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Disproportionation reaction of diarylmethylisopropyl ethers: a versatile access to diarylmethanes from diarylcarbinols speeded up by the use of microwave irradiation

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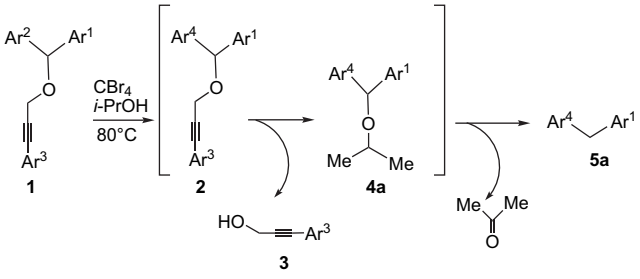
Abstract—An efficient synthesis of diarylmethanes under classical thermal conditions and under microwave heating is described from diarylcarbinols via a new disproportionation reaction. The key step involves a selective hydride transfer of isopropyl ether intermediates. Mild reaction conditions i.e., catalytic CBr_4 or TfOH in *i*-PrOH and good yields render this method useful and competitive to the conventional approaches relying on application of external reducing agents.

1. Introduction

During our research on the synthesis of low generation poly(arylpropargylether) dendrimers,[1] we hoped to cleave a methoxyethoxymethyl- (MEM-) protected phenol under mild conditions as previously described by Lee.[2] However, when ether **1** was reacted with a catalytic amount of CBr_4 in *i*-PrOH at 80 °C, the expected triarylether **2** was not detected. Instead, the only products isolated were the propargylic alcohol **3** (92%) and the diarylmethane **5a** (70%). On the contrary, performing the reaction at a lower temperature (55 °C; 24 h) resulted in the formation of **3** and unsymmetrical ether **4a** (90%).

To explain the formation of **5a** from **1**, we believe that the deprotection of the MEM group occurred and subsequently, the intermediate **2**, unstable under these acidic conditions, cleaved to give the propargylic alcohol **3** together with **5a** having a free phenolic group. The formation of the latter compound would probably result from a selective disproportionation reaction of the unsymmetrical ether **4a** via a concerted selective hydride transfer as in the Meerwein–Ponndorf–Verley-reduction[3] (Scheme 1). The high selectivity of this dismutation requiring catalytic acidic conditions,[4] could be explained by a preferable hydride transfer to the more electrophilic bis-benzylic carbon centre.



Ar^1= 4-$MeOC_6H_4$; Ar^2= 4-$MEMOC_6H_4$; Ar^3= 4-$EtO_2CC_6H_4$; Ar^4= 4-HOC_6H_4

Scheme 1. Plausible mechanism for the formation of **5a** from **1**.

The simplicity of this transformation and the interest of diarylmethane derivatives in organic chemistry led us to investigate this reaction.

Diarylmethane derivatives are of considerable interest as biological and medicinal substrates,[5] models for analogous thermally robust linkages present in fuel resources such as coal[6] and components in acid- or alkali-treated lignins.[7] Besides this, some diarylmethanes are frequently used as subunits in the design of supramolecular structures.[8] A number of methods have been proposed for their synthesis including transition metal-catalyzed cross coupling between aryl or benzyl nucleophiles with benzyl or aryl halides, respectively.[9,10] Alternative routes consist in the reduction of diaryl ketones[11] or benzhydrols[12] using, in most cases, a hydride donor agent (e.g., Et_3SiH, $NaBH_4$, H_2, PMHS, $LiAlH_4$,…) in the presence of TFA or a Lewis acid ($BF_3 \cdot Et_2O$, $AlCl_3$, $InCl_3$…).

Keywords: Disproportionation; Diarylcarbinols; Diarylmethanes; *i*-PrOH; CBr_4; TfOH; Microwave heating.
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Some examples of disproportionation reactions giving access to diarylmethane derivatives[13] were mentioned in the literature. Most of the described methods are sometimes harsh, need strong acidic activations and are often associated with low yields. In this letter, we report a simple and convenient procedure for the synthesis of a range of substituted diarylmethane derivatives from diarylcarbinols mediated by CBr_4 or TfOH (triflic acid) in *i*-PrOH.

2. Results and discussion

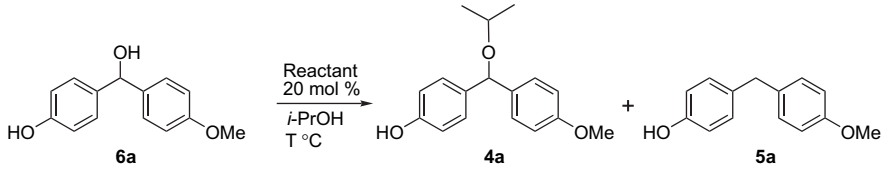
At the outset of this work, we evaluated the effect of a variety of catalysts on the disproportionation of carbinol **6a** chosen as a model substrate. Table 1 summarizes the results of our investigations.

After screening a series of catalysts, we were delighted to find that the use of catalytic amount of CBr_4, PTSA (*p*-toluenesulfonic acid), TfOH and aqueous HBr (entries 1, 2, 4 and 7), in contrast to TFA (trifluoroacetic acid), HCO_2H and Amberlyst 15 (entries 3, 5 and 6) allowed complete conversion of intermediate **4a** into **5a**. The best yield (83%, entry 1) was obtained with CBr_4 (20 mol %) in boiling *i*-PrOH for 24 h.

