

## **Supporting Information**

### **Dual-Reagent Catalysis within Ir-Sn Domain: Highly Selective Alkylation of Arenes and Heteroarenes with Aromatic Aldehydes**

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## **1. General methods:**

All preparations and manipulations were performed under a dry, oxygen-free argon atmosphere using standard vacuum lines and Schlenk techniques. All solvents, used for the synthesis, were dried and distilled by standard methods and previously deoxygenated in the vacuum line. Pre-coated silica gel 60F<sub>254</sub> was used for thin layer chromatography and silica gel 60-120 mesh was used for column chromatography. IrCl<sub>3</sub>.xH<sub>2</sub>O, 1,5-cyclooctadiene and tin tetrachloride were commercially available. All mono and bimetallic transition metal complexes were synthesized according to the literature procedure.<sup>1</sup>

<sup>1</sup>H (200 MHz) and <sup>13</sup>C NMR (54.6 MHz) spectra were recorded on 200 MHz spectrometer at 298 K. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (in <sup>1</sup>H NMR spectra δ<sub>H</sub> = 2.49 ppm for DMSO-d<sub>6</sub> and 7.26 ppm for CDCl<sub>3</sub> and in <sup>13</sup>C NMR spectra δ<sub>C</sub> = 39.52 ppm for DMSO-d<sub>6</sub> and 77.0 ppm for CDCl<sub>3</sub>). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constant (Hz). Melting points are uncorrected.

### **2.1 General procedure to study the catalytic reactivity of “Tm-Sn” bimetallic combinations in the bisarylation of aldehyde (refer to Scheme 1 and Table 1)**

A 10-mL Schlenk flask equipped with a magnetic bar, was charged with low valent late transition metal organometallic complex (0.01 mmol), along with SnCl<sub>4</sub> (0.04 mmol) and anisole (3 mmol). The flask was degassed with argon and placed into a constant temperature bath at 90 °C. After the mixture was stirred vigorously for 5 min, 4-nitrobenzaldehyde (1 mmol) was added to it, and the reaction was allowed to continue at 90 °C for 1.5 h. After completion the reaction mixture was quenched with aqueous NH<sub>4</sub>F solution, extracted with diethyl ether (10 mL) and washed with water (10 mL x 3), brine (10 mL) and dried over anhydrous MgSO<sub>4</sub>. After removing the solvent the residue was subjected to silica gel column chromatography (60-120 mesh, 3% ethylacetate in pet ether) to yield the product.

### **2.2 General procedure to study the catalytic reactivity of “Ir-LA” bimetallic combinations in the bisarylation of aldehyde (refer to Table 2)**

The procedure as in section 2.1 was followed for the reaction of 4-nitrobenzaldehyde (1 mmol), and anisole (3 mmol) with catalytic [Ir(COD)Cl]<sub>2</sub> (0.01 mmol) and Lewis acid (0.04 mmol). A blank reaction was also performed in each case with catalytic Lewis acid but in the absence of [Ir(COD)Cl]<sub>2</sub>.

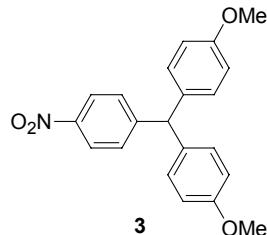
### **2.3 FT-IR and $^{13}\text{C}$ -NMR Studies on Aldehyde Interaction:**

The carbonyl stretching frequency ( $\nu$ ,  $\text{cm}^{-1}$ ) of 4-methylbenzaldehyde (**A**) appeared at  $1700\text{ cm}^{-1}$  (neat or solution), and the  $^{13}\text{C}$  NMR signal ( $\delta$ , ppm) of -CHO appeared at  $191.12\text{ ppm}$  (in  $\text{CDCl}_3$ ), and  $190.24\text{ ppm}$  (in  $\text{C}_6\text{D}_6$ ). Addition of  $\text{SnCl}_4$  or a combination of  $\text{Tm-SnCl}_4$  caused a lowering in the carbonyl frequency, and downfield shift of the -CHO resonance. The corresponding shifts ( $\Delta\nu$ ,  $\text{cm}^{-1}$ , and  $\Delta\delta$ , ppm) are shown in the Table below.

#	Compound/Combination	$\Delta\nu$ , $\text{cm}^{-1}$	$\Delta\delta$ , ppm
1.	4-methylbenzaldehyde ( <b>A</b> )	0	0
2.	<b>A</b> + $\text{SnCl}_4$	111	6.62
3.	<b>A</b> + Complex <b>27</b>	102	0.52
4	<b>A</b> + $[\text{Ir}(\text{COD})\text{Cl}]_2/4\text{SnCl}_4$	112	0.79
5.	<b>A</b> + $\text{IrCl}(\text{CO})(\text{PPh}_3)_2/4\text{SnCl}_4$	109	-
6.	<b>A</b> + $\text{RhCl}(\text{CO})(\text{PPh}_3)_2/4\text{SnCl}_4$	105	-

**2.4 Spectroscopic & Analytical Data of Products [For known compounds CAS registry no. & Lit. Ref. are also given]:**

All products gave satisfactory spectral and analytical data and were compared with authentic samples wherever possible.



