

# Gold–Catalyzed Intermolecular Hydrophenoxylation of Unactivated Internal Alkynes

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## SUPPORTING INFORMATION

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### General Experimental

All the reactions were performed in an oven-dried Schlenk flask under an argon atmosphere. Commercial grade solvents were distilled prior to use. Column chromatography was performed using silica gel (100-200 Mesh). Flash column chromatography was performed using silica gel (230-400 Mesh). Thin layer chromatography (TLC) was performed on silica gel GF254 plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm) and staining over I<sub>2</sub> chamber or an aqueous alkaline KMnO<sub>4</sub> solution followed by heating.

Proton and carbon nuclear magnetic resonance spectra (<sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>19</sup>F NMR) were recorded on a Bruker Avance 400 (<sup>1</sup>H NMR, 400 MHz; <sup>13</sup>C NMR, 101 MHz; <sup>19</sup>F NMR, 376 MHz) spectrometer, Bruker Avance 500 (<sup>1</sup>H NMR, 500 MHz; <sup>13</sup>C NMR, 126 MHz; <sup>19</sup>F NMR, 470 MHz) spectrometer having solvent resonance as internal standard (<sup>1</sup>H NMR, CHCl<sub>3</sub> at 7.26 ppm; <sup>13</sup>C NMR, CDCl<sub>3</sub> at 77.0 ppm). Few cases tetramethylsilane (TMS) at 0.00 ppm was used as reference standard. Data for <sup>1</sup>H NMR are reported as follows: chemical shift (ppm),

multiplicity (s = singlet; br s = broad singlet; d = doublet; br d = broad doublet, t = triplet; br t = broad triplet; q = quartet; m = multiplet), coupling constants,  $J$ , in (Hz), and integration. Data for  $^{13}\text{C}$  NMR,  $^{19}\text{F}$  NMR were reported in terms of chemical shift (ppm). GC analysis was performed on GCMS equipped with ZB-1 column (30 m x 0.25 mm, pressure = 20.0 kPa, detector = EI, 300 °C) with helium gas as carrier. IR spectra were recorded on FT/IR-5300 spectrometer and reported in  $\text{cm}^{-1}$ . LC-MS spectra were obtained (EI-positive/ negative mode) with ionization voltage of 70eV; data was reported in the form of  $m/z$  (intensity relative to base peak = 100). HPLC analysis of the samples was performed using Daicel Chiralpak AS-H column/Chiralcel OD-H column, hexanes-*i*-PrOH as eluent, flow rate = 0.3-1.0 mL/min at  $\lambda = 254$  nm with SPD-20A detector. Elemental (C, H, N) analysis were carried out using FLASH EA 1112 analyzer. Melting points were determined on electro-thermal melting point apparatus and are uncorrected. X-ray data was collected at 298K on a SMART APEX CCD single crystal diffractometer using graphite monochromated Mo-K $\alpha$  radiation (0.71073 Å).

**Materials:** Unless otherwise noted, all the reagents and intermediates were obtained commercially and used without purification. Dichloromethane (DCM), nitromethane and 1,2-Dichloroethane (DCE) were distilled over  $\text{CaH}_2$ . THF was freshly distilled over sodium/benzophenone ketyl under dry nitrogen. Gold(III)chloride ( $\text{AuCl}_3$ , 99%) was purchased from Sigma Aldrich Ltd. and used as received. Buchwald biaryl ligands are purchased from Aldrich Ltd. and Strem Chemicals Inc. and used as received. Diphenylacetylene (**2a**), 4-octyne (**2b**), 1-phenyl-1-propyne (**4b**) are purchased from Sigma Aldrich Ltd. Alkynes such as 1,2-bis(4-methoxyphenyl)ethyne (**2c**),<sup>1</sup> 1,2-bis(4-chlorophenyl)ethyne (**2d**),<sup>1</sup> 1,2-bis(3-(trifluoromethyl)phenyl)ethyne (**2g**),<sup>1</sup> 1-methoxy-4-(phenylethynyl)benzene (**5a**),<sup>2</sup> 1-(phenylethynyl)-3-(trifluoromethyl)benzene (**5c**)<sup>2</sup> were prepared according to the respective literature procedure. Analytical and spectral data of all those known alkynes are exactly matching with the reported values.

## **Experimental Procedures:**

### **General procedure for the reaction of activated phenols with alkynes (GP-1; condition-A):**

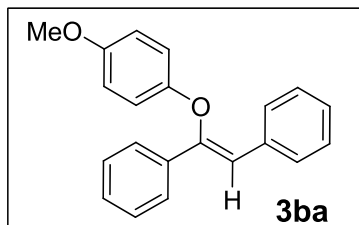
In an oven dried pressure tube, phenol (2.0 mmol), alkyne (1.0 mmol), and  $\text{Ag}_2\text{CO}_3$  (2.0 mmol) were taken. The tube was evacuated and backfilled with argon for three times. In a separate Schlenk flask, heterogeneous solution of  $\text{AuCl}_3$  (0.03 mmol) and ligand [4b (JohnPhos), 2-(di-*tert*-butylphosphino)biphenyl, 0.03 mmol] in DCM (1.0 mL) was freshly prepared and introduced to the parent reaction mixture under an argon atmosphere. The resulting reaction mixture was heated at 100 °C. Progress of the reaction was monitored by GC analysis while noticing complete consumption of alkynes employed. Reaction was continued for the time shown in the respective Tables, and brought to room temperature. The reaction mixture was diluted with dichloromethane (5 mL), and filtered over a small pad of celite. Solvent was evaporated under reduced pressure and the crude reaction mixture was purified using silica gel column chromatography.

### **General Procedure for the reaction of unactivated phenols to alkynes (GP-2; condition-B):**

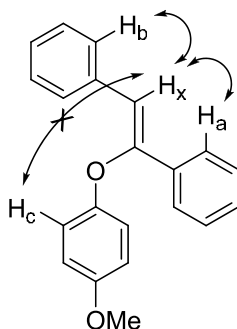
In an oven dried Schlenk flask, phenol (2.0 mmol), alkyne (1.0 mmol),  $\text{K}_2\text{CO}_3$  (2.0 mmol) were taken. The flask was evacuated and backfilled with argon for three times. A solution of  $\text{AuCl}_3$  (0.05 mmol) and 4b (JohnPhos, 0.05 mmol) in THF (1.0 mL) was freshly prepared in a separate Schlenk flask and introduced to the parent mixture under an argon atmosphere. The resulting reaction mixture was heated at 100 °C. Progress of the reaction was monitored by GC analysis while noticing complete consumption of alkynes employed. Reaction was continued for the time shown in the respective Tables, and allowed to cool down to room temperature. The reaction mixture was diluted with dichloromethane (5 mL), and filtered over a small pad of celite. Solvent was evaporated under reduced pressure and the crude reaction mixture was purified using silica gel column chromatography.

### Spectral and analytical data

#### **(Z)-(1-(4-methoxyphenoxy)ethene-1,2-diyl)dibenzene (3ba):**

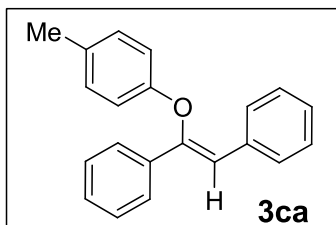


Following the general procedure (GP-2) in condition B; a mixture of 4-methoxyphenol (**1b**; 248 mg, 2.0 mmol), diphenylacetylene (**2a**; 178 mg, 1.0 mmol), K<sub>2</sub>CO<sub>3</sub> (276 mg, 2.0 mmol) in the presence of AuCl<sub>3</sub> (15 mg, 0.05 mmol) and **4b** (15 mg, 0.05 mmol) in THF (1.0 mL) was heated at 100 °C for 96 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (49:1) to afford **3ba** (251 mg) in 83% yield as colorless solid.



The Z-configuration of **3ba** is established based on the NOESY studies; NOEs between vinyl-H ( $\delta$  = 6.62 ppm) and *ortho*-hydrogens ( $\delta$  = 7.60, 7.68 ppm) of the phenyl groups of **3ba** is clearly seen while the NOEs between vinyl-H ( $\delta$  = 6.62 ppm) and *ortho*-hydrogens ( $\delta$  = 6.78 ppm) of 4-methoxyphenyl moiety of **3ba** is not observed.

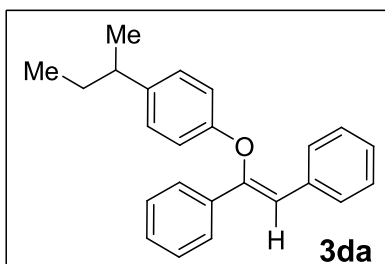
#### **(Z)-(1-(4-methylphenoxy)ethene-1,2-diyl)dibenzene (3ca):**



Following the general procedure (GP-2) in condition B; a mixture of 4-methylphenol (**1c**; 216 mg, 2.0 mmol), diphenylacetylene (**2a**; 178 mg, 1.0 mmol), K<sub>2</sub>CO<sub>3</sub> (276 mg, 2.0 mmol) in the

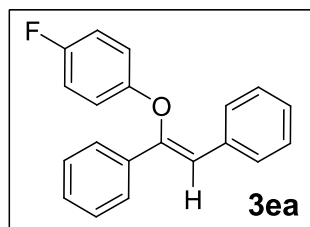
presence of  $\text{AuCl}_3$  (15 mg, 0.05 mmol) and **4b** (15 mg, 0.05 mmol) in THF (1.0 mL) was heated at 100 °C for 96 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane to afford **3ca** (198 mg) in 69% yield as colorless solid.

