Supporting Information

A Convenient, General Synthesis of 1,1-Dimethylallyl Esters as Protecting Groups for Carboxylic Acids

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Experimental Procedures

Reagents and Solvents. All reactions were performed under nitrogen atmosphere. All solvents were purified and dried on alumina columns before use. Reactions were carried out in oven or flame dried glassware. 3-chloro 3-methylbut-1-yne was purchased from Alfa Aesar. All amino acids purchased from Novabiochem. All other reagents and catalysts were purchased from commercially available sources (Aldrich, Strem Chemicals, VWR International)

Instrumentation. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian Inova 300 MHz NMR in CDCl_3 . Chemical shifts (δ values) were reported in parts per million (ppm) and coupling constants (J values) in Hz. Multiplicity is indicated using the following abbreviations: s for a singlet, d for a doublet, t for a triplet, m for a multiplet, br s for a broad singlet, etc. Infrared spectra were recorded on a Perkin-Elmer Spectrum on FT-IR spectrometer MIR with MIRIGS detector. Thin-layer chromatography (TLC) was performed with pre-coated Whatman SIL G/UV254, glass backed, 250 μm , 20X20 cm TLC plates. The silica gel used for flash chromatography was ICN silica 32-63, 60 Å particle size.

General Procedure For Synthesis Of 1,1-Dimethylpropargyl Esters (6a-6l).

A solution of carboxylic acid (0.50 mmol), Cs_2CO_3 (1mmol), KI (0.85 mmol) and CuI (0.01 mmol) in DMF (5 ml) at 25° C was treated with 3-chloro-3-methylbut-1-yne (1 mmol) under nitrogen atmosphere. The mixture was stirred and monitored by TLC until completion (1.5-6 h). The mixture was filtered and the filtrate was evaporated under reduced pressure. The crude product was then purified by flash column chromatography using ethyl acetate / petroleum ether (1: 9).

General Procedure For The Synthesis Of 1,1-Dimethylallyl Esters (7a-7l).

To a solution of 1,1-dimethylpropargyl ester (1 mmol) in methanol (10 ml), was added 5% Palladium on barium sulfate (0.01 mmol) and quinoline (0.3 mmol). The reaction was connected to a hydrogen balloon and the hydrogenation reaction was monitored by TLC until completion. The mixture was filtered through Celite^R and the filtrate was evaporated in vacuo. The crude product was purified by flash column chromatography using ethyl acetate / petroleum ether.

General Procedure For Deprotection Of 1,1-Dimethylallyl Esters (5a-5l).

$(\text{Ph}_3\text{P})_4\text{Pd}$ (10 mol%) was added under nitrogen to a solution of dimethylallyl ester (1 mmol) in THF (5 ml) at room temperature and the resulting mixture treated dropwise with (3 mmol) *N*-methyl morpholine. After completion of the reaction as judged by TLC, solvent was removed in vacuo. The residue was redissolved in dichloromethane (20 ml) and the resulting solution washed with 2N HCl (15 ml) and water (15 ml). The organic layer was dried over MgSO_4 and evaporated in vacuo. The residue was dissolved in ether (20 ml), filtered and the filtrate evaporated. The crude product was purified by flash column chromatography using dichloromethane-methanol. Instead of *N*-methylmorpholine, PhSiH_3 , Potassium 2-ethyl Hexanoate or *p*-Toluene sulfonic acid sodium salt could be used successfully in this reaction as well.

General Procedure For Fmoc Deprotection.

A solution of Fmoc-protected amino acid 1,1-dimethylallyl ester (1 mmol) in methanol (2 ml) was cooled to 0° C and treated with diethyl amine (10 mmol). The mixture was stirred at 25° C and monitored by TLC for completion. Solvent was evaporated and the crude product was purified using size exclusion (Sephadex LH-20) chromatography to obtain desired Fmoc-deprotected product.

Spectral Data

Fmoc-Val-dimethylpropargyl ester (6a).

