Supporting Information

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Section 1. $^1$H and $^{13}$C NMR Comparison between enantiomeric pairs
Comparison between the $^1$H NMR spectra of (+)-24 and (-)-15 (500 MHz, CDCl$_3$)

[Diagram showing the NMR spectra of compounds 15 and 24]
Comparison between the $^{13}$C NMR spectra of (+)-24 and (-)-15 (125 MHz, CDCl$_3$) [marked peaks at $\delta$ 137.9, 129.1, 128.2, and 125.3 are from residual toluene]
Comparison between the $^1$H NMR spectra of (+)-25 and (-)-16 (500 MHz, CDCl$_3$)

[Diagram showing the NMR spectra of (+)-25 and (-)-16 with their respective chemical structures and physical properties.]
Comparison between the $^{13}$C NMR spectra of (+)-25 and (-)-16 (125 MHz, CDCl$_3$)
Comparison between the $^1$H NMR spectra of ($-$)-26 and ($+$)-17 (500 MHz, CDCl$_3$)
Comparison between the $^{13}$C NMR spectra of (-)-26 and (+)-17 (125 MHz, CDCl$_3$)
Comparison between the $^1$H NMR spectra of (+)-27 and (-)-18 (500 MHz, CDCl$_3$)
Comparison between the $^{13}$C NMR spectra of (+)-27 and (-)-18 (125 MHz, CDCl$_3$)

$\text{[\alpha]_D^{25} = -166.67}$

$\text{[\alpha]_D^{25} = +161.67}$

(-) enantiomer from D-tryptophan

(+)-enantiomer from D-tryptophan
Comparison between the $^1$H NMR spectra of (+)-29 and (-)-19 (500 MHz, CDCl$_3$)
Comparison between the $^{13}$C NMR spectra of (+)-29 and (-)-19 (125 MHz, CDCl$_3$)
Comparison between the $^1$H NMR spectra of (+)-28 and (-)-20 (500 MHz, CDCl$_3$)
Comparison between the $^{13}$C NMR spectra of (+)-28 and (-)-20 (125 MHz, CDCl$_3$)

$[\alpha]_D^{25} = -149.00$ for the (-) enantiomer from D-tryptophan

$[\alpha]_D^{25} = +154.78$ for the (+)-enantiomer from D-tryptophan
Comparison between the $^1$H NMR spectra of (+)-30 and (-)-21 (500 MHz, CDCl$_3$)

$[\alpha]_D^{25} = -191.30$

$[\alpha]_D^{25} = +188.89$

(-) enantiomer from D-tryptophan

(+) enantiomer from D-tryptophan
Comparison between the $^1$H NMR spectra of (+)-30 and (-)-21 (125 MHz, CDCl$_3$)
Comparison between the $^1$H NMR spectra of (+)-31 and (-)-22 (500 MHz, CDCl$_3$)
Comparison between the $^{13}$C NMR spectra of (+)-31 and (-)-22 (125 MHz, CDCl$_3$)

[Diagram showing two NMR spectra side by side. The (+)-enantiomer 31 is labeled with $[\alpha]_D^{25} = +3.99$ and the (-)-enantiomer 22 is labeled with $[\alpha]_D^{25} = -2.38$.]

(-) enantiomer from D-tryptophan

(+)-enantiomer from D-tryptophan
Comparison between the $^1\text{H}$ NMR spectra of (+)-32 and (-)-23 (500 MHz, CDCl$_3$).
Comparison between the $^{13}$C NMR spectra of (+)-32 and (-)-23 (125 MHz, CDCl$_3$)

[Image of NMR spectra]

$[\alpha]_D^{25} = -48.25$ for (-)-enantiomer from D-tryptophan

$[\alpha]_D^{25} = +50.86$ for (+)-enantiomer from D-tryptophan
Section 2. $^1$H, $^{13}$C, HSQC and COSY NMR Spectra of the compounds 24-32, 38, 40, and 42
$^1$H NMR spectrum of 24 (500 MHz, CDCl$_3$)

$[^\alpha]_D^{25} = +118.80$
$\text{C NMR spectrum of 24 (125 MHz, CDCl}_3$)
HSQC NMR spectrum of 24 (500 MHz, 125 MHz, CDCl$_3$)

$[\alpha]_D^{25} = +118.80$
COSY NMR spectrum of 24 (500 MHz, CDCl₃)
$^1$H NMR spectrum of 25 (500 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 25 (125 MHz, CDCl$_3$)

$[\alpha]_D^{25} = +143.20$
HSQC NMR spectrum of 25 (500 MHz, 125 MHz, CDCl₃)

[α]₀²⁵ = +143.20
COSY NMR spectrum of 25 (500 MHz, CDCl₃)

\[ [\alpha]_D^{25} = +143.20 \]
$[\alpha]_D^{25} = -32.31$

$^1$H NMR spectrum of 26 (500 MHz, CDCl$_3$)
HSQC NMR spectrum of 26 (500 MHz, 125 MHz, CDCl₃)

