

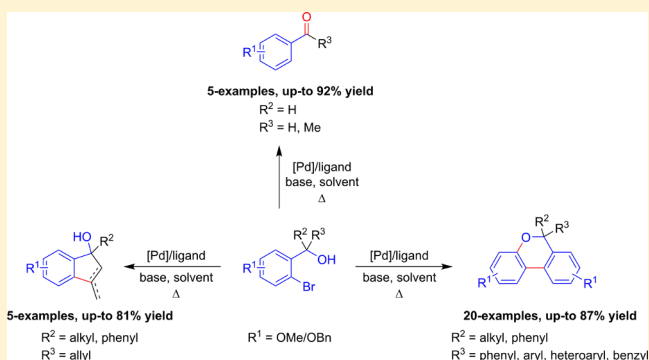
Substitution Controlled Functionalization of *ortho*-Bromobenzyl Alcohols via Palladium Catalysis: Synthesis of Chromenes and Indenols

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S Supporting Information

ABSTRACT: An efficient domino Pd-catalyzed transformation of simple *ortho*-bromobenzyl tertiary alcohols to chromenes is presented. Their formation is believed to proceed via the formation of a five-membered palladacycle, which, in turn, involves in an intermolecular homocoupling with the second *ortho*-bromobenzyl tertiary alcohol to yield the homo-biaryl bond followed by intramolecular C–O bond formation. Interestingly, when there is an allylic substituent on the benzylic carbon atom, a chemoselective switch was observed, which preferred intramolecular Heck coupling and gave indenols. Further, it has been confirmed that the tertiary alcohol functionality is indispensable to give the coupled products, whereas the use of primary/secondary benzylic alcohols furnished the simple carbonyl products via a possible reductive debromination followed by oxidation due to the availability of β -hydrogen(s).



INTRODUCTION

Domino reactions facilitate construction of complex molecules in one-pot operation without the need to isolate reaction intermediates.¹ Transition metal catalysis plays a major role in the development of useful synthetic methods, particularly in the organic synthesis,² as it enables construction of both C–C as well as C–X (heteroatom) bonds most efficiently, through which it is possible to achieve molecular complexity. In this context, palladium plays a special role, since it can be able to drive a wide variety of organic transformations. For example, in one case, a palladium catalyst can be used for reduction (catalytic hydrogenation), whereas, on the other hand, it can be applied for oxidation (Wacker oxidation), while there are many coupling reactions (Heck, Stille, Suzuki, Shonogashira, Buchwald–Hartwig, etc.) that fall in-between these two extreme cases. This sort of diversity, in Pd-catalysis, is feasible because of the reason that the fate of Pd-catalyzed transformations can be changed by the environment (i.e., reaction conditions) around the palladium–metal center as well as the nature of the reactant. Of late, many domino processes have been developed by using Pd-catalysis,³ predominantly for the construction of useful heterocyclic systems.⁴ Particularly, a unique and rare method was reported that involves a Pd-catalyzed β -carbon cleavage via the coordination of hydroxy group to the Pd-metal center. This type of process is selectively observed in the case of tertiary alcohols such as 2-methyl-4-arylbut-3-yn-2-ol⁵ and α,α -disubstituted arylmethanols⁶ through cleavage of $sp(C)$ – $sp^3(C)$ and $sp^2(C)$ – $sp^3(C)$ bonds, respectively (Scheme 1). In addition, Pd-catalyzed ring-opening

transformations through the disconnection of $sp^3(C)$ – $sp^3(C)$ bond, in strained cyclic systems, have also been reported.^{7–10} Furthermore, it was also noticed that the $sp^3(C)$ – $sp^3(C)$ bond fission is facilitated by a six-membered palladium-cyclic transition state.¹¹

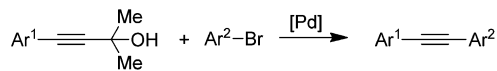
In continuation of our ongoing interest in the development of transition catalysis,¹² very recently we have developed a novel method¹³ involving a palladium-catalyzed domino reaction for the conversion of α,α -disubstituted-(2-haloaryl)-methanols to 6,6-dialkyl-6H-benzo[*c*]chromenes via homo-biaryl coupling. During the course of this process, the reaction drives to form two bonds (C–C and C–O) in a sequential fashion. Herein, we report a successful application and thorough study of the method, the conversion of various *ortho*-bromobenzyl tertiary alcohols to the corresponding chromenes. In addition, it was observed that when there is an olefin substituent on the benzylic carbon atom, preferred intramolecular Heck coupling furnished indenols. Overall, this entire study relies on preferential chemoselective coordination of the initially formed arylpalladium species either with the hydroxy group or insertion into the double bond of olefin. Moreover, it was further proved that the tertiary alcohol functionality is vital to promote the coupling, whereas the reaction of primary/secondary bromobenzyl alcohols, under the adopted reaction conditions,¹³ furnished simple carbonyl compounds as shown in Scheme 1.

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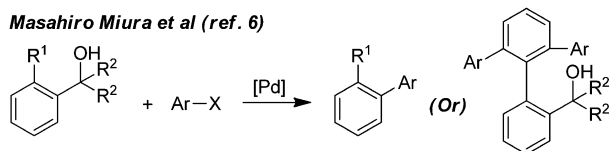
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Scheme 1. Representative Previous Approaches vs Present Study on Pd-Mediated Propargyl/Benzyl Tertiary Alcohol Cleavage Followed by Coupling

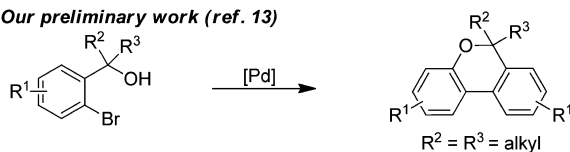
Hak-Fun Chow *et al.* (ref. 5)



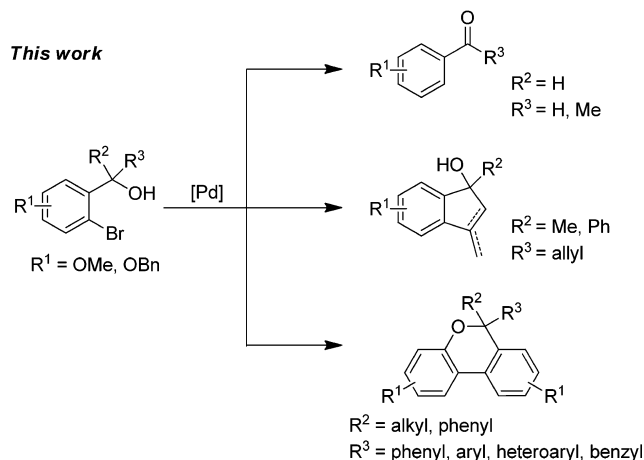
Masahiro Miura *et al.* (ref. 6)



Our preliminary work (ref. 13)



This work



RESULTS AND DISCUSSION

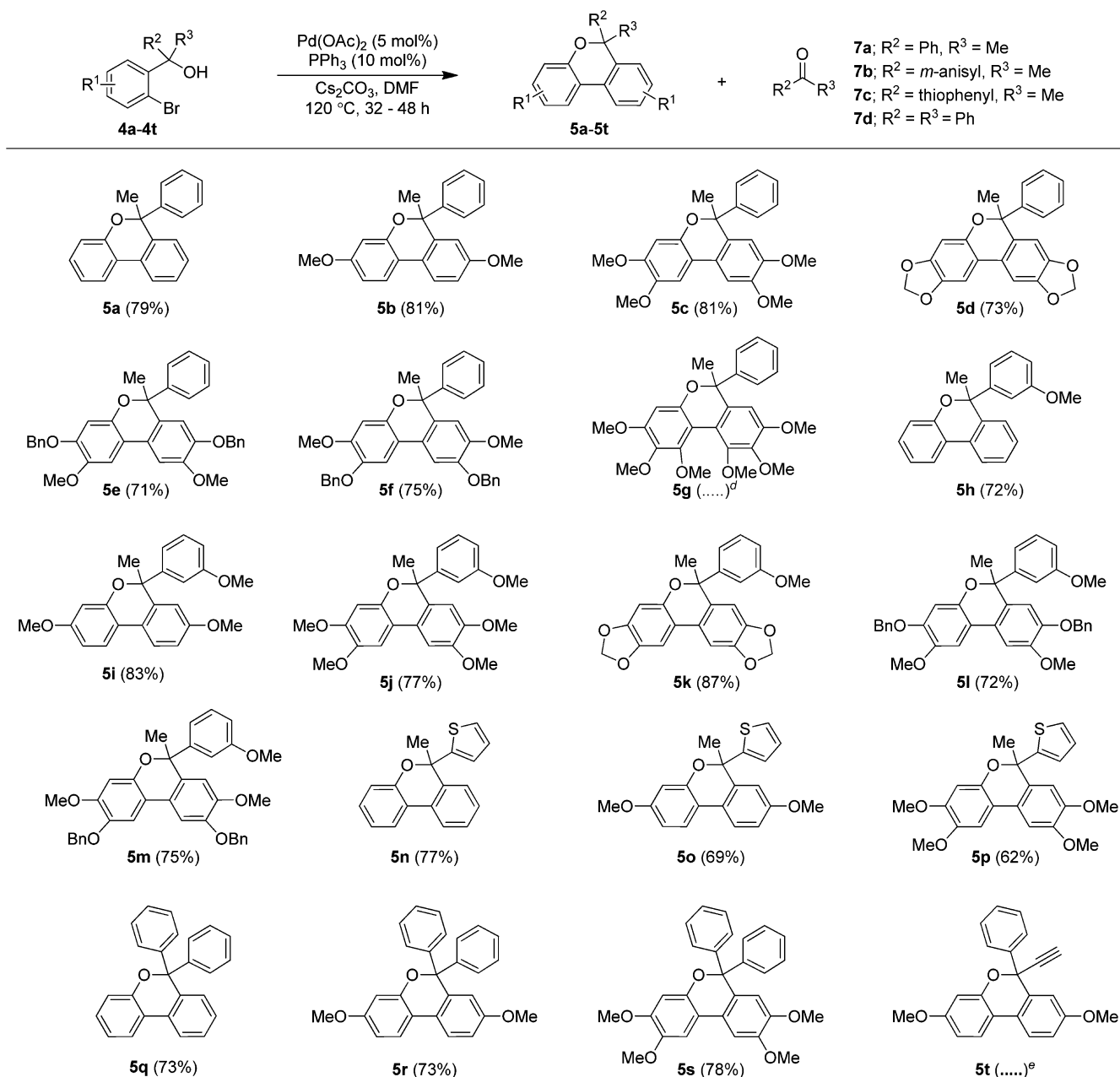
The study was initiated with the preparation of requisite tertiary bromobenzyl alcohols **4** from 2-bromobenzaldehydes **1** using the protocol of arylmagnesiumbromide addition, followed by oxidation of the resulting secondary alcohol **2** to the corresponding ketone and then alkylmagnesiumiodide reaction of the ketone **3**. Unlike the previous study,¹³ herein, the second aromatic substituent of the tertiary alcohol **4a** may pose a chemoselectivity problem in competition to the hydroxyl group. Therefore, if there is a preferential intramolecular coordination of the hydroxy group to the arylpalladium species, the chromene **5a** would result. On the other hand, if the arylpalladium species preferentially inserts into the second aromatic ring, the intramolecular Heck product fluorene **6a** would be the end product. With the tertiary alcohols **4** in hand, initially the key Pd-mediated domino catalysis was attempted on tertiary bromobenzyl alcohol **4a**. Thus, the reaction under established conditions [$\text{Pd}(\text{OAc})_2$ (5 mol %), PPh_3 (10 mol %), Cs_2CO_3 (2 equiv), DMF (2 mL), 80 °C for 12 h],¹³ led to the chromene **5a** as the end product, in a highly chemoselective manner along with a considerable amount of starting material recovery. Even prolonged reaction time (24 h) at the same temperature (80 °C) was still unable to convert all the starting material to product. Gratifyingly, further prolonged reaction time (48 h) at high temperature variation (120 °C) was successful to deliver

all the starting material to the product **5a**. This extra activation required for the present systems can be attributed to the steric constraints. The selective formation of chromene **5a** over fluorene **6a** may be justified on the basis of the preferential chelation of hydroxy group with arylpalladium species. Recently, the research group of Catellani reported the synthesis of such 6*H*-dibenzo[*b,d*]pyrans using sequential Pd/norbornene-catalysis through heterobiaryl coupling.¹⁴ Very recently, Nishihara and co-workers reported the synthesis of triphenylenes by coupling between tertiary bromobenzyl alcohols and *ortho*-iodobiphenyls.¹⁵

To further check the scope and generality of the method, these optimized reaction conditions were applied to other systems. In general, these results were fairly comparable to that obtained for chromene **5a** and furnished chromenes **5b–5f** possessing simple as well as electron rich 2-bromoaryl moiety (i.e., $\text{R}^1 = \text{H}/\text{OMe}/\text{OBn}$, $\text{R}^2 = \text{alkyl}$, $\text{R}^3 = \text{phenyl}$), in very good yields (Table 1). However, the formation of chromene **5g** was impeded, maybe due to the presence of *o,o'* dimethoxy groups that might induce tremendous strain and thus would prevent both aromatic rings to adopt coplanar structure, since the entire tricyclic chromene core is in plane. Further, it was observed that the method was applicable to other tertiary alcohols **4h–4m**, with *meta*-anisyl substituent on the benzylic carbon center (i.e., $\text{R}^1 = \text{H}/\text{OMe}/\text{OBn}$, $\text{R}^2 = \text{alkyl}$, $\text{R}^3 = m\text{-MeOC}_6\text{H}_4$), therefore giving the corresponding products **5h–5m**. Also, the reaction was successful on alcohols **4n–4p** with heteroaryl substituent (i.e., $\text{R}^1 = \text{H}/\text{OMe}/\text{OBn}$, $\text{R}^2 = \text{alkyl}$, $\text{R}^3 = \text{thiophene}$) and furnished the chromenes **5n–5p**. Furthermore, the diphenyl substituted tertiary alcohols **4q–4s** (i.e., $\text{R}^1 = \text{H}/\text{OMe}$, $\text{R}^2 = \text{R}^3 = \text{phenyl}$) smoothly transformed into the corresponding chromenes **5q–5s**. However, it was noticed that the reaction of the tertiary alcohol **4t** with acetylene substituent was unclear and failed to deliver the chromene **5t**. This is presumably due to the interfering ability of the reactive triple bond with the so-formed aryl palladium intermediate. It is worth mentioning that in each of the reaction, the formation of cleaved byproduct ketone **7** has also been isolated. The carbonyl byproducts (**7a**, **7b**, and **7d**) were isolated in most of the cases and characterized by NMR spectroscopy (except for the ketone **7c**, for which the TLC spot was not clean and therefore unable to obtain a clean NMR spectrum), which, in turn, supports the reaction mechanism proposed in our previous report.

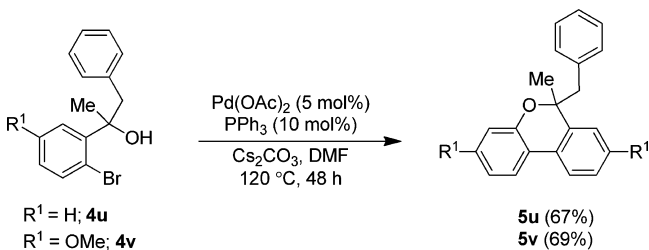
Further, to check the scope and applicability of the method and to extend for other chromene derivatives, we explored the reaction with benzyl substituent (i.e., $\text{R}^1 = \text{H}/\text{OMe}$, $\text{R}^2 = \text{alkyl}$, $\text{R}^3 = \text{benzyl}$). The required alcohols **4u**, **4v** were prepared using α -arylation (this α -arylation was specifically developed on 2-bromoacetophenones, very recently, in our laboratory)^{12j} followed by methylmagnesium iodide addition of 2-bromoacetophenones **3a**, **3b** (for details, see the Supporting Information). Gratifyingly, the method was found to be amenable and furnished the expected chromenes **5u**, **5v** in fair yields (Scheme 2).

Moreover, it was concluded that the tertiary alcohol functionality of **4** is essential to selectively deliver to the coupled (chromene) product **5**, because the corresponding primary **9a**, **9b**¹³ or secondary alcohols **9c–9e** were unable to furnish the expected chromenes **5**, rather furnishing the benzaldehydes/ketones **10a–10e**, as shown in Table 2. The formation of benzaldehydes **10a**, **10b** can be explained via the oxidation followed by reductive debromination sequence, after the formation of five-membered palladacycle (for details, see the plausible mechanism

Table 1. Synthesis of Chromenes 5 from Tertiary Alcohols 4 under Optimized Conditions^{a,b,c}

^aReaction conditions: **4a-4t** (100 mg, 0.21–0.47 mmol), Cs₂CO₃ (2 equiv), Pd(OAc)₂ (5 mol %), PPh₃ (10 mol %), 0.14–0.23 M in DMF, at 120 °C for 24–48 h. ^bYields in the parentheses are isolated yields of chromatographically pure products. ^cThe corresponding ketone byproducts **7** have been isolated in most of the cases and characterized by NMR spectroscopic data. ^dMost of the starting material was recovered. ^eThe reaction was not clean.

Scheme 2. Pd-Catalyzed Transformation of Tertiary Alcohols 4 to the Chromenes 5



as described in Scheme 6). It is worth mentioning that the standard catalytic [Pd(OAc)₂ (5 mol %)/PPh₃ (10 mol %), DMF] conditions are suitable only for primary alcohols **9a, 9b**

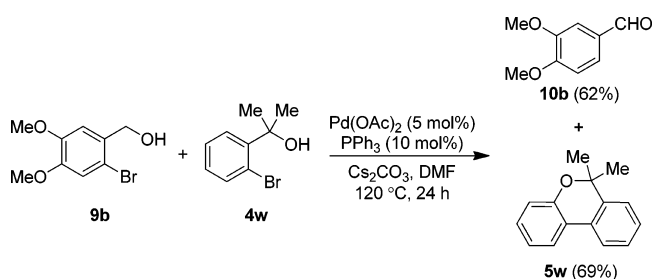
to give the corresponding ketones **10a, 10b**, whereas the secondary alcohols **9c-9e** furnished a mixture of unclear products. Interestingly, for such systems **9c-9e**, the catalyst Pd(dppf)₂Cl₂ (5 mol %) was found to be the best and gave the corresponding ketones **10c-10e** (Table 2).

Further, to better understand whether homo-biaryl coupling is preferred or not, reaction was performed with the primary and tertiary alcohols (**9b** and **4w**) together. As a result, the products obtained are the benzaldehyde **10b** and the chromene **5w**. On the basis of this observation, we realized that the compound **4w** predominantly reacted in its own independent tandem path, without much intervention from the other alcohol **9b** (i.e., majorly preferred homocoupling rather than the heterocoupling), as described in Scheme 3.

