A squaramide-based organocatalyst as a novel versatile chiral solvating agent for carboxylic acids

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Figure S13. ^{13}C NMR (150 MHz, 40 mM, DMSO-d_6 + 2 equiv of TFA, 25 °C) spectrum of compound **I**. * Indicate resonances belonging to TFA.

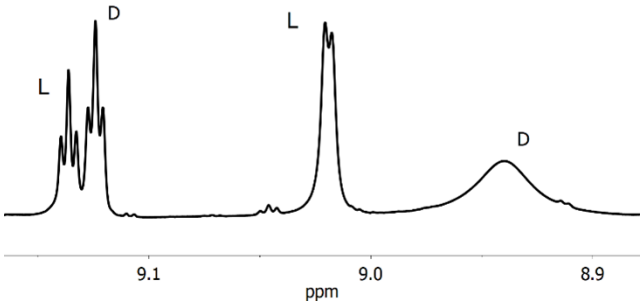

Figure S1. Spectral region of the ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) spectrum of compound **1** (10 mM) in equimolar CSA/**1**/DABCO mixture, including DNB resonances. Enantiomeric composition is 40% L- and 60% D-**1**.

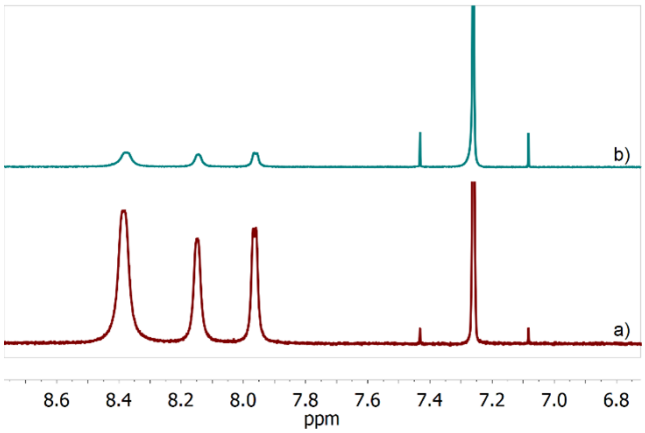

Figure S2. Spectral region of ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) spectra involving amide nuclei of substrate **4** in 1:2 mixtures of CSA/**4** with: a) [CSA]=10 mM; b) [CSA]=0.7 mM.

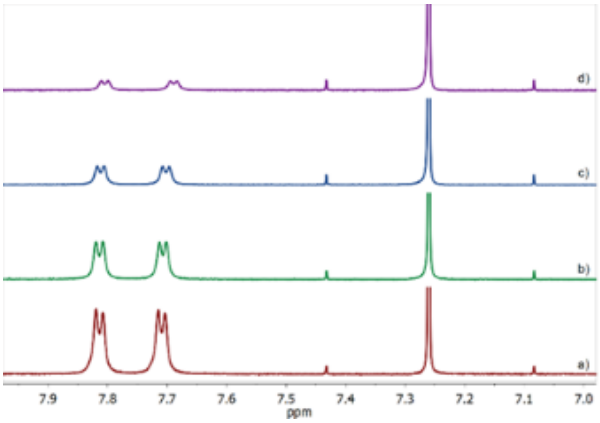

Figure S3. Spectral region of ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) spectra involving amide nuclei of substrate **7** in 1:2 mixtures of CSA/**7** with: a) [CSA]=10 mM; b) [CSA]=5 mM; c) [CSA]=2.5 mM; d) [CSA]=1.25 mM.

