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Formation of Arenes *via* Diallylarenes: Strategic Utilization of Suzuki–Miyaura Cross-Coupling, Claisen Rearrangement and Ring-Closing Metathesis

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Abstract: Two new synthetic strategies for benzoannulation are reported. The first strategy is based on the Suzuki–Miyaura cross-coupling reaction. To this end, various *ortho*-diallylbenzene derivatives were prepared from the corrresponding diiodo derivatives by an allylation strategy using an allylboronate as coupling partner. These diallyl derivatives were subjected to a ring-closing metathesis (RCM) and one-pot dichlorodicyanoquinone (DDQ) oxidation sequence to deliver 2-substituted naphthalenes. In the second strategy, a double Claisen rearrangement and RCM protocol have been used as key steps to give highly functionalized benzoannulated quinone derivatives.

Keywords: benzoannulation; Claisen rearrangement; diallylarenes; 2-naphthalene derivatives; ring-closing metathesis; Suzuki–Miyaura cross-coupling

Introduction

Functionalized aromatics are found to be useful building blocks in organic synthesis and medicinal chemistry. Generally they are accessible by functional group manipulation of preformed aromatic derivatives. These strategies provide aromatics with limited substitution patterns. To this end, the benzoannulation reaction, a single or multi-step process which involves appending an aromatic ring starting with readily available substrates seems to be a useful strategy to afford highly functionalized aromatics. Various biologically active quinones or naphthalene derivatives have become easily available because of the advancement of such reactions. A variety of synthetic methodologies have been reported for benzoannulation starting with acyclic or cyclic precursors.[1] Recently reported, Pd-catalyzed benzoannulation strategies furnish diverse polysubstituted aromatics. In this respect, Yamamoto's group reported the [4+2]-benzoannulation of enyne-ynes to give 1,4- or 1,2,4-substituted benzene derivatives[2] while Takahashi and co-workers disclosed the coupling of *o*-diiodoarene with alkynes to give tetrasubstituted naphthalene derivatives in moderate to good yields.[3] The Dötz annulation provides a unique class of quinone derivatives with additional functionality.[4] Surprisingly, a benzoannulation strategy based on ring-closing metathesis (RCM) is relatively less explored.[5]

As part of a major program involving metathesis sequences, two new strategies for benzoannulation involving RCM as a key step were conceived. Both of these strategies rely on common types of intermediates involving diallylarenes (Figure 1). In the first approach, diallylarenes are derived by application of the Suzuki–Miyaura (SM) cross-coupling[6] with *o*-substituted dihalo aromatics. In the second strategy, a double Claisen rearrangement generated the quinone-based diallylarenes.[7] Subsequently, these diallylarenes on reaction with Grubbs' ruthenium-based reagent generate ring-closing products which, on DDQ or MnO_2 oxidation, gave the benzoannulated products. Here, the full details of these strategies are disclosed.

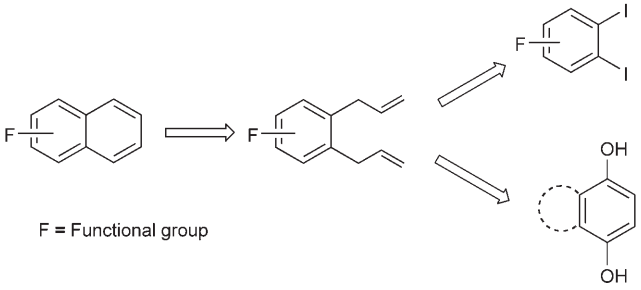


Figure 1.

Results and Discussion

In recent times, RCM involving the ruthenium catalysts **1** and **2** (Figure 2) has become a useful tool for

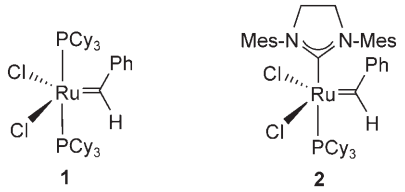
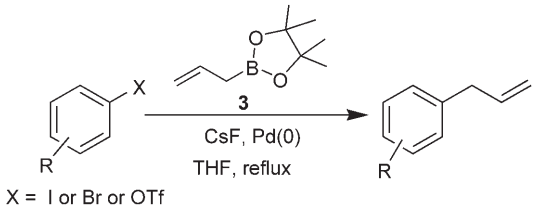


Figure 2.

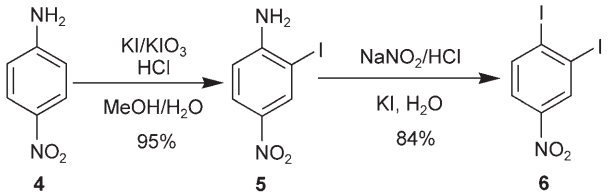
synthetic chemists and has found various applications for the preparation of diverse heterocyclic, carbocyclic and macrocyclic molecules.[8] Earlier we have demonstrated a simple protocol for the allylation of aromatic halides *via* the SM cross-coupling reaction using the allylboronate **3** as a coupling partner (Scheme 1).[9] As an extension of this methodology, extrapolation of the diallylation protocol with aromatic substrates can give useful precursors suitable for the benzoannulation strategy.



Scheme 1.

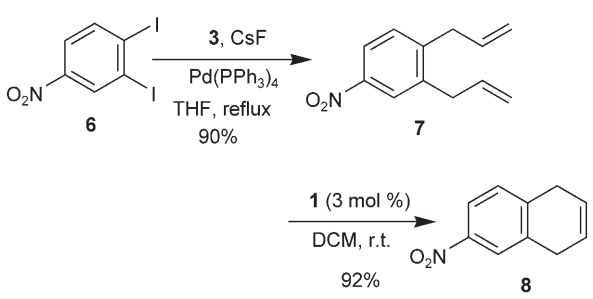
In this regard, it was found that 1,2-diallylbenzene derivatives can be prepared by diallylation of the corresponding diiodo derivatives *via* SM cross-coupling with allylboronate **3**. Since aromatic iodides with the electron-withdrawing groups gave good yields of the cross-coupling products, the preparation of various *o*-diiodobenzene derivatives was undertaken.

The required 1,2-diiodo derivatives were prepared by adopting a tactical combination of the existing literature methods.[10] For example, 2-iodoaniline derivatives on diazotization followed by treatment with aqueous potassium iodide gave various 1,2-diiodobenzene derivatives. In another series, $KI/KIO_3/HCl$ conditions were employed as a source of iodine which exclusively gave the 2-iodo-4-nitroaniline **5** in 95% yield when using 4-nitroaniline **4** as starting material. Diazotization of the 2-iodoaniline derivative **5** with sodium nitrite in HCl/H_2O (1:1), followed by treatment with aqueous potassium iodide gave 3,4-diiodonitrobenzene **6** in 84% yield (Scheme 2).



Scheme 2.

Having prepared several diiodo derivatives, the stage was set for the SM cross-coupling reaction. When the 3,4-diiodonitrobenzene **6** was subjected to the SM cross-coupling reaction with allylboronate **3**, 3,4-diallylnitrobenzene **7** was isolated in 90% yield (Scheme 3). The diallyl derivative **7** was characterized by its complementary spectral (^{1}H NMR, ^{13}C NMR and mass) data.

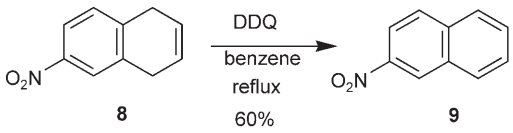


Scheme 3.

Next, the diallylnitrobenzene **7** was treated with the Grubbs' catalyst **1** (3 mol%) in dry dichloromethane at room temperature (Scheme 3) and the reaction was completed after 20 min. The dihydronaphthalene derivative **8** was isolated in 92% yield and its structure was confirmed on the basis of routine spectral data.

Then, the dihydronaphthalene derivative **8** was subjected to DDQ oxidation in refluxing benzene. Here, monitoring of the reaction with the aid of TLC appears to be difficult as the RCM product and the aromatized product have the same R_f value. So the oxidation reaction was continued for an extended period (*ca.* 48 h) to ensure the completion of the reaction and the dehydrogenated product, 2-nitronaphthalene **9** was isolated in 60% yield (Scheme 4).

Having demonstrated the benzoannulation strategy with the first substrate, our attention was directed towards the generalization of this strategy. Various sub-



Scheme 4.