Table 2. Pd-Catalysis of Primary and Secondary Alcohols (2 and 9)

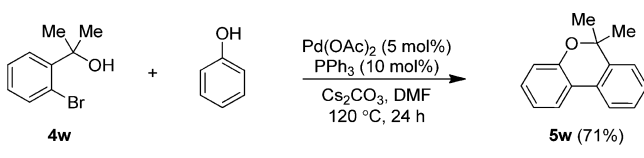
Reaction Conditions		
$R^1 = H, R^2 = OMe$ $R^3 = H$; 9a	Pd(OAc) ₂ (5 mol%)/PPh ₃ (10 mol%) Cs ₂ CO ₃ (2 equiv), DMF, 120 °C, 24 h	10a (72%)
$R^1 = R^2 = OMe$ $R^3 = H$; 9b	"	10b (86%)
$R^1 = H, R^2 = OMe$ $R^3 = Me$; 9c	Pd(dppf)Cl ₂ (5 mol%) Cs ₂ CO ₃ (2 equiv), DMF, 120 °C, 24 h	10c (89%)
$R^1 = R^2 = OMe$ $R^3 = Me$; 9d	"	10d (92%)
$R^1 = R^2 = OCH_2O$ $R^3 = Me$; 9e	"	10e (90%)

Scheme 3. Pd-Catalysis of Primary and Tertiary Alcohols (9b and 4w)

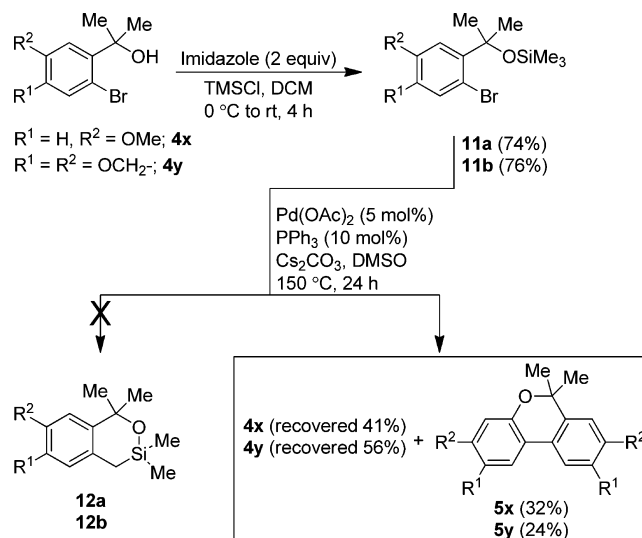


Similarly, to check whether the intermolecular Buchwald–Hartwig coupling or formation of chromene **5w** product, the reaction was carried out in the presence of phenol as an external coupling agent. However, the chromene **5w** was obtained as the sole product, which clearly indicates that the intramolecular trapping of the aryl palladium intermediate by the hydroxy group works efficiently rather than the intermolecular coupling (Scheme 4).

Scheme 4. Pd-Catalysis of 4w in the Presence of External Phenol



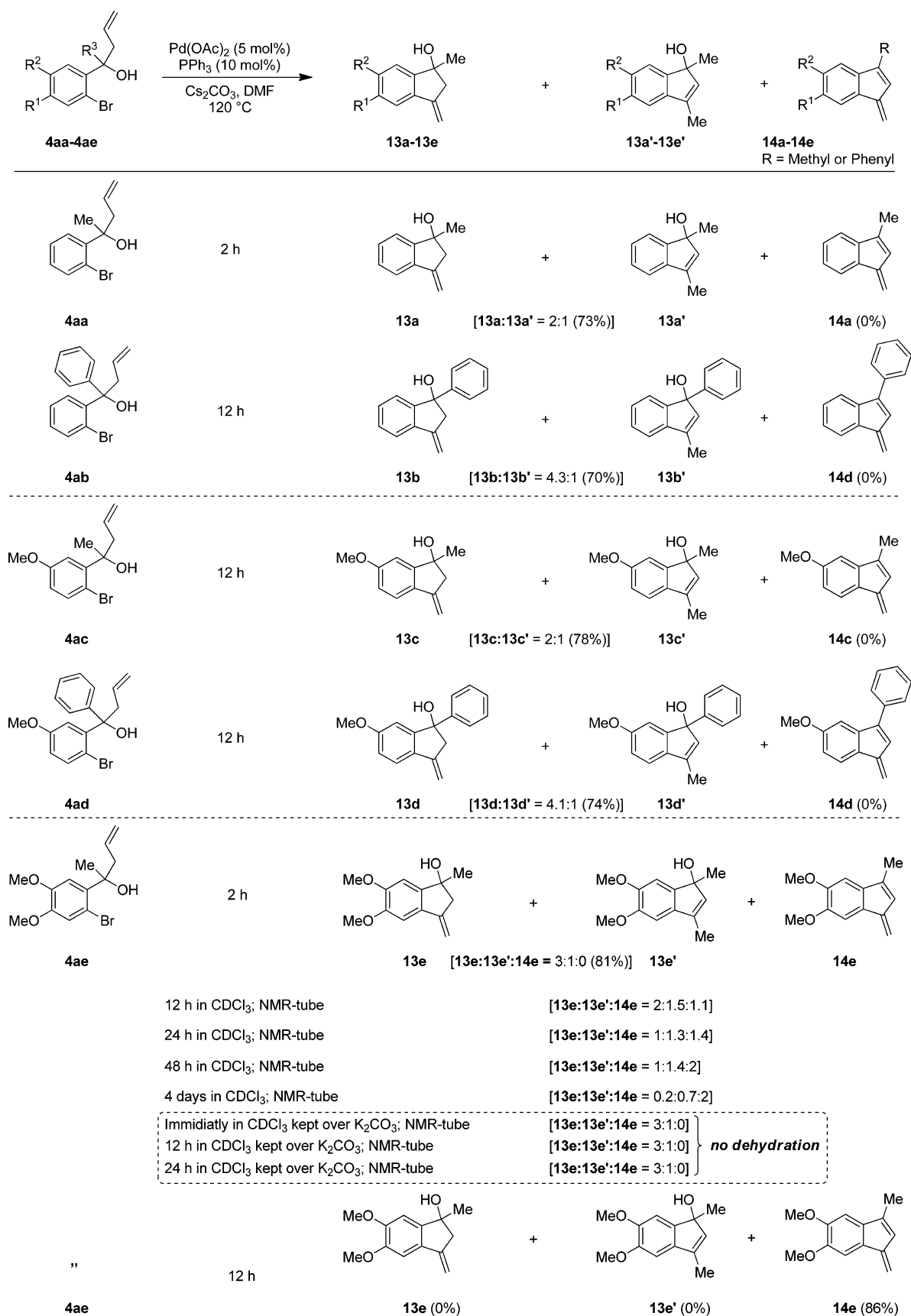
Furthermore, to check the scope and application of the method, we attempted the reaction of silyl ether, anticipating intramolecular sp^3 C–H activation to generate cyclic silyl ethers **12a**, **12b** (Scheme 5). This sort of sp^3 C–H activation of methyl groups of silyl group is expected on the basis of the existing reports.¹⁶ However, the reaction failed to furnish the expected cyclic silyl ethers **12a**, **12b**, rather producing simple chromenes **5x–5y** along with the recovery of TMS-group deprotected starting tertiary alcohols **4x–4y**. The formation of simple chromenes **5x–5y** can be explained on the basis of in situ deprotection of TMS-group (this would be feasible under

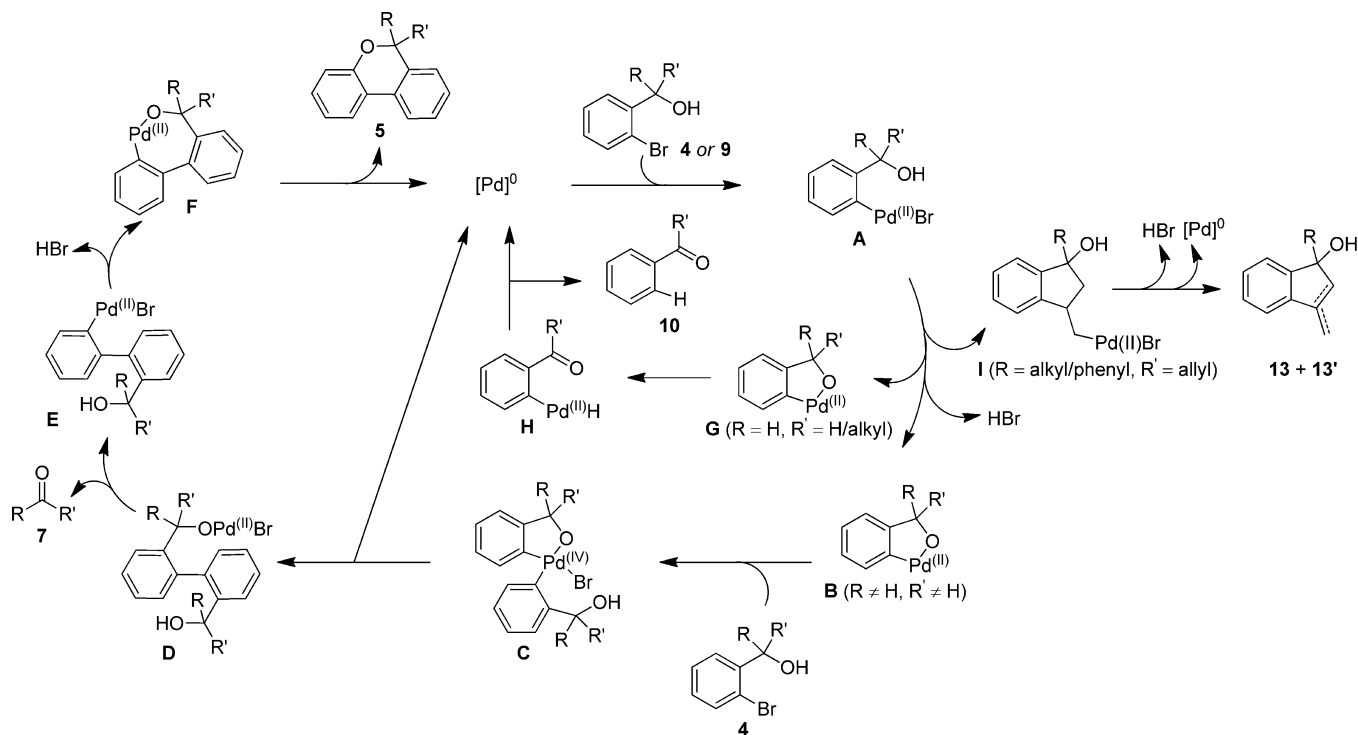
Scheme 5. Reaction of Silyl Ethers **11** in the Presence of Pd Catalyst

basic reaction conditions) followed by the usual Pd-catalyzed transformation of tertiary alcohols **4x–4y**. The deprotection of TMS-group was further confirmed by a blank reaction in the presence of base, without the palladium catalyst.¹⁷ The slow rate of the reaction and the isolation of the deprotected tertiary alcohols **4x–4y** in the presence of active Pd catalyst even after 24 h may be due to the interference of deprotected silyl species with the Pd catalyst.

In addition to the spectroscopic identification of the compounds **5**, the complete structures were further confirmed by single crystal X-ray diffraction analysis of compounds **5b** and **5r** (for details, see the Supporting Information).

To further understand the scope and limitations of the method, olefin variants were also explored (i.e., $R^1 = R^2 = H/OMe$, $R^3 = \text{methyl/phenyl}$). Thus, in contrary to our expectation, unlike the above case [Table 1 and Scheme 2], the fate of chemoselectivity totally changed in the presence of an isolated double bond, therefore furnishing unusual regioisomeric mixture of indenols **13a–13d** (major regioisomer) and **13a'–13d'** (minor regioisomer), as inseparable mixture, from alcohols **4aa–4ad**, via simple intramolecular Heck coupling. The observed chemoselectivity switch may be justified on the basis of preferential insertion of arylpalladium species into reactive isolated double bond. In addition, this chemoselectivity switch is in good agreement with that reported by Oestreich et al.,¹⁸ wherein preferential involvement of olefin was observed to give the Heck product. Interestingly, in the case of electron rich bromoaryl moiety, the formation of indenene **14e**¹⁹ was observed from the indenols (**13e** and **13e'**), after leaving the sample in CDCl₃ within the NMR tube, for a reasonable amount of time, 12 h (Table 3). This could be due to mild acidic nature of the NMR solvent CDCl₃, when electron rich aromatic ring is in conjugation to the hydroxy group connected carbon atom. To better understand this phenomenon, the NMR sample of the mixture (**13e** + **13e'** + **14e**) was left as such in CDCl₃ in the NMR tube, and NMR spectra were measured after 24 h, 48 h, and four days, respectively. As expected, the slow dehydration of the indenols (**13e** and **13e'**) mixture was observed with increase in concentration of **14e**, as described in Table 3. To further prove that the dehydration may be triggered by acidic DCl component of CDCl₃, we

Table 3. Pd-Catalyzed Chemoselective Intramolecular Heck Coupling of Tertiary Alcohols **4** to the Region-Isomeric Mixture of Indenols **13** and Indenenes **14**

Scheme 6. Plausible Catalytic Cycle Reaction Mechanism for the Formation of Chromenes 5 and the Carbonyl Compounds 10^a

^aFor simplicity, ligands are omitted.

recorded the NMR spectra in regular intervals, with the CDCl_3 kept over K_2CO_3 . As anticipated, no dehydration product **14e** was observed. Moreover, when the reaction was performed for sufficiently longer reaction time (12 h), the indene **14e** was formed as the sole product (Table 3). This can be explained by the electron releasing effect of the aromatic ring that facilitates the dehydration of the chelated intermediate of the tertiary alcohol with the palladium species.

The reaction mechanism for the formation of chromenes **5** can be explained via the formation of five-membered palladacycle(II) **B** through the insertion of the initially formed aryl-palladium(II) species **A** from **4a–4v**, onto the O–H bond of the tertiary alcohol (Scheme 6). Now, the oxidative addition of second aryl bromide on to the palladacycle(II) **B** would generate new Pd(IV) intermediate **C**. Intramolecular migration of aryl group leads to the Pd(II) intermediate **D** via simultaneous reductive ring-opening of palladacycle(IV) and homobiaryl bond formation. Now β -carbon cleavage of biaryl intermediate **D** gives the ketone byproduct **7** and the biaryl-palladium(II) species **E**. Finally, intramolecular coupling of the 7-membered palladacycle(II) **F** via a reductive elimination delivers the active Pd(0) catalyst as well as the end product chromene **5**. Though the formation of transmetalation intermediate that contains two Pd(II) centers would also be possible between two Pd(II)-centers (**A** and **B**) for those less sterically hindered Pd(II)-intermediates followed by aryl migration,²⁰ the present case seems probable for the formation of higher oxidation state Pd(IV) intermediate, since sterically crowded palladacycle(II) prefers oxidative addition with second aryl halide.²¹ In the case of primary/secondary benzylic alcohols **9a–9e** the same intermediacy of five-membered palladacycle **G** can be predicted to that of **B**. Because of the availability of β -hydrogen the five-membered palladacycle opens up to the intermediate **H**, which upon reductive elimination regenerates

the Pd(0) catalyst along with the formation of corresponding carbonyl product **10**. On the other hand, the aryl palladium species **A** from **4aa–4ad** insert into the double bond rather than coupling with the hydroxy group and yields the five-membered intermediate **I**, which on reductive elimination and double bond isomerization furnishes the regioisomeric mixture of cyclic olefins **13** and **13'**.

CONCLUSION

In summary, we developed an efficient domino Pd-catalysis for the conversion of simple *ortho*-bromobenzyl tertiary alcohols to chromenes. The reaction might proceed via the formation of a five-membered palladacycle, which in turn couples with the second aryl bromide to facilitate biaryl C–C bond followed by intramolecular C–O bond formation. Interestingly, when there is isolated double bond functionality in the near vicinity a chemoselective switch is preferred, furnishing indenols via intramolecular Heck reaction. Overall, the study has been carried out in a reasonably divergent fashion to show the ability and applicability of Pd-catalysis, which in turn reveals the potentiality of transition metal catalysis.

EXPERIMENTAL SECTION

General Considerations. IR spectra were recorded on a FTIR spectrophotometer. ^1H NMR spectra were recorded on 400 MHz spectrometer at 295 K in CDCl_3 ; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) ($\delta_{\text{H}} = 0.00$ ppm) or CHCl_3 ($\delta_{\text{H}} = 7.25$ ppm). ^{13}C NMR spectra were recorded on 100 MHz spectrometer at RT in CDCl_3 ; chemical shifts (δ ppm) are reported relative to CHCl_3 [$\delta_{\text{C}} = 77.00$ ppm (central line of triplet)]. In the ^{13}C NMR, the nature of carbons (C, CH, CH_2 , and CH_3) was determined by recording the DEPT-135 spectra and is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for CH_2) and q = quartet (for CH_3). In the ^1H NMR, the

following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, m = multiplet and br s. = broad singlet. The assignment of signals was confirmed by ^1H , ^{13}C CPD, and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded using Q-TOF multimode source. Melting points were determined on an electrothermal melting point apparatus and are uncorrected. Benzaldehydes, aryl halides, allyl bromide, methyl iodide, Zn and Mg metal, lithium acetylide, Pd(OAc)₂, Pd(dppf)₂Cl₂, PPh₃, xantphos, Cs₂CO₃, ^tBuOK, Phenol, imidazole and trimethylsilyl chloride, Na₂SO₄ and NH₄Cl were commercially available and used without further purification. All dry solvents were used, diethylether and THF were dried over sodium metal, DCM and DMF were dried over calcium hydride, and dry DMSO was purchased from Sigma Aldrich. All these solvents (diethylether, THF, DCM, DMF, and DMSO) are commercially available. All small scale dry reactions were carried out using standard syringe-septum technique. Reactions were monitored by TLC on silica gel using a combination of petroleum ether and ethyl acetate as eluents. Reactions were generally run under argon or a nitrogen atmosphere. Solvents were distilled prior to use; petroleum ether with a boiling range of 40 to 60 °C was used. Acme's silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per one gram of crude material).

General Procedure GP-1 for Alcohols (2 or 4). To a cold (0 °C), magnetically stirred solution of a bromobenzaldehyde **1** or ketone **3** (1 mmol) in dry THF or dry ether (2 mL) was added phenylmagnesium bromide (5 mmol) [prepared from magnesium (5 mmol) and bromobenzene or bromothiophene or 3-bromoanisole or methyl iodide (5 mmol) and a catalytic amount of iodine in 10 mL of dry THF or dry ether]. The reaction mixture was stirred at 0 °C to room temperature for 3 h. It was then poured into saturated aqueous NH₄Cl solution and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried (Na₂SO₄) and concentrated in vacuo. The crude secondary alcohol **2** or tertiary alcohol **4** was purified by column chromatography on silica using petroleum ether/ethyl acetate as eluent.

General Procedure GP-2 for Ketones (3). To a magnetically stirred solution of the secondary alcohol **2** (1 mmol) in dry CH₂Cl₂ (10 mL) was added a homogeneous mixture (1:1) of PCC (3 mmol) and silica gel. The resulting reaction mixture was stirred at room temperature for 2 h. Filtration of the reaction mixture through a short silica column with excess CH₂Cl₂ furnished the pure ketone **3**.

General Procedure GP-3 for α -Aryl Ketones (8). In an oven-dried Schlenk tube under nitrogen atmosphere were added aryl iodide (0.50 mmol), *ortho*-bromoacetophenone **3** (0.55 mmol), Pd(OAc)₂ (2 mol %), xantphos (4 mol %) and ^tBuOK (0.65 mmol) followed by addition of dry toluene (4 mL). The resulting reaction mixture was stirred at 80 °C for 45 min. Progress of the reaction was monitored by TLC until the reaction is completed. The reaction mixture was then quenched with saturated aqueous NH₄Cl, and the aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried (Na₂SO₄) and concentrated in vacuo. The crude ketone **8** was purified by column chromatography on silica using petroleum ether/ethyl acetate as eluent.

