Electronic Supplementary Information for

A new practical synthesis of triaryl and trisindolylmethanes under solvent-free reaction conditions

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General Information

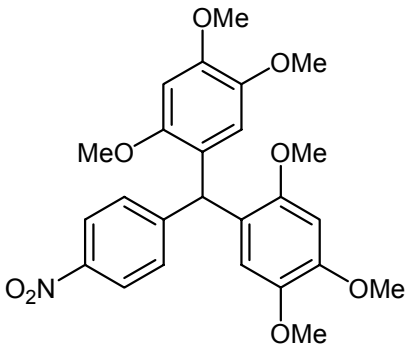
All the reactions were run in vials using analytical grade reagents, and were monitored by TLC, GC, GC-MS and NMR spectrometry. GC-MS spectra were recorded with an AT5973N mass selective detector connected to an AT6890N GC cross-linked methyl silicone capillary column. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ with a Bruker Avance 200 spectrometer at 200 MHz and 50 MHz, respectively; chemical shifts are given in ppm relative to $CDCl_3$. TLC were performed on Fluka silica gel TLCPET foils GF 254, 2–25 μm, layer thickness 0.2 mm, medium pore diameter 60 A˚. Plates were visualized using UV light (254 nm). Column chromatography was carried out on SiO_2 (pore size 70 Å, 70–230 mesh). Petroleum ether refers to the fraction boiling in the range 40–60 °C and is abbreviated as PE. Commercially available reagents and solvents were purchased from Aldrich and were used without purification or distillation prior to use; Dowex 50X8 ion-exchange resin was purchased from Fluka. *o*-Benzenedisulfonimide (**1**) was prepared as described in literature.[1] Details for the reactions and yields for the pure (GC, GC-MS, TLC, ^{1}H NMR) isolated products are listed in Table 2, 4 and 5. Structure and purity of all the products were confirmed by comparison of their physical and spectral data (IR, MS, ^{1}H NMR and ^{13}C NMR) with those reported in literature. For triarylmethanes **5d-e**, **6b** and **8b**, ^{1}H NMR spectra are reported for the *p,p* isomer, always predominant, along with distinctive signals for the *o,p* minor isomer.
By the work-up of the reaction mixtures, *o*-benzenedisulfonimide could be recovered by evaporating aqueous phases, purified by elution on Dowex ion-exchange resin and recycled in other reactions. When OBS was used adsorbed onto SiO_2, at the end of the reaction, the solid mixture was extracted with small portions of CH_2Cl_2 (6 x 3 mL) under stirring; the heterogeneous catalyst was then directly recycled after drying under vacuum.

[1] M. Barbero, M. Crisma, I. Degani, R. Fochi and P. Perracino, *Synthesis*, 1998, 1171.

General Procedures

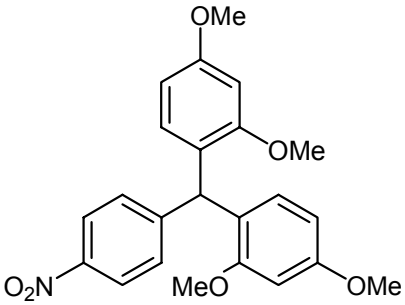
Preparation of 10% w/w silica-gel supported *o*-benzenedisulfonimide:
To a solution of *o*-benzenedisulfonimide (**1**) (0.66 g, 3 mmol) in water (10 mL), silica gel (column chromatographic grade, 70 Å, 70-230 mesh; 6.60 g) was added. The mixture was stirred for 5 min and then water was evaporated under heating at reduced pressure until a free-flowing white solid was obtained. The catalyst was ready to use.

General procedure for acid catalysed Friedel-Crafts hydroxyalkylation reactions:
A mixture of aldehyde **2** (1.0 mmol), aromatic compound **4** (mmol as in Table 4) and *o*-benzenedisulfonimide (**1**, 10 mol%, 0.022 g) was stirred at r.t. (or under heating, as in Table 4) in a vial until TLC analyses showed almost complete conversion of **2**. The reaction mixture was then treated with CH_2Cl_2–H_2O (1:1, 20 mL). The aqueous phase was extracted with CH_2Cl_2 (2 x 20 mL). The organic extracts were dried with Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by column chromatography on a short column of silica gel.
When 10% w/w silica-gel supported *o*-benzenedisulfonimide was used as the catalyst, at the end of the reaction, after extraction of the solid phase with CH_2Cl_2 (3 mL) and further few washings with small amounts of solvent (6 x 3 mL), the solid catalyst was dried and immediately recycled. Organic extracts were dried with Na_2SO_4 and the work-up was as above.