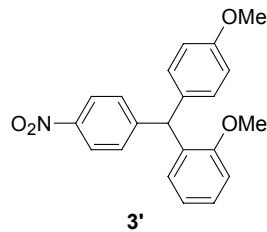
[128527-22-0]<sup>2</sup>

$\delta_{\text{H}}$ (200 MHz,  $\text{CDCl}_3$ ) 3.79 (6H, s, 2  $\text{OCH}_3$ ), 5.53 (1H, s,  $\text{CH}$ ), 6.84 (4H, d,  $J = 8.7$  Hz,  $\text{CH}$  aromat.), 6.99 (4H, d,  $J = 8.7$  Hz,  $\text{CH}$  aromat.), 7.26 (2H, d,  $J = 8.6$  Hz,  $\text{CH}$  aromat.), 8.13 (2H, d,  $J = 8.6$  Hz,  $\text{CH}$  aromat.).

$\delta_{\text{C}}$ (54.6 MHz,  $\text{CDCl}_3$ ) 54.9, 55.2, 113.9, 123.4, 130.0, 130.1, 134.7, 146.3, 152.3, 158.3.

HRMS calcd for  $\text{C}_{21}\text{H}_{19}\text{NO}_4 + \text{H}^+$  350.1392 found 350.1384.

Anal. ( $\text{C}_{21}\text{H}_{19}\text{NO}_4$ ) calcd, C: 72.18, H: 5.48 N: 4.01; found, C: 72.29, H: 5.50 N: 4.03.

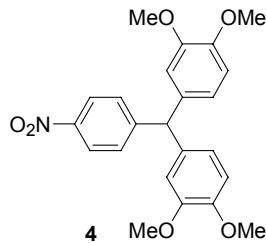


$\delta_{\text{H}}$ ( $\text{CDCl}_3$ ) 3.71 (3H, s,  $\text{OCH}_3$ ), 3.79 (3H, s,  $\text{OCH}_3$ ), 5.91 (1H, s,  $\text{CH}$ ), 6.77-7.00 (8H, m,  $\text{CH}$  aromat.), 7.23 (2H, d,  $J = 8.8$  Hz,  $\text{CH}$  aromat.), 8.11 (2H, d,  $J = 8.8$  Hz,  $\text{CH}$  aromat.).

$\delta_{\text{C}}$ ( $\text{CDCl}_3$ ) 48.9, 55.1, 55.4, 110.7, 113.8, 120.4, 123.3, 128.1, 129.8, 129.9, 130.3, 131.3, 134.1, 146.3, 152.3, 156.8, 158.2.

HRMS calcd for  $\text{C}_{21}\text{H}_{19}\text{NO}_4 + \text{H}^+$  350.1392 found 350.1375.

Anal. ( $\text{C}_{21}\text{H}_{19}\text{NO}_4$ ) calcd, C: 72.18, H: 5.48 N: 4.01; found, C: 72.31, H: 5.60 N: 4.09.

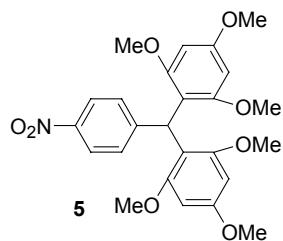


[494868-45-0]<sup>3</sup>

$\delta_H$ (CDCl<sub>3</sub>) 3.77 (6H, s, 2 OCH<sub>3</sub>), 3.87 (6H, s, 2 OCH<sub>3</sub>), 5.52 (1H, s, CH), 6.52-6.63 (4H, m, CH aromat.), 6.80 (2H, d, *J* = 8.2 Hz, CH aromat.), 7.28 (2H, d, *J* = 8.4 Hz, CH aromat.), 8.14 (2H, d, *J* = 8.4 Hz, CH aromat.).

$\delta_C$ (CDCl<sub>3</sub>) 55.5, 55.7, 110.8, 112.3, 121.2, 123.3, 129.9, 134.8, 146.3, 147.7, 148.8, 151.9.

Anal. (C<sub>23</sub>H<sub>23</sub>NO<sub>6</sub>) calcd, C: 65.46, H: 5.66 N: 3.42; found, C: 65.29, H: 5.78 N: 3.31.



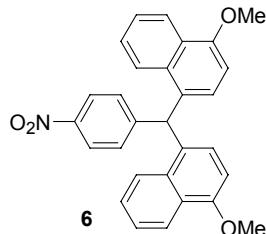
[54921-80-1]<sup>4</sup>

$\delta_H$ (CDCl<sub>3</sub>) 3.52 (12H, s, 4 OCH<sub>3</sub>), 3.79 (6H, s, 2 OCH<sub>3</sub>), 6.10 (4H, s, CH aromat.), 6.26 (1H, s, CH), 7.16 (2H, d, *J* = 8.6 Hz, CH aromat.), 8.01 (2H, d, *J* = 8.6 Hz, CH aromat.).

$\delta_C$ (CDCl<sub>3</sub>) 37.2, 55.1, 55.8, 91.5, 112.2, 122.4, 128.4, 145.1, 154.9, 159.6, 159.7.

