

Supporting Information-SI

Reactivity and Selectivity of Organotin Reagents in Allylation and Arylation: Nucleophilicity Parameter as a Guide

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Fukui Functions calculation

All calculations of organotin and allyl metal reagents were performed at the B3LYP1/LANL2DZ, 6-31G* level of theory using the Gaussian 03 software package.^{S-1} Density functional theory offers a very convenient framework for the discussion of chemical reactivity. The Fukui function,^{S-2} launched by Parr and Yang and defined as the initial response of the electron density due to an infinitesimal perturbation in the total number of electrons N , at constant external (i.e. due to the nuclei) potential $v(r)$. Due to the discontinuity of the electron density with respect to the number of electrons, three different Fukui functions can be introduced, representing the case of a nucleophilic attack $f^+(r)$, an electrophilic attack $f^-(r)$ or a neutral (radical) attack $f^0(r)$. The Fukui function for electrophilic attack $f^-(r)$ and nucleophilic attack $f^+(r)$ can be computed as follows:

$$f^-(r) = \left(\frac{\partial \rho(r)}{\partial N} \right)_{v(r)}^- = \rho_N(r) - \rho_{N-1}(r) \quad (1)$$

$$f^+(r) = \left(\frac{\partial \rho(r)}{\partial N} \right)_{v(r)}^+ = \rho_{N+1}(r) - \rho_N(r) \quad (2)$$

using the Finite Differences Approximation (FDA), where $\rho_N(r)$, $\rho_{N-1}(r)$, and $\rho_{N+1}(r)$ are the densities of the N and $N-1$ and $N+1$ electron system, computed at the geometry of the N -electron system. This Fukui function can be condensed to atoms, using electronic population analyses. In this paper, atomic populations were obtained with the Natural population analysis (NPA) method.^{S-3a}

Chemical potential (μ), Hardness (η) and softness (s) calculation

The electronic chemical potential and the chemical hardness have to be known for the calculation of electrophilicity and nucleophilicity index. The electronic chemical potential is the negative of electronegativity χ , is defined for an N -electron system with external potential $v(r)$ and total energy E as the partial derivative of the energy to the number of electrons at constant external potential and in absence of a magnetic field:^{S-4}

$$\mu = -\chi = \left(\frac{\partial E}{\partial N} \right)_{V(r)} \approx -\frac{I + A}{2} \quad (3)$$

where I and A are the vertical ionization energy and electron affinity, respectively. These two quantities were calculated, again by using the B3LYP methods and LANL2DZ, 6-31G* as basis set. Hardness is defined as the corresponding second derivative as proposed by Parr and Pearson.^{S-5}

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{V(r)} \approx (I - A) \quad (4)$$

It is now common to exclude the factor $\frac{1}{2}$ in the above definition. In this paper we calculated the chemical hardness as the difference between the vertical ionization energy I and electron affinity A.

Softness (S) is the reciprocal of hardness (η).

$$S = \frac{1}{\eta} = \frac{1}{I - A} \quad (5)$$

Where $I = E_{\text{HOMO}}$ = Ionization potential (IP) and $A = E_{\text{LUMO}}$ = Electron affinity (EA)

Electrophilicity Calculation

$$\omega = \frac{\mu^2}{2\eta} \quad (8)^{S-6}$$

where ω represents the electrophilicity defined by parr et al^{S-6} as $\omega = \frac{\mu^2}{2\eta}$ μ is chemical potential and η is hardness

Equation used in two different methods for Nucleophilicity and one equation for electrophilicity calculation

Method I

$$\omega^- = \frac{I^2}{2(I - A)} \quad (6)^{S-7}$$

I is HOMO energy and A is LUMO energy.

Method II

$$\omega^- = \frac{(3I + A)^2}{16(I - A)} \quad (7)^{S-7}$$

I is HOMO energy and A is LUMO energy.

Table SI-1: HOMO and LUMO energy, Chemical potential(μ), Hardness (η), softness (S) of all the 99 Organotin reagents.

