A One-Pot Cross-Pinacol Coupling/Rearrangement Procedure

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Dedicated to *Dieter Seebach* on the occasion of his 75th birthday

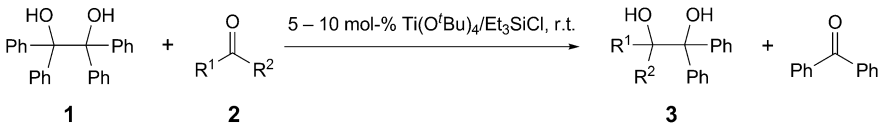
A new catalytic *retro*-pinacol/cross-pinacol reaction, followed by subsequent rearrangement or deoxygenation of the intermediately formed vicinal diols, is described. This operationally simple one-pot protocol allows isolation of geminal α,α-diphenyl ketones or 1,1-diphenyl alkenes with high yields and selectivities.

Introduction. – Vicinal diols are not only substructures in a variety of natural products but they also serve as important functional-group units for the synthesis various structure elements [1]. A very effective method for the construction of vicinal diols is the pinacol coupling due to the direct one-step reaction of carbonyl compounds and thus high atom economy. Usually, the application of pinacol coupling is restricted to the synthesis of symmetrical diols. In addition, stoichiometric amounts of reducing metals are required for full conversion.

Recently, we have reported a new method for the construction of pinacol cross-coupling products. This new methodology is based on a *retro*-pinacol/cross-pinacol coupling process. The unsymmetrical 1,2-diols **3** were obtained in excellent yields. Corresponding symmetrically pinacol products were not detected. The reaction proceeds with very high yields under real catalytic conditions (*Scheme 1*) [2].

Here, we report the combination of this new transformation with further reactions.

Scheme 1. *Catalytic* retro-*Pinacol/Pinacol-Cross Coupling*

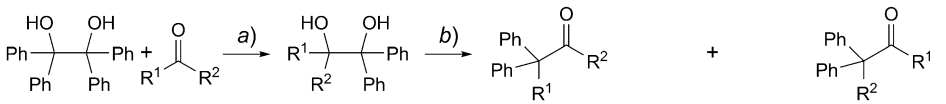


1 **2** **3**

Results and Discussion. – To extend the scope of this new transformation, we have investigated several suitable reactions for the successive application in a one-pot procedure. In a first series, we have tested a subsequent *Brønsted*-acid catalyzed pinacol rearrangement [3]. This reaction sequence was exemplified with different aldehydes **2a**–**2d** and ketones **2e**–**2k**. Several strong acids proved to be catalysts for the subsequent pinacol rearrangement. *para*-Toluenesulfonic acid (TsOH) turned out to be an optimal catalyst and was used for more intensive studies. This transformation is

characterized by operationally simple and very mild conditions. The initial cross-pinacol coupling process is monitored by TLC. Upon completion of this process, 20 mol-% TsOH were added to the resulting mixture. Depending on the substrates, the rearrangement process was completed after 2–6 h at room temperature. Results of these investigations are compiled in *Scheme 2*.

Scheme 2. *One-Pot Cross-Pinacol Coupling/Pinacol Rearrangement*



1	R^1 R^2	R^1 R^2	R^1 R^2	Yield [%] (Ratio **4**:**5**)	R^1 R^2
2a	H ^{i}Pr	**3a** H ^{i}Pr	**4a** H ^{i}Pr	93 (100:0)	**5a** H ^{i}Pr
2b	H ^{sec}Bu	**3b** H ^{sec}Bu	**4b** H ^{sec}Bu	95 (100:0)	**5b** H ^{sec}Bu
2c	H Et_2CH	**3c** H Et_2CH	**4c** H Et_2CH	96 (100:0)	**5c** H Et_2CH
2d	H Ph	**3d** H Ph	**4d** H Ph	91 (100:0)	**5d** H Ph
2e	Me Me	**3e** Me Me	**4e** Me Me	83 (100:0)	**5e** Me Me
2f	Et Et	**3f** Et Et	**4f** Et Et	87 (100:0)	**5f** Et Et
2g	$-(CH_2)_4-$	**3g** $-(CH_2)_4-$	**4g** $-(CH_2)_4-$	91 (100:0)	**5g** $-(CH_2)_4-$
2h	Ph Me	**3h** Ph Me	**4h** Ph Me	92 (>99:<1)	**5h** Ph Me
2i	Bn Me	**3i** Bn Me	**4i** Bn Me	89 (96:4)	**5i** Bn Me
2k	^{i}Bu Me	**3k** ^{i}Bu Me	**4k** ^{i}Bu Me	84 (67:33)	**5k** ^{i}Bu Me

a) 5–10 mol-% $Ti(O^tBu)_4/Et_3SiCl$, 3 equiv. of aldehydes or 4 equiv. ketones, r.t., 8 h–3 d. *b*) 20 mol-% TsOH, 2–6 h.

