

Supplementary Materials

TFA-PROTECTED α -AMINO ACID N-HYDROXYSUCCINIMIDE ESTER: APPLICATION FOR INTER- AND INTRAMOLECULAR ACYLATION

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SM-1. Procedure for the preparation of TFA-L-/D-phenylalanine (TFA-L-/D-Phe, L-/D-2) and TFA-L-/D-proline (TFA-L-/D-Pro, L-/D-20)

The TFA- α -amino acid was prepared with reported procedure^{1,2} with slightly modification. Triethylamine (33 mmol, 1.5 equiv.) was added to a solution of α -amino acid (22 mmol) in MeOH (22 mL). After 5 min, ethyl trifluoroacetate (29 mmol, 1.3 equiv.) was added and the reaction was allowed to stir for 24 h. The solvent was removed by rotary evaporation and the residue that remained was dissolved in H₂O and acidified with concentrated HCl. The mixture was extracted with ethyl acetate for several times and the organic layers were combined and washed with brine, dried by MgSO₄, filtered, and concentrated by rotary evaporation. Further subjection into high vacuum for overnight, if needed to solidify the product (TFA-L-/D-Phe, L-/D-2 and TFA-L-/D-Pro, L-/D-20).

(S)-3-phenyl-2-(2,2,2-trifluoroacetamido)propanoic acid (TFA-L-Phe, L-2). Colorless amorphous mass. $[\alpha]_D = +13$ (*c* 1.0, MeOH); Lit.³ $[\alpha]_D = +17.2$ (*c* 2, Ethanol). IR (neat) ν : 3319, 3099, 3033, 2929, 1739, 1706 cm⁻¹. ¹H-NMR (270 MHz, CDCl₃) δ : 7.38–7.30 (3H, m, Ar-H), 7.14 (2H, d, *J* = 7.6 Hz, Ar-H), 6.72 (1H, br s, NH), 4.94 (1H, dt, *J* = 7.6, 5.6 Hz, CHNH), 3.31 (1H, dd, *J* = 14.2, 5.6 Hz, CH₂CH), 3.22 (1H, dd, *J* = 14.2, 5.6 Hz, CH₂CH) ppm. ¹³C-NMR (67.5 MHz, CDCl₃) δ : 174.2, 156.7 (q, ²*J*_{CF} = 38.2 Hz), 134.2, 129.2 (2 x CH), 129.0 (2 x CH), 127.8, 115.5 (q, ¹*J*_{CF} = 287.2 Hz), 53.2, 36.9 ppm. HRMS-ESI (*m/z*) [M + H]⁺ calcd for C₁₁H₁₁F₃NO₃ 262.0691, found 262.0699.

(R)-3-phenyl-2-(2,2,2-trifluoroacetamido)propanoic acid (TFA-D-Phe, D-2). Colorless amorphous mass. $[\alpha]_D = -13$ (*c* 1.0, MeOH); Lit.⁴ $[\alpha]_D = -17.2$ (*c* 2, Ethanol). IR (neat) ν : 3320, 3093, 3033, 2934, 1740, 1702 cm⁻¹. ¹H-NMR (270 MHz, CDCl₃) δ : 7.34–7.30 (3H, m, Ar-H), 7.14 (2H, d, *J* = 7.3 Hz, Ar-H), 6.69 (1H, br s, NH), 4.94 (1H, dt, *J* = 7.9, 5.8 Hz, CHNH), 3.32 (1H, dd, *J* = 14.2, 5.6 Hz, CH₂CH), 3.22 (1H, dd, *J* = 14.2, 5.6 Hz, CH₂CH) ppm. ¹³C-NMR (67.5 MHz, CDCl₃) δ : 174.6, 156.8 (q, ²*J*_{CF} = 38.4 Hz), 134.2, 129.2 (2 x CH), 129.0 (2 x CH), 127.8, 115.5 (q, ¹*J*_{CF} = 287.3 Hz), 53.3, 36.9 ppm. HRMS-ESI (*m/z*) [M + H]⁺ calcd for C₁₁H₁₁F₃NO₃ 262.0691, found 262.0694.

(S)-1-(2,2,2-Trifluoroacetyl)pyrrolidine-2-carboxylic acid (TFA-L-Pro, L-20).

Colorless amorphous mass. $[\alpha]_D = -86$ (*c* 1.0, CHCl₃); Lit.⁵ $[\alpha]_D = -65.19$ (*c* 1.08, Ph-H). IR (neat) ν : 1739, 1705 cm⁻¹. ¹H-NMR (270 MHz, CDCl₃) δ : 4.59 (1H, dd, *J* = 8.4, 3.8 Hz, CH₂CH), 3.90–3.69 (2H, m, CH₂), 2.36–1.99 (4H, m, 2 x CH₂) ppm. ¹³C-NMR (67.5 MHz, CDCl₃) δ : 176.2, 176.0, 156.1 (q, ²*J*_{CF} = 37.8 Hz), 116.0 (q, ¹*J*_{CF} = 287.0 Hz), 60.0, 59.1 (q, *J* = 3.4 Hz), 48.0, 47.2 (q, *J* = 3.4 Hz), 31.5, 28.3, 24.8, 21.0 ppm. HRMS-ESI (*m/z*) [M + H]⁺ calcd for C₇H₉F₃NO₃ 212.0535, found 212.0536.

(R)-1-(2,2,2-Trifluoroacetyl)pyrrolidine-2-carboxylic acid (TFA-D-Pro, D-20).

Colorless amorphous mass. $[\alpha]_D = +86$ (*c* 1.0, CHCl₃). IR (neat) ν : 1738, 1709 cm⁻¹. ¹H-NMR (270 MHz, CDCl₃) δ : 4.59 (1H, dd, *J* = 8.2, 3.6 Hz, CH₂CH), 3.87–3.67 (2H, m, CH₂), 2.37–1.96 (4H, m, 2 x CH₂) ppm. ¹³C-NMR (67.5 MHz, CDCl₃) δ : 175.9, 175.7, 156.1 (q, ²*J*_{CF} = 37.8 Hz), 116.0 (q, ¹*J*_{CF} = 286.8 Hz), 60.0, 59.1 (q, *J* = 3.4 Hz), 48.0, 47.2 (q, *J* = 3.4 Hz), 31.5, 28.3, 24.8, 21.0 ppm. HRMS-ESI (*m/z*) [M + H]⁺ calcd for C₇H₉F₃NO₃ 212.0535, found 212.0555.

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- (1) Curphey, T. J. *J. Org. Chem.* **1979**, *44* (2), 2805–2807.
 - (2) Deblander, J.; Van Aeken, S.; Jacobs, J.; De Kimpe, N.; Tehrani, K. A. *Eur. J. Org. Chem.* **2009**, No. 28, 4882–4892.
 - (3) Weygand, F.; Ropsch, A. *Chem. Ber.* **1959**, *92*, 2095–2099.
 - (4) Fones, W. S.; Lee, M. *J. Biol. Chem.* **1954**, *210* (1), 227–238.
 - (5) Ookawa, A.; Soai, K. *J. Chem. Soc., Perkin Trans. I* **1987**, 1465–1471.

SM-2. Procedure for the preparation of TFA-L-/D-tyrosine (L-/D-15).

Triethylamine (136 mmol, 8 equiv.) was added to a solution of α -amino acid (17 mmol) in MeOH (40 mL). After 5 min, ethyl trifluoroacetate (51 mmol, 3 equiv.) was added and the reaction was allowed to stir for 7 d. The solvent was removed by rotary evaporation and the residue that remained was dissolved in H₂O and acidified with concentrated HCl. The mixture was extracted with ethyl acetate for several times and the organic layers were combined and washed with brine, dried by MgSO₄, filtered, and concentrated by rotary evaporation. Further subjection into high vacuum for overnight, if needed to solidify the product (TFA-L-/D-Tyr, L-/D-15).

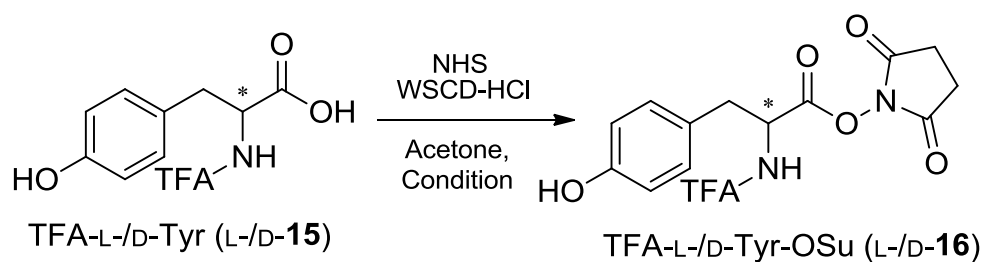
(S)-3-(4-hydroxyphenyl)-2-(2,2,2-trifluoroacetamido)propanoic acid (TFA-L-Tyr, L-15).

Yellowish amorphous mass. $[\alpha]_D = +26$ (*c* 1.0, MeOH). IR (neat) ν : 3302, 3098, 2932, 1734 cm⁻¹. ¹H-NMR (270 MHz, ACETONE-D₆) δ : 8.55 (1H, br s, OH), 7.19 (2H, d, *J* = 8.2 Hz, Ar-H), 6.83 (2H, d, *J* = 8.6 Hz, Ar-H), 4.78 (1H, td, *J* = 8.7, 4.5 Hz, CHNH), 3.31 (1H, dd, *J* = 14.2, 4.6 Hz, CH₂CH), 3.08 (1H, dd, *J* = 14.0, 9.7 Hz, CH₂CH) ppm. ¹³C-NMR (67.5 MHz, ACETONE-D₆) δ : 171.6, 157.3 (q, ²*J*_{CF} = 36.9 Hz), 157.1, 131.0 (2 x CH), 128.2, 116.8 (q, ¹*J*_{CF} = 287.2 Hz), 116.0 (2 x CH), 55.0, 36.4 ppm. HRMS-ESI (*m/z*) [M + Na]⁺ calcd for C₁₁H₁₀F₃NO₄Na 300.0460, found 300.0444.

(R)-3-(4-hydroxyphenyl)-2-(2,2,2-trifluoroacetamido)propanoic acid (TFA-D-Tyr, D-15).

Yellowish amorphous mass. $[\alpha]_D = -26$ (*c* 1.0, MeOH). IR (neat) ν : 3295, 3098, 2932, 1732 cm⁻¹. ¹H-NMR (270 MHz, ACETONE-D₆) δ : 8.51 (1H, br s, OH), 7.15 (2H, d, *J* = 8.2 Hz, Ar-H), 6.80 (2H, d, *J* = 8.2 Hz, Ar-H), 4.78 (1H, td, *J* = 8.7, 4.9 Hz, CHNH), 3.29 (1H, dd, *J* = 14.2, 4.9 Hz, CH₂CH), 3.05 (1H, dd, *J* = 14.2, 9.6 Hz, CH₂CH) ppm. ¹³C-NMR (67.5 MHz, ACETONE-D₆) δ : 171.9, 157.5 (q, ²*J*_{CF} = 37.1 Hz), 157.0, 131.0 (2 x CH), 128.1, 116.8 (q, ¹*J*_{CF} = 287.3 Hz), 116.1 (2 x CH), 55.0, 36.4 ppm. HRMS-ESI (*m/z*) [M + Na]⁺ calcd for C₁₁H₁₀F₃NO₄Na 300.0460, found 300.0469.

SM-4. Optimization of TFA-L-/D-tyrosine-OSu (L-/D-16) synthesis

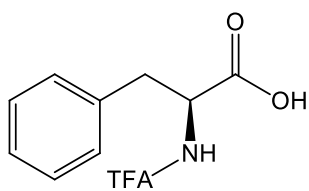


Entry ^a	Start Material	NHS (equiv.)	WSCD-HCl (equiv.)	Condition	%Yield
1	L-15 ^c	1.1	1.0	2h, rt	66% ^g
2	D-15 ^c	1.1	1.0	2h, rt	70% ^g
3	L-15 ^d	1.3	1.0	2h, rt	60% ^g
4	D-15 ^d	1.3	1.0	2h, rt	66% ^g
5 ^b	L-15 ^d	1.3	1.0	3h, rt	75%
6 ^b	D-15 ^d	1.3	1.0	3h, rt	74%
7	L-15 ^e	1.3	1.0 ^f	2h, rt	70% ^g
8	D-15 ^e	1.3	1.0 ^f	2h, rt	72% ^g
9	L-15 ^c	1.3	1.4	2h, rt	68% ^g
10	D-15 ^c	1.3	1.4	2h, rt	63% ^g
11	L-15 ^c	1.8	1.0	2h, rt	58% ^g
12	D-15 ^c	1.8	1.0	2h, rt	54% ^g

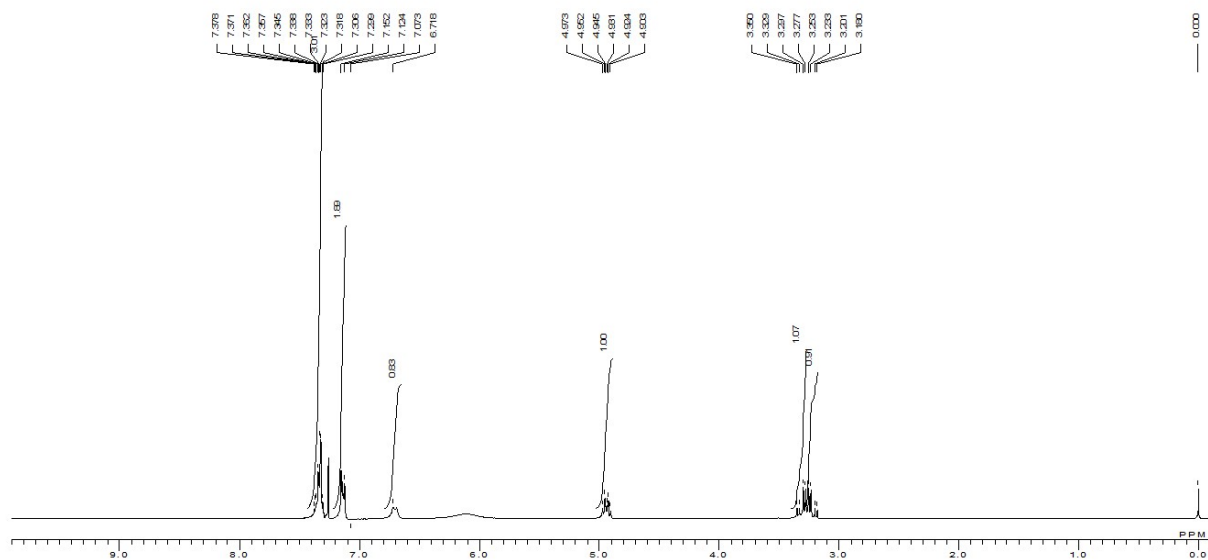
^aSolvent was removed under reduced pressure. Then, residue was dissolve in ethyl acetate and washed by sat. NaCl and NaHCO₃ 0.1M. ^bSolvent was removed under reduced pressure. Then, residue was dissolve in ethyl acetate and washed by sat. NaCl and NaHCO₃ 0.01M. ^cConc. 0.08M in acetone. ^dConc. 0.04M in acetone. ^eConc. 0.06M in acetone. ^fWSCD-HCl was dissolved in CH₂Cl₂ (0.06M) before addition at 0 °C. ^gContaminated with unidentified compounds, observed by appearance of other α -protons in ¹H-NMR (ratio 1.00 : 0.01~0.18).

SM-5. NMR Spectra

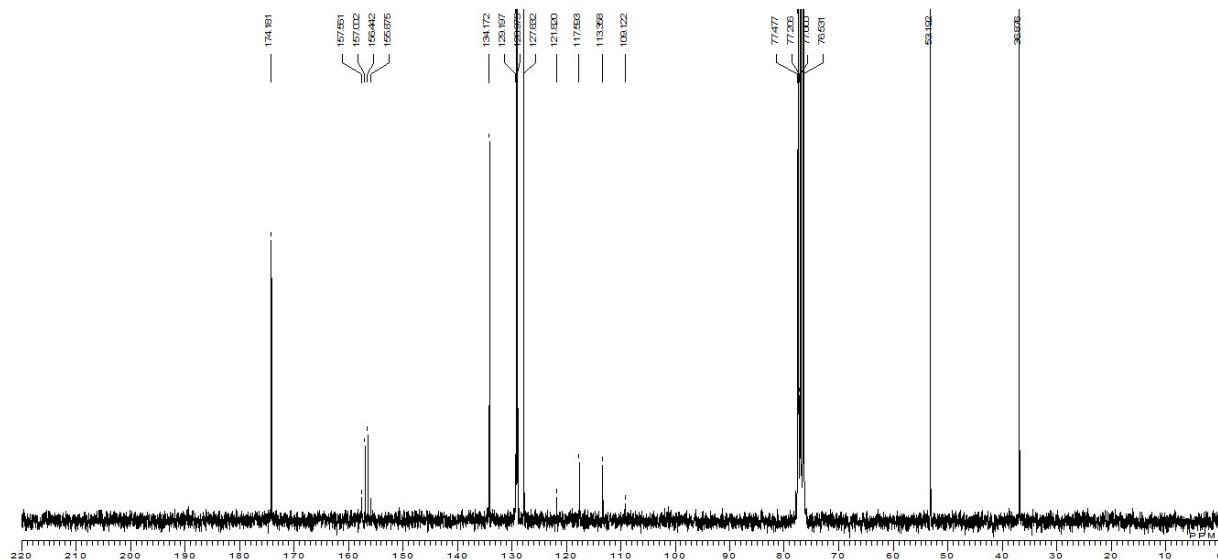
(S)-3-phenyl-2-(2,2,2-trifluoroacetamido)propanoic acid (TFA-L-Phe, L-2)



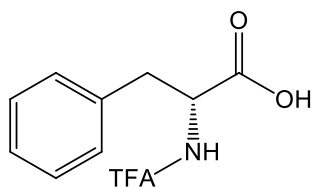
$^1\text{H-NMR}$ (270 MHz, CDCl_3)



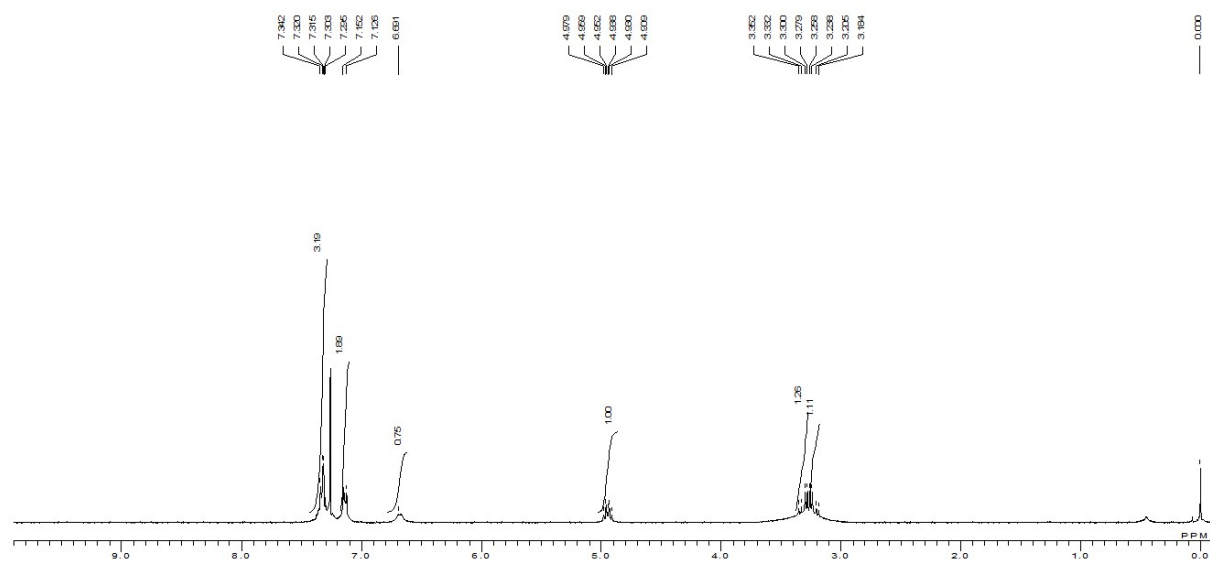
$^{13}\text{C-NMR}$ (67.5 MHz, CDCl_3)



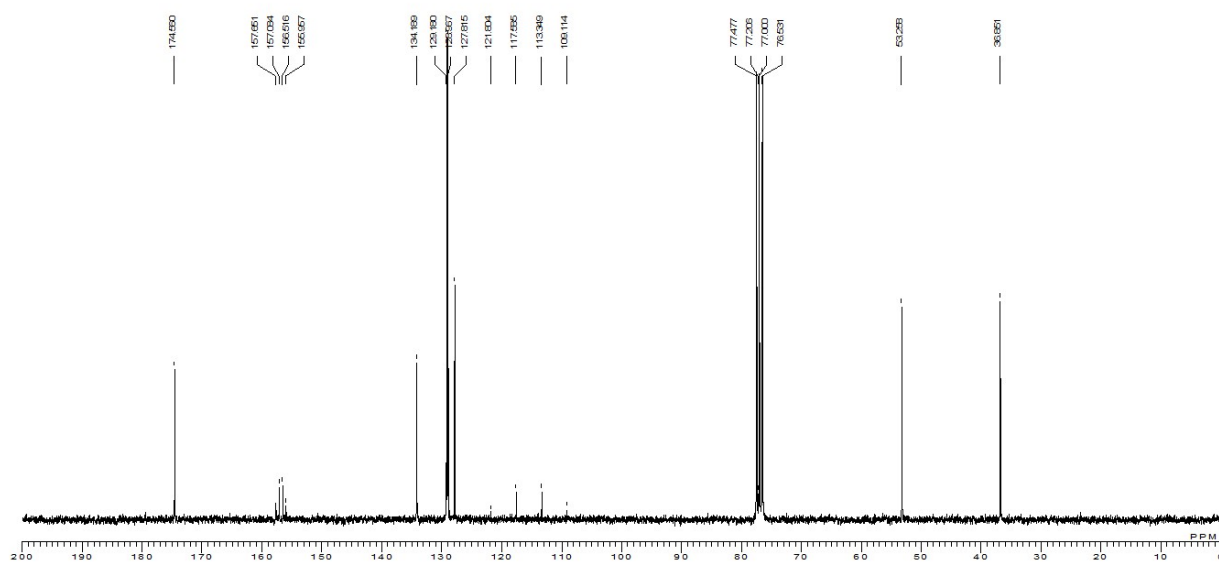
(R)-3-phenyl-2-(2,2,2-trifluoroacetamido)propanoic acid (TFA-D-Phe, D-2)



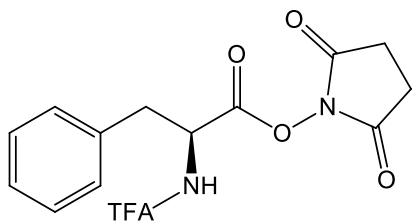
¹H-NMR (270 MHz, CDCl₃)



