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Rapid Communication

Synthesis of symmetrical and unsymmetrical trisubstituted benzene derivatives through ring-closing alkyne metathesis strategy and depropargylation with various catalysts

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Alkyne trimerization by application of the Grubbs ruthenium first generation catalyst has been demonstrated. In this regard, triaryloxymethylbenzene derivatives have been generated by co-trimerization of propargylated phenol derivatives with the aid of the Grubbs catalyst. Depropargylation under various catalysts have been studied.

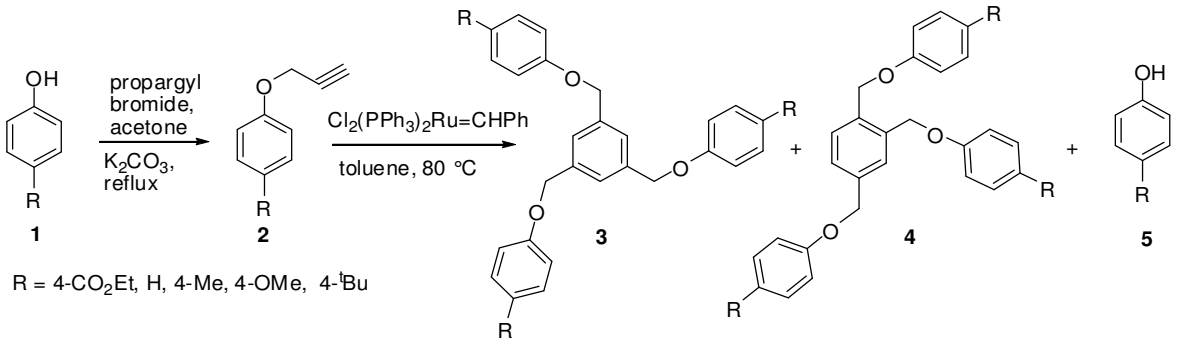
Keywords: Metathesis, C_3-symmetric molecules, Grubbs catalyst, benzene derivatives, depropargylation

Functionalized aromatics such as 1,3,5-triarylbenzenes are valuable building blocks in organic synthesis and they are also useful synthons in supramolecular chemistry[1,2]. Their preparations through condensation of acetophenones have been considered as a general methodology and this protocol has been realized in the presence of catalysts such as $SiCl_4$ (ref. 3) or $TiCl_4$ (ref. 4). Several interesting C_3-symmetric aromatic building blocks prepared by this strategy have shown to be useful in catalysis, material science and crystal engineering. To this end, cyclotrimerization of the acetylene derivatives to annulated benzenes seems to be another reliable method for the synthesis of highly functionalized aromatic compounds, was first developed by Reppe *et al*. in 1948. However, adaptations of this reaction to prepare substituted aromatic compounds from three different, unsymmetrical acetylenes, a variety of products are possible. Thus, regiochemical control in these situations is a formidable synthetic challenge. In this regard, various transition metal catalysts based on Pd[5], Co[6], Mo[7] and Ti[8] are used for cyclotrimerization of acetylenes to generate the functionalized benzene derivatives.

Grubbs ruthenium metathesis catalysts have found several applications in the synthesis of both natural and non-natural products[9]. However, limited applications are available where the benzene derivatives are formed by these ruthenium catalysts by trimerization strategy involving a tandem alkyne metathesis sequence. For example, Roy and Das prepared multifunctional carbohydrate derivatives by the Grubbs ruthenium-catalyzed cyclotrimerization of the terminal alkynes containing a carbohydrate moiety[10]. In another event, Undheim and co-workers reported a intramolecular Ru(II)-catalyzed cascade involving the ring-closing metathesis (RCM) approach for the construction of the bis-indane-based α–amino acid derivatives[11]. The mechanistic pathway for the isomerization of triynes to the annulated benzene derivatives using the Grubbs catalyst was reported by Blechert and Peters[12]. A cascade of four metathesis steps are involved in this process. Our group has also utilized the Grubbs catalysts for synthesis of the diverse polycyclic compounds[13]. In continuation of our metathesis work using ruthenium catalysts and also utilization of [2+2+2] cyclo-addition[14] strategies for the synthesis of diverse polycylics, we were interested in cyclotrimerization of alkynes to prepare triaryloxymethylbenzenes. Herein, we report our efforts in this direction using the Grubbs ruthenium based catalysts.