**(Z)-(1-(4-*sec*-butylphenoxy)ethene-1,2-diyl)dibenzene (3da):**



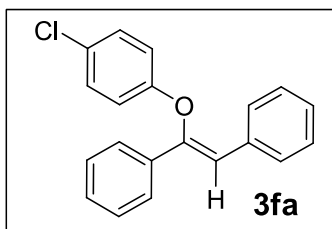
Following the general procedure (GP-2) in condition B; a mixture of 4-*sec*-butylphenol (**1d**; 300 mg, 2.0 mmol), diphenylacetylene (**2a**; 178 mg, 1.0 mmol),  $\text{K}_2\text{CO}_3$  (276 mg, 2.0 mmol) in the presence of  $\text{AuCl}_3$  (15 mg, 0.05 mmol) and **4b** (15 mg, 0.05 mmol) in THF (1.0 mL) was heated at 100 °C for 96 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane to afford **3da** (233 mg) in 71% yield as colorless solid.

**(Z)-(1-(4-fluorophenoxy)ethene-1,2-diyl)dibenzene (3ea):**

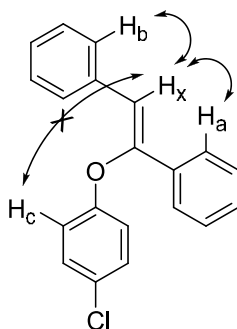


Following the general procedure (GP-2) in condition B; a mixture of 4-fluorophenol (**1e**; 224 mg, 2.0 mmol), diphenylacetylene (**2a**; 178 mg, 1.0 mmol),  $\text{K}_2\text{CO}_3$  (276 mg, 2.0 mmol) in the presence of  $\text{AuCl}_3$  (15 mg, 0.05 mmol) and **4b** (15 mg, 0.05 mmol) in THF (1.0 mL) was heated at 100 °C for 84 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane to afford **3ea** (262 mg) in 90% yield as colorless solid.

**(Z)-(1-(4-chlorophenoxy)ethene-1,2-diyl)dibenzene (3fa):**

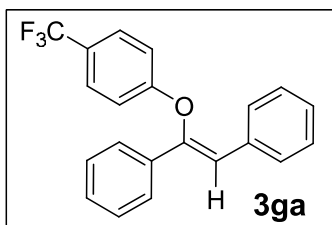


Following the general procedure (GP-2) in condition B; a mixture of 4-chlorophenol (**1f**; 257 mg, 2.0 mmol), diphenylacetylene (**2a**; 178 mg, 1.0 mmol), K<sub>2</sub>CO<sub>3</sub> (276 mg, 2.0 mmol) in the presence of AuCl<sub>3</sub> (15 mg, 0.05 mmol) and **4b** (15 mg, 0.05 mmol) in THF (1.0 mL) was heated at 100 °C for 46 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane to afford **3fa** (270 mg) in 88% yield as colorless solid.



The Z-configuration of **3fa** is established based on the NOESY studies; NOEs between vinyl-H ( $\delta$  = 6.67 ppm) and *ortho*-hydrogens ( $\delta$  = 7.61, 7.57 ppm) of the phenyl groups of **3fa** is clearly seen while the NOEs between vinyl-H ( $\delta$  = 6.67 ppm) and *ortho*-hydrogens ( $\delta$  = 6.95 ppm) of 4-chlorophenyl moiety of **3fa** is not observed.

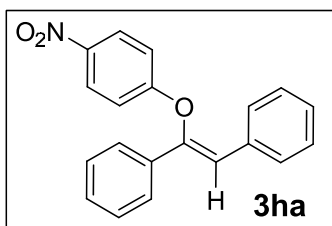
**(Z)-(1-(4-(trifluoromethyl)phenoxy)ethene-1,2-diyl)dibenzene (3ga):**



Following the general procedure (GP-1) in condition A; a mixture of 4-trifluoromethylphenol (**1g**; 324 mg, 2.0 mmol), diphenylacetylene (**2a**; 178 mg, 1.0 mmol), Ag<sub>2</sub>CO<sub>3</sub> (551 mg, 2.0 mmol) in the presence of AuCl<sub>3</sub> (9.0 mg, 0.03 mmol) and **4b** (8.9 mg, 0.03 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.0

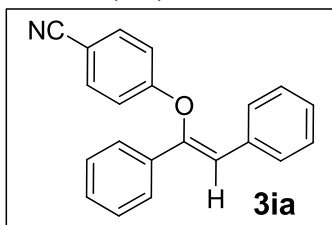
mL) was heated at 100 °C for 24 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane to afford **3ga** (279 mg) in 82% yield as colorless solid.

**(Z)-(1-(4-nitrophenoxy)ethene-1,2-diyl)dibenzene (3ha):**



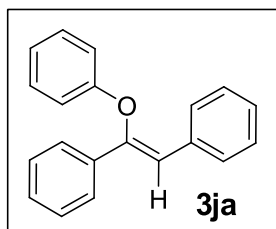
Following the general procedure (GP-1) in condition A; a mixture of 4-nitrophenol (**1h**; 278 mg, 2.0 mmol), diphenylacetylene (**2a**; 178 mg, 1.0 mmol), Ag<sub>2</sub>CO<sub>3</sub> (551 mg, 2.0 mmol) in the presence of AuCl<sub>3</sub> (9.0 mg, 0.03 mmol) and **4b** (8.9 mg, 0.03 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) was heated at 100 °C for 24 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (49:1) to afford **3ha** (273 mg) in 86% yield as pale yellow thick liquid.

**(Z)-4-(1,2-diphenylvinyl)oxybenzonitrile (3ia):**



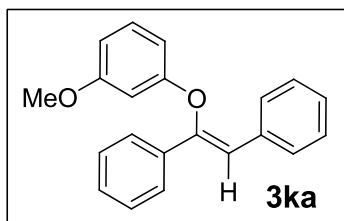
Following the general procedure (GP-1) in condition A; a mixture of 4-cyanophenol (**1i**; 238 mg, 2.0 mmol), diphenylacetylene (**2a**; 178 mg, 1.0 mmol), Ag<sub>2</sub>CO<sub>3</sub> (551 mg, 2.0 mmol) in the presence of AuCl<sub>3</sub> (9.0 mg, 0.03 mmol) and **4b** (8.9 mg, 0.03 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) was heated at 100 °C for 72 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane:ethyl acetate (49:1) to afford **3ia** (259 mg) in 87% yield as colorless solid.

**(Z)-(1-phenoxyethene-1,2-diyl)dibenzene (3ja):**



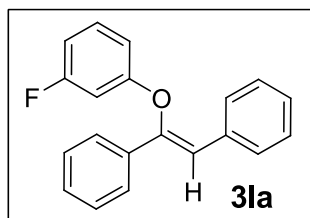
Following the general procedure (GP-2) in condition B; a mixture of phenol (**1j**; 188 mg, 2.0 mmol), diphenylacetylene (**2a**; 178 mg, 1.0 mmol),  $K_2CO_3$  (276 mg, 2.0 mmol) in the presence of  $AuCl_3$  (15 mg, 0.05 mmol) and **4b** (15 mg, 0.05 mmol) in THF (1.0 mL) was heated at 100 °C for 144 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane to afford **3ja** (96 mg) in 35% yield as colorless solid.

**(Z)-(1-(3-methoxyphenoxy)ethene-1,2-diyl)dibenzene (3ka):**



Following the general procedure (GP-2) in condition B; a mixture of 3-methoxyphenol (**1k**; 248 mg, 2.0 mmol), diphenylacetylene (**2a**; 178 mg, 1.0 mmol),  $K_2CO_3$  (276 mg, 2.0 mmol) in the presence of  $AuCl_3$  (15 mg, 0.05 mmol) and **4b** (15 mg, 0.05 mmol) in THF (1.0 mL) was heated at 100 °C for 120 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (49:1) to afford **3ka** (155 mg) in 51% yield as colorless solid.

**(Z)-(1-(3-fluorophenoxy)ethene-1,2-diyl)dibenzene (3la):**

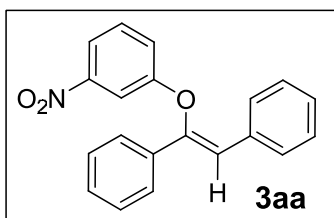


Following the general procedure (GP-2) in condition B; a mixture of 3-fluorophenol (**1l**; 224 mg, 2.0 mmol), diphenylacetylene (**2a**; 178 mg, 1.0 mmol),  $K_2CO_3$  (276 mg, 2.0 mmol) in the



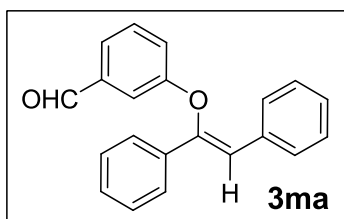
presence of  $\text{AuCl}_3$  (15 mg, 0.05 mmol) and **4b** (15 mg, 0.05 mmol) in THF (1.0 mL) was heated at 100 °C for 96 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane to afford **3la** (209 mg) in 72% yield as colorless solid.