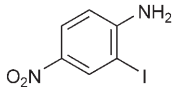
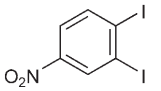
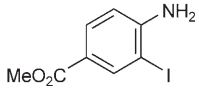
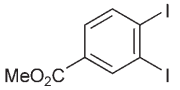
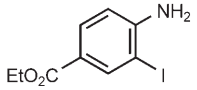
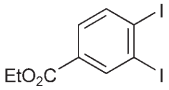
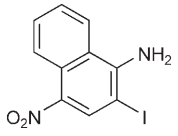
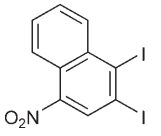
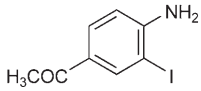
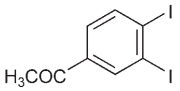
strates prepared in this venture are included in Table 1. The 2-iodoaniline derivatives **10**–**13**, precursors of diiodo derivatives, were prepared by adopting a similar protocol as that employed in the preparation of 2-iodo-4-nitroaniline **5**. The requisite diiodo derivatives were prepared in a moderate to good yield (Table 1) by diazotization of 2-iodoaniline derivatives **10**–**13** by adopting standard diazotization conditions followed by treatment with aqueous potassium iodide. Diazotization of anilines such as **12** and **13** with sodium nitrite in HCl/H_2O (1:1), followed by treatment with aqueous potassium iodide gave unstable products. However, diazotization of compound **12** under $H_2SO_4/NaNO_2$ conditions, followed by treatment with aqueous KI afforded the diiodo derivative **16** in 40% yield (Table 1, entry 4).[11] Surprisingly, the diazotization of compound **13** under similar reaction conditions gave diiodo derivative **17** in 48% yield (Table 1, entry 5).

Along similar lines, the diiodo derivatives **14**–**17** were subjected to SM cross-coupling conditions and the corresponding diallyl derivatives **18**–**21** were isolated in good to excellent yields (Table 1, entrie 2–5). When the diallyl derivative **18** was treated with Grubbs' catalyst **1**, the reaction was completed after 20 mins. Unfortunately, the corresponding dihydro derivative was found to be unstable. So, it was decided to oxidize the crude RCM product and, therefore, a one-pot RCM and DDQ sequence was planned. Thus, the diallyl derivative **18** was treated with catalyst **1** in dry dichloromethane and at the conclusion of the reaction (20 min, TLC monitoring), the reaction mixture was treated with DDQ (2.5 equivalents, based on complete conversion to RCM product) in benzene (10 mL). The resulting reaction mixture was heated at reflux temperature for 48 h and the aromatized product **22** was isolated in 86% yield (Table 2, entry 2). RCM followed by one-pot DDQ oxidation of the diallyl derivatives **19**–**21** gave the aromatized products **23**–**25** in good yields (Table 2, entries 3–5).

In the second benzoannulation strategy, a sequential combination of the Claisen rearrangement[12] and RCM protocol has been employed for the synthesis of various quinone derivatives. It seems that suitably functionalized quinones are useful therapeutic compounds for the treatment of a wide variety of disorders. For example, anthracycline antibiotics[13] such as idarubicin (**26**), doxorubicin (**27**) and daunorubicin (**28**) have widely been used as clinically effective antitumor agents against acute leukemia, Hodgkin's disease, lymphomas, breast carcinomas and sarcomas (Figure 3).[14] Additionally, various naphthacenediones are found to exhibit potent biological activity. More specifically, XR651 (**29**) is identified as a novel naphthacene-5,12-dione derivative that inhibits interleukin-1 signal transduction in carcinoma cells.[15]

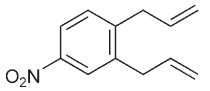
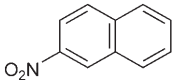
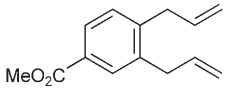
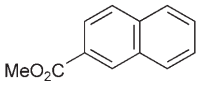
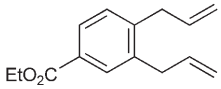
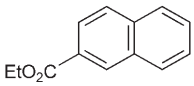
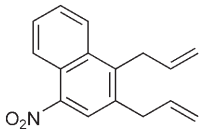
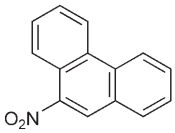
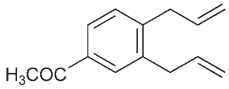
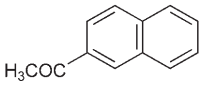
The required precursors suitable for double Claisen rearrangement were prepared *via* *O*-allylation of the corresponding 1,4-dihydroxybenzene derivatives by following the conventional allylation conditions using allyl bromide, potassium carbonate in acetone at room temperature (Scheme 5). The desired di-olefinic precursors required for the RCM were obtained *via* double Claisen rearrangement of bis-allyloxybenzene derivatives under different reaction conditions. The allyloxyanthraquinone **33** is somewhat resistant to the

Table 1. List of 2-iodoaniline derivatives and diiodo derivatives isolated.

Entry	2-Iodoaniline Derivatives		Yield [%]	Diazotization Method[a]	3,4-Diiodo Derivatives		Yield [%][b]
1	**5**		95	**A**	**6**		84
2	**10**		84	**A**	**14**		67
3	**11**		95	**A**	**15**		68
4	**12**		93	**B**	**16**		40
5	**13**		70[b]	**B**	**17**		48

[a] **A:** (i) HCl/H_2O, $NaNO_2$; (ii) KI. **B:** (i) H_2SO_4, $NaNO_2$; (ii) KI.
[b] Isolated yield after column chromatography.

Table 2. List of 3,4-diallyl derivatives and naphthalene derivatives prepared.

Entry	Cross-Coupling Product	Yield [%][a]	Aromatized Product	Yield [%][b]
1	**7** 	90	**9** 	60[c]
2	**18** 	95	**22** 	86
3	**19** 	92	**23** 	82
4	**20** 	71	**24** 	82
5	**21** 	89	**25** 	82

[a] Isolated yield after column chromatography.
[b] Overall yield after RCM and DDQ oxidation sequence.
[c] Isolated yield of aromatized product of dihydronaphthalene derivative **8** after DDQ oxidation.

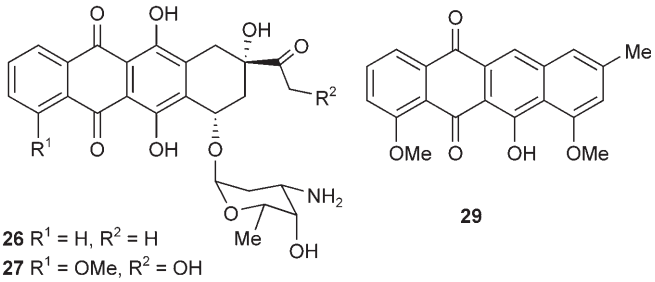
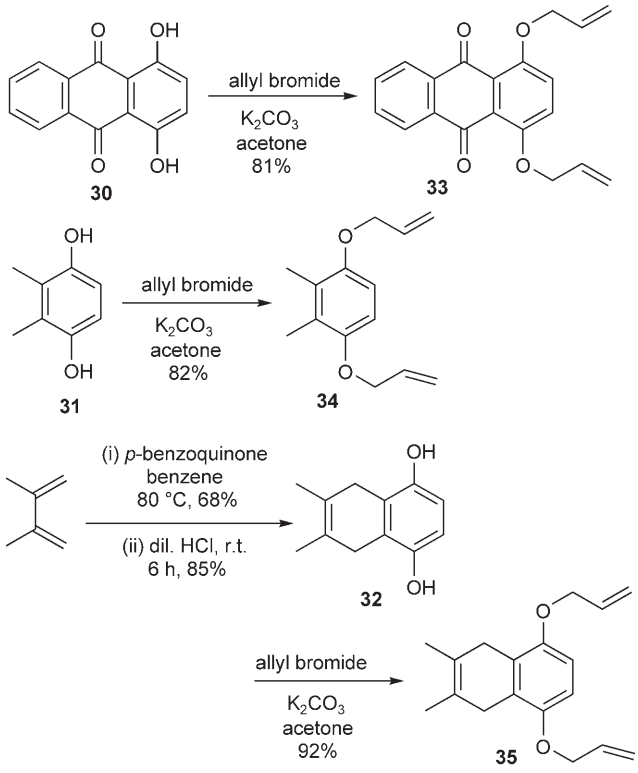


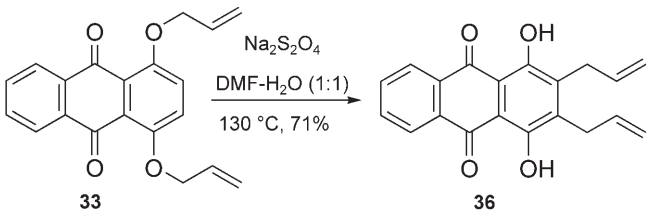
Figure 3.