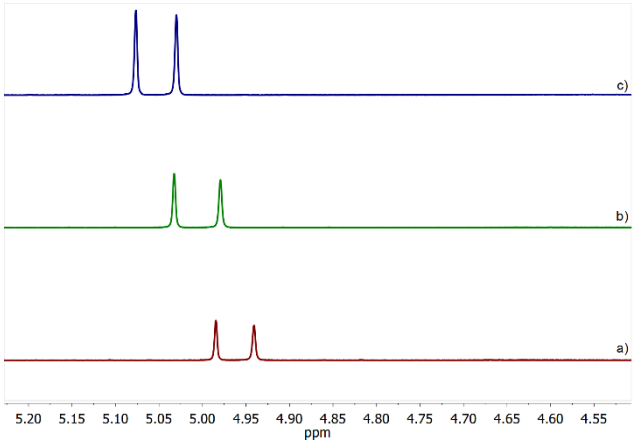

Figure S4. Spectral region of ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) spectra involving chiral methine of substrate **9** in mixtures of CSA/**9** ([CSA]=5 mM) at the following CSA/substrate molar ratios: a) 1:2; b) 1:3; c) 1:4.

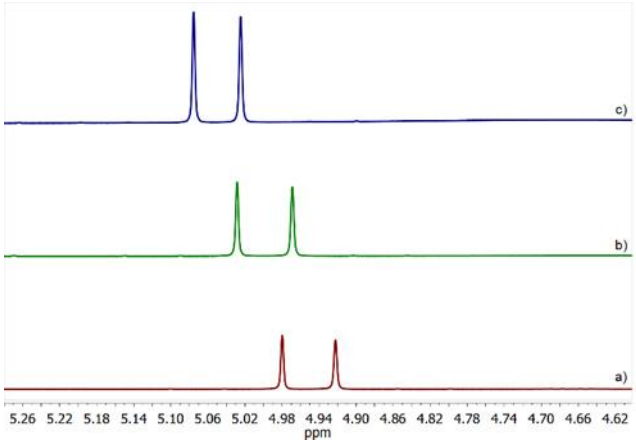

Figure S5. Spectral region of ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) spectra involving chiral methine of substrate **10** in mixtures of CSA/**10** ([CSA]=5 mM) at the following CSA/substrate molar ratios: a) 1:2; b) 1:3; c) 1:4.

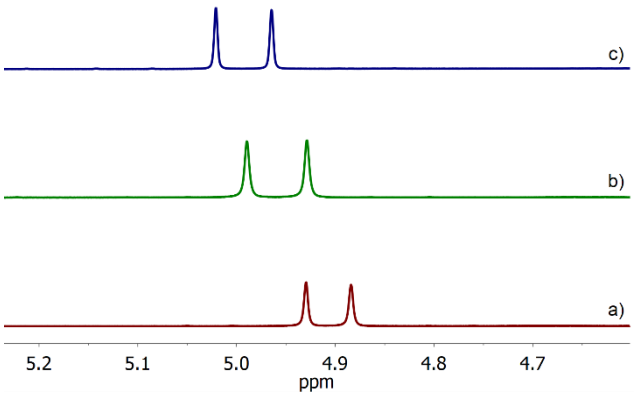

Figure S6. Spectral region of ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) spectra involving chiral methine of substrate **11** in mixtures of CSA/**11** ([CSA]=5 mM) at the following CSA/substrate molar ratios: a) 1:2; b) 1:3; c) 1:4.

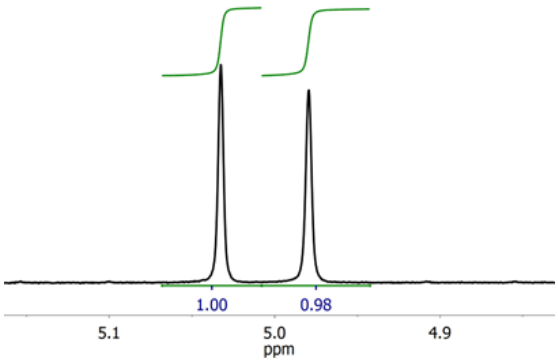

Figure S7. Spectral region of the ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) spectrum, including the chiral methine proton of substrate **9** in the presence of CSA (5 mM) at the stoichiometric ratio CSA/**9** 1:3.