General Procedure GP-4 for Homoallylic Alcohol (4). Allyl bromide (0.60 mL–0.70 mL, 6.98–8.04 mmol) in THF (1 mL) was added dropwise to a sonicated suspension of zinc dust (457 mg–525 mg, 6.98–8.04 mmol) or lithium acetylide in THF (2 mL) at room temperature, and the mixture was further sonicated for 30 min, and then *ortho*-bromoacetophenone **3** (400 mg, 1.74–2.01 mmol) in THF (3 mL) was added and continued sonication at room temperature for 2 h. Progress of the reaction was monitored by TLC. The reaction mixture was quenched by addition of aqueous NH₄Cl solution and extracted with ethyl acetate (3 × 15 mL). The collected organic layers were dried (Na₂SO₄) and concentrated in vacuo. Purification of the residue on a silica gel column chromatography (petroleum ether/ethyl acetate) as eluent furnished homoallylic alcohol **4**.

General Procedure GP-5 for Trimethylsilylether (11). To a magnetically stirred solution of the tertiary alcohol **4** (1.5 mmol) and imidazole (3 mmol) in dry CH₂Cl₂ (6 mL) trimethylsilyl chloride (3 mmol) was added at 0 °C. The resulting reaction mixture was

stirred at room temperature for 4 h. The reaction mixture was quenched and extracted with CH₂Cl₂ (3 × 15 mL). The collected organic layers were dried (Na₂SO₄) and concentrated under reduced pressure. Purification of the residue on a silica gel column chromatography (petroleum ether/ethyl acetate) as eluent furnished trimethylsilylether of corresponding alcohol **11**.

General Procedure GP-6 for Cyclization (5). In an oven-dried Schlenk tube under nitrogen atmosphere were added Pd(OAc)₂ (5 mol %), PPh₃ (10 mol %), Cs₂CO₃ (1.0 mmol), and tertiary alcohol **4** (0.50 mmol) followed by addition of DMF (2 mL) [or DMSO (2 mL) in case of silyl ethers **11a**, **11b**]. The resulting reaction mixture was stirred at 120 °C for 24–48 h. Progress of the reaction was monitored by TLC until the reaction is completed. The reaction mixture was quenched by addition of aq. NH₄Cl solution and extracted with CH₂Cl₂ (3 × 10 mL). The organic layers were dried (Na₂SO₄) and concentrated in vacuo. Purification of the residue on a silica gel column chromatography using petroleum ether/ethyl acetate as eluent furnished the cyclic ethers **5**.

[5-(Benzyloxy)-2-bromo-4-methoxyphenyl](phenyl)methanol (2e). This compound was prepared according to the GP-1 and isolated as yellow color viscous liquid 96% yield (597 mg): ^1H NMR (CDCl₃, 400 MHz) δ = 7.41 (d, 2H, *J* = 7.4 Hz), 7.37 (d, 2H, *J* = 7.8 Hz), 7.35–7.28 (m, 5H), 7.25 (t, 1H, *J* = 7.8 Hz), 7.08 (s, 1H), 7.02 (s, 1H), 6.08 (s, 1H), 5.07 (s, 2H), 3.79 (s, 3H), 2.61 (br. s, 1H) ppm; ^{13}C NMR (CDCl₃, 100 MHz) δ = 149.3 (C_q), 148.0 (C_q), 142.4 (C_q), 136.3 (C_q), 135.2 (C_q), 128.5 (2 × CH), 128.3 (2 × CH), 128.0 (CH), 127.6 (CH), 127.3 (2 × CH), 126.7 (2 × CH), 117.6 (CH), 112.3 (C_q), 111.3 (CH), 74.3 (CH), 71.1 (CH₂), 56.0 (C_q) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{max} = 3552, 2939, 1499, 1379, 1257, 1152, 1027, 809, 735, 697 cm⁻¹; HR-MS (ESI+) *m/z* calculated for [C₂₁H₁₈⁷⁹BrO₂]⁺ = [(M + H) – H₂O]⁺ 381.0485, found 381.0486.

[4-(Benzyloxy)-2-bromo-5-methoxyphenyl](phenyl)methanol (2f). This compound was prepared according to the GP-1 and isolated as brown color viscous liquid 96% yield (597 mg): ^1H NMR (CDCl₃, 400 MHz) δ = 7.38 (d, 2H, *J* = 7.1 Hz), 7.32 (dd, 4H, *J* = 7.5 and 7.1 Hz), 7.29–7.24 (m, 3H), 7.21 (d, 1H, *J* = 7.1 Hz), 7.04 (s, 1H), 6.98 (s, 1H), 6.02 (s, 1H), 5.02 (s, 2H), 3.74 (s, 3H), 2.75 (br. s, 1H) ppm; ^{13}C NMR (CDCl₃, 100 MHz) δ = 149.1 (C_q), 147.9 (C_q), 142.3 (C_q), 136.2 (C_q), 135.2 (C_q), 128.5 (2 × CH), 128.3 (2 × CH), 128.0 (CH), 127.5 (CH), 127.3 (2 × CH), 126.6 (2 × CH), 117.4 (CH), 112.2 (C_q), 111.2 (CH), 74.2 (CH), 71.0 (CH₂), 55.9 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{max} = 3505, 2934, 1497, 1383, 1257, 1154, 1044, 865, 737, 698 cm⁻¹; HR-MS (ESI+) *m/z* calculated for [C₂₁H₁₈⁷⁹BrO₂]⁺ = [(M + H) – H₂O]⁺ 381.0485, found 381.0486.

(2-Bromo-3,4,5-trimethoxyphenyl)(phenyl)methanol (2g). This compound was prepared according to the GP-1 and isolated as brown color viscous liquid 98% yield (632 mg): ^1H NMR (CDCl₃, 400 MHz) δ = 7.39 (d, 2H, *J* = 7.3 Hz), 7.33 (dd, 2H, *J* = 7.8 and 6.8 Hz), 7.27 (d, 1H, *J* = 6.8 Hz), 6.97 (s, 1H), 6.18 (s, 1H), 3.86 (s, 6H), 3.82 (s, 3H), 2.52 (br. s, 1H) ppm; ^{13}C NMR (CDCl₃, 100 MHz) δ = 152.9 (C_q), 150.6 (C_q), 142.4 (C_q), 142.1 (C_q), 138.1 (C_q), 128.4 (2 × CH), 127.7 (CH), 126.9 (2 × CH), 109.1 (C_q), 107.0 (CH), 74.6 (CH), 61.0 (2 × CH₃), 56.1 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{max} = 3450, 2937, 1568, 1479, 1391, 1324, 1237, 1159, 1104, 1007, 921, 816, 700, 607 cm⁻¹; HR-MS (ESI+) *m/z* calculated for [C₁₆H₁₆⁷⁹BrO₃]⁺ = [(M + H) – H₂O]⁺ 335.0283, found 335.0287.

(2-Bromo-5-methoxyphenyl)(3-methoxyphenyl)methanol (2i). This compound was prepared according to the GP-1 and isolated as colorless viscous liquid 94% yield (706 mg): ^1H NMR (CDCl₃, 400 MHz) δ = 7.45 (d, 1H, *J* = 8.8 Hz), 7.29 (dd, 1H, *J* = 8.2 and 8.1 Hz), 7.20 (d, 1H, *J* = 2.9 Hz), 7.03 (d, 2H, *J* = 7.5 Hz), 6.86 (dd, 1H, *J* = 7.0 and 2.5 Hz), 6.74 (dd, 1H, *J* = 8.8 and 2.9 Hz), 6.13 (s, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 2.79 (br. s, 1H) ppm; ^{13}C NMR (CDCl₃, 100 MHz) δ = 159.5 (C_q), 159.1 (C_q), 143.6 (C_q), 143.4 (C_q), 133.3 (CH), 129.4 (CH), 119.2 (CH), 114.9 (CH), 113.8 (CH), 113.0 (CH), 112.9 (C_q), 112.7 (CH), 74.4 (CH), 55.3 (CH₃), 55.1 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{max} = 3416, 2937, 1593, 1465, 1235, 1149, 1038, 907, 874, 729, 693 cm⁻¹; HR-MS (ESI+) *m/z*

calculated for $[C_{15}H_{14}^{79}BrO_2]^+ = [(M + H) - H_2O]^+ 305.0172$, found 305.0164.

(2-Bromo-4, 5-dimethoxyphenyl)(3-methoxyphenyl)methanol (2j). This compound was prepared according to the GP-1 and isolated as colorless viscous liquid 95% yield (684 mg): 1H NMR ($CDCl_3$, 400 MHz) $\delta = 7.25$ (dd, 1H, $J = 8.1$ and 8.1 Hz), 7.07 (s, 1H), 7.03 – 6.93 (m, 3H), 6.81 (dd, 1H, $J = 8.1$ and 2.3 Hz), 6.11 (s, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 3.79 (s, 3H), 2.65 (br. s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 159.6$ (C_q), 148.9 (C_q), 148.7 (C_q), 144.2 (C_q), 134.7 (C_q), 129.4 (CH), 118.9 (CH), 115.3 (CH), 112.8 (CH), 112.6 (C_q), 112.4 (CH), 110.9 (CH), 74.2 (CH), 56.1 (CH_3), 56.0 (CH_3), 55.1 (CH_3) ppm; IR (MIR-ATR, 4000 – 600 cm^{-1}) $\nu_{max} = 3486$, 2934 , 1599 , 1498 , 1378 , 1253 , 1148 , 1027 , 809 , 740 , 697 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[C_{16}H_{16}^{79}BrO_3]^+ = [(M + H) - H_2O]^+ 335.0277$, found 335.0269.

(6-Bromobenzo[d][1,3]dioxol-5-yl)(3-methoxyphenyl)methanol (2k). This compound was prepared according to the GP-1 and isolated as pale yellow viscous liquid 88% yield (650 mg): 1H NMR ($CDCl_3$, 400 MHz) $\delta = 7.27$ (d, 1H, $J = 8.2$ and 8.0 Hz), 7.08 – 7.94 (m, 4H), 6.83 (dd, 1H, $J = 8.2$ and 2.3 Hz), 6.13 (s, 1H), 5.98 (d, 1H, $J = 1.2$ Hz), 5.95 (d, 1H, $J = 1.4$ Hz), 3.81 (s, 3H), 2.60 (br. s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 159.6$ (C_q), 147.7 (C_q), 147.6 (C_q), 144.0 (C_q), 136.0 (C_q), 129.5 (CH), 118.9 (CH), 113.1 (C_q), 112.9 (CH), 112.4 (CH), 112.3 (CH), 108.3 (CH), 101.7 (CH_2), 74.2 (CH), 55.2 (CH_3) ppm; IR (MIR-ATR, 4000 – 600 cm^{-1}) $\nu_{max} = 3394$, 2900 , 1473 , 1230 , 1105 , 1035 , 905 , 726 , 647 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[C_{15}H_{12}^{79}BrO_3]^+ = [(M + H) - H_2O]^+ 318.9964$, found 318.9950.

[5-(Benzoyloxy)-2-bromo-4-methoxyphenyl](3-methoxyphenyl)methanol (2l). This compound was prepared according to the GP-1 and isolated as white solid 93% yield (623 mg): mp 110 – 112 $^{\circ}C$; 1H NMR ($CDCl_3$, 400 MHz) $\delta = 7.44$ – 7.26 (m, 5H), 7.23 (dd, 1H, $J = 8.0$ and 7.8 Hz), 7.08 (s, 1H), 7.03 (s, 1H), 6.92 (s, 1H), 6.88 (d, 1H, $J = 7.8$ Hz), 6.82 (dd, 1H, $J = 8.0$ and 2.5 Hz), 6.01 (s, 1H), 5.11 (d, 1H, $J = 12.2$ Hz), 5.10 (d, 1H, $J = 12.2$ Hz), 3.87 (s, 3H), 3.78 (s, 3H), 2.42 (br. s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 159.6$ ($2 \times C_q$), 149.6 (C_q), 147.6 (C_q), 144.0 (C_q), 136.5 (C_q), 134.5 (C_q), 129.4 (CH), 128.5 ($2 \times CH$), 127.9 (CH), 127.5 ($2 \times CH$), 118.9 (CH), 115.8 (CH), 113.8 (CH), 113.0 (CH), 112.3 (CH), 74.2 (CH), 71.0 (CH_2), 56.2 (CH_3), 55.1 (CH_3) ppm; IR (MIR-ATR, 4000 – 600 cm^{-1}) $\nu_{max} = 3479$, 2937 , 1496 , 1377 , 1254 , 1146 , 1028 , 908 , 729 , 695 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[C_{22}H_{20}^{79}BrO_3]^+ = [(M + H) - H_2O]^+ 411.0590$, found 411.0578.

[4-(Benzoyloxy)-2-bromo-5-methoxyphenyl](3-methoxyphenyl)methanol (2m). This compound was prepared according to the GP-1 and isolated as pale yellow solid 92% yield (615 mg): mp 108 – 110 $^{\circ}C$; 1H NMR ($CDCl_3$, 400 MHz) $\delta = 7.40$ (d, 2H, $J = 7.4$ Hz), 7.35 (dd, 2H, $J = 7.4$ and 7.0 Hz), 7.30 (d, 1H, $J = 7.0$ Hz), 7.23 (dd, 1H, $J = 8.0$ and 8.0 Hz), 7.06 (s, 1H), 7.02 (s, 1H), 6.99 – 6.90 (m, 2H), 6.79 (dd, 1H, $J = 8.0$ and 2.5 Hz), 6.07 (d, 1H, $J = 3.5$ Hz), 5.08 (s, 2H), 3.81 (s, 3H), 3.77 (s, 3H), 2.37 (d, 1H, $J = 3.5$ Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 159.6$ ($2 \times C_q$), 149.3 (C_q), 148.1 (C_q), 144.1 (C_q), 136.3 (C_q), 135.0 (C_q), 129.5 (CH), 128.6 ($2 \times CH$), 128.1 (CH), 127.4 ($2 \times CH$), 119.0 (CH), 117.6 (CH), 112.9 (CH), 112.4 (CH), 111.3 (CH), 74.3 (CH), 71.2 (CH_2), 56.1 (CH_3), 55.2 (CH_3) ppm; IR (MIR-ATR, 4000 – 600 cm^{-1}) $\nu_{max} = 3476$, 2939 , 1495 , 1374 , 1253 , 1152 , 1023 , 904 , 725 , 694 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[C_{22}H_{20}^{79}BrO_3]^+ = [(M + H) - H_2O]^+ 411.0590$, found 411.0579.

(2-Bromo-5-methoxyphenyl)(thiophen-2-yl)methanol (2o). This compound was prepared according to the GP-1 and isolated as black color semisolid 93% yield (646 mg): 1H NMR ($CDCl_3$, 400 MHz) $\delta = 7.38$ (d, 1H, $J = 8.8$ Hz), 7.23 (dd, 2H, $J = 7.3$ and 3.4 Hz), 6.90 (s, 2H), 6.70 (dd, 1H, $J = 8.3$ and 2.5 Hz), 6.28 (s, 1H), 3.76 (s, 3H), 2.98 (br. s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 159.2$ (C_q), 146.0 (C_q), 143.0 (C_q), 133.3 (CH), 126.6 (CH), 125.5 (CH), 125.4 (CH), 115.4 (CH), 113.0 (CH), 112.5 (C_q), 70.9 (CH), 55.4 (CH_3) ppm; IR (MIR-ATR, 4000 – 600 cm^{-1}) $\nu_{max} = 3515$, 2914 , 1487 , 1380 , 1237 , 1144 , 1014 , 835 , 735 , 688 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[C_{12}H_{11}^{79}BrNaSO_2]^+ = [M + Na]^+ 322.9535$, found 322.9523.

(2-Bromo-4,5-dimethoxyphenyl)(thiophen-2-yl)methanol (2p). This compound was prepared according to the GP-1 and isolated as black semisolid 90% yield (604 mg): 1H NMR ($CDCl_3$, 400 MHz) $\delta = 7.27$ (dd, 1H, $J = 5.4$ and 1.5 Hz), 7.21 (s, 1H), 6.96 (s, 1H), 6.92 (dd, 1H, $J = 5.4$ and 3.4 Hz), 6.88 (d, 1H, $J = 3.4$ Hz), 6.01 (s, 1H), 3.86 (s, 3H), 3.80 (s, 3H), 1.59 (br. s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 149.2$ (C_q), 148.9 (C_q), 144.4 (C_q), 132.2 (C_q), 126.5 (CH), 126.1 (CH), 125.7 (CH), 114.9 (CH), 112.7 (C_q), 110.7 (CH), 75.6 (CH), 56.1 (CH_3), 56.0 (CH_3) ppm; IR (MIR-ATR, 4000 – 600 cm^{-1}) $\nu_{max} = 3525$, 2924 , 1492 , 1382 , 1254 , 1153 , 1042 , 862 , 734 , 692 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[C_{13}H_{12}^{79}BrSO_2]^+ = [(M + H) - H_2O]^+ 310.9736$, found 310.9737.

(6-Bromobenzo[d][1,3]dioxol-5-yl)(phenyl)methanone (3d). This compound was prepared according to the GP-2 and isolated as white solid 96% yield (476 mg): mp 110 – 115 $^{\circ}C$; 1H NMR ($CDCl_3$, 400 MHz) $\delta = 7.80$ (d, 2H, $J = 7.1$ Hz), 7.57 (dd, 1H, $J = 7.7$ and 7.1 Hz), 7.44 (dd, 2H, $J = 7.8$ and 7.7 Hz), 7.05 (s, 1H), 6.81 (s, 1H), 6.03 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 195.1$ (C_q), 149.7 (C_q), 147.1 (C_q), 136.3 ($2 \times C_q$), 133.5 (CH), 130.1 ($2 \times CH$), 128.5 ($2 \times CH$), 113.2 (CH), 111.4 (C_q), 109.2 (CH), 102.2 (CH_2) ppm; IR (MIR-ATR, 4000 – 600 cm^{-1}) $\nu_{max} = 2932$, 1663 , 1592 , 1434 , 1331 , 1262 , 1170 , 1021 , 853 , 715 , 699 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[C_{14}H_{10}^{79}BrO_3]^+ = [M + H]^+ 304.9808$, found 304.9806.

[5-(Benzoyloxy)-2-bromo-4-methoxyphenyl](phenyl)methanone (3e). This compound was prepared according to the GP-2 and isolated as white solid 96% yield (477 mg): mp 108 – 110 $^{\circ}C$; 1H NMR ($CDCl_3$, 400 MHz) $\delta = 7.72$ (d, 2H, $J = 7.3$ Hz), 7.57 (dd, 1H, $J = 7.4$ and 7.3 Hz), 7.41 (dd, 2H, $J = 7.8$ and 7.8 Hz), 7.38 – 7.26 (m, 5H), 7.10 (s, 1H), 6.92 (s, 1H), 5.08 (s, 2H), 3.93 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 195.3$ (C_q), 151.6 (C_q), 146.9 (C_q), 136.5 (C_q), 136.0 (C_q), 133.3 (CH), 131.9 (CH), 130.2 ($2 \times CH$), 128.6 ($2 \times CH$), 128.5 ($2 \times CH$), 128.1 (CH), 127.4 ($2 \times CH$), 116.3 (CH), 115.1 (CH), 111.7 (C_q), 71.2 (CH_2), 56.3 (CH_3) ppm; IR (MIR-ATR, 4000 – 600 cm^{-1}) $\nu_{max} = 2934$, 1666 , 1593 , 1439 , 1330 , 1261 , 1174 , 1024 , 850 , 718 , 697 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[C_{21}H_{18}^{79}BrO_3]^+ = [M + H]^+ 397.0434$, found 397.0435.

