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STEREOSELECTIVE FORMAL TOTAL SYNTHESIS OF NOVEL ANTIBIOTIC (–)-CENTROLOBINE

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Abstract – A concise and stereoselective formal total synthesis of (–)-centrolobine is achieved utilizing Mioskowski's Lewis acid mediated epoxide opening followed by ring-closing metathesis as the key reaction.

INTRODUCTION

Syntheses of natural products and analogues thereof embodying substituted tetrahydropyrans are of substantial interest to organic chemistry and chemical biology.^{1,2} Several natural products possessing 2,6-disubstituted tetrahydropyran, tetrahydrofurans, and oxepanes such as (–)-centrolobine,³ de-*O*-methylcentrolobine, calyxins,⁴ diospongins,⁵ annonaceae acetogenins,⁶ ionophores,⁷ etc. exhibit a wide range of biological activities. Owing to the challenges posed by the substitution pattern as well as the widespread occurrence of substituted tetrahydropyran moieties in natural products with interesting biological activities,⁸ has inspired the development of numerous creative synthetic approaches to this important structural subunit.

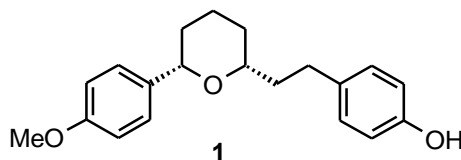


Figure 1. Structure of (–)-centrolobine **1**.

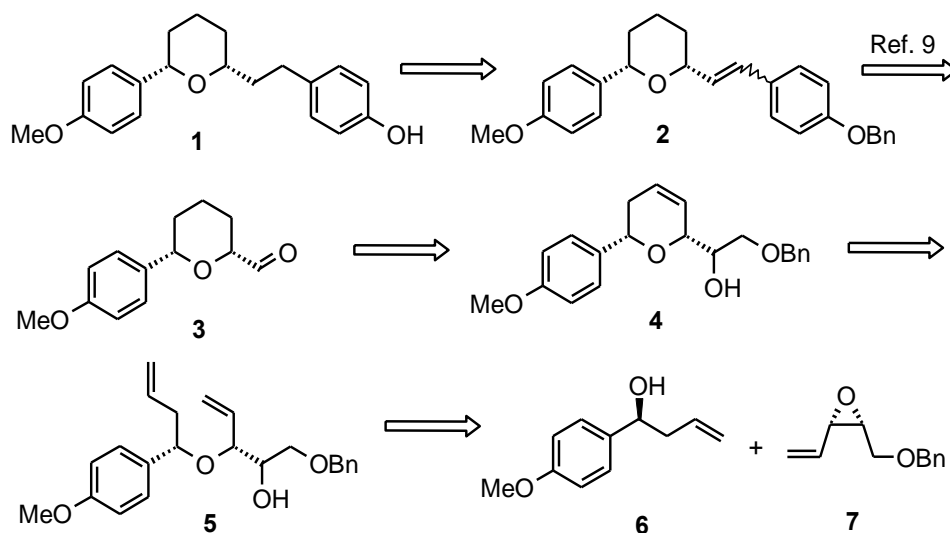
(–)-Centrolobine, 6-[β-(*p*-hydroxyphenyl)ethyl]-2-(*p*-methoxyphenyl)tetrahydropyran, is a crystalline substance (Figure 1) isolated from the heartwood of *Centrolobine robustum* and from the stem of *Brosinium*

This paper is dedicated to Prof. Akira Suzuki on the occasion of his 80th birthday.

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potabile in the amazon rain forest in 1962. Although the basic structure of (–)-centrolobine was elucidated in 1964,¹ its absolute configuration was only established in 2002 by an enantioselective total synthesis.⁹ Afterward several research groups have accomplished the total synthesis of (–)-centrolobine. A variety of approaches starting with optically active building blocks, obtained by well-established asymmetric reactions or the chiral pool method, have been devised to provide access to the *cis*-2,6-disubstituted tetrahydropyran rings. These include the Prins and related cyclizations^{10a,h,k,o} reductive etherifications,^{9,10b} one-pot cross metathesis–hydrogenation–lactonization procedure,^{10c} radical cyclization,^{10e} nucleophilic addition–stereoselective reduction protocol,^{10f} intramolecular oxy-Michael reaction,^{10g} diastereoselective ring rearrangement metathesis–isomerization sequence,¹⁰ⁱ FeCl₃-mediated cyclization of 1,5-diol,^{10m} hetero-Diels-Alder reaction.¹⁰ⁿ

