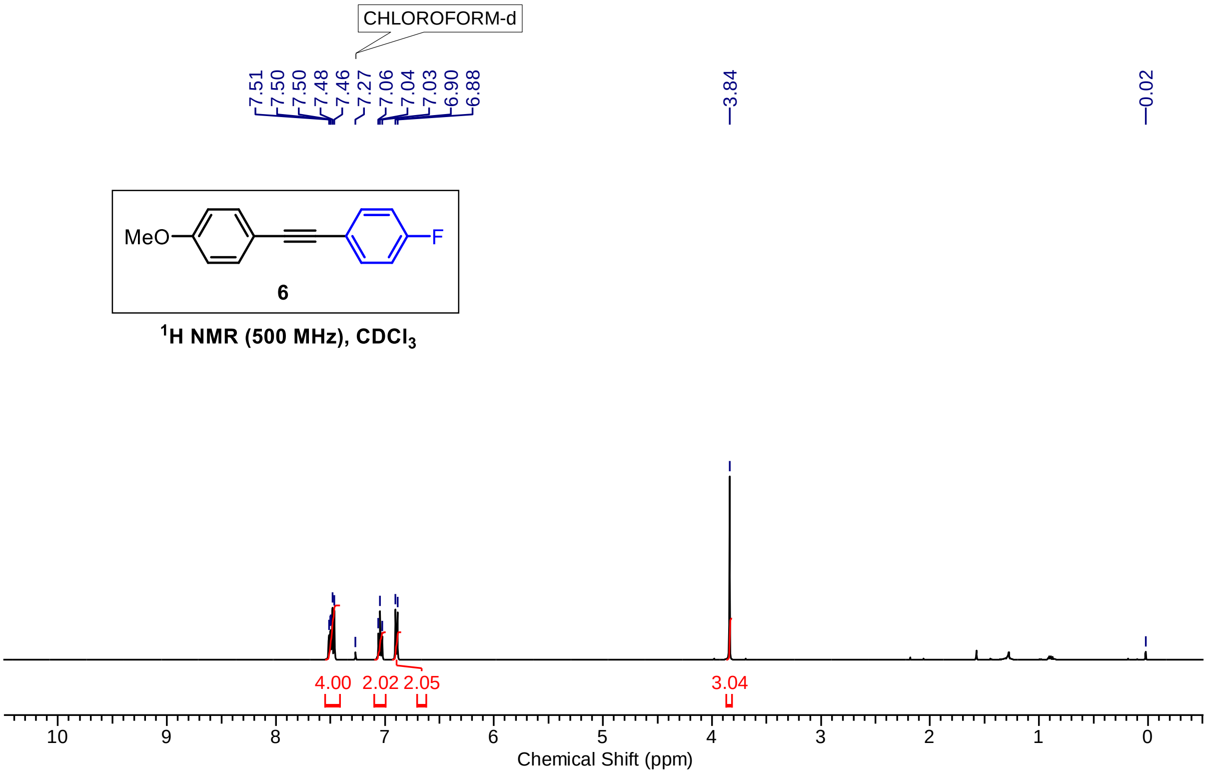
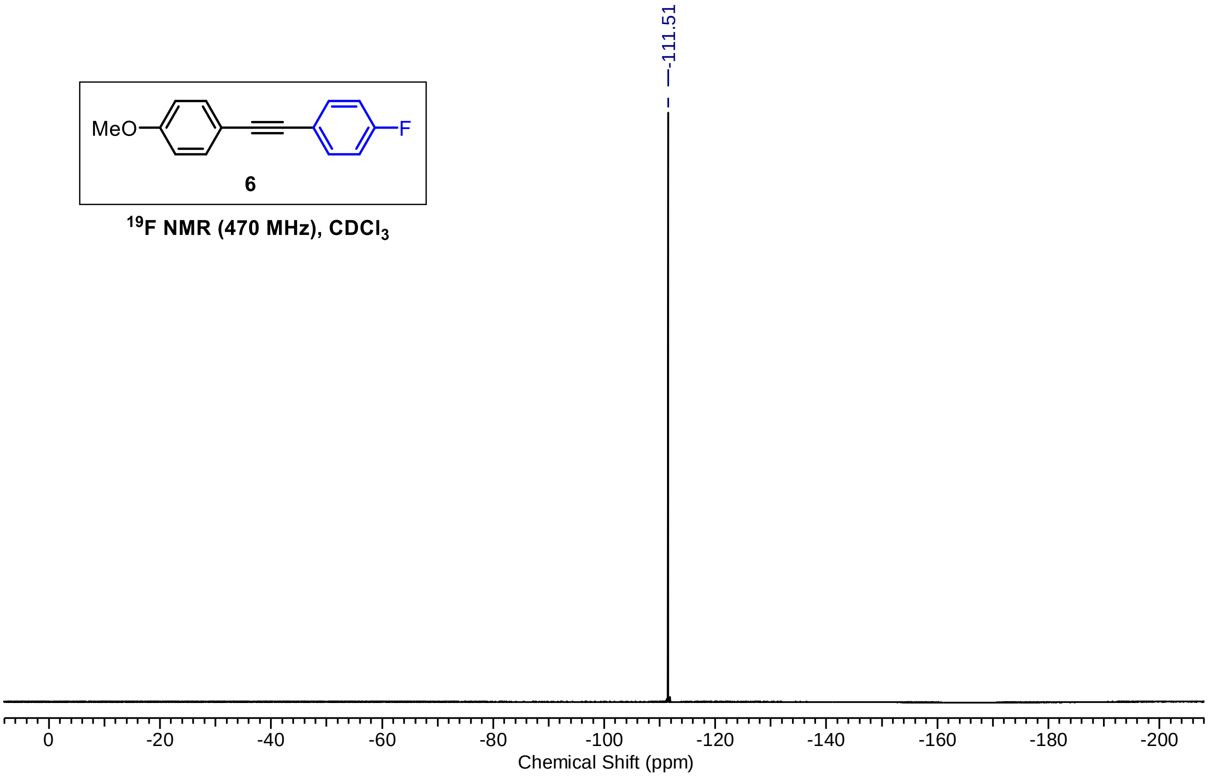
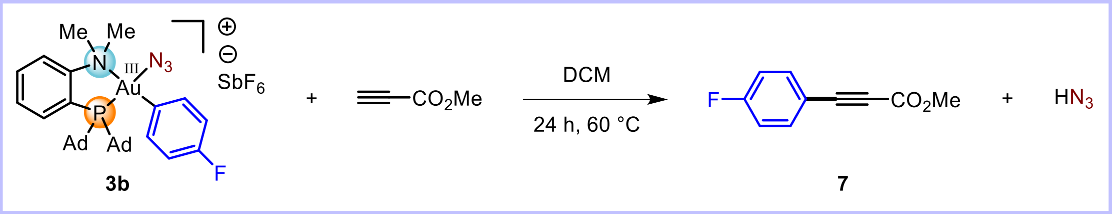
6) T. Li, X. Qu, G. Xie, J. Mao, *Chem. Asian J.*, 2011, **6**, 1325–1330.

87% yield, **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.51 - 7.46 (m, 4 H), 7.04 (t, *J* = 8.7 Hz, 2 H), 6.91 - 6.87 (d, *J* = 8.8 Hz, 2 H), 3.84 (s, 3 H). **^{19}F NMR (470 MHz, CHLOROFORM-d)** δ = -111.51.



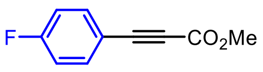


3.4. Reaction of Au(III)-azide complex with terminal alkyne:



An oven dried vial was charged with Au(III)-azide complex **3b** (0.2 mmol, 1 equiv) in dichloromethane. Methyl propiolate (1 mmol, 5 equiv) was added, and the reaction mixture was stirred for 48 hours at 60 ºC. The formation of methyl 3-(4-fluorophenyl)propiolate **7** was indicated by TLC analysis and the product was further isolated and characterized by ^{1}H NMR spectroscopy.

methyl 3-(4-fluorophenyl)propiolate (7):[7]



7

96% yield, **^{1}H NMR (500 MHz, CHLOROFORM-d)** δ = 7.62 - 7.59 (m, 2 H), 7.12 - 7.08 (m, 2 H), 3.86 (s, 3 H). **^{19}F NMR (470 MHz, CHLOROFORM-d)** δ = -106.27.

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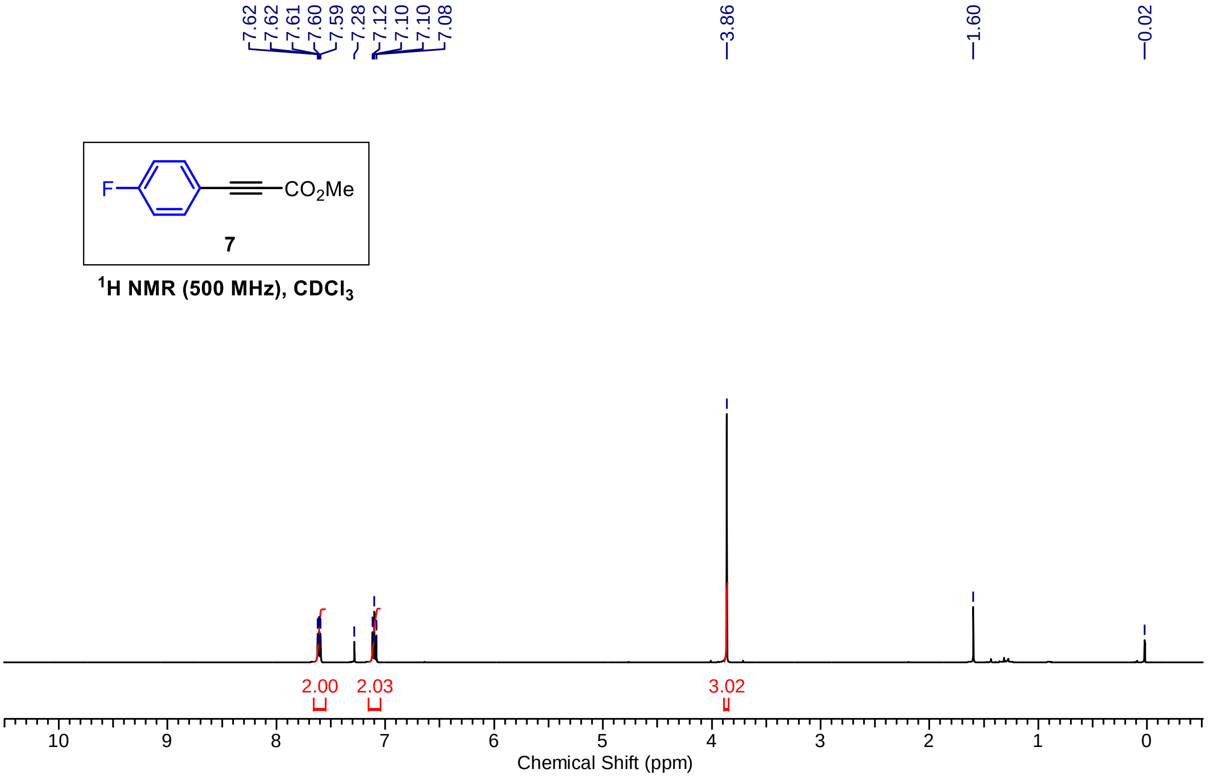
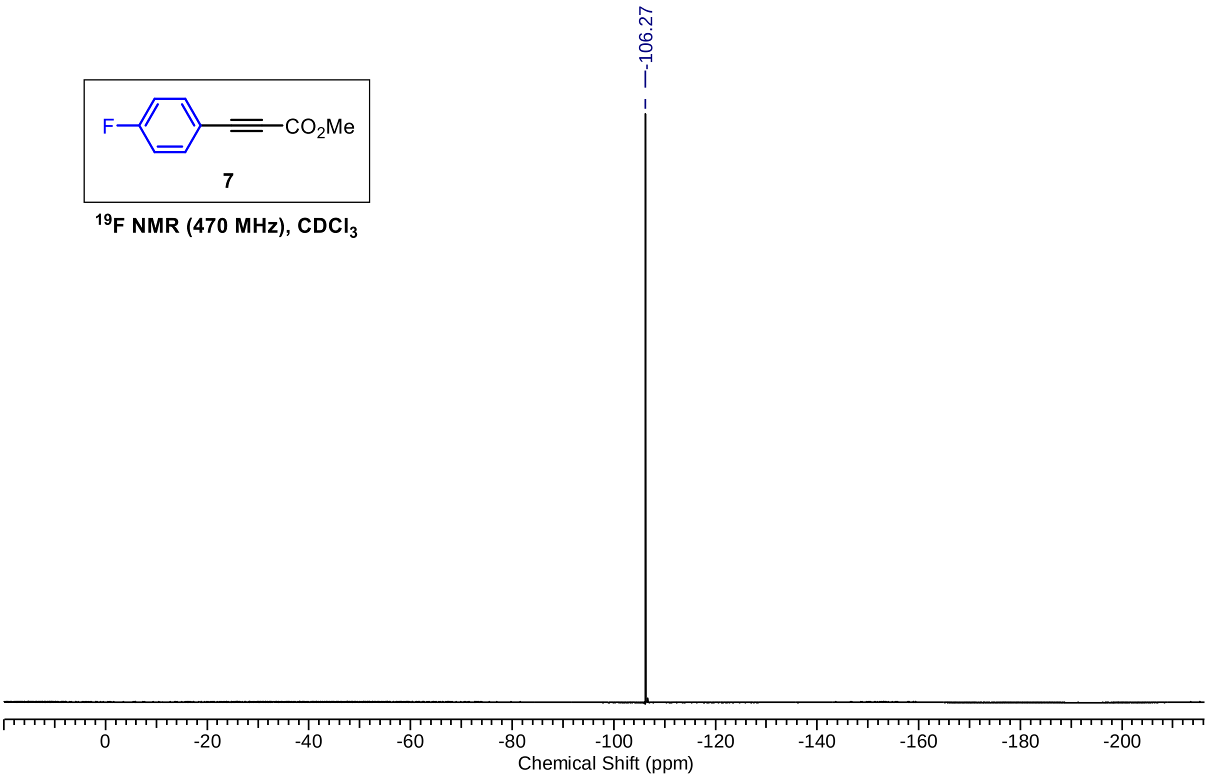
[7] Y.-L. Zhu, N. Zhao, X.-L. Fu, X.-Y. Zhao, Y.-L. Li, Y.-D. Shao, J. Chen, Y. Lu, *Org. Lett.*, 2024, **26**, 12–17.



