Supporting Information

Rh(III)-catalyzed double C-H activation towards peptide-benzazepine conjugates

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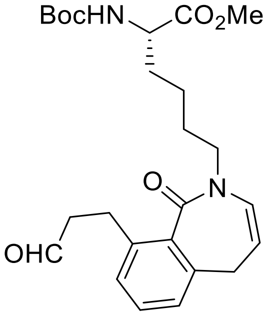
1、General Information

All other reagents were used as received from commercial sources. Reactions were monitored through thin layer chromatography (TLC) on 0.25-mm silica gel plates and visualized under UV light. Flash column chromatography (FCC) was performed using Flash silica gel (90-Å pore size, 200-300 μm). NMR spectra were recorded on Bruker Avance-400 or -600 instrument, calibrated to $CD(H)Cl_3$ as the internal reference (7.26 and 77.0 ppm for ^1H and ^{13}C NMR spectra, respectively). ^1H NMR spectral data were reported in terms of chemical shift (δ, ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR spectral data were reported in terms of chemical shift (δ, ppm). The following abbreviations indicated the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. High-resolution mass spectra were recorded using a SCIEX X500R LC-Q-TOF, ESI ion Source.

2、Product Preparation

In a seal capped flask equipped with a stirring bar, **1** (0.1 mmol, 1 equiv.), **2** (0.3 mmol, 3 equiv.), $[RhCp^*Cl_2]_2$ (0.005 mmol, 0.05 equiv.), $AgSbF_6$ (0.02 mmol, 0.2 equiv.), TMBA (0.2 mmol, 2 equiv.) and DCE (1 mL, 0.1 M.) were added. The reaction mixture was put in an oil bath and heated at 40 °C for 2 h, cooled to room temperature. The solvent was removed in *vacuo* and the remaining residue was purified by a silica gel column chromatography (EtOAc/*n*-hexane from 1:20 to 1:2, then EtOAc/*n*-hexane 1:2) to afford the products **3a-3aa**.



3a

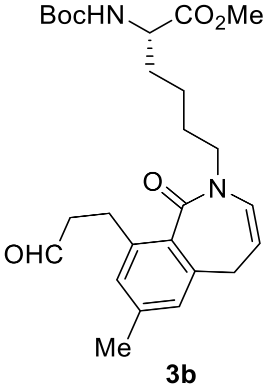
Following general procedure, **1a** (0.1 mmol, 36.4 mg) and **2a** (0.3 mmol, 20 μL) were used to give product **3a**. 33.0 mg, 72%. Pale yellow liquid oil. $R_f = 0.4$ (EtOAc/*n*-hexane, 1:2).

In a seal capped flask equipped with a stirring bar, **1a** (1.5 mmol, 546.3 mg), **2a** (4.5 mmol, 0.3 mL), $[RhCp^*Cl_2]_2$ (0.075 mmol, 46.4 mg), $AgSbF_6$ (0.3 mmol, 103.1 mg), TMBA (3.0 mmol, 492.3 mg) and DCE (15 mL) were added. The reaction mixture was put in an oil bath and heated at 40 °C for 2 h, cooled to room temperature. The solvent was removed in vacuo and the remaining residue was purified by a silica gel column chromatography (EtOAc/*n*-hexane from 1:20 to 1:2, then EtOAc/*n*-hexane 1:2) to afford the product **3a**. 308.7 mg, 45%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (s, 1H), 7.25 – 7.19 (m, 1H), 7.11 (dd, J = 7.7, 2.2 Hz, 1H), 6.92 (dd, J = 7.3, 2.3 Hz, 1H), 5.88 (dd, J = 7.3, 2.4 Hz, 1H), 5.78 – 5.69 (m, 1H), 5.15 (s, 1H), 4.28 (s, 1H), 4.09 (s, 1H), 3.72 (s, 3H), 3.27 (s, 2H), 3.09 – 2.88 (m, 4H), 2.69 (s, 1H), 1.85 (s, 1H), 1.75 – 1.64 (m, 3H), 1.44 – 1.38 (m, 11H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 173.1, 169.2, 155.3, 144.9, 141.7, 133.0, 129.8, 129.1, 128.6, 123.8, 121.1, 79.7, 53.2, 52.2, 47.6, 46.0, 32.3, 31.4, 28.2, 28.0, 27.0, 22.5.

HRMS (ESI, m/z) calcd for $C_{25}H_{35}N_2O_6$ $[M + H]^+$: 459.2490, found: 459.2480.



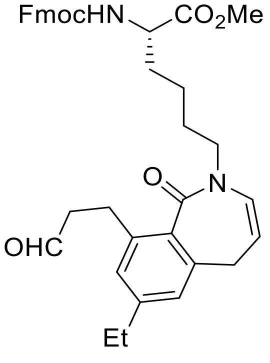
3b

Following general procedure, **1b** (0.1 mmol, 37.8 mg) and **2a** (0.3 mmol, 20 μL) were used to give product **3b**. 35.4 mg, 75%. White viscous liquid oil. R_f = 0.5 (EtOAc/*n*-hexane, 1:2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 6.94 (s, 1H), 6.76 (s, 1H), 5.89 (d, *J* = 7.4 Hz, 1H), 5.74 (q, *J* = 7.4 Hz, 1H), 5.13 (s, 1H), 4.30 (s, 1H), 4.11 (s, 1H), 3.75 (s, 3H), 3.26 (s, 2H), 3.09 – 2.87 (m, 4H), 2.68 (d, *J* = 17.5 Hz, 1H), 2.30 (s, 3H), 1.86 (s, 1H), 1.70 (q, *J* = 8.1, 7.6 Hz, 3H), 1.47 – 1.39 (m, 11H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2, 173.2, 169.2, 155.4, 144.9, 141.8, 140.1, 130.2, 129.5, 129.3, 124.7, 120.9, 79.8, 53.3, 52.2, 48.0, 46.2, 32.2, 31.5, 28.2, 28.1, 27.1, 22.5, 21.0.

HRMS (ESI, m/z) calcd for $C_{26}H_{37}N_2O_6$ $[M + H]^+$: 473.2646, found: 473.2641.



