Supporting informations

All experiments were carried out with rhodium complexes, phosphines, aryl boronic acids, and methyl vinyl ketone purchased from Aldrich or Acros and used as received. Potassium aryltrifluoroborates salts were purchased from Aldrich and kept under vacuum for at least 3 days before use. Methanol was previously dried over $Mg(OMe)_2$ and other organic solvents were used as received.

GLC analyses were performed on a varian CP 3900 apparatus equipped with a flame ionisation detector and a CPSil 5CB (25 m × 0.32 mm, Chrompack) column. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on an AC-300 Bruker spectrometer at 23 °C; ^{1}H and ^{13}C chemical shifts are reported in ppm downfield from TMS, ^{19}F chemical shifts are reported in ppm downfield from $CFCl_3$.

Purification and characterizations of the products obtained from methyl vinyl ketone are detailed in reference 9 of the manuscript and are thus not included in the supporting information.

(H. Chochois, M. Sauthier, E. Maerten, Y. Castanet, A. Mortreux, *Tetrahedron* 2006, **62**, 11740)

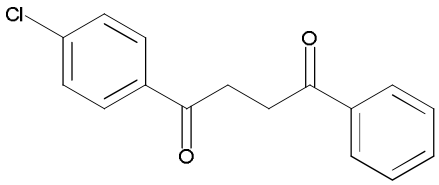
For the products obtained from aryl vinyl ketone : After reaction in methanol according to the typical catalytic experiment, the reaction mixture already containing crystals at room temperature was stored at -20°C in a freezer for three days. The crystals are finally collected by simple filtration and dried under vacuum at room temperature for 3 days. The products were obtained solvent free in pure form according to ^{1}H and ^{13} C NMR. The collected data are identical to those reported in the following reference:

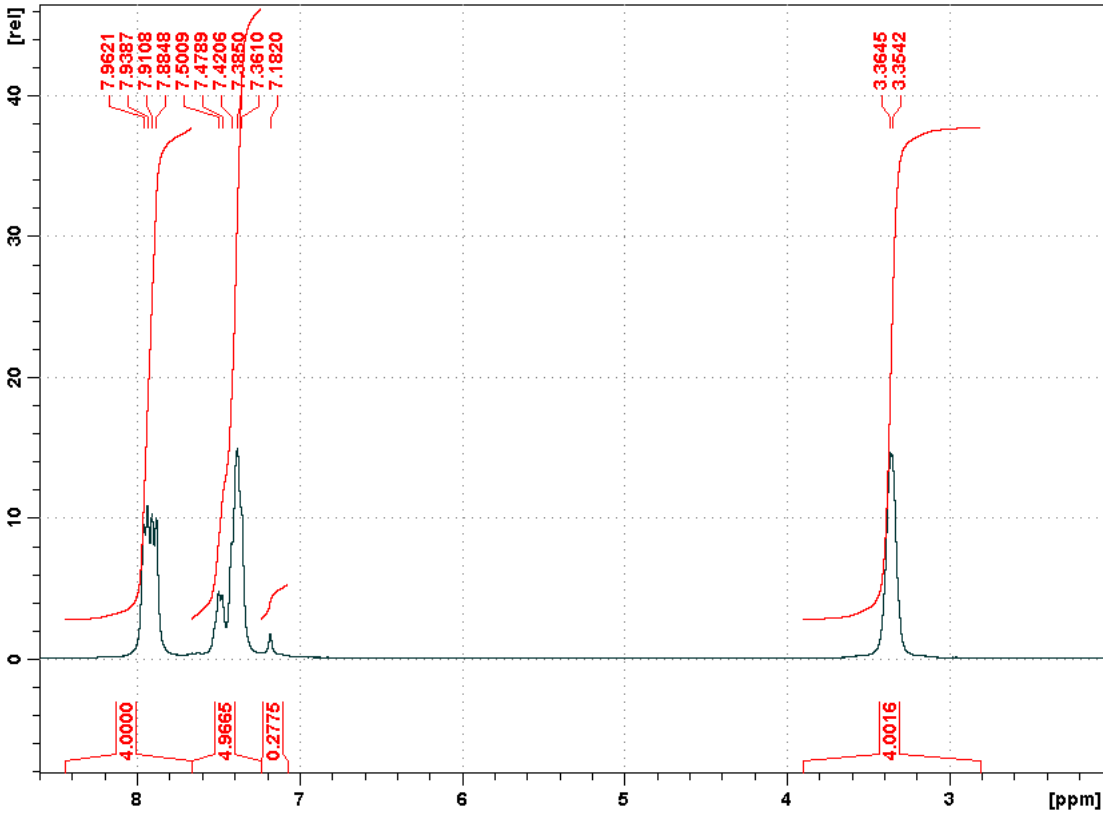
M. Yasuda, S. Tsuji; Y Shigeyoshi, A. Baba *J. Am. Chem. Soc.* 2002, **124**, 7440.

