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# Annulation selectivity in the coupling of Fischer carbene complexes with *o*-alkynylbiphenyl and *o*-alkynylstyrene derivatives☆

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**Abstract**—The coupling of various Fischer carbene complexes with o-ethynylbiphenyl and an *o*-alkynylstyrene derivatives has been examined. In coupling reactions with methylcarbene and cyclopropylcarbene complexes, the major products are derived from C–H or C–C activation processes. In coupling reactions with phenylcarbene complexes, the major products are derived from the Dötz reaction.


## 1. Introduction

In recent papers, the coupling of carbene complexes with *Z* phenylvinylacetylenes (e.g. **1**, Scheme 1)[2] and dienylacetylenes (e.g. **7**)[3] was reported. These coupling reactions afforded benzannulation products (e.g. **6** and **9**). In each case, the anticipated phenol derivative (**5** or **8**) was unstable under the reaction conditions, and ultimately resulted in either the ketal or benzofuran derivatives, depending upon the workup conditions. The design of the reaction processes in Scheme 1 is based on the well-known benzannulation that occurs in the coupling of alkynes with arylcarbene- or alkenylcarbene–chromium complexes (**10**, Scheme 2), commonly known as the Dötz reaction.[4] Isolated dienylcarbene complexes (e.g. **13**) also lead to cyclization/benzannulation products under photochemical conditions.[5] A common feature of all of the reaction processes in Schemes 1 and 2 is the intermediacy of an α,β,γ,δ-unsaturated carbene complex (e.g. **3**, **11**, and **13**), also known as a metallahexatriene.[6] Arylcarbene and alkenylcarbene complexes both participate in the Dötz reaction with similar efficiency. Derivatives of complex **13** where either one or both of the double bonds of the α,β,γ,δ-unsaturated system are contained within an aromatic ring undergo bennzannulation reactions with similar efficiency. In this paper, the analogous reaction processes involving the coupling of carbene complexes with *o*-ethynylbiphenyl derivative **16** (Scheme 3) and *o*-alkynylstyrene derivative **17** are examined. Unlike the conversion of **13** to **15** in Scheme 2, placement of the central alkene within an aromatic ring is detrimental to the success of the benzannulation reaction pathway in these systems.

## 2. Results

### 2.1. Synthesis of compounds 16 and 17

Compounds **16** and **17** were synthesized according to the sequence of reactions depicted in Scheme 4. Compound **16** was prepared from 2-biphenylmethanol (**18**) via oxidation to aldehyde **19** followed by Corey–Fuchs alkynylation.[7] Styrenyl compound **17** was prepared from *o*-bromobenaldehyde **20** via Sonogashira coupling[8] followed by Wittig reaction.

### 2.2. Coupling of *o*-alkynylstyrene derivative 17 and carbene complexes

The coupling of carbene complex **2** with alkynylstyrene derivative **17** afforded none of the expected benzannulation products **26** or **27** (Scheme 5). A complex mixture of five-membered ring derivatives **22**–**25** was produced in this reaction. Similar products were obtained from the coupling of alkynylstyrene derivative **17** with cyclopropylcarbene complex **28** using 99:1 dioxane/water as the solvent. Related cyclopentenone structures have been obtained from the coupling of simple alkynes with methylcarbene complex **2**[9] or cyclopropylcarbene complex **28**,[10] thus the pendant alkene appears to have no effect on the reaction processes in Scheme 5. Coupling of alkynylstyrene

☆ See Ref. 1.

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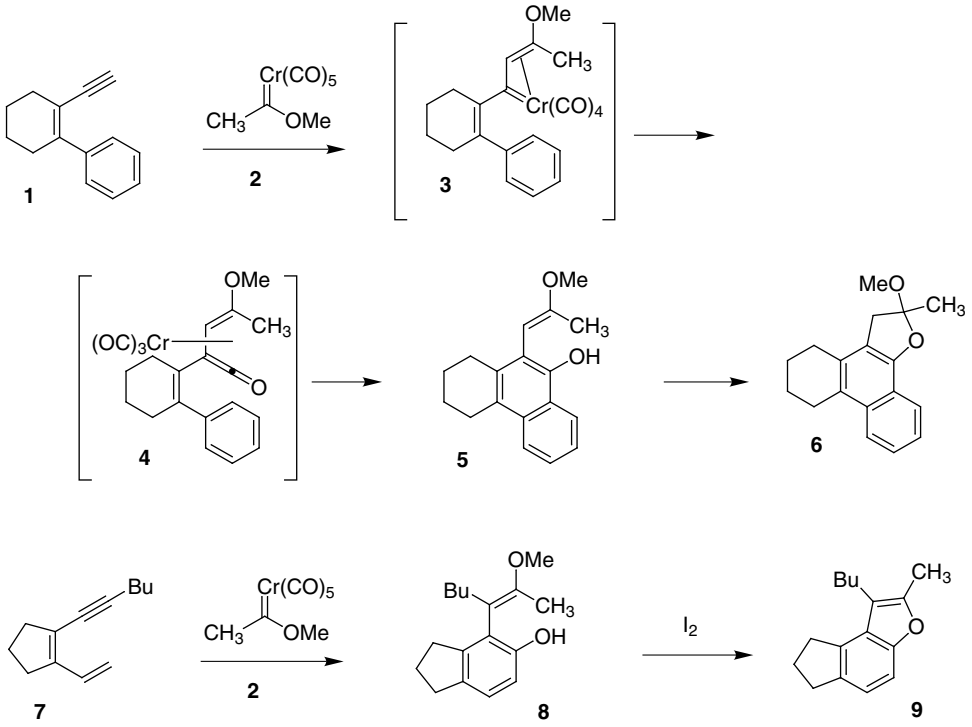
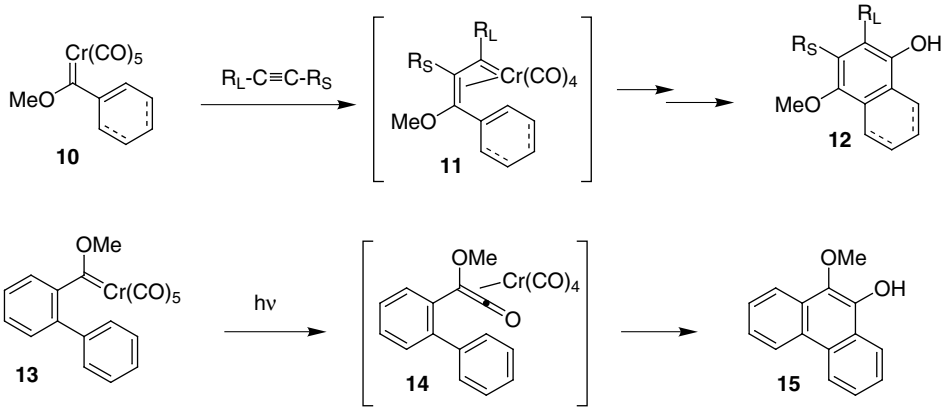
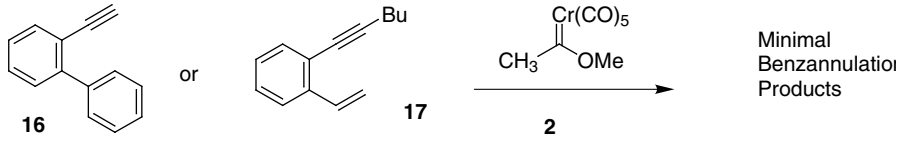



