Org. Lett. – Supporting Information

A Novel Palladium-Catalyzed Arylation-Dehydroaromatization Reaction: Synthesis of 7- Aryltetralones

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Experimental Details

General. ^1H and ^{13}C NMR: Bruker Avance 400, spectra were recorded at 295 K in CDCl_3 ; chemical shifts are calibrated to added TMS (δH 0.00 ppm) and the residual carbon resonance of the solvent CDCl_3 (δC 77.0 ppm). Melting points: Büchi Melting Point B-540, uncorrected. EI-MS: Finnigan Triple-Stage-Quadrupol (TSQ-70). HRMS (EI): Intectra AMD MAT-711A. Analytical LC-MS: HP 1100 Series connected with an ESI MS detector Agilent G1946C, positive mode with fragmentor voltage of 40 eV, column: Nucleosil 100-5, C-18 HD, 5 mm, 70×3 mm Machery Nagel, eluent: NaCl solution (5 mM)/acetonitrile, gradient: 0-10-15-17-20 min with 20-80-80-99-99% acetonitrile, flow: 0.5 mL min^{-1} . Flash chromatography: J. T. Baker silica gel 43-60 μm . Thin-layer chromatography Machery-Nagel Polygram Sil G/UV₂₅₄. All solvents used in the reactions were purified before use. Dry tetrahydrofuran and toluene were distilled from sodium and benzophenone, whereas dry dichloromethane and dimethylformamide were distilled from CaH_2 . Petroleum ether with a boiling range of 40-60 $^\circ\text{C}$ was used. Reactions were generally run under nitrogen atmosphere. All commercially available compounds (Acros, Aldrich, Fluka, Merck) were used as received unless stated otherwise.

Cs_2CO_3 (Aldrich) was dried at 150 $^\circ\text{C}$ under vacuum for 6 h. The aryl halides were used without further purification.

For the estimation of the product yields by LC-MS the enone **4** was mixed with biphenyl (10 mol%) as internal standard and the mixture diluted with acetonitrile. The integrals of the UV signal of both compounds were measured at 254 nm and the ratio of the integrals was calculated (ratio-1 = area **4**/area biphenyl). The same measurement was run with compound **7a** (ratio-2 = area **7a**/area biphenyl). The coupling reactions were then performed with biphenyl (10 mol%) as internal standard and samples checked by LC-MS. Now area **4**/area biphenyl was determined and divided by ratio-1 which reflects the conversion. The determination of area **7a**/area biphenyl and its division by ratio-2 gave a value which reflects the yield of the reaction. In runs where compound **7a** was isolated, the LC-MS yields and the isolated yields turned out to be comparable.

Starting materials

2-(3-Bromopropyl)-1,3-dioxolane (2):¹ DIBAL (100 mL of 1 M solution in hexane) was added dropwise to a solution of ethyl 4-bromobutanoate (19.5 g, 0.1 mol) in CH_2Cl_2 (180 mL) under N_2 at -70 $^\circ\text{C}$. After stirring for 1 h at -65 to -70 $^\circ\text{C}$ the reaction mixture was poured into an ice-cold 10 % HCl solution, and the mixture stirred at 0 $^\circ\text{C}$ for 1 h. After separation of the organic layer, the aqueous phase was extracted with CH_2Cl_2 ($2 \times 50 \text{ mL}$). The combined organic phases were washed with water, brine, dried with sodium sulphate, filtered, and concentrated in vacuo. The residue (16 g) was dissolved in benzene (350 mL), then ethylene glycol (46 g, 0.75 mol) and *p*-TsOH (0.68 g, 4 mmol) were added, followed by refluxing of the mixture with a Dean-Stark trap. After 3 h, the mixture was allowed to cool, and NaHCO_3 (3 g) were added. After stirring for 10 min, the contents were washed with saturated NaHCO_3 solution, dried with K_2CO_3 , and filtered. The solvent was evaporated and the residue distilled resulting in 17.2 g (88%) of 2-(3-bromopropyl)-1,3-dioxolane (**2**), b.p. 87-88 $^\circ\text{C}$ (10 torr). ^1H NMR (400 MHz, CDCl_3): δ [ppm] = 1.72-1.81 (m, 2H, CH_2), 1.90-2.01 (m, 2H, CH_2), 3.39 (t, J = 6.7 Hz, 2H, CH_2Br), 3.79 (bt, J = 6.8 Hz, 2H, CH_2O), 3.90 (bt, J = 6.8 Hz, 2H, CH_2O), 4.83 (t, J = 4.6 Hz, 1H, CH); ^{13}C NMR (100 MHz, CDCl_3): δ [ppm] = 27.6 (C_2), 32.7 (C_1), 34.0 (C_3), 65.3 (CH_2O), 104.1 (CH).

