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Iodine-catalyzed disproportionation of aryl-substituted ethers under solvent-free reaction conditions†

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Iodine was demonstrated to be an efficient catalyst for disproportionation of aryl-substituted ethers under solvent-free reaction conditions. Variously substituted 1,1,1′,1′-tetraaryldimethyl ethers were transformed into the corresponding diarylketone and diarylmethane derivatives. I_2-catalyzed transformation of 4-methoxyphenyl substituted ethers yielded mono- and dialkylated Friedel–Crafts products as well. Treatment of trityl alkyl and trityl benzyl ethers with a catalytic amount of iodine produced triphenylmethane and the corresponding aldehydes and ketones. The electron-donating substituents facilitated the reaction, while the electron-withdrawing groups retarded it; the difference in reactivity is not very high. Such an observation may be in favour of hydride transfer, predominantly from the less electron rich side of the ether with more stable carbocation formation. With the isotopic studies it was established that a substantial portion of the C–H bond scission took place in the rate-determining step, while the carbonyl oxygen atom originated from the starting ether, and not from the air. The transformation took place under air and under argon, and HI was not a functioning catalyst.

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Introduction

Iodine[1] as a mild oxidizer and poor electrophile[2–5] displays tolerance to a broad range of functional groups and possesses excellent polarizability, which is presumably of vital importance for its fascinating catalytic potential.[6–8] It interacts particularly effectively with molecules bearing oxygen functional groups; there has been a boom of iodine-catalyzed transformations in recent years.[9–16] It has several advantages over the hazardous, toxic, hygroscopic and expensive metallic Lewis acids. One of the major disadvantages is its relatively high molar mass. Iodine exhibits high catalytic activity in a dilute solution, under highly concentrated reaction conditions and under solvent-free reaction conditions (SFRC). The latter conditions are particularly important in terms of green chemistry since they contribute to waste reduction, enhanced cost-efficiency, health-hazard minimization and energy efficiency.[17,18] These demands have been gaining increasing importance due to the sharpened environmental circumstances that are consequently reflected in more stringent safety precautions and in more rigorous legislation.[19–21]

Clean and environmentally benign synthesis has been an exceedingly important issue in chemistry. The reaction medium shares a great deal of 'nongreen' reaction attributes, the key goal remaining to reduce the use of volatile organic solvents.[22] The best reaction medium is 'no medium' and therefore SFRCs are the conditions of choice.[23–27]

The disproportionation reactions appear to be uncommon in organic chemistry;[28–30] they are often performed with unusual reagents[31,32] or with acids[33] or strong bases.[34,35] Disproportionation of ethers is a rare and challenging transformation that represents an atom-economical[36] approach to the carbonyl and the alkane derivatives. It was accomplished with trityl salts,[37] CF_3SO_3H,[38,39] CBr_4,[40] *o*-benzenedisulfonimide,[41] and under supercritical conditions.[42,43]

One of the principal advantages of iodine is its ability to substitute strongly acidic catalysts, for example, in esterification reactions,[44,45] in the Ritter reaction[46] and in Beckmann rearrangement.[47] These transformations require species with appreciably negative pK_a values, which may not be compatible with the sensitive functional groups. Iodine is also an important catalyst in protection/deprotection chemistry,[6,8] the removal of the trityl group with 1% I_2 in MeOH yielded a deprotected alcohol derivative, trityl methyl ether and a significant amount of triphenylmethane.[48] The course of the redox process is unclear as is the source of hydride. The unprecedented role of iodine prompted us to investigate the transformations of different ethers with a catalytic amount of iodine.

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†Electronic supplementary information (ESI) available: Copies of NMR spectra. See DOI: 10.1039/c3ob27267b

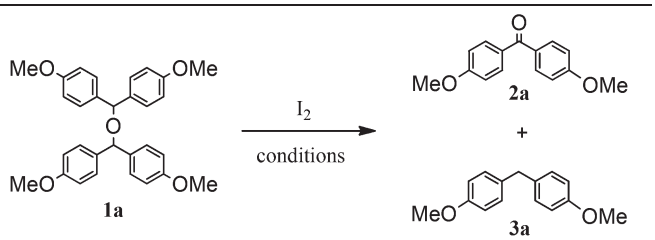
Results and discussion

Initially the reactivity of ether **1a** in the presence of iodine in different solvents was examined; the results are summarized in Table 1.

The starting material remained almost completely unreacted in the halogenated solvents, as well as in toluene and ethyl acetate (Table 1, entries 1–5).

Substitution took place in the protic solvents (MeOH and 1,1,1,3,3,3-hexafluoroisopropanol (HFIP), entries 6 and 7), while the crucial breakthrough was SFRC (entry 8), where the complete conversion of the dimeric ether to the 4,4′-dimethoxybenzophenone **2a** and the 4,4′-dimethoxydiphenylmethane **3a** derivative occurred in the presence of air. The reaction successfully took place also under an Ar atmosphere (entry 9). A concentrated aqueous solution of HI under SFRC has been tested and found to be effective under both air and Ar (entries 10 and 11). There is an ongoing debate regarding iodine-catalyzed reactions,[9] since the highly successful reactions are often attributed, though not experimentally proven, to the *in situ* formed HI.[49] In our case, it is likely that iodine polarized the starting ether, and that the reaction took place without HI formation. The formation of HI under our reaction conditions (aryl-substituted ether and iodine under SFRC) seems unlikely, because iodine was recovered after the reaction (see below). Successful disproportionation with HI (entries 10 and 11) is in accordance with the literature data that strong Brønsted acids catalyzed disproportionation of the ethers.[39,50] Two different catalytic pathways of disproportionation became obvious; HI acts as a Brønsted acid, while I_2 as a Lewis acid. In contrast, I_2-catalyzed oxidation of alcohols with the proposed HI formation and oxidation into I_2 was reported.[51] Encouraged by the results, we undertook the synthesis of the starting ethers **1** and examined their reactivity with a catalytic amount of iodine under SFRC; the results are in Table 2.

Table 1 The role of the reaction conditions in the I_2-catalyzed transformation of ether **1a**



Entry	Conditions	Conversion[a] [%]
1	CH_2Cl_2	9
2	$CDCl_3$	3
3	CCl_4	2
4	Toluene	2
5	EtOAc	7
6	MeOH	100[b]
7	HFIP	100[c]
8	SFRC, air	100[d]
9	SFRC, Ar	100
10	SFRC, HI, air	100[e]
11	SFRC, HI, Ar	100

[a] 0.2 mmol of **1a**, 10 mol% of I_2 stirred in 2 mL of solvent or under SFRC at 85 °C for 15 min. Conversion determined from ^{1}H NMR spectra of the crude reaction mixture. [b] Bis(*p*-anisyl)methyl methyl ether **2aa** was formed. [c] Bis(*p*-anisyl)methyl bis(trifluoromethyl)methyl ether **2ab** was formed. [d] Ratio **2a**/**3a** was 1/1. [e] 10 mol% of a 57% solution of HI was added.

The bicyclic ethers **1b** and **1c** exhibited similar reactivity to **1a** and furnished the corresponding ketones **2b** and **2c** and suberane **3b** and suberene **3c** (entries 2 and 3). Bis-*p*-methyl-substituted derivative **1d** yielded benzophenone **2d** and diphenylmethane derivative **3d**. Tetramethyl-substituted derivative **1e** yielded products **2e** and **3e**, and it was significantly less reactive than **1a**; ether **1f** exhibited good reactivity. Introduction of the thiomethyl groups retarded the reaction of **1g** and **1h** considerably (entries 7 and 8). The anomalously large difference could be possibly ascribed to the additional complexation of iodine to sulfur.

The reaction mixture of **1b** was diluted with MeCN after the reaction, and iodine was titrated with $Na_2S_2O_3$. We found that iodine was neither consumed nor transformed to any other species, but it was fully recovered.

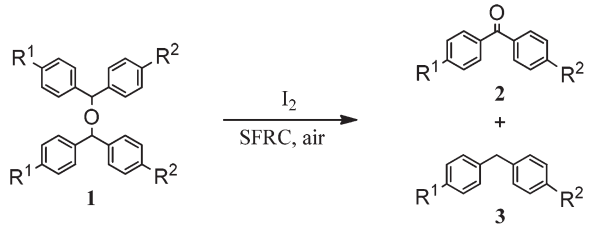
The chlorine atoms considerably reduced the reactivity of **1i** (entry 9). The sterically more demanding naphthalenyl-substituted derivatives **1j** and **1k** smoothly yielded the corresponding ketones **2j** and **2k** and the diarylmethane derivatives **3j** and **3k** (entries 10 and 11).

Next, the reactivity of other substrates bearing the *p*-substituted aryl ring was examined. Hexamethoxy **1l** and its cyclic analogue **1m** were converted to the benzophenone derivatives **2l** and **2m** and diphenylmethanes **3l** and **3m** (Table 1, entries 12 and 13) and exhibited high reactivity. Substrate **1n** exhibited similar reactivity giving **2n** and **3n**. *m*-Bromo substituted substrates **1o** and **1p** afforded the corresponding **2o**, **3o** and **2p** and **3p** derivatives; the bromine atom decreased the reactivity of the substrates presumably due to the negative inductive effect (entries 15 and 16).

Further, the sterically hindered **1q** and **1r** disproportionated smoothly giving **2q** and **3q** and **2r** and **3r** (entries 17 and 18). In addition, we examined the reactivity of the sterically congested *o*-disubstituted phenyl ethers **1s–1v**. All of these ethers reacted well, regardless of the steric hindrance yielding the corresponding benzophenone and diphenylmethane derivatives **2s–2v** and **3s–3v** (entries 19–22). 3,4,5-Trisubstituted ether **1vv** smoothly yielded the expected products **2vv** and **3vv** in a short reaction time (entry 23). It appears that steric hindrance was not an obstacle for the disproportionation; however, the attempted reaction of highly sterically hindered bis[(2,3,4,5,6-pentamethylphenyl)(phenyl)methyl] ether furnished a complex reaction mixture.

In the cases of substrates **1f**, **1i** and **1n** a side reaction also took place. Friedel–Crafts products **3ff**, **3ii** and **3nn** were obtained (Scheme 1); consequently, whether iodine activated the methylene C–H bond in diphenylmethanes **3f**, **3i** and **3n** was investigated. In an independent experiment we treated

Table 2 Iodine-catalyzed disproportionation of ethers under SFRC



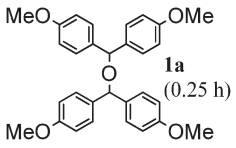
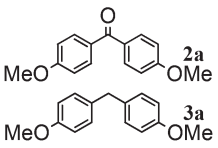
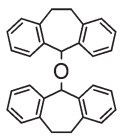
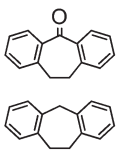
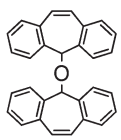
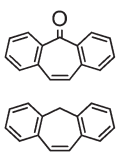
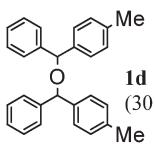
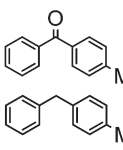
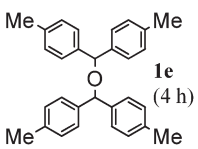
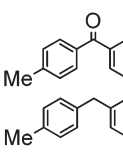
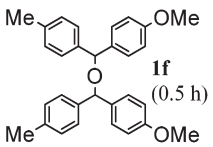
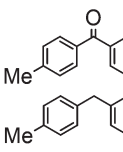
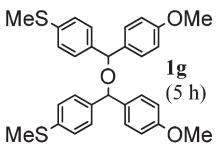
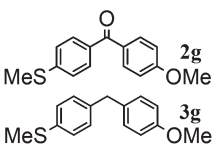
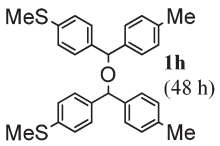
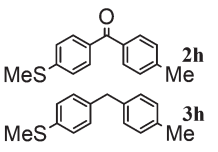
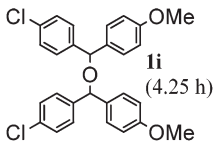
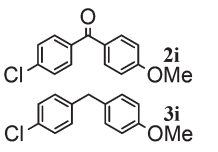
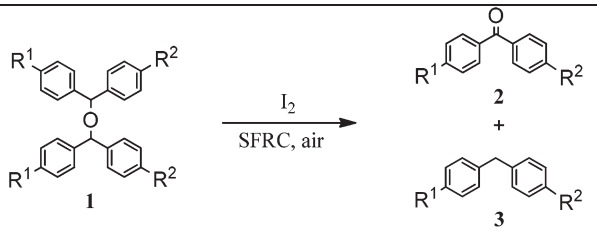
	Substrate[a]	Products	Yield [%]
1	 **1a** (0.25 h)	 **2a** **3a**	(74) **2a** (91) **3a**
2	 **1b** (0.5 h)	 **2b** **3b**	(90) **2b** (79) **3b**
3	 **1c** (0.33 h)	 **2c** **3c**	(79) **2c** (73) **3c**
4	 **1d** (30 h)	 **2d** **3d**	(93) **2d** (84) **3d**
5	 **1e** (4 h)	 **2e** **3e**	(88) **2e** (85) **3e**
6	 **1f** (0.5 h)	 **2f** **3f**	(67) **2f** (38) **3f**
7	 **1g** (5 h)	 **2g** **3g**	(77) **2g** (63) **3g**
8	 **1h** (48 h)	 **2h** **3h**	(96) **2h** (70) **3h**
9	 **1i** (4.25 h)	 **2i** **3i**	(51) **2i** (16) **3i**

Table 2 *(Contd.)*



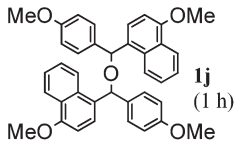
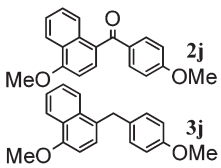
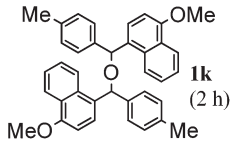
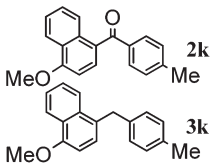
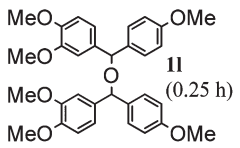
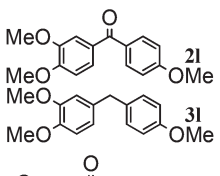
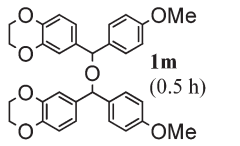
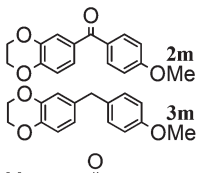
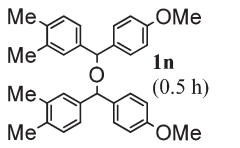
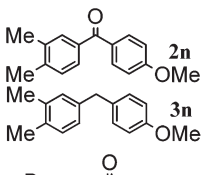
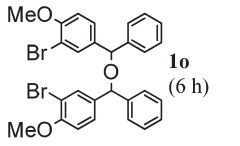
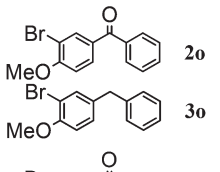
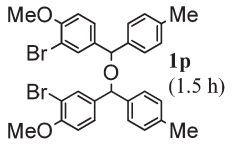
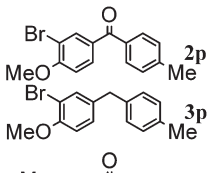
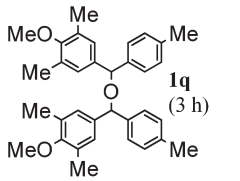
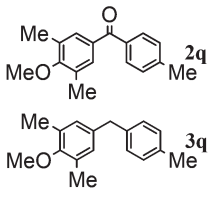
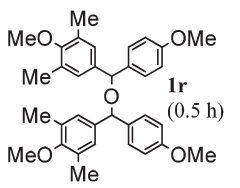
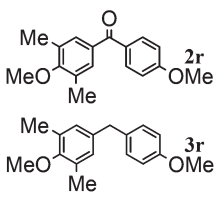
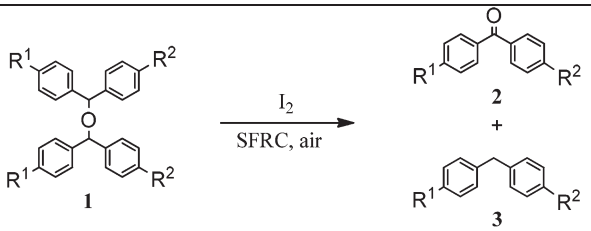
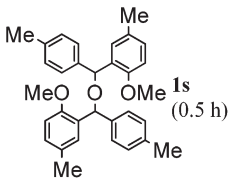
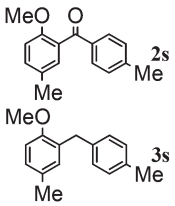
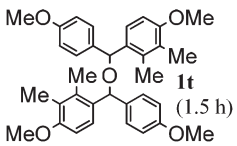
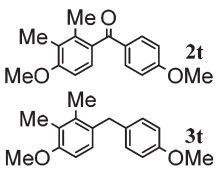
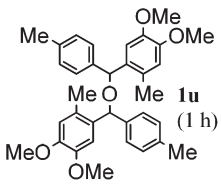
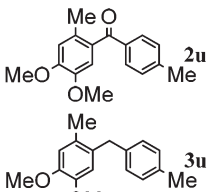
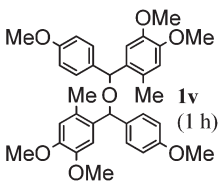
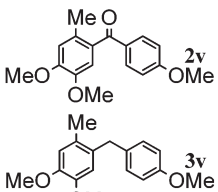
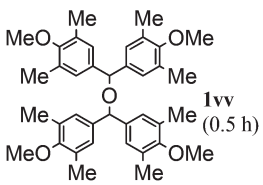
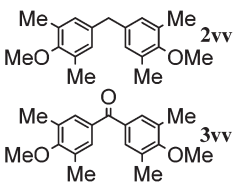
	Substrate[a]	Products	Yield [%]
10	 **1j** (1 h)	 **2j** **3j**	(88) **2j** (61) **3j**
11	 **1k** (2 h)	 **2k** **3k**	(78) **2k** (59) **3k**
12	 **1l** (0.25 h)	 **2l** **3l**	(45) **2l** (42) **3l**
13	 **1m** (0.5 h)	 **2m** **3m**	(81) **2m** (59) **3m**
14	 **1n** (0.5 h)	 **2n** **3n**	(73) **2n** (49) **3n**
15	 **1o** (6 h)	 **2o** **3o**	(85) **2o** (91) **3o**
16	 **1p** (1.5 h)	 **2p** **3p**	(87) **2p** (86) **3p**
17	 **1q** (3 h)	 **2q** **3q**	(93) **2q** (93) **3q**
18	 **1r** (0.5 h)	 **2r** **3r**	(94) **2r** (68) **3r**

Table 2 *(Contd.)*



	Substrate[a]	Products	Yield [%]
19	 **1s** (0.5 h)	 **2s** **3s**	(83) **2s** (66) **3s**
20	 **1t** (1.5 h)	 **2t** **3t**	(83) **2t** (62) **3t**
21	 **1u** (1 h)	 **2u** **3u**	(99) **2u** (83) **3u**
22	 **1v** (1 h)	 **2v** **3v**	(76) **2v** (54) **3v**
23	 **1vv** (0.5 h)	 **2vv** **3vv**	(97) **2vv** (92) **3vv**

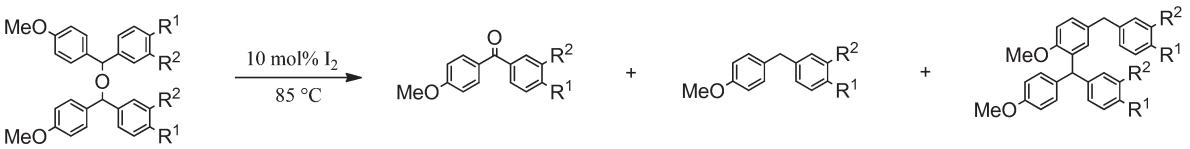
[a] 0.2 mmol of **1**, 10 mol% I_2 stirred under SFRC at 85 °C under air. Reaction times are in the brackets.

anisole with 4,4′-dimethoxydiphenylmethane in the presence of I_2. Under the same reaction conditions, only unreacted reactants were recovered, thus indicating the other reaction pathway than C–H activation. It is also known that iodine-catalyzed alkylation of electron-rich arenes with aryl-aldehydes furnished triphenylmethanes.[52]

All the starting substrates examined in Table 2 could disproportionate in only one way, giving the expected products. The reactivity of the non-symmetrically substituted ethers **1w**, **1x** and **1y** was examined in order to establish which part of the molecule was the better hydrogen donor, Scheme 2. The given relative ratios are based on the isolated yields of the products.

