Supplementary Information for

Empowering Alcohols as Carbonyl Surrogates for Grignard-Type Reactions

Chen-Chen Li, Haining Wang, Malcolm M. Sim, Zihang Qiu, Zhang-Pei Chen, Rustam Z. Khaliullin and Chao-Jun Li*

Department of Chemistry and FQRNT Centre for Green Chemistry and Catalysis, McGill University, 801 Sherbrooke Street West, Montreal, Quebec H3A 0B8, Canada. * Email: cj.li@mcgill.ca

Table of Content

I. General experimental information	2
II. Experimental procedures	3
i. Preparation of hydrazone or hydrazone solution	3
ii. General procedure for Table 1-2, Scheme 2-4	4
III. Synthesis of active species	7
i. Preparation of Ru-PNP-1	7
ii. Preparation of Ru-PNP-2	7
IV. Mechanistic study	9
i. DFT study for the dehydrogenation step	9
ii. Proposed mechanism1	1
V. Spectroscopic data of products1	2
VI. NMR spectra of products2	5
VII. Supplementary references	9

I. General experimental information

Reaction Setup: All reactions were carried out in flame-dried V-shaped microwave reaction vials which were covered by aluminum seals with PTFE-faced silicone septa, under an atmosphere of nitrogen unless otherwise stated. All reaction temperatures corresponded to oil bath temperatures. All air and moisture-sensitive catalysts, ligands, and reagents were stored and charged in MBRAUN UNIIab Pro Glove Box Workstation unless otherwise stated.

Purifications: All work-up and purification procedures were carried out with reagent-grade solvents. Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 pre-coated plates (0.25 mm). Flash column chromatography was performed with E. Merck silica gel P60 (40–63 µm particle size, 230–400 mesh) (SiO₂). Unless otherwise specified, "SiO₂" refers to P60 grade silica gel. Visualization was accomplished with UV light and/or iodine (I₂) or Vanillin solution. Retention factor (R_f) values reported were measured using a 10 × 2 cm TLC plate in a developing chamber containing the solvent system (10 mL) described. Automated flash column chromatography was performed on Biotage IsoleraTM Spektra Systems with ACITM.

Solvents: 2-methyl-tetrahydrofuran (2-Me-THF), ordered from Sigma Aldrich without any purification. Solvents for filtration, transfers and chromatography, were dichloromethane (CH₂Cl₂) (ACS grade, amylene stabilized), acetone (ACS grade), ethyl acetate (EtOAc) (Fisher, ACS grade), hexane (Fisher, ACS grade), pentane (ACS grade), methanol (ACS grade).

Chemicals: In the model study, benzaldehyde (Aldrich) were distilled prior to use. Other chemicals that are commercially available and used without further purification: 2-penten-1-ol (Aldrich), Ru(PPh₃)₄Cl₂ (Aldrich), Ru(PPh₃)₃Cl₂ (Aldrich), dcypf (Aspira), potassium phosphate (Aldrich), hydrazine hydrate (Reagent Grade, 64–65% wt, Aldrich), mesitylene (Aldrich), 1,3,5-trimethoxylbenzene (Aldrich), anhydrous sodium sulfate. All liquid carbonyls were distilled, and solid ones were recrystallized prior to use. The **PNP** pincer ligands (**L1**, **L2**, **L3**) were purchased from Aldrich. All the alcohol substrates are commercially available (Aldrich, Oakwood & Combi Block) *NMR Spectroscopy:* Nuclear magnetic resonance (¹H and ¹³C NMR) spectra were recorded on a Bruker AV500 equipped with a 60-position Sample Xpress sample changer (¹H, 500 MHz; ¹³C, 125 MHz), a Varian MERCURY plus-500 spectrometer (¹H, 500 MHz; ¹³C, 125 MHz) or Bruker AV400 spectrometer (¹H, 400 MHz; ¹³C, 100 MHz). Chemical shifts for both ¹H NMR and ¹³C NMR spectra are expressed in parts per million (ppm) units downfield from TMS, with the solvent residue peak as the chemical shift standard (CDCl₃: δ 7.28 ppm in ¹H NMR; δ 77.00 ppm in ¹³C NMR). Data are reported as following: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, td = triplet of doublets, q = quartet, quin = quintet, sep = septet, m = multiplet), coupling constants *J* (Hz), and integration.

Mass Spectrometry: Mass spectrometry (MS) was performed by the McGill Chemistry Department Mass Spectrometry Facility. High resolution mass spectra were recorded using electrospray ionization (ESI+) and/or atmospheric pressure chemical ionization APCI (+/-), performed either on "Exactive Plus Orbitrap" a ThermoScientific high resolution accurate mass (HR/AM) FT mass spectrometer, or a Bruker Daltonics Maxis Impact quadrupole-time of flight (QTOF) mass spectrometer.

Characterization of Products: For the products, most of which are known compounds, we report the virtual states, NMR spectra and HRMS data.

DFT calculation: All the calculations were carried out at the B3LYP/6-31G(d,p) level (LANL2DZ for Ru), using the Gaussian 16, Rev A.03 suite of programs.¹ Harmonic frequencies were calculated at the same level to characterize the stationary points and to determine the zeropoint energies (ZPE). Intrinsic reaction coordinate (IRC) studies were performed in ambiguous cases to confirm the relation of the transition states with the corresponding minima.

II. Experimental procedures

i. Preparation of hydrazone or hydrazone solution



Procedure A: For Table 1: 2-Me-THF (4 mL) was added first into a small bottle with a stir bar. Then, hydrazine monohydrate (0.35 mL, 7 mmol) was added into the bottle. After that, 0 (5 mmol)* was added dropwise into the stirred solution and the mixture was stirred for 5 min. Next, proper amount of anhydrous Na₂SO₄ was added to remove water. After stirring for another 3h, the so-formed solution was ready to use.



Procedure B: For Table 2, Figure 2, Figure 3: MeOH (5 mL) was added first into a small bottle with a stir bar. Then, hydrazine monohydrate (0.75 mL, 15 mmol) was added into the bottle. After that, 0 (10.0 mmol) was added dropwise into the stirred solution and the mixture was stirred for 5 min. After stirring for 3 h, *a*. if the solution is a homogeneity, the so-formed solution was concentrated by vacuum to dryness. Next, the crude hydrazone was frozen-dried under vacuum for three times to remove excess amount of hydrazine hydrate. The so formed hydrazone was directly used without further purification. *b*. if precipitates formed from the solution, the solid was filtered and washed with small potion of MeOH and then dried under vacuum, after which the hydrazone can be used directly without further purifications.

