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Synthesis of Polycyclic Chromene Cores through Gold (I)-Catalyzed Intramolecular Hydroarylation Reaction (IMHA)

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Dedicated to Prof. Franco Cozzi in occasion of his 70th birthday.

A regioselective gold (I)-catalyzed approach for the construction of polycyclic chromene cores has been developed. The reaction proceeds in good to excellent yields under mild condition with a broad range of substrates providing a simple and efficient tool for the synthesis of pyranochromene derivatives. Moreover, the regiochemical control of the annulation of unsymmetrically substituted propargylic ethers has been investigated focusing on electronic/steric effects of the ligands of gold complexes as well as on the electronic effects of the groups on the aromatic rings.

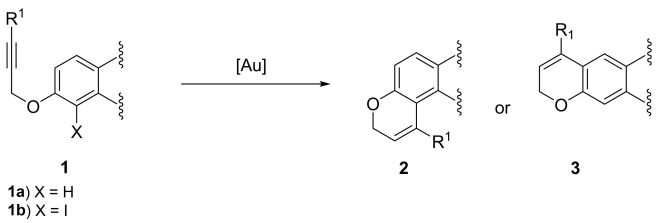
Introduction

The addition reaction of a broad range of nucleophiles with alkynes catalyzed by gold(I) complexes has emerged as a powerful tool in organic synthesis.[1] In the case of arenes as nucleophiles, alkynes undergo gold(I)-catalyzed Friedel-Crafts-type reactions to give hydroarylation products, which are applied in the context of the synthesis of polycyclic and polyheterocyclic derivatives.[2]

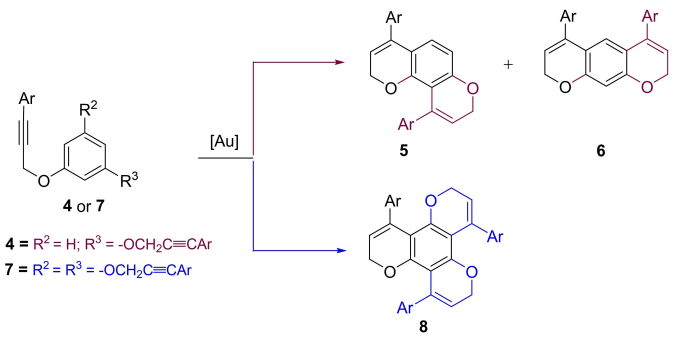
We previously described the regioselective access to the angular pyranocumarine derivatives **2** through the gold-catalyzed intramolecular hydroarylation of readily available 7-(prop-2-yn-1-yloxy)-2*H*-chromen-2-ones **1 a** at their C-8 congested position by tuning the electronic and steric properties of the ligand on the gold complex.[3] On the other hand, the combination of the JohnPhosAu(MeCN)SbF_6 catalyzed intramolecular hydroarylation of 8-iodo-7-(prop-2-yn-1-yloxy)-2*H*-chromen-2-one derivatives **1 b** followed by selective palladium/formate C–I reduction allows for the exclusive formation of the corresponding linear isomer **3** (Scheme 1).

Subsequently, we envisaged to investigate the intramolecular gold-catalyzed hydroarylation of the readily available 1,3-bis((3-arylprop-2-yn-1-yl)oxy)benzene derivatives **4** to the corresponding 4,6-diaryl-2*H*,8*H*-pyrano[3,2-*g*]chromenes **5** and/or 4,10-diaryl-2*H*,8*H*-pyrano[2,3-*f*]chromenes **6** (Scheme 2) and of the 1,3,5-tris((3-arylprop-2-yn-1-yl)oxy)benzene derivatives **7** to 4,8,12-triaryl-2*H*,6*H*,10*H*-dipyrano[2,3-*f*:2′,3′-*h*]chromenes **8** (Scheme 2).

As 2*H*-chromene derivatives, these cyclization products appeared to us very attractive for different remarkable features. Indeed, the 2*H*-chromene ring system is the core structure of numerous biologically active natural products,[4] and was proved to code useful photochromic properties[5] opening new perspectives on materials science. In this regard, for instance,



Scheme 1. Our previous work: IMHA of 7-(prop-2-yn-1-yloxy)-2*H*-chromen-2-one derivatives **1 a** or **1 b**.



Scheme 2. Work hypothesis.

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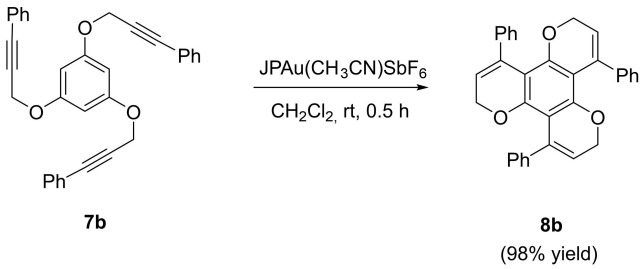
this heterocyclic motif has been linked to photochromic crystals[6] and to photochromic organogelators.[7] Due to its importance, several studies in the field of gold catalysis have been focused on providing access to this relevant heterocyclic scaffold,[8] but to the best of our knowledge, there is a lack of approaches to dipyranochromene derivatives, while only limited synthetic methodologies of pyranochromenes are reported in the literature.[9] This aspect may justify our efforts to develop a new and efficient protocol for their preparation. Hereafter we report the results of our investigation



7b **8b** (98% yield)

Scheme 4. Au(I)-catalyzed IMHA of (((5-(((phenylethynyl)oxy)methyl)-1,3-phenylene)bis(oxy))bis(prop-1-yne-3,1-diyl))dibenzene **7b**.

Results and Discussion

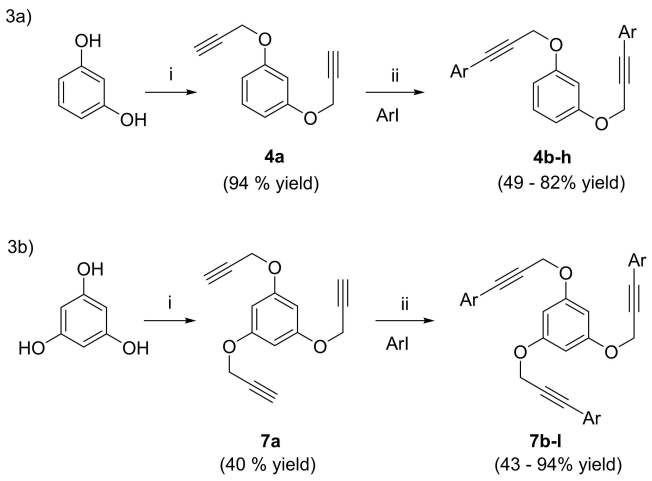
The 1,3-bis((3-arylprop-2-yn-1-yl)oxy)benzene derivatives **4b–h** and the 1,3,5-tris((3-arylprop-2-yn-1-yl)oxy)benzene building blocks **7b–l** were easily obtained from the corresponding cheap phenols through a two- step procedure outlined in the following Scheme 3.

We started our work performing the cyclization of the compound **7b** in the presence of the commercially available gold catalyst JohnPhosAu(CH_3CN)SbF_6: pleasingly, using the 4 mol% of catalyst in CH_2Cl_2 at room temperature (Scheme 4)[3,11] we observed the formation of compound **8b** rapidly and in excellent yield.

Remarkably, this triple hydroarylation achieves the simultaneous formation of all three C–C bonds in a *one-pot* transformation.[12]

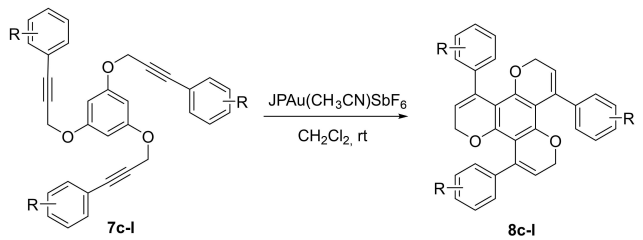
As an almost quantitative yield was obtained no further screening experiments were carried out and we turned our attention on the evaluation of the substrate scope (Table 1).

As expected, the introduction of an electron-donating group in the *para*-position of the three aromatic rings attached



Scheme 3. 3a) Synthesis of 1,3-bis((3-arylprop-2-yn-1-yl)oxy)benzene derivatives **4b-h**. *Reagents and conditions*: (i) K_2CO_3 (2.5 equiv.), propargyl bromide (2.5 equiv.), DMF, rt; (ii) substituted iodobenzene (2.2 equiv.), $Pd(PPh_3)_2Cl_2$ (0.02 equiv.), CuI (0.04 equiv.), DMF–Et_3N, r.t. 3b) Synthesis of 1,3,5-tris((3-arylprop-2-yn-1-yl)oxy)benzene derivatives **7b-l**. *Reagents and conditions*: (i) K_2CO_3 (3.5 equiv.), propargyl bromide (3.5 equiv.), DMF, rt; (ii) substituted iodobenzene (3.3 equiv.), $Pd(PPh_3)_2Cl_2$ (0.02 equiv.), CuI (0.04 equiv.), DMF–Et_3N, r.t.

Table 1. Substrate Scope.



Entry[a]	(**7**) R =	Time [h]	(**8**) Yield [%][b]
1	(**7c**) 4-(Me)	0.75	(**8c**) 95
2	(**7d**) 4-(OMe)	0.25	(**8d**) 98
3	(**7e**) 3-(OMe)	0.5	(**8e**) 91
4	(**7f**) 4-(COMe)	1.0	(**8f**) 90
5	(**7g**) 4-(CO_2Me)	0.25	(**8g**) 99
6	(**7h**) 4-(CN)	0.50	(**8h**) 99
7	(**7i**) 3-(CF_3)	0.25	(**8i**) 98
8	(**7j**) 4-Cl	0.25	(**8j**) 98
9	(**7k**) 4-Br	0.25	(**8k**) 99
10	(**7l**) 3-Br	0.75	(**8l**) 95

[a] Reactions were carried out on 0.3 mmol of **7c–l** in 2 mL of CH_2Cl_2 at room temperature in the presence of 0.04 equiv. of JohnPhosAu(CH_3CN)SbF_6. [b] Yields are given for isolated products.

to the alkyne moiety of the starting ethers **7** efficiently promoted the triple hydroarylation reaction (Table 1, entries 1 and 2). It is worth emphasizing that the reaction is also allowed in almost quantitative yield even in the presence of strong withdrawing substituents (Table 1, entries 4–7). Furthermore, the reaction is totally compatible with aryl halides due to the inertness of gold(I) catalysts towards oxidative addition reactions under homogeneous conditions allowing further functionalization of the halide substituted dipyranochromenes (Table 1, entries 8–10).

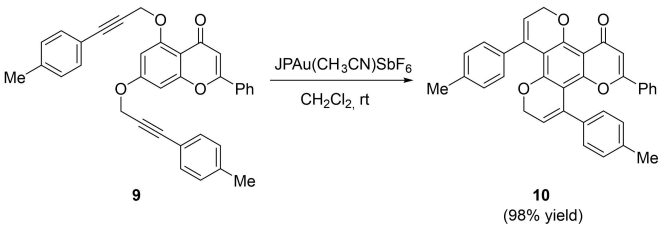
Based on the above results and considering the relevance of flavonoid derivatives in developing potent anticancer agents,[13] we investigated the gold-catalyzed IMHA of the propargyl

ethers of the 5,7-dihidroxyflavone (chrysin). The dipropargyl ether 2-phenyl-5,7-bis((*p*-tolyl)prop-2-yn-1-yl)oxy)-4*H*-chromene-4-one **9** lead to the formation of the 4,11-di-*p*-tolyl-*2H*,*8H*,*12H*-dipyrano[2,3-*f*.*2*′,*3*′-*h*]chromen-8-one **10** in almost quantitative yield (Scheme 5).

