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# Cobalt-catalyzed *ortho*-alkenylation of aromatic aldimines via chelation-assisted C–H bond activation

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ABSTRACT

An *ortho*-alkenylation reaction of an aromatic aldimine with an internal alkyne is efficiently promoted by a cobalt catalyst generated from $CoBr_2$, triarylphosphine, and $^{i}PrMgBr$. The reaction takes place under mild room-temperature conditions to afford, upon acidic hydrolysis, a variety of *ortho*-alkenylated aromatic aldehydes in moderate to excellent yields. The neighboring formyl and alkenyl groups in the product can be utilized as synthetic handles for the facile construction of indene and naphthalene carbocycles.



## 1. Introduction

Since the groundbreaking work of Murai and coworkers on the ruthenium-catalyzed *ortho*-alkylation reaction of aromatic ketones with olefins,[1] chelation-assisted C–H bond activation has been extensively practiced as a powerful strategy for the regioselective functionalization of arenes.[2] Besides the precise regiocontrol of C–H functionalization, this strategy is particularly attractive for the construction of carbo- and heterocycles through intramolecular reaction between the directing group and the newly introduced functional group (Scheme 1a). This can be achieved by two complementary approaches, that is, (1) simple C–H bond functionalization followed by appropriate functional group interconversion and intramolecular cyclization and (2) direct annulation through sequential C–H bond functionalization/intramolecular cyclization. While the latter direct approach allows straightforward construction of a single type of carbo- or heterocycle in one shot, the former stepwise approach enables, depending on the versatility of the directing group, construction of a diverse set of cyclic structures in a flexible manner.[3]

In the above context, aromatic aldimines and alkynes have proven to be useful starting materials for the construction of carbo- and heterocycles based on the direct annulation approach. Kuninobu, Takai and coworkers developed a rhenium-catalyzed annulation reaction for the synthesis of indene derivatives, which supposedly involves intramolecular nucleophilic attack of an alkenylrhenium intermediate to the C=N bond as the key cyclization step.[4,5] Fagnou and coworkers developed a rhodium-catalyzed oxidative annulation reaction leading to isoquinolines through C–N reductive elimination of an alkenylrhodium(III) intermediate.[6–8] On the other hand, aldimine has rarely been used as a directing group for simple *ortho*-alkenylation reaction with alkynes, regardless of the versatility of aldimine and its hydrolyzed form (i.e., aldehyde).[9,10] Recently, we reported on a cobalt-catalyzed *ortho*-alkenylation reaction of aromatic ketimines with alkynes under mild room-temperature conditions.[11] Upon extension of the scope of the cobalt catalysis,[12–14] we have successfully developed a new cobalt-based catalytic system that allows efficient *ortho*-alkenylation of aromatic aldimines with internal alkynes, which is reported herein. The resulting *ortho*-alkenylated aromatic aldehyde serves as a useful platform for the construction of indene and naphthalene carbocycles.

## 2. Results and discussion

Our initial study focused on the screening of reaction conditions for the alkenylation of *o*-tolualdehyde-derived aldimine **1a** with diphenylacetylene **2a** (Table 1). The catalytic system consisting of $CoBr_2$ (5 mol %), $P(3\text{-}ClC_6H_4)_3$ (10 mol %), $^{t}BuCH_2MgBr$ (50 mol %), and pyridine (80 mol %), which we previously used for the *ortho*-alkenylation of aromatic ketimines,[11] promoted the reaction at room temperature (25 °C) to only a moderate extent, affording the adduct **3aa** in 29% GC yield (entry 1). Pyridine was not a critical additive, as the product yield increased to 39% in its absence (entry 2). A serious

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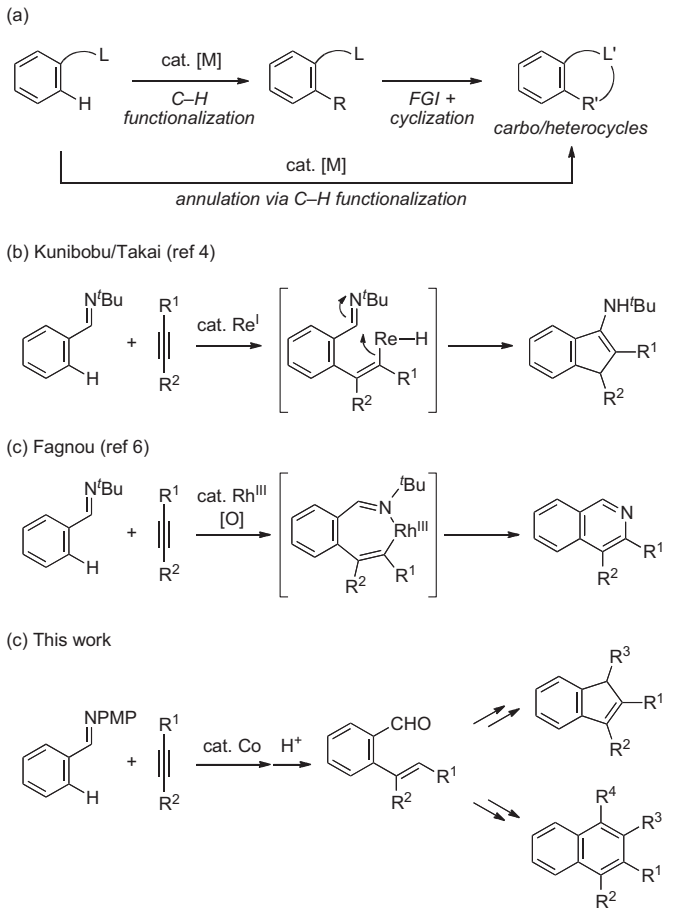
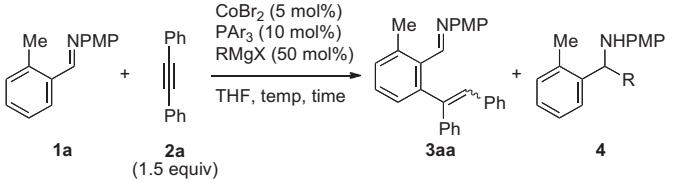



