Supporting Information

"Pd(0)/Au(I) RedOx Incompatibilities as Revealed by Pd-Catalyzed Homo-Coupling of Arylgold(I)-Complexes"

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I. General Information:

Reactions were run under positive N_2 pressure at the indicated temperature using dry tetrahydrofuran that had been freshly distilled over a suspension of sodium and benzophenone. Grignard reagents, gold chloride precursors, palladium salts, mercury, and phosphine ligands were used as purchased from Aldrich, Fisher Scientific, or Strem. NMR data were acquired using a BRUKER AVANCE 400 MHz, 500 MHz, or 600 MHz spectrometer. Spectra were referenced to TMS (0.00 ppm) using residual proton or carbon signals of the deuterated solvent. ^{31}P spectra were referenced to $P(OPh)_3$ in $CDCl_3$ (-18.0 ppm) or concentrated H_3PO_3 (0 ppm) as external standards. ESI high resolution mass spectra (HRMS-ESI+) were obtained on a BRUKER APEX-QE. An internal CsOAc standard was used to calibrate the spectrometer. GC-MS data was obtained on an Agilent 6850 GC-System with an HP-5MS column (length: 30 m; I.D. 0.250 mm) connected to an Agilent 5973 *Network* Mass Selective Detector. The GC method consisted of the following parameters: inlet temperature was set to 250°C, oven temperature was held at 125°C for 3 minutes and ramped at 20°C/min until the target temperature of 250°C was reached. The oven temperature was held constant at 250°C for 5 minutes. The column flow rate was set to 1.2 mL/min and the detector temperature was 280°C.

*II. Synthesis of Au-Complexes **A, B, 1a, 1b, 1c, 1d**:*

Synthesis of Au-vinyls **A** and **B**:
Compounds **A** and **B** were synthesized as reported.[1,2]

General Procedure for the Synthesis of Au-aryls **1a-d**:
In a flame-dried Schlenk flask under nitrogen atmosphere, the corresponding LAuCl complex was dissolved in dry THF. The solution was cooled to 0°C with an ice-water bath and 1.3 equivalents of a 0.5 M solution of (3,5-dimethyl)phenyl magnesium bromide in THF were added dropwise. The reaction mixture was stirred for 30 minutes at 0°C and followed by an additional hour at RT. The reaction was quenched with H_2O and extracted with diethyl ether. The combined organic layers were dried over K_2CO_3 and concentrated *in vacuo*. The residue was dissolved in a minimum amount of methylene chloride, layered with an excess amount (200-300 mL) of pentanes, and stored in the freezer. After 24 hours a crystalline material was obtained in the case of **1a**. In the case of **1b** a brown foam instead of a crystalline solid was obtained. In the cases of **1c**, and **1d**, a white crystalline solid was obtained after concentration *in vacuo*.

NMR data for **1a**:
^{1}H-NMR (CD_2Cl_2, 400 MHz, δ): 7.46-7.64 (m, 15H), 7.12 (d, $^{4}J_{PH}$ = 4.8 Hz, 2H), 6.71 (s, 1H), 2.23 (s, 6H). ^{13}C {^{1}H} (CD_2Cl_2, 125 MHz, δ): 171.9 (d, $^{2}J_{PC}$ = 115.3 Hz), 137.5 (s), 136.5 (d, $^{3}J_{PC}$ = 6.4 Hz), 134.9 (d, $^{3}J_{PC}$ = 13.6 Hz), 131.7 (d, $^{1}J_{PC}$ = 48.5 Hz), 131.7 (d, $^{4}J_{PC}$ = 2.3 Hz), 129.6 (d, $^{2}J_{PC}$ = 10.6 Hz), 127.8 (s), 21.9 (s). ^{31}P {^{1}H} (CD_2Cl_2, 202 MHz, δ): 43.1 (s). HRMS-ESI+: m/z

697.0335 calculated for $[M+Cs]^+$, found m/z 697.0340. (m/z 721.1488 for $[(Ph_3P)_2Au]^+$ and m/z 1023.1856 for $[M+Ph_3PAu]^+$ were also found). R_f (Hex:EA = 4:1) = 0.46.

NMR data for **1b**:
^{1}H-NMR (CD_2Cl_2, 400 MHz, δ): 7.49 (d, $^3J_{HH}$ = 8.0 Hz, 6H), 7.46 (d, $^3J_{HH}$ = 8.0 Hz, 6H), 7.10 ($^4J_{PH}$ = 5.2 Hz, 2H), 6.69 (s, 1H), 2.40 (s, 12H), 2.22 (s, 6H). ^{13}C {^{1}H} (CD_2Cl_2, 125 MHz, δ): 172.8 (d, $^2J_{PC}$ = 115.0 Hz), 142.2 (s), 137.6 (s), 136.5 (d, $^4J_{PC}$ = 6.3 Hz), 134.7 (d, $^3J_{PC}$ = 13.8 Hz), 130.3 (d, $^2J_{PC}$ = 11.3 Hz), 128.8 (d, $^1J_{PC}$ = 50.0 Hz), 127.7 (s), 21.9 (s), 21.7 (s). ^{31}P {^{1}H} (CD_2Cl_2, 202 MHz, δ): 42.0 (s). HRMS-ESI+: m/z 739.0805 calculated for $[M+Cs]^+$, found m/z 739.0781. (m/z 805.2427 for $[(tol_3P)_2Au]^+$ and m/z 1107.2797 for $[M+tol_3PAu]^+$ were also found.)

NMR data for **1c**:
^{1}H-NMR (CD_2Cl_2, 400 MHz, δ): 7.52 (t, $^3J_{HH}$ = 8.0 Hz, 2H), 7.33 (d, $^3J_{HH}$ = 8.0 Hz, 4H), 7.19 (s, 2H), 6.56 (s, 2H), 6.42 (s, 1H), 2.66 (septet, $^3J_{HH}$ = 6.8 Hz, 4H), 2.02 (s, 6H), 1.40 (d, $^3J_{HH}$ = 6.8 Hz, 12H), 1.24 (d, $^3J_{HH}$ = 6.8 Hz, 12H). ^{13}C {^{1}H} (CD_2Cl_2, 125 MHz, δ): 169.2 (s), 146.4 (s), 138.3 (s), 135.4 (s), 135.2 (s), 130.6 (s), 126.2 (s), 124.4 (s), 123.5 (s), 29.3 (s), 24.8 (s), 24.2 (s), 21.7 (s). HRMS-ESI+: m/z 823.2302 calculated for $[M+Cs]^+$, found m/z 823.2265. (m/z 973.5422 for $[IPr_2Au]^+$ and m/z 1275.5792 for $[M+IPrAu]^+$ were also found.)