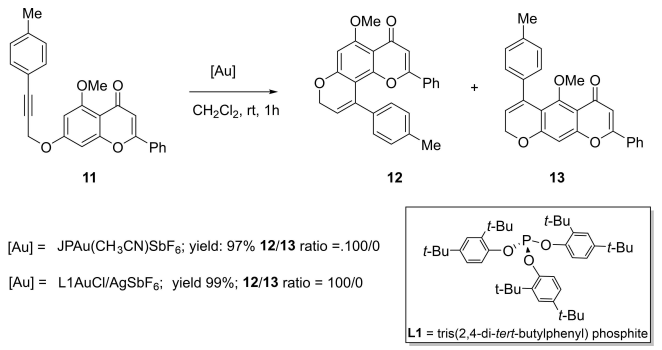
Switching to the 5-methoxy-2-phenyl-7-((3-(*p*-tolyl)prop-2-yn-1-yl)oxy)-4*H*-chromen-4-one **11** the formation of two isomeric products was expected (**12** and **13**): in our hypothesis Au(I)-catalyzed regiodivergent IMHA to the *ortho*- and *para*-position of the -OMe group would have be established by tuning the electronic and steric properties of the ligand on the gold complex. Indeed, altering three-coordinate Au(I) complexes was reported to play a key role in the adjacent cyclization.[10]

Surprisingly, a regioselective cyclization at the *para*-position leading the exclusive formation of **12** was observed both in the presence of JohnPhosAu(CH_3CN)SbF_6 and with the electron-deficient tris(2,4-di-*tert*-butylphenyl) phosphite ligand (L1). Formation of **13** was not observed (Scheme 6).

Subsequently, we went on further study to achieve a regiodivergent annulation reaction and explore the site control of the gold-catalyzed IMHA. To this purpose we selected the IMHA of the aryl propargyl ethers **4b**–**h** as suitable substrates to evaluate the possibility to selectively prepare the corresponding regioisomeric linear products **5b**–**h** and/ or angular **6b**–**h** regioisomers by appropriately choosing the catalyst or by modifying the reaction conditions. Regiodivergent methodologies are included as the key factor in the concept of efficiency and atom economy in synthetic organic chemistry. In order to achieve the desired regioselective control of the gold (I)-catalyzed IMHA of the substrates **4b**–**h**, we explored the annulation reaction with three different catalysts. Our results, summarized in the Table 2, showed that the robust air stable JohnPhosAu(CH_3CN)SbF_6 **catalyst 1** (see Figure 1) is a suitable catalyst to afford regioselectively the 4,5-diaryl-*2H*,*8H*-pyrano-[3,2-*g*]chromenes **6b**–**h** in high yields and a good tolerance for both the functional groups and steric hindrance. A worsening of the selectivity was observed in the presence of a strong electron withdrawing at the 4-position of the aryl moiety bonded to the alkyne moiety (Table 2, entries 10–15). The **catalyst 2** as well as the **catalyst 3** (see Figure 1) resulted also efficient catalysts but failed to achieve the regiocontrol of the annulation reaction of **4b**–**h**.

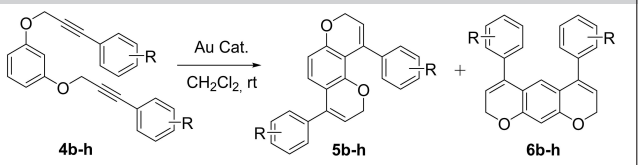


Scheme 5. Au(I)-catalyzed IMHA of 2-phenyl-5,7-bis((*p*-tolyl)prop-2-yn-1-yl) oxy)-4*H*-chromene-4-one **9.**



Scheme 6. Regioselective Au(I)-catalyzed IMHA of 5-methoxy-2-phenyl-7-((3-(*p*-tolyl)prop-2-yn-1-yl)oxy)-4*H*-chromen-4-one one **11** to **12**: reactions were carried out on 0.3 mmol of **11** in 2 mL of CH_2Cl_2 at room temperature under the presence of 0.04 equiv. of the catalyst.

Table 2. Au(I)-catalyzed IMHA of aryl propargyl ethers **4b**–**h**.[a]



Entry	(4) R=	Catalyst	Time [h]	Overall yield [%][b]	5/6 Ratio[c]
1		Cat. 1	0.5	95	2/98
2	**(4b)**	Cat. 2	0.5	90	40/60
3	H	Cat. 3	0.5	96	46/54
4		Cat. 1	1	98	0/100
5	**(4c)**	Cat. 2	1	98	39/61
6	4-Me	Cat. 3	1	98	42/58
7		Cat. 1	4.5	98	0/100
8	**(4d)**	Cat. 2	3	99	7/93
9	4-OMe	Cat. 3	1.75	98	28/72
10		Cat. 1	2.5	99	39/61
11	**(4e)**	Cat. 2	1.5	97	40/60
12	4-COMe	Cat. 3	3	97	42/58
13		Cat. 1	1	92	13/87
14	**(4f)**	Cat. 2	0.5	98	41/59
15	4-CO_2Me	Cat. 3	0.5	96	43/57
16		Cat. 1	0.5	89	5/95
17	**(4g)**	Cat. 2	0.5	89	28/72
18	4-Cl	Cat. 3	0.5	96	39/61
19		Cat. 1	1	93	4/96
20	**(4h)**	Cat. 2	0.5	95	29/71
21	2-Br	Cat. 3	0.5	92	30/70

[a] Reactions were carried out on 0.3 mmol of **4** in 2 ml of CH_2Cl_2 at room temperature under the presence of 0.04 equiv. of **catalyst 1** or **catalyst 2** or **catalyst 3**. [b] Overall yield refers to the mixture of regiosomers **5**+**6**. [c] Isomeric ratios were calculated from the ^{1}H NMR analyses.

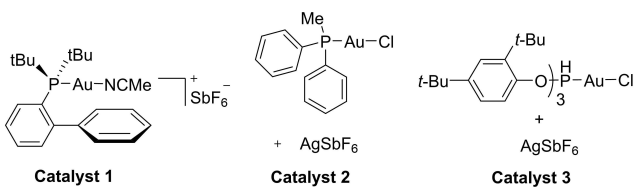


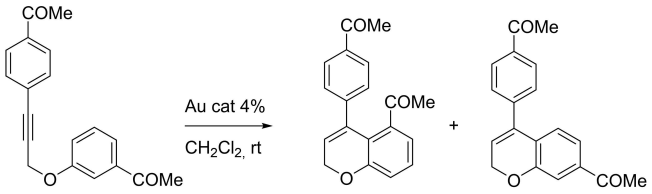
Figure 1. Catalysts used to explore the regiochemical outcome of the Au(I)-catalyzed IMHA: **catalyst 1**: (acetonitrile)[(2-biphenyl)di-*tert*-butylphosphine] gold(I) hexafluoroantimonate; **catalyst 2**: chloro(methyldiphenylphosphine) gold(I) and $AgSbF_6$; **catalyst 3**: [Tris(2,4-di-*tert*-butylphenyl)phosphite]gold(I) chloride and $AgSbF_6$

Conversely, these latter catalysts accomplished the highly regioselective IMHA of the propargyl ether **14a** to afford the 1-(4-(5-acetyl-2*H*-chromen-4-yl)phenyl)ethan-1-one **15a** in about quantitative yield (Table 3, entries 1, 10).

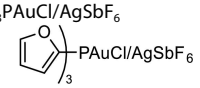
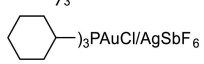
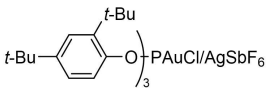
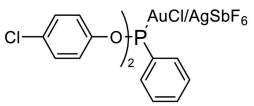
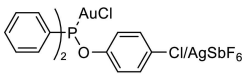
Indeed, in order to determine the pivotal role of the structural features of the propargylic ethers derivatives and of the catalytic system on the regioselective outcome of the IMHA, we screened a variety of Au(I)complexes generating in situ the active catalysts by the combined use of LAuCl complexes and $AgSbF_6$.[14] Accordingly to the remarkable applicability of the $Ph_3PAuCl/AgSbF_6$ catalytic system for the regioselective formation of complex coumarins useful as neuroimaging[11] and the better results provided by triphenylphosphine-gold(I) catalysis results in terms of yield and selectivity compared to the platinum-catalyzed IMHA of functionalised propargyl ethers agents,[15] we observed the regioselective formation of **15a** in high yield and with good regioselectivity in the presence of the gold(I) catalyst bearing methyldiphenylphosphine, triphenylphosphine, tris-(4-chlorophenyl)-phosphine, tris-(4-trifluormethylphenyl)-phosphine and tri(furan-2-yl)phosphine (Table 3, entries 1, 4–6, 8). Likely, the reaction completely failed with the tris-(pentafluorophenyl)phosphine gold(I)chloride/$AgSbF_6$ because of the rapid decomposition of the catalytic system under the reaction conditions (Table 3, entry 7). A worsening of the effectiveness and of the regioselectivity occurred in the presence of the gold(I) catalyst bearing the tricyclohexyl phosphine moiety (Table 3, entry 9). Control experiments with either the gold catalyst alone or the silver salt showed no conversions (Table 3, entries 2–3). Excellent results were observed with the electron-deficient phosphite ligands (Table 3, entries 10–12) and best results in terms of the regioselective outcome were observed using the electron-deficient tris(2,4-di-*tert*-butylphenyl) phosphite ligand (**catalyst 3**) (Table 3, entry 10). Conversely, disappointing results were observed with Au(I) complexes coordinated with the rigid, bulky electron-rich ligands (Table 3, entries 13–19).

However, the IMHA reaction of a variety propargylic ethers **14** in the presence of the **catalyst 3** showed the relevance of

Table 3. Au(I)-catalyzed IMHA of the (4-(3-(3-acetylphenoxy)prop-1-yn-1-yl)phenyl)ethan-1-one **14a**.[a]



14a **15a** **16a**

Entry	Catalyst	Time [h]	Overall yield [%][b]	Ratio **15a**/**16a**[c]
1	$Me(Ph)_2PAuCl/AgSbF_6$	3	99	90/10
2	$Me(Ph)_2PAuCl$	3	–[d]	–
3	$AgSbF_6$	3	–[d]	-
4	$Ph_3PAuCl/AgSbF_6$	5	99	94/6
5	$(p\text{-}Cl\text{-}C_6H_4)_3PAuCl/AgSbF_6$	8	99	90/10
6	$(p\text{-}CF_3\text{-}C_6H_4)_3PAuCl/AgSbF_6$	3	99	92/8
7	$(C_6F_5)_3PAuCl/AgSbF_6$	–[e]	–	–
8		1	99	95/5
9		24	75[f]	75/25
10		3	99	98/2
11		1	99	95/5
12		2	99	94/6
13	$JPAuCl/AgSbF_6$	1	99	41/59
14	$CyJPAuCl/AgSbF_6$	1.5	99	53/47
15	$XPhosAuCl/AgSbF_6$	4	99	63/37
16	$t\text{-}BuXPhosAuCl/AgSbF_6$	3	99	43/57
17	$RuPhosAuCl/AgSbF_6$	7	99	43/57
18	$DavePhosAuCl/AgSbF_6$	8.5	99	84/16
19	$SPhosAuCl/AgSbF_6$	3	99	63/37

[a] Reactions were carried out on 0.3 mmol of **14a** in 2 ml of CH_2Cl_2 at room temperature under the presence of 0.04 equiv. of the catalyst. [b] Overall yield is referred to the mixture of regiosomers **15a**+**16a**. [c] Isomeric ratios were calculated from the ^1H NMR analyses [d] The starting **14a** was quantitatively recovered. [e] Instantaneous precipitation of the catalyst. [f] The starting **14a** was recovered in 11% yield.

the features of the starting alkyne to address a high regiochemical control of the cyclization reaction (see Table 4).

The high regioselective formation of the regioisomers **15** was observed by reacting starting alkynes, bearing withdrawing substituents in both the aromatic rings (Table 4 entries 1 and 2), while the reversing of the regioselectivity occurred with the same catalyst in the presence of electron donating substituents (Table 4, entries 4, 5, and 7).

