

Supporting Information

Organocatalyst based Cross-Catalytic System

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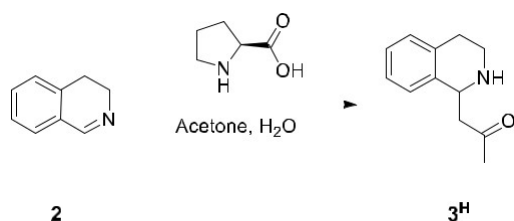
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1. General experimental information

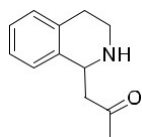
Unless otherwise indicated, reagents and substrates were purchased from commercial sources and used as received. Reactions were monitored by ^1H -NMR. Purification of the products was performed by column chromatography using Merck 60 Å 230-400 mesh silica gel. Components were visualised by UV and KMnO_4 or Ninhydrin staining of thin layer chromatography (TLC) plates. NMR data was collected on a Varian MercuryPlus (^1H at 400 MHz; ^{13}C at 101 MHz) equipped with a 400 Autosw probe, a Varian 400MR (^1H at 400 MHz; ^{13}C at 101 MHz) equipped with a OneNMR probe, a Varian Inova (^1H at 500 MHz; ^{13}C at 126 MHz) equipped with either a HCN93 or ID probe and a Bruker NEO (^1H at 600 MHz; ^{13}C at 151 MHz) equipped with a SmartProbe BBFO. Chemical shifts are reported in parts per million (ppm) relative to residual solvent peak. Coupling constants are reported in Hertz (Hz). Multiplicity is reported with the usual abbreviations (s: singlet, d: doublet, dd: doublet of doublets, t: triplet, q: quadruplet, m: multiplet). Exact mass spectra were recorded on a LTQ Orbitrap XL apparatus with ESI ionization. 3,4-dihydroisoquinoline (**2**) was synthesised by a known literature procedure.¹

2. General procedure for the formation of Mannich product



L-proline (**Pro**) (2.6 mg, 10 mol%) and 3,4-dihydroisoquinoline (**2**) (26 mg, 0.2 mmol) were dissolved in 1.5 ml of acetone. Then 36 μ l of H₂O was added and the reaction mixture was stirred at room temperature overnight. The complete reaction mixture was loaded on a SiO₂ column (The column was loaded using pentane:EtOAc 1:1 as the eluent, then it was changed to EtOAc:MeOH:Et₃N, 98.5:1:0.5 to elute). Mannich product (**3^H**) was recovered as a yellow oil which turns dark over time (20 mg, 54% yield).

1-(1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (**3^H**)



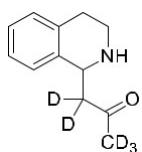
¹H-NMR (300 MHz, Acetone-*d*₆) δ 7.16-7.03 (m, 4H), 4.40 (dd, *J*=9.6, 3.4 Hz, 1H), 3.12 (dt, *J*=11.7, 5.6 Hz, 1H), 3.01-2.91 (m, 2H), 2.91-2.75 (m, 3H), 2.70 (dd, *J* = 12.3, 6.2 Hz, 1H), 2.15 (s, 3H).

¹³C NMR (151 MHz, Acetone-*d*₆) δ 207.2, 138.9, 135.7, 129.2, 125.9, 125.8, 125.6, 52.1, 50.0, 40.4, 29.7, 29.5

HRMS (ESI⁺, *m/z*) calcd. for C₁₂H₁₅NO [M+H]⁺: 190.1226, found: 190.1228.

To circumvent traces of L-proline in product **3^H** an L-proline free method² was used to synthesise this product when used for seeding experiments.

1-(1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one-1,1,3,3,3-d₅ (**3**)



¹H-NMR (600 MHz, Acetone-*d*₆) δ 7.24 – 7.01 (m, 4H), 4.37 (s, 1H), 3.10 (m, 1H), 2.88 (m, 1H), 2.80 – 2.73 (m, 1H), 2.67 (m, 1H).

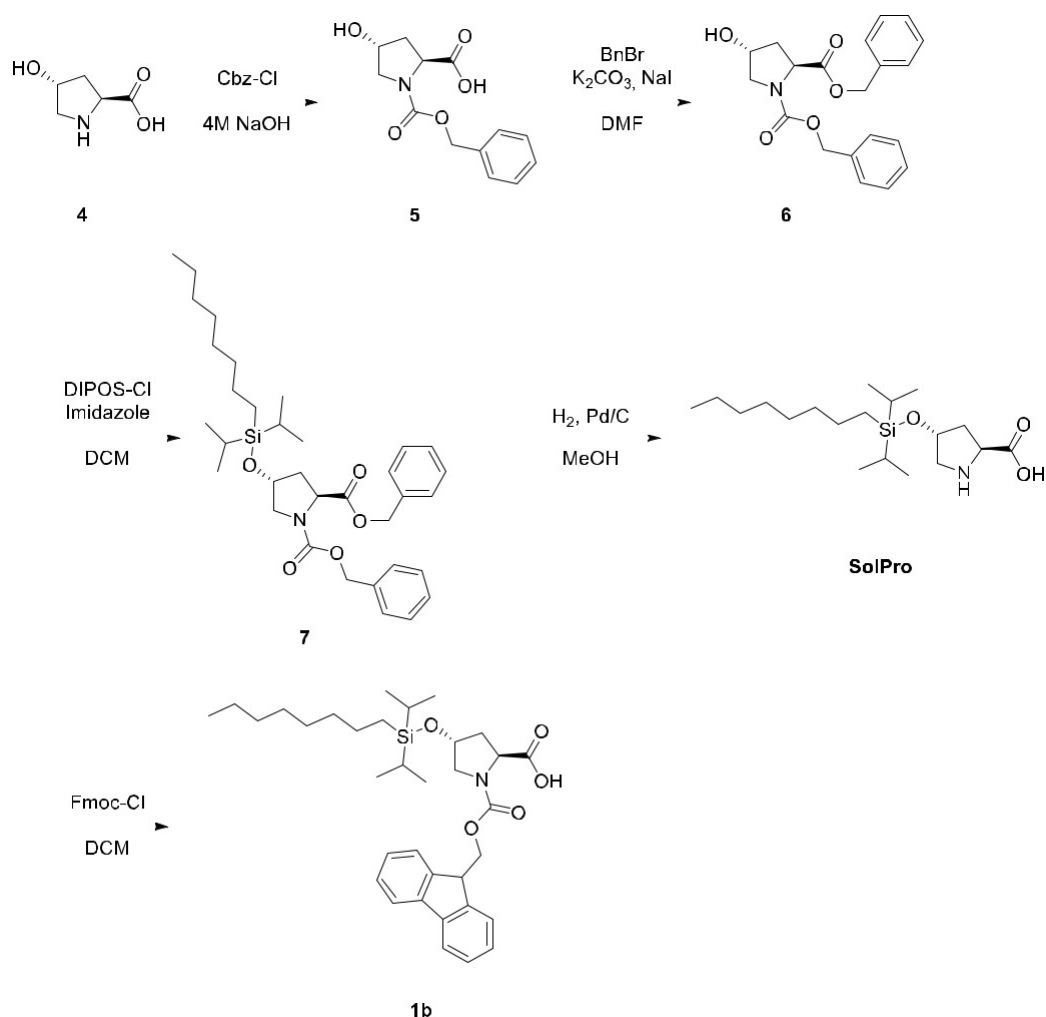
¹³C-NMR (151 MHz, Acetone-*d*₆) δ 208.2, 138.6, 135.5, 129.2, 125.9, 125.9, 125.7, 51.8, 49.1 (p, *J* = 19.5 Hz), 40.4, 29.4, 29.0*.

* Carbon resonances of the CD₃ could not be read due to overlap with acetone-*d*₆.

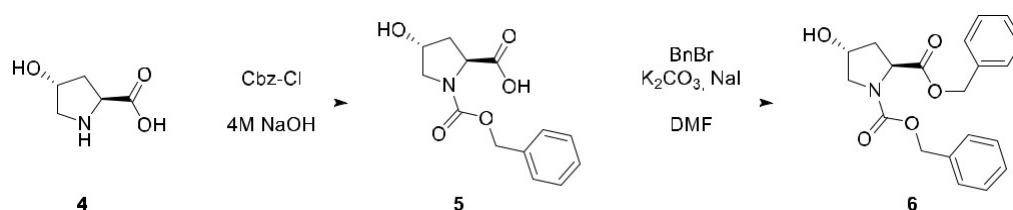
HRMS (ESI⁺, *m/z*) calcd. for C₁₂H₁₀D₅NO [M+H]⁺: 195.1540, found: 195.1536.

NMR spectra were recorded from the crude mixture. A ¹H-NMR spectrum after column chromatography showed a doublet of doublets at 4.40 ppm, showing that the proton α to the nitrogen couples with other protons thereby confirming that proton exchange takes place and **3** cannot be isolated.

3. Synthesis of SolPro³ and 1b



Synthesis of dibenzyl (2S,4R)-4-hydroxyproline-1,2-dicarboxylate (6):³



4-Hydroxy-L-proline (**4**) was dissolved in 4M sodium hydroxide (aqueous solution) and the solution was cooled in an ice-salt bath. Benzyl chloroformate was added slowly with magnetic stirring to this alkaline solution. The reaction mixture was stirred for 30 minutes at 0 °C and was extracted with diethylether and the ether layer discarded. The product was precipitated as an oil by addition of concentrated hydrochloric acid to the aqueous solution cooled to 0 °C. The oil was extracted into ethyl acetate and washed with water and brine. After drying and removal of the ethyl acetate, the product **5** was obtained as a colourless oil in 96% yield, which was used without further purification.

Compound **5** (4g, 15 mmol) was dissolved in DMF (10 mL) along with K₂CO₃ (1.7 g, 12 mmol, 0.8 equiv.), BnBr (1.8 mL, 15 mmol, 1 equiv.), and NaI (18 mg, 0.12 mmol), and the mixture was vigorously stirred for 16 hours. Then 10 ml of water was added and the mixture was extracted with diethylether. The organic layer was extracted with water (2 x 10 ml), the water layer back extracted with diethylether

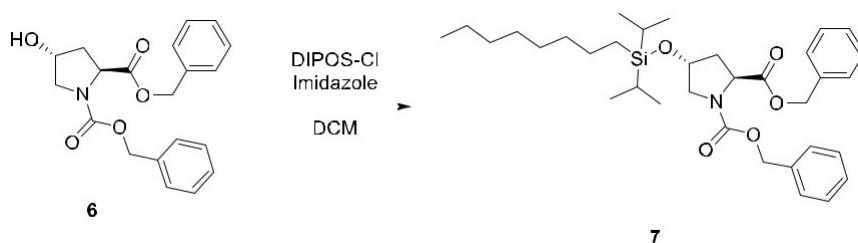
(20 ml) and the combined organic layers washed with brine. Then the organic layer was dried over MgSO₄ and removed under reduced pressure. The residue was purified by chromatography (Pentane:Et₂O 4:1) and the product was obtained in 70% yield.

¹H-NMR (600 MHz, CDCl₃) δ 7.43-7.21 (m, 10H), 5.28-4.98 (m, 4H), 4.58 (dt, *J* = 28.6, 7.9 Hz, 1H), 4.51-4.48 (m, 1H), 3.71 (dt, *J* = 11.7, 4.1 Hz, 1H), 3.67-3.56 (m, 1H), 2.39-2.27 (m, 1H), 2.10 (ddd, *J* = 13.1, 7.9, 4.8 Hz, 1H), 2.02 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 172.7, 172.5, 155.2, 154.7, 136.6, 136.4, 135.7, 135.5, 128.6, 128.6, 128.5, 128.4, 128.3, 128.2, 128.2, 128.1, 128.0, 128.0, 70.3, 69.5, 67.4, 67.1, 67.0, 58.2, 57.9, 55.4, 54.8, 39.3, 38.5.

Analytical data were in agreement with those reported in literature.⁴

Synthesis of dibenzyl (2S,4R)-4-((diisopropyl(octyl)silyl)oxy)pyrrolidine-1,2-dicarboxylate (7):³



In a round bottom flask, **6** (4g, 11.3, mmol) and imidazole (1.8g, 26 mmol, 2.3 equiv.) were dissolved in DCM (30 ml), diisopropyloctylsilyl chloride (3.3g, 12.5 mmol, 1.1 equiv.) was added and the mixture was stirred at room temperature overnight. The mixture was washed with sat. NaHCO₃, two times with sat. NH₄Cl and finally with brine. The organic fraction was dried over MgSO₄ and the solvent was removed under reduced pressure. The product was obtained after column chromatography (Pentane:EtOAc 20:1) in 72% yield.

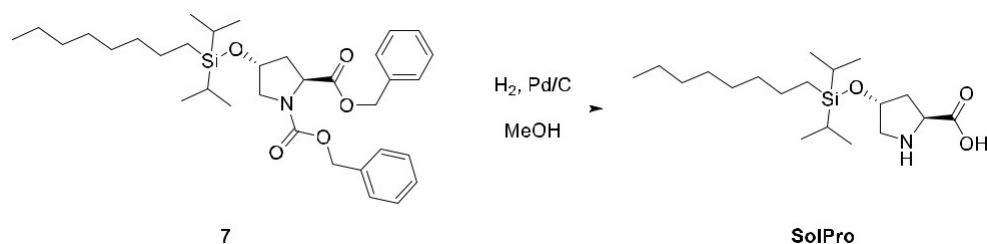
¹H-NMR (600 MHz, CDCl₃) δ 7.40 – 7.23 (m, 10H), 5.27 – 4.96 (m, 4H), 4.59 (t, *J*=7.5 Hz, 1H, α), 4.52 (t, *J*=7.5 Hz, 1H, β), 4.50 – 4.48 (m, 1H), 3.73 (dd, *J*=11.1, 4.8 Hz, 1H, α), 3.69 (dd, *J*=10.9, 4.8 Hz, 1H, β), 3.55 (dd, *J*=10.9, 2.8 Hz, 1H, α), 3.48 (dd, *J*=10.9, 2.8 Hz, 1H, β), 2.29 – 2.23 (m, 1H), 2.12 – 2.03 (m, 1H), 1.38 – 1.24 (m, 12H), 1.05 – 0.98 (m, 17H), 0.64 (q, *J*=9.4 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃, 2 rotamers α and β) δ 172.8 (α), 172.6 (β), 155.2 (α), 154.5 (β), 136.8 (α), 136.6 (β), 135.8 (α), 135.6 (β), 128.7 (α), 128.6 (α), 128.5 (β), 128.5 (α), 128.4 (β), 128.3 (α), 128.2 (β), 128.1 (α), 128.0 (β), 127.9 (β), 70.6 (α), 69.9 (β), 67.2 (α), 67.2 (β), 67.0 (α), 66.9 (β), 58.4 (α), 58.1 (β), 55.4 (α), 55.0 (β), 40.1 (α), 39.1 (β), 34.1 (α), 32.0 (β), 29.4 (α), 29.3 (β), 23.5 (α), 22.8 (β), 17.7, 14.2, 12.6, 10.9.

