Electronic Supplementary Material (ESI) for ChemComm.

Mechanistic and asymmetric investigations of the Au-catalysed cross-coupling between cryldiazonium salts and arylboronic acids using (P,N) gold complexes

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Electronic Supplementary Information

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A) General methods

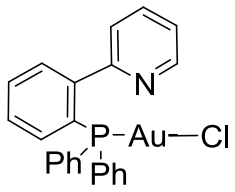
All commercial materials were used without further purification, unless indicated. ^{1}H NMR, ^{18}F NMR, ^{31}P NMR and ^{13}C NMR were recorded on a BRUKER AVANCE I 300 MHz spectrometer (^{1}H: 300MHz, ^{13}C: 75.3MHz, ^{18}F: 282MHz, ^{31}P: 121.5MHz). The chemical shifts for the NMR spectra are reported in ppm relative to the solvent residual peak.[1] Coupling constants *J* are reported in hertz (Hz). The following abbreviations are used for the multiplicities : s, singlet; d, doublet; t, triplet; q, quartet; qt, quintet; st, sextet; m, multiplet; br, broad; dd, doublet of doublet. Yields refer to isolated material determined to be pure by NMR spectroscopy and thin-layer chromatography (TLC), unless specified in the text. Analytical TLC was performed on Fluka Silica Gel 60 F254. High resolution mass spectra were performed by the CESAMO (Talence, France) and were recorded on a Qq-TOF tadem mass spectrometer (API Q-STAR Pulsari, Applied Biosystems). Positive ion mode ESI-MS was used for the analyses. Blue light irradiations were performed with a Flexled INSPIRE LED lamp (1.5m, 45LED, 25 LUMEN, 3.45W, λ = 465 nm) coiled inside a glass tube.[2] All the reactions were performed in sealed tubes. When the irradiation was turned on, the internal temperature of the photochemical system slightly increased and stabilised at 30°C. Analytical chiral HPLC were performed on a JASCO LC-NetII/ADC with a JASCO MD-2010-Plus diode array detector using DAICEL CHIRAL PAK columns (5µm, 4.6*250mm), and analysed using the JASCO ChromNAV 1.12.01 software (chromatogram wavelength: 223 nm).

[1] Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw,J. E.; Goldberg, K. I. *Organometallics* **2010**, 29, 2176

[2] Cornilleau, T.; Hermange, P.; Fouquet, E. *Chem. Commun.* **2016**, *52*, 10040.

B) Stoichiometric mechanistic investigations with L1AuCl

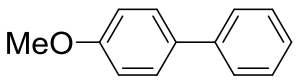
Chloro[2-(2-(diphenylphosphanyl)phenyl)pyridine] gold(I) L1AuCl



L1AuCl

Under inert atmosphere, 2-(2-(diphenylphosphanyl)phenyl)pyridine **L1** (74.6 mg, 0.22 mmol, 1.0 eq.) and chloro(dimethylsulfide)gold(I) (64.9 mg, 0.22 mmol, 1.0 eq.) were dissolved in dichloromethane (2.2 mL). The reaction mixture was stirred in the dark for 2 hours, the solvent was removed and the residue was triturated in pentane to give the product (120 mg, 0.21 mmol, 95%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.31-8.27 (m, 1H), 7.78-7.70 (m, 2H), 7.65-7.59 (m, 1H), 7.58-7.36 (m, 12H), 7.28-7.23 (m,1H), 7.12-7.05 (ddd, *J* = 12.3 Hz, *J* = 7.8 Hz, *J* =1.0 Hz, 1H). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ (ppm): 30.3. The spectral data was in accordance with the literature.[3]

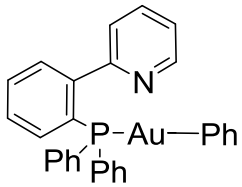
4-Methoxy-1,1'-biphenyl 3a (Catalytic experiment)



3a

In a vial were added phenylboronic acid (30.5 mg, 0.25 mmol, 1.0 eq.), 4-methoxybenzene diazonium tetrafluoroborate (83 mg, 0.38 mmol, 1.5 eq.), **L1**AuCl (14.3 mg, 0.025 mmol, 0.1 eq.), $Ru(bpy)_3(PF_6)_2$ (4.3 mg, 5 µmol, 0.02 eq.) and CsF (76 mg, 0.5 mmol, 2.0 eq.). The vial was purged three times with nitrogen and CH_3CN (2 mL) was added. The reaction was placed inside the turned-off photochemical reactor and stirred under blue light irradiation for 16h. The solvent was evaporated under reduced pressure. Then, the residue was purified by preparative TLC (90/10:cyclohexane/diethyl ether, R_f: 0.6) to give product **3a** (18 mg, 0.096 mmol, 39%) as a white solid.

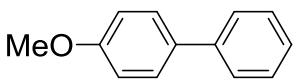
Phenyl [2-(2-(diphenylphosphanyl)phenyl)pyridine] gold(I) B1



B1

In a vial were added **L1**AuCl (29 mg, 0.05 mmol, 1.0 eq.), phenylboronic acid (6.1 mg, 0.05 mmol, 1.0 eq.) and CsF (15.2 mg, 0.1 mmol, 2.0 eq.). The vial was purged three times with nitrogen and CH_3CN (1 mL) was added. The reaction was stirred at 50°C overnight. The mixture was filtered throught a celite pad and the filtrate was evaporated under reduced pressure. Then, the residue was triturated with pentane to give the product **B1** (29 mg, 0.047 mmol, 94%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.34 (d, *J* = 4.4 Hz, 1H), 7.74-7.69 (m, 2H), 7.64-7.60 (m, 5H), 7.58-7.54 (m, 1H), 7.45-7.39 (m, 6H), 7.39-7.35 (m, 1H), 7.20-7.14 (m, 5H), 7.11-7.07 (m, 1H), 7.00-6.96 (m, 1H). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ (ppm): 42.5. ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 172.9, 157.7, 148.5, 145.7, 145.4, 139.6, 136.8, 135.6 (d, *J* = 3.8 Hz), 134.4 (d, *J* = 13.8 Hz), 133.8, 133.3, 130.9, 130.7, 130.5, 130.3 (d, *J* = 7.4 Hz), 130.2, 128.8 (d, *J* = 10.7 Hz), 128.5 (d, *J* = 7.2 Hz), 127.3 (d, *J* = 6.2 Hz), 125.5, 123.5, 122.7.

4-Methoxy-1,1'-biphenyl 3a (from B1)



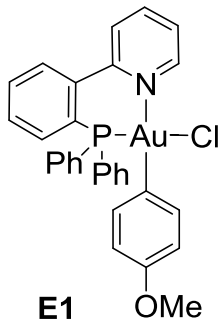
3a

In a vial were added complex **B1** (29 mg, 0.047 mmol, 1.0 eq.), 4-methoxybenzene diazonium tetrafluoroborate (10.4 mg, 0.047 mmol, 1.0 eq.) and $Ru(bpy)_3(PF_6)_2$ (0.8 mg, 0.9 µmol, 0.02 eq.). The vial was purged

[3] Huang, L.; Rominger, F.; Rudolph, M; Hashmi, A. S. K. *Chem. Commun.*, **2016**, 52, 6435.

three times with nitrogen and CH_3CN (1 mL) was added. The reaction was placed inside the turned-off photochemical reactor and stirred under blue light irradiation for 3h. The end of the reaction was confirmed by ^{31}P NMR. The solvent was evaporated under reduced pressure and the residue was purified by preparative TLC (90/10:cyclohexane/diethyl ether, R_f: 0.6) to give the product **3a** (2.6 mg, 0.014 mmol, 30%) as a white solid.

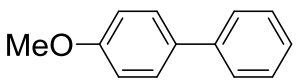
[(4-methoxyphenyl)-((2-(2-(diphenylphosphanyl)phenyl)pyridine)]Chloro gold(III) tetrafluoroborate E1



E1

In a vial were added complex **L1**AuCl (29 mg, 0.05 mmol, 1.0 eq.), 4-methoxybenzene diazonium tetrafluoroborate (11.1 mg, 0.05 mmol, 1.0 eq.) and $Ru(bpy)_3(PF_6)_2$ (0.9 mg, 1 µmol, 0.02 eq.). The vial was purged three times with nitrogen and CH_3CN (1 mL) was added. The reaction was placed inside the turned-off photochemical reactor and stirred under blue light irradiation for 2h. The end of the reaction was confirmed by ^{31}P NMR. The mixture was filtered and the solvent was evaporated under reduced pressure. Then, the residue was triturated with diethyl ether to give the product **E1** (36 mg, 0.047 mmol, 94%) as an orange solid. ^1H NMR (300 MHz, $(CD_3)_2CO$) δ (ppm): 9.30 (dd, *J* = 5.8 Hz, *J* = 1.5 Hz, 1H), 8.35-8.32 (m, 1H), 8.26-8.23 (m,1H), 8.10-8.07 (m, 1H), 7.92-7.87 (m, 2H), 7.70-7.47 (m, 11H), 7.14 (dd, *J* = 8.6 Hz, *J* = 1.9 Hz, 2H), 6.51 (d, *J* = 8.6 Hz, 2H), 3.66 (s, 3H). ^{31}P NMR (121.5 MHz, $(CD_3)_2CO$) δ (ppm): 30.0. The spectral data was in accordance with the literature.[3]

4-Methoxy-1,1'-biphenyl 3d (from E1)



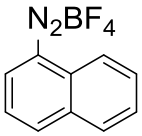
3a

In a vial were added complex **E1** (36 mg, 0.047 mmol, 1.0 eq.), phenylboronic acid (6.1 mg, 0.047 mmol, 1.0 eq.) and CsF (15.2 mg, 0.094 mmol, 2.0 eq.). The vial was purged three times with nitrogen and CH_3CN (1 mL) was added. The reaction was stirred at 50°C for 16h. The solvent was evaporated under reduced pressure. Then the residue was purified by preparative TLC (90/10:cyclohexane/diethyl ether, R_f: 0.6) to give the product **3a** (3.2 mg, 0.017 mmol, 35%) as a white solid.

C) Asymmetric induction

*a) Syntheses of diazonium salts **1b-e***

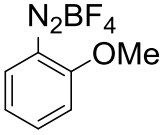
Naphthalene-1-diazonium tetrafluoroborate 1b



1b

To a solution of boron trifluoride ethyl etherate (0.84 mL, 6.6 mmol, 3.3 eq.) at -50°C were added successively a solution of naphtylamine (286 mg, 2 mmol, 1.0 eq.) in THF (2 mL), and a solution of tert-butyl nitrite (0.72 mL, 6 mmol, 3.0 eq.) in THF (4 mL). The reaction mixture was stirred for 30 min at -50°C. Methanol (2 mL) was added dropwise, the mixture was warmed at rt and the resulting solids were filtered, washed with ice-cold methanol (5 mL) to give product **1b** (260 mg, 1.07 mmol, 54%) as a purple solid. ^{1}H NMR (300 MHz, CD_3CN) δ (ppm): 8.97 (dd, *J* = 7.9 Hz, *J* = 1.1 Hz, 1H), 8.86 (d, *J* = 8.3 Hz, 1H), 8.36 (d, *J* = 8.3 Hz, 1H), 8.29-8.25 (m, 1H), 8.10 (ddd, *J* = 8.4 Hz, *J* = 7.1 Hz, *J* = 1.2 Hz, 1H), 7.99-7.94 (m, 2H). ^{19}F NMR (282 MHz, CD_3CN δ (ppm): -151.4, -151.5. ^{13}C NMR (75 MHz, CD_3CN) δ (ppm): 145.3, 138.5, 134.2, 134.1, 131.9, 131.3, 129.3, 127.5, 123.2, 122.4.

2-Methoxybenzenediazonium tetrafluoroborate 1c



1c

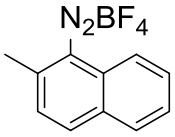
To a solution of 2-methoxyaniline (0.23 mL, 2 mmol, 1.0 eq.) in ethanol (0.6 mL) at rt was added an aqueous solution of HBF_4 (48% w/w, 0.52 mL, 4 mmol, 2.0 eq.). The reaction mixture was stirred for 2 min. The mixture was cooled to 0 °C and tert-butyl nitrite (0.48 mL, 4 mmol, 2.0 eq.) was added dropwise. After addition, the mixture was stirred for 15 min at 0 °C and for 1 h then at rt. Diethyl ether (4 mL) was added to the reaction mixture and the resulting solids were filtered, washed with diethyl ether and dried under high vacuum to give product **1c** (374.2 mg, 1.67 mmol, 84%) as a white solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm): 8.51 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 1H), 8.24 (ddd, *J* = 8.7 Hz, *J* = 7.4 Hz, *J* = 1.6 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.45 (ddd, *J* = 8.7 Hz, *J* = 7.4 Hz, *J* = 0.8 Hz, 1H). ^{19}F NMR (282 MHz, DMSO-d_6) δ (ppm): -148.2, -148.3. ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm): 162.1, 143.8, 132.4, 122.9, 114.9, 102.3, 58.7.

2-Bromobenzenediazonium tetrafluoroborate 1d

1d

To a suspension of 2-bromoaniline (172 mg, 1 mmol, 1.0 eq.) in water (1mL) at rt was added an aqueous solution of HBF_4 (48% w/w, 0.26 mL, 2 mmol, 2.0 eq.) and the reaction mixture was stirred for 2 min. The mixture was cooled to 0 °C and a solution of $NaNO_2$ (69 mg, 1 mmol, 1.0 eq.) in water (0.15 mL) was added dropwise. After addition the reaction mixture was stirred at 0 °C for 15 min. The solids were filtered, washed with ice-cold water (5 mL) and diethyl ether (10 mL) to give product **1d** (122.8 mg, 0.45 mmol, 45%) as brown solid. ^{1}H NMR (300 MHz, CD_3CN) δ (ppm): 8.61-8.58 (m, 1H), 8.18-8.11 (m, 2H), 7.94-7.89 (m, 1H). ^{19}F NMR (282 MHz, CD_3CN δ (ppm): -151.5, -151.6. ^{13}C NMR (75 MHz, CD_3CN) δ (ppm): 144.0, 137.0, 136.2, 131.8, 126.0.

2-Methylnaphthalene-1-diazonium tetrafluoroborate 1e

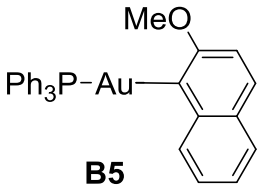


1e

To a solution of boron trifluoride ethyl etherate (0.42 mL, 3.3 mmol, 3.3 eq.) at -50°C were added successively a solution of 2-methyl-1-naphtylamine (0.09 mL, 1 mmol, 1.0 eq.) in THF (1 mL) and a solution of tert-butyl nitrite (0.36 mL, 3 mmol, 3.0 eq.) in THF (2 mL). The reaction mixture was stirred for 30 min at -50°C. Methanol (1 mL) was added dropwise and the mixture was warmed at rt. The resulting solids were filtered, washed with ice-cold methanol (5 mL) to give product **1e** (101.5 mg, 0.40 mmol, 40%) as a yellow solid. ^{1}H NMR (300 MHz, CD_3CN) δ (ppm): 8.70 (d, *J* = 8.5 Hz, 1H), 8.30 (d, *J* = 8.2 Hz, 1H), 8.19 (dd, *J* = 8.2 Hz, *J* = 1.2 Hz, 1H), 8.06 (ddd, *J* = 8.5 Hz, *J* = 7.1 Hz, *J* = 1.2 Hz, 1H), 7.90 (ddd, *J* = 8.2 Hz, *J* = 7.1 Hz, *J* = 1.2 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 2.96 (s, 3H). ^{19}F NMR (282 MHz, CD_3CN δ (ppm): -151.5, -151.6. ^{13}C NMR (75 MHz, CD_3CN) δ (ppm): 152.9, 144.4, 134.0, 132.5, 131.9, 130.6, 130.1, 129.6, 128.9, 121.9, 20.5.

b) Racemic experiments with Ph_3AuCl

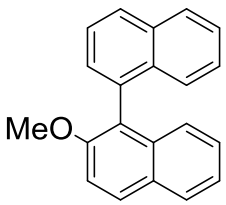
2-Methoxynaphtyl(triphenylphosphine) gold(I) B5



B5

In a vial were added PPh_3AuCl (74.3 mg, 0.15 mmol, 1.0 eq.), 2-methoxy-1-naphtaleneboronic acid **2b** (30 mg, 0.15 mmol, 1.0 eq.) and CsF (45.6 mg, 0.3 mmol, 2.0 eq.). The vial was purged three times with nitrogen and CH_3CN (1.5 mL) was added. The reaction was stirred at 50°C for 16h. The mixture was filtered throught a celite pad and the filtrate was evaporated under reduced pressure. Then, the residue was triturated with pentane to give the crude product **B5** (77.3 mg, 0.125 mmol, 91%) as a white solid. Traces of triphenylphosphine oxide were detected by ^{31}P NMR, but compound **B5** was engaged in the following step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.48 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.73-7.66 (m, 6H), 7.52-7.46 (m, 10H), 7.38-7.33 (m, 2H), 7.28-7.23 (m, 1H), 3.99 (s, 3H). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ (ppm): 44.6.

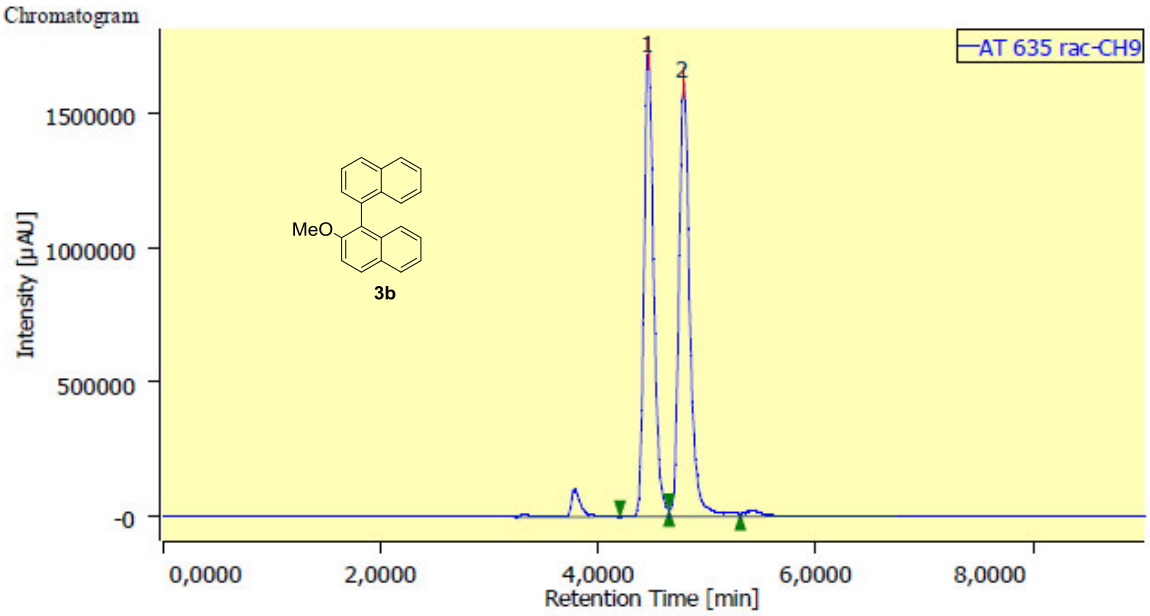
2-Methoxy-1,1'-binaphthalene 3b (from B5)



3b

In a vial were added complex **B5** (20.0 mg, 0.032 mmol, 1.0 eq.), naphthalene-1-diazonium tetrafluoroborate **1b** (7.8 mg, 0.032 mmol, 1.0 eq.) and $Ru(bpy)_3(PF_6)_2$ (1.1 mg, 1.3 µmol, 0.04 eq.). The vial was purged three times with nitrogen and CH_3CN (1 mL) was added. The reaction was placed inside the turned-off photochemical reactor and stirred under blue light irradiation for 3h. The completion of the reaction was confirmed by NMR ^{31}P. The solvent was evaporated under reduced pressure and the residue was purified by preparative TLC (90/10 : cyclohexane/ethyl acetate, R_f: 0.7) to give product **3b** (5.1 mg, 0.018 mmol, 57%) as a colorless oil. ^{1}H NMR (300 MHz,) δ (ppm): 8.0-7.92 (m, 3H), 7.88-7.86 (m, 1H), 7.64-7.52 (m, 1H), 7.48-7.42 (m, 3H), 7.33-7.27 (m, 3H), 7.25-7.22 (m, 1H), 7.17-7.12 (m, 1H), 3.76 (s, 3H). The spectral data was in accordance with the literature.[4] Chiral HPLC analysis (CHIRAL PAK ID column (5µm, 4.6*250mm), isopropanol/hexane 2/98, flow rate 1.0mL/min): <2% e.e. (retention times: 4.5 min and 4.8 min).

[4] Alvarez-Casao, Y.; Estepa, B.; Monge, D.; Ros, A.; Iglesias-Sigüenza, J.; Alvarez, E.; Fernadez, R.; Lassaletta J. M. *Tetrahedron*. **2016**, *72*, 5184.



Peak Information

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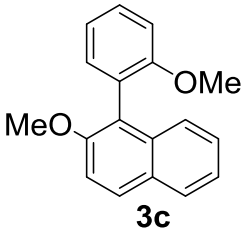
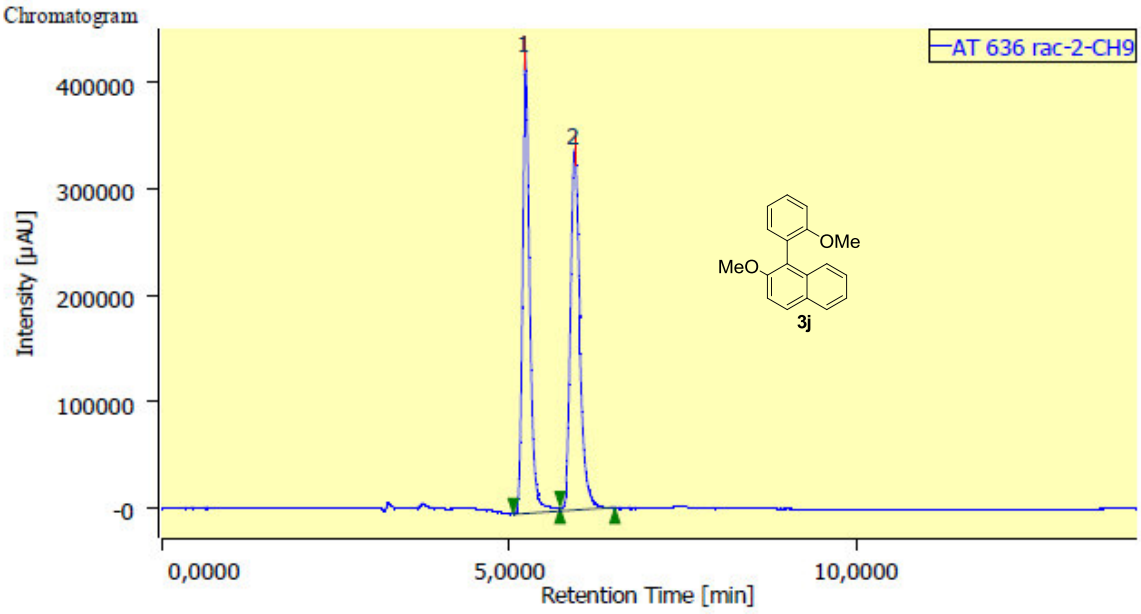
2-Methoxy-1-(2-methoxyphenyl)naphthalene 3c (from B5)



In a vial were added complex **B5** (20.0 mg, 0.032 mmol, 1.0 eq.), 2-methoxybenzenediazonium tetrafluoroborate **1c** (7.1 mg, 0.032 mmol, 1.0 eq.) and $Ru(bpy)_3(PF_6)_2$ (1.1 mg, 1.3 µmol, 0.04 eq.). The vial was purged three times with nitrogen and CH_3CN (1 mL) was added. The reaction was placed inside the turned-off photochemical reactor and stirred under blue light irradiation for 3h. The completion of the reaction was confirmed by ^{31}P NMR. The solvent was evaporated under reduced pressure and the residue was purified by preparative layer TLC (90/10 : cyclohexane/ethyl acetate, R_f: 0.4) to give product **3c** (5.5 mg, 0.021 mmol, 65%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.88 (d, *J* = 9.0 Hz, 1H), 7.83-7.80 (m, 1H), 7.42-7.29 (m, 5H), 7.23-7.20 (m, 1H), 7.11-7.06 (m, 2H), 3.84 (s, 3H), 3.69 (s, 3H). The spectral data was in accordance with the literature.[5] Chiral HPLC analysis (CHIRAL PAK ID column, isopropanol/hexane 2/98, flow rate 1.0mL /min): <1% e.e. (retention times: 5.2 min and 5.9 min).

[5] Jumde, V. R.; Iuliano, A. *Tetrahedron : Asymmetry*, **2011**, *22*, 2151.



Peak Information

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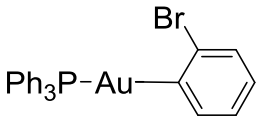
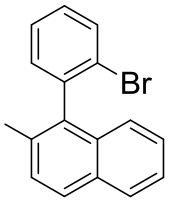
2-Bromophenyl(triphenylphosphine) gold(I) B6



B6

In a vial were added $AuPPh_3Cl$ (49.5 mg, 0.1 mmol, 1.0 eq.), 2-bromophenylboronic acid **2e** (20.1 mg, 0.1 mmol, 1.0 eq.) and CsF (30.4 mg, 0.2 mmol, 2.0 eq.). The vial was purged three times with nitrogen and CH_3CN (1 mL) was added. The reaction was stirred at 50°C for 16h. The mixture was filtered throught a celite pad and the filtrate was evaporated under reduced pressure. Then, the residue was triturated with pentane to give the crude product **B6** (56 mg, 0.085 mmol, 85%) as a white solid. Traces of triphenylphosphine oxide were detected by ^{31}P NMR, but compound **B6** was engaged in the following step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.67-7.60 (m, 6H), 7.51-7.46 (m, 10H), 7.39 (ddd, *J* = 7.4 Hz, *J* = 5.6 Hz, *J* = 1.8 Hz, 1H), 7.21 (tt, *J* = 7.2 Hz, *J* = 1.2 Hz, 1H), 6.98-6.92 (m, 1H). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ (ppm): 41.2.