**Scheme 1.**




**Scheme 2.**

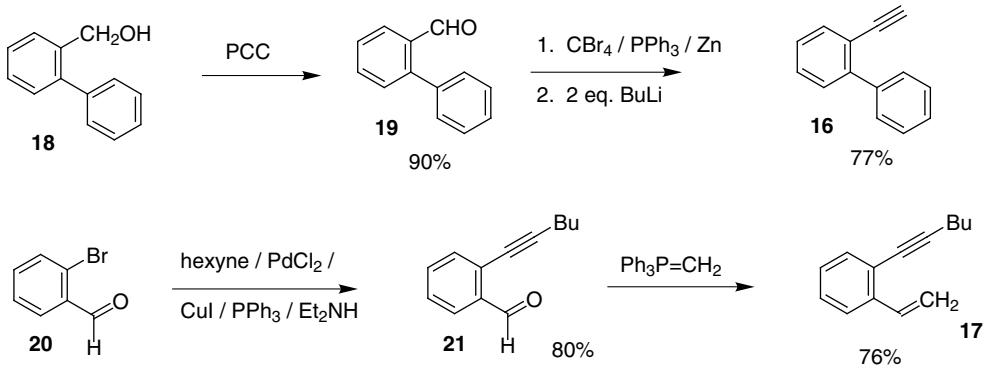



**Scheme 3.**

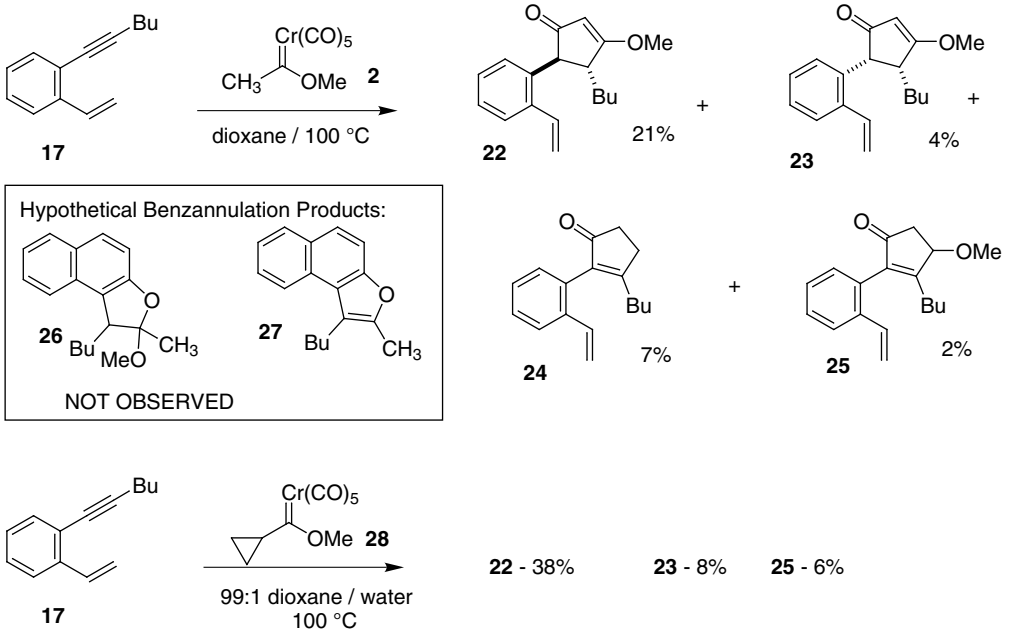
derivative **17** with phenylcarbene complex **29** led exclusively to the Dötz benzannulation product **30** (Scheme 6). None of the products from benzannulation onto the styrenyl system, naphthalenes **31** or **32**, were observed in the reaction.

### 2.3. Coupling of 2-ethynylbiphenyl (16) with carbene complexes

The reaction of 2-ethynylbiphenyl (**16**) with carbene complex **2** led to a mixture of oxidized benzannulation product **33A** and cyclopentannulation product **34** (Scheme 7). Phenanthrene **33A** is likely derived from air oxidation of enol ether **35A** or ketal **36A**. In the initial separation of the reaction mixture by flash chromatography, a fraction containing **33A** and a compound consistent with enol ether **35A** could be isolated. Attempts to separate **33A** and **35A** were not successful. Optimal weight recoveries were obtained if the reaction mixture was separated by

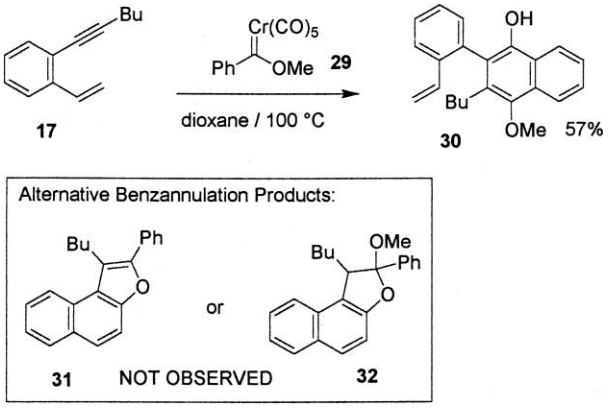



**Scheme 4.**




**Scheme 5.**

preparative TLC. Under these conditions only oxidized product **33A** and cyclopentenone **34** were obtained from the reaction. Similar products were obtained from coupling of alkyne **16** with cyclopropylcarbene complex **28**; the yield of cyclopentannulation product **34** was much higher in this case. An unusual multiple benzannulation product **38** was obtained from the coupling of phenylcarbene complex **29** and alkyne **16** (Scheme 8). This product is more likely derived from Dötz benzannulation product **37** and not the alternative benzannulation product **39** based on the more appropriate location of the oxygens in **37** vs the oxygens of **39**. A trace amount of alternative benzannulation product **33C** (2% yield) was also obtained from this reaction.