**(Z)-(1-(3-nitrophenoxy)ethene-1,2-diyl)dibenzene (3aa):**

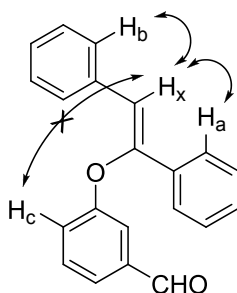


Following the general procedure (GP-1) in condition A; a mixture of 3-nitrophenol (**1a**; 278 mg, 2.0 mmol), diphenylacetylene (**2a**; 178 mg, 1.0 mmol),  $\text{Ag}_2\text{CO}_3$  (551 mg, 2.0 mmol) in the presence of  $\text{AuCl}_3$  (9.0 mg, 0.03 mmol) and **4b** (8.9 mg, 0.03 mmol) in  $\text{CH}_2\text{Cl}_2$  (1.0 mL) was heated at 100 °C for 24 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (49:1) to afford **3aa** (270 mg) in 85% yield as pale yellow solid.

**(Z)-3-(1,2-diphenylvinyl)benzaldehyde (3ma):**

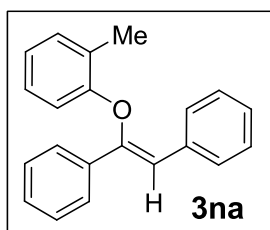


Following the general procedure (GP-1) in condition A; a mixture of 3-hydroxybenzaldehyde (**1m**; 244 mg, 2.0 mmol), diphenylacetylene (**2a**; 178 mg, 1.0 mmol),  $\text{Ag}_2\text{CO}_3$  (551 mg, 2.0 mmol) in the presence of  $\text{AuCl}_3$  (9.0 mg, 0.03 mmol) and **4b** (8.9 mg, 0.03 mmol) in  $\text{CH}_2\text{Cl}_2$  (1.0 mL) was heated at 100 °C for 24 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (49:1) to afford **3ma** (151 mg) in 50% yield as yellow solid.



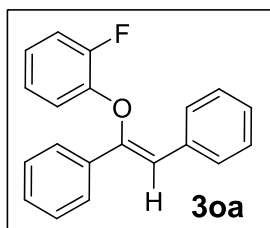
The *Z*-configuration of **3ma** is established based on the NOESY studies; NOEs between vinyl-H ( $\delta = 6.73$  ppm) and *ortho*-hydrogens ( $\delta = 7.63, 7.61$  ppm) of the phenyl groups of **3ma** is clearly seen while the NOEs between vinyl-H ( $\delta = 6.73$  ppm) and *ortho*-hydrogens ( $\delta = 7.23$  ppm) of 3-hydroxybenzaldehyde moiety of **3ma** is not observed.

**(*Z*)-(1-(*o*-tolyloxy)ethene-1,2-diyl)dibenzene (**3na**):**



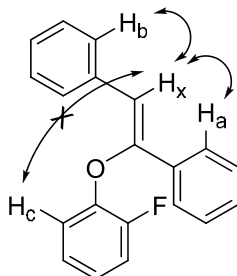
Following the general procedure (GP-2) in condition B; a mixture of 2-methylphenol (**1n**; 216 mg, 2.0 mmol), diphenylacetylene (**2a**; 178 mg, 1.0 mmol),  $K_2CO_3$  (276 mg, 2.0 mmol) in the presence of  $AuCl_3$  (15 mg, 0.05 mmol) and **4b** (15 mg, 0.05 mmol) in THF (1.0 mL) was heated at 100 °C for 146 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane to afford **3na** (129 mg) in 45% yield as colorless solid.

**(*Z*)-(1-(2-fluorophenoxy)ethene-1,2-diyl)dibenzene (**3oa**):**



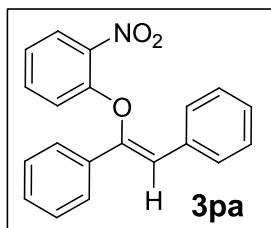
Following the general procedure (GP-2) in condition B; a mixture of 2-fluorophenol (**1o**; 224 mg, 2.0 mmol), diphenylacetylene (**2a**; 178 mg, 1.0 mmol),  $K_2CO_3$  (276 mg, 2.0 mmol) in the presence of  $AuCl_3$  (15 mg, 0.05 mmol) and **4b** (15 mg, 0.05 mmol) in THF (1.0 mL) was heated

at 100 °C for 72 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane to afford **3oa** (262 mg) in 90% yield as colorless thick liquid.



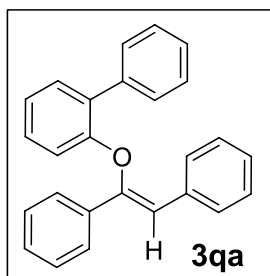
The *Z*-configuration of **3oa** is established based on the NOESY studies; NOEs between vinyl-H ( $\delta = 6.69$  ppm) and *ortho*-hydrogens ( $\delta = 7.70, 7.68$  ppm) of the phenyl groups of **3oa** is clearly seen while the NOEs between vinyl-H ( $\delta = 6.69$  ppm) and *ortho*-hydrogens ( $\delta = 6.88$  ppm) of 2-fluorophenyl moiety of **3oa** is not observed.

**(Z)-(1-(2-nitrophenoxy)ethene-1,2-diyl)dibenzene (3pa):**



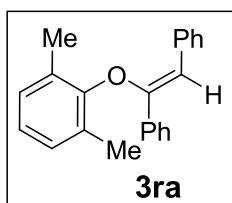
Following the general procedure (GP-1) in condition A; a mixture of 2-nitrophenol (**1p**; 278 mg, 2.0 mmol), diphenylacetylene (**2a**; 178 mg, 1.0 mmol),  $\text{Ag}_2\text{CO}_3$  (551 mg, 2.0 mmol) in the presence of  $\text{AuCl}_3$  (9.0 mg, 0.03 mmol) and **4b** (8.9 mg, 0.03 mmol) in  $\text{CH}_2\text{Cl}_2$  (1.0 mL) was heated at 100 °C for 96 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane to afford **3pa** (70 mg) in 22% yield as pale yellow thick liquid.

**(Z)-(2-(1,2-diphenylvinyl)oxy)biphenyl (3qa):**



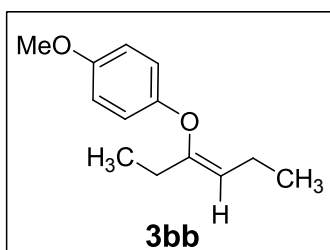
Following the general procedure (GP-2) in condition B; a mixture of 2-phenylphenol (**1q**; 340 mg, 2.0 mmol), diphenylacetylene (**2a**; 178 mg, 1.0 mmol),  $K_2CO_3$  (276 mg, 2.0 mmol) in the presence of  $AuCl_3$  (15 mg, 0.05 mmol) and **4b** (15 mg, 0.05 mmol) in THF (1.0 mL) was heated at 100 °C for 144 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane to afford **3qa** (237 mg) in 68% yield as colorless solid.

**(Z)-(1-(2,6-dimethylphenoxy)ethene-1,2-diyl)dibenzene (3ra):**



Following the general procedure (GP-2) in condition B; a mixture of 2,6-xyleneol (**1r**; 244 mg, 2.0 mmol), diphenylacetylene (**2a**; 178 mg, 1.0 mmol),  $K_2CO_3$  (276 mg, 2.0 mmol) in the presence of  $AuCl_3$  (15 mg, 0.05 mmol) and **4b** (15 mg, 0.05 mmol) in THF (1.0 mL) was heated at 100 °C for 146 h. Unfortunately, the reaction failed completely; the desired product **3rb** was not detected in GC analysis.

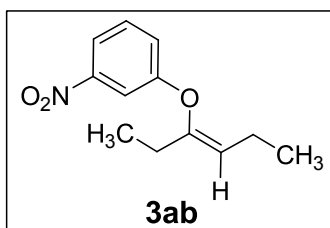
**(Z)-1-(hex-3-en-3-yloxy)-4-methoxybenzene (3bb):**



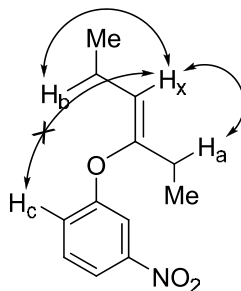
Following the general procedure (GP-2) in condition B; a mixture of 4-methoxyphenol (**1b**; 248 mg, 2.0 mmol), 3-hexyne (**2b**; 82 mg, 1.0 mmol),  $K_2CO_3$  (276 mg, 2.0 mmol) in the presence of

AuCl<sub>3</sub> (15 mg, 0.05 mmol) and **4b** (15 mg, 0.05 mmol) in THF (1.0 mL) was heated at 100 °C for 48 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane to afford **3bb** (194 mg) in 94% yield as colorless liquid.

**(Z)-1-(hex-3-en-3-yloxy)-3-nitrobenzene (3ab):**

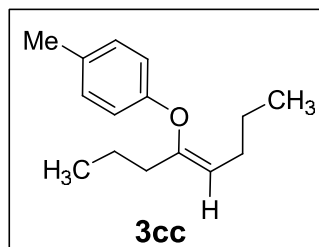


Following the general procedure (GP-1) in condition A; a mixture of 3-nitrophenol (**1a**; 278 mg, 2.0 mmol), 3-hexyne (**2b**; 82 mg, 1.0 mmol), Ag<sub>2</sub>CO<sub>3</sub> (551 mg, 2.0 mmol) in the presence of AuCl<sub>3</sub> (9 mg, 0.03 mmol) and **4b** (9 mg, 0.03 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) was heated at 100 °C for 48 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane to afford **3ab** (122 mg) in 55% yield as pale yellow liquid.