On the other hand, employing a substrate with opposite electronic effect on the two aromatic moieties, the ring closing reaction is mainly driven by the group on the phenol ring (R^1). Indeed, when an electron-withdrawing substituent is linked to the phenol ring, reaction gives compound **15** as the main component of the isomeric mixtures in spite of the presence of a strong electron-donating group on the other ring (Table 4, entry 2). Using a starting alkyne bearing a mild electron-donating group R^1 and a strong electron -withdrawing group R^2 the site control of the cyclization results to be poorer even with a slight prevalence of the isomer **15** (Table 4, entry 6). In all the examined cases about a quantitative yield of the IMHA products was observed.

Conclusion

In conclusion, we developed an efficient protocol for the synthesis of pyranochromene derivatives through a gold (I)-catalyzed intramolecular hydroarylation reaction (IMHA) that proceeds in good to excellent yields under mild conditions, being compatible with different functional groups such as ether, bromo, trifluoromethyl, acetyl, cyano, and carbomethoxy. The cyclization of unsymmetrically substituted propargylic ethers allows the formation of two isomeric derivatives: both electronic/steric effects of the ligands of gold complexes and electronic effects of the substituents on the aromatic rings of the of the starting alkyne prove to be crucial for the selectivity.

Experimental Section

General information

All the commercially available reagents, catalysts, bases and solvents were used as purchased, without further purification. Reaction products **5b/6b**–**5h/6h** and **15a/16a**–**15g/16g** were obtained as isomeric mixtures by filtration on a pad of SiO_2 to eliminate the catalysts before calculating the isomeric ratio from ^{1}H NMR analyses. When possible, to obtain suitable NMR spectra of each compound, the isomeric mixtures were further purified by semi-preparative HPLC under normal phase condition using a Nucleodur 100–5 column (762007.100) and eluting with *n*-hexane/AcOEt mixtures. Isomeric mixture **15d**+**16d**, **15f**+**16f**, **15g**+**16g** revealed to be inseparable and were characterized without further purification. ^{1}H NMR (400.13 MHz), ^{13}C NMR (100.6 MHz), and ^{19}F spectra (376.5 MHz) were recorded with a Bruker Avance 400 spectrometer, equipped with Nanobay console and Cryoprobe Prodigy probe. Splitting patterns are designed as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), or bs (broad singlet). IR spectra were recorded with a PerkinElmer SpectrumOne FT-ATR spectrophotometer. HRMS were recorded with an Orbitrap Exactive Mass spectrometer with ESI source. Melting points were determined with a Büchi B-545 apparatus and are uncorrected.

Synthetic procedures

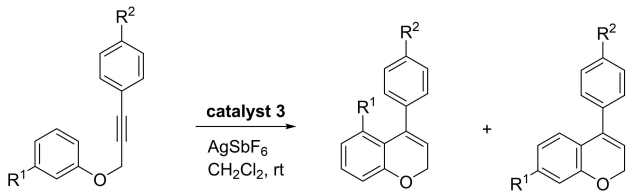
Starting materials has been prepared according to the literature through a two-step procedure.[16]

The typical procedures for the preparation of compounds **4b**, **7b**, **14a** and for the synthesis of **5b/6b** are reported below. Compounds **8** and **15**/**16** were synthetized according to the same procedure outlined for compounds **5b**/**6b**.

Typical procedure for the preparation of 4b

A flask equipped with a magnetic stirring bar was charged with $PdCl_2(PPh_3)_2$ (42 mg, 0.06 mmol, 0.02 equiv.) and CuI (22.8 mg, 0.12 mmol, 0.04 equiv.) dissolved in diisopropylamine (6 mL) and *N,N*-dimethylformamide (3 mL). The resultant solution was stirred under nitrogen at room temperature for 10 minutes before adding

Table 4. Au(I)-catalyzed IMHA of phenyl propargyl ethers **14a–g** in the presence of **catalyst 3.**[a]



14 a-g **15 a-g** **16 a-g**

Entry	14	R^1	R^2	Time [h]	Overall yield [%][b]	Ratio 15/16[c]
1	**14a**	COMe	COMe	3	99	98/2
2	**14b**	COMe	OMe	0.5	99	74/26
3	**14c**	COMe	Cl	2	98	94/6
4	**14d**	OMe	COMe	1.5	99	34/66
5	**14e**	OMe	Cl	0.5	99	36/64
6	**14f**	Me	COMe	1.5	99	60/40
7	**14g**	Me	OMe	0.5	97	23/77

[a] Reactions were carried out on a 0.4 mmol of **14** in 2 ml of CH_2Cl_2 at room temperature under the presence of 0.04 equiv. of the **Catalyst 3**. [b] Overall yield is referred to the mixture of regiosomers **15**+**16**. [c] Isomeric ratios were calculated from the ^{1}H NMR analyses.

iodobenzene (1387 mg, 760 μl, 6.8 mmol, 2.2 equiv.) and 1,3-bis (prop-2-yn-1-yloxy)benzene (576 mg, 3.1 mmol, 1.0 equiv.) and stirred for 4 hours at room temperature. After this time, the reaction mixture was diluted with Et_2O and washed with a saturated NH_4Cl solution, HCl 2 N and with brine. The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by chromatography on SiO_2 (25–40 μm), eluting with a 95/5 (v/v) *n*-hexane/AcOEt mixture (R_f = 0.24) to obtain 813 mg (77% yield) of 1,3-bis((3-phenylprop-2-yn-1-yl)oxy) benzene **4b**.

Compound 4b: Yield: 77% (813 mg); *n*-hexane/AcOEt mixture 95/5 (v/v) R_f = 0.24; pale yellow solid.

Mp = 61–62 °C; IR (neat): 2907, 2223, 1587, 1488, 1365, 1257 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.48–7.46 (m, 4 H), 7.35–7.25 (m, 7 H), 6.76 (t, J = 2.3 Hz, 1 H), 6.72 (dd, J_1 = 8.2 Hz, J_2 = 2.3 Hz, 2 H), 4.93 (s, 4 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 159.2, 132.0, 130.1, 128.8, 128.4, 122.4, 108.1, 102.7, 87.3, 83.9, 56.9; HRMS: *m/z* $[M+H]^+$ calcd for $C_{24}H_{19}O_2$: 339.1380; found: 339.1379.

Typical procedure for the preparation of 7b

A flask equipped with a magnetic stirring bar was charged with $PdCl_2(PPh_3)_2$ (29.2 mg, 0.042 mmol, 0.02 equiv.) and CuI (15.8 mg, 0.083 mmol, 0.04 equiv.) dissolved in diisopropylamine (10 mL) and *N,N*-dimethylformamide (5 mL). The resultant solution was stirred under nitrogen at room temperature for 10 minutes before adding iodobenzene (1401 mg, 768 μl, 6.87 mmol, 3.3 equiv.) and 1,3,5-tris (prop-2-yn-1-yloxy)benzene (500 mg, 2.08 mmol, 1.0 equiv.) and stirred for 24 hours at room temperature. After this time, the reaction mixture was diluted with Et_2O and washed with a saturated NH_4Cl solution, HCl 2 N and with brine. The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by chromatography on SiO_2 (25-40 μm), eluting with a 85/15 (v/v) *n*-hexane/AcOEt mixture (R_f = 0.24) to obtain 584 mg (60% yield) of 1,3,5-tris((3-phenylprop-2-yn-1-yl)oxy)benzene **7b**.

Compound **7b**: Yield: 60% (584 mg); *n*-hexane/AcOEt mixture 85/15 (v/v) R_f = 0.24; white solid.

Mp = 76-77 °C; IR (neat): 2921, 2233, 1716, 1601, 1508, 1350 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.48–7.46 (m, 6 H), 7.36–7.28 (m, 9 H), 6.41 (s, 3 H), 4.91 (s, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 159.8, 132.0, 128.8, 128.4, 123.4, 95.7, 87.4, 83.7, 57.1; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{33}H_{24}O_3Na$: 491.1618; found: 491.1629.

Typical procedure for the preparation of **14a:**

A flask equipped with a magnetic stirring bar was charged with $PdCl_2(PPh_3)_2$ (56.0 mg, 0.08 mmol, 0.02 equiv.) and CuI (30.0 mg, 0.16 mmol, 0.04 equiv.) dissolved in diisopropylamine (5 mL) and *N,N*-dimethylformamide (4 mL). The resultant solution was stirred under nitrogen at room temperature for 10 minutes before adding 1-(4-iodophenyl)ethan-1-one (1180 mg, 4.8 mmol, 1.2 equiv.) in diisopropylamine (3 mL) and 1-(3-(prop-2-yn-1-yloxy)phenyl)ethan-1-one (700 mg, 4.0 mmol, 1.0 equiv.) and stirred for 1 hour at room temperature. After this time, the reaction mixture was diluted with Et_2O and washed with a saturated NH_4Cl solution, HCl 2 N and with brine. The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by chromatography on SiO_2 (25–40 μm), eluting with a 75/25 (v/v) *n*-hexane/AcOEt mixture (R_f = 0.23) to obtain 1063 mg (91% yield) of 1-(4-(3-(3-acetylphenoxy)prop-1-yn-1-yl)phenyl)ethan-1-one **14a.**

Compound **14a**: Yield: 91% (1063 mg); *n*-hexane/AcOEt mixture 75/25 (v/v); R_f = 0.23; pale yellow solid.

Mp: 73–74; °C; IR (neat): 2920, 2227, 1683, 1592, 1448, 1361, 1258, 1026 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.90 (d, J = 8.4 Hz, 2 H), 7.65 (s, 1 H), 7.61 (d, J = 7.6 Hz, 1 H) 7.53 (d, J = 8.4 Hz, 2 H), 7.43 (t, J = 8.0 Hz, 1 H), 7.26–7.23 (m, 1 H), 5.0 (s, 2H), 2.62 (s, 3 H), 2.60 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 197.7, 197.2, 157.8, 138.5, 136.7, 132.0, 129.7, 128.2, 126.9, 122.0, 120.4, 113.7, 86.7, 86.6, 56.7, 26.7, 26.6; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{19}H_{16}O_3$ Na: 315.0992, found: 315.0992.

Typical procedure for the preparation of **5b/6b:**

A flask equipped with a magnetic stirring bar was charged with 1,3-bis((3-phenylprop-2-yn-1-yl)oxy)benzene (101.5 mg, 0.3 mmol, 1 equiv) and CH_2Cl_2 (2 mL) before adding catalyst 1 or 2 or 3 (catalyst 1: JohnPhosAu(MeCN)SbF_6, 9.2 mg, 0.012 mmol, 0.04 equiv; catalyst 2: $MePh_2PAuCl$, 5.2 mg, 0.012 mmol, 0.04 equiv. and $AgSbF_6$, 4.1 mg, 0.012 mmol, 0.04 equiv; catalyst 3: [Tris(2,4-di-*tert*-butylphenyl)phosphite]gold chloride, 10.5 mg, 0.012 mmol, 0.04 equiv. and $AgSbF_6$, 4.1 mg, 0.012 mmol, 0.04 equiv).The resulting mixture was stirred for 30 minutes, then it was concentrated under reduced pressure and the residue was filtered on a pad of SiO_2 to afford 96.2 mg of isomeric mixture **5b** + **6b** (95% overall yield) using catalyst 1 or 91.5 mg of isomeric mixture **5b** + **6b** (90% overall yield) using catalyst 2 or 97.3 mg of isomeric mixture **5b** + **6b** (96% overall yield) using catalyst 3. Regioisomeric ratio was calculated by ^1H NMR analyses on the residue obtained after filtration. Afterwards, the two isomers were separated by semi-preparative HPLC to obtain suitable NMR spectra of each compound.

HPLC eluent = *n*-hexane/AcOEt mixture 95/5 (v/v); R_f = 0.22

Overall yield (catalyst 1): 95% (96.2 mg); **5b**/**6b** = 2/98.

