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First total synthesis of 7(*S*),17(*S*)-Resolvin D5, a potent anti-inflammatory docosanoid

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Abstract—The first total synthesis of 7(*S*),17(*S*)-Resolvin D5, a lipid mediator derived from docosahexaenoic acid, has been achieved. The chiral centers were generated via a Co-salen hydrolytic kinetic resolution of a terminal epoxide with >99% ee. Key steps include Takai olefination, Pd^0/Cu^I coupling and simultaneous deprotection and ester cleavage with lipase from *Candida rugosa*.

Serhan et al. have recently described that docosahexaenoic and eicosapentaenoic acids are converted in vivo to a new class of lipid mediators named Resolvins (resolution phase interaction products).[1–6] These novel lipid mediators have potent anti-inflammatory activities in the pico to nanomolar range, explaining the health benefit of ω-3 fatty acids in humans.[7] Their extremely low availability from natural sources and our interest to explore their biological activities prompt us to prepare these compounds by total chemical synthesis. We recently reported the total synthesis of Resolvin D2.[8]

In this communication, we wish to report the first total synthesis of 7(*S*),17(*S*)-Resolvin D5 (**1**). Our synthetic strategy is based on the retrosynthetic analysis shown in Figure 1. Both chiral centers, 7(*S*) and 17(*S*), were obtained from (+)-benzyl glycidyl ether (**7**). The similarity of the structure around the chiral centers allowed the use

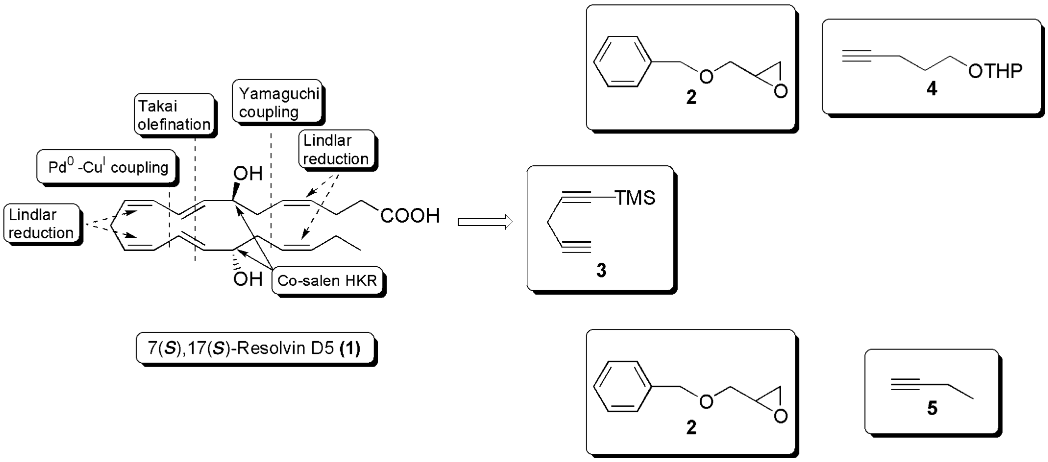

Figure 1.

Keywords: Resolvins; Hydrolytic kinetic resolution; Palladium catalyst; Takai reaction; Lindlar reduction.

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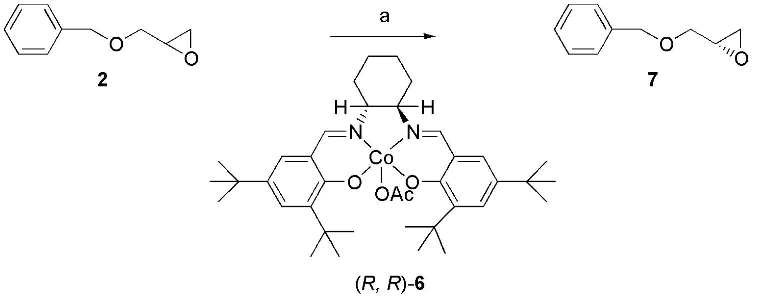
of the same strategy to build up the key intermediates. All cis double bonds were obtained via Lindlar reduction whereas the trans double bonds resulted from Takai olefination.