¹H NMR (300 MHz, CDCl₃) δ 7.81 (d, J = 7.30 Hz, 2H), 7.63 (d, J = 7.03 Hz, 2H), 7.40 (t, J = 7.25 Hz, 2H), 7.31 (t, J = 7.03 Hz, 2H), 5.40 (d, J = 8.49 Hz, 1H), 4.45 (d, J = 6.01 Hz, 2H), 4.30 (t, J = 6.66 Hz, 1H), 2.62 (s, 1H), 2.20 (d, J = 5.57 Hz, 1H), 1.75 (d, J = 8.35 Hz, 6H), 1.01 (dd, J = 6.37 Hz, 6H). ¹³C NMR (300 MHz, CDCl₃) δ 17.6, 17.6, 27.5, 27.6, 32.5, 47.1, 57.2, 67.8, 67.9, 71.2, 84.6, 124.1, 125.2, 127.1, 127.7, 130.1, 130.6, 141.3, 143.8, 155.5, 169.9. IR (Neat): 3425.5, 3297.8, 3049.6, 2971.6, 2304.9, 1723.4, 1510.6, 1446.8, 1265.9, 1127.6 cm⁻¹.

Fmoc-Pro-dimethylpropargyl ester (6b).

¹H NMR (300 MHz, CDCl₃) δ 7.79 (d, J = 7.33 Hz, 2H), 7.63 (m, 2H), 7.40 (t, J = 7.33 Hz, 2H), 7.28 (t, J = 7.03 Hz, 2H), 4.22-4.58 (m, 4H), 3.78-3.5 (m, 2H), 2.55 (d, J = 16.11 Hz, 1H), 2.40 (m, 2H), 1.90 (m, 2H), 1.62 (d, J = 5.56 Hz, 6H). ¹³C NMR (300 MHz, CDCl₃) δ 23.4, 24.3, 28.5, 28.7, 28.9, 29.1, 29.7, 46.5, 47.0, 47.3, 59.6, 67.7, 72.5, 84.1, 119.9, 125.1, 125.2, 127.0, 127.1, 127.7, 141.3, 143.6, 143.9, 156.4, 170.9. IR (Neat): 3483.4, 3284.1, 3062.7, 2981.5, 2944.6, 2878.2, 2250.9, 2118.0, 1749.3, 1671.8, 1413.8, 1351.1, 1236.8, 1188.9, 1122.5 cm⁻¹.

Fmoc-Thr(Trt)dimethylpropargyl ester (6c).

¹H NMR (300 MHz, CDCl₃) δ 7.90 (d, J = 7.18 Hz, 2H), 7.81 (t, J = 7.39 Hz, 2H), 7.60 (d, J = 7.33 Hz, 7H), 7.25 (m, 12H), 6.03 (d, J = 9.52 Hz, 1H), 4.50 (m, 2H), 4.41 (d, J = 7.91 Hz, 1H), 4.01 (d, J = 6.0 Hz, 1H), 2.4 (s, 1H), 1.62 (d, J = 16.26 Hz, 6H), 1.38 (t, J = 7.18 Hz, 3H). ¹³C NMR (300 MHz, CDCl₃) δ 18.5, 28.6, 29.0, 47.3, 59.8, 67.3, 73.1, 73.2, 84.1, 86.6, 125.2, 126.7, 127.2, 127.7, 127.8, 128.6, 129.1, 141.4, 143.9, 144.1, 144.7, 156.6, 171.0. IR (Neat): 3057.9, 2985.5, 2681.1, 2297.1, 1721.7, 1508.6, 1447.2, 1418.2, 1262.9, 1129.2 cm⁻¹.

Fmoc-Abu-dimethylpropargyl ester (6d).

¹H NMR (300 MHz, CDCl₃) δ 7.80 (d, J = 7.32 Hz, 2H), 7.62 (d, J = 7.32 Hz, 2H), 7.41 (t, J = 7.39 Hz, 2H), 7.32 (t, J = 7.03 Hz, 2H), 5.61 (d, J = 7.91 Hz, 1H), 4.40 (d, J = 7.03 Hz, 2H), 4.21 (t, J = 7.03 Hz, 1H), 2.61 (s, 1H), 1.90 (m, 2H), 1.81 (m, 2H), 1.72 (d, J = 8.06 Hz, 6H), 1.01 (t, J = 7.39 Hz, 2H). ¹³C NMR (300 MHz, CDCl₃) δ 21.0, 25.3, 25.6, 25.9, 26.3, 26.4, 47.2, 55.2, 60.4, 68.2, 71.2, 90.4, 120.1, 125.1, 126.5, 127.1, 127.7, 128.8, 141.3, 141.9, 143.9, 155.9, 171.1. IR (Neat): 3579.3, 3298.8, 3062.7, 2974.1, 2937.2, 2878.2, 2250.9, 2118.0, 1712.4, 1520.7, 1447.0, 1236.8, 1126.2 cm⁻¹.