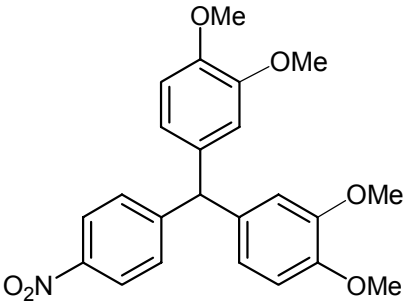


bis(2,4,5-Trimethoxyphenyl)(4-nitrophenyl)methane (5a).[2]
Chromatographic eluent: PE–AcOEt (6:4); yellow solid (0.47 g, quantitative yield); mp 125–126 °C (EtOH) [lit.[2] 123–124 °C].
^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.58 (s, 6H), 3.61 (s, 6H), 3.83 (s, 6H), 6.04 (s, 1H), 6.32 (s, 2H), 6.49 (s, 2H), 7.13 (d, *J* = 9.0 Hz, 2H), 8.03 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 42.8, 55.9 (2C), 56.4 (2C), 56.5 (2C), 97.8 (2C), 114.2 (2C), 122.1 (2C), 123.0 (2C), 129.4 (2C), 142.6 (2C), 145.9, 148.4 (2C), 151.3 (2C), 152.7.
MS (EI): *m/z* (%) 469 [M^+](100), 438 (40), 181 (25), 151 (25).

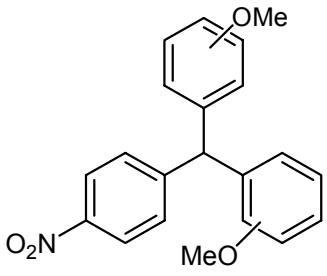
[2] Y. Leng, F. Chen, L. Zuo and W. Duan, *Tetrahedron Lett.*, **2010**, *51*, 2370



bis(2,4-Dimethoxyphenyl)(4-nitrophenyl)methane (5b).[2]
Chromatographic eluent: PE–AcOEt (7:3); light yellow solid (0.41 g, quantitative yield); mp 151.8–152.4 °C (CH_2Cl_2–PE) [lit.[2] 148–149 °C].
^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.62 (s, 6H), 3.73 (s, 6H), 5.99 (s, 1H), 6.32 (dd, *J* = 8.4 and 2.4 Hz, 2H), 6.41 (d, *J* = 2.4 Hz, 2H), 6.58 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 2H), 8.02 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 42.3, 55.1 (2C), 55.4 (2C), 98.6 (2C), 103.5 (2C), 123.0 (2C), 123.2 (2C), 129.5 (2C), 130.1 (2C), 145.9, 153.1 (2C), 157.8 (2C), 159.5.
MS (EI): *m/z* (%) 409 [M^+](100), 378 (40), 287 (50), 234 (40).



bis(3,4-Dimethoxyphenyl)(4-nitrophenyl)methane (5c).[3]
Chromatographic eluent: PE–AcOEt (6:4); light yellow oil (0.39 g, 95% yield).
^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.70 (s, 6H), 3.80 (s, 6H), 5.46 (s, 1H), 6.50 (dd, *J* = 8.2 and 2.0 Hz, 2H), 6.57 (d, *J* = 2.0 Hz, 2H), 6.74 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 2H), 8.08 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 55.5, 55.7 (4C), 110.8 (2C), 112.3 (2C), 121.2 (2C), 123.3 (2C), 129.9 (2C), 134.8 (2C), 146.3 , 147.7 (2C), 148.8 (2C), 151.9.
MS (EI): *m/z* (%) 409 [M^+](100), 378 (70), 287 (45).

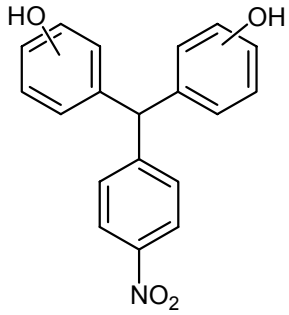


5d

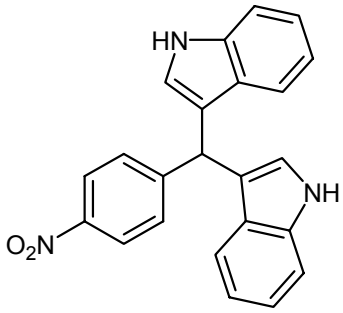
bis(4-Methoxyphenyl)(4-nitrophenyl)methane (5d) and isomer.[2]

[3] S. Podder, J. Choudhury, U. K. Roy and S. Roy, *J. Org. Chem*., **2007**, *72*, 3100.

