Supplementary material for the article:

Ajdačić, V.; Nikolić, A.; Kerner, M.; Wipf, P.; Opsenica, I. M. Reevaluation of the Palladium/Carbon-Catalyzed Decarbonylation of Aliphatic Aldehydes. Synlett 2018, 29 (13), 1781-1785. https://doi.org/10.1055/s-0037-1610433

Supporting Information
for DOI: 10.1055/s-0037-1610433
© Georg Thieme Verlag KG Stuttgart • New York 2018

Thieme

## Supporting Information

## Reevaluation of the Pd/C-Catalyzed Decarbonylation of Aliphatic Aldehydes

Vladimir Ajdačić, ${ }^{\text {a }}$ Andrea Nikolić, ${ }^{\text {a }}$ Michael Kerner, ${ }^{\text {b }}$ Peter Wipf, , Igor M. Opsenica*, ${ }^{\text {a }}$<br>${ }^{\text {a }}$ University of Belgrade-Faculty of Chemistry, PO Box 51, Studentski trg 16, 11158 Belgrade, Serbia<br>${ }^{\mathrm{b}}$ Department of Chemistry, University of Pittsburgh, 219 Parkman Avenue, Pittsburgh, Pennsylvania 15260, United States<br>* Corresponding authors.<br>igorop@chem.bg.ac.rs (I. M. Opsenica)

Supporting Information Contents: ..... Page

1) General Information ..... 2
2) Experimental Procedures and Characterization Data for Products ..... 2
3) ${ }^{1} \mathrm{H}$ NMR, ${ }^{13} \mathrm{C}$ NMR Copies of Products ..... 9
4) GC-MS Analysis ..... 25
5) References ..... 31

## General Information

$\mathrm{Pd} / \mathrm{C}(10 \mathrm{wt} . \%$ loading) was purchased from Sigma Aldrich. All aldehydes were obtained from commercial sources and used without further purification, except for the hydrocinnamaldehyde which was distilled prior to use since it is highly unstable. Unless stated otherwise, solvents and other reagents were obtained from commercial sources and used without further purification. Dry-flash chromatography was performed on $\mathrm{SiO}_{2}(0.018-0.032 \mathrm{~mm})$. IR spectra were recorded on a Thermo-Scientific Nicolet 6700 FT-IR Diamond Crystal instrument. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra were recorded on a Bruker Ultrashield Avance III spectrometer (at 500 and 125 MHz , respectively) using $\mathrm{CDCl}_{3}$ (unless stated otherwise) as the solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts are expressed in parts per million ( ppm ) on the ( $\delta$ ) scale. Chemical shifts were calibrated relative to those of the solvent. GC-MS spectra of the synthesized compounds were acquired on an Agilent Technologies 7890A apparatus equipped with a DB-5 MS column ( $30 \mathrm{~m} \times 0.25 \mathrm{~mm} \times 0.25 \mu \mathrm{~m}$ ), a 5975 C MSD and FID detector. The selected values are as follows: carrier gas was $\mathrm{He}(1.0 \mathrm{~mL} / \mathrm{min})$, temperature linearly increased from $40-315^{\circ} \mathrm{C}$ $\left(10^{\circ} \mathrm{C} / \mathrm{min}\right)$, injection volume: $1 \mu \mathrm{~L}$, temperature: $250^{\circ} \mathrm{C}$, temperature (FID detector): $300^{\circ} \mathrm{C}$, and EI mass spectra range: $\mathrm{m} / \mathrm{z} 40-550$. For determination of NMR and GC-MS yield, the internal standard (naphthalene or methyl benzoate) was added to the reaction mixture after the workup. Compound $\mathbf{1 0}$ was analyzed by high resolution tandem mass spectrometry using LTQ Orbitrap XL (Thermo Fisher Scientific Inc., USA) mass spectrometer. The sample was dissolved in MeCN and it was injected directly. Ionization was done in positive mode on heated electrospray ionization (HESI) probe. HESI parameters were: spray voltage 4.7 kV , vaporizer temperature $60^{\circ} \mathrm{C}$, sheath and auxiliary gas flow 24 and 10 (arbitrary units), respectively, capillary voltage 49 V , capillary temperature $275^{\circ} \mathrm{C}$, tube lens voltage 80 V , resolution (at $\mathrm{m} / \mathrm{z}$ 400): 30000 .