Next, in the continuation of our work to develop rapid and efficient methodologies, we choose to promote and accelerate the synthesis of **5a** using microwave-assisted irradiation.[14] Because heating was not foreseen to cause any serious decomposition problems, we gradually increased the temperature. We were pleased to observe that, in the presence of CBr_4 (20 mol %) and using microwave irradiation at 140 °C, **6a** was totally transformed into **5a** in only 15 min with a good yield (78%, entry 9). Under these conditions (microwave heating at 140 °C), **6a** was reacted with the other previously tested catalysts (TFA, HCOOH, Amberlyst 15) and the disappearance of the ether **4a** occurred in favour of the diarylmethane **5a** (compare entries 3 and 11, 5 and 13, 6 and 14). Moreover, when using CBr_4, PTSA, TfOH under microwave irradiation, the yields obtained at 140 °C were similar to or better than those observed under classical thermal conditions (compare entries 1 and 9, 2 and 10, 4 and 12). Finally, the amount of the catalyst was then studied. With 5 mol % of either CBr_4 or PTSA, the transformation was efficient and no starting material or intermediate ether **4a** was detected (entries 15, 16). As a control experiment, **6a** was heated in *i*-PrOH with CBr_4 (5 mol %) in a sealed tube at 140 °C for 15 min. Comparison of the results obtained using convectional or microwave heating indicated clearly the efficiency of the latter method (70%, entry 15 vs 40%, entry 17).

Having optimized the reaction parameters, we then examined the reaction with a wide variety of benzhydrols **6**, prepared from Grignard reagents and aromatic aldehydes (Table 2). All benzhydrols subjected to the CBr_4/*i*-PrOH system produced the corresponding diarylmethane derivatives but with variable amounts of their corresponding ether intermediate **4** except in the case of **5b** (entry 1). Thus, when using CBr_4 (20 mol %) in *i*-PrOH for 15 min under microwave irradiation at 140 °C, **5c** and **5d** were obtained together with their isopropylether precursors (entries 2 and 4). On the contrary, replacing CBr_4 by TfOH resulted in a complete disproportionation reaction with higher yields and easier purifications (entries 3 and 5). In this way, reduced phenstatin[15]

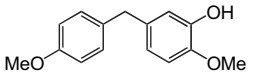
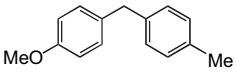
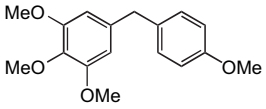
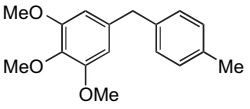
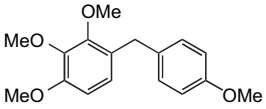
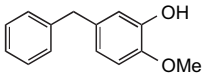
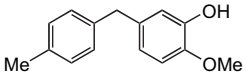
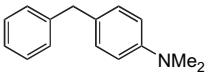
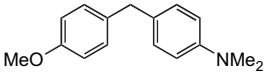
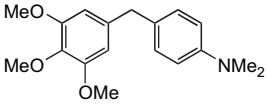
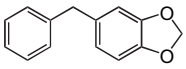
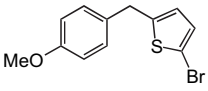
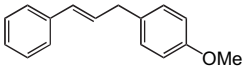
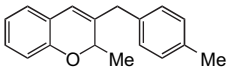
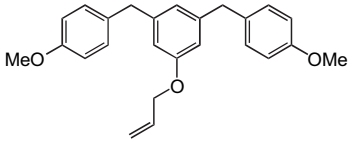
Table 1. Reduction of **6a** in *i*-PrOH



Entry	Reactant	Temperature (°C)	Conditions[a]	Time (h)	**4a**/**5a**[b]	**5** Yield[c] (%)
1	CBr_4	80	A	24	0/100	83
2	PTSA	80	**A**	24	0/100	74
3	TFA	80	A	24	100/0[d]	—
4	TfOH	80	A	24	0/100	70
5	HCO_2H	80	A	24	100/0[d]	—
6	Amberlyst 15	80	A	24	30/70	—
7	Aqueous HBr	80	A	24	0/100	57
8	CBr_4	100	B	0.25	0/100[e]	40
9	CBr_4	140	B	0.25	0/100	78
10	PTSA	140	B	0.25	0/100	80
11	TFA	140	B	0.25	22/78	—
12	TfOH	140	B	0.25	0/100	81
13	HCO_2H	140	B	0.25	50/50	—
14	Amberlyst 15	140	B	0.25	0/100	60
15	CBr_4[f]	140	B	0.25	0/100	70
16	PTSA	140	B	0.25	0/100	65
17	CBr_4[f]	140	C	0.25	0/100	40

[a] Method: **A**: thermal conditions; **B**: microwave irradiation; **C**: sealed tube.
[b] Ratio determined by ^1H NMR analysis ($CDCl_3$) of the crude reaction mixtures.
[c] Yield of isolated product after column chromatography.
[d] Isolated yield of **4a**: 82% (TFA); 76% (HCO_2H).
[e] The ^1H NMR spectrum of the crude mixture revealed the presence of an unidentified by-product.
[f] The reaction was carried out using 5 mol % of CBr_4.

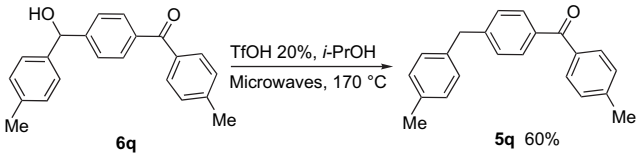
Table 2. Synthesis of diarylmethanes **5** from diarylcarbinols **6** under microwave irradiation

Entry	Alcohols **6**	Diarylmethanes **5**		Reactant (20 mol %)	Yield[a] (%)
1	**6b**		**5b**	CBr_4	70
2 3	**6c**		**5c**	CBr_4 TfOH	61[b] 85
4 5	**6d**		**5d**	CBr_4 TfOH	62[b] 70
6	**6e**		**5e**	TfOH	72
7	**6f**		**5f**	TfOH	80
8	**6g**		**5g**	TfOH	64
9	**6h**		**5h**	TfOH	78
10	**6i**		**5i**	TfOH	87
11	**6j**		**5j**	TfOH	64
12	**6k**		**5k**	TfOH	86
13	**6l**		**5l**	TfOH	75[c]
14	**6m**		**5m**	TfOH	86
15	**6n**		**5n**	TfOH	80[d]
16	**6o**		**5o**	TfOH	51[e]
17	**6p**		**5p**	TfOH	67

[a] Yield of isolated product after column chromatography.
[b] Unsymmetrical diarylmethylisopropyl ether (15–20%) was also isolated.
[c] Reaction time: 1 h.
[d] Obtained as a 1/1 mixture of double bond transposed isomers.
[e] Obtained as a 1/4 mixture of double bond transposed isomers.

analogues **5e** and **5f** were prepared with 72% and 80% isolated yields, respectively (entries 6 and 7). As shown with the model benzhydrol **6a** (Table 1), phenolic benzhydrols as well as amino derivatives afforded the expected diarylmethanes **5g–5k** with good yields (entries 8–12). We have also noticed that the disproportionation was efficient with methylenedioxyaryl analogue, but required a prolonged reaction time (1 h, entry 13). Because various functional groups survived under the reaction conditions, we have applied this process to the brominated thiophene **6m** and we were pleased to observe its total transformation affording the reduced compound **5m** with an excellent yield (86%, entry 14). The protocol was also applied to alcohols **6n**, **6o**. The expected diarylmethane derivatives **5n**, **5o** were then obtained with fair to good yields accompanied by isomers resulting in the double bond migration (entries 15 and 16). Disproportionation was also successful (67% entry 17) with compound **6p** containing two benzydrol units. In that case, we were delighted to find that this process took place with only 10% of TfOH per hydroxyl and preserved the allylic ether function (entry 17).

Finally, we have tested this microwave protocol (catalytic TfOH in *i*-PrOH) with the hydroxyketone **6q**. After stirring for 2 h at 170 °C[16] using microwave heating, we were pleased to observe that the disproportionation process occurred (60%). Careful examination of the crude mixture by ^{1}H NMR did not reveal the presence of reduced by-products (alcohols or diarylmethanes), demonstrating in this manner the selectivity of the present reductive method (Scheme 2).



Scheme 2. Reduction of **6q** preserving the ketone function.

To confirm the selectivity of this process, we have carried out the following experiment. When the model **6a** and benzophenone (as external carbonyl compound) were reacted together for 30 min at 140 °C using microwave heating, we were pleased to observe that the disproportionation of **6a** occurred without affecting the benzophenone, which was recovered totally unchanged (95%). However, we have noticed that under these conditions (TfOH 20%, *i*-PrOH, microwaves, 140 °C) several benzaldehydes were partially reduced under these conditions even in the absence of **6a**.

3. Conclusion

We have described herein a fast and efficient synthesis of functionalized diarylmethane derivatives under classical thermal conditions and in a faster way under microwave irradiation.[17] This process is chemoselective since several functional groups are tolerated (hydroxy, allyl, ketone) in contrary to some of the previously reported methods.[11,12] The key step involves a highly selective disproportionation reaction of diarylmethylisopropyl ether intermediates obtained from the corresponding carbinols. Further developments will be disclosed in due course.

4. Experimental

4.1. Materials

All glasswares were oven-dried at 140 °C. THF was distilled from sodium-benzophenone ketyl.

4.2. Instrumentation

All microwave experiments were performed using an Emrys Optimizer in 2–5 mL Pyrex reaction vessels. Each contained a Teflon stir bar and Teflon coated reaction vessel cap.

The compounds were all identified by usual physical methods, i.e., ^{1}H NMR, ^{13}C NMR, IR and elemental analysis. ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ with a Bruker Avance 300. ^{1}H chemical shifts are reported in parts per million from the peak of residual chloroform (7.27 ppm). ^{13}C chemical shifts are reported in parts per million from the central peak of deuteriochloroform (77.14 ppm). IR spectra were measured on a Bruker Vector 22 spectrophotometer (neat, cm^{-1}). Elemental analyses were performed with a Perkin–Elmer 240 analyser. Analytical TLC was performed on Merck precoated silica gel 60F plates. Merck silica gel 60 (230–400 mesh) was used for column chromatography. Melting points (mp) were recorded on a Büchi B-450 apparatus and were uncorrected.

4.3. Typical procedure for the preparation of diarylcarbinols 6

At −40 °C, a 1 M solution of Grignard reagent (1.5 mL; 1.5 mmol) was added dropwise to a solution of aldehyde (1 mmol) in THF (10 mL). The mixture was then stirred for 12 h at rt and then hydrolyzed with H_2O (10 mL). The organic phase was separated and the water phase was extracted with ether (2×10 mL). The combined extracts were dried (Na_2SO_4) and the solvent was evaporated under reduced pressure to give alcohols **6**, which were further purified by flash chromatography on silica gel.

Alcohols **6a**, **6c**, **6d**, **6g**, **6i**, **6j**, **6k**, **6l** and **6n** are known and gave satisfactory data. All new compounds were characterized by ^{1}H, ^{13}C NMR, IR and elemental analysis.

4.3.1. (4-Methoxyphenyl)-(3-hydroxy-4-methoxyphenyl)-methanol 6b. Yield: 78%.

Mp: 96 °C.

TLC: R_f 0.34 (cyclohexane/AcOEt 60/40, SiO_2).

Anal. Calcd for **6b** ($C_{15}H_{16}O_4$): C, 69.22; H, 6.20. Found: C, 69.10; H, 6.33.

IR (neat) ν_{max}/cm^{-1}: 3447, 3204, 1610, 1510, 1247, 1127, 1025.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.10 (d, 1H, J=3.3 Hz), 3.78 (s, 3H), 3.86 (s, 3H), 5.59 (s, 1H), 5.71 (d, 1H, J=3.3 Hz), 6.78–6.92 (m, 5H), 7.27 (d, 2H, J=8.4 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 55.3 (OCH_3), 55.9 (OCH_3), 75.4 (CH), 110.4 (CH), 112.9 (CH), 113.8 (2CH), 118.0

(CH), 127.7 (2CH), 136.2 (C), 137.6 (C), 145.5 (C), 145.6 (C), 159.0 (C).

4.3.2. (3,4,5-Trimethoxyphenyl)-(4-tolyl)methanol 6e. Yield: 76%.

Mp: 95 °C.

TLC: R_f 0.63 (cyclohexane/AcOEt 80/20, SiO_2).

Anal. Calcd for **6e** ($C_{17}H_{20}O_4$): C, 70.81; H, 6.99. Found: C, 70.89; H, 7.13.

IR (neat) ν_{max}/cm^{-1}: 3349, 1590, 1509, 1459, 1422, 1326, 1266, 1128, 1059, 1039, 1004.

^1H NMR (300 MHz, $CDCl_3$) δ: 2.15 (d, 1H, J=3.3 Hz), 2.34 (s, 3H), 3.82 (s, 3H), 3.83 (s, 6H), 5.75 (d, 1H, J=3.3 Hz), 6.61 (s, 2H), 7.16 (d, 2H, J=7.8 Hz), 7.27 (d, 2H, J=7.8 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 21.1 (CH_3), 56.0 ($2OCH_3$), 60.7 (OCH_3), 76.0 (CH), 103.4 (2CH), 126.4 (2CH), 129.1 (2CH), 137.1 (C), 137.3 (C), 139.6 (C), 140.7 (C), 153.1 (2C).

4.3.3. (3,4,5-Trimethoxyphenyl)-(4-methoxyphenyl)-methanol 6f. Yield: 83%.

TLC: R_f 0.44 (cyclohexane/AcOEt 60/40, SiO_2).

Anal. Calcd for **6f** ($C_{17}H_{20}O_5$): C, 67.09; H, 6.62. Found: C, 66.65; H, 6.86.

IR (neat) ν_{max}/cm^{-1}: 3500, 1601, 1510, 1493, 1462, 1243, 1172, 1092, 1009.

^1H NMR (300 MHz, $CDCl_3$) δ: 2.86 (d, 1H, J=5.7 Hz), 3.68 (s, 3H), 3.81 (s, 3H), 3.87 (s, 6H), 5.91 (d, 1H, J=5.7 Hz), 6.66 (d, 1H, J=8.7 Hz), 6.88 (d, 2H, J=8.7 Hz), 7.00 (d, 1H, J=8.7 Hz), 7.29 (d, 2H, J=8.7 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 55.2 (OCH_3), 55.9 (OCH_3), 60.6 ($2OCH_3$), 71.9 (CH), 106.9 (CH), 114.4 (2CH), 122.0 (CH), 128.6 (2CH), 130.1 (C), 136.2 (C), 142.1 (C), 151.2 (C), 153.3 (C), 158.7 (C).

4.3.4. (3-Hydroxy-4-methoxyphenyl)-(4-tolyl)methanol 6h. Yield: 73%.

Mp: 101–102 °C.

TLC: R_f 0.55 (cyclohexane/AcOEt 80/20, SiO_2).

Anal. Calcd for **6h** ($C_{15}H_{16}O_3$): C, 73.75; H, 6.60. Found: C, 73.61; H, 6.78.

IR (neat) ν_{max}/cm^{-1}: 3412, 3229, 1509, 1445, 1277, 1125, 1038, 947.

^1H NMR (300 MHz, $CDCl_3$) δ: 2.07 (d, 1H, J=3.3 Hz), 2.32 (s, 3H), 3.87 (s, 3H), 5.57 (s, 1H), 5.73 (d, 1H, J=3.3 Hz), 6.79–6.94 (m, 3H), 7.13 (d, 2H, J=7.8 Hz), 7.26 (d, 2H, J=7.8 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 21.1 (CH_3), 55.9 (OCH_3), 79.2 (CH), 110.4 (CH), 113.6 (CH), 118.9 (CH), 126.3 (2CH), 129.1 (2CH), 136.0 (C), 136.8 (C), 139.5 (C), 145.4 (C), 145.8 (C).

4.3.5. (5-Bromothiophen-2-yl)-(4-methoxyphenyl)-methanol 6m. Yield: 61%.

TLC: R_f 0.62 (cyclohexane/AcOEt 80/20, SiO_2).

Anal. Calcd for **6h** ($C_{12}H_{11}BrO_2S$): C, 48.17; H, 3.71. Found: C, 48.37; H, 3.68.

IR (neat) ν_{max}/cm^{-1}: 1610, 1509, 1439, 1244, 1172, 1029, 966.

^1H NMR (300 MHz, $CDCl_3$) δ: 2.91 (s, 1H), 3.80 (s, 3H), 5.83 (s, 1H), 6.57 (d, 1H, J=3.8 Hz), 6.86 (m, 3H), 7.30 (d, 2H, J=8.4 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 55.3 (OCH_3), 72.1 (CH), 112.1 (C), 114.0 (2CH), 124.9 (CH), 127.7 (2CH), 129.4 (CH), 134.8 (C), 150.1 (C), 159.5 (C).

*We have noticed that after few days **6m** was not stable in $CDCl_3$.*

4.3.6. (2-Methyl-2*H*-chromenyl)-(4-tolyl)methanol 6o. Yield: 80% (mixture of diastereoisomers).

TLC: R_f 0.61 (cyclohexane/AcOEt 70/30, SiO_2).

Anal. Calcd for **6o** ($C_{18}H_{18}O_2$): C, 81.17; H, 6.81. Found: C, 80.87; H, 6.95.

IR (neat) ν_{max}/cm^{-1}: 3404, 1605, 1513, 1485, 1364, 1235, 1206, 1142, 1105, 1040, 1022.

^1H NMR (300 MHz, $CDCl_3$) δ: 1.26 (d, 1.5H, J=6.6 Hz), 1.27 (d, 1.5H, J=6.6 Hz), 2.02–2.10 (br s, 1H), 2.36 (s, 3H), 4.69 (q, 0.5H, J=6.6 Hz), 4.94 (q, 0.5H, J=6.6 Hz), 5.25 (s, 0.5H), 5.32 (s, 0.5H), 6.32 (s, 0.5H), 6.58 (s, 0.5H), 6.70–7.30 (m, 8H).

^{13}C NMR (75 MHz, $CDCl_3$) δ: (the presence of diastereoisomers complicates the spectrum; only the most significant resonances are listed) 19.5 (CH_3), 20.0 (CH_3), 21.2 ($2CH_3$), 71.7 (2CH), 74.0 (CH), 75.0 (CH), 116.3 (CH), 116.4 (CH), 118.1 (CH), 120.0 (CH), 121.2 (CH), 121.3 (CH), 122.2 (2C), 126.6 (2CH), 126.8 (2CH), 129.1 (2CH), 129.3 (2CH), 129.5 (2CH), 130.0 (2CH), 137.7 (C), 138.2 (2C), 138.4 (C), 140.1 (C), 140.2 (C), 153.6 (2C).

4.3.7. Compound 6p. Compound **6p** was prepared from 5-allyloxy-isophthalic acid dimethyl ester in three steps as follows.

4.3.7.1. 3,5-Bis(hydroxymethyl)-(1-allyloxy)-phenyl. Under argon, were mixed $LiAlH_4$ in 110 mL of THF (8.7 g; 230.4 mmol) and 5-allyloxy-isophthalic acid dimethyl ester (14.4 g; 57.6 mmol) in 80 mL of THF. The stirred solution was then refluxed for 3 h. After cooling at 0 °C, the solution was hydrolyzed dropwise with H_2O

(100 mL), filtered and concentrated under vacuo to give 10.7 g (55.1 mmol) of the diol.

Yield: 96%.

TLC: R_f 0.52 (CH_2Cl_2/MeOH 90/10, SiO_2).

Mp: 54–55 °C.

IR (neat) ν_{max}/cm^{-1}: 3335, 3251, 3015, 2930, 2876, 1594.

^1H NMR (300 MHz, MeOD) δ: 4.54 (dt, 2H, J=5.1 Hz, J=1.6 Hz), 4.56 (s, 4H), 5.23 (dq, 1H, J=10.5 Hz; J=1.6 Hz), 5.39 (dq, 1H, J=17.2 Hz, J=1.6 Hz), 6.02 (m, 1H), 6.84 (s, 2H), 6.91 (s, 1H), (OH not seen).

^{13}C NMR (75 MHz, MeOD) δ: 65.1 (CH_2), 69.7 ($2CH_2$), 113.0 (CH), 117.4 (CH_2), 118.7 (2CH), 135.0 (CH), 144.4 (2C), 160.4 (C).

4.3.7.2. 5-Allyloxyisophthalaldehyde. A solution of the diol (350 mg; 1.80 mmol) in CH_2Cl_2 (11 mL) was mixed with PCC (1.24 g; 5.7 mmol) and stirred for 2 h at rt. The mixture was then diluted in Et_2O (15 mL) and filtered over SiO_2. The filtrate was concentrated under vacuo to give 5-allyloxyisophthalaldehyde (280 mg, 1.47 mmol) as a white solid.

Yield: 85%.

TLC: R_f 0.33 (cyclohexane/AcOEt 80/20, SiO_2).

Mp: (cyclohexane) 67–68 °C.

IR (neat) ν_{max}/cm^{-1}: 3000, 2832, 1681, 1592.

^1H NMR (300 MHz, $CDCl_3$) δ: 4.59 (dt, 2H, J=5.2 Hz, J=1.4 Hz), 5.27 (dq, 1H, J=10.5 Hz; J=1.4 Hz), 5.39 (dq, 1H, J=17.2 Hz, J=1.4 Hz), 6.00 (m, 1H), 7.59 (s, 2H), 7.89 (s, 1H), 9.98 (s, 2H).

^{13}C NMR (75 MHz, MeOD) δ: 69.3 (CH_2), 118.4 (CH), 120.0 (2CH), 124.1 (CH), 132.0 (CH), 138.2 (2C), 157.9 (C), 190.7 (2C).

4.3.7.3. 3,5-Bis[(4-methoxyphenyl)hydroxymethyl]-1-allyloxy-benzene 6p. Yield: 50%.

Mp: 101–103 °C.

TLC: R_f 0.13 (cyclohexane/AcOEt 60/40, SiO_2).

Anal. Calcd for **6p** ($C_{25}H_{26}O_5$): C, 73.87; H, 6.45. Found: C, 73.71; H, 6.48.

IR (neat) ν_{max}/cm^{-1}: 3347, 1611, 1509, 1441, 1282, 1247, 1168, 1111, 1028.

^1H NMR (300 MHz, $CDCl_3$) δ: 3.03 (s, 6H), 3.77 (d, 2H, J=5.0 Hz), 3.88 (d, 2H, J=4.0 Hz), 4.47 (d, 1H, J=10.4 Hz), 4.64 (d, 1H, J=17.2 Hz), 4.97 (d, 2H, J=4.0 Hz), 5.21–5.40 (m, 1H), 6.10–6.14 (m, 6H), 6.34 (s, 1H), 6.57 (d, 4H, J=8.4 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 56.5 ($2OCH_3$), 70.2 (CH_2), 76.8 (2CH), 112.9 (2CH), 115.2 (4CH), 118.3 (CH), 118.9 (CH), 129.6 (4CH), 135.8 (CH), 139.5 (2C), 149.1 (2C), 160.5 (2C), 160.7 (C).

4.3.8. {4-[(4-Tolyl)-hydroxymethyl]-phenyl}-(4-tolyl)-methanone 6q. Compound **6q** was obtained as a by-product (22%) of the reaction between *p*-tolyl magnesium bromide (1 equiv) and terephthaldicarboxaldehyde (2 equiv) as follows: to a solution of terephthaldicarboxaldehyde (2.68 g, 22 mmol) in 40 mL of THF was added dropwise at −40 °C under argon, 11 mL (11 mmol) of a 1 M solution of *p*-tolyl magnesium bromide. After stirring for a night at rt, the mixture was treated with H_2O (30 mL) and extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were then dried with $MgSO_4$ and evaporated to dryness. Purification by flash chromatography afforded **6q** as a white solid.

Yield: 22% (not optimized).

Mp: 108 °C.

TLC: R_f 0.63 (cyclohexane/AcOEt 80/20, SiO_2).

Anal. Calcd for **6q** ($C_{22}H_{20}O_2$): C, 83.51; H, 6.37. Found: C, 83.29; H, 6.22.

IR (neat) ν_{max}/cm^{-1}: 3483, 2918, 1637, 1604, 1569, 1413, 1316, 1279, 1177, 1043, 1017.

^1H NMR (300 MHz, $CDCl_3$) δ: 1.75 (s, 3H), 1.84 (s, 3H), 2.40 (s, 1H, OH), 5.25 (s, 1H), 6.56 (d, 2H, J=7.8 Hz), 6.67 (d, 4H, J=7.8 Hz), 6.88 (d, 2H, J=8.4 Hz), 7.10 (d, 2H, J=7.8 Hz), 7.13 (d, 2H, J=8.4 Hz).

^{13}C NMR (75 MHz) δ: 21.1 (CH_3), 21.6 (CH_3), 60.4 (CH), 126.6 (2CH), 127.2 (2CH), 128.9 (2CH), 129.8 (2CH), 130.1 (2CH), 130.2 (2CH), 134.8 (C), 136.7 (C), 137.5 (C), 140.5 (C), 143.1 (C), 148.3 (C), 196.2 (C).

4.4. Typical procedure for the disproportionation of carbinols under thermal conditions

To a flask containing **6a** (1 mmol) was added CBr_4 (66 mg, 0.2 mmol) in *i*-PrOH (8 mL). The mixture was then stirred at 80 °C for 24 h. After cooling to rt, the crude mixture was hydrolyzed with H_2O (5 mL) and extracted with CH_2Cl_2 (3×5 mL). The combined organic layers were then dried with $MgSO_4$ and evaporated to dryness. Purification by flash chromatography afforded the diarylmethane derivative **5a**.

4.5. Typical procedure for the disproportionation of carbinols under microwave irradiation

To an Emrys Optimizer 2–5 mL Pyrex reaction vessel were added 0.2 mL of a 1 M solution of TfOH in *i*-PrOH, 1 mmol of diarylcarbinol and *i*-PrOH (3 mL). The reaction vessel was then placed in the Emrys Optimizer and exposed to microwave irradiation according to the following specifications: temperature: 140 °C, time 900 s, fixed hold time: on, sample absorption: high, pre-stirring: 60 s. After cooling to rt, the crude mixture was treated as above.

Diarylmethanes **5a**, **5c**, **5d**, **5f**, **5g**, **5i**, **5j**, **5l** and **5n** are known and gave satisfactory data.

4.5.1. (4-Methoxyphenyl)-(3-hydroxy-4-methoxyphenyl)-methane 5b. Yield: 70%.

Mp: 61–62 °C.

TLC: R_f 0.48 (cyclohexane/AcOEt 60/40, SiO_2).

Anal. Calcd for **5b** ($C_{15}H_{16}O_3$): C, 73.75; H, 6.60. Found: C, 73.71; H, 6.67.

IR (neat) ν_{max}/cm^{-1}: 3467, 1609, 1586, 1508, 1463, 1444, 1271, 1223, 1202, 1178, 1130, 1020.

^1H NMR (300 MHz, $CDCl_3$) δ: 3.78 (s, 3H), 3.83 (s, 2H), 3.85 (s, 3H), 5.56 (s, 1H), 6.66 (dd, 1H, J=8.2 Hz, J=1.8 Hz), 6.76 (d, 1H, J=1.8 Hz), 6.77 (d, 1H, J=8.2 Hz), 6.82 (d, 2H, J=8.4 Hz), 7.10 (d, 2H, J=8.4 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 40.4 (CH_2) 55.2 (OCH_3), 56.0 (OCH_3), 110.6 (CH), 113.8 (2CH), 115.1 (CH), 120.0 (CH), 129.7 (2CH), 133.5 (C), 135.0 (C), 144.9 (C), 145.5 (C), 157.9 (C).

4.5.2. (4-Tolyl)-(3,4,5-trimethoxyphenyl)methane 5e. Yield: 80%.

Mp: 53 °C.

TLC: R_f 0.40 (cyclohexane/AcOEt 80/20, SiO_2).

Anal. Calcd for **5e** ($C_{17}H_{20}O_3$): C, 74.97; H, 7.40. Found: C, 74.89; H, 7.29.

IR (neat) ν_{max}/cm^{-1}: 1588, 1506, 1465, 1421, 1324, 1240, 1120, 1001.

^1H NMR (300 MHz, $CDCl_3$) δ: 2.34 (s, 3H), 3.82 (s, 6H), 3.84 (s, 3H), 3.90 (s, 2H), 6.42 (s, 2H), 7.12 (s, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 20.9 (CH_3), 41.7 (CH_2), 56.0 ($2OCH_3$), 60.8 (OCH_3), 105.8 (2CH), 128.6 (2CH), 129.1 (2CH), 135.6 (C), 136.2 (C), 136.9 (C), 137.8 (C), 153.1 (2C).

4.5.3. (4-Tolyl)-(3-hydroxy-4-methoxyphenyl)methane 5h. Yield: 64%.

Mp: 80–81 °C.

TLC: R_f 0.20 (cyclohexane/AcOEt 70/30, SiO_2).

Anal. Calcd for **5h** ($C_{15}H_{16}O_2$): C, 78.92; H, 7.06. Found: C, 78.87; H, 7.05.

IR (neat) ν_{max}/cm^{-1}: 3435, 1587, 1502, 1468, 1446, 1351, 1302, 1238, 1127, 1020.

^1H NMR (300 MHz, $CDCl_3$) δ: 2.32 (s, 3H), 3.86 (s, 5H), 5.56 (s, 1H, OH), 6.67 (dd, 1H, J=10.0 Hz, J=2.1 Hz), 6.76–6.80 (m, 2H), 7.09 (s, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 21.0 (CH_3), 40.9 (CH_2), 56.0 (OCH_3), 110.6 (CH), 115.1 (CH), 120.1 (CH), 128.7 (2CH), 129.1 (2CH), 134.8 (C), 135.4 (C), 138.3 (C), 144.9 (C), 145.5 (C).

4.5.4. (4-Methoxyphenyl)-(4-*N*,*N*-dimethylaminophenyl)-methane 5k. Yield: 86%.

Mp: 77 °C.

TLC: R_f 0.26 (cyclohexane/AcOEt 80/20, SiO_2).

Anal. Calcd for **5k** ($C_{18}H_{23}NO_3$): C, 71.73; H, 7.69; N, 4.65. Found: C, 71.55; H, 7.95; N, 4.50.

IR (neat) ν_{max}/cm^{-1}: 1614, 1588, 1521, 1505, 1461, 1421, 1237, 1123, 1006.

^1H NMR (300 MHz, $CDCl_3$) δ: 2.93 (s, 6H), 3.82 (s, 9H), 3.84 (s, 2H), 6.41 (s, 2H), 6.73 (d, 2H, J=8.7 Hz), 7.08 (d, 2H, J=8.7 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 40.8 ($2NCH_3$), 41.2 (CH_2), 56.0 ($2OCH_3$), 60.8 (OCH_3), 105.7 (2CH), 113.0 (2CH), 129.3 (2CH), 136.1 (C), 137.7 (2C), 149.1 (C), 153.1 (2C).

4.5.5. 2-Bromo-5-(4-methoxybenzyl)thiophene 5m. Yield: 86%.

TLC: R_f 0.59 (cyclohexane/AcOEt 50/50, SiO_2).

Anal. Calcd for **5m** ($C_{12}H_{11}BrOS$): C, 50.90; H, 3.92; S, 11.32. Found: C, 50.20; H, 3.78; S, 11.08.

IR (neat) ν_{max}/cm^{-1}: 1614, 1588, 1521, 1505, 1461, 1421, 1237, 1123, 1006.

