

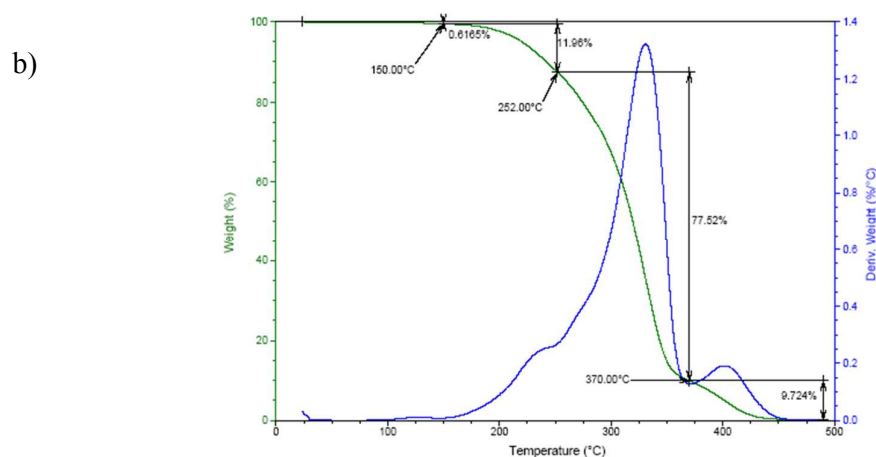
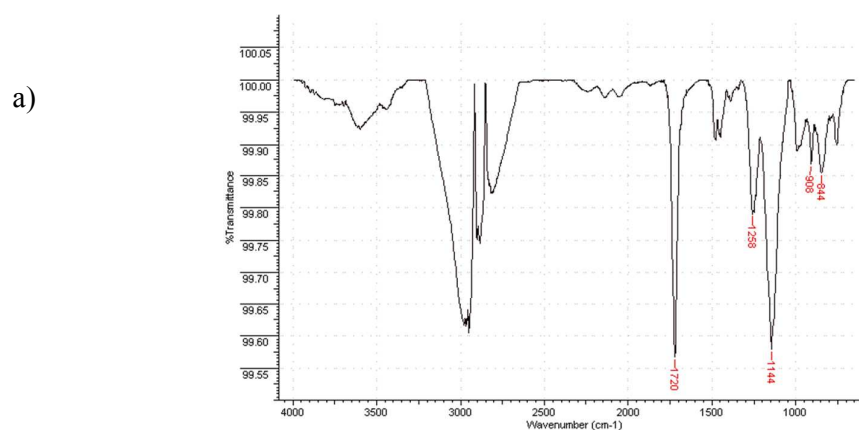
## Supporting Information

Covalent Immobilization of *Pseudomonas stutzeri* lipase on a porous polymer: an efficient biocatalyst for a scalable production of enantiopure benzoin esters under sustainable conditions.

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**Table S1.** Pore volume distribution in poly(GMA-co-HDDMA).

| Radius (nm)                       | < 5 | 5-10 | 10-15 | 15-20 | 20-30 | 30-50 | 50-100 | >100 |
|-----------------------------------|-----|------|-------|-------|-------|-------|--------|------|
| Pore Volume Distribution (vol. %) | 2   | 2    | 3     | 4     | 11    | 24    | 33     | 21   |