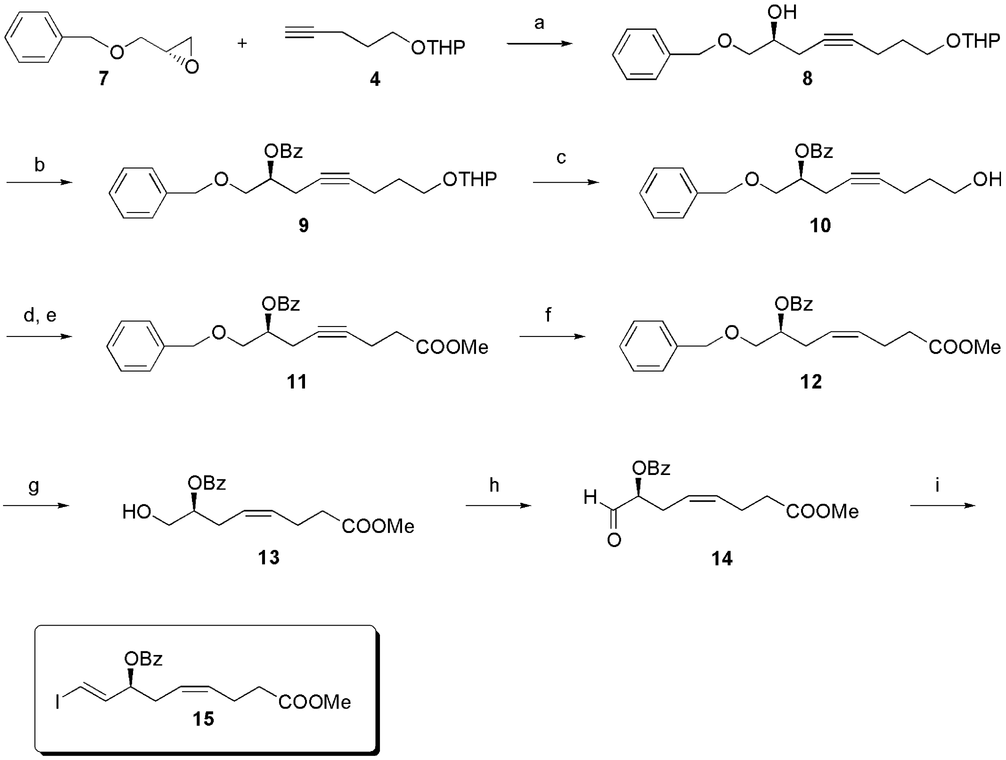
As outlined in Scheme 1, compound **7** was obtained from racemic benzyl glycidyl ether (**2**) via Jacobsen hydrolytic kinetic resolution with 0.55 equiv of H_2O in the presence of 0.1% (*R*,*R*)-salen-Co catalyst **6** [45% yield (90% theoretical) and >99% ee].[9,10]

The C_1–C_9 fragment **15** was obtained from **7** and commercial 2-(4-pentynyloxy)tetrahydro-2*H*-pyran (**4**),[11] as outlined in Scheme 2. Lithiation of **4** with BuLi in THF at −70 °C, followed by warming to rt, and reaction with **7** under Yamaguchi conditions ($BF_3 \cdot Et_2O$ at −78 °C) gave **8** in 85% isolated yield.[12–14] Compound **8** was converted into the benzoate **9** in 92% yield with 2 equiv of benzoyl chloride in pyridine. The THP group was removed with a catalytic amount of pyridinium *p*-toluenesulfonate (PPTS) in MeOH at rt to give **10** (88%). Compound **10** was transformed via Jones oxidation, followed by in situ esterification with 2,2-dimethoxypropane, MeOH, 10% TMSCl, into the methyl ester **11** in 93% yield.[15] Lindlar reduction of **11** in hexane at rt gave **12** in 98% yield. The deprotection of the benzyl group in the presence of the benzoate and the methyl ester was achieved with EtSH, $AlCl_3$ in CH_2Cl_2 at −35 °C to give **13** in 86% yield.[16] Swern oxidation with $Py \cdot SO_3$ in CH_2Cl_2 at rt gave the aldehyde **14** in 86% yield after chromatography. The C_1–C_9 fragment **15** was obtained via Takai olefination of **14** $CrCl_2$/CHI_3/THF at rt in 52% isolated yield.[17]