The corresponding ketones **4a**–**4k** were obtained in high yields under comparatively mild conditions[1]). Regioselectivity of the rearrangement is usually very high. This is due to the more stable corresponding diphenylcarbenium ions, which are exclusively formed as intermediates, when used with pinacol-cross-coupling products **3a**–**3k**. As a consequence α,α-diphenylketones **4a**–**4k** or **5a**–**5k** are detected exclusively as the main products. The ratio of the two possible regioisomers **4a**–**4k** and **5a**–**5k** is dictated by migratory aptitude of the substituents R^1 and R^2. Based on the results collected in *Scheme 2*, the following migration tendency is observed: H $\gg$ Ph > Bn > Alkyl > Me. The extremely high migration tendency of H resulted in a very fast and selective rearrangement (reactions of aldehydes **2a**–**2d**, $R^1 = H$; *Scheme 2*).

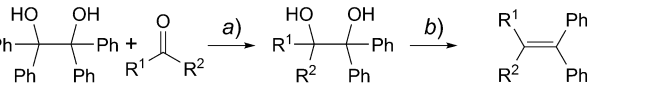
Another possible consecutive reaction is the deoxygenation of vicinal diols to yield the corresponding alkenes [12]. This is of special interest, since the formation of the corresponding alkenes is not observed during the initial *retro*-pinacol/pinacol-coupling reaction (*Scheme 1*). On the other hand, these compounds were found as by-products in mixtures of pinacol couplings. In *McMurry* reactions, alkenes were found as the main products, alongside varying amounts of the corresponding diols [13].

To exploit the described selectivity, we have adopted the reaction conditions of *Barua* and *Sharma* [4] in a one-pot procedure, as the *retro*-pinacol/pinacol coupling can be accomplished in different solvents, also in MeCN. This method for the deoxygenation of vicinal diols represents a mild and operationally easy access to highly substituted alkenes. Again, the initial cross-pinacol coupling process is monitored by

[1]) Compare with the results in [4–11].

TLC. Upon completion of this process, 2 equiv. of NaI and Me_3SiCl were added to the mixture. Depending on the substrates, the deoxygenation was completed after 1–12 h at room temperature. Tetrasubstituted alkenes **6e**–**6k** were isolated in high yields (*Scheme 3*)[2]).

Scheme 3. *Synthesis of Alkenes* via *Cross*-retro-*Pinacol/Reductive Elimination*



1	R^1	R^2		R^1	R^2		R^1	R^2	Yield [%]
2a	H	^{i}Pr	**3a**	H	^{i}Pr	**6a**	H	^{i}Pr	–[2])
2b	H	^{sec}Bu	**3b**	H	^{sec}Bu	**6b**	H	^{sec}Bu	–[2])
2c	H	Et_2CH	**3c**	H	Et_2CH	**6c**	H	Et_2CH	–[2])
2d	H	Ph	**3d**	H	Ph	**6d**	H	Ph	44[2])
2e	Me	Me	**3e**	Me	Me	**6e**	Me	Me	78
2f	Et	Et	**3f**	Et	Et	**6f**	Et	Et	76
2g	$-(CH_2)_4-$		**3g**	$-(CH_2)_4-$		**6g**	$-(CH_2)_4-$		75
2h	Ph	Me	**3h**	Ph	Me	**6h**	Ph	Me	84
2i	Bn	Me	**3i**	Bn	Me	**6i**	Bn	Me	77
2k	^{i}Bu	Me	**3k**	^{i}Bu	Me	**6k**	^{i}Bu	Me	74

a) 5–10 mol-% $Ti(O^{t}Bu)_4/Et_3SiCl$, 3 equiv. of aldehydes or 4 equiv. ketones, r.t., 8 h–3 d. *b*) NaI, Me_3SiCl.