NMR data for **1d**:
^{1}H-NMR (CD_2Cl_2, 500 MHz, δ): 7.11 (s, 2H), 7.07 (s, 4H), 6.64 (s, 2H), 6.46 (s, 1H), 2.37 (s, 6H), 2.20 (s, 12H), 2.07 (s, 6H). ^{13}C {^{1}H} (CD_2Cl_2, 125 MHz, δ): 196.0 (s), 169.3 (s), 139.9 (s), 138.2 (s), 136.0 (s), 135.6 (s), 129.9 (s), 129.6 (s), 126.4 (s), 122.6 (s), 21.7 (s), 21.5 (s), 18.3 (s). HRMS-ESI+: m/z 739.1363 calculated for $[M+Cs]^+$, found m/z 739.1317. (m/z 805.3544 for $[(IMes)_2Au]^+$ was also found.)

Representative procedure for attempted cross-coupling of **1a** with TolOTf:
In the glove box, 5-10 mol% [Pd], 5-10 mol% ligand, and a stir bar were added to a septum vial. The vial was removed from the glove box. After addition of 2 mL of THF, the solution was stirred for 2 minutes at RT under positive N_2 pressure. After addition of 2 equivalents of TolOTf, the reaction mixture was stirred for another 5 minutes. A solution of 18 μmol of **1a** in 2 mL of THF was added at RT and the vial containing the reaction mixture was lowered into an oil bath which had been pre-heated to 58°C. The progress of the reaction was monitored by TLC. Once TLC indicated complete consumption of **1a** (or incomplete reaction after the time listed in Table 1), a GC-MS spectrum was obtained.

Representative procedure for homo-coupling of **1a-d** in the absence of TolOTf:
In the glove box, 5-10 mol% [Pd], 5-10 mol% ligand, and a stir bar were added to a septum vial. The vial was removed from the glove box. After addition of 2 mL of THF, the solution was stirred for 2 minutes at RT under positive N_2 pressure. A solution of 18 μmol of **1** in 2 mL of THF was added at RT and the vial containing the reaction mixture was lowered into an oil bath which was pre-heated to 58°C. The progress of the reaction was monitored by TLC. Once TLC indicated complete consumption of **1** (or incomplete reaction after the times listed in Table 2), a GC-MS spectrum was obtained.

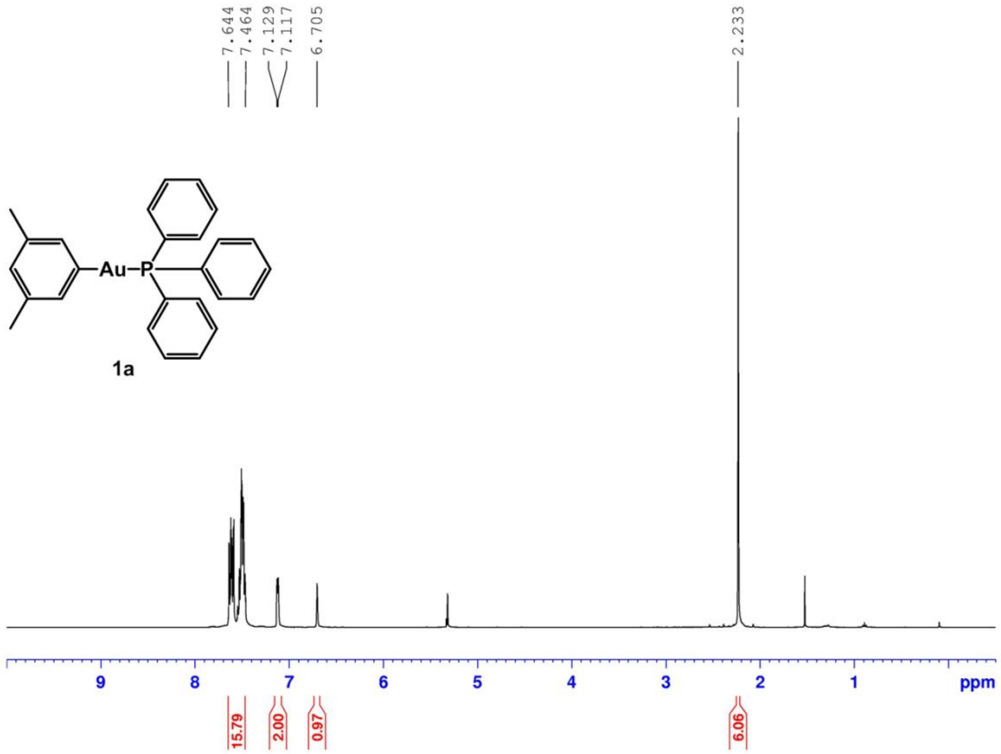
Representative procedure for the ligand free homo-coupling of **1a**:
In the glove box, 5-10 mol% $Pd(OAc)_2$ and a stir bar were added to a septum vial. The vial was removed from the glove box. After addition of 2 mL of THF a solution of 10 mg **1a** (18 μmol) in 2 mL of THF was added at RT under positive N_2 pressure and the vial containing the reaction mixture was lowered into an oil bath which was pre-heated to 58°C. The progress of the

reaction was monitored by TLC. Once TLC indicated complete consumption of **1a**, a GC-MS spectrum was obtained.

Isolation of a mixture of **3**[3] and **4**:[4]
In the glove box, 5-10 mol% Pd(OAc)$_2$ and a stir bar were added to a septum vial. The vial was removed from the glove box. After addition of 2 mL of THF a solution of 10 mg **1a** (18 µmol) in 2 mL of THF was added at RT under positive N$_2$ pressure and the vial containing the reaction mixture was lowered into an oil bath which was pre-heated to 58°C. Once TLC indicated complete consumption of **1a**, a mini-pipette column was prepared with a silica slurry in hexanes.The concentrated reaction mixture was loaded with a minimum amount of DCM. Hexanes was used as an eluent and 1.0 mg of a mixture of **3** and **4** was obtained. The ratio of **3** and **4** was determined by NMR (84:16) and GC-MS (83:17), which corresponds to an isolated yield of 45% **3** and 5 % **4**.
NMR data for **3**:
^{1}H-NMR (CD$_2$Cl$_2$, 600 MHz, δ): 7.19 (dd, $^4J_{HH}$ = 0.6 Hz, $^4J_{HH}$ = 0.6 Hz, 4H), 6.98 (m, 2H), 2.36 (d, $^4J_{HH}$ = 0.6 Hz, 12H).
NMR data for **4**:
^{1}H-NMR (CD$_2$Cl$_2$, 600 MHz, δ): 7.58 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.2 Hz, 2H), 7.42 (dd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.8 Hz, 2H), 7.32 (tt, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.2 Hz, 1H), 7.21 (dd, $^4J_{HH}$ = 1.2 Hz, $^4J_{HH}$ = 1.2 Hz, 2H), 7.00 (m, 1H), 2.37 (d, $^4J_{HH}$ = 0.6 Hz, 6H).

