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Broad Scope Aminocyclization of Enynes with Cationic JohnPhos–Gold(I) Complex as the Catalyst

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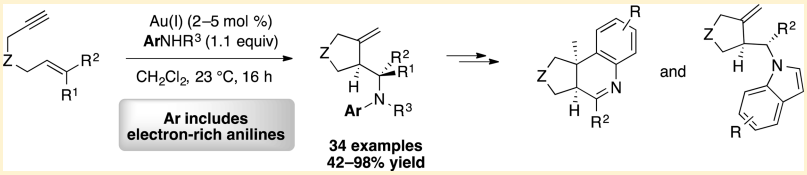
Supporting Information

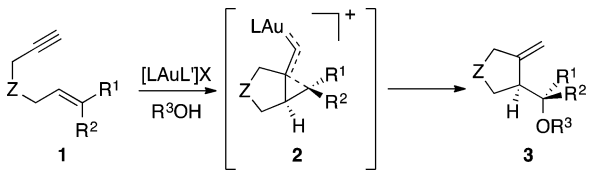


ABSTRACT: A practical aminocyclization of 1,6-enynes with a wide variety of substituted anilines, including *N*-alkyl anilines, has been achived by using cationic [JohnPhosAu(MeCN)]SbF_6 as a general purpose catalyst. The resulting adducts can be easily converted into polycyclic compounds by palladium- and gold-catalyzed reactions.

1. INTRODUCTION

Gold(I) complexes are very active and selective catalysts for the addition of nucleophiles on 1,n-enynes.[1,2] The most emblematic transformation in this area is the addition of alcohols and water on 1,6-enynes **1** (alkoxy- or hydroxycyclization), which occurs stereospecifically to form adducts **3** in the presence of gold(I) catalysts[3,4] under much milder conditions than with other electrophilic metal catalysts (Scheme 1).[5,6] According to

Scheme 1. Gold(I)-Catalyzed Alkoxy- or Hydroxycyclization of 1,6-Enynes



DFT calculations, this reaction proceeds through intermediates **2**, whose structures are intermediate between cyclopropyl gold(I) carbenes and gold(I)-stabilized homoallyl carbocations.[7] It is interesting to note that the hydroxycyclization is usually much faster than the direct nucleophilic addition of water on the terminal alkyne to form the corresponding methyl ketone.[8] Enantioselective hydroxy- and alkoxycyclizations of 1,6-enynes have been achieved with moderate to good enantioselectivities with a variety of chiral phosphines or NHC-gold catalysts.[9] The hydroxy- and alkoxycyclizations of 1,5-[4b,10,11] and 1,7-enynes take place similarly.[12]

A few examples of intramolecular amination of 1,5-enynes have been described.[10] The intermolecular reaction of 1,6-enynes with carbamates $ROCONH_2$ (R = Et, Bn) and anilines also takes place using Ph_3PAuCl and $AgSbF_6$ (5 mol %).[13] However, in the latter case, only less basic anilines bearing strongly electron-withdrawing groups (*p*-NO_2, *o*-CN, *o*-CF_3, *p*-Cl) were used as the nucleophiles. We decided to study the scope and limitations of the intermolecular amination of 1,6-enynes with a broader range of anilines using gold(I) complexes with JohnPhos and related bulky biphenyl-based phosphines (Buchwald ligands), which are often the catalysts of choice in gold(I)-catalyzed reactions.[14]

2. RESULTS AND DISCUSSION

The aminocyclization of enynes was initially studied with dimethyl 2-*trans*-cinnamyl-2-(prop-2-yn-1-yl)malonate (**1a**) as the substrate and a slight excess of the aniline using 2−5 mol % of the gold catalyst in CH_2Cl_2 (Table 1). The best result for the addition of aniline was obtained using 2 mol % of commercially available cationic JohnPhos−gold(I) catalyst **A**, leading to adduct **4a** in excellent yield (Table 1, entry 1). Increasing the catalyst loading to 5 mol % was required for the addition of *p*-anisidine to form **4b** in 58% yield after a 19 h reaction time (Table 1, entry 2). This result with an electron-rich aniline is remarkable since this reaction had only been reported with deactivated amines.[13] Lower yields were obtained with gold(I) complexes with other phosphine, NHC, or phosphite ligands (Table 1, entries 3−7). Tetrahydrofuran was also evaluated as solvent in the reaction with aniline; however, the yield was significantly reduced.[15]

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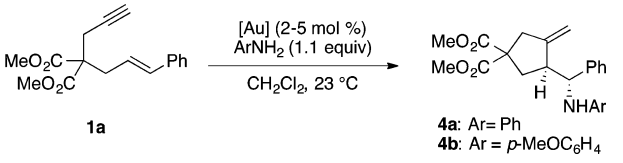
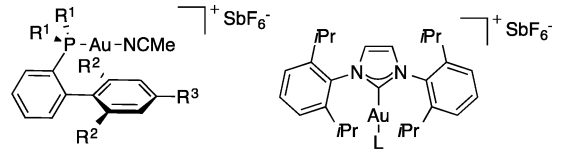
Table 1. Gold(I)-Catalyzed Aminocyclization of 1,6-Enyne 1a



1a — **4a**: Ar= Ph; **4b**: Ar = *p*-MeOC$_6$H$_4$

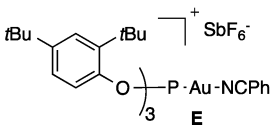
entry	Ar	[Au], mol %	time (h)	product, yield (%)[a]
1	Ph	**A** (2)	16	**4a** (95[a], 93[b])
2	*p*-MeOC$_6$H$_4$	**A** (5)	19	**4b** (58)
3	*p*-MeOC$_6$H$_4$	**B** (5)	19	**4b** (42)
4	*p*-MeOC$_6$H$_4$	**C** (5)	19	**4b** (30)
5	*p*-MeOC$_6$H$_4$	**D$_1$** (5)	19	**4b** (10)
6	*p*-MeOC$_6$H$_4$	**E** (5)	19	**4b** (23)
7	*p*-MeOC$_6$H$_4$	$PPh_3AuCl/AgSbF_6$ (5)	19	**4b** (7[b])

[a]Yields determined by ^{1}H NMR. [b]Isolated yield.



A: R^1 = *t*Bu, R^2 = R^3 = H
B: R^1 = Cy, R^2 = OMe, R^3 = H
C: R^1 = *t*Bu, R^2 = R^3 = *i*Pr

D$_1$: L = PhCN

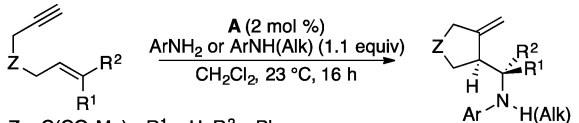


E

It is important to note that the reaction of anilines and aliphatic amines with complex **A** forms complexes [(JohnPhos)Au(NH$_2$R)]SbF$_6$ by ligand substitution, which have been characterized by X-ray diffraction and show diminished catalytic activity in the reaction of cyclopropenes with *p*-anisidine.[16] However, in our system, these less active amino complexes presumably formed in situ under the amination reaction still undergo ligand exchange with the enynes at a sufficient rate so as to generate the catalytically active (η^2-alkyne)gold(I) species.[15]

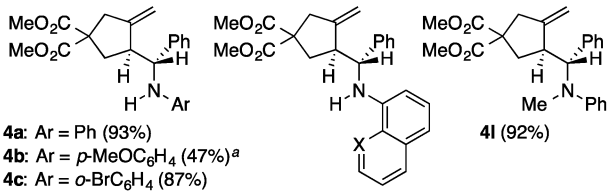
The substrate generality under these reaction conditions was tested with different enynes and a wide range of anilines (Table 2). In general, moderate to excellent yields were obtained for the different combinations of 1,6-enynes and anilines examined (42−98%). Concerning the anilines, electron-rich as well as electron-poor anilines participated efficiently in this reaction without significant differences in the isolated yields. Anilines substituted at the *ortho*-position also gave rise to the corresponding adducts **4c**, **4e**, **4h**, **4o**, **4w**, and **4y** in satisfactory yields. Secondary anilines, such as *N*-methylaniline, *N*-allylaniline, indoline, or tetrahydroquinoline also reacted to give the corresponding adducts in moderate to good yields (**4l**, **4t**, **4ad**−**ag**). Different substitution patterns on the enyne were also used, and all led efficiently to the desired product. The presence of a dimethyl or phenyl substituent on the alkene did not give significantly different results in terms of reactivity. The relative configuration of the aminocyclization products was assigned by determining the structures of compounds **4d**, **4i**, and **4x** by X-ray crystallography analysis,[17] confirming the *anti*-type addition of the nucleophile to the 1,6-enyne.

Table 2. Gold(I)-Catalyzed Aminocyclization of 1,6-Enynes 1a−f with Different Anilines



1a: Z = C(CO$_2$Me)$_2$, R^1 = H, R^2 = Ph
1b: Z = C(SO$_2$Ph)$_2$, R^1 = R^2 = Me
1c: Z = C(CO$_2$Me)$_2$, R^1 = R^2 = Me
1d: Z = 2,2-dimethyl-1,3-dioxane, R^1 = H, R^2 = Ph
1e: Z = C(CH$_2$OPMB)$_2$, R^1 = H, R^2 = Ph
1f: Z = C(CH$_2$OMe)$_2$, R^1 = H, R^2 = Ph

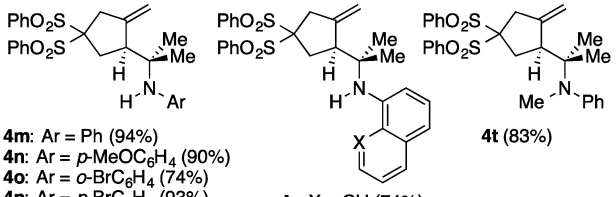
4a-ae



4a: Ar = Ph (93%)
4b: Ar = *p*-MeOC$_6$H$_4$ (47%)[a]
4c: Ar = *o*-BrC$_6$H$_4$ (87%)
4d: Ar = *p*-BrC$_6$H$_4$ (74%)
4e: Ar = *o*-IC$_6$H$_4$ (98%)
4f: Ar = 4-Br,2-IC$_6$H$_3$ (90%)
4g: Ar = 5-Cl,2-IC$_6$H$_3$ (85%)
4h: Ar = 2,4,6-Me$_3$C$_6$H$_2$ (82%)
4i: Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$ (89%)

4j: X = CH (51%)
4k: X = N (46%)

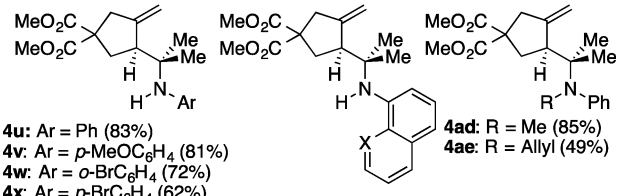
4l (92%)



4m: Ar = Ph (94%)
4n: Ar = *p*-MeOC$_6$H$_4$ (90%)
4o: Ar = *o*-BrC$_6$H$_4$ (74%)
4p: Ar = *p*-BrC$_6$H$_4$ (93%)
4q: Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$ (48%)

4r: X = CH (74%)
4s: X = N (72%)

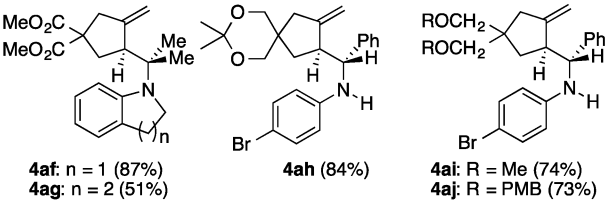
4t (83%)



4u: Ar = Ph (83%)
4v: Ar = *p*-MeOC$_6$H$_4$ (81%)
4w: Ar = *o*-BrC$_6$H$_4$ (72%)
4x: Ar = *p*-BrC$_6$H$_4$ (62%)
4y: Ar = *o*-IC$_6$H$_4$ (58%)
4z: Ar = *p*-MeCOC$_6$H$_4$ (74%)
4aa: Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$ (42%)

4ab: X = CH (78%)
4ac: X = N (81%)

4ad: R = Me (85%)
4ae: R = Allyl (49%)



4af: n = 1 (87%)
4ag: n = 2 (51%)

4ah (84%)

4ai: R = Me (74%)
4aj: R = PMB (73%)

[a]5 mol % catalyst.

To illustrate the synthetic potential of this gold(I) catalyzed reaction, additional transformations were carried out on several halogenated derivatives, in order to increase the molecular complexity. First, an intramolecular Heck reaction was successfully applied for compounds bearing iodine in the *ortho* position (Scheme 2, **4e**−**g**). Under standard conditions, good yields of the desired *cis*-fused tricyclic structures **5e**−**g** were obtained after selective 6-*exo* cyclization. This outcome represents an easy access to these tetrahydro-1*H*-cyclopenta-[*c*]quinoline derivatives. The use of *o*-Br derivative **4c** or dimethyl substituted compound **4y** only led to the recovery of the starting material. It is interesting to note that the initial

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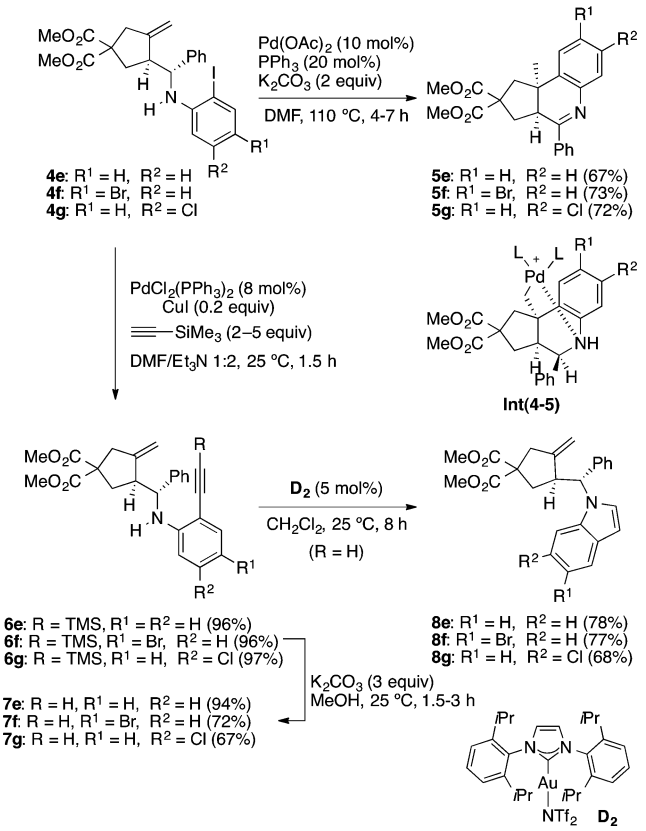
Scheme 2. Transformation of Adducts 4e−g into Tetrahydro-1*H*-cyclopenta[*c*]quinoline and Indole Derivatives via Pd(0)-Catalyzed Cross-Coupling and Au(I)-Catalyzed Cyclization



alkyl-palladium(II) species of the Heck reaction evolves by an intramolecular redox process presumably via *β*-hydride elimination from the benzylic position of cationic intermediate **Int(4−5)**, followed by reductive elimination.

