Supporting Information

β-Arylation of Oxime Ethers Using Diaryliodonium Salts through Activation of Inert C(sp3)-H Bond with Palladium Catalyst

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I. General Comments

All the reactions were carried out in a pre-dried screwcapped tube with a Teflon-lined septum under N₂ atmosphere. Diaryliodonium salts except Ph₂IPF₆ and (4- Bu-Ph)₂IOTf were prepared according to the literature[1]. Column chromatography was performed on silica gel (particle size 10-40 μm, Ocean Chemical Factory of Qingdao, China). ¹H NMR and ¹³C NMR spectra were recorded on a JEOL AL-300MHz, AL-400MHz or AL-600MHz spectrometer at ambient temperature with CDCl₃ as the solvent. Chemical shifts (δ) were given in ppm, referenced to the residual proton resonance of CDCl₃ (7.26), to the carbon resonance of CDCl₃ (77.16). Coupling constants (J) were given in Hertz (Hz). The term m, dq, q, t, d, s referred to multiplet, doublet quartet, quartet, triplet, doublet, singlet.

HRMS experiments were carried out on a Thermo Scientific LTQ Orbitrap Discovery (Bremen, Germany). Melting points were gained by mini-Lamp. MS data were monitored by GC-MS. The reaction progress was monitored by TLC and GC-MS if applicable.
II. Experimental Procedures for the Preparation of Starting Materials

1. General Procedure for Preparing Oximes (1a-1h, 1m)[2]

\[
\begin{align*}
\text{R}^1 \quad \text{R}^2 & \quad \overset{\text{CH}_3\text{ONH}_2 \cdot \text{HCl}}{\text{NaOAc}} \quad \overset{\text{H}_2\text{O}/\text{MeOH} (2:1), 80^\circ\text{C}}{\text{R}^1 \quad \text{R}^2} \\
\end{align*}
\]

Methoxylamine hydrochloride (1.5 equiv) and NaOAc (2.5 equiv) were placed in a schlenk tube and charge with N₂. Solvent, H₂O (10 ml)/MeOH (5 mL), were added into the tube alongside with ketone (5 mmol) and the mixture was stirred at 80°C for 5h. After cooling down to room temperature, dichloromethane (10 mL) and water (10 mL) were added. The aqueous layer was extracted with dichloromethane and the combined organic extracts were dried over MgSO₄, filtered, and concentrated under reduced pressure.

Note: Aimed ketoximes were obtained quantitively after concentration under reduced pressure without any further purification.

2. Procedure for Preparing Compound 1i[2]

A stirred solution of fenchone (5.0 mmo, 760 mg) and methoxylamine hydrochloride (5.5 mmol, 456.5 mg) in pyridine (10 mL) was heated at 115°C for overnight. Pyridine was removed under reduced pressure. The residue was diluted with diethyl ether (10 mL) and then washed with water (10 mL). The organic phase was dried over MgSO₄, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to give desired 1i (500 mg, 55%).

3. Procedure for Preparing Compound 1j[3]

\[
\begin{align*}
\text{(+)-Carvol} & \quad \overset{1, \text{H}_2, \text{PtO}_2, \text{THF}}{\text{2. MeONH}_2 \cdot \text{HCl}} \quad \overset{\text{H}_2\text{O}/\text{MeOH}}{\text{(+)-Carvol}} \\
\end{align*}
\]

PtO₂ (0.05 mmol, 11 mg) in 50 mL THF were placed in a round bottom flask. (+)-Carvol (10 mmol, 1.56 mL) was slowly added and the mixture was stirred at room temperature under
an atmosphere of hydrogen gas (balloon). Progress was monitored by GC/MS with full conversion achieved after 5.5 h. The resulting mixture was filtered through celite and washed with EtOAc (10ml × 3). The filtrate was evaporated under reduced pressure and the pure 5-isopropyl-2-methylcyclohex-2-enone were obtained by column chromatography on silica gel (Hexane/EtOA = 1/50). (1.31 g, 86%).

The aimed product (1j) (1.45 g, 93%) were prepare from 5-isopropyl-2-methylcyclohex-2-enone according to the general procedure for preparing oximes above.

4. Procedure for Preparing Compound 1k

PtO₂ (0.05 mmol, 11 mg) in 50 mml THF were placed in a round bottom flask and Lanosterol (10 mmol, 4.26 g) was slowly added. The mixture was stirred at room temperature under an atmosphere of hydrogen gas (balloon). Progress was monitored by GC/MS with full conversion achieved after 6h. The resulting mixture was filtered through celite and washed with EtOAc. The filtrate was evaporated under reduced pressure and the residue was used without further purification. To a stirred solution of the residue in dichloromethane (100 mL) was added Dess-Martin periodinane (15 mmol, 6.36 g). After stirring for one hour at room temperature, 100μl water was added into the mixture to accelerate the conversion. The reaction was quenched after another 3h. The resulting mixture was extracted with EtOAc (50 ml×3) while the organic layers were combined, dried over MgSO₄, filtered, and concentrated. The residue was purified by column chromatography on silica gel (Hexane/EtOA = 1/30) to give the ketone. (3.00 g, 70%).

Hydroxylamine hydrochloride (1.58 g, 18.8 mmol) and NaOAc (2.51 g, 30.8 mmol) were added to the above ketone (3g, 7 mmol) in H₂O (20 mL)/MeOH (10 mL)/DCM (5 mL) and the mixture was stirred at 75 °C for 4 h. After cooling down to room temperature, EtOAc (15 mL) and water (10 mL) were added. The aqueous layer was extracted with EtOAc (15 mL x 3) and the combined organic extracts were dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Hexane/EtOAc = 50/1) to afford ketoxime 1k (2.96g, 93%).
5. Procedure for Preparing Compound 1l\textsuperscript{[5,6]}

To a solution of Glycyrrhetinic Acid (2.35 g, 5 mmol) in dichloromethane (50 mL) was added Dess-Martin periodinane (5.5 mmol, 2.33 g). After stirring for 1h at room temperature, 100μl water was added into the mixture to facilitate the conversion. The reaction was quenched after another 3h and the resulting mixture was extracted with EtOAc (30 ml×3). The organic layers were combined, dried over MgSO\textsubscript{4}, filtered and concentrated without further purification to give the corresponding ketone \textsuperscript{[6]} quantitatively.

Solid K\textsubscript{2}CO\textsubscript{3} (3.12 g, 22.5 mmol) as well as neat MeI (4.67 mL, 75.3 mmol) were added to a room temperature DMF solution (30 mL) of glycyrrhetic acid (2.35 g, 5 mmol). After stirring for 8h, solution was filtered followed by evaporating filtration. The residual DMF was portioned between H\textsubscript{2}O (200 mL) and EtOAc (200 mL) while aqueous layer was separated and extracted with EtOAc. Then the combined organic layers were washed with 5 % Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}, saturated NaHCO\textsubscript{3}, brine and then dried (Mg\textsubscript{2}SO\textsubscript{4}). Concentration afforded the crude ester that was purified by chromatography (1:20 EtOAc/hexanes) to afford corresponding ester (1l') as a white solid (1.70 g, 73%).\textsuperscript{[6]}

Hydroxylamine hydrochloride (677 mg, 8.1 mmol) and NaOAc (1.08 g, 13.2 mmol) were added to the above ketone (1.45g, 3 mmol) in H\textsubscript{2}O (10 mL)/MeOH (5 mL)/DCM (2.5 mL) and the mixture was stirred at 75 °C for 4 h. After cooling down to room temperature, EtOAc (10 mL) and water (10 mL) were added. The aqueous layer was extracted with EtOAc (15 mL x 3) and the combined organic extracts were dried over MgSO\textsubscript{4}, filtered, and concentrated under reduced pressure. 1l can be obtained quantitively after concentration.
6. Spectroscopic Data of Prepared Oximes

\textit{(E)-2-methylcyclohexanone O-methyl oxime (1a)}: colorless liquid.

\begin{align*}
\text{H} & \text{NMR (400 MHz, CHLOROFORM-D)} \; \delta \; 3.81 \text{ (s, 3H), } 2.84 - 2.71 \text{ (m, 1H), } 2.36 - \\
& 2.27 \text{ (m, 1H), } 2.11 - 2.03 \text{ (m, 1H), } 1.88 - 1.76 \text{ (m, 1H), } 1.75 - 1.64 \text{ (m, 2H), } 1.54 - \\
& 1.44 \text{ (m, 2H), } 1.40 - 1.33 \text{ (m, 1H), } 1.10 \text{ (d, } J = 6.8 \text{ Hz, 3H). } \text{\textsuperscript{13}} \text{C NMR (101 MHz,} \\
& \text{CHLOROFORM-D)} \; \delta \; 163.0, 61.1, 36.8, 35.4, 26.3, 24.1, 24.0, 17.3. \text{EI-MS: 141 (M\textsuperscript{+})}
\end{align*}

\textit{pentan-3-one O-methyl oxime (1b)}: colorless liquid

\begin{align*}
\text{H} & \text{NMR (301 MHz, CHLOROFORM-D)} \; \delta \; 3.79 \text{ (s, 3H), } 2.28 \text{ (q, } J = 7.6 \text{ Hz, 2H), } 2.17 \\
& (q, J = 7.6 \text{ Hz, 2H), } 1.07 \text{ (t, } J = 5.5 \text{ Hz, 2H), } 1.03 \text{ (t, } J = 5.5 \text{ Hz, 1H). } \text{\textsuperscript{13}} \text{C NMR (76 MHz,} \\
& \text{CHLOROFORM-D)} \; \delta \; 163.5, 61.1, 27.1, 21.2, 11.3, 10.5. \text{EI-MS: 115 (M\textsuperscript{+})}
\end{align*}

\textit{3-methylbutan-2-one O-methyl oxime (1c)}: colorless liquid; obtained as a mixture of two isomers in a ratio \(E/Z=6:1\)

\begin{align*}
\text{major isomer (}\textit{(E)3-methylbutan-2-one O-methyl oxime}\text{): } \text{H} & \text{NMR (400 MHz,} \\
& \text{CHLOROFORM-D)} \; \delta \; 3.8 \text{ (s, 3H), } 2.55 - 2.37 \text{ (m, 1H), } 1.73 \text{ (s, 3H), } 1.04 \text{ (d, } J = 6.9, \\
& \text{Hz, 6H).} \text{\textsuperscript{13}} \text{C NMR (101 MHz, CHLOROFORM-D)} \; \delta \; 162.0, 61.1, 34.3, 20.0, 10.8. \\
& \text{EI-MS: 115 (M\textsuperscript{+})}
\end{align*}

\textit{(E)-3,3-dimethylbutan-2-one O-methyl oxime (1d)}: colorless liquid

\begin{align*}
\text{H} & \text{NMR (400 MHz, CHLOROFORM-D)} \; \delta \; 3.81 \text{ (s, 3H), } 1.77 \text{ (s, 3H), } 1.10 \text{ (s, 9H).} \text{\textsuperscript{13}} \text{C NMR (101 MHz,} \\
& \text{CHLOROFORM-D)} \; \delta \; 163.4, 61.1, 37.1, 27.8 10.5. \text{EI-MS: 129 (M\textsuperscript{+})}
\end{align*}