Results and Discussion

To test the idea of the trimerization of the acetylene derivatives using ruthenium based catalysts, ethyl-4-(prop-2-ynyloxy)benzoate **2a**[15] was prepared by reacting the ethyl-4-hydroxybenzoate **1a**, with the propargyl bromide under refluxing acetone with potassium carbonate as a base. The resulting propargylated compound **2a** was heated in presence of the Grubbs first generation catalyst (7.5 mole%) in toluene at 80°C and two new products on TLC[16] were observed. Purification of the crude reaction-mixture with flash column chromatography yielded a white solid (mixture of **3a** and **4a**) along with a white crystalline compound **5a**. Careful analysis of the product[17] (mixture of **3a** and **4a**) by ^1H and ^{13}C NMR spectral data revealed that, it is a mixture of



Scheme I

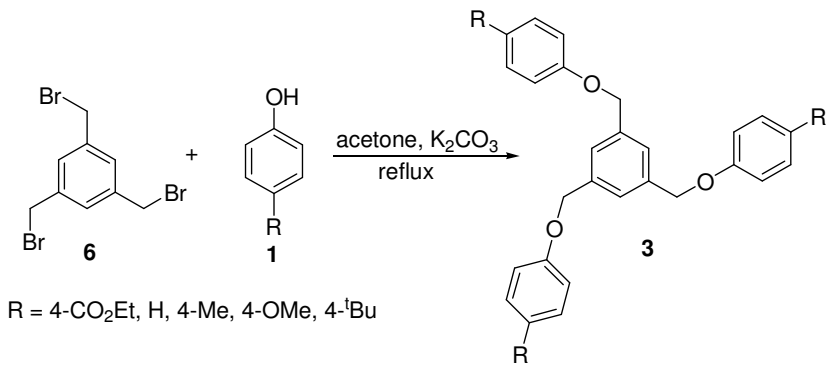
Table I — Preparation of substituted phenylpropargyl ether **2a-e**

Entry	**1**	**2**	Time (hr)	Yield (%)
a	R = 4-CO_2Et	R = 4-CO_2Et	27	98
b	R = H	R = H	23	97
c	R = 4-Me	R = 4-Me	22	72
d	R = 4-OMe	R = 4-OMe	22	87
e	R = 4-^{t}Bu	R = 4-^{t}Bu	22	95

symmetrical 1,3,5- and unsymmetrical 1,2,4-triarylbenzene (**3a** and **4a** respectively) derivatives **(Scheme I)**. Attempts to separate these two compounds by column chromatography were unsuccessful. Similarly, the reaction of the substituted phenols **1b-e** was then extended with propargyl bromide to get **2b-e**[18] **(Table I)** and carried out the trimerization reaction with the Grubbs ruthenium first generation catalyst (5-7.5 mole%) and obtained **3b-e**, **4b-e**[17] and **5b-e** respectively **(Table II)**. The identity of the products **3a-e** has been established by an

Table II — Preparation of 1,3,5- and 1,2,4-triaryloxymethylbenzenes **3a-e**, **4a-e** and depropargylated product **5a-e**

Entry	R	G-I (mol %)	Time (hr)	Yield (%)			Integration ratio
				3 & **4**	**5**	**3** & **4**:**5**	**4**:**3**
a	4-CO_2Et	7.5	54	60	37	1.6:1	1.3:1
b	H	5.0	27	37	25	1.5:1	1.3:1
c	4-Me	5.0	26	33	13	2.6:1	1.4:1
d	4-OMe	5.0	24	71	-	-	1.2:1
e	4-^{t}Bu	5.0	50	24	22	1.1:1	1.4:1



Scheme II

Table III — Preparation of 1,3,5-triaryloxymethylbenzenes **3a-e** from **6** and **1**

Entry	**1**	**3**	Time (hr)	Yield (%)
a	R = 4-CO_2Et	R = 4-CO_2Et	7	87
b	R = H	R = H	5	100
c	R = 4-Me	R = 4-Me	5	99
d	R = 4-OMe	R = 4-OMe	5	84
e	R = 4-^{t}Bu	R = 4-^{t}Bu	8	95

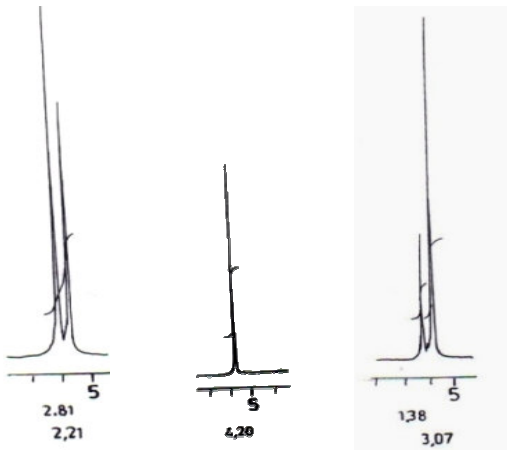


Figure 1 **Figure 2** **Figure 3**

^{1}H NMR spectrum of trimerized product (benzylic protons are shown).