thermal Claisen rearrangement. Although one of the allyl group rearranges under normal conditions, rearrangement of the second allyl group is sluggish and consequently the other possible side reactions are expected to compete. To circumvent these problems, the carbonyl groups of the anthraquinone are reduced *in situ* to give an anthraquinone radical anion or dianion under appropriate conditions amenable for Claisen rearrangement. In this regard, treatment of the bis-allyloxyanthraquinone **33** with sodium dithionite (1.0 mol equiv.) in the presence of sodium hydroxide (4 mol equivs.) in dimethylformamide-water (1:1) with heating for 1 h furnished the desired doubly rearranged product **36** in good yield (Scheme 6).[16]

Thermal Claisen rearrangement of the 1,4-bis-[allyloxy]-2,3-dimethylbenzene (**34**) and 5,8-bis-[allyloxy]-2,3-dimethyl-1,4-dihydronaphthalene (**35**) gave the corresponding bis-allylquinones **38** and **40**, respectively, instead of 1,4-bis-hydroxybenzene derivatives **37** and **39** during purification on a silica gel column (Scheme 7). This critical observation prompted the exploration of the Claisen rearrangement on a silica gel support to obtain a one-pot conversion of 1,4-bis-allyloxybenzene derivatives to 2,3-bis-allyl-1,4-quinone derivatives.



Scheme 5.

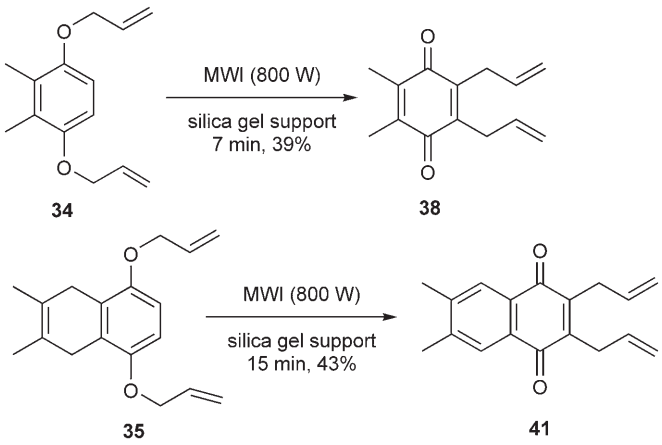


Scheme 6.

In recent years, solvent-free reactions using either organic or inorganic solid supports have received increasing attention.[17] There are multiple advantages for executing the synthetic sequence in dry media. These include: (i) short reaction times, (ii) increased safety, (iii) economic advantages due to the absence of solvent. Silica gel is effective because the end products can easily be separated. Moreover, silica gel can function as a convenient medium and act as a mild acidic catalyst.

Microwave irradiation (MWI) has become an established and popular tool in organic synthesis, because of the rate enhancements, higher yields and often improved selectivity, with respect to conventional reaction conditions.[18] In addition, solvent-free MWI processes are also clean and efficient.

In view of the several advantages of silica gel-supported organic synthesis and MWI under solvent-free conditions, compound **34** was heated in an unmodified domestic MW oven with a maximum power (800 W) on a silica gel support for 7 min to produce the corresponding bis-allylated ketone **38**. Consequently, a significant rate enhancement and improved yield of the rearranged product was observed under MWI conditions on a silica gel support compared to the conventional reaction conditions. It is worth mentioning that, under similar reaction conditions, compound **35** upon irradiation for 15 min gave the aromatized quinone **41** in 43% yield (Scheme 8).[19] The reaction time was optimized by monitoring the individual reaction with



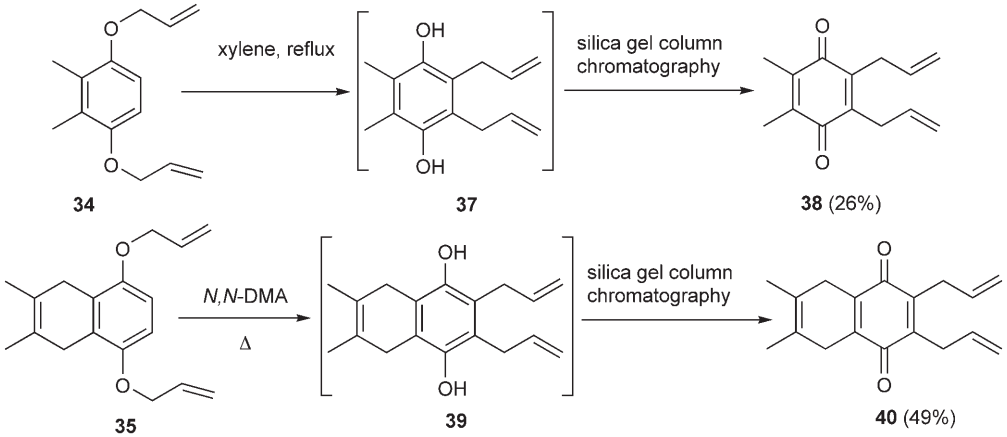
Scheme 8.

the aid of TLC at regular intervals. It was found that a prolonged MWI gave an intractable polymeric material, thereby reducing the yield of the required product. To avoid the polymerization problem, the MWI power level was reduced which, in turn, increased the total exposure time.

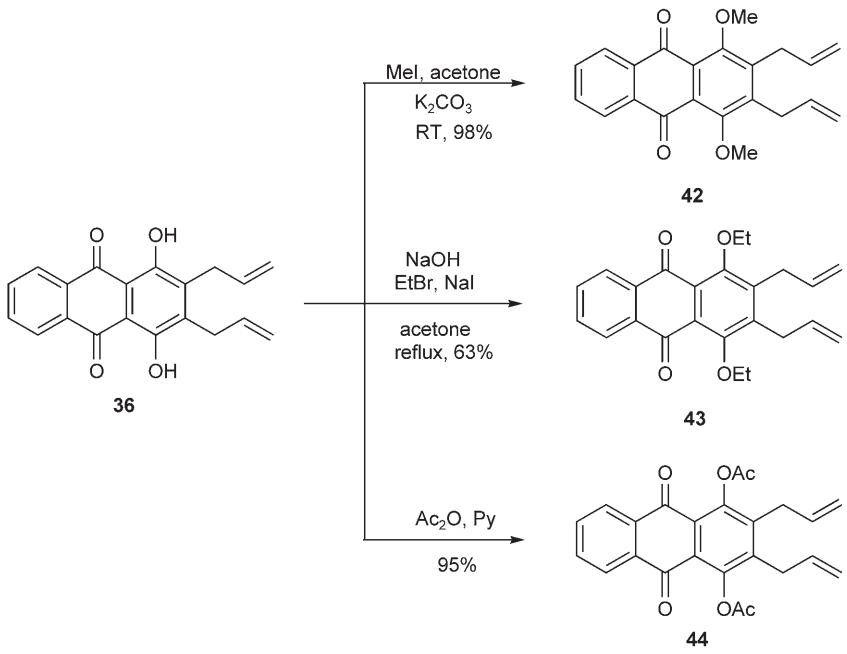
Among the various solid supports (e.g., silica gel, alumina and the highly acidic montmorillonite clay) tested for the Claisen rearrangement, silica gel was found to be the most efficient medium. Here, the role of silica gel may be twofold: (i) enhancement of reaction rate due to physisorption of reactants on the silica surface which, in turn, increases the local concentration of substrate and (ii) the silica surface being acidic in nature, promotes the autooxidation of phenol to the corresponding quinone derivative.[20]

Having the diallylated derivatives in hand, the RCM with compound **36** was attempted. In this context, Grubbs' catalysts **1** and **2** failed to give the desired product, and a complex mixture of products was formed as indicated by TLC.

Next, the free hydroxy groups of **36** were protected (Scheme 9) and these modified tetracyclic derivatives



Scheme 7.



Scheme 9.

successfully underwent the RCM (without isolation) and, on aromatization with DDQ, gave a moderate overall yield of the benzoannulated products (Table 3, entries 1 and 2). Surprisingly, no product formation was observed when compound **44** was exposed to the Grubbs' catalyst **1** which could be attributed to the complexation of the catalyst with the acetyl group. The use of the more reactive Grubbs' catalyst **2**, however, afforded the desired product in good yield (Table 3, entry 3). Along similar lines, exposure of compounds **38**, **40** and **41** to the Grubbs' catalyst **1** followed by one-pot aromatization with DDQ afforded compounds **54**, **55** and **55**, respectively, in good yields (Table 3, entries 4–6).