3-[3-(1,3-Dioxolan-2-yl)propyl]cyclohexanone (3):² This compound was prepared by CuI-catalyzed conjugate addition of the Grignard reagent derived from **2**.³ To a Mg turnings (0.62 g, 25.4 mmol) in 10 mL THF was added 2-(3-Bromopropyl)-1,3-dioxolane (2.67 g, 12.6 mmol) at 22-24 $^\circ\text{C}$ over a period of 15 min. After being stirred for 1 h, the mixture was cooled to -30 $^\circ\text{C}$ and CuI (0.2 g, 1.05 mmol) was added at once. The mixture was stirred for 15 min and cooled to -78 $^\circ\text{C}$. Then, a solution of cyclohex-2-en-1-one (0.6 g, 6.24 mmol) in THF (5 mL) was added dropwise. The mixture was warmed to 0 $^\circ\text{C}$ within 1 h and quenched with saturated NH_4Cl solution (adj pH 8). After stirring for 30 min, the mixture was extracted with CH_2Cl_2 , dried, filtered (MgSO_4), and concentrated in vacuo. Purification of the residue by flash chromatography (hexane/EtOAc, 5:1) afforded 1.22 g (92%) of ketone **3** as a colorless oil. TLC (hexane/EtOAc, 5:1): R_f 0.2; ^1H NMR (400 MHz, CDCl_3): δ [ppm] = 1.16-2.41 (m, 15H), 3.75-3.92 (m, 4H, CH_2O), 4.77 (t, J = 4.8 Hz, 1H, CH); ^{13}C NMR (100 MHz, CDCl_3): δ [ppm] = 21.5 (CH_2), 25.7 (CH_2), 31.5 (CH_2), 34.3 (CH_2), 36.8 (CH_2), 39.4 (CH), 41.9 ($\alpha\text{-CH}_2$), 48.5 ($\alpha\text{-CH}_2$), 65.3 (CH_2O), 104.8 (CH-O), 212.4 (C=O).

¹ Wenkert, D.; Ferguson, S. B.; Porter, B.; Qvarnstrom, A.; McPhail, A. T. *J. Org. Chem.* **1985**, 50, 4114-4119.

² Bal, S. A.; Marfat, A.; Helquist, P. *J. Org. Chem.* **1982**, 47, 5045-5050.

³ Tsantali, G. G.; Takakis, I. M. *J. Org. Chem.* **2003**, 68, 6455-6458.

3,4,4a,5,6,7-Hexahydronaphthalen-1(2H)-one (4):² 3-[3-(1,3-Dioxolan-2-yl)propyl]cyclohexanone (**3**) (1.2 g, 5.66 mmol) was slowly refluxed 3-4 h with 1 N HCl (15 mL) and THF (15 mL) (TLC monitoring). After cooling, the solution was neutralized with a NaHCO₃ solution, and extracted with CH₂Cl₂. The organic layers were dried (MgSO₄), filtered and concentrated in vacuo. Purification of the residue by flash chromatography (hexane/EtOAc, 10:1) furnished the enone **4** (721 mg, 85%) as a colorless oil. TLC (hexane/EtOAc, 5:1): R_f 0.5; ¹H NMR (400 MHz, CDCl₃): δ[ppm] = 1.44-2.54 (m, 13H), 6.63-6.68 (m, 1H, CH). ¹³C NMR (100 MHz, CDCl₃): δ[ppm] = 21.8 (CH₂), 23.0 (CH₂), 26.6 (CH₂), 30.7 (CH₂), 32.0 (CH₂), 38.2 (CH), 40.6 (CH₂), 136.2 (CH=C), 140.3 (CH=C), 201.5 (C=O).

