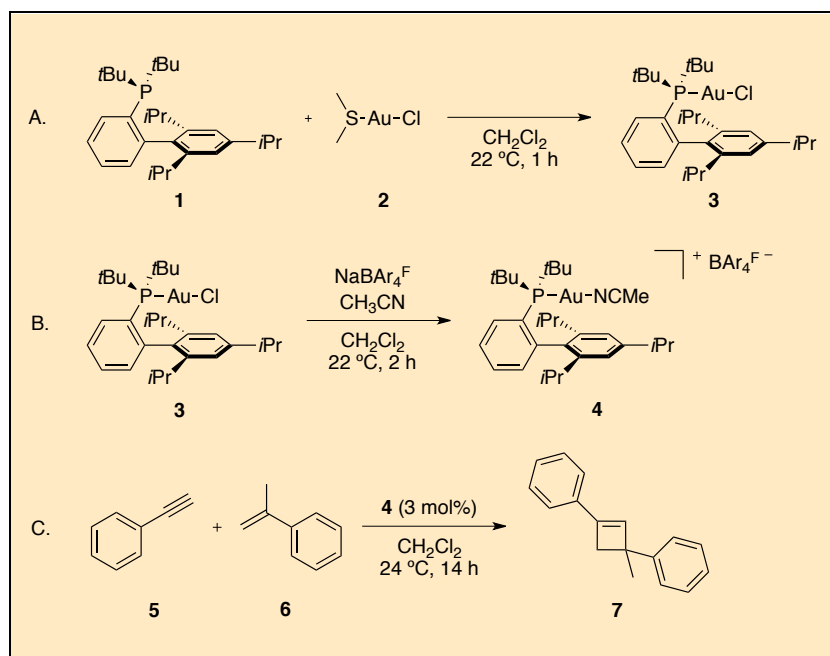# Intermolecular [2+2] Cycloaddition of Alkynes with Alkenes Catalyzed by Gold(I)

M. Elena de Orbe, and Antonio M. Echavarren*[1]

Institute of Chemical Research of Catalonia (ICIQ),
Av. Països Catalans 16, 43007 Tarragona, Spain.

Checked by Giulia Rusconi, Estíbaliz Merino and Cristina Nevado

Procedure

A. *Chloro[(2′,4′,6′-triisopropyl-1,1′-biphenyl-2-yl)di-tert-butylphosphine]-gold(I) (3)*. A one-necked (B14, diameter: 2.0 cm) 10-mL round-bottomed

flask open to air, equipped with a 1-cm Teflon-coated cylindrical magnetic stirring bar is charged with di-*tert*-butyl(2',4',6'-triisopropyl-[1,1'-biphenyl]-2-yl)phosphine (**1**) (0.500 g, 1.14 mmol, 1.00 equiv) and chloro(dimethylsulfide)gold(I) (**2**) (0.345 g, 1.14 mmol, 1.00 equiv) (Note 1). Dichloromethane (6 mL) is added via syringe (Note 2) and the flask is fitted with a glass stopper. The resulting colorless solution is stirred (600 rpm) at 22 °C for 1 h. The volatiles are removed by rotatory evaporation (300 mmHg, 40 °C bath temperature) and then, under vacuum for 19 h (0.2 mmHg) to afford gold(I) chloride complex **3** (735 mg, 98% yield) as a white solid (Note 3) (Figure 1).

Figure 1. White solid produced in Step A

B.   *(Acetonitrile)[(2 ′,4 ′,6 ′-triisopropyl-1,1 ′-biphenyl-2-yl)di-tert-butylphos-phine]gold(I) tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (**4**)*. A one-necked (B29, diameter: 3.5 cm) 100-mL round-bottomed flask open to air, equipped with a Teflon-coated egg-shaped magnetic stirring bar (19 × 10 mm) is charged with gold(I) chloride complex **3** (0.600 g, 0.913 mmol, 1.0 equiv) and dichloromethane (45 mL) (Note 2). Acetonitrile (119 µL, 2.28 mmol, 2.5 equiv) is added via Hamilton syringe (Note 4), the flask is fitted with a septum and the resulting colorless solution (Figure 2A) is stirred (600 rpm) at 22 °C for 5 min. Then, sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (876 mg, 0.959 mmol, 1.05 equiv) is added in one portion (Note 5) and the flask is again fitted with the septum. The resulting white suspension is stirred (600 rpm) at 22 °C for 2 h (in this time, the solution becomes purple) (Figure 2B) (Note 6).   The reaction mixture is
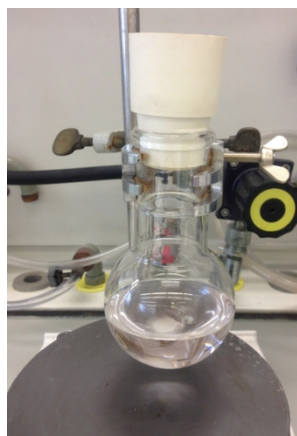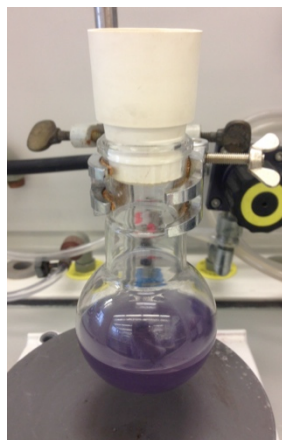
Figure 2A. Colorless Solution   **Figure 2B. Purple Solution in Step B**

