Supporting Information

Thiourea catalysed reduction of α-keto substituted acrylate compounds using Hantzsch ester as reducing agent in water

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General Methods: All starting materials were of the commercially available (analytical grade) and used without further purification. All the solvents are used after redistillation. Reactions were monitored by thin layer chromatography using silica gel HSGF254 plates. Flash chromatography was performed using silica gel HG/T2354-92. Melting points were measured with SGW X-4 melting point apparatus. \textsuperscript{1}H NMR (400 MHz) spectra were recorded in CDCl\textsubscript{3} or DMSO. \textsuperscript{1}H NMR chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constants (Hz) and integration. \textsuperscript{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard. Chemical yields refer to pure isolated substances. All products were prepared according to the general procedure. Products 6a-6g, 6k-6s, 6u-6z are known compounds and their \textsuperscript{1}H NMR data matched the literature data\textsuperscript{[1-10]}.

General experimental procedures for preparing of Cat 1-6:

\[
\text{R}^\text{1}\text{NH}_2 + \text{F}_3\text{C}-\text{NC}_\text{S} \rightarrow \text{R}^\text{2}\text{NH} + \text{F}_3\text{C}-\text{SCF}_3
\]

Under an argon atmosphere, to a solution of 3,5-bis(trifluoromethyl)aniline (2 mmol) in THF (5 mL), n-BuLi (2.4 mmol) was added slowly at -78\textdegree C. After stirring for 15 minutes, the reaction mixture was then allowed to warm to room temperature and stirring for another 15 minutes, a solution of isothiocyanate (2.2 mmol) in THF (2 mL) was added dropwise, stirred at room temperature overnight. The products was purified by a flash chromatography on silica gel.

Experimental procedure for preparing of Cat 7:

\[
\text{Ph}_2\text{NH} + \text{CH}_3\text{SO}_2\text{Cl} \rightarrow \text{Ph}_2\text{NH} + \text{CH}_3\text{SO}_2\text{Cl}
\]

To a stirred solution of (1R,2S)-2-amino-1,2-diphenylethanol (1 mmol) and triethylamine (1.2 mmol) in DCM (3 mL), methanesulfonyl chloride (1.1 mmol) was added dropwise. The reaction mixture was stirred for 12h at room temperature. The product was purified by a flash chromatography on silica gel.

Experimental procedure for preparing of Cat 8:
To a stirred solution of (1R,2S)-2-amino-1,2-diphenylethanol (1 mmol) and triethylamine (1.2 mmol) in DCM (3 mL), trifluoromethanesulfonic anhydride (1 mmol) was added dropwise at room temperature. The reaction mixture was stirred overnight under room temperature. The product was purified by a flash chromatography on silica gel.

**General procedure for preparation of α-keto substituted acrylate compounds 5:**

\[
\begin{align*}
\text{Cat 2} & \quad \text{H}_2\text{O}, 100^\circ \text{C}, 24 \text{h} \\
\end{align*}
\]

The mixture of β-Keto esters (10 mmol), aromatic aldehyde (12 mmol) and proline (2 mmol) in EtOH (40 mL) was stirred at room temperature for 2d. The solvent was removed under reduced pressure. The product was purified by a flash chromatography on silica gel.

**General procedure for synthesis of α-alkyl-β-ketoesters:**

\[
\begin{align*}
\text{Cat 2} & \quad \text{H}_2\text{O}, 100^\circ \text{C}, 24 \text{h} \\
\end{align*}
\]

The 5 (0.2 mmol), dihydropyridine esters (0.24 mmol) and catalyst (0.04 mmol) were refluxed at 100°C in H₂O (2 mL) for 24 hours. After the reaction mixtures were cooled to room temperature, the crude solution was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were washed with brine and dried over anhydrous Na₂SO₄. After removal of solvents under reduced pressure, the residue was purified through column chromatograph on silica gel to give the pure products.

