

“CF₃-groups enhance critically the binding of thiourea catalysts to ketones – a NMR and FT-IR study”

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Supporting Information

¹H-NMR spectra of 4CF-DPTU + 1,3-Diphenyl-2-propenone mixtures in DCM

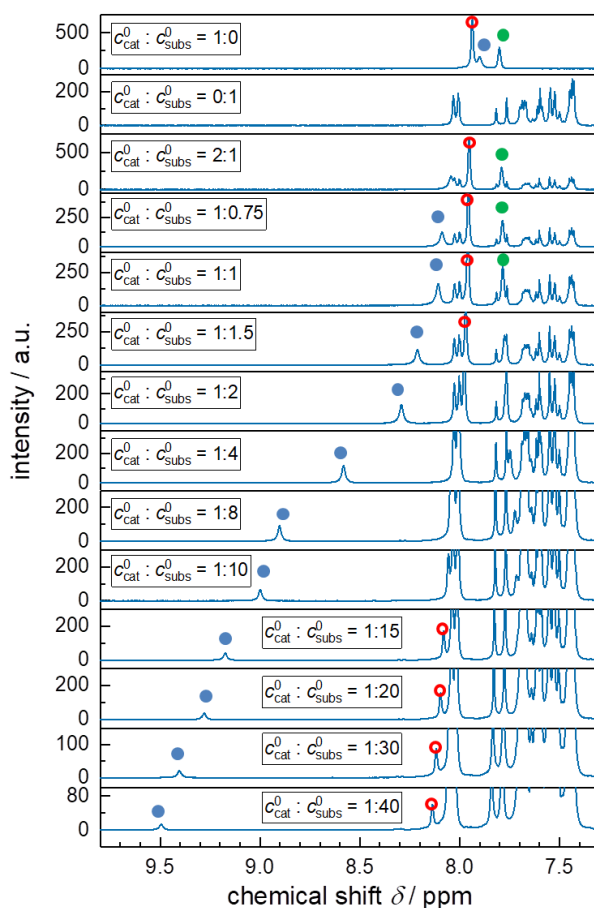


Figure S1: ¹H-NMR spectra for 4CF-DPTU (cat) and 1,3-Diphenyl-2-propenone (subs) mixtures in DCM. The chemical shift of the NH-, the ortho- and the para-proton of 4CF-DPTU are marked with a blue circle (NH), red circle (ortho) and green circle

(para), respectively. The change of chemical shift of the ortho- and para protons is less pronounced than for the NH proton.

Association constants from the chemical shift of the ortho- and para protons of 4CF-DPTU and ^{13}C chemical shifts of 1,3-diphenyl-2-propenones C=O group

In Figure S2 we show the ^{13}C chemical shift of the carbonyl carbon atom of the substrate with varying substrate concentration c_{subs}^0 for a solution of 0.01 mol/L 4CF-DPTU in DCM. We find the variation of the chemical shift to be consistent with the association equilibria as extracted from the ^1H -NMR results (Figure 2 of the main manuscript): Using $K_{\text{NMR}}(4\text{CF-DPTU,DCM}) = 15.8 \text{ L/mol}$ the experimental ^{13}C data can be excellently described using eq S1:

$$\delta = \delta_{\text{subs}} \frac{[\text{subs}]}{c_{\text{subs}}^0} + \delta_{\text{complex}} \frac{[\text{complex}]}{c_{\text{subs}}^0} \quad (\text{S1})$$

with $\delta_{\text{subs}}=190.57 \text{ ppm}$ and $\delta_{\text{complex}}=196.76 \text{ ppm}$.

