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Gram-Scale Synthesis of Substituted Triarylmethanes

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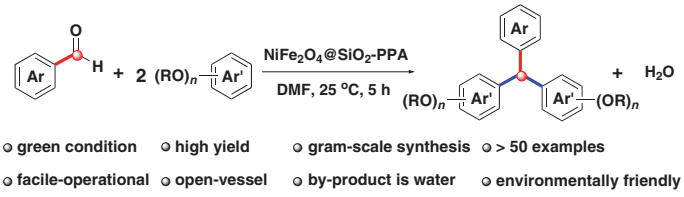

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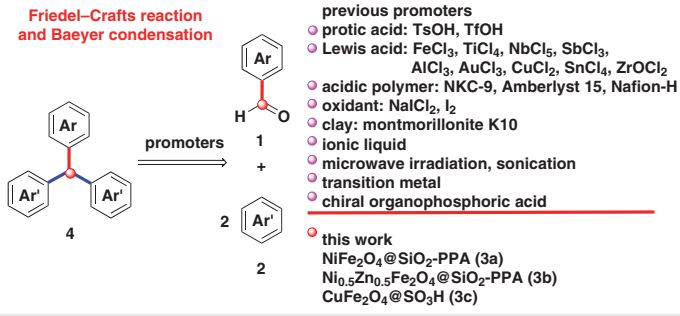
Abstract A high-yield, open-vessel route for the facile-operational, gram-scale synthesis of functionalized triarylmethanes (TRAMs) is described via silica-coated magnetic nanoparticles of modified polyphosphoric acid ($NiFe_2O_4$@SiO_2-PPA)-mediated intermolecular Friedel–Crafts reaction of substituted aryl aldehydes with 2 equivalents of oxygenated arenes under environmentally friendly reaction conditions. Among the overall reaction process, only water was generated as the by-product. Various reaction conditions are investigated for efficient transformation.

Key words gram-scale synthesis, triarylmethanes, magnetic nanoparticles, Friedel–Crafts reaction, environmentally friendly

For the related applications of triarylmethanes (TRAMs) and their derivatives, there are several review articles documented. In 1993, Duxbury outlined the first photochemical and photophysical dyestuff properties of triphenylmethane.[1] Afterward, Shchepinov and Korshun provided a discussion for the applications of a bifunctional trityl cation (a deprotonated TRAMs).[2] The Nair group summarized the synthetic chemistry of triaryl- and triheteroarylmethanes.[3] Panda and co-worker analyzed these elegant synthetic methodologies of diversified TRAMs.[4] Subsequently, by focusing the transition metal catalysis, Nambo and Crudden compared the synthetic routes of chiral TRAMs.[5] Very recently, the Saha, Huang, and Nandi teams described the advanced development in the progress of catalytic and stoichiometric synthesis of TRAMs.[6] These review papers demonstrated that the core system of symmetrically and asymmetrically substituted TRAMs could exhibit numerous unique properties, including organic functionalized materials, biologically active molecules, chemoselective metal-ion sensors, and useful synthetic building blocks.

Traditionally, the Friedel–Crafts reaction and Baeyer condensation have been two of the most commonly employed tools for the formation of TRAMs in the presence of different promoters. Several promoters have been reported, as shown in Scheme 1, including protic acid (TsOH,[7] TfOH[8]), Lewis acid ($FeCl_3$,[9] $TiCl_4$,[10] $NbCl_5$,[11] $SbCl_3$,[12] $AlCl_3$,[13] $AuCl_3$,[14] $CuCl_2$,[15] $SnCl_4$,[16] $ZrOCl_2$[17]), acidic polymer (NKC-9,[18] Amberlyst-15,[19] Nafion-H[20]), oxidant ($NaICl_2$,[21] I_2[22]), clay (K10),[23] ionic liquid,[24] microwave irradiation, and sonication.[25]

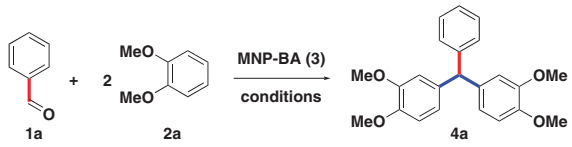


Scheme 1 Synthetic routes of triarylmethanes (TRAMs)

Recently, a number of transition-metal-catalyzed methods have emerged as an alternative route to provide structurally diverse TRAMs.[5] The main drawbacks of the synthetic routes for these catalysts were that they were corrosive or expensive, and the apparatus for microwaving and sonication was infrequently put to use. Moreover, the desired TRAMs required a tedious workup process. Motivated by the above-mentioned literature survey, herein, we chose excellent silica-coated magnetic nanoparticles (MNP) of modified polyphosphoric acid (PPA) as a reusable, facile-operational and green solid support for the gram-scale generation of TRAMs under a mild reaction condition and open-vessel conditions. Among these synthetic catalysts towards TRAMs, to the best of our knowledge, no MNP-mediated synthetic reports have been documented.[26–30] However, recent examples on chiral organophosphoric acid (OrganoPPA)-mediated enantioselective synthesis of TRAMs have been developed.[31–35] To deserve to be mentioned, Zhao[36] and Walsh[37] have reported the novel and efficient synthesis of TRAMs via palladium-catalyzed cross-coupling reaction. For the synthetic applications on the combination of MNP and PPA, a few examples have been reported on the establishment of thioxoquinazolinone, β-acetamido ketone, pyranopyrazole, and chromeno[4,3-*b*]chromene skeletons.[38–41] On the basis of the above recorded observations, we present an efficient, one-step synthetic route towards TRAMs **4** via a Friedel–Crafts reaction and Baeyer condensation of substituted aryl aldehydes **1** and oxygenated arenes **2** in the presence of freshly prepared silica-coated magnetic nanoparticles of modified Brønsted acids (MNP-BA) **3a–c**. Among the overall reaction processes, only water was generated as the by-product. The use of nanostructured materials as support for different types of functional transformations remains an attractive field to organic chemists. The nature of the magnetic nanoparticle catalysts usually allows for facile-operational purification, an easy-recovered process and repeated-cycling activation.

The initial study commenced with the treatment of simple benzaldehyde (**1a**; Ar = Ph, 0.53 g, 5.0 mmol) with veratrole [**2a**; Ar′ = 3,4-$(MeO)_2C_6H_3$; 1.38 g, 10.0 mmol]. After perusing review articles on MNP-BA-promoted synthetic applications,[26–30] three that are known and well-prepared, $NiFe_2O_4$@SiO_2-PPA (**3a**),[38,39] $Ni_{0.5}Zn_{0.5}Fe_2O_4$@SiO_2-PPA (**3b**),[38] and $CuFe_2O_4$@SO_3H (**3c**),[41] were examined. First, by using **3a** (10 mol%), only a 12% yield of **4a** was obtained in the presence of MeCN (1 mL) at 25 °C for 5 hours (Table 1, entry 1). By changing the solvent to toluene, a similar yield (20%) was obtained (entry 2). However, $CHCl_3$ and DME provided modest yields (47% and 61%, entries 3, 4). For $MeNO_2$ and DMF, better yields (70% and 90%) were observed (entries 5, 6). From the results, we found that more polar solvent could increase the yield of **4a**. With the results in mind, the optimal reaction time was surveyed next by controlling **3a** as the promoter and DMF as the solvent. To increase the isolated yield, elongated times (10, 15, and 20 h) were investigated. In entries 7–9, we found that three reaction times provided yields of nearly 85%, 82%, and 80%, respectively. From the experimental results, we understood that longer reaction times (10, 15 or 20 h) did not enhance the yield of **4a**.

Table 1 Reaction Conditions[a]



Entry	MNP-BA **3a–c**	Solvent	Time (h)	Yield (%)[b]
1	$NiFe_2O_4$@SiO_2-PPA **3a**	MeCN	5	12
2	$NiFe_2O_4$@SiO_2-PPA **3a**	toluene	5	20
3	$NiFe_2O_4$@SiO_2-PPA **3a**	$CHCl_3$	5	47
4	$NiFe_2O_4$@SiO_2-PPA **3a**	DME	5	61
5	$NiFe_2O_4$@SiO_2-PPA **3a**	$MeNO_2$	5	70
6	$NiFe_2O_4$@SiO_2-PPA **3a**	DMF	5	90
7	$NiFe_2O_4$@SiO_2-PPA **3a**	DMF	10	85
8	$NiFe_2O_4$@SiO_2-PPA **3a**	DMF	15	82
9	$NiFe_2O_4$@SiO_2-PPA **3a**	DMF	20	80
10	$NiFe_2O_4$@SiO_2-PPA **3a**	DMF	10	70[c]/39[d]
11	$NiFe_2O_4$@SiO_2-PPA **3a**	DMF[e]	10	78
12	$NiFe_2O_4$@SiO_2-PPA **3a**	–[f]	10	82
13	$NiFe_2O_4$@SiO_2-PPA **3a**[g]	DMF	10	85
14	$Ni_{0.5}Zn_{0.5}Fe_2O_4$@SiO_2-PPA **3b**	DMF	10	70
15	$CuFe_2O_4$@SO_3H **3c**	DMF	10	63[h]
16	SiO_2-PPA	DMF	10	80

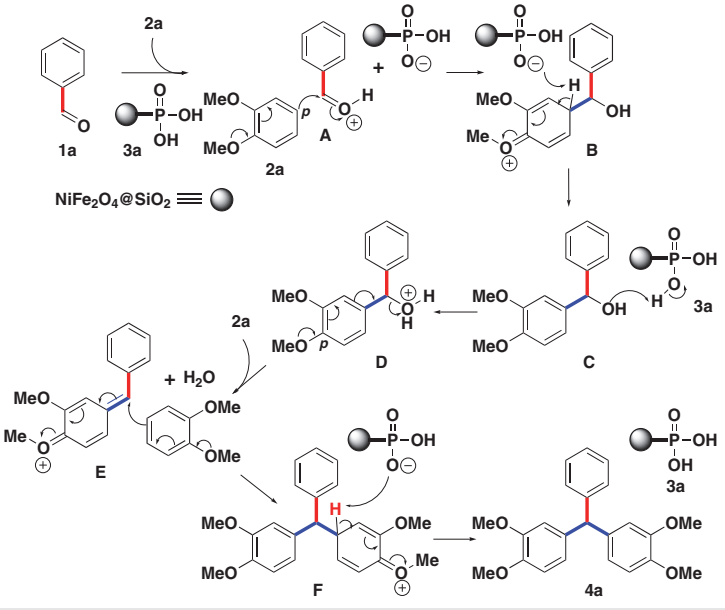
[a] Reactions were run on a 5.0 mmol scale with **1a** (530 mg), **2a** (1380 mg, 10.0 mmol), solvent (1 mL), and **3a–c** (250 mg, ~10 mol%) at 25 °C.
[b] Isolated yields.
[c] At 80 °C.
[d] Reflux (154 °C).
[e] DMF (5 mL).
[f] Solvent-free condition.
[g] Amount of **3a** used: 500 mg, ~20 mol%.
[h] Complex unknown mixture (~10%) was isolated.

