Supporting Information

Functionalization of α-hydroxyphosphonates as a convenient route to N-tosyl-α-aminophosphonates

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1. \[^1\text{H}, ^{13}\text{C}, ^{19}\text{F}, ^{31}\text{P}\] and 2D NMR Spectra of Compounds

\[^1\text{H}\] NMR of rac 1a

rac 1a

rac 1a
$^{13}$C NMR of rac 1a

rac 7a

$^1$H NMR of rac 7a

rac 7a

$^{13}$C NMR of rac 7a
$\text{F}_3\text{C}$

$\begin{array}{c}
\text{N} \\
\text{H} \\
\text{OH} \\
\text{P(O)(OEt)₂}
\end{array}$

rac 7a

$^{31}\text{P}(1\text{H})$ NMR of rac 7a

$\text{F}_3\text{C}$

$\begin{array}{c}
\text{N} \\
\text{H} \\
\text{OH} \\
\text{P(O)(OEt)₂}
\end{array}$

rac 7b

$^1\text{H}$ NMR of rac 7b
$^{13}\text{C}$ NMR of \textit{rac} 7b

$^{31}\text{P}(/^2\text{H})$ NMR of \textit{rac} 7b
H NMR of rac 8b – major rotamer

\[ \text{rac 8b} \]

\[ \text{F}_3\text{C} \]

\[ \text{Boc} \]

\[ \text{N} \]

\[ \text{OH} \]

\[ \text{P(O)(OEt)}_2 \]

C NMR of rac 8b – major rotamer

\[ \text{rac 8b} \]

\[ \text{F}_3\text{C} \]

\[ \text{Boc} \]

\[ \text{N} \]

\[ \text{OH} \]

\[ \text{P(O)(OEt)}_2 \]

\[ ^{13}\text{C NMR of rac 8b – major rotamer} \]

S6
$\text{S}$

$\text{7}$

$\text{P}$

{/$\text{1}$

$\text{H}$

$\text{NMR}$

of

$\text{rac 8b}$

$\text{1}$

$\text{H}$

$\text{NMR}$

of

$\text{rac 8b}$

$\text{b} - \text{minor rotamer}$

$\text{31P}$($\text{1H}$) $\text{NMR}$ of rac 8b – major rotamer

$\text{rac 8b}$

$\text{1H}$ $\text{NMR}$ of rac 8b – minor rotamer

$\text{S7}$
$^{13}$C NMR of rac 8b – minor rotamer

$^{31}$P/$^1$H NMR of rac 8b – minor rotamer
$^{31}P(^1H)$ NMR of rac 9a

$^1H$ NMR of rac 9b
$^{31}$P($^1$H) NMR of rac 9b

$^{13}$C NMR of rac 9b
$^1$H NMR of 11a. Mixture of 11a and 11b [1.9:1, d.r.]

$^{13}$C NMR of 11a. Mixture of 11a and 11b [1.9:1, d.r.]
$^{31}$P/$^1$H NMR of 11a and 11b [1.9:1, d.r.]

HSQC of 11a. Mixture of 11a and 11b [1.9:1, d.r.]
$^1$H NMR of 12a. Mixture of 12a and 12b [2.7:1, d.r.]

$^{13}$C NMR of 12a. Mixture of 12a and 12b [2.7:1, d.r.]
$^{31}$P/$^1$H NMR of 12a and 12b [2.7:1, d.r.]

HSQC of 12a. Mixture of 12a and 12b [2.7:1, d.r.]
$^1$H NMR of 14a. Mixture of 14a and 14b [5.4:1, d.r.]

$^{13}$C NMR of 14a. Mixture of 14a and 14b [5.4:1, d.r.]
$^{31}$P/$^1$H NMR of 14a and 14b [5.4:1, d.r.]

$^1$H NMR of 15a. Mixture of 15a and 15b [1.7:1, d.r.]
$^{13}$C NMR of 15a. Mixture of 15a and 15b [1.7:1, d.r.]

$^{31}$P($^1$H) NMR of of 15a and 15b [1.7:1, d.r.]
HSQC of 15a. Mixture of 15a and 15b [1.7:1, d.r.]

1H NMR of 16a. Mixture of 16a and 16b [10.8:1, d.r.]
$^{13}$C NMR of 16a. Mixture of 16a and 16b [10.8:1, d.r.]

$^{31}$P/$^1$H NMR of 16a. Mixture of 16a and 16b [10.8:1, d.r.]
$^{31}$P/$^{1}$H NMR of 16b

$^{1}$H NMR of 18a (3:1, r.r.)
$^{13}$C NMR of 18a (3:1, r.r.)

$^{31}$P(1H) NMR of 18a (3:1, r.r.)
$^{1}$H NMR of 18b (8.3:1, r.r.)

$^{13}$C NMR of 18b (8.3:1, r.r.)
$^3\text{P}(^1\text{H})$ NMR of 18b (8.3:1, r.r.)

$^1\text{H}$ NMR of 19a

S25
$^{13}$C NMR of 19a

$^{31}$P/$^1$H NMR of 19a
$^{1}H$ NMR of 19a and 19b [2.6:1, d.r.]

