

Appendices

Calibration for Gas Chromatography analysis of the rhodium catalysed conjugate addition reaction.

Calibration curve sample preparation

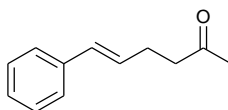
Dihexylether (1 mL, 4.26 mmol) was used as a standard and dissolved in dioxane (3 mL) to afford a 1.42 M stock solution. A number of solutions of each of the following samples over a range of concentrations were made up and an aliquot of the standard stock solution was added to each.

The samples were analysed by GC and the area response recorded. The ratio of the area of sample to standard was calculated and the ratio of sample concentration was calculated. To calculate the Response Factor 'F':

$$\frac{C_{unk}}{C_{std}} = F_{unk} \frac{A_{unk}}{A_{std}}$$

Where C_{unk} = Concentration of unknown, C_{std} = Concentration of standard, A_{unk} = Area of unknown, A_{std} = area of standard. Therefore a plot of C_{unk}/C_{std} against A_{unk}/A_{std} will afford linear plots with gradient = the response factor. To extrapolate the sample concentration from the calibration curve the sample response must be linear throughout the range of concentrations used.

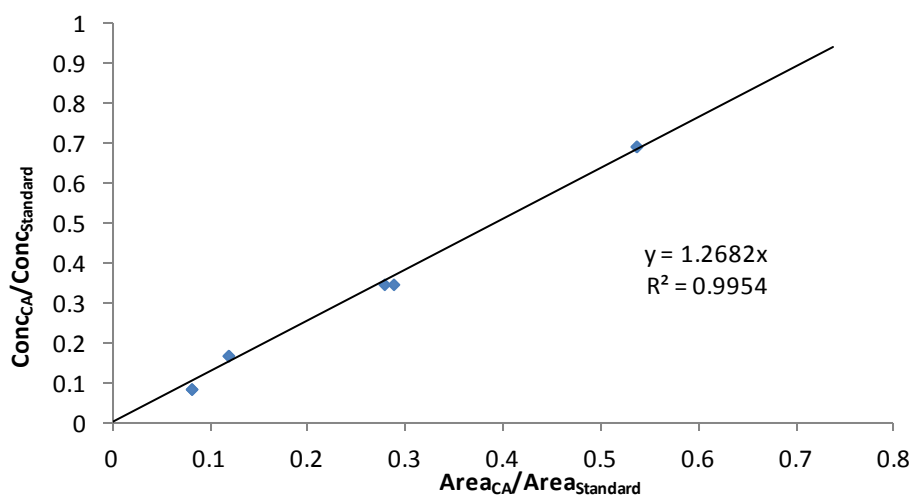
Relative response factor (RRF) for 6-phenyl-hex-5-en-2-one (3.34)



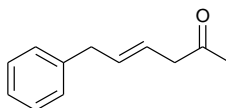
6-Phenyl-hex-5-en-2-one (0.213 g, 0.1225 mmol) was dissolved in dioxane (2 ml). 0.1 mL, 0.2 mL, 0.3 mL, 0.4 mL and 0.5 mL aliquots were taken, and 0.05 mL of the standard stock solution added and each diluted to 1 mL (dioxane) for analysis. Conjugate addition R factor = 1.2682

Entry	[CA]	[Standard]	Area _{CA}	Area _{Standard}	$\frac{Area_{CA}}{Area_{Standard}}$	$\frac{Conc_{CA}}{Conc_{Standard}}$
1	0.0059	0.071	202.8	2465.4	0.082258	0.08309859
2	0.0059	0.071	205.8	2500.3	0.08231	0.08309859
3	0.0071	0.0426	308.5	2573.3	0.119885	0.16666667
4	0.0071	0.0426	302.9	2523.6	0.120027	0.16666667
5	0.0147	0.0426	602.8	2156.2	0.279566	0.34507042
6	0.0147	0.0426	617.8	2137.6	0.289016	0.34507042
7	0.0294	0.0426	1221.8	2273.1	0.537504	0.69014085
8	0.0294	0.0426	1210.6	2250.5	0.537925	0.69014085
9	0.0059	0.071	202.8	2465.4	0.082258	0.08309859
10	0.0059	0.071	205.8	2500.3	0.08231	0.08309859