Then, we envisioned a second gold-catalyzed aminocyclization to form *N*-substituted indoles (Scheme 2). The alkyne was introduced at the *ortho* position by Sonogashira cross-coupling of the iodoarenes with trimethylsilylacetylene to form **6e−g** in near-quantitative yields, followed by deprotection of the TMS-alkynyl compounds by methanolysis to give **7e−g**. The new gold(I)-catalyzed aminocyclization proceeded efficiently using catalyst $\mathbf{D_2}$ with IPr as the NHC ligand, leading to indole derivatives **8e−g** in good yields. The presence of chlorine or bromine atoms in **5f−g** and **8f−g** could allow their further functionalizations by cross-coupling reactions or other tranformations.

3. CONCLUSIONS

Although amines coordinate to Lewis acidic gold(I) complexes, thus reducing their availability to activate alkynes and other substrates, robust cationic gold(I) complex [JohnPhosAu(MeCN)]SbF_6 is the catalyst of choice for the broad-scope aminocyclization of 1,6-enynes. The reaction proceeds under mild conditions in moderate to excellent yields with a wide variety of substituted anilines, including electron-rich as well as secondary *N*-alkyl anilines to give the corresponding adducts, which can be further derivatized to form polycyclic compounds by palladium- and gold-catalyzed reactions.

EXPERIMENTAL SECTION

General Experimental Procedures. Solvents were dried by passing through an activated alumina column on a solvent purification system. Analytical thin layer chromatography was carried out using TLC-aluminum sheets with 0.2 mm of silica gel (Merck GF254) using UV light as the visualizing agent or an acidic solution of vanillin in ethanol as the developing agent. Purifications by chromatography were carried out using flash grade silica gel (SDS Chromatogel 60 ACC, 40−60 mm). Preparative TLC was performed on 20 cm × 20 cm silica gel plates (2.0 mm thick, catalogue number 02015, Analtech). Organic solutions were concentrated under reduced pressure on a rotary evaporator. Unless otherwise stated, NMR spectra were recorded at 298 K on 300, 400, and 500 MHz devices. ^{1}H and ^{13}C chemical shifts (δ) are given in ppm relative to TMS, and coupling constants (J), in Hz. The solvent signals were used as references, and the chemical shifts were converted to the TMS scale. Mass spectra were recorded employing TOF mass analyzers (ESI, EI, CI). Melting points were determined by observation of the fusion of the solids placed in a capillary, through a magnifying glass. Crystal structure determinations were carried out using a diffractomer equipped with an APPEX 2 4K CCD area detector, an FR591 rotating anode with Mo Kα radiation, Montel mirrors as the monochromator, and a Kryoflex low temperature device (T = −173 °C). Full-sphere data collection was used with w and j scans. Programs used: Data collection APEX-2, data reduction Bruker Saint V/.60A and absorption correction SADABS. Structure Solution and Refinement: Crystal structure solution was achieved using direct methods as implemented in SHELXTL and visualized using the program XP. Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least-squares refinement on F2 using all measured intensities was carried out using the program SHELXTL. All non-hydrogen atoms were refined including anisotropic displacement parameters.

Compounds **1a**,[18] **1b**,[19] and **1c**[19] were prepared according to reported methods. Gold complexes **A**, **B**, and **C** are commercialy available; $\mathbf{D_1}$,[2] $\mathbf{D_2}$,[4c] and **E**[2] were prepared according to literature procedures.

2-Cinnamyl-2-(prop-2-yn-1-yl)propane-1,3-diol. $LiAlH_4$ (461 mg, 12.1 mmol) was suspended in anhydrous THF (30 mL), and the slurry was cooled to 0 °C. A solution of malonate **1a** (1.58 g, 5.52 mmol) in anhydrous THF (2 mL) was added dropwise at 0 °C. When effervescence had ceased, the mixture was allowed to warm to room temperature and was then heated at 45 °C and stirred vigorously for 3.5 h. TLC (c-hexane/EtOAc 8:1 and 1:1) showed full consumption of the starting malonate and clean conversion. The mixture was diluted with wet diethyl ether (30 mL) and quenched by addition of sodium sulfate decahydrate (ca. 2 g) slowly, to control the effervescence. After stirring for 1 h at rt, a few drops of saturated aqueous NH_4Cl were added, until the suspension became white. The solids were filtered off over Celite, and the cake was washed thoroughly with diethyl ether (200 mL). The filtrate was concentrated *in vacuo*, and the residue was purified by column chromatography on silica gel eluting with pentane/diethyl ether 1:1 to straight diethyl ether to afford 1.15 g of a colorless solid (90%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39−7.35 (m, 2H), 7.34−7.29 (m, 2H), 7.25−7.21 (m, 1H), 6.50 (d, J = 15.6 Hz, 1H), 6.23 (dt, J = 15.6, 7.7 Hz, 1H), 3.76−3.67 (m, 4H), 2.43−2.37 (m, 2H), 2.33 (dd, J = 7.7, 1.4 Hz, 2H), 2.32 (d, J = 2.8 Hz, 2H), 2.08 (t, J = 2.7 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.2, 133.6, 128.5, 127.3, 126.1, 124.8, 80.9, 71.0, 67.5, 42.7, 35.2, 21.6 ppm. **HRMS-APCI** calcd for $C_{15}H_{19}O_2^+$ $[M + H]^+$: 231.1380; found: 231.1386. **Mp** 100−102 °C.

*5-Cinnamyl-2,2-dimethyl-5-(prop-2-yn-1-yl)-1,3-dioxane (**1d**).* In a dry flask, 2-cinnamyl-2-(prop-2-yn-1-yl)propane-1,3-diol (600 mg, 2.61 mmol) was dissolved in anhydrous acetone (2 mL) and *p*TsOH·H_2O (25 mg, 0.13 mmol) was added, followed by addition of $MgSO_4$ (300 mg). The suspension was stirred vigorously at rt for 24 h. TLC showed clean conversion to a new product and only traces of starting material. Acetone was removed under a stream of nitrogen, and the mixture was loaded on silica gel and purified by column chromatography eluting with pentane/diethyl ether 95:5 to 9:1 to

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afford 650 mg of a colorless oil (92%). *Remark:* melting point close to room temperature. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39−7.35 (m, 2H), 7.35−7.30 (m, 2H), 7.26−7.21 (m, 1H), 6.51 (d, J = 15.8 Hz, 1H), 6.19 (dt, J = 15.6, 7.7 Hz, 1H), 3.73 (s, 4H), 2.42 (d, J = 2.8 Hz, 2H), 2.37 (dd, J = 7.8, 1.3 Hz, 2H), 2.08 (t, J = 2.7 Hz, 1H), 1.46 (s, 3H), 1.44 (s, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.2, 133.9, 128.5, 127.3, 126.1, 124.0, 98.2, 80.6, 71.1, 66.7, 36.1, 36.0, 25.3, 22.5, 22.2 ppm. **HRMS-ESI** calcd for $C_{18}H_{22}O_2Na^+$ $[M + Na]^+$: 293.1512; found: 293.1512.

*(E)-(4,4-Bis(methoxymethyl)hept-1-en-6-yn-1-yl)benzene (**1e**).*[20] In a dry flask, 2-cinnamyl-2-(prop-2-yn-1-yl)propane-1,3-diol (200 mg, 0.87 mmol) was dissolved in anhydrous THF (2 mL), and NaH (80 mg, 2 mmol), MeI (135 mL, 2.17 mmol), and TBAI (48 mg, 0.13 mmol) were added sequentially. The suspension was stirred vigorously at rt for 24 h. TLC showed full consumption of starting material and conversion to diprotected alcohol with traces of monoprotection. The mixture was quenched by careful addition of saturated aqueous NH_4Cl (30 mL) and extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with brine (2 × 15 mL), dried over $MgSO_4$, and filtered, and the solvent was removed under vacuum. The resulting mixture was purified by column chromatography on silica gel eluting with c-hexane/EtOAc 10:1 to afford 210 mg of a colorless oil (94%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39−7.35 (m, 2H), 7.34−7.29 (m, 2H), 7.25−7.20 (m, 1H), 6.47 (d, J = 15.8 Hz, 1H), 6.23 (dt, J = 15.6, 7.7 Hz, 1H), 3.36 (s, 6H), 3.34−3.28 (m, 4H), 2.34 (dd, J = 7.7, 1.3 Hz, 2H), 2.27 (d, J = 2.7 Hz, 2H), 2.02 (t, J = 2.7 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.7, 133.1, 128.5, 127.0, 126.1, 125.7, 81.3, 74.3, 70.1, 59.3, 42.4, 35.4, 22.2 ppm. **HRMS-APCI** calcd for $C_{17}H_{23}O_2^+$ $[M + H]^+$: 259.1693; found: 259.1690.

*4,4′-(((2-Cinnamyl-2-(prop-2-yn-1-yl)propane-1,3diyl)bis(oxy))-bis(methylene)) Bis(methoxybenzene) (**1f**).*[20] In a dry flask, 2-cinnamyl-2-(prop-2-yn-1-yl)propane-1,3-diol (200 mg, 0.87 mmol) was dissolved in anhydrous THF (2 mL), and NaH (73 mg, 1.82 mmol), PMB-Cl (0.26 mL, 1.91 mmol), and TBAI (48 mg, 0.13 mmol) were added sequentially. The suspension was stirred vigorously at rt for 24 h. TLC showed full consumption of starting material and conversion to mono- and diprotected alcohols (diprotection major). The mixture was quenched by careful addition of saturated aqueous NH_4Cl (30 mL) and extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with brine (2 × 15 mL), dried over $MgSO_4$, and filtered, and the solvent was removed under vacuum. The resulting mixture was purified by column chromatography on silica gel eluting with c-hexane/EtOAc 10:1 to afford 230 mg of a colorless oil (64%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34−7.23 (m, 8H), 7.23−7.18 (m, 1H), 6.89−6.84 (m, 4H), 6.39 (d, J = 15.7 Hz, 1H), 6.12 (dt, J = 15.6, 7.7 Hz, 1H), 4.45 (s, 4H), 3.81 (s, 6H), 3.42−3.36 (m, 4H), 2.35 (dd, J = 7.7, 1.3 Hz, 2H), 2.31 (d, J = 2.7 Hz, 2H), 1.98 (t, J = 2.7 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.0, 137.7, 132.9, 130.8, 129.1, 128.4, 126.9, 126.1, 125.9, 113.7, 81.4, 72.9, 71.4, 70.2, 55.2, 42.6, 35.4, 22.4 ppm. **HRMS-ESI** calcd for $C_{31}H_{34}O_4Na^+$ $[M + Na]^+$: 493.2349; found: 493.2362.

General Procedure for the Aminocyclization of 1,6-Enynes (GP-I). Enyne (1 equiv) and aniline (1.1 equiv) were placed in a dry flask, and $[JohnPhosAu(MeCN)]SbF_6$ (**A**) (2 mol %) was added as a solution in anhydrous CH_2Cl_2 (overall 0.15 M). The solution was stirred vigorously at rt for 16 h.

*Dimethyl 3-Methylene-4-(phenyl(phenylamino)methyl)cyclopentane-1,1-dicarboxylate (**4a**).* Obtained using catalyst **A** (2.2 mg, 2.8 μmol), enyne **1a** (0.14 mL, 1.0 M in dry CH_2Cl_2, 0.14 mmol), and aniline (0.30 mL, 0.5 M in dry CH_2Cl_2, 0.154 mmol) as the nucleophile in CH_2Cl_2 (0.6 mL) according to General Procedure I. Preparative TLC (c-hexane/EtOAc 5:1) yielded 49 mg (93%) of the aminated product as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41−7.40 (m, 2H), 7.39−7.36 (m, 2H), 7.26 (tt, J = 4.2, 1.5 Hz, 1H), 7.10 (dd, J = 8.6, 7.4 Hz, 2H), 6.67 (tt, J = 7.4, 1.2 Hz, 1H), 6.54 (dd, J = 8.6, 1.2 Hz, 2H), 5.10−5.08 (m, 1H), 4.80−4.78 (m, 1H), 4.57 (d, J = 5.0 Hz, 1H), 4.34 (s, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 3.16−3.07 (m, 2H), 3.01−2.96 (m, 1H), 2.39−2.33 (m, 1H), 2.28−2.24 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.4, 171.8, 147.8, 147.2, 142.3, 129.0, 128.5, 127.0, 126.7, 117.5, 113.7, 109.1, 59.0, 58.2, 52.9, 52.8, 49.4, 42.0, 34.9 ppm. **HRMS-ESI** calcd for $C_{23}H_{26}NO_4^+$ $[M + H]^+$: 380.1856; found: 380.1865.