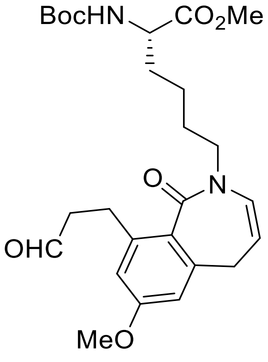
3c

Following general procedure, **1c** (0.1 mmol, 51.4 mg) and **2a** (0.3 mmol, 20 μL) were used to give product **3c**. 39.8 mg, 68%. Pale yellow liquid oil. R_f = 0.5 (EtOAc/*n*-hexane, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.7 Hz, 2H), 6.95 (s, 1H), 6.74 (d, *J* = 8.8 Hz, 1H), 5.89 (d, *J* = 7.4 Hz, 1H), 5.75 (t, *J* = 7.7 Hz, 1H), 5.67 – 5.48 (m, 1H), 4.40 (q, *J* = 6.1 Hz, 3H), 4.16 (d, *J* = 36.9 Hz, 2H), 3.77 (s, 3H), 3.34 (d, *J* = 2.8 Hz, 2H), 3.29 (s, 1H), 3.10 – 2.89 (m, 3H), 2.58 (q, *J* = 7.7 Hz, 3H), 1.94 (s, 1H), 1.80 – 1.63 (m, 3H), 1.48 (dd, *J* = 16.5, 8.2 Hz, 2H), 1.22 (d, *J* = 7.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 202.3, 172.9, 169.3, 156.0, 146.3, 146.0, 145.0, 143.8, 143.7, 142.9, 141.8, 141.2, 130.4, 129.2, 128.4, 128.3, 127.6, 127.0, 125.1, 123.4, 121.0, 119.89, 119.87, 104.1, 66.9, 53.7, 52.4, 47.1, 46.1, 34.2, 31.5, 29.4, 28.3, 28.0, 27.1, 22.4, 15.0.

HRMS (ESI, m/z) calcd for $C_{37}H_{41}N_2O_6$ $[M + H]^+$: 609.2959, found: 609.2952



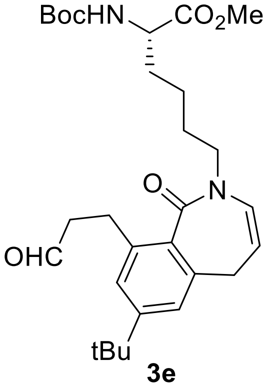
3d

Following general procedure, **1d** (0.1 mmol, 39.4 mg) and **2a** (0.3 mmol, 20 μL) were used to give product **3d**. 27.4 mg, 56%. Pale yellow liquid oil. R_f = 0.5 (EtOAc/*n*-hexane, 1:2).

^{1}H NMR (400 MHz, CDCl$_3$) δ 9.81 (s, 1H), 6.66 (s, 1H), 6.47 (s, 1H), 5.90 (d, *J* = 7.4 Hz, 1H), 5.74 (q, *J* = 7.4 Hz, 1H), 5.13 (s, 1H), 4.30 (s, 1H), 4.11 (s, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 3.27 (s, 2H), 3.12 – 2.89 (m, 4H), 2.73 (s, 1H), 1.86 (d, *J* = 10.7 Hz, 1H), 1.69 (d, *J* = 9.7 Hz, 3H), 1.47 – 1.39 (m, 11H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 202.2, 173.2, 168.9, 160.4, 155.4, 146.8, 144.2, 129.6, 125.8, 120.5, 114.1, 109.3, 79.8, 55.2, 53.3, 52.3, 47.5, 46.1, 32.3, 31.9, 28.3, 28.2, 27.4, 22.6.

HRMS (ESI, m/z) calcd for $C_{26}H_{37}N_2O_7$ $[M + H]^+$: 489.2596, found: 489.2589.



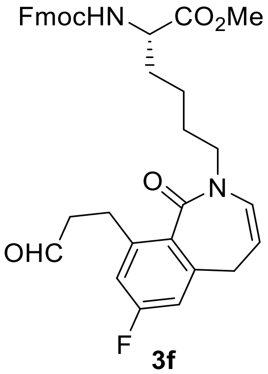
3e

Following general procedure, **1e** (0.1 mmol, 42.0 mg) and **2a** (0.3 mmol, 20 μL) were used to give product **3e**. 28.1 mg, 55%. Pale yellow liquid oil. R_f = 0.4 (EtOAc/*n*-hexane, 1:2).

^{1}H NMR (400 MHz, CDCl$_3$) δ 9.95 (s, 1H), 7.28 (d, *J* = 2.0 Hz, 1H), 7.07 (d, *J* = 1.9 Hz, 1H), 6.03 (d, *J* = 7.4 Hz, 1H), 5.90 (q, *J* = 7.2 Hz, 1H), 5.28 (s, 1H), 4.44 (s, 1H), 4.27 (d, *J* = 7.0 Hz, 1H), 3.88 (s, 3H), 3.43 (s, 2H), 3.17 (d, *J* = 42.0 Hz, 4H), 2.86 (s, 1H), 2.00 (s, 1H), 1.85 (s, 3H), 1.60 – 1.54 (m, 11H), 1.44 (s, 9H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 202.4, 173.2, 169.3, 156.0, 153.2, 144.7, 141.5, 130.2, 129.2, 125.9, 121.0, 79.8, 53.3, 52.2, 47.2, 46.3, 34.6, 31.9, 31.1, 28.3, 27.5, 22.6.

HRMS (ESI, m/z) calcd for $C_{29}H_{43}N_2O_6$ $[M + H]^+$: 515.3116, found: 515.3115.



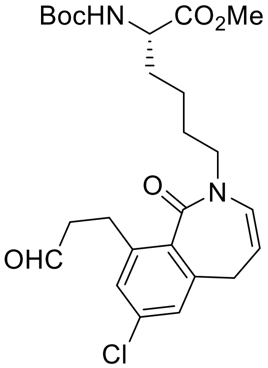
3f

Following general procedure, **1f** (0.1 mmol, 50.4 mg) and **2a** (0.3 mmol, 20 μL) were used to give product **3f**. 28.2 mg, 47%. Pale yellow liquid oil. $R_f = 0.5$ (EtOAc/*n*-hexane, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.78 (d, *J* = 7.7 Hz, 2H), 7.60 (d, *J* = 7.4 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 7.7 Hz, 2H), 6.83 (d, *J* = 9.6 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 5.91 (d, *J* = 7.4 Hz, 1H), 5.74 (t, *J* = 7.6 Hz, 1H), 5.48 (d, *J* = 8.1 Hz, 1H), 4.40 (t, *J* = 9.4 Hz, 3H), 4.23 (s, 1H), 4.11 (s, 1H), 3.78 (s, 3H), 3.31 (d, *J* = 14.6 Hz, 2H), 3.05 (s, 2H), 2.95 (d, *J* = 10.7 Hz, 2H), 2.72 (s, 1H), 1.94 (s, 1H), 1.72 (s, 3H), 1.51 – 1.37 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.5, 172.8, 168.5, 161.6, 156.3, 147.3 (d, *J* = 8.1 Hz), 145.0, 143.8, 141.3, 129.6, 129.3, 127.7, 127.0, 125.1, 120.5, 120.0, 115.3 (d, *J* = 21.0 Hz), 110.9 (d, *J* = 21.6 Hz), 67.0, 53.7, 52.4, 47.1, 45.8, 31.4, 28.1, 27.1, 22.5.