Fmoc-Tyr(*t*-Bu)dimethylpropargyl ester (6e).

¹H NMR (300 MHz, CDCl₃) δ 7.70 (d, J = 7.47 Hz, 2H), 7.52 (d, J = 7.18 Hz, 2H), 7.30 (t, J = 7.32 Hz, 2H), 7.21 (t, J = 7.33 Hz, 2H), 7.04 (d, J = 7.76 Hz, 2H), 6.82 (d, J = 7.33 Hz, 2H), 5.71 (d, J = 7.81 Hz, 1H), 4.50 (m, 1H), 4.31 (m, 2H), 4.20 (t, J = 6.81 Hz, 1H), 3.12 (d, J = 5.42 Hz, 2H), 2.59 (s, 1H), 1.60 (d, J = 5.86 Hz, 6H), 1.25 (s, 9H). ¹³C NMR (300 MHz, CDCl₃) δ 28.7, 28.9, 36.5, 47.2, 55.08, 67.03, 73.2, 78.4, 84.0, 120.034, 124.1, 125.2, 127.1, 127.7, 130.1, 130.6, 141.3, 143.8, 154.4, 155.5, 169.9. IR (Neat): 3579.3, 3424.3, 3291.5, 3062.7, 2981.5, 2937.2, 2243.5, 2118.0, 1719.8, 1671.8, 1498.6, 1388.0, 1240.5, 1126.2 cm⁻¹.

Fmoc-Orn(Boc)dimethylpropargyl ester (6f).

¹H NMR (300 MHz, CDCl₃) δ 7.76 (d, J = 7.34 Hz, 2H), 7.60 (d, J = 6.88 Hz, 2H), 7.41 (t, J = 7.25 Hz, 2H), 7.30 (t, J = 7.17 Hz, 2H), 5.90 (br t, J = 6.16 Hz, 1H), 5.02 (br s, 1H), 4.41 (dd, J = 6.74 Hz, J = 5.71 Hz, 2H), 4.21 (t, J = 6.59 Hz, 1H), 3.17 (br s, 2H), 2.60 (s, 1H), 1.90 (br s, 2H), 1.67 (d, J = 6.73 Hz, 6H), 1.43 (s, 9H). ¹³C NMR (300 MHz, CDCl₃) δ 25.9, 28.4, 28.7, 29.0, 29.9, 36.5, 47.2, 53.8, 67.02, 73.1, 73.3, 83.9, 120.0, 125.1, 127.1, 127.7, 141.3, 143.8, 155.9, 171.6. IR (Neat): 3291.5, 3055.3, 2974.1, 2929.8, 2870.8, 2243.5, 2118.0, 1712.4, 1524.4, 1447.0, 1255.2, 1129.9 cm⁻¹.

Fmoc-Glu(*t*-Bu)dimethylpropargyl ester (6g).

¹H NMR (300 MHz, CDCl₃) δ 7.80 (d, J = 7.32 Hz, 2H), 7.61 (d, J = 7.03 Hz, 2H), 7.40 (t, J = 7.32 Hz, 2H), 7.30 (t, J = 7.32 Hz, 2H), 5.61 (d, J = 7.62 Hz, 1H), 4.40 (d, J = 6.74 Hz, 2H), 4.30 (d, J = 4.25 Hz, 1H), 4.22 (t, J = 6.81, 1H), 2.60 (s, 1H), 2.50-1.95 (m, 4H), 1.7 (s, 6H), 1.45 (s, 9H). ¹³C NMR (300 MHz, CDCl₃) δ 27.7, 28.0, 28.9, 28.9, 31.0, 31.4, 36.4, 47.2, 53.9, 67.0, 72.0, 72.5, 82.4, 84.6, 120.0, 125.1, 127.1, 127.7, 141.3, 143.8, 144.0, 156.0, 162.6, 171.1. IR (Neat): 3579.3, 3291.5, 3055.3, 2974.1, 2250.9, 2118.0, 1959.4, 1918.8, 1716.1, 1671.8, 1524.4, 1450.6, 1384.3, 1236.8, 1126.2 cm⁻¹.

Fmoc-Me-Val dimethylpropargyl ester (6h).