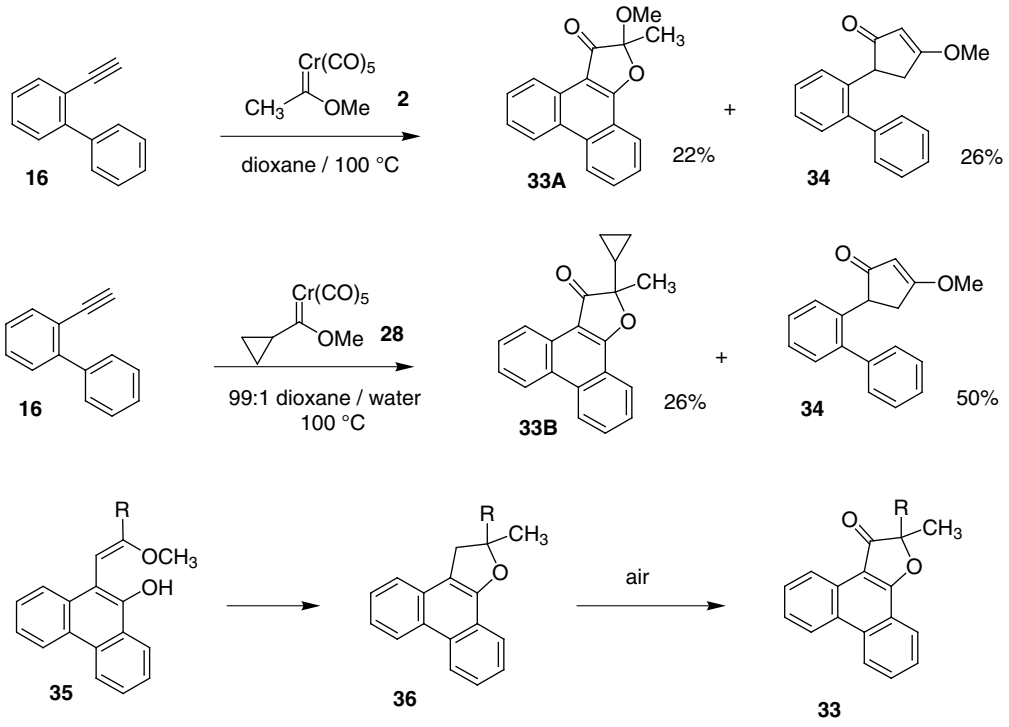



**Scheme 6.**

## 3. Discussion

### 3.1. Benzannulation vs cyclopentannulation in the coupling of methylcarbene complex 2 or cyclopropylcarbene complex 28 with alkynes 16 and 17

The results in Schemes 5–8 all show that 2-ethynylbiphenyl (**16**) and *o*-alkynylstyrene **17** are very reluctant to undergo benzannulation reactions with Fischer carbene complexes in contrast to the systems depicted in Scheme 1. In the reactions of Schemes 5 and 7, C–H or C–C activation processes are preferred over benzannulation processes. Previous

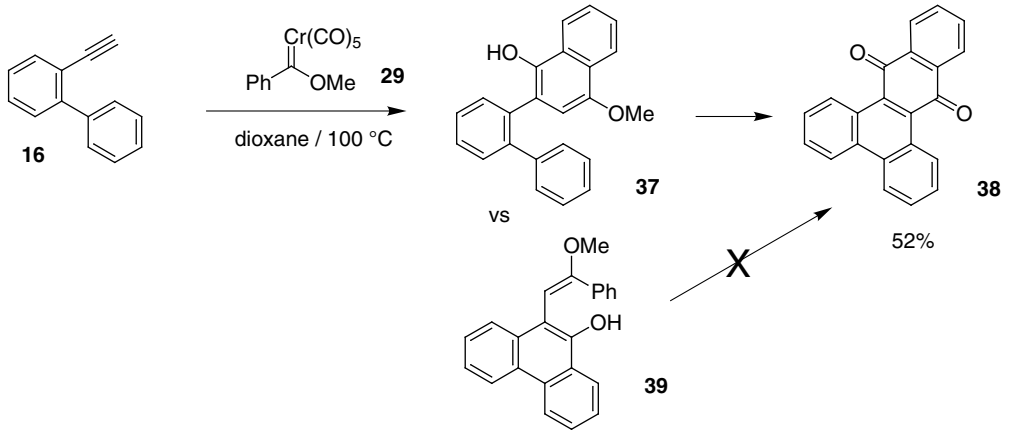



**Scheme 7.**

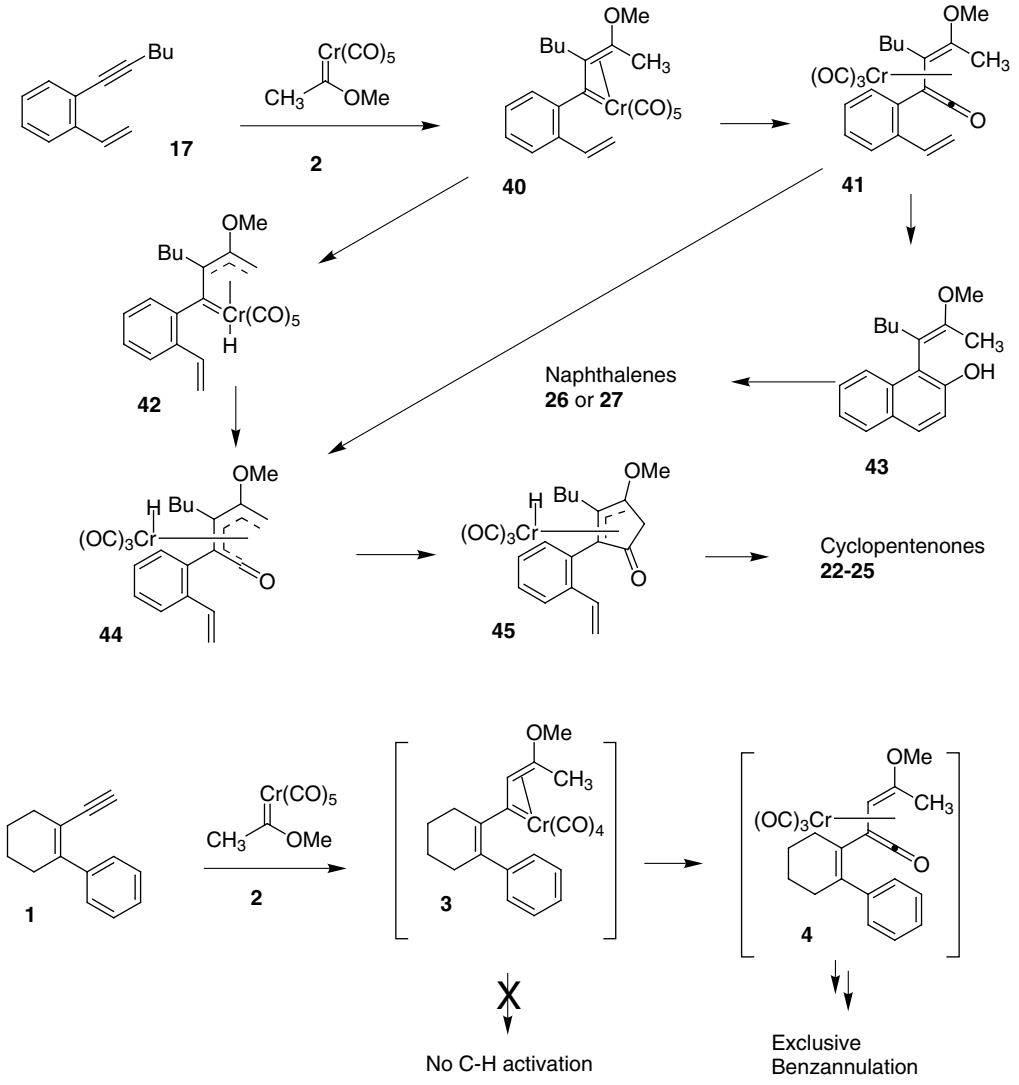
reports of the cyclopentannulation reactions depicted in Schemes 5 and 7[9,10] suggested mechanistic alternatives, where the C–H activation process occurred at either the vinylketene or vinylcarbene stages (Scheme 9). No definitive experiment was presented that could delineate which intermediate was involved in the C–H(C–C) activation event. Very strong evidence however supports the intermediacy of vinylketene complexes in the benzannulation event.[11]

