Supporting Information

Photoinduced Oxidative Activation of Electron-rich Arene: Alkenylation with H₂ Evolution under External-oxidant-free Conditions

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General Information

Unless otherwise stated, analytical grade solvents and commercially available reagents were used without further purification. 9-Mesityl-10-methylacridinium perchlorate (Acr\(^+\)-Mes ClO\(_4\)^-) is purchased from Tokyo Chemical Industry (TCI). The substituted styrene derivatives were prepared following references.\(^1\) All manipulations were carried out by using standard schlenk techniques. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200–300 mesh silica gel in petroleum ether (bp. 60–90 °C). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum ether to the ethyl acetate. All new compounds were characterized by \(^1\)H NMR, \(^13\)C NMR and HRMS. The known compounds were characterized by \(^1\)H NMR and \(^13\)C NMR. The \(^1\)H and \(^13\)C NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. The chemical shifts (δ) were given in part per million relative to internal tetramethyl silane (TMS, 0 ppm for \(^1\)H), CDCl\(_3\) (77.0 ppm for \(^13\)C). High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument and accurate masses were reported for the molecular ion + Hydrogen (M+H). IR spectra were recorded on a Mettler Toledo React IR 15 spectrometer using a diamond comb. GC-MS data was measured with a Shimadzu GC-MS-QP2010. Hydrogen gas content was analyzed by gas chromatography (7890-II, Tianmei, China, TCD, argon as a carrier gas and 5 Å molecular sieve column, a thermal conductivity detector). The source of the blue LEDs is the LED lights made by ourselves. The power of each blue light is 3W. There is 3.0 cm distance between the reactor and LEDs. The photographs of this photochemical setup were show below.
Experimental Procedures

1. **Preparation of Co(dmgH)$_2$(4-NMe$_2$Py)Cl$_2$:**

   A 500 mg (1.48 mmol) sample of [Co(dmgH)(dmgH)Cl]$_2$ was suspended in 50 mL of methanol. 4-(Dimethylamino)pyridine (361 mg, 2.96 mmol, 2 equiv) was then added to the flask, after 6 h, the green suspension change to a brown precipitate. The suspension was filtered and the precipitate washed with water (10 mL), ethanol (10 mL), and diethyl ether (10 mL) respectively to give [Co(dmgH)$_2$(4-NMe$_2$Py)Cl].

2. **General procedure for external-oxidant-free oxidative cross-coupling of electron-rich arenes and styrenes:**

   \[
   \begin{array}{c}
   \text{R}^1_3 \text{R}^2 + \text{R}^4_4 \text{R}^3_3 \rightarrow \text{R}^1_3 \text{R}^2_2 \text{R}^3_3 + \text{H}_2 \\
   \text{DCE, blue LEDs, r.t.}
   \end{array}
   \]

   A schlenk tube equipped with a stir bar was loaded with 9-mesityl-10-methylacridinium perchlorate 4 (0.006 mmol, 3 mol %), Co(dmgH)$_2$(4-NMe$_2$Py)Cl 6 (0.02 mmol, 10 mol %), arene 1 (0.2 mmol) and styrenes 2 (0.4 mmol) in degased dry DCE (4 mL) under N$_2$ atmosphere. The solution was then stirred at room temperature under the irradiation of 12W blue LED for 24 h. After completion of the reaction, the products were determined by TLC and GC-MS. Then the pure product was obtained by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 50:1) to afford corresponding products 3.

3. **Gram scale synthesis:**

   \[
   \begin{array}{c}
   \text{OMe} \text{MeO} + \text{Ph} \text{Ph} \rightarrow \text{OMe} \text{MeO} \\
   \text{MeO} 1.68 g \text{OMe} \text{MeO} \text{Ph} \text{Ph} \text{MeO} \text{MeO} \\
   1a, 10 mmol 2j, 20 mmol 3aj, 2.43 g, 70% yield
   \end{array}
   \]

   A 100 mL schlenk flask equipped with a stir bar was loaded with 9-mesityl-10-methylacridinium perchlorate 4 (12 mg, 0.03 mmol, 0.3 mol %), Co(dmgH)$_2$(4-NMe$_2$Py)Cl 6 (45 mg, 0.1 mmol, 1 mol %), 1,3,5-trimethoxybenzene 1a (1.68 g, 10 mmol) and 1,1-diphenylethylene 2j (3.6 g, 20 mmol) in
degased dry DCE (20 mL) under N\textsubscript{2} atmosphere. The solution then stirred at room temperature under the irradiation of 30W blue LED for 48 h. After completion of the reaction, the product was determined by TLC and GC-MS. Then the pure product was obtained by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 50:1) to afford corresponding stilbene derivatives \textit{3aj} in 70\% yield (2.43 g).

4. **Condition optimization of the alkenylation of anisole:**

![Chemical structure image]

| entry | catalyst | solvent      | yield(%) |
|-------|----------|--------------|----------|
| 1     | 4        | DCE          | n.d.     |
| 2     | 4        | DCE/HFIP     | trace    |
| 3     | 8        | DCE/HFIP     | 5        |
| 4     | 8        | CHCl\textsubscript{3}/HFIP | 15       |

5. **Kinetic isotope effect (KIE) experiment:**

**Synthesis of 1,3,5-trimethoxybenzene-d3.**

![Chemical structure image]

In an oven dried schlenk tube equipped with a stir-bar, 1,3,5-trimethoxybenzene (2.0 mmol) was added. The reaction tube was allowed to be vacuumed and purged with nitrogen for three times. Then, 1,2-dichloroethane (2 mL) and deuterium chloride solution (1 mL, 35 wt. % in D\textsubscript{2}O, 99 atom % D (Aldrich)) was added by syringe under nitrogen. Finally, the schlenk tube was allowed to stir at room temperature for 30 min. After completion of the reaction, the reaction mixture was extracted with dichloromethane (3 x 5 mL). The organic layers were combined and dried over sodium sulfate. The desired product (92 atom % D) was obtained after removing the solvent. \textsuperscript{1}H NMR spectra for the product was shown as follow:
**Procedure for KIE measurement.**

\[
\text{OMe} + \text{MeO} + \text{OMe} \xrightarrow{3 \text{ mol} \% 4, 10 \text{ mol} \% 6} \text{DCE, blue LED, 2h} \xrightarrow{3 \text{ aj/3 aj-d3, 30\%, } k_H/k_D = 1.2}
\]

A schlenk tube equipped with a stir bar was loaded with 9-mesityl-10-methylacridinium perchlorate 4 (0.006 mmol, 3 mol %), Co(dmgH)\(_2\)(4-NMe\(_2\)Py)Cl 6 (0.02 mmol, 10 mol %), 1,3,5-trimethoxybenzene 1a (0.1 mmol), 1,3,5-trimethoxybenzene-d3 1a-d3 (0.1 mmol), and 1,1-diphenylene 2j (0.4 mmol) in degased dry DCE (4 mL) under N\(_2\) atmosphere. The solution then stirred at room temperature under the irradiation of 12W blue LED for 2 h. After then, the products was determined by TLC and GC-MS. Then the pure product was obtained by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 50:1) to afford corresponding stilbene derivatives 3aj/3aj-d3 in 30% yield. \(^1\)H NMR spectra for the isolated product was shown as follow, which indicate that the ratio of 3aj:3aj-d3 is 1.2:1.
6. Kinetic studies by using Operando-IR.

General procedure of in-situ IR experiments

General procedure: In a self-prepared three-necked micro reactor with a magnetic stirrer, Acr⁺-Mes ClO₄⁻ (12.0 mg, 0.03 mmol), Co(dmgH)₂(4-NMe₂Py)Cl (45 mg, 0.1 mmol) and 1,3,5-trimethoxybenzene 1a (168 mg, 1 mmol) were added. The reactor was allowed to be vacuumed and purged with nitrogen for three times. Then 10 mL degassed DCE was added via a syringe. After complete dissolution of catalysts, the alkene (2 mmol) was added. The mixture was allowed to stir at 40 °C and recorded by React IR. 5 mins later, a 30 W blue LED lamp was turned on. The course of the reaction could be observed from the characteristic IR band of olefin. After 4 hours, the reaction was stopped. The yield of corresponding product was detected by GC-FID using naphthalene as the internal standard.

According to operation of aforementioned general procedure of Operando-IR, the olefination of 1a with 1,1-diphenylene 2j was monitored by React IR 15. Absorption peak of the 1a at 1150 cm⁻¹ was found. And with the decrease in absorption of this peak, a new peak at 1025 cm⁻¹ belonged to the product 3aj can be observed through in-situ IR. After 4 hours, 0.5 mmol of 3aj was afforded. The reaction was recorded by React IR as shown in Fig. S1. The 2D spectroscopy was also shown.
Figure S1. Kinetic plots of olefination of 1a with 1,1-diphenylene.