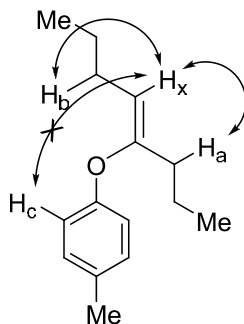


The *Z*-configuration of **3ab** is established based on the NOESY studies; NOEs between vinyl-H ( $\delta = 5.12$  ppm) and *ortho*-hydrogens ( $\delta = 2.16, 1.98$  ppm) of the methylene groups of **3ab** is clearly seen while the NOEs between vinyl-H ( $\delta = 5.12$  ppm) and *ortho*-hydrogens ( $\delta = 7.25$  ppm) of 3-nitrophenyl moiety of **3ab** is not observed.

**(Z)-1-methyl-4-(oct-4-en-4yloxy) benzene (3cc):**

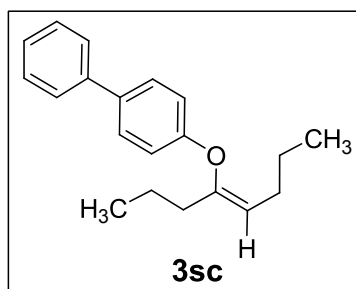


Following the general procedure (GP-2) in condition B; a mixture of 4-methylphenol (**1c**; 216 mg, 2.0 mmol), 4-octyne (**2c**; 110 mg, 1.0 mmol), K<sub>2</sub>CO<sub>3</sub> (276 mg, 2.0 mmol) in the presence of AuCl<sub>3</sub> (15 mg, 0.05 mmol) and **4b** (15 mg, 0.05 mmol) in THF (1.0 mL) was heated at 100 °C for 96 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane to afford **3cc** (172 mg) in 79% yield as colorless thick liquid.



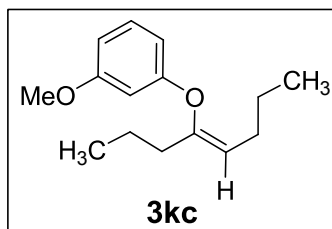
The *Z*-configuration of **3cc** is established based on the NOESY studies; NOEs between vinyl-H ( $\delta = 5.02$  ppm) and *ortho*-hydrogens ( $\delta = 2.11, 2.03$  ppm) of the methylene groups of **3cc** is clearly seen while the NOEs between vinyl-H ( $\delta = 5.02$  ppm) and *ortho*-hydrogens ( $\delta = 6.85$  ppm) of 4-methylphenyl moiety of **3cc** is not observed.

**(Z)-4-(oct-4-en-4-yloxy)biphenyl (3sc):**



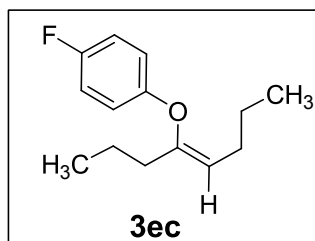
Following the general procedure (GP-2) in condition B; a mixture of 4-phenylphenol (**1s**; 340 mg, 2.0 mmol), 4-octyne (**2c**; 110 mg, 1.0 mmol), K<sub>2</sub>CO<sub>3</sub> (276 mg, 2.0 mmol) in the presence of AuCl<sub>3</sub> (15 mg, 0.05 mmol) and **4b** (15 mg, 0.05 mmol) in THF (1.0 mL) was heated at 100 °C for 72 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane to afford **3sc** (268 mg) in 96% yield as colorless liquid.

**(Z)-1-methoxy-3-(oct-4-en-4-yloxy)benzene (3kc):**



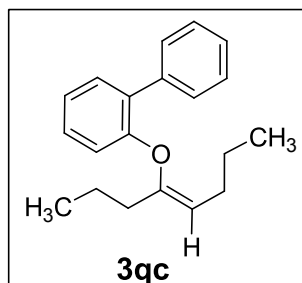
Following the general procedure (GP-2) in condition B; a mixture of 3-methoxyphenol (**1k**; 248 mg, 2.0 mmol), 4-octyne (**2c**; 110 mg, 1.0 mmol),  $K_2CO_3$  (276 mg, 2.0 mmol) in the presence of  $AuCl_3$  (15 mg, 0.05 mmol) and **4b** (15 mg, 0.05 mmol) in THF (1.0 mL) was heated at 100 °C for 50 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane to afford **3kc** (217 mg) in 93% yield as colorless liquid.

**(Z)-1-fluoro-4-(oct-4-en-4-yloxy)benzene (3ec):**



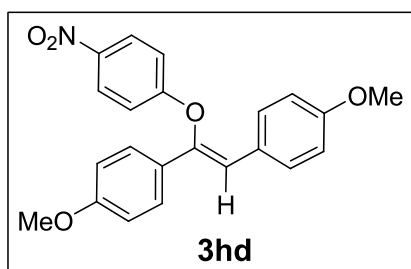
Following the general procedure (GP-2) in condition B; a mixture of 4-fluorophenol (**1e**; 224 mg, 2.0 mmol), 4-octyne (**2c**; 110 mg, 1.0 mmol),  $K_2CO_3$  (276 mg, 2.0 mmol) in the presence of  $AuCl_3$  (15 mg, 0.05 mmol) and **4b** (15 mg, 0.05 mmol) in THF (1.0 mL) was heated at 100 °C for 48 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane to afford **3ec** (210 mg) in 95% yield as colorless liquid.

**(Z)-2-(oct-4-en-4-yloxy)biphenyl (3qc):**

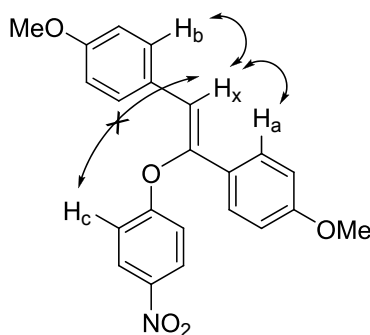


Following the general procedure (GP-2) in condition B; a mixture of 2-phenylphenol (**1q**; 340 mg, 2.0 mmol), 4-octyne (**2c**; 110 mg, 1.0 mmol), K<sub>2</sub>CO<sub>3</sub> (276 mg, 2.0 mmol) in the presence of AuCl<sub>3</sub> (15 mg, 0.05 mmol) and **4b** (15 mg, 0.05 mmol) in THF (1.0 mL) was heated at 100 °C for 120 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane to afford **3qc** (187 mg) in 67% yield as colorless thick liquid.

**(Z)-4,4'-(1-(4-nitrophenoxy)ethene-1,2-diyl)bis-methoxybenzene (3hd):**



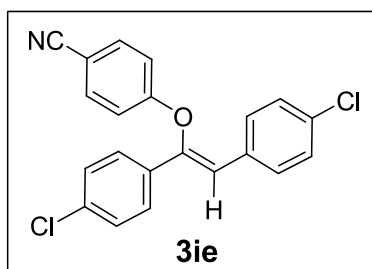
Following the general procedure (GP-1) in condition A; a mixture of 4-nitrophenol (**1h**; 139 mg, 1.0 mmol), 1,2-bis(4-methoxyphenyl)ethyne (**2d**; 119 mg, 0.5 mmol), Ag<sub>2</sub>CO<sub>3</sub> (275 mg, 1.0 mmol) in the presence of AuCl<sub>3</sub> (4.5 mg, 0.015 mmol) and **4b** (4.5 mg, 0.015 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) was heated at 100 °C for 36 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (19:1) to afford **3hd** (157 mg) in 83% yield as thick yellow liquid.



The *Z*-configuration of **3hd** is established based on the NOESY studies; NOEs between vinyl-H ( $\delta$  = 6.62 ppm) and *ortho*-hydrogens ( $\delta$  = 7.46, 7.49 ppm) of the phenyl groups of **3hd** is clearly seen while the NOEs between vinyl-H ( $\delta$  = 6.62 ppm) and *ortho*-hydrogens ( $\delta$  = 7.11 ppm) of 4-nitrophenyl moiety of **3hd** is not observed.

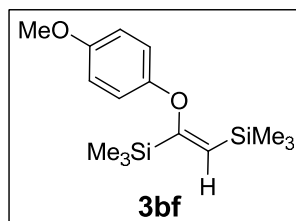


**(Z)-4-(1,2-bis(4-chlorophenyl)vinyl)oxybenzonitrile (**3ie**):**



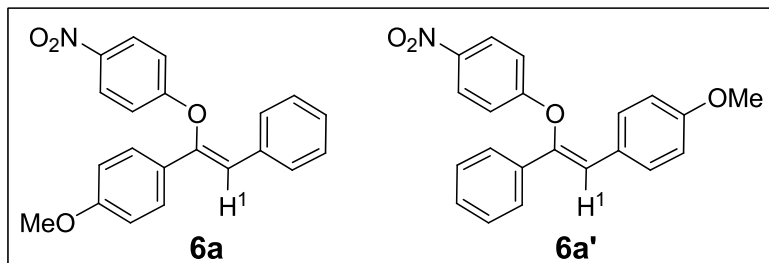
Following the general procedure (GP-1) in condition A; a mixture of 4-cyanophenol (**1i**; 238 mg, 2.0 mmol), 1,2-bis(4-chlorophenyl)ethyne (**2e**; 247 mg, 1.0 mmol),  $\text{Ag}_2\text{CO}_3$  (551 mg, 2.0 mmol) in the presence of  $\text{AuCl}_3$  (9.0 mg, 0.03 mmol) and **4b** (8.9 mg, 0.03 mmol) in  $\text{CH}_2\text{Cl}_2$  (1.0 mL) was heated at 100 °C for 72 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (49:1) to afford **3ie** (250 mg) in 68% yield as colorless thick liquid.

