Supporting information for:

One-Pot Halide and Silver-Free Synthesis of Echavarren's Catalyst

Mohammad Albayer,[a] Robert Corbo,[a] Anthony F. Hill[b] and Jason L. Dutton[a]*

[a] *Department of Chemistry and Physics, La Trobe Institute of Molecular Sciences, La Trobe University, Melbourne, Victoria, Australia.*
[b]*Research School of Chemistry, Australian National University, Canberra, Australian Capital Territory, Australia.*
*Corresponding author: Email: j.dutton@latrobe.edu.au

Experimental

All manipulations were carried out under an atmosphere of dry dinitrogen or argon using standard Schlenk and vacuum line or dry-box techniques. Acetonitrile was dried by distillation under nitrogen from calcium hydride. Gold powder (1.3-2.5 mm) was obtained from Precious Metals Online and [NO]BF4 was obtained from Sigma-Aldrich. All remaining reagents were ordered from Sigma-Aldrich and used as received. ^{1}H, ^{13}C and $^{31}P\{1H\}$ NMR spectra were obtained using a Bruker spectrometer. Best results were obtained by protecting the reaction vessel from direct light with aluminium foil.

Synthesis of [Au(NCMe)(P^{t}Bu$_2$C$_6$H$_4$Ph-2)]BF$_4$ [1]BF$_4$

A 54 mg (0.46 mmol) of $NOBF_4$ in 5mL acetonitrile was added to 100 mg (0.51 mmol) of Au powder in 10 mL acetonitrile. The reaction mixture was then stirred for 3 h in the absence of visible light with a positive nitrogen flow. The reaction mixture was filtered to remove unreacted Au powder. P^{t}Bu$_2$C$_6$H$_4$Ph-2 **(**JohnPhos) (137 mg, 0.46 mmol) was then added, and the reaction mixture was stirred for a further 6 h. The resulting solution was concentrated under reduced pressure, and the addition of Et_2O gave Echavarren's catalyst as a white solid (167 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.88-783 (m, 1 H), 7.60–7.54 (m, 5 H), 7.33–7.29 (m, 1 H), 7.15-7.14 (m, 2 H), 2.50 (s, 3 H), 1.40 (d, J = 16.0 *Hz*, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 149.11 (d, $J_{^{13}C,^{31}P}$ = 12.00 *Hz*), 142.39, 133.32 (d, $J_{^{13}C,^{31}P}$ = 7.0 *Hz*), 133.06 (d, $J_{^{13}C,^{31}P}$ = 4.0 *Hz*), 131.55 (d, $J_{^{13}C,^{31}P}$ = 2.0 Hz), 129.43,

129.30, 127.70, 127.62, 123.52, 119.58, 38.11 (d, $J_{^{13}C,^{31}P}$ = 28.0 *Hz*), 30.84, 2.410. ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) = 57.19.

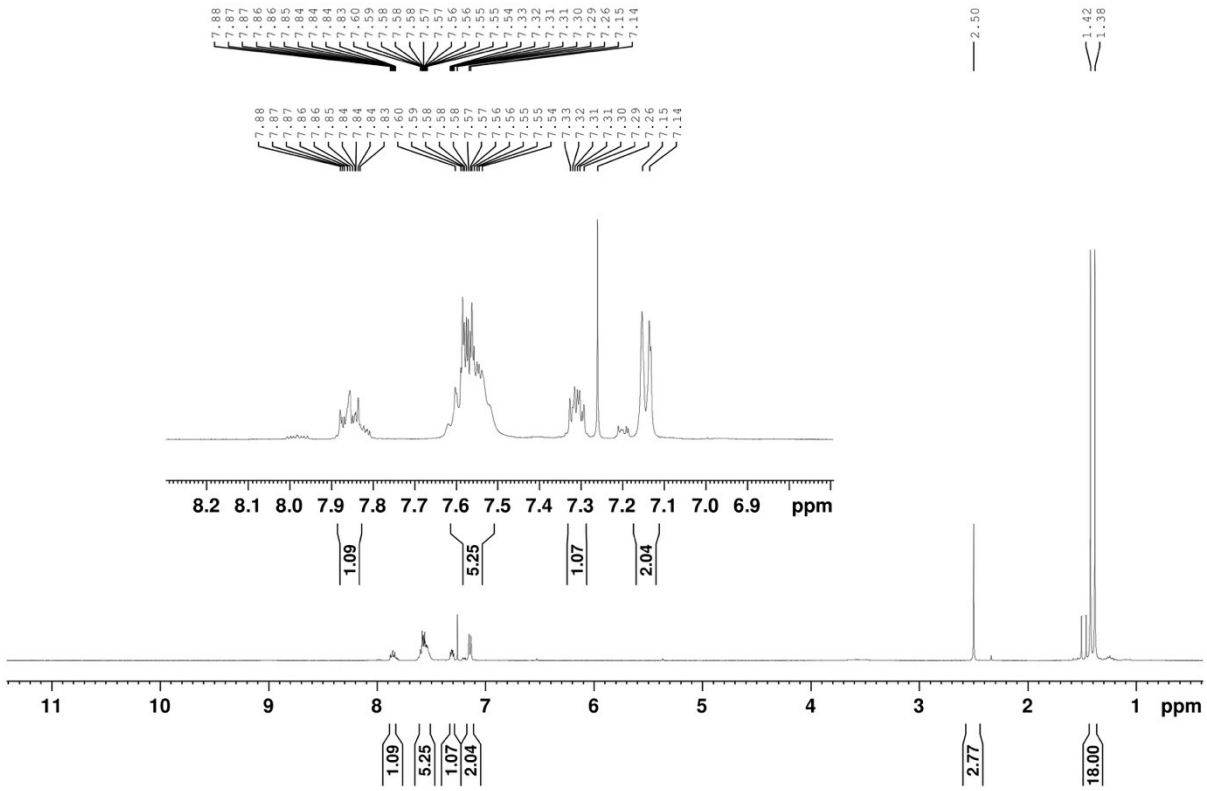

Figure 1. ^{1}H NMR spectrum of **[1]BF_4**.