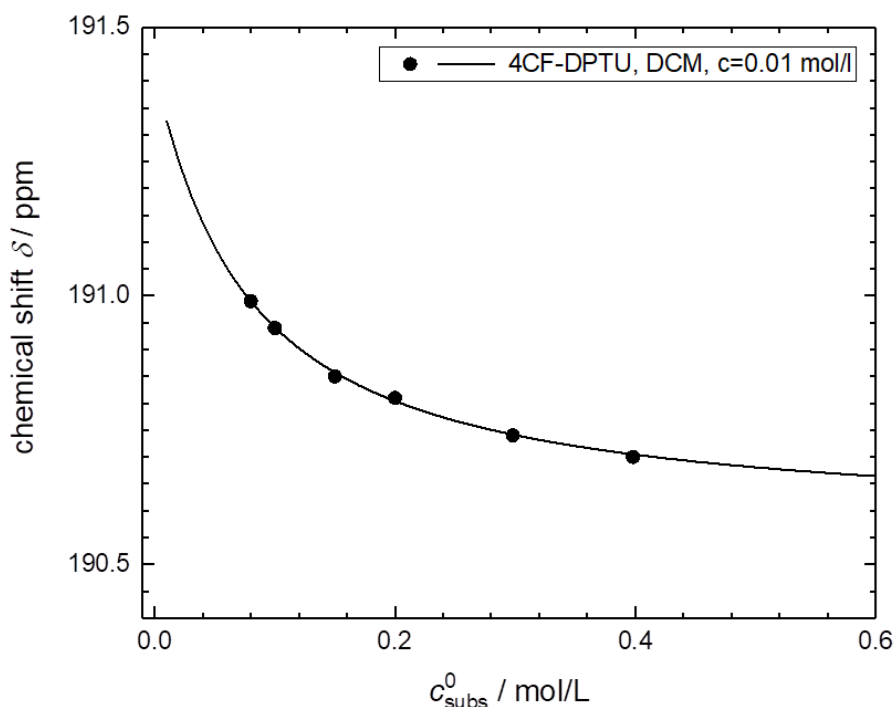


Figure S2: ^{13}C Chemical Shift of the carbon of the carbonyl group of the substrate as a function of substrate concentration c_{subs}^0 . Solutions in DCM contained a constant concentration of 0.01 mol/L 4CF-DPTU. The symbols represent the experimental data and the solid lines show the association model (eq. 1 and eq. S1) with a fixed value of $K_{\text{NMR}} = 15.8 \text{ L/mol}$.

Similar to our analysis of the chemical shift of the NH proton in the main manuscript, the variation of the ortho- and the para-protons of 4CF-DPTU with substrate concentration can be used to extract the association equilibria. In analogy to the analysis shown in Figure 2 of the main manuscript, we also extract K values from these data. Using the ortho-proton we find $K = 16.6 \text{ L/mol}$, in excellent agreement with the value extracted from the NH protons (Figure S3). The para-proton, which is most distant from the hydrogen-bonding NH group, exhibits the least variation of the chemical shift. From this variation we extract (Figure S3) $K = 25.3 \text{ L/mol}$, which is somewhat higher than the value extracted from the ortho- and the NH protons. Given the low sensitivity of the chemical shift of the para-protons to intermolecular binding, this value is still consistent with the association constants determined from the chemical shifts of the ortho- and the NH-proton.

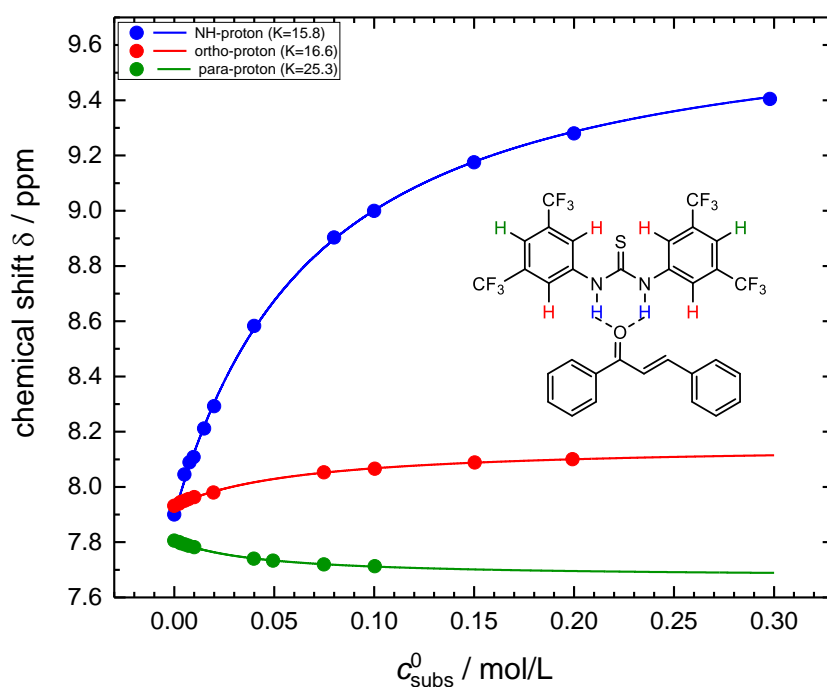


Figure S3. Chemical shift of the NH protons (blue), ortho-protons (red) and para-protons (green) as a function of substrate concentration, c_{subs}^0 for 4CF-DPTU at a constant catalyst concentration ($c_{\text{cat}}^0 = 0.01 \text{ mol/L}$) in the solvent DCM. Solid lines show fits with the association model (eq. 2).