**The gram-scale synthesis of ethyl 2-benzyl-3-oxo-3-phenylpropanoate:**

\[
\begin{align*}
\text{Cat 2} & \quad \text{H}_2\text{O}, 100^\circ \text{C}, 24 \text{h} \\
\end{align*}
\]

The 5a (4 mmol, 1.12g), dihydropyridine esters (4.8 mmol, 1.01g) and catalyst 2 (0.8 mmol, 387mg) were refluxed at 100°C in H₂O (30mL) for 24 hours. After the reaction mixtures were cooled to room temperature, the crude solution was extracted with ethyl acetate (3 x 50 mL). The combined organic layers were washed with brine and dried over anhydrous Na₂SO₄. After removal of solvents under reduced pressure, the residue was purified through column chromatograph on silica gel to give the pure products.
ethyl 2-benzyl-3-oxo-3-phenylpropanoate (6a): The crude mixture was purified by column chromatography to yield 6a as light yellow liquid with 93% yield. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.96 (d, $J = 7.98$ Hz, 2H), 7.56 (t, $J = 7.26$ Hz, 1H), 7.45 (d, $J = 7.50$ Hz, 2H), 7.23 - 7.27 (m, 5H), 7.19 (t, $J = 7.08$ Hz, 1H), 4.62 (t, $J = 7.26$ Hz, 1H), 4.11 (q, $J = 6.96$ Hz, 2H), 3.30 - 3.37 (m, 2H), 1.11 (t, $J = 7.02$ Hz, 3H).

ethyl 2-(4-methylbenzyl)-3-oxo-3-phenylpropanoate (6b): The crude mixture was purified by column chromatography to yield 6b as colorless liquid with 88% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.98 - 8.00 (m, 2H), 7.59 - 7.60 (m, 1H), 7.48 (m, 2H), 7.14 (d, $J = 8.0$ Hz, 2H), 7.09 (d, $J = 7.92$ Hz, 2H), 4.63 (t, $J = 7.28$ Hz, 1H), 4.09 - 4.17 (m, 2H), 3.30 - 3.33 (m, 2H), 2.31 (s, 3H), 1.15 (t, $J = 7.12$ Hz, 3H).

ethyl 2-(4-methoxybenzyl)-3-oxo-3-phenylpropanoate (6c): The crude mixture was purified by column chromatography to yield 6c as colorless liquid with 76% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.98 (d, $J = 7.56$ Hz, 2H), 7.58 (t, $J = 7.36$ Hz, 1H), 7.47 (t, $J = 7.84$ Hz, 2H), 7.17 (d, $J = 8.56$ Hz, 2H), 6.81 (d, $J = 8.60$ Hz, 2H), 4.60 (t, $J = 7.32$ Hz, 1H), 4.12 (q, $J = 7.16$ Hz, 2H), 3.78 (s, 3H), 3.29 (dd, $J = 2.28$, 7.64 Hz, 2H), 1.14 (t, $J = 7.12$ Hz, 3H).

ethyl 2-(4-bromobenzyl)-3-oxo-3-phenylpropanoate (6d): The crude mixture was purified by column chromatography to yield 6d as colorless liquid with 94% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.99 - 7.96 (m, 2H), 7.60 (t, $J = 7.36$ Hz, 1H), 7.48 (t, $J = 7.92$ Hz, 2H), 7.39 - 7.41 (m, 2H), 7.13 (d, $J = 8.36$ Hz, 2H), 4.60 (t, $J = 7.36$ Hz, 1H), 4.07 - 4.16 (m, 2H), 3.30 (d, $J = 7.36$ Hz, 2H), 1.14 (t, $J = 7.12$ Hz, 3H).
ethyl 2-(4-fluorobenzyl)-3-oxo-3-phenylpropanoate (6e): The crude mixture was purified by column chromatography to yield 6e as colorless liquid with 90% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.98 - 7.96 (m, 2H), 7.61 - 7.57 (m, 1H), 7.49 - 7.46 (m, 2H), 7.24 - 7.20 (m, 2H), 6.99 - 6.93 (m, 2H), 4.60 (t, \(J = 7.36\) Hz, 1H), 4.18 - 4.08 (m, 2H), 3.32 (d, \(J = 7.40\) Hz, 2H), 1.14 (t, \(J = 7.12\) Hz, 3H).