[α]D²⁵ = -32.31
COSY NMR spectrum of 26 (500 MHz, CDCl₃)

COSY of Na-H (R,R,S)-enol-TIPS

[α]D²⁵ = -32.31
[^\text{H}]_D^{25} = +161.67

$^1$H NMR spectrum of 27 (500 MHz, CDCl$_3$)
\[ [\alpha]_D^{25} = +161.67 \]

\[^{13}\text{C} \text{NMR spectrum of 27 (125 MHz, CDCl}_3] \]
HSQC NMR spectrum of 27 (500 MHz, 125 MHz, CDCl₃)
COSY NMR spectrum of 27 (500 MHz, CDCl$_3$)

$\lbrack \alpha \rbrack_D^{25} = +161.67$
$[^1]H$ NMR spectrum of 28 (500 MHz, CDCl$_3$)

$[\alpha]_D^{25} = +154.78$
$[\alpha]_D^{25} = +154.78$

$^{13}$C NMR spectrum of 28 (125 MHz, CDCl$_3$)
HSQC NMR spectrum of 28 (500 MHz, 125 MHz, CDCl₃)
COSY spectrum of 28 (500 MHz, CDCl₃)

COSY of Nα-H (R,R,R)-alkyne

[α]₀²⁵ = +154.78

COSY NMR spectrum of 28 (500 MHz, CDCl₃)
$^1$H NMR spectrum of 29 (500 MHz, CDCl$_3$)

$[^{13}C]_{D}^{26} = +170.59$
$^{13}$C NMR spectrum of 29 (125 MHz, CDCl$_3$)

$\alpha_d^{25} = +170.59$
HSQC NMR spectrum of 29 (500 MHz, 125 MHz, CDCl₃)

[α]₀²⁵ = +170.59
COSY NMR spectrum of 29 (500 MHz, CDCl₃)

COSY of Na-Me (R,R,R)-Ketone-TiPS

[α]D²⁵ = +170.59
$^1$H NMR spectrum of 30 (500 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 30 (125 MHz, CDCl$_3$)
HSQC NMR spectrum of 30 (500 MHz, 125 MHz, CDCl₃)

[α]₀²⁵ = +188.89
COSY NMR spectrum of 30 (500 MHz, CDCl₃)
\(^1\)H NMR spectrum of 31 (500 MHz, CDCl\(_3\))
$\left[\alpha\right]_D^{25} = +3.99$

$^{13}$C NMR spectrum of 31 (125 MHz, CDCl$_3$)
HSQC NMR spectrum of 31 (500 MHz, 125 MHz, CDCl₃)
COSY NMR spectrum of 31 (500 MHz, CDCl₃)
$^1$H NMR spectrum of 32 (500 MHz, CDCl$_3$)

$[^{25}\alpha]_D$ = +50.85
$[^{13}\text{C}] \nu^{25} = +50.85$

$^{13}$C NMR spectrum of 32 (125 MHz, CDCl$_3$)
HSQC NMR spectrum of 32 (500 MHz, 125 MHz, CDCl₃)
COSY NMR spectrum of 32 (500 MHz, CDCl$_3$)

COSY of $\alpha$-H (P,R,S)-alkyne

$[\alpha]_0^{25} = +50.85$
$[\alpha]_D^{25} = 17.0$

$^1$H NMR spectrum of 38 (500 MHz, CDCl$_3$)
$[\alpha]^2_{D} = +17.0$

$^{13}$C NMR spectrum of 38 (125 MHz, CDCl$_3$)
HSQC NMR spectrum of 38 (500 MHz, 125 MHz, CDCl₃)

$[\alpha]_D^{25} = +17.0$
COSY NMR spectrum of 38 (500 MHz, CDCl₃)

COSY of Nα-Me (R,R,R)-THBC

[α]D²⁵ = +17.0
$^1$H NMR spectrum of 40 (500 MHz, CDCl$_3$)
$^13$C NMR spectrum of 40 (125 MHz, CDCl$_3$)
HSQC NMR spectrum of 40 (500, 125 MHz, CDCl$_3$)

$[\alpha]_D^{25} = +3.01$
COSY NMR spectrum of 40 (500 MHz, CDCl₃)
$^1$H NMR spectrum of 42 (500 MHz, CDCl$_3$)

$[\alpha]_D^{25} = +88.14$
$^{13}$C NMR spectrum of 42 (125 MHz, CDCl$_3$)
HSQC NMR spectrum of 42 (500, 125 MHz, CDCl₃)
COSY NMR spectrum of 42 (500 MHz, CDCl$_3$)

$\alpha$D$^{26} = +88.14$