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Application of Ring Closing Metathesis towards functionalized 1,4-dihydro-9,10-anthraquinones and anthraquinones using Grubbs' Catalyst[#]

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Abstract

A [illegible] and s[illegible] a[illegible] o[illegible] a d syn[illegible] s s of an[illegible] a [illegible] nomes[illegible] as de[illegible] o[illegible] ed, n[illegible] d a y a[illegible] on of [illegible],4 na[illegible] o [illegible] nomes, [illegible] o[illegible] ed by [illegible] n [illegible] os n Me[illegible] s s ([illegible] M) of [illegible] s [illegible] n d a y na[illegible] o [illegible] nomes[illegible] bbs' ca[illegible] a ys[illegible] and s bse[illegible] en[illegible] de[illegible] yd o[illegible] na[illegible] on s[illegible] n [illegible] d/ a[illegible] o ded[illegible] de s[illegible] ed an[illegible] a [illegible] nomes[illegible] o con[illegible] o of s bs[illegible] en s and n ood y[illegible] ds.

An[illegible] a [illegible] nomes a[illegible] des[illegible] ad n na[illegible] as[illegible] ys o o ca y ac[illegible] cons[illegible] en s of an s, c oo an s s, nsec s and a me an a s.[3] [illegible] a[illegible] ac[illegible] b o o ca ac[illegible] s of [illegible] se an[illegible] a [illegible] nomes, [illegible] o[illegible] xa[illegible] an[illegible] o a[illegible] s a[illegible] an[illegible] ome,[4] [illegible] oxan[illegible] ome[4] and[illegible] na[illegible] a ad a yc me,[5] [illegible] x a n[illegible] a[illegible] n[illegible] s[illegible] n[illegible] nome o[illegible] y as a[illegible] a[illegible] n o an c syn[illegible] s s. Many syn[illegible] c s[illegible] a[illegible] s[illegible] o a ds[illegible] syn[illegible] s s of an[illegible] a [illegible] nomes[illegible] a[illegible] a[illegible] ady been de[illegible] o[illegible] ed, s[illegible] as [illegible] de[illegible] a[illegible] s[illegible] ac[illegible] ons,[illegible] s A de[illegible] ac[illegible] ons,[illegible] a de an on s[illegible] a[illegible] s,[2,8] and a y me ann[illegible] a on[illegible] ac[illegible] ons. [illegible] o[illegible] e[illegible] o[illegible] ed[illegible] ods s[illegible] a[illegible] so[illegible] d a bac s s[illegible] as[illegible] a s[illegible] ac on cond[illegible] ons, o[illegible] y[illegible] ds o a d[illegible] c[illegible] ocon[illegible] o. [illegible] s reason, [illegible] de[illegible] o[illegible] en[illegible] of a me[illegible] and[illegible] me a[illegible] od [illegible] o[illegible] syn[illegible] s s of an[illegible] a [illegible] nomes s of sc[illegible] en[illegible] c n[illegible] es[illegible].

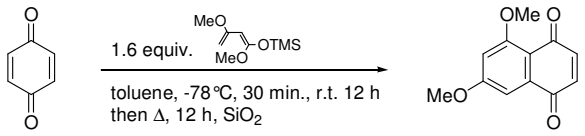
In[illegible] as[illegible] decade, [illegible] n [illegible] os n Me[illegible] s s ([illegible] M) of [illegible] oa[illegible] o [illegible] nc[illegible] ona[illegible] zed d[illegible] emes[illegible] as been [illegible] sen[illegible] ed as a o[illegible] e[illegible] od [illegible] o[illegible] cons[illegible] c on of an[illegible] e b oaden n an[illegible] e of ca bocyc[illegible] es and[illegible] e ocyc[illegible] es.[0] [illegible] y[illegible] ecen[illegible] y, a me[illegible] o oco [illegible] o benzoann[illegible] a on n o n do b[illegible] a sen[illegible] a an[illegible] en and [illegible] n [illegible] os n Me[illegible] s s ([illegible] M) as been [illegible] sen[illegible] ed[illegible] o a ds 2,3 d[illegible] y , 0 an[illegible] a [illegible] nome. In con[illegible] n a on of o[illegible] n[illegible] es[illegible] n[illegible] syn[illegible] s s of na[illegible] a y occ[illegible] n co o nds,[2] s co[illegible] n ca on d sc os[illegible] s a o[illegible] e me a[illegible] odo o y [illegible] o[illegible] e n cons[illegible] c on of [illegible] nome sys[illegible] s[illegible] z n [illegible] n [illegible] os n Me[illegible] s s[illegible] o a ds and/o[illegible] s bs[illegible] ed d[illegible] yd oan[illegible] a [illegible] nomes and an[illegible] a [illegible] nomes[illegible] o con[illegible] o of s bs[illegible] en s.