Compounds	HOMO	LUMO	HOMO (EV)	LUMO (EV)	η	μ	S
1	-0.19677	0.03878	-5.3541117	1.0552038	6.4093155	2.149454	1.560229
2	-0.18475	0.01304	-5.0270475	0.3548184	5.3818659	2.336115	1.858092
3	-0.20363	0.03042	-5.5407723	0.8277282	6.3685005	2.356522	1.570228
4	-0.20993	0.0284	-5.7121953	0.772764	6.4849593	2.469716	1.54203
5	-0.21227	0.02885	-5.7758667	0.7850085	6.5608752	2.495429	1.524187
6	-0.19758	0.00919	-5.3761518	0.2500599	5.6262117	2.563046	1.777395
7	-0.21433	0.02668	-5.8319193	0.7259628	6.5578821	2.552978	1.524883
8	-0.21848	0.02896	-5.9448408	0.7880016	6.7328424	2.57842	1.485257
9	-0.2191	0.02387	-5.961711	0.6495027	6.6112137	2.656104	1.512582
10	-0.21884	0.02315	-5.9546364	0.6299115	6.5845479	2.662362	1.518707
11	-0.222	0.02318	-6.04062	0.6307278	6.6713478	2.704946	1.498947
12	-0.21816	0.01843	-5.9361336	0.5014803	6.4376139	2.717327	1.553371
13	-0.24502	0.05002	-6.6669942	1.3610442	8.0280384	2.652975	1.245634
14	-0.20895	0.00074	-5.6855295	0.0201354	5.7056649	2.832697	1.752644
15	-0.21323	0.00426	-5.8019883	0.1159146	5.9179029	2.843037	1.689788
16	-0.21652	0.0022	-5.8915092	0.059862	5.9513712	2.915824	1.680285
17	-0.22475	0.00992	-6.1154475	0.2699232	6.3853707	2.922762	1.56608
18	-0.23028	0.01186	-6.2659188	0.3227106	6.5886294	2.971604	1.517766
19	-0.19814	-0.02226	-5.3913894	-0.6056946	4.7856948	2.998542	2.089561
20	-0.23122	-0.00147	-6.2914962	-0.0399987	6.2514975	3.165747	1.599617
21	-0.22926	-0.00468	-6.2381646	-0.1273428	6.1108218	3.182754	1.636441
22	-0.23984	0.00559	-6.5260464	0.1521039	6.6781503	3.186971	1.497421
23	-0.2418	0.00524	-6.579378	0.1425804	6.7219584	3.218399	1.487662
24	-0.23499	-0.00341	-6.3940779	-0.0927861	6.3012918	3.243432	1.586976
25	-0.23765	-0.00639	-6.4664565	-0.1738719	6.2925846	3.320164	1.589172
26	-0.24036	-0.00391	-6.5401956	-0.1063911	6.4338045	3.323293	1.55429
27	-0.238	-0.01119	-6.47598	-0.3044799	6.1715001	3.39023	1.620352
28	-0.24218	-0.00761	-6.5897178	-0.2070681	6.3826497	3.398393	1.566747
29	-0.24202	-0.00865	-6.5853642	-0.2353665	6.3499977	3.410365	1.574804
30	-0.23935	-0.01378	-6.5127135	-0.3749538	6.1377597	3.443834	1.629259
32	-0.24229	-0.01201	-6.5927109	-0.3267921	6.2659188	3.459752	1.595935
31	-0.24557	-0.00903	-6.6819597	-0.2457063	6.4362534	3.463833	1.553699
33	-0.21627	-0.03355	-5.8847067	-0.9128955	4.9718112	3.398801	2.011339
34	-0.24245	-0.01342	-6.5970645	-0.3651582	6.2319063	3.481111	1.604645
35	-0.21691	-0.03383	-5.9021211	-0.9205143	4.9816068	3.411318	2.007384
36	-0.24054	-0.01622	-6.5450934	-0.4413462	6.1037472	3.49322	1.638338
37	-0.21917	-0.03315	-5.9636157	-0.9020115	5.0616042	3.432814	1.975658
38	-0.2476	-0.01108	-6.737196	-0.3014868	6.4357092	3.519341	1.55383
39	-0.21787	-0.03547	-5.9282427	-0.9651387	4.963104	3.446691	2.014868
40	-0.21482	-0.03872	-5.8452522	-1.0535712	4.791681	3.449412	2.08695
41	-0.2349	-0.02819	-6.391629	-0.7670499	5.6245791	3.579339	1.777911
42	-0.2172	-0.04074	-5.910012	-1.1085354	4.8014766	3.509274	2.082693
43	-0.24824	-0.02017	-6.7546104	-0.5488257	6.2057847	3.651718	1.6114
45	-0.23524	-0.03052	-6.4008804	-0.8304492	5.5704312	3.615665	1.795193
44	-0.24497	-0.02325	-6.6656337	-0.6326325	6.0330012	3.649133	1.65755