HRMS (ESI⁺, *m/z*) calcd. for C₃₄H₅₁NO₅Si [M+H]⁺: 582.3609, found: 582.3603.

Analytical data was in agreement with those reported in literature.³

Synthesis of (2S,4R)-4-((diisopropyl(octyl)silyl)oxy)pyrrolidine-2-carboxylic acid (**SolPro**):



In a round bottom flask **7** (5.5g, 9.5 mmol) was dissolved in methanol (55 ml) and Pd/C (10w%) was added under an atmosphere of nitrogen. The atmosphere was removed and replaced by hydrogen three times before the mixture was stirred overnight at room temperature. Filtration of the mixture over celite and removal of the solvent in vacuum yielded the product in 96% yield.

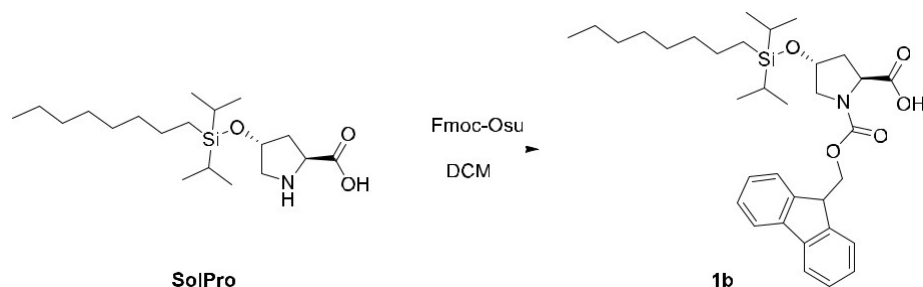
¹H-NMR (600 MHz, CDCl₃) δ 4.49 (m, 1H), 4.18 (t, *J* = 8.2 Hz, 1H), 3.53 – 3.47 (m, 1H), 3.18 (m, 2H), 2.27-2.11 (m, 2H), 1.33-1.25 (m, 12H), 1.01 – 0.95 (m, 14H), 0.87 (t, *J* = 7.0 Hz, 3H), 0.63 – 0.56 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 173.7, 71.2, 60.2, 52.9, 39.3, 34.2, 32.1, 29.4, 29.3, 23.5, 22.8, 17.7, 14.2, 12.5, 10.9.

HRMS (ESI⁺, *m/z*) calcd. for C₁₉H₃₉NO₃Si [M+H]⁺: 358.2772, found: 358.2772.

Analytical data was in agreement with those reported in literature.³

Synthesis of (2S,4R)-1-(((9H-fluoren-9-yl)methoxy)carbonyl)-4-((diisopropyl(octyl)silyl)oxy)pyrrolidine-2-carboxylic acid (**1b**)



SolPro (0.53g, 1.5 mmol) was dissolved in DCM (4 ml) and Fmoc-Osu (0.55g, 1.6 mmol, 1.1 equiv.) was added to this solution. The solution was stirred at room temperature overnight. Water was added and the aqueous layer was extracted thrice with DCM and the combined organic layers were dried over MgSO₄ and the mixture was concentrated *in vacuo*. The product was obtained in 88% yield as an oil.

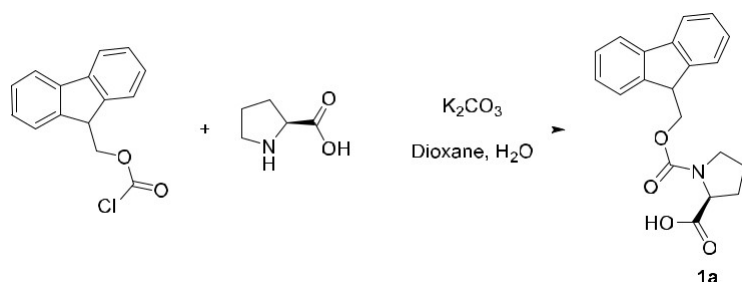
¹H NMR (600 MHz, Acetone-*d*₆) δ 11.08 (br s, 1H), 7.88-7.85 (m, 2H), 7.74-7.68 (m, 2H), 7.41 (q, *J*=7.7 Hz, 2H), 7.33 (m, 2H), 4.68-4.64 (m, 1H), 4.51 (dt, *J*=104.1, 7.6 Hz, 1H), 4.39-4.19 (m, 3H), 3.67 (ddd, *J*=28.0, 10.9, 4.4 Hz, 1H), 3.54 (dd, *J*=26.1, 11.0 Hz, 1H), 2.44-2.27 (m, 1H), 2.21 (m, 1H), 1.48-1.34 (m, 4H), 1.28 (m, 8H), 1.11-1.00 (m, 14H), 0.86 (q, *J*=6.8 Hz, 3H), 0.78-0.71 (m, 2H).

¹³C NMR (151 MHz, Acetone-*d*₆, 2 rotamers α and β) δ 174.3 (α), 173.8 (β), 155.6 (α), 155.3 (β), 145.3 (α), 145.3 (β), 145.1 (α), 145.1 (β), 142.3, 142.2 (α), 142.2 (β), 128.7, 128.1 (α), 128.1 (β), 128.1, 126.4 (α), 126.3 (β), 126.2 (α), 126.1 (β), 121.0 (α), 121.0 (β), 121.0 (α), 120.9 (β), 71.9 (α), 71.1 (β), 68.5 (α), 68.1 (β), 59.0 (α), 58.6 (β), 56.4 (α), 56.0 (β), 48.2 (α), 48.2 (β), 41.1 (α), 40.0 (β), 34.8 (α), 32.8 (β), 30.1 (α), 30.0 (β), 24.3 (α), 23.5 (β), 18.1 (α), 18.1 (β), 14.5, 13.5 (α), 13.5 (β), 11.7 (α), 11.6 (β).

HRMS (ESI⁺, *m/z*) calcd. for C₃₄H₄₉NO₅Si [M+H]⁺: 580.3453, found: 580.3451.

4. Synthesis of Fmoc-Pro-OH derivatives

Synthesis of (((9H-fluoren-9-yl)methoxy)carbonyl)-L-proline (FmocPro-OH)(**1a**):



L-proline (1 g, 8.7 mmol) was dissolved in 1,4-dioxane (4 mL) and H_2O (15 mL), and cooled to 0 °C. K_2CO_3 (3.24 g, 23 mmol) was added, and then (9H-fluoren-9-yl)methyl chloroformate (2.3 g, 8.3 mmol) was added in portions. The mixture was stirred at room temperature overnight and H_2O (10 mL) was added. The mixture was extracted with Et_2O (2 × 20 mL). The aqueous phase was acidified with aqueous HCl (1 M) to pH 2–3, and extracted with DCM (3 × 50 mL). Combined organic layers were dried over Na_2SO_4 , filtered, concentrated to dryness to give **1a** as a white solid (2.6 g, 89% yield).

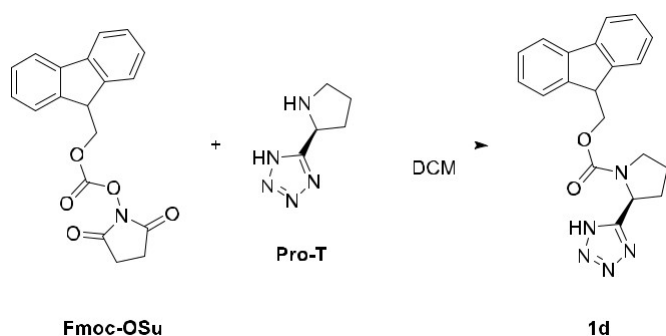
1H -NMR (600 MHz, Acetone- d_6) δ 7.88 (dd, J = 11.2, 7.6 Hz, 2H), 7.72 (q, J = 9.0, 7.9 Hz, 2H), 7.43 (q, J = 7.7 Hz, 2H), 7.35 (m, 2H), 4.49 – 4.35 (m, 1H), 4.41 – 4.19 (m, 3H), 3.67 – 3.44 (m, 2H), 2.34 (dddd, J = 55.1, 17.7, 13.2, 9.1 Hz, 1H), 2.15 – 2.08 (m, 1H), 2.04 – 1.92 (m, 2H).

^{13}C -NMR (243 MHz, Acetone- d_6 , 2 rotamers α and β) δ 173.4 (α), 172.9 (β), 154.4 (α), 154.0 (β), 144.3 (α), 144.3 (β), 144.2 (α), 144.1 (β), 141.3 (α), 141.2 (β), 141.2 (α), 141.1 (β), 127.7 (2 × C), 127.1, 127.1, 125.3 (α), 125.3 (β), 125.2 (α), 125.2 (β), 119.9 (2 × C)(α), 119.9 (2 × C)(β), 67.2 (α), 67.0 (β), 59.0 (α), 58.5 (β), 47.2 (α), 47.1 (β), 46.8 (α), 46.3 (β), 30.8 (α), 29.5 (β), 24.1 (α), 23.1 (β).

HRMS (ESI⁺, m/z) calcd. for $C_{20}H_{19}NO_4$ [$M+Na$]⁺: 360.1206, found: 360.1210.

Compound **6a** has been reported before in $CDCl_3$.⁵

Synthesis of 1-pyrrolidinecarboxylic acid, 2-(2H-tetrazol-5-yl)-, 9H-fluoren-9-ylmethyl ester (Fmoc-Pro-T)(**1d**):



(S)-5-(pyrrolidin-2-yl)-1H-tetrazole (**Pro-T**) (200 mg, 1.437 mmol, 1 equiv.) was added to a round bottom flask and DCM was added (3 ml). Fmoc-OSu (485 mg, 1.437 mmol, 1 equiv.) was added to this suspension and the mixture was stirred at room temperature overnight. Water was added and the aqueous layer was extracted with DCM three times. The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography to afford the product as a white solid (412 mg, 78% yield).

¹H-NMR (600 MHz, CDCl₃) δ 13.21 (br, 1H), 7.76 (t, J=7.8 Hz, 2H), 7.56 (dd, J=20.0, 7.5 Hz, 2H), 7.41 (q, J=7.3 Hz, 2H), 7.31 (t, J=7.8 Hz, 2H), 5.07 (dd, J=8.2, 2.3 Hz, 1H), 4.58-4.49 (m, 2H), 4.24 (t, J= 6.6 Hz, 1H), 3.45-3.37 (m, 2H), 2.99-2.95 (m, 1H), 2.36-2.29 (m, 1H), 2.18-2.05 (m, 2H)

¹³C-NMR (243 MHz, CDCl₃, 2 rotamers α and β) δ 156.7, 143.5 (α), 143.3 (β), 141.4 (α), 141.4 (β), 128.0 (α), 127.9 (β), 127.2 (α), 127.1 (β), 124.9 (α), 124.8 (β), 120.1 (α), 120.1 (β), 68.0, 51.4, 47.3, 47.1, 28.4, 24.7

To confirm that the two sets of signals are due to rotamers, the ¹³C-NMR spectrum was recorded at elevated temperature (55 °C) and the two sets coalesce at this temperature.

HRMS (ESI⁺, m/z) calcd. for C₂₀H₁₉N₅O₂ [M+H]⁺: 362.1611, found: 362.1617.

5. Kinetic studies

Kinetic experiments described in this work were performed using $^1\text{H-NMR}$ (500 MHz) at 25 °C. $^1\text{H-NMR}$ spectra were automatically acquired periodically every 5 or 10 minutes for a period of up to 12 hours (number of scans (nt) = 8, relaxation delay (d1) = 25 sec). Reaction progress was determined by monitoring the disappearance of characteristic signals of imine protons in **2a** (8.32 ppm), and appearance of protons in product **5'** (4.40 ppm) and **DBF** (6.25 ppm). Stock solutions of the corresponding internal standard in the corresponding solvent were freshly prepared: HMDSO in acetone-*d*6 (1 vol%) and 1,3,5-trimethoxybenzene in DMSO-*d*6 (2.7 mM).

5.1 Mannich reaction

3,4-Dihydroisoquinoline (**2a**) (17.4 mg, 0.13 mmol, 1 equiv.) was dissolved in 1 ml of the acetone-*d*6 stock solution. The catalyst (2 mol%) was added and 0.6 ml of the resulting solution was added to an NMR tube. The reaction was followed at regular time intervals by $^1\text{H-NMR}$. The time of mixing is referred to as $t=0$.

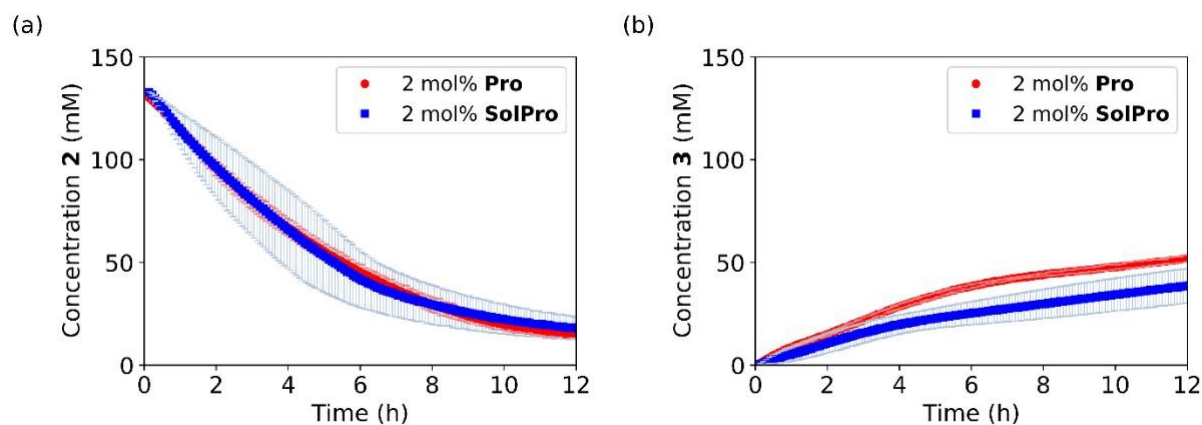


Figure S1. Kinetic reactions examining the addition of acetone-*d*6 to **2** (133 mM) catalysed by **Pro** and **SolPro** at 25°C in acetone-*d*6. The reaction catalysed by 2 mol% of **Pro** (red circles) and the reaction catalysed by 2 mol% of **SolPro** (blue squares). (a) Concentration over time of **2**, (b) Concentration over time of **3**.