**Kinetic studies**

**Reaction order for 1a.** The reaction order with respect to 1a was determined by studying the initial rate of reaction with different concentration of 1a. Using the above mentioned general procedure, 1a (0.5 ~ 2 mmol), Acr⁺-Mes ClO₄⁻ (12.0 mg, 0.03 mmol), Co(dmgH)₂(4-NMe₂Py)Cl (45 mg, 0.1 mmol) and 1,1-diphenylene 2j (2 mmol) were added. Product yield from the corresponding reaction was monitored by GC-FID using naphthalene as the internal standard. Finally, the profiles of relative concentrations vs time for product 3aj could be obtained to analyse the initial rate of reaction. A plot of initial rate (Δ[3aj]/Δt) versus [1a] gave a straight line (R² = 0.99422), indicative of a first order with respect to [1a].

Figure S2. First order kinetic experiment dependence on [1a].

**Reaction orders for alkene, photosensitizer and cobalt complex.** The reaction orders with respect to alkene, photosensitizer, and cobalt complex were also determined by the same method. From Figure S3-S5, the initial rate of reaction was changeless when using different concentrations of alkene and cobalt complex. Therefore, these results indicated a zero order reaction dependence on [Co(dmgH)₂(4-NMe₂py)Cl] and [2j]. When the concentration of photosensitizer is low, the initial
rate constant is linearly related to the concentration of photosensitizer. The reaction rate is saturated in high concentration of photosensitizer. This may be due to the limited number of photons of the used LED lamp.

**Figure S3.** The profiles of relative initial rate vs time in different [2].

**Figure S4.** The profiles of relative initial rate vs time in different [Co(dmgH)\(_2\)(4-NMe\(_3\)py)Cl].

**Figure S5.** The profiles of relative initial rate vs time in different [Acr\(^+\)-Mes ClO\(_4\) ].

7. Emission quenching experiments for Acr\(^+\)-Mes ClO\(_4\) .
Emission intensities were recorded using a HITACHI F-4500 Fluorescence Spectrometer. All Acr⁺-Mes ClO₄⁻ solutions were excited at 450 nm and the emission intensity at 512 nm was observed. DCE was degassed with a stream of N₂ for 30 min and then moved to glove box. All the solutions were prepared in the glove box. In a typical experiment, the emission spectrum of a 5×10⁻⁴ M solution of Acr⁺-Mes ClO₄⁻ in DCE was collected. Then, appropriate amount of quencher was added to the measured solution and the emission spectrum of the sample was collected.

Figure S6. Acr⁺-Mes ClO₄⁻ emission quenching by 1,3,5-trimethoxybenzene.

Figure S7. Acr⁺-Mes ClO₄⁻ emission quenching by styrene.
**Figure S8.** Acr⁺-Mes ClO₄⁻ emission quenching by 1,1-diphenylethene.

**Figure S9.** Acr⁺-Mes ClO₄⁻ emission quenching by 4-cyanostyrene.

**Figure S10.** Stern–Volmer emission quenching studies of Acr⁺-Mes ClO₄⁻ by 1,3,5-trimethoxybenzene, styrene, 1,1-diphenylethene and 4-cyanostyrene.

8. General Computational Calculation Details
DFT calculations were performed using the M06-2X levels of theory\(^3\) with the Gaussian09 program\(^4\). The 6-311+G(d,p) basis set was used for the C, H and O. Frequency calculations at the same level of theory have been performed to identify all of the stationary points as minima (zero imaginary frequencies) and to provide free energies at 298.15 K. The solvation energies were calculated with SMD model\(^5\). Solvation effect was taken into consideration during geometry optimization with dichloroethane as the solvent.

\[
\begin{align*}
\text{MeO} &\quad \text{MeO} &\quad \text{OMe} &\quad \text{OMe} &\quad \text{OMe} \\
+ &\quad \text{Ph} &\quad \text{MeO} &\quad \text{OMe} &\quad \text{OMe} &\quad \text{OMe} \\
\rightarrow &\quad \text{Ph} &\quad \text{MeO} &\quad \text{OMe} &\quad \text{OMe} &\quad \text{OMe} &\quad \text{OMe} \\
\Delta G &= 7.1 \text{ kcal/mol (in DCE)}
\end{align*}
\]

\[
\begin{align*}
\text{MeO} &\quad \text{MeO} &\quad \text{OMe} &\quad \text{OMe} &\quad \text{OMe} \\
+ &\quad \text{Ph} &\quad \text{Ph} &\quad \text{MeO} &\quad \text{OMe} &\quad \text{OMe} \\
\rightarrow &\quad \text{Ph} &\quad \text{Ph} &\quad \text{MeO} &\quad \text{OMe} &\quad \text{OMe} &\quad \text{OMe} \\
\Delta G &= -13.5 \text{ kcal/mol (in DCE)}
\end{align*}
\]

\[
\begin{align*}
\text{MeO} &\quad \text{MeO} &\quad \text{OMe} &\quad \text{OMe} \\
+ &\quad \text{Ph} &\quad \text{Ph} &\quad \text{MeO} &\quad \text{OMe} &\quad \text{OMe} \\
\rightarrow &\quad \text{Ph} &\quad \text{Ph} &\quad \text{MeO} &\quad \text{OMe} &\quad \text{OMe} &\quad \text{OMe} \\
\Delta G &= -4.2 \text{ kcal/mol (in DCE)}
\end{align*}
\]

\[
\begin{align*}
\text{MeO} &\quad \text{MeO} &\quad \text{OMe} &\quad \text{OMe} \\
+ &\quad \text{Ph} &\quad \text{Ph} &\quad \text{MeO} &\quad \text{OMe} &\quad \text{OMe} \\
\rightarrow &\quad \text{Ph} &\quad \text{Ph} &\quad \text{MeO} &\quad \text{OMe} &\quad \text{OMe} &\quad \text{OMe} \\
\Delta G &= -9.5 \text{ kcal/mol (in DCE)}
\end{align*}
\]

Thermal correction to Gibbs Free Energy= 0.102753

Sum of electronic and thermal Free Energies= -309.490807

C
-1.77871400 -1.03990900 -0.00000600
C
-0.40771500 -1.28153300 0.00000000
C
 0.51005000 -0.22572000 0.00000600
C
 0.01737800 1.08621000 0.00000600
C
-1.34984600 1.32862100 0.00000000
C
-2.25458100 0.26688900 -0.00000700
H
-2.47276500 -1.87270600 -0.00001100
H
-0.03861100 -2.30218600 0.00000100
H
 0.70494300 1.92426400 0.00001300
H
-1.71381000 2.34987300 0.00000000

\[512\]
Thermal correction to Gibbs Free Energy = 0.102833
Sum of electronic and thermal Free Energies = -309.255993
Thermal correction to Gibbs Free Energy = 0.177691
Sum of electronic and thermal Free Energies = -540.439138

|       |       |       |       |
|-------|-------|-------|-------|
| C     | 0.00000000 | 2.50736400 | -0.00000700 |
| H     | 0.92472200  | 3.07029600  | -0.06643300 |
| H     | -0.92472300 | 3.07029600  | 0.06641600  |
| C     | 0.00000000  | 1.16932800  | -0.00000300 |
| C     | 1.27539500  | 0.39991000  | -0.04174000 |
| C     | 1.38498800  | -0.74509400 | -0.83962600 |
| C     | 2.39013300  | 0.81372600  | 0.69459900  |
| C     | 2.58588700  | -1.44122900 | -0.91996800 |
| H     | 0.52687000  | -1.08390700 | -1.41061600 |
| C     | 3.58976300  | 0.11201100  | 0.62078400  |
| H     | 2.31031900  | 1.68149400  | 1.34030700  |
| C     | 3.69261900  | -1.01551400 | -0.18902600 |
| H     | 2.65605900  | -2.31882100 | -1.55273700 |
| H     | 4.44214900  | 0.44096700  | 1.20461800  |
| H     | 4.62652500  | -1.56300400 | -0.24531400 |
| C     | -1.27539500 | 0.39991000  | 0.04173700  |
| C     | -1.38499000 | -0.74508500 | 0.83963600  |
| C     | -2.39013100 | 0.81372000  | -0.69460800 |
| C     | -2.58588900 | -1.44121900 | 0.91998100  |
| H     | -0.52687400 | -1.08389200 | 1.41063000  |
| C     | -3.58976100 | 0.11200600  | -0.62079000 |
| H     | -2.31031400 | 1.68148100  | -1.34032500 |
| C     | -3.69261900 | -1.01551100 | 0.18903200  |
| H     | -2.65606400 | -2.31880500 | 1.55275900  |
H   -4.44214500  0.44095500  -1.20463000
H   -4.62652500 -1.56300000  0.24532300

Thermal correction to Gibbs Free Energy=  0.176393
Sum of electronic and thermal Free Energies= -540.208888

\[
\begin{array}{ccc}
\text{C} & 0.00000000 & 2.50039700 \\
\text{H} & 0.92604900 & 3.06115500 \\
\text{H} & -0.92604900 & 3.06115300 \\
\text{C} & 0.00000100 & 1.10582800 \\
\text{C} & 1.26100100 & 0.38751000 \\
\text{C} & 1.34335900 & -0.85205500 \\
\text{C} & 2.42323900 & 0.92189900 \\
\text{C} & 2.54653200 & -1.53106700 \\
\text{H} & 0.47035100 & -1.24335400 \\
\text{C} & 3.61311600 & 0.22250000 \\
\text{H} & 2.37396200 & 1.85806900 \\
\text{C} & 3.67864900 & -1.00076900 \\
\text{H} & 2.60972300 & -2.46824000 \\
\text{H} & 4.49505500 & 0.62262100 \\
\text{H} & 4.61938500 & -1.53706300 \\
\text{C} & -1.26100000 & 0.38751000 \\
\text{C} & -1.34336100 & -0.85205000 \\
\text{C} & -2.42323600 & 0.92189600 \\
\text{C} & -2.54653600 & -1.53106100 \\
\text{H} & -0.47035400 & -1.24334700 \\
\text{C} & -3.61311400 & 0.22249800 \\
\end{array}
\]
H  -2.37395700  1.85806300  -1.10519200
C  -3.67865000 -1.00076700  0.15951700
H  -2.60972800 -2.46823000  1.31715700
H  -4.49505000  0.62261600 -0.99843600
H  -4.61938600 -1.53705900  0.20784600