Chromatographic eluent: PE–AcOEt (7:3); light yellow oil (0.32 g, 91% yield). Mixture of isomers (*p,p* and *o,p*, the former always prevalent) not completely separable.
^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.66 (s, 3H) (*o,p*), 3.74 (s, 6H) (*p,p*), 3.76 (s, 3H) (*o,p*), 5.49 (s, 1H) (*p,p*), 5.87 (s, 1H) (*o,p*), 6.80 (d, *J* = 8.8 Hz, 4H), 6.95 (d, *J* = 8.8 Hz, 4H), 7.22 (d, *J* = 8.6 Hz, 2H), 8.07 (d, *J* = 8.8 Hz, 2H).
MS (EI): *m/z* (%) 349 [M^+](100), 318 (65), 227 (100) (*p,p* isomer); 349 [M^+](100), 319 (40), 227 (55), 121 (55) (*o,p* isomer).

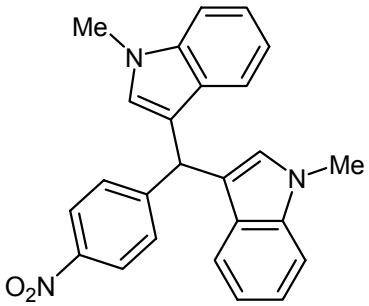


bis(4-Hydroxyphenyl)(4-nitrophenyl)methane (5e) and isomer.[2]
Chromatographic eluent: PE–EE (1:1); oil (0.32 g, quantitative yield). Mixture of isomers (*p,p* and *o,p*, the former always prevalent) not completely separable.
^{1}H NMR (200 MHz, CD_3OD): δ = 5.42 (s, 1H) (*p,p*), 5.82 (s, 1H) (*o,p*), 6.64 (d, *J* = 8.6 Hz, 4H), 6.81 (d, *J* = 8.6 Hz, 4H), 7.19 (d, *J* = 8.8 Hz, 2H), 8.01 (d, *J* = 8.8 Hz, 2H).
MS (EI): *m/z* (%) 321 [M^+](100), 228 (30), 199 (80) (*p,p* isomer); 321 [M^+](100), 228 (100), 199 (50), 181 (60) (*o,p* isomer).

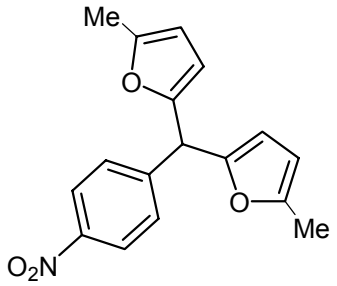


bis(3-Indolyl)(4-nitrophenyl)methane (5f).[4]
Chromatographic eluent: PE–CH_2Cl_2 (2:8); yellow needles (0.35 g, 95% yield); mp 221.9–222.3 °C (AcOEt–PE) [lit.[4] 218–220 °C].
^{1}H NMR (200 MHz, CD_3CN): δ = 6.00 (s, 1H), 6.75 (d, *J* = 2.4 Hz, 2H), 6.88 (t, *J* = 7. 5 Hz, 2H), 7.06 (t, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 2H), 8.06 (d, *J* = 8.8 Hz, 2H), 9.10 (br s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 40.0, 111.1 (2C), 117.9 (2C), 119.3 (2C), 119.4 (2C), 122.2 (2C), 123.4 (4C), 126.4 (2C), 129.3 (2C), 136.5 (2C), 146.4, 151.6.

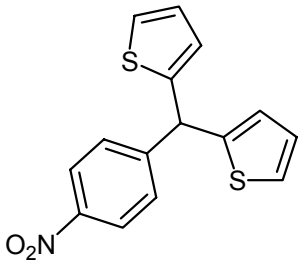
[4] K. Rad-Moghadam and M. Sharifi-Kiasaraie, *Tetrahedron*, **2009**, *65*, 8816



bis(1-Methyl-3-indolyl)(4-nitrophenyl)methane (5g).[5]
Chromatographic eluent: PE–CH_2Cl_2 (4:6); yellow needles (0.39 g, 99% yield); mp 210.0–211.0 °C (CH_2Cl_2–PE) [lit.[5] 215–217 °C].
^{1}H NMR (200 MHz, CD_3CN): δ = 3.65 (s, 6H), 5.93 (s, 1 H), 6.50 (s, 2H), 6.92–7.02 (m, 2H), 7.14–7.35 (m, 6H), 7.45 (d, *J* = 8.6 Hz, 2H), 8.08 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 32.6, 39.9, 109.2 (2C), 116.4 (2C), 118.9 (2C), 119.5 (2C), 121.7 (2C), 123.4 (2C), 126.9 (2C), 128.1 (2C) 129.3 (2C), 137.3 (2C), 146.3, 152.2.