Attempted cross-coupling under published conditions:[5]
In the glove box, 5-10 mol% PdCl$_2$(PPh$_3$)$_2$ and a stir bar were added to a septum vial. The vial was removed from the glove box. After addition of 2 mL of THF and 1 equiv. of aryl-triflate a solution of 10 mg **1a** or PhAuPPh$_3$ (18 µmol) in 2 mL of THF was added at RT under positive N$_2$ pressure. The reaction was stirred at RT and monitored by TLC. Only an initial burst of product formation was observed. For 4 h no further conversion was observed by TLC.

III. *NMR data:*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P
1a
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8
7
6
5
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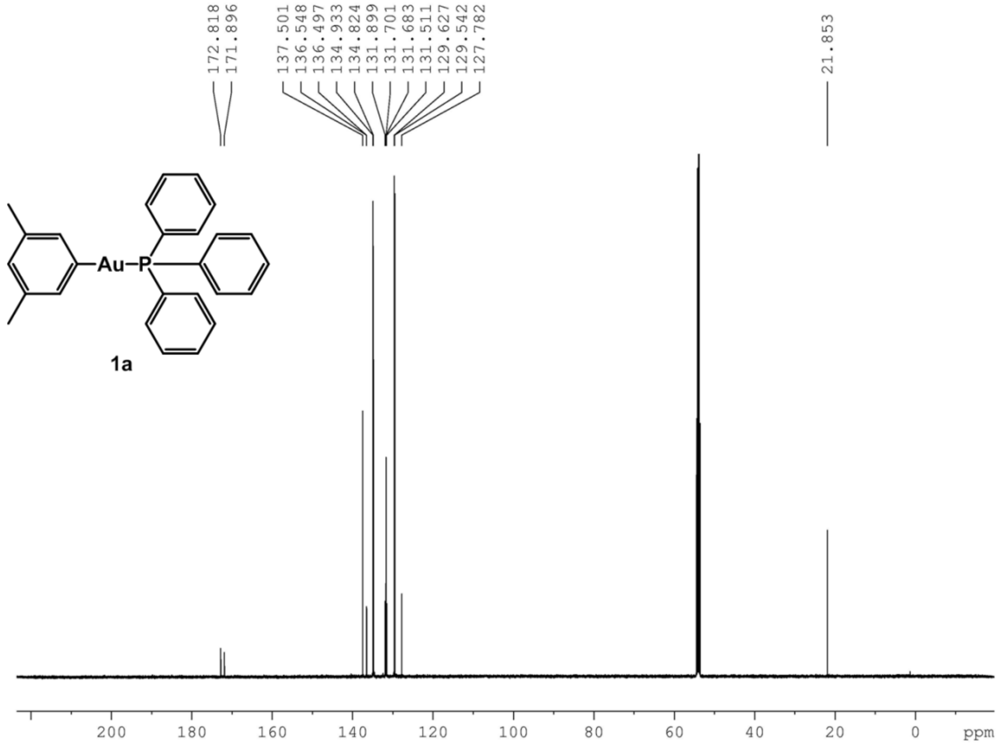
3
2
1
ppm
15.79
2.00
0.97
6.06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136.548
136.497
134.933
134.824
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129.627
