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Intriguing formal [2+3] cycloaddition promoted by a hypervalent iodine reagent

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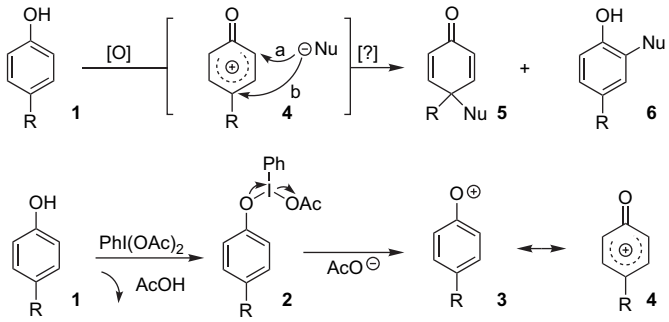
ABSTRACT

Treatment of various substituted phenols in the presence of iodobenzene diacetate, perfluorinated alcohols and furan, allylsilanes or cyclic enol ethers promotes an oxidative annulation process in moderate to useful yields. In only one step, this method produces different heterocyclic rings such as dihydrofuranobenzofurans, tetrahydrofuranobenzofurans, tetrahydropyranofurans, and dihydrobenzofurans.

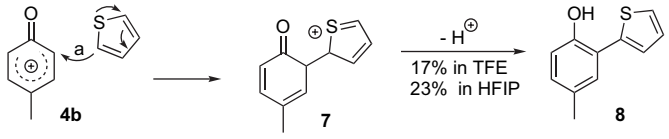
1. Introduction

The potential of iodobenzene diacetate (DIB), an environmentally benign and inexpensive reagent, is now well known.[1] This reagent promotes noteworthy oxidative transformations of phenol[2] and aniline[3] derivatives, in a manner consistent with the recent requirements for green chemical processes. As observed by Kita,[4] DIB reactions generally occur best in solvents such as trifluoroethanol (TFE) or hexafluoroisopropanol (HFIP).[5] Under these conditions, oxidative attack of phenols in the presence of unhindered heteronucleophiles[6] tends to proceed through pathway b to afford compound **5**. The species **4** would arise through DIB activation of the phenol **1**, Scheme 1.



Scheme 1.

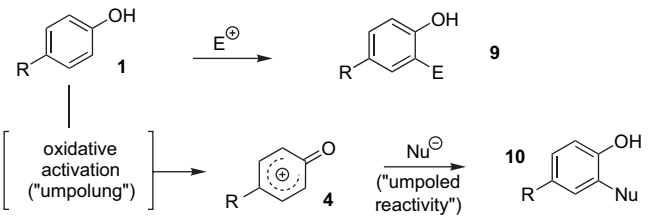
However, we recently determined that carbon-based nucleophiles such as thiophene[7] attack the presumed intermediate **4** at a position adjacent to the carbonyl group (pathway a), resulting in the formation of products **8**, albeit in low yield (Scheme 2).



Scheme 2.

Although compound **8** is obtained in low yield, this result opens a new opportunity in organic synthesis. As a matter of fact, this transformation would proceed by an electrophilic substitution on position 2 of thiophene with intriguing electrophile species **4**. Formally, this transformation may be termed as an 'aromatic ring umpolung'. Whereas an electron-rich aromatic nucleus, such as a phenol, normally reacts as a nucleophile and suitable oxidative activation can convert it to a reactive electrophilic intermediate. The high electronegativity of the oxygen atom in **3** was likely to render this transient intermediate short-lived, excessively electrophilic, and consequently very reactive, which may be intercepted with external mild nucleophiles such as thiophene (Scheme 3).

In order to develop and improve this 'novel' transformation, different carbon-based nucleophiles have been envisaged for the



Scheme 3.

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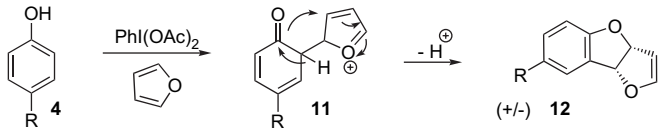
formation of new C–C bonds. These attempts have led to an unexpected reaction that proceeds via a formal [2+3] cycloaddition.

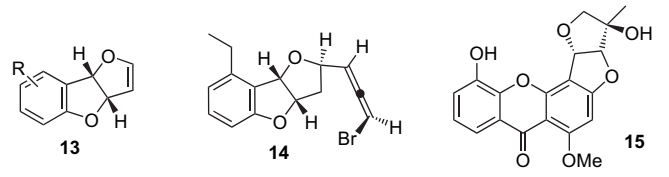
2. Formal cycloaddition with furan

Interestingly, the use of furan in lieu of thiophene in the same reaction produces none of the biaryl. Instead, it efficiently leads to tricyclic compounds **12** resulting from a formal oxidative [2+3] cycloaddition (Scheme 4). The reaction, in this case, is best carried out in TFE as the solvent (not HFIP; vide infra) and in the presence of furan.[8]



Scheme 4.

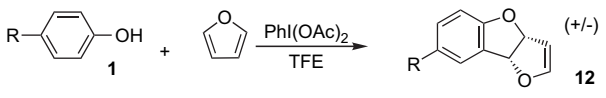
The difference between the behavior of thiophene and furan in otherwise identical reactions may be rationalized considering that the formation of the biaryl versus the tricyclic compound **12** depends on the stability of the sulfonium **7** versus the oxonium **11** generated in the media. These results can be explained if we consider that furan has a weaker aromatic character than thiophene. Thus, the formed oxonium can be trapped by a nucleophilic attack of the hydroxy and leads to **12**, whereas the sulfonium is transformed faster to the thiophene derivative via an elimination of the first order leading to the biaryl **8**. This latter species, electron richer than the starting material is probably rapidly over oxidized into inextractable tars of by-products; this may explain the low yield of this transformation with thiophene. However, this intriguing novel cyclization allows expeditious entry to the unusual dihydrofurobenzofuran[9] skeleton **13**, a ring system present in natural products such as panacene **14**, a shark antifeedant,[10] psorofebrin **15**, an antileukemic xanthone,[11] and other bioactive substances[12] (Scheme 5).



Scheme 5.

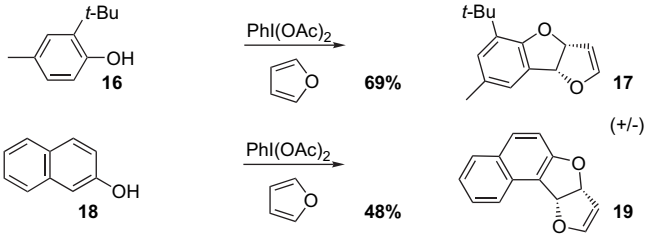
Thus, to verify the scope of this novel reaction, various substituted phenols were converted to **12** in 38–61% yield. A summary of representative experiments with *para*-substituted phenols appears in Table 1. It is worthy of note that the reaction tolerates moderately nucleophilic functionalities, such as a sulfonamide, which may be present on the substrate phenol (cf. entry **e**). A 4-trimethylsilyl group is also readily tolerated (cf. entry **f**).

Table 1



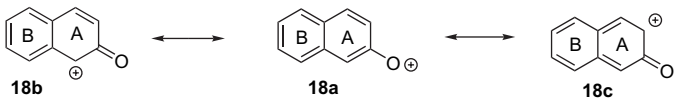
Entry	R	Yield
a	*t*-Bu	61
b	Me	38
c	OMe	41
d	CH_2COOMe	52
e	CH_2CH_2NHTs	47
f	$SiMe_3$	59

This reaction can be usefully extended to polysubstituted aromatic phenols such as **16** or polycyclic ones such as 2-naphthol **18** (Scheme 6). In the case of **17**, it seems to indicate that the process is fairly insensitive to steric effects. In fact, **16** is quickly converted to **17** in good yield despite the presence of a bulky *tert*-butyl group at the *ortho* position of the phenolic OH. Moreover, a unique cycloadduct is observed with 2-naphthol.