Conclusions

We have demonstrated two simple strategies for benzoannulation. The first benzoannulation strategy has been accomplished *via* the SM cross-coupling reaction and RCM as key steps. The required 3,4-diiodobenzene derivatives were prepared by diazotization with sodium nitrite in HCl/H_2O or H_2SO_4 in moderate to good yields (40–84%). The SM cross-coupling reaction afforded 3,4-diallylbenzene derivatives in good to excellent yields (71–95%). RCM followed by one-pot aromatization using DDQ gave acceptable yields of the aromatized products (82–86%, two steps). The second strategy for benzoannulation is based on a double Claisen rearrangement and RCM followed by one-pot DDQ oxidation to yield the benzoannulated quinone derivatives. It is worth mentioning that the RCM products **45**, **46** or **47** are advanced precursors for the synthesis of potent anticancer analogues such as idarubicin (**26**) using simple transformations.

Experimental Section

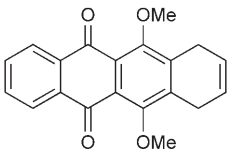
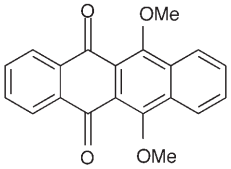
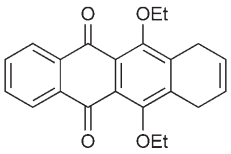
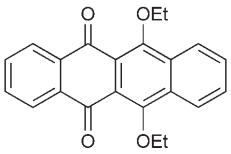
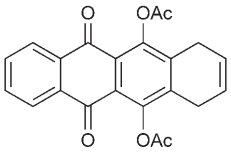
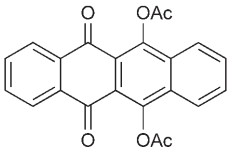
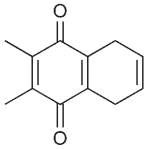
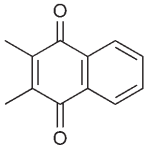
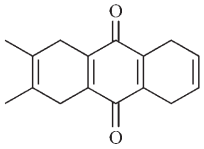
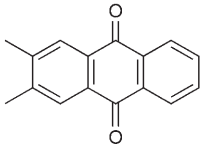
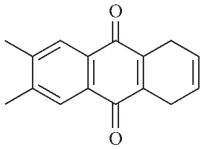
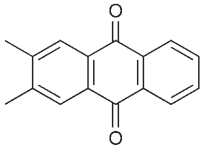
General Remarks

All the commercial grade reagents were used without further purification. Grubbs' catalysts (**1** and **2**), allylboronate (**3**), 4-dihydroxyanthraquinone (**30**), 2,3-dimethylbenzene-1,4-diol (**31**), 2,3-dimethyl-1,3-butadiene, and methyl iodide were purchased from Aldrich Chemical Co., Inc. (Milwaukee, WI, USA). 4-Aminoacetophenone, sodium dithionite (Spectrochem), acetic anhydride, ethyl bromide and allyl bromide (s. d. fine-Chem Limited) were used as received. 4-Nitroaniline (**4**) and 4-aminobenzoic acid were commercially available. 1-Nitronaphthalene was purchased from Alfa Aesar Ltd. UK. 2-Iodo-4-nitroaniline (**5**),[10] methyl 4-aminobenzoate,[24] ethyl 4-aminobenzoate,[26] 4-nitronaphthylamine,[30] 3,4-diiodo-1-nitro naphthalene (**16**),[11] 1,4-bis-allyloxyanthraquinone (**33**),[35] 1,4-bis[allyloxy]-2,3-dimethylbenzene (**34**),[36] 6,7-dimethyl-5,8-dihydronaphthalene-1,4-diol (**32**),[37] and 2,3-diallyl-1,4-dihydroxyanthraquinone (**36**)[38] were prepared according to the reported procedures.

General Procedure for Preparation of 2-Iodoaniline Derivatives

To a stirred solution of aniline derivative (1 equiv.) in a methanol-water mixture, potassium iodide (0.75 equivs.), potassium iodate (0.375 equivs.) were added. The resulting

Table 3. List of various benzoannulated quinones prepared by the RCM and DDQ oxidation sequence.

Entry	Diene	Conditions[a]	RCM product	Aromatized Products	Yield [%][b]
1	**42**	**A**	**45** 	**51** 	49
2	**43**	**A**	**46** 	**52** 	37
3	**44**	**B**	**47** 	**53** 	51
4	**38**	**A**	**48** 	**54** 	54
5	**40**	**A**	**49** 	**55** 	85
6	**41**	**A**	**50** 	**55** 	91

[a] **A:** (i) Catalyst **1**, dry dichloromethane, reflux, 24 h; (ii) DDQ, benzene, reflux. **B:** (i) Catalyst **2**, dry dichloromethane, reflux, 24 h; (ii) DDQ, benzene, reflux.
[b] Yield refers to the overall yield obtained after the RCM and aromatization sequence.

mixture was stirred for 2–5 min and then dilute HCl (1 equiv.) was added during a period of 45–60 min. The reaction mixture was stirred at room temperature for 6 h and then filtered. The solid was washed with water and dilute sodium thiosulfate solution and dried at room temperature or in an oven to give the corresponding 2-iodoaniline derivatives; yield: 85–96%.

General Procedure for Preparation of 3,4-Diiodobenzene Derivatives from 2-Iodoaniline Derivatives

Method A: To a cooled solution of 2-iodoaniline derivative at 0 °C in HCl-water (1:1), an aqueous solution of sodium nitrite was added within 10 min. The resulting solution was stirred at 0–5 °C for 30 min. To the above mixture, an aqueous solution of KI was added during a period of 10–15 min. The reaction mixture was stirred at room temperature for 20–24 h and then extracted with dichloromethane (40 mL × 3). The combined organic layers were washed with dilute sodium thiosulfate solution, water and brine. The solvent was evaporated and the crude product was purified by silica gel column chromatography. Elution of the column with petroleum ether or 1–2% ethyl acetate/petroleum ether mixture gave the desired diiodo derivatives; yield: 63–84%.

Method B: To cooled, concentrated H_2SO_4 at 0 °C (1 mL), $NaNO_2$ was added. Then, the amine in glacial acetic acid was added at the same temperature during a period of 10 min. The resulting mixture was stirred at low temperature for 30 min and aqueous KI solution was added within 5–10 min. The reaction mixture was extracted with dichloromethane (30 mL × 3) and combined organic layers were washed with dilute sodium thiosulfate solution, water and brine. The solvent was evaporated to give the crude product which was purified by column chromatography. Elution of the column with petroleum ether or 1% ethyl acetate/petroleum ether mixture gave the desired diiodo derivatives.

General Procedure for Preparation of *o*-Diallylbenzene Derivatives *via* Suzuki–Miyaura Cross-Coupling Reaction

In a three-necked, round-bottom flask, the diiodo compound was charged and THF was added followed by CsF and $Pd(PPh_3)_4$. The resulting suspension was stirred at room temperature for 30 min and allylboronate **3** in THF was added. The reaction mixture was refluxed (70–75 °C oil-bath temperature). After completion of the reaction (TLC monitoring), the reaction mixture was quenched with water and extracted with dichloromethane (30 mL × 3). The combined organic layers were washed with water and brine. The solvent was evaporated to give the crude product which was purified by silica gel column chromatography. Elution of the column with petroletum ether or 1–2 % ethyl aetate/petroleum ether mixture gave the desired diallyl derivative; yield: 71–95 %.

General Procedure for RCM and One-Pot Oxidation by DDQ

To a stirred solution of diallyl derivatives in dry DCM, the Grubbs' catalyst **1** was added. After completion of the reaction (20–25 min, TLC monitoring), benzene and DDQ were added to the reaction mixture and refluxed for 48 h. Then, the solvent was evaporated under reduced pressure and the crude product was purified by silica gel column chromatography. Elution of the column with 1–2 % ethyl acetate/petroleum ether mixture gave the desired aromatized product; yield: 82–86 %.

3,4-Diiodonitrobenzene (6)

2-Iodoaniline (**5**; 1.0 g, 3.78 mmol), $NaNO_2$ (340 mg, 4.92 mmol), and KI (900 mg, 5.42 mmol) were treated as described in method A for diazotization. Elution of the column with petroleum ether gave the desired product **6** as a yellow solid; yield: 1.2 g (84 %); mp 109–112 °C (Lit. mp 108–110 °C).[21] ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.87$ (dd, $J = 8.4$ Hz, 2.4 Hz, 1 H), 8.06 (d, $J = 8.4$ Hz , 1 H), 8.64 (d, $J =$ 2.4 Hz, 1 H).