**Scheme 1.** Construction of carbo- and heterocycles via chelation-assisted C–H bond functionalization.

**Table 1**
Screening of reaction conditions[a]



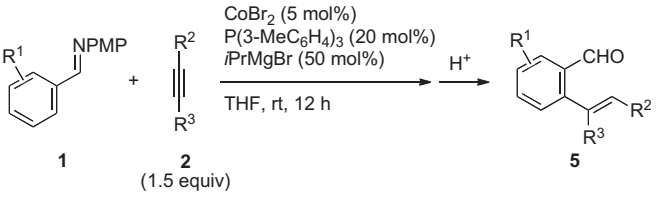

| Entry | PAr$_3$ | RMgX | Temp (°C) | Yield (%)[b] | |
|---|---|---|---|---|---|
| | | | | **3aa** (*E*/*Z*) | **4** |
| 1[c] | P(3-ClC$_6$H$_4$)$_3$ | $^{t}$BuCH$_2$MgBr | 25 | 29 (N.D.)[d] | 0 |
| 2 | P(3-ClC$_6$H$_4$)$_3$ | $^{t}$BuCH$_2$MgBr | 25 | 39 (N.D.)[d] | 0 |
| 3 | P(4-MeOC$_6$H$_4$)$_3$ | $^{t}$BuCH$_2$MgBr | 25 | 26 (62/38) | 0 |
| 4 | P(4-MeOC$_6$H$_4$)$_3$ | $^{t}$BuCH$_2$MgBr | 60 | 44 (41/59) | 0 |
| 5 | P(4-MeOC$_6$H$_4$)$_3$ | PhMgBr | 60 | 55 (25/75) | 0 |
| 6 | P(4-MeOC$_6$H$_4$)$_3$ | MeMgCl | 60 | 60 (17/83) | 6 |
| 7 | P(4-MeOC$_6$H$_4$)$_3$ | $^{n}$BuMgBr | 60 | 68 (22/78) | 32 |
| 8 | P(4-MeOC$_6$H$_4$)$_3$ | $^{i}$PrMgBr | 60 | 88 (18/82) | 12 |
| 9[e] | P(4-MeOC$_6$H$_4$)$_3$ | $^{i}$PrMgBr | 25 | 76 (79/21) | 2 |
| 10[e] | P(3-MeC$_6$H$_4$)$_3$ | $^{i}$PrMgBr | 25 | 87 (79/21) | 4 |

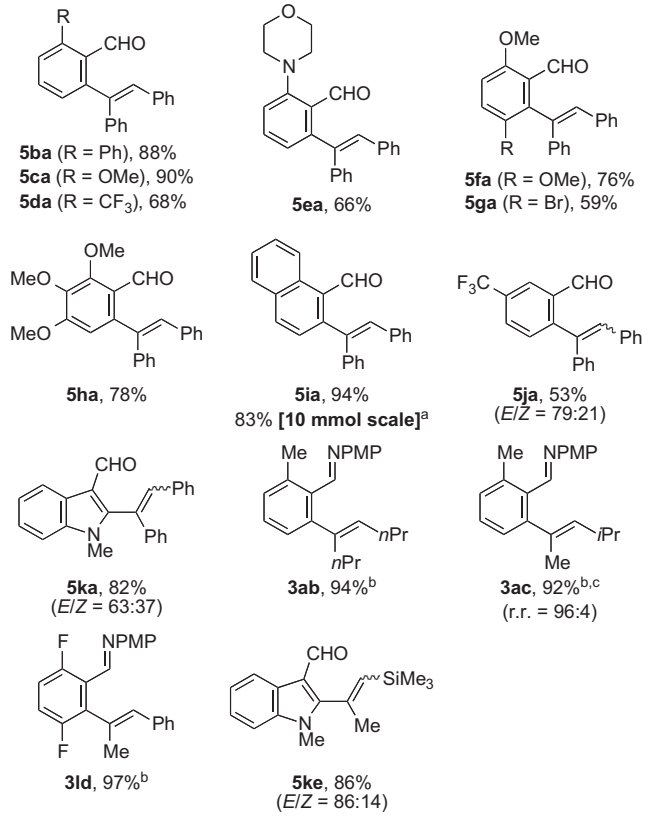
[a] Reaction was performed on a 0.3 mmol scale.
[b] Determined by GC (entries 1 and 2) or $^{1}$H NMR (entries 3–10).
[c] Pyridine (80 mol %) was added.
[d] N.D.=not determined.
[e] 20 mol % of ligand was used.

problem we observed in these reactions was a poor mass balance. Thus, for entries 1 and 2, the aldimine **1a** was recovered only in 13% and 6% yields, respectively, for unknown reasons. Throughout screening of other triarylphosphine ligands, we observed a better mass balance achieved with P(4-MeOC$_6$H$_4$)$_3$ (entry 3). While it did not particularly improve the product yield (26%), **1a** was recovered in a much better yield of 68%. We also noted that the product **3aa** consisted of a mixture of *E*/*Z* isomers (62/38) by $^{1}$H NMR analysis. Increasing the reaction temperature to 60 °C slightly improved the product yield to 44% maintaining a reasonable mass balance (48% recovery), while the *Z* isomer became the major isomer (*E*/*Z*=41/59).

Next, we screened a series of Grignard reagents including PhMgBr, MeMgCl, $^{n}$BuMgBr, and $^{i}$PrMgBr to observe their significant influences on the catalytic activity (entries 5–8). Among them, $^{i}$PrMgBr gave rise to the highest catalytic activity,[14] resulting in the formation of **3aa** in 88% yield with an *E*/*Z* ratio of 18:82 (entry 8). However, the reaction with $^{i}$PrMgBr (as well as MeMgBr and $^{n}$BuMgBr) was accompanied by a nonnegligible amount of amine **4** arising from Grignard addition to the C=N bond. This side reaction could be suppressed by lowering the temperature to 25 °C and increasing the loading of P(4-MeOC$_6$H$_4$)$_3$–20 mol %, with a slight decrease in the product yield (entry 9). With additional fine-tuning of the reaction conditions, we eventually identified the combination of CoBr$_2$ (5 mol %), P(3-MeC$_6$H$_4$)$_3$ (20 mol %), and $^{i}$PrMgBr (50 mol %) as the optimum catalytic system, affording **3aa** in 87% yield with an *E*/*Z* ratio of ca. 4:1 (entry 10). Efforts to improve the *E*/*Z* ratio were unsuccessful.

With the optimized catalytic system in hand, we explored the scope of the *ortho*-alkenylation reaction (Scheme 2). A variety of



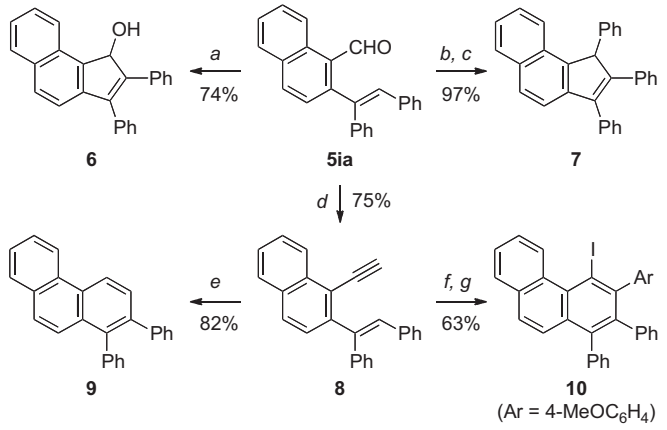

**Scheme 2.** Scope of cobalt-catalyzed *ortho*-alkenylation of aromatic aldimines. The reaction was performed on a 0.3 mmol scale unless otherwise noted. [a]The reaction was performed on a 10 mmol scale for 24 h. [b]The products were obtained without acidic hydrolysis. [c]r.r.=regioisomer ratio. The major regioisomer is shown.