Compounds $\quad$ 3,3-diphenylpropanal (1b), ${ }^{1} \quad$ 2-(adamantan-1-yl)acetaldehyde ( $\mathbf{1 j}$ ), ${ }^{2}$ 2-(4methoxyphenyl)octanal (1n) ${ }^{3}$ and $3 \alpha, 7 \alpha, 12 \alpha$-triacetoxy- $5 \beta$-cholan-24-al $(4)^{4,5}$ were synthesized according to the previously reported procedures.

## General procedure A for decarbonylation of aliphatic aldehydes

Decarbonylation of 3-phenylpropanal to ethylbenzene (2a) [CAS Reg. No. 100-41-4]
Dry glass reaction tube purged with argon and equipped with a magnetic stir bar was charged with molecular sieves ( $3-4 \AA, 100 \mathrm{mg}$ ), aldehyde $\mathbf{1 a}(50 \mu \mathrm{~L}, 0.38 \mathrm{mmol}), \mathrm{Pd} / \mathrm{C}(20 \mathrm{mg}, 5 \mathrm{~mol} \%$ $\mathrm{Pd})$, and cyclohexane ( 1 mL ) and the sealed tube was heated at $130{ }^{\circ} \mathrm{C}$ for 24 h . The reaction
mixture was cooled to room temperature, filtered through a pad of Celite, and washed with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(15-20 \mathrm{~mL})$. Compound 2a was obtained, GC-MS yield: $67 \%$, based on naphthalene as a standard. GC-MS: $\mathrm{m} / \mathrm{z}=106.1[\mathrm{M}]^{+}$.

## NMR spectroscopic analysis:

## General procedure B for decarbonylation of aliphatic aldehydes

Dry glass reaction tube purged with argon and equipped with a magnetic stir bar was charged with molecular sieves ( $3-4 \AA, 100 \mathrm{mg}$ ), aldehyde $\mathbf{1 a}(40 \mu \mathrm{~L}, 0.30 \mathrm{mmol}), \mathrm{Pd} / \mathrm{C}(16 \mathrm{mg}, 5 \mathrm{~mol} \%$ $\mathrm{Pd})$, and $\mathrm{C}_{6} \mathrm{D}_{6}(1 \mathrm{~mL})$ and the sealed tube was heated at $130{ }^{\circ} \mathrm{C}$ for 24 h . The reaction mixture was cooled to room temperature, filtered through a short pad of $\mathrm{SiO}_{2}$ to remove the catalyst, and the $\mathrm{SiO}_{2}$ was washed with $\mathrm{C}_{6} \mathrm{D}_{6}(2 \times 0.5 \mathrm{~mL})$. Compound 2a was obtained, NMR yield: $78 \%$, based on methyl benzoate as a standard. ${ }^{1} \mathrm{H}$ NMR $\left(500 \mathrm{~Hz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)=7.10-7.00(\mathrm{~m}, 5 \mathrm{H}), 2.43(\mathrm{q}, \mathrm{J}$ $=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 1.06(\mathrm{t}, J=7.5 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}\left(125 \mathrm{~Hz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)=144.28,128.59,128.09$, 125.91, 29.15, 15.80.

## Decarbonylation of 3,3-diphenylpropanal to 1,1-diphenylethane (2b) ${ }^{6}$

Following the general procedure A for the decarbonylation, compound $\mathbf{2 b}$ was obtained after column chromatography $\left(\mathrm{SiO}_{2}\right.$ : hexane) as a colorless oil. Alongside the desired product, ${ }^{1} \mathrm{H}$ NMR analysis showed the formation of a side product, 1,1-diphenylethylene $\mathbf{3 b}$. The ratio between the main product and the side product was determined by ${ }^{1} \mathrm{H}$ NMR $(78 \% \mathbf{2 b}, 6 \% \mathbf{3 b})$. 1,1-Diphenylethane: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{~Hz}, \mathrm{CDCl}_{3}$ ) $\delta 7.29-7.15(\mathrm{~m}, 10 \mathrm{H}), 4.15(\mathrm{q}, J=7 \mathrm{~Hz}, 1 \mathrm{H})$, $1.64(\mathrm{~d}, J=7 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}\left(125 \mathrm{~Hz}, \mathrm{CDCl}_{3}\right) \delta 146.35,128.33$, 127.60, 125.99, 44.75, 21.83; GCMS m/z $182.1[\mathrm{M}]^{+}$.
1,1-Diphenylethylene: ${ }^{1} \mathrm{H}$ NMR $\left(500 \mathrm{~Hz}, \mathrm{CDCl}_{3}\right) \delta 7.35-7.30(\mathrm{~m}, 10 \mathrm{H}), 5.46(\mathrm{~s}, 2 \mathrm{H})$.