¹H NMR (300 MHz, CDCl₃) δ 7.81 (d, J = 7.03 Hz, 2H), 7.70 (d, J = 7.03 Hz, 2H), 7.40 (t, J = 7.32 Hz, 2H), 7.30 (t, J = 7.03 Hz, 2H), 4.50 (d, J = 6.44 Hz, 2H), 4.30 (t, J = 6.45 Hz, 1H), 4.19 (d, J = 10.55 Hz, 1H), 2.92 (d, J = 2.93, 3H), 2.60 (s, 1H), 2.20 (br s, 1H), 1.62 (d, J = 6.45 Hz, 6H), 1.01 (m, 6H). ¹³C NMR (300 MHz, CDCl₃) δ 19.0, 19.6, 27.9, 28.8, 29.1, 30.2, 47.3, 64.1, 67.7, 72.5, 72.9, 84.4, 120.0, 125.0, 127.1, 127.7, 141.4, 143.9, 144.1, 144.2, 156.3, 169.1. IR (Neat): 3410.1, 3254.5, 3049.6, 2978.7, 2297.8, 1741.1, 1695.0, 1475.9, 1262.4, 1117.0 cm⁻¹.

Fmoc-Gly dimethylpropargyl ester (6i).

¹H NMR (300 MHz, CDCl₃) δ 7.81 (d, J = 7.47 Hz, 2H), 7.63 (d, J = 7.32 Hz, 2H), 7.40 (t, J = 7.32 Hz, 2H), 7.30 (t, J = 7.32 Hz, 2H), 5.70 (br s, 1H), 4.42 (d, J = 7.18 Hz, 2H), 4.30 (t, J = 7.10 Hz, 1H), 4.01 (d, J = 5.56 Hz, 2H), 2.60 (s, 1H), 1.77 (s, 6H). ¹³C NMR (300 MHz, CDCl₃) δ 28.3, 28.9, 43.1, 47.1, 67.2, 73.2, 73.3, 84.1, 120.0, 125.2, 126.6, 127.1, 127.7, 140.7, 141.3, 143.3, 143.9, 156.4, 168.5. IR (Neat): 3413.0, 3297.1, 3065.2, 2992.7, 2942.0, 2246.3, 2115.9, 1718.1, 1667.5, 1526.6, 1450.8, 1382.1, 1237.6, 1194.2, 1129.2 cm⁻¹.

Fmoc-Ala dimethylpropargyl ester (6j).

¹H NMR (300 MHz, CDCl₃) δ 7.80 (d, J = 7.32 Hz, 2H), 7.61 (d, J = 7.17 Hz, 2H), 7.40 (t, J = 7.32 Hz, 2H), 7.30 (t, J = 7.32 Hz, 2H), 5.62 (d, J = 6.89 Hz, 1H), 4.40 (d, J = 7.03 Hz, 3H), 2.60 (s, 1H), 1.72 (d, J = 6.59 Hz, 6H), 1.43 (d, J = 6.74 Hz, 3H).

¹³C NMR (300 MHz, CDCl₃) δ 18.64, 28.7, 28.9, 47.23, 49.9, 67.0, 72.5, 73.0, 84.1, 120.0, 124.6, 125.2, 126.6, 127.1, 127.7, 141.3, 143.9, 144.0, 155.7, 162.6, 171.4. IR (Neat): 3579.3, 3306.2, 2981.5, 2937.2, 2118.0, 1952.0, 1712.4, 1531.7, 1447.0, 1211.0, 1133.6, 1074.6 cm⁻¹.

Fmoc-Val-dimethylallyl ester (7a).

¹H NMR (300 MHz, CDCl₃) δ 7.85 (d, J = 7.47 Hz, 2H), 7.70 (d, J = 7.32 Hz, 2H), 7.42 (t, J = 7.39 Hz, 2H), 6.18 (dd, J = 10.84 Hz, 1H), 5.39 (d, J = 9.08 Hz, 1H), 5.18 (dd, J = 14.13 Hz, 2H), 4.42 (m, 2H), 4.25 (t, J = 6.59 Hz, 1H), 4.20 (q, J = 7.1 Hz, 1H), 2.22 (t, J = 5.71 Hz, 1H), 1.60 (s, 6H), 1.01 (dd, J = 6.81 Hz, 6H). ¹³C NMR (300 MHz, CDCl₃) δ 17.5, 19.0, 26.3, 26.5, 31.5, 47.3, 59.2, 67.0, 82.3, 113.4, 120.0, 125.1, 127.1, 127.7, 141.3, 141.9, 143.9, 144.0, 156.3, 170.9. IR (Neat): 3340.4, 3063.8, 2957.4, 2872.3, 1716.3, 1521.2, 1468.0, 1312.0, 1241.1, 1209.2, 1124.1 cm⁻¹.