129.542
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P
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160
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120
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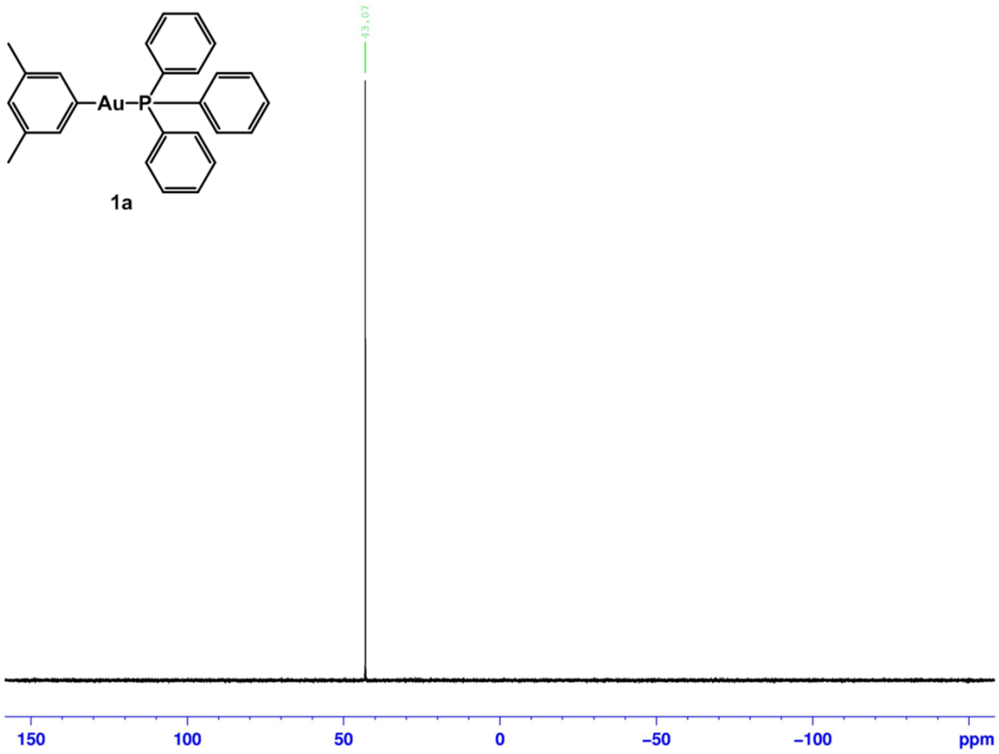
80
60
40
20
0
ppm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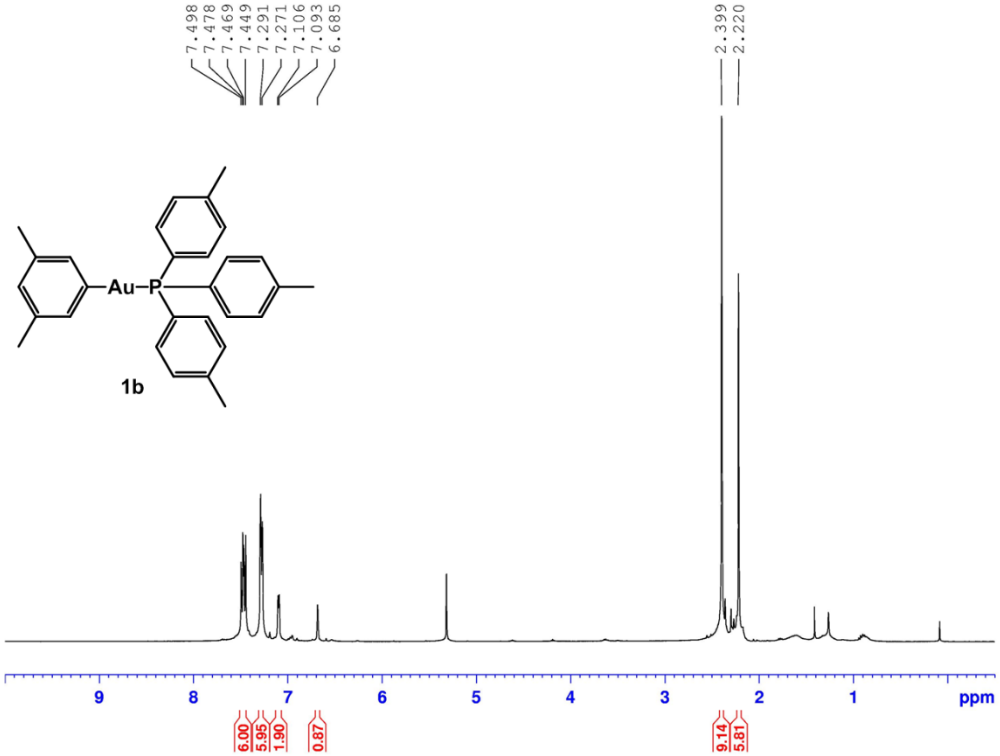
–50
–100
ppm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P
1b
9
8
7
6
5
4
3
2
1
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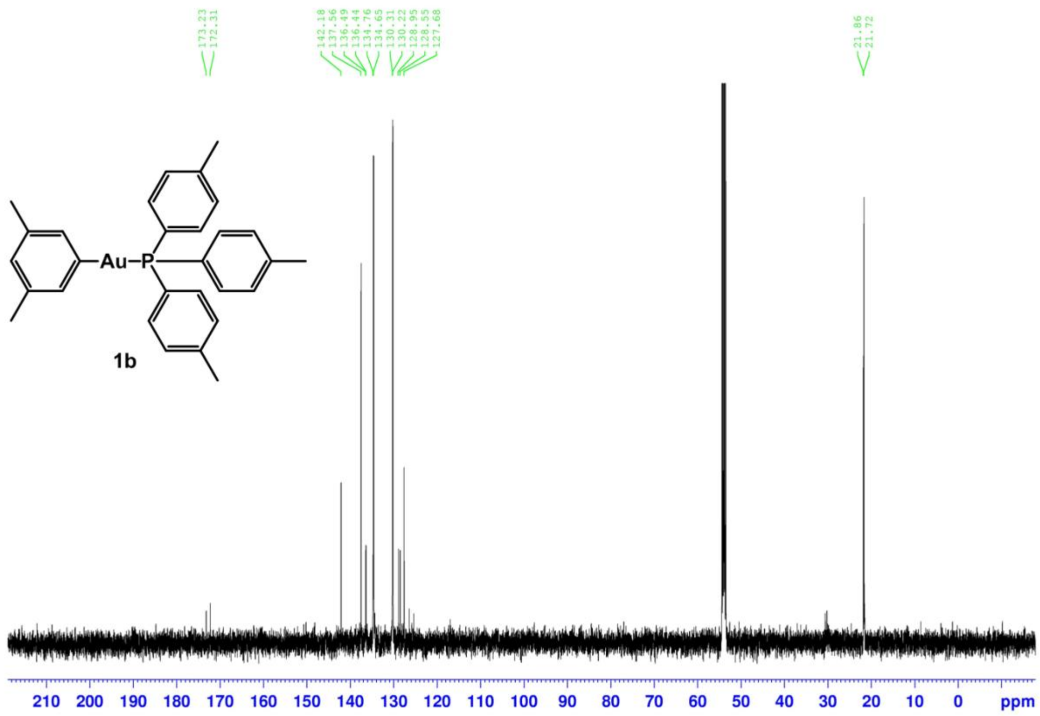
9.14
5.81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21.86
21.72
Au
P
1b
210
200
190
180
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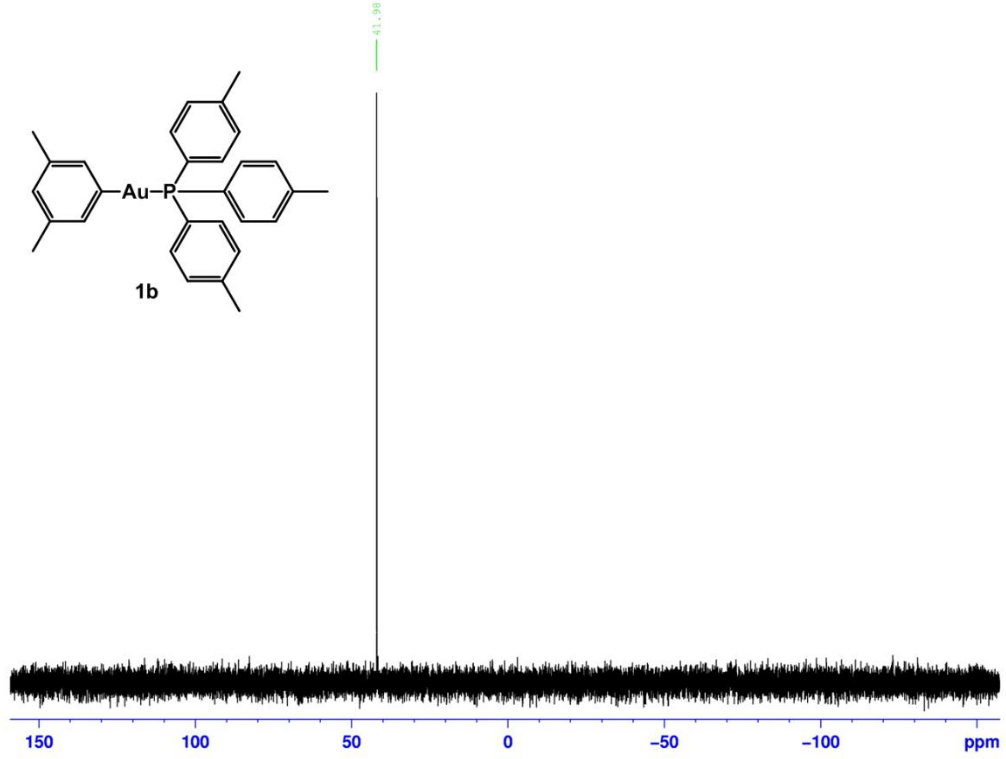
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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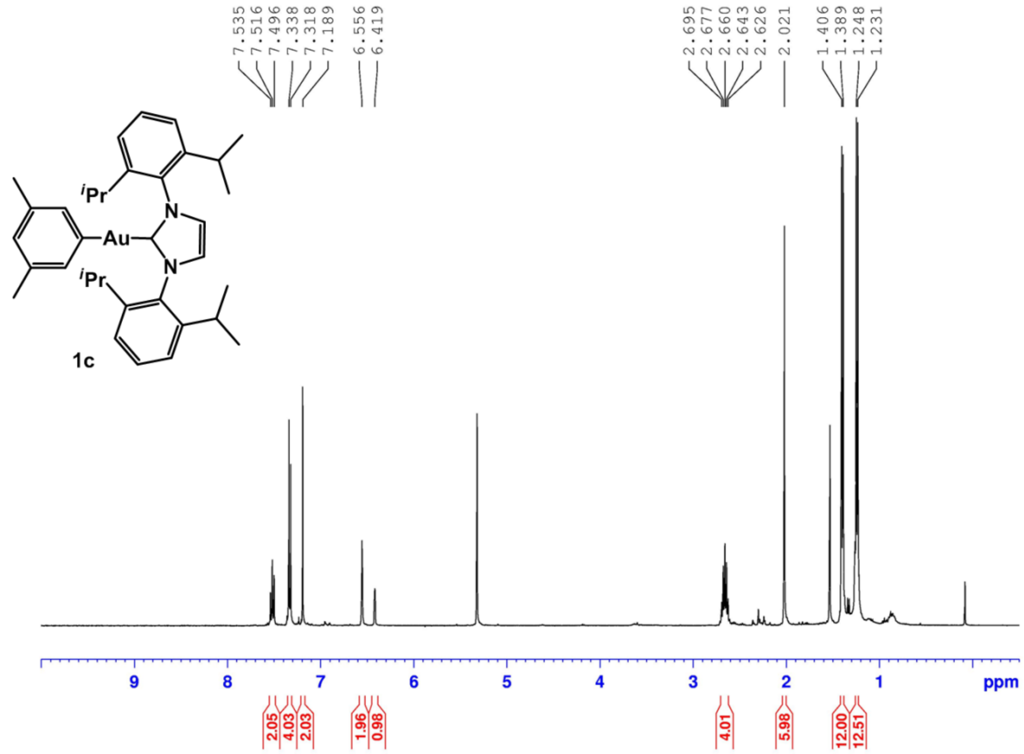