3,4-Diallylnitrobenzene (7)

3,4-Diiodonitrobenzene (**6**; 100 mg, 0.26 mmol), CsF (162 mg, 1.06 mmol), $Pd(PPh_3)_4$ (37 mg, 12 mol %) and allylboronate **3** (180 mg, 1.07 mmol) were treated as described in a general procedure for diallylation. After completion of the reaction (8 h, TLC monitoring), work-up according to the general procedure gave the crude product. Elution of the column with 1 % ethyl acetate/petroleum ether mixture gave the desired product **7** as a yellow liquid; yield: 49 mg (90 %); IR (neat): $\tilde{\nu} = 3080$, 1520, 1344, 992, 915, 840, 812 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 3.47$ (d, $J =$ 5.2 Hz, 4 H), 5.19–4.99 (m, 4 H), 6.00–5.90 (m, 2 H), 7.32 (d, $J = 8.4$ Hz, 1 H), 8.01–8.05 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = 36.9$, 37.1, 117.3, 117.4, 121.7, 124.5, 130.5, 135.3, 135.37, 139.93, 145.9, 146.9; HR-MS (Q-ToF): $m/z =$ 226.0852, calcd. for $C_{12}H_{13}NO_2Na$ (M + Na): 226.0844.

5,8-Dihydro-2-nitronaphthalene (8)

3,4-Diallylnitrobenzene (**7**; 44.0 mg, 0.22 mmol), Grubbs' catalyst **1** (4.4 mg, 3 mol %) in dry dichloromethane (5 mL) was treated as described in the general procedure for RCM reaction. At the conclusion of the reaction (20 min, TLC monitoring), the solvent was evaporated and the resulting crude product was purified by silica gel column chromatography. Elution of the column with 1 % ethyl acetate/petroleum ether mixture gave the desired product **8** as a pale yellow liquid; yield: 35 mg (92 %); ^{1}H NMR ($CDCl_3$, 400 MHz):[22] $\delta = 3.49$ (d, $J = 1.6$ Hz, 4 H), 5.92–5.94 (m, 2 H), 7.23–7.26 (m, 1 H), 7.96–7.98 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = 29.9$, 30.1, 121.1, 123.5, 124.0 124.3, 129.35, 135.9, 142.2, 146.4.

2-Nitronaphthalene (9)

To a stirred solution of dihydronaphthalene derivative **8** (32 mg, 0.18 mmol) in benzene (8 mL), DDQ (118 mg, 0.46 mmol) was added and the resulting mixture was refluxed for 48 h. Then, the solvent was evaporated under reduced pressure and the crude product was purified by silica gel column chromatography. Elution of the column with 2 % ethyl acetate/petroleum ether mixture gave the desired product **9** as a yellow solid; yield: 18 mg (60 %); mp 75–78 °C (Lit. mp 77.8–78.6 °C).[23] ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.61$–7.93 (m, 2 H), 7.93–7.97 (m, 2 H), 8.03 (d, $J = 7.8$ Hz, 1 H), 8.24 (dd, $J = 9.0$ Hz, 2.1 Hz, 1 H), 8.80 (d, $J =$ 2.1 Hz,1 H).

Methyl 3-Iodo-4-aminobenzoate (10)

Methyl 4-aminobenzoate[24] (500 mg, 3.31 mmol), KI (370 mg, 2.23 mmol), KIO_3 (236 mg, 1.10 mmol), HCl (0.5 mL diluted to 5 mL) in methanol/water (3 mL/15 mL) were treated as described in the general procedure for iodination. The desired product **10** was obtained as a white solid; yield: 770 mg (84 %); mp 84–88 °C (Lit. mp 89–90 °C).[25]

Methyl 3,4-Diiodobenzoate (14)

2-Iodoaniilne (**10**; 700 mg, 2.53 mmol), $NaNO_2$ (277 mg in 2 mL water, 4.92 mmol), KI (609 mg, 3.63 mmol) were treated as described in method A for diazotization. Elution of the column with 1 % ethyl acetate/petroleum ether mixture gave the desired product **14** as a pale yellow solid; yield: 635 mg (67 %); mp 74–76 °C; IR (neat): $\tilde{\nu} = 3060$, 2941, 2840, 1720, 1280, 1110, 890, 838, 755 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 3.83$ (s, 3 H), 7.56 (dd, $J = 8.4$ Hz, 1.6 Hz, 1 H), 7.90 (d, $J = 8.4$ Hz, 1 H), 8.39 (d, $J = 1.6$ Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = 52.7$, 108.1, 114.6, 129.8, 131.1, 139.6, 140.2, 156.4; HR-MS (Q-ToF): $m/z = 388.8546$, calcd. for $C_8H_7I_2O_2$ (M + H): 388.8536.

Methyl 3,4-Diallylbenzoate (18)

Methyl 3,4-diiodobenzoate (**14**; 150 mg, 0.39 mmol), CsF (235 mg , 1.54 mmol), $Pd(PPh_3)_4$ (53.5 mg, 12 mol %) and allylboronate **3** (260 mg, 1.54 mmol) were treated as described in the general procedure for diallylation. After completion of the reaction (48 h, TLC monitoring), reaction mixture was quenched with water, extracted with dichloromethane

(30 mL × 3). Combined organic layers were washed with water and brine. Evaporation of the solvent gave the crude product which was purified by silica gel column chromatography. Elution of the column with 1% ethyl acetate/petroleum ether mixture gave the desired product **18** as a thick yellow liquid; yield: 80 mg (95%). IR (neat): $\tilde{\nu}$ = 3080, 1720, 1634, 1110, 992, 919, 845, 796, 760 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 3.43 (d, J = 5.7 Hz, 4H), 3.90 (s, 3H), 5.12–4.95 (m, 4H), 6.03–5.87 (m, 2H), 7.24 (d, J = 8.4 Hz, 1H), 7.83–7.85 (m, 2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 37.0, 37.2, 52.1, 115.6, 116.5, 127.9, 128.5, 129.8, 130.9, 136.2, 136.4, 138.4, 143.6, 167.3; HR-MS (Q-ToF): m/z = 217.1230, calcd. for $C_{14}H_{18}NO_2$ (M + H): 217.1229.

Methyl 2-Naphthoate (22)

To a stirred solution of methyl 3,4-diallylbenzoate (**18**; 80.0 mg, 0.37 mmol) in dry dichloromethane (5 mL), Grubbs' catalyst **1** (9.0 mg, 3 mol%) was added. At the conclusion of the reaction (25 min, TLC monitoring), DDQ (255.0 mg, 0.92 mmol) and benzene (10 mL) were added. The resulting mixture was heated to reflux for 48 h and the solvent was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography. Elution of the column with 1% ethyl acetate/petroleum ether mixture gave the desired product **22** as a white solid; yield: 59.0 mg (82%); mp 76–78 °C (Lit. mp 75–76 °C).[26] ^1H NMR ($CDCl_3$, 400 MHz): δ = 3.98 (s, 3H), 7.60–7.52 (m, 2H), 7.88 (d, J = 8.8 Hz, 2H), 7.95 (d, J = 8.0 Hz, 1H), 8.06 (dd, J = 8.8 Hz, 1.6 Hz, 1H), 8.61 (s, 1H).

Ethyl 3-Iodo-4-aminobenzoate (11)

Ethyl 4-aminobenzoate[27] (2.0 g, 12.1 mmol), KI (1.34 g, 8.07 mmol), KIO_3 (870 mg, 4.04 mmol), HCl (1.3 mL diluted to 10 mL) in methanol/water (10 mL/60 mL) were treated as described in the general procedure for iodination to provide the desired product **11** as a white solid; yield: 3.4 g (95%); mp 82–86 °C (Lit. mp 83 °C).[28]

Ethyl 3,4-Diiodobenzoate (15)

2-Iodoaniline (**11**; 1.5 g, 5.15 mmol), $NaNO_2$ (462 mg, 6.70 mmol), KI (1.2 g, 7.22 mmol) were treated as described in method A for diazotization. Elution of the column with 1% ethyl acetate/petroleum ether mixture gave the desired product **15** as a white solid; yield: 1.3 g (68%); mp 74–76 °C. IR (neat): $\tilde{\nu}$ = 3076, 2933, 2896, 1715, 1275, 1110, 755, 890, 838 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.39 (t, J = 7.2 Hz, 3H), 4.37 (q, J = 7.2 Hz, 2H), 7.66 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 8.47 (d, J = 1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 14.3, 61.6, 107.9, 114.3, 129.8, 131.5, 139.5, 140.1, 164.8; HR-MS (Q-ToF): m/z = 402.8691, calcd. for $C_9H_9O_2I_2$ (M + H): 402.8692.