General procedure for the synthesis of 5 and 6: To the solution of enone **4** (30 mg, 0.2 mmol) and amine (0.25 mmol) in dry CH₂Cl₂ (5 mL) (entry 1,2,3,5,6), or (THF/ DMF 1:1, entry 4) TIPSOtF (69 mg, 0.21 mmol) was added dropwise, and the reaction stirred at N₂ under the conditions shown in Table 1. After completion of the reaction, the mixture was diluted with 10% NaHCO₃ solution, extracted with hexane, dried with Na₂SO₄, filtered, concentrated. The residue was purified by filtration through a pad (length 2 cm) of silica gel (1% Et₃N in hexane). The yield of **5** + **6** was 80-95 %. However, the isomers could not be separated by column chromatography. The ratio of **5** and **6** was determined by ¹H NMR. The assignments of the isomers **5** and **6** was done by comparison of the ¹H NMR shifts of the vinylic hydrogens with that of similar compounds.⁴

entry	conditions	ratio 5 : 6	yield of 5 + 6 (%)
1	2,6-lutidine, CH ₂ Cl ₂ , -20 °C, 1 h	0:100	95
2	2,6-diisopropyl-N,N-dimethylaniline, CH ₂ Cl ₂ , -20 °C, 24 h	0:100	96
3	Cy ₂ NEt, CH ₂ Cl ₂ , -78 °C, 2 h	30:70	89
4	KN(SiMe ₃) ₂ , THF/DMF (1:1), -78 °C, 24 h	50:50	82
5	<i>i</i> Pr ₂ EtN, CH ₂ Cl ₂ , -20 °C, 24 h	58:42	95
6	<i>i</i> Pr ₂ EtN, CH ₂ Cl ₂ , -78 °C, 24 h	68:32	98

Under thermodynamic conditions (entry 1 and 2) only dienol ether **6** was formed. Under kinetic control (entry 3-6) mixtures of **5** and **6** were observed. The two isomers could not be separated by chromatography. The thermodynamic isomer **6** (trimethylsilyl derivative) was also obtained under modified Kharash conditions.⁵

tri-Isopropylsilyl 2,3,4,4a,5,6-hexahydro-1-naphthalenyl ether (5): colorless oil. TLC (hexane): R_f 0.7; ¹H NMR (400 MHz, CDCl₃): δ[ppm] = 1.02 (d, *J* = 6.8 Hz, 18H, CH₃), 1.07-1.21 (m, 5H), 1.37-1.51 (m, 1H), 1.62-1.79 (m, 3H), 1.96-2.18 (m, 5 H), 5.50-5.56 (m, 1H, C-7), 6.50 (d, *J* = 9.8 Hz, 1H, C-8); ¹³C NMR (100 MHz, CDCl₃): δ[ppm] = 13.2 (CH-Si), 18.1 (d, *J* = 2.9 Hz, CH-Si), 22.6 (CH₂), 25.9 (CH₂), 30.6 (CH₂), 30.7 (CH₂), 30.9 (CH₂), 35.2 (C-4'), 106.2 (C-7), 123.1 (C-8), 135.0 (C'-8), 144.2 (C-1).

tri-Isopropylsilyl 3,4,4a,5,6,7-hexahydro-1-naphthalenyl ether (6): colorless oil. TLC (hexane): R_f 0.7. ¹H NMR (400 MHz, CDCl₃): δ[ppm] = 1.02 (d, *J* = 6.8 Hz, 18H, CH₃), 1.07-1.21 (m, 5H), 1.37-1.51 (m, 1H), 1.62-1.79 (m, 3H), 1.96-2.18 (m, 5 H), 4.92 (bd, *J* = 5.1 Hz, 1H, C-2), 5.96 (bs, 1H, C-8); ¹³C NMR (100 MHz, CDCl₃): δ[ppm] = 12.9 (CH-Si), 18.1 (CH₃), 18.2 (CH₃), 22.3 (CH₂), 24.1 (CH₂), 25.7 (CH₂), 30.7 (CH₂), 30.8 (CH₂), 36.3 (C-4'), 105.8 (C-2), 120.1 (C-8), 135.0 (C'-8), 148.3 (C-1); HRMS (EI): [M]⁺ calcd for C₁₉H₃₄OSi 306.23789, found 306.23548.

⁴ a) Munslow, W. D.; Reusch, W. J. *J. Org. Chem.* **1982**, 47, 5096-5099; b) Kato, M.; Watanabe, M.; Awen, B. Z. *J. Org. Chem.* **1993**, 58, 5145-5152.

⁵ Krafft, M. E.; Holton, R. A. *J. Am. Chem. Soc.* **1984**, 106, 7619-7621.