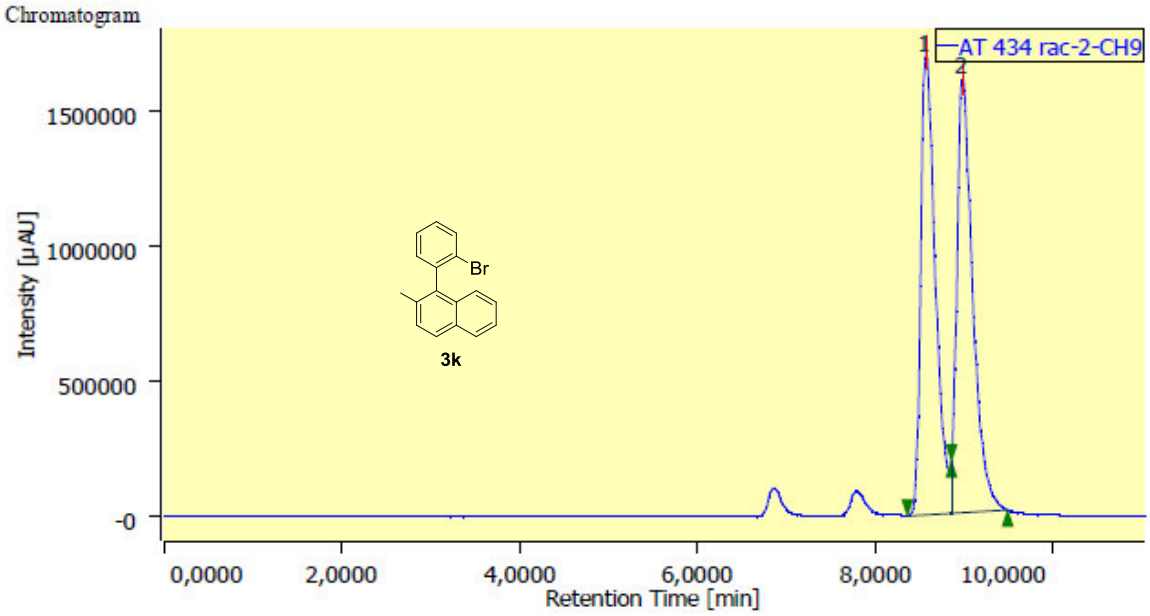
1-(2-Bromophenyl)-2-methylnaphthalene 3d (from B6)



3d

In a vial were added complex **B6** (21.3 mg, 0.034 mmol, 1.0 eq.), 2-methylnaphthalene-1-diazonium tetrafluoroborate **1e** (8.7 mg, 0.034 mmol, 1.0 eq.) and $Ru(bpy)_3(PF_6)_2$ (1.2 mg, 1.4 µmol, 0.04 eq.). The vial was purged three times with nitrogen and CH_3CN (1 mL) was added. The reaction was placed inside the turned-off photochemical reactor and stirred under blue light irradiation for 3h. The end of the reaction was confirmed by ^{31}P NMR. The solvent was evaporated under reduced pressure and the residue was purified by preparative TLC (cyclohexane, R_f: 0.4) to give product **3d** (3.0 mg, 0.01 mmol, 30%) as a white solid. ^{1}H NMR (300

MHz, $CDCl_3$) δ (ppm): 7.87-7.82 (m, 2H), 7.76 (dd, *J* = 8.0 Hz, *J* = 1.1 Hz, 1H), 7.48-7.29 (m, 5H), 7.26-7.20 (m, 2H), 2.20 (s, 3H). The spectral data was in accordance with the literature.[6] Chiral HPLC analysis (CHIRAL PAK IB column, hexane, flow rate 1.0mL/min) : <2 % e.e. (retention times: 8.6 min and 9.0 min).

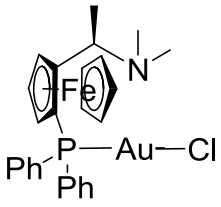


Peak Information

#	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%
1	9	8,560	19379745	1706973	49,314
2	9	8,973	19918713	1601571	50,686

*c) Experiments with **L2**AuCl*

Chloro[(*R*)-(−)-*N*,*N*-dimethyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine] gold(I) L2AuCl



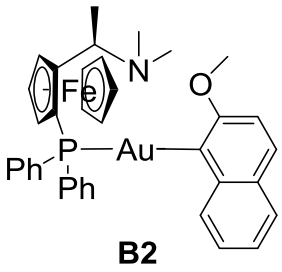
L2AuCl

Under inert atmosphere, (*R*)-(−)-*N*,*N*-Dimethyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine **L2** (56.3 mg, 0.13 mmol, 1.0 eq.) and chloro(dimethylsulfide)gold(I) (38.0 mg, 0.13 mmol, 1.0 eq.) were dissolved in dichloromethane (1 mL). The reaction mixture was stirred in the dark for 2 hours. Then, the solvent was removed under reduced pressure and the residue was triturated in pentane to give product **L2**AuCl (77.3 mg, 0.115 mmol, 88%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.82-7.77 (m, 2H), 7.54-7.44 (m, 5H), 7.37-7.32 (m, 3H), 4.84-4.79 (m, 1H), 4.53-4.51 (m, 1H), 4.34-4.31 (m, 1H), 4.19 (s, 4H), 3.83-3.81 (m, 1H), 1.63 (s, 6H), 1.17 (d, *J* = 7.0 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 1H). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ (ppm): 26.8. ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 134.8 (d, *J* = 13.9 Hz), 132.7 (d, *J* = 14.3 Hz), 132.6, 131.7, 131.4 (d, *J* = 2.0 Hz), 131.3, 130.6 (d, *J* = 1.9 Hz), 130.5, 128.6 (d, *J* = 11.3 Hz), 128.2 (d, *J* = 12.3 Hz), 74.1 (d, *J* = 5.6 Hz), 71.8 (d, *J* = 6.8 Hz), 71.0, 70.1, 69.1 (d, *J* = 8.4 Hz), 58.1, 38.8, 7.6. HRMS (ESI/TOF$^+$) $C_{26}H_{28}AuClFeNP$ $[M+H]^+$ calculated 674.0735 found 674.0747.

[6] Hsiao, C.-C.; Lin, Y.-K.; Liu, C.-J.; Wu, T.-C.; Wu, Y.-T. *Adv. Synth. Catal.* **2010**, 352, 3267.

Pathway I

2-Methoxynaphtyl-[(R)-(−)-N,N-Dimethyl-1-[(S)-2-(diphenylphosphino)ferrocenyl]ethylamine] gold(I) B2

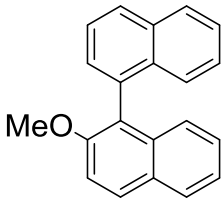


B2

In a vial were added complex **L2**AuCl (1.0 eq.), 2-methoxy-1-naphtaleneboronic acid **2b** (1.5 eq. or 1 eq.) and CsF (2.0 eq.). The vial was purged three times with nitrogen and CH_3CN (1 mL) was added. The reaction was stirred at 50°C for 16h. The mixture was filtered throught a celite pad and the filtrate was evaporated under reduced pressure. Then, residue was triturated with pentane to give the crude product **B2** as a yellow solid, which was engaged in the following step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.63 (d, *J* = 8.3 Hz, 1H), 8.04-7.94 (m, 2H), 7.81-7.76 (m, 2H), 7.72-7.69 (m, 3H), 7.48-7.45 (m, 3H), 7.39-7.36 (m, 4H), 7.30-7.25 (m, 1H), 5.24-5.18 (m, 1H), 4.50-4.48 (m, 1H), 4.34-4.33 (m, 1H), 4.32 (s, 4H), 4.00 (s, 3H), 3.85-3.83 (m, 1H), 3.62 (br s, 1H), 1.68 (s, 6H), 1.19 (d, *J* = 6.7 Hz, 3H). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ (ppm): 37.9.

Experience	Conditions	Mass of of B2 (Crude yield)
Exp 1, step 1	**L2**AuCl (16.8 mg, 25 µmol), **2b** (7.6 mg, 37.5 µmol), CsF (7.6 mg, 50 µmol)	18.0 mg (90%)
Exp 2, step 1	**L2**AuCl (16.8 mg, 25 µmol), **2b** (7.6 mg, 37.5 µmol), CsF (7.6 mg, 50 µmol)	16.0 mg (80%)
Exp 3, step 1	**L2**AuCl (16.8 mg, 25 µmol), **2b** (7.6 mg, 37.5 µmol), CsF (7.6 mg, 50 µmol)	13.9 mg (70%)
Exp 4, step 1	**L2**AuCl (14.1 mg, 21 µmol), **2b** (4.3 mg, 21 µmol), CsF (6.4 mg, 42 µmol)	16.0 mg (95%)

2-Methoxy-1,1'-binaphthalene 3b (from B2)

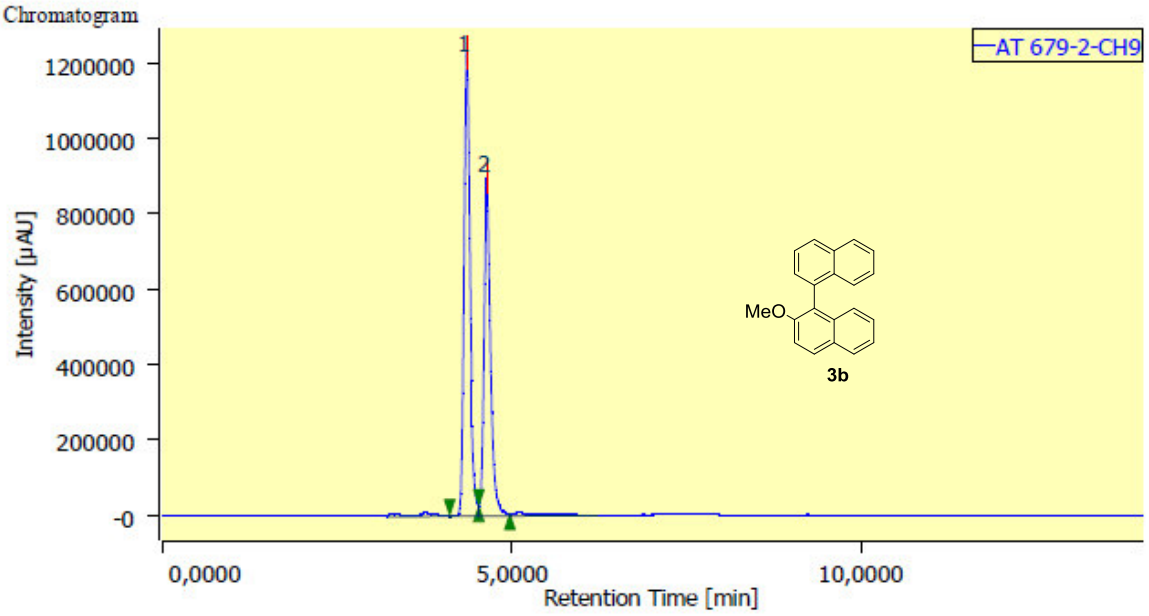


3b

In a vial were added complex **B2** (1.0 eq.), naphthalene-1-diazonium tetrafluoroborate **1b** (1.0 eq.) and $Ru(bpy)_3(PF_6)_2$ (0.02 eq.). The vial was purged three times with nitrogen and CH_3CN (1 mL) was added. The reaction was placed inside the turned-off photochemical reactor and stirred under blue light irradiation for 3h. The completion of the reaction was confirmed by ^{31}P NMR. The solvent was evaporated under reduced pressure, and the residue was purified by preparative TLC (90/10 : cyclohexane/ethyl acetate, Rf : 0.7) to give product **3b** as a colorless oil. The yield was calculated over the two steps of Pathway I. Enantiomeric excess was determined by Chiral HPLC analysis (CHIRAL PAK ID column (5µm, 4.6*250mm), isopropanol/hexane 2/98, flow rate 1.0mL/min, retention times: 4.4 to 4.9 min and 4.7 to 5.3 min). Plus sign was arbitrary attributed if the major enantiomer of **3b** corresponded to the HLPC pic with the lower retention time, and minus sign in the opposite case.

Experience	Conditions	Mass of 3b (yield over the two steps)	e.e. of 3b
Exp 1, step 2	**B2** (18.0 mg, 23 µmol), **1b** (5.5 mg, 23 µmol), $Ru(bpy)_3(PF_6)_2$ (0.5 mg, 0.5 µmol)	2.2 mg (31%)	+ 8%
Exp 2, step 2	**B2** (16.0 mg, 20 µmol), **1b** (5.0 mg, 20 µmol), $Ru(bpy)_3(PF_6)_2$ (0.3 mg, 0.4 µmol)	2.9 mg (41%)	+ 4%
Exp 3, step 2	**B2** (14.0 mg, 18 µmol), **1b** (4.4 mg, 18 µmol), $Ru(bpy)_3(PF_6)_2$ (0.3 mg, 0.4 µmol)	2.0 mg (28%)	+ 3%
Exp 4, step 2	**B2** (16 mg, 20 µmol), **1b** (5.0 mg, 20 µmol), $Ru(bpy)_3(PF_6)_2$ (0.4 mg, 0.5 µmol)	2.0 mg (33%)	+ 4%

- **Experience 1**



Peak Information

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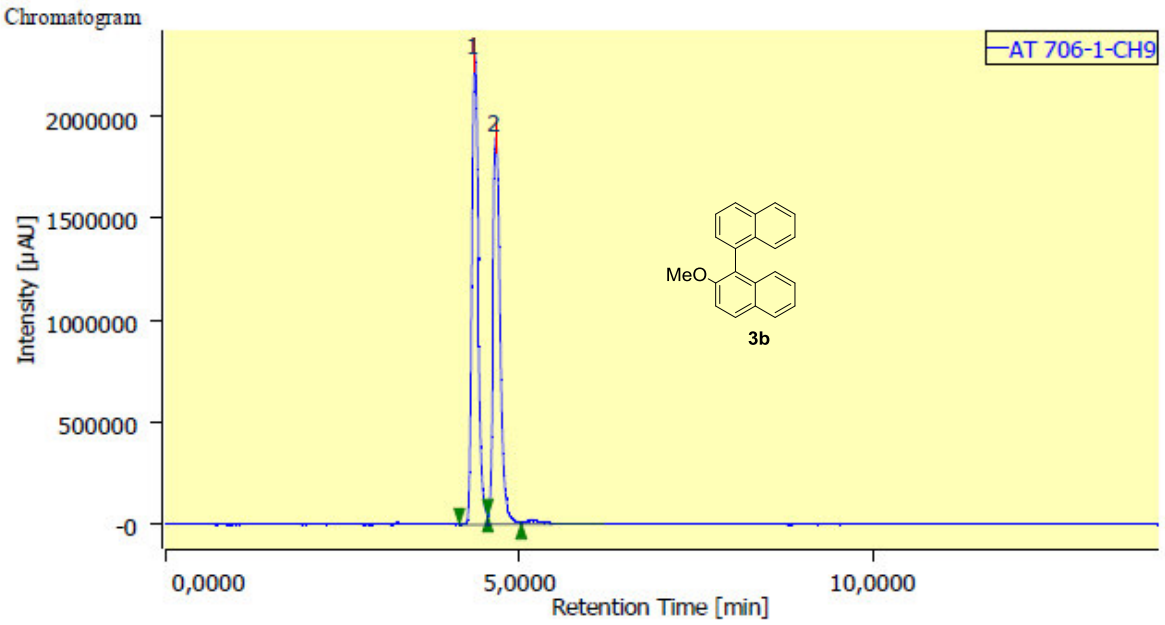
2	9	4,653	6002334	895129	45,879

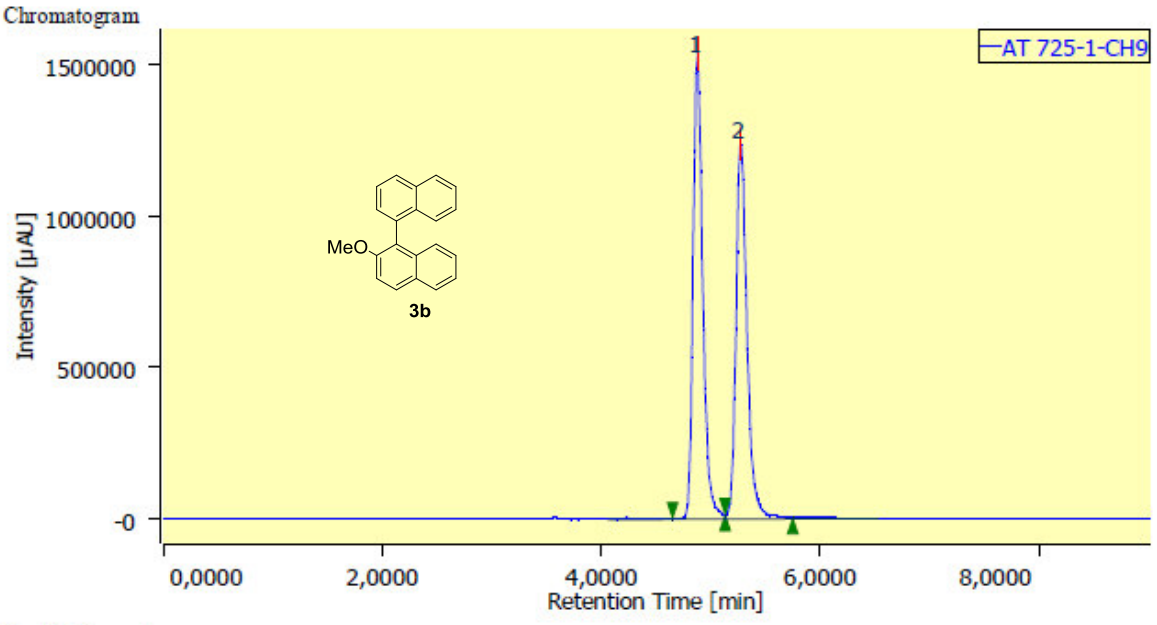
- **Experience 2**



Peak Information

#	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%
1	9	4,373	14588201	2295564	52,199
2	9	4,680	13359213	1894529	47,801

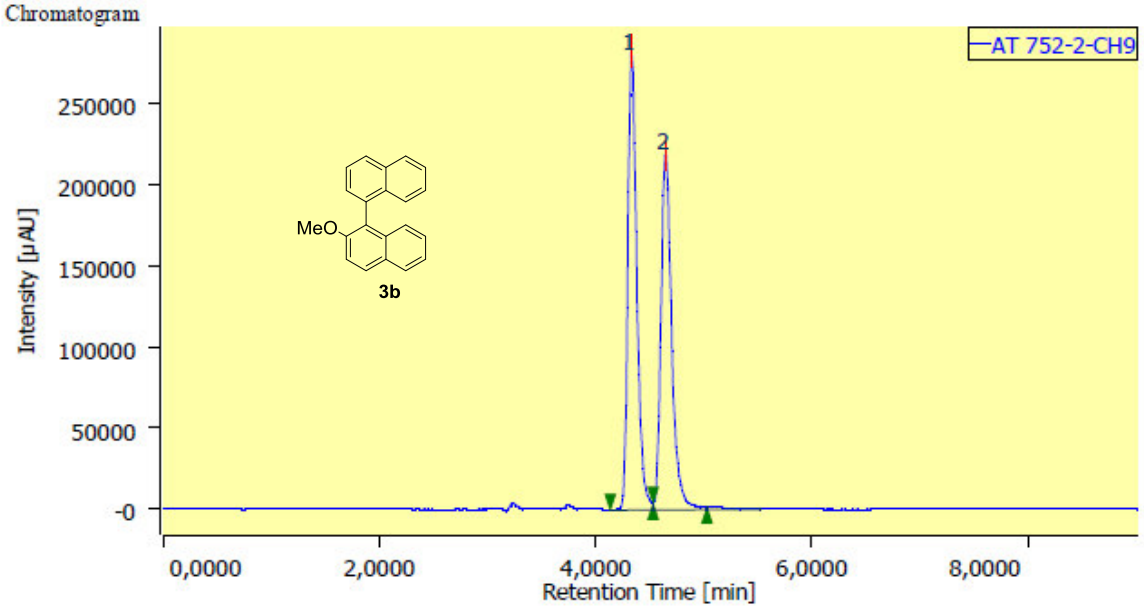
- **Experience 3**



Peak Information

#	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%
1	9	4,880	9316406	1535243	51,586
2	9	5,267	8743448	1235684	48,414

- **Experience 4**

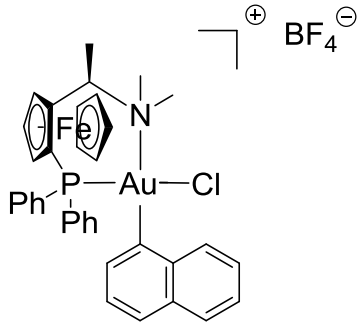


Peak Information

#	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%
1	9	4,333	1608414	282249	51,807
2	9	4,653	1496216	218794	48,193

Pathway II

[(naphthyl)-((*R*)-(−)-*N*,*N*-Dimethyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine)]chloro gold(III) tetrafluoroborate E2

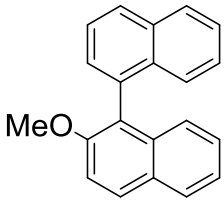


E2

In a vial were added **L2**AuCl (1.0 eq.), naphthalene-1-diazonium tetrafluoroborate **1b** (1.0 eq.) and $Ru(bpy)_3(PF_6)_2$ (0.02 eq.). The vial was purged three times with nitrogen and CH_3N (1 mL) was added. The reaction was placed inside the turned-off photochemical reactor and stirred under blue light irradiation for 2h. The completion of the reaction was confirmed by ^{31}P NMR. The mixture was filtered and the solvent was evaporated under reduced pressure. Then, the residue was triturated with diethyl ether to give the crude product **E2** as a dark red solid, which was engaged in the following step without further purification despite detection by ^{31}P NMR of traces of a minor side product (δ :13.2 ppm, <10%). ^{1}H NMR (300 MHz, CD_3CN) δ (ppm): 8.52 (d, *J* = 7.8 Hz, 1H), 8.04-8.01 (m, 2H), 7.92-7.90 (m, 2H), 7.75-7.73 (m, 1H), 7.65-7.63 (m, 4H), 7.54-7.52 (m, 3H), 7.43-7.38 (m, 2H), 7.35-7.26 (m, 2H), 5.28 (br s, 1H), 5.00 (br s, 1H), 4.89 (br s, 1H), 4.46 (br s, 1H), 4.32 (br s, 1H), 4.23 (br s, 4H), 3.47-3.40 (m, 3H), 2.39 (d, *J* = 4.0 Hz, 3H), 2.30 d, *J* = 3.7 Hz, 3H). ^{31}P NMR (121.5 MHz, CD_3CN) δ (ppm): 20.6.

Experience	Conditions	Mass of of E2 (Crude yield)
Exp 1, step 1	**L2**AuCl (16.8 mg, 25 µmol), **1b** (6.1 mg, 25 µmol), $Ru(bpy)_3(PF_6)_2$ (0.5 mg, 0.5 µmol)	21.0 mg (95%)
Exp 2, step 1	**L2**AuCl (16.8 mg, 25 µmol), **1b** (6.1 mg, 25 µmol), $Ru(bpy)_3(PF_6)_2$ (0.5 mg, 0.5 µmol)	22.0 mg (98%)
Exp 3, step 1	**L2**AuCl (16.8 mg, 25 µmol), **1b** (6.1 mg, 25 µmol), $Ru(bpy)_3(PF_6)_2$ (0.5 mg, 0.5 µmol)	21.0 mg (95%)
Exp 4, step 1	**L2**AuCl (16.8 mg, 25 µmol), **1b** (6.1 mg, 25 µmol), $Ru(bpy)_3(PF_6)_2$ (0.5 mg, 0.5 µmol)	20.0 mg (90%)
Exp 5, step 1	**L2**AuCl (16.8 mg, 25 µmol), **1b** (6.1 mg, 25 µmol), $Ru(bpy)_3(PF_6)_2$ (0.5 mg, 0.5 µmol)	20.9 mg (94%)
Exp 6, step 1	**L2**AuCl (15.0 mg, 22 µmol), **1b** (6.0 mg, 22 µmol), $Ru(bpy)_3(PF_6)_2$ (0.54mg, 0.4 µmol), 4h	17.0 mg (87%)

2-Methoxy-1,1'-binaphthalene 3b (from E2)

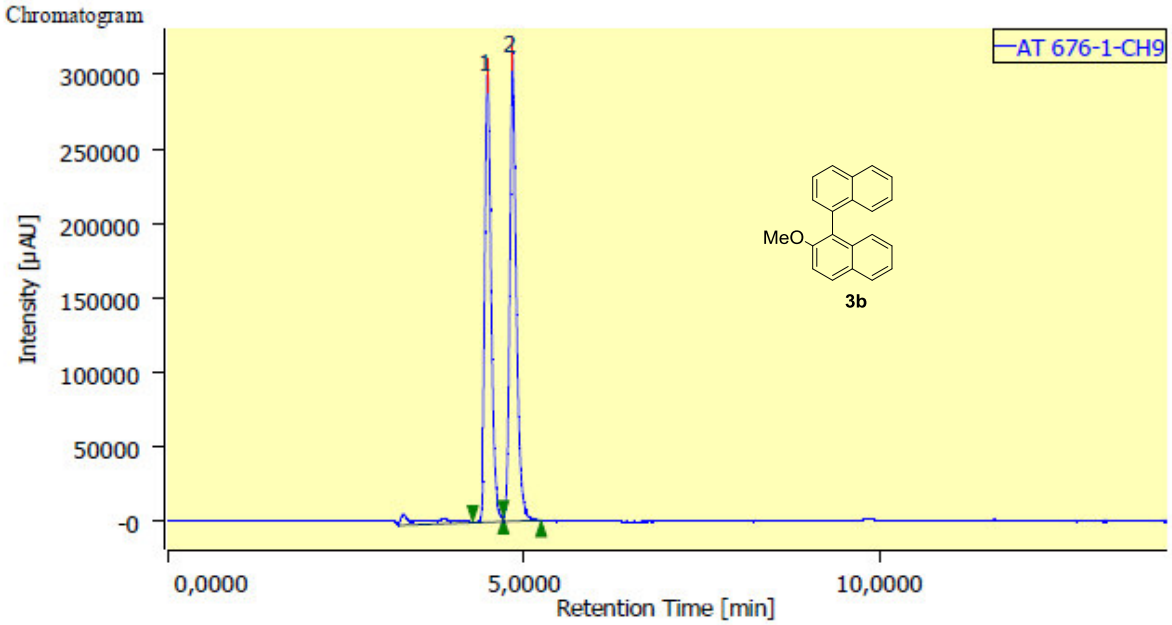


3b

In a vial were added the complex **E2** (1.0 eq.), 2-methoxy-1-naphtaleneboronic acid **2b** (1.0 eq.) and CsF (2.0 eq.). The vial was purged three times with nitrogen and CH_3CN (1 mL) was added. The reaction was stirred at 50°C for 16h. The solvent was evaporated under reduced pressure, and the residue was purified by preparative TLC (90/10 : cyclohexane/ethyl acetate, R_f : 0.7) to give the product as a colorless oil. The yield was calculated over the two steps of Pathway II. Enantiomeric excess was determined by Chiral HPLC analysis (CHIRAL PAK ID column (5µm, 4.6*250mm), isopropanol/hexane 2/98, flow rate 1.0mL/min, retention times: 4.3 to 4.5 min and 4.6 to 4.9 min). Plus sign was arbitrary attributed if the major enantiomer of **3b** corresponded to the HLPC pic with the lower retention time, and minus sign in the opposite case.