HRMS (ESI, m/z) calcd for $C_{35}H_{36}FN_2O_6$ [M + H]$^+$: 599.2552, found: 599.2548



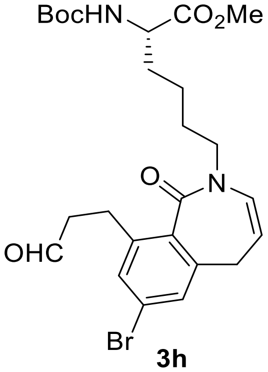
3g

Following general procedure, **1g** (0.1 mmol, 39.8 mg) and **2a** (0.3 mmol, 20 μL) were used to give product **3g**. 15.7 mg, 32%. Pale yellow liquid oil. $R_f = 0.5$ (EtOAc/*n*-hexane, 1:2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.13 (d, *J* = 2.1 Hz, 1H), 6.96 (d, *J* = 2.1 Hz, 1H), 5.92 (d, *J* = 7.4 Hz, 1H), 5.75 (q, *J* = 7.2 Hz, 1H), 5.12 (s, 1H), 4.31 (s, 1H), 4.10 (s, 1H), 3.75 (s, 3H), 3.27 (s, 2H), 3.09 – 2.89 (m, 4H), 2.73 (d, *J* = 10.0 Hz, 1H), 1.86 (s, 1H), 1.69 (s, 3H), 1.48 – 1.40 (m, 11H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.5, 173.2, 168.4, 155.4, 146.3, 143.9, 135.6, 131.6, 129.6, 128.6, 123.9, 120.6, 79.9, 53.2, 52.3, 47.8, 45.8, 31.3, 29.3, 28.3, 28.1, 26.9, 22.5.

HRMS (ESI, m/z) calcd for $C_{25}H_{34}ClN_2O_6$ [M + H]$^+$: 493.2100, found: 493.2096.



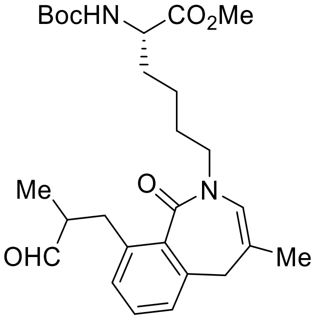
3h

Following general procedure, **1h** (0.1 mmol, 44.2 mg) and **2a** (0.3 mmol, 20 μL) were used to give product **3h**. 21.4 mg, 40%. Pale yellow liquid oil. R_f = 0.4 (EtOAc/*n*-hexane, 1:2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.28 (s, 1H), 7.11 (s, 1H), 5.91 (d, *J* = 7.4 Hz, 1H), 5.74 (q, *J* = 7.5 Hz, 1H), 5.10 (s, 1H), 4.30 (s, 1H), 4.11 (d, *J* = 15.9 Hz, 1H), 3.75 (s, 3H), 3.28 (d, *J* = 14.2 Hz, 2H), 3.05 (d, *J* = 11.3 Hz, 2H), 2.93 (d, *J* = 14.8 Hz, 2H), 2.72 (d, *J* = 12.6 Hz, 1H), 1.86 (s, 1H), 1.74 – 1.65 (m, 3H), 1.45 – 1.40 (m, 11H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.4, 173.2, 168.4, 146.5, 144.0, 132.0, 131.5, 129.5, 126.8, 124.0, 120.7, 79.8, 53.2, 52.3, 47.9, 45.9, 32.2, 31.2, 28.3, 28.1, 26.8, 22.5.

HRMS (ESI, m/z) calcd for $C_{25}H_{34}BrN_2O_6$ $[M + H]^+$: 537.1595, found: 537.1596.



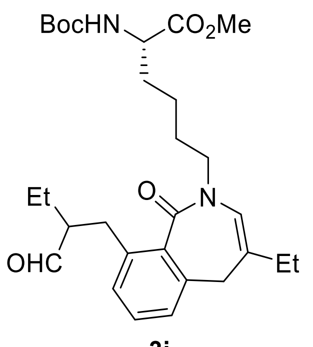
3i

Following general procedure, **1a** (0.1 mmol, 36.4 mg),**2b** (1 mmol, 82 μL) and Pivalic acid (0.2 mmol, 20.4 mg) at 60°C for 12 h were used to give product **3i**. 30.2 mg, 62%. Pale yellow liquid oil. R_f = 0.6 (EtOAc/*n*-hexane, 1:2). Dr = 1.2:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 – 9.63 (m, 1H), 7.22 (q, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 7.7 Hz, 1H), 6.94 (dd, *J* = 7.6, 4.1 Hz, 1H), 5.68 – 5.57 (m, 1H), 5.20 – 5.04 (m, 1H), 4.30 (s, 1H), 4.16 – 4.02 (m, 1H), 3.74 (d, *J* = 3.4 Hz, 4H), 3.58 – 3.36 (m, 2H), 3.27 – 3.03 (m, 2H), 2.99 – 2.53 (m, 4H), 1.88 – 1.83 (m, 1H), 1.76 – 1.69 (m, 3H), 1.46 – 1.41 (m, 11H), 1.06 (dd, *J* = 7.4, 2.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.9, 173.3, 168.9, 168.8, 155.4, 144.3, 144.2, 140.1, 133.1, 132.9, 132.8, 132.7, 131.2, 130.8, 129.6, 129.5, 126.6, 125.8, 123.9, 123.2, 123.1, 79.8, 53.4, 52.3, 48.1, 48.0, 47.6, 47.2, 37.6, 35.0, 34.8, 32.5, 32.2, 28.3, 28.0, 27.9, 22.7, 20.2, 19.8, 13.7, 13.2.

