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Cp*Co^{III}–Catalyzed *syn*-Selective C–H Hydroarylation of Alkynes Using Benzamides: An Approach Toward Highly Conjugated Organic Frameworks

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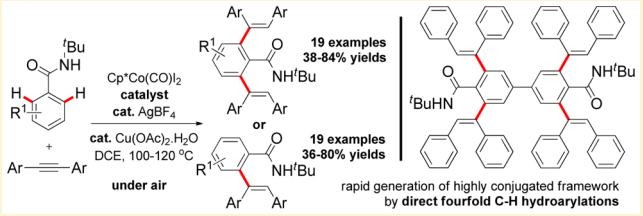
Supporting Information

ABSTRACT: Hydroarylation of internal alkynes by cost-effective Co^{III}-catalysis, directed by *N*-*tert*-butyl amides, is achieved to avail mono- or dihydroarylated amide products selectively in an atom and step economic way. Several important functional groups were tolerated under the reaction conditions, and *syn*-hydroarylation products were exclusively isolated. Notably, a 4-fold C–H hydroarylation provided a highly conjugated organic framework in one step. Kinetic study with extensive deuterium labeling experiments were performed to support the proposed mechanism.



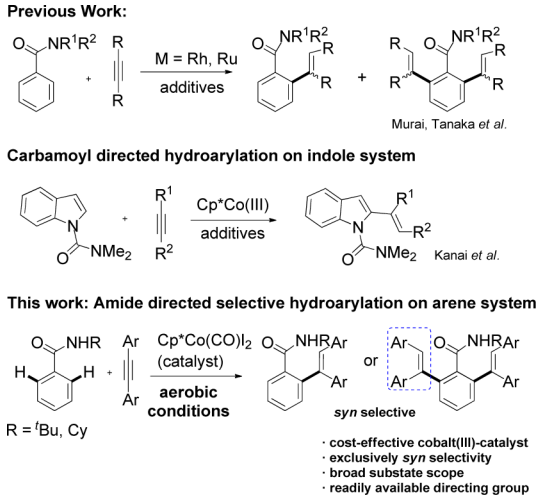
INTRODUCTION

Transition metal catalyzed C–H activation has emerged as a powerful atom and step economic method to functionalize inert C–H bonds to install desired functional groups of great synthetic interest.[1] Compared to noble metals, C–H bond functionalization based on the corresponding first row transition metal catalysts are much under developed and recently gained considerable attention due to their low cost and ready availability. In this line low valent cobalt catalysts have played a crucial role for directed C–H bond functionalization.[2,3] However, in many cases, reactive Grignard reagents used to generate active low valent cobalt catalyst restrict its application for many substrates having reactive functionalities. In this direction, recently high valent cationic Co^{III}-catalyzed C–H bond functionalization has gained significant attention. Kanai, Matsunaga, and co-workers have first reported the cationic Co^{III}-catalyzed insertion reaction of C–H bond to alkynes (Scheme 1), imines, and enones.[4] Later on Glorius, Ackermann, and Chang groups reported Co^{III}-catalyzed cyanation, halogenation, and allylation reactions.[5] Ellman and co-workers has applied this Cp*Co^{III}-catalyst for the synthesis of indazole and furan by C–H functionalization strategy.[6] Since then this catalyst has been an attractive choice to achieve some remarkable transformations by site selective functionalization of unactivated C–H bonds.[7−10]

Installation of alkenyl moieties on the aryl unit by classical cross-coupling methods faces some limitations, such as this need to use the corresponding prefunctionalized aryl dihalides which requires tedious synthetic efforts.[11]

Alkenylated aryls are very important molecules as they are key starting precursors for the synthesis of conjugated LED materials.[12,13] Hydroarylation of alkynes by C–H bond activation is a highly efficient, atom and step economic method to synthesize alkenylated arenes.[14] More importantly, manifold C–H hydroarylation is a highly promising method to generate highly conjugated organic frameworks in just one step. Amide directed rhodium and ruthenium catalyzed hydroarylation was previously reported by Tanaka[14c] and Miura et al. (Scheme 1).[14e] Previously, Kisch and Yoshikai groups[15a−d] reported a low valent cobalt catalyzed hydroarylation reaction on azobenzene and aromatic imines system, but limited scope and sensitive catalytic system with complex reaction conditions restrict its broad application. Although Petit et al. reported an *anti*-selective hydroarylation reaction, but catalytic system

Scheme 1. Amide Directed C–H Hydroarylations



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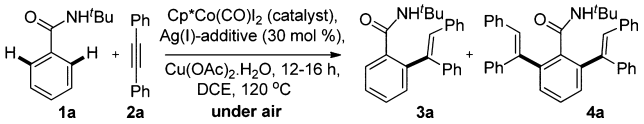
involves highly combustible and air sensitive $Co(PMe_3)_4$ catalyst.[1Se,f] Later on using internal alkyne, Kanai et al.[4c] introduced stable high valent Co^{III}-catalyzed carbamoyl directed hydroarylation on indole system, and here we have revealed our results on amide directed cost-effective Co^{III}-catalyzed *syn*-hydroarylation on arene system using internal alkynes under robust reaction conditions. We advanced the scope of hydroarytion by synthesizing mono- and dihydroarylated products selectively, and extended our methodology to 4-fold C−H activation strategy.

RESULTS AND DISCUSSION

We optimized the reaction conditions by using *N*-(*tert*-butyl)benzamide **1a** and diphenylacetylene **2a** (Table 1). The $Cp^*Co(CO)I_2$ catalyst was employed in combination with Ag(I)-salt and hydrated $Cu(OAc)_2$ additives.

Table 1. Optimization of the Reaction Conditions[a]



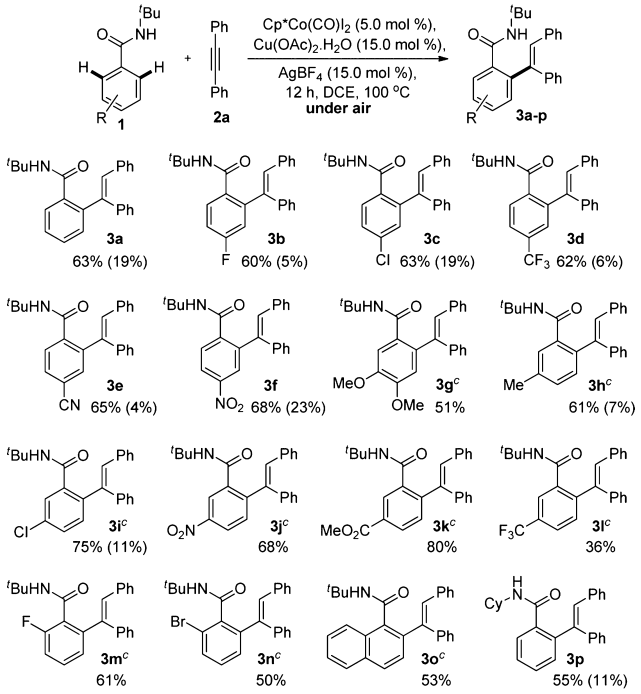
entry	catalyst [mol%]	Ag(I)-additive	$Cu(OAc)_2{\cdot}H_2O$ [equiv]	yield [%][b] 3a	4a
1	10	$AgSbF_6$	1.05	52	8
2	0	$AgSbF_6$	1.05	0	0
3	10	no	1.05	0	0
4	10	$AgBF_4$	1.05	56	8
5	10	$AgBF_4$	2.1	35	4
6	10	$AgBF_4$	0.50	45	15
7	10	$AgBF_4$	0.15	38	27
8[c]	10	$AgBF_4$	0.15	0	82
9[c]	10	$AgBF_4$	0	4	70
10[d]	5	$AgBF_4$	0.15	58	17
11[d,e]	5	$AgBF_4$	0.15	63	19

[a]Reaction conditions: **1a** (0.25 mmol), **2a** (0.25 mmol), 12−16 h. [b]Isolated yields. [c]2.5 equiv of **2a** was used. [d]15 mol% $AgBF_4$ was used and reaction temp = 100 °C. [e]1.3 equiv of **2a** was used.

For this reaction 1,2-dichloroethane was found to be the best solvent (entry 1). Cp^*Co^{III}-catalyst and $AgSbF_6$ additive were mandatory for our reaction (entries 2 and 3). On changing the additive to $AgBF_4$, the yield of **3a** slightly improved to 56% (entry 4). On increasing the amount of $Cu(OAc)_2{\cdot}H_2O$ additive, the yield of **3a** and **4a** decreased (entry 5). Interestingly, on decreasing the $Cu(OAc)_2{\cdot}H_2O$ additive, although the yield of **3a** decreased, it favored the formation of **4a** (entries 6 to 7). Gratifyingly, on using 2.5 equiv of **2a**, all **3a** was converted to **4a** and isolated as sole product in 82% yield (entry 8). Even without $Cu(OAc)_2{\cdot}H_2O$ additive, **4a** was isolated in 70% yield (entry 9). Further optimization by decreasing the catalyst loading to 5.0 mol% provided **3a** selectively (entry 7 vs 10). Finally, the yield of **3a** was further improved on increasing the amount of **2a** to 1.3 equiv (entry 11). Screening of different benzamides revealed that free N−H-functional group is necessary for this hydroarylation reaction.

With optimized conditions in hand, the scope of the monohydroarylation reaction was studied first by varying several amides **1**. The reaction proceeds with good to excellent yields for several amides having wide range of functional groups (Scheme 2). 4-Fluoro and 4-chloro benzamide reacted smoothly to provide monoalkenylated product **3b** and **3c** in

Scheme 2. Scope of Monohydroarylation Reaction[a,b]



[a]Reaction conditions: **1** (0.25 mmol), **2** (0.33 mmol), $Cp^*Co(CO)I_2$ (0.0125 mmol), $AgBF_4$ (0.0375 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.0375 mmol), DCE (1.0 mL), 12 h. [b]In parentheses isolated yields of the corresponding dialkenylated products **4** were given. [c]10 mol% catalyst and 30 mol% $AgBF_4$ were used.

60% and 63% yields, respectively. In both cases, dialkenylated products were also isolated in low yields as shown in the parentheses (5% and 19%, respectively).

Amides having electron withdrawing trifluoromethyl, cyanide, and nitro groups at the *para* position also reacted selectively to provide monoalkenylated products **3d**−**3f** in 62−68% yields. For *meta* substituted benzamides, less sterically hindered *ortho*-C−H-bond underwent reaction which was confirmed by ^1H NMR analysis. Amides having electron donating methoxy and methyl substitutions at the *meta* position provided products **3g** and **3h** in 51% and 61% yields, respectively. Several electron withdrawing functional groups at the *meta* position of amides also reacted smoothly to provide products **3i**−**3l** in 36 to 80% yields. 2-Fluoro and sterically hindered 2-bromo benzamides also provided desired product **3m** and **3n** in moderate yields. 1-Naphthamide was also a suitable substrate for our reaction and product **3o** was isolated in 53% yield. On changing the amine part of the amide to cyclohexyl, product **3p** was isolated in 55% yield along with 11% of dialkenylated product.