ethyl 2-(4-chlorobenzyl)-3-oxo-3-phenylpropanoate (6f): The crude mixture was purified by column chromatography to yield 6f as colorless liquid with 92% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.97 (d, \(J = 7.24\) Hz, 2H), 7.60 (t, \(J = 7.36\) Hz, 1H), 7.48 (t, \(J = 7.92\) Hz, 2H), 7.26 (t, \(J = 8.48\) Hz, 2H), 7.19 (d, \(J = 8.48\) Hz, 2H), 4.60 (t, \(J = 7.36\) Hz, 1H), 4.16 - 4.08 (m, 2H), 3.31 (d, \(J = 7.36\) Hz, 2H), 1.14 (t, \(J = 7.12\) Hz, 3H).

ethyl 2-(4-nitrobenzyl)-3-oxo-3-phenylpropanoate (6g): The crude mixture was purified by column chromatography to yield 6g as light yellow liquid with 90% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.14 (d, \(J = 8.68\) Hz, 2H), 7.99 - 7.97 (m, 2H), 7.61 (t, \(J = 7.48\) Hz, 1H), 7.51 - 7.42 (m, 4H), 4.66 (t, \(J = 7.36\) Hz, 1H), 4.15 - 4.11 (m, 2H), 3.45 (d, \(J = 7.48\) Hz, 2H), 1.14 (t, \(J = 7.12\) Hz, 3H).

ethyl 2-(3-nitrobenzyl)-3-oxo-3-phenylpropanoate (6h): The crude mixture was purified by column chromatography to yield 6h as light yellow liquid with 86% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)): 8.15 (s, 1H), 8.09 (d, \(J = 8.16\) Hz, 1H), 7.99 (d, \(J = 7.32\) Hz, 2H), 7.61 (t, \(J = 7.40\) Hz, 2H), 7.51 - 7.44 (m, 3H), 4.67 (t, \(J = 7.40\) Hz, 1H), 4.13 (q, \(J = 7.12\) Hz, 2H), 3.45 (d, \(J = 7.40\) Hz, 2H), 1.14 (t, \(J = 7.12\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 193.6, 168.7, 148.3, 140.5, 135.8, 135.5, 133.8, 129.4, 128.8, 128.6, 123.8, 121.9, 61.9, 55.6, 34.2, 13.9.
ethyl 2-(2-nitrobenzyl)-3-oxo-3-phenylpropanoate (6i): The crude mixture was purified by column chromatography to yield 6i as light yellow liquid with 83% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.01 - 7.97 (m, 3H), 7.60 - 7.37 (m, 6H), 4.94 (t, $J = 7.68$ Hz, 1H), 4.19 - 4.06 (m, 2H), 3.68 - 3.55 (m, 2H), 1.11 (t, $J = 7.12$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): 194.3, 168.9, 149.2, 136.1, 133.7, 133.6, 133.5, 128.7, 128.1, 125.1, 61.6, 54.2, 32.5, 13.9.

ethyl 2-(naphthalen-2-ylmethyl)-3-oxo-3-phenylpropanoate (6j): The crude mixture was purified by column chromatography to yield 6j as light yellow liquid with 93% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.08 (d, $J = 8.40$ Hz, 1H), 7.92 - 7.87 (m, 3H), 7.74 (d, $J = 7.92$ Hz, 1H), 7.59 - 7.50 (m, 3H), 7.57 - 7.47 (m, 2H), 7.43 - 7.34 (m, 4H), 4.84 (t, $J = 7.16$ Hz, 1H), 4.13 - 4.08 (m, 2H), 3.86 (d, $J = 7.16$ Hz, 2H), 1.11 (t, $J = 7.12$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): 194.7, 169.5, 136.3, 134.2, 133.9, 133.5, 131.7, 129.0, 128.6, 127.5, 127.4, 126.2, 125.6, 125.4, 123.3, 61.6, 54.9, 31.7, 13.9.

ethyl 2-(furan-2-ylmethyl)-3-oxo-3-phenylpropanoate (6k): The crude mixture was purified by column chromatography to yield 6k as colorless liquid with 88% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.02 - 8.00 (m, 2H), 7.62 - 7.59 (m, 1H), 7.50 - 7.47 (m, 2H), 7.30 - 7.29 (m, 1H), 6.26 - 6.25 (m, 1H), 6.08 - 6.07 (m, 1H), 4.77 (t, $J = 7.24$ Hz, 1H), 4.18 - 4.12 (m, 2H), 3.44 - 3.32 (m, 2H), 1.17 (t, $J = 7.12$ Hz, 3H).