^{1}H NMR (500 MHz), $CDCl_3$

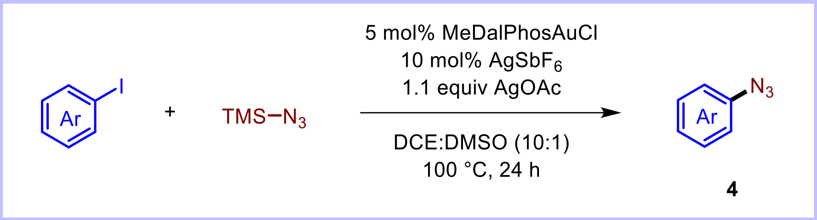


^{19}F NMR (470 MHz), $CDCl_3$

4. General procedure for the gold-catalyzed azidation of aryl iodides:

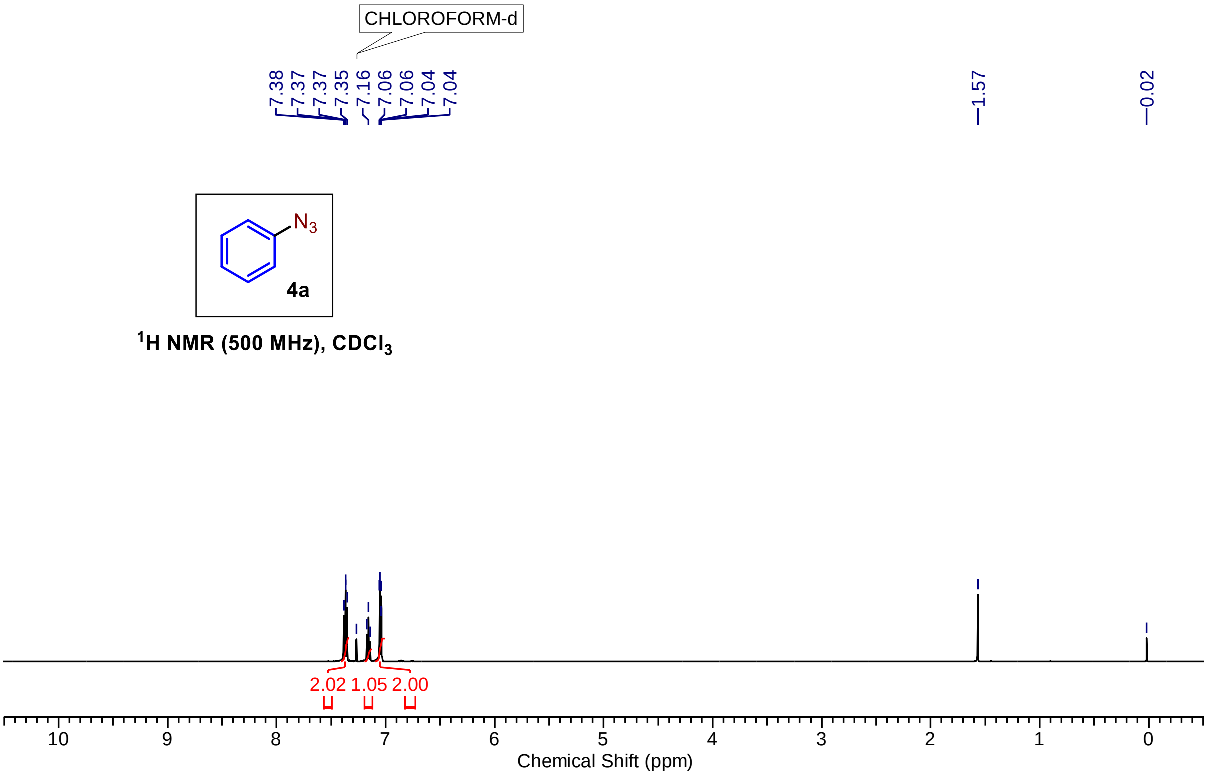
We began the development of gold-catalyzed azidation reaction of aryl iodides by performing the reaction of iodobenzene (1 equiv) with sodium azide (1 equiv) in the presence of 5 mol%

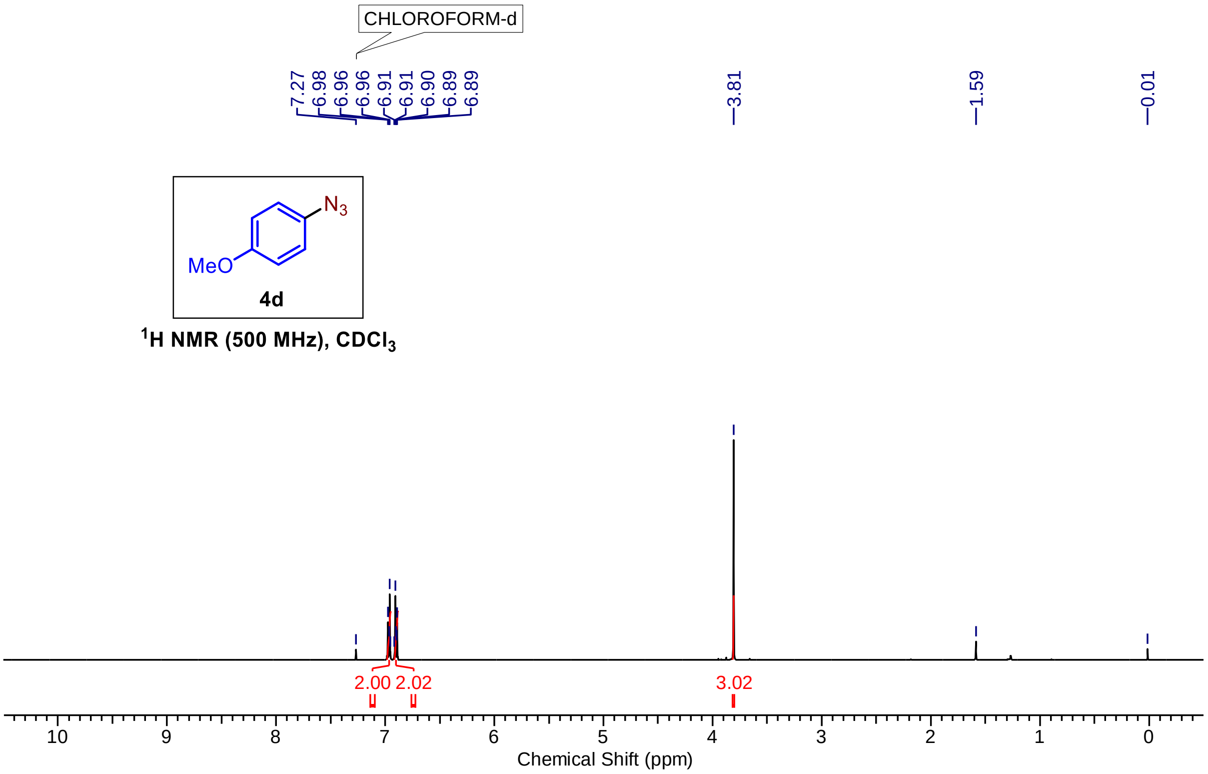
MeDalPhosAuCl, 10 mol% $AgSbF_6$ and 1.1 equiv AgOAc in DCE:DMSO (10:1) at 100 ºC for 24 hours. The formation of the desired product was observed in trace amounts. Next, we moved our attention towards screening of other sources of azide such as $TMSN_3$ and diphenyl phosphoryl azide. By utilizing $TMSN_3$ as the coupling partner, the yield of the reaction was increased to 84%.

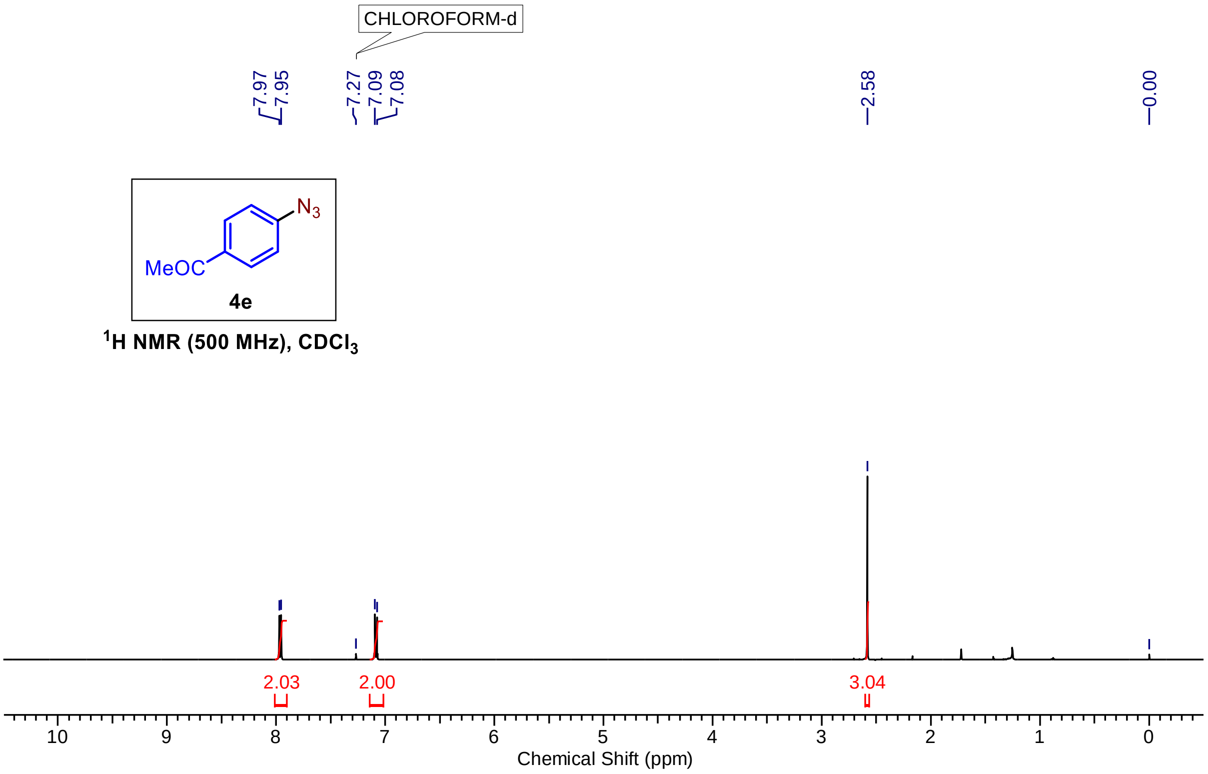


An oven-dried screw-cap vial, equipped with a magnetic stir bar, was loaded with $TMSN_3$ (0.2 mmol, 1.0 equiv), AgOAc (0.22 mmol, 1.1 equiv) and DMSO (0.2 ml) and allowed to stir at 100 ºC for 1 h. In another vial, aryl iodide (0.2 mmol, 1.0 equiv), MeDalPhosAuCl (0.01 mmol, 0.05 equiv), and DCE (2 ml) was added and stirred at room temperature. This mixture was then added to the screw-cap vial by using a syringe equipped with a needle. The resulting reaction mixture was stirred at room temperature for 5 min, then $AgSbF_6$ (0.02 mmol, 0.1 equiv) was added and the mixture was allowed to stir at 100 ºC for 24 h. After completion of the reaction, as monitored by TLC, it was diluted with DCM (5 mL), filtered through a short pad of celite, concentrated and subsequently purified by silica gel column chromatography to afford the desired cross-coupled product **4**.

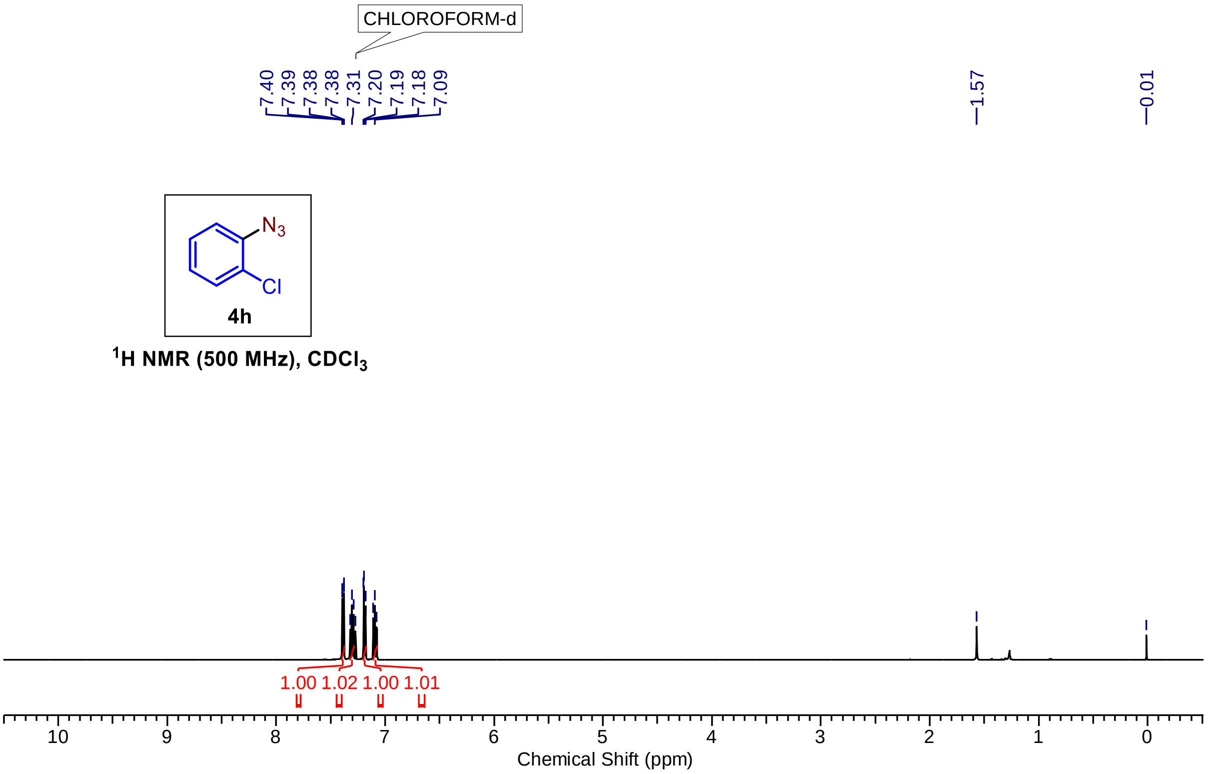
NMR Spectra for azidoarenes (4):


CHLOROFORM-d
7.38
7.37
7.37
7.35
7.16
7.06
7.06
7.04
7.04
1.57
0.02
N$_3$
4a
^{1}H NMR (500 MHz), CDCl$_3$
2.02
1.05
2.00
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


CHLOROFORM-d
7.27
6.98
6.96
6.96
6.91
6.91
6.90
6.89
6.89
3.81
1.59
0.01
N$_3$
MeO
4d
^{1}H NMR (500 MHz), CDCl$_3$
2.00
2.02
3.02
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)



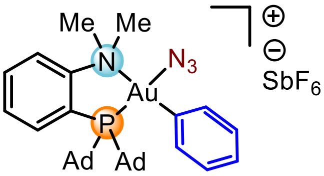
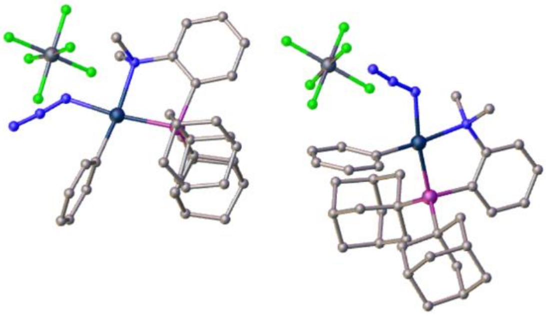
^{1}H NMR (500 MHz), $CDCl_3$