Overall yield (catalyst 2): 90% (91.5 mg); **5b**/**6b** = 40/60;

Overall yield (catalyst 3): 96% (97.3 mg); **5b**/**6b** = 46/54;

Compound **5b**: yellow solid; mp: 139–140 °C; IR (neat): 2919, 2838, 1676, 1599, 1575, 1489 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.32–7.21 (m, 10 H), 6.81 (d, J = 8.4 Hz, 1 H), 6.47 (d, J = 8.4 Hz, 1 H), 5.78 (t, J = 4.5 Hz, 1 H), 5.50 (t, J = 3.9 Hz, 1 H), 4.59 (d, J = 4.5 Hz, 2 H), 4.27 (d, J = 3.9 Hz, 2 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 157.0, 151.2, 141.3, 138.7, 137.2, 136.3, 128.8, 128.5, 127.8, 127.7, 127.1, 127.0, 126.7, 121.0, 118.9, 117.4, 113.2, 109.1, 65.0, 64.4; HRMS: *m/z* $[M+H]^+$ calcd for $C_{24}H_{19}O_2$: 339.1380; found: 339.1376.

Compound **6b**: white solid; mp: 176–177 °C; IR (neat): 2962, 2826, 1599, 1487, 1252, 1158 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.33–7.26 (m, 10 H), 6.79 (s, 1 H), 6.54 (s, 1 H), 5.69 (t, J = 4.0 Hz, 2 H), 4.85 (d, J = 4.0 Hz, 4 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 156.2, 138.2, 137.0, 128.5, 128.3, 127.9, 123.7, 117.2, 117.1, 104.4, 65.7; HRMS: *m/z* $[M+H]^+$ calcd for $C_{24}H_{19}O_2$: 339.1380; found: 339.1376.

Characterization data of 4c–h, 7c–l, 9, 11, 14b–g

Compound **4c**: Yield: 82% (901.5 mg); *n*-hexane/AcOEt mixture 97/3 (v/v); R_f = 0.24; known Compound;[16] white solid;

Mp = 120-121 °C; IR (neat): 2914, 2229, 1587, 1488, 1366, 1153, 1039 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.34 (d, J = 8.0 Hz, 4 H), 7.23 (t, J = 8.2 Hz, 1 H), 7.10 (d, J = 8.0 Hz, 4 H), 6.73 (t, J = 2.3 Hz, 1 H), 6.68 (dd, J_1 = 8.2 Hz, J_2 = 2.3 Hz, 2 H), 4.89 (s, 4 H), 2.34 (s, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 159.2, 139.0, 131.9, 130.0, 129.2, 119.3, 108.0, 102.7, 87.5, 83.3, 57.0, 21.6; HRMS: *m/z* $[M+H]^+$ calcd for $C_{26}H_{23}O_2$: 367.1693; found: 367.1688.

Compound **4d**: Yield: 49% (625.0 mg); *n*-hexane/AcOEt mixture 90/10 (v/v); R_f = 0.24; known Compound;[16] white solid.

Mp = 123-124 °C ; IR (neat): 2964, 2228, 1603, 1487, 1247, 1142, 1036 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.38 (d, J = 8.9 Hz, 4 H), 7.23 (t, J = 8.2 Hz, 1 H), 6.82 (d, J = 8.9 Hz, 4 H), 6.73 (t, J = 2.4 Hz, 1 H), 6.67 (dd, J_1 = 8.2 Hz, J_2 = 2.4 Hz, 2 H), 4.88 (s, 4 H), 3.80 (s, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 160.0, 159.2, 133.5, 130.0, 114.5, 114.0, 108.0, 102.7, 87.3, 82.6, 57.0, 55.4; HRMS: m/z $[M+H]^+$ calcd for $C_{26}H_{23}O_4$: 399.1591; found: 399.1588.

Compound **4e**: Yield: 50% (612.3 mg); *n*-hexane/AcOEt mixture 80/20 (v/v); R_f = 0.25; pale yellow solid.

Mp = 127-129 °C ; IR (neat): 2957, 2167, 1682, 1489, 1261, 1141, 841 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.87 (d, J = 8.6 Hz, 4 H), 7.50 (d, J = 8.6 Hz, 4 H), 7.26 (t, J = 8.3 Hz, 1 H), 6.72-6.71 (m, 1 H), 6.69 (dd, J_1 = 8.3 Hz, J_2 = 2.2 Hz, 2 H), 4.92 (s, 4 H), 2.58 (s, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 197.4, 159.1, 136.8, 132.1, 130.2, 128.3, 127.1, 108.1, 102.7, 87.2, 86.5, 56.8, 26.7; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{28}H_{22}O_4Na$: 445.1410; found: 445.1405.

Compound **4f**: Yield: 47% (641.1 mg); *n*-hexane/AcOEt mixture 90/10 (v/v); R_f = 0.24; yellow solid.

Mp = 111-112 °C ; IR (neat): 2904, 2234, 1709, 1588, 1489, 1153, 765 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.96 (d, J = 8.5 Hz, 4 H), 7.48 (d, J = 8.5 Hz, 4 H), 7.25 (t, J = 8.2 Hz, 1 H), 6.72-6.71 (m, 1 H), 6.69 (dd, J_1 = 8.2 Hz, J_2 = 2.2 Hz, 2 H), 4.92 (s, 4 H), 3.91 (s, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 166.5, 159.1, 131.9, 130.2, 130.1, 129.6, 127.0, 108.1, 102.7, 86.8, 86.5, 56.8, 52.4; HRMS: *m/z* $[M+H]^+$ calcd for $C_{28}H_{23}O_6$: 455.1489; found: 455.1482.

Compound **4g**: Yield: 79% (965.8 mg); *n*-hexane/AcOEt mixture 93/7 (v/v); R_f = 0.24; known Compound;[16] white solid.

Mp = 120-121 °C ; IR (neat): 2932, 2228, 1610, 1585, 1488, 1142, 750 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.38 (d, J = 8.6 Hz, 4 H), 7.29 (d, J = 8.6 Hz, 4 H), 7.27-7.25 (m, 1 H) 6.74-6.72 (m, 1 H), 6.70 (dd, J_1 = 8.2 Hz, J_2 = 2.3 Hz, 2 H), 4.91 (s, 4 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 159.1, 134.9, 133.2, 130.1, 128.8, 120.8, 108.1, 102.7, 86.2, 84.9, 56.8; HRMS: *m/z* $[M+H]^+$ calcd for $C_{24}H_{17}Cl_2O_2$: 407.0600; found: 407.0604.

Compound **4h**: Yield: 66% (1015.4 mg); *n*-hexane/AcOEt mixture 95/5 (v/v) R_f = 0.24; White solid.

Mp = 94-95 °C ; IR (neat): 2926, 2234, 1610, 1585, 1467, 1141, 847 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.56 (dd, J_1 = 7.9 Hz, J_2 = 1.2 Hz, 2 H), 7.46 (dd, J_1 = 7.6 Hz, J_2 = 1.7 Hz, 2 H), 7.25-7.21 (m, 3 H), 7.16 (dt, J_1 = 7.9 Hz, J_2 = 1.8 Hz, 2 H), 6.80 (t, J = 2.4 Hz, 1 H), 6.72 (dd, J_1 = 8.2 Hz, J_2 = 2.4 Hz, 2 H), 4.96 (s, 4 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 159.1, 133.9, 132.5, 130.04, 129.97, 127.1, 125.8, 124.6, 108.4, 103.0, 88.6, 85.8, 56.9; HRMS: *m/z* $[M+H]^+$ calcd for $C_{24}H_{17}Br_2O_2$: 496.9569; found: 496.9563.

Compound **7c**: Yield: 46% (470.1 mg); *n*-hexane/AcOEt mixture 90/10 (v/v); R_f = 0.25; pale brown solid.

Mp = 101–102 °C; IR (neat): 2924, 2236, 1601, 1434, 1329, 1240 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.33 (d, J = 8.0 Hz, 6 H), 7.09 (d, J = 8.0 Hz, 6 H), 6.37 (s, 3 H), 4.87 (s, 6 H), 2.33 (s, 9 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 159.8, 139.0, 131.9, 129.2, 119.3, 95.7, 87.6, 83.1, 57.1, 21.6; HRMS: *m/z* $[M+H]^+$ calcd for $C_{36}H_{31}O_3$: 511.2268; found: 511.2274.

Compound **7d**: Yield: 40% (469 mg); *n*-hexane/AcOEt mixture 90/10 (v/v) R_f = 0.23; white solid.

Mp = 109–111 °C; IR (neat): 2922, 2241, 1602, 1471, 1433, 1328 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.38 (d, J = 8.9 Hz, 6 H), 6.81 (d, J = 8.9 Hz, 6 H), 6.37 (s, 3 H), 4.86 (s, 6 H), 3.79 (s, 9 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 160.0, 159.8, 133.5, 114.4, 114.0, 95.6, 87.4, 82.4, 57.1, 55.4; HRMS: *m/z* $[M+H]^+$ calcd for $C_{36}H_{31}O_6$: 559.2115; found: 559.2130.

Compound **7e**: Yield: 65% (726.69 mg); *n*-hexane/AcOEt mixture 85/15 (v/v); R_f = 0.24; orange oil.

IR (neat): 2935, 2230, 1716, 1598, 1466, 1143 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.20 (t, J = 8.0 Hz, 3 H), 7.04 (d, J = 7.6 Hz, 3 H), 6.98 (m, 3 H), 6.88 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 3 H), 6.38 (s, 3 H), 4.88 (s, 6 H), 3.78 (s, 9 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 159.8, 159.4,129.5, 124.5, 123.3, 116.7, 115.5, 95.7, 87.4, 83.6, 57.0, 55.4; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{36}H_{30}O_6Na$: 581.1935; found: 581.1946.

Compound **7f**: Yield: 60% (713.0 mg); *n*-hexane/AcOEt mixture 80/20 (v/v); R_f = 0.22; pink solid.

Mp = 118–120 °C; IR (neat): 2916, 2857, 2223, 1681, 1599, cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.86 (d, J = 8.4 Hz, 6 H), 7.50 (d, J = 8.4 Hz, 6 H), 6.38 (s, 3 H), 4.91 (s, 6 H), 2.58 (s, 9 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 197.3, 159.6, 136.7, 131.9, 128.2, 126.9, 95.6, 86.8, 86.5, 56.8, 26.6; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{39}H_{30}O_6Na$: 617.1935; found: 617.1943.

Compound **7g**: Yield: 65% (835.8 mg); *n*-hexane/AcOEt mixture 85/15 (v/v); R_f = 0.25; white solid.

Mp = 148–149 °C; IR (neat): 2923, 2235, 1601, 1469, 1434, 1329 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.94 (d, J = 8.5 Hz, 6 H), 7.47 (d, J = 8.5 Hz, 6 H), 6.38 (s, 3 H), 4.90 (s, 6 H), 3.91 (s, 9 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 166.5, 159.7, 131.9, 130.1, 129.6, 126.9, 95.7, 86.7, 86.6, 56.9, 52.4; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{39}H_{30}O_9Na$: 665.1782; found: 665.1791.

Compound **7h**: Yield: 93% (960.5 mg); *n*-hexane/AcOEt mixture 70/30 (v/v); R_f = 0.27; yellow solid.

Mp = 173–174 °C; IR (neat): 2910, 2226, 1599, 1508, 1364, 1141 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.59 (d, J = 8.2 Hz, 6 H), 7.51 (d, J = 8.2 Hz, 6 H), 6.34 (s, 3 H), 4.90 (s, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 159.6, 132.4, 132.1, 127.0, 118.3, 112.3, 95.5, 87.9, 85.7, 56.7; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{36}H_{21}N_3O_3Na$: 566.1475; found: 566.1476.

Compound **7i**: Yield: 94% (1138 mg); *n*-hexane/AcOEt mixture 85/15 (v/v); R_f = 0.25; orange solid.