filtered under vacuum through a plug of Celite (20 mm diameter × 20 mm height) (Figure 3A) (Note 7), which is washed with dichloromethane (1 x 25 mL) (Note 2). The filtrate is concentrated by rotatory evaporation (300 mmHg, 40 °C bath temperature) to a volume of approximately 2 mL and filtered through two 0.2 μm Teflon filters (13 mm diameter), which are washed with dichloromethane (1 x 4 mL) (Note 2). The solvent of the filtrate is removed by rotatory evaporation (300 mmHg, 40 °C bath temperature), and then the residue is dried under vacuum (0.3 mmHg) for 19 h to afford cationic gold(I) complex **4** (1.37 g, >99% yield) as a white solid (Figure 3B) (Note 8).

C. *1,3-Diphenyl-3-methylcyclobut-1-ene (7)*. A one-necked (B29, diameter: 3.5 cm) 100-mL round-bottomed flask open to air, equipped with a Teflon-coated egg-shaped magnetic stirring bar (19 × 10 mm) is charged with dichloromethane (50 mL) (Note 2). α-Methylstyrene (**6**) (7.00 mL, 6.39 g, 53.5 mmol, 2.00 equiv) and ethynylbenzene (**5**) (3.00 mL, 2.79 g, 26.8 mmol, 1.00 equiv) are successively added via syringe (Note 9) while stirring (800 rpm) at 24 °C. Afterwards, cationic gold(I) complex **4** (1.225 g, 0.803 mmol, 0.03 equiv) is added in one portion, the flask is fitted with a septum and the solution is stirred (800 rpm) at 24 °C for 14 h (Note 10). During the course of the reaction, the solution turns progressively from

Figure 3A. Filtration of Step B

Figure 3B. White product of Step B

colorless to yellow and finally to orange (Figure 4). Triethylamine (1.6 mL) is added via syringe (Note 11) to quench the reaction while stirring. At this point, the solution becomes yellow. Volatiles are removed using a rotary evaporator under reduced pressure (375 mmHg and then 20 mmHg, 40 °C bath temperature). The resulting residue is dissolved in dichloromethane (20 mL) and poured into a 250-mL round-bottomed flask containing florisil (22 g) (Note 12). After removing the solvent by rotatory evaporation (375 mbar and then 20 mbar, 40 °C bath temperature), the crude material adsorbed on florisil is charged on a 390 g silica gel column (7 cm diameter × 25 cm height) (Note 13), packed with cyclohexane (600 mL) and eluted with cyclohexane (about 6 L) under compressed air (1.5 atm) (Note 14 and 15). Fractions 26-40 containing pure product are concentrated by rotary evaporation (110 mmHg and then 20 mmHg, 40 °C bath temperature) and the resultant residue is dried under vacuum (0.2 mmHg) for 20 h to afford cyclobutene **7** (5.8 g, 98% yield) as a dense yellow oil (Note 16).
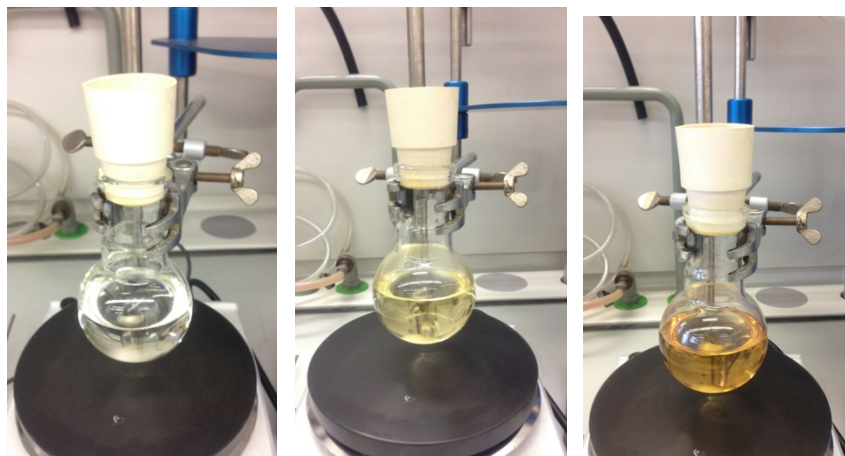
Figure 4. Progression of color from colorless to yellow to orange in Step C

Notes

1. Di-*tert*-butyl(2',4',6'-triisopropyl-[1,1'-biphenyl]-2-yl)phosphine (97%) and chloro(dimethylsulfide)gold(I) (97.5%) were purchased from Sigma-Aldrich Chemical Co. (Ref. 638080 and 420727, respectively) and used as received.