When used with 1,2-diols **3a**–**3d** (pinacol-coupling products of aldehydes **2a**–**2d**), the elimination process was observed to only a small degree. The high migration tendency of H prevents a reductive elimination of secondary alcohols **3a**–**3d** ($R^1 = H$), since the diphenylcarbenium ion is also a reactive intermediate during this reductive elimination. Instead, the corresponding rearranged ketones **4a**–**4d** were obtained as the major products. Thus, the reductive elimination is restricted to the deployment of ketones only.

In conclusion, 1,1-diphenyl alkenes or geminal α,α-diphenyl ketones are accessible by a new one-pot procedure. This process includes a catalytic *retro*-pinacol/pinacol-coupling reaction, followed by rearrangement or reductive elimination. Comparisons of the results of the one-pot reactions with separately accomplished reaction steps reveal no relevant difference in yields and selectivity. Thus, by the one-pot procedure described here, extensive purification steps can be avoided. The products are obtained in high yields by operationally simple protocols and mild reaction conditions. These observations further emphasize the efficiency and the advantages of the *retro*-pinacol/pinacol-coupling process.

Experimental Part

General. Commercially available aldehydes were freshly distilled before use. All other chemicals used in the syntheses were purchased from *Sigma–Aldrich* and were used without further purification. Air- and/or moisture-sensitive reactions were carried out in anh. solvents in oven- or flame-dried glassware. TLC: silica gel *60 F254* TLC plates; used to monitor the progress of the reactions. Column

[2]) Compounds **4a**, **4b**, **4c**, and **4d** are identified as the major products.

chromatography (CC): silica gel *60* (particle size 0.04–0.063 mm). Yields were determined after CC. ^{1}H- and ^{13}C-NMR: at 500 and 125 MHz, resp.; chemical shifts δ in ppm and coupling constants J in Hz. EI-MS: *Concept-H* mass spectrometer (*MSI*). ESI-MS: *LTQ-FT* mass spectrometer (*Thermo Industries*).

General Procedure for the Synthesis of α,α-Diphenyl-Ketones **4a**–**4k**. In a typical experiment, 366 mg benzopinacol **1** (1.0 mmol) and 3 equiv. of the corresponding aldehyde **2a**–**2d** (4 equiv. of the corresponding ketones **2e**–**2k**) were dissolved in 3.0 ml of dry CH_2Cl_2. One ml of a separately prepared soln. containing 0.05M $Ti(O^tBu)_4$ and Et_3SiCl (0.1M for the reaction of ketones) was added. The resulting soln. was stirred at ambient temp. in a sealed reaction tube. The reaction was continously monitored by TLC (hexane/acetone 9:1). At the end of the reaction (when **1** is no more detectable (1 h to 3 d for aldehydes or 12 h to 5 d for ketones)), $TsOH \cdot H_2O$ (38 mg, 0.2 mmol) was added. Again the reaction was monitored by TLC and was complete after 2–6 h (hexane/acetone 9:1). The resulting mixture was extracted with CH_2Cl_2, and successively by sat. aq. NH_4Cl and $NaHCO_3$ soln. The org. layers were separated, dried ($MgSO_4$), and the solvent was removed *in vacuo*. The residue was purified by flash CC (hexane/acetone 19:1 to 9:1).

3-Methyl-1,1-diphenylbutan-2-one (**4a**) [5]. Yield: 93% (over two reaction steps). Colorless oil. ^{1}H-NMR: 1.17 (*d*, J = 7.2, 6 H); 2.86 (*sept.*, J = 6.9, 1 H); 5.36 (*s*, 1 H); 7.28–7.88 (*m*, 10 H). ^{13}C-NMR: 18.6; 40.9; 62.1; 127.1; 128.6; 128.9; 138.6; 212.1. HR-EI-MS: 238.1358 (M^+, $C_{17}H_{18}O^+$; calc. 238.1358).

4-Methyl-1,1-diphenylpentan-2-one (**4b**). Yield: 95% (over two reaction steps). Colorless oil. ^{1}H-NMR: 0.85 (*t*, J = 7.4, 3 H); 1.13 (*d*, J = 7.0, 3 H); 1.39–1.48 (*m*, 1 H); 1.73–1.81 (*m*, 1 H); 2.68 (*pseudo-sext.*, J = 6.8, 1 H); 5.30 (*s*, 1 H); 7.27–7.36 (*m*, 10 H). ^{13}C-NMR: 11.6; 16.2; 26.0; 47.9, 62.8; 127.1; 128.6; 129.0; 138.6; 211.6. HR-ESI-MS: 275.1406 ($[M + Na]^+$, $C_{18}H_{20}NaO^+$; calc. 275.1412).