HRMS (ESI, m/z) calcd for $C_{27}H_{39}N_2O_6$ $[M + H]^+$: 487.2803, found: 487.2796



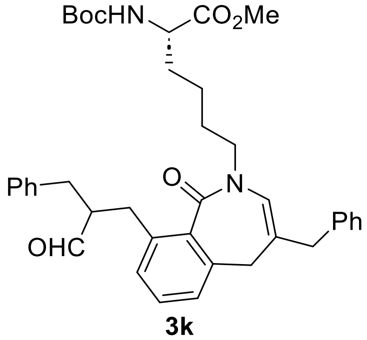
3j

Following general procedure, **1a** (0.1 mmol, 36.4 mg), **2c** (2 mmol, 196 μL) and Pivalic acid (0.2 mmol, 20.4 mg) at 60°C for 12 h were used to give product **3j**. 26.6 mg, 52%. Pale yellow liquid oil. *R*f = 0.5 (EtOAc/*n*-hexane, 1:4). Dr = 1:1.

^{1}H NMR (400 MHz, CDCl$_3$) δ 9.60 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.24 – 7.17 (m, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.93 (dd, *J* = 7.3, 2.8 Hz, 1H), 5.62 (d, *J* = 25.1 Hz, 1H), 5.18 – 5.04 (m, 1H), 4.31 (s, 1H), 4.15 – 4.03 (m, 1H), 3.75 (d, *J* = 3.8 Hz, 4H), 3.39 (dd, *J* = 13.2, 4.7 Hz, 1H), 3.27 – 3.11 (m, 2H), 3.00 – 2.79 (m, 2H), 2.75 – 2.53 (m, 2H), 2.15 (q, *J* = 7.7 Hz, 2H), 1.87 (s, 1H), 1.73 (d, *J* = 7.6 Hz, 2H), 1.64 (s, 1H), 1.46 – 1.42 (m, 11H), 1.03 (t, *J* = 7.4 Hz, 3H), 0.95 – 0.90 (m, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 205.2, 205.1, 173.2, 168.9, 168.8, 155.5, 144.7, 140.2, 140.1, 138.4, 133.0, 131.2, 130.8, 129.5, 129.3, 129.2, 126.5, 125.8, 124.0, 123.9, 122.4, 122.3, 79.8, 55.0, 54.9, 53.4, 52.3, 47.7, 36.3, 33.1, 33.0, 32.5, 32.2, 28.31, 28.29, 28.0, 27.9, 27.4, 22.8, 22.7, 22.4, 21.9, 12.4, 11.5, 11.4.

HRMS (ESI, m/z) calcd for $C_{29}H_{43}N_2O_6$ $[M + H]^+$: 515.3116, found: 515.3112



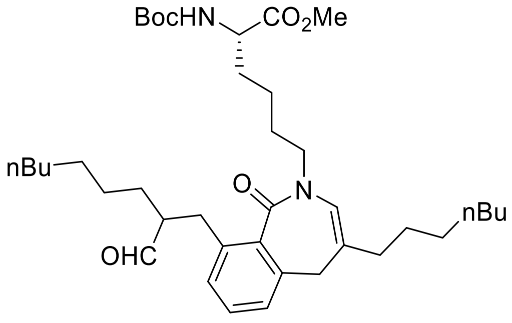
3k

Following general procedure, **1a** (0.1 mmol, 36.4 mg) and **2d** (2 mmol, 292.4 mg) at 60°C for 12 h were used to give product **3k**. 31.6 mg, 50%. Pale yellow liquid oil. *R*f = 0.5 (EtOAc/*n*-hexane, 1:4). Dr = 1.2:1.

^{1}H NMR (400 MHz, CDCl$_3$) δ 9.64 (d, *J* = 2.3 Hz, 1H), 7.26 – 7.23 (m, 3H), 7.20 (dd, *J* = 7.1, 5.3 Hz, 2H), 7.15 (dd, *J* = 9.1, 2.7 Hz, 2H), 7.11 – 7.06 (m, 3H), 7.05 – 6.99 (m, 2H), 6.57 (d, *J* = 8.3 Hz, 1H), 5.69 (d, *J* = 6.1 Hz, 1H), 5.11 (dd, *J* = 27.1, 9.5 Hz, 1H), 4.33 (s, 1H), 4.19 – 4.07 (m, 1H), 3.75 (d, *J* = 2.7 Hz, 3H), 3.42 (d, *J* = 4.1 Hz, 2H), 3.34 (d, *J* = 13.3 Hz, 1H), 3.26 – 3.10 (m, 2H), 3.04 – 2.96 (m, 2H), 2.83 – 2.63 (m, 3H), 1.88 (s, 1H), 1.71 (q, *J* = 7.2 Hz, 3H), 1.47 – 1.41 (m, 11H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 204.4, 172.8, 169.1, 155.3, 144.4, 139.7, 139.2, 137.9, 135.6, 133.0, 129.5, 129.4, 129.1, 129.0, 128.5, 128.4, 126.6, 126.3, 124.5, 124.3, 124.2, 79.9, 55.3, 54.9, 53.6, 52.3, 47.6, 47.1, 40.4, 35.7, 35.3, 33.7, 33.5, 32.6, 31.4, 28.3, 22.8.

HRMS (ESI, m/z) calcd for $C_{39}H_{47}N_2O_6$ $[M + H]^+$: 639.3429, found: 639.3425.