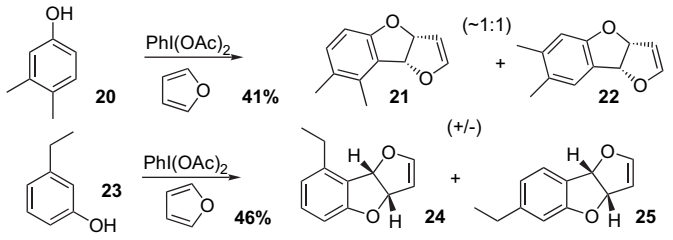
Scheme 6.

The selectivity observed on compound **19** might be explained by the fact that the electronegative oxygen in **18a** would delocalize the presumed cationic charge into ring A, with aromatic ring B in **18b** making this mesomer a stronger contributor to the overall delocalized system in comparison to **18c**. No O-alkylation is observed; we thought this point would be the key aspect of the transformation (Scheme 7).



Scheme 7.

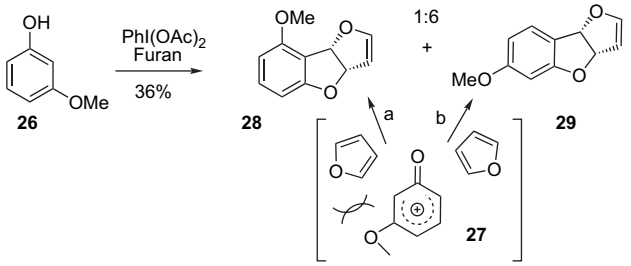
On the other hand, a very poor selectivity is observed with *meta* alkyl substituted phenol. Indeed, oxidation of 3,4-xylenol **20** leads to an inseparable ~1:1[13] mixture of compounds **21** and **22** in 41% yield (Scheme 8). Evidently, the methyl group at the *meta* position exerts an insufficient degree of regiocontrol. In addition, oxidation of 3-ethyl phenol **23** at −10 °C leads to a mixture 2:3 of compounds **24** and **25** with a global yield of 46%. It should be stressed that, if the reaction is conducted at −30 °C, we observe a small augmentation of the selectivity to 11:14.[13] Experiments carried out at lower temperature did not provide better results.



Scheme 8.

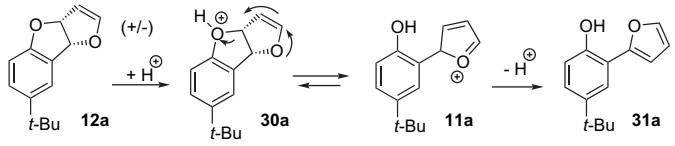
This reaction on 3-methoxy phenol **26** leads to corresponding cycloadducts **28** and **29** with selectivity (~1:6) in favor of **29**.[13] It should be noted that the methoxy group at position 3 exerts a better degree of regiocontrol than the ethyl group of **23**, probably due to a stereoelectronic control. Indeed, electronic repulsion of the lone pairs of oxygen would disfavor the approach of the furan by pathway a in favor of pathway b (Scheme 9).

Compounds such as **12** are stable under neutral conditions and can be chromatographed without incident. However, substoichiometric amounts of strong protonic acids, such as TFA, induce rapid and quantitative isomerization to biaryls. This is exemplified in Scheme 10 by the conversion of **12a** to **31a**. Phenols **31** are significantly more electron-rich than the starting species **4**.



Scheme 9.

Consequently, they are more readily oxidized by DIB than the corresponding starting phenols, resulting in the formation of intractable polymeric materials. Thus, it is essential to minimize formation of **31** during the main oxidative process. In a sense, the heterobicyclic system in **12** serves as a protecting group for the phenolic functionality, and it prevents undesirable side reactions of the latter and would explain why this reaction is rather inefficient with thiophene.



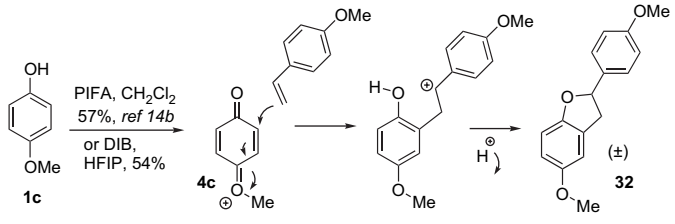
Scheme 10.

Available evidence suggests that compounds **12** are fairly stable in media containing moderately acidic TFE. In contrast, the significantly more acidic HFIP appears to promote the conversion to **31** in many cases, resulting in over oxidation and the ultimate formation of much polymeric matter. We believe this to be the reason why TFE, not HFIP, is the optimal reaction solvent in the present case. Even so, we suspect that some loss of product through the above sequence of events (formation of **31** and further oxidation) may occur even during reactions run in TFE, because more than 1 equiv of DIB is required to oxidize all the starting phenol.

3. Electrons-rich alkenes

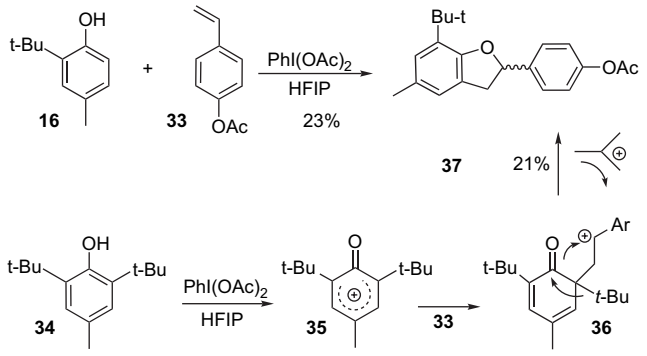
We have also been interested in checking whether this reaction could be extended to general alkenes sufficiently reactive to lead to cycloadducts. In the literature and especially in the work of Swenton's group, a similar process is described in aprotic solvents between electrons-rich aromatics such as methoxy phenol derivatives or isoeugenol and alkenes such as 4-methoxystyrene derivatives.[14] In such case, it would proceed through a quinonium intermediate due to the presence of a methoxy group at position 4. In the presence of a quinonium species, this reaction is efficient in protic or aprotic solvents with a similar yield (Scheme 11). Other similar processes using quinonium or radical species deserve to be mentioned.[15]

This reaction can be extended to regular substituted phenols in protic solvents to produce the corresponding dihydrobenzofuran core. The difference in reactivity between formal cycloaddition



Scheme 11.

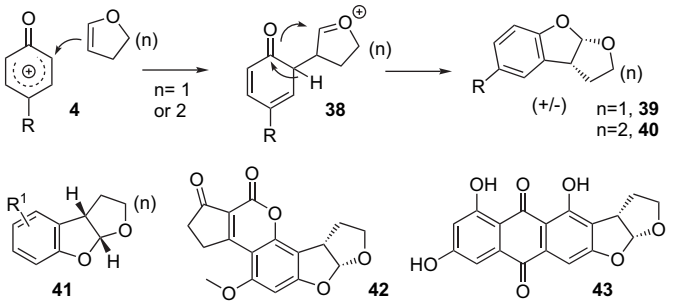
developed in aprotic versus protic solvents may result in the difference in stability of the electrophilic species **4**. Indeed, in aprotic solvents, the excessively reactive intermediate should quickly polymerize, if it is not stabilized by a lone pair of a donor group such as a methoxy (via a quinonium species). In protic and poor nucleophilic solvents, such as TFE or HFIP (Kita's conditions), this corresponding electrophilic intermediate would be stabilized by the solvent and would be sufficiently 'stable' to react with alkenes. Thus, these protic conditions would allow this formal cycloaddition to be extended to a large range of phenols. With a slightly electron-rich alkene such as 4-acetoxystyrene **33**, we observe a loss of yield. Indeed, oxidation of compound **16** in the presence of **33**, under these conditions, leads to **37** in 23% yield and demonstrates that this reaction is more efficient with electron richer-alkenes. The presence of a hypothetical cation on **4** is intriguing.[16] To bring a new element, the same reaction has been carried out with **34**. The oxidation of the latter leads to **37** with an unprecedented *ipso* rearrangement, probably due to the stability of the tertiary carbocation generated in situ; it would confirm the presence of a cationic species (Scheme 12).



Scheme 12.

