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Niobium Pentachloride Mediated (Hetero)aromatic Aldehyde Friedel–Crafts Hydroxyalkylation with Arenes: An Efficient Strategy to Synthesize Triarylmethanes

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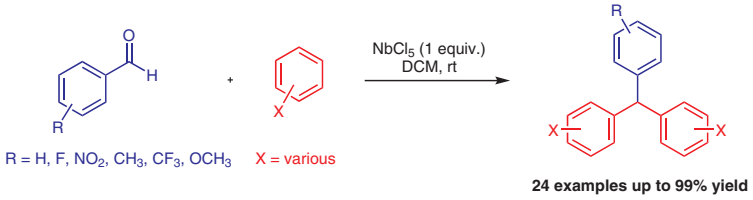
This paper is dedicated to Professor Mauricio Gomes Constantino on the occasion of his 75th birthday.



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Abstract Niobium pentachloride is an efficient and useful Lewis acid to conduct Friedel–Crafts hydroxyalkylation between arenes and (hetero)aromatic aldehydes, to generate triarylmethanes. This practical methodology offers several advantages, such as short reaction time, mild experimental conditions, and excellent yields.

Keywords triarylmethanes, niobium pentachloride, Friedel–Crafts hydroxyalkylation, carbocations, (hetero)aromatic aldehydes

Triarylmethanes are well-known substructures in several areas including dyes,[1] photochromic agents,[2] materials science,[3] and medicinal chemistry (acting as anticancer,[4] antitubercular,[5] and antifungal agents[6]), among other fields.[7] Due to the importance of triarylmethane compounds, considerable attention has been given to the development of different and efficient methods to synthesize these compounds.[7]

Friedel–Crafts hydroxyalkylation is a common strategy to prepare triarylmethanes.[7] Various Lewis or protic acids, such as $AuCl_3$/AgOTf,[8] $Yb(OTf)_3$,[9] $AlCl_3$,[10] $BF_3{\cdot}H_2O$,[11] $FeCl_3$,[12] $ZrOCl_2$,[13] TfOH,[14] $[Ir(COD)Cl]_2$–$SnCl_4$,[6,15] $ZnBr_2/SiO_2$,[16] and $FeCl_3/Ac_2O$,[17] have been employed.[7] However, these methods have disadvantages: they demand the use of superacids and corrosive acids as well as additives like co-oxidants or co-catalysts, experimental conditions are harsh, reaction times are long, and yields are low.

In this context, the use of niobium(V) chloride ($NbCl_5$) offers many advantages: it is easy to handle and can act as an excellent acid system for numerous reactions under mild conditions, including allylic halide synthesis,[18] intramolecular alkene hydrofunctionalization,[19] benzylic alcohol nucleophilic substitution reactions,[20] dithioacetal deprotection,[21] Mannich reactions,[22] multicomponent reactions,[23] and Diels–Alder reactions,[24] among others.[25]

As part of our interest in developing new synthetic methodologies, we report an efficient and simple procedure to obtain triarylmethanes through Friedel–Crafts-type hydroxyalkylation mediated by $NbCl_5$ under mild conditions.

First, we optimized the experimental conditions by using benzaldehyde as the common substrate. Different arenes were screened in the presence of various amounts of $NbCl_5$, using several kinds of solvents, at room temperature. One equivalent of $NbCl_5$ and dichloromethane as solvent provided the best results. Although the aldehyde was completely converted within a few hours, we routinely added saturated aqueous sodium carbonate solution after 24 hours to quench the reactions (Table 1).

Toluene (**2a**) was the first arene we used under these conditions (Table 1, entry 1), but the reaction with benzaldehyde (**1a**) did not produce any compound **3a**, and we completely recovered benzaldehyde. On the other hand, the reaction between benzaldehyde (**1a**) and xylenes **2b–d** resulted in the desired triarylmethanes **3b–d** (Table 1, entries 2–4) in good yields (59–66%). The fact that xylenes possess two electron-donating methyl groups and are thus more nucleophilic arenes than toluene explains the results. These reactions furnished only one regioisomeric product in which the methyne group attached to the aryl carbon is located at the *para* position relative to an electron-donating methyl group (Table 1, entries 2 and 3). In the case of *p*-xylene (**2d**), the *para* position is blocked, so the carbonyl group was added at the *ortho* position (Table 1, entry 4). Reaction of benzaldehyde (**1a**) with anisole (**2e**) produced compound **3e** in 58% yield (Table 1, entry 5). When we used 1,4-dimethoxybenzene (**2f**), the reaction afforded the desired compound **3f** in 75% yield (Table 1, entry 6). Furthermore, the reaction between a more electron-rich arene

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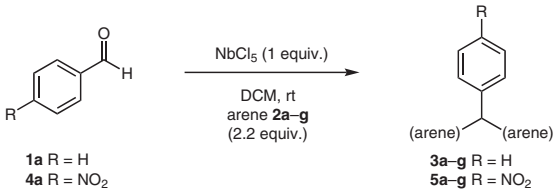
such as 1,2,4-trimethoxybenzene (**2g**) and benzaldehyde (**1a**) gave the triarylmethane **3g** in 90% yield (Table 1, entry 7).

To work around this issue, we performed the reaction under the same conditions, but used 4-nitrobenzaldehyde (**4a**) as electrophile. As expected, the reaction between **4a** and toluene (**2a**) produced the desired triarylmethane **5a** in moderate yield (67%) (Table 1, entry 8). In addition, the reactions with 4-nitrobenzaldehyde (**4a**) and xylenes **2b–d** furnished the corresponding triarylmethanes **5b–d** in higher yields (72–77%) (Table 1, entries 9–11) than the corresponding reactions employing benzaldehyde (**1a**) as substrate (Table 1, entries 2–4).