ethyl 3-oxo-3-phenyl-2-(thiophen-2-ylmethyl)propanoate (6l): The crude mixture was purified by column chromatography to yield 6l as colorless liquid with 77% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.01 (d, $J = 7.24$ Hz, 2H), 7.60 (t, $J = 7.36$ Hz, 1H), 7.48 (t, $J = 7.88$ Hz, 2H), 7.12 (d, $J = 1.16$ Hz, 1H), 6.90 - 6.86 (m, 2H), 4.68 (t, $J = 7.20$ Hz, 1H), 4.16 - 4.13 (m, 2H), 3.59 - 3.56 (dd, $J = 3.72$, 7.28 Hz, 2H), 1.17 (t, $J = 7.12$ Hz, 3H).

ethyl 2-benzyl-3-oxo-3-(p-tolyl)propanoate (6m): The crude mixture was
purified by column chromatography to yield 6m as colorless liquid with 87% yield. 1H NMR (400 MHz, CDCl3): δ 7.89 (d, J=8.12 Hz, 2H), 7.31-7.22 (m, 7H), 4.62 (t, J=7.32 Hz, 1H), 4.14-4.09 (m, 2H), 3.34 (dd, J=4.56, 7.64 Hz, 2H), 2.42 (s, 3H), 1.14 (t, J=7.12 Hz, 3H).

ethyl 2-benzyl-3-(4-methoxyphenyl)-3-oxopropanoate (6n): The crude mixture was purified by column chromatography to yield 6n as colorless liquid with 82% yield. 1H NMR (400 MHz, CDCl3): δ 7.99 - 7.97 (m, 2H), 7.29 - 7.23 (m, 5H), 6.95 - 6.93 (m, 2H), 4.60 (t, J = 7.24 Hz, 1H), 4.13 - 4.10 (m, 2H), 3.88 (s, 3H), 3.35 - 3.29 (m, 2H), 1.15 (t, J=7.12 Hz, 3H).

ethyl 2-benzyl-3-(4-bromophenyl)-3-oxopropanoate (6o): The crude mixture was purified by column chromatography to yield 6o as colorless liquid with 90% yield. 1H NMR (400 MHz, CDCl3): δ 7.83 (d, J= 8.56 Hz, 2H), 7.60 (d, J= 8.56 Hz, 2H), 7.30 - 7.21 (m, 5H), 4.58 (t, J= 7.36 Hz, 1H), 4.16 - 4.09 (m, 2H), 3.34 (dd, J= 1.60, 7.48 Hz, 2H), 1.14 (t, J= 7.12 Hz, 3H).

ethyl 2-benzyl-3-(4-fluorophenyl)-3-oxopropanoate (6p): The crude mixture was purified by column chromatography to yield 6p as colorless liquid with 95% yield. 1H NMR (400 MHz, CDCl3): δ 8.03 - 7.99 (m, 2H), 7.30 - 7.18 (m, 5H), 7.13 (t, J = 7.36 Hz, 2H), 4.60 (t, J = 7.2 Hz, 1H), 4.17 - 4.09 (m, 2H), 3.39 - 3.30 (dd, J= 2.84, 7.44 Hz, 2H), 1.14 (t, J= 7.12 Hz, 3H).

ethyl 2-benzyl-3-(4-chlorophenyl)-3-oxopropanoate (6q): The crude mixture was purified by column chromatography to yield 6q as colorless liquid with 92% yield. 1H NMR (400 MHz, CDCl3): δ 7.91 (d, J= 8.56 Hz, 2H), 7.43 (d, J= 8.52 Hz, 2H), 7.29 - 7.19 (m, 5H), 4.59 (t, J= 7.36 Hz, 1H), 4.16 - 4.09 (m, 2H), 3.34 (dd, J= 1.80, 7.44 Hz, 2H), 1.14 (t, J= 7.12 Hz, 3H).