Table S1. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) nonequivalences ($\Delta\Delta\delta$, ppm) for selected resonances of racemic mixtures of substrates **15**-**20** in the presence of CSA **I** at different concentrations and molar ratios.

Substrate	CSA/Substrate	Concentrations	$\Delta\Delta\delta$ (ppm)
15	1:1	CSA: 5 mM Substrate: 5 mM	CH: 0.007 CH_3: 0.001
	1:2	CSA: 5 mM Substrate: 10 mM	CH: 0.015 CH_3: 0.003
	1:3	CSA: 5 mM Substrate: 15 mM	CH: 0.005 CH_3: 0.001
	1:4	CSA: 5 mM Substrate: 20 mM	CH: 0.001
	1:2	CSA: 10 mM Substrate: 20 mM	CH: 0.019 CH_3: 0.003
	1:2	CSA: 20 mM Substrate: 40 mM	CH: 0.023 CH_3: 0.003
16	1:2	CSA: 5 mM Substrate: 10 mM	CH: 0.130 Ar-CH*o*: 0.007; Ar-CH*m*: 0.005; Ar-CH*p*: 0.003
	1:3	CSA: 5 mM Substrate: 15 mM	CH: 0.089 Ar-CH*m*: 0.002
	1:4	CSA: 5 mM Substrate: 20 mM	CH: 0.070
17	1:1	CSA: 5 mM Substrate: 5 mM	One of the diastereotopic protons of CH_2: 0.030 Ar-CH*o*: 0.026
	1:2	CSA: 5 mM Substrate: 10 mM	CH: 0.013 One of the diastereotopic protons of CH_2: 0.076 Ar-CH*o*: 0.017 COOH: 0.548* CH: 0.311* CH_2: 0.421*
	1:3	CSA: 5 mM Substrate: 15 mM	CH: 0.006 One of the diastereotopic protons of CH_2: 0.052
19	1:1	CSA: 5 mM Substrate: 5 mM	CH: 0.007 CH_3 (propyl fragment): 0 CH_3 (isopropyl fragment): 0.003
	1:2	CSA: 5 mM Substrate: 10 mM	CH: 0.012 CH_3 (propyl fragment): 0.003 CH_3 (isopropyl fragment): 0.002
	1:3	CSA: 5 mM Substrate: 15 mM	CH: 0.012 CH_3 (propyl fragment): 0.003 CH_3 (isopropyl fragment): 0
	1:4	CSA: 5 mM Substrate: 20 mM	CH: 0.009 CH_3 (propyl fragment): 0.003
20	1:2	CSA: 5 mM Substrate: 10 mM	CH: 0.003 CH_3: 0.010
	1:3	CSA: 5 mM Substrate: 15 mM	CH: 0.005 CH_3: 0.009
	1:4	CSA: 5 mM Substrate: 20 mM	CH: 0.006 CH_3: 0.008
	1:5	CSA: 5 mM Substrate: 25 mM	CH: 0.005 CH_3: 0.007
	1:4	CSA: 10 mM Substrate: 40 mM	CH: 0.010 CH_3: 0.008

*^{13}C NMR (150 MHz, $CDCl_3$, 25 °C) nonequivalences ($\Delta\Delta\delta$, ppm).

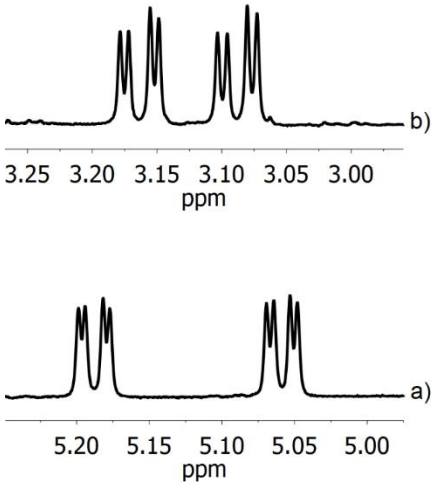

Figure S8. Spectral region of the ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) spectra, including the chiral methine of substrate **16** (a) and one of the two diastereotopic methylene protons of substrate **17** (b) in the presence of the CSA (5 mM) at CSA/substrate stoichiometric ratio of 1:2.