5.2 Deprotection reaction

The Fmoc-protected amino acid (266 mM) was dissolved in the appropriate stock solution. In addition, the desired deprotecting agent (266 mM) was dissolved in the appropriate stock solution. Then 0.3 ml of each of these solutions was added to the NMR tube. The reaction was followed at regular time intervals by $^1\text{H-NMR}$. The time of mixing is referred to as $t=0$.

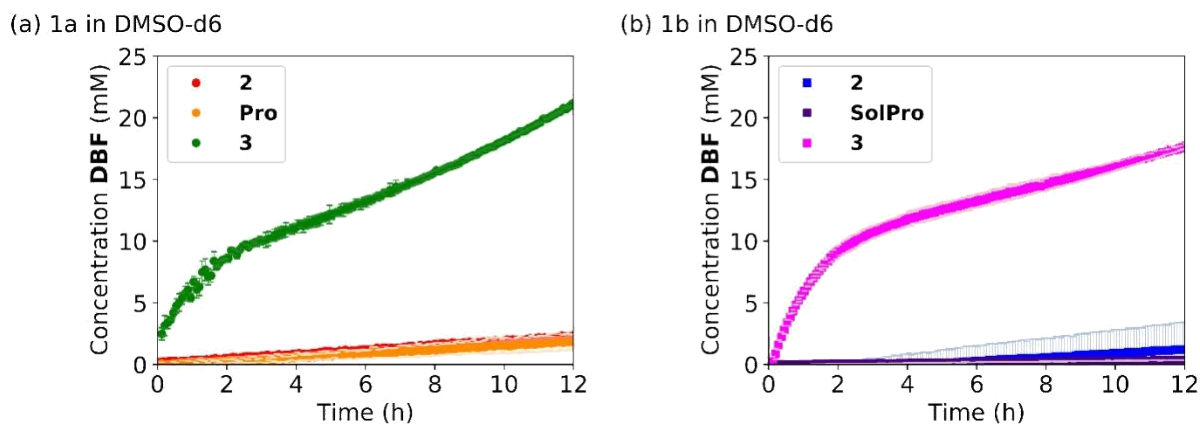


Figure S2. Kinetic reactions examining the deprotection of **1a** and **1b** (133 mM) respectively at 25°C in DMSO-d6 (a) Deprotection of **1a** with 1 equiv. of **2** (red circles), 1 equiv. of **Pro** (orange circles) and 1 equiv. of **3** (green circles). (b) Deprotection of **1b** with 1 equiv. of **2** (blue squares), concentrated solution of **SolPro** (purple squares) and 1 equiv. of **3** (pink squares).

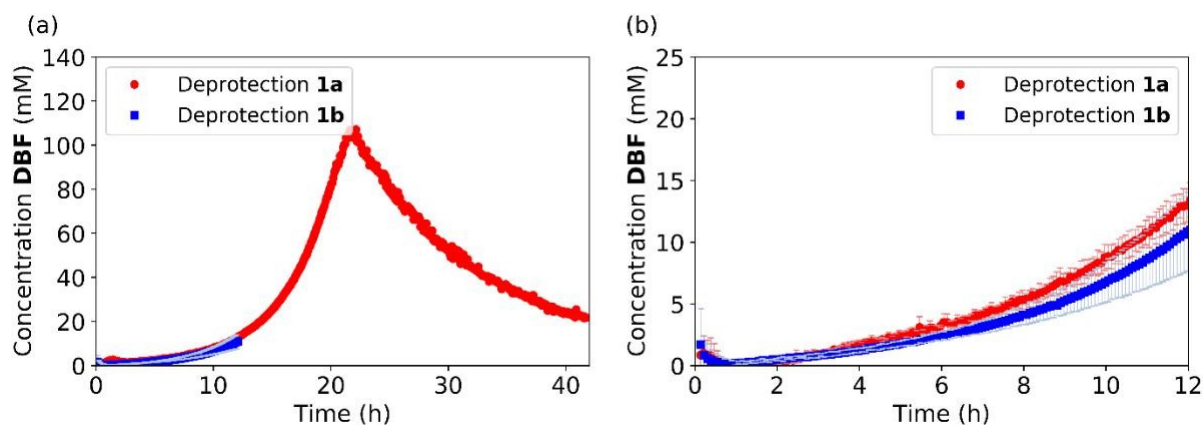
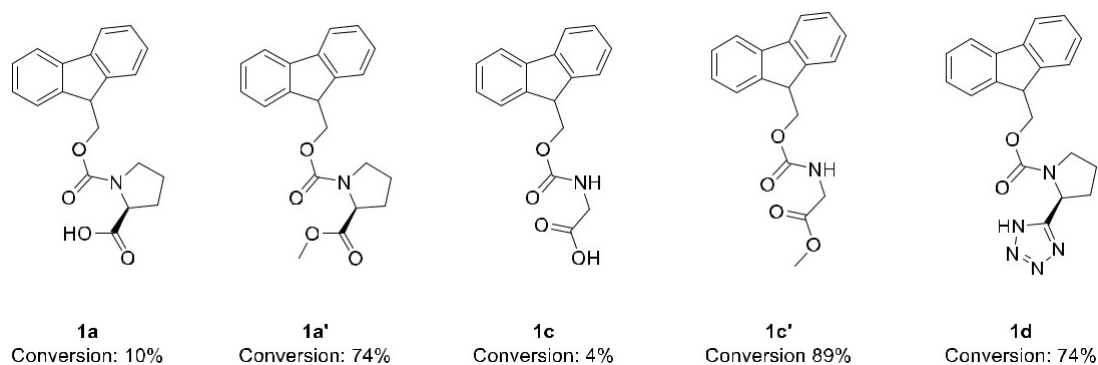


Figure S3. (a) Kinetic reactions examining the deprotection of **1a** (red circles) and **1b** (blue squares) (133 mM) with 1 equiv. of **3** at 25°C in acetone-d6. (b) Zoom-in of the first 12 hours of reaction.

5.2.1 Deprotection of Fmoc protected amino acid derivatives

Different Fmoc protected amino acids and amino acid derivatives (Scheme S1) were deprotected with 1 equiv. of **3** in acetone-d6.



Scheme S1 Fmoc-protected amino acids and amino acid derivatives used in this study.

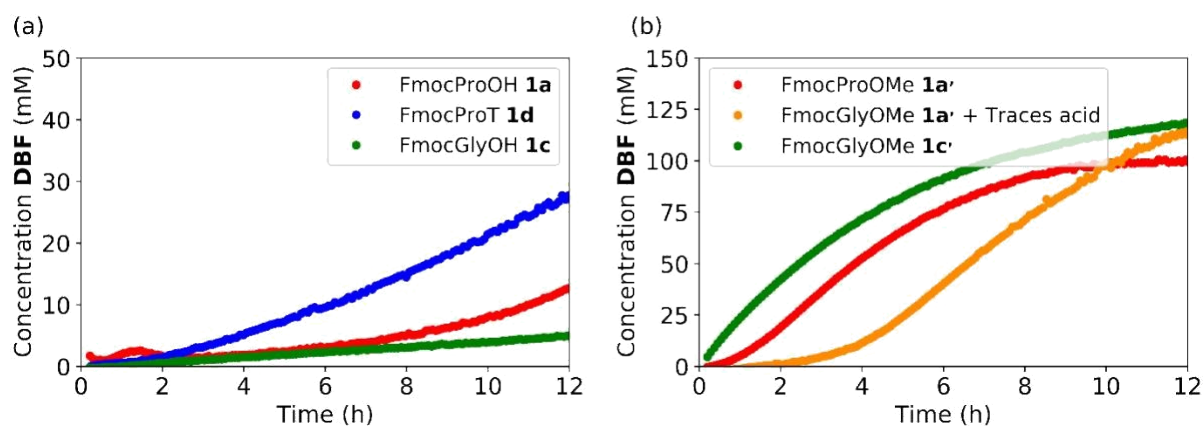


Figure S4. Deprotection reaction of the different amino-acids protected with the Fmoc protecting group.

The deprotection of **1a**, **1c** and **1d** with 1 equivalent of **3** were all slow, however the deprotection of **1d** was slightly faster which can be explained by the less acidic proton of the tetrazole group (Figure S4a). When there is no acid proton (**1a'** and **1c'**) the reaction reaches full conversion in 12 hours. As **1a'** was synthesised in the presence of H_2SO_4 , we found that when traces of this acid are still present, first a lag period is observed. After washing the reagent with neutral water and thereby removing some of these acids, the lag period was decreased (Figure S4b).

5.3 Cross-catalysis

The appropriate Fmoc protected proline (0.266 mmol, 1 eq.) was dissolved in 1 ml of the acetone- d_6 stock solution. 3,4 dihydroisoquinoline (**2a**) (17.4 mg, 0.133 mmol, 1 eq.) was dissolved in 1 ml of the same stock solution. Then 0.3 ml of each solution was added to an NMR tube. The reaction was followed at regular time intervals by ^1H -NMR.

When seeding experiments were carried out, the two solutions (of 3,4-dihydroisoquinoline (**2a**) and Fmoc protected proline (**1a-d**)) were mixed in a vial containing the appropriate amount of **Pro** or Mannich product **3^H**. The time of mixing is referred to as $t=0$ sec.

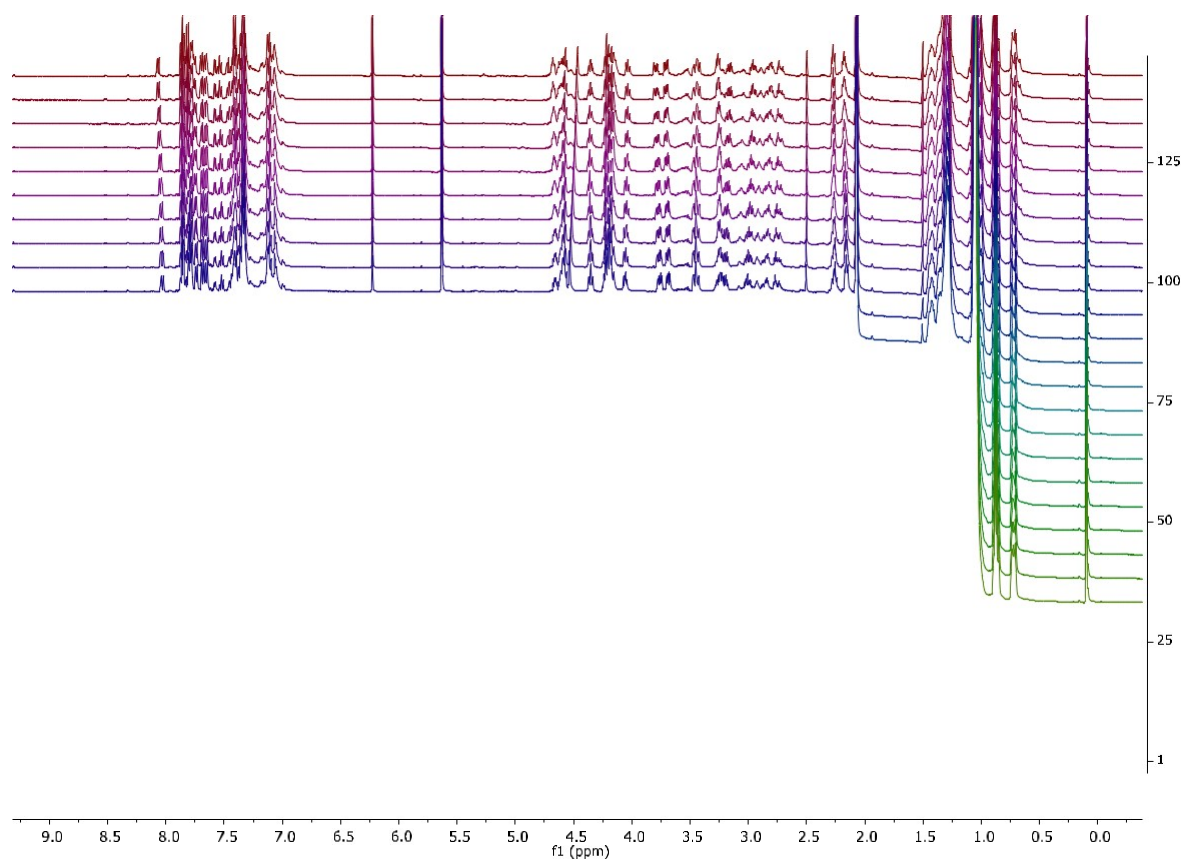


Figure S5 Typical array of spectra of a cross-catalytic reaction.