Experience	Conditions	Mass of 3b (yield over the two steps)	e.e. of 3b
Exp 1, step 2	**E2** (21.0 mg), **2b** (5.1 mg, 25 µmol), CsF (7.6 mg, 50 µmol)	1.9 mg (27%)	- 8%
Exp 2, step 2	**E2** (22.0 mg), **2b** (5.1 mg, 25 µmol), CsF (7.6 mg, 50 µmol)	0 mg (0%)	-
Exp 3, step 2	**E2** (21.0 mg), **2b** (5.1 mg, 25 µmol), CsF (7.6 mg, 50 µmol)	2.0 mg (28%)	- 8%
Exp 4, step 2	**E2** (20.0 mg), **2b** (4.8 mg, 24 µmol), CsF (7.3 mg, 48 µmol)	0 mg (0%)	-
Exp 5, step 2	**E2** (20.9 mg), **2b** (4.8 mg, 24 µmol), CsF (7.3 mg, 48 µmol)	0 mg (0%)	-
Exp 6, step 2	**E2** (17.0mg), **2b** (4.2 mg, 22 µmol), CsF (6.8 mg, 48 µmol)	0 mg (0%)	-

- **Experience 1**



Peak Information

#	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%
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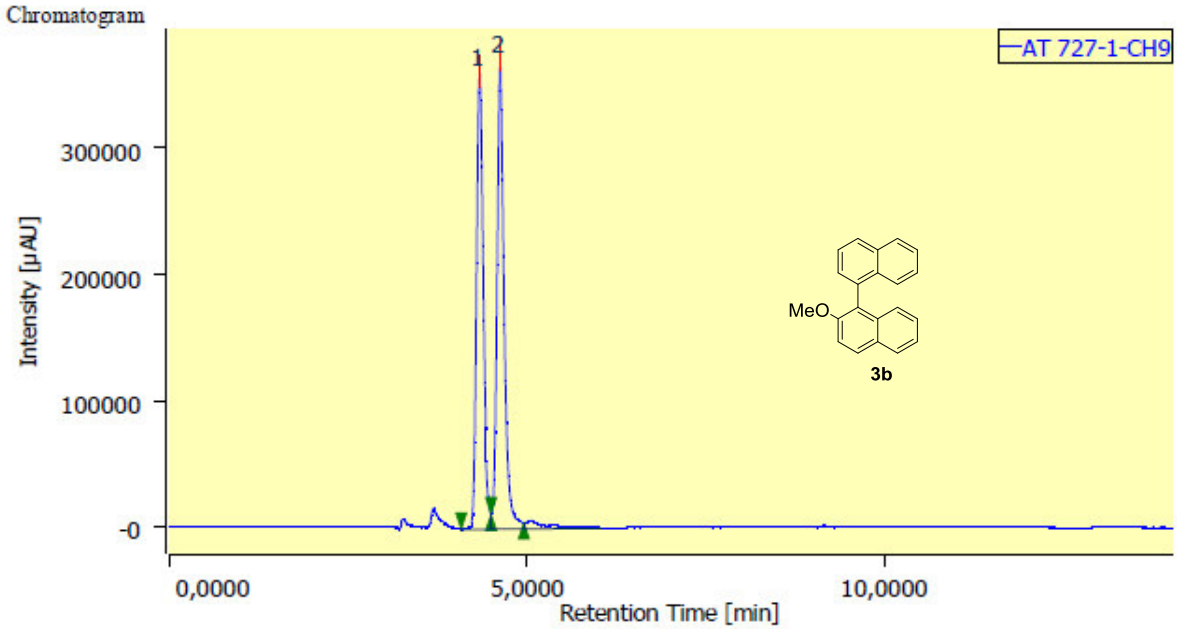
2	9	4,853	2111929	313321	53,985

- **Experience 3**

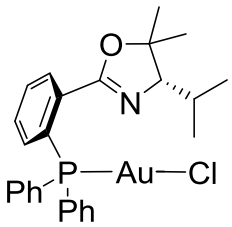


Peak Information

#	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%
1	9	4,347	2256422	361582	45,899
2	9	4,627	2659600	374837	54,101

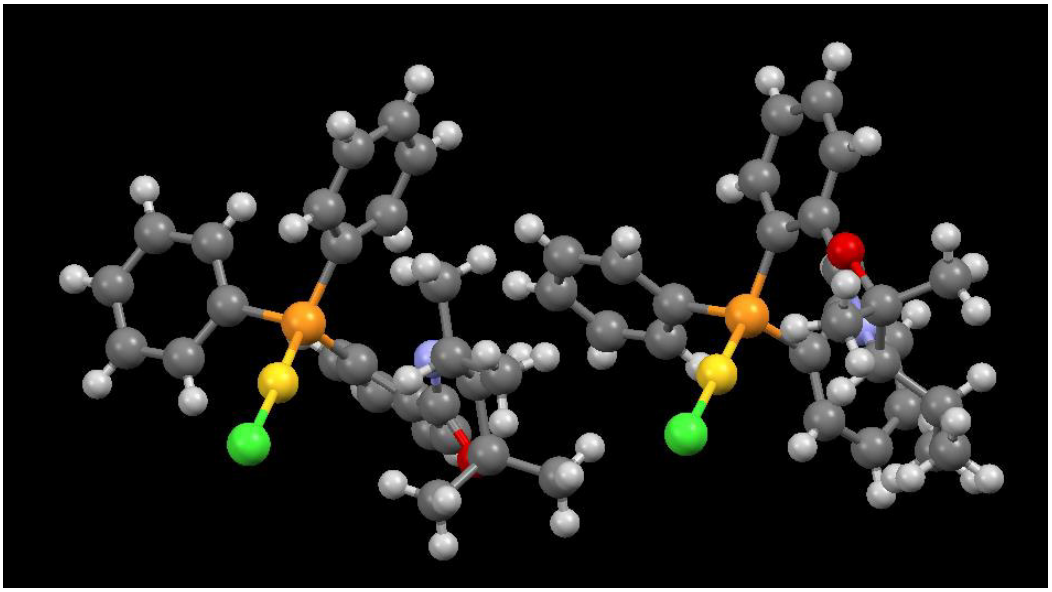
*d) Experiments with **L3**AuCl*

Chloro[(4*S*)-2-[2-(diphenylphosphino)phenyl]-4,5-dihydro-5,5-dimethyl-4-(1-methylethyl)-oxazole]gold(I) L3AuCl



L3AuCl

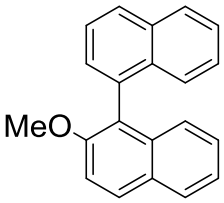
Under inert atmosphere, (4S)-2-[2-(diphenylphosphino)phenyl]-4,5-dihydro-5,5-dimethyl-4-(1-methylethyl)-oxazole **L3** (80.2 mg, 0.2 mmol, 1.0 eq.) and chloro(dimethylsulfide)gold(I) (59.0 mg, 0.2 mmol, 1.0 eq.) were dissolved in dichloromethane (2 mL). The reaction mixture was stirred in the dark for 2 hours. Then, the solvent was removed under reduced pressure and the residue was triturated in pentane to give product **L3**AuCl (118.6 mg, 0.19 mmol, 95%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.05-8.01 (m, 1H), 7.59-7.35 (m, 12H), 6.89-6.82 (m, 1H), 3.27 (d, *J* = 9.3 Hz, 1H), 1.74-1.62 (m, 1H), 1.47 (s, 3H), 1.26 (s, 3H), 0.78 (dd, *J* = 7.6 Hz, *J* = 6.7 Hz, 6H). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ (ppm): 33.5. ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 134.8 (d, *J* = 7.2 Hz), 134.4 (d, *J* = 6.9 Hz), 134.2 (d, *J* = 6.9 Hz), 131.3 (m), 130.8 (m), 130.6 (m), 129.4, 129.1, 128.9, 128.7, 28.8, 28.6, 21.7, 21.5, 20.8. HRMS (ESI/TOF$^+$) $C_{26}H_{28}AuClNOP$ $[M+Na]^+$ calculated 656.1154 found 656.1158. Slow vapor diffusion of Et_2O in a solution of **L3**AuCl in CH_2Cl_2 allowed to produce suitable monocrystals for X-ray diffraction analysis. Crystallographic data were acquired at CESAMO (UMR 5255) on a Bruker APEX 2 DUO. A single crystal was mounted and immersed in a stream of nitrogen gas [*T* = 150(2) K]. Data were collected, using a microfocus sealed tube of Mo K_α radiation (*k* = 0.71073 Å) on a KappaCCD diffractometer. Data collection and cell refinement were performed using APEX2 2013.10-0 (Bruker AXS Inc.), and SAINT v8.34A (Bruker AXS Inc.). Data reduction was performed using SAINT v8.34A (Bruker AXS Inc.). Correction for absorption was performed using multi-scan integration as included in SADABS V2012/1 (Bruker AXS). Structure solutions were found by charge flipping methods (SUPERFLIP (Palatinus & Chapuis, 2007) EDMA (Palatinus et al., 2012)) and refined with (SHELXL).[7] Full crystallographic data for this structure has been deposited with the Cambridge Crystallographic Data (CCDC 1843202).



*Mercury drawing of the crystalline structure of **L3**AuCl obtained by X-Ray diffraction analysis (50% thermal ellipsoids)*

[7] Sheldrick, G. M. *Acta Crystallographica Section A*. **2008**, 64, 112.

2-Methoxy-1,1'-binaphthalene 3b

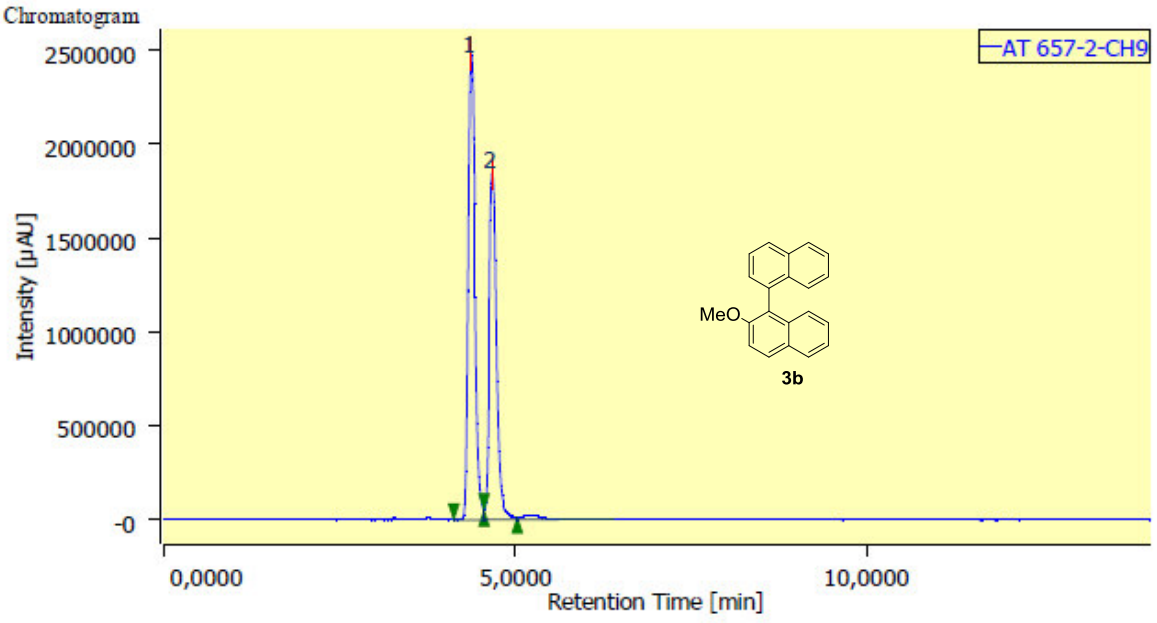


3b

Pathway I (from L3AuCl via B3)

In a vial were added complex **L3**AuCl (31.6 mg, 0.05 mmol, 1.0 eq.), 2-methoxy-1-naphtaleneboronic acid **2b** (15.5 mg, 0.075 mmol, 1.5 eq.) and CsF (15.2 mg, 0.1 mmol, 2.0 eq.). The vial was purged three times with nitrogen and CH_3CN (1 mL) was added. The reaction was stirred at 50°C for 16h. The mixture was filtered throught a celite pad and the filtrate was evaporated under reduced pressure. Then, the residue was triturated with pentane to give the intermediate crude product 2-methoxynaphtyl-[(4*S*)-2-[2-(diphenylphosphino)phenyl]-4,5-dihydro-5,5-dimethyl-4-(1-methylethyl)-oxazole]gold(I) **B3** (30.0 mg, 0.039 mmol, 78%) as a white solid, which was engaged in the following step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.47 (d, *J* = 8.1 Hz, 1H), 8.03 (dd, *J* = 6.4 Hz and *J* = 4.0 Hz, 1H), 7.76-7.69 (m, 6H), 7.63 (d, *J* = 8.7 Hz, 1H), 7.56-7.51 (m, 1H), 7.44-7.36 (m, 5H), 7.32-7.28 (m, 2H), 7.25-7.14 (m, 2H), 6.97 (dd, *J* = 10.1 Hz, *J* = 8.2 Hz, 1H), 3.96 (s, 3H), 3.37 (d, *J* = 9.2 Hz, 1H), 1.33-1.30 (m, 1H), 1.24 (s, 3H), 1.16 (s, 3H), 0.74 (d, , *J* = 6.5 Hz, 3H), 0.68 (d, *J* = 6.5 Hz, 3H). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ (ppm): 47.4.

Then, in a vial were added the complex **B3** (20.0 mg, 0.026 mmol, 1.0 eq), naphthalene-1-diazonium tetrafluoroborate **1b** (6.4 mg, 0.026 mmol, 1.0 eq.) and $Ru(bpy)_3(PF_6)_2$ (0.6 mg, 0.5 µmol, 0.02 eq.). The vial was purged three times with nitrogen and CH_3CN (1 mL) was added. The reaction was placed inside the turned-off photochemical reactor and stirred under blue light irradiation for 3h. The solvent was evaporated under reduced pressure and the residue was purified by preparative TLC (90/10 : cyclohexane/ethyl acetate, R_f: 0.7) to give product **3b** (4.0 mg, 0.014 mmol, 42% over the two steps) as a colorless oil. Enantiomeric excess was determined by Chiral HPLC analysis (CHIRAL PAK ID column (5µm, 4.6*250mm), isopropanol/hexane 2/98, flow rate 1.0mL/min): +12% ee (retention times: 4.4 min and 4.7 min, plus sign was arbitrary attributed if the major enantiomer of **3i** corresponded to the HLPC pic with the lower retention time, and minus sign in the opposite case).



Peak Information

#	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%
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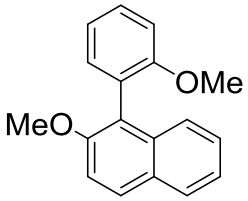
2	9	4,680	13167769	1842315	44,176

2-Methoxy-1-(2-methoxyphenyl)naphthalene 3c

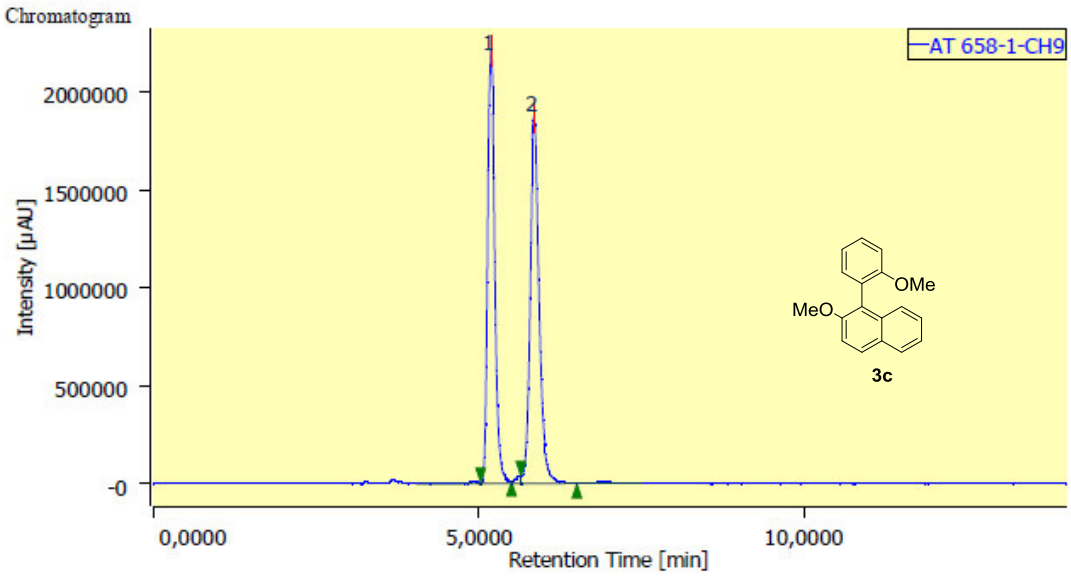


3c

*Pathway I (from **L3**AuCl via **B3**)*

In a vial were added complex **L3**AuCl (31.6 mg, 0.05 mmol, 1.0 eq.), 2-methoxy-1-naphtaleneboronic acid **2b** (15.5 mg, 0.075 mmol, 1.5 eq.) and CsF (15.2 mg, 0.1 mmol, 2.0 eq.). The vial was purged three times with nitrogen and CH_3CN (1 mL) was added. The reaction was stirred at 50°C for 16h. The mixture was filtered throught a celite pad and the filtrate was evaporated under reduced pressure. Then, the residue was triturated with pentane to give the intermediate crude product 2-methoxynaphtyl-[(4*S*)-2-[2-(diphenylphosphino)phenyl]-4,5-dihydro-5,5-dimethyl-4-(1-methylethyl)-oxazole]gold(I) **B3** (30.0 mg, 0.039 mmol, 78%) as a white solid, which was engaged in the following step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.47 (d, *J* = 8.1 Hz, 1H), 8.03 (dd, *J* = 6.4 Hz and *J* = 4.0 Hz, 1H), 7.76-7.69 (m, 6H), 7.63 (d, *J* = 8.7 Hz, 1H), 7.56-7.51 (m, 1H), 7.44-7.36 (m, 5H), 7.32-7.28 (m, 2H), 7.25-7.14 (m, 2H), 6.97 (dd, *J* = 10.1 Hz, *J* = 8.2 Hz, 1H), 3.96 (s, 3H), 3.37 (d, *J* = 9.2 Hz, 1H), 1.33-1.30 (m, 1H), 1.24 (s, 3H), 1.16 (s, 3H), 0.74 (d, , *J* = 6.5 Hz, 3H), 0.68 (d, *J* = 6.5 Hz, 3H). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ (ppm): 47.4.

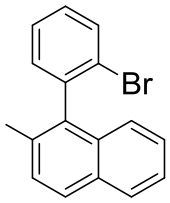
Then, in a vial were added the complex **B3** (10.0 mg, 0.013 mmol, 1.0 eq), 2-methoxybenzenediazonium tetrafluoroborate **1c** (3.2 mg, 0.013 mmol, 1.0 eq.) and $Ru(bpy)_3(PF_6)_2$ (0.3 mg, 0.3 µmol, 0.02 eq.). The vial was purged three times with nitrogen and CH_3CN (1 mL) was added. The reaction was placed inside the turned-off photochemical reactor and stirred under blue light irradiation for 3h. The solvent was evaporated under reduced pressure and the residue was purified by preparative TLC (90/10 : cyclohexane/ethyl acetate, R_f: 0.5) to give product **3c** (1.0 mg, 3.8 µmol, 23% over the two steps) as a colorless oil. Enantiomeric excess was determined by Chiral HPLC analysis (CHIRAL PAK ID column (5µm, 4.6*250mm), isopropanol/hexane 2/98, flow rate 1.0mL/min): -3% ee (retention times: 5.2 min and 5.9 min, plus sign was arbitrary attributed if the major enantiomer of **3c** corresponded to the HLPC pic with the lower retention time, and minus sign in the opposite case).



Peak Information

#	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%
1	9	5,187	17301716	2207633	48,726
2	9	5,853	18206677	1868119	51,274

1-(2-Bromophenyl)-2-methylnaphthalene 3d (from 1d and 2d)



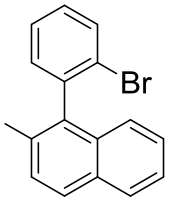
3d

*Pathway I (from **L3**AuCl via **B3'**)*

In a vial were added complex **L3**AuCl (15.8 mg, 0.025 mmol, 1.0 eq.), 2-methyl-1-naphtaleneboronic acid **2d** (6.0 mg, 0.025 mmol, 1.0 eq.) and CsF (7.6 mg, 0.05 mmol, 2.0 eq.). The vial was purged three times with nitrogen and CH_3CN (1 mL) was added. The reaction was stirred at 50°C for 72h. The mixture was filtered throught a celite pad and the filtrate was evaporated under reduced pressure. Then, the residue was triturated with pentane to give a mixture of product 2-methylnaphthyl-[(4*S*)-2-[2-(diphenylphosphino)phenyl]-4,5-dihydro-5,5-dimethyl-4-(1-methylethyl)-oxazole]gold(I) **B3'** and starting **L3**AuCl (13.9 mg, 2:3 ratio determined by ^{31}P NMR) as a white solid. This crude mixture which was engaged in the following step without further purification. ^{31}P NMR (121.5 MHz, $CDCl_3$) δ (ppm): 47.9.

Then, in a vial were added the mixture containing complex **B3'** (13.9 mg), 2-bromobenzenediazonium tetrafluoroborate **1d** (4.9 mg, 0.018 mmol, 1.0 eq.) and $Ru(bpy)_3(PF_6)_2$ (0.3 mg, 0.4 µmol, 0.02 eq.). The vial was purged three times with nitrogen and CH_3CN (1 mL) was added. The reaction was placed inside the turned-off photochemical reactor and stirred under blue light irradiation for 3h. The solvent was evaporated under reduced pressure and the residue was purified by preparative TLC (cyclohexane, R_f: 0.5) to give product **3d** in mixture with multiple side-products, as determined by the chiral HPLC analysis (0.8 mg, <10%). A second purification by preparative TLC did not improved the purity of the sample, which precluded any e.e. determination.

1-(2-Bromophenyl)-2-methylnaphthalene 3d (from 1e and 2e)



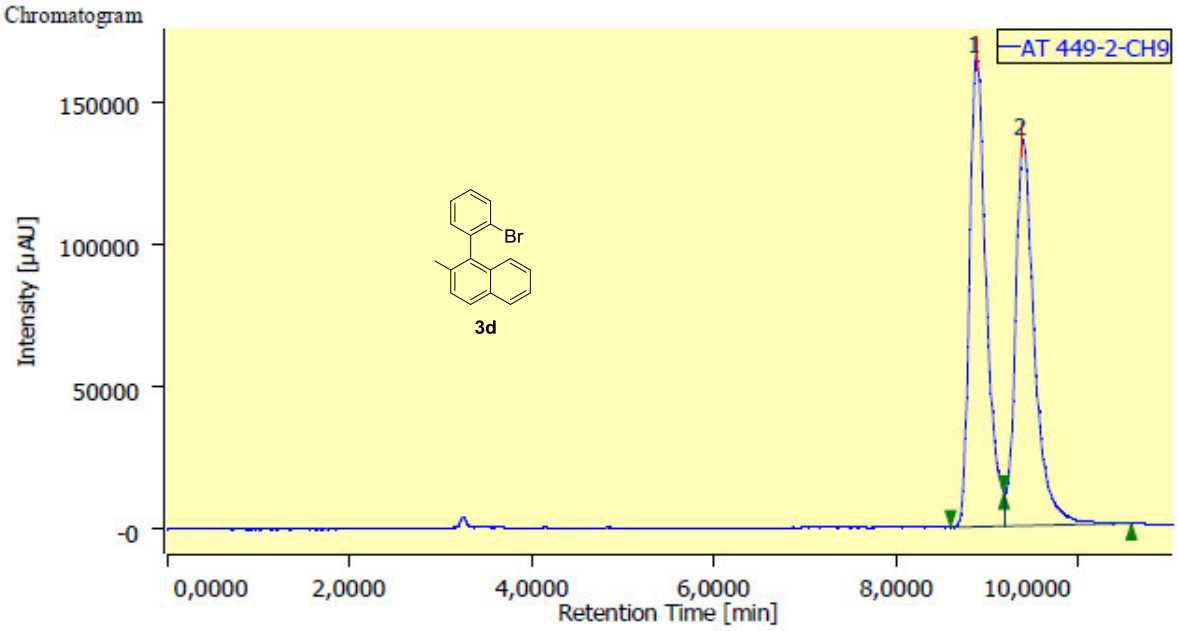
3d

*Pathway I (from **L3**AuCl via **B3''**)*

In a vial were added complex **L3**AuCl (43.8 mg, 0.067 mmol, 1.0 eq.), 2-bromophenylboronic acid **2e** (13.5 mg, 0.067 mmol, 1.0 eq.) and CsF (20.4 mg, 0.13 mmol, 2.0 eq.). The vial was purged three times with nitrogen and CH_3CN (2 mL) was added. The reaction was stirred at 50°C for 2h. The mixture was filtered throught a celite pad and the filtrate was evaporated under reduced pressure. Then, the residue was triturated with pentane to give a mixture of product 2-bromophenyl-[(4*S*)-2-[2-(diphenylphosphino)phenyl]-4,5-dihydro-5,5-dimethyl-4-(1-methylethyl)-oxazole]gold(I) **B3''** and starting **L3**AuCl (22.9 mg, 7:3 ratio determined by ^{31}P NMR) as a white solid. This crude mixture which was engaged in the following step without further purification. ^{31}P NMR (121.5 MHz, $CDCl_3$) δ (ppm): 43.7.