The preferential C–H bond scission obviously took place on the less electron-rich side of the ethers, giving ketones **2d**, **2e** and **2h** as the major, and **2a** as the minor products. The side of the C–H scission strongly suggests two things: (a) the generation of the more stable carbocation, and (b) the formation and transfer of the hydride. The quantity of the corresponding diphenylmethane products **3d**, **3e** and **3h** was substantially lower than expected; moreover, no **3a** was obtained, because it was fully consumed in the Friedel–Crafts alkylation, giving the mono- and disubstituted products **3ww–yy** and **10ww–yy**. In the disproportionation of **1w**, the most probable alkylation agent was ether **1d** formed *in situ* from **1w**. This can be concluded from an independent experiment in the presence of I_2, where **2a** was treated with **1d**, yielding the double Friedel–Crafts product **10ww**, Scheme 3. The reaction mixture contained (relative ratio) 67% of **3ww** and 33% of **10ww** after 45 minutes, while after 8 h only traces of **3ww** were detected. Alkylating agents in Friedel–Crafts alkylation are likely to be formed in this way.

The 4-methoxyphenyl group is obviously a crucial fragment for further alkylation. In Scheme 2 (below), the methoxy group in the starting ethers had both free *o*-positions. We were interested in what happens when they are blocked, Scheme 2 (above). Ethers **1z**, **1aa** and **1bb** yielded ketones **2zz**, **2d**, **2e** and diphenylmethanes **3d**, **3e**, and again C–H scission preferentially took place on the less electron-rich side (**2zz** > **3zz**); while transetherification yielded ethers **1zz** and **1d**. **1e** and **1vv** were not isolated because they disproportionated further, and examples of **1d**, **1e** and **1vv** are already described in Table 2, while **1zz** failed to disproportionate. The growing level of disproportionation of **1zz**, **1d** and **1e** is consistent with the increasing electron density from **1zz** to **1e**.



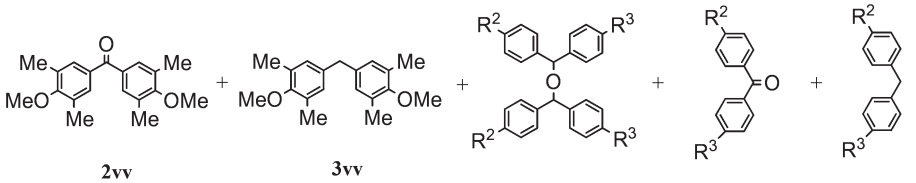
1f: R^1 = Me; R^2 = H
1i: R^1 = Cl; R^2 = H
1n: R^1 = R^2 = Me

2f: R^1 = Me; R^2 = H (67%)
2i: R^1 = Cl; R^2 = H (51%)
2n: R^1 = R^2 = Me (73%)

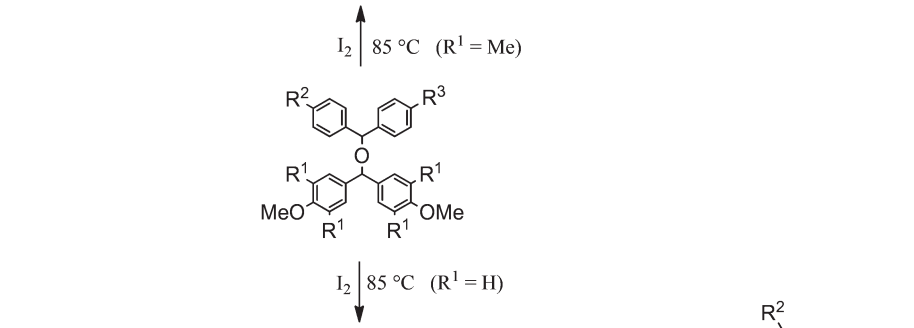
3f: R^1 = Me; R^2 = H (38%)
3i: R^1 = Cl; R^2 = H (16%)
3n: R^1 = R^2 = Me (49%)

3ff: R^1 = Me; R^2 = H (22%)
3ii: R^1 = Cl; R^2 = H (15%)
3nn: R^1 = R^2 = Me (24%)

Scheme 1 Friedel–Crafts side reaction giving triphenylmethane derivatives.

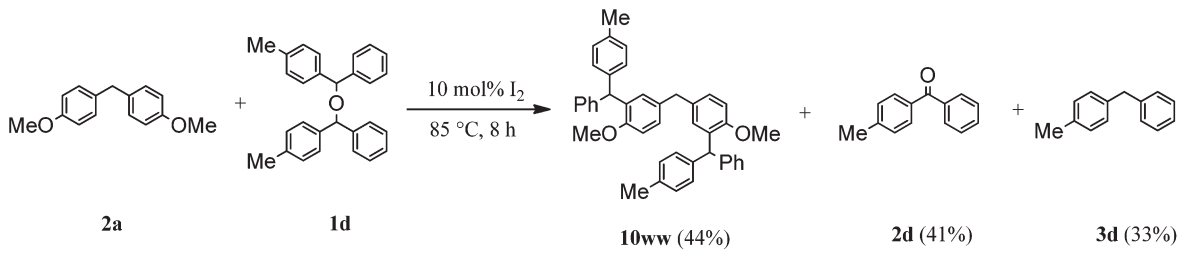


1z: R^2, R^3 = H	2.5	/	3.2	/	2.1 (**1zz**)	/	1 (**2zz**)	/	0 (**3zz**)	(8 h)
1aa: R^2 = H, R^3 = Me	4.3	/	5.5	/	3.1 (**1d**)	/	3.4 (**2d**)	/	1 (**3d**)	(0.6 h)
1bb: R^2, R^3 = Me	1.2	/	1.4	/	0 (**1e**)	/	1.2 (**2e**)	/	1 (**3e**)	(1.5 h)



1w: R^2 = H, R^3 = Me (0.75 h)	8.6	/	12 (**2d**)	/	0	/	1 (**3d**)	/	3.5 (**3ww**)	/	3.1 (**10ww**)
1x: R^2, R^3 = Me (0.25 h)	4.9	/	6 (**2e**)	/	0	/	1.6 (**3e**)	/	2.7 (**3xx**)	/	1 (**10xx**) (+ traces of **1d**)
1y: R^2 = SMe, R^3 = Me (1.5 h)	9.3	/	10.8 (**2h**)	/	0	/	3.5 (**3h**)	/	3.8 (**3yy**)	/	1 (**10yy**)

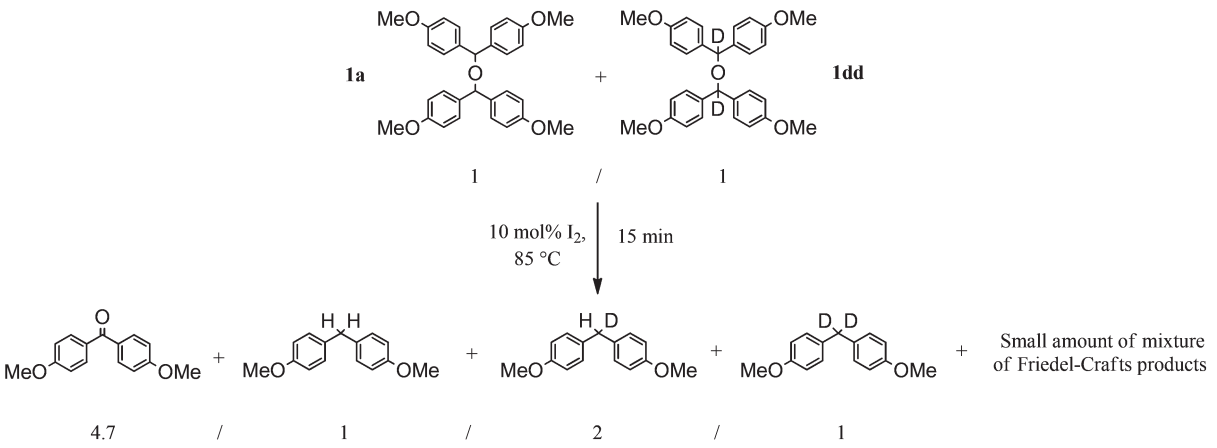
Scheme 2 I_2-catalyzed transformation of non-symmetrically substituted ethers.



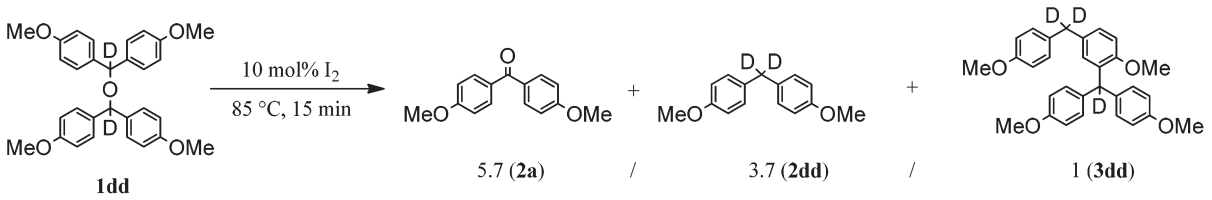
Scheme 3 Dimeric ether **1d** as an alkylating agent.

The isotope-labelled experiments were also performed. The I_2-catalyzed scrambling experiment of **1a** and its D_2-counterpart **1dd** yielded a mixture of products, Scheme 4. **1a** and **1dd** were fully transformed, and the overall product ratio suggested that approximately one half of **1a** and **1dd** disproportionated, giving the benzophenone and diphenylmethane derivatives (H_2 and D_2). The second half of **1a** and **1dd** was likely to transetherificate, giving mixed (HD) dimeric ether, which upon disproportionation yielded the benzophenone and mixed (HD) diphenylmethane products. A small amount of the mixture of Friedel–Crafts products was also isolated.

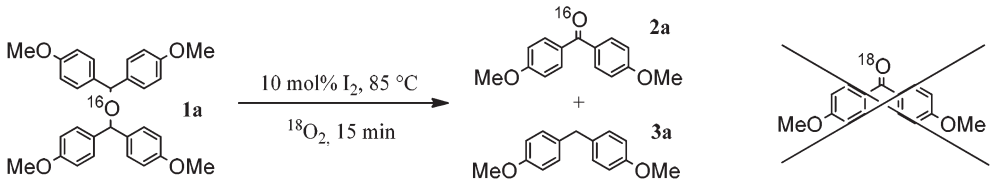
The scrambling experiment of **1a** and **1dd** was done also in $CHCl_3$ at 85 °C (conditions from Table 1, reaction time was 72 h). The ratio of diphenylmethane derivatives (H_2 *vs.* HD) was the same as it was under SFRC (1/2), which is an indication of transetherification followed by disproportionation; while some **1dd** remained unreacted. Next, the transformation of **1dd** was examined, Scheme 5. Ketone **2a** and diphenylmethane **2dd** were the expected products; in addition, Friedel–Crafts alkylation giving **3dd** also took place. As established above, the dimeric ethers acted as alkylating agents, and **3dd** was formed by the alkylation of **2dd** with **1dd**.



Scheme 4 Deuterium scrambling experiment under SFRC.



Scheme 5 I_2-catalyzed disproportionation of **1dd** under SFRC.



Scheme 6 I_2-catalyzed disproportionation of **1a** under the $^{18}O_2$ atmosphere.

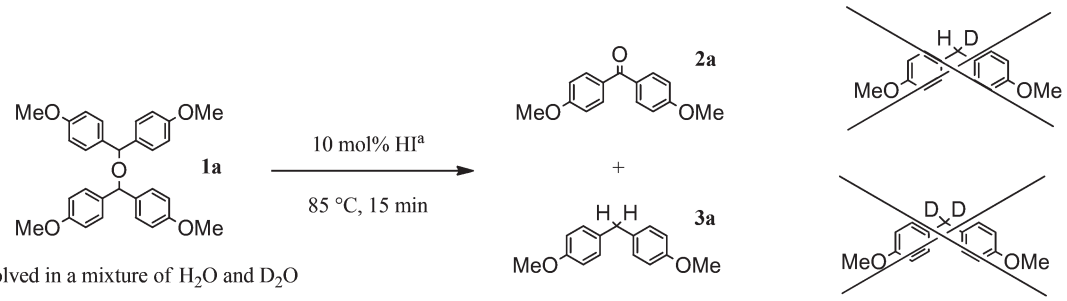
The formation of **3dd** was in substantial contrast with **1a**, where only traces of the Friedel–Crafts product were detected. It is evident that the cleavage of the C–D(H) bond played an important role in this reaction, since a considerable part of C–H(D) is broken in the transition state. The higher activation barrier made **1dd** less reactive for disproportionation, and the alkylation became a competitive process; while in the case of **1a** the reaction barrier is lower, and disproportionation was much faster than alkylation, and almost completely prevailed. It may be concluded that the primary kinetic isotope effect is considerable.[53]

The fate of an oxygen atom was studied with the isotopically pure $^{18}O_2$, Scheme 6. I_2-catalyzed disproportionation of **1a** under SFRC under an $^{18}O_2$ atmosphere furnished products **2a** and **3a** in a ratio of 1/1. No ^{18}O incorporation in ketone **2a** was established. The experiment confirmed that the carbonyl oxygen originated from the starting ether and not from the air.

Further, the role of HI was investigated in the presence of D_2O, Scheme 7. Disproportionation of **1a** with a catalytic amount of a 57% aqueous solution of HI in the presence of a small amount of D_2O yielded **2a** and **3a**, and no deuterium incorporation was noted. This is in strong support of the intramolecular hydrogen migration, because in the case of the intermolecular migration some incorporation of deuterium would have been observed.

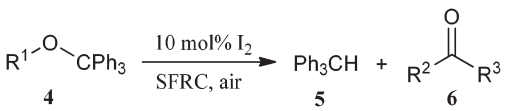
In continuation, we examined the reactivity of various trityl ethers in iodine-catalyzed transformation under SFRC; the results are summarized in Table 3. Trityl ethyl ether **4a** smoothly afforded triphenylmethane **5** and ethanal as the exclusive products; the latter as highly volatile was observed in ^1H NMR spectra (entry 1).

Trityl benzyl ether **4b** exhibited the lowest reactivity among the tested substrates, but the reaction was very efficient and without side-products (entry 2). 2-Octyl trityl ether **4c** was efficiently transformed into **5** and 2-octanone as the sole products in a short reaction time. 1-Phenylethyl trityl ether **4d** exhibited similar reactivity as **4c** did, affording **5** and acetophenone (entry 4). Trityl cyclohexyl ether **4e** completely disproportionated into cyclohexanone and **5**, which was isolated in high yield.



Scheme 7 HI-catalyzed disproportionation of **1a** in the presence of D_2O.

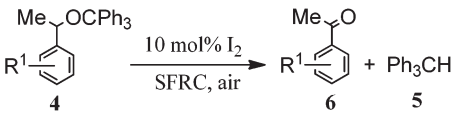
Table 3 I_2-catalyzed disproportionation of the trityl ethers



	R^1 (**4**)[a]	R^2	R^3	t [h]	**5**[b] [%]
1	R^1 = Et (**4a**)	Me	H	12	90
2	R^1 = CH_2Ph (**4b**)	Ph	H	20	96
3	R^1 = CH(Me)C_6H_{13}(**4c**)	C_6H_{13}	Me	2	76
4	R^1 = CH(Me)Ph (**4d**)	Ph	Me	2	88
5	R^1 = $CH(CH_2)_5$ (**4e**)	–$(CH_2)_5$–		2	94

[a] 0.2 mmol of **4**, 10 mol% I_2 stirred under SFRC at 85 °C. [b] 100% conversion in all cases, isolated yield of **5**. PhCHO, PhCOMe and 2-octanone were also isolated. Ethanal and cyclohexanone were observed in ^{1}H NMR spectra of the crude reaction mixture.

Table 4 The role of substituents in I_2-catalyzed disproportionation of trityl ethers



	R^1	**6**	t [h]	Conversion[a] [%]	**5**[b]
1	*p*-Me (**4f**)	(**6f**)	1	100 (89)	(86)
2	*m*-Me (**4g**)	(**6g**)	3	100 (92)	(89)
3	*m*-MeO (**4h**)	(**6h**)	2	100 (88)	(84)
4	*p*-F (**4i**)	(**6i**)	5	100 (84)	(90)
5	*p*-Cl (**4j**)	(**6j**)	3	89 (78)	(75)
6	*p*-Br (**4k**)	(**6k**)	3	89 (75)	(77)
7	*m*-NO_2 (**4l**)	(**6l**)	6	94 (81)	(83)
8	*p*-NO_2 (**4m**)	(**6m**)	8	92 (79)	(80)
9	*p*-CF_3 (**4n**)	(**6n**)	20	91 (77)	(78)

[a] 0.2 mmol of **4**, 10 mol% I_2 stirred under SFRC at 85 °C. Conversion determined from ^{1}H NMR spectra of the crude reaction mixture. [b] Values in the brackets refer to the isolated products.

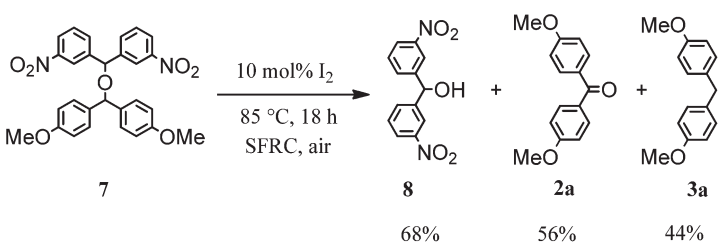
In order to obtain a deeper insight into this transformation, we studied the reactivity of the variously substituted 1-phenylethyl trityl ethers; the results are collected in Table 4.

Due to the SFRC, the transformation took place in a heterogeneous, highly viscous reaction mixture, and the Hammett correlation was not an objective.

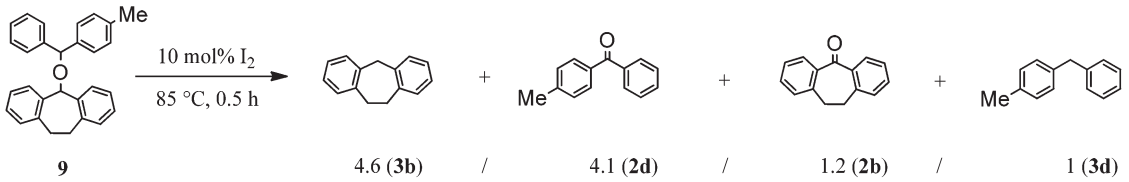
Reactions proceeded highly selectively without any other products. The difference in reactivity between activated and deactivated substrates is not extremely high; it can be concluded that only a moderate amount of charge is being developed in the transition state.

As can be seen from Table 4, a loose general trend could be observed; the electron-donating groups facilitated the transformation, and the electron-withdrawing groups retarded the reaction. Similar behaviour in disproportionation of trityl ethers in dichloromethane was observed,[37] as well as in disproportionation of dibenzhydryl ethers.[39] This is consistent with the hydride shift and carbocation with moderate charge formation, rather than the proton transfer.[37,41]

The electron-withdrawing groups deteriorated the disproportionation. We were interested in the reactivity of ether **7**, consisting of the electron-rich and the electron-poor fragment. According to the observed reactivity so far, one might expect the formation of 3,3′-dinitrobenzophenone and 4,4′-dimethoxydiphenylmethane as the main products; however, the reaction course was substantially different, Scheme 8.



Scheme 8 Transformation of the 'push–pull' substrate **7**.



Scheme 9 I_2-catalyzed disproportionation of the non-symmetrical ether **9**.

The transformation most probably began with the I_2-catalyzed transformation of **7** giving **8** and 4,4′-dimethoxydiphenylmethanol which was not isolated, since it reacted further giving the dimeric ether **1a**. The isolated products **2a** and **3a** were thus formed in a disproportionation of **1a**, while **8** was too deactivated to dimerize and also failed to disproportionate.

An additional test was performed with **9**, consisting of a highly reactive dibenzosuberanyl- and poorly reactive 4′-methylbenzhydryl moiety (Table 2, entries 2 and 4), Scheme 9.