2. Dichloromethane (CHROMASOLV®, for HPLC, ≥99.8%) was purchased from Sigma-Aldrich Chemical Co. (Ref. 34856) and used as received.

3. The physical and spectroscopic properties of gold(I) chloride complex **3** are as follows: mp = 255–257 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) : 0.91 (d, J = 6.6 Hz, 6H), 1.28 (d, J = 6.8 Hz, 6H), 1.35 (d, J = 6.9 Hz, 6H), 1.39 (s, 9H), 1.44 (s, 9H), 2.36 (hept, J = 6.7 Hz, 2H), 2.95 (hept, J = 6.9 Hz, 1H), 7.06 (s, 2H), 7.27–7.32 (m, 1H), 7.47–7.57 (m, 2H), 7.88–7.94 (m, 1H). ^{13}C {^{1}H} NMR (101 MHz, CD_2Cl_2) δ: 23.0 (s), 24.5 (s), 26.3 (s), 31.1 (s), 31.4 (d, J (^{13}C-^{31}P) = 6.4 Hz), 34.7 (s), 38.6 (d, J (^{13}C-^{31}P) = 26.6 Hz), 122.0 (s), 126.9 (d, J (^{13}C-^{31}P) = 6.9 Hz), 128.3 (s), 128.8 (s), 130.7 (d, J (^{13}C-^{31}P) = 2.4 Hz), 135.0 (d, J (^{13}C-^{31}P) = 3.0 Hz), 135.2 (d, J (^{13}C-^{31}P) = 8.1 Hz), 136.3 (d, J (^{13}C-^{31}P) = 5.5 Hz), 146.3 (s), 148.5 (d, J (^{13}C-^{31}P) = 14.0 Hz), 150.3 (s). ^{31}P {^{1}H} NMR (162 MHz, CD_2Cl_2) δ: 58.69. IR (neat) : 2970, 1739, 1444, 1365, 1228, 1217, 1206, 775, 528 cm^{-1}. HRMS-ESI$^+$ m/z calcd for $C_{29}H_{45}AuClNaP^+$ [M+Na]$^+$ 679.2505, found 679.2516. Anal. calcd for $C_{29}H_{45}AuClP$: C, 53.01; H, 6.90; found: C, 52.65; H, 6.77.

4. Acetonitrile (CHROMASOLV® gradient grade, for HPLC, ≥99.9%) was purchased from Sigma-Aldrich Chemical Co. (Ref. 34851) and used as received.

5. Sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (97%, may contain 1-5% water) was purchased from Alfa Aesar (Ref. H30014) and used as received.

6. **Important:** It is necessary to use an excess of acetonitrile (2.5 equiv) and sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (1.05 equiv) in order to obtain pure cationic gold(I) complex **4**. If not, the reaction outcome can be a mixture of desired product **4**, unreacted gold(I) chloride complex **3** and other different species.

7. Merck Celite 545 (particle size 0.02-0.1 mm) was used.

8. The physical and spectroscopic properties of cationic gold(I) complex **4** are as follows: mp = 148–150 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ: 0.93 (d, J = 6.6 Hz, 6H), 1.26 (d, J = 6.8 Hz, 6H), 1.32 (d, J = 6.9 Hz, 6H), 1.40 (d, J = 16.3 Hz, 18H), 2.22 (broad s, 3H), 2.34 (hept, J = 6.7 Hz, 2H), 2.95 (hept, J = 6.9 Hz, 1H), 7.17 (s, 2H), 7.31–7.35 (m, 1H), 7.58 (s, 4H), 7.56–7.62 (m, 2H), 7.74–7.75 (m, 8H), 7.87–7.91 (m, 1H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ: 3.0 (s), 23.2 (s), 24.3 (s), 26.1 (s), 31.3 (d, J (^{13}C-^{31}P) = 5.5 Hz), 31.4 (s), 34.5 (s), 39.1 (d, J (^{13}C-^{31}P) = 28.2 Hz), 117.9 (p, J (^{13}C-^{19}F) = 3.9 Hz), 118.9 (s), 122.3 (s), 125.1 (q, J (^{13}C-^{19}F) = 272.4 Hz), 125.9 (d, J (^{13}C-^{31}P) = 49.8 Hz), 128.0 (d, J (^{13}C-^{31}P) = 7.9 Hz), 129.3 (qq, J (^{13}C-^{19}F) = 31.6 Hz and J (^{13}C-^{11}B) = 2.7 Hz), 130.3 (s), 132.0 (d, J (^{13}C-^{31}P) = 2.4 Hz), 134.6 (d, J (^{13}C-^{31}P) = 4.3 Hz), 135.2 (s), 135.3 (s), 136.6 (d, J (^{13}C-^{31}P) = 6.3 Hz), 147.4 (d, J (^{13}C-^{31}P) = 11.7 Hz), 147.9 (s), 150.3 (s), 162.2 (q, J (^{13}C-^{11}B) = 49.8 Hz). ^{31}P {^{1}H} NMR (162 MHz, CD_2Cl_2) δ: 55.35. ^{19}F {^{1}H} NMR (376 MHz, CD_2Cl_2) δ: –62.83. ^{11}B {^{1}H} NMR (128 MHz, CD_2Cl_2) δ: –6.56. ESI$^+$ m/z calcd for $C_{31}H_{48}AuNP^+$ [M-$C_{32}H_{12}BF_{24}$]$^+$ 662.3184, found 662.3186. Anal. calcd for $C_{63}H_{60}AuBF_{24}NP$: C, 49.59; H, 3.96; N, 0.92; found: C, 49.52; H, 3.95; N, 0.58.