Decarbonylation of 2,2-diphenylacetaldehyde to diphenylmethane (2c) [CAS Reg. No. 101-81-5]

Following the general procedure A for decarbonylation, compound 2c was obtained after dryflash column chromatography $\left(\mathrm{SiO}_{2}\right.$ : hexane) as a colorless oil in $69 \%$ yield. Diphenylmethane ${ }^{1} \mathrm{H}$ NMR $\left(500 \mathrm{~Hz}, \mathrm{CDCl}_{3}\right)=7.31-7.27(\mathrm{~m}, 4 \mathrm{H}), 7.22-7.18(\mathrm{~m}, 6 \mathrm{H}), 4.00(\mathrm{~s}, 2 \mathrm{H}) . \mathrm{GC}-\mathrm{MS}: \mathrm{m} / \mathrm{z}=$ $168.0[\mathrm{M}]^{+}$.

Decarbonylation of phenylacetaldehyde to toluene (2d) [CAS Reg. No. 108-88-3]
Following the general procedure A for decarbonylation, compound 2d was obtained. GC-MS yield: $82 \%$, based on naphthalene as a standard. GC-MS: $\mathrm{m} / \mathrm{z}=92.0[\mathrm{M}]^{+}$.

## Decarbonylation of octanal to $n$-heptane (2e) [CAS Reg. No. 142-82-5]

Following the general procedure A for decarbonylation, compound $\mathbf{2 e}$ was obtained. GC-MS yield: $64 \%$, based on naphthalene as a standard. GC-MS: $m / z=100.0[M]^{+}$.

## Decarbonylation of nonanal to $\boldsymbol{n}$-octane (2f) [CAS Reg. No. 111-65-9]

Following the general procedure A for decarbonylation, compound $2 f$ was obtained. GC-MS yield: $50 \%$, based on naphthalene as a standard. GC-MS: $m / z=114.1[M]^{+}$.

## Decarbonylation of decanal to n-nonane (2g) [CAS Reg. No. 111-84-2]

Following the general procedure A for decarbonylation, compound $\mathbf{2 g}$ was obtained. GC-MS yield: $54 \%$, based on naphthalene as a standard. GC-MS: $\mathrm{m} / \mathrm{z}=128.1[\mathrm{M}]^{+}$.

## Decarbonylation of undecanal to $\boldsymbol{n}$-decane (2h) [CAS Reg. No. 124-18-5]

Following the general procedure A for decarbonylation, compound $\mathbf{2 h}$ was obtained. GC-MS yield: $99 \%$, based on naphthalene as a standard. GC-MS: $m / z=142.1[M]^{+}$.

## Decarbonylation of cyclohexanecarbaldehyde to cyclohexane (2i) [CAS Reg. No. 110-82-7]

Dry glass reaction tube purged with argon and equipped with a magnetic stir bar was charged with molecular sieves ( $3-4 \AA, 100 \mathrm{mg}$ ), aldehyde $\mathbf{1 i}(40 \mu \mathrm{~L}, 0.33 \mathrm{mmol}), \mathrm{Pd} / \mathrm{C}(18 \mathrm{mg}, 5 \mathrm{~mol} \%$ $\mathrm{Pd})$, and $\mathrm{C}_{6} \mathrm{D}_{6}(1 \mathrm{~mL})$ and the sealed tube was heated at $130{ }^{\circ} \mathrm{C}$ for 24 h . The reaction mixture was cooled to room temperature, filtered through a short pad of $\mathrm{SiO}_{2}$ to remove the catalyst, and the $\mathrm{SiO}_{2}$ was washed with $\mathrm{C}_{6} \mathrm{D}_{6}(2 \times 0.5 \mathrm{~mL})$. Compound $\mathbf{2 i}$ was obtained, NMR yield: $74 \%$, based on naphthalene as a standard. ${ }^{1} \mathrm{H} \operatorname{NMR}\left(500 \mathrm{~Hz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)=1.41(\mathrm{~s}, 12 \mathrm{H}) .{ }^{13} \mathrm{C}\left(125 \mathrm{~Hz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ $=27.18$