Mp = 64–66 °C; IR (neat): 2925, 2238, 1602, 1471, 1433, 1328 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.69 (bs, 3 H), 7.60–7.55 (m, 6 H), 7.41 (t, J = 7.8 Hz, 3 H), 6.38 (s, 3 H), 4.90 (s, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 159.8, 135.0, 131.1 (q, J_{CF} = 32.5 Hz), 129.0, 128.8 (q, J_{CF} = 3.7 Hz), 125.5 (q, J_{CF} = 4.1 Hz), 123.7 (q, J_{CF} = 270.6 Hz), 123.2, 95.7, 85.9, 85.3, 56.8; ^{19}F NMR (376.5 MHz) ($CDCl_3$): δ = -63.0; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{36}H_{21}F_9O_3Na$: 695.1239; found: 695.1240.

Compound **7j**: Yield: 73% (835.0 mg); *n*-hexane/AcOEt mixture 90/10 (v/v); R_f = 0.26; white solid.

Mp = 131–132 °C; IR (neat): 2916, 2224, 1599, 1470, 1362, 1247 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.27 (d, J = 8.6 Hz, 6H), 7.18 (d, J = 8.6 Hz, 6H), 6.28 (s, 3H), 4.79 (s, 6H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 159.8, 135.0, 133.2, 128.8, 120.8, 95.7, 86.3, 84.7, 56.9; HRMS: *m/z* $[M+H]^+$ calcd for $C_{33}H_{22}Cl_3O_3$: 571.0629; found: 571.0641.

Compound **7k**: Yield: 402% (621.9 mg); *n*-hexane/AcOEt mixture 90/10 (v/v); R_f = 0.25; pale brown solid.

Mp = 142–143 °C; IR (neat): 2913, 2224, 1682, 1597, 1468, 1361 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.41 (d, J = 8.6 Hz, 6 H), 7.27 (d, J = 8.6 Hz, 6 H), 6.35 (s, 3 H), 4.86 (s, 6 H); ^{13}C NMR

(100.6 MHz) ($CDCl_3$): δ = 159.7, 133.4, 131.7, 123.2, 121.2, 95.7, 86.4, 84.9, 56.9; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{33}H_{21}Br_3O_3Na$: 726.8913; found: 726.8912.

Compound **7l**: Yield: 85% (1198.3 mg); *n*-hexane/AcOEt mixture 90/10 (v/v); R_f = 0.24; yellow oil.

IR (neat): 2915, 2242, 1712, 1591, 1405, 1278 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.58–7.57 (m, 3 H), 7.46–7.43 (m, 3 H), 7.36–7.34 (m, 3 H), 7.15 (t, *J* = 7.9 Hz, 3 H), 6.36 (s, 3 H), 4.88 (s, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 159.7, 134.7, 132.0, 130.5, 129.9, 124.3, 122.2, 95.7, 85.9, 85.1, 56.9; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{33}H_{21}Br_3O_3Na$: 726.8913; found: 726.8914.

Compound **9**: Yield: 92% (1407 mg); *n*-hexane/AcOEt mixture 90/10 (v/v); R_f = 0.26; yellow solid.

Mp = 162–163 °C; IR (neat): 2926, 2220, 1638, 1598, 1483, 1365, 1161, 1100, 814 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.88–7.86 (m, 2 H), 7.50–7.48 (m, 3 H), 7.35–7.31 (m, 4 H), 7.10 (d, *J* = 7.9 Hz, 2 H), 7.07 (d, *J* = 7.9 Hz, 2 H), 6.79 (d, *J* = 2.3 Hz, 1 H), 6.77 (d, *J* = 2.3 Hz, 1 H), 6.68 (s, 1 H), 5.10 (s, 2 H), 5.00 (s, 2 H), 2.33 (s, 3 H), 2.31 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 177.4, 161.9, 160.8, 159.6, 158.9, 139.2, 138.9, 131.8 (overlapping, 2 C), 131.5, 131.2, 129.1, 129.0, 128.9, 126.0, 119.1, 118.7, 110.3, 109.1, 99.3, 95.1, 88.4, 88.3, 82.5, 81.9, 58.1, 57.3, 21.5, 21.4; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{35}H_{26}O_4Na$: 533.1723, found: 533.1727.

Compound **11**: Yield: 95% (1126 mg); *n*-hexane/AcOEt mixture 90/10 (v/v); R_f = 0.25; yellow solid.

Mp = 172–173 °C; IR (neat): 2922, 2224, 1639, 1614, 1493, 1376, 1260, 1024, 820 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.81–7.78 (m, 2H), 7.43–7.40 (m, 3 H), 7.27 (d, *J* = 8.1 Hz, 2 H), 7.04 (d, *J* = 8.1 Hz, 2 H), 6.65 (d, *J* = 2.3 Hz, 1 H), 6.61 (s, 1 H), 6.42 (d, *J* = 2.3 Hz, 1 H), 4.93 (s, 2 H), 3.89 (s, 3 H), 2.26 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 177.6, 162.1, 161.0, 160.8, 159.7, 139.3, 131.7, 131.5, 131.2, 129.2, 128.9, 126.0, 118.7, 109.7, 109.1, 96.7, 94.1, 88.4, 81.9, 57.2, 56.5, 21.6; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{26}H_{20}O_4Na$: 419.1254, found: 419.1247.

Compound **14b**: Yield: 93% (1039 mg); *n*-hexane/AcOEt mixture 75/25 (v/v) R_f = 0.24; pale yellow solid.

Mp = 49–50 °C; IR (neat): 2934, 2227, 1682, 1581, 1508, 1246, 1026, 832 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.73–7.69 (m, 2 H), 7.41–7.37 (m, 3 H), 7.25 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1 H), 6.85 (d, *J* = 8.4 Hz, 2 H), 4.97 (s, 2 H), 3.94 (s, 3 H), 3.82 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 166.9, 159.9, 157.7, 133.4, 131.5, 129.4, 122.6, 120.3, 115.4, 114.2, 113.9, 87.6, 82.1, 56.9, 55.3, 52.2; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{18}H_{16}O_3Na$: 303.0992, found: 303.0991.

Compound **14c**: Yield: 93% (1055 mg); *n*-hexane/AcOEt mixture 75/25 (v/v) R_f = 0.25; pale yellow solid.

Mp = 58–60 °C; IR (neat): 2920, 2227, 1683, 1591, 1484, 1437, 1265, 1013, 825 cm^{-1};^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.56–7.55 (m, 1 H), 7.52 (d, *J* = 7.6 Hz, 1 H), 7.33 (t, *J* = 7.9 Hz, 1 H), 7.29 (d, *J* = 8.5 Hz, 2 H), 7.20 (d, *J* = 8.5 Hz, 2 H), 7.15 (dd, J_1 = 7.9 Hz, J_2 = 2.4 Hz, 1 H), 4.88 (s, 2 H), 2.53 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 197.7, 157.9, 138.5, 134.9, 133.1, 129.7, 128.7, 121.9, 120.6, 120.4, 113.7, 86.5, 84.3, 56.7, 26.8; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{17}H_{13}O_2ClNa$: 307.0496, found: 307.0497.

Compound **14d**: Yield: 90% (1010 mg); *n*-hexane/AcOEt mixture 75/25 (v/v) R_f = 0.25; brown solid.

Mp = 64–65 °C; IR (neat): 2919, 2220, 1678, 1592, 1483, 1448, 1360, 1257, 1026, 835 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.81 (d, *J* = 8.4 Hz, 2 H), 7.44 (d, *J* = 8.4 Hz, 2 H), 7.14 (t, *J* = 8.4 Hz, 1 H), 6.57–6.48 (m, 3 H), 4.84 (s, 2 H), 3.72 (s, 3 H), 2.51 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 197.2, 160.8, 158.9, 136.6, 131.9, 129.9, 128.2, 127.1, 107.2, 106.9, 101.6, 87.2, 86.3, 56.6, 55.3, 26.6; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{18}H_{16}O_3Na$: 303.0992, found: 303.0990 m/z.

Compound **14e**: Yield: 90% (1010 mg); *n*-hexane/AcOEt mixture 80/20 (v/v); R_f = 0.26; pale yellow solid.

Mp = 35–36 °C; IR (neat): 2928, 2221, 1682, 1591, 1484, 1437, 1357, 1258, 1014, 825 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.29 (d, *J* = 8.4 Hz, 2 H), 7.20 (d, *J* = 8.4 Hz, 2 H), 7.14 (t, *J* = 8.0 Hz, 1 H), 6.52 (m, 3 H), 4.80 (s, 2 H), 3.72 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 160.8, 159.9, 134.8, 133.1, 129.9, 128.7, 120.8, 107.1, 106.9, 101.5, 86.0, 84.9, 56.6, 55.3; HRMS: *m/z* $[M+H]^+$ calcd for $C_{16}H_{14}O_2Cl$: 273.0677, found: 273.0674

Compound **14f**: Yield: 89% (940 mg); *n*-hexane/AcOEt mixture 75/25 (v/v); R_f = 0.24; pale yellow solid; known compound.[11]

Mp = 78–80 °C; IR (neat): 2910, 2210, 1673, 1598, 1492, 1403, 1357, 1257, 1026, 825 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.92 (d, *J* = 8.5 Hz, 2 H), 7.54 (d, *J* = 8.5 Hz, 2 H), 7.25–7.21 (m, 1 H), 6.86–6.84 (m, 3 H), 4.93 (s, 2 H), 2.62 (s, 3 H), 2.38 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 197.3, 157.7, 139.6, 136.6, 131.9, 129.2, 128.2, 127.2, 122.4, 115.9, 111.7, 87.4, 86.2, 56.5, 26.6, 21.6; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{18}H_{16}O_2Na$: 287.1043, found: 287.1040.

Compound **14g**: Yield: 95% (940 mg); *n*-hexane/AcOEt mixture 80/20 (v/v); R_f = 0.27; yellow oil; known compound.[11]

IR (neat): 2916, 2224, 1604, 1584, 1508, 1488, 1244, 1150, 1031, 830 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.27 (d, *J* = 8.8 Hz, 2 H), 7.08 (t, *J* = 7.2 Hz, 1 H), 6.74–6.64 (m, 5 H), 4.75 (s, 2 H), 3.66 (s, 3 H), 2.23 (s, 3H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 159.9, 158.0, 139.6, 133.4, 129.2, 122.2, 115.9, 114.5, 114.0, 111.8, 87.1, 82.8, 56.7, 55.3, 21.6; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{17}H_{16}O_2Na$: 275.1043, found: 275.1039.

Characterization data of **5c–h**, **6c–h**, **8b–l**, **10a**, **12a**, **15a–g**, **16a–g**

Isomeric mixture 5c + 6c

HPLC eluent = *n*-hexane/AcOEt mixture 95/5 (v/v); R_f = 0.21

Overall yield (catalyst 1): 98% (107.9 mg); **5c**/**6c** = 0/100

Overall yield (catalyst 2): 98% (108.3 mg); **5c**/**6c** = 39/61

Overall yield (catalyst 3): 98% (107.5 mg); **5c**/**6c** = 42/58

Compound **5c**: white solid; mp = 168–170 °C; IR (neat): 2919, 2846, 1678, 1602, 1489, 1259 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.19–7.06 (m, 8 H), 6.82 (d, *J* = 8.4 Hz, 1 H), 6.46 (d, *J* = 8.4 Hz, 1 H), 5.76 (t, *J* = 4.4 Hz, 1 H), 5.48 (t, *J* = 3.7 Hz, 1 H), 4.57 (d, *J* = 4.4 Hz, 2 H), 4.29 (d, *J* = 3.7 Hz, 2 H), 2.31 (s, 3 H), 2.30 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 157.0, 151.3, 138.3, 137.6, 137.1, 136.6, 136.2, 135.8, 129.1, 128.7, 128.4, 127.0, 126.7, 120.6, 119.0, 116.9, 113.2, 109.0, 64.9, 64.4, 21.4, 21.3; HRMS: *m/z* $[M+H]^+$ calcd for $C_{26}H_{23}O_2$: 367.1693; found: 367.1691.