Thermal correction to Gibbs Free Energy=         0.159348
Sum of electronic and thermal Free Energies=         -575.593010

C    1.38987300  0.20498000 -0.00002800
C    0.85084900 -1.09294500  0.00006500
C   -0.51792500 -1.30555400  0.00003600
C   -1.37204800 -0.18986000 -0.00005400
C    0.52092900  1.28363500 -0.00011400
H    2.46468000  0.31831100  0.00001200
H   -0.95862400 -2.29251600  0.00009600
H   -1.50764300  1.97651000 -0.00009600
O    1.76718900 -2.09133900  0.00011200
O   -2.69482200 -0.48458100  0.00003600
O    0.92813900  2.57630300 -0.00010800
C    2.32530100  2.83066400 -0.00004900
H    2.43316900  3.91363400 -0.00008300
H    2.79975100  2.41781900  0.89461700
H    2.79985000  2.41776000 -0.89463500
C   -3.61572600  0.59637600 -0.00003500
H   -4.60651400  0.14624200  0.00012500
|     | X         | Y         | Z         |
|-----|-----------|-----------|-----------|
| H   | -3.49652900 | 1.21472200 | 0.89402700 |
| H   | -3.49672400 | 1.21450000 | -0.89426800 |
| C   | 1.29065800  | -3.42904400 | 0.00016000 |
| H   | 0.69621300  | -3.63462800 | -0.89448200 |
| H   | 2.17563400  | -4.06262900 | 0.00026400 |
| H   | 0.69606500  | -3.63456200 | 0.89471200 |

Thermal correction to Gibbs Free Energy= 0.161502
Sum of electronic and thermal Free Energies= -575.369515

|     | X         | Y         | Z         |
|-----|-----------|-----------|-----------|
| C   | -1.24413500 | 0.24176800 | -0.00001400 |
| C   | -0.90131000 | -1.09166900 | -0.00000300 |
| C   | 0.47523400  | -1.49726500 | -0.00002000 |
| C   | 1.51458300  | -0.52487500 | -0.00005100 |
| C   | 1.19148000  | 0.80512000  | -0.00009600 |
| C   | -0.18887000 | 1.17918600  | -0.00006800 |
| H   | -2.27445100 | 0.56318400  | -0.00001500 |
| H   | 0.71920800  | -2.55303600 | -0.00000300 |
| H   | 1.92855900  | 1.59632400  | -0.00012500 |
| O   | -1.74912100 | -2.10210300 | 0.00001500 |
| O   | 2.74415800  | -1.03206400 | -0.00002900 |
| O   | -0.38165600 | 2.47085200  | -0.00010400 |
| C   | -1.71418900 | 3.01634400  | 0.00015500 |
| H   | -1.57922400 | 4.09368100  | 0.00025300 |
| H   | -2.24380400 | 2.70013500  | -0.89920800 |
| H   | -2.24352700 | 2.69992600  | 0.89960600 |
| C   | 3.83984500  | -0.11273200 | -0.00002000 |
H   4.73778900  -0.72475800  0.00000800
H   3.81262000  0.51035200  -0.89741500
H   3.81258300  0.51038100   0.89735300
C   -3.15352700 -1.81565600  0.00012400
H   -3.42137400 -1.25444800 -0.89738000
H   -3.64888400 -2.78220400  0.00022300
H   -3.42122100 -1.25434900   0.89761100

Thermal correction to Gibbs Free Energy=  0.290104
Sum of electronic and thermal Free Energies=  -884.881809

C   2.81460900  -1.04799600  -0.03585600
C   3.40072300   0.22345700   0.12766800
C   2.65457400   1.43270500   0.03755200
C   1.31306300   1.36736000  -0.22039000
C   0.66589700   0.09804900  -0.41500900
C   1.46254700  -1.10225100  -0.29197900
H   3.40886000  -1.94531200   0.04105800
H   3.18123300   2.36562900   0.18251000
O   0.50131200   2.41770100  -0.32046000
O   4.67426300   0.39741600   0.37871900
O   0.77030800  -2.21734700  -0.45062800
C   1.45266500  -3.47338500  -0.36077000
H   1.91127500  -3.58350600   0.62399700
H   0.68758300  -4.23130400  -0.50450900
H   2.20719600  -3.54686300  -1.14678200
C  1.07152800  3.71907100  -0.16110500
H  1.83036900  3.89619900  -0.92675600
H  0.24892900  4.41829700  -0.28462000
H  1.50534000  3.82524000  0.83588900
C  5.55355300  -0.73312600  0.51020400
H  5.55587500  -1.31484200  -0.41216700
H  6.53732500  -0.30804000  0.68743200
H  5.24869900  -1.34609000  1.35952400
C  -0.79179600  0.02293400  -0.66189600
H  -1.03572500  -0.88248500  -1.21698800
H  -1.11477100  0.89645400  -1.22948100
C  -1.55478200  0.00264700  0.69615700
H  -1.22271000  -0.85962600  1.27883000
H  -1.30737000  0.90873400  1.25420300
C  -3.03933900  -0.07389600  0.45396400
C  -3.69598300  -1.30532100  0.44864800
C  -3.77290800  1.08476900  0.18789200
C  -5.06173000  -1.37914700  0.18734100
H  -3.13345600  -2.21059900  0.65646100
C  -5.13757200  1.01408000  -0.07452100
H  -3.26848500  2.04666900  0.19187900
C  -5.78527500  -0.21924600  -0.07602300
H  -5.56104300  -2.34151800  0.19164700
H  -5.69612800  1.92135500  -0.27582600
H  -6.84871500  -0.27477100  -0.27866300
Thermal correction to Gibbs Free Energy = 0.367010

Sum of electronic and thermal Free Energies = -1115.823738

| Atom | x           | y           | z           |
|------|-------------|-------------|-------------|
| C    | -2.98210900 | 0.23610800  | -0.78559900 |
| C    | -3.41606300 | -0.83943700 | 0.01287900  |
| C    | -2.56740300 | -1.92613100 | 0.37167500  |
| C    | -1.26517700 | -1.91459000 | -0.04399800 |
| C    | -0.75240900 | -0.81560200 | -0.81902600 |
| C    | -1.67164800 | 0.23078400  | -1.21194900 |
| H    | -3.65798700 | 1.03096100  | -1.06072100 |
| H    | -2.99048900 | -2.72013400 | 0.97127100  |
| O    | -0.36518700 | -2.85925200 | 0.22398900  |
| O    | -4.63576000 | -0.93928800 | 0.47974500  |
| O    | -1.13177100 | 1.15646900  | -1.98177700 |
| C    | -1.89112700 | 2.32904100  | -2.29183100 |
| H    | -2.20445900 | 2.82565600  | -1.37075600 |
| H    | -1.21966700 | 2.97082600  | -2.85638200 |
| H    | -2.75869200 | 2.06776800  | -2.90191700 |
| C    | -0.78218600 | -3.97936900 | 1.00903400  |
| H    | -1.58590000 | -4.51903200 | 0.50325200  |
| H    | 0.09366000  | -4.61615300 | 1.10078800  |
| H    | -1.11018400 | -3.64874500 | 1.99727800  |
| C    | -5.60442000 | 0.08856800  | 0.20983300  |
| H    | -5.78840300 | 0.15458700  | -0.86341100 |
| H    | -6.50605200 | -0.22744100 | 0.72663800  |
|     | X          | Y          | Z          |
|-----|------------|------------|------------|
| H   | -5.2561620 | 1.0425730  | 0.6074640  |
| C   | 0.7051590  | -0.7139460 | -1.0825010 |
| H   | 0.9078570  | 0.0085410  | -1.8715810 |
| H   | 1.0873200  | -1.6917580 | -1.3797690 |
| C   | 1.4389870  | -0.2757890 | 0.2339780  |
| H   | 1.2058180  | -1.0343700 | 0.9862920  |
| C   | 2.9464470  | -0.3294320 | 0.0183130  |
| C   | 3.7777440  | 0.7887530  | 0.0751680  |
| C   | 3.5277030  | -1.5804280 | -0.2245460 |
| C   | 5.1532250  | 0.6618980  | -0.1220830 |
| H   | 3.3656880  | 1.7672020  | 0.2877180  |
| C   | 4.8967180  | -1.7090090 | -0.4185520 |
| H   | 2.8984090  | -2.4658240 | -0.2473260 |
| C   | 5.7170030  | -0.5823430 | -0.3737700 |
| H   | 5.7819530  | 1.5439780  | -0.0740100 |
| H   | 5.3262900  | -2.6882450 | -0.5982060 |
| H   | 6.7859020  | -0.6785890 | -0.5260270 |
| C   | 0.8825220  | 1.0435470  | 0.7314620  |
| C   | 0.2731260  | 1.1077770  | 1.9849990  |
| C   | 0.8990880  | 2.1932630  | -0.0651280 |
| C   | -0.3003160 | 2.2935180  | 2.4416830  |
| H   | 0.2474040  | 0.2192170  | 2.6087600  |
| C   | 0.3277000  | 3.3777350  | 0.3859030  |
| H   | 1.3536930  | 2.1591700  | -1.0502680 |
| C   | -0.2753760 | 3.4310890  | 1.6417140  |
| H   | -0.7661920 | 2.3253190  | 3.4201280  |
| H   | 0.3485910  | 4.2598790  | -0.2446550 |
| H   | -0.7198000 | 4.3551640  | 1.9938320  |
Characterization of Products