Ethyl 3,4-Diallylbenzoate (19)

Ethyl 3,4-diiodobenzoate (**15**; 150 mg, 0.37 mmol), CsF (227 mg , 1.49 mmol), $Pd(PPh_3)_4$ (51.0 mg, 12 mol%) and allylboronate **3** (250 mg, 1.49 mmol) were treated as described in the general procedure for diallylation. At the conclusion of reaction (48 h, TLC monitoring), general work-up with dichloromethane gave crude product which was purified by silica gel column chromatography. Elution of the column with 0.4% ethyl acetate/petroleum ether mixture gave the desired product **19** as a yellow liquid; yield: 81 mg (92%). IR (neat): $\tilde{\nu}$ = 3076, 1724, 1634, 1370, 996, 910, 845, 755 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.39 (t, J = 7.2 Hz, 3H), 3.43 (d, J = 6.4 Hz, 4H), 4.36 (q, J = 7.2 Hz, 2H), 5.11–4.96 (m, 4H), 6.01–5.89 (m 2H), 7.23 (d, J = 8.0 Hz, 1H), 7.86–7.83 (m, 2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 14.5, 37.1, 37.2, 61.0, 116.4, 116.6, 127.9, 128.9, 129.8, 130.9, 136.3, 136.6, 138.3, 143.6, 166.9; HR-MS (Q-ToF): m/z = 231.1385, calcd. for $C_{15}H_{17}O_2$ (M + H): 231.1385.

Ethyl 2-Naphtholate (23)

To a stirred solution of ethyl 3,4-diallylbenzoate (**19**; 68.0 mg, 0.29 mmol) in dry dichloromtehane (5 mL), Grubbs' catalyst **1** (7.3 mg, 3 mol%) was added. At the conclusion of the reaction (25 min, TLC monitoring), DDQ (244.0 mg, 0.88 mmol) and benzene (10 mL) were added. The resulting mixture was heated to reflux for 48 h and solvent was evaporated under reduced pressure and the crude product was purified by silica gel column chromatography. Elution of the column with 1% ethyl acetate/petroleum ether mixture gave the desired product **23** as a pale yellow liquid; yield: 59.0 mg (82%). ^1H NMR ($CDCl_3$, 300 MHz):[29] δ = 1.45 (t, J = 7.2 Hz, 3H), 4.45 (q, J = 7.2 Hz, 2H), 7.61–7.51 (m, 2H), 7.88 (d, J = 9.0 Hz, 2H), 7.95 (d, J = 8.7 Hz, 1H), 8.07 (dd, J = 8.7 Hz, 1.5 Hz, 1H), 8.61 (s, 1H).

2-Iodo-4-nitro-1-naphthylamine (12)

4-Nitro-1-naphthylamine[30] (2.0 g, 10.6 mmol), KI (1.17 g, 7.1 mmol), KIO_3 (0.76 g, 3.05 mmol), HCl (1.2 mL diluted to 10 mL) in methanol/water (10 mL/60 mL) were treated as described in the general procedure to give the title compound **12** as a yellow solid; yield: 3.1 g (93%); mp 232–234 °C (Lit. mp 232 °C).[31] ^1H NMR ($CDCl_3$, 400 MHz): δ = 5.46 (bs, 2H), 7.60–7.56 (m, 1H), 7.76–7.71 (m, 1H), 7.84 (d, J = 8.8 Hz, 1H), 8.76 (s, 1H), 8.90 (d, J = 8.8 Hz, 1H).

3,4-Diallyl 1-Nitronaphthalene (20)

3,4-Diiodo-1-nitronaphthalene[11] (**16**; 150 mg, 0.35 mmol), CsF (215 mg, 1.42 mmol), $Pd(PPh_3)_4$ (45.0 mg, 12 mol%) and allylboronate **3** (240 mg, 1.42 mmol) were treated as described in the general procedure for diallylation. After completion of reaction (48 h, TLC monitoring), general work-up as described in a general procedure gave the crude product which was purified by silica gel column chromatography. Elution of the column with petroleum ether gave the desired product **20** as a yellow liquid; yield: 63 mg (71%); IR (neat): $\tilde{\nu}$ = 3092, 1520, 1344, 990, 923, 825, 740 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ = 3.62–3.60 (m, 2H), 3.91–3.89 (m, 2H), 4.89–4.83 (m, 1H), 5.20–5.01 (m, 3H), 6.09–5.96 (m, 2H), 7.68–7.59 (m, 2H), 8.08 (s, 1H), 8.11 (d, J = 8.0 Hz 1H), 8.53 (dd, J = 8.0 Hz, 1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ = 32.8, 37.6, 116.9, 117.3, 123.5, 124.4, 125.1, 126.1, 127.5, 128.3, 133.6, 134.9, 135.1, 135.7, 140.7, 145.7; HR-MS (Q-ToF): m/z = 254.1184, calcd. for $C_{16}H_{16}NO_2$ (M + H) : 254.1181.

9-Nitrophenanthrene (24)

To a stirred solution of 3,4-diallyl-1-nitronaphthalene (**20**; 53.0 mg, 0.21 mmol) in dry dichloromethane (5 mL), Grubbs' catalyst **1** (5.2 mg, 3 mol %) was added. At the conclusion of the reaction (30 min, TLC monitoring), DDQ (244.0 mg, 0.88 mmol) and benzene (10 mL) were added. The resulting mixture was heated to reflux for 48 h and the solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography. Elution of the column with 1% ethyl acetate/petroleum ether mixture gave the desired product **25** as a pale yellow solid; yield: 38.0 mg (82%); mp 114–117 °C (Lit. mp 115–117 °C).[31] ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.86$–7.69 (m, 4H), 8.02 (d, $J = 7.6$ Hz, 1H), 8.48 (s, 1H), 8.50 (dd, $J = 7.6$ Hz, 2.0 Hz, 1H), 8.71 (d, $J = 8.4$ Hz, 1H), 8.77 (dd, $J = 6.8$ Hz, 2.0 Hz, 1H).

3-Iodo-4-aminoacetophenone (13)

4-Aminoacetophenone (2.0 g, 12.1 mmol), KI (1.34 g, 8.07 mmol), KIO_3 (870 mg, 4.04 mmol), HCl (1.3 mL diluted to 10 mL) in methanol/water (10 mL/60 mL) were treated according to the general procedure for iodination to provide the desired product **13** as a yellow solid; yield: 2.56 g (70%); mp 53–55 °C (Lit. mp 50–52 °C).[33] ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 8.28$ (d, $J = 2.0$ Hz, 1H), 7.76 (dd, $J = 8.4$ Hz, 2.0 Hz, 1H), 6.71 (d, $J = 8.8$ Hz, 1H), 4.61 (bs, 2H), 2.50 (s, 3H).

3,4-Diiodoacetophenone (17)

2-Iodo aniline (**13**; 800 mg, 3.05 mmol) in AcOH (6 mL), $NaNO_2$ (275 mg, 3.98 mmol), KI (738 mg, 4.45 mmol) and concentrated H_2SO_4 (1 mL) were treated as described in method B for diazotization. Elution of the column with 1% ethyl acetate/petroleum ether mixture gave the desired product **17** as a yellow crystalline solid; yield: 550 mg (48%); mp 73–76 °C. IR (neat): $\tilde{\nu} = 3060$, 2917, 2847, 1683, 1564, 1090, 900, 808 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 2.56$ (s, 3H), 7.57 (dd, $J = 8.4$ Hz, 2.0 Hz, 1H), 7.98 (d, $J = 8.4$ Hz, 1H), 8.38 (d, $J = 2.0$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): $\delta = 26.7$, 108.7, 114.9, 128.5, 137.8, 139.0, 139.8, 196.2. HR-MS (Q-ToF): $m/z = 372.8596$, calcd. for $C_8H_7OI_2$ (M+H): 372.8586.

3,4-Diallylacetophenone (21)

3,4-Diiodoacetophenone (**17**; 150 mg, 0.40 mmol), CsF (245 mg, 1.61 mmol), $Pd(PPh_3)_4$ (56.0 mg, 12 mol %) and allylboronate **3** (250 mg, 1.49 mmol) were treated as described in the general procedure for diallylation. At the conclusion of the reaction (TLC monitoring, 48 h), work-up procedure as described in a general procedure gave the crude product which was purified by silica gel column chromatography. Elution of the column with 2% ethyl acetate/petroleum ether mixture and careful removal of solvent at lower temperature (< 40 °C) under reduced pressure gave the desired product **21** as a colorless liquid which turned yellowish green on standing; yield: 70 mg (89%) **Note:** *The product is volatile.* IR (neat): $\tilde{\nu} = 3080$, 1680, 1634, 1356, 996, 910, 830, 755 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 2.59$ (s, 3H), 3.44 (dd, $J = 6.4$ Hz, 1.6 Hz, 4H), 5.00 (dd, $J = 8.8$ Hz, 1.6 Hz, 2H), 5.10 (dd, $J = 8.8$ Hz, 1.6 Hz, 2H), 5.99–5.89 (m 2H), 7.27 (d, $J = 8.8$ Hz, 1H,), 7.77–7.75 (m, 2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = 26.6$, 37.0, 37.1, 116.4, 116.7, 128.7, 129.6, 129.9, 135.6, 136.0, 136.3, 138.5, 143.9, 198.1; HR-MS (Q-ToF): $m/z = 201.1286$, calcd. for $C_{14}H_{17}O$ (M+H): 201.1279.