[4-(Benzoyloxy)-2-bromo-5-methoxyphenyl](phenyl)methanone (3f). This compound was prepared according to the GP-2 and isolated as white solid 94% yield (468 mg): mp 120 – 122 $^{\circ}C$; 1H NMR ($CDCl_3$, 400 MHz) $\delta = 7.82$ (d, 2H, $J = 7.6$ Hz), 7.58 (dd, 1H, $J = 7.6$ and 7.0 Hz), 7.51 – 7.42 (m, 4H), 7.40 (dd, 2H, $J = 7.6$ and 7.0 Hz), 7.34 (d, 1H, $J = 7.0$ Hz), 7.13 (s, 1H), 6.91 (s, 1H), 5.17 (s, 2H), 3.83 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 195.5$ (C_q), 150.0 (C_q), 148.7 (C_q), 136.5 (C_q), 135.8 (C_q), 133.4 (CH), 132.7 (C_q), 130.2 ($2 \times CH$), 128.6 ($2 \times CH$), 128.5 ($2 \times CH$), 128.2 (CH), 127.4 ($2 \times CH$), 117.8 (CH), 112.6 (CH), 110.6 (C_q), 71.2 (CH_2), 56.2 (CH_3) ppm; IR (MIR-ATR, 4000 – 600 cm^{-1}) $\nu_{max} = 2928$, 1649 , 1588 , 1497 , 1379 , 1264 , 1146 , 987 , 839 , 719 , 696 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[C_{21}H_{18}^{79}BrO_3]^+ = [M + H]^+ 397.0434$, found 397.0425.

(2-Bromo-3,4,5-trimethoxyphenyl)(phenyl)methanone (3g). This compound was prepared according to the GP-2 and isolated as yellow color solid 97% yield (482 mg): mp 72 – 73 $^{\circ}C$; 1H NMR ($CDCl_3$, 400 MHz) $\delta = 7.82$ (d, 2H, $J = 7.8$ Hz), 7.60 (t, 1H, $J = 7.3$ Hz), 7.46 (dd, 2H, $J = 7.8$ and 7.3 Hz), 6.69 (s, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 3.83 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 195.4$ (C_q), 153.0 ($2 \times C_q$), 151.1 (C_q), 144.3 (C_q), 136.1 (C_q), 133.7 (CH), 130.2 ($2 \times CH$), 128.6 ($2 \times CH$), 107.7 (CH), 106.3 (C_q), 61.2 (CH_3), 61.1 (CH_3), 56.3 (CH_3) ppm; IR (MIR-ATR, 4000 – 600 cm^{-1}) $\nu_{max} = 2937$, 1669 , 1562 , 1479 , 1383 , 1336 , 1227 , 1162 , 1103 , 1003 , 926 , 837 , 726 , 689 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[C_{16}H_{15}^{79}BrNaO_4]^+ = [M + Na]^+ 373.0046$, found 373.0042.

(2-Bromo-5-methoxyphenyl)(3-methoxyphenyl)methanone (3i). This compound was prepared according to the GP-2 and isolated as white solid 98% yield (486 mg): mp 63 – 70 $^{\circ}C$; 1H NMR ($CDCl_3$, 400 MHz) $\delta = 7.49$ (d, 1H, $J = 8.8$ Hz), 7.44 (s, 1H), 7.34 (dd, 1H, $J = 7.8$ and 7.8 Hz), 7.29 (d, 1H, $J = 7.6$ Hz), 7.14 (ddd, 1H, $J = 8.8$, 7.8 , and 2.5 Hz), 6.88 (dd, 1H, $J = 8.8$ and 3.0 Hz), 6.86 (d, 1H, $J = 3.0$ Hz), 3.84 (s, 3H), 3.79 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 195.4$ (C_q), 159.9 (C_q), 158.7 (C_q), 141.4 (C_q), 137.2

(C_q), 133.9 (CH), 129.6 (CH), 123.5 (CH), 120.5 (CH), 117.3 (CH), 114.1 (CH), 113.7 (CH), 109.7 (C_q), 55.6 (CH₃), 55.4 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 2937, 1671, 1593, 1464, 1288, 1019, 788, 681 cm⁻¹; HR-MS (ESI+) m/z calculated for [C₁₅H₁₃⁷⁹BrKO₃]⁺ = [M + K]⁺ 358.9680, found 358.9674.

(4,5-Dimethoxy-2-methylphenyl)(3-methoxyphenyl)methanone (3j). This compound was prepared according to the GP-2 and isolated as brown viscous liquid 98% yield (487 mg): ¹H NMR (CDCl₃, 400 MHz) δ = 7.30 (s, 1H), 7.24–7.14 (m, 2H), 7.02 (d, 1H, J = 7.7 Hz), 6.97 (s, 1H), 6.78 (s, 1H), 3.81 (s, 3H), 3.73 (s, 6H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 195.3 (C_q), 159.8 (C_q), 150.9 (C_q), 148.2 (C_q), 138.0 (C_q), 132.4 (C_q), 129.5 (CH), 123.3 (CH), 120.0 (CH), 115.9 (CH), 113.9 (CH), 112.3 (CH), 110.9 (C_q), 56.3 (CH₃), 56.2 (CH₃), 55.4 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 2936, 1665, 1593, 1373, 1256, 1172, 1034, 751, 629 cm⁻¹; HR-MS (ESI+) m/z calculated for [C₁₆H₁₅⁷⁹BrNaO₄]⁺ = [M + Na]⁺ 373.0046, found 373.0056.

(6-Bromobenzo[d][1,3]dioxol-5-yl)(3-methoxyphenyl)methanone (3k). This compound was prepared according to the GP-2 and isolated as yellow color solid 98% yield (490 mg): mp 98–100 °C; ¹H NMR (CDCl₃, 400 MHz) δ = 7.41 (dd, 1H, J = 2.4 and 1.5 Hz), 7.33 (d, 1H, J = 7.8 Hz), 7.29 (ddd, 1H, J = 7.8, 6.3, and 1.4 Hz), 7.17–7.08 (m, 1H), 7.06 (s, 1H), 6.81 (s, 1H), 6.05 (s, 2H), 3.84 (s, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 195.0 (C_q), 159.8 (C_q), 149.7 (C_q), 147.2 (C_q), 137.7 (C_q), 133.7 (C_q), 129.5 (CH), 123.3 (CH), 120.2 (CH), 113.8 (CH), 113.3 (CH), 111.5 (C_q), 109.2 (CH), 102.3 (CH₂), 55.5 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 2933, 1668, 1500, 1450, 1381, 1263, 1038, 843, 737, 698 cm⁻¹; HR-MS (APCI+) m/z calculated for [C₁₅H₁₁⁷⁹BrNaO₄]⁺ = [M + Na]⁺ 356.9733, found 356.9717.

[5-(Benzyloxy)-2-bromo-4-methoxyphenyl](3-methoxyphenyl)methanone (3l). This compound was prepared according to the GP-2 and isolated as pale yellow color solid 98% yield (489 mg): mp 106–108 °C; ¹H NMR (CDCl₃, 400 MHz) δ = 7.42–7.23 (m, 7H), 7.19 (d, 1H, J = 7.7 Hz), 7.11 (dd, 1H, J = 8.7 and 2.6 Hz), 7.10 (s, 1H), 6.92 (s, 1H), 5.08 (s, 2H), 3.92 (s, 3H), 3.82 (s, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 195.1 (C_q), 159.8 (C_q), 151.6 (C_q), 147.0 (C_q), 137.9 (C_q), 136.1 (C_q), 132.1 (C_q), 129.4 (CH), 128.6 (2 × CH), 128.1 (CH), 127.4 (2 × CH), 123.3 (CH), 120.1 (CH), 116.4 (CH), 115.1 (CH), 113.7 (CH), 111.7 (C_q), 71.2 (CH₂), 56.3 (CH₃), 55.4 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 2932, 1667, 1590, 1510, 1448, 1391, 1260, 1036, 841, 735, 693 cm⁻¹; HR-MS (ESI+) m/z calculated for [C₂₂H₂₀⁷⁹BrO₄]⁺ = [M + H]⁺ 427.0539, found 427.0521.

[4-(Benzyloxy)-2-bromo-5-methoxyphenyl](3-methoxyphenyl)methanone (3m). This compound was prepared according to the GP-2 and isolated as white color solid 97% yield (483 mg): mp 104–106 °C; ¹H NMR (CDCl₃, 400 MHz) δ = 7.45 (d, 2H, J = 7.1 Hz), 7.42–7.37 (m, 3H), 7.36–7.26 (m, 3H), 7.18–7.08 (m, 2H), 6.89 (s, 1H), 5.17 (s, 2H), 3.84 (s, 6H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 195.4 (C_q), 159.8 (C_q), 150.0 (C_q), 148.7 (C_q), 137.9 (C_q), 135.9 (C_q), 132.8 (C_q), 129.5 (CH), 128.7 (2 × CH), 128.3 (CH), 127.4 (2 × CH), 123.4 (CH), 120.2 (CH), 117.9 (CH), 113.7 (CH), 112.5 (CH), 110.6 (C_q), 71.2 (CH₂), 56.2 (CH₃), 55.4 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 2933, 1668, 1591, 1500, 1450, 1381, 1263, 1038, 843, 738, 698 cm⁻¹; HR-MS (ESI+) m/z calculated for [C₂₂H₂₀⁷⁹BrO₄]⁺ = [M + H]⁺ 427.0539, found 427.0527.

(2-Bromophenyl)(thiophen-2-yl)methanone (3n). This compound was prepared according to the GP-2 and isolated as black color viscous liquid 98% yield (486 mg): ¹H NMR (CDCl₃, 400 MHz) δ = 7.75 (dd, 1H, J = 4.9 and 1.5 Hz), 7.64 (d, 1H, J = 7.8 Hz), 7.45–7.37 (m, 3H), 7.36–7.30 (m, 1H), 7.11 (dd, 1H, J = 4.9 and 3.9 Hz) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 187.8 (C_q), 143.4 (C_q), 140.4 (C_q), 136.0 (CH), 135.6 (CH), 133.3 (CH), 131.3 (CH), 128.7 (CH), 128.3 (CH), 127.0 (CH), 119.4 (C_q) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 2936, 1669, 1583, 1371, 1253, 1171, 1032, 750, 622 cm⁻¹; HR-MS (ESI+) m/z calculated for [C₁₁H₈⁷⁹BrOS]⁺ = [(M + H)]⁺ 266.9474, found 266.9475.

(2-Bromo-5-methoxyphenyl)(thiophen-2-yl)methanone (3o). This compound was prepared according to the GP-2 and isolated

as black color solid 97% yield (477 mg): mp 84–86 °C; ¹H NMR (CDCl₃, 400 MHz) δ = 7.74 (d, 1H, J = 4.9 Hz), 7.49 (d, 1H, J = 8.8 Hz), 7.41 (d, 1H, J = 3.4 Hz), 7.10 (dd, 1H, J = 4.9 and 3.9 Hz), 6.92 (d, 1H, J = 2.9 Hz), 6.88 (dd, 1H, J = 8.8 and 2.9 Hz), 3.79 (s, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 187.5 (C_q), 158.5 (C_q), 143.1 (C_q), 141.1 (C_q), 136.1 (CH), 135.7 (CH), 134.0 (CH), 128.3 (CH), 117.3 (CH), 114.1 (CH), 109.5 (C_q), 55.6 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 2932, 1662, 1591, 1373, 1252, 1171, 1035, 753, 628 cm⁻¹; HR-MS (ESI+) m/z calculated for [C₁₂H₁₃⁸¹BrNO₂S]⁺ = [M + NH₄]⁺ 315.9824, found 315.9811.

(2-Bromo-4,5-dimethoxyphenyl)(thiophen-2-yl)methanone (3p). This compound was prepared according to the GP-2 and isolated as black color solid 95% yield (472 mg): mp 118–120 °C; ¹H NMR (CDCl₃, 400 MHz) δ = 7.71 (dd, 1H, J = 4.9 and 1.0 Hz), 7.43 (dd, 1H, J = 3.4 and 1.0 Hz), 7.09 (dd, 1H, J = 4.9 and 3.4 Hz), 7.06 (s, 1H), 6.92 (s, 1H), 3.90 (s, 3H), 3.82 (s, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 187.3 (C_q), 150.8 (C_q), 147.9 (C_q), 143.5 (C_q), 135.7 (CH), 135.3 (CH), 132.2 (C_q), 128.2 (CH), 115.9 (CH), 111.8 (CH), 110.5 (C_q), 56.2 (CH₃), 56.1 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 2931, 1668, 1591, 1378, 1259, 1178, 1035, 752, 628 cm⁻¹; HR-MS (ESI+) m/z calculated for [C₁₃H₁₁⁷⁹BrNaO₃S]⁺ = [(M + Na)]⁺ 348.9504, found 348.9495.

1-(2-Bromo-5-methoxyphenyl)-1-phenylethanol (4b). This compound was prepared according to the GP-1 and isolated as brown color viscous liquid 96% yield (405 mg): ¹H NMR (CDCl₃, 400 MHz) δ = 7.40 (dd, 2H, J = 8.6 and 3.1 Hz), 7.33–7.20 (m, 5H), 6.72 (dd, 1H, J = 8.6 and 3.1 Hz), 3.84 (s, 3H), 3.42 (br. s, 1H), 1.94 (s, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 158.7 (C_q), 147.3 (C_q), 146.0 (C_q), 135.4 (CH), 128.1 (2 × CH), 126.9 (CH), 125.6 (2 × CH), 115.4 (CH), 113.5 (CH), 112.4 (C_q), 77.3 (C_q), 55.5 (CH₃), 29.9 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 3458, 2936, 1569, 1463, 1289, 1039, 764, 699 cm⁻¹; HR-MS (ESI+) m/z calculated for [C₁₅H₁₄⁷⁹BrO]⁺ = [(M + H) – H₂O]⁺ 289.0223, found 289.0222.

1-(2-Bromo-4,5-dimethoxyphenyl)-1-phenylethanol (4c). This compound was prepared according to the GP-1 and isolated as brown color viscous liquid 98% yield (411 mg): ¹H NMR (CDCl₃, 400 MHz) δ = 7.33 (s, 1H), 7.27–7.12 (m, 5H), 6.92 (s, 1H), 3.86 (s, 3H), 3.78 (s, 3H), 1.89 (s, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 148.5 (C_q), 147.7 (C_q), 147.5 (C_q), 137.6 (C_q), 128.1 (2 × CH), 126.9 (CH), 125.7 (2 × CH), 117.6 (CH), 112.1 (C_q), 111.7 (CH), 77.0 (C_q), 56.1 (2 × CH₃), 29.8 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 3514, 2935, 1598, 1500, 1442, 1373, 1255, 1157, 1027, 764, 618 cm⁻¹; HR-MS (ESI+) m/z calculated for [C₁₆H₁₆⁷⁹BrO₂]⁺ = [(M + H) – H₂O]⁺ 319.0328, found 319.0327.

1-(6-bromo-1,3-benzodioxol-5-yl)-1-phenylethanol (4d). This compound was prepared according to the GP-1 and isolated as yellow color viscous liquid 97% yield (410 mg): ¹H NMR (CDCl₃, 400 MHz) δ = 7.32 (s, 1H), 7.28–7.18 (m, 5H), 6.94 (s, 1H), 5.99 (d, 1H, J = 1.4 Hz), 5.98 (d, 1H, J = 1.4 Hz), 3.34 (br. s, 1H), 1.87 (s, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 147.7 (C_q), 147.4 (C_q), 147.2 (C_q), 138.8 (C_q), 128.1 (2 × CH), 126.9 (CH), 125.5 (2 × CH), 114.7 (CH), 112.9 (C_q), 108.8 (CH), 102.0 (CH₂), 77.2 (C_q), 30.5 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 3514, 2936, 1597, 1502, 1432, 1353, 1245, 1151, 1047, 761, 675 cm⁻¹; HR-MS (ESI+) m/z calculated for [C₁₅H₁₂⁷⁹BrO₂]⁺ = [(M + H) – H₂O]⁺ 303.0015, found 303.0011.

1-[5-(Benzyloxy)-2-bromo-4-methoxyphenyl]-1-phenylethanol (4e). This compound was prepared according to the GP-1 and isolated as yellow color viscous liquid 97% yield (405 mg): ¹H NMR (CDCl₃, 400 MHz) δ = 7.37 (d, 2H, J = 7.3 Hz), 7.31 (d, 2H, J = 7.0 Hz), 7.28 (s, 1H), 7.24 (d, 1H, J = 7.0 Hz), 7.23–7.05 (m, 5H), 6.94 (s, 1H), 5.13 (s, 2H), 3.79 (s, 3H), 1.76 (s, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 149.3 (C_q), 147.6 (C_q), 146.5 (C_q), 137.2 (C_q), 136.6 (C_q), 128.6 (2 × CH), 128.1 (3 × CH), 127.6 (2 × CH), 126.8 (CH), 125.6 (2 × CH), 118.1 (CH), 115.2 (CH), 112.9 (C_q), 77.0 (C_q), 71.5 (CH₂), 56.2 (CH₃), 30.2 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 3512, 2933, 1596, 1494, 1373, 1252, 1151, 1023, 760, 691 cm⁻¹; HR-MS (ESI+) m/z calculated for [C₂₂H₂₀⁷⁹BrO₂]⁺ = [(M + H) – H₂O]⁺ 395.0641, found 395.0639.

1-[4-(Benzyloxy)-2-bromo-5-methoxyphenyl]-1-phenylethanol (4f). This compound was prepared according to the GP-1 and isolated as brown color viscous liquid 98% yield (408 mg): $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ = 7.43 (dd, 3H, J = 7.5 and 6.3 Hz), 7.38 (dd, 2H, J = 7.5 and 7.1 Hz), 7.33 (d, 1H, J = 7.1 Hz), 7.31–7.22 (m, 5H), 7.05 (d, 1H, J = 7.1 Hz), 5.10 (s, 2H), 3.94 (s, 3H), 1.96 (s, 3H) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ = 148.3 (C_q), 147.7 (C_q), 147.5 (C_q), 138.0 (C_q), 136.3 (C_q), 128.6 (2 \times CH), 128.1 (3 \times CH), 127.4 (2 \times CH), 126.9 (CH), 125.7 (2 \times CH), 119.9 (CH), 112.2 (CH), 112.0 (C_q), 77.1 (C_q), 71.2 (CH_2), 56.3 (CH_3), 29.9 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3511, 2934, 1598, 1497, 1370, 1253, 1154, 1025, 763, 699 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{22}\text{H}_{20}^{79}\text{BrO}_2]^+ = [(\text{M} + \text{H}) - \text{H}_2\text{O}]^+$ 395.0641, found 395.0637.