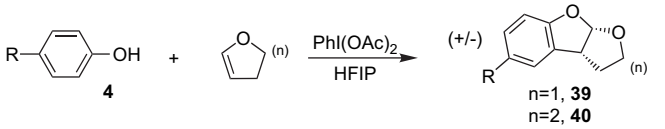
In the case of **34**, it seems to indicate that the oxidation process is fairly insensitive to steric effects. On this basis, this reaction would proceed through a cationic intermediate. To verify this hypothesis, we have investigated the reactivity of numerous alkenes. A reasonable choice to extend this reaction to enol ethers could be the use of compounds such as dihydrofuran (DHF, n=1) due to their similarity to furan. Indeed, our first results led to the corresponding tricyclic rings in moderate yield. This reaction occurs also with dihydropyran (DHP, n=2). The selectivity observed is consistent with a cationic process to afford tetrahydrofurobenzofuran **39** or dihydropyranobenzofuran cores **40** (Scheme 14). Moreover, this novel extension of this reaction would be potentially useful in the synthesis of natural products. Indeed, this system occurs in compounds (n=1) such as aflatoxin B_2, **42**, a food borne mutagenic metabolite of *Aspergillus flavus* and versicolorin B_2, **43**, isolated from *Aspergillus parasiticus*.[17] The 'direct oxidative [2+3] cycloaddition' between a phenol and DHF, according to the format of Scheme 13, seems to be a potentially short route to synthesize these compounds. In the literature, different ways are known to get such tricyclic acetal ring systems.[18]

However, for the enol ether variant, the best solvent for this reaction is HFIP. Indeed, reaction with TFE provides a mixture (~1:1) of desired compound and a byproduct such as **5** resulting from a nucleophilic attack of TFE in the *para* position (as shown in Scheme 1, pathway b). This information lets us suppose that furan reacts faster than enol ether. Indeed, no compound such as **5** is observed in the same conditions with furan. Fortunately, the tricyclic acetal ring is sufficiently stable to survive in acidic conditions generated in the medium by HFIP. A summary of representative experiments with *para*-substituted phenols appears in Table 2.



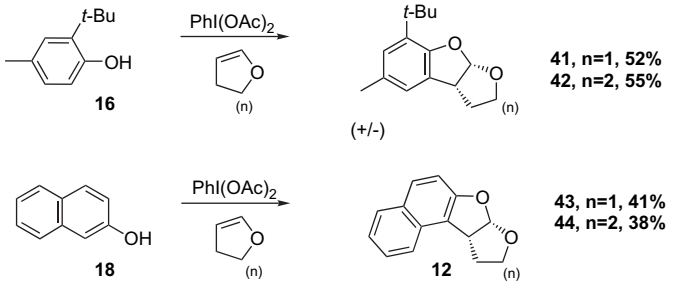
Scheme 13.

Table 2



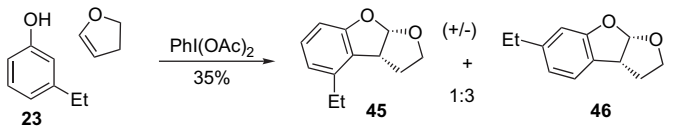
Entry	R	Yield (n=1)	Yield (n=2)
a	*t*-Bu	52	55
b	Cl	37	40
c	Br	30	32
d	$SiMe_3$	42	41
e	Ph	32	29

This reaction also succeeds with polysubstituted phenols such as **16** and with polycyclic ones such as β-naphthol **18** (Scheme 14).



Scheme 14.

To verify the influence of the steic effect of a substituent at the *meta* position, 3-ethyl phenol was oxidized. Although the cycloaddition occurs with furan, as previously, a different ratio (1:3) is obtained. Indeed, 3-ethyl phenol **23** leads to **45** and **46** in 35% yield (Scheme 15). The increasing selectivity is due to a new approach to the double bond (attack 1–3) with more steric interactions compared to the furan approach (attack 1–5) as described in Scheme 9.

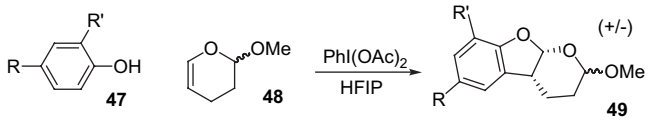


Scheme 15.

This reaction can be extended to 3,4-dihydro-2-methoxy-2*H*-pyran **48** to quickly yield the corresponding tricyclic compound **49** in an epimeric mixture of ~1:1 (Table 3).

It should be stressed that this unusual bis-ketal structure **49** has never been reported with a tetrahydrofurobenzopyran ring center and should find useful applications in synthesis or in medicinal

Table 3



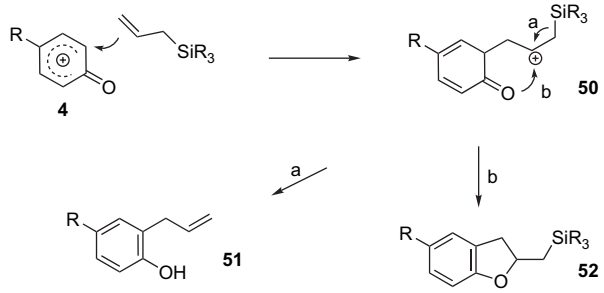
Entry	R	R′	Yield
a	*t*-Bu	H	44
b	Cl	H	32
c	Br	H	33
d	Ph	H	23
e	Me	*t*-Bu	37

chemistry. Similar examples of tetrahydrofurobenzofuran cores are known.[19]

Although global yields of this transformation are moderate, this ring making method is an impressive short access to the corresponding tricyclic acetal core. This extension to cyclic enol ethers is slightly less efficient than the one conducted with furan. It is probably due to the fact that, even if phenols react faster with DIB than enol ethers, they are not inert in the presence of DIB and are oxidized into by-products. Moreover, a quite hindered base such as lutidine is used to trap the acetic acid liberated in the medium limiting possible cationic polymerization. Other attempts to generalize this reaction to unsubstituted aliphatic enol ethers such as *tert*-butyl vinyl ether, vinyl acetate or ethyl vinyl ether were not successful, probably due to the fact than polymerization of vinyl occurred first.

4. Formal cycloaddition with allylsilanes

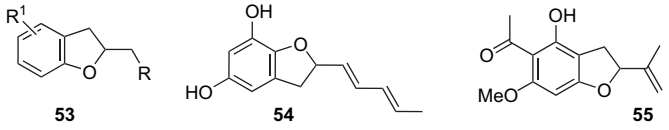
It should be noted that this oxidative annulation process occurs only with quite electron-rich alkenes. Indeed, with alkenes that are not electron-rich, such as styrene, indene, allyl bromine or allyl acetate, no cycloaddition occurred and it led to the formation of intractable polymeric materials. However, very important alkenes, such as allylsilanes, are known to be good nucleophiles reacting on electrophilic carbons efficiently.[20] Allylsilanes should interact with electrophilic intermediate **4** to afford **50**. From this intermediate two compounds should be obtained: a regular Sakurai (pathway a) should lead to **51** or a cyclization (pathway b) could produce **52**, Scheme 16.



Scheme 16.

Surprisingly, only small amounts (5–10%) of compounds such as **50** and **51** were sometimes detected. The main product isolated is the corresponding cycloadduct **52** resulting from the oxidative annulation process. The formation of a cycloadduct (pathway b) instead of the product **51** of a regular Sakurai reaction (pathway a) would be explained by the stability of the electrophilic intermediate **50** due to the use of a protic solvent. Indeed, under this condition, the cationic charge of **50** would be more stabilized by the high ionizing power of the solvent and would be sufficiently stable.

Thus, the formed carbocation **50** can be trapped by a nucleophilic attack of the oxygen and leads to **52** instead of the elimination of the TMS group. Once again, this method leads to heterocyclic compounds such as dihydrofuran **53** in only one step. This structure is equally present in many natural products such as arthrographol **54**,[21] a natural product isolated from *Aspergillus oryzae* or *Arthrographis pinicola*, remirol **55**,[22] isolated from *Remiria maritima*, and other bioactive substances (Scheme 17).[23] While a number of useful routes to substructure **54** are reported,[24] we have become interested in an 'oxidative cycloaddition' approach between phenols and alkenes.[25]

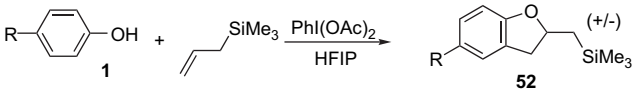


Scheme 17.