Furthermore, reaction temperature screening was performed. By elevating the temperature to 80 °C, a 70% yield of **4a** was isolated, but when the reaction was conducted at a reflux temperature (154 °C), the yield of **4a** was quickly decreased to 39% (Table 1, entry 10). It is obvious that the reaction was appropriate under a room temperature-dependent condition. A possible reason could be that elevating the temperature could destroy the magnetic nanoparticle's structure stepwise such that catalytic amounts of **3a** could not promote the generation of **4a** efficiently. On the basis of the above-mentioned data, DMF volumes were studied. After diluting the reaction concentration from 1 mL to 5 mL, a slightly lower yield (78%) was obtained (entry

11). Under solvent-free conditions, however, a neat solution system provided similar yields (82%, entry 12). Compared with entry 6 (1 mL DMF), neither of them obtained higher yields of **4a**. In entry 13, increasing the catalytic amounts (10 → 20 mol%) of **3a**, the same yield (85%) of **4a** was isolated. This meant that 10 mol% amount of **3a** was enough to produce a better yield of **4a**. Subsequently, **3b** and **3c** were checked. When the reaction was treated with **3b**, the provided yield (70%) was lower than **3a** (entry 14). According to the results, we found that $NiFe_2O_4$ had more reactive magnetic nanoparticles than $Ni_{0.5}Zn_{0.5}Fe_2O_4$ due to the higher component of nickel increasing the yield of **4a**. On the other hand, changing the source of the Brønsted acid from phosphoric acid to sulfonic acid, **3c** was tested. However, **4a** was isolated in a lower yield (63%) along with a 10% yield of a complex unknown mixture (entry 15). For the phenomenon of low yield, we envisioned that the sulfonic acid residue on **3c** was a stronger Brønsted acid than PPA such that complex products were detected. Finally, by removing MNP-dispersion, a simple solid support of SiO_2-PPA (250 mg) was tested,[42] and the obtained yield (80%, entry 16) was lower than **3a**. Compared with **3a** (entry 6, 90%) and SiO_2-PPA (entry 16, 80%), **3a** provided a higher yield than SiO_2-PPA. On the basis of the results, we envisioned that MNP should also play the Lewis acid role to catalyze the reaction process such that the yield of **4a** was improved from 80% to 90%. From these observations, we concluded that entry 6 provided optimal conditions for the formation of **4a** (90%) via a **3a**-promoted intermolecular Friedel–Crafts reaction and Baeyer condensation of **1a** with **2a**.

On the basis of our experimental results, a plausible mechanism for the formation of **4a** is illustrated in Scheme 2. Initially, coupling **1a** with **3a** yields **A** via an intermolecular proton exchange. With the involvement of **2a**, the methoxy group on **2a** can trigger the *para*-carbon to attack the protonated carbonyl group of **1a** yielding **B** and **3a** with a *phosphate* ion. Following the aromatization process, **3a** with a phosphate ion abstracts the proton from **B** to lead to **C**. After protonation of the hydroxyl group on **C** with the resulting **3a**, **D** having an oxonium ion, can be formed. Then, by the electron-donating ability of the *para*-methoxy group, water can be removed from the dibenzylic position to afford **E**. Subsequently, by the involvement of another **2a**, **F** is generated via the above-mentioned intermolecular addition. Finally, after dehydrogenative aromatization by **3a** with a phosphate ion, **4a** can be formed spontaneously along with the recovery of **3a**.

To explore the substrate scope and limitations of this route, diversified aryl aldehydes **1a–x** were reacted with substituted oxygenated arenes **2a–i** to afford functionalized TRAMs **4a–t**, **4u–ah** in the presence of **3a**, as shown in Table 2. With optimal conditions established (Table 1, entry 6) and a plausible mechanism proposed (Scheme 2), we found that this route allowed a direct Friedel–Crafts reaction and Baeyer condensation under mild conditions in the range of moderate to good yields (Table 2, entries 1–34, 80–94%). By controlling dioxygenated **2a** as the arene source, entries 1–23 showed that different Ar groups of **1a–x** with halogen (fluoro, bromo, dichloro), electron-neutral (methyl, dimethyl), electron-withdrawing (nitro, trifluoromethyl, methyl ketone, formyl) and electron-releasing (mono-, di- or trioxygenated) groups, and carbocyclic (2-naphthyl) and heterocyclic (2-thienyl, 2-pyridyl, 2-furyl) groups, etc. did not affect the efficient formations of **4a–x** except for **4t**. The

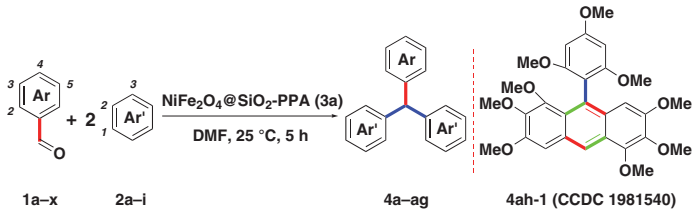


Scheme 2 Plausible mechanism

molecular structure of **4e** was determined by single-crystal X-ray analysis.[43] Also deserving mention, entry 13 showed that Ar with both one electron-withdrawing nitro group and two electron-donating oxygenated groups produced **4m** in an 84% yield.

Unexpectedly, **1s** could produce an 84% yield of the product **4s**. However, when treatment of **2a** with **1t** with a 2-furyl group was undertaken, no desired product **4t** was isolated, and only an unidentified and unknown complex mixture was detected due to the low aromaticity of the furan ring resulting in the phenomenon (Table 2, entry 20). By the use of SiO_2-PPA (Table 1, entry 16), **4t** could not be still obtained. From the results, we believe that 2-furyl group was unstable under the PPA/DMF condition. For the bis-formyl group of **1u**, in particular, the optimal reaction condition controlled one formyl group of **1u** to react with two equivalents of **3a** selectively, and the asymmetrical **4u** with one formyl residue could be generated in a 90% yield (entry 21). On the other hand, when treatment of **2a** (2.0 equiv) was undertaken with **1v** having two kinds of different carbonyl synthons, the formyl and acetyl, respectively, only the formyl group could be converted to **4v** (entry 22). However, the acetyl substituent was not initiated in the Friedel–Crafts reaction. In entry 23, **1w** with one formyl and one nitrile groups showed similar results.

Table 2 Synthesis of **4a–ag** and **4ah–1**[a]



1a–x 2a–i 4a–ag 4ah-1 (CCDC 1981540)

Entry	**1**, Ar =	**2**, Ar′ =	**4**, Yield (%)[b]
1	**1a**, Ph	**2a**, 1,2-$(MeO)_2C_6H_4$	**4a**, 90
2	**1b**, 3-FC_6H_4	**2a**, 1,2-$(MeO)_2C_6H_4$	**4b**, 94
3	**1c**, 4-MeC_6H_4	**2a**, 1,2-$(MeO)_2C_6H_4$	**4c**, 94
4	**1d**, 4-$MeOC_6H_4$	**2a**, 1,2-$(MeO)_2C_6H_4$	**4d**, 90
5	**1e**, 3,4-$(MeO)_2C_6H_3$	**2a**, 1,2-$(MeO)_2C_6H_4$	**4e**, 94
6	**1f**, 3,4-$CH_2O_2C_6H_3$	**2a**, 1,2-$(MeO)_2C_6H_4$	**4f**, 93
7	**1g**, 4-PhC_6H_4	**2a**, 1,2-$(MeO)_2C_6H_4$	**4g**, 91
8	**1h**, 2-naphthyl	**2a**, 1,2-$(MeO)_2C_6H_4$	**4h**, 87
9	**1i**, 2-Br,4,5-$(MeO)_2C_6H_2$	**2a**, 1,2-$(MeO)_2C_6H_4$	**4i**, 89
10	**1j**, 3-$MeOC_6H_4$	**2a**, 1,2-$(MeO)_2C_6H_4$	**4j**, 90
11	**1k**, 2-$NO_2C_6H_4$	**2a**, 1,2-$(MeO)_2C_6H_4$	**4k**, 86
12	**1l**, 3-$CF_3C_6H_4$	**2a**, 1,2-$(MeO)_2C_6H_4$	**4l**, 87
13	**1m**, 3-MeO,4-OH,5-$NO_2C_6H_2$	**2a**, 1,2-$(MeO)_2C_6H_4$	**4m**, 84
14	**1n**, 3,5-$(Me)_2C_6H_3$	**2a**, 1,2-$(MeO)_2C_6H_4$	**4n**, 88
15	**1o**, 3,4-$Cl_2C_6H_3$	**2a**, 1,2-$(MeO)_2C_6H_4$	**4o**, 90
16	**1p**, 4-HOC_6H_4	**2a**, 1,2-$(MeO)_2C_6H_4$	**4p**, 90
17	**1q**, 4-ClC_6H_4	**2a**, 1,2-$(MeO)_2C_6H_4$	**4q**, 91
18	**1r**, 4-NO_2,2-thienyl	**2a**, 1,2-$(MeO)_2C_6H_4$	**4r**, 83
19	**1s**, 3-pyridyl	**2a**, 1,2-$(MeO)_2C_6H_4$	**4s**, 84
20	**1t**, 2-furyl	**2a**, 1,2-$(MeO)_2C_6H_4$	**4t**, –[c]
21	**1u**, 4-$CHOC_6H_4$	**2a**, 1,2-$(MeO)_2C_6H_4$	**4u**, 90
22	**1v**, 3-Me(C=O)C_6H_4	**2a**, 1,2-$(MeO)_2C_6H_4$	**4v**, 90
23	**1w**, 4-NCC_6H_4	**2a**, 1,2-$(MeO)_2C_6H_4$	**4w**, 93
24	**1x**, 3,4,5-$(MeO)_3C_6H_2$	**2a**, 1,2-$(MeO)_2C_6H_4$	**4x**, 89

Table 2 (continued)

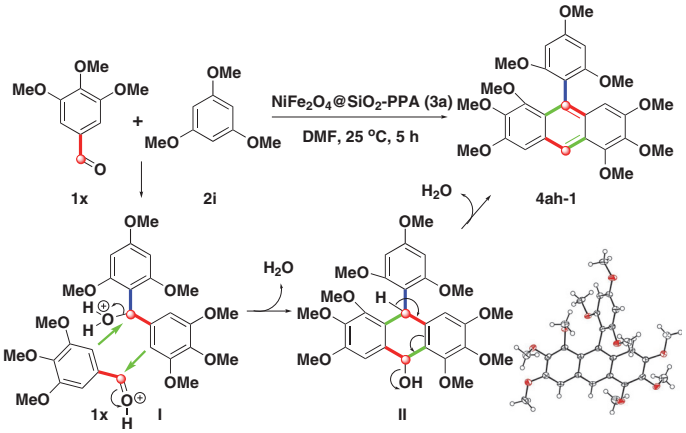
Entry	**1**, Ar =	**2**, Ar′ =	**4**, Yield (%)[b]
25	**1x**, 3,4,5-$(MeO)_3C_6H_2$	**2b**, 1,2-$CH_2O_2C_6H_4$	**4y**, 84
26	**1o**, 3,4-$Cl_2C_6H_3$	**2c**, 1,2-$(C_4H_9O)_2C_6H_4$	**4z**, 85
27	**1h**, 2-naphthyl	**2c**, 1,2-$(C_4H_9O)_2C_6H_4$	**4aa**, 85
28	**1x**, 3,4,5-$(MeO)_3C_6H_2$	**2c**, 1,2-$(C_4H_9O)_2C_6H_4$	**4ab**, 84
29	**1x**, 3,4,5-$(MeO)_3C_6H_2$	**2d**, 1,2-$(C_8H_{17}O)_2C_6H_4$	**4ac**, 89
30	**1x**, 3,4,5-$(MeO)_3C_6H_2$	**2e**, 1,2-$(C_{12}H_{25}O)_2C_6H_4$	**4ad**, 80
31	**1x**, 3,4,5-$(MeO)_3C_6H_2$	**2f**, 1,2,3-$(MeO)_3C_6H_3$	**4ae**, 80
32	**1x**, 3,4,5-$(MeO)_3C_6H_2$	**2g**, 1,2,3-$(C_4H_9O)_3C_6H_3$	**4af**, 82
33	**1x**, 3,4,5-$(MeO)_3C_6H_2$	**2h**, 1,2,3-$(C_8H_{17}O)_3C_6H_3$	**4ag**, 81
34	**1x**, 3,4,5-$(MeO)_3C_6H_2$	**2i**, 1,3,5-$(MeO)_3C_6H_3$	**4ah**, –[d]

[a] Reactions were run on a 5.0 mmol scale with **1a–x**, **2a–i** (10.0 mmol), $NiFe_2O_4$@SiO_2-PPA (**3a**; 250 mg, ~10 mol%), DMF (1 mL), 10 h at 25 °C.
[b] Isolated yields.
[c] Complex unknown mixture was isolated.
[d] Product **4ah–1** (30%) was isolated.