\[(E)-1,3,5\text{-Trimethoxy-2-styrylbenzene (3aa)}, \text{37.8 mg, 70\% yield, yellow oil. Only the data of E-}\]
\[\text{isomer was shown here.}^{1}H \text{ NMR (400 MHz, CDCl}_3\text{) }\delta 7.54 (d, J = 7.3 \text{ Hz, 2H}), 7.49 (d, J = 16.8 \text{ Hz, 1H}), 7.42 (d, J = 16.6 \text{ Hz, 1H}), 7.34 (t, J = 7.7 \text{ Hz, 2H}), 7.21 (t, J = 7.3 \text{ Hz, 1H}), 6.19 (s, 2H), 3.90 (s, 6H), 3.85 (s, 3H); ^{13}C \text{ NMR (150 MHz, CDCl}_3\text{) }\delta 160.2, 159.5, 139.7, 129.9, 128.4, 126.5, 126.1, 119.8, 108.1, 90.8, 55.8, 55.3; \text{HRMS (ESI) calcd for C}_{17}H_{19}O_3^+, [M+H]^+, 271.1329 found 271.1321.\]

\[(E)-1,3,5\text{-Trimethoxy-2-(4-methylstyryl)benzene (3ab)}, \text{34.6 mg, 61\% yield, white solid. Only the}\]
\[\text{data of E-isomer was shown here.}^{1}H \text{ NMR (400 MHz, CDCl}_3\text{) }\delta 7.43 (d, J = 17.1 \text{ Hz, 2H}), 7.39 (s, 1H), 7.34 (d, J = 16.6 \text{ Hz, 1H}), 7.12 (d, J = 8.0 \text{ Hz, 2H}), 6.15 (s, 2H), 3.86 (s, 6H), 3.81 (s, 3H), 2.33 (s, 3H); ^{13}C \text{ NMR (101 MHz, CDCl}_3\text{) }\delta 160.0, 159.3, 136.8, 136.2, 129.8, 129.1, 126.0, 118.8, 108.2, 90.7, 55.7, 55.2, 21.2; \text{HRMS (ESI) calcd for C}_{18}H_{21}O_3^+, [M+H]^+, 285.1485 found 285.1488.\]

\[(E)-1,3,5\text{-Trimethoxy-2-(4-methoxystyryl)benzene (3ac)}, \text{31.8 mg, 53\% yield, white solid. Only the}\]
\[\text{data of E-isomer was shown here.}^{1}H \text{ NMR (400 MHz, CDCl}_3\text{) }\delta 7.49 – 7.34 (m, 3H), 7.24 (d, J = 9.6 \text{ Hz, 1H}), 6.86 (d, J = 8.7 \text{ Hz, 2H}), 6.16 (s, 2H), 3.87 (s, 6H), 3.83 (s, 3H), 3.81 (s, 3H); ^{13}C \text{ NMR (101 MHz, CDCl}_3\text{) }\delta 159.8, 159.2, 158.5, 132.4, 129.5, 127.2, 117.8, 113.8, 108.3, 90.8, 55.7, 55.3, 55.3; \text{HRMS (ESI) calcd for C}_{18}H_{21}O_4^+, [M+H]^+, 301.1434 found 301.1424.\]
Only the data of E-isomer was shown here. (E)-2-(4-(Tert-butyl)styryl)-1,3,5-trimethoxybenzene (3ad), 41.7 mg, 64% yield, white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48 (s, 1H), 7.45 (d, $J = 7.7$ Hz, 2H), 7.38 (d, $J = 2.7$ Hz, 2H), 7.35 (d, $J = 5.6$ Hz, 1H), 6.18 (s, 2H), 3.89 (s, 6H), 3.85 (s, 3H), 1.35 (s, 9H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 160.0, 159.4, 149.5, 137.0, 129.9, 125.9, 125.4, 119.2, 108.4, 90.9, 55.8, 55.3, 34.5, 31.4; HRMS (ESI) calcd for C$_{21}$H$_{27}$O$_3$+, [M+H]$^+$, 327.1955 found 327.1951.

(Z, E)-2-(4-Fluorostyryl)-1,3,5-trimethoxybenzene (3ae), 37.4 mg, 65% yield, white solid. A mixture of Z/E isomers was isolated (Z/E = 1: 13 ratio determined based on GC). $^1$H NMR (400 MHz, CDCl$_3$) of E-isomer: $\delta$ 7.50 – 7.37 (m, 3H), 7.29 (d, $J = 16.6$ Hz, 1H), 7.04 – 6.95 (m, 2H), 6.16 (s, 2H), 3.87 (s, 6H), 3.83 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) mixture of Z/E isomers: $\delta$ 163.0 ($\nu_{CF} = 245.2$ Hz), 160.2, 159.4, 158.3, 135.8, 135.7, 129.8, 129.4, 129.3, 128.6, 127.5, 127.4, 119.6, 119.5, 115.20 ($\nu_{CF} = 21.5$ Hz), 114.4 (d, $J = 21.2$ Hz), 107.9, 90.7, 55.7, 55.3; $^{19}$F NMR (377 MHz, CDCl$_3$) mixture of Z/E isomers: $\delta$ -115.57, -116.25; HRMS (ESI) calcd for C$_{17}$H$_{18}$FO$_3$+, [M+H]$^+$, 289.1234 found 289.1227.

(E)-2-(4-Chlorostyryl)-1,3,5-trimethoxybenzene (3af), 31.6 mg, 52% yield, white solid. Only the data of E-isomer was shown here. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 (d, $J = 8.6$ Hz, 2H), 7.38 (d, $J = 4.6$ Hz, 2H), 7.29 – 7.23 (m, 2H), 6.16 (s, 2H), 3.88 (s, 6H), 3.83 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 160.4, 159.6, 138.2, 131.9, 128.5, 128.5, 127.3, 120.5, 107.8, 90.7, 55.8, 55.4; HRMS (ESI) calcd for C$_{17}$H$_{18}$ClO$_3$+, [M+H]$^+$, 305.0939 found 305.0938.
(E)-2-(4-Bromostyryl)-1,3,5-trimethoxybenzene (3ag), 36.3 mg, 52% yield, white solid. Only the data of E-isomer was shown here. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49 – 7.44 (m, 2H), 7.42 (s, 2H), 7.42 – 7.36 (m, 2H), 6.20 (s, 2H), 3.91 (s, 6H), 3.87 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 160.5, 159.6, 138.7, 131.5, 128.5, 127.7, 120.6, 120.0, 107.7, 90.7, 55.8, 55.4; HRMS (ESI) calcd for C$_{17}$H$_{18}$BrO$_3^+$, [M+H]$^+$, 349.0434 found 349.0427.

![Structure of (E)-2-(4-Bromostyryl)-1,3,5-trimethoxybenzene](image)

(E)-1,3,5-Trimethoxy-2-(2,4,6-trimethylstyryl)benzene (3ah), 58.0 mg, 93% yield, white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 (d, $J$ = 17.0 Hz, 1H), 6.92 (s, 2H), 6.81 (d, $J$ = 17.0 Hz, 1H), 6.21 (s, 2H), 3.87 (s, 6H), 3.87 (s, 3H), 2.40 (s, 6H), 2.32 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 160.0, 159.3, 136.4, 135.9, 135.4, 128.8, 128.6, 124.4, 108.7, 91.0, 55.9, 55.4, 21.2, 21.0; HRMS (ESI) calcd for C$_{20}$H$_{25}$O$_3^+$, [M+H]$^+$, 313.1798 found 313.1794.

![Structure of (E)-1,3,5-Trimethoxy-2-(2,4,6-trimethylstyryl)benzene](image)

(Z, E)-4-(2,4,6-trimethoxystyryl)benzonitrile (3ai), 43% yield, 25.4 mg, white solid. A mixture of Z/E isomers was isolated (Z/E = 1: 6 ratio determined based on $^1$H NMR and GC). $^1$H NMR (400 MHz, CDCl$_3$) of E-isomer $\delta$ 7.45 (d, $J$ = 8.4 Hz, 2H), 7.30 – 7.23 (m, 2H), 6.63 – 6.55 (m, 2H), 6.10 (s, 2H), 3.84 (s, 3H), 3.58 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) of E-isomer $\delta$ 161.7, 158.5, 144.3, 131.7, 129.2, 128.5, 124.7, 119.6, 109.7, 107.1, 90.8, 55.6, 55.6; HRMS (ESI) calcd for C$_{20}$H$_{25}$O$_3^+$, [M+H]$^+$, 296.1281 found 296.1289.