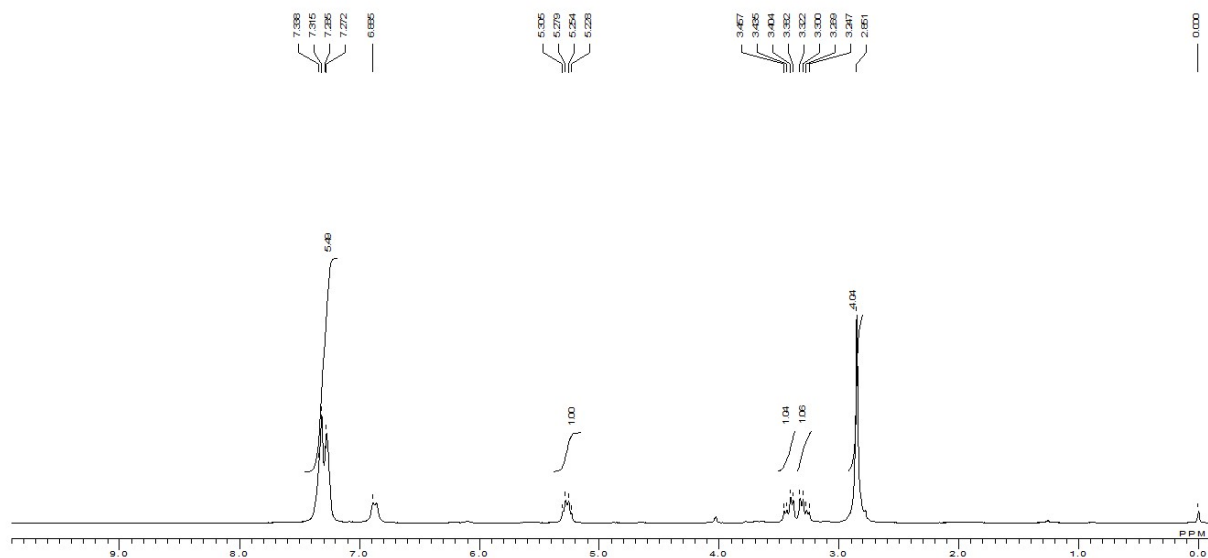
¹³C-NMR (67.5 MHz, CDCl₃)



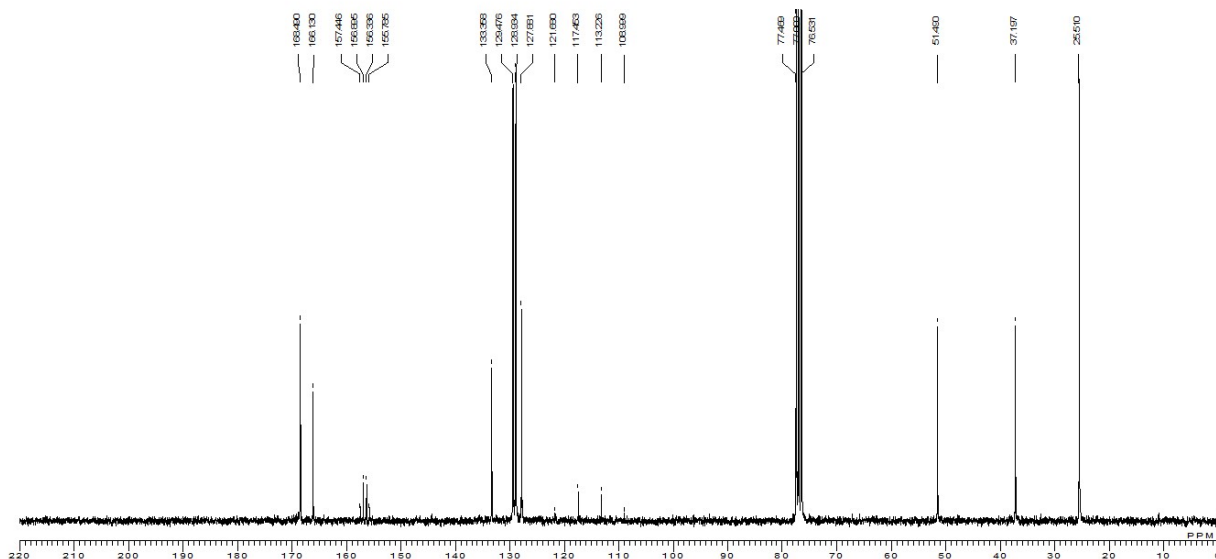
(S)-2,5-dioxopyrrolidin-1-yl 3-phenyl-2-(2,2,2-trifluoroacetamido)propanoate (TFA-L-Phe-OSu, L-3)



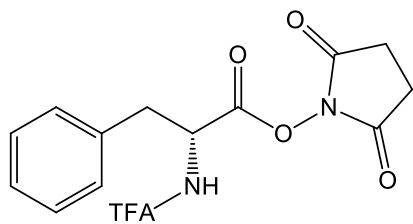
$^1\text{H-NMR}$ (270 MHz, CDCl_3)



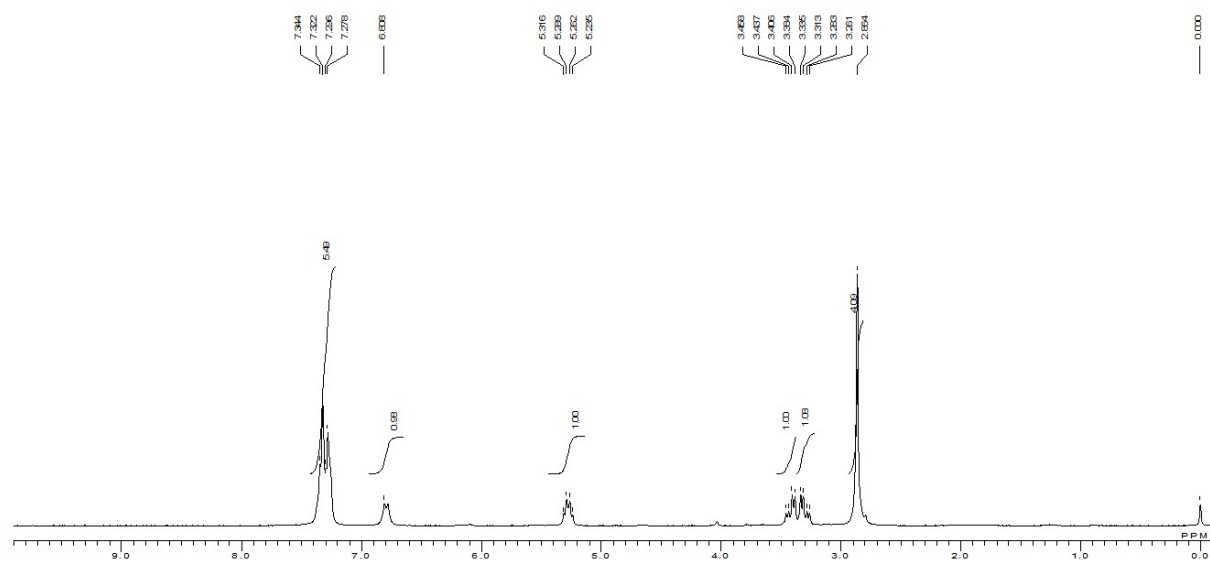
$^{13}\text{C-NMR}$ (67.5 MHz, CDCl_3)



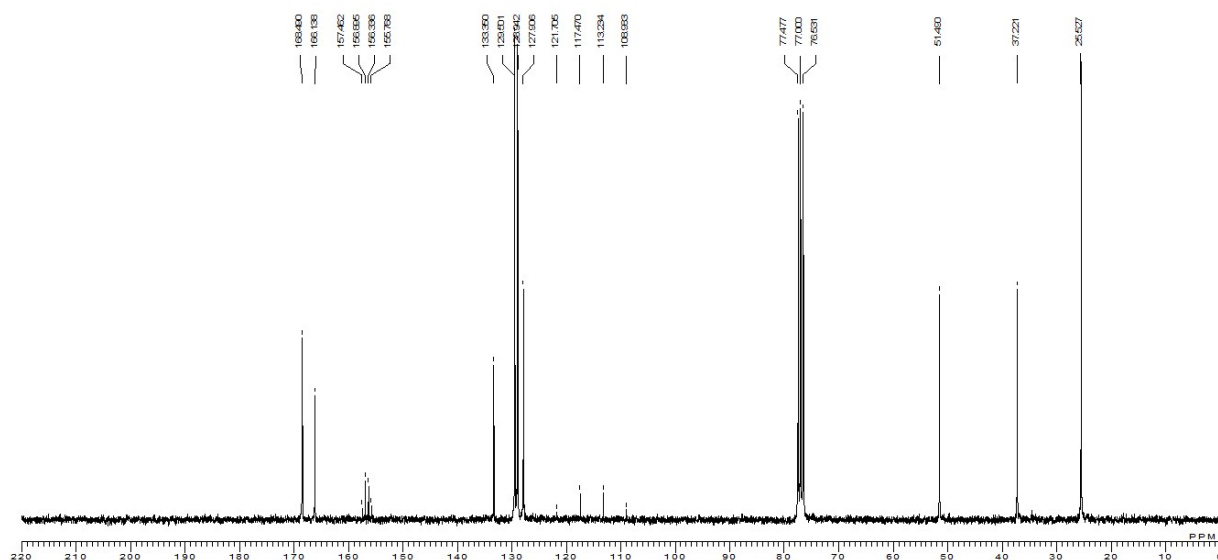
(R)-2,5-dioxopyrrolidin-1-yl 3-phenyl-2-(2,2,2-trifluoroacetamido)propanoate (TFA-D-Phe-OSu, D-3)



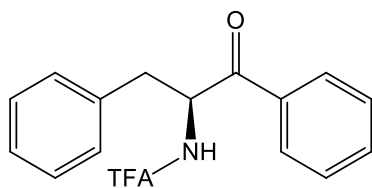
$^1\text{H-NMR}$ (270 MHz, CDCl_3)



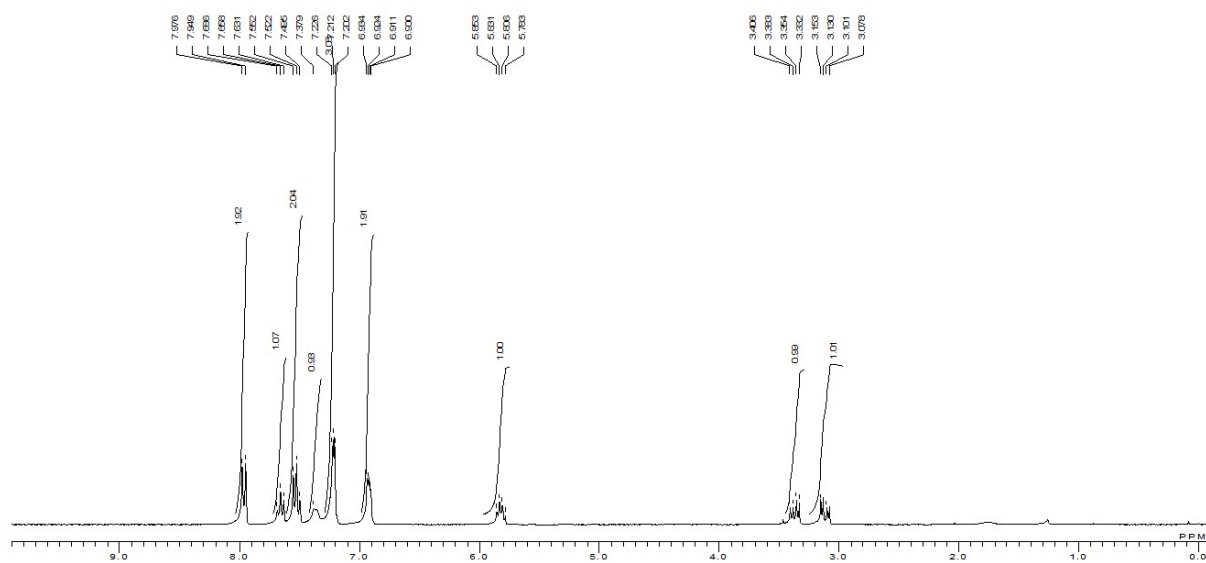
$^{13}\text{C-NMR}$ (67.5 MHz, CDCl_3)



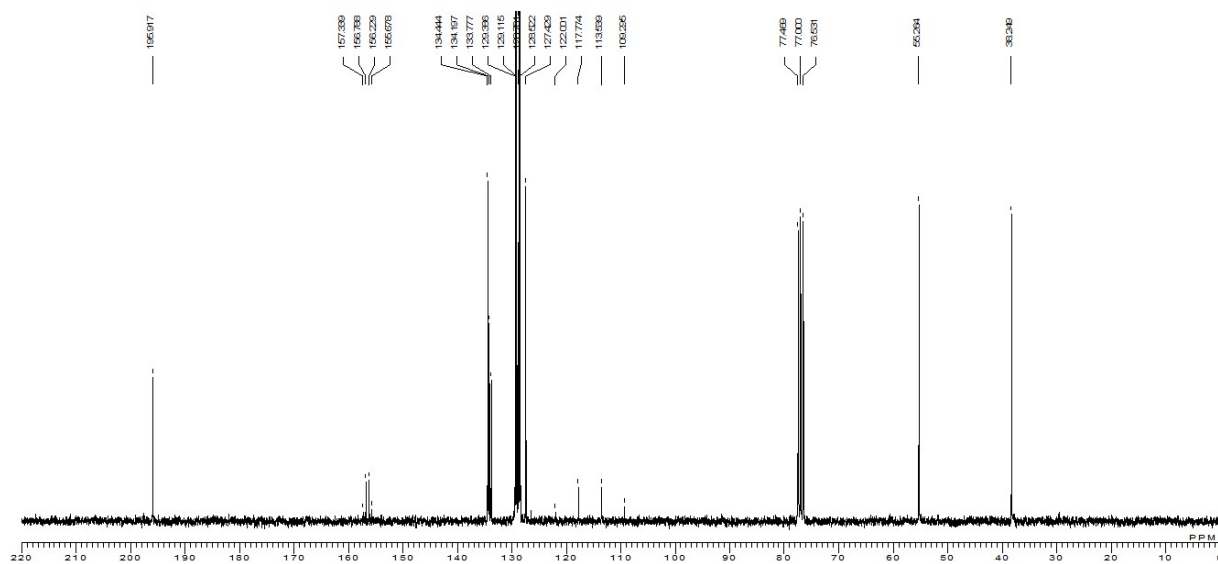
(S)-2,2,2-trifluoro-N-(1-oxo-1,3-diphenylpropan-2-yl)acetamide (TFA-L-Phe-Ph, L-4)



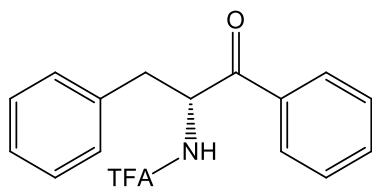
¹H-NMR (270 MHz, CDCl₃)



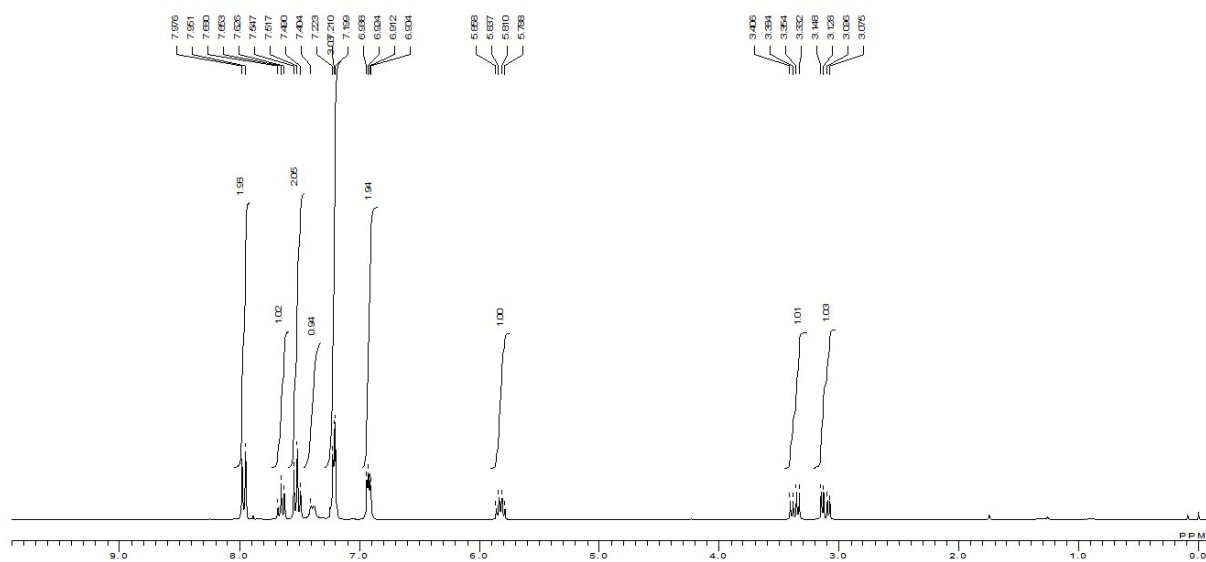
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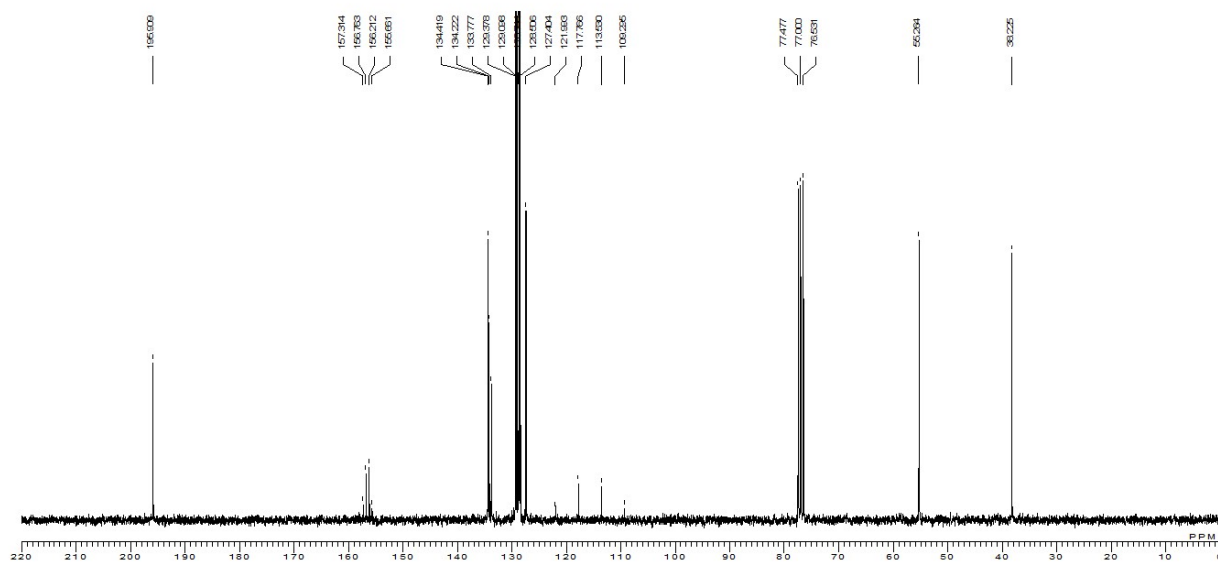
(R)-2,2,2-trifluoro-N-(1-oxo-1,3-diphenylpropan-2-yl)acetamide (TFA-D-Phe-Ph, D-4)



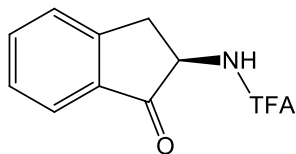
¹H-NMR (270 MHz, CDCl₃)



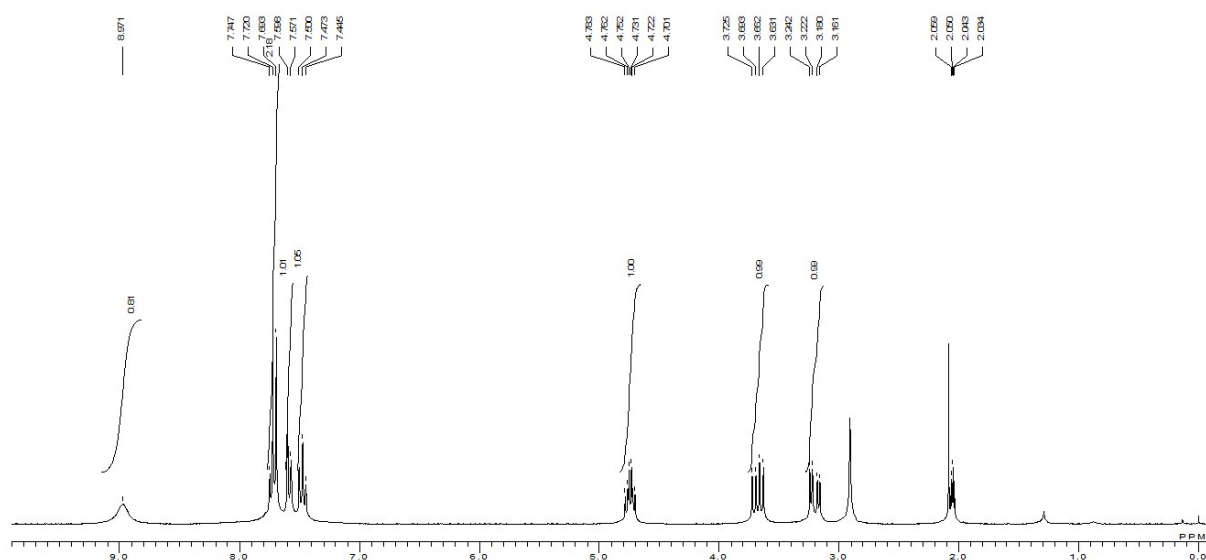
¹³C-NMR (67.5 MHz, CDCl₃)