Fmoc-Pro-dimethylallyl ester (7b).

¹H NMR (300 MHz, CDCl₃) δ 7.80 (d, J = 7.12 Hz, 2H), 7.60-7.80 (m, 2H), 7.40 (t, J = 7.33 Hz, 2H), 7.33 (t, J = 7.32 Hz, 2H), 6.10 (m, 1H), 5.20 (dd, J = 7.32 Hz, 1H), 5.09 (dd, J = 7.47 Hz, 1H), 4.58-4.20 (m, 4H), 3.80-3.56 (m, 2H), 2.40 (m, 2H), 1.90 (m, 2H), 1.61 (t, J = 6.15 Hz, 6H). ¹³C NMR (300 MHz, CDCl₃) δ 23.3, 26.4, 26.4, 26.5, 29.8, 47.3, 47.4, 59.8, 67.4, 81.6, 112.9, 120.0, 125.2, 125.4, 127.0, 127.1, 127.7, 141.2, 141.3, 142.0, 142.2, 144.0, 144.4, 154.8, 171.5. IR (Neat): 3379.3, 3331.7, 3055.3, 2974.1, 2878.2, 1738.2, 1705.0, 1498.6, 1450.7, 1413.8, 1347.4, 1203.6, 1148.3, 1118.8 cm⁻¹.

Fmoc-Thr(Trt)dimethylallyl ester (7c).

¹H NMR (300 MHz, CDCl₃) δ 7.90 (d, J = 7.18 Hz, 2H), 7.80 (t, J = 8.13 Hz, 2H), 7.57 (d, J = 7.33 Hz, 7H), 7.40 (m, 12H), 6.05 (dd, J = 10.99 Hz, 1H), 5.90 (t, J = 7.47 Hz, 1H), 5.07 (dd, J = 14.13 Hz, 2H), 4.57 (m, 2H), 4.40 (t, J = 7.03 Hz, 1H), 4.30 (t, J = 7.91 Hz, 1H), 4.02 (d, J = 4.1 Hz, 1H), 1.49 (d, J = 16.24 Hz, 6H), 1.35 (m, 3H). ¹³C NMR (300 MHz, CDCl₃) δ 18.7, 18.8, 26.2, 26.3, 47.3, 60.1, 67.3, 71.4, 82.5, 84.7, 113.1, 125.2, 126.6, 126.7, 127.2, 127.3, 127.7, 127.8, 127.9, 128.5, 129.1, 141.4, 142.1, 143.9, 144.1, 144.6, 156.6, 171.1. IR (Neat): 3432.6, 3056.7, 2978.7, 2936.1, 2297.8, 1957.4, 1723.4, 1507.0, 1446.8, 1262.4, 1081.5 cm⁻¹.

Fmoc-Abu-dimethylallyl ester (7d).

¹H NMR (300 MHz, CDCl₃) δ 7.82 (d, J = 7.47 Hz, 2H), 7.64 (d, J = 7.32 Hz, 2H), 7.41 (t, J = 7.32 Hz, 2H), 7.38 (t, J = 7.18 Hz, 2H), 6.10 (dd, J = 10.83 Hz, 1H), 5.41 (d, J = 7.47 Hz, 1H), 5.18 (dd, J = 14.21 Hz, 2H), 4.40 (d, J = 7.03 Hz, 2H), 4.22 (t, J = 7.10 Hz, 1H), 1.93 (m, 2H), 1.80 (m, 2H), 1.60 (s, 6H), 1.01 (m, 2H). ¹³C NMR (300 MHz, CDCl₃) δ 21.0, 25.3, 25.6, 25.9, 26.3, 26.4, 32.6, 47.2, 55.2, 60.4, 66.9, 82.2, 84.3, 113.3, 120.0, 125.1, 126.5, 127.1, 127.7, 127.8, 141.3, 141.9, 143.9, 155.9, 171.1. IR (Neat): 3579.3, 3335.7, 3055.3, 2966.7, 2937.2, 2870.8, 1719.8, 1524.4, 1450.6, 1351.1, 1211.0, 1122.5 cm⁻¹.

Fmoc-Tyr(*t*-Bu)dimethylallyl ester (7e).