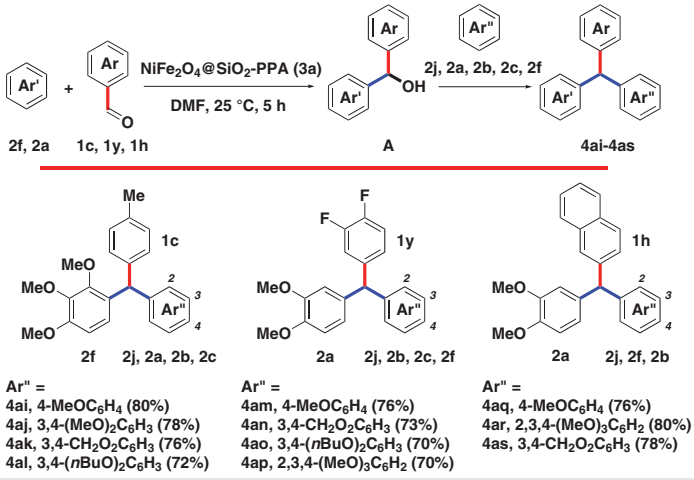
Furthermore, after elongating the dioxygenated aliphatic carbon chain from a one-carbon **2a**, **2b** to a four-carbon side chain, **2c** was examined. In Table 2, entries 26–28, **2c** with a shorter bis-*n*-butoxy arm provided **4z**, **4aa**, and **4ab** in 85%, 85% and 74% yield, respectively. With these results in hand, both **4ac** (medium *n*-octyloxy chain) and **4ad** (longer *n*-dodecyloxy group) could be obtained in good yields (89% and 80%, entries 29, 30).

This was a quite convenient route used to obtain TRAMs skeleton having different lipid-containing side chains. After increasing the chain number from dimethoxy **2a** to trimethoxy (for **2f**), the yield of **4ae** could be maintained (80%, Table 2, entry 31), and both contiguous 1,2,3-tri-*n*-butyloxy (**2g**) and 1,2,3-tri-*n*-octyloxy (**2h**) also produced **4af** and **4ag** in good yields (82% and 81%, entries 32, 33). By the use of cold hexane as the solvent, interestingly, these nonpolar products with four-carbon, eight-carbon, and twelve-carbon side chains were dissolved easily such that the overall purification process was easy to handle. After searching the literature on the preparation of TRAMs with two to six lipid chains, however, no studies were found on related synthetic work. Therefore, the present work provides a novel route for synthesizing the TRAMs with four or six lipid-conjugated arms. In particular, no desired **4ah** was detected, and **4ah-1** was obtained in only a 30% yield via the reaction of **1x** (1.0 equiv) and **2i** (2.0 equiv) with a separated 1,3,5-trimethoxy group (entry 34). Especially, two equivalents of **1x** were installed into the formation of **4ah-1** in the presence of excess amounts of **2l** (Scheme 3). This reasonable mechanism showed that the initial intermediate **I** was formed by the reaction of the same equivalent of **1x** and **2l**. In the next reaction of **I**, a competitive behavior between **1x** and **2i** was formed. When the reaction of **I** treated **2i**, the expected **4ah** could be formed, but we could not isolate **4ah**. Therefore, we envisioned that **I** preferred to react with **1x** over **2l**. For the generation of intermediate **II**, a possible reason could be that the oxygenated group on **I** can promote the *para*-carbon to easily attack the formyl group of **1x**. After accomplishing the aromatization of **II**, the desired **4ah-1** was generated. This synthetic route provided highly effective four C–C bond formations. The unique tricyclic molecular structure of **4ah-1,** with an anthracene core, was determined by single-crystal X-ray analysis.[43]

Encouraged by the above experimental results, synthesis of the asymmetrical TRAMs skeletons was investigated next (Scheme 4). By involvement of $NiFe_2O_4$@SiO_2-PPA (**3a**) as the acidic support, the initial reaction of model *p*-tolualdehyde (**1c**) with the same equivalent of two oxygenated arenes **2f** (1.0 equiv) and **2j** (1.0 equiv) produced **4ai** in an 80% yield. The experiment revealed that the formyl group on **1c** could be reacted with **2f** first to generate a secondary alcohol moiety (for the generation of intermediate **A**) followed by the sequential introduction of anisole (**2j**) via a well-ordered intermolecular Friedel–Crafts reaction sequence. Controlling the starting substrates **1c** and **2f**, **2a**, **2b**, and **2c** produced **4aj**, **4ak**, and **4al** in 78%, 76% and 72% yield, respectively. By similar reaction conditions, after adjusting aldehyde **1c** with an electron-neutral group to **2f** with an electron-withdrawing group and changing **2f** with a trimethoxy group to **2a** with a dimethoxy group, four TRAMs **4am–ap** were produced in a range of 70–76% yields by the reaction of **2j**, **2b**, **2c**, and **2f**. Furthermore, **4aq–as** were obtained in 76–80% yields by the combination of bicyclic **1h**, **2a**, and **2j**, **2f** and **2b**. This was an efficient transformation for the magnetic nanoparticle-mediated preparation of asymmetrical TRAMs skeletons.

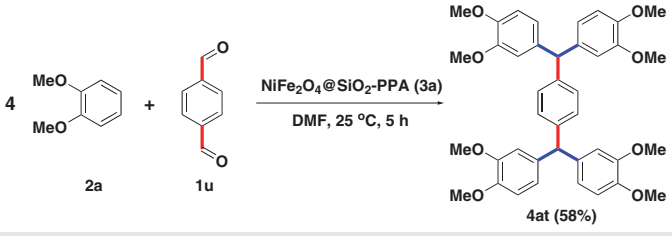


Scheme 3 Plausible mechanism of formation of **4ah-1**

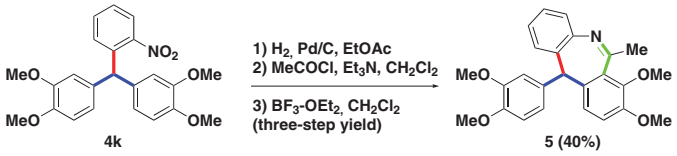


Scheme 4 Stepwise synthesis of **4ai–as**

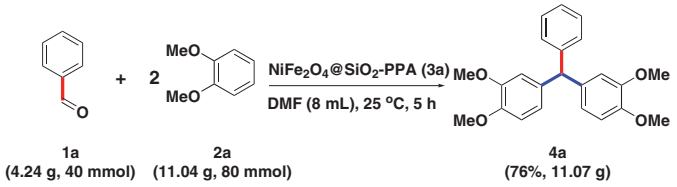
On the basis of the abovementioned results, a linear dendrimer-like TRAMs structure was examined next (Scheme 5). Double condensation of 1,4-diformylbenzene (**1u**) with four equivalents of **2a** produced **4at** in a 58% yield along with two equivalents of water. As an extension of the $NiFe_2O_4$@SiO_2-PPA (**3a**)-mediated synthesis of triarylmethanes (TRAMs), we were able to synthesize 11*H*-dibenzo[*b*,*e*]azepine skeleton (Scheme 6). 11*H*-Dibenzo[*b*,*e*]azepine is a versatile core in useful synthetic intermediates[44,45] and bioactive molecules.[46,47] Furthermore, by using **4k** as the starting material, tricyclic **5** was obtained in a 40% yield in three-steps including: (1) reduction of the nitro group on **4k**, (2) *N*-acylation of the resulting amine with excess acetyl chloride in the presence of triethylamine (Et_3N), and (3) trifluoroboron etherate (BF_3·OEt_2)-mediated Bischler-Napieralski cyclization of the corresponding amide.



Scheme 5 Synthesis of **4at**



Scheme 6 Synthesis of **5**



Scheme 7 Large-scale synthesis of **4a**

Because of the potential application of this protocol in synthesis of various TRAMs, attempts at large scale-up of the transformation would improve the significance of the results. Thus, the development of a re-used **3a**-mediated 10 grams-scale route was highly in demand. As shown in Scheme 7, re-cycled **3a** (2.0 g)-mediated reaction of benzaldehyde (**1a**; 4.24 g, 40 mmol) and veratrole (**2a**; 11.04 g, 80 mmol) could produce **4a** in a 76% yield (11.07 g) in DMF (8 mL) at 25 °C for 5 hours. Compared with 5 mmol scale of **1a** (90%, Table 2, entry 1), 40 mmol scale provided a lower yield (76%). Although the obtained yield was lower, the 10 grams-scale synthetic route of TRAMs was well-established.

In summary, we have developed a gram-scale, environmentally friendly, one-step Friedel–Crafts type route for the synthesis of symmetrical and asymmetrical functionalized triarylmethanes (TRAMs) via silica coated magnetic nanoparticles of modified polyphosphoric acid ($NiFe_2O_4$@SiO_2-PPA)-mediated intermolecular condensation of substituted aryl aldehydes with 2 equivalents of oxygenated arenes. A related plausible mechanism has been proposed. The uses of various reaction conditions were investigated for efficient transformation. Further investigations regarding the synthetic application of TRAMs will be conducted and published in due course.

All reagents and solvents were obtained from commercial sources and used without further purification. Reactions were routinely carried out under an atmosphere of dry N_2 with magnetic stirring. Products in organic solvents were dried with anhyd $MgSO_4$ before concentration in vacuo. Melting points were determined with a SMP3 melting apparatus. ^1H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 spectrometer operating at 400 and at 100 MHz, respectively. Chemical shifts (δ) are reported in parts per million (ppm) and the coupling constants (*J*) are given in hertz (Hz). High-resolution mass spectra (HRMS) were recorded on a Finnigan/Thermo Quest MAT 95XL mass spectrometer. X-ray crystal structures were obtained with an Enraf-Nonius FR-590 diffractometer (CAD4, Kappa CCD).

The starting substrates **1a–y** and **2a–j** were purchased commercially and used without further purification. For three freshly prepared silica-coated magnetic nanoparticles of modified Brønsted acids (MNP-BA), $NiFe_2O_4$@SiO_2-PPA (**3a**), $Ni_{0.5}Zn_{0.5}Fe_2O_4$@SiO_2-PPA (**3b**) and $CuFe_2O_4$@SO_3H (**3c**), these compounds were known and preparation methods were identical with those in the literature.[38–41]

Triarylmethanes 4a–s, 4u–ag, and 4ah-1; General Procedure 1

$NiFe_2O_4$@SiO_2-PPA (**3a**; 250 mg, 10 mol%) was added to a stirred solution of aryl aldehyde **1** (5.0 mmol) and oxygenated arene **2** (10.0 mmol) in DMF (1 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 5 h. Upon completion, **3a** could be placed on the side wall of the reaction vessel with the aid of an external magnet, then **3a** was isolated, washed with CH_2Cl_2 (3 × 5 mL) and dried to reuse in the next run. Then, combined DMF and CH_2Cl_2 solutions were concentrated under reduced pressure to afford the crude product. Purification on silica gel (hexanes/EtOAc 50:1 to 10:1) afforded compounds **4a–s**, **4u–ag**, and **4ah-1**.

4,4′-(Phenylmethylene)bis(1,2-dimethoxybenzene) (4a)

Prepared according to the general procedure 1 from **1a** (530 mg, 5.0 mmol) and **2a** (1380 mg, 10.0 mmol); yield: 90% (1639 mg); white solid; mp 126–128 °C (recrystallized from hexanes and EtOAc).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.26 (m, 2 H), 7.21–7.18 (m, 1 H), 7.14–7.12 (m, 2 H), 6.78 (d, *J* = 8.4 Hz, 2 H), 6.69 (d, *J* = 2.0 Hz, 2 H), 6.61 (dd, *J* = 2.0, 8.4 Hz, 2 H), 5.46 (s, 1 H), 3.84 (s, 6 H), 3.75 (s, 6 H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 148.5 (2 ×), 147.2 (2 ×), 144.1, 136.5, 129.0 (2 ×), 128.0 (2 ×), 126.0 (2 ×), 121.2 (2 ×), 112.6 (2 ×), 110.7 (2 ×), 55.7, 55.6 (2 ×), 55.5 (2 ×).

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{23}H_{25}O_4$: 365.1753; found: 365.1745.