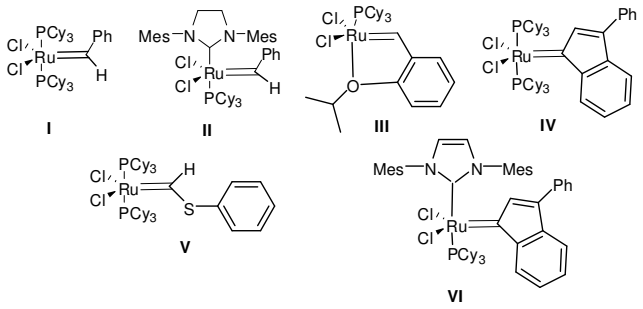


Figure 4 — Various metathesis catalysts used for depropargylation

independent synthesis of 1,3,5-triarylbenzene derivatives as discussed here **(Scheme II)** and yields are reported in **Table III**.

To this end 1,3,5-*tris*-(bromomethyl)benzene **6** was reacted with **1a**[19] to deliver the compound **3a**[20]. Later on, the reaction of **1b-e** was then extended with compound **6** to obtain the symmetrical triaryloxymethylbenzenes **3b-e**[20], respectively **(Scheme II)**. The ^{1}H NMR and ^{13}C NMR spectral data of these compounds has been used to establish their presence in the earlier experiments where the symmetrical and the unsymmetrical products were obtained.

The ^{1}H NMR spectral data of the mixture (symmetrical and unsymmetrical isomers **3a** and **4a** respectively), showed two characteristic peaks at δ 5.14 and 5.22 for the two types of benzylic protons **(Figure 1)**, whereas the ^{1}H NMR of the 1,3,5-triarylbenzene derivative **3a**, obtained from **Scheme II** shows only one benzylic proton peak at δ 5.15 **(Figure 2)**. The assignment of the two benzylic peaks in the ^{1}H NMR of mixture was done on the basis of a simple experiment. In this regard, an artificial mixture containing increased amount of symmetrical isomer (**3a**, 3 mg) was prepared, which was obtained from **Scheme II** and trimerized products (**3a** and **4a**, 3 mg) obtained from **Scheme I**. The ^{1}H NMR spectral data **(Figure 3)** of the above artificial mixture shows enhancement in the peak at δ 5.14, which confirms that this peak corresponds to the symmetrical isomer **3a** and other signal at δ 5.22 was due to the unsymmetrical isomer **4a**. Further, the regioisomeric ratio was determined from the relative integration ratio of these two benzylic protons in **Figure 1** and is shown in **Table II**. LC-Mass spectral studies (LC-MS-MS ion trap) using acetonitrile as an eluent shows the formation of two regioisomers. The first isomer shows peak at *m/z* 612 (M^+ peak) and other one gave peak corresponding to the sodium adduct at *m/z* 635 (M^++Na peak). In addition to the trimerized product (TLC analysis) a white crystalline compound **5a** was formed during the trimerization reaction. A careful analysis of the ^{1}H and ^{13}C NMR spectral data of **5a** shows that it was a depropargylated product **(Scheme I)**. To investigate the role of the Grubbs catalyst in the formation of the depropargylated product **5a**, the substrate **2a** was heated in toluene at 80^{o}C in the absence of the catalyst. Under these conditions the starting material was recovered even after 48 hr. This confirms that the trimerization and the depropargylation processes were aided by the Grubbs first generation catalyst. During the preparation of this manuscript, it was found that Tae and co-workers have also observed deprotection of propargyl ethers under the Grubbs catalyst (10-20 mole%) conditions[21]. It seems worth while to investigate the scope of the depropargylation of

Table IV — Yields of **3a**, **4a** and **5a** under variuos catalysts

Entry	Catalyst (mol %)	Time (hr)	Yield (%)			Integration ratio
			3a & **4a**	**5a**	**5a**:**3a** & **4a**	**4a**:**3a**
a	I (7.5)	54	60	37	0.6:1	1.3:1
b	I (15)	30	41	50	1.2:1	1.5:1
c	II (7.5)	66	27	41	1.5:1	1.2:1
d	III (7.5)	68	26	51	2.0:1	1.1:1
e	IV (7.5)	82	30	57	2.0:1	1.3:1
f	V (7.5)	90	21	53	2.5:1	1.2:1
g	VI (7.5)	112	17	50	3.0:1	1.0:1

substrate **2a** under different catalyst conditions **(Table IV)**.