![Structure of (Z, E)-4-(2,4,6-trimethoxystyryl)benzonitrile](image)

(2-(2,4,6-Trimethoxyphenyl)ethene-1,1-diyl)dibenzene (3ajj), 68.5 mg, 99% yield, white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 – 7.40 (m, 2H), 7.37 – 7.28 (m, 3H), 7.25 – 7.17 (m, 3H), 7.17 – 7.09 (m, 2H), 6.79 (s, 1H), 6.04 (s, 2H), 3.83 (s, 3H), 3.50 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 160.6,
158.4, 143.9, 143.5, 142.5, 129.5, 128.4, 127.9, 127.4, 127.0, 126.5, 119.8, 109.0, 90.3, 55.3, 55.2; HRMS (ESI) calcd for C_{23}H_{22}O_3^+, [M+H]^+, 347.1642 found 347.1635.

4,4′-(2-(2,4,6-Trimethoxyphenyl)ethene-1,1-diyl)bis(methylbenzene) (3ak), 67.3 mg, 89% yield, white solid. 1H NMR (400 MHz, CDCl_3) δ 7.26 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 6.96 (s, 4H), 6.65 (s, 1H), 5.99 (s, 2H), 3.78 (s, 3H), 3.45 (s, 6H), 2.34 (s, 3H), 2.28 (s, 3H); 13C NMR (101 MHz, CDCl_3) δ 160.3, 158.3, 143.3, 141.2, 139.5, 136.6, 135.8, 129.3, 128.5, 128.2, 128.0, 118.6, 109.3, 90.4, 55.2, 55.1, 21.2, 21.1; HRMS (ESI) calcd for C_{25}H_{17}O_3^+, [M+H]^+, 375.1955 found 375.1946.

4,4′-(2-(2,4,6-Trimethoxyphenyl)ethene-1,1-diyl)bis(methoxybenzene) (3al), 80.4 mg, 99% yield, white solid. 1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.25 (m, 2H), 7.03 – 6.93 (m, 2H), 6.86 – 6.75 (m, 2H), 6.74 – 6.63 (m, 2H), 6.58 (s, 1H), 6.00 (s, 2H), 3.81 (s, 3H), 3.78 (s, 3H), 3.76 (s, 3H), 3.48 (s, 6H). 13C NMR (101 MHz, CDCl_3) δ = 13C NMR (101 MHz, CDCl_3) δ 160.3, 158.3, 158.2, 158.1, 142.6, 136.7, 135.1, 130.5, 129.4, 117.4, 113.1, 112.7, 109.4, 90.3, 55.2, 55.2, 55.2, 55.1; HRMS (ESI) calcd for C_{25}H_{27}O_5^+, [M+H]^+, 407.1853 found 407.1826.

4,4′-(2-(2,4,6-Trimethoxyphenyl)ethene-1,1-diyl)bis(fluorobenzene) (3am), 71.0 mg, 93% yield, white solid. 1H NMR (400 MHz, CDCl_3) δ 7.32 – 7.27 (m, 2H), 7.10 – 7.00 (m, 2H), 6.99 – 6.94 (m, 2H), 6.90 – 6.81 (m, 2H), 6.65 (s, 1H), 6.00 (s, 2H), 3.78 (s, 3H), 3.49 (s, 6H); 13C NMR (101 MHz, CDCl_3) δ 163.1 (J_{CF} = 63.5 Hz), 160.71, 160.67 (J_{CF} = 62.7 Hz), 158.2, 141.4, 139.7 (J_{CF} = 62.7 Hz),
138.2 ($\delta_{\text{C-F}} = 3.3$ Hz), 130.9 ($\delta_{\text{C-F}} = 7.8$ Hz), 129.7 ($\delta_{\text{C-F}} = 7.9$ Hz), 119.8, 114.7 ($\delta_{\text{C-F}} = 21.3$ Hz), 114.3 ($\delta_{\text{C-F}} = 21.1$ Hz), 108.4, 90.2, 55.2, 55.1; $^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ -115.72, -115.92; HRMS (ESI) calcd for C$_{25}$H$_{20}$F$_2$O$_3^+$, [M+H]$^+$, 383.1453 found 383.1444.

OMe

OMe

OMe

OMe

Cl

Cl

4,4'-(2-(2,4,6-Trimethoxyphenyl)ethene-1,1-diyl)bis(chlorobenzene) (3an), 77.1 mg, 93% yield, white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.25 (s, 4H), 7.15 (d, $J = 8.5$ Hz, 2H), 7.00 (d, $J = 8.5$ Hz, 2H), 6.71 (s, 1H), 5.99 (s, 2H), 3.78 (s, 3H), 3.48 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 160.9, 158.1, 141.8, 140.9, 140.5, 132.9, 132.1, 130.6, 129.4, 128.0, 127.7, 120.8, 108.1, 90.2, 55.2, 55.0; HRMS (ESI) calcd for C$_{23}$H$_{21}$Cl$_2$O$_3^+$, [M+H]$^+$, 415.0862 found 415.0852.

OMe

OMe

OMe

OMe

OMe

Br

Br

4,4'-(2-(2,4,6-Trimethoxyphenyl)ethene-1,1-diyl)bis(bromobenzene) (3ao), 75.3 mg, 75% yield, white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 (d, $J = 8.5$ Hz, 2H), 7.30 (d, $J = 8.4$ Hz, 2H), 6.94 (d, $J = 8.4$ Hz, 2H), 6.72 (s, 1H), 5.99 (s, 2H), 3.79 (s, 3H), 3.48 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.0, 158.2, 142.2, 141.0, 140.9, 131.0, 130.7, 129.8, 121.2, 120.9, 120.4, 108.1, 90.3, 55.2, 55.1; HRMS (ESI) calcd for C$_{23}$H$_{21}$Br$_2$O$_3^+$, [M+H]$^+$, 502.9852 found 502.9810.

OMe

OMe

OMe

OMe

OMe

OMe

E-isomer

Z-isomer

(Z, E)-1,3,5-Trimethoxy-2-(2-phenyl-2-(p-tolyl)vinyl)benzene (3ap), 71.3 mg, 99% yield, white solid. A mixture of $E$/Z isomers was isolated (53:47 ratio determined based on GC and $^1$H NMR). $^1$H NMR (400 MHz, CDCl$_3$) of $E$-isomer $\delta$ 7.36 – 7.29 (m, 3H), 7.24 – 7.18 (m, 2H), 7.17 – 7.11 (m, 2H), 7.02 (s, 2H), 6.75 (s, 1H), 6.03 (s, 2H), 3.82 (s, 3H), 3.49 (s, 6H), 2.40 (s, 3H); $^1$H NMR (400 MHz, CDCl$_3$)
of Z-isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 – 7.37 (m, 2H), 7.36 – 7.26 (m, 2H), 7.24 – 7.17 (m, 1H), 7.17 – 7.11 (m, 2H), 7.02 (s, 2H), 6.74 (s, 1H), 6.05 (s, 2H), 3.83 (s, 3H), 3.51 (s, 3H), 2.34 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) mixture of Z/E isomers: $\delta$ 160.4, 158.3, 158.3, 144.0, 143.4, 143.2, 142.5, 141.0, 139.4, 136.6, 135.8, 129.4, 129.3, 128.5, 128.3, 128.2, 128.0, 127.8, 127.3, 126.9, 126.3, 119.3, 119.0, 109.2, 109.0, 90.3, 90.3, 55.2, 55.1, 21.2, 21.1; HRMS (ESI) calcd for C$_{24}$H$_{25}$O$_3$*, [M+H]$^+$, 361.1798 found 361.1789.

(Z,E)-4-(1-Phenyl-2-(2,4,6-trimethoxyphenyl)vinyl)-1,1'-biphenyl (3aq), 83.6 mg, 99% yield, white solid. A mixture of E/Z isomers was isolated (59:41 ratio determined based on GC and $^1$H NMR). $^1$H NMR (400 MHz, CDCl$_3$) of E-isomer: $\delta$ 7.65 – 7.56 (m, 2H), 7.56 – 7.51 (m, 1H), 7.50 – 7.38 (m, 5H), 7.36 – 7.26 (m, 2H), 7.25 – 7.04 (m, 4H), 6.81 (s, 1H), 6.00 (s, 2H), 3.77 (s, 3H), 3.46 (s, 6H); $^1$H NMR (400 MHz, CDCl$_3$) of Z-isomer: $\delta$ 7.65 – 7.56 (m, 2H), 7.56 – 7.51 (m, 1H), 7.50 – 7.38 (m, 5H), 7.36 – 7.26 (m, 2H), 7.25 – 7.04 (m, 4H), 6.77 (s, 1H), 6.00 (s, 2H), 3.77 (s, 3H), 3.46 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) mixture of Z/E isomers $\delta$ $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 160.61, 160.59, 158.3, 143.8, 142.90, 142.85, 142.3, 141.6, 141.0, 140.9, 139.6, 138.9, 129.8, 129.4, 128.7, 128.6, 128.4, 127.9, 127.4, 127.1, 127.0, 126.9, 126.8, 126.5, 126.4, 125.9, 120.0, 119.9, 108.9, 90.3, 90.3, 55.2, 55.1; HRMS (ESI) calcd for C$_{29}$H$_{27}$O$_3$*, [M+H]$^+$, 423.1955 found 423.1943.