*ortho*-monosubstituted aromatic aldimines smoothly participated in the reaction with diphenylacetylene to afford, upon acidic hydrolysis, the corresponding *ortho*-alkenylated aromatic aldehydes **5ba**–**5ia** in moderate to good yields. It is notable that, unlike the model substrate **1a**, these aldimine substrates afforded *cis*-alkenylation products (i.e., *E* isomers) with exclusive stereoselectivity. The reaction tolerated both electron-donating (i.e., methoxy, morpholino) and electron-withdrawing (i.e., trifluoromethyl) groups. A bromide substituent on the aldimine substrate remained untouched under the reaction conditions (see compound **5ga**), which would be useful for further synthetic transformations. The reaction of 1-naphthyl aldimine could be performed on a 10 mmol scale to afford the alkenylation product **5ia** in multigram quantities without significant decrease in the reaction efficiency. The presence of a *meta*-trifluoromethyl group directed the reaction to take place exclusively at the sterically less hindered position to afford the adduct **5ja** in 53% yield with an *E*/*Z* ratio of ca. 4:1. The C2 position of indole was also alkenylated with diphenylacetylene in 82% yield with extensive *E*/*Z* isomerization (see the product **5ka**).

It was rather curious to find that parent benzaldimine was nearly unreactive toward diphenylacetylene under the present conditions, where formation of only a trace amount of a monoalkenylation product was indicated by GC–MS analysis. At this moment, we do not have a rationale for this observation. It should also be noted that the PMP group was a much better *N*-substituent than others. Thus, the reaction of 1-naphthaldimine derivatives bearing *N*-phenyl and *N*-*tert*-butyl groups with diphenylacetylene afforded the alkenylated aldehyde **5ia** in 58% and 2% yields, respectively.

The present reaction was applicable to other alkynes such as 5-decyne, 4-methylpent-2-yne, 1-phenyl-1-propyne, and 1-trimethylsilyl-1-propyne, which afforded the adducts **3ab**, **3ac**, **3ld**, and **5ke**, respectively, in good yields. The reaction of the latter three alkynes took place with exclusive regioselectivity, where the new C–C bond was formed on the less hindered acetylenic carbon atom.[11,13b,15] Note that the products **3ab**, **3ac**, and **3ld** as well as **3aa** in Table 1 were isolated in the form of aldimine without hydrolysis, as the acidic treatment of the crude reaction mixture caused not only the desired hydrolysis but also intramolecular cyclization of the aldimine and the alkenyl moieties, resulting in a mixture of an alkenylated aldehyde and an aminoindene derivative.[11a]

As discussed in the Introduction, the *ortho* formyl/alkenyl groups in the present alkenylation product serve as versatile synthetic handles for the construction of carbocycles. As a demonstration of this idea, the adduct **5ia** was diversified into indene and naphthalene derivatives (Scheme 3). $BF_3$-mediated cyclization of **5ia** afforded indenol **6** in 74% yield. Alternatively, **5ia** was first subjected to the addition of phenyllithium followed by $BF_3$-mediated cyclization, affording indene **7** in 97% overall yield. Facile conversion of the formyl group to an ethynyl group using lithiated trimethylsilyldiazomethane provides further opportunities for carbocyclization. Thus, the enyne **8** readily participated in $PtCl_2$-catalyzed carbocyclization to afford a phenanthrene derivative **9** in 82% yield.[16] Furthermore, Sonogashira coupling of **8** with 4-iodoanisole was followed by *N*-iodosuccinimide-mediated iodocarbocyclization to afford a polyarylated iodophenanthrene **10** in 63% overall yield.[17]




**Scheme 3.** Transformation of ortho-alkenylation product. Reaction conditions: a) $BF_3{\cdot}OEt_2$ (2 equiv), $CH_2Cl_2$, 0 °C; b) PhLi (1.5 equiv), THF, −78 °C; c) $BF_3{\cdot}OEt_2$ (2 equiv), $CH_2Cl_2$, rt; d) $Me_3SiCHN_2$ (1.2 equiv), BuLi (1.2 equiv), THF, −78 °C to rt; e) $PtCl_2$ (10 mol %), toluene, 90 °C; f) $PdCl_2(PPh_3)_2$ (2 mol %), CuI (1 mol %), 4-$MeOC_6H_4I$ (2 equiv), $NEt_3$, 55 °C; g) NIS (3 equiv), $CH_2Cl_2$, 50 °C.

## 3. Conclusion

In summary, we have developed an *ortho*-alkenylation reaction of aromatic aldimines with internal alkynes promoted by a cobalt catalyst generated from $CoBr_2$, triarylphosphine, and $^i$PrMgBr. The reaction affords a variety of *ortho*-alkenylated aromatic aldehydes in moderate to excellent yields under mild room-temperature conditions. The reaction generally takes place with *cis*-stereoselectivity, while significant *E*/*Z* isomerization is observed in some cases for currently unknown reasons. The formyl and alkenyl groups in the product allow convenient preparation of indene and naphthalene carbocycles, and should also hold promise for further structural diversification. Further studies on the mechanism, development, and application of C–H alkenylation reactions are currently in progress in our laboratory.

## 4. Experimental section

### 4.1. General

All reactions dealing with air- and moisture-sensitive compounds were performed by standard Schlenk techniques in oven-dried reaction vessels under nitrogen atmosphere. Analytical thin-layer chromatography (TLC) was performed on Merck 60 F254 silica gel plates. Flash chromatography was performed using 40–63 μm silica gel (Si 60, Merck). 1H and 13C nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECA-400 (400 MHz) spectrometer, and are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm) and $CHCl_3$ (77 ppm), respectively. Gas chromatographic (GC) analysis was performed on a Shimadzu GC-2010 system equipped with an FID detector and a capillary column, DB-5 (Agilent J&W, 0.25 mm i.d.×30 m, 0.25 μm film thickness). High-resolution mass spectra (HRMS) were recorded with a Q-Tof Premier LC HR mass spectrometer. Unless otherwise noted, commercial reagents were purchased from Aldrich, Alfa Aesar, and other commercial suppliers and were used as received. Cobalt(II) bromide (99%) were purchased from Aldrich. THF was distilled over Na/benzophenone before use.

### 4.2. General procedure for preparation of aromatic aldimine

To a solution of aromatic aldehyde (50 mmol) in EtOH (100 mL) was added *p*-anisidine (60 mmol) at room temperature. After stirring for 12 h, the reaction mixture was concentrated under reduced pressure. The crude product was purified by recrystallization or silica gel chromatography. Spectral data of **1a**,[18] **1b**,[19] **1h**,[20] **1i**,[21] and **1k**[22] showed good agreement with the literature data.

*4.2.1. (E)-4-Methoxy-N-(2-methoxybenzylidene)aniline (**1c**).* Purified by recrystallization from hexane/$CH_2Cl_2$. Yellow solid (58%); Mp=43–44 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.83 (s, 3H), 3.90 (s, 3H), 6.91–6.96 (m, 3H), 7.03 (t, *J*=7.8 Hz, 1H), 7.24 (app. d,

$J$=9.1 Hz, 2H), 7.42 (td, $J$=8.0 Hz, 1.8 Hz, 1H), 8.14 (dd, $J$=7.8, 1.8 Hz, 1H), 8.94 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 55.6, 55.7, 111.2, 114.4 (2C), 121.0, 122.5 (2C), 125.1, 127.5, 132.5, 145.8, 154.6, 158.2, 159.5; HRMS (ESI+) Calcd for $C_{15}H_{16}NO_2$ $[M+H]^+$ 242.1181, found 242.1184.