$^{13}C$ NMR of 19a and 19b [2.6:1, d.r.]
$^3$P($^1$H) NMR of 19a and 19b [2.6:1, d.r.]

HSQC of 19a and 19b [2.6:1, d.r.]
$^1$H NMR of 21a (1.8:1, r.r.)

$^{13}$C NMR of 21a (1.8:1, r.r.)
$^{31}$P/$^1$H NMR of 21a (1.8:1, r.r.)

HSQC of 21a (1.8:1, r.r.)
$^1$H NMR of rac 22

$^{13}$C NMR of rac 22
$^{31}\text{P}(^{1}\text{H})$ NMR of rac 22

$^1\text{H}$ NMR of rac 23a
$^{13}$C NMR of rac 23a

$^{31}$P($^1$H) NMR of rac 23a
$^1$H NMR of rac 23b

$^{13}$C NMR of rac 23b
$^{31}P(1^H)$ NMR of rac 23b

$^1H$ NMR of rac 24a. Mixture of rac 24a and 24b [6:1, d.r.]
\[ \text{C NMR of rac 24a. Mixture of rac 24a and 24b [6:1, d.r.]} \]

\[ \text{\( ^{31}P(\text{H}) \) NMR of rac 24a and rac 24b [6:1, d.r.]} \]
\[ ^1\text{H NMR of 26a} \]

\[ ^13\text{C NMR of 26a} \]
$^{31}\text{P}/^{1}\text{H}$ NMR of 26a

$^{1}\text{H}$ NMR of 27a
$^{13}$C NMR of 27a

$^{31}$P($^1$H) NMR of 27a
$^1$H NMR of 27b. Mixture of 27a and 27b [1:3.5, d.r.]

$^{13}$C NMR of 27b. Mixture of 27a and 27b [1:3.5, d.r.]

\[ \text{27b} \]
$^3\text{P}({}^1\text{H})$ NMR of 27b and 27a [3.5:1, d.r.]

$^1\text{H}$ NMR of 28a. Mixture of 28a and 28b [10.6:1, d.r.]
$^{13}$C NMR of 28a. Mixture of 28a and 28b [10.6:1, d.r.]

$^{31}$P($^1$H) NMR of 28a and 28b [10.6:1, d.r.]
1H NMR of 30a

13C NMR of 30a
$^3\text{P}(/	ext{^1H})$ NMR of 30a

$^1\text{H}$ NMR of 31a
$^{13}$C NMR of 31a

$^{31}$P/$^1$H NMR of 31a
$^1$H NMR of 33a (1.5:1, r.r.) and 33b (2.2:1, r.r) [4.4:1, d.r.]

$^{13}$C NMR of 33a (1.5:1, r.r.) and 33b (2.2:1, r.r) [4.4:1, d.r.]
$^{31}\text{P}(^1\text{H})$ NMR of 33a (1.5:1, r.r.) and 33b (2.2:1, r.r.) [4.4:1, d.r.]

HSQC of 33a (1.5:1, r.r.) and 33b (2.2:1, r.r.) [4.4:1, d.r.]
$^1$H NMR of rac 34a (2.5:1, r.r.) and rac 34b (4.5:1, r.r.) [3.7:1, d.r.]

$^{13}$C NMR of rac 34a (2.5:1, r.r.) and rac 34b (4.5:1, r.r.) [3.7:1, d.r.]
$^{31}\text{P}/(H)$ NMR of rac 34a (2.5:1, r.r.) and rac 34b (4.5:1, r.r.) [3.7:1, d.r.]

HSQC of rac 34a (2.5:1, r.r.) and rac 34b (4.5:1, r.r.) [3.7:1, d.r.]
H NMR of rac 36a (1.4:1, r.r.)

$^1$H NMR of rac 36a (1.4:1, r.r.)

$^{13}$C NMR of rac 36a (1.4:1, r.r.)

$^{13}$C NMR of rac 36a (1.4:1, r.r.)
$^{31}$P/$^{1}$H NMR of rac 36a (1.4:1, r.r.)

HSQC of rac 36a (1.4:1, r.r.)
H NMR of 37a (1.2:1, r.r.)

C NMR of 37a (1.2:1, r.r.)
$^{31}$P/$^1$H NMR of 37a (1.2:1, r.r.)

HSQC of 37a (1.2:1, r.r.)
H NMR of rac 38

\[ \text{CbzHN} - \text{O} - \text{P(O)(OEt)\(_2\)}} \]

rac 38

\[ \text{\( ^{1}H \) NMR of rac 38} \]

\[ \text{\( ^{13}C \) NMR of rac 38} \]
2. Crystallographic Data

Figure 1. Chain of hydrogen-bonded 4-fold screw related molecules of 10a, as seen approximately along y-direction. Hydrogen bonds are shown as thin blue lines.
Figure 2. Centrosymmetric, hydrogen-bonded dimers observed in the crystal structures of a) 9a, b) 23a, c) 34a, d) 36a, e) 38. Hydrogen bonds are shown as dashed blue lines; for 23a the dimers created by both symmetry-independent molecules are shown.