[#] [illegible] an, [illegible]; [illegible] oo[illegible] e, M.; [illegible] yn, S.; [illegible] e, [illegible] *Synlett* **2004**, [illegible]

[illegible] : +00[illegible]2 2[illegible]45[illegible]5[illegible], [illegible] ax: +00[illegible]2 2[illegible]4[illegible]24[illegible]

,4 Na t o nomes a re t re co re c a y a a abre o reas y access b re co o nds, w t c a res t re a ac t re s a t n a re a s n na t a od c syn t res s. 5, w t oxy ,4 na t o nome **2a** w as re a red f o ,4 benzo nome **1** s n a w re no n re s A de t odo o y 3 w t ,3 d t oxy t t y s y oxy ,3 b ad reme 4 (Sc re re). S nce on y t re na t o nomes **2b** and **2d** a re co re c a y a a abre, t re t y a red ana o re **2c** of na t o nome **2b** ad t o be re a red z n 4 re a ren s of odo t ame and 3 re a ren s of A 2 n re x n 2 2 f o 2 o s (Sc re re 2).

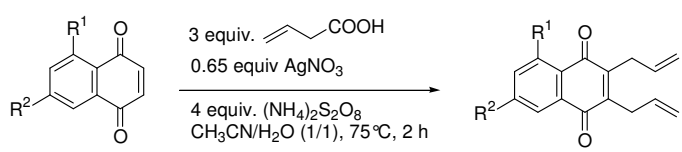
Sc re re



1 **2a** (59%)

2,3 a y na t o nomes **3** w re re re a red n ood y re ds (2% %) f o na t o nomes **2** on reac on w t 3 re a ren s of 3 b reno c ac d n ace on t re n t re resence of 4 re a ren s of d a on t re s f a re and a ca a y c a o n of s re n a re. A do b re ad ca M c ae add t on on na t o nomes **2** a f o ded t re des red a y a red co o nd **3** (Sc re re 2). o re y, d a y a t on of ,4 na t o nomes w t ace c ac d nde t rese cond t ons as red o 2,3 d t y ,4 na t o nome ad ca add t ons. 5 A so a y a t on of na t o nomes as been ren t omed n t re t a t re.

Sc re re 2



2a R^1 = OMe, R^2 = OMe
2b R^1 = OH, R^2 = H
2c R^1 = OMe, R^2 = H
2d R^1 = R^2 = H

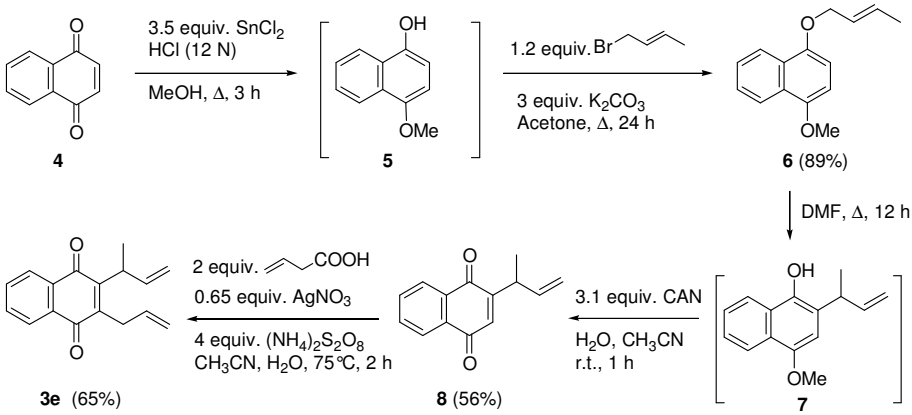
4 equiv. MeI, 3 equiv. Ag_2O, CH_2Cl_2, Δ, 12 h, 93%