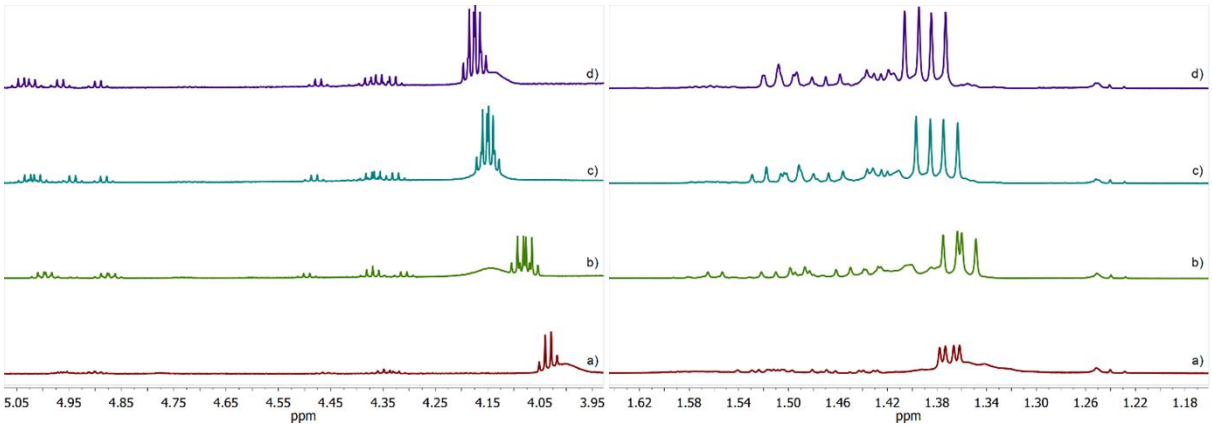

Figure S9. Spectral regions of ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) spectra, including the chiral methine (left) and methyl (right) protons of racemic mixtures of substrate **18** in the presence of the CSA (5 mM) at the following CSA/substrate stoichiometric ratios: a) 1:1; b) 1:2; c) 1:3; d) 1:4.

Table S2. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) nonequivalences ($\Delta\Delta\delta$, ppm) for selected resonances of racemic mixtures of substrates **21**-**24** in the presence of CSA **I** at different concentrations and molar ratios.