Table 1 Reactions of Benzaldehyde (**1a**) and 4-Nitrobenzaldehyde (**4a**) with Several Arenes[a]



1a R = H
4a R = NO_2

3a–g R = H
5a–g R = NO_2

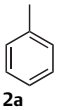
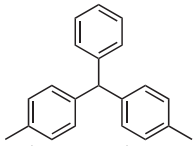
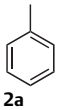
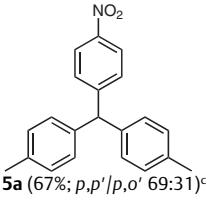
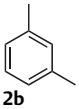
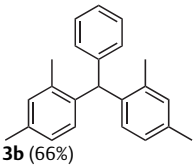
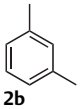
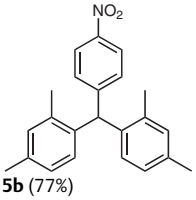
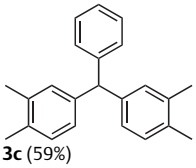
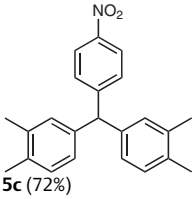
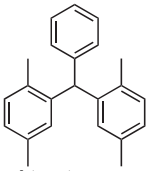
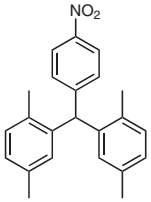
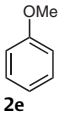
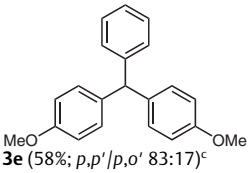
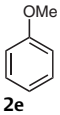
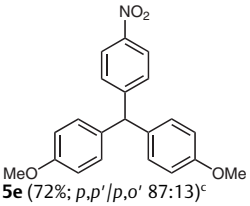
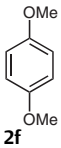
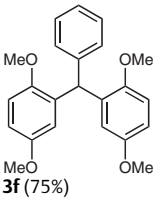
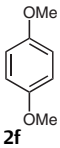
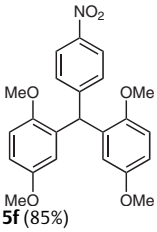
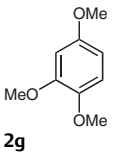
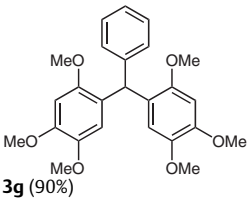
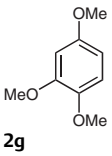
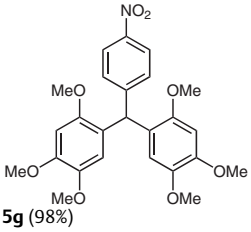
Reactions with benzaldehyde (**1a**)			Reactions with 4-nitrobenzaldehyde (**4a**)		
Entry	Arene	Triarylmethane **3** (Yield)[b]	Entry	Arene	Triarylmethane **5** (Yield)[b]
1	 **2a**	 **3a** (no reaction)	8	 **2a**	 **5a** (67%; *p*,*p*′/*p*,*o*′ 69:31)[c]
2	 **2b**	 **3b** (66%)	9	 **2b**	 **5b** (77%)
3	 **2c**	 **3c** (59%)	10	 **2c**	 **5c** (72%)
4	 **2d**	 **3d** (62%)	11	 **2d**	 **5d** (75%)

Table 1 (continued)

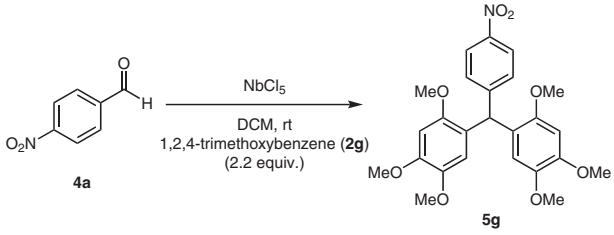
Reactions with benzaldehyde (**1a**)			Reactions with 4-nitrobenzaldehyde (**4a**)		
Entry	Arene	Triarylmethane **3** (Yield)[b]	Entry	Arene	Triarylmethane **5** (Yield)[b]
5	 **2e**	 **3e** (58%; *p*,*p*′/*p*,*o*′ 83:17)[c]	12	 **2e**	 **5e** (72%; *p*,*p*′/*p*,*o*′ 87:13)[c]
6	 **2f**	 **3f** (75%)	13	 **2f**	 **5f** (85%)
7	 **2g**	 **3g** (90%)	14	 **2g**	 **5g** (98%)

[a] Reaction conditions: arene (2.2 mmol), aldehyde (1.0 mmol), $NbCl_5$ (1.0 mmol), DCM (5 mL), room temperature, 24 h.
[b] Isolated yield.
[c] Ratio determined by NMR spectroscopy.

The reaction between 4-nitrobenzaldehyde (**4a**) and anisole (**2e**) led to the expected triarylmethane **5e** in very good yield (72%) (Table 1, entry 12). When we used 1,4-dimethoxybenzene (**2f**), the reaction proceeded very well and gave compound **5f** in excellent yield (85%) (Table 1, entry 13). Likewise, when the reaction was conducted with electron-rich arenes like 1,2,4-trimethoxybenzene (**2g**) and 4-nitrobenzaldehyde (**4a**), the triarylmethane **5g** emerged in very high yield (98%).

At this point, we decided to verify whether the high yields obtained in the previous reactions could be maintained even at lower $NbCl_5$ concentrations, mainly by using a highly electrophilic aldehyde, such as 4-nitrobenzaldehyde (**4a**), and a very nucleophilic arene, like 1,2,4-trimethoxybenzene (**2g**) (Table 2). The reactions between **4a** and **2g** with fewer equivalents of $NbCl_5$ produced low yields of triarylmethane **5g** (Table 2, entries 2 and 3). We also performed the control reaction without $NbCl_5$, but the desired product was not obtained (Table 2, entry 4), which demonstrates that the presence of 1 equivalent of $NbCl_5$ is important in this type of reaction.

Table 2 Reactions of **2g** with **4a** in the Presence of Different Amounts of $NbCl_5$[a]

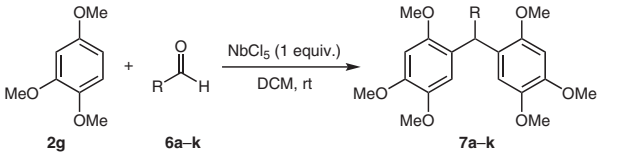


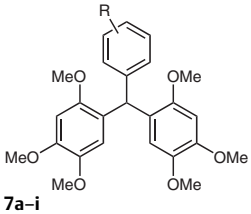
Entry	Equivalents of $NbCl_5$	Yield (%)[b] of triarylmethane **5g**
1	1.0	98
2	0.5	75
3	0.1	24
4	0	0

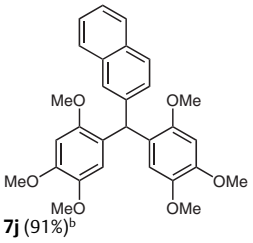
[a] Reaction conditions: arene **2g** (2.2 mmol), aldehyde **4a** (1.0 mmol), DCM (5 mL), room temperature, 24 h.
[b] Isolated yield.