Procedure C: For Figure 2, 3ks, 3ls: 2-Me-THF (5 mL) was added first into a small bottle with a stir bar. Then, hydrazine monohydrate (0.4 mL, 8 mmol) was added into the bottle. After that, **0** (6 mmol) was added dropwise into the stirred solution and the mixture was stirred for 5 min. Next, proper amount of anhydrous Na₂SO₄ was added to remove water. After stirring for another 3h, the so-formed solution was ready to use.

ii. General procedure for Table 1-2, Scheme 2-4



General procedure for Table 1: Ru(PPh₃)₂Cl₂ (0.01 mmol), dcypf (0.01 mmol), K₃PO₄ (0.22 mmol), oxidant (0.4 mmol, 2 equiv)* were added into a V-shaped reaction tube with a stir bar in the glovebox. Then, the reaction tube was sealed and moved out of the glovebox. After that, **1a** solution (prepared through *Procedure A*, 0.22 mL, 0.25 mmol) was added first and followed by the addition of **2a** (25.0 μ L, 0.2 mmol). The mixture was stirred for 24h. Then, 1,3,5-trimethoxylbenzene (11.2 mg, 0.067 mmol) was added in the mixture as standard. Then, the solution was filtered by celite and concentrated to dryness. The crude mixture was diluted by CDCl₃ to run the ¹H NMR test to determine the ¹H NMR yield.

*For entry 2, the reaction tube was sealed before exposed to air for 5 min. For entry 3, after removing reaction tube out of the glovebox, it was charged with O_2 via 3 times vacuum-refill by oxygen balloon.



General procedure for Table 2: Ru(PPh₃)₂Cl₂ (0.01 mmol), ligand (0.01 mmol), K₃PO₄ (0.4 mmol) were added into a V-shaped reaction tube with a stir bar in the glovebox. Then, the reaction tube was sealed and moved out of the glovebox. After that, 0.5 mL 2-Me-THF was added and followed by the addition of corresponding amount of **1a** (prepared through *Procedure B*) and **2a** (25.0 μ L, 0.2 mmol). The mixture was stirred for 24h under N₂ at 70 °C. After completion, the solution was filtered by celite and concentrated to dryness. Then, 1,3,5-trimethoxylbenzene (11.2 mg, 0.067 mmol) was added in the mixture as standard. The crude mixture was diluted by CDCl₃ to run the ¹H NMR test to determine the ¹H NMR yield.



General procedure for Figure 3, Figure 4: Ru(PPh₃)₃Cl₂ (0.01 mmol), L1 (0.01 mmol) and K₃PO₄ (0.4 mmol) and solid substrates were added into a V-shaped reaction tube with a stir bar in the glovebox. Then, the reaction tube was sealed and moved out of the glovebox. After that, 0.5 mL 2-Me-THF was added first followed by the addition of liquid substrates. The mixture was stirred under 70 °C for 24h. The reaction mixture was filtered through a celite plug with 2-3 mL CH₂Cl₂. The solvent was removed by a

rotary evaporator and the residue was purified by column chromatography on silica gel (using hexane and ethyl acetate as eluent) to give the pure product.

General procedure for Figure 3, 3as, 3at, 3au, 3hv and 3hw: Ru-PNP-3 (0.01 mmol), and K_3PO_4 (0.4 mmol) and solid substrates were added into a V-shaped reaction tube with a stir bar in the glovebox. Then, the reaction tube was sealed and moved out of the glovebox. After that, 0.5 mL 2-Me-THF was added first followed by the addition of liquid substrates. The mixture was stirred under 100 °C for 24h. The reaction mixture was filtered through a celite plug with 2-3 mL CH₂Cl₂. The solvent was removed by a rotary evaporator and the residue was purified by column chromatography on silica gel (using hexane and ethyl acetate as eluent) to give the pure product.

General procedure for Figure 3ax-3az: **Ru-PNP-1** (0.01 mmol), K₃PO₄ (0.4 mmol) and solid alcohol (0.2 mmol, if applicable) were added into a V-shaped reaction tube with a stir bar in the glovebox. Then, the reaction tube was sealed and moved out of the glovebox. After that, 0.5 mL 2-Me-THF was added first followed by the addition of **1a** (0.6 mmol, 3 equiv.) and liquid alcohols (0.2 mmol, if applicable). The mixture was stirred under 70 °C for 24h. The reaction mixture was filtered through a celite plug with 2-3 mL CH₂Cl₂. The solvent was removed by a rotary evaporator and the residue was purified by column chromatography on silica gel (using hexane and ethyl acetate as eluent) to give the pure product. Specifically, for **3ay**, the mixture was diluted with CDCl₃ and run the ¹H NMR test to determine trace amount of desired product.

Procedure for Figure 3 (3ks, 3ls): Ru(PPh₃)₃Cl₂ (0.01 mmol), L3 (0.006 mmol) and K₃PO₄ (0.4 mmol) were added into a V-shaped reaction tube with a stir bar in the glovebox. Then, the reaction tube was sealed and moved out of the glovebox. After that, 1 solution (prepared through *Procedure B*, 0.55 mL, 0.6 mmol) was added. The mixture was stirred at 100 °C for 24h. The reaction mixture was filtered through a celite plug with 2-3 mL CH₂Cl₂. The solvent was removed by a rotary evaporator and the residue was added mesitylene as internal standard. The mixture was diluted with CDCl₃ and run the ¹H NMR test to determine trace amount of desired product based on the standard spectrum from literature.^{2, 3}

III. Synthesis of active species

i. Preparation of Ru-PNP-1



To a solution of Ru(PPh₃)₃Cl₂ (958 mg, 1 mmol) in THF (8 mL) was dropwise added bis(2-(diisopropylphosphino)ethyl)amine (3.5 mL, 10 w% in THF, 1 mmol). The mixture was stirred at room temperature for 2h. Then, most of THF was evaporated by rotavapor followed by the addition of pentane (25 mL) while stirring. At this period, solid was precipitated. It was placed at 4 °C for 1h. Then, the solid was collected by filtration which was washed by ether and dried under vacuum to give **Ru-PNP-1** as a light brown solid. The characterization was reported by previous literature.⁴

ii. Preparation of Ru-PNP-2



To a solution of Ru(PPh₃)₃Cl₂ (958 mg, 1 mmol) in THF (8 mL) was dropwise added bis(2-(diethylphosphino)ethyl)amine (250 mg, 1 mmol). The mixture was stirred at room temperature for 2h. Then, most of THF was evaporated by rotavapor followed by the addition of pentane (25 mL) while stirring. At this period, solid was precipitated. It was placed at 4 °C for 1h. Then, the solid was collected by filtration which was washed by ether and dried under vacuum to give **Ru-PNP-2** as a green to yellow solid.