1,3,5-Trimethoxy-2-(2-phenylallyl)benzene (3ar), 27.3 mg, 48% yield, white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 (d, $J$ = 7.3 Hz, 2H), 7.33 (t, $J$ = 7.5 Hz, 2H), 7.26 (t, $J$ = 7.3 Hz, 1H), 6.17 (s, 2H), 5.22 (d, $J$ = 1.2 Hz, 1H), 4.60 (d, $J$ = 1.5 Hz, 1H), 3.83 (s, 3H), 3.76 (s, 6H), 3.71 (s, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.7, 159.1, 147.0, 142.3, 128.0, 127.1, 126.1, 110.8, 108.8, 90.6, 55.8, 55.3, 27.9.
(E)-1,3,5-Trimethoxy-2-(2-phenylprop-1-en-1-yl)benzene (3as), 26.7 mg, 47%, white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.63 – 7.55 (m, 2H), 7.34 (t, $J = 7.6$ Hz, 2H), 7.24 (d, $J = 4.0$ Hz, 1H), 6.61 (d, $J = 1.0$ Hz, 1H), 6.18 (s, 2H), 3.84 (s, 3H), 3.80 (s, 6H), 1.96 (d, $J = 1.1$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 160.4, 158.5, 143.2, 138.1, 128.0, 126.7, 125.9, 118.6, 108.7, 90.5, 55.7, 55.3, 17.9.

2-(2,4,6-Trimethoxyphenyl)-1H-indene (3at), 19.2 mg, 34%, white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 (d, $J = 7.3$ Hz, 1H), 7.38 (d, $J = 7.5$ Hz, 1H), 7.24 (dd, $J = 8.1$, 6.6 Hz, 1H), 7.13 (td, $J = 7.4$, 1.1 Hz, 1H), 7.01 (s, 1H), 6.20 (s, 2H), 3.85 (s, 3H), 3.83 (s, 2H), 3.79 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 160.3, 158.9, 145.5, 143.9, 140.0, 131.5, 125.9, 123.8, 123.1, 120.5, 108.4, 90.9, 55.8, 55.3, 42.4.

(2-(2,4-Dimethoxyphenyl)ethene-1,1-diyl) dibenzene 3ba and (2-(2,6-dimethoxyphenyl)ethene-1,1-diyl) dibenzene 3ba', 27.2 mg, 43% yield, yellow solid. A mixture of regioisomers was isolated (3ba: 3ba' = 85:15 ratio determined based on GC). $^1$H NMR (400 MHz, CDCl$_3$) of 3ba $\delta$ 7.34 – 7.22 (m, 8H), 7.22 – 7.16 (m, 2H), 7.10 – 7.02 (m, 1H), 6.67 (d, $J = 8.6$ Hz, 1H), 6.41 (d, $J = 2.5$ Hz, 1H), 6.14 (dd, $J = 8.6$, 2.4 Hz, 1H), 3.79 (d, $J = 4.6$ Hz, 3H), 3.74 (s, 3H); $^1$H NMR (400 MHz, CDCl$_3$) of 3ba' $\delta$ 7.85 – 7.75 (m, 3H), 7.63 – 7.56 (m, 2H), 7.43 – 7.34 (m, 4H), 7.17 – 7.10 (m, 3H), 6.79 (s, 1H), 6.39 (s, 1H), 3.47 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) mixture of isomers: $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.8, 158.8, 157.6, 144.5, 143.9, 143.5, 142.0, 140.9, 140.7, 137.5, 132.4, 130.7, 130.6, 130.0, 129.4, 128.3, 128.2, 128.0, 127.9, 127.7, 127.3, 127.1, 127.0, 126.9, 126.6, 122.7, 119.8, 119.4, 103.9, 103.5, 97.9, 55.4, 55.2, 55.1; HRMS (ESI) calcd for C$_{22}$H$_{21}$O$_2$+, [M+H]$^+$, 317.1536 found 317.1535.
(2-(2,4-Dimethoxy-6-methylphenyl)ethene-1,1-diyl)dibenzene 3bb and (2-(2,6-dimethoxy-4-methylphenyl)ethene-1,1-diyl)dibenzene 3bb’, 35.0 mg, 53% yield, yellow solid. A mixture of regioisomers was isolated (3bb: 3bb’ = 78:22 ratio determined based on GC and $^1$H NMR).

$^1$H NMR (400 MHz, CDCl$_3$) of 3bb: $\delta$ 7.39 – 7.35 (m, 2H), 7.33 – 7.26 (m, 3H), 7.16 – 7.12 (m, 3H), 7.06 – 6.98 (m, 2H), 6.74 (s, 1H), 6.21 (s, 2H), 3.75 (s, 3H), 3.54 (s, 3H), 1.98 (s, 3H); $^1$H NMR (400 MHz, CDCl$_3$) of 3bb’: $\delta$ 7.86 – 7.77 (m, 3H), 7.66 – 7.56 (m, 1H), 7.48 (t, $J$ = 7.6 Hz, 3H), 7.34 – 7.33 (m, 1H), 7.11 – 7.05 (m, 2H), 6.77 (s, 1H), 6.22 (s, 2H), 3.45 (s, 6H), 2.30 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.36, 158.31, 157.42, 144.27, 143.98, 143.80, 143.59, 142.35, 141.24, 138.64, 138.11, 137.59, 132.47, 130.11, 129.86, 129.48, 128.39, 128.36, 128.31, 128.02, 127.87, 127.60, 127.37, 127.26, 127.06, 126.78, 126.49, 123.69, 120.03, 119.57, 113.04, 106.07, 104.52, 95.74, 55.19, 55.13, 22.21, 20.67; HRMS (ESI) calcd for C$_{23}$H$_{23}$O$_2$+, [M+H]$^+$, 331.1693 found 331.1697.

(2-(2-Chloro-4,6-dimethoxyphenyl)ethene-1,1-diyl)dibenzene (3bc), 52.5 mg, 75% yield, yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41 – 7.35 (m, 2H), 7.34 – 7.27 (m, 3H), 7.21 – 7.11 (m, 3H), 7.05 (dd, $J$ = 6.6, 3.1 Hz, 2H), 6.68 (s, 1H), 6.48 (d, $J$ = 2.3 Hz, 1H), 6.16 (d, $J$ = 2.3 Hz, 1H), 3.74 (s, 3H), 3.35 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.6, 158.1, 145.6, 142.9, 141.2, 135.1, 130.0, 129.6, 128.3, 128.0, 127.5, 127.4, 126.9, 120.9, 119.3, 105.4, 97.3, 55.4, 55.1; HRMS (ESI) calcd for C$_{23}$H$_{22}$O$_2$+, [M+H]$^+$, 331.1693 found 331.1697.

N-(2-(2,2-Diphenylvinyl)-3,5-dimethoxyphenyl)acetamide (3bd), 32.1 mg, 43% yield, white solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 – 7.31 (m, 6H), 7.25 – 7.19 (m, 3H), 7.17 – 7.10 (m, 2H), 7.07 (s, 1H), 6.73 (s, 1H), 6.25 (d, $J$ = 1.9 Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 1.82 (s, 3H); $^{13}$C NMR (101 MHz,
CDCl₃ δ 167.9, 160.3, 159.0, 144.6, 142.8, 139.6, 135.2, 129.6, 128.5, 128.4, 128.3, 128.2, 127.9, 121.3, 109.6, 97.5, 94.8, 55.6, 55.4, 24.9; HRMS (ESI) calcd for C₂₂H₂₄NO₃⁺, [M+H]⁺, 373.1678 found 373.1673.

2-(2,2-Diphenylvinyl)-3,5-dimethoxyphenol (3be), 38.5 mg, 58% yield, white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.34 (m, 5H), 7.34 – 7.28 (m, 3H), 7.28 – 7.21 (m, 2H), 6.81 (s, 1H), 6.11 (d, J = 2.3 Hz, 1H), 5.97 (d, J = 2.3 Hz, 1H), 5.11 (s, 1H), 3.79 (s, 3H), 3.77 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 160.9, 159.5, 153.1, 143.7, 142.8, 139.3, 129.7, 128.6, 128.3, 128.1, 127.7, 120.6, 106.5, 92.9, 91.2, 55.6, 55.2; HRMS (ESI) calcd for C₂₂H₂₁O₃⁺, [M+H]⁺, 333.1485 found 333.1486.