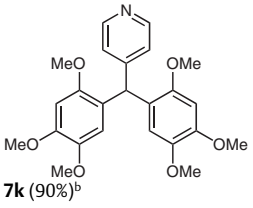
With these results in hand, we fixed $NbCl_5$ at 1 equivalent and 1,2,4-trimethoxybenzene (**2g**) as starting arene, and studied the generality of the reaction through experiments carried out with different aldehydes as electrophiles (Table 3). When we applied the experimental conditions to 3-nitrobenzaldehyde and 2-nitrobenzaldehyde, the reactions produced the corresponding triarylmethanes **7a** and **7b** in very high yields (98% and 95%, respectively). Benzaldehyde derivatives bearing an electron-withdrawing group (CF_3, Cl, Br, or F) at the *para* position also afforded the desired triarylmethanes **7c–f** in very high yields (96–99%) (Table 3).

Table 3 Scope of the Reaction of 1,2,4-Trimethoxybenzene (**2g**) with Respect to the Aldehyde[a]









7a	R = 3-NO_2	(98%)[b]
7b	R = 2-NO_2	(95%)[b]
7c	R = 4-CF_3	(97%)[b]
7d	R = 4-Cl	(99%)[b]
7e	R = 4-Br	(96%)[b]
7f	R = 4-F	(98%)[b]
7g	R = 4-CH_3	(93%)[b]
7h	R = 4-OMe	(95%)[b]
7i	R = 3,4,5-$(OMe)_3$	(98%)[b]

[a] Reaction conditions: arene **2g** (2.2 mmol), aldehyde **6a–k** (1.0 mmol), $NbCl_5$ (1.0 mmol), DCM (5 mL), room temperature, 24 h.
[b] Isolated yield.

Furthermore, when we employed benzaldehydes bearing an electron-donating substituent [4-CH_3, 4-OCH_3, or 3,4,5-$(OMe)_3$], the reaction provided very good yields (**7g–i**, 93–98%) (Table 3). Similarly, 2-naphthaldehyde reacted with 1,2,4-trimethoxybenzene (**2g**) to produce the triarylmethane **7j** in 91% yield. The reaction between pyridine-4-carbaldehyde and **2g** under the same reaction conditions afforded the corresponding diaryl(heteroaryl)methane **7k** in high yield (90%) (Table 3). The latter reaction attests to the great versatility of the methodology developed with the use of $NbCl_5$, which is important because diaryl(heteroaryl)methanes are essential structural moieties in natural products, biologically active molecules, and synthetic materials.[26]

In contrast, the reactions with other aromatic and aliphatic aldehydes, including cinnamaldehyde, phenylacetaldehyde, valeraldehyde, and octanal, did not give the desired triarylmethanes, probably because carbocations that were not at the benzylic position originated in the medium. To guarantee the success of this methodology, the resulting carbocation needs to be simultaneously stabilized by the mesomeric effect of the oxygen atom and the phenyl group.

In summary, we have developed a simple and straightforward method to synthesize triarylmethanes by Friedel–Crafts hydroxyalkylation by means of a practical protocol based on niobium pentachloride. The results clearly demonstrate an excellent tolerance to the various types of functional groups, where both aromatic aldehydes with electron-donating and electron-withdrawing groups react well to produce triarylmethanes in excellent yields.

All solvents were obtained from commercial sources and were purified according to standard procedures. Melting points were determined on a Reichert Kofler block apparatus, with a non-calibrated thermometer, installed under a Bristoline microscope. NMR spectroscopy was performed on a Bruker DPX-300, Bruker DRX-400, or Bruker DRX-500 instrument, operating at 300, 400, or 500 MHz for ^1H and at 75, 100, or 125 MHz for ^{13}C, respectively. TMS was used as internal standard. The chemical shifts are reported in ppm (δ); coupling constants (*J*) are given in hertz (Hz). The following abbreviations are employed to designate chemical shift multiplicities: s = singlet, br s = broad singlet, d = doublet, dd = double doublet, t = triplet, dt = double triplet, m = multiplet. Mass spectra were recorded on a Shimadzu GC/MS QP-2010 spectrometer (Shimadzu Corporation, Kyoto, Japan) fitted with an electron-impact ionization (EI) source operating at 70 eV. GC analyses were conducted on a Shimadzu GC-2010 Plus instrument equipped with a fused silica capillary column (Restek Rtx-5, 30 m length × 0.25 mm i.d.) operating at temperatures ranging from 100 to 310 °C at 5 °C/min. High-resolution electrospray ionization mass spectra (HRESIMS) were measured on a micrOTOF-Q II (Bruker Daltonics) spectrometer. IR spectra were recorded on a Perkin Elmer Spectrum RX I FTIR system, in KBr pellets or plates. All reactions were monitored by TLC on pre-coated aluminum sheets (silica gel 60 F_{254}) as the stationary phase.

Condensation Reaction of Aldehydes with Arenes in the Presence of $NbCl_5$ as Acid Catalyst; General Procedure

A suspension of aldehyde (1 mmol) and $NbCl_5$ (1 mmol) in DCM (5 mL) was stirred at 0 °C. Then, arene (2.2 mmol) was added. The reaction was allowed to reach room temperature. The end of the reaction was monitored via TLC. Next, the reaction mixture was quenched with saturated Na_2CO_3 solution (15 mL) and extracted with Et_2O (3 × 20 mL). The organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by flash column chromatography (silica gel; hexane–EtOAc, 9.5:0.5 to 8:2 v/v) to afford the pure compounds. All obtained products were characterized by their spectroscopic data [^1H, ^{13}C, and ^{19}F NMR, IR, MS (EI)].

1,1′-(Phenylmethanediyl)bis(2,4-dimethylbenzene) (3b)

Pale yellow oil; yield: 198 mg (66%).