\textit{(E)-pivalaldehyde O-methyl oxime (1e)}: colorless liquid

\begin{align*}
\text{H} & \text{NMR (301 MHz, CHLOROFORM-D)} \; \delta \; 7.29 \text{ (s, 1H), } 3.80 \text{ (s, 3H), } 1.09 \text{ (s, 9H).} \text{\textsuperscript{13}} \text{C NMR (76 MHz,} \\
& \text{CHLOROFORM-D)} \; \delta \; 158.3, 61.2, 33.6, 27.7 \text{EI-MS: 115 (M\textsuperscript{+})}
\end{align*}

\textit{2,4-dimethylpentan-3-one O-methyl oxime (1f)}: colorless liquid

\begin{align*}
\text{H} & \text{NMR (400 MHz, CHLOROFORM-D)} \; \delta \; 3.75 \text{ (s, 3H), } 2.98 \text{ (m, 1H), } 2.48 \text{ (m, 1H), } \\
& 1.10 \text{ (d, } J = 7.1 \text{ Hz, 6H), } 1.07 \text{ (d, } J = 6.9 \text{ Hz, 6H).} \text{\textsuperscript{13}} \text{C NMR(101 MHz,} \\
& \text{CHLOROFORM-D)} \; \delta \; 168.5, 61.1, 31.2, 28.1, 21.3, 19.1. \text{EI-MS: 143 (M\textsuperscript{+})}
\end{align*}
1-cyclohexylethanone O-methyl oxime (1g): colorless liquid; obtained as a mixture of two isomers in a ratio E/Z=10:1

\[ \text{major isomer (}(E)\text{-1-cyclohexylethanone O-methyl oxime):} \]
\[ ^1\text{H NMR (301 MHz, CHLOROFORM-D)} \delta 3.77 (s, 3H), 2.21 – 2.03 (m, 1H), 1.77 – 1.62 (m, 8H), 1.31 – 1.14 (m, 5H). ^13\text{C NMR (76 MHz, CHLOROFORM-D)} \delta 161.4, 61.0, 44.5, 30.2, 26.1, 11.6. EI-MS: 155 (M^+) \]

(R,E)-5-isopropyl-2-methylcyclohex-2-enone O-methyl oxime (1j): colorless liquid
\[ ^1\text{H NMR (400 MHz, CHLOROFORM-D)} \delta 5.98 (d, J = 5.7 Hz, 1H), 3.90 (s, 3H), 3.14 – 3.01 (m, 1H), 2.25 – 2.09 (m, 1H), 1.91 – 1.84 (m, 1H), 1.82 (s, 3H), 1.79 – 1.71 (m, 1H), 1.56 – 1.42 (m, 2H), 0.93 – 0.89 (m, 6H). ^13\text{C NMR (101 MHz, CHLOROFORM-D)} \delta 157.0, 133.1, 130.5, 61.8, 39.7, 32.3, 28.8, 26.7, 19.97 (s), 19.8, 17.8. EI-MS: 181 (M^+). [\alpha]_D^{23} -12.6^\circ (1, DCM) \]

1,3,3-trimethylbicyclo[2.2.1]heptan-2-one O-methyl oxime (1i): Pale orange liquid, obtained as a mixture of two isomers in a ratio E/Z=12:1

\[ \text{major isomer:} (E)\text{-1,3,3-trimethylbicyclo[2.2.1]heptan-2-one O-methyl oxime:} \]
\[ ^1\text{H NMR (400 MHz, CHLOROFORM-D)} \delta 3.71 (s, 3H), 1.78 – 1.71 (m, 2H), 1.69 – 1.64 (m, 1H), 1.51 (m, 2H), 1.43 – 1.38 (m, 1H), 1.29 (m, 1H), 1.22 (s, 3H), 1.20 (s, 3H), 1.18 (s, 3H). ^13\text{C NMR (101 MHz, CHLOROFORM-D)} \delta 172.8, 61.1, 50.0, 48.7, 44.7, 43.5, 34.5, 25.4, 23.5, 22.6, 17.3. EI-MS: 181 (M^+). [\alpha]_D^{23} -23.6^\circ (1, DCM) \]

(E)-1-((3r,5r,7r)-adamantan-1-yl)ethanone O-methyl oxime (1h): pale orange liquid
\[ ^1\text{H NMR (400 MHz, CHLOROFORM-D)} \delta 3.81 (s, 3H), 2.01 (s, 3H), 1.76 – 1.64 (m, 15H) ^13\text{C NMR (101 MHz, CHLOROFORM-D)} \delta 163.7, 61.1, 39.6, 39.0, 36.9, 28.3, 9.5. EI-MS: 207 (M^+) \]

(E)-ethyl 2-(methoxyimino)-1-methylcyclohexanecarboxylate (1n): Pale yellow liquid.
\[ ^1\text{H NMR (400 MHz, CHLOROFORM-D)} \delta 4.23 – 4.07 (m, 2H), 3.82 (s, 3H), 3.19 – 3.03 (m, 1H), 2.38 – 2.28 (m, 1H), 1.90-1.82 (m, 1H), 1.77 – 1.69 (m, 1H), 1.69-1.62 (m, 1H), 1.51 – 1.42 (m, 1H), 1.42 – 1.33 (m, 2H), 1.32 (s, 3H), 1.23 (t, J = 7.1 Hz, 3H). ^13\text{C NMR (101 MHz, CHLOROFORM-D)} \delta 175.0, 159.7, 61.4, 61.0, 49.9, 38.2, 25.7, 23.6, 23.0, 22.7, 14.3. EI-MS: 213 (M^+) \]
(8R,9S,10S,13S,14S,17S,E)-17-hydroxy-2,10,13,17-tetramethyltetradecahydro-1H-cyclopenta[a]phenanthren-3(2H)-one O-methyl oxime (1m): colorless solid, m.p. 156°C-158°C

\[ \delta \]

\[ 3.79 (s, 3H), 2.93 \text{ (dd, } J = 14.6, 3.2 \text{ Hz, 1H}), 2.38-2.30 \text{ (m, 1H), 1.85 (dd, } J = 12.9, 4.8 \text{ Hz, 2H), 1.77 - 1.57 \text{ (m, 4H), 1.58 - 1.40 \text{ (m, 4H), 1.39 - 1.30 \text{ (m, 2H), 1.29 - 1.18 \text{ (m, 5H), 1.18 (s, 3H), 1.04 (d, } J = 6.2 \text{ Hz, 3H), 0.91 (d, } J = 5.2 \text{ Hz, 3H), 0.88 (s, 2H), 0.83 (s, 3H), 0.64-0.58 \text{ (m, 1H)})} \]

\[ \delta \]

\[ 162.3, 81.8, 61.1, 54.2, 50.7, 48.7, 46.2, 45.6, 39.0, 36.4, 36.2, 32.9, 31.7, 31.6, 28.5, 27.9, 25.9, 23.3, 20.9, 16.7, 14.1, 12.44. \]

EI-MS: 347 (M+). HRMS (ESI, m/z) calcd for C\(_{22}\)H\(_{37}\)NO\(_2\) [M+H]+: 348.2897, found: 348.2896. \[ [\alpha]_D^{23} +14.3^\circ \] (1, DCM)

\[ \alpha \]

(10S,13R,14R,17R,E)-4,4,10,13,14-pentamethyl-17-((R)-6-methylheptan-2-yl)-4,5,6,7,10,11,12,13,14,15,16,17-dodecahydro-1H-cyclopenta[a]phenanthren-3(2H)-one O-methyl oxime (1k): colorless solid, m.p. 113°C-115°C

\[ \delta \]

\[ 3.81 (s, 3H), 3.00 \text{ (ddd, } J = 15.3, 5.1, 3.6 \text{ Hz, 1H), 2.14 (ddd, } J = 15.3, 12.8, 5.6 \text{ Hz, 1H), 2.07 - 1.99 \text{ (m, 4H), 1.96 - 1.89 \text{ (m, 1H), 1.81 (ddd, } J = 12.8, 5.5, 3.7 \text{ Hz, 1H), 1.70 (m, 3H), 1.61 - 1.51 \text{ (m, 3H), 1.47 - 1.42 \text{ (m, 1H), 1.37 - 1.29 \text{ (m, 6H), 1.16 (s, 3H), 1.15 - 1.09 \text{ (m, 4H), 1.08 (s, 3H), 1.07 (s, 3H), 1.00 - 0.97 \text{ (m, 1H), 0.89 (d, } J = 6.5 \text{ Hz, 3H), 0.87 (d, } J = 3.1 \text{ Hz, 3H), 0.86 (d, } J = 2.2 \text{ Hz, 6H), 0.70 (s, 3H).} \]

\[ \delta \]

\[ 166.2, 135.0, 134.0, 61.2, 51.6, 50.7, 50.0, 44.6, 40.2, 39.7, 37.2, 36.6, 35.9, 31.2, 31.0, 28.4, 28.2, 27.2, 26.6, 24.4, 24.3, 23.4, 23.0, 22.7, 21.2, 19.1, 18.8, 18.3, 16.0. \] EI-MS: 455 (M+). HRMS (ESI, m/z) calcd for C\(_{31}\)H\(_{37}\)NO\(_3\) [M+H]+: 456.4200, found: 456.4199. \[ [\alpha]_D^{23} +17.7^\circ \] (1, DCM)

\[ \alpha \]

(2S,4aS,6aS,6bR,12aS,12bR,14bS)-methyl 2,4a,6a,6b,9,9,12a-heptamethyl-10,13-dioxo-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12a,12b,13,14b-icosahydropicene-2-carboxylate (1l'): colorless solid, m.p. 113°C-115°C

\[ \delta \]

\[ 5.70 (s, 1H), 3.70 (s, 3H), 2.96 (ddd, } J = 13.4, 7.0, 4.1 \text{ Hz, 1H), 2.62 (ddd, } J = 15.9, 11.0, 7.1 \text{ Hz, 1H), 2.36 (ddd, } J = 15.8, 6.5, 4.1 \text{ Hz, 1H), 2.15 - 1.83 \text{ (m, 5H), 1.76 - 1.67 \text{ (m, 1H), 1.64 (dd, } J = 24.1, 10.6 \text{ Hz, 2H), 1.55 (d, } J = 8.7 \text{ Hz, 2H), 1.51 - 1.41 \text{ (m, 3H), 1.39 (s, 3H), 1.32 (dd, } J = 9.4, 5.1 \text{ Hz, 4H), 1.27 (s, 3H), 1.22 (d, } J = 4.4 \text{ Hz, 1H), 1.17 (s, 3H), 1.15 (s, 3H), 1.11 (s, 3H), 1.07 (s, 3H), 0.83 (s, 3H).} \]

\[ \delta \]

\[ 216.9, 199.2, 176.7, 169.6, 128.3, 61.0, 55.3, 51.7, 48.3, 47.6, 45.1, 44.0, 43.2, 41.1, 39.6, 37.7, 36.6, 34.1, 32.0, 31.8, 31.0, 28.5, 28.2, 26.5, 26.4, 26.3, 23.3, 21.3, 18.7, 18.4, 15.6. \]
(2S,4aS,6aS,6bR,12aS,12bR,14bS,E)-methyl 10-(methoxyimino)-2,4a,6a,6b,9,9,12a-heptamethyl-13-oxo-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-icosahydropice ne-2-carboxylate (I): colorless solid, m.p. 251°C-253°C