^{1}H NMR (500 MHz), $CDCl_3$

5. X-ray crystallographic information

Sr. No.	Compound structure	ORTEP diagram

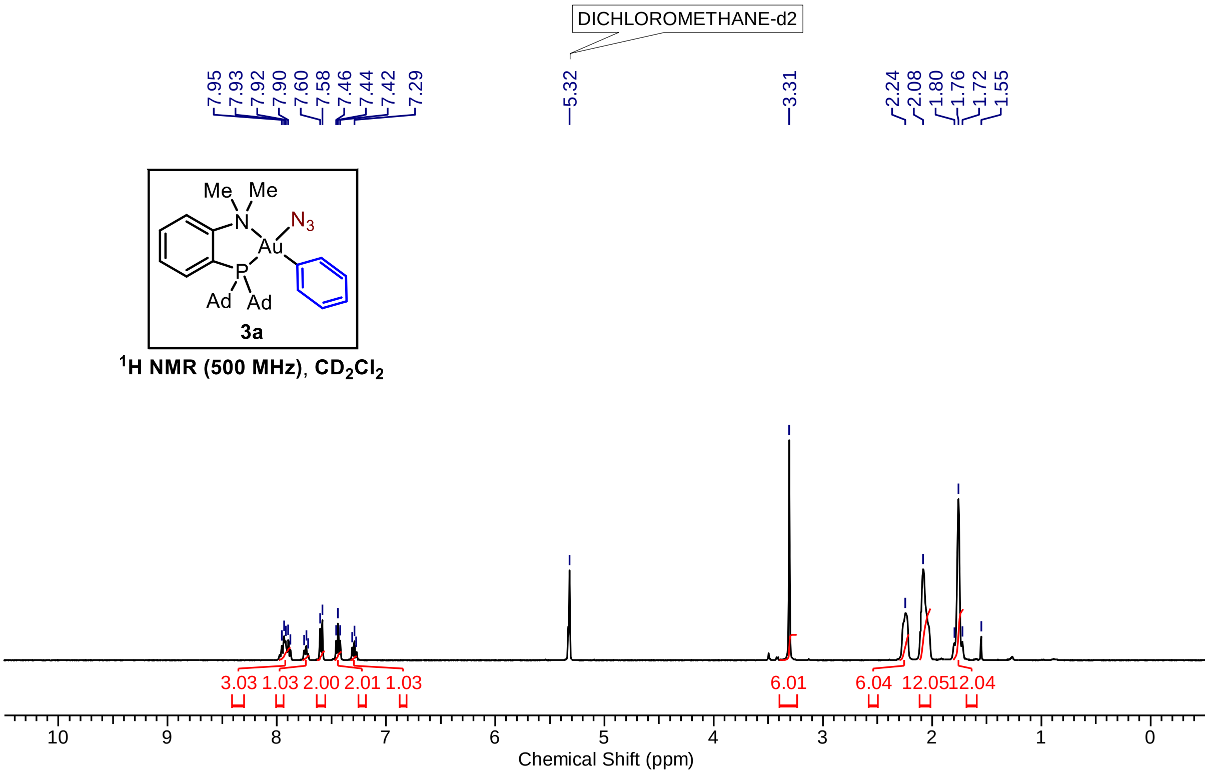
1	 **3a**	 **CCDC** = 2425771

Crystal Parameters

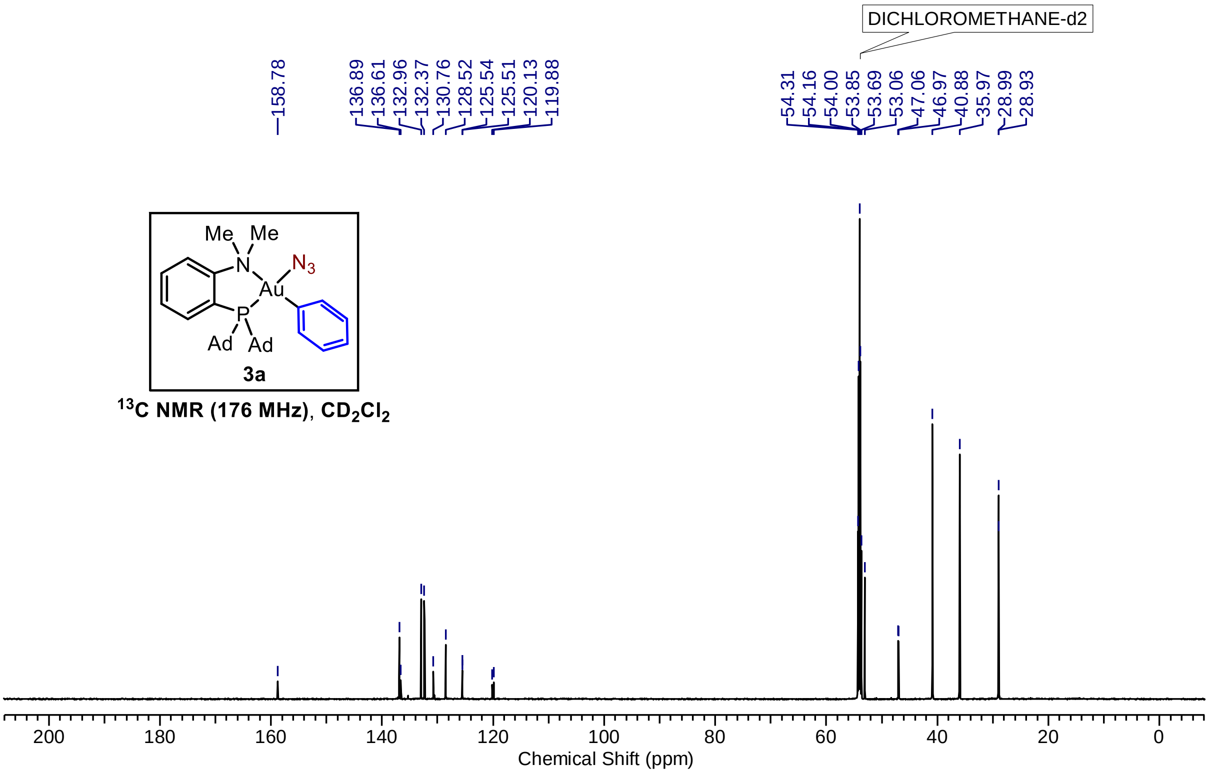
Empirical formula	C68 H90 Au2 F12 N8 P2 Sb2	
Formula weight	1946.85	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 20.424(9) Å	α = 90°.
	b = 11.606(5) Å	β = 107.44(2)°.
	c = 32.783(19) Å	γ = 90°.
Volume	7414(6) Å^3	
Z	4	
Density (calculated)	1.744 Mg/m^3	
Absorption coefficient	4.784 mm^{-1}	
F(000)	3808	
Theta range for data collection	1.919 to 26.408°.	
Index ranges	-25<=h<=25, -14<=k<=14, -40<=l<=40	
Reflections collected	98147	
Independent reflections	15173 [R(int) = 0.1871]	
Completeness to theta = 25.242°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15173 / 51 / 851	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0688, wR2 = 0.1343	
R indices (all data)	R1 = 0.1249, wR2 = 0.1582	
Largest diff. peak and hole	1.950 and -1.082 e.Å^{-3}	

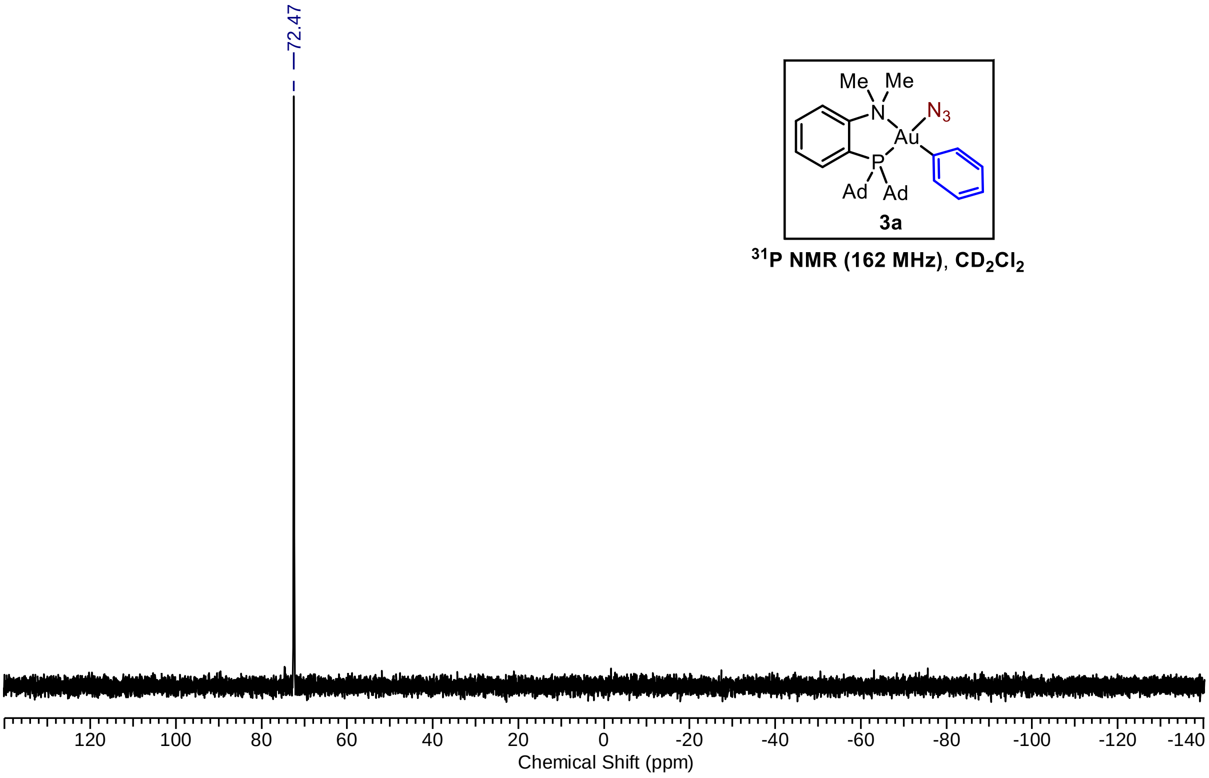
Justification for omission of elemental analysis data: Elemental analysis data could not be obtained for the (P^N)Au(III)-azide complexes due to their thermal instability. These complexes undergo reductive elimination at 100 °C. Alternative characterization data, including ^{1}H, ^{31}P and ^{13}C NMR, HRMS, and X-ray crystallography (wherever applicable), have been provided to confirm the purity of the compounds.

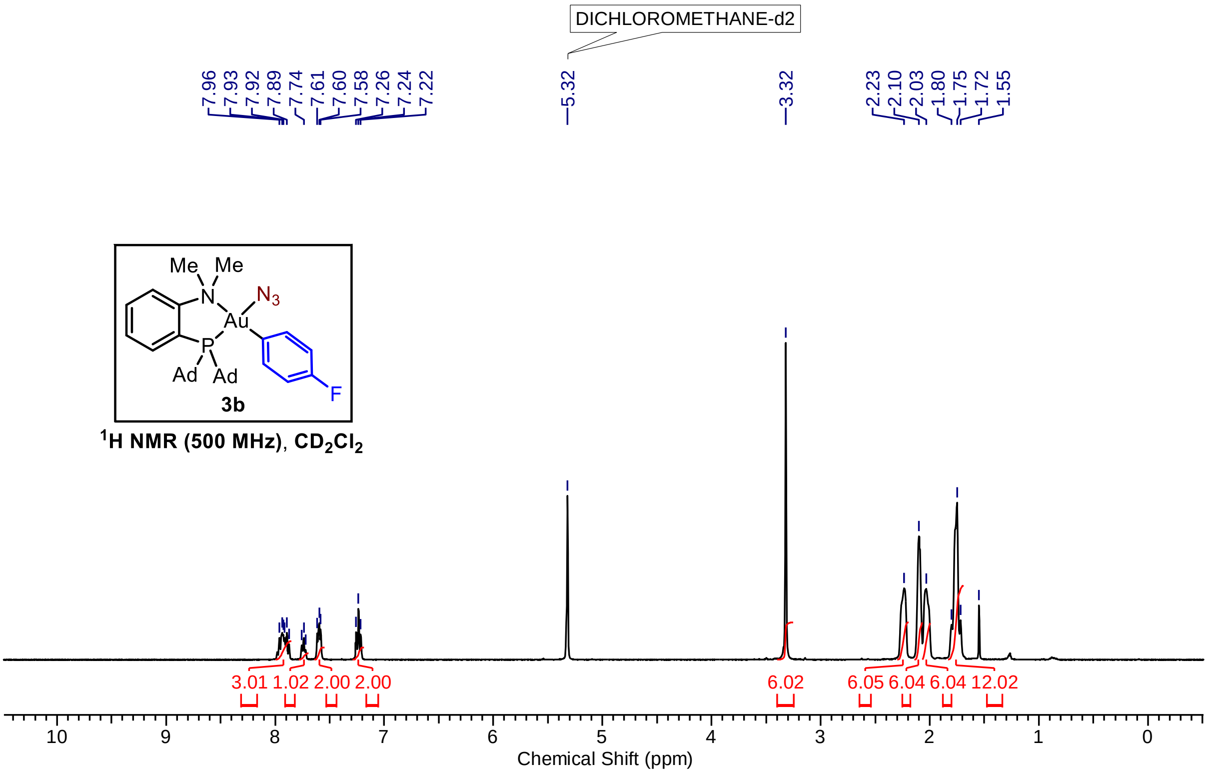
6. NMR Spectra:



^{1}H NMR (500 MHz), CD_2Cl_2

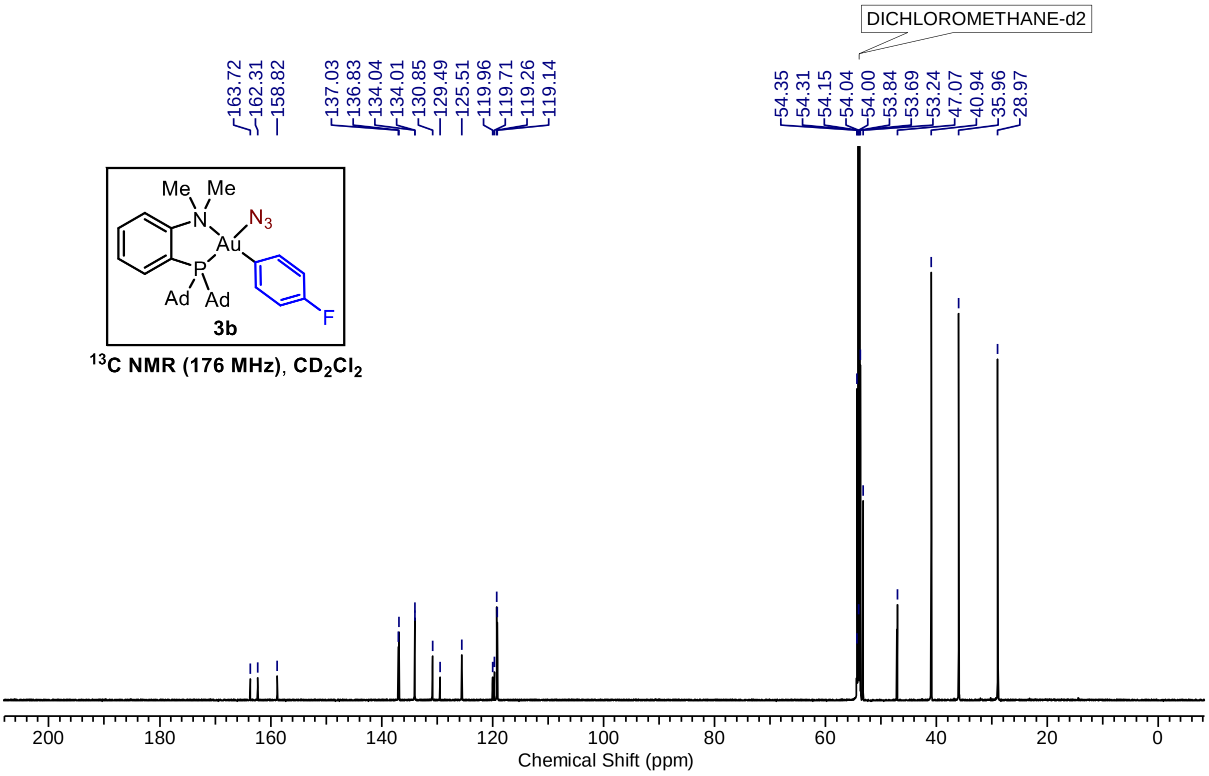

DICHLOROMETHANE-d2
158.78
136.89
136.61
132.96
132.37
130.76
128.52
125.54
125.51
120.13
119.88
54.31
54.16
54.00
53.85
53.69
53.06
47.06
46.97
40.88
35.97
28.99
28.93
Me
Me
N
N3
Au
P
Ad
Ad
3a
13C NMR (176 MHz), CD2Cl2
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


72.47
Me
Me
N
N3
Au
P
Ad
Ad
3a
31P NMR (162 MHz), CD2Cl2
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
Chemical Shift (ppm)