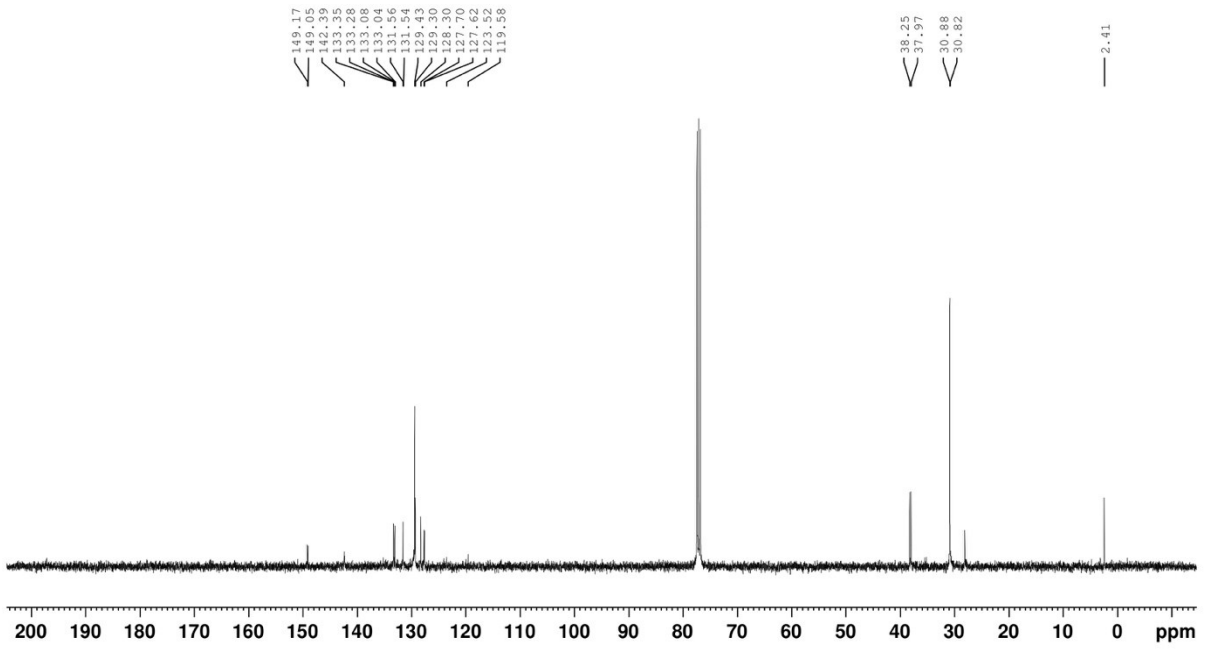

Figure 2. ^{13}C NMR spectrum of **[1]BF_4**.

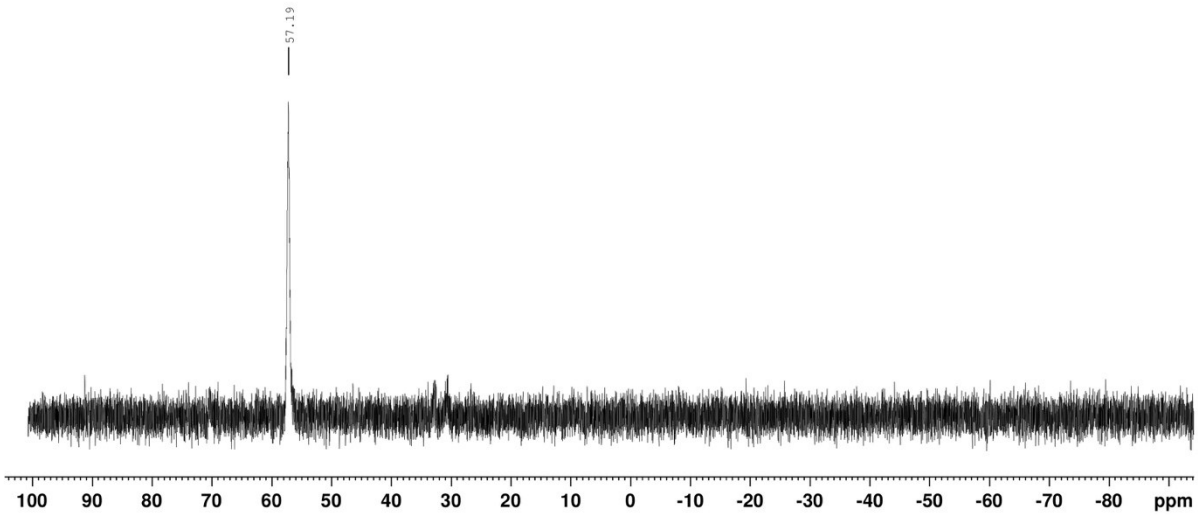

Figure 3. ^{31}P NMR spectrum of **[1]BF$_4$**.