¹**H NMR** (500 MHz, C₆D₆) δ 8.32 –8.10 (m, 6H), 7.13 – 7.00 (m, 9H), 3.83 – 3.61 (m, 1H), 2.96 – 2.79 (m, 2H), 2.31 – 2.13 (m, 2H), 2.00 – 1.82 (m, 4H), 1.73 – 1.57 (m, 2H), 1.52 – 1.31 (m, 4H), 1.04 – 0.86 (m, 8H), 0.82 (p, *J* = 7.1 Hz, 6H). ¹³**C NMR** (126 MHz, C₆D₆) δ 143.6 (d, *J* = 36.5 Hz), 136.1 (d, *J* = 9.5 Hz), 129.1, 127.7 (d, *J* = 8.5 Hz), 48.9, 26.3, 14.4 (t, *J* = 10.8 Hz), 13.4 (t, *J* = 10.3 Hz), 9.5, 9.0. ³¹**P NMR** (203 MHz, C₆D₆) δ 42.7 (t, *J* = 28.1 Hz), 33.7 (d, *J* = 28.0 Hz). **HRMS:** (APCI, *m/z*): calcd. for C₃₀H₄₄ClNP₃Ru[M-Cl]⁺ 648.1410, found: 648.1413.

¹HNMR spectrum



¹³C NMR spectrum





IV. Mechanistic study

i. DFT study for the dehydrogenation step



Supplementary Figure 1. Energy diagram of the dehydrogenation step based on DFT calculation. DFT calculation was conducted by Gaussian 16. The IRC study clearly shows the possibility of proposed six-membered ring transition state for dehydrogenation step.

Since the first step (dehydrogenation) is the key step of this dehydrogenative Grignard reaction, we mainly did the calculation for the first step. The result shows that the six-membered-ring transition state we proposed is reasonable in this case (Supplementary Figure 1). Furthermore, we also predicted a four-membered-ring transition state which is the corresponding to the classic β -hydride elimination process and the preliminary calculation shows that the free energy of transition state is 54.3 kcal/mol higher than the six-membered-ring one and the intermediate does not show a perfect match with transition state possibly due to the geometry mismatch (thus we did not show on the diagram), which suggested that the six-membered ring transition state is a more favorable transition state in this case. For the 1,2 addition step, we already did several studies in previous work done by us and others.^{2,5}

ii. Proposed mechanism



Supplementary Figure 2. Proposed mechanism for alcohol surrogated Grignard reaction. The proposed mechanism starts from the tetracoordinated ruthenium complex. The whole process includes a dehydrogenation step and a C-C bond formation step which are all experience six-membered-ring transition states.

In this proposed mechanism, the intermediate A was proposed refer to the previous literature about a similar structure study.⁶ In that case, it is shown that the PNP

ruthenium complex would form a square planar structure with the presence of base. The dehydrogenation process **A** to **C**, it is also supported by the DFT calculation and other related literature.⁷ For the hydrogen releasing step **C** to **D**, it also has the literature support which suggested that the hydride would protonated to hydrogen gas while nitrogen can serve as an internal base to assist the coordination of hydrazine.^{8,9} For the 1,2-addition step, it is already illustrated in our previous work.^{2,5}

V. Spectroscopic data of products

Note: references of the characterization data of some known compounds are marked before our characterization data.

(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 95:5 as eluent, light brown oil, 28 mg, yield: 73%): ¹**H NMR** (500 MHz, CDCl₃) δ 7.38 – 7.31 (m, 2H), 7.31 – 7.16 (m, 3H), 3.90 – 3.79 (m, 1H), 2.86 (dd, *J* = 13.6, 4.2 Hz, 1H), 2.68 (dd, *J* = 13.5, 8.4 Hz, 1H), 1.73 – 1.46 (m, 4H), 1.46 – 1.21 (m, 5H), 0.93 (t, *J* = 6.9 Hz, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ 138.6, 129.4, 128.5, 126.4, 72.7, 44.0, 36.8, 31.8, 25.4, 22.6, 14.0. **HRMS:** (ESI, *m/z*): calcd. for C₁₃H₂₀ONa[M+Na]⁺ 215.1406, found: 215.1404.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 95:5 as eluent, light brown oil, 31.5 mg, yield: 70%) ¹**H NMR** (500 MHz, CDCl₃) δ 7.38 – 7.31 (m, 2H), 7.31 – 7.16 (m, 3H), 3.90 – 3.79 (m, 1H), 2.86 (dd, *J* = 13.6, 4.2 Hz, 1H), 2.67 (dd, *J* = 13.6, 8.4 Hz, 1H), 1.70 – 1.46 (m, 4H), 1.46 – 1.18 (m, 9H), 1.00 – 0.84 (m, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ 138.6, 129.4, 128.5, 126.4, 72.7, 44.0, 36.8, 31.8, 29.6, 29.3, 25.7, 22.6, 14.1. **HRMS:** (ESI, *m/z*): calcd. for C₁₅H₂₄ONa[M+Na]⁺ 243.1719, found: 243.1717.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 95:5 as eluent, light brown oil, 33 mg, yield: 66%) ¹**H NMR** (500 MHz, CDCl₃) δ 7.41 – 7.30 (t, *J* = 7.4 Hz, 2H), 7.30 – 7.18 (m, 3H), 3.90 – 3.79 (m, 1H), 2.86 (dd, *J* = 13.5, 4.2 Hz, 1H), 2.67 (dd, *J* = 13.5, 8.4 Hz, 1H), 1.68 – 1.46 (m, 4H), 1.45 – 1.16 (m, 13H), 0.92 (t, *J* = 6.9 Hz, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ 138.6, 129.4, 128.5, 126.4, 72.7, 44.0, 36.8, 31.9, 29.6, 29.6, 29.6, 29.3, 25.7, 22.7, 14.1. **HRMS:** (ESI, *m/z*): calcd. for C₁₇H₂₈ONa[M+Na]⁺ 271.2032, found: 271.2038.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 94:6 as eluent, colorless oil, 31 mg, yield: 70%) ¹**H NMR** (500 MHz, CDCl₃) δ 7.43 – 7.18 (m, 10H), 3.94 – 3.83 (m, 1H), 2.97 – 2.84 (m, 2H), 2.83 – 2.68 (m, 2H), 1.97 – 1.80 (m, 2H), 1.60 (s, 1H). ¹³**C NMR** (126 MHz, CDCl₃) δ 142.0, 138.3, 129.4, 128.6, 128.4, 128.4, 126.5, 125.8, 71.9, 44.1, 38.4, 32.1. **HRMS:** (ESI, *m/z*): calcd. for C₁₆H₁₈ONa[M+Na]⁺ 249.1250, found: 249.1247.