**(E)-1-(4-methoxyphenoxy)ethene-1,2-diylbis(trimethylsilane) (**3bf**):**



Following the general procedure (GP-2) in condition B; a mixture of 4-methoxyphenol (**1b**; 248 mg, 2.0 mmol), bis(trimethylsilyl)acetylene (**2f**; 170 mg, 1.0 mmol),  $\text{K}_2\text{CO}_3$  (276 mg, 2.0 mmol) in the presence of  $\text{AuCl}_3$  (15 mg, 0.05 mmol) and **4b** (15 mg, 0.05 mmol) in THF (1.0 mL) was heated at 100 °C for 146 h. Unfortunately, the reaction failed completely; the desired product **3bf** was not detected in GC analysis.

**(Z)-1-methoxy-4-(1-(4-nitrophenoxy)-2-phenylvinyl)benzene (6a); (Z)-1-methoxy-4-(2-(4-nitrophenoxy)-2-phenylvinyl)benzene (6a'):**



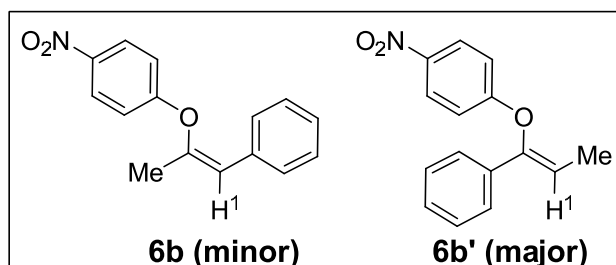
Following the general procedure (GP-1) in condition A; a mixture of 4-nitrophenol (278 mg, 2.0 mmol), 1-methoxy-4-(phenylethynyl)benzene (**5a**, 208 mg, 1.0 mmol), Ag<sub>2</sub>CO<sub>3</sub> (551 mg, 2.0 mmol) in the presence of AuCl<sub>3</sub> (9.0 mg, 0.03 mmol) and **4b** (8.9 mg, 0.03 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) was heated at 100 °C for 96 h. Upon usual work-up, the crude reaction was purified by silica gel column chromatography eluting with hexane: ethyl acetate (49:1) to afford a mixture of **6a+6a'** (326 mg) in 94% yield as yellow thick liquid. Purification of the in-separable regioisomers **6a** and **6a'** was failed through repeated flash column chromatography.

Ratio of both regioisomers **6a** : **6a'** was determined based on the characteristic H<sup>1</sup> proton integration. Furthermore HPLC data reconfirms the amount of regioisomers obtained in the reaction.

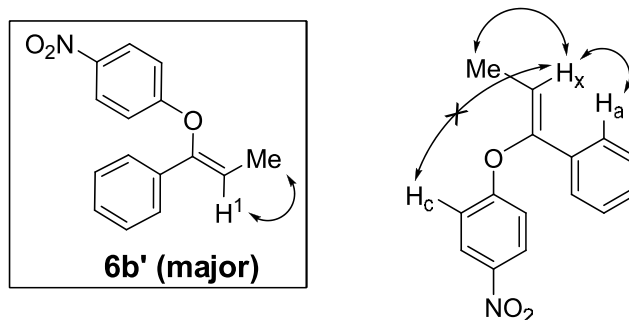
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) H<sup>1</sup> for **6a/6a'**: δ = 6.73 (s, 1H, 31%; minor) / 6.64 (s, 1H, 69%; major).

HPLC analysis (Daicel Chiralpak AS-H column, hexanes-*i*-PrOH = 97:3 for elution, flow rate = 1.0 mL/min; λ = 254 nm) for **6a/6a'** = t<sub>R</sub> (7.87 min, 37%; minor)/(8.47 min, 63%; major).

**(Z)-1-nitro-4-(1-phenylprop-1-en-2-yloxy)benzene (6b); (Z)-1-nitro-4-(1-phenylprop-1-enyloxy)benzene (6b'):**

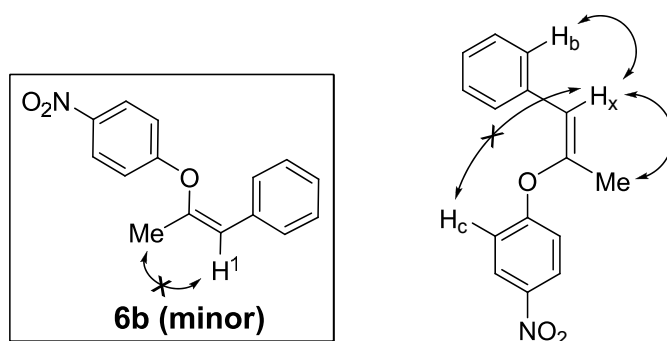


Following the general procedure (GP-1) in condition A; a mixture of 4-nitrophenol (**1h**, 278 mg, 2.0 mmol), 1-phenyl-1-propyne (**5b**, 116 mg, 1.0 mmol),  $\text{Ag}_2\text{CO}_3$  (551 mg, 2.0 mmol) in the presence of  $\text{AuCl}_3$  (9.0 mg, 0.03 mmol) and **4b** (8.9 mg, 0.03 mmol) in  $\text{CH}_2\text{Cl}_2$  (1.0 mL) was heated at 100 °C for 72 h. Upon usual work-up, the crude reaction was purified by silica gel column chromatography eluting with hexane: ethyl acetate (49:1) to afford a mixture of **6b+6b'** (237 mg) in 93% yield as yellow thick liquid. Purification of the regioisomers **6b** (minor) and **6b'** (major) was successfully carried out through repeated flash column chromatography. Ratio of both regioisomers **6b** : **6b'** was determined based on the characteristic  $^1\text{H}$  proton integration. Furthermore HPLC data reconfirms the amount of regioisomers obtained in the reaction.



**6b'** (major product) was obtained as light yellow thick liquid.

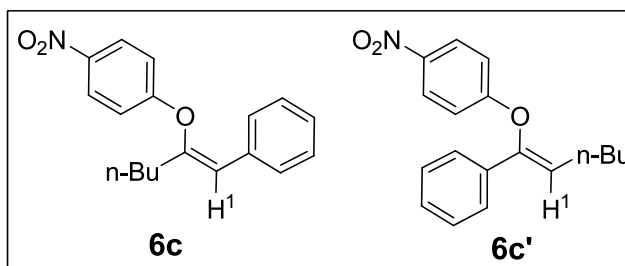
The *Z*-configuration of **6b'** is established based on the NOESY studies; NOEs between vinyl- $\text{H}$  ( $\delta = 6.01$  ppm) and *ortho*-hydrogens ( $\delta = 7.42, 1.74$  ppm) of the phenyl and methyl groups respectively of **6b'** is clearly seen while the NOEs between vinyl- $\text{H}$  ( $\delta = 6.01$  ppm) and *ortho*-hydrogens ( $\delta = 7.03$  ppm) of 4-nitrophenyl moiety of **6b'** is not observed.



**6b** (minor product) was obtained as light yellow thick liquid.

The *Z*-configuration of **6b** is established based on the NOESY studies; NOEs between vinyl-H ( $\delta$  = 6.06 ppm) and *ortho*-hydrogens ( $\delta$  = 7.39, 2.04 ppm) of the phenyl and methyl groups respectively of **6b** is clearly seen while the NOEs between vinyl-H ( $\delta$  = 6.06 ppm) and *ortho*-hydrogens ( $\delta$  = 7.06 ppm) of 4-nitrophenyl moiety of **6b** is not observed.

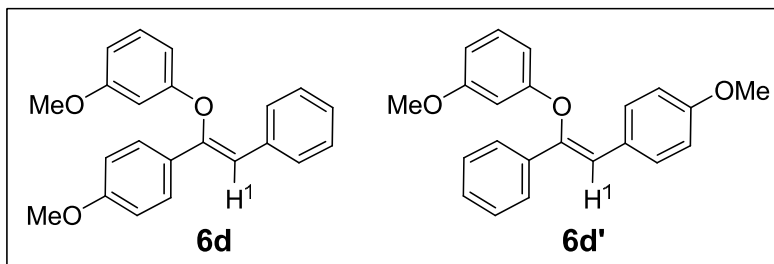
**(Z)-1-nitro-4-(1-phenylhex-1-en-2-yloxy)benzene (6c); (Z)-1-nitro-4-(1-phenylhex-1-enyloxy)benzene (6c'):**



Following the general procedure (GP-1) in condition A; a mixture of 4-nitrophenol (278 mg, 2.0 mmol), hex-1-ynylbenzene (**5c**, 158 mg, 1.0 mmol), Ag<sub>2</sub>CO<sub>3</sub> (551 mg, 2.0 mmol) in the presence of AuCl<sub>3</sub> (9.0 mg, 0.03 mmol) and **4b** (8.9 mg, 0.03 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) was heated at 100 °C for 72 h. Upon usual work-up, the crude reaction was purified by silica gel column chromatography eluting with hexane: ethyl acetate (49:1) to afford a mixture of **6c+6c'** (241 mg) in 81% yield as yellow thick liquid. Purification of the in-separable regioisomers **6c** and **6c'** was failed through repeated flash column chromatography.

Ratio of both regioisomers **6c** : **6c'** was determined based on the characteristic H<sup>1</sup> proton integration. Furthermore HPLC data reconfirms the amount of regioisomers obtained in the reaction.