46	-0.24449	-0.02375	-6.6525729	-0.6462375	6.0063354	3.649405	1.664909
47	-0.2544	-0.01723	-6.922224	-0.4688283	6.4533957	3.695526	1.549572
48	-0.25095	-0.02097	-6.8283495	-0.5705937	6.2577558	3.699472	1.598017
49	-0.25419	-0.01997	-6.9165099	-0.5433837	6.3731262	3.729947	1.569089
50	-0.2549	-0.02243	-6.935829	-0.6103203	6.3255087	3.773075	1.580901
51	-0.25616	-0.02294	-6.9701136	-0.6241974	6.3459162	3.797156	1.575817
52	-0.25627	-0.02289	-6.9731067	-0.6228369	6.3502698	3.797972	1.574736
53	-0.24077	-0.03606	-6.5513517	-0.9811926	5.5701591	3.766272	1.795281
54	-0.25771	-0.02396	-7.0122891	-0.6519516	6.3603375	3.83212	1.572244
55	-0.26002	-0.02678	-7.0751442	-0.7286838	6.3464604	3.901914	1.575681
57	-0.25446	-0.03513	-6.9238566	-0.9558873	5.9679693	3.939872	1.675612
56	-0.25582	-0.03419	-6.9608622	-0.9303099	6.0305523	3.945586	1.658223
58	-0.2499	-0.04453	-6.799779	-1.2116613	5.5881177	4.00572	1.789511
59	-0.26233	-0.03607	-7.1379993	-0.9814647	6.1565346	4.059732	1.62429
60	-0.26233	-0.03642	-7.1379993	-0.9909882	6.1470111	4.064494	1.626807
61	-0.26309	-0.03785	-7.1586789	-1.0298985	6.1287804	4.094289	1.631646
62	-0.2658	-0.03624	-7.232418	-0.9860904	6.2463276	4.109254	1.600941
63	-0.25717	-0.04331	-6.9975957	-1.1784651	5.8191306	4.08803	1.71847
64	-0.25316	-0.04848	-6.8884836	-1.3191408	5.5693428	4.103812	1.795544
65	-0.24441	-0.05427	-6.6503961	-1.4766867	5.1737094	4.063541	1.932849
66	-0.25834	-0.04814	-7.0294314	-1.3098894	5.719542	4.16966	1.748392
67	-0.26814	-0.04237	-7.2960894	-1.1528877	6.1432017	4.224489	1.627816
68	-0.25954	-0.0481	-7.0620834	-1.308801	5.7532824	4.185442	1.738138
69	-0.25774	-0.05149	-7.0131054	-1.4010429	5.6120625	4.207074	1.781876
70	-0.26796	-0.04697	-7.2911916	-1.2780537	6.0131379	4.284623	1.663025
71	-0.26272	-0.05548	-7.1486112	-1.5096108	5.6390004	4.329111	1.773364
72	-0.27119	-0.06065	-7.3790799	-1.6502865	5.7287934	4.514683	1.745568
73	-0.27182	-0.06093	-7.3962222	-1.6579053	5.7383169	4.527064	1.742671
74	-0.26328	-0.06552	-7.1638488	-1.7827992	5.3810496	4.473324	1.858374
75	-0.27213	-0.0612	-7.4046573	-1.665252	5.7394053	4.534955	1.742341
76	-0.27262	-0.06188	-7.4179902	-1.6837548	5.7342354	4.550873	1.743912
77	-0.26559	-0.06678	-7.2267039	-1.8170838	5.4096201	4.521894	1.848559
78	-0.27333	-0.06415	-7.4373093	-1.7455215	5.6917878	4.591415	1.756917
79	-0.26674	-0.06942	-7.2579954	-1.8889182	5.3690772	4.573457	1.862517
80	-0.23884	-0.08779	-6.4988364	-2.3887659	4.1100705	4.443801	2.433048
81	-0.23733	-0.08978	-6.4577493	-2.4429138	4.0148355	4.450332	2.490762
82	-0.23978	-0.08931	-6.5244138	-2.4301251	4.0942887	4.477269	2.442427
83	-0.24676	-0.08854	-6.7143396	-2.4091734	4.3051662	4.561757	2.322791
84	-0.22919	-0.09319	-6.2362599	-2.5356999	3.70056	4.38598	2.702294
85	-0.22952	-0.09357	-6.2452392	-2.5460397	3.6991995	4.395639	2.703288
86	-0.24804	-0.09032	-6.7491684	-2.4576072	4.2915612	4.603388	2.330154
87	-0.24818	-0.09048	-6.7529778	-2.4619608	4.291017	4.607469	2.33045
88	-0.23011	-0.0948	-6.2612931	-2.579508	3.6817851	4.420401	2.716074
89	-0.26965	-0.08585	-7.3371765	-2.3359785	5.001198	4.836578	1.999521
90	-0.25742	-0.09138	-7.0043982	-2.4864498	4.5179484	4.745424	2.213394
91	-0.25964	-0.09268	-7.0648044	-2.5218228	4.5429816	4.793314	2.201198
92	-0.26116	-0.09256	-7.1061636	-2.5185576	4.587606	4.812361	2.179786
93	-0.26516	-0.09203	-7.2150036	-2.5041363	4.7108673	4.85957	2.122751
94	-0.26117	-0.09343	-7.1064357	-2.5422303	4.5642054	4.824333	2.190962
95	-0.28176	-0.08833	-7.6666896	-2.4034593	5.2632303	5.035074	1.899974