(2-(2-(Allyloxy)-4,6-dimethoxyphenyl)ethene-1,1-diyl)dibenzene (3bf), 46.9 mg, 63% yield, white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.34 (m, 2H), 7.31 – 7.22 (m, 3H), 7.20 – 7.12 (m, 3H), 7.11 – 7.02 (m, 2H), 6.72 (s, 1H), 6.01 – 5.97 (m, 2H), 5.86 – 5.73 (m, 1H), 5.23 (ddd, J = 17.3, 3.1, 1.5 Hz, 1H), 5.14 (dd, J = 10.5, 1.5 Hz, 1H), 4.25 (dt, J = 5.1, 1.5 Hz, 2H), 3.76 (s, 3H), 3.44 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 160.3, 158.4, 157.4, 143.9, 143.6, 142.2, 133.7, 129.6, 128.3, 127.3, 126.9, 126.4, 119.9, 116.8, 109.5, 91.6, 90.5, 69.1, 55.2, 55.1; HRMS (ESI) calcd for C₂₅H₂₅O₅⁺, [M+H]⁺, 373.1798 found 373.1789.

2-(2,2-Diphenylvinyl)thiophene (3bg), 23.6 mg, 45% yield, colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.52 – 7.41 (m, 3H), 7.37 – 7.21 (m, 8H), 7.03 (d, J = 5.0 Hz, 1H), 6.96 – 6.90 (m, 1H), 6.89 – 6.84 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 141.7, 141.3, 139.7, 139.4, 130.3, 129.3, 128.9, 128.3, 128.0, 127.3, 126.7, 126.3, 126.2, 120.8. HRMS (ESI) calcd for C₁₈H₁₅S⁺, [M+H]⁺, 263.0889 found 263.0843.

2-(2,2-Diphenylvinyl)thiophene (3bg), 23.6 mg, 45% yield, colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.52 – 7.41 (m, 3H), 7.37 – 7.21 (m, 8H), 7.03 (d, J = 5.0 Hz, 1H), 6.96 – 6.90 (m, 1H), 6.89 – 6.84 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 141.7, 141.3, 139.7, 139.4, 130.3, 129.3, 128.9, 128.3, 128.0, 127.3, 126.7, 126.3, 126.2, 120.8. HRMS (ESI) calcd for C₁₈H₁₅S⁺, [M+H]⁺, 263.0889 found 263.0843.
2-(2,2-Diphenylvinyl)-3-methylthiophene 3bh and 2-(2,2-diphenylvinyl)-4-methylthiophene 3bh', 39.2 mg, 71% yield, yellow solid. A mixture of regioisomers was isolated (3bh: 3bh' = 2:1 ratio determined based on $^1$H NMR). $^1$H NMR (400 MHz, CDCl$_3$) of 3bh δ 7.48–7.40 (m, 3H), 7.37–7.19 (m, 8H), 6.93 (d, $J = 5.1$ Hz, 1H), 6.72 (d, $J = 5.1$ Hz, 1H), 2.33 (s, 3H); $^1$H NMR (400 MHz, CDCl$_3$) of 3bh' δ 7.52–7.39 (m, 3H), 7.35–7.19 (m, 8H), 6.73 (s, 1H), 6.61 (s, 1H), 2.13 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) of mixture $^{13}$C NMR (101 MHz, CDCl$_3$) δ 142.5, 141.9, 141.1, 139.5, 139.5, 139.4, 139.3, 137.6, 136.7, 134.8, 131.5, 130.7, 130.4, 129.3, 129.2, 129.2, 128.4, 128.1, 127.3, 127.0, 126.8, 125.0, 122.1, 121.0, 119.4, 15.5, 14.6. HRMS (ESI) calcd for C$_{19}$H$_{17}$S, [M+H]$^+$, 277.1045 found 277.1004.

2-(2,2-Diphenylvinyl)-3,4-dimethylthiophene (3bi), 44.7 mg, 77% yield, colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.48–7.39 (m, 3H), 7.34–7.22 (m, 8H), 6.64 (s, 1H), 2.21 (s, 3H), 2.09 (d, $J = 0.7$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 142.5, 139.7, 139.2, 137.2, 136.8, 134.9, 130.7, 129.0, 128.2, 127.9, 127.2, 126.9, 121.2, 120.0, 15.0, 13.0. HRMS (ESI) calcd for C$_{20}$H$_{19}$S, [M+H]$^+$, 291.1205 found 291.1205.

5-(2,2-Diphenylvinyl)-2,3-dihydrothieno[3,4-b][1,4]dioxine (3bj), 51.2 mg, 80% yield, colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.51–7.40 (m, 3H), 7.37–7.24 (m, 7H), 7.24–7.18 (m, 1H), 6.06 (s, 1H), 4.25 (dd, $J = 7.4$, 3.6 Hz, 2H), 4.18 (dd, $J = 7.4$, 3.5 Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 141.8,
141.0, 140.6, 139.3, 137.3, 130.2, 128.2, 127.0, 126.6, 116.2, 116.0, 100.3, 64.8, 64.6.

HRMS (ESI) calcd for C\textsubscript{20}H\textsubscript{17}O\textsubscript{2}S, [M+H]\textsuperscript{+}, 321.0944 found 321.0951.

![Ph-Ph-O](image)

2-(2,2-Diphenylvinyl)-5-ethylfuran (3bk), 31.8 mg, 58% yield, colorless oil. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.50 – 7.35 (m, 3H), 7.34 – 7.16 (m, 7H), 6.93 (s, 1H), 5.80 (d, \(J = 2.7\) Hz, 1H), 5.38 (d, \(J = 3.0\) Hz, 1H), 2.54 (d, \(J = 7.5\) Hz, 2H), 1.13 (t, \(J = 7.6\) Hz, 3H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 157.0, 151.4, 141.8, 140.5, 138.4, 129.6, 128.8, 128.2, 127.4, 127.1, 126.7, 116.2, 110.1, 106.2, 21.4, 12.0; HRMS (ESI) calcd for C\textsubscript{20}H\textsubscript{18}O, [M]\textsuperscript{+}, 274.1358 found 274.1351.

![Ph-Ph](image)

2-(2,2-Diphenylvinyl)-1-(p-tolyl)-1H-pyrrole (3bl), 52.3 mg, 78% yield, white solid. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.47 – 7.37 (m, 3H), 7.32 – 7.24 (m, 6H), 7.23 – 7.14 (m, 5H), 6.76 (dd, \(J = 2.6, 1.7\) Hz, 1H), 6.72 (s, 1H), 6.13 – 5.93 (m, 1H), 5.39 (dd, \(J = 3.8, 1.5\) Hz, 1H), 2.42 (s, 3H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 142.7, 141.1, 138.1, 137.2, 137.1, 131.1, 130.0, 129.8, 129.0, 128.2, 127.4, 126.8, 126.8, 126.2, 122.9, 116.9, 110.7, 109.2, 21.1; HRMS (ESI) calcd for C\textsubscript{25}H\textsubscript{22}N\textsuperscript{+}, [M+H]\textsuperscript{+}, 333.1485 found 333.1486.

![Ph immunol](image)

3-(2,2-Diphenylvinyl)-2-phenylimidazo[1,2-a]pyridine (3bm), 72.2 mg, 97% yield, white solid. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.95 (d, \(J = 7.4\) Hz, 2H), 7.57 (d, \(J = 9.0\) Hz, 1H), 7.52 (d, \(J = 6.9\) Hz, 1H), 7.47 – 7.43 (m, 2H), 7.42 – 7.35 (m, 5H), 7.30 (t, \(J = 7.3\) Hz, 1H), 7.16 – 6.99 (m, 7H), 6.45 (t, \(J = 6.7\) Hz, 1H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 146.2, 144.7, 144.7, 144.6, 142.3, 139.7, 134.6, 129.1, 128.6, 128.4, 128.3, 128.3, 128.0, 128.0, 127.7, 124.4, 124.1, 118.7, 117.0, 115.0, 111.4; HRMS (ESI) calcd for C\textsubscript{27}H\textsubscript{22}N\textsuperscript{+}, [M+H]\textsuperscript{+}, 373.1699 found 373.1690.
3-(2,2-Diphenylvinyl)-2-(3-methoxyphenyl)imidazo[1,2-a]pyridine (3bn), 71.6 mg, 89% yield, white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.61 – 7.53 (m, 2H), 7.53 – 7.47 (m, 2H), 7.43 (dd, $J$ = 6.7, 3.1 Hz, 2H), 7.40 – 7.34 (m, 3H), 7.27 (t, $J$ = 8.2 Hz, 1H), 7.14 – 6.98 (m, 7H), 6.90 – 6.82 (m, 1H), 6.46 (td, $J$ = 6.8, 1.1 Hz, 1H), 3.81 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.9, 160.3, 159.0, 144.6, 142.8, 139.6, 135.2, 129.6, 128.5, 128.4, 128.3, 128.2, 127.9, 121.3, 109.6, 94.8, 55.6, 55.4, 24.9; HRMS (ESI) calcd for C$_{28}$H$_{23}$N$_2$O$^+$, [M+H]$^+$, 403.1805 found 403.1800.