2-Acetylnaphthalene (25)

To a stirred solution of 3,4-diallylacetophenone (**21**; 25.0 mg, 0.11 mmol) in dry dichloromethane (5 mL), Grubbs' catalyst **1** (2.7 mg, 3 mol %) was added. At the conclusion of the reaction (25 min, TLC monitoring), DDQ (255.0 mg, 0.92 mmol) and benzene (10 mL) were added. The resulting reaction mixture was heated to reflux for 48 h and solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography. Elution of the column with 2% ethyl acetate/petroleum ether mixture gave the desired product **25** as a white solid; yield: 18.0 mg (82%); mp 76–78 °C (Lit. mp 76–77 °C).[34] ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 2.73$ (s, 3H), 7.62–7.54 (m, 2H), 7.89 (t, $J = 8.4$ Hz, 6.4 Hz, 2H), 7.97 (d, $J = 7.6$ Hz, 1H), 8.04 (dd, $J = 8.8$ Hz, 1.6 Hz, 1H), 8.47 (s, 1H).

5,8-Bis[allyloxy]-2,3-dimethyl-1,4-dihydronaphthalene (35)

To a solution of diol **32**[37] (1.1 g, 5.7 mmol) in dry acetone, potassium carbonate (3.2 g, 22.8 mmol) and allyl bromide (2.1 gm, 17.1 mmol) were added. The reaction mixture was stirred at room temperature for 24 h and then filtered through a celite pad. The residue was washed with dichloromethane (3 × 30 mL). Evaporation of the solvent gave the crude product, which was charged on a silica gel column. Elution of the column with 1% ethyl acetate/petroleum ether mixture gave the compound **35** as a white crystalline solid; yield: 1.24 g (81%); mp 97 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.77$ (s, 6H), 3.24 (s, 4H), 4.49 (dt, $J = 5.1$, 1.7 Hz, 4H), 5.26 (dd, $J = 10.5$, 1.5 Hz, 2H); 5.41 (dd, $J = 17.3$, 1.5 Hz, 2H); 6.0–6.13 (m, 2H), 6.59 (s, 2H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): $\delta = 18.6$, 31.1, 69.1, 108.1, 116.8, 122.4, 125.5, 133.9, 149.7; anal. calcd. (%) for $C_{18}H_{22}O_2$: C 79.96, H 8.20; found: C 79.90, H 7.74.

Claisen Rearrangement of Compound 34 under Conventional Heating Conditions

A solution of **34** (464 mg, 2.12 mmol) in xylene (8 mL) was refluxed for 12 h. Xylene was distilled off under reduced pressure and the crude reaction mixture was directly charged on a silica gel column. Elution of the column with petroleum ether gave 2,3-diallyl-5,6-dimethyl[1,4]benzoquinone (**38**) as a yellow liquid; yield: 121 mg (26%); $R_f = 0.5$ (silica gel, EtOAc/petroleum ether, 1:49). IR (neat): $\tilde{\nu} = 1651$ cm^{-1} (C=O); UV ($CHCl_3$): λ_{max} (ε) = 276 nm (3542 mol^{-1} dm^3 cm^{-1}); ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 2.03$ (s, 6H), 3.27 (dt, $J = 6.4$, 1.6 Hz, 4H), 5.02–5.09 (m, 4H), 5.75–5.85 (m, 2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = 12.5$, 30.6, 116.8, 134.2, 140.8, 142.3, 187.2; HR-MS (Q-ToF): $m/z = 217.1228$, calcd. for $C_{14}H_{17}O_2$ (M+H): 217.1229.

Claisen Rearrangement of Compound 35 under Conventional Heating Conditions

A solution of **35** (100 mg, 0.37 mmol) in *N,N*-dimethylaniline (8 mL) was refluxed for 12 h. The solvent was distilled off under reduced pressure and the crude reaction mixture was charged on a silica gel column. Elution of the column with 1% ethyl acetate/petroleum ether gave 2,3-diallyl-6,7-dimethylnaphthalene-1,4-(5*H*,8*H*)-dione (**40**) as a yellow liquid; yield: 49 mg (49%); $R_f = 0.26$ (silica gel, EtOAc/petroleum ether, 1:49). IR (neat): $\tilde{\nu} = 1656$; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 1.73$ (s, 6H), 3.0 (s, 4H), 3.27 (d, $J = 6.0$ Hz, 4H), 5.03–5.09 (m, 4H), 5.75–5.85 (m, 2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = 18.2$, 30.2, 30.6, 116.7, 121.9, 134.0, 139.3, 142.0, 186.6; MS (Q-ToF): *m/z* 269.0 [$C_{18}H_{17}O_2$ (M + H)].

General Procedure for Claisen Rearrangement under MWI using Silica Gel Support

To a dichloromethane solution of starting material in a beaker, was added pre-activated (pre-activation of the silica gel was achieved by MWI [Ken Star, OM-992E] for 5 min) silica gel (100–200 mesh, 4–10 times the weight of the starting substrate) and then the solvent was evaporated. The resulting homogeneous mixture of the substrate and silica gel was then irradiated in a microwave oven (power 800 watt) for optimized time. The crude reaction mixture was purified by flash chromatography. Elution of the column with an appropriate mixture of ethyl acetate and petroleum ether gave the desired product.

2,3-Diallyl-5,6-dimethyl[1,4]benzoquinone (38)

Compound **34** (517 mg, 2.37 mmol) was mixed with silica gel (2.4 g) and then irradiated in a microwave oven for 7 min by following a general procedure. The crude reaction mixture was then directly charged on a silica gel column. Elution of the column with petroleum ether gave the compound **38** as a yellow liquid; yield: 200 mg (39%). The ^{1}H NMR spectral data of this compound were found to be identical to those of the earlier reported compound.

2,3-Diallyl-6,7-dimethyl[1,4]naphthoquinone (41)

Compound **35** (113 mg, 0.42 mmol) was mixed with silica gel (3.9 g) and then irradiated in a microwave oven for 15 min by following a general procedure. The crude reaction mixture was charged on a silica gel column. Elution of the column with 1% Ethyl acetate/petroleum ether gave compound **41** as a yellow liquid; yield: 48 mg (43%). IR (neat): $\tilde{\nu} = 1661$ cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 2.38$ (s, 6H); 3.41 (dt, $J = 6.4$, 1.6 Hz, 4H); 5.05–5.14 (m, 4H); 5.82–5.92 (m, 2H); 7.81 (s, 2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = 20.3$, 30.9, 116.9, 127.5, 130.2 121.9, 134.2, 143.4, 144.9, 185.0; HR-MS (Q-Tof): *m/z* = 267.1382, calcd. for $C_{18}H_{19}O_2$ (M + H): 267.1385.

2,3-Diallyl-1,4-dimethoxyanthraquinone (42)[39]

To a solution of **36** (102 mg, 0.32 mmol) in dry acetone, potassium carbonate (221 mg, 1.6 mmol) and methyl iodide (0.2 mL, 3.2 mmol) were added. The reaction mixture was then allowed to stir at room temperataure for 24 h. and then filtered through a celite pad. The residue was washed with dichloromethane (3 × 10 mL). Evaporation of the solvent gave the crude product, which was charged on a silica gel column. Elution of the column with 3% ethyl acetate in petroleum ether gave the compound **42** as a yellow liquid; yield: 109 mg (98%). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 3.59$ (dt, $J = 3.9$, 1.8 Hz, 4H), 3.91 (s, 6H; 2 × OCH_3), 4.94 (d, $J = 17.2$ Hz, 2H), 5.08 (d, $J = 10.2$ Hz, 2H), 5.92–6.05 (m, 2H), 7.71–7.76 (m, 2H), 8.19 (dd, 2H, $J = 5.7$, 3.3 Hz).