## General procedure $\mathbf{C}$ for decarbonylation of aliphatic aldehydes

## Decarbonylation of 2-(adamantan-1-yl)acetaldehyde to 1-methyladamantane (2j) ${ }^{7}$

Dry glass reaction tube purged with argon and equipped with a magnetic stir bar was charged with molecular sieves ( $3-4 \AA, 100 \mathrm{mg}$ ), aldehyde $\mathbf{1 j}(180 \mathrm{mg}, 1.01 \mathrm{mmol}), \mathrm{Pd} / \mathrm{C}(107 \mathrm{mg}, 10$ $\mathrm{mol} \% \mathrm{Pd}$ ), and cyclohexane ( 1 mL ) and the sealed tube was heated at $130{ }^{\circ} \mathrm{C}$ for 48 h . The
reaction mixture was cooled to room temperature, filtered through a pad of Celite, washed with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(15-20 \mathrm{~mL})$ and the solvents were removed under the reduced pressure. The crude product was purified by dry-flash column chromatography $\left(\mathrm{SiO}_{2}\right.$ : pentane) to afford product $\mathbf{2 j}$ as a colorless powder ( $119 \mathrm{mg}, 78 \%$ ). IC $(\mathrm{ATR})=2900,2844,1453 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H} \mathrm{NMR}(500 \mathrm{~Hz}$, $\left.\mathrm{CDCl}_{3}\right)=1.92(\mathrm{~s}, 3 \mathrm{H}), 1.70-1.55(\mathrm{~m}, 6 \mathrm{H}), 1.50-1.41(\mathrm{~m}, 6 \mathrm{H}), 0.76(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}(125 \mathrm{~Hz}$, $\left.\mathrm{CDCl}_{3}\right)=44.64,36.94,31.44,29.80,28.89 . \operatorname{GC}-\mathrm{MS}: \mathrm{m} / \mathrm{z}=150.1[\mathrm{M}]^{+}$.

## Deuterium labeling experiment



## [11 $\mathrm{D}_{1}$ ]1-methyladamantane ( $\mathbf{d - 2 j}$ )

Round-bottom flask, purged with argon and equipped with a magnetic stir bar was charged with aldehyde $\mathbf{1 j}$ ( $452 \mathrm{mg}, 2.53 \mathrm{mmol}$ ) and $\mathrm{MeOH}(7 \mathrm{~mL}) . \mathrm{NaBD}_{4}(106 \mathrm{mg}, 2.53,1$ equiv) was added to the solution in portions, over 5 minutes. The resulting mixture was stirred at room temperature for 3 h . The reaction was quenched with $\mathrm{H}_{2} \mathrm{O}(15 \mathrm{~mL})$ and the mixture was extracted with $\mathrm{Et}_{2} \mathrm{O}$ (2 $\times 20 \mathrm{~mL}$ ). The organic solution was dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and the solvents were removed under the reduced pressure. The crude product was used in the next reaction without further purification. Compound $\mathbf{1 0}$ was obtained as a colorless powder ( $396 \mathrm{mg}, 86 \%$ ). $\mathrm{Mp}=65-$ $68^{\circ} \mathrm{C}$. IC $(\mathrm{ATR})=3300,2902,2846,1450 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H} \operatorname{NMR}\left(500 \mathrm{~Hz}, \mathrm{CDCl}_{3}\right)=3.64(\mathrm{t}, \mathrm{J}=7.5 \mathrm{~Hz}$, $1 \mathrm{H}), 1.90(\mathrm{~s}, 3 \mathrm{H}), 1.66(\mathrm{~d}, \mathrm{~J}=12.0 \mathrm{~Hz}, 3 \mathrm{H}), 1.59(\mathrm{~d}, J=12.0 \mathrm{~Hz}, 3 \mathrm{H}), 1.54-1.41(\mathrm{~m}, 7 \mathrm{H}), 1.34$ $(\mathrm{d}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}\left(125 \mathrm{~Hz}, \mathrm{CDCl}_{3}\right)=58.31(\mathrm{t}, J=21.6 \mathrm{~Hz}), 47.05,42.72,37.03,31.79$, 28.59. GC-MS: $m / z=181.1[M]^{+}$.

Alcohol 10 ( $100 \mathrm{mg}, 0.55 \mathrm{mmol}$ ) was dissolved in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(8 \mathrm{~mL})$ and $\mathrm{PCC}(178 \mathrm{mg}, 0.83 \mathrm{mmol}$, 1.5 equiv) was added to the solution. The resulting mixture was stirred at room temperature for 2 hour. The mixture was filtered through a pad of $\mathrm{SiO}_{2}$ and the $\mathrm{SiO}_{2}$ was washed with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(20$ $\mathrm{mL})$. The solvent was removed under the reduced pressure to yield a pure $\boldsymbol{d} \mathbf{- 1} \mathbf{j}(95 \mathrm{mg}, 96 \%)$ as a colorless oil. IC $(\mathrm{ATR})=2903,2849,1707,1450 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR $\left(500 \mathrm{~Hz}, \mathrm{CDCl}_{3}\right)=9.87(\mathrm{~m}$, $0.15 \mathrm{H}), 2.12(\mathrm{~m}, 2 \mathrm{H}), 1.99(\mathrm{~s}, 3 \mathrm{H}), 1.76-1.64(\mathrm{~m}, 12 \mathrm{H}) .{ }^{13} \mathrm{C}\left(125 \mathrm{~Hz}, \mathrm{CDCl}_{3}\right)=203.61(\mathrm{C}-\mathrm{H})$, $203.32(\mathrm{t}, \mathrm{J}=26.1 \mathrm{~Hz}, \mathrm{C}-\mathrm{D}), 57.06(\mathrm{t}, J=3.5 \mathrm{~Hz}), 42.70,36.60,33.28$, 28.43. GC-MS: $\mathrm{m} / \mathrm{z}=$ $179.1[\mathrm{M}]^{+}$.