The observed results in Schemes 5–7 suggest that the C–H(C–C) activation events occur at the vinylketene stage. If the C–H(C–C) events occur at the vinylcarbene stage, the competitive process is C–H(C–C) activation vs CO insertion (i.e. conversion of **40** to **42** vs conversion of **40** to **41**, Scheme 9). Occurrence of the C–H(C–C) activation event at the vinylcarbene stage would likely result in similar reaction pathways for the coupling of carbene complexes **2** or **28** with alkynes **16**, **17**, or **1**. Since neither intermediate **40** nor intermediate **3** can directly undergo the benzannulation event, the competition between CO insertion and C–H(C–C) activation should be similar for these two intermediates. The vinylketenes derived from these intermediates (**41** and **4**) however differ greatly in the placement of aromatic rings and cyclization to the phenols (**43** or **5**) will likely occur at different rates. As noted in Ref. 2, benzannulation is the exclusive reaction pathway for the coupling of alkyne **1** with carbene complexes **2** and **28**.

The less facile benzannulation of vinylketene **41** relative to vinylketene **4** is not consistent with a recent theoretical study of the Dötz reaction.[12] In the energetically most




**Scheme 8.**

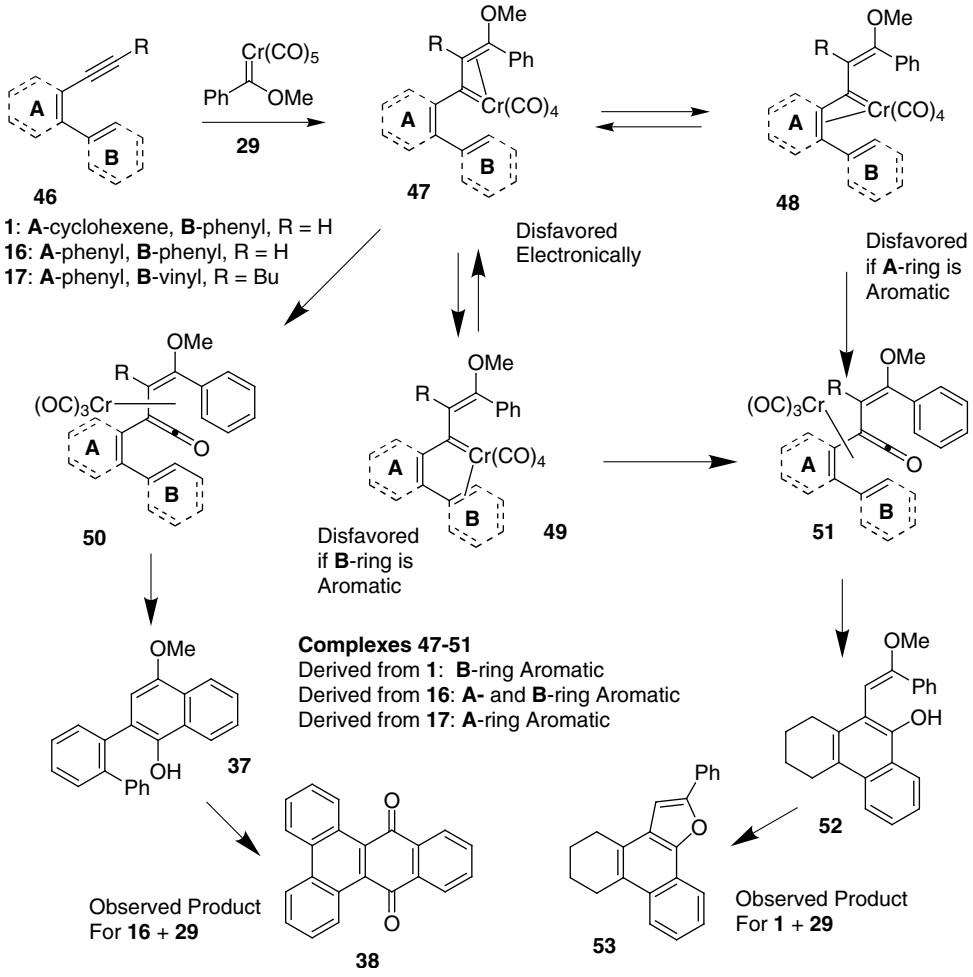



**Scheme 9.**

reasonable pathway for this reaction, coordination of the metal to the γ,δ-double bond of a dienylcarbene intermediate was suggested as an important event. This event should be more favorable for complex **40** than for complex **3** since coordination to the monosubstituted alkene of **40** would be more favorable than $\eta^2$-coordination to the aromatic ring in intermediate **3**.[13]