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7.496
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6.556
6.419
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2.660
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2.626
2.021
1.406
1.389
1.248
1.231
ⁱPr
Au
N
N
ⁱPr
1c
9
8
7
6
5
4
3
2
1
ppm
2.05
4.03
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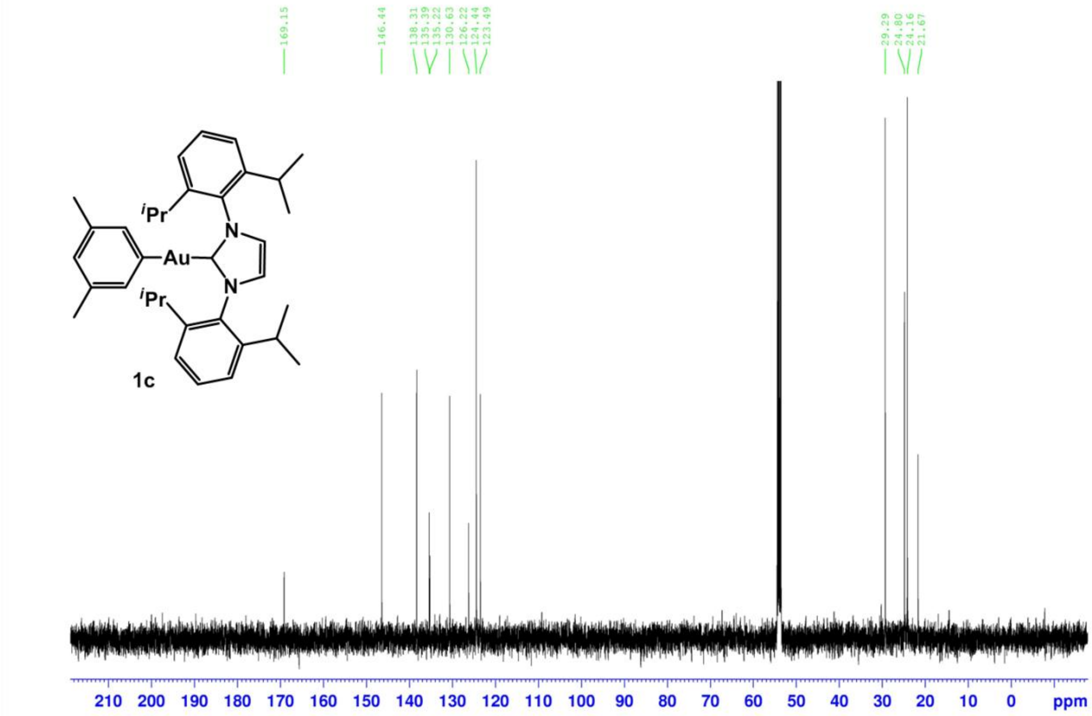
1.96
0.98
4.01
5.98
12.00
12.51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130.63
126.22
124.44
123.49
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ⁱPr
Au
N
N
ⁱPr
1c
210
200
190
180
170
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150
140
130
120
110
100
90
80
70
60
50
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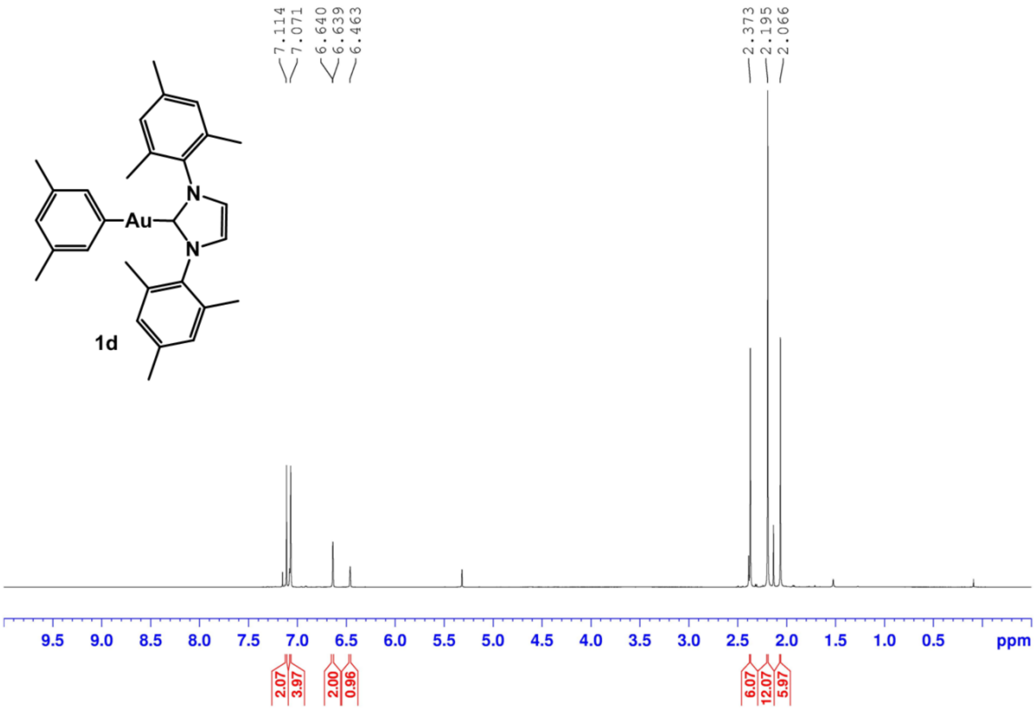
30
20
10
0
ppm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6.639