After successfully studying the scope of the monohydroarylation method, we investigated the scope of the dihydroarylation method (Scheme 3). It provided many important 1,3-dialkenylated benzamides, a key building block present in important conjugated PPVs polymers. In general, the reaction was highly efficient and in most of the cases clean formation of dialkenylated product **4** was observed. Amides having fluoro, chloro, and bromo functionalities at the *para* position reacted

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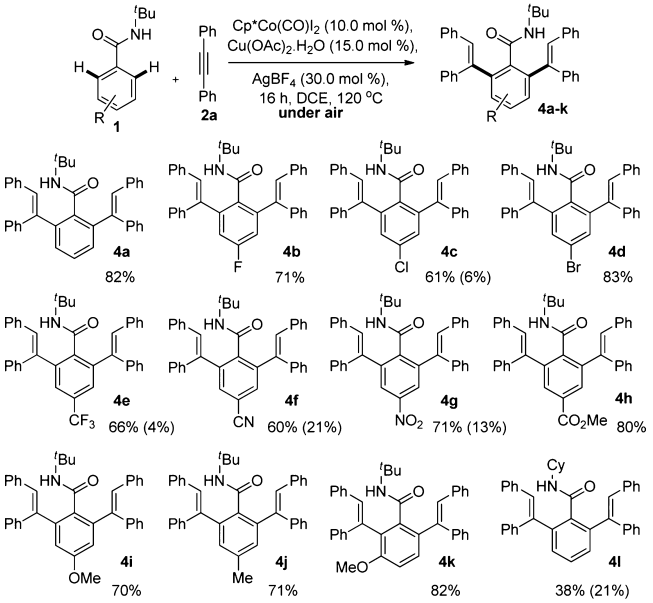
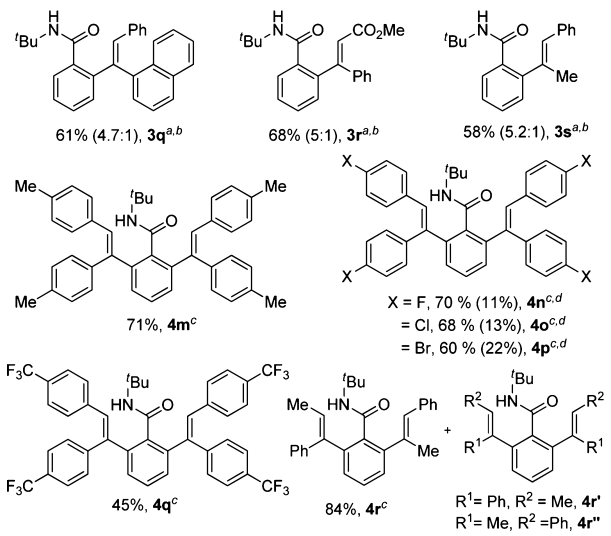
Scheme 3. Scope of Dihydroarylation Reaction[a,b]



[a]Reaction conditions: **1** (0.25 mmol), **2** (0.63 mmol), Cp*Co(CO)I_2 (0.025 mmol), $AgBF_4$ (0.075 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.0375 mmol), DCE (1.0 mL), 16 h. [b]In parentheses the isolated yields of **3** were given.

Scheme 4. Scope of Alkyne for Hydroarylation Reaction[a,b,c,d]



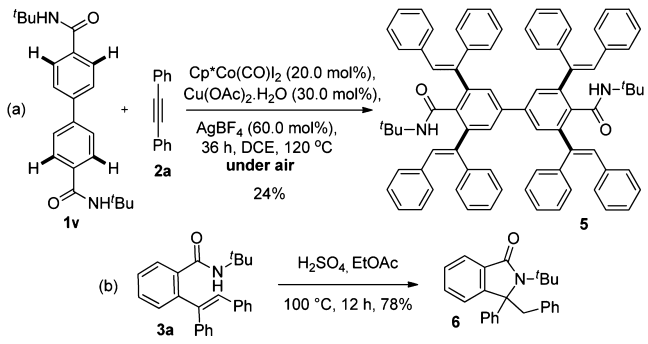
[a]Reaction conditions: As described under Scheme 2. [b]In the parentheses regioselectivities are given. [c]Reaction conditions: As described under Scheme 3. [d]In parentheses the isolated yields of **3** were provided.

smoothly to provide products **4b**–**4d** in moderate to excellent yields (61–83%). Electron withdrawing trifluoromethyl, cyanide, nitro, and ester substitutions at the *para* position of the benzamide also reacted smoothly to provide **4e**–**4h** in 60–80% yields. 4-Methoxy and 4-methyl substituted benzamide also provided dialkenylated products **4i** and **4j** in 70% and 71% yields, respectively. Finally, 3-methoxybenzamide also provided desired product **4k** in excellent yield. On changing the amide functional groups from *tert*-butyl to cyclohexyl, product **4l** was obtained in decent yield.

Finally, we explored the scope of this reaction with various internal symmetrical and unsymmetrival alkynes (Scheme 4). Unsymmetrical arylalkyne, 1-(phenylethynyl)naphthalene, reacted with **1a** selectively to provide **3q** in 61% yield as a 4.7:1 regioisomeric mixture. Two other unsymmetrical aryl alkylalkynes, methyl phenylpropiolate and 1-phenyl-1-propyne, have also taken part in the reaction and products **3r** and **3s** were isolated in moderate yields and regioselectivities. Electron donating methyl and fluoro substituted alkynes reacted smoothly to provide dialkenylated products **4m** and **4n** in good yields. Symmetrical 4-chloro and 4-bromo substituted diarylalkynes were also suitable substrates for the reaction. Electron deficient 1,2-bis(4-(trifluoromethyl)phenyl) ethyne reacted under our reaction conditions to provide dialkenylated product **4q** in 45% yield. 1-Phenyl-1-propyne also readily reacted under dihydroarylation conditions, and all three isomers **4r**, **4r**′, and **4r**″ were isolated in a combined yield of 84% as an inseparable mixture. Single crystal X-ray analysis of products **3m** and **4a** confirmed that hydroarylation occurred in *syn*-fashion (Figure S7).[20] The alkene geometry of products **3a**–**l**, **3n**–**p**, and **4b**–**q** are assigned in analogy to **3m** and **4a**, respectively.

Organic frameworks containing arenes with conjugated π-systems show potential utility as organic electronic materials.[16] Synthesizing them directly from simple starting materials are highly demanding area of research. Besides the cross-coupling reactions, C–H activation has already been introduced to prepare them in highly efficient way.[17] To show the efficiency of our method, biphenyl based diamide **1w** was subjected under the optimized reaction conditions to achieve 4-fold C–H hydroarylations in a single step. To our delight, the desired highly conjugated poly aromatic tetra-alkenylated framework **5** was obtained albeit in relatively low yield from **1v** (24%, Scheme 5a). Due to extended π-conjugation, compound **5** was

Scheme 5. 4-fold C–H Activation and Hydroamination of Hydroarylated Product



found to be fluorescence active. It absorbs UV (in methanol) at λ_{max} 288 nm and fluoresces at λ_{max} 390 nm (Figure S8).[20] In presence of sulfuric acid, hydroarylated product **3a** leads to the formation of isoindolinone structure **6** with *N*-substituted quaternary center which is a privileged structural motif present in many natural products and biologically active molecules (Scheme 5b).[18]

To gain insight in to the catalyst's mode of action we performed intermolecular competition experiment using electronically different benzamides, and we found electron rich benzamides are converted more efficiently with almost 3.4:1 ratio (**4i**/**4h**, Scheme 6a).[20] This result can be explained

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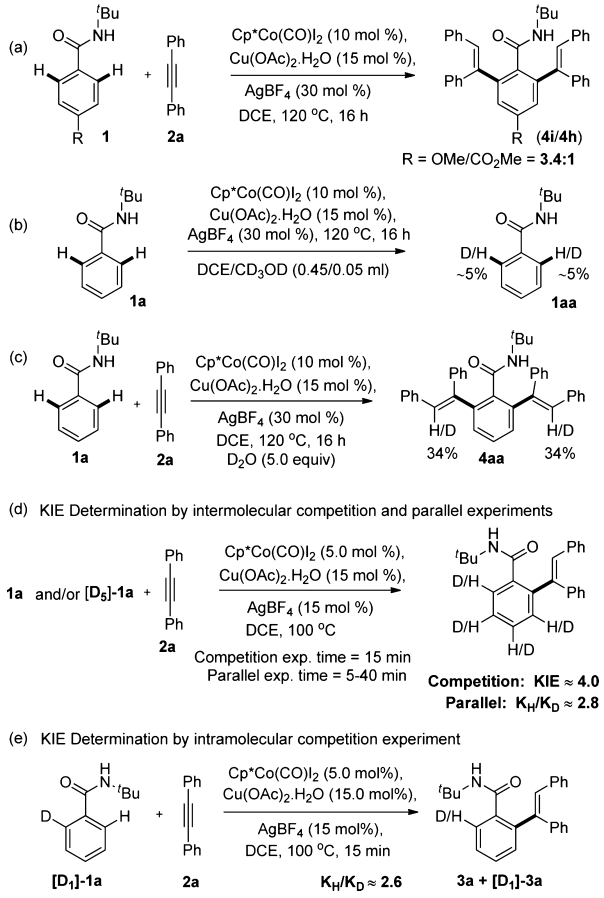
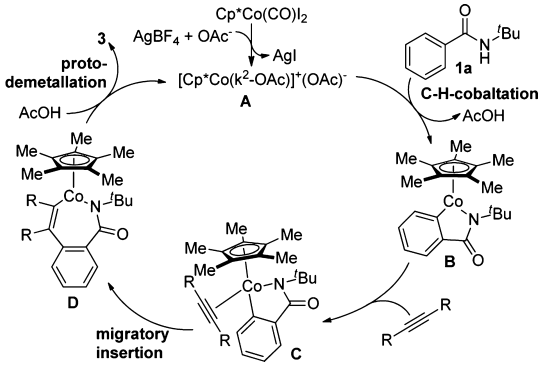
Scheme 6. Intermolecular Competition Experiment, Deuterium Labeling Study, and Kinetic Isotopic Effect Study



by a base assisted intermolecular electrophilic substitution reaction (BIES) type mechanism.[1c,19a−d] Deuterium exchange experiments using CD_3OD cosolvent under the same reaction conditions did not show a significant amount of H/D scrambling at the *ortho*-positions, suggesting an irreversible C−H-activation step. Further mechanistic investigation with alkyne also reveals that the alkene proton is deuterated partially (~34%) by the external deuterium source (Scheme 6c). Parallel experiment, intermolecular and intramolecular competition experiments have been performed to study kinetic isotopic effect. A KIE value of 4.0 and a K_H/K_D value of 2.8 were observed from the intermolecular competition experiment and parallel experiment, respectively (Scheme 6d). Finally, an intramolecular competition experiment has also been conducted and it showed a KIE value of 2.6 (Scheme 6e). All these results indicate that C−H activation probably occurs in the rate-determining step (RDS) of the reaction.[19b]

Based on the above experiments and previous reports, we propose that cobalt(III)-catalyzed C−H hydroarylation proceeds via a facile BIES-type C−H cobaltation step (Scheme 7).[1c,19] In the presence of copper acetate additive, *in situ* prepared Cp*Co(III)-complex **A** generates metallacycle **B** through the acetate assisted C−H activation.[1c] Thereafter subsequent alkyne co-ordination to the cyclometalated intermediate **B** delivers **C** followed by the migratory insertion to produce intermediate **D**. Finally in the presence of acid, proto-demetalation takes place to provide hydroarylated product **3** along with the regenerated active catalyst **A**, completing the catalytic cycle.