2-(4-Chlorophenyl)-3-(2,2-diphenylvinyl)imidazo[1,2-a]pyridine (3bo), 64.9 mg, 80% yield, white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 (d, $J$ = 8.3 Hz, 2H), 7.56 (t, $J$ = 7.7 Hz, 2H), 7.47 – 7.36 (m, 5H), 7.32 (d, $J$ = 8.3 Hz, 2H), 7.13 – 7.02 (m, 4H), 7.00 – 6.91 (m, 3H), 6.49 (t, $J$ = 6.8 Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 146.97, 144.70, 143.11, 142.05, 139.43, 133.45, 133.45, 133.04, 129.14, 129.05, 128.54, 128.42, 128.31, 128.27, 128.00, 124.64, 123.99, 118.91, 117.00, 114.31, 111.65; HRMS (ESI) calcd for C$_{27}$H$_{20}$ClN$_2^+$, [M+H]$^+$, 407.1310 found 407.1303.

3-(2,2-Diphenylvinyl)-2-(4-(methylsulfonyl)phenyl)imidazo[1,2-a]pyridine (3bp), 45.9 mg, 51% yield, white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.04 (d, $J$ = 8.6 Hz, 2H), 7.89 (d, $J$ = 8.6 Hz, 2H), 7.71 (d, $J$ = 6.9 Hz, 1H), 7.60 (d, $J$ = 9.1 Hz, 1H), 7.48 – 7.35 (m, 5H), 7.18 – 7.14 (m, 1H), 7.11 – 7.06 (m, 1H), 7.04 – 7.01 (m, 2H), 6.97 (s, 1H), 6.95 – 6.85 (m, 2H), 6.61 (td, $J$ = 6.8, 1.0 Hz, 1H), 3.05 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 148.4, 144.9, 141.8, 141.6, 140.1, 139.1, 138.8, 129.1, 128.7, 128.5,
128.5, 128.4, 128.2, 128.1, 127.4, 125.2, 124.0, 120.3, 117.3, 113.4, 112.2, 44.5; HRMS (ESI) calcd for C_{28}H_{23}N_{2}O_{2}S^{+}, [M+H]^{+}, 451.1475 found 451.1466.

3-(2,2-Diphenylvinyl)-2,6-dimethoxypyridine (3bq), 52.6 mg, 83% yield, white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.35 – 7.22 (m, 8H), 7.20 (d, \(J = 2.0\) Hz, 1H), 7.18 (d, \(J = 1.6\) Hz, 1H), 7.01 (s, 1H), 6.87 (d, \(J = 8.3\) Hz, 1H), 5.96 (d, \(J = 8.3\) Hz, 1H), 3.95 (s, 3H), 3.87 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 161.6, 160.6, 143.5, 141.3, 140.6, 140.5, 130.4, 128.5, 128.0, 127.6, 127.2, 127.2, 121.4, 112.0, 100.3, 53.5, 53.4; HRMS (ESI) calcd for C_{21}H_{20}NO_{2}^{+}, [M+H]^{+}, 318.1489 found 318.1496.

2-(2,2-Diphenylvinyl)-1-(naphthalen-1-yl)-1H-pyrrole (3br), 66.8 mg, 90% yield, white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.94 (d, \(J = 7.8\) Hz, 2H), 7.65 – 7.37 (m, 8H), 7.35 – 7.26 (m, 2H), 7.13 – 7.03 (m, 3H), 7.02 – 6.87 (m, 2H), 6.84 – 6.77 (m, 1H), 6.39 (s, 1H), 6.20 – 6.10 (m, 1H), 5.45 (d, \(J = 2.8\) Hz, 1H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 142.5, 141.1, 138.0, 136.2, 134.1, 132.8, 131.4, 129.9, 129.0, 128.8, 128.0, 128.0, 127.4, 127.3, 126.7, 126.6, 126.5, 125.8, 125.2, 124.3, 123.4, 116.5, 109.8, 109.1; HRMS (ESI) calcd for C_{28}H_{22}N_{2}^{+}, [M+H]^{+}, 372.1747 found 372.1751.

3-(2,2-Diphenylvinyl)imidazo[1,2-b]pyridazine (3bs), 42.8 mg, 72% yield, white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.37 (d, \(J = 3.2\) Hz, 1H), 7.88 (d, \(J = 9.0\) Hz, 1H), 7.65 (s, 1H), 7.53 – 7.41 (m, 5H), 7.39 – 7.24 (m, 5H), 7.00 (dd, \(J = 9.1, 4.4\) Hz, 1H), 6.66 (s, 1H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 142.7, 142.2, 141.4, 140.5, 138.7, 133.6, 129.4, 129.3, 128.3, 128.1, 127.7, 127.2, 127.0, 125.6, 116.2, 111.8; HRMS (ESI) calcd for C_{20}H_{16}N_{3}^{+}, [M+H]^{+}, 298.1339 found 298.1334.
3-(2,2-Diphenylvinyl)-2-phenylimidazo[1,2-a]pyrimidine (3bt), 53.7 mg, 72% yield, white solid. \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.40 (dd, \(J = 4.1, 2.0\) Hz, 1H), 8.12 (dd, \(J = 5.2, 3.3\) Hz, 2H), 7.72 (dd, \(J = 6.9, 2.0\) Hz, 1H), 7.55 – 7.33 (m, 8H), 7.24 – 7.10 (m, 5H), 7.05 (s, 1H), 6.49 (dd, \(J = 6.9, 4.1\) Hz, 1H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 149.2, 147.7, 146.5, 146.2, 141.8, 139.4, 133.9, 131.4, 129.0, 128.7, 128.6, 128.4, 128.3, 128.3, 117.0, 114.3, 107.6; HRMS (ESI) calcd for C\(_{26}\)H\(_{20}\)N\(_3\), [M+H]\(^+\), 374.1652 found 374.1649.

(2-(4-Methoxyphenyl)ethene-1,1-diyl)dibenzene (3bu), 8.6 mg, 15% yield, white solid. \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.38 – 7.18 (m, 10H), 6.95 (d, \(J = 8.7\) Hz, 2H), 6.91 (s, 1H), 6.67 (d, \(J = 8.8\) Hz, 2H), 3.74 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 158.3, 143.5, 140.6, 140.5, 130.8, 130.4, 130.0, 128.7, 128.1, 127.6, 127.4, 127.2, 113.4, 55.1.

1,3,5-Trimethoxy-2-((4-methoxyphenyl)ethynyl)benzene (10), 20.2 mg, 34% yield, white solid. \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.56 – 7.46 (m, 2H), 6.85 (d, \(J = 8.9\) Hz, 2H), 6.12 (s, 2H), 3.89 (s, 6H), 3.84 (s, 3H), 3.81 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 162.0, 161.3, 159.1, 133.0, 116.4, 113.7, 96.2, 94.6, 90.4, 80.3, 56.1, 55.4, 55.2.

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**NMR spectra**
- Chemical structures are shown with labels:
  - 3ah and 3ah'

- Spectroscopic data is presented:
  - 5.96, 3.00, 1.95, 2.00, 2.06, 1.99, 3.84, 5.96, 55.60, 55.62

- Peak assignments include:
  - 3.58 ppm
  - 7.45 ppm
  - 3.8 ppm
  - 3.08 ppm

- Additional data points and chemical shifts are indicated.
3bd

O
Me

Ph


PM

MeO

3bd


PM

MeO

3bd
\[ \text{N} \]

\[ \text{N} \]

\[ \text{Ph} \]

\[ \text{Ph} \]

\[ \text{3bm} \]

\[ \text{N} \]

\[ \text{N} \]

\[ \text{Ph} \]

\[ \text{Ph} \]

\[ \text{3bm} \]
| f1 (ppm) | 1.90 | 1.94 | 2.01 | 2.04 | 2.91 | 3.00 | 3.81 |
|----------|------|------|------|------|------|------|------|
| 3.50     | 6.85 | 6.85 | 6.85 | 6.87 | 6.87 | 6.87 | 6.87 |
| 4.00     | 7.01 | 7.02 | 7.03 | 7.04 | 7.05 | 7.06 | 7.07 |
| 4.50     | 7.08 | 7.09 | 7.10 | 7.25 | 7.27 | 7.29 | 7.37 |
| 5.00     | 7.38 | 7.38 | 7.39 | 7.42 | 7.43 | 7.44 | 7.44 |

N  N  Ph  Ph  3bn

| f1 (ppm) | 112.57 | 114.10 | 114.93 | 116.98 | 118.89 | 120.60 | 124.02 |
|----------|--------|--------|--------|--------|--------|--------|--------|
| 124.39   | 127.88 | 128.26 | 128.27 | 128.56 | 129.05 | 129.35 | 135.91 |
| 135.91   | 139.62 | 142.22 | 144.61 | 146.44 | 159.63 | 164.04 | 168.63 |
| 168.63   | 171.37 | 172.57 | 175.05 | 177.45 | 185.62 | 189.62 | 194.01 |

N  N  Ph  Ph  3bn
| f1 (ppm) | 1.00 | 0.98 | 0.99 | 0.94 | 1.95 | 3.00 | 2.17 | 8.31 | 2.03 | 5.44 | 5.45 | 6.14 | 6.15 | 6.16 | 6.39 | 7.07 | 7.07 | 7.08 | 7.30 | 7.31 | 7.32 | 7.43 | 7.45 | 7.47 | 7.53 | 7.54 | 7.56 |
|---------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|

![Chemical Structure](image1)

![Chemical Structure](image2)

![Chemical Structure](image3)