6.463
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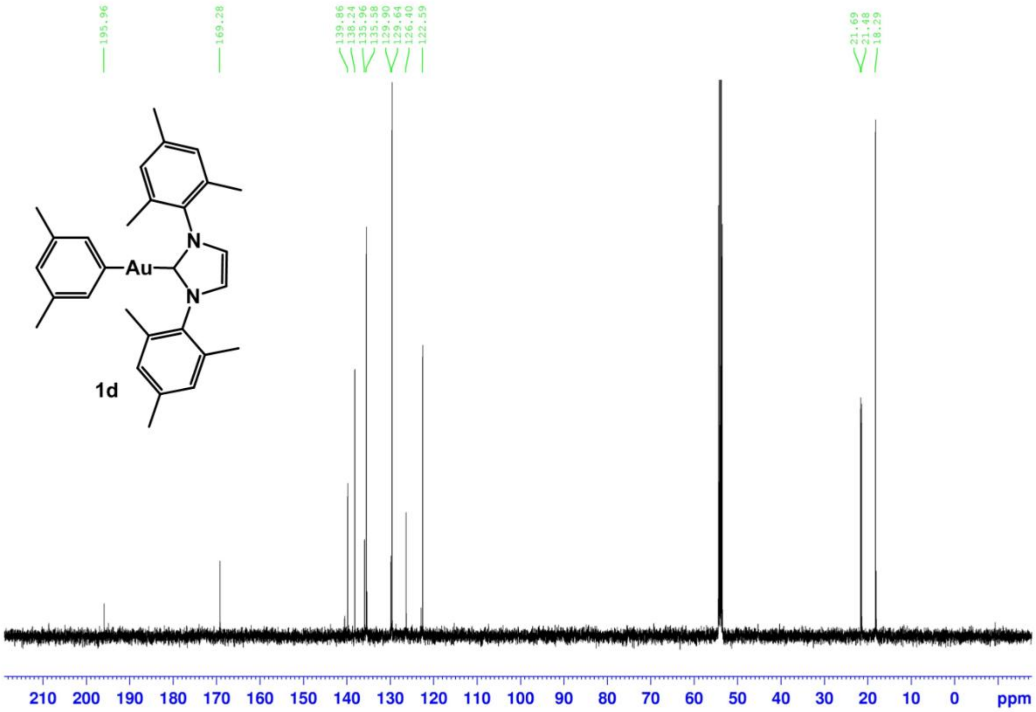
2.195
2.066
Au
N
N
1d
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.07
3.97
2.00
0.96
6.07
12.07
5.97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139.86
138.24
135.96
135.58
129.90
129.64
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N
N
1d
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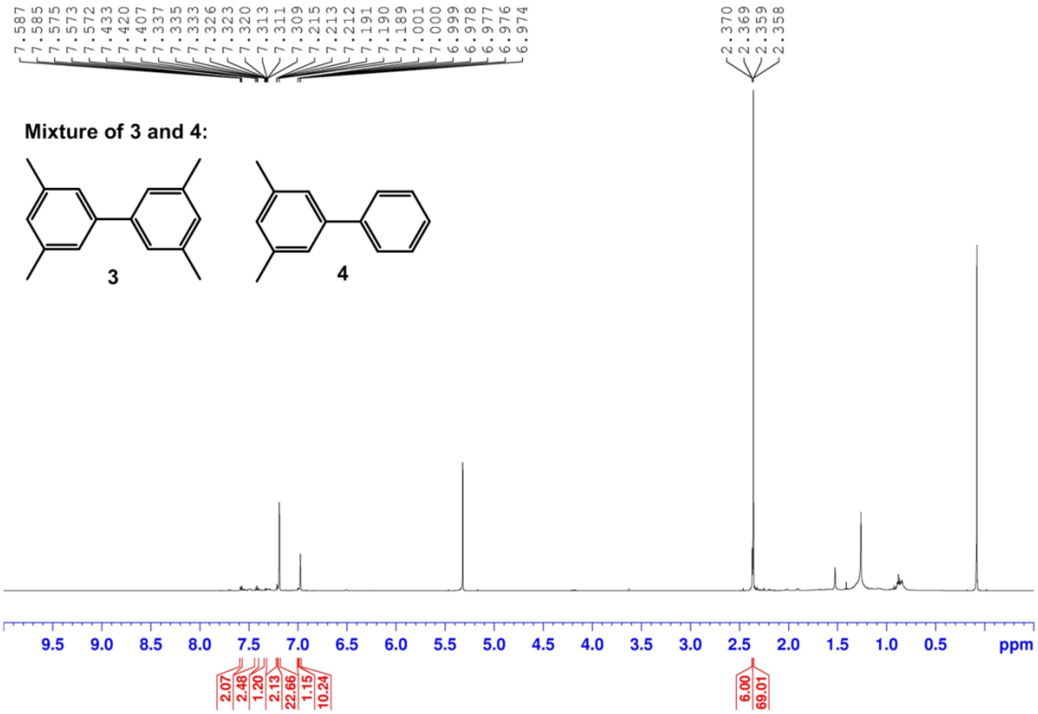
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7.323
7.320
7.313
7.311
7.309
7.215
7.213
7.212
7.191
7.190
7.189
7.001
7.000
6.999
6.978
6.977
6.976
6.974
2.370
2.369
2.359
2.358
Mixture of 3 and 4:
3
4
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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2.07
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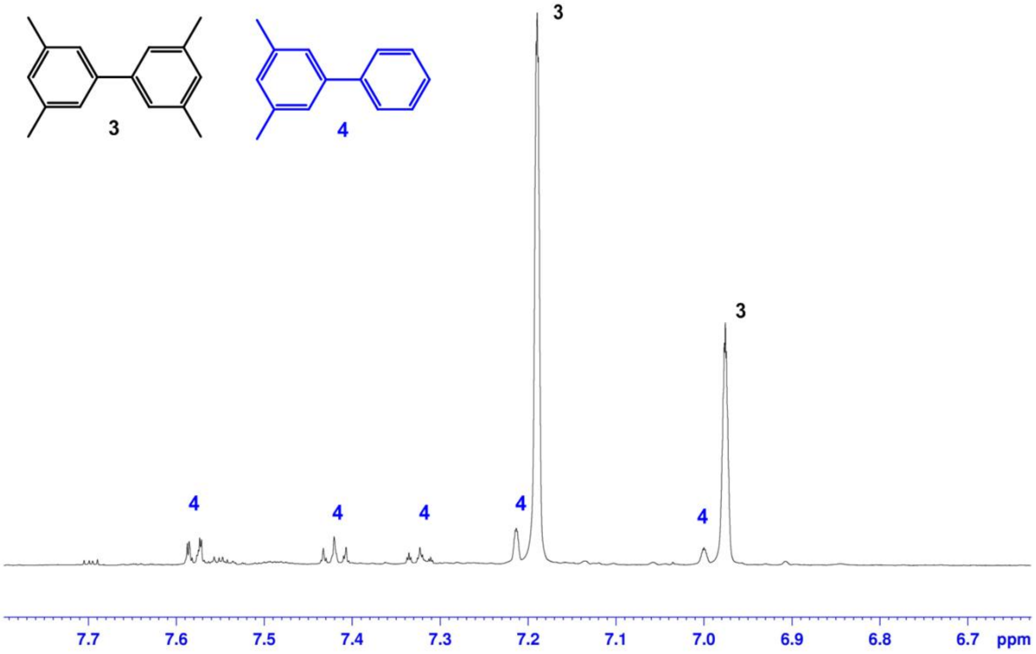
2.13
22.66
1.15
10.24
6.00
69.01