*Dimethyl 3-(((4-Methoxyphenyl)amino)(phenyl)methyl)-4-methylenecyclopentane-1,1-dicarboxylate (**4b**).* Obtained using catalyst **A** (5.6 mg, 7.4 μmol), enyne **1a** (42 mg, 0.15 mmol) and *p*-anisidine (19 mg, 0.16 mol) as the nucleophile in CH_2Cl_2 (1.0 mL) according to the General Procedure I. Purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded 28 mg (47%) of the aminated product as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38−7.18 (m, 5H), 6.70−6.65 (m, 2H), 6.47−6.42 (m, 2H), 5.06 (br s, 1H), 4.77 (br s, 1H), 4.44 (d, J = 4.6 Hz, 1H), 3.98 (s, 1H), 3.73 (s, 3H), 3.67 (s, 6H), 3.20−2.95 (m, 3H), 2.32 (dd, J = 13.6, 9.8 Hz, 1H), 2.23 (dd, J = 13.6, 8.7 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.4, 172.0, 152.2, 147.6, 142.6, 142.2, 128.7, 127.1, 126.9, 115.1, 114.8, 109.1, 60.0, 57.9, 55.8, 53.0, 52.9, 49.7, 42.1, 35.0 ppm. **HRMS-ESI** calcd for $C_{24}H_{28}NO_5^+$ $[M + H]^+$: 410.1962; found: 410.1984.

*Dimethyl 3-(((2-Bromophenyl)amino)(phenyl)methyl)-4-methylenecyclopentane-1,1-dicarboxylate (**4c**).* Obtained using catalyst **A** (2.2 mg, 2.8 μmol), enyne **1a** (0.14 mL, 1.0 M in dry CH_2Cl_2, 0.14 mmol), and 2-bromoaniline (26 mg, 0.15 mmol) as the nucleophile in CH_2Cl_2 (0.85 mL) according to General Procedure I. Preparative TLC (c-hexane/EtOAc 5:1) yielded 56 mg (87%) of the aminated product as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (dd, J = 7.9, 1.4 Hz, 1H), 7.35−7.31 (m, 4H), 7.27−7.24 (m, 1H), 6.99 (dt, J = 7.6, 1.4 Hz, 1H), 6.53 (dt, J = 7.6, 1.4 Hz, 1H), 6.36 (dd, J = 7.6, 1.4 Hz, 1H), 5.09 (m, 1H), 4.80 (d, J = 4.7 Hz, 1H), 4.72 (m, 1H), 4.52 (t, J = 5.3 Hz, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 3.18−3.16 (m, 1H), 3.03 (s, 2H), 2.45 (dd, J = 13.7, 8.2 Hz, 1H), 2.29 (dd, J = 13.7, 9.9 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.8, 171.7, 146.9, 144.3, 141.2, 132.2, 128.5, 128.2, 127.3, 126.8, 118.1, 112.9, 110.3, 109.9, 60.3, 58.1, 52.9, 52.8, 49.4, 42.1, 35.5 ppm. **HRMS-ESI** calcd for $C_{23}H_{25}BrNO_4^+$ $[M + H]^+$: 458.0961; found: 458.0969.

*Dimethyl 3-(((4-Bromophenyl)amino)(phenyl)methyl)-4-methylenecyclopentane-1,1-dicarboxylate (**4d**).* Obtained using catalyst **A** (5.7 mg, 7.4 μmol), enyne **1a** (42 mg, 0.15 mmol), and 4-bromoaniline (31 mg, 0.18 mol) as the nucleophile in CH_2Cl_2 (1.0 mL) according to General Procedure I. Purification by column chromatography (pentane/diethyl ether 9:1 to 4:1) yielded 50 mg (74%) of the aminated product as a white solid, which was further crystallized from Et_2O/pentane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40−7.22 (m, 5H), 7.18−7.14 (m, 2H), 6.43−6.36 (m, 2H), 5.08 (br s, 1H), 4.78 (br s, 1H), 4.55−4.50 (m, 2H), 3.78 (s, 3H), 3.71 (s, 3H), 3.14−3.05 (m, 2H), 2.99−2.92 (m, 1H), 2.35 (dd, J = 14.0, 9.3 Hz, 1H), 2.21 (dd, J = 14.0, 9.3 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.7, 171.9, 147.2, 146.9, 141.9, 131.8, 128.8, 127.3, 126.7, 115.3, 109.2, 109.1, 58.9, 57.7, 53.1, 52.9, 49.3, 42.2, 34.7 ppm. **HRMS-ESI** calcd for $C_{23}H_{25}BrNO_4^+$ $[M + H]^+$: 458.0961; found: 458.0971. **Mp** 124−126 °C.

*Dimethyl 3-(((2-Iodophenyl)amino)(phenyl)methyl)-4-methylenecyclopentane-1,1-dicarboxylate (**4e**).* Obtained using catalyst **A** (15 mg, 20 μmol), enyne **1a** (286 mg, 1 mmol), and 2-iodoaniline (234 mg, 1.07 mmol) as the nucleophile in CH_2Cl_2 (4 mL) according to General Procedure I. Purification by column chromatography (pentane/diethyl ether 9:1 to 4:1) yielded 489 mg (98%) of the aminated product as a colorless solid. Note: on 2.79 mmol scale, the reaction afforded the desired compound in 90% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 (dd, J = 7.8, 1.5 Hz, 1H), 7.36−7.30 (m, 4H), 7.28−7.22 (m, 1H), 7.00 (ddd, J = 8.2, 6.8, 1.5 Hz, 1H), 6.39 (ddd, J = 7.8, 7.3, 1.5 Hz, 1H), 6.27 (dd, J = 8.2, 1.5 Hz, 1H), 5.10 (q, J = 2.2 Hz, 1H), 4.76 (q, J = 2.2 Hz, 1H), 4.61 (d, J = 4.6 Hz, 1H), 4.52 (t, J = 5.1 Hz, 1H), 3.73 (s, 3H), 3.70 (s, 3H), 3.16 (dtt, J = 12.3, 5.5, 2.3 Hz, 1H), 3.11−2.99 (m, 2H), 2.42 (ddd, J = 13.7, 8.1, 1.4 Hz, 1H), 2.28 (dd, J = 13.7, 10.1 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.8, 171.7, 147.0, 146.4, 141.1, 138.8, 129.1, 128.6, 127.3, 126.8, 119.0, 112.2, 110.0, 86.2, 60.7, 58.2, 52.9, 52.8, 49.5, 42.1, 35.5 ppm. **HRMS-ESI** calcd for $C_{23}H_{24}INO_4Na^+$ $[M + Na]^+$: 528.0642, found 528.0637. **Mp** 129−131 °C.

*Dimethyl 3-(((4-Bromo-2-iodophenyl)amino)(phenyl)methyl)-4-methylenecyclopentane-1,1-dicarboxylate (**4f**).* Obtained using

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catalyst **A** (19 mg, 24 μmol), enyne **1a** (350 mg, 1.22 mmol), and 4-bromo-2-iodoaniline (401 mg, 1.35 mmol) as the nucleophile in CH_2Cl_2 (8 mL) according to General Procedure I. Purification by column chromatography (pentane/Et_2O 9:1) yielded 644 mg (90%) of the aminated product as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 2.3 Hz, 1H), 7.35−7.21 (m, 5H), 7.07 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.11 (d, *J* = 8.7 Hz, 1H), 5.10 (q, *J* = 2.2 Hz, 1H), 4.74 (q, *J* = 2.2 Hz, 1H), 4.61 (d, *J* = 4.5 Hz, 1H), 4.47 (t, *J* = 5.0 Hz, 1H), 3.72 (s, 3H), 3.69 (s, 3H), 3.18−3.11 (m, 1H), 3.03 (bs, 2H), 2.39 (dd, *J* = 13.7, 8.2 Hz, 1H), 2.24 (dd, *J* = 13.7, 10.2 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.9, 171.8, 147.1, 145.8, 140.7, 140.3, 132.0, 128.8, 127.7, 126.9, 113.3, 110.3, 109.4, 86.3, 60.9, 58.3, 53.1, 53.0, 49.5, 42.3, 35.6 ppm. **HRMS-ESI** calcd for $C_{23}H_{23}BrINO_4Na^+$ [M + Na]$^+$: 605.9747; found: 605.9747. **Mp** 123−125 °C.

*Dimethyl 3-(((5-Chloro-2-iodophenyl)amino)(phenyl)methyl)-4-methylenecyclopentane-1,1-dicarboxylate (**4g**).* Obtained using catalyst **A** (19 mg, 24 μmol), enyne **1a** (350 mg, 1.22 mmol), and 5-chloro-2-iodoaniline (341 mg, 1.35 mmol) as the nucleophile in CH_2Cl_2 (8 mL) according to General Procedure I. Purification by column chromatography (pentane/Et_2O 9:1) yielded 562 mg (85%) of the aminated product as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.3 Hz, 1H), 7.37−7.29 (m, 4H), 7.28−7.23 (m, 1H), 6.39 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.24 (d, *J* = 2.3 Hz, 1H), 5.09 (q, *J* = 2.1 Hz, 1H), 4.73 (q, *J* = 2.2 Hz, 1H), 4.68 (d, *J* = 5.0 Hz, 1H), 4.49 (t, *J* = 5.3 Hz, 1H), 3.72 (s, 3H), 3.69 (s, 3H), 3.20−3.12 (m, 1H), 3.05−2.99 (m, 2H), 2.42 (dd, *J* = 13.7, 8.1 Hz, 1H), 2.23 (dd, *J* = 13.7, 10.1 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.9, 171.8, 147.5, 147.0, 140.5, 139.4, 135.4, 128.9, 127.7, 126.9, 119.1, 112.2, 110.3, 83.2, 60.7, 58.3, 53.1, 53.0, 49.4, 42.3, 35.6 ppm. **HRMS-ESI** calcd for $C_{23}H_{23}ClINO_4Na^+$ [M + Na]$^+$: 562.0253; found: 562.0262. **Mp** 143−145 °C.

*Dimethyl 3-((Mesitylamino)(phenyl)methyl)-4-methylenecyclopentane-1,1-dicarboxylate (**4h**).* Obtained using catalyst **A** (2.2 mg, 2.8 μmol), enyne **1a** (0.14 mL, 1.0 M in dry CH_2Cl_2, 0.14 mmol), and 2,4,6-trimethylaniline (0.31 mL, 0.5 M in CH_2Cl_2, 0.15 mmol) as the nucleophile in CH_2Cl_2 (0.6 mL) according to General Procedure I. Preparative TLC (c-hexane/EtOAc 5:1) yielded 48 mg (82%) of the aminated product as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21−7.14 (m, 5H), 6.68 (s, 2H), 4.86 (d, *J* = 1.7 Hz, 1H), 4.36 (d, *J* = 1.7 Hz, 1H), 4.22 (d, *J* = 8.4 Hz, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 3.45 (s, 1H), 3.29−3.25 (m, 1H), 2.98−2.87 (m, 3H), 2.42 (dd, *J* = 13.8, 9.5 Hz, 1H), 2.16 (s, 3H), 2.10 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.2, 172.0, 148.2, 142.8, 141.5, 130.2, 129.6, 128.4, 128.0, 127.4, 127.0, 110.0, 64.0, 58.1, 52.9, 52.8, 47.9, 42.2, 37.8, 20.4, 19.3 ppm. **HRMS-ESI** calcd for $C_{26}H_{32}NO_4^+$ [M + H]$^+$: 422.2326; found: 422.2331.

*Dimethyl 3-(((3,5-Bis(trifluoromethyl)phenyl)amino)(phenyl)-methyl)-4-methylenecyclopentane-1,1-dicarboxylate (**4i**).* Obtained using catalyst **A** (5.7 mg, 7.4 μmol), enyne **1a** (41 mg, 0.14 mmol) and 3,5-bistrifluoromethylaniline (25 μL, 0.16 mol) as the nucleophile in CH_2Cl_2 (1.0 mL) according to General Procedure I. Purification by column chromatography (c-hexane/EtOAc 12:1) yielded 67 mg (89%) of the aminated product as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36−7.30 (m, 4H), 7.30−7.23 (m, 1H), 7.07 (br s, 1H), 6.85−6.81 (m, 2H), 5.27 (d, *J* = 4.6 Hz, 1H), 5.10−5.05 (m, 1H), 4.79−4.76 (m, 1H), 4.62 (dd, *J* = 4.6 Hz, 1H), 3.78 (s, 3H), 3.69 (s, 3H), 3.20−3.13 (m, 1H), 3.13−3.08 (m, 1H), 2.93−2.86 (m, 1H), 2.39 (dd, *J* = 14.2, 8.5 Hz, 1H), 2.18 (dd, *J* = 14.6, 10.4 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.2, 171.7, 148.6, 147.0, 140.7, 132.2 (q, *J* = 32.9 Hz), 129.1, 127.8, 126.6, 123.6 (q, *J* = 273.4 Hz), 112.7, 110.3 (sept, *J* = 4.1 Hz), 109.2, 58.4, 57.6, 53.4, 53.0, 48.8, 42.4, 34.4 ppm. **^{19}F NMR** (376.49 MHz, $CDCl_3$) δ −63.0 ppm. **HRMS-ESI** calcd for $C_{25}H_{23}F_6NO_4Na^+$ [M + Na]$^+$: 538.1423; found: 538.1437. **Mp** 143−145 °C.

*Dimethyl 3-Methylene-4-((naphthalen-1-ylamino)(phenyl)-methyl)cyclopentane-1,1-dicarboxylate (**4j**).* Obtained using catalyst **A** (2.2 mg, 2.8 μmol), enyne **1a** (0.14 mL, 1.0 M in dry CH_2Cl_2, 0.14 mmol), and naphtalen-1-amine (20 mg, 0.14 mmol) as the nucleophile in CH_2Cl_2 (0.8 mL) according to General Procedure I. Preparative TLC (c-hexane/EtOAc 5:1) yielded 31 mg (51%) of the aminated product as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (br d, *J* = 7.9 Hz, 1H), 7.80 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.54−7.44 (m, 4H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.28−7.24 (m, 1H), 7.21−7.14 (m, 2H), 6.33 (dd, *J* = 7.2, 1.2 Hz, 1H), 5.09 (d, *J* = 2.2 Hz, 1H), 4.85 (d, *J* = 2.2 Hz, 1H), 4.80 (d, *J* = 4.7 Hz, 1H), 3.82 (s, 3H), 3.73 (s, 3H), 3.32−3.28 (m, 1H), 3.15 (d, *J* = 16.2 Hz, 1H), 3.02 (dd, *J* = 16.2, 1.9 Hz, 1H), 2.58 (dd, *J* = 14.0, 9.6 Hz, 1H), 2.30 (dd, *J* = 14.0, 9.6 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.5, 171.8, 147.2, 142.6, 141.9, 134.2, 128.6, 127.1, 126.6, 126.4, 125.6, 124.7, 123.9, 120.2, 117.5, 109.1, 106.4, 58.7, 57.6, 52.9, 52.7, 49.4, 42.3, 34.7 ppm. **HRMS-ESI** calcd for $C_{27}H_{28}NO_4^+$ [M + H]$^+$: 430.2013; found: 430.2020.