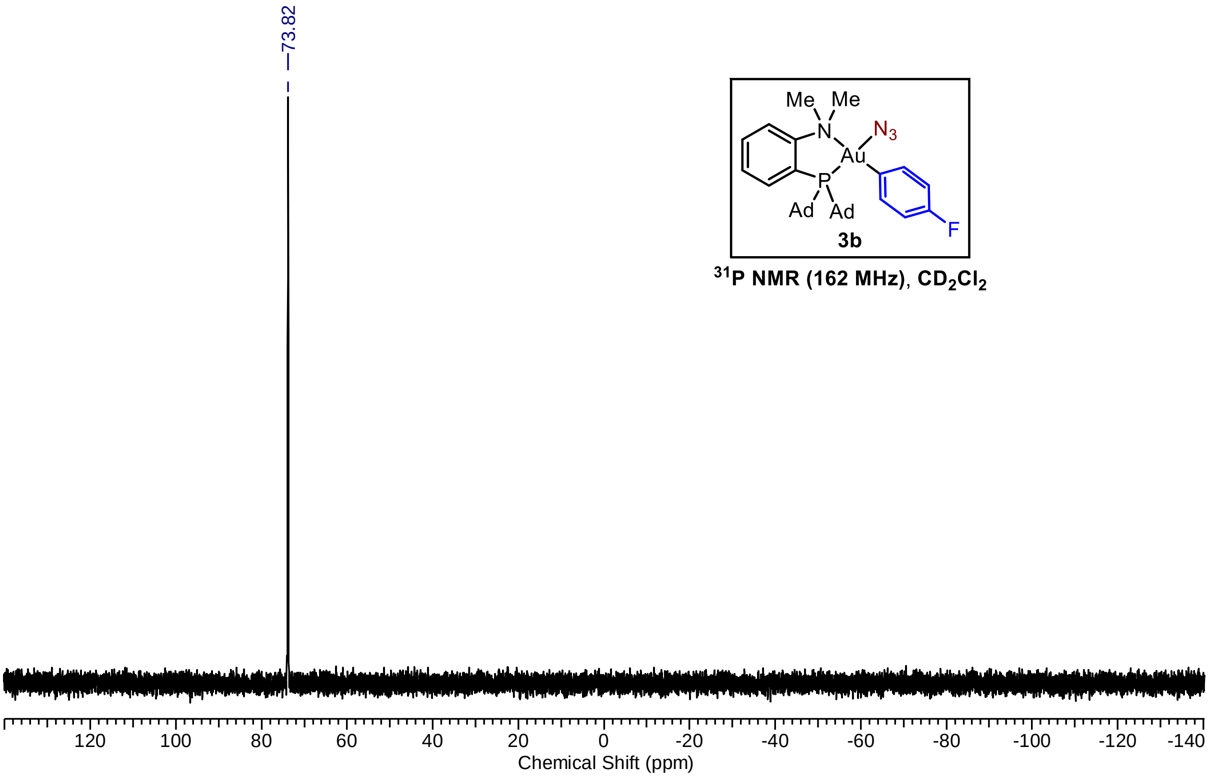
3b

^{1}H NMR (500 MHz), **CD_2Cl_2**



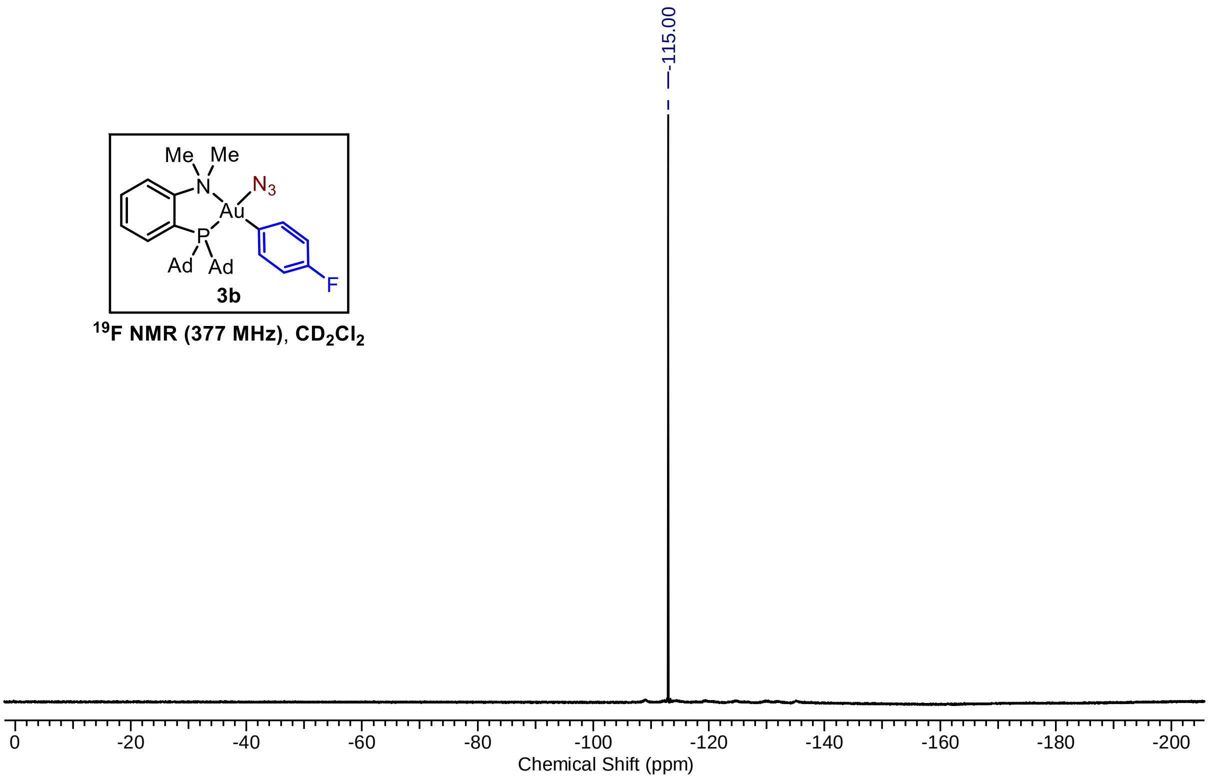
3b

^{13}C NMR (176 MHz), **CD_2Cl_2**



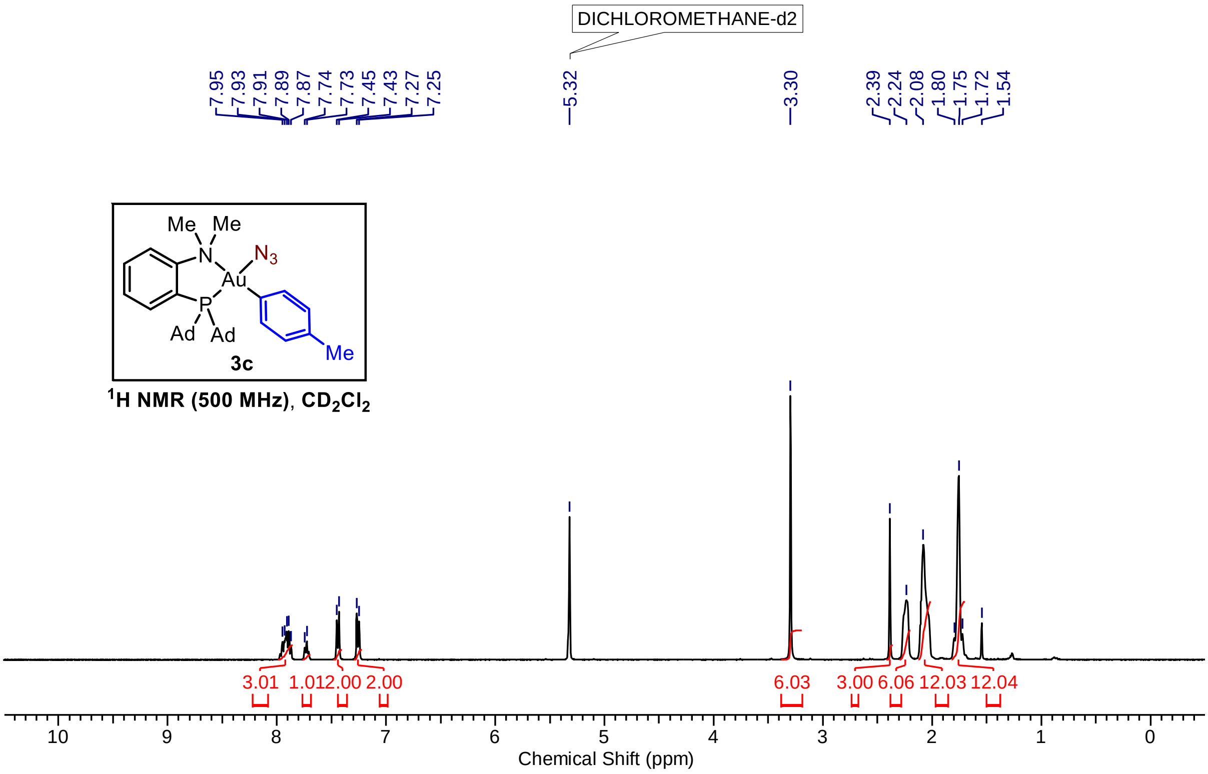
3b

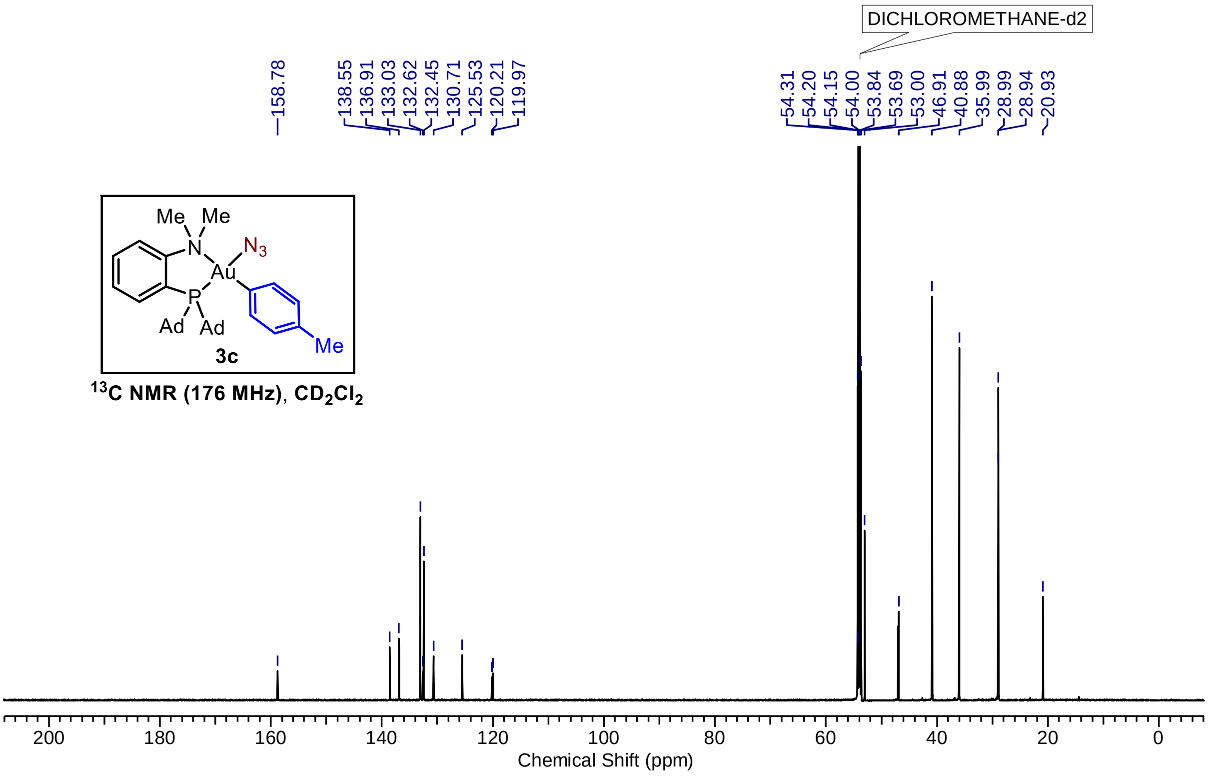
^{31}P NMR (162 MHz), CD$_2$Cl$_2$

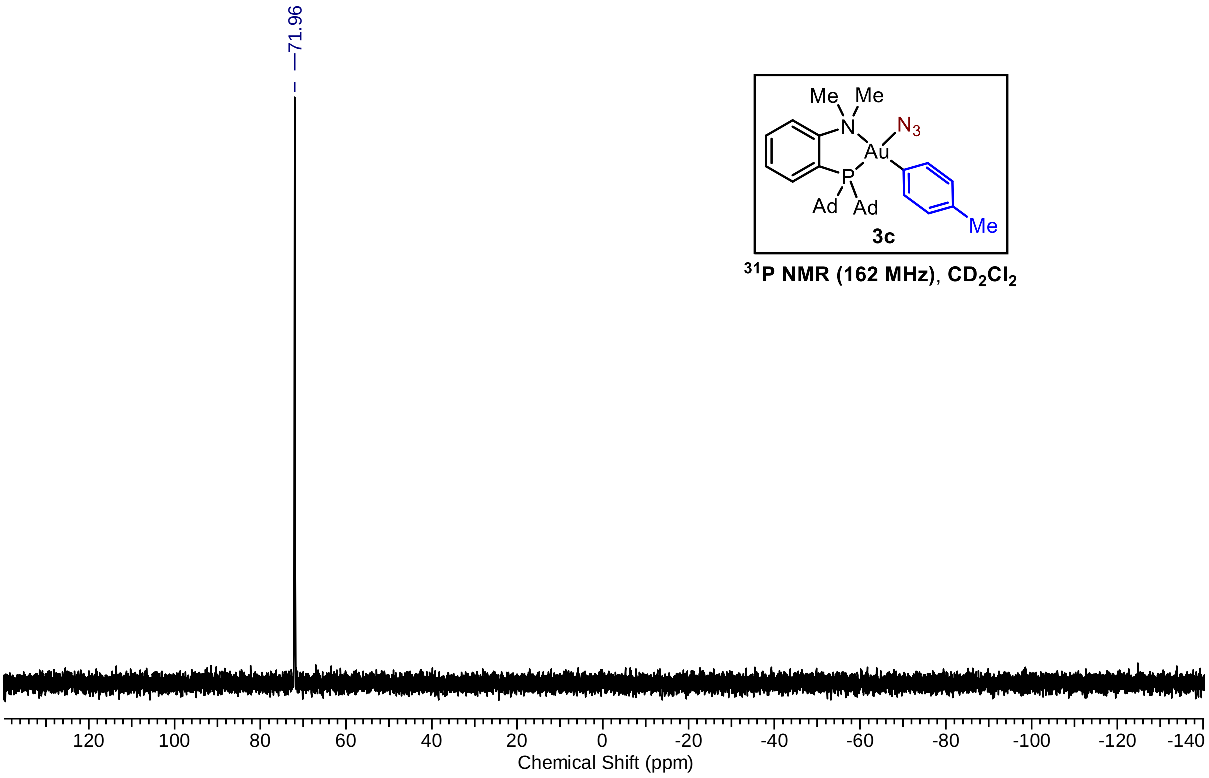


3b

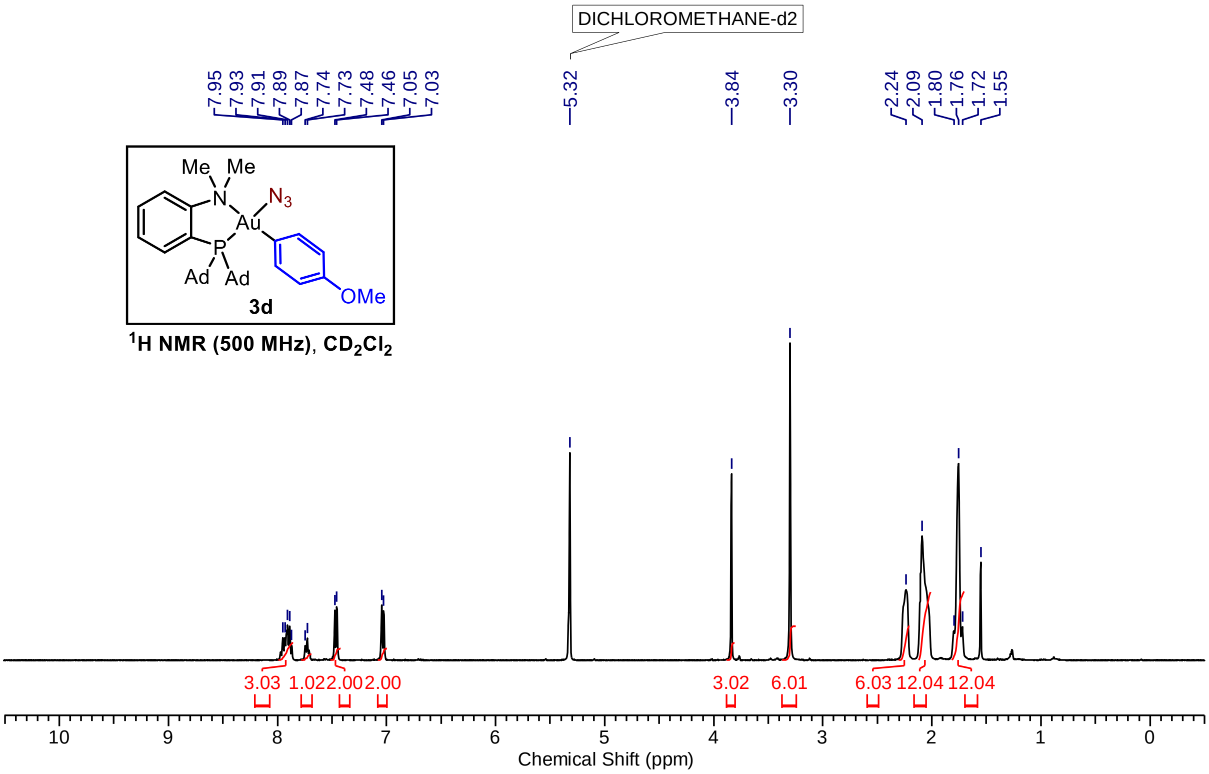
^{19}F NMR (377 MHz), CD$_2$Cl$_2$


DICHLOROMETHANE-d2
7.95
7.93
7.91
7.89
7.87
7.74
7.73
7.45
7.43
7.27
7.25
5.32
3.30
2.39
2.24
2.08
1.80
1.75
1.72
1.54
Me
Me
N
N3
Au
P
Ad
Ad
Me
3c
1H NMR (500 MHz), CD2Cl2
3.01
1.01
2.00
2.00
6.03
3.00
6.06
12.03
12.04
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

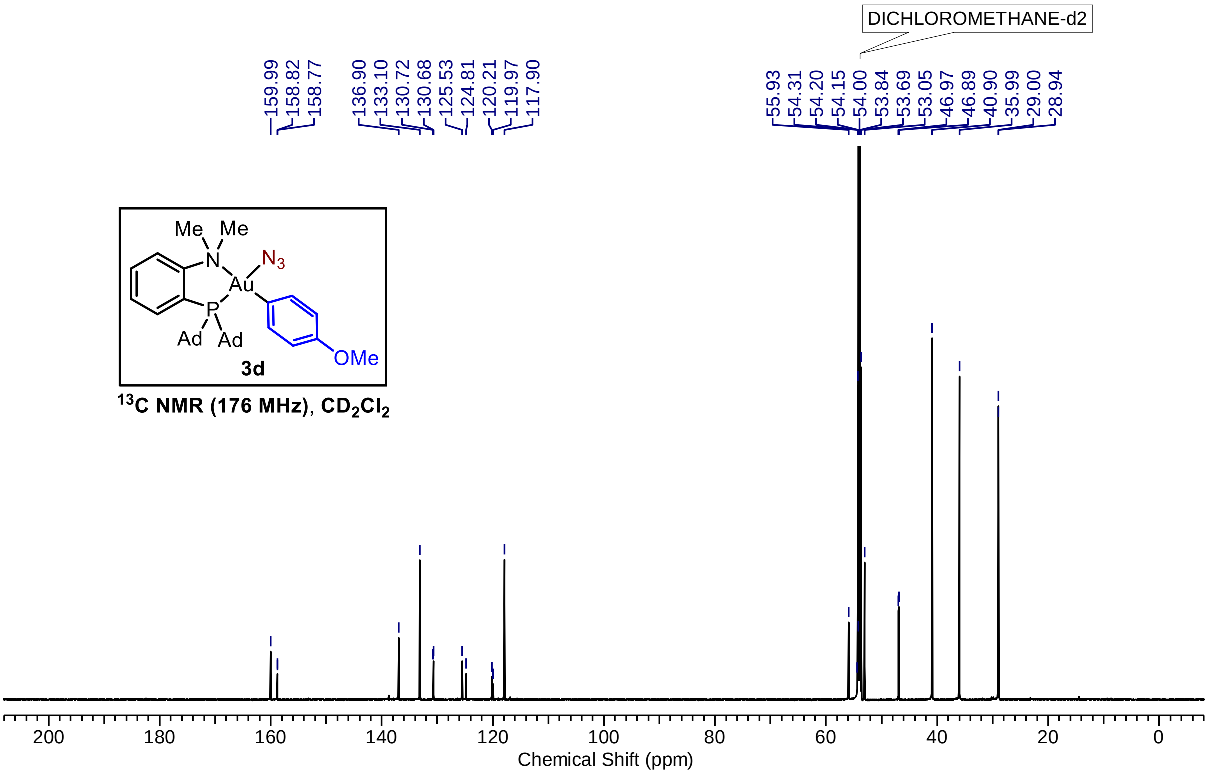

DICHLOROMETHANE-d2