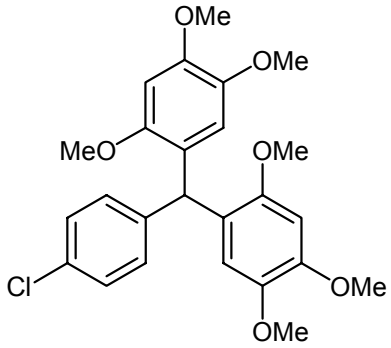
bis(5-Methyl-2-furyl)(4-nitrophenyl)methane (5h).[6]
Chromatographic eluent: PE–EE (7:3); white needles (0.39 g, 95% yield); mp 81.7–82.7 °C (CH_2Cl_2–PE) [lit.[6] 89–91 °C].
^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.19 (s, 6H), 5.37 (s, 1H), 5.84–5.89 (m, 4H), 7.35 (d, *J* = 8.8 Hz, 2H), 8.11 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.37 (2C), 44.63, 106.1 (2C), 108.6 (2C), 123.5 (2C), 129.1 (2C), 146.8, 147.3, 150.8 (2C), 151.9 (2C).
MS (EI): *m/z* (%) 297 [M^+](90), 175 (100).



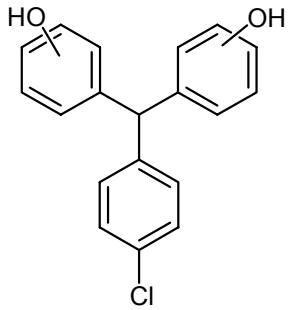
bis(2-Thienyl)(4-nitrophenyl)methane (5i).[3]
Chromatographic eluent: PE–EE (7:3); pink needles (0.22 g, 74% yield); mp 81.7.8–82.7.4 °C (CH_2Cl_2–PE) [lit.[3] 89–91 °C];

[5] B.-S. Liao, J.-T. Chen and S.-T. Liu, *Synthesis*, **2007**, 3125
[6] S. Ch. Gagieva, T. A. Sukhova, D. V. Savinov, V. A. Tuskaev, K. A. Lyssenko, N. M. Bravaya, Yu. N. Belokon and B. M. Bulychev, *Russ. Chem. Bull. Int. Ed*., **2006**, *55*, 1794

^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.92 (s, 1H), 5.75–5.79 (m, 2H), 6.88–6.95 (m, 2H), 7.18–7.22 (m, 2H), 7.40 (d, *J* = 9.0 Hz, 2H), 8.12 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 46.9, 123.7 (2C), 125.2 (2C), 126.4 (2C), 126.7 (2C), 129.1 (2C), 145.4 (2C), 146.8, 150.6.
MS (EI): *m/z* (%) 301 [M^+](100), 179 (40).

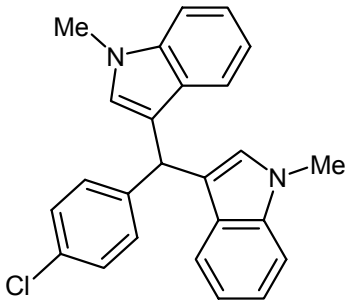


(4-Chlorophenyl)bis(2,4,5-trimethoxyphenyl)methane (6a).[7]
Chromatographic eluent: PE–AcOEt (6:4); white needles (0.46 g, 90% yield); mp 167.8–168.2 °C (CH_2Cl_2–PE) [lit.[7] 168–169 °C].
^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.57 (s, 6H), 3.60 (s, 6H), 3.81 (s, 6H), 5.96 (s, 1H), 6.33 (s, 2H), 6.47 (s, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 41.9, 55.9 (2C), 56.5 (2C), 56.7 (2C), 98.0 (2C), 114.2 (2C), 123.6 (2C), 127.9 (2C), 130.1 (2C), 131.2, 142.5 (2C), 142.8, 148.0 (2C), 151.3 (2C).
MS (EI): *m/z* (%) 458 [M^+](100), 427 (55).