Background subtraction from FT-IR spectra

In Figure 3 of the main manuscript, we show FT-IR spectra corrected for background absorption due to the solvent and due to the substrate. The raw spectra (before subtraction) are shown in Fig. S4. To account for the background, we subtract the spectrum of the solvent from all samples.

The FT-IR spectra of the pure substrate (blue dashed-dotted line in Figure S4) reveals a structured absorption at the frequencies characteristic to the NH stretching band of thiourea. To remove these contributions, we subtract a concentration weighted infrared spectrum at a high substrate concentration from the sample spectra. All spectra are additionally corrected for a constant offset due to reflection losses.

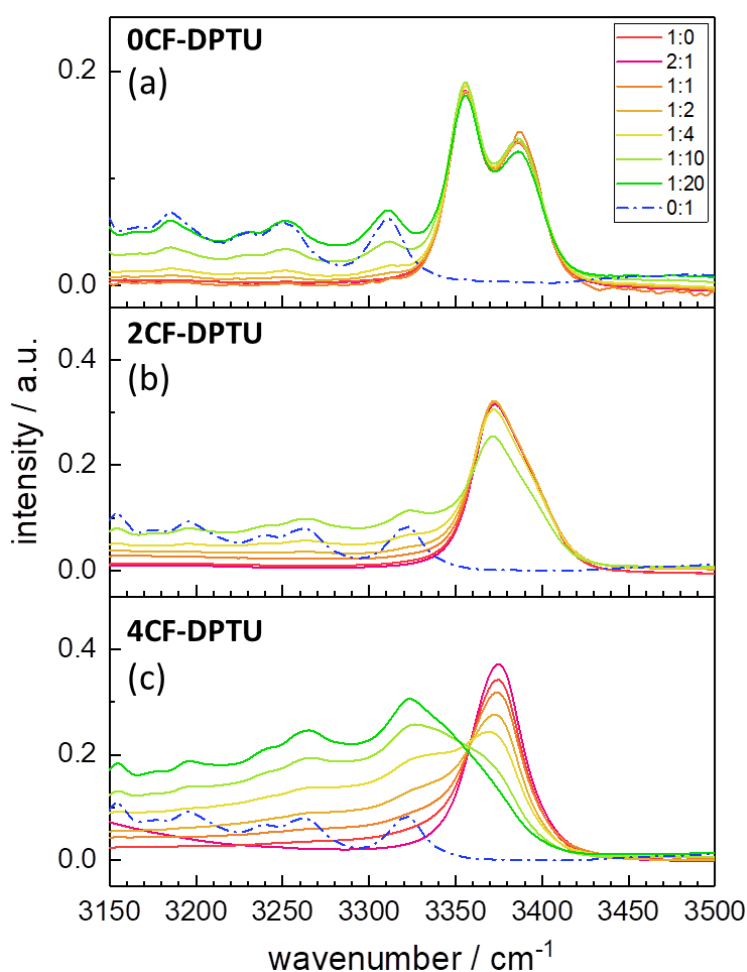


Figure S4. Raw FT-IR spectra of the catalysts 0CF-DPTU (a), 2CF-DPTU (b) and 4CF-DPTU (c) upon association with the substrate in DCM. Solutions of only the substrate in DCM (blue dashed-dotted) exhibit a structured absorption overlapping with the frequency range, where we observe the hydrogen-bonded NH-stretching vibration.

Degree of association from IR spectra

From the analysis in Figure 4 of the main manuscript, we obtain the extinction coefficient of both, ε_{cat} and $\varepsilon_{\text{complex}}$. Accordingly, the degree of association, α , can be determined from both the absorbance of the catalyst-substrate complexes (eq 6 of the main manuscript) or the absorbance of the free catalyst $\alpha = \frac{c_{\text{cat}}^0 - [\text{cat}]}{c_{\text{cat}}^0}$. As can be seen from Figure S5, both values agree very well and yield very similar association constants.