158.78
138.55
136.91
133.03
132.62
132.45
130.71
125.53
120.21
119.97
54.31
54.20
54.15
54.00
53.84
53.69
53.00
46.91
40.88
35.99
28.99
28.94
20.93
Me
Me
N
N3
Au
P
Ad
Ad
Me
3c
13C NMR (176 MHz), CD2Cl2
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

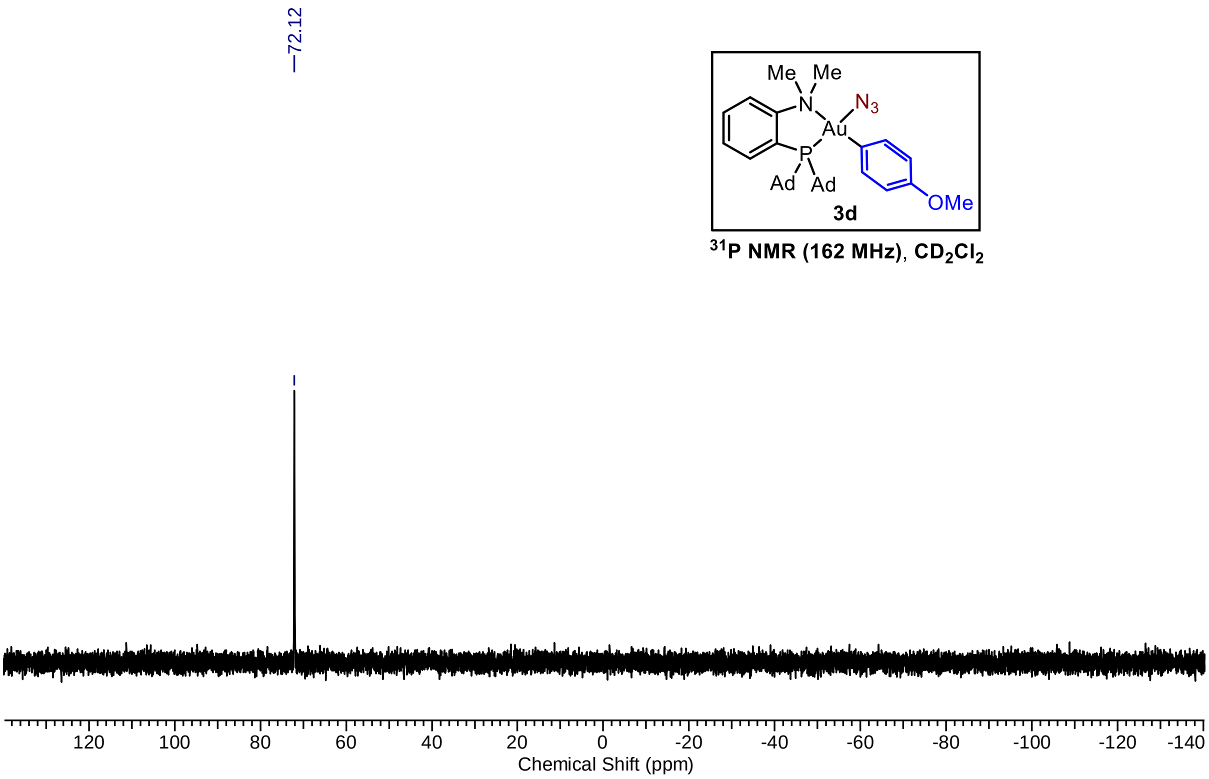

3c

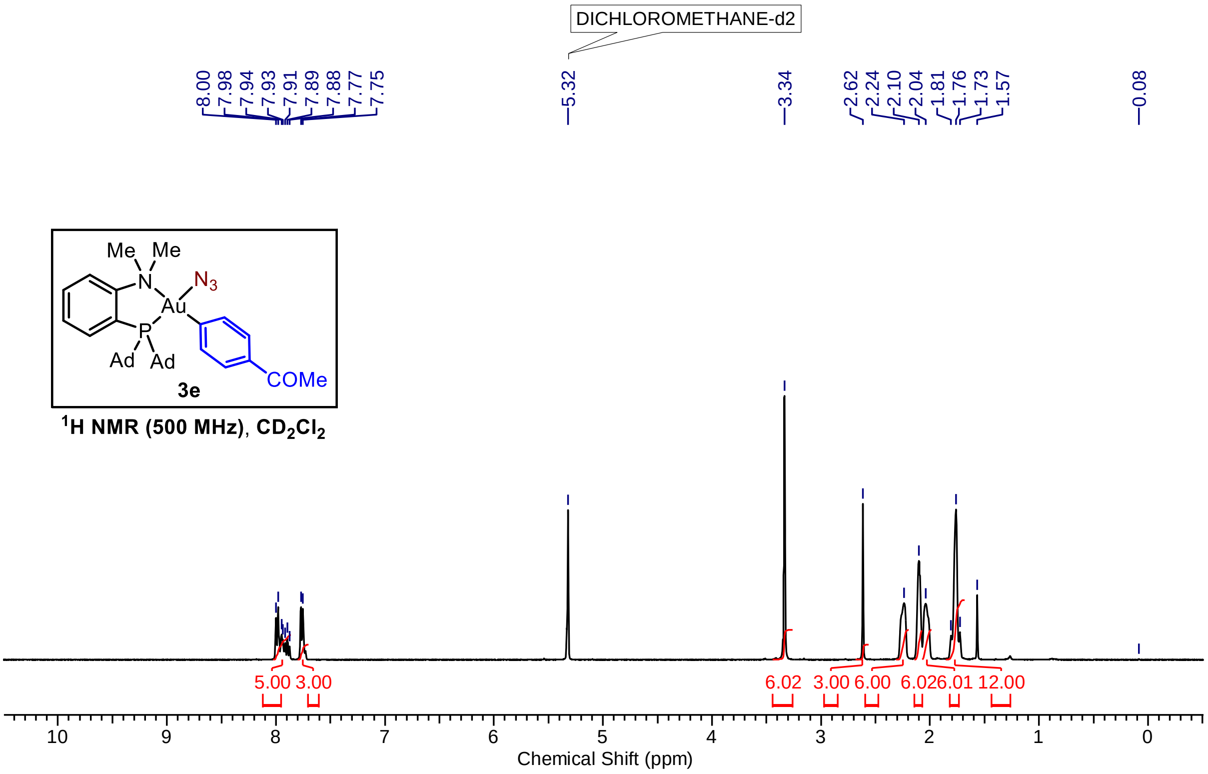
^{31}P NMR (162 MHz), CD_2Cl_2


3d

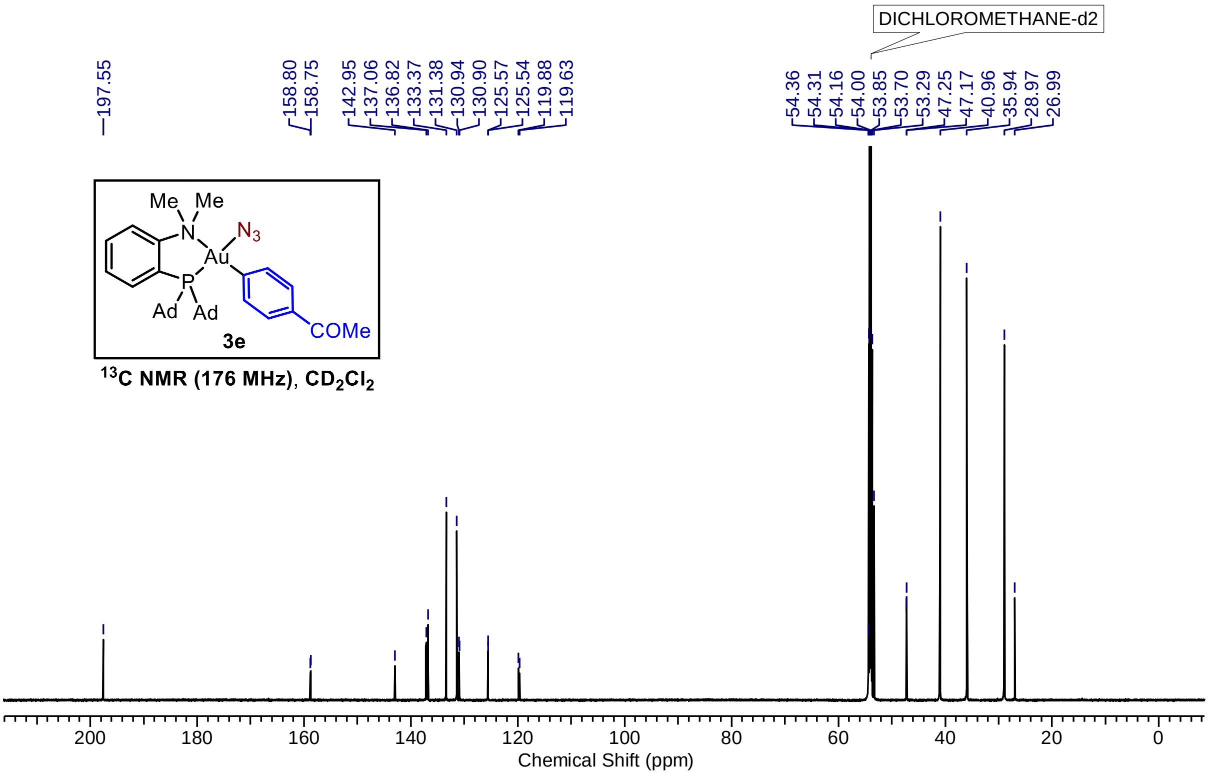
^{1}H NMR (500 MHz), CD_2Cl_2


DICHLOROMETHANE-d2
159.99
158.82
158.77
136.90
133.10
130.72
130.68
125.53
124.81
120.21
119.97
117.90
55.93
54.31
54.20
54.15
54.00
53.84
53.69
53.05
46.97
46.89
40.90
35.99
29.00
28.94
Me
Me
N
N3
Au
P
Ad
Ad
OMe
3d
13C NMR (176 MHz), CD2Cl2
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