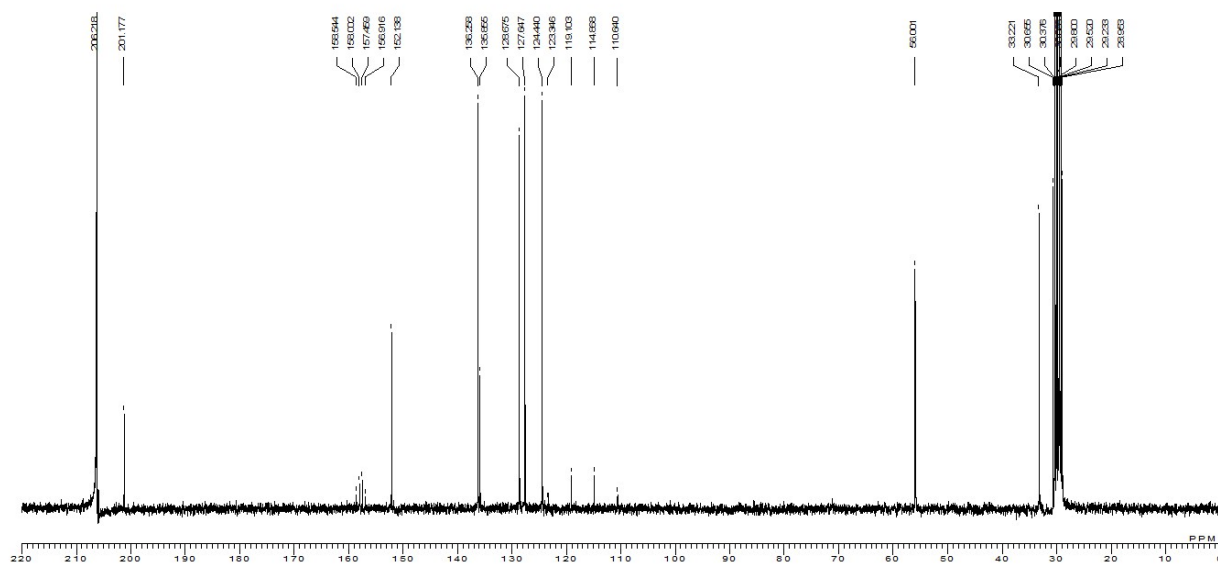
(S)-2,2,2-trifluoro-N-(1-oxo-2,3-dihydro-1H-inden-2-yl)acetamide (TFA-L-cPhe, L-5)



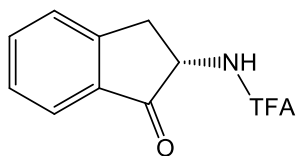
¹H-NMR (270 MHz ACETONE-D₆)



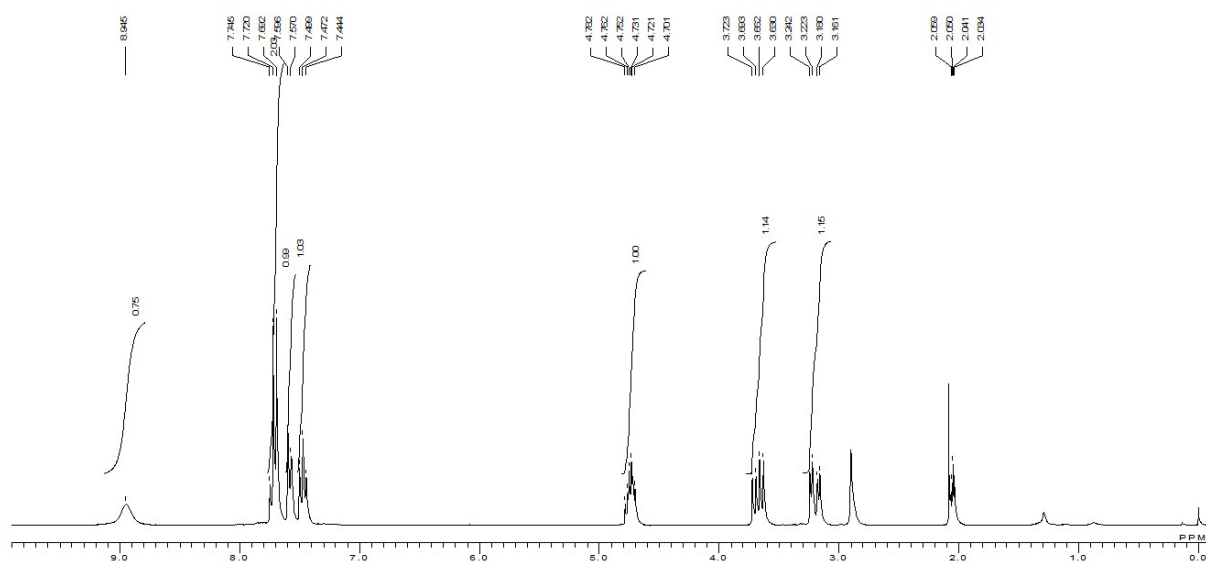
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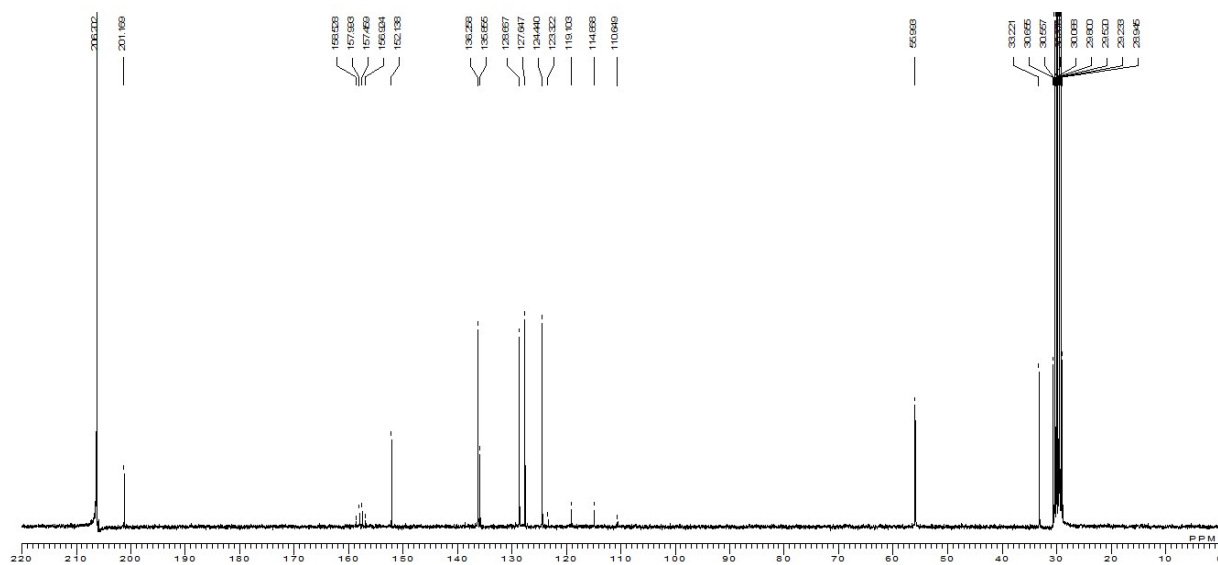
(R)-2,2,2-trifluoro-N-(1-oxo-2,3-dihydro-1H-inden-2-yl)acetamide (TFA-D-cPhe, D-5)



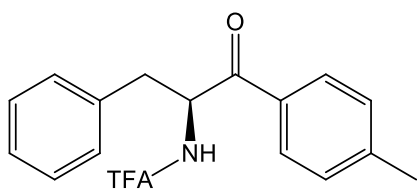
¹H-NMR (270 MHz, ACETONE-D₆)



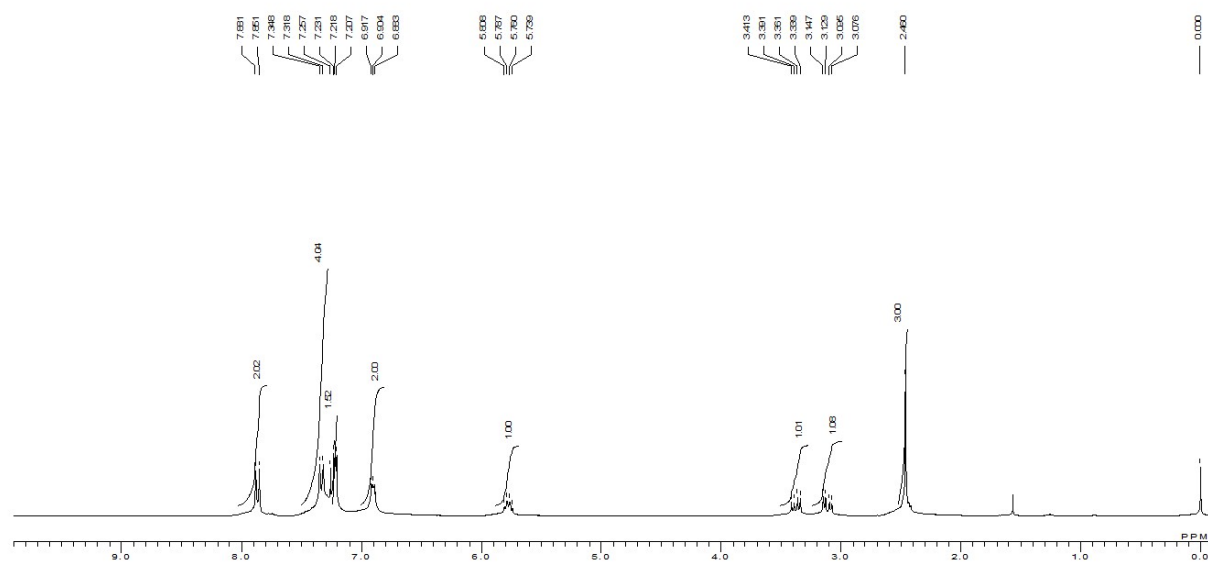
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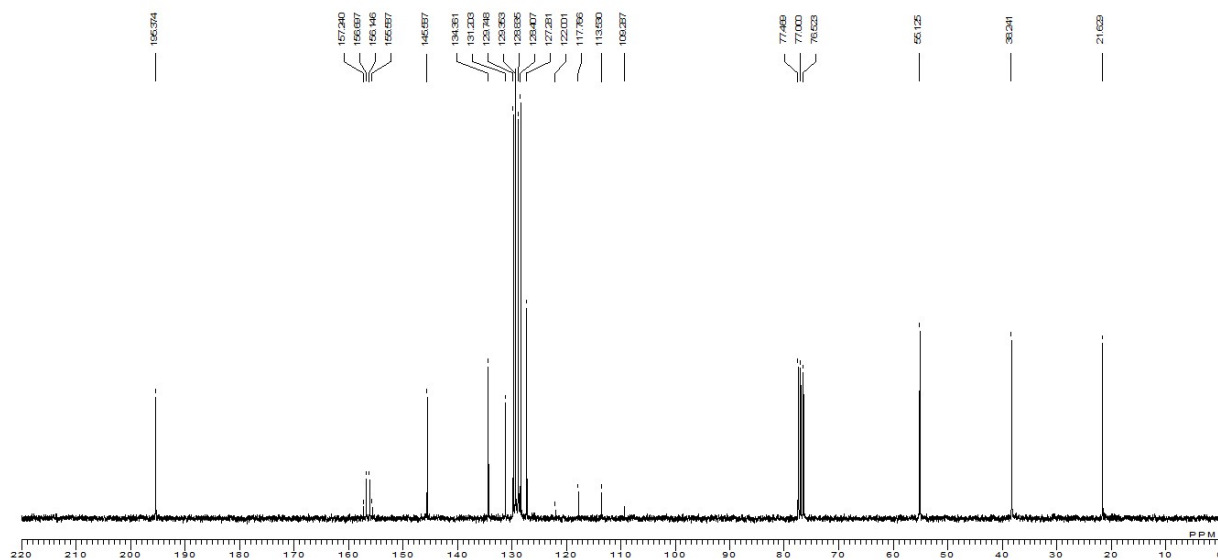
(S)-2,2,2-trifluoro-N-(1-oxo-3-phenyl-1-(p-tolyl)propan-2-yl)acetamide (TFA-L-Phe-Ph(4-Me), L-6)



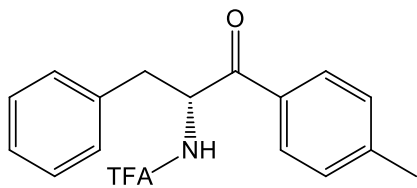
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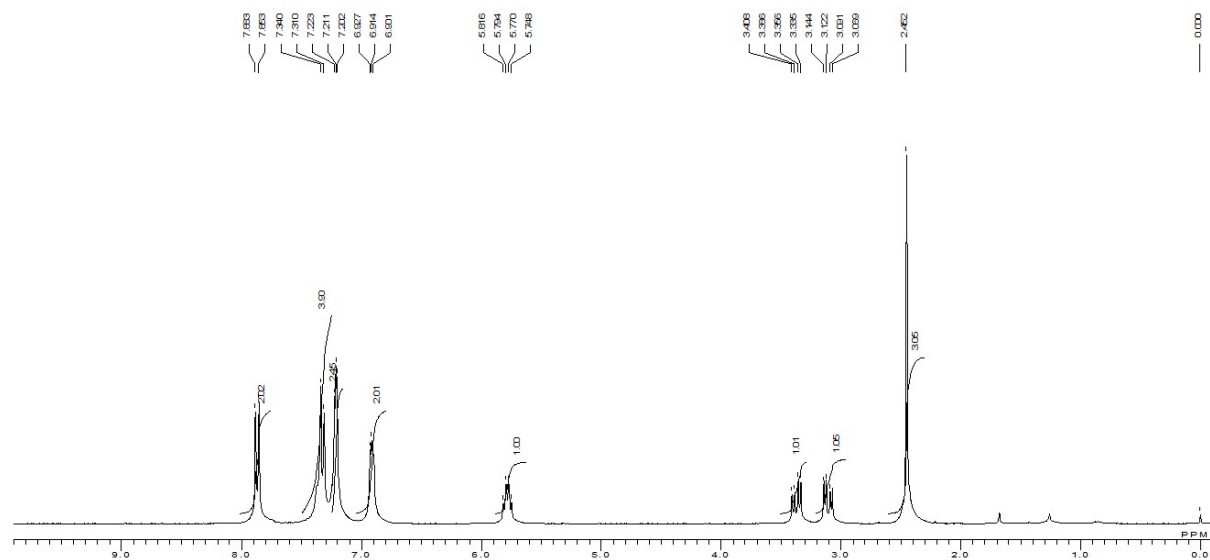
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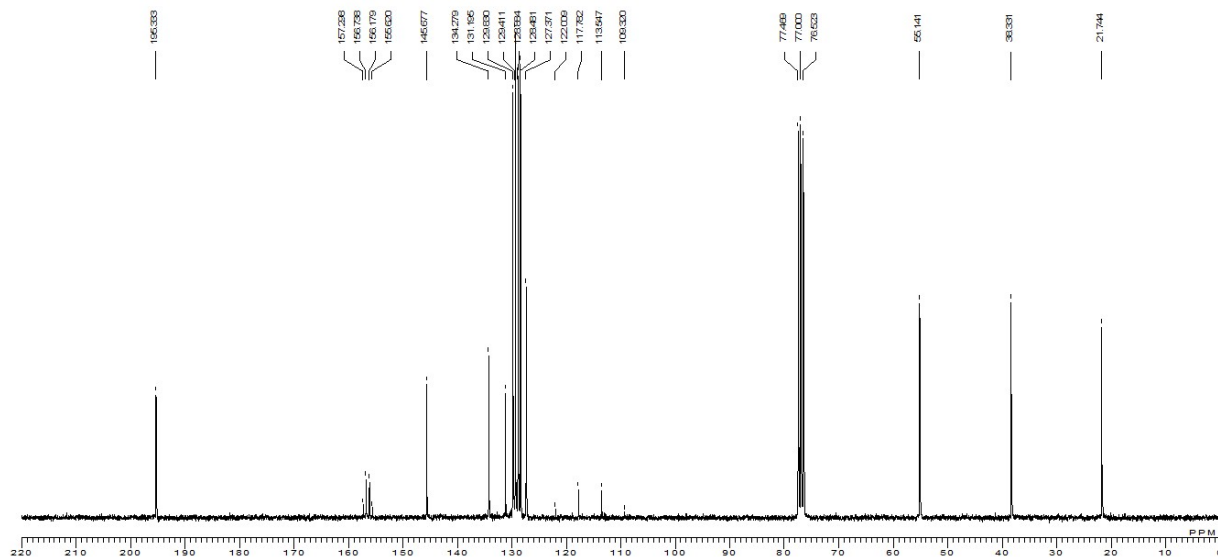
(R)-2,2,2-trifluoro-N-(1-oxo-3-phenyl-1-(p-tolyl)propan-2-yl)acetamide (TFA-D-Phe-Ph(4-Me), D-6)



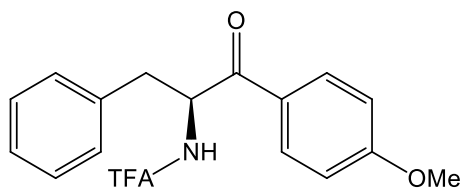
¹H-NMR (270 MHz, CDCl₃)



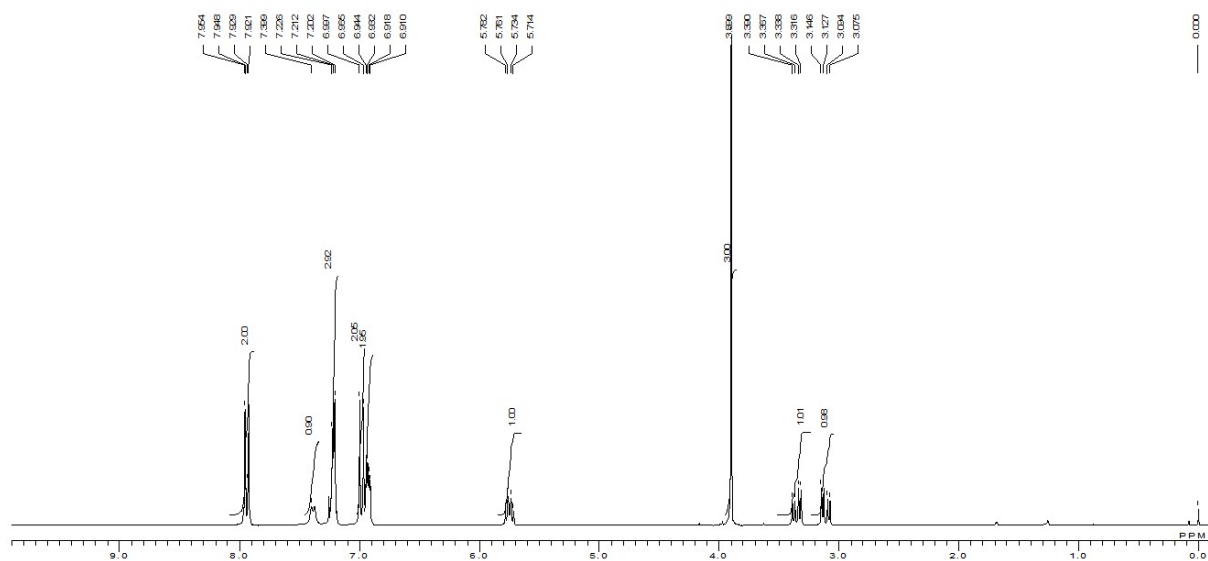
¹³C-NMR (67.5 MHz, CDCl₃)



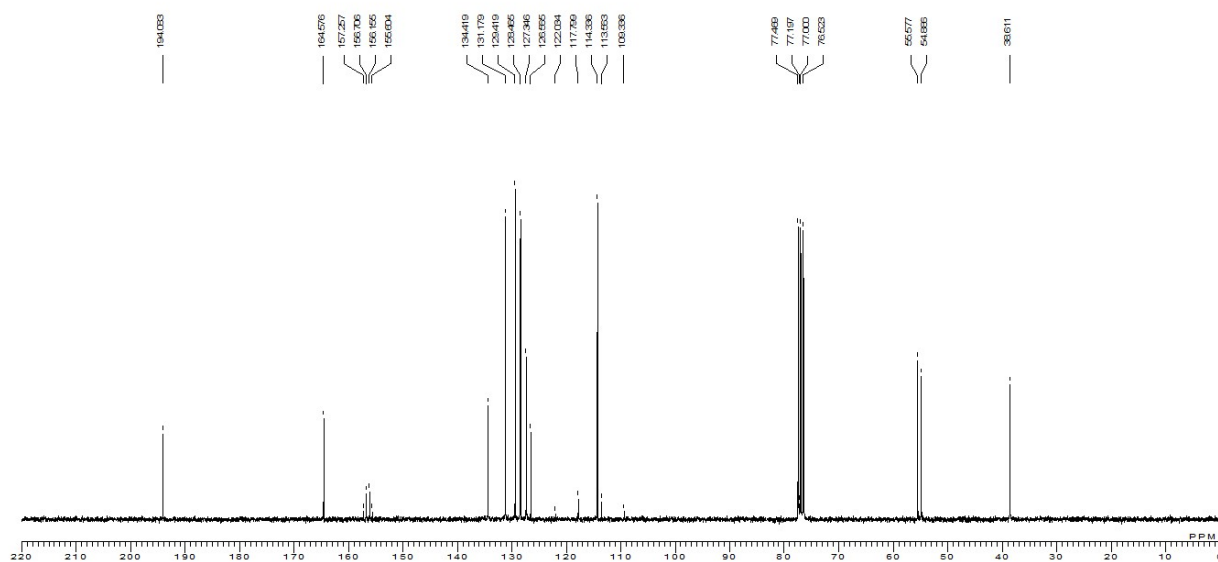
(S)-2,2,2-trifluoro-N-(1-(4-methoxyphenyl)-1-oxo-3-phenylpropan-2-yl)acetamide (TFA-L-Phe-Ph(4-OMe), L-7)



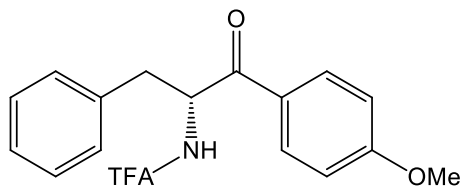
¹H-NMR (270 MHz, CDCl₃)



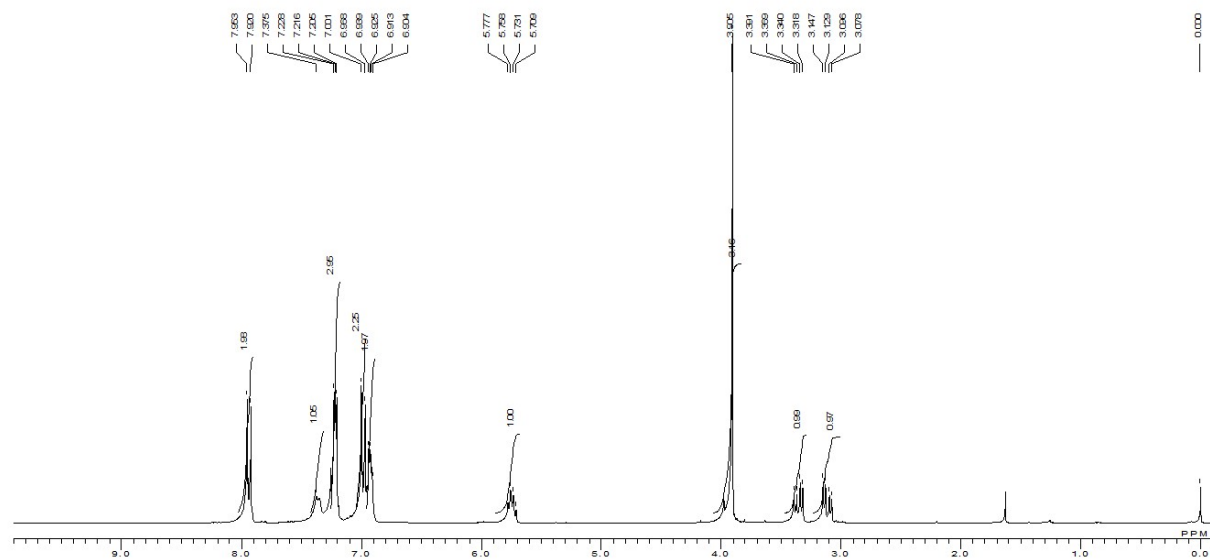
¹³C-NMR (67.5 MHz, CDCl₃)