*Dimethyl 3-Methylene-4-(phenyl(quinolin-8-ylamino)methyl)-cyclopentane-1,1-dicarboxylate (**4k**).* Obtained using catalyst **A** (2.2 mg, 2.8 μmol), enyne **1a** (0.14 mL, 1.0 M in dry CH_2Cl_2, 0.14 mmol), and quinolin-8-amine (20 mg, 0.14 mmol) as the nucleophile in CH_2Cl_2 (0.8 mL) according to General Procedure I. Preparative TLC (c-hexane/EtOAc 5:1) yielded 28 mg (46%) of the aminated product as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.79 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.05 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.38 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.24−7.19 (m, 2H), 7.01 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.78 (d, *J* = 6.0 Hz, 1H), 6.45 (dd, *J* = 7.6, 0.8 Hz, 1H), 5.01 (d, *J* = 2.0 Hz, 1H), 4.62 (t, *J* = 6.4 Hz, 1H), 4.58 (d, *J* = 2.0 Hz, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 3.29−3.25 (m, 1H), 3.13 (qd, *J* = 16.4, 2.4 Hz, 1H), 3.01 (qd, *J* = 16.4, 2.4 Hz, 1H), 2.63 (ddd. *J* = 14.0, 9.6, 1.6, Hz, 1H), 2.39 (dd, *J* = 14.0, 9.6 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 171.8, 147.1, 147.0, 143.9, 142.0, 138.4, 135.9, 128.5, 128.4, 127.5, 127.2, 127.1, 121.3, 114.2, 109.9, 106.2, 60.3, 58.4, 52.8, 49.4, 41.9, 36.2 ppm. **HRMS-ESI** calcd for $C_{26}H_{27}N_2O_4^+$ [M + H]$^+$: 431.1965; found: 431.1954.

*Dimethyl 3-((Methyl(phenyl)amino)(phenyl)methyl)-4-methylenecyclopentane-1,1-dicarboxylate (**4l**).* Obtained using catalyst **A** (2.2 mg, 2.8 μmol), enyne **1a** (0.14 mL, 1.0 M in dry CH_2Cl_2, 0.14 mmol), and *N*-methylaniline (0.3 mL, 0.5 M in dry CH_2Cl_2, 0.15 mmol) as the nucleophile in CH_2Cl_2 (0.6 mL) according to General Procedure I. Preparative TLC (c-hexane/EtOAc 5:1) yielded 50 mg (92%) of the aminated product as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27−7.23 (m, 7H), 6.89−6.86 (m, 2H), 6.75 (tt, *J* = 7.2, 1.0 Hz, 1H), 4.86−4.81 (m, 2H), 4.22 (d, *J* = 2.1 Hz, 1H), 3.79 (s, 3H), 3.70 (s, 3H), 3.60−3.57 (m, 1H), 3.24 (qd, *J* = 16.5, 2.1 Hz, 1H), 3.01 (dd, *J* = 16.6, 2.1 Hz, 1H), 2.74 (ddd, *J* = 13.5, 7.7, 1.5 Hz, 1H), 2.67 (s, 3H), 2.12 (dd, *J* = 13.5, 9.9 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.4, 171.9, 150.1, 148.6, 138.9, 129.2, 128.1, 128.0, 127.3, 117.3, 113.9, 109.8, 65.7, 57.6, 52.9, 52.8, 43.4, 41.8, 38.6, 31.8 ppm. **HRMS-ESI** calcd for $C_{24}H_{28}NO_4^+$ [M + H]$^+$: 394.2013; found: 394.2026.

*N-(2-(2-Methylene-4,4-bis(phenylsulfonyl)cyclopentyl)propan-2-yl)aniline (**4m**).* Obtained using catalyst **A** (1.9 mg, 2.5 μmol), enyne **1b** (0.12 mL, 1.0 M in dry CH_2Cl_2, 0.12 mmol), and aniline (0.25 mL, 0.5 M in CH_2Cl_2, 0.124 mmol) as the nucleophile in CH_2Cl_2 (0.6 mL) according to General Procedure I. Preparative TLC (c-hexane/EtOAc 5:1) yielded 58 mg (94%) of the aminated product as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 6.4, 0.8 Hz, 2H), 7.97 (dd, *J* = 5.6, 0.8 Hz, 2H), 7.75−7.69 (m, 2H), 7.62 (t, *J* = 6.0 Hz, 2H), 7.54 (t, *J* = 6.4 Hz, 2H), 7.19 (dd, *J* = 6.8, 6.0 Hz, 2H), 6.81 (t, *J* = 6.0 Hz, 2H), 6.68 (dd, *J* = 7.2, 6.8 Hz, 1H), 5.02 (br s, 2H), 3.63 (br s, 1H), 3.55 (qd, *J* = 14.0, 2.0 Hz, 1H), 3.35 (dt, *J* = 14.0, 2.0 Hz, 1H), 2.91−2.82 (m, 2H), 2.67 (ddd, *J* = 12.4, 7.2, 1.2, Hz, 1H), 1.39 (s, 3H), 1.30 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.6, 145.8, 137.2, 135.8, 134.7, 134.5, 131.0, 130.9, 129.2, 128.7, 128.6, 118.5, 116.8, 111.3, 91.7, 56.4, 50.2, 41.0, 33.6, 26.2, 25.4 ppm. **HRMS-ESI** calcd for $C_{27}H_{30}NO_4S_2^+$ [M + H]$^+$: 496.1611; found: 496.1638.

*4-Methoxy-N-(2-(2-methylene-4,4-bis(phenylsulfonyl)-cyclopentyl)propan-2-yl)aniline (**4n**).* Obtained using catalyst **A** (1.9 mg, 2.5 μmol), enyne **1b** (0.12 mL, 1.0 M in dry CH_2Cl_2, 0.12 mmol), and 4-methoxyaniline (15 mg, 0.12 mmol) as the nucleophile in CH_2Cl_2 (0.8 mL) according to General Procedure I. Preparative TLC (c-hexane/EtOAc 5:1) yielded 59 mg (90%) of the aminated product as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.0, 0.8 Hz, 2H), 7.99 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.75−7.71 (m, 2H), 7.62 (t, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 8.0 Hz, 2H), 6.78 (d, *J* = 9.2 Hz, 2H), 6.72

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(d, J = 9.2 Hz, 2H), 5.08 (s, 1H), 5.04 (s, 1H), 3.80 (s, 3H), 3.56 (qd, J = 17.2, 2.4 Hz, 1H), 3.16 (dt, J = 8.4, 2.0 Hz, 1H), 2.92−2.83 (m, 2H), 2.69 (ddd, J = 16.8, 8.8, 1.2, Hz, 1H), 1.27 (s, 3H), 1.20 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.9, 146.8, 139.1, 137.2, 135.9, 134.6, 134.5, 131.0, 131.0, 128.7, 128.6, 121.4, 114.4, 111.4, 91.8, 57.0, 55.6, 51.3, 40.9, 33.8, 26.2, 25.3 ppm. **HRMS-ESI** calcd for $C_{28}H_{32}NO_5S_2^+$ $[M + H]^+$: 526.1716; found: 526.1726.

*2-Bromo-N-(2-(2-methylene-4,4-bis(phenylsulfonyl)cyclopentyl)-propan-2-yl)aniline (**4o**).* Obtained using catalyst **A** (1.9 mg, 2.5 μmol), enyne **1b** (0.12 mL, 1.0 M in dry CH_2Cl_2, 0.12 mmol), and 2-bromoaniline (21 mg, 0.124 mmol) as the nucleophile in CH_2Cl_2 (0.8 mL) according to General Procedure I. Preparative TLC (c-hexane/EtOAc 5:1) yielded 53 mg (74%) of the aminated product as a colorless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (dd, J = 8.8, 1.2 Hz, 2H), 8.01 (dd, J = 8.8, 1.2 Hz, 2H), 7.74−7.70 (m, 2H), 7.63−7.54 (m, 4H), 7.46 (dd, J = 7.6, 1.2 Hz, 1H), 7.15 (dt, J = 8.4, 2.0 Hz, 1H), 6.90 (dd, J = 8.4, 2.4 Hz, 1H), 6.61 (dt, J = 8.0, 1.2 Hz, 1H), 5.06 (s, 1H), 5.00 (s, 1H), 4.43 (br s, 1H), 3.61 (qd, J = 17.2, 2.4 Hz, 1H), 3.47 (t, J = 7.6 Hz, 1H), 2.84 (d, J = 17.6 Hz, 1H), 2.73 (dd, J = 15.6, 8.4 Hz, 1H), 2.58 (ddd, J = 15.6, 9.2, 1.6 Hz, 1H), 1.49 (s, 3H), 1.34 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.4, 142.7, 137.0, 135.7, 134.7, 134.6, 132.9, 131.1, 131.0, 128.7, 128.7, 128.2, 118.5, 114.5, 111.9, 111.5, 91.7, 56.7, 49.4, 40.7, 33.7, 26.2, 25.2 ppm. **HRMS-ESI** calcd for $C_{27}H_{28}BrNO_4S_2Na^+$ $[M + Na]^+$: 596.0535; found: 596.0566. **Mp** 191−192 °C.

*4-Bromo-N-(2-(2-methylene-4,4-bis(phenylsulfonyl)cyclopentyl)-propan-2-yl)aniline (**4p**).* Obtained using catalyst **A** (1.9 mg, 2.5 μmol), enyne **1b** (0.12 mL, 1.0 M in dry CH_2Cl_2, 0.124 mmol), and 4-bromoaniline (21.4 mg, 0.12 mmol) as the nucleophile in CH_2Cl_2 (0.8 mL) according to General Procedure I. Preparative TLC (c-hexane/EtOAc 5:1) yielded 67 mg (93%) of the aminated product as a colorless foam. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (dd, J = 8.4, 1.2 Hz, 2H), 7.05 (dd, J = 8.4, 1.2 Hz, 2H), 7.76−7.70 (m, 2H), 7.64−7.53 (m, 4H), 7.27−7.25 (m, 2H), 6.58−6.55 (m, 2H), 5.03 (s, 1H), 5.00 (s, 1H), 3.70 (br s, 1H), 3.53 (qd, J = 17.2, 2.4 Hz, 1H), 3.32 (dt, J = 8.4, 2.4 Hz, 1H), 2.87 (d, J = 17.2 Hz, 1H), 2.79 (dd, J = 15.6, 8.8, Hz 1H), 2.62 (ddd, J = 15.6, 8.8, 1.6 Hz, 1H), 1.48 (s, 3H), 1.33 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.5, 144.9, 137.1, 135.7, 134.7, 134.6, 132.0, 131.9, 131.0, 128.7, 128.6, 118.1, 116.7, 111.3, 91.6, 56.5, 49.9, 41.0, 33.5, 26.1, 25.3 ppm. **HRMS-ESI** calcd for $C_{27}H_{27}BrNO_4S_2^-$ $[M - H]^-$: 572.0570; found: 572.0593. **Mp** 116−118 °C.

*N-(2-(2-Methylene-4,4-bis(phenylsulfonyl)cyclopentyl)propan-2-yl)-3,5-bis(trifluoromethyl)aniline (**4q**).* Obtained using catalyst **A** (1.9 mg, 2.5 μmol), enyne **1b** (0.12 mL, 1.0 M in dry CH_2Cl_2, 0.12 mmol) and 3,5-bis(trifluoromethyl)aniline (0.25 mL, 0.5 M in CH_2Cl_2, 0.12 mmol) as the nucleophile in CH_2Cl_2 (0.6 mL) according to General Procedure I. Preparative TLC (c-hexane/EtOAc 5:1) yielded 38 mg (48%) of the aminated product as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (dd, J = 8.4, 1.2 Hz, 2H), 7.98 (dd, J = 8.4, 1.2 Hz, 2H), 7.77−7.69 (m, 2H), 7.64−7.61 (m, 2H), 7.56−7.52 (m, 2H), 7.21 (br s, 1H), 7.00 (br s, 2H), 5.02 (s, 1H), 4.93 (s, 1H), 4.20 (s, 1H), 3.54 (qd, J = 17.6, 2.4, Hz, 1H), 3.24 (t, J = 9.2 Hz, 1H), 2.97 (d, J = 17.6 Hz, 1H), 2.83 (dd, J = 16.0, 8.4 Hz, 1H), 2.67 (ddd, J = 16.0, 8.4, 1.6 Hz, 1H), 1.45 (s, 3H), 1.38 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.6, 146.1, 137.0, 135.8, 134.9, 134.7, 132.4 (q, J = 32.0 Hz), 131.0, 130.9, 128.8, 128.7, 123.4 (q, J = 271.0 Hz), 114.4 (q, J = 4.0 Hz), 111.8, 110.8 (sept, J = 4.0 Hz), 92.3, 56.7, 50.2, 41.0, 33.3, 25.9, 25.2 ppm. **HRMS-ESI** calcd for $C_{29}H_{26}F_6NO_4S_2^-$ $[M - H]^-$: 630.1213; found: 630.1215.