Scheme 7. Proposed Mechanism for Hydroarylation Reaction



CONCLUSION

In conclusion, we have developed an elegant method to synthesize several mono- and dialkenylated benzamides selectively using readily available *tert*-butylbenzamides derivatives and internal alkyne as starting precursors. An inexpensive cobalt(III)-catalyst was employed to achieve the goal. Several important functional groups such as chloride, bromide, cyanide, ester, and nitro were tolerated under the reaction conditions. The reaction showed excellent scope as several amides and alkynes were suitable substrates for our reaction. This method is highly effective to build structurally defined extended π-conjugated frameworks in a single step.

EXPERIMENTAL SECTION

General Information. All reactions were carried out in an oven-dried sealed tube. Unless otherwise stated, all solvents were dried by following standard procedure. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates. Column chromatography was performed through silica gel (100−200 mesh) using a proper solvent system. ^{1}H NMR and ^{13}C NMR were recorded on a (400 MHz) and (600 MHz) spectrometer in $CDCl_3$. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated as br (broad), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants (J) are given in Hertz (Hz). Chemical shift for ^{1}H NMR spectra were reported with respect to the residual signal of $CHCl_3$ at 7.26 ppm present in $CDCl_3$. Chemical shifts for ^{13}C NMR spectra were mentioned in ppm with respect to the center of a triplet at 77.16 ppm of chloroform-*d*. High-resolution mass spectra (HRMS) were recorded in TOF, ESI (+ Ve) method. Other chemicals were obtained from commercial sources and used without further purification. Single crystal X-ray data of the crystal was collected at 293 K on a CCD diffractometer. Infrared (IR) spectra were recorded by FTIR spectrometer and reported in cm^{-1}.

General Procedure for the Preparation of Aromatic Amides: (GP I). The benzamides **1a−w** were prepared according to the literature procedure from the corresponding acid chloride or acid.[10d] For the preparation of acid chloride, the carboxylic acid (10.0 mmol) and thionyl chloride (5.0 mL) were mixed and refluxed for 2 h. After completion of the reaction, volatiles were removed in vacuo to obtain crude acid chloride which was directly used for the next step without further purification. For the synthesis of aryl amides, to a solution of the corresponding benzoyl chloride (10.0 mmol) in diethyl ether (0.5 mmol/mL), triethylamine (2.0 equiv) was added and the reaction mixture was allowed to cool at 0 °C for 15 min. To this cooled reaction mixture amine was added slowly and then stirring was continued at room temperature for 3 h. The reaction mixture was quenched using 1.0 N HCl and extracted with ethyl acetate (30 mL × 2). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was further

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purified by silica gel column chromatography using hexane/ethyl acetate eluent.

General Procedure for Mono C−H Hydroarylation with *N*-(*tert*-Butyl)benzamide (GP IIA). *N*-(*tert*-butyl)benzamide **1** (0.25 mmol, 1.0 equiv) was taken in a 12.0 mL screw capped reaction tube, and 1.0 mL of anhydrous 1,2-dichloroethane was added. Then alkyne **2** (0.33 mmol, 1.3 equiv), catalyst $Cp^*Co(CO)I_2$ (6.0 mg, 0.0125 mmol, 5.0 mol%), $AgBF_4$ (7.3 mg, 0.0375 mmol, 15.0 mol%) and $Cu(OAc)_2{\cdot}H_2O$ (7.5 mg, 0.0375 mmol, 15.0 mol%) were added to the reaction mixture. The resultant reaction mixture was allowed to stir at 100 °C for 12 h. After completion of the reaction as indicated by TLC, the crude product was directly purified by silica gel column chromatography using petroleum ether/ethyl acetate eluent.

General Procedure for Mono C−H Hydroarylation with *N*-(*tert*-Butyl)benzamide (GP IIB). Similar to **GP IIA**, except catalyst $Cp^*Co(CO)I_2$ (11.9 mg, 0.025 mmol, 10.0 mol%) and additive $AgBF_4$ (14.6 mg, 0.075 mmol, 30.0 mol%) amounts were changed.

General Procedure for Di C−H Hydroarylation with *N*-(*tert*-Butyl)benzamide (GP III). *N*-(*tert*-butyl)benzamide **1** (0.25 mmol, 1.0 equiv) was taken in a 12.0 mL screw capped reaction tube, and 1.0 mL of anhydrous 1,2-dichloroethane was added. Then alkyne **2** (0.63 mmol, 2.5 equiv), catalyst $Cp^*Co(CO)I_2$ (11.9 mg, 0.025 mmol, 10.0 mol%), additive $AgBF_4$ (14.6 mg, 0.075 mmol, 30.0 mol%), and $Cu(OAc)_2{\cdot}H_2O$ (7.5 mg, 0.0375 mmol, 15.0 mol%) were added to the reaction mixture. The resultant reaction mixture was allowed to stir at 120 °C for 16 h. After completion of the reaction as indicated by TLC, the crude product was directly purified by silica gel column chromatography using petroleum ether/ethyl acetate eluent.

*N-(tert-Butyl)benzamide (**1a**).* The title compound **1a** was synthesized according to the GP I and isolated as white solid (1.50 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.72 (d, J = 6.5 Hz, 2H), 7.47−7.41 (m, 3H), 5.95 (br s, 1H), 1.47 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.1, 136.0, 131.2, 128.6, 126.8, 51.8, 29.0.

*N-(tert-Butyl)-4-fluorobenzamide (**1b**).* The title compound **1b** was synthesized according to the GP I and isolated as white solid (1.52 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.73−7.69 (m, 2H), 7.08−7.04 (m, 2H), 5.93 (br s, 1H), 1.45 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 166.0, 164.6 (d, J = 251.2 Hz), 132.2, 129.1 (d, J = 8.8 Hz), 115.5 (d, J = 21.7 Hz), 51.9, 29.0.

*N-(tert-Butyl)-4-chlorobenzamide (**1c**).* The title compound **1c** was synthesized according to the GP I and isolated as white solid (1.69 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.64 (d, J = 7.2 Hz, 2H), 7.36 (d, J = 7.2 Hz, 2H), 5.92 (br s, 1H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.0, 137.4, 134.4, 128.8, 128.3, 51.9, 29.0.

*4-Bromo-N-(tert-butyl)benzamide (**1d**).* The title compound **1d** was synthesized according to the GP I and isolated as white solid (2.18 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.58 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.3 Hz, 2H), 5.92 (br s, 1H), 1.45 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.0, 134.9, 131.8, 128.5, 125.8, 51.9, 29.0.

*N-(tert-Butyl)-4-(trifluoromethyl)benzamide (**1e**).* The title compound **1e** was synthesized according to the GP I and isolated as white solid (1.59 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.82 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.1 Hz, 2H), 5.98 (br s, 1H), 1.48 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 165.8, 139.4, 133.0 (q, J = 32.5 Hz), 127.3, 125.7 (q, J = 3.8 Hz), 123.9 (q, J = 272.2 Hz), 52.1, 28.9.

*N-(tert-Butyl)-4-cyanobenzamide (**1f**).* The title compound **1f** was synthesized according to the GP I and isolated as white solid (1.37 g, 68%). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.80 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 8.3 Hz, 2H), 5.98 (br s, 1H), 1.47 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 165.2, 140.0, 132.5, 127.6, 118.2, 114.8, 52.3, 28.9.

*N-(tert-Butyl)-4-nitrobenzamide (**1g**).* The title compound **1g** was synthesized according to the GP I and isolated as white solid (1.73 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.24 (d, J = 8.5 Hz, 2H), 7.86 (d, J = 8.5 Hz, 2H), 6.02 (br s, 1H), 1.48 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 165.0, 149.4, 141.7, 128.1, 123.9, 52.4, 28.9.

*Methyl 4-(tert-Butylcarbamoyl)benzoate (**1h**).* The title compound **1h** was synthesized according to the GP I and isolated as white solid (1.98 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.03 (d, J = 7.8 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H), 6.06 (s, 1H), 3.91 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.5, 166.2, 140.0, 132.4, 129.8, 126.9, 52.4, 52.0, 28.9.

*N-(tert-Butyl)-4-methoxybenzamide (**1i**).* The title compound **1i** was synthesized according to the GP I and isolated as white solid (1.76 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.68 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 8.4 Hz, 2H), 5.88 (br s, 1H), 3.83 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.7, 162.0, 128.6, 128.3, 113.8, 55.5, 51.6, 29.1.

*N-(tert-Butyl)-4-methylbenzamide (**1j**).* The title compound **1j** was synthesized according to the GP I and isolated as white solid (1.43 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.61 (d, J = 7.7 Hz, 2H), 7.19 (d, J = 7.6 Hz, 2H), 5.94 (br s, 1H), 2.37 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.9, 141.5, 133.1, 129.2, 126.8, 51.6, 29.0, 21.5.

*N-(tert-Butyl)-3,4-dimethoxybenzamide (**1k**).* The title compound **1k** was synthesized according to the GP I and isolated as white solid (1.52 g, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.38 (s, 1H), 7.17 (d, J = 8.1 Hz, 1H), 6.78 (d, J = 8.1 Hz, 1H), 5.98 (br s, 1H), 3.87 (s, 3H), 3.865 (s, 3H), 1.43 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.5, 151.4, 148.9, 128.5, 118.9, 110.5, 110.1, 56.00, 55.98, 51.6, 28.9.

*N-(tert-Butyl)-3-methoxybenzamide (**1l**).* The title compound **1l** was synthesized according to the GP I and isolated as white solid (1.68 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.32−7.27 (m, 2H), 7.20 (d, J = 7.3 Hz, 1H), 7.00 (d, J = 7.8 Hz, 1H), 5.95 (br s, 1H), 3.84 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.8, 159.9, 137.5, 129.5, 118.5, 117.5, 112.3, 55.6, 51.8, 29.0.