### 3.2. Competitive benzannulation in the coupling of phenylcarbene complex 29 with alkynes 16 and 17

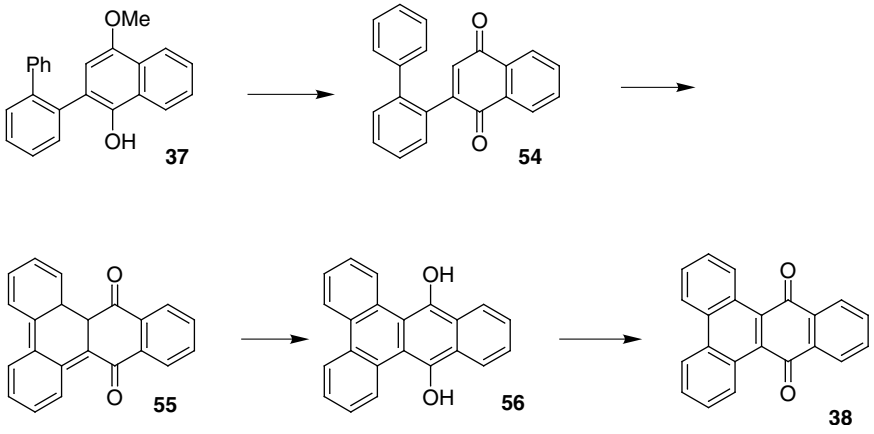
The reaction of phenylcarbene complex **29** with alkynes **16** or **17** led to predominantly products derived from benzannulation onto the phenyl ring originating from the carbene complex. Coupling of carbene complex **29** with alkyne **1** afforded predominantly benzofuran **53** (Scheme 10),[2] which is derived from benzannulation onto the phenyl ring originating from the enyne. The different reaction pathways of alkynes **1** vs alkynes **16** and **17** can be attributed to ligation preferences in the intermediate vinylcarbene complex intermediates (e.g. **47**–**49**). The coupling of carbene complex **29** with generic alkyne **46** should initially produce vinylcarbene complex **47**. An electronically favorable ligand isomerization would then afford alternative vinylcarbene complex intermediate **48**. This isomerization is observed when the **A**-ring is not aromatic, as in complexes derived from alkyne **1**, and thus the preferred reaction pathway is isomerization of **47** to **48** followed by CO-insertion to give vinylketene **51** and electrocyclic ring closure in the coordination sphere of chromium to afford phenol **52** and ultimately benzofuran **53**. When the **A**-ring is aromatic, as in intermediates derived from alkynes **16** and **17**, the isomerization of **47** to **48** is disfavored since the isomerization step involves the formation of a partially coordinated aromatic ring.[13] The observed reaction pathway in this case is conversion of initially generated vinylcarbene complex **47** to vinylketene **50** and electrocyclic ring closure in the coordination sphere of chromium to afford phenol **37** and ultimately quinone **38**. An alternative scenario for alkyne **17** is conversion of **47** to **49** and subsequent benzannulation onto the vinyl group,[12] however, this event does not seem to be important since the only product of this reaction is also derived from benzannulation onto the phenyl ring originating at the carbene complex (naphthol **30**, Scheme 6).




**Scheme 10.**

### 3.3. Formation of dibenzoanthraquinone 38 and not naphthol 37

In the coupling of alkyne **16** with phenylcarbene complex **29**, the expected benzannulation product **37** was not isolated. Only the double benzannulation product **38** was obtained from the reaction. A possible reason for this benzannulation is a secondary cyclization process emanating from naphthoquinone **54**, as depicted in Scheme 11.[14] These series of events are surprising in that no deliberate attempt to oxidize naphthol **37** to naphthoquinone **54** has been attempted. In the first attempt to purify the products of this reaction by flash chromatography, quinone **38** was observed as the major product, contaminated with a compound featuring a methoxy group and no protons in the bay region. This product is likely the Dötz reaction product **37**, however, it could not be obtained free of anthraquinone **38**.




**Scheme 11.**

## 4. Conclusion

The coupling of carbene complexes with phenylacetylene derivatives featuring unsaturated ortho-substituents has been explored. Benzannulation involving the unsaturated acetylene system is never more than a minor reaction pathway in these systems, which is in contrast to the efficient benzannulation reactions previously reported for coupling of carbene complexes and dienylacetylene derivatives where the central alkene is not in an aromatic ring. The reduced benzannulation efficiency has been attributed to poorer ligation ability of an aromatic ring relative to a simple alkene.

## 5. Experimental

### 5.1. General considerations

Nuclear magnetic resonance ($^1$H and $^{13}$C) spectra were recorded on a Bruker AF200 (200 MHz) or Bruker AF400 (400 MHz) spectrometer. Chemical shifts are reported in parts per million ($\delta$) downfield from an internal tetramethylsilane reference. Coupling constants ($J$ values) are reported in hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Infrared spectra were recorded on a Nicolet 5DXC FT-IR spectrometer. Band positions are reported in reciprocal centimeters ($cm^{-1}$). Band intensities are reported relative to the most intense band and are listed as: br (broad), vs (very strong), s (strong), m (medium), w (weak). Only diagnostic bands occurring outside of the region 2800–3100 $cm^{-1}$ are reported. Mass spectra (MS) were obtained on a VG 7070E spectrometer using electron impact (EI) or chemical ionization (CI) or on a Hewlett-Packard GC-Mass Spec 5970B with Mass Selection Detector; *m/e* values are reported, followed by the relative intensity in parentheses. Flash column chromatography was performed using thick-walled glass columns and 'flash grade' silica (Bodmann 230–400 mesh). Routine thin layer chromatography (TLC) was performed by using precoated 250 μm mm silica gel plates purchased from Whatman. Preparative thin layer chromatography (prep TLC) was performed by using precoated 1000 μm silica gel plates purchased from Whatman. The relative proportion of solvents in mixed chromatography solvents refers to the volume: volume ratio. All commercially available reagents and reactants were obtained in reagent grade and used without purification. All reaction solvents were distilled for purity. Diethyl ether, THF and dioxane were distilled from sodium-benzophenone ketyl, dichloromethane from calcium hydride prior to use. All reactions were performed in an inert atmosphere created by a slight positive pressure (ca. 0.1 psi) of nitrogen. Carbene complexes were prepared according to literature procedures.[15]

**5.1.1. Synthesis of 2-biphenylcarboxaldehyde (19).** To a suspension of Celite (6.25 g) and pyridinium chlorochromate (6.25 g, 29.0 mmol) in dichloromethane (90 mL) was added dropwise a solution of 2-biphenylmethanol (2.68 g, 15.0 mmol) in dichloromethane (20 mL). The mixture was allowed to stir for a 12 h period and diluted with ether (50 mL). The mixture was then filtered, dried over magnesium sulfate, and the solvent was removed on a rotary evaporator. Final purification was achieved by flash chromatography on silica gel using 9:1 hexane/ethyl acetate as eluent. After solvent removal, a yellow oil identified as 2-biphenylcarboxaldehyde (**19**) (2.40 g, 90%) was obtained. $^1$H NMR ($CDCl_3$): $\delta$ 9.95 (s, 1H), 8.02 (m, 1H), 7.51 (m, 8H). The spectral data are in agreement with those previously reported for this compound.[16]