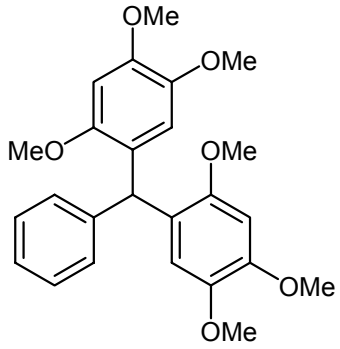


(4-Chlorophenyl)bis(4-hydroxyphenyl)methane (6b) and isomer.[8]
Chromatographic eluent: PE–AcOEt (6:4); viscous oil (0.24 g, 77% yield). Mixture of isomers (*p,p* and *o,p*, the former always prevalent) not completely separable.
^{1}H NMR (200 MHz, CD_3OD): δ = 5.25 (s, 1H) (*p,p*), 5.71 (s, 1H) (*o,p*), 6.63 (d, *J* = 8.6 Hz, 4H), 6.79 (d, *J* = 8.4 Hz, 4H), 6.94 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.6 Hz, 2H).
MS (EI): *m/z* (%) 310 [M^+](100), 275 (40), 217 (40), 199 (70), 181 (80) (*p,p* isomer); 310 [M^+](40), 181 (100), 275 (30), 217 (35) (*o,p* isomer).

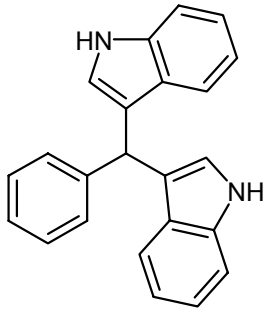
[7] P. Thirupathi and S. S. Kim, *J. Org. Chem*., **2010**, 75, 5240.
[8] N. Mibu, K. Yokomizo, M. Uyeda and K. Sumoto, *Chem. Pharm. Bull.*, **2003**, *51*, 1325.



(4-Chlorophenyl)bis(1-methyl-3-indolyl)methane (6c).[9]
Chromatographic eluent: PE–CH_2Cl_2 (4:6); white solid (0.38 g, quantitative yield); mp 206–207 (CH_2Cl_2–PE) [lit.[9] 208–209 °C].
^{1}H NMR (200 MHz, CD_3CN): δ = 3.64 (s, 6H), 5.83 (s, 1H), 6.49 (s, 2H), 6.95–7.02 (m, 2H), 7.14–7.35 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 32.5 (2C), 39.3, 109.0 (2C), 117.6 (2C), 118.6 (2C), 119.8 (2C), 121.4 (2C), 127.1 (2C), 128.1 (2C), 128.2, (2C) 129.9 (2C), 131.4, 137.3 (2C), 142.9.



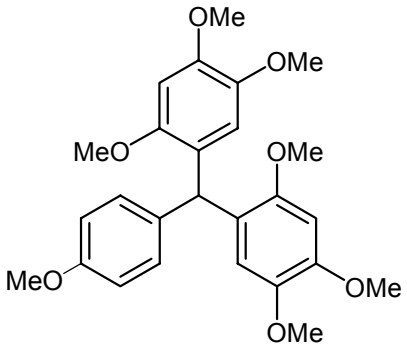
bis(2,4,5-Trimethoxyphenyl)phenylmethane (7a).[7]
Chromatographic eluent: PE–AcOEt (7:3); white solid (0.39 g, 93% yield); mp 129.9–130.5 °C (CH_2Cl_2–PE) [lit.[7] 126–127 °C].
^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.57 (s, 6H), 3.60 (s, 6H), 3.82 (s, 6H), 6.02 (s, 1H), 6.37 (s, 2H), 6.48 (s, 2H), 6.95–7.05 (m, 2H), 7.10–7.22 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 42.3, 55.9 (2C), 56.4 (2C), 56.8 (2C), 98.2 (2C), 114.3 (2C), 124.3 (2C), 125.6, 127.8 (2C), 128.8 (2C), 142.5 (2C), 144.1, 147.8 (2C), 151.4 (2C).
MS (EI): *m/z* (%) 424 [M^+] (100), 393 (50).



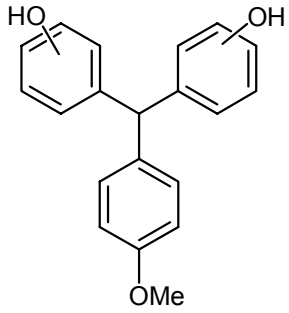
bis(3-Indolyl)phenylmethane (7b).[7]

[9] J.-T. Li, M.-X. Sun, G.-Y. He and X.-Y. Xu, *Ultrason. Sonochem.*, **2011**, *18*, 412.