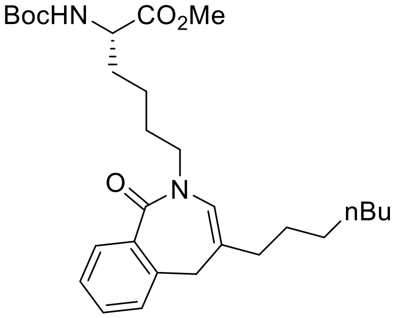
3l

Following general procedure, **1a** (0.1 mmol, 36.4 mg), **2e** (2 mmol, 308.3 mg) and Pivalic acid (0.2 mmol, 20.4 mg) at 60°C for 12 h were used to give product **3l**. 23.3 mg, 36%. Pale yellow liquid oil. *R*f = 0.5 (EtOAc/*n*-hexane, 1:4). Dr = 1:1.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.58 (dd, *J* = 8.6, 2.7 Hz, 1H), 7.19 (q, *J* = 7.4 Hz, 1H), 7.08 (dd, *J* = 10.8, 7.7 Hz, 1H), 6.92 (dd, *J* = 7.5, 2.7 Hz, 1H), 5.57 (d, *J* = 4.4 Hz, 1H), 5.18 – 5.06 (m, 1H), 4.36 – 4.24 (m, 1H), 4.17 – 4.08 (m, 1H), 3.75 (s, 3H), 3.52 – 3.32 (m, 2H), 3.24 – 3.13 (m, 2H), 2.98 – 2.80 (m, 2H), 2.70 – 2.54 (m, 2H), 2.17 – 2.01 (m, 3H), 1.86 (s, 1H), 1.75 – 1.58 (m, 6H), 1.45 – 1.42 (m, 11H), 1.24 (t, *J* = 12.3 Hz, 16H), 0.88 (d, *J* = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.1, 204.9, 173.2, 168.83, 168.76, 155.4, 144.7, 140.1, 140.0, 136.73, 136.69, 133.0, 132.9, 129.4, 129.2, 124.00, 123.96, 123.10, 123.05, 79.8, 79.7, 53.6, 53.4, 52.2, 47.6, 47.2, 42.4, 36.1, 34.5, 33.4, 33.3, 32.47, 32.45, 31.74, 31.70, 29.5, 29.14, 29.12, 29.0, 28.95, 28.90, 28.8, 28.3, 28.2, 28.1, 28.0, 27.9, 27.3, 27.0, 26.9, 22.7, 22.62, 22.57, 22.5, 14.03, 14.01.

HRMS (ESI, m/z) calcd for $C_{39}H_{63}N_2O_6$ $[M + H]^+$: 655.4681, found: 655.4679.



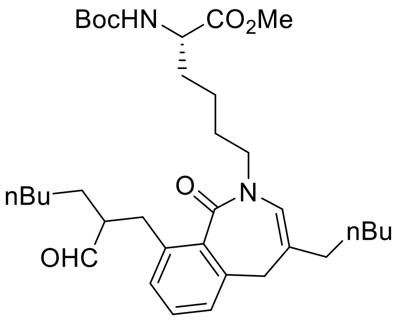
3l'

Following general procedure, **1a** (0.1 mmol, 36.4 mg), **2e** (2 mmol, 308.3 mg) and Pivalic acid (0.2 mmol, 20.4 mg) at 60°C for 12 h were used to give product **3l'**. 13.0 mg, 26%. Pale yellow liquid oil. *R*f = 0.5 (EtOAc/*n*-hexane, 1:4).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.39 – 7.34 (m, 1H), 7.31 – 7.26 (m, 1H), 7.07 (dd, *J* = 7.5, 1.3 Hz, 1H), 5.66 – 5.60 (m, 1H), 5.15 (d, *J* = 8.4 Hz, 1H), 4.30 (d, *J* = 6.6 Hz, 1H), 3.74 (s, 3H), 3.66 (s, 2H), 3.18 (s, 2H), 2.18 – 2.11 (m, 2H), 1.95 – 1.81 (m, 2H), 1.79 – 1.60 (m, 5H), 1.49 – 1.37 (m, 14H), 1.25 – 1.20 (m, 4H), 0.87 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 173.3, 168.8, 155.4, 142.9, 134.0, 133.8, 131.2, 130.8, 126.4, 125.8, 123.6, 79.8, 53.3, 52.2, 47.7, 35.9, 34.8, 32.2, 31.7, 29.0, 28.9, 28.3, 27.9, 27.6, 22.6, 22.5, 14.0.

HRMS (ESI, m/z) calcd for $C_{29}H_{45}N_2O_5$ [M + H]$^+$: 501.3323, found: 501.3324.



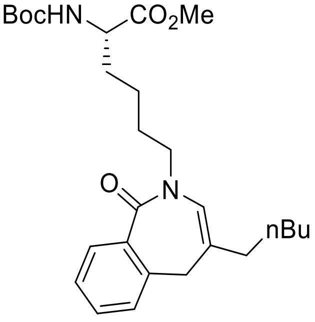
3m

Following general procedure, **1a** (0.1 mmol, 36.4 mg), **2f** (2 mmol, 252.2 mg) and Pivalic acid (0.2 mmol, 20.4 mg) at 60°C for 12 h were used to give product **3m**. 27.9 mg, 47%. Pale yellow liquid oil. *R*$_f$ = 0.5 (EtOAc/*n*-hexane, 1:4). Dr = 1:1.

^{1}H NMR (400 MHz, CDCl$_3$) δ 9.58 (t, *J* = 3.3 Hz, 1H), 7.23 – 7.16 (m, 1H), 7.09 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 5.58 (s, 1H), 5.19 – 5.05 (m, 1H), 4.31 (s, 1H), 4.18 – 4.07 (m, 1H), 3.75 (s, 3H), 3.54 – 3.32 (m, 2H), 3.26 – 3.10 (m, 2H), 2.99 – 2.78 (m, 2H), 2.72 – 2.54 (m, 2H), 2.20 – 2.02 (m, 3H), 1.86 (s, 1H), 1.44 (d, *J* = 12.5 Hz, 14H), 1.29 – 1.24 (m, 11H), 0.88 (dd, *J* = 13.2, 5.6 Hz, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 205.2, 205.0, 173.3, 168.9, 155.2, 144.7, 140.0, 136.7, 132.7, 129.5, 129.2, 124.0, 123.1, 79.7, 53.6, 53.4, 52.3, 47.6, 47.3, 36.1, 34.4, 33.4, 32.5, 31.9, 31.8, 31.5, 31.4, 31.0, 30.1, 29.3, 29.1, 28.9, 28.29, 28.26, 27.0, 26.7, 26.6, 22.74, 22.66, 22.4, 22.3, 14.0, 13.9.

HRMS (ESI, m/z) calcd for $C_{35}H_{55}N_2O_6$ [M + H]$^+$: 599.4055, found: 599.4058.