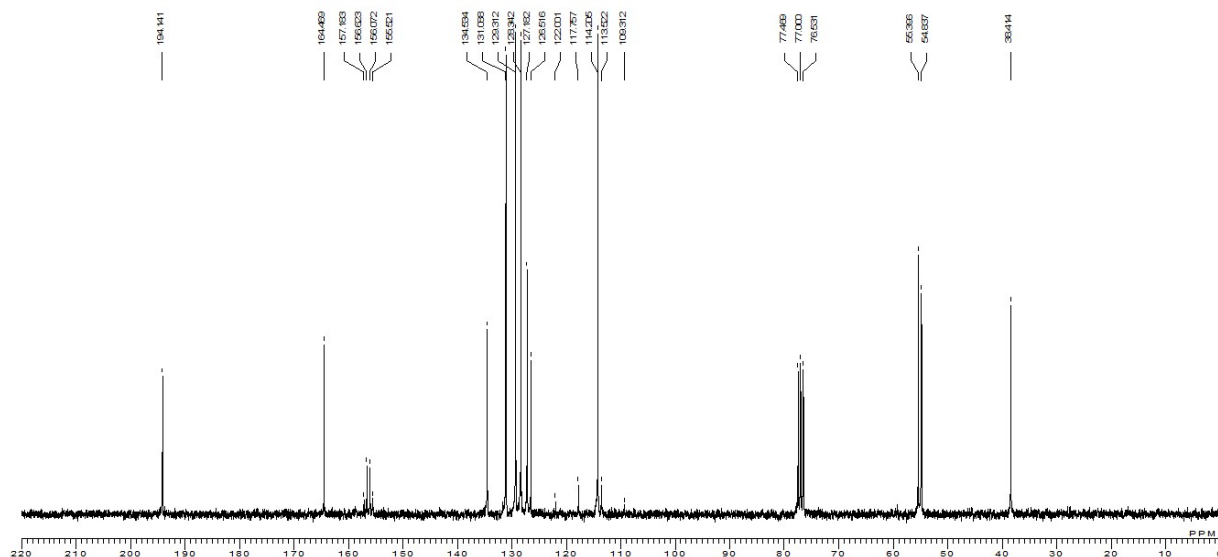
(R)-2,2,2-trifluoro-N-(1-(4-methoxyphenyl)-1-oxo-3-phenylpropan-2-yl)acetamide (TFA-d-Phe-Ph(4-OMe), d-7)



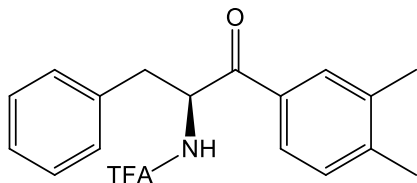
¹H-NMR (270 MHz, CDCl₃)



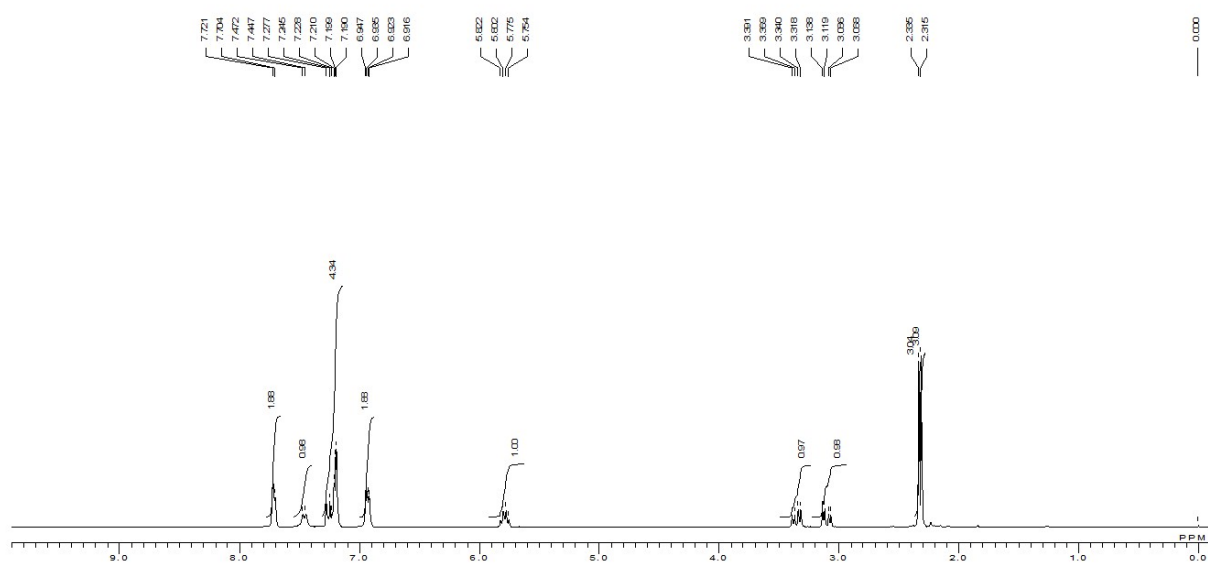
¹³C-NMR (67.5 MHz, CDCl₃)



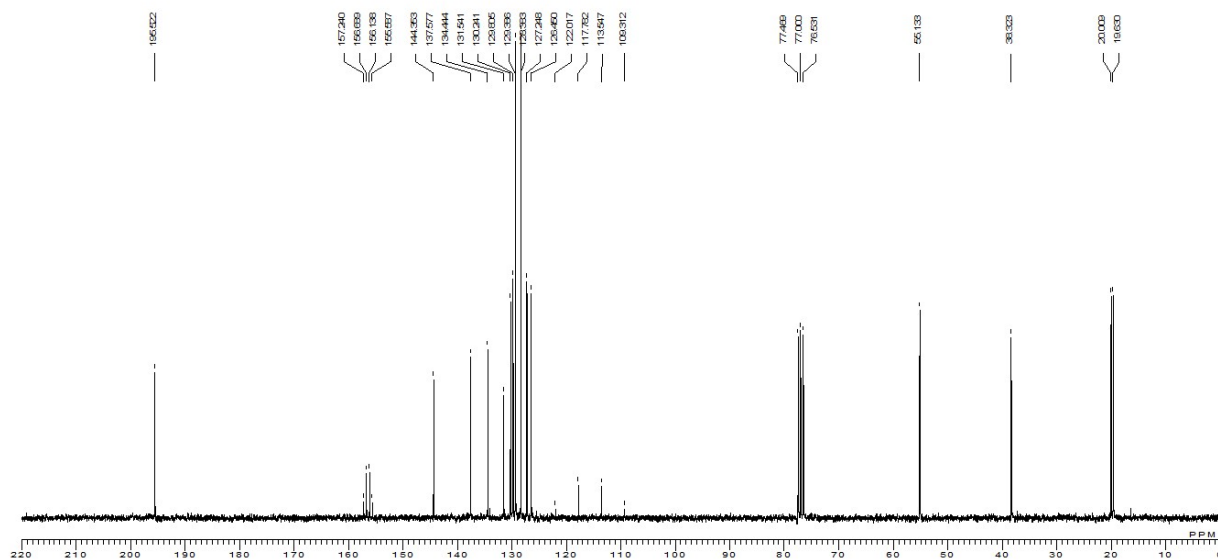
(S)-N-(1-(3,4-dimethylphenyl)-1-oxo-3-phenylpropan-2-yl)-2,2,2-trifluoroacetamide (TFA-L-Phe-Ph(3,4-Me), L-8)



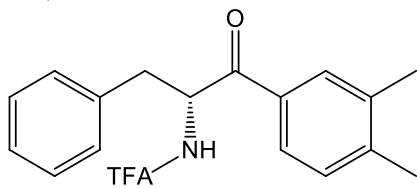
$^1\text{H-NMR}$ (270 MHz, CDCl_3)



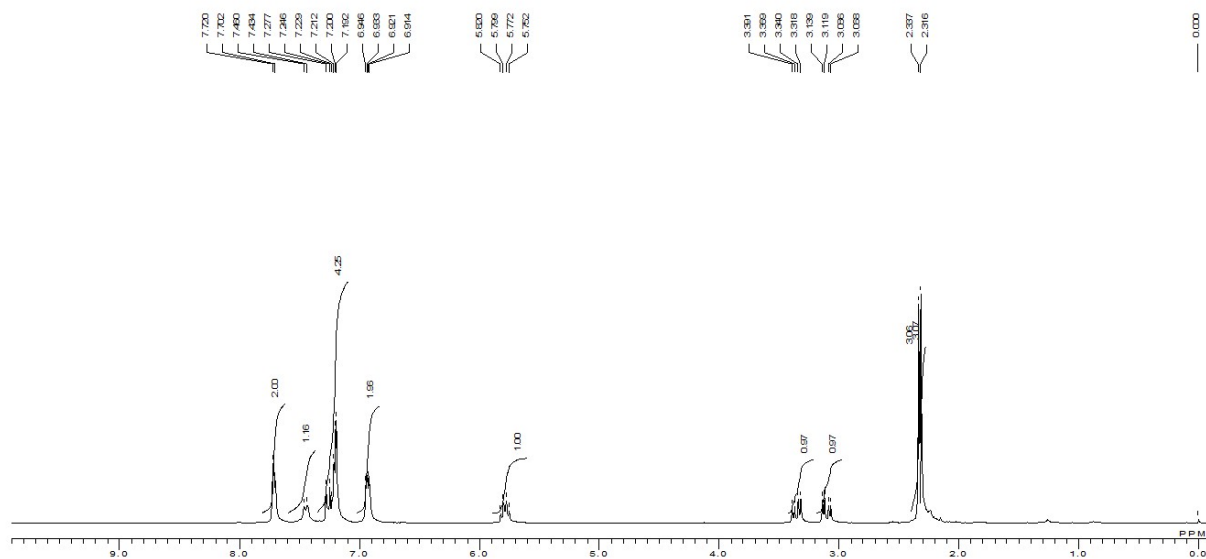
$^{13}\text{C-NMR}$ (67.5 MHz, CDCl_3)



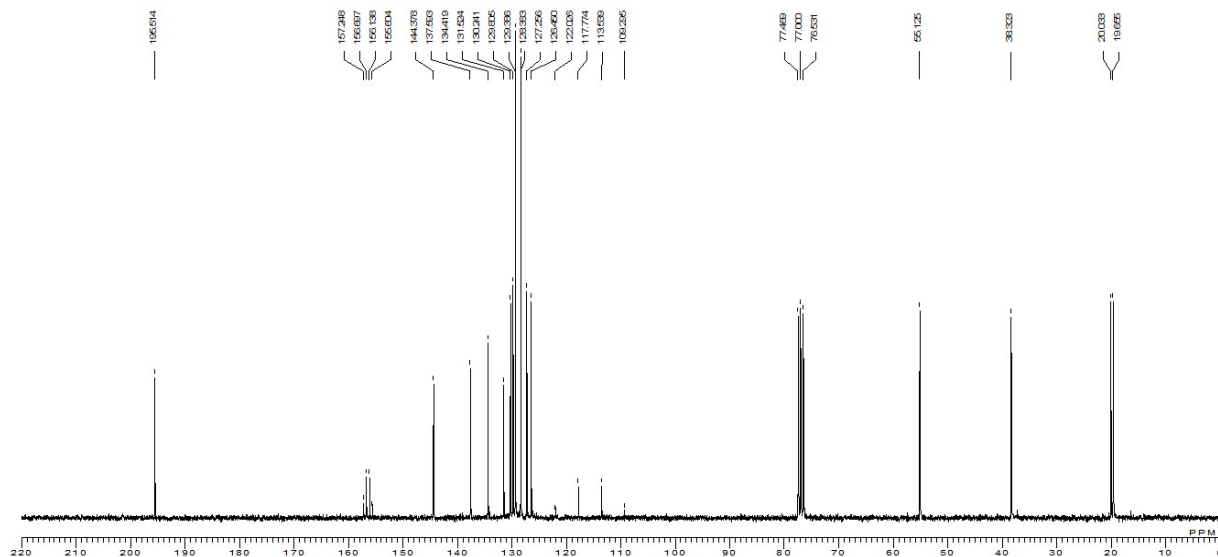
(R)-N-(1-(3,4-dimethylphenyl)-1-oxo-3-phenylpropan-2-yl)-2,2,2-trifluoroacetamide (TFA-D-Phe-Ph(3,4-Me), D-8)



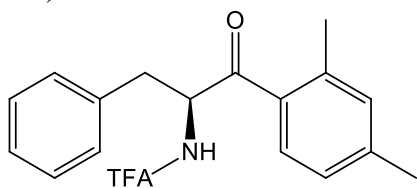
¹H-NMR (270 MHz, CDCl₃)



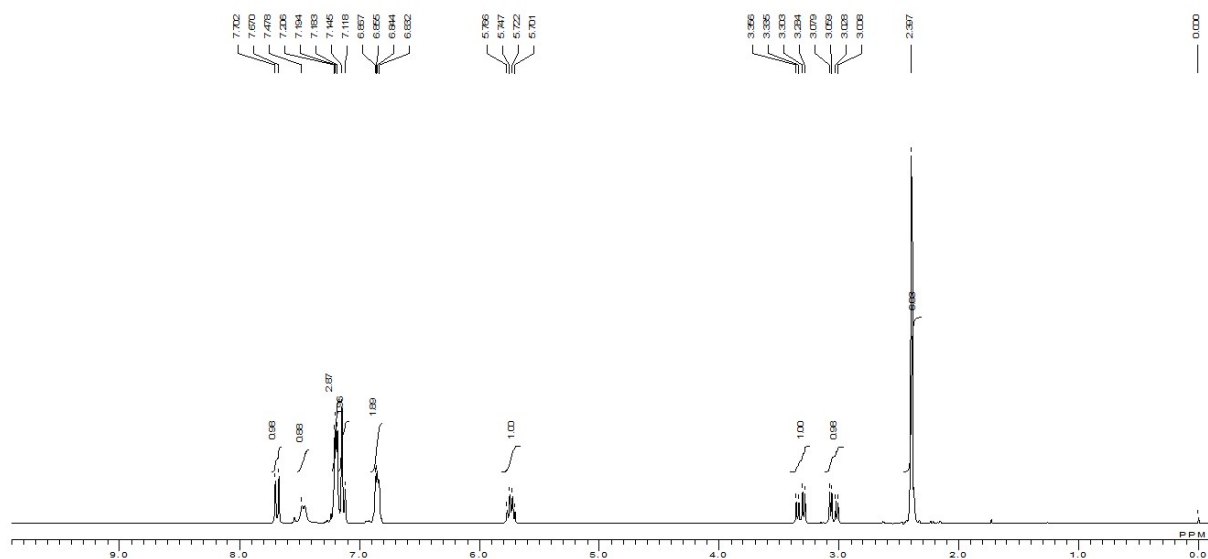
¹³C-NMR (67.5 MHz, CDCl₃)



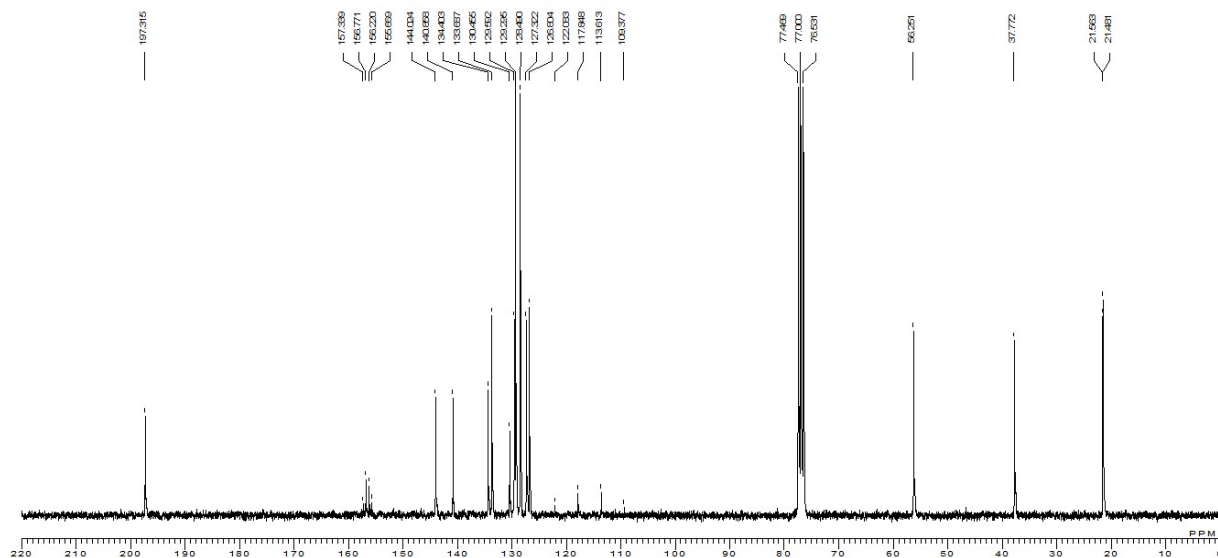
(S)-N-(1-(2,4-dimethylphenyl)-1-oxo-3-phenylpropan-2-yl)-2,2,2-trifluoroacetamide (TFA-L-Phe-Ph(2,4-Me), L-9)



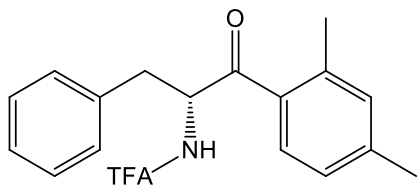
¹H-NMR (270 MHz, CDCl₃)



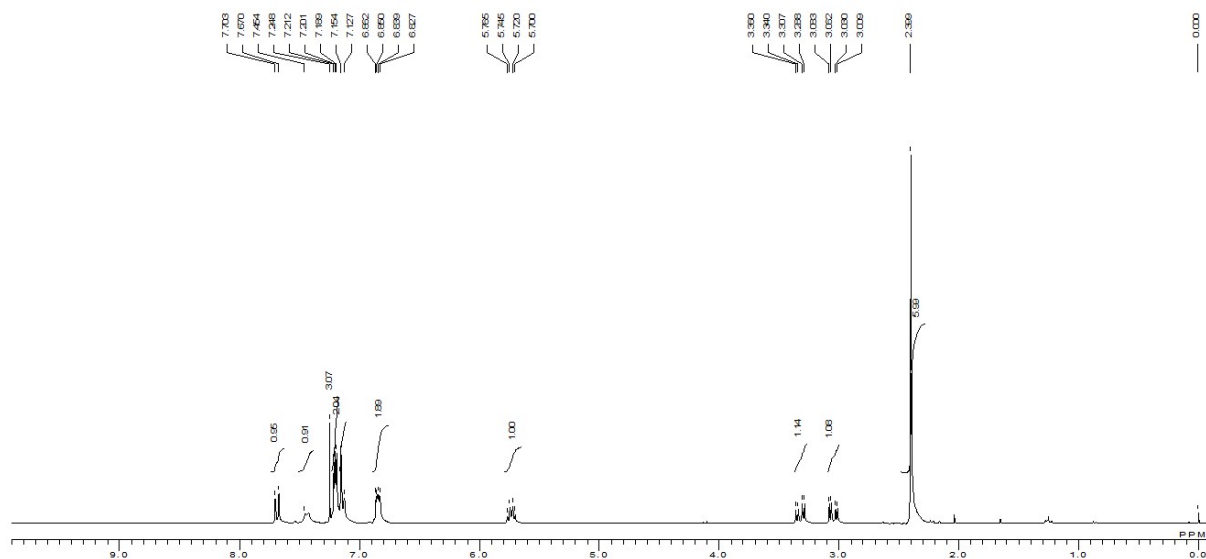
¹³C-NMR (67.5 MHz, CDCl₃)



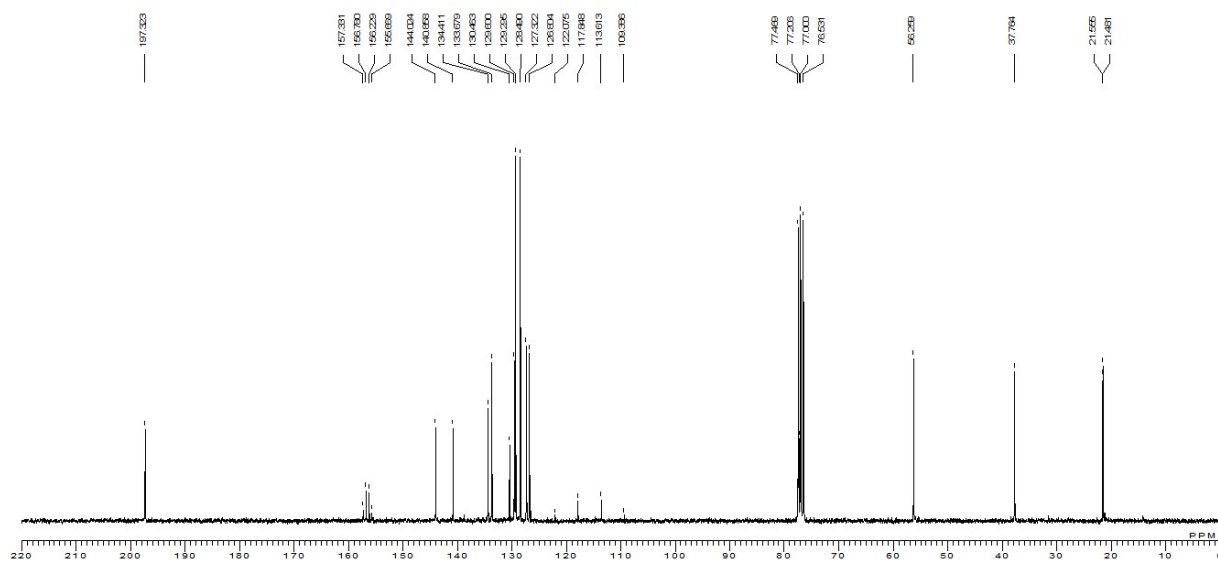
(R)-N-(1-(2,4-dimethylphenyl)-1-oxo-3-phenylpropan-2-yl)-2,2,2-trifluoroacetamide (TFA-D-Phe-Ph(2,4-Me), D-9)