IR: 3054, 2927, 2852, 1712, 1266, 739 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.12 (s, 6 H), 2.28 (s, 6 H), 5.61 (s, 1 H), 6.62 (d, *J* = 7.80 Hz, 2 H), 6.87 (d, *J* = 7.80 Hz, 2 H), 6.97 (s, 2 H), 7.02 (d, *J* = 7.96 Hz, 2 H), 7.18–7.24 (m, 3 H).

^{13}C NMR (100 MHz $CDCl_3$): δ = 19.5 (2 CH_3), 20.9 (2 CH_3), 49.9 (CH),126.0 (CH), 126.3 (2 CH), 128.2 (2 CH), 129.1 (2 CH), 129.7 (2 CH), 131.2 (2 CH),135.6 (2 C), 136.3 (2 C), 139.1 (2 C), 143.2 (C).

MS (EI): *m*/*z* (%) = 300 (80) [M⁺], 285 (100), 223 (15), 207 (19), 193 (28), 179 (51), 165 (21), 91 (6), 77 (5).

1,1′-(Phenylmethanediyl)bis(3,4-dimethylbenzene) (3c)

Pale yellow oil; yield: 177 mg (59%).

IR: 3056, 2925, 2853, 1713, 1266, 739 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.19 (s, 6 H), 2.22 (s, 6 H), 5.41 (s, 1 H), 6.82 (d, *J* = 7.41 Hz, 2 H), 6.91 (s, 2 H), 7.03 (d, *J* = 7.64 Hz, 2 H), 7.11 (d, *J* = 7.41 Hz, 2 H), 7.18–7.24 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.3 (2 CH_3), 19.8 (2 CH_3), 56.2 (CH), 126.0 (CH), 126.8 (2 CH), 128.2 (2 CH), 129.4 (2 CH), 129.5 (2 CH), 130.7 (2 CH), 134.3 (2 C), 136.3 (2 C), 141.6 (2 C), 144.5 (C).

MS (EI): *m*/*z* (%) = 300 (45) [M⁺], 285 (100), 223 (13), 207 (11), 193 (17), 179 (19), 165 (13), 91 (3), 77 (3).

1,1′-(Phenylmethanediyl)bis(2,5-dimethylbenzene) (3d)

Pale yellow solid; mp 80–82 °C; yield: 186 mg (62%).

IR: 3056, 2932, 2836, 1712, 1266, 738 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.11 (s, 6 H), 2.20 (s, 6 H), 5.63 (s, 1 H), 6.54 (s, 2 H), 6.95 (d, *J* = 7.58 Hz, 2 H), 7.02 (d, *J* = 7.08 Hz, 2 H), 7.04 (d, *J* = 7.08 Hz, 2 H), 7.18–7.22 (m, 1 H), 7.25–7.29 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.2 (2 CH_3), 21.2 (2 CH_3), 50.5 (CH), 126.1 (CH), 126.9 (2 CH), 128.2 (2 CH), 129.8 (2 CH), 129.9 (2 CH), 130.1 (2 CH), 133.4 (2 C), 134.9 (2 C), 141.8 (2 C), 142.9 (C).

MS (EI): *m*/*z* (%) = 300 (70) [M⁺], 285 (100), 223 (7), 207 (17), 193 (30), 179 (69), 165 (21), 91 (6), 77 (5).

1,1′-(Phenylmethanediyl)bis(4-methoxybenzene) (3e)

Pale yellow oil; yield: 176 mg (58%); ratio of isomers *p*,*p*′ (**3e**)/*p*,*o*′ (**3e′**) = 83:17.

IR: 2915, 1598, 1493, 1260, 809, 746, 699 cm^{-1}.

Major Isomer

^1H NMR (300 MHz, $CDCl_3$): δ = 3.78 (s, 6 H), 5.45 (s, 1 H), 6.82 (d, *J* = 8.66 Hz, 4 H), 7.02 (d, *J* = 8.66 Hz, 4 H), 7.09–7.11 (m, 2 H), 7.16–7.23 (m, 2 H), 7.27–7.30 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 48.7 (CH), 55.2 (2 CH_3O), 113.6 (2 CH), 126.1 (CH), 128.2 (2 CH), 129.3 (2 CH), 130.3 (2 CH), 136.5 (2 C), 144.6 (2 C), 158.7 (2 C).

MS (EI): *m*/*z* (%) = 304 (100) [M⁺], 289 (6), 273 (58), 227 (85), 197 (30), 181 (17), 153 (21), 113 (11).

Minor Isomer

MS (EI): *m*/*z* (%) = 304 (100) [M⁺], 289 (32), 273 (34), 227 (29), 197 (26), 165 (21), 121 (49), 91 (23).

1,1′-(Phenylmethanediyl)bis(2,5-dimethoxybenzene) (3f)

Pale yellow, viscous oil; yield: 273 mg (75%).

IR: 2950, 2832, 1590, 1493, 1219, 1049, 801, 709 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.69 (s, 6 H), 3.72 (s, 6 H), 6.23 (s, 1 H), 6.52 (d, *J* = 3.03 Hz, 2 H), 6.78 (dd, *J* = 8.85, 2.53 Hz, 2 H), 6.85 (d, *J* = 8.59 Hz, 2 H), 7.16 (d, *J* = 7.33 Hz, 2 H), 7.23 (t, *J* = 7.33 Hz, 1 H), 7.31 (d, *J* = 7.33 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.5 (CH), 55.4 (2 CH_3O), 56.4 (2 CH_3O), 110.7 (2 CH), 111.9 (2 CH), 117.2 (2 CH), 125.8 (CH), 127.9 (2 CH), 129.2 (2 CH), 133.9 (2 C), 143.3 (C), 151.6 (2 C), 157.3 (2 C).

MS (EI): *m*/*z* (%) = 364 (100) [M⁺], 333 (24), 241 (11), 213 (17), 151 (13), 121 (30).

1,1′-(Phenylmethanediyl)bis(2,4,5-trimethoxybenzene) (3g)

White solid; mp 123–124 °C (Lit.[27] 126–127 °C); yield: 382 mg (90%).

