MECHANISTIC STUDIES ON THE HECK-MIZOROKI CROSS-COUPLING REACTION OF A HINDERED VINYLBORONATE ESTER AS A KEY APPROACH TO DEVELOPING A HIGHLY STEREOSELECTIVE SYNTHESIS OF A C1-C7 *Z,Z,E,*-TRIENE SYNTHON FOR VIRIDENOMYCIN.

ANDREI S. BATSANOV, JONATHAN KNOWLES AND ANDREW WHITING
Department of Chemistry, University of Durham, Science laboratories, South Road, Durham DH1 3LE, UK. Email: andy.whiting@durham.ac.uk

LIST OF CONTENTS in file ESI1 **PAGE**

LIST OF CONTENTS (^{1}H, ^{13}C and ^{19}F NMR spectra) in file ESI2 **PAGE**

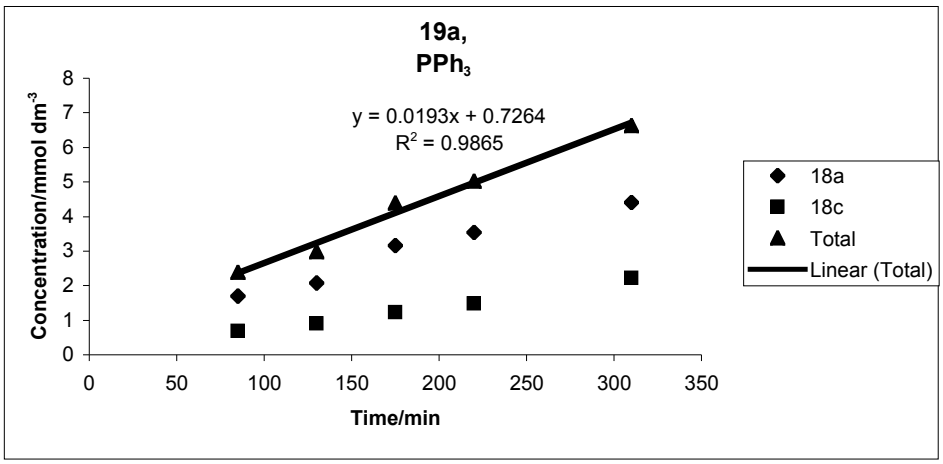
General experimental

All ^{1}H NMR spectra were recorded on either a 400 or 500 spectrometers. ^{13}C NMR spectra were _recorded on the 100 MHz. ^{11}B NMR spectra were _recorded at 128 MHz. Chemical shifts are expressed as _parts per million downfield from the internal _standard TMS. GC-MS analysis was integrated manually using WSearch32 (available by free download from http://www.wsearch.com.au/). Column chromatography was performed _on silica gel, 60 mesh. TLC was _performed on plastic backed _silica gel plates with visualization achieved _using a UV lamp. All glassware was oven dried (130 °C) _before use and cooled under a positive pressure _of argon. Dry solvents were dried by _distillation from CaH_2 (DCM, hydrocarbons) or _sodium-benzophenone ketyl (THF), or by drying using a commercial solvent purification system. All other _materials were purchased directly from standard chemical suppliers and used without further _purification, unless stated otherwise.

Triphenylphosphine catalysis data.

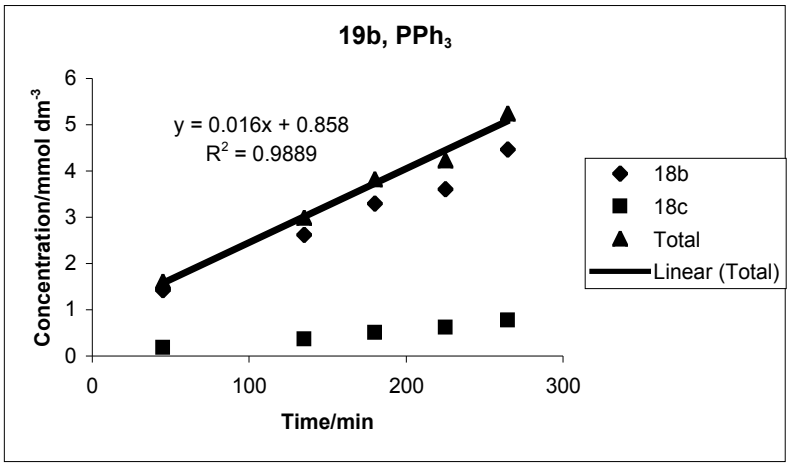
4-Iodoanisole.