$^1$H NMR (400 MHz, CHLOROFORM-D) $\delta$ 5.66 (s, 1H), 3.79 (s, 3H), 3.67 (s, 3H), 2.92 (dt, J = 15.5, 4.2 Hz, 1H), 2.85 – 2.74 (m, 1H), 2.36 (s, 1H), 2.20 (ddd, J = 15.8, 12.8, 5.7 Hz, 1H), 2.11 – 2.03 (m, 1H), 2.02 – 1.94 (m, 2H), 1.90 (d, J = 13.7 Hz, 1H), 1.83 (dd, J = 13.7, 4.0 Hz, 1H), 1.72 – 1.64 (m, 1H), 1.60 (d, J = 13.8 Hz, 2H), 1.48 (t, J = 12.5 Hz, 1H), 1.41 (d, J = 12.4 Hz, 2H), 1.33 (s, 3H), 1.29 (d, J = 9.5 Hz, 2H), 1.22 (s, 3H), 1.20 (s, 1H), 1.16 (s, 3H), 1.13 (s, 6H), 1.05 (s, 3H), 0.98 (m, 3H), 0.79 (s, 3H). $^{13}$C NMR (101 MHz, CHLOROFORM-D) $\delta$ 200.0, 177.0, 169.5, 165.8, 128.6, 61.47 (s), 61.1, 55.7, 51.9, 48.5, 45.5, 44.2, 43.4, 41.2, 40.2, 39.2, 37.9, 37.1, 32.6, 32.0, 31.3, 28.7, 28.4, 27.4, 26.6, 26.5, 23.6, 23.4, 18.8, 18.3, 17.9, 15.8. HRMS (ESI, m/z) calcd for C_{32}H_{49}NO_4 [M+H]^+: 512.3734 , found: 512.3732. $\alpha_{D}^{25}+49.2^\circ$ (1, DCM)
III. Experimental Procedure for the Optimization Study

The yield of the product was confirmed by NMR using trichloroethylene as an internal.

1. Selection for catalyst and preliminary optimization on solvent.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (5 mmol%)</th>
<th>solvent</th>
<th>Temp (°C)</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CuCl</td>
<td>DCE</td>
<td>50</td>
<td>N.R.</td>
</tr>
<tr>
<td>2</td>
<td>CuBr</td>
<td>DCE</td>
<td>50</td>
<td>N.R.</td>
</tr>
<tr>
<td>3</td>
<td>Cu(OTf)₂</td>
<td>DCE</td>
<td>50</td>
<td>N.R.</td>
</tr>
<tr>
<td>4</td>
<td>CuCl</td>
<td>Toluene</td>
<td>50</td>
<td>N.R.</td>
</tr>
<tr>
<td>5</td>
<td>Pd(OAc)₂</td>
<td>DCE</td>
<td>85</td>
<td>17%</td>
</tr>
<tr>
<td>6</td>
<td>Pd(OAc)₂</td>
<td>DCE</td>
<td>60</td>
<td>trace</td>
</tr>
<tr>
<td>7</td>
<td>Pd(OAc)₂</td>
<td>CH₃CN</td>
<td>80</td>
<td>N.R.</td>
</tr>
<tr>
<td>8</td>
<td>Pd(OAc)₂</td>
<td>DCM/DMSO</td>
<td>80</td>
<td>N.R.</td>
</tr>
<tr>
<td>9</td>
<td>Pd(OAc)</td>
<td>EtOH</td>
<td>80</td>
<td>N.R.</td>
</tr>
<tr>
<td>10</td>
<td>PdCl₂</td>
<td>DCE</td>
<td>80</td>
<td>N.R.</td>
</tr>
<tr>
<td>11</td>
<td>Pd(COOCF₃)₂</td>
<td>DCE</td>
<td>80</td>
<td>N.R.</td>
</tr>
<tr>
<td>12</td>
<td>PdCl₂(PPh₃)₂</td>
<td>DCE</td>
<td>80</td>
<td>N.R.</td>
</tr>
</tbody>
</table>
2. Further optimization for solvent, base, additive and reacting time.

```
Entry Solvent X Base Additive Time Yield
1  DCE PF₆ K₂CO₃ (1 equiv) None 12h 10%
2  DCE PF₆ NaHCO₃ (1 equiv) None 12h 15%
3  DCE PF₆ Na₂CO₃ (1 equiv) None 12h 8%
4  DCE PF₆ Ag₂CO₃ (1 equiv) None 12h 23%
5  DCE:tert-Butanol (4:1) PF₆ Ag₂CO₃ (2 equiv) None 12h 27%
6  DCE PF₆ Ag₂CO₃ (2 equiv) PivOH (0.3 equiv) 12h 44%
7  DCE:tert-Butanol (4:1) PF₆ Ag₂CO₃ (2 equiv) PivOH (0.6 equiv) 12h 57%
8  DCE:HFIP(3:1) PF₆ Ag₂CO₃ (2 equiv) PivOH (0.6 equiv) 12h 82%
9  DCE:HFIP(1:1) PF₆ Ag₂CO₃ (2 equiv) PivOH (0.6 equiv) 12h 40%
10 DCE:HFIP(1:1) PF₆ Ag₂CO₃ (2 equiv) PivOH (0.6 equiv) 12h 51%
11 DCE:HFIP(3:1) OTf Ag₂CO₃ (2 equiv) PivOH (0.6 equiv) 5h 87%
12 DCE:HFIP(3:1) BF₄ Ag₂CO₃ (2 equiv) PivOH (0.6 equiv) 5h trace
13 DCE PF₆ Ag₂CO₃ (2 equiv) PivOH (0.6 equiv) 5h 50%
14a DCE:HFIP(3:1) OTf Ag₂CO₃ (2 equiv) None 5h 30%
15a DCE:HFIP(3:1) OTf Ag₂CO₃ (2 equiv) PivOH (0.6 equiv) 5h 68%
```

a 5 mol% of Pd(OPiv)₂ was employed catalyst instead of Pd(OAc)₂
IV. Experimental Procedure for the $sp^3$ C–H Arylation

1. **General Procedure for the Pd-Catalyzed Arylation of Oximes.**

   Diaryliodonium salts (0.25 mmol), Pd(OAc)$_2$ (0.0125 mmol, 2.8 mg) along with Ag$_2$CO$_3$ (0.5 mmol, 137.9 mg) were placed in a schlenk tube. The tube was evacuated and recharged with N$_2$ for 3 times. Mixing solvent of DCE (1.5 ml) and HFIP (0.5 ml) was dropped in under N$_2$ atmosphere. Then appropriate ketoximes (0.25 mmol) and PivOH (0.15 mmol, 16.9 μl) was slowly added to the mixture. The tube was sealed and the mixture was allowed to stir at 70-90 °C for 5h. After completion which was monitored by GC/MS, the mixture was cooled to room temperature, then NaHCO$_3$ aq. (5 mL) was added. The mixture was extracted with ethyl acetate (5 mL x 3) and dried over anhydrous MgSO$_4$. Evaporation of the solvent followed by purification on silica gel (petroleum ether/ethyl acetate 100/1 to 50/1) provided the corresponding ketoximes.

2. **General Procedure for Obtaining Arylated Ketone and Aldehydes**

   Diaryliodonium salts (0.25 mmol), Pd(OAc)$_2$ (0.0125 mmol, 2.8 mg) and Ag$_2$CO$_3$ (0.5 mmol, 137.9mg) were placed in a tube. The tube was evacuated and recharged with N$_2$ for 3 times. Mixing solvent of DCE (1.5 ml) and HFIP (0.5 ml) was dropped in. Then appropriate ketoximes (0.25 mmol) and PivOH (0.15 mmol, 16.9 μl) was slowly added to the mixture. The tube was sealed and the mixture was allowed to stir at 70-90 °C for 5h. After completion, the mixture was filtered through celite and THF (2 ml) was added in the filtrate. Then 35% aqueous formaldehyde solution (1ml) as well as 10% aqueous HCl solution (0.5 ml) was added to the reaction mixture. Being stirred at 35°C for 5 h, the mixture was diluted with ethyl acetate (10 mL), neutralized with NaHCO$_3$ aq. and washed with water (10 mL). The organic layer was dried over anhydrous MgSO$_4$. Evaporation of the solvent followed by purification on silica gel (petroleum ether/ethyl acetate 100/1 to 50/1) provided the corresponding ketones.
3. Spectroscopic Data of Corresponding Products

**(E)-2-benzylcyclohexanone O-methyl oxime (3aa):** colorless liquid; yield: 83%

\[ H^1 \text{NMR} \ (301 \text{ MHz, CHLOROFORM-D}) \delta \ 7.31 – 7.23 \ (m, 2H), 7.18 \ (dd, J = 6.9, 4.5 \text{ Hz, } 3H), 3.83 \ (s, 3H), 3.12 \ (dd, J = 13.4, 4.7 \text{ Hz, } 1H), 2.82 – 2.70 \ (m, 1H), 2.59 \ (dd, J = 13.4, 9.8 \text{ Hz, } 1H), 2.53 – 2.41 \ (m, 1H), 2.20 \ (m, 1H), 1.75 – 1.63 \ (m, 3H), 1.65 – 1.51 \ (m, 2H), \] 1.39 \ (m, 2H)\n
\[ H^{13} \text{C NMR} \ (76 \text{ MHz, CHLOROFORM-D}) \delta 162.0, 140.9, 129.4, 128.3, 126.0, 61.2, 43.8, 37.3, 31.8, 26.4, 24.3, 23.8. \text{ IR (neat, } \nu_{C=\text{N}} \text{) 1736 cm}^{-1}. \text{EI-MS: 217} \ (M^+) \text{. HRMS (ESI, m/z) calcd for } C_{14}H_{19}NO [M+H]^+: 218.1539, \text{ found: 218.1535} \]

*GC-MS spectra of the extracted reaction mixture: red arrow indicated the peak of the product*

**(E)-2-(4-bromobenzyl)cyclohexanone O-methyl oxime (3ad):** colorless liquid; yield: 80%

\[ H^1 \text{NMR} \ (400 \text{ MHz, CHLOROFORM-D}) \delta \ 7.39 \ (d, J = 8.3 \text{ Hz, } 2H), 7.06 \ (d, J = 8.3 \text{ Hz, } 2H), 3.08 \ (dd, J = 13.7, 5.3 \text{ Hz, } 1H), 2.80 \ (dt, J = 13.7, 5.6 \text{ Hz, } 1H), 2.54 \ (dd, J = 13.7, 9.6 \text{ Hz, } 1H), 2.41 \ (dt, J = 8.5, 4.5 \text{ Hz, } 1H), 2.13 \ (dd, J = 14.0, 9.6, 4.5 \text{ Hz, } 1H), 1.76 – 1.65 \ (m, 3H), 1.60 – 1.50 \ (m, 1H), 1.42 \ (dt, J = 9.0, 6.2 \text{ Hz, } 1H), 1.33 – 1.22 \ (m, 1H). \text{IR (neat, } \nu_{C=\text{N}} \text{) 1736 cm}^{-1}. \text{EI-MS: 295} \ (M^+) \text{. HRMS (ESI, m/z) calcd for } C_{14}H_{18}BrNO [M+Na]^+: 296.0645, \text{ found: 296.0646} \]