3-Ethyl-1,1-diphenylpentan-2-one (**4c**). Yield: 96% (over two reaction steps). Colorless oil. ^{1}H-NMR: 0.82 (*t*, J = 7.4, 3 H); 1.48–1.60 (*m*, 2 H); 1.69–1.82 (*m*, 2 H); 2.57 (*quint.*, J = 6.4, 1 H); 5.29 (*s*, 1 H); 7.28–7.38 (*m*, 10 H). ^{13}C-NMR: 11.6; 23.6; 55.1; 63.2; 127.1; 128.5; 129.1; 138.3; 210.8. HR-ESI-MS: 289.1561 ($[M + Na]^+$, $C_{19}H_{22}NaO^+$; calc. 289.1568).

1,2,2-Triphenylethanone (**4d**) [6]. Yield: 91% (over two reaction steps). White solid. M.p. 137.9°. ^{1}H-NMR: 5.96 (*s*, 1 H); 7.15–7.26 (*m*, 10 H); 7.31–7.34 (*m*, 2 H); 7.41–7.45 (*m*, 1 H), 7.92–7.94 (*m*, 2 H). ^{13}C-NMR: 59.4; 127.1; 128.6; 128.7; 129.0; 129.1; 133.0; 136.8; 139.1; 198.2. HR-ESI-MS: 295.1094 ($[M + Na]^+$, $C_{20}H_{16}NaO^+$; calc. 295.1099).

3,3-Diphenylbutan-2-one (**4e**) [7]. Yield: 83% (over two reaction steps). Colorless oil. ^{1}H-NMR: 1.92 (*s*, 3 H); 2.16 (*s*, 3 H); 7.24–7.39 (*m*, 10 H). ^{13}C-NMR: 26.4; 27.6, 62.2; 126.9; 128.2; 128.3; 143.5; 209.1. HR-ESI-MS: 247.1094 ($[M + Na]^+$, $C_{16}H_{16}NaO^+$; calc. 247.1099).

4,4-Diphenylhexan-3-one (**4f**) [8]. Yield: 87% (over two reaction steps). Colorless oil. ^{1}H-NMR: 0.71 (*t*, J = 7.5, 3 H); 0.91 (*t*, J = 7.5, 3 H); 2.33–2.43 (*m*, 4 H); 7.27–7.39 (*m*, 10 H). ^{13}C-NMR: 9.0; 9.4; 30.0; 32.4; 66.6; 126.7; 128.1; 129.4; 141.5; 211.4. HR-ESI-MS: 275.1406 ($[M + Na]^+$, $C_{18}H_{20}NaO^+$; calc. 275.1412).

2,2-Diphenylcyclohexanone (**4g**) [9]. Yield: 91% (over two reaction steps). White solid. M.p. 103.2°. ^{1}H-NMR: 1.82–1.87 (*m*, 2 H); 1.93–1.99 (*m*, 2 H); 2.51–2.57 (*m*, 2 H); 2.59–2.65 (*m*, 2 H); 7.07–7.08 (*m*, 4 H); 7.24–7.34 (*m*, 6 H). ^{13}C-NMR: 22.1; 27.7; 39.1; 40.6; 63.9; 126.8; 128.3; 128.5; 142.3; 211.2. HR-ESI-MS: 273.1250 ($[M + Na]^+$, $C_{18}H_{18}NaO^+$; calc. 273.1255).

1,1,1-Triphenylpropan-2-one (**4h**) [10]. Yield: 92% (over two reaction steps). White solid. M.p. 137.9°. ^{1}H-NMR: 2.15 (*s*, 3 H); 7.26–7.37 (*m*, 15 H). ^{13}C-NMR: 29.7; 73.1; 126.7; 128.1; 130.3; 142.2; 205.9. HR-ESI-MS: 309.1252 ($[M + Na]^+$, $C_{21}H_{18}NaO^+$; calc. 309.1255).