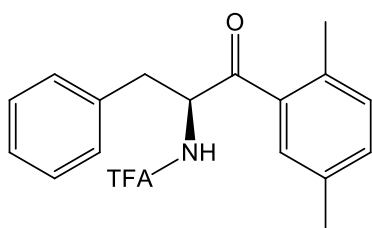
¹H-NMR (270 MHz, CDCl₃)



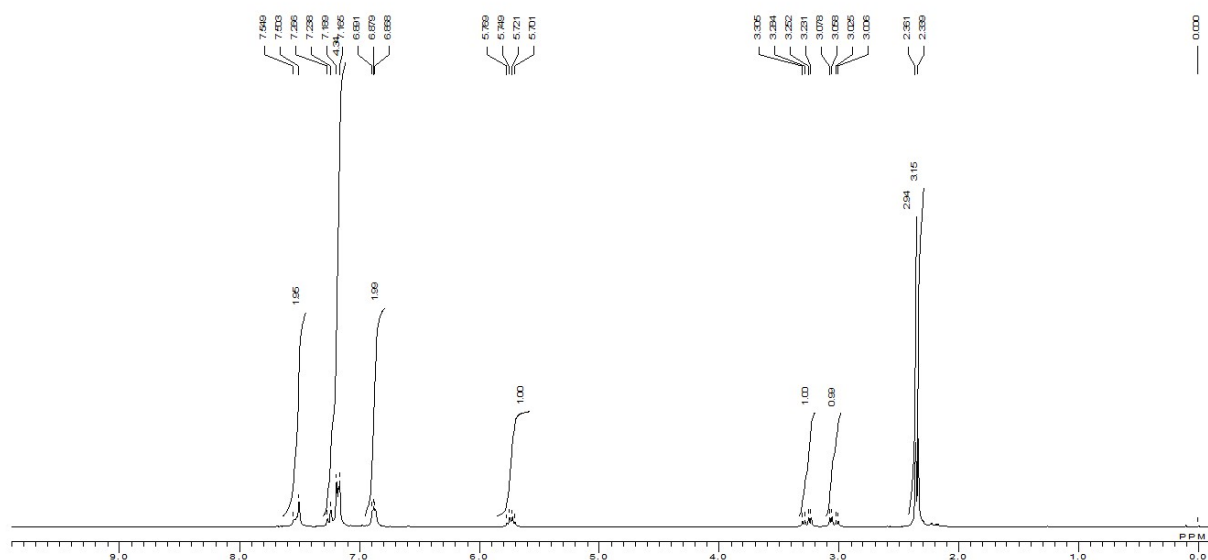
¹³C-NMR (67.5 MHz, CDCl₃)



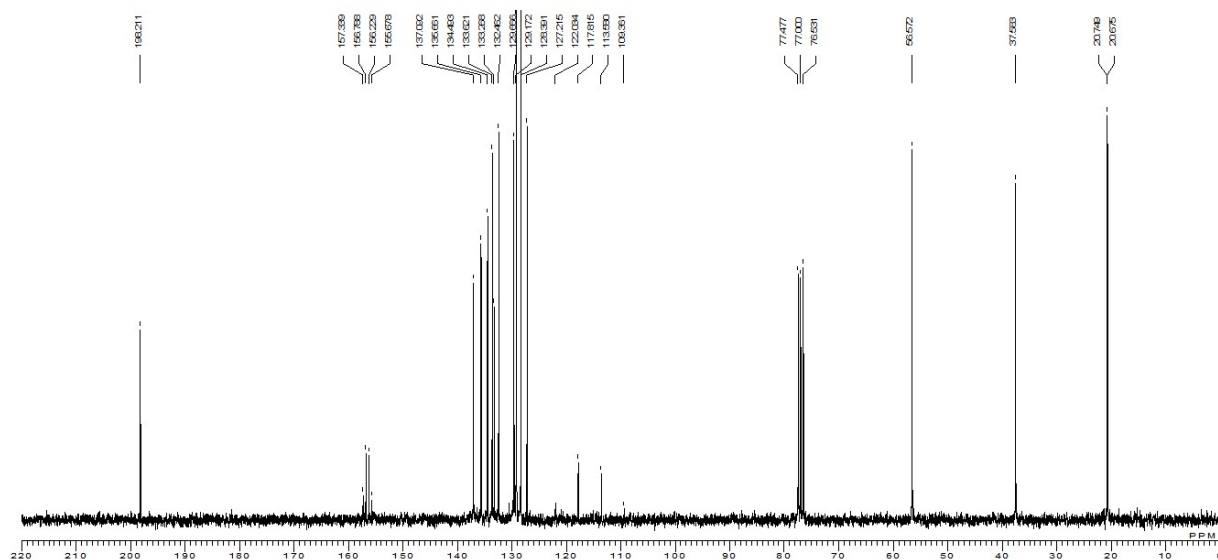
(S)-N-(1-(2,5-dimethylphenyl)-1-oxo-3-phenylpropan-2-yl)-2,2,2-trifluoroacetamide (TFA-L-Phe-Ph(2,5-Me), L-10)



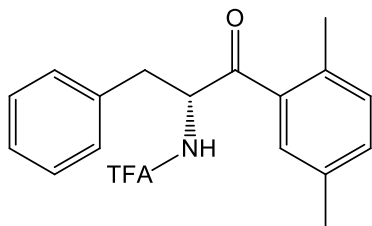
¹H-NMR (270 MHz, CDCl₃)



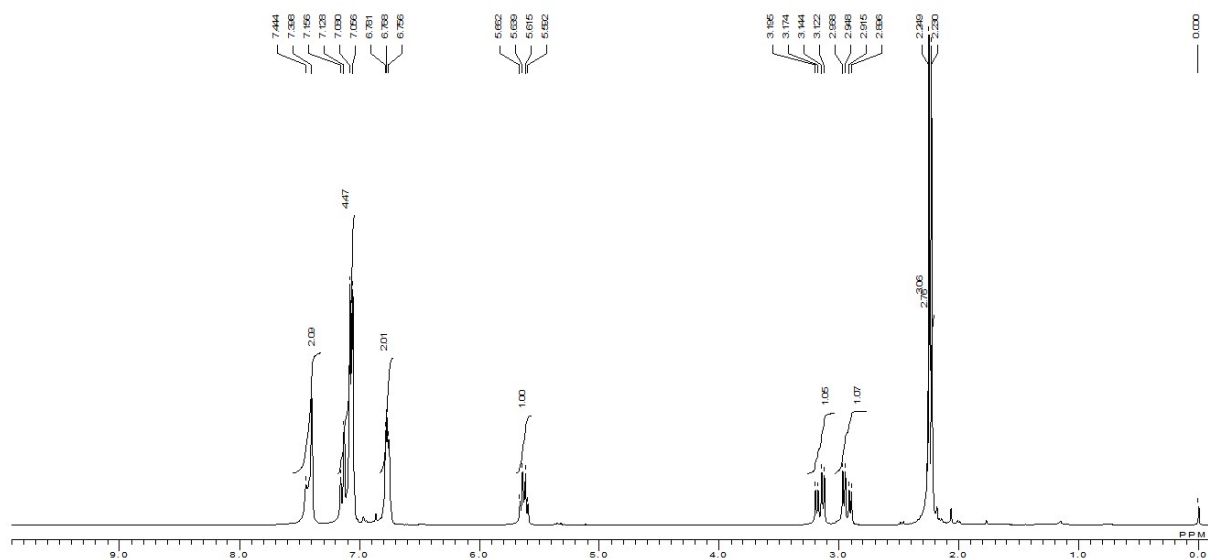
¹³C-NMR (67.5 MHz, CDCl₃)



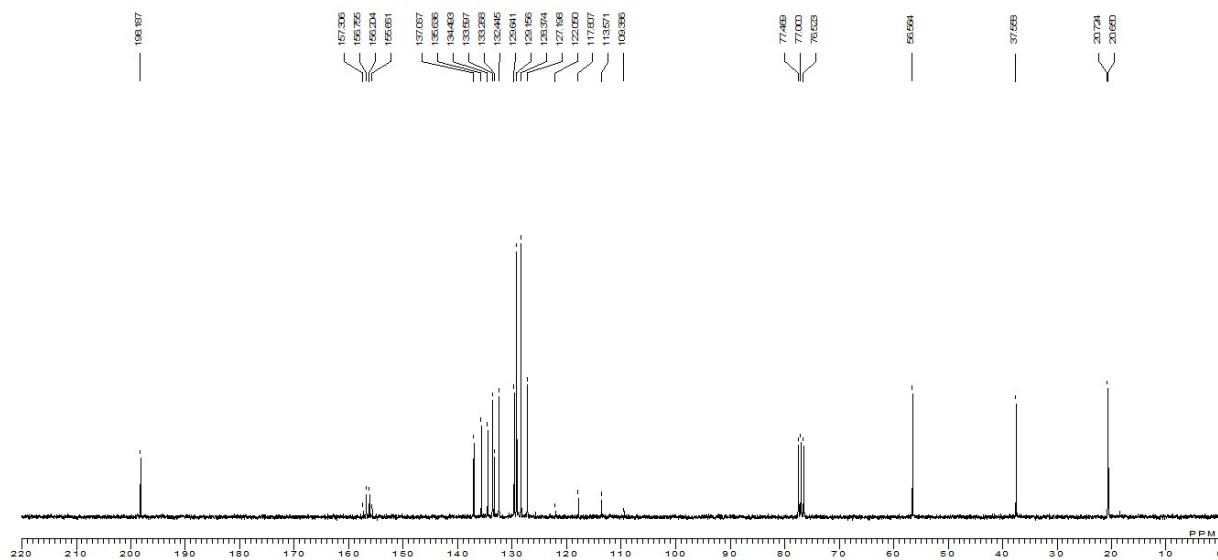
(R)-N-(1-(2,5-dimethylphenyl)-1-oxo-3-phenylpropan-2-yl)-2,2,2-trifluoroacetamide (TFA-D-Phe-Ph(2,5-Me), D-10)



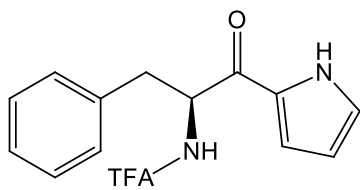
¹H-NMR (270 MHz, CDCl₃)



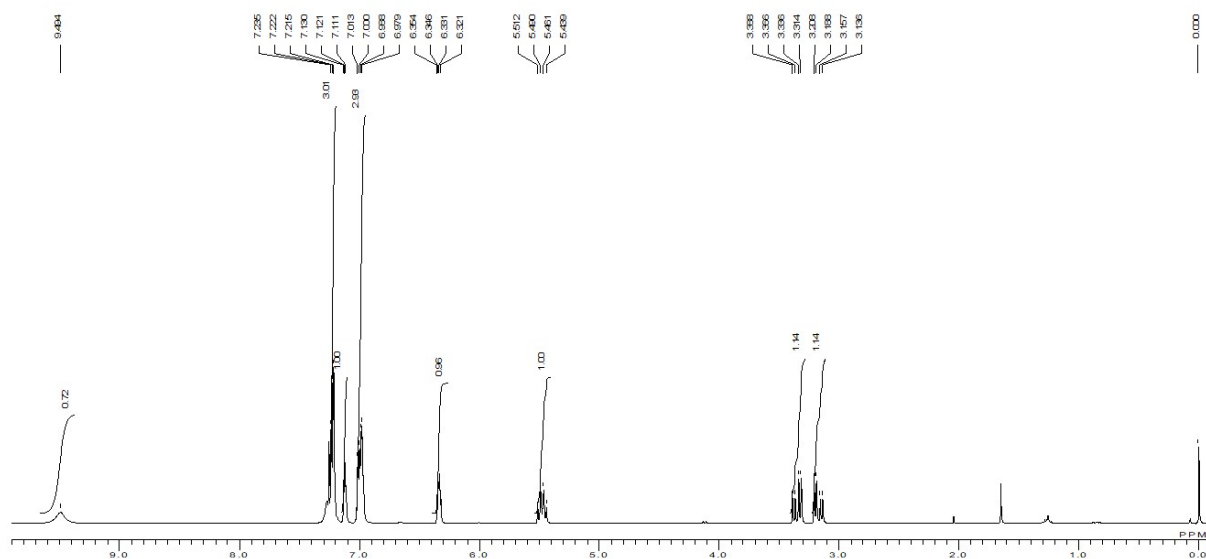
¹³C-NMR (67.5 MHz, CDCl₃)



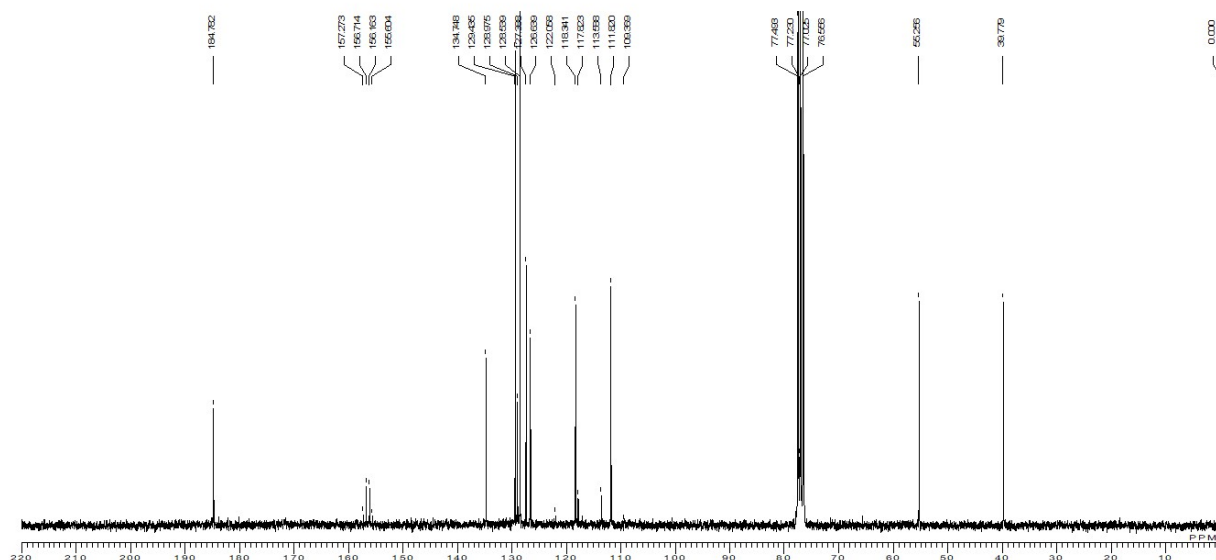
(S)-2,2,2-trifluoro-N-(1-oxo-3-phenyl-1-(1H-pyrrol-2-yl)propan-2-yl)acetamide (TFA-L-Phe-(2-Pyr), L-11)



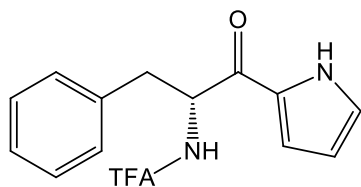
¹H-NMR (270 MHz, CDCl₃)



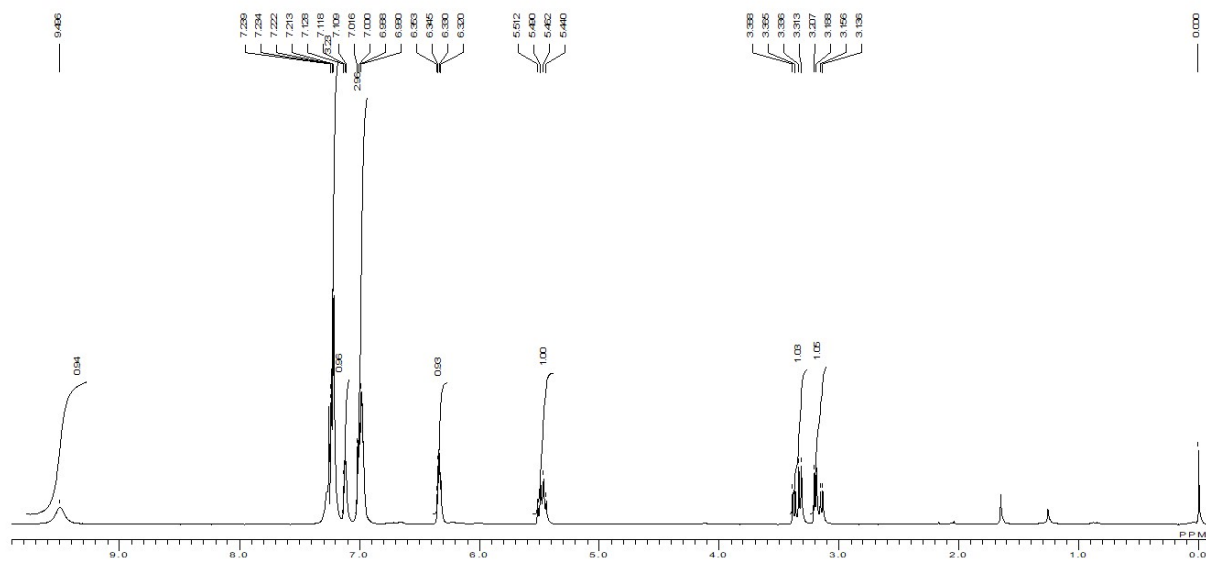
¹³C-NMR (67.5 MHz, CDCl₃)



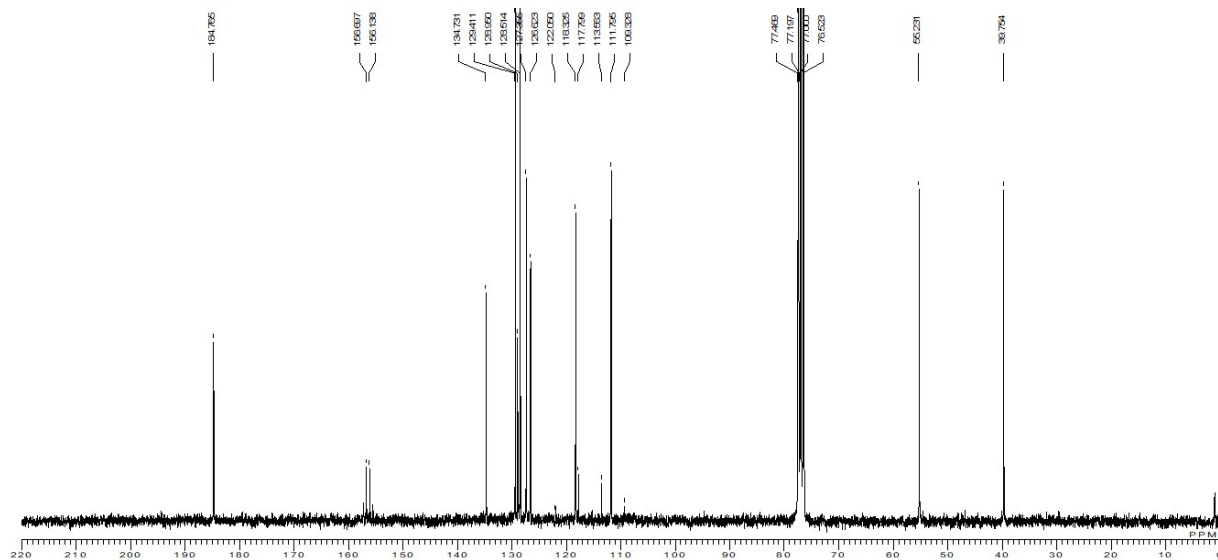
(R)-2,2,2-trifluoro-N-(1-oxo-3-phenyl-1-(1H-pyrrol-2-yl)propan-2-yl)acetamide (TFA-D-Phe-(2-Pyr), D-11)



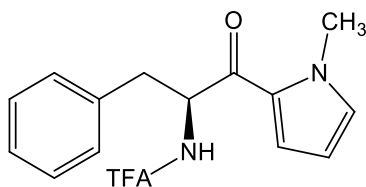
¹H-NMR (270 MHz, CDCl₃)



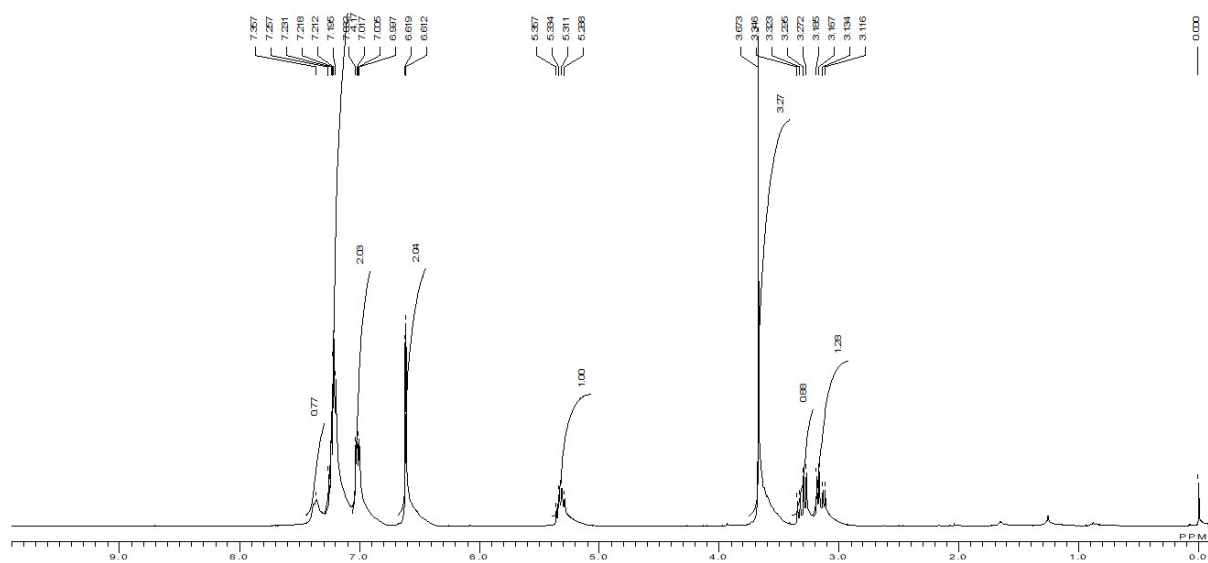
¹³C-NMR (67.5 MHz, CDCl₃)



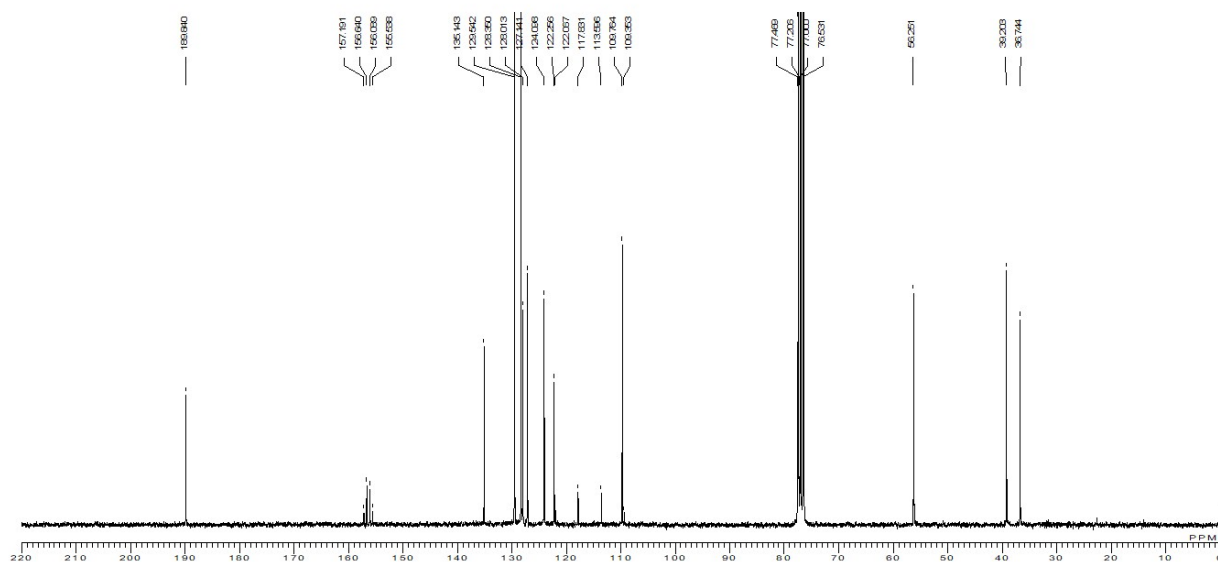
(S)-2,2,2-trifluoro-N-(1-(1-methyl-1H-pyrrol-2-yl)-1-oxo-3-phenylpropan-2-yl)acetamide (TFA-L-Phe-(2-(N-Me)Pyr), 1-12).