ESI-MS: for C<sub>25</sub>H<sub>27</sub>NO<sub>8</sub> [M], [M+H]<sup>+</sup> = 470.17.

Anal. (C<sub>25</sub>H<sub>27</sub>NO<sub>8</sub>) calcd, C: 63.94, H: 5.80 N: 2.98; found, C: 64.12, H: 5.94 N: 3.07.

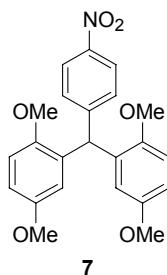


$\delta_H$ (CDCl<sub>3</sub>) 3.96 (6H, s, 2 OCH<sub>3</sub>), 6.63 (2H, d, *J* = 8 Hz, CH aromat.), 6.73 (2H, d, *J* = 8 Hz, CH aromat.), 6.81 (1H, s, CH), 7.29-7.47 (6H, m, CH aromat.), 7.79 (2H, d, *J* = 7.7 Hz, CH aromat.), 8.12 (2H, d, *J* = 8.7 Hz, CH aromat.), 8.33 (2H, d, *J* = 8.7 Hz, CH aromat.).

$\delta_C$ (CDCl<sub>3</sub>) 48.5, 55.4, 103.0, 122.7, 123.5, 123.6, 125.1, 126.1, 126.9, 127.8, 130.3, 130.5, 132.3, 146.6, 152.2, 154.8.

HRMS calcd for C<sub>29</sub>H<sub>23</sub>NO<sub>4</sub> + H<sup>+</sup> 450.1705 found 450.1704.

Anal. ( $C_{29}H_{23}NO_4$ ) calcd, C: 77.48, H: 5.16 N: 3.12; found, C: 77.33, H: 5.31 N: 3.24.



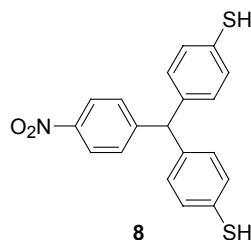
[353750-75-1]<sup>5</sup>

$\delta_H$ (CDCl<sub>3</sub>) 3.64 (6H, s, 2 OCH<sub>3</sub>), 3.67 (6H, s, 2 OCH<sub>3</sub>), 6.17 (1H, s, CH), 6.35 (2H, d, <sup>4</sup>J = 2.9 Hz, CH aromat.), 6.69- 6.84 (4H, m, CH aromat.), 7.20 (2H, d, J = 8.7 Hz, CH aromat.), 8.09 (2H, d, J = 8.7 Hz, CH aromat.).

$\delta_C$ (CDCl<sub>3</sub>) 43.7, 55.4, 56.1, 111.2, 111.8, 117.1, 123.2, 129.8, 131.9, 146.2, 151.4, 151.9, 153.4.

ESI-MS: for C<sub>23</sub>H<sub>23</sub>NO<sub>6</sub> [M], [M+H]<sup>+</sup> = 410.21.

Anal. (C<sub>23</sub>H<sub>23</sub>NO<sub>6</sub>) calcd, C: 65.46, H: 5.66 N: 3.42; found, C: 65.61, H: 5.47 N: 3.28.

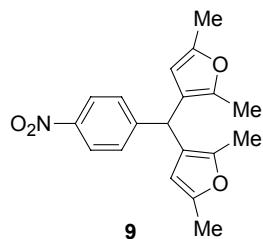


$\delta_H$ (CDCl<sub>3</sub>) 5.43 (1H, s, CH), 7.22-7.37 (8H, m, CH aromat.), 7.44 (2H, d, J = 8.7 Hz, CH aromat.), 8.09 (2H, d, J = 8.7 Hz, CH aromat.).

$\delta_C$ (CDCl<sub>3</sub>) 59.7, 123.6, 128.5, 128.7, 129.0, 133.1, 133.2, 147.1, 147.2.

ESI-MS: for C<sub>19</sub>H<sub>15</sub>NO<sub>2</sub>S<sub>2</sub> [M], [M-H]<sup>-</sup> = 352.01.

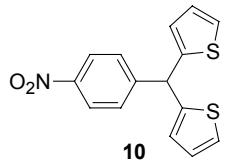
Anal. (C<sub>19</sub>H<sub>15</sub>NO<sub>2</sub>S<sub>2</sub>) calcd, C: 64.58, H: 4.28 N: 3.96; found, C: 64.74, H: 4.45 N: 3.79.



$\delta_H$ (CDCl<sub>3</sub>) 2.13 (6H, s, 2 CH<sub>3</sub>), 2.20 (6H, s, 2 CH<sub>3</sub>), 4.99 (1H, s, CH), 5.66 (2H, s, CH heteroaromat.), 7.33 (2H, d, J = 8.7 Hz, CH aromat.), 8.12 (2H, d, J = 8.7 Hz, CH aromat.).

$\delta_C$ (CDCl<sub>3</sub>) 11.6, 13.4, 37.9, 106.8, 120.6, 123.4, 128.9, 145.7, 146.3, 149.7, 151.7.