*4.2.2. (E)-4-Methoxy-N-(2-(trifluoromethyl)benzylidene)aniline (**1d**).* Purified by silica gel chromatography (eluent: hexane/EtOAc/$NEt_3$=20:1:1). Yellow solid (96%); Mp=55–56 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.84 (s, 3H), 6.96 (app. d, $J$=8.7 Hz, 2H), 7.27 (app. d, $J$=8.7 Hz, 2H), 7.54 (t, $J$=8.2 Hz, 1H), 7.65 (t, $J$=7.3 Hz, 1H), 7.73 (d, $J$=8.2 Hz, 1H), 8.44 (d, $J$=7.8 Hz, 1H), 8.84–8.85 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 55.7, 114.7 (2C), 122.7 (2C), 124.5 (q, $^1J_{C-F}$=277.8 Hz), 125.9 (q, $^3J_{C-F}$=5.7 Hz), 128.4, 129.6 (q, $^2J_{C-F}$=31.6 Hz), 130.5, 132.2, 134.6, 144.6, 154.2, 159.0; HRMS (ESI+) Calcd for $C_{15}H_{13}NOF_3$ $[M+H]^+$ 280.0949, found 280.0950.

*4.2.3. (E)-4-Methoxy-N-(2-morpholinobenzylidene)aniline (**1e**).* Purified by recrystallization from hexane/$CH_2Cl_2$. Yellow solid (80%); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.02–3.04 (m, 4H), 3.85 (s, 3H), 3.86–3.89 (m, 4H), 6.95 (app. d, $J$=9.2 Hz, 2H), 7.12 (dd, $J$=8.2, 0.9 Hz, 1H), 7.17 (t, $J$=7.3 Hz, 1H), 7.23 (app. d, $J$=11.9 Hz, 2H), 7.41–7.46 (m, 1H), 8.09 (dd, $J$=7.8, 1.6 Hz, 1H), 8.87 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 53.7, 55.5, 67.1, 114.4, 118.8, 122.2, 123.7, 128.3, 129.8, 131.7, 145.4, 153.3, 156.3, 158.2; HRMS (ESI+) Calcd for $C_{18}H_{21}N_2O_2$ $[M+H]^+$ 297.1603, found 297.1602.

*4.2.4. (E)-N-(2,5-Dimethoxybenzylidene)-4-methoxyaniline (**1f**).* Purified by recrystallization from hexane/EtOAc/$CHCl_3$. Yellow solid (78%); Mp=76–77 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.83 (s, 3H), 3.86 (s, 3H), 3.86 (s, 3H), 6.88–7.01 (m, 5H), 7.24 (s, 3H), 7.68 (d, $J$=3.2 Hz, 1H), 8.90 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 55.6, 56.0, 56.4, 110.4, 113.0, 114.5 (2C), 119.6, 122.6 (2C), 125.6, 145.7, 154.0, 154.2, 154.5, 158.3; HRMS (ESI+) Calcd for $C_{16}H_{18}NO_3$ $[M+H]^+$ 272.1287, found 272.1284.

*4.2.5. (E)-N-(5-Bromo-2-methoxybenzylidene)-4-methoxyaniline (**1g**).* Purified by recrystallization from hexane/EtOAc/$CHCl_3$. Yellow solid (59%); Mp=100–101 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.84 (s, 3H), 3.89 (s, 3H), 6.83 (d, $J$=8.7 Hz, 1H), 6.93 (app. d, $J$=9.2, 2H), 7.24–7.26 (m, 2H), 7.50 (dd, $J$=9.2, 2.7 Hz, 1H), 8.26 (d, $J$=2.7 Hz, 1H), 8.84 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 55.7, 56.0, 113.1, 113.8, 114.5 (2C), 122.6 (2C), 126.9, 130.0, 134.7, 145.1, 152.8, 158.4, 158.6; HRMS (ESI+) Calcd for $C_{15}H_{15}NO_2Br$ $[M+H]^+$ 322.0286, found 322.0286.

*4.2.6. (E)-4-Methoxy-N-(3-(trifluoromethyl)benzylidene)aniline (**1j**).* Purified by silica gel chromatography (eluent: hexane/EtOAc/$NEt_3$=20:1:1). Dark brown solid (98%); Mp=42–43 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.84 (s, 3H), 6.94 (app. d, $J$=8.7 Hz, 2H), 7.26 (app. d, $J$=8.7 Hz, 2H), 7.58 (t, $J$=8.2 Hz, 1H), 7.70 (d, $J$=7.8 Hz, 1H), 8.05 (d, $J$=7.8 Hz, 1H), 8.17 (s, 1H), 8.52 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 55.7, 114.7 (2C), 122.6 (2C), 124.2 (q, $^1J_{C-F}$=274.0 Hz), 125.3 (q, $^3J_{C-F}$=3.8 Hz), 127.5 (q, $^3J_{C-F}$=3.8 Hz), 129.4, 131.5 (q, $^2J_{C-F}$=32.6 Hz), 131.9, 137.4, 144.3, 156.4, 158.9; HRMS (ESI+) Calcd for $C_{15}H_{13}NOF_3$ $[M+H]^+$ 280.0949, found 280.0952.

*4.2.7. (E)-N-(2,5-Difluorobenzylidene)-4-methoxyaniline (**1l**).* Purified by recrystallization from hexane. Yellow solid (70%); Mp=66–67 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.84 (s, 3H), 6.94 (app. d, $J$=9.2 Hz, 2H), 7.08–7.12 (m, 2H), 7.27 (app. d, $J$=8.7 Hz, 2H), 7.85–7.89 (m, 1H), 8.74 (d, $J$=2.3 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 55.7, 113.6 (dd, $^2J_{C-F}$=24.9 Hz), 114.6 (2C), 117.2 (dd, $^2J_{C-F}$, $^3J_{C-F}$=24.9, 8.6 Hz), 119.2 (dd, $^2J_{C-F}$, $^3J_{C-F}$=24.9, 8.6 Hz), 122.7 (2C), 125.6–125.8 (m, 1C), 114.3, 149.9, 158.8 (q, $^1J_{C-F}$=248.1 Hz), 159.07, 159.09 (d, $^1J_{C-F}$=244.3 Hz); HRMS (ESI+) Calcd for $C_{14}H_{12}NOF_2$ $[M+H]^+$ 248.0887, found 248.0888.