96	-0.26806	-0.09331	-7.2939126	-2.5389651	4.7549475	4.916439	2.103073
97	-0.27536	-0.09558	-7.4925456	-2.6007318	4.8918138	5.046639	2.044232
98	-0.27831	-0.10321	-7.5728151	-2.8083441	4.764471	5.19058	2.098869
99	-0.28423	-0.11306	-7.7338983	-3.0763626	4.6575357	5.40513	2.147058

Table SI-2: Nucleophilicity of all the 99 organotin reagents in two different methods.

Compounds	N (MI)	N (MII)
1	4.47163958	4.553405
2	4.25928686	3.970673
3	4.14883895	4.084515
4	3.97494529	3.874875
5	3.93330341	3.835965
6	3.89316687	3.570449
7	3.85629801	3.731024
8	3.81020188	3.707208
9	3.72022625	3.560794
10	3.71403046	3.547104
11	3.65662602	3.488974
12	3.6538237	3.438787
13	3.61226233	3.696924
14	3.53016027	3.145342
15	3.51596168	3.167345
16	3.42920868	3.068939
17	3.4147556	3.126665
18	3.35625964	3.088474
19	3.29286248	2.719494
20	3.158684	2.795857
21	3.14062407	2.754058
22	3.13607088	2.831443
23	3.10567595	2.80092
24	3.08250465	2.713688
25	3.00972169	2.627989
26	3.00826701	2.64525
27	2.94313198	2.536005
28	2.93966182	2.559142
29	2.92849149	2.54217
30	2.89411597	2.47658
32	2.88327917	2.480275
31	2.88307159	2.501043
33	2.87140849	2.307546
34	2.86384461	2.45424
35	2.86011311	2.297256
36	2.84967175	2.422898
37	2.84641932	2.293097
38	2.83575067	2.447118

39	2.82443394	2.258796
40	2.80486127	2.218608
41	2.75357498	2.262952
42	2.7493377	2.164706
43	2.72035819	2.292248
44	2.71918894	2.220818
45	2.71569204	2.268165
46	2.71431528	2.263749
47	2.69356211	2.289725
48	2.68421392	2.258404
49	2.66445573	2.249067
50	2.6298362	2.206304
51	2.61242972	2.189491
52	2.61197822	2.189444
53	2.59558805	2.092995
54	2.58696487	2.163358
55	2.53565976	2.106782
56	2.48977698	2.022687
57	2.48920699	2.027918
58	2.41716304	1.914414
59	2.41664756	1.963976
60	2.41290926	1.959272
61	2.39187396	1.935976
62	2.38829361	1.942364
63	2.37678778	1.894077
64	2.34739777	1.843687
65	2.33957516	1.802867
66	2.31499925	1.824129
67	2.30804609	1.851425
68	2.30717216	1.819121
69	2.28208472	1.783129
70	2.26221635	1.794974
71	2.20693106	1.712185
72	2.1042083	1.619886
73	2.09794754	1.614554
74	2.09702771	1.589396
75	2.09356748	1.610447
76	2.08416934	1.601142
77	2.07164932	1.56767
78	2.05800777	1.57351
79	2.03843218	1.534205
80	1.94629227	1.372983
81	1.92546394	1.349681
82	1.92364737	1.35307
83	1.9099118	1.354355
84	1.90304489	1.311883
85	1.89687885	1.306811

86	1.88427713	1.33195
87	1.88191319	1.329932
88	1.87828013	1.290738
89	1.85800172	1.349848
90	1.84174545	1.308997
91	1.82041619	1.292318
92	1.81696141	1.291817
93	1.80991326	1.29246
94	1.80755497	1.282591
95	1.7908805	1.304921
96	1.78753524	1.275702
97	1.74277421	1.24449
98	1.66161337	1.169883
99	1.55736093	1.079169

Table SI-3: HOMO and LUMO energy, Chemical potential(μ), Hardness (η), softness (S) of all the 12 allylmetal reagents and two allyl tin(II) reagents.