*GC-MS spectra of the extracted reaction mixture: red arrow indicated the peak of the product*

**(E)-2-(4-(trifluoromethyl)benzyl)cyclohexanone O-methyl oxime (3ah):** colorless liquid; yield: 86%

\[ H^1 \text{NMR} \ (400 \text{ MHz, CHLOROFORM-D}) \delta \ 7.52 \ (d, J = 8.0 \text{ Hz, } 2H), 7.29 \ (d, J = 8.0 \text{ Hz, } 2H), 3.19 \ (dd, J = 13.8, 5.3 \text{ Hz, } 1H), 2.84 \ (dt, J = 13.8, 5.3 \text{ Hz, } 1H), 2.64 \ (dd, J = 13.7, 9.0 \text{ Hz, } 1H), 2.54 – 2.39 \ (m, 1H), 2.14-2.08 \ (m, 1H), 1.75 – 1.67 \ (m, 3H), 1.57 – 1.50 \ (m, 1H), 1.47 – 1.39 \ (m, 1H), 1.39 – 1.31 \ (m, 1H). \text{IR (neat, } \nu_{C=\text{N}} \text{) 1736 cm}^{-1}. \text{EI-MS: 295} \ (M^+) \text{. HRMS (ESI, m/z) calcd for } C_{14}H_{18}BrNO [M+Na]^+: 296.0645, \text{ found: 296.0646} \]

*GC-MS spectra of the extracted reaction mixture: red arrow indicated the peak of the product*
CHLOROFORM-D) δ 161.2, 145.2, 129.7, 128.35 (d, J = 32.2 Hz), 125.2, 61.3, 43.7, 37.2, 32.3, 26.3, 24.5, 24.1. IR (neat, ν\textsubscript{C=\textit{N}}) 1737 cm\textsuperscript{-1}. EI-MS: 285 (M'). EI-MS: 295 (M'). HRMS (ESI, m/z) calcd for C\textsubscript{15}H\textsubscript{18}F\textsubscript{3}NO [M+Na]\textsuperscript{+}: 286.1413, found: 286.1417.

**GC-MS spectra of the extracted reaction mixture: red arrow indicated the peak of the product**

(E)-2-(2-fluorobenzyl)cyclohexanone O-methyl oxime (3aj): colorless liquid; yield: 78%

\textsuperscript{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.18 (m, 2H), 7.02 (m, 2H), 3.81 (s, 3H), 3.11 (dd, J = 13.7, 5.6 Hz, 1H), 2.86 – 2.76 (m, 1H), 2.70 (dd, J = 13.7, 9.2 Hz, 1H), 2.56 – 2.43 (m, 1H), 2.16 (m, 1H), 1.77 – 1.64 (m, 3H), 1.56 (dd, J = 8.8, 4.0 Hz, 1H), 1.42 (m, 2H). \textsuperscript{13}C NMR (101 MHz, CHLOROFORM-D) δ 161.5 (d, J = 244.8 Hz), 161.5, 131.8 (d, J = 5.0 Hz), 127.7 (d, J = 8.2 Hz), 123.9 (s), 115.2 (d, J = 22.4 Hz), 61.2, 42.7, 32.2, 30.6, 24.3, 24.0. IR (neat, ν\textsubscript{C=\textit{N}}) 1737 cm\textsuperscript{-1}. EI-MS: 235 (M'). HRMS (ESI, m/z) calcd for C\textsubscript{15}H\textsubscript{18}F\textsubscript{3}NO [M+Na]\textsuperscript{+}: 236.1445 , found: 236.1442.

**GC-MS spectra of the extracted reaction mixture: red arrow indicated the peak of the product**

(E)-2-(2-chlorobenzyl)cyclohexanone O-methyl oxime (3ak): colorless liquid; yield: 72%

\textsuperscript{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.25 (d, J = 7.5 Hz, 1H), 7.16 (dd, J = 9.2, 4.2 Hz, 1H), 7.06 (dt, J = 7.3, 4.2 Hz, 2H), 3.74 (s, 3H), 3.17 (dd, J = 13.7, 5.5 Hz, 1H), 2.80 (dt, J = 13.8, 5.1 Hz, 1H), 2.68 (dd, J = 13.7, 8.9 Hz, 1H), 2.55 – 2.42 (m, 1H), 2.07 – 1.94 (m, 1H), 1.74 – 1.58 (m, 3H), 1.52 – 1.41 (m, 1H), 1.40 – 1.25 (m, 2H). \textsuperscript{13}C NMR (101 MHz, CHLOROFORM-D) δ 161.4, 138.6, 134.5 131.9, 129.6, 127.5, 126.5, 61.2, 42.2, 34.9, 32.5, 26.4, 24.5, 24.4. IR (neat, ν\textsubscript{C=\textit{N}}) 1737 cm\textsuperscript{-1}. EI-MS: 251 (M'). HRMS (ESI, m/z) calcd for C\textsubscript{15}H\textsubscript{18}Cl\textsubscript{3}NO [M+H]\textsuperscript{+}: 252.1150 , found: 252.1152.

**GC-MS spectra of the extracted reaction mixture: red arrow indicated the peak of the product**
**(E)**-**methyl 4-((2-(methoxyimino)cyclohexyl)methyl)benzoate (3ag):** colorless solid; yield: 87%; m.p. 67-69°C

1H NMR (301 MHz, CHLOROFORM-D) δ 7.95 (m, 2H), 7.25 (m, 2H), 3.90 (s, 3H), 3.81 (s, 3H), 3.19 (dd, J = 13.6, 5.3 Hz, 1H), 2.83 (m, 1H), 2.63 (dd, J = 13.6, 9.2 Hz, 1H), 2.47 (tt, J = 8.8, 4.4 Hz, 1H), 2.12 (m, 1H), 1.70 (m, 3H), 1.58 – 1.48 (m, 1H), 1.48 – 1.24 (m, 2H).

13C NMR (76 MHz, CHLOROFORM-D) δ 167.2, 161.2, 146.6, 129.6, 129.4, 128.0, 61.2, 52.1, 43.6, 37.4, 32.2, 26.3, 24.4, 24.0. IR (neat, νC=O) 1722 cm⁻¹ (The peak of νC=N was overlapped). EI-MS: 275 (M⁺). HRMS (ESI, m/z) calcd for C₁₆H₂₁NO₃ [M+H]⁺: 276.1594, found: 276.1591. [α]D 23 +49.2° (1, DCM)

**GC-MS spectra of the extracted reaction mixture: red arrow indicated the peak of the product**

**(E)-2-(4-methoxybenzyl)cyclohexanone O-methyl oxime (3ai):** colorless liquid yield: 80%

1H NMR (400 MHz, CHLOROFORM-D) δ 7.08 (m, 2H), 6.81 (m, 2H), 3.81 (s, 3H), 3.77 (s, 3H), 3.03 (dd, J = 13.7, 5.0 Hz, 1H), 2.78 – 2.67 (m, 1H), 2.53 (dd, J = 13.7, 9.7 Hz, 1H), 2.42 (dt, J = 12.9, 4.7 Hz, 1H), 2.22 (m, 1H), 1.68 (mz, 3H), 1.57 (m, 1H), 1.44 – 1.34 (m, 2H).

13C NMR (101 MHz, CHLOROFORM-D) δ 162.1, 158.0, 132.8, 130.3, 113.7, 61.2, 55.4, 43.9, 36.4, 31.6, 26.4, 24.2, 23.7. IR (neat, νC=N) 1737 cm⁻¹, EI-MS: 251 (M⁺). HRMS (ESI, m/z) calcd for C₁₅H₂₁NO₂ [M+H]⁺: 248.1645, found: 248.1645.

**GC-MS spectra of the extracted reaction mixture: red arrow indicated the peak of the product**

**(R,E)-methyl4-((4-isopropyl-6-(methoxyimino)cyclohex-1-en-1-yl)methyl)benzoate (3jg):** colorless liquid; yield: 38%

1H NMR (400 MHz, CHLOROFORM-D) δ 7.93 (m, 2H), 7.29 (m, 2H), 5.88 (m, 1H), 3.90 (s, 3H), 3.86 (s, 3H), 3.61 (m, 2H), 3.06 (dd, J = 16.5, 2.5 Hz, 1H), 2.27 – 2.12 (m, 1H), 1.87 (m, 1H), 1.77 (dd, J = 16.5, 12.7 Hz, 1H), 1.56 – 1.43 (m, 2H), 0.89 (m, 6H).

13C NMR (101 MHz, CHLOROFORM-D) δ 167.4, 155.2, 146.6, 134.2, 133.8, 129.5, 129.4, 127.8, 61.9, 52.1, 39.4, 37.2, 32.2, 28.9, 26.7, 19.9, 19.8. IR (neat, νC=O) 1723 cm⁻¹ (The peak of νC=N was overlapped). EI-MS: 315 (M⁺). HRMS (ESI, m/z)
calcd for C₁₉H₂₅NO₃ [M+H]⁺: 316.1907, found: 316.1911. [α]D²³ -15.8° (1, DCM)

GC-MS spectra of the extracted reaction mixture: red arrow indicated the peak of the product

**Methyl 4-((1S,2R,3S,5R,7S)-1-((E)-1-(methoxyimino)ethyl)adamantan-2-yl)benzoate (3hg):** colorless liquid; yield: 47%

1H NMR (400 MHz, CHLOROFORM-D) δ 7.90 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 8.3 Hz, 2H), 3.89 (s, 3H), 3.77 (s, 3H), 3.24 (m, 1H), 2.58 (d, J = 13.6 Hz, 1H), 2.11 (dd, J = 6.0, 3.0 Hz, 3H), 2.05 – 1.94 (m, 4H), 1.75 (s, 2H), 1.67 (s, 1H), 1.59 (d, J = 9.0 Hz, 1H), 1.54 (s, 3H), 1.48 (d, J = 13.1 Hz, 1H). 13C NMR (101 MHz, CHLOROFORM-D) δ 167.3, 162.2, 150.0, 129.3, 129.0, 127.5, 61.3, 52.1, 51.5, 44.3, 42.0, 39.7, 37.5, 36.4, 35.1, 30.5, 28.5, 27.9, 9.5. IR (neat, νC=O) 1723 cm⁻¹ (The peak of νC=N was overlapped). EI-MS: 342 (M⁺). HRMS (ESI, m/z) calcd for C₁₉H₂₅NO₃ [M+H]⁺: 342.2064, found: 342.2069

**(E)-methyl 4-((3-(methoxyimino)-2,4-dimethylbicyclo[2.2.1]heptan-2-yl)methyl)benzoate (3ig):** colorless solid; yield: 65%; m.p. 74-76°C