9. α-Methylstyrene (99%, stab. with 10-20 ppm 4-*tert*-butylcatechol) was purchased from Alfa Aesar (Ref. L03609). Ethynylbenzene (>98.0%) was purchased from Tokyo Chemical Industry Co. (Ref. E0196). Both were used as received.

10. The gold(I)-catalyst is neither sensitive to oxygen nor moisture, so the reaction was performed under air (with *ca.* 80% relative humidity).

11. Triethylamine (puriss. p.a., ≥99.5%) was purchased from Sigma-Aldrich Chemical Co. (Ref. 90340) and used as received.

12. Florisil (60-100 mesh) was purchased from Acros Organics.

13. Silica gel (technical grade, pore size 60 Å, 230-400 mesh particle size, 40-63 μm particle size) was purchased from Sigma-Aldrich Chemical Co.

14. Column fractions were checked by TLC analysis on Merck Silica Gel 60 F_{254} aluminium sheets, using cyclohexane as eluent. Visualization is accomplished with 254 nm UV light and subsequently with vanillin staining (solution of 12 g of vanillin and 2 mL of concentrated sulphuric acid in 200 mL of absolute ethanol) by immersion and heating with a heat gun. The starting α-methylstyrene has Rf = 0.71 (UV active; blue after staining) whereas the cyclobutene product **7** has Rf = 0.50 (UV active; purple after staining).

15. Fractions of 60 mL (about 1.5 L, 25 fractions in total) are collected until all α-methylstyrene is eluted and then, fractions of 60 mL (about 0.9 L, 15 fractions) and 500 mL (about 4 L, 8 fractions in total) are collected until no more product elutes.

16. The physical and spectroscopic properties of cyclobutene **7** are as follows: ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.64 (s, 3H), 2.96 (q, J = 12.5 Hz, 2H), 6.74 (s, 1H), 7.18–7.23 (m, 1H), 7.25–7.29 (m, 1H), 7.31–7.37 (m, 4H), 7.39–7.42 (m, 4H). ^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$) δ: 27.6, 44.3, 46.0, 124.6, 125.7, 125.8, 127.8, 128.1, 128.3, 133.7, 134.7, 143.8, 147.7. IR (neat): 3025, 2953, 1741, 1736, 1727, 1490, 1445, 1368, 1229, 1216, 1206, 748, 690 cm^{-1}. HRMS-APCI m/z calculated for $C_{17}H_{17}$ [M+H]$^+$ 221.1325, found 221.1324. Anal. calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32; found: C, 92.69; H, 7.30.

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Discussion

The synthesis of cyclobutenes by metal-catalyzed intermolecular [2+2] cycloaddition of alkynes with alkenes is normally restricted to strained bicyclic olefins.[2] Otherwise, internal or terminal alkynes react with electron-deficient alkenes to give cyclobutenes using rhodium (I)[3] or (II)[4] catalysts, respectively. Cyclobutenes are also obtained in the intermolecular reaction of 1,3-enynes with alkenes catalyzed by nickel[5] or cobalt[6] complexes. Apart from that, in the presence of cobalt catalysts, only cyclopentene and cycloheptene were found to undergo cycloaddition with internal alkynes to generate cyclobutene derivatives.[7] In this context, the gold(I)-catalyzed intermolecular [2+2] cycloaddition of terminal alkynes with differently-substituted alkenes, whose procedure is reported herein, is an important method for the formation of cyclobutenes.[8]

The key point for the development of this transformation was the use of a gold(I)-catalyst bearing a sterically hindered ligand such as *t*BuXPhos, which allows the selective activation of the alkyne towards nucleophilic attack of the alkene and reduces competitive pathways leading to oligomers.[8a] Further mechanistic studies revealed the impact of the more bulky, non-coordinating and less basic BAr_4^{F-} as counterion in the gold

catalyst in order to decrease the deprotonation of terminal alkynes forming unreactive α,π-(acetylide)digold complexes.[8b]

The optimized [tBuXPhosAu(MeCN)]BAr$_4^F$ catalyst can be easily synthesized in two steps, starting from the phosphine tBuXPhos and chloro(dimethylsulfide)gold(I) to form the gold(I) chloride complex[9] and then, treating with slight excess of NaBAr$_4^F$ and acetonitrile to obtain the corresponding cationic gold(I) complex.