### 4.3. General procedure for cobalt-catalyzed *ortho*-alkenylation of aromatic aldimines

In a Schlenk tube equipped with a stirrer bar were placed aldimine (0.3 mmol), P(3-$MeC_6H_4$)$_3$ (18.3 mg, 0.06 mmol, 20 mol %), $CoBr_2$ (0.075 M solution in THF, 0.2 mL, 0.015 mmol, 5 mol %), and THF (0.21 mL). To the mixture was added a THF solution of $^i$PrMgBr (1.03 M, 0.14 mL, 0.15 mmol) dropwise at 0 °C. After stirring for 30 min, diphenylacetylene (0.23 M solution in THF, 0.2 mL, 0.45 mmol) was added. The resulting mixture was allowed to room temperature and stirred for 12 h, followed by dilution with THF (1 mL) and quenching with water (0.5 mL) and 1 N HCl (0.5 mL). The resulting mixture was stirred for 1 h and then extracted with EtOAc (4 mL×3). The combined organic layer was dried over $Na_2SO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel chromatography to afford the desired *ortho*-alkenylated aryl aldehyde. Characterization data for the compound **5ka** have been reported in the literature.[9b]

*4.3.1. (E)-N-(2-((E)-1,2-Diphenylvinyl)benzylidene)-4-methoxyaniline (**3aa**).* The reaction mixture was not treated with aq HCl (i.e., imine was not hydrolyzed). Purified by silica gel chromatography (eluent: hexane/EtOAc/$NEt_3$=100:1:2). Red oil (78%) consisting of a 79:21 mixture of alkene *E*/*Z* isomers as determined by $^1$H NMR analysis; $R_f$ 0.41 (hexane/EtOAc=10:1); $^1$H NMR (400 MHz, $CDCl_3$, *E*-isomer): $\delta$ 2.71 (s, 3H), 3.75 (s, 3H), 6.72–6.77 (m, 4H), 6.99 (d, $J$=6.4 Hz, 2H), 7.05–713 (m, 5H), 7.22–7.34 (m, 7H), 8.50 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, *E*-isomer): $\delta$ 22.3, 55.6, 114.2 (2C), 121.9 (2C), 127.1 (2C), 127.3, 127.7, 128.3 (2C), 128.6 (2C), 128.9, 129.4, 129.5 (2C), 130.1, 131.4, 133.6, 137.1, 139.4, 140.9, 142.3, 143.1, 146.1, 158.0, 159.6; HRMS (ESI+) Calcd for $C_{29}H_{26}NO$ $[M+H]^+$ 404.2014, found 404.2014.

*4.3.2. 3-(1,2-Diphenylvinyl)-[1,1′-biphenyl]-2-carbaldehyde (**5ba**).* Purified by silica gel chromatography (eluent: hexane/EtOAc=25:1). Red oil (88%); $R_f$ 0.21 (hexane/EtOAc=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 6.95–6.97 (m, 2H), 7.07–7.15 (m, 4H), 7.22–7.43 (m, 12H), 7.56 (t, $J$=7.8 Hz, 1H), 9.78 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 127.1 (3C), 127.6, 128.0, 128.2, 128.39 (2C), 128.42 (2C), 128.8 (2C), 129.4 (2C), 129.9 (2C), 130.7, 131.4, 132.7, 133.8, 137.1, 139.0, 141.2, 142.1, 142.6, 146.0, 192.5; HRMS (ESI+) Calcd for $C_{27}H_{21}O$ $[M+H]^+$ 361.1592, found 361.1590.

*4.3.3. (E)-2-(1,2-Diphenylvinyl)-6-methoxybenzaldehyde (**5ca**).* Purified by silica gel chromatography (eluent: hexane/EtOAc=10:1). Red solid (90%); Mp=127–128 °C; $R_f$ 0.13 (hexane/EtOAc=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.95 (s, 3H), 6.82 (d, $J$=7.8 Hz, 1H), 6.96–7.07 (m, 3H), 7.08–7.14 (m, 4H), 7.22–7.29 (m, 5H), 7.49 (t, $J$=8.2 Hz, 1H), 10.3 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 56.1, 111.3, 124.0, 124.3, 126.9 (2C), 127.2, 127.7, 128.3 (2C), 128.5 (2C), 128.9, 129.5 (2C), 135.4, 137.1, 140.6, 142.5, 144.5, 162.0, 190.5; HRMS (ESI+) Calcd for $C_{22}H_{19}O_2$ $[M+H]^+$ 315.1385, found 315.1389.

*4.3.4. (E)-2-(1,2-Diphenylvinyl)-6-(trifluoromethyl)benzaldehyde (**5da**).* Purified by silica gel chromatography (eluent: hexane/EtOAc=25:1) Red solid (68%); Mp=78–79 °C; $R_f$ 0.12 (hexane/EtOAc=25:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 6.88–6.90 (m, 2H), 7.11–7.15 (m, 4H), 7.23–7.34 (m, 4H), 7.46 (d, $J$=7.8 Hz, 1H), 7.61 (t, $J$=7.8 Hz, 1H), 7.79 (d, $J$=7.8 Hz, 1H), 10.7 (q, $J$=2.3 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 126.2 (q, $^3J_{C-F}$=5.8 Hz), 127.2 (2C), 127.7, 128.2, 128.5 (2C), 128.8 (2C), 129.5 (2C), 130.3 (q, $^2J_{C-F}$=32.5 Hz), 130.5, 132.5, 134.9, 136.1, 136.4, 139.2, 142.0, 143.6, 190.7. The signal

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of $CF_3$ carbon could not be identified because of signal overlapping of other peaks; HRMS (ESI+) Calcd for $C_{22}H_{16}OF_3$ $[M+H]^+$ 353.1153, found 353.1151.

*4.3.5. (E)-2-(1,2-Diphenylvinyl)-6-morpholinobenzaldehyde (**5ea**).* Purified by silica gel chromatography (eluent: hexane/EtOAc=25:1). Red oil (66%); $R_f$ 0.17 (hexane/EtOAc=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.02–3.14 (m, 4H), 3.84–3.91 (m, 4H), 6.91–6.93 (m, 3H), 7.07–7.17 (m, 5H), 7.23–7.35 (m, 5H), 7.50 (t, $J$=7.8 Hz, 1H), 10.2 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 53.9, 67.2, 118.2, 125.7, 127.0 (2C). 127.2, 127.5, 127.8, 128.3 (2C), 128.6 (2C), 129.5 (2C), 129.7, 134.8, 137.0, 140.5, 142.7, 145.9, 154.9, 190.7; HRMS (ESI+) Calcd for $C_{25}H_{24}NO_2$ $[M+H]^+$ 370.1807, found 370.1805.

*4.3.6. (E)-2-(1,2-Diphenylvinyl)-3,6-dimethoxybenzaldehyde (**5fa**).* Purified by silica gel chromatography (eluent: hexane/EtOAc=15:85). Red solid (76%); Mp=118–119; $R_f$ 0.10 (hexane/EtOAc=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.55 (s, 3H), 3.89 (s, 3H), 6.96–7.01 (m, 3H), 7.08–7.15 (m, 4H), 7.19 (s, 1H), 7.23–7.35 (m, 5H), 10.2 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 56.4, 56.9, 112.2, 118.4, 124.3, 126.5 (2C), 127.2, 127.6, 128.3 (2C), 128.5 (2C), 128.8 (2C), 130.3, 133.1, 137.3, 142.0, 151.3, 155.5, 1991.1; HRMS (ESI+) Calcd for $C_{23}H_{21}O_3$ $[M+H]^+$ 345.1491, found 345.1488.