Time/min	Concentration 1**9a** /mmol dm^{-3}	Concentration 1**9c** /mmol dm^{-3}	Total concentration /mmol dm^{-3}
85	1.69	0.69	2.38
130	2.09	0.90	2.99
175	3.15	1.24	4.39
220	3.54	1.47	5.02
310	4.41	2.21	6.63



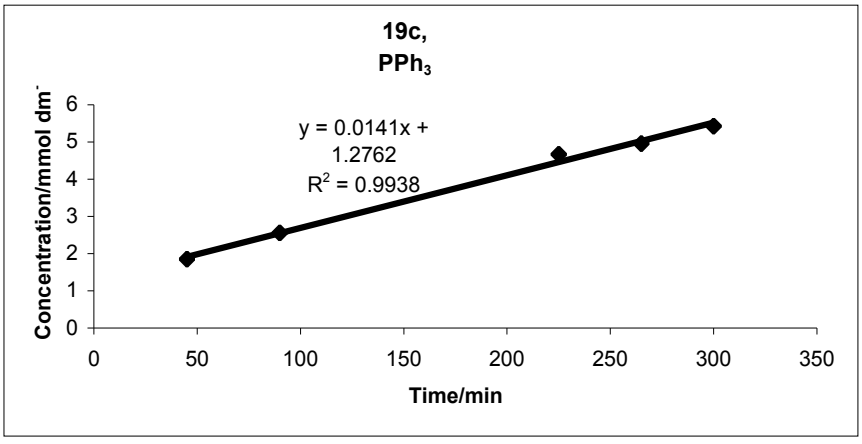
4-Iodotoluene.

Time/min	Concentration 19**b** /mmol dm^{-3}	Concentration 19**c** /mmol dm^{-3}	Total concentration /mmol dm^{-3}
45	1.42	0.19	1.60
135	2.62	0.37	2.99
180	3.30	0.51	3.81
225	3.60	0.62	4.22
265	4.47	0.77	5.24



Iodobenzene

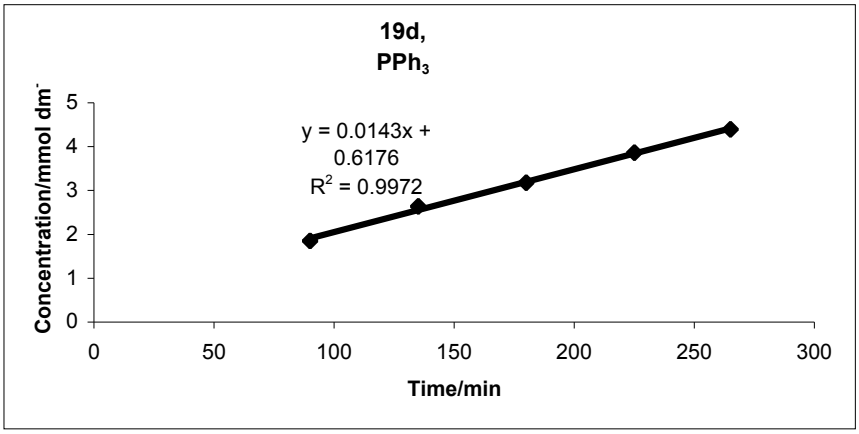
Time/min	Concentration **19c** /mmol dm^{-3}
45	1.86
90	2.55
225	4.67
265	4.95
300	5.43



4-Iodofluorobenzene.

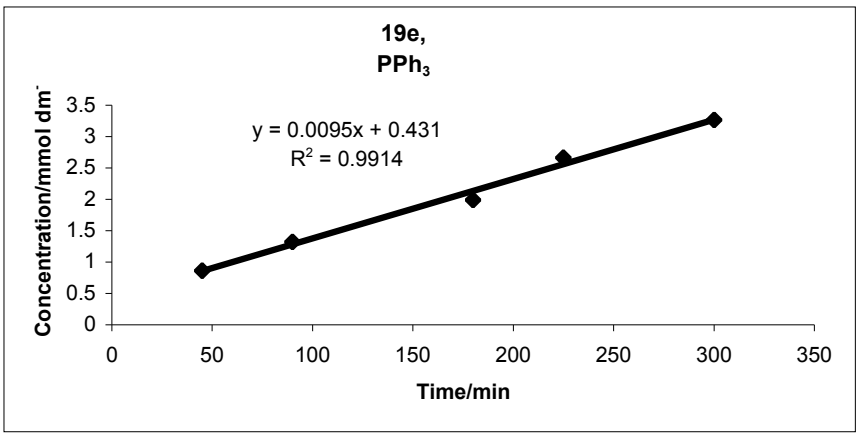
Time/min	Concentration **19d** /mmol dm^{-3}
90	1.85