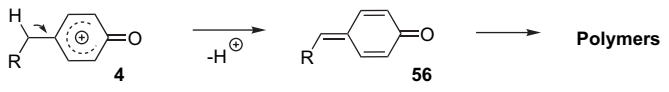
This novel extension described between various substituted phenols and allyltrimethylsilane must be carried out in the presence of an excess of allyltrimethylsilane and also in solvents such as TFE or HFIP with similar yield.[26] As a matter of fact, corresponding dihydrofuran cores **52** are quite stable in such acidic conditions. A summary of representative experiments with *para*-substituted phenols appears in Table 4. Regardless, the various examples provided herein suggest that the reaction is certainly synthetically useful to obtain dihydrobenzofuran skeleton such as **52** quickly.

It should be stressed that the reaction is not efficient when a benzylic hydrogen atom is in the *para* position (cf. entries **f** and **g**).

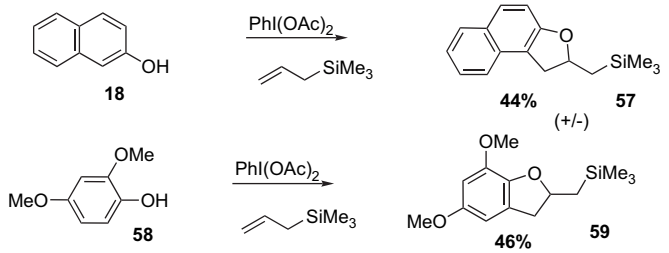
Table 4



Entry	R	Yield
a	*t*-Bu	58
b	Cl	52
c	Br	53
d	I	41
e	OMe	43
f	CH_2CH_2OH	21
g	CH_2CH_2NHTs	35
h	$SiMe_3$	53
i	OPh	40



Scheme 18.

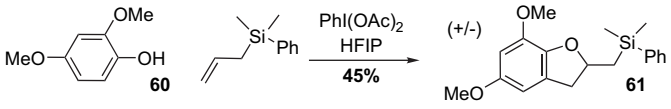


Scheme 19.

Reaction with *para* cresol occurs in low yields (20%). These latter results show some limits of our method and these unsatisfactory results could be explained by formation of the corresponding quinone methide **56** that leads to inextractable tars of by-products, Scheme 18. This problem could be overcome considering that the reaction with bromine **52c** or with iodine **52d** would allow different R chains with the palladium chemistry to be introduced.

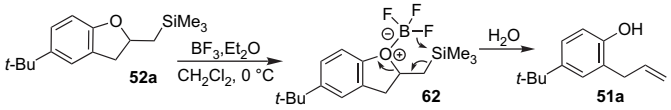
Of course, this reaction also occurs with polycyclic phenols such as β-naphthol **18** (44% of a single isomer) and with polysubstituted ones such as **58** with a similar yield, Scheme 19.

Moreover, this reaction can be extended to dimethylphenylallylsilane to lead to compound **61**, a potential precursor of arthrographol, via a potential Tamao–Fleming process[27] (Scheme 20).



Scheme 20.

If a compound such as **51** is almost not observed during the oxidative reaction, the latter is produced by a treatment of **52a** with a Lewis acid such as boron trifluoride diethyl etherate (Scheme 21).



Scheme 21.

5. Conclusion

In conclusion, formal [2+3] cycloaddition is based on a common electrophilic intermediate generated by an environmentally benign hypervalent iodine reagent (DIB) in perfluorinated protic solvents. This intermediate can react with different sufficiently reactive alkenes to lead in one step to different heterocyclic rings such as dihydrofuranobenzofurans, tetrahydrofuranobenzofurans, tetrahydropyranofurans, and dihydrobenzofurans. All these structures are present in a number of natural products and could potentially lead to a short route to these molecules. This transformation expands novel strategic opportunities in the chemical synthesis of heterooxygenated substances with an intriguing concept that could be termed as an 'aromatic ring umpolung'. New results in ongoing investigations in this field will be disclosed in due course.

6. Experimental protocols

6.1. General

Unless otherwise noted, NMR spectra were recorded in $CDCl_3$ at 300 MHz for ^1H and 75 MHz or 150 MHz for ^{13}C. Chemical shift (δ) are in parts per million and coupling constants (J) are in hertz. Multiplicities are reported as: 's' (singlet), 'd' (doublet), 'dd' (doublet of doublets), 't' (triplet), 'q' (quartet), 'm' (multiplet), 'c' (complex), and 'br' broad. All reactions were monitored by TLC. Reagents and solvents were commercial products and were used as received, including trifluoroethanol (TFE) and hexafluoroisopropanol (HFIP).

*6.1.1. Cycloaddition with furan **12***

At −10 °C (ice/NaCl), a solution of $PhI(OAc)_2$ ('DIB', 98 mg, 0.3 mmol, 1.5 equiv) in CF_3CH_2OH ('TFE', 0.35 mL) was added dropwise for 1 min to a vigorously stirred solution of phenol **1** (0.2 mmol, 1 equiv) in furan (164 mg, 2.4 mmol, 12 equiv) and TFE