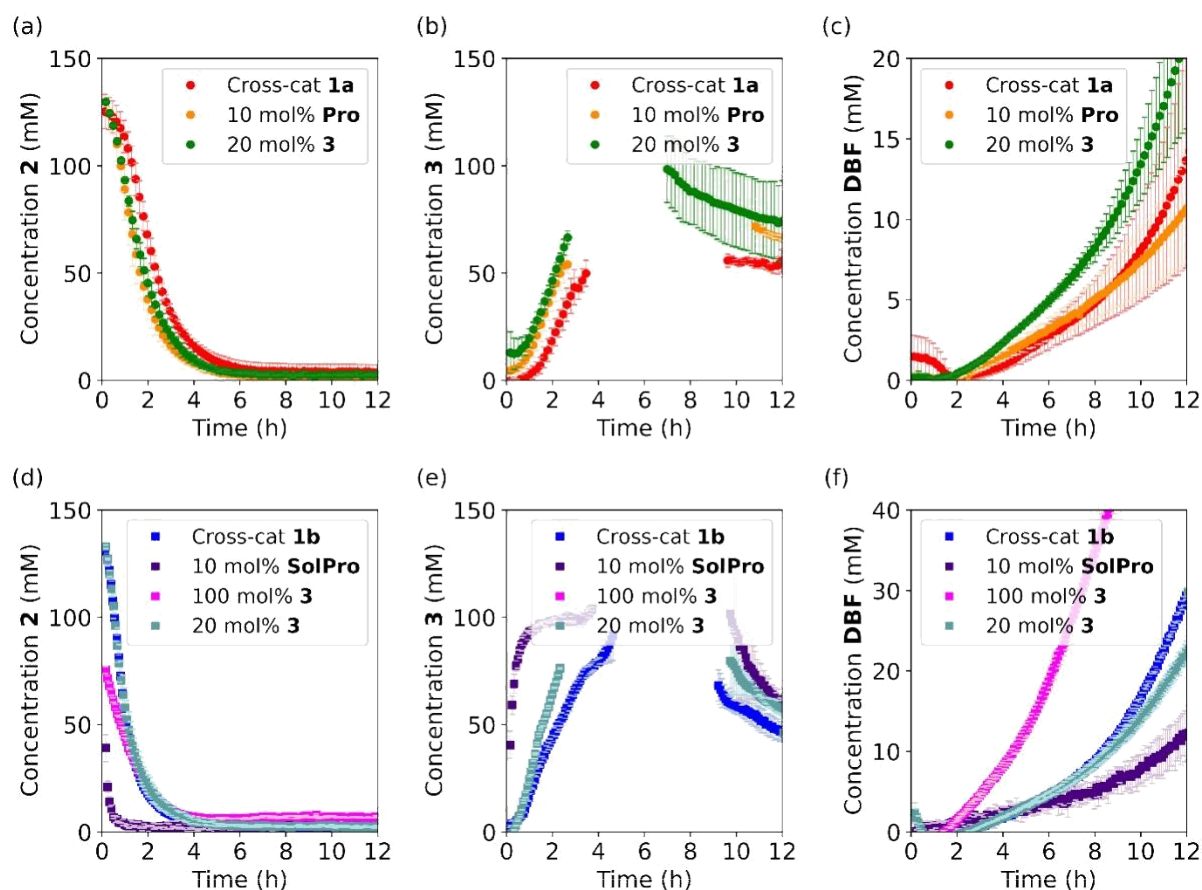


Figure S6 Kinetic experiments examining the reactions of **1a** and **1b** with **2** and the different seeding reactions in the cross-catalytic reaction with **1a** (red circles), the reaction that was seeded with 10 mol% of L-proline (**Pro**) at $t=0$ (orange circles) and the reaction that was seeded with 20 mol% of **3** at $t=0$ (green circles). The cross-catalytic reaction with **1b** (blue squares), the reaction that was seeded with 10 mol% of **SolPro** at $t=0$ (purple squares), the reaction that was seeded with 20 mol% of **3** at $t=0$ (blue grey squares) and the reaction that was seeded with 100 mol% of **3** at $t=0$ (pink squares). (a) and (d) Concentration over time of **2**, (b) and (e) Concentration over time of **3**, (c) and (f) Concentration over time of DBF.

All reaction kinetics as reported in Figure S6 were based on at least two experiments, where most were done in triplo. Averages of these individual reaction are reported, error bars are included based on standard deviations as calculated by the STDEV.S function in Excel.

The Mannich seeding reactions as displayed in figure S6d-f were performed using a Mannich product **3** which was synthesised by the proline free method precisely described by Klussman *et al.*²

Figure S6b and S6e show the decrease of the concentration of **3** after longer reaction times.

* Note: Initial higher concentrations of DBF in the first hours of the reaction are an artefact as there is a broad peak observed around 6 ppm when starting the reaction. The integrations of the DBF peak at the start of the reactions are therefore always higher than in reality, part of the broad peak is integrated as well.

** Note: As the peak of **d-3** shifts over time and increasingly overlaps with a peak of a side product, the formation of the Mannich product could be followed only for the first 4 hours. After 8 hours of reaction the peak of **d-3** that is followed is an isolated peak in the ¹H-NMR spectrum again as the side product peak is not shifting were the **d-3** product peak is. From this point on it is possible to follow the formation of **d-3** again as the peak is an isolated peak and can be integrated without the interference of the side product.

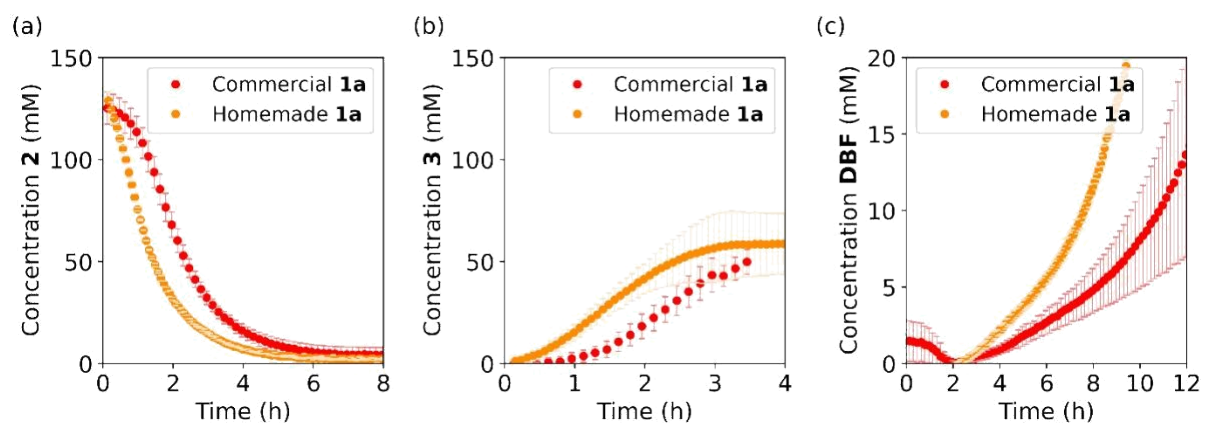
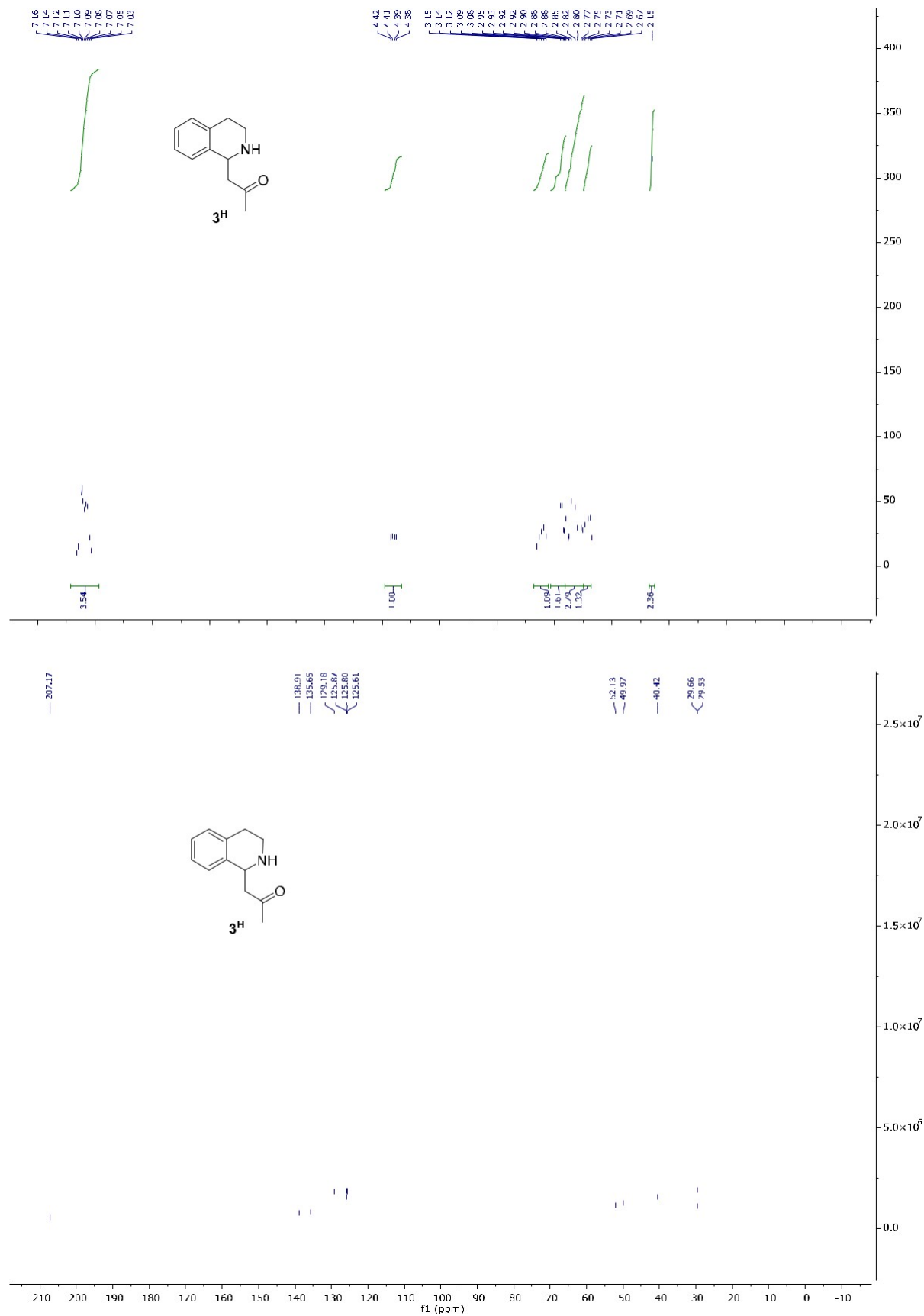
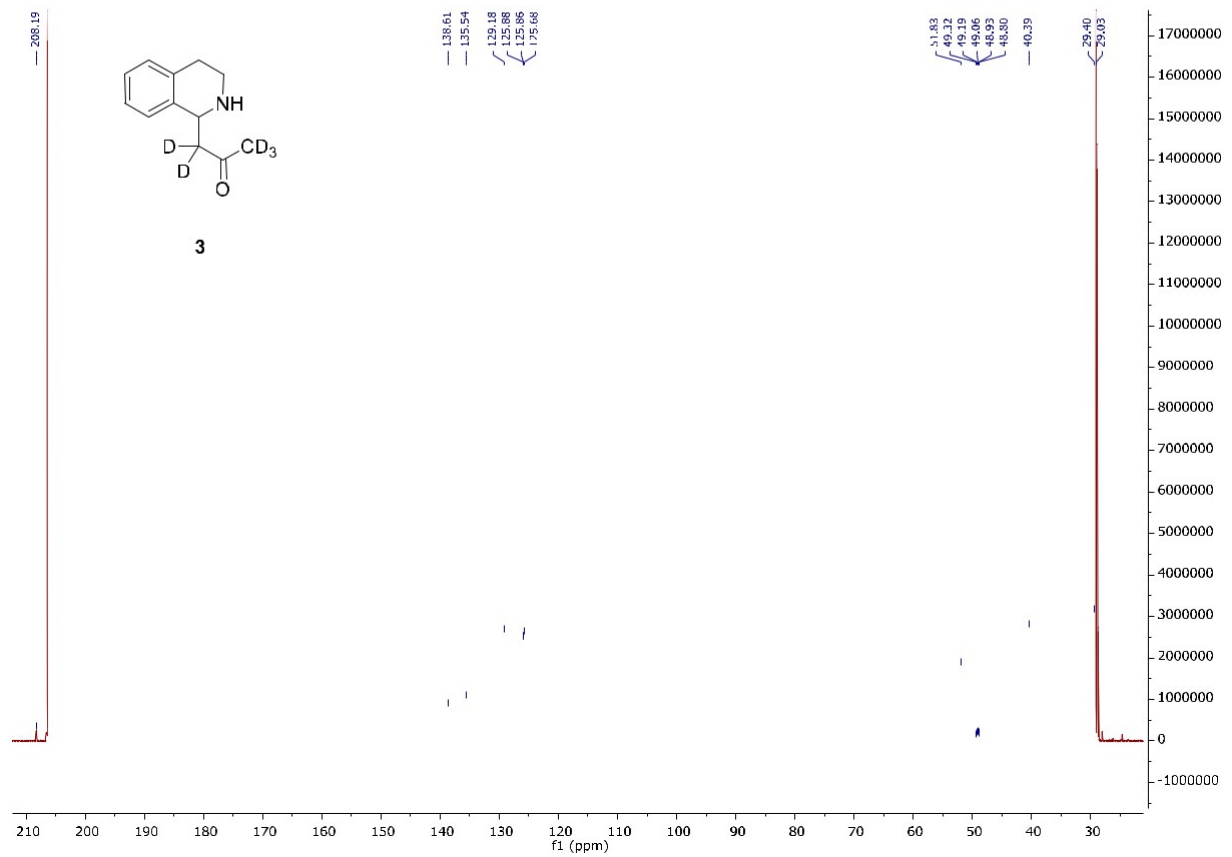
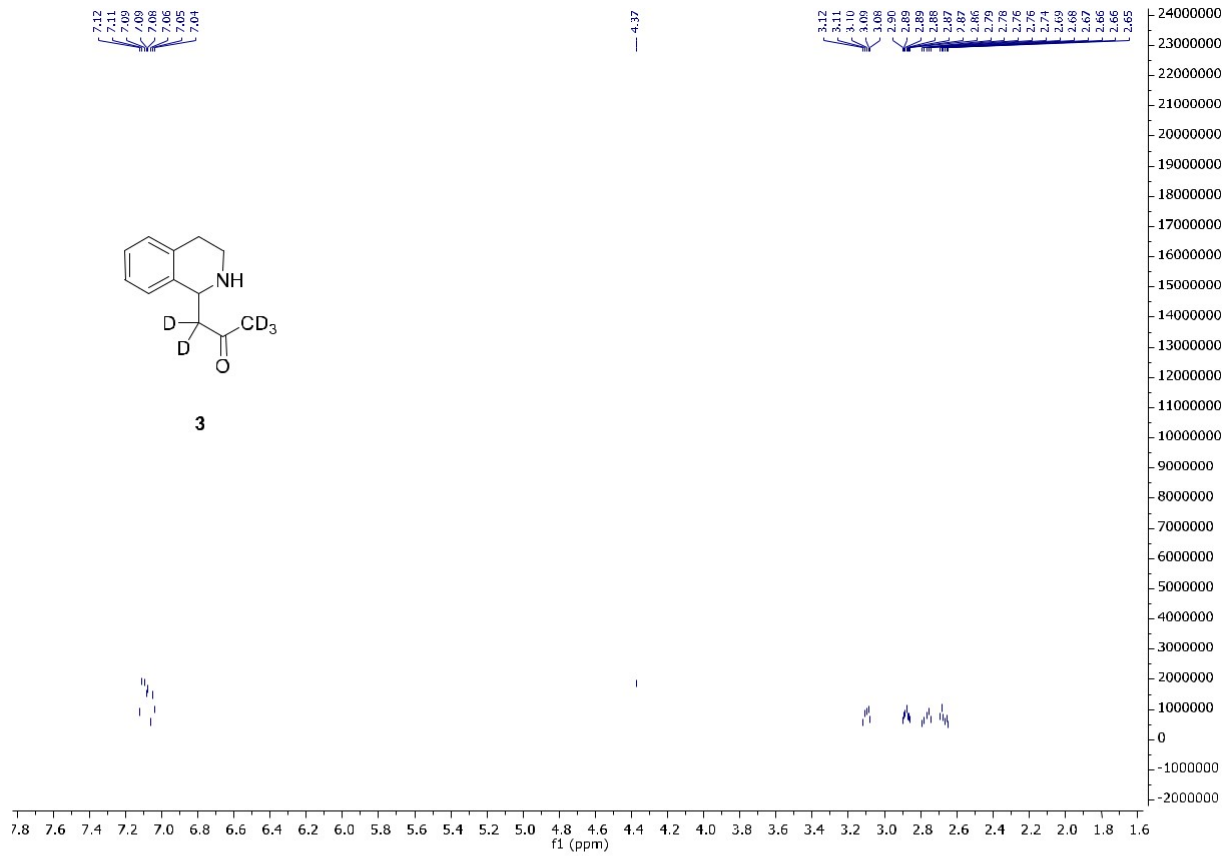
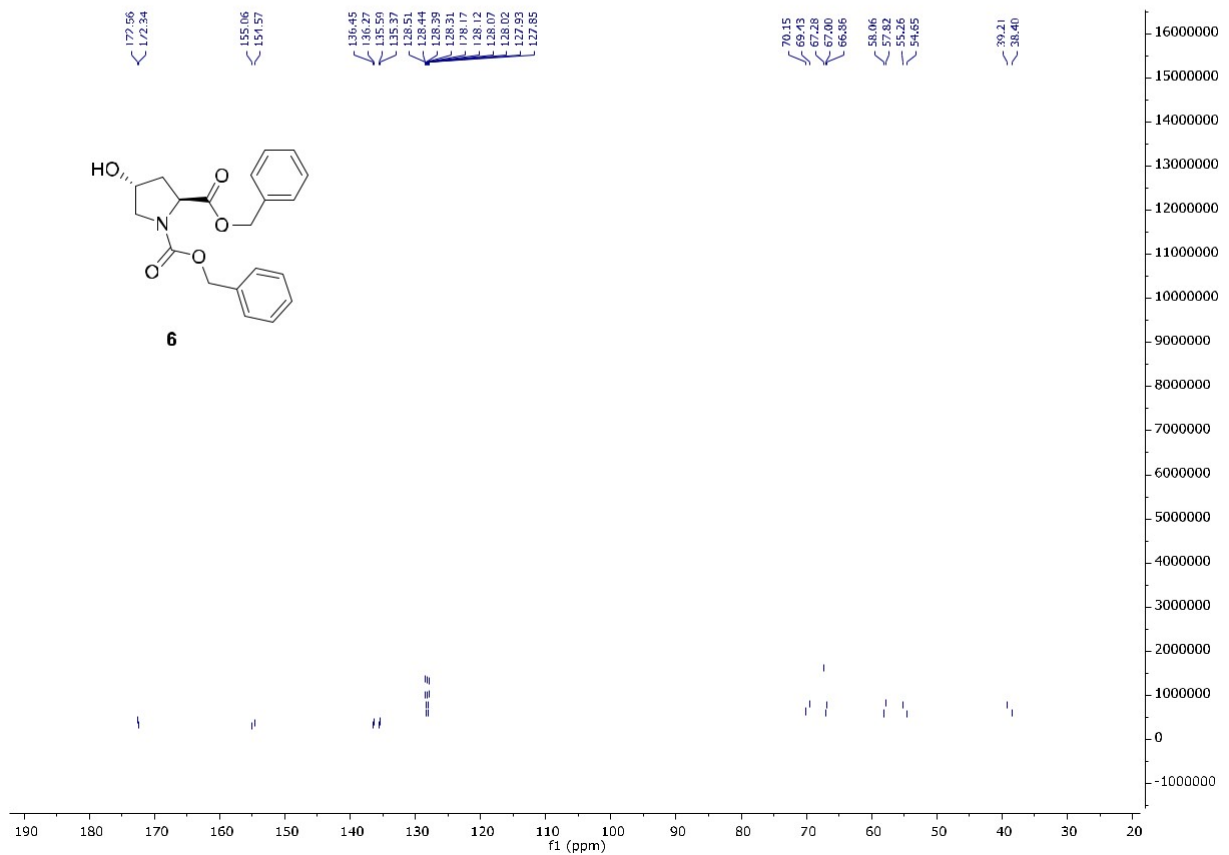
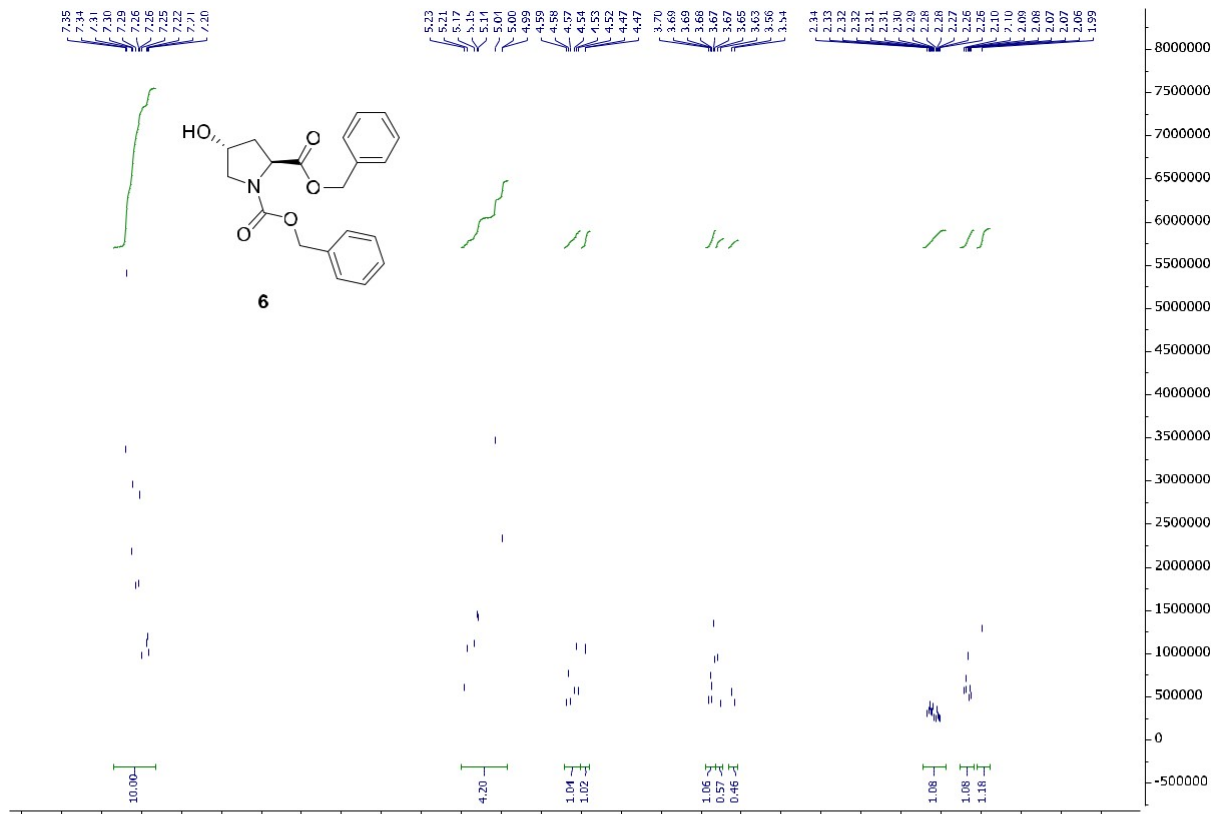