1H NMR (400 MHz, CHLOROFORM-D) δ 7.94 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 3.90 (s, 3H), 3.80 (s, 3H), 3.10 (d, J = 13.6 Hz, 1H), 2.91 (d, J = 13.6 Hz, 1H), 1.75 (m, 2H), 1.71 – 1.41 (m, 3H), 1.43 – 1.31 (m, 2H), 1.26 (s, 3H), 1.17 (s, 3H). 13C NMR (101 MHz, CHLOROFORM-D) δ 171.6, 167.4, 145.5, 130.6, 129.2, 127.9, 61.4, 54.3, 52.1, 47.9, 45.0, 40.1, 37.3, 31.4, 24.8, 23.2, 22.7. IR (neat, νC=O) 1723 cm⁻¹ (The peak of νC=N was overlapped), EI-MS: 315 (M⁺). HRMS (ESI, m/z) calcd for C₁₉H₂₂NO₃ [M+H]⁺: 316.1907, found: 316.1911. [α]D²³ +13.7° (1, DCM)

GC-MS spectra of the extracted reaction mixture: red arrow indicated the peak of the product
dimethyl 4,4’-(((6aR,6bS,8aS,11S,12aS,14aR,14bS,E)-11-(methoxycarbonyl)-3-(methoxylimino)-6a,6b,8a,11,14b-pentamethyl-14-oxo-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12a,14,14a,14b-icosahydropicene-4,4-diyl)bis(methylene))dibenzoate (3lg): colorless solid; yield: 73%; m.p.277°C-279°C

\[ \text{1H NMR (400 MHz, CHLOROFORM-D)} \delta 7.92 (d, J = 8.2 Hz, 2H), 7.86 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 5.61 (s, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.70 (s, 3H), 3.67 (s, 3H), 3.38 (d, J = 13.7 Hz, 1H), 3.17 (t, J = 14.5 Hz, 2H), 2.78 (t, J = 14.6 Hz, 2H), 2.54 (d, J = 13.9 Hz, 1H), 2.17 (dd, J = 14.5, 4.9 Hz, 1H), 2.06 (m, 1H), 2.00 (d, J = 14.5 Hz, 2H), 1.83 (m, 2H), 1.76 (m, 2H), 1.53 (m, 2H), 1.42 (s, 3H), 1.38 (m, 4H), 1.30 (s, 1H), 1.27 (m, 2H), 1.15 (s, 3H), 1.11 (s, 3H), 1.02 (s, 3H), 0.86 (m 2H), 0.78 (s, 3H).

\[ \text{13C NMR (101 MHz, CHLOROFORM-D)} \delta 199.7, 177.0, 169.5, 167.4, 167.3, 158.1, 146.0, 143.2, 131.5, 131.3, 129.0, 128.7, 128.3, 128.3, 127.9, 61.7, 61.5, 52.1, 52.1, 51.9, 49.5, 49.2, 48.6, 45.4, 44.1, 43.3, 42.1, 41.1, 39.2, 37.8, 37.3, 36.7, 32.0, 31.6, 31.3, 28.7, 28.4, 27.1, 26.4, 23.0, 19.2, 18.5, 18.4, 16.0. IR (neat, νC=O) 1724 cm\(^{-1}\) (The peak of νC=N was overlapped). HRMS (ESI, m/z) calcd for C\(_{48}\)H\(_{61}\)NO\(_8\) [M+H]+: 780.4470, found: 780.4474. [α]D\(^{23}\)+54.8° (1, DCM)

dimethyl4,4’-(((10S,13R,14R,17R,E)-3-(methoxyimino)-10,13,14-trimethyl-17-(R)-6-methylheptan-2-yl)-2,3,4,5,6,7,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene-4,4-diyl)bis(methylene))dibenzoate: colorless solid; yield: 73%; m.p.143-145°C

\[ \text{1H NMR (400 MHz, CHLOROFORM-D)} \delta 7.93 (d, J = 8.2 Hz, 2H), 7.83 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 7.10 (d, J = 8.2 Hz, 2H), 3.91 (s, 3H), 3.87 (s, 3H), 3.71 (s, 3H), 3.30 (d, J = 13.5 Hz, 1H), 3.18 (d, J = 13.5 Hz, 1H), 2.77 (d, J = 13.3 Hz, 1H), 2.59 (d, J = 13.6 Hz, 1H), 2.15 – 1.73 (m, 10H), 1.65 (m, 2H), 1.51 (m, 2H), 1.31 (m, 8H), 1.21 (s, 3H), 1.12 (m, 3H), 1.02 – 0.91 (m, 2H), 0.86 (m, 9H), 0.67 (d, J = 4.0 Hz, 6H).

\[ \text{13C NMR (101 MHz, CHLOROFORM-D)} \delta 167.4, 158.2, 145.6, 143.7, 135.0, 134.1 131.5, 131.5, 128.7, 128.1, 127.7, 61.5, 52.1, 52.1, 50.6, 49.9, 49.2, 45.1, 44.5, 42.0, 39.6, 39.1, 36.9, 36.6, 34.2, 31.0, 30.9, 29.9, 28.3, 28.1, 25.8, 24.2, 24.3, 24.1, 23.0, 22.7, 21.1, 19.4, 19.3, 19.1, 18.8, 16.0. IR (neat, νC=O, νC=N, νC=O) 1724, 1717, 1709 cm\(^{-1}\). HRMS (ESI, m/z) calcd for C\(_{47}\)H\(_{65}\)NO\(_5\) [M+Na]+: 746.4755, found: 746.4753. [α]D\(^{23}\)+20.5° (1, DCM)
X-ray crystal structure analysis of compound 3kg: Single crystals suitable for X-ray analysis were obtained by slow evaporation of its solution in hexane. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 1057827. Formula: C₄₇H₆₅NO₅, \( M = 724.00 \), colourless crystal, 0.28 x 0.15 x 0.05 mm, \( a = 35.188(7) \), \( b = 7.4837(15) \), \( c = 16.526(3) \) Å, \( \alpha = 90.00 \), \( \beta = 98.87(3) \), \( \gamma = 90.00 \), \( V = 4299.8(15) \) Å³, \( \rho_{\text{calc}} = 1.118 \) gcm⁻³, \( \mu = 0.071 \) mm⁻¹, \( Z = 4 \), Monoclinic, space group C2, \( \lambda = 0.71073 \) Å, \( T = 173(2) \) K. Data completeness = 0.998, Theta (max) = 27.48
2-benzylcyclohexanone (4aa)\[8\]: colorless liquid; yield: 80%

\[^1\text{H}\text{ NMR (301 MHz, CHLOROFORM-D) \(\delta \)}

7.27 (dd, \(J = 9.4, 4.8\) Hz, 2H), 7.21 – 7.10 (m, 3H), 3.24 (dd, \(J = 13.7, 4.6\) Hz, 1H), 2.62 – 2.49 (m, 1H), 2.42 (dt, \(J = 13.4, 6.4\) Hz, 2H), 2.31 (dd, \(J = 13.4, 5.8\) Hz, 1H), 2.13 – 1.98 (m, 2H), 1.90 – 1.78 (m, 1H), 1.72 – 1.54 (m, 2H), 1.35 (ddd, \(J = 24.8, 12.4, 3.5\) Hz, 1H).\[^1\text{C}\text{ NMR (76 MHz, CHLOROFORM-D) \(\delta \)}

212.7, 140.5, 129.3, 128.4 126.1, 52.6, 42.3, 35.6, 33.6, 28.2, 25.2. IR (neat, \(\nu_{C=O}\)) 1706 cm\(^{-1}\). EI-MS: 188 (M\(^+\)). HRMS (ESI, m/z) calcd for C\(_{13}\)H\(_{16}\)O [M+Na\(^+\)]: 211.1093, found: 211.1093.

2-(4-fluorobenzyl)cyclohexanone (4ab)\[8\]: colorless liquid; yield: 80%

\[^1\text{H}\text{ NMR (400 MHz, CHLOROFORM-D) \(\delta \)}

7.18 – 7.04 (m, 2H), 6.94 (m, 2H), 3.17 (dd, \(J = 13.9, 4.6\) Hz, 1H), 2.58 – 2.45 (m, 1H), 2.48 – 2.28 (m, 3H), 2.12 – 1.97 (m, 2H), 1.84 (dd, \(J = 10.6, 2.4\) Hz, 1H), 1.73 – 1.53 (m, 2H), 1.39 – 1.28 (m, 1H).\[^1\text{C}\text{ NMR (101 MHz, CHLOROFORM-D) \(\delta \)}

212.5, 161.4 (d, \(J = 243.7\) Hz), 136.0, 130.6 (d, \(J = 7.8\) Hz), 115.1 (d, \(J = 21.1\) Hz), 52.64 (s), 42.3, 34.8, 33.6, 28.1, 25.2. IR (neat, \(\nu_{C=O}\)) 1711 cm\(^{-1}\). EI-MS: 206 (M\(^+\)). EI-MS: 188 (M\(^+\)). HRMS (ESI, m/z) calcd for C\(_{13}\)H\(_{15}\)FO [M+Na\(^+\)]: 229.0999, found: 229.0997.

2-(4-chlorobenzyl)cyclohexanone (4ac)\[9\]: colorless liquid; yield: 78%

\[^1\text{H}\text{ NMR (400 MHz, CHLOROFORM-D) \(\delta \)}

7.23 (d, \(J = 8.4\) Hz, 2H), 7.09 (d, \(J = 8.3\) Hz, 2H), 3.17 (dd, \(J = 13.9, 5.1\) Hz, 1H), 2.60 – 2.46 (m, 1H), 2.47 – 2.36 (m, 2H), 2.34 – 2.24 (m, 1H), 2.04 (dddd, \(J = 21.8, 12.9, 5.8, 2.7\) Hz, 2H), 1.84 (ddd, \(J = 11.6, 5.6, 3.3\) Hz, 1H), 1.74 – 1.53 (m, 2H), 1.34 (ddd, \(J = 25.0, 12.3, 3.6\) Hz, 1H).\[^1\text{C}\text{ NMR (101 MHz, CHLOROFORM-D) \(\delta \)}

212.3, 139.0, 131.8, 130.6, 128.5, 52.5, 42.3 35.0, 33.61, 28.1, 25.2. IR (neat, \(\nu_{C=O}\)) 1709 cm\(^{-1}\). EI-MS: 226 (M\(^+\)). HRMS (ESI, m/z) calcd for C\(_{14}\)H\(_{15}\)ClO [M+Na\(^+\)]: 245.0704, found: 245.0708.

GC-MS spectra of the extracted reaction mixture: red arrow indicated the peak of the aimed product in form of oxime without hydrolysis

2-(4-chlorobenzyl)cyclohexanone (4ac)\[9\]: colorless liquid; yield: 78%

\[^1\text{H}\text{ NMR (400 MHz, CHLOROFORM-D) \(\delta \)}

7.23 (d, \(J = 8.4\) Hz, 2H), 7.09 (d, \(J = 8.3\) Hz, 2H), 3.17 (dd, \(J = 13.9, 5.1\) Hz, 1H), 2.60 – 2.46 (m, 1H), 2.47 – 2.36 (m, 2H), 2.34 – 2.24 (m, 1H), 2.04 (dddd, \(J = 21.8, 12.9, 5.8, 2.7\) Hz, 2H), 1.84 (ddd, \(J = 11.6, 5.6, 3.3\) Hz, 1H), 1.74 – 1.53 (m, 2H), 1.34 (ddd, \(J = 25.0, 12.3, 3.6\) Hz, 1H).\[^1\text{C}\text{ NMR (101 MHz, CHLOROFORM-D) \(\delta \)}

212.3, 139.0, 131.8, 130.6, 128.5, 52.5, 42.3 35.0, 33.61, 28.1, 25.2. IR (neat, \(\nu_{C=O}\)) 1709 cm\(^{-1}\). EI-MS: 226 (M\(^+\)). HRMS (ESI, m/z) calcd for C\(_{14}\)H\(_{15}\)ClO [M+Na\(^+\)]: 245.0704, found: 245.0708.

GC-MS spectra of the extracted reaction mixture: red arrow indicated the peak of the aimed product in form of oxime without hydrolysis
2-(4-bromobenzyl)cyclohexanone (4ad)\textsuperscript{[10]}: colorless liquid; yield: 78%

$\text{\textsuperscript{1}H NMR (400 MHz, CHLOROFORM-D)} \delta 7.38 (d, J = 8.3 Hz, 2H), 7.03 (d, J = 8.3 Hz, 2H), 3.16 (dd, J = 13.9, 5.1 Hz, 1H), 2.56 – 2.47 (m, 1H), 2.45 – 2.26 (m, 3H), 2.04 (dddd, J = 12.8, 8.2, 5.9, 2.7 Hz, 2H), 1.88 – 1.80 (m, 1H), 1.70 – 1.56 (m, 2H), 1.40 – 1.29 (m, 1H). $\textsuperscript{13}C NMR (101 MHz, CHLOROFORM-D) \delta 212.3, 139.5, 131.5, 131.1, 120.0, 52.5, 42.3, 35.1, 33.6, 28.2, 25.3. IR (neat, $\nu \text{C}=\text{O}$) 1708 cm\textsuperscript{-1}. EI-MS: 266 (M\textsuperscript{+}). HRMS (ESI, m/z) calcd for C\textsubscript{13}H\textsubscript{15}BrO \[M+Na\]^+: 289.0198, found: 289.0199.

2-(4-(trifluoromethyl)benzyl)cyclohexanone (4ah): colorless liquid; yield: 84%

$\text{\textsuperscript{1}H NMR (400 MHz, CHLOROFORM-D)} \delta 7.52 (d, J = 7.9 Hz, 2H), 7.27 (d, J = 9.6 Hz, 2H), 3.26 (dd, J = 13.6, 4.8 Hz, 1H), 2.63 – 2.53 (m, 1H), 2.53 – 2.42 (m, 2H), 2.33 (td, J = 13.0, 5.9 Hz, 1H), 2.05 (dd, J = 26.0, 12.4 Hz, 2H), 1.85 (d, J = 12.0 Hz, 1H), 1.65 (dt, J = 21.7, 12.6 Hz, 2H), 1.38 (dt, J = 21.6, 7.8 Hz, 1H). $\textsuperscript{13}C NMR (101 MHz, CHLOROFORM-D) \delta 212.02 (s), 144.8, 129.6, 128.5 (d, J = 32.3 Hz), 125.3 (d, J = 3.7 Hz), 124.5 (d, J = 271.9 Hz), 52.3, 42.3, 35.5, 33.8, 28.1, 25.3. IR (neat, $\nu \text{C}=\text{O}$) 1711 cm\textsuperscript{-1}, EI-MS: 256 (M\textsuperscript{+}). HRMS (ESI, m/z) calcd for C\textsubscript{14}H\textsubscript{15}F\textsubscript{3}O \[M-H\]-: 255.1002, found: 255.1005.

2-(4-methylbenzyl)cyclohexanone (4ae): colorless liquid; yield: 77%

$\text{\textsuperscript{1}H NMR (400 MHz, CHLOROFORM-D)} \delta 7.05 (m, 4H), 3.18 (dd, J = 13.9, 4.7 Hz, 1H), 2.56 – 2.47 (m, 1H), 2.46 – 2.31 (m, 3H), 2.28 (m, 3H), 2.09 – 1.96 (m, 2H), 1.71 – 1.52 (m, 2H), 1.40 – 1.29 (m, 1H). $\textsuperscript{13}C NMR (76 MHz, CHLOROFORM-D) \delta 212.9, 137.4, 135.6, 129.2, 129.1, 52.7, 42.3, 35.1, 33.5, 28.2, 25.2, 21.1. IR (neat, $\nu \text{C}=\text{O}$) 1711 cm\textsuperscript{-1}, EI-MS: 202 (M\textsuperscript{+}). HRMS (ESI, m/z) calcd for C\textsubscript{14}H\textsubscript{18}O \[M+Na\]^+: 225.1250, found: 225.1245.

GC-MS spectra of the extracted reaction mixture: red arrow indicated the peak of the aimed product in form of oxime without hydrolysis.

2-(2-chlorobenzyl)cyclohexanone (4ak): colorless liquid; yield: 69%

$\text{\textsuperscript{1}H NMR (301 MHz, CHLOROFORM-D)} \delta 7.33 (dd, J = 7.2, 2.1 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.20 – 7.08 (m, 2H), 3.33 (dd, J = 13.6, 5.0 Hz, 1H), 2.75 – 2.63 (m, 1H), 2.64 – 2.51 (m, 1H), 2.47 – 2.28 (m, 2H), 2.10 – 1.94 (m, 2H), 1.90 – 1.80 (m, 1H), 1.75 – 1.59 (m, 2H), 1.41 (m, 1H). $\textsuperscript{13}C NMR (76 MHz, CHLOROFORM-D) \delta 212.4, 138.2, 134.3, 132.0, 129.6, 127.7, 126.7, 50.7, 42.4, 33.8, 33.5, 28.3, 25.4. IR (neat, $\nu \text{C}=\text{O}$) 1709 cm\textsuperscript{-1}, EI-MS: 222 (M\textsuperscript{+}). HRMS (ESI, m/z) calcd for C\textsubscript{14}H\textsubscript{15}Cl\textsubscript{5}O \[M+Na\]^+: 245.0704, found: 245.0707.
2-(2-fluorobenzyl)cyclohexanone (4aj): colorless liquid; yield: 74%

\[
\begin{align*}
\text{1H NMR (301 MHz, CHLOROFORM-D)} & \ \delta \ 7.22 - 7.08 \ (m, 2H), \ 7.14 - 6.93 \ (m, 2H), \ 3.20 \ (dd, J = 13.2, 4.1 Hz, 1H), \ 2.68 - 2.30 \ (m, 4H), \ 2.11 - 1.96 \ (m, 2H), \\
& \ 1.93 - 1.78 \ (m, 1H), \ 1.77 - 1.58 \ (m, 2H), \ 1.49 - 1.34 \ (m, 1H). \\
\text{13C NMR (76 MHz, CHLOROFORM-D)} & \ \delta \ 212.5 \ (s), \ 161.4 \ (d, J = 244.5 Hz), \ 131.9 \ (d, J = 5.0 Hz), \ 127.9 \ (d, J = 8.2 Hz), \ 127.3 \ (d, J = 15.8 Hz), \ 124.0, \ 115.3 \ (d, J = 22.2 Hz), \ 51.2, \ 42.3, \ 33.6 \\
& \ 28.2, \ 25.2. \ IR \ (neat, \ \nu_{C=O}) \ 1709 \text{cm}^{-1}, \ EI-MS: \ 206 \ (M^+). \ HRMS (ESI, m/z) \ \text{calcd for } C_{14}H_{15}FO \ [M+Na]^+: \ 229.0999, \ \text{found: 229.0996.}
\end{align*}
\]

2-(2-bromobenzyl)cyclohexanone (4al): colorless liquid; yield: 56%

\[
\begin{align*}
\text{1H NMR (400 MHz, CHLOROFORM-D)} & \ \delta \ 7.45 \ (d, J = 8.0 Hz, 1H), \ 7.22 - 7.09 \ (m, 2H), \ 6.98 \ (m, 1H), \ 3.28 \ (dd, J = 13.8, 5.2 Hz, 1H), \ 2.68 - 2.59 \ (m, 1H), \ 2.49 \\
& \ (dd, J = 13.8, 8.1 Hz, 1H), \ 2.36 \ (dd, J = 13.6, 3.5 Hz, 1H), \ 2.27 \ (td, J = 12.9, 5.8 Hz, 1H), \ 1.83 - 1.71 \ (m, 1H), \ 1.68 - 1.51 \ (m, 2H), \ 1.45 - 1.31 \ (m, 1H). \\
\text{13C NMR (101 MHz, CHLOROFORM-D)} & \ \delta \ 212.3, \ 139.9, \ 132.9, \ 127.9, \ 124.9, \ 50.7 \ 42.4, \ 35.9, \ 33.9, \ 28.3, \ 25.4. \ IR \ (neat, \ \nu_{C=O}) \ 1711 \text{cm}^{-1}, \ EI-MS: \ 266 \ (M^+). \ HRMS (ESI, m/z) \ \text{calcd for } C_{14}H_{15}BrO \ [M+Na]^+: \ 289.0198, \ \text{found: 289.0194.}
\end{align*}
\]

methyl 4-((2-oxocyclohexyl)methyl)benzoate (4ag): colorless liquid; yield: 81%

\[
\begin{align*}
\text{1H NMR (301 MHz, CHLOROFORM-D)} & \ \delta \ 7.94 \ (d, J = 8.2 \text{ Hz, } 2H), \ 7.23 \ (d, J = 8.1 \text{ Hz, } 2H), \ 3.90 \ (s, 3H), \ 3.27 \ (dd, J = 13.4, 4.5 Hz, 1H), \\
& \ 2.95 - 2.68 \ (m, 1H), \ 2.58 - 2.32 \ (m, 3H), \ 2.14 - 1.95 \ (m, 2H), \ 1.84 \ (d, J = 9.7 \text{ Hz, } 1H), \ 1.73 - 1.51 \ (m, 1H). \\
\text{13C NMR (76 MHz, CHLOROFORM-D)} & \ \delta \ 212.1, \ 167.2, \ 146.2, \ 129.8, \ 129.3, \ 128.1, \ 52.3, \ 52.2, \ 42.3, \ 35.7, \ 33.7, \ 28.1, \ 25.3. \ IR \ (neat, \ \nu_{C=O}) \ 1709, \ 1722 \text{ cm}^{-1}, \ EI-MS: \ 246 \ (M^+). \ HRMS (ESI, m/z) \ \text{calcd for } C_{15}H_{18}O_3 \ [M+Na]^+: \ 269.1148, \ \text{found: 269.1150.}
\end{align*}
\]

2-(4-methoxybenzyl)cyclohexanone (4ai): colorless liquid; yield: 76%

\[
\begin{align*}
\text{1H NMR (400 MHz, CHLOROFORM-D)} & \ \delta \ 7.07 \ (d, J = 8.3 \text{ Hz, } 2H), \ 6.82 \ (d, J = 8.3 \text{ Hz, } 2H), \ 3.78 \ (s, 3H), \ 3.16 \ (dd, J = 13.9, 4.3 \text{ Hz, } 1H), \ 2.38 \ (dd, J = 19.3, 18.9, 5.4 \text{ Hz, } 4H), \\
& \ 2.04 \ (s, 2H), \ 1.83 \ (d, J = 13.1 \text{ Hz, } 1H), \ 1.75 - 1.56 \ (m, 2H), \ 1.41 - 1.32 \ (m, 1H). \\
\text{13C NMR (101 MHz, CHLOROFORM-D)} & \ \delta \ 212.9, \ 158.0, \ 132.5, \ 130.2, \ 113.8, \ 55.4, \ 52.8, \ 42.3, \ 34.7, \ 33.5, \ 28.2, \ 25.2. \ IR \ (neat, \ \nu_{C=O}) \ 1709, \ 1722 \text{ cm}^{-1}, \ EI-MS: \ 218 \ (M^+). \ HRMS (ESI, m/z) \ \text{calcd for } C_{14}H_{18}O_2 \ [M+H]^+: \ 241.1199, \ \text{found: 241.1193.}
\end{align*}
\]