Looking at the reaction time of **1d** (Table 2, entry 4), r.t. = 30 h, the disproportionation of **9** took place surprisingly rapidly (0.5 h). Only the expected products **2b**, **3b**, **2d** and **3d** were formed, and their relative ratios clearly confirmed the predominant hydrogen transfer that occurred from the electron-poorer side. There were no EDGs on the aryls, and (as expected) no Friedel–Crafts alkylation took place. The postulated hydride transfer and formation of the more stable carbocation appeared to be the most probable reaction pathway.

Finally, the proposed mechanism is depicted in Scheme 10. It appears that there are two different reaction pathways (α and β), where iodine played a crucial role in the polarization of the substrate. A direct disproportionation (path α) likely took place in two different modes, (i) and (ii), Scheme 10 (above). Hydrogen migration from the electron-poorer side was the major process (i), and from the electron-richer side was the minor process (ii); consequently a non-equal distribution of products was obtained. The electron-richer substrates exhibited higher reactivity, thus indicating the formation of the carbocationic intermediate and hydride migration, where stability of the carbocation was of prime importance.

An indirect disproportionation (β way) also took place with polarization of ether A, thus generating an electron-deficient centre (δ+) or carbocation. Transetherification with the second A furnished ethers B and C, where B was not isolated because it was more electron rich and more reactive than C and rapidly disproportionated further into D and E. Ether C disproportionated only partly due to its lower reactivity furnishing F and G; moreover, in a competing process, C acted as an alkylating agent of E, giving Friedel–Crafts products H and I.

Iodine has a remarkable catalytic potential and it is a substitute of choice for numerous metallic Lewis acids. Due to its mild nature and compatibility with the sensitive functional groups, research into the role of iodine in transformation of alcohols is currently underway in our laboratory.

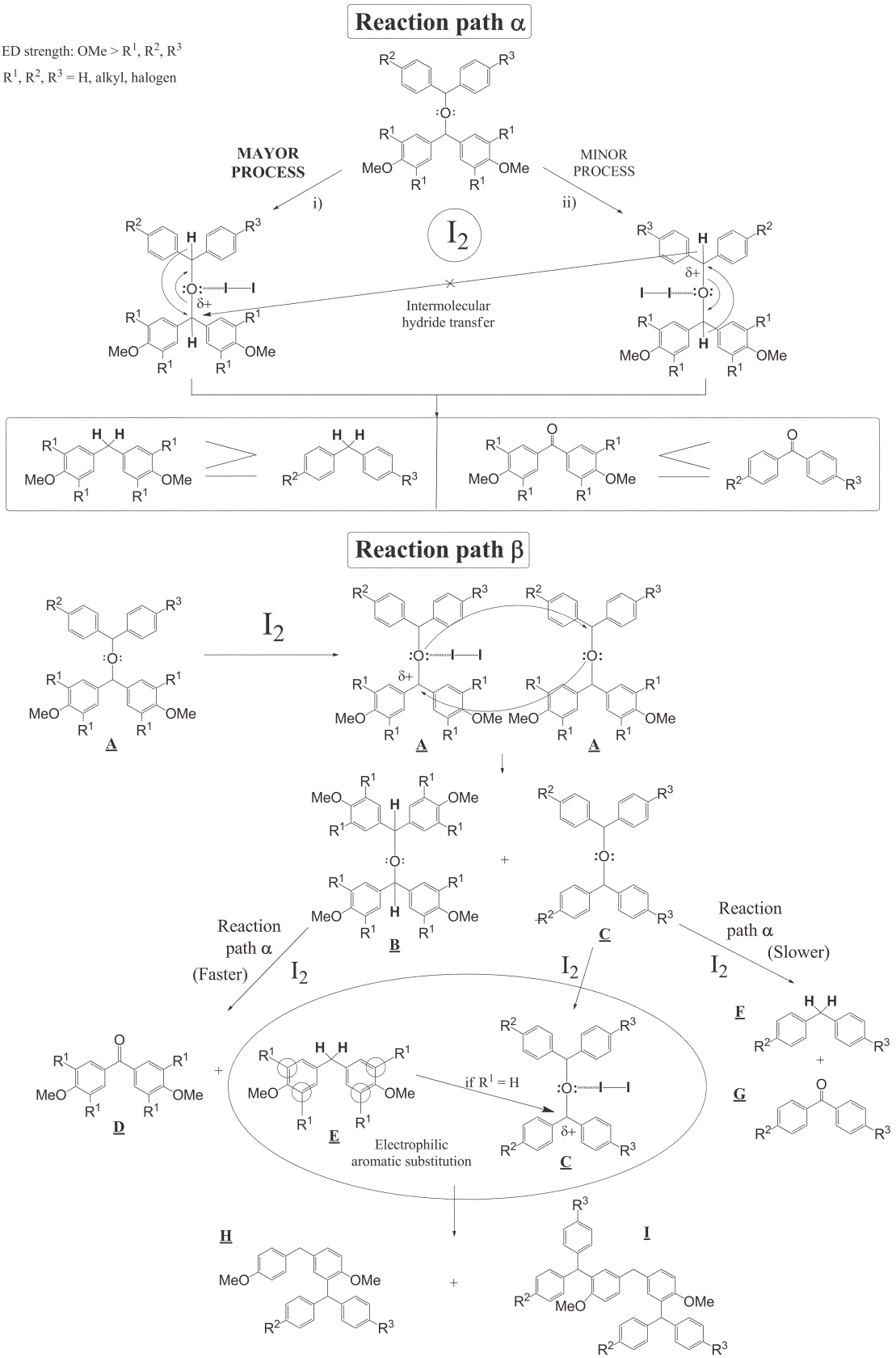
Conclusions

Iodine was shown to be an efficient, highly active and selective catalyst for disproportionation of the aryl-substituted ethers. Iodine's remarkable feature to replace strong acids as catalysts was demonstrated. This reaction has several advantages over other methods and is therefore amenable for scale-up and broader use. From a synthetic point of view, the reaction protocol is very simple; the transformation took place under mild reaction conditions, in the presence of air and moisture, without exotic, expensive, highly acidic or sensitive catalysts, yielding two classes of easily separable products – alkanes and ketones – in one step. The prevalent hydrogen transfer occurred from the electron poorer side, thus indicating hydride migration and formation of the more stable carbocation. An intramolecular hydride transfer was more likely than an intermolecular one. A substantial proportion of the C–H bond is being disrupted in the rate-determining step. The carbonyl oxygen atom originated from the starting ether, and not from the present air. In the cases of some 4-methoxyphenyl substituted ethers Friedel–Crafts mono- and dialkylation took place. This transformation also shares important green chemistry attributes, since it is conducted without organic solvents, thus contributing to operational simplicity, health-hazard minimization, improved atom- and cost-efficiency and waste-reduction.

Experimental section

General information

Reactions were carried out with 10 mol% of I_2 under an air atmosphere in tightly closed conical vials with stirring at 85 °C. Considerably viscous reaction mixtures were formed, because no solvent was used; however stirring was not prevented. Iodine remained in the closed reaction vial in spite of a high temperature (85 °C); no loss of iodine from the vial was noted. The basic chemicals were obtained from commercial sources, and the targeting ethers were synthesized. Column chromatography was performed on 70–230 mesh silica gel. TLC was performed on silica gel coated plates, using mixtures of hexane and CH_2Cl_2. Crude reaction mixtures were directly subjected to column chromatography. All starting ethers and products were characterized by their NMR spectra, HRMS, IR, melting points and elemental analysis; additionally COSY, HSQC and HMBC spectra were utilized to establish the



Scheme 10 The proposed reaction pathways of disproportionation under SFRC.

structures **3ff**, **3ii**, **3nn**, **3xx**, **3ww** and **10ww**. Spectroscopic properties of products **6** and **2zz** were identical to the commercially available compounds. HRMS were obtained by using electrospray ionization (ESI) with TOF mass analyzer type. The ^{1}H NMR spectra were recorded at 300 and 500 MHz, ^{13}C NMR spectra were recorded at 75 and 125 MHz. ^{19}F NMR spectra were recorded in acetone-d_6 at 470 MHz and are referred to (0.00 ppm) $CFCl_3$. Chemical shifts in ^{1}H NMR spectra are referred to (0.00 ppm) TMS or to 7.26 ppm in $CDCl_3$ or to 2.05 ppm (central line) in acetone-d_6 or to 2.50 ppm (central line) in DMSO-d_6. ^{13}C NMR shifts are always referred to the central line of the solvent peak – 77.00 ppm in $CDCl_3$, 30.83 ppm in acetone-d_6, and 39.43 ppm in DMSO-d_6.

Typical procedure for synthesis of the starting ethers 1

All ethers **1** were obtained by dimerization of the precursory diarylmethanols as exemplified in the cases of **1b** and **1d**. Diarylmethanols were prepared by reduction of the corresponding ketone derivatives; the latter were either commercially available or prepared by the Friedel–Crafts reaction using commercial starting materials. The crude ethers **1** were purified by crystallization or by column chromatography.

(a) Synthesis of 1 in dichloromethane: all but two of the ethers were synthesized in this way. Dibenzosuberol 1.05 g (5 mmol) was dissolved in 1 mL of CH_2Cl_2 and iodine 38 mg (0.15 mmol) was added. The reaction mixture was quenched after 10 minutes of stirring at room temperature with finely powdered $Na_2S_2O_3$; the stirring was continued until the iodine disappeared. After filtration of solids, the solvent was evaporated and the crude product crystallized from hexane/CH_2Cl_2 affording 0.86 g (85%) of **1b**.

(b) Synthesis of 1 under SFRC: only 1d and 1s were prepared in this way. (Phenyl)(*p*-tolyl)methanol 0.99 g (5 mmol) and iodine 38 mg (0.15 mmol) were stirred for 30 minutes at 85 °C. The reaction mixture was dissolved in CH_2Cl_2 and stirred further with finely powdered $Na_2S_2O_3$ until the disappearance of iodine. After concentration, the crude reaction mixture was chromatographed on silica gel (hexane/CH_2Cl_2 = 7/3) yielding 0.86 g (91%) of **1d**.

Typical procedure for synthesis of the starting trityl ethers 4a–e

Trityl ethers were prepared *via* a modified literature procedure[54] as follows. To a stirred solution of trityl chloride 4.18 g (15 mmol) and benzyl alcohol 1.78 g (16.5 mmol) in CH_2Cl_2 (6.5 mL), DBU 2.74 g (18 mmol) was added. The reaction mixture was stirred at room temperature for 24 h and chromatographed over silica gel (hexane/CH_2Cl_2 = 7.5/2.5), giving **4b** as a white solid; yield: 1.26 g (24%).

Typical procedure for synthesis of the starting trityl ethers 4f–4n

Trityl ethers were prepared *via* a modified literature procedure[54] as follows. To a stirred solution of 1-(4-methylphenyl)-ethanol 0.5 g (3.7 mmol) and trityl chloride 3.09 g (11.1 mmol) in CH_2Cl_2 (6 mL), DBU 1.69 g (11.1 mmol) was added. The reaction mixture was stirred at room temperature for 24 h and chromatographed over silica gel (hexane/CH_2Cl_2 = 7.5/2.5), giving **4f** as a white solid; yield 0.85 g (61%).

Synthesis of the starting ether 7

4,4′-Dimethoxybenzhydrol 733 mg (3 mmol) and 3,3′-dinitrobenzhydrol[55] 2.47 g (9 mmol) were dissolved in CH_2Cl_2 9 mL and iodine 23 mg (0.09 mmol) was added. The reaction mixture was quenched after 1 h of stirring at room temperature with finely powdered $Na_2S_2O_3$; the stirring was continued until the disappearance of iodine. After concentration, the crude reaction mixture was chromatographed over silica gel (CH_2Cl_2) giving 1.05 g (70%) of **7**.

Typical procedure for disproportionation of ethers 1

In a closed conical vial ether **1a** (94 mg, 0.2 mmol) and iodine (5 mg, 0.02 mmol) were stirred at 85 °C for 15 minutes. After the reaction was complete as monitored by TLC, the crude reaction mixture was dissolved in CH_2Cl_2 and subjected to preparative chromatography on silica gel (hexane/CH_2Cl_2 = 6/4) to afford **2a** as a white solid; yield: 36 mg (74%) and **3a** as a white solid; yield: 42 mg (91%).

Typical procedure for disproportionation of trityl ethers 4

In a closed conical vial trityl ether **4d** (73 mg, 0.2 mmol) and iodine (5 mg, 0.02 mmol) were stirred at 85 °C for 2 h. After the reaction was complete as monitored by TLC, the crude reaction mixture was dissolved in CH_2Cl_2 and subjected to preparative chromatography on silica gel (hexane/CH_2Cl_2 = 6/4) to afford **5** as a white solid; yield: 43 mg (88%) and **6d** as a colorless liquid; yield: 18 mg (76%). The characterization data of triphenylmethane **5**, benzaldehyde **6b**, 2-octanone **6c** and acetophenones **6d** and **6f–n** were identical to the properties of the commercially available compounds.

Experimental procedure for independent synthesis of compound 10ww

In a closed conical vial bis(*p*-anisyl)methane **2a** (46 mg, 0.2 mmol), **1d** (76 mg, 0.2 mmol) and iodine (5 mg, 0.02 mmol) were stirred at 85 °C for 8 hours. After the reaction was complete as monitored by TLC, the crude reaction mixture was dissolved in CH_2Cl_2 and subjected to preparative chromatography on silica gel (hexane/CH_2Cl_2 = 1/1) to afford **10ww** as a white solid; yield: 52 mg (44%).

Experimental procedure for disproportionation of a mixture of ethers 1a and 1dd

In a closed conical vial ether **1a** (47 mg, 0.1 mmol), **1dd** (47 mg, 0.1 mmol) and iodine (5 mg, 0.02 mmol) were stirred at 85 °C for 15 minutes. After the reaction was complete, the crude reaction mixture was dissolved in CH_2Cl_2 and subjected to preparative chromatography on silica gel (hexane/CH_2Cl_2 = 1/1) to afford ketone **2a**, Friedel–Crafts products and a mixture of **3a** and its isotopologues which was further analyzed with ^{1}H and ^{13}C-NMR spectroscopy.

Experimental procedure for disproportionation of ether 1dd

In a closed conical vial ether **1dd** (95 mg, 0.2 mmol) and iodine (5 mg, 0.02 mmol) were stirred at 85 °C for 15 minutes. After the reaction was complete, the crude reaction mixture was dissolved in CH_2Cl_2 and subjected to preparative chromatography on silica gel (hexane/CH_2Cl_2 = 1/1) to afford **2a** as a white solid; yield: 42 mg (87%), **2dd** as a white solid; yield: 26 mg (56%) and **3dd** as a white solid; yield: 14 mg (23%).

Experimental procedure for disproportionation of ether 1a under an $^{18}O_2$ atmosphere

In a closed conical vial ether **1a** (94 mg, 0.2 mmol) and iodine (5 mg, 0.02 mmol) were stirred at 85 °C under an $^{18}O_2$ atmosphere for 15 minutes. After the reaction was complete, the crude reaction mixture was dissolved in CH_2Cl_2 and subjected to preparative chromatography on silica gel (hexane/CH_2Cl_2 = 1/1) to afford **2a**, which was further analyzed on ^{18}O content with MS.

Experimental procedure for disproportionation of ether 1a with HI/D_2O

In a closed conical vial ether **1a** (94 mg, 0.2 mmol), HI (57 wt% in H_2O, 5 mg, 0.02 mmol) and D_2O (4 mg, 0.2 mmol) were stirred at 85 °C for 15 minutes. After the reaction was complete, the crude reaction mixture was dissolved in CH_2Cl_2 and subjected to preparative chromatography on silica gel (hexane/CH_2Cl_2 = 1/1) to afford **3a**, which was further analyzed with ^1H and ^{13}C NMR spectroscopy.

Experimental procedure for disproportionation of ether 7

In a closed conical vial ether **7** (140 mg, 0.28 mmol) and iodine (7 mg, 0.028 mmol) were stirred at 85 °C for 18 hours. After the reaction was complete as monitored by TLC, the crude reaction mixture was dissolved in CH_2Cl_2 and subjected to preparative chromatography on silica gel (CH_2Cl_2) to afford **8** as a yellow solid; yield: 52 mg (68%), **2a** as a white solid; yield: 19 mg (56%) and **3a** as a white solid; yield: 14 mg (44%).

Experimental procedure for disproportionation of ether 9

In a closed conical vial ether **9** (293 mg, 0.75 mmol) and iodine (19 mg, 0.075 mmol) were stirred at 85 °C for 30 minutes under air. After the reaction was complete as monitored by TLC, the crude reaction mixture was dissolved in CH_2Cl_2 and subjected to preparative chromatography on silica gel (hexane/CH_2Cl_2 = 8/2) to afford **2b** as a colorless oil; yield: 35 mg (22%), **2d** as a yellow oil; yield: 111 mg (75%), **3b** as a white solid; yield: 102 mg (70%) and **3d** as a colorless oil; yield: 20 mg (15%).

Spectroscopic and analytic data

[Bis(4-methoxy-3,5-dimethylphenyl)]methyl (phenyl)(*p*-tolyl)-methyl ether (1aa). (1.3 mmol (0.39 g) bis(4-methoxy-3,5-dimethylphenyl)methanol, 3.9 mmol (0.77 g) (phenyl)(*p*-tolyl)-methanol, 4 mL CH_2Cl_2, 0.04 mmol (10 mg) I_2, r.t. = 0.75 h, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 6/4); white solid (0.37 g, 65%); mp: 42.8–51.5 °C; ^1H-NMR (300 MHz, CD_3COCD_3): δ 7.42–7.20 (m, 7H), 7.18–7.10 (m, 2H), 7.05 (s, 4H), 5.39 (s, 1H), 5.23 (s, 1H), 3.67 (s, 6H), 2.30 (s, 3H), 2.21 (s, 12H); ^{13}C-NMR (75 MHz, CD_3COCD_3): δ 158.2, 158.1, 144.8, 141.6, 139.9, 139.8, 138.7, 132.2, 132.2, 130.8, 130.1, 129.2, 129.1, 129.1, 129.0, 128.9, 81.7, 81.6, 60.7, 22.1, 17.3; IR(neat): 2921, 1482, 1451, 1219, 1133, 1062, 1009, 873, 697 cm^{-1}; MS (ESI): 503.3 $(M + Na)^+$; HRMS: calcd for $C_{33}H_{36}O_3Na$: 503.2562; found: 503.2560; Anal. Calcd for $C_{33}H_{36}O_3$: C, 82.46; H, 7.55. Found: C, 82.47; H, 7.59.

[Bis(4-methoxy-3,5-dimethylphenyl)]methyl bis(*p*-tolyl)-methyl ether (1bb). (1.1 mmol (0.33 g) bis(4-methoxy-3,5-dimethylphenyl)methanol, 3.3 mmol (0.70 g) bis(*p*-tolyl)-methanol, 3 mL CH_2Cl_2, 0.03 mmol (8 mg) I_2, r.t. = 0.75 h, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 6/4); white solid (0.41 g, 76%); mp: 50.9–52.8 °C; ^1H-NMR (300 MHz, CD_3COCD_3): δ 7.25 (d, J = 8.0 Hz, 4H), 7.13 (d, J = 8.0 Hz, 4H), 7.04 (s, 4H), 5.35 (s, 1H), 5.22 (s, 1H), 3.67 (s, 6H), 2.29 (s, 6H), 2.21 (s, 12H); ^{13}C-NMR (75 MHz, CD_3COCD_3): δ 158.1, 141.8, 139.9, 138.5, 132.2, 130.7, 129.1, 128.9, 81.6, 81.5, 60.7, 22.1, 17.3; IR(neat): 2921, 1482, 1219, 1133, 1064, 1011, 874, 807, 764, 653 cm^{-1}; MS (ESI): 517.3 $(M + Na)^+$; HRMS: calcd for $C_{34}H_{38}O_3Na$: 517.2719; found: 517.2721; Anal. Calcd for $C_{34}H_{38}O_3$: C, 82.55; H, 7.74. Found: C, 82.63; H, 7.95.

Bis[(phenyl)(*p*-tolyl)methyl] ether (1d). From 5 mmol (0.99 g) of (phenyl)(*p*-tolyl)methanol under SFRC (0.15 mmol (38 mg) I_2, r.t. = 30 min, 85 °C); preparative chromatography (SiO_2, CH_2Cl_2); colorless oil[56] (0.86 g, 91%); ^1H-NMR (300 MHz, $CDCl_3$): δ 7.38–7.18 (m, 14H), 7.14–7.06 (m, 4H), 5.36 (s, 2H), 2.31 (s, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 142.6, 142.5, 139.3, 139.2, 137.0, 137.0, 129.1, 129.0, 128.3, 128.3, 127.3, 127.2, 127.2, 127.1, 79.7, 21.1; IR(neat): 3057, 3027, 2921, 2866, 1603, 1510, 1493, 1450, 1176, 1082, 1057, 1020, 799, 733, 698 cm^{-1}; MS (ESI): 401.2 $(M + Na)^+$.