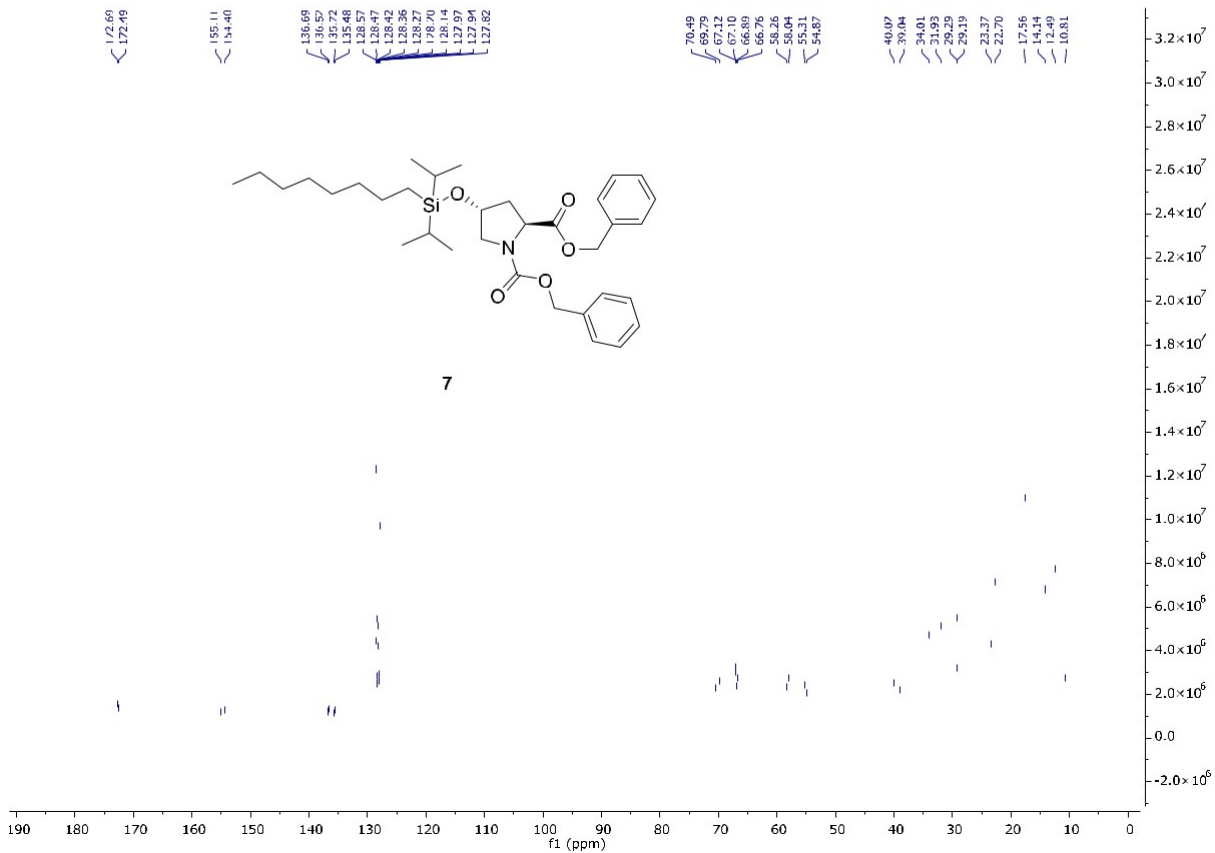
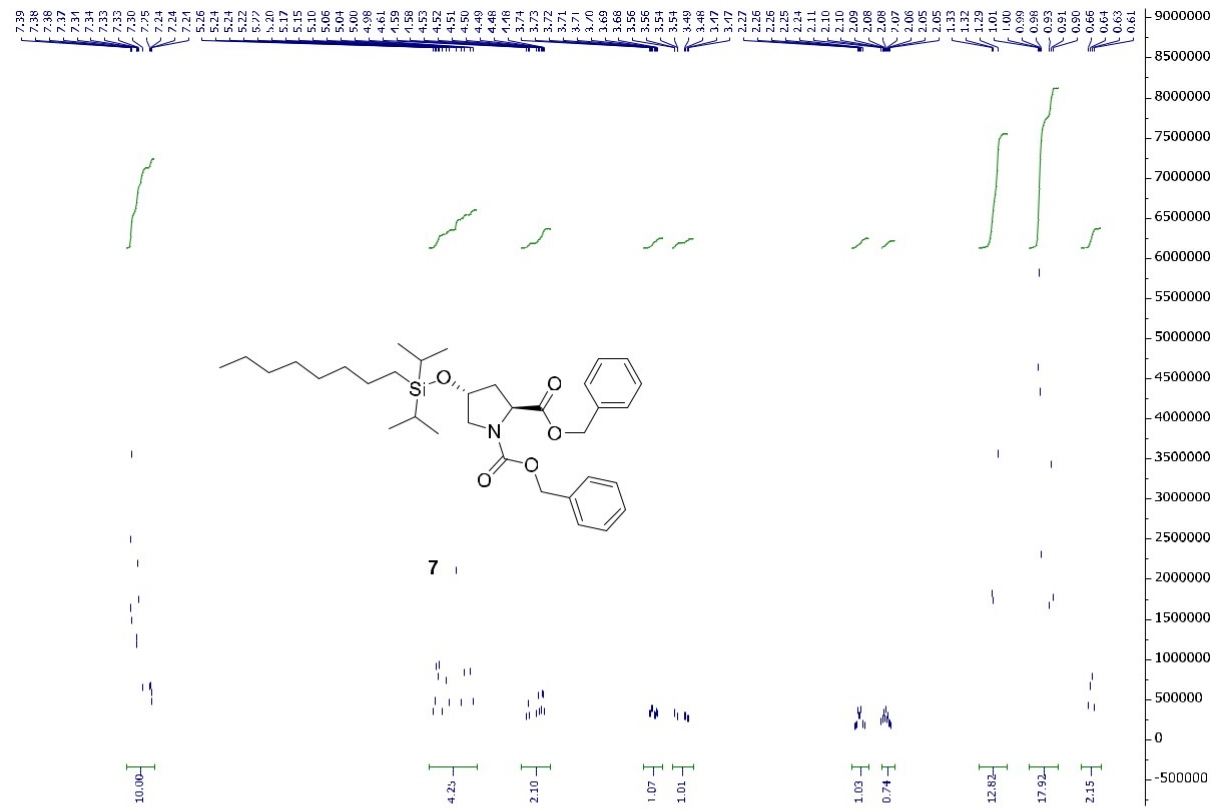
Figure S7 Kinetic experiments examining the cross-catalytic reactions between **2** (133mM) and respectively commercial available **1a** (133 mM) (red circles) and **1a** synthesised in house (133 mM) (orange circles). (a) Concentration over time of **2**, (b) concentration over time of **3**, (c) concentration over time of **DBF**.