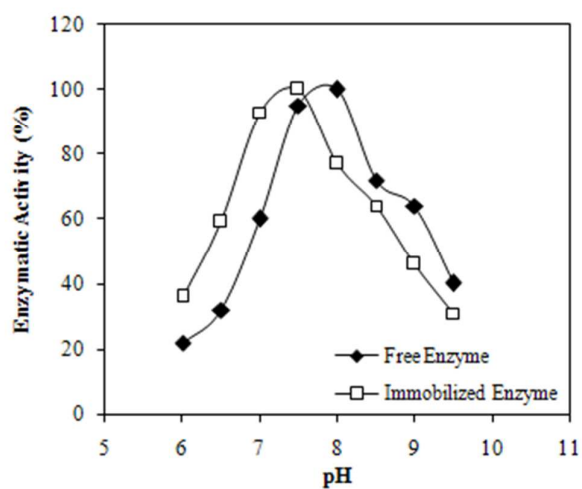


**Figure S1.** a) FT-IR spectrum of the poly(GMA-co-HDDMA); b) Termogravimetric analysis of the poly(GMA-co-HDDMA).

**Table S2.** Results of the immobilization of Lipase from *P. stutzeri* at different ratios of support/lipase.

| Entry | Support            | Derivative Code | Support (mg) | Lipase (mg) | Bound protein (%) | Loading (mg enzyme mg support <sup>-1</sup> ) | stationary effectiveness factor $\eta^a$ |
|-------|--------------------|-----------------|--------------|-------------|-------------------|-----------------------------------------------|------------------------------------------|
| 1     | Poly(GMA-co-HDDMA) | TL-PGcH-1       | 100          | 1           | 100               | 0.010                                         | 0.76                                     |
| 2     |                    | TL-PGcH-2       | 100          | 2           | 78                | 0.016                                         | 0.80                                     |
| 3     |                    | TL-PGcH-3       | 100          | 3           | 60                | 0.018                                         | 0.65                                     |
| 4     | Eupergit C         | TL-EuC          | 100          | 1           | 72                | 0.007                                         | 0.45                                     |

<sup>a</sup>Ratio of hydrolysis rate of *p*-nitrophenyl-palmitate by the immobilized enzyme compared to the same amount of native enzyme, as described.<sup>12</sup> Enzymatic activity of native lipase from *P. stutzeri* was 105 U/mg crude enzyme, equivalent to  $\eta=1$ .