135	2.64
180	3.18
225	3.87
265	4.39



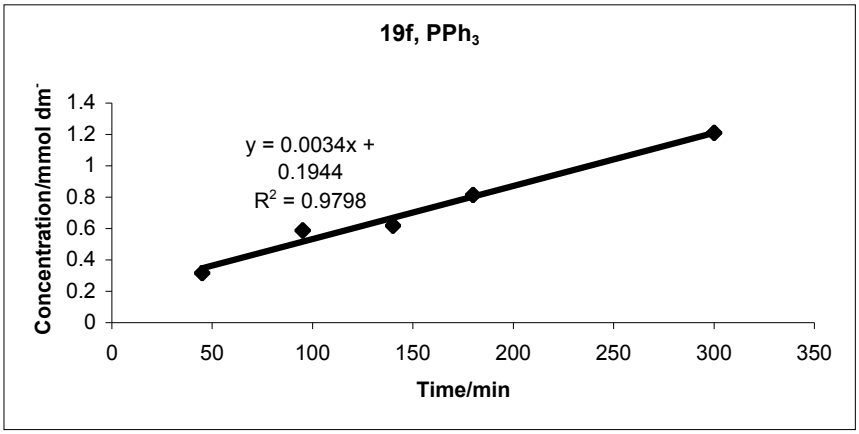
4-Iodochlorobenzene.

Time/min	Concentration **19e** /mmol dm^{-3}
45	0.86
90	1.32
180	1.99
225	2.66
300	3.26



4-Iodonitrobenzene.

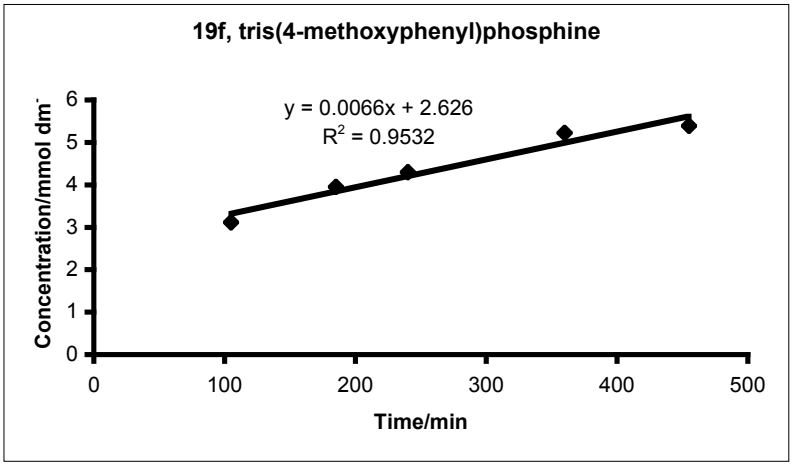
Time/min	Concentration **19f** /mmol dm^{-3}
45	0.28
95	0.51
140	0.54
180	0.71
300	1.05



Tris(4-methoxyphenyl)phosphine catalysis data.

4-Iodonitrobenzene.