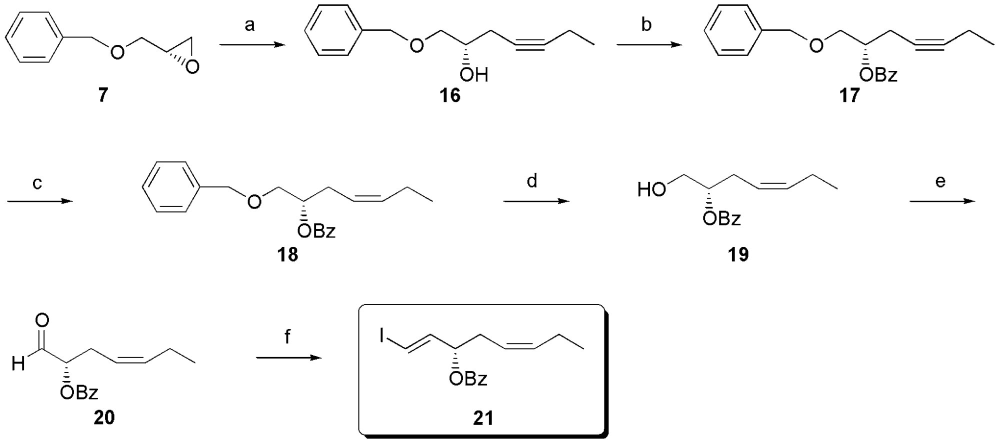
The C_{15}–C_{22} fragment **21** was obtained from the chiral glycidyl ether **7** as outlined in Scheme 3. Lithiation of 1-butyne (**5**) in THF with BuLi at −70 °C, followed by warming to rt, and subsequent reaction with **7** under



Scheme 1. Reagents and conditions: (a) (*R*,*R*)-(salen)Co(III)(OAc) catalyst (**6**), H_2O, 0 °C to rt.



Scheme 2. Reagents and conditions: (a) *n*-BuLi, $BF_3 \cdot Et_2O$, THF, −70 °C; (b) BzCl, pyridine, 0 °C to rt; (c) pyridinium *p*-toluenesulfonate, MeOH, rt; (d) Jones reagent, acetone, 0 °C; (e) 10% TMSCl, MeOH, 2,2-dimethoxypropane, rt; (f) H_2, Lindlar cat., hexane; (g) EtSH, $AlCl_3$, CH_2Cl_2, −35 °C; (h) $Py \cdot SO_3$, DMSO, CH_2Cl_2, Et_3N; (i) $CrCl_2$, CHI_3, THF, rt.