3,3,4-Triphenylbutan-2-one (**4i**) [11]. Yield: 89% (mixture **4i**/**5i**: 96/4; over two reaction steps). White solid. M.p. 44.3° (recryst. petroleum ether (PE)/Et_2O). ^{1}H-NMR: 2.09 (*s*, 3 H); 3.71 (*s*, 2 H); 6.66–6.68 (*m*, 2 H); 6.99–7.02 (*m*, 2 H); 7.06–7.07 (*m*, 1 H); 7.25–7.34 (*m*, 10 H). ^{13}C-NMR: 27.3; 43.5, 68.6; 125.9; 127.0; 127.2; 128.0; 129.8; 130.9; 137.7; 140.3; 207.3. HR-ESI-MS: 323.1407 ($[M + Na]^+$, $C_{22}H_{20}NaO^+$; calc. 323.1412).

5-Methyl-3,3-diphenylhexan-2-one (**4k**) [14]. Yield: 84% (mixture **4k**/**5k**: 67/33, over two reaction steps). Colorless oil. ^{1}H-NMR: 0.67 (*d*, J = 6.7, 6 H); 1.37–1.42 (*m*, 1 H); 2.06 (*s*, 3 H); 2.31 (*d*, J = 5.4, 2 H); 7.21–7.37 (*m*, 10 H). ^{13}C-NMR: 22.4; 24.3; 24.9; 45.9; 66.5; 126.8; 128.1; 129.5; 141.9; 208.0. HR-ESI-MS: 289.1563 ($[M + Na]^+$, $C_{19}H_{22}NaO^+$; calc. 289.1568).

5-Methyl-2,2-diphenylhexan-3-one (**5k**). Yield: 84% (mixture of **4k** and **5k**: 67/33; over two reaction steps). ^{1}H-NMR: 0.81 (*d*, *J* = 6.7, 1 H); 1.88–1.92 (*m*, 9 H); 2.07–2.12 (*m*, 1 H); 2.34 (*d*, *J* = 6.7, 2 H); 7.21–7.37 (*m*, 10 H). ^{13}C-NMR: 24.3; 26.4; 27.2; 47.9; 62.1; 126.8; 128.2; 128.5; 143.7; 210.4.

General Procedure for the Synthesis of 1,1-Diphenyl Alkenes **6a**–**6k**. In a typical experiment, 366 mg of **1** (1.0 mmol) and 3 equiv. of the corresponding aldehyde **2a**–**2d** (4 equiv. of the corresponding ketone **2e**–**2k**) were dissolved in 3.0 ml of dry MeCN. One ml of a separately prepared soln. containing 0.05M $Ti(O^tBu)_4$ and Et_3SiCl (0.1M for the reaction of ketones) was added. The resulting soln. was stirred at ambient temp. in a sealed reaction tube.

The reaction was continuously monitored by TLC (hexane/acetone 9:1). The reaction was complete after 1 h to 3 d for aldehydes and 12 h to 5 d for ketones (**1** was no more detectable).

A soln. of NaI (2.0 mmol) in 4.0 ml of MeCN was added. After 15 min, the mixture was treated with Me_3SiCl (2.0 mmol). The reaction was completed after 1–12 h (pinacol-cross-coupling products **3a**–**3k** were not detectable). The resulting mixture was extracted with Et_2O, and successively washed with sat. aq. $Na_2S_2O_3$ and NaCl solns. The org. layers were separated, dried ($MgSO_4$), and the solvent was removed *in vacuo*. The residue was purified by flash CC (hexane/Et_2O 49:1 to 9:1).

1,1,2-Triphenylethene (=*1,1′,1″-Ethene-1,1,2-triyltribenzene*; **6d**) [15]. Yield: 44% (over two reaction steps). White solid. M.p. 71.2°. ^{1}H-NMR: 6.89 (*s*, 1 H); 6.94–6.96 (*m*, 2 H); 7.00–7.06 (*m*, 3 H); 7.12–7.15 (*m*, 2 H); 7.19–7.26 (*m*, 8 H). ^{13}C-NMR: 126.7; 127.4; 127.5; 127.6; 127.9; 128.1; 128.2; 128.6; 129.5; 130.4; 137.4; 140.3; 142.6; 143.4. HR-EI-MS: 256.1252 (M^+, $C_{20}H_{16}^+$; calc. 256.1252).