Anal. (C<sub>19</sub>H<sub>19</sub>NO<sub>4</sub>) calcd, C: 70.14, H: 5.89 N: 4.31; found, C: 69.94, H: 5.66 N: 3.83.

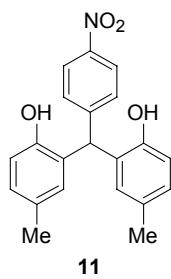


$\delta_{\text{H}}(\text{CDCl}_3)$  5.97 (1H, s, CH), 6.83 (2H, d,  $J = 2.9$  Hz, CH heteroaromat.), 6.97 (2H, dd,  $J = 2.9, 4.1$  Hz, CH heteroaromat.), 7.26 (2H, d,  $J = 4.1$  Hz, CH heteroaromat.), 7.46 (2H, d,  $J = 8.5$  Hz, CH aromat.), 8.18 (2H, d,  $J = 8.5$  Hz, CH aromat.).

$\delta_{\text{C}}(\text{CDCl}_3)$  47.0, 123.8, 125.3, 126.5, 126.8, 129.2, 145.5, 146.9, 150.7.

HRMS calcd for  $\text{C}_{15}\text{H}_{11}\text{NO}_2\text{S}_2 + \text{H}^+$  302.0309 found 302.0323.

Anal. ( $\text{C}_{15}\text{H}_{11}\text{NO}_2\text{S}_2$ ) calcd, C: 59.80, H: 3.68; found, C: 59.97, H: 3.56.

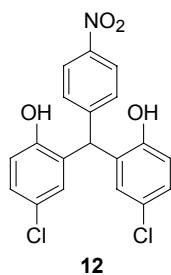


[54764-80-6]<sup>6</sup>

$\delta_{\text{H}}(\text{CDCl}_3 + \text{DMSO-d}_6)$  1.75 (6H, s,  $\text{CH}_3$ ), 3.53 (2H, br s, OH), 5.76 (1H, s, CH), 6.13 (2H, s, CH aromat.), 6.32 (2H, d,  $J = 8.0$  Hz, CH aromat.), 6.45 (2H, d,  $J = 8.0$  Hz, CH aromat.), 6.87 (2H, d,  $J = 8.6$  Hz, CH aromat.), 7.68 (2H, d,  $J = 8.6$  Hz, CH aromat.).

$\delta_{\text{C}}(\text{DMSO-d}_6)$  20.4, 43.1, 115.0, 123.2, 126.9, 127.9, 128.4, 130.0, 145.6, 152.6, 152.9.

Anal. ( $\text{C}_{21}\text{H}_{19}\text{NO}_4$ ) calcd, C: 72.18, H: 5.48 N: 4.01; found, C: 71.98, H: 5.69 N: 4.21.

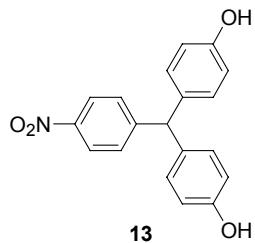


$\delta_{\text{H}}(\text{CDCl}_3 + \text{DMSO-d}_6)$  4.91 (2H, br s, 2 OH), 6.05 (1H, s, CH), 6.69 (2H, d,  ${}^4J = 2.5$  Hz, CH aromat.), 6.79 (2H, d,  $J = 8.7$  Hz, CH aromat.), 7.04 (2H, dd,  $J = 8.7$  Hz,  ${}^4J = 2.5$  Hz, CH aromat.), 7.26 (2H, d,  $J = 8.8$  Hz, CH aromat.), 8.11 (2H, d,  $J = 8.8$  Hz, CH aromat.).

$\delta_{\text{C}}(\text{CDCl}_3 + \text{DMSO-d}_6)$  43.3, 116.2, 122.6, 122.9, 127.0, 128.7, 129.4, 129.7, 145.7, 150.3, 153.1.

ESI-MS: for  $\text{C}_{19}\text{H}_{13}\text{Cl}_2\text{NO}_4$  [M],  $[\text{M}-\text{H}]^- = 387.98$ .

Anal. ( $\text{C}_{19}\text{H}_{13}\text{Cl}_2\text{NO}_4$ ) calcd, C: 58.48, H: 3.36 N: 3.59; found, C: 58.83, H: 3.28 N: 3.64.



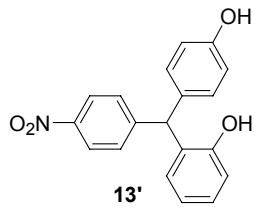
[63647-37-0]<sup>7</sup>

$\delta_{\text{H}}$ (CDCl<sub>3</sub>) 3.14 (2H, br s, OH), 5.49 (1H, s, CH), 6.77 (4H, d, *J* = 8.2 Hz, CH aromat.), 6.92 (4H, d, *J* = 8.2 Hz, CH aromat.), 7.25 (2H, d, *J* = 8.6 Hz, CH aromat.), 8.12 (2H, d, *J* = 8.6 Hz, CH aromat.).

$\delta_{\text{C}}$ (CDCl<sub>3</sub> + DMSO-d<sub>6</sub>) 55.7, 116.5, 124.3, 131.0, 131.2, 134.3, 147.1, 154.2, 157.2.