Arylation of **5 and **6**:** A flask containing Cs₂CO₃ (165 mg, 0.5 mmol), and PPh₃ (5.3 mg, 0.02 mmol) was evacuated and flushed with nitrogen for 3 times. Then a solution of **5** + **6** (60 mg, 0.2 mmol), PhBr (150 mg, 1.0 mmol) and Pd(OAc)₂ (2.23 mg, 0.01 mmol) in absolute DMF (1.5 mL) was injected and the mixture stirred at 100 °C for 12 h. After completion of the reaction (disappearance of **5** + **6**, TLC-monitoring), the mixture was poured onto water, extracted with CH₂Cl₂, dried (MgSO₄), filtered, and concentrated in vacuo. The residue was purified by flash chromatography.

5 : 6	yield of 7a [%]
0 : 100	42
68 : 32	45

The yield of **7a** is comparable to the yield obtained for the direct arylation of **4** under the same conditions. Moreover, **4** was observed in the reaction mixture by HPLC-MS. It seems, that **5** and **6** are first converted to enone **4** which is then arylated as usual. The high temperature is required for this reaction.

General procedure for palladium-catalyzed arylation of $\Delta^{8,9}$ -octal-1-one (**4**)

A flask containing Cs₂CO₃ (340 mg, 1.0 mmol), TBAB (128 mg, 0.4 mmol) and PPh₃ (10.5 mg, 0.04 mmol) was evacuated and flushed with nitrogen for 3 times. Then, a solution of enone **4** (60 mg, 0.4 mmol), aryl halide (2.0 mmol) and Pd(OAc)₂ (4.45 mg, 0.02 mmol) in degassed DMF (2.5 mL) was injected by syringe and the mixture stirred at rt for 3-5 days. After completion of the reaction (TLC-monitoring), the mixture was poured onto water and extracted with CH₂Cl₂. The organic layer was dried (MgSO₄), filtered, and concentrated in vacuo. The residue was purified by flash chromatography. During the optimization studies biphenyl (10 mol% based on **4**) was added as internal standard.

7-Phenyl-3,4-dihydronaphthalen-1(2H)-one (7a**):**⁶ yield 63 mg (71%), colorless oil. TLC (hexane/EtOAc, 4:1): R_f 0.55; ¹H NMR (400 MHz, CDCl₃): δ [ppm] = 2.06-2.16 (m, 2H, C-3), 2.62 (t, *J* = 6.3 Hz, 2H, C-4), 2.93 (t, *J* = 6.1 Hz, 2H, C-2), 7.24-7.30 (m, 2H, C-5 and C-4'), 7.37 (t, *J* = 7.6 Hz, 2H, C-3'), 7.54 (d, *J* = 7.6 Hz, 2H, C-2'), 7.64 (dd, *J* = 7.8, 1.8 Hz, 1H, C-6), 8.22 (d, *J* = 1.8 Hz, 1H, C-8); ¹³C NMR (100 MHz, CDCl₃): δ [ppm] = 23.2 (C-3), 29.4 (C-4), 39.2 (C-2), 125.5, 127.0, 127.5, 128.8, 129.4, 131.9, 132.9, 139.6, 140.0, 143.4, 198.4 (C-1).

7-(4-Methylphenyl)-3,4-dihydronaphthalen-1(2H)-one (7b**):**⁶ yield 48 mg (51%), colorless crystals, m.p. 76-77 °C. TLC (hexane/EtOAc, 4:1): R_f 0.6; ¹H NMR (400 MHz, CDCl₃): δ [ppm] = 2.09 (tt, 2H, *J* = 6.3 Hz, *J* = 6.1 Hz, C-3), 2.32 (s, 3H, CH₃), 2.61 (t, 2H, *J* = 6.3 Hz, C-4), 2.92 (t, 2H, *J* = 6.1 Hz, C-2), 7.17 (d, 2H, *J* = 7.9 Hz, C-3'), 7.24 (d, 1H, *J* = 7.8 Hz, C-5), 7.45 (d, 2H, *J* = 7.9 Hz, C-2'), 7.64 (dd, 1H, *J* = 7.8, *J* = 1.8 Hz, C-6), 8.20 (d, 1H, *J* = 1.8 Hz, C-8); ¹³C NMR (100 MHz, CDCl₃): δ [ppm] = 21.1 (CH₃), 23.3 (C-3), 29.4 (C-4), 39.2 (C-2), 125.2, 126.8, 129.3, 129.5, 131.7, 132.8, 137.1, 137.4, 139.5, 143.1, 198.4 (C-1).

⁶ Shiraishi, M.; Aramaki, Y.; Seto, M.; Imoto, H.; Nishikawa, Y.; Kanzaki, N.; Okamoto, M.; Sawada, H.; Nishimura, O.; Baba, M.; Fujino, M. *J. Med. Chem.* **2000**, *43*, 2049-2063.

