Supporting Information

Introverted Brønsted Acid Cavitands

for Selective Conjugate Addition Reactions

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Dedicated to Professor François Diederich who sadly passed away on the 23rd of September 2020.

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3. 1H NMR and 13C NMR and 31P NMR spectra for all new compounds of 1•CsH5N, 1, 2•CsH5N, 2, 3•CsH5N, 3, 4•CsH5N, 4, 5, 6, and 7.

4. HRMS (ESI) data for the 1•CsH5N complex.
1. Portions of NMR spectra of $1\cdot C_5H_5N$ (Figure 1S).

Figure 1S. Portions of the spectra of $1\cdot C_5H_5N$ for (a) $^1H$ NMR (400 MHz, CD$_2$Cl$_2$, 298 K) from 3.8 to 5.9 ppm, and (b) $^{13}C$ NMR (100 MHz, CD$_2$Cl$_2$, 298 K) from 122.1 to 125.2 ppm and from 134.8 to 140.4 ppm. ●: The broad peaks of 5.58, 4.70, and 4.14 ppm correspond to 2-, 4-, and 3-positioned protons of an interior pyridine with properly integral values of 2 : 1 : 2, respectively; ■: Three kinds of carbon peaks in an encapsulated pyridine located at 139.9, 138.9, 124.1 ppm for 2-, 4-, 3-positioned carbons, respectively.
2. $^1$H NMR spectra of 1•(2-vinyl)pyridine, 2•(2-vinyl)pyridine, 3•(2-vinyl)pyridine, 4•(2-vinyl)pyridine. (Figure 2S (a)-(d)).

Compound 1•(2-vinyl)pyridine ($^1$H NMR spectrum in CDCl$_3$)

Figure 2S (a). $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1•(2-vinyl)pyridine: 8.27 (s, 2H), 7.94 (m, 2H), 7.75 (m, 2H), 7.61 (m, 2H), 7.49 (m, 4H), 7.32 (m, 4H), 7.29 (s, 2H), 7.23 (s, 2H), 6.23 (brs, 1H, C_H$_2$=CH-), 5.73 (t, $J$ = 8.0 Hz, 1H), 5.60 (t, $J$ = 8.0 Hz, 2H), 5.22 (brs, 1H, C_H$_2$=CH-), 4.92 (brs, 1H) 2.36-2.26 (m, 8H), 1.45-1.28 (m, 72H), 0.90-0.87 (m, 12H) ppm.
Compound 2•(2-vinyl)pyridine (1H NMR spectrum in CDCl3)

Figure 2S (b). 1H NMR (400 MHz, CDCl3) spectrum of 2•(2-vinyl)pyridine: 8.41 (s, 1H), 8.08 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.71 (d, J = 8.1 Hz, 1H), 7.66 (d, J = 8.1 Hz, 1H), 7.55-7.48 (m, 4H, including one proton of the pyridine ring), 7.35 (s, 1H), 7.33 (s, 1H), 7.20 (m, 2H), 7.18 (s, 1H), 7.13 (s, 1H), 7.00 (brs, 1H, CH2=CH-), 6.47 (s, 1H), 5.90 (brs, 1H, CH2=CH-), 5.73 (t, J = 8.0 Hz, 1H), 5.70 (t, J = 8.0 Hz, 1H), 5.52 (d, J = 7.2 Hz, 1H, -O-CH2-O-), 5.21 (brs, 1H, CH2=CH-), 4.79 (t, J = 8.0 Hz, 1H), 4.69 (t, J = 8.0 Hz, 1H), 4.10 (d, J = 7.2 Hz, 1H, -O-CH2-O-), 2.29-2.22 (m, 8H), 1.45-1.27 (m, 72H), 0.90-0.87 (m, 12H) ppm.
Compound 3•(2-vinyl)pyridine (1H NMR spectrum in CDCl₃)

Figure 2S (c). 1H NMR (400 MHz, CDCl₃) spectrum of 3•(2-vinyl)pyridine: 8.25 (brs, 1H, 6-positioned proton of pyridine ring), 7.89 (brs, 1H, 3-positioned proton of the pyridine ring), 7.77 (d, J = 7.8 Hz, 2H), 7.72 (d, J = 7.8 Hz, 2H), 7.52-7.44 (m, 5H, including 4-positioned proton of the pyridine ring), 7.39 (s, 2H), 7.33 (s, 2H), 7.22 (s, 2H), 7.19 (s, 2H), 7.13 (brs, 1H, 5-positioned proton of the pyridine ring), 6.90 (dd, J = 17.2, 12.4 Hz, 1H, CH₂=CH), 6.25 (d, J = 17.2 Hz, 1H, C=CH), 5.80-5.65 (br, 1H, C=CH), 5.75 (d, J = 7.4 Hz, 1H, -O-CH₂-O-), 5.69 (t, J = 8.2 Hz, 2H), 4.84 (t, J = 8.2 Hz, 1H), 4.73 (t, J = 8.2 Hz, 1H), 4.26 (d, J = 7.4 Hz, 1H, -O-CH₂-O-), 2.27 (m, 8H), 1.44-1.27 (m, 72H),
0.91-0.86 (m, 12H) ppm.
Compound 4•(2-vinyl)pyridine (1H NMR spectrum in CDCl₃)