3m'

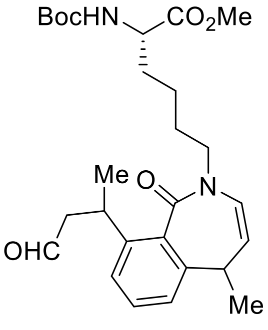
Following general procedure, **1a** (0.1 mmol, 36.4 mg), **2f** (2 mmol, 252.2 mg) and Pivalic acid (0.2 mmol, 20.4 mg) at 60°C for 12 h were used to give product **3m'**. 4.9 mg, 11%. Pale yellow liquid oil. *R*$_f$ = 0.5 (EtOAc/*n*-hexane, 1:4).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.84 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.40 – 7.34 (m, 1H), 7.31 – 7.27 (m, 1H), 7.08 (dd, *J* = 7.5, 1.3 Hz, 1H), 5.65 (d, *J* = 1.4 Hz, 1H), 5.15 (d, *J* = 8.4 Hz, 1H), 4.30 (q, *J* = 8.2, 7.3 Hz, 1H), 3.77 – 3.65 (m, 5H), 3.18 (s, 2H), 2.17 – 2.10

(m, 2H), 1.85 (dd, J = 11.0, 5.5 Hz, 1H), 1.76 – 1.63 (m, 5H), 1.47 – 1.41 (m, 13H), 1.19 – 1.12 (m, 2H), 0.85 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 168.7, 155.4, 142.9, 134.0, 133.8, 131.2, 130.8, 126.4, 125.8, 123.6, 79.8, 53.3, 52.2, 47.7, 35.8, 34.8, 32.2, 31.2, 28.3, 27.9, 27.2, 22.5, 22.3, 13.9.

HRMS (ESI, m/z) calcd for $C_{27}H_{41}N_2O_5$ $[M + H]^+$: 473.3010, found: 473.3015.



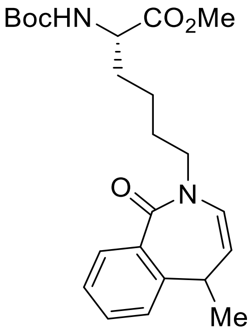
3n

Following general procedure, **1a** (0.1 mmol, 36.4 mg) and **2g** (2 mmol, 164 μL) at 60°C for 12 h were used to give product **3n**. 17.6 mg, 36%. Pale yellow liquid oil. R_f = 0.5 (EtOAc/*n*-hexane, 1:4). Dr = 1:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ [9.76 (t), 9.51 (q), 1H], 7.35 (q, J = 7.7 Hz, 1H), 7.21 (dd, J = 12.1, 7.8 Hz, 1H), 7.02 (dd, J = 11.2, 7.7 Hz, 1H), 5.93 – 5.80 (m, 1H), 5.48 – 5.34 (m, 1H), 5.24 – 5.01 (m, 1H), 4.39 – 4.23 (m, 1H), 4.19 – 3.98 (m, 1H), 3.85 – 3.76 (m, 1H), [3.75 (s), 3.65 (s), 3H], 3.45 (d, J = 7.5 Hz, 1H), 3.41 – 3.24 (m, 1H), [2.97 (m), 2.62 (m), 2H], 1.94 – 1.84 (m, 1H), 1.78 – 1.67 (m, 3H), 1.47 (dd, J = 7.0, 4.5 Hz, 3H), 1.43 (d, J = 8.9 Hz, 11H), 1.29 – 1.19 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.8, 201.9, 173.3, 169.9, 155.5, 148.7, 145.9, 133.2, 132.6, 129.84, 129.79, 128.9, 127.4, 124.8, 124.6, 119.1, 119.0, 79.9, 53.3, 52.5, 52.3, 52.0, 47.5, 47.2, 34.0, 32.4, 32.1, 30.7, 28.31, 28.29, 28.2, 22.74, 22.65, 21.8, 15.8.

HRMS (ESI, m/z) calcd for $C_{27}H_{39}N_2O_6$ $[M + H]^+$: 487.2803, found: 487.2803.



3n'

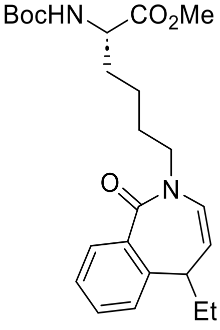
Following general procedure, **1a** (0.1 mmol, 36.4 mg) and **2g** (2 mmol, 164 μL) at 60°C for 12 h were used to give product **3n′**. 11.4 mg, 27%. Pale yellow liquid oil. R_f = 0.6 (EtOAc/*n*-hexane, 1:4). Dr = 1:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.80 (m, 1H), 7.49 – 7.40 (m, 1H), 7.31 (dd, J = 7.7, 1.2 Hz, 1H), 7.16 (d, J = 7.7 Hz, 1H), 5.91 – 5.86 (m, 1H), 5.40 (dd, J = 7.7, 6.6 Hz, 1H), 5.14 (d, J = 7.8 Hz, 1H), 4.31 (d, J = 8.1 Hz, 1H), 4.08 – 3.89 (m, 1H), 3.74

(d, *J* = 2.3 Hz, 3H), 3.54 – 3.38 (m, 2H), 1.92 – 1.83 (m, 1H), 1.77 – 1.69 (m, 3H), 1.47 (d, *J* = 7.1 Hz, 3H), 1.44 (d, *J* = 9.8 Hz, 11H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.3, 169.4, 155.5, 147.14, 147.11, 131.4, 131.1, 127.9, 126.3, 125.1, 122.2, 79.8, 53.3, 52.3, 47.9, 47.8, 34.3, 32.3, 32.1, 28.33, 28.30, 28.05, 27.98, 22.6, 16.3.

HRMS (ESI, m/z) calcd for $C_{23}H_{33}N_2O_5$ $[M + H]^+$: 417.2384, found: 417.2388.



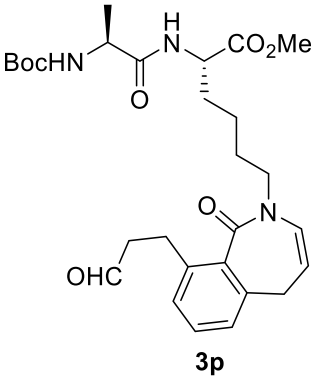
3o'

Following general procedure, **1a** (0.1 mmol, 36.4 mg) and **2h** (2 mmol, 196 µL) at 60°C for 12 h were used to give product **3o′**. 10.8 mg, 25%. Pale yellow liquid oil. *R*f = 0.5 (EtOAc/*n*-hexane, 1:4). Dr = 1:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 1H), 7.45 – 7.37 (m, 1H), 7.31 – 7.26 (m, 1H), 7.10 (d, *J* = 7.7 Hz, 1H), 5.91 (d, *J* = 7.8 Hz, 1H), 5.47 (t, *J* = 7.6 Hz, 1H), 5.14 (d, *J* = 8.3 Hz, 1H), 4.37 – 4.22 (m, 1H), 3.74 (d, *J* = 1.5 Hz, 5H), 3.14 (q, *J* = 7.6 Hz, 1H), 1.92 – 1.83 (m, 2H), 1.81 – 1.64 (m, 4H), 1.44 (d, *J* = 4.2 Hz, 11H), 0.99 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 169.4, 155.5, 146.4, 133.6, 131.4, 131.3, 128.3, 126.3, 123.5, 79.8, 53.4, 52.3, 48.0, 47.9, 42.8, 32.2, 32.1, 28.3, 27.93, 27.87, 23.9, 22.6, 22.5, 12.4.