Compound **6c**: yellow solid; mp = 184–185 °C; IR (neat): 2922, 2838, 1676, 1489, 1257, 1117 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.18 (d, *J* = 8.0 Hz, 4 H), 7.12 (d, *J* = 8.0 Hz, 4 H), 6.84 (s, 1 H), 6.52 (s, 1 H), 5.66 (t, *J* = 4.0 Hz, 2 H), 4.81 (d, *J* = 4.0 Hz, 4 H), 2.35 (s, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 156.2, 137.5, 136.9, 135.3, 129.0, 128.3, 123.8, 117.2, 116.8, 104.3, 65.6, 21.3; HRMS: *m/z* $[M+H]^+$ calcd for $C_{26}H_{23}O_2$: 367.1693; found: 367.1689.

Isomeric mixture 5d + 6d

HPLC eluent = *n*-hexane/AcOEt mixture 90/10 (v/v); R_f = 0.21

Overall yield (catalyst 1): 98% (116.9 mg); **5d**/**6d** = 0/100

Overall yield (catalyst 2): 99% (118.4 mg); **5d**/**6d** = 7/93

Overall yield (catalyst 3): 98% (117.3 mg); **5d**/**6d** = 28/72

Compound **5d**: yellow solid; mp = 90–91 °C; IR (neat): 2922, 2846, 1677, 1601, 1489, 1247 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.26–7.23 (m, 4 H), 6.92–6.86 (m, 5 H), 6.53 (d, *J* = 8.4 Hz, 1 H), 5.81 (t, *J* = 4.6 Hz, 1 H), 5.54 (t, *J* = 3.9 Hz, 1 H), 4.64 (d, *J* = 4.6 Hz, 2 H), 4.37 (d, *J* = 3.9 Hz, 2 H), 3.84 (s, 6H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 159.4, 158.8, 157.1, 151.4, 136.8, 135.9, 133.7, 131.1, 129.9, 128.2, 126.7, 120.2, 119.1, 116.6, 113.9, 113.2, 113.1, 109.0, 64.9, 64.5, 55.5, 55.4; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{26}H_{22}O_4Na$: 421.1410; found: 421.1405.

Compound **6d**: white solid; mp = 185–186 °C; IR (neat): 2916, 2839, 1677, 1610, 1489, 1257 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.20 (d, *J* = 8.8 Hz, 4 H), 6.83 (d, *J* = 8.8 Hz, 4 H), 6.80 (s, 1 H), 6.50 (s, 1 H), 5.62 (t, *J* = 4.0 Hz, 2 H), 4.80 (d, *J* = 4.0 Hz, 4 H), 3.80 (s, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 159.3, 156.2, 136.6, 130.7, 129.6, 123.7, 117.3, 116.4, 113.7, 104.4, 65.7, 55.4; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{26}H_{22}O_4Na$: 421.1410; found: 421.1405.

Isomeric mixture 5e + 6e

HPLC eluent = *n*-hexane/AcOEt mixture 80/20 (v/v); R_f = 0.22

Overall yield (**catalyst 1**): 99% (131.0 mg); **5e**/**6e** = 39/61

Overall yield (**catalyst 2**): 97% (128.8 mg); **5e**/**6e** = 40/60

Overall yield (**catalyst 3**): 97% (128.6 mg); **5e**/**6e** = 42/58

Compound **5e**: yellow solid; mp = 157–158 °C; IR (neat): 2922, 2838, 1674, 1601, 1489, 1258 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.98 (d, *J* = 8.4 Hz, 2 H), 7.95 (d, *J* = 8.4 Hz, 2 H), 7.42–7.39 (m, 4 H), 6.85 (d, *J* = 8.4 Hz, 1 H), 6.56 (d, *J* = 8.4 Hz, 1 H), 5.92 (t, *J* = 4.6 Hz, 1 H), 5.64 (t, *J* = 4.0 Hz, 1 H), 4.69 (d, *J* = 4.6 Hz, 2 H), 4.35 (d, *J* = 4.0 Hz, 2 H), 2.64 (s, 3 H), 2.63 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 198.0, 197.8, 157.1, 151.0, 146.2, 136.6, 136.5, 135.8, 135.4, 128.9, 128.6, 128.0, 127.3, 126.8, 122.5, 120.6, 118.4, 118.3, 112.7, 109.4, 64.9, 64.3, 26.82, 26.79; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{26}H_{22}O_4Na$: 445.1410; found: 445.1402.

Compound **6e**: yellow solid; mp = 190–191 °C; IR (neat): 2959, 2814, 1676, 1576, 1488, 1257 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.88 (d, *J* = 8.2 Hz, 4 H), 7.34 (d, *J* = 8.2 Hz, 4 H), 6.57 (s, 1 H), 6.53 (s, 1 H), 5.74 (t, *J* = 4.0 Hz, 2 H), 4.85 (d, *J* = 4.0 Hz, 4 H), 2.58 (s, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 197.7, 156.4, 143.1, 136.6, 136.2, 128.7, 128.5, 123.2, 118.6, 116.8, 104.7, 65.6, 26.7; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{26}H_{22}O_4Na$: 445.1410; found: 445.1402.

Isomeric mixture 5f + 6f

HPLC Eluent = *n*-hexane/AcOEt mixture 90/10 (v/v); R_f = 0.20

Overall yield (catalyst 1): 92% (125.4 mg); **5f**/**6f** = 13/87;

Overall yield (catalyst 2): 98% (133.4 mg); **5f**/**6f** = 41/59;

Overall yield (catalyst 3): 96% (130.9 mg); **5f**/**6f** = 43/57;

Compound **5f**: white solid; mp = 176–177 °C; IR (neat): 2924, 2848, 1678, 1601, 1259, 1157 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 8.05 (d, *J* = 8.4 Hz, 2 H), 8.02 (d, *J* = 8.4 Hz, 2 H), 7.38 (dd, J_1 = 8.4 Hz, J_2 = 2.8 Hz, 4 H), 6.84 (d, *J* = 8.4 Hz, 1 H), 6.55 (d, *J* = 8.4 Hz, 1 H), 5.91 (t, *J* = 4.5 Hz, 1 H), 5.63 (t, *J* = 4.0 Hz, 1 H), 4.69 (d, *J* = 4.5 Hz, 2 H), 4.34 (d, *J* = 4.0 Hz, 2 H), 3.94 (s, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 167.2, 167.0, 157.1, 151.0, 146.0, 143.3, 136.5, 135.5, 129.8, 129.6, 129.2, 128.7, 127.1, 126.8, 122.3, 118.34, 118.30, 112.8, 109.4, 64.9, 64.3, 52.3, 52.2; HRMS: *m/z* $[M+H]^+$ calcd for $C_{28}H_{23}O_6$: 455.1489; found: 455.1484.

Compound **6f**: white solid; mp = 216–217 °C; IR (neat): 3070, 2866, 1713, 1653, 1575, 1161 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.95 (d, *J* = 8.2 Hz, 4 H), 7.31 (d, *J* = 8.2 Hz, 4 H), 6.60 (s, 1 H), 6.52 (s, 1 H), 5.72 (t, *J* = 4.0 Hz, 2 H), 4.83 (d, *J* = 4.0 Hz, 4 H), 3.91 (s, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 166.9, 156.4, 142.9, 136.3, 129.74, 129.70, 128.4, 123.1, 118.6, 116.8, 104.7, 65.5, 52.3; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{28}H_{22}O_6Na$: 477.1309; found: 477.1299.

Isomeric mixture 5g + 6g

HPLC Eluent = *n*-hexane/AcOEt mixture 95/5 (v/v); R_f = 0.21

Overall yield (catalyst 1): 89% (108.9 mg); **5g**/**6g** = 5/95

Overall yield (catalyst 2): 89% (109.1 mg); **5g**/**6g** = 28/72

Overall yield (catalyst 3): 96% (117.2 mg); **5g**/**6g** = 39/61

Compound **5g**: yellow solid; mp = 132–133 °C; IR (neat): 2960, 2840, 1587, 1486, 1401, 1088 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.27 (d, *J* = 8.4 Hz, 2 H), 7.22 (d, *J* = 8.4 Hz, 2 H), 7.19–7.15 (m, 4 H), 6.76 (d, *J* = 8.4 Hz, 1 H), 6.46 (d, *J* = 8.4 Hz, 1 H), 5.76 (t, *J* = 4.6 Hz, 1 H), 5.50 (t, *J* = 4.0 Hz, 1 H), 4.58 (d, *J* = 4.6 Hz, 2 H), 4.29 (d, *J* = 4.0 Hz, 2 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 157.1, 151.1, 140.0, 137.0, 136.3, 135.2, 133.8, 132.7, 130.1, 128.7, 128.5, 128.0, 126.7, 121.5, 118.5, 117.6, 112.8, 109.3, 64.9, 64.3; HRMS: *m/z* $[M+H]^+$ calcd for $C_{24}H_{17}Cl_2O_2$: 407.0600; found: 407.0598.

Compound **6g**: white solid; mp = 179–180 °C; IR (neat): 2962, 2836, 1615, 1484, 1398, 1155 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.27 (d, *J* = 8.5 Hz, 4 H), 7.18 (d, *J* = 8.5 Hz, 4 H), 6.62 (s, 1 H), 6.51 (s, 1 H), 5.66 (t, *J* = 4.0 Hz, 2 H), 4.81 (d, *J* = 4.0 Hz, 4 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 156.4, 136.7, 136.0, 133.9, 130.0, 128.6, 123.1, 117.8, 116.9, 104.6, 65.6; HRMS: *m/z* $[M+H]^+$ calcd for $C_{24}H_{17}Cl_2O_2$: 407.0600; found: 407.0606.

Isomeric mixture 5h + 6h

HPLC eluent = *n*-hexane/AcOEt mixture 95/5 (v/v); R_f = 0.22

Overall yield (catalyst 1): 93% (138.2 mg); **5h**/**6h** = 4/96

Overall yield (catalyst 2): 95% (141.4 mg); **5h**/**6h** = 29/71

Overall yield (catalyst 3): 92% (137.2 mg); **5h**/**6h** = 30/70

Compound **5h**: yellow oil; IR (neat): 2930, 2835, 1676, 1575, 1490, 1427 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.55-7.47 (m, 2 H), 7.27-6.98 (m, 6 H), 6.36 (s, 2 H), 5.65 (bs, 1 H), 5.39 (bs, 1 H), 4.76–4.61 (m, 2 H), 4.42–4.33 (m, 1 H), 4.22–4.14 (m, 1 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 155.7, 150.6, 142.6, 139.4, 136.5, 135.3, 133.0, 132.0, 131.4, 130.0, 129.3, 128.3, 127.5, 127.0, 126.3, 123.8, 122.6, 122.2, 118.9, 117.8, 112.4, 109.3, 65.0, 64.9; HRMS: *m/z* $[M+H]^+$ calcd for $C_{24}H_{17}Br_2O_2$: 496.9569; found: 496.9565.

Compound **6h**: white solid; mp = 159–161 °C; IR (neat): 2925, 2837, 1676, 1576, 1488, 1427 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.45 (m, 2 H), 7.19–7.16 (m, 3 H), 7.06 (dt, J_1 = 7.6 Hz, J_2 = 1.8 Hz, 3 H), 6.42 (s, 1 H), 5.80–5.74 (m, 1 H), 5.55 (s, 2 H), 4.95–4.88 (m, 4 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 155.4, 138.7, 136.0, 132.6, 131.2, 129.1, 127.2, 123.7, 123.2, 118.5, 116.4, 104.0, 65.7; HRMS: *m/z* $[M+H]^+$ calcd for $C_{24}H_{17}Br_2O_2$: 496.9569; found: 496.9565.

