Direct Cross-coupling of Organic Halides with Allylic Acetates

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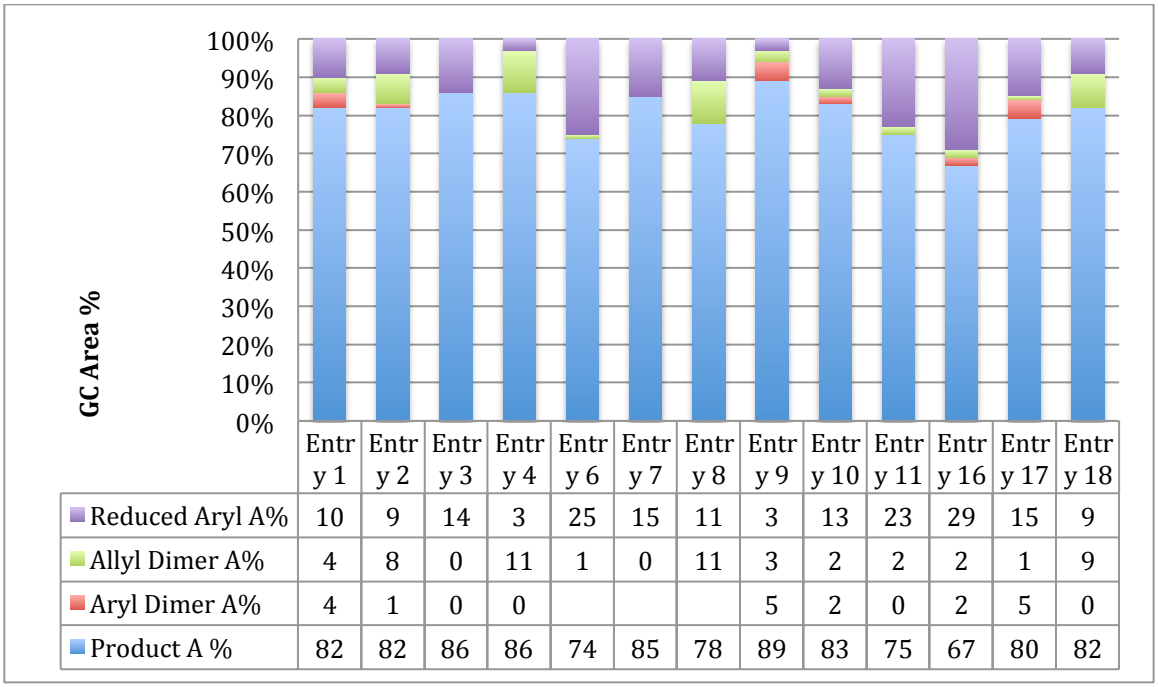
Supporting Information

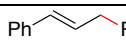
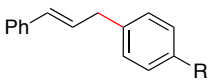
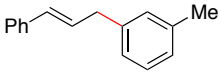
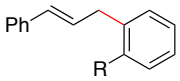
Table of Contents

Table S1: Selectivity Data for the Coupling Reactions of Iodoarenes with Cinnamyl Acetate in Table 2[a]