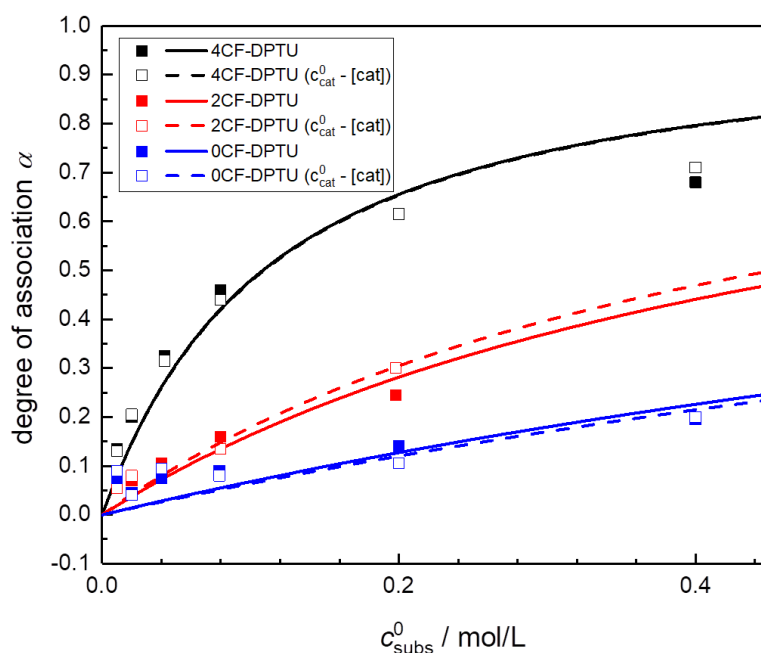


Figure S5: Degree of association, α , as obtained from the IR experiments for 4CF-DPTU (black symbols), 2CF-DPTU (red symbols) and 0CF-DPTU (blue symbols) in DCM ($c_{\text{cat}}^0 = 0.02 \text{ mol/L}$). Solid lines show fits using the bimolecular association model (eq 1, main manuscript) to $\alpha = \frac{[\text{complex}]}{c_{\text{cat}}^0}$ values (filled symbols) and dashed lines show fits to $\alpha = \frac{c_{\text{cat}}^0 - [\text{cat}]}{c_{\text{cat}}^0}$ values (open symbols). Note, that in case of 4CF-DPTU the two fits overlap.

Vibrational spectra of catalyst-substrate complexes

To isolate the vibrational spectra of the catalyst-substrate complexes, we subtract scaled spectra of the neat catalyst in solution from the spectrum with a molar ratio of catalyst:substrate (1:10) such that the absorbance at $>3400\text{cm}^{-1}$ remains positive. These spectra for 0CF-DPTU (blue), 2CF-DPTU (red) and 4CF-DPTU (black) are shown in Figure S5 and reveal that the band shape of the catalyst-substrate

complexes is quite similar for the three catalysts. The similarity suggests that the strength of the hydrogen-bonds of the catalyst is comparable.