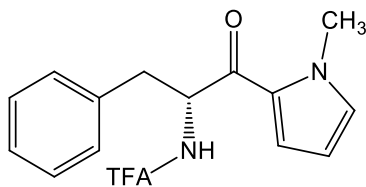
¹H-NMR (270 MHz, CDCl₃)



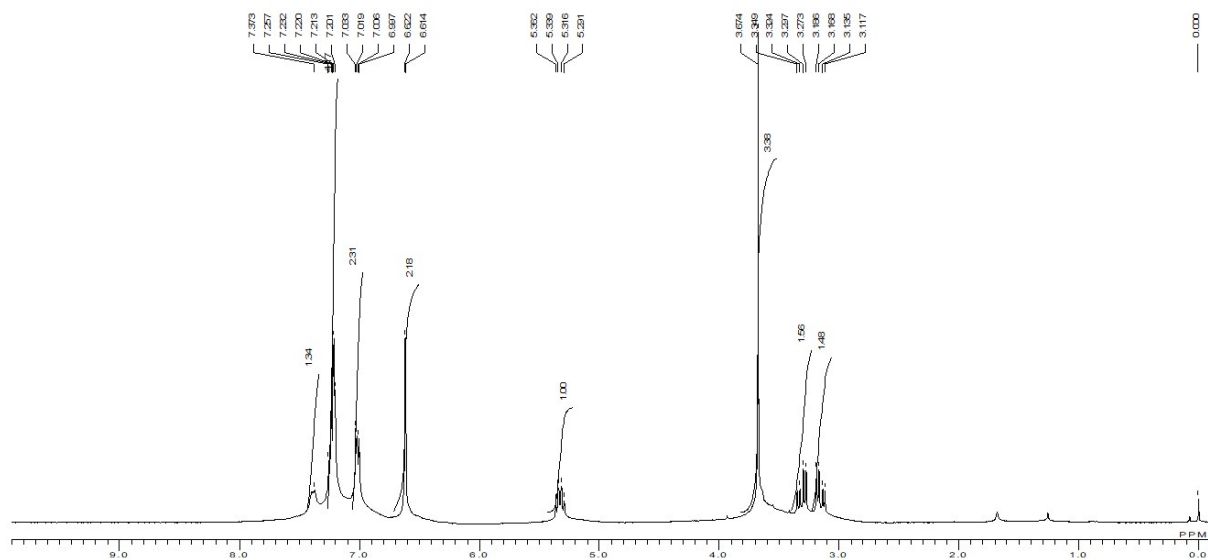
¹³C-NMR (67.5 MHz, CDCl₃)



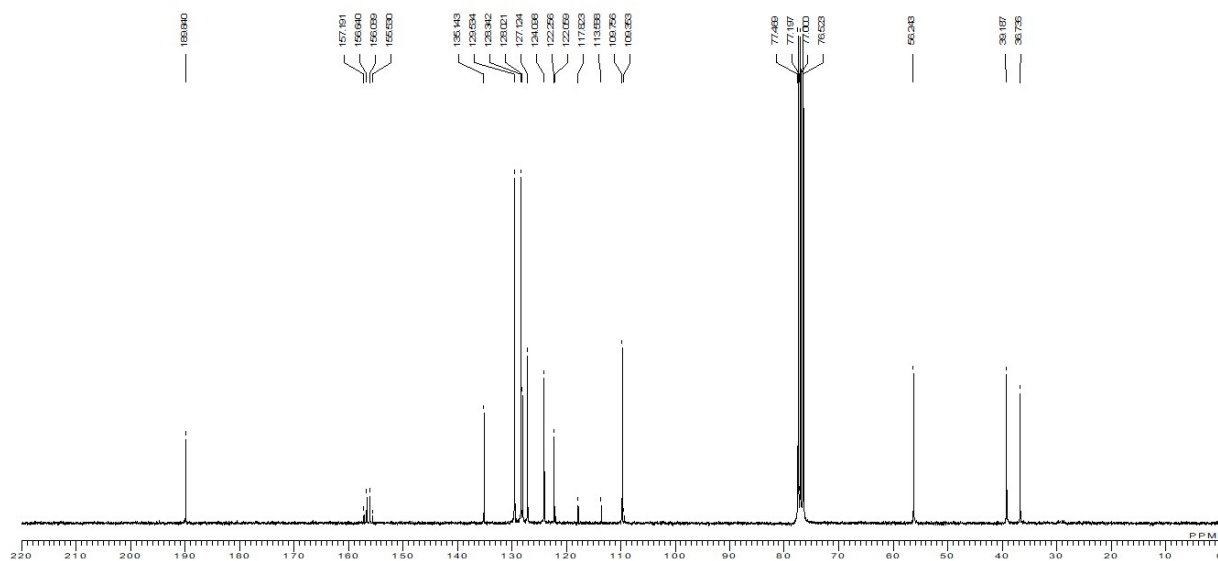
(R)-2,2,2-trifluoro-N-(1-(1-methyl-1H-pyrrol-2-yl)-1-oxo-3-phenylpropan-2-yl)acetamide (TFA-D-Phe-(2-(N-Me)Pyr), D-12).



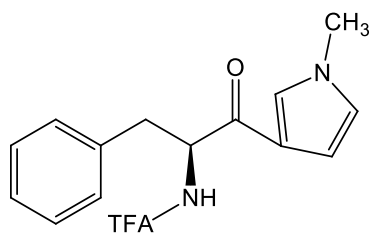
¹H-NMR (270 MHz, CDCl₃)



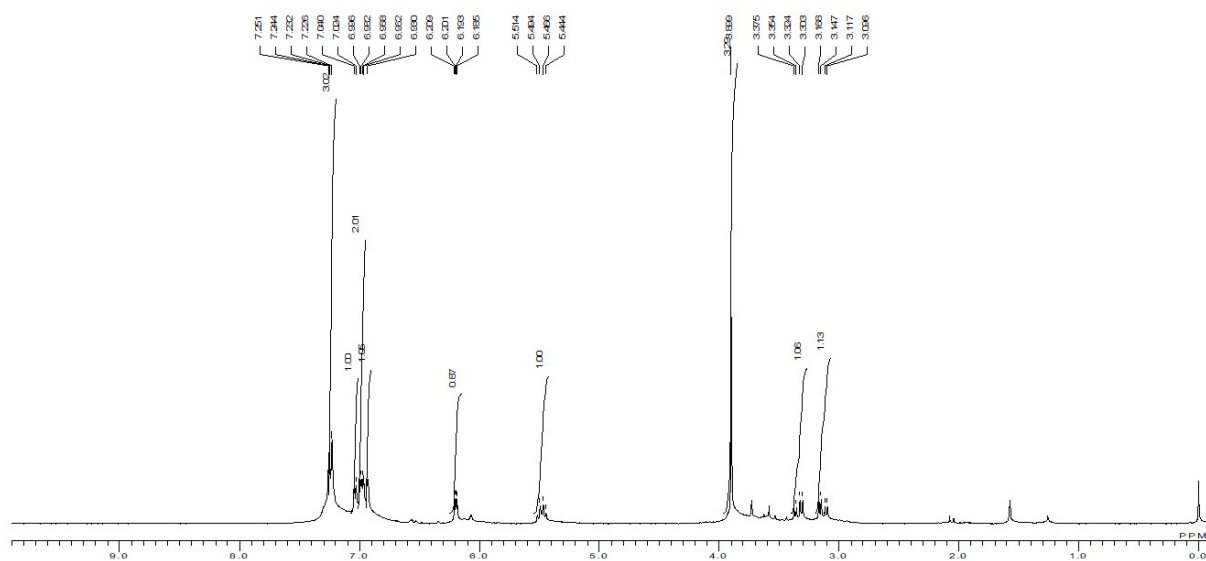
¹³C-NMR (67.5 MHz, CDCl₃)



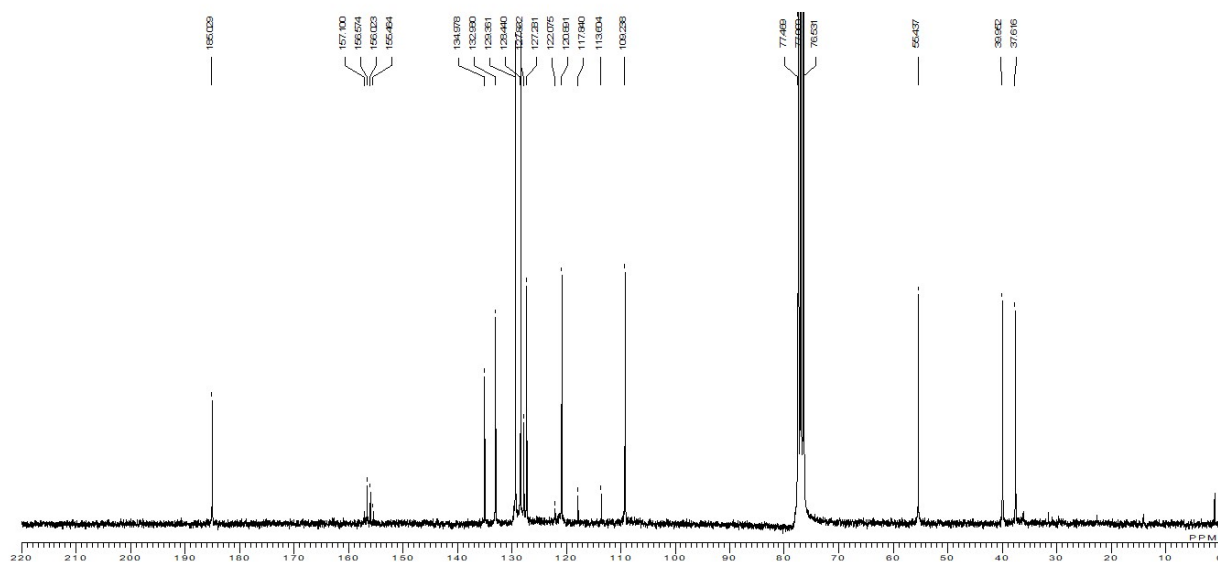
(S)-2,2,2-trifluoro-N-(1-(1-methyl-1H-pyrrol-3-yl)-1-oxo-3-phenylpropan-2-yl)acetamide (TFA-L-Phe-(3-(N-Me)Pyr), L-13).



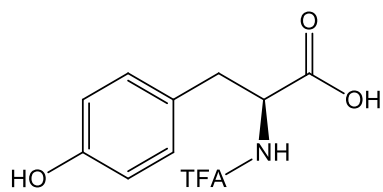
¹H-NMR (270 MHz, CDCl₃)



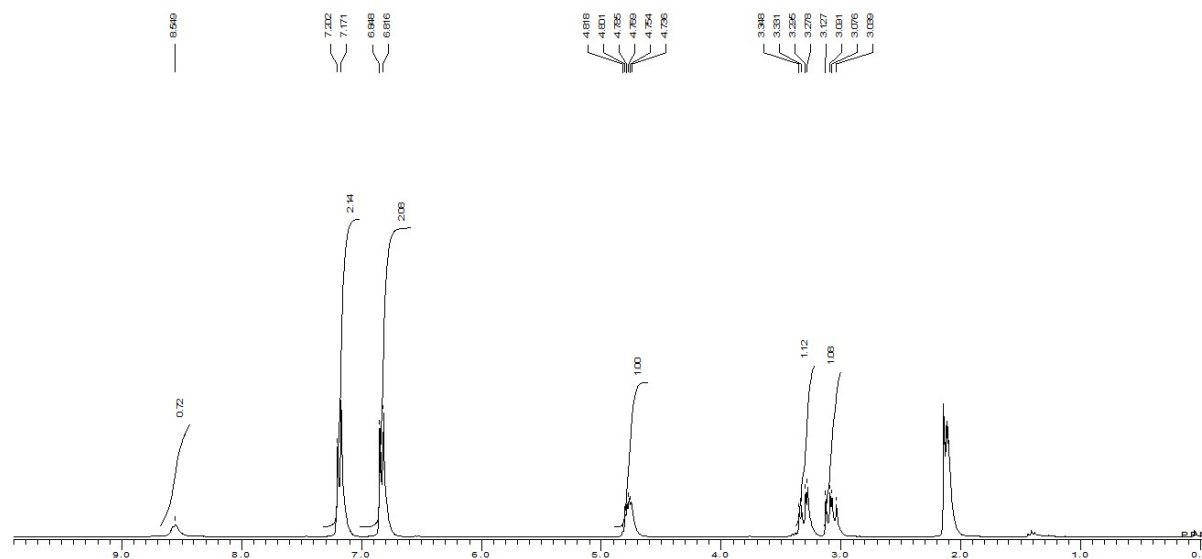
¹³C-NMR (67.5 MHz, CDCl₃)



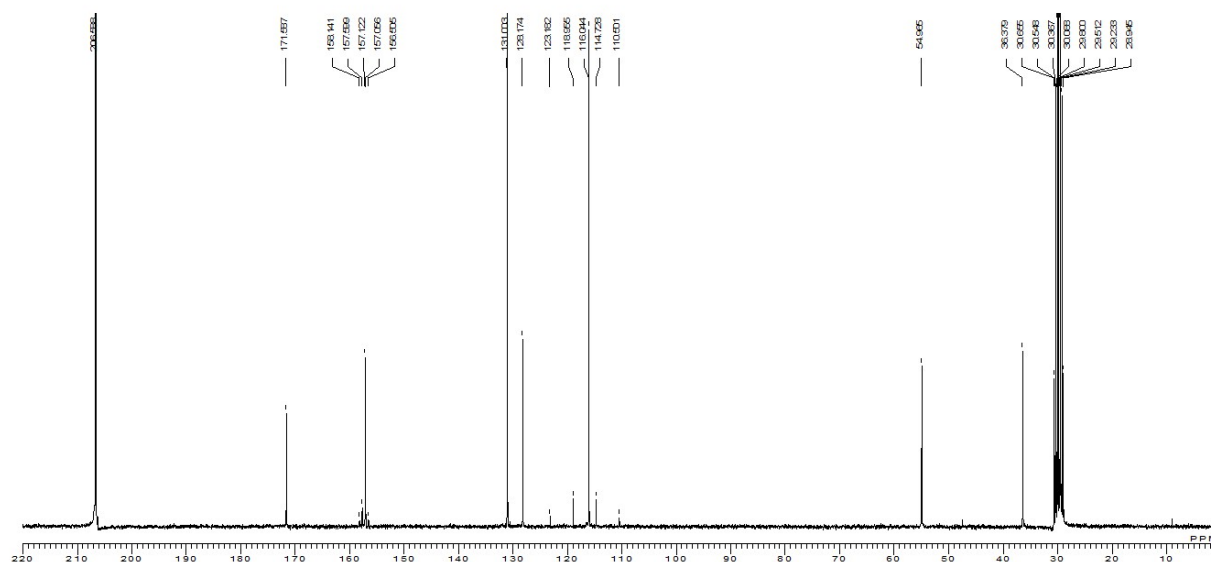
(S)-3-(4-hydroxyphenyl)-2-(2,2,2-trifluoroacetamido)propanoic acid (TFA-L-Tyr, L-15).



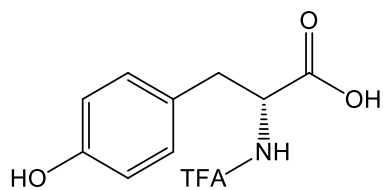
¹H-NMR (270 MHz, ACETONE-D₆)



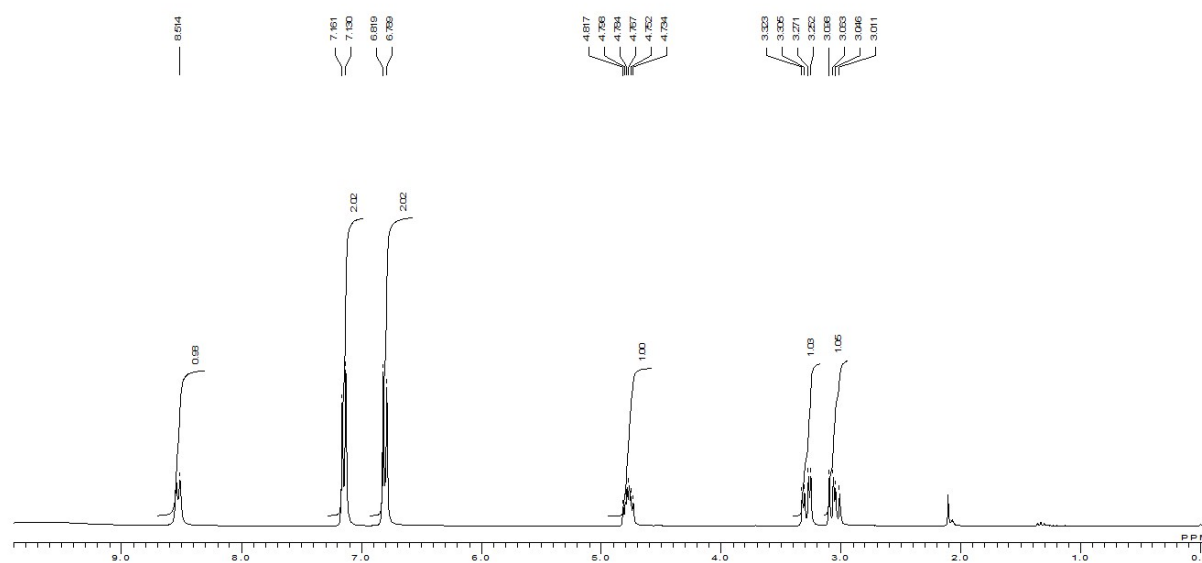
¹³C-NMR (67.5 MHz, ACETONE-D₆)



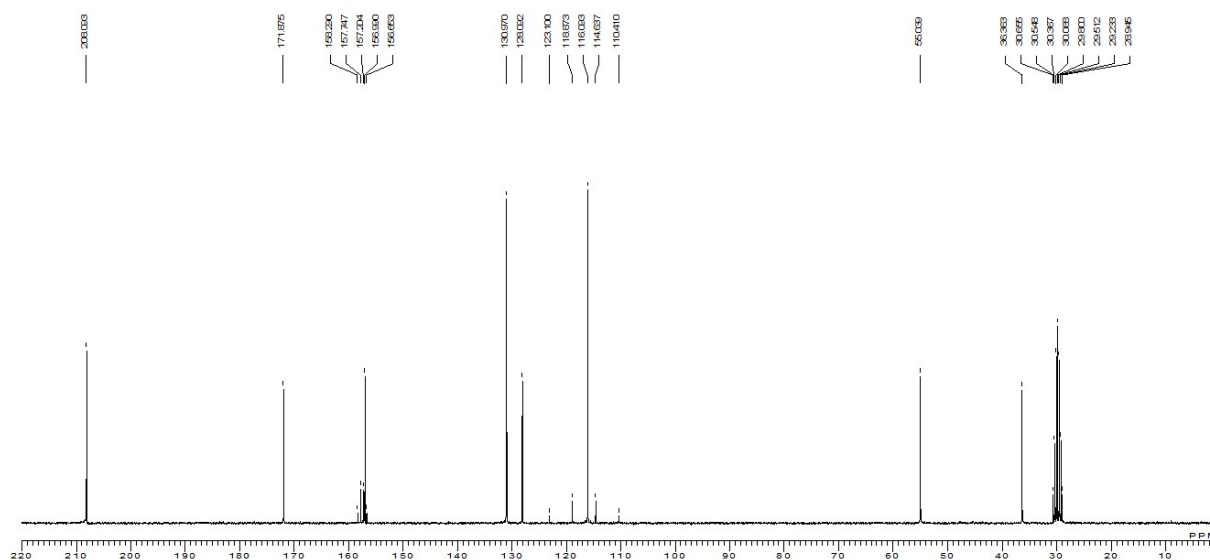
(R)-3-(4-hydroxyphenyl)-2-(2,2,2-trifluoroacetamido)propanoic acid (TFA-D-Tyr, D-15).