7-(4-Methoxyphenyl)-3,4-dihydronaphthalen-1(2H)-one (7c):⁷ yield 62 mg (62%), colorless crystals, m.p. 120-121 °C. TLC (hexane/EtOAc, 4:1): R_f 0.3. ^1H NMR (400 MHz, CDCl_3): δ [ppm] = 2.08 (tt, J = 6.3, 6.1 Hz, 2H, C-3), 2.61 (t, J = 6.3 Hz, 2H, C-4), 2.91 (t, J = 6.1 Hz, 2H, C-2), 3.77 (s, 3H, OCH_3), 6.90 (d, J = 8.3 Hz, 2H, C-3'), 7.23 (d, J = 7.8 Hz, 1H, C-5), 7.48 (d, J = 8.3 Hz, 2H, C-2'), 7.60 (dd, J = 7.8, 1.5 Hz, 1H, C-6), 8.16 (d, J = 1.5 Hz, 1H, C-8); ^{13}C NMR (100 MHz, CDCl_3): δ [ppm] = 23.3 (C-3), 29.4 (C-4), 39.2 (C-2), 55.3 (OCH_3), 114.2, 124.9, 128.0, 129.3, 131.5, 132.5, 132.8, 139.2, 142.7, 159.3 (C-4'), 198.5 (C-1).

7-(4-tert-Butylphenyl)-3,4-dihydronaphthalen-1(2H)-one (7d): yield 65 mg (59%), colorless oil. TLC (hexane/EtOAc, 4:1): R_f 0.7. ^1H NMR (400 MHz, CDCl_3): δ [ppm] = 1.28 (s, 9H, CH_3), 2.09 (tt, J = 6.3, 6.1 Hz, 2H, C-3), 2.61 (t, J = 6.3 Hz, 2H, C-4), 2.92 (t, J = 6.1 Hz, 2H, C-2), 7.24 (d, J = 7.8 Hz, 1H, C-5), 7.39 (d, J = 8.6 Hz, 2H, C-3'), 7.50 (d, J = 8.6 Hz, 2H, C-2'), 7.64 (dd, J = 7.8, 1.8 Hz, 1H, C-6), 8.21 (d, J = 1.8 Hz, 1H, C-8); ^{13}C NMR (100 MHz, CDCl_3): δ [ppm] = 23.3 (C-3), 29.4 (C-4), 31.3 (CH_3), 34.5 (CMe_3), 39.2 (C-2), 125.2, 125.8, 126.6, 129.3, 131.8, 132.8, 137.0, 139.4, 143.1, 150.6, 198.4 (C-1); HRMS (EI): $[M]^+$ calcd for $\text{C}_{20}\text{H}_{22}\text{O}$ 278.16706, found 278.16580.

7-[4-(Dimethylamino)phenyl]-3,4-dihydronaphthalen-1(2H)-one (7e): yield 50 mg (47%), yellowish crystals, m.p. 110-111 °C. TLC (hexane/EtOAc, 4:1): R_f 0.35. ^1H NMR (400 MHz, CDCl_3): δ [ppm] = 2.07 (tt, J = 6.3, 6.1 Hz, 2H, C-3), 2.59 (t, J = 6.3 Hz, 2H, C-4), 2.89 (t, J = 6.1 Hz, 2H, C-2), 2.91 (s, 6H, CH_3), 6.71 (d, J = 8.3 Hz, 2H, C-3'), 7.19 (d, J = 7.8 Hz, 1H, C-5), 7.45 (d, J = 8.3 Hz, 2H, C-2'), 7.60 (dd, J = 7.8, 2.2 Hz, 1H, C-6), 8.17 (d, J = 2.2 Hz, 1H, C-8); ^{13}C NMR (100 MHz, CDCl_3): δ [ppm] = 23.3 (C-3), 29.3 (C-4), 39.2 (C-2), 40.5 (CH_3), 112.6, 124.2, 127.5, 127.8, 129.2, 131.1, 132.7, 139.6, 142.0, 150.1, 198.6 (C-1); HRMS (EI): $[M]^+$ calcd for $\text{C}_{18}\text{H}_{19}\text{NO}$ 265.14665, found 265.14554.