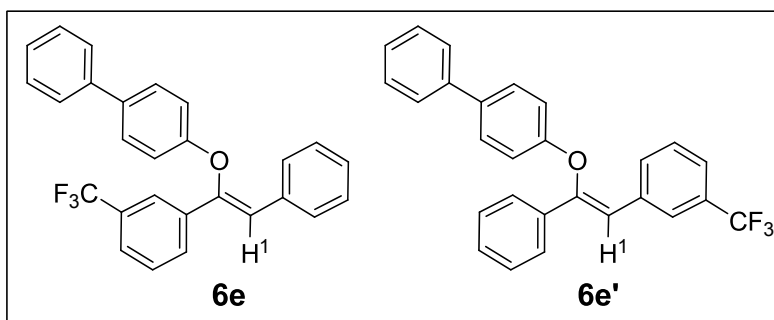
**(Z)-1-methoxy-3-(1-(4-methoxyphenyl)-2-phenylvinyl)oxy)benzene (6d); (Z)-1-methoxy-3-(2-(4-methoxyphenyl)-1-phenylvinyl)oxy)benzene (6d'):**



Following the general procedure (GP-2) in condition B; a mixture of 3-methoxyphenol (**1k**, 119 mg, 0.96 mmol), 1-methoxy-4-(phenylethynyl)benzene (**5a**, 100 mg, 0.48 mmol), K<sub>2</sub>CO<sub>3</sub> (133 mg, 0.96 mmol) in the presence of AuCl<sub>3</sub> (7.3 mg, 0.024 mmol) and **4b** (7.3 mg, 0.024 mmol) in THF (1.0 mL) was heated at 100 °C for 120 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (19:1) to afford a mixture of **6d+6d'** (101 mg) in 63% yield as pale yellow solid. Purification of the in-separable regioisomers **6d** and **6d'** was failed through repeated flash column chromatography.

Ratio of both regioisomers **6d/6d'** was unable to determine based on the characteristic H<sup>1</sup> proton integration. However, HPLC data confirms the amount of regioisomers obtained in the reaction.

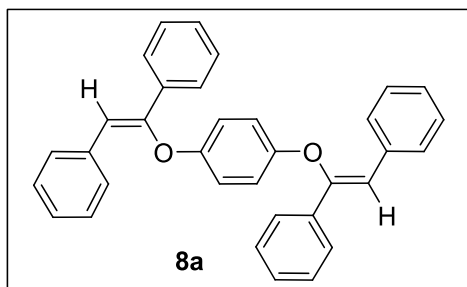
**(Z)-4-(2-phenyl-1-(3-(trifluoromethyl)phenyl)vinyl)oxybiphenyl (6e); (Z)-4-(1-phenyl-2-(3-(trifluoromethyl)phenyl)vinyl)oxybiphenyl (6e')**:



Following the general procedure (GP-2) in condition B; a mixture of 4-Phenylphenol (**1r**, 139 mg, 0.82 mmol), 1-(phenylethynyl)-3-(trifluoromethyl)benzene (**5c**, 100 mg, 0.41 mmol), K<sub>2</sub>CO<sub>3</sub> (112 mg, 0.82 mmol) in the presence of AuCl<sub>3</sub> (6.2 mg, 0.02 mmol) and **4b** (6.2 mg, 0.02 mmol) in THF (1.0 mL) was heated at 100 °C for 140 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (49:1) to afford a mixture of **6e+6e'** (147 mg) in 35% yield as pale yellow thick liquid. Purification of the in-separable regioisomers **6e** and **6e'** was failed through repeated flash column chromatography.

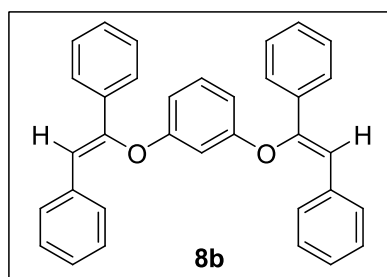
Ratio of both regioisomers **6e/6e'** was determined based on the characteristic H<sup>1</sup> proton integration. Furthermore HPLC data reconfirms the amount of regioisomers obtained in the reaction.

**1,4-bis[(Z)-1,2-diphenylvinyl]oxybenzene (8a):**

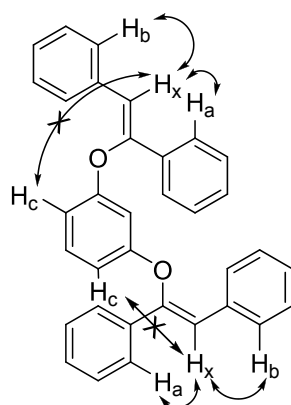


Following the general procedure (GP-2) in condition B; a mixture of hydroquinone (**7a**, 110 mg, 1.0 mmol), diphenylacetylene (**2a**, 712 mg, 4.0 mmol),  $K_2CO_3$  (553 mg, 4.0 mmol) in the presence of  $AuCl_3$  (30.3 mg, 0.1 mmol) and **4b** (30.0 mg, 0.1 mmol) in THF (2.0 mL) was heated at 100 °C for 96 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (95:5) to afford **8a** (256 mg) in 55% yield as colorless solid.

**1,3-bis[(Z)-1,2-diphenylvinyl]oxybenzene (8b):**

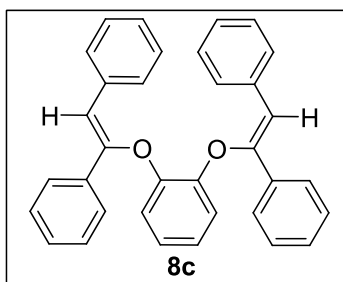


Following the general procedure (GP-2) in condition B; a mixture of resorcinol (**7b**, 110 mg, 1.0 mmol), diphenylacetylene (**2a**, 712 mg, 4.0 mmol),  $K_2CO_3$  (553 mg, 4.0 mmol) in the presence of  $AuCl_3$  (30.3 mg, 0.1 mmol) and **4b** (30.3 mg, 0.1 mmol) in THF (2.0 mL) was heated at 100 °C for 96 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (95:5) to afford **8b** (440 mg) in 94% yield as colorless solid.

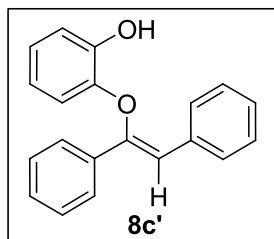


The Z-configuration of **8b** is established based on the NOESY studies; NOEs between vinyl-H ( $\delta = 6.60$  ppm) and *ortho*-hydrogens ( $\delta = 7.57, 7.49$  ppm) of the phenyl groups of **8b** is clearly seen while the NOEs between vinyl-H ( $\delta = 6.60$  ppm) and *ortho*-hydrogens ( $\delta = 6.75$  ppm) of resorcinol moiety of **8b** is not observed.

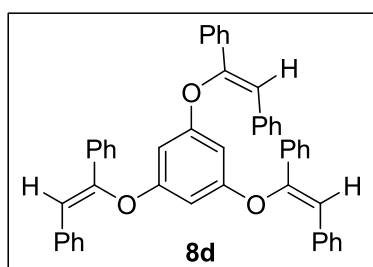
**1,2-bis[(Z)-1,2-diphenylvinyl]oxybenzene (8c):**



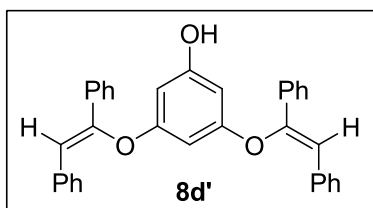
Following the general procedure (GP-2) in condition B; a mixture of catechol (**7c**, 110 mg, 1.0 mmol), diphenylacetylene (**2a**, 712 mg, 4.0 mmol),  $K_2CO_3$  (553 mg, 4.0 mmol) in the presence of  $AuCl_3$  (30.3 mg, 0.1 mmol) and **4b** (30.3 mg, 0.1 mmol) in THF (2.0 mL) was heated at 100 °C for 168 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (19:1) to afford di-substituted **8c** (33 mg) in 7% yield as colorless solid and mono-substituted **8c'** (97 mg) in 34% yield as colorless thick liquid.



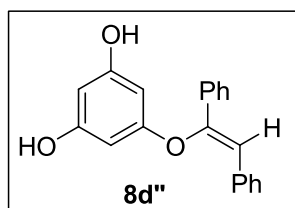
**1,3,5-tris[(Z)-1,2-diphenylvinyl]oxybenzene (**8d**):**



Following the general procedure (GP-2) in condition B; a mixture of phloroglucinol (**7d**, 126 mg, 1.0 mmol), diphenylacetylene (**2a**, 1.07 g, 6.0 mmol),  $K_2CO_3$  (828 mg, 6.0 mmol) in the presence of  $AuCl_3$  (45 mg, 0.15 mmol) and **4b** (45 mg, 0.15 mmol) in THF (2.0 mL) was heated at 100 °C for 168 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (19:1) to afford tri-substituted **8d** (38 mg) in 6% yield as colorless solid, di-substituted **8d'** (44 mg) in 9% yield as pale-brown thick liquid and mono-substituted **8d''** (99 mg) in 32% yield as pale brown thick liquid.



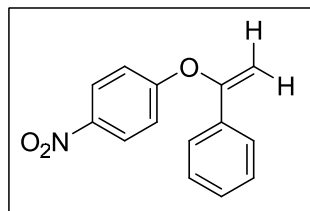
Compound (**8d'**) was purified through column chromatography eluting with hexane;ethyl acetate (9:1) mixture.





Compound (**8d''**) was purified through column chromatography eluting with hexane;ethyl acetate (3:2) mixture.