ethyl 2-benzyl-3-(2-chlorophenyl)-3-oxopropanoate (6r): The crude mixture was purified by column chromatography to yield 6r as colorless liquid with 82% yield. 1H NMR (400 MHz, CDCl3): δ 7.48 - 7.26 (m, 10H), 4.62 - 4.58 (t, J = 7.42 Hz, 1H), 4.13 - 4.06 (m, 2H), 3.38 - 3.28 (m, 2H), 1.14 - 1.10 (t, J= 7.12 Hz, 3H).
ethyl 2-benzyl-3-(3-chlorophenyl)-3-oxopropanoate (6s): The crude mixture was purified by column chromatography to yield 6s as colorless liquid with 85% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.94 (s, 1H), 7.83 (d, J = 7.84 Hz, 1H), 7.55 (d, J = 7.00 Hz, 1H), 7.40 (t, J = 7.90 Hz, 1H), 7.30 - 7.20 (m, 5H), 4.58 (t, J = 7.36 Hz, 1H), 4.18 - 4.10 (m, 2H), 3.35 (d, J = 7.36 Hz, 2H), 1.15 (t, J = 7.12 Hz, 3H).

ethyl 2-benzyl-3-(naphthalen-2-yl)-3-oxopropanoate (6t): The crude mixture was purified by column chromatography to yield 6t as colorless liquid with 88% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 8.50 (s, 1H), 8.05 (dd, J = 1.6, 8.72 Hz, 1H), 7.96 (d, J = 7.26 Hz, 1H), 7.89 (t, J = 8.20 Hz, 2H), 7.65-7.56 (m, 2H), 7.30 - 7.29 (m, 4H), 7.23 - 7.20 (m, 1H), 4.81 (t, J = 7.32 Hz, 1H), 4.18 - 4.09 (m, 2H), 3.42 (dd, J = 2.04, 7.60 Hz, 2H), 1.14 (t, J = 7.12 Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 197.3, 168.6, 138.3, 138.1, 132.0, 131.2, 130.6, 130.1, 129.9, 129.3, 128.5, 127.9, 126.8, 125.7, 61.6, 59.8, 34.3, 13.9.

ethyl 2-benzyl-3-oxo-3-(thiophen-2-yl)propanoate (6u): The crude mixture was purified by column chromatography to yield 6u as colorless liquid with 78% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.78 (dd, J = 0.96, 3.84 Hz, 1H), 7.69 (dd, J = 1.0, 4.96 Hz, 1H), 7.30 - 7.21 (m, 5H), 7.13 (t, J = 8.80 Hz, 1H), 4.48 (t, J = 7.40 Hz, 3H), 4.18 - 4.12 (m, 2H), 3.37 - 3.35 (m, 2H), 1.18 (t, J = 7.12 Hz, 3H).

ethyl 2-benzyl-3-oxobutanoate (6v): The crude mixture was purified by column chromatography to yield 6v as colorless liquid with 38% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.32-7.28 (m, 2H), 7.32 - 7.19 (m, 5H), 4.20 - 4.14 (m, 2H), 3.80 (t, J = 7.64 Hz, 1H), 3.19 (d, J = 7.16 Hz, 2H), 2.21 (s, 3H), 1.23 (t, J = 7.12 Hz, 3H).

ethyl 2-benzoylpentanoate (6w): The crude mixture was purified by column chromatography to yield 6w as colorless liquid with 62% yield. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta 7.97-8.00 (m, 2H), 7.55 - 7.60 (m, 1H), 7.44 - 7.49 (m, 2H), 4.30 (t, J = 7.14 Hz, 1H), 4.12 (q, J = 7.11 Hz, 2H), 1.93 - 2.03 (m, 2H), 1.35 - 1.42 (m, 2H), 1.17 (t, J = 7.11 Hz, 3H), 0.95 (t, J = 7.26 Hz, 3H).
methyl 2-benzyl-3-oxo-3-phenylpropanoate (6x): The crude mixture was purified by column chromatography to yield 6x as colorless liquid with 89% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.97 (d, $J = 7.36$ Hz, 2H), 7.53 - 7.45 (m, 3H), 7.28 - 7.21 (m, 5H), 4.68 (t, $J = 7.38$ Hz, 1H), 3.67 (s, 3H), 3.30 - 3.40 (m, 2H).