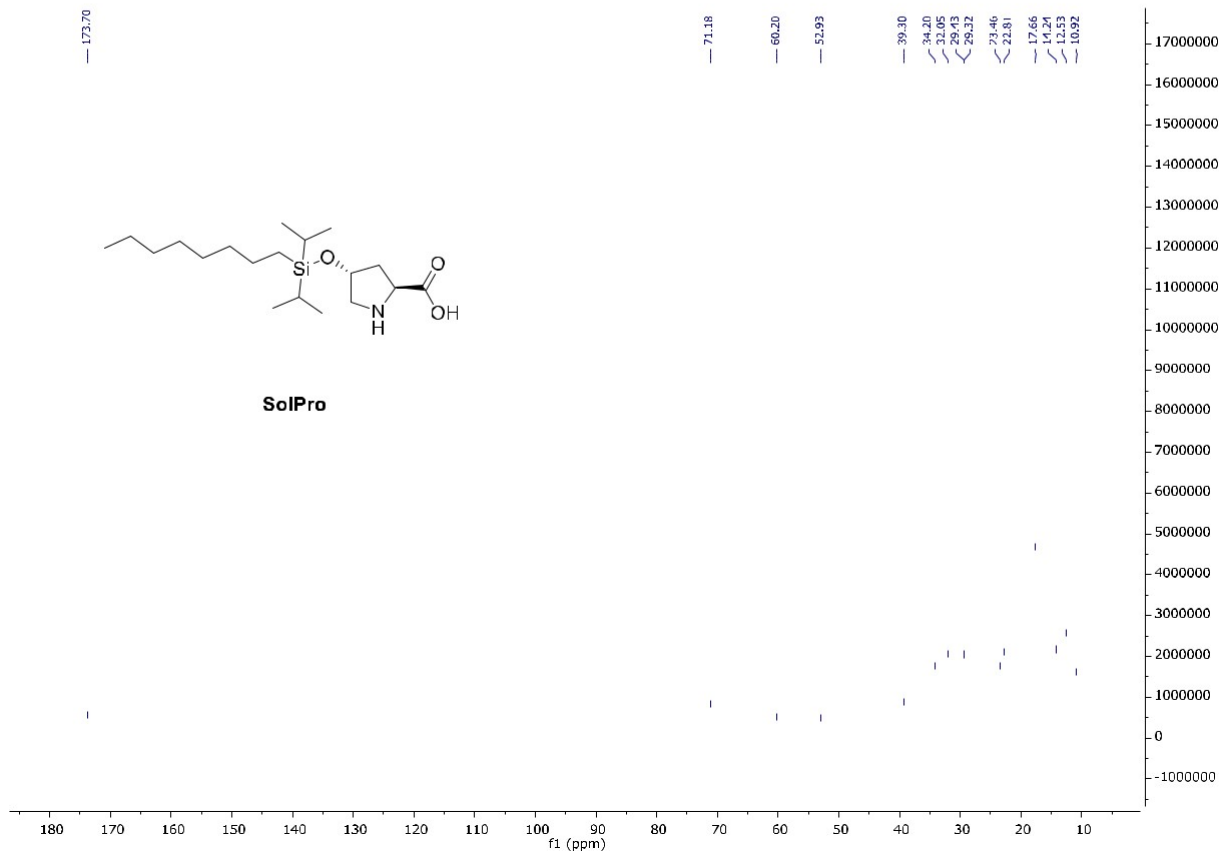
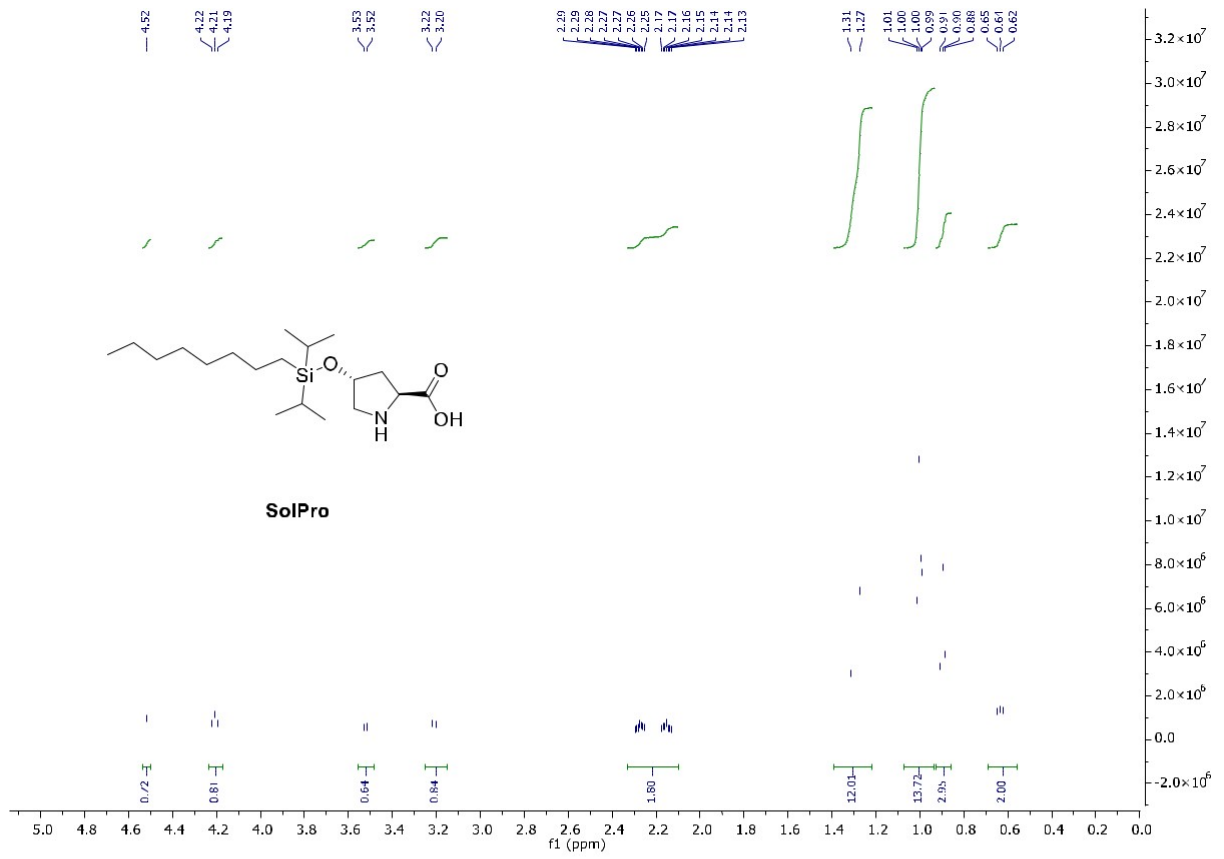
6. NMR spectra

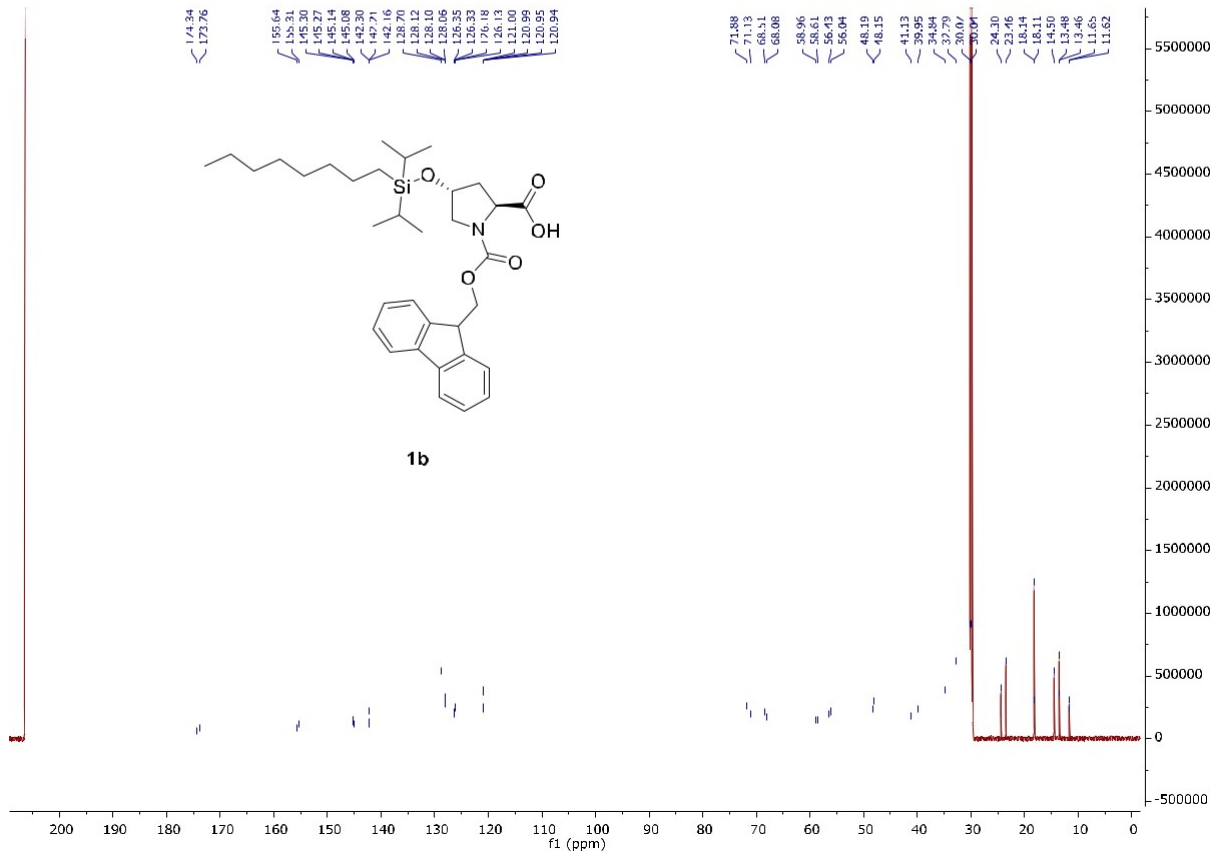
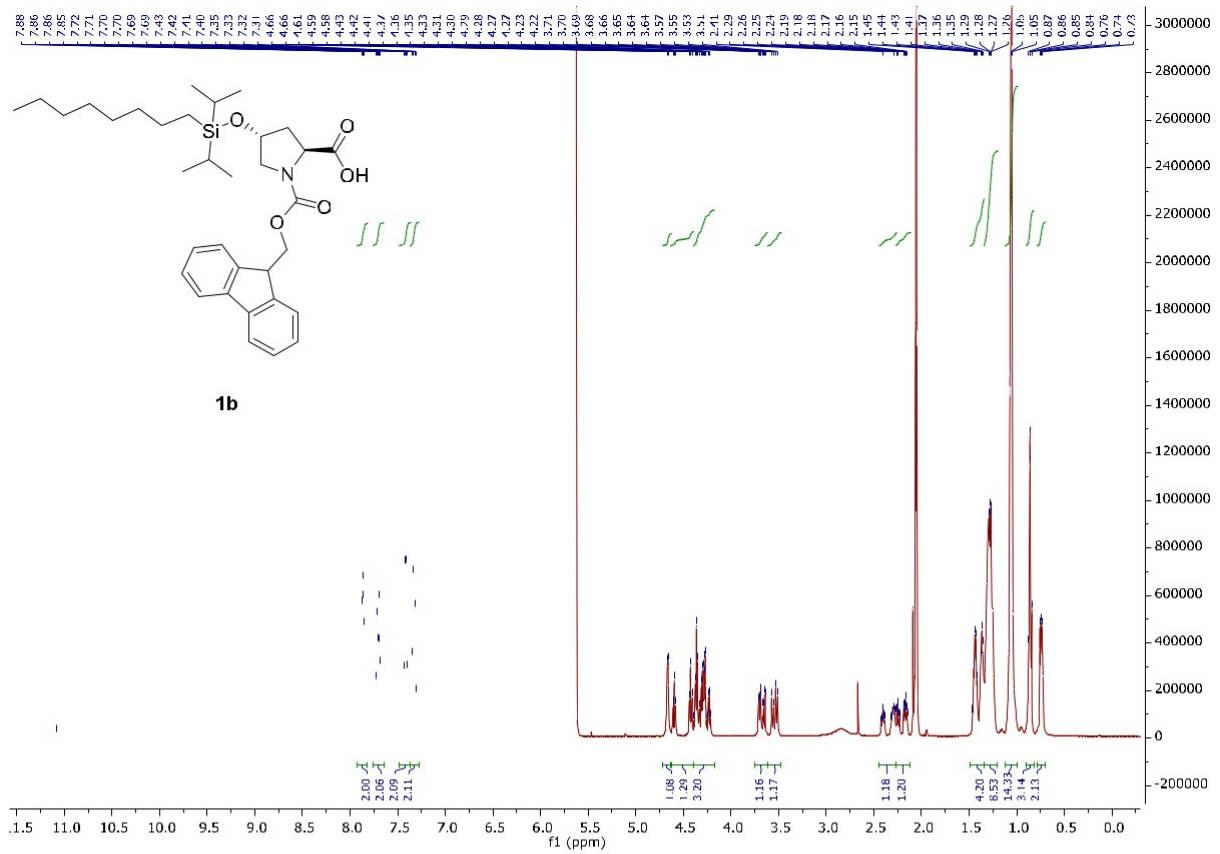