^1H NMR (300 MHz, $CDCl_3$) δ: 3.78 (s, 3H), 3.99 (s, 2H), 6.52 (d, 1H, J=4.0 Hz), 6.82–6.85 (m, 3H), 7.13 (d, 2H, J=8.4 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 35.6 (CH_2), 55.2 (OCH_3), 109.9 (C), 114.0 (2CH), 125.1 (CH), 129.5 (CH), 129.6 (CH), 130.9 (CH), 131.6 (C), 146.6 (C), 158.4 (C).

4.5.6. 2-Methyl-3-(4-methylbenzyl)-2*H*-chromene 5o. Yield: 51%.

TLC: R_f 0.40 (cyclohexane/AcOEt 80/20, SiO_2).

IR (neat) ν_{max}/cm^{-1}: (mixture of isomers) 2922, 1766, 1657, 1607, 1578, 1514, 1487, 1456, 1370, 1236, 1207, 1108, 1039.

^1H NMR (300 MHz, $CDCl_3$) (obtained as an inseparable mixture (4/1) with its minor double bond transposed isomer) *major isomer* ***5o*** δ: 1.33 (d, 3H, J=6.6 Hz), 2.35 (s, 3H), 3.36 (d, 1H, J=15.9 Hz), 3.46 (d, 1H, J=15.9 Hz), 4.79 (q, 1H, J=6.6 Hz), 6.07 (s, 1H), 6.78 (d, 1H, J=8.1 Hz), 6.84 (t, 1H, J=16.0 Hz), 6.93 (dd, 1H, J=6.0 Hz, J=1.3 Hz), 7.05–7.13 (m, 5H). *2-Methyl-3-(4-methylbenzylidene)chromane (minor isomer)*: (only the most significant resonances are listed) δ: 1.50 (d, 3H, J=6.6 Hz), 2.36 (s, 3H), 3.38

(d, 1H, J=19.0 Hz), 3.87 (d, 1H, J=19.0 Hz), 5.37 (d, 1H, J=6.6 Hz), 6.56 (s, 1H), 6.89 (d, 2H, J=7.2 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) *major isomer* ***5o*** δ: 18.9 (CH_3), 29.9 (CH_3), 39.3 (CH_2), 73.7 (CH), 115.9 (CH), 119.6 (CH), 120.9 (CH), 122.5 (C), 125.9 (CH), 128.4 (CH), 129.0 (2CH), 129.2 (2CH), 134.8 (C), 136.0 (C), 138.5 (C), 151.5 (C). ^{13}C NMR (75 MHz, $CDCl_3$) *minor isomer*: (only the most significant resonances are listed) δ: 21.1 (CH_3), 29.6 (CH_3), 31.6 (CH_2), 70.1 (C), 117.1 (CH), 120.3 (CH), 125.4 (CH), 127.4 (CH), 128.5 (CH), 153.0 (C).

4.5.7. 3,5-Bis(4-methoxybenzyl)-1-allyloxybenzene 5p. Yield: 67%.

TLC: R_f 0.47 (cyclohexane/AcOEt 90/10, SiO_2).

Anal. Calcd for **5p** ($C_{25}H_{26}O_3$): C, 80.18; H, 7.00. Found: C, 80.12; H, 6.98.

IR (neat) ν_{max}/cm^{-1}: 1592, 1509, 1453, 1241, 1175, 1107, 1034.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.80 (s, 6H), 3.86 (s, 4H), 4.44 (dt, 2H, J=5.7 Hz, J=1.5 Hz), 5.28 (dq, 1H, J=10.5 Hz, J=1.5 Hz), 5.36 (dq, 1H, J=17.4 Hz, J=1.5 Hz), 5.95–6.08 (m, 1H), 6.56 (s, 2H), 6.65 (s, 1H), 6.83 (d, 4H, J=8.7 Hz), 7.10 (d, 4H, J=8.7 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 41.0 ($2CH_2$), 55.2 ($2OCH_3$), 68.6 (CH_2), 112.9 (2CH), 113.8 (4CH), 117.6 (CH_2), 122.1 (CH), 129.8 (4CH), 133.0 (2C), 133.3 (CH), 143.0 (2C), 157.9 (2C), 158.9 (C).

4.5.8. [4-(4-Methylbenzyl)-phenyl]-(4-tolyl)methanone 5q. Yield: 61%.

TLC: R_f 0.55 (cyclohexane/AcOEt 90/10, SiO_2).

Anal. Calcd for **5q** ($C_{22}H_{20}O$): C, 87.96; H, 6.71. Found: C, 87.94; H, 6.66.

IR (neat) ν_{max}/cm^{-1}: 1652, 1605, 1312, 1276, 1177, 1114.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.43 (s, 3H), 2.53 (s, 3H), 4.11 (s, 2H), 7.21 (s, 4H), 7.35–7.40 (m, 4H), 7.79–7.83 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 21.0 (CH_3), 21.6 (CH_3), 41.5 (CH_2), 120.1 (2CH), 129.3 (4CH), 130.1 (2CH), 130.2 (2CH), 130.3 (2CH), 135.1 (C), 135.7 (C), 135.8 (C), 137.1 (C), 143.0 (C), 146.1 (C), 196.1 (C).

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16. At 140 °C, the disproportionation was incomplete (30% of **4q** was observed in the crude mixture).
17. The experimental microwave experiments described in this letter are well established and controlled and can be safely and beneficially reproduced.