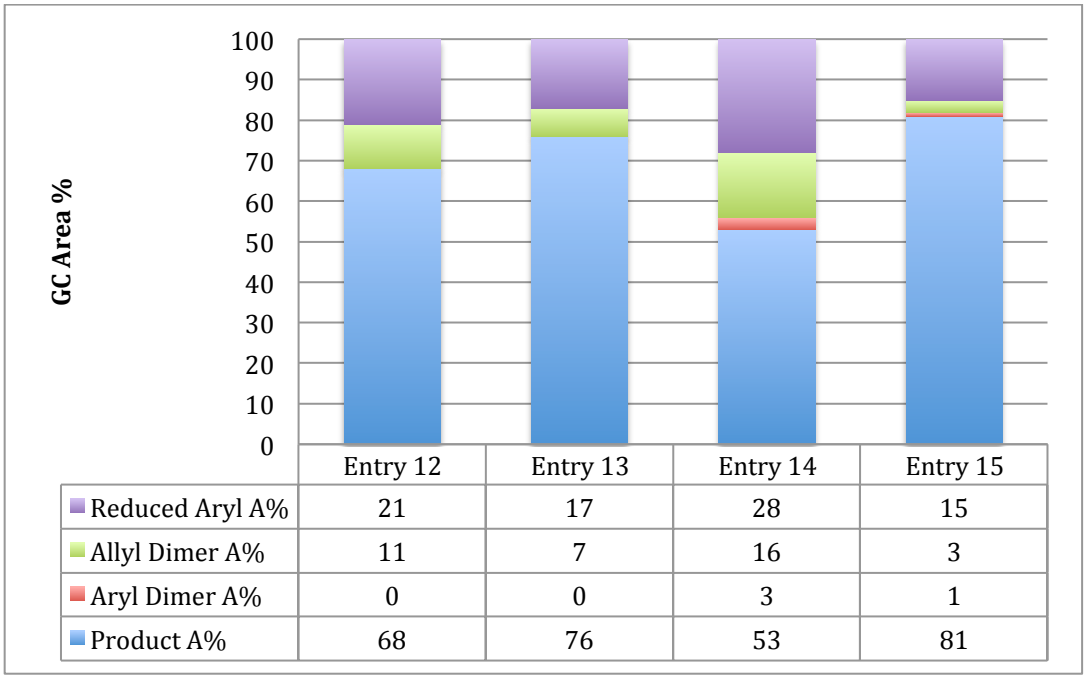
	Entry 1	Entry 2	Entry 3	Entry 4	Entry 6	Entry 7	Entry 8	Entry 9	Entry 10	Entry 11	Entry 16	Entry 17	Entry 18
Reduced Aryl A%	10	9	14	3	25	15	11	3	13	23	29	15	9
Allyl Dimer A%	4	8	0	11	1	0	11	3	2	2	2	1	9
Aryl Dimer A%	4	1	0	0				5	2	0	2	5	0
Product A %	82	82	86	86	74	85	78	89	83	75	67	80	82

[a] GC area% ratios are uncorrected. The high molecular weight of both the product and the aryl dimer for entry 5 prevented GC analysis. The similarly, the high MW for the aryl dimer of entries 6, 7 &8 prevented detection by GC.

Entry	Ar-X	product	yield[b]
		 (**3a**)	
1	I	1 mmol scale, set up in glovebox	88
2	I	10 mmol scale, set up on benchtop	81
			
3	I	R = C(O)Me (**3b**)	71
4	I	R = CHO (**3c**)	70
6	I	R = NHC(O)CF_3 (**3e**)	64
7	I	R = CH_2OTBS (**3f**)	80
8	I	R = NMe_2 (**3g**)	55
9	I	R = Me (**3h**)	86
10	I	R = OMe (**3i**)	83
11	I	R = Br (**3j**)	64
16	I	 (**3n**) 	78
17	I	R = CN (**3o**)	86
18	I	R = OMe (**3p**)	80

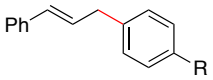
[b] Isolated yields from Table 2.

Table S2: Selectivity Data for the Coupling Reactions of Bromoarenes with Cinnamyl Acetate in Table 2[a]



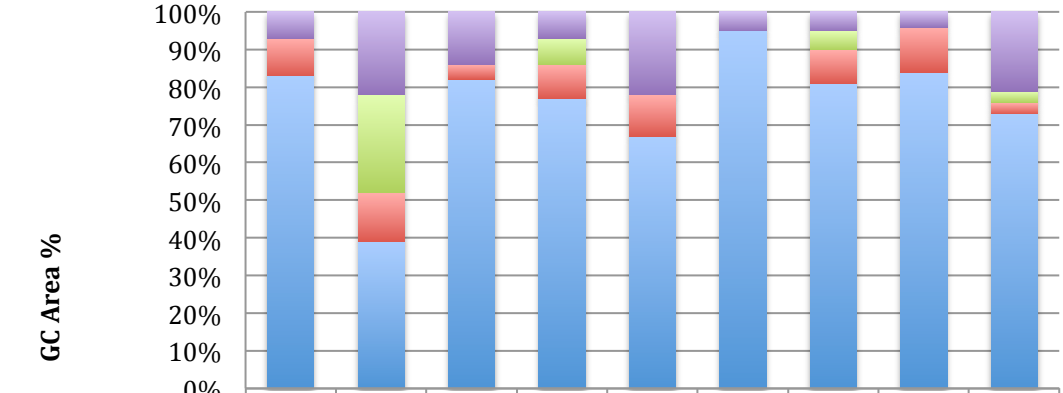
	Entry 12	Entry 13	Entry 14	Entry 15
Reduced Aryl A%	21	17	28	15
Allyl Dimer A%	11	7	16	3
Aryl Dimer A%	0	0	3	1
Product A%	68	76	53	81