4,4′-((3-Fluorophenyl)methylene)bis(1,2-dimethoxybenzene) (4b)

Prepared according to the general procedure 1 from **1b** (620 mg, 5.0 mmol) and **2a** (1380 mg, 10.0 mmol); yield: 94% (1796 mg); colorless liquid.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.22 (m, 1 H), 6.92–6.88 (m, 2 H), 6.82–6.79 (m, 1 H), 6.79 (d, *J* = 8.4 Hz, 2 H), 6.65 (d, *J* = 2.0 Hz, 2 H), 6.59 (dd, *J* = 2.0, 8.0 Hz, 2 H), 5.43 (s, 1 H), 3.86 (s, 6 H), 3.77 (s, 6 H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 162.5 (d, *J* = 245.6 Hz), 148.8 (2 ×), 147.6 (2 ×), 147.0 (d, *J* = 6.9 Hz), 136.0 (2 ×), 130.1 (d, *J* = 7.6 Hz), 125.9 (d, *J* = 3.1 Hz), 121.3 (2 ×), 120.9 (d, *J* = 21.3 Hz), 117.0 (d, *J* = 23.5 Hz), 112.6 (2 ×), 110.9 (2 ×), 55.82 (2 ×), 55.79 (2 ×), 55.6 (d, *J* = 1.5 Hz).

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{23}H_{24}FO_4$: 383.1659; found: 383.1664.

4,4′-(*p*-Tolylmethylene)bis(1,2-dimethoxybenzene) (4c)

Prepared according to the general procedure 1 from **1c** (600 mg, 5.0 mmol) and **2a** (1380 mg, 10.0 mmol); yield: 94% (1777 mg); white solid; mp 141–143 °C (recrystallized from hexanes and EtOAc).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.10 (d, *J* = 8.0 Hz, 2 H), 7.02 (d, *J* = 8.0 Hz, 2 H), 6.78 (d, *J* = 8.0 Hz, 2 H), 6.69 (d, *J* = 2.0 Hz, 2 H), 6.61 (dd, *J* = 2.0, 8.4 Hz, 2 H), 5.42 (s, 1 H), 3.86 (s, 6 H), 3.77 (s, 6 H), 2.33 (s, 3 H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 148.6 (2 ×), 147.3 (2 ×), 141.2, 136.8 (2 ×), 135.6, 129.0 (2 ×), 128.8 (2 ×), 121.2 (2 ×), 112.7 (2 ×), 110.7 (2 ×), 55.72 (2 ×), 55.68 (2 ×), 55.4, 20.9.

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{24}H_{27}O_4$: 379.1909; found: 379.1915.

4,4′-((4-Methoxyphenyl)methylene)bis(1,2-dimethoxybenzene) (4d)

Prepared according to the general procedure 1 from **1d** (680 mg, 5.0 mmol) and **2a** (1380 mg, 10.0 mmol); yield: 90% (1774 mg); colorless liquid.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.03 (d, *J* = 8.4 Hz, 2 H), 6.83 (d, *J* = 8.8 Hz, 2 H), 6.78 (d, *J* = 8.4 Hz, 2 H), 6.67 (d, *J* = 2.0 Hz, 2 H), 6.60 (dd, *J* = 2.0, 8.4 Hz, 2 H), 5.40 (s, 1 H), 3.85 (s, 6 H), 3.78 (s, 3 H), 3.76 (s, 6 H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 157.9, 148.6 (2 ×), 147.3 (2 ×), 137.0, 136.4 (2 ×), 130.9 (2 ×), 121.2 (2 ×), 113.5 (2 ×), 112.6 (2 ×), 110.7 (2 ×), 55.74 (2 ×), 56.69 (2 ×), 55.1, 55.0.

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{24}H_{27}O_5$: 395.1859; found: 395.1866.

Tris(3,4-dimethoxyphenyl)methane (4e)

Prepared according to the general procedure 1 from **1e** (830 mg, 5.0 mmol) and **2a** (1380 mg, 10.0 mmol); yield: 94% (1994 mg); white solid; mp 142–144 °C (recrystallized from hexanes and EtOAc).

^1H NMR (400 MHz, $CDCl_3$): δ = 6.78 (d, *J* = 8.4 Hz, 3 H), 6.66 (d, *J* = 2.0 Hz, 3 H), 6.59 (dd, *J* = 2.0, 8.0 Hz, 3 H), 5.38 (s, 1 H), 3.86 (s, 9 H), 3.76 (s, 9 H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 148.7 (3 ×), 147.4 (3 ×), 136.9 (3 ×), 121.3 (3 ×), 112.7 (3 ×), 110.8 (3 ×), 55.81 (3 ×), 55.78 (3 ×), 55.4.

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{25}H_{29}O_6$: 425.1964; found: 425.1963.

Single-Crystal X-ray Data

Crystals of compound **4e** were grown by slow diffusion of EtOAc into a solution of compound **4e** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 2_1, *a* = 10.0496(9) Å, *b* = 8.4754(10) Å, *c* = 14.0842(18) Å, *V* = 1149.9(2) Å^3, *Z* = 2, d_{calcd} = 1.226 g/cm^3, *F*(000) = 452, 2θ range 1.508–25.086°, R indices (all data) R1 = 0.1487, wR2 = 0.1290.

5-(Bis(3,4-dimethoxyphenyl)methyl)benzo[*d*][1,3]dioxole (4f)

Prepared according to the general procedure 1 from **1f** (750 mg, 5.0 mmol) and **2a** (1380 mg, 10.0 mmol); yield: 93% (1898 mg); colorless liquid.

^1H NMR (400 MHz, $CDCl_3$): δ = 6.78 (d, *J* = 8.0 Hz, 2 H), 6.72 (d, *J* = 7.6 Hz, 1 H), 6.66 (d, *J* = 2.0 Hz, 2 H), 6.60 (t, *J* = 2.4 Hz, 2 H), 6.57 (dt, *J* = 2.0, 8.0 Hz, 2 H), 5.91 (s, 2 H), 5.35 (s, 1 H), 3.82 (s, 6 H), 3.73 (s, 6 H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 148.7 (2 ×), 147.4 (2 ×), 147.5, 145.9, 138.3, 136.7, 122.2 (2 ×), 121.2 (2 ×), 112.6 (2 ×), 110.8 (2 ×), 109.7, 107.9, 100.8 (2 ×), 55.79 (2 ×), 55.77, 55.5.

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{24}H_{25}O_6$: 409.1651; found: 409.1659.

4-(Bis(3,4-dimethoxyphenyl)methyl)-1,1′-biphenyl (4g)

Prepared according to the general procedure 1 from **1g** (910 mg, 5.0 mmol) and **2a** (1380 mg, 10.0 mmol); yield: 91% (2003 mg); colorless liquid.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.61–7.59 (m, 2 H), 7.54 (d, *J* = 8.4 Hz, 2 H), 7.45–7.41 (m, 2 H), 7.35–7.31 (m, 1 H), 7.21 (d, *J* = 8.4 Hz, 2 H), 6.82 (d, *J* = 8.0 Hz, 2 H), 6.73 (d, *J* = 2.0 Hz, 2 H), 6.66 (dd, *J* = 2.0, 8.0 Hz, 2 H), 5.50 (s, 1 H), 3.88 (s, 6 H), 3.79 (s, 6 H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 148.7 (2 ×), 147.5 (2 ×), 143.4, 140.7, 139.0, 136.6 (2 ×), 129.6 (2 ×), 128.7 (2 ×), 127.1, 126.89 (2 ×), 126.86 (2 ×), 121.3 (2 ×), 112.7 (2 ×), 110.8 (2 ×), 55.78 (2 ×), 55.76 (2 ×), 55.5.

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{29}H_{29}O_4$: 441.2066; found: 441.2078.

2-(Bis(3,4-dimethoxyphenyl)methyl)naphthalene (4h)

Prepared according to the general procedure 1 from **1h** (780 mg, 5.0 mmol) and **2a** (1380 mg, 10.0 mmol); yield: 87% (1802 mg); white solid; mp 162–164 °C (recrystallized from hexanes and EtOAc).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.81 (m, 1 H), 7.78 (d, *J* = 8.8 Hz, 1 H), 7.75–7.72 (m, 1 H), 7.49 (s, 1 H), 7.67–7.43 (m, 2 H), 7.33 (dd, *J* = 2.0, 8.4 Hz, 1 H), 6.81 (d, *J* = 8.4 Hz, 2 H), 6.76 (d, *J* = 2.0 Hz, 2 H), 6.67 (dd, *J* = 2.0, 8.4 Hz, 2 H), 5.63 (s, 1 H), 3.88 (s, 6 H), 3.78 (s, 6 H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 148.7 (2 ×), 147.4 (2 ×), 141.9, 136.4, 133.3, 132.0, 127.9, 127.8, 127.7, 127.5, 127.4 (2 ×), 125.9, 125.5, 121.5 (2 ×), 112.7 (2 ×), 110.8 (2 ×), 55.9, 55.74 (2 ×), 55.71 (2 ×).

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{27}H_{27}O_4$: 415.1909; found: 415.1918.

4,4′-((2-Bromo-4,5-dimethoxyphenyl)methylene)bis(1,2-dimethoxybenzene) (4i)

Prepared according to the general procedure 1 from **1i** (1220 mg, 5.0 mmol) and **2a** (1380 mg, 10.0 mmol); yield: 89% (2234 mg); colorless liquid.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.04 (s, 1 H), 6.77 (d, *J* = 8.4 Hz, 2 H), 6.63 (d, *J* = 2.0 Hz, 2 H), 6.52 (dd, *J* = 2.0, 8.4 Hz, 2 H), 6.45 (s, 1 H), 5.71 (s, 1 H), 3.85 (s, 9 H), 3.76 (s, 6 H), 3.62 (s, 3 H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 148.7 (2 ×), 148.1, 148.0, 147.5 (2 ×), 135.6, 135.5, 121.3 (2 ×), 115.6 (2 ×), 115.2, 113.8, 112.7 (2 ×), 110.7 (2 ×), 56.1, 55.9, 55.8 (2 ×), 55.7 (2 ×), 54.6.

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{25}H_{28}BrO_6$: 503.1069; found: 503.1077.

4,4′-((3-Methoxyphenyl)methylene)bis(1,2-dimethoxybenzene) (4j)

Prepared according to the general procedure 1 from **1j** (680 mg, 5.0 mmol) and **2a** (1380 mg, 10.0 mmol); yield: 90% (1774 mg); white solid; mp 108–110 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 (t, *J* = 8.0 Hz, 1 H), 6.78 (d, *J* = 8.4 Hz, 2 H), 6.76–6.66 (m, 5 H), 6.81 (dd, *J* = 2.0, 8.4 Hz, 2 H), 5.41 (s, 1 H), 3.85 (s, 6 H), 3.77 (s, 6 H), 3.74 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 159.5, 148.7 (2 ×), 147.4 (2 ×), 145.9, 136.5, 129.1 (2 ×), 121.7, 121.3 (2 ×), 115.3, 112.6 (2 ×), 111.2, 110.8 (2 ×), 55.81, 55.75 (2 ×), 55.7 (2 ×), 55.0.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{27}O_5$: 395.1859; found: 395.1864.

4,4′-((2-Nitrophenyl)methylene)bis(1,2-dimethoxybenzene) (4k)

Prepared according to the general procedure 1 from **1k** (755 mg, 5.0 mmol) and **2a** (1380 mg, 10.0 mmol); yield: 86% (1759 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (dd, *J* = 1.2, 8.4 Hz, 1 H), 7.48 (dt, *J* = 1.2, 7.6 Hz, 1 H), 7.37 (dt, *J* = 1.2, 8.4 Hz, 1 H), 7.09 (d, *J* = 7.6 Hz, 1 H), 6.77 (d, *J* = 8.0 Hz, 2 H), 6.62 (d, *J* = 2.0 Hz, 2 H), 6.51 (dd, *J* = 2.0, 8.4 Hz, 2 H), 6.17 (s, 1 H), 3.85 (s, 6 H), 3.76 (s, 6 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 149.7, 148.9 (2 ×), 147.8 (2 ×), 138.5, 134.6, 132.3, 131.7, 127.4 (2 ×), 124.6, 121.3 (2 ×), 112.8 (2 ×), 110.8 (2 ×), 55.81 (2 ×), 55.79 (2 ×), 50.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{24}NO_6$: 410.1604; found: 410.1598.