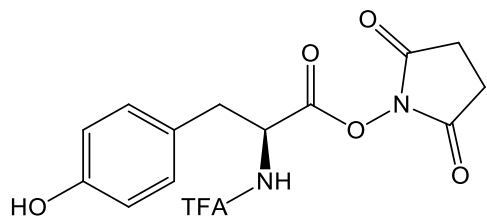
¹H-NMR (270 MHz, ACETONE-D₆)



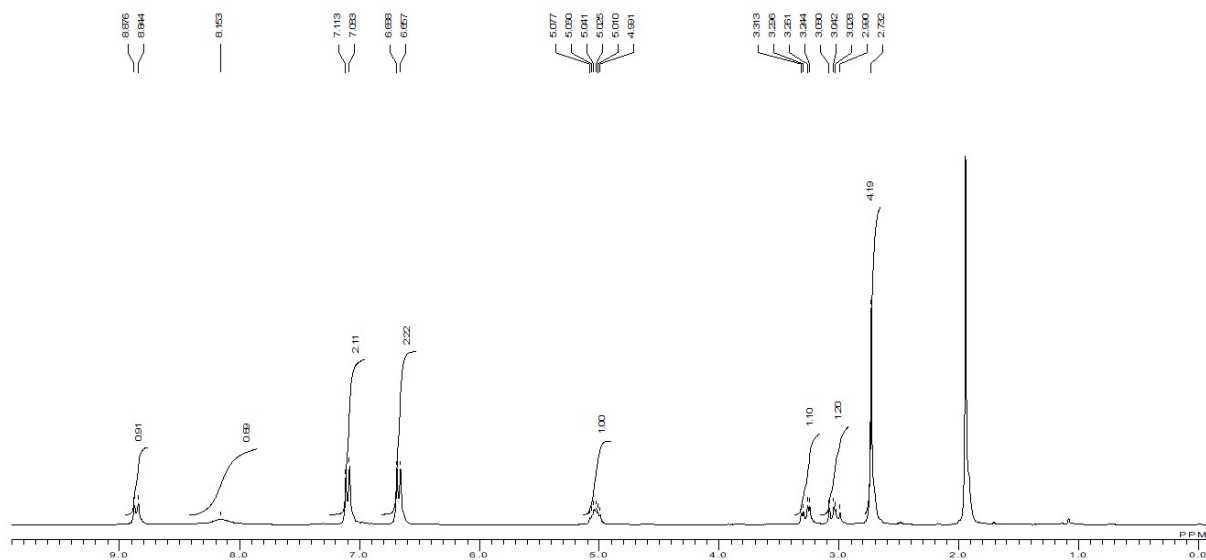
¹³C-NMR (67.5 MHz, ACETONE-D₆)



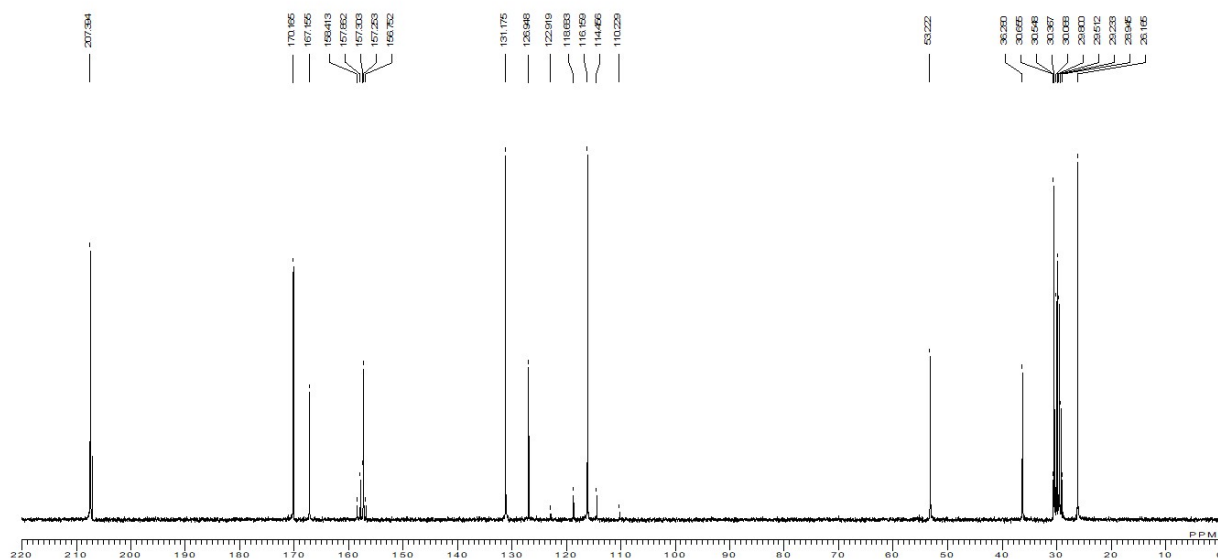
(S)-2,5-dioxopyrrolidin-1-yl 3-(4-hydroxyphenyl)-2-(2,2,2-trifluoroacetamido)propanoate (TFA-L-Tyr-OSu, L-16).



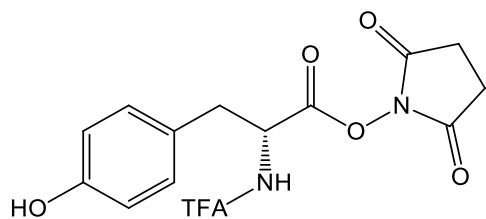
¹H-NMR (270 MHz, ACETONE-D₆)



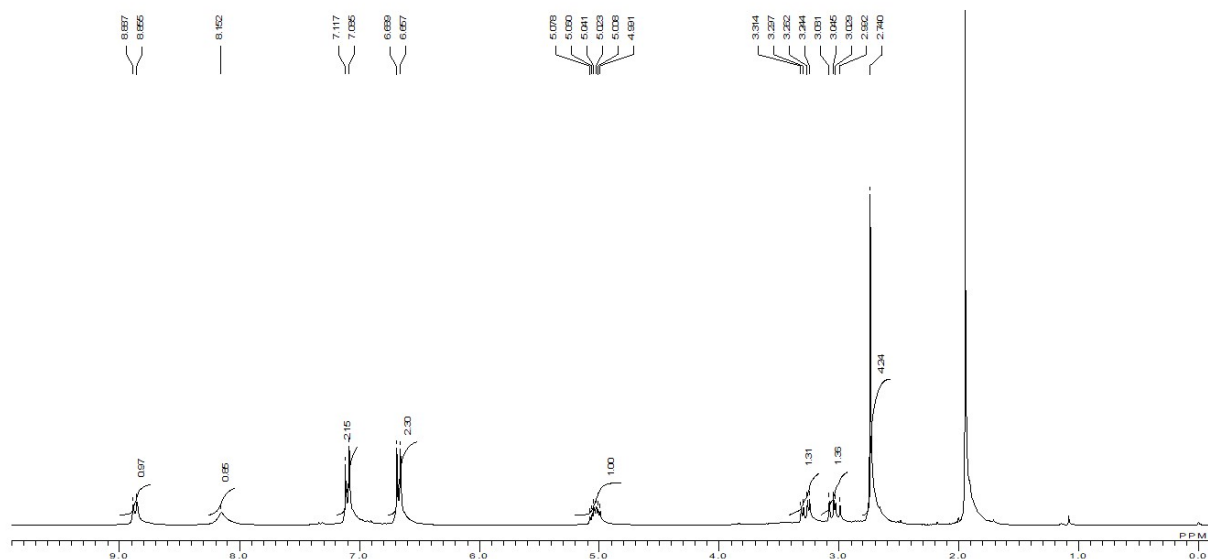
¹³C-NMR (67.5 MHz, ACETONE-D₆)



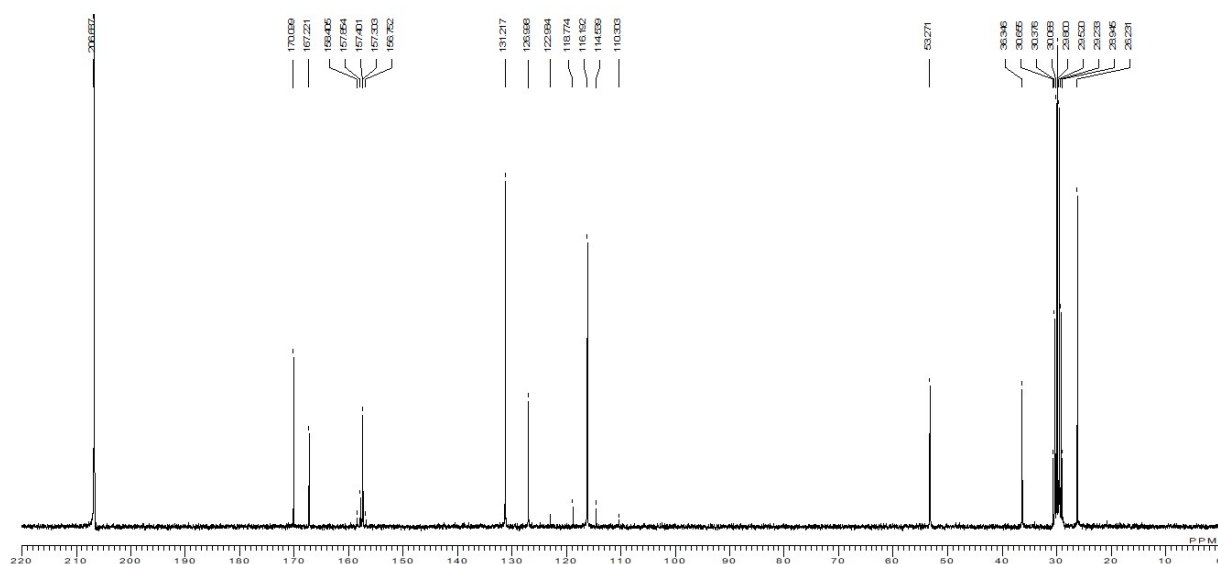
(R)-2,5-dioxopyrrolidin-1-yl 3-(4-hydroxyphenyl)-2-(2,2,2-trifluoroacetamido)propanoate (TFA-D-Tyr-OSu, D-16).



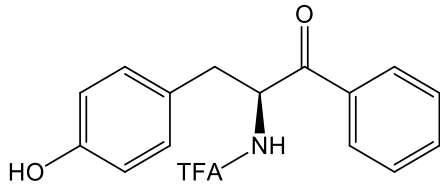
¹H-NMR (270 MHz, ACETONE-D₆)



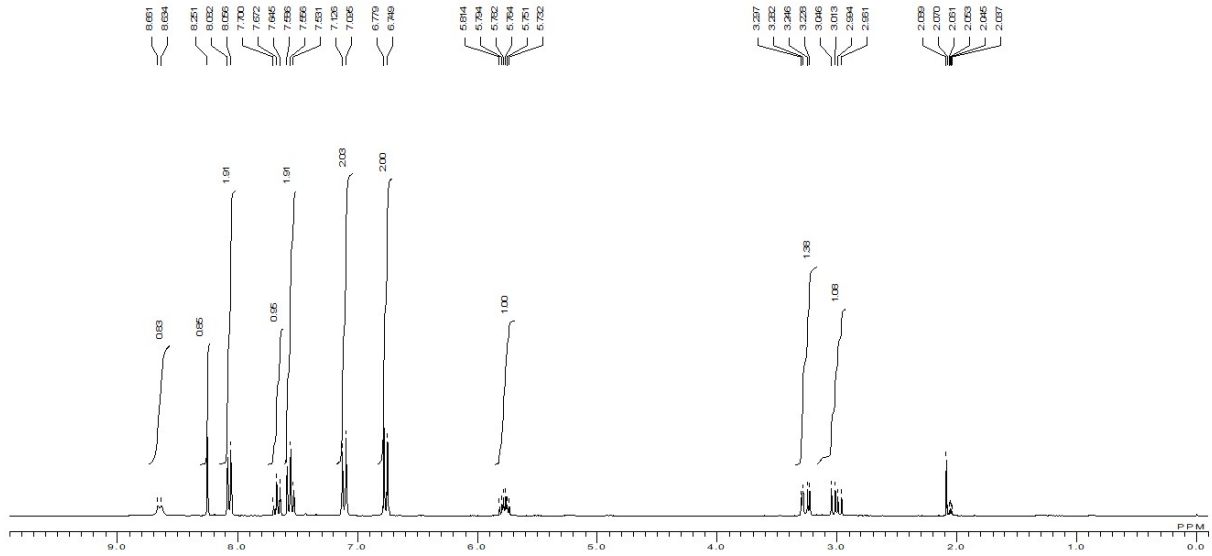
¹³C-NMR (67.5 MHz, ACETONE-D₆)



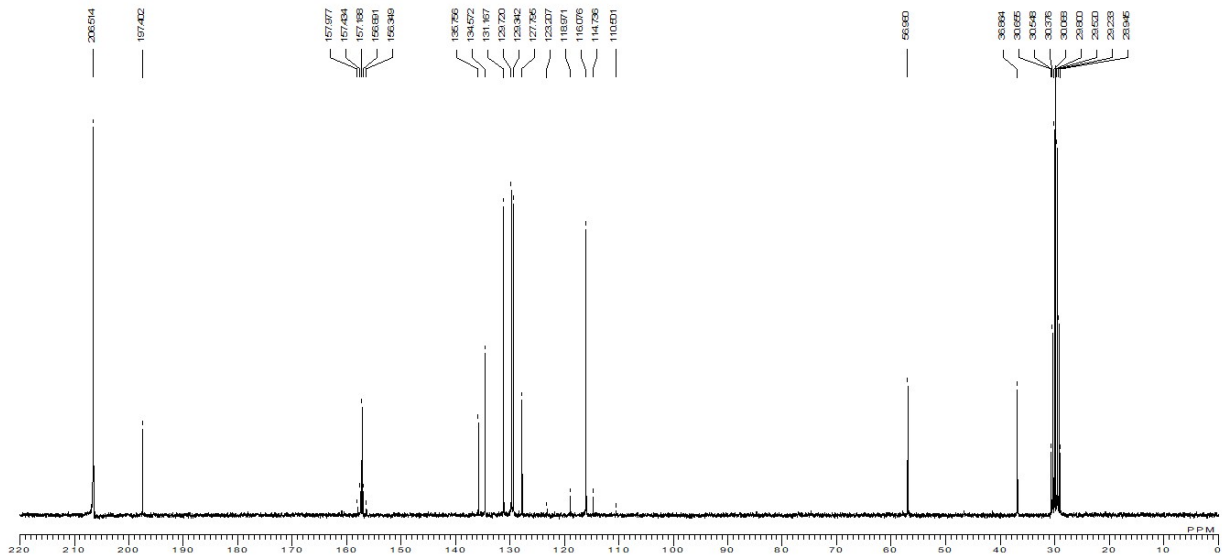
(S)-2,2,2-trifluoro-N-(3-(4-hydroxyphenyl)-1-oxo-1-phenylpropan-2-yl)acetamide (TFA-L-Tyr-Ph, L-17).



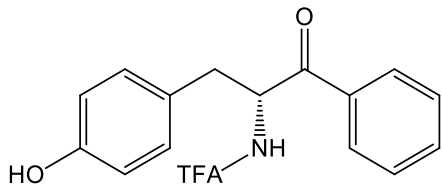
¹H-NMR (270 MHz, ACETONE-D₆)



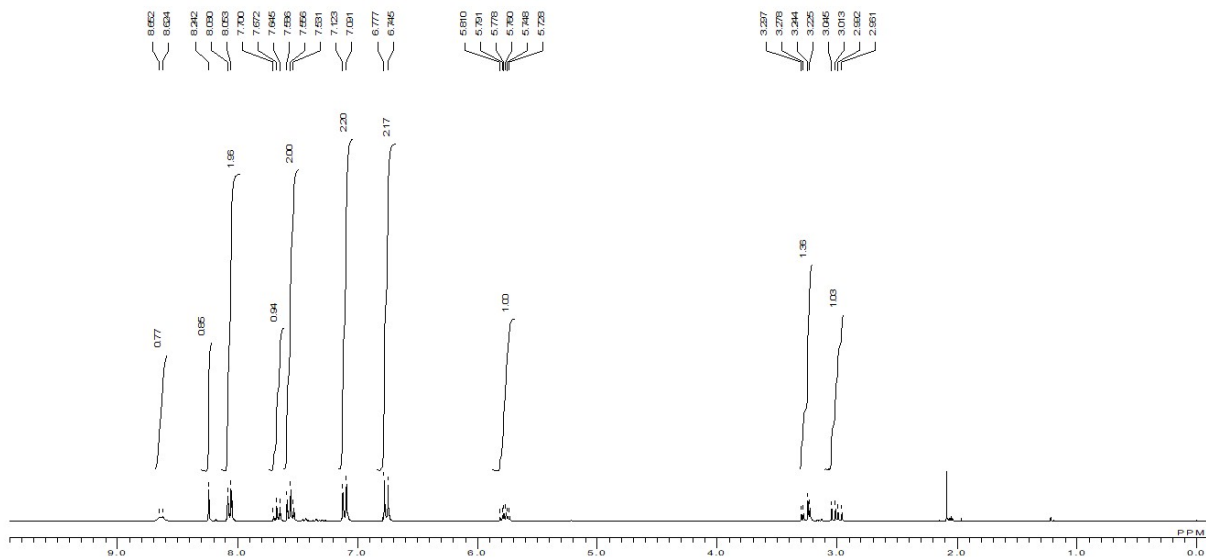
¹³C-NMR (67.5 MHz, ACETONE-D₆)



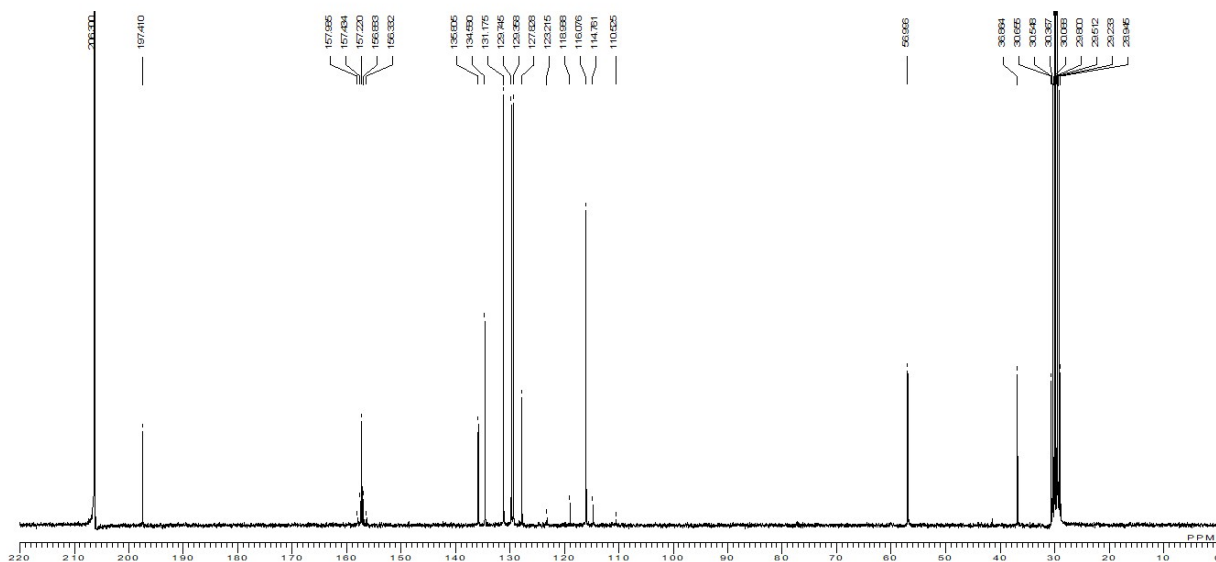
(R)-2,2,2-trifluoro-N-(3-(4-hydroxyphenyl)-1-oxo-1-phenylpropan-2-yl)acetamide (TFA-D-Tyr-Ph, D-17).



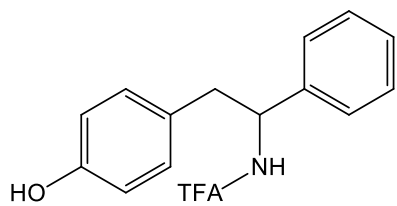
¹H-NMR (270 MHz, ACETONE-D₆)



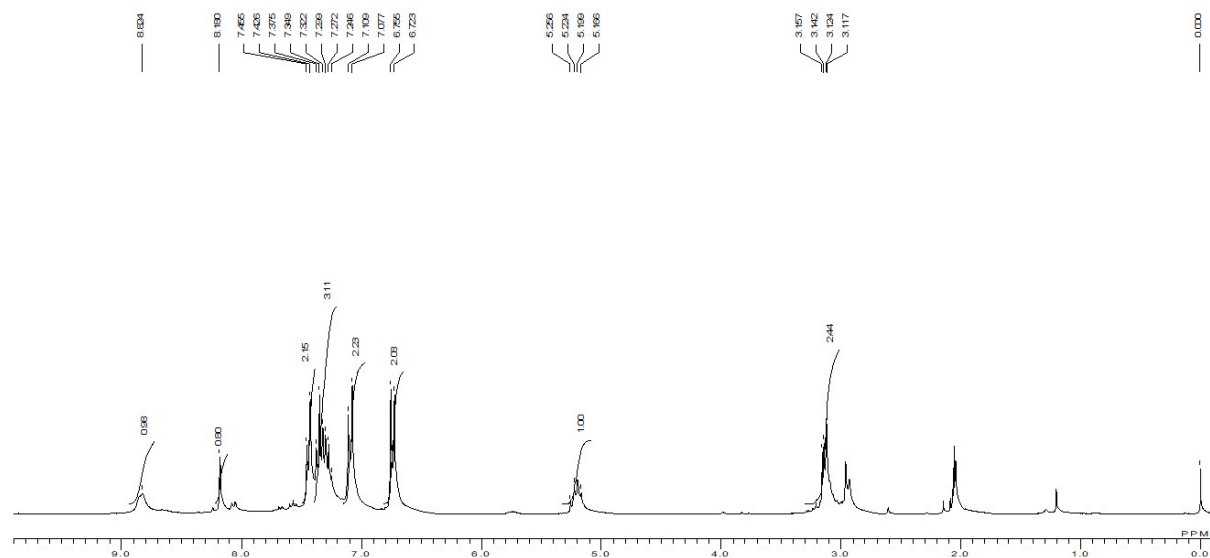
¹³C-NMR (67.5 MHz, ACETONE-D₆)



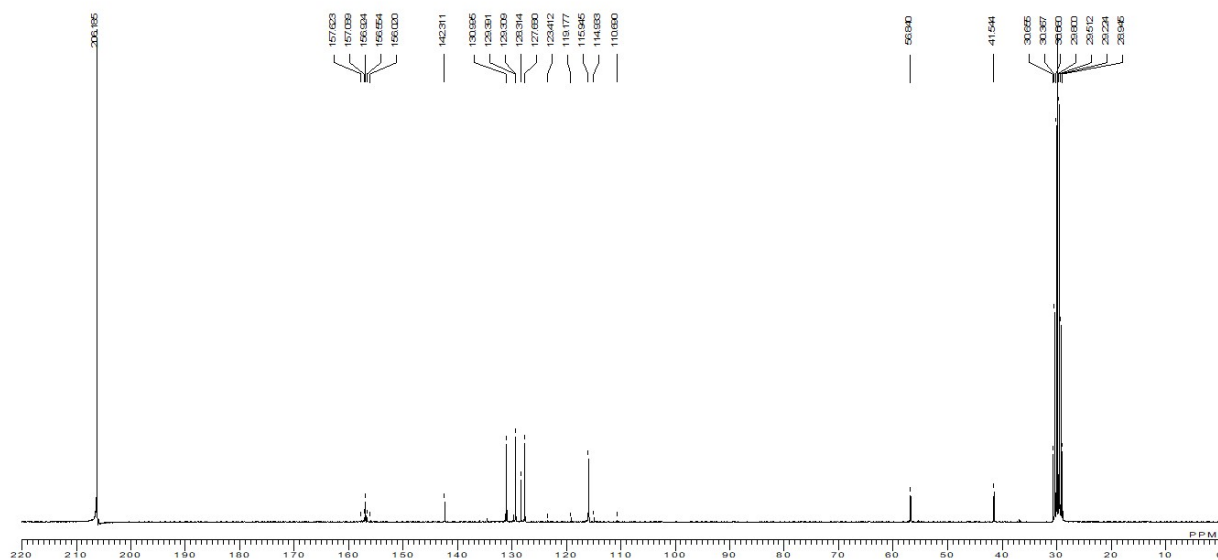
2,2,2-trifluoro-N-(2-(4-hydroxyphenyl)-1-phenylethyl)acetamide (18).