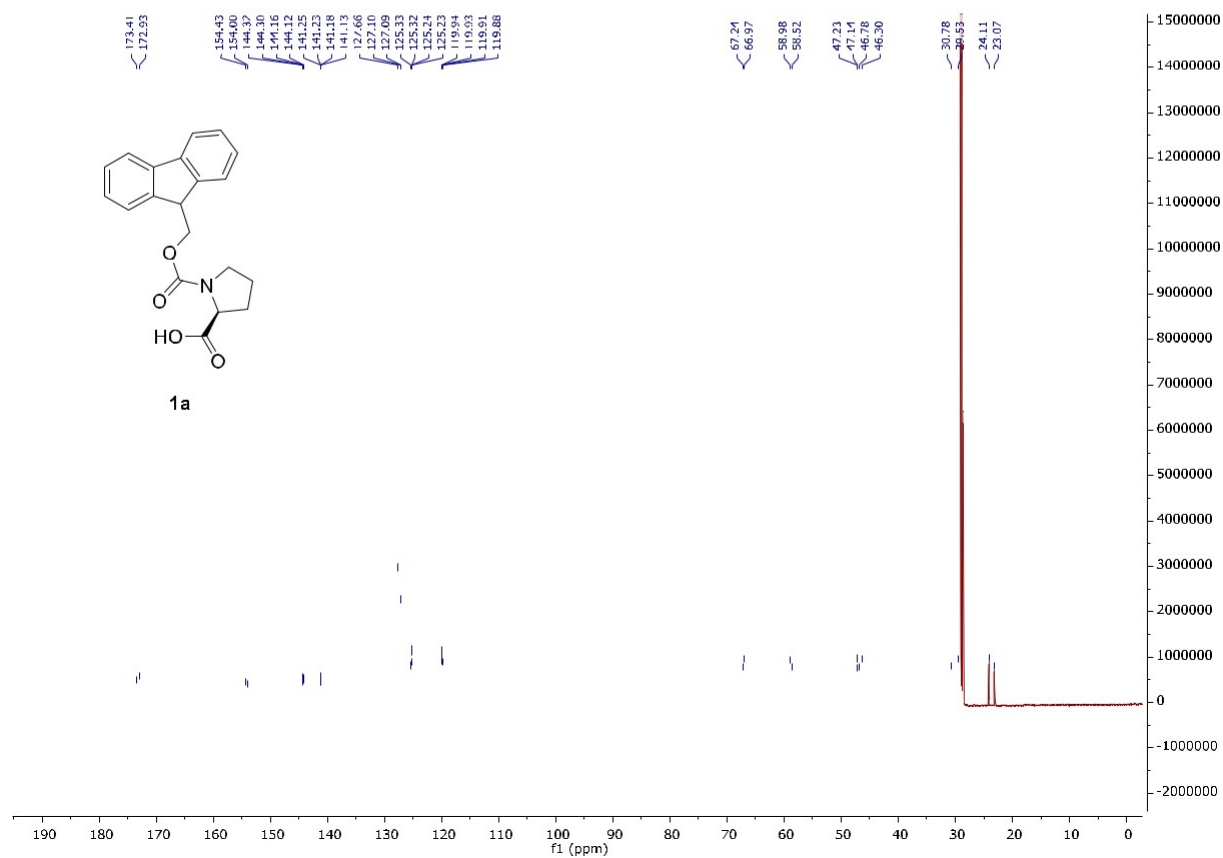
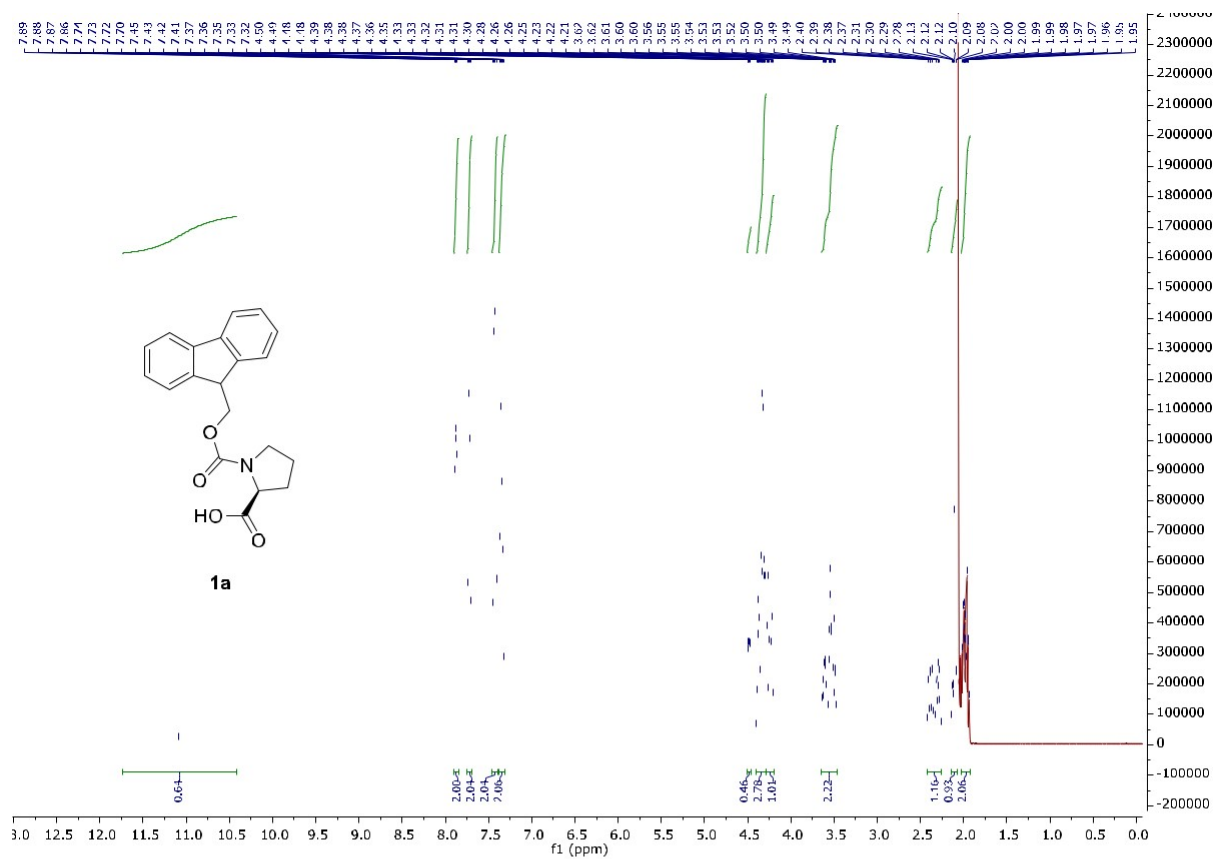


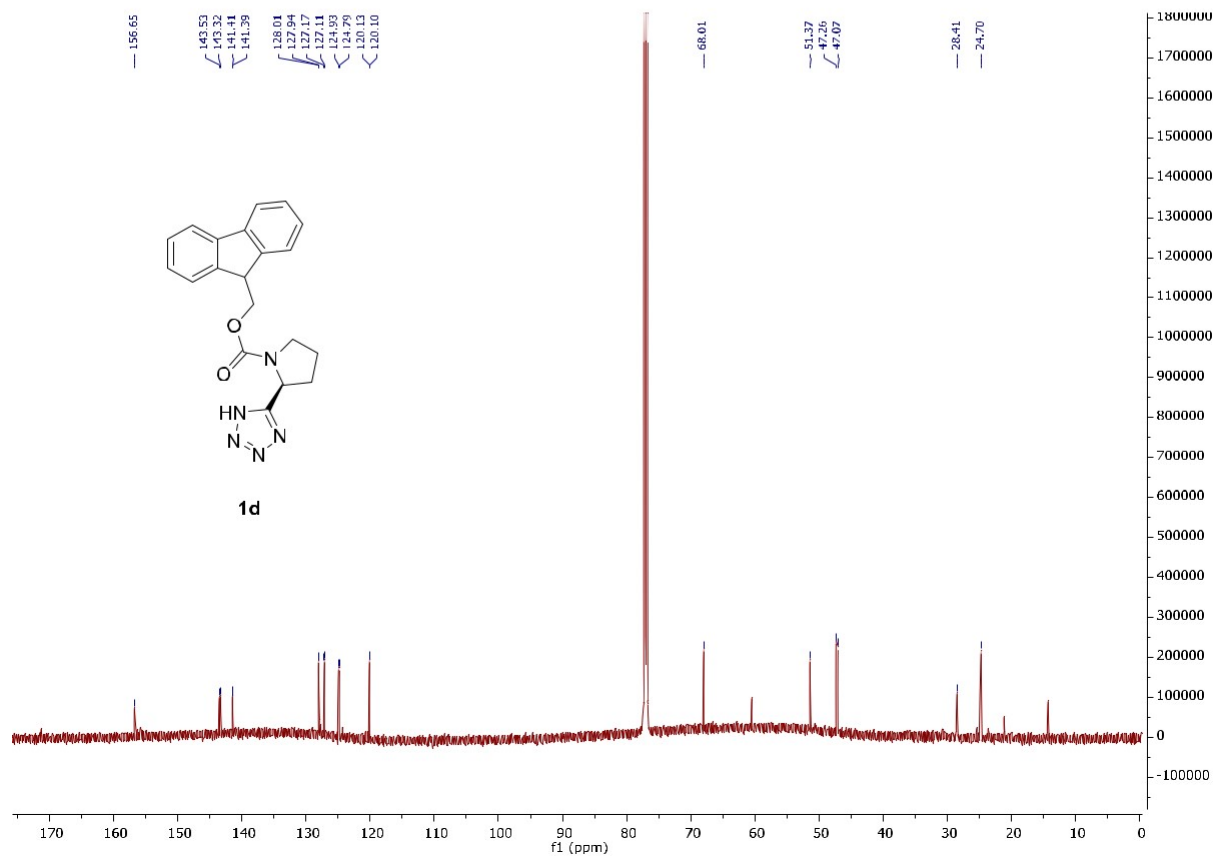
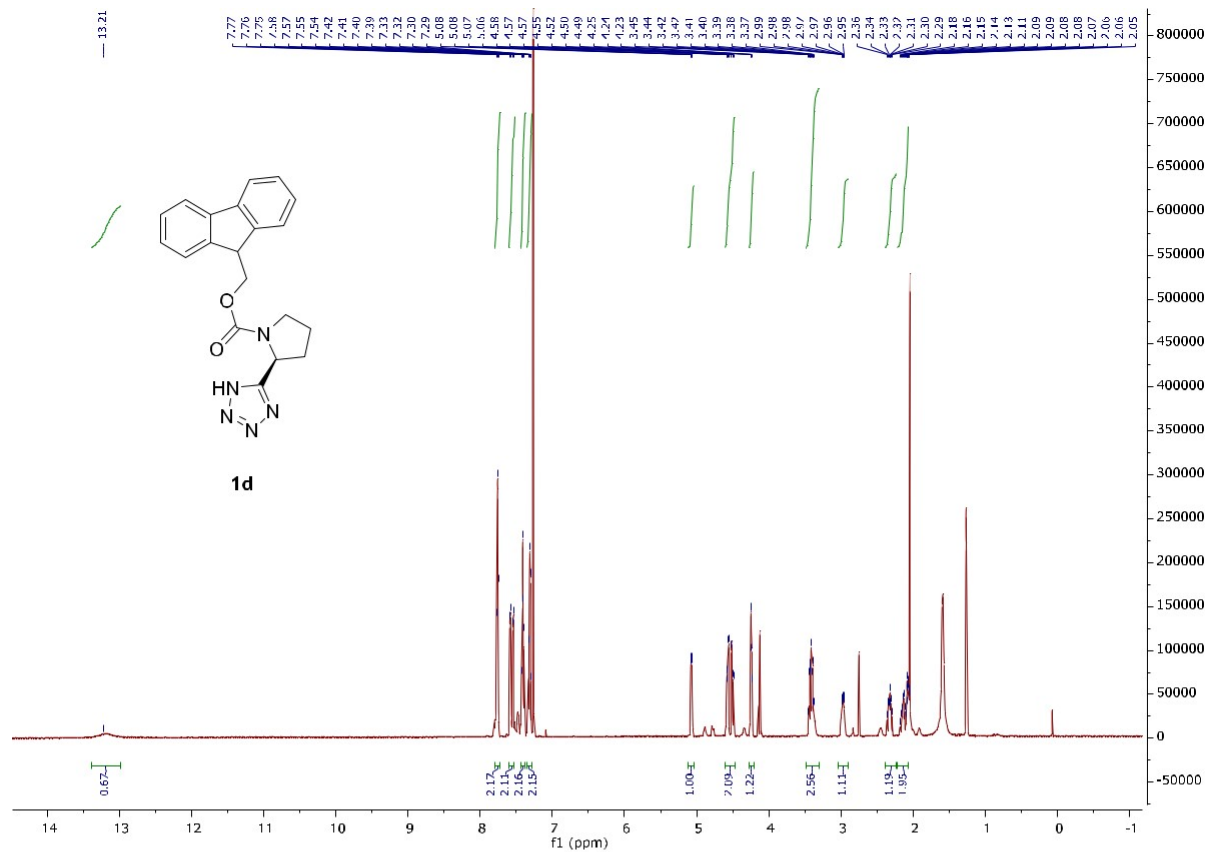