Compounds	HOMO	LUMO	HOMO (EV)	LUMO (EV)	η	μ	S
102	-0.24123	0.01654	-6.56387	0.450053	7.013922	3.056907	1.425736
100	-0.19578	-0.02673	-5.32717	-0.72732	4.599851	3.027249	2.173984
103	-0.24444	0.01811	-6.65121	0.492773	7.143986	3.07922	1.399779
101	-0.2126	-0.02606	-5.78485	-0.70909	5.075753	3.246969	1.970151
104	-0.22566	-0.01938	-6.14021	-0.52733	5.612879	3.333769	1.781617
110	-0.20987	-0.03768	-5.71056	-1.02527	4.68529	3.367918	2.13434
105	-0.20872	-0.0481	-5.67927	-1.3088	4.37047	3.494036	2.288083
111	-0.23095	-0.04538	-6.28415	-1.23479	5.04936	3.75947	1.980449
106	-0.22528	-0.04907	-6.12987	-1.33519	4.794674	3.732532	2.085647
107	-0.25787	-0.04439	-7.01664	-1.20785	5.808791	4.112247	1.721529
108	-0.24918	-0.05644	-6.78019	-1.53573	5.244455	4.15796	1.906776
109	-0.24502	-0.07269	-6.66699	-1.97789	4.689099	4.322445	2.132606

Table SI-4: Nucleophilicity of all the 12 allyl metal reagents in two different methods.

Compounds	N (MI)	N (MII)
102	3.255901	3.031103
100	3.241753	2.636154
103	3.22975	3.018119
101	3.03352	2.488917
104	2.977484	2.501387
110	2.873483	2.273894
105	2.710023	2.077477
111	2.557251	2.002239
106	2.552036	1.971759
107	2.359701	1.87604
108	2.281639	1.753367
109	2.109887	1.553096

In order to analyze the regioselectivity issue in carbonyl allylation via allylstannane, some of the generalized selected examples are provided in Table5-9 and Scheme 1&2.

All the selectivity refers to six membered cyclic transition state and open antiperiplanar transition state. Regioselectivity arising out of mechanism involving Tin-Transition metal (Tm), Tin-Tin, and Tm-tin are excluded.

Table SI-5:

X = OH, OAc, OCO₂Me α-isomer γ-isomer						
X	Solvent	Temp(°C)	Time(h)	Yield(%)	$\gamma:\alpha$	Ref
OCOMe	DMI	50	20	69	100:0	S-8a, S-8e
OCO ₂ Me	DMI	10	84	95	100:0	S-8e
OH	DMI	25	36	63	100:0	S-8b
OH	DMF	25	63	89	100:0	S-8c
OH	DMSO	25	136	34	100:0	S-8d
OH	EG	25	37	78	100:0	S-8d
OH	THF	-10	139	81	100:0	S-8d
OH	Et ₂ O, ultrasound	25	4	76	25:75	S-8f, S-8g

Table SI-6:

$\text{RCHO} + \begin{array}{c} \text{R}^3 \\ \\ \text{R}^1 - \text{C} = \text{C} - \text{X} \\ \\ \text{R}^2 \end{array} \xrightarrow[\text{Cu salt (cat.)}]{\text{SnCl}_2 \cdot 2\text{H}_2\text{O}} \begin{array}{c} \text{OH} \quad \text{R}^3 \\ \quad \\ \text{R} - \text{C} - \text{C} - \text{X} \\ \quad \\ \text{R}^1 \quad \text{R}^2 \end{array}$ Solvent, rt									
R ¹	R ²	R ³	R	X	Cu salt	Solvent	Yield(%)	$\gamma:\alpha$	Ref
Me	H	H	4-ClC ₆ H ₄	Br	CuCl ₂ ·2H ₂ O	DCM-H ₂ O	91	100:0	S-9
Ph	H	H	4-ClC ₆ H ₄	Br	CuCl ₂ ·2H ₂ O	DCM-H ₂ O	72	100:0	S-9
Me	H	H	C ₆ H ₅	Cl	(CuCl + 30% aq NH ₄ F)	THF or Et ₂ O	94	100:0	S-10