Following the general procedure C for decarbonylation, compound $\mathbf{d} \mathbf{-} \mathbf{2} \mathbf{j}$ was obtained after dryflash column chromatography $\left(\mathrm{SiO}_{2}\right.$ : pentane) as a colorless foam ( $49 \mathrm{mg}, 61 \%$ ). IC $(\mathrm{ATR})=$ $2955,2924,2853,1460 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR $\left(500 \mathrm{~Hz}, \mathrm{CDCl}_{3}\right)=1.92(\mathrm{~s}, 3 \mathrm{H}), 1.71-1.57(\mathrm{~m}, 6 \mathrm{H}), 1.47-$ $1.42(\mathrm{~m}, 6 \mathrm{H}), 0.76\left(\mathrm{~s}, \mathrm{CH}_{3}\right), 0.74\left(\mathrm{t}, J=1.5 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{D}\right) .{ }^{13} \mathrm{C}\left(125 \mathrm{~Hz}, \mathrm{CDCl}_{3}\right)=44.61,36.92$, 31.43, $31.11\left(\mathrm{t}, \mathrm{J}=18.9 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{D}\right), 29.76$, 28.87. GC-MS: $\mathrm{m} / \mathrm{z}=151.1[\mathrm{M}]^{+}$.

Decarbonylation of adamantane-1-carbaldehyde to adamantane (2k) [CAS Reg. No. 281-232]
Following the general procedure C for decarbonylation, compound $\mathbf{2 k}$ was obtained after dryflash column chromatography $\left(\mathrm{SiO}_{2}\right.$ : pentane) as a colorless powder ( $\left.88 \mathrm{mg}, 54 \%\right)$. $\mathrm{IC}(\mathrm{ATR})=$ 2904, 2848, $1450 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H} \operatorname{NMR}\left(500 \mathrm{~Hz}, \mathrm{CDCl}_{3}\right)=1.87(\mathrm{~s}, 4 \mathrm{H}), 1.75(\mathrm{~s}, 12 \mathrm{H}) .{ }^{13} \mathrm{C}(125 \mathrm{~Hz}$, $\left.\mathrm{CDCl}_{3}\right)=37.75,28.35 . \mathrm{GC}-\mathrm{MS}: \mathrm{m} / \mathrm{z}=136.0[\mathrm{M}]^{+}$.

## Decarbonylation of undec-10-enal to dec-1-ene (21) [CAS Reg. No. 872-05-9]

Following the general procedure A for decarbonylation, compound $\mathbf{2 l}$ was obtained. GC-MS yield: $72 \%$, based on naphthalene as a standard. GC-MS: $\mathrm{m} / \mathrm{z}=140.2[\mathrm{M}]^{+}$.

## Decarbonylation of 3-(3-chlorophenyl)propionaldehyde to 1-chloro-3-ethylbenzene (2m)

 [CAS Reg. No. 620-16-6]Following the general procedure B for decarbonylation, compound $\mathbf{2 m}$ was obtained, NMR yield: $51 \%$, based on methyl benzoate as a standard. ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{~Hz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) $=7.15-7.00(\mathrm{~m}, 2 \mathrm{H})$, $6.85-6.83(\mathrm{~m}, 1 \mathrm{H}), 6.73-6.70(\mathrm{~m}, 1 \mathrm{H}), 2.22(\mathrm{q}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 0.91(\mathrm{t}, J=7.5 \mathrm{~Hz}, 3 \mathrm{H})$.