4,4′-((3-(Trifluoromethyl)phenyl)methylene)bis(1,2-dimethoxybenzene) (4l)

Prepared according to the general procedure 1 from **1l** (870 mg, 5.0 mmol) and **2a** (1380 mg, 10.0 mmol); yield: 87% (1880 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 7.6 Hz, 1 H), 7.42–7.38 (m, 2 H), 7.29 (d, *J* = 8.0 Hz, 1 H), 6.80 (d, *J* = 8.0 Hz, 2 H), 6.64 (d, *J* = 2.0 Hz, 2 H), 6.57 (dd, *J* = 2.0, 8.4 Hz, 2 H), 5.49 (s, 1 H), 3.86 (s, 6 H), 3.77 (s, 6 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 148.9 (2 ×), 147.7 (2 ×), 145.3, 135.7, 132.6, 130.6 (q, *J* = 31.0 Hz), 128.6 (2 ×), 125.9 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 269.9 Hz), 123.2 (q, *J* = 3.8 Hz), 121.3 (2 ×), 112.6 (2 ×), 111.0 (2 ×), 55.81 (2 ×), 55.79 (2 ×), 55.6.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{24}F_3O_4$: 433.1627; found: 433.1634.

4-(Bis(3,4-dimethoxyphenyl)methyl)-2-methoxy-6-nitrophenol (4m)

Prepared according to the general procedure 1 from **1m** (985 mg, 5.0 mmol) and **2a** (1380 mg, 10.0 mmol); yield: 84% (1912 mg); white solid; mp 143–145 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.68 (s, 1 H), 7.35 (d, *J* = 1.6 Hz, 1 H), 6.92 (d, *J* = 2.0 Hz, 1 H), 6.78 (d, *J* = 8.4 Hz, 2 H), 6.62 (d, *J* = 2.0 Hz, 2 H), 6.55 (dd, *J* = 2.0, 8.0 Hz, 2 H), 5.36 (s, 1 H), 3.83 (s, 6 H), 3.79 (s, 3 H), 3.75 (s, 6 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 149.6, 148.8 (2 ×), 147.7 (2 ×), 144.9, 135.6, 135.0 (2 ×), 133.4, 121.1 (2 ×), 119.0, 115.7, 112.3 (2 ×), 110.9 (2 ×), 56.5, 55.70 (2 ×), 55.68 (2 ×), 55.0.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{26}NO_8$: 456.1659; found. 456.1668.

4,4′-((3,5-Dimethylphenyl)methylene)bis(1,2-dimethoxybenzene) (4n)

Prepared according to the general procedure 1 from **1n** (670 mg, 5.0 mmol) and **2a** (1380 mg, 10.0 mmol); yield: 88% (1726 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.86 (s, 1 H), 6.79 (d, *J* = 8.0 Hz, 2 H), 6.74 (s, 2 H), 6.70 (d, *J* = 2.0 Hz, 2 H), 6.61 (dd, *J* = 2.0, 8.4 Hz, 2 H), 5.38 (s, 1 H), 3.86 (s, 6 H), 3.78 (s, 6 H), 2.26 (s, 6 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 148.6 (2 ×), 147.3 (2 ×), 144.1 (2 ×), 137.5, 136.8, 127.8 (2 ×), 127.0 (2 ×), 121.3 (2 ×), 112.7 (2 ×), 110.7 (2 ×), 55.73, 55.70 (4 ×), 21.2 (2 ×).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{25}H_{29}O_4$: 393.2066; found: 393.2074.

4,4′-((3,4-Dichlorophenyl)methylene)bis(1,2-dimethoxybenzene) (4o)

Prepared according to the general procedure 1 from **1o** (870 mg, 5.0 mmol) and **2a** (1380 mg, 10.0 mmol); yield: 90% (1944 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 8.4 Hz, 1 H), 7.18 (d, *J* = 2.4 Hz, 1 H), 6.94 (dd, *J* = 2.4, 8.4 Hz, 1 H), 6.78 (d, *J* = 8.0 Hz, 2 H), 6.63 (d, *J* = 2.0 Hz, 2 H), 6.55 (dd, *J* = 2.0, 8.4 Hz, 2 H), 5.37 (s, 1 H), 3.85 (s, 6 H), 3.76 (s, 6 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 148.8 (2 ×), 147.7 (2 ×), 144.7, 135.3 (2 ×), 132.2, 131.0, 130.1, 130.0, 128.6, 121.2 (2 ×), 112.4 (2 ×), 110.9 (2 ×), 55.7 (4 ×), 54.9.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{23}Cl_2O_4$: 433.0973; found: 433.0968.

4,4′-((4-Hydroxyphenyl)methylene)bis(1,2-dimethoxybenzene) (4p)

Prepared according to the general procedure 1 from **1p** (610 mg, 5.0 mmol) and **2a** (1380 mg, 10.0 mmol); yield: 90% (1711 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.96 (d, *J* = 8.8 Hz, 2 H), 6.78 (d, *J* = 8.0 Hz, 2 H), 6.75 (d, *J* = 8.8 Hz, 2 H), 6.66 (d, *J* = 2.0 Hz, 2 H), 6.59 (dd, *J* = 2.0, 8.4 Hz, 2 H), 5.37 (s, 1 H), 5.20 (br s, 1 H), 3.85 (s, 6 H), 3.76 (s, 6 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 154.0, 148.7 (2 ×), 147.3 (2 ×), 137.1 (2 ×), 136.4, 130.3 (2 ×), 121.3 (2 ×), 115.0 (2 ×), 112.7 (2 ×), 110.8 (2 ×), 55.81 (2 ×), 55.77 (2 ×), 55.0.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{25}O_5$: 381.1702; found: 381.1709.

4,4′-((4-Chlorophenyl)methylene)bis(1,2-dimethoxybenzene) (4q)

Prepared according to the general procedure 1 from **1q** (700 mg, 5.0 mmol) and **2a** (1380 mg, 10.0 mmol); yield: 91% (1811 mg); white solid; mp 159–160 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 (d, *J* = 8.4 Hz, 2 H), 7.04 (d, *J* = 8.0 Hz, 2 H), 6.78 (d, *J* = 8.0 Hz, 2 H), 6.64 (d, *J* = 2.4 Hz, 2 H), 6.57 (dd, *J* = 2.0, 8.4 Hz, 2 H), 5.41 (s, 1 H), 3.85 (s, 6 H), 3.76 (s, 6 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 148.7 (2 ×), 147.5 (2 ×), 142.8, 136.0 (2 ×), 131.9, 130.5 (2 ×), 128.3 (2 ×), 121.2 (2 ×), 112.5 (2 ×), 110.8 (2 ×), 55.73 (2 ×), 55.71 (2 ×), 55.1.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{24}ClO_4$: 399.1363; found: 399.1369.

2-[Bis-(3,4-dimethoxyphenyl)methyl]-5-nitrothiophene (4r)

Prepared according to the general procedure 1 from **1r** (785 mg, 5.0 mmol) and **2a** (1380 mg, 10.0 mmol); yield: 83% (1723 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 4.0 Hz, 1 H), 6.82 (d, *J* = 8.8 Hz, 2 H), 6.73–6.70 (m, 5 H), 5.53 (s, 1 H), 3.87 (s, 6 H), 3.80 (s, 6 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 158.3, 150.4, 149.1, 148.4, 134.3 (2 ×), 128.5 (2 ×), 125.8 (2 ×), 120.7 (2 ×), 111.9 (2 ×), 111.1 (2 ×), 55.9 (2 ×), 55.8 (2 ×), 51.9.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{22}NO_6S$: 416.1168; found: 416.1175.

3-[Bis-(3,4-dimethoxyphenyl)methyl]pyridine (4s)

Prepared according to the general procedure 1 from **1s** (535 mg, 5.0 mmol) and **2a** (1380 mg, 10.0 mmol); yield: 84% (1534 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (d, *J* = 4.4 Hz, 1 H), 8.43 (s, 1 H), 7.50 (d, *J* = 8.0 Hz, 1 H), 7.30 (dd, *J* = 4.8, 8.0 Hz, 1 H), 6.80 (d, *J* = 8.4 Hz, 2 H), 6.63 (d, *J* = 2.0 Hz, 2 H), 6.56 (dd, *J* = 2.0, 8.0 Hz, 2 H), 5.46 (s, 1 H), 3.86 (s, 6 H), 3.77 (s, 6 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 149.4, 149.1 (2 ×), 147.9 (2 ×), 146.5 (2 ×), 140.5, 137.8, 135.0, 123.6, 121.3 (2 ×), 112.5 (2 ×), 111.1 (2 ×), 55.88 (2 ×), 55.86 (2 ×), 53.4.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{24}NO_4$: 366.1705; found: 366.1714.

4-[Bis-(3,4-dimethoxyphenyl)methyl]benzaldehyde (4u)

Prepared according to the general procedure 1 from **1u** (670 mg, 5.0 mmol) and **2a** (1380 mg, 10.0 mmol); yield: 90% (1765 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.96 (s, 1 H), 7.79 (d, *J* = 8.0 Hz, 2 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 6.79 (d, *J* = 8.4 Hz, 2 H), 6.64 (d, *J* = 2.0 Hz, 2 H), 6.57 (dd, *J* = 2.0, 8.0 Hz, 2 H), 5.50 (s, 1 H), 3.85 (s, 6 H), 3.75 (s, 6 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 191.8, 151.5, 148.8 (2 ×), 147.7 (2 ×), 135.4 (2 ×), 134.6, 129.9 (2 ×), 129.7 (2 ×), 121.3 (2 ×), 112.5 (2 ×), 110.9 (2 ×), 55.9, 55.8 (2 ×), 55.7 (2 ×).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{25}O_5$: 393.1702; found: 393.1711.

1-(3-(Bis(3,4-dimethoxyphenyl)methyl)phenyl)ethan-1-one (4v)

Prepared according to the general procedure 1 from **1v** (740 mg, 5.0 mmol) and **2a** (1380 mg, 10.0 mmol); yield: 90% (1828 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (dt, *J* = 1.2, 7.6 Hz, 1 H), 7.76 (t, *J* = 1.6 Hz, 1 H), 7.38 (t, *J* = 8.0 Hz, 1 H), 7.31 (dt, *J* = 0.4, 8.0 Hz, 1 H), 6.79 (d, *J* = 8.0 Hz, 2 H), 6.65 (d, *J* = 2.0 Hz, 2 H), 6.57 (dd, *J* = 2.0, 8.0 Hz, 2 H), 5.49 (s, 1 H), 3.86 (s, 6 H), 3.76 (s, 6 H), 2.54 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 198.2, 148.8 (2 ×), 147.6 (2 ×), 145.0, 137.2, 136.0 (2 ×), 133.9, 129.0, 128.5, 126.4, 121.3 (2 ×), 112.6 (2 ×), 110.9 (2 ×), 55.82 (4 ×), 55.76, 26.6.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{25}H_{27}O_5$: 407.1859; found: 407.1853.

4-[Bis-(3,4-dimethoxyphenyl)methyl]benzonitrile (4w)

Prepared according to the general procedure 1 from **1w** (655 mg, 5.0 mmol) and **2a** (1380 mg, 10.0 mmol); yield: 93% (1810 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.4 Hz, 2 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 6.79 (d, *J* = 8.0 Hz, 2 H), 6.61 (d, *J* = 2.0 Hz, 2 H), 6.54 (dd, *J* = 2.0, 8.4 Hz, 2 H), 5.47 (s, 1 H), 3.86 (s, 6 H), 3.76 (s, 6 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 150.0, 149.0 (2 ×), 147.9 (2 ×), 135.1 (2 ×), 132.1 (2 ×), 130.0 (2 ×), 121.3 (2 ×), 118.9, 112.6 (2 ×), 111.0 (2 ×), 110.2, 55.88, 55.85 (2 ×), 55.8 (2 ×).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{24}NO_4$: 390.1705; found: 390.1711.