*4.3.7. (E)-3-Bromo-2-(1,2-diphenylvinyl)-6-methoxybenzaldehyde (**5ga**).* Purified by silica gel chromatography (eluent: hexane/EtOAc=10:1). Yellow solid (59%) Mp=138–139 °C; $R_f$ 0.07 (hexane/EtOAc=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.92 (s, 3H), 6.93–6.97 (m, 3H), 7.12–7.15 (m, 3H), 7.21 (s, 1H), 7.25–7.32 (m, 5H), 7.78 (d, $J$=9.2 Hz, 2H), 10.1 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 56.3, 113.2, 116.6, 125.7, 126.7 (2C), 127.6, 127.9, 128.5 (2C), 128.7 (2C), 128.9 (2C), 130.6, 136.6, 137.7, 139.0, 140.5, 144.0, 160.5, 190.2; HRMS (ESI+) Calcd for $C_{22}H_{18}O_2Br$ $[M+H]^+$ 393.0490, found 393.0487.

*4.3.8. (E)-6-(1,2-Diphenylvinyl)-2,3,4-trimethoxybenzaldehyde (**5ha**).* Purified by silica gel chromatography (eluent: hexane/EtOAc=9:1). Red oil (78%); $R_f$ 0.10 (hexane/EtOAc=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.76 (s, 3H), 3.95 (s, 3H), 3.97 (s, 3H), 6.50 (s, 1H), 6.93–6.96 (m, 2H), 7.09–7.13 (m, 4H), 7.26–7.34 (m, 5H), 10.1 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 56.4, 61.4, 62.6, 110.6, 122.5, 126.8 (2C), 127.3, 127.9, 128.4 (2C), 128.6 (2C), 129.2, 129.4 (2C), 136.9, 140.1, 140.2, 142.0, 142.2, 157.0, 158.4, 189.3; HRMS (ESI+) Calcd for $C_{24}H_{23}O_4$ $[M+H]^+$ 375.1596, found 375.1599.

*4.3.9. (E)-2-(1,2-Diphenylvinyl)-1-naphthaldehyde (**5ia**).* Purified by silica gel chromatography (eluent: hexane/EtOAc=50:1). Red solid (94%) Mp=130–131 °C; $R_f$ 0.32 (hexane/EtOAc=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 6.92–6.94 (m, 2H), 7.03–7.07 (m, 3H), 7.27–7.39 (m, 7H), 7.56–7.61 (m, 1H), 7.67 (t, $J$=8.2 Hz, 1H), 7.91 (d, $J$=8.2 Hz), 8.08 (d, $J$=8.7 Hz, 1H), 9.25 (d, $J$=8.7 Hz), 10.5 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 126.3, 127.1 (2C), 127.2, 127.7, 128.2, 128.6 (3C), 128.9 (2C), 129.0, 129.1, 129.4, 129.6 (2C), 131.1, 131.5, 133.6, 135.6, 136.3, 138.7, 142.7, 147.2, 194.5; HRMS (ESI+) Calcd for $C_{25}H_{19}O$ $[M+H]^+$ 335.1436, found 335.1432.

*4.3.10. (E)-2-(1,2-Diphenylvinyl)-5-(trifluoromethyl)benzaldehyde (**5ja**).* Purified by silica gel chromatography (eluent: hexane/EtOAc=50:1). Orange oil (53%) consisting of ca. 79:21 mixture of $E/Z$ isomers as determined by $^1$H NMR analysis; $R_f$ 0.24 (hexane/EtOAc=10:1); $^1$H NMR (400 MHz, $CDCl_3$, $E$-isomer): $\delta$ 6.62 (s, 1H), 7.13–7.38 (m, 11H), 7.43 (d, $J$=8.2 Hz), 7.75 (dd, $J$=8.2 Hz, 2.3 Hz, 1H), 10.3 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, $E$-isomer): $\delta$ 125.2 (q, $^3J_{C-F}$=3.8 Hz), 128.2, 128.4 (3C), 129.0 (2C), 129.7 (2C), 130.1 (2C), 131.8, 135.3, 135.9, 136.0, 137.4, 139.6, 151.0, 190.7; The signals of the $CF_3$ carbon and the aromatic carbon next to $CF_3$ could not be identified because of signal overlapping with other peaks; HRMS (ESI+) Calcd for $C_{22}H_{16}OF_3$ $[M+H]^+$ 353.1153, found 353.1160.

*4.3.11. (E)-4-Methoxy-N-(2-methyl-6-((E)-oct-4-en-4-yl)benzylidene)aniline (**3ab**).* Purified by silica gel chromatography (eluent: hexane/EtOAc/$NEt_3$=100:0.5:2.5). Yellow oil (94%); $R_f$ 0.40 (hexane/EtOAc=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.86 (t, $J$=7.3 Hz, 3H), 0.89 (t, $J$=7.3 Hz, 3H), 1.28–1.34 (m, 2H), 1.37–1.43 (m, 2H), 2.16 (q, $J$=7.3 Hz, 2H), 2.33–2.37 (m, 2H), 2.66 (s, 3H), 6.92 (app. d, $J$=9.2 Hz, 2H), 7.04 (d, $J$=7.3 Hz, 1H), 7.13–7.16 (m, 3H), 7.20–7.25 (m, 1H), 8.64 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 14.1, 14.4, 21.6, 22.1, 23.2, 30.6, 35.0, 55.7, 114.5 (2C), 122.1 (2C), 127.0, 129.0, 130.1, 132.9, 133.0, 138.2, 139.9, 146.0, 147.0, 158.2, 160.7; HRMS (ESI+) Calcd for $C_{23}H_{30}NO$ $[M+H]^+$ 336.2327, found 336.2326.

*4.3.12. (E)-4-Methoxy-N-(2-methyl-6-((E)-4-methylpent-2-en-2-yl) benzylidene)aniline (**3ac**).* Purified by silica gel chromatography (eluent: hexane/$NEt_3$=100:2.5). Yellow oil (97%); $R_f$ 0.43 (hexane/EtOAc=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.97 (d, $J$=6.4 Hz, 6H), 1.96 (d, $J$=1.4 Hz, 3H), 2.62–2.668 (m, 4H), 3.82 (s, 3H), 5.19 (dd, $J$=9.2 Hz, 1.4 Hz, 1H), 6.91–6.94 (m, 4H), 7.06–7.19 (m, 4H), 7.22–7.25 (m, 1H), 8.61 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 19.1, 22.0, 23.1 (2C), 28.0, 55.7, 114.5 (2C), 122.1 (2C), 126.4, 129.2, 130.0, 132.6, 1332.7, 138.3, 140.4, 145.9, 147.9, 158.2, 160.4; HRMS (ESI+) Calcd for $C_{21}H_{26}NO$ $[M+H]^+$ 308.2014, found 308.2016.