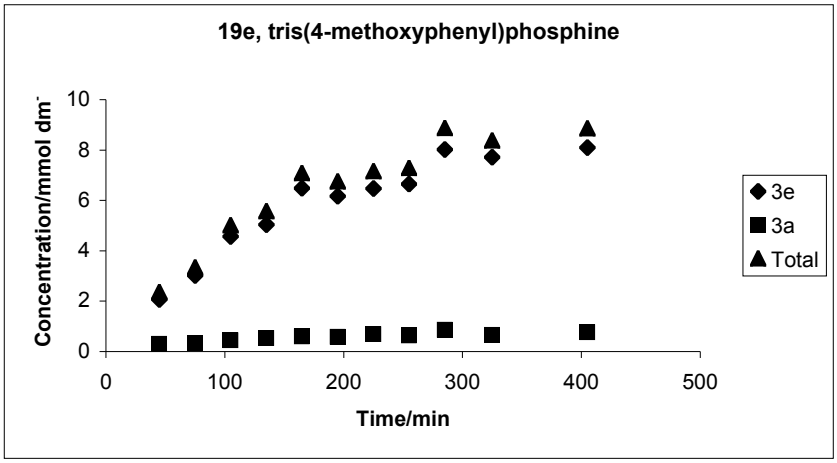
Time/min	Concentration **19f** /mmol dm^{-3}
105	0.91
185	1.74
240	2.09
360	3.02
455	3.18



4-Iodochlorobenzene.

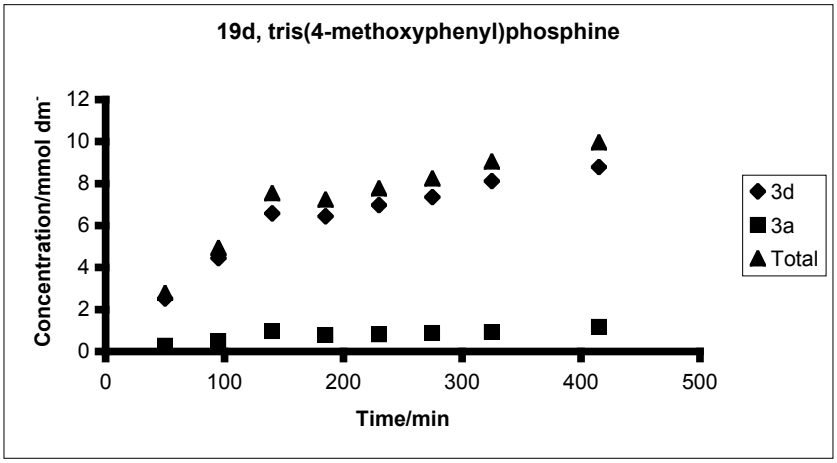
Time/min	Concentration **19e** /mmol dm^{-3}	Concentration **19a** /mmol dm^{-3}	Total concentration /mmol dm^{-3}
45	2.06	0.30	2.36
75	3.02	0.32	3.34
105	4.57	0.44	5.01
135	5.04	0.54	5.58
165	6.49	0.60	7.09
195	6.17	0.58	6.75
225	6.47	0.68	7.15

255	6.65	0.63	7.28
285	8.01	0.86	8.87
325	7.71	0.66	8.37
405	8.10	0.76	8.85



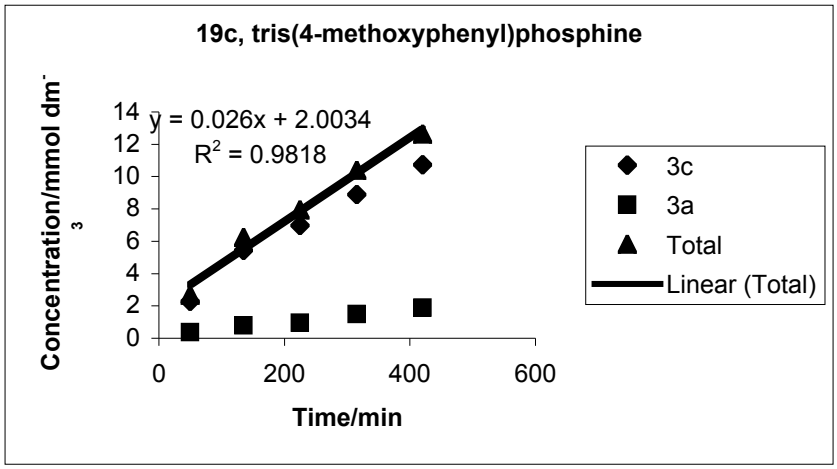
4-Iodofluorobenzene.