[a] GC area% ratios are uncorrected.

Entry	Ar-X	product	yield[b]
			
12	Br	R = CO_2Me (**3k**)	65
13	Br	R = C(O)Me (**3b**)	48
14	Br	R = CF_3 (**3l**)	51
15	Br	R = CN (**3m**)	77

[b] Isolated yields from Table 2.

Table S3: Selectivity Data for the Coupling Reactions of Substituted Allylic Acetates with Iodoarenes in Table 3[a]



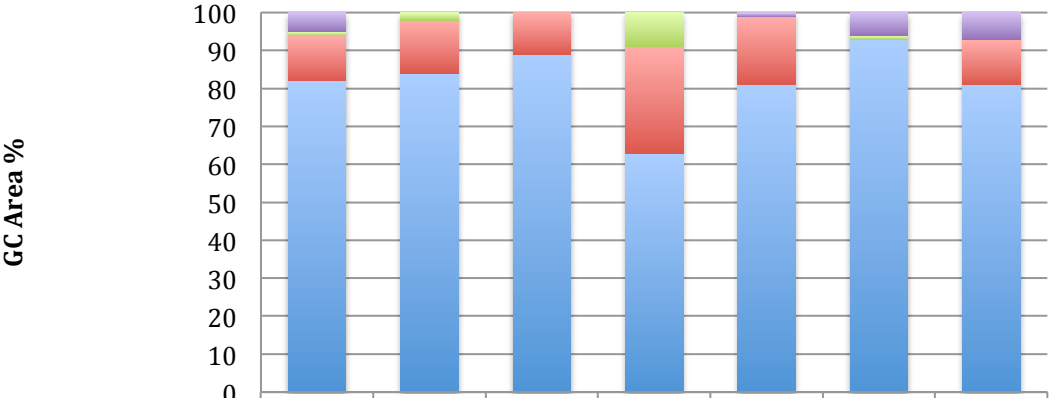
	Entry 1	Entry 2	Entry 3	Entry 4	Entry 5	Entry 6	Entry 7	Entry 8	Entry 9
Reduced Aryl A%.	7	22	14	7	22	5	5	4	21
Allyl Dimer A%	0	26	0	7	0	0	5	0	3
Aryl Dimer A%	10	13	4	9	11	0	9	12	3
Product A%	83	39	83	77	67	95	81	84	73

[a] GC area% ratios are uncorrected.

Entry	allylic acetate	Product	yield[b]
1	OAc (**2b**)	Ph (**4a**)	81
2	OAc, Ph (**2c**)	Ph, Ph (**3a**)	52
3	Ph, OAc (**2d**)	Ph, Ph (**3a**)	75
4	*c*-C_6H_{11}, OAc (**2e**)	*c*-C_6H_{11}, Ph (**4b**)	97
5	OAc (**2f**)	Ac (**4c**)	55
6	OAc (**2g**)	Ph (**4d**)	65
7	OAc (**2h**)	Ph (**4e**)	52
8	OAc (**2i**)	Ph (**4f**)	80
9	OAc, Ph, Me (**2j**)	Ph, Ph, Me (**4g**)	73

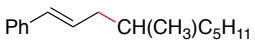
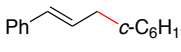
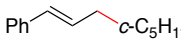
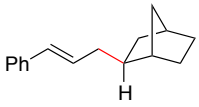
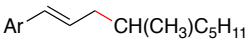
[b] Isolated yields from Table 3.