Relative response factor (RRF) plot for conjugate addition product



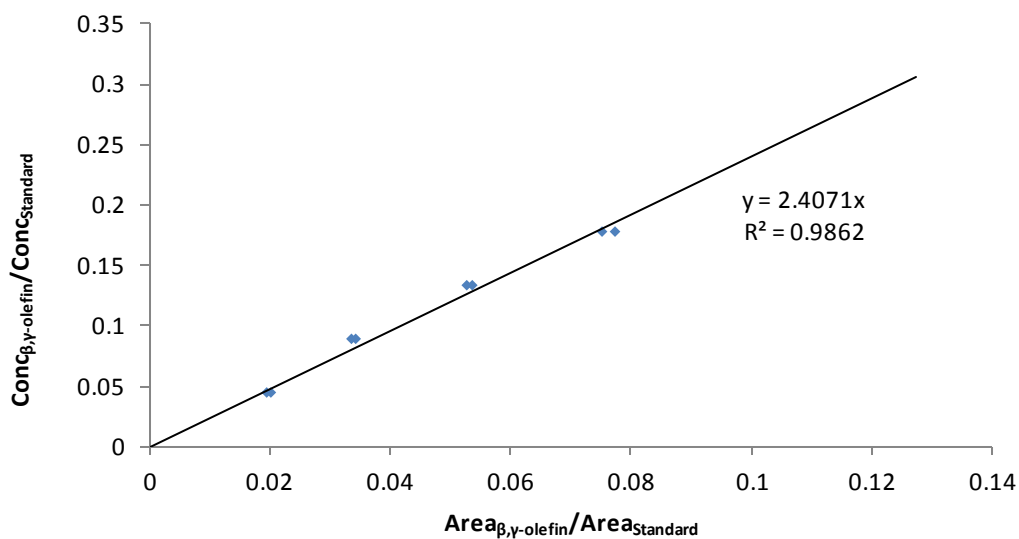
Relative response factor (RRF) for 6-phenyl-hex-4-en-2-one (3.35)



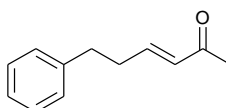
6-Phenyl-hex-4-en-2-one (0.022 g, 0.126 mmol) was dissolved in dioxane (1 ml). 0.1 mL, 0.2 mL, 0.3 mL and 0.4 mL aliquots were taken, 0.2 mL of the standard stock solution was added and each diluted to 1 mL (dioxane) for analysis. β,γ -Olefin R factor = 2.4071

Entry	[β,γ -olefin]	[Standard]	Area $_{\beta,\gamma\text{-olefin}}$	Area $_{\text{Standard}}$	$\frac{\text{Area}_{\beta,\gamma\text{-o}}}{\text{Area}_{\text{Standard}}}$	$\frac{\text{Conc}_{\beta,\gamma\text{-o}}}{\text{Conc}_{\text{Standard}}}$
1	0.0126	0.284	286.5	14248.7	0.020107097	0.044366197
2	0.0126	0.284	280.8	14461.6	0.019416939	0.044366197
3	0.0252	0.284	505.5	15091.6	0.033495454	0.088732394
4	0.0252	0.284	521.7	15254	0.034200865	0.088732394
5	0.0378	0.284	773.3	14685.8	0.052656307	0.133098592
6	0.0378	0.284	746.8	13939.4	0.053574759	0.133098592
7	0.0504	0.284	1086.7	14463.2	0.075135516	0.177464789
8	0.0504	0.284	1105.6	14304	0.077293065	0.177464789