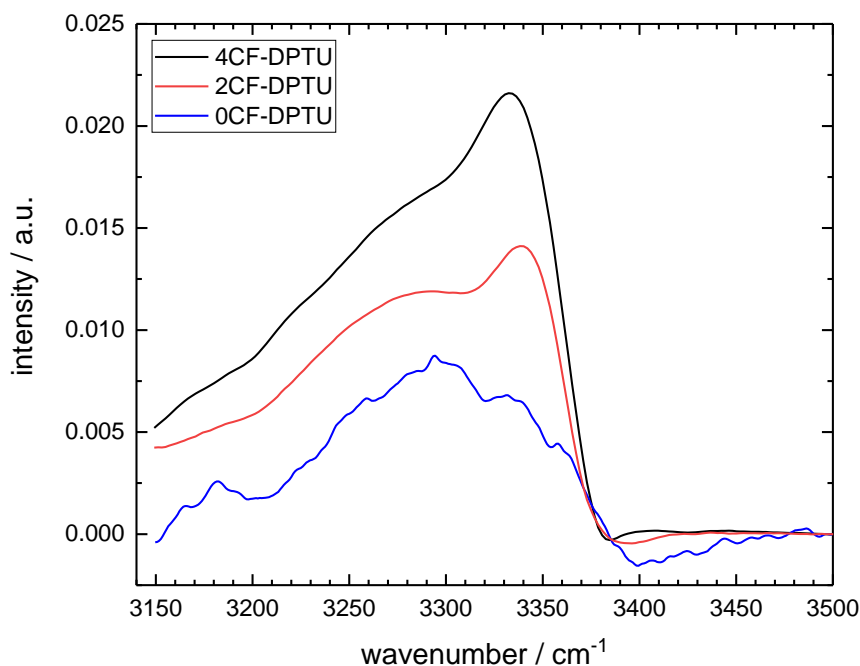


Figure 6: FT-IR spectra of the catalyst-substrate complex with 4CF-DPTU (black), 2CF-DPTU (red) and 0CF-DPTU (blue) for a molar ratio of catalyst:substrate (1:10). For details see text.

Association equilibria as obtained from NMR in toluene

The change of the chemical shift of the NH-proton of 4CF-DPTU (black), 2CF-DPTU (red) and 0CF-DPTU (blue) as a function of increasing substrate concentration c_{subs}^0 in the solvent toluene is shown in Figure S7. The largest variation of the chemical shift is observed for 4CF-DPTU and the smallest change for 0CF-DPTU. The association model fit (eq. 1 and eq. 2 of the main manuscript, solid lines in Figure S7) yields $K_{\text{NMR}}(4\text{CF-DPTU}) = 27.7 \pm 1.3 \text{ L/mol}$, $K_{\text{NMR}}(2\text{CF-DPTU}) = 2.98 \pm 0.1 \text{ L/mol}$, and $K_{\text{NMR}}(0\text{CF-DPTU}) = 1.65 \pm 0.2 \text{ L/mol}$ and the chemical shift of the complex as $\delta_{\text{complex}}(4\text{CF-DPTU}) = 9.54 \pm 0.04 \text{ ppm}$, $\delta_{\text{complex}}(2\text{CF-DPTU}) = 10.46 \pm 0.03 \text{ ppm}$ and $\delta_{\text{complex}}(0\text{CF-DPTU}) = 8.89 \pm 0.07 \text{ ppm}$, respectively. The measured chemical shifts of the free catalyst, which are used for the fit are $\delta_{\text{cat}}(4\text{CF-DPTU}) = 6.59 \text{ ppm}$, $\delta_{\text{cat}}(2\text{CF-DPTU}) = 6.98 \text{ ppm}$ and $\delta_{\text{cat}}(0\text{CF-DPTU}) = 7.77 \text{ ppm}$. Note, that for 2CF-DPTU the signal of the NH overlaps with the solvent peak at 6.98 ppm and we thus take this value as δ_{cat} .

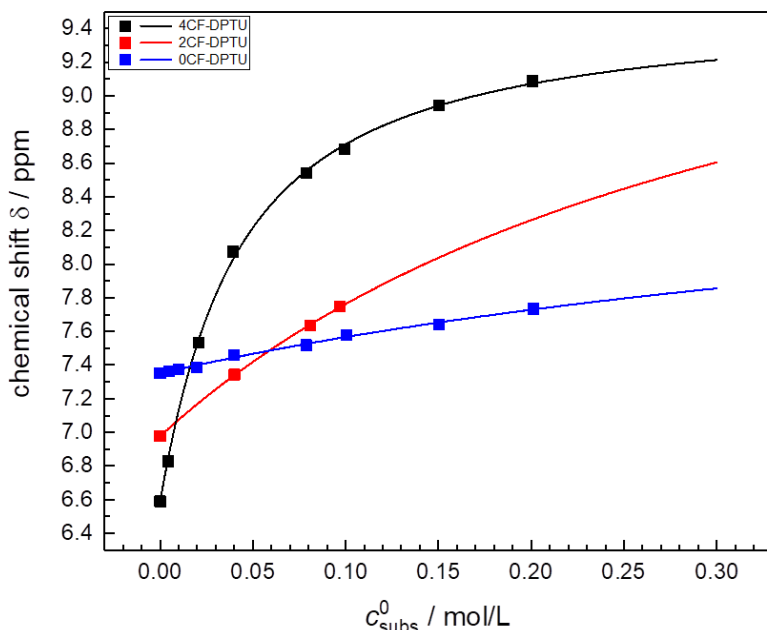


Figure S7. Chemical shift of the NH proton as a function of substrate concentration, c_{subs}^0 for 4CF-DPTU (black symbols), 2CF-DPTU (red symbols), and 0CF-DPTU (blue-symbols) at a constant catalyst concentration ($c_{\text{cat}}^0 = 0.01 \text{ mol/L}$) in the solvent toluene. Solid lines show fits with the association model (eq. 1 and 2 of the main manuscript).