Chromatographic eluent: PE–AcOEt (8:2); light yellow solid (0.41 g, 75% yield); mp 110–112 °C (CH_2Cl_2–PE) [lit.[7] 141–142 °C].
^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.84 (s, 1H), 6.57 (d, *J* = 3.2 Hz, 2H), 6.90–7.00 (m, 2H), 7.05–7.38 (m, 11H), 7.77 (br s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 40.0, 110.9 (2C), 119.0 (2C), 119.5 (2C), 119.8 (2C), 121.7 (2C), 123.4 (2C), 126.0, 126.9 (2C), 128.0 (2C), 128.5 (2C), 136.5 (2C), 143.8.
MS (EI): *m/z* (%) 322 [M^+] (100), 245 (60).

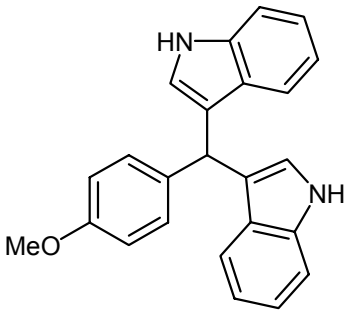


bis(2,4,5-Trimethoxyphenyl)(4-methoxyphenyl)methane (8a).[7]
Chromatographic eluent: PE–AcOEt (6:4); white solid (0.40 g, 91% yield); mp 129.9–130.2 °C (CH_2Cl_2–PE) [lit.[7] 131 °C];
^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.58 (s, 6H), 3.60 (s, 6H), 3.71 (s, 3H), 3.81 (s, 6H), 5.96 (s, 1H), 6.36 (s, 2H), 6.47 (s, 2H), 6.72 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 41.5, 55.0, 55.9 (2C), 56.5 (2C), 56.9 (2C), 98.3 (2C), 113.2 (2C), 114.3 (2C), 124.8 (2C), 129.7 (2C), 136.1, 142.5 (2C), 147.7 (2C), 151.3 (2C), 157.4.
MS (EI): *m/z* (%) 454 [M^+] (100), 423 (9).

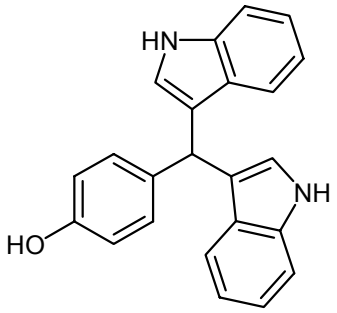


bis(4-Hydroxyphenyl)(4-methoxyphenyl)methane (8b) and isomer.[10]
Chromatographic eluent: PE–AcOEt (6:4); oil (0.25 g, 82% yield). Mixture of isomers (*p,p* and *o,p*, the former always prevalent) not completely separable.
^{1}H NMR (200 MHz, CD_3OD): δ = 3.67 (s, 3H), 5.23 (s, 1H) (*p,p*), 5.68 (s, 1H) (*o,p*), 6.53–6.92 (m, 12H).
MS (EI): *m/z* (%) 306 [M^+](100), 275 (40), 213 (60), 197 (45) (*p,p* isomer); 306 [M^+](75), 213 (40), 197 (100), 181 (80) (*o,p* isomer).

[10] N. Mibu and K. Sumoto, *Chem. Pharm. Bull*., **2000**, *48*, 1810.



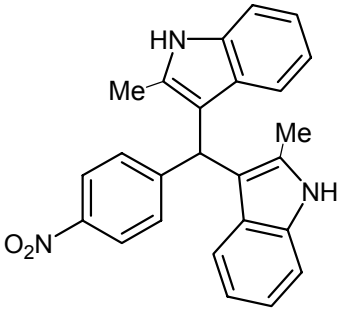
bis(3-Indolyl)(4-methoxyphenyl)methane (8c).[7]
Chromatographic eluent: PE–AcOEt (6:4); brown solid (0.31 g, 89% yield); mp 195.5–196.5 °C (CH_2Cl_2–PE) [lit.[7] 187 °C].
^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.73 (s, 3H), 5.79 (s, 1H), 6.56 (d, *J* = 1.6 Hz, 2H), 6.77 (d, *J* = 8.6 Hz, 2H), 6.96 (t, *J* = 7.8 Hz, 2H), 7.05–7.23 (m, 4H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.76 (br s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 39.1, 55.0, 110.8 (2C), 113.4 (2C), 119.0 (2C), 119.9 (4C), 121.7 (2C), 123.4 (2C), 126.9 (2C), 129.4 (2C), 136.0, 136.5 (2C), 157.7.