3
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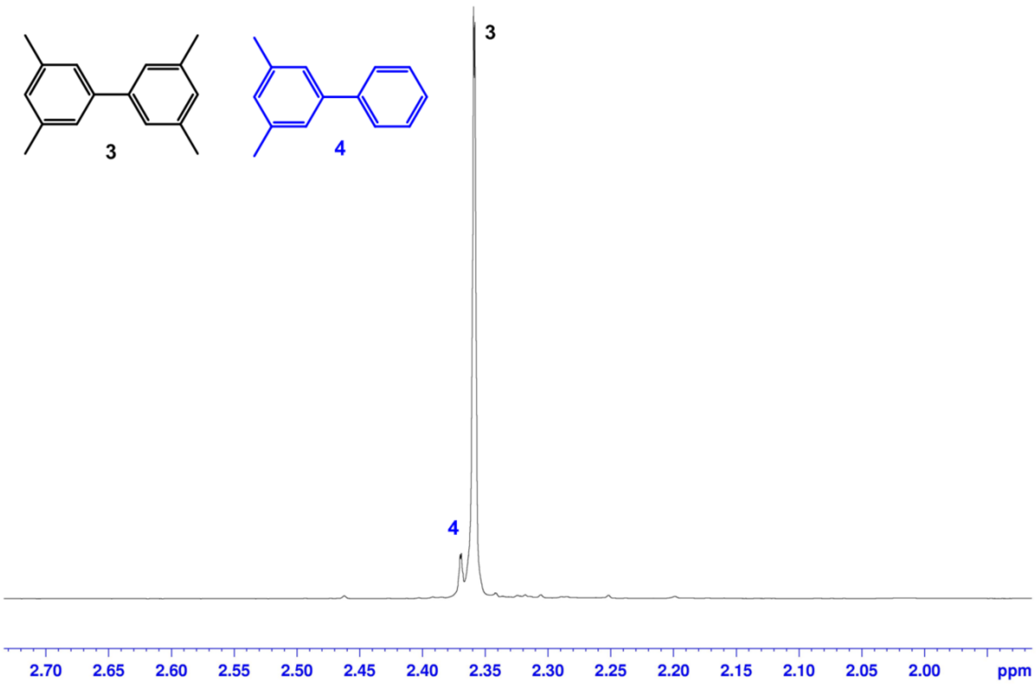
6.8
6.7
ppm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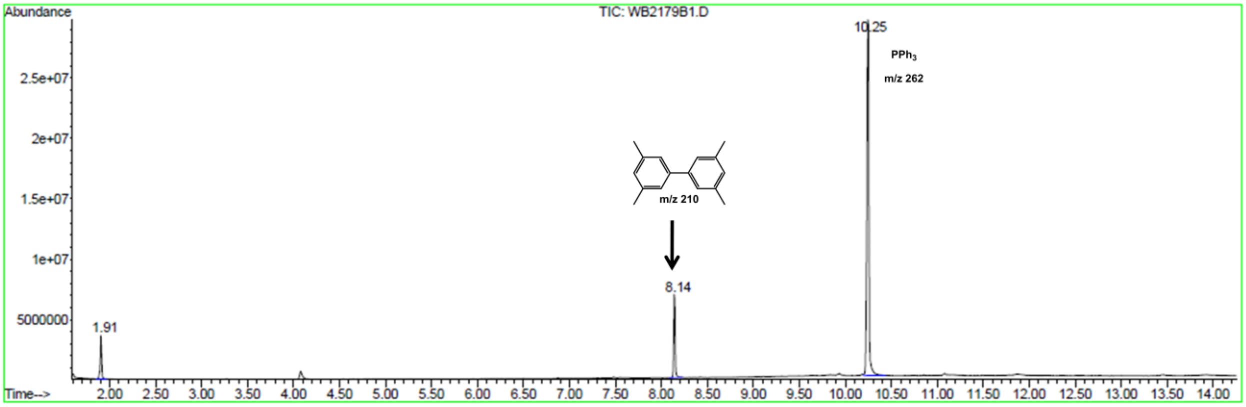
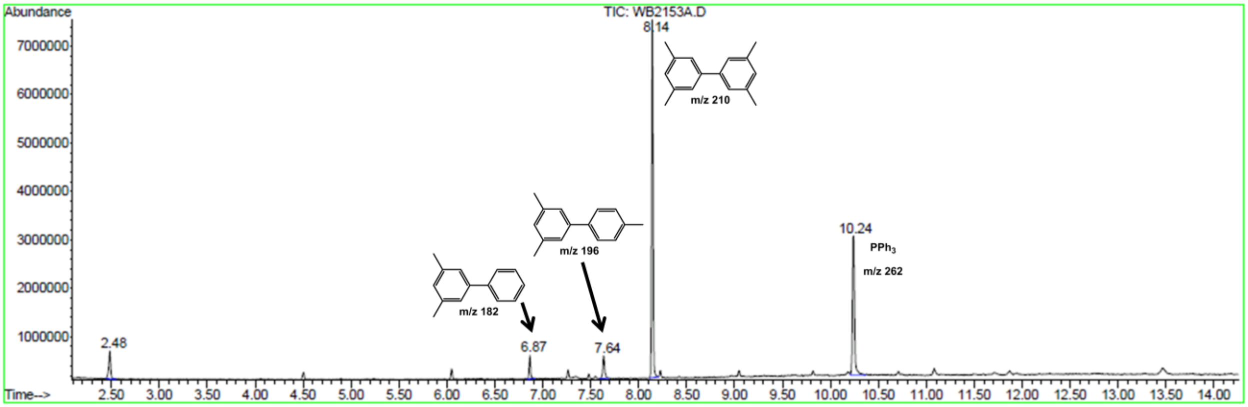
2.40
2.35
2.30
2.25
2.20
2.15
2.10
2.05
2.00
ppm