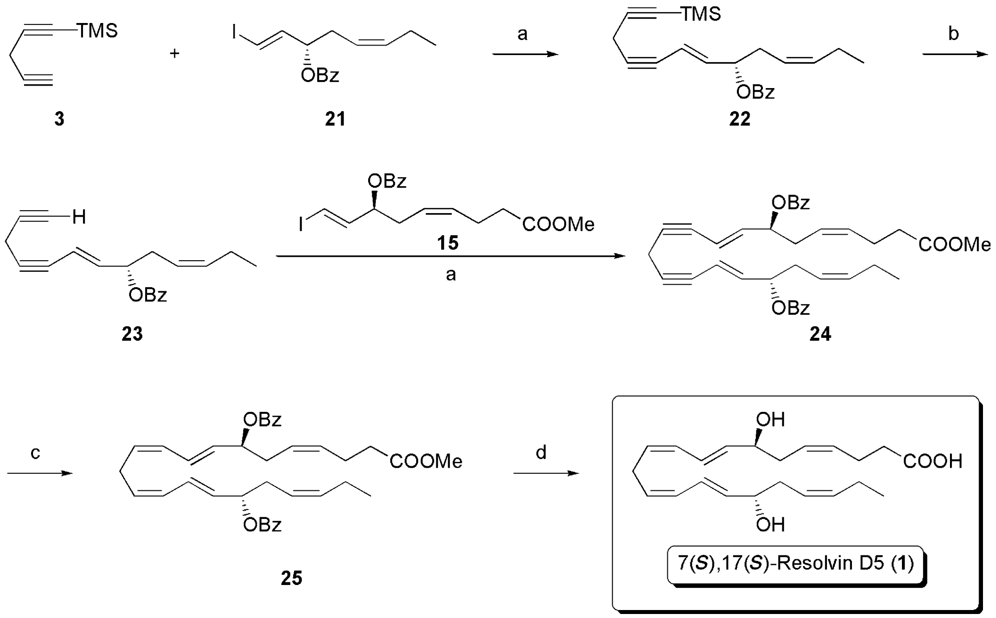


Scheme 3. Reagents and conditions: (a) 1-butyne (**5**), *n*-BuLi, $BF_3{\cdot}Et_2O$, THF, −70 °C; (b) BzCl, pyridine, 0 °C to rt; (c) H_2, Lindlar cat., hexane; (d) EtSH, $AlCl_3$, CH_2Cl_2, −35 °C; (e) $Py{\cdot}SO_3$, DMSO, CH_2Cl_2, Et_3N; (f) $CrCl_2$, CHI_3, THF, rt.

Yamaguchi conditions produced **16** in 80% yield.[12–14] Compound **16** was converted into the benzoate **17** with 2 equiv of benzoyl chloride in pyridine (94%). Lindlar hydrogenation of **17** in hexane produced **18** in 96% yield. Deprotection of the benzyl group was achieved as described in the synthesis of the C_1–C_9 fragment **15** with EtSH, $AlCl_3$ in CH_2Cl_2 at −35 °C to give **19** in 85% yield after chromatography. Swern oxidation with $Py{\cdot}SO_3$ in CH_2Cl_2 at rt gave the aldehyde **20** (84%). The *trans*-vinyl iodide **21** was generated using the Takai olefination.[17] The ^1H NMR spectrum of **21** showed the presence of 20% of the *cis*-vinyl iodide that was difficult to remove at this stage.

The Pd^0/Cu^I coupling of crude **21** with 2 equiv of 1-trimethylsilyl-1,4-pentadiyne (**3**)[18] in benzene for 1 h gave exclusive the *trans*-ene-diyne **22** in 50% yield. Under these conditions only the more reactive *trans*-vinyl iodide **21** reacted. The cleavage of the terminal TMS group to generate **23** was achieved using Nicolaou's procedure with $AgNO_3$ in MeOH followed by short treatment with NaCN.[19,20] The second Pd^0/Cu^I coupling of **15** with **23** produced the Resolvin precursor **24** in 54% yield. Compound **25** was obtained from **24** by controlled hydrogenation (Lindlar catalyst, deactivated with Et_3N, in hexane) in 84% yield. Hydrolysis of **25** under mild basic conditions cleaved the methyl ester but not the benzoate groups. Stronger alkaline conditions led to the decomposition of the product. Simultaneous cleavage of the benzoate protective groups and hydrolysis of the methyl ester was achieved using lipase from *Candida rugosa* (EC 3.1.1.3, type VII, Sigma) at pH 7.2 affording Resolvin D5 (**1**) (75%) (Scheme 4).[21,22]

In summary, a concise total synthesis of 7(*S*),17(*S*)-Resolvin D5 has been achieved, making this novel anti-inflammatory lipid mediator from docosahexaenoic acid available for further biological investigations. The synthesis of other Resolvins, Docosatrienes, and Neuroprotectins will be reported in due course.