Table 1. Other cyclobutenes synthesized following this procedure.
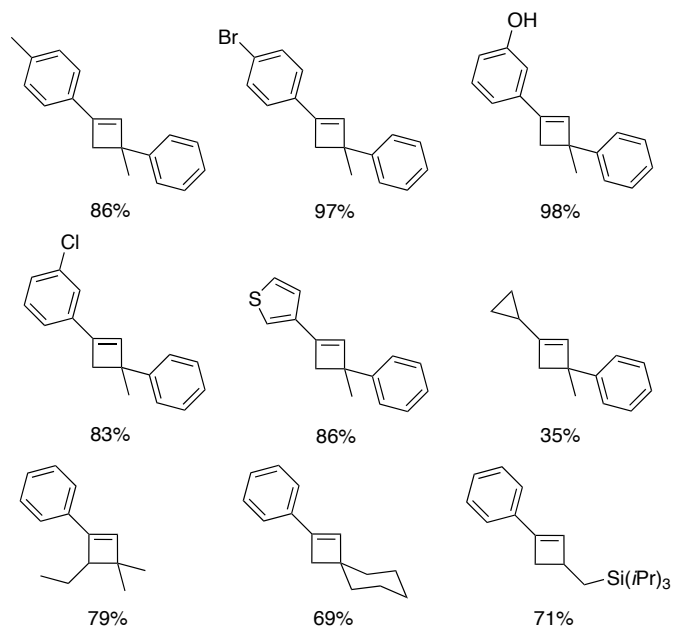
In the presence of this efficient gold(I)-catalyst, terminal arylalkynes react with mono-, di- and trisubstituted alkenes to build regioselectively cyclobutenes containing a wide variety of functional groups in moderate to excellent yields (Table 1). Ethynylcyclopropane also undergoes the cycloaddition in moderate yields, but internal alkynes such as 1-phenyl-1-propyne are unreactive under these conditions.

It is worth mentioning that this gold(I)-catalyzed transformation proceeds at room temperature and under air. Thus, our procedure represents a facile method for the preparation of substituted cyclobutenes under mild conditions.

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1. Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans 16, 43007 Tarragona, Spain. E-mail: aechavarren@iciq.es. We thank MINECO (project CTQ2013-42106-P, Severo Ochoa Excellence Accreditation SEV-2013-0319 and Severo Ochoa predoctoral fellowship), European Research Council (Advanced Grant No. 321066), AGAUR (2014 SGR 818, and the ICIQ Foundation for financial support.

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Appendix
Chemical Abstracts Nomenclature (Registry Number)

Di-*tert*-butyl(2',4',6'-triisopropyl-[1,1'-biphenyl]-2-yl)phosphine: Phosphine, bis(1,1-dimethylethyl)[2',4',6'-tris(1-methylethyl)[1,1'-biphenyl]-2-yl]-; (564483-19-8)

Chloro(dimethylsulfide)gold(I): Gold, chloro[thiobis[methane]]-; (29892-37-3)

Chloro[(2′,4′,6′-triisopropyl-1,1′-biphenyl-2-yl)di-tert-butylphosphine]gold(I): Gold, [bis(1,1-dimethylethyl)[2',4',6'-tris(1-methylethyl)[1,1'-biphenyl]-2-yl]phosphine]chloro-; (1312108-97-6)

Sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate: Borate(1-), tetrakis[3,5-bis(trifluoromethyl)phenyl]-, sodium (1:1) (79060-88-1)

(Acetonitrile)[(2′,4′,6′-triisopropyl-1,1′-biphenyl-2-yl)di-tert-butylphosphine]gold(I) tetrakis[3,5-bis(trifluoromethyl)phenyl] borate; (1610790-72-1)

Ethynylbenzene: Benzene, ethynyl-; (536-74-3)

α-Methylstyrene: Benzene, (1-methylethenyl)-; (98-83-9)

(1,3-Diphenyl-3-methylcyclobut-1-ene: Benzene, 1,1'-(3-methyl-1-cyclobutene-1,3-diyl)bis-; (1235453-87-8)

M. Elena de Orbe was born in Madrid (Spain) in 1991. She graduated with a degree in Chemistry from the Universidad Complutense de Madrid with the Extraordinary Award in 2013. In 2014, she completed the Master in Synthesis, Catalysis and Molecular Design at the Universitat Rovira i Virgili (Tarragona, Spain) and joined the group of Prof. Antonio M. Echavarren at the Institute of Chemical Research of Catalonia (ICIQ) to perform her Ph.D. studies.