(0.6 mL). The mixture was then stirred for 20 s, diluted with 6 mL of ethyl acetate, poured into a separatory funnel, and washed with 3 mL of a satd solution of K_2CO_3 and 3 mL of brine. The solution was concentrated under vacuum and the residue was purified by silica gel chromatography with an appropriate mixture of ethyl acetate/hexane. *NMR data*. Compound **12a**: ^{1}H (300 MHz, $CDCl_3$) δ=7.48 (d, 1H, J=1.8 Hz), 7.34 (dd, 1H, J=8.2, 1.8 Hz), 6.82 (d, 1H, J=8.2 Hz), 6.65 (d, 1H, J=2.9 Hz), 6.06 (d, 1H, J=7.6 Hz), 5.97 (dd, 1H, J=7.6, 2.3 Hz), 5.31 (t, 1H, J=2.3 Hz), 1.33 (s, 9H). ^{13}C (75 MHz, $CDCl_3$) δ=157.1, 151.1, 143.8, 128.4, 124.1, 122.9, 110.1, 100.0, 89.0, 85.5, 34.3, 31.6. HMRS (ESI): calcd for $C_{14}H_{17}O_2$ (MH^+): 217.1223; found: 217.1228. Compound **12b**: ^{1}H (300 MHz, $CDCl_3$) δ=7.24 (d, 1H, J=1.8 Hz), 7.08 (dd, 1H, J=8.2, 1.8 Hz), 6.77 (d, 1H, J=8.2 Hz), 6.63 (d, 1H, J=2.9 Hz), 6.03 (d, 1H, J=7.6 Hz), 5.97 (dd, 1H, J=7.6, 2.3 Hz), 5.31 (t, 1H, J=2.3 Hz), 2.31 (s, 3H). ^{13}C (75 MHz, $CDCl_3$) δ=157.2, 151.0, 131.8, 130.1, 126.5, 124.5, 110.4, 100.1, 88.8, 85.3, 20.6. HMRS (ESI): calcd for $C_{11}H_{11}O_2$ (MH^+): 175.0754; found: 175.0749. Compound **12c**: ^{1}H (300 MHz, $CDCl_3$) δ=6.99 (d, 1H, J=2.7 Hz), 6.86 (dd, 1H, J=8.8, 2.7 Hz), 6.78 (d, 1H, J=8.8 Hz), 6.63 (d, 1H, J=2.7 Hz), 6.03 (d, 1H, J=7.6 Hz), 5.97 (dd, 1H, J=7.6, 2.7 Hz), 5.29 (t, 1H, J=2.7 Hz), 3.77 (s, 3H). ^{13}C (75 MHz, $CDCl_3$) δ=154.1, 150.9, 150.9, 125.0, 117.8, 111.1, 110.7, 100.2, 89.0, 85.5, 56.0. HMRS (ESI): calcd for $C_{11}H_{11}O_3$ (MH^+): 191.0703; found: 191.0704. Compound **12d**: ^{1}H (300 MHz, $CDCl_3$) δ=7.36 (d, 1H, J=1.8 Hz), 7.18 (dd, 1H, J=8.2, 1.8 Hz), 6.82 (d, 1H, J=8.2 Hz), 6.63 (d, 1H, J=2.3 Hz), 6.04 (d, 1H, J=7.6 Hz), 5.97 (dd, 1H, J=7.6, 2.3 Hz), 5.30 (t, 1H, J=2.3 Hz), 3.69 (s, 3H), 3.58 (s, 2H). ^{13}C (75 MHz, $CDCl_3$) δ=172.2, 151.2, 132.2, 130.3, 127.1, 126.2, 125.0, 110.8, 99.9, 89.2, 85.0, 52.0, 40.3. HMRS (ESI): calcd for $C_{13}H_{13}O_4$ (MH^+): 233.0808; found: 233.0808. Compound **12e**: ^{1}H (300 MHz, $CDCl_3$) δ=7.69 (d, 2H, J=8.2 Hz), 7.28 (d, 2H, J=8.2 Hz), 6.97 (dd, 1H, J=8.2, 1.7 Hz), 6.74 (d, 1H, J=8.2 Hz), 6.61 (d, 1H, J=2.7 Hz), 5.97 (m, 2H), 5.29 (t, 1H, J=2.7 Hz), 4.56 (t, 1H, J=7.1 Hz), 3.17 (q, 2H, J=7.2 Hz), 2.70 (t, 2H, J=7.2 Hz), 2.42 (s, 3H). ^{13}C (75 MHz, $CDCl_3$) δ=154.1, 150.9, 150.9, 125.0, 117.8, 111.1, 110.7, 100.2, 89.0, 85.5, 56.0. HMRS (ESI): calcd for $C_{19}H_{20}O_4N_1S_1$ (MH^+): 358.1108; found: 358.1112. Compound **12f**: ^{1}H (300 MHz, $CDCl_3$) δ=7.59 (d, 1H, J=1.6 Hz), 7.42 (dd, 1H, J=8.2, 1.6 Hz), 6.87 (d, 1H, J=8.2 Hz), 6.61 (d, 1H, J=2.7 Hz), 6.04 (d, 1H, J=7.7 Hz), 5.94 (dm, 1H, J=7.7 Hz), 5.28 (t, 1H, J=2.7 Hz), 0.23 (s, 9H). ^{13}C (75 MHz, $CDCl_3$) δ=160.1, 151.2, 136.5, 131.8, 131.4, 124.4, 110.5, 99.9, 88.9, 85.1, −0.8. HMRS (ESI): calcd for $C_{13}H_{17}O_2Si$ (MH^+): 233.0992; found: 233.0997. Compound **17**: ^{1}H (300 MHz, $CDCl_3$) δ=7.12 (s, 1H), 7.04 (s, 1H), 6.60 (d, 1H, J=2.3 Hz), 6.03 (d, 1H, J=8.2 Hz), 5.96 (dm, 1H, J=8.2 Hz), 5.30 (t, 1H, J=2.3 Hz), 2.32 (s, 3H), 1.35 (s, 9H). ^{13}C (75 MHz, $CDCl_3$) δ=150.5, 133.8, 129.7, 128.5, 125.0, 123.9, 100.5, 87.8, 85.3, 34.0, 29.1, 20.8. HMRS (ESI): calcd for $C_{15}H_{19}O_2$ (MH^+): 231.1380; found: 231.1378. Compound **19**: ^{1}H (300 MHz, $CDCl_3$) δ=7.92 (d, 1H, J=8.2 Hz), 7.84 (d, 1H, J=8.2 Hz), 7.82 (d, 1H, J=8.2 Hz), 7.56 (td, 1H, J=8.2, 1.2 Hz), 7.37 (td, 1H, J=8.2, 1.2 Hz), 7.15 (d, 1H, J=9.4 Hz), 6.69 (d, 1H, J=2.9 Hz), 6.52 (d, 1H, J=7.6 Hz), 6.17 (dm, 1H, J=7.0 Hz), 5.38 (t, 1H, J=2.9 Hz). ^{13}C (75 MHz, $CDCl_3$) δ=157.5, 151.2, 137.4, 132.4, 130.9, 130.1, 128.6, 127.5, 123.3, 122.1, 112.8, 99.9, 89.8, 85.1. HMRS (ESI): calcd for $C_{14}H_{11}O_2$ (MH^+): 211.0754; found: 211.0746. Compound **29**: ^{1}H (300 MHz, $CDCl_3$) δ=7.33 (d, 1H, J=8.2 Hz), 6.63 (d, 1H, J=2.2 Hz), 6.50 (dd, 1H, J=8.2, 2.2 Hz), 6.42 (d, 1H, J=2.2 Hz), 6.02 (m, 2H), 5.29 (t, 1H, J=2.2 Hz), 3.78 (s, 3H). ^{13}C (75 MHz, $CDCl_3$) δ=162.7, 161.0, 151.3, 126.6, 116.9, 107.4, 99.8, 96.2, 90.0, 85.0, 55.4. HMRS (ESI): calcd for $C_{11}H_{11}O_3$ (MH^+): 191.0703; found: 191.0704.

*Biaryl **31a***. To a stirred solution of **12a** (22 mg, 0.1 mmol) in dichloromethane (1 mL) under argon at 0 °C was added TFA (24 mg, 0.02 mmol). The solution was stirred at room temperature for 20 min (verified by TLC) and quenched with satd aq $NaHCO_3$ (2 mL). The aqueous phase was extracted with ethyl acetate (2×5 mL), the combined organic layers were washed with brine (4 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was quickly filtered by chromatography (*n*-hexane/EtOAc, 85:15) to afford compound **31a** (21 mg, 0.095 mmol, 95%) as an oil. ^{1}H (300 MHz, $CDCl_3$) δ=7.54 (m, 2H), 7.25 (dd, 1H, J=8.2, 2.3 Hz), 7.04 (br, 1H), 6.92 (d, 1H, J=8.2 Hz), 6.72 (d, 1H, J=3.5 Hz), 6.55 (dd, 1H, J=3.5, 1.8 Hz), 1.34 (s, 9H). ^{13}C (75 MHz, $CDCl_3$) δ=150.1, 143.3, 141.1, 131.1, 126.5, 122.8, 116.7, 115.7, 111.6, 106.3, 34.1, 31.4. HMRS (ESI): calcd for $C_{14}H_{17}O_2$ (MH^+): 217.1223; found: 217.1225.

6.1.2. Cycloaddition with 4-acetoxystyrene *37*

At 0 °C (ice/NaCl), a solution of $PhI(OAc)_2$ ('DIB', 100 mg, 0.31 mmol, 1.55 equiv) in $(CF_3)_2CHOH$ ('HFIP', 0.35 mL) was added over 10 s to a vigorously stirred solution of phenol **16** or **34** (0.2 mmol, 1 equiv) in HFIP (0.6 mL) and 4-acetoxystyrene **33** (1.6 mmol, 8 equiv). The mixture was then stirred for 30 s, concentrated under vacuum and the residue was purified by silica gel chromatography with a mixture of ethyl acetate/hexane (5:95). ^{1}H (300 MHz, $CDCl_3$) δ=7.41 (d, 2H, J=8.2 Hz), 7.07 (d, 2H, J=8.2 Hz), 6.91 (s, 1H), 6.86 (s, 1H), 5.73 (t, 1H, J=8.2 Hz), 3.55 (dd, 1H, J=15.4, 9.4 Hz), 3.08 (dd, 1H, J=15.4, 8.2 Hz), 2.31 (s, 3H), 2.29 (s, 3H), 1.39 (s, 9H). ^{13}C (150 MHz, $CDCl_3$) δ=169.4, 155.3, 150.0, 140.5, 132.3, 129.6, 126.6, 126.6, 125.4, 122.9, 121.6, 82.8, 38.6, 34.0, 29.3, 21.1, 21.0 HMRS (ESI): calcd for $C_{17}H_{17}O_4$ (MH^+): 285.1121; found: 285.1125.

6.1.3. Cycloaddition with cyclic enol ethers *39/40/49*

At −10 °C (ice/NaCl), a solution of $PhI(OAc)_2$ ('DIB', 100 mg, 0.31 mmol, 1.55 equiv) in $(CF_3)_2CHOH$ ('HFIP', 0.35 mL) was added over 10 s to a vigorously stirred solution of phenol **1** (0.2 mmol, 1 equiv) in HFIP (0.6 mL), lutidine (66.4 mg, 0.62 mmol, 3.1 equiv), and enol ether (3 mmol, 15 equiv). The mixture was then stirred for 30 s, concentrated under vacuum, and the residue was purified by silica gel chromatography with a mixture of ethyl acetate/hexane (5:95). *NMR data of dihydrofurans*. Compound **39a**: ^{1}H (300 MHz, $CDCl_3$) δ=7.21 (d, 1H, J=1.7 Hz), 7.17 (dd, 1H, J=8.2, 1.7 Hz), 6.73 (d, 1H, J=8.2 Hz), 6.30 (d, 1H, J=6.0 Hz), 4.06 (t, 1H, J=7.7 Hz), 3.99 (dd, 1H, J=8.2, 6.0 Hz), 3.65 (ddd, 1H, J=12.1, 8.2, 4.9 Hz), 2.30 (m, 1H), 2.08 (dd, 1H, J=11.5, 4.4 Hz), 1.30 (s, 9H). ^{13}C (75 MHz, $CDCl_3$) δ=157.1, 144.1, 127.1, 125.4, 121.4, 111.0, 108.3, 67.1, 46.7, 34.3, 33.5, 31.6. HMRS (ESI): calcd for $C_{14}H_{19}O_2$ (MH^+): 219.1380; found: 219.1374. Compound **39b**: ^{1}H (300 MHz, $CDCl_3$) δ=7.14 (d, 1H, J=1.7 Hz), 7.09 (dd, 1H, J=8.2, 1.7 Hz), 6.72 (d, 1H, J=8.2 Hz), 6.31 (d, 1H, J=6.0 Hz), 4.08 (t, 1H, J=7.7 Hz), 3.98 (dd, 1H, J=8.2, 6.0 Hz), 3.63 (ddd, 1H, J=12.1, 8.2, 4.9 Hz), 2.30 (m, 1H), 2.04 (dd, 1H, J=11.5, 4.4 Hz). ^{13}C (75 MHz, $CDCl_3$) δ=158.0, 129.5, 128.5, 125.7, 124.7, 111.4, 110.1, 67.2, 46.5, 33.3. HMRS (ESI): calcd for $C_{10}H_{10}O_2Cl$ (MH^+): 197.0364; found: 197.0371. Compound **39c**: ^{1}H (300 MHz, $CDCl_3$) δ=7.29 (d, 1H, J=1.7 Hz), 7.24 (dd, 1H, J=8.2, 1.7 Hz), 6.68 (d, 1H, J=8.2 Hz), 6.31 (d, 1H, J=6.0 Hz), 4.08 (t, 1H, J=7.7 Hz), 3.98 (dd, 1H, J=8.2, 6.0 Hz), 3.61 (ddd, 1H, J=12.1, 8.2, 4.9 Hz), 2.30 (m, 1H), 2.05 (dd, 1H, J=11.5, 4.4 Hz). ^{13}C (75 MHz, $CDCl_3$) δ=158.5, 131.5, 130.1, 127.7, 112.8, 111.4, 110.7, 67.2, 46.4, 33.4. HMRS (ESI): calcd for $C_{11}H_{10}O_2Br$ (MH^+): 240.9859; found: 240.5851. Compound **39d**: ^{1}H (300 MHz, $CDCl_3$) δ=7.31 (d+s, 2H, J=8.2 Hz), 6.82 (d, 1H, J=8.2 Hz), 6.31 (d, 1H, J=5.5 Hz), 4.08 (t, 1H, J=8.2 Hz), 4.0 (t, 1H, J=7.1 Hz), 3.63 (m, 1H), 2.32 (m, 1H), 2.09 (dd, 1H, J=12.0, 4.9 Hz), 0.25 (s, 9H). ^{13}C (75 MHz, $CDCl_3$) δ=160.1, 134.8, 134.0, 132.1, 129.6, 110.9, 108.8, 67.2, 46.3, 33.5, −0.8. HMRS (ESI): calcd for $C_{13}H_{19}O_2Si$ (MH^+): 235.1149; found: 235.1152. Compound **39e**: ^{1}H (300 MHz, $CDCl_3$) δ=7.53 (d, 2H, J=8.2 Hz), 7.46–7.36 (m, 4H), 7.29 (t, 1H, J=7.5 Hz), 6.87 (d, 1H, J=8.2 Hz), 6.37 (d, 1H, J=5.6 Hz), 4.15–4.03 (m, 2H), 3.68 (m, 1H), 2.35 (m, 1H), 2.13 (dd, 1H, J=12.0, 4.9 Hz). ^{13}C (75 MHz, $CDCl_3$) δ=159.0, 141.0, 134.7, 128.7, 128.3, 127.7, 126.7, 126.6, 123.5, 111.3, 109.3, 67.2, 46.5, 33.5. HMRS (ESI): calcd for $C_{16}H_{15}O_2$ (MH^+): 239.1067; found: 239.1070. Compound **41**: ^{1}H (300 MHz, $CDCl_3$) δ=6.89 (s, 1H), 6.86 (s, 1H), 6.30 (d, 1H, J=6.0 Hz), 4.04 (t, 1H, J=8.2 Hz), 3.92 (t, 1H, J=7.0 Hz), 3.57 (m, 1H), 2.29 (m+s, 4H), 2.02 (dd, 1H, J=12.3, 4.7 Hz), 1.36 (s, 9H). ^{13}C (75 MHz, $CDCl_3$) δ=157.1, 144.1, 127.1, 125.4, 121.4, 111.0, 108.3, 67.1, 46.7, 34.3, 33.5, 31.7.

HMRS (ESI): calcd for $C_{15}H_{21}O_2$ (MH^+): 233.1536; found: 233.1531. Compound **43**: ^1H (300 MHz, $CDCl_3$) δ=7.83 (d, 1H, J=8.2 Hz), 7.71 (d, 2H, J=8.8 Hz), 7.52 (t, 1H, J=7.6 Hz), 7.34 (t, 1H, J=7.6 Hz), 7.12 (d, 1H, J=8.8 Hz), 6.51 (d, 1H, J=5.5 Hz), 4.34 (t, 1H, J=7.1 Hz), 4.12 (t, 1H, J=8.2 Hz), 3.64 (m, 1H), 2.41 (m, 1H), 2.30 (m, 1H). ^{13}C (75 MHz, $CDCl_3$) δ=156.7, 130.1, 129.7, 129.6, 129.0, 126.9, 123.0, 122.0, 118.3, 111.8, 111.6, 67.4, 45.9, 31.8. HMRS (ESI): calcd for $C_{14}H_{13}O_2$ (MH^+): 213.0910; found: 213.0912. *NMR data of dihydropyrans*. Compound **40a**: ^1H (300 MHz, $CDCl_3$) δ=7.17 (d+s, 2H, J=8.2 Hz), 6.79 (d, 1H, J=8.2 Hz), 5.87 (d, 1H, J=6.6 Hz), 3.85–3.65 (m, 2H), 3.29 (dd, 1H, J=11.5, 5.5 Hz), 2.05 (m, 1H), 1.92 (m, 1H), 1.60 (m, 2H), 1.31 (s, 9H). ^{13}C (75 MHz, $CDCl_3$) δ=156.0, 144.0, 128.9, 124.9, 120.6, 108.8, 104.2, 61.1, 38.9, 34.3, 31.7, 22.8, 20.1. HMRS (ESI): calcd for $C_{15}H_{21}O_2$ (MH^+): 233.1536; found: 233.1542. Compound **40b**: ^1H (300 MHz, $CDCl_3$) δ=7.08 (d+s, 2H, J=8.2 Hz), 6.74 (d, 1H, J=8.2 Hz), 5.86 (d, 1H, J=6.6 Hz), 3.81–3.62 (m, 2H), 3.27 (dd, 1H, J=11.5, 5.5 Hz), 2.01 (m, 1H), 1.83 (m, 1H), 1.54 (m, 2H). ^{13}C (75 MHz, $CDCl_3$) δ=156.9, 129.4, 128.1, 125.7, 124.0, 110.7, 104.5, 61.0, 38.8, 22.5, 19.8. HMRS (ESI): calcd for $C_{11}H_{12}O_2Cl$ (MH^+): 211.0520; found: 211.0511. Compound **40c**: ^1H (300 MHz, $CDCl_3$) δ=7.26 (d+s, 2H, J=8.2 Hz), 6.74 (d, 1H, J=8.2 Hz), 5.89 (d, 1H, J=6.6 Hz), 3.83–3.65 (m, 2H), 3.31 (dd, 1H, J=11.5, 5.5 Hz), 2.04 (m, 1H), 1.87 (m, 1H), 1.60 (m, 2H). ^{13}C (75 MHz, $CDCl_3$) δ=157.4, 131.9, 131.0, 126.9, 112.8, 111.3, 104.5, 61.0, 38.7, 22.5, 19.8. HMRS (ESI): calcd for $C_{11}H_{10}O_2Br$ (MH^+): 255.0015; found: 255.0011. Compound **40d**: ^1H (300 MHz, $CDCl_3$) δ=7.28 (d, 1H, J=8.2 Hz), 6.79 (d, 1H, J=8.8 Hz), 5.89 (d, 1H, J=6.6 Hz), 3.83–3.64 (m, 2H), 3.31 (dd, 1H, J=11.5, 5.5 Hz), 2.05 (m, 1H), 1.86 (m, 1H), 1.60 (m, 2H), 1.31 (s, 9H). ^{13}C (75 MHz, $CDCl_3$) δ=159.1, 133.6, 131.9, 129.2, 128.5, 109.3, 104.2, 61.0, 38.5, 22.7, 20.0, −0.7. HMRS (ESI): calcd for $C_{14}H_{21}O_2Si$ (MH^+): 249.1305; found: 249.1310. Compound **40e**: ^1H (300 MHz, $CDCl_3$) δ=7.55 (d, 2H, J=8.2 Hz), 7.48–7.37 (m, 4H), 7.32 (t, 1H, J=7.2 Hz), 6.94 (d, 1H, J=8.2 Hz), 5.96 (d, 1H, J=6.6 Hz), 3.89–3.69 (m, 2H), 3.39 (dd, 1H, J=11.5, 6.0 Hz), 2.10 (m, 1H), 1.97 (m, 1H), 1.62 (m, 2H). ^{13}C (75 MHz, $CDCl_3$) δ=157.9, 141.1, 134.6, 130.0, 128.6, 127.2, 126.7, 126.5, 122.6, 109.8, 104.5, 61.0, 38.7, 22.6, 19.9. HMRS (ESI): calcd for $C_{17}H_{17}O_2$ (MH^+): 253.1223; found: 253.1226. Compound **42**: ^1H (300 MHz, $CDCl_3$) δ=6.91 (s, 1H), 6.82 (s, 1H), 5.89 (d, 1H, J=6.0 Hz), 3.71 (m, 2H), 3.26 (q, 1H, J=5.5 Hz), 3.57 (m, 1H), 2.31 (s, 3H), 2.04 (m, 1H), 1.87 (dd, 1H, J=13.7, 5.0 Hz), 1.62 (m, 1H), 1.52 (m, 1H), 1.38 (s, 9H). ^{13}C (75 MHz, $CDCl_3$) δ=154.3, 132.5, 129.8, 129.5, 125.5, 121.9, 103.5, 60.5, 38.5, 33.9, 29.2, 22.4, 21.1, 19.8. HMRS (ESI): calcd for $C_{16}H_{23}O_2$ (MH^+): 247.1693; found: 247.1693. Compound **44**: ^1H (300 MHz, $CDCl_3$) δ=7.82 (d, 1H, J=8.2 Hz), 7.71 (d, 1H, J=8.8 Hz), 7.66 (d, 1H, J=8.2 Hz), 7.47 (t, 1H, J=8.2 Hz), 7.31 (t, 1H, J=8.2 Hz), 7.16 (d, 1H, J=8.8 Hz), 6.12 (d, 1H, J=6.6 Hz), 3.94 (m, 2H), 3.63 (q, 1H, 7.1 Hz), 2.29 (m, 1H), 1.75 (m, 2H), 1.57 (m, 1H). ^{13}C (75 MHz, $CDCl_3$) δ=154.7, 130.3, 129.4, 129.1, 129.0, 126.6, 122.9, 122.4, 122.1, 112.1, 105.6, 61.2, 37.3, 24.0, 20.5. HMRS (ESI): calcd for $C_{15}H_{15}O_2$ (MH^+): 227.1067; found: 227.1071.

6.1.4. Cycloaddition with allylsilanes *52*

A solution of $PhI(OAc)_2$ ('DIB', 98 mg, 0.3 mmol, 1.5 equiv) in $(CF_3)_2CHOH$ ('HFIP', 0.35 ml) was added dropwise over 30 s to a vigorously stirred solution of phenol **1** (0.2 mmol, 1 equiv) in allyltrimethylsilane (230 mg, 2 mmol, 10 equiv) and HFIP (0.6 ml). The mixture was then stirred for 30 s, concentrated under vacuum, and the residue was purified by silica gel chromatography with a mixture of ethyl acetate/hexane (5:95). Compound **52a**: ^1H (300 MHz, $CDCl_3$) δ=7.31 (d, 1H, J=1.7 Hz), 7.27 (dd, 1H, J=8.2, 1.7 Hz), 6.76 (d, 1H, J=8.2 Hz), 4.92 (m, 1H), 3.29 (dd, 1H, J=15.4, 8.2 Hz), 2.81 (dd, 1H, J=15.4, 8.2 Hz), 1.34 (dd, 1H, J=14.3, 6.6 Hz), 1.11 (dd, 1H, J=14.3, 8.8 Hz), 0.24 (s, 9H), 0.11 (s, 9H). ^{13}C (75 MHz, $CDCl_3$) δ=156.8, 130.8, 128.7, 128.6, 126.4, 122.5, 122.5, 118.5, 112.1, 82.9, 36.9, 25.6, −0.7. HMRS (ESI): calcd for $C_{16}H_{27}OSi$ (MH^+): 263.1826; found: 263.1817. Compound **52b**: ^1H (300 MHz, $CDCl_3$) δ=7.32 (d, 1H, J=1.7 Hz), 7.08 (dd, 1H, J=8.2, 1.7 Hz), 6.66 (d, 1H, J=8.2 Hz), 4.90 (m, 1H), 3.26 (dd, 1H, J=15.4, 8.2 Hz), 2.82 (dd, 1H, J=15.4, 8.2 Hz), 1.26 (m+s, 4H), 1.05 (dd, 1H, J=14.3, 8.8 Hz), 0.09 (s, 9H). ^{13}C (75 MHz, $CDCl_3$) δ=158.0, 129.4, 127.6, 124.8, 118.4, 110.0, 82.9, 38.1, 25.1, −0.8. HMRS (ESI): calcd for $C_{12}H_{18}OClSi$ (MH^+): 241.0810; found: 241.0811. Compound **52c**: ^1H (300 MHz, $CDCl_3$) δ=7.23 (d, 1H, J=1.7 Hz), 7.18 (dd, 1H, J=8.2, 1.7 Hz), 6.60 (d, 1H, J=8.2 Hz), 4.93 (m, 1H), 3.27 (dd, 1H, J=15.4, 8.2 Hz), 2.79 (dd, 1H, J=15.4, 8.2 Hz), 1.30 (dd, 1H, J=14.3, 6.6 Hz), 1.09 (dd, 1H, J=14.3, 8.8 Hz), 0.09 (s, 9H). ^{13}C (75 MHz, $CDCl_3$) δ=158.0, 129.4, 127.6, 124.8, 118.4, 110.0, 82.9, 38.1, 25.1, −0.8. HMRS (ESI): calcd for $C_{12}H_{18}OBrSi$ (MH^+): 285.0305; found: 285.0313. Compound **52d**: ^1H (300 MHz, $CDCl_3$) δ=7.41 (d, 1H, J=1.7 Hz), 7.36 (dd, 1H, J=8.2, 1.7 Hz), 6.51 (d, 1H, J=8.2 Hz), 4.92 (m, 1H), 3.26 (dd, 1H, J=15.4, 8.2 Hz), 2.77 (dd, 1H, J=15.4, 8.2 Hz), 1.29 (dd, 1H, J=14.3, 6.6 Hz), 1.07 (dd, 1H, J=14.3, 8.8 Hz), 0.08 (s, 9H). ^{13}C (75 MHz, $CDCl_3$) δ=159.3, 136.6, 133.5, 130.4, 111.5, 82.8, 37.8, 25.1, −0.9. HMRS (ESI): calcd for $C_{12}H_{18}OISi$ (MH^+): 333.0166; found: 333.0162. Compound **52e**: ^1H (300 MHz, $CDCl_3$) δ=6.71 (s, 1H), 6.62 (d, 1H, J=8.2 Hz), 6.58 (d, 1H, J=8.2 Hz), 4.85 (m, 1H), 3.71 (s, 3H), 3.21 (dd, 1H, J=15.4, 8.2 Hz), 2.74 (dd, 1H, J=15.4, 8.2 Hz), 1.28 (dd, 1H, J=14.3, 6.6 Hz), 1.07 (dd, 1H, J=14.3, 8.8 Hz), 0.07 (s, 9H). ^{13}C (75 MHz, $CDCl_3$) δ=153.7, 128.3, 113.1, 112.5, 111.3, 108.9, 82.3, 56.0, 38.6, 25.1, −0.8. HMRS (ESI): calcd for $C_{13}H_{21}O_2Si$ (MH^+): 237.1305; found: 237.1296. Compound **52f**: ^1H (300 MHz, $CDCl_3$) δ=7.01 (d, 1H, J=1.7 Hz), 6.94 (dd, 1H, J=8.2, 1.7 Hz), 6.67 (d, 1H, J=8.2 Hz), 4.91 (m, 1H), 3.81 (t, 2H, J=6.4 Hz), 3.26 (dd, 1H, J=15.4, 8.2 Hz), 2.79 (m, 3H), 1.33 (dd, 1H, J=14.3, 6.6 Hz), 1.09 (dd, 1H, J=14.3, 8.8 Hz), 0.10 (s, 9H). ^{13}C (75 MHz, $CDCl_3$) δ=158.1, 129.7, 128.3, 127.8, 125.4, 109.0, 82.3, 63.9, 38.5, 38.2, 25.2, −0.8. HMRS (ESI): calcd for $C_{14}H_{23}O_2Si$ (MH^+): 251.1462; found: 251.1463. Compound **52g**: ^1H (300 MHz, $CDCl_3$) δ=7.68 (d, 2H, J=8.2 Hz), 7.29 (d, 2H, J=8.2 Hz), 6.85 (d, 1H, J=1.7 Hz), 6.76 (dd, 1H, J=8.2, 1.7 Hz), 6.60 (d, 1H, J=8.2 Hz), 4.89 (m, 1H), 4.40 (t, 1H, J=6.6 Hz), 3.21 (dd, 1H, J=15.4, 8.2 Hz), 3.15 (q, 2H, J=6.6 Hz), 2.74 (dd, 1H, J=15.4, 8.2 Hz), 2.66 (t, 2H, J=6.6 Hz), 2.42 (s, 3H), 1.31 (dd, 1H, J=14.3, 6.6 Hz), 1.09 (dd, 1H, J=14.3, 8.8 Hz), 0.09 (s, 9H). ^{13}C (75 MHz, $CDCl_3$) δ=158.3, 143.3, 136.8, 129.6, 128.8, 128.0, 127.9, 127.0, 125.1, 109.1, 82.4, 44.5, 38.1, 35.0, 25.2, 21.5, −0.9. HMRS (ESI): calcd for $C_{21}H_{30}NO_3SSi$ (MH^+): 404.1710; found: 404.1720. Compound **52h**: ^1H (300 MHz, $CDCl_3$) δ=7.31 (d, 1H, J=1.7 Hz), 7.27 (dd, 1H, J=8.2, 1.7 Hz), 6.76 (d, 1H, J=8.2 Hz), 4.92 (m, 1H), 3.29 (dd, 1H, J=15.4, 8.2 Hz), 2.81 (dd, 1H, J=15.4, 8.2 Hz), 1.34 (dd, 1H, J=14.3, 6.6 Hz), 1.11 (dd, 1H, J=14.3, 8.8 Hz), 0.24 (s, 9H), 0.11 (s, 9H). ^{13}C (75 MHz, $CDCl_3$) δ=160.2, 133.3, 130.5, 129.7, 127.0, 108.9, 82.2, 38.0, 25.3, −0.7. HMRS (ESI): calcd for $C_{15}H_{27}OSi_2$ (MH^+): 279.1595; found: 279.1599. Compound **52i**: ^1H (300 MHz, $CDCl_3$) δ=7.29 (t, 2H, J=8.2 Hz), 7.02 (t, 1H, J=8.2 Hz), 6.94 (d, 2H, J=8.2 Hz), 6.85 (d, 1H, J=1.7 Hz), 6.79 (dd, 1H, J=8.2, 1.7 Hz), 6.68 (d, 1H, J=8.2 Hz), 4.93 (m, 1H), 3.26 (dd, 1H, J=15.4, 8.2 Hz), 2.79 (dd, 1H, J=15.4, 8.2 Hz), 1.34 (dd, 1H, J=14.3, 6.6 Hz), 1.13 (dd, 1H, J=14.3, 8.8 Hz), 0.10 (s, 9H). ^{13}C (75 MHz, $CDCl_3$) δ=158.8, 155.7, 149.6, 129.4, 128.7, 122.0, 119.3, 117.3, 117.0, 109.3, 82.7, 38.4, 25.2, −0.8. HMRS (ESI): calcd for $C_{18}H_{23}O_2Si$ (MH^+): 299.1462; found: 299.1455. Compound **57**: ^1H (300 MHz, $CDCl_3$) δ=7.76 (d, 1H, J=8.2 Hz), 7.63 (d, 1H, J=8.2 Hz), 7.54 (d, 1H, J=8.2 Hz), 7.43 (t, 1H, J=8.2 Hz), 7.27 (d, 1H, J=8.2 Hz), 7.05 (d, 1H, J=8.2 Hz), (m, 1H), 5.10 (m, 1H), 3.56 (dd, 1H, J=14.8, 8.8 Hz), 3.03 (dd, 1H, J=14.8, 8.2 Hz), 1.37 (dd, 1H, J=13.7, 6.6 Hz), 1.18 (dd, 1H, J=14.3, 8.8 Hz), 0.11 (s, 9H). ^{13}C (75 MHz, $CDCl_3$) δ=156.8, 130.8, 128.9, 128.7, 128.6, 126.4, 122.5, 122.5, 118.5, 112.1, 82.9, 36.9, 25.6, −0.7. HMRS (ESI): calcd for $C_{16}H_{21}OSi$ (MH^+): 257.1356; found: 257.1350. Compound **59**: ^1H (300 MHz, $CDCl_3$) δ=6.35 (s, 2H), 4.92 (m, 1H), 3.84 (s, 3H), 3.77 (s, 3H), 3.22 (dd, 1H, J=15.4, 8.2 Hz), 2.79 (dd, 1H, J=15.4, 8.2 Hz), 1.42 (dd, 1H, J=14.3, 6.6 Hz), 1.19 (dd, 1H, J=14.3, 8.8 Hz), 0.10 (s, 9H). ^{13}C (75 MHz, $CDCl_3$) δ=154.4, 144.3, 141.9, 128.3, 101.4, 99.1, 82.9, 56.0, 38.9, 30.9, 25.0, −0.9. HMRS (ESI): calcd for $C_{14}H_{23}O_3Si$ (MH^+): 267.1411; found: 267.1414. Compound **61**: ^1H (300 MHz, $CDCl_3$)

δ=7.53 (m, 2H), 7.36 (m, 3H), 6.33 (s, 1H), 6.29 (s, 1H), 4.89 (m, 1H), 3.83 (s, 3H), 3.73 (s, 3H), 3.06 (dd, 1H, *J*=15.4, 8.2 Hz), 2.69 (dd, 1H, *J*=15.4, 8.2 Hz), 1.69 (dd, 1H, *J*=4.3, 6.6 Hz), 1.39 (dd, 1H, *J*=14.3, 8.8 Hz), 0.38 (s, 3H), 0.37 (s, 3H). ^{13}C (75 MHz, $CDCl_3$) δ=154.4, 144.3, 141.8, 138.2, 133.5, 129.1, 128.2, 127.8, 101.3, 99.1, 82.6, 55.9, 38.7, 24.3, −2.2, −2.4. HMRS (ESI): calcd for $C_{19}H_{25}O_3Si$ (MH^+): 329.1567; found: 329.1573.

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