(4-Hydroxyphenyl)bis(3-indolyl)methane (9a).[11]
Chromatographic eluent: PE–AcOEt (4:6); red solid (0.25 g, 73% yield); mp 213–214 °C (CH_2Cl_2–PE) [lit.[11] 210–211 °C].
^{1}H NMR (200 MHz, CD_3CN): δ = 5.76 (s, 1H), 6.64–6.70 (m, 4H), 6.82–6.91 (m, 2H), 6.99–7.14 (m, 4H), 7.24–7.35 (m, 4H), 8.99 (br s, 2H); ^{13}C NMR (50 MHz, CD_3CN): δ = 38.9, 111.4 (2C), 114.6 (2C), 118.4 (2C), 119.2 (4C), 121.2 (2C), 123.3 (2C), 126.8 (2C), 129.3 (2C), 136.0, 136.7 (2C), 154.9.

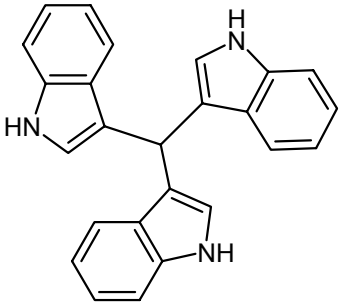
General procedure for Friedel-Crafts hydroxyalkylation in the absence of catalyst:
A mixture of aldehyde **2a** (1.0 mmol) and aromatic compound **4** (2 mmol) was stirred under heating at 100 °C in a vial until TLC analyses showed almost complete conversion of the starting reagents. The reaction mixture was then treated with CH_2Cl_2–H_2O (1:1, 20 mL). The aqueous phase was extracted with CH_2Cl_2 (2 x 20 mL). The organic extracts were dried with Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by column chromatography on a short column of silica gel. Details are reported in Table 4.

[11] H. Firouzabadi, N. Iranpoor and A. A. Jafari, *J. Mol. Catal. A: Chem.*, **2006**, *244*, 168.



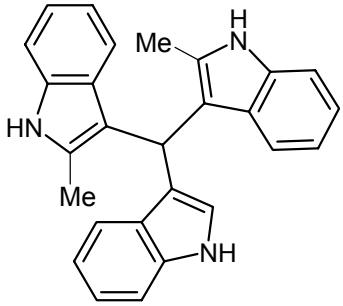
bis(2-Methyl-3-indolyl)(4-nitrophenyl)methane (5j).[12]
Chromatographic eluent: PE–AcOEt (4:6); yellow solid (0.38 g, quantitative yield); dp 239–242 °C (CH_2Cl_2–PE) [lit.[12] 241–243 °C].
^{1}H NMR (200 MHz, CD_3CN): δ = 2.05 (s, 6H), 6.06 (s, 1H), 6.69–6.81 (m, 4H), 6.88–6.96 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 9.0 Hz, 2H), 8.05 (d, *J* = 9.0 Hz, 2H), 9.01 (br s, 2H); ^{13}C NMR (50 MHz, CD_3CN): δ = 11.1 (2C), 38.9, 110.3 (2C), 111.2 (2C), 118.4 (2C), 118.5 (2C), 120.2 (2C), 123.0 (2C), 128.0 (2C), 129.6 (2C), 132.6 (2C), 135.2 (2C), 146.2, 152.5.

General procedure for trisindolylmethane 11a–c synthesis:
A mixture of 3-formylindole **2f** (0.15 g, 1.0 mmol), aromatic compound **4** (2.2 mmol) and *o*-benzenedisulfonimide (**1**, mol% as in Table 5) in EtOH (2 mL) was stirred at r.t. in a vial until TLC analyses showed almost complete conversion of **2f**. The reaction mixture was then treated with CH_2Cl_2–H_2O (1:1, 20 mL). The aqueous phase was extracted with CH_2Cl_2 (2 x 20 mL). The organic extracts were dried with Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by column chromatography on a short column of silica gel; eluent: PE–AcOEt (6:4).