¹H NMR (300 MHz, CDCl₃) δ 7.84 (d, J = 7.62 Hz, 2H), 7.67 (d, J = 7.03 Hz, 2H), 7.49 (t, J = 7.32 Hz, 2H), 7.40 (t, J = 7.33 Hz, 2H), 7.16 (d, J = 8.20 Hz, 2H), 7.00 (d, J = 7.03 Hz, 2H), 6.04 (dd, J = 10.83 Hz, 1H), 5.47 (d, J = 7.62 Hz, 1H), 5.14 (m, 2H), 4.63 (m, 1H), 4.40 (m, 2H), 4.27 (t, J = 6.73 Hz, 1H), 3.15 (d, J = 5.86 Hz, 2H), 1.56 (s, 6H), 1.42 (s, 9H). ¹³C NMR (300 MHz, CDCl₃) δ 26.2, 26.4, 28.9, 37.9, 47.2, 55.2, 67.0, 78.4, 82.6, 113.4, 120.0, 124.2, 125.1, 127.1, 127.8, 130.1, 130.9, 141.4, 141.8, 143.9, 154.4, 155.6, 170.4. IR (Neat): 3424.3, 3343.1, 3055.3, 2966.7, 2929.8, 1701.3, 1609.2, 1509.6, 1447.0, 1362.2, 1159.4 cm⁻¹.

Fmoc-Orn(Boc)dimethylallyl ester (7f).

¹H NMR (300 MHz, CDCl₃) δ 8.20 (d, J = 8.35 Hz, 1H), 7.80 (d, J = 7.47 Hz, 2H), 7.62 (d, J = 7.17 Hz, 2H), 7.41 (t, J = 7.39 Hz, 2H), 7.38 (t, J = 7.54 Hz, 2H), 6.15 (dd, J = 10.83 Hz, 1H), 5.62 (d, J = 6.30 Hz, 1H), 5.20 (m, 2H), 4.80 (br s, 1H), 4.42 (d, J = 6.88 Hz, 2H), 4.22 (t, J = 6.88 Hz, 1H), 3.20 (d, J = 4.68 Hz, 2H), 1.90 (m, 2H), 1.60 (s, 6H), 1.50 (s, 9H). ¹³C NMR (300 MHz, CDCl₃) δ 25.3, 25.5, 27.9, 28.4, 30.2, 42.4, 47.2, 54.0, 66.9, 79.1, 82.5, 113.5, 120.0, 125.1, 126.8, 127.1, 127.7, 141.3, 141.7, 143.8, 143.9, 156.0, 171.4. IR (Neat): 3335.7, 3055.3, 2974.1, 2937.2, 1708.7, 1513.3, 1447.0, 1365.8, 1247.9, 1166.8, 1126.2, 1048.8 cm⁻¹.

Fmoc-Glu(*t*Bu)dimethylallyl ester (7g).

¹H NMR (300 MHz, CDCl₃) δ 7.80 (d, J = 7.47 Hz, 2H), 7.62 (d, J = 7.18 Hz, 2H), 7.40 (t, J = 7.32 Hz, 2H), 7.30 (t, J = 7.32 Hz, 2H), 6.10 (dd, J = 10.91 Hz, 1H), 5.60 (d, J = 7.76 Hz, 1H), 5.10 (dd, J = 14.20 Hz, 2H), 4.40 (d, J = 7.33 Hz, 2H), 4.32 (m, 1H), 4.22 (t, J = 7.03 Hz, 1H), 2.50-1.95 (m, 4H), 1.55 (s, 9H), 1.45 (s, 6H). ¹³C NMR (300 MHz, CDCl₃) δ 26.5, 28.0, 47.2, 54.0, 67.0, 82.4, 113.6, 125.1, 127.1, 127.7, 130.1, 130.9, 141.3, 141.5, 143.8, 143.9, 156.0, 172.1. IR (Neat): 3579.3, 3424.3, 3055.3, 2981.5, 2302.5, 1723.5, 1505.9, 1447.0, 1421.1, 1369.5, 1262.6, 1152.0 cm⁻¹.

Fmoc-Me-Val dimethylallyl ester (7h).