ESI-MS: for C<sub>19</sub>H<sub>15</sub>NO<sub>4</sub> [M], [M-H]<sup>-</sup> = 320.06.

Anal. (C<sub>19</sub>H<sub>15</sub>NO<sub>4</sub>) calcd, C: 71.06, H: 4.71 N: 4.36; found, C: 71.31, H: 4.54 N: 4.22.



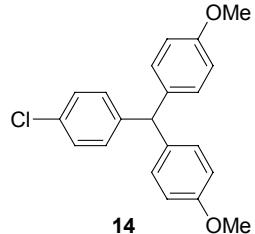
[63118-62-7]<sup>8</sup>

$\delta_{\text{H}}$ (CDCl<sub>3</sub> + DMSO-d<sub>6</sub>) 4.04 (2H, br s, 2 OH), 5.82 (1H, s, CH), 6.69-6.87 (8H, m, CH aromat), 7.22 (2H, d, *J* = 8.6 Hz, CH aromat.), 8.03 (2H, d, *J* = 8.6 Hz, CH aromat.).

$\delta_{\text{C}}$ (CDCl<sub>3</sub> + DMSO-d<sub>6</sub>) 48.3, 114.7, 118.5, 122.4, 127.0, 129.0, 129.2, 129.4, 129.6, 132.2, 145.7, 152.4, 154.1, 155.3, 162.4.

ESI-MS: for C<sub>19</sub>H<sub>15</sub>NO<sub>4</sub> [M], [M-H]<sup>-</sup> = 320.06.

Anal. (C<sub>19</sub>H<sub>15</sub>NO<sub>4</sub>) calcd, C: 71.06, H: 4.71 N: 4.36; found, C: 71.29, H: 4.56 N: 4.23.

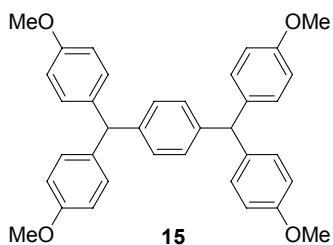


$\delta_{\text{H}}$ (CDCl<sub>3</sub>) δ = 3.79 (6H, s, 2 OCH<sub>3</sub>), 5.42 (1H, s, CH), 6.82 (4H, d, *J* = 8.7 Hz, CH aromat.), 6.99 (4H, d, *J* = 8.7 Hz, CH aromat.), 7.03 (2H, d, *J* = 8.5 Hz, CH aromat.), 7.24 (2H, d, *J* = 8.5 Hz, CH aromat.).

$\delta_{\text{C}}$ (CDCl<sub>3</sub>) 54.5, 55.2, 113.7, 128.3, 130.2, 130.6, 131.9, 135.9, 143.2, 158.1.

ESI-MS: for C<sub>21</sub>H<sub>19</sub>ClO<sub>2</sub> [M] [M+H]<sup>+</sup> = 339.10.

Anal. (C<sub>21</sub>H<sub>19</sub>ClO<sub>2</sub>) calcd, C: 74.44, H: 5.65; found, C: 74.35, H: 5.82.

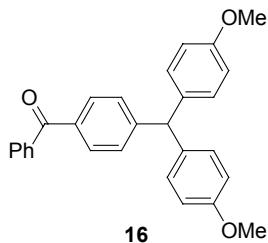


[103268-69-5]<sup>9</sup>

$\delta_{\text{H}}(\text{CDCl}_3)$  3.77 (12H, s, 4 OCH<sub>3</sub>), 5.40 (2H, s, 2 CH), 6.80 (8H, d, *J* = 8.4 Hz, CH aromat.), 6.98 (4H, s, CH aromat.), 7.01 (8H, d, *J* = 8.4 Hz, CH aromat.).

$\delta_{\text{C}}(\text{CDCl}_3)$  5.1, 54.8, 113.6, 129.0, 130.2, 136.5, 142.2, 157.9.

Anal. (C<sub>36</sub>H<sub>34</sub>O<sub>4</sub>) calcd, C: 81.47, H: 6.46; found, C: 81.27, H: 6.62.

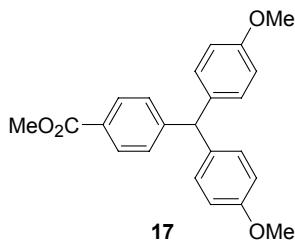


$\delta_{\text{H}}(\text{CDCl}_3)$  3.79 (6H, s, 2 OCH<sub>3</sub>), 5.52 (1H, s, CH), 6.84 (4H, d, *J* = 8.7 Hz, CH aromat.), 7.03 (4H, d, *J* = 8.7 Hz, CH aromat.), 7.22 (2H, d, *J* = 8.3 Hz, CH aromat.), 7.43-7.58 (3H, m, CH aromat.), 7.71-7.82 (4H, m, CH aromat.).

$\delta_{\text{C}}(\text{CDCl}_3)$  55.2, 113.8, 128.2, 129.2, 129.9, 130.2, 132.2, 135.5, 137.7, 149.6, 158.2, 196.3.