*N-(2-(2-Methylene-4,4-bis(phenylsulfonyl)cyclopentyl)propan-2-yl)naphthalen-1-amine (**4r**).* Obtained using catalyst **A** (1.9 mg, 2.5 μmol), enyne **1b** (0.12 mL, 1.0 M in dry CH_2Cl_2, 0.12 mmol), and naphtalen-1-amine (18 mg, 0.12 mmol) as the nucleophile in CH_2Cl_2 (0.8 mL) according to General Procedure I. Preparative TLC (c-hexane/EtOAc 5:1) yielded 50 mg (74%) of the aminated product as a colorless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (dd, J = 8.4, 1.2 Hz, 2H), 7.98 (dd, J = 8.4, 1.2 Hz, 2H), 7.84−7.80 (m, 2H), 7.71−7.66 (m, 2H), 7.56−7.47 (m, 6H), 7.36−7.31 (m, 2H), 6.87 (dd, J = 7.2, 1.6 Hz, 1H), 5.04 (br s, 1H), 4.98 (br s, 1H), 4.39 (br s, 1H), 3.65−3.60 (m, 2H), 2.91−2.85 (m, 2H), 2.64 (ddd, J = 15.6, 8.8, 1.6 Hz, 1H), 1.53 (s, 3H), 1.45 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.7, 140.9, 137.2, 135.8, 134.7, 134.6, 134.5, 131.0, 130.9, 128.7, 128.6, 125.6, 125.0, 124.9, 119.9, 118.3, 111.4, 109.1, 91.7, 56.5, 49.7, 40.9, 33.7, 26.1, 25.4 ppm. **HRMS-ESI** calcd for $C_{31}H_{31}NO_4S_2Na^+$ $[M + Na]^+$: 568.1587; found: 568.1591. **Mp** 89−92 °C.

*N-(2-(2-Methylene-4,4-bis(phenylsulfonyl)cyclopentyl)propan-2-yl)quinolin-8-amine (**4s**).* Obtained using catalyst **A** (1.9 mg, 2.5 μmol), enyne **1b** (0.12 mL, 1.0 M in dry CH_2Cl_2, 0.12 mmol), and quinolin-8-amine (20 mg, 0.12 mmol) as the nucleophile in CH_2Cl_2 (0.8 mL) according to General Procedure I. Preparative TLC (c-hexane/EtOAc 5:1) yielded slightly contaminated product. Recrystallization from c-hexane/EtOAc yielded 49 mg (72%) of the pure aminated product as a pale yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.77 (dd, J = 4.0, 1.6 Hz, 1H), 8.07 (dd, J = 8.4, 2.0 Hz, 1H), 8.04 (dd, J = 8.8, 1.2 Hz, 2H), 7.98 (dd, J = 8.8, 1.2 Hz, 2H), 7.71−7.41 (m, 6H), 7.38 (dd, J = 8.4, 4.4 Hz, 1H), 7.34 (t, J = 8.4 Hz, 1H), 7.08 (dd, J = 8.0, 0.8 Hz, 1H), 6.89 (dd, J = 8.4, 0.8 Hz, 1H), 6.66 (s, 1H), 5.04 (s, 1H), 4.97 (s, 1H), 3.69−3.59 (m, 2H), 2.86−2.77 (m, 2H), 2.53 (ddd, J = 15.6, 8.8, 1.6 Hz), 1.57 (s, 3H), 1.45 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.8, 146.7, 142.0, 138.6, 137.0, 136.2, 135.6, 134.7, 134.5, 131.0, 130.9, 130.8, 129.6, 129.1, 128.9, 128.7, 128.6, 128.5, 127.5, 121.4, 114.3, 111.2, 107.2, 91.6, 55.9, 48.4, 40.8, 33.6, 25.8, 25.0 ppm. **HRMS-ESI** calcd for $C_{30}H_{31}N_2O_4S_2^+$ $[M + H]^+$: 547.1720; found: 547.1720. **Mp** 82−85 °C.

*N-Methyl-N-(2-(2-methylene-4,4-bis(phenylsulfonyl)cyclopentyl)-propan-2-yl)aniline (**4t**).* Obtained using catalyst **A** (1.9 mg, 2.5 μmol), enyne **1b** (0.12 mL, 1.0 M in dry CH_2Cl_2, 0.12 mmol), and *N*-methylaniline (0.25 mL, 0.5 M in CH_2Cl_2, 0.12 mmol) as the nucleophile in CH_2Cl_2 (0.6 mL) according to General Procedure I. Preparative TLC (c-hexane/EtOAc 5:1) yielded 53 mg (83%) of the aminated product as a colorless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (dd, J = 7.6, 1.2 Hz, 2H), 8.07 (dd, J = 7.6, 1.2 Hz, 2H), 7.77−7.71 (m, 2H), 7.66−7.58 (m, 4H), 7.33−7.30 (m, 2H), 7.17−7.14 (m, 3H), 5.12 (s, 1H), 5.05 (s, 1H), 3.56 (qd, J = 17.2, 2.0 Hz, 1H), 3.22 (t, J = 7.6 Hz, 1H), 3.08 (dd, J = 15.6, 8.0 Hz, 1H), 2.80 (d, J = 17.2 Hz, 1H), 2.72−2.69 (m, 1H+3H), 1.18 (s, 3H), 0.85 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.5, 147.3, 137.3, 135.9, 134.6, 134.5, 131.1, 131.0, 128.7, 128.6, 128.2, 128.1, 124.4, 111.3, 91.9, 60.4, 50.4, 40.9, 36.4, 34.0, 21.8, 20.7 ppm. **HRMS-ESI** calcd for $C_{28}H_{31}NO_4S_2Na^+$ $[M + Na]^+$: 532.1587; found: 532.1586. **Mp** 171−172 °C.

*Dimethyl 3-Methylene-4-(2-(phenylamino)propan-2-yl)cyclopentane-1,1-dicarboxylate (**4u**).* Obtained using catalyst **A** (2.2 mg, 2.8 μmol), enyne **1c** (35 mg, 0.15 mmol), and aniline (15 μL, 0.16 mol) as the nucleophile in CH_2Cl_2 (1.0 mL) according to General Procedure I. Purification by column chromatography (c-hexane/EtOAc 13:1) yielded 40 mg (83%) of the aminated product as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17−7.11 (m, 2H), 6.76−6.69 (m, 3H), 5.07 (br s, 1H), 4.97 (br s, 1H), 3.72 (s, 3H), 3.70 (s, 3H), 3.61 (br s, 1H), 3.23−3.19 (m, 1H), 2.94−2.84 (m, 2H), 2.63 (ddd, J = 13.5, 8.4, 1.2 Hz, 1H), 2.05 (dd, J = 13.5, 9.4 Hz, 1H), 1.31 (s, 3H), 1.29 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.0, 171.9, 148.5, 146.3, 129.2, 118.3, 117.2, 111.1, 58.6, 56.3, 52.8, 49.1, 44.0, 36.4, 27.0, 25.9, 25.8 ppm. **HRMS-ESI** calcd for $C_{19}H_{26}NO_4^+$ $[M + H]^+$: 332.1856; found: 332.1857.

*Dimethyl 3-(2-((4-Methoxyphenyl)amino)propan-2-yl)-4-methylenecyclopentane-1,1-dicarboxylate (**4v**).* Obtained using catalyst **A** (2.3 mg, 3.0 μmol), enyne **1c** (36 mg, 0.15 mmol), and *p*-anisidine (20 mg, 0.16 mmol) as the nucleophile in CH_2Cl_2 (1 mL) according to General Procedure I. Purification by column chromatography (c-hexane/EtOAc 8:1) yielded 44 mg (81%) of the aminated product as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.75 (br s, 4H), 5.10 (br s, 1H), 5.04 (br s, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 3.71 (s, 3H), 3.16 (br s, 1H), 3.03−2.83 (m, 3H), 2.64 (ddd, J = 13.4, 8.5, 1.7 Hz, 1H), 2.12 (dd, J = 13.4, 9.3 Hz, 1H), 1.21 (s, 3H), 1.19 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.1, 172.0, 154.0, 148.7, 139.4, 122.0, 114.4, 111.3, 58.7, 56.9, 55.6, 52.8, 50.4, 44.0, 36.4, 27.0,

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25.9, 25.7 ppm. **HRMS-ESI** calcd for $C_{20}H_{27}NO_5Na^+$ $[M + Na]^+$: 384.1781; found: 384.1801.

*Dimethyl 3-(2-((2-Bromophenyl)amino)propan-2-yl)-4-methylenecyclopentane-1,1-dicarboxylate (**4w**).* Obtained using catalyst **A** (34 mg, 0.04 mmol), enyne **1c** (525 mg, 2.20 mmol), and 2-bromoaniline (417 mg, 2.42 mmol) as the nucleophile in CH_2Cl_2 (14 mL) according to General Procedure I. Purification by column chromatography (pentane/Et_2O 9:1) yielded 649 mg (72%) of the aminated product as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 (dd, J = 7.9, 1.5 Hz, 1H), 7.12 (ddd, J = 8.6, 7.4, 1.6 Hz, 1H), 6.95 (dd, J = 8.3, 1.5 Hz, 1H), 6.55 (ddd, J = 7.9, 7.3, 1.5 Hz, 1H), 5.08 (t, J = 2.3 Hz, 1H), 4.91 (ddt, J = 2.9, 1.8, 0.9 Hz, 1H), 4.43 (s, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 3.27 (ddd, J = 9.4, 8.5, 2.0 Hz, 1H), 2.95 (dq, J = 15.3, 2.6 Hz, 1H), 2.88 (ddt, J = 15.2, 1.9, 1.1 Hz, 1H), 2.62 (ddd, J = 13.6, 8.6, 1.9 Hz, 1H), 2.02 (dd, J = 13.6, 9.5 Hz, 1H), 1.38 (s, 3H), 1.36 (s, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.0, 171.9, 147.9, 143.3, 133.0, 128.2, 118.1, 114.8, 112.1, 111.5, 58.7, 56.7, 52.9, 48.8, 44.1, 36.4, 25.7, 25.6 ppm. **HRMS-ESI** calcd for $C_{19}H_{24}BrNO_4Na^+$ $[M + Na]^+$: 432.0781; found: 432.0785.

*Dimethyl 3-(2-((4-Bromophenyl)amino)propan-2-yl)-4-methylenecyclopentane-1,1-dicarboxylate (**4x**).* Obtained using catalyst **A** (2.3 mg, 3.0 μmol), enyne **1c** (35 mg, 0.15 mmol), and 4-bromoaniline (28 mg, 0.16 mmol) as the nucleophile in CH_2Cl_2 (1.0 mL) according to General Procedure I. Purification by column chromatography (c-hexane/EtOAc 9:1) yielded 37 mg (62%) of the aminated product as a colorless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27−7.24 (m, 2H), 6.65−6.58 (m, 2H), 5.09 (br s, 1H), 4.95 (br s, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 3.69 (br s, 1H), 3.23−3.17 (m, 1H), 2.90 (br s, 2H), 2.62 (dd, J = 13.5, 8.4 Hz, 1H), 2.03 (dd, J = 13.5, 9.3 Hz, 1H), 1.32 (s, 3H), 1.29 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.0, 171.8, 148.3, 145.4, 132.0, 118.4, 111.2, 110.1, 58.6, 56.4, 52.9, 48.9, 44.0, 36.4, 25.8 ppm. **HRMS-ESI** calcd for $C_{19}H_{25}BrNO_4^+$ $[M + H]^+$: 410.0961; found: 410.0947. **Mp** 116−118 °C.

*Dimethyl 3-(2-((2-Iodophenyl)amino)propan-2-yl)-4-methylenecyclopentane-1,1-dicarboxylate (**4y**).* Obtained using catalyst **A** (34.2 mg, 0.04 mmol), enyne **1c** (500 mg, 2.1 mmol), and 2-iodoaniline (492 mg, 2.25 mmol) as the nucleophile in CH_2Cl_2 (6.0 mL) according to General Procedure I. Purification by column chromatography (pentane/Et_2O 10:1 to 4:1) yielded 553 mg (58%) of the aminated product as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 (dd, J = 7.9, 1.6 Hz, 1H), 7.16 (ddd, J = 8.5, 7.2, 1.6 Hz, 1H), 6.91 (dd, J = 8.4, 1.5 Hz, 1H), 6.42 (ddd, J = 8.0, 7.3, 1.4 Hz, 1H), 5.10 (br s, 1H), 4.92 (br s, 1H), 4.25 (s, 1H), 3.74 (s, 3H), 3.72 (s, 3H), 3.31−3.25 (m, 1H), 2.97 (dq, J = 15.2, 2.6 Hz, 1H), 2.90 (d, J = 15.3 Hz, 1H), 2.63 (ddd, J = 13.7, 8.6, 2.0 Hz, 1H), 2.04 (dd, J = 13.6, 9.5 Hz, 1H), 1.40 (s, 3H), 1.36 (s, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.7, 171.7, 147.7, 145.4, 139.6, 129.0, 118.8, 113.8, 111.4, 88.7, 58.5, 56.9, 52.7, 48.6, 43.9, 36.2, 25.6, 25.3 ppm. **HRMS-ESI** calcd for $C_{19}H_{24}INO_4Na^+$ $[M + Na]^+$: 480.0642, found 480.0638.

*Dimethyl 3-(2-((4-Acetylphenyl)amino)propan-2-yl)-4-methylenecyclopentane-1,1-dicarboxylate (**4z**).* Obtained using catalyst **A** (2.3 mg, 2.9 μmol), enyne **1c** (0.15 mL, 1.0 M in dry CH_2Cl_2, 0.15 mmol), and 1-(4-aminophenyl)ethanone (20 mg, 0.15 mmol) as the nucleophile in CH_2Cl_2 (0.8 mL) according to General Procedure I. Preparative TLC (c-hexane/EtOAc 5:1) yielded 40 mg (74%) of the aminated product as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87−7.85 (m, 2H), 6.69−6.66 (m, 2H), 5.09 (s, 1H), 4.91 (s, 1H), 4.31 (s, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 3.37 (t, J = 9.2 Hz, 1H), 2.92 (s, 2H), 2.65 (dd, J = 13.6, 8.8 Hz, 1H), 2.51 (s, 3H), 2.00 (dd, J = 13.6, 8.8 Hz, 1H), 1.41 (s, 3H), 1.39 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.2, 171.8, 171.6, 150.5, 147.9, 130.7, 126.6, 113.7, 111.0, 58.4, 56.3, 52.8, 48.0, 43.9, 36.2, 26.0, 25.5, 25.4 ppm. **HRMS-ESI** calcd for $C_{21}H_{26}NO_5^-$ $[M - H]^-$: 372.1816; found: 372.1817.