IR: 2956, 1512, 1204, 1037, 816, 707 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.63 (s, 6 H), 3.66 (s, 6 H), 3.88 (s, 6 H), 6.08 (s, 1 H), 6.43 (s, 2 H), 6.54 (s, 2 H), 7.04–7.06 (d, *J* = 7.02 Hz, 2 H), 7.14–7.24 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.5 (CH), 55.9 (2 CH_3O), 56.6 (2 CH_3O), 56.9 (2 CH_3O), 98.4 (2 CH), 114.6 (2 CH), 124.5 (C), 125.7 (CH), 127.8 (2 CH), 128.9 (2 CH), 142.7 (2 C), 144.2 (2 C), 148.0 (2 C), 151.5 (2 C).

MS (EI): *m*/*z* (%) = 424 (100) [M⁺], 393 (67), 347 (14), 241 (10), 181 (29), 151 (23), 91 (15).

1,1′-[(4-Nitrophenyl)methanediyl]bis(4-methylbenzene) (5a)

Yellow oil; yield: 213 mg (67%); ratio of isomers *p*,*p*′ (**5a**)/*p*,*o*′ (**5a′**) = 69:31.

IR: 2927, 1712, 1347, 1267, 748 cm^{-1}.

Major Isomer

^1H NMR (500 MHz, $CDCl_3$): δ = 2.33 (s, 6 H), 5.55 (s, 1 H), 6.97 (d, *J* = 7.91 Hz, 4 H), 7.12 (d, *J* = 7.91 Hz, 4 H), 7.27 (d, *J* = 8.69 Hz, 2 H), 8.12 (d, *J* = 8.69 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.0 (2 CH_3), 55.9 (CH), 123.5 (2 CH), 129.1 (4 CH), 129.3 (4 CH), 130.2 (2 CH), 136.5 (2 C), 139.6 (2 C), 146.5 (C), 152.1 (C).

MS (EI): *m*/*z* (%) = 317 (78) [M⁺], 302 (100), 256 (10), 239 (10), 226 (11), 195 (39), 179 (44), 165 (37), 152 (9), 107 (12).

Minor Isomer

^1H NMR (500 MHz, $CDCl_3$): δ = 2.20 (s, 3 H), 2.34 (s, 3 H), 5.71 (s, 1 H), 6.75 (d, *J* = 7.52 Hz, 1 H), 6.91 (d, *J* = 8.04 Hz, 2 H), 7.12–7.15 (m, 4 H), 7.20 (d, *J* = 8.82 Hz, 2 H), 7.23–7.26 (m, 1 H), 8.13 (d, *J* = 8.82 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.8 (CH_3), 21.0 (CH_3), 53.0 (CH), 123.5 (2 CH), 126.1 (CH), 126.9 (CH), 129.2 (CH), 129.4 (2 CH), 129.5 (2 CH), 130.3 (2 CH), 130.7 (CH), 136.5 (2 C), 138.8 (C), 141.0 (C), 146.6 (C), 151.6 (C).

MS (EI): *m*/*z* (%) = 317 (84) [M⁺], 302 (100), 256 (10), 239 (9), 226 (16), 195 (27), 179 (54), 165 (37), 152 (10), 107 (9).

1,1′-[(4-Nitrophenyl)methanediyl]bis(2,4-dimethylbenzene) (5b)

Pale yellow solid; mp 134–137 °C; yield: 265 mg (77%).

IR: 3066, 2974, 2917, 1519, 1342, 812, 744 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.12 (s, 6 H), 2.30 (s, 6 H), 5.70 (s, 1 H), 6.55 (d, *J* = 7.80 Hz, 2 H), 6.90 (d, *J* = 7.80 Hz, 2 H), 7.01 (s, 2 H), 7.19 (d, *J* = 8.74 Hz, 2 H), 8.12 (d, *J* = 8.74 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.5 (2 CH_3), 20.9 (2 CH_3), 49.7 (CH), 123.5 (2 CH), 126.7 (2 CH), 129.0 (2 CH), 130.4 (2 CH), 131.5 (2 CH), 136.2 (2 C), 136.4 (2 C), 137.6 (2 C), 146.5 (C), 151.4 (C).

MS (EI): *m*/*z* (%) = 345 (74) [M$^+$], 330 (100), 240 (12), 222 (34), 207 (20), 193 (44), 178 (40), 165 (9).

1,1′-[(4-Nitrophenyl)methanediyl]bis(3,4-dimethylbenzene) (5c)

Yellow oil; yield: 248 mg (72%).

IR: 3056, 2929, 1712, 1267, 738 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.20 (s, 6 H), 2.24 (s, 6 H), 5.49 (s, 1 H), 6.79 (d, *J* = 7.58 Hz, 2 H), 6.87 (s, 2 H), 7.06 (d, *J* = 7.58 Hz, 2 H), 7.28 (d, *J* = 8.72 Hz, 2 H), 8.12 (d, *J* = 8.72 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.3 (2 CH_3), 19.8 (2 CH_3), 56.0 (CH), 123.5 (2 CH), 126.6 (2 CH), 129.8 (2 CH), 130.2 (2 CH), 130.5 (2 CH), 135.1 (2 C), 136.8 (2 C), 140.0 (2 C), 146.4 (C), 152.3 (C).

MS (EI): *m*/*z* (%) = 345 (46) [M$^+$], 330 (100), 222 (21), 207 (17), 193 (19), 178 (15), 165 (5).

1,1′-[(4-Nitrophenyl)methanediyl]bis(2,5-dimethylbenzene) (5d)

Yellow solid; mp 103–106 °C; yield: 259 mg (75%).

IR: 3076, 2972, 2917, 1518, 1346, 813, 737 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.11 (s, 6 H), 2.21 (s, 6 H), 5.72 (s, 1 H), 6.46 (br s, 2 H), 6.98 (d, *J* = 7.80 Hz, 2 H), 7.08 (d, *J* = 7.80 Hz, 2 H), 7.20 (d, *J* = 8.59 Hz, 2 H), 8.14 (d, *J* = 8.59 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.1 (2 CH_3), 21.2 (2 CH_3), 50.3 (CH), 123.5 (2 CH), 127.6 (2 CH), 129.7 (CH), 129.8 (CH), 130.5 (2 CH), 130.6 (2 CH), 133.3 (2 C), 135.5 (2 C), 140.3 (2 C), 146.6 (C), 151.2 (C).

MS (EI): *m*/*z* (%) = 345 (93) [M$^+$], 330 (100), 240 (12), 222 (69), 207 (27), 193 (68), 178 (59), 165 (12).