3ae (Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 93:7 as eluent, white solid, 28 mg, yield: 67%) ¹**H** NMR (500 MHz, CDCl₃) δ 7.40 – 7.30 (m, 2H), 7.30 – 7.18 (m, 3H), 3.93 – 3.82 (m, 1H), 2.86 (dd, *J* = 13.7, 4.3 Hz, 1H), 2.69 (dd, *J* = 13.2, 8.5 Hz, 1H), 2.55 (t, *J* = 7.0 Hz, 2H), 2.13 (s, 3H), 1.92 – 1.80 (m, 1H), 1.78 – 1.54 (m, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 138.3, 129.4, 128.6, 126.5, 72.2, 44.2, 35.8, 34.2, 25.3, 15.5. **HRMS:** (ESI, *m/z*): calcd. for C₁₂H₁₈OSNa[M+Na]⁺ 233.0971, found: 233.0967.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 94:6 as eluent, colorless oil, 29 mg, yield: 68%) ¹**H NMR** (500 MHz, CDCl₃) δ 7.41 – 7.31 (m, 4H), 7.31 – 7.20 (m, 6H), 4.15 – 4.05 (m, 1H), 2.90 (dd, *J* = 13.5, 4.7 Hz, 2H), 2.80 (dd, *J* = 13.5, 8.2 Hz, 2H), 1.71 (s, 1H). ¹³**C NMR** (126 MHz, CDCl₃) δ 138.4, 129.4, 128.5, 126.5, 73.5, 43.3. **HRMS:** (ESI, *m/z*): calcd. for C₁₅H₁₆ONa[M+Na]⁺ 235.1093, found: 235.1092.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 94:6 as eluent, colorless oil, 30 mg, yield: 69%) ¹**H NMR** (500 MHz, CDCl₃) δ 7.42 – 7.30 (m, 2H), 7.30 – 7.18 (m, 3H), 4.00 – 3.92 (m, 1H), 2.84 (dd, *J* = 13.6, 4.2 Hz, 1H), 2.66 (dd, *J* = 13.6, 8.4 Hz, 1H), 1.88 – 1.78 (m, 1H), 1.78 – 1.64 (m, 4H), 1.64 – 1.43 (m, 3H), 1.43 – 1.11 (m, 4H), 1.05 – 0.82 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 138.6, 129.4, 128.5, 126.4, 70.0, 44.7, 44.6, 34.1, 32.8, 26.6, 26.3, 26.2. **HRMS:** (ESI, *m/z*): calcd. for C₁₅H₂₂ONa[M+Na]⁺ 241.1563, found: 241.1556.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 80:20 as eluent, colorless oil, 45 mg, yield: 71%) ¹**H NMR** (500 MHz, CDCl₃) δ 7.39 – 7.30 (m, 2H), 7.30 – 7.16 (m, 3H), 4.08 (s, 2H), 4.00 – 3.84 (m, 1H), 2.82 (dd, *J* = 13.5, 4.2 Hz, 1H), 2.77 – 2.62 (m, 3H), 1.90 – 1.56 (m, 4H), 1.56 – 1.31 (m, 11H), 1.24 – 0.96 (m, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ 154.8, 138.2, 129.3, 128.6, 126.5, 79.2, 69.7, 44.8, 43.5, 32.9, 32.5, 28.4. **HRMS:** (ESI, *m*/*z*): calcd. for C₁₉H₂₉O₃NNa[M+Na]⁺ 342.2040, found: 342.2041.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 94:6 as eluent, colorless oil, 35 mg, yield: 80%) ¹H NMR (500 MHz, CDCl₃) δ 7.44 – 7.32 (m, 2H), 7.32 – 7.24 (m, 3H), 7.24 – 7.18 (m, 1H), 7.05 – 6.97 (m, 1H), 6.97 – 6.87 (m, 1H), 4.18 – 4.02 (m, 1H), 3.11 (dd, *J* = 14.7, 4.4 Hz, 1H), 3.01 (dd, *J* = 14.7, 7.8 Hz, 1H), 2.92 (dd, *J* = 13.6, 4.8 Hz, 1H), 2.80 (dd, *J* = 13.6, 8.0 Hz, 1H), 1.92 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 140.4, 138.1, 129.4, 128.5, 126.9, 126.5, 126.0, 124.2, 73.2, 43.0, 37.2. HRMS: (ESI, *m/z*): calcd. for C₁₃H₁₄OSNa[M+Na]⁺ 241.0658, found: 241.0650.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 93:7 as eluent, white solid, 32 mg, yield: 63%) ¹**H NMR** (500 MHz, CDCl₃) δ 8.00 – 7.79 (m, 3H), 7.69 (s, 1H), 7.59 – 7.44 (m, 2H), 7.40 – 7.31 (m, 1H), 4.02 – 3.87 (m, 1H), 3.02 (dd, *J* = 13.6, 4.1 Hz, 1H), 2.86 (dd, *J* = 13.6, 8.7 Hz, 1H), 2.51 – 2.34 (m, 1H), 2.31 – 2.13 (m, 1H), 1.97 – 1.85 (m, 1H), 1.85 – 1.72 (m, 1H), 1.67 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 135.1, 133.6, 132.4, 130.7, 128.5, 128.0, 127.7, 127.5, 127.5, 127.4 (q, *J* = 276.6 Hz), 126.3, 125.8, 71.1, 44.3, 30.4 (q, *J* = 28.9 Hz), 29.0 (q, *J* = 2.7 Hz). ¹⁹F NMR (471 MHz, CDCl₃) δ - 66.3. **HRMS:** (ESI, *m/z*): calcd. for C₁₅H₁₅OF₃Na[M+Na]⁺ 291.0967, found: 291.0972.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 90:10 as eluent, white solid, 24 mg, yield: 67%) ¹**H NMR** (500 MHz, CDCl₃) δ 7.95 – 7.77 (m, 3H), 7.70 (s, 1H), 7.56 – 7.44 (m, 2H), 7.43 – 7.33 (m, 1H), 4.20 – 4.08 (m, 1H), 2.98 (dd, *J* = 13.5, 4.8 Hz, 1H), 2.89 (dd, *J* = 13.5, 8.0 Hz, 1H), 1.67 (s, 1H), 1.32 (d, *J* =6.3 Hz, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ 136.0, 133.5, 132,2, 128.1, 127.8, 127.7, 127.6, 127.5, 126.1, 125.5, 68.7, 45.9, 22.8. **HRMS:** (ESI, *m/z*): calcd. for C₁₃H₁₄ONa[M+Na]⁺ 209.0937, found: 209.0935.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 92:8 as eluent, colorless oil, 30 mg, yield: 64%) ¹**H NMR** (500 MHz, CDCl₃) δ 7.40 – 7.31 (m, 2H), 7.31 – 7.22 (m, 3H), 7.22 – 7.13 (m, 2H), 6.94 – 6.84 (m, 2H), 6.97 – 6.87 (m, 1H), 4.11 – 3.99 (m, 1H), 3.82 (s, 3H), 2.94 – 2.68 (m, 4H), 1.68 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 158.3, 138.5, 130.3, 129.4, 128.5, 126.4, 113.9, 73.6, 55.2, 43.3, 42.4. **HRMS:** (ESI, *m/z*): calcd. for C₁₆H₁₈O₂Na[M+Na]⁺ 265.1199, found: 265.1197.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 95:5 as eluent, white solid, 24 mg, yield: 61%)² ¹**H NMR** (500 MHz, CDCl₃) δ 7.42 – 7.37 (m, 4H), 7.37 – 7.30 (m, 3H), 7.30 – 7.26 (m, 1H), 7.26 – 7.20 (m, 2H), 4.93 (dd, *J* = 8.5, 4.9 Hz, 1H), 3.11 – 2.99 (m, 2H), 2.02 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 143.8, 138.0, 129.5, 128.5, 128.4, 127.6, 126.6, 125.9, 75.3, 46.1. **HRMS:** (ESI, *m/z*): calcd. for C₁₄H₁₄ONa[M+Na]⁺ 221.0937, found: 221.0942.