HRMS calcd for C<sub>28</sub>H<sub>24</sub>O<sub>3</sub> + H<sup>+</sup> 409.1804 found 409.1784.

Anal. (C<sub>28</sub>H<sub>24</sub>O<sub>3</sub>) calcd, C: 82.32, H: 5.93; found, C: 82.17, H: 6.05.

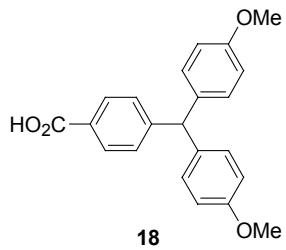


$\delta_{\text{H}}(\text{CDCl}_3)$  3.78 (6H, s, 2 OCH<sub>3</sub>), 3.89 (3H, s, COOCH<sub>3</sub>), 5.49 (1H, s, CH), 6.82 (4H, d, *J* = 8.7 Hz, CH aromat.), 6.99 (4H, d, *J* = 8.7 Hz, CH aromat.), 7.17 (2H, d, *J* = 8.2 Hz, CH aromat.), 7.94 (2H, d, *J* = 8.2 Hz, CH aromat.).

$\delta_{\text{C}}(\text{CDCl}_3)$  52.0, 55.2, 113.8, 128.1, 129.3, 129.6, 130.2, 135.6, 150.0, 158.2, 167.0.

HRMS calcd for C<sub>23</sub>H<sub>22</sub>O<sub>4</sub> + H<sup>+</sup> 363.1596 found 363.1601.

Anal. (C<sub>23</sub>H<sub>22</sub>O<sub>4</sub>) calcd, C: 76.21, H: 6.12; found, C: 76.38, H: 6.27.



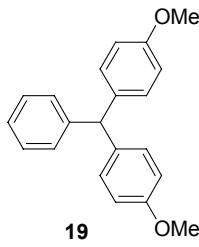
[166110-06-1]<sup>10</sup>

$\delta_H$ (CDCl<sub>3</sub>) 3.79 (6H, s, 2 OCH<sub>3</sub>), 5.51 (1H, s, CH), 6.83 (4H, d, *J* = 8.7 Hz, CH aromat.), 7.00 (4H, d, *J* = 8.7 Hz, CH aromat.), 7.21 (2H, d, *J* = 8.3 Hz, CH aromat.), 8.01 (2H, d, *J* = 8.3 Hz, CH aromat.).

$\delta_C$ (CDCl<sub>3</sub>) 55.2, 113.8, 127.3, 129.4, 130.1, 130.2, 135.4, 151.1, 158.2, 172.1.

ESI-MS: for C<sub>22</sub>H<sub>20</sub>O<sub>4</sub> [M] [M-H]<sup>-</sup> = 347.08.

Anal. (C<sub>22</sub>H<sub>20</sub>O<sub>4</sub>) calcd, C: 75.83, H: 5.79; found, C: 75.60, H: 5.98.

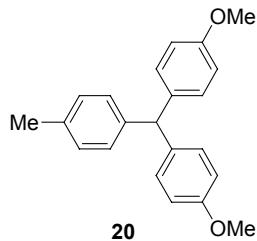


[7500-67-7]<sup>11</sup>

$\delta_H$ (CDCl<sub>3</sub>) 3.78 (6H, s, 2 OCH<sub>3</sub>), 5.45 (1H, s, CH), 6.82 (4H, d, *J* = 8.7 Hz, CH aromat.), 7.02 (4H, d, *J* = 8.7 Hz, CH aromat.), 7.08-7.28 (5H, m, CH aromat.).

$\delta_C$ (CDCl<sub>3</sub>) 48.8, 55.2, 113.7, 126.2, 128.3, 129.3, 130.3, 136.5, 144.6, 158.0.

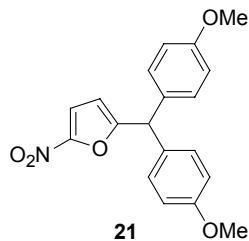
Anal. (C<sub>21</sub>H<sub>20</sub>O<sub>2</sub>) calcd, C: 82.85, H: 6.63; found, C: 83.02, H: 6.79.



$\delta_H$ (CDCl<sub>3</sub>) 2.33 (3H, s, CH<sub>3</sub>), 3.79 (6H, s, 2 OCH<sub>3</sub>), 5.43 (1H, s, CH), 6.80 (4H, d, *J* = 7.8 Hz, CH aromat.), 6.97-7.12 (8H, m, CH aromat.).

$\delta_C$ (CDCl<sub>3</sub>) 20.9, 54.6, 55.2, 113.6, 128.9, 129.2, 130.2, 135.6, 136.7, 141.6, 157.9.

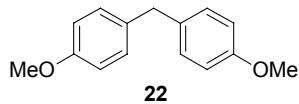
Anal. (C<sub>22</sub>H<sub>22</sub>O<sub>2</sub>) calcd, C: 82.98, H: 6.97; found, C: 83.07, H: 6.77.