Antonio M. Echavarren was born in Bilbao (Spain) in 1955 and obtained his Ph.D. at the Universidad Autónoma de Madrid in 1982 with Francisco Fariña. After postdoctoral stays at Boston College with T. Ross Kelly and at Colorado State University with John K. Stille he joined the Institute of Organic Chemistry (CSIC) in Madrid, where he stayed until 1992. That year he returned to the UAM as a Professor of Organic Chemistry. He moved in 2004 to Tarragona as a Group Leader at the Institute of Chemical Research of Catalonia (ICIQ).

Giulia Rusconi graduated with a degree in Chemistry from the Università degli Studi di Milano in 2010. In 2012, she completed the Master in Organic Chemistry at the same university and joined the group of Prof. Cristina Nevado at the University of Zurich to perform her Ph.D. studies.
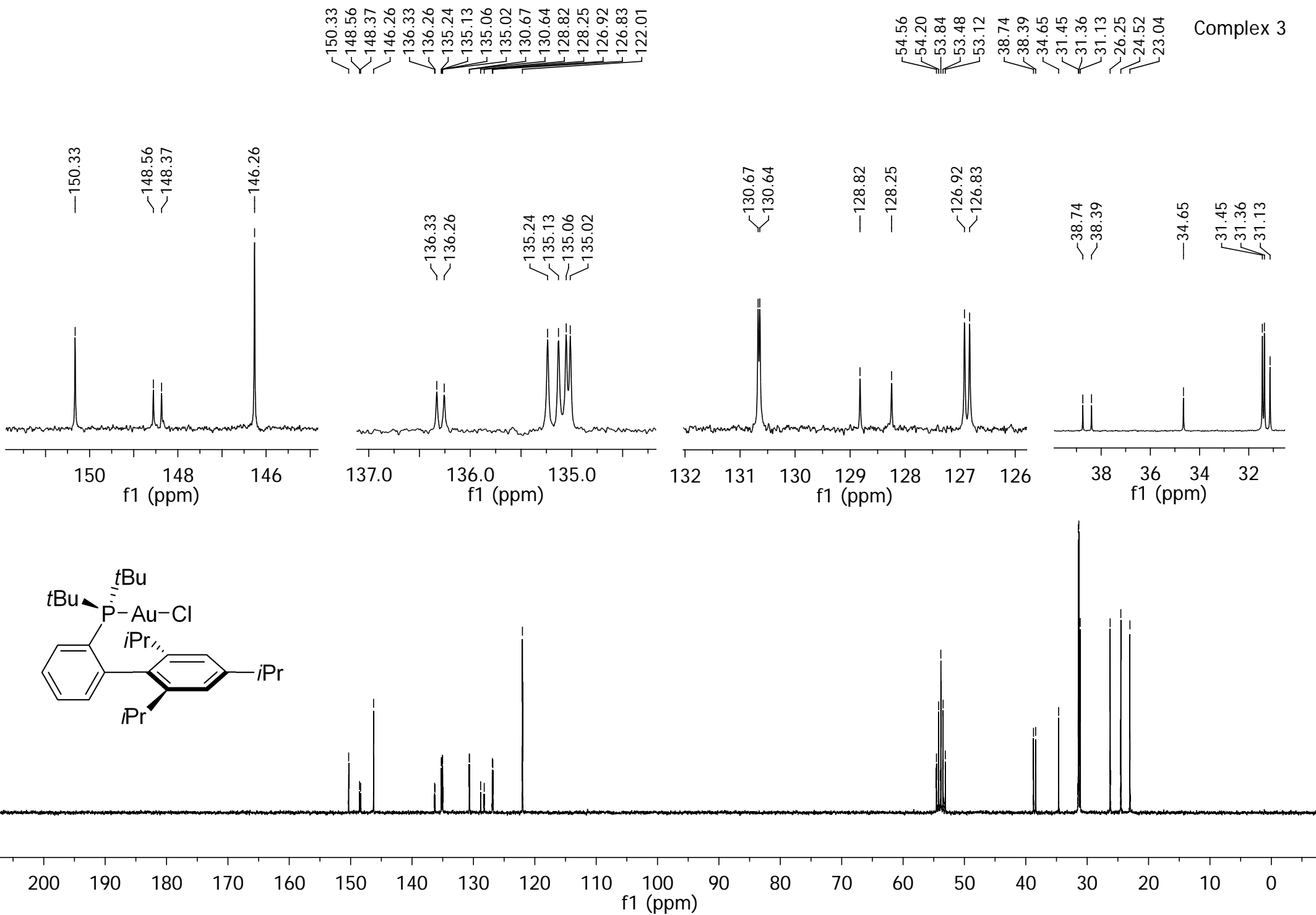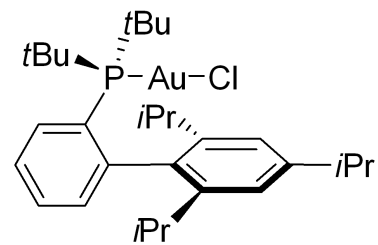
Estíbaliz Merino obtained her Ph.D. at the University Autónoma de Madrid. After a postdoctoral stay with Prof. Magnus Rueping at Goethe University Frankfurt and RWTH-Aachen University in Germany, she worked with Prof. Avelino Corma in Instituto de Tecnología Química-CSIC (Valencia) and Prof. Félix Sánchez in Instituto de Química Orgánica General-CSIC (Madrid) Spain. At present, she is a research associate in Prof. Cristina Nevado´s group in University of Zürich.
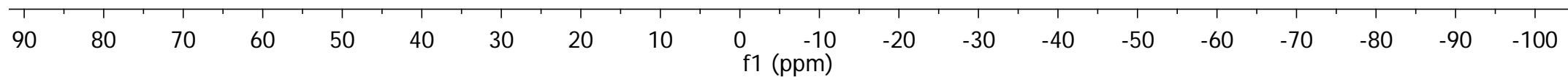
Complex 3