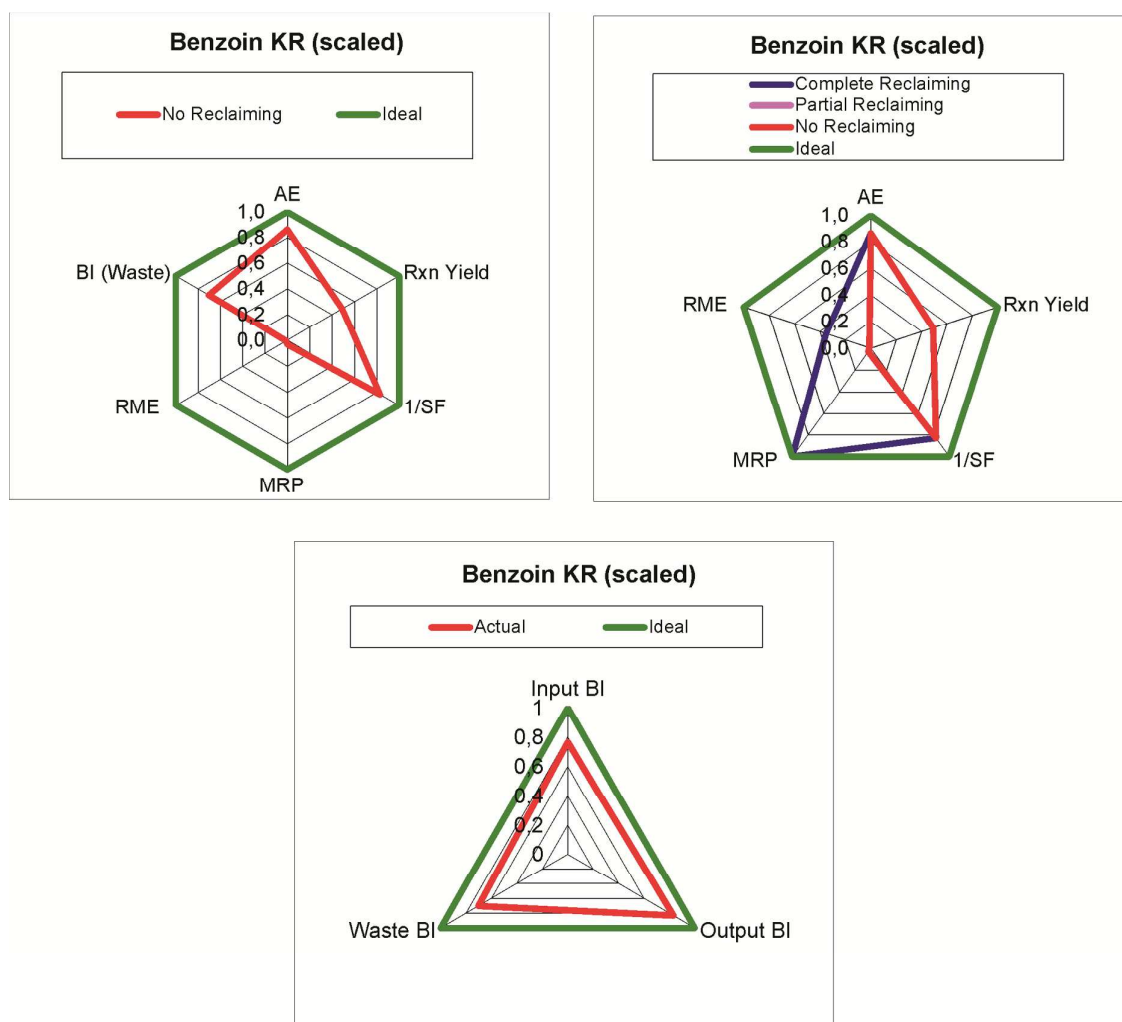


**Figure S2.** Effect of pH on the activity of free and immobilized lipase from *P. stutzeri*.

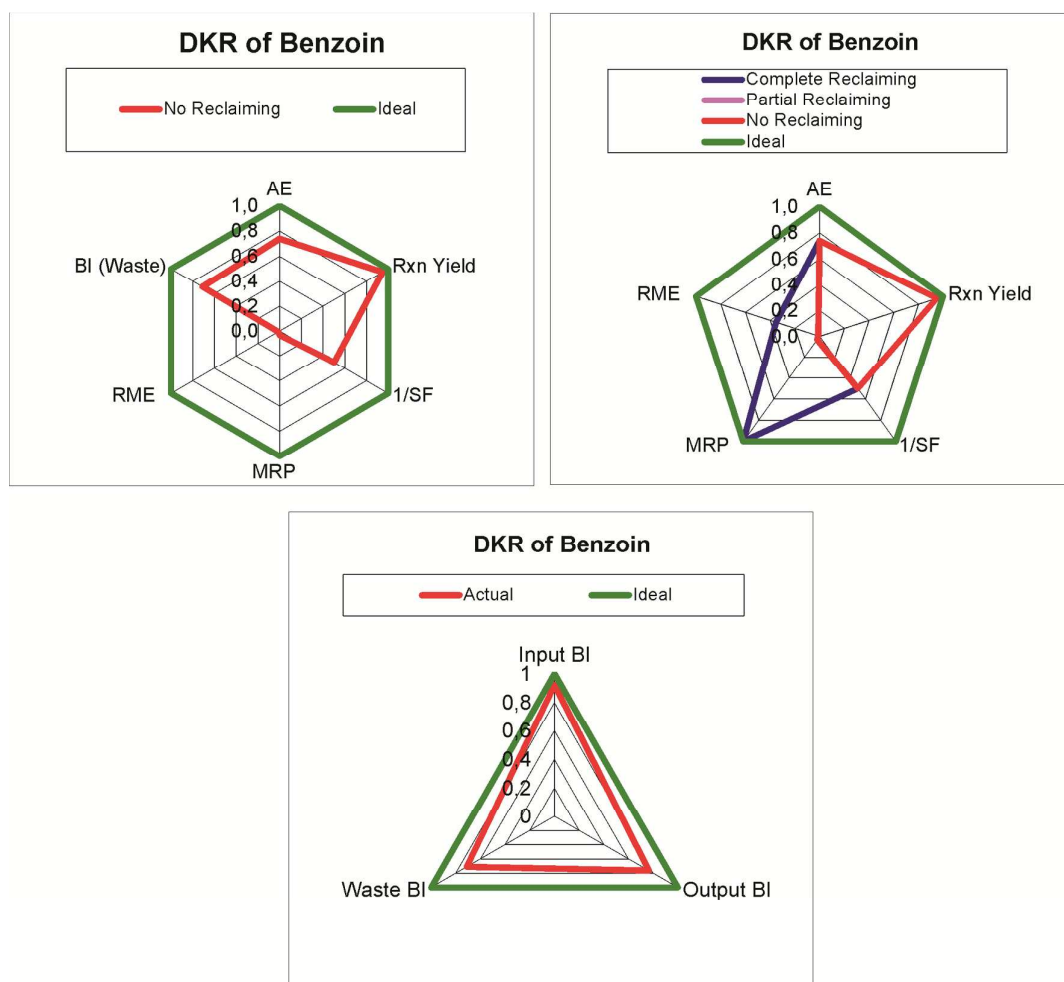
**Table S3.** Green chemistry calculations