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 92:8 as eluent, white solid, 33 mg, yield: 54%) ¹**H NMR** (500 MHz, CDCl₃) δ 7.56 – 7.41 (m, 4H), 7.41 – 7.18 (m, 7H), 7.11 – 7.04 (m, 1H), 7.04 – 6.89 (m, 2H), 5.09 (s, 2H), 4.91 (dd, *J* = 8.5, 4.8 Hz, 1H), 3.11 – 2.98 (m, 2H), 2.07 (s, 1H). ¹³**C NMR** (126 MHz, CDCl₃) δ 158.9, 145.5, 138.0, 137.0, 129.5, 129.4, 128.5, 128.5, 127.9, 127.5, 126.6, 118.5, 114.0, 112.3, 75.2, 69.9, 46.0. **HRMS:** (ESI, *m/z*): calcd. for C₂₁H₂₀O₂Na[M+Na]⁺ 327.1356, found: 327.1360.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 93:7 as eluent, white solid, 26 mg, yield: 53%) ¹**H** NMR (500 MHz, CDCl₃) δ 7.36 – 7.24 (m, 7H), 7.24 – 7.19 (m, 2H), 4.88 (dd, *J* = 8.1, 5.1 Hz, 1H), 3.09 – 2.95 (m, 2H), 2.51 (s, 3H), 2.01 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 140.7, 137.8, 137.5, 129.5, 128.5, 126.6, 126.4, 74.9, 45.9, 15.9. **HRMS:** (ESI, *m/z*): calcd. for C₁₅H₁₆OSNa[M+Na]⁺ 267.0814, found: 267.0813.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 95:5 as eluent, colorless oil, 24 mg, yield: 69%): ¹H NMR (500 MHz, CDCl₃) δ 7.39 – 7.31 (m, 2H), 7.31 – 7.18 (m, 3H), 3.83 – 3.70 (m, 1H), 2.79 (dd, *J* = 13.7, 3.9 Hz, 1H), 2.56 (dd, *J* = 13.7, 8.4 Hz, 1H), 2.48 – 2.34 (m, 1H), 2.12 – 1.90 (m, 4H), 1.90 – 1.79 (m, 2H), 1.58 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 138.6, 129.4, 128.4, 126.3, 76.4, 40.9, 40.7, 24.4, 24.2, 17.8. HRMS: (ESI, *m/z*): calcd. for C₁₂H₁₆ONa[M+Na]⁺ 199.1093, found: 199.1095.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 95:5 as eluent, colorless oil, 21 mg, yield: 50%)¹ ¹**H NMR** (500 MHz, CDCl₃) δ 7.44 – 7.31 (m, 2H), 7.31 – 7.16 (m, 3H), 3.65 – 3.56 (m, 1H), 2.91 (dd, *J* = 13.6, 3.4 Hz, 1H), 2.56 (dd, *J* = 13.6, 9.6 Hz, 1H), 2.00 – 1.90 (m, 1H), 1.88 – 1.75 (m, 3H), 1.75 – 1.65 (m, 1H), 1.60 – 1.37 (m, 2H), 1.37 – 1.03 (m, 5H). ¹³**C NMR** (126 MHz, CDCl₃) δ 139.2, 129.4, 128.5, 126.3, 76.9, 43.2, 40.8, 29.3, 28.0, 26.5, 26.3, 26.1. **HRMS:** (ESI, *m/z*): calcd. for C₁₄H₂₀ONa[M+Na]⁺ 227.1406, found: 227.1415.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 82:18 as eluent, white solid, 31 mg, yield: 50%): ¹**H NMR** (500 MHz, CDCl₃) δ 7.38 – 7.30 (m, 2H), 7.30 – 7.18 (m, 3H), 4.19 (s, 2H), 3.68 – 3.56 (m, 1H), 2.91 (dd, *J* = 13.5, 3.3 Hz, 1H), 2.80 – 2.54 (m, 3H), 1.97 – 1.85 (m, 1H), 1.80 – 1.54 (m, 3H), 1.54 – 1.21 (m, 12H). ¹³**C NMR** (126 MHz, CDCl₃) δ 154.8, 138.5, 129.3, 128.6, 126.5, 79.3, 75.9, 43.5, 41.6, 40.8, 28.4. **HRMS:** (ESI, *m/z*): calcd. for C₁₈H₂₇O₃NNa[M+Na]⁺ 328.1883, found: 328.1887.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 96:4 as eluent, colorless oil, 23 mg, yield: 54%)² ¹**H NMR** (500 MHz, CDCl₃) δ 7.47 – 7.41 (m, 2H), 7.41 – 7.33 (m, 2H), 7.33 – 7.19 (m, 4H), 7.08 – 6.98 (m, 2H), 3.17 (d, *J* = 13.4 Hz, 1H), 3.06 (d, *J* = 13.4 Hz, 1H), 1.90 (s, 1H), 1.60 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 147.5, 136.7, 130.6, 128.0, 126.6, 124.9, 74.4, 50.5, 29.4. **HRMS:** (ESI, *m/z*): calcd. for C₁₅H₁₆ONa[M+Na]⁺ 235.1093, found: 235.1096.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 96:4 as eluent, colorless oil, 10 mg, yield: 23%) ¹**H** NMR (500 MHz, CDCl₃) δ 7.37 – 7.30 (m, 2H), 7.30 – 7.19 (m, 3H), 2.78 (dd, *J* = 29.4, 13.3 Hz, 2H), 1.55 – 1.40 (m, 4H), 1.40 – 1.24 (m, 7H), 1.16 (s, 3H), 0.92 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 137.6, 130.5, 128.2, 126.4, 72.5, 48.0, 41.9, 31.9, 29.8, 26.5, 24.0, 22.6, 14.1. **HRMS:** (ESI, *m/z*): calcd. for C₁₅H₂₄ONa[M+Na]⁺ 243.1719, found: 243.1728.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 95:5 as eluent, white solid, 34 mg, yield: 85%) ¹**H NMR** (500 MHz, CDCl₃) δ 7.91 – 7.78 (m, 3H), 7.71 (s, 1H), 7.56 – 7.45 (m, 2H), 7.41 (dd, *J* = 8.4, 1.8 Hz, 1H), 2.97 (s, 2H), 1.56 (s, 1H), 1.31 (s, 6H). ¹³**C NMR** (126 MHz, CDCl₃) δ 135.4, 133.3, 132.2, 129.0, 128.8, 127.6, 127.6, 126.0, 125.4, 70.9, 49.8, 29.2. **HRMS:** (ESI, *m/z*): calcd. for C₁₄H₁₆ONa[M+Na]⁺ 223.1093, found: 223.1094.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 95:5 as eluent, white solid, 26 mg, yield: 61%) ¹**H NMR** (500 MHz, CDCl₃) δ 7.92 – 7.77 (m, 3H), 7.71 (s, 1H), 7.57 – 7.45 (m, 2H), 7.41 (dd, *J* = 8.4, 1.8 Hz, 1H), 2.95 (q, *J* = 13.3 Hz, 2H), 1.59 (q, *J* = 7.5 Hz, 2H), 1.47 (s, 1H), 1.21 (s, 3H), 1.04 (t, *J* = 7.5 Hz, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ 135.3, 133.3, 132.2, 129.1, 128.9, 127.6, 126.0, 125.4, 72.9, 47.6, 34.3, 26.0, 8.3. **HRMS:** (ESI, *m/z*): calcd. for C₁₅H₁₈ONa[M+Na]⁺ 237.1250, found: 237.1254.