*Dimethyl 3-(2-((3,5-Bis(trifluoromethyl)phenyl)amino)propan-2-yl)-4-methylenecyclopentane-1,1-dicarboxylate (**4aa**).* Obtained using catalyst **A** (2.4 mg, 3 μmol), enyne **1c** (35 mg, 0.14 mmol), and 3,5-bis(trifluoromethyl)aniline (25 μL, 0.16 mmol) as the nucleophile in CH_2Cl_2 (1.0 mL) according to General Procedure I. Preparative TLC (c-hexane/EtOAc 15:1) yielded 28 mg (42%) of the aminated product as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 (s, 1H), 7.04 (s, 2H), 5.15−5.12 (m, 1H), 4.99−4.96 (m, 1H), 4.17 (br s, 1H), 3.74 (s, 3H), 3.72 (s, 3H), 3.18 (dddd, J = 10.3, 8.6, 4.0, 2.0 Hz, 1H), 2.94 (dq, J = 15.3, 1.2 Hz, 1H), 2.88 (dq, J = 15.4, 2.6 Hz, 1H), 2.62 (ddd, J = 13.6, 8.5, 1.8 Hz, 1H), 2.04 (dd, J = 13.6, 9.6 Hz, 1H), 1.40 (s, 3H), 1.36 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.7, 171.5, 147.8, 147.0, 132.3 (q, J = 32.7 Hz), 123.5 (q, J = 272.7 Hz), 114.6 (app. d, J = 4.2 Hz), 111.4, 110.5 (quintet, J = 3.7 Hz), 58.3, 56.5, 52.8, 52.8, 49.0, 43.8, 36.1, 25.6, 25.3 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ − 63.3 ppm. **HRMS-ESI** calcd for $C_{21}H_{23}F_6NO_4Na^+$ $[M + Na]^+$: 490.1423; found: 490.1430.

*Dimethyl 3-Methylene-4-(2-(naphthalen-1-ylamino)propan-2-yl)cyclopentane-1,1-dicarboxylate (**4ab**).* Obtained using catalyst **A** (2.3 mg, 2.9 μmol), enyne **1c** (0.15 mL, 1.0 M in dry CH_2Cl_2, 0.15 mmol), and naphtalen-1-amine (21 mg, 0.15 mmol) as the nucleophile in CH_2Cl_2 (0.8 mL) according to General Procedure I. Preparative TLC (c-hexane/EtOAc 5:1) yielded 44 mg (78%) of the aminated product as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82−7.78 (m, 2H), 7.48−7.43 (m, 2H), 7.34 (t, J = 8.0 Hz, 1H), 7.26 (d, J = 8.0 Hz, 1H), 6.97 (d, J = 7.6 Hz, 1H), 5.10 (br s, 1H), 4.94 (br s, 1H), 4.41 (s, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 3.48 (dt, J = 9.2, 1.6 Hz, 1H), 3.03−2.92 (m, 2H), 2.72 (ddd, J = 13.6, 8.8, 1.6 Hz, 1H), 2.14 (dd, J = 13.6, 8.8 Hz, 1H), 1.47 (s, 3H), 1.46 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 171.8, 148.3, 140.9, 134.7, 128.9, 126.2, 125.5, 125.1, 124.8, 120.1, 117.9, 111.2, 109.3, 58.6, 55.5, 52.8, 48.7, 44.0, 36.4, 25.5 ppm. **HRMS-ESI** calcd for $C_{23}H_{28}NO_4^+$ $[M + H]^+$: 382.2013; found: 382.2022.

*Dimethyl 3-Methylene-4-(2-(quinolin-8-ylamino)propan-2-yl)-cyclopentane-1,1-dicarboxylate (**4ac**).* Obtained using catalyst **A** (2.3 mg, 2.94 μmol), enyne **1c** (0.15 mL, 1.0 M in dry CH_2Cl_2, 0.15 mmol), and quinolin-8-amine (21 mg, 0.15 mmol) as the nucleophile in CH_2Cl_2 (0.8 mL) according to General Procedure I. Preparative TLC (c-hexane/EtOAc 5:1) yielded 45 mg (81%) of the aminated product as a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.71 (dd, J = 4.0, 1.6 Hz, 1H), 8.05 (dd, J = 8.4, 1.6 Hz, 1H), 7.38−7.33 (m, 2H), 7.05 (d, J = 8.0 Hz, 1H), 6.98 (d, J = 8.4 Hz, 1H), 6.65 (s, 1H), 5.05 (s, 1H), 4.89 (s, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.59−3.55 (m, 1H), 3.01 (qd, J = 15.2, 2.0 Hz, 1H), 2.92 (d, J = 15.2 Hz, 1H), 2.66 (ddd, J = 13.6, 8.4, 1.6 Hz, 1H), 2.07 (dd, J = 13.6, 8.4 Hz, 1H), 1.57 (s, 3H), 1.53 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 171.8, 148.1, 146.6, 142.3, 138.7, 136.1, 128.9, 127.5, 121.2, 113.5, 110.9, 106.9, 58.6, 55.6, 52.7, 47.5, 44.0, 36.3, 30.9, 25.2, 25.0 ppm. **HRMS-ESI** calcd for $C_{22}H_{27}N_2O_4^+$ $[M + H]^+$: 383.1965; found: 383.1975.

*Dimethyl 3-(2-(Methyl(phenyl)amino)propan-2-yl)-4-methylenecyclopentane-1,1-dicarboxylate (**4ad**).* Obtained using catalyst **A** (3.2 mg, 4.2 μmol), enyne **1c** (0.21 mL, 1.0 M in dry CH_2Cl_2, 0.21 mmol), and *N*-methylaniline (0.46 mL, 0.5 M in CH_2Cl_2, 0.23 mmol) as the nucleophile in CH_2Cl_2 (0.5 mL) according to General Procedure I. Preparative TLC (c-hexane/EtOAc 5:1) yielded 61 mg (85%) of the aminated product as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25−7.23 (m, 2H), 7.19−7.14 (m, 2H), 7.13−7.08 (m, 1H), 5.14 (br s, 1H), 5.08 (br s, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 3.10−3.05 (m, 1H), 2.97−2.84 (m, 2H), 2.73 (s, 3H), 2.63 (ddd, J = 13.8, 8.6, 1.7 Hz, 1H), 2.21 (dd, J = 13.8, 9.3 Hz, 1H), 1.08 (s, 3H), 0.89 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 171.8, 150.9, 148.9, 128.3, 128.0, 124.1, 110.8, 60.0, 58.4, 52.7, 48.8, 44.0, 36.6, 36.3, 21.5, 20.8 ppm. **HRMS-ESI** calcd for $C_{20}H_{28}NO_4^+$ $[M + H]^+$: 346.2013; found: 346.2015.

*Dimethyl 3-(2-(Allyl(phenyl)amino)propan-2-yl)-4-methylenecyclopentane-1,1-dicarboxylate (**4ae**).* Obtained using catalyst **A** (11 mg, 15.0 μmol), enyne **1c** (0.29 mL, 1.0 M in dry CH_2Cl_2, 0.29 mmol), and *N*-allylaniline (70 mg, 0.29 mmol) as the nucleophile in CH_2Cl_2 (1.5 mL) according to General Procedure I. Flash column chromatography (c-hexane/EtOAc 5:1) yielded 54 mg (49%) of the aminated product as a colorless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (t, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.11 (t, J = 8.0 Hz, 1H), 5.66−5.58 (m, 1H), 5.16 (s, 1H), 5.11 (s, 1H), 4.98 (dd, J = 17.5, 1.5 Hz, 1H), 4.85 (dd, J = 17.5, 1.5 Hz, 1H), 3.79 (s, 3H), 3.77−3.76 (m, 3H + 2H), 3.13−3.07 (m, 1H), 2.96−2.87 (m, 2H), 2.66 (ddd, J =

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14.0, 8.5, 1.5 Hz, 1H), 2.30 (dd, *J* = 13.5, 9.0 Hz, 1H), 1.11 (s, 3H), 0.88 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.2, 172.1, 149.1, 147.9, 137.2, 130.0, 127.9, 124.8, 115.7, 110.9, 60.4, 58.5, 52.7, 52.6, 50.6, 49.2, 44.1, 36.7, 22.2, 21.9 ppm. **HRMS-ESI** calcd for $C_{22}H_{30}NO_4^+$ $[M + H]^+$: 372.2169; found: 372.2156. **Mp** 75−77 °C.

*Dimethyl 3-(2-(Indolin-1-yl)propan-2-yl)-4-methylenecyclopentane-1,1-dicarboxylate (**4af**).* Obtained using catalyst **A** (11 mg, 15.0 μmol), enyne **1c** (0.29 mL, 1.0 M in dry CH_2Cl_2, 0.29 mmol), and indoline (0.29 mL, 1.0 M in dry CH_2Cl_2, 0.29 mmol) as the nucleophile in CH_2Cl_2 (1.5 mL) according to General Procedure I. Flash column chromatography (c-hexane/EtOAc 5:1) yielded 92 mg (87%) of the aminated product as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.06 (dd, *J* = 7.5, 0.5 Hz, 1H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.63 (dd, *J* = 7.5, 0.5 Hz, 1H), 5.07 (br s, 2H), 3.76 (s, 3H), 3.75 (s, 3H), 3.60 (t, *J* = 10.0 Hz, 1H), 3.52−3.41 (m, 2H), 2.93 (br s, 2H), 2.88 (t, *J* = 8.5 Hz, 2H), 2.63 (ddd, *J* = 13.5, 8.5, 1.5 Hz, 1H), 2.10 (dd, *J* = 13.5, 9.0 Hz, 1H), 1.37 (s, 3H), 1.27 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.0, 171.9, 149.8, 148.5, 131.6, 126.9, 124.4, 116.6, 110.6, 109.8, 58.7, 58.3, 52.8, 52.7, 49.6, 48.5, 44.0, 36.2, 28.1, 21.4, 21.0 ppm. **HRMS-ESI** calcd for $C_{21}H_{28}NO_4^+$ $[M + H]^+$: 358.2013; found: 358.2025.

*Dimethyl 3-(2-(3,4-Dihydroquinolin-1(2H)-yl)propan-2-yl)-4-methylenecyclopentane-1,1-dicarboxylate (**4ag**).* Obtained using catalyst **A** (11 mg, 15.0 μmol), enyne **1c** (0.29 mL, 1.0 M in dry CH_2Cl_2, 0.29 mmol), and 1,2,3,4-tetrahydroquinoline (0.29 mL, 1.0 M in dry CH_2Cl_2, 0.29 mmol) as the nucleophile in CH_2Cl_2 (1.5 mL) according to General Procedure I. Washing with 10% aqueous solution of NaOH to remove excess 1,2,3,4-tetrahydroquinoline, flash column chromatography (c-hexane/EtOAc 5:1), and subsequent preparative TLC (CH_2Cl_2/c-hexane 1:2) yielded 56 mg (51%) of the aminated product as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.06−7.04 (m, 2H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.74 (dt, *J* = 6.5, 2.5 Hz, 1H), 5.06 (s, 1H), 4.98 (s, 1H), 3.75 (s, 3H), 3.72 (s, 3H), 3.62 (dt, *J* = 10.0, 2.0 Hz, 1H), 3.33−3.28 (m, 1H), 3.23−3.18 (m, 1H), 2.97−2.89 (m, 2H), 2.65 (t, J = 6.5 Hz, 2H), 2.55 (ddd, *J* = 13.6, 8.0, 1.5 Hz, 1H), 2.06 (dd, *J* = 13.5, 9.5 Hz, 1H), 1.89 (quin, *J* = 6.5 Hz, 2H), 1.43 (s, 3H), 1.32 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.1, 171.9, 148.9, 145.9, 131.1, 128.4, 125.4, 119.8, 118.3, 110.5, 60.8, 58.4, 52.8, 52.7, 48.8, 44.3, 44.1, 36.6, 28.0, 25.3, 24.3, 23.6 ppm. **HRMS-ESI** calcd for $C_{22}H_{30}NO_4^+$ $[M + H]^+$: 372.2169; found: 372.2162.

*4-Bromo-N-((8,8-dimethyl-3-methylene-7,9-dioxaspiro[4,5]decan-2-yl)(phenyl)methyl)aniline (**4ah**).* Obtained using catalyst **A** (4.6 mg, 0.006 mmol), enyne **1d** (81 mg, 0.30 mmol), and 4-bromoaniline (57 mg, 0.33 mmol) as the nucleophile in CH_2Cl_2 (0.9 mL) according to General Procedure I (stirred vigorously at rt for 5 h). Purification by column chromatography (pentane/Et_2O 95:5 to 9:1) yielded 125 mg of colorless gum (94%, contains ca. 3−5% impurities) that was further crystallized from 0.4 mL of diethyl ether layered with 1.2 mL of pentane (sonication initiated the crystallization) to yield 110 mg of colorless crystals (84%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 (app. d, *J* = 4.3 Hz, 4H), 7.25 (ddd, *J* = 8.7, 4.9, 3.9 Hz, 1H), 7.17−7.12 (m, 2H), 6.40−6.35 (m, 2H), 5.07 (br s, 1H), 4.77 (q, *J* = 2.1 Hz, 1H), 4.43 (d, *J* = 5.2 Hz, 1H), 4.02 (br s, 1H), 3.72 (d, *J* = 11.2 Hz, 1H), 3.66 (d, *J* = 11.4 Hz, 1H), 3.55−3.48 (m, 2H), 2.99 (dddt, *J* = 10.6, 7.9, 5.2, 2.2 Hz, 1H), 2.53 (dq, *J* = 16.5, 1.6 Hz, 1H), 2.18 (dq, *J* = 16.4, 2.4 Hz, 1H), 1.67 (dd, *J* = 13.6, 8.2 Hz, 1H), 1.50 (dd, *J* = 13.6, 10.3 Hz, 1H), 1.40 (s, 3H), 1.38 (s, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.0, 146.7, 141.7, 131.7, 128.5, 127.2, 126.8, 115.5, 109.5, 109.5, 97.9, 69.4, 67.5, 59.9, 48.8, 41.7, 39.4, 34.0, 24.7, 22.8 ppm. **HRMS-ESI** calcd for $C_{24}H_{28}BrNO_2Na^+$ $[M + Na]^+$: 464.1196; found: 464.1197. **Mp** 110−112 °C.