isopropyl 2-benzyl-3-oxo-3-phenylpropanoate (6y): The crude mixture was purified by column chromatography to yield 6y as colorless liquid with 86% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.00 - 7.98 (m, 2H), 7.58 (t, $J = 7.60$ Hz, 1H), 7.47 (t, $J = 7.60$ Hz, 2H), 7.31 - 7.21 (m, 5H), 5.0 - 4.93 (m, 1H), 4.59 (t, $J = 7.40$ Hz, 1H), 3.34 (d, $J = 7.36$ Hz, 2H), 1.14 (d, $J = 6.24$ Hz, 3H), 1.05 (d, $J = 6.28$ Hz, 3H).

tert-butyl 2-benzyl-3-oxo-3-phenylpropanoate (6z): The crude mixture was purified by column chromatography to yield 6z as light yellow liquid with 85% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.99 - 7.97 (m, 2H), 7.60 - 7.56 (m, 1H), 7.49 - 7.45 (m, 2H), 7.29 - 7.27 (m, 6H), 7.23 - 7.13 (m, 4H), 4.53 (t, $J = 7.36$ Hz, 1H), 3.32 (d, $J = 7.36$ Hz, 2H), 1.31 (s, 9H).

benzyl 2-benzyl-3-oxo-3-phenylpropanoate (6aa): The crude mixture was purified by column chromatography to yield 6aa as colorless liquid with 88% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.96 - 7.94 (m, 2H), 7.58 (t, $J = 7.42$ Hz, 1H), 7.44 (t, $J = 7.76$ Hz, 2H), 7.30 - 7.27 (m, 6H), 7.23 - 7.13 (m, 4H), 5.09 (s, 2H), 4.69 (t, $J = 7.36$ Hz, 1H), 3.36 (d, $J = 7.24$ Hz, 2H).

1-(3,5-bis(trifluoromethyl)phenyl)-3-((1S,2R)-2-hydroxy-1,2-diphenylethyl)thiourea (Cat 2): The crude mixture was purified by column chromatography to yield Cat 2 as colorless liquid with 72% yield. $^1$HNMR (400 MHz, DMSO): $\delta$ 10.35 (s, 1H), 8.72 (d, $J = 8.60$ Hz, 1H), 8.28 (s, 2H), 7.75 (s, 1H), 7.09 - 7.26 (m, 10H), 5.85 (d, $J = 4.12$ Hz, 1H), 5.67 - 5.64 (m, 1H), 5.12 (s, 1H).

1-(3,5-bis(trifluoromethyl)phenyl)-3-((1R,2R)-2-hydroxy-1,2-diphenylethyl)thiourea (Cat 3):
diphenylethylthiourea (Cat 3): The crude mixture was purified by column chromatography to yield Cat 3 as colorless liquid with 68% yield. $^1$HNMR (400 MHz, DMSO): $\delta$ 10.54 (s, 1H), 8.69 (d, $J = 8.24$ Hz, 1H), 8.33 (s, 2H), 7.71 (s, 1H), 7.23 - 7.51 (m, 10H), 6.00 (d, $J = 4.36$ Hz, 1H), 5.59 (d, $J = 6.96$ Hz, 1H), 4.97 (d, $J = 3.60$ Hz, 1H).

Cat 5

1-(3,5-bis(trifluoromethyl)phenyl)-3-(1R,2S)-2-hydroxy-1,2-diphenylethylthiourea (Cat 5): The crude mixture was purified by column chromatography to yield Cat 5 as colorless liquid with 70% yield. $^1$HNMR (400 MHz, DMSO): $\delta$ 10.35 (s, 1H), 8.72 (d, $J = 8.52$ Hz, 1H), 8.28 (s, 2H), 7.75 (s, 1H), 7.09 - 7.25 (m, 10H), 5.84 (d, $J = 4.04$ Hz, 1H), 5.85 (d, $J = 4.04$ Hz, 1H), 5.64 - 5.67 (m, 1H), 5.13 (s, 1H).