## Decarbonylation of 2-(4-methoxyphenyl)octanal to 1-heptyl-4-methoxybenzene (2n) ${ }^{8}$

Following the general procedure A for decarbonylation, compound $\mathbf{2 n}$ was obtained after dryflash column chromatography $\left(\mathrm{SiO}_{2}\right.$ : pentane) as a colorless oil ( $35 \mathrm{mg}, 95 \%$ ). IC $(\mathrm{ATR})=2998$, 2955, 2927, 2854, 1612, 1513, 1462, 1299, 1246, 1178, 1040, $827 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 500 Hz , $\left.\mathrm{CDCl}_{3}\right)=7.12-7.05(\mathrm{~m}, 2 \mathrm{H}), 6.86-6.77(\mathrm{~m}, 2 \mathrm{H}), 3.78(\mathrm{~s}, 3 \mathrm{H}), 2.59-2.50(\mathrm{~m}, 2 \mathrm{H}), 1.60-1.53$ $(\mathrm{m}, 2 \mathrm{H}), 1.35-1.21(\mathrm{~m}, 8 \mathrm{H}), 0.92-0.85(\mathrm{~m}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}\left(125 \mathrm{~Hz}, \mathrm{CDCl}_{3}\right)=157.58,135.07$, $129.22,113.63,55.23,35.03,31.83,31.76,29.24,29.18,22.66,14.08 . G C-M S: m / z=206.1$ $[\mathrm{M}]^{+}$.

## Decarbonylation of 2-(4-acetylphenyl)octanal (10) to 4-n-heptylacetophenone (20) ${ }^{9}$

Dry glass reaction tube equipped with a magnetic stir bar was charged with $\mathrm{Pd}(\mathrm{OAc})_{2}(5 \mathrm{mg}, 0.02$ $\mathrm{mmol}, 4 \mathrm{~mol} \%$ ), rac-BINAP ( $20 \mathrm{mg}, 0.03 \mathrm{mmol}, 6 \mathrm{~mol} \%$ ), $\mathrm{Cs}_{2} \mathrm{CO}_{3}(208 \mathrm{mg}, 0.64 \mathrm{mmol})$ and 4bromoacetophenone ( $106 \mathrm{mg}, 0.53 \mathrm{mmol}, 1$ equiv). The reaction tube was evacuated and backfilled with argon followed by the addition of octanal ( $100 \mu \mathrm{~L}, 0.64 \mathrm{mmol}, 1.2$ equiv) and $1,4-$ dioxane ( 2 mL ) and the sealed reaction tube was heated at $80^{\circ} \mathrm{C}$ for 9 h . The reaction mixture was cooled to room temperature, filtered through a pad of Celite, washed with EtOAc ( 25 mL ) and the solvents were removed under reduced pressure. The crude product was purified by dryflash column chromatography $\left(\mathrm{SiO}_{2}\right.$ : hexane/ethyl acetate $\left.=9 / 1\right)$ to afford 2-(4acetylphenyl)octanal $1 \mathbf{1 o}$ as a yellow oil ( $45 \mathrm{mg}, 34 \%$ ). IC (ATR) $=3401,2928,2858,1683,1608$, $1462,1415,1360,1270 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR $\left(500 \mathrm{~Hz}, \mathrm{CDCl}_{3}\right)=9.69(\mathrm{~d}, J=2 \mathrm{~Hz}, 1 \mathrm{H}), 7.97(\mathrm{~d}, J=8.5$ $\mathrm{Hz}, 2 \mathrm{H}), 7.30(\mathrm{~d}, \mathrm{~J}=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 3.60-3.55(\mathrm{~m}, 1 \mathrm{H}), 2.61(\mathrm{~s}, 3 \mathrm{H}), 2.15-2.05(\mathrm{~m}, 1 \mathrm{H}), 1.80-$ $1.70(\mathrm{~m}, 1 \mathrm{H}), 1.40-1.15(\mathrm{~m}, 8 \mathrm{H}), 0.90-0.80(\mathrm{~m}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}\left(125 \mathrm{~Hz}, \mathrm{CDCl}_{3}\right)=200.14,197.58$, $142.03,136.37,128.99,59.13,31.50,29.75,29.03,27.00,26.58,22.51,13.98 . \mathrm{GC}-\mathrm{MS}: \mathrm{m} / \mathrm{z}=$ $246.2[\mathrm{M}]^{+}$. HRMS (HESI) m/z ([M + H] $\left.{ }^{+}\right)$calcd for $\mathrm{C}_{16} \mathrm{H}_{23} \mathrm{O}_{2}: 247.16980$, found 247.16864.