Scheme 4. Reagents and conditions: (a) $Pd(PPh_3)_4$, CuI, *n*-$PrNH_2$, benzene, rt; (b) $AgNO_3$, MeOH, H_2O, NaCN; (c) H_2, Lindlar cat., Et_3N, hexane; (d) lipase from *Candida rugosa*, H_2O ($CaCl_2$, NaCl), THF.

Acknowledgements

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22. Satisfactory spectroscopic data were obtained for all compounds. Selected physical data: Compound **10**: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.1–8.0 (m, 2H), 7.6–7.5 (m, 1H), 7.5–7.4 (m, 2H), 7.4–7.2 (m, 5H), 5.4–5.2 (m, 1H), 4.7–4.5 (2d ABsystem, J = 12.3 Hz, 2H), 3.8–3.7 (m, 2H), 3.7–3.6 (t, J = 6.3 Hz, 2H), 2.8–2.6 (m, 2H), 2.3–2.2 (m, 2H), 1.8–1.6 (quint., J = 6.3 Hz, 2H); ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ 166.07, 138.19, 133.07, 130.40, 129.83 (2C), 128.44 (2C), 128.40 (2C), 127.72, 127.69 (2C), 81.77, 75.65, 73.32, 71.77, 70.02, 61.68, 31.35, 21.36, 15.17. Compound **11**: ^{1}H NMR (CDCl$_3$, 300 MHz): 8.1–8.0 (m, 2H), 7.6–7.5 (m, 1H), 7.5–7.4 (m, 2H), 7.4–7.2 (m, 5H), 5.4–5.2 (m, 1H), 4.7–4.5 (2d ABsystem, J = 12.0 Hz, 2H), 3.8–3.7 (m, 2H), 3.6 (s, 3H), 2.8–2.6 (m, 2H), 2.5–2.4 (m, 4H); ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ 172.50, 166.03, 138.18, 133.06, 130.38, 129.84 (2C), 128.44 (2C), 128.39 (2C), 127.72, 127.69 (2C), 80.54, 75.86, 73.31, 71.65, 69.86, 51.59, 33.55, 21.23, 14.61. Compound **12**: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.1–8.0 (m, 2H), 7.6–7.5 (m, 1H), 7.5–7.4 (m, 2H), 7.4–7.2 (m, 5H), 5.5–5.4 (m, 2H), 5.4–5.2 (m, 1H), 4.7–4.5 (2d ABsystem, J = 12.0 Hz, 2H), 3.7–3.6 (m, 2H), 3.6 (s, 3H), 2.6–2.5 (m, 2H), 2.5–2.2 (m, 4H); ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ 173.41, 166.07, 138.08, 132.89, 130.75, 130.40, 129.67 (2C), 128.35 (2C), 128.30 (2C), 127.61, 127.57 (2C), 125.35, 73.16, 72.90, 70.59, 51.43, 33.74, 28.87, 22.76. Compound **14**: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 9.6 (d, J = 0.9 Hz, 1H), 8.1–8.0 (m, 2H), 7.6–7.5 (m, 1H), 7.5–7.4 (m, 2H), 5.6–5.4 (m, 2H), 5.3–5.2 (m, 1H), 3.6 (s, 3H), 2.8–2.6 (m, 2H), 2.5–2.2 (m, 4H); ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ 198.13, 173.27, 166.07, 133.57, 131.91, 129.87 (2C), 129.17, 128.54 (2C), 123.67, 78.02, 51.43, 33.48, 27.03, 22.69. Compound **15**: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.0 (m, 2H), 7.6–7.5 (m, 1H), 7.5–7.4 (m, 2H), 6.7–6.6 (dd, J = 15.0, 6.3 Hz, 1H), 6.6–6.4 (d, J = 15.0 Hz, 1H), 5.6–5.4 (m, 3H), 3.7 (s, 3H), 2.7–2.4 (m, 2H), 2.4–2.3 (m, 4H); ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ 173.41, 165.59, 143.50, 133.21, 131.46, 130.16, 129.74 (2C), 128.50 (2C), 124.48, 80.00, 75.43, 51.48, 