In continuation of our research on the synthesis of biologically active natural products containing tetrahydrofuran and tetrahydropyran rings,¹¹ we herein disclose a new strategy towards the synthesis of tetrahydropyran derivatives using Mioskowski's Lewis acid¹² catalyzed regioselective epoxide opening followed by ring-closing metathesis as the key steps. This novel strategy was applied for the synthesis of (–)-centrolobine. Retrosynthetic analysis of (–)-centrolobine (**1**), as depicted in Scheme 1, revealed two fragments **6** and **7**.

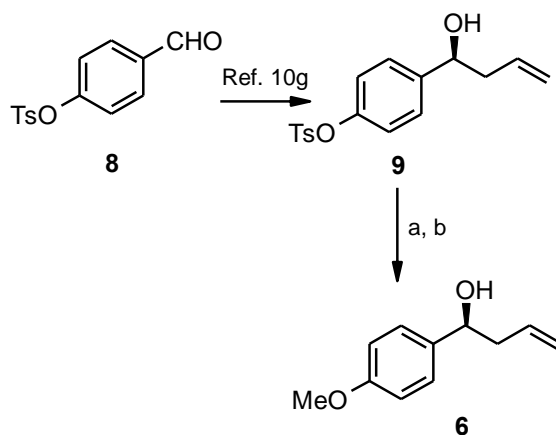


Scheme 1. Retrosynthetic analysis.

RESULTS AND DISCUSSION

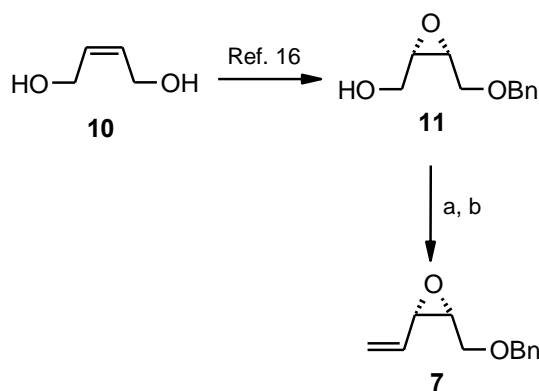
As summarized in Scheme 1, one of the stereogenic centers of (–)-centrolobine was established in a reagent-controlled fashion, whereas the other capitalized on a stereocontrolled asymmetric allylation. For synthesizing fragment **6**, we followed Keck allylation on 4-tosyloxybenzaldehyde.¹³ Detosylation¹⁴

followed by selective methylation^{10a} of phenolic hydroxy group accomplished the fragment **6** in 83% yield over two steps.



Scheme 2. Reagents and conditions: (a) Mg, MeOH, rt, 3 h, 94%; (b) MeI, K₂CO₃, acetone, rt, 12 h, 88%.