Then, in a vial were added the mixture containing complex **B3''** (22.9 mg), 2-methyl-1-naphtalene diazonium tetrafluoroborate **1e** (7.7 mg, 0.03 mmol, 1.0 eq.) and $Ru(bpy)_3(PF_6)_2$ (0.5 mg, 0.6 µmol, 0.02 eq.). The vial was purged three times with nitrogen and CH_3CN (1 mL) was added. The reaction was placed inside the turned-off photochemical reactor and stirred under blue light irradiation for 3h. The solvent was evaporated under reduced pressure and the residue was purified by preparative TLC (cyclohexane, R_f: 0.5) to give product **3d** (1.0 mg, 3.3 µmol, 5% over the two steps) as a white solid. Enantiomeric excess was determined by Chiral HPLC analysis (CHIRAL PAK IB column (5µm, 4.6*250mm), isopropanol/hexane 2/98, flow rate 1.0mL/min): +3% ee (retention times: 8.9 min and

9.4 min, plus sign was arbitrary attributed if the major enantiomer of **3d** corresponded to the HLPC pic with the lower retention time, and minus sign in the opposite case).

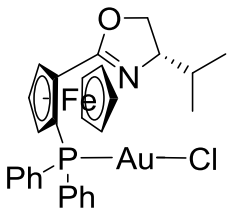


Peak Information

#	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%
1	9	8,867	2092518	165689	51,492
2	9	9,373	1971278	135170	48,508

*e) Experiments with **L4**AuCl*

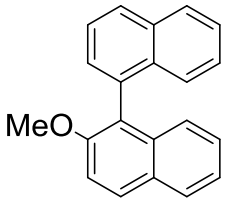
Chloro[(*S*)[(*Sp*)-2-(diphenylphosphino)ferrocenyl]-4-isopropyloxazoline] gold(I) L4AuCl



L4AuCl

Under inert atmosphere, (S)[(Sp)-2-(Diphenylphosphino)ferrocenyl]-4-isopropyloxazoline **L4** (48.1 mg, 0.1 mmol, 1.0 eq.) and chloro(dimethylsulfide)gold(I) (29.5 mg, 0.1 mmol, 1.0 eq.) were dissolved in dichloromethane (1 mL). The reaction mixture was stirred in the dark for 2 hours. Then, the solvent was removed under reduced pressure and the residue was triturated in pentane to give product **L4**AuCl (49.8 mg, 0.089 mmol, 70%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.77-7.70 (m, 2H), 7.53-7.36 (m, 8H), 5.07(br s, 1H), 4.49 (br s, 1H), 4.42 (s, 5H), 4.29-4.24 (m, 1H), 3.87-3.81 (m, 1H), 3.74-3.65 (m, 2H), 1.93 (dq, *J* = 13.3 Hz, *J* = 6.5 Hz, 1H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.81 (d, *J* = 6.7 Hz, 3H). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ (ppm): 30.5. ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 163.0, 134.9 (d, *J* = 14.5 Hz), 132.9 (d, *J* = 14.2 Hz), 131.9, 131.8 (d, *J* = 2.3 Hz), 131.1 (d, *J* = 2.1 Hz), 131.0, 130.2, 128.8 (d, *J* = 14.2 Hz), 128.7 (d, *J* = 15.0 Hz), 76.2 (d, *J* = 5.9 Hz), 75.4 (d, *J* = 11.5 Hz), 74.3 (d, *J* = 6.0 Hz), 73.5, 72.2, 71.5 (d, *J* = 7.5 Hz), 71.2, 70.3, 70.2, 32.3, 20.0, 18.2. HRMS (ESI/TOF^{+}) $C_{28}H_{28}AuClFeNOP$ $[M+H]^{+}$ calculated 714.0684 found 714.0710.

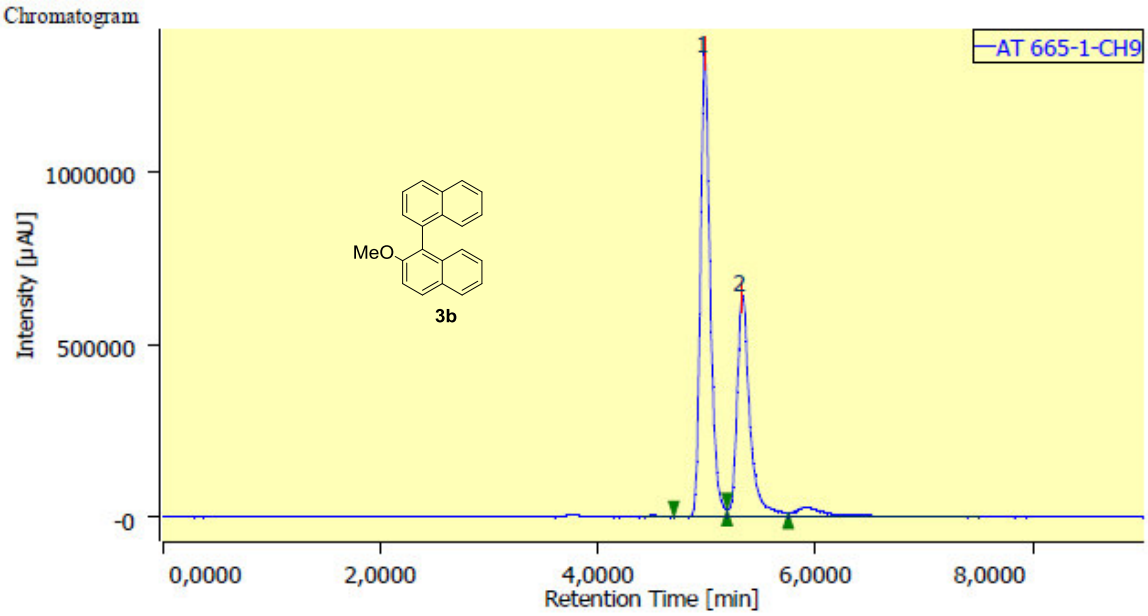
2-Methoxy-1,1'-binaphthalene 3b (from L4AuCl via B4)



3b

In a vial were added complex **L4**AuCl (17.8 mg, 0.025 mmol, 1.0 eq.), 2-methoxy-1-naphtaleneboronic acid **2b** (7.6 mg, 0.0375 mmol, 1.5 eq.) and CsF (7.6 mg, 0.05 mmol, 2.0 eq.). The vial was purged three times with nitrogen and CH_3CN (1 mL) was added. The reaction was stirred at 50°C for 16h. The mixture was filtered throught a celite pad and the filtrate was evaporated under reduced pressure. Then, the residue was triturated with pentane to give the intermediate crude product 2-methoxynaphtyl-[(*S*)[(*Sp*)-2-(diphenylphosphino)ferrocenyl]-4-isopropyloxazoline]gold(I) **B4** (17.6 mg, 0.021 mmol, 84%) as a yellow solid, which was engaged in the following step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.61 (d, *J* = 8.3 Hz, 1H), 7.94-7.88 (m, 2H), 7.80-7.73 (m, 2H), 7.65-7.61 (m, 3H), 7.49-7.46 (m, 3H), 7.34-7.37 (m, 3H), 7.29-7.23 (m, 1H), 7.17-7.14 (m, 1H), 5.15 (br s, 1H), 4.58 (s, 5H), 4.52-4.50 (m, 1H), 4.30-4.24 (m, 1H), 3.99 (s, 3H), 3.81-3.73 (m, 2H), 3.64-3.59 (m, 1H), 1.64 (dq, *J* = 13.1 Hz and *J* = 6.6 Hz, 1H), 0.71 (d, *J* = 6.7 Hz, 3H), 0.55 (d, *J* = 6.7 Hz, 3H). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ (ppm): 43.0.

Then, in a vial were added the complex **B4** (17.6 mg, 0.021 mmol, 1.0 eq), naphthalene-1-diazonium tetrafluoroborate **1b** (5.1 mg, 0.021 mmol, 1.0 eq.) and $Ru(bpy)_3(PF_6)_2$ (0.4 mg, 0.4 µmol, 0.02 eq.). The vial was purged three times with nitrogen and CH_3CN (1 mL) was added. The reaction was placed inside the turned-off photochemical reactor and stirred under blue light irradiation for 3h. The solvent was evaporated under reduced pressure and the residue was purified by preparative TLC (90/10 : cyclohexane/ethyl acetate, R_f: 0.7) to give product **3b** (3.1 mg, 0.011 mmol, 44% over the two steps) as a colorless oil. Enantiomeric excess was determined by Chiral HPLC analysis (CHIRAL PAK ID column (5µm, 4.6*250mm), isopropanol/hexane 2/98, flow rate 1.0mL/min): +26% ee (retention times: 5.0 min and 5.3 min, plus sign was arbitrary attributed if the major enantiomer of **3b** corresponded to the HLPC pic with the lower retention time, and minus sign in the opposite case).



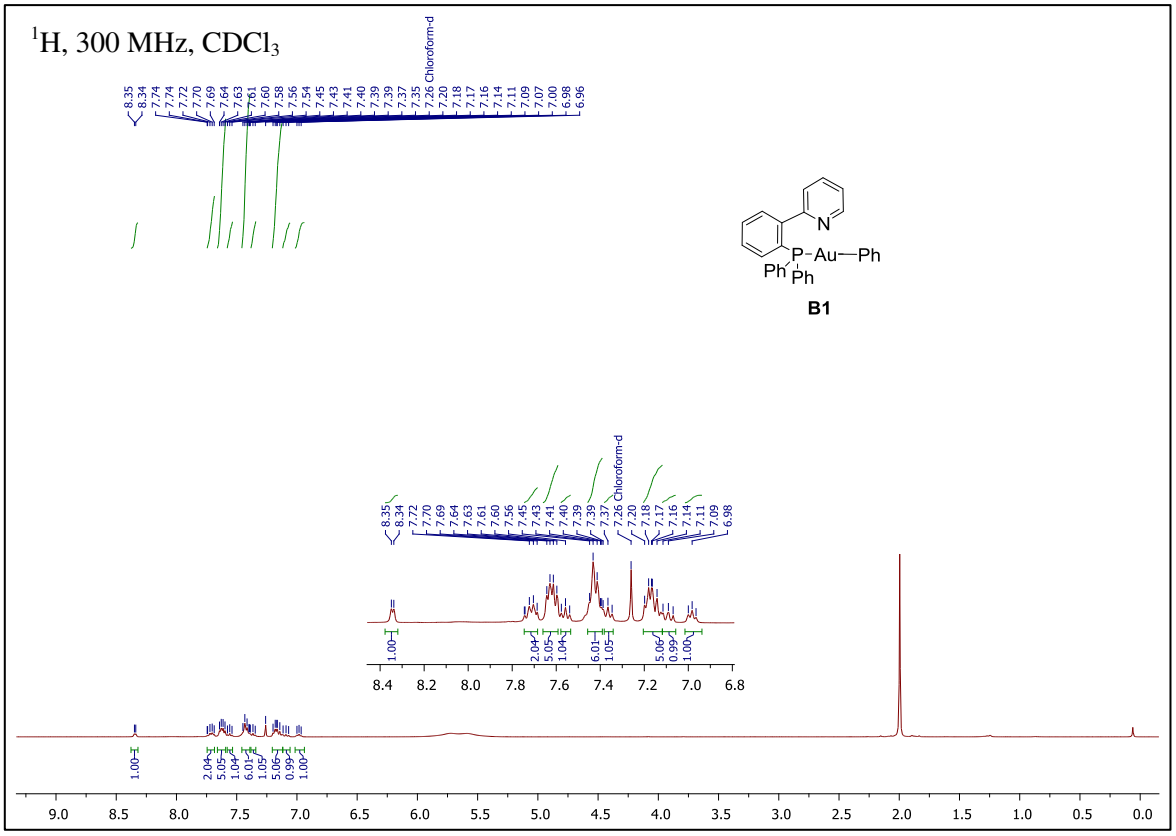
Peak Information

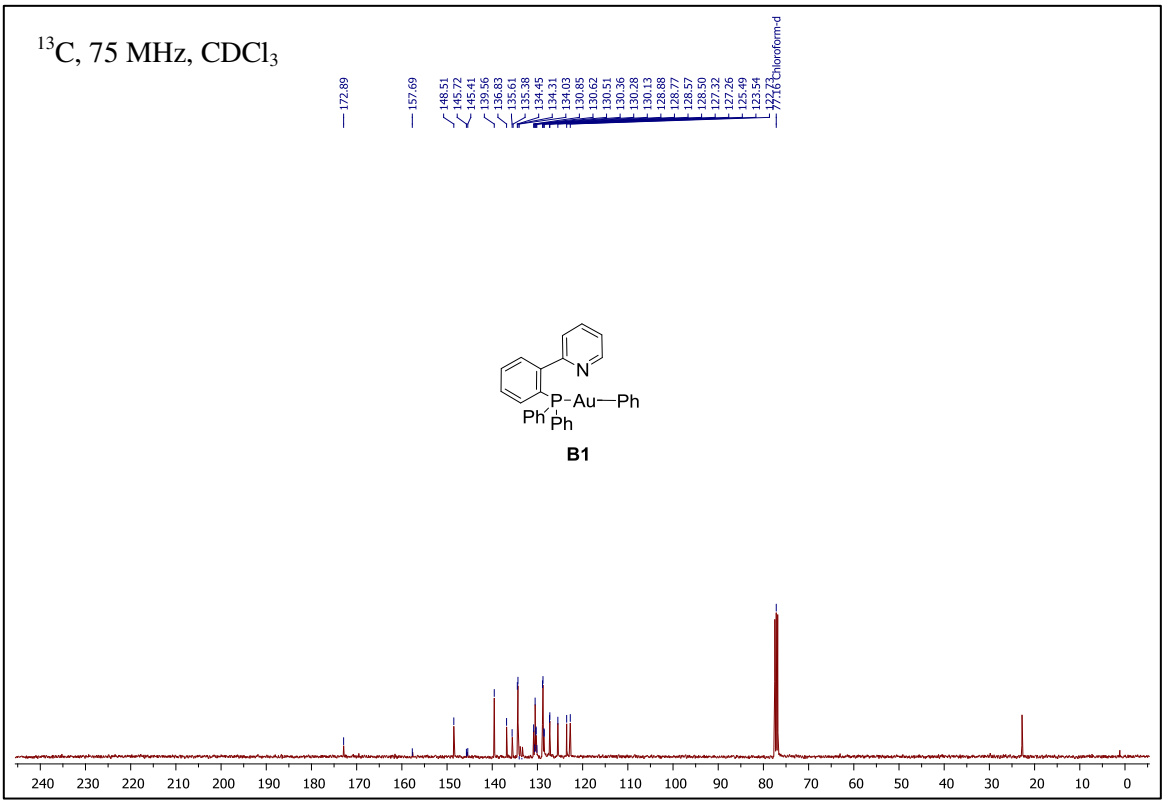
#	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%
1	9	4,987	8480684	1339019	61,691
2	9	5,320	5266279	637224	38,309

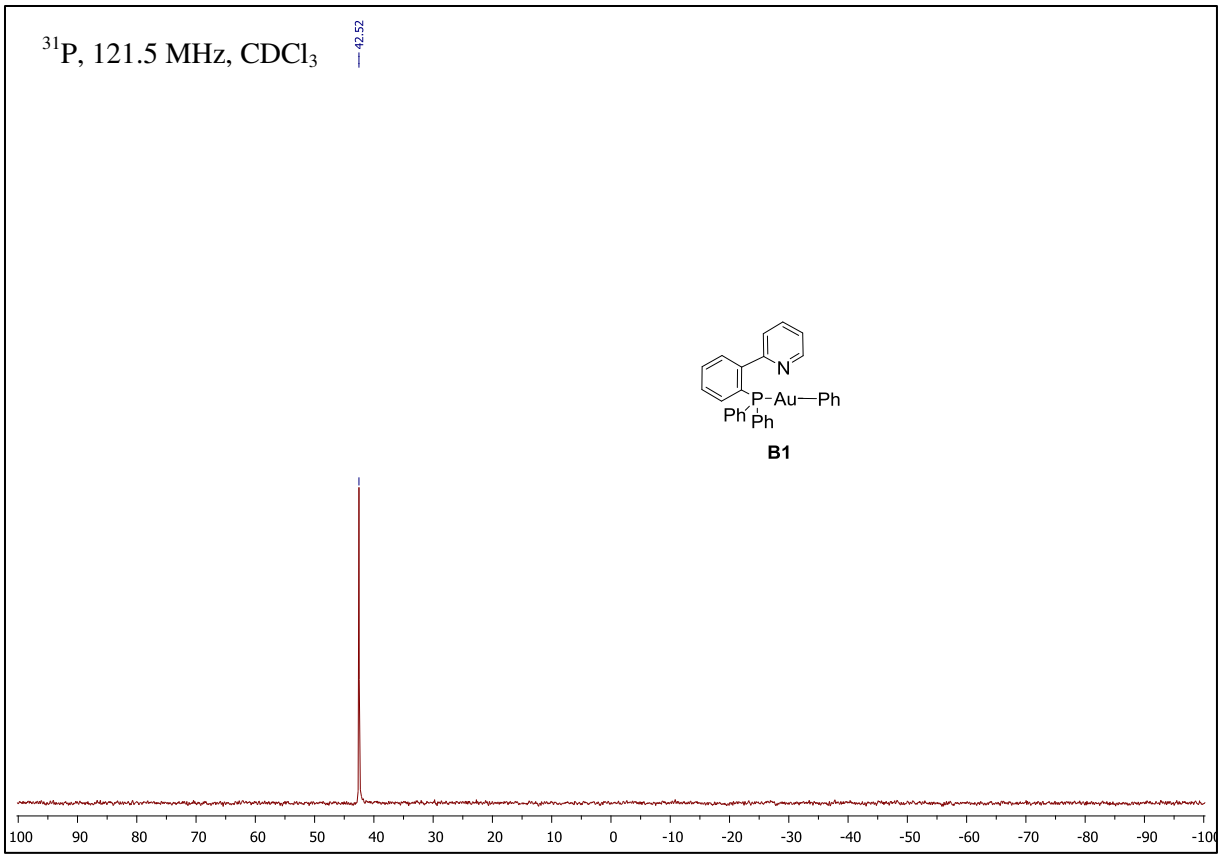
f) ^{1}H, ^{13}C *NMR,* ^{31}P *NMR and* ^{19}F *NMR Spectra*

Stoichiometric mechanistic investigations with L1AuCl

Phenyl [2-(2-(diphenylphosphanyl)phenyl)pyridine] gold(I) B1



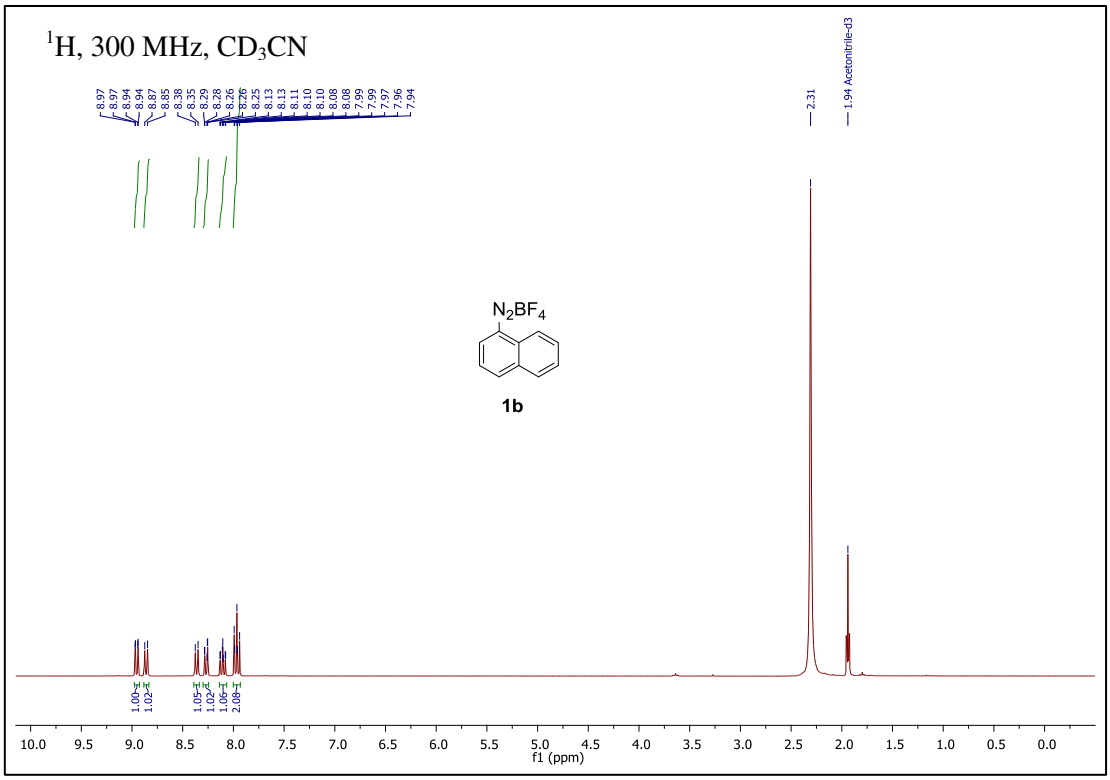




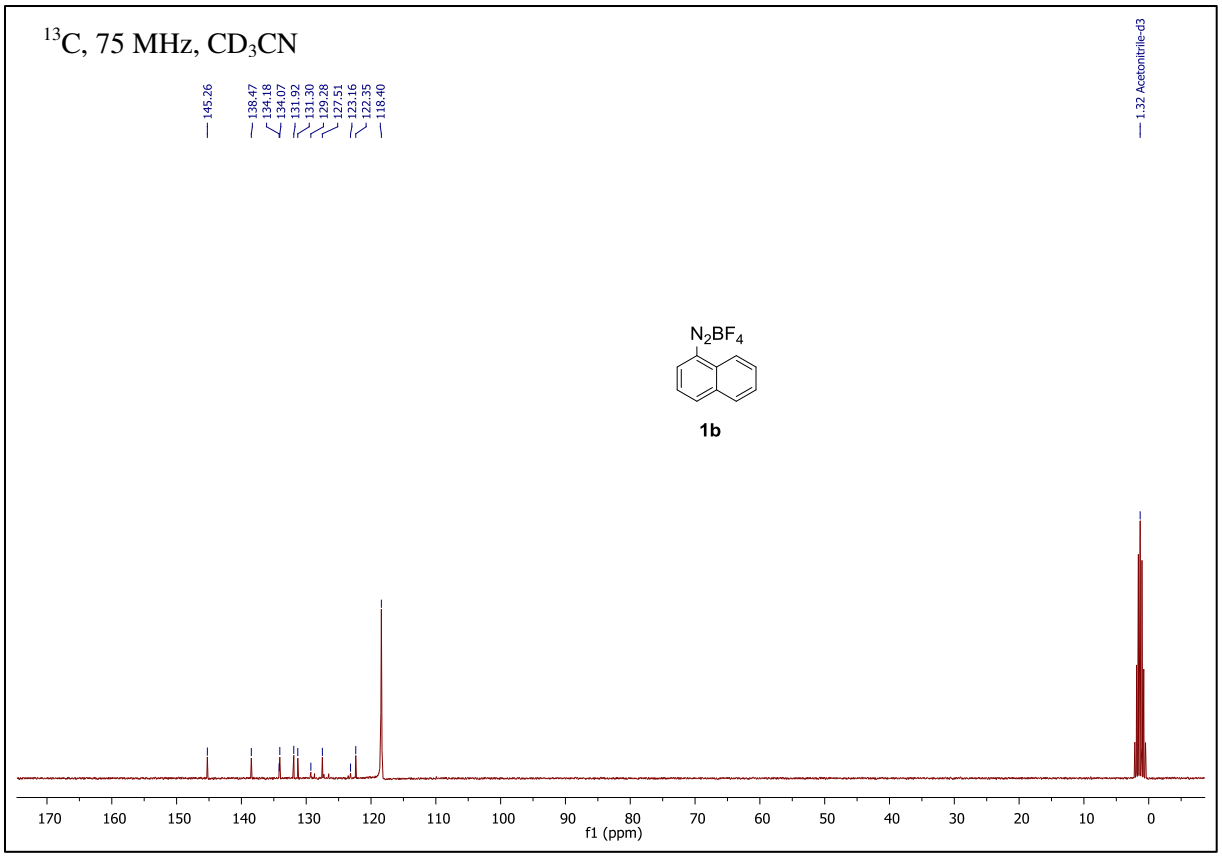
Asymmetric induction

*Syntheses of diazonium salts **1b-e***

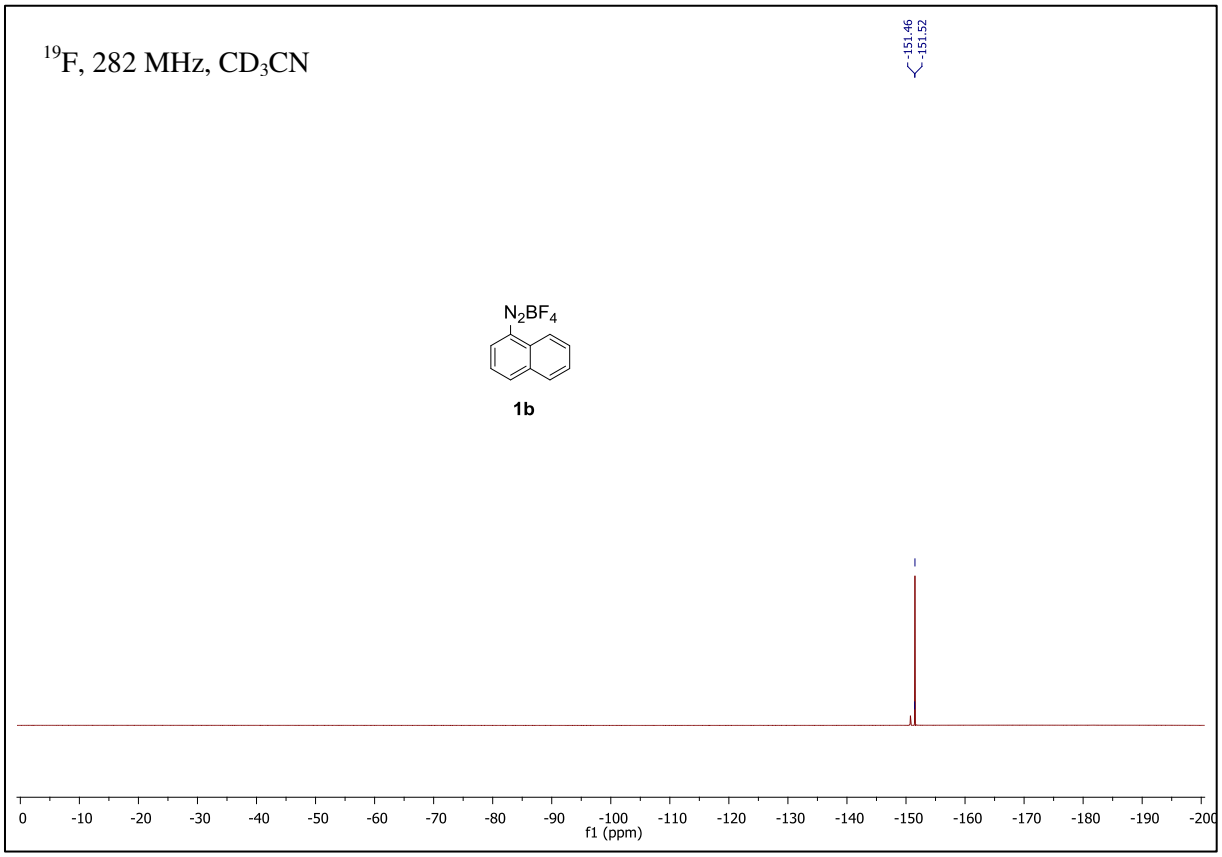
Naphthalene-1-diazonium tetrafluoroborate 1b