Table SI-7:

$\text{R}^1 - \text{CH}=\text{CH}-\text{CH}_2-\text{Y} + \text{R}-\text{CHO} \xrightarrow[\text{condition}]{\text{SnX}_2} \begin{array}{c} \text{R}^1 \\ \\ \text{CH}=\text{CH}-\text{CH}(\text{OH})-\text{R} \\ \\ \text{H} \end{array} + \begin{array}{c} \text{R}^1 \\ \\ \text{CH}=\text{CH}-\text{CH}(\text{OH})-\text{R} \\ \\ \text{H} \end{array}$ $\gamma-$ $\alpha-$							
#	R ¹	Y	carbonyl	SnX ₂ , condition	Yield (%)	$\gamma:\alpha$	Ref
2	ⁿ Pr	OH	ⁿ PrCHO	SnI ₂ , Me ₃ SiCl, NaI, MeCN-H ₂ O	64	3:97	S-11a
5	Me	Br	PhCHO	SnCl ₂ ·2H ₂ O, [bmim]BF ₄ , H ₂ O, 24h	96	90:10	S-11b
6	Me	Cl	PhCHO	SnCl ₂ ·2H ₂ O, KI, H ₂ O	79	65:35	S-12
7	Ph	Cl	PhCHO	SnCl ₂ ·2H ₂ O, KI, H ₂ O	80	57:43	S-12

Table SI-8:

$\text{R}-\text{CH}=\text{CH}-\text{CH}_2-\text{Br} + \text{PhCHO} \xrightarrow[\text{condition}]{\text{Sn}} \begin{array}{c} \text{R} \\ \\ \text{CH}=\text{CH}-\text{CH}(\text{OH})-\text{Ph} \\ \\ \text{H} \end{array} + \begin{array}{c} \text{R} \\ \\ \text{CH}=\text{CH}-\text{CH}(\text{OH})-\text{Ph} \\ \\ \text{H} \end{array}$ $\gamma-$ $\alpha-$						
#	R	Nature of Sn(0)	Condition	Yield(%)	$\gamma:\alpha$	Ref
1	CO ₂ Et	powder	H ₂ O, rt	71	100:0	S-15
2	CO ₂ Et	powder	CTAB, ^c H ₂ O, rt	81	100:0	S-15
3	CO ₂ Et	powder	<i>n</i> Bu ₄ NBr, H ₂ O, rt	73	100:0	S-15
4	CO ₂ Et	powder	PEG, ^d H ₂ O, rt	71	100:0	S-15
5	CO ₂ Et	powder	Silica gel, H ₂ O, rt	74	100:0	S-15
6	CO ₂ Et	20 nm	H ₂ O, rt, 12 h	61	100:0	S-16
7	Me	commercial ^a	THF, rt, 12 h	76	100:0	S-17a
8	Me	powder	DCM-H ₂ O, rt, 48 h	83	45:55	S-17b
9	Me	325 mesh (99.8%)	H ₂ O, aq. HCl, ^c rt, 5 min	90	100:0	S-17c
10	Me	commercial-powder	bmim, ^b rt, overnight	75	100:0	S-17d
11	Me	commercial-powder	emim, ^f rt, overnight	75	100:0	S-17d
12	Me	20 nm	H ₂ O, rt, 24 h	85	61:39	S-16
13	Me	powder	H ₂ O, NaBF ₄ , rt, 10 h	73	0:100	S-17e
14	Ph	powder	H ₂ O, rt, 3 day	80	1:99	S-17b

Table SI-9:

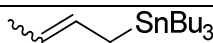
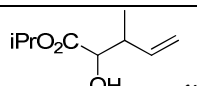
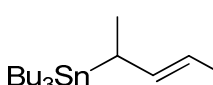
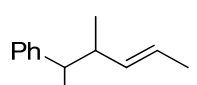
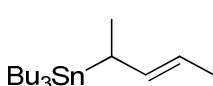
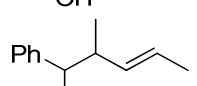
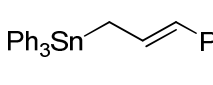
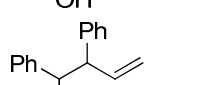
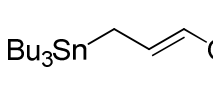
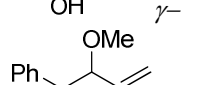
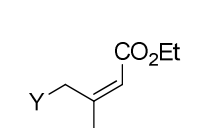
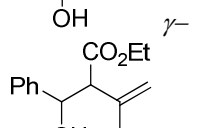
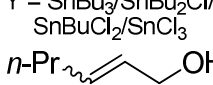
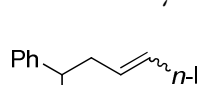
#	allyltin	aldehyde	condition	Product	Ref
1		CHOCO ₂ iPr	BF ₃ .Et ₂ O, CH ₂ Cl ₂ , -78 °C	 γ-	S-18
6		PhCHO	150 °C, neat, 18h	 γ-	S-19
7		PhCHO	BF ₃ .Et ₂ O, CH ₂ Cl ₂ , -78 °C, 4h	 γ-	S-19
8		PhCHO	BF ₃ .Et ₂ O, CH ₂ Cl ₂ , -78 °C	 γ-	S-20
9		PhCHO	BF ₃ .Et ₂ O, CH ₂ Cl ₂ , -78 °C	 γ-	S-13
10	 Y = SnBu ₃ /SnBu ₂ Cl/ SnBuCl ₂ /SnCl ₃	PhCHO	BF ₃ .Et ₂ O, CH ₂ Cl ₂ , -78 °C, Bu ₄ NF, THF	 γ-	S-14
11		PhCHO	PdCl ₂ (MeCN) ₂ , SnCl ₂ , Et ₂ O, 10-15 °C, ultrasound	 α-;γ- = 98:2	S-8f

Chart SI-1 Tin(II) halide promoted reaction of allyl halide and aldehyde in presence of tetraalkylammonium halides as additive in biphasic medium. ^{S-21}

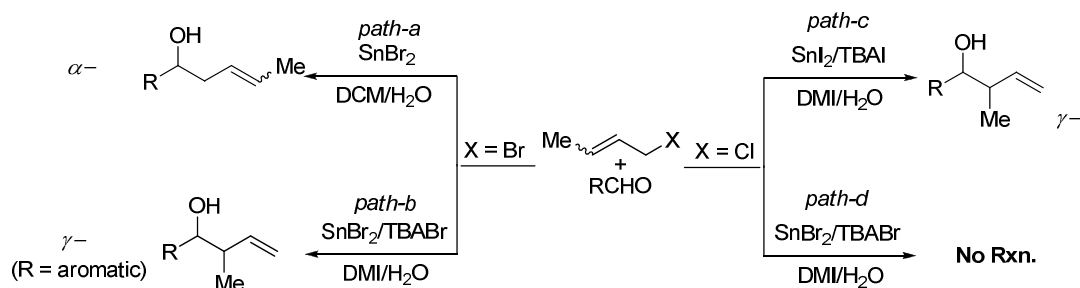
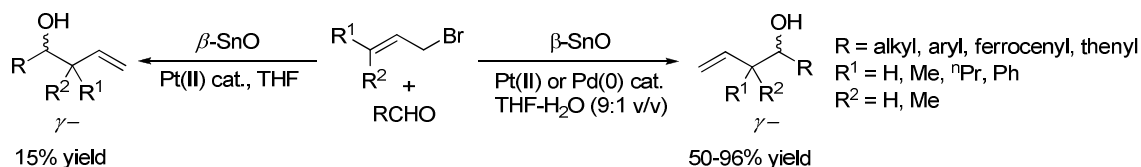


Chart SI- 2 In an interesting development towards heterogenous-Barbier allylation of various aldehydes using tetragonal blue-black tin(II) oxide (β -SnO). ^{S-22}



References:

1. (a) Frisch, M. J.; et al. Gaussian 03, Revision C.02; Gaussian, Inc.: Wallingford, CT, **2004**.
2. (a) Fukui, K.; Yonezawa, T.; Shingu, H. *J. Chem. Phys.* **1952**, 20, 722. (c) Fukui, K.; Yonezawa, T.; Nagata, C.; Shingu, H. *J. Chem. Phys.* **1954**, 22, 1433.
3. (a) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, 88, 899. (b) Mulliken, R. S. *J. Chem. Phys.* **1934**, 2, 782–793.
4. Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *Journal of Chemical Physics* **1978**, 68, 3801-3807.
5. Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, 105, 7512-7516.
6. Parr, R. G.; von Szentpaly, L.; Liu, S. *J. Am. Chem. Soc.* **1999**, 121, 1922.
7. Gazquez, J. L.; Cedillo, A.; Vela, A. *J. Phys. Chem. A* **2007**, 111, 1966.
8. (a) Masuyama, Y.; Hayasi, R.; Otake, K.; Kurusu, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 44; (b) Masuyama, Y.; Takahara, J. P.; Kurusu, Y. *J. Am. Chem. Soc.* **1988**, 110, 4473; (c) Masuyama, Y.; Takahara, J. P.; Kurusu, Y. *Tetrahedron Lett.* **1989**, 30, 3437; (d) Takahara, J. P.; Masuyama, Y.; Kurusu, Y. *J. Am. Chem. Soc.* **1992**, 114, 2577; (e) Masuyama, Y.; Otake, K.; Kurusu, Y. *Tetrahedron Lett.* **1988**, 29, 3563.; (f) Masuyama, Y.; Hayakawa, A.; Kurusu, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 1102; (g) Masuyama, Y.; Hayakawa, A.; Kishida, M.; Kurusu, Y. *Inorg. Chim. Acta* **1994**, 220, 155.