4,4′-((3,4,5-Trimethoxyphenyl)methylene)bis(1,2-dimethoxybenzene) (4x)

Prepared according to the general procedure 1 from **1x** (980 mg, 5.0 mmol) and **2a** (1380 mg, 10.0 mmol); yield: 89% (2021 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.77 (d, *J* = 8.4 Hz, 2 H), 6.66 (d, *J* = 2.0 Hz, 2 H), 6.59 (dd, *J* = 2.0, 8.0 Hz, 2 H), 6.31 (s, 2 H), 5.35 (s, 1 H), 3.84 (s, 6 H), 3.82 (s, 3 H), 3.76 (s, 6 H), 3.71 (s, 6 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 152.8 (2 ×), 148.6 (2 ×), 147.4 (2 ×), 139.8 (2 ×), 136.4 (2 ×), 121.2 (2 ×), 112.5 (2 ×), 110.7 (2 ×), 106.4 (2 ×), 60.7, 55.9 (3 ×), 55.70 (2 ×), 55.68 (2 ×).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{31}O_7$: 455.2070; found: 455.2076.

5,5′-((3,4,5-Trimethoxyphenyl)methylene)bis(benzo[*d*][1,3]dioxole) (4y)

Prepared according to the general procedure 1 from **1x** (980 mg, 5.0 mmol) and **2b** (1220 mg, 10.0 mmol); yield: 84% (1773 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.73 (d, *J* = 8.8 Hz, 2 H), 6.60 (d, *J* = 2.0 Hz, 2 H), 6.57 (dd, *J* = 2.0, 8.0 Hz, 2 H), 6.31 (s, 2 H), 5.94 (d, *J* = 2.0 Hz, 2 H), 5.90 (d, *J* = 1.2 Hz, 2 H), 5.30 (s, 1 H), 3.83 (s, 3 H), 3.75 (s, 6 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 153.0 (2 ×), 147.6 (2 ×), 146.0 (2 ×), 139.6, 137.8 (2 ×), 136.5, 122.3 (2 ×), 109.7 (2 ×), 108.0 (2 ×), 106.5 (2 ×), 100.9 (2 ×), 60.8, 56.2, 56.1 (2 ×).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{23}O_7$: 423.1444; found: 423.1452.

4,4′-((3,4-Dichlorophenyl)methylene)bis(1,2-di-*n*-butoxybenzene) (4z)

Prepared according to the general procedure 1 from **1o** (870 mg, 5.0 mmol) and **2c** (2222 mg, 10.0 mmol); yield: 85% (2551 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 8.4 Hz, 1 H), 7.18 (d, *J* = 2.0 Hz, 1 H), 6.93 (dd, *J* = 2.0, 8.4 Hz, 1 H), 6.78 (d, *J* = 8.0 Hz, 2 H), 6.61 (d, *J* = 2.0 Hz, 2 H), 6.52 (dd, *J* = 2.0, 8.4 Hz, 2 H), 5.31 (s, 1 H), 3.97 (t, *J* = 6.8 Hz, 4 H), 3.88 (t, *J* = 6.8 Hz, 4 H), 1.82–1.69 (m, 8 H), 1.54–1.40 (m, 8 H), 0.97 (t, *J* = 7.2 Hz, 6 H), 0.94 (t, *J* = 7.6 Hz, 6 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 149.0 (2 ×), 148.0 (2 ×), 145.0, 135.6 (2 ×), 132.2, 131.2, 130.1, 130.0, 128.7, 121.6 (2 ×), 115.3 (2 ×), 113.6 (2 ×), 69.0 (2 ×), 68.9 (2 ×), 55.0, 31.4 (2 ×), 31.3 (2 ×), 19.23 (2 ×), 19.18 (2 ×), 13.9 (4 ×).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{35}H_{47}Cl_2O_4$: 601.2851; found: 601.2858.

2-(Bis(3,4-di-*n*-butoxyphenyl)methyl)naphthalene (4aa)

Prepared according to the general procedure 1 from **1h** (780 mg, 5.0 mmol) and **2c** (2222 mg, 10.0 mmol); yield: 85% (2475 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.82 (m, 1 H), 7.78 (d, *J* = 8.4 Hz, 1 H), 7.76–7.73 (m, 1 H), 7.51 (s, 1 H), 7.48–7.44 (m, 2 H), 7.35 (dd, *J* = 1.6, 8.4 Hz, 1 H), 6.84 (d, *J* = 8.0 Hz, 2 H), 6.77 (d, *J* = 2.0 Hz, 2 H), 6.66 (dd, *J* = 2.0, 8.0 Hz, 2 H), 5.60 (s, 1 H), 4.02 (t, *J* = 6.8 Hz, 4 H), 3.92 (t, *J* = 6.8 Hz, 4 H), 1.87–1.72 (m, 8 H), 1.59–1.43 (m, 8 H), 1.02 (t, *J* = 7.2 Hz, 6 H), 0.96 (t, *J* = 7.6 Hz, 6 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 148.9 (2 ×), 147.6 (2 ×), 142.2, 136.6 (2 ×), 133.3, 132.1, 128.1, 127.8, 127.6, 127.5, 127.4, 125.8, 125.4, 121.8 (2 ×), 115.6 (2 ×), 113.5 (2 ×), 68.88 (2 ×), 68.87 (2 ×), 55.9, 31.4 (2 ×), 31.3 (2 ×), 19.2 (2 ×), 19.1 (2 ×), 13.83 (2 ×), 13.81 (2 ×).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{39}H_{51}O_4$: 583.3787; found: 583.3796.

4,4′-((3,4,5-Trimethoxyphenyl)methylene)bis(1,2-di-*n*-butoxybenzene) (4ab)

Prepared according to the general procedure 1 from **1x** (980 mg, 5.0 mmol) and **2c** (2222 mg, 10.0 mmol); yield: 84% (2614 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.79 (d, *J* = 8.0 Hz, 2 H), 6.66 (d, *J* = 2.0 Hz, 2 H), 6.58 (dd, *J* = 2.0, 8.4 Hz, 2 H), 6.32 (s, 2 H), 5.31 (s, 1 H), 3.97 (t, *J* = 6.8 Hz, 4 H), 3.89 (t, *J* = 6.8 Hz, 4 H), 3.83 (s, 3 H), 3.72 (s, 6 H), 1.82–1.69 (m, 8 H), 1.54–1.40 (m, 8 H), 0.97 (t, *J* = 7.2 Hz, 6 H), 0.93 (t, *J* = 7.6 Hz, 6 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 152.9 (2 ×), 148.8 (2 ×), 147.6 (2 ×), 140.2, 136.8, 136.2 (2 ×), 121.6 (2 ×), 115.5 (2 ×), 113.5 (2 ×), 106.5 (2 ×), 69.0 (2 ×), 68.9 (2 ×), 60.8, 56.0 (2 ×), 55.9, 31.4 (2 ×), 31.3 (2 ×), 19.21 (2 ×), 19.15 (2 ×), 13.8 (4 ×).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{38}H_{55}O_7$: 623.3948; found: 623.3955.

4,4′-((3,4,5-Trimethoxyphenyl)methylene)bis(1,2-bis(*n*-octyloxy)benzene) (4ac)

Prepared according to the general procedure 1 from **1x** (980 mg, 5.0 mmol) and **2d** (3343 mg, 10.0 mmol); yield: 89% (3768 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.88 (s, 2 H), 6.79 (d, *J* = 8.0 Hz, 2 H), 6.67 (d, *J* = 2.0 Hz, 2 H), 6.58 (dd, *J* = 2.0, 8.4 Hz, 2 H), 6.32 (s, 2 H), 5.32 (s, 1 H), 4.01–3.89 (m, 4 H), 3.88–3.84 (m, 4 H), 3.84 (s, 3 H), 3.72 (s, 6 H), 1.83–1.73 (m, 12 H), 1.47–1.29 (m, 34 H), 0.90–0.87 (m, 12 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 152.9 (2 ×), 148.8 (2 ×), 147.6 (2 ×), 140.2, 136.8, 136.2 (2 ×), 130.0 (2 ×), 115.4 (2 ×), 113.4 (2 ×), 106.5 (2 ×), 69.3 (2 ×), 69.2 (2 ×), 60.8, 56.0 (2 ×), 55.9, 31.8 (4 ×), 29.4 (4 ×), 29.3 (4 ×), 29.2 (4 ×), 26.03 (2 ×), 26.00 (2 ×), 22.6 (4 ×), 14.0 (4 ×).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{54}H_{87}O_7$: 847.6452; found: 847.6448.

4,4′-((3,4,5-Trimethoxyphenyl)methylene)bis(1,2-bis(*n*-dodecyloxy)benzene) (4ad)

Prepared according to the general procedure 1 from **1x** (980 mg, 5.0 mmol) and **2e** (4464 mg, 10.0 mmol); yield: 80% (4284 mg); white solid; mp 59–61 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.78 (d, *J* = 8.4 Hz, 2 H), 6.66 (d, *J* = 2.0 Hz, 2 H), 6.57 (dd, *J* = 2.0, 8.4 Hz, 2 H), 6.31 (s, 2 H), 5.31 (s, 1 H), 3.96 (t, *J* = 6.8 Hz, 4 H), 3.87 (t, *J* = 6.8 Hz, 4 H), 3.83 (s, 3 H), 3.72 (s, 6 H), 1.83–1.70 (m, 12 H), 1.49–1.26 (m, 68 H), 0.90–0.86 (m, 12 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 152.9 (2 ×), 148.5 (2 ×), 147.2 (2 ×), 140.2, 136.8 (2 ×), 136.2, 121.6 (2 ×), 115.5 (2 ×), 113.5 (2 ×), 106.5 (2 ×), 69.30 (2 ×), 69.26 (2 ×), 60.8, 55.01 (2 ×), 55.96, 31.9 (2 ×), 29.71 (2 ×), 29.69 (2 ×), 29.6 (8 ×), 29.5 (2 ×), 29.39 (4 ×), 29.36 (4 ×), 29.3 (4 ×), 26.1 (4 ×), 26.0 (4 ×), 22.7 (4 ×), 14.1 (4 ×).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{70}H_{119}O_7$: 1071.8956; found: 1071.8966.

4,4′-((3,4,5-Trimethoxyphenyl)methylene)bis(1,2,3-trimethoxybenzene) (4ae)

Prepared according to the general procedure 1 from **1x** (980 mg, 5.0 mmol) and **2f** (1681 mg, 10.0 mmol); yield: 80% (2057 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.56 (d, *J* = 8.8 Hz, 2 H), 6.50 (d, *J* = 8.8 Hz, 2 H), 6.30 (s, 2 H), 5.98 (s, 1 H), 3.86 (s, 6 H), 3.82 (s, 6 H), 3.81 (s, 3 H), 3.72 (s, 6 H), 3.58 (s, 6 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 152.9 (2 ×), 152.2 (2 ×), 151.5 (2 ×), 142.4 (2 ×), 139.5, 136.2, 130.6 (2 ×), 124.0 (2 ×), 106.6 (2 ×), 106.4 (2 ×), 60.8, 60.7 (2 ×), 60.4 (2 ×), 56.0 (2 ×), 55.8 (2 ×), 43.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{35}O_9$: 515.2281; found: 515.2290.

4,4′-((3,4,5-Trimethoxyphenyl)methylene)bis(1,2,3-tri-*n*-butoxybenzene) (4af)

Prepared according to the general procedure 1 from **1x** (980 mg, 5.0 mmol) and **2g** (2942 mg, 10.0 mmol); yield: 82% (3143 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.50 (d, *J* = 8.8 Hz, 2 H), 6.43 (d, *J* = 8.4 Hz, 2 H), 6.28 (s, 2 H), 6.03 (s, 1 H), 3.97–3.91 (m, 8 H), 3.80 (s, 3 H), 3.69 (s, 6 H), 3.62 (t, *J* = 6.8 Hz, 4 H), 1.82–1.69 (m, 8 H), 1.55–1.40 (m, 12 H), 1.30–1.24 (m, 4 H), 0.98–0.93 (m, 12 H), 0.82 (t, *J* = 7.2 Hz, 6 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 152.7 (2 ×), 152.0 (2 ×), 151.2 (2 ×), 141.7 (2 ×), 140.7 (2 ×), 136.0, 130.4, 124.0 (2 ×), 107.0 (2 ×), 106.7 (2 ×), 73.0 (2 ×), 72.8 (2 ×), 68.2 (2 ×), 60.8, 55.9 (2 ×), 43.7, 32.4 (2 ×), 32.3 (2 ×), 31.4 (2 ×), 19.3 (2 ×), 19.2 (2 ×), 19.1 (2 ×), 13.92 (2 ×), 13.89 (2 ×), 13.8 (2 ×).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{46}H_{71}O_9$: 767.5098; found: 767.5089.