**5.1.2. Synthesis of 2-ethynylbiphenyl (16).** A mixture of zinc dust (220 mg, 3.29 mmol), triphenylphosphine (860 mg, 3.29 mmol), and carbon tetrabromide (1.09 g, 3.29 mmol) in dichloromethane (100 mL) was stirred at room temperature under nitrogen for a 24 h period. To this solution was added 2-biphenylcarboxaldehyde (**19**) (300 mg, 1.65 mmol) and the reaction was allowed to stir for a 2 h period. Pentane (350 mL) was added and the suspension was filtered. The solvent was removed from the filtrate using a rotary evaporator; the residue after evaporation was dissolved in THF (100 mL), placed under nitrogen, and cooled to −78°C. *n*-Butyllithium (2.06 mL of a 1.6 M hexane solution, 3.30 mmol) was added and the solution was kept at −78°C for 1 h. The reaction mixture was then allowed to warm to room temperature and stirred for 1 h. Water (1 mL) was added and the mixture was poured into a mixture of water and pentane in a separatory funnnel and shaken vigorously. The pentane layer was dried over magnesium sulfate and the solvent was removed on a rotary evaporator. Final purification was achieved by flash chromatography on silica gel using 24:1 hexane:ethyl acetate as eluent. After solvent removal, a colorless oil identified as 2-ethynylbiphenyl (16) (230 mg, 77%) was obtained. $^1$H NMR ($CDCl_3$): $\delta$ 7.67–7.59 (m, 3H), 7.50–7.32 (m, 6H), 3.05 (s, 1H); $^{13}$C NMR ($CDCl_3$): $\delta$ 144.3, 140.3, 133.9, 129.6, 129.3, 129.0, 128.0, 127.6, 127.1, 120.7, 83.0, 80.1; IR ($CCl_4$): 3313 (s), 2106 (w) $cm^{-1}$; MS (EI): 178 (M, 100), 151 (17); HRMS: calcd for $C_{14}H_{10}$—178.07825, found 178.07728.

**5.1.3. Synthesis of butynylstyrene 17.** A mixture of methyltriphenylphosphonium iodide (6.84 g, 17.0 mmol), aldehyde **21**[8] (2.10 g, 11.0 mmol), and sodium hydroxide (0.68 g, 17.0 mmol) in THF (150 mL) and water (1 mL) was heated to reflux for a 24 h period. The solution was filtered and the solvent was removed on a rotary evaporator. Final purification was achieved by flash chromatography on silica gel using pure hexane as eluent. After solvent removal, a colorless oil identified as alkyne **17** (1.54 g, 76%) was obtained. $^1$H NMR ($CDCl_3$): $\delta$ 7.56 (d, 1H, $J$=8.0 Hz), 7.39 (d, 1H, $J$=8.0 Hz), 7.20 (m, 3H), 5.76 (d, 1H, $J$=17.6 Hz), 5.31 (d, 1H, $J$=11.0 Hz), 2.46 (t, 2H, $J$=6.9 Hz) 1.54 (m, 4H), 0.95 (t, 3H, $J$=7.1 Hz); $^{13}$C NMR ($CDCl_3$): $\delta$ 138.9, 135.3, 132.5, 127.6, 127.4, 124.5, 115.0, 95.3, 78.9, 30.9, 22.0, 19.3, 13.6; IR ($CCl_4$): 2215 (w) $cm^{-1}$; MS (EI): 184 (M, 3), 154 (100), 141 (49)128 (24), 115 (39); HRMS: calcd for $C_{14}H_{16}$—181.12520, found 181.12586.

**5.1.4. General procedure for the coupling of alkynes with carbene complexes.** To a two-neck round bottom flask equipped with a reflux condenser, stirrer, and a septum under nitrogen was added dioxane (10 mL). The dioxane was brought to a gentle reflux. To this refluxing dioxane,

with the aid of a syringe pump was added carbene complex (1.0 equiv.) and enyne (1.2 equiv.) in dioxane (10 mL) dropwise over a 2 h period. After the addition was complete, the mixture was allowed to reflux for a 24 h period. The reaction mixture was then allowed to cool to room temperature and then concentrated in vacuo. Ethyl acetate (50 mL) was added and the green chromium residue was filtered over a bed of Celite. The solvent was removed on a rotary evaporator. Final purification was achieved by either flash chromatography on silica gel or prep TLC on silica gel. In all reactions involving cyclopropylcarbene complex **28**, the reaction solvent was 99:1 dioxane/water.

**5.1.5. Coupling of methylcarbene complex 2 with butynylstyrene 17.** The general procedure was followed using carbene complex **2** (44 mg, 0.14 mmol) and enyne **17** (39 mg, 0.21 mmol). After purification on prep TLC using 9:1 hexane/ethyl acetate followed by 5:1 ethyl acetate as the eluent, five fractions were isolated. The product in the first fraction was the starting enyne **17**. The product in the second fraction (3 mg, 7% yield) was identified as cyclopentenone **24**. The product in the third fraction (1 mg, 2% yield) was identified as cyclopentenone **25**. The product in the fourth fraction (10 mg, 21% yield) was identified as cyclopentenone **22**. The product in the fifth fraction (2 mg, 4% yield) was identified as cyclopentenone **23**.

*Cyclopentenone **24***: $^1$H NMR ($CDCl_3$): $\delta$ 7.64 (dd, 1H, $J$=9.1, 2.5 Hz), 7.33 (m, 2H), 7.07 (dd, 1H, $J$=9.0, 2.6 Hz), 6.57 (dd, 1H, $J$=17.5, 11.0 Hz), 5.72 (d, 1H, $J$=17.5 Hz), 5.25 (d, 1H, $J$=11.0 Hz), 2.74 (m, 2H), 2.52 (t, 2H, $J$=4.2 Hz), 2.04 (t, 2H, $J$=7.3 Hz), 1.18 (m, 4H), 0.71 (t, 3H, $J$=7.1 Hz); $^{13}$C NMR ($CDCl_3$): $\delta$ 209.5, 161.5, 156.1, 134.3, 134.2, 128.7, 127.8, 127.0, 126.1, 125.8, 115.8, 34.7, 32.2, 29.8, 23.5, 22.6, 13.7; IR ($CCl_4$): 1706 (s) cm$^{-1}$; MS (EI): 240 (M, 18), 213 (14), 198 (15), 183 (56), 141 (100); HRMS: calcd for $C_{17}H_{20}O$—240.15141, found 240.15147.