$\delta_{\text{H}}(\text{CDCl}_3)$  3.83 (6H, s, 2  $\text{OCH}_3$ ), 5.40 (1H, s,  $\text{CH}$ ), 6.11 (1H, d,  $J = 3.8\text{Hz}$ ,  $\text{CH}$  heteroaromat.), 6.86 (4H, d,  $J = 8.7\text{ Hz}$ ,  $\text{CH}$  aromat.), 7.04 (4H, d,  $J = 8.7\text{ Hz}$ ,  $\text{CH}$  aromat.), 7.22 (1H, d,  $J = 3.8\text{ Hz}$ ,  $\text{CH}$  heteroaromat.).

$\delta_{\text{C}}(\text{CDCl}_3)$  49.5, 55.3, 111.7, 112.6, 114.2, 129.6, 131.9, 151.8, 158.9, 161.6.

Anal. ( $\text{C}_{19}\text{H}_{17}\text{NO}_5$ ) calcd, C: 67.23, H: 5.05 N: 4.13; found, C: 67.47, H: 4.92 N: 4.29.



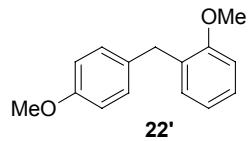
[726-18-1]<sup>12</sup>

$\delta_{\text{H}}(\text{CDCl}_3)$  3.78 (6H, s, 2  $\text{OCH}_3$ ), 3.86 (2H, s,  $\text{CH}_2$ ), 6.82 (4H, d,  $J = 8.5\text{ Hz}$ ,  $\text{CH}$  aromat.), 7.09 (4H, d,  $J = 8.5\text{ Hz}$ ,  $\text{CH}$  aromat.).

$\delta_{\text{C}}(\text{CDCl}_3)$  40.1, 55.2, 113.8, 129.7, 133.7, 157.9.

ESI-MS: for  $\text{C}_{15}\text{H}_{16}\text{O}_2$  [M]  $[\text{M}+\text{H}]^+ = 229.12$ .

Anal. ( $\text{C}_{15}\text{H}_{16}\text{O}_2$ ) calcd, C: 78.91, H: 7.07; found, C: 79.09, H: 7.31.



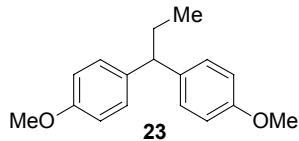
[30567-87-4]<sup>12</sup>

$\delta_{\text{H}}(\text{CDCl}_3)$  3.73 (3H, s,  $\text{OCH}_3$ ), 3.80 (3H, s,  $\text{OCH}_3$ ), 3.91 (2H, s,  $\text{CH}_2$ ), 6.79-6.90 (4H, m,  $\text{CH}$  aromat.), 7.02-7.23 (4H, m,  $\text{CH}$  aromat.).

$\delta_{\text{C}}(\text{CDCl}_3)$  34.9, 55.2, 55.3, 110.4, 113.7, 120.4, 127.3, 129.8, 130.4, 133.1, 157.3, 157.8.

ESI-MS: for  $\text{C}_{15}\text{H}_{16}\text{O}_2$  [M]  $[\text{M}+\text{H}]^+ = 229.11$ .

Anal. ( $\text{C}_{15}\text{H}_{16}\text{O}_2$ ) calcd, C: 78.91, H: 7.07; found, C: 79.02, H: 7.34.



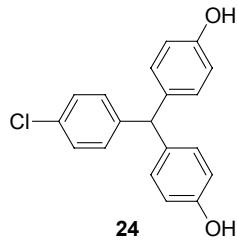
[4792-39-6]<sup>13</sup>

$\delta_H$ (CDCl<sub>3</sub>) 0.88 (3H, t, *J* = 7.2 Hz, CH<sub>2</sub>CH<sub>3</sub>), 1.96-2.07 (2H, m, CH<sub>2</sub>CH<sub>3</sub>), 3.69 (1H, t, *J* = 6.3 Hz, CH),

3.77 (6H, s, 2 OCH<sub>3</sub>), 6.85 (4H, d, *J* = 8.1 Hz, CH aromat.), 7.13 (4H, d, *J* = 8.1 Hz, CH aromat.).

$\delta_C$ (CDCl<sub>3</sub>) 12.8, 28.9, 51.5, 55.1, 113.7, 128.7, 137.7, 157.7.

Anal. (C<sub>17</sub>H<sub>20</sub>O<sub>2</sub>) calcd, C: 79.64, H: 7.87; found, C: 79.82, H: 8.01.



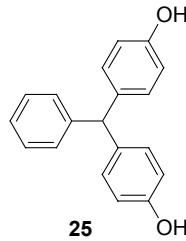
[21825-11-6]<sup>14</sup>

$\delta_H$ (CDCl<sub>3</sub>) 5.38 (1H, s, CH), 6.73 (4H, d, *J* = 8.9 Hz, CH aromat.), 6.93 (4H, d, *J* = 8.9 Hz, CH aromat.),

7.00 (2H, d, *J* = 8.4 Hz, CH aromat.), 7.24 (2H, d, *J* = 8.4 Hz, CH aromat.).