Ethyl 4-(8-oxo-5,6,7,8-tetrahydronaphthalen-2-yl)benzoate (7f): yield 56 mg (48%), colorless crystals, m.p. 79-80 °C. TLC (hexane/EtOAc, 4:1): R_f 0.35. ^1H NMR (400 MHz, CDCl_3): δ [ppm] = 1.34 (t, J = 7.1 Hz, 3H, CH_3), 2.10 (tt, J = 6.3, 6.1 Hz, 2H, C-3), 2.63 (t, J = 6.3 Hz, 2H, C-4), 2.94 (t, J = 6.1 Hz, 2H, C-2), 4.31 (q, J = 6.1 Hz, 2H, OCH_2), 7.29 (d, J = 7.8 Hz, 1H, C-5), 7.61 (d, J = 8.3 Hz, 2H, C-2'), 7.67 (dd, J = 7.8, 1.8 Hz, 1H, C-6), 8.04 (d, J = 8.3 Hz, 2H, C-3'), 8.24 (d, J = 1.8 Hz, 1H, C-8); ^{13}C NMR (100 MHz, CDCl_3): δ [ppm] = 14.3 (CH_3), 23.1 (C-3), 29.4 (C-4), 39.1 (C-2), 61.0 (CH_2O), 125.7, 126.8, 129.5, 129.5, 130.1, 131.9, 132.9, 138.4, 144.3, 166.4 (CO_2Et), 198.2 (C-1); HRMS (EI): $[M]^+$ calcd for $\text{C}_{19}\text{H}_{18}\text{O}_3$ 294.12558, found 294.12690.

6,7-Dihydro-2,2'-binaphthalen-8(5H)-one (7g): yield 54 mg (50%), colorless crystals, m.p. 152 °C. TLC (hexane/EtOAc, 4:1): R_f 0.6. ^1H NMR (400 MHz, CDCl_3): δ [ppm] = 2.08 (tt, J = 6.3, 6.1 Hz, 2H, C-3), 2.61 (t, J = 6.3 Hz,

⁷ Bailey, A. S.; Dale, G. A.; Shuttleworth, A. J.; Weizmann, D. P. *J. Chem. Soc.* **1964**, 5110-5118.

2H, C-4), 2.91 (t, $J = 6.1$ Hz, 2H, C-2), 7.26 (d, $J = 7.8$ Hz, 1H, C-5), 7.35-7.45 (m, 2H), 7.67 (dd, $J = 7.8, 1.5$ Hz, 1H, C-6), 7.73-7.85 (m, 4H), 7.98 (s, 1H), 8.33 (d, $J = 1.5$ Hz, 1H, C-8); ^{13}C NMR (100 MHz, CDCl_3): $\delta[\text{ppm}] = 23.2$ (C-3), 29.4 (C-4), 39.2 (C-2), 125.1, 125.6, 125.7, 126.1, 126.3, 127.6, 128.2, 129.4, 132.1, 133.7, 132.7, 132.9, 133.6, 137.2, 139.4, 143.5, 198.4 (C-1); HRMS (EI): $[\text{M}]^+$ calcd for $\text{C}_{20}\text{H}_{16}\text{O}$ 272.12011, found 272.1161.

3-(4-*tert*-Butylphenyl)cyclohex-1-ene-1-carbaldehyde (9): This compound was prepared by the general procedure on a 1 mmol scale, yield 97 mg, 41%, pale yellow oil. TLC (hexane/EtOAc, 4:1): R_f 0.6. ^1H NMR (400 MHz, CDCl_3): $\delta[\text{ppm}] = 1.32$ (s, 9H, $(\text{CH}_3)_3$), 1.59-1.69 (m, 2H, CH_2), 1.81-1.90 (m, 1H, CH_2), 2.05-2.43 (m, 3H, CH_2), 3.62 (br s, 1H, C-3), 6.79 (br s, 1H, C-2), 7.11 (d, $J = 8.2$ Hz, 2H, Ar), 7.35 (d, $J = 8.2$ Hz, 2H, Ar), 9.48 (s, 1H, CHO). ^{13}C NMR (100 MHz, CDCl_3): $\delta[\text{ppm}] = 20.5$ (CH_2), 21.3 (CH_2), 31.3 (CH_3), 31.9 (CH_2), 34.4 ($\text{C}(\text{CH}_3)_3$), 42.7 (C-3), 125.6 (Ar), 127.4 (Ar), 140.8, 141.8, 149.7, 153.4 (C-2), 194.6 (CHO); HRMS (EI): $[\text{M}]^+$ calcd for $\text{C}_{17}\text{H}_{22}\text{O}$ 242.1728, found 242.1671.