*Cyclopentenone **25***. $^1$H NMR ($CDCl_3$): $\delta$ 7.62 (d, 1H, $J$=8.0 Hz), 7.25 (m, 2H), 7.01 (m, 1H), 6.49 (m, 1H), 5.69 (2 d's 1H, $J$=17.0 Hz), 5.19 and 5.18 (2 d's, 1H, $J$=11.0 Hz), 4.61 (m, 1H), 3.48 (s, 3H), 2.85 (dd, 1H, $J$=16.7, 5.0 Hz), 2.70–2.10 (m, 3H), 1.35 (m, 4H), 0.81 (t, 3H, $J$=6.9 Hz) (this compound appears to be a mixture of diastereomeric rotamers based on the appearance of the alkene Hs); $^{13}$C NMR ($CDCl_3$): $\delta$ 200.1, 135.1, 134.9, 131.7, 130.5, 129.8, 128.8, 127.6, 125.7, 115.6, 104.9, 57.3, 41.2, 29.7, 29.4, 28.6, 22.6, 13.7; IR ($CCl_4$): 1706 (s) cm$^{-1}$; Mass spec (EI): 270 (M, 18), 242 (13), 240 (20), 238 (22), 212 (73), 181 (64), 156 (95), 142 (100); HRMS: calcd for $C_{18}H_{22}O_2$—270.16199, found 270.16224.

*Cyclopentenone **22***. $^1$H NMR ($CDCl_3$): $\delta$ 7.45 (dd, 1H, $J$=9.1, 2.6 Hz), 7.20 (m, 2H), 7.00 (m, 1H), 6.92 (dd, 1H, $J$=17.0, 11.0 Hz), 5.62 (dd, 1H, $J$=17.0, 1.4 Hz), 5.38 (s, 1H), 5.30 (dd, 1H, $J$=11.0, 1.4 Hz), 3.89 (s, 3H), 3.63 (d, 1H, $J$=3.1 Hz), 2.89 (m, 1H), 1.80 (m, 1H), 1.22 (m, 5H), 0.83 (br t, 3H, $J$=6.9 Hz); $^{13}$C NMR ($CDCl_3$): $\delta$ 204.6, 191.0, 144.9, 134.9, 131.2, 128.1, 128.0, 127.1, 126.9, 117.1, 103.5, 58.9, 55.5, 49.9, 31.3, 28.4, 22.6, 13.8; IR ($CCl_4$): 1705 (s), 1599 (vs) cm$^{-1}$; Mass spec (EI): 270 (M, 100), 255 (20), 227 (33), 216 (58), 215 (60); HRMS: calcd for $C_{18}H_{22}O_2$—270.16199, found 270.16267.

*Cyclopentenone **23***. $^1$H NMR ($CDCl_3$): $\delta$ 7.44 (m, 1H), 7.19 (m, 2H), 7.00 (m, 2H), 5.59 (dd, 1H, $J$=17.2, 1.4 Hz), 5.45 (s, 1H), 5.29 (dd, 1H, $J$=11.0, 1.4 Hz), 4.17 (d, 1H, $J$=7.4 Hz) 3.86 (s, 3H), 3.09 (q, 1H, $J$=7.4 Hz), 2.64 (m, 1H), 1.26–0.83 (m, 5H), 0.60 (br t, 3H, $J$=6.9 Hz); $^{13}$C NMR ($CDCl_3$): $\delta$ 205.3, 192.9, 138.9, 134.9, 129.8, 128.2, 127.5, 127.2, 126.3, 116.9, 104.1, 58.6, 44.8, 29.6, 29.2, 29.0, 22.4, 13.5; IR ($CCl_4$): 1705 (s), 1599 (vs) cm$^{-1}$; Mass spec (EI): 270 (M, 100), 255 (19), 227 (28), 213 (55); HRMS: calcd for $C_{18}H_{22}O_2$—270.16199, found 270.16169.

**5.1.6. Coupling of cyclopropylcarbene complex 28 with butynylstyrene 17.** The general procedure was followed using carbene complex **28** (36 mg, 0.13 mmol) and enyne **17** (28 mg, 0.15 mmol). After purification on prep TLC using 9:1 hexane/ethyl acetate followed by 5:1 ethyl acetate as the eluent, four fractions were isolated. The product in the first fraction was the starting enyne **17**. The product in the second fraction (2 mg, 6% yield) was identified as cyclopentenone **25**. The product in the third fraction (13 mg, 38% yield) was identified as cyclopentenone **22**. The product in the fourth fraction (3 mg, 8% yield) was identified as cyclopentenone **23**. The spectral data were identical to those reported in the previous experiment.

**5.1.7. Coupling of phenylcarbene complex 29 with butynylstyrene 17.** The general procedure was followed using carbene complex **29** (47 mg, 0.15 mmol) and enyne **17** (33 mg, 0.18 mmol). After purification using flash chromatography and 9:1 hexane/ethyl acetate as eluent, naphthol **30** (28 mg, 57% yield) was isolated. $^1$H NMR ($CDCl_3$): $\delta$ 8.21 (d, 1H, $J$=8.1 Hz), 8.07 (d, 1H, $J$=8.1 Hz), 7.79 (d, 1H, $J$=8.1 Hz), 7.47 (m, 4H), 7.28 (d, 1H, $J$=7.1 Hz), 6.41 (dd, 1H, $J$=17.4, 11.0 Hz), 5.73 (d, 1H, $J$=17.5 Hz), 5.13 (d, 1H, $J$=11.0 Hz), 4.87 (s, 1H), 3.92 (s, 3H), 2.59 (dt, 1H, $J$=14.4, 6.5 Hz), 2.33 (dt, 1H, $J$=14.4, 6.5 Hz), 1.35 (m, 2H), 1.19 (quintet, 2H, $J$=6.5 Hz), 0.67 (t, 3H, $J$=6.5 Hz); $^{13}$C NMR ($CDCl_3$): $\delta$ 147.3, 144.6, 137.8, 134.2, 133.3, 131.9, 130.6, 129.0, 128.4, 128.3, 126.4, 125.7, 124.8, 123.5, 122.7, 121.8, 120.7, 115.8, 62.2, 32.2, 27.5, 22.8, 13.5; IR ($CCl_4$): 3550 (m), 1594 (m) cm$^{-1}$; Mass spec (EI): 332 (M, 100), 317 (16), 275 (22), 261 (67), 260 (46), 259 (66); HRMS: calcd for $C_{23}H_{24}O_2$—332.17764, found 332.17768.