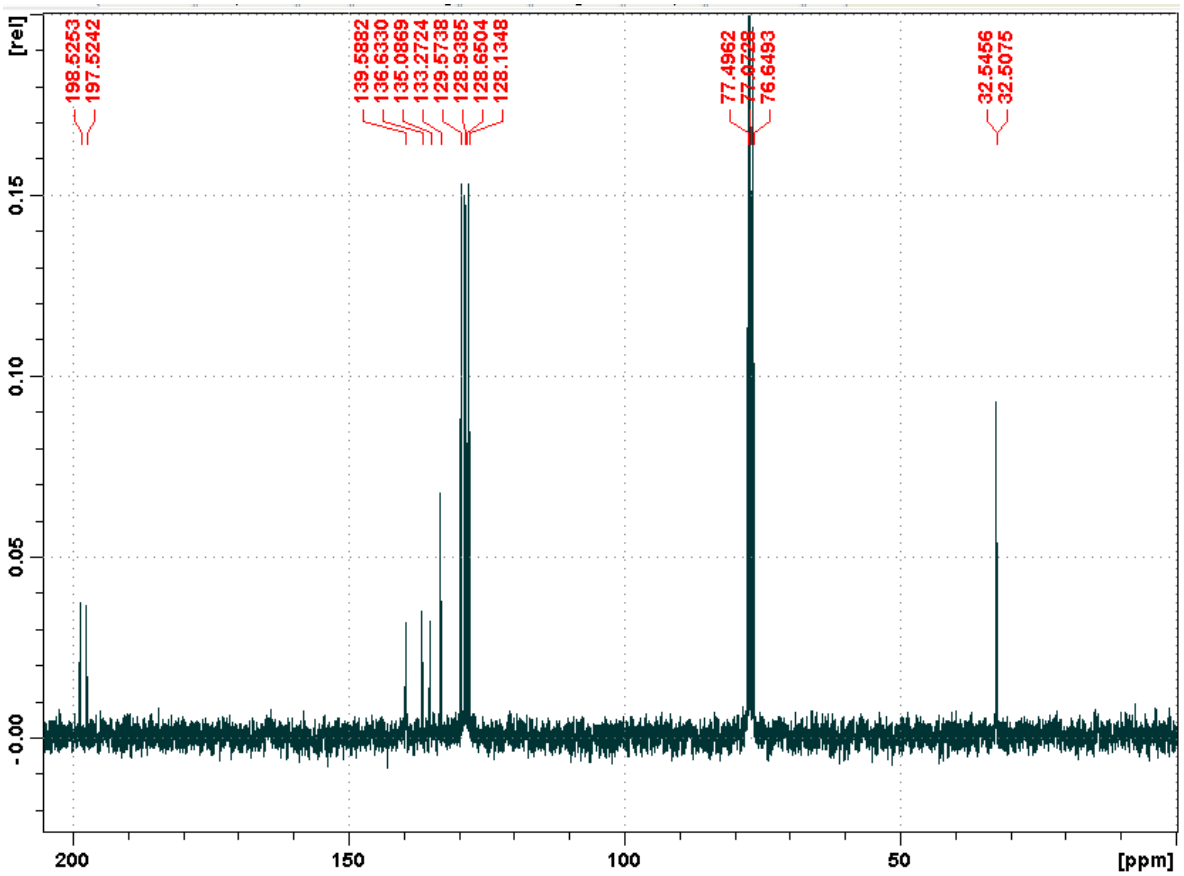
In addition, no remaining boron salt was present according to ^{19}F NMR of a suspension of the products in D_2O.

1-(4-chlorophenyl)-4-phenylbutane-1,4-dione : white crystals, 59 % yield. ^{1}H NMR : (300 MHz, $CDCl_3$) : δ = 7.94 (m, 4H, C*H* aromatic); 7.10-730 (m, 5H, C*H* aromatic); 3.36 (m, 4H, CH_2). ^{13}C NMR : ($CDCl_3$, 75 MHz) δ = 198.52 (s, 1C, Ar*C*O); 197.52 (s, 1C, Ar*C*O); 139.58 (s, 1C, Cl*C* or *C*CO); 136.63 (s, 1C, Cl*C* or *C*CO); 135.09 (s, 1C, Cl*C* or *C*CO); 133.27 (s,

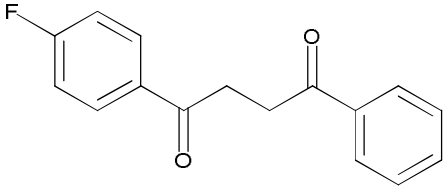
1C, *C*H aromatic); 129.57 (s, 2C, *C*H aromatic); 128.94 (s, 2C, *C*H aromatic); 128.65 (s, 2C, *C*H aromatic); 128.13 (s, 2C, *C*H aromatic); 32.54 (s, 1C, CH_2); 32.50 (s, 1C, CH_2).