33.72, 31.77, 22.88. Compound **16**: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.4–7.2 (m, 5H), 4.6–4.5 (s, 2H), 4.0–3.8 (m, 1H), 3.6–3.4 (m, 2H), 2.5–2.4 (m, 2H), 2.2–2.0 (m, 2H), 1.1 (t, J = 7.5 Hz, 3H); ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ 138.17, 128.48 (2C), 127.80, 127.76 (2C), 84.28, 74.86, 73.43, 73.08, 69.20, 23.89, 14.02, 12.28. Compound **17**: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.1 (m, 2H), 7.6–7.5 (m, 1H), 7.5–7.4 (m, 2H), 7.4–7.2 (m, 5H), 5.4–5.2 (m, 1H), 4.7–4.5 (2d ABsystem, J = 12.3 Hz, 2H), 3.8 (m, 2H), 2.8–2.6 (m, 2H), 2.2–2.0 (m, 2H), 1.1 (t, J = 7.5 Hz, 3H); ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ 166.01, 138.24, 132.95, 130.50, 129.82 (2C), 128.39 (2C), 128.33 (2C), 127.65 (3C), 84.03, 74.20, 73.29, 71.87, 69.98, 21.27, 13.93, 12.23. Compound **18**: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.1 (m, 2H), 7.6–7.5 (m, 1H), 7.5–7.4 (m, 2H), 7.4–7.2 (m, 5H), 5.6–5.5 (m, 1H), 5.5–5.3 (m, 2H), 4.7–4.5 (2d ABsystem, J = 12.0 Hz, 2H), 3.7 (m, 2H), 2.6–2.5 (m, 2H), 2.2–2.0 (m, 2H), 1.0 (t, J = 7.5 Hz, 3H); ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ 166.18, 138.28, 134.99, 132.85, 130.67, 129.73 (2C), 128.39 (2C), 128.31 (2C), 127.62, 127.60 (2C), 123.05, 73.19 (2C), 70.70, 28.81, 20.51, 13.94. Compound **19**: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.0 (m, 2H), 7.5 (m, 1H), 7.4 (m, 2H), 5.6–5.4 (m, 1H), 5.4–5.3 (m, 1H), 5.2–5.0 (m, 1H), 3.8 (m, 2H), 2.7–2.6 (m, 1H), 2.6–2.4 (m, 2H), 2.2–2.0 (m, 2H), 0.9 (t, J = 7.5 Hz, 3H); ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ 166.72, 135.07, 133.00, 130.31, 129.67 (2C), 128.33 (2C), 122.81, 75.76, 64.11, 28.47, 20.46, 13.84. Compound **20**: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 9.6 (d, J = 0.6 Hz, 1H), 8.1 (m, 2H), 7.6 (m, 1H), 7.5–7.4 (m, 2H), 5.7–5.5 (m, 1H), 5.5–5.3 (m, 1H), 5.3–5.2 (br t, J = 6.4 Hz, 1H), 2.8–2.6 (m, 2H), 2.2–2.0 (m, 2H), 0.9 (t, J = 7.5 Hz, 3H); ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ 198.27, 166.16, 136.09, 133.55, 129.93 (2C), 129.36, 128.56 (2C), 121.34, 78.27, 27.11, 20.55, 13.80. Compound **22**: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.1–8.0 (m, 2H), 7.6–7.5 (m, 1H), 7.5–7.4 (m, 2H), 6.2–6.1 (dd, J = 15.9, 6.6 Hz, 1H), 5.8–5.7 (m, 1H), 5.6–5.4 (m, 2H), 5.4–5.2 (m, 1H), 3.3 (d, J = 2.1 Hz, 2H), 2.6–2.4 (m, 2H), 2.2–2.0 (m, 2H), 1.0–0.9 (t, J = 7.5 Hz, 3H), 0.2 (s, 9H); ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ 165.72, 140.40, 135.34, 133.06, 130.43, 129.71 (2C), 128.42 (2C), 122.45, 112.19, 99.38, 85.40, 84.73, 78.40, 73.76, 32.11, 20.65, 13.91, 11.43, –0.24 (3C).