**5.1.8. Coupling of methylcarbene complex 2 with 2-ethynylbiphenyl (16).** The general procedure was followed using carbene complex **2** (48 mg, 0.19 mmol) and 2-ethynylbiphenyl (**16**) (38 mg, 0.21 mmol). After purification on prep TLC using 9:1 hexane/ethyl acetate followed by 5:1 ethyl acetate as the eluent, two fractions were isolated. The product in the first fraction (11.5 mg, 22% yield) was identified the as the oxidized phenanthrene derivative **33A**. The product in the second fraction (13.2 mg, 26% yield) was identified as cyclopentenone **34**.

*Phenanthrene **33***. $^1$H NMR ($CDCl_3$): $\delta$ 8.85 (d, 1H, $J$=7.6 Hz), 8.75 (d, 1H, $J$=7.6 Hz), 8.58 (d, 1H, $J$=7.6 Hz), 8.41 (d, 1H, $J$=7.6 Hz), 7.91 (t, 1H, $J$=7.6 Hz), 7.65 (m,

3H), 3.34 (s, 3H), 1.73 (s, 3H); $^{13}$C NMR ($CDCl_3$): $\delta$ 217.0, 132.5, 129.1,127.8, 125.8, 125.7, 124.0, 123.8, 122.9, 111.8, 109.6, 55.3, 23.1; IR ($CCl_4$): 1703 (s) $cm^{-1}$; MS (EI): 278 (M, 100), 263 (11), 248 (10), 247 (13), 221 (12), 204 (35); HRMS: calcd for $C_{18}H_{14}O_3$—278.09430, found 278.09440.

When the final purification was conducted using flash chromatography, the following compound, contaminated with **33A**, could also be isolated. This compound is consistent with the enol ether structure **36A**: $^1$H NMR ($CDCl_3$): $\delta$ 8.70 (d, 1H, $J$=7.6 Hz), 8.66 (d, 1H, $J$=7.6 Hz), 8.12 (d, 1H, $J$=7.6 Hz), 7.99 (d, 1H, $J$=7.6 Hz), 7.50 (m, 4H), 5.30 (br s, 1H), 3.45 (s, 3H), 1.72 (s, 3H).

*Cyclopentenone* ***34***. $^1$H NMR ($CDCl_3$): $\delta$ 7.42–7.25 (m, 8H), 7.10 (d, 1H, $J$=7.3 Hz), 5.38 (s, 1H), 3.88 (dd, 1H, $J$=6.4, 2.3 Hz). 3.85 (s, 3H), 2.91 (dd, 1H, $J$=18.0, 6.4 Hz), 2.58 (dd, 1H, $J$=18.0, 2.3 Hz); $^{13}$C NMR ($CDCl_3$): $\delta$ 206.0, 190.1, 142.9, 141.2, 137.9, 130.2, 129.8, 128.1, 127.1, 126.7, 126.5, 104.3, 58.7, 48.0, 39.3; IR ($CCl_4$): 1705 (s), 1603 (s) $cm^{-1}$; MS (EI): 264 (M, 100), 263 (23), 205 (20), 203 (23), 179 (26), 177 (30), 165 (64); HRMS: calcd for $C_{18}H_{16}O_2$—264.11502, found 264.11592.

**5.1.9. Coupling of cyclopropylcarbene complex 28 with 2-ethynylbiphenyl (16).** The general procedure was followed using carbene complex **28** (32 mg, 0.14 mmol) and 2-ethynylbiphenyl (**16**) (26 mg, 0.14 mmol). After purification on prep TLC using 9:1 hexane:ethyl acetate followed by 5:1 ethyl acetate as the eluent, two fractions were isolated. The product in the first fraction (9 mg, 26% yield) was identified the as the oxidized phenanthrene derivative **33B**. The product in the second fraction (15 mg, 50% yield) was identified as cyclopentenone **34**.

*Phenanthrene* ***33B***. $^1$H NMR ($CDCl_3$): $\delta$ 8.71 (d, 1H, $J$=7.6 Hz), 8.68 (d, 1H, $J$=7.6 Hz), 8.35 (d, 1H, $J$=7.6 Hz), 8.00 (d, 1H, $J$=7.6 Hz), 7.91 (t, 1H, $J$=7.6 Hz), 7.65 (m, 3H), 3.40 (s, 3H), 1.50 (m, 1H), 1.00 (m, 1H), 0.70 (m, 1H), 0.41 (m, 2H); $^{13}$C NMR ($CDCl_3$): $\delta$ 217.6, 132.0, 129.5, 128.9, 126.0, 124.0, 123.7, 123.3, 122.9, 109.9, 52.7, 14,8, 1.6, 0.5; IR ($CCl_4$): 1703 (s) $cm^{-1}$; MS (EI): 304 (M, 85), 276 (69), 233 (10), 220 (14), 217 (15), 203 (76), 176 (100); HRMS: calcd for $C_{20}H_{16}O_3$—304.10995, found 304.10921.

**5.1.10. Coupling of phenylcarbene complex 29 with 2-ethynylbiphenyl (16).** The general procedure was followed using carbene complex **29** (40 mg, 0.13 mmol) and 2-ethynylbiphenyl (**16**) (27 mg, 0.15 mmol). After purification on prep TLC using 9:1 hexane:ethyl acetate as the eluent, two fractions were isolated. The product in the first fraction (1 mg, 2% yield) was the as the oxidized phenanthrene derivative **33C**. The product in the second fraction (21 mg, 52% yield) was identified as dibenzoanthraquinone **38**.

*Dibenzoanthraquinone*(***38***). mp 178–181°C; $^1$H NMR ($CDCl_3$): $\delta$ 9.35 (d, 2H, $J$=8.0 Hz), 8.74 (d, 2H, $J$=8.0 Hz), 8.20 (m, 2H), 7.76 (m, 6H); $^{13}$C NMR ($CDCl_3$): $\delta$ 187.0, 134.2, 133.6, 133.4, 132.8, 129.8, 129.5, 128.6, 128.3, 127.3, 126.3, 122.7; MS (EI): 308 (M, 100), 280 (21), 252 (28), 250 (30). The spectral data are in agreement with those previously reported for this compound.[17]

*Phenanthrene* ***33C***. $^1$H NMR ($CDCl_3$): $\delta$ 8.83 (d, 1H, $J$=7.6 Hz), 8.70 (d, 1H, $J$=7.6 Hz), 8.59 (d, 1H, $J$=7.6 Hz), 8.38 (d, 1H, $J$=7.6 Hz), 7.80–7.30 (m, 9H), 3.39 (s, 3H); MS (EI): 340 (M, 30), 311 (23), 310 (20), 281 (23), 204 (67), 176 (100); HRMS: calcd for $C_{23}H_{16}O_3$—340.10995, found 304.10953.

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