Substrate	CSA/Substrate	Concentrations	ΔΔδ (ppm)
21	1:1	CSA: 5 mM Substrate: 5 mM	CH_3 (main chain): 0.004 CH_3 (bound to CH): 0.007
	1:1	CSA: 10 mM Substrate: 10 mM	CH_3 (main chain): 0.004 CH_3 (bound to CH): 0.008
	1:2	CSA: 5 mM Substrate: 10 mM	CH_3 (main chain): 0.003 CH_3 (bound to CH): 0.004
	1:3	CSA: 5 mM Substrate: 15 mM	CH_3 (main chain): 0.002 CH_3 (bound to CH): 0.003
22	1:1	CSA: 5 mM Substrate: 5 mM	CH: 0.069 CH_3 (Ar): 0.012 CH_3 (Aliphatic chain): 0.012 CH(*meta* to CH_3 (Ar)): 0.026
	1:2	CSA: 5 mM Substrate: 10 mM	CH: superimposed signals CH_3 (Ar): 0.002 CH_3 (Aliphatic chain): 0.002 CH(*meta* to CH_3 (Ar)): 0.009
	1:3	CSA: 5 mM Substrate: 15 mM	CH: superimposed signals CH_3 (Aliphatic chain): 0.006 CH(*meta* to CH_3 (Ar)): 0.004
23	1:1	CSA: 5 mM Substrate 5 mM	CH_3(a): 0.006 CH_3(b): 0.007
	1:2	CSA: 5 mM Substrate 10 mM	CH_3(a): 0.007 CH_3(b): 0.003
	1:3	CSA: 5 mM Substrate 15 mM	CH_3(a): 0.006
24	1:1	CSA: 5 mM Substrate: 5 mM	CH: 0.025 Ar-CH*o*: 0.007; Ar-CH*m*: 0.003; Ar-CH*p*: 0.006
	1:2	CSA: 5 mM Substrate: 10 mM	CH: 0.026 Ar-CH*o*: 0.007; Ar-CH*m*: 0.003; Ar-CH*p*: 0.004
	1:3	CSA: 5 mM Substrate: 15 mM	CH: 0.025 Ar-CH*o*: 0.006; Ar-CH*m*: 0.003; Ar-CH*p*: 0.003
	1:4	CSA: 5 mM Substrate: 20 mM	CH: 0.010 Ar-CH*o*: 0.005; Ar-CH*m*: 0.002; Ar-CH*p*: 0.003
	1:5	CSA: 5 mM Substrate: 25 mM	CH: 0.009 Ar-CH*o*: 0.005; Ar-CH*m*: 0.002; Ar-CH*p*: 0.003
	1:6	CSA: 5 mM Substrate: 30 mM	CH: 0.006

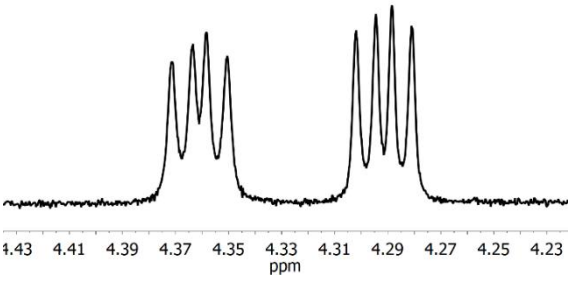

Figure S10. Spectral region of the ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) spectrum including the chiral methine proton of substrate **22** in the presence of CSA (5 mM) at equimolar ratio.

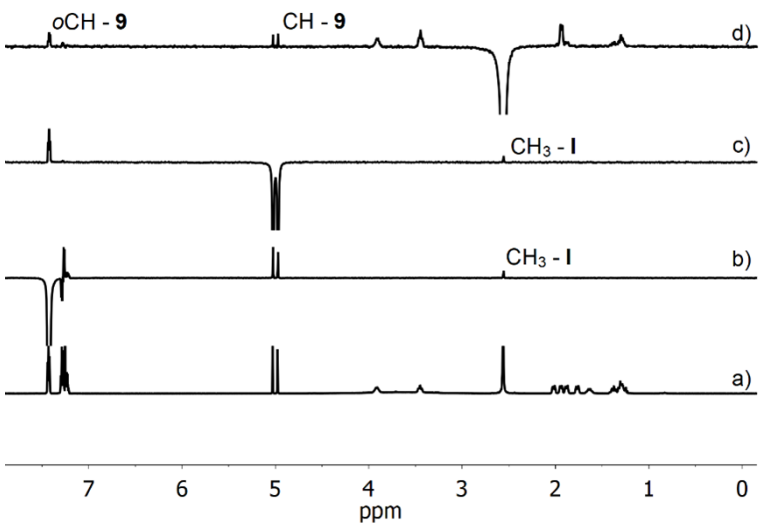

Figure S11. ^{1}H NMR (600 MHz, $CDCl_3$, 25°C) spectrum of **9/I** mixture at the composition of 1:3 ([CSA] = 5 mM) (a) and 1D ROESY (600 MHz, $CDCl_3$, 25 °C, mixing time = 500 ms) spectra of the same mixture corresponding to: b) *ortho*-CH of substrate **9**; c) CH of substrate **9**; d) CH_3 of squaramide **I**. Protons involved in intermolecular ROE effects are indicated in the spectra.