Compound **8b**: yield (catalyst 1): 98% (137.8 mg); white solid.

Mp = 222–223 °C; IR (neat): 2831, 1623, 1571, 1490, 1425, 1320 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.36–7.28 (m, 15 H), 5.67 (t, *J* = 4.6 Hz, 3 H), 4.25 (d, *J* = 4.6 Hz, 6 H); ^{13}C NMR (100.6 MHz)

($CDCl_3$): δ = 153.8, 141.4, 136.1, 127.7, 127.1, 126.9, 118.9, 107.9, 64.2; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{33}H_{24}O_3Na$: 491.1618; found: 491.1624.

Compound **8c**: yield (catalyst 1): 95% (145.7 mg); white solid.

Mp = 214–216 °C; IR (neat): 2984, 2831, 1624, 1571, 1425, 1120 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.17 (d, *J* = 8.0 Hz, 6 H), 7.12 (d, *J* = 8.0 Hz, 6 H), 5.63 (t, *J* = 4.6 Hz, 3 H), 4.23 (d, *J* = 4.6 Hz, 6 H), 2.36 (s, 9 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 153.9, 138.4, 136.4, 136.0, 128.4, 127.0, 118.4, 108.0, 64.2, 21.3; HRMS: *m/z* $[M+H]^+$ calcd for $C_{36}H_{31}O_3$: 511.2268; found: 511.2276.

Compound **8d**: yield (catalyst 1): 98% (164.1 mg); white solid.

Mp = 260–261 °C; IR (neat): 2941, 2832, 1722, 1574, 1482, 1287 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.20 (d, *J* = 8.7 Hz, 6 H), 6.85 (d, *J* = 8.7 Hz, 6 H), 5.61 (t, *J* = 4.6 Hz, 3 H), 4.24 (d, *J* = 4.6 Hz, 6 H), 3.83 (s, 9H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 158.7, 153.9, 135.7, 133.9, 128.2, 117.9, 113.1, 107.9, 64.2, 55.4; HRMS: *m/z* $[M+H]^+$ calcd for $C_{36}H_{31}O_6$: 559.2115; found: 559.2128.

Compound **8e**: yield (catalyst 1): 91% (152.7 mg); white solid.

Mp = 162–164 °C; IR (neat): 3023, 2831, 1624, 1570, 1424, 1118 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.28–7.22 (m, 3 H), 6.90–6.83 (m, 9 H), 5.69 (t, *J* = 4.6 Hz, 3 H), 4.26 (d, *J* = 4.6 Hz, 6 H), 3.82 (s, 9 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 159.3, 153.7, 142.9, 136.0, 128.7, 119.8, 118.9, 112.7, 112.5, 108.0, 64.2, 55.4; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{36}H_{30}O_6Na$: 581.1935; found: 581.1947.

Compound **8f**: yield (catalyst 1): 90% (161.0 mg); white solid.

Mp = 234–235 °C; IR (neat): 3023, 2831, 1682, 1624, 1571, 1426 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.93 (d, *J* = 8.3 Hz, 6 H), 7.36 (d, *J* = 8.3 Hz, 6 H), 5.71 (t, *J* = 4.6 Hz, 3 H), 4.24 (d, *J* = 4.6 Hz, 6 H), 2.62 (s, 9 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 198.0, 153.6, 146.2, 135.8, 135.2, 128.0, 127.3, 120.3, 107.6, 64.1, 26.8; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{39}H_{30}O_6Na$: 617.1935; found: 617.1942.

Compound **8g**: yield (catalyst 1): 99% (190.2 mg); white solid.

Mp = 240–242 °C; IR (neat): 2957, 1716, 1597, 1467, 1286, 1143 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.99 (d, *J* = 8.4 Hz, 6 H), 7.33 (d, *J* = 8.4 Hz, 6 H), 5.69 (t, *J* = 4.6 Hz, 3 H), 4.23 (d, *J* = 4.6 Hz, 6 H), 3.92 (s, 9 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 167.2, 153.5, 146.0, 135.3, 129.2, 128.7, 127.1, 120.1, 107.6, 64.1, 52.2; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{39}H_{30}O_9Na$: 665.1782; found: 665.1787.

Compound **8h**: yield (catalyst 1): 99% (161.3 mg); pale yellow solid.

Mp = 187–188 °C; IR (neat): 2941, 2228, 1723, 1573, 1424, 1286 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.62 (d, *J* = 8.1 Hz, 6 H), 7.35 (d, *J* = 8.1 Hz, 6 H), 5.71 (t, *J* = 4.5 Hz, 3 H), 4.25 (d, *J* = 4.5 Hz, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 153.4, 145.8, 134.6, 131.7, 127.8, 120.8, 119.2, 110.7, 107.3, 64.1; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{36}H_{21}N_3O_3Na$: 566.1475; found: 566.1475.

Compound **8i**: yield (catalyst 1): 98% (197.4 mg); orange solid.

Mp = 154–156 °C; IR (neat): 2831, 1624, 1571, 1488, 1426, 1120 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.55–7.51 (m, 6 H), 7.48–7.42 (m, 6 H), 5.70 (t, *J* = 4.6 Hz, 3 H), 4.24 (d, *J* = 4.6 Hz, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 153.6, 141.9, 134.9, 130.5, 130.1 (q, J_{CF} = 31.7 Hz), 128.3, 124.4 (q, J_{CF} = 270.6 Hz), 124.1 (q, J_{CF} = 3.7 Hz), 123.7 (q, J_{CF} = 3.7 Hz), 120.1, 107.5, 64.0; ^{19}F NMR (376.5 MHz) ($CDCl_3$): δ = m, (-62.3)–(-62.9); HRMS: *m/z* $[M+Na]^+$ calcd for $C_{36}H_{21}F_9O_3Na$: 695.1239; found: 695.1242.

Compound **8j**: yield (catalyst 1): 98% (168.0 mg); white solid.

Mp = 231–233 °C; IR (neat): 2958, 1723, 1572, 1454, 1422, 1287 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.28 (d, *J* = 8.5 Hz, 6 H), 7.19 (d, *J* = 8.5 Hz, 6 H), 5.64 (t, *J* = 4.6 Hz, 3 H), 4.24 (d, *J* = 4.6 Hz, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 153.6, 139.7, 135.1, 132.7, 128.5, 127.9, 119.3, 107.7, 64.1; HRMS: *m/z* $[M+H]^+$ calcd for $C_{33}H_{22}Cl_3O_3$: 571.0629; found: 571.0638.

Compound **8k**: yield (catalyst 1): 99% (209.5 mg); pale brown solid.

Mp = 244–245 °C; IR (neat): 3023, 2830, 1624, 1571, 1490, 1425 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.43 (d, *J* = 8.4 Hz, 6 H), 7.13 (d, *J* = 8.4 Hz, 6 H), 5.64 (t, *J* = 4.6 Hz, 3 H), 4.24 (d, *J* = 4.6 Hz, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 153.6, 140.2, 135.1, 130.9, 128.8, 120.8, 119.3, 107.6, 64.1; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{33}H_{21}Br_3O_3Na$: 726.8913; found: 726.8912.

Compound **8l**: yield (catalyst 1): 95% (201.3 mg); brown solid.

Mp = 201–204 °C; IR (neat): 2958, 2832, 1723, 1572, 1423, 1287 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.43–7.37 (m, 6 H), 7.21–7.16 (m, 6 H), 5.68 (t, *J* = 4.6 Hz, 3 H), 4.27 (d, *J* = 4.6 Hz, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 153.5, 143.3, 134.7, 130.2, 129.9, 129.3, 125.8, 121.7, 119.8, 107.6, 64.1; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{33}H_{21}Br_3O_3Na$: 726.8913; found: 726.8914.

Compound **10**: yield (catalyst 1): 98% (150.0 mg); pale yellow solid.

Mp = 171–173 °C; IR (neat): 2919, 1643, 1558, 1446, 1357, 1261, 1118, 832 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.32 (t, *J* = 7.4 Hz, 1 H), 7.21 (d, *J* = 8.1 Hz, 2 H), 7.15–7.11 (m, 8 H), 6.72 (d, *J* = 7.4 Hz, 2 H), 6.65 (s, 1 H), 5.87 (t, *J* = 4.7 Hz, 1 H), 5.79 (t, *J* = 4.7 Hz, 1 H), 4.89 (d, *J* = 4.7 Hz, 2 H), 4.29 (d, *J* = 4.7 Hz, 2 H), 2.37 (s, 3 H), 2.29 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 176.5, 159.8, 157.3, 155.8, 153.2, 136.8, 136.7, 136.3, 135.8, 134.2, 134.0, 129.9, 129.7, 128.2, 127.6, 127.3, 126.2, 125.7, 124.9, 118.6, 118.3, 110.0, 109.3, 107.2, 105.9, 64.8, 63.3, 20.3, 20.2; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{35}H_{26}O_4Na$: 533.1723, found: 533.1727.

Compound **12**: yield (catalyst 1): 97% (115.1 mg); **12/13**: 100/0.

Yield (catalyst 3): 99% (117.9 mg); **12/13**: 100/0; pale yellow solid.

Mp = 195–196 °C; IR (neat): 2922, 1642, 1566, 1475, 1450, 1384, 1260, 1111, 861 cm^{-1}; ^1H NMR (400.13 MHz) ($DMSOd_6$): δ = 7.38 (t, *J* = 7.4 Hz, 1 H), 7.21–7.12 (m, 6 H), 6.78 (d, *J* = 7.4 Hz, 2 H), 6.72 (d, *J* = 6.0 Hz, 2 H), 5.94 (t, *J* = 4.7 Hz, 1 H), 4.76 (d, *J* = 4.7 Hz, 2 H), 3.89 (s, 3 H), 2.25 (s, 3 H); ^{13}C NMR (100.6 MHz) ($DMSOd_6$): δ = 176.2, 161.4, 161.0, 159.7, 154.6, 137.6, 137.2, 134.2, 130.5, 129.5, 128.7, 125.9, 120.6, 110.1, 108.2, 105.5, 97.5, 65.4, 56.8, 21.1; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{26}H_{20}O_4Na$: 419.1254, found: 419.1249.

Isomeric mixture 15a + 16a

HPLC eluent = *n*-hexane/AcOEt mixture 80/20 (v/v); R_f = 0.21

Overall yield (catalyst 3): 99% (116.0 mg); **15a/16a**: 98/2.

Compound **15a**: pale yellow solid; mp = 147–148 °C; IR (neat): 2922, 1674, 1603, 1569, 1490, 1254, 1080, 829 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.92 (d, *J* = 8.3 Hz, 2 H), 7.31–7.28 (m, 3 H), 7.19–7.15 (m, 2 H), 6.09 (t, *J* = 4.8 Hz, 1 H), 4.74 (d, *J* = 4.8 Hz, 2 H), 2.62 (s, 3 H), 2.10 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 201.8, 197.5, 157.0, 145.4, 139.4, 136.7, 136.1, 129.2, 128.8, 127.2, 123.2, 122.2, 121.5, 119.6, 64.4, 29.2, 26.6; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{19}H_{16}O_3Na$: 315.0992, found: 315.0991.

Compound **16a**: pale yellow solid; mp = 109–110 °C; IR (neat): 2923, 1675, 1606, 1569, 1490, 1255, 1080, 830 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 8.02 (d, *J* = 8.3 Hz, 2 H), 7.49–7.43 (m, 4 H), 7.04 (d, *J* = 7.9 Hz, 1 H), 6.01 (t, *J* = 3.9 Hz, 1 H), 4.9 (d, *J* = 3.9 Hz, 2 H), 2.7 (s, 3 H), 2.6 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 197.6, 197.2, 154.7, 142.4, 138.0, 136.7, 135.9, 128.7, 128.6, 127.2, 125.6, 123.7, 121.4,

116.1, 65.3, 26.7, 26.6; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{19}H_{16}O_3Na$: 315.0992, found: 315.0991.