During these studies it was observed that the yield of the depropargylated product **5a** was increased and also time required for the completion of the reaction decreased with the increased catalyst (G-I) loading preferably at the beginning of the reaction **(Table IV, entries a** and **b)**. In general, G-I is more effective for the trimerization as compared to G-II **(Table IV, entries a-c)**. With the catalysts III-VI **(Figure 4)** it was found that the relative yield of the depropargylated product increased as compare to the trimerized product **(Table IV, entries d-g)**. Finally with the imidazole indene catalyst VI **(Table IV, entry g)** the depropargylated product and the trimerized product were obtained in 3:1 ratio respectively. Therefore, it was concluded that the catalyst with fast initiation and slow propagation rates facilitated the formation of the depropargylated product. Moreover, in all the instances the yield of the unsymmetrical isomer was more as compared to the symmetrical isomer **(Table IV)**.

Conclusion

In summary, usefulness of various ruthenium catalysts for the alkyne trimerization reaction to generate the triarylbenzenes, apart from the regular metathesis protocol is demonstrated. The presence of two regioisomers was confirmed from ^{1}H NMR and LC-MS-MS studies. The present methodology opens up a new route for the alkyne trimerization reactions leading to various C_3-symmetric molecules. Depropargylation under various metathesis catalysts has been tested. Tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphe-nyl)imidazol-2-ylidene][3-phenyl-1*H*-indene-ylidene]ruthenium(II)dichloride catalyst **VI** gave best selectivity towards depropargylation.

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15 **Spectral data for compound 2a obtained from 1a**
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (3H, t, *J* = 7.2Hz), 2.56 (1H, t, *J* = 2.4Hz), 4.34 (2H, q, *J* = 7.2Hz), 4.74 (2H, d, *J* = 2.4Hz), 6.99-7.00 (2H, m), 8.00-8.03(2H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.4, 55.9, 60.8, 76.1, 76.8, 114.5, 123.9, 131.6, 161.2, 166.3; m.p.: 42-44^{o}C; I.R. (cm^{-1}): 1709, 2124, 3301.

16 **General procedure for trimerization**
To a solution of **2a-e** in dry degassed toluene (15 mL) was added catalysts I-VI (5-7.5 mole%). The reaction- mixture was heated at 80^{o}C under inert atmosphere. At the conclusion of the reaction (TLC monitoring) the reaction-mixture was concentrated on a rotary evaporator. The crude material obtained was purified using silica gel column chromatography. Elution of column with ethyl acetate-petroleum ether gave the trimerized compounds (mixture of **3a-e** and **4a-e**).

17 **Spectral data for inseparable isomers 3a and 4a obtained from 2a**
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.38 (18H, t, *J* = 6.8 Hz), 4.35 (12H, q, *J* = 6.8 Hz), 5.14 (6H, s), 5.22 (6H, s), 6.98-6.99 (12H, m), 7.45-7.59(6H, m), 7.98- 8.02 (12H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 60.8, 68.0, 68.1, 69.7, 69.8, 114.5, 114.6, 123.6, 123.8, 127.7, 128.2, 129.7, 131.8, 134.6, 135.2,137.2, 162.2, 162.3, 166.4; m.p.: 136-38^{o}C; HRMS (Q-Tof): *m/z* [M+ Na]$^+$ Calcd for $C_{36}H_{36}O_9Na$: 635.2257; Found: 635.2276.

Spectral data for inseparable isomers 3b and 4b obtained from 2b
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.08 (6H, s), 5.17 (6H, s), 6.95-6.99 (18H, m), 7.25-7.29(12H, m), 7.42-7.60 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 67.8, 68.0, 69.6, 115.0, 121.3, 127.4, 128.0, 129.3, 129.7, 135.0, 135.6, 137.5, 158.7, 158.8; HRMS (Q-Tof): *m/z* [M+ H]$^+$ Calcd for $C_{27}H_{25}O_3$: 397.1804; Found: 397.1794.

Spectral data for inseparable isomers 3c and 4c obtained from 2c
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.29 (18H, s), 5.05 (6H, s), 5.13 (6H, s), 6.85- 6.87 (12H, m), 7.06- 7.08 (12H, m), 7.42-7.58 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.6, 68.0, 68.2, 69.9, 70.0, 114.9, 126.0, 127.3, 128.0, 129.2, 130.1, 135.1,135.7, 137.6, 156.7; m.p.: 62- 64^{o}C; HRMS (Q-Tof): *m/z* [M+ Na]$^+$ Calcd for $C_{30}H_{30}O_3Na$: 461.2093; Found: 461.2078.