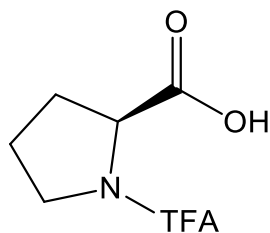
$^1\text{H-NMR}$ (270 MHz, ACETONE- D_6)



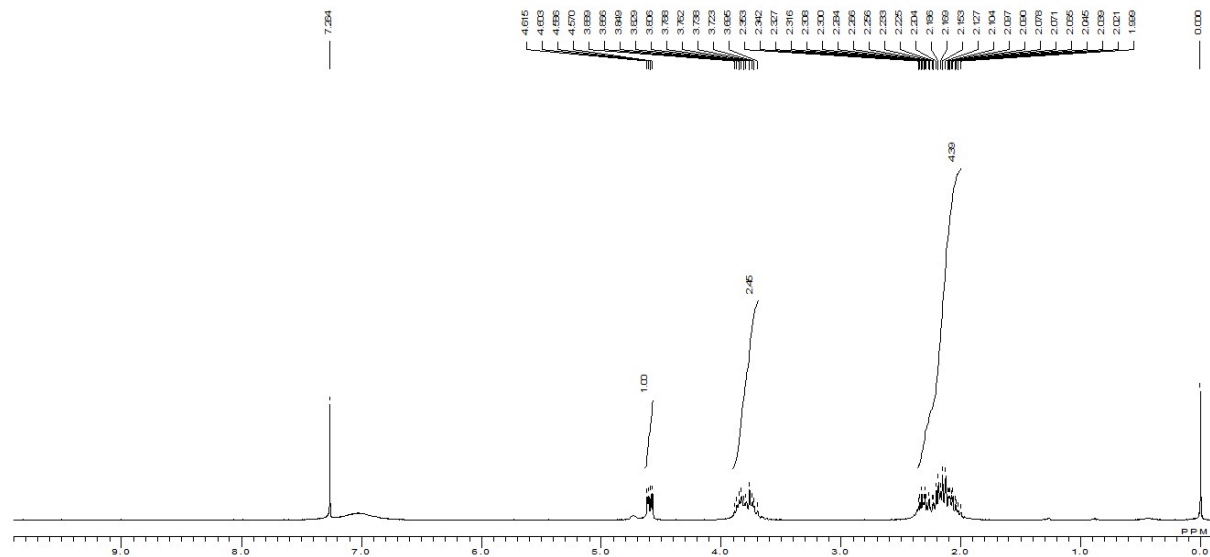
$^{13}\text{C-NMR}$ (67.5 MHz, ACETONE- D_6)



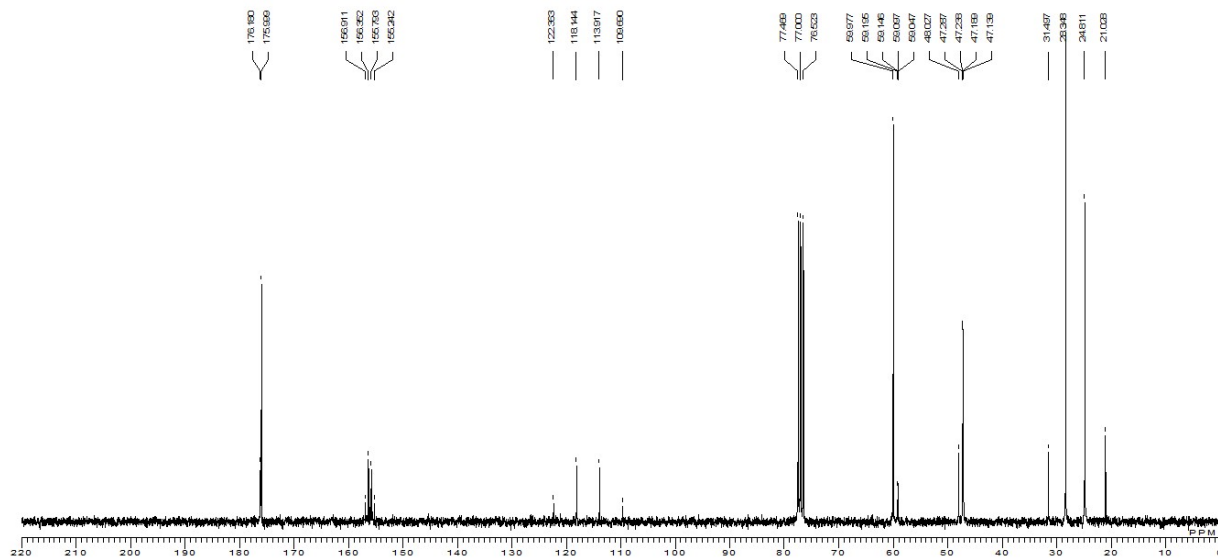
(S)-1-(2,2,2-Trifluoroacetyl)pyrrolidine-2-carboxylic acid (TFA-L-Pro, L-20).



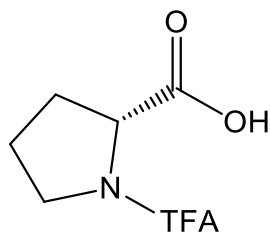
¹H-NMR (270 MHz, CDCl₃)



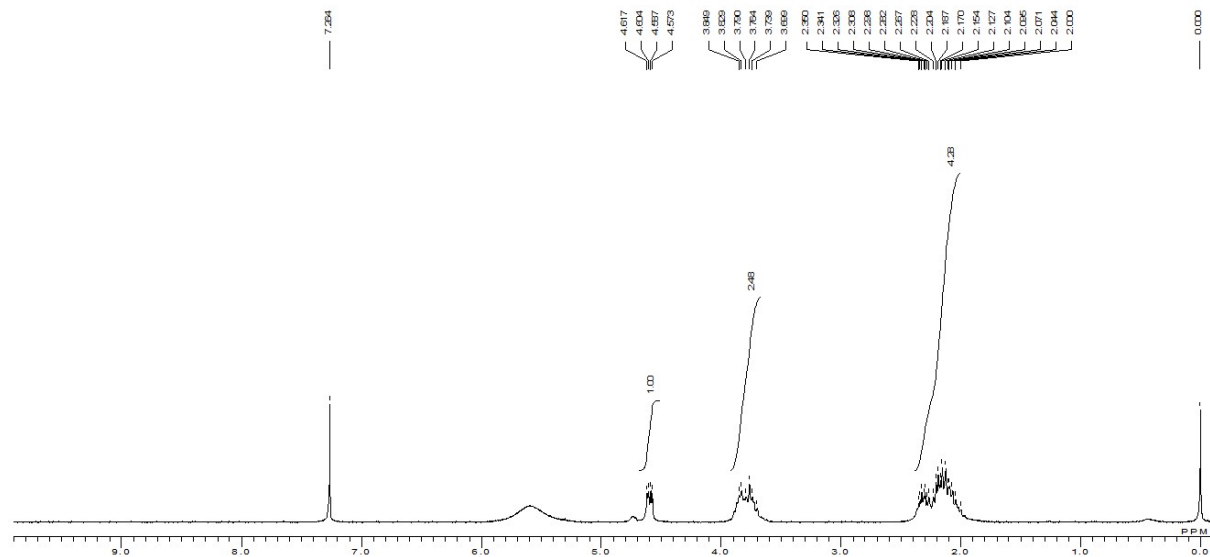
¹³C-NMR (67.5 MHz, CDCl₃)



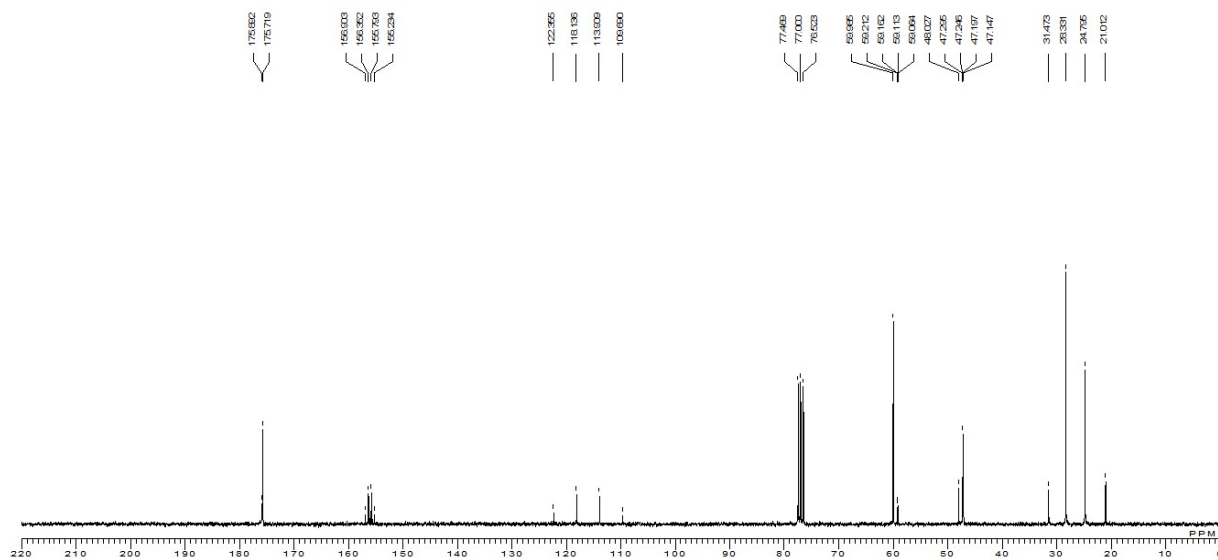
(R)-1-(2,2,2-Trifluoroacetyl)pyrrolidine-2-carboxylic acid (TFA-D-Pro, D-20).



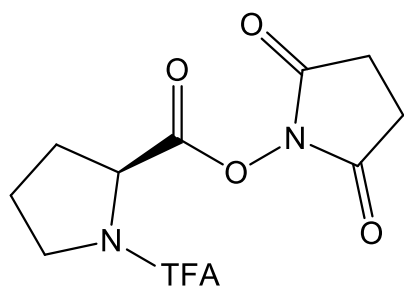
¹H-NMR (270 MHz, CDCl₃)



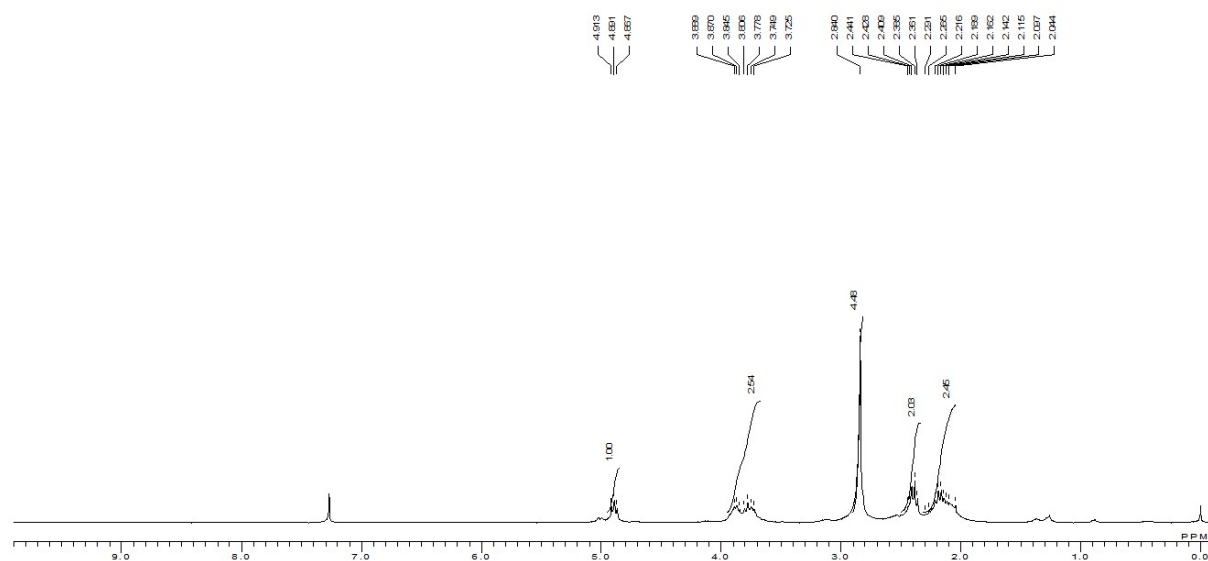
¹³C-NMR (67.5 MHz, CDCl₃)



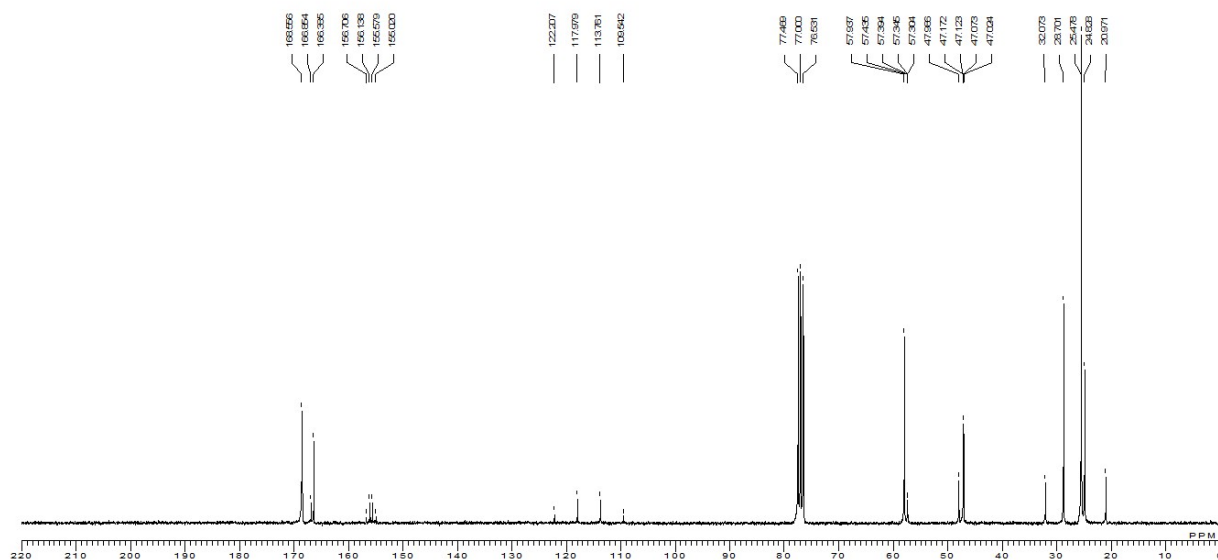
(S)-2,5-dioxypyrrolidin-1-yl 1-(2,2,2-trifluoroacetyl)pyrrolidine-2-carboxylate (TFA-L-Pro-OSu, L-21).



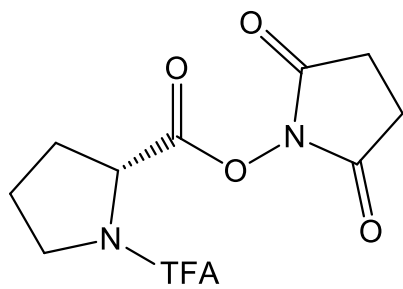
$^1\text{H-NMR}$ (270 MHz, CDCl_3)



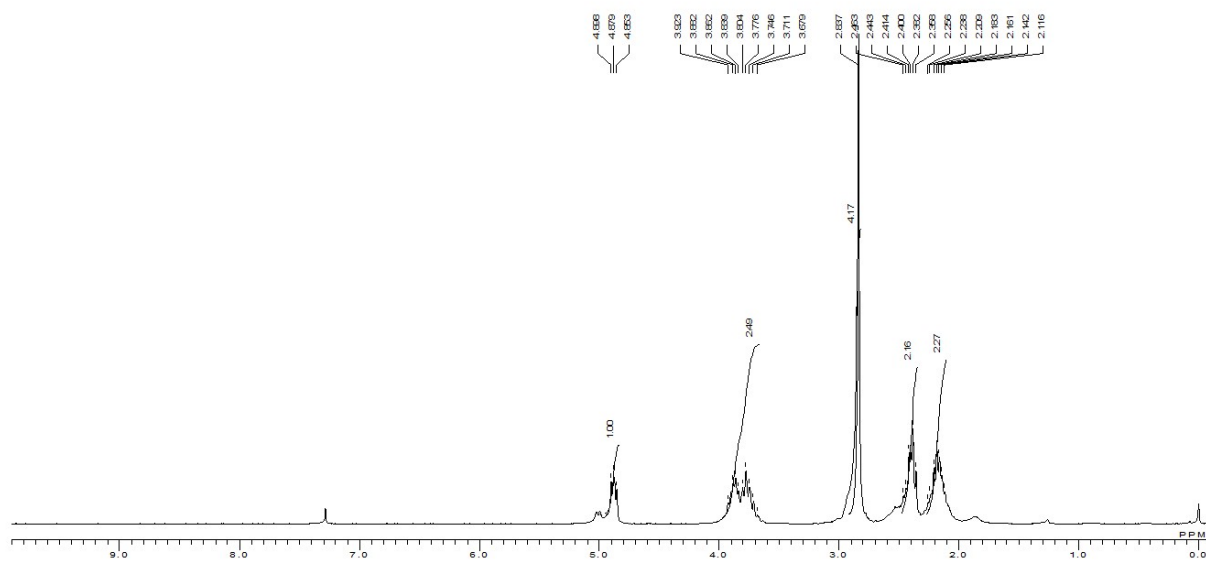
$^{13}\text{C-NMR}$ (67.5 MHz, CDCl_3)



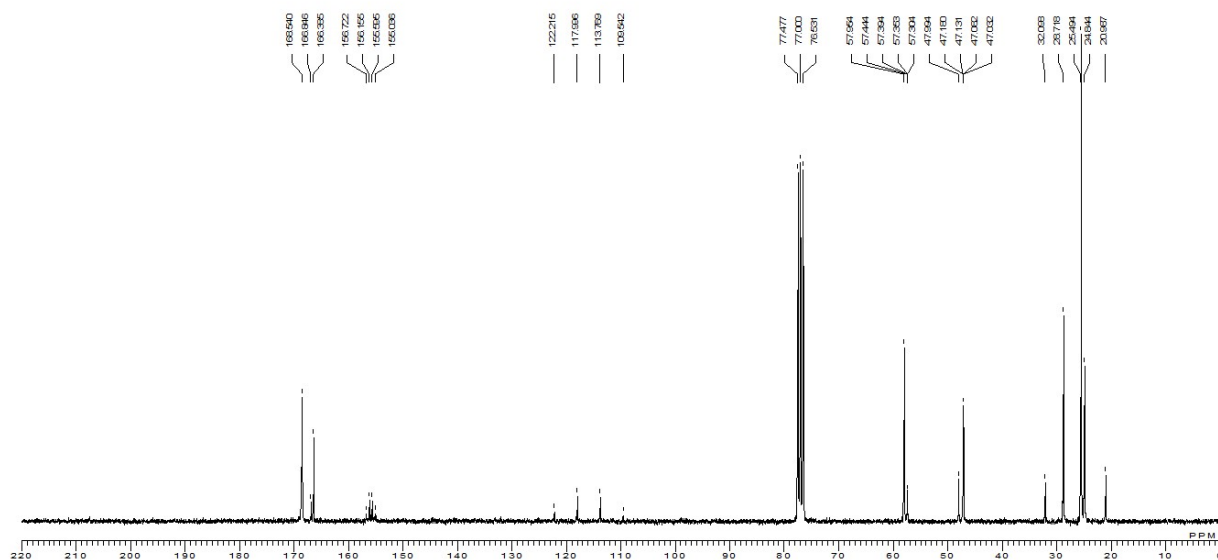
(R)-2,5-dioxopyrrolidin-1-yl 1-(2,2,2-trifluoroacetyl)pyrrolidine-2-carboxylate (TFA-D-Pro-OSu, D-21).



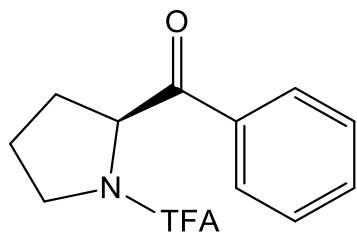
¹H-NMR (270 MHz, CDCl₃)



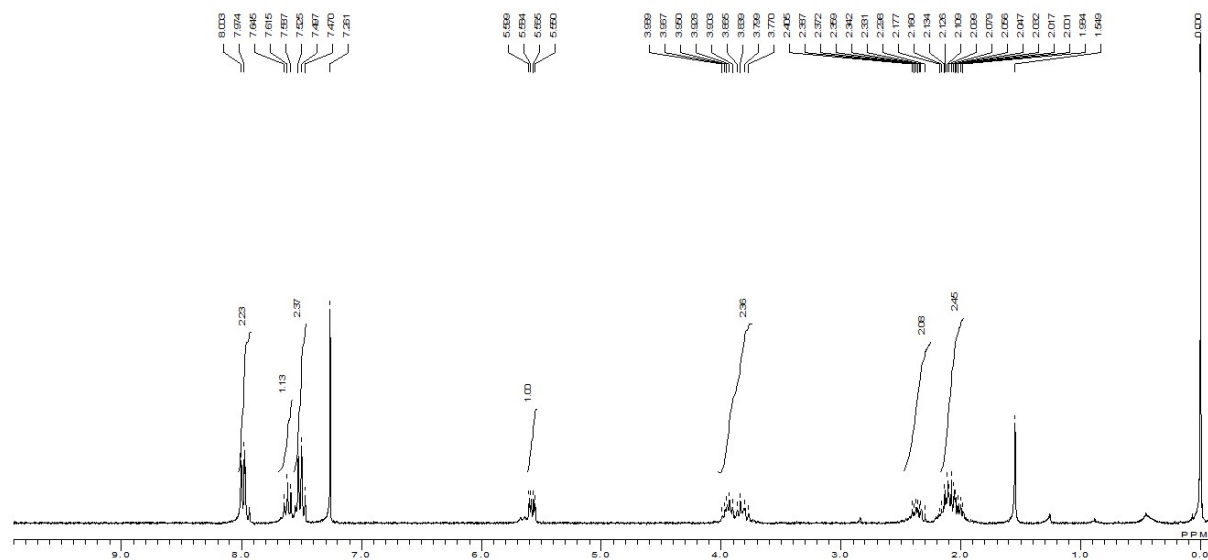
¹³C-NMR (67.5 MHz, CDCl₃)



(S)-1-(2-benzoylpyrrolidin-1-yl)-2,2,2-trifluoroethanone (TFA-L-Pro-Ph, L-22).



¹H-NMR (270 MHz, CDCl₃)



¹³C-NMR (67.5 MHz, CDCl₃)