Table S4: Selectivity Data for the Coupling Reactions of Allylic Acetates with Alkyl Bromides in Table 4[a]



	Entry 1	Entry 2	Entry 3	Entry 4	Entry 5	Entry 6	Entry 7
Reduced Alkyl A%	5	0	0	0	1	6	7
Alkyl Dimer A%	1	2	0	9	0	1	0
Allyl Dimer A%	12	14	11	28	18	0	12
Product A%	82	84	89	63	81	93	81

[a] GC area% ratios are uncorrected. All entries except entry 3 are an average of 2 runs. The alkyl reduction products of entries 2-4 were too low boiling and would elute with solvent, preventing detection by GC analysis. The allyl dimer for entry 6 was too high boiling for GC analysis on our instrument.

Entry	product	yield[b]
1	 (**5a**)	79
2	 (**5b**) Set up in glovebox	88
3	Set up in the benchtop[c]	90
4	 (**5c**)	68
5	 (**5d**)	78
6	 Ar = *p*-MeO-C_6H_4 (**5e**)	79
7	Ar = *p*-F_3C-C_6H_4 (**5f**)	66

[b] Isolated yields from Table 4.

Table S5: Selectivity Data for the Coupling Reactions of Allylic Substrates with a Vinyl Bromide in Tables 5 and 6[a]

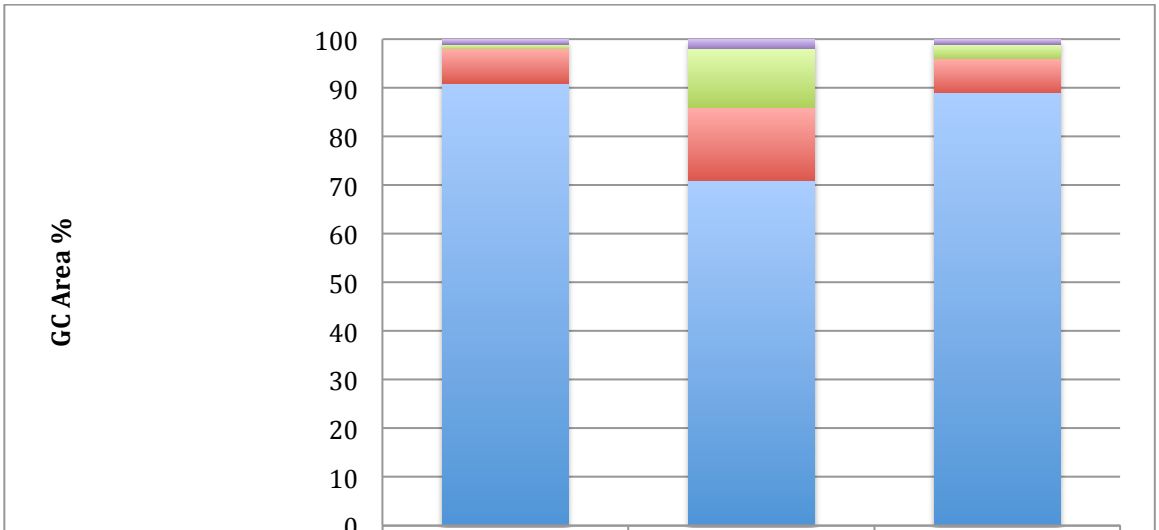
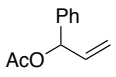
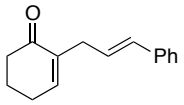
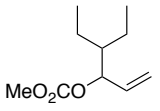
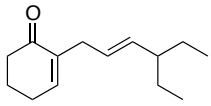
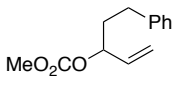
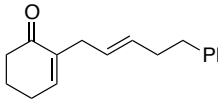