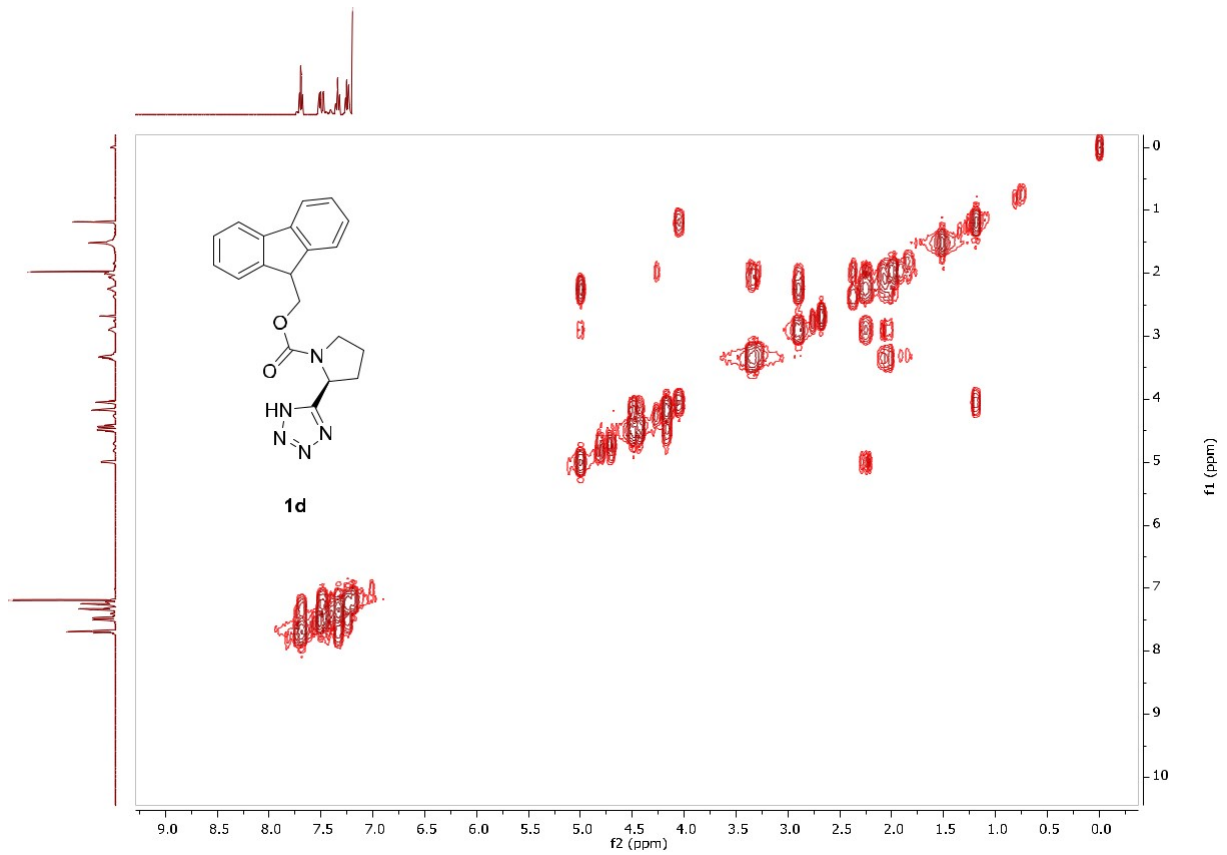




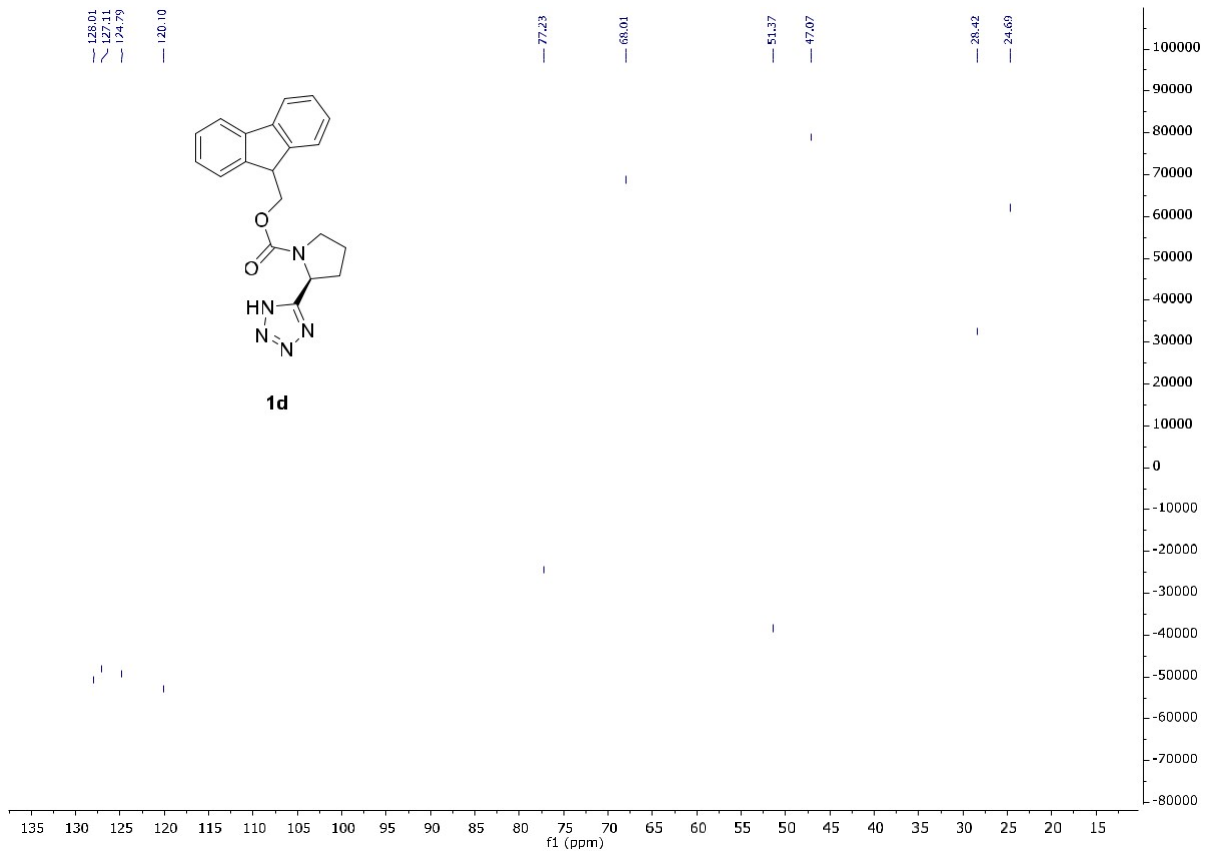




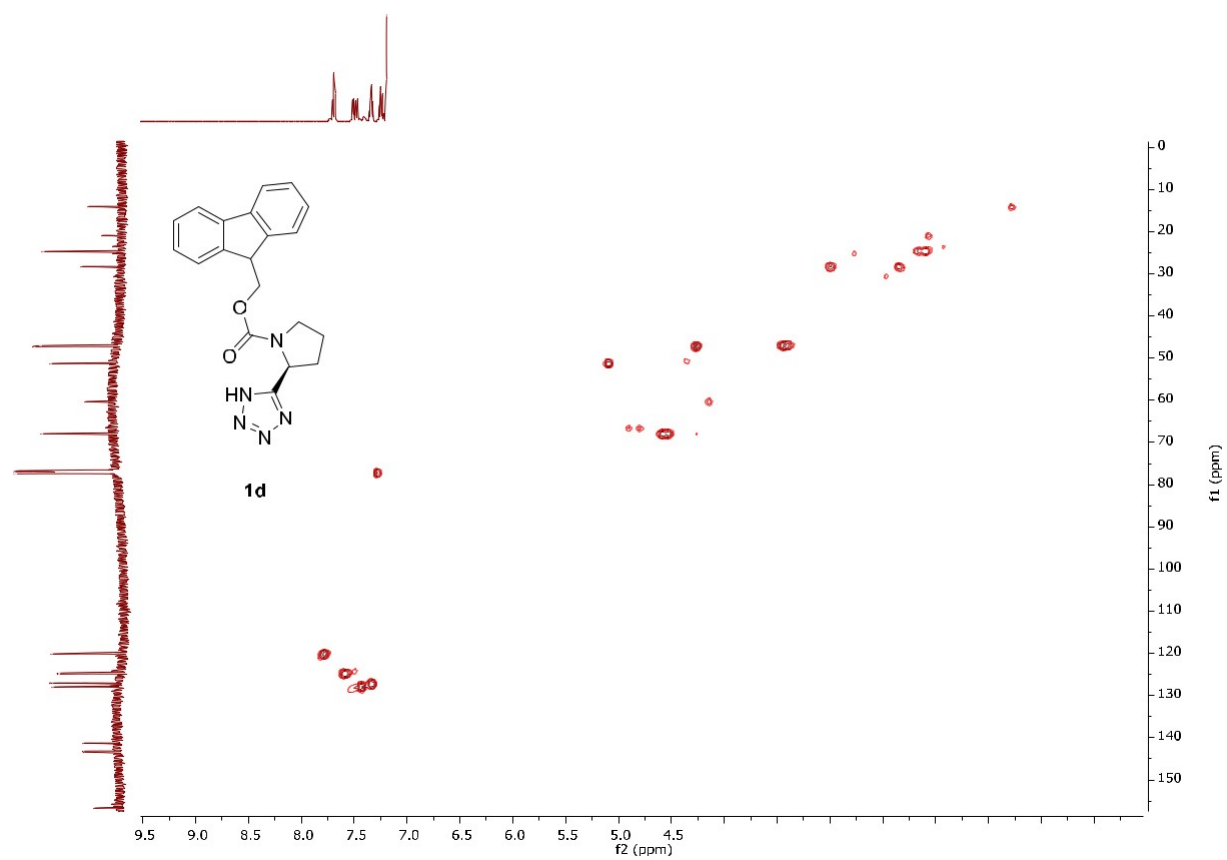
COSY:



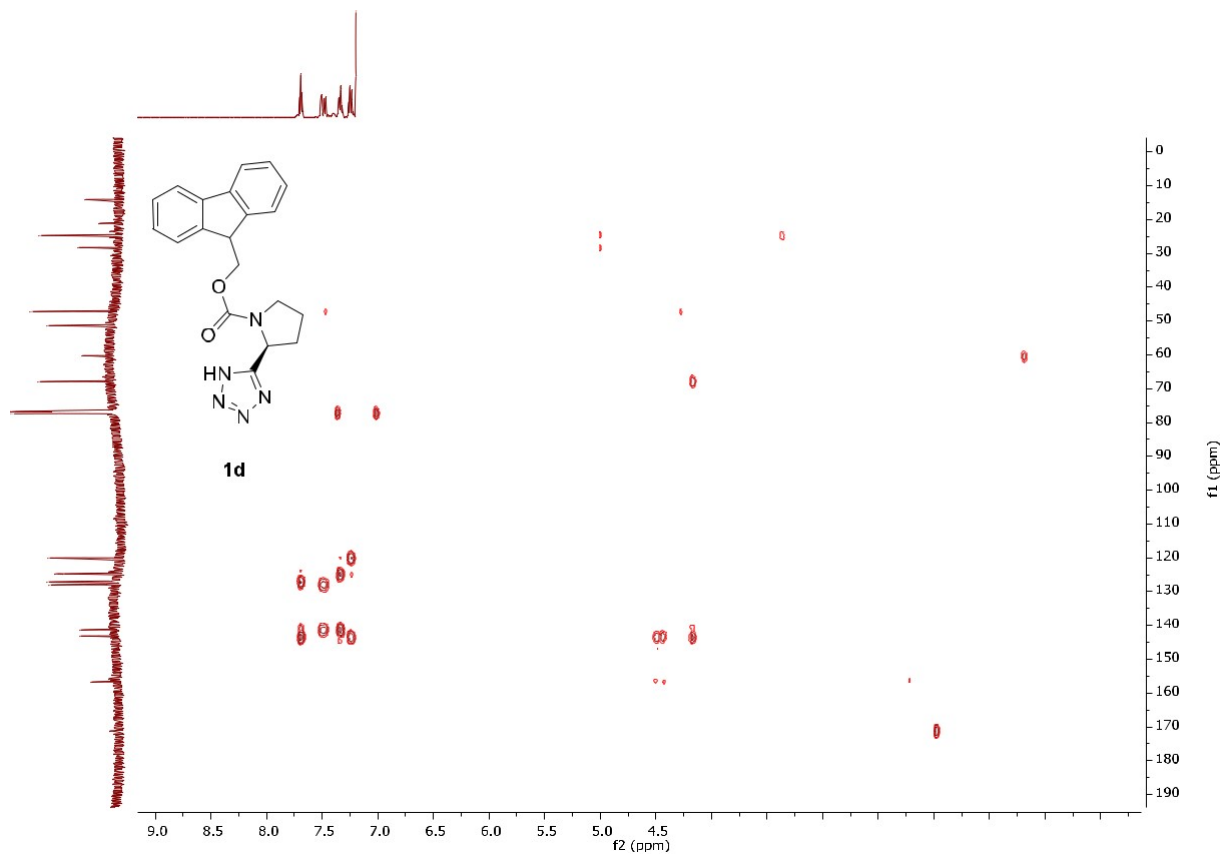
DEPT:



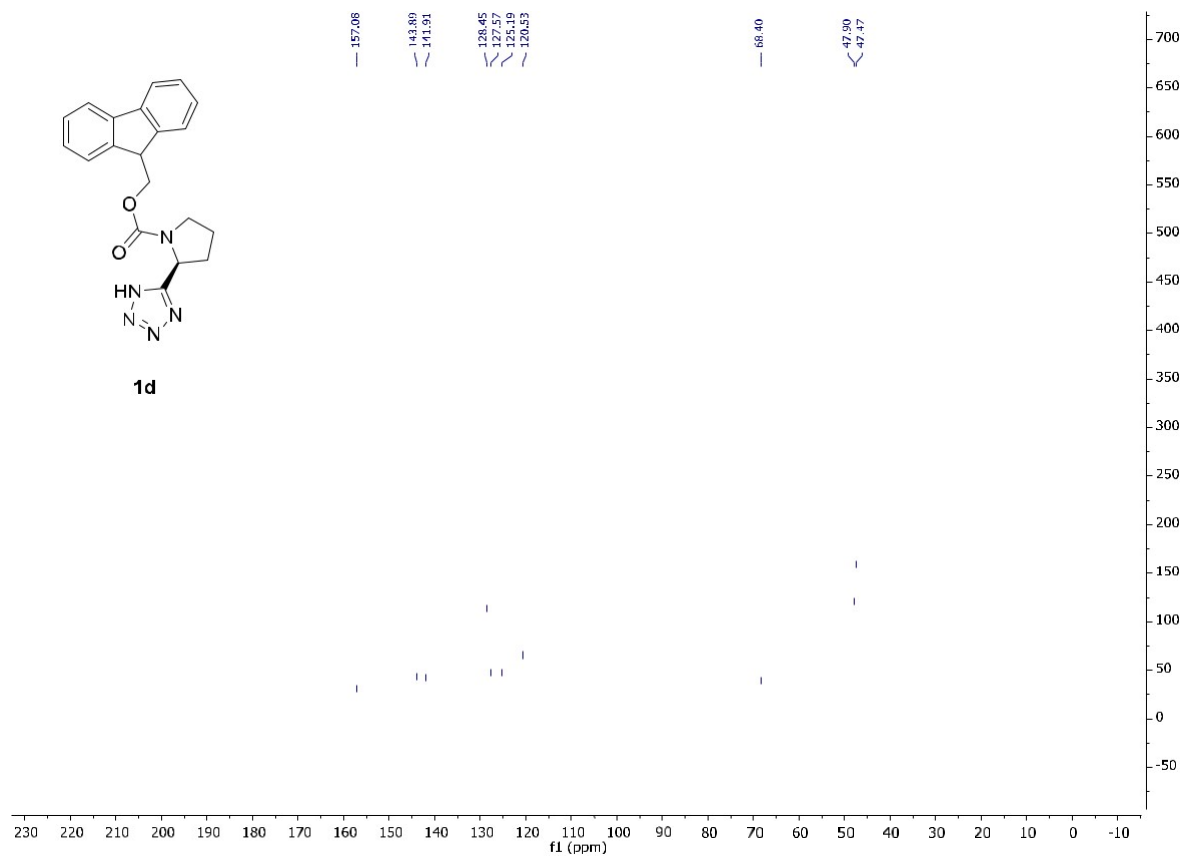
HSQC:



HMBC:



^{13}C -NMR at 55 °C:



7. References

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