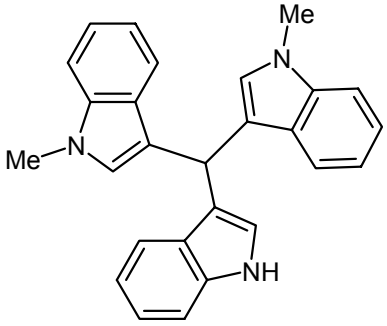


Tris(3-indolyl)methane (11a).[13]
Chromatographic eluent: PE–AcOEt (4:6); light orange solid (0.33 g, 92% yield); dp 229–234 °C (Acetone–PE) [lit.[13] 240 °C];
^{1}H NMR (200 MHz, CD_3CN): δ = 6.08 (m, 1H), 6.80–6.90 (m, 6H), 6.95–7.08 (m, 3H), 7.27–7.40 (m, 6H), 9.07 (br s, 3H); ^{13}C NMR (50 MHz, CD_3CN): δ = 31.0, 111.1 (3C), 118.3 (3C), 118.7 (3C), 119.2 (3C), 121.1 (3C), 123.0 (3C), 126.8 (3C), 136.7 (3C).

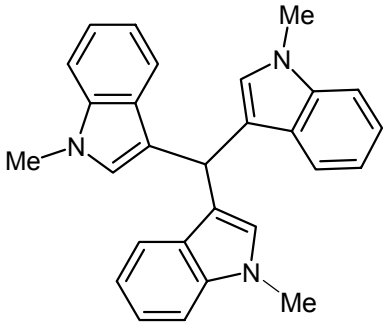
[12] A. Hasaninejad, A. Zare, H. Sharghi, K. Niknam and M. Shekouhy, *Arkivoc*, **2007**, (*xiv*), 39.
[13] A. Hazra, P. Paira, K. B. Sahu, S. Banerjee and N. B. Mondal, *Catal. Commun*., **2008**, *9*, 1681.



Bis(2-methyl-3-indolyl)(3-indolyl)methane (11b).[13]
Chromatographic eluent: PE–AcOEt (4:6); orange solid (0.28 g, 72% yield); dp 250–255 °C (Acetone–PE) [lit.[13] 260–262 °C].
^{1}H NMR (200 MHz, DMSO-d_6): δ = 2.04 (s, 6H), 5.96 (s, 1H), 6.50–6.67 (m, 3H), 6.69–6.87 (m, 3H), 6.90–7.00 (m, 3H), 7.05–7.15 (m, 3H), 7.25–7.30 (m, 1H), 10.57 (br s, 3H); ^{13}C NMR (50 MHz, DMSO-d_6): δ = 12.1, 30.5, 110.4, 111.6, 112.9 118.0, 118.3, 118.7, 119.2, 119.6, 121.1, 123.5, 127.5, 128.6, 131.5, 135.2, 136.8.



Bis(1-methyl-3-indolyl)(3-indolyl)methane (11c).[14]
Chromatographic eluent: PE–AcOEt (4:6); orange solid (0.35 g, 90% yield); dp 218–223 °C (CH_2Cl_2–PE) [lit.[14] 219–220 °C];
^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.60 (s, 6H), 6.12 (s, 1H), 6.58 (s, 2H), 6.69 (d, *J* = 2.2 Hz, 1H), 6.90–7.00 (m, 3H), 7.11–7.31 (m, 6H), 7.43–7.48 (m, 3H), 7.76 (br s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 30.1, 32.5, 108.8, 110.8, 117.8, 118.2 118.8, 119.6, 120.0, 121.0, 121.5, 123.1, 127.0, 127.3, 127.8, 136.5, 137.2.



Tris(1-methyl-3-indolyl)methane (11d).[13]

[14] H. Koshima and W. Matsusaka, *J. Heterocycl. Chem*., **2002**, *39*, 1089.

Title product was isolated when **2f** and 1-methylindole (**4g**) were reacted in the presence of OBS 10 mol%. The immediate formation of two products was observed: the expected TIM **11c** and the symmetric TIM **11d**. The reaction was heated to 50 °C and stopped after 24 h. After usual work-up and chromatographic purification, TIM **11d** was obtained as orange solid (0.16 g, 41% yield). GC and GC-MS analyses confirmed indole (**4f**) formation in the reaction mixture (MS (EI): *m/z* (%) 117 [M^+] (100), 90 (45)).
Dp 244 °C (CH_2Cl_2–PE) [lit.[13] 255–257 °C].
^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.60 (s, 9H), 6.09 (s, 1H), 6.57 (s, 3H), 6.93–6.99 (m, 3H), 7.13–7.22 (m, 6H), 7.40–7.48 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 32.5, 108.8, 118.0, 118.2, 120.0, 121.0, 127.3, 127.8, 137.2.