*N-(tert-Butyl)-3-methylbenzamide (**1m**).* The title compound **1m** was synthesized according to the GP I and isolated as white solid (1.36 g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.54 (s, 1H), 7.49−7.47 (m, 1H), 7.31−7.27 (m, 2H), 5.94 (br s, 1H), 2.38 (s, 3H), 1.47 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 167.4, 138.4, 136.0, 131.9, 128.5, 127.6, 123.8, 51.7, 29.0, 21.5.

*N-(tert-Butyl)-3-chlorobenzamide (**1n**).* The title compound **1n** was synthesized according to the GP I and isolated as white solid (1.6 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.68 (s, 1H), 7.57 (d, J = 7.6 Hz, 1H), 7.42 (d, J = 7.5 Hz, 1H), 7.34−7.31 (m, 1H), 5.95 (s, 1H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 165.7, 137.8, 134.7, 131.2, 129.9, 127.2, 125.0, 52.0, 28.9.

*N-(tert-Butyl)-3-nitrobenzamide (**1o**).* The title compound **1o** was synthesized according to the GP I and isolated as white solid (1.55 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.50 (s, 1H), 8.29 (d, J = 8.1 Hz, 1H), 8.09 (d, J = 7.7 Hz, 1H), 7.59 (t, J = 7.9 Hz, 1H), 6.14 (br s, 1H), 1.48 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 164.6, 148.2, 137.6, 133.2, 129.8, 125.8, 121.7, 52.4, 28.9.

*Methyl 3-(tert-Butylcarbamoyl)benzoate (**1p**).* The title compound **1p** was synthesized according to the GP I and isolated as white solid (1.93 g, 82%). IR (KBr): 3277, 2983, 2955, 1723, 1635, 1536 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.28 (s, 1H), 8.10 (d, J = 7.6 Hz, 1H), 7.97 (d, J = 7.5 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 6.07 (br s, 1H), 3.92 (s, 3H), 1.47 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.6, 166.0, 136.4, 132.1, 131.8, 130.4, 128.9, 127.4, 52.5, 52.0, 29.0. LCMS (ESI): calculated for $C_{13}H_{18}NO_3$ ($[M+H]^+$): 236.1; found 236.3.

*N-(tert-Butyl)-3-(trifluoromethyl)benzamide (**1q**).* The title compound **1q** was synthesized according to the GP I and isolated as white solid (1.76 g, 72%). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.97 (s, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.72 (d, J = 7.7 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 5.98 (s, 1H), 1.48 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 165.61, 136.85, 131.15 (q, J = 33 Hz), 130.17, 129.25, 127.83 (q, J = 3.6 Hz), 123.894 (q, J = 270.9 Hz), 123.894 (q, J = 3.8 Hz), 52.17, 28.93.

*N-(tert-Butyl)-2-fluorobenzamide (**1r**).* The title compound **1r** was synthesized according to the GP I and isolated as white solid (1.6 g, 82%). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.05−8.02 (m, 1H), 7.43−7.40 (m, 1H), 7.24−721 (m, 1H), 7.09−7.05 (m, 1H), 6.58 (d, J

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= 10.4 Hz, 1H), 1.46 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 162.42 (d, J = 3.3 Hz), 160.51 (d, J = 244.5 Hz), 132.94 (d, J = 9.3 Hz), 131.91, 124.84 (d, J = 3.0 Hz), 122.44 (d, J = 11.7 Hz), 116.0 (d, J = 25.5 Hz), 51.88, 28.99.

*2-Bromo-N-(tert-butyl)benzamide (**1s**).* The title compound **1s** was synthesized according to the GP I and isolated as white solid (2.05 g, 80%). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.55 (d, J = 8.0 Hz, 1H), 7.48 (dd, J = 7.6, 1.1 Hz, 1H), 7.34−7.31 (m, 1H), 7.24−7.22 (m, 1H), 5.73 (br s, 1H), 1.47 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 167.1, 139.2, 133.3, 131.0, 129.4, 127.6, 119.3, 52.4, 28.9.

*N-(tert-Butyl)-1-naphthamide (**1t**).* The title compound **1t** was synthesized according to the GP I and isolated as white solid (1.84 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.26 (d, J = 7.9 Hz, 1H), 7.86 (t, J = 8.1 Hz, 2H), 7.56−7.21 (m, 3H), 7.43 (t, J = 7.4 Hz, 1H), 5.83 (br s, 1H), 1.53 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.3, 136.1, 133.8, 130.2, 130.1, 128.4, 127.1, 126.4, 125.4, 124.9, 124.5, 52.2, 29.0.

*N-Cyclohexylbenzamide (**1u**).* The title compound **1u** was synthesized according to the GP I and isolated as white solid (1.75 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.75 (d, J = 7.7 Hz, 2H), 7.49−7.45 (m, 1H), 7.42−7.39 (m, 2H), 6.06 (s, 1H), 4.02−3.92 (m, 1H), 2.04−2.01 (m, 2H), 1.77−1.73 (m, 2H), 1.66−1.63 (m, 1H), 1.47−1.37 (m, 2H), 1.28−1.18 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.8, 135.1, 131.2, 128.5, 127.0, 48.8, 33.2, 25.6, 25.0.

*N^4,$N^{4'}$-Di-tert-butyl-[1,1′-biphenyl]-4,4′-dicarboxamide (**1v**).* The title compound **1w** was synthesized according to the GP I and isolated as white solid (0.5 mmol scale, 68 mg, 56%). IR (KBr): 3283, 2965, 1610, 1640, 1543, 1492 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.80 (d, J = 8.1 Hz, 4H), 7.64 (d, J = 8.1 Hz, 4H), 5.98 (s, 2H), 1.49 (s, 18H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 166.6, 142.9, 135.3, 127.5, 127.4, 51.9, 29.1. HRMS (ESI): calculated for $C_{22}H_{29}N_2O_2$ ([M+H]$^+$): 353.2224; found 353.2237.

*(E)-N-(tert-Butyl)-2-(1,2-diphenylvinyl)benzamide (**3a**).* The title compound **3a** was synthesized according to the GP IIA and the crude product was purified by using 10:90 ethyl actetate/hexane eluent. The product **3a** was isolated as white solid (56 mg, 63%) and in a second fraction the product **4a** was also isolated as white solid (25 mg, 19%). mp 124−126 °C. IR (KBr): 3292, 2965, 1629, 1535, 1452, 1261 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.58−7.55 (m, 1H), 7.36−7.32 (m, 2H), 7.24−7.10 (m, 11H), 6.75 (s, 1H), 5.72 (br s, 1H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.8, 142.2, 141.4, 139.8, 137.6, 137.3, 131.1, 131.0, 130.5, 129.6, 129.5, 128.5, 128.4, 128.2, 127.7, 127.6, 127.1, 51.6, 28.7. HRMS (ESI): calculated for $C_{25}H_{26}NO$ ([M+H]$^+$): 356.2009; found 356.2008.

*(E)-N-(tert-Butyl)-2-(1,2-diphenylvinyl)-4-fluorobenzamide (**3b**).* The title compound **3b** was synthesized according to the GP IIA. The crude product was purified by using 10:90 ethyl actetate/hexane eluent. The product **3b** was isolated as white solid (54.4 mg, 60%) and in a second fraction the product **4b** was also isolated as white solid (7 mg, 5%). mp 146−148 °C. IR (KBr): 2924, 2854, 1737, 1634, 1539, 1456 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.57 (dd, J = 8.3, 6.0 Hz, 1H), 7.24−7.23 (m, 3H), 7.17−7.16 (m, 5H), 7.10−7.09 (m, 2H), 7.02 (td, J = 8.3, 2.1 Hz, 1H), 6.92 (dd, J = 9.5, 2.0 Hz, 1H), 6.76 (s, 1H), 5.70 (s, 1H), 1.20 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 167.9, 163.0 (d, J = 249.9 Hz), 144.8 (d, J = 7.8 Hz), 140.3 (d, J = 1.1 Hz), 139.2, 136.8, 133.8 (d, J = 3.2 Hz), 131.70, 130.68 (d, J = 8.6 Hz), 130.4, 129.5, 128.6, 128.3, 128.0, 127.5, 117.8 (d, J = 21.7 Hz), 114.6 (d, J = 21.3 Hz), 51.7, 28.7. HRMS (ESI): calculated for $C_{25}H_{25}FNO$ ([M+H]$^+$): 374.1915; found 374.1935.

*(E)-N-(tert-Butyl)-5-chloro-2-(1,2-diphenylvinyl)benzamide (**3c**).* The title compound **3c** was synthesized according to the GP IIA and the crude product was purified by using 10:90 ethyl actetate/hexane eluent. The product **3c** was isolated as white solid (61.5 mg, 63%) and in a second fraction the product **4c** was also isolated as white solid (27 mg, 19%). mp 186−190 °C. **IR** (KBr): 2966, 3286, 1632, 1591, 1541, 1446 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.52 (d, J = 8.3 Hz, 1H), 7.31 (dd, J = 8.3, 1.7 Hz, 1H), 7.24−7.22 (m, 4H), 7.17−7.16 (m, 5H), 7.10−7.09 (m, 2H), 6.75 (s, 1H), 5.70 (br s, 1H), 1.19 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 167.7, 144.0, 140.3, 139.1, 136.8, 136.0, 135.5, 131.8, 130.9, 130.4, 130.0, 129.5, 128.6, 128.3, 128.0, 127.8, 127.5, 51.8, 28.7. HRMS (ESI): calculated for $C_{25}H_{25}ClNO$ ([M+H]$^+$): 390.1619; found 390.1618.

*(E)-N-(tert-Butyl)-2-(1,2-diphenylvinyl)-4-(trifluoromethyl)-benzamide (**3d**).* The title compound **3d** was synthesized according to the GP IIA and the crude product was purified by using 10:90 ethyl actetate/hexane eluent. The product **3d** was isolated as white solid (65.4 mg, 62%) and in a second fraction the product **4e** was also isolated as white solid (9 mg, 6%). mp 160−164 °C. IR (KBr): 3296, 2927, 2968, 1637, 1542, 1327 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.66 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 7.9 Hz, 1H), 7.50 (s, 1H), 7.24−7.23 (m, 3H), 7.17 (s, 5H), 7.11−7.10 (m, 2H), 6.77 (s, 1H), 5.67 (s, 1H), 1.20 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 167.5, 143.0, 140.8, 140.2, 139.0, 136.8, 132.1, 131.65 (q, J = 32.4 Hz), 130.5, 129.6, 129.0, 128.6, 128.3, 128.1, 127.9, 127.9 (q, J = 3.7 Hz), 127.6, 124.5 (q, J = 3.7 Hz), 52.0, 28.6. HRMS (ESI): calculated for $C_{26}H_{25}F_3NO$ ([M+H]$^+$): 424.1883; found 424.1885.