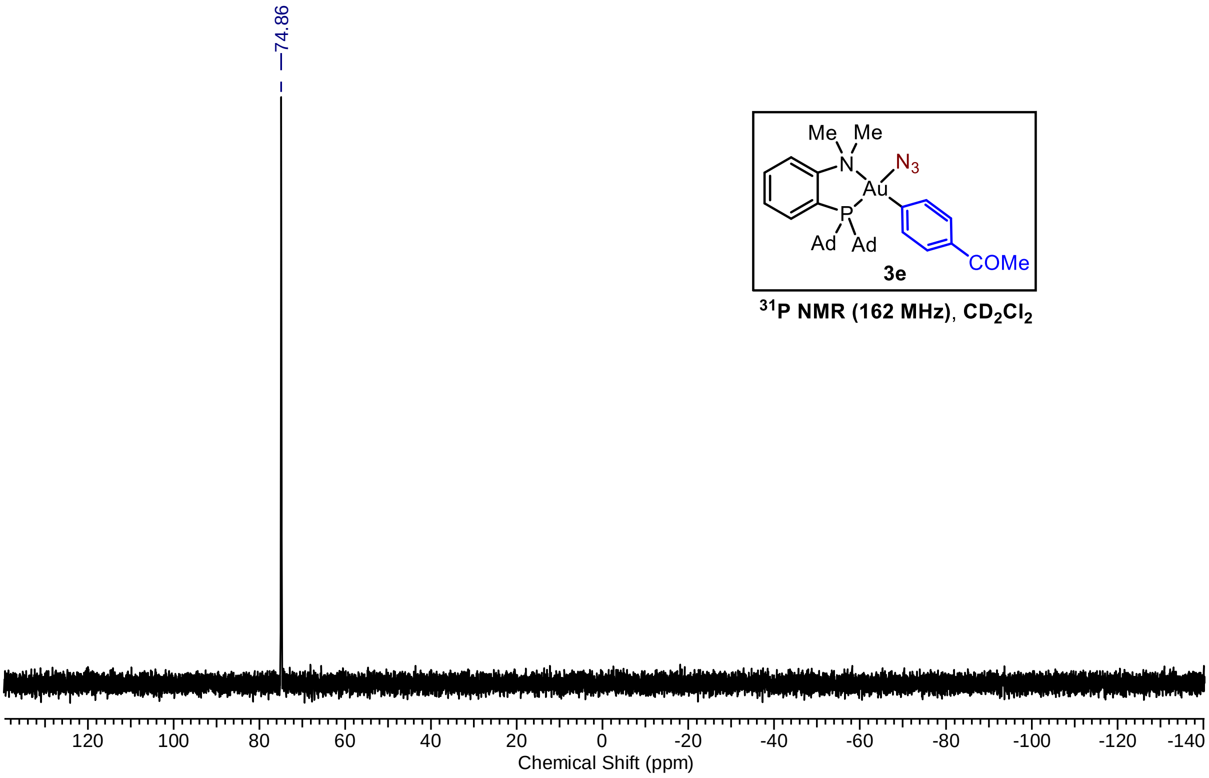

72.12
Me
Me
N
N3
Au
P
Ad
Ad
OMe
3d
31P NMR (162 MHz), CD2Cl2
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
Chemical Shift (ppm)