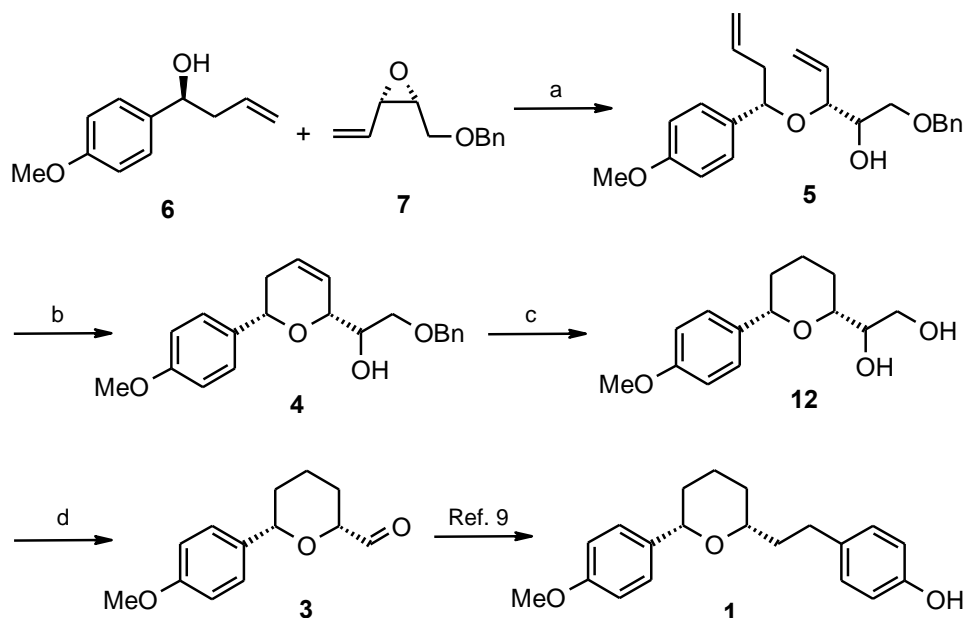
The other fragment **7** was synthesized starting from *cis*-2-butene-1,4-diol. Accordingly, the alcohol **10** was mono protected as its benzyl ether with NaH and benzyl bromide followed by Sharpless asymmetric epoxidation with L-(+)-DET, TBHP afforded the epoxy alcohol **11**.¹⁵ IBX oxidation of the primary hydroxyl group to the corresponding aldehyde and Wittig reaction using methyltriphenylphosphonium bromide¹¹ afforded vinyl substituted epoxide **7** in an overall yield of 86% in two steps.



Scheme 3. Reagents and conditions: (a) IBX, DMSO, THF, 0 °C - rt, 4 h; (ii) Ph₃P⁺CH₃Br⁻, NaHMDS, THF, 0 °C - rt, 12 h, 86% over two steps.

After having enantiomerically pure homoallylic alcohol **6** and the vinyl epoxide derivative **7** in hand, we proceeded further for the Mioskowski's Lewis acid mediated epoxide opening reaction. Accordingly, the two segments were treated with BF₃·OEt₂ in dichloromethane to afford the diene **5** in 67% yield. Barely detectable amounts of isomeric diene could be detected in the product by HPLC analysis or by NMR spectroscopy. Now, the stage is set to effect the ring-closing metathesis reaction. On exposure of **5** to

Grubbs second generation catalyst¹⁶ furnished the pyran ring in 73% yield. The product was assigned by ¹H, ¹³C NMR, mass and elemental analysis.



Scheme 4. Reagents and conditions: (a) $\text{BF}_3\text{-OEt}_2$, CH_2Cl_2 , rt, 45 min, 67%; (b) Grubbs second generation catalyst, toluene, 70 °C, 73%; (c) Pd/C, HCl EtOH:EtOAc:H₂O (5:1:1), 1 h, 75%; (d) NaIO_4 (impregnated over silica gel, CH_2Cl_2 , rt, 30 min, 92%.

Double bond reduction as well as benzyl ether cleavage was accomplished in one pot by exposure of **4** to Pd/C catalyst under hydrogen atmosphere^{10g} to afford the diol **12** in 75% yield. Compound **12** was then treated with NaIO_4 impregnated over silica gel in dichloromethane to afford the aldehyde **3** in 92% yield. The analytical data were exactly matching with the reported values. Though this constitutes a formal synthesis of (–)-centrolobine, we were interested to complete its synthesis and compare the data with the natural product. The Wittig reaction between the 4-benzyloxybenzyltriphenylphosphonium bromide^{9b} and the aldehyde **3** was carried out in the presence of *n*-BuLi to obtain **2** followed by simultaneous reduction of the double bond and deprotection of the benzyl ether by catalytic hydrogenation gave (–)-centrolobine (**1**) in 78% yield over two steps. ¹H and ¹³C NMR spectra, IR, melting point, and optical rotation ($[\alpha]_{\text{D}}^{25} -91.5$ (*c* 1.2, CHCl_3)) of **1** were in good agreement with the natural product.¹⁰

CONCLUSION

In summary, a new synthetic approach has been designed for the stereoselective formal synthesis of (–)-centrolobine following Lewis acid mediated epoxide opening followed by ring-closing metathesis

reaction for the first time. Total syntheses of other pyran ring containing natural products are in progress in our laboratory following the above approach and will be reported in due course.