1,1′-[(4-Nitrophenyl)methanediyl]bis(4-methoxybenzene) (5e)

Yellow oil; yield: 251 mg (72%); ratio of isomers *p*,*p*′ (**5e**)/*p*,*o*′ (**5e′**) = 87:13.

IR: 3056, 2921, 1712, 1266, 738 cm^{-1}.

Major Isomer

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.79 (s, 6 H), 5.53 (s, 1 H), 6.84 (d, *J* = 8.46 Hz, 4 H), 6.99 (d, *J* = 8.46 Hz, 4 H), 7.26 (d, *J* = 8.59 Hz, 2 H), 8.13 (d, *J* = 8.59 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 48.9 (CH), 55.3 (2 CH_3O), 114.0 (4 CH), 123.5 (2 CH), 130.1 (2 CH), 130.2 (4 CH), 134.8 (2 C), 146.4 (C), 152.4 (2 C), 158.4 (C).

MS (EI): *m*/*z* (%) = 349 (98) [M$^+$], 334 (4), 318 (59), 227 (100), 121 (4), 91 (2).

Minor Isomer

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.0 (CH_3O), 55.3 (CH_3O), 55.5 (CH), 113.9 (2 CH), 120.4 (CH), 123.3 (2 CH), 128.5 (2 CH), 129.9 (1 CH), 130.0 (CH), 130.4 (2 CH), 131.3 (CH), 134.2 (2 C), 146.3 (C), 156.9 (2 C), 158.3 (C).

MS (EI): *m*/*z* (%) = 349 (100) [M$^+$], 334 (28), 318 (28), 227 (32), 121 (63), 91 (13).

1,1′-[(4-Nitrophenyl)methanediyl]bis(2,5-dimethoxybenzene) (5f)

Yellow solid; mp 135–137 °C; yield: 348 mg (85%).

IR: 2937, 2832, 1516, 1495, 1345, 1217, 1045, 834, 709 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.64 (s, 6 H), 3.67 (s, 6 H), 6.18 (s, 1 H), 6.37 (d, *J* = 2.96 Hz, 2 H), 6.75 (dd, *J* = 8.89, 2.96 Hz, 2 H), 6.82 (d, *J* = 8.74 Hz, 2 H), 7.22 (d, *J* = 8.89 Hz, 2 H), 8.10 (d, *J* = 8.74 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 43.8 (CH), 55.5 (2 CH_3O), 56.3 (2 CH_3O), 111.3 (2 CH), 111.9 (2 CH), 117.3 (2 CH), 123.3 (2 CH), 129.9 (2 CH), 132.0 (C), 146.3 (2 C), 151.5 (2 C), 151.9 (C), 153.5 (2 C).

MS (EI): *m*/*z* (%) = 409 (100) [M$^+$], 378 (6), 258 (13), 241 (8), 151 (15), 121 (42).

1,1′-[(4-Nitrophenyl)methanediyl]bis(2,4,5-trimethoxybenzene) (5g)

Orange solid; mp 60–61 °C; yield: 460 mg (98%).

IR: 3001, 2936, 1512, 1203, 1033, 887, 742 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.65 (s, 6 H), 3.68 (s, 6 H), 3.90 (s, 6 H), 6.11 (s, 1 H), 6.39 (s, 2 H), 6.56 (s, 2 H), 7.20 (d, *J* = 8.66 Hz, 2 H), 8.10 (d, *J* = 8.66 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.0 (CH), 56.0 (2 CH_3O), 56.5 (2 CH_3O), 56.7 (2 CH_3O), 98.1 (2 CH), 114.5 (2 CH), 122.3 (2 C), 123.1 (2 CH), 129.5 (2 CH), 142.8 (2 C), 146.1 (C), 148.6 (2 C), 151.5 (2 C), 152.8 (C).

MS (EI): *m*/*z* (%) = 469 (100) [M$^+$], 438 (48), 181 (21), 151 (27).

HRESIMS: *m*/*z* calcd for $C_{25}H_{27}NNaO_8$ [M + Na]$^+$: 492.1634; found: 492.1628.

1,1′-[(3-Nitrophenyl)methanediyl]bis(2,4,5-trimethoxybenzene) (7a)

Yellow solid; mp 101–104 °C (Lit.[28] 117 °C); yield: 459 mg (98%).

IR: 2963, 1512, 1201, 1034, 815, 763, 668 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.65 (s, 6 H), 3.68 (s, 6 H), 3.91 (s, 6 H), 6.12 (s, 1 H), 6.40 (s, 2 H), 6.58 (s, 2 H), 7.37–7.39 (m, 1 H), 7.40 (t, *J* = 6.82 Hz, 1 H), 7.92 (br s, 1 H), 8.00 (dt, *J* = 6.82, 2.52 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.7 (CH), 56.1 (2 CH_3O), 56.6 (2 CH_3O), 56.8 (2 CH_3O), 98.1 (2 CH), 114.6 (2 CH), 120.9 (C), 122.4 (2 C), 123.6 (CH), 128.6 (CH), 134.9 (CH), 142.8 (CH), 147.0 (2 C), 148.2 (2 C), 148.7 (2 C), 151.6 (C).

MS (EI): *m*/*z* (%) = 469 (100) [M$^+$], 438 (37), 181 (35), 151 (28).

HRESIMS: *m*/*z* calcd for $C_{25}H_{27}NNaO_8$ [M + Na]$^+$: 492.1634; found: 492.1625.

1,1′-[(2-Nitrophenyl)methanediyl]bis(2,4,5-trimethoxybenzene) (7b)

Orange solid; mp 134–135 °C; yield: 446 mg (95%).

IR: 3004, 2935, 2835, 1511, 1463, 1202, 1033, 851, 737 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.62 (s, 6 H), 3.68 (s, 6 H), 3.88 (s, 6 H), 6.35 (s, 1 H), 6.54 (s, 2 H), 6.55 (s, 2 H), 7.07 (dd, *J* = 7.83, 1.26 Hz, 1 H), 7.34 (dt, *J* = 7.83, 7.83, 1.39 Hz, 1 H), 7.44 (dt, *J* = 7.83, 7.83, 1.26 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.9 (CH), 56.0 (2 CH_3O), 56.7 (2 CH_3O), 56.8 (2 CH_3O), 98.3 (2 CH), 114.3 (2 CH), 122.3 (2 C), 124.4 (CH), 126.8 (CH), 131.1 (CH), 131.9 (CH), 139.0 (2 C), 142.7 (2 C), 148.6 (2 C), 149.8 (C), 151.7 (C).