4,4′-((3,4,5-Trimethoxyphenyl)methylene)bis(1,2,3-tris(*n*-octyloxy)benzene) (4ag)

Prepared according to the general procedure 1 from **1x** (980 mg, 5.0 mmol) and **2h** (4624 mg, 10.0 mmol); yield: 81% (4467 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.49 (d, *J* = 8.4 Hz, 2 H), 6.42 (d, *J* = 8.4 Hz, 2 H), 6.28 (s, 2 H), 6.03 (s, 1 H), 3.96–3.89 (m, 8 H), 3.81 (s, 3 H), 3.69 (s, 6 H), 3.63 (t, *J* = 6.8 Hz, 4 H), 1.83–1.71 (m, 12 H), 1.50–1.40 (m, 12 H), 1.33–1.22 (m, 48 H), 0.90–0.83 (m, 18 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 152.7 (2 ×), 152.0 (2 ×), 151.3 (2 ×), 141.7 (2 ×), 140.7 (2 ×), 136.0, 130.5, 124.0 (2 ×), 107.0 (2 ×), 106.7 (2 ×), 73.3 (2 ×), 73.2 (2 ×), 68.5 (2 ×), 60.8, 55.9 (2 ×), 43.7, 31.91 (2 ×), 31.88 (2 ×), 31.8 (2 ×), 30.42 (2 ×), 30.36 (2 ×), 29.7 (2 ×), 29.62 (2 ×), 29.57 (2 ×), 29.44 (2 ×), 29.41 (2 ×), 29.37 (4 ×), 29.3 (2 ×), 26.20 (2 ×), 26.17 (2 ×), 26.1 (2 ×), 22.68 (2 ×), 22.66 (2 ×), 14.8 (6 ×).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{70}H_{119}O_9$: 1103.8854; found: 1103.8847.

1,2,3,5,6,7-Hexamethoxy-9-(2,4,6-trimethoxyphenyl)anthracene (4ah-1)

Yield: 30% (786 mg); white solid; mp 169–171 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (s, 1 H), 7.11 (s, 1 H), 6.56 (s, 1 H), 6.32 (s, 2 H), 4.11 (s, 3 H), 4.01 (s, 3 H), 3.99 (s, 3 H), 3.94 (s, 3 H), 3.90 (s, 3 H), 3.70 (s, 3 H), 3.58 (s, 6 H), 3.38 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 160.3, 158.5 (2 ×), 151.9, 151.5, 149.2, 146.3, 142.2, 140.2, 128.9, 128.1, 125.0, 123.9, 123.4, 118.9, 112.4, 102.6, 99.8 (2 ×), 90.6, 61.3, 61.1, 61.0, 60.5, 55.9 (2 ×), 55.6, 55.42, 55.38.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{29}H_{33}O_9$: 525.2125; found: 525.2130.

Single-Crystal X-ray Data

Crystals of compound **4ah-1** were grown by slow diffusion of EtOAc into a solution of compound **4ah-1** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the triclinic crystal system, space group P-1, *a* = 10.9208(3) Å, *b* = 12.8617(4) Å, *c* = 19.3099(4) Å, *V* = 2675.59(12) Å^3, *Z* = 4, d_{calcd} = 1.302 g/cm^3, *F*(000) = 1112.0, 2θ range 3.18–52°, R indices (all data) R1 = 0.0912, wR2 = 0.1457.

Triarylmethanes 4ai–at; General Procedure 2

$NiFe_2O_4$@SiO_2-PPA (**3a**; 250 mg, ~10 mol%) was added to a stirred solution of aryl aldehyde **1c**, **1y**, or **1h** (5.0 mmol) and oxygenated arene **2a** or **2f** (5.0 mmol) in DMF (0.5 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 5 h. Then, a solution of oxygenated arene **2j**, **2a**, **2b**, **2c**, or **2f** (5.0 mmol) in DMF (0.5 mL) at 25 °C was added to the mixture. The reaction mixture was stirred at 25 °C for 5 h. Upon completion, **3a** could be placed on the side wall of the reaction vessel with the aid of an external magnet, then **3a** was isolated, washed with CH_2Cl_2 (3 × 5 mL) and dried to reuse in the next run. Then, the combined DMF and CH_2Cl_2 solutions were concentrated under reduced pressure to afford the crude product. Purification on silica gel (hexanes/EtOAc 50:1 to 10:1) afforded compounds **4ai–at**.

1,2,3-Trimethoxy-4-((4-methoxyphenyl)(*p*-tolyl)methyl)benzene (4ai)

Prepared according to the general procedure 2 from **1c** (600 mg, 5.0 mmol), **2f** (840 mg, 5.0 mmol), and **2j** (540 mg, 5.0 mmol); yield: 80% (1513 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09 (d, *J* = 8.0 Hz, 2 H), 7.04 (d, *J* = 8.8 Hz, 2 H), 7.01 (d, *J* = 8.0 Hz, 2 H), 6.83 (d, *J* = 8.4 Hz, 2 H), 6.58 (d, *J* = 8.8 Hz, 1 H), 6.55 (d, *J* = 8.4 Hz, 1 H), 5.78 (s, 1 H), 3.88 (s, 3 H), 3.84 (s, 3 H), 3.79 (s, 3 H), 3.54 (s, 3 H), 2.33 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 157.8, 152.1, 151.6, 142.3, 141.3, 136.4, 135.4, 131.1, 130.2 (2 ×), 129.2 (2 ×), 128.8 (2 ×), 124.2, 113.5 (2 ×), 106.6, 60.60, 60.57, 55.8, 55.1, 48.6, 21.0.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{27}O_4$: 379.1909; found: 379.1915.

1-((3,4-Dimethoxyphenyl)(*p*-tolyl)methyl)-2,3,4-trimethoxybenzene (4aj)

Prepared according to the general procedure 2 from **1c** (600 mg, 5.0 mmol), **2f** (840 mg, 5.0 mmol), and **2a** (690 mg, 5.0 mmol); yield: 78% (1592 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08 (d, *J* = 8.0 Hz, 2 H), 6.99 (d, *J* = 8.0 Hz, 2 H), 6.77 (d, *J* = 8.4 Hz, 1 H), 6.69 (d, *J* = 1.6 Hz, 1 H), 6.59 (dd, *J* = 2.4, 8.4 Hz, 1 H), 6.57 (d, *J* = 8.8 Hz, 1 H), 6.53 (d, *J* = 8.8 Hz, 1 H), 5.75 (s, 1 H), 3.87 (s, 3 H), 3.85 (s, 3 H), 3.83 (s, 3 H), 3.77 (s, 3 H), 3.52 (s, 3 H), 2.32 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 152.2, 151.6, 148.6, 147.2, 142.2, 141.2, 136.8, 135.5, 130.9, 129.1 (2 ×), 128.8 (2 ×), 124.1, 121.3, 112.7, 110.7, 106.5, 60.6, 55.8 (2 ×), 55.7 (2 ×), 49.0, 20.9.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{25}H_{29}O_5$: 409.2015; found: 409.2022.

5-(*p*-Tolyl(2,3,4-trimethoxyphenyl)methyl)benzo[*d*][1,3]dioxole (4ak)

Prepared according to the general procedure 2 from **1c** (600 mg, 5.0 mmol), **2f** (840 mg, 5.0 mmol), and **2b** (610 mg, 5.0 mmol); yield: 76% (1490 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08 (d, *J* = 7.6 Hz, 2 H), 6.99 (d, *J* = 8.0 Hz, 2 H), 6.71 (d, *J* = 8.4 Hz, 1 H), 6.62–6.56 (m, 4 H), 5.91 (s, 2 H), 5.72 (s, 1 H), 3.87 (s, 3 H), 3.83 (s, 3 H), 3.56 (s, 3 H), 2.32 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 152.3, 151.6, 147.5, 145.7, 142.3, 141.1, 138.3, 135.6, 130.8, 129.1 (2 ×), 128.9 (2 ×), 124.2, 122.3, 109.9, 107.8, 106.6, 100.8, 60.8, 60.6, 55.9, 49.1, 21.0.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{25}O_5$: 393.1702; found: 393.1710.

1-((3,4-Di-*n*-butoxyphenyl)(*p*-tolyl)methyl)-2,3,4-trimethoxybenzene (4al)

Prepared according to general synthetic procedure 2 from **1c** (600 mg, 5.0 mmol), **2f** (840 mg, 5.0 mmol), and **2c** (1111 mg, 5.0 mmol); yield: 72% (1772 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08 (d, *J* = 7.6 Hz, 2 H), 7.00 (d, *J* = 8.0 Hz, 2 H), 6.78 (d, *J* = 8.4 Hz, 1 H), 6.69 (d, *J* = 2.0 Hz, 1 H), 6.58–6.53 (m, 3 H), 5.73 (s, 1 H), 3.98 (t, *J* = 6.8 Hz, 2 H), 3.91 (t, *J* = 6.8 Hz, 2 H), 3.88 (s, 3 H), 3.83 (s, 3 H), 3.52 (s, 3 H), 2.32 (s, 3 H), 1.83–1.70 (m, 4 H), 1.53–1.43 (m, 4 H), 0.98 (t, *J* = 7.6 Hz, 3 H), 0.95 (t, *J* = 7.2 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 152.1, 151.6, 148.8, 147.4, 142.2, 141.3, 136.9, 135.4, 131.1, 129.1 (2 ×), 128.8 (2 ×), 124.2, 121.6, 115.6, 113.5, 106.5, 68.9 (2 ×), 60.57, 60.55, 55.8, 49.0, 31.4, 31.3, 20.9, 19.2, 19.1, 13.8 (2 ×).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{31}H_{41}O_5$: 493.2954; found: 493.2960.

4-((3,4-Difluorophenyl)(4-methoxyphenyl)methyl)-1,2-dimethoxybenzene (4am)

Prepared according to the general procedure 2 from **1y** (710 mg, 5.0 mmol), **2a** (690 mg, 5.0 mmol), and **2j** (540 mg, 5.0 mmol); yield: 76% (1407 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09–7.03 (m, 1 H), 7.01 (d, *J* = 8.8 Hz, 2 H), 6.93–6.87 (m, 2 H), 6.85 (d, *J* = 8.4 Hz, 2 H), 6.80 (d, *J* = 8.8 Hz, 1 H), 6.63 (d, *J* = 2.0 Hz, 1 H), 6.57 (dd, *J* = 2.0, 8.4 Hz, 1 H), 5.40 (s, 1 H), 3.86 (s, 3 H), 3.79 (s, 3 H), 3.78 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 158.2, 150.7 (dd, *J* = 12.1, 127.3 Hz), 148.9, 148.2 (dd, *J* = 10.7, 125.1 Hz), 147.7, 141.6 (t, *J* = 4.6 Hz), 135.9, 135.3, 130.1 (2 ×), 125.0 (dd, *J* = 3.8, 6.1 Hz), 121.2, 118.0 (d, *J* = 17.5 Hz), 116.8 (d, *J* = 16.7 Hz), 113.8 (2 ×), 112.5, 110.9, 55.80, 55.76, 55.2, 54.6.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{21}F_2O_3$: 371.1459; found: 371.1468.