*N-((4,4-Bis(methoxymethyl)-2-methylenecyclopropentyl(phenyl)-methyl)-4-bromoaniline (**4ai**).* Obtained using catalyst **A** (3.9 mg, 0.005 mmol), enyne **1f** (64.6 mg, 0.25 mmol), and 4-bromoaniline (47 mg, 0.275 mmol) as the nucleophile in CH_2Cl_2 (1.0 mL) according to General Procedure I (stirred vigorously at r.t. for 5 h). Purification by column chromatography (pentane/Et_2O 95:5 to 85:15) yielded 80 mg (74%) of the aminated product as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35−7.28 (m, 4H), 7.25−7.20 (m, 1H), 7.15−7.11 (m, 2H), 6.37−6.32 (m, 2H), 4.98 (q, *J* = 2.1 Hz, 1H), 4.75 (q, *J* = 2.1 Hz, 1H), 4.50−4.46 (m, 2H), 3.41 (s, 3H), 3.32 (s, 2H), 3.27 (s, 3H), 3.12 (s, 2H), 3.02 (t, *J* = 8.2 Hz, 1H), 2.40 (dq, *J* = 16.3, 2.3 Hz, 1H), 2.31 (d, *J* = 16.2 Hz, 1H), 1.75 (dd, *J* = 13.9, 9.1 Hz, 1H), 1.51 (dd, *J* = 13.9, 9.3 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.2, 147.0, 142.3, 131.6, 128.5, 126.9, 126.7, 115.1, 108.7, 107.7, 77.7, 76.2, 60.4, 59.3, 59.3, 49.7, 45.4, 40.5, 32.2 ppm. **HRMS-ESI** calcd for $C_{23}H_{28}BrNO_2Na^+$ $[M + Na]^+$: 452.1196; found: 452.1197.

*N-((4,4-Bis(((4-methoxybenzyl)oxy)methyl)-2-methylenecyclopentyl)(phenyl)methyl)-4-bromoaniline (**4aj**).* Obtained using catalyst **A** (2.0 mg, 0.0026 mmol), enyne **1e** (61 mg, 0.13 mmol), and 4-bromoaniline (57 mg, 0.143 mmol) as the nucleophile in CH_2Cl_2 (0.6 mL) according to General Procedure I (stirred vigorously at rt for 5 h). Purification by column chromatography (pentane/Et_2O 95:5 to 85:15) yielded 61 mg (73%) of the aminated product as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34−7.21 (m, 7H), 7.18−7.13 (m, 2H), 7.10−7.06 (m, 2H), 6.92−6.88 (m, 2H), 6.87−6.83 (m, 2H), 6.20−6.15 (m, 2H), 4.97 (q, *J* = 2.1 Hz, 1H), 4.74 (q, *J* = 2.1 Hz, 1H), 4.49 (s, 2H), 4.47 (t, *J* 3.0 Hz, 1H), 4.37 (s, 2H), 4.34 (br s, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.46−3.39 (m, 2H), 3.23−3.17 (m, 2H), 2.99 (dddt, *J* = 9.3, 6.9, 4.5, 2.2 Hz, 1H), 2.46 (dq, *J* = 16.4, 2.3 Hz, 1H), 2.35 (d, *J* = 16.2 Hz, 1H), 1.78 (dd, *J* = 14.0, 9.2 Hz, 1H), 1.52 (dd, *J* = 13.9, 9.3 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.2, 159.0, 151.5, 146.9, 142.3, 131.5, 130.6, 129.3, 128.9, 128.4, 126.9, 126.6, 115.1, 113.8, 113.7, 108.7, 107.5, 74.9, 73.3, 73.1, 72.8, 60.3, 55.3, 55.2, 49.7, 45.5, 40.6, 32.1 ppm. **HRMS-ESI** calcd for $C_{37}H_{40}BrNO_4Na^+$ $[M + Na]^+$: 664.2033; found: 664.2030.

*Dimethyl 9b-Methyl-4-phenyl-1,3,3a,9b-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate (**5e**).* A solution of compound **4e** (40 mg, 0.08 mmol) in degassed DMF (0.5 mL) was treated with $Pd(OAc)_2$ (1.8 mg, 8 μmol), PPh_3 (4.2 mg, 16 μmol), and K_2CO_3 (22 mg, 0.16 mmol) under a N_2 atmosphere, and the solution was heated at 110 °C for 7 h. Purification by flash column chromatography (pentane/Et_2O 9:1) provided product **5e** (20 mg, 67%) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.12−8.07 (m, 2H), 7.54−7.45 (m, 4H), 7.38 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.28 (td, *J* = 7.5, 1.6 Hz, 1H), 7.23 (td, *J* = 7.4, 1.5 Hz, 1H), 3.79 (s, 3H), 3.50 (s, 3H), 3.45 (d, *J* = 14.2 Hz, 1H), 3.31 (dd, *J* = 12.4, 7.8 Hz, 1H), 2.66 (dd, *J* = 13.8, 7.8 Hz, 1H), 2.54 (d, *J* = 14.2 Hz, 1H), 2.17 (dd, *J* = 13.8, 12.4 Hz, 1H), 1.20 (s, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.4, 171.4, 165.8, 142.4, 138.7, 131.7, 130.8, 128.8, 128.6, 127.9, 127.7, 127.0, 125.7, 58.5, 53.2, 52.9, 46.9, 46.5, 44.5, 38.8, 28.7 ppm. **HRMS-ESI** calcd for $C_{23}H_{24}NO_4^+$ $[M + H]^+$: 378.1700; found: 378.1697.

*Dimethyl 8-Bromo-9b-methyl-4-phenyl-1,3,3a,9b-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate (**5f**).* A solution of compound **4f** (60 mg, 0.11 mmol) in degassed DMF (0.7 mL) was treated with $Pd(OAc)_2$ (2.3 mg, 10 μmol), PPh_3 (5.4 mg, 21 μmol), and K_2CO_3 (28 mg, 0.21 mmol) under a N_2 atmosphere, and the solution was heated at 110 °C for 4 h. Purification by flash column chromatography (pentane/Et_2O 9:1) provided product **5f** (34 mg, 73%) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.15−8.04 (m, 2H), 7.52−7.45 (m, 4H), 7.42−7.35 (m, 2H), 3.78 (s, 3H), 3.58 (s, 3H), 3.33 (d, *J* = 14.3 Hz, 1H), 3.28 (dd, *J* = 12.2, 8.1 Hz, 1H), 2.63 (dd, *J* = 13.9, 8.1 Hz, 1H), 2.58 (d, *J* = 14.3 Hz, 1H), 2.21 (dd, *J* = 13.9, 12.2 Hz, 1H), 1.20 (s, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.1, 171.2, 166.4, 141.6, 138.3, 133.9, 131.1, 130.9, 130.2, 128.8, 128.8, 127.0, 120.9, 58.5, 53.3, 53.1, 46.8, 46.1, 44.7, 38.9, 28.4 ppm. **HRMS-ESI** calcd for $C_{23}H_{23}BrNO_4^+$ $[M + H]^+$: 456.0805; found: 456.0798.

*Dimethyl 7-Chloro-9b-methyl-4-phenyl-1,3,3a,9b-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate (**5g**).* A solution of compound **4g** (60 mg, 0.11 mmol) in degassed DMF (0.75 mL) was treated with $Pd(OAc)_2$ (2.5 mg, 11 μmol), PPh_3 (5.8 mg, 22 μmol), and K_2CO_3 (31 mg, 0.22 mmol) under a N_2 atmosphere, and the solution was heated at 110 °C for 4 h. Purification by flash column chromatography (pentane/Et_2O 9:1) provided product **5g** (33 mg, 72%) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.12−8.06 (m, 2H), 7.57−7.44 (m, 4H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.20 (dd, *J* = 8.2, 2.3 Hz, 1H), 3.79 (s, 3H), 3.53 (s, 3H), 3.42 (d, *J* = 14.3 Hz, 1H), 3.32 (dd, *J* = 12.4, 7.7 Hz, 1H), 2.68 (dd, *J* = 13.8, 7.7 Hz, 1H), 2.50 (d, *J* = 14.4 Hz, 1H), 2.10 (dd, *J* = 13.8, 12.4 Hz, 1H), 1.18 (s, 3H) ppm. **^{13}C**

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NMR (126 MHz, $CDCl_3$) δ 173.2, 171.3, 167.3, 143.7, 138.2, 133.0, 131.2, 130.3, 128.8, 128.4, 127.6, 127.1, 127.0, 58.4, 53.3, 53.0, 46.7, 46.4, 44.4, 38.9, 28.6 ppm. **HRMS-ESI** calcd for $C_{23}H_{23}ClNO_4^+$ $[M + H]^+$: 412.1310; found: 412.1320.

*Dimethyl 3-Methylene-4-(phenyl((2-((trimethylsilyl)ethynyl)-phenyl)amino)methyl)cyclopentane-1,1-dicarboxylate (**6e**).* A dry 10 mL MW vial was charged with $PdCl_2(PPh_3)_2$ (56 mg, 0.079 mmol), CuI (38 mg, 0.20 mmol), and 2-iodoaniline **4e** (500 mg, 0.99 mmol), and the MW vial was sealed and left under argon. Degassed Et_3N (7 mL) and degassed DMF (3 mL) were added followed by trimethylsilylacetylene (0.68 mL, 4.95 mmol, 5 equiv) at 25 °C. The resulting mixture was stirred at 25 °C for 1.5 h (complete conversion monitored by GC-MS). The dark brown mixture was partitioned between water (50 mL) and diethyl ether (20 mL). The aqueous layer was re-extracted with diethyl ether (2 × 20 mL). The combined ethereal extracts were dried over sodium sulfate and concentrated. The title product was obtained after purification by chromatography on silica gel eluting with pentane/Et_2O 9:1 to 4:1 as a pale brown crystalline solid (451 mg, 96%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38−7.22 (m, 6H), 6.99 (ddd, J = 8.6, 7.4, 1.6 Hz, 1H), 6.56 (td, J = 7.5, 1.0 Hz, 1H), 6.30 (d, J = 8.3 Hz, 1H), 5.14 (d, J = 4.9 Hz, 1H), 5.08 (q, J = 2.6 Hz, 1H), 4.72 (q, J = 2.5 Hz, 1H), 4.51 (t, J = 5.4 Hz, 1H), 3.70 (s, 3H), 3.70 (s, 3H), 3.18−3.10 (m, 1H), 3.04 (dq, J = 16.4, 1.6 Hz, 1H), 2.95 (dq, J = 16.5, 2.6 Hz, 1H), 2.43 (ddd, J = 13.6, 7.8, 1.7 Hz, 1H), 2.22 (dd, J = 13.5, 10.4 Hz, 1H), 0.30 (s, 9H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.7, 171.4, 148.6, 146.6, 141.5, 132.1, 129.9, 128.5, 127.2, 126.9, 116.6, 111.1, 110.0, 108.0, 102.0, 100.2, 59.8, 58.0, 52.8, 52.7, 49.3, 41.8, 35.4, − 0.1 ppm. **HRMS-ESI** calcd for $C_{28}H_{34}NO_4Si^+$ $[M + H]^+$: 476.2252; found: 476.2247. **Mp** 108−109 °C.

*Dimethyl 3-(((4-Bromo-2-((trimethylsilyl)ethynyl)phenyl)amino)-(phenyl)methyl)-4-methylenecyclopentane-1,1-dicarboxylate (**6f**).* Prepared according to the procedure for **6e**, with **4f** (440 mg, 0.753 mmol), $PdCl_2(PPh_3)_2$ (42 mg, 0.06 mmol), and CuI (29 mg, 0.15 mmol) in degassed DFM/Et_3N (1:2, 6.75 mL) to which was added TMS-acetylene (208 μL, 1.51 mmol, 2 equiv), followed by stirring at 25 °C for 1.5 h. Obtained as a pale yellow oil after purification by column chromatography on silica gel eluting with pentane/Et_2O 9:1 to 4:1 (400 mg, 96%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38−7.31 (m, 4H), 7.30−7.24 (m, 1H), 7.19 (d, J = 8.2 Hz, 1H), 6.53 (dd, J = 8.2, 2.0 Hz, 1H), 6.29 (d, J = 1.9 Hz, 1H), 5.19 (d, J = 5.3 Hz, 1H), 5.07 (dq, J = 2.5, 1.5 Hz, 1H), 4.71−4.68 (m, 1H), 4.48 (t, J = 5.6 Hz, 1H), 3.70 (s, 3H), 3.69 (s, 3H), 3.19−3.09 (m, 1H), 3.02 (dq, J = 16.4, 1.6 Hz, 1H), 2.91 (dq, J = 16.5, 2.6 Hz, 1H), 2.43 (ddd, J = 13.5, 7.8, 1.7 Hz, 1H), 2.16 (dd, J = 13.5, 10.4 Hz, 1H), 0.31 (s, 9H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.7, 171.4, 149.4, 146.5, 140.7, 135.7, 132.9, 128.6, 127.5, 126.8, 116.7, 111.1, 110.2, 106.6, 101.2, 100.9, 59.7, 58.0, 52.8, 52,8, 49.1, 41.8, 35.8, 0.0 ppm. **HRMS-ESI** calcd for $C_{28}H_{32}BrNO_4SiNa^+$ $[M + Na]^+$: 576.1176; found: 576.1196.