Relative response factor (RRF) plot for β,γ -olefin



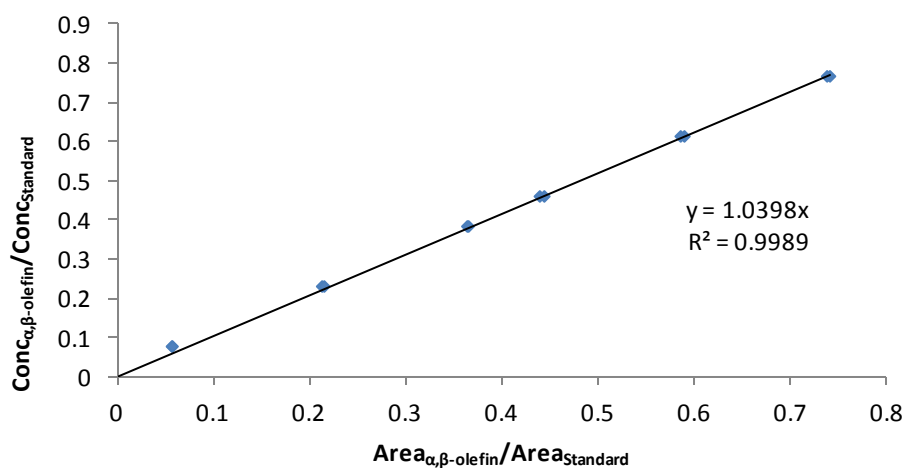
Relative response factor (RRF) for 6-phenyl-hex-3-en-2-one (3.36)



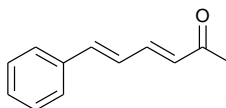
6-Phenyl-hex-3-en-2-one (0.100 g, 0.5739 mmol) was dissolved in dioxane (3.5 ml). 0.1 mL, 0.3 mL, 0.5 mL, 0.6 mL, 0.8 mL and 1 mL aliquots were taken, known volumes of the standard stock solution added and each diluted to 1 mL (dioxane) for analysis. α,β -olefin R factor = 1.0398

Entry	[α,β -olefin]	[Standard]	Area $_{\alpha,\beta\text{-olefin}}$	Area $_{\text{Standard}}$	$\frac{\text{Area}_{\alpha,\beta\text{-o}}}{\text{Area}_{\text{Standard}}}$	$\frac{\text{Conc}_{\alpha,\beta\text{-o}}}{\text{Conc}_{\text{Standard}}}$
1	0.0163	0.213	796.6	13870.7	0.05743041	0.076525822
2	0.0163	0.213	799.6	13772.9	0.05805604	0.076525822
3	0.0489	0.213	2386.9	11174.1	0.21361005	0.229577465
4	0.0489	0.213	2198.6	10185.2	0.21586223	0.229577465
5	0.0815	0.213	3774.2	10352.4	0.36457247	0.382629108
6	0.0815	0.213	3761	10278.2	0.36592010	0.382629108
7	0.0978	0.213	4679.9	10636.7	0.43997668	0.45915493
8	0.0978	0.213	4551.9	10237.3	0.44463872	0.45915493
9	0.1304	0.213	6130.1	10384.4	0.59031817	0.612206573
10	0.1304	0.213	5143.8	8771.2	0.58644199	0.612206573
11	0.163	0.213	6870.8	9263.9	0.74167467	0.765258216
12	0.163	0.213	8013.2	10847.9	0.73868675	0.765258216

Relative response factor (RRF) plot for α,β -olefin product



Relative response factor (RRF) for 6-phenyl-hexa-3,5-dien-2-one (3.37)