Following the general procedure A for decarbonylation, compound $\mathbf{2 0}$ was obtained after dryflash column chromatography $\left(\mathrm{SiO}_{2}\right.$ : pentane/EtOAc $\left.=95 / 5\right)$ as a yellow oil $(64 \mathrm{mg}, 76 \%)$. IC $(A T R)=2956,2928,2856,1684,1606,1462,1412,1358,1268,1182 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 500 Hz , $\left.\mathrm{CDCl}_{3}\right)=7.88(\mathrm{~d}, \mathrm{~J}=8 \mathrm{~Hz}, 2 \mathrm{H}), 7.26(\mathrm{~d}, J=8 \mathrm{~Hz}, 2 \mathrm{H}), 2.70-2.60(\mathrm{~m}, 2 \mathrm{H}), 2.58(\mathrm{~s}, 3 \mathrm{H}), 1.70-$ $1.55(\mathrm{~m}, 2 \mathrm{H}), 1.40-1.20(\mathrm{~m}, 8 \mathrm{H}), 0.95-0.80(\mathrm{~m}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}\left(125 \mathrm{~Hz}, \mathrm{CDCl}_{3}\right)=197.85,148.81$, $134.88,128.56,128.43,35.95,31.73,31.08,29.18,29.08,26.48,22.60,14.04 . G C-M S: m / z=$ $218.2[\mathrm{M}]^{+}$.

## Decarbonylation of $3 \alpha, 7 \alpha, 12 \alpha$-triacetoxy- $5 \beta$-cholan-24-al to $3 \alpha, 7 \alpha, 12 \alpha$-triacetoxy-24-nor-5 $\beta$ cholane (5) ${ }^{10}$

Dry glass reaction tube purged with argon and equipped with a magnetic stir bar was charged with molecular sieves ( $3-4 \AA, 100 \mathrm{mg}$ ), aldehyde $4(46 \mathrm{mg}, 0.09 \mathrm{mmol}), \mathrm{Pd} / \mathrm{C}(5 \mathrm{mg}, 5 \mathrm{~mol} \%$ $\mathrm{Pd})$, and cyclohexane ( 1 mL ) and the sealed tube was heated at $130^{\circ} \mathrm{C}$ for 24 h . The reaction mixture was cooled to room temperature, filtered through a pad of Celite, washed with $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ $(15-20 \mathrm{~mL})$ and the solvents were removed under the reduced pressure. The residue was dissolved in $\mathrm{EtOH}(2 \mathrm{~mL})$ and the solution was purged with argon, followed by addition of $\mathrm{Pd} / \mathrm{C}$ $(4 \mathrm{mg})$. The reaction mixture, connected to a balloon of hydrogen, was stirred at room temperature overnight. The reaction mixture was filtered through short pad of $\mathrm{SiO}_{2}$, to remove
the catalyst, and $\mathrm{SiO}_{2}$ was washed with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(25 \mathrm{~mL})$. The solvents were removed under the reduced pressure to afford the pure 5 as a colorless oil ( $37 \mathrm{mg}, 85 \%$ ). IC $(A T R)=2958,2872$, $1733,1376,1249,1025,736 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H} \operatorname{NMR}\left(500 \mathrm{~Hz}, \mathrm{CDCl}_{3}\right)=5.01(\mathrm{~s}, 1 \mathrm{H}), 4.95-4.90(\mathrm{~m}, 1 \mathrm{H})$, $4.63-4.54(\mathrm{~m}, 1 \mathrm{H}), 2.13(\mathrm{~s}, 3 \mathrm{H}), 2.08(\mathrm{~s}, 3 \mathrm{H}), 2.05(\mathrm{~s}, 3 \mathrm{H}), 2.01-1.37(\mathrm{~m}, 16 \mathrm{H}), 1.33-1.22$ $(\mathrm{m}, 4 \mathrm{H}), 1.25-0.99(\mathrm{~m}, 3 \mathrm{H}), 0.92(\mathrm{~s}, 3 \mathrm{H}), 0.84-0.78(\mathrm{~m}, 5 \mathrm{H}), 0.73(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}(125 \mathrm{~Hz}$, $\left.\mathrm{CDCl}_{3}\right)=170.53,170.49,170.35,75.51,74.09,70.74,47.21,44.96,43.34,40.95,37.75,36.24$, $34.69,34.61,34.33,31.25,28.90,28.06,27.16,26.87,25.55,22.83,22.54,21.59,21.45,21.38$, 17.23, 12.19, 10.22.