*Dimethyl 3-(((4-Chloro-2-((trimethylsilyl)ethynyl)phenyl)amino)-(phenyl)methyl)-4-methylenecyclopentane-1,1-dicarboxylate (**6g**).* Prepared according to the procedure for **6e**, with **4g** (550 mg, 1.02 mmol), $PdCl_2(PPh_3)_2$ (57.2 mg, 0.08 mmol), CuI (39 mg, 0.20 mmol) in degassed DFM/Et_3N (1:2, 7.5 mL) to which was added TMS-acetylene (282 μL, 2.04 mmol, 2 equiv), followed by stirring at 25 °C for 1.5 h. Obtained as a yellow oil after purification by column chromatography on silica gel eluting with pentane/Et_2O 9:1 to 4:1 (502 mg, 97%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 (d, J = 2.4 Hz, 1H), 7.36−7.30 (m, 4H), 7.28−7.23 (m, 1H), 7.05 (dd, J = 8.8, 2.3 Hz, 1H), 6.16 (d, J = 8.8 Hz, 1H), 5.11 (d, J = 4.8 Hz, 1H), 5.08 (q, J = 2.5 Hz, 1H), 4.71 (q, J = 2.5 Hz, 1H), 4.47 (t, J = 5.3 Hz, 1H), 3.70 (s, 3H), 3.69 (s, 3H), 3.13 (dddd, J = 10.4, 8.0, 5.6, 2.3 Hz, 1H), 3.03 (dq, J = 16.5, 1.6 Hz, 1H), 2.92 (dq, J = 16.5, 2.6 Hz, 1H), 2.40 (ddd, J = 13.6, 7.8, 1.7 Hz, 1H), 2.18 (dd, J = 13.5, 10.5 Hz, 1H), 0.30 (s, 9H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.7, 171.4, 147.5, 146.5, 140.9, 134.2, 132.5, 128.6, 127.4, 126.8, 112.7, 110.1, 110.0, 107.8, 101.7, 100.3, 59.8, 58.0, 52.8, 52,8, 49.2, 41.8, 35.7, 0.0 ppm. **HRMS-ESI** calcd for $C_{28}H_{32}ClNO_4SiNa^+$ $[M + Na]^+$: 532.1681; found: 532.1693.

*Dimethyl 3-(((2-Ethynylphenyl)amino)(phenyl)methyl)-4-methylenecyclopentane-1,1-dicarboxylate (**7e**).* Substrate **6e** (150 mg, 0.32 mmol) was suspended in methanol (1 mL) at 25 °C, and K_2CO_3 (131 mg, 0.95 mmol) was added. The mixture was stirred vigorously at 25 °C for 3 h (disappearance of starting material monitored by GC-MS). The volatiles were then removed under a stream of nitrogen, and the residue was purified by column chromatography on silica gel eluting with pentane/Et_2O 4:1 to afford 120 mg of colorless oil (94%). Note: alternatively the deprotection of the TMS group can be carried out on the crude mixture after Sonogashira coupling to afford the title alkyne in 81% yield over 2 steps (1 g scale of iodoaniline substrate [1.98 mmol], 650 mg [1.61 mmol] of alkyne obtained). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38−7.29 (m, 5H), 7.27−7.22 (m, 1H), 7.03 (ddd, J = 8.6, 7.4, 1.6 Hz, 1H), 6.58 (td, J = 7.5, 1.0 Hz, 1H), 6.31 (d, J = 8.4 Hz, 1H), 5.14 (d, J = 5.1 Hz, 1H), 5.07 (q, J = 2.1 Hz, 1H), 4.73 (q, J = 2.1 Hz, 1H), 4.55 (t, J = 5.4 Hz, 1H), 3.72 (s, 3H), 3.70 (s, 3H), 3.52 (s, 1H), 3.22−3.13 (m, 1H), 3.08−2.96 (m, 2H), 2.45 (dd, J = 13.7, 8.2 Hz, 1H), 2.26 (dd, J = 13.7, 9.9 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.8, 171.7, 148.8, 147.0, 141.4, 132.3, 130.1, 128.5, 127.2, 126.8, 116.5, 111.0, 110.0, 106.8, 83.2, 80.7, 60.0, 58.2, 52.8, 49.3, 42.1, 35.4 ppm. **HRMS-ESI** calcd for $C_{25}H_{25}NO_4Na^+$ $[M + Na]^+$: 426.1676; found: 426.1681.

*Dimethyl 3-(((4-Bromo-2-ethynylphenyl)amino)(phenyl)methyl)-4-methylenecyclopentane-1,1-dicarboxylate (**7f**).* Prepared according to the procedure for **7e**, with **6f** (115 mg, 0.21 mmol) and K_2CO_3 (86 mg, 0.62 mmol) in methanol (0.7 mL), followed by stirring at 25 °C for 1.5 h. Obtained as a colorless oil after purification by column chromatography on silica gel eluting with pentane/Et_2O 9:1 to 4:1 (72 mg, 72%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 (d, J = 2.4 Hz, 1H), 7.35−7.29 (m, 4H), 7.27−7.23 (m, 1H), 7.09 (dd, J = 8.8, 2.4 Hz, 1H), 6.17 (d, J = 8.9 Hz, 1H), 5.13 (d, J = 5.1 Hz, 1H), 5.07 (q, J = 2.1 Hz, 1H), 4.71 (q, J = 2.1 Hz, 1H), 4.49 (t, J = 5.4 Hz, 1H), 3.72 (s, 3H), 3.70 (s, 3H), 3.54 (s, 1H), 3.19−3.12 (m, 1H), 3.05−2.95 (m, 2H), 2.42 (dd, J = 13.7, 8.2 Hz, 1H), 2.21 (dd, J = 13.8, 9.8 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.7, 171.7, 147.8, 146.9, 140.9, 134.4, 132.9, 128.6, 127.4, 126.7, 112.6, 110.0, 108.7, 107.7, 84.3, 79.2, 60.0, 58.1, 52.9, 52.8, 49.2, 42.2, 35.4 ppm. **HRMS-ESI** calcd for $C_{25}H_{24}BrNO_4Na^+$ $[M + Na]^+$: 504.0781; found: 504.0778.

*Dimethyl 3-(((4-Chloro-2-ethynylphenyl)amino)(phenyl)methyl)-4-methylenecyclopentane-1,1-dicarboxylate (**7g**).* Prepared according to the procedure for **7e**, with **6g** (135 mg, 0.27 mmol) and K_2CO_3 (110 mg, 0.79 mmol) in methanol (1 mL), followed by stirring at 25 °C for 2.5 h. Obtained as a pale yellow oil after purification by column chromatography on silica gel eluting with pentane/Et_2O 9:1 to 4:1 (78 mg, 67%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36−7.31 (m, 4H), 7.29−7.24 (m, 1H), 7.22 (d, J = 8.1 Hz, 1H), 6.55 (dd, J = 8.2, 2.0 Hz, 1H), 6.29 (d, J = 1.9 Hz, 1H), 5.21 (d, J = 5.5 Hz, 1H), 5.07 (q, J = 2.1 Hz, 1H), 4.71 (q, J = 2.1 Hz, 1H), 4.51 (t, J = 5.6 Hz, 1H), 3.72 (s, 3H), 3.70 (s, 3H), 3.54 (s, 1H), 3.20−3.12 (m, 1H), 3.04−2.94 (m, 2H), 2.44 (dd, J = 13.7, 8.3 Hz, 1H), 2.20 (dd, J = 13.8, 9.8 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.7, 171.7, 149.6, 146.8, 140.6, 136.0, 133.1, 128.7, 127.5, 126.7, 116.7, 111.0, 110.1, 105.3, 84.0, 79.8, 59.9, 58.2, 52.8, 49.2, 42.2, 35.4 ppm. **HRMS-ESI** calcd for $C_{25}H_{24}ClNO_4Na^+$ $[M + Na]^+$: 460.1286; found: 460.1286.

*Dimethyl 3-((1H-Indol-1-yl)(phenyl)methyl)-4-methylenecyclopentane-1,1-dicarboxylate (**8e**).* In a dry vial, **7e** (100 mg, 0.25 mmol) was dissolved in dry CH_2Cl_2 (2.5 mL) and IPrAuNTf$_2$ (**D$_2$**) (10.7 mg, 12 μmol) was added in one portion. The mixture was stirred at 25 °C for 8 h (monitored by GC-MS). The solvent was removed under a stream of nitrogen, and the crude mixture was loaded on silica gel and purified by column chromatography on silica gel eluting with pentane/Et_2O 9:1 to 4:1 to afford the title product as a colorless solid (78 mg, 78%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 (d, J = 7.9 Hz, 1H), 7.47−7.42 (m, 2H), 7.40−7.34 (m, 2H), 7.32−7.18 (m, 4H), 7.09 (ddd, J = 7.9, 7.0, 1.0 Hz, 1H), 6.60 (d, J = 3.2 Hz, 1H), 5.29 (d, J = 11.0 Hz, 1H), 4.90 (q, J = 2.0 Hz, 1H), 4.18−4.14 (m, 1H), 3.87−3.78 (m, 1H), 3.75 (s, 3H), 3.63 (s, 3H), 3.23 (dq, J = 16.3, 2.4 Hz, 1H), 2.97 (dq, J = 16.3, 1.5 Hz, 1H), 2.66 (ddd, J = 13.9, 7.9, 1.6 Hz, 1H), 1.88 (dd, J = 13.8, 8.2 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.9, 171.7, 146.7, 139.8, 136.4, 128.4, 128.3, 127.8, 127.6,

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124.6, 121.7, 120.9, 119.6, 111.6, 109.7, 102.5, 63.4, 58.1, 52.9, 52.8, 46.3, 41.7, 38.4 ppm. **HRMS-ESI** calcd for $C_{25}H_{26}NO_4^+$ $[M + H]^+$: 404.1856; found: 404.1853. **Mp** 52−54 °C.

*Dimethyl 3-((5-Bromo-1H-indol-1-yl)(phenyl)methyl)-4-methylenecyclopentane-1,1-dicarboxylate (**8f**).* Prepared according to the procedure for **8e**, with **7f** (61 mg, 0.13 mmol) and $IPrAuNTf_2$ ($\mathbf{D_2}$) (5.5 mg, 6.3 μmol) in CH_2Cl_2 (1.2 mL), followed by stirring at 25 °C for 8 h. Obtained as a colorless foamy solid after purification by column chromatography on silica gel eluting with pentane/Et_2O 9:1 to 4:1 (47 mg, 77%). ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.71 (d, J = 1.6 Hz, 1H), 7.40 (d, J = 3.3 Hz, 1H), 7.34−7.21 (m, 7H), 6.51 (d, J = 3.5 Hz, 1H), 5.22 (d, J = 10.9 Hz, 1H), 4.89 (q, J = 1.9 Hz, 1H), 4.16 (q, J = 1.7 Hz, 1H), 3.81−3.74 (m, 1H), 3.73 (s, 3H), 3.63 (s, 3H), 3.19 (dq, J = 16.3, 2.3 Hz, 1H), 2.96 (dq, J = 16.4, 1.5 Hz, 1H), 2.59 (ddd, J = 13.8, 7.9, 1.5 Hz, 1H), 1.84 (dd, J = 13.8, 8.2 Hz, 1H) ppm. ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 171.8, 171.7, 146.6, 139.4, 135.0, 130.0, 128.6, 128.1, 127.5, 125.9, 124.5, 123.4, 112.9, 111.7, 111.2, 102.1, 63.7, 58.0, 52.9, 52.9, 46.3, 41.6, 38.3 ppm. **HRMS-ESI** calcd for $C_{25}H_{25}BrNO_4^+$ $[M + H]^+$: 482.0961; found: 482.0959. **Mp** 55−56 °C.

*Dimethyl 3-((5-Chloro-1H-indol-1-yl)(phenyl)methyl)-4-methylenecyclopentane-1,1-dicarboxylate (**8g**).* Prepared according to the procedure for **8e**, with **7g** (62 mg, 0.14 mmol) and $IPrAuNTf_2$ ($\mathbf{D_2}$) (6.1 mg, 7.1 μmol) in CH_2Cl_2 (1.3 mL), followed by stirring at 25 °C for 8 h. Obtained as a colorless foamy solid after purification by column chromatography on silica gel eluting with pentane/Et_2O 9:1 to 4:1 (42 mg, 68%). ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.49 (d, J = 8.4 Hz, 1H), 7.41−7.39 (m, 2H), 7.36−7.33 (m, 2H), 7.32−7.28 (m, 2H), 7.27−7.22 (m, 1H), 7.04 (dd, J = 8.4, 1.8 Hz, 1H), 6.55 (dd, J = 3.3, 1.8 Hz, 1H), 5.18 (d, J = 11.0 Hz, 1H), 4.89 (q, J = 2.0 Hz, 1H), 4.14 (dd, J = 2.7, 1.5 Hz, 1H), 3.81−3.75 (m, 1H), 3.74 (s, 3H), 3.64 (s, 3H), 3.20 (dq, J = 16.4, 2.4 Hz, 1H), 2.96 (dq, J = 16.3, 1.5 Hz, 1H), 2.61 (ddd, J = 13.8, 7.9, 1.6 Hz, 1H), 1.83 (dd, J = 13.8, 8.2 Hz, 1H) ppm. ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 171.8, 171.6, 146.5, 139.4, 136.8, 128.6, 128.1, 127.8, 127.6, 126.8, 125.3, 121.7, 120.3, 111.7, 109.7, 102.8, 63.6, 58.1, 52.9, 52.9, 46.3, 41.6, 38.3 ppm. **HRMS-ESI** calcd for $C_{25}H_{24}ClNO_4Na^+$ $[M + Na]^+$: 460.1286; found: 460.1281. **Mp** 49−50 °C.

■ ASSOCIATED CONTENT

Supporting Information

. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02607.

Crystallographic data files for **4i**, **4d**, and **4x** (ZIP)

Spectral data for all new compounds and X-ray crystallography data for compounds **4d**, **4i**, and **4x**(PDF)

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Notes

The authors declare no competing financial interest.

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