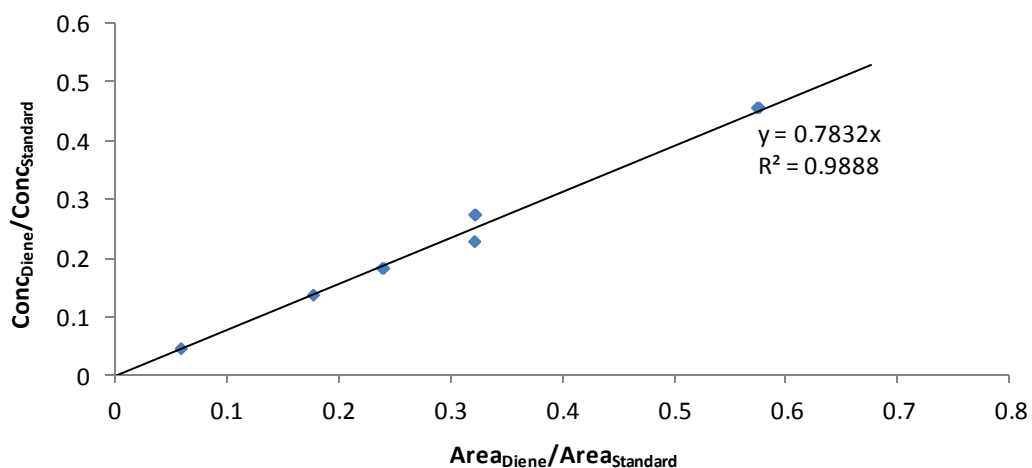


6-Phenyl-hex-3,5-dien-2-one (0.100 g, 0.5807 mmol) was dissolved in dioxane (3.0 ml). 0.1 mL, 0.3 mL, 0.4 mL, 0.5 mL, 0.6 mL and 1 mL aliquots were taken, known volumes of the standard stock solution added and each diluted to 1 mL (dioxane) for analysis.

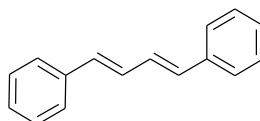
Diene addition product R factor = 0.7832

Entry	[Diene]	[Standard]	Area _{Diene}	Area _{Standard}	$\frac{Area_{Diene}}{Area_{Standard}}$	$\frac{Conc_{Diene}}{Conc_{Standard}}$
1	0.0194	0.426	1004.3	16905.5	0.059406702	0.045539906
2	0.0194	0.426	970.1	16311.3	0.059474107	0.045539906
3	0.0582	0.426	2921.1	16457.5	0.177493544	0.136619718
4	0.0582	0.426	2918.4	16429.5	0.177631699	0.136619718
5	0.0776	0.426	3878.2	16125	0.240508527	0.182159624
6	0.0776	0.426	3999.5	16728.5	0.239083002	0.182159624
7	0.097	0.426	5172.7	16072.9	0.321827424	0.227699531
8	0.097	0.426	5050.4	15708.7	0.321503371	0.227699531
9	0.1164	0.426	5922.3	18421	0.321497204	0.273239437
10	0.1164	0.426	5856.4	18145.2	0.322752023	0.273239437
11	0.194	0.426	10089.6	17573.6	0.574133928	0.455399061
12	0.194	0.426	10174.9	17664.9	0.575995335	0.455399061