Complex 3

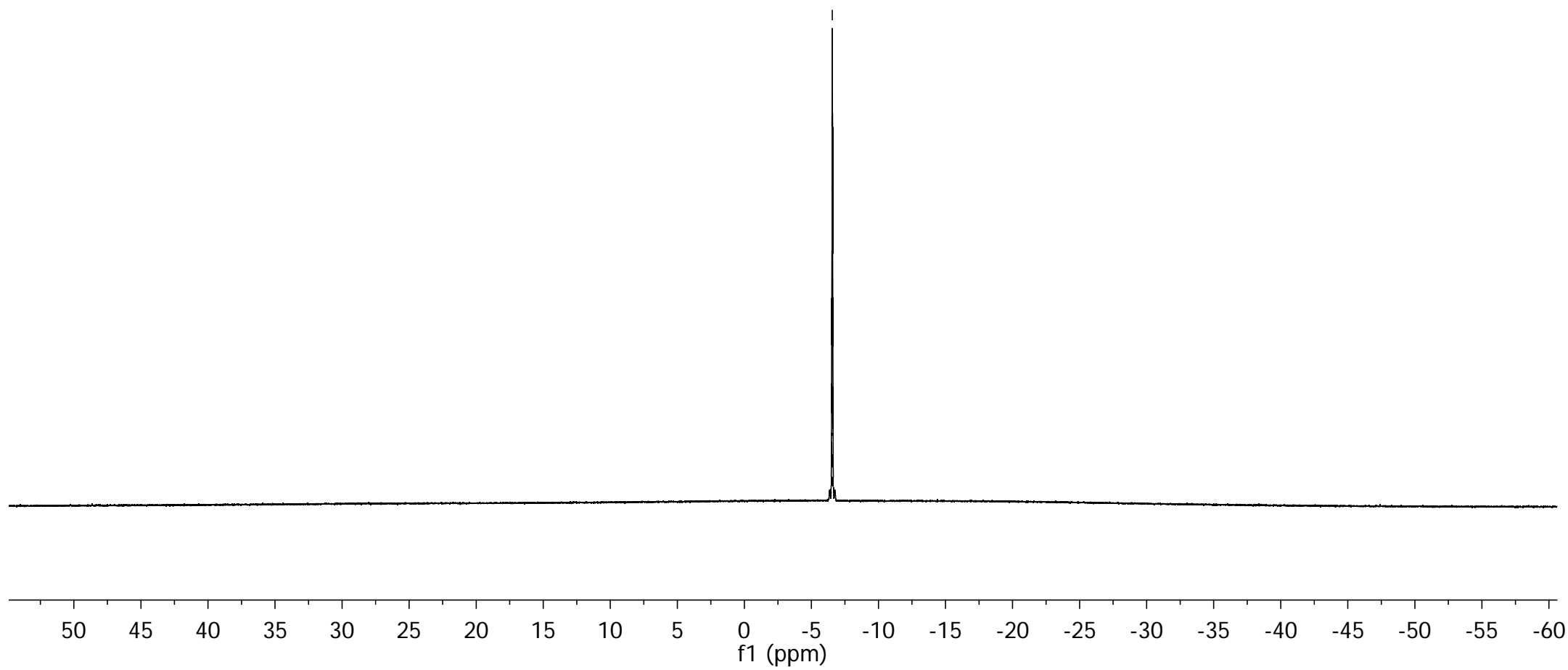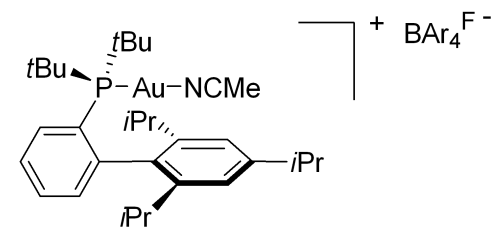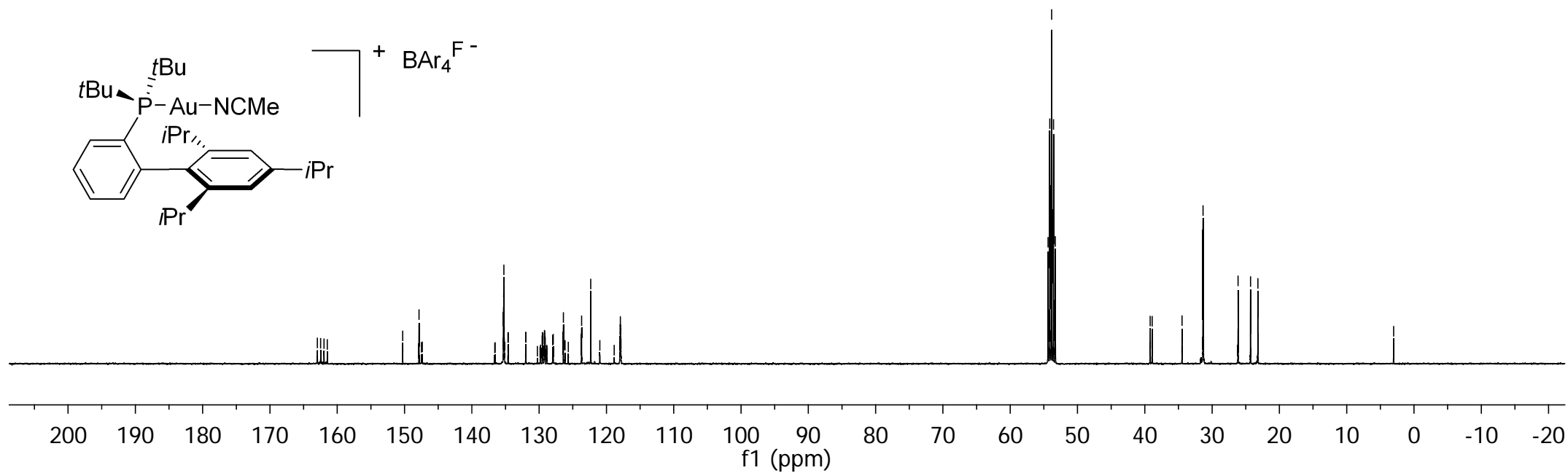Complex 3