9. Kundu, A.; Prabhakar, S.; Vairamani, M.; Roy, S. *Organometallics* **1997**, *16*, 4796.
10. Imai, T.; Nishida, S. *J. Chem. Soc., Chem. Commun.* **1994**, 277.
11. (a) Kanagawa, Y.; Nishiyama, Y.; Ishii, Y. *J. Org. Chem.* **1992**, *57*, 6988. (b) Tang, L.; Ding, L.; Chang, W. -X.; Li, J. *Tetrahedron Lett.* **2006**, *47*, 303.
12. (a) Gremyachinskiy, D. E.; Smith, L. L.; Gross, P. H.; Samoshin, V. V. *Green Chem.*, **2002**, *4*, 317; (b) Samoshin, V. V.; Gremyachinskiy, D. E.; Smith, L. L.; Bliznets, I. V.; Gross, P. H. *Tetrahedron Lett.* **2002**, *43*, 6329; (c) Houllémare, D.; Outurquin, F.; Paulmier, C. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1629; (d) Imai, T.; Nishida, S. *Synthesis* **1993**, 395.
13. Koreeda, M.; Tanaka, Y. *Tetrahedron Lett.* **1987**, 28, 143.
14. Yamamoto, Y.; Hatsuya, S.; Yamada, J. *J. Chem. Soc., Chem. Commun.* **1987**, 561.
15. Zha, Z.; Wang, Y.; Yang, G.; Zhang, L.; Wang, Z. *Green Chem.* **2002**, *4*, 578.
16. (a) Wang, Z.; Zha, Z.; Zhou, C. *Org. Lett.* **2002**, *4*, 1683; (b) Zha, Z.; Qiao, S.; Jiang, J.; Wang, Y.; Miao, Q.; Wang, Z. *Tetrahedron* **2005**, *61*, 2521.
17. (a) Mukaiyama, T.; Harda, T. *Chem. Lett.* **1981**, 1527. (b) Tan, K. T.; Chng, S. S.; Cheng, H. S.; Loh, T. P. *J. Am. Chem. Soc.* **2003**, *125*, 2958. (c) Guimaraes, R. L.; Lima, D. J. P.; Barros, M. E. S. B.; Cavalcanti, L. N.; Hallwass, F.; Navarro, M.; Bieber, L. W.; Malvestiti, I. *Molecules* **2007**, *12*, 2089. (d) Law, M. C.; Wong, K. -Y.; Chan, T. H. *Green Chem.* **2002**, *4*, 161. (e) Zha, Z.; Xie, Z.; Zhou, C.; Chang, M.; Wang, Z. *New J. Chem.* **2003**, *27*, 1297.
18. Yamamoto, Y.; Maeda, N.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1983**, 774.
19. Hull, C.; Mortlock, S. V.; Thomas, E. J. *Tetrahedron* **1989**, *45*, 1007.
20. Koreeda, M.; Tanaka, Y. *Chem. Lett.* **1982**, 1299.
21. (a) Ito, A.; Kishida, M.; Kurusu, Y.; Masuyama, Y. *J. Org. Chem.* **2000**, *65*, 494; (b) Masuyama, Y.; Kishida, M.; Kurusu, Y. *J. Chem. Soc., Chem. Commun.* **1995**, 1405;

(c) Masuyama, Y.; Kishida, M.; Kurusu, Y. *Tetrahedron Lett.* **1996**, 37, 7103; (d) Masuyama, Y.; Ito, T.; Tachi, K.; Ito, A.; Kurusu, Y. *Chem. Commun.* **1999**, 1261.

22. Sinha, P.; Roy, S. *Chem. Commun.* **2001**, 1798.