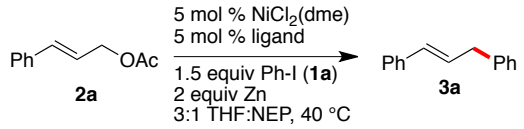
	Table 5, Entry 3	Table 6, Entry 3	Table 6, Entry 4
Cyclohex-2-en-1-one A%	1	2	1
Vinyl Dimer A%	1	12	3
Allyl Dimer A%	7	15	7
Product A%	91	71	89

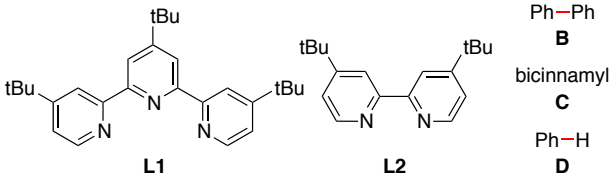
[a] GC area% ratios are uncorrected.

Entry	Starting Material	Product	Yield[b]
Table 5, Entry 3	 **(2c)**	 **(7a)**	78
Table 6, Entry 3	 **(2m)**	 **(7b)**	51
Table 6, Entry 4	 **(2n)**	 **(7c)**	67

[b] Isolated yields from Tables 5 and 6.

Table S6: Control reactions for the coupling of cinnamyl acetate with iodobenzene[a]



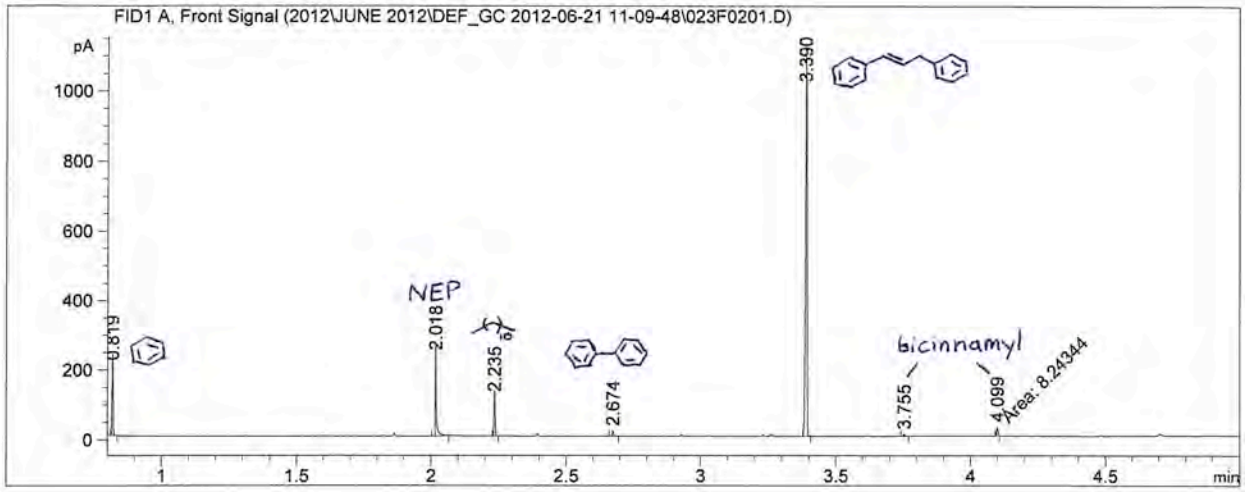


entry	alterations from scheme	time (h)	yield **3a** (%)[b]	yield **D** (%)[b]
1	No alterations	22	90	18
2	No $NiCl_2$(dme)	48	0	2
3	No $NiCl_2$(dme) and no L1	48	0	2
4	No Zn	48	0	0

[a] Reactions were run on a 0.5 mmol scale in 1 ml of 3:1 THF:NEP. [b] Corrected GC yields vs. an internal standard (dodecane). Amount of **4** and **5** produced was negligable in all cases but the standard reaction.