Bis[bis(*p*-anisyl)deuteromethyl] ether (1dd). From 2 mmol (491 mg) of bis(*p*-anisyl)deuteromethanol (4 mL CH_2Cl_2, 0.06 mmol (15 mg) I_2, r.t. = 5 min, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); colorless oil (376 mg, 80%); ^1H-NMR (300 Hz, CD_3COCD_3): δ 7.28 (d, J = 8.7 Hz, 8H), 6.88 (d, J = 8.7 Hz, 8H), 3.77 (s, 12H); ^{13}C-NMR (75 MHz, CD_3COCD_3): δ 160.9, 136.8, 130.1, 115.5, 80.4 (t, J = 22 Hz), 56.5; IR(neat): 2999, 2953, 2834, 1608, 1506, 1461, 1440, 1299, 1239, 1168, 1067, 1028, 806, 767 cm^{-1}; MS (ESI): 495.2 $(M + Na)^+$; HRMS: calcd for $C_{30}H_{28}D_2O_5Na$: 495.2116; found: 495.2133; Anal. Calcd for $C_{30}H_{28}D_2O_5$: C, 76.25; H, 6.82. Found: C, 75.97; H, 6.58.

Bis[bis(*p*-tolyl)methyl] ether (1e). From 5 mmol (1.06 g) of bis(*p*-tolyl)methanol (1 mL CH_2Cl_2, 0.15 mmol (38 mg) I_2, r.t. = 90 min, 25 °C); preparative chromatography (SiO_2, CH_2Cl_2); pale orange solid (1 g, 98%); mp: 116.0–117.2 °C (lit[57] 117 °C); ^1H-NMR (300 MHz, $CDCl_3$): δ 7.18 (d, J = 8.0 Hz, 8H), 7.06 (d, J = 8.0 Hz, 8H), 5.26 (s, 2H), 2.31 (s, 12H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 139.6, 136.8, 129.0, 127.1, 79.5, 21.1; IR(KBr): 3024, 2919, 2872, 1511, 1176, 1115, 1080, 1019, 806, 765 cm^{-1}; MS (ESI): 429.2 $(M + Na)^+$; HRMS: calcd for $C_{30}H_{30}ONa$: 429.2194;

found: 429.2212; Anal. Calcd for $C_{30}H_{30}O$: C, 88.63; H, 7.44. Found: C, 88.90; H, 7.62.

Bis[(*p*-anisyl)(*p*-tolyl)methyl] ether (1f). From 5 mmol (1.14 g) of (*p*-anisyl)(*p*-tolyl)methanol (1 mL CH_2Cl_2, 0.15 mmol (38 mg) I_2, r.t. = 1 h, 25 °C); preparative chromatography (SiO_2, CH_2Cl_2); white solid (1.01 g, 92%); mp: 80.0–88.7 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.23–7.15 (m, 8H), 7.07 (d, J = 7.9 Hz, 4H), 6.79 (d, J = 8.6 Hz, 4H), 5.25 (s, 2H), 3.77 (s, 6H), 2.32 (s, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 158.8, 158.8, 139.7, 139.6, 136.8, 136.8, 134.8, 134.7, 129.0, 129.0, 128.5, 128.5, 127.1, 113.7, 113.7, 79.1, 55.2, 21.1; IR(KBr): 2951, 2833, 1608, 1509, 1458, 1302, 1241, 1170, 1068, 1033, 808, 773 cm^{-1}; MS (ESI): 461.2 (M + Na)$^+$; HRMS: calcd for $C_{30}H_{30}O_3Na$: 461.2093; found: 461.2095; Anal. Calcd for $C_{30}H_{30}O_3$: C, 82.16; H, 6.89. Found: C, 82.24; H, 7.04.

Bis[(*p*-anisyl)(4-methylthiophenyl)methyl] ether (1g). From 5 mmol (1.30 g) of (*p*-anisyl)(4-methylthiophenyl)methanol (1 mL CH_2Cl_2, 0.15 mmol (38 mg) I_2, r.t. = 1 h, 25 °C); preparative chromatography (SiO_2, CH_2Cl_2); white solid (1.03 g, 82%); mp: 115.6–118.0 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.29–7.15 (m, 12H), 6.84 (d, J = 8.4 Hz, 4H), 5.28 (s, 2H), 3.78 (s, 6H), 2.46 (s, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 159.0, 159.0, 139.6, 139.4, 137.3, 137.2, 134.2, 134.1, 128.5, 128.4, 127.6, 127.6, 126.6, 113.8, 113.8, 79.0, 55.2, 15.9; IR(KBr): 2831, 1607, 1508, 1460, 1437, 1300, 1241, 1171, 1069, 1032, 810 cm^{-1}; MS (ESI): 525.2 (M + Na)$^+$; HRMS: calcd for $C_{30}H_{30}O_3S_2Na$: 525.1534; found: 525.1519; Anal. Calcd for $C_{30}H_{30}O_3S_2$: C, 71.68; H, 6.02. Found: C, 71.83; H, 6.06.

Bis[(4-methylthiophenyl)(*p*-tolyl)methyl] ether (1h). From 5 mmol (1.22 g) of (4-methylthiophenyl)(*p*-tolyl)methanol (1 mL CH_2Cl_2, 0.15 mmol (38 mg) I_2, r.t. = 2 h, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); white solid (1.04 g, 88%); mp: 120.9–126.0 °C; ^{1}H-NMR (300 MHz, DMSO): δ 7.31–7.18 (m, 12H), 7.16–7.10 (m, 4H), 5.30 (s, 2H), 2.43 (s, 6H), 2.26 (s, 6H); ^{13}C-NMR (75 MHz, DMSO): δ 139.0, 139.0, 139.0, 138.9, 137.0, 136.9, 136.5, 136.4, 128.9, 127.1, 127.1, 126.4, 126.4, 125.9, 78.8, 20.6, 14.6; IR(KBr): 3022, 2919, 2876, 1595, 1511, 1489, 1435, 1403, 1189, 1071, 1014, 967, 862, 805, 772, 730, 615 cm^{-1}; MS (ESI): 493.2 (M + Na)$^+$; HRMS: calcd for $C_{30}H_{30}OS_2Na$: 493.1636; found: 493.1646; Anal. Calcd for $C_{30}H_{30}OS_2$: C, 76.55; H, 6.42. Found: C, 76.86; H, 6.67.

Bis[(*p*-anisyl)(4-chlorophenyl)methyl] ether (1i). From 5 mmol (1.24 g, of (*p*-anisyl)(4-chlorophenyl)methanol (1 mL CH_2Cl_2, 0.15 mmol (38 mg) I_2, r.t. = 1 h, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); white solid (0.92 g, 77%); mp: 108.5–116.6 °C (lit[58] 118–119 °C); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.32–7.15 (m, 12H), 6.90–6.80 (m, 4H), 5.28 (s, 2H), 3.79 (s, 3H), 3.78 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 159.2, 159.2, 141.1, 140.8, 133.7, 133.4, 133.1, 133.0, 128.6, 128.6, 128.4, 128.4, 128.3, 114.0, 113.9, 78.9, 78.9, 55.2; IR(KBr): 3000, 2953, 2833, 1610, 1511, 1489, 1300, 1244, 1171, 1069, 1034, 1011, 860, 807 cm^{-1}; MS (ESI): 517.1 (M + K)$^+$; HRMS: calcd for $C_{28}H_{24}O_3Cl_2K$: 517.0740; found: 517.0740.

Bis[(*p*-anisyl)(4-methoxynaphthalen-1-yl)methyl] ether (1j). From 5 mmol (1.47 g) of (*p*-anisyl)(4-methoxynaphthalen-1-yl)-methanol (1 mL CH_2Cl_2, 0.15 mmol (38 mg) I_2, r.t. = 1 h, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); pale orange solid (1.13 g, 79%); mp: 96.9–117.2 °C; ^{1}H-NMR (300 MHz, DMSO): δ 8.23–8.10 (m, 2H), 7.92–7.83 (m, 1H), 7.79–7.65 (m, 2H), 7.60–7.51 (m, 1H), 7.48–7.14 (m, 8H), 7.04–6.95 (m, 2H), 6.90–6.76 (m, 4H), 5.96 (s, 1H), 5.90 (s, 1H), 3.99 (s, 3H), 3.96 (s, 3H), 3.70 (s, 3H), 3.67 (s, 3H); ^{13}C-NMR (75 MHz, DMSO): δ 158.3, 158.2, 154.6, 154.4, 133.9, 131.2, 130.9, 128.9, 128.3, 128.0, 126.3, 126.1, 126.1, 125.4, 125.2, 125.1, 124.8, 124.7, 124.2, 123.9, 121.9, 121.8, 113.6, 113.4, 103.6, 103.5, 77.7, 76.9, 55.5, 55.4, 54.9; IR(KBr): 2999, 2955, 2834, 1609, 1585, 1511, 1460, 1391, 1298, 1244, 1168, 1092, 1053, 1030, 814, 763, 710 cm^{-1}; MS (ESI): 593.2 (M + Na)$^+$; HRMS: calcd for $C_{38}H_{34}O_5Na$: 593.2304; found: 593.2315; Anal. Calcd for $C_{38}H_{34}O_5$: C, 79.98; H, 6.01. Found: C, 79.93; H, 6.12.

Bis[(4-methoxynaphthalen-1-yl)(*p*-tolyl)methyl] ether (1k). From 5 mmol (1.39 g) of (4-methoxynaphthalen-1-yl)(*p*-tolyl)-methanol (1 mL CH_2Cl_2, 0.15 mmol (38 mg) I_2, r.t. = 30 min, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); pale yellow solid (1.12 g, 83%); mp: 94.2–120.1 °C; ^{1}H-NMR (300 MHz, DMSO): δ 8.23–8.11 (m, 2H), 7.95–7.87 (m, 1H), 7.78–7.71 (m, 1H), 7.70–7.63 (m, 1H), 7.59–7.50 (m, 1H), 7.47–6.94 (m, 14H), 5.97 (s, 1H), 5.90 (s, 1H), 3.98 (s, 3H), 3.95 (s, 3H), 2.24 (s, 3H), 2.20 (s, 3H); ^{13}C-NMR (75 MHz, DMSO): δ 154.7, 154.4, 139.0, 138.9, 136.3, 136.1, 131.2, 130.9, 128.7, 128.6, 128.1, 126.9, 126.6, 126.5, 126.1, 126.0, 125.6, 125.4, 125.1, 124.8, 124.7, 124.2, 123.9, 121.9, 121.8, 103.5, 103.5, 78.1, 77.4, 55.4, 55.4, 20.5, 20.5; IR(KBr): 3003, 2953, 2922, 1623, 1585, 1512, 1462, 1392, 1269, 1241, 1218, 1157, 1093, 1056, 818, 762, 713 cm^{-1}; MS (ESI): 538.3 (M)$^+$; HRMS: calcd for $C_{38}H_{34}O_3$: 538.2508; found: 538.2515; Anal. Calcd for $C_{38}H_{34}O_3$: C, 84.73; H, 6.36. Found: C, 84.84; H, 6.83.

Bis[(*p*-anisyl)(3,4-dimethoxyphenyl)methyl] ether (1l). From 5 mmol (1.37 g) of (*p*-anisyl)(3,4-dimethoxyphenyl)methanol (1 mL CH_2Cl_2, 0.15 mmol (38 mg) I_2, r.t. = 45 min, 25 °C); preparative chromatography (SiO_2, CH_2Cl_2); white solid (0.85 g, 64%); mp: 40.5–51.5 °C; ^{1}H-NMR (300 MHz, DMSO): δ 7.26 (d, J = 8.5 Hz, 4H), 6.94–6.81 (m, 10H), 5.27 (s, 2H), 3.72 (s, 12H), 3.68 (s, 3H), 3.67 (s, 3H); ^{13}C-NMR (75 MHz, DMSO): δ 158.3, 148.6, 148.5, 147.9, 135.0, 134.8, 134.6, 134.4, 127.8, 127.8, 118.8, 118.7, 113.6, 113.6, 111.7, 110.4, 110.3, 78.8, 78.8, 55.4, 55.3, 55.3, 54.9; IR(KBr): 2998, 2833, 1609, 1510, 1459, 1416, 1253, 1172, 1137, 1027, 835, 809, 747, 633 cm^{-1}; MS (ESI): 530.2 (M)$^+$; HRMS: calcd for $C_{32}H_{34}O_7$: 530.2305; found: 530.2319; Anal. Calcd for $C_{32}H_{34}O_7$: C, 72.43; H, 6.46. Found: C, 72.66; H, 6.67.

Bis[(*p*-anisyl)(2,3-dihydro-benzo[1,4]dioxin-6-yl)methyl] ether (1m). From 5 mmol (1.36 g) of (*p*-anisyl)(2,3-dihydro-benzo-[1,4]dioxin-6-yl)methanol (1 mL CH_2Cl_2, 0.15 mmol (38 mg) I_2, r.t. = 40 min, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); white solid (1.16 g, 88%); mp: 57.5–71.8 °C; ^{1}H-NMR (300 MHz, DMSO): δ 7.26–7.17 (m, 4H), 6.93–6.85 (m, 4H), 6.82–6.72 (m, 6H), 5.19 (s, 2H), 4.20 (s, 8H), 3.72 (s, 3H), 3.72 (s, 3H); ^{13}C-NMR (75 MHz, DMSO): δ 158.3, 143.0, 142.4, 135.7, 135.6, 134.3, 134.2, 127.7, 119.2, 116.8, 115.0, 113.7, 78.2, 63.9, 63.9, 54.9; IR(KBr): 2931, 2873, 2835, 1601, 1590, 1505, 1459, 1432, 1286, 1248, 1173, 1110, 1065,

1033, 920, 888, 816, 786, 714 cm^{-1}; MS (ESI): 549.2 $(M + Na)^+$; HRMS: calcd for $C_{32}H_{30}O_7Na$: 549.1889; found: 549.1899; Anal. Calcd for $C_{32}H_{30}O_7$: C, 72.99; H, 5.74. Found: C, 72.99; H, 5.74.

Bis[(*p*-anisyl)(3,4-dimethylphenyl)methyl] ether (1n). From 5 mmol (1.21 g) of (*p*-anisyl)(3,4-dimethylphenyl)methanol (1 mL CH_2Cl_2, 0.15 mmol (38 mg) I_2, r.t. = 1 h, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); yellow oil (0.86 g, 74%); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.25 (d, J = 8.5 Hz, 4H), 7.12–7.03 (m, 6H), 6.83 (d, J = 8.5 Hz, 4H), 5.28 (s, 2H), 3.76 (s, 6H), 2.22 (s, 6H), 2.21 (s, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 58.8, 140.2, 140.1, 136.3, 135.4, 135.0, 134.9, 129.5, 128.4, 124.6, 124.6, 113.7, 79.3, 55.2, 19.9, 19.4; IR(neat): 3000, 2932, 2835, 1610, 1584, 1508, 1456, 1298, 1247, 1172, 1109, 1057, 1036, 826, 783, 737 cm^{-1}; MS (ESI): 489.2 $(M + Na)^+$; HRMS: calcd for $C_{32}H_{34}O_3Na$: 489.2406; found: 489.2418; Anal. Calcd for $C_{32}H_{34}O_3$: C, 82.37; H, 7.34. Found: C, 82.75; H, 7.68.

Bis[(3-bromo-4-methoxyphenyl)(phenyl)methyl] ether (1o). From 5 mmol (1.47 g) of (3-bromo-4-methoxyphenyl)(phenyl)-methanol (1 mL CH_2Cl_2, 0.15 mmol (38 mg) I_2, r.t. = 3 h, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); white solid (1 g, 70%); mp: 52.6–70.9 °C; ^{1}H-NMR (300 MHz, DMSO): δ 7.51–7.46 (m, 2H), 7.41–7.22 (m, 12H), 7.12–7.04 (m, 2H), 5.38 (s, 2H), 3.82 (s, 6H); ^{13}C-NMR (75 MHz, DMSO); δ 154.6, 141.9, 141.8, 135.8, 135.7, 130.9, 128.4, 127.4, 127.2, 126.4, 112.7, 112.6, 110.5, 78.6, 78.5, 56.1; IR(KBr): 1603, 1495, 1456, 1255, 1183, 1055, 1020, 808, 698, 669 cm^{-1}; MS (ESI): 589.0 $(M + Na)^+$, 591.0 $(M + 2 + Na)^+$, 593.0 $(M + 4 + Na)^+$; HRMS: calcd for $C_{28}H_{24}Br_2O_3Na$: 588.9990; found: 589.0010; Anal. Calcd for $C_{28}H_{24}Br_2O_3$: C, 59.18; H, 4.26. Found: C, 59.47; H, 4.23.

Bis[(3-bromo-4-methoxyphenyl)(*p*-tolyl)methyl] ether (1p). From 5 mmol (1.54 g) of (3-bromo-4-methoxyphenyl)(*p*-tolyl)-methanol (1 mL CH_2Cl_2, 0.15 mmol (38 mg) I_2, r.t. = 1 h, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); white solid (1.21 g, 81%); mp: 55.2–65.7 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.54–746 (m, 2H), 7.26–7.09 (m, 10H), 6.87–6.79 (m, 2H), 5.25 (s, 2H), 3.86 (s, 3H), 3.86 (s, 3H), 2.33 (s, 3H), 2.33 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 155.1, 155.1, 138.7, 138.6, 137.4, 137.3, 136.2, 136.0, 132.1, 132.0, 129.2, 129.2, 127.3, 127.2, 127.0, 111.8, 111.7, 111.6, 111.6, 78.9, 78.9, 56.2, 21.1; IR(KBr): 1602, 1496, 1256, 1180, 1054, 1018, 814, 771, 674 cm^{-1}; MS (ESI): 617.0 $(M + Na)^+$, 619.0 $(M + 2 + Na)^+$, 621.0 $(M + 4 + Na)^+$; HRMS: calcd for $C_{30}H_{28}Br_2O_3Na$: 617.0303; found: 617.0316; Anal. Calcd for $C_{30}H_{28}Br_2O_3$: C, 60.42; H, 4.73. Found: C, 60.82; H, 4.80.

Bis[(4-methoxy-3,5-dimethylphenyl)(*p*-tolyl)methyl] ether (1q). From 5 mmol (1.28 g) of (4-methoxy-3,5-dimethylphenyl)-(*p*-tolyl)methanol (1 mL CH_2Cl_2, 0.15 mmol (38 mg) I_2, r.t. = 1 h, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); white solid (0.87 g, 70%); mp: 44.9–53.3 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.19 (d, J = 7.7 Hz, 4H), 7.08 (d, J = 7.7 Hz, 4H), 6.90 (s, 4H), 5.18 (s, 1H), 5.18 (s, 1H), 3.68 (s, 3H), 3.67 (s, 3H), 2.33 (s, 6H), 2.22 (s, 12H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 156.1, 156.1, 139.6, 139.6, 137.7, 137.7, 136.8, 136.8, 130.4, 129.0, 127.7, 127.6, 127.2, 127.1, 79.6, 79.5, 59.6, 21.1, 16.2; IR(KBr): 1509, 1481, 1454, 1307, 1221, 1177, 1136, 1067, 1013, 884, 820, 773, 637 cm^{-1}; MS (ESI): 517.3 $(M + Na)^+$; HRMS: calcd for $C_{34}H_{38}O_3Na$: 517.2719; found: 517.2733; Anal. Calcd for $C_{34}H_{38}O_3$: C, 82.55; H, 7.74. Found: C, 82.95; H, 8.03.