| <i>KR scaled TL-PGc-2H</i> |                     |                    |               |       |                 |        |       |
|----------------------------|---------------------|--------------------|---------------|-------|-----------------|--------|-------|
| Raw Materials Footprint    |                     |                    |               |       |                 |        |       |
| Parameter                  | Complete Reclaiming | Partial Reclaiming | No Reclaiming | Ideal | Parameter       | Actual | Ideal |
| AE                         | 0.865               | 0.865              | 0.865         | 1     | Input BI        | 0.77   | 1     |
| Rxn Yield                  | 0.49                | 0.49               | 0.49          | 1     | Output BI       | 0.83   | 1     |
| 1/SF                       | 0.830               | 0.838              | 0.838         | 1     | Waste BI        | 0.70   | 1     |
| MRP                        | 1                   | 0.031              | 0.031         | 1     | E <sub>MW</sub> | 0.16   | 0     |
| RME                        | 0.352               | 0.011              | 0.011         | 1     |                 |        |       |
| BI (Waste)                 | 1                   | 1                  | 0.70          | 1     |                 |        |       |
| E                          | 1.8                 | 90.3               | 90.3          | 0     |                 |        |       |
| MI=(E+1)                   | 2.8                 | 91.3               | 91.3          | 1     |                 |        |       |

| <i>DKR TL-PGc-2H/Shvo's catalyst</i> |                     |                    |               |       |                 |        |       |
|--------------------------------------|---------------------|--------------------|---------------|-------|-----------------|--------|-------|
| Raw Materials Footprint              |                     |                    |               |       |                 |        |       |
| Parameter                            | Complete Reclaiming | Partial Reclaiming | No Reclaiming | Ideal | Parameter       | Actual | Ideal |
| AE                                   | 0.738               | 0.738              | 0.738         | 1     | Input BI        | 0.92   | 1     |
| Rxn Yield                            | 0.950               | 0.950              | 0.950         | 1     | Output BI       | 0.77   | 1     |
| 1/SF                                 | 0.502               | 0.502              | 0.502         | 1     | Waste BI        | 0.71   | 1     |
| MRP                                  | 1                   | 0.032              | 0.032         | 1     | E <sub>MW</sub> | 0.35   | 0     |
| RME                                  | 0.352               | 0.011              | 0.011         | 1     |                 |        |       |
| BI (Waste)                           | 1                   | 1                  | 0.71          | 1     |                 |        |       |
| E                                    | 1.8                 | 86.9               | 86.9          | 0     |                 |        |       |
| MI=(E+1)                             | 2.8                 | 87.9               | 87.9          | 1     |                 |        |       |



**Figure S3.** Plots for KR of **1a** at higher scale with TL-PGc-2H



**Figure S4.** Plots for DKR of **1a** with TL-PGc-2H

## NMR of reaction products:

### 1. (1S)-2-oxo-1,2-diphenylethyl butyrate (2a).

Colorless oil (12 mg, 90% isolated yield),  $[\alpha]_D^{20}$ : + 118.7 (c 2 CHCl<sub>3</sub>). <sup>1</sup>H-RMN (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 0.97 (t, 3H, J= 7.38 Hz), 1.71 (m, 2H, J= 7.40 Hz), 2.44 (m, 2H), 6.86 (s, 1H), 7.33 (m, 1H), 7.35 (m, 2H), 7.40 (m, 2H), 7.46 (m, 2H), 7.51 (m, 2H). <sup>13</sup>C-RMN (75.5 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 13.56, 18.35, 35.85, 77.36, 128.57, 128.74, 129.04, 133.36, 133.70, 173.10, 193.92.