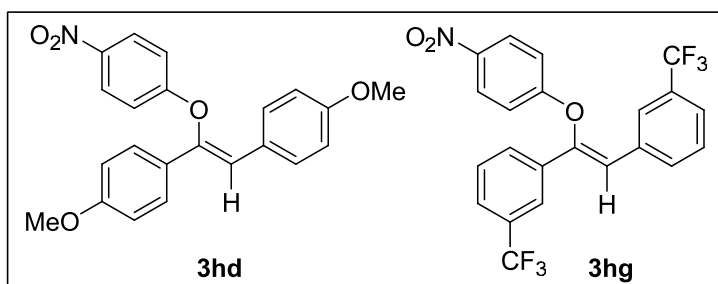
**1-nitro-4-(1-phenylvinyl)oxybenzene :**



Following the general procedure (GP-1) in condition A; a mixture of 4-nitrophenol (**1h**; 278 mg, 2.0 mmol), phenylacetylene (102 mg, 1.0 mmol),  $\text{Ag}_2\text{CO}_3$  (551 mg, 2.0 mmol) in the presence of  $\text{AuCl}_3$  (9.0 mg, 0.03 mmol) and **4b** (8.9 mg, 0.03 mmol) in  $\text{CH}_2\text{Cl}_2$  (1.0 mL) was heated at 100 °C for 48 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane to afford the desired product (58 mg) in 24% yield as pale yellow liquid.

mp 116–117 °C;  $R_f$  = 0.35 (49:1 hexane/EtOAc);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.23–8.018 (m, 2H), 7.61–7.50 (m, 2H), 7.42–7.25 (m, 3H), 7.16–7.10 (m, 2H), 5.43 (d,  $J$  = 2.4 Hz, 1H), 4.93 (d,  $J$  = 2.4 Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.3, 156.9, 142.6, 133.6, 129.3, 128.7, 125.8, 125.5, 117.4, 117.2, 98.9; IR (KBr)  $\nu_{\text{max}}$  3109, 3082, 2930, 2851, 1637, 1340, 1163, 1026, 920  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%) 240 ( $\text{M}^+ - 1$ , 16), 234 (5), 213 (18), 197 (9), 154 (9), 138 (100).

**Competitive experiment:**



Following the general procedure (GP-1) in condition A; a mixture of 4-nitrophenol (**1h**; 30 mg, 0.21 mmol), 1,2-bis(4-methoxyphenyl)ethyne (**2d**, 50 mg, 0.21 mmol) and 1,2-bis(3-(trifluoromethyl)phenyl)ethyne (**2g**, 65 mg, 0.21 mmol),  $\text{Ag}_2\text{CO}_3$  (115 mg, 0.42 mmol) in the presence of  $\text{AuCl}_3$  (1.9 mg, 0.0063 mmol) and **4b** (1.8 mg, 0.0063 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.5 mL) was heated at 100 °C for 72 h. Upon usual work-up, the crude mixture was analyzed by  $^1\text{H}$

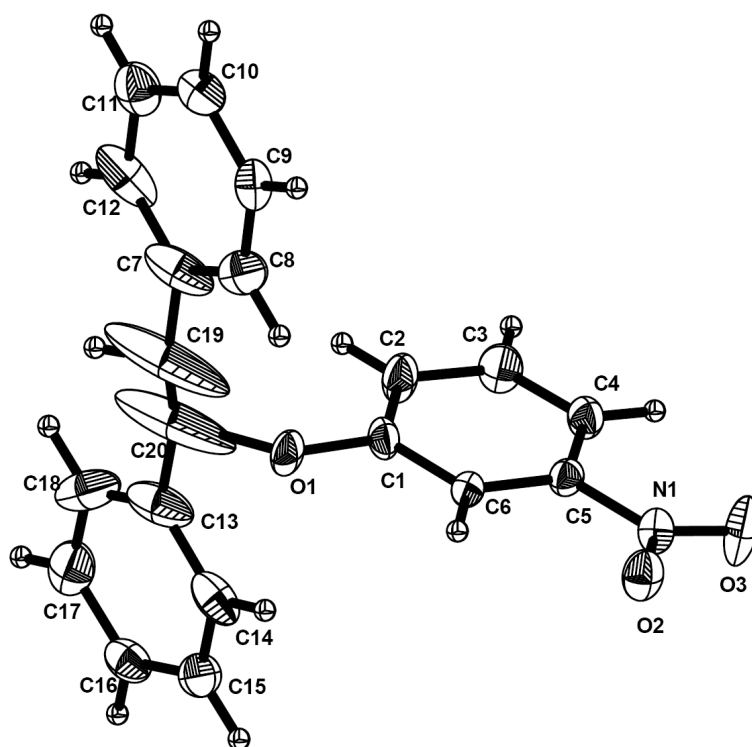
NMR. The respective vinyl-hydrogen integration in the crude  $^1\text{H}$  NMR spectrum showed the formation of the corresponding products **3hd** and **3hg** in 2:1 ratio, respectively.

**References:**

1. M. J. Mio, L. C. Kopel, J. B. Braun, T. L. Gadzikwa, K. L. Hull, R. G. Brisbois, C. J. Markworth, P. A. Grieco, *Org. Lett.* **2002**, 4, 3199.
2. P. Li, L. Wang, M. Wang, F. You, *Eur. J. Org. Chem.* **2008**, 5946.

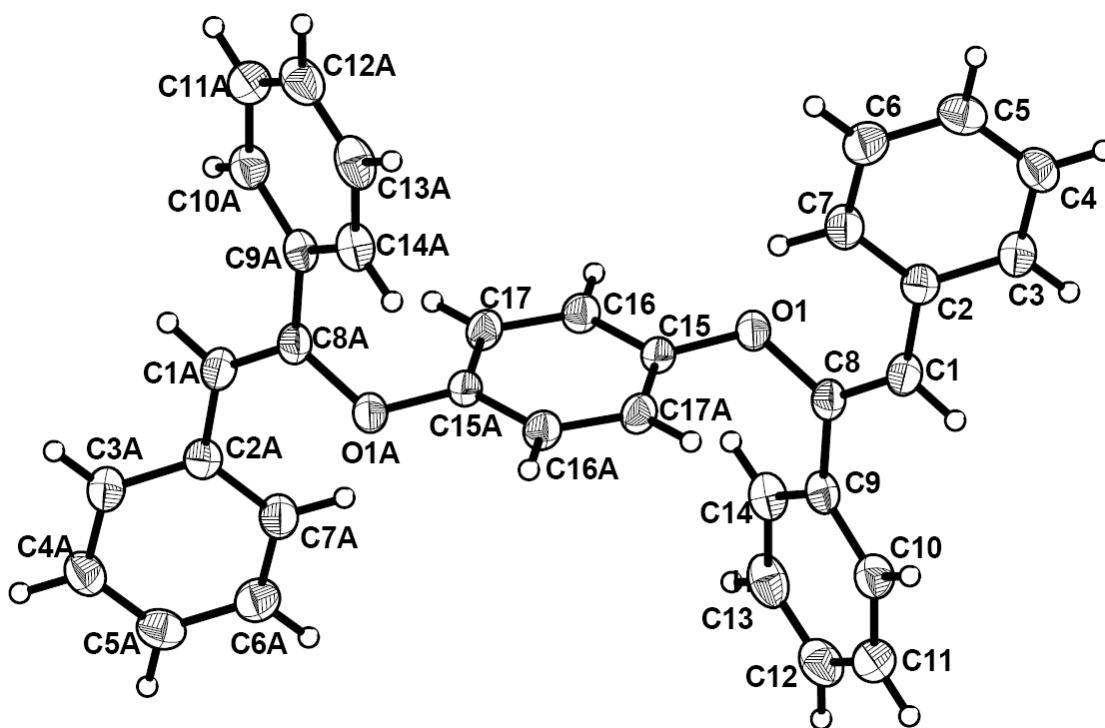
**X-ray crystallography:** Single crystal X-ray data for the compounds **3aa** and **8a** were collected at on a Bruker SMART APEX CCD area detector system [ $\lambda(\text{Mo-K}\alpha) = 0.71073 \text{ \AA}$ ] at 100K, (**3aa**) and 298K (**8a**) respectively, graphite monochromator with a  $\omega$  scan width of  $0.3^\circ$ , crystal-detector distance 60 mm, collimator 0.5 mm. The SMART software<sup>1</sup> was used for the intensity data acquisition and the SAINTPLUS Software<sup>1</sup> was used for the data extraction. In each case, absorption correction was performed with the help of SADABS program,<sup>1</sup> an empirical absorption correction using equivalent reflections was performed with the program. The structure was solved using SHELXS-97,<sup>2</sup> and full-matrix least-squares refinement against  $F^2$  was carried out using SHELXL-97.<sup>2</sup> All non-hydrogen atoms were refined anisotropically. Aromatic and methyl hydrogens were introduced on calculated positions and included in the refinement riding on their respective parent atoms.

#### 1) X-ray crystal structure and data for **3aa** & **8a**:



**Figure 1.** Thermal ellipsoidal plot of compound **3aa** with atom labeling scheme. Displacement ellipsoids are drawn at 50% probability level except for the H atoms, which are shown as circles of arbitrary radius.

In the crystal structure of compound **3aa**, two carbon atoms C19 and C20 are disordered. Intensity data for **3aa** was collected for three times using crystals from three different batches, both at 100K as well as 298K and noticed the disorder in every crystal structure. However, the overall topology of the molecule shows (*Z*)-olefinic stereochemistry, which was further confirmed by crystallographic analysis of compound **8a**.