Spectral data for inseparable isomers 3d and 4d obtained from 2d
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.77 (18H, s), 5.03 (6H, s), 5.11 (6H, s), 6.81- 6.91 (24H, m), 7.41- 7.57 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.5, 68.7, 68.9, 70.5, 114.9, 116.1, 127.4, 128.0, 129.3, 135.2, 135.8, 137.7, 153.0, 154.3; m.p.: 66- 68 ^{o}C. HRMS (Q-Tof): *m/z* [M+ Na]$^+$ Calcd for $C_{30}H_{30}O_6Na$: 509.1940; Found: 509.1939.

Spectral data for inseparable isomers 3e and 4e obtained from 2e
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.29 (54H, s), 5.05 (6H, s), 5.14 (6H, s), 6.89- 6.92 (12H, m), 7.28- 7.31 (12H, m), 7.41-7.58 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.7, 34.2, 67.9, 68.2, 69.8, 114.5, 126.4, 127.4, 128.1, 129.3, 135.2, 135.8, 137.7, 144.0, 156.6, 156.7; m.p.: 78- 80^{o}C; HRMS (Q-Tof): *m/z* [M- 3x C_4H_8+ H]$^+$ Calcd for $C_{27}H_{25}O_3$: 397.1804; Found: 397.1813.

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19 **General procedure for trimerization with K_2CO_3**
To a solution of 1,3,5-tris(bromomethyl)benzene **6** (1 equiv.) and phenol derivatives **1a-e** (4 equiv.) in dry acetone, finely powdered K_2CO_3 (10 equiv.) was added and refluxed (till the completion of the reaction, TLC monitoring). The reaction-mixture was cooled and filtered off over celite pad with the help of sintered funnel to remove unwanted salts. The combined organic layer was concentrated on a rotary evaporator. The crude material obtained was purified using silica gel column chromatography. Elution of column with ethyl acetate- petroleum ether gave the compounds **3a-e**.

20 **Spectral data for compound 3a obtained from 6**
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.38 (9H, t, *J* = 7.2 Hz), 4.35 (6H, q, *J* = 7.2Hz), 5.15 (6H, s), 6.99- 7.00 (6H, m), 7.48 (3H, s), 8.00- 8.02 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$): 14.5, 60.8, 69.8, 114.6, 123.7, 126.2, 131.8, 137.7, 162.3, 166.4; m.p.: 118- 20 ^{o}C; HRMS (Q-Tof): *m/z* [M+ H]$^+$ Calcd for $C_{36}H_{37}O_9$: 613.2438; Found: 613.2434.

Spectral data for compound 3b obtained from 6
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.08 (6H, s), 6.95- 6.98 (9H, m), 7.27- 7.31 (6H, m), 7.47 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 69.8, 115.0, 121.2, 126.0, 129.6, 138.1, 158.8; m.p.: 58- 60^{o}C; HRMS (Q-Tof): *m/z* [M+ Na]$^+$ Calcd for $C_{27}H_{24}O_3Na$: 419.1623; Found: 419.1625.

Spectral data for compound 3c obtained from 6
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.28 (9H, s), 5.03 (6H, s), 6.84- 6.87 (6H, m), 7.06- 7.08 (6H, m), 7.43 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.7, 70.0, 115.0, 126.0, 130.1, 130.4, 138.3, 156.8; m.p.: 50- 51^{o}C; HRMS (Q-Tof): *m/z* [M+ Na]$^+$ Calcd for $C_{30}H_{30}O_3Na$: 461.2093; Found: 461.2078.

Spectral data for compound 3d obtained from 6
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.77 (9H, s), 5.01 (6H, s), 6.83- 6.92 (12H, m), 7.42 (3H, s); ^{13}C NMR (100 MHz,

$CDCl_3$): 55.9, 70.3, 114.9, 116.1, 127.6, 138.6, 153.0, 154.3; m.p.: 86- 88°C; HRMS (Q-Tof): *m/z* [M+ Na]$^+$ Calcd for $C_{30}H_{30}O_6Na$: 509.1940; Found: 509.1939.

Spectral data for compound 3e obtained from 6

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.29 (27H, s), 5.05 (6H, s), 6.90- 6.92 (6H, m), 7.30- 7.32 (6H, m), 7.45 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.6, 34.2, 69.9, 114.4, 126.0, 126.4, 138.2, 143.8, 156.6; m.p.: 80- 82°C; HRMS (Q-Tof):*m/z* [M- 3x C_4H_8+ H]$^+$ Calcd for $C_{27}H_{25}O_3$: 397.1804; Found: 397.1813.

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