Time/min	Concentration **19d** /mmol dm^{-3}	Concentration **19a** /mmol dm^{-3}	Total concentration /mmol dm^{-3}
50	2.53	0.27	2.79
95	4.45	0.49	4.94
140	6.58	0.96	7.54
185	6.45	0.78	7.23
230	6.97	0.80	7.77
275	7.35	0.89	8.24
325	8.11	0.93	9.05
415	8.79	1.18	9.96



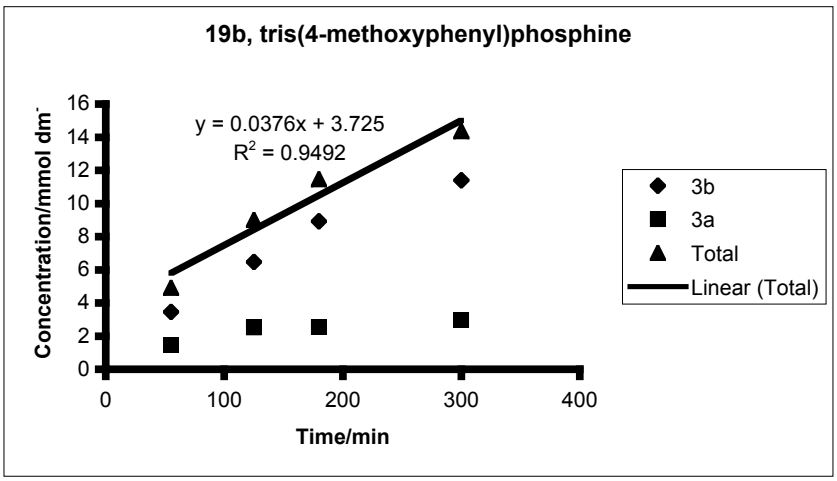
Iodobenzene.

Time/min	Concentration **19c** /mmol dm^{-3}	Concentration **19a** /mmol dm^{-3}	Total concentration /mmol dm^{-3}
50	2.29	0.37	2.67
135	5.44	0.79	6.23
225	6.98	0.95	7.94
315	8.90	1.49	10.39
420	10.74	1.88	12.61



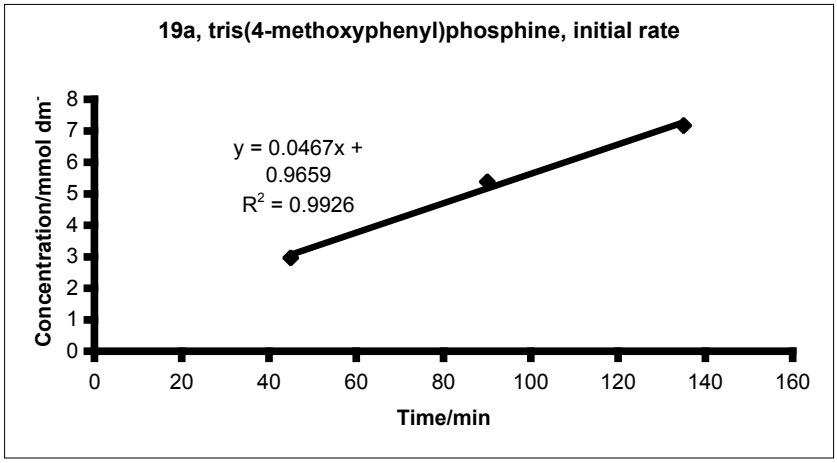
4-Iodotoluene.

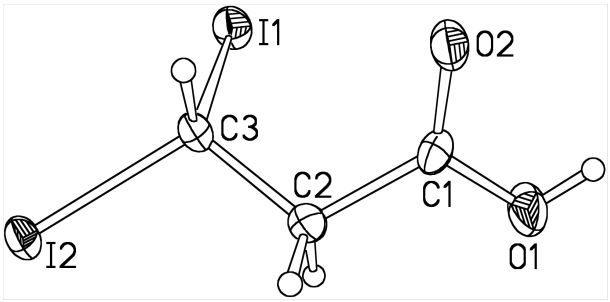
Time/min	Concentration **19b** /mmol dm^{-3}	Concentration **19a** /mmol dm^{-3}	Total concentration /mmol dm^{-3}
55	3.47	1.45	4.92
125	6.48	2.52	9.00
180	8.92	2.53	11.45
300	11.40	2.96	14.36



4-Iodoanisole.

Time/min	Concentration **19a** /mmol dm^{-3}
45	2.96
90	5.38
135	7.17
180	7.52
225	7.70
260	8.77
290	8.59





Single crystal X-ray molecular structure of
3,3-diiodopropionic acid (50% thermal ellipsoids).