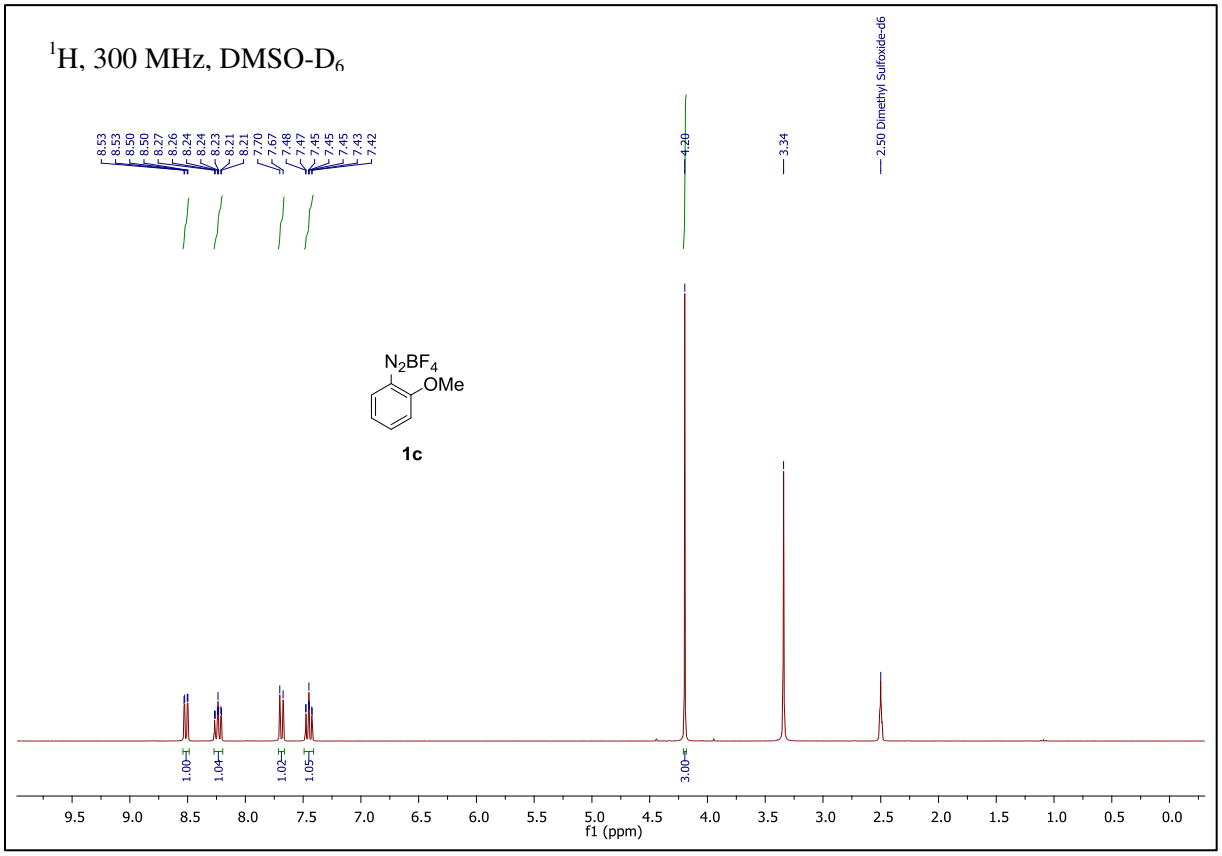
^{13}C, 75 MHz, CD_3CN

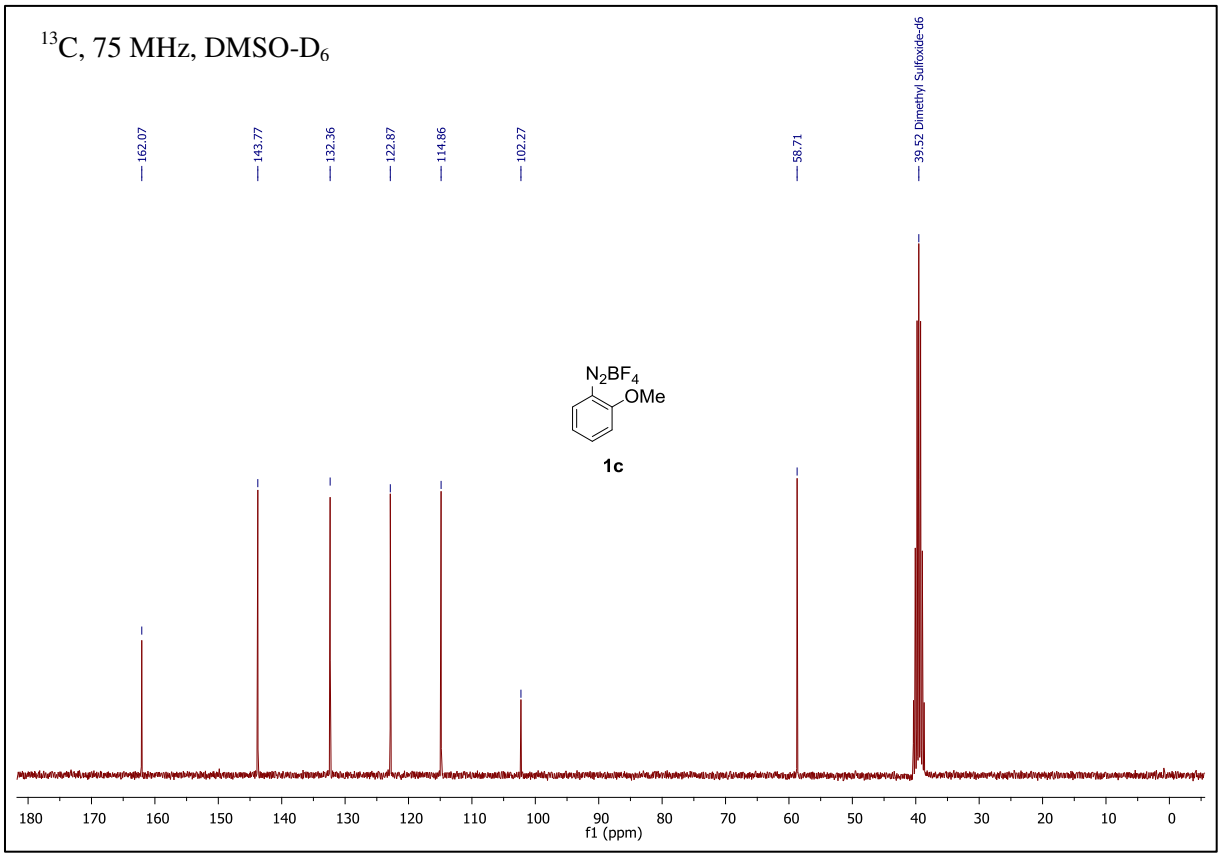


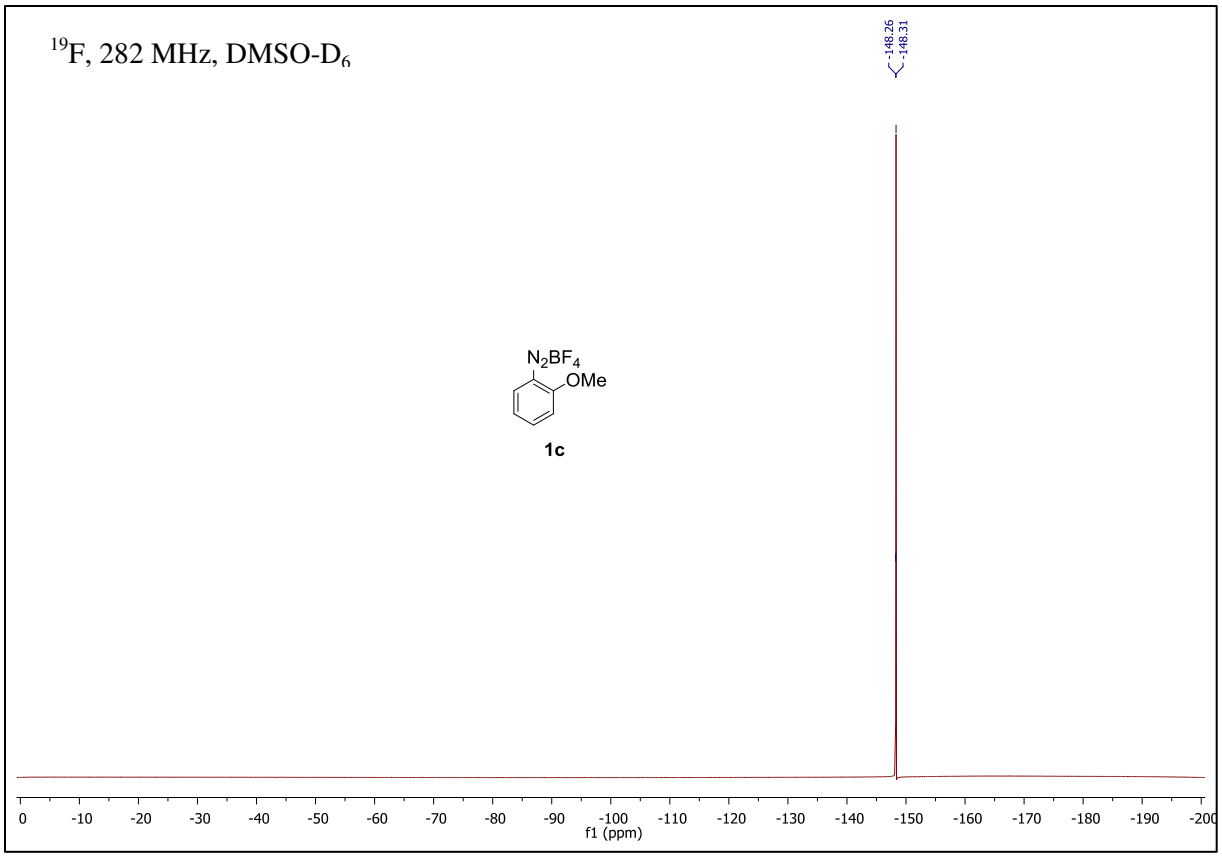
^{19}F, 282 MHz, CD_3CN



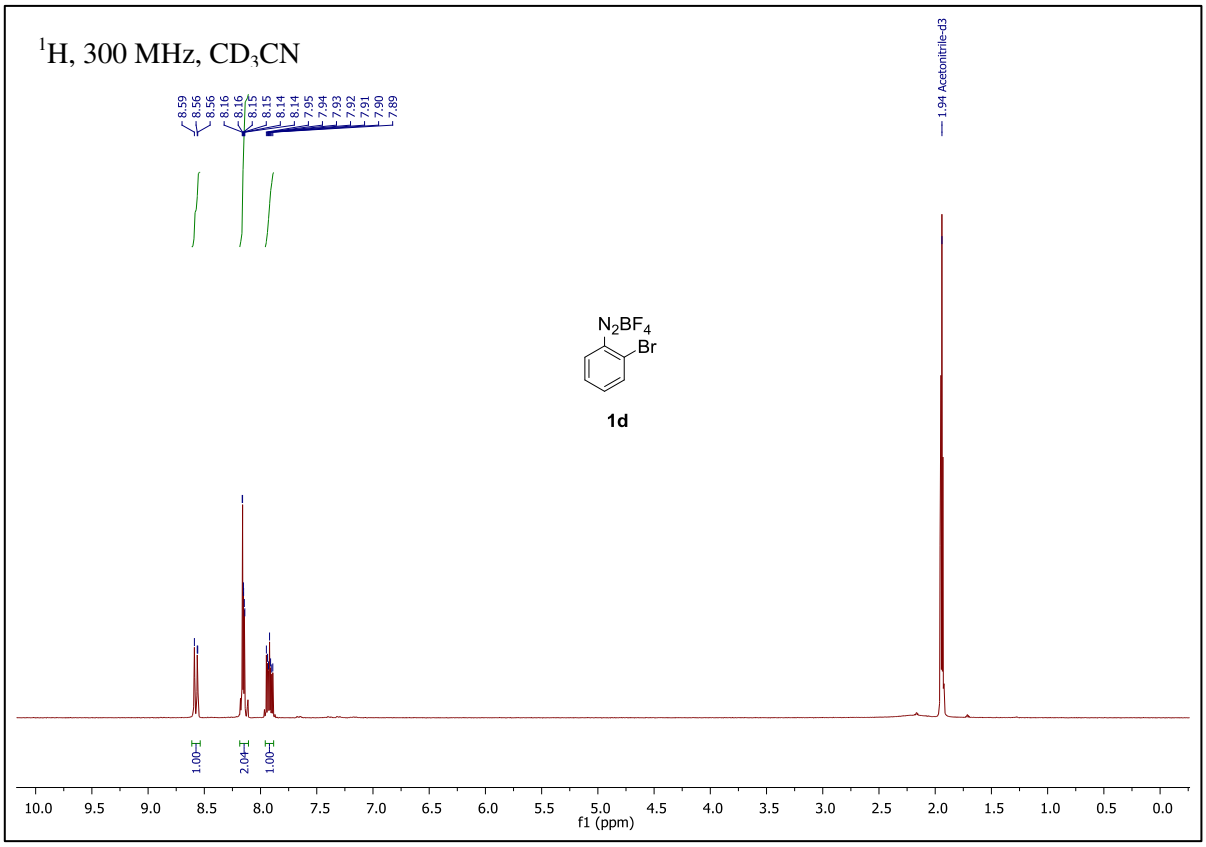
2-Methoxybenzenediazonium tetrafluoroborate 1c



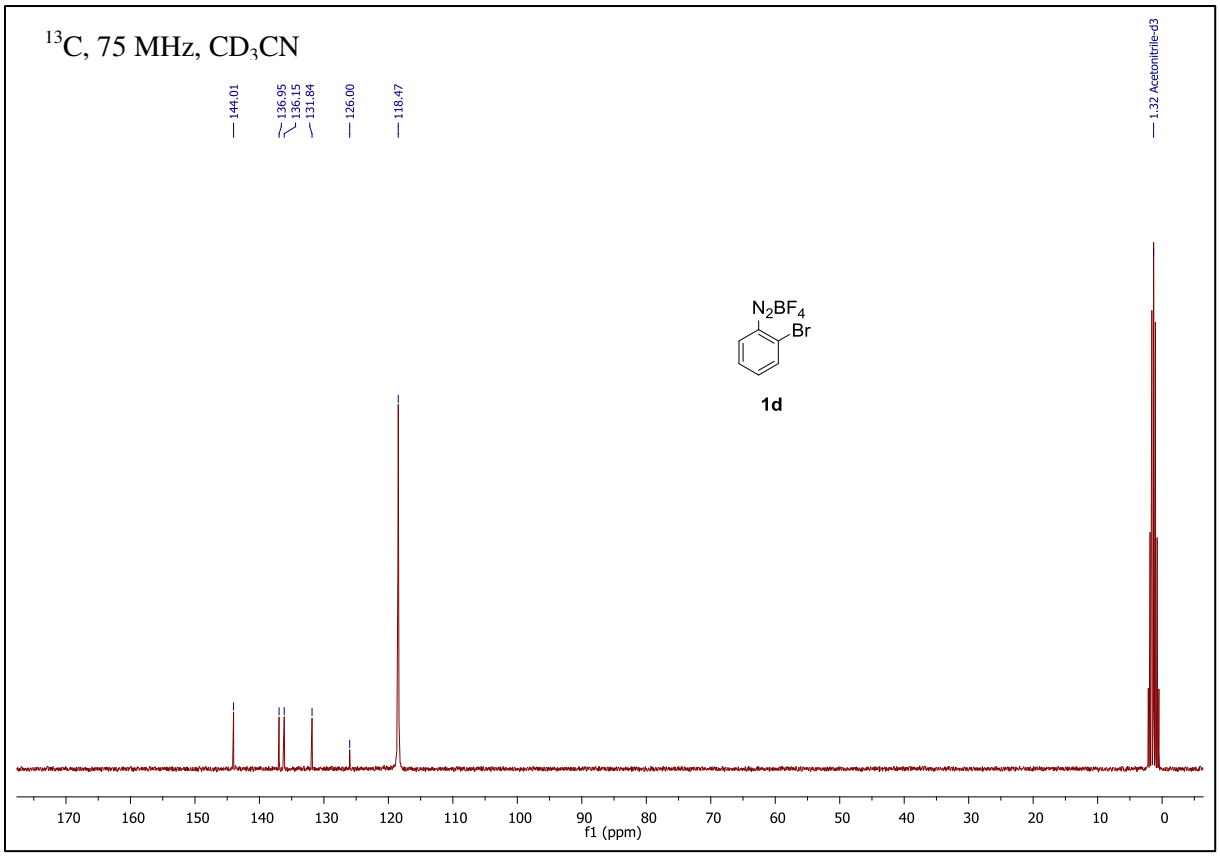




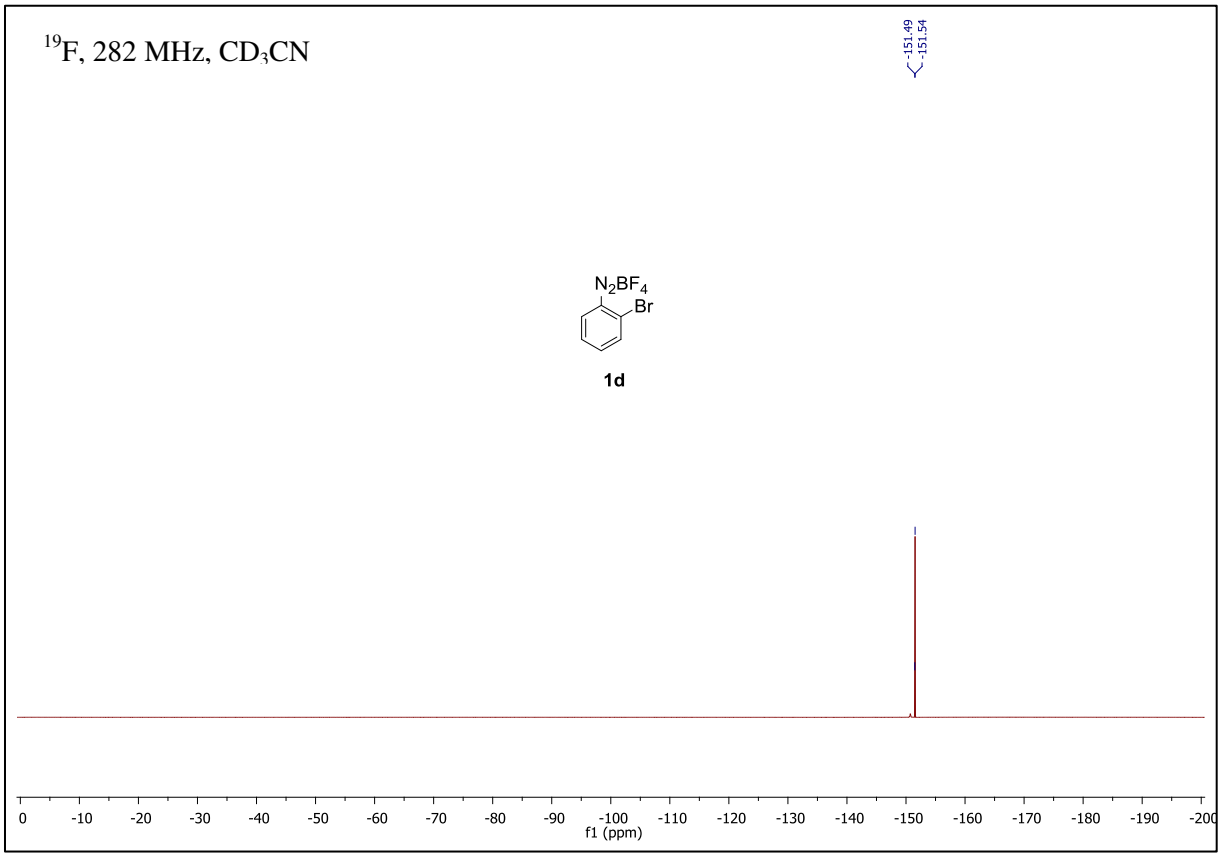
2-Bromobenzenediazonium tetrafluoroborate 1d