MS (EI): *m*/*z* (%) = 469 (26) [M$^+$], 421 (100), 406 (23), 256 (39), 242 (36), 232 (20), 195 (43), 168 (35).

HRESIMS: *m*/*z* calcd for $C_{25}H_{27}NNaO_8$ [M + Na]$^+$: 492.1634; found: 492.1610.

1,1′-{[4-(Trifluoromethyl)phenyl]methanediyl}bis(2,4,5-trimethoxybenzene) (7c)

Pale yellow solid; mp 50–51 °C; yield: 478 mg (97%).

IR: 2937, 1510, 1324, 1206, 1035, 887, 768 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.65 (s, 6 H), 3.67 (s, 6 H), 3.89 (s, 6 H), 6.11 (s, 1 H), 6.41 (s, 2 H), 6.58 (s, 2 H), 7.17 (d, *J* = 7.78 Hz, 2 H), 7.50 (d, *J* = 7.78 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 42.7 (CH), 56.1 (2 CH_3O), 56.7 (4 CH_3O), 98.5 (2 CH), 114.9 (2 CH), 123.3 (2 C), 124.4 (q, J_{CF} = 271 Hz, CF_3), 124.8 (q, J_{CF} = 3.84 Hz, 2 $CHCCF_3$), 128.2 (q, J_{CF} = 32.6 Hz, CCF_3), 129.2 (2 CH), 142.9 (2 C), 148.5 (2 C), 148.8 (C), 151.7 (2 C).

^{19}F NMR (471 MHz, $CDCl_3$): δ = –63.24.

MS (EI): *m*/*z* (%) = 492 (100) [M$^+$], 461 (16), 347 (10), 181 (21), 151 (27), 69 (5).

HRESIMS: *m*/*z* calcd for $C_{26}H_{27}F_3NaO_6$ [M + Na]$^+$: 515.1657; found: 515.1643.

1,1′-[(4-Chlorophenyl)methanediyl]bis(2,4,5-trimethoxybenzene) (7d)

White solid; mp 157–159 °C (Lit.[27] 168–169 °C); yield: 454 mg (99%).

IR: 2932, 1513, 1450, 1203, 1036, 886, 761 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.64 (s, 6 H), 3.67 (s, 6 H), 3.89 (s, 6 H), 6.02 (s, 1 H), 6.39 (s, 2 H), 6.54 (s, 2 H), 6.98 (d, *J* = 8.42 Hz, 2 H), 7.21 (d, *J* = 8.42 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.1 (CH), 56.0 (2 CH_3O), 56.7 (2 CH_3O), 56.8 (2 CH_3O), 98.3 (2 CH), 114.5 (2 CH), 123.8 (2 C), 128.0 (2 CH), 130.3 (2 CH), 131.4 (C), 142.8 (C), 143.0 (2 C), 148.2 (2 C), 151.5 (2 C).

MS (EI): *m*/*z* (%) = 458 (100) [M$^+$], 427 (72), 181 (25), 151 (30), 125 (17).

HRESIMS: *m*/*z* calcd for $C_{25}H_{27}ClNaO_6$ [M + Na]$^+$: 481.1394; found: 481.1370.

1,1′-[(4-Bromophenyl)methanediyl]bis(2,4,5-trimethoxybenzene) (7e)

Orange solid; mp 137–138 °C (Lit.[29] 141 °C); yield: 483 mg (96%).

IR: 2933, 1511, 1451, 1200, 1035, 884, 761 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.64 (s, 6 H), 3.67 (s, 6 H), 3.88 (s, 6 H), 6.01 (s, 1 H), 6.40 (s, 2 H), 6.54 (s, 2 H), 6.92 (d, *J* = 8.47 Hz, 2 H), 7.35 (d, *J* = 8.47 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.1 (CH), 56.1 (2 CH_3O), 58.7 (2 CH_3O), 58.8 (2 CH_3O), 98.3 (2 CH), 114.6 (2 CH), 119.5 (C), 123.7 (2 C), 130.7 (2 CH), 131.0 (2 CH), 142.8 (C), 143.5 (2 C), 148.3 (2 C), 151.6 (2 C).

MS (EI): *m*/*z* (%) = 504 (100) [M$^+$], 502 (98), 473 (63), 471 (62), 347 (16), 208 (12), 181 (37), 151 (40).

HRESIMS: *m*/*z* calcd for $C_{25}H_{27}BrNaO_6$ [M + Na]$^+$: 525.0889; found: 525.0873.

1,1′-[(4-Fluorophenyl)methanediyl]bis(2,4,5-trimethoxybenzene) (7f)

White solid; mp 100–101 °C; yield: 433 mg (98%).

IR: 2956, 1508, 1320, 1204, 1038, 884, 764 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.64 (s, 6 H), 3.66 (s, 6 H), 3.88 (s, 6 H), 6.05 (s, 1 H), 6.41 (s, 2 H), 6.55 (s, 2 H), 6.89–6.95 (m, 2 H), 6.99–7.04 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 41.8 (CH), 55.9 (2 CH_3O), 56.5 (2 CH_3O), 56.6 (2 CH_3O), 98.3 (2 CH), 114.4 (d, J_{CF} = 21.1 Hz, 2 CH), 114.6 (2 CH), 124.1 (2 C), 130.2 (d, J_{CF} = 7.7 Hz, 2 CH), 139.9 (d, J_{CF} = 2.9 Hz, C), 142.6 (2 C), 148.1 (2 C), 151.4 (2 C), 160.9 (d, J_{CF} = 243 Hz, C).

^{19}F NMR (471 MHz, $CDCl_3$): δ = –118.7.

MS (EI): *m*/*z* (%) = 442 (100) [M$^+$], 411 (70), 347 (7), 181 (17), 151 (20), 109 (20).

HRESIMS: *m*/*z* calcd for $C_{25}H_{27}FNaO_6$ [M + Na]$^+$: 465.1689; found: 465.1680.

1,1′-[(4-Methylphenyl)methanediyl]bis(2,4,5-trimethoxybenzene) (7g)

White solid; mp 134–137 °C (Lit.[29] 142–143 °C); yield: 408 mg (93%).