IV. Sample GC-MS data

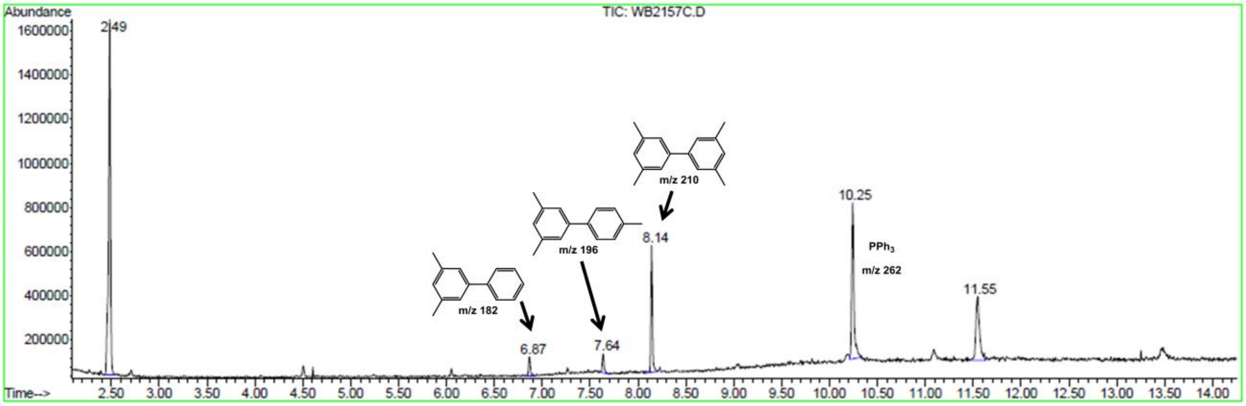
Solution of **1a** in THF and EtOAc (eluent) after silica plug:



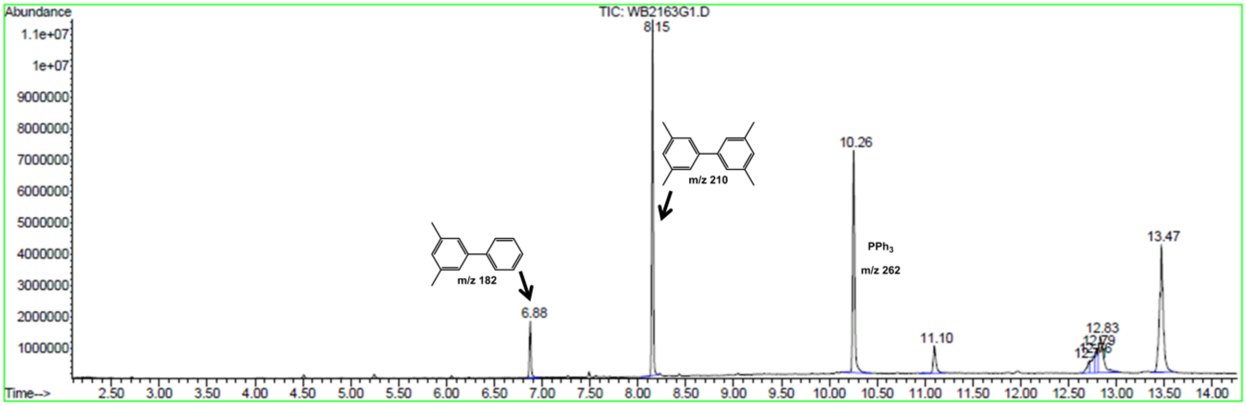
Homo-coupling of **1a** with 5-10 mol% Pd(OAc)$_2$, 5-10 mol% **L1**, >2 equiv. of TolOTf at 58°C in THF:



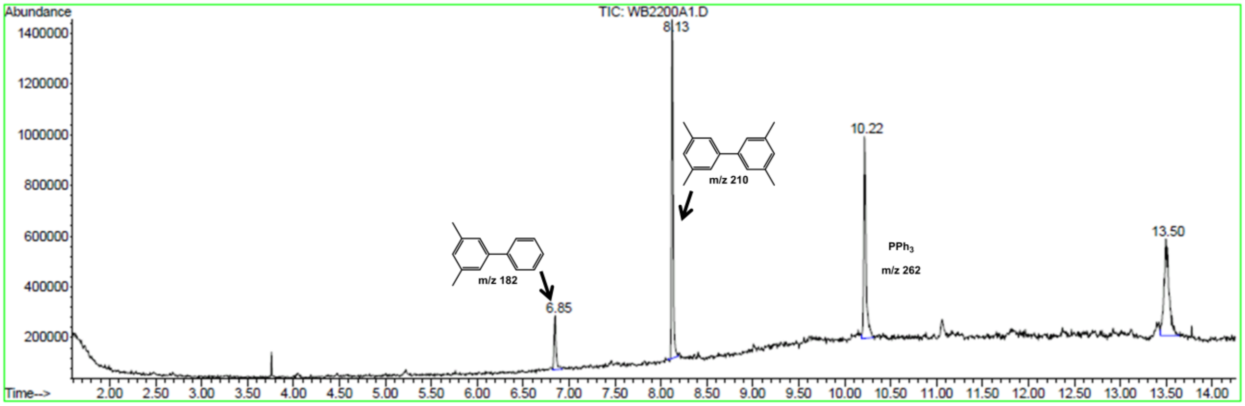
Homo-coupling of **1a** with 5-10 mol% Pd$_2$(dba)$_3$, 5-10 mol% **L1**, >2 equiv. of TolOTf at 58°C in THF:



Homo-coupling of **1a** with 5-10 mol% Pd(OAc)$_2$, 5-10 mol% **L2** at 58°C in THF:



Homo-coupling of **1a** with 5-10 mol% Pd(OAc)$_2$ at 58°C in THF:



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[1] (*a*) D. Weber, M. A. Tarselli, M. R. Gagné, *Angew. Chem. Int. Ed.*, 2009, **48**, 5733–5736; (*b*) D. Weber, M. R. Gagné, *Org. Lett.*, 2009, **11**, 4962–4965.

[2] (*a*) L.-P. Liu, B. Xu, M. S. Mashuta, G. B. Hammond, *J. Am. Chem. Soc.*, 2008, **130**, 17642–17643; (*b*) L.-P. Liu, G. B. Hammond, *Chem. Asian J.*, 2009, **4**, 1230–1236.

[3] H.-T. Yang, S. Zhou, F.-S. Chang, C.-R. Chen, H.-M. Gau, *Organometallics*, 2009, **28**, 5715-5721.

[4] A. V. Vorogushin, X. Huang, S. L. Buchwald, *J. Am. Chem. Soc.*, 2005, **127**, 8146-8149.

[5] M. Pena-López, M. Ayán-Varela, L. A. Sandareses, J. P. Sestelo, *Chem. Eur. J.*, 2010, **16**, 9905–9909.