Bis[(*p*-anisyl)(4-methoxy-3,5-dimethylphenyl)methyl] ether (1r). From 5 mmol (1.36 g) of (*p*-anisyl)(4-methoxy-3,5-dimethylphenyl)methanol (15 mmol toluene, 3 mol% I_2, r.t. = 30 min, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); white solid (0.76 g, 58%); mp: 45.8–46.9 °C; ^{1}H-NMR (300 MHz, DMSO): δ 7.22 (d, J = 8.5 Hz, 4H), 6.95 (s, 4H), 6.91–6.84 (m, 4H), 5.19 (s, 1H), 5.19 (s, 1H), 3.72 (s, 6H), 3.61 (s, 3H), 3.61 (s, 3H), 2.17 (s, 12H); ^{13}C-NMR (75 MHz, DMSO): δ 158.4, 158.3, 155.5, 155.5, 137.7, 137.5, 134.4, 134.2, 129.9, 129.9, 127.8, 127.7, 126.9, 126.7, 113.7, 113.7, 78.8, 78.7, 59.1, 54.9, 15.8; IR(KBr): 1611, 1511, 1481, 1303, 1246, 1222, 1172, 1135, 1063, 1020, 1008, 833, 777, 635 cm^{-1}; MS (ESI): 549.3 $(M + Na)^+$; HRMS: calcd for $C_{34}H_{38}O_5Na$: 549.2617; found: 549.2629; Anal. Calcd for $C_{34}H_{38}O_5$: C, 77.54; H, 7.27. Found: C, 77.90; H, 7.65.

Bis[(2-methoxy-5-methylphenyl)(*p*-tolyl)methyl] ether (1s). From 5 mmol (1.21 g) of (2-methoxy-5-methylphenyl)(*p*-tolyl)-methanol (0.15 mmol (38 mg) I_2, r.t. = 25 min, 85 °C); preparative chromatography (SiO_2, CH_2Cl_2); white solid (0.78 g, 67%); mp: 117.0–141.7 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.37 (dd, J = 9.7 Hz, J = 1.7 Hz, 2H), 7.24–7.16 (m, 4H), 7.07–6.99 (m, 4H), 6.99–6.91 (m, 2H), 6.69–6.63 (m, 2H), 5.72 (s, 1H), 5.71 (s, 1H), 3.61 (s, 3H), 3.60 (s, 3H), 2.30 (s, 6H), 2.27 (s, 3H), 2.25 (s, 3H); ^{13}C-NMR (75 MHz, DMSO): δ 154.2, 153.9, 139.2, 139.1, 136.0, 130.1, 128.9, 128.5, 128.4, 126.9, 126.8, 126.6, 110.9, 73.1, 73.0, 55.3, 55.3, 20.5, 20.3; IR(KBr): 2996, 2916, 1609, 1501, 1460, 1285, 1246, 1178, 1119, 1070, 1028, 808, 735 cm^{-1}; MS (ESI): 489.2 $(M + Na)^+$; HRMS: calcd for $C_{32}H_{34}O_3Na$: 489.2406; found: 489.2417; Anal. Calcd for $C_{32}H_{34}O_3$: C, 82.37; H, 7.34. Found: C, 82.74; H, 7.64.

Bis[(*p*-anisyl)(4-methoxy-2,3-dimethylphenyl)methyl] ether (1t). From 5 mmol (1.36 g) of (*p*-anisyl)(4-methoxy-2,3-dimethylphenyl)methanol (1 mL CH_2Cl_2, 0.15 mmol (38 mg) I_2, r.t. = 1 h, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); white solid (0.96 g, 73%); mp: 63.3–72.7 °C; ^{1}H-NMR (300 MHz, DMSO): δ 7.35 (d, J = 8.6 Hz, 1H), 7.25 (d, J = 8.6 Hz, 1H), 7.16–7.06 (m, 4H), 6.91–6.80 (m, 6H), 5.43 (s, 1H), 5.41 (s, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 3.71 (s, 3H), 3.70 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 1.88 (s, 3H), 1.86 (s, 3H); ^{13}C-NMR (75 MHz, DMSO): δ 158.2, 158.1, 156.2, 156.0, 135.2, 134.6, 134.1, 133.8, 131.9, 131.4, 128.3, 127.9, 125.8, 124.9, 124.3, 124.1, 113.5, 113.4, 107.7, 107.7, 76.7, 76.4, 55.2, 54.9, 14.9, 14.9, 11.6, 11.6; IR(KBr): 2997, 2935, 2834, 1605, 1511, 1481, 1464, 1248, 1172, 1107, 1069, 1034, 810 cm^{-1}; MS (ESI): 549.3 $(M + Na)^+$; HRMS: calcd for $C_{34}H_{38}O_5Na$: 549.2617; found: 549.2626; Anal. Calcd for $C_{34}H_{38}O_5$: C, 77.54; H, 7.27. Found: C, 77.67; H, 7.27.

Bis[(4,5-dimethoxy-2-methylphenyl)(*p*-tolyl)methyl] ether (1u). From 5 mmol (1.36 g) of (4,5-dimethoxy-2-methylphenyl)-(*p*-tolyl)methanol (1 mL CH_2Cl_2, 0.15 mmol (38 mg) I_2, r.t. = 1 h, 25 °C); preparative chromatography (SiO_2, CH_2Cl_2); white solid (0.93 g, 71%); mp: 52.3–64.1 °C; ^{1}H-NMR (300 MHz, DMSO): δ 7.20–7.07 (m, 8H), 7.04 (s, 1H), 7.03 (s, 1H),

6.76 (s, 1H), 6.71 (s, 1H), 5.42 (s, 1H), 5.40 (s, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 3.67 (s, 3H), 3.61 (s, 3H), 2.26 (s, 3H), 2.25 (s, 3H), 1.94 (s, 6H); ^{13}C-NMR (75 MHz, DMSO): δ 147.7, 147.6, 146.8, 146.7, 138.8, 138.6, 136.3, 136.1, 131.8, 131.0, 128.8, 128.6, 127.7, 127.1, 126.8, 126.6, 114.1, 114.1, 110.9, 110.9, 76.7, 76.3, 55.4, 55.4, 55.3, 20.5, 20.5, 18.2, 18.0; IR(KBr): 2997, 2930, 2848, 1609, 1513, 1460, 1263, 1213, 1099, 1039, 849, 811, 753 cm^{-1}; MS (ESI): 526.3 (M)$^+$; HRMS: calcd for $C_{34}H_{38}O_5$: 526.2719; found: 526.2729; Anal. Calcd for $C_{34}H_{38}O_5$: C, 77.54; H, 7.27. Found: C, 77.79; H, 7.58.

Bis[(*p*-anisyl)(4,5-dimethoxy-2-methylphenyl)methyl] ether (1v). From 5 mmol (1.44 g) of (*p*-anisyl)(4,5-dimethoxy-2-methylphenyl)methanol (1 mL CH_2Cl_2, 0.15 mmol (38 mg) I_2, r.t. = 1 h, 25 °C); preparative chromatography (SiO_2, CH_2Cl_2); white solid (0.77 g, 55%); mp: 50.2–64.7 °C; ^{1}H-NMR (300 MHz, DMSO): δ 7.21–7.12 (m, 4H), 7.08–7.03 (m, 2H), 6.92–6.82 (m, 4H), 6.78–6.69 (m, 2H), 5.39 (s, 1H), 5.37 (s, 1H), 3.74 + 3.72 + 3.71 + 3.68 + 3.62 (18H), 1.93 (s, 6H); ^{13}C-NMR (75 MHz, DMSO): δ 158.3, 158.2, 147.6, 147.5, 146.8, 146.7, 133.7, 133.5, 131.9, 131.2, 128.2, 128.0, 127.6, 127.0, 114.1, 114.1, 113.6, 113.5, 110.8, 110.7, 76.4, 76.1, 55.4, 55.4, 55.4, 54.9, 18.2, 18.0; IR(KBr): 2998, 2933, 2834, 1610, 1511, 1462, 1302, 1249, 1211, 1172, 1099, 1033, 831, 755 cm^{-1}; MS (ESI): 558.3 (M)$^+$; HRMS: calcd for $C_{34}H_{38}O_7$: 558.2618; found: 558.2615; Anal. Calcd for $C_{34}H_{38}O_7$: C, 73.10; H, 6.86. Found: C, 73.27; H, 7.07.

Bis[bis(4-methoxy-3,5-dimethylphenyl)methyl] ether (1vv). (0.75 mmol (0.23 g) bis(4-methoxy-3,5-dimethylphenyl)methanol, 3 mL CH_2Cl_2, 0.02 mmol (6 mg) I_2, r.t. = 1.5 h, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); white solid (0.15 g, 69%); mp: 150.3–157.2 °C; ^{1}H-NMR (300 MHz, CD_3COCD_3): δ 7.01 (s, 8H), 5.20 (s, 2H), 3.68 (s, 12H), 2.21 (s, 24H); ^{13}C-NMR (75 MHz, CD_3COCD_3): δ 158.1, 139.8, 132.1, 129.3, 81.8, 60.7, 17.3; IR(neat): 2920, 2864, 2824, 1481, 1416, 1317, 1294, 1218, 1132, 1082, 1014, 886, 877, 865, 785, 748, 703, 676, 641 cm^{-1}; MS (ESI): 605.3 (M + Na)$^+$; HRMS: calcd for $C_{38}H_{46}O_5Na$: 605.3243; found: 605.3232; Anal. Calcd for $C_{38}H_{46}O_5$: C, 78.32; H, 7.96. Found: C, 78.24; H, 7.98.

Bis(*p*-anisyl)methyl (phenyl)(*p*-tolyl)methyl ether (1w). (2 mmol (0.49 g) bis(*p*-anisyl)methanol, 6 mmol (1.19 g) (phenyl)(*p*-tolyl)methanol, 6 mL CH_2Cl_2, 0.06 mmol (15 mg) I_2, r.t. = 30 min, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 2.5/7.5); colorless oil (0.81 g, 95%); ^{1}H-NMR (300 MHz, DMSO): δ 7.38–7.18 (m, 11H), 7.17–7.10 (m, 2H), 6.93–6.83 (m, 4H), 5.31 (s, 1H), 5.27 (s, 1H), 3.72 (s, 6H), 2.26 (s, 3H); ^{13}C-NMR (75 MHz, DMSO): δ 158.4, 158.3, 142.4, 139.2, 136.4, 134.4, 134.3, 128.9, 128.2, 127.8, 127.7, 127.1, 126.5, 126.4, 113.7, 113.6, 79.0, 78.5, 54.9, 20.6; IR(neat): 2834, 1609, 1508, 1453, 1301, 1242, 1169, 1030, 776, 730, 698 cm^{-1}; MS (ESI): 447.2 (M + Na)$^+$; HRMS: calcd for $C_{29}H_{28}O_3Na$: 447.1936; found: 447.1940; Anal. Calcd for $C_{29}H_{28}O_3$: C, 82.05; H, 6.65. Found: C, 81.88; H, 6.84.

Bis(*p*-anisyl)methyl bis(*p*-tolyl)methyl ether (1x). (2 mmol (0.49 g) bis(*p*-anisyl)methanol, 6 mmol (1.27 g) bis(*p*-tolyl)-methanol, 6 mL CH_2Cl_2, 0.06 mmol (15 mg) I_2, r.t. = 30 min, 25 °C); preparative chromatography (SiO_2, CH_2Cl_2); pink solid (0.54 g, 61%); mp: 78.6–82.3 °C; ^{1}H-NMR (300 MHz, DMSO): δ 7.29–7.04 (m, 12H), 6.96–6.79 (m, 4H), 5.27 (s, 1H), 5.25 (s, 1H), 3.72 (s, 6H), 2.26 (s, 6H); ^{13}C-NMR (75 MHz, DMSO): δ 158.3, 139.4, 136.3, 134.4, 128.8, 127.7, 126.5, 113.6, 78.8, 78.4, 54.9, 20.5; IR(neat): 2833, 1608, 1507, 1462, 1302, 1239, 1170, 1065, 1031, 811, 774, 764 cm^{-1}; MS (ESI): 461.2 (M + Na)$^+$; HRMS: calcd for $C_{30}H_{30}O_3Na$: 461.2093; found: 461.2076; Anal. Calcd for $C_{30}H_{30}O_3$: C, 82.16; H, 6.89. Found: C, 82.19; H, 7.05.

Bis(*p*-anisyl)methyl (4-methylthiophenyl)(*p*-tolyl)methyl ether (1y). (2 mmol (0.49 g) bis(*p*-anisyl)methanol, 6 mmol (1.47 g) (4-methylthiophenyl)(*p*-tolyl)methanol, 6 mL CH_2Cl_2, 0.06 mmol (15 mg) I_2, r.t. = 30 min, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 2.5/7.5); white solid (0.83 g, 88%); mp: 102.4–105.4 °C; ^{1}H-NMR (300 MHz, CD_3COCD_3): δ 7.37–7.18 (m, 10H), 7.18–7.09 (m, 2H), 6.93–6.82 (m, 4H), 5.36 (s, 1H), 5.34 (s, 1H), 3.77 (s, 6H), 2.46 (s, 3H), 2.29 (s, 3H); ^{13}C-NMR (75 MHz, CD_3COCD_3): δ 161.0, 161.0, 141.6, 141.5, 139.5, 138.7, 136.7, 136.6, 130.8, 130.1, 130.1, 129.4, 128.8, 128.1, 115.5, 115.5, 81.1, 81.1, 56.5, 22.1, 16.5; IR(neat): 2833, 1607, 1507, 1462, 1302, 1239, 1169, 1066, 1031, 810, 775 cm^{-1}; MS (ESI): 493.2 (M + Na)$^+$; HRMS: calcd for $C_{30}H_{30}O_3SNa$: 493.1813; found: 493.1815; Anal. Calcd for $C_{30}H_{30}O_3S$: C, 76.56; H, 6.43. Found: C, 76.68; H, 6.50.

[Bis(4-methoxy-3,5-dimethylphenyl)]methyl diphenylmethyl ether (1z). (2 mmol (0.60 g) bis(4-methoxy-3,5-dimethylphenyl)methanol, 6 mmol (1.11 g) diphenylmethanol, 6 mL CH_2Cl_2, 0.06 mmol (15 mg) I_2, r.t. = 0.5 h, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 6/4); white solid (0.37 g, 40%); mp: 94.3–101.4 °C; ^{1}H-NMR (300 MHz, CD_3COCD_3): δ 7.44–7.37 (m, 4H), 7.37–7.29 (m, 4H), 7.29–7.21 (m, 2H), 7.06 (s, 4H), 5.43 (s, 1H), 5.24 (s, 1H), 3.67 (s, 6H), 2.21 (s, 12H); ^{13}C-NMR (75 MHz, CD_3COCD_3): δ 158.2, 144.6, 139.7, 132.2, 130.2, 129.2, 129.1, 128.9, 81.9, 81.7, 60.7, 17.3; IR(neat): 1482, 1448, 1220, 1132, 1062, 1010, 761, 735, 700 cm^{-1}; MS (ESI): 489.2 (M + Na)$^+$; HRMS: calcd for $C_{32}H_{34}O_3Na$: 489.2406; found: 489.2404; Anal. Calcd for $C_{32}H_{34}O_3$: C, 82.37; H, 7.34. Found: C, 82.56; H, 7.39.

[Bis(*p*-anisyl)methyl][methyl] ether (2aa). From 1 mmol (0.24 g) of bis(*p*-anisyl)methanol (1 mL MeOH, 0.06 mmol (15 mg) I_2, r.t. = 30 min, 55 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 7.5/2.5); white solid[59] (0.23 g, 88%); mp: 34.4–35.4 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.16 (d, J = 8.7 Hz, 4H), 6.78 (d, J = 8.7 Hz, 4H), 5.08 (s, 1H), 3.76 (s, 6H), 3.30 (s, 3H); ^{13}C-NMR (125 MHz, CD_3COCD_3): δ 160.8, 136.9, 129.8, 115.3, 85.9, 57.6, 56.4; IR(neat): 2995, 2934, 2904, 2831, 1610, 1510, 1460, 1300, 1245, 1171, 1088, 1034, 814, 596, 574 cm^{-1}; MS (ESI): 281.1 (M + Na)$^+$; HRMS: calcd for $C_{16}H_{18}O_3Na$: 281.1154; found: 281.1148.

[Bis(*p*-anisyl)methyl][bis(trifluoromethyl)methyl] ether (2ab). From 1 mmol (0.24 g) of bis(*p*-anisyl)methanol, (1 mL $(CF_3)_2COH$, 0.06 mmol (15 mg) I_2, r.t. = 30 min, 55 °C); preparative chromatography (Al_2O_3 (basic), hexane/CH_2Cl_2 = 6/4); colorless oil (30 mg, 76%), ^{1}H-NMR (500 MHz, CD_3COCD_3): δ 7.34 (d, J = 8.7 Hz, 4H), 6.94 (d, J = 8.7 Hz, 4H), 5.91 (s, 1H), 4.90 (septet, J = 6.2 Hz, 1H), 3.79 (s, 6H); ^{13}C-NMR (125 MHz,

CD_3COCD_3): δ 161.6, 133.7, 130.7, 124.0 (qq, J = 284 Hz, J = 4 Hz), 115.6, 87.5, 74.5 (septet, J = 32 Hz), 56.5; ^{19}F-NMR (470 MHz, CD_3COCD_3): δ −72.7 (d, J = 6.2 Hz, 6F); IR(neat): 3006, 2936, 2840, 1613, 1586, 1514, 1465, 1365, 1284, 1254, 1194, 1102, 1035, 977, 887, 832, 815, 779, 743, 688 cm^{-1}; MS (ESI): 417.1 (M + Na)$^+$; HRMS: calcd for $C_{18}H_{16}F_6O_3Na$: 417.0901; found: 417.0885. Anal. Calcd for $C_{18}H_{16}F_6O_3$: C, 54.83; H, 4.09. Found: C, 54.99; H, 3.79.

Bis(*p*-anisyl)dideuteromethane (2dd). From 0.2 mmol (95 mg) of **1dd** (0.02 mmol (5 mg) I_2, r.t. = 15 min, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 6/4); white solid (26 mg, 56%); mp: 49.8–50.8 °C; ^{1}H-NMR (500 MHz, CD_3COCD_3): δ 7.12 (d, J = 8.7 Hz, 4H), 6.83 (d, J = 8.7 Hz, 4H), 3.74 (s, 6H); ^{13}C-NMR (125 MHz, CD_3COCD_3): δ 159.9, 135.7, 131.4, 115.5, 56.4, 40.9 (quintet, J = 19 Hz); IR(neat): 3031, 3006, 2962, 2935, 2836, 1607, 1579, 1507, 1455, 1295, 1235, 1173, 1106, 1028, 1000, 878, 830, 804, 778, 749, 716 cm^{-1}; MS (ESI): 228.1 (M − D)$^+$; HRMS: calcd for $C_{15}H_{14}DO_2$: 228.1135; found: 228.1130.

(*p*-Anisyl)(4-methylthiophenyl)methanone (2g). From 0.2 mmol (101 mg) of **1g** (0.02 mmol (5 mg) I_2, r.t. = 5 h, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 6/4); white solid (40 mg, 77%); mp: 124.1–125.1 °C (lit[60] 126–127 °C); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.79 (d, J = 7.9 Hz, 2H), 7.70 (d, J = 7.7 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 6.95 (d, J = 7.7 Hz, 2H), 3.89 (s, 3H), 2.54 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 194.6, 163.0, 144.5, 134.3, 132.3, 130.4, 130.3, 124.8, 113.5, 55.5, 14.9; IR(KBr): 2839, 1642, 1592, 1503, 1397, 1312, 1289, 1252, 1171, 1148, 1088, 1022, 926, 847, 826, 759, 677, 617 cm^{-1}; MS (ESI): 259.1 (M + H)$^+$.

(4-Methylthiophenyl)(*p*-tolyl)methanone (2h). From 0.2 mmol (94 mg) of **1h** (0.02 mmol (5 mg) I_2, r.t. = 48 h, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); white solid (47 mg, 96%); mp: 85.5–86.3 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.72 (d, J = 8.5 Hz, 2H), 7.68 (d, J = 8.1 Hz, 2H), 7.32–7.23 (m, 4H), 2.55 (s, 3H), 2.45 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 195.6, 144.8, 143.0, 135.0, 133.9, 130.5, 130.1, 128.9, 124.8, 21.6, 14.8; IR(KBr): 1643, 1591, 1396, 1287, 1084, 926, 845, 816, 745, 673 cm^{-1}; MS (ESI): 243.1 (M + H)$^+$; HRMS: calcd for $C_{15}H_{15}OS$: 243.0844; found: 243.0838; Anal. Calcd for $C_{15}H_{14}OS$: C, 74.34; H, 5.82. Found: C, 73.97; H, 5.63.