2-Methyl-1,1-diphenylprop-1-ene (=*1,1′-(2-Methylprop-1-ene-1,1-diyl)dibenzene*; **6e**) [16]. Yield: 78% (over two reaction steps). Colorless oil. M.p. 11.0°. ^{1}H-NMR: 1.72 (*s*, 6 H); 7.05–7.11 (*m*, 6 H); 7.17–7.20 (*m*, 4 H). ^{13}C-NMR: 22.5; 126.0; 127.8; 129.8; 131.0; 137.1; 143.3. HR-EI-MS: 208.1253 (M^+, $C_{16}H_{16}^+$; calc. 208.1252).

2-Ethyl-1,1-diphenylbut-1-ene (=*1,1′-(2-Ethylbut-1-ene-1,1-diyl)dibenzene*; **6f**) [17]. Yield: 76% (over two reaction steps). Colorless oil. ^{1}H-NMR: 0.94 (*t*, *J* = 7.5, 6 H); 2.07 (*q*, *J* = 7.4, 4 H); 7.07–7.12 (*m*, 6 H); 7.18–7.21 (*m*, 4 H). ^{13}C-NMR: 13.3; 24.3; 126.0; 128.0; 129.2; 137.1; 142.1; 143.5. HR-EI-MS: 236.1565 (M^+, $C_{18}H_{20}^+$; calc. 236.1565).

1-(Cyclopentylidene(phenyl)methyl)benzene (=*1,1′-(Cyclopentylidenemethanediyl)dibenzene*; **6g**) [18]. Yield: 75% (over two reaction steps). White solid. M.p. 62.1°. ^{1}H-NMR: 1.56–1.60 (*m*, 4 H); 2.23–2.25 (*m*, 4 H); 7.09–7.12 (*m*, 6 H); 7.19–7.22 (*m*, 4 H). ^{13}C-NMR: 26.9; 33.2; 126.0; 127.9; 129.2; 132.9; 143.4; 143.5. HR-EI-MS: 234.1409 (M^+, $C_{18}H_{18}^+$; calc. 234.1409).

1,1,2-Triphenylprop-1-ene (=*1,1′,1″-Prop-1-ene-1,1,2-triyltribenzene*; **6h**) [19]. Yield: 84% (over two reaction steps). White solid. M.p. 90.0°. ^{1}H-NMR: 2.06 (*s*, 3 H); 6.81–6.83 (*m*, 2 H); 6.91–6.96 (*m*, 3 H); 7.00–7.03 (*m*, 2 H); 7.05–7.07 (*m*, 3 H); 7.16–7.19 (*m*, 3 H); 7.25–7.28 (*m*, 2 H). ^{13}C-NMR: 23.3; 125.8; 126.2; 126.4; 126.5; 127.4; 127.8; 128.1; 129.3; 130.0; 130.8; 135.6; 139.3; 143.0; 143.5; 144.0. HR-EI-MS: 270.1408 (M^+, $C_{21}H_{18}^+$; calc. 270.1409).

2-Benzyl-1,1-diphenylprop-1-ene (=*1,1′,1″-(2-Methylprop-1-en-3-yl-1-ylidene)trisbenzene*; **6i**) [20]. Yield: 77% (over two reaction steps). White solid. M.p. 66.3°. ^{1}H-NMR: 1.61 (*s*, 3 H); 3.43 (*s*, 2 H); 6.94–7.26 (*m*, 15 H). ^{13}C-NMR: 19.7; 41.4; 125.9; 126.2; 126.4; 127.9; 128.1; 128.3; 128.6; 129.4; 129.6; 133.1; 139.3; 140.5; 143.0; 143.0. HR-EI-MS: 284.1565 (M^+, $C_{22}H_{20}^+$; calc. 284.1565).

2,4-Dimethyl-1,1-diphenylpent-1-ene (=*1,1′-(2,4-Dimethylpent-1-ene-1,1-diyl)dibenzene*; **6k**). Yield: 74% (over two reaction steps). Colorless oil. ^{1}H-NMR: 0.74 (*d*, *J* = 6.6, 6 H); 1.68 (*s*, 3 H); 1.78–1.83 (*m*, 1 H); 1.96 (*d*, *J* = 7.5, 2 H); 7.04–7.12 (*m*, 6 H); 7.17–7.20 (*m*, 4 H). ^{13}C-NMR: 19.7; 22.3; 26.7, 44.3; 125.9; 126.0; 127.9; 127.9; 129.6; 129.8; 134.1; 138.6; 143.5; 143.7. HR-EI-MS: 250.1722 (M^+, $C_{19}H_{22}^+$; calc. 250.1722).

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