*(E)-N-(tert-Butyl)-4-cyano-2-(1,2-diphenylvinyl)benzamide (**3e**).* The title compound **3e** was synthesized according to the GP IIA and the crude product was purified by using 10:90 ethyl actetate/hexane eluent. The product **3e** was isolated as white solid (62.0 mg, 65%) and in a second fraction the product **4f** was also isolated as white solid (5.8 mg, 4%). mp 106−108 °C. IR (KBr): 3285, 2967, 2927, 2230, 1633, 1544 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.63−7.58 (m, 2H), 7.50 (s, 1H), 7.27−7.24 (m, 3H), 7.17−7.14 (m, 5H), 7.10−7.08 (m, 2H), 6.76 (s, 1H), 5.70 (br s, 1H), 1.21 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 167.1, 143.4, 141.5, 139.1, 138.8, 136.5, 134.6, 132.6, 130.9, 130.4, 129.5, 129.2, 128.8, 128.3, 128.2, 127.7, 118.2, 113.4, 52.2, 28.6. HRMS (ESI): calculated for $C_{26}H_{25}N_2O$ ([M+H]$^+$): 381.1961; found 381.1975.

*(E)-N-(tert-Butyl)-2-(1,2-diphenylvinyl)-4-nitrobenzamide (**3f**).* The title compound **3f** was synthesized according to the GP IIA and the crude product was purified by using 10:90 ethyl actetate/hexane eluent. The product **3f** was isolated as light yellow solid (68 mg, 68%) and in a second fraction the product **4g** was also isolated as yellow solid (33.5 mg, 23%). mp 128−130 °C. IR (KBr): 3274, 3060, 2969, 1633, 1523, 1349 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.16 (dd, J = 8.4, 1.7 Hz, 1H), 8.09 (d, J = 1.6 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.27−7.26 (m, 3H), 7.18 (s, 5H), 7.11−7.10 (m, 2H), 6.80 (s, 1H), 5.68 (br s, 1H), 1.22 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 166.9, 148.3, 144.0, 143.1, 139.3, 138.7, 136.4, 132.7, 130.4, 129.6, 128.8, 128.3, 128.3, 127.8, 125.9, 122.4, 52.3, 28.6. HRMS (ESI): calculated for $C_{25}H_{25}N_2O_3$ ([M+H]$^+$): 401.1860; found 401.1862.

*(E)-N-(tert-Butyl)-2-(1,2-diphenylvinyl)-4,5-dimethoxybenzamide (**3g**).* The title compound **3g** was synthesized according to the GP IIB. The crude product was purified by using 20:80 ethyl actetate/hexane eluent and isolated as white solid (52.8 mg, 51%). mp 156−158 °C. IR (KBr): 3385, 2970, 1663, 1594, 1498, 1451 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.23−7.22 (m, 3H), 7.19−7.16 (m, 6H), 7.14−7.13 (m, 2H), 6.75 (s, 1H), 6.65 (s, 1H), 6.00 (s, 1H), 3.94 (s, 3H), 3.81 (s, 3H), 1.20 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 167.9, 149.8, 148.4, 141.2, 139.4, 137.1, 135.0, 131.2, 130.3, 129.5, 129.4, 128.5, 128.3, 127.9, 127.3, 113.7, 112.1, 56.3, 56.2, 51.6, 28.6. HRMS (ESI): calculated for $C_{27}H_{30}NO_3$ ([M+H]$^+$): 416.2220; found 416.2221.

*(E)-N-(tert-Butyl)-2-(1,2-diphenylvinyl)-5 methylbenzamide (**3h**).* The title compound **3h** was synthesized according to the GP IIB. The crude product was purified by using 10:90 ethyl actetate/hexane eluent and the product **3h** was isolated as white solid (56.5 mg, 61%). In a second fraction the corresponding dialkenylated product was also isolated as white solid (10 mg, 7%). mp 116−118 °C. IR (KBr): 3249, 3056, 2966, 1630, 1545, 1447 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.49 (d, J = 7.8 Hz, 1H), 7.22−7.21 (m, 3H), 7.19−7.17 (m, 2H), 7.16−7.13 (m, 4H), 7.11−7.10 (m, 2H), 7.04 (s, 1H), 6.73 (s, 1H), 5.76 (br s, 1H), 2.33 (s, 3H), 1.20 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 168.7, 142.2, 141.7, 139.8, 139.7, 137.3, 134.8, 131.7, 130.8, 130.5, 129.5, 128.7, 128.4, 128.4, 128.2, 127.7, 127.1, 51.5, 28.7, 21.4. HRMS (ESI): calculated for $C_{26}H_{28}NO$ ([M+H]$^+$): 370.2165; found 370.2176.

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*(E)-N-(tert-Butyl)-5-chloro-2-(1,2-diphenylvinyl)benzamide (**3i**).* The title compound **3i** was synthesized according to the GP IIB. The crude product was purified by using 10:90 ethyl acetate/hexane eluent and the product **3i** was isolated as white solid (73 mg, 75%). In a second fraction the corresponding dialkenylated product was also isolated as white solid (15.5 mg, 11%). mp 162−164 °C. IR (KBr): 3279, 3054, 2970, 1628, 1541, 1454 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.53 (d, J = 2.0 Hz, 1H), 7.32 (dd, J = 8.3, 2.1 Hz, 1H), 7.23−7.22 (m, 3H), 7.17−7.15 (m, 6H), 7.10−7.08 (m, 2H), 6.73 (s, 1H), 5.67 (br s, 1H), 1.20 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 167.4, 140.7, 140.2, 139.5, 139.0, 137.0, 133.6, 132.5, 131.4, 130.5, 129.6, 129.6, 129.5, 128.5, 128.2, 127.9, 127.4, 51.9, 28.6. HRMS (ESI): calculated for $C_{25}H_{25}ClNO$ ($[M+H]^+$): 390.1619; found 390.1634.

*(E)-N-(tert-Butyl)-2-(1,2-diphenylvinyl)-5-nitrobenzamide (**3j**).* The title compound **3j** was synthesized according to the GP IIB. The crude product was purified by using 15:85 ethyl acetate/hexane eluent and isolated as light yellow solid (68 mg, 68%). IR (KBr): 3406, 3272, 2924, 1631, 1521, 1343 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.37 (d, J = 2.4 Hz, 1H), 8.18 (dd, J = 8.5, 2.4 Hz, 1H), 7.40 (d, J = 8.5 Hz, 1H), 7.27−7.24 (m, 3H), 7.18−7.15 (m, 5H), 7.11−7.09 (m, 2H), 6.81 (s, 1H), 5.69 (br s, 1H), 1.23 (s, 9H). ^{13}C NMR (150 MHz, CDCl3): δ (ppm) 166.6, 149.0, 146.8, 139.6, 138.9, 138.8, 136.4, 132.9, 132.2, 130.5, 129.6, 128.8, 128.3, 128.3, 127.9, 124.2, 123.6, 52.2, 28.6. HRMS (ESI): calculated for $C_{25}H_{25}N_2O_3$ ($[M+H]^+$): 401.1860; found 401.1875.

*(E)-Methyl 3-(tert-Butylcarbamoyl)-4-(1,2-diphenylvinyl) benzoate (**3k**).* The title compound **3k** was synthesized according to the GP IIB. The crude product was purified by using 15:85 ethyl acetate/hexane eluent and isolated as white solid (82.5 mg, 80%). mp 190−194 °C. IR (KBr): 3273, 3055, 2961, 1724, 1624, 1543 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.17 (d, J = 1.6 Hz, 1H), 7.99 (dd, J = 8.0, 1.6 Hz, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.23−7.21 (m, 3H), 7.17−7.15 (m, 5H), 7.10−7.09(m, 2H), 6.78 (s, 1H), 5.68 (br s, 1H), 3.93 (s, 3H), 1.21 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 168.0, 166.5, 147.1, 140.7, 139.4, 138.0, 136.9, 131.7, 131.3, 130.5, 130.4, 129.6, 129.4, 129.2, 128.5, 128.2, 127.9, 127.4, 52.4, 51.9, 28.7. HRMS (ESI): calculated for $C_{27}H_{28}NO_3$ ($[M+H]^+$): 414.2064; found 414.2063.

*(E)-N-(tert-Butyl)-2-(1,2-diphenylvinyl)-5-(trifluoromethyl) benzamide (**3l**).* The title compound **3l** was synthesized according to the GP IIB. The crude product was purified by using 10:90 ethyl acetate/hexane eluent and isolated as white solid (37 mg, 36%). mp 192−196 °C. IR (KBr): 3286, 1720, 1629, 1542, 1494, 1457 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.81 (s, 1H), 7.59 (d, J = 7.9 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.25−7.22 (m, 3H), 7.17 (s, 5H), 7.12−7.10 (m, 2H), 6.78 (s, 1H), 5.72 (s, 1H), 1.22 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 167.4, 145.8, 140.1, 139.2, 138.2, 136.7, 132.1, 131.6, 130.4, 129.79 (q, J = 33.0 Hz), 129.6, 128.7, 128.3, 128.1, 127.6, 126.2 (q, J = 3.6 Hz), 125.5 (q, J = 3.8 Hz), 123.9 (q, J = 272.2 Hz), 52.0, 28.7. HRMS (ESI): calculated for $C_{26}H_{25}F_3NO$ ($[M+H]^+$): 424.1883; found 424.1882.

*(E)-N-(tert-Butyl)-2-(1,2-diphenylvinyl)-6-fluorobenzamide (**3m**).* The title compound **3m** was synthesized according to the GP IIB. The crude product was purified by using 10:90 ethyl acetate/hexane eluent and isolated as white solid (57 mg, 61%). IR (KBr): 3291, 3056, 2966, 1640, 1542, 1450 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.22−7.20 (m, 6H), 7.12 (s, 3H), 7.07−7.05 (m, 2H), 7.02−7.00 (m, 2H), 6.79 (s, 1H), 5.49 (br s, 1H), 1.22 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 163.8, 159.4 (d, J = 247.0 Hz), 144.9 (d, J = 3.4 Hz), 140.1 (d, J = 2.1 Hz), 140.0, 137.1, 131.3, 130.6, 130.0 (d, J = 8.9 Hz), 129.6, 128.5, 128.1, 127.6, 127.1, 126.5 (d, J = 2.9 Hz), 126.3 (d, J = 17.9 Hz), 114.7 (d, J = 22.5 Hz), 52.1, 28.8. HRMS (ESI): calculated for $C_{25}H_{25}FNO$ ($[M+H]^+$): 374.1915; found 374.1927.