**Figure 2.** Thermal ellipsoidal plot of compound **8a** with atom labeling scheme. Displacement ellipsoids are drawn at 30% probability level except for the H atoms, which are shown as circles of arbitrary radius. Atoms shown with (A) are generated through symmetry relation and the relevant symmetry codes are: (A)  $-x, -y+1, -z$ .

**Table 1. Crystal data for 3aa and 8a.**

	<b>Compound 1</b>	<b>Compound 2</b>
Identification code	<b>3aa</b>	<b>8a</b>
Formula	C <sub>20</sub> H <sub>15</sub> NO <sub>3</sub>	C <sub>34</sub> H <sub>26</sub> O <sub>2</sub>
$F_w$	317.33	466.55
$T$ (K)	100(2)	298(2)
$\lambda$ (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$
$a$ (Å)	23.1476(16)	7.7422(8)
$b$ (Å)	11.0330(8)	14.6183(15)
$c$ (Å)	16.6135(11)	10.9539(11)
$\alpha$ (°)	90	90
$\beta$ (°)	132.3450(10)	94.865(2)
$\gamma$ (°)	90	90
$V$ (Å <sup>3</sup> )	3135.9(4)	1235.3(2)
$Z$	8	2
$\rho_{\text{calcd}}$ (Mg m <sup>-3</sup> )	1.344	1.254
$\mu$ (mm <sup>-1</sup> )	0.091	0.076
$F(000)$	1328	492
Crystal Size (mm)	0.60 × 0.24 × 0.10	0.24 × 0.20 × 0.14
2 $\theta$ range/deg	2.20 / 25.02	2.33 / 25.09
Reflections collected	14736	11710
Unique reflections	2768	2191
Completeness to 2 $\theta$ (%)	25.02 (100.0)	25.09 (99.9)
$T_{\text{max}}, T_{\text{min}}$	0.9910, 0.9475	0.9894, 0.9819
Parameters	217	163
GOF ( $F^2$ )	1.087	1.036
$RI, wR2 [I > 2\sigma(I)]$	0.0798, 0.1912	0.0366, 0.0870

<i>R</i> 1, <i>wR</i> 2 (all data)	0.0829, 0.1932	0.0500, 0.0940
Largest diff. Peak and hole (e·Å <sup>-3</sup> )	1.029 and -0.928	0.120 and -0.126

## Check CIF/ Platon report (full structure check) for 3aa:

Bond precision:	C-C = 0.0067 Å	Wavelength=0.71073
Cell:	a=23.1476(16)    b=11.0330(8)    c=16.6135(11)	
	alpha=90    beta=132.345(1)    gamma=90	
Temperature:	100 K	
	Calculated	Reported
Volume	3135.9(4)	3135.9(4)
Space group	C 2/c	C2/c
Hall group	-C 2yc	?
Moiety formula	C14 H11, C6 H4 N O3	C20 H15 N O3
Sum formula	C20 H15 N O3	C20 H15 N O3
Mr	317.33	317.33
Dx, g cm <sup>-3</sup>	1.344	1.344
Z	8	8
Mu (mm <sup>-1</sup> )	0.091	0.091
F000	1328.0	1328.0
F000'	1328.64	
h,k,lmax	27,13,19	27,13,19
Nref	2768	2768
Tmin,Tmax	0.974,0.991	0.947,0.991
Tmin'	0.947	
Correction method=	EMPIRICAL	
Data completeness=	1.000	Theta(max)= 25.020
R(reflections)=	0.0798( 2617)	wR2(reflections)= 0.1932( 2768)
S =	1.087	Npar= 217

The following ALERTS were generated. Each ALERT has the format **test-name\_ALERT\_alert-type\_alert-level**.  
Click on the hyperlinks for more details of the test.

### Alert level A

<a href="#">PLAT351_ALERT_3_A</a>	Long C-H Bond (0.96Å)	C20 - H19 ... 1.43 Ång.
<a href="#">PLAT366_ALERT_2_A</a>	Short? C(sp?)-C(sp?) Bond	C19 - C20 ... 0.97 Ång.
<a href="#">PLAT432_ALERT_2_A</a>	Short Inter X...Y Contact	O1 .. C20 .. 1.78 Ång.
<a href="#">PLAT432_ALERT_2_A</a>	Short Inter X...Y Contact	O1 .. C19 .. 1.98 Ång.
<a href="#">PLAT432_ALERT_2_A</a>	Short Inter X...Y Contact	O1 .. C13 .. 2.65 Ång.
<a href="#">PLAT432_ALERT_2_A</a>	Short Inter X...Y Contact	C1 .. C20 .. 2.68 Ång.

### Alert level B

<a href="#">DIFMN02_ALERT_2_B</a>	The minimum difference density is < -0.1*ZMAX*1.00	
	_refine_diff_density_min given =	-0.928
	Test value =	-0.800
<a href="#">DIFMX01_ALERT_2_B</a>	The maximum difference density is > 0.1*ZMAX*1.00	

```

_refine_diff_density_max given =      1.029
Test value =      0.800
PLAT097_ALERT_2_B Large Reported Max. (Positive) Residual Density 1.03 eA-3
PLAT098_ALERT_2_B Large Reported Min. (Negative) Residual Density -0.93 eA-3
PLAT213_ALERT_2_B Atom C19 has ADP max/min Ratio ..... 4.70 prola
PLAT213_ALERT_2_B Atom C20 has ADP max/min Ratio ..... 4.80 prola
PLAT220_ALERT_2_B Large Non-Solvent C Ueq(max)/Ueq(min) ... 4.44 Ratio
PLAT222_ALERT_3_B Large Non-Solvent H Ueq(max)/Ueq(min) ... 4.53 Ratio
PLAT241_ALERT_2_B Check High Ueq as Compared to Neighbors for C19
PLAT241_ALERT_2_B Check High Ueq as Compared to Neighbors for C20
PLAT250_ALERT_2_B Large U3/U1 Ratio for Average U(i,j) Tensor .... 4.43
PLAT432_ALERT_2_B Short Inter X...Y Contact O1 .. C7 .. 2.74 Ang.
PLAT432_ALERT_2_B Short Inter X...Y Contact O1 .. C14 .. 2.84 Ang.
PLAT432_ALERT_2_B Short Inter X...Y Contact O1 .. C8 .. 2.86 Ang.
PLAT432_ALERT_2_B Short Inter X...Y Contact C1 .. C19 .. 2.92 Ang.
PLAT432_ALERT_2_B Short Inter X...Y Contact C2 .. C20 .. 2.99 Ang.

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### ●Alert level C

```

ABSTY02_ALERT_1_C An _exptl_absorpt_correction_type has been given without
a literature citation. This should be contained in the
_exptl_absorpt_process_details field.
Absorption correction given as empirical
DIFMN03_ALERT_1_C The minimum difference density is < -0.1*ZMAX*0.75
The relevant atom site should be identified.
DIFMX02_ALERT_1_C The maximum difference density is > 0.1*ZMAX*0.75
The relevant atom site should be identified.
PLAT230_ALERT_2_C Hirshfeld Test Diff for C13 -- C18 .. 5.34 su
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C7
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C13
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor .... 2.16
PLAT309_ALERT_2_C Single Bonded Oxygen (C-O .GT. 1.3 Ang) ..... 01
PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds (x 1000) Ang .. 7
PLAT042_ALERT_1_C Calc. and Reported MoietyFormula Strings Differ ?
PLAT234_ALERT_4_C Large Hirshfeld Difference C19 -- C20 .. 0.16 Ang.

```

### ●Alert level G

```

PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large. 21.22
PLAT343_ALERT_2_G Check Angle Range in Main Residue for .. C20

```

## Check CIF/ Platon report (full structure check) for 8a:

```

Bond precision: C-C = 0.0020 A Wavelength=0.71073
Cell: a=7.7422(8) b=14.6183(15) c=10.9539(11)
alpha=90 beta=94.865(2) gamma=90
Temperature: 298 K

```

	Calculated	Reported
Volume	1235.3(2)	1235.3(2)
Space group	P 21/c	P2(1)/c
Hall group	-P 2ybc	?
Moiety formula	C34 H26 O2	C34 H26 O2
Sum formula	C34 H26 O2	C34 H26 O2
Mr	466.55	466.55

Dx,g cm-3	1.254	1.254
Z	2	2
Mu (mm-1)	0.076	0.076
F000	492.0	492.0
F000'	492.21	
h,k,lmax	9,17,13	9,17,13
Nref	2195	2191
Tmin,Tmax	0.982,0.989	0.982,0.989
Tmin'	0.982	
Correction method= EMPIRICAL		
Data completeness=	0.998	Theta(max)= 25.090
R(reflections)=	0.0366( 1728)	wR2(reflections)= 0.0940( 2191)
S =	1.036	Npar= 163

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The following ALERTS were generated. Each ALERT has the format  
**test-name\_ALERT\_alert-type\_alert-level**.  
Click on the hyperlinks for more details of the test.

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### ●Alert level C

[PLAT125\\_ALERT\\_4\\_C](#) No \_symmetry\_space\_group\_name\_Hall Given ..... ?

### References:

1. Bruker SMART V5.630 and SAINT-PLUS V6.45, Bruker-Nonius Analytical X-ray Systems Inc.:Madison, Wisconsin, USA 2003. SADABS, Empirical absorption correction program, Bruker AXS Inc., Madison, Wisconsin, USA 1997.
2. Sheldrick G M, *Acta Crystallogr* 64A (2008) 112.