3ax

(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 90:10 as eluent, colorless oil, 35 mg, yield: 59%) ¹**H NMR** (500 MHz, CDCl₃) δ 8.00 (s, 1H), 7.93 (d, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.37 – 7.14 (m, 5H), 4.97 (dd, *J* = 8.7, 4.7 Hz, 1H), 3.16 – 2.89 (m, 2H), 2.16 (s, 1H), 1.63 (s, 9H). ¹³**C NMR** (126 MHz, CDCl₃) δ 165.7, 144.0, 137.7, 132.1, 129.9, 129.5, 128.6, 128.5, 128.2, 126.8, 126.7,

81.1, 74.9, 46.0, 28.2. **HRMS:** (ESI, *m*/*z*): calcd. for C₁₉H₂₂O₃Na[M+Na]⁺ 321.1461, found: 321.1470.



3az

(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 65:35 as eluent, white solid, 30 mg, yield: 48%) ¹**H NMR** (500 MHz, CDCl₃) δ 7.56 – 7.45 (m, 2H), 7.44 – 7.30 (m, 3H), 7.31 – 7.13 (m, 5H), 4.12 – 3.98 (m, 1H), 2.85 (ddd, *J* = 14.2, 9.7, 4.7 Hz, 2H), 2.81 – 2.65 (m, 2H), 1.73 (s, 1H), 1.34 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 176.5, 138.4, 136.4, 134.2, 129.8, 129.4, 128.5, 126.4, 120.2, 73.5, 43.2, 42.7, 39.5, 27.6. **HRMS:** (ESI, *m/z*): calcd. for C₂₀H₂₅O₂NNa[M+Na]⁺ 334.1777, found: 334.1775.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 94:6 as eluent, white solid, 40 mg, yield: 75%): ¹**H** NMR (500 MHz, CDCl₃) δ 7.70 – 7.56 (m, 4H), 7.54 – 7.43 (m, 2H), 7.42 – 7.29 (m, 3H), 4.00 – 3.77 (m, 1H), 2.91 (dd, *J* = 13.6, 4.2 Hz, 1H), 2.73 (dd, *J* = 13.6, 8.4 Hz, 1H), 1.73 – 1.50 (m, 4H), 1.50 – 1.19 (m, 5H), 0.95 (t, *J* = 6.9 Hz, 3H). ¹³**C** NMR (126 MHz, CDCl₃) δ 140.9, 139.3, 137.7, 129.8, 128.7, 127.2, 127.1, 127.0, 72.7, 43.6, 36.9, 31.8, 25.4, 22.6, 14.0. **HRMS:** (ESI, *m/z*): calcd. for C₁₉H₂₄ONa[M+Na]⁺ 291.1719, found: 291.1730.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 94:6 as eluent, white solid, 29 mg,