II. Example GC Yield Calculation

GC chromatogram from Table 1, Entry 1 (with terpyridine **L1**):




```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Retention Time
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A, Front Signal

Peak RetTime Sig Type    Area      Height     Area
  #   [min]            [pA*s]      [pA]       %
----|-------|---|----|----------|----------|--------|
   1   0.819  1  BB     64.71152  201.13582 10.38658
   2   2.018  1  BB     72.92727  231.00208 11.70526
   3   2.235  1  BB     37.65450  112.79506  6.04377
   4   2.674  1  BB      5.44882   14.77481  0.87457
   5   3.390  1  BB    431.64377 1054.72852 69.28137
   6   3.755  1  BB      2.40078    5.21727  0.38534
   7   4.099  1  MM      8.24344   24.97758  1.32312

Totals :               623.03010 1644.63112
```

$$mmol\ Product = \frac{(Area\ Product) \times (mmol\ Internal\ Standard)}{(Area\ Internal\ Standard) \times (Correction\ Factor)}$$

$$mmol\ Product\ = \frac{431.64377 \times 0.044}{37.65450 \times 1.12}$$

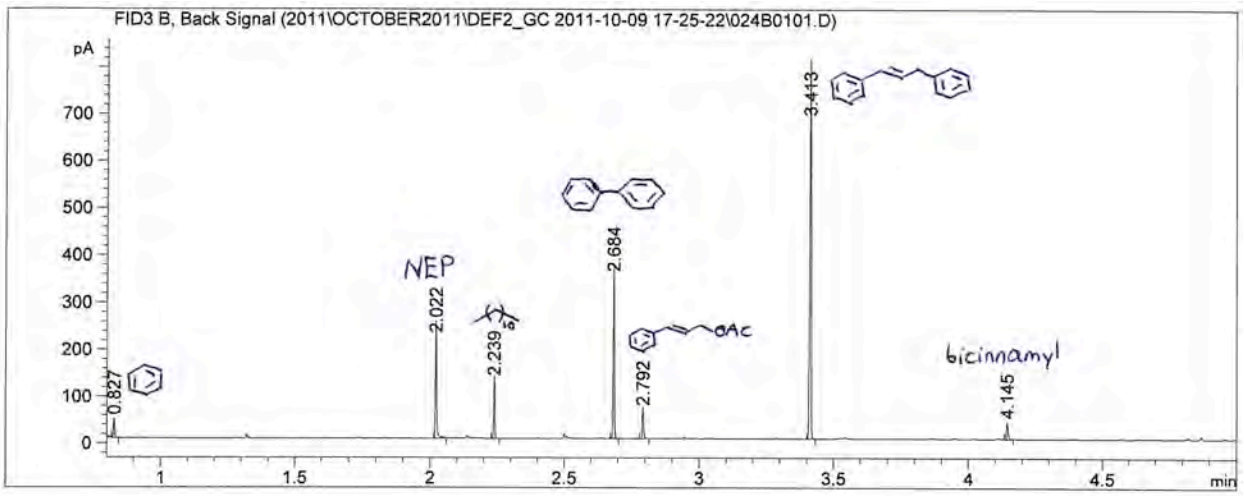
$$mmol\ Product\ = 0.45$$

$$GC\ Yield = \frac{mmol\ Product}{mmol\ Theoretical} \times 100\%$$

$$GC\ Yield = \left(\frac{0.45}{0.50}\right) \times 100\%$$

$$GC\ Yield = 90\%$$

GC chromatogram from Table 1, Entry 2 (with bipyridine **L2**):

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=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Retention Time
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: FID3 B, Back Signal

Peak RetTime Sig Type    Area      Height     Area
  #   [min]             [pA*s]      [pA]       %
----|-------|---|----|----------|----------|--------|
   1   0.827  1  VB     14.26214   38.55714  2.38767
   2   2.022  1  BB     79.97160  214.97862 13.38831
   3   2.239  1  BB     38.76766  123.18441  6.49022
   4   2.684  1  BB    114.61913  344.47751 19.18877
   5   2.792  1  BB     23.92602   59.99182  4.00553
   6   3.413  1  BB    309.75629  675.46704 51.85733
   7   4.145  1  BB     16.02118   34.36098  2.68216

Totals :              597.32401 1491.01752
```

Similar to above, the calculated GC Yield is 62%.