*4.3.13. (E)-N-(3,6-Difluoro-2-((E)-1-phenylprop-1-en-2-yl)benzylidene)-4-methoxyaniline (**3ld**).* Purified by silica gel chromatography (eluent: hexane/EtOAc=25:1). Red oil (92%) consisting of 96:4 mixture of regioisomers as determined by $^1$H NMR analysis; $R_f$ 0.22 (hexane/EtOAc=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.23 (d, $J$=0.9 Hz, 3H), 3.80 (s, 3H), 6.44 (d, $J$=0.9 Hz, 1H), 6.89 (app. d, $J$=9.2 Hz, 2H), 7.05–7.12 (m, 2H), 7.18 (app. d, $J$=9.2 Hz, 2H), 7.24–7.39 (m, 6H), 8.59 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 20.0, 55.7, 114.6 (2C), 115.8 (dd, $J$=25.9 Hz, 9.6 Hz), 118.1 (dd, $J$=25.9 Hz, 9.6 Hz), 122.4 (2C), 124.0 (dd, $J$=10.5 Hz, 3.8 Hz), 127.2, 128.5 (2C), 129.2 (2C), 131.1, 132.6, 134.9 (d, $J$=19.2 Hz), 137.2, 145.2, 152.8, 155.9 (dd, $J$=240.4 Hz), 157.8 (dd, $J$=258.7 Hz, 8.6 Hz), 158.8; HRMS (ESI+) Calcd for $C_{23}H_{18}NOF_2$ $[M+H]^+$ 362.1356, found 362.1362.

*4.3.14. (E)-1-Methyl-2-(1-(trimethylsilyl)prop-1-en-2-yl)-1H-indole-3-carbaldehyde (**5ke**).* Purified by silica gel chromatography (eluent: hexane/EtOAc=10:1). White solid (86%) consisting of ca. 86:14 mixture of $E/Z$ isomers as determined by $^1$H NMR analysis; Mp=89–91 °C; $R_f$ 0.20 (hexane/EtOAc=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.31 (s, 9H), 2.25 (d, $J$=0.9 Hz, 3H), 3.70 (s, 3H), 5.94 (d, $J$=0.9 Hz, 1H), 7.29–7.36 (m, 3H), 8.37–8.39 (m, 1H), 9.93 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ −0.2 (3C), 23.3, 30.7, 109.7, 113.7, 122.2, 123.2, 123.9, 125.3, 137.0, 140.8, 140.9, 156.9, 186.0; HRMS (ESI+) Calcd for $C_{16}H_{22}NOSi$ $[M+H]^+$ 272.1471, found 272.1467.

### 4.4. Transformation of *ortho*-alkenylated aromatic aldehyde 5ia

*4.4.1. 2,3-Diphenyl-1H-cyclopenta[a]naphthalen-1-ol (**6**).* To solution of **5ia** (16.7 mg, 0.05 mol) in $CH_2Cl_2$ was added $BF_3{\cdot}OEt_2$ (12.7 μL, 0.10 mmol) at 0 °C. After stirring for 10 min, the reaction mixture was quenched with water. The aqueous layer was extracted with EtOAc (1 mL×3). The combined organic layer was dried over $Na_2SO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (eluent: hexane/EtOAc=10:1) to afford the title compound as a white solid (12.8 mg, 74%); Mp=206–207 °C; $R_f$ 0.12 (hexane/EtOAc=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ f6.07 (d, $J$=9.2 Hz), 7.23–7.31 (m, 4H), 7.35 (d, $J$=8.2 Hz, 1H), 7.40–7.48 (m, 8H), 7.57 (t, $J$=7.8 Hz, 1H), 7.82

(d, $J$=8.2 Hz, 1H), 7.88 (d, $J$=8.2 Hz, 1H), 8.40 (d, $J$=8.2 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 77.5, 119.6, 124.4, 125.5, 127.1, 127.5, 128.1, 128.6 (2C), 129.0, 129.2 (2C), 129.4 (2C), 129.5 (2C), 129.7, 130.0, 132.9, 134.1, 135.1, 139.3, 140.0, 141.6, 144.2; HRMS (ESI+) Calcd for $C_{25}H_{19}O$ $[M+H]^+$ 335.1436, found 335.1437.

*4.4.2. (E)-(2-(1,2-Diphenylvinyl)naphthalen-1-yl)(phenyl)methanol (**7′**).* To a solution of bromobenzene (23.6 mg, 0.15 mmol) in THF (1.0 mL) was added $^n$BuLi (1.6 M in hexane, 94 μL, 0.15 mmol) at −78 °C. After stirring for 20 min, aldehyde **5ia** (33.4 mg, 0.098 mol) was added. The reaction mixture was stirred for 90 min and then quenched with water while being allowed to room temperature. The aqueous layer was extracted with EtOAc (1 mL×3), and the combined organic layer was dried over $Na_2SO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (eluent: hexane/EtOAc=10:1) to afford the title compound (37.2 mg, 98%). This compound existed as a 55:45 mixture of rotamers as judged from $^1$H NMR analysis. Mp=83–85 °C; $R_f$ 0.24 (hexane/EtOAc=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.46–1.48 (m, 1H, major), 1.94–1.95 (m, 1H, minor), 6.41 (d, $J$=4.1 Hz, 1H, minor), 6.53 (d, $J$=3.2 Hz, 1H, major), 7.04–7.95 (m, 21H, major, 20H, minor), 8.02 (d, $J$=8.7 Hz, 1H, minor); $^{13}$C NMR (100 MHz, $CDCl_3$): peaks of the major and the minor isomers could not be distinguished. $\delta$ 72.6, 73.0, 125.87, 125.93, 125.96, 126.01, 126.4, 126.5, 126.7, 127.4, 127.5, 127.6, 127.8, 128.0, 128.07, 128.15, 128.23, 128.4, 128.62, 128.64, 128.80, 128.84, 129.1, 129.2, 129.5, 129.8, 129.9, 130.0, 131.9, 132.1, 134.6, 134.9, 136.1, 136.78, 137.15, 137.9, 138.5, 141.2, 141.5, 142.2, 143.3, 143.5, 143.6; HRMS (ESI+) Calcd for $C_{31}H_{25}O$ $[M+H]^+$ 413.1905, found 413.1905.

*4.4.3. 1,2,3-Triphenyl-1H-cyclopenta[a]naphthalene (**7**).* To a solution of **7′** (19.3 mg, 0.05 mmol) in $CH_2Cl_2$ (0.5 mL) was added $BF_3\cdot OEt_2$ (12.7 μL, 0.10 mmol) at 0 °C then the reaction mixture was warmed to room temperature. After stirring for 15 min, the reaction mixture was quenched with water. The aqueous layer was extracted with $Et_2O$ (1 mL×3). The combined organic layer was dried over $Na_2SO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (eluent=hexane/$CH_2Cl_2$=95:5 to 90:10) to afford the title compound as a white solid (18.2 mg, 99%), (two steps, 97%); Mp=86–88 °C; $R_f$ 0.40 (hexane/EtOAc=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 5.41 (s, 1H), 7.06–7.13 (m, 6H), 7.16–7.17 (m, 4H), 7.29 (m, 8H), 7.53 (d, $J$=8.7 Hz, 1H), 7.78 (d, $J$=7.8 Hz, 1H), 7.84 (t, $J$=7.8 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 58.2, 119.7, 123.6, 124.8, 126.4, 126.7, 126.8, 127.5, 127.9 (2C), 128.3, 128.6 (2C), 128.8 (4C), 129.0 (2C), 129.56 (2C), 129.62, 129.8 (2C), 132.5, 135.6, 139.7, 140.2, 143.2, 143.7, 148.1; HRMS (ESI+) Calcd for $C_{31}H_{22}$ $[M+H]^+$ 395.1800, found 395.1804.