$\delta_C$ (CDCl<sub>3</sub>) 54.5, 115.2, 128.4, 130.4, 130.6, 132.0, 136.0, 143.0, 154.0.

Anal. (C<sub>19</sub>H<sub>15</sub>ClO<sub>2</sub>) calcd, C: 73.53, H: 4.87; found, C: 75.75, H: 5.01.



[4081-02-1]<sup>15</sup>

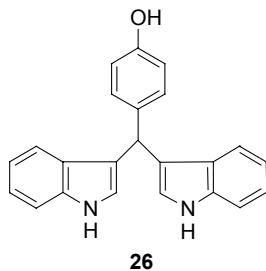
$\delta_H$ (CDCl<sub>3</sub>) 5.42 (1H, s, CH), 6.74 (4H, d, *J* = 8.2 Hz, CH aromat.), 6.96 (4H, d, *J* = 8.4 Hz, CH aromat.),

7.09 (2H, d, *J* = 7.8 Hz, CH aromat.), 7.22-7.33 (3H, m, CH aromat.).

$\delta_C$ (CDCl<sub>3</sub> + DMSO-d<sub>6</sub>) 54.8, 114.8, 125.5, 127.7, 128.8, 129.8, 134.8, 144.7, 155.0.

ESI-MS: for C<sub>19</sub>H<sub>16</sub>O<sub>2</sub> [M] [M-H]<sup>-</sup> = 275.11.

Anal. (C<sub>19</sub>H<sub>16</sub>O<sub>2</sub>) calcd, C: 82.57, H: 5.84; found, C: 82.34, H: 5.71.



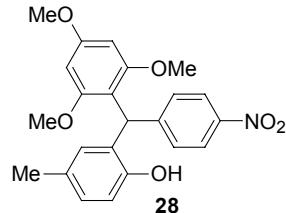
[151358-47-3]<sup>16</sup>

$\delta_H$ (CDCl<sub>3</sub>) 4.77 (1H, br s, OH), 5.74 (1H, s, CH), 6.58 (2H, s, CH aromat. of indole ring), 6.71 (2H, d, *J* = 8.4 Hz, CH aromat.), 6.88-6.96 (2H, m, CH aromat.), 7.05-7.13 (4H, m, CH aromat. of indole ring), 7.27-7.36 (4H, m, CH aromat. of indole ring), 8.45 (2H, br s, NH).

$\delta_C$ (CDCl<sub>3</sub> + DMSO-d<sub>6</sub>) 59.8, 110.8, 114.5, 117.9, 118.9, 119.1, 120.7, 123.2, 126.5, 128.9, 134.9, 136.3, 154.6.

ESI-MS: for C<sub>23</sub>H<sub>18</sub>N<sub>2</sub>O [M] [M-H]<sup>-</sup> = 337.11.

Anal. (C<sub>23</sub>H<sub>18</sub>N<sub>2</sub>O) calcd, C: 81.63, H: 5.36 N 8.28; found, C: 81.45, H: 5.52 N 8.46.

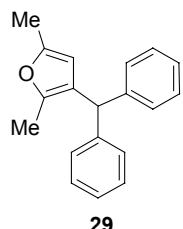


$\delta_H$ (CDCl<sub>3</sub>) 2.23 (3H, s, CH<sub>3</sub>), 3.69 (6H, s, OCH<sub>3</sub>), 3.82 (3H, s, OCH<sub>3</sub>), 6.07 (1H, s, CH), 6.19 (2H, s, CH aromat.), 6.76 (1H, d, *J* = 8.1 Hz, CH aromat.), 6.91-6.98 (2H, m, CH aromat.), 7.26 (2H, d, *J* = 8.7 Hz, CH aromat.), 8.08(2H, d, *J* = 8.7 Hz, CH aromat.).

$\delta_C$ (CDCl<sub>3</sub>) 20.6, 40.7, 55.4, 55.9, 91.9, 109.9, 116.3, 122.9, 126.6, 128.6, 128.7, 129.1, 131.9, 145.9, 150.8, 152.2, 158.3, 160.8.

ESI-MS: for C<sub>23</sub>H<sub>23</sub>NO<sub>6</sub> [M] [M-H]<sup>-</sup> = 408.12.

Anal. (C<sub>23</sub>H<sub>23</sub>NO<sub>6</sub>) calcd, C: 67.47, H: 5.66, N: 3.42; found, C: 67.59, H: 5.51, N: 3.50.



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$\delta_{\text{H}}$ (CDCl<sub>3</sub>) 2.08 (3H, s, CH<sub>3</sub>), 2.17 (3H, s, CH<sub>3</sub>), 5.19 (1H, s, CH), 5.64 (1H, s, CH heteroaromat.), 7.12-7.31 (m, 10H, CH aromat.).

$\delta_{\text{C}}$ (CDCl<sub>3</sub>) 11.7, 13.6, 47.5, 107.7, 121.8, 126.2, 128.3, 128.8, 144.1, 145.8, 149.2.

Anal. (C<sub>19</sub>H<sub>18</sub>O) calcd, C: 86.99, H: 6.92; found, C: 86.71, H: 7.01.

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## 2.6 $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of products:

