Construction of a quaternary carbon at the carbonyl carbon of the cyclohexane ring

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<sup>a</sup> isomer: The corresponding regioisomer. <sup>b</sup> 100:0: The isomer was not seen in the expanded 1<sup>H</sup> NMR spectroscopy. <sup>c</sup> nd: Not determined. <sup>d</sup> The ratio of 5h : 6h : alcohol : 4B = 0.29:61:10. A mixture of 5r and the regioisomer 6r were obtained only in <10% yield.
General

Infrared (IR) spectra are reported in wave numbers (cm\(^{-1}\)). The \(^1\)H NMR (300 MHz) and \(^{13}\)C NMR (75 MHz) spectra were measured in CDCl\(_3\), using SiMe\(_4\) (δ = 0 ppm) and the center line of CDCl\(_3\) triplet (δ = 77.1 ppm) as internal standards, respectively. Signal patterns are indicated as br s, broad singlet; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants (J) are given in hertz (Hz). Chemical shifts of carbons accompany plus (for CH and CH\(_3\)) and minus (for C and CH\(_2\)) signs of APT experiments. After the reactions, organic extracts were concentrated by using a rotary evaporator and the residues were purified by chromatography on silica gel (Kanto, silica gel 60N).

Synthesis of Picolinates

2-(4-tert-Butylcyclohexylidene)ethyl Picolinate (4A)

![Chemical Structure]

To a suspension of LiCl (593 mg, 14.0 mmol) in MeCN (10 mL) were added DBU (1.80 mL, 12.0 mmol) and triethyl phosphonoacetate (2.60 mL, 13.0 mmol) at 0 °C. The mixture was stirred at 0 °C for 30 min, and ketone 3A (1.54 g, 9.98 mmol) was added. The reaction was carried out at room temperature overnight and quenched by addition of saturated NaHCO\(_3\). The mixture was extracted with EtOAc three times. The combined extracts were washed with brine, dried over MgSO\(_4\) and concentrated. The residue was purified by chromatography on silica gel (hexane/EtOAc) to afford the corresponding ester (2.22 g, 99%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 0.86 (s, 9 H), 1.28 (t, J = 7 Hz, 3 H), 1.10–1.33 (m, 3 H), 1.76–1.99 (m, 3 H), 2.16 (dt, J = 3, 14 Hz, 1 H), 2.31 (dm, J = 14 Hz, 1 H), 3.87 (dm, J = 14 Hz, 1 H), 4.14 (q, J = 7 Hz, 2 H), 5.60 (s, 1 H). The spectrum was identical with the data reported.¹

To a solution of the above ester (765 mg, 3.64 mmol) in THF (7 mL) was added DIBAL (7.80 mL, 1.03 M in hexane, 8.03 mmol) dropwise at −78 °C. After 1 h at −78 °C, the reaction was quenched by addition of water. The cooling bath was removed, and 1 N HCl was added. The mixture was extracted with EtOAc three times. The combined extracts were washed with saturated NaHCO\(_3\) and brine successively, dried over Na\(_2\)SO\(_4\) and concentrated to afford the corresponding alcohol (616 mg), which was used for the next reaction without further purification: \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 0.85 (s, 9 H), 0.82–1.26 (m, 4 H), 1.75 (tm, J = 14 Hz, 1 H), 1.80–1.94 (m, 2 H), 2.02 (tm, J = 13 Hz, 1 H), 2.26 (tq, J = 14, 3 Hz, 1 H), 2.69 (tq, J = 14, 3 Hz, 1 H), 4.09–4.20 (m, 1 H), 5.36 (t, J = 7 Hz, 1 H). The spectrum was identical with that reported.²
To an ice-cold solution of the above alcohol in CH₂Cl₂ (11 mL) were added picolinic acid (538 mg, 4.37 mmol), DMAP (133 mg, 1.09 mmol) and DCC (976 mg, 4.73 mmol). The mixture was stirred at room temperature for 1 h, diluted with ether, and filtered through a pad of Celite. The filtrate was concentrated to afford a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to furnish picolinate 4A (958 mg, 92% from the ester): mp. 55–56 °C; IR (nujol) 1730, 1302, 1135 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.85 (s, 9 H), 0.78–1.29 (m, 3 H), 1.74–1.96 (m, 3 H), 2.06 (tm, J = 13 Hz, 1 H), 2.25 (dm, J = 13 Hz, 1 H), 2.82 (dm, J = 14 Hz, 1 H), 4.95 (d, J = 7 Hz, 2 H), 5.46 (t, J = 7 Hz, 1 H), 7.47 (ddd, J = 8, 5, 1 Hz, 1 H), 7.84 (ddd, J = 8, 8, 2 Hz, 1 H), 8.15 (ddd, J = 8, 1, 1 Hz, 1 H), 8.77 (dm, J = 5 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 27.5 (+), 28.2 (−), 28.7 (−), 28.8 (−), 32.4 (−), 36.8 (−), 48.1 (+), 62.2 (−), 114.6 (+), 125.0 (+), 126.7 (+), 136.9 (+), 147.0 (−), 148.3 (−), 149.8 (+), 165.2 (−); HRMS (FAB) calcd for C₁₈H₂₆NO₂ [(M+H)⁺] 288.1964, found 288.1958.

2-(4-Phenylcyclohexylidene)ethyl Picolinate (4B)

To an ice-cold suspension of LiCl (342 mg, 8.07 mmol) in MeCN (6 mL) were added DBU (1.0 mL, 6.70 mmol) and triethyl phosphonoacetate (1.5 mL, 7.49 mmol). The mixture was stirred 0 °C for 30 min, and a solution of ketone 3B (987 mg, 5.67 mmol) was added dropwise. The reaction was carried out at 0 °C for 3 h and quenched by addition of saturated NH₄Cl. The resulting mixture was extracted with EtOAc three times. The combined extracts were dried over MgSO₄ and concentrated to give a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to afford the corresponding ester (1.37 g, 97%): ¹H NMR (300 MHz, CDCl₃) δ 1.29 (t, J = 7 Hz, 3 H), 1.55–1.72 (m, 2 H), 1.96–2.12 (m, 3 H), 2.27–2.42 (m, 2 H), 2.78 (tt, J = 12, 3.5 Hz, 1 H), 3.93–4.02 (m, 1 H), 4.16 (q, J = 7 Hz, 2 H), 5.68 (s, 1 H), 7.15–7.34 (m, 5 H); ¹³C NMR (75 MHz, CDCl₃) δ 14.4 (+), 29.4 (−), 34.8 (−), 35.6 (−), 37.7 (−), 44.1 (+), 59.6 (−), 113.8 (+), 126.2 (+), 126.8 (+), 128.5 (+), 146.0 (−), 161.9 (−), 166.8 (−). The spectra were identical with those reported.³

To a solution of the above ester (632 mg, 2.58 mmol) in THF (5 mL) was added DIBAL (5.5 mL, 1.03 M in hexane, 5.69 mmol) dropwise at −78 °C. After 1 h at −78 °C, the reaction was quenched by addition of water. The cooling bath was removed, and 1 N HCl was added. The resulting mixture was extracted with EtOAc three times. The combined extracts were washed with saturated NaHCO₃ and brine successively, dried over Na₂SO₄ and concentrated to give a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to afford the corresponding allylic alcohol (466 mg, 89%): IR (neat) 3331, 1493, 987, 699 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.39–1.65 (m, 3 H), 1.88–2.07 (m, 3 H), 2.16–2.41 (m, 2 H), 2.65–2.84 (m, 2 H), 4.18 (d, J = 7 Hz, 2 H), 5.45 (t, J = 7
Hz, 1 H), 7.15–7.33 (m, 5 H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 28.6 (–), 35.0 (–), 35.6 (–), 36.8 (–), 44.6 (+), 58.7 (–), 121.1 (+), 126.1 (+), 126.9 (+), 128.4 (+), 143.0 (–), 146.7 (–).

To an ice-cold solution of the above alcohol (439 mg, 2.17 mmol) in CH$_2$Cl$_2$ (11 mL) were added picolinic acid (321 mg, 2.61 mmol), DMAP (79.7 mg, 0.65 mmol) and DCC (583 mg, 2.82 mmol). The mixture was stirred at room temperature for 2 h, diluted with Et$_2$O and filtered through a pad of Celite. The filtrate was concentrated to afford a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to furnish picolinate 4B (661 mg, 99%): IR (neat) 1718, 1301, 1127, 700 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.92 (m, 5 H), 2.02 (m, 3 H), 2.47 (m, 3 H), 3.54 (dt, $J$ = 7.5 Hz, 1 H), 7.16–7.33 (m, 5 H), 7.44 (ddd, $J$ = 8, 5, 1 Hz, 1 H), 7.86 (ddd, $J$ = 8, 8, 2 Hz, 1 H), 8.17 (ddd, $J$ = 8, 1, 1 Hz, 1 H), 8.78 (ddd, $J$ = 5, 2, 1 Hz, 1 H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 28.8 (–), 34.8 (–), 35.3 (–), 36.7 (–), 44.4 (+), 62.2 (–), 115.8 (+), 125.2 (+), 126.1 (+), 126.81 (+), 126.85 (+), 128.4 (+), 137.0 (+), 145.8 (–), 146.5 (–), 148.3 (–), 149.9 (+), 165.2 (–); HRMS (FAB) calcd for C$_{20}$H$_{22}$NO$_2$ [(M+H)$^+$] 308.1651, found 308.1651.

(E)- and (Z)-2-(2-Methylcyclohexylidene)ethyl Picolinate (4C)

To a suspension of LiCl (297 mg, 7.01 mmol) in MeCN (5 mL) were added DBU (0.90 mL, 6.03 mmol) and triethyl phosphonoacetate (1.30 mL, 6.49 mmol) at 0 °C. The mixture was stirred at 0 °C for 30 min, and ketone 3C (0.60 mL, 4.97 mmol) was added. The reaction was carried out at room temperature overnight and quenched by addition of saturated NaHCO$_3$. The resulting mixture was extracted with EtOAc three times. The combined extracts were washed with brine, dried over MgSO$_4$ and concentrated to give a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to afford the corresponding ester (647 mg, 71%) as a 4:1 mixture of the E/Z stereoisomers by $^1$H NMR spectroscopy. The (E)-isomer: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.07 (d, $J$ = 7 Hz, 3 H), 1.29 (t, $J$ = 7 Hz, 3 H), 1.01–1.92 (m, 5 H), 2.02–2.47 (m, 3 H), 3.54 (dt, $J$ = 13, 5 Hz, 1 H), 4.15 (q, $J$ = 7 Hz, 2 H), 5.58 (s, 1 H). The (Z)-isomer: $^1$H NMR $\delta$ 4.14 (q, $J$ = 7 Hz, 2 H), 5.55 (d, $J$ = 2 Hz, 1 H).

To a solution of the above ester (647 mg, 3.55 mmol) in THF (7 mL) was added DIBAL (7.60 mL, 1.03 M in hexane, 7.83 mmol) dropwise at −78 °C. After 1 h at −78 °C, the reaction was quenched by addition of water. The cooling bath was removed, and 1 N HCl was added. The mixture was extracted with EtOAc three times. The combined extracts were washed with saturated NaHCO$_3$ and brine successively, dried over Na$_2$SO$_4$ and concentrated to afford the corresponding alcohol as a 4:1 mixture of the E/Z stereoisomers by $^1$H NMR spectroscopy. The mixture was used
for the next reaction without further purification. The (E)-isomer: $^1$H NMR (300 MHz, CDCl$_3$) δ 1.08 (d, $J = 7$ Hz, 3 H), 0.92–2.18 (m, 8 H), 2.54 (dm, $J = 14$ Hz, 1 H), 4.14–4.23 (m, 1 H), 5.34 (t, $J = 7$ Hz, 1 H). The (Z)-isomer: $^1$H NMR δ 2.84–2.96 (m, 1 H). The signals for the isomers were identical with those reported.$^2$

To an ice-cold solution of the above alcohol in CH$_2$Cl$_2$ (14 mL) were added picolinic acid (524 mg, 4.26 mmol), DMAP (130 mg, 1.06 mmol) and DCC (952 mg, 4.62 mmol). The mixture was stirred at room temperature for 1 h, diluted with ether and filtered through a pad of Celite. The filtrate was concentrated to afford a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to furnish picolinate 4C (756 mg, 87% from the ester) as a 4:1 mixture of the E/Z stereoisomers by $^1$H NMR spectroscopy. The (E)-isomer: IR (neat) 1739, 1717, 1307, 1289 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 1.07 (d, $J = 7$ Hz, 3 H), 0.80–2.20 (m, 8 H), 2.58–2.70 (m, 1 H), 4.91–5.07 (m, 2 H), 5.43 (t, $J = 7$ Hz, 1 H), 7.48 (ddd, $J = 8, 5, 1.5$ Hz, 1 H), 7.84 (ddm, $J = 8, 8$ Hz, 1 H), 8.07 (d, $J = 8$ Hz, 1 H), 8.76 (dm, $J = 5$ Hz, 1 H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 18.3 (+), 25.3 (–), 27.9 (–), 28.7 (–), 36.4 (–), 38.4 (+), 62.2 (–), 112.4 (+), 125.0 (+), 126.6 (+), 136.8 (+), 148.1 (–), 149.7 (+), 150.7 (–), 165.0 (–); HRMS (FAB) calcd for C$_{15}$H$_{20}$NO$_2$ [(M+H)$^+$] 246.1494, found 246.1497.

**(E)- and (Z)-2-(3-Methylcyclohexylidene)ethyl Picolinate (4D)**

![Structural diagram](image)

To a suspension of LiCl (297 mg, 7.01 mmol) in MeCN (5 mL) were added DBU (0.90 mL, 6.03 mmol) and triethyl phosphonoacetate (1.30 mL, 6.49 mmol) at 0 °C. The mixture was stirred at 0 °C for 30 min, and ketone 3D (0.61 mL, 5.00 mmol) was added. The reaction was carried out at room temperature overnight and quenched by addition of saturated NaHCO$_3$. The resulting mixture was extracted with EtOAc three times. The combined extracts were washed with brine, dried over MgSO$_4$ and concentrated to give a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to afford the corresponding ester (801 mg, 88%) as a 1:1 mixture of the stereoisomers by $^1$H NMR spectroscopy. The mixture: $^1$H NMR (300 MHz, CDCl$_3$) δ 0.95 and 0.98 (2 d, $J = 6.5$ and 6.5 Hz, 1:1, total 3 H), 1.02–2.30 (m, 11 H), 3.59–3.72 (m, 1 H), 4.14 (q, $J = 7$ Hz, 2 H), 5.60 and 5.61 (2 s, 1:1, total 1 H).

To a solution of the above ester (801 mg, 4.39 mmol) in THF (8 mL) was added DIBAL (9.40 mL, 1.03 M in hexane, 9.68 mmol) dropwise at −78 °C. After 1 h at −78 °C, the reaction was quenched by addition of water. The cooling bath was removed, and 1 N HCl was added. The mixture was extracted with EtOAc three times. The combined extracts were washed with saturated NaHCO$_3$ and brine successively, dried over Na$_2$SO$_4$ and concentrated to afford the corresponding
alcohol, which was used for the next reaction without further purification: \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 0.91 and 0.94 (2 d, \(J = 7\) and 7 Hz, 1:1, total 3 H), 0.87–2.04 (m, 8 H), 2.12–2.23 (m, 1 H), 2.54 (dm, \(J = 10\) Hz, 1 H), 4.14 (dm, \(J = 6\) Hz, 2 H), 5.36 and 5.39 (2 t, \(J = 6\) and 6 Hz, 1:1, total 1 H). The spectrum of the alcohol was identical with that reported.\(^2\)

To an ice-cold solution of the above alcohol (571 mg) in CH\(_2\)Cl\(_2\) (16 mL) were added picolinic acid (649 mg, 5.27 mmol), DMAP (161 mg, 1.32 mmol) and DCC (1.18 g, 5.72 mmol). The mixture was stirred at room temperature for 1 h, diluted with ether and filtered through a pad of Celite. The filtrate was concentrated to afford a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to furnish picolinate 4D (997 mg, 93% from ester) as a 1:1 mixture of the stereoisomers by \(^1\)H NMR spectroscopy. The mixture: IR (neat) 1740, 1718, 1301, 1289, 1246, 1129 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 0.90 and 0.95 (2 d, \(J = 6\) and 6 Hz, 1:1, total 3 H), 0.83–2.04 (m, 7 H), 2.14–2.26 (m, 1 H), 2.59–2.72 (m, 1 H), 4.94 (d, \(J = 7\) Hz, 2 H), 5.42–5.52 (m, 1 H), 7.46 (ddd, \(J = 8\), 5, 1 Hz, 1 H), 7.83 (ddd, \(J = 8\), 8, 1 Hz, 1 H), 8.14 (d, \(J = 8\) Hz, 1 H), 8.76 (d, \(J = 5\) Hz, 1 H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 22.0 (+), 22.1 (+), 26.8 (–), 26.8 (–), 28.3 (–), 33.5 (+), 34.0 (+), 34.7 (–), 36.3 (–), 37.0 (–), 45.0 (–), 61.9 (–), 62.0 (–), 115.0 (+), 124.9 (+), 126.6 (+), 136.8 (+), 146.4 (–), 148.1 (–), 149.6 (+), 165.0 (–); HRMS (FAB) calcd for C\(_{15}\)H\(_{20}\)NO\(_2\) [(M+H)+] 246.1494, found 246.1495.

\((E)\)- and \((Z)\)-2-(3,3,5-Trimethylcyclohexylidene)ethyl Picolinate (4E)

\[(\text{E})\] [\(\text{Z}\)]

\(\text{3E} \quad \text{4E} \quad [\text{E}]/[\text{Z} = 7:3]\)

To an ice-cold suspension of LiCl (396 mg, 9.34 mmol) in MeCN (12 mL) were added DBU (1.27 mL, 8.51 mmol) and triethyl phosphonoacetate (1.71 mL, 8.54 mmol). The mixture was stirred 0 °C for 30 min, and a solution of ketone 3E (990 mg, 7.06 mmol) in MeCN (2 mL) was added dropwise. The reaction was carried out at 0 °C overnight and quenched by addition of saturated NH\(_4\)Cl. The resulting mixture was extracted with EtOAc three times. The combined extracts were dried over MgSO\(_4\) and concentrated to give a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to afford the corresponding ester (1.08 g, 73%) as a 7:3 mixture of the \(E/Z\) stereoisomers by \(^1\)H NMR spectroscopy. The mixture: \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 0.81 (s, 2.1 H) and 0.83 (s, 0.9 H), 0.93 (d, \(J = 6\) Hz, 0.9 H) and 0.96 (d, \(J = 6.5\) Hz, 2.1 H), 0.98 (s, 2.1 H) and 1.02 (s, 0.9 H), 1.27 (q, \(J = 7\) Hz, 0.9 H) and 1.28 (q, \(J = 7\) Hz, 2.1 H), 1.24–2.24 (m, 6 H), 3.58 (ddd, \(J = 13\), 3, 2 Hz, 0.3 H) and 3.83 (ddddd, \(J = 13\), 3, 2, 2 Hz, 0.7 H), 4.08–4.20 (m, 2 H), 5.55–5.58 (m, 0.7 H) and 5.68–5.70 (m, 0.3 H). The \(E\) and \(Z\) stereochemistries were assigned to the major and minor isomers by converting the isomers to the known alcohols (see below).

To a solution of the above ester (897 mg, 4.26 mmol) in THF (8.5 mL) was added DIBAL (12.3
mL, 1.04 M in hexane, 12.8 mmol) dropwise at –78 °C. After 1 h at –78 °C, the reaction was quenched by addition of water. The cooling bath was removed, and 1 N HCl was added. The resulting mixture was extracted with EtOAc three times. The combined extracts were washed with saturated NaHCO₃ and brine successively, dried over Na₂SO₄ and concentrated to give a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to afford the corresponding alcohol (707 mg, 98%) as a 7:3 mixture of the E/Z stereoisomers by ¹H NMR spectroscopy. The mixture: ¹H NMR (300 MHz, CDCl₃) δ 0.80 (s, 3 H), 0.89 (d, J = 6 Hz, 0.9 H) and 0.92 (d, J = 6.5 Hz, 2.1 H), 0.94 (s, 2.1 H) and 0.98 (s, 0.9 H), 0.86–1.92 (m, 6.7 H), 2.17 (dm, J = 11 Hz, 0.3 H), 2.26 (dm, J = 13 Hz, 0.3 H), 2.58 (dm, J = 13 Hz, 0.7 H), 4.08–4.21 (m, 2 H), 5.34 (tm, J = 7 Hz, 0.7 H) and 5.49 (tm, J = 7 Hz, 0.3 H). The major and minor signals were identical with the data reported for the E and Z stereoisomers.¹

To an ice-cold solution of the above alcohol (702 mg, 4.17 mmol) in CH₂Cl₂ (14 mL) were added picolinic acid (621 mg, 5.05 mmol), DMAP (517 mg, 4.23 mmol) and DCC (1.12 g, 5.43 mmol). The mixture was stirred at room temperature for 2.5 h, diluted with Et₂O and filtered through a pad of Celite. The filtrate was concentrated to afford a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to furnish picolinate 4E (1.12 g, 98%): as a 7:3 mixture of the E/Z stereoisomers by ¹H NMR spectroscopy. The mixture: ¹H NMR (300 MHz, CDCl₃) δ 0.79 (s, 2.1 H) and 0.80 (s, 0.9 H), 0.89 (d, J = 6.5 Hz, 0.9 H) and 0.93 (d, J = 6.5 Hz, 2.1 H), 0.94 (s, 2.1 H) and 0.96 (s, 0.9 H), 0.86–1.94 (m, 5.7 H), 2.20 (dm, J = 11 Hz, 0.3 H), 2.38 (dm, J = 13 Hz, 0.3 H), 2.71 (dm, J = 13 Hz, 0.7 H), 4.87–5.00 (m, 2 H), 5.43 (tm, J = 7.5 Hz, 0.7 H) and 5.59 (tm, J = 7.5 Hz, 0.3 H), 7.47 (ddm, J = 8, 5 Hz, 1 H), 7.84 (ddm, J = 8, 8 Hz, 1 H), 8.13 (dm, J = 8 Hz, 1 H), 8.77 (dm, J = 5 Hz, 1 H); HRMS (FAB) calcd for C₁₇H₂₄NO₂ [(M+H)⁺] 274.1807, found 274.1806.

(⁴-E)- and (⁴-Z)-2-(2-Methoxycyclohexylidene)ethyl Picolinate (4F)

To an ice-cold suspension of LiCl (262 mg, 6.18 mmol) in MeCN (12 mL) were added DBU (0.78 mL, 5.22 mmol) and triethyl phosphonoacetate (1.12 mL, 5.59 mmol). The mixture was stirred 0 °C for 30 min, and a solution of ketone 3F (554 mg, 4.32 mmol) in MeCN (8 mL) was added dropwise. The reaction was carried out at 0 °C overnight and quenched by addition of saturated NH₄Cl. The resulting mixture was extracted with EtOAc three times. The combined extracts were dried over MgSO₄ and concentrated to give a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to afford the corresponding ester (811 mg, 95%) as a 2:3 mixture of the E/Z stereoisomers by ¹H NMR spectroscopy. The mixture: ¹H NMR (300 MHz, CDCl₃) δ 1.288 (t, J...
AB) calcd for C\textsubscript{24}H\textsubscript{24}O\textsubscript{2}C\textsubscript{d}, –34 – –2:34 6 –15, the above ester (876 mg, 4.42 mmol) in THF (9 mL) was added a t 22 H\textsubscript{13}C\textsubscript{6} extracts were washed with saturated NaHCO\textsubscript{3} by addition of 3 N HCl. The resulting mixture was extracted with EtOAc three time (ratio = 4:1) and a solution of the picolinate 4F (1.05 g, 93%) as a 2:3 mixture of the E/Z stereoisomers by 1H NMR spectroscopy. The mixture: 1H NMR (300 MHz, CDCl\textsubscript{3}) δ 1.30–2.42 (m, 8 H), 3.247 (s, 1.8 H) and 3.254 (s, 1.2 H), 3.56–3.61 (m, 0.4 H) and 4.27–4.33 (m, 0.6 H), 4.98–5.04 (m, 2 H), 5.64–5.74 (m, 1 H), 7.48 (ddm, J = 8, 5 Hz, 1 H), 7.85 (ddd, J = 8, 8, 2 Hz, 1 H), 8.15 (dm, J = 8 Hz, 1 H), 8.77 (dm, J = 5 Hz, 1 H); HRMS (FAB) calcd for C\textsubscript{15}H\textsubscript{26}NO\textsubscript{3} [(M+H)\textsuperscript{+}] 262.1443, found 262.1442.

(E)- and (Z)-2-(2-Hexyl-1-(phenoxycarbonyl)piperidin-4-ylidene)ethyl Picolinate (4G)

According to the literature procedure\textsuperscript{6} C\textsubscript{6}H\textsubscript{13}MgBr (3.07 mL, 0.85 M in THF, 2.60 mmol) and phenyl chloroformate (0.33 mL, 2.63 mmol) were added to a solution of 4-methoxypyridine (258 mg, 2.37 mmol) in THF (24 mL) dropwise at –23 ºC. After 4 h at –23 ºC, the reaction was quenched by addition of 3 N HCl. The resulting mixture was extracted with EtOAc three times. The combined extracts were washed with saturated NaHCO\textsubscript{3} and brine successively, dried over MgSO\textsubscript{4} and
concentrated to afford the corresponding enone, which was used for the next reaction without further purification.

A solution of the above enone and 10% Pd/C (75 mg) in MeOH (10 mL) was stirred at room temperature for 3 h under hydrogen, diluted with EtOAc and filtered through a pad of Celite. The filtrate was concentrated to afford a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to give ketone 3G (494 mg, 63% from 4-methoxypyridine): \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 0.88 (t, \(J = 7\) Hz, 3 H), 1.18–1.70 (m, 10 H), 2.34–2.47 (m, 2 H), 2.61 (ddd, \(J = 15, 12, 7\) Hz, 1 H), 2.71–2.84 (m, 1 H), 3.21–3.50 (m, 1 H), 4.42–4.58 (m, 1 H), 4.77 (br s, 1 H), 7.12 (d, \(J = 8\) Hz, 2 H), 7.23 (dd, \(J = 8, 8\) Hz, 1 H), 7.39 (dd, \(J = 8, 8\) Hz, 2 H).

To an ice-cold suspension of 60% NaH (7.2 mg, 0.18 mmol) in THF (0.7 mL) was added triethyl phosphonoacetate (0.028 mL, 0.14 mmol). The mixture was stirred at 0 °C for 10 min, and a solution of ketone 3G (38.9 mg, 0.128 mmol) in THF (0.8 mL) was added dropwise. The reaction was carried out at 0 °C for 2.5 h and quenched by addition of saturated NH\(_4\)Cl. The resulting mixture was extracted with EtOAc three times. The combined extracts were dried over MgSO\(_4\) and concentrated to give a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to afford the corresponding ester (41 mg, 86%) as a 4:1 mixture of the stereoisomers by \(^1\)H NMR spectroscopy. The mixture: \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 0.82–0.92 (m, 3 H), 1.1–1.8 (m, 13 H), 2.16–2.69 (m, 3 H), 2.92–3.24 (m, 1 H), 3.75–3.93 (m, 1 H), 4.18 (q, \(J = 7\) Hz, 2 H), 4.12–4.38 (m, 1 H), 4.53 (br s, 1 H), 5.74 (s, 0.8 H) and 5.85 (s, 0.2 H), 7.10 (d, \(J = 8\) Hz, 2 H), 7.20 (dd, \(J = 8, 8\) Hz, 1 H), 7.37 (dd, \(J = 8, 8\) Hz, 2 H).

To a solution of the above ester (40 mg, 0.107 mmol) in THF (1 mL) was added DIBAL (0.31 mL, 1.03 M in hexane, 0.32 mmol) dropwise at −78 °C. After 1 h at −78 °C, the reaction was quenched by addition of water. The cooling bath was removed, and 1 N HCl was added. The resulting mixture was extracted with EtOAc three times. The combined extracts were washed with saturated NaHCO\(_3\) and brine successively, dried over Na\(_2\)SO\(_4\) and concentrated to give a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to afford the corresponding alcohol (34 mg, 95%), which was used for the next reaction without further purification: \(^1\)H NMR of the mixture (300 MHz, CDCl\(_3\)) \(\delta\) 0.80–0.94 (m, 3 H), 1.1–1.8 (m, 10 H), 2.0–3.2 (m, 8 H), 2.82–3.08 (m, 1 H), 4.06–4.31 (m, 3 H), 4.47 (br s, 1 H), 5.51 (t, \(J = 6.5\) Hz, 0.8 H) and 5.65 (t, \(J = 6.5\) Hz, 0.2 H), 7.10 (d, \(J = 7.5\) Hz, 2 H), 7.20 (dd, \(J = 7.5, 7.5\) Hz, 1 H), 7.37 (dd, \(J = 7.5, 7.5\) Hz, 2 H).

To an ice-cold solution of the above alcohol (291 mg, 0.877 mmol) in CH\(_2\)Cl\(_2\) (9 mL) were added picolinic acid (130 mg, 1.06 mmol), DMAP (110 mg, 0.90 mmol) and DCC (240 mg, 1.17 mmol). The mixture was stirred at room temperature for 5 h, diluted with Et\(_2\)O, and filtered through a pad of Celite. The filtrate was concentrated to afford a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to furnish picolinate 4G (382 mg, 99%) as a 4:1
mixture of the stereoisomers by $^1$H NMR spectroscopy. The mixture: $^1$H NMR (300 MHz, CDCl$_3$) δ 0.80–0.94 (m, 3 H), 1.1–3.2 (m, 17 H), 4.21–4.36 (m, 1 H), 4.40–4.64 (m, 1.2 H) and 4.90–5.12 (m, 1.8 H), 5.63 (t, $J = 6.5$ Hz, 0.8 H) and 5.80 (t, $J = 6.5$ Hz, 0.2 H), 7.11 (d, $J = 7.5$ Hz, 2 H), 7.20 (dd, $J = 7.5$, 7.5 Hz, 1 H), 7.37 (dd, $J = 7.5$, 7.5 Hz, 2 H), 7.49 (ddm, $J = 8$, 5 Hz, 1 H), 7.86 (dd, $J = 8$, 8 Hz, 1 H), 8.16 (d, $J = 8$ Hz, 1 H), 8.78 (d, $J = 5$ Hz, 1 H); HRMS (FAB) calcd for C$_{26}$H$_{33}$N$_2$O$_4$ [(M+H)$^+$] 437.2440, found 437.2439.

(4a$^R$,8a$^R$)-Octahydronaphthalen-2(1H)-one (3H)

To a flask containing NH$_3$ (ca. 25 mL) at −70 °C were added a solution of the octalenone (421 mg, 2.80 mmol) in THF (1 mL), tBuOH (0.21 mL, 2.2 mmol) and Li (ca. 170 mg, 24 mg-atom). After 15 min at −70 °C, saturated NH$_4$Cl was added to the solution with vigorous stirring. The product was extracted with Et$_2$O several times. The combined extracts were dried over MgSO$_4$ and concentrated to afford a mixture of trans-octalone 3H and the corresponding alcohol. A solution of the mixture in acetone (20 mL) was cooled to 0 °C and Jones reagent (1.4 mL, 4.0 M, 5.6 mmol) was added to the solution. The mixture was stirred for 15 min and the excess reagent was destroyed by addition of iPrOH. The mixture was diluted with EtOAc and the solution isolated by decantation was rinsed with brine, dried over MgSO$_4$ and concentrated. The residue was purified by chromatography on silica gel (hexane/EtOAc) to afford octalone 3H (281 mg, 66%). $^1$H NMR (300 MHz, CDCl$_3$) δ 0.84–1.48 (m, 7 H), 1.63–1.84 (m, 4 H), 1.90–2.15 (m, 2 H), 2.25–2.44 (m, 3 H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 25.6 (–), 26.2 (–), 32.7 (–), 33.7 (–), 34.3 (–), 41.65 (–), 41.70 (+), 43.4 (+), 48.7 (–), 211.8 (–). The $^{13}$C NMR spectrum was identical with that reported for the trans isomer.

(4a$^R$,8a$^R$)-Octahydronaphthalen-2(1H)-ylidene)ethyl Picolinate (4H)

To an ice-cold suspension of LiCl (80 mg, 1.88 mmol) in MeCN (10 mL) were added DBU (0.23 mL, 1.54 mmol) and triethyl phosphonoacetate (0.34 mL, 1.70 mmol). The mixture was stirred 0 °C for 30 min, and a solution of ketone 3H (196 mg, 1.29 mmol) in MeCN (3 mL) was added dropwise. The reaction was carried out at 0 °C overnight and quenched by addition of saturated NH$_4$Cl. The resulting mixture was extracted with EtOAc three times. The combined extracts were
dried over MgSO₄ and concentrated to give a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to afford the corresponding ester (242 mg, 90%) as a 1:1 mixture of the stereoisomers by ¹H NMR spectroscopy. The mixture: ¹H NMR (300 MHz, CDCl₃) δ 0.84–1.94 (m, 13 H), 1.27 (q, J = 7 Hz, 3 H), 2.10–2.31 (m, 2 H), 3.72–3.79 (m, 0.5 H) and 3.81–3.90 (m, 0.5 H), 4.14 (q, J = 7 Hz, 2 H), 5.59 (br s, 1 H).

To a solution of the above ester (185 mg, 0.832 mmol) in THF (8 mL) was added DIBAL (2.40 mL, 1.04 M in hexane, 2.47 mmol) dropwise at -78 °C. After 1.5 h at -78 °C, the reaction was quenched by addition of water. The cooling bath was removed and 1 N HCl was added. The resulting mixture was extracted with EtOAc three times. The combined extracts were washed with saturated NaHCO₃ and brine successively, dried over Na₂SO₄ and concentrated to give a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to afford the corresponding alcohol, which was used for the next reaction without further purification: ¹H NMR (300 MHz, CDCl₃) δ 0.82–2.25 (m, 16 H), 2.46–2.55 (m, 0.5 H) and 2.59–2.69 (m, 0.5 H), 4.14 (d, J = 7 Hz, 2 H), 5.39 (tm, J = 7 Hz, 1 H).

To an ice-cold solution of the above alcohol in CH₂Cl₂ (8 mL) were added picolinic acid (164 mg, 1.33 mmol), DMAP (104 mg, 0.85 mmol) and DCC (319 mg, 1.54 mmol). The mixture was stirred at room temperature overnight, diluted with Et₂O and filtered through a pad of Celite. The filtrate was concentrated to afford a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to furnish picolinate 4H (209 mg, 88% from the ester) as a 1:1 mixture of the stereoisomers by ¹H NMR spectroscopy. The mixture: ¹H NMR (300 MHz, CDCl₃) δ 0.84–2.30 (m, 15 H), 2.59–2.68 (m, 0.5 H) and 2.63–2.83 (m, 0.5 H), 4.95 (d, J = 7 Hz, 2 H), 5.46 (t, J = 7 Hz, 1 H), 7.47 (dd, J = 8, 5, 1.5 Hz, 1 H), 7.84 (dd, J = 8, 8, 1.5 Hz, 1 H), 8.14 (dm, J = 8 Hz, 1 H), 8.77 (d, J = 5 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 26.3 (−), 26.5 (−), 28.8 (−), 33.4 (−), 33.5 (−), 33.9 (−), 34.2 (−), 34.6 (−), 35.1 (−), 36.2 (−), 36.8 (−), 43.29 (+), 43.35 (+), 44.0 (+), 44.1 (−), 44.6 (+), 62.26 (−), 62.33 (−), 114.09 (+), 115.0 (+), 125.0 (−), 126.8 (+), 137.0 (+), 146.8 (−), 147.0 (−), 148.4 (−), 149.9 (+), 165.3 (+); HRMS (FAB) calcd for C₁₈H₂₄NO₅ [(M+H)⁺] 286.1807, found 286.1806.


![Chemical Structure](image)

To an ice-cold solution of stanolone (329 mg, 1.13 mmol) in DMF (4 mL) were added imidazole
(369 mg, 5.42 mmol) and TBSCI (508 mg, 3.37 mmol). The mixture was stirred at room
temperature overnight and diluted with EtOAc and saturated NaHCO₃. The organic layer was
separated, and the aqueous layer was extracted with EtOAc three times. The combined organic
layers were dried over MgSO₄ and concentrated to afford a residue, which was purified by
chromatography on silica gel (hexane/EtOAc) to furnish the above ester (393 mg, 0.828 mmol) in THF (2 mL) was added
and filtered through a pad of Celite. The filtrate was concentrated to afford a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to furnish picolinic acid (324 mg), which was used for the next reaction without further purification:

\[ \text{H NMR (300 MHz, CDCl₃) } \delta = \begin{array}{l}
0.00 (s, 3 H), 0.69 (s, 3 H), 0.87 (s, 12 H), 0.56–2.55 (m, 23 H), 3.53 (t, } J = 8 \text{ Hz, 1 H), 4.02–4.24 (m, 2 H), 5.26–5.43 (m, 1 H) \end{array} \]

To an ice-cold suspension of LiCl (53 mg, 1.25 mmol) in MeCN (1 mL) were added DBU (0.160 mL, 1.07 mmol) and triethyl phosphonoacetate (0.23 mL, 1.15 mmol). The mixture was stirred at 0 °C for 30 min, and 3I (363 mg, 0.897 mmol) was added. The reaction was carried out at room temperature overnight and quenched by addition of saturated NaHCO₃. The resulting mixture was extracted with EtOAc three times. The combined extracts were washed with brine, dried over MgSO₄ and concentrated to give a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to afford the corresponding ester (415 mg, 97%) as a 1:1 mixture of the stereoisomers by \( ^1H \) NMR spectroscopy: \( ^1H \) NMR (300 MHz, CDCl₃) \( \delta = \begin{array}{l}
0.00 (s, 3 H), 0.69 (s, 3 H), 0.87 (s, 12 H), 0.56–2.40 (m, 21 H), 0.69 (s, 3 H), 0.86 (s, 9 H), 0.91 (s, 3 H), 1.26 (t, } J = 7 \text{ Hz, 3 H), 3.47 and 3.72 (2 dm, } J = 15 \text{ and 15 Hz, 1:1, total 1 H) } \end{array} \]

To a solution of the above ester (393 mg, 0.828 mmol) in THF (2 mL) was added DIBAL (1.8 mL, 1.03 M in hexane, 1.85 mmol) dropwise at −78 °C. After 1 h at −78 °C, the reaction was quenched by addition of water. The cooling bath was removed, and 1 N HCl was added. The mixture was extracted with EtOAc three times. The combined extracts were washed with saturated NaHCO₃ and brine successively, dried over Na₂SO₄ and concentrated to afford the corresponding alcohol (324 mg), which was used for the next reaction without further purification: \( ^1H \) NMR (300 MHz, CDCl₃) \( \delta = \begin{array}{l}
0.00 (s, 3 H), 0.69 (s, 3 H), 0.87 (s, 12 H), 0.56–2.55 (m, 23 H), 3.53 (t, } J = 8 \text{ Hz, 1 H), 4.02–4.24 (m, 2 H), 5.26–5.43 (m, 1 H) \end{array} \]

To an ice-cold solution of the above alcohol (324 mg) in CH₂Cl₂ (3 mL) were added picolinic acid (122 mg, 0.991 mmol), DMAP (30 mg, 0.246 mmol) and DCC (222 mg, 1.08 mmol). The mixture was stirred at room temperature for 1 h, diluted with ether and filtered through a pad of Celite. The filtrate was concentrated to afford a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to furnish picolinate 4I (398 mg, 89% from ester) as a 1:1 mixture of the stereoisomers by \( ^1H \) NMR spectroscopy. The mixture: \( [\alpha]_{D}^{23} = +15 \) (c 0.72, CHCl₃); IR (neat) 1740, 1718, 1302, 1247, 1124, 1094 cm⁻¹; \( ^1H \) NMR (300 MHz, CDCl₃) \( \delta = \begin{array}{l}
0.66 (s, 3 H), 0.84 (s, 9 H), 0.85 (s, 3 H), 0.52–2.30 (m, 21 H), 2.31 and 2.60 (2d, } J = 14 \text{ and 15 Hz, 1:1, total 1 H) } \end{array} \]

4.13 (q, } J = 7 \text{ Hz, 2 H), 5.64–5.60 (m, 1 H).

To an ice-cold suspension of LiCl (53 mg, 1.25 mmol) in MeCN (1 mL) were added DBU (0.160 mL, 1.07 mmol) and triethyl phosphonoacetate (0.23 mL, 1.15 mmol). The mixture was stirred at 0 °C for 30 min, and 3I (363 mg, 0.897 mmol) was added. The reaction was carried out at room temperature overnight and quenched by addition of saturated NaHCO₃. The resulting mixture was extracted with EtOAc three times. The combined extracts were washed with brine, dried over MgSO₄ and concentrated to give a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to afford the corresponding ester (415 mg, 97%) as a 1:1 mixture of the stereoisomers by \( ^1H \) NMR spectroscopy: \( ^1H \) NMR (300 MHz, CDCl₃) \( \delta = \begin{array}{l}
0.00 (s, 3 H), 0.69 (s, 3 H), 0.87 (s, 12 H), 0.56–2.40 (m, 21 H), 0.69 (s, 3 H), 0.86 (s, 9 H), 0.91 (s, 3 H), 1.26 (t, } J = 7 \text{ Hz, 3 H), 3.47 and 3.72 (2 dm, } J = 15 \text{ and 15 Hz, 1:1, total 1 H) } \end{array} \]

To a solution of the above ester (393 mg, 0.828 mmol) in THF (2 mL) was added DIBAL (1.8 mL, 1.03 M in hexane, 1.85 mmol) dropwise at −78 °C. After 1 h at −78 °C, the reaction was quenched by addition of water. The cooling bath was removed, and 1 N HCl was added. The mixture was extracted with EtOAc three times. The combined extracts were washed with saturated NaHCO₃ and brine successively, dried over Na₂SO₄ and concentrated to afford the corresponding alcohol (324 mg), which was used for the next reaction without further purification: \( ^1H \) NMR (300 MHz, CDCl₃) \( \delta = \begin{array}{l}
0.00 (s, 3 H), 0.69 (s, 3 H), 0.87 (s, 12 H), 0.56–2.55 (m, 23 H), 3.53 (t, } J = 8 \text{ Hz, 1 H), 4.02–4.24 (m, 2 H), 5.26–5.43 (m, 1 H) \end{array} \]

To an ice-cold solution of the above alcohol (324 mg) in CH₂Cl₂ (3 mL) were added picolinic acid (122 mg, 0.991 mmol), DMAP (30 mg, 0.246 mmol) and DCC (222 mg, 1.08 mmol). The mixture was stirred at room temperature for 1 h, diluted with ether and filtered through a pad of Celite. The filtrate was concentrated to afford a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to furnish picolinate 4I (398 mg, 89% from ester) as a 1:1 mixture of the stereoisomers by \( ^1H \) NMR spectroscopy. The mixture: \( [\alpha]_{D}^{23} = +15 \) (c 0.72, CHCl₃); IR (neat) 1740, 1718, 1302, 1247, 1124, 1094 cm⁻¹; \( ^1H \) NMR (300 MHz, CDCl₃) \( \delta = \begin{array}{l}
0.66 (s, 3 H), 0.84 (s, 9 H), 0.85 (s, 3 H), 0.52–2.30 (m, 21 H), 2.31 and 2.60 (2d, } J = 14 \text{ and 15 Hz, 1:1, total 1 H) } \end{array} \]

3.49 (t, } J = 8 \text{ Hz, 1 H), 4.83–4.99 (m, 2 H), 5.36–5.45 (m, 1 H), 7.42 (ddd, } J = 8, 5, 1
Hz, 1 H), 7.80 (ddd, J = 8, 8, 2 Hz, 1 H), 8.11 (dm, J = 8 Hz, 1 H), 8.73 (d, J = 5 Hz, 1 H); 13C NMR (75 MHz, CDCl3) δ −4.8 (+), −4.5 (+), 11.4 (+), 11.8 (+), 11.9 (+), 18.1 (−), 20.7 (−), 20.8 (−), 23.5 (−), 24.8 (−), 25.9 (+), 28.6 (−), 28.9 (−), 30.9 (−), 31.55 (−), 31.61 (−), 32.5 (−), 35.5 (+), 36.46 (−), 36.49 (−), 37.2 (−), 37.9 (−), 39.4 (−), 43.3 (−), 47.4 (+), 48.0 (+), 50.6 (+), 54.5 (+), 54.6 (+), 62.16 (−), 62.20 (−), 81.8 (−), 114.5 (−), 114.7 (−), 125.1 (+), 126.8 (+), 137.0 (+), 146.9 (−), 147.1 (−), 148.3 (−), 149.9 (+), 165.2 (−), 165.3 (−).

**General procedure for the Allylation**

(1s,4s)-4-tert-Butyl-1-methyl-1-vinylcyclohexane (5a)

![Chemical Structure](image)

**Allylation with ZnBr2** (Table 1, Entry 3): To an ice-cold suspension of CuBr·Me2S (26.7 mg, 0.130 mmol) and ZnBr2 (28.8 mg, 0.128 mmol) in THF (1 mL) was added MeMgBr (0.28 mL, 0.93 M in THF, 0.260 mmol) slowly. The mixture was stirred at 0 °C for 30 min, cooled to −40 °C and added a solution of picolinate 4A (24.9 mg, 0.0866 mmol) in THF (1 mL). The mixture was allowed to warm to −10 °C over 1 h and diluted with hexane and saturated NH4Cl with vigorous stirring. The layers were separated and the aqueous layer was extracted with hexane twice. The combined extracts were washed with brine, dried over MgSO4 and concentrated to give a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to afford 5a (14.7 mg, 94%): IR (neat) 3081, 1364, 910 cm−1; 1H NMR (300 MHz, CDCl3) δ 0.77–1.03 (m, 3 H), 0.83 (s, 9 H), 0.94 (s, 3 H), 1.06–1.30 (m, 4 H), 1.46–1.59 (s, 2 H), 1.67–1.78 (m, 2 H), 4.96 (dm, J = 18 Hz, 1 H), 5.02 (dm, J = 11 Hz, 1 H), 5.76 (dd, J = 18, 11 Hz, 1 H); 13C NMR (75 MHz, CDCl3) δ 23.5 (−), 27.7 (−), 31.5 (−), 32.5 (−), 36.6 (−), 38.5 (−), 48.3 (+), 112.0 (−), 146.3 (+). The stereochemistry was determined as drawn by comparison of the 13C NMR data with that reported.9

**Allylation with ZnI2** (Table 1, Entry 6): To an ice-cold suspension of CuBr·Me2S (27.9 mg, 0.136 mmol) and ZnI2 (43.4 mg, 0.136 mmol) in THF (1 mL) was added MeMgBr (0.29 mL, 1.0 M in THF, 0.27 mmol) slowly. The resulting mixture was stirred at 0 °C for 30 min and cooled to −40 °C. A solution of 4A (26.0 mg, 0.0905 mmol) in THF (1 mL) was added to the mixture dropwise. The mixture was allowed to warm to −10 °C over 1 h and diluted with hexane and saturated NH4Cl with vigorous stirring. The product was extracted with hexane and purified as described above to afford 5a (13.9 mg, 85%).

**Allylation with ZnCl2** (Table 1, Entry 7): To an ice-cold suspension of CuBr·Me2S (37.7 mg, 0.183 mmol) and ZnCl2 (24.2 mg, 0.178 mmol) in THF (1 mL) was added MeMgBr (0.34 mL, 1.06 M in THF, 0.36 mmol) slowly. The resulting mixture was stirred at 0 °C for 30 min and cooled to
–40 °C. A solution of 4A (34.5 mg, 0120 mmol) in THF (1 mL) was added to the mixture dropwise. The resulting mixture was allowed to warm to –10 °C over 1 h and diluted with hexane and saturated NH₄Cl with vigorous stirring. The product was extracted with hexane and purified as described above to afford 5a (18.6 mg, 86%).

**Allylation Products**

**4-tert-Butyl-1-ethyl-1-vinylcyclohexane (5b)**

![Structural formula of 5b]

Table 1, Entry 11: According to the general procedure a solution of 4A (36.8 mg, 0.128 mmol) in THF (1 mL) was added to a mixture of EtMgBr (0.38 mL, 1.0 M in THF, 0.38 mmol), CuBr·Me₂S (39.5 mg, 0.192 mmol) and ZnI₂ (61.3 mg, 0.192 mmol) in THF (1.5 mL) at –40 °C, and the mixture was allowed to warm to 0 °C over 1 h to afford 5b (21.5 mg, 86%): IR (neat) 3079, 1639, 1365, 1000, 910 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.76 (t, J = 7.5 Hz, 3 H), 0.81 (s, 9 H), 0.73–1.17 (m, 5 H), 1.22 (q, J = 7.5 Hz, 2 H), 1.46–1.58 (m, 2 H), 1.73–1.81 (m, 2 H), 4.92 (dd, J = 18, 2 Hz, 1 H), 5.14 (dd, J = 11, 2 Hz, 1 H), 5.50 (dd, J = 18, 11 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 7.9 (+), 23.4 (--), 23.7 (+), 32.5 (--), 36.1 (–), 36.9 (–), 40.0 (–), 48.8 (+), 114.0 (–), 144.9 (+).

**4-tert-Butyl-1-butyl-1-vinylcyclohexane (5c)**

![Structural formula of 5c]

Table 1, Entry 13: According to the general procedure a solution of 4A (27.5 mg, 0.0957 mmol) in THF (1.0 mL) was added to a mixture of BuMgBr (0.25 mL, 1.09 M in THF, 0.273 mmol), CuBr·Me₂S (29.5 mg, 0.143 mmol) and ZnI₂ (45.8 mg, 0.144 mmol) in THF (1.0 mL) at –40 °C, and the mixture was warmed to –10 °C over 1 h to afford 5c (20.1 mg, 94%): ¹H NMR (300 MHz, CDCl₃) δ 0.81 (s, 9 H), 0.80–1.28 (m, 13 H), 1.47–1.58 (m, 3 H), 1.75–1.82 (m, 2 H), 4.92 (dd, J = 17.5, 1.5 Hz, 1 H), 5.12 (dd, J = 11, 1.5 Hz, 1 H), 5.52 (dd, J = 17.5, 11 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 14.3 (+), 23.4 (–), 23.6 (–), 25.7 (+), 27.7 (+), 32.5 (–), 36.6 (–), 39.8 (–), 44.7 (–), 48.7 (+), 113.7 (–), 145.4 (+).

**4-tert-Butyl-1-isopropyl-1-vinylcyclohexane (5d)**

S15
Table 1, Entry 15: According to the general procedure a solution of 4A (34.4 mg, 0.120 mmol) in THF (1 mL) was added to a mixture of iPrMgBr (0.89 mL, 0.81 M in THF, 0.721 mmol), CuBr·Me₂S (73.8 mg, 0.359 mmol) and ZnI₂ (114.6 mg, 0.359 mmol) in THF (1 mL) at –40 ºC, and the mixture was warmed to 0 ºC over 3 h to afford 5d (23.1 mg, 93%): IR (neat) 3079, 1636, 1365, 911 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.79 (d, J = 7 Hz, 6 H), 0.81 (s, 9 H), 0.76–1.20 (m, 6 H), 1.25–1.38 (m, 1 H), 1.48–1.56 (m, 2 H), 1.84–1.92 (m, 2 H), 4.90 (dd, J = 18, 2 Hz, 1 H), 5.20 (dd, J = 11, 2 Hz, 1 H), 5.46 (dd, J = 18, 11 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 17.3 (+), 23.5 (–), 27.6 (+), 32.4 (–), 34.2 (–), 39.1 (+), 42.4 (–), 48.6 (+), 115.3 (–), 142.8 (+).

1-Methyl-4-phenyl-1-vinylcyclohexane (5e)

With ZnBr₂: According to the general procedure a solution of 4B (28.8 mg, 0.0937 mmol) in THF (1 mL) was added to a mixture of MeMgBr (0.27 mL, 1.06 M in THF, 0.286 mmol), CuBr·Me₂S (29.5 mg, 0.144 mmol) and ZnBr₂ (31.7 mg, 0.141 mmol) in THF (1 mL) at –40 ºC, and the mixture was warmed to 5 ºC over 3 h to afford 5e (16.4 mg, 87%): IR (neat) 3080, 1636, 910, 698 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.01 (s, 3 H), 1.34–1.47 (m, 2 H), 1.55–1.73 (m, 4 H), 1.77–1.87 (m, 2 H), 2.40–2.52 (m, 1 H), 5.04 (dd, J = 17.5, 1.5 Hz, 1 H), 5.09 (dd, J = 11, 1.5 Hz, 1 H), 5.84 (dd, J = 17.5, 11 Hz, 1 H), 7.14–7.30 (m, 5 H); ¹³C NMR (75 MHz, CDCl₃) δ 30.4 (–), 31.6 (+), 36.4 (–), 38.1 (–), 44.5 (+), 112.5 (–), 125.9 (+), 127.0 (+), 128.3 (+), 146.3 (+), 147.7 (–); HRMS (EI) calcd for C₁₅H₂₀ [M⁺] 200.1565, found 200.1567.

With ZnI₂: According to the general procedure a solution of 4B (31.4 mg, 0.102 mmol) in THF (1 mL) was added to a mixture of MeMgBr (0.33 mL, 0.93 M in THF, 0.307 mmol), CuBr·Me₂S (31.1 mg, 0.151 mmol) and ZnI₂ (49.2 mg, 0.154 mmol) in THF (1 mL) at –40 ºC and the mixture was warmed to –5 ºC over 2 h to afford 5e (19.7 mg, 96%).

1-Ethyl-4-phenyl-1-vinylcyclohexane (5f)

According to the general procedure a solution of 4B (80 mg, 0.274 mmol) in THF (2 mL) was added to a mixture of EtMgBr (0.95 mL, 0.85 M in THF, 0.81 mmol), CuBr·Me₂S (83.3 mg, 0.405 mmol) and ZnBr₂ (243 mg, 1.08 mmol) in THF (5 mL) at –40 ºC. The mixture was warmed to 0 ºC
over 2 h to give a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to afford 5f (47.5 mg, 81%): 1H NMR (300 MHz, CDCl$_3$) δ 0.81 (t, J = 7 Hz, 3 H), 1.22–1.42 (m, 4 H), 1.56–1.76 (m, 4 H), 1.82–1.95 (m, 2 H), 2.41–2.54 (m, 1 H), 5.01 (dd, J = 18, 2 Hz, 1 H), 5.24 (dd, J = 11, 2 Hz, 1 H), 5.60 (dd, J = 18, 11 Hz, 1 H), 7.12–7.36 (m, 5 H); 13C NMR (75 MHz, CDCl$_3$) δ 7.9, 30.3, 35.8, 36.9, 39.8, 45.0, 114.5, 125.9, 126.9, 128.3, 144.6, 147.9.

1-Butyl-4-phenyl-1-vinylcyclohexane (5g)

According to the general procedure a solution of 4B (31.2 mg, 0.102 mmol) in THF (1 mL) was added to a mixture of BuMgBr (0.31 mL, 0.975 M in THF, 0.302 mmol), CuBr·Me$_2$S (31.2 mg, 0.152 mmol) and ZnI$_2$ (48.3 mg, 0.151 mmol) in THF (1 mL) at –40 °C, and the mixture was allowed to warm to –5 °C over 2 h to afford 5g (21.6 mg, 88%): IR (neat) 3079, 1451, 1002, 910, 698 cm$^{-1}$; 1H NMR (300 MHz, CDCl$_3$) δ 0.89 (t, J = 7 Hz, 3 H), 1.19–1.43 (m, 8 H), 1.54–1.72 (m, 4 H), 1.83–1.92 (m, 2 H), 2.39–2.52 (m, 1 H), 4.99 (dd, J = 18, 1.5 Hz, 1 H), 5.20 (dd, J = 11, 1.5 Hz, 1 H), 5.61 (dd, J = 18, 11 Hz, 1 H), 7.13–7.32 (m, 5 H); 13C NMR (75 MHz, CDCl$_3$) δ 14.3 (+), 23.6 (–), 25.7 (–), 30.3 (–), 36.3 (–), 39.7 (–), 44.6 (–), 44.9 (+), 114.2 (–), 125.9 (+), 126.9 (+), 128.3 (+), 145.0 (+), 147.9 (–); HRMS (FAB) calcd for C$_{18}$H$_{26}$ [M$^+$] 242.2035, found 242.2041.

1-Isopropyl-4-phenyl-1-vinylcyclohexane (5h)

According to the general procedure a solution of 4B (71.0 mg, 0.239 mmol) in THF (1 mL) was added to a mixture of iPrMgBr (0.80 mL, 0.90 M in THF, 0.72 mmol), CuBr·Me$_2$S (74 mg, 0.36 mmol) and ZnBr$_2$ (216 mg, 0.710 mmol) in THF (5 mL) at –40 °C. The resulting mixture was allowed to warm to 0 °C over 2 h to afford 5h (45.5 mg, 83%): IR (neat) 3027, 912, 756, 698 cm$^{-1}$; 1H NMR (300 MHz, CDCl$_3$) δ 0.84 (d, J = 7 Hz, 3 H), 1.28–1.47 (m, 3 H), 1.52–1.74 (m, 4 H), 1.96 (dm, J = 14 Hz, 2 H), 2.43 (tt, J = 16, 4 Hz, 1 H), 4.98 (dd, J = 18, 2 Hz, 1 H), 5.28 (dd, J = 11, 2 Hz, 1 H), 5.55 (dd, J = 18, 11 Hz, 1 H), 7.12–7.33 (m, 5 H); 13C NMR (75 MHz, CDCl$_3$) δ 17.2 (+), 30.4 (–), 33.9 (–), 39.1 (+), 42.3 (–), 44.8 (+), 115.8 (–), 125.9 (+), 126.9 (+), 128.3 (+), 142.4 (+), 147.9 (–).

(1R*,2R*)-1,2-Dimethyl-1-vinylcyclohexane (5i)
According to the general procedure a solution of 4C (75 mg, 0.306 mmol) in THF (2 mL) was added to a mixture of MeMgBr (0.93 mL, 1.0 M in THF, 0.93 mmol), CuBr·Me₂S (95 mg, 0.462 mmol) and ZnBr₂ (276 mg, 1.23 mmol) in THF (6 mL) at −40 ºC, and the resulting mixture was warmed to 0 ºC over 3 h to afford 5i (26 mg, 61%): IR (neat) 3075, 1260, 911 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.79 (d, J = 7 Hz, 3 H), 0.99 (s, 3 H), 0.70–2.15 (m, 9 H), 4.96 (dd, J = 18, 2 Hz, 1 H), 5.04 (dd, J = 11, 2 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 16.7 (+), 22.5 (–), 26.6 (–), 27.0 (+), 31.1 (–), 39.5 (–), 39.8 (–), 41.3 (+), 112.8 (–), 142.7 (+).

**Determination of the stereochemistry of 5i**

To an ice-cold solution of 5i (25 mg, 0.181 mmol) in H₂O-CCl₅-MeCN (3 : 1 : 1, 1.8 mL) were added NaIO₄ (162 mg, 0.76 mmol) and RuCl₃·nH₂O (1 mg). After 5 h at 0 ºC, the mixture was diluted with Et₂O and aqueous Na₂SO₃. The layers were separated and the aqueous layer was extracted with Et₂O twice. The combined extracts were dried over MgSO₄ and concentrated to give a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to afford acid S₁ (21 mg, 73%): ¹H NMR (300 MHz, CDCl₃) δ 084–1.74 (m, 8 H), 1.06 (d, J = 7 Hz, 3 H), 1.29 (s, 3 H), 1.96–2.06 (m, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 16.8, 22.8, 24.5, 25.2, 30.2, 35.2, 39.6, 45.7, 183.3. The ¹³C NMR spectrum was identical with that reported,¹⁰ thus establishing the relative stereochemistry as drawn above.

**1-Butyl-2-methyl-1-vinylcyclohexane (5j)**

According to the general procedure a solution of 4C (26.5 mg, 0.108 mmol) in THF (1 mL) was added to a mixture of BuMgBr (0.38 mL, 0.85 M in THF, 0.323 mmol), CuBr·Me₂S (32.8 mg, 0.160 mmol) and ZnI₂ (52.7 mg, 0.165 mmol) in THF (1 mL) at −40 ºC and the mixture was warmed to −5 ºC over 2.5 h to afford 5j (14.8 mg, 76%): ¹H NMR (300 MHz, CDCl₃) δ 0.81 (d, J = 7 Hz, 3 H), 0.89 (d, J = 7 Hz, 3 H), 1.09–1.69 (m, 15 H), 4.91 (dd, J = 18, 2 Hz, 1 H), 5.10 (dd, J = 11, 2 Hz, 1 H), 5.83 (dd, J = 18, 11 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 14.3 (+), 16.0 (+), 22.2 (–), 23.7 (–), 25.5 (–), 25.9 (–), 31.1 (–), 32.6 (–), 38.8 (–), 39.2 (+), 42.2 (–), 113.5 (–), 142.4 (+).
1-Ethyl-3-methyl-1-vinylcyclohexane (5k)

According to the general procedure a solution of 4D (36.7 mg, 0.150 mmol) in THF (1 mL) was added to a mixture of EtMgBr (0.45 mL, 1.0 M in THF, 0.45 mmol), CuBr·Me₂S (46.3 mg, 0.225 mmol) and ZnI₂ (71.8 mg, 0.225 mmol) in THF (2 mL) at –40 °C. The resulting mixture was allowed to warm to 0 °C over 1 h to afford 5k (14.2 mg, 62%): IR (neat) 3079, 1458, 1001, 909 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.75 (t, J = 7 Hz, 3 H), 0.83 (d, J = 6 Hz, 3 H), 0.68–0.94 (m, 3 H), 1.02 (dt, J = 5, 13 Hz, 1 H), 1.18–1.75 (m, 7 H), 4.88 (dd, J = 18, 2 Hz, 1 H), 5.11 (ddd, J = 11, 2, 1 Hz, 1 H), 5.52 (dd, J = 18, 11 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 7.7 (+), 22.6 (–), 23.2 (+), 28.4 (+), 35.1 (–), 35.6 (–), 37.1 (–), 40.9 (–), 44.8 (–), 113.7 (–), 145.2 (+).

1-Butyl-3-methyl-1-vinylcyclohexane (5l)

According to the general procedure a solution of 4D (28.7 mg, 0.117 mmol) in THF (1 mL) was added to a mixture of BuMgBr (0.41 mL, 0.85 M in THF, 0.349 mmol), CuBr·Me₂S (36.0 mg, 0.175 mmol) and ZnI₂ (55.1 mg, 0.173 mmol) in THF (1 mL) at –40 ºC, and the mixture was warmed to –5 ºC over 2 h to afford 5l (16.8 mg, 79%): IR (neat) 3079, 1458, 1001, 910 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.84 (d, J = 7 Hz, 3 H), 0.87 (t, J = 6.5 Hz, 3 H), 0.69–1.74 (m, 15 H), 4.89 (dd, J = 18, 2 Hz, 1 H), 5.10 (dd, J = 11, 2 Hz, 1 H), 5.55 (dd, J = 18, 11 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 14.2 (+), 22.6 (–), 23.2 (+), 23.6 (–), 25.5 (–), 28.4 (+), 35.6 (–), 40.7 (–), 44.9 (–), 45.2 (–), 113.4 (–), 145.7 (+); HRMS (EI) calcd for C₁₃H₂₄ [M⁺] 180.1878, found 180.1877.

1-Butyl-3,3,5-trimethyl-1-vinylcyclohexane (5m)

According to the general procedure a solution of 4E (32.4 mg, 0.119 mmol) in THF (1 mL) was added to a mixture of BuMgBr (0.48 mL, 0.738 M in THF, 0.354 mmol), CuBr·Me₂S (36.6 mg, 0.178 mmol) and ZnI₂ (57.4 mg, 0.180 mmol) in THF (1 mL) at –40 ºC, and the mixture was warmed to –5 ºC over 2 h to afford 5m (18.7 mg, 76%): IR (neat) 3078, 1458, 1004, 906 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.54–1.36 (m, 22 H), 1.43 (dm, J = 14 Hz, 1 H), 1.63–1.78 (m, 1 H), 1.87 (dm, J = 14 Hz, 1 H), 4.87 (dd, J = 18, 1.5 Hz, 1 H), 4.99 (dd, J = 11, 1.5 Hz, 1 H), 5.67 (dd, J = 18, 11 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 14.3 (+), 23.0 (+), 23.6 (–), 24.6 (+), 25.3 (–), 27.2
(+), 32.1 (−), 34.7 (+), 40.7 (−), 42.2 (−), 46.3 (−), 49.2 (−), 51.3 (−), 111.2 (−), 147.3 (+); HRMS (EI) calcd for C_{15}H_{28} [M^{+}] 208.2191, found 208.2197.

1-Butyl-2-methoxy-1-vinylecyclohexane (5n)

According to the general procedure a solution of 4F (28.0 mg, 0.107 mmol) in THF (1 mL) was added to a mixture of BuMgBr (0.34 mL, 0.938 M in THF, 0.319 mmol), CuBr·Me$_2$S (33.0 mg, 0.161 mmol) and ZnI$_2$ (52.3 mg, 0.164 mmol) in THF (1 mL) at −40 ºC, and the mixture was warmed to 5 ºC over 3 h to afford 5n (14.6 mg, 70%): IR (neat) 3075, 1104, 909 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 0.88 (t, J = 7 Hz, 3 H), 1.08–1.86 (m, 14 H), 2.91 (dd, J = 9.5, 3.5 Hz, 1 H), 3.33 (s, 3 H), 4.97 (dd, J = 18, 11 Hz, 1 H), 5.15 (dd, J = 11, 2 Hz, 1 H), 5.85 (dd, J = 18, 11 Hz, 1 H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 14.3 (+), 21.5 (−), 23.6 (−), 24.0 (−), 25.5 (−), 26.0 (−), 31.1 (−), 38.1 (−), 45.0 (−), 57.1 (+), 85.6 (+), 113.9 (−), 141.9 (+).

Phenyl 2-Hexyl-4-methyl-4-vinylpiperidine-1-carboxylate (5o)

According to the general procedure a solution of 4G (47.8 mg, 0.110 mmol) in THF (1 mL) was added to a mixture of MeMgBr (0.31 mL, 1.06 M in THF, 0.329 mmol), CuBr·Me$_2$S (33.8 mg, 0.164 mmol) and ZnI$_2$ (52.4 mg, 0.164 mmol) in THF (1 mL) at −40 ºC, and the mixture was warmed to 5 ºC over 3 h to afford 5o (26.1 mg, 72%): IR (neat) 1718, 1419, 1204, 749, 688 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 0.87 (t, J = 7 Hz, 3 H), 1.00 (s, 3 H), 1.2–2.1 (m, 14 H), 3.03–3.37 (m, 1 H), 4.06 (d, J = 13.5 Hz, 1 H), 4.25–4.44 (m, 1 H), 5.03 (d, J = 17.5 Hz, 1 H), 5.04 (d, J = 11 Hz, 1 H), 5.91 (dd, J = 17.5, 11 Hz, 1 H), 7.07–7.39 (m, 5 H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 14.3 (+), 22.7 (−), 26.7 (−), 29.2 (−), 31.9 (−), 32.0 (−), 32.3 (+), 34.6 (−), 34.8 (−), 36.7 (−), 40.6 (−), 52.0 (+), 111.2 (−), 121.8 (+), 125.1 (+), 129.3 (+), 146.8 (+), 151.7 (−); HRMS (FAB) calcd for C$_{21}$H$_{32}$NO$_2$ [(M+H)$^+$] 330.2433, found 330.2438.

Phenyl 4-Butyl-2-hexyl-4-vinylpiperidine-1-carboxylate (5p)

According to the general procedure a solution of 4G (47.3 mg, 0.108 mmol) in THF (1 mL) was added to a mixture of BuMgBr (0.42 mL, 0.738 M in THF, 0.323 mmol), CuBr·Me$_2$S (33.4 mg,
0.163 mmol) and ZnI₂ (52.3 mg, 0.164 mmol) in THF (1 mL) at –40 °C. The mixture was warmed to –5 °C over 2 h to afford 5p (34.0 mg, 84%): IR (neat) 1718, 1419, 1204 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.87 (t, J = 7 Hz, 6 H), 1.1–1.9 (m, 19 H), 1.95 (d, J = 13.5 Hz, 1 H), 3.00–3.25 (m, 1 H), 4.05 (d, J = 13.5 Hz, 1 H), 4.22–4.45 (m, 1 H), 4.98 (dd, J = 18, 1 Hz, 1 H), 5.14 (dd, J = 11, 1 Hz, 1 H), 5.76 (dd, J = 18, 11 Hz, 1 H), 7.06–7.39 (m, 5 H); ¹³C NMR (75 MHz, CDCl₃) δ 14.2 (+), 22.7 (–), 23.3 (–), 25.1 (–), 26.8 (–), 29.2 (–), 31.9 (–), 32.1 (–), 32.6 (–), 36.5 (–), 37.8 (–), 39.9 (–), 45.0 (–), 52.1 (+), 112.7 (–), 121.8 (+), 125.1 (+), 129.3 (+), 145.2 (+), 151.7 (–), 154.0 (–); HRMS (FAB) calcd for C₂₄H₃₈NO₂ [(M+H)⁺] 372.2903, found 372.2900.

(4aS*,8aS*)-2-Methyl-2-vinyldecahydronaphthalene (5q)

According to the general procedure a solution of 4H (34.1 mg, 0.119 mmol) in THF (1 mL) was added to a mixture of MeMgBr (0.34 mL, 1.06 M in THF, 0.360 mmol), CuBr·Me₂S (36.8 mg, 0.179 mmol) and ZnI₂ (57.0 mg, 0.179 mmol) in THF (1 mL) at –40 °C. The mixture was allowed to warm to –5 °C over 2 h to afford 5q (16.2 mg, 76%): IR (neat) 3079, 1448, 909 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.93 (s, 3 H), 0.77–1.73 (m, 16 H), 4.95 (dd, J = 17.5, 1.5 Hz, 1 H), 4.99 (dd, J = 11, 1.5 Hz, 1 H), 5.79 (dd, J = 17.5, 11 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 26.7 (–), 26.8 (–), 30.3 (–), 31.7 (+), 33.8 (–), 34.3 (–), 37.5 (–), 37.8 (–), 38.9 (+), 43.5 (+), 45.9 (–), 111.8 (–), 147.2 (+).

(4aS*,8aS*)-2-Butyl-2-vinyldecahydronaphthalene (5r)

According to the general procedure a solution of 4H (33.3 mg, 0.117 mmol) in THF (1 mL) was added to a mixture of BuMgBr (0.47 mL, 0.738 M in THF, 0.347 mmol), CuBr·Me₂S (36.4 mg, 0.177 mmol) and ZnI₂ (55.9 mg, 0.175 mmol) in THF (1 mL) at –40 °C, and the mixture was warmed to –5 °C over 2 h to afford 5r (24.6 mg, 96%): IR (neat) 3078, 1418, 1001, 909 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.77–1.78 (m, 25 H), 4.89 (dd, J = 18, 2 Hz, 1 H), 5.10 (dd, J = 11, 2 Hz, 1 H), 5.57 (dd, J = 18, 11 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 26.7 (–), 26.8 (–), 30.2 (–), 33.8 (–), 34.3 (–), 35.9 (–), 38.7 (–), 43.5 (+), 44.1 (–), 44.8 (–), 113.4 (–), 145.9 (+); HRMS (EI) calcd for C₁₆H₂₈ [M⁺] 220.2191, found 220.2185.

tert-Butyl(((10S,13S,17S)-3-ethyl-10,13-dimethyl-3-vinylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)oxy)dimethylsilane (5s)
According to the general procedure a solution of 4I (40.7 mg, 0.0757 mmol) in THF (1 mL) was added to a mixture of EtMgBr (0.23 mL, 1.0 M in THF, 0.230 mmol), CuBr·Me₂S (23.3 mg, 0.113 mmol) and ZnI₂ (36.4 mg, 0.114 mmol) in THF (1 mL) at –40 °C. The resulting mixture was allowed to warm to 0 °C over 1 h to give 5s (29.3 mg, 87%): [α]D²³ +23 (c 0.53, CHCl₃); IR (neat) 3078, 1472, 1255, 1119, 1081, 909, 835 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ –0.011 (s, 3 H), –0.004 (s, 3 H), 0.67 (s, 3 H), 0.745 (t, J = 8 Hz, 3 H), 0.754 (s, 3 H), 0.87 (s, 9 H), 1.20 (q, J = 8 Hz, 2 H), 0.54–1.91 (m, 22 H), 3.51 (t, J = 8 Hz, 1 H), 4.91 (dd, J = 18, 1 Hz, 1 H), 5.12 (dd, J = 11, 1 Hz, 1 H), 5.51 (dd, J = 18, 11 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ –4.7 (+), –4.4 (+), 7.8 (+), 11.5 (+), 12.1 (+), 18.2 (–), 20.7 (–), 23.6 (–), 26.0 (+), 28.9 (–), 30.4 (–), 31.0 (–), 31.7 (–), 34.9 (–), 35.7 (+), 36.4 (–), 36.9 (–), 37.3 (–), 39.0 (–), 40.6 (–), 42.1 (+), 43.4 (–), 50.8 (+), 54.9 (+), 82.0 (+), 113.5 (–), 145.6 (+).

tert-Butyl((3R,10S,13S,17S)-3-butyl-10,13-dimethyl-3-vinylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yloxy)dimethylsilane (5t)

According to the general procedure a solution of 4I (31.0 mg, 0.0576 mmol) in THF (0.7 mL) was added to a mixture of BuMgBr (0.18 mL, 0.96 M in THF, 0.173 mmol), CuBr·Me₂S (17.8 mg, 0.0866 mmol) and ZnI₂ (28.3 mg, 0.0887 mmol) in THF (0.8 mL) at –40 °C, and the mixture was warmed to –5 °C over 2 h to afford 5t (21.7 mg, 80%): IR (neat) 1249, 1087, 909, 834, 774 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ –0.01 (s, 3 H), 0.00 (s, 3 H), 0.67 (s, 3 H), 0.76 (s, 3 H), 0.87 (s, 9 H), 0.54–1.91 (m, 31 H), 3.51 (t, J = 8 Hz, 1 H), 4.90 (dd, J = 18, 1.5 Hz, 1 H), 5.09 (dd, J = 11, 1.5 Hz, 1 H), 5.53 (dd, J = 18, 11 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ –4.7 (+), –4.4 (+), 11.5 (+), 12.1 (+), 14.2 (+), 18.2 (–), 20.7 (–), 23.6 (–), 25.6 (–), 26.0 (+), 28.9 (–), 30.97 (–), 31.01 (–), 31.7 (–), 34.9 (–), 35.7 (+), 36.4 (–), 37.3 (–), 39.3 (–), 40.5 (–), 42.1 (+), 43.4 (–), 44.7 (–), 50.8 (+), 54.9 (+), 82.0 (+), 113.2 (–), 146.1 (+); HRMS (El) calcd for C₃₁H₆₆OSi [M⁺] 472.4100, found 472.4094.

Determination of the stereochemistry of 5t
A stream of ozone was bubbled to a solution of 5t (51.5 mg, 0.109 mmol) in CH₂Cl₂ (3 mL) at −78 °C for 30 min, Ar was bubbled to remove excess O₃, and Me₂S (0.10 mL) was added. The solution was stirred at room temperature for 20 min and diluted with CH₂Cl₂. The solution was washed with brine, dried over MgSO₄ and concentrated to give a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to afford the corresponding aldehyde (29.6 mg, 57%).

To a solution of the above aldehyde (29.6 mg, 0.0623 mmol) in CH₂Cl₂ (1 mL) was added mCPBA (16.1 mg, 0.0933 mmol). The mixture was stirred at room temperature for 48 h and diluted with saturated NH₄Cl. The product was extracted with EtOAc three times. The combined extracts were washed with brine, dried over MgSO₄ and concentrated to afford the corresponding formate, which was used for the next reaction without further purification.

To a solution of the above formate in MeOH (1 mL) was added KOH (7 mg, 0.12 mmol). The mixture was stirred at room temperature overnight and diluted with EtOAc. The product was extracted with EtOAc three times. The combined extracts were washed with brine, dried over MgSO₄ and concentrated to give a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to afford alcohol S₂ (10.2 mg, 20% from the aldehyde): ¹H NMR (300 MHz, CDCl₃) δ −0.073 (s, 3 H), −0.066 (s, 3 H), 0.62 (s, 3 H), 0.67 (s, 3 H), 0.80 (s, 9 H), 0.6–1.9 (m, 32 H), 3.47 (t, J = 8 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃) δ −4.7 (+), −4.4 (+), 11.3 (+), 11.5 (+), 14.2 (+), 18.2 (−), 20.7 (−), 23.4 (−), 23.6 (−), 25.4 (−), 26.0 (+), 28.6 (−), 31.0 (−), 31.7 (−), 33.2 (−), 34.0 (−), 35.7 (+), 36.0 (−), 37.3 (−), 40.0 (−), 41.1 (+), 43.4 (−), 44.3 (−), 50.8 (+), 54.6 (+), 71.7 (−), 81.9 (+). The ¹H and ¹³C NMR spectra except APT were consistent with those reported.⁸
References

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
OCO(2-Py) 4C

$^1$H NMR (300 MHz, CDCl$_3$)

OCO(2-Py) 4C

$^{13}$C NMR (75 MHz, CDCl$_3$)
\[
\text{OCO(2-Py)}
\]

4D

$^1\text{H NMR (300 MHz, CDCl}_3\text{)}$

\[
\text{OCO(2-Py)}
\]

4D

$^{13}\text{C NMR (75 MHz, CDCl}_3\text{)}$

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**4E**

$^1$H NMR (300 MHz, CDCl$_3$)

**4F**

$^1$H NMR (300 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
(2-Py)COO

$^1$H NMR (300 MHz, CDCl$_3$)

(2-Py)COO

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)

S33
$^1$H NMR (300 MHz, CDCl$_3$)

$^1$C NMR (75 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)

$^1$C NMR (75 MHz, CDCl$_3$)
Ph

5e

$^1$H NMR (300 MHz, CDCl$_3$)

Ph

5e

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{1}H$ NMR (300 MHz, CDCl$_3$)

$^{13}C$ NMR (75 MHz, CDCl$_3$)
$^{1}H$ NMR (300 MHz, CDCl$_3$)

$^{13}C$ NMR (75 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{1}H$ NMR (300 MHz, CDCl$_3$)

$^{13}C$ NMR (75 MHz, CDCl$_3$)
**5o**

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{1}H$ NMR (300 MHz, CDCl$_3$)

$^{13}C$ NMR (75 MHz, CDCl$_3$)

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$^{1}$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
**$^{1}$H NMR (300 MHz, CDCl$_3$)**

![H NMR spectrum](image)

**$^{13}$C NMR (75 MHz, CDCl$_3$)**

![C NMR spectrum](image)
5s

$^1$H NMR (300 MHz, CDCl$_3$)

5s

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)

S52