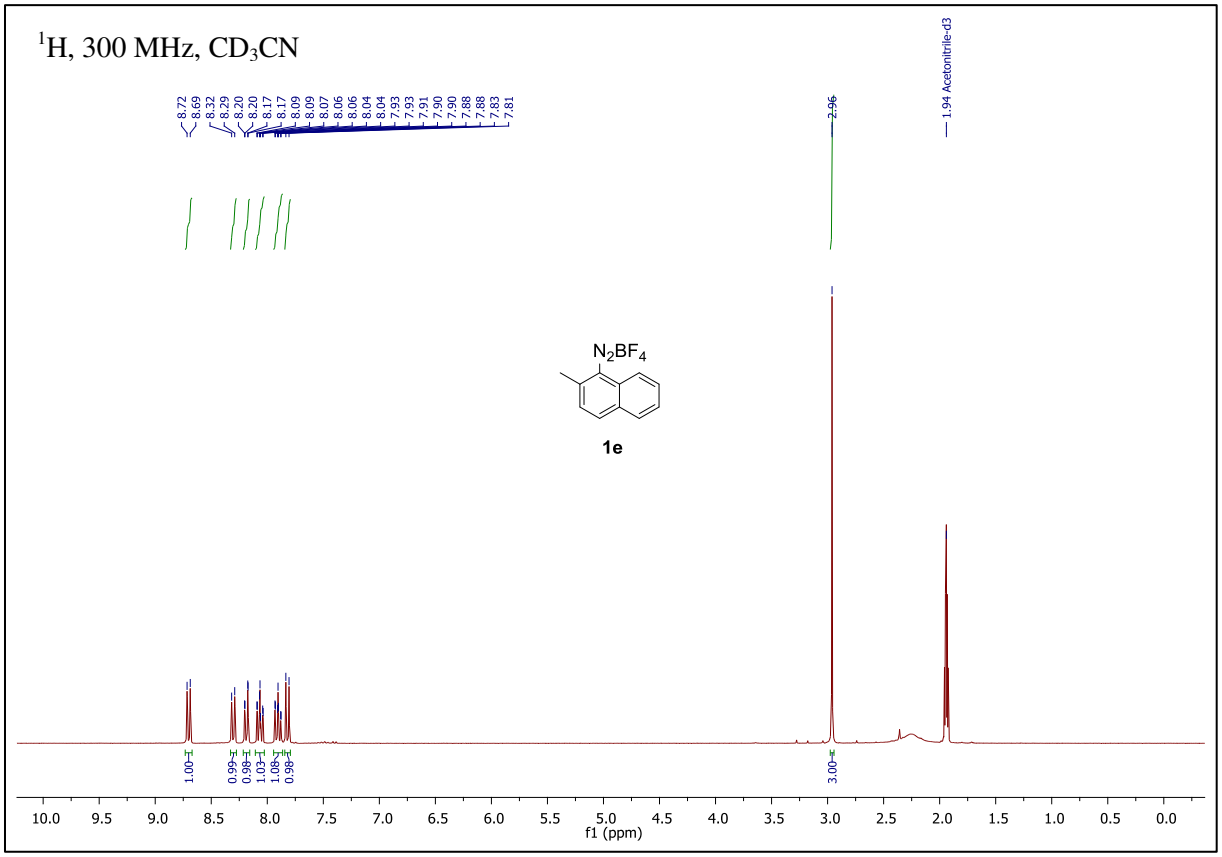
^{13}C, 75 MHz, CD_3CN

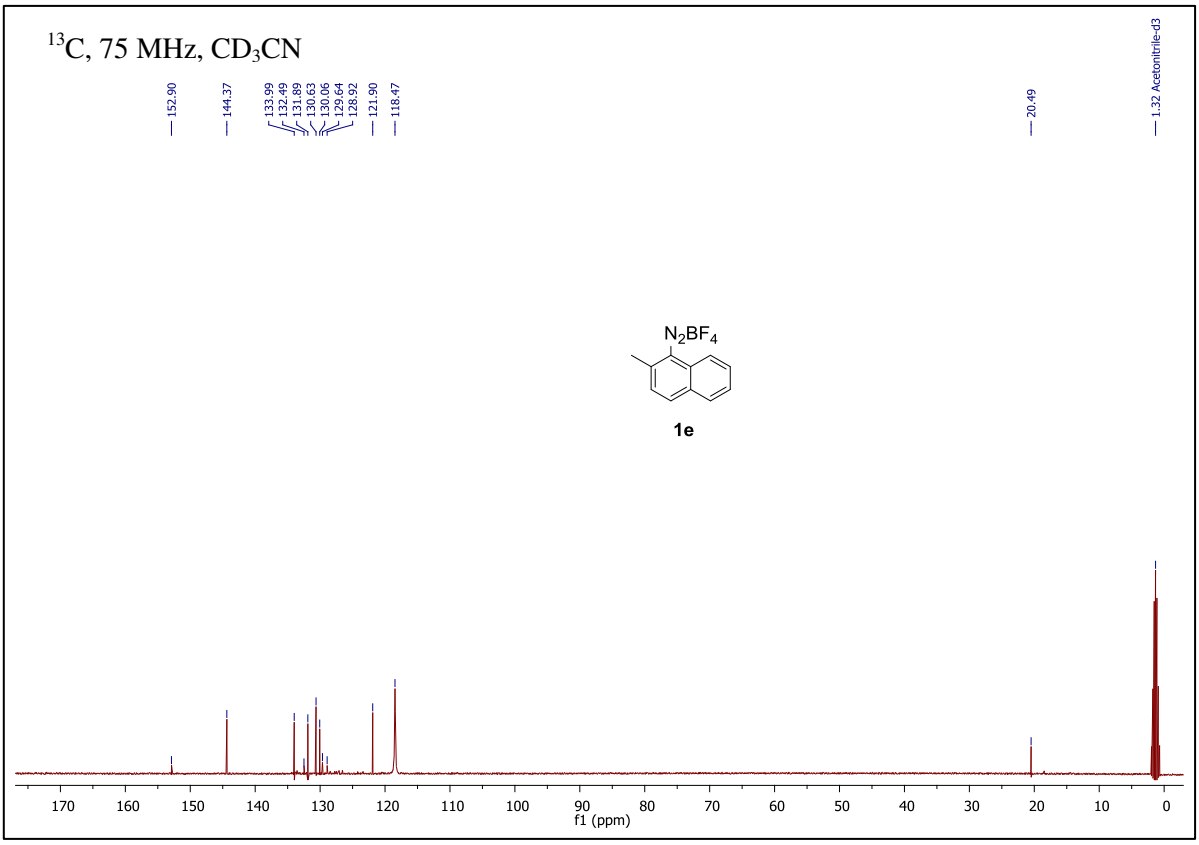


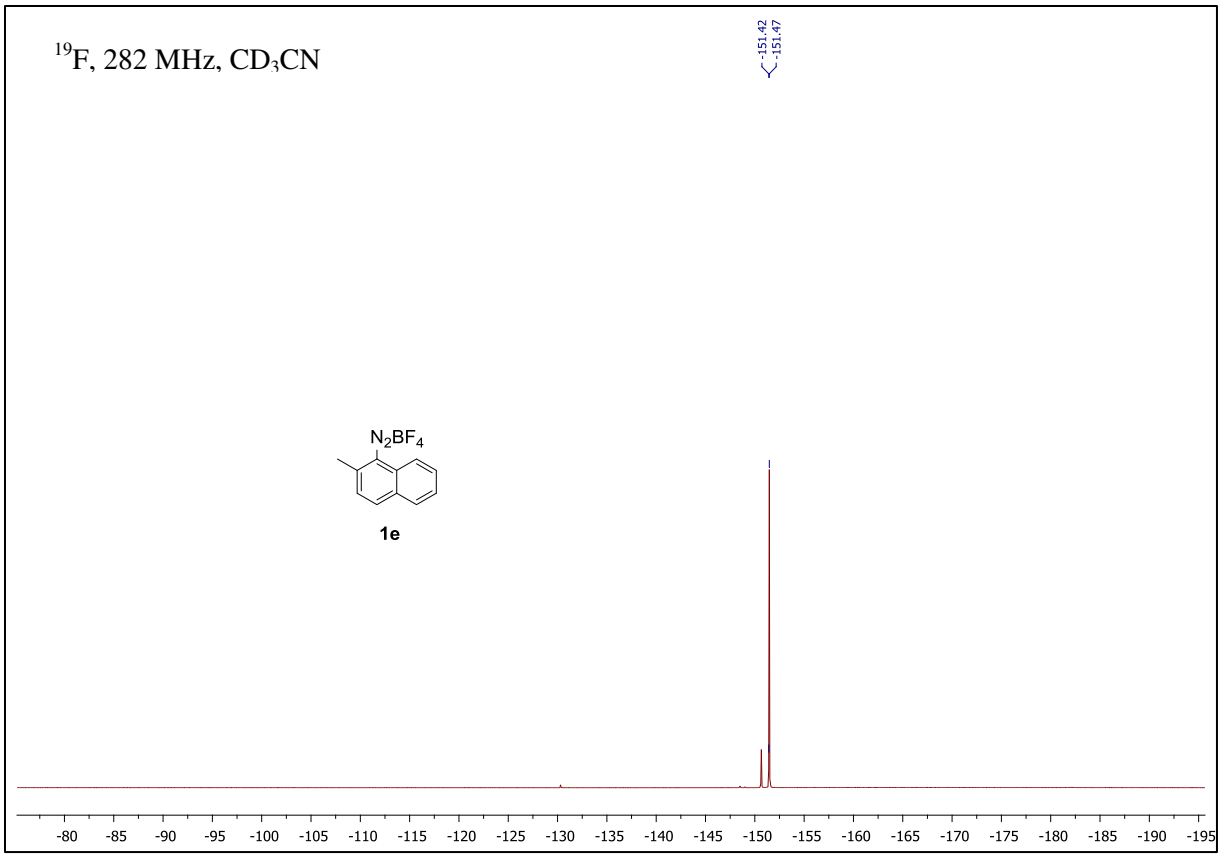
^{19}F, 282 MHz, CD_3CN



2-Methylnaphthalene-1-diazonium tetrafluoroborate 1e

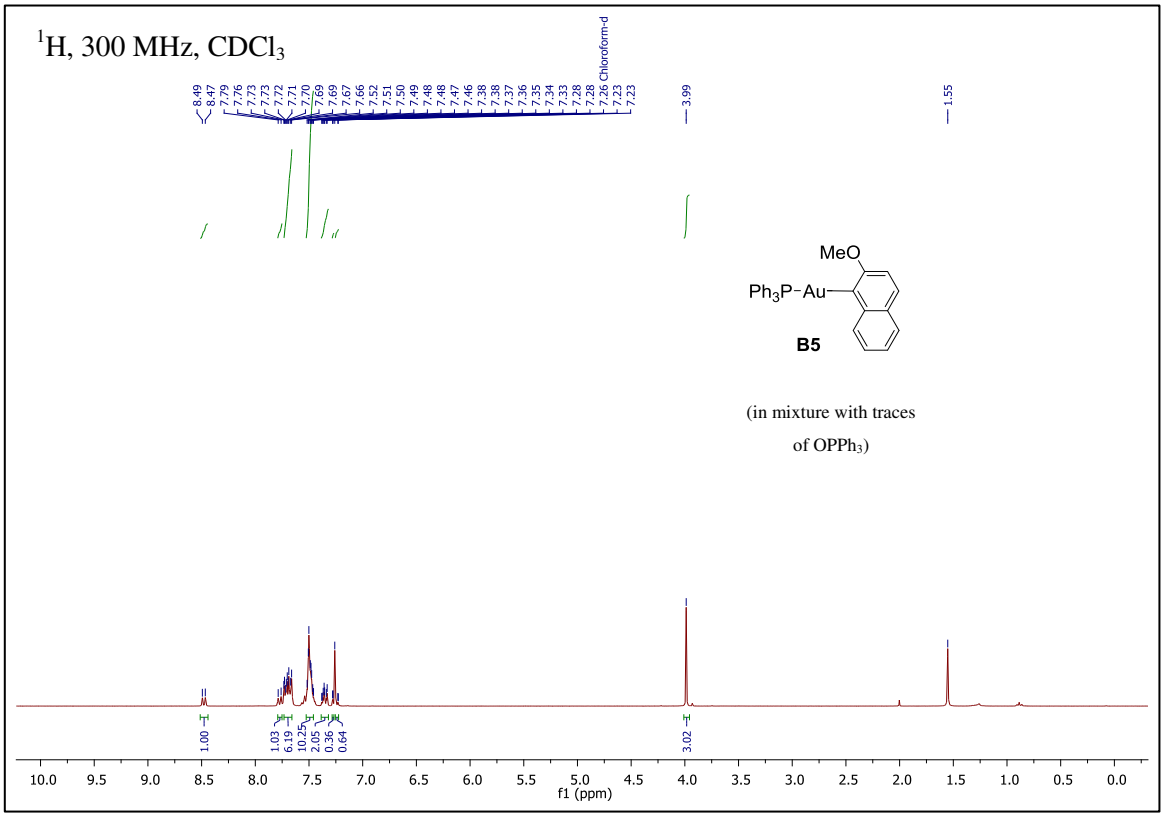


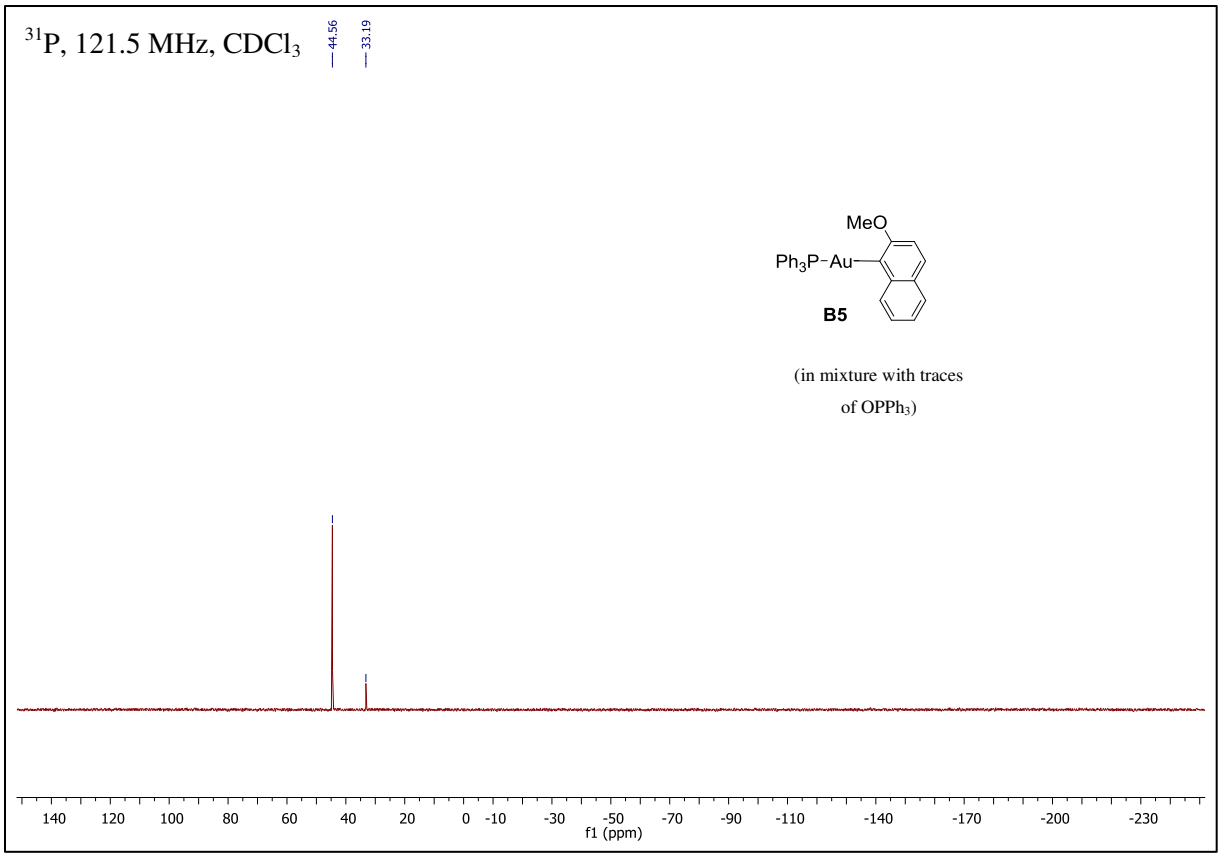




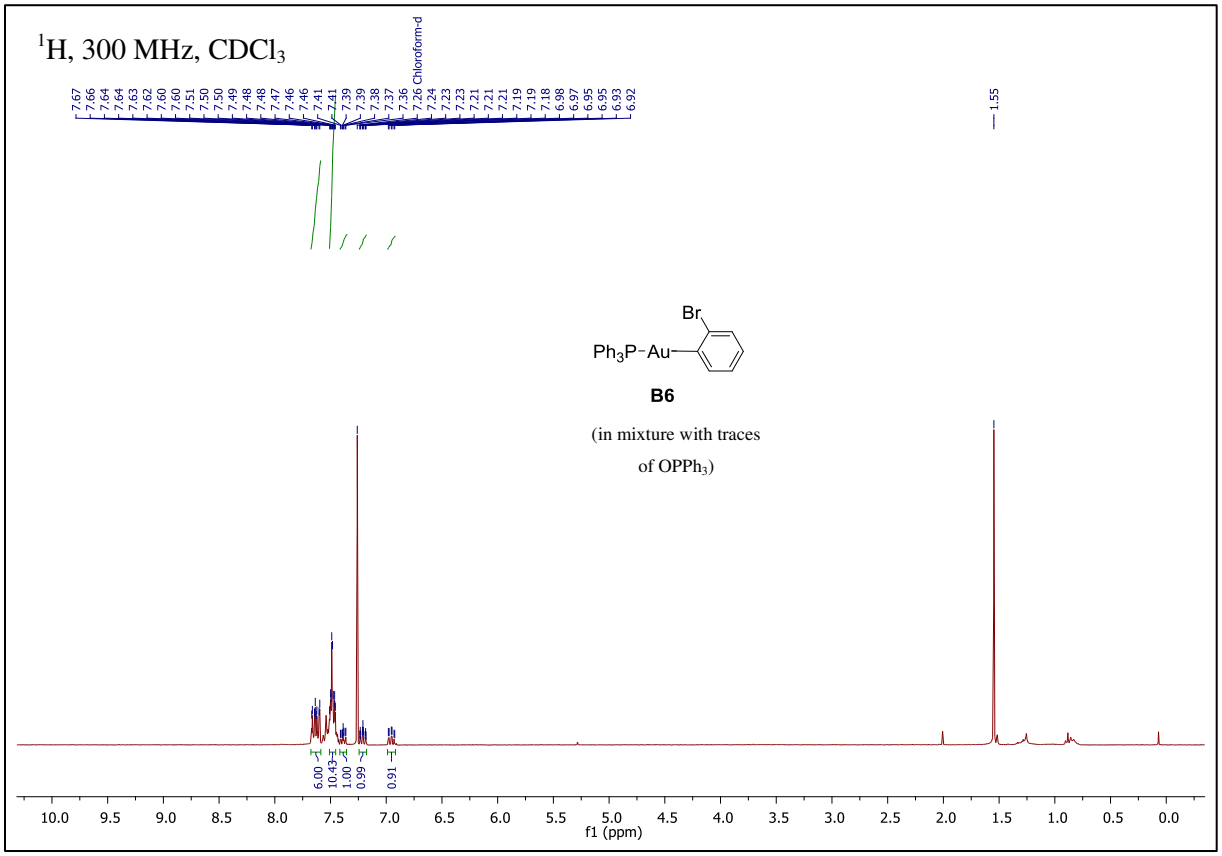
Racemic experiments with Ph_3AuCl

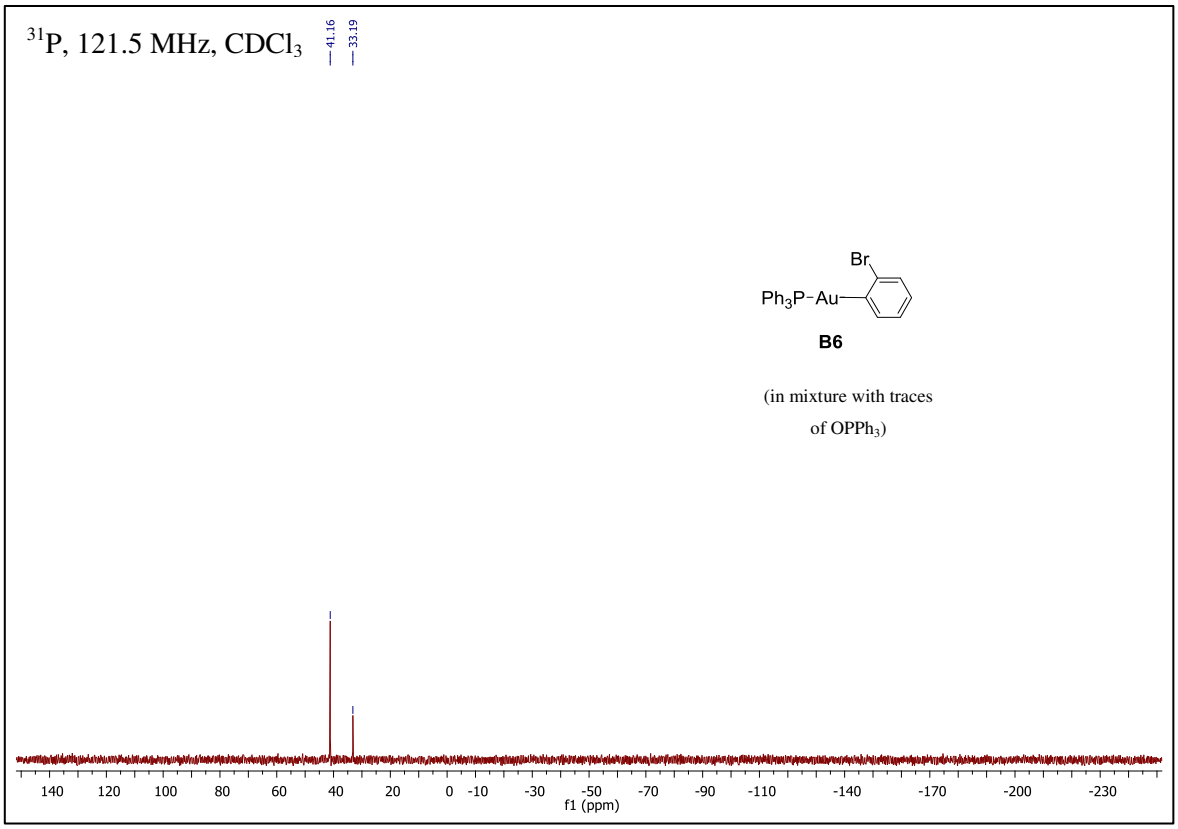
2-Methoxynaphtyl(triphenylphosphine) gold(I) B5





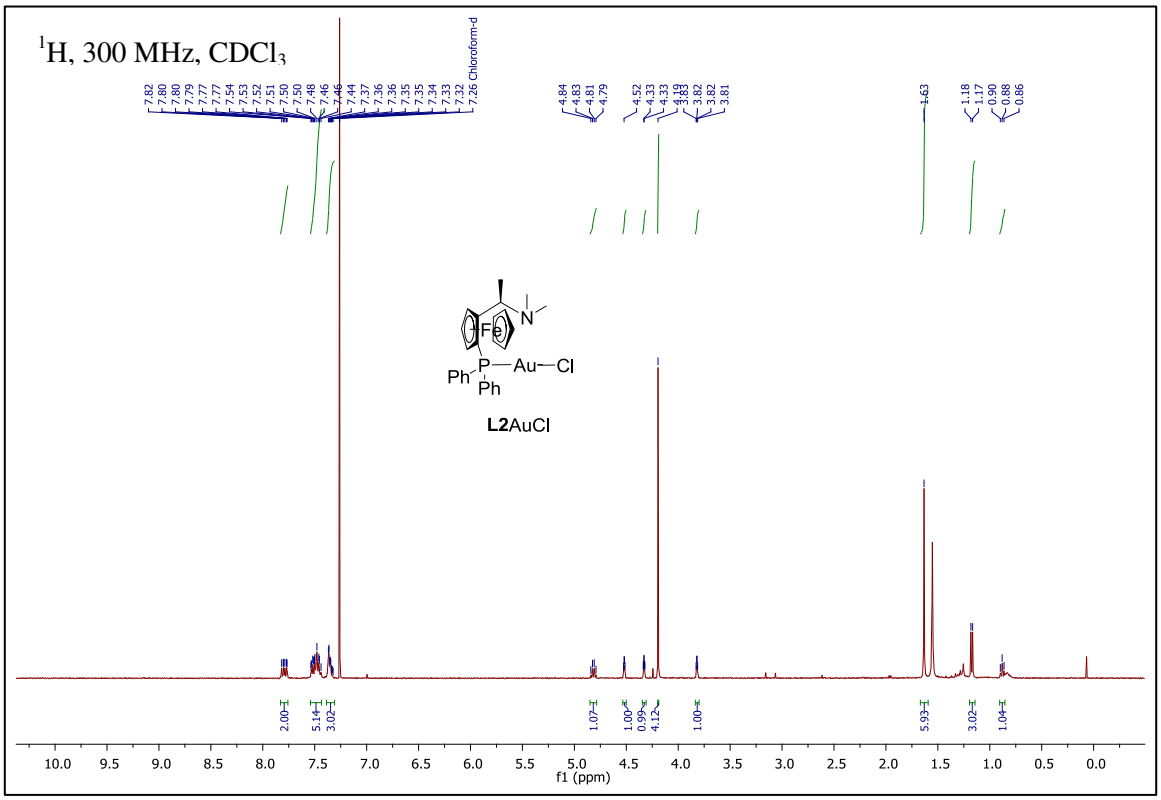
2-Bromophenyl(triphenylphosphine) gold(I) B6



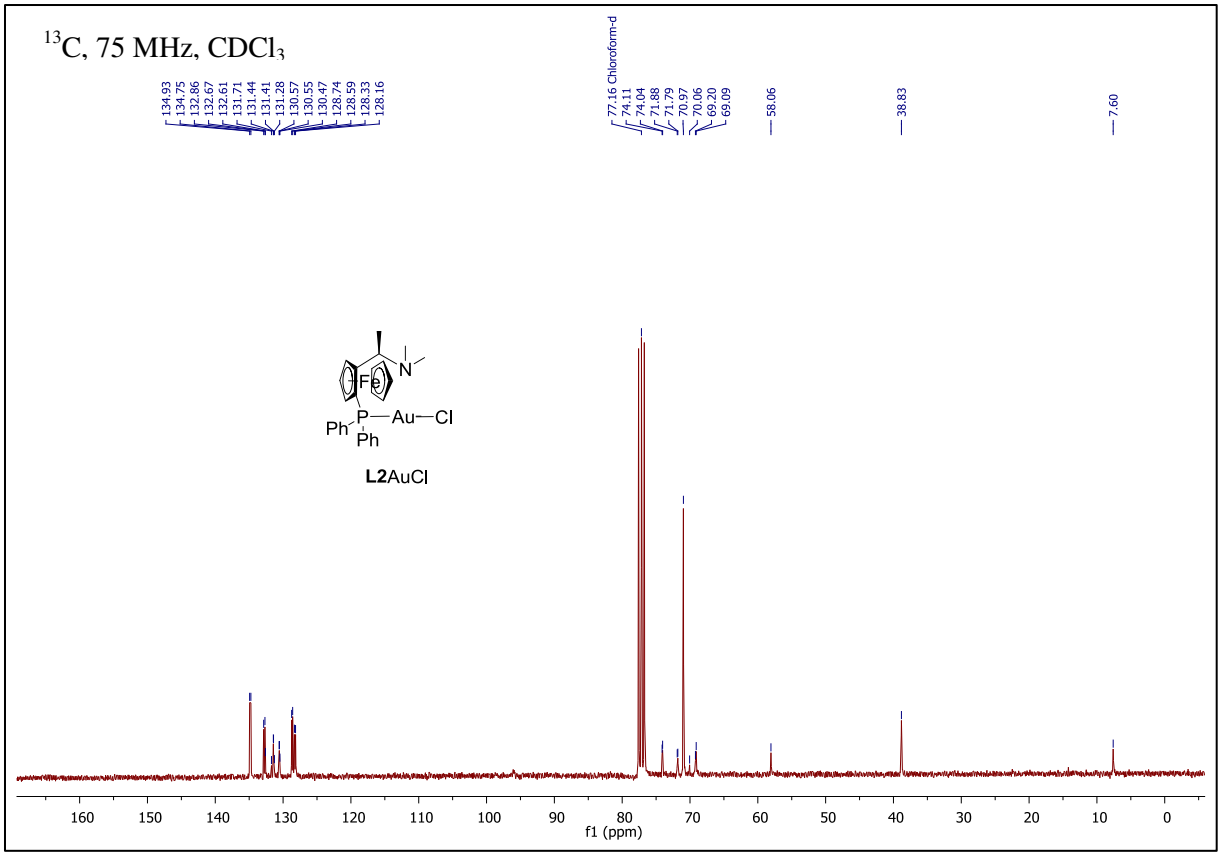


*Experiments with **L2**AuCl*

Chloro[(*R*)-(−)-*N*,*N*-dimethyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine] gold(I) L2AuCl