### 2.2.7.2. (1S)-1,2-bis(4-methoxyphenyl)-2-oxoethyl butyrate (2b).

Colorless oil (19 mg, 86% isolated yield),  $[\alpha]_D^{20}$ : + 104.1 (c 2 CHCl<sub>3</sub>). <sup>1</sup>H-RMN (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 0.96 (t, 3H, J= 7.34 Hz), 1.70 (m, 2H, J= 7.40 Hz), 2.42 (m, 2H), 3.75 (s, 3H), 3.80 (s, 3H), 6.80 (s, 1H), 6.85 (m, 4H), 7.37 (m, 2H), 7.91 (m, 2H). <sup>13</sup>C-RMN (75.5 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 13.59, 18.36, 35.85, 55.21, 55.38, 76.68, 113.78, 114.46, 126.18, 127.55, 130.02, 131.07, 160.18, 163.60, 173.19, 192.25.

### 2.2.7.3. (1S)-1,2-bis(4-isopropylphenyl)-2-oxoethyl butyrate (2c).

Colorless oil (15 mg, 87% isolated yield),  $[\alpha]_D^{20}$ : + 101.3 (c 2 CHCl<sub>3</sub>). <sup>1</sup>H-RMN (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 0.96 (t, 3H, J= 7.38 Hz), 1.20 (d, 6H, J= 7.00 Hz), 1.21 (d, 6H, J= 7.00 Hz), 1.70 (m, 2H, J= 7.40 Hz), 2.42 (m, 2H), 2.88 (m, 2H), 6.82 (s, 1H), 7.22 (m, 4H), 7.38 (m, 2H), 7.89 (m, 2H). <sup>13</sup>C-RMN (75.5 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 13.63, 18.36, 23.58, 23.81, 33.87, 34.26, 35.91, 77.14, 126.76, 127.19, 128.66, 129.10, 131.20, 132.57, 150.00, 154.95, 173.22, 193.50.

### 2.2.7.4. (1S)-1-(4-methoxyphenyl)-2-oxo-2-phenylethyl butyrate (2d).

Colorless oil (12 mg, 80% isolated yield),  $[\alpha]_D^{20}$ : + 138.1 (c 2 CHCl<sub>3</sub>). <sup>1</sup>H-RMN (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 0.97 (t, 3H, J= 7.34 Hz), 1.37 (t, 3H, J= 7.06 Hz), 1.70 (m, 2H, J= 7.40 Hz), 2.43 (m, 2H), 3.98 (q, 2H, J= 6.99 Hz), 6.81 (s, 1H), 6.85 (m, 2H), 7.36 (m, 2H), 7.37 (m, 2H), 7.49 (m, 1H), 7.91 (m, 2H). <sup>13</sup>C-RMN (75.5 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 13.60, 14.71, 18.38, 35.88, 63.46, 77.02, 115.02, 125.44, 128.55, 128.73, 130.12, 133.26, 134.79, 159.70, 173.23, 193.96.

**2.2.7.5. (1S)-2-(4-methoxyphenyl)-2-oxo-1-phenylethyl butyrate (2e).**

Colorless oil (12.5 mg, 85% isolated yield),  $[\alpha]_D^{20}$ : + 124.9 (c 2 CHCl<sub>3</sub>). <sup>1</sup>H-RMN (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 0.96 (t, 3H, J= 7.44 Hz), 1.39 (t, 3H, J= 7.06 Hz), 1.70 (m, 2H, J= 7.44 Hz), 2.44 (m, 2H), 4.04 (q, 2H, J= 6.93 Hz), 6.83 (s, 1H), 6.84 (m, 2H), 7.33 (m, 2H), 7.34 (m, 1H), 7.45 (m, 2H), 7.91 (m, 2H). <sup>13</sup>C-RMN (75.5 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 13.60, 14.58, 18.38, 35.90, 63.73, 77.05, 114.25, 125.44, 127.35, 128.52, 128.99, 129.06, 131.13, 134.27, 163.14, 173.11, 193.96.