*(E)-2-Bromo-N-(tert-butyl)-6-(1,2-diphenylvinyl)benzamide (**3n**).* The title compound **3n** was synthesized according to the GP IIB. The crude product was purified by using 10:90 ethyl acetate/hexane eluent and isolated as white solid (54.4 mg, 50%). IR (KBr): 3293, 3054, 2965, 1639, 1537, 1445 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.48 (dd, J = 7.7, 1.1 Hz, 1H), 7.25−7.24 (m, 3H), 7.22−7.20 (m, 2H), 7.14−7.11 (m, 4H), 7.10−7.08 (m, 1H), 7.07−7.05 (m, 2H), 6.82 (s, 1H), 5.42 (br s, 1H), 1.27 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 166.7, 144.1, 140.2, 139.7, 139.0, 136.9, 131.8, 131.7, 130.4, 129.6, 129.6, 129.5, 128.6, 128.1, 127.7, 127.2, 120.4, 52.3, 28.7. HRMS (ESI): calculated for $C_{25}H_{25}BrNO$ ($[M+H]^+$): 434.1114; found 434.1111.

*(E)-N-(tert-Butyl)-2-(1,2-diphenylvinyl)-1-naphthamide (**3o**).* The title compound **3o** was synthesized according to the GP IIB. The crude product was purified by using 10:90 ethyl acetate/hexane eluent and isolated as white solid (54 mg, 53%). IR (KBr): 3419, 2959, 2922, 1666, 1509, 1452 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.08 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.72 (d, J = 8.6 Hz, 1H), 7.57−7.55 (m, 1H), 7.51−7.49 (m, 1H), 7.26−7.23 (m, 6H), 7.16−7.10 (m, 5H), 6.98 (s, 1H), 5.73 (br s, 1H), 1.35 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 168.7, 140.5, 140.3, 138.6, 137.2, 135.0, 132.6, 132.1, 130.6, 130.4, 129.8, 128.7, 128.5, 128.1, 127.7, 127.6, 127.6, 127.3, 127.1, 126.4, 125.7, 52.3, 28.9. HRMS (ESI): calculated for $C_{29}H_{28}NO$ ($[M+H]^+$): 406.2165; found 406.2165.

*(E)-N-Cyclohexyl-2-(1,2-diphenylvinyl)benzamide (**3p**).* The title compound **3p** was synthesized according to the GP IIA and the crude product was purified by using 10:90 ethyl acetate/hexane eluent. The product **3p** was isolated as white solid (52.4 mg, 55%) and in a second fraction the corresponding dihydroarylated product was also isolated as white solid (15.5 mg, 11%). IR (KBr): 2929, 2372, 2342, 1738, 1526, 1442 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.53 (d, J = 7.5 Hz, 1H), 7.37 (t, J = 7.0 Hz, 1H), 7.33 (t, J = 7.4 Hz, 1H), 7.28 (d, J = 7.5 Hz, 1H), 7.22−7.21 (m, 3H), 7.18−7.12 (m, 5H), 7.09 (d, J = 6.6 Hz, 2H), 6.75 (s, 1H), 5.65 (d, J = 7.4 Hz, 1H), 3.66−3.62 (m, 1H), 1.75−1.73 (m, 2H), 1.64−1.51 (m, 4H), 1.11−1.07 (m, 1H), 0.99−0.93 (m, 2H), 0.89−0.84 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 168.6, 142.4, 141.5, 139.8, 137.2, 137.0, 133.1, 131.8, 131.0, 130.9, 130.6, 129.7, 129.6, 128.3, 128.2, 127.7, 127.2, 48.7, 33.0, 25.6, 24.8. HRMS (ESI): calculated for $C_{27}H_{28}NO$ ($[M+H]^+$): 382.2165; found 382.2165.

*(E)-N-(tert-Butyl)-2-(2-(naphthalen-2-yl)-1-phenylvinyl)-benzamide (**3q**).* The title compound **3q** was synthesized according to the GP IIA and the crude product was purified by using 10:90 ethyl acetate/hexane eluent. The product **3q** was isolated as white solid (61.6 mg, 61%) and in a second fraction the corresponding dihydroarylated product was also isolated as white solid (11.3 mg, 7%). IR (KBr): 3056, 2966, 1656, 1506, 1446, 1364 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.13 (d, J = 8.4 Hz, 1H), 7.85−7.84 (m, 2H), 7.49 (d, J = 7.3 Hz, 1H), 7.45−7.40 (m, 3H), 7.34 (t, J = 7.5 Hz, 1H), 7.24 (d, J = 7.7 Hz, 1H), 7.21−7.17 (m, 1H), 7.13 (s, 1H), 7.07 (d, J = 7.9 Hz, 1H), 6.99−6.95 (m, 3H), 6.86 (d, J = 7.0 Hz, 2H), 5.79 (s, 1H), 1.31 (s, 9H). (major isomer). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 170.0, 142.2, 138.4, 138.0, 137.4, 136.9, 134.1, 133.8, 131.7, 130.5, 129.8, 129.3, 129.2, 128.7, 128.3, 128.2, 128.00, 127.98, 127.2, 127.1, 126.5, 126.0, 125.9, 51.8, 28.8 (major isomer). HRMS (ESI): calculated for $C_{29}H_{27}NNaO$ ($[M+Na]^+$): 428.1985; found 428.1989. The regioselectivity was determined by cleaving the alkene moiety of **3q**.

*(E)-Methyl 3-(2-(tert-Butylcarbamoyl)phenyl)-3-phenyl acrylate (**3r**).* The title compound **3r** was synthesized according to the GP IIA and the crude product was purified by using 20:80 ethyl acetate/hexane eluent. The product **3r** was isolated as white solid (57 mg, 68%) and in a second fraction the corresponding dihydroarylated product was also isolated as white solid (5 mg, 4%). IR (KBr): 2964, 1710, 1662, 1528, 1450, 1362 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.64−7.62 (m, 1H), 7.44−7.42 (m, 2H), 7.36−7.30 (m, 5H), 7.10−7.08 (m, 1H), 6.55 (s, 1H), 6.23 (s, 1H), 3.64 (s, 3H), 1.20 (s, 9H) (major isomer). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 168.1, 167.4, 139.0, 137.5, 136.8, 130.1, 129.8, 129.2, 128.8, 128.6, 128.5, 128.0, 127.9, 116.6, 51.7, 51.5, 28.5. (major isomer). HRMS (ESI): calculated for $C_{21}H_{23}NNaO_3$ ($[M+Na]^+$): 360.1570; found 360.1544.

*(E)-N-(tert-Butyl)-2-(1-phenylprop-1-en-2-yl)benzamide (**3s**).* The title compound **3s** was synthesized according to the GP IIA and the crude product was purified by using 10:90 ethyl acetate/hexane eluent. The product **3s** was isolated as white solid (42.7 mg, 58%) and in a second fraction the corresponding dihydroarylated product was

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also isolated as white solid (12.1 mg, 12%). IR (KBr): 2928, 2856, 1656, 1528, 1444, 1384 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.69 (dd, J = 7.6, 1.2 Hz, 1H), 7.42−7.33 (m, 6H), 7.29−7.27 (m, 2H), 6.58 (s, 1H), 6.04 (s, 1H), 2.24 (d, J = 1.4 Hz, 3H), 1.36 (s, 9H) (major isomer). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 168.4, 143.6, 139.6, 137.5, 135.6, 130.2, 130.0, 129.1, 129.0, 128.9, 128.5, 127.6, 127.1, 51.6, 28.8, 20.7. (major isomer). HRMS (ESI): calculated for $C_{20}H_{23}NNaO$ ($[M+Na]^+$): 316.1672; found 316.1678.

*N-(tert-Butyl)-2,6-bis((E)-1,2-diphenylvinyl)benzamide (**4a**).* The title compound **4a** was synthesized according to the GP III. The crude product was purified by using 5:95 ethyl actetate/hexane eluent and isolated as white solid (109.0 mg, 82%). mp 168−172 °C. IR (KBr): 3410, 3057, 2968, 1669, 1506, 1449 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.31−7.28 (m, 4H), 7.27−7.25 (m, 5H), 7.20−7.17 (m, 2H), 7.15−7.06 (m, 12H), 6.84 (s, 2H), 5.47 (br s, 1H), 1.04 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 168.25, 142.36, 140.77, 140.61, 137.45, 137.35, 131.09, 130.41, 129.64, 129.41, 128.54, 128.06, 127.92, 127.50, 126.91, 51.76, 28.69. HRMS (ESI): calculated for $C_{39}H_{36}NO$ ($[M+H]^+$): 534.2791; found 534.2791.

*N-(tert-Butyl)-2,6-bis((E)-1,2-diphenylvinyl)-4-fluorobenzamide (**4b**).* The title compound **4b** was synthesized according to GP III and the crude product was purified by using 5:95 ethyl actetate/hexane eluent. The product **4b** was isolated as white solid (98.0 mg, 71%) and in a second fraction the product **3b** was also isolated as white solid (3.5 mg, 3%). IR (KBr): 3430, 2964, 2921, 1666, 1585, 1495 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.30−7.27 (m, 10H), 7.15−7.12 (m, 6H), 7.08−7.07 (m, 4H), 6.85 (s, 2H), 6.76 (d, J = 9.2 Hz, 2H), 5.44 (br s, 1H), 1.03 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 167.6, 161.6 (d, J = 248.9 Hz), 144.8 (d, J = 7.9 Hz), 140.0, 139.8 (d, J = 1.4 Hz), 137.0, 131.6, 130.3, 129.7, 129.4 (d, J = 4.9 Hz), 128.7, 128.1, 127.8, 127.2, 116.2 (d, J = 21.5 Hz), 51.9, 28.7. HRMS (ESI): calculated for $C_{39}H_{35}FNO$ ($[M+H]^+$): 552.2697; found 552.2699.

*N-(tert-Butyl)-4-chloro-2,6-bis((E)-1,2-diphenylvinyl)benzamide (**4c**).* The title compound **4c** was synthesized according to the GP III and the crude product was purified by using 5:95 ethyl actetate/hexane eluent. The product **4c** was isolated as white solid (86.5 mg, 61%) and in a second fraction the product **3c** was also isolated as white solid (6 mg, 6%). mp 152−156 °C. IR (KBr): 3411, 3055, 2966, 1668, 1567, 1505 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.30−7.27 (m, 10H), 7.16−7.13 (m, 6H), 7.09−7.07 (m, 6H), 6.84 (s, 2H), 5.43 (br s, 1H), 1.03 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 167.4, 144.2, 139.9, 139.6, 136.9, 136.0, 133.8, 131.8, 130.3, 129.6, 129.2, 128.7, 128.1, 127.8, 127.2, 51.9, 28.6. HRMS (ESI): calculated for $C_{39}H_{35}ClNO$ ($[M+H]^+$): 568.2402; found 568.2418.

*4-Bromo-N-(tert-butyl)-2,6-bis((E)-1,2-diphenylvinyl)benzamide (**4d**).* The title compound **4d** was synthesized according to the GP III. The crude product was purified by using 5:95 ethyl actetate/hexane eluent and isolated as white solid (125 mg, 82%). IR (KBr): 3420, 3022, 2971, 1672, 1560, 1445 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.30−7.27 (m, 10H), 7.21 (s, 2H), 7.15−7.12 (m, 6H), 7.08−7.06 (m, 4H), 6.82 (s, 2H), 5.40 (br s, 1H), 1.01 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 167.4, 144.3, 139.8, 139.5, 136.9, 136.5, 132.1, 131.9, 130.4, 129.6, 128.7, 128.1, 127.8, 127.2, 122.0, 51.9, 28.7. HRMS (ESI): calculated for $C_{39}H_{35}BrNO$ ($[M+H]^+$): 612.1897; found 612.1909.

*N-(tert-Butyl)-2,6-bis((E)-1,2-diphenylvinyl)-4-(trifluoromethyl)-benzamide (**4e**).* The title compound **4e** was synthesized according to the GP III and the crude product was purified by using 5:95 ethyl actetate/hexane eluent. The product **4e** was isolated as white solid (100 mg, 66%) and in a second fraction the product **3d** was also isolated as white solid (4.5 mg, 4%). IR (KBr): 3428, 2961, 2925, 1669, 1508, 1445 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.33−7.27 (m, 12H), 7.17−7.13 (m, 6H), 7.09−7.08 (m, 4H), 6.84 (s, 2H), 5.41 (br s, 1H), 1.03 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) δ 167.1, 143.4, 140.4, 139.7, 139.6, 136.9, 132.2, 130.4 (q, J = 32.4), 130.3, 129.6, 128.8, 128.2, 127.9, 127.3, 126.1 (q, J = 3.7 Hz), 123.7 (q, J = 272.6 Hz), 52.1, 28.7. HRMS (ESI): calculated for $C_{40}H_{35}F_3NO$ ($[M+H]^+$): 602.2665; found 602.2687.

*N-(tert-Butyl)-4-cyano-2,6-bis((E)-1,2-diphenylvinyl)benzamide (**4f**).* The title compound **4f** was synthesized according to the GP III and the crude product was purified by using 5:95 ethyl actetate/hexane eluent. The product **4f** was isolated as white solid (84 mg, 60%) and in a second fraction the product **3e** was also isolated as white solid (20 mg, 21%). mp 226−228 °C. IR (KBr): 3357, 2960, 2233, 1672, 1520, 1447 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.31−7.26 (m, 12H), 7.15−7.14 (m, 6H), 7.09−7.07 (m, 4H), 6.86 (s, 2H), 5.55 (br s, 1H), 1.05 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 166.6, 143.7, 141.1, 139.6, 138.7, 136.6, 132.6, 132.5, 130.3, 129.6, 128.9, 128.2, 128.1, 127.5, 118.2, 112.1, 52.3, 28.6. HRMS (ESI): calculated for $C_{40}H_{35}N_2O$ ($[M+H]^+$): 559.2744; found 559.2736.

*N-(tert-Butyl)-2,6-bis((E)-1,2-diphenylvinyl)-4-nitrobenzamide (**4g**).* The title compound **4g** was synthesized according to the GP III and the crude product was purified by using 5:95 ethyl actetate/hexane eluent. The product **4g** was isolated as yellow solid (103 mg, 71%) and in a second fraction the product **3f** was also isolated as light yellow solid (13 mg, 13%). IR (KBr): 3401, 3055, 2964, 1667, 1516, 1346 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.91 (s, 2H), 7.33−7.31 (m, 10H), 7.17−7.16 (m, 6H), 7.11−7.10 (m, 4H), 6.88 (s, 2H), 5.49 (br s, 1H), 1.06 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 166.5, 147.2, 144.3, 142.6, 139.3, 138.7, 136.5, 132.6, 130.3, 129.6, 128.9, 128.21, 128.16, 127.5, 124.0, 52.3, 28.6. HRMS (ESI): calculated for $C_{39}H_{35}N_2O_3$ ($[M+H]^+$): 579.2642; found 579.2637.

*Methyl 4-(tert-Butylcarbamoyl)-3,5-bis((E)-1,2-diphenylvinyl)-benzoate (**4h**).* The title compound **4h** was synthesized according to the GP III. The crude product was purified by using 10:90 ethyl actetate/hexane eluent and isolated as white solid (121 mg, 82%). IR (KBr): 3391, 2970, 1717, 1665, 1517, 1237 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.73 (s, 2H), 7.26−7.24 (m, 10H), 7.11−7.06 (m, 10H), 6.79 (s, 2H), 5.38 (br s, 1H), 3.80 (s, 3H), 1.01 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.4, 166.5, 142.8, 141.2, 140.0, 139.9, 137.1, 131.7, 130.4, 130.4, 129.8, 129.6, 128.6, 128.1, 127.8, 127.1, 52.4, 52.0, 28.7. HRMS (ESI): calculated for $C_{41}H_{38}NO_3$ ($[M+H]^+$): 592.2846; found 592.2864.

*N-(tert-Butyl)-2,6-bis((E)-1,2-diphenylvinyl)-4-methoxybenzamide (**4i**).* The title compound **4i** was synthesized according to the GP III. The crude product was purified by using 10:90 ethyl actetate/hexane eluent and isolated as white solid (98 mg, 70%). IR (KBr): 3424, 2963, 1657, 1588, 1507, 1447 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.29−7.26 (m, 9H), 7.12−7.07 (m, 11H), 6.82 (s, 2H), 6.60 (s, 2H), 5.41 (br s, 1H), 3.66 (s, 3H), 1.00 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.2, 158.7, 144.1, 140.8, 140.3, 137.3, 130.9, 130.9, 130.4, 129.6, 128.5, 128.1, 127.5, 126.9, 114.9, 55.4, 51.6, 28.7. HRMS (ESI): calculated for $C_{40}H_{38}NO_2$ ($[M+H]^+$): 564.2897; found 564.2898.

*N-(tert-Butyl)-2,6-bis((E)-1,2-diphenylvinyl)-4-methylbenzamide (**4j**).* The title compound **4j** was synthesized according to the GP III. The crude product was purified by using 5:95 ethyl actetate/hexane eluent and isolated as white solid (97 mg, 71%). IR (KBr): 3428, 2963, 1663, 1596, 1496, 1444 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.32−7.25 (m, 10H), 7.15−7.12 (m, 5H), 7.11−7.08 (m, 5H), 6.89 (s, 2H), 6.81 (s, 2H), 5.46 (br s, 1H), 2.21 (s, 3H), 1.03 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.4, 142.4, 141.0, 140.6, 137.7, 137.4, 135.0, 130.9, 130.4, 130.0, 129.6, 128.5, 128.0, 127.5, 126.8, 51.6, 28.7, 21.2. HRMS (ESI): calculated for $C_{40}H_{38}NO$ ($[M+H]^+$): 548.2948; found 548.2971.

*N-(tert-Butyl)-2,6-bis((E)-1,2-diphenylvinyl)-3-methoxybenzamide (**4k**).* The title compound **4k** was synthesized according to the GP III. The crude product was purified by using 10:90 ethyl actetate/hexane eluent and isolated as white solid (113 mg, 80%). mp 192−194 °C. IR (KBr): 3422, 2963, 1665, 1494, 1447, 1287 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.41 (d, J = 7.2 Hz, 2H), 7.28−7.26 (m, 5H), 7.22−7.16 (m, 4H), 7.14−7.09 (m, 7H), 7.07−7.02 (m, 3H), 6.87 (s, 1H), 6.77 (d, J = 8.6 Hz, 1H), 6.67 (s, 1H), 5.44 (br s, 1H), 3.59 (s, 3H), 1.04 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 167.9, 156.6, 141.1, 140.4, 140.3, 139.2, 137.5, 137.4, 134.3, 131.4, 130.89, 130.85, 130.5, 130.4, 130.2, 129.7, 129.6, 128.6, 128.4, 128.01, 127.96, 127.9, 127.4, 126.9, 126.8, 126.7, 111.6, 56.1, 51.7, 28.7. HRMS (ESI): calculated for $C_{40}H_{38}NO_2$ ($[M+H]^+$): 564.2897; 564.2896.

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*N-Cyclohexyl-2,6-bis((E)-1,2-diphenylvinyl)benzamide (**4l**).* The title compound **4l** was synthesized according to the GP III and the crude product was purified by using 5:95 ethyl actetate/hexane eluent. The product **4l** was isolated as white solid (53 mg, 38%) and in a second fraction the product **3p** was also isolated as white solid (20.2 mg, 21%). IR (KBr): 3428, 3053, 2925, 1658, 1494, 1444 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.27−7.23 (m, 11H), 7.17−7.15 (m, 2H), 7.13−7.09 (m, 6H), 7.05 (d, J = 7.2 Hz, 4H), 6.81 (s, 2H), 5.22 (d, J = 7.1 Hz, 1H), 3.33−3.29 (m, 1H), 1.46−1.43 (m, 2H), 1.39−1.37 (m, 3H), 1.10−1.04 (m, 2H), 0.99−0.95 (m, 1H), 0.76-.071 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 168.0, 142.5, 140.9, 140.4, 137.3, 136.8, 131.1, 130.5, 129.6, 128.4, 128.2, 128.0, 127.5, 126.9, 48.6, 32.6, 25.6, 24.5. HRMS (ESI): calculated for $C_{41}H_{38}NO$ ($[M+H]^+$): 560.2948; found 560.2941.

*N-(tert-Butyl)-2,6-bis((E)-1,2-di-p-tolylvinyl)benzamide (**4m**).* The title compound **4m** was synthesized according to the GP III. The crude product was purified by using 5:95 ethyl actetate/hexane eluent and isolated as white solid (105 mg, 71%). IR (KBr): 3428, 2924, 1720, 1661, 1508, 1451 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.18−7.12 (m, 6H), 7.07−7.06 (m, 4H), 7.03−7.02 (m, 2H), 6.99−6.98 (m, 4H), 6.94−6.93 (m, 3H), 6.73 (s, 2H), 5.44 (s, 1H), 2.33 (s, 6H), 2.26 (s, 6H), 1.02 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 168.4, 142.7, 139.9, 137.9, 137.5, 137.1, 136.5, 134.7, 130.6, 130.3, 129.5, 129.2, 128.8, 127.8, 127.1, 51.7, 28.7, 21.43, 21.37. HRMS (ESI): calculated for $C_{43}H_{44}NO$ ($[M+H]^+$): 590.3417; found 590.3431.

*2,6-Bis((E)-1,2-bis(4-fluorophenyl)vinyl)-N-(tert-butyl)benzamide (**4n**).* The title compound **4n** was synthesized according to the GP III and the crude product was purified by using 5:95 ethyl actetate/hexane eluent. The product **4n** was isolated as white solid (106 mg, 70%) and in a second fraction the corresponding monohydroarylated product was also isolated as white solid (11 mg, 11%). IR (KBr): 3433, 3058, 2967, 1665, 1599, 1506 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.25−7.20 (m, 4H), 7.05−7.03 (m, 7H), 6.97 (t, J = 8.6 Hz, 4H), 6.85 (t, J = 8.6 Hz, 4H), 6.76 (s, 2H), 5.46 (s, 1H), 1.05 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 168.2, 162.3 (d, J = 246 Hz), 161.8 (d, J = 246 Hz), 142.0, 139.7 (d, J = 0.9 Hz), 137.4, 136.2 (d, J = 3.5 Hz), 133.2 (d, J = 3.3 Hz), 132.1 (d, J = 8.0 Hz), 131.2 (d, J = 7.9 Hz), 130.0, 129.5, 128.2, 115.7 (d, J = 21.3 Hz), 115.2 (d, J = 21.4 Hz), 51.9, 28.7. HRMS (ESI): calculated for $C_{39}H_{32}F_4NO$ ($[M+H]^+$): 606.2415; found 606.2429.

*2,6-Bis((E)-1,2-bis(4-chlorophenyl)vinyl)-N-(tert-butyl)benzamide (**4o**).* The title compound **4o** was synthesized according to the GP III and the crude product was purified by using 5:95 ethyl actetate/hexane eluent. The product **4o** was isolated as white solid (114 mg, 68%) and in a second fraction the corresponding monohydroarylated product was also isolated as white solid (13.9 mg, 13%). IR (KBr): 3422, 2963, 1721, 1663, 1586, 1489 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.26−7.24 (m, 3H), 7.20−7.19 (m, 5H), 7.14−7.10 (m, 5H), 7.03−6.99 (m, 6H), 6.76 (s, 2H), 5.44 (s, 1H), 1.04 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 168.0, 141.7, 140.3, 138.5, 137.5, 135.4, 133.8, 133.0, 131.7, 130.8, 130.3, 129.6, 129.0, 128.6, 128.3, 52.0, 28.8. HRMS (ESI): calculated for $C_{39}H_{32}Cl_4NO$ ($[M+H]^+$): 670.1233; found 670.1232.

*2,6-Bis((E)-1,2-bis(4-bromophenyl)vinyl)-N-(tert-butyl)benzamide (**4p**).* The title compound **4p** was synthesized according to the GP III and the crude product was purified by using 5:95 ethyl actetate/hexane eluent. The product **4p** was isolated as white solid (128.4 mg, 60%) and in a second fraction the corresponding monohydroarylated product was also isolated as white solid (25.5 mg, 22%). IR (KBr): 3427, 2966, 1659, 1566, 1500, 1446 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.42 (d, J = 8.2 Hz, 4H), 7.31 (d, J = 8.3 Hz, 4H), 7.15 (d, J = 8.3 Hz, 5H), 7.04 (d, J = 7.7 Hz, 2H), 6.96 (d, J = 8.3 Hz, 4H), 6.76 (s, 2H), 5.43 (s, 1H), 1.06 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 168.0, 141.6, 140.4, 138.9, 137.4, 135.8, 132.0, 131.9, 131.5, 131.1, 130.3, 129.6, 128.3, 122.0, 121.3, 52.0, 28.8. HRMS (ESI): calculated for $C_{39}H_{32}Br_4NO$ ($[M+H]^+$): 845.9212; found 845.9231.

*Spectral data for Monohydroarylated Product (**3t**).* IR (KBr): 3415, 2924, 1720, 1653, 1586, 1511 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.47 (d, J = 7.3 Hz, 1H), 7.37−7.32 (m, 4H), 7.30 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 7.1 Hz, 1H), 7.03 (d, J = 8.3 Hz, 2H), 6.95 (d, J = 8.3 Hz, 2H), 6.66 (s, 1H), 5.58 (s, 1H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm). δ 168.8, 141.9, 141.5, 138.5, 137.9, 136.0, 132.3, 131.6, 131.5, 131.1, 129.8, 129.7, 128.0, 121.9, 121.2, 51.7, 28.7. HRMS (ESI): calculated for $C_{25}H_{24}Br_2NO$ ($[M+H]^+$): 512.0219; found 512.0235.

*2,6-Bis((E)-1,2-bis(4-(trifluoromethyl)phenyl)vinyl)-N-(tert-butyl)-benzamide (**4q**).* The title compound **4q** was synthesized according to the GP III. The crude product was purified by using 5:95 ethyl actetate/hexane eluent and isolated as white solid (90 mg, 45%). IR (KBr): 3438, 2965, 1740, 1664, 1506, 1411 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.55 (d, J = 8.1 Hz, 4H), 7.44 (d, J = 8.2 Hz, 5H), 7.39 (d, J = 8.0 Hz, 4H), 7.17 (d, J = 8.1 Hz, 4H), 7.06 (d, J = 7.7 Hz, 2H), 6.94 (s, 2H), 5.49 (s, 1H), 1.04 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 167.9, 143.3, 141.6, 141.3, 140.1, 137.4, 131.0, 130.7, 130.1 (q, J = 32.7 Hz), 129.9, 129.7, 129.4 (q, J = 32.5 Hz), 128.6, 125.8 (q, J = 3.6 Hz), 125.4 (q, J = 3.7 Hz), 124.1 (q, J = 272.2 Hz), 52.14, 28.74. HRMS (ESI): calculated for $C_{43}H_{32}F_{12}NO$ ($[M+H]^+$): 806.2287; found 806.2286.

*N-(tert-Butyl)-2,6-bis((E)-1-phenylprop-1-en-1-yl)benzamide (**4r**).* The title compound **4r** was synthesized according to the GP III. The crude product was purified by using 10:90 ethyl actetate/hexane eluent and isolated as mixture of three possible isomers (combined yields, 86.3 mg, 84%). IR (KBr): 3428, 2964, 1656, 1509, 1445, 1261 cm^{-1}. ^1H NMR (600 MHz, CDCl3): δ (ppm) 7.37−7.28 (m, 19H), 7.25−7.22 (m, 6H), 7.17 (d, J = 7.6 Hz, 1H), 7.13- 7.11 (m, 0.6 H), 7.06 (d, J = 7.6 Hz, 1H), 6.96 (d, J = 7.7 Hz, 1H), 6.51 (s, 2H), 5.98−5.93 (m, 2H), 5.55 (s, 0.6H minor), 5.33 (s, 1H major), 5.22 (s, 0.45H minor), 2.28 (s, 3H), 2.26 (s, 3H), 1.86−1.83 (m, 6H), 1.28 (s, 6H minor), 1.19 (s, 9H major), 1.18 (s, 4H minor). ^{13}C NMR (150 MHz, CDCl3): δ (ppm) 168.6, 168.5, 168.4, 144.0, 143.8, 142.4, 142.1, 140.7, 140.4, 140.3, 140.1, 138.7, 138.6, 137.93, 137.88, 137.3, 136.2, 135.4, 130.1, 129.9, 129.6, 129.47, 129.45, 129.1, 129.09, 129.0, 128.7, 128.3, 128.13, 128.06, 127.7, 127.44, 127.35, 127.2, 127.1, 126.88, 126.85, 126.7, 51.6, 51.51, 51.49, 28.8, 28.69, 28.67, 20.6, 20.5, 15.81, 15.76. HRMS (ESI): calculated for C29H32NO ($[M+H]^+$): 410.2478; found 410.2476.

*N^4,$N^{4\prime}$-Di-tert-butyl-3,3′,5,5′-tetrakis((E)-1,2-diphenylvinyl)-[1,1′-biphenyl]-4,4′-dicarboxamide (**5**).* N^4,$N^{4\prime}$-Di-*tert*-butyl-[1,1′-biphenyl]-4,4′-dicarboxamide **1w** (35.5 mg, 0.1 mmol, 1.0 equiv) was taken in a 10.0 mL screw capped reaction tube and 1.0 mL of anhydrous 1,2-dichloroethane was added. Then alkyne **2a** (0.5 mmol, 5.0 equiv), $Cp^*Co(CO)I_2$ (9.5 mg, 0.02 mmol, 20.0 mol%), additive $AgBF_4$ (11.6 mg, 0.06 mmol, 60.0 mol%), and $Cu(OAc)_2{\cdot}H_2O$ (6.0 mg, 0.03 mmol, 30.0 mol%) were added to the reaction mixture. The resultant reaction mixture was allowed to stir at 120 °C for 36 h. After completion of the reaction as indicated by TLC, the crude product was purified by using 15:85 ethyl actetate/hexane eluent and isolated as white solid (25.4 mg, 24%). IR (KBr): 3428, 3054, 2854, 1723, 1663, 1496 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.29−7.24 (m, 24H), 7.14−7.07 (m, 20H), 6.80 (s, 4H), 5.41 (br s, 2H), 1.01 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.0, 142.9, 140.5, 140.2, 140.0, 137.2, 131.3, 131.2, 130.4, 130.3, 130.3, 129.6, 129.4, 129.3, 128.5, 128.2, 128.1, 127.5, 127.0, 51.8, 28.7. HRMS (ESI): calculated for $C_{78}H_{69}N_2O_2$ ($[M+H]^+$): 1065.5354; found 1065.5356.

*3-Benzyl-2-(tert-butyl)-3-phenylisoindolin-1-one (**6**).* (*E*)-*N*-(*tert*-Butyl)-2-(1,2-diphenylvinyl)benzamide **3a** (71 mg, 0.2 mmol, 1.0 equiv) was taken in a 10.0 mL screw capped reaction tube. Then 1.0 mL ethyl acetate and 2 mL of 12 (N) H_2SO_4 were added, respectively. The resultant reaction mixture was allowed to stir at 100 °C for 12 h. The reaction mixture was diluted with ice cold water (15 mL), and extracted with ethyl acetate (2 × 10 mL). The combined organic extracts were saturated $NaHCO_3$ solution (2 × 10 mL) and brine solution, respectively. The crude product was purified by column chromatography using 5:95 ethyl actetate/hexane as eluent, and isolated as white sticky solid (55 mg, 78%). IR (KBr): 3029, 2968, 2867, 1696, 1496, 1470 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.62 (d, J = 7.7 Hz, 1H), 7.54 (d, J = 8.7 Hz, 2H), 7.47−7.45 (m, 2H), 7.34 (t, J = 7.7 Hz, 2H), 7.33−7.27 (m, 2H), 7.10−7.04 (m, 3H), 6.90

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(d, J = 7.0 Hz, 2H), 3.65−3.60 (m, 2H), 1.41 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 154.9, 147.5, 142.8, 135.0, 132.2, 130.89, 130.86, 128.61, 128.57, 127.8, 127.77, 126.79, 125.5, 123.9, 122.3, 91.8, 53.6, 47.0, 30.5. HRMS (ESI): calculated for $C_{25}H_{26}NO$ ([M+H]$^+$): 356.2009; found 356.2003.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02516.

Experimental details, analytical data for all new compounds, crystallographic data (**3m** and **4a**), and NMR spectra (PDF)

X-ray crystallographic data of compounds **3m** and **4a** (CIF)

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Notes

The authors declare no competing financial interest.

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