yield: 64%): ¹**H NMR** (500 MHz, CDCl₃) δ 7.37 – 7.25 (m, 2H), 7.21 – 7.12 (m, 2H), 3.88 – 3.72 (m, 1H), 2.81 (dd, *J* = 13.7, 4.3 Hz, 1H), 2.65 (dd, *J* = 13.7, 8.3 Hz, 1H), 1.67 – 1.44 (m, 4H), 1.44 – 1.21 (m, 5H), 0.92 (t, *J* = 6.9 Hz, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ 137.2, 132.2, 130.7, 128.6, 72.5, 43.3, 36.8, 31.8, 25.4, 22.6, 14.0. **HRMS**: (ESI, *m/z*): calcd. for C₁₃H₁₉OClNa[M+Na]⁺ 249.1017, found: 249.1019.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 94:6 as eluent, white solid, 38 mg, yield: 64%): ¹**H NMR** (500 MHz, CDCl₃) δ 7.54 – 7.32 (m, 5H), 7.17 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 5.09 (s, 1H), 3.88 – 3.74 (m, 1H), 2.81 (dd, *J* = 13.7, 4.2 Hz, 1H), 2.62 (dd, *J* = 13.7, 8.4 Hz, 1H), 1.71 – 1.46 (m, 4H), 1.46 – 1.23 (m, 5H), 0.94 (t, *J* = 6.9 Hz, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ 157.5, 137.1, 130.9, 130.3, 128.5, 127.9, 127.4, 114.9, 72.7, 70.0, 43.1, 36.7, 31.8, 25.4, 22.6, 14.0. **HRMS:** (ESI, *m/z*): calcd. for C₂₀H₂₆O₂Na[M+Na]⁺ 321.1825, found: 321.1825.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 94:6 as eluent, colorless oil, 26 mg, yield: 50%): ¹H NMR (500 MHz, CDCl₃) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 3.95 – 3.78 (m, 1H), 2.89 (dd, *J* = 13.6, 4.1 Hz, 1H), 2.75 (dd, *J* = 13.6, 8.3 Hz, 1H), 1.67 – 1.46 (m, 4H), 1.46 – 1.22 (m, 5H), 0.92 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 143.0, 129.7, 128.7 (q, *J* = 32.4 Hz), 125.3 (q, *J* = 3.2 Hz), 124.3 (q, *J* = 271.2 Hz), 72.5, 43.7, 37.0, 31.8, 25.3, 22.6, 14.0. ¹⁹F NMR (471 MHz, CDCl₃) δ -62.4. HRMS: (ESI, *m*/*z*): calcd. for C₁₄H₁₉OF₃Na[M+Na]⁺ 283.1280, found: 283.1277.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 93:7 as eluent, colorless oil, 31 mg, yield: 65%): ¹H NMR (500 MHz, CDCl₃) δ 7.24 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 3.87 – 3.75 (m, 1H), 2.81 (dd, *J* = 13.6, 4.3 Hz, 1H), 2.63 (dd, *J* = 13.6, 8.3 Hz, 1H), 2.50 (s, 3H), 1.63 – 1.44 (m, 4H), 1.44 – 1.20 (m, 5H), 0.92 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 136.1, 135.6, 129.9, 127.0, 72.6, 43.4, 36.8, 31.8, 25.4, 22.6, 16.1, 14.0. HRMS: (ESI, *m*/*z*): calcd. for C₁₄H₂₂OSNa[M+Na]⁺ 261.1284, found: 261.1284.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 95:5 as eluent, colorless oil, 26 mg, yield: 62%): ¹H NMR (500 MHz, CDCl₃) δ 7.33 – 7.16 (m, 2H), 7.16 – 6.97 (m, 2H), 3.96 – 3.80 (m, 1H), 2.92 (dd, *J* = 13.8, 4.4 Hz, 1H), 2.71 (dd, *J* = 13.8, 8.2 Hz, 1H), 2.50 (s, 3H), 1.66 – 1.46 (m, 4H), 1.46 – 1.22 (m, 5H), 0.92 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 161.4 (d, *J* = 244.7 Hz), 131.8 (d, *J* = 4.7 Hz), 128.2 (d, *J* = 8.1 Hz), 125.7 (d, *J* = 15.6 Hz), 124.0 (d, *J* = 3.5 Hz), 115.4 (d, *J* = 22.4 Hz), 71.7, 37.2, 37.0, 31.8, 25.4, 22.6, 14.1. ¹⁹F NMR (471 MHz, CDCl₃) δ -117.7. HRMS: (ESI, *m/z*): calcd. for C₁₃H₁₉OFNa[M+Na]⁺ 233.1312, found: 233.1315.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 94:6 as eluent, white solid, 33 mg, yield: 68%): ¹**H NMR** (500 MHz, CDCl₃) δ 7.92 – 7.77 (m, 1H), 7.71 (s, 1H), 7.55 – 7.44 (m, 2H), 7.43 – 7.34 (m, 1H), 4.01 – 3.87 (m, 1H), 3.03 (dd, *J* = 13.6, 4.2 Hz, 1H),