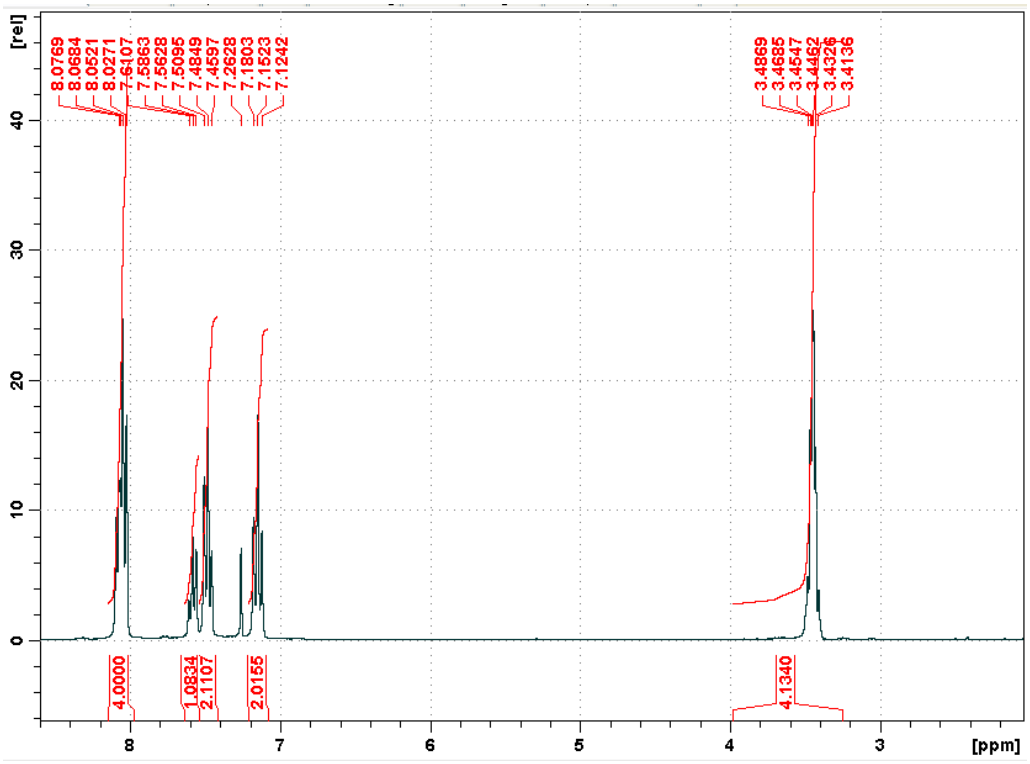


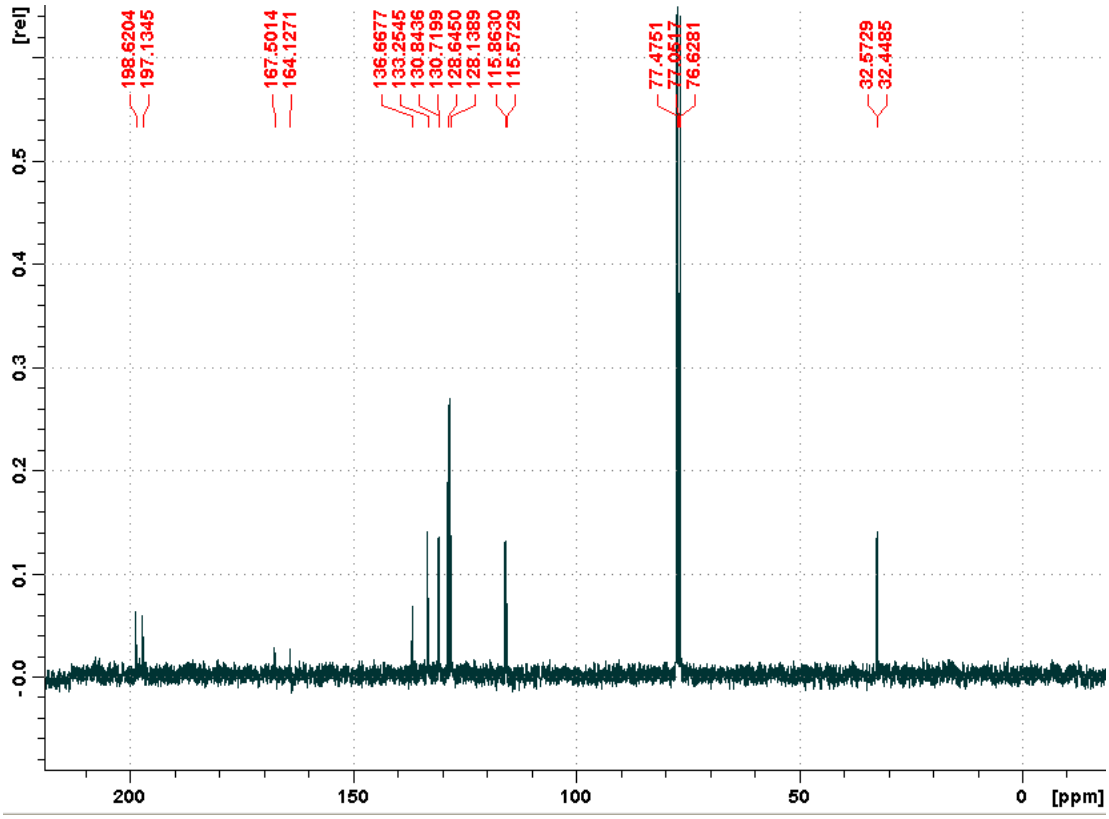




1-(4-fluorophenyl)-4-phenylbutane-1,4-dione : white crystals, 52 % yield. ^{1}H NMR : (300 MHz, $CDCl_3$) : δ = 8.0-8.1 (m, 4H, C*H* aromatic); **7**.58 (t, 1H, $^{3}J_{H-H}$= 7.2 Hz, C*H* aromatic); **7**.48 (dd, 2H, $^{3}J_{H-H}$= 7.2 Hz, $^{3}J_{H-H}$= 7.5 Hz, C*H* aromatic); **7**.15 (dd, 2H, $^{3}J_{H-H}$= 8.4 Hz, $^{3}J_{F-H}$= 8.4 Hz, C*H* aromatic); 3.45 (m, 4H, CH_2). ^{13}C NMR : ($CDCl_3$, 75 MHz) δ = 198,62 (s, 1C, Ar*C*O); 197.13 (s, 1C, Ar*C*O); 165.81 (d, 1C, $^{1}J_{F-C}$= 254.4 Hz, F*C*); 136.67 (s, 1C, *C*CO); 133.25 (s, 1C, *C*H aromatic); 130.77 (d, 2C, $^{2}J_{F-C}$= 9 Hz, *C*H aromatic); 128.64 (s, 2C, *C*H aromatic); 128.13 (s, 2C, *C*H aromatic); 115.1 (d, 2C, $^{3}J_{F-C}$= 21.7 Hz, *C*H aromatic); 32.57 (s, 1C, CH_2); 32.45 (s, 1C, CH_2); ^{19}F NMR : (282 MHz, $CDCl_3$) : δ = -105.2.