*4.4.4. (E)-2-(1,2-Diphenylvinyl)-1-ethynylnaphthalene (**8**).* To a solution of diisopropylamine (168 μL, 1.2 mmol) was added *n*-BuLi (1.6 M in hexane, 750 μL, 1.2 mmol) at −78 °C. The resulting mixture was allowed to room temperature, stirred for 15 min, and then cooled again to −78 °C, followed by the addition of trimethylsilyldiazomethane (2.0 M in hexane, 600 μL, 1.2 mmol). After stirring for 45 min, aldehyde **5ia** (334 mg, 1.0 mol) was added at the same temperature. The reaction mixture was stirred for 1 h, warmed to room temperature, and then stirred for additional 10 h before quenching with water. The aqueous layer was extracted with $Et_2O$ (30 mL×3), and the combined organic layer was washed with brine, dried over $Na_2SO_4$, and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (eluent: hexane/EtOAc=50:1) to afford the title compound as a white solid (250 mg, 75%); Mp=83–85 °C; $R_f$ 0.29 (hexane/EtOAc=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.30 (s, 1H), 6.99–7.07 (m, 5H), 7.17 (s, 1H), 7.24–7.34 (m, 6H), 7.52–7.60 (m, 2H), 7.82–7.88 (m, 2H), 8.38 (d, $J$=7.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 80.4, 86.1, 120.0, 126.6, 126.7, 127.2, 127.3 (3C), 127.6, 128.3 (2C), 128.4 (4C), 129.4 (2C), 129.6, 129.9, 132.5, 134.3, 137.4, 141.3, 142.6, 142.9; HRMS (ESI+) Calcd for $C_{26}H_{18}$ $[M+H]^+$ 331.1487, found 331.1487.

*4.4.5. 1,2-Diphenylphenanthreneaphthalene (**9**).* A mixture of **6** (33.1 mg, 0.1 mmol) and $PtCl_2$ (2.9 mg, 0.01 mmol) in toluene (1.0 mL) was stirred at 90 °C for 24 h. The reaction was cooled to room temperature and then quenched with water. The aqueous layer was extracted with EtOAc (1 mL×3), and the combined organic layer was dried over $Na_2SO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (eluent: hexane) to afford the title compound as a red solid (27.0 mg, 82% yield). Mp=148–149 °C; $R_f$ 0.28 (hexane/EtOAc=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.17–7.21 (m, 7H), 7.27–7.32 (m, 3H), 7.57–7.68 (m, 4H), 7.72 (d, $J$=8.7 Hz, 1H), 7.85 (d, $J$=7.8 Hz, 1H), 8.76 (t, $J$=8.7 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 122.1, 122.8, 125.2, 126.2, 126.66 (2C), 126.71, 127.0, 127.6 (2C), 127.8 (2C), 128.4, 127.5, 129.6, 130.0 (2C), 130.1 (2C), 130.8, 131.5, 131.6, 138.5, 139.3, 139.3, 141.8; HRMS (ESI+) Calcd for $C_{26}H_{19}$ $[M+H]^+$ 331.1487, found 331.1487.

*4.4.6. (E)-2-(1,2-Diphenylvinyl)-1-((4-methoxyphenyl)ethynyl)naphthalene (**10′**).* To a solution of **8** (332 mg, 1.0 mmol) and 4-iodoanisole (470 mg, 2.0 mmol) in $NEt_3$ (16 mL) were added $Pd(PPh_3)_2Cl_2$ (14.0 mg, 0.02 mmol) and CuI (2.2 mg, 0.01 mmol). The resulting mixture was stirred at 55 °C for 3 h, followed by quenching with water at room temperature. The aqueous layer was extracted with EtOAc (5 mL×3), and the combined organic layer was dried over $Na_2SO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (eluent: hexane/EtOAc=25:1) to afford the title compound as a white solid (304 mg, 70% yield). Mp=65–66 °C; $R_f$ 0.23 (hexane/EtOAc=10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.78 (s, 3H), 6.77 (d, $J$=8.7 Hz, 2H), 7.02–7.06 (m, 5H), 7.17–7.33 (m, 7H), 7.38 (d, $J$=8.3 Hz, 2H), 7.51–7.59 (m, 2H), 7.76 (d, $J$=8.7 Hz, 1H), 7.85 (d, $J$=7.8 Hz, 1H), 8.45 (d, $J$=8.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 54.5, 85.5, 98.9, 114.0 (2C), 115.8, 121.5, 126.6, 126.8, 127.0, 127.1, 127.4 (2C), 127.5, 128.2 (2C), 128.39, 128.43 (2C), 128.5, 128.8, 129.6 (2C), 129.8, 132.7, 133.2 (2C), 134.0, 137.5, 141.6, 142.1, 143.1, 159.7; HRMS (ESI+) Calcd for $C_{33}H_{25}O$ $[M+H]^+$ 437.1905, found 437.1907.

*4.4.7. 4-Iodo-3-(4-methoxyphenyl)-1,2-diphenylphenanthrene (**10**).* To a solution of **10′** (14 mg, 0.03 mmol) in $CH_2Cl_2$ was added NIS (21 mg, 0.09 mmol) at room temperature. The reaction mixture was stirred at 50 °C for 12 h, followed by quenching with water at room temperature. The aqueous layer was extracted with EtOAc (1 mL×3), and the combined organic layer was dried over $Na_2SO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (eluent: hexane) to afford the title compound as a white solid (15.2 mg, 90% yield). Mp=245 °C; $R_f$ 0.40 (hexane/EtOAc=10/1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.75 (s, 3H), 6.73–6.89 (m, 7H), 7.04 (app. d, $J$=7.8 Hz, 2H), 7.12–7.25 (m, 5H), 7.35 (d, $J$=9.2 Hz, 1H), 7.59–7.61 (m, 3H), 7.81–7.84 (m, 1H), 9.80–9.82 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 55.0, 97.0, 112.7 (2C), 123.7, 124.8, 125.6, 126.6 (3C), 127.4, 127.56 (3C), 127.63, 128.5, 130.8 (2C), 131.0 (3C), 131.5, 132.0 (2C), 132.7, 133.1, 139.1, 139.8, 140.0, 140.1, 140.5, 148.1, 158.2; HRMS (ESI+) Calcd for $C_{33}H_{24}IO$ $[M+H]^+$ 563.0870, found 563.0872.

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## Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.02.092.

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