Relative response factor (RRF) plot for diene addition product



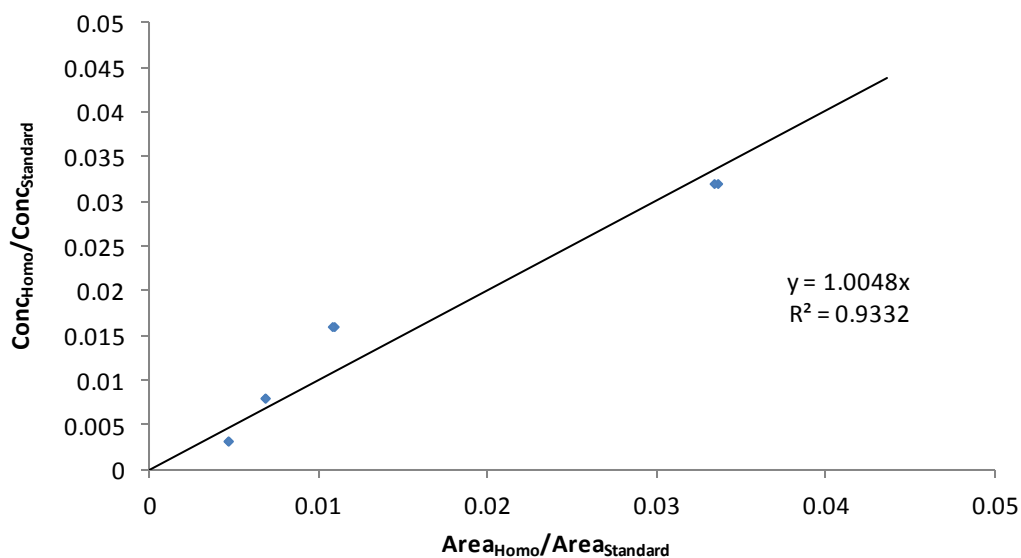
Relative response factor (RRF) for (*E,E*)-1,4-diphenyl-1,3-butadiene (3.38)



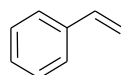
Homocoupled product, (*E,E*)-1,4-diphenyl-1,3-butadiene (0.0014 g, 0.00680 mmol) was dissolved in dioxane (0.3 ml). 0.01 mL, 0.025 mL, 0.05 mL and 0.1 mL aliquots were taken, known volumes of the standard stock solution added and each diluted to 1 mL (dioxane) for analysis. Homocoupled R factor = 1.0048

Entry	[Homocoupled]	[Standard]	Area _{Homo}	Area _{Standard}	$\frac{Area_{Homo}}{Area_{Standard}}$	$\frac{Conc_{Homo}}{Conc_{Standard}}$
1	0.000224	0.07	12.4	2666.1	0.004651	0.0032
2	0.000224	0.07	12.4	2649	0.004681	0.0032
3	0.00056	0.07	18.1	2648.2	0.006835	0.008
4	0.00056	0.07	18.1	2636.2	0.006866	0.008
5	0.00112	0.07	27.8	2542.1	0.010936	0.016
6	0.00112	0.07	28.2	2605.8	0.010822	0.016
7	0.00224	0.07	90.1	2680.6	0.033612	0.032
8	0.00224	0.07	90.1	2697.9	0.033396	0.032

Relative response factor (RRF) plot for homocoupled product



Relative response factor (RRF) styrene (3.39)



Protodeboronated product styrene (0.05 mL, 4.36 mmol) was dissolved in dioxane (4 ml). 0.05 mL, 0.1 mL, 0.4 mL, 0.6 mL, 0.6 mL and 0.8 mL aliquots were taken, 0.3 mL of the standard stock solution added and each diluted to 1.1 mL (dioxane) for analysis. Homocoupled R factor = 1.2439

Entry	[Styrene]	[Standard]	Area _{Styrene}	Area _{Standard}	$\frac{Area_{styrene}}{Area_{standard}}$	$\frac{Conc_{styrene}}{Conc_{standard}}$
1	0.049545455	0.387272727	1566.5	14970.1	0.10464192	0.127934272
2	0.049545455	0.387272727	1550.8	14934.8	0.103838016	0.127934272
3	0.099090909	0.387272727	3113.8	14680	0.212111717	0.255868545
4	0.099090909	0.387272727	3173.5	14942.2	0.212385057	0.255868545
7	0.396363636	0.387272727	13763.5	15214.4	0.904636397	1.023474178
8	0.396363636	0.387272727	13526	15035.8	0.899586321	1.023474178
9	0.594545455	0.387272727	18749.1	15317.1	1.224063302	1.535211268
10	0.594545455	0.387272727	18458	15214.2	1.213208713	1.535211268
11	0.792727273	0.387272727	25385.1	15789.1	1.60776105	2.046948357
12	0.792727273	0.387272727	25750	15930.6	1.616386075	2.046948357

Relative response factor (RRF) plot for protodeboronated product