Decarbonylation of ( $\pm$ )-citronellal to 2,6-dimethylhept-2-ene (7) [CAS Reg. No. 5557-98-2], 2,6-dimethylheptane (8) [CAS Reg. No. 1072-05-5] and p-cimene (9) [CAS Reg. No. 99-87-6] Following the general procedure A for decarbonylation, compounds 7, $\mathbf{8}$ and 9 were obtained. GC-MS yield of 7: $36 \%$, based on naphthalene as a standard. GC-MS: $m / z=126.1[M]^{+}$. GC-MS yield of 8: $8 \%$, based on naphthalene as a standard. GC-MS: $m / z=128.1[M]^{+}$. GC-MS yield of 9: $23 \%$, based on naphthalene as a standard. GC-MS: $m / z=134.1[M]^{+}$.





Decarbonylation of cyclohexanecarbaldehyde
${ }^{1} \mathrm{H}$ NMR spectroscopic analysis of the reaction mixtures in $\mathrm{C}_{6} \mathrm{D}_{6}$ before filtration through a short pad of $\mathrm{SiO}_{2}$; naphthalene was used as an internal standard







1-chloro-3-ethylbenzene (2m)






ю




$\| \mid I I$
$I\|\|$





20
 VA424.010.001.1r.esp






## Decarbonylation of citronellal

${ }^{1} \mathrm{H}$ NMR spectroscopic analysis of the reaction mixtures in $\mathrm{C}_{6} \mathrm{D}_{6}$; naphthalene was used as an internal standard


## Decarbonylation of ( $\pm$ )-citronellal; naphthalene as a standard








## References

${ }^{1}$ Lu, X.; Lin, S.; Pd(II)-bipyridine catalyzed conjugate addition of arylboronic acid to $\alpha, \beta-$ unsaturated carbonyl compounds, J. Org. Chem., 2005, 70, 9651-9653.
${ }^{2}$ Gopalan, B.; Ponpandian, T.; Kachhadia, V.; Bharathimohan, K.; Vignesh, R.; Sivasudar, V.; Narayanan, S.; Mandar, B.; Praveen, R.; Saranya, N.; Rajagopal, S.; Rajagopal, S.; Discovery of adamantane based highly potent HDAC inhibitors, Bioorg. Med. Chem. Lett., 2013, 23, 25322537.
${ }^{3}$ Martín, R.; Buchwald, S. L.; An improved protocol for the Pd-catalyzed R-arylation of aldehydes with aryl halides, Org. Lett., 2008, 10, 4561.
${ }^{4}$ Tot, M.; Opsenica, D. M.; Mitrić, M.; Burnett, J. C.; Gomba, L.; Bavari, S.; Šolaja, B. A.; New 9-aminoacridine derivatives as inhibitors of botulinum neurotoxins and P. falciparum malaria, J. Serb. Chem. Soc., 2013, 78, 1847-1864.
${ }^{5}$ Videnović, M.; Opsenica, D. M.; Burnett, J. C.; Gomba, L.; Nuss, J. E.; Selaković, Ž.;
Konstantinović, J.; Krstić, M.; Šegan, S.; Zlatović, M.; Sciotti, R. J.; Bavari, S.; Šolaja, B. A.; Second generation steroidal 4-aminoquinolines are potent, dual-target inhibitors of the botulinum neurotoxin Serotype A metalloprotease and P. falciparum malaria, J. Med. Chem., 2014, 57, 4134-4153.
${ }^{6}$ Hattori, T.; Takakura, R.; Ichikawa, T.; Sawama, Y.; Monguchi, Y.; Sajiki H. Switching the cleavage sites in palladium on carbon-catalyzed carbon-carbon bond disconnection. J. Org. Chem. 2016, 81, 2737.
${ }^{7}$ Aoyama, M.; Hara, S.; Synthesis of functionalized adamantanes from fluoroadamantanes, Tetrahedron, 2009, 65, 3682-3687.
${ }^{8}$ Ejiri, S.; Odo, S.; Takahashi, H.; Nishimura, Y.; Gotoh, K.; Nishihara, Y.; Takagi, K.; Negishi alkyl-aryl cross-coupling catalyzed by Rh: efficiency of novel tripodal 3-diphenylphosphino-2-(diphenylphosphino)methyl-2-methylpropyl acetate ligand, Org. Lett., 2010, 12, 1692-1695.
${ }^{9}$ Krasovskiy, A.; Duplais, C.; Lipshutz, B. H.; Zn-Mediated, Pd-Catalyzed Cross-Couplings in Water at Room Temperature Without Prior Formation of Organozinc Reagents, J. Am. Chem. Soc., 2009, 131, 15592-15593.
${ }^{10}$ Skidmore, M. A.; Schiesser, C. H.; Toward chiral stannane reducing agents derived from cholic acid and cholestanol, Phosphorus, Sulfur Silicon Relat. Elem., 1999, 150, 177-191.