2,3-Diallyl-1,4-diethoxyanthraquinone (43)

To a solution of **36** (68 mg, 0.21 mmol) in dry acetone, ethyl bromide (0.2 mL, 2.9 mmol) sodium iodide (319 mg, 2.1 mmol) and sodium hydroxide (85 mg, 2.1 mmol) were added. The reaction mixture was then allowed to reflux for 24 h. It was then filtered through a celite pad. The residue was washed with dichloromethane (3 × 10 mL). Evaporation of the solvent gave the crude product, which was charged on a silica gel column. Elution of the column with 3% ethyl acetate in petroleum ether gave compound **43** as a yellow crystalline solid; yield: 50 mg (63%); mp 70 °C. IR (neat): $\tilde{\nu} = 1673$ cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.52$ (t, $J = 7$ Hz, 6H), 3.59 (dt, $J = 5.6$, 2 Hz, 4H), 4.01(q, $J = 6.8$ Hz, 4H), 4.92 (d, $J = 17.2$ Hz, 2H), 5.06 (d, $J = 10.2$ Hz, 2H) 5.93–6.03 (m, 2H), 7.69–7.74 (m, 2H), 8.18 (dd, $J = 5.6$, 3.2 Hz, 2H); HR-MS (Q-ToF): *m/z* = 377.1769, calcd. for $C_{24}H_{25}O_4$ (M + H): 377.1753.

2,3-Diallyl-9,10-dioxo-9,10-dihydroanthracene-1,4-diyl Diacetate (44)[40]

To a solution of **36** (64 mg, 0.2 mmol) in dry pyridine (2 mL), acetic anhydride (0.1 mL, 1 mmol) was added. The reaction mixture was then allowed to stir at room temperature for 24 h. Water (30 mL) and diethyl ether (30 mL) were added and the solution was washed with 1 N HCl and saturated aqueous $NaHCO_3$ (10 mL), then dried over anhydrous $MgSO_4$. Evaporation of the solvent gave the crude product, which was charged on a silica gel column. Elution of the column with 6% ethyl acetate in petroleum ether gave the compound **44** as a yellow crystalline solid; yield: 77 mg (95%); mp 151 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 2.49$ (s, 6H), 3.49 (m, 4H), 5.02 (d, $J = 17.2$ Hz, 2H), 5.09 (d, $J = 10.2$ Hz, 2H), 5.79–5.89 (m, 2H), 7.7–7.74 (m, 2H), 8.14 (dd, $J = 5.8$, 3.4 Hz, 2H).

6,11-Dimethoxytetracene-5,12-dione (51)

To a solution of compound **42** (49 mg, 0.14 mmol) in dry degassed DCM (12 mL) was added the Grubbs' catalyst **1** (6 mg, 5 mol%). The reaction mixture was refluxed for 24 h. In the same pot DDQ (48 mg, 0.21 mmol) dissolved in dry benzene (15 mL) was added and refluxed for an additional 24 h. Then, the reaction mixture was concentrated and the crude product was purified by a silica gel column. Elution of the column with 3% ethyl acetate/petroleum ether gave compound **51** as a yellow crystalline solid; yield: 22 mg (47%); $R_f = 0.55$ (silica gel, EtOAc/petroleum ether 1:9); mp 188 °C (Lit. mp 183–184 °C).[41] ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 4.14$ (s, 6H), 7.74–7.78 (m, 4H; ArH), 8.27 (dd, $J = 5.9$, 3.5 Hz, 2H), 8.42 (dd, $J = 6.3$, 3.3 Hz, 2H);

^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 63.3, 120.8, 124.8, 126.8, 130, 132.8, 133.6, 134.9, 155.8 (C-6, C-11), 182.7 (C-5, C-12).

6,11-Diethoxytetracene-5,12-dione (52)

To a solution of compound **43** (42 mg, 0.11 mmol) in dry degassed DCM (12 mL) was added the Grubbs' catalyst **1** (5 mg, 5 mol%). The reaction mixture was refluxed for 24 h. In the same pot DDQ (39 mg, 0.17 mmol) dissolved in dry benzene (15 mL) was added and refluxed for 24 h. Then, the reaction mixture was concentrated and the crude product was purified by a silica gel column. Elution of the column with 4% ethyl acetate/petroleum ether gave the compound **52** as a yellow crystalline solid; yield: 14 mg (37%); R_f = 0.6 (silica gel, EtOAc/petroleum ether, 1:9); mp 152–153 °C. IR (neat): $\tilde{\nu}$ = 1675 cm^{-1} (C=O); UV ($CHCl_3$): λ_{max} (ε) = 297 nm (10159 mol^{-1} dm^3 cm^{-1}); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.66 (t, J = 6.9 Hz, 6H), 4.26 (q, J = 7 Hz, 4H), 7.71–7.78 (m, 4H), 8.27 (dd, J = 5.7, 3.3 Hz, 2H), 8.43 (dd, J = 6.6, 3.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 15.8, 72.0, 121, 125, 126.8, 129.9, 133.2, 133.5, 135.1, 154.9, 183.0; HR-MS (Q-ToF): m/z = 347.1290, calcd. for $C_{22}H_{19}O_4$ (M+H): 347.1283.

6,11-Diacetoxytetracene-5,12-dione (53)[42]

To a solution of compound **44** (37 mg, 0.09 mmol) in dry degassed DCM (12 mL) was added the Grubbs' catalyst **2** (4 mg, 5 mol%). The reaction mixture was refluxed for 24 h. In the same pot DDQ (31 mg, 0.14 mmol) dissolved in dry benzene (15 mL) was added and refluxed for 24 h. Then, the reaction mixture was concentrated and the crude product was purified by a silica gel column. Elution of the column with 10% ethyl acetate/petroleum ether gave the compound **53** as a yellow crystalline solid; yield: 17 mg (51%); R_f = 0.22 (silica gel, EtOAc/petroleum ether, 3:47). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.66 (s, 6H), 7.74–7.8 (m, 4H), 8.19 (dd, J = 7.7, 3 Hz, 2H), 8.24 (dd, J = 6, 3.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 21.3, 119.9, 124, 127.1, 130.7, 131.3, 134.4, 135.1, 146.4, 169.3, 181.7.

2,3-Dimethyl[1,4]naphthoquinone (54)

To a solution of compound **38** (56 mg, 0.26 mmol) in dry degassed DCM (12 mL) was added the Grubbs' catalyst **1** (11 mg, 5 mol%). The reaction mixture was refluxed for 24 h. In the same pot DDQ (89 mg, 0.39 mmol) dissolved in dry benzene (15 mL) was added and refluxed for 24 h. Then, the reaction mixture was concentrated and the crude product was purified by a silica gel column. Elution of the column with 1% ethyl acetate/petroleum ether gave the compound **54** as a yellow crystalline solid; yield: 26 mg (54%); R_f = 0.45 (silica gel, EtOAc/petroleum ether, 1:49); mp 130 °C (Lit. mp 123–126 °C).[43] ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.18 (s, 6H), 7.69 (dd, J = 5.7, 3.3 Hz, 2H), 8.07 (dd, J = 5.7, 3.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 13.0, 126.3, 132.2, 133.4, 143.5, 185.0.

One-Pot RCM and Aromatization of 40

To a solution of compound **40** (19 mg, 0.07 mmol) in dry degassed dichloromethane (4 mL) was added the Grubbs' catalyst **1** (4 mg, 5 mol%). The reaction mixture was stirred for 6 h. at room temperature. In the same pot DDQ (48 mg, 0.21 mmol) dissolved in dry benzene (15 mL) was added and refluxed for 24 h. Then, the reaction mixture was concentrated and the crude product was purified by a silica gel column. Elution of the column with 1% ethyl acetate/petroleum ether gave 2,3-dimethyl-anthraquinone (**55**) as a yellow crystalline solid; yield: 21 mg (91%); R_f = 0.15 (silica gel, EtOAc/petroleum ether, 1:49); mp 212–213 °C (Lit. mp 210–212 °C).[44]

One-Pot RCM and Aromatization of 41

To a solution of compound **41** (26 mg, 0.097 mmol) in dry degassed DCM (5 mL) was added the Grubbs' catalyst **1** (4 mg, 5 mol%). The reaction mixture was stirred for 6 h at room temperature. In the same pot DDQ (33 mg, 0.14 mmol) dissolved in dry benzene (15 mL) was added and refluxed for 24 h. Then, the reaction mixture was concentrated and the crude product was purified by a silica gel column. Elution of the column with 1% ethyl acetate/petroleum ether gave 2,3-dimethyl-anthraquinone **(55)** as a yellow crystalline solid; yield: 21 mg (91%). The melting point of this compound was found to be identical to that of the earlier reported compound.

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