EXPERIMENTAL

General

All chemicals used in this study were purchased from Aldrich, Fluka or Lancaster and used as received. All the moisture-sensitive reactions were performed in an inert atmosphere of either N₂ or Ar using dry solvents. The elemental analyses were recorded on Elmentar-Vario-EL (Heraeus Company Ltd. Germany). The NMR spectra were obtained on a Bruker 200, 400, or 500 Fourier transform spectrometer. Optical rotations were measured with a JASCO DIP 370 digital polarimeter. All reactions are monitored by Thin Layer Chromatography (TLC) carried out on 0.25 mm E- Merck silica gel plates (60F-254) with UV, I₂ or anisaldehyde in ethanol as development reagents.

(2R,3S)-2-(Benzyloxymethyl)-3-vinyloxirane (7)

To a solution of IBX (6.5 g, 23.19 mmol) in DMSO (14 mL), was added pyridine (5 mL) followed by epoxy alcohol **11** (3.0 g, 15.46 mmol) in dry THF (20 mL) at rt and stirred for 4 h. After completion of the reaction (monitored by TLC), water (H₂O) (30 mL) was added, and diluted with Et₂O (50 mL). The solid was filtered through a pad of Celite and organic layer was separated. The aqueous layer was extracted with Et₂O (2 x 50 mL). The combined organic layer was washed with brine, dried over Na₂SO₄, concentrated to give crude aldehyde (2.9 g, crude product) which was used immediately for the next reaction.

To a suspension of methyltriphenylphosphonium bromide salt (16.56 g, 46.39 mmol) in THF (50 mL) at 0 °C, was added NaHMDS (31.0 mL, 1M solution in toluene) drop-wise. The reaction mixture was stirred for 1 h and the crude aldehyde (2.9 g in 20 mL THF) was added slowly. After 2 h, the reaction was quenched with saturated solution of NH₄Cl and extracted with EtOAc. The organic layers were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. Purification of the crude product by silica gel (60-120 mesh) column chromatography afforded vinyl epoxide **7** (2.5 g, 86% over two steps) as a yellow color liquid. $[\alpha]_D^{25} -1.95$ (*c* 1.65, CHCl₃); IR (CHCl₃): 3030, 2989, 2920, 2860, 1639, 1496, 1453, 1387, 1148, 1096, 1028, 929, 739.cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ 3.24 (dt, *J* = 4.4, 5.9 Hz, 1H), 3.38 (dd, *J* = 4.4, 6.7 Hz, 1H), 3.45-3.62 (m, 2H), 4.44 (d, *J* = 11.9 Hz, 1H), 4.53 (d, *J* = 11.9 Hz, 1H), 5.22-5.44 (m, 2H), 5.51-5.68 (m, 1H), 7.17-7.27 (m, 5H) ppm; ¹³C NMR (50 MHz, CDCl₃): δ 56.0, 56.7, 67.8, 73.2, 120.8, 127.7, 128.38, 131.9, 137.8 ppm; ESI-MS *m/z* 213.2 [M+Na]⁺; Anal. Calcd for C₁₂H₁₄O₂: C, 75.76; H, 7.42. Found: C, 75.59; H, 7.35.

(2S,3R)-1-(Benzyloxy)-3-((S)-1-(4-methoxyphenyl) but-3-enyloxy)pent-4-en-2-ol (5)

To a mixture of epoxide **7** (250 mg 1.31 mmol) and homoallyl alcohol **6** (350 mg, 1.97 mmol) in CH₂Cl₂ (20 mL) was added drop-wise a 19% solution of BF₃·Et₂O (0.4 mL, 0.065 mmol) in freshly dried CH₂Cl₂ at rt. After 45 minutes of stirring at rt, the solution was diluted with CH₂Cl₂ and washed with saturated aqueous NaHCO₃ solution and brine. The organic layer was dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (light petroleum/EtOAc: 9/1) to afford diene **5** (0.32 g, 67%) as a colorless liquid. [α]_D²⁵ +3.8 (*c* 2.6, CHCl₃); IR (CHCl₃): 3436, 3009, 2906, 2862, 1639, 1611, 1512, 1496, 1454, 1302, 1247, 1175, 1035, 923, 832, 755, 698 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ 2.24-2.58 (m, 2H), 3.30-3.65 (m, 3H), 3.71 (s, 3H), 3.84-3.96 (m, 1H), 4.24-4.48 (m, 3H), 4.88-5.25 (m, 4H), 5.40-5.76 (m, 2H), 6.72-6.80 (m, 2H), 7.07-7.25 (m, 7H) ppm; ¹³C NMR (50 MHz, CDCl₃): δ 43.7, 55.1, 70.8, 72.9, 73.2, 77.4, 77.6, 113.6, 116.8, 118.0, 127.0, 127.6, 128.2, 133.0, 134.6, 134.8, 135.1, 159.1 ppm; ESI-MS *m/z* 391.48 [M + Na]⁺; Anal. Calcd for C₂₃H₂₈O₄: C, 74.97; H, 7.66. Found: C, 74.79; H, 7.49.