2.85 (dd, J = 13.6, 8.4 Hz, 1H), 1.72 - 1.50 (m, 4H), 1.50 - 1.24 (m, 5H), 0.94 (t, J = 6.9 Hz, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ 136.2, 133.5, 132.2, 128.1, 127.8, 127.8, 127.6, 127.5, 126.0, 125.4, 72.6, 44.2, 36.9, 31.8, 25.4, 22.6, 14.0. **HRMS:** (ESI, m/z): calcd. for C₁₇H₂₂ONa[M+Na]⁺ 265.1563, found: 265.1564.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 94:6 as eluent, white solid, 26 mg, yield: 57%): ¹**H NMR** (500 MHz, CDCl₃) δ 7.33 – 7.19 (m, 3H), 7.17 – 7.08 (m, 1H), 3.89 – 3.75 (m, 1H), 2.81 (dd, *J* = 13.7, 4.2 Hz, 1H), 2.65 (dd, *J* = 13.6, 8.4 Hz, 1H), 1.63 – 1.45 (m, 4H), 1.45 – 1.23 (m, 5H), 0.92 (t, *J* = 6.9 Hz, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ 140.8, 134.2, 129.7, 129.5, 127.6, 126.6, 72.5, 43.6, 36.9, 31.8, 25.4, 22.6, 14.0. **HRMS:** (ESI, *m/z*): calcd. for C₁₃H₁₉OClNa[M+Na]⁺ 249.1017, found: 249.1020.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 92:8 as eluent, colorless oil, 27 mg, yield: 61%): ¹H NMR (500 MHz, CDCl₃) δ 7.32 – 7.20 (m, 1H), 6.90 – 6.71 (m, 3H), 3.89 – 3.76 (m, 4H), 2.83 (dd, *J* = 13.5, 4.2 Hz, 1H), 2.64 (dd, *J* = 13.5, 8.5 Hz, 1H), 1.72 – 1.46 (m, 4H), 1.46 – 1.21 (m, 5H), 0.92 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 159.7, 140.2, 129.5, 121.7, 115.1, 111.7, 72.6, 55.1, 44.1, 36.8, 31.8, 25.4, 22.6, 14.0. HRMS: (ESI, *m/z*): calcd. for C₁₄H₂₂O₂Na[M+Na]⁺ 245.1512, found: 245.1521.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 95:5 as eluent, colorless oil, 33 mg, yield: 67%, mixture of two diastereomers, d.r. = 1:1) ¹H NMR (500 MHz, CDCl₃) δ

7.43 – 7.31 (m, 2H), 7.31 – 7.15 (m, 3H), 5.23 – 5.05 (m, 1H), 4.02 – 3.88 (m, 1H), 2.94 – 2.77 (m, 1H), 2.77 – 2.58 (m, 1H), 2.13 – 1.90 (m, 2H), 1.80 – 1.12 (m, 12H), 1.06 – 0.81 (m, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ 138.6, 138.6, 131.2, 131.2, 129.4, 128.5, 126.4, 126.4, 124.7, 70.7, 70.3, 44.8, 44.3, 44.2, 44.2, 37.9, 36.6, 29.3, 28.9, 25.7, 25.5, 25.3, 20.2, 19.1, 17.6. **HRMS:** (ESI, *m/z*): calcd. for C₁₇H₂₆ONa[M+Na]⁺ 269.1876, found: 269.1875.



(Generated following the corresponding general procedure, isolated by column chromatography on silica gel with hexane: EtOAc = 95:5 as eluent, colorless oil, 32 mg, yield: 62%, mixture of two diastereomers, d.r. = 1:1) ¹**H** NMR (500 MHz, CDCl₃) δ 7.41 – 7.30 (m, 2H), 7.30 – 7.16 (m, 3H), 5.48 – 5.34 (m, 1H), 3.93 – 3.78 (m, 1H), 2.88 – 2.73 (m, 2H), 2.48 – 2.38 (m, 1H), 2.38 – 2.11 (m, 5H), 2.11 – 2.00 (m, 1H), 1.92 – 1.74 (m, 1H), 1.30 (d, *J* = 2.6 Hz, 3H), 1.24 – 1.11 (m, 1H), 0.89 (d, *J* = 2.2 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 145.3, 145.0, 138.8, 138.8, 129.4, 128.4, 128.3, 126.3, 120.3, 120.0, 69.8, 69.6, 45.9, 45.6, 45.0, 44.7, 43.4, 43.4, 40.7, 40.6, 38.0, 37.7, 32.0, 31.7, 31.4, 31.4, 26.2, 26.2, 21.3, 21.2. HRMS: (ESI, *m/z*): calcd. for C₁₈H₂₄ONa[M+Na]⁺ 279.1719, found: 279.1728.

VI. NMR spectra of products



















































































































































VII. Supplementary references

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

2 Wang, H., Dai, X.-J. & Li, C.-J. Aldehydes as Alkyl Carbanion Equivalents for Additions to Carbonyl Compounds. *Nat. Chem.* **9**, 374-378 (2017)

Too, P. C., Tnay, Y. L. & Chiba, S. Copper-Catalyzed Aerobic Aliphatic C–H Oxygenation with Hydroperoxides. *Beilstein J. Org. Chem.* 9, 1217-1225 (2013).

4 Abdur-Rashid, K.; Graham, T.; Tsang, C.-W.; Chen, X.; Guo, R.; Jia, W.; Amoroso, D.; Sui-Seng, C. Method for the Production of Hydrogen from Ammonia Borane. US Patent WO 2008/141439 (2008).

5 Yan, S.-S. et al. Ruthenium-Catalyzed Umpolung Carboxylation of Hydrazones with Co2. Chem. Sci. 9, 4873-4878 (2018).

6 Askevold, B., Khusniyarov, M. M., Herdtweck, E., Meyer, K. & Schneider, S. A Square-Planar Ruthenium(II) Complex with a Low-Spin Configuration. *Angew. Chem. Int. Ed.* **49**, 7566-7569 (2010).

7 Sandoval, C. A., Ohkuma, T., Muñiz, K. & Noyori, R. Mechanism of Asymmetric Hydrogenation of Ketones Catalyzed by BINAP/1,2-Diamine–Ruthenium(II) Complexes. *J. Am. Chem. Soc.* **125**, 13490-13503 (2003).

8 Das, U. K., Chakraborty, S., Diskin-Posner, Y. & Milstein, D. Direct Conversion of Alcohols into Alkenes by Dehydrogenative Coupling with Hydrazine/Hydrazone Catalyzed by Manganese. *Angew. Chem.* **130**, 13632-13636 (2018).

Garbe, M. *et al.* Manganese(I)-Catalyzed Enantioselective Hydrogenation of Ketones Using a Defined Chiral PNP Pincer Ligand. *Angew. Chem. Int. Ed.* 56, 11237-11241 (2017).