3a (62%)
3b (65%)
3c (64%)
3d (67%)

In o de t of n s s bs t t ed an t a nomes, a a sen rea an ren t a oac w as a red o a ds t re syn t res s of 2 (t y 2 o reny) ,4 na t o nome **8** a re ono *O* a y a t on of t re a o a re s bs t a re (Sc re re 3). Na t o nome **4** w as t ans f o red n o t yd oxy 4 t oxyna t a reme **5** n t ano n t re resence of 3.5 re a ren s of Sn 2 and 2 M yd oc o c ac d. S bse ren y, t re f ree yd oxy o of co o nd **5** w as a y a red w t .2 re a ren s of c o y b o de n ace ome nde bas c cond t ons (3

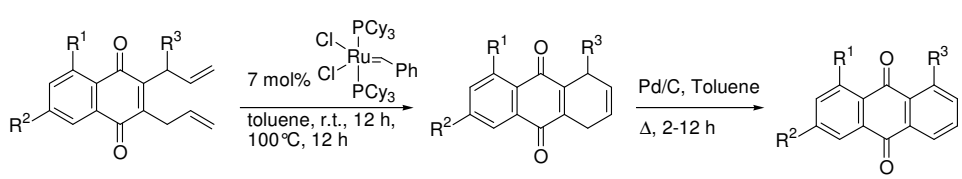
[illegible] 3). [illegible] (*E*) (2' b [illegible]noxy) 4 [illegible] oxyna[illegible] **6** [illegible] as [illegible] as a s [illegible] a [illegible] yd oxyna[illegible] **7**, [illegible] as [illegible] y ox d zed [illegible] 3. [illegible] a [illegible] on [illegible] (A [illegible]) [illegible] a [illegible] ace on [illegible] (/) [illegible] n [illegible] o [illegible] **8**. [illegible] y, a y a on [illegible] 3 b [illegible] c ac d n [illegible] esence of d a on [illegible] and A 2 [illegible] d [illegible] y s [illegible] d na[illegible] o [illegible] **3e** n [illegible]5% y [illegible] d (Sc[illegible] 3).

Sc[illegible] 3



[illegible] y s [illegible] n [illegible] d sc os[illegible] d syn[illegible] s s of an[illegible] a [illegible] nomes co [illegible] ses a [illegible] n [illegible] os n Me[illegible] s s of 2,3 d a y na[illegible] o [illegible] nomes **3** s n [illegible] bbs' [illegible] s [illegible] a on ca a ys. [illegible] s [illegible] ay, d yd oan[illegible] a [illegible] nomes **9** [illegible] syn[illegible] s zed n [illegible] y [illegible] ds and [illegible] y [illegible] z n [illegible] o % of b[illegible]nzy d[illegible] b s(cyc o [illegible] xy [illegible] os [illegible] me)d c o o [illegible] n [illegible] n o [illegible] on [illegible] a n (Sc[illegible] 4). [illegible] a [illegible] na s [illegible] , [illegible] as y ob a med d yd oan[illegible] a [illegible] nomes **9** [illegible] a o a zed by [illegible] ans of a ad [illegible] on ac [illegible] ca bon n o [illegible] nde [illegible] x, [illegible] n [illegible] n [illegible] a [illegible] ed an[illegible] a [illegible] nomes **10** n [illegible] xce [illegible] n [illegible] y [illegible] ds (88% [illegible]%).

Sc[illegible] 4



3a ($R^1 = R^2 = OMe$, $R^3 = H$)	**9a** (91%)	**10a** (91%)
3b ($R^1 = OH$, $R^2 = R^3 = H$)	**9b** (93%)	**10b** (96%)
3c ($R^1 = OMe$, $R^2 = R^3 = H$)	**9c** (94%)	**10c** (92%)
3d ($R^1 = R^2 = R^3 = H$)	**9d** (88%)	**10d** (94%)
3e ($R^1 = R^2 = H$, $R^3 = Me$)	**9e** (89%)	**10e** (88%)

In conclusion, a theoretical and statistical foundation for synthetic design of novel organic compounds has been developed. Application of Hammett's equation, originally developed for benzene derivatives, as extended to other aromatic systems and to aliphatic compounds has been reviewed. The theoretical basis for the correlations obtained and the limitations of the method have been discussed.

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