NMR and FT-IR spectra of 4CF-DPTU + 1,3-Diphenyl-2-propenone in ACN

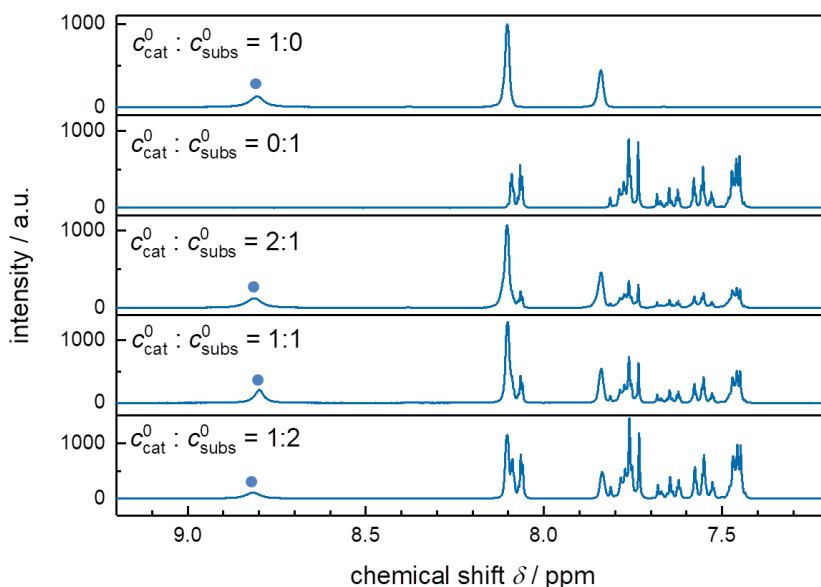


Figure S8: $^1\text{H-NMR}$ spectra for 4CF-DPTU (cat) and 1,3-Diphenyl-2-propenone (subs) mixtures in ACN. The chemical shift of the NH protons (blue circle) at $\sim 8.8\text{ppm}$ is found independent of substrate concentration, indicating no appreciable association of the catalyst with the substrate.

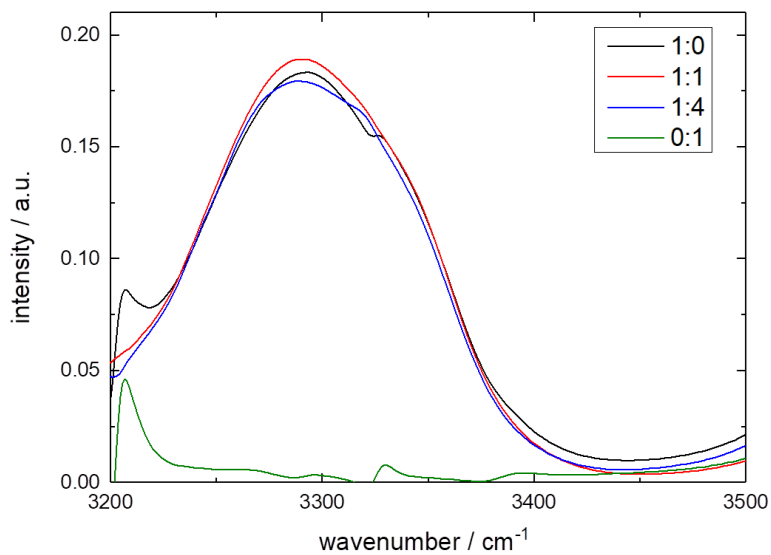


Figure S9: Infrared absorption spectra for solutions of $c_{\text{cat}}^0 = 0.02 \text{ mol/L}$ 4CF-DPTU (cat) in ACN for different DPTU:substrate (1,3-Diphenyl-2-propenone) ratios.