1-phenyl-4-p-tolylbutane-1,4-dione : white crystals, 62 % yield. ^{1}H NMR : (300 MHz, $CDCl_3$) : δ = 8.04 (d, 2H, $^{3}J_{H-H}$= 7.6 Hz, C*H* aromatic); 7.93 (d, 2H, $^{3}J_{H-H}$= 7.8 Hz, C*H* aromatic); **7**.54 (t, 1H, $^{3}J_{H-H}$= 7.2 Hz, C*H* aromatic); **7**.47 (dd, 2H, $^{3}J_{H-H}$= 7.2 Hz, $^{3}J_{H-H}$= 7.6 Hz, C*H* aromatic); 7.26 (d, 2H, $^{3}J_{H-H}$= 7.8 Hz, C*H* aromatic); 3.44 (s, 4H, CH_2); 2.41 (s, 3H, CH_3). ^{13}C NMR : ($CDCl_3$, 75 MHz) δ = 198.83 (s, 1C, Ar*C*O); 198.33 (s, 1C, Ar*C*O); 143.95 (s, 1C, CH_3C); 136.79 (s, 1C, *C*CO); 134.28 (s, 1C, *C*CO); 133.16 (s, 1C, *C*H aromatic); 129.29 (s, 2C, *C*H aromatic); 128.61 (s, 2C, *C*H aromatic); 128.26 (s, 2C, *C*H aromatic); 128.15 (s, 2C, *C*H aromatic); 32.62 (s, 1C, *C*H_2); 32.48 (s, 1C, *C*H_2); 21.69 (s, 1C, Ar*C*H_3).