Figure 2S (d). 1H NMR (400 MHz, CDCl₃) spectrum of 4•(2-vinyl)pyridine: 8.69 (d, J = 5.7 Hz, 1H, 6-positioned proton of the pyridine ring), 8.16 (dd, J = 7.8, 7.8 Hz, 1H, 4-positioned proton of the pyridine ring), 7.95 (d, J = 7.8 Hz, 1H, 3-positioned proton of the pyridine ring), 7.91 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.64-7.54 (m, 3H, including 5-positioned proton of the pyridine ring), 7.46 (s, 1H), 7.42 (s, 1H), 7.17 (s, 1H), 7.15 (s, 1H), 7.12 (s, 1H), 7.10 (s, 1H), 7.09 (dd, J = 14.6, 11.2 Hz, 1H, CH₂=CH⁻), 6.56 (s, 1H), 6.43 (d, J = 14.6 Hz, 1H, CH₂=CH⁻), 6.42 (s, 1H), 5.85 (d, J = 11.2 Hz, 1H, CH₂=CH⁻), 5.76 (t, J = 7.8 Hz, 1H), 5.72 (d, J = 7.2 Hz, 1H, -O-CH₂-O⁻), 5.52 (d, J = 7.2 Hz, 1H, -O-CH₂-O⁻), 4.78 (t, J = 7.8 Hz, 1H), 4.69 (t, J = 7.8 Hz, 2H), 4.45 (d, J = 7.2
Hz, 1H, -O-CH₂-O-), 4.44 (d, $J = 7.2$ Hz, 1H, -O-CH₂-O-), 2.32-2.21 (m, 8H), 1.47-1.27 (m, 72H), 0.89-0.86 (m, 12H) ppm.
3. $^1$H NMR and $^{13}$C NMR and $^{31}$P NMR spectra for all new compounds of $^1$CsH$_5$N, 1, 2•CsH$_5$N, 2, 3•CsH$_5$N, 3, 4•CsH$_5$N, 4, 5, 6, and 7.

Compound $^1$CsH$_5$N ($^1$H NMR spectrum in CD$_2$Cl$_2$)
Compound 1\(\cdot\)C\(_5\)H\(_5\)N (\(^1\)H NMR spectrum in CDCl\(_3\))
Compound 1•C₅H₅N (³¹P NMR spectrum in CDCl₃)
Compound 1•C₅H₅N (¹³C NMR spectrum in CD₂Cl₂)
Compound $\text{1} \cdot \text{C}_6\text{H}_5\text{N}$ ("$^{13}$C NMR spectrum in CDCl$_3$")
Compound free acid 1 (\(^1\)H NMR spectrum in CDCl\(_3\))
Compound free acid 1 (^{13}C NMR spectrum in CDCl₃)
Compound free acid 1 ($^{31}$P NMR spectrum in CDCl$_3$)
Compound 2•C₆H₅N (¹H NMR spectrum in CD₂Cl₂)
Compound 2·C₅H₅N (¹³C NMR spectrum in CD₂Cl₂)
Compound 2·C₅H₅N (³¹P NMR spectrum in CD₂Cl₂)

R = C₁₁H₂₃
Compound free acid 2 (\(^1\)H NMR spectrum in CD\(_2\)Cl\(_2\))
Compound free acid 2 ($^{13}$C NMR spectrum in CD$_2$Cl$_2$)
Compound free acid 2 ($^{31}$P NMR spectrum in CD$_2$Cl$_2$)
Compound 3•C₅H₅N (¹H NMR spectrum in CD₂Cl₂)
Compound 3•C₅H₅N ($^{13}$C NMR spectrum in CD$_2$Cl$_2$)
Compound 3•C₅H₅N \(^{31}\text{P NMR spectrum in CD}_2\text{Cl}_2\)
Compound free acid 3 ($^1$H NMR spectrum in CD$_2$Cl$_2$)
Compound free acid 3 ($^{13}$C NMR spectrum in CD$_2$Cl$_2$)
Compound free acid 3 (\(^{31}\)P NMR spectrum in CD\(_2\)Cl\(_2\))
Compound 4•C₅H₅N (¹H NMR spectrum in CDCl₃)
Compound 4 • C₅H₅N₁₃C NMR spectrum in CDCl₃
Compound 4•C₅H₅N (³¹P NMR spectrum in CDCl₃)
Compound free acid 4 ($^1$H NMR spectrum in CDCl$_3$)

$\delta$/ppm

$R = C_{11}H_{23}$
Compound free acid 4 ($^{13}$C NMR spectrum in CDCl$_3$)
Compound free acid 4 ($^{31}$P NMR spectrum in CDCl$_3$)

$$R = C_{11}H_{23}$$
Compound 5 ($^1$H NMR spectrum in CDCl₃)

\[ R = C_{17}H_{23} \]
Compound 5 \( (^{13}\text{C} \text{ NMR spectrum in CDCl}_3) \)
Compound 6 (\(^1\)H NMR spectrum in CDCl\(_3\))
Compound 6 ($^{13}$C NMR spectrum in CDCl$_3$)
Compound 7 (\textsuperscript{1}H NMR spectrum in CDCl\textsubscript{3})
Compound 7 ($^{13}$C NMR spectrum in CDCl$_3$)
4. HRMS (ESI) data of 1·C₅H₅N.