Compound **23**: ^{1}H NMR ($CDCl_3$, 300 MHz): 8.0 (m, 2H), 7.6–7.5 (m, 1H), 7.4 (m, 2H), 6.2–6.1 (dd, $J = 15.9$, 6.6 Hz, 1H), 5.8–5.7 (m, 1H), 5.6–5.4 (m, 2H), 5.4–5.2 (m, 1H), 3.3–3.2 (br s, 2H), 2.6–2.4 (m, 2H), 2.2–2.0 (m, 3H), 1.0–0.9 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 165.68, 140.65, 135.34, 133.04, 130.43, 129.70 (2C), 128.42 (2C), 122.42, 111.97, 84.28, 78.64, 77.75, 73.70, 68.88, 32.09, 20.64, 13.89, 10.10. Compound **24**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.0 (m, 4H), 7.6–7.5 (m, 2H), 7.5–7.3 (m, 4H), 6.2–6.0 (2dd, $J = 15.9$, 6.3 Hz, 2H), 5.8–5.7 (m, 2H), 5.6–5.2 (m, 6H), 3.6 (s, 3H), 3.4–3.3 (br s, 2H), 2.6–2.4 (m, 4H), 2.4–2.2 (m, 4H), 2.1–1.9 (m, 2H), 1.0–0.9 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 173.31, 165.52, 165.48, 140.39, 140.17, 135.22, 133.01, 132.97, 131.04, 130.19 (2C), 129.58 (4C), 128.34 (4C), 124.70, 122.31, 112.16, 111.94, 84.78, 84.59, 78.41, 78.33, 73.68, 73.49, 51.51, 33.72, 32.14, 32.10, 22.91, 20.70, 14.01, 11.06. Compound **25**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.1–8.0 (m, 4H), 7.6–7.5 (m, 2H), 7.5–7.3 (m, 4H), 6.6 (m, 2H), 6.0–5.9 (m, 2H), 6.2–6.0 (m, 2H), 5.6–5.3 (m, 8H), 3.6 (s, 3H), 3.1–3.0 (br t, $J = 7.5$ Hz, 2H), 2.7–2.4 (m, 4H), 2.4–2.2 (m, 4H), 2.1–1.9 (m, 2H), 0.9 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 173.36, 165.78 (2C), 134.84, 132.85, 132.80, 131.54, 131.31, 130.68 (2C), 130.49, 130.24, 130.15, 129.62, (4C), 128.34 (2C), 128.31 (2C), 128.22 (2C), 127.85, 127.68, 125.30, 122.94, 74.72, 74.53, 51.48, 33.85, 32.65, 32.57, 26.63, 23.01, 20.75, 14.06. Compound **1**: ^{1}H NMR (CD_3CN, 300 MHz): δ 6.6 (br dd, $J = 15.0$, 11.1 Hz, 2H), 6.1–6.0 (t, $J = 11.1$ Hz, 2H), 6.2–6.0 (dd, $J = 15.0$, 6.0 Hz, 2H), 5.6–5.3 (m, 6H), 4.1–4.2 (m, 2H), 3.1 (br t, $J = 7.6$ Hz, 2H), 2.4–2.2 (m, 8H), 2.2–2.1 (m, 2H), 1.0–0.9 (t, $J = 47.5$ Hz, 3H). UV (CH_3CN) λ_{max} 225, 244 nm. HPLC/API–ES/MS (m/z): 383.6 $[M+Na^+]^+$.