5-((3,4-Difluorophenyl)(3,4-dimethoxyphenyl)methyl)benzo[*d*][1,3]dioxole (4an)

Prepared according to the general procedure 2 from **1y** (710 mg, 5.0 mmol), **2a** (690 mg, 5.0 mmol), and **2b** (610 mg, 5.0 mmol); yield: 73% (1402 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.06 (dt, *J* = 8.4, 10.4 Hz, 1 H), 6.90 (dt, *J* = 2.4, 7.6 Hz, 1 H), 6.85–6.82 (m, 1 H), 6.80 (d, *J* = 8.4 Hz, 1 H), 6.74 (d, *J* = 8.0 Hz, 1 H), 6.63 (d, *J* = 2.0 Hz, 1 H), 6.58–6.53 (m, 3 H), 5.93 (s, 2 H), 5.36 (s, 1 H), 3.86 (s, 3 H), 3.78 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 150.7 (dd, *J* = 12.9, 122.8 Hz), 148.9, 148.2 (dd, *J* = 12.9, 122.0 Hz), 147.8, 146.2, 141.3 (t, *J* = 3.8 Hz), 137.1, 135.6, 125.0 (t, *J* = 3.0 Hz), 124.9, 122.2, 121.2, 118.0 (d, *J* = 17.5 Hz), 116.8 (d, *J* = 17.4 Hz), 112.5, 111.0, 109.6, 108.1, 101.0, 55.8 (2 ×), 55.1.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{19}F_2O_4$: 385.1252; found: 385.1247.

1,2-Di-*n*-butoxy-4-((3,4-difluorophenyl)(3,4-dimethoxyphenyl)methyl)benzene (4ao)

Prepared according to the general procedure 2 from **1y** (710 mg, 5.0 mmol), **2a** (690 mg, 5.0 mmol), and **2c** (1111 mg, 5.0 mmol); yield: 70% (1695 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09–7.02 (m, 1 H), 6.93–6.88 (m, 1 H), 6.85–6.78 (m, 3 H), 6.64 (br s, 2 H), 6.59–6.54 (m, 2 H), 5.37 (s, 1 H), 3.98 (t, *J* = 6.8 Hz, 2 H), 3.90 (t, *J* = 6.8 Hz, 2 H), 3.86 (s, 3 H), 3.77 (s, 3 H), 1.83–1.70 (m, 4 H), 1.53–1.43 (m, 4 H), 0.98 (t, *J* = 7.6 Hz, 3 H), 0.95 (t, *J* = 7.2 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 150.6 (dd, *J* = 12.2, 126.6 Hz), 148.9, 148.8, 148.1 (dd, *J* = 12.2, 125.9 Hz), 147.9, 147.6, 141.5 (t, *J* = 4.6 Hz), 135.8, 135.7, 125.0 (dd, *J* = 3.8, 6.1 Hz), 121.4, 121.2, 118.0 (d, *J* = 17.4 Hz), 116.7 (d, *J* = 16.7 Hz), 115.3, 113.5, 112.5, 110.9, 68.9, 68.8, 55.74, 55.71, 54.9, 31.3, 31.2, 19.2, 19.1, 13.8 (2 ×).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{29}H_{35}F_2O_4$: 485.2504; found: 485.2511.

1-((3,4-Difluorophenyl)(3,4-dimethoxyphenyl)methyl)-2,3,4-trimethoxybenzene (4ap)

Prepared according to the general procedure 2 from **1y** (710 mg, 5.0 mmol), **2a** (690 mg, 5.0 mmol), and **2f** (840 mg, 5.0 mmol); yield: 70% (1506 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.05 (dt, *J* = 8.4, 10.4 Hz, 1 H), 6.89 (dt, *J* = 2.4, 7.6 Hz, 1 H), 6.83–6.80 (m, 1 H), 6.78 (d, *J* = 8.4 Hz, 1 H), 6.63 (d, *J* = 2.0 Hz, 1 H), 6.58 (d, *J* = 8.4 Hz, 1 H), 6.54 (dd, *J* = 2.0, 8.8 Hz, 1 H), 6.48 (d, *J* = 8.8 Hz, 1 H), 5.72 (s, 1 H), 3.862 (s, 3 H), 3.856 (s, 3 H), 3.84 (s, 3 H), 3.78 (s, 3 H), 3.54 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 152.6, 151.5, 150.7 (dd, *J* = 12.2, 131.9 Hz), 148.9, 148.2 (dd, *J* = 12.8, 128.8 Hz), 147.6, 142.3, 141.5 (t, *J* = 3.8 Hz), 135.7, 129.8, 125.01 (t, *J* = 3.8 Hz), 123.9, 121.2, 118.0 (d, *J* = 16.7 Hz), 116.7 (d, *J* = 17.4 Hz), 112.6, 110.9, 106.7, 60.64, 60.63, 55.9, 55.8 (2 ×), 48.7.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{25}F_2O_5$: 431.1670; found: 431.1675.

2-((3,4-Dimethoxyphenyl)(4-methoxyphenyl)methyl)naphthalene (4aq)

Prepared according to the general procedure 2 from **1h** (780 mg, 5.0 mmol), **2a** (690 mg, 5.0 mmol), and **2j** (540 mg, 5.0 mmol); yield: 76% (1460 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.81 (m, 1 H), 7.77 (d, *J* = 8.8 Hz, 1 H), 7.74–7.72 (m, 1 H), 7.48 (s, 1 H), 7.47–7.43 (m, 2 H), 7.32 (dd, *J* = 2.0, 8.8 Hz, 1 H), 7.09 (d, *J* = 8.4 Hz, 2 H), 6.86 (d, *J* = 8.8 Hz, 2 H), 6.81 (d, *J* = 8.4 Hz, 1 H), 6.74 (d, *J* = 2.0 Hz, 1 H), 6.65 (dd, *J* = 2.0, 8.4 Hz, 1 H), 5.63 (s, 1 H), 3.88 (s, 3 H), 3.81 (s, 3 H), 3.77 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 158.0, 148.8, 147.5, 142.1, 136.6, 136.0, 133.4, 132.1, 130.4 (2 ×), 128.0, 127.8, 127.7, 127.5 (2 ×), 125.9, 125.5, 121.5, 113.7 (2 ×), 112.8, 110.9, 55.81, 55.77, 55.6, 55.2.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{25}O_3$: 385.1804; found: 385.1812.

2-((3,4-Dimethoxyphenyl)(2,3,4-trimethoxyphenyl)methyl)naphthalene (4ar)

Prepared according to the general procedure 2 from **1h** (780 mg, 5.0 mmol), **2a** (690 mg, 5.0 mmol), and **2f** (840 mg, 5.0 mmol); yield: 80% (1777 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82–7.79 (m, 1 H), 7.76 (d, *J* = 8.4 Hz, 1 H), 7.73–7.70 (m, 1 H), 7.44–7.42 (m, 3 H), 7.32 (dd, *J* = 1.6, 8.4 Hz, 1 H), 6.80 (d, *J* = 8.0 Hz, 1 H), 6.74 (d, *J* = 2.0 Hz, 1 H), 6.63 (dd, *J* = 2.0, 8.4 Hz, 1 H), 6.58 (s, 2 H), 5.96 (s, 1 H), 3.89 (s, 3 H), 3.87 (s, 3 H), 3.85 (s, 3 H), 3.77 (s, 3 H), 3.53 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 152.4, 151.7, 148.7, 147.4, 142.3, 142.0, 136.4, 133.3, 132.1, 130.5, 128.2, 127.8, 127.7, 127.5, 127.4, 125.8, 125.4, 124.4, 121.5, 112.9, 110.8, 106.6, 60.7, 60.6, 55.84, 55.79 (2 ×), 49.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{29}O_5$: 445.2015; found: 445.2022.

5-((3,4-Dimethoxyphenyl)(naphthalen-2-yl)methyl)benzo[*d*][1,3]dioxole (4as)

Prepared according to the general procedure 2 from **1h** (780 mg, 5.0 mmol), **2a** (690 mg, 5.0 mmol), and **2b** (610 mg, 5.0 mmol); yield: 78% (1553 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.80 (m, 1 H), 7.77 (d, *J* = 8.4 Hz, 1 H), 7.75–7.72 (m, 1 H), 7.48 (br s, 1 H), 7.46–7.43 (m, 2 H), 7.31 (dd, *J* = 1.6, 8.4 Hz, 1 H), 6.81 (d, *J* = 8.4 Hz, 1 H), 6.76 (d, *J* = 8.0 Hz, 1 H), 6.73 (d, *J* = 2.0 Hz, 1 H), 6.67–6.61 (m, 3 H), 5.94 (s, 2 H), 5.58 (s, 1 H), 3.88 (s, 3 H), 3.77 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 148.8, 147.7, 147.6, 146.0, 141.8, 137.9, 136.3, 133.3, 132.1, 127.9, 127.84, 127.81, 127.5 (2 ×), 126.0, 125.6, 122.5, 121.5, 112.8, 110.9, 110.0, 108.0, 100.9, 56.1, 55.84, 55.81.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{23}O_4$: 399.1596; found: 399.1603.

1,4-Bis(bis(3,4-dimethoxyphenyl)methyl)benzene (4at)

Prepared according to the general procedure 2 from **1u** (670 mg, 5.0 mmol), **2a** (2761 mg, 20.0 mmol); yield: 58% (1886 mg); white solid; mp 82–84 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.04 (s, 4 H), 6.77 (d, *J* = 8.0 Hz, 4 H), 6.66 (d, *J* = 2.0 Hz, 4 H), 6.60 (dd, *J* = 2.0, 8.4 Hz, 4 H), 5.41 (s, 2 H), 3.85 (s, 12 H), 3.76 (s, 12 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 148.7 (4 ×), 147.4 (4 ×), 142.2 (2 ×), 136.7 (4 ×), 129.1 (4 ×), 121.3 (4 ×), 112.7 (4 ×), 110.8 (4 ×), 55.8 (4 ×), 55.7 (4 ×), 55.5 (2 ×).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{40}H_{43}O_8$: 651.2958; found: 651.2966.

11-(3,4-Dimethoxyphenyl)-8,9-dimethoxy-6-methyl-11*H*-dibenzo[*b*,*e*]azepine (5)

Pd/C (10%, 30 mg) was added to a solution of **4k** (409 mg, 1.0 mmol) in EtOAc (10 mL) at 25 °C. H_2 gas was installed to the reaction mixture at 25 °C. The mixture was stirred at 25 °C for 20 h. The mixture was filtered and the solvent was concentrated to afford the crude product. Without further purification, Et_3N (223 mg, 2.2 mmol) was added to a stirred solution of the resulting amine in CH_2Cl_2 (10 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 10 min. AcCl (314 mg, 4.0 mmol) was added to the mixture at 25°C and stirred at 0 °C for 10 h. The residue was diluted with H_2O (10 mL) and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford the crude product under reduced pressure. Without further purification, $BF_3{\cdot}OEt_2$ (280 mg, 2.0 mmol) was added to a stirred solution of the resulting amide in CH_2Cl_2 (10 mL) at 25 °C. The mixture was stirred at 25 °C for 10 h. The residue was diluted with sat. aq $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford the crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc 10:1 to 1:1) afforded compound **5**; yield: 40% (161 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (s, 1 H), 7.55–7.40 (m, 3 H), 7.26 (br s, 1 H), 7.08 (br s, 1 H), 6.59 (s, 1 H), 6.06 (br s, 2 H), 5.31 (s, 1 H), 4.04 (s, 3 H), 3.98 (s, 3 H), 3.75 (s, 3 H), 3.58 (s, 3 H), 3.02 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 176.1, 156.1, 148.7, 148.4, 148.3, 142.0, 137.2, 133.6, 131.1, 130.8, 129.5, 128.6, 125.7, 120.4, 119.0, 113.1, 112.2, 110.8, 110.2, 57.1, 56.8, 56.0, 55.7, 54.2, 24.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{25}H_{26}NO_4$: 404.1862; found: 404.1854.

Large-Scale Synthesis of Compound 4a

Recycled $NiFe_2O_4$@SiO_2-PPA (**3a**; 2.0 g, ~10 mol%) was added to a stirred solution of benzaldehyde (**1a**; 4.24 g, 40 mmol) and veratrole (**2a**; 11.04 g, 80 mmol) in DMF (8 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 5 h. Upon completion, **3a** could be placed on the side wall of the reaction vessel with the aid of an external magnet, then **3a** was isolated, washed with CH_2Cl_2 (3 × 5 mL) and dried to reuse in the next run. Then, the combined DMF and CH_2Cl_2 solutions were concentrated to afford the crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc 50:1 to 10:1) afforded compound **4a**; yield: 11.07 g (76%).

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

Scanned photocopies of NMR spectral data for all compounds and X-ray analysis data of **4e** and **4ah-1**. Supporting information for this article is available online at https://doi.org/10.1055/a-1863-3443.

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