HRMS (ESI, m/z) calcd for $C_{24}H_{35}N_2O_5$ $[M + H]^+$: 431.2541, found: 431.2545.



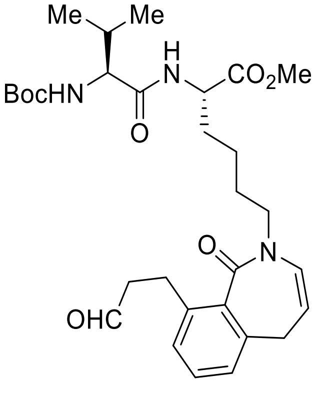
3p

Following general procedure, **1p** (0.1 mmol, 43.5 mg) and **2a** (0.3 mmol, 20 µL) were used to give product **3p**. 27.6 mg, 52%. Pale yellow liquid oil. *R*f = 0.5 (EtOAc/*n*-hexane, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.27 – 7.22 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.79 (s, 1H), 5.89 (d, *J* = 7.5 Hz, 1H), 5.78 (q, *J* = 6.3, 5.2 Hz, 1H), 5.16 (s, 1H), 4.58 (s, 1H), 4.15 (s, 2H), 3.75 (s, 3H), 3.29 (s, 2H), 3.00 (d, *J* = 14.4 Hz, 4H), 2.74 (s, 1H), 1.93 (s, 1H), 1.77 – 1.61 (m, 3H), 1.47 – 1.44 (m, 11H), 1.34 – 1.29 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.6, 172.5, 169.8, 145.0, 141.7, 133.0, 130.0, 129.1, 128.7, 123.9, 121.5, 80.3, 52.4, 52.0, 50.0, 46.0, 31.8, 31.5, 28.3, 28.0, 27.1, 22.3, 18.1.

HRMS (ESI, m/z) calcd for $C_{28}H_{40}N_3O_7$ $[M + H]^+$: 530.2861, found: 530.2861.



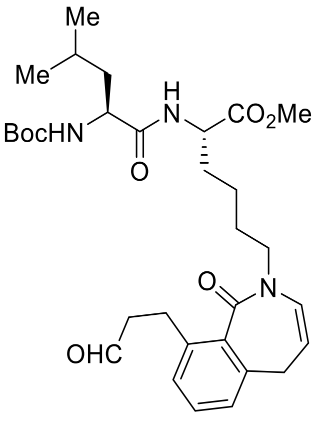
3q

Following general procedure, **1q** (0.1 mmol, 46.3 mg) and **2a** (0.3 mmol, 20 μL) were used to give product **3q**. 36.5 mg, 66%. Pale yellow liquid oil. *R*f = 0.5 (EtOAc/*n*-hexane, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.4 Hz, 1H), 6.71 (d, *J* = 59.0 Hz, 1H), 5.88 (d, *J* = 7.4 Hz, 1H), 5.77 (q, *J* = 7.2 Hz, 1H), 5.15 (d, *J* = 8.8 Hz, 1H), 4.56 (q, *J* = 6.7 Hz, 1H), 4.13 (s, 1H), 3.94 (d, *J* = 14.4 Hz, 1H), 3.74 (s, 3H), 3.27 (s, 2H), 3.04 (d, *J* = 54.9 Hz, 4H), 2.74 (s, 1H), 1.93 (s, 1H), 1.82 (s, 1H), 1.76 – 1.57 (m, 3H), 1.50 – 1.40 (m, 11H), 0.88 (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2, 172.4, 171.7, 169.7, 155.8, 145.0, 141.7, 133.1, 130.0, 129.1, 128.7, 124.0, 121.6, 79.7, 53.4, 52.3, 52.1, 47.1, 46.1, 31.5, 31.2, 28.3, 28.0, 27.1, 22.5, 19.1, 17.7.

HRMS (ESI, m/z) calcd for $C_{30}H_{44}N_3O_7$ $[M + H]^+$: 558.3174, found: 558.3167.



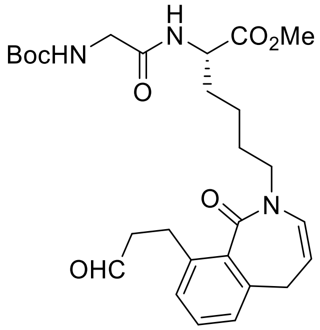
3r

Following general procedure, **1r** (0.1 mmol, 47.7 mg) and **2a** (0.3 mmol, 20 μL) were used to give product **3r**. 29.4 mg, 49%. Pale yellow liquid oil. R_f = 0.5 (EtOAc/*n*-hexane, 4:1).

H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.13 (dd, *J* = 7.7, 1.3 Hz, 1H), 6.94 (dd, *J* = 7.6, 1.3 Hz, 1H), 6.75 (s, 1H), 5.89 (d, *J* = 7.4 Hz, 1H), 5.77 (q, *J* = 7.2 Hz, 1H), 5.02 (d, *J* = 27.1 Hz, 1H), 4.58 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 3H), 3.28 (s, 2H), 3.04 (d, *J* = 44.2 Hz, 4H), 2.73 (s, 1H), 1.94 (s, 1H), 1.80 (s, 1H), 1.68 – 1.60 (m, 3H), 1.49 – 1.42 (m, 11H), 1.27 (d, *J* = 1.7 Hz, 2H), 0.90 (d, *J* = 5.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.5, 173.7, 168.5, 156.2, 146.4, 141.9, 133.1, 130.0, 129.1, 128.6, 124.0, 80.1, 53.1, 52.3, 52.0, 47.5, 46.0, 31.7, 31.5, 28.3, 28.0, 27.1, 24.7, 22.9, 22.3, 21.8.

HRMS (ESI, m/z) calcd for $C_{31}H_{46}N_3O_7$ $[M + H]^+$: 572.3331, found: 572.3323.