(*p*-Anisyl)(4-methoxynaphthalen-1-yl)methanone (2j). From 0.2 mmol (114 mg) of **1j** (0.02 mmol (5 mg) I_2, r.t. = 1 h, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 6/4); pale green solid (51 mg, 88%); mp: 104.3–105.5 °C (lit[61] 115–116 °C); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.38–8.30 (m, 1H), 8.24–8.17 (m, 1H), 7.84 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 8.0 Hz, 1H), 7.54–7.47 (m, 2H), 6.92 (d, J = 8.0 Hz, 2H), 6.80 (d, J = 8.0 Hz, 1H), 4.06 (s, 3H), 3.87 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$); δ 196.1, 163.3, 157.8, 132.6, 132.5, 131.9, 129.8, 128.9, 127.7, 125.7, 122.2, 113.5, 102.0, 55.7, 55.5; IR(KBr): 1639, 1597, 1576, 1506, 1462, 1424, 1321, 1291, 1256, 1175, 1152, 1088, 1052, 1024, 979, 866, 843, 819, 770 cm^{-1}; MS (ESI): 293.1 (M + H)$^+$.

(4-Methoxynaphthalen-1-yl)(*p*-tolyl)methanone (2k). From 0.2 mmol (108 mg) of **1k** (0.02 mmol (5 mg) I_2, r.t. = 2 h, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 6/4); pale green solid (43 mg, 78%); mp: 108.8–109.6 °C (lit[62] 110–111 °C); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.34–8.22 (m, 2H), 7.72 (d, J = 8.1 Hz, 2H), 7.54 (d, J = 8.0 Hz, 1H), 7.57–7.45 (m, 2H), 7.22 (d, J = 8.1 Hz, 2H), 6.76 (d, J = 8.0 Hz, 1H), 4.06 (s, 3H), 2.43 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 197.0, 158.0, 143.3, 136.6, 132.5, 130.6, 130.4, 128.9, 128.5, 127.8, 125.7, 122.2, 101.9, 55.7, 21.6; IR(neat): 3050, 3004, 2938, 2842, 1649, 1601, 1579, 1511, 1460, 1424, 1327, 1252, 1178, 1157, 1094, 1054, 1026, 983, 872, 821, 769, 745 cm^{-1}; MS (ESI): 277.1 (M + H)$^+$.

(*p*-Anisyl)(3,4-dimethoxyphenyl)methanone (2l). From 0.2 mmol (106 mg) of **1l** (0.02 mmol (5 mg) I_2, r.t. = 15 min, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); white solid (25 mg, 45%); mp: 98.3–99.2 °C (lit[63] 96–97 °C); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.77 (d, J = 8.8 Hz, 2H), 7.41 (d, J = 1.9 Hz, 1H), 7.32 (dd, J = 8.3 Hz, J = 1.9 Hz, 1H), 6.94 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.3 Hz, 1H), 3.95 (s, 3H), 3.94 (s, 3H), 3.89 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 194.4, 162.8, 152.6, 148.9, 132.2, 130.8, 130.7, 124.7, 113.4, 112.3, 109.7, 56.0, 56.0, 55.4; IR(KBr): 3068, 2934, 2837, 1643, 1601, 1514, 1449, 1414, 1315, 1264, 1236, 1167, 1133, 1020, 868, 837, 757, 700 cm^{-1}; MS (ESI): 273.1 (M + H)$^+$.

(*p*-Anisyl)(2,3-dihydro-benzo[1,4]dioxin-6-yl)methanone (2m). From 0.2 mmol (105 mg) of **1m** (0.02 mmol (5 mg) I_2, r.t. = 30 min, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); orange solid (44 mg, 81%), mp: 98.0–100.8 °C (lit[64] 130–133 °C); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.79 (d, J = 8.7 Hz, 2H), 7.37–7.29 (m, 2H), 6.98–6.89 (m, 3H), 4.35–4.23 (m, 4H), 3.88 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 194.1, 162.9, 147.2, 143.1, 132.2, 131.6, 130.5, 124.0, 119.5, 116.9, 113.4, 64.6, 64.2, 55.4; IR(KBr): 2839, 1641, 1602, 1578, 1504, 1460, 1423, 1304, 1256, 1169, 1112, 1066, 1024, 890, 844, 766 cm^{-1}; MS (ESI): 271.1 (M + H)$^+$.

(*p*-Anisyl)(3,4-dimethylphenyl)methanone (2n). From 0.2 mmol (93 mg) of **1n** (0.02 mmol (5 mg) I_2, r.t. = 30 min, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 6/4); orange solid (35 mg, 73%); mp: 66.7–70.4 °C (lit[65] 75 °C); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.81 (d, J = 8.8 Hz, 2H), 7.56 (d, J = 1.3 Hz, 1H), 7.49 (dd, J = 7.8 Hz, J = 1.3 Hz, 1H), 7.22 (d, J = 7.8 Hz, 1H), 6.96 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H), 2.34 (s, 3H), 2.32 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 195.5, 162.9, 141.3, 136.6, 135.9, 132.4, 130.9, 130.5, 129.3, 127.6, 113.4, 55.4, 20.0, 19.8; IR(KBr): 1647, 1599, 1504, 1450, 1400, 1305, 1251, 1171, 1115, 1025, 974, 839, 788, 765, 687 cm^{-1}; MS (ESI): 241.1 (M + H)$^+$; Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.98; H, 6.86.

(3-Bromo-4-methoxyphenyl)(*p*-tolyl)methanone (2p). From 0.2 mmol (119 mg) of **1p** (0.02 mmol (5 mg) I_2, r.t. = 1.5 h, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 6/4); white solid (53 mg, 87%); mp: 104.8–105.4 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.04–7.99 (m, 1H), 7.76 (d, J = 8.3 Hz, 1H), 7.64 (d, J = 7.7 Hz, 2H), 7.26 (d, J = 7.7 Hz, 2H), 6.93 (d, J = 8.3 Hz, 1H), 3.98 (s, 3H), 2.45 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$); δ 194.0, 159.1, 143.1, 135.4, 134.9, 131.6, 131.3, 129.9, 129.0, 111.6, 110.9, 56.5, 21.6; IR(KBr): 2843, 1645, 1592, 1490,

1287, 1267, 1180, 1153, 1051, 1020, 907, 837, 811, 750 cm^{-1}; MS (ESI): 305.0 $(M + H)^+$, 307.0 $(M + 2 + H)^+$; HRMS: calcd for $C_{15}H_{14}BrO_2$: 305.0177; found: 305.0182; Anal. Calcd for $C_{15}H_{13}BrO_2$: C, 59.04; H, 4.29. Found: C, 59.31; H, 4.02.

(4-Methoxy-3,5-dimethylphenyl)(*p*-tolyl)methanone (2q). From 0.2 mmol (99 mg) of **1q** (0.02 mmol (5 mg) I_2, r.t. = 3 h, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 6/4); white solid (47 mg, 93%); mp: 76.2–77.3 °C (lit[66] 75–77 °C); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.67 (d, J = 7.5 Hz, 2H), 7.44 (s, 2H), 7.25 (d, J = 7.5 Hz, 2H), 3.77 (s, 3H), 2.45 (s, 3H), 2.32 (s, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 196.0, 160.5, 142.8, 135.3, 133.4, 131.0, 130.8, 130.1, 128.8, 59.7, 21.6, 16.2; IR(KBr): 1649, 1599, 1317, 1217, 1177, 1123, 1002, 901, 837, 768, 748, 610 cm^{-1}; MS (ESI): 255.1 $(M + H)^+$.

(*p*-Anisyl)(4-methoxy-3,5-dimethylphenyl)methanone (2r). From 0.2 mmol (105 mg) of **1r** (0.02 mmol (5 mg) I_2, r.t. = 30 min, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); white solid (51 mg, 94%); mp: 81.5–82.6 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.76 (d, J = 8.9 Hz, 2H), 7.40 (s, 2H), 6.92 (d, J = 8.9 Hz, 2H), 3.88 (s, 3H), 3.76 (s, 3H), 2.32 (s, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 195.0, 162.9, 160.3, 133.7, 132.3, 130.8, 130.7, 130.5, 113.4, 59.6, 55.4, 16.1; IR(neat): 2938, 2837, 1646, 1599, 1507, 1456, 1416, 1317, 1256, 1218, 1166, 1126, 1015, 899, 847, 770, 640, 613 cm^{-1}; MS (ESI): 271.1 $(M + H)^+$; HRMS: calcd for $C_{17}H_{19}O_3$: 271.1334; found: 271.1335; Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.53; H, 6.63.

(2-Methoxy-5-methylphenyl)(*p*-tolyl)methanone (2s). From 0.2 mmol (93 mg) of **1s** (0.02 mmol (5 mg) I_2, r.t. = 30 min, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); white solid (40 mg, 83%); mp: 77.4–78.8 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.69 (d, J = 8.0 Hz, 2H), 7.25–7.16 (m, 3H), 7.12 (d, J = 1.9 Hz, 1H), 6.85 (d, J = 8.4 Hz, 1H), 3.70 (s, 3H), 2.43 (s, 3H), 2.33 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 196.3, 155.2, 143.7, 135.3, 131.9, 130.0, 129.8, 129.8, 129.0, 128.9, 111.5, 55.8, 21.7, 20.3; IR(KBr): 2921, 1656, 1603, 1499, 1413, 1290, 1248, 1210, 1181, 1116, 1028, 967, 839, 813, 768, 724 cm^{-1}; MS (ESI): 241.1 $(M + H)^+$; HRMS: calcd for $C_{16}H_{17}O_2$: 241.1229; found: 241.1228; Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.94; H, 6.38.

(*p*-Anisyl)(4-methoxy-2,3-dimethylphenyl)methanone (2t). From 0.2 mmol (105 mg) of **1t** (0.02 mmol (5 mg) I_2, r.t. = 1.5 h, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); yellow solid (45 mg, 83%); mp: 112.5–113.6 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.79 (d, J = 8.6 Hz, 2H), 7.14 (d, J = 8.4 Hz, 1H), 6.91 (d, J = 8.6 Hz, 2H), 6.73 (d, J = 8.4 Hz, 1H), 3.86 (s, 6H), 2.22 (s, 3H), 2.20 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$); δ 197.5, 163.4, 158.7, 136.6, 132.4, 132.4, 131.4, 127.0, 126.1, 113.5, 106.6, 55.5, 55.4, 17.2, 11.6; IR(KBr): 3007, 2965, 2936, 2835, 1638, 1599, 1573, 1425, 1308, 1281, 1255, 1160, 1105, 1065, 1028, 963, 848, 812, 770, 697, 617 cm^{-1}; MS (ESI): 271.1 $(M + H)^+$; HRMS: calcd for $C_{17}H_{19}O_3$: 271.1334; found: 271.1326; Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.80; H, 6.94.

(4,5-Dimethoxy-2-methylphenyl)(*p*-tolyl)methanone (2u). From 0.2 mmol (105 mg) of **1u** (10 mol% I_2, r.t. = 1 h, 85 °C); preparative chromatography (SiO_2, CH_2Cl_2); yellow solid (54 mg, 99%); mp: 66.0–67.2 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.67 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 6.84 (s, 1H), 6.72 (s, 1H), 3.92 (s, 3H), 3.79 (s, 3H), 2.43 (s, 3H), 2.28 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$); δ 197.5, 150.4, 146.1, 143.6, 135.8, 130.8, 130.6, 130.1, 129.0, 113.7, 112.6, 56.0, 55.9, 21.6, 19.9; IR(KBr): 3007, 2934, 2847, 1653, 1603, 1576, 1510, 1450, 1350, 1264, 1210, 1165, 1096, 903, 839, 758 cm^{-1}; MS (ESI): 271.1 $(M + H)^+$; HRMS: calcd for $C_{17}H_{19}O_3$: 271.1334; found: 271.1329; Anal. calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.63; H, 6.41.

(*p*-Anisyl)(4,5-dimethoxy-2-methylphenyl)methanone (2v). From 0.2 mmol (112 mg) of **1v** (10 mol% I_2, r.t. = 1 h, 85 °C); preparative chromatography (SiO_2, CH_2Cl_2); white solid (44 mg, 76%); mp: 82.0–83.4 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.75 (d, J = 8.9 Hz, 2H), 6.89 (d, J = 8.9 Hz, 2H), 6.82 (s, 1H), 6.71 (s, 1H), 3.92 (s, 3H), 3.87 (s, 3H), 3.81 (s, 3H), 2.26 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$); δ 196.6, 163.4, 150.2, 146.2, 132.3, 131.1, 130.9, 130.2, 113.7, 113.6, 112.2, 56.1, 55.9, 55.4, 19.7; IR(KBr): 2934, 2845, 1655, 1596, 1508, 1454, 1350, 1312, 1257, 1209, 1157, 1096, 1020, 903, 849, 760 cm^{-1}; MS (ESI): 287.1 $(M + H)^+$; HRMS: calcd for $C_{17}H_{19}O_4$: 287.1283; found: 287.1271; Anal. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.36; H, 6.05.

Bis(4-methoxy-3,5-dimethylphenyl)methanone (2vv). From 0.18 mmol (105 mg) of **1vv** (0.02 mmol (5 mg) I_2, r.t. = 30 min, 85 °C); preparative chromatography (SiO_2, CH_2Cl_2); white solid (52 mg, 97%); mp: 108.8–110.1 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.46 (s, 4H), 3.79 (s, 6H), 2.33 (s, 12H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 195.8, 160.5, 133.6, 130.9, 130.8, 59.7, 16.2; IR(neat): 2919, 1653, 1594, 1479, 1455, 1412, 1321, 1153, 1118, 899, 769, 671 cm^{-1}; MS (ESI): 299.2 $(M + H)^+$; HRMS: calcd for $C_{19}H_{23}O_3$: 299.1647; found: 299.1641; Anal. Calcd for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43. Found: C, 76.74; H, 7.08.

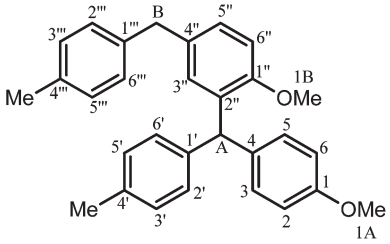
10,11-Dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene (3b). From 0.2 mmol (81 mg) of **1b** (0.02 mmol (5 mg) I_2, r.t. = 30 min, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 6/4); white solid (31 mg, 79%); mp: 73.0–74.0 °C (lit[67] 76–77 °C); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.19–7.03 (m, 8H), 4.11 (s, 2H), 3.17 (s, 4H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 139.2, 138.9, 129.5, 129.0, 126.6, 126.0, 41.0, 32.5; IR(KBr): 3057, 2928, 2831, 1487, 1450, 1354, 1290, 1096, 947, 702, 619 cm^{-1}; MS (ESI): 195.1 $(M + H)^+$.

4-(4-Methoxy-dideuterobenzyl)-2-[bis(*p*-anisyl)deuteromethyl]-1-methoxybenzene (3dd). From 0.2 mmol (95 mg) of **1dd** (0.02 mmol (5 mg) I_2, r.t. = 15 min, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 6/4); white solid (14 mg, 23%); mp: 84.9–85.7 °C; ^{1}H-NMR (500 MHz, CD_3COCD_3): δ 7.04–6.98 (m, 3H), 6.96 (d, J = 8.5 Hz, 4H), 6.87 (d, J = 8.3 Hz, 1H), 6.83–6.76 (m, 7H), 3.75 (s, 6H), 3.74 (s, 3H), 3.69 (s, 3H); ^{13}C-NMR (125 MHz, CD_3COCD_3): δ 158.9, 158.9, 156.3, 137.1, 134.6, 134.1, 133.8, 131.4, 131.0, 130.4, 128.4, 114.5, 114.2, 111.7, 56.0, 55.4, 48.3 (*t*, J = 20 Hz), 40.1 (quintet, J = 20 Hz); IR(neat): 3011, 2959, 2837, 1608, 1579, 1508, 1494, 1462, 1298, 1239, 1173, 1126, 1109, 1026, 833, 809, 778,

767 cm^{-1}; MS (ESI): 457.2 $(M)^+$; HRMS: calcd for $C_{30}H_{27}D_3O_4$: 457.2332; found: 457.2334.

Bis(*p*-tolyl)methane (3e). From 0.2 mmol (81 mg) of **1e** (0.02 mmol (5 mg) I_2, r.t. = 4 h, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 6/4); colorless oil (33 mg, 85%); (lit[68] mp: 28 °C); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.06 (s, 8H), 3.89 (s, 2H), 2.30 (s, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 138.3, 135.4, 129.1, 128.7, 41.1, 21.0; IR(neat): 3044, 3017, 2916, 2858, 1512, 1440, 1378, 1182, 1106, 847, 799, 749 cm^{-1}; MS (ESI): 195.1 $(M - H)^+$.

4-(4-Methylbenzyl)-2-((*p*-anisyl)(*p*-tolyl)methyl)-1-methoxybenzene (3ff).

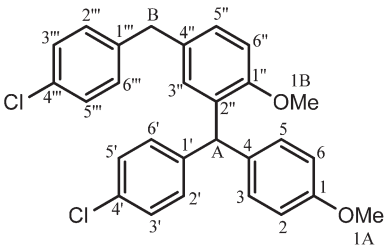


From 0.2 mmol (88 mg) of **1f** (0.02 mmol (5 mg) I_2, r.t. = 30 min, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 6/4); white solid (12 mg, 22%); mp: 73.1–74.8 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.08–7.03 (m, H_3', H_5', H_3''', H_5''', 4H), 7.01–6.92 (m, H_2', H_2''', H_6', H_6''', H_3, H_5, H_5'', 7H), 6.81–6.72 (m, H_2, H_6, H_6'', H_3'', 4H), 5.81 (s, H_A, 1H), 3.79 (s, H_B, 2H), 3.79 (s, H_{1A}, 3H), 3.68 (s, H_{1B}, 3H), 2.32 (s, 3H), 2.31 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 157.7 (C_1), 155.4 (C_1''), 141.2 (C_1'), 138.6 (C_1'''), 136.3 (C_4), 135.3 (C_4' or C_4'''), 135.2 (C_4''' or C_4'), 132.9 (C_2'' or C_4''), 132.9 (C_4'' or C_2''), 130.9 (C_3''), 130.3 (C_3, C_5), 129.2 (C_2', C_6'), 129.0 (C_3''', C_5''' or C_3', C_5'), 128.7 (C_3', C_5' or C_3''', C_5'''), 128.5 (C_2''', C_6'''), 127.4 (C_5''), 113.4 (C_2, C_6), 110.8 (C_6''), 55.7 (C_{1B}), 55.2 (C_{1A}), 48.3 (C_A), 40.6 (C_B), 21.0, 21.0; IR(KBr): 2838, 1608, 1509, 1496, 1442, 1289, 1244, 1174, 1106, 1029, 804 cm^{-1}; MS (ESI): 422.2 $(M)^+$; HRMS: calcd for $C_{30}H_{30}O_2$: 422.2246; found: 422.2236; Anal. Calcd for $C_{30}H_{30}O_2$: C, 85.27; H, 7.16. Found: C, 85.14; H, 7.41.

(*p*-Anisyl)(4-methylthiophenyl)methane (3g). From 0.2 mmol (101 mg) of **1g** (0.02 mmol (5 mg) I_2, r.t. = 5 h, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 6/4); colorless oil[69] (31 mg, 63%); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.20 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.7 Hz), 3.89 (s, 2H), 3.79 (s, 3H), 2.46 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 158.0, 138.7, 135.6, 133.1, 129.8, 129.3, 127.2, 113.9, 55.2, 40.5, 16.3; IR(neat): 2996, 2914, 2833, 1609, 1508, 1438, 1298, 1246, 1176, 1094, 1036, 842, 797, 756 cm^{-1}; MS (ESI): 243.1 $(M - H)^+$.

(4-Methylthiophenyl)(*p*-tolyl)methane (3h). From 0.2 mmol (94 mg), of **1h** (0.02 mmol (5 mg) I_2, r.t. = 48 h, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1) and hexane/CH_2Cl_2 = 8.5/1.5; white solid (32 mg, 70%); mp: 49.3–50.2 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.21 (d, J = 8.2 Hz, 2H), 7.16–7.04 (m, 6H), 3.91 (s, 2H), 2.47 (s, 3H), 2.33 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 138.5, 137.9, 135.6, 129.4, 129.1, 128.7, 127.2, 40.9, 21.0, 16.3; IR(KBr): 2914, 1634, 1510, 1492, 1437, 1090, 1016, 955, 853, 795, 748, 652 cm^{-1}; MS (ESI): 228.1 $(M)^+$; HRMS: calcd for $C_{15}H_{16}S$: 228.0973; found: 228.0965; Anal. Calcd for $C_{15}H_{16}S$: C, 78.90; H, 7.06. Found: C, 79.03; H, 7.29.

4-(4-Chlorobenzyl)-2-((*p*-anisyl)(4-chlorophenyl)methyl)-1-methoxybenzene (3ii).