2-(4-(tert-butyl)benzyl)cyclohexanone (4af): colorless liquid; yield: 67%

\[
\begin{align*}
\text{1H NMR (400 MHz, CHLOROFORM-D)} & \ \delta \ 7.29 \ (d, J = 8.2 \text{ Hz, } 3H), \ 7.28 \ (s, 2H), \ 7.08 \ (d, J = 8.1 \text{ Hz, } 2H), \ 7.08 \ (d, J = 8.1 \text{ Hz, } 2H), \ 3.20 \ (dd, J = 14.0, 4.7 \text{ Hz, } 1H), \ 3.20 \ (dd, J = 14.0, 4.7 \text{ Hz, } 1H), \ 2.53 \ (dd, J = 7.7, 4.4}
\end{align*}
\]
Hz, 1H), 2.53 (dd, J = 7.7, 4.4 Hz, 1H), 2.38 (m, 3H), 2.38 (m, 3H), 2.21 – 1.94 (m, 2H), 2.13 – 2.01 (m, 2H), 1.94 – 1.75 (m, 1H), 1.87 – 1.77 (m, 1H), 1.75 – 1.53 (m, 2H), 1.73 – 1.55 (m, 2H), 1.43 – 1.34 (m, 2H), 1.30 (s, 9H). 13C NMR (101 MHz, CHLOROFORM-D) δ 212.9, 148.9, 137.4, 128.9, 125.3, 52.6, 42.3, 35.0, 34.5, 33.6, 31.5, 28.2, 25.2. IR (neat, νC=O) 1709 cm⁻¹, EI-MS: 244 (M⁺). HRMS (ESI, m/z) calcd for C₁₇H₂₄O [M+H]⁺: 245.1900, found: 245.1900.

GC-MS spectra of the extracted reaction mixture: red arrow indicated the peak of the aimed product in form of oxime without hydrolysis.

4-(4-bromophenyl)-3-methylbutan-2-one (4bd): colorless liquid; yield: 80%

1H NMR (400 MHz, CHLOROFORM-D) δ 7.38 (d, J = 8.3 Hz, 2H), 7.01 (d, J = 8.3 Hz, 2H), 2.94 (dd, J = 13.6, 7.0 Hz, 1H), 2.78 (dd, J = 14.2, 7.1 Hz, 1H), 2.50 (dd, J = 13.6, 7.4 Hz, 1H), 2.08 (s, 3H), 1.07 (d, J = 7.0 Hz, 3H). 13C NMR (101 MHz, CHLOROFORM-D) δ 211.8, 138.8, 131.6, 130.8, 120.2, 48.8, 38.3 29.0, 16.5. IR (neat, νC=O) 1712 cm⁻¹, EI-MS: 240 (M⁺). HRMS (ESI, m/z) calcd for C₁₁H₁₃BrO[M+Na]⁺: 263.0072, found: 263.0074.

GC-MS spectra of the extracted reaction mixture: red arrow indicated the peak of the aimed product in form of oxime without hydrolysis.

1-(4-bromophenyl)pentan-3-one(4cd): colorless liquid; yield: 75%

1H NMR (400 MHz, CHLOROFORM-D) δ 7.38 (d, J = 8.3 Hz, 2H), 7.05 (d, J = 8.2 Hz, 2H), 2.85 (t, J = 7.5 Hz, 2H), 2.70 (t, J = 7.4 Hz, 2H), 2.40 (q, J = 7.3 Hz, 2H), 1.04 (t, J = 7.3 Hz, 3H). 13C NMR (101 MHz, CHLOROFORM-D) δ 210.3, 140.3, 131.6, 130.3, 120.0, 43.7, 36.3, 29.3, 7.9. IR (neat, νC=O) 1712 cm⁻¹, EI-MS: 240 (M⁺). HRMS (ESI, m/z) calcd for C₁₁H₁₃BrO[M+Na]⁺: 263.0042, found: 263.0041.

GC-MS spectra of the extracted reaction mixture: red arrow indicated the peak of the aimed product in form of oxime without hydrolysis.
4-(4-bromophenyl)-3,3-dimethylbutan-2-one (4dd): colorless liquid; yield: 83%

$^1$H NMR (400 MHz, CHLOROFORM-D) $\delta$ 7.36 (d, $J = 8.2$ Hz, 2H), 6.95 (d, $J = 8.3$ Hz, 2H), 2.75 (s, 2H), 2.10 (s, 3H), 1.10 (s, 6H).$^{13}$C NMR (101 MHz, CHLOROFORM-D) $\delta$ 213.6, 137.0, 132.1, 131.3, 120.5, 48.6, 44.6, 26.2, 24.5. IR (neat, $\nu_{C=O}$) 1705 cm$^{-1}$, EI-MS: 254 (M$^+$$)$. HRMS (ESI, m/z) calcd for C$_{12}$H$_{15}$BrO [M+Na]$^+$: 277.0193 , found: 277.0190.

GC-MS spectra of the extracted reaction mixture: red arrow indicated the peak of the aimed product in form of oxime without hydrolysis.

3-(4-bromophenyl)-2,2-dimethylpropanal (4ed): colorless liquid; yield: 65%

$^1$H NMR (400 MHz, CHLOROFORM-D) $\delta$ 9.56 (s, 1H), 7.39 (d, $J = 8.2$ Hz, 2H), 6.97 (d, $J = 8.3$ Hz, 2H), 2.73 (s, 2H), 1.04 (s, 6H).$^{13}$C NMR (101 MHz, CHLOROFORM-D) $\delta$ 205.7 136.1 132.1 131.4, 120.7, 47.0, 42.5 21.5. IR (neat, $\nu_{C=O}$) 1736 cm$^{-1}$. EI-MS: 240 (M$^+$). HRMS (ESI, m/z) calcd for C$_{11}$H$_{13}$BrO [M+Na]$^+$: 263.0042 , found: 263.0044.

GC-MS spectra of the extracted reaction mixture: red arrow indicated the peak of the aimed product in form of oxime without hydrolysis

1-(4-bromophenyl)-2,4-dimethylpentan-3-one (4fd): colorless liquid: 85%

$^1$H NMR (301 MHz, CHLOROFORM-D) $\delta$ 7.37 (d, $J = 8.3$ Hz, 2H), 7.00 (d, $J = 8.3$ Hz, 2H), 3.05 – 2.83 (m, 2H), 2.64 – 2.42 (m, 2H), 1.07 (d, $J = 6.6$ Hz, 3H), 1.01 (d, $J = 6.9$ Hz, 3H), 0.87 (d, $J = 6.9$ Hz, 3H).$^{13}$C NMR (76 MHz, CHLOROFORM-D) $\delta$ 217.5, 139.2, 131.5, 130.9, 120.1, 46.5, 40.43 (s), 38.9, 18.1, 18.0, 17.4. IR (neat, $\nu_{C=O}$) 1709 cm$^{-1}$, EI-MS: 268 (M$^+$), HRMS (ESI, m/z) calcd for C$_{12}$H$_{17}$BrO [M+Na]$^+$: 291.0355 , found: 291.0343.

GC-MS spectra of the extracted reaction mixture: red arrow indicated the peak of the aimed product in form of oxime without hydrolysis.
1-(2-(4-bromophenyl)cyclohexyl)ethanone (4gd): colorless liquid; yield: 42%

$^1$H NMR (400 MHz, CHLOROFORM-D) $\delta$ 7.38 (d, $J = 8.3$ Hz, 2H), 7.05 (d, $J = 8.3$ Hz, 2H), 2.84 – 2.64 (m, 2H), 1.99 – 1.85 (m, 4H), 1.84 (s, 3H), 1.48 – 1.35 (m, 4H). $^{13}$C NMR (101 MHz, CHLOROFORM-D) $\delta$ 211.8, 144.1, 131.7, 129.2, 120.2, 57.3, 45.7, 34.4, 30.1, 29.7, 26.3, 25.6. IR (neat, $\nu_{C=O}$) 1706 cm$^{-1}$, EI-MS: 280 (M$^+$. HRMS (ESI, m/z) calcld for C$_{14}$H$_{17}$BrO [M+Na$^+$]: 303.0355, found: 303.0352.

1-(4'-bromo-[1,1'-biphenyl]-2-yl)propan-1-one (4od): colorless liquid; yield: 64%

$^1$H NMR (400 MHz, CHLOROFORM-D) $\delta$ 7.55 (d, $J = 8.3$ Hz, 2H), 7.49 (d, $J = 9.0$ Hz, 2H), 7.43 (d, $J = 8.1$ Hz, 1H), 7.35 (d, $J = 6.9$ Hz, 1H), 7.19 (d, $J = 8.4$ Hz, 2H), 2.35 (qd, $J = 7.2$, 2.5 Hz, 2H), 0.94 (tt, $J = 17.4$, 8.7 Hz, 3H). $^{13}$C NMR (101 MHz, CHLOROFORM-D) $\delta$ 208.2, 140.9, 139.8, 138.9, 131.9, 130.7, 130.2, 130.0, 128.0, 127.9, 122.3, 36.3, 8.7. IR (neat, $\nu_{C=O}$) 1706 cm$^{-1}$, EI-MS: 288 (M$^+$). HRMS (ESI, m/z) calcld for C$_{15}$H$_{13}$BrO [M+Na$^+$]: 311.0042, found: 303.0039, 313.0013

GC-MS spectra of the extracted reaction mixture: red arrow indicated the peak of the aimed product in form of oxime without hydrolysis.

ethyl 1-(4-bromobenzyl)-2-oxocyclohexanecarboxylate (4nd): colorless solid; yield: 80%, m.p. 65°C

$^1$H NMR (400 MHz, CHLOROFORM-D) $\delta$ 7.35 (d, $J = 7.6$ Hz, 2H), 7.01 (d, $J = 7.8$ Hz, 2H), 4.17 – 4.01 (m, 2H), 3.23 (d, $J = 13.8$ Hz, 1H), 2.82 (d, $J = 13.8$ Hz, 1H), 2.44 (qd, $J = 13.1$, 6.1 Hz, 3H), 2.02 (dd, $J = 6.5$, 3.8 Hz, 1H), 1.80 – 1.59 (m, 3H), 1.43 (td, $J = 12.7$, 4.5 Hz, 1H), 1.17 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (101 MHz, CHLOROFORM-D) $\delta$ 207.3, 171.1, 135.8, 132.3, 131.2, 120.8, 62.2, 61.5, 41.4, 40.0, 36.3, 27.7, 22.7, 14.1. IR (neat, $\nu_{C=O}$) 1709 cm$^{-1}$, 1722 cm$^{-1}$, EI-MS: 288 (M$^+$). HRMS (ESI, m/z) calcld for C$_{16}$H$_{19}$BrO$_3$ [M+Na$^+$]: 361.0410, found: 361.0407, 363.0380

GC-MS spectra of the extracted reaction mixture: red arrow indicated the peak of the aimed product in form of oxime without hydrolysis.