IR: 2918, 1512, 1200, 1037, 854, 760 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.30 (s, 3 H), 3.64 (s, 6 H), 3.66 (s, 6 H), 3.88 (s, 6 H), 6.04 (s, 1 H), 6.44 (s, 2 H), 6.54 (s, 2 H), 6.93 (d, *J* = 7.96 Hz, 2 H), 7.04 (d, *J* = 7.96 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0 (CH_3), 42.1 (CH), 56.1 (2 CH_3O), 56.7 (2 CH_3O), 57.0 (2 CH_3O), 98.5 (2 CH), 114.7 (2 CH), 125.0 (2 C), 128.7 (2 CH), 128.9 (2 CH), 135.1 (C), 141.0 (C), 142.7 (2 C), 148.0 (2 C), 151.6 (2 C).

MS (EI): *m*/*z* (%) = 438 (100) [M$^+$], 407 (83), 347 (9), 181 (19), 151 (17), 105 (24).

HRESIMS: *m*/*z* calcd for $C_{26}H_{30}NaO_6$ [M + Na]$^+$: 461.1940; found: 461.1930.

1,1′-[(4-Methoxyphenyl)methanediyl]bis(2,4,5-trimethoxybenzene) (7h)

White solid; mp 125–130 °C (Lit.[29] 131 °C); yield: 432 mg (95%).

IR: 2960, 1507, 1205, 1029, 880, 815, 764 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.64 (s, 6 H), 3.66 (s, 6 H), 3.78 (s, 3 H), 3.88 (s, 6 H), 6.02 (s, 1 H), 6.42 (s, 2 H), 6.54 (s, 2 H), 6.79 (d, *J* = 8.59 Hz, 2 H), 6.96 (d, *J* = 8.59 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 41.7 (CH), 55.1 (CH_3O), 56.1 (2 CH_3O), 56.7 (2 CH_3O), 57.1 (2 CH_3O), 98.6 (2 CH), 113.3 (2 CH), 114.6 (2 CH), 125.0 (C), 129.9 (2 CH), 136.3 (2 C), 142.8 (2 C), 148.0 (2 C), 151.6 (2 C), 157.6 (C).

MS (EI): *m*/*z* (%) = 454 (94) [M$^+$], 423 (100), 347 (6), 271 (10), 181 (14), 151 (12), 121 (37).

HRESIMS: *m*/*z* calcd for $C_{26}H_{30}NaO_7$ [M + Na]$^+$: 477.1889; found: 477.1882.

1,1′-[(3,4,5-Trimethoxyphenyl)methanediyl]bis(2,4,5-trimethoxybenzene) (7i)

Yellow solid; mp 103–104 °C (Lit.[27] 97–99 °C); yield: 504 mg (98%).

IR: 3002, 2935, 2834, 1588, 1512, 1454, 1205, 1126, 1031, 880, 763 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.65 (s, 6 H), 3.70 (s, 6 H), 3.71 (s, 6 H), 3.82 (s, 3 H), 3.89 (s, 6 H), 6.01 (s, 1 H), 6.28 (s, 2 H), 6.54 (s, 2 H), 6.55 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.6 (CH), 56.0 (4 CH_3O), 56.8 (2 CH_3O), 57.1 (2 CH_3O), 60.8 (CH_3O), 98.4 (2 CH), 106.4 (2 CH), 114.5 (2 CH), 124.5 (2 C), 136.1 (C), 139.8 (C), 142.7 (2 C), 148.1 (2 C), 151.6 (2 C), 152.8 (2 C).

MS (EI): *m*/*z* (%) = 514 (100) [M$^+$], 483 (92), 347 (12), 331 (18), 181 (38), 151 (14).

HRESIMS: *m*/*z* calcd for $C_{28}H_{34}NaO_9$ [M + Na]$^+$: 537.2101; found: 537.2093.

2-[Bis(2,4,5-trimethoxyphenyl)methyl]naphthalene (7j)

White solid; mp 155–159 °C; yield: 432 mg (91%).

IR: 2962, 1512, 1196, 1034, 878, 818, 762 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.61 (s, 6 H), 3.67 (s, 6 H), 3.90 (s, 6 H), 6.24 (s, 1 H), 6.47 (s, 2 H), 6.57 (s, 2 H), 7.25–7.28 (m, 1 H), 7.35 (br s, 1 H), 7.39–7.42 (m, 2 H), 7.67–7.81 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 42.7 (CH), 56.1 (2 CH_3O), 56.8 (2 CH_3O), 57.0 (2 CH_3O), 98.7 (2 CH), 115.0 (2 CH), 124.5 (2 C), 125.1 (CH), 125.6 (CH), 126.9 (CH), 127.4 (CH), 127.5 (CH), 127.9 (CH), 128.3 (CH), 132.1 (C), 133.5 (C), 142.0 (C), 142.9 (2 C), 148.3 (2 C), 151.8 (2 C).

MS (EI): *m*/*z* (%) = 474 (100) [M$^+$], 443 (76), 347 (7), 181 (14), 151 (12), 141 (22).

HRESIMS: *m*/*z* calcd for $C_{29}H_{30}NaO_6$ [M + Na]$^+$: 497.1940; found: 497.1929.

4-[Bis(2,4,5-trimethoxyphenyl)methyl]pyridine (7k)

Yellow solid; mp 94–95 °C; yield: 382 mg (90%).

IR: 2957, 2935, 1595, 1512, 1451, 1317, 1204, 1038, 890, 765 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.65 (s, 6 H), 3.68 (s, 6 H), 3.90 (s, 6 H), 6.02 (s, 1 H), 6.40 (s, 2 H), 6.55 (s, 2 H), 6.97–6.98 (m, 2 H), 8.45–8.46 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.4 (CH), 56.1 (2 CH_3O), 56.6 (2 CH_3O), 56.7 (2 CH_3O), 98.1 (2 CH), 114.5 (2 CH), 122.2 (2 C), 124.2 (2 CH), 142.8 (2 C), 148.6 (2 C), 149.3 (2 CH), 151.6 (2 C), 153.9 (C).

MS (EI): *m*/*z* (%) = 425 (100) [M$^+$], 394 (39), 347 (19), 181 (31), 151 (25).

HRESIMS: *m*/*z* calcd for $C_{24}H_{28}NO_6$ [M + H]$^+$: 426.1917; found: 426.1905.

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Supporting Information

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