

Figure S1. <sup>1</sup>H NMR spectrum of S4.



Figure S2.  ${}^{13}C{}^{1}H$  NMR spectrum of S4.

Figure S3. <sup>1</sup>H NMR spectrum of S5.





**Figure S4.**  ${}^{13}C{}^{1}H$  NMR of **S5**.









Figure S7. <sup>1</sup>H NMR spectrum of S8.





Figure S8.  ${}^{13}C{}^{1}H$  NMR spectrum of S8.

**Figure S9.** Partial <sup>19</sup>F NMR spectra of the Mosher ester of *rac*-**36** (left spectrum) and the Mosher ester of (*S*)–**36** (right spectrum, 84% ee).





-71.95 -72.00 -72.05 -72.10 -72.15 -72.20 -72.25 -72.30 -72.35 -72



**Figure S10.** <sup>1</sup>H NMR spectrum of **8** in CDCl<sub>3</sub>.



Figure S11. <sup>13</sup>C NMR spectrum of 8 in CDCl<sub>3</sub>.



Figure S12. <sup>1</sup>H NMR spectrum for 12 (Table 1, entry 10) in CDCl<sub>3</sub> at 50 °C.











**Figure S15.** <sup>13</sup>C $\{^{1}H\}$  NMR of *tert*-butyl 4,4-diphenyl-2-vinyl-pyrrolidine-1-carboxylate.



**Figure S16**. <sup>1</sup>H NMR spectrum for **S20** at 60 °C.



Figure S17. <sup>13</sup>C NMR spectrum for S20 at 60 °C.



Figure S18. COSY NMR spectrum for *trans*-S20.



Figure S19. NOESY NMR spectrum for *trans*-S20.

Figure S20. <sup>1</sup>H NMR spectrum of S21.