From 0.2 mmol (96 mg) of **1i** (0.02 mmol (5 mg) I_2, r.t. = 4.25 h, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); white solid (9 mg, 15%), mp: 86.5–88.5 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.24–7.20 (m, H_3', H_5', H_3''', H_5''', 4H), 7.03–6.91 (m, H_2', H_6', H_2''', H_6''', H_3, H_5, H_5'', 7H), 6.84–6.76 (m, H_2, H_6, H_6'', 3H), 6.62 (d, J = 2 Hz, H_3'', 1H), 5.79 (s, H_A, 1H), 3.79 (s, Me_{1A}, 3H), 3.79 (s, H_B, 2H), 3.68 (s, Me_{1B}, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 157.9 (C_1), 155.5 (C_1''), 142.7 (C_1'), 140.0 (C_1'''), 135.2 (C_4), 132.4 (C_2''), 132.2 (C_4''), 131.7 (C_4' or C_4'''), 131.6 (C_4''' or C_4'), 130.7 (C_3''), 130.6 (C_3, C_5), 130.2 (C_2', C_6'), 130.0 (C_2''', C_6'''), 128.4 (C_3', C_5' or C_3''', C_5'''), 128.2 (C_3''', C_5''' or C_3', C_5'), 127.7 (C_5''), 113.6 (C_2, C_6), 110.8 (C_6''), 55.7 (C_{1B}), 55.2 (C_{1A}), 48.2 (C_A), 40.3 (C_B); IR(KBr): 2998, 2833, 1609, 1510, 1489, 1239, 1175, 1112, 1090, 1033, 835, 808 cm^{-1}; Anal. Calcd for $C_{28}H_{24}Cl_2O_2$: C, 72.57; H, 5.22. Found: C, 72.30; H, 5.42.

(*p*-Anisyl)(4-methoxynaphthalen-1-yl)methane (3j). From 0.2 mmol (114 mg) of **1j** (0.02 mmol (5 mg) I_2, r.t. = 1 h, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 6/4); yellow oil (34 mg, 61%); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.34–8.24 (m, 1H), 7.95–7.86 (m, 1H), 7.49–7.39 (m, 2H), 7.16 (d, J = 7.8 Hz, 1H), 7.09 (d, J = 8.6 Hz, 2H), 6.79 (d, J = 8.6 Hz, 2H), 6.74 (d, J = 7.8 Hz, 1H), 4.30 (s, 2H), 3.98 (s, 3H), 3.75 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 157.8, 154.5, 133.1, 132.9, 129.5, 128.9, 126.9, 126.4, 126.0, 124.8, 124.1, 122.5, 113.8, 103.3, 55.5, 55.2, 37.7; IR(neat): 3069, 3000, 2951, 2834, 1585, 1508, 1460, 1390, 1244, 1177, 1158, 1091, 1032, 814, 766 cm^{-1}; MS (ESI): 278.1 $(M)^+$; HRMS: calcd for $C_{19}H_{18}O_2$: 278.1307; found: 278.1305; Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 82.24; H, 6.59.

(4-Methoxynaphthalen-1-yl)(*p*-tolyl)methane (3k). From 0.2 mmol (108 mg) of **1k** (0.02 mmol (5 mg) I_2, r.t. = 2 h, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 6/4); white solid (31 mg, 59%); mp: 75.6–76.3 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.34–8.25 (m, 1H), 7.94–7.86 (m, 1H), 7.49–7.40 (m, 2H), 7.17 (d, J = 7.8 Hz, 1H), 7.06 (s, 4H), 6.74 (d, J = 7.8 Hz, 1H), 4.32 (s, 2H), 3.98 (s, 3H), 2.29 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 154.5, 138.0, 135.3, 132.9, 129.1, 128.8, 128.5, 127.0, 126.4, 126.0, 124.8, 124.1, 122.5, 103.3, 55.5, 38.2, 21.0; IR(KBr): 3012, 2963, 2843, 1584, 1512, 1461, 1390, 1277, 1247, 1224, 1158, 1088, 1023, 805, 769, 710 cm^{-1}; MS (ESI): 263.1 $(M + H)^+$; HRMS: calcd for $C_{19}H_{19}O$: 263.1436; found:

263.1432; Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92. Found: C, 87.02; H, 6.67.

(*p*-Anisyl)(2,3-dihydro-benzo[1,4]dioxin-6-yl)methane (3m). From 0.2 mmol (105 mg) of **1m** (0.02 mmol (5 mg) I_2, r.t. = 30 min, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); colorless oil (30 mg, 59%); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.10 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 6.78 (d, J = 8.1 Hz, 1H), 6.70–6.62 (m, 2H), 4.22 (s, 4H), 3.82 (s, 2H), 3.79 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 157.9, 143.3, 141.7, 135.0, 133.4, 129.7, 121.6, 117.4, 117.1, 113.9, 64.4, 64.3, 55.2, 40.3; IR(neat): 3030, 2930, 2835, 1610, 1587, 1504, 1461, 1435, 1286, 1244, 1204, 1177, 1125, 1067, 1035, 919, 886, 809, 767, 740 cm^{-1}; MS (ESI): 256.1 $(M)^+$; HRMS: calcd for $C_{16}H_{16}O_3$: 256.1099; found: 256.1102; Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.96; H, 6.43.

4-(3,4-Dimethylbenzyl)-2-((*p*-anisyl)(3,4-dimethylphenyl)methyl)-1-methoxybenzene (3nn). From 0.2 mmol (93 mg) of **1n** (0.02 mmol (5 mg) I_2, r.t. = 30 min, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 6/4); colorless oil (14 mg, 24%); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.06–6.94 (m, 5H), 6.91–6.75 (m, 8H), 5.82 (s, 1H), 3.80 (s, 3H), 3.79 (s, 2H), 3.71 (s, 3H), 2.24 (s, 3H), 2.24 (s, 3H), 2.22 (s, 3H), 2.20 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 157.6, 155.4, 141.6, 139.1, 136.4, 136.3, 136.0, 133.9, 133.8, 132.9, 132.9, 131.0, 130.7, 130.3, 130.0, 129.5, 129.2, 127.4, 126.7, 126.0, 113.3, 110.8, 55.8, 55.2, 48.1, 40.6, 19.8, 19.7, 19.4, 19.3; IR(neat): 3001, 2932, 2834, 1609, 1509, 1498, 1456, 1245, 1177, 1109, 1035, 808 cm^{-1}; MS (ESI): 450.3 $(M)^+$; HRMS: calcd for $C_{32}H_{34}O_2$: 450.2559; found: 450.2545; Anal. Calcd for $C_{32}H_{34}O_2$: C, 85.29; H, 7.61. Found: C, 85.36; H, 7.23.

(3-Bromo-4-methoxyphenyl)(phenyl)methane (3o). From 0.2 mmol (114 mg) of **1o** (0.02 mmol (5 mg) I_2, r.t. = 6 h, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 6/4); colorless oil (50 mg, 91%); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.38 (d, J = 2.0 Hz, 1H), 7.35–7.27 (m, 2H), 7.25–7.20 (m, 1H), 7.20–7.14 (m, 2H), 7.08 (dd, J = 8.4 Hz, J = 2.0 Hz, 1H), 6.82 (d, J = 8.4 Hz, 1H), 3.91 (s, 2H), 3.87 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 154.3, 140.7, 134.8, 133.6, 128.8, 128.5, 126.2, 112.0, 111.6, 56.3, 40.7; IR(neat): 3060, 3026, 2936, 2904, 2835, 1603, 1493, 1453, 1439, 1403, 1281, 1255, 1182, 1055, 1022, 797, 770, 728, 698, 671, 619 cm^{-1}; Anal. Calcd for $C_{14}H_{13}BrO$: C, 60.67; H, 4.73. Found: C, 60.77; H, 4.65.

(3-Bromo-4-methoxyphenyl)(*p*-tolyl)methane (3p). From 0.2 mmol (119 mg) of **1p** (0.02 mmol (5 mg) I_2, r.t. = 1.5 h, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 6/4); white solid (50 mg, 86%); mp: 37.7–38.4 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.37 (d, J = 2.1 Hz, 1H), 7.14–7.03 (m, 5H), 6.81 (d, J = 8.4 Hz, 1H), 3.86 (s, 5H), 2.33 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 154.2, 137.7, 135.7, 135.2, 133.6, 129.2, 128.7, 128.7, 112.0, 111.6, 56.3, 40.2, 21.0; IR(KBr): 2914, 2849, 1609, 1494, 1439, 1259, 1187, 1051, 1020, 893, 796, 748, 670, 605 cm^{-1}; Anal. Calcd for $C_{15}H_{15}BrO$: C, 61.87; H, 5.19. Found: C, 62.12; H, 5.35.

(4-Methoxy-3,5-dimethylphenyl)(*p*-tolyl)methane (3q). From 0.2 mmol (99 mg) of **1q** (0.02 mmol (5 mg) I_2, r.t. = 3 h, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 6/4); colorless oil[66] (45 mg, 93%); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.07 (s, 4H), 6.80 (s, 2H), 3.81 (s, 2H), 3.69 (s, 3H), 2.32 (s, 3H), 2.24 (s, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 155.2, 138.4, 136.6, 135.4, 130.6, 129.1, 129.1, 128.7, 59.7, 40.9, 21.0, 16.1; IR(neat): 2997, 2920, 2859, 2510, 1484, 1440, 1376, 1310, 1223, 1143, 1016, 877, 811, 761, 644 cm^{-1}; MS (ESI): 241.2 $(M + H)^+$.

(*p*-Anisyl)(4-methoxy-3,5-dimethylphenyl)methane (3r). From 0.2 mmol (105 mg) of **1r** (0.02 mmol (5 mg) I_2, r.t. = 30 min, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); colorless oil (35 mg, 68%); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.11 (d, J = 8.6 Hz, 2H), 6.87–6.80 (m, 4H), 3.81 (s, 2H), 3.79 (s, 3H), 3.70 (s, 3H), 2.25 (s, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 157.9, 155.2, 136.8, 133.6, 130.6, 129.8, 129.1, 113.8, 59.7, 55.2, 40.4, 16.1; IR(neat): 2995, 2932, 2834, 1611, 1508, 1484, 1298, 1244, 1223, 1177, 1142, 1106, 1016, 819, 766, 635 cm^{-1}; MS (ESI): 256.1 $(M)^+$; HRMS: calcd for $C_{17}H_{20}O_2$: 256.1463; found: 256.1464; Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.53; H, 8.05.

(2-Methoxy-5-methylphenyl)(*p*-tolyl)methane (3s). From 0.2 mmol (93 mg) of **1s** (0.02 mmol (5 mg) I_2, r.t. = 30 min, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); colorless oil (30 mg, 66%); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.10 (d, J = 8.3 Hz, 2H), 7.06 (d, J = 8.3 Hz, 2H), 6.96 (dd, J = 8.2 Hz, J = 1.8 Hz, 1H), 6.87 (d, J = 1.8 Hz, 1H), 6.75 (d, J = 8.2 Hz, 1H), 3.89 (s, 2H), 3.78 (s, 3H), 2.30 (s, 3H), 2.22 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 155.3, 138.1, 135.1, 131.0, 129.6, 129.6, 128.9, 128.8, 127.5, 110.5, 55.5, 35.3, 21.0, 20.5; IR(neat): 3001, 2921, 2833, 1611, 1500, 1460, 1252, 1182, 1122, 1036, 805, 767, 720 cm^{-1}; MS (ESI): 225.1 $(M - H)^+$; HRMS: calcd for $C_{16}H_{17}O$: 225.1279; found: 225.1282; Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.90; H, 8.25.

(*p*-Anisyl)(4-methoxy-2,3-dimethylphenyl)methane (3t). From 0.2 mmol (105 mg) of **1t** (0.02 mmol (5 mg) I_2, r.t. = 1.5 h, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); white solid (32 mg, 62%); mp: 66.9–67.6 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.01 (d, J = 8.5 Hz, 2H), 6.92 (d, J = 8.3 Hz, 1H), 6.80 (d, J = 8.5 Hz, 2H), 6.67 (d, J = 8.3 Hz, 1H), 3.90 (s, 2H), 3.80 (s, 3H), 3.77 (s, 3H), 2.16 (s, 3H), 2.12 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 157.7, 156.1, 136.4, 133.3, 131.4, 129.4, 127.7, 125.4, 113.7, 107.6, 55.5, 55.2, 38.8, 15.8, 12.0; IR(KBr): 3001, 2909, 2832, 1611, 1585, 1510, 1460, 1306, 1254, 1172, 1102, 1064, 1034, 806, 752 cm^{-1}; MS (ESI): 256.1 $(M)^+$; HRMS: calcd for $C_{17}H_{20}O_2$: 256.1463; found: 256.1461; Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.77; H, 7.81.

(4,5-Dimethoxy-2-methylphenyl)(*p*-tolyl)methane (3u). From 0.2 mmol (105 mg) of **1u** (0.02 mmol (5 mg) I_2, r.t. = 1 h, 85 °C); preparative chromatography (SiO_2, CH_2Cl_2) white solid (43 mg, 83%); mp: 70.5–72.4 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.07 (d, J = 7.9 Hz, 2H), 6.99 (d, J = 7.9 Hz, 2H), 6.69 (s, 1H), 6.65 (s, 1H), 3.88 (s, 2H), 3.85 (s, 3H), 3.80 (s, 3H), 2.30 (s, 3H), 2.18 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 147.2, 146.9, 137.6, 135.3, 130.9, 129.0, 128.5, 128.3, 56.0, 55.9, 38.5, 20.9, 19.1; IR(KBr): 2955, 2920, 1607, 1514, 1462, 1341, 1225, 1200, 1161, 1099, 997, 867, 841, 800, 755 cm^{-1}; MS (ESI): 256.1 $(M)^+$; HRMS: calcd for $C_{17}H_{20}O_2$: 256.1463; found: 256.1463; Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.65; H, 7.54.

(*p*-Anisyl)(4,5-dimethoxy-2-methylphenyl)methane (3v). From 0.2 mmol (112 mg) of **1v** (0.02 mmol (5 mg) I_2, r.t. = 1 h, 85 °C); preparative chromatography (SiO_2, CH_2Cl_2) pale orange solid (29 mg, 54%); mp: 62.9–64.6 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.02 (d, J = 8.7 Hz, 2H), 6.81 (d, J = 8.7 Hz, 2H), 6.69 (s, 1H), 6.63 (s, 1H), 3.86 (s, 5H), 3.80 (s, 3H), 3.78 (s, 3H), 2.18 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 157.8, 147.2, 146.9, 132.8, 131.1, 129.4, 128.5, 113.8, 113.7, 56.0, 55.9, 55.2, 38.1, 19.1; IR(KBr): 3020, 2959, 2914, 2835, 1609, 1510, 1442, 1346, 1271, 1227, 1171, 1100, 1026, 999, 869, 812, 756 cm^{-1}; MS (ESI): 273.1 (M + H)$^+$; HRMS: calcd for $C_{17}H_{21}O_3$: 273.1491; found: 273.1487; Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 75.30; H, 7.62.

Bis(4-methoxy-3,5-dimethylphenyl)methane (3vv). From 0.18 mmol (105 mg) of **11** (0.02 mmol (5 mg) I_2, r.t. = 30 min, 85 °C); preparative chromatography (SiO_2, CH_2Cl_2); white solid (47 mg, 92%); mp: 77.8–80.8 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 6.82 (s, 4H), 3.73 (s, 2H), 3.69 (s, 6H), 2.24 (s, 12H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 155.2, 136.6, 130.6, 129.1, 59.7, 40.7, 16.1; IR(neat): 2920, 1482, 1445, 1418, 1372, 1216, 1138, 1008, 880, 861, 766, 692, 667 cm^{-1}; MS (ESI): 285.2 (M + H)$^+$; HRMS: calcd for $C_{19}H_{25}O_2$: 285.1855; found: 285.1852; Anal. Calcd for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found: C, 80.22; H, 8.89.

4-(4-Methoxybenzyl)-2-[(*p*-anisyl)(phenyl)methyl]-1-methoxybenzene (3ww). From 0.4 mmol (170 mg) of **1w** (0.04 mmol (10 mg) I_2, r.t. = 45 min, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); white solid (36 mg, 44%); mp: 66.6–67.6 °C; ^{1}H-NMR (500 MHz, CD_3COCD_3): δ 7.28–7.22 (m, 2H), 7.20–7.15 (m, 1H), 7.09–7.04 (m, 4H), 7.03–6.98 (m, 3H), 6.97–6.92 (m, 2H), 6.91–6.87 (m, 1H), 6.82–6.76 (m, 3H), 5.85 (s, 1H), 3.74 (s, 5H), 3.69 (s, 3H), 2.28 (s, 3H); ^{13}C-NMR (125 MHz, CD_3COCD_3): δ 159.9, 157.3, 146.1, 142.8, 137.1, 135.6, 135.2, 134.2, 132.5, 131.3, 131.1, 131.1, 130.5, 129.9, 129.5, 127.8, 115.5, 112.7, 57.0, 56.4, 51.0, 41.7, 22.0; IR(neat): 3007, 2835, 1607, 1509, 1493, 1455, 1438, 1233, 1175, 1106, 1028, 807, 735, 700 cm^{-1}; MS (ESI): 408.2 (M)$^+$; HRMS: calcd for $C_{29}H_{28}O_2$: 408.2089; found: 408.2088; Anal. Calcd for $C_{29}H_{28}O_2$: C, 85.26; H, 6.91. Found: C, 85.20; H, 6.93.

4-(4-Methoxybenzyl)-2-[bis(*p*-tolyl)methyl]-1-methoxybenzene (3xx). From 0.6 mmol (263 mg) of **1x** (0.06 mmol (15 mg) I_2, r.t. = 15 min, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); white solid (59 mg, 47%); mp: 98.9–99.6 °C; ^{1}H-NMR (300 MHz, DMSO): δ 7.06 (d, J = 7.9 Hz, 4H), 7.03–6.98 (m, 3H), 6.94 (d, J = 7.9 Hz, 4H), 6.87 (d, J = 8.3 Hz, 1H), 6.82–6.77 (m, 3H), 5.81 (s, 1H), 3.74 (s, 5H), 3.68 (s, 3H), 2.28 (s, 6H); ^{13}C-NMR (75 MHz, DMSO): δ 159.9, 157.3, 143.0, 137.0, 135.6, 135.1, 134.4, 132.5, 131.3, 131.0, 130.5, 129.4, 115.5, 112.6, 56.9, 56.4, 50.5, 41.7, 22.0; IR(neat): 3002, 2837, 1607, 1510, 1493, 1235, 1177, 1105, 1029, 807, 772, 743, 607 cm^{-1}; MS (ESI): 422.2 (M)$^+$; HRMS: calcd for $C_{30}H_{30}O_2$: 422.2246; found: 422.2240; Anal. Calcd for $C_{30}H_{30}O_2$: C, 85.27; H, 7.16. Found: C, 85.35; H, 7.41.

4-(4-Methoxybenzyl)-2-[(4-methylthiophenyl)(*p*-tolyl)methyl]-1-methoxybenzene (3yy). From 0.75 mmol (353 mg) of **1y** (0.075 mmol (19 mg) I_2, r.t. = 90 min, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1 and Al_2O_3, hexane/CH_2Cl_2 = 8/2); white solid (23 mg, 13%); mp: 55.7–57.8 °C; ^{1}H-NMR (500 MHz, CD_3COCD_3): δ 7.18–7.14 (m, 2H), 7.09–7.05 (m, 2H), 7.04–6.97 (m, 5H), 6.97–6.92 (m, 2H), 6.90–6.86 (m, 1H), 6.82–6.76 (m, 3H), 5.80 (s, 1H), 3.75 (s, 2H), 3.74 (s, 3H), 3.69 (s, 3H), 2.45 (s, 3H), 2.28 (s, 3H); ^{13}C-NMR (125 MHz, CD_3COCD_3): δ 159.9, 157.3, 143.0, 142.7, 137.8, 137.2, 135.6, 135.2, 134.1, 132.4, 131.6, 131.3, 131.0, 130.6, 129.5, 127.9, 115.5, 112.7, 57.0, 56.4, 50.5, 41.7, 22.0, 16.6; IR(neat): 2954, 2919, 1491, 1461, 1439, 1240, 1107, 1092, 1031, 804, 775, 640, 621 cm^{-1}; Anal. Calcd for $C_{30}H_{30}O_2S$: C, 79.26; H, 6.65. Found: C, 79.20; H, 6.68.