¹H NMR (300 MHz, CDCl₃) δ 7.82 (d, J = 7.32 Hz, 2H), 7.68 (d, J = 7.18 Hz, 2H), 7.47 (t, J = 7.25 Hz, 2H), 7.38 (t, J = 7.18 Hz, 2H), 6.11 (m, 1H), 5.21 (m, 2H), 4.50 (d, J = 6.44 Hz, 2H), 4.30 (t, J = 6.45 Hz, 1H), 4.19 (d, J = 10.55 Hz, 1H), 2.96 (s, 3H), 2.20 (d, J = 6.45 Hz, 1H), 1.56 (s, 6H), 1.01 (m, 6H). ¹³C NMR (300 MHz, CDCl₃) δ 19.0, 19.7, 27.5, 27.7, 30.2, 47.4, 67.6, 81.7, 113.1, 120.0, 125.0, 127.1, 127.7, 141.4, 142.0, 142.2, 144.0, 144.1, 156.9, 170.1. IR (Neat): 3453.8, 3062.7, 2966.7, 2937.2, 2870.8, 2354.2, 2332.1, 1734.5, 1701.3, 1609.2, 1469.1, 1447.0, 1306.9, 1203.6 cm⁻¹.

Fmoc-Gly dimethylallyl ester (7i).

¹H NMR (300 MHz, CDCl₃) δ 7.81 (d, J = 7.47 Hz, 2H), 7.62 (d, J = 7.17 Hz, 2H), 7.40 (t, J = 7.32 Hz, 2H), 7.30 (t, J = 7.32 Hz, 2H), 6.08 (dd, J = 10.83 Hz, 1H), 5.60 (br s, 1H), 5.17 (dd, J = 14.21 Hz, 2H), 4.41 (d, J = 7.03 Hz, 2H), 4.30 (t, J = 6.81 Hz, 1H), 3.90 (d, J = 5.28 Hz, 2H), 1.50 (s, 6H). ¹³C NMR (300 MHz, CDCl₃) δ 25.5, 26.4, 43.4, 47.2, 60.4, 67.1, 82.4, 113.4, 120.0, 125.2, 126.5, 127.1, 127.7, 141.3, 141.8, 143.9,

156.4, 169.2. IR (Neat): 3645.4, 3340.4, 3056.7, 2978.7, 2929.0, 1723.4, 1524.8, 1450.3, 1365.2, 1212.7, 1156.0, 1049.6 cm^{-1} .

Fmoc-Ala dimethylallyl ester (7j).

^1H NMR (300 MHz, CDCl_3) δ 7.82 (d, J = 7.47 Hz, 2H), 7.70 (d, J = 7.33 Hz, 2H), 7.40 (t, J = 7.16 Hz, 2H), 7.39 (t, J = 7.40 Hz, 2H), 6.11 (dd, J = 10.84 Hz, 1H), 5.60 (d, J = 6.88 Hz, 1H), 5.18 (dd, J = 14.20 Hz, 2H), 4.40 (m, 3H), 4.25 (t, J = 6.95 Hz, 1H), 1.62 (d, J = 2.05 Hz, 6H), 1.50 (t, J = 6.88 Hz, 3H). ^{13}C NMR (300 MHz, CDCl_3) δ 18.8, 18.9, 25.4, 25.6, 26.4, 26.4, 33.5, 43.2, 50.1, 67.0, 82.2, 84.4, 113.3, 120.0, 125.2, 127.1, 127.7, 141.3, 141.9, 143.9, 144.0, 155.7, 172.0. IR (Neat): 3579.3, 3328.4, 2974.1, 2937.2, 1719.8, 1524.4, 1447.0, 1336.4, 1247.9, 1214.7, 1122.5 cm^{-1} .

H_2N -Val-dimethylallyl ester (8a).

^1H NMR (300 MHz, CDCl_3) δ 6.05 (dd, J = 10.84 Hz, 1H), 5.05 (dd, J = 14.27 Hz, 2H), 3.18 (d, J = 4.69 Hz, 2H), 2.01 (m, 1H), 1.53 (s, 6H), 1.36 (m, 1H), 0.90 (dd, J = 6.88 Hz, 6H). ^{13}C NMR (300 MHz, CDCl_3) δ 17.2, 17.3, 26.6, 26.7, 31.5, 60.4, 82.3, 113.4, 145.2, 170.9. IR (Neat): 3520.9, 3382.9, 3312.0, 3085.1, 2964.5, 2929.0, 1730.4, 1641.8, 1606.3, 1464.5, 1368.8, 1226.9, 1187.9, 1124.1 cm^{-1} .

H_2N -Pro-dimethylallyl ester (8b).