1-(2-Bromo-3,4,5-trimethoxyphenyl)-1-phenylethanol (4g). This compound was prepared according to the GP-1 and isolated as brown color solid 92% yield (385 mg): mp 68–69 $^\circ\text{C}$; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ = 7.38–7.28 (m, 5H), 7.25 (s, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 3.82 (s, 3H), 3.47 (br. s, 1H), 1.95 (s, 3H) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ = 152.0 (C_q), 151.4 (C_q), 147.4 (C_q), 142.2 (C_q), 140.8 (C_q), 128.1 (2 \times CH), 126.9 (CH), 125.5 (2 \times CH), 109.0 (C_q), 107.8 (CH), 77.5 (C_q), 61.0 (CH_3), 60.9 (CH_3), 56.2 (CH_3), 29.9 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3516, 2945, 1588, 1487, 1360, 1251, 1158, 1024, 754, 686 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{17}\text{H}_{18}^{79}\text{BrO}_3]^+ = [(\text{M} + \text{H}) - \text{H}_2\text{O}]^+$ 349.0434, found 349.0430.

1-(2-Bromophenyl)-1-(3-methoxyphenyl)ethanol (4h). This compound was prepared according to the GP-1 and isolated as colorless viscous liquid 94% yield (397 mg): $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ = 7.78 (dd, 1H, J = 7.9 and 1.1 Hz), 7.53 (d, 1H, J = 7.9 Hz), 7.38 (dd, 1H, J = 7.6 and 7.5 Hz), 7.24–7.10 (m, 2H), 6.88 (s, 1H), 6.78 (d, 2H, J = 8.6 Hz), 3.76 (s, 3H), 3.54 (br. s, 1H), 1.94 (s, 3H) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ = 159.5 (C_q), 149.5 (C_q), 144.7 (C_q), 134.8 (CH), 129.1 (2 \times CH), 128.4 (CH), 127.3 (CH), 122.4 (C_q), 118.0 (CH), 111.8 (CH), 111.7 (CH), 77.4 (C_q), 55.1 (CH_3), 30.3 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3453, 2937, 1582, 1429, 1249, 1129, 1037, 754, 698 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{15}\text{H}_{14}^{79}\text{BrO}]^+ = [(\text{M} + \text{H}) - \text{H}_2\text{O}]^+$ 289.0223, found 289.0223.

1-(2-Bromo-5-methoxyphenyl)-1-(3-methoxyphenyl)ethanol (4i). This compound was prepared according to the GP-1 and isolated as pale yellow color viscous liquid 95% yield (399 mg): $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ = 7.40 (d, 1H, J = 8.7 Hz), 7.37 (d, 1H, J = 3.0 Hz), 7.19 (dd, 1H, J = 8.0 and 8.0 Hz), 6.89 (dd, 1H, J = 2.0 and 1.9 Hz), 6.85–6.74 (m, 2H), 6.70 (dd, 1H, J = 8.7 and 3.0 Hz), 3.84 (s, 3H), 3.76 (s, 3H), 3.45 (br. s, 1H), 1.92 (s, 3H) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ = 159.5 (C_q), 158.8 (C_q), 149.1 (C_q), 145.9 (C_q), 135.4 (CH), 129.1 (CH), 118.1 (CH), 115.4 (CH), 113.6 (CH), 112.5 (C_q), 112.0 (CH), 111.8 (CH), 77.3 (C_q), 55.5 (CH_3), 55.2 (CH_3), 30.0 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3472, 2937, 1584, 1462, 1234, 1159, 1036, 755, 700 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{16}\text{H}_{16}^{79}\text{BrO}_2]^+ = [(\text{M} + \text{H}) - \text{H}_2\text{O}]^+$ 319.0328, found 319.0329.

1-(2-Bromo-4,5-dimethoxyphenyl)-1-(3-methoxyphenyl)ethanol (4j). This compound was prepared according to the GP-1 and isolated as yellow color solid 96% yield (402 mg): mp 72–74 $^\circ\text{C}$; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ = 7.35 (s, 1H), 7.20 (dd, 1H, J = 8.0 and 7.9 Hz), 6.99 (s, 1H), 6.88 (dd, 1H, J = 2.0 and 2.0 Hz), 6.82 (d, 1H, J = 7.6 Hz), 6.77 (dd, 1H, J = 8.0 and 2.0 Hz), 3.92 (s, 3H), 3.85 (s, 3H), 3.76 (s, 3H), 3.29 (br. s, 1H), 1.93 (s, 3H) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ = 159.5 (C_q), 149.4 (C_q), 148.5 (C_q), 147.7 (C_q), 137.4 (C_q), 129.1 (CH), 118.2 (CH), 117.5 (CH), 112.3 (C_q), 112.0 (CH), 111.7 (CH), 111.6 (CH), 77.0 (C_q), 56.1 (2 \times CH_3), 55.2 (CH_3), 29.9 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3465, 2937, 1584, 1461, 1232, 1153, 1032, 751, 646 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{17}\text{H}_{17}^{79}\text{BrO}_3]^+ = [\text{M} - \text{H}_2\text{O}]^+$ 348.0356, found 348.0354.

1-(6-Bromo-1,3-benzodioxol-5-yl)-1-(3-methoxyphenyl)ethanol (4k). This compound was prepared according to the GP-1 and isolated as white color solid 96% yield (405 mg): mp 74–76 $^\circ\text{C}$; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ = 7.32 (s, 1H), 7.19 (dd, 1H, J = 8.0

and 7.9 Hz), 6.97 (s, 1H), 6.88 (dd, 1H, J = 2.3 and 2.0 Hz), 6.81 (d, 1H, J = 7.8 Hz), 6.77 (dd, 1H, J = 8.0 and 2.5 Hz), 6.01 (d, 2H, J = 1.4 Hz), 3.77 (s, 3H), 3.44 (br. s, 1H), 1.88 (s, 3H) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ = 159.5 (C_q), 149.6 (C_q), 147.4 (C_q), 147.2 (C_q), 138.7 (C_q), 129.2 (CH), 118.1 (CH), 114.7 (CH), 113.0 (C_q), 111.9 (CH), 111.8 (CH), 108.8 (CH), 102.0 (CH_2), 77.2 (C_q), 55.2 (CH_3), 30.5 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3545, 2898, 1583, 1473, 1230, 1100, 1031, 928, 863, 701, 634 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{16}\text{H}_{14}^{79}\text{BrO}_3]^+ = [(\text{M} + \text{H}) - \text{H}_2\text{O}]^+$ 333.0121, found 333.0127.

1-[5-(Benzyloxy)-2-bromo-4-methoxyphenyl]-1-(3-methoxyphenyl)ethanol (4l). This compound was prepared according to the GP-1 and isolated as yellow color viscous liquid 96% yield (402 mg): $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ = 7.44 (d, 2H, J = 7.0 Hz), 7.39 (s, 1H), 7.38 (dd, 2H, J = 7.5 and 7.0 Hz), 7.33 (d, 1H, J = 7.0 Hz), 7.21 (dd, 1H, J = 7.9 and 7.9 Hz), 7.06 (s, 1H), 6.89 (dd, 1H, J = 2.0 and 2.0 Hz), 6.83 (d, 1H, J = 7.7 Hz), 6.78 (dd, 1H, J = 8.0 and 2.3 Hz), 5.10 (s, 2H), 3.93 (s, 3H), 3.77 (s, 3H), 3.32 (br. s, 1H), 1.94 (s, 3H) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ = 159.4 (C_q), 149.4 (C_q), 148.3 (C_q), 147.7 (C_q), 137.8 (C_q), 136.3 (C_q), 129.1 (CH), 128.6 (2 \times CH), 128.0 (CH), 127.4 (2 \times CH), 119.9 (CH), 118.1 (CH), 112.2 (CH), 112.1 (C_q), 112.0 (CH), 111.7 (CH), 77.0 (C_q), 71.2 (CH₂), 56.2 (CH_3), 55.1 (CH_3), 29.9 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3446, 2937, 1597, 1495, 1369, 1249, 1152, 1025, 735, 697 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{23}\text{H}_{22}^{79}\text{BrO}_3]^+ = [(\text{M} + \text{H}) - \text{H}_2\text{O}]^+$ 425.0747, found 425.0757.

1-[4-(Benzyloxy)-2-bromo-5-methoxyphenyl]-1-(3-methoxyphenyl)ethanol (4m). This compound was prepared according to the GP-1 and isolated as pale yellow color viscous liquid 97% yield (405 mg): $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ = 7.44 (d, 2H, J = 7.0 Hz), 7.38 (dd, 3H, J = 7.5 and 6.9 Hz), 7.32 (d, 1H, J = 7.0 Hz), 7.21 (dd, 1H, J = 8.0 and 7.9 Hz), 7.06 (s, 1H), 6.90 (s, 1H), 6.83 (d, 1H, J = 7.6 Hz), 6.78 (dd, 1H, J = 8.0 and 2.5 Hz), 5.09 (s, 2H), 3.92 (s, 3H), 3.76 (s, 3H), 3.52 (br. s, 1H), 1.95 (s, 3H) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ = 159.4 (C_q), 149.3 (C_q), 148.3 (C_q), 147.7 (C_q), 137.9 (C_q), 136.3 (C_q), 129.1 (CH), 128.6 (2 \times CH), 128.1 (CH), 127.4 (2 \times CH), 119.9 (CH), 118.2 (CH), 112.3 (CH), 112.1 (C_q), 112.0 (CH), 111.8 (CH), 77.0 (C_q), 71.2 (CH₂), 56.2 (CH_3), 55.1 (CH_3), 29.9 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3443, 2934, 1598, 1497, 1370, 1253, 1154, 1025, 763, 699 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{23}\text{H}_{22}^{79}\text{BrO}_3]^+ = [(\text{M} + \text{H}) - \text{H}_2\text{O}]^+$ 425.0747, found 425.0755.

1-(2-Bromophenyl)-1-thien-2-ylethanol (4n). This compound was prepared according to the GP-1 and isolated as black color viscous liquid 97% yield (412 mg): $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ = 7.83 (dd, 1H, J = 7.8 and 2.0 Hz), 7.56 (dd, 1H, J = 7.8 and 1.5 Hz), 7.37 (ddd, 1H, J = 8.8, 7.8, and 1.5 Hz), 7.23 (dd, 1H, J = 4.9 and 1.5 Hz), 7.17 (ddd, 1H, J = 8.8, 7.8, and 1.5 Hz), 6.91 (dd, 1H, J = 4.9 and 3.4 Hz), 6.73 (dd, 1H, J = 3.4 and 1.5 Hz), 3.39 (br. s, 1H), 2.10 (s, 3H) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ = 152.5 (C_q), 144.6 (C_q), 134.9 (CH), 129.2 (CH), 127.9 (CH), 127.3 (CH), 126.6 (CH), 124.7 (CH), 124.4 (CH), 122.1 (C_q), 75.2 (C_q), 30.2 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3456, 2933, 1595, 1498, 1363, 1247, 1151, 1023, 733, 692 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{12}\text{H}_{10}^{79}\text{BrS}]^+ = [(\text{M} + \text{H}) - \text{H}_2\text{O}]^+$ 264.9681, found 264.9679.

1-(2-Bromo-5-methoxyphenyl)-1-thien-2-ylethanol (4o). This compound was prepared according to the GP-1 and isolated as yellow color viscous liquid 93% yield (410 mg): $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ = 7.47–7.37 (m, 2H), 7.22 (dd, 1H, J = 4.9 and 1.0 Hz), 6.90 (dd, 1H, J = 4.9 and 3.4 Hz), 6.75 (dd, 1H, J = 3.4 and 1.0 Hz), 6.71 (dd, 1H, J = 8.8 and 3.4 Hz), 3.81 (s, 3H), 3.34 (br. s, 1H), 2.07 (s, 3H) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ = 158.7 (C_q), 152.0 (C_q), 145.8 (C_q), 135.3 (CH), 126.5 (CH), 124.8 (CH), 124.6 (CH), 114.5 (CH), 113.9 (CH), 112.2 (C_q), 74.9 (C_q), 55.4 (CH_3), 29.7 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3441, 2933, 1595, 1494, 1368, 1247, 1153, 1024, 738, 692 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{13}\text{H}_{12}^{79}\text{BrOS}]^+ = [(\text{M} + \text{H}) - \text{H}_2\text{O}]^+$ 294.9787, found 294.9790.

1-(2-Bromo-4,5-dimethoxyphenyl)-1-thien-2-ylethanol (4p). This compound was prepared according to the GP-1 and isolated as

black color semisolid 95% yield (400 mg): ^1H NMR (CDCl_3 , 400 MHz) δ = 7.42 (s, 1H), 7.20 (d, 1H, J = 4.9 Hz), 6.99 (s, 1H), 6.89 (dd, 1H, J = 4.9 and 3.9 Hz), 6.79 (d, 1H, J = 3.4 Hz), 3.88 (s, 3H), 3.84 (s, 3H), 3.19 (br. s, 1H), 2.07 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ = 152.3 (C_q), 148.4 (C_q), 147.6 (C_q), 137.2 (C_q), 126.5 (CH), 124.8 (CH), 124.6 (CH), 117.4 (CH), 111.9 (C_q), 111.0 (CH), 74.5 (C_q), 56.0 (CH_3), 55.9 (CH_3), 29.7 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3441, 2933, 1596, 1495, 1362, 1249, 1151, 1024, 735, 697 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{14}\text{H}_{15}^{79}\text{BrO}_3\text{S}]^+ = [\text{M}]^+ 343.9900$, found 343.9887.

(2-Bromophenyl)(diphenyl)methanol (4q). This compound was prepared according to the GP-1 and isolated as colorless viscous liquid 91% yield (460 mg): ^1H NMR (CDCl_3 , 400 MHz) δ = 7.38 (dd, 2H, J = 8.3 and 1.5 Hz), 7.34–7.18 (m, 12H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ = 145.5 ($2 \times \text{C}_q$), 145.0 (C_q), 134.8 (CH), 131.9 (CH), 129.2 (CH), 127.9 ($8 \times \text{CH}$), 127.3 ($2 \times \text{CH}$), 126.8 (CH), 122.9 (C_q), 83.1 (C_q) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3544, 3057, 1583, 1446, 1338, 1265, 1158, 1023, 890, 755, 698 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{19}\text{H}_{14}^{79}\text{Br}]^+ = [(\text{M} + \text{H}) - \text{H}_2\text{O}]^+ 321.0273$, found 321.0277.

(2-Bromo-5-methoxyphenyl)(diphenyl)methanol (4r). This compound was prepared according to the GP-1 and isolated as colorless viscous liquid 61% yield (310 mg): ^1H NMR (CDCl_3 , 400 MHz) δ = 7.45 (d, 1H, J = 8.8 Hz), 7.33–7.17 (m, 10H), 6.65 (dd, 1H, J = 8.8 and 2.9 Hz), 6.25 (d, 1H, J = 2.9 Hz), 4.53 (s, 1H), 3.55 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ = 158.1 (C_q), 146.1 (C_q), 145.3 ($2 \times \text{C}_q$), 135.3 (CH), 127.9 ($4 \times \text{CH}$), 127.8 ($4 \times \text{CH}$), 127.3 ($2 \times \text{CH}$), 119.0 (CH), 113.6 (CH), 113.1 (C_q), 83.0 (C_q), 55.1 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3542, 3053, 1573, 1443, 1358, 1265, 1155, 1024, 893, 752, 695 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{20}\text{H}_{16}^{79}\text{BrO}]^+ = [(\text{M} + \text{H}) - \text{H}_2\text{O}]^+ 351.0379$, found 351.0383.

(2-Bromo-4,5-dimethoxyphenyl)(diphenyl)methanol (4s). This compound was prepared according to the GP-1 and isolated as colorless viscous liquid 81% yield (402 mg): ^1H NMR (CDCl_3 , 400 MHz) δ = 7.35–7.18 (m, 10H), 7.02 (s, 1H), 6.19 (s, 1H), 4.39 (s, 1H), 3.82 (s, 3H), 3.42 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ = 148.5 (C_q), 147.0 (C_q), 145.7 ($2 \times \text{C}_q$), 137.4 (C_q), 127.9 ($8 \times \text{CH}$), 127.3 ($2 \times \text{CH}$), 117.4 (CH), 115.3 (CH), 112.9 (C_q), 82.9 (C_q), 56.1 (CH_3), 55.4 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3545, 3059, 2933, 1597, 1500, 1442, 1369, 1253, 1149, 1019, 730, 699 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{21}\text{H}_{18}^{79}\text{BrO}_2]^+ = [(\text{M} + \text{H}) - \text{H}_2\text{O}]^+ 381.0485$, found 381.0482.

1-(2-Bromo-5-methoxyphenyl)-1-phenylprop-2-yn-1-ol (4t). This compound was prepared according to the GP-4 and isolated as pale yellow color crystalline solid 63% yield (275 mg): mp 97–98 °C; ^1H NMR (CDCl_3 , 400 MHz) δ = 7.64 (d, 1H, J = 2.9 Hz), 7.50 (dd, 2H, J = 7.8 and 1.5 Hz), 7.43 (d, 1H, J = 8.8 Hz), 7.38–7.28 (m, 3H), 6.75 (dd, 1H, J = 8.8 and 2.9 Hz), 3.82 (s, 3H), 3.38 (br. s, 1H), 2.88 (s, 1H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ = 158.7 (C_q), 142.5 (C_q), 142.4 (C_q), 135.4 (CH), 128.3 ($2 \times \text{CH}$), 128.1 (CH), 126.7 ($2 \times \text{CH}$), 114.9 (CH), 114.8 (CH), 111.9 (C_q), 84.1 (C_q), 76.2 (CH), 74.5 (C_q), 55.5 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3436, 3286, 1591, 1463, 1290, 1236, 1019, 815, 767, 698 cm^{-1} .

2-(2-Bromophenyl)-1-phenylpropan-2-ol (4u). This compound was prepared according to the GP-1 and isolated as colorless viscous liquid 83% yield (351 mg): ^1H NMR (CDCl_3 , 400 MHz) δ = 7.63 (d, 1H, J = 7.8 Hz), 7.47 (d, 1H, J = 7.8 Hz), 7.23–7.13 (m, 4H), 7.08 (ddd, 1H, J = 9.3, 7.8, and 1.5 Hz), 7.04–6.96 (m, 2H), 3.66 (d, 1H, J = 13.2 Hz), 3.26 (d, 1H, J = 13.2 Hz), 2.44 (br. s, 1H), 1.75 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ = 144.9 (C_q), 136.7 (C_q), 135.0 (CH), 130.5 ($2 \times \text{CH}$), 129.7 (C_q), 128.5 (CH), 128.3 (CH), 128.1 ($2 \times \text{CH}$), 127.4 (CH), 126.6 (CH), 75.5 (C_q), 46.0 (CH₂), 27.3 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3456, 2932, 1561, 1462, 1283, 1033, 762, 694 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{15}\text{H}_{14}^{79}\text{Br}]^+ = [(\text{M} + \text{H}) - \text{H}_2\text{O}]^+ 273.0273$, found 273.0271.