(S)-2-(Benzyloxy)-1-((2R,6S)-6-(4-methoxyphenyl)-5,6-dihydro-2H-pyran-2-yl)ethanol (4). A mixture of compound **5** (0.31 g, 0.84 mmol) and Grubbs' II catalyst (0.021 g, 0.025 mmol) in degassed toluene (60 mL) was heated at 70 °C for 12 h. After completion of the reaction (monitored by TLC), solvent was evaporated under reduced pressure and the crude purified on silica gel column chromatography by eluting with light petroleum: EtOAc (19:1) to afford **4** (0.21 g, 73%) as a colorless viscous liquid. [α]_D²⁵ +4.3 (*c* 1.4, CHCl₃); IR (CHCl₃): 3401, 2922, 2851, 1612, 1514, 1454, 1385, 1303, 1247, 1174, 1085, 829, 770 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ 2.19-2.31 (m, 2H), 2.58 (bs, 1H), 3.53-3.72 (m, 2H), 3.78 (s, 3H), 3.78-3.90 (m, 1H), 4.48-4.61 (m, 4H), 5.74-5.80 (m, 1H), 5.94-6.04 (m, 1H), 6.85 (d, *J* = 8.7 Hz, 2H), 7.22-7.33 (m, 7H) ppm; ¹³C NMR (50 MHz, CDCl₃): δ 32.9, 55.2, 70.9, 72.3, 73.4, 75.2, 75.7, 113.7, 126.8, 126.8, 127.0, 127.7, 128.4, 134.5, 138.1, 159.0 ppm; ESI-MS *m/z* 363.4 (M + Na)⁺; Anal. Calcd for C₂₁H₂₄O₄: C, 74.09; H, 7.11. Found: C, 73.97; H, 7.00.

(S)-1-((2R,6S)-6-(4-Methoxyphenyl)tetrahydro-2H-pyran-2-yl)ethane-1,2-diol (12). A solution of **4** (0.34 g, 1.0 mmol) in EtOH:EtOAc:water (25:5:5) was hydrogenated in the presence of 10% Pd/C (20 mg) under acidic condition (conc. HCl) at rt. After 1 h, the reaction mixture was filtered through a pad of Celite, concentrated and the residue purified on silica gel column chromatography using EtOAc: light petroleum (1:4) to afford **12** (0.19 g, 75%) as a colorless liquid. [α]_D²⁵ +4.8 (*c* 1.25, CHCl₃); IR (CHCl₃): 3392, 2932, 1613, 1514, 1384, 1246, 1175, 1035, 830, 771 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 1.43-1.48 (m, 2H), 1.56 (m, 1H), 1.61 (m, 1H), 1.70-1.73 (m, 1H), 1.89-1.93 (m, 1H), 2.55 (bs, 2H), 3.52-3.57 (m, 2H), 3.59 (dd, *J* = 4.5, 11.7 Hz, 1H), 3.67 (dd, *J* = 11.7, 3.4 Hz, 1H), 3.73 (s, 3H), 4.28 (dd, *J* = 11.4, 2.1 Hz, 1H), 6.80 (d, *J* = 8.7 Hz, 2H), 7.18 (d, *J* = 8.7 Hz, 2H) ppm; ¹³C NMR (50 MHz, CDCl₃): δ 23.3, 26.8, 33.2, 55.2, 63.6, 74.2, 79.1, 79.7, 113.6, 127.1, 134.9, 158.9 ppm; ESI-MS *m/z* 275.1 [M + Na]⁺; Anal. Calcd for C₁₄H₂₀O₄: C,

66.65; H, 7.99. Found: C, 66.54; H, 7.80.