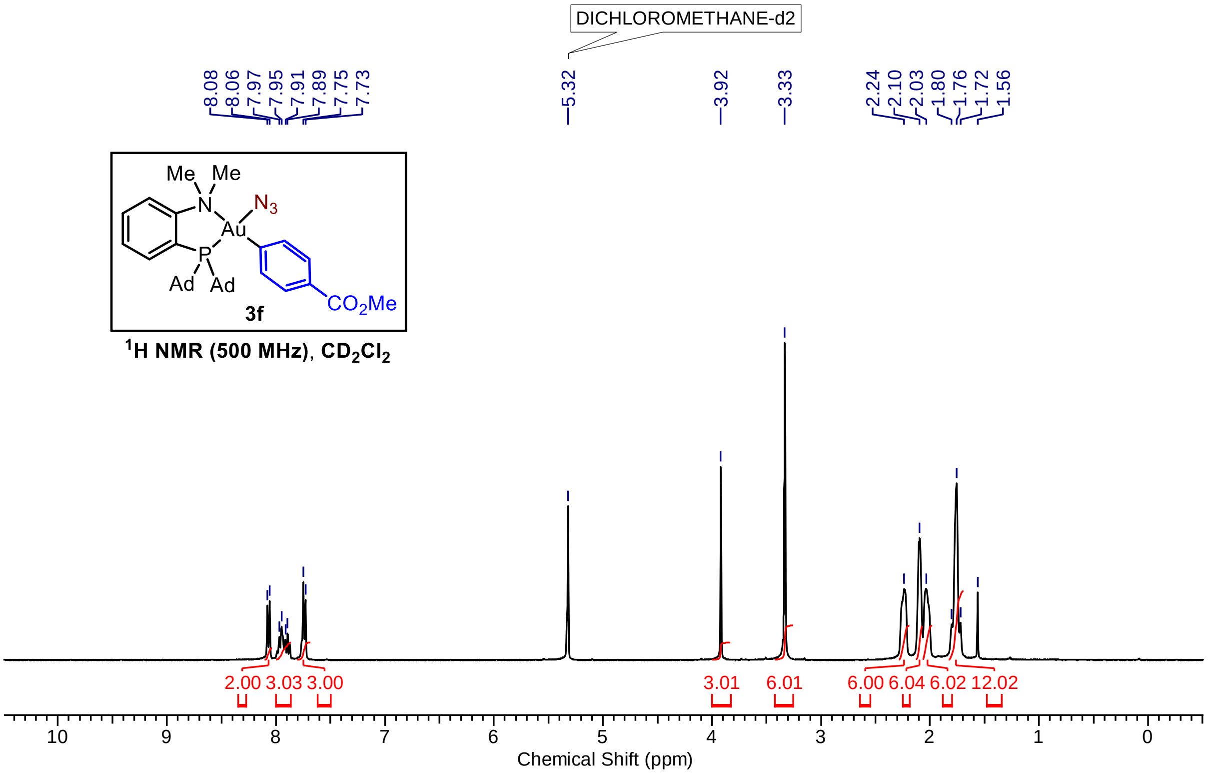
^{1}H NMR (500 MHz), CD_2Cl_2



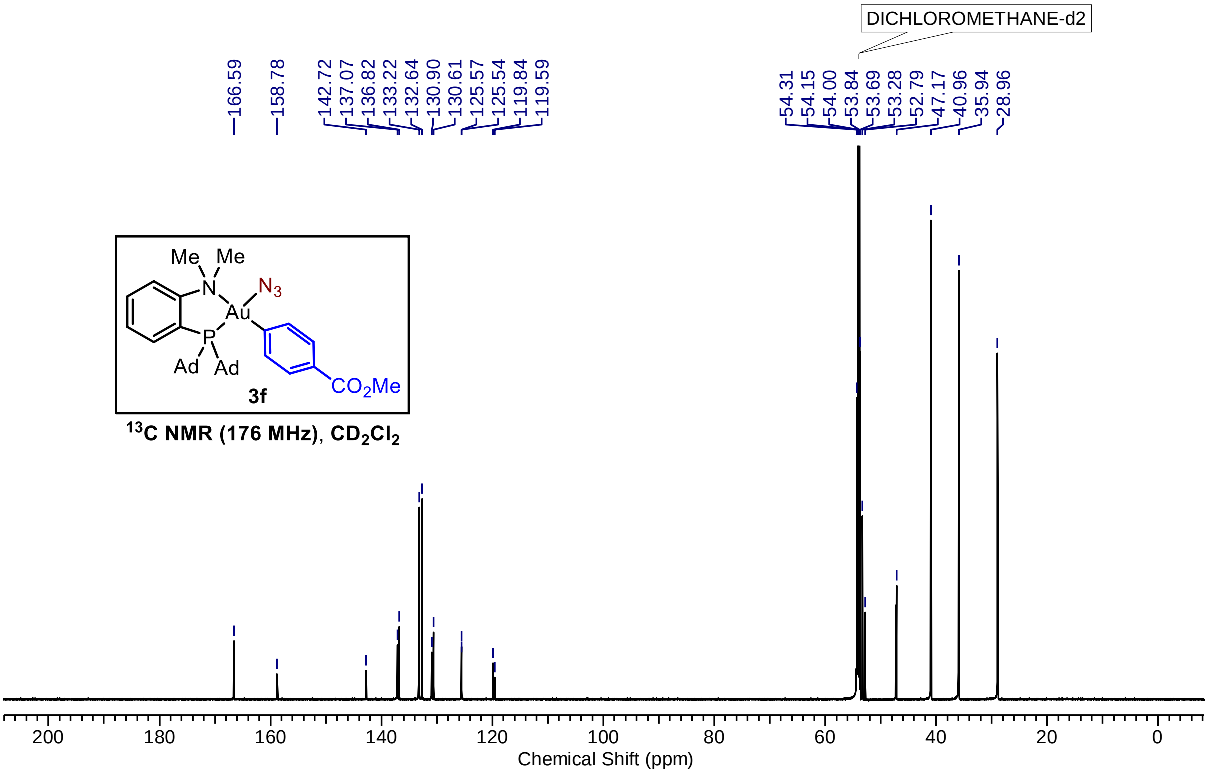
^{13}C NMR (176 MHz), CD_2Cl_2



^{31}P NMR (162 MHz), CD_2Cl_2

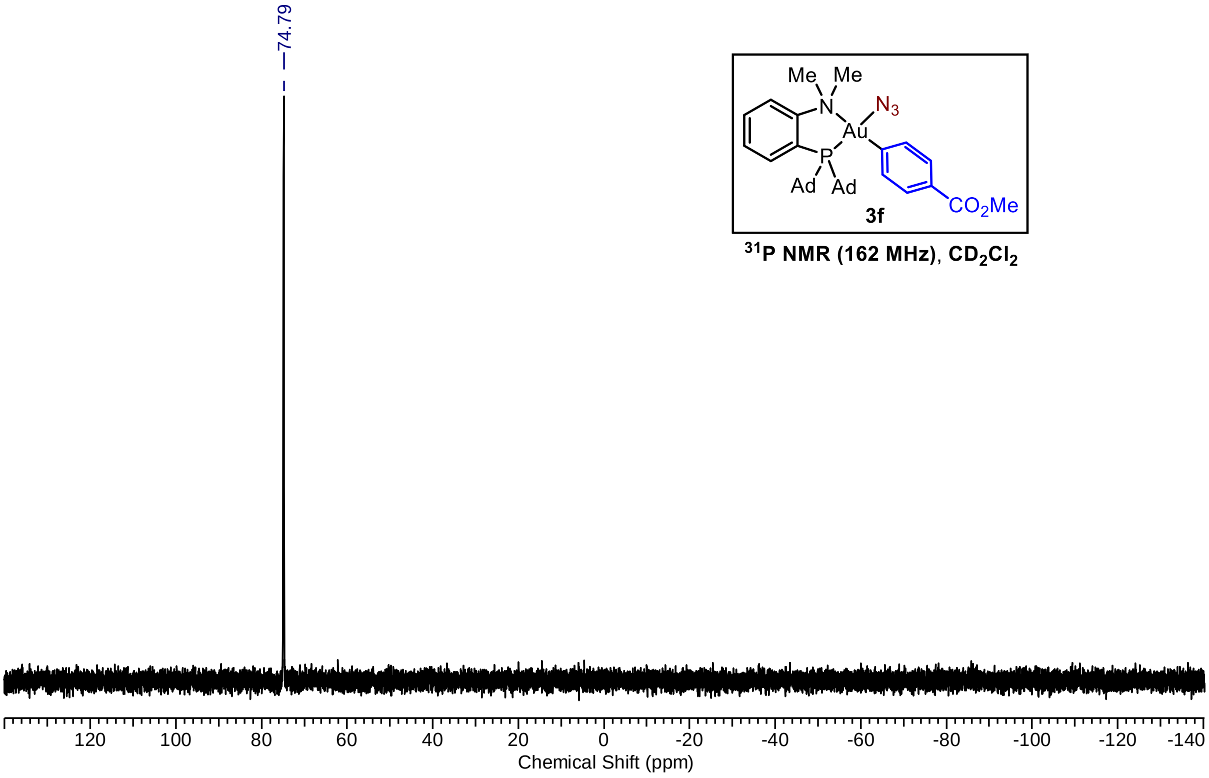


^{1}H NMR (500 MHz), CD_2Cl_2



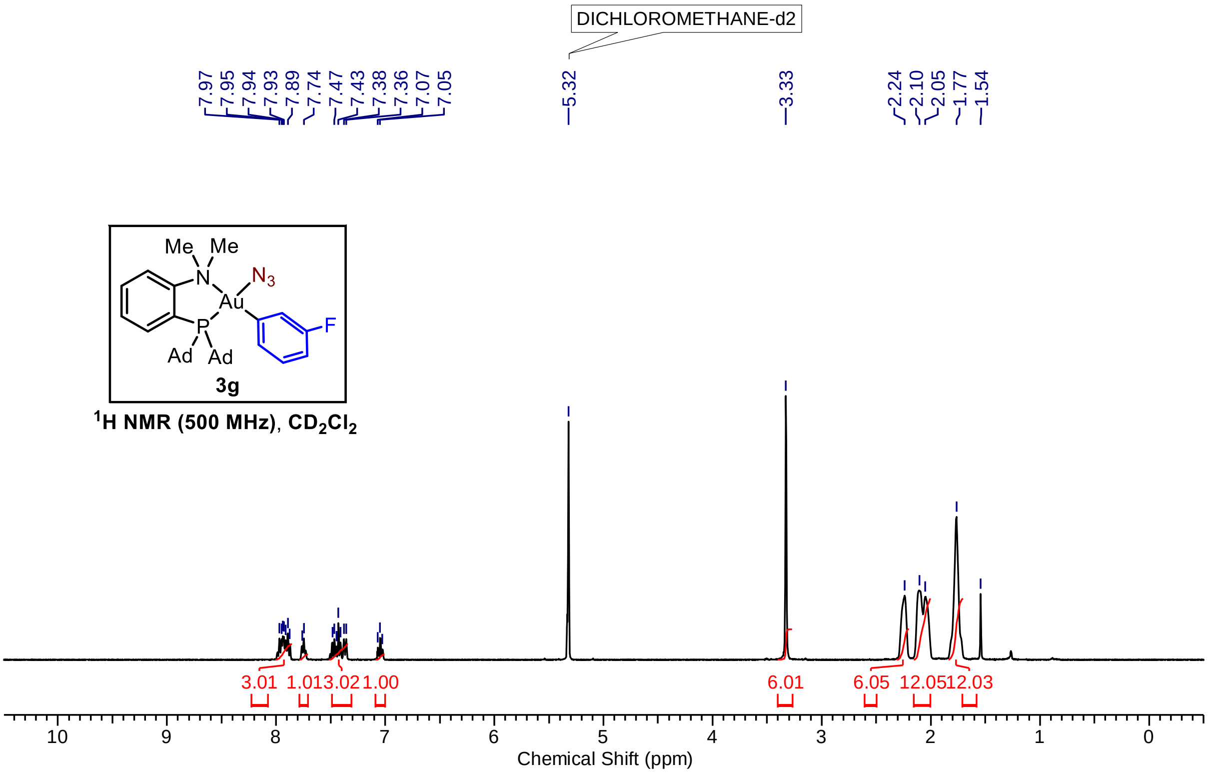
3f

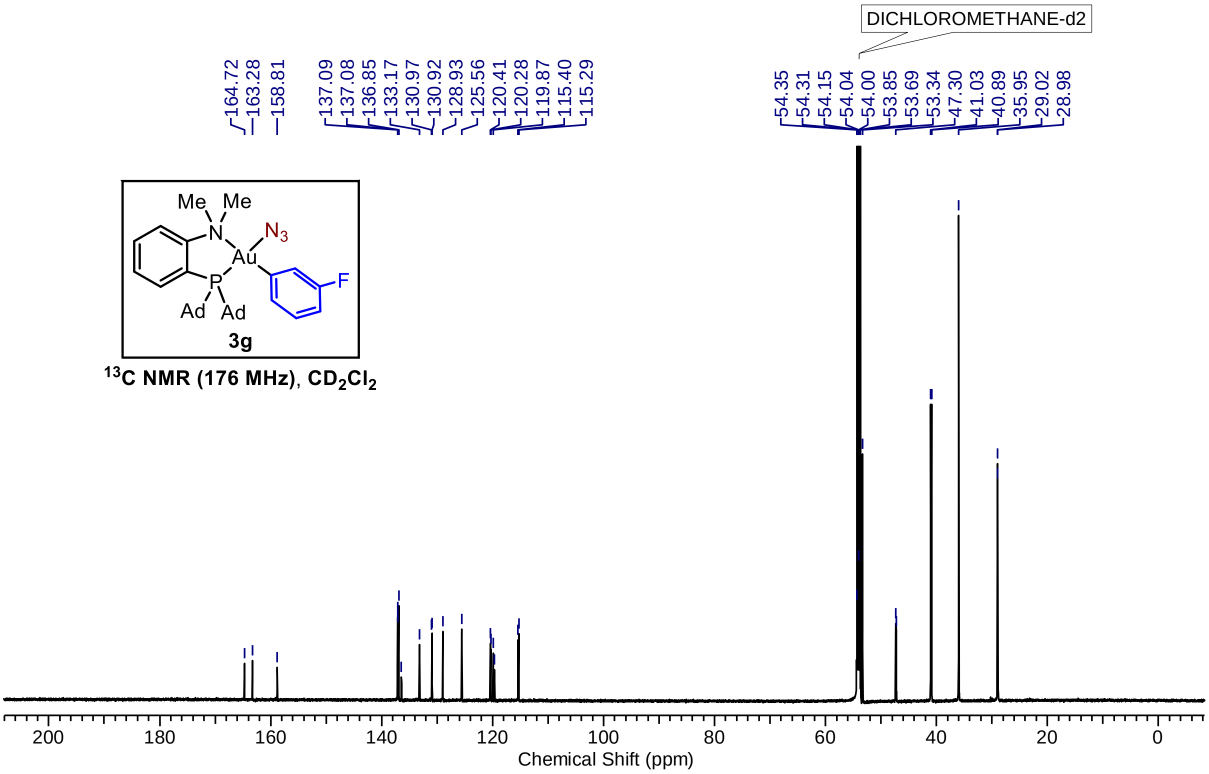
^{13}C NMR (176 MHz), CD$_2$Cl$_2$

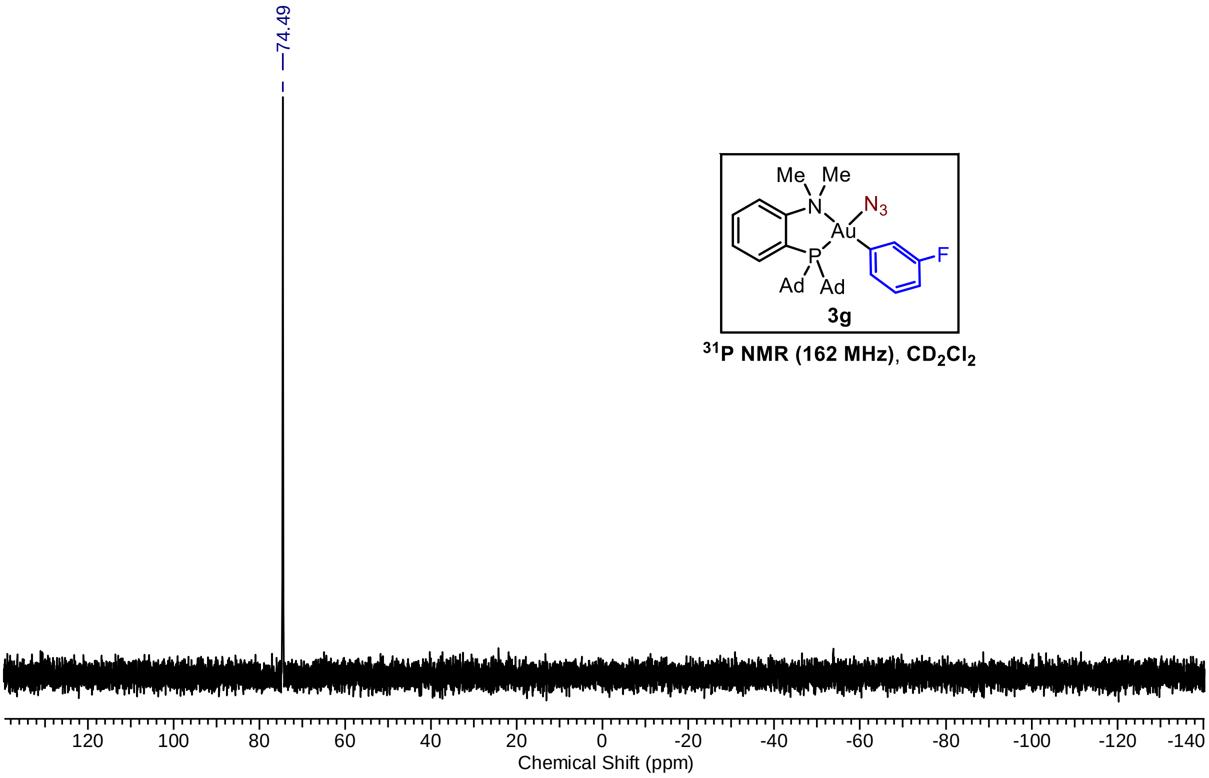


3f

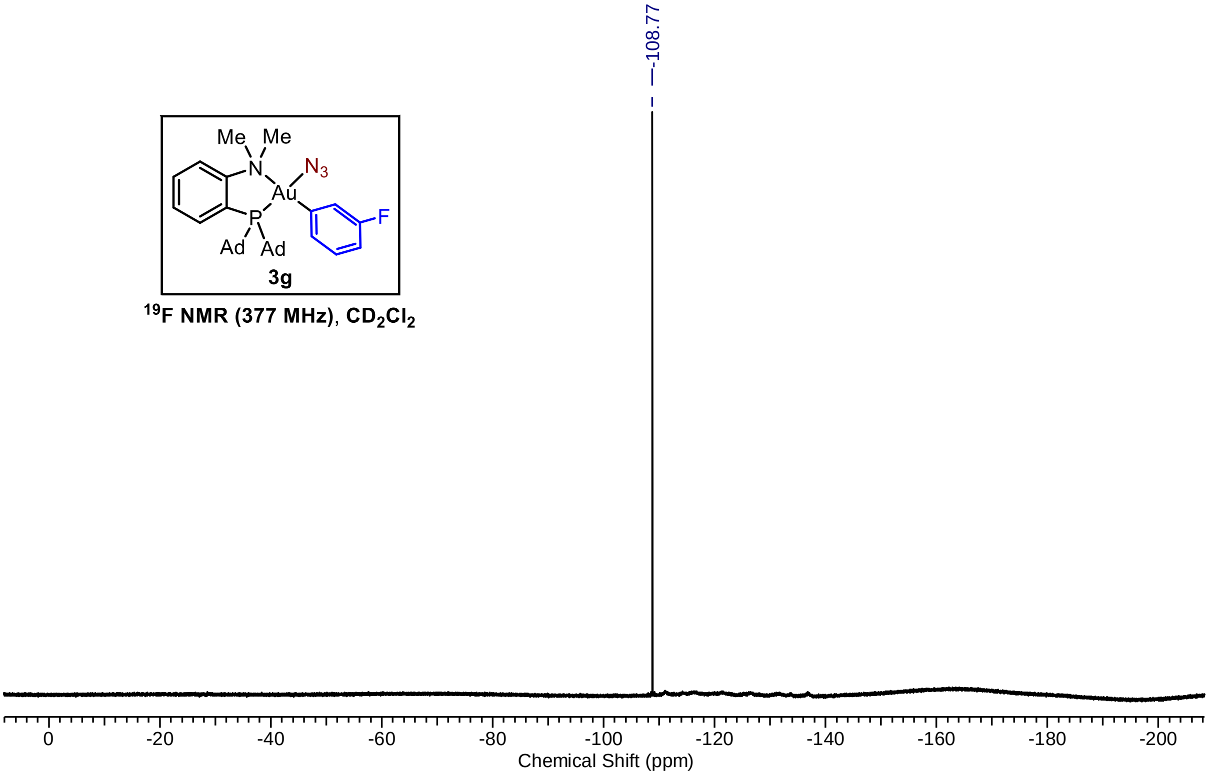
^{31}P NMR (162 MHz), CD$_2$Cl$_2$


DICHLOROMETHANE-d2
7.97
7.95
7.94
7.93
7.89
7.74
7.47
7.43
7.38
7.36
7.07
7.05
5.32
3.33
2.24
2.10
2.05
1.77
1.54
Me
Me
N
N3
Au
F
P
Ad
Ad
3g
¹H NMR (500 MHz), CD₂Cl₂
3.01
1.01
3.02
1.00
6.01
6.05
12.05
12.03
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

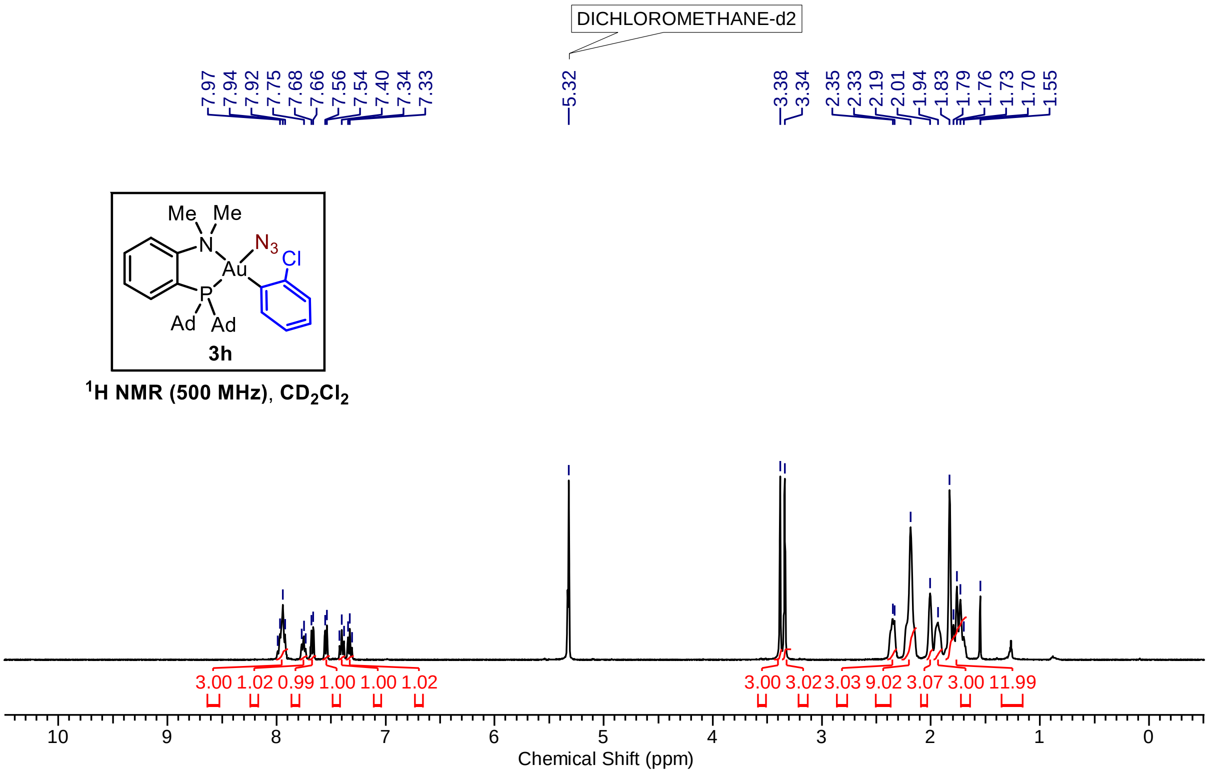

DICHLOROMETHANE-d2
164.72
163.28
158.81
137.09
137.08
136.85
133.17
130.97
130.92
128.93
125.56
120.41
120.28
119.87
115.40
115.29
54.35
54.31
54.15
54.04
54.00
53.85
53.69
53.34
47.30
41.03
40.89
35.95
29.02
28.98
Me
Me
N
N3
Au
F
P
Ad
Ad
3g
¹³C NMR (176 MHz), CD₂Cl₂
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



^{31}P NMR (162 MHz), CD_2Cl_2

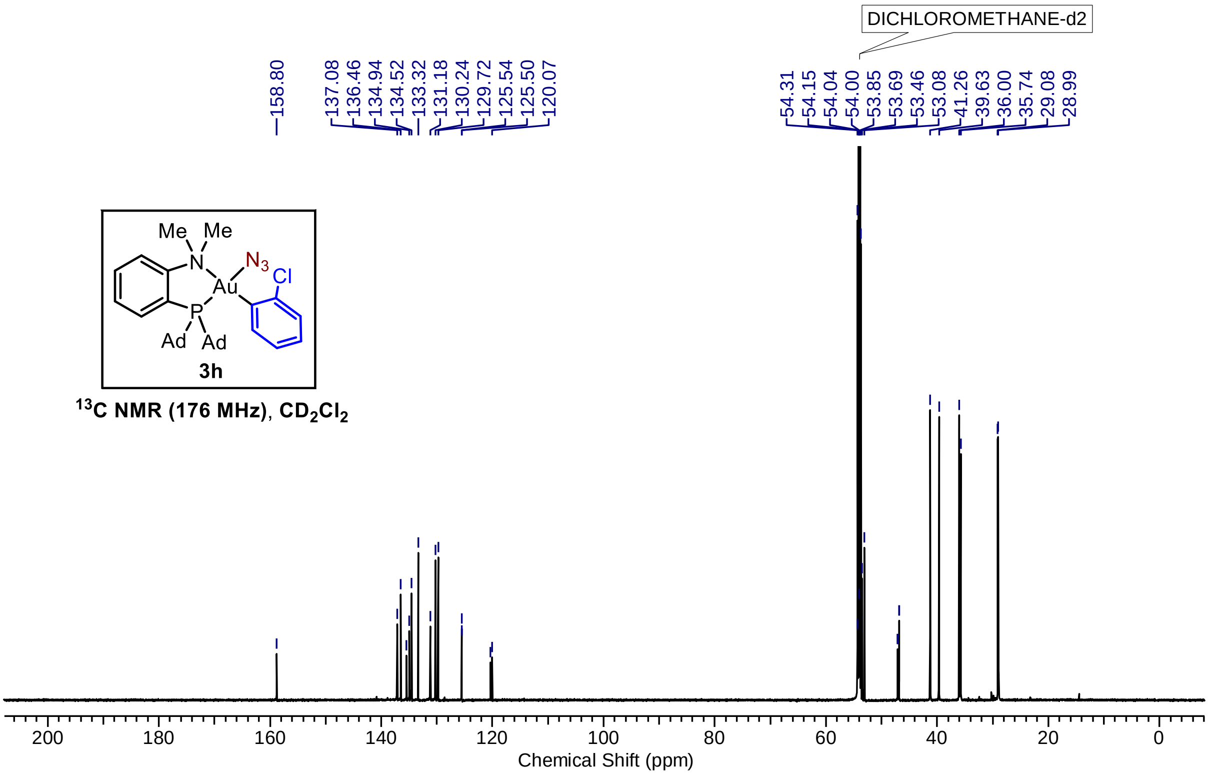


^{19}F NMR (377 MHz), CD_2Cl_2



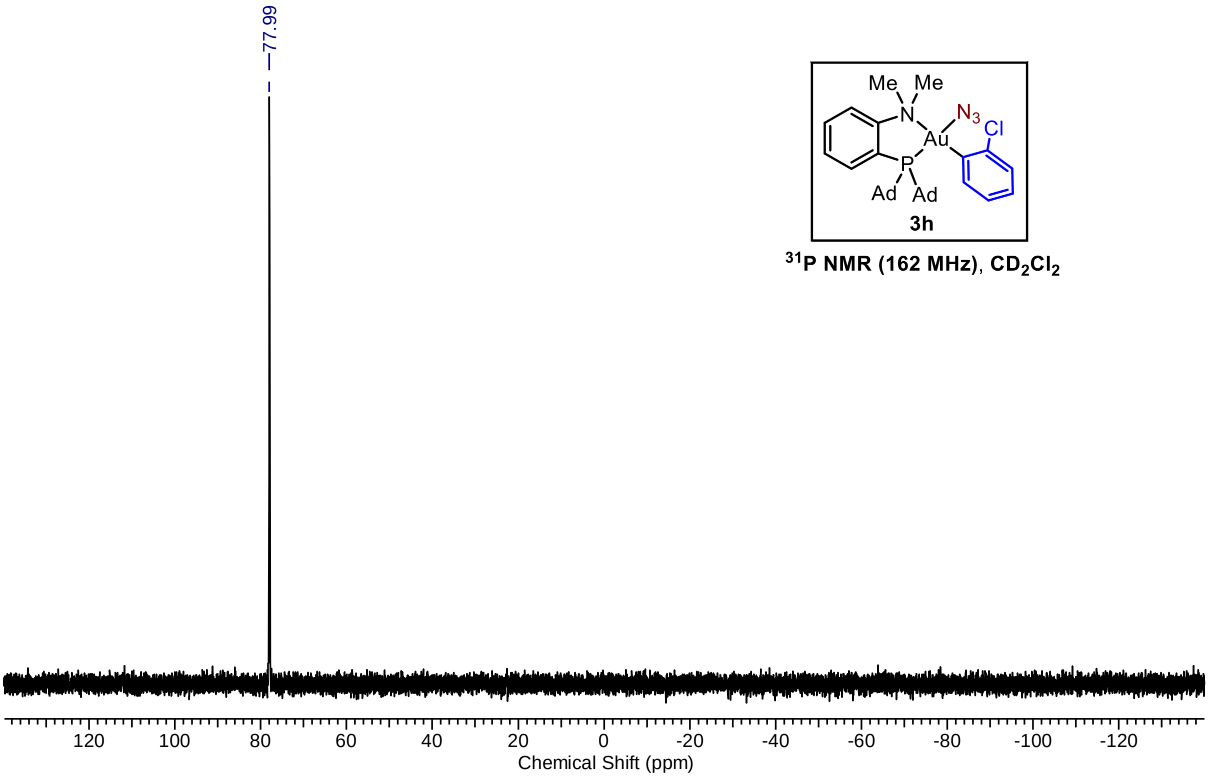
3h

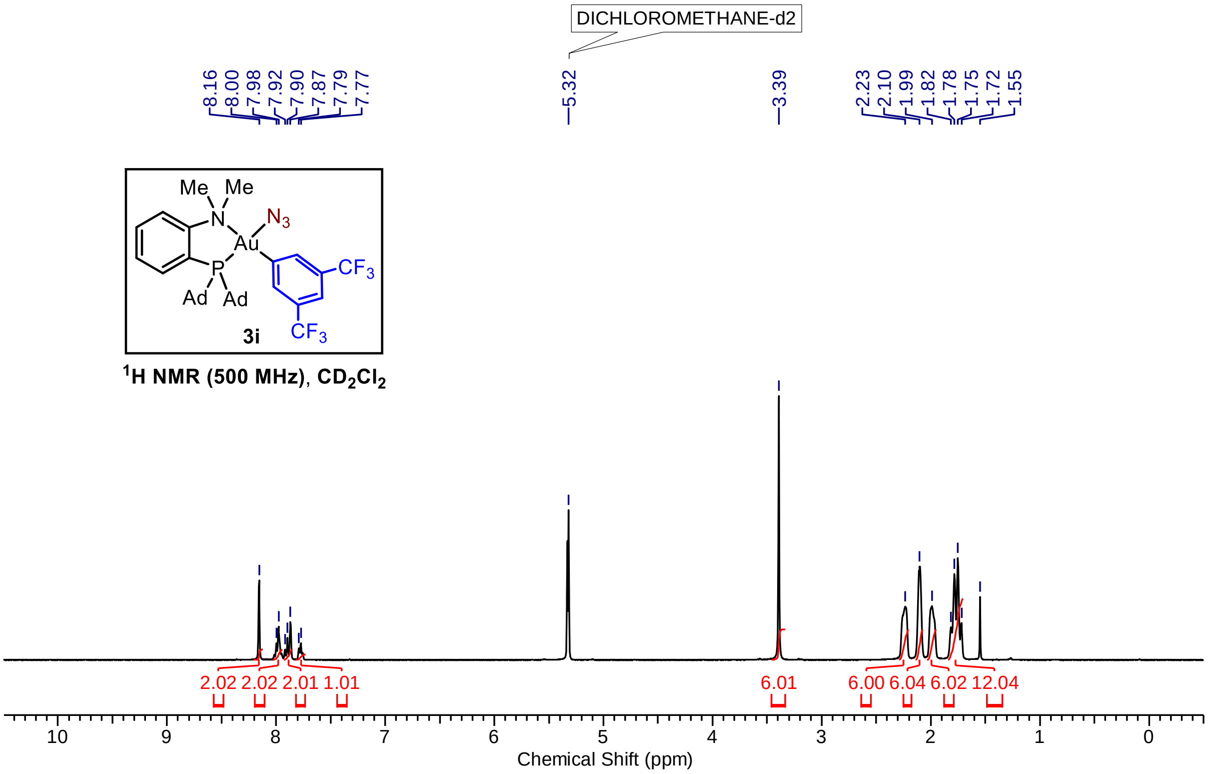
^{1}H NMR (500 MHz), CD$_2$Cl$_2$

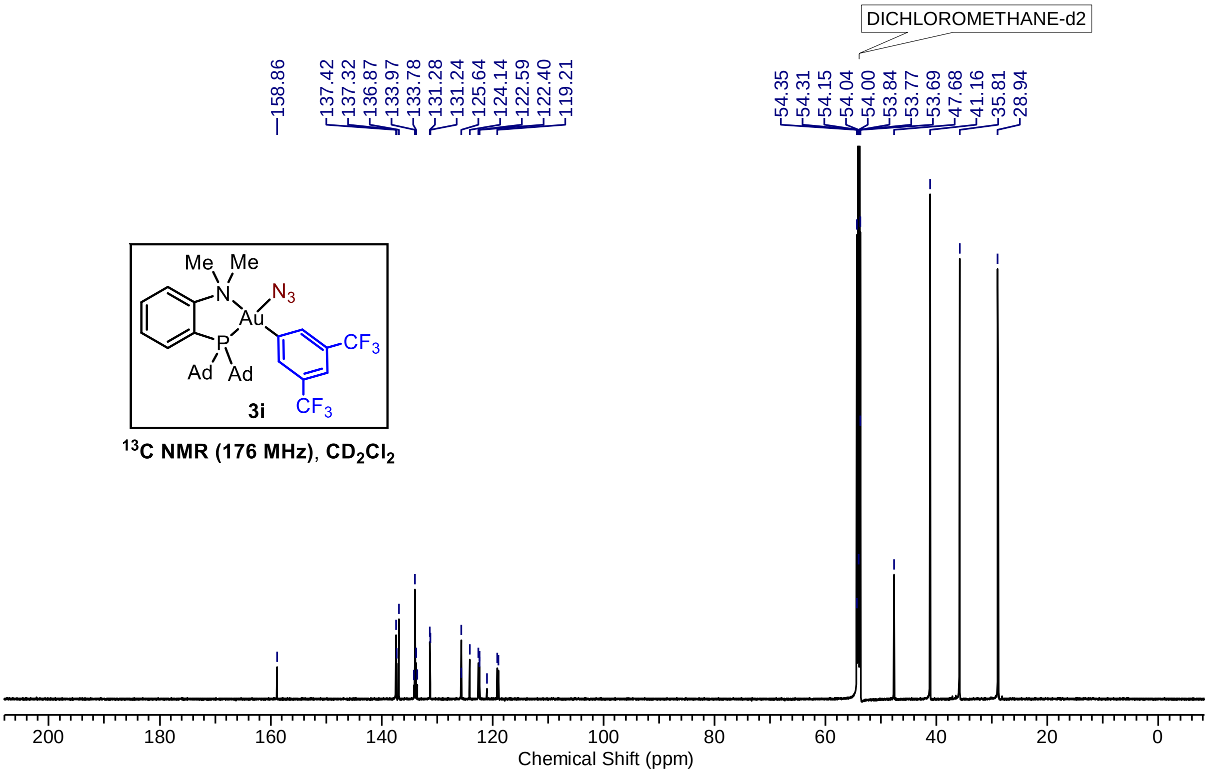


3h

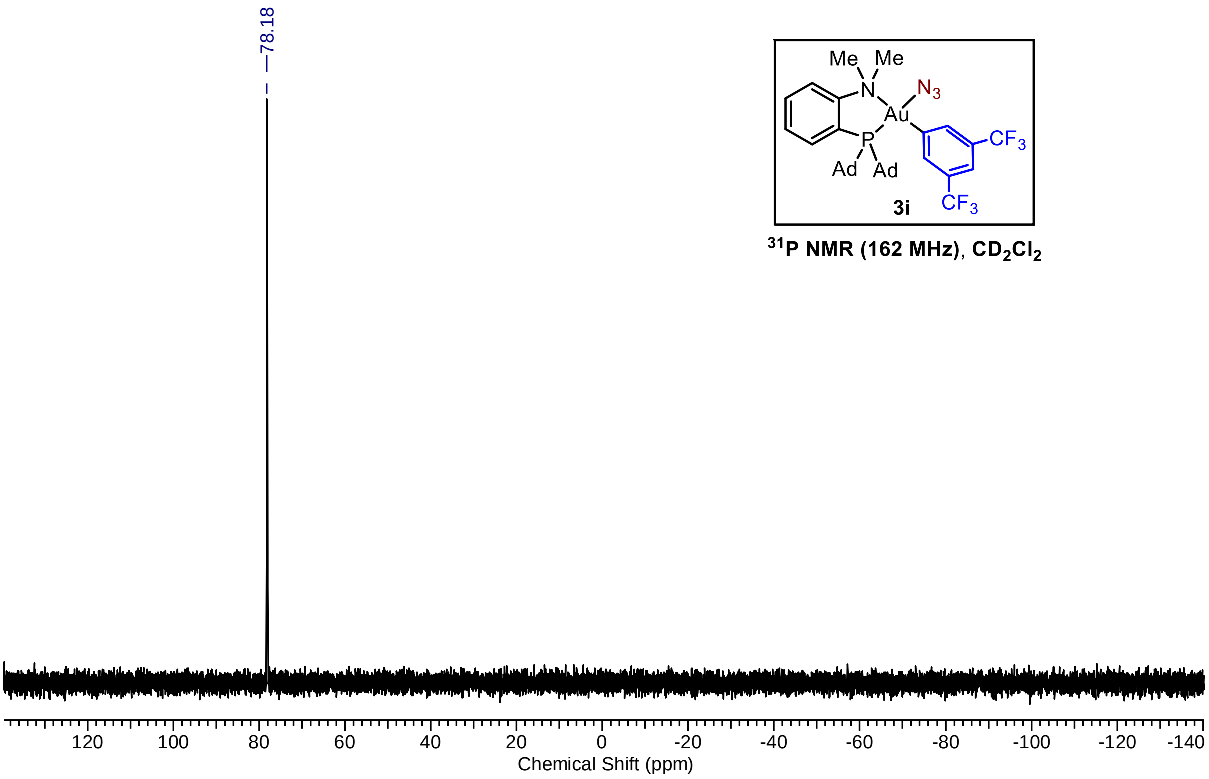
^{13}C NMR (176 MHz), CD$_2$Cl$_2$


77.99
Me
Me
N
N3
Au
Cl
P
Ad
Ad
3h
^{31}P NMR (162 MHz), CD$_2$Cl$_2$
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
Chemical Shift (ppm)

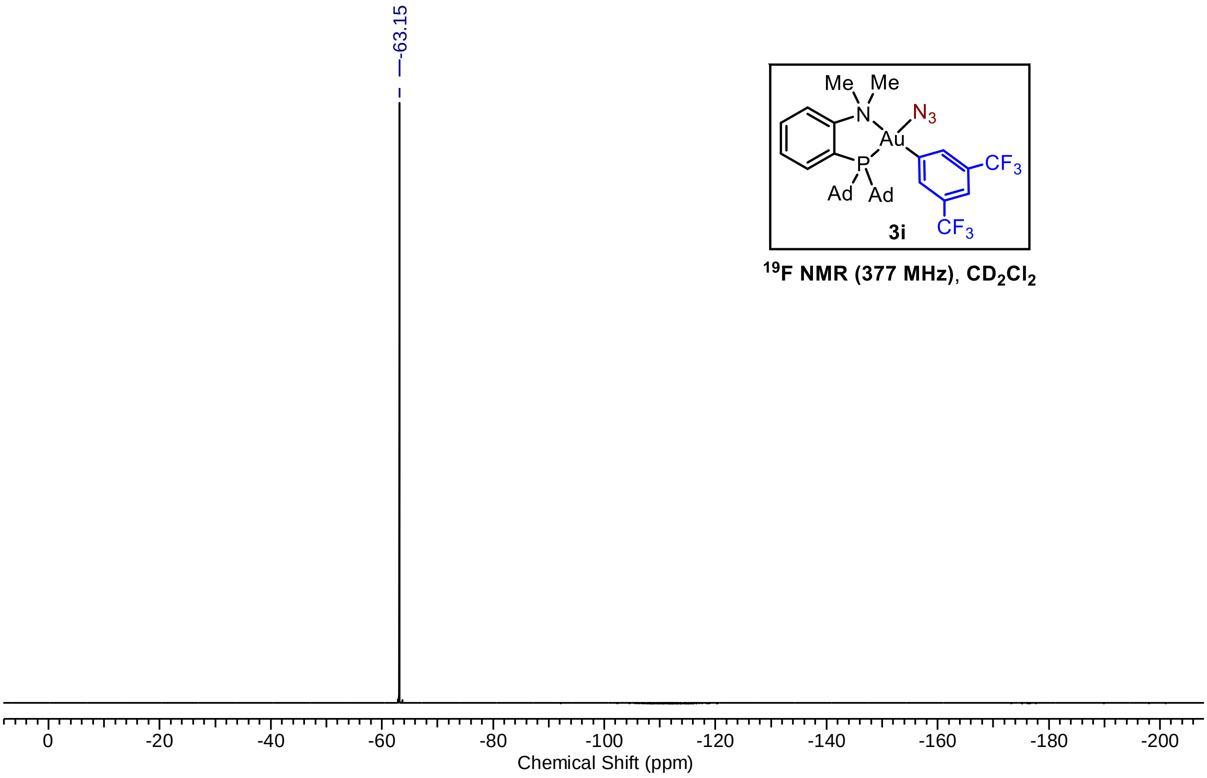

DICHLOROMETHANE-d2
8.16
8.00
7.98
7.92
7.90
7.87
7.79
7.77
5.32
3.39
2.23
2.10
1.99
1.82
1.78
1.75
1.72
1.55
Me
Me
N
N3
Au
CF3
P
Ad
Ad
3i
CF3
^{1}H NMR (500 MHz), CD$_2$Cl$_2$
2.02
2.02
2.01
1.01
6.01
6.00
6.04
6.02
12.04
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)



^{13}C NMR (176 MHz), CD$_2$Cl$_2$



^{31}P NMR (162 MHz), CD$_2$Cl$_2$



^{19}F NMR (377 MHz), CD_2Cl_2