Isomeric mixture 15b+16b

HPLC eluent = *n*-hexane/AcOEt mixture 80/20 (v/v); $R_f = 0.22$

Overall yield (catalyst 3): 99% (111.6 mg); 15b/16b: 74/26

Compound **15b**: pale yellow solid; mp = 137–138 °C; IR (neat): 2920, 1680, 1602, 1578, 1480, 1265, 1060, 856 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.27 (t, *J* = 7.9 Hz, 1 H), 7.15–7.07 (m, 4 H), 6.84 (d, *J* = 8.7 Hz, 2 H), 5.96 (t, *J* = 4.8 Hz, 1 H), 4.70 (d, *J* = 4.8 Hz, 2 H), 3.81 (s, 3 H), 2.04 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 202.7, 159.4, 157.0, 140.2, 136.8, 132.9, 129.0, 128.8, 123.0, 121.2, 120.5, 119.1, 114.0, 64.6, 55.3, 29.8; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{18}H_{16}O_3Na$: 303.0992, found: 303.0991.

Compound **16b**: pale yellow solid; mp = 111–112 °C; IR (neat): 2932, 1675, 1605, 1575, 1491, 1255, 1080, 860 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.38–7.36 (m, 2 H), 7.18 (d, *J* = 8.6 Hz, 2 H), 7.03 (d, *J* = 8.5 Hz, 1 H), 6.87 (d, *J* = 8.6 Hz, 2 H) 5.81 (t, *J* = 4.0 Hz, 1 H), 4.82 (d, *J* = 4.0 Hz, 2 H), 3.78 (s, 3 H), 2.49 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 197.5, 159.6, 154.9, 137.8, 136.3, 130.0, 129.8, 128.4, 126.0, 122.0, 121.4, 116.1, 114.1, 65.6, 55.5, 26.8; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{18}H_{16}O_3Na$: 303.0992, found: 303.0989.

Isomeric mixture 15c+16c

HPLC eluent = *n*-hexane/AcOEt mixture 85/15 (v/v); $R_f = 0.21$

Overall yield (catalyst 3): 98% (111.5 mg); **15c/16c**: 94/6.

Compound **15c**: pale yellow solid; mp = 130–132 °C; IR (neat): 2922, 1680, 1593, 1485, 1232, 1020, 830 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.22–7.18 (m, 4 H), 7.07–7.04 (m, 3 H), 5.91 (t, *J* = 4.8 Hz, 1 H), 4.62 (d, *J* = 4.8 Hz, 2 H), 2.01 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 202.1, 157.1, 140.2, 139.8, 139.1, 136.5, 133.7, 129.3, 128.9, 128.7, 122.5, 122.2, 121.4, 119.5, 64.5, 29.5; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{17}H_{13}O_2ClNa$: 307.0496 m/z, found: 307.0497.

Compound **16c**: pale yellow solid; mp = 107–108 °C; IR (neat): 2930, 1676, 1569, 1492, 1255, 1020, 830 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.38–7.36 (m, 2 H), 7.32 (d, *J* = 8.4 Hz, 2 H), 7.28 (d, *J* = 8.4 Hz, 2 H), 6.95 (d, *J* = 8.2 Hz, 1 H) 5.84 (t, *J* = 3.9 Hz, 1 H), 4.83 (d, *J* = 3.9 Hz, 2 H), 2.49 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 197.4, 154.8, 138.1, 136.1, 135.8, 134.2, 130.0, 129.0, 127.7, 125.7, 123.1, 121.5, 116.2, 64.5, 26.8; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{17}H_{13}O_2ClNa$: 307.0496, found: 307.0495 m/z.

Isomeric mixture 15d+16d

Overall yield (catalyst 3): 99% (111.0 mg); 15d/16d: 34/66

Pale yellow oil; IR (neat): 2922, 1676, 1601, 1512, 1250, 1030, 837 cm^{-1};

Reported NMR spectra refer to an isomeric mixtures **15d+16d** in the ratio 34/66; ^1H NMR signals have been assigned to each specific isomer while ^{13}C NMR signals have not been assigned.

^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.98 (d, *J* = 8.6 Hz, 2 H, **16d**), 7.90 (d, *J* = 8.6 Hz, 2 H, **15d**), 7.44 (d, *J* = 8.6 Hz, 2 H **16d**), 7.31 (d, *J* = 8.6 Hz, 2 H, **15d**), 7.18 (t, *J* = 8.2 Hz, 1 H, **15d**), 6.87 (d, *J* = 8.2 Hz, 1 H, **16d**), 6.87 (d, *J* = 8.2 Hz, 1 H **15d**), 6.50 (m, 2H, **15d+16d**), 6.42 (dd, J_1 = 8.4 Hz, J_2 = 2.5, 1 H, **16d**), 5.88 (t, *J* = 4.6 Hz, 1 H, **15d**), 5.72 (t, *J* = 3.9 Hz, 1 H **16d**), 4.84 (d, *J* = 3.9 Hz, 2 H, **16d**), 4.65 (d, *J* = 4.6 Hz, 2 H, **15d**), 3.41 (s, 3 H, **15d**), 2.63 (s, 3 H, **16d**), 2.62 (s, 3 H, **15d**); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 197.9, 197.7, 160.9, 157.0, 156.3, 156.1, 146.1, 143.4, 136.4, 136.3, 135.7, 135.5, 130.0, 128.8, 128.6, 128.5, 127.8, 127.1, 126.5, 121.8, 118.1, 116.3, 112.9, 109.5, 107.1, 105.3, 102.1, 65.4, 64.5, 55.4, 55.2, 26.7, 26.6. HRMS: *m/z* $[M+Na]^+$ calcd for $C_{18}H_{16}O_3Na$: 303.0992, found: 303.0990 m/z.

Isomeric mixture 15e+16e

Overall yield (catalyst 3): 99% (107.3 mg); **15e/16e**: 36/64.

HPLC eluent = *n*-hexane/AcOEt mixture 90/10 (v/v); $R_f = 0.22$

Compound **15e**: pale yellow solid; mp = 101–102 °C; IR (neat): 2925, 1608, 1488, 1248, 1034, 837; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.33 (d, *J* = 8.2 Hz, 2 H), 7.24–7.20 (m, 3 H), 6.72 (d, *J* = 7.6 Hz, 1 H), 6.56 (d, *J* = 7.6 Hz, 1 H), 5.87 (t, *J* = 4.6 Hz, 1 H), 4.68 (d, *J* = 4.6 Hz, 2 H), 3.52 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 157.2, 156.5, 139.6, 135.6, 132.4, 129.9, 128.4, 127.7, 121.0, 113.2,109.6, 105.4, 64.6, 55.4; HRMS: *m/z* $[M+H]^+$ calcd for $C_{16}H_{14}O_2Cl$: 273.0677, found: 273.0674.

Compound **16e**: pale yellow solid; mp = 88–90 °C; IR (neat): 2927, 1605, 1490, 1255, 1030, 830 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.38–7.36 (m, 3 H), 7.32 (d, *J* = 8.4 Hz, 2 H), 7.28 (d, *J* = 8.4 Hz, 2 H), 6.95 (d, *J* = 8.2 Hz, 1 H) 5.84 (t, *J* = 3.9 Hz, 1 H), 4.83 (d, *J* = 3.9 Hz, 2 H), 2.49 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 197.4, 154.8, 138.1, 136.1, 135.8, 134.2, 130.0, 129.0, 127.7, 125.7, 123.1, 121.5, 116.2, 64.5, 26.8; HRMS: *m/z* $[M+H]^+$ calcd for $C_{16}H_{14}O_2Cl$: 273.0677, found: 273.0675.

Isomeric mixture 15f+16f

Overall yield (catalyst 3): 99% (104.4 mg); 15f/16f: 60/40

Pale yellow oil; IR (neat): 2932, 1684, 1604, 1565, 1463, 1262, 1016, 841 cm^{-1}; HRMS: *m/z* $[M+H]^+$ calcd for $C_{18}H_{17}O_2$: 265.1223, found: 265.1219.

Reported NMR spectra refer to an isomeric mixtures **15f+16f** in the ratio 60/40; ^1H NMR signals have been assigned to each specific isomer while ^{13}C NMR signals have not been assigned.

^1H NMR (400.13 MHz) ($CDCl_3$): δ = 8.01 (d, *J* = 8.3 Hz, 2 H, **16f**), 7.96 (d, *J* = 8.0 Hz, 2 H, **15f**), 7.47 (d, *J* = 8.3 Hz, 2 H, **16f**), 7.36 (d, *J* = 8.0 Hz, 2 H, **15f**), 7.15 (t, *J* = 7.8 Hz, 1 H, **15f**), 6.90 (d, *J* = 7.8 Hz, 1 H, **15f**), 6.87 (d, *J* = 7.8 Hz, 1 H, **16f**), 6.78 (d, *J* = 7.8 Hz, 1 H, **15f**), 6.77 (s, 1 H, **16f**), 6.70 (bd, *J* = 7.8 Hz, 1 H, **16f**), 6.00 (t, *J* = 4.7 Hz, 1 H, **15f**), 5.83 (t, *J* = 4.0 Hz, 1 H, **16f**), 4.86 (d, *J* = 4.0 Hz, 2 H, **16f**), 4.62 (d, *J* = 4.7 Hz, 2 H, **15f**), 2.66 (s, 3 H, **16f**), 2.64 (s, 3 H, 15f), 2.33 (s, 3 H, **16f**), 1.77 (s, 3 H, **15f**); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 197.69, 197.67, 156.5, 154.6, 146.1, 143.4, 143.3, 140.1, 137.7, 136.5, 136.4, 136.0, 135.6, 129.1, 128.8, 128.6, 128.5, 127.6, 125.4, 125.0, 123.9, 123.1, 122.1, 120.4, 119.9, 116.9, 114.1, 65.2, 64.2, 29.7, 26.7, 26.6, 22.7, 21.4.

16f: Known Compound.[11]

Isomeric mixture 15g+16g

Overall yield (catalyst 3): 97% (97.6 mg); 15 g/16 g: 23/77

Pale yellow oil; IR (neat): 2924, 1615, 1450, 1260, 1024, 874 cm^{-1}; HRMS: *m/z* $[M+Na]^+$ calcd for $C_{17}H_{16}O_2Na$: 275.1043, found: 275.1039.

Reported NMR spectra refer to an isomeric mixtures **15g+16g** in the ratio 23/77; ^1H NMR signals have been assigned to each specific isomer while ^{13}C NMR signals have not been assigned.

^{1}H NMR (400.13 MHz) ($CDCl_3$): δ 7.19 (d, J=8.9 Hz, 2 H, **16g**), 7.07 (d, J=8.7 Hz, 2 H, **15g**), 7.01 (t, J=7.8 Hz, 1 H, 15 g), 6.97 (d, J=7.8 Hz, 1 H, **15g**), 6.85–6.83 (m, 3 H, **16g**), 6.80–6.74 (m, 3 H, **15g**), 6.64 (bs, 1 H, **16g**), 6.60 (bd, J=7.8 Hz, 1 H, **16g**), 5.79 (t, J=4.7 Hz, 1 H, **15g**), 5.62 (t, J=3.9 Hz, 1 H, **16g**), 4.72 (d, J=3.9 Hz, 2 H, **16g**), 4.48 (t, J=4.7 Hz, 2 H, **16g**), 3.76 (s, 3 H, **16g**), 3.75 (s, 3 H, **15g**), 2.22 (s, 3 H, **16g**), 1.70 (s, 3 H, **15g**); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ=159.3, 159.0, 156.5, 154.8, 139.5, 137.9, 136.7, 136.0, 133.7, 130.8, 130.3, 129.7, 129.5, 128.6, 125.7, 125.0, 121.9, 121.6, 121.31, 121.38, 118.1, 116.7, 114.0, 113.7, 65.3, 64.3, 55.31, 55.27, 22.6, 21.3;

1**6g**: Known Compound.[11]

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Conflict of Interest

The authors declare no conflict of interest.

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