(2R,6S)-2-(4-(Benzyloxy)styryl)-6-(4-methoxyphenyl)tetrahydro-2H-pyran (2). Compound **12** (0.08 g, 0.32 mmol) in CH₂Cl₂ (5 mL) was stirred with sodium metaperiodate impregnated over silica gel (0.64 g, 2.0 g/ mmol) for 0.5 h. Silica was separated by filtration, organic layer concentrated under reduced pressure and the crude aldehyde **3** used for the next reaction without further purification.

To a stirred solution of *p*-benzyoxybenzyltriphenylphosphonium bromide (0.41 g, 0.95 mmol) in THF (5 mL) under nitrogen was added (0.63 mL, of 1.6 M solution in hexane) of *n*-butyllithium. After stirring for 0.5 h, crude aldehyde **3** was added with THF (3 mL) and the reaction mixture stirred for an additional 1 h. The reaction mixture was quenched with saturated aqueous NH₄Cl and diluted with Et₂O. The organic layer was separated and washed with water, brine and dried over Na₂SO₄. Solvent was evaporated under reduced pressure and the crude product purified by silica gel column chromatography eluting with EtOAc: light petroleum (3:97) to afford product **2** (0.07 g, 55%) as a colorless liquid. $[\alpha]_D^{25} +15.0$ (*c* 1.2, CHCl₃); IR (CHCl₃): 3368, 2929, 2853, 1607, 1511, 1454, 1382, 1247, 1174, 1074, 1029, 834, 769 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ 1.51-2.24 (m, 6H), 3.71 (s, 3H), 4.03-4.13 (m, 0.27H), 4.27-4.35 (m, 1.63H), 4.97 (s, 0.55H), 4.99 (s, 1.42H), 5.58 (dd, *J* = 8.7, 11.6 Hz, 0.68H), 6.06 (dd, *J* = 5.9, 16.0 Hz, 0.27H), 6.41 (d, *J* = 11.8 Hz, 0.8H), 6.63 (d, *J* = 16.0 Hz, 0.17H), 6.76-7.37 (m, 13H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 23.9, 24.1, 31.6, 31.8, 32.9, 33.4, 55.2, 69.9, 74.9, 78.8, 79.0, 79.6, 113.6, 114.5, 114.8, 127.2, 127.3, 127.4, 127.6, 127.9, 128.0, 128.5, 128.6, 129.0, 129.2, 129.9, 130.1, 130.8, 131.5, 135.4, 135.6, 137.0, 158.0, 158.3, 159.0 ppm; ESI-MS *m/z* 423.5 [M + Na]⁺; Anal. Calcd for C₂₇H₂₈O₃: C; 80.97, H; 7.05. Found: C; 80.78, H; 6.89.

4-(2-((2R,6S)-6-(4-Methoxyphenyl)tetrahydro-2H-pyran-2-yl)ethyl)phenol (1). Compound **2** was hydrogenated by the same procedure as used for the transformation of **4** to **12**. The crude product was purified by silica gel column chromatography eluting with EtOAc: light petroleum (1:10) to obtain (–)-centrolobine (**1**) (0.02 g, 89%). $[\alpha]_D^{25} -91.5$ (*c* 1.2, CHCl₃), lit.,³ $[\alpha]_D^{25} -92.2$ (*c* 1.0, CHCl₃); IR (CHCl₃): 3420, 2930, 1650, 1490, 1220, 1110 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ 1.42-1.58 (m, 4H), 1.61-1.69 (m, 2H), 1.78-1.89 (m, 2H), 2.54-2.69 (m, 2H), 3.34-3.39 (m, 1H), 3.73 (s, 3H), 4.22 (dd, *J* = 1.9, 11.1 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H) ppm; ¹³C NMR (50 MHz, CDCl₃): δ 24.0, 30.7, 31.3, 33.3, 38.3, 55.3, 77.1, 79.1, 113.6, 115.1, 127.1, 129.6, 134.7, 135.9, 153.5, 158.7 ppm; ESI-MS *m/z* 344.4 [M + Na]⁺; Anal. Calcd for C₂₀H₂₄O₃: C; 76.89, H; 7.74. Found: C; 76.66, H; 7.67.

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