2-(2-Bromo-5-methoxyphenyl)-1-phenylpropan-2-ol (4v). This compound was prepared according to the GP-1 and isolated as colorless viscous liquid 87% yield (366 mg): ^1H NMR (CDCl_3 ,

400 MHz) δ = 7.51 (d, 1H, J = 8.8 Hz), 7.24–7.14 (m, 3H), 7.11 (d, 1H, J = 2.9 Hz), 7.05 (dd, 2H, J = 7.3 and 2.9 Hz), 6.64 (dd, 1H, J = 8.8 and 3.4 Hz), 3.70 (s, 3H), 3.67 (d, 1H, J = 13.7 Hz), 3.26 (d, 1H, J = 13.7 Hz), 2.44 (br. s, 1H), 1.73 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ = 158.8 (C_q), 146.3 (C_q), 136.6 (C_q), 135.5 (CH), 130.4 ($2 \times \text{CH}$), 128.1 ($2 \times \text{CH}$), 126.6 (CH), 114.5 (CH), 113.7 (CH), 110.4 (C_q), 75.3 (C_q), 55.3 (CH_3), 45.8 (CH₂), 27.1 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3454, 2939, 1560, 1461, 1289, 1037, 762, 699 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{16}\text{H}_{16}^{79}\text{BrO}]^+ = [(\text{M} + \text{H}) - \text{H}_2\text{O}]^+ 303.0379$, found 303.0370.

2-(2-Bromophenyl)pent-4-en-2-ol (4aa). This compound was prepared according to the GP-4 and isolated as colorless viscous liquid 95% yield (460 mg): ^1H NMR (CDCl_3 , 400 MHz) δ = 7.69 (dd, 1H, J = 7.9 and 1.6 Hz), 7.57 (dd, 1H, J = 7.9 and 1.1 Hz), 7.29 (ddd, 1H, J = 8.0, 6.9, and 1.1 Hz), 7.08 (ddd, 1H, J = 9.2, 7.4, and 1.6 Hz), 5.65–5.45 (m, 1H), 5.13 (d, 1H, J = 17.1 Hz), 5.08 (d, 1H, J = 10.2 Hz), 3.27 (dd, 1H, J = 14.0 and 6.4 Hz), 2.64 (m, 2H), 1.72 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ = 145.0 (C_q), 135.0 (CH), 133.6 (CH), 128.5 (CH), 128.2 (CH), 127.4 (CH), 119.9 (C_q), 119.3 (CH₂), 74.6 (C_q), 45.0 (CH₂), 27.3 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3443, 2932, 1591, 1490, 1367, 1240, 1151, 1024, 735, 697 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{11}\text{H}_{12}^{79}\text{Br}]^+ = [(\text{M} + \text{H}) - \text{H}_2\text{O}]^+ 223.0117$, found 223.0117.

1-(2-Bromophenyl)-1-phenylbut-3-en-1-ol (4ab). This compound was prepared according to the GP-4 and isolated as colorless viscous liquid 89% yield (413 mg): ^1H NMR (CDCl_3 , 400 MHz) δ = 7.80 (dd, 1H, J = 7.9 and 1.5 Hz), 7.49 (d, 1H, J = 7.9 Hz), 7.35 (dd, 1H, J = 7.9 and 7.4 Hz), 7.32–7.18 (m, 5H), 7.12 (ddd, 1H, J = 7.7, 7.5, and 1.4 Hz), 5.78–5.58 (m, 1H), 5.11 (dd, 1H, J = 17.2 and 1.4 Hz), 5.06 (d, 1H, J = 10.2 Hz), 3.42 (dd, 1H, J = 14.1 and 6.6 Hz), 3.22 (br. s, 1H), 2.99 (dd, 1H, J = 14.1 and 7.3 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ = 145.5 (C_q), 143.9 (C_q), 135.0 (CH), 133.6 (CH), 129.1 (CH), 128.9 (CH), 128.0 ($2 \times \text{CH}$), 127.1 (CH), 127.0 (CH), 126.5 ($2 \times \text{CH}$), 122.1 (C_q), 118.9 (CH₂), 78.3 (C_q), 44.8 (CH₂) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3440, 2942, 1581, 1450, 1360, 1230, 1156, 1021, 739, 689 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{16}\text{H}_{14}^{79}\text{Br}]^+ = [(\text{M} + \text{H}) - \text{H}_2\text{O}]^+ 285.0273$, found 285.0280.

2-(2-Bromo-5-methoxyphenyl)pent-4-en-2-ol (4ac). This compound was prepared according to the GP-4 and isolated as colorless viscous liquid 94% yield (445 mg): ^1H NMR (CDCl_3 , 400 MHz) δ = 7.43 (d, 1H, J = 8.6 Hz), 7.29 (d, 1H, J = 3.0 Hz), 6.62 (dd, 1H, J = 8.6, and 3.0 Hz), 5.65–5.45 (m, 1H), 5.12 (d, 1H, J = 17.1 Hz), 5.07 (d, 1H, J = 10.0 Hz), 3.76 (s, 3H), 3.27 (dd, 1H, J = 14.0 and 6.3 Hz), 2.67 (br. s, 1H), 2.60 (dd, 1H, J = 14.0 and 8.5 Hz), 1.69 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ = 158.8 (C_q), 146.3 (C_q), 135.5 (CH), 133.5 (CH), 119.2 (CH₂), 114.4 (CH), 113.5 (CH), 110.0 (C_q), 74.4 (C_q), 55.3 (CH₃), 44.8 (CH₂), 27.1 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3442, 2932, 1591, 1493, 1366, 1242, 1150, 1025, 735, 698 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{12}\text{H}_{14}^{79}\text{BrO}]^+ = [(\text{M} + \text{H}) - \text{H}_2\text{O}]^+ 253.0223$, found 253.0220.

1-(2-Bromo-5-methoxyphenyl)-1-phenylbut-3-en-1-ol (4ad). This compound was prepared according to the GP-4 and isolated as red color viscous liquid 91% yield (416 mg): ^1H NMR (CDCl_3 , 400 MHz) δ = 7.40 (d, 1H, J = 3.0 Hz), 7.36 (d, 1H, J = 8.7 Hz), 7.30–7.15 (m, 5H), 6.65 (dd, 1H, J = 8.7 and 3.1 Hz), 5.78–5.60 (m, 1H), 5.11 (dd, 1H, J = 17.1 and 1.6 Hz), 5.05 (dd, 1H, J = 10.2 and 1.6 Hz), 3.79 (s, 3H), 3.42 (dd, 1H, J = 14.2 and 6.6 Hz), 3.17 (br. s, 1H), 2.99 (dd, 1H, J = 14.2 and 7.3 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ = 158.5 (C_q), 145.2 (C_q), 144.9 (C_q), 135.5 (CH), 133.6 (CH), 128.0 ($2 \times \text{CH}$), 127.1 (CH), 126.5 ($2 \times \text{CH}$), 118.8 (CH₂), 115.9 (CH), 113.7 (CH), 112.2 (C_q), 78.1 (C_q), 55.4 (CH₃), 44.4 (CH₂) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3435, 2930, 1581, 1496, 1366, 1230, 1156, 1029, 734, 686 cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{17}\text{H}_{16}^{79}\text{BrO}]^+ = [(\text{M} + \text{H}) - \text{H}_2\text{O}]^+ 315.0379$, found 315.0388.

2-(2-Bromo-4,5-dimethoxyphenyl)pent-4-en-2-ol (4ae). This compound was prepared according to the GP-4 and isolated as colorless viscous liquid 92% yield (427 mg): ^1H NMR (CDCl_3 , 400 MHz) δ = 7.32 (s, 1H), 7.05 (s, 1H), 5.70–5.50 (m, 1H), 5.17 (d, 1H,

$J = 17.4$ Hz), 5.13 (d, 1H, $J = 10.2$ Hz), 3.89 (s, 3H), 3.88 (s, 3H), 3.31 (dd, 1H, $J = 14.1$ and 6.3 Hz), 2.62 (dd, 1H, $J = 14.1$ and 8.5 Hz), 2.53 (br. s, 1H), 1.72 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 147.9$ (C_q), 147.8 (C_q), 137.6 (C_q), 133.7 (CH), 119.4 (CH_2), 117.7 (CH), 111.3 (CH), 109.4 (C_q), 74.3 (C_q), 56.1 (CH_3), 55.9 (CH_3), 45.1 (CH_2), 27.5 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) $\nu_{\text{max}} = 3423, 2938, 1583, 1428, 1321, 1243, 1151, 1035, 745, 696$ cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{13}\text{H}_{16}^{79}\text{BrO}_2]^+ = [(\text{M} + \text{H}) - \text{H}_2\text{O}]^+$ 283.0328, found 283.0323.

[1-(2-Bromo-5-methoxyphenyl)-1-methylethoxy](trimethyl)silane (11a). This compound was prepared according to the GP-5 and isolated as 74% yield (383 mg) as colorless viscous liquid: ^1H NMR (CDCl_3 , 400 MHz) $\delta = 7.44$ (d, 1H, $J = 8.3$ Hz), 7.32 (d, 1H, $J = 3.4$ Hz), 6.61 (dd, 1H, $J = 8.3$ and 3.4 Hz), 3.79 (s, 3H), 1.75 (s, 3H), 0.16 (s, 9H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 158.6$ (C_q), 148.5 (C_q), 135.7 (CH), 114.0 (CH), 113.1 (CH), 110.6 (C_q), 76.3 (C_q), 55.2 (CH_3), 29.8 ($2 \times \text{CH}_3$), 2.4 ($3 \times \text{CH}_3$) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) $\nu_{\text{max}} = 2950, 2874, 1532, 1454, 1372, 1230, 1128, 1022, 831, 750, 694$ cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{13}\text{H}_{19}^{81}\text{BrSiKO}]^+ = [(\text{M} + \text{K}) - \text{H}_2\text{O}]^+$ 339.0001, found 339.0011.

[1-(6-Bromo-1,3-benzodioxol-5-yl)-1-methylethoxy](trimethyl)silane (11b). This compound was prepared according to the GP-5 and isolated as white color solid 76% yield (388 mg): mp 47–48 °C; ^1H NMR (CDCl_3 , 400 MHz) $\delta = 7.23$ (s, 1H), 7.02 (s, 1H), 5.95 (s, 2H), 1.72 (s, 6H), 0.14 (s, 9H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 147.2$ (C_q), 146.8 (C_q), 141.3 (C_q), 115.0 (CH), 110.7 (C_q), 108.1 (CH), 101.8 (CH_2), 76.4 (C_q), 30.2 ($2 \times \text{CH}_3$), 2.6 ($3 \times \text{CH}_3$) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) $\nu_{\text{max}} = 2957, 2894, 1502, 1474, 1375, 1231, 1126, 1032, 832, 752, 690$ cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{13}\text{H}_{19}^{79}\text{BrSiNaO}_3]^+ = [(\text{M} + \text{Na})]^+$ 353.0179, found 353.0172.

6-Methyl-6-phenyl-6H-benzo[*c*]chromene (5a). This compound was prepared according to the GP-6 and isolated as white color solid 79% yield (54 mg): mp 120–122 °C, byproduct ketone 7a (20 mg, 68%) as colorless oil; ^1H NMR (CDCl_3 , 400 MHz) $\delta = 7.74$ (dd, 1H, $J = 7.8$ and 1.0 Hz), 7.65 (dd, 1H, $J = 7.8$ and 1.5 Hz), 7.41 (ddd, 1H, $J = 8.8, 7.4$, and 1.5 Hz), 7.35 (dd, 1H, $J = 7.6$ and 1.2 Hz), 7.31 (dd, 2H, $J = 8.8$ and 1.5 Hz), 7.27 (dd, 1H, $J = 7.6$ and 1.2 Hz), 7.24–7.12 (m, 4H), 7.02 (dd, 1H, $J = 8.0$ and 1.0 Hz), 6.95 (ddd, 1H, $J = 8.8, 7.8$, and 1.0 Hz), 2.04 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 152.9$ (C_q), 144.8 (C_q), 137.5 (C_q), 129.5 (C_q), 129.4 (CH), 128.1 (CH), 127.9 ($2 \times \text{CH}$), 127.5 (CH), 127.3 (CH), 126.5 ($2 \times \text{CH}$), 125.6 (CH), 122.9 (CH), 122.8 (C_q), 122.5 (CH), 121.7 (CH), 118.2 (CH), 81.0 (C_q), 28.4 (C_q) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) $\nu_{\text{max}} = 3060, 2925, 2852, 1591, 1438, 1371, 1245, 1137, 1066, 928, 755, 698$ cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{20}\text{H}_{17}\text{O}]^+ = [(\text{M} + \text{H})]^+$ 273.1274, found 273.1262.

3,8-Dimethoxy-6-methyl-6-phenyl-6H-benzo[*c*]chromene (5b). This compound was prepared according to the GP-6 and isolated as yellow color solid 81% yield (68 mg): mp 130–132 °C, byproduct ketone 7a (19 mg, 63%) as colorless oil; ^1H NMR (CDCl_3 , 400 MHz) $\delta = 7.59$ (d, 1H, $J = 8.5$ Hz), 7.48 (d, 1H, $J = 8.5$ Hz), 7.35 (d, 2H, $J = 7.8$ Hz), 7.29–7.14 (m, 3H), 6.93 (dd, 1H, $J = 8.7$ and 2.6 Hz), 6.78 (d, 1H, $J = 2.0$ Hz), 6.59 (d, 1H, $J = 2.0$ Hz), 6.52 (dd, 1H, $J = 8.5$ and 2.6 Hz), 3.82 (s, 3H), 3.77 (s, 3H), 2.01 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 160.2$ (C_q), 158.5 (C_q), 153.3 (C_q), 144.7 (C_q), 138.0 (C_q), 128.0 ($2 \times \text{CH}$), 127.4 (CH), 126.5 ($2 \times \text{CH}$), 123.2 (CH), 123.1 (CH), 122.8 (C_q), 115.9 (C_q), 113.0 (CH), 112.0 (CH), 108.3 (CH), 103.2 (CH), 81.4 (C_q), 55.4 (CH_3), 55.3 (CH_3), 28.3 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) $\nu_{\text{max}} = 3061, 2928, 2853, 1592, 1438, 1371, 1246, 1156, 1067, 929, 757, 698$ cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{22}\text{H}_{21}\text{O}_3]^+ = [(\text{M} + \text{H})]^+$ 333.1485, found 333.1482.

2,3,8,9-Tetramethoxy-6-methyl-6-phenyl-6H-benzo[*c*]chromene (5c). This compound was prepared according to the GP-6 and isolated as brown color solid 81% yield (80 mg): mp 158–160 °C, byproduct ketone 7a (22 mg, 72%) as colorless oil; ^1H NMR (CDCl_3 , 400 MHz) $\delta = 7.30$ (d, 2H, $J = 7.8$ Hz), 7.22 (dd, 2H, $J = 7.8$ and 6.9 Hz), 7.18 (d, 1H, $J = 6.9$ Hz), 7.08 (s, 1H), 7.00 (s, 1H), 6.73 (s, 1H), 6.57 (s, 1H), 3.98 (s, 3H), 3.87 (s, 6H), 3.85 (s, 3H), 1.99

(s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 149.9$ (C_q), 149.0 (C_q), 148.0 (C_q), 147.0 (C_q), 145.1 (C_q), 144.1 (C_q), 129.2 (C_q), 127.9 ($2 \times \text{CH}$), 127.4 (CH), 126.4 ($2 \times \text{CH}$), 123.0 (C_q), 114.5 (C_q), 109.3 (CH), 105.9 (CH), 105.1 (CH), 102.1 (CH), 80.9 (C_q), 56.7 (CH_3), 56.2 ($2 \times \text{CH}_3$), 55.9 (CH_3), 28.2 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) $\nu_{\text{max}} = 2933, 2833, 1504, 1443, 1332, 1266, 1139, 1035, 910, 861, 770$ cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{24}\text{H}_{23}\text{O}_5]^+ = [(\text{M} + \text{H})]^+$ 393.1697, found 393.1689.

6-Methyl-6-phenyl-6H-[1,3]benzodioxolo[5,6-*c*][1,3]dioxolo[4,5-*g*]chromene (5d). This compound was prepared according to the GP-6 and isolated as colorless oil 73% yield (66 mg), byproduct ketone 7a (18 mg, 61%) as colorless oil: ^1H NMR (CDCl_3 , 400 MHz) $\delta = 7.27$ (dd, 2H, $J = 7.8$ and 1.0 Hz), 7.21 (dd, 2H, $J = 7.8$ and 6.8 Hz), 7.18 (d, 1H, $J = 6.9$ Hz), 7.01 (s, 1H), 6.90 (s, 1H), 6.75 (s, 1H), 6.53 (s, 1H), 6.00 (d, 2H, $J = 1.6$ Hz), 5.88 (d, 1H, $J = 1.0$ Hz), 5.85 (d, 1H, $J = 1.0$ Hz), 1.94 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 147.7$ (C_q), 147.6 ($2 \times \text{C}_q$), 146.6 (C_q), 144.9 (C_q), 142.7 (C_q), 130.3 (C_q), 127.9 ($2 \times \text{CH}$), 127.4 (CH), 126.4 ($2 \times \text{CH}$), 124.6 (C_q), 116.0 (C_q), 106.2 (CH), 102.5 (CH), 102.0 (CH), 101.2 (CH_2), 101.1 (CH_2), 100.1 (CH), 81.2 (C_q), 28.4 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) $\nu_{\text{max}} = 2899, 1502, 1477, 1371, 1255, 1168, 1037, 935, 861, 770, 699$ cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{22}\text{H}_{17}\text{O}_5]^+ = [(\text{M} + \text{H})]^+$ 361.1071, found 361.1062.

3,8-Bis(benzyloxy)-2,9-dimethoxy-6-methyl-6-phenyl-6H-benzo[*c*]chromene (5e). This compound was prepared according to the GP-6 and isolated as colorless oil 76% yield (102 mg), byproduct ketone 7a (21 mg, 71%) as colorless oil: ^1H NMR (CDCl_3 , 400 MHz) $\delta = 7.46$ –7.26 (m, 11H), 7.20–7.05 (m, 5H), 7.02 (s, 1H), 6.74 (s, 1H), 6.59 (s, 1H), 5.18 (d, 1H, $J = 12.4$ Hz), 5.17 (d, 1H, $J = 12.4$ Hz), 5.13 (s, 2H), 3.99 (s, 3H), 3.87 (s, 3H), 1.84 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 149.8$ (C_q), 149.0 (C_q), 147.0 (C_q), 146.6 (C_q), 145.0 (C_q), 144.6 (C_q), 136.9 (C_q), 136.7 (C_q), 129.2 (C_q), 128.6 ($2 \times \text{CH}$), 128.5 ($2 \times \text{CH}$), 127.9 ($2 \times \text{CH}$), 127.8 (CH), 127.7 ($2 \times \text{CH}$), 127.5 ($2 \times \text{CH}$), 127.3 ($2 \times \text{CH}$), 127.1 (CH), 126.2 (CH), 123.4 (C_q), 115.0 (C_q), 113.0 (CH), 106.9 (CH), 105.7 (CH), 104.5 (CH), 80.8 (C_q), 71.5 (CH_2), 70.8 (CH_2), 57.0 (CH_3), 56.3 (CH_3), 28.4 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) $\nu_{\text{max}} = 3061, 2932, 1608, 1499, 1443, 1374, 1257, 1166, 1019, 905, 848, 737, 696$ cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{36}\text{H}_{32}\text{NaO}_5]^+ = [(\text{M} + \text{Na})]^+$ 567.2142, found 567.2123.

2,9-Bis(benzyloxy)-3,8-dimethoxy-6-methyl-6-phenyl-6H-benzo[*c*]chromene (5f). This compound was prepared according to the GP-6 and isolated as colorless oil 75% yield (104 mg), byproduct ketone 7a (18 mg, 61%) as colorless oil: ^1H NMR (CDCl_3 , 400 MHz) $\delta = 7.68$ (dd, 1H, $J = 8.4$ and 1.4 Hz), 7.65 (dd, 1H, $J = 8.4$ and 1.5 Hz), 7.53 (ddd, 1H, $J = 7.8, 7.5$, and 1.5 Hz), 7.50–7.26 (m, 10H), 7.16–7.09 (m, 2H), 7.08 (s, 1H), 7.02 (s, 1H), 6.73 (s, 1H), 6.59 (s, 1H), 5.18 (d, 1H, $J = 12.4$ Hz), 5.17 (d, 1H, $J = 12.4$ Hz), 5.13 (s, 2H), 3.99 (s, 3H), 3.86 (s, 3H), 1.84 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 149.9$ (C_q), 148.1 (C_q), 147.1 (C_q), 146.7 (C_q), 145.1 (C_q), 144.7 (C_q), 136.9 (C_q), 136.8 (C_q), 133.0 (C_q), 132.2 (CH), 132.1 (CH), 132.0 (CH), 128.6 (CH), 128.5 ($2 \times \text{CH}$), 127.9 (CH), 127.8 ($2 \times \text{CH}$), 127.5 ($2 \times \text{CH}$), 127.3 (C_q), 127.1 (CH), 126.2 (CH), 125.7 (C_q), 123.5 (C_q), 115.1 (C_q), 113.1 (CH), 107.0 (CH), 105.7 (CH), 104.5 (CH), 80.9 (C_q), 71.5 (CH_2), 70.8 (CH_2), 57.1 (CH_3), 56.3 (CH_3), 28.4 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) $\nu_{\text{max}} = 3061, 2932, 1500, 1458, 1377, 1261, 1199, 1031, 909, 857, 740, 698$ cm^{-1} ; HR-MS (ESI+) m/z calculated for $[\text{C}_{36}\text{H}_{33}\text{O}_5]^+ = [(\text{M} + \text{H})]^+$ 545.2323, found 545.2313.

6-(3-Methoxyphenyl)-6-methyl-6H-benzo[*c*]chromene (5h). This compound was prepared according to the GP-6 and isolated as colorless oil 72% yield (55 mg), byproduct ketone 7a 68% yield (25 mg) as colorless oil: ^1H NMR (CDCl_3 , 400 MHz) $\delta = 7.74$ (d, 1H, $J = 7.8$ Hz), 7.65 (dd, 1H, $J = 7.8$ and 1.1 Hz), 7.41 (ddd, 1H, $J = 7.7, 7.3$, and 1.1 Hz), 7.34 (dd, 1H, $J = 7.7$ and 7.3 Hz), 7.29 (d, 1H, $J = 7.5$ Hz), 7.20 (ddd, 1H, $J = 8.5, 8.0$, and 1.1 Hz), 7.13 (dd, 1H, $J = 8.0$ and 7.9 Hz), 7.04 (d, 1H, $J = 8.0$ Hz), 6.96 (dd, 1H, $J = 7.5$ and 7.5 Hz), 6.90 (s, 1H), 6.87 (d, 1H, $J = 8.5$ Hz), 6.70 (dd, 1H, $J = 8.0$ and 2.5 Hz), 3.70 (s, 3H), 2.03 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 159.2$ ($2 \times \text{C}_q$), 152.9 (C_q), 146.6 (C_q), 137.4 (C_q),

129.4 (CH), 128.8 (CH), 128.2 (CH), 127.5 (CH), 125.5 (CH), 122.9 (CH), 122.8 (C_q), 122.4 (CH), 121.8 (CH), 119.0 (CH), 118.2 (CH), 112.8 (CH), 112.4 (CH), 81.0 (C_q), 55.1 (CH₃), 28.5 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 3068, 2933, 1582, 1482, 1371, 1242, 1167, 1039, 928, 876, 726, 616 cm⁻¹; HR-MS (ESI+) m/z calculated for [C₂₁H₂₃NO]⁺ = [(M + NH₄) + (-H₂O)]⁺ 305.1774, found 305.1763.

3,8-Dimethoxy-6-(3-methoxyphenyl)-6-methyl-6H-benzo[c]-chromene (5i). This compound was prepared according to the GP-6 and isolated as red color solid 83% yield (76 mg): mp 74–76 °C, byproduct ketone **7b** 55% yield (20 mg) as colorless oil; ¹H NMR (CDCl₃, 400 MHz) δ = 7.57 (d, 1H, J = 8.3 Hz), 7.47 (d, 1H, J = 8.3 Hz), 7.27 (d, 1H, J = 8.3 Hz), 7.15 (d, 1H, J = 2.0 Hz), 7.12 (d, 1H, J = 7.8 Hz), 6.97–6.84 (m, 4H), 6.77 (d, 1H, J = 2.4 Hz), 6.71 (dd, 1H, J = 8.3 and 2.4 Hz), 6.57 (d, 1H, J = 2.4 Hz), 6.51 (dd, 1H, J = 8.8 and 2.4 Hz), 3.82 (s, 3H), 3.77 (s, 3H), 3.71 (s, 3H), 1.98 (s, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 160.2 (C_q), 159.2 (C_q), 158.5 (C_q), 153.3 (C_q), 146.4 (C_q), 137.8 (C_q), 128.9 (CH), 123.1 (CH), 123.0 (CH), 122.7 (C_q), 120.5 (CH), 119.0 (CH), 115.9 (C_q), 112.8 (CH), 112.4 (CH), 111.9 (CH), 109.6 (CH), 108.3 (CH), 103.1 (CH), 81.3 (C_q), 55.7 (CH₃), 55.4 (CH₃), 55.3 (CH₃), 55.1 (CH₃), 28.2 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 3038, 2937, 2830, 1605, 1489, 1375, 1253, 1194, 1036, 907, 852, 787, 695 cm⁻¹; HR-MS (ESI+) m/z calculated for [C₂₃H₂₃O₄]⁺ = [M + H]⁺ 363.1591, found 363.1577.

2,3,8,9-Tetramethoxy-6-(3-methoxyphenyl)-6-methyl-6H-benzo[c]chromene (5j). This compound was prepared according to the GP-6 and isolated as brown color viscous liquid 77% yield (82 mg), byproduct ketone **7b** 58% yield (21 mg) colorless oil: ¹H NMR (CDCl₃, 400 MHz) δ = 7.13 (dd, 1H, J = 8.2 and 8.2 Hz), 7.07 (s, 1H), 7.00 (s, 1H), 6.90–6.82 (m, 2H), 6.75 (s, 1H), 6.70 (dd, 1H, J = 8.2 and 2.5 Hz), 6.58 (s, 1H), 3.97 (s, 3H), 3.87 (s, 6H), 3.84 (s, 3H), 3.70 (s, 3H), 1.98 (s, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 159.1 (C_q), 149.8 (C_q), 149.0 (C_q), 148.0 (C_q), 146.9 (2 × C_q), 144.0 (C_q), 129.0 (C_q), 128.8 (CH), 122.9 (C_q), 118.9 (CH), 114.5 (C_q), 112.8 (CH), 112.2 (CH), 109.2 (CH), 105.9 (CH), 105.1 (CH), 102.1 (CH), 80.8 (C_q), 56.6 (CH₃), 56.1 (2 × CH₃), 55.9 (CH₃), 55.0 (CH₃), 28.3 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 2932, 2834, 1605, 1498, 1371, 1252, 1138, 1036, 908, 852, 730, 695 cm⁻¹; HR-MS (ESI+) m/z calculated for [C₂₅H₂₇O₆]⁺ = [M + H]⁺ 423.1802, found 423.1786.

6-(3-Methoxyphenyl)-6-methyl-6H-[1,3]benzodioxolo[5,6-c][1,3]dioxolo[4,5-g]chromene (5k). This compound was prepared according to the GP-6 and isolated as yellow color semisolid 87% yield (86 mg), byproduct ketone **7b** 57% yield (21 mg) colorless oil: ¹H NMR (CDCl₃, 400 MHz) δ = 7.13 (dd, 1H, J = 8.3 and 8.1 Hz), 7.01 (s, 1H), 6.91 (s, 1H), 6.87–6.80 (m, 2H), 6.76 (s, 1H), 6.71 (ddd, 1H, J = 8.3, 2.4, and 0.9 Hz), 6.54 (s, 1H), 5.99 (s, 2H), 5.88 (d, 1H, J = 1.4 Hz), 5.86 (d, 1H, J = 1.4 Hz), 3.72 (s, 3H), 1.94 (s, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 159.2 (C_q), 147.7 (C_q), 147.6 (2 × C_q), 146.7 (C_q), 146.6 (C_q), 142.7 (C_q), 130.2 (C_q), 128.8 (CH), 124.6 (C_q), 118.9 (CH), 116.0 (C_q), 112.9 (CH), 112.2 (CH), 106.2 (CH), 102.5 (CH), 102.0 (CH), 101.2 (CH₂), 101.0 (CH₂), 100.0 (CH), 81.1 (C_q), 55.1 (CH₃), 28.4 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 3030, 2932, 2835, 1604, 1499, 1371, 1253, 1194, 1036, 908, 852, 777, 695 cm⁻¹; HR-MS (ESI+) m/z calculated for [C₂₃H₁₈NaO₆]⁺ = [M + Na]⁺ 413.0996, found 413.0977.

3,8-Bis(benzyloxy)-2,9-dimethoxy-6-(3-methoxyphenyl)-6-methyl-6H-benzo[c]chromene (5l). This compound was prepared according to the GP-6 and isolated as red color viscous liquid 72% yield (104 mg), byproduct ketone **7b** 75% yield (28 mg) colorless oil: ¹H NMR (CDCl₃, 400 MHz) δ = 7.47–7.27 (m, 11H), 7.07 (s, 1H), 7.03 (s, 1H), 6.78 (dd, 1H, J = 2.0 and 2.0 Hz), 6.73 (s, 1H), 6.68 (dd, 2H, J = 8.3 and 2.0 Hz), 6.64 (d, 1H, J = 8.3 Hz), 6.59 (s, 1H), 5.15 (d, 2H, J = 2.0 Hz), 5.20–5.05 (m, 4H), 3.98 (s, 3H), 3.87 (s, 3H), 3.64 (s, 3H), 1.83 (s, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 159.1 (C_q), 149.9 (C_q), 149.2 (C_q), 147.0 (C_q), 146.8 (2 × C_q), 144.7 (C_q), 136.9 (C_q), 136.8 (C_q), 129.2 (C_q), 128.8 (CH), 128.5 (4 × CH), 127.9 (CH), 127.8 (CH), 127.5 (2 × CH), 127.3 (2 × CH), 123.4 (C_q), 118.8 (CH), 115.1 (C_q), 112.9 (CH), 112.4 (2 × CH), 107.0

(CH), 105.7 (CH), 104.4 (CH), 80.8 (C_q), 71.5 (CH₂), 70.9 (CH₂), 57.1 (CH₃), 56.3 (CH₃), 55.1 (CH₃), 28.2 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 3063, 2932, 1604, 1499, 1458, 1371, 1253, 1167, 1036, 908, 852, 731, 695 cm⁻¹; HR-MS (ESI+) m/z calculated for [C₃₇H₃₅O₆]⁺ = [M + H]⁺ 575.2428, found 575.2410.

2,9-Bis(benzyloxy)-3,8-dimethoxy-6-(3-methoxyphenyl)-6-methyl-6H-benzo[c]chromene (5m). This compound was prepared according to the GP-6 and isolated as yellow color semisolid 75% yield (108 mg), byproduct ketone **7b** 68% yield (25 mg) as colorless oil: ¹H NMR (CDCl₃, 400 MHz) δ = 7.48 (d, 2H, J = 7.2 Hz), 7.46–7.27 (m, 7H), 7.15 (dd, 1H, J = 8.3 and 8.2 Hz), 6.95 (s, 1H), 6.91 (s, 1H), 6.90–6.84 (m, 2H), 6.76–6.68 (m, 2H), 6.58 (s, 1H), 5.16 (s, 2H), 5.08 (d, 1H, J = 12.0 Hz), 5.04 (d, 1H, J = 12.0 Hz), 3.87 (s, 3H), 3.85 (s, 3H), 3.72 (s, 3H), 1.98 (s, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 159.1 (C_q), 150.7 (C_q), 148.6 (C_q), 148.2 (C_q), 147.4 (C_q), 146.8 (C_q), 143.0 (C_q), 137.6 (C_q), 137.0 (C_q), 129.5 (C_q), 128.8 (CH), 128.6 (2 × CH), 128.5 (2 × CH), 128.0 (CH), 127.8 (CH), 127.5 (2 × CH), 127.4 (2 × CH), 122.7 (C_q), 118.9 (CH), 114.4 (C_q), 112.8 (CH), 112.3 (CH), 109.8 (CH), 109.6 (CH), 107.8 (CH), 102.2 (CH), 80.9 (C_q), 72.3 (CH₂), 71.3 (CH₂), 56.3 (CH₃), 56.0 (CH₃), 55.1 (CH₃), 28.2 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 3063, 2931, 1604, 1499, 1372, 1253, 1167, 1036, 908, 852, 731, 695 cm⁻¹; HR-MS (ESI+) m/z calculated for [C₃₇H₃₅NO₆]⁺ = [M + NH₄]⁺ 592.2694, found 592.2687.

6-Methyl-6-thien-2-yl-6H-benzo[c]chromene (5n). This compound was prepared according to the GP-6 and isolated as yellow color viscous liquid 77% yield (107 mg), byproduct ketone **7c** 69% yield (21 mg) as black color viscous liquid: ¹H NMR (CDCl₃, 400 MHz) δ = 7.77 (d, 1H, J = 7.8 Hz), 7.70 (dd, 1H, J = 7.8 and 1.5 Hz), 7.42 (ddd, 1H, J = 8.8, 7.3, and 1.5 Hz), 7.33 (ddd, 1H, J = 8.8, 7.8, and 1.5 Hz), 7.27 (dd, 1H, J = 7.3 and 1.5 Hz), 7.23–7.14 (m, 2H), 6.99 (dd, 2H, J = 7.3 and 7.3 Hz), 6.78 (dd, 1H, J = 4.9 and 3.4 Hz), 6.67 (dd, 1H, J = 3.4 and 1.5 Hz), 2.13 (s, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 152.4 (C_q), 149.6 (C_q), 137.4 (C_q), 129.5 (CH), 129.2 (C_q), 128.5 (CH), 127.8 (CH), 125.9 (CH), 125.8 (CH), 125.6 (CH), 124.8 (CH), 122.9 (CH), 122.5 (C_q), 122.3 (CH), 122.0 (CH), 118.3 (CH), 79.0 (C_q), 29.0 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 3062, 2980, 1591, 1480, 1431, 1245, 1136, 1066, 915, 824, 748, 647 cm⁻¹; HR-MS (ESI+) m/z calculated for [C₁₈H₁₃S]⁺ = [(M + H) - H₂O]⁺ 261.0732, found 261.0735.

3,8-Dimethoxy-6-methyl-6-thien-2-yl-6H-benzo[c]chromene (5o). This compound was prepared according to the GP-6 and isolated as brown color semisolid 69% yield (59 mg), byproduct ketone **7c** 70% yield (22 mg) black color viscous liquid: ¹H NMR (CDCl₃, 400 MHz) δ = 7.22–7.11 (m, 3H), 7.09 (d, 1H, J = 2.4 Hz), 7.07 (d, 1H, J = 2.4 Hz), 6.96 (dd, 1H, J = 8.3 and 2.9 Hz), 6.90 (dd, 1H, J = 8.8 and 2.9 Hz), 6.87 (dd, 1H, J = 4.9 and 3.9 Hz), 6.68 (d, 1H, J = 3.9 Hz), 3.87 (s, 3H), 3.84 (s, 3H), 1.96 (s, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 159.2 (C_q), 158.7 (C_q), 142.6 (C_q), 141.6 (C_q), 134.5 (C_q), 133.1 (CH), 132.4 (C_q), 132.1 (CH), 131.5 (C_q), 127.0 (CH), 126.9 (CH), 126.1 (CH), 116.9 (CH), 115.3 (CH), 113.3 (CH), 112.7 (CH), 55.4 (2 × CH₃), 29.4 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 3063, 2980, 1590, 1484, 1437, 1248, 1139, 1065, 918, 825, 746, 647 cm⁻¹; HR-MS (ESI+) m/z calculated for [C₂₀H₁₇O₂S]⁺ = [(M + H) - H₂O]⁺ 321.0944, found 321.0940.

2,3,8,9-Tetramethoxy-6-methyl-6-thien-2-yl-6H-benzo[c]chromene (5p). This compound was prepared according to the GP-6 and isolated as yellow color solid 62% yield (62 mg): mp 126–128 °C, byproduct ketone **7c** 55% yield (17 mg) black color viscous liquid; ¹H NMR (CDCl₃, 400 MHz) δ = 7.18 (dd, 1H, J = 4.9 and 1.0 Hz), 7.09 (s, 1H), 7.05 (s, 1H), 6.80 (dd, 1H, J = 4.9 and 3.9 Hz), 6.73 (s, 1H), 6.69 (dd, 1H, J = 3.4 and 1.5 Hz), 6.54 (s, 1H), 3.99 (s, 3H), 3.90 (s, 3H), 3.86 (s, 3H), 3.84 (s, 3H), 2.09 (s, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 149.9 (2 × C_q), 149.3 (C_q), 148.2 (C_q), 146.5 (C_q), 144.3 (C_q), 129.1 (C_q), 125.9 (CH), 125.6 (2 × CH), 122.7 (C_q), 114.2 (C_q), 108.4 (CH), 105.9 (CH), 104.9 (CH), 102.2 (CH), 78.9 (C_q), 56.7 (CH₃), 56.1 (2 × CH₃), 55.9 (CH₃), 28.8 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{\max} = 3062, 2982, 1592, 1481, 1433, 1245, 1137, 1067, 918, 824, 745, 648 cm⁻¹; HR-MS (ESI+)

m/z calculated for $[C_{22}H_{22}SO_3]^+ = [(M + Na)]^+$ 421.1080, found 421.1064.

6,6-Diphenyl-6H-benzo[c]chromene (5q). This compound was prepared according to the GP-6 and isolated as colorless viscous liquid 73% yield (60 mg), byproduct ketone **7d** 58% yield (26 mg) white crystals: 1H NMR ($CDCl_3$, 400 MHz) $\delta = 7.77$ (d, 1H, $J = 7.8$ Hz), 7.65 (dd, 1H, $J = 7.8$ and 1.5 Hz), 7.40 (ddd, 1H, $J = 8.8$, 7.8, and 1.5 Hz), 7.34–7.12 (m, 12H), 7.04 (dd, 1H, $J = 8.3$ and 1.5 Hz), 6.94 (ddd, 1H, $J = 8.8$, 7.8, and 1.5 Hz), 6.71 (dd, 1H, $J = 7.3$ and 1.0 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 152.8$ (C_q), 143.6 ($2 \times C_q$), 137.1 (C_q), 130.1 (C_q), 129.5 (CH), 128.9 ($5 \times CH$), 128.3 ($2 \times CH$), 127.7 ($5 \times CH$), 127.0 (CH), 123.0 (C_q), 122.9 (CH), 122.3 (CH), 121.9 (CH), 118.6 (CH), 86.6 (C_q) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) $\nu_{max} = 3060, 3032, 1591, 1437, 1302, 1234, 1038, 988, 757, 699$ cm^{-1} ; HR-MS (ESI+) m/z calculated for $[C_{25}H_{18}O]^+ = [M + H]^+$ 334.1352, found 334.1355.

3,8-Dimethoxy-6,6-diphenyl-6H-benzo[c]chromene (5r). This compound was prepared according to the GP-6 and isolated as white color solid 73% yield (71 mg): mp 118–120 °C, byproduct ketone **7d** 53% yield (24 mg) white crystals; 1H NMR ($CDCl_3$, 400 MHz) $\delta = 7.61$ (d, 1H, $J = 8.8$ Hz), 7.47 (d, 1H, $J = 8.8$ Hz), 7.35–7.17 (m, 10H), 6.92 (dd, 1H, $J = 8.3$ and 2.4 Hz), 6.59 (d, 1H, $J = 2.4$ Hz), 6.49 (dd, 1H, $J = 8.8$ and 2.4 Hz), 6.25 (d, 1H, $J = 2.4$ Hz), 3.76 (s, 3H), 3.69 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 160.2$ (C_q), 158.0 (C_q), 153.3 (C_q), 143.5 ($2 \times C_q$), 137.4 (C_q), 128.8 ($5 \times CH$), 127.8 (CH), 127.7 ($4 \times CH$), 123.5 (C_q), 123.1 (CH), 122.9 (CH), 116.1 (C_q), 114.7 (CH), 113.1 (CH), 108.4 (CH), 103.5 (CH), 86.9 (C_q), 55.3 (CH_3), 55.2 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) $\nu_{max} = 3060, 2935, 2834, 1617, 1484, 1273, 1157, 1048, 1008, 907, 834, 727, 699$ cm^{-1} ; HR-MS (ESI+) m/z calculated for $[C_{27}H_{22}O_3]^+ = [(M + H)]^+$ 395.1642, found 395.1635.

2,3,8,9-Tetramethoxy-6,6-diphenyl-6H-benzo[c]chromene (5s). This compound was prepared according to the GP-6 and isolated as brown color semisolid 78% yield (88 mg), byproduct ketone **7d** 71% yield (32 mg) white crystals: 1H NMR ($CDCl_3$, 400 MHz) $\delta = 7.36$ –7.16 (m, 10H), 7.10 (s, 1H), 7.00 (s, 1H), 6.60 (s, 1H), 6.18 (s, 1H), 3.98 (s, 3H), 3.86 (s, 3H), 3.82 (s, 3H), 3.60 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 149.9$ (C_q), 149.1 (C_q), 147.5 (C_q), 146.9 (C_q), 144.2 (C_q), 143.8 ($2 \times C_q$), 129.6 (C_q), 128.7 ($5 \times CH$), 127.7 ($5 \times CH$), 123.6 (C_q), 114.7 (C_q), 112.0 (CH), 105.8 (CH), 104.8 (CH), 102.5 (CH), 86.6 (C_q), 56.6 (CH_3), 56.1 (CH_3), 55.9 ($2 \times CH_3$) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) $\nu_{max} = 2930, 2834, 1502, 1440, 1259, 1197, 1119, 1014, 910, 860, 729, 700$ cm^{-1} ; HR-MS (ESI+) m/z calculated for $[C_{29}H_{26}O_5]^+ = [M]^+$ 454.1775, found 454.1772.

6-Benzyl-6-methyl-6H-benzo[c]chromene (5u). This compound was prepared according to the GP-6 and isolated as pale yellow color viscous liquid 67% yield (48 mg): 1H NMR ($CDCl_3$, 400 MHz) $\delta = 7.76$ (ddd, 2H, $J = 7.3, 7.3$, and 1.5 Hz), 7.36 (ddd, 1H, $J = 8.3, 7.3$, and 1.0 Hz), 7.29 (dd, 1H, $J = 8.3$ and 2.0 Hz), 7.24–7.14 (m, 4H), 7.05 (dd, 1H, $J = 7.8$ and 1.5 Hz), 7.02 (d, 2H, $J = 7.3$ Hz), 7.00–6.94 (m, 2H), 3.15 (d, 1H, $J = 13.2$ Hz), 2.87 (d, 1H, $J = 13.2$ Hz), 1.67 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 152.4$ (C_q), 138.0 (C_q), 136.6 (C_q), 130.7 ($2 \times CH$), 129.6 (CH), 128.7 (C_q), 127.8 (CH), 127.7 ($2 \times CH$), 127.6 (CH), 126.3 (CH), 124.5 (CH), 122.9 (CH), 122.3 (C_q), 122.0 (CH), 121.6 (CH), 118.2 (CH), 79.7 (C_q), 45.6 (CH_2), 24.5 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) $\nu_{max} = 3028, 2923, 2851, 1592, 1484, 1437, 1377, 1250, 1154, 1087, 938, 756, 702$ cm^{-1} ; HR-MS (ESI+) m/z calculated for $[C_{21}H_{18}O]^+ = [M + H]^+$ 287.1430, found 287.1436.

6-Benzyl-3,8-dimethoxy-6-methyl-6H-benzo[c]chromene (5v). This compound was prepared according to the GP-6 and isolated as pale yellow color viscous liquid 69% yield (60 mg): 1H NMR ($CDCl_3$, 400 MHz) $\delta = 7.59$ (d, 2H, $J = 8.8$ Hz), 7.24–7.15 (m, 3H), 7.00 (dd, 2H, $J = 7.8$ and 2.4 Hz), 7.87 (dd, 1H, $J = 8.8$ and 2.9 Hz), 6.61 (dd, 1H, $J = 8.3$ and 2.4 Hz), 6.55 (d, 1H, $J = 2.4$ Hz), 6.51 (d, 1H, $J = 2.4$ Hz), 3.83 (s, 3H), 3.75 (s, 3H), 3.13 (d, 1H, $J = 13.7$ Hz), 2.85 (d, 1H, $J = 13.7$ Hz), 1.64 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 160.4$ (C_q), 158.5 (C_q), 152.8 (C_q), 138.4 (C_q), 136.6 (C_q), 130.8 ($2 \times CH$), 127.7 ($2 \times CH$), 126.4 (CH), 123.1 (CH), 122.6 (CH), 121.9 (C_q), 115.4 (C_q), 113.1 (CH), 110.4 (CH), 108.2 (CH),

103.1 (CH), 80.1 (C_q), 55.4 (CH_3), 55.3 (CH_3), 45.6 (CH_2), 24.5 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) $\nu_{max} = 3002, 2920, 2851, 1580, 1440, 1361, 1236, 1149, 1057, 924, 755, 693$ cm^{-1} ; HR-MS (ESI+) m/z calculated for $[C_{23}H_{22}O_3]^+ = [(M + H)]^+$ 347.1642, found 347.1634.

1-Methyl-3-methyleneindan-1-ol (13a) and 1,3-Dimethyl-1H-inden-1-ol (13a'). This compound was prepared according to the GP-6 and isolated as colorless viscous liquid 73% yield (58 mg): 1H NMR ($CDCl_3$, 400 MHz) (for major isomer) $\delta = 7.42$ (dd, 1H, $J = 4.9$ and 3.9 Hz), 7.35 (dd, 1H, $J = 5.5$ and 3.3 Hz), 7.28–7.21 (m, 2H), 5.44 (t, 1H, $J = 2.3$ and 2.3 Hz), 5.01 (s, 1H), 2.85 (q, 2H, $J = 16.4$ and 7.5 Hz), 1.84 (br. s, 1H), 1.51 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 150.4$ (C_q), 145.9 (C_q), 142.7 (CH), 129.0 (CH), 128.6 (CH), 122.9 (CH), 120.6 (CH), 104.4 (CH_2), 78.7 (C_q), 49.4 (CH_2), 28.1 (CH_3) ppm; 1H NMR ($CDCl_3$, 400 MHz) (for minor isomer) $\delta = 7.31$ (d, 1H, $J = 7.6$ Hz), 7.18 (d, 1H, $J = 8.4$ Hz), 7.13 (dd, 1H, $J = 7.4$ and 7.3 Hz), 7.07 (d, 1H, $J = 7.6$ Hz), 5.90 (s, 1H), 1.98 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 143.0$ (C_q), 142.7 (C_q), 139.4 (C_q), 137.7 (C_q), 128.3 (CH), 126.3 (CH), 121.2 (CH), 119.2 (CH), 78.7 (C_q), 23.8 (CH_3), 12.7 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) $\nu_{max} = 3062, 2923, 2855, 1591, 1434, 1373, 1240, 1150, 1063, 924, 754, 699$ cm^{-1} ; HR-MS (ESI+) m/z calculated for $[C_{11}H_{12}O]^+ = [(M + Na)]^+$ 183.0780, found 183.0787.

3-Methylene-1-phenylindan-1-ol (13b) and 3-Methyl-1-phenyl-1H-inden-1-ol (13b'). This compound was prepared according to the GP-6 and isolated as colorless viscous liquid 70% yield (78 mg): 1H NMR ($CDCl_3$, 400 MHz) (for major isomer) $\delta = 7.56$ (d, 1H, $J = 7.5$ Hz), 7.37 (d, 2H, $J = 8.0$ Hz), 7.33–7.20 (m, 5H), 7.13 (d, 1H, $J = 7.5$ Hz), 5.59 (s, 1H, $J = 2.3$ and 2.3 Hz), 5.12 (s, 1H), 3.19 (q, 2H, $J = 19.7$ and 6.7 Hz), 2.30 (br. s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 150.3$ (C_q), 146.5 (C_q), 146.1 (C_q), 140.2 (C_q), 129.3 (CH), 128.8 (CH), 128.1 ($2 \times CH$), 126.8 (CH), 125.2 ($2 \times CH$), 124.6 (CH), 120.6 (CH), 104.8 (CH_2), 82.5 (C_q), 51.8 (CH_2) ppm; 1H NMR ($CDCl_3$, 400 MHz) (for minor isomer) $\delta = 7.41$ (dd, 1H, $J = 7.6$ Hz), 7.33 (d, 1H, $J = 7.4$ Hz), 7.30–7.21 (m, 5H), 7.20–7.15 (m, 2H), 6.07 (s, 1H), 2.10 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 150.5$ (C_q), 148.0 (C_q), 143.7 (C_q), 140.0 (C_q), 137.9 (CH), 128.4 (CH), 128.2 ($2 \times CH$), 127.3 (CH), 126.7 (CH), 125.8 ($2 \times CH$), 122.8 (CH), 119.5 (CH), 84.8 (C_q), 12.8 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) $\nu_{max} = 3042, 2913, 2845, 1565, 1443, 1337, 1220, 1105, 1066, 923, 765, 656$ cm^{-1} .

6-Methoxy-1-methyl-3-methyleneindan-1-ol (13c) and 6-Methoxy-1,3-dimethyl-1H-inden-1-ol (13c'). This compound was prepared according to the GP-6 and isolated as colorless viscous liquid 78% yield (69 mg): 1H NMR ($CDCl_3$, 400 MHz) (for major isomer) $\delta = 7.39$ (d, 1H, $J = 8.4$ Hz), 6.91 (d, 1H, $J = 2.3$ Hz), 6.86 (dd, 1H, $J = 8.4$ and 2.4 Hz), 5.34 (t, 1H, $J = 2.3$ and 2.1 Hz), 4.95 (t, 1H, $J = 1.9$ and 1.8 Hz), 3.82 (s, 3H), 2.91 (q, 2H, $J = 16.4$ and 11.0 Hz), 1.56 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 160.8$ (C_q), 152.1 (C_q), 145.3 (C_q), 135.8 (C_q), 121.8 (CH), 115.9 (CH), 106.7 (CH), 102.1 (CH_2), 78.6 (C_q), 55.5 (CH_3), 49.8 (CH_2), 28.0 (CH_3) ppm; 1H NMR ($CDCl_3$, 400 MHz) (for minor isomer) $\delta = 7.02$ (d, 1H, $J = 8.2$ Hz), 6.98 (d, 1H, $J = 2.4$ Hz), 6.76 (dd, 1H, $J = 8.2$ and 2.4 Hz), 5.86 (d, 1H, $J = 1.5$ Hz), 2.01 (d, 3H, $J = 1.5$ Hz), 1.54 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 159.1$ (C_q), 138.7 (C_q), 135.8 (C_q), 132.2 (C_q), 119.8 (CH), 112.6 (CH), 108.5 (CH), 80.8 (C_q), 55.6 (CH_3), 24.0 (CH_3), 12.8 (CH_3) ppm; IR (MIR-ATR, 4000–600 cm^{-1}) $\nu_{max} = 3067, 2923, 2851, 1582, 1448, 1361, 1241, 1150, 1062, 922, 758, 699$ cm^{-1} ; HR-MS (ESI+) m/z calculated for $[C_{12}H_{14}O_2]^+ = [(M + Na)]^+$ 213.0893, found 213.0886.

6-Methoxy-3-methylene-1-phenylindan-1-ol (13d) and 6-Methoxy-3-methyl-1-phenyl-1H-inden-1-ol (13d'). This compound was prepared according to the GP-6 and isolated as colorless viscous liquid 74% yield (93 mg): 1H NMR ($CDCl_3$, 400 MHz) (for major isomer) $\delta = 7.49$ (d, 1H, $J = 8.3$ Hz), 7.38 (d, 2H, $J = 6.8$ Hz), 7.31 (dd, 2H, $J = 7.8$ and 6.8 Hz), 7.24 (d, 1H, $J = 5.8$ Hz), 6.90 (dd, 1H, $J = 8.3$ and 2.4 Hz), 6.63 (d, 1H, $J = 2.4$ Hz), 5.43 (dd, 1H, $J = 2.4$ and 2.0 Hz), 5.00 (dd, 1H, $J = 2.0$ and 1.5 Hz), 3.73 (s, 3H), 3.33–3.08 (m, 2H), 2.32 (br. s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 160.9$ (C_q), 151.9 (C_q), 146.4 (C_q), 145.5 (C_q), 133.2 (C_q), 128.1

(2 × CH), 126.9 (CH), 125.1 (2 × CH), 121.8 (CH), 116.5 (CH), 108.0 (CH), 102.4 (CH₂), 82.5 (C_q), 55.4 (CH₃), 52.4 (CH₂) ppm; ¹H NMR (CDCl₃, 400 MHz) (for minor isomer) δ = 7.43 (d, 1H, J = 6.8 Hz), 7.38 (d, 2H, J = 6.8 Hz), 7.31 (dd, 1H, J = 7.8 and 6.8 Hz), 7.24 (d, 1H, J = 5.8 Hz), 7.09 (d, 1H, J = 7.8 Hz), 6.80 (dd, 1H, J = 3.9 and 2.0 Hz), 6.78 (d, 1H, J = 2.0 Hz), 5.98 (d, 1H, J = 7.8 Hz), 2.10 (d, 3H, J = 2.0 Hz) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 160.9 (C_q), 151.9 (C_q), 146.4 (C_q), 145.5 (C_q), 136.1 (C_q), 128.3 (2 × CH), 127.2 (CH), 125.2 (2 × CH), 120.1 (CH), 113.0 (CH), 110.0 (CH), 82.5 (C_q), 55.5 (CH₃), 12.9 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{max} = 3072, 2934, 2845, 1590, 1454, 1345, 1256, 1140, 1054, 943, 756, 645 cm⁻¹; HR-MS (ESI+) *m/z* calculated for [C₁₇H₁₆NaO₂]⁺ = [(M + Na)]⁺ 275.1043, found 275.1039.

5,6-Dimethoxy-1-methyl-3-methyleneindan-1-ol (13e) and 5,6-Dimethoxy-1,3-dimethyl-1H-inden-1-ol (13e'). This compound was prepared according to the GP-6 and isolated as colorless viscous liquid 81% yield (89 mg): ¹H NMR (CDCl₃, 400 MHz) (for major isomer) δ = 6.92 (s, 1H), 6.89 (s, 1H), 5.31 (dd, 1H, J = 2.4 and 2.0 Hz), 4.95 (dd, 1H, J = 2.0 and 1.5 Hz), 3.91 (s, 3H), 3.90 (s, 3H), 3.05–2.80 (m, 2H), 1.83 (br. s, 1H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 150.8 (C_q), 150.2 (C_q), 145.8 (C_q), 143.1 (C_q), 131.9 (C_q), 104.9 (CH), 102.5 (CH), 101.8 (CH₂), 78.7 (C_q), 56.0 (2 × CH₃), 49.8 (CH₂), 28.1 (CH₃) ppm; ¹H NMR (CDCl₃, 400 MHz) (for minor isomer) δ = 7.00 (s, 1H), 6.70 (s, 1H), 5.91 (d, 1H, J = 2.0 Hz), 3.87 (s, 3H), 3.85 (s, 3H), 2.03 (d, 3H, J = 1.5 Hz) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 149.2 (C_q), 148.0 (C_q), 142.5 (C_q), 138.5 (C_q), 136.6 (C_q), 133.7 (C_q), 105.7 (CH), 103.6 (CH), 81.0 (C_q), 56.3 (2 × CH₃), 24.0 (CH₂), 12.9 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{max} = 3085, 2924, 2835, 1580, 1452, 1325, 1252, 1142, 1044, 942, 751, 642 cm⁻¹; HR-MS (ESI+) *m/z* calculated for [C₁₃H₁₇O₃]⁺ = [(M + H)]⁺ 221.1172, found 221.1175.

5,6-Dimethoxy-3-methyl-1-methylene-1H-indene (14e). This compound was prepared according to the GP-6 and isolated as colorless viscous liquid 86% yield (87 mg): ¹H NMR (CDCl₃, 400 MHz) δ = 6.43 (s, 1H), 6.01 (s, 1H), 5.39 (s, 1H), 5.07 (s, 1H), 4.76 (s, 1H), 3.18 (s, 3H), 3.19 (s, 3H), 1.42 (s, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 162.5 (C_q), 149.5 (C_q), 147.5 (C_q), 146.8 (C_q), 142.3 (C_q), 137.8 (C_q), 129.2 (C_q), 124.5 (CH), 110.0 (CH₂), 104.3 (CH), 102.7 (CH), 56.3 (CH₃), 56.1 (CH₃), 13.1 (CH₃) ppm; IR (MIR-ATR, 4000–600 cm⁻¹) ν_{max} = 2930, 2861, 1581, 1450, 1380, 1240, 1140, 1022, 926, 770, 689 cm⁻¹; HR-MS (ESI+) *m/z* calculated for [C₁₃H₁₅O₂]⁺ = [(M + H)]⁺ 202.1067, found 202.1073.

■ ASSOCIATED CONTENT

● Supporting Information

Experimental procedures and characterization for all new compounds, copies of NMR spectra, and CIF files for **5b** and **5r**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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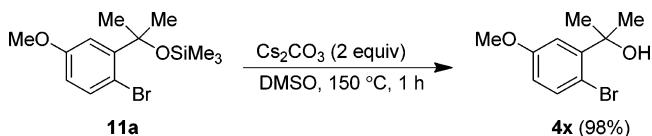
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