1-Phenylethyl trityl ether (4d). From 15 mmol (4.18 g) of Ph_3CCl (16.5 mmol of 1-phenylethanol in 6.5 mL CH_2Cl_2, 18 mmol (2.74 g) of DBU, r.t. = 24 h, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 6/4); yellow solid (0.49 g, 9%); mp: 114.3–115.6 °C (lit[54] 118–119 °C); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.48–7.40 (m, 6H), 7.22–7.01 (m, 14H), 4.60 (q, J = 6.3 Hz, 1H), 1.05 (d, J = 6.3 Hz, 3H); ^{13}C-NMR (125 MHz, CD_3COCD_3): δ 148.3, 147.0, 130.8, 129.6, 129.4, 128.7, 128.0, 127.3, 89.5, 74.5, 27.2; IR(KBr): 3057, 2976, 2922, 1597, 1489, 1447, 1366, 1225, 1065, 1023, 992, 915, 744, 696, 629 cm^{-1}; MS (ESI): 387.2 (M + Na)$^+$; HRMS: calcd for $C_{27}H_{24}ONa$: 387.1725; found: 387.1738.

1-(4-Methylphenyl)trityl ether (4f). From 11.1 mmol (3.09 g) of Ph_3CCl (3.7 mmol (0.5 g) of 1-(4-methylphenyl)ethanol in 6 mL CH_2Cl_2, 11.1 mmol of DBU, r.t. = 24 h, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 7.5/2.5); white solid (0.85 g, 61%); mp: 116.5–119.2 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.51–7.43 (m, 6H), 7.33–7.13 (m, 9H), 7.05 (d, J = 8.1 Hz, 2H), 6.99 (d, J = 8.1 Hz, 2H), 4.59 (q, J = 6.3 Hz, 1H), 2.92 (s, 3H), 0.96 (d, J = 6.3 Hz, 3H); ^{13}C-NMR (125 MHz, CD_3COCD_3): δ 147.1, 145.4, 137.3, 130.8, 130.3, 129.4, 128.7, 127.3, 89.5, 74.4, 27.1, 22.1; IR(KBr): 3058, 2978, 1489, 1448, 1366, 1219, 1066, 1024, 914, 816, 763, 744, 697, 632 cm^{-1}; Anal. Calcd for $C_{28}H_{26}O$: C, 88.85; H, 6.92. Found: C, 88.85; H, 7.04.

1-(3-Methylphenyl)trityl ether (4g). From 11.1 mmol (3.09 g) of Ph_3CCl (3.7 mmol (0.5 g) of 1-(3-methylphenyl)ethanol in 6 mL CH_2Cl_2, 11.1 mmol of DBU, r.t. = 24 h, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 7.5/2.5); white solid (0.95 g, 68%); mp: 92.5–93.9 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.52–7.46 (m, 6H), 7.25–7.13 (m, 9H), 7.10–6.83 (m, 4H), 4.60 (q, J = 6.3 Hz, 1H), 2.26 (s, 3H), 1.07 (d, J = 6.3 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 146.2, 145.0, 137.1, 129.0, 127.9, 127.7, 127.5, 126.8, 126.3, 122.6, 87.7, 72.9, 25.7, 21.3; IR(KBr): 3059, 3023, 2967, 2918, 1609, 1487, 1445, 1365, 1219, 1156, 1067, 1032, 898, 772, 744, 697, 628 cm^{-1}; Anal. Calcd for $C_{28}H_{26}O$: C, 88.85; H, 6.92. Found: C, 89.10; H, 7.12.

1-(3-Methoxyphenyl)trityl ether (4h). From 9.9 mmol (2.76 g) of Ph_3CCl (3.3 mmol (0.5 g) of 1-(3-methoxyphenyl)-ethanol in 6 mL CH_2Cl_2, 9.9 mmol of DBU, r.t. = 24 h, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 6/4); white solid (0.79 g, 61%); mp: 82.0–83.9 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.52–7.41 (m, 6H), 7.34–7.11 (m, 9H), 7.09–7.00 (m, 1H), 6.73–6.59 (m, 3H), 4.60 (q, J = 6.3 Hz, 1H), 3.73 (s, 3H), 1.07 (d, J = 6.3 Hz, 3H); ^{13}C-NMR (125 MHz, CD_3COCD_3): δ 161.3, 149.9, 147.0, 130.8, 130.7, 129.4, 128.7, 119.6, 113.6,

112.9, 89.5, 74.5, 56.3, 27.1; IR(KBr): 3021, 2978, 2830, 1596, 1487, 1447, 1348, 1314, 1271, 1252, 1153, 1061, 1028, 999, 899, 861, 765, 744, 697, 632 cm^{-1}; Anal. Calcd for $C_{28}H_{26}O_2$: C, 85.25; H, 6.64. Found: C, 85.61; H, 6.65.

1-(4-Fluorophenyl)trityl ether (4i). From 10.8 mmol (3.01 g) of Ph_3CCl (3.6 mmol (0.5 g) of 1-(4-fluorophenyl)ethanol in 6 mL CH_2Cl_2, 10.8 mmol of DBU, r.t. = 24 h, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 7.5/2.5); white solid (0.88 g, 64%); mp: 139.4–141.1 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.49–7.41 (m, 6H), 7.25–7.12 (m, 9H), 7.02 (dd, J = 8.7 Hz, J = 5.6 Hz, 2H), 6.78 (dd, J = 8.7 Hz, J = 8.7 Hz, 2H), 4.61 (q, J = 6.3 Hz, 1H), 1.13 (d, J = 6.3 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 161.1 (d, J = 243 Hz), 144.8, 142.1 (d, J = 3 Hz), 129.0, 127.6, 127.0 (d, J = 8 Hz), 126.9, 114.4, (d, J = 21 Hz), 87.7, 72.2, 26.0; ^{19}F-NMR (470 MHz, CD_3COCD_3): δ −117.4-(−117.5) (m, 1F); IR(KBr): 3060, 2987, 2927, 1599, 1507, 1489, 1449, 1368, 1221, 1152, 1068, 1025, 915, 831, 764, 743, 697, 630 cm^{-1}; Anal. Calcd for $C_{27}H_{23}FO$: C, 84.79; H, 6.06. Found: C, 85.04; H, 6.16.

1-(4-Chlorophenyl)trityl ether (4j). From 9.6 mmol (2.68 g) of Ph_3CCl (3.2 mmol (0.5 g) of 1-(4-chlorophenyl)ethanol in 6 mL CH_2Cl_2, 9.6 mmol of DBU, r.t. = 24 h, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 7.5/2.5); white solid (0.71 g, 56%); mp: 133.7–136.8 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.50–7.41 (m, 6H), 7.25–7.12 (m, 9H), 7.07 (d, J = 8.5 Hz, 2H), 6.99 (d, J = 8.5 Hz, 2H), 4.60 (q, J = 6.3 Hz, 1H), 1.12 (d, J = 6.3 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 144.8, 144.8, 131.5, 129.0, 127.8, 127.6, 126.9, 126.9, 87.8, 72.2, 25.9; IR(KBr): 3058, 2991, 2929, 1595, 1487, 1448, 1405, 1369, 1221, 1068, 1025, 913, 824, 763, 744, 696, 632 cm^{-1}; Anal. Calcd for $C_{27}H_{23}ClO$: C, 81.29; H, 5.81. Found: C, 80.92; H, 5.91.

1-(4-Bromophenyl)trityl ether (4k). From 7.5 mmol (2.09 g) of Ph_3CCl (2.5 mmol (0.5 g) of 1-(4-bromophenyl)ethanol in 6 mL CH_2Cl_2, 7.5 mmol of DBU, r.t. = 24 h, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 7.5/2.5); white solid (0.64 g, 58%); mp: 131.2–131.8 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.50–7.37 (m, 6H), 7.27–7.10 (m, 11H), 6.97–6.89 (m, 2H), 4.58 (q, J = 6.1 Hz, 1H), 1.11 (d, J = 6.1 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 145.4, 144.7, 130.7, 129.0, 127.6, 127.3, 126.9, 119.7, 87.8, 72.2, 25.8; IR(KBr): 3059, 3032, 2933, 2903, 1591, 1487, 1441, 1397, 1366, 1206, 1153, 1076, 1029, 999, 818, 787, 749, 709, 698, 629 cm^{-1}; Anal. Calcd for $C_{27}H_{23}BrO$: C, 73.14; H, 5.23. Found: C, 73.55; H, 5.01.

1-(3-Nitrophenyl)trityl ether (4l). From 9 mmol (2.51 g) of Ph_3CCl (3 mmol (0.5 g) of 1-(3-nitrophenyl)ethanol in 6 mL CH_2Cl_2, 9 mmol of DBU, r.t. = 24 h, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 6/4); white solid (0.57 g, 46%); mp: 158.5–159.3 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.87–7.80 (m, 1H), 7.71–7.67 (m, 1H), 7.49–7.41 (m, 6H), 7.39–7.33 (m, 1H), 7.24–7.09 (m, 10H), 4.74 (q, J = 6.4 Hz, 1H), 1.40 (d, J = 6.4 Hz, 3H); ^{13}C-NMR (125 MHz, CD_3COCD_3): δ 150.2, 149.4, 146.4, 133.8, 130.7, 130.7, 129.5, 128.9, 122.6, 122.2, 89.6, 73.7, 27.3; IR(KBr): 3061, 2992, 2972, 1525, 1489, 1445, 1346, 1204, 1080, 1063, 1032, 997, 902, 808, 753, 738, 701, 633 cm^{-1}; Anal. Calcd for $C_{27}H_{23}NO_3$: C, 79.20; H, 5.66; N, 3.42. Found: C, 79.25; H, 5.67; N, 3.30.

1-(4-Nitrophenyl)trityl ether (4m). From 9 mmol (2.51 g) of Ph_3CCl (3 mmol (0.5 g) of 1-(4-nitrophenyl)ethanol, 6 mL CH_2Cl_2, 9 mmol of DBU, r.t. = 24 h, 25 °C); preparative chromatography two times: (SiO_2, hexane/CH_2Cl_2 = 7.5/2.5) and (SiO_2, hexane/CH_2Cl_2 = 1/1); white solid (0.53 g, 43%); mp: 172.1–172.6 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.89 (d, J = 8.7 Hz, 2H), 7.47–7.41 (m, 6H), 7.30–7.10 (m, 11H), 4.74 (q, J = 6.4 Hz, 1H), 1.32 (d, J = 6.4 Hz, 3H); ^{13}C-NMR (125 MHz, CD_3COCD_3): δ 155.8, 148.0, 146.5, 130.8, 129.5, 128.9, 128.4, 124.5, 89.7, 73.8, 27.1; IR(KBr): 3063, 2968, 2928, 2893, 1598, 1522, 1489, 1445, 1344, 1219, 1156, 1071, 1028, 995, 901, 851, 747, 702, 632 cm^{-1}; Anal. Calcd for $C_{27}H_{23}NO_3$: C, 79.20; H, 5.66; N, 3.42. Found: C, 79.18; H, 5.65; N, 3.51.

1-[(4-Trifluoromethyl)phenyl]trityl ether (4n). From 7.8 mmol (2.17 g) of Ph_3CCl (2.6 mmol (0.5 g) of 1-(4-trifluoromethylphenyl)ethanol in 6 mL CH_2Cl_2, 7.8 mmol of DBU, r.t. = 24 h, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 7.5/2.5); white solid (0.66 g, 59%); mp: 122.8–124.3 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.49–7.41 (m, 6H), 7.35–7.29 (m, 2H), 7.24–7.09 (m, 11H), 4.68 (q, J = 6.3 Hz, 1H), 1.22 (d, J = 6.3 Hz, 3H); ^{13}C-NMR (125 MHz, CD_3COCD_3): δ 152.6 (q, J = 1 Hz), 146.6, 130.8, 129.5, 128.9, 128.0, 126.4 (q, J = 271 Hz), 126.3 (q, J = 4 Hz), 89.6, 74.0, 27.2; ^{19}F-NMR (470 MHz, CD_3COCD_3): δ −61.7 (s, 3F); IR(KBr): 3057, 2965, 2926, 1619, 1491, 1445, 1410, 1367, 1324, 1152, 1123, 1074, 1031, 997, 838, 777, 760, 746, 702, 631 cm^{-1}; Anal. Calcd for $C_{28}H_{23}F_3O$: C, 77.76; H, 5.36. Found: C, 77.83; H, 5.35.

[Bis(*p*-anisyl)methyl][bis(*m*-nitrophenyl)methyl] ether (7). (3 mmol (0.73 g) bis(*p*-anisyl)methanol, 9 mmol (2.47 g) bis(*m*-nitrophenyl)methanol, 9 mL CH_2Cl_2, 0.09 mmol (22 mg) I_2, r.t. = 1 h, 25 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 7.5/2.5); white solid (1.05 g, 70%); mp: 142.6–143.7 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.23–8.13 (m, 4H), 7.73–7.67 (m, 2H), 7.57–7.50 (m, 2H), 7.22 (d, J = 8.7 Hz, 4H), 6.88 (d, J = 8.7 Hz, 4H), 5.56 (s, 1H), 5.30 (s, 1H), 3.80 (s, 6H); ^{13}C-NMR (75 MHz, CD_3COCD_3): δ 161.2, 150.5, 146.0, 135.8, 135.3, 132.0, 130.2, 124.6, 123.6, 115.7, 82.4, 80.1, 56.5; IR(KBr): 2932, 2838, 1608, 1534, 1509, 1348, 1303, 1269, 1246, 1172, 1032, 993, 931, 899, 858, 833, 807, 738, 702 cm^{-1}; MS (ESI): 523.1 $(M + Na)^+$; HRMS: calcd for $C_{28}H_{24}N_2O_7Na$: 523.1481; found: 523.1472; Anal. Calcd for $C_{28}H_{24}N_2O_7$: C, 67.19; H, 4.83; N, 5.60. Found: C, 66.86; H, 4.58; N, 5.52.

3,3′-Dinitrobenzhydrol (8). (6.6 mmol (1.8 g) bis(*m*-nitrophenyl)methanone, 13.2 mmol (0.5 g) $NaBH_4$, 14 mL EtOH, r.t. = 30 min, reflux); yellow solid; mp: 101.7–104.1 °C (lit[70] 106.5–106.9 °C); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.31–8.26 (m, 2H), 8.21–8.15 (m, 2H), 7.76–7.70 (m, 2H), 7.60–7.53 (m, 2H), 6.05 (s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 148.4, 144.6, 132.5, 129.9, 123.1, 121.4, 74.3; IR(KBr): 1534, 1348, 1092, 1042, 901, 826, 803, 738, 712, 674 cm^{-1}; MS (ESI): 297.0 $(M + Na)^+$; HRMS: calcd for $C_{13}H_{10}N_2O_5Na$: 297.0487; found: 297.0477.

10,11-Dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene-5-yl (phenyl)-(*p*-tolyl)methyl ether (9). (2 mmol (0.42 g) 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene-5-ol, 6 mmol (1.19 g) (phenyl)-(*p*-tolyl)methanol, 6 mL CH_2Cl_2, 0.06 mmol (15 mg) I_2, r.t. = 15 min, 25 °C); preparative chromatography (SiO_2, hexane/

CH_2Cl_2 = 7/3); white solid (0.71 g, 91%); mp: 87.6–94.4 °C; ^{1}H-NMR (300 MHz, CD_3COCD_3): δ 7.44–7.09 (m, 17H), 5.49 (br s, 1H), 5.44 (s, 1H), 3.54 (br s, 2H), 3.09–2.83 (m, 2H), 2.29 (s, 3H); ^{13}C-NMR (75 MHz, CD_3COCD_3): δ 143.2, 140.0, 137.3, 130.7, 130.6, 129.4, 128.7, 128.4, 127.6, 127.4, 127.3, 126.2, 80.6, 32.4, 32.3, 20.6; IR(neat): 3017, 1493, 1447, 1030, 1017, 811, 723, 694 cm^{-1}; MS (ESI): 413.2 $(M + Na)^+$; HRMS: calcd for $C_{29}H_{26}ONa$: 413.1881; found: 413.1883; Anal. Calcd for $C_{29}H_{26}O$: C, 89.19; H, 6.71. Found: C, 88.97; H, 6.84.

Bis[[4-methoxy-3-[(phenyl)(*p*-tolyl)methyl]]phenyl]methane (10ww). From 0.4 mmol (170 mg) of **1w** (0.04 mmol (10 mg) I_2, r.t. = 45 min, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); white solid (46 mg, 39%); mp: 63.5–65.0 °C; ^{1}H-NMR (500 MHz, CD_3COCD_3): δ 7.25–7.19 (m, 4H), 7.19–7.14 (m, 2H), 7.06–6.99 (m, 8H), 6.97–6.88 (m, 6H), 6.88–6.82 (m, 2H), 6.68–6.65 (m, 2H), 5.82 (s, 2H), 3.68 (s, 6H), 3.63 (s, 2H), 2.27 (s, 6H); ^{13}C-NMR (125 MHz, CD_3COCD_3): δ 157.3, 146.1, 142.8, 137.0, 135.2, 135.2, 134.1, 132.2, 131.1, 131.0, 130.5, 129.8, 129.4, 127.7, 112.7, 57.0, 51.1, 42.0, 42.0, 22.0; IR(neat): 3022, 2918, 2833, 1493, 1450, 1240, 1108, 1030, 802, 740, 698 cm^{-1}; MS (ESI): 588.3 $(M)^+$; HRMS: calcd for $C_{43}H_{40}O_2$: 588.3028; found: 588.3027; Anal. Calcd for $C_{43}H_{40}O_2$: C, 87.72; H, 6.85. Found: C, 87.71; H, 6.83.

Bis[[4-methoxy-3-[bis(*p*-tolyl)methyl]]phenyl]methane (10xx). From 0.6 mmol (263 mg) of **1x** (0.06 mmol (15 mg) I_2, r.t. = 15 min, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1); white solid (52 mg, 28%); mp: 84.7–88.9 °C; ^{1}H-NMR (500 MHz, CD_3COCD_3): δ 7.03 (d, J = 8.0 Hz, 8H), 6.94 (dd, J = 8.3 Hz, J = 2.2 Hz, 2H), 6.90 (d, J = 8.0 Hz, 8H), 6.85 (d, J = 8.3 Hz, 2H), 6.68 (d, J = 2.2 Hz, 2H), 5.87 (s, 2H), 3.68 (s, 6H), 3.63 (s, 2H), 2.27 (s, 12H); ^{13}C-NMR (125 MHz, CD_3COCD_3): δ 157.3, 143.1, 136.9, 135.2, 134.3, 132.2, 131.0, 130.5, 129.3, 112.6, 57.0, 50.6, 42.0, 22.0; IR(neat): 2954, 2920, 2855, 1510, 1491, 1461, 1241, 1106, 1033, 822, 807, 769, 718, 653, 640 cm^{-1}; MS (ESI): 615.3 $(M - H)^+$; HRMS: calcd for $C_{45}H_{43}O_2$: 615.3263; found: 615.3275.

Bis[[4-methoxy-3-[(4-methylthiophenyl)(*p*-tolyl)methyl]]phenyl]-methane (10yy). From 0.75 mmol (353 mg) of **1y** (0.075 mmol (19 mg) I_2, r.t. = 90 min, 85 °C); preparative chromatography (SiO_2, hexane/CH_2Cl_2 = 1/1 and Al_2O_3, hexane/CH_2Cl_2 = 8/2); white solid (73 mg, 29%); mp: 84.9–87.9 °C; ^{1}H-NMR (500 MHz, CD_3COCD_3): δ 7.14–7.09 (m, 4H), 7.07–7.02 (m, 4H), 6.99–6.92 (m, 6H), 6.92–6.88 (m, 4H), 6.88–6.83 (m, 2H), 6.68–6.63 (m, 2H), 5.78 (s, 2H), 3.69 (s, 6H), 3.64 (s, 2H), 2.43 (s, 6H), 2.27 (s, 6H); ^{13}C-NMR (125 MHz, CD_3COCD_3): δ 157.2, 143.0, 143.0, 142.7, 142.7, 137.7, 137.7, 137.1, 137.1, 135.3, 135.3, 134.0, 132.1, 132.1, 131.6, 131.0, 130.6, 129.4, 112.6, 57.0, 50.5, 42.0, 42.0, 22.0, 16.6; IR(neat): 3005, 2833, 1611, 1510, 1492, 1461, 1435, 1292, 1232, 1176, 1107, 1029, 817, 803 cm^{-1}; Anal. Calcd for $C_{45}H_{44}O_2S_2$: C, 79.37; H, 6.51. Found: C, 79.39; H, 6.62.

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