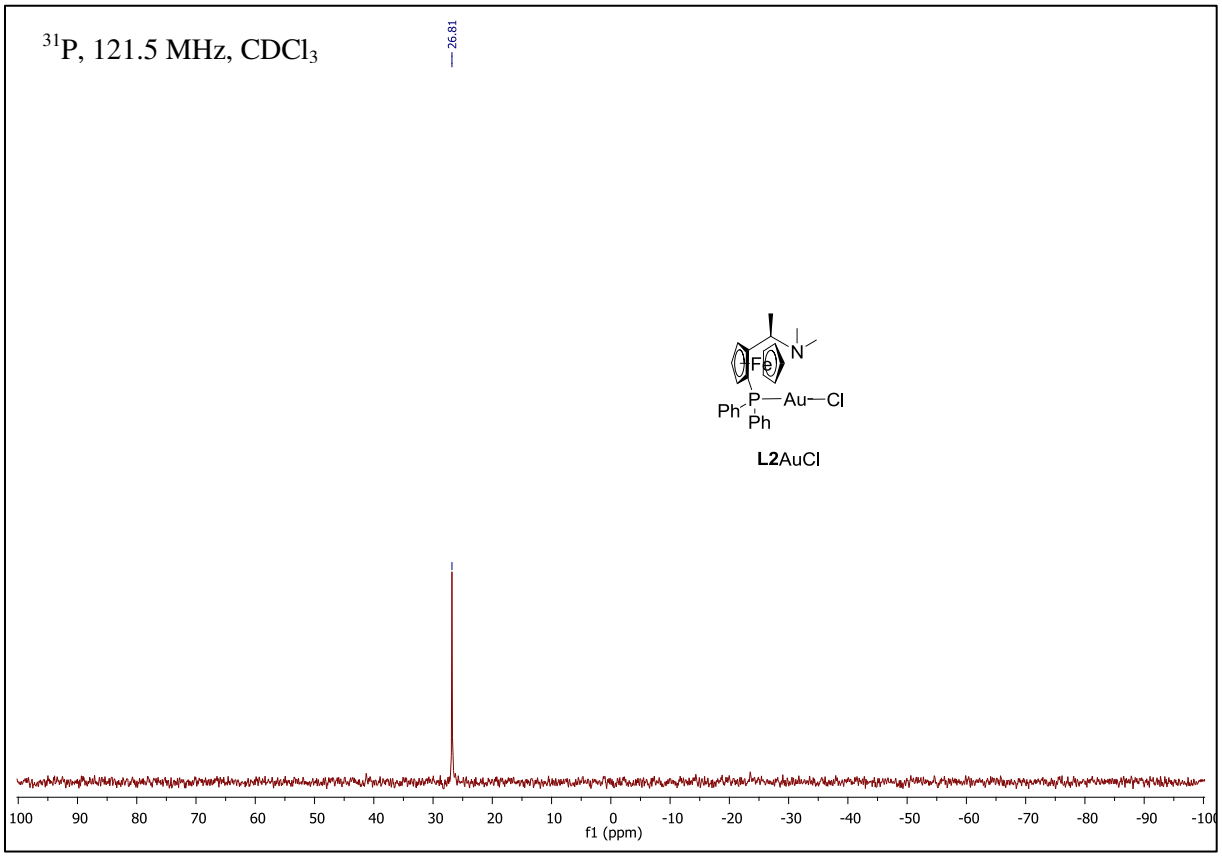


^{13}C, 75 MHz, $CDCl_3$



L2AuCl

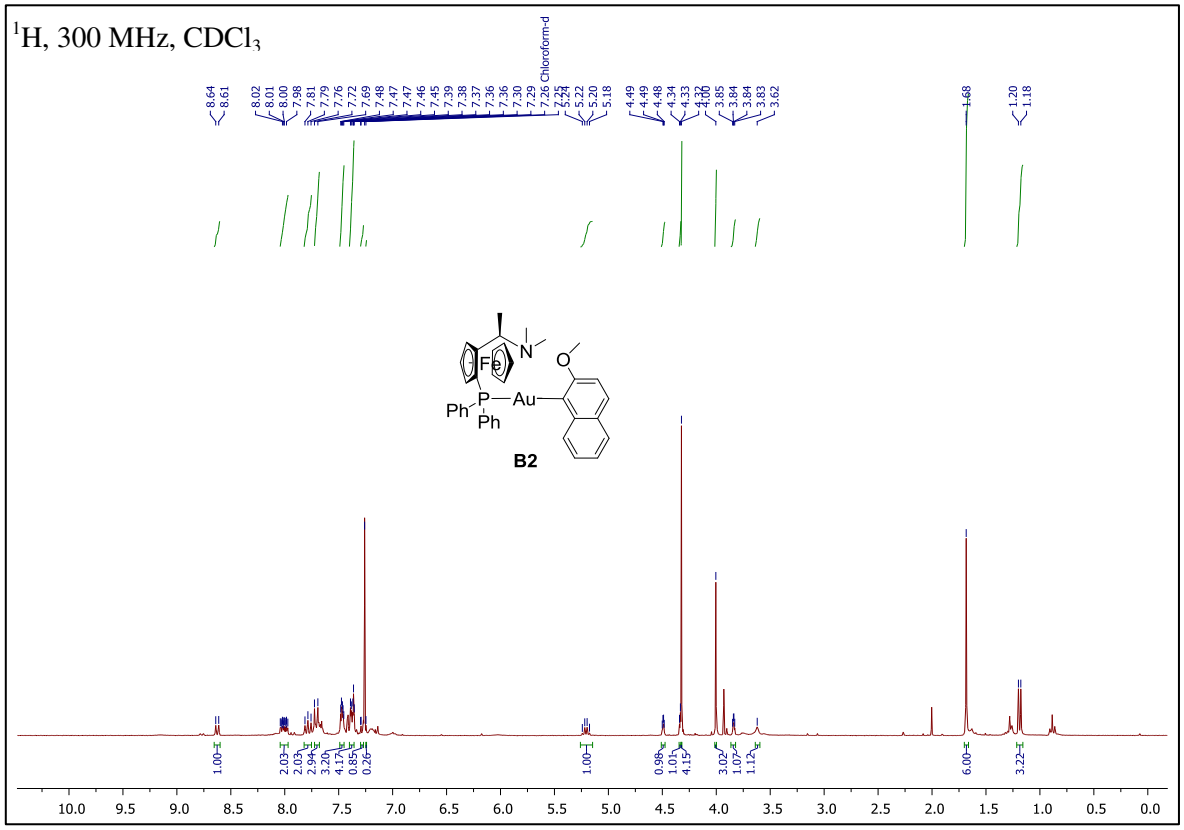
^{31}P, 121.5 MHz, $CDCl_3$



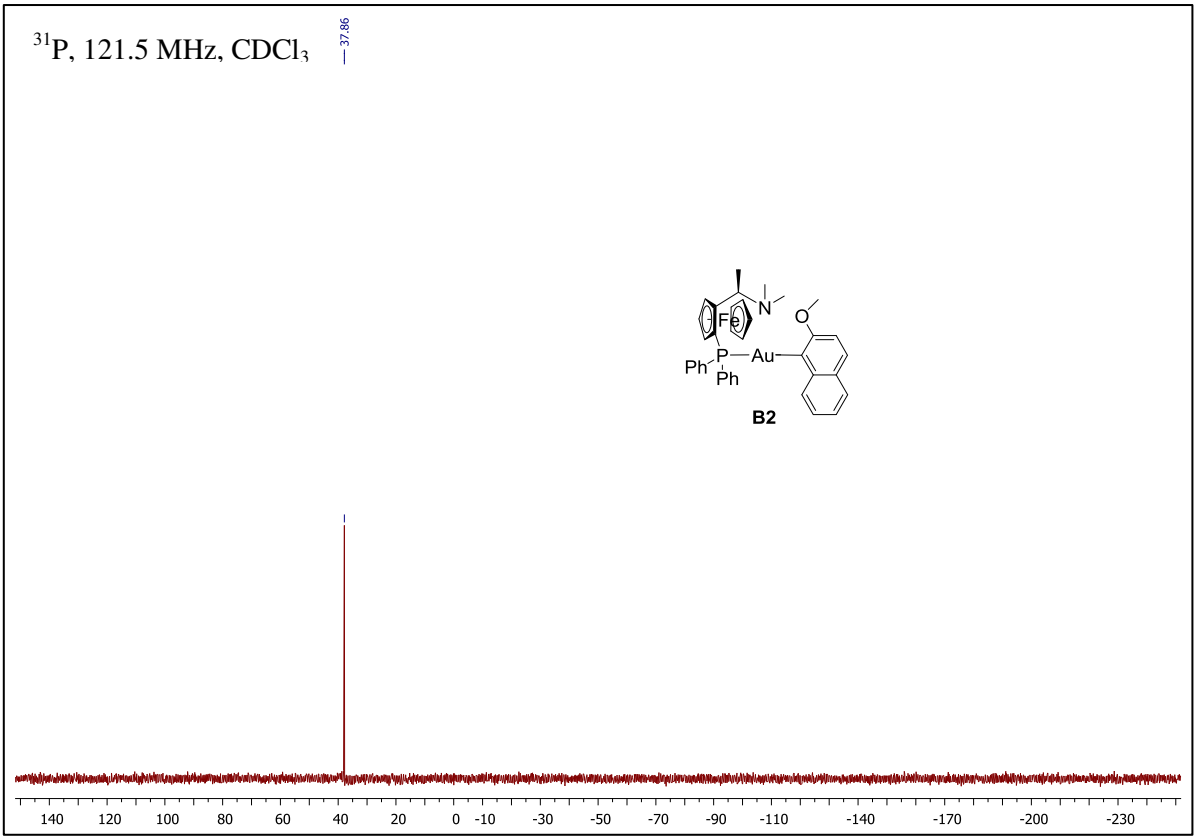
L2AuCl

2-Methoxynaphtyl-[(R)-(−)-N,N-Dimethyl-1-[(S)-2-(diphenylphosphino)ferrocenyl]ethylamine] gold(I) B2

^{1}H, 300 MHz, $CDCl_3$

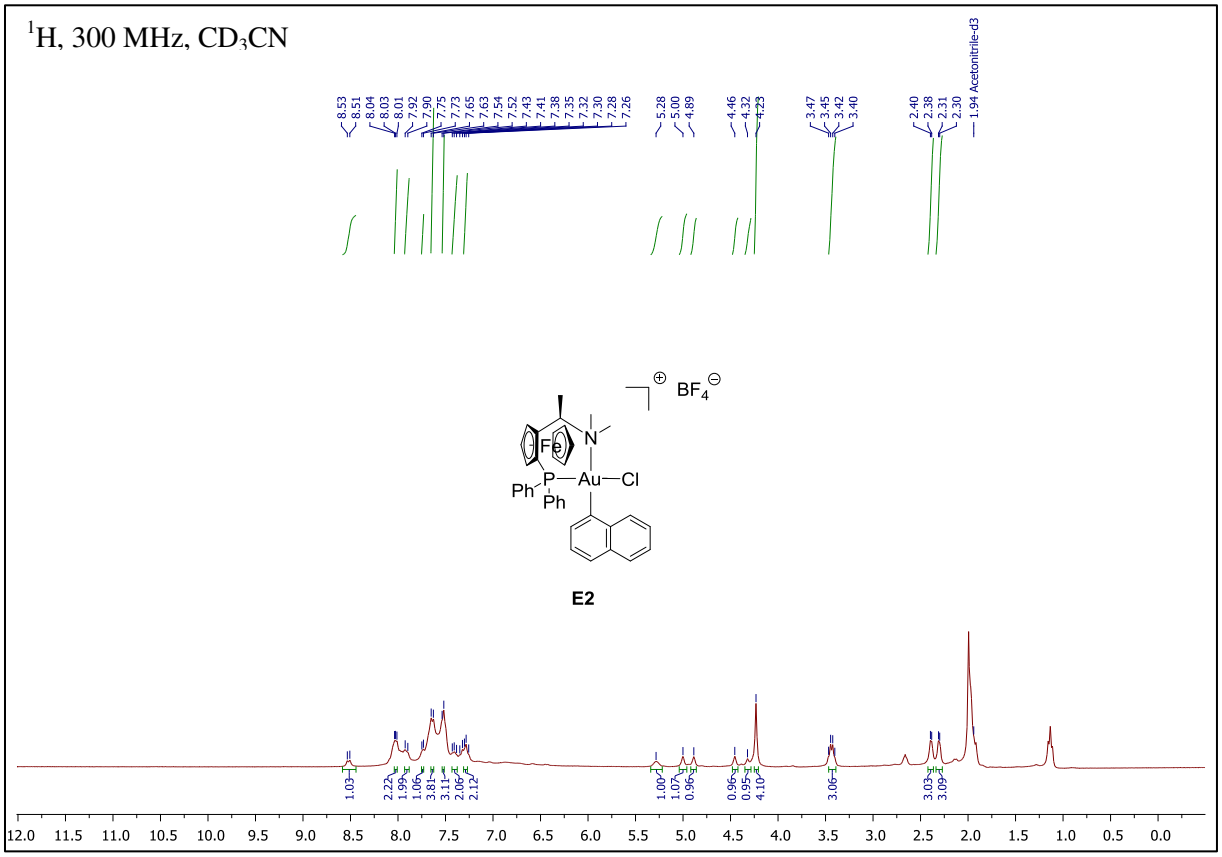


^{31}P, 121.5 MHz, $CDCl_3$

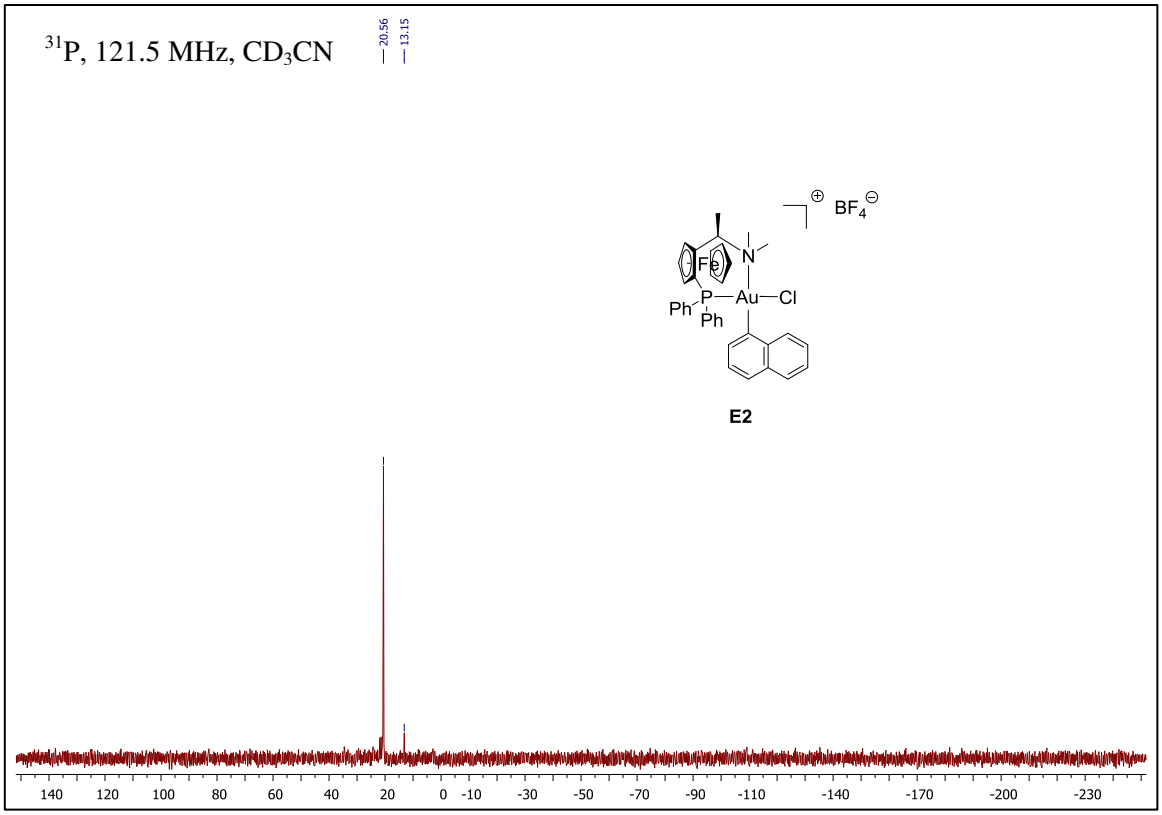


[(Naphthyl)-((*R*)-(−)-*N*,*N*-Dimethyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine)]chloro gold(III) tetrafluoroborate E2

^{1}H, 300 MHz, CD_3CN

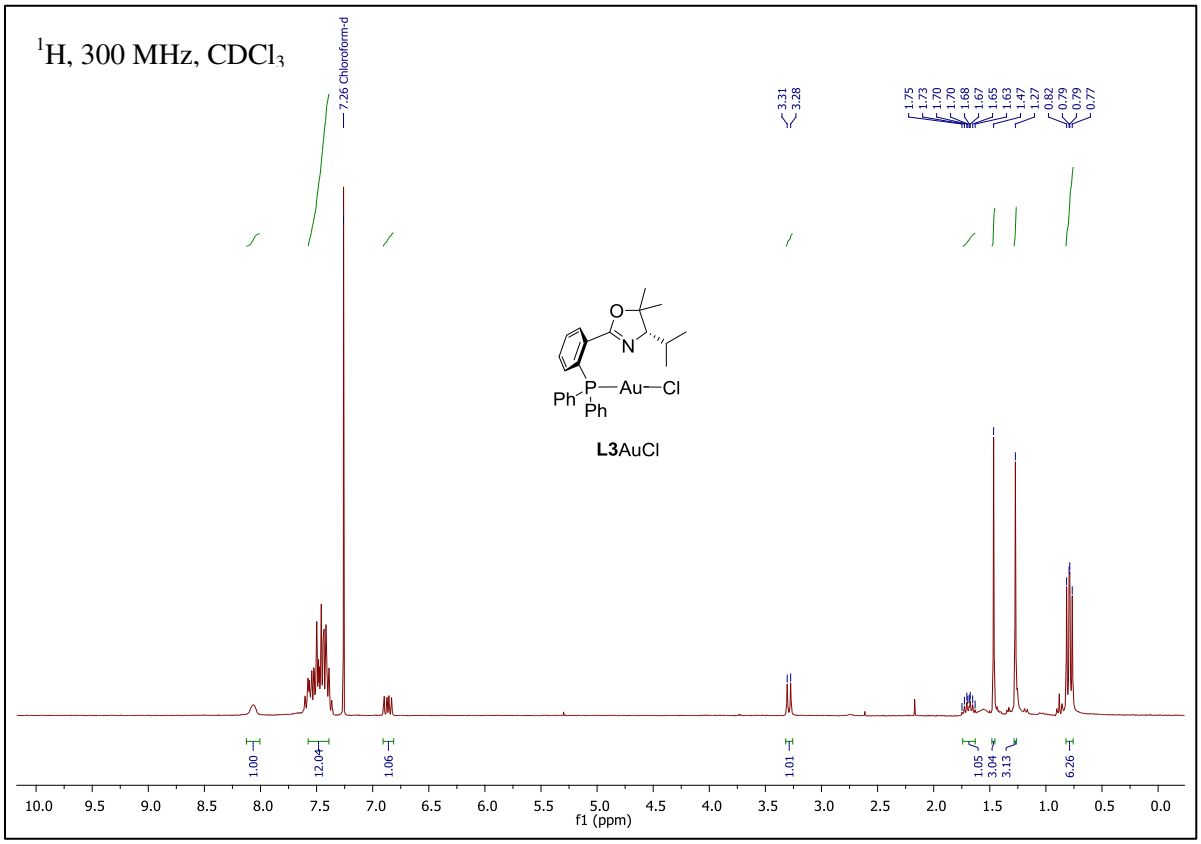


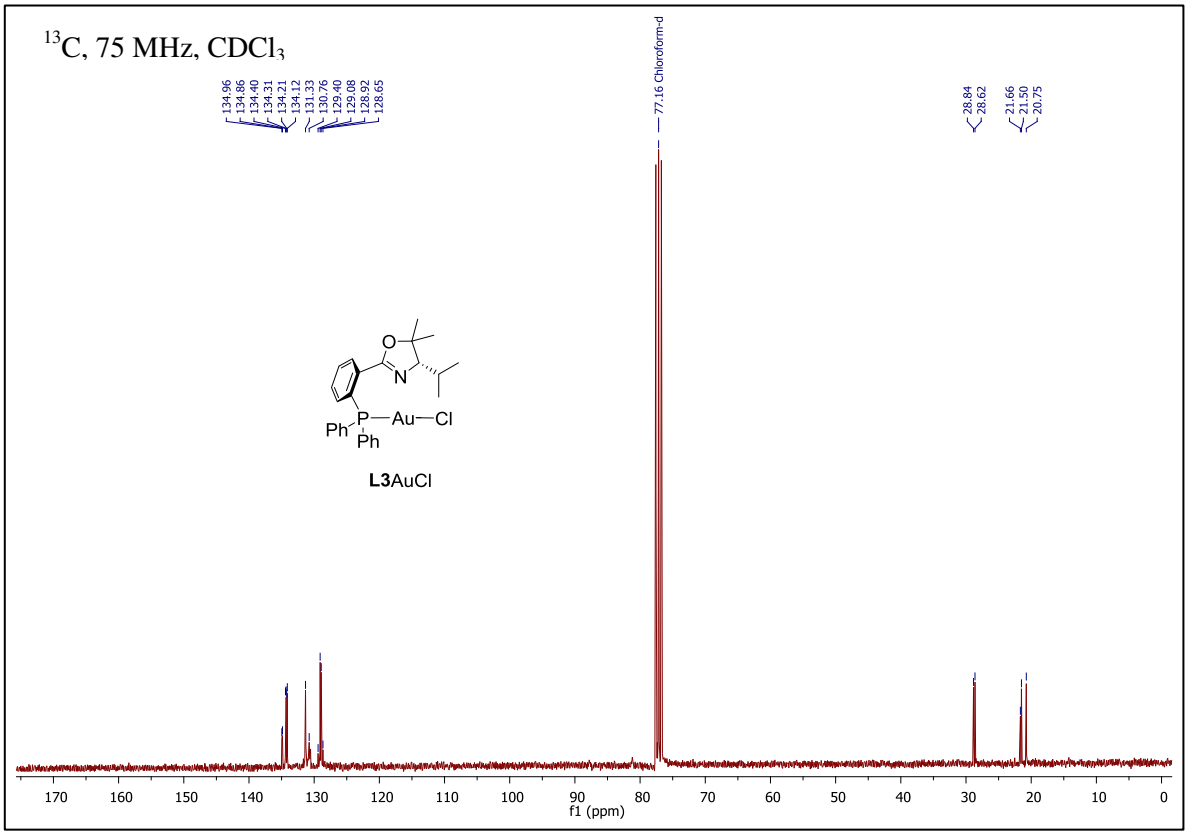
^{31}P, 121.5 MHz, CD_3CN

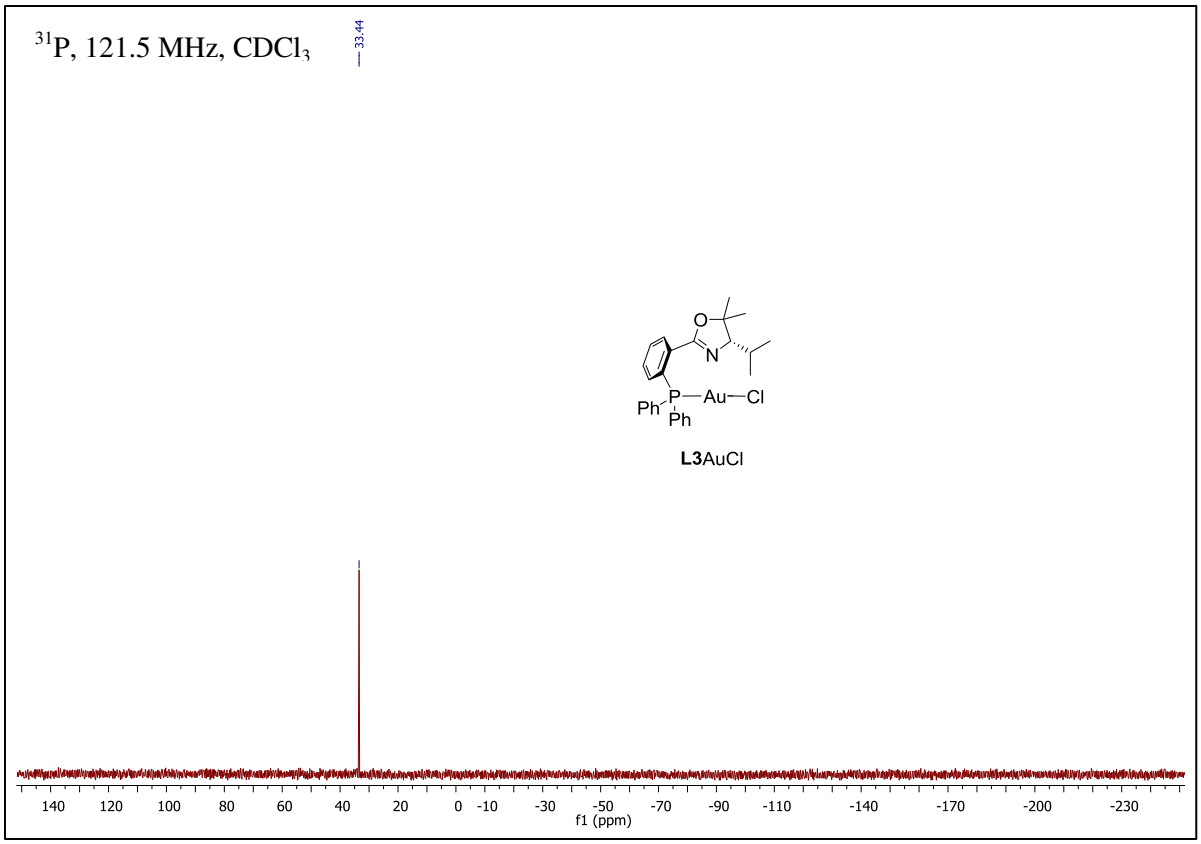


*Experiments with **L3**AuCl*

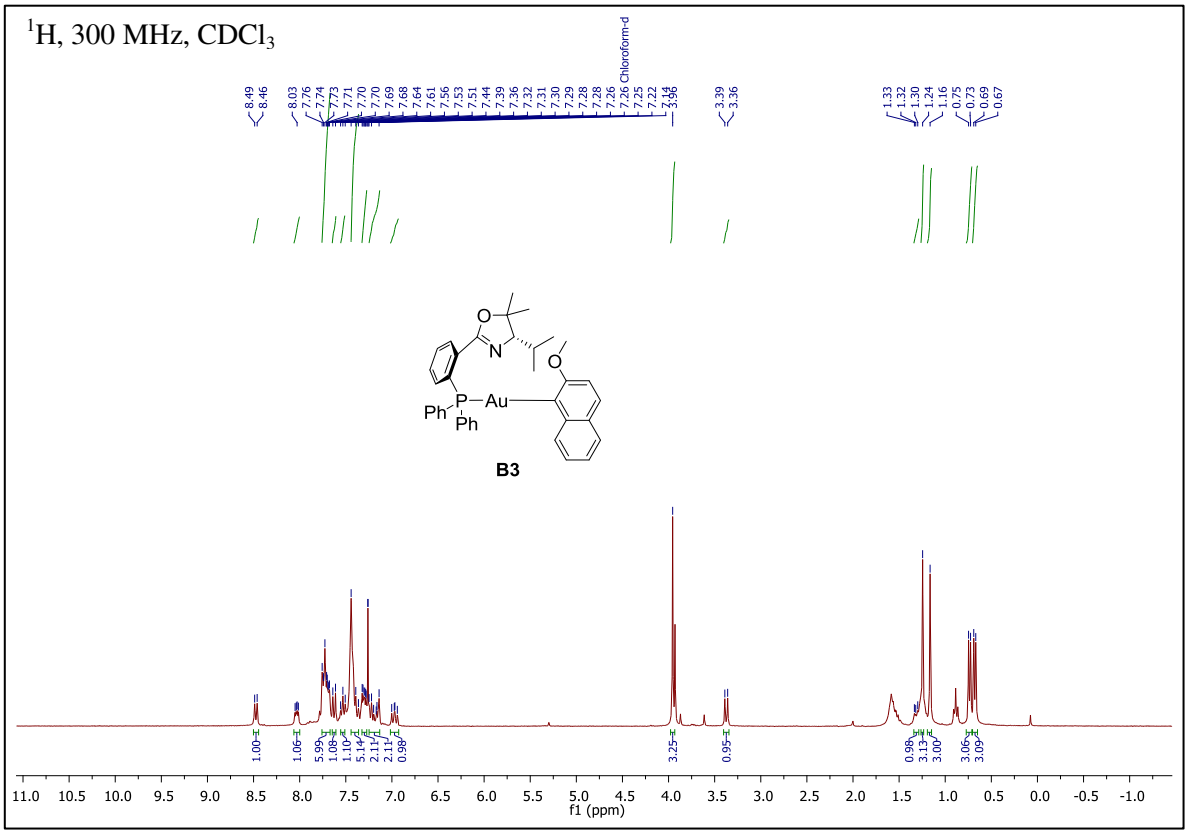
Chloro[(4*S*)-2-[2-(diphenylphosphino)phenyl]-4,5-dihydro-5,5-dimethyl-4-(1-methylethyl)-oxazole]gold(I) L3AuCl