^1H NMR (300 MHz, CDCl_3) δ 8.20 (d, J = 8.23 Hz, 1H), 6.00 (m, 1H), 5.2 (dd, J = 7.76 Hz, 1H), 5.01 (dd, J = 7.47 Hz, 1H), 4.25 (m, 1H), 3.70-3.50 (m, 2H), 2.38 (m, 2H), 1.90 (m, 2H), 1.50 (t, J = 6.10 Hz, 6H). ^{13}C NMR (300 MHz, CDCl_3) δ 23.4, 26.4, 26.5, 30.1, 47.3, 59.8, 81.6, 112.9, 144.5, 171.5. IR (Neat): 3514.7, 3365.6, 2974.6, 2877.4, 1738.9, 1705.4, 1499.8, 1451.7, 1414.1, 1348.4, 1203.5, 1148.9, 1117.2 cm^{-1} .

H_2N -Abu-dimethylallyl ester (8d).

^1H NMR (300 MHz, CDCl_3) δ 6.02 (dd, J = 10.73 Hz, 1H), 5.40 (d, J = 7.47 Hz, 1H), 5.04 (dd, J = 14.21 Hz, 2H), 2.00 (s, 2H), 1.93 (m, 2H), 1.81 (m, 2H), 1.60 (s, 6H), 1.01 (m, 2H). ^{13}C NMR (300 MHz, CDCl_3) δ 26.3, 26.4, 35.2, 44.6, 82.2, 113.3, 143.9, 171.1. IR (Neat): 3511.7, 3345.9, 2971.8, 2966.9, 2938.4, 2872.4, 1720.6, 1528.7, 1453.6, 1352.2, 1211.9, 1121.8 cm^{-1} .

H_2N -Tyr(*t*-Bu)dimethylallyl ester (8e).

^1H NMR (300 MHz, CDCl_3) δ 7.20 (d, J = 8.49 Hz, 2H), 6.83 (d, J = 8.35 Hz, 2H), 5.92 (dd, J = 10.84 Hz, 1H), 5.02 (dd, J = 14.21 Hz, 2H), 3.58 (t, J = 6.66 Hz, 1H), 2.90 (dd, J = 5.86 Hz, 1H), 2.79 (dd, J = 7.32 Hz, 1H), 1.50 (br s, 2H), 1.45 (s, 6H), 1.30 (s, 9H). ^{13}C NMR (300 MHz, CDCl_3) δ 26.3, 26.4, 28.8, 40.6, 56.3, 78.3, 81.5, 112.9, 124.2, 129.8, 132.2, 142.2, 154.1, 171.6. IR (Neat): 3542.6, 3375.8, 3304.9, 2971.6, 2921.9, 2865.2, 1730.5, 1602.8, 1507.0, 1365.2, 1237.5, 1163.1 cm^{-1} .

H_2N -Orn(Boc)dimethylallyl ester (8f).

^1H NMR (300 MHz, CDCl_3) δ 6.08 (dd, J = 10.9 Hz, 1H), 5.13 (dd, J = 14.13 Hz, 2H), 4.75 (br s, 2H), 3.4 (t, J = 6.0 Hz, 1H), 3.18 (br s, 2H), 1.90 (m, 2H), 1.7 (m, 2H), 1.50 (s, 6H), 1.43 (s, 9H). ^{13}C NMR (300 MHz, CDCl_3) δ 25.3, 25.5, 27.9, 28.4, 30.2, 42.4, 54.0,

79.1, 82.6, 113.5, 144.0, 156.0, 171.4. IR (Neat): 3550.4, 3368.7, 2971.6, 2929.0, 2872.3, 1705.6, 1521.2, 1450.3, 1361.7, 1248.2, 1170.2, 1127.6 cm^{-1} .

H₂N-Glu(*t*Bu)dimethylallyl ester (8g).

¹H NMR (300 MHz, CDCl₃) δ 6.00 (dd, *J* = 10.84 Hz, 1H), 5.02 (dd, *J* = 14.27 Hz, 2H), 3.30 (m, 1H), 2.1-1.58 (m, 4H), 1.5 (s, 9H), 1.38 (s, 6H). ¹³C NMR (300 MHz, CDCl₃) δ 26.9, 27.1, 28.5, 28.6, 28.7, 29.1, 29.7, 54.0, 82.4, 82.8, 113.6, 144.0, 172.1. IR (Neat): 3501.6, 3375.8, 3049.6, 2978.7, 2936.1, 2886.5, 1723.4, 1457.4, 1365.2, 1265.9, 1152.4 cm^{-1} .

(9b)