| Table 1. Crystal data and refinement details |
|---------------------------------------------|
| **Compound** | **9a** | **10a** | **23a** | **34a** | **36a** | **38** |
| Formula | C_{10}H_{21}F_{3} | C_{27}H_{34}NO | C_{22}H_{28}F_{3}N | C_{22}H_{37}N_{2} | C_{22}H_{37}N_{2}O_{8} | C_{10}H_{21}F_{3} |
| Formula | 411.31 | 467.52 | 520.49 | 524.55 | 520.56 | 411.31 |
| Crystal | triclinic | Tetragonal | triclinic | triclinic | triclinic | triclinic |
| Space | P-1 | P-1 | P-1 | P-1 | P-1 | P-1 |
| a(Å) | 9.2602(5) | 18.3893(4) | 9.4187(3) | 9.1196(7) | 11.2960(6) | 10.1589(16) |
| b(Å) | 9.4720(4) | 18.3893(4) | 11.5503(5) | 11.0522(9) | 12.0965(6) | 10.3309(11) |
| c(Å) | 11.9414(4) | 15.9702(8) | 25.4175(1) | 13.6480(1) | 12.4628(6) | 10.8732(11) |
| α(°) | 107.154(4) | 90 | 90.406(3) | 71.568(8) | 112.998(5) | 108.225(10) |
| β(°) | 96.395(3) | 90 | 99.189(3) | 77.690(7) | 110.653(4) | 112.480(12) |
| γ(°) | 95.550(4) | 90 | 113.524(4) | 87.393(6) | 98.152(4) | 90.483(10) |
| V(A³) | 985.29(8) | 5400.6(4) | 2495.13(1) | 1274.7(2) | 1387.41(16) | 990.8(2) |
| Z | 2 | 8 | 4 | 2 | 2 | 2 |
| d(Å) | 1.39 | 1.15 | 1.39 | 1.37 | 1.25 | 1.38 |
| F(000) | 428 | 2000 | 1088 | 556 | 556 | 428 |
| μ(mm⁻¹) | 0.198 | 0.132 | 0.251 | 0.236 | 0.219 | 0.197 |
| Θ range (°) | 3.27 – 3.38 – 3.22 – 3.31 – 3.37 – 3.64 – |
| Reflections collected | 17923 | 14476 | 18335 | 8392 | 16691 | 6885 |
| unique | 3448 | 5216 | 9637 | 4881 | 5328 | 3461 |
| with | 2844 | 4155 | 7875 | 3446 | 4503 | 1499 |
| R(F) | 0.074 | 0.044 | 0.041 | 0.085 | 0.059 | 0.118 |
| wR(F²) | 0.212 | 0.103 | 0.099 | 0.191 | 0.173 | 0.306 |
| R(F) [all] | 0.084 | 0.061 | 0.053 | 0.117 | 0.068 | 0.222 |
| wR(F²) [all] | 0.220 | 0.114 | 0.106 | 0.205 | 0.181 | 0.366 |
| Goodness | 1.14 | 1.03 | 1.04 | 1.02 | 1.08 | 1.03 |
| max/min | 0.68/-0.32 | 0.14/-0.17 | 0.55/-0.45 | 1.80/-1.03 | 0.70/-0.48 | 0.71/-0.35 |

| Table 2. Hydrogen bond data (Å, °) with s.u.’s in parentheses |
|---------------------------------------------|
| **D** | **H** | **A** | **D-H** | **H···A** | **D···A** | **D-H···A** |
| 8a | | | | | | |
| O10 | H10 | O2' | 0.82 | 1.85 | 2.665(4) | 173 |
| 10a | | | | | | |
| O10 | H10 | O2'' | 0.82 | 1.95 | 2.764(3) | 175 |
| 23a | | | | | | |
| N10A | H10A | O2A'''' | 0.80(2) | 1.99(2) | 2.783(2) | 175(2) |
| N10B | H10B | O2B'''' | 0.78(2) | 2.02(2) | 2.800(2) | 173(2) |
| N3 | H3N | O1'''' | 0.87(2) | 2.32(2) | 3.1049(17) | 151.5(19) |
| C3 | H3 | O13 | 1.00 | 2.29 | 3.0590(19) | 133 |
| 34a | | | | | | |
| N10 | H10 | O2'''' | 0.88 | 1.94 | 2.801(6) | 166 |
| 36a | | | | | | |
| N10 | H10 | O24'''' | 0.86 | 2.12 | 2.956(3) | 163 |

S56
|    |    |    |     |    |    |    |
|----|----|----|-----|----|-----|-----|
| N17 | H17 | O2\textsuperscript{vii} | 0.88 | 1.92 | 2.778(6) | 166 |

Symmetry codes: \( ^{i} 1-x,1-y,-z \); \( ^{ii} 3/2-y,1/2+x,1/4+z \); \( ^{iii} 2-x,1-y,-z \); \( ^{iv} -x,2-y,1-z \); \( ^{v} 1-x,1-y,2-z \); \( ^{vi} 1-x,-y,-z \); \( ^{vii} 1-x,1-y,1-z \).