Cat 5

1-(3,5-bis(trifluoromethyl)phenyl)-3-(1S,2R)-2-methoxy-1,2-diphenylethylthiourea (Cat 5): The crude mixture was purified by column chromatography to yield Cat 5 as colorless liquid with 63% yield. $^1$HNMR (400 MHz, DMSO): $\delta$ 10.27 (s, 1H), 8.72 (d, $J = 8.76$ Hz, 1H), 8.24 (s, 1H), 7.75 (s, 1H), 7.07 - 7.29 (m, 10H), 5.70 - 5.73 (m, 1H), 4.75 (d, $J = 4.84$, 1H), 3.22 (s, 3H).

Cat 5

1-benzyl-3-(3,5-bis(trifluoromethyl)phenyl)thiourea (Cat 6): The crude mixture was purified by column chromatography to yield Cat 6 as colorless liquid with 65% yield. $^1$HNMR (400 MHz, CDCl$_3$): colorless liquid; $^1$HNMR (400 MHz, DMSO) $\delta$ 8.04 (s, 1H), 7.76 (s, 2H), 7.72 (s, 1H), 7.35 - 7.42 (m, 5H), 6.40 (s, 1H), 4.85 (d, $J = 4.0$ Hz, 2H).

Cat 6

N-((1S,2R)-2-hydroxy-1,2-diphenylethyl)methanesulfonamide (Cat 7): The crude mixture was purified by column chromatography to yield Cat 7 as colorless liquid with 53% yield. $^1$HNMR (400 Hz, CDCl$_3$): $\delta$ 7.27 - 7.32 (m, 6H), 7.07 - 7.13 (m, 4H), 5.32 (d, $J = 8.56$ Hz, 1H), 5.14 - 5.16 (m, 1H), 4.76 (dd, $J = 4.68$ Hz, 8.64 Hz, 1H), 2.58 (s, 3H), 2.43 (d, $J = 3.96$ Hz, 1H).

Cat 7

1,1,1-trifluoro-N-((1S,2R)-2-hydroxy-1,2-diphenylethyl)methanesulfonamide (Cat 8): The crude mixture was purified by column
chromatography to yield Cat 8 as colorless liquid with 67% yield. $^1$HNMR (400 MHz, CDCl$_3$): 10.00 (d, $J = 9.12$ Hz, 1H), 7.25 - 7.33 (m, 10H), 5.68 (d, $J = 5.0$ Hz, 1H), 4.73 (dd, $J = 5.04$, 7.60 Hz, 12.0 Hz, 1H), 4.43 (t, $J = 8.52$ Hz, 1H).

References
\textbf{\textsuperscript{1}H NMR Spectra:}

\textbf{The \textsuperscript{1}H NMR Spectra of 6a}

\textbf{The \textsuperscript{1}H NMR Spectra of 6b}
The $^1$H NMR Spectra of 6c

The $^1$H NMR Spectra of 6d
The $^1$H NMR Spectra of 6e

The $^1$H NMR Spectra of 6f
The \textsuperscript{1}H NMR Spectra of 6g
The $^1$H NMR Spectra of 6h

The $^1$H NMR Spectra of 6i
The $^1$H NMR Spectra of 6j
The $^1$H NMR Spectra of 6k
The $^1$H NMR Spectra of 6l
The $^1$H NMR Spectra of 6m

The $^1$H NMR Spectra of 6n
The $^1$H NMR Spectra of 6o

The $^1$H NMR Spectra of 6p
The $^1$H NMR Spectra of 6q

The $^1$H NMR Spectra of 6r
The $^1$H NMR Spectra of 6s

The $^1$H NMR Spectra of 6t
The $^1$H NMR Spectra of 6u
The $^1$H NMR Spectra of 6v

The $^1$H NMR Spectra of 6w
The $^1$H NMR Spectra of 6y

The $^1$H NMR Spectra of 6z
The $^1$H NMR Spectra of 6aa

The $^1$H NMR Spectra of Cat 2
The $^1$H NMR Spectra of Cat 3

The $^1$H NMR Spectra of Cat 4
The $^1$H NMR Spectra of Cat 5

The $^1$H NMR Spectra of Cat 6
The $^1$H NMR Spectra of Cat 7

The $^1$H NMR Spectra of Cat 8