58.69

90   80   70   60   50   40   30   20   10   0   -10   -20   -30   -40   -50   -60   -70   -80   -90   -100
f1 (ppm)

Complex 4

−6.56

50   45   40   35   30   25   20   15   10   5   0   -5   -10   -15   -20   -25   -30   -35   -40   -45   -50   -55   -60
f1 (ppm)

Complex 4

Peak labels (top expansions, left to right):

162.96, 162.47, 161.97, 161.47, 150.27, 147.85, 147.48, 147.36, 135.23, 134.63, 134.59, 132.00, 131.97, 129.54, 129.51, 129.49, 129.46, 129.23, 129.20, 129.17, 129.14, 129.11, 127.99, 127.91, 126.40, 123.69, 122.33, 117.96, 117.93, 117.89, 117.85, 54.38, 54.11, 53.84, 53.57, 53.30, 39.19, 38.91, 34.46, 31.35, 31.30, 26.14, 24.29, 23.19

3.02

Expansion insets:

162.96, 162.47, 161.97, 161.47 — f1 (ppm) 163 162 161

147.85, 147.48, 147.36 — f1 (ppm) 148.0 147.6 147.2

136.60, 136.54, 135.31, 135.23, 134.63, 134.59 — f1 (ppm) 137 135

132.00, 131.97 — f1 (ppm) 132.1

130.26, 129.80, 129.54, 129.51, 129.49, 129.46, 129.23, 129.20, 129.17, 129.14, 129.11, 128.92, 128.89, 128.86, 127.99, 127.91 — f1 (ppm) 130.5 129.5 128.5

117.96, 117.93, 117.89, 117.85 — f1 (ppm) 118.0

39.19, 38.91 — f1 (ppm) 39.0

f1 (ppm): 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20

31P of Complex 4

—55.35

tBu
tBu—P—Au—NCMe
iPr
iPr
iPr

$+$ $BAr_4{}^{F-}$

90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

−−62.83

Compound 7

Compound 7

Peaks (ppm): 147.68, 143.80, 134.69, 133.72, 128.30, 128.10, 127.78, 125.84, 125.66, 124.57, 77.32, 77.00, 76.68, 45.95, 44.25, 27.55

Inset (ppm): 128.30, 128.10, 127.78, 125.84, 125.66, 124.57