**2.2.7.6. (1S)-1-(3,4-dichlorophenyl)-2-oxo-2-phenylethyl butyrate (2f).**

Colorless oil (14.5 mg, 88% isolated yield),  $[\alpha]_D^{20}$ : + 102.4 (c 2 CHCl<sub>3</sub>). <sup>1</sup>H-RMN (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 0.96 (t, 3H, J= 7.34 Hz), 1.70 (m, 2H, J= 7.44 Hz), 2.43 (m, 2H), 6.79 (s, 1H), 7.27 (dd, 1H, J= 2.10, 8.20 Hz), 7.40 (m, 1H), 7.44 (m, 2H), 7.53 (m, 1H), 7.56 (m, 1H), 7.90 (m, 2H). <sup>13</sup>C-RMN (75.5 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 13.57, 18.32, 35.76, 75.70, 127.65, 128.72, 128.82, 130.32, 131.00, 133.30, 133.64, 133.83, 133.87, 134.36, 172.83, 193.31.

**2.2.7.7. (1S)-2-(3,4-dichlorophenyl)-2-oxo-1-phenylethyl butyrate (2g).**

Colorless oil (14 mg, 83% isolated yield),  $[\alpha]_D^{20}$ : + 96.0 (c 2 CHCl<sub>3</sub>). <sup>1</sup>H-RMN (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 0.97 (t, 3H, J= 7.44 Hz), 1.70 (m, 2H, J= 7.44 Hz), 2.45 (m, 2H), 6.72 (s, 1H), 7.36 (m, 1H), 7.38 (m, 2H), 7.40 (m, 1H), 7.42 (m, 2H), 7.46 (m, 1H, J= 8.39), 7.73 (dd, 1H, J= 2.10, 8.39 Hz), 8.00 (d, 1H, J= 2.10). <sup>13</sup>C-RMN (75.5 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 13.57, 18.35, 35.78, 77.29, 127.67, 128.51, 129.28, 129.57, 130.73, 132.90, 133.44, 134.24, 138.07, 173.16, 191.98.

**2.2.7.8. (1S)-1,2-di-2-furyl-2-oxoethyl butyrate (2h).**

Colorless oil (11 mg, 91% isolated yield),  $[\alpha]_D^{20}$ : + 103.8 (c 2 CHCl<sub>3</sub>). <sup>1</sup>H-RMN (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 0.96 (t, 3H, J= 7.44 Hz), 1.70 (m, 2H, J= 7.40 Hz), 2.43 (m, 2H), 6.36 (dd, 1H, J= 1.91, 3.24 Hz), 6.48 (d, 1H, J= 3.05 Hz), 6.50 (dd, 1H, J= 1.72, 3.62 Hz), 6.76 (s, 1H), 7.24 (dd, 1H, J= 0.57, 3.62 Hz), 7.43 (dd, 1H, J= 0.57, 3.62 Hz), 7.56 (dd, 1H, J= 0.76, 1.72 Hz). <sup>13</sup>C-RMN (75.5 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 13.48, 18.25, 35.55, 70.13, 110.95, 111.53, 112.40, 119.05, 144.07, 146.58, 147.08, 150.19, 172.70, 179.73.

**2.2.7.9. (1*S*)-2-oxo-1,2-di-3-thienylethyl butyrate (2i).**

Colorless oil (13 mg, 82% isolated yield),  $[\alpha]_D^{20}$ : +92.1 (c 2 CHCl<sub>3</sub>). **<sup>1</sup>H-RMN** (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 0.96 (t, 3H, J= 7.44 Hz), 1.70 (m, 2H, J= 7.40 Hz), 2.44 (m, 2H), 6.74 (s, 1H), 7.13 (dd, 1H, J= 1.24, 5.05 Hz), 7.26 (dd, 1H, J= 2.86, 5.15 Hz), 7.31 (dd, 1H, J= 2.96, 5.05 Hz), 7.41 (dd, 1H, J= 0.86, 2.96 Hz), 7.52 (dd, 1H, J= 1.14, 5.15 Hz), 8.09 (dd, 1H, J= 1.34, 2.86 Hz). **<sup>13</sup>C-RMN** (75.5 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 13.54, 18.31, 35.78, 73.85, 125.50, 126.32, 126.88, 126.92, 127.23, 133.24, 134.28, 138.81, 172.94, 187.62.