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Reactions of 2-hydroxybenzophenones with Corey–Chaykovsky reagent

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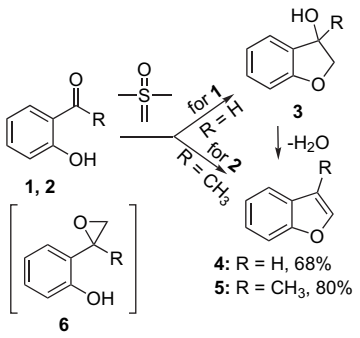
Abstract

A variety of 2-hydroxybenzophenones on reaction with Corey–Chaykovsky reagent underwent unprecedented rearrangements leading to 3-substituted benzofurans **8** and one-carbon homologated compounds **9** and **12**. Compounds **9** could further be quantitatively transformed to 2-substituted benzofuran derivatives **10**.

1. Introduction

Dimethylsulfoxonium methylide, often called as Corey–Chaykovsky reagent (CCR)[1] has proven to be a versatile nucleophilic agent to achieve variety of chemical transformations and provide new compounds with potential application. In general trimethylsulfoxonium iodide when reacted with a strong base such as NaH will generate CCR, which can then be used as a methylene-transfer reagent. Most often CCR is employed for the preparation of epoxides[2] from carbonyl compounds, aziridines from imines,[2] cyclopropanes[2] from α,β-unsaturated carbonyl compounds, and *O*-, *N*-, and *S*-alkylated compounds.[1e] Corey–Chaykovsky reaction is mostly a reliable strategy in many of the synthetic applications and was successfully applied for the total synthesis of variety of natural products with distinct molecular framework and also for the synthesis of biologically important molecules.[3] A number of modified CCRs were recently utilized for enantioselective synthesis with excellent selectivities.[4] Lowe and Holt found that CCR on reaction with an aromatic carbonyl compound having a *o*-hydroxyl substituent led to a novel protocol for the synthesis of benzofuran derivatives in moderate to good yields (Scheme 1).[5] 2-Hydroxyacetophenone (**2**) provided 3-methylbenzofuran (**5**) as a single isolated product in excellent yield (Scheme 1).[5] Based on the isolation of hydroxyl intermediate **3** (for various benzaldehydes utilized in their study) and the CCR ability to form epoxides with carbonyl functionalities, one of the possible reaction pathways for the formation of the observed products might be through a hydroxy-epoxide intermediate like **6** (Scheme 1). However, Lowe and Holt pointed out the fact that they did not detect any hydroxy-epoxide intermediate in these reactions.



Scheme 1. CCR mediated synthesis of benzofurans.

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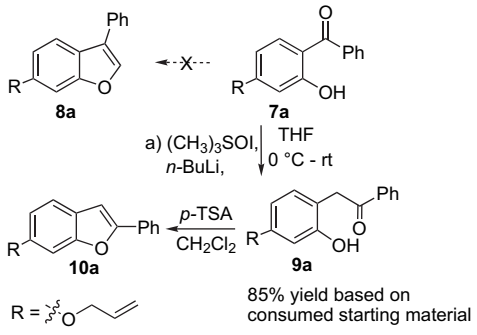
Benzo[*b*]furans and their derivatives have received much attention in recent years because of their occurrence in natural substances and their physiological activity.[6] These are also used for organic materials with light-emitting capability, which can then be used as organic light-emitting devices.[7] General routes for the synthesis of benzo[*b*]furans are widely described in literature.[8] During our study on the design, synthesis, and structure–activity relationship of novel peroxisome-proliferator-activated receptor (PPAR) agonists, we needed 3-substituted benzofurans as building blocks.[9a] 3-Phenyl-7-propylbenzofuran-6-ol was found to be a good building block for providing selective PPAR agonists when attached to different scaffolds.[9b]

2. Results and discussion

In an attempt to obtain 3-phenyl-6-allyloxy-benzofuran (**8a**) from 4-allyloxy-2-hydroxybenzophenone (**7a**) employing Lowe and Holt sequence led to the serendipitous discovery of a novel rearrangement product 2-[4-(allyloxy)-2-hydroxyphenyl]-1-phenyl-1-ethanone (**9a**). Compound **9a** on subsequent cyclization provided 2-phenyl-6-allyloxybenzofuran (**10a**, Scheme 2).[9a,10] In the view of importance of benzo[*b*]furans, it appeared for us to study the generality of this unprecedented reaction.



Scheme 2. One-carbon homologation with CCR leading to 2-substituted benzofuran **10a**.

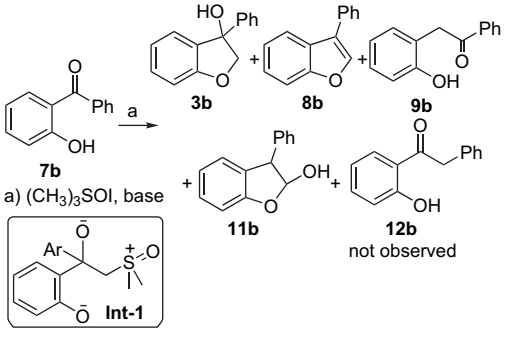
Initially, compound **8a** was of interest. Accordingly, when the corresponding benzophenone **7a** was subjected to sulfoxonium ylide prior generated in the presence of *n*-BuLi/THF (Method A), underwent incomplete reaction furnishing a new compound as indicated by TLC. The newly formed product purified by column chromatography shows in its ^{1}H NMR spectrum, no peak at around 7.8–8.0 ppm, a diagnostic value for C-2 proton of benzofuran, instead a singlet at 4.19 ppm accounting for 2 protons. After long standing in $CDCl_3$ the peak at 4.19 ppm disappeared and a new peak showed up as a singlet at 6.94 ppm, a diagnostic peak of C-3 proton of a benzofuran. Careful analysis of all the obtained analytical data (IR, ^{1}H NMR, ^{13}C NMR and DEPT, HRMS) provided the structures of the newly formed compounds as **9a** and **10a**, respectively. The slight acid in $CDCl_3$ solvent caused cyclization of **9a** into **10a**. This finding is surprising and contemplated to be due to the change of reaction condition from usual NaH/DMSO to *n*-BuLi/THF to generate CCR. After our initial results,[9a,10] base dependent and solvent dependent product distribution in Corey–Chaykovsky reaction was also observed by other research groups.[11]

At the outset the reaction was performed with 2-hydroxybenzophenone (**7b**) under NaH and *n*-BuLi conditions (Table 1). After several trials we found that 4 equiv of CCR was required for the completion of the reaction with compound **7b**. Sulfoxonium ylide generated utilizing NaH as base in DMSO on reaction with **7b** at 60 °C led to the formation of 3-phenylbenzofuran (**8b**) in 50% yield with 20% recovery of starting material (Table 1, entry 1). When solvent was changed to THF, reaction did not proceed. In an intriguing observation when *n*-BuLi was used as base furnished products **3b**, **11b**, and **9b** in 70% total yield (Table 1, entry 2).

The presence of compounds **3b** and **11b** could be witnessed from the ^{1}H NMR of the crude reaction mixtures; however, several attempts to obtain the pure compounds **3b** and **11b** by column chromatography were unsuccessful providing mixture of **3b** or **11b** along with the dehydrated product 3-phenylbenzofuran (**8b**). Consequently, after isolating the one-carbon homologated compound **9b** by column chromatography, the mixture of **3b**, **11b**, and **8b** was subjected to *p*-TSA/CH_2Cl_2 condition to obtain 3-phenylbenzofuran (**8b**) as the sole product. Formation of compounds **3b** and **8b** is in accord with the Lowe and Holt's result.

Consequently, when this reaction was extended to 2-hydroxybenzophenone **7c** with R^4=OMe furnished 45% of one-carbon homologated product **9c** and 20% of 3-substituted benzofuran **8c** (Table 2). In providing compounds **9a**, **9b**, **9c** sulfur ylide is effecting a methylene insertion to the benzophenone. But this insertion can in principle be at two different positions of benzophenone. One of the possible reasons for highly selective methylene insertion product in these cases

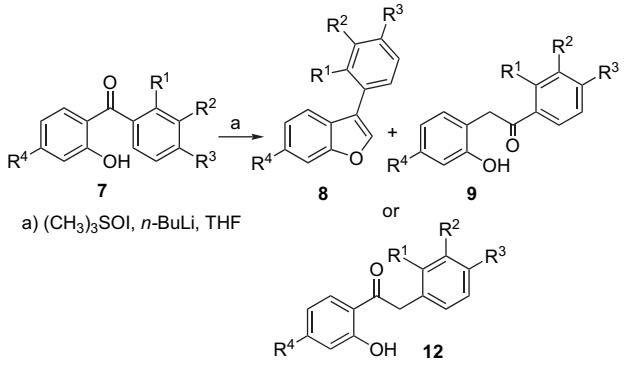
Table 1
Unprecedented rearrangements of 2-hydroxybenzophenone on reaction with CCR



Entry	Method:[a] base/solvent	DMSY (equiv)	Time (h)/ Temp.	Yield (%)			
				3b	11b	8b	9b
1[b]	B: NaH/DMSO	4	24/60 °C	—[c]	—[c]	50	—[c]
2	A: *n*-BuLi/THF	4	4/60 °C	—[d]	—[d]	50	20

[a] See Section 4.
[b] 20% recovery of SM.
[c] Not observed.
[d] Compounds **3b** and **11b** could be seen from ^{1}H NMR of the crude sample.

Table 2
Reactions of various 2-hydroxybenzophenones with CCR



Entry	2-Hydroxybenzophenones	Products/yield (%)
1	**7b**:R^1=R^2=R^3=R^4=H	**8b**/50+**9b**/20
2	**7c**:R^1=R^2=R^3=H; R^4=OMe	**8c**/20+**9c**/45
3	**7d**:R^1=R^2=R^4=H; R^3=Me	**8d**/45+**9d**/20
4	**7e**:R^1=R^2=R^4=H; R^3=OMe	**8e**/32+**9e**/32
5	**7f**:R^1=R^2=R^4=H; R^3=F	**8f**/42+**9f**/22
6	**7g**:R^1=R^2=R^4=H; R^3=CN	**8g**/42+**9g**/12
7	**7h**:R^1=R^2=R^4=H; R^3=CF_3	**8h**/36+**9h**/15
8	**7i**:R^1=R^2=R^4=H; R^3=NO_2	**12i**/70
9	**7j**:R^1=R^4=H; R^2=Me; R^3=NO_2	**12j**/50 (20% SM recovered)

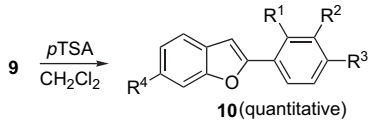
may be due to electronic factors. Thus, we pursued this reaction with a few selected 2-hydroxybenzophenones to come up with a probable reaction mechanism and possible scope and limitation of these novel rearrangements.

Initially, several substituted 2-hydroxybenzophenones were prepared (see Supplementary data). Thus, electron-rich aryl groups and electron-deficient aryl groups were connected to 2-hydroxybenzoyl moiety to give 2-hydroxybenzophenones **7**, which may provide varying electronic effects during the reaction with CCR.

When R^3 is an electron-donating substituent like methyl- or methoxy-group furnished the one-carbon homologated products **9d** (20%) and **9e** (32%) along with 3-substituted benzofurans **8d** (45%) and **8e** (32%). A weakly electron-withdrawing substitution like fluorine for R^3 gave 22% of **9f**, a one-carbon homologated product, beside 42% of **8f**, a 3-substituted benzofuran. By changing R^3 to cyano- (**7g**) and trifluoromethyl- (**7h**) provided low yields (**9g**-12% and **9h**-15%) of the one-carbon homologated products and moderate yields of 3-substituted benzofurans (**8g**-42% and **8h**-36%). In all the cases studied, products similar to **3b** or **11b** were not easy to isolate. Thus, after separating the rearranged product **9** from the crude sample, the remaining reaction mixture was treated with *p*-TSA in CH_2Cl_2 to obtain 3-phenylbenzofurans **8** as sole products. In a turn around situation with a nitro substitution for R^3 provided compound **12i** as a single product in 70% yield. Here the methylene insertion took place at the other alternative position of benzophenone. Compound **7j** also gave a similar rearranged product **12j** in 50% yield with 20% recovery of the starting material.

All the one-carbon homologated products **9** on treatment with *p*-TSA in CH_2Cl_2 quantitatively converted to the corresponding 2-aryl substituted benzofurans **10** (Eq. 1).

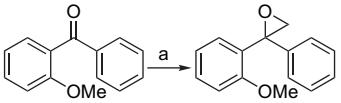
The structures of all the new compounds were assigned on the basis of their IR, ^{1}H NMR and ^{13}C NMR, DEPT, and low- and high-resolution mass spectral analyses. The ^{1}H NMR data of the known compounds **8b**,[12] **8c**,[13] **8e**,[14] **9b**,[15] **9e**,[16] **10b**,[21] **10d**,[17] **10e**,[17] **12i**[18] were compared with the data reported in literature.



(1)

b:R^1 = R^2 = R^3 = R^4 = H
c:R^1 = R^2 = R^3 = H; R^4 = OMe
d:R^1 = R^2 = R^4 = H ; R^3 = Me
e:R^1 = R^2 = R^4 = H ; R^3 = OMe
f:R^1 = R^2 = R^4 = H ; R^3 = F
g:R^1 = R^2 = R^4 = H ; R^3 = CN
h:R^1 = R^2 = R^4 = H ; R^3 = CF_3

To understand the participation of the hydroxyl group in this CCR mediated reaction, compound **13** was subjected to standard reaction conditions that provided epoxide **14** in 63% yield (Eq. 2). During a recent study on synthesis of diazonamide A by Nicolaou's group,[19] hydroxyl functionality in the 2-hydroxybenzophenone was protected and epoxide formation at the ketone moiety could be carried out in near quantitative yield.

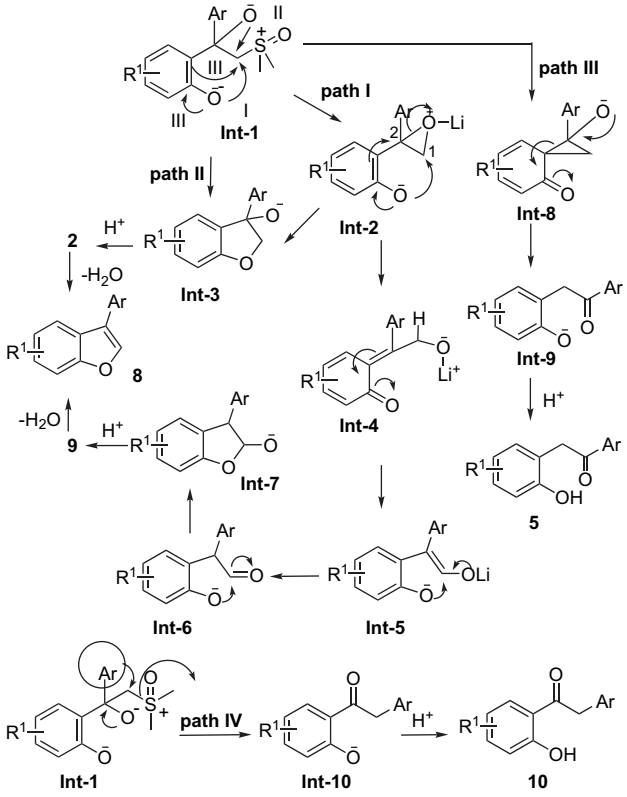


a) $(CH_3)_3SOI$, *n*-BuLi, THF, rt

(2)

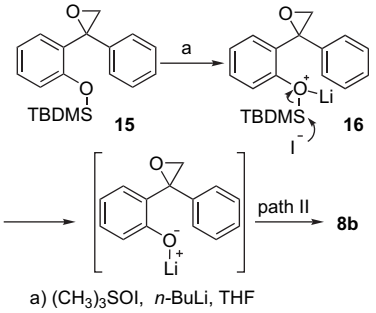
Although the reaction mechanism involved for the formation of observed products is not completely understood, we propose the following pathways. When a 2-hydroxybenzophenone substrate is added to the in situ generated ylide, initial formation of **Int-1** takes place. Thus **Int-1** is now open for a number of reaction pathways. If the nucleophilic oxygen near to the sulfoxonium cation kicks out the dimethyl sulfoxide leaving group, it can provide the epoxide **Int-2** (Scheme 3, path I). The phenoxide ion then opens the epoxide ring at carbon-1 to give **Int-3**; subsequent protonation and dehydration leads to 3-substituted benzofuran **3** (Scheme 3, path I or II). If the epoxide formed in path I is opened at carbon-2 by the phenoxide, then formation of **Int-4**, which upon consequent cyclization provides **Int-7**, subsequent protonation (Scheme 3, path II) and further dehydration leads to 3-substituted benzofuran **8**. This pathway is proposed based up on the observed product **11**, but we never isolated or detected the intermediate hydroxyl aldehyde (leading from **Int-6**). Formation of one-carbon homologation process is still not clearly understood. It appears as a cyclopropane type **Int-8** (Scheme 3, path III) that opens up to provide the 2-substituted benzofuran precursor **9**. As shown in path IV, migration of a phenyl ring provides compound **12**. The formation of compound **5** can also be expected to form by the aromatic ring migration depending upon the substitution pattern on these substrates.

In order to determine the presence of hydroxy-epoxide intermediate leading to the formation of 3-substituted



Scheme 3. Plausible reaction mechanisms for the formation of observed products.

benzofuran, epoxide **15** was synthesized (Scheme 4). Compound **15** under $(CH_3)_3SOI$, *n*-BuLi, THF condition transformed to product **8b** (trace amount of **3b** was observed in ^1H NMR of crude reaction mixture). Though, this proves the presence of hydroxy-epoxide intermediate, other possible reaction mechanisms leading to compound **8b** cannot be ruled out.



Scheme 4. Presence of hydroxy-epoxide intermediate in CCR mediated reactions.

3. Summary

In conclusion, though the reaction offered mixture of products, the novel rearrangement reaction observed here to provide the one-carbon homologated products, which were subsequently transformed to 2-substituted benzofuran derivatives is noteworthy and unprecedented. Electron-releasing substitution on either of the aryl group provided the methylene insertion to give compound **9**. Weakly electron-withdrawing substitutions provided low yields of the one-carbon homologated product. Surprisingly, a strongly electron-withdrawing substitution as in **7i** or **7j** gave one-carbon homologated product with a different regioselectivity. In summary, 2-hydroxybenzophenones on reaction with Corey–Chaykovsky reagent unprecedented rearrangement reactions to provide one-carbon homologated products, which in turn could be transformed to 2-substituted benzofurans.

4. Experimental section

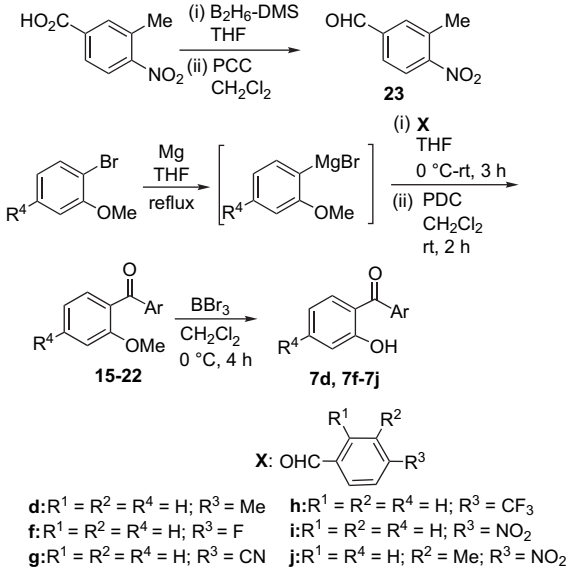
4.1. Method A

Trimethylsulfoxonium iodide in dry THF was placed in a flask, which was cooled to −78 °C. To this 1 equiv *n*-BuLi was added. After the addition of base, reaction mixture was brought to rt. Typically it took 10–15 min for the complete formation of CCR. To this reaction mixture, starting material (benzophenone) in dry THF was added and heated the reaction mixture to 60 °C for 4 h. Reaction was quenched with water and extracted with ether. The combined layers of ether was dried over anhydrous $MgSO_4$ and evaporated to yield the crude reaction mixture, which was then subjected to column chromatography to obtain the pure products.

4.2. Method B

A weighed amount of NaH (60% mineral oil dispersion) was washed with hexane to remove the mineral oil. This was dispersed in dry DMSO. Trimethyloxosulfonium iodide (1 equiv) in dry DMSO was added and stirred for 10–15 min during which time formation of DMSY took place. Now the starting material (benzophenones) in dry DMSO was added and heated the reaction mixture to 60 °C until the disappearance of starting material. Reaction was quenched with water and extracted with ether. The combined layers of ether was dried over anhydrous $MgSO_4$ and evaporated to yield the crude reaction mixture, which was then subjected to column chromatography to obtain the pure products.

Benzophenones **7a**, **7b**, **7c**, and **7e** are commercially available. 3-Methyl-4-nitrobenzaldehyde (**23**) was prepared from commercially available 3-methyl-4-nitrobenzoic acid in two steps (Scheme 5). In a general synthetic sequence, Grignard reaction of a substituted benzaldehyde **X** with 2-methoxyphenylmagnesium bromide furnished crude diaryl carbinol after usual workup. Thus obtained diaryl carbinol required no further purification and on subsequent PDC oxidation[20] gave the corresponding benzophenone derivatives **15**–**22** in good yield. Demethylation of the 2-methoxybenzophenones **15**–**22** in the presence of BBr_3[21] afforded the 2-hydroxybenzophenones **7d**, **7f**–**7j** required for the present study. Most of the substituted benzaldehydes were bought from commercial sources.



Scheme 5. Synthesis of 2-hydroxybenzophenones.

4.3. General procedure for the preparation of 2-methoxybenzophenones

Place in the flask 1.5 mmol of Mg turnings and 10 mL of dry THF. To this 2-bromoanisoles (1.2 mmol) are added and allowed to gently reflux while stirring until most of the Mg turnings are utilized for the reaction. The reaction flask was cooled to 0 °C and corresponding benzaldehydes (1.0 mmol) in dry THF are dropwise added and allowed to stir for 3 h. Reaction was quenched by adding crushed ice and the precipitated magnesium compounds by the addition of 10% aq hydrochloric acid with stirring until the precipitate has disappeared. Extraction was performed using ethylacetate and the extracts were dried over $MgSO_4$. This crude reaction mixture in CH_2Cl_2 is added to a stirred solution of PDC (2.0 mmol) and 4 Å molecular sieves in CH_2Cl_2 and the reaction is stirred until completion, then filtered through Celite and concentrated under reduced pressure. Purification by column chromatography furnished 2-methoxybenzophenones.

4.4. General procedure for demethylation to provide 2-hydroxybenzophenones

A solution of 1.0 mmol of 2-methoxybenzophenones in 6 mL of CH_2Cl_2 was added during 5 min to a well-stirred solution of 1.5 mmol of BBr_3 (1.0 M in CH_2Cl_2) at 0 °C. The reaction mixture was then quenched by the addition of crushed ice and NH_4Cl (aq). Extraction was performed using ethylacetate, the extracts were dried over $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography furnished the required 2-hydroxybenzophenones.

4.4.1. (2-Methoxyphenyl)(4-methylphenyl)methanone (**16**)

IR (neat) ν 3027 (w), 2944 (w), 2858 (w), 1664 (s), 1601 (s), 1488 (s), 1459 (s), 1435 (s), 1297 (s), 1262 (s), 1244 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 3.71 (s, 3H), 6.98 (d, J=8.4 Hz, 1H), 7.03 (t, J=7.6 Hz, 1H), 7.22 (d, J=8.0 Hz, 2H), 7.33 (dd, J=1.6, 7.6 Hz, 1H), 7.45 (ddd, J=1.6, 7.6, 8.4 Hz, 1H), 7.73 (d, J=8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5 (CH_3), 55.5 (CH_3), 111.4 (CH), 120.3 (CH), 128.8 (2×CH), 129.2 (CH), 129.9 (2×CH), 131.4 (CH), 135.2 (C), 143.6 (2×C), 157.1 (C), 195.9 (C); MS (EI, 70 eV) *m/z* (relative intensity) 226 (M^+, 88), 209 (32), 135 (100), 91 (65), 77 (41), 65 (37); HRMS (EI) calcd for $C_{15}H_{14}O_2$ (M^+) 226.0993, found 226.1003.

4.4.2. (4-Fluorophenyl)(2-methoxyphenyl)methanone (**18**)

IR (neat) ν 3074 (m), 3066 (w), 2944 (m), 2839 (m), 1677 (s), 1598 (s), 1488 (s), 1305 (s), 1295 (s), 1261 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.68 (s, 3H), 7.08–6.95 (m, 4H), 7.33–7.31 (m, 1H), 7.46–7.41 (m, 1H), 7.81–7.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4 (CH_3), 111.4 (CH), 115.2 (d, J=22.9 Hz, 2×CH), 120.5 (CH), 128.5 (C), 129.3 (CH), 131.9 (CH), 132.2 (d, J=9.2 Hz, 2×CH), 134.2 (C), 157.1 (C), 165.6 (d, J=253.5 Hz, CF), 194.7 (C); MS (EI, 70 eV) *m/z* (relative intensity) 230 (M^+, 69), 185 (14), 135 (100), 123 (79), 95 (97), 92 (45); HRMS (EI) calcd for $C_{14}H_{11}FO_2$ (M^+) 230.0743, found 230.0741.

4.4.3. 4-(2-Methoxybenzoyl)benzonitrile (**19**)

IR (neat) ν 3455 (br), 2834 (w), 2230 (m), 1658 (s), 1598 (s), 1487 (s), 1404 (m), 1311 (s), 1296 (s), 1259 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.67 (s, 3H), 6.98 (dd, J=0.8, 7.6 Hz, 1H), 7.06 (ddd, J=0.8, 7.6, 8.4 Hz, 1H), 7.41 (dd, J=2.0, 7.6 Hz, 1H), 7.51 (ddd, J=2.0, 7.6, 8.4 Hz, 1H), 7.70 (dd, J=2.0, 8.4 Hz, 2H), 7.84 (dd, J=2.0, 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5 (CH_3), 111.5 (CH), 115.7 (C), 118.2 (C), 120.9 (CH), 127.4 (C), 129.8 (CH×2), 130.1 (CH), 132.0 (CH×2), 133.1 (CH), 141.4 (C), 157.6 (C), 195.0 (C); MS (EI, 70 eV) *m/z* (relative intensity) 237 (M^+, 50), 206 (5), 135 (100), 130 (16), 107 (3), 102 (30); HRMS (EI) calcd for $C_{15}H_{11}NO_2$ 237.0799, found 237.0790.

4.4.4. (2-Methoxyphenyl)[4-(trifluoromethyl)phenyl]-methanone (**20**)

IR (neat) ν 3335 (w), 3069 (m), 3017 (m), 2972 (m), 2839 (w), 1675 (s), 1603 (s), 1510 (s), 1451 (s), 1326 (s), 1295 (s), 1245 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.69 (s, 3H), 6.98 (dd, J=1.2, 8.0 Hz, 1H), 7.05 (ddd, J=1.2, 6.8, 7.2 Hz, 1H), 7.40 (dd, J=1.8, 7.2 Hz, 1H), 7.49 (ddd, J=1.8, 6.8, 7.2 Hz, 1H), 7.67 (dd, J=0.8, 8.0 Hz, 2H), 7.87 (dd, J=0.8, 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.2 (CH_3), 111.3 (CH), 120.6 (CH), 123.6 (q, ^1J=270.1 Hz, CF_3), 125.0 (q, ^3J=3.8 Hz, CH×2), 127.7 (C), 129.6 (CH×2), 129.8 (CH), 132.6 (CH), 133.6 (q, ^2J=32.2 Hz, C), 140.8 (C), 157.4 (C), 195.1 (C); MS (EI, 70 eV) *m/z* (relative intensity) 280 (M^+, 43), 211 (12), 173 (17), 145 (38), 135 (100), 107 (7); HRMS (EI) calcd for $C_{15}H_{11}F_3O_2$ 280.0711, found 280.0713.

4.4.5. (2-Methoxyphenyl)(4-nitrophenyl)methanone (**21**)

IR (neat) ν 3105 (m), 2937 (m), 2838 (m), 1674 (s), 1602 (s), 1488 (m), 1465 (m), 1354 (s), 1261 (s) cm^{-1}; ^1H NMR

(400 MHz, $CDCl_3$) δ 3.64 (s, 3H), 6.97 (d, J=8.0 Hz, 1H), 7.04 (t, J=8.0 Hz, 1H), 7.42 (dd, J=1.6, 7.6 Hz, 1H), 7.49 (ddd, J=1.6, 7.6, 8.0 Hz, 1H), 7.86 (d, J=8.8 Hz, 2H), 8.21 (d, J=8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3 (CH_3), 111.5 (CH), 120.8 (2×CH), 123.2 (2×CH), 127.3 (CH), 130.1 (2×CH), 133.1 (CH), 143.0 (C), 149.8 (C), 157.5 (C), 194.5 (C); MS (EI, 70 eV) *m/z* (relative intensity) 257 (M^+, 28), 240 (18), 210 (16), 185 (9), 135 (100); HRMS (EI) calcd for $C_{14}H_{11}NO_4$ (M^+) 257.0688, found 257. 0675.

4.4.6. (2-Methoxyphenyl)(3-methyl-4-nitrophenyl)-methanone (**22**)

IR (neat) ν 3074 (w), 2937 (m), 2839 (m), 1674 (s), 1599 (s), 1578 (s), 1483 (s), 1349 (s), 1297 (s), 1257 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.58 (s, 3H), 3.67 (s, 3H), 6.98 (dd, J=0.8, 8.4 Hz, 1H), 7.04 (ddd, J=0.8, 7.6, 7.6 Hz, 1H), 7.40 (dd, J=2.0, 7.6 Hz, 1H), 7.49 (ddd, J=2.0, 7.6, 8.4 Hz, 1H), 7.63 (dd, J=1.2, 8.4 Hz, 1H), 7.74 (d, J=1.2 Hz, 1H), 7.91 (d, J=8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.1 (CH_3), 55.4 (CH_3), 111.4 (CH), 120.7 (CH), 124.3 (CH), 127.3 (C), 127.9 (CH), 130.0 (CH), 133.0 (CH), 133.3 (C), 133.3 (CH), 141.2 (C), 151.1 (C), 157.4 (C), 194.8 (C); MS (EI, 70 eV) *m/z* (relative intensity) 271 (M^+, 33), 256 (3), 164 (6), 136 (10), 135 (100), 121 (29), 77 (27); HRMS (EI) calcd for $C_{15}H_{13}NO_4$ 271.0845, found 271.0842.

4.4.7. 3-Methyl-4-nitrobenzaldehyde (**23**)

IR (neat) ν 3104 (w), 2854 (m), 2748 (w), 1703 (s), 1686 (s), 1519 (s), 1507 (s), 1459 (m), 1381 (s), 1358 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.63 (s, 3H), 7.82–7.84 (m, 2H), 8.02 (d, J=8.4 Hz, 1H), 10.05 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9 (CH_3), 125.2 (CH), 127.8 (CH), 133.8 (CH), 134.2 (C), 138.5 (C), 190.4 (CH); MS (EI, 70 eV) *m/z* (relative intensity) 165 (M^+, 13), 148 (100), 120 (17), 91 (40), 77 (17); HRMS (EI) calcd for $C_8H_7NO_3$ 165.0426, found 165.0424.

4.4.8. (2-Hydroxyphenyl)(4-methylphenyl)methanone (**7d**)

IR (neat) ν 3029 (br), 2912 (m), 2857 (m), 1624 (s), 1602 (s), 1483 (s), 1331 (m), 1304 (m), 1243 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 3H), 6.82–6.86 (m, 1H), 7.04 (d, J=8.0 Hz, 1H), 7.27 (d, J=7.6 Hz, 2H), 7.46 (t, J=8.0 Hz, 1H), 7.57 (d, J=7.6 Hz, 2H), 7.60 (d, J=1.6 Hz, 1H), 12.07 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4 (CH_3), 118.1 (CH), 118.3 (CH), 119.0 (C), 128.8 (2×CH), 129.3 (2×CH), 133.3 (CH), 134.9 (C), 135.9 (CH), 142.5 (C), 162.9 (C), 201.1 (C); MS (EI, 70 eV) *m/z* (relative intensity) 212 (M^+, 87), 211 (72), 197 (100), 121 (47), 120 (38), 119 (48); HRMS (EI) calcd for $C_{14}H_{12}O_2$ (M^+) 212.0837, found 212.0845.

4.4.9. (2-Hydroxyphenyl)(4-fluorophenyl)methanone (**7f**)

IR (neat) ν 3076 (br), 3053 (w), 1676 (w), 1627 (s), 1603 (s), 1590 (s), 1483 (s), 1446 (s), 1244 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (td, J=7.2, 1.2 Hz, 1H), 7.05 (d, J=8.0 Hz, 1H), 7.14–7.18 (m, 2H), 7.46–7.50 (m, 1H), 7.54 (dd, J=1.6, 8.0 Hz, 1H), 7.67–7.71 (m, 2H), 11.88 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.4 (d, J=22.4 Hz, 2×CH), 118.4 (CH), 118.9 (C), 131.7 (d, J=7.6 Hz, 2×CH), 133.1 (CH), 134.0 (C), 136.3 (CH), 163.1 (C), 165.9 (d, J=252 Hz, C), 199.8 (C); MS (EI, 70 eV) *m/z* (relative intensity) 216 (M^+, 100), 133 (4), 123 (53), 120 (34), 75 (14); HRMS (EI) calcd for $C_{13}H_9FO_2$ (M^+) 216.0588, found 216.0597.

4.4.10. 4-(2-Hydroxybenzoyl)benzonitrile (**7g**)

IR (neat) ν 2967 (w), 2930 (w), 2858 (w), 2233 (m), 1626 (s), 1590 (s), 1482 (s), 1439 (s), 1335 (s), 1244 (s), 1221 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (ddd, J=0.8, 7.2, 8.0 Hz, 1H), 7.08 (dd, J=0.8, 8.4 Hz, 1H), 7.43 (dd, J=1.6, 8.0 Hz, 1H), 7.54 (ddd, J=1.6, 7.2, 8.4 Hz, 1H), 7.74 (dd, J=2.0, 8.4 Hz, 2H), 7.80 (dd, J=2.0, 8.4 Hz, 2H), 11.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.2 (C), 117.8 (C), 118.4 (C), 118.7 (CH), 119.0 (CH), 129.4 (CH×2), 132.2 (CH×2), 137.2 (CH), 141.5 (C), 163.3 (C), 199.7 (C); MS (EI, 70 eV) *m/z* (relative intensity) 223 (M^+, 98), 222 (100), 197 (6), 130 (23), 121 (91), 102 (35), 93 (15); HRMS (EI) calcd for $C_{14}H_9NO_2$ 223.0633, found 223.0632.

4.4.11. (2-Hydroxyphenyl)[4-(trifluoromethyl)phenyl]-methanone (**7h**)

IR (neat) ν 3078 (w), 2926 (w), 1628 (s), 1612 (s), 1576 (s), 1483 (s), 1408 (s), 1324 (s), 1245 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (ddd, J=1.2, 7.2, 8.0 Hz, 1H), 7.07 (dd, J=1.2, 8.4 Hz, 1H), 7.48 (dd, J=1.6, 8.0 Hz, 1H), 7.52 (ddd, J=1.6, 7.2, 8.4 Hz, 1H), 7.79 (m, 4H), 11.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.6 (CH), 118.7 (C), 118.9 (CH), 123.6 (q, ^1J=270.9 Hz, CF_3), 125.39 (q, ^3J=3.8 Hz, CH×2), 129.3 (CH×2), 133.2 (CH), 133.3 (q, ^2J=32.9 Hz, C), 136.9 (CH), 141.0 (C), 163.4 (C), 200.3 (C); MS (EI, 70 eV) *m/z* (relative intensity) 266 (M^+, 82), 265 (50), 173 (22), 145 (35), 121 (100); HRMS (EI) calcd for $C_{14}H_9F_3O_2$ 266.0555, found 266.0555.

4.4.12. (2-Hydroxyphenyl)(4-nitrophenyl)methanone (**7i**)

IR (neat) ν 3105 (br), 3076 (s), 2937 (s), 2838 (s), 1674 (s), 1602 (s), 1488 (m), 1465 (s), 1354 (s), 1261 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (ddd, J=0.8, 7.6, 8.0 Hz, 1H), 7.09 (dd, J=0.8, 8.0 Hz, 1H), 7.42 (dd, J=1.6, 8.0 Hz, 1H), 7.55 (ddd, J=1.6, 7.6, 8.0 Hz, 1H), 7.81 (d, J=8.8 Hz, 2H), 8.35 (d, J=8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.5 (C), 118.8 (CH), 119.0 (CH), 123.6 (2×CH), 129.8 (2×CH), 133.0 (CH), 137.3 (CH), 143.1 (C), 149.5 (C), 163.4 (C), 199.5 (C); MS (EI, 70 eV) *m/z* (relative intensity) 243 (M^+, 100), 226 (54), 196 (89), 151 (12), 121 (98), 102 (12), 92 (7); HRMS (EI) calcd for $C_{13}H_9NO_4$ (M^+) 243.0532, found 243.0528.

4.4.13. (2-Hydroxyphenyl)(3-methyl-4-nitrophenyl) methanone (**7j**)

IR (neat) ν 3083 (w), 3043 (w), 2935 (w), 2864 (w), 1628 (s), 1605 (s), 1583 (s), 1522 (s), 1483 (s), 1446 (s), 1337 (s), 1310 (s), 1247 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65

(s, 3H), 6.88 (ddd, J=1.2, 8.0, 9.2 Hz, 1H), 7.08 (dd, J=0.8, 8.4 Hz, 1H), 7.45 (dd, J=1.2, 8.0 Hz, 1H), 7.54 (ddd, J=1.6, 8.0, 9.2 Hz, 1H), 7.58 (dd, J=1.6, 8.0 Hz, 1H), 7.61 (d, J=0.8 Hz, 1H), 8.05 (d, J=8.4 Hz, 1H), 11.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3 (CH_3), 118.6 (C), 118.7 (CH), 119.1 (CH), 124.6 (CH), 127.3 (CH), 133.0 (CH), 133.1 (CH), 133.9 (C), 137.2 (CH), 141.6 (C), 150.7 (C), 163.4 (C), 199.7 (C); MS (EI, 70 eV) *m/z* (relative intensity) 257 (M^+, 97), 242 (100), 240 (22), 211 (12), 197 (12), 121 (56); HRMS (EI) calcd for $C_{14}H_{11}NO_4$ 257.0688, found 257.0678.

*4.4.14. 3-(4-Methylphenyl)benzo[b]furan (**8d**)*

IR (neat) ν 3025 (w), 2919 (w), 2854 (w), 1578 (s), 1508 (s), 1451 (s), 1341 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.50 (s, 3H), 7.35–7.45 (m, 4H), 7.62–7.65 (m, 3H), 7.83 (s, 1H), 7.93 (dd, J=1.2, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1 (CH_3), 111.6 (CH), 120.3 (CH), 122.1 (C), 122.8 (CH), 124.4 (CH), 126.6 (C), 127.6 (C), 127.3 (2×CH), 129.0 (C), 129.6 (2×CH), 137.1 (C), 140.9 (CH), 155.8 (C); MS (EI, 70 eV) *m/z* (relative intensity) 208 (M^+, 100), 207 (12), 115 (11), 102 (4); HRMS (EI) calcd for $C_{15}H_{12}O$ (M^+) 208.0888, found 208.0884.

*4.4.15. 4-(1-Benzofuran-3-yl)benzonitrile (**8g**)*

IR (neat) ν 3448 (br), 3103 (w), 2233 (m), 2226 (s), 1611 (s), 1577 (m), 1449 (s), 1343 (w), 1276 (w), 1219 (s), 1109 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (ddd, J=1.2, 7.2, 7.2 Hz, 1H), 7.38 (ddd, J=1.6, 7.2, 7.2 Hz, 1H), 7.56 (dd, J=1.2, 7.2 Hz, 1H), 7.72 (m, 4H), 7.79 (dd, J=1.6, 7.2 Hz, 1H), 7.85 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.8 (C), 112.0 (CH), 118.8 (C), 119.9 (CH), 120.8 (C), 123.5 (CH), 125.1 (CH), 125.4 (C), 127.6 (CH×2), 132.7 (CH×2), 136.9 (C), 142.5 (CH), 155.8 (C); MS (EI, 70 eV) *m/z* (relative intensity) 220 (M+1, 22), 219 (M^+, 100), 190 (53); HRMS (EI) calcd for $C_{15}H_9NO$ 219.0684, found 219.0688.

*4.4.16. 3-(4-Fluorophenyl)benzo[b]furan (**8f**)*

IR (neat) ν 3056 (w), 1596 (m), 1570 (m), 1505 (s), 1452 (s), 1341 (m), 1271 (s), 1108 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (m, 2H), 7.32–7.41 (m, 2H), 7.58–7.62 (m, 2H), 7.75 (s, 1H), 7.81 (ddd, J=0.8, 0.8, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.7 (CH), 115.8 (d, J=21.4 Hz, 2×CH), 120.0 (CH), 121.3 (C), 123.0 (CH), 124.6 (CH), 126.3 (C), 128.0 (C), 129.0 (d, J=7.6 Hz, 2×CH), 141.1 (CH), 155.7 (C), 162.2 (d, J=244 Hz, CF); MS (EI, 70 eV) *m/z* (relative intensity) 212 (M^+, 100), 184 (6), 183 (42), 182 (4); HRMS (EI) calcd for $C_{14}H_9OF$ (M^+) 212.0637, found 212.0647.

*4.4.17. 3-[4-(Trifluoromethyl)phenyl]-1-benzofuran (**8h**)*

IR (neat) ν 3120 (w), 3057 (w), 1912 (w), 1683 (m), 1652 (s), 1622 (s), 1558 (m), 1506 (m), 1451 (s), 1413 (s), 1327 (s), 1265 (s), 1219 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (ddd, J=1.2, 7.2, 7.2 Hz, 1H), 7.38 (ddd, J=1.6, 7.2, 7.2 Hz, 1H), 7.57 (dd, J=1.2, 7.2 Hz, 1H), 7.71–7.76 (m, 4H), 7.81 (dd, J=1.6, 7.2 Hz, 1H), 7.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.3 (C), 111.9 (CH), 120.1 (CH), 121.1 (C), 123.3 (CH), 124.2 (q, ^1J=270.2 Hz, CF_3), 124.9 (CH), 125.9 (q, ^3J=3.8 Hz, CH×2), 127.5 (CH×2), 129.4 (q, ^2J=32.5 Hz, C), 135.8 (C), 142.0 (CH), 155.8 (C); MS (EI, 70 eV) *m/z* (relative intensity) 263 (M^++1, 11), 262 (M^+, 100), 165 (28); HRMS (EI) calcd for $C_{15}H_9F_3O$ 262.0605, found 262.0607.

*4.4.18. 2-[4-(Allyloxy)-2-hydroxyphenyl]-1-phenyl-1-ethanone (**9a**)*

IR (film) ν 3150 (m), 3041 (w), 1690 (s), 1640 (m), 1589 (m), 743 (s), 693 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.19 (s, 2H), 4.46 (d, J=4.8 Hz, 2H), 5.24 (dd, J=1.2, 8.4 Hz, 1H), 5.35 (dd, J=1.2, 14.0 Hz, 1H), 5.97–6.04 (m, 1H), 6.44 (dd, J=2.8, 8.8 Hz, 1H), 6.53 (d, J=2.4 Hz, 1H), 7.03 (d, J=8.0 Hz, 1H), 7.48 (t, J=8.0 Hz, 2H), 7.60 (t, J=7.2 Hz, 1H), 8.07 (d, J=7.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.3 (CH_2), 68.8 (CH_2), 104.0 (CH), 107.4 (CH), 113.3 (C), 117.6 (CH_2), 128.8 (2×CH), 129.0 (2×CH), 131.3 (CH), 133.1 (CH), 134.0 (CH), 135.7 (C), 156.5 (C), 159.3 (C), 201.4 (C); MS (EI, 70 eV) *m/z* (relative intensity) 268 (27), 250 (24), 210 (15), 209 (86), 163 (86), 152 (10), 105 (28); HRMS (EI) calcd for $C_{17}H_{16}O_3$ (M^+) 268.1099, found 268.1101.

*4.4.19. 2-(2-Hydroxy-4-methoxyphenyl)-1-phenyl-1-ethanone (**9c**)*

IR (neat) ν 3378 (s), 2909 (s), 2837 (s), 1677 (s), 1619 (s), 1596 (s), 1465 (m), 1447 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (s, 3H), 4.19 (s, 2H), 6.42 (dd, J=2.8, 8.4 Hz, 1H), 6.51 (d, J=2.4 Hz, 1H), 7.03 (d, J=8.4 Hz, 1H), 7.45–7.49 (m, 2H), 7.57–7.60 (m, 1H), 8.05–8.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.4 (CH_2), 55.3 (CH_3), 103.3 (CH), 106.8 (CH), 113.1 (C), 128.8 (2×CH), 129.0 (2×CH), 131.4 (CH), 134.0 (CH), 135.8 (C), 156.7 (C), 160.5 (C), 201.4 (C); MS (EI, 70 eV) *m/z* (relative intensity) 242 (M^+, 26), 151 (15), 137 (100), 105 (45), 77 (42); HRMS (EI) calcd for $C_{15}H_{14}O_3$ (M^+) 242.0943, found 242.0954.

*4.4.20. 2-(2-Hydroxyphenyl)-1-(4-methylphenyl)-1-ethanone (**9d**)*

IR (neat) ν 3424 (br), 3024 (w), 2961 (w), 2915 (w), 1675 (s), 1608 (m), 1596 (m), 1456 (m), 1341 (m), 1268 (w), 1224 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 4.24 (s, 2H), 6.85 (t, J=7.6 Hz, 1H), 6.93 (d, J=7.6 Hz, 1H), 7.14 (t, J=7.6 Hz, 2H), 7.27 (d, J=8.4 Hz, 2H), 7.98 (d, J=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6 (CH_3), 40.8 (CH_2), 117.5 (CH), 120.6 (CH), 121.2 (C), 128.8 (CH), 129.1 (2×CH), 129.4 (2×CH), 130.8 (CH), 133.3 (C), 145.0 (C), 155.6 (C), 200.7 (C); MS (EI, 70 eV) *m/z* (relative intensity) 226 (M^+, 14), 121 (100), 95 (27); HRMS (EI) calcd for $C_{15}H_{14}O_2$ (M^+) 226.0993, found 226.1004.

*4.4.21. 1-(4-Fluorophenyl)-2-(2-hydroxyphenyl)-1-ethanone (**9f**)*

IR (neat) ν 3424 (s), 2538 (s), 1677 (s), 1598 (s), 1454 (s), 1464 (m), 1344 (m), 1217 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.24 (s, 2H), 6.86 (dd, J=7.2, 7.6 Hz, 1H), 6.93 (d, J=7.6 Hz, 1H), 7.18–7.13 (m, 4H), 8.13–8.09 (m, 2H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 40.8 (CH_2), 116.0 (CH), 116.4 (d, J=22.9 Hz, 2×CH), 120.5 (CH), 123.0 (C), 129.2 (CH), 132.0 (CH), 132.4 (d, J=9.2 Hz, 2×CH), 134.7 (C), 156.2 (C), 167.0 (d, J=250.4 Hz, CF), 199.3 (C); MS (EI, 70 eV) *m/z* (relative intensity) 230 (M^+, 30), 123 (100), 107 (9), 95 (30); HRMS (EI) calcd for $C_{14}H_{11}FO_2$ (M^+) 230.0743, found 230.0736.

*4.4.22. 4-[(2-Hydroxyphenyl)acetyl]benzonitrile (**9g**)*

IR (neat) ν 3431 (s), 3068 (w), 2924 (w), 2852 (w), 2242 (m), 1683 (s), 1558 (s), 1506 (s), 1457 (s), 1401 (s), 1339 (s), 1268 (m), 1213 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.28 (s, 2H), 6.43 (br, 1H), 6.87 (dd, J=1.2, 7.6 Hz, 1H), 6.99 (ddd, J=1.2, 7.2, 7.6 Hz, 1H), 7.14 (dd, J=1.6, 7.2 Hz, 1H), 7.17 (ddd, J=1.6, 7.6, 7.6 Hz, 1H), 7.77 (dd, J=2.0, 6.4 Hz, 2H), 8.14 (dd, J=2.0, 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.9 (CH_2), 116.8 (C), 117.0 (CH), 117.8 (C), 120.3 (C), 121.2 (CH), 129.2 (CH×2), 129.2 (CH), 131.1 (CH), 132.6 (CH×2), 139.1 (C), 154.6 (C), 198.5 (C); MS (EI, 70 eV) *m/z* (relative intensity) 238 (M+1, 12), 237 (M^+, 72), 130 (100), 107 (36), 102 (16); HRMS (EI) calcd for $C_{15}H_{11}NO_2$ 237.0790, found 237.0778.

*4.4.23. 2-(2-Hydroxyphenyl)-1-[4-(trifluoromethyl)phenyl]-ethanone (**9h**)*

IR (neat) ν 3435 (s), 1682 (s), 1596 (m), 1458 (m), 1405 (m), 1341 (m), 1327 (m), 1312 (m), 1259 (m), 1118 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.29 (s, 2H), 6.83 (br, 1H), 6.86–6.90 (m, 2H), 7.14–7.18 (m, 2H), 7.73 (dd, J=0.8, 8.0 Hz, 2H), 8.16 (dd, J=0.8, 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.9 (CH_2), 117.1 (CH), 120.5 (C), 121.1 (CH), 123.5 (q, ^1J=270.9 Hz, CF_3), 125.8 (q, ^3J=3.8 Hz, CH×2), 129.1 (CH), 129.2 (CH×2), 131.0 (CH), 134.9 (q, ^2J=32.5 Hz, C), 138.7 (C), 154.8 (C), 199.3 (C); MS (EI, 70 eV) *m/z* (relative intensity) 280 (M^+, 26), 173 (100), 145 (41), 107 (57), 77 (29); HRMS (EI) calcd for $C_{15}H_{11}F_3O_2$ 280.0711, found 280.0714.

*4.4.24. 6-Allyloxy-2-phenyl-1-benzofuran (**10a**)*

IR (film) ν 3082 (m), 2915 (w), 1619 (s), 1566 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.60 (d, J=5.2 Hz, 2H), 5.33 (dd, J=1.2, 5.2 Hz, 1H), 5.47 (dd, J=1.2, 8.8 Hz, 1H), 6.07–6.16 (m, 1H), 6.91 (dd, J=2.4, 4.4 Hz, 1H), 6.94 (s, 1H), 7.09 (d, J=1.2 Hz, 1H), 7.32 (dt, J=0.4, 7.2 Hz, 1H), 7.41–7.45 (m, 3H), 7.82 (d, J=4.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 69.4 (CH_2), 97.1 (CH), 101.1 (CH), 112.6 (CH), 117.7 (CH_2), 121.0 (CH), 122.8 (C), 124.5 (2×CH), 128.0 (CH), 128.7 (2×CH), 130.7 (C), 133.3 (CH), 155.2 (C), 155.8 (C), 157.0 (C); MS (EI, 70 eV) *m/z* (relative intensity) 250 (24), 209 (100), 153 (15.3), 152 (33.2), 128 (64), 105 (14.2); HRMS (EI) calcd for $C_{17}H_{14}O_2$ (M^+) 250.0994, found 250.0986.

*4.4.25. 6-Methoxy-2-phenylbenzo[b]furan (**10c**)*

IR (neat) ν 3113 (w), 3007 (w), 2965 (w), 2838 (w), 1615 (s), 1560 (s), 1488 (s), 1450 (s), 1298 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 6.86 (dd, J=2.0, 8.4 Hz, 1H), 6.94 (s, 1H), 7.07 (d, J=2.0 Hz, 1H), 7.29–7.33 (m, 1H), 7.40–7.44 (m, 3H), 7.80–7.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.7 (CH_3), 95.9 (CH), 101.1 (CH), 111.9 (CH), 120.9 (CH), 122.6 (C), 124.4 (2×CH), 128.0 (CH), 128.7 (2×CH), 130.7 (C), 155.2 (C), 156.0 (C), 158.1 (C); MS (EI, 70 eV) *m/z* (relative intensity) 224 (M^+, 82) 209 (100), 153 (33), 77 (15); HRMS (EI) calcd for $C_{14}H_{12}O_4$ (M^+) 224.0837, found 224.0825. Anal. Calcd for $C_{14}H_{12}O_4$: C, 80.34; H, 5.39. Found: C, 80.46; H, 5.44.

*4.4.26. 2-(4-Fluorophenyl)benzo[b]furan (**10f**)*

IR (neat) ν 3066 (w), 2928 (w), 2853 (w), 1600 (s), 1504 (s), 1452 (s), 1300 (m), 1234 (m), 1097 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.93 (s, 1H), 7.10–7.15 (m, 2H), 7.21–7.30 (m, 2H), 7.50 (d, J=8.0 Hz, 1H), 7.57 (dd, J=0.8, 8.0 Hz, 1H), 7.80–7.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 101.0 (CH), 111.1 (CH), 115.8 (d, J=22.9 Hz, 2×CH), 120.8 (CH), 123.0 (CH), 124.2 (CH), 126.7 (d, J=7.6 Hz, 2×CH), 129.2 (C), 154.9 (C), 155.0 (C), 162.9 (d, J=247.3 Hz, C); MS (EI, 70 eV) *m/z* (relative intensity) 212 (M^+, 100), 183 (34), 157 (4), 106 (3); HRMS (EI) calcd for $C_{14}H_{12}O_4$ (M^+) 212.0637, found 212.0629.

*4.4.27. 4-(1-Benzofuran-2-yl)benzonitrile (**10g**)*

IR (neat) ν 2226 (m), 1734 (m), 1684 (s), 1653 (s), 1558 (s), 1506 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, J=0.8 Hz, 1H), 7.25 (ddd, J=0.8, 7.2, 7.6 Hz, 1H), 7.34 (ddd, J=1.2, 7.2, 8.4 Hz, 1H), 7.52 (dd, J=0.8, 8.4 Hz, 1H), 7.61 (ddd, J=0.8, 1.2, 7.6 Hz, 1H), 7.70 (dd, J=1.6, 8.0 Hz, 2H), 7.92 (dd, J=1.6, 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 104.3 (CH), 111.4 (CH), 111.5 (C), 118.7 (C), 121.5 (CH), 123.4 (CH), 125.1 (CH×2), 125.5 (CH), 128.6 (C), 132.6 (CH×2), 134.4 (C), 153.5 (C), 155.2 (C); MS (EI, 70 eV) *m/z* (relative intensity) 220 (M+1, 24), 219 (M^+, 100), 190 (68), 164 (19), 163 (11); HRMS (EI) calcd for $C_{15}H_9NO$ 219.0684, found 219.0697.

*4.4.28. 2-[4-(Trifluoromethyl)phenyl]-1-benzofuran (**10h**)*

IR (neat) ν 2919 (w), 2851 (w), 1681 (w), 1652 (w), 1610 (w), 1506 (m), 1472 (m), 1412 (m), 1326 (m), 1294 (m), 1163 (s), 1108 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J=0.8 Hz, 1H), 7.24 (ddd, J=0.8, 7.2, 7.6 Hz, 1H), 7.32 (ddd, J=1.2, 7.2, 8.4 Hz, 1H), 7.53 (dd, J=0.8, 8.4 Hz, 1H), 7.60 (ddd, J=0.8, 1.2, 7.6 Hz, 1H), 7.68 (dd, J=0.8, 8.0 Hz, 1H), 7.95 (dd, J=0.8, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 103.2 (CH), 111.3 (CH), 121.3 (CH), 123.3 (CH), 124.1 (q, ^1J=270.1 Hz, CF_3), 124.9 (CH×2), 125.1 (CH), 125.8 (q, ^3J=3.8 Hz, CH×2), 128.8 (C), 130.1 (q, ^2J=32.2 Hz, C), 133.7 (C), 154.2 (C), 155.1 (C); MS (EI, 70 eV) *m/z* (relative intensity) 263 (M+1, 18), 262 (M^+, 100), 165 (36), 106 (10); HRMS (EI) calcd for $C_{15}H_9F_3O$ 262.0605, found 262.0602.

*4.4.29. 1-(2-Hydroxyphenyl)-2-(3-methyl-4-nitrophenyl)-ethanone (**12j**)*

IR (neat) ν 3056 (br), 2973 (w), 2931 (w), 2856 (w), 1636 (s), 1612 (s), 1581 (m), 1520 (s), 1487 (s), 1447 (s), 1340 (s), 1273 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.59 (s, 3H), 4.35 (s, 2H), 6.92 (ddd, J=1.2, 7.6, 8.0 Hz, 1H), 6.99 (dd,

J=1.2, 8.4 Hz, 1H), 7.21–7.23 (m, 2H), 7.49 (ddd, J=1.6, 7.6, 8.4 Hz, 1H), 7.81 (dd, J=1.6, 8.0 Hz, 1H), 7.96 (d, J=8.4 Hz, 1H), 11.99 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6 (CH_3), 44.4 (CH_2), 118.7 (C), 118.8 (CH), 119.2 (CH), 125.1 (CH), 128.1 (CH), 130.0 (CH), 134.0 (CH), 134.2 (C), 137.0 (CH), 139.5 (C), 148.1 (C), 162.8 (C), 202.3 (C); MS (EI, 70 eV) *m/z* (relative intensity) 271 (M^+, 3), 121 (100), 93 (10), 65 (14); HRMS (EI) calcd for $C_{15}H_{13}NO_4$ 271.0845, found 271.0850.

*4.4.30. tert-Butyl(dimethyl)[2-(1-phenylvinyl)phenoxy]-silane (**24**)*

IR (neat) ν 3059 (m), 3028 (m), 2956 (s), 2929 (s), 2884 (m), 2857 (s), 1942 (w), 1800 (w), 1612 (m), 1596 (s), 1574 (m), 1495 (s), 1486 (s), 1448 (s), 1276 (s), 1249 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.03 (s, 6H), 1.69 (s, 9H), 5.27, 5.30 (abq, J=1.2 Hz, 2H), 6.80 (dd, J=0.8, 8.4 Hz, 1H), 6.95 (ddd, J=1.2, 7.2, 7.2 Hz, 1H), 7.19–7.29 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.9 (C), 25.4 ($CH_3\times5$), 115.2 (CH_2), 119.2 (CH), 121.0 (CH), 126.5 (CH×2), 127.3 (CH), 128.0 (CH×2), 128.7 (CH), 131.7 (CH), 133.3 (C), 140.6 (C), 147.5 (C), 153.1 (C); MS (EI) *m/z* (relative intensity) 254 (M−56, 21), 53 (M−57, 100), 151 (11), 57 (8); HRMS (EI) calcd for $C_{20}H_{26}OSi$ 310.1753, found 253.1046 (M−57).

*4.4.31. tert-Butyl(dimethyl)[2-(2-phenyloxiran-2-yl)-phenoxy]silane (**15**)*

IR (neat) ν 3068 (m), 3041 (m), 2960 (s), 2933 (s), 2891 (m), 2856 (s), 1728 (w), 1597 (m), 1574 (m), 1493 (s), 1460 (s), 1450 (s), 1276 (s), 1253 (s), 1097 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.14 (s, 3H), 0.19 (s, 3H), 0.76 (s, 9H), 3.19, 3.26 (abq, J=5.6 Hz, 2H), 6.84 (dd, J=0.8, 8.0 Hz, 1H), 6.96 (ddd, J=1.2, 7.2, 7.2 Hz, 1H), 7.16–7.25 (m, 6H), 7.40 (dd, J=1.6, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.9 (C), 25.4 ($CH_3\times5$), 57.5 (CH_2), 59.2 (C), 117.8 (CH), 120.7 (CH), 126.0 (CH×2), 127.4 (CH), 127.9 (CH×2), 129.2 (CH), 129.7 (C), 130.2 (CH), 140.1 (C), 154.2 (C); MS (EI) *m/z* (relative intensity) 326 (M^+, 16), 270 (23), 269 (100), 195 (2), 77 (3); HRMS (EI) calcd for $C_{20}H_{26}O_2Si$ 326.1702, found 326.1718.

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Supplementary data

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