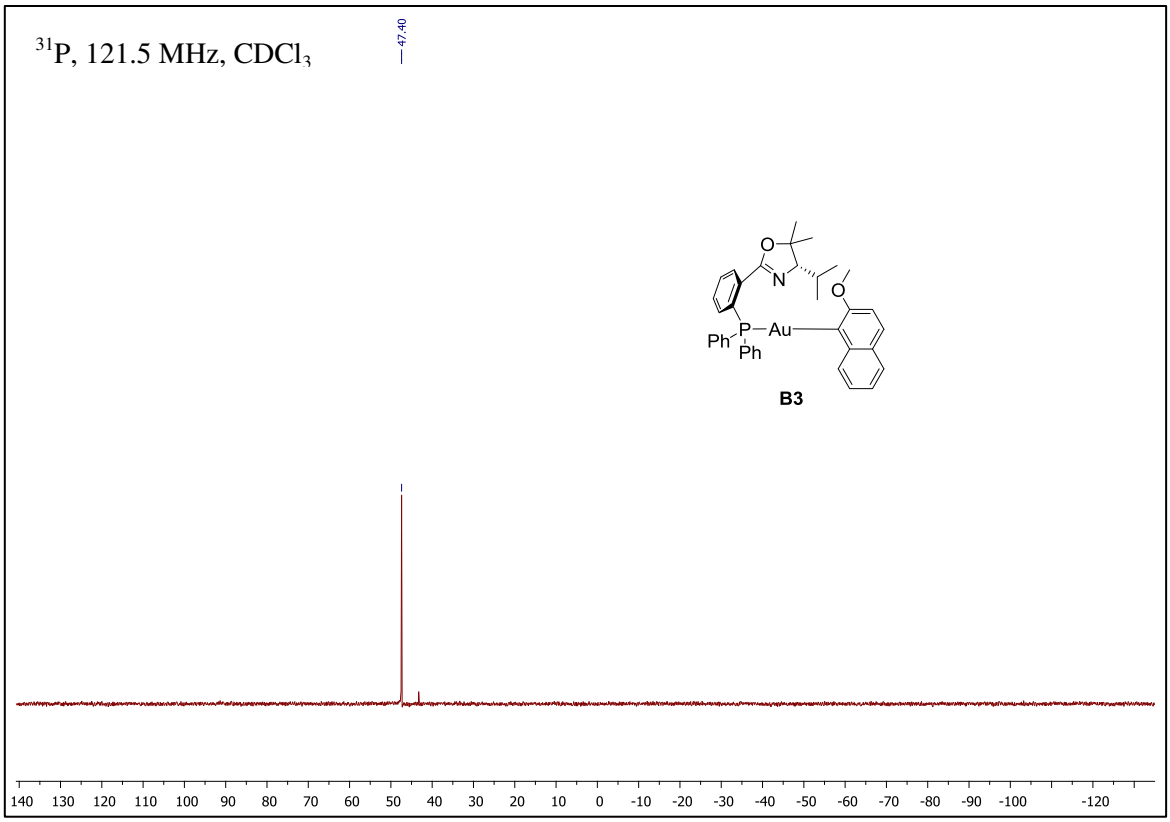




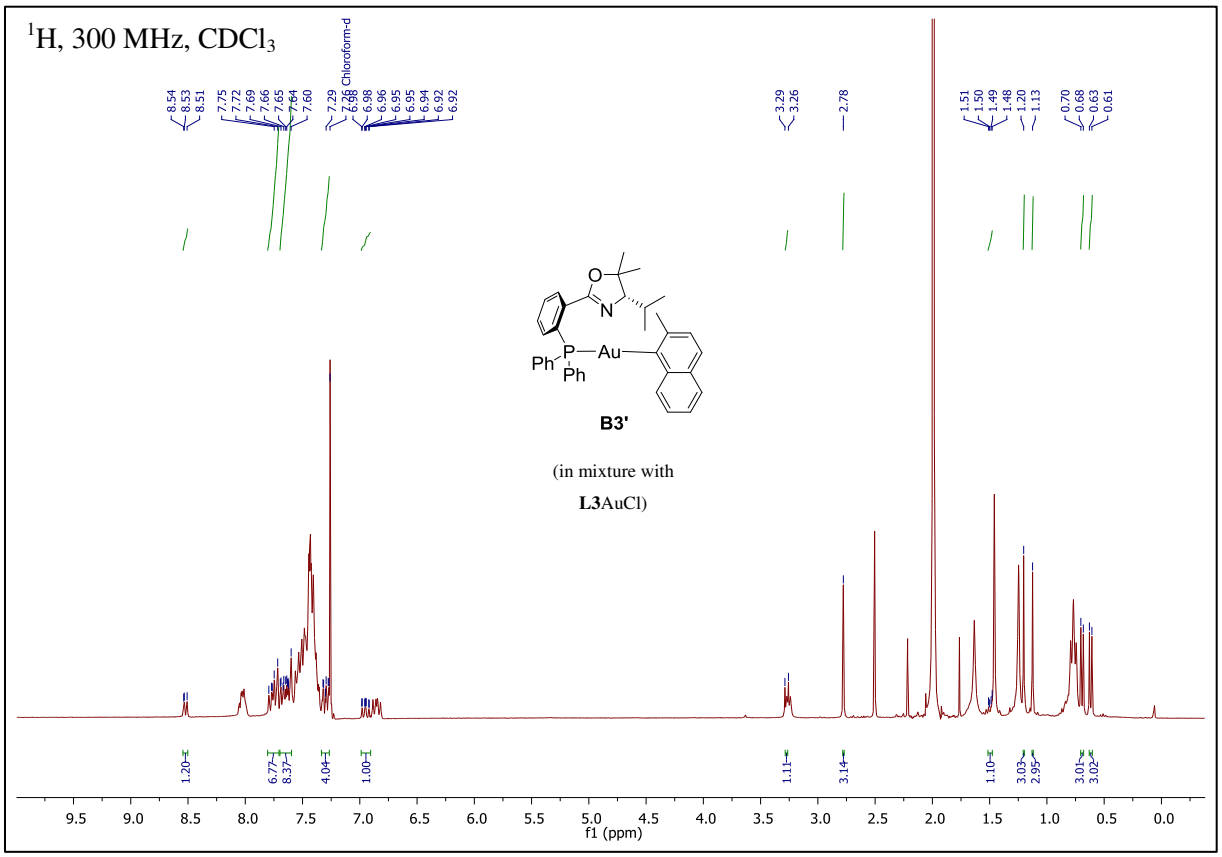


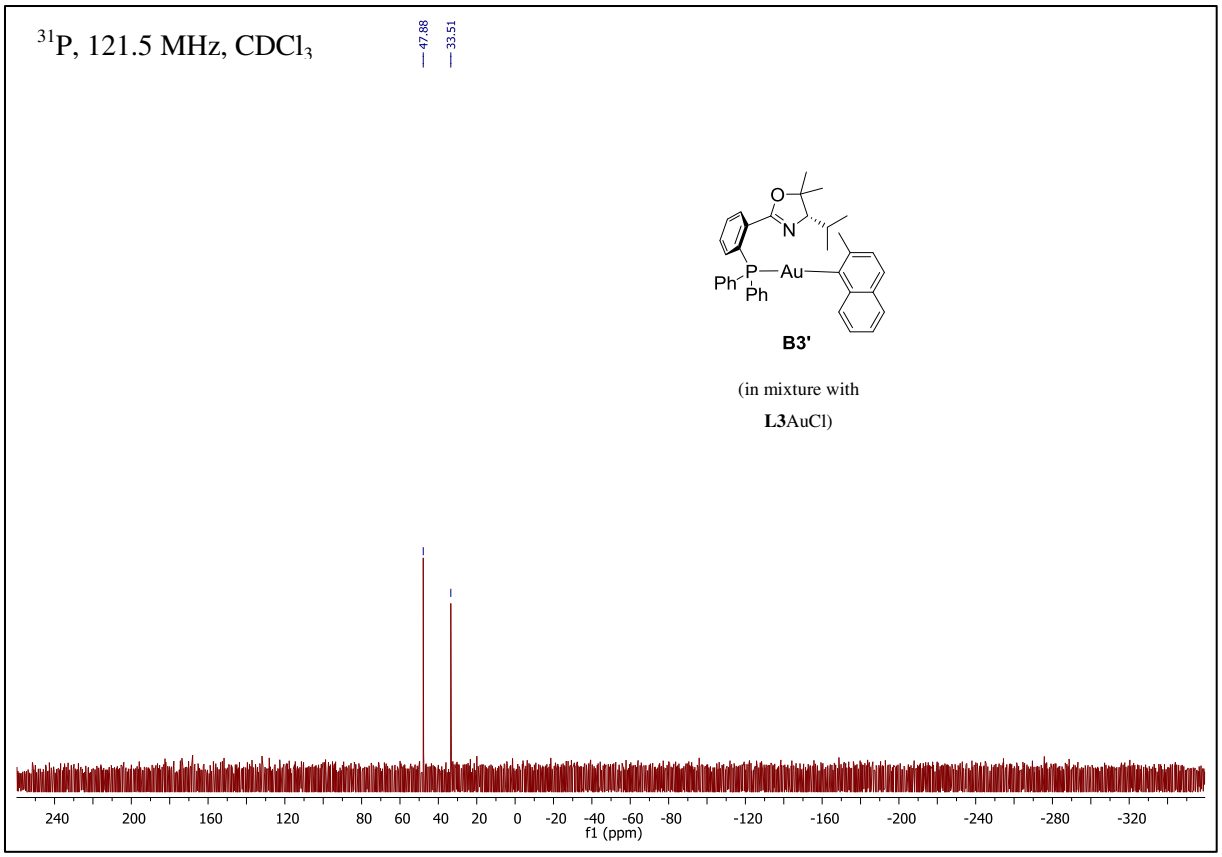
2-Methoxynaphtyl-[(4*S*)-2-[2-(diphenylphosphino)phenyl]-4,5-dihydro-5,5-dimethyl-4-(1-methylethyl)-oxazole]gold(I) B3



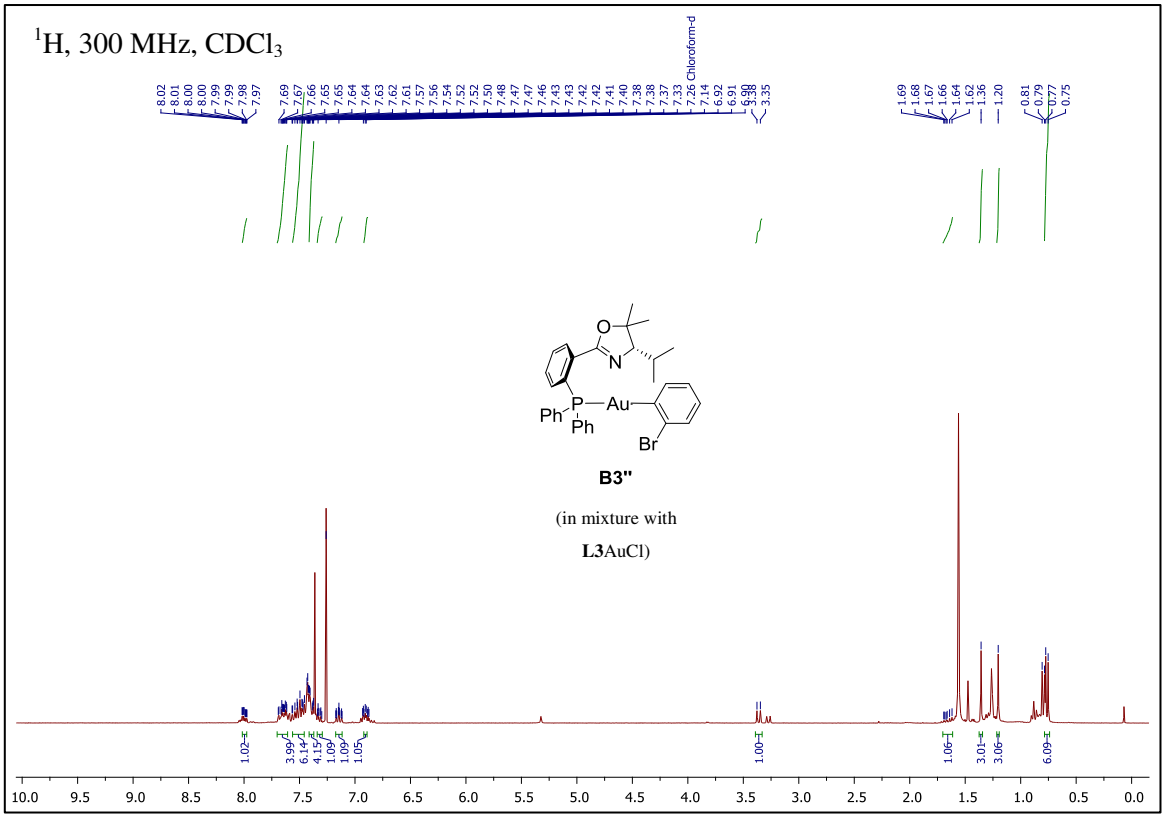


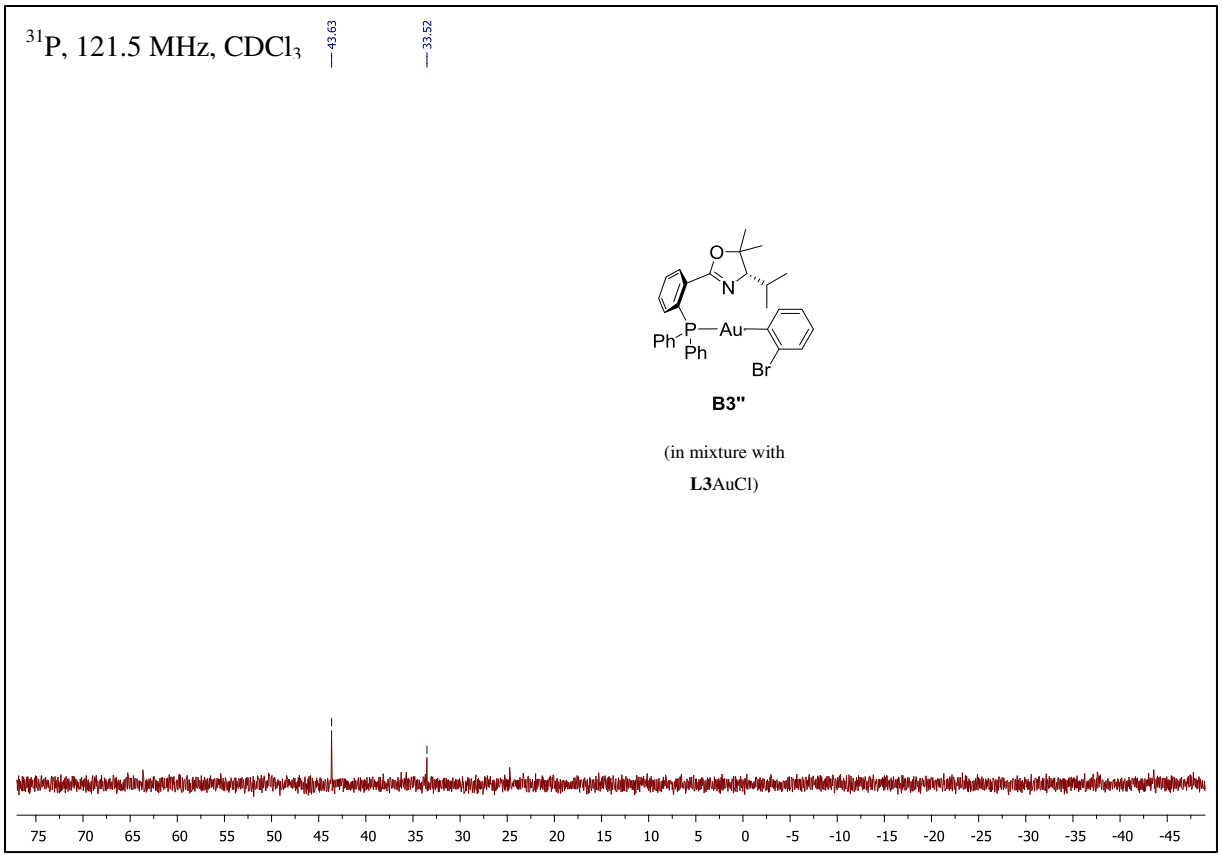
2-Methylnaphthyl-[(4*S*)-2-[2-(diphenylphosphino)phenyl]-4,5-dihydro-5,5-dimethyl-4-(1-methylethyl)-oxazole]gold(I) B3'





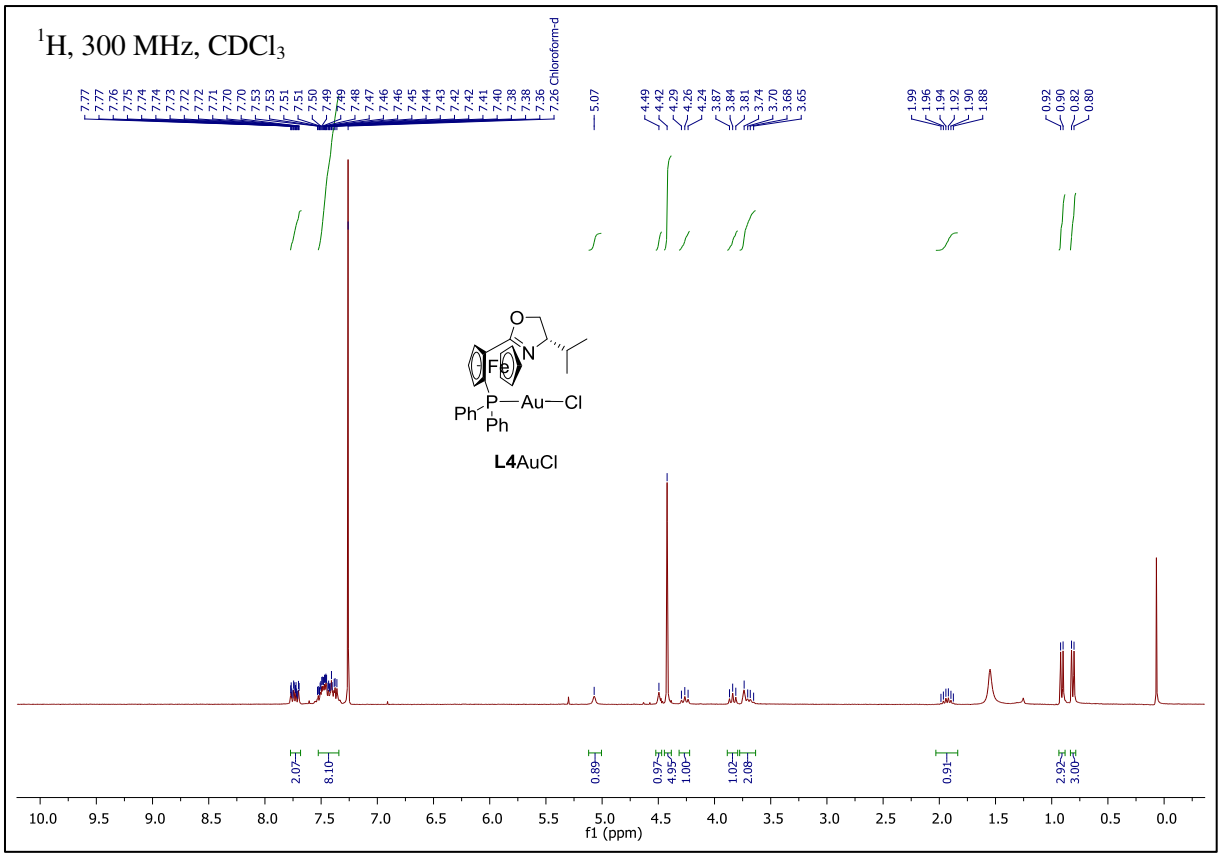
2-Bromophenyl-[(4*S*)-2-[2-(diphenylphosphino)phenyl]-4,5-dihydro-5,5-dimethyl-4-(1-methylethyl)-oxazole]gold(I) B3''



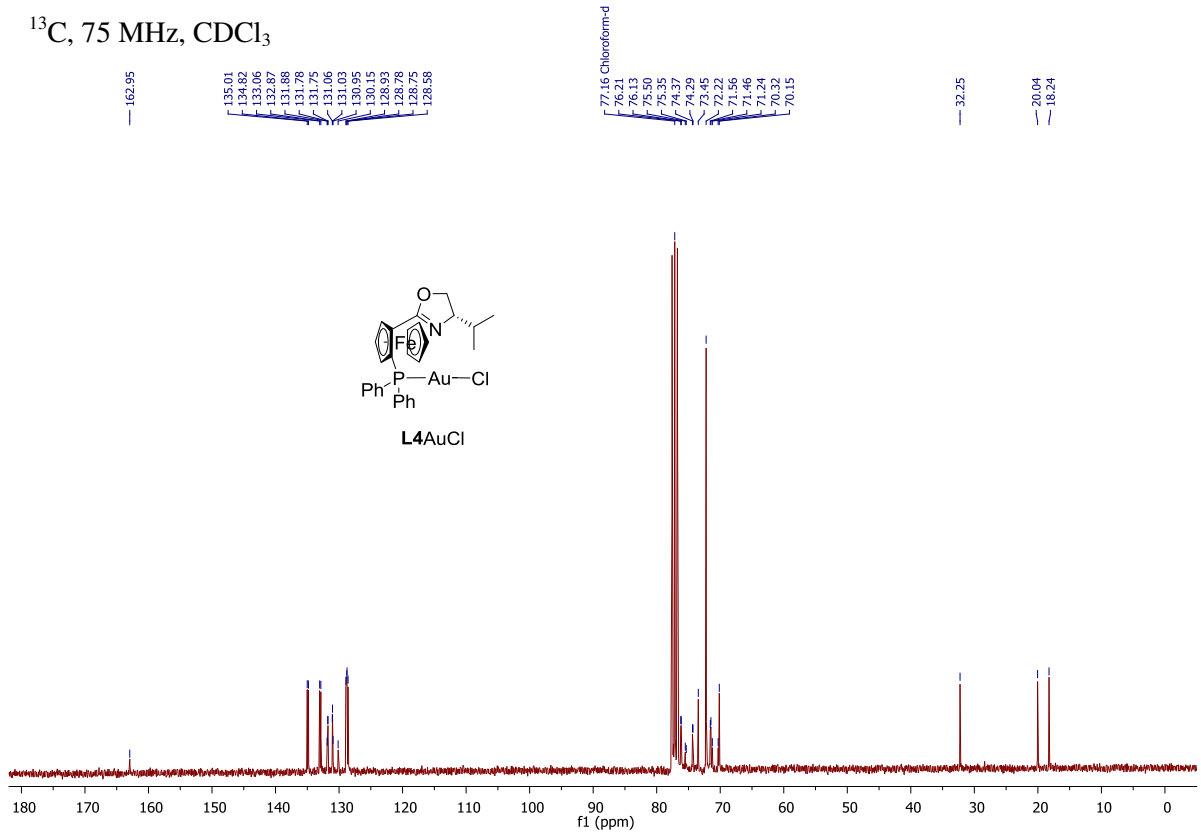


*Experiments with **L4**AuCl*

Chloro[(*S*)[(*Sp*)-2-(diphenylphosphino)ferrocenyl]-4-isopropyloxazoline] gold(I) L4AuCl

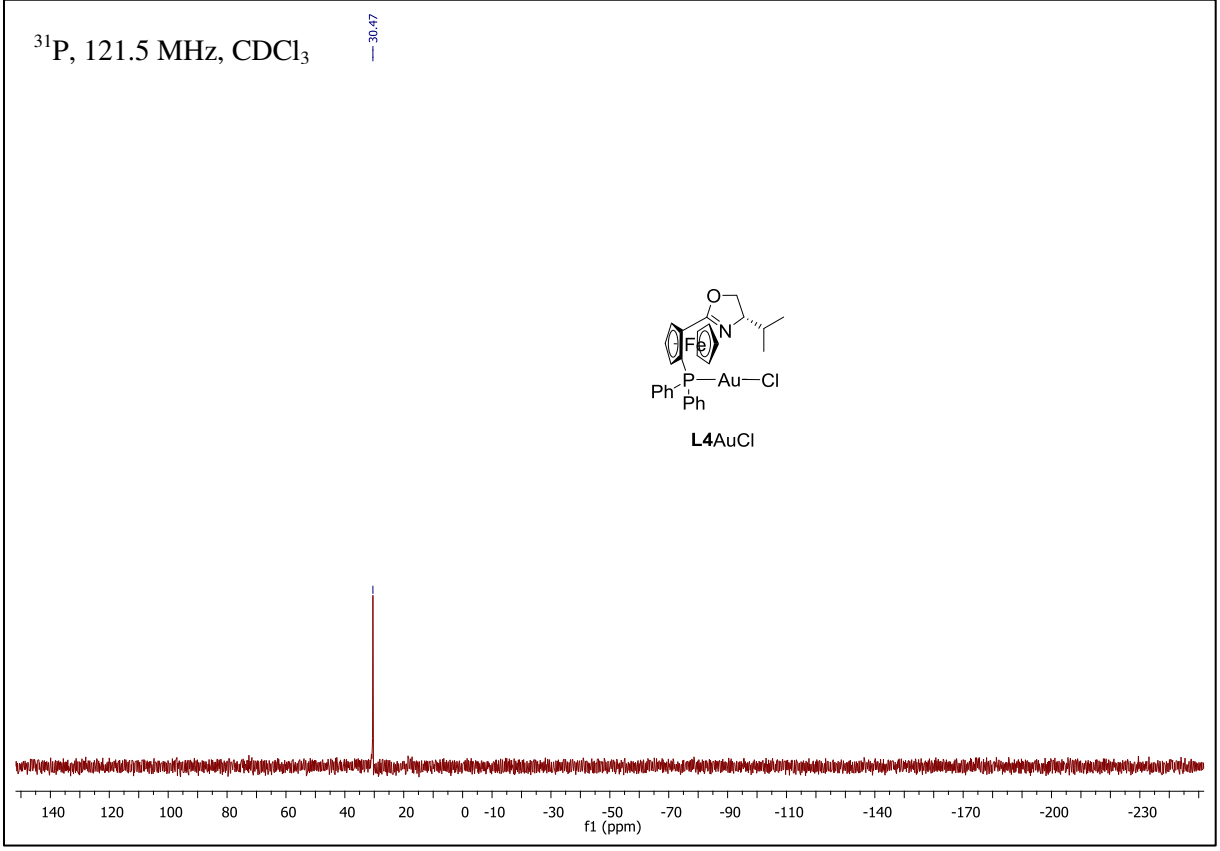


^{13}C, 75 MHz, $CDCl_3$



L4AuCl

^{31}P, 121.5 MHz, $CDCl_3$



L4AuCl

2-Methoxynaphtyl-[(*S*)[(*Sp*)-2-(diphenylphosphino)ferrocenyl]-4-isopropyloxazoline]gold(I) B4