$^1$H NMR (301 MHz, CHLOROFORM-D) $\delta$ 7.45 – 7.33 (m, 2H), 7.03 (d, $J = 8.3$ Hz, 2H), 3.19 (dd, $J = 14.0$, 5.0 Hz, 1H), 2.59 (td, $J = 13.0$, 5.5 Hz, 1H), 2.11 (dd, $J = 14.0$, 3.6 Hz, 1H), 1.97 (dd, $J = 13.0$, 5.8 Hz, 1H), 1.88 – 1.65 (m, 4H), 1.59 – 1.41 (m, 6H), 1.39 – 1.25 (m, 7H), 1.20 (s, 3H), 1.11 – 1.03 (m, 1H), 1.00 (s, 3H), 0.90 (t, $J = 5.4$ Hz, 1H), 0.82 (d, $J = 9.9$ Hz, 3H), 0.74 – 0.61 (m, 1H). $^{13}$C NMR (76 MHz, CHLOROFORM-D) $\delta$ 211.7, 139.6, 131.5, 131.0, 119.8, 81.8, 54.0, 50.6, 48.4, 48.2, 46.0, 45.7, 45.1, 39.1, 36.6, 36.2, 34.9, 31.6, 31.7, 28.7, 26.0, 23.4, 21.3, 14.1, 12.6. IR (neat, νC=O) 1711 cm$^{-1}$.

HRMS (ESI, m/z) calcd for C$_{27}$H$_{37}$BrO$_2$ [M+Na]$^+$: 497.1853, found: 497.1851. [$\alpha$]$_{D}^{23}$-24.7° (1, DCM)
V. Experimental Procedure of hydrogenation

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\text{(E)-2-benzylcyclohexanone O-methyl oxime, 3aa (108.3 mg, 0.5 mmol) in acetic acid (5 mL) was hydrogenated over platinum(IV) oxide (11.3 mg, 0.05 mmol) under hydrogen pressure (5 bar) for 24h. Then, the mixture filtered through celite and washed between dichloromethane and aqueous Na}_2\text{CO}_3\text{ solution. The organic layer was concentrated purified on silica gel (petroleum ether/ethyl acetate 100/1) to give provide 3aa-H (78.8 mg, 0.36 mmol, 72%) as a colorless liquid.}
\]

\[
\text{N-(2-benzylcyclohexyl)-O-methylhydroxylamine (3aa-H): colorless liquid; Yield: 72%}
\]

\[
\begin{align*}
\text{\text{MeO}N} & \quad \text{H}_2, \text{PtO}_2 \quad \text{AoOH} \\
\text{3aa} & \quad \text{MeO}NH \\
\text{3aa-H: 72%}
\end{align*}
\]

\[
\begin{align*}
\text{1H NMR (400 MHz, CHLOROFORM-D) } & \delta 7.29 – 7.24 (m, 2H), 7.21 – 7.15 (m, 3H), 3.56 (s, 3H), 3.10 (dt, J = 7.1, 3.4 Hz, 1H), 2.79 (dd, J = 13.5, 5.5 Hz, 1H), 2.49 (dd, J = 13.4, 9.9 Hz, 1H), 2.08 – 1.93 (m, 1H), 1.74 – 1.64 (m, 2H), 1.62 – 1.57 (m, 1H), 1.44 – 1.23 (m, 6H). \\
\text{13C NMR (101 MHz, CHLOROFORM-D) } & \delta 141.6, 129.2, 128.3, 125.8, 62.2, 59.5, 40.3, 35.7, 27.1, 23.5, 22.6. \\
\text{IR (neat, } \nu_{\text{N-H}}, \nu_{\text{C-N}} \text{) } & 2928, 1452 \text{ cm}^{-1}. \\
\text{EI-MS: } & 219 (M^+) \text{, HRMS (ESI, m/z) calcd for C}_{14}\text{H}_{21}\text{NO }[\text{M+H}^+]^*: 220.1695, \text{ found: 220.1690.}
\end{align*}
\]
VI. Palladium Complex\textsuperscript{[7]}

A schlenk tube was charged with Pd(OAc)$_2$ (157 mg, 0.7 mmol) and a solution of (E)-3,3-dimethylbutan-2-one O-methyl oxime (64.5 mg, 0.5 mmol) in dichloroethane (1.5 mL) and HFIP (0.5 mL). The tube was sealed and stirred at 85°C for 4 h. After this time the reaction mixture was cooled to room temperature and treated with triphenylphosphine (466 mg, 0.7 mmol). The tube was sealed 80 °C for another 2 hours. After this time the reaction mixture was cooled to room temperature and filtered through a thin pad of Celite, eluting with ethyl acetate (30 mL) and CH$_2$Cl$_2$ (10 mL) and the filtrate was concentrated under reduced pressure. The residue was then re-dissolved in CH$_2$Cl$_2$ (20 mL), washed with brine (2 x 20 mL) and dried over Mg$_2$SO$_4$ and concentrated under vacuum. The crude reaction mixture was purified by flash column chromatography (silica gel, gradient elution: 0% acetone in CH$_2$Cl$_2$ to 2.5% acetone in CH$_2$Cl$_2$) to provide the complex as a colorless solid (236 mg, 89%). Crystals were grown by vial-in-vial diffusion of ether into dichloromethane solution of the title complex.

NMR: $^1$H NMR (400 MHz, CHLOROFORM-D) $\delta$ 7.78 – 7.67 (m, 6H), 7.47 – 7.34 (m, 9H), 4.15 (s, 3H), 1.95 (s, 3H), 1.51 (d, $J = 3.8$ Hz, 2H), 1.06 (s, 6H).$^{13}$C NMR (101 MHz, CHLOROFORM-D) $\delta$ 183.4, 134.7, 134.6, 131.8, 131.3, 130.3 128.3, 128.2, 62.8, 48.8, 46.1, 29.1, 27.0, 12.7
X-ray crystal structure analysis of compound 6: Single crystals suitable for X-ray analysis were obtained by slow evaporation of its solution in hexane. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 1048079. Formula: C_{15}H_{29}ClNOPd, $M = 532.31$, colourless crystal, 0.33 x 0.21 x 0.11 mm, $a = 16.151(3)$, $b = 9.5824(19)$, $c = 16.403(3)$ Å, $\alpha = 90.00$, $\beta = 111.38(3)$, $\gamma = 90.00$, $V = 2363.9(8)$ Å$^3$, $\rho_{\text{calc}} = 1.496$ g cm$^{-3}$, $\mu = 0.982$ mm$^{-1}$, $Z = 4$, Monoclinic, space group P2(1)/n, $\lambda = 0.71073$ Å, $T = 173(2)$ K. Data completeness = 0.985, Theta (max) = 25.00
VII. Discussions on Negative Results

1. Application of diaryliodonium salts bearing heteroaromatic rings

![Diagrams of diaryliodonium salts](images)

When 2m was employed to react with 1a, the transformation of phenyl group was observed to generate 3aa. As to 2n, it is noted in the manuscript that asymmetric diaryliodonium salts Ar-I’-MesX’ are not applicable in this reaction. And for 2o and 2p, no desired products were obtained probably due to the coordination of pyridine group with palladium catalysts.

2. Examination of aromatic oxime ether under the standard condition

![Chemical reaction](images)

3. Results of the methylene C-H bond activation.

![Oximes](images)

Listed above are the oximes we examined under the optimized condition of this method with diaryliodonium salts 2d. 1q-1s were not able be arylated while the arylated product of 1t was observed with trace amounts in GC/MS. The scope of substrates is somehow limited for arylation on methylene C-H bond and it likely depends on the angle between the directing groups and aimed activated bonds. 1g and 1h can be arylated in only moderate yields since the conversion rate of starting materials were comparably low. We failed to further increase the yield by adding legands, additives, etc., while it helped a little by using more diaryliodonium salts as well as higher reacting temperature.
VIII. Copies of $^1$H and $^{13}$C NMR spectra

$^1$H NMR and $^{13}$C NMR spectra of compound 1j
\(^1\)H NMR and \(^{13}\)C NMR spectra of compound 1i
$^1$H NMR and $^{13}$C NMR spectra of compound 1m
$^1$H NMR and $^{13}$C NMR spectra of compound 1k
$^1$H NMR and $^{13}$C NMR spectra of compound 11'
$^{1}$H NMR and $^{13}$C NMR spectra of compound 11
$^{1}H$ NMR and $^{13}C$ NMR spectra of compound 3aa
$^1$H NMR and $^{13}$C NMR spectra of compound 3ad
$^1$H NMR and $^{13}$C NMR spectra of compound $3\text{ah}$
$^{1}H$ NMR and $^{13}C$ NMR spectra of compound 3aj
$^1$H NMR and $^{13}$C NMR spectra of compound 3ak
$^1$H NMR and $^{13}$C NMR spectra of compound $3ag$
$^1$H NMR and $^{13}$C NMR spectra of compound 3ai
\(^1\text{H NMR and }^{13}\text{C NMR spectra of compound }3\text{ig}\)
$^1$H NMR and $^{13}$C NMR spectra of compound 3jg
$^1$H NMR and $^{13}$C NMR spectra of compound 3hg
$^1$H NMR and $^{13}$C NMR spectra of compound 3kg
$^1$H NMR and $^{13}$C NMR spectra of compound 3jg
$^1$H NMR and $^{13}$C NMR spectra of compound 4ab
$^1$H NMR and $^{13}$C NMR spectra of compound 4ac
$^1$H NMR and $^{13}$C NMR spectra of compound 4ad
$^1$H NMR and $^{13}$C NMR spectra of compound 4ae
$^1$H NMR and $^{13}$C NMR spectra of compound 4af
$^1$H NMR and $^{13}$C NMR spectra of compound 4ag
$^1$H NMR and $^{13}$C NMR spectra of compound 4ah
$^1$H NMR and $^{13}$C NMR spectra of compound 4ai
$^1$H NMR and $^{13}$C NMR spectra of compound 4aj
$^1$H NMR and $^{13}$C NMR spectra of compound 4ak
$^1$H NMR and $^{13}$C NMR spectra of compound 4al
$^1$H NMR and $^{13}$C NMR spectra of compound 4bd
$^1$H NMR and $^{13}$C NMR spectra of compound 4cd
$^1$H NMR and $^{13}$C NMR spectra of compound 4dd
$^1$H NMR and $^{13}$C NMR spectra of compound 4ed
$^1$H NMR and $^{13}$C NMR spectra of compound 4fd
$^{1}H$ NMR and $^{13}C$ NMR spectra of compound 4gd
$^1$H NMR and $^{13}$C NMR spectra of compound 4od
$^1$H NMR and $^{13}$C NMR spectra of compound 4nd
$^1$H NMR and $^{13}$C NMR spectra of compound 4md
$^1$H NMR and $^{13}$C NMR spectra of compound 6
$^1$H NMR and $^{13}$C NMR spectra of compound 3aa-H
IX. References