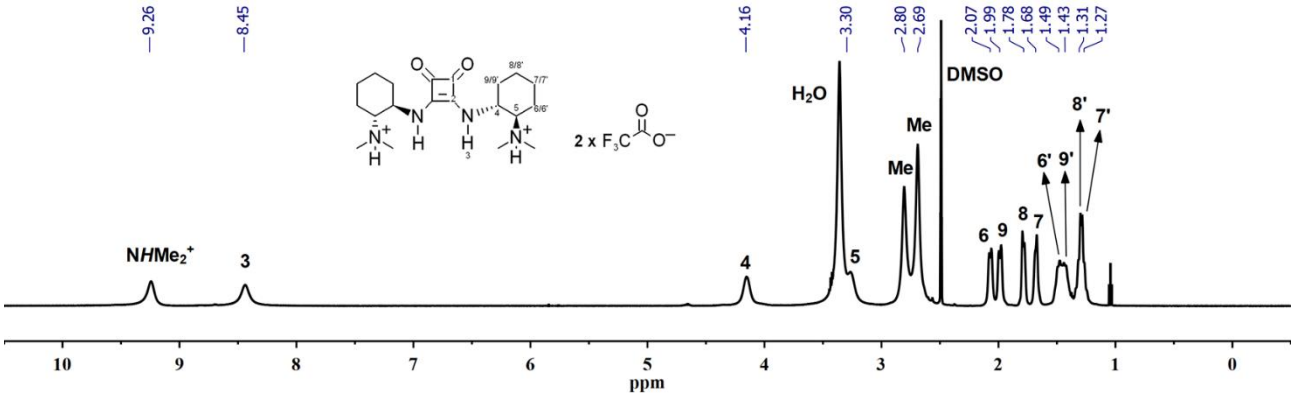

Figure S12. ^{1}H NMR (600 MHz, 40 mM, DMSO-d_6 + 2 equiv of TFA, 25 °C) spectrum of compound **I**. The apex indicates the axial proton.

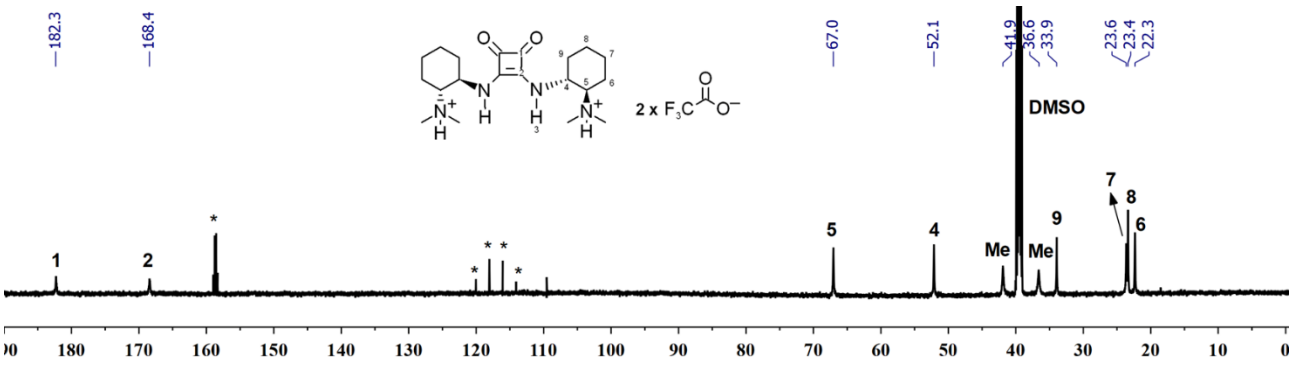

Figure S13. ^{13}C NMR (150 MHz, 40 mM, DMSO-d_6 + 2 equiv of TFA, 25 °C) spectrum of compound **I**. * Indicate resonances belonging to TFA.