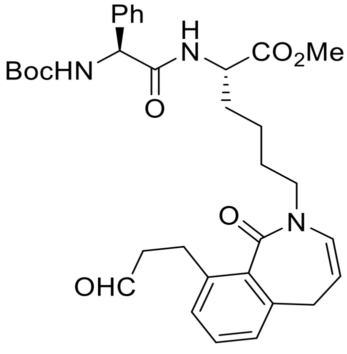
3s

Following general procedure, **1s** (0.1 mmol, 42.1 mg) and **2a** (0.3 mmol, 20 μL) were used to give product **3s**. 17.1 mg, 34%. Pale yellow liquid oil. R_f = 0.5 (EtOAc/*n*-hexane, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.24 (dd, *J* = 7.5, 2.4 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 1H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.85 – 6.72 (m, 1H), 5.90 (dd, *J* = 7.3, 2.5 Hz, 1H), 5.83 – 5.72 (m, 1H), 5.25 (s, 1H), 4.62 (s, 1H), 4.09 (s, 1H), 3.86 – 3.71 (m, 5H), 3.30 (s, 2H), 3.04 (d, *J* = 35.5 Hz, 4H), 2.74 (s, 1H), 1.94 (s, 1H), 1.80 (s, 3H), 1.47 (d, *J* = 2.4 Hz, 11H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2, 172.5, 169.3, 145.0, 141.7, 133.0, 130.0, 129.0, 128.7, 124.0, 121.4, 80.4, 52.4, 52.0, 47.2, 46.1, 44.2, 31.8, 31.5, 28.3, 27.9, 27.1, 22.3.

HRMS (ESI, m/z) calcd for $C_{27}H_{38}N_3O_7$ $[M + H]^+$: 516.2705, found: 516.2697.



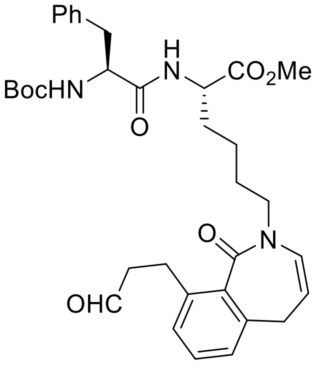
3t

Following general procedure, **1t** (0.1 mmol, 49.7 mg) and **2a** (0.3 mmol, 20 μL) were used to give product **3t**. 32.8 mg, 56%. Pale yellow liquid oil. $R_f = 0.5$ (EtOAc/*n*-hexane, 1:1). Mixture of rotamers (7:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.31 (d, *J* = 11.0 Hz, 5H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.14 (dd, *J* = 7.8, 1.3 Hz, 1H), 6.95 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.63 (d, *J* = 52.6 Hz, 1H), 5.88 (d, *J* = 7.4 Hz, 1H), 5.84 – 5.69 (m, 2H), 5.17 (d, *J* = 32.0 Hz, 1H), 4.54 (s, 1H), 4.13 (d, *J* = 7.0 Hz, 1H), [3.75 (s), 3.65 (s), 3H], 3.25 (d, *J* = 16.4 Hz, 2H), 3.04 (d, *J* = 55.5 Hz, 4H), 2.74 (d, *J* = 7.1 Hz, 1H), 1.94 (s, 1H), 1.75 – 1.54 (m, 3H), 1.51 – 1.34 (m, 11H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2, 172.0, 170.1, 169.7, 154.9, 145.0, 141.6, 133.0, 130.0, 129.0, 128.8, 128.6, 128.2, 127.2, 123.9, 121.5, 80.0, 58.2, 52.3, 47.0, 46.0, 31.5, 28.2, 27.9, 27.0, 22.0.

HRMS (ESI, m/z) calcd for $C_{33}H_{42}N_3O_7$ $[M + H]^+$: 592.3018, found: 592.3011.



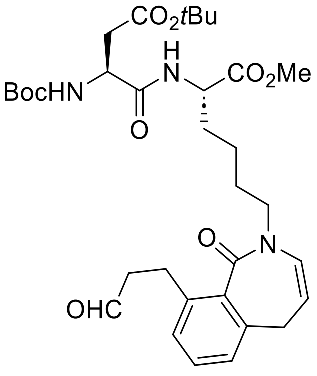
3u

Following general procedure, **1u** (0.1 mmol, 51.1 mg) and **2a** (0.3 mmol, 20 μL) were used to give product **3u**. 39.6 mg, 65%. Pale yellow liquid oil. $R_f = 0.6$ (EtOAc/*n*-hexane, 1:2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.27 (s, 1H), 7.25 (d, *J* = 3.4 Hz, 2H), 7.23 (d, *J* = 2.2 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 3H), 6.94 (d, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 7.6 Hz, 1H), 5.89 (d, *J* = 7.4 Hz, 1H), 5.77 (q, *J* = 7.2 Hz, 1H), 5.13 (d, *J* = 34.0 Hz, 1H), 4.60 – 4.51 (m, 1H), 4.37 (s, 1H), 4.10 (d, *J* = 27.8 Hz, 1H), 3.72 (s, 3H), 3.27 (s, 2H), 3.03 (d, *J* = 39.5 Hz, 6H), 2.72 (s, 1H), 1.94 – 1.84 (m, 1H), 1.70 (s, 3H), 1.44 – 1.34 (m, 11H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2, 172.1, 171.1, 169.4, 155.3, 145.0, 141.7, 136.6, 133.0, 130.0, 129.3, 129.1, 128.6, 128.5, 126.8, 123.9, 121.4, 80.1, 55.6, 52.3, 52.1, 47.4, 46.0, 38.3, 31.8, 31.5, 28.2, 28.0, 27.0, 22.2.

HRMS (ESI, m/z) calcd for $C_{34}H_{44}N_3O_7$ $[M + H]^+$: 606.3174, found: 606.3172.



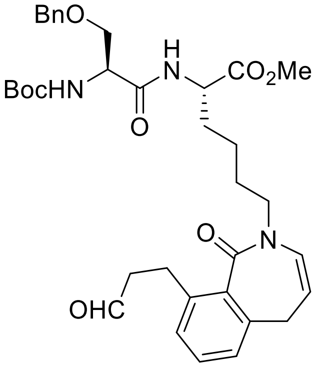
3v

Following general procedure, **1v** (0.1 mmol, 60.6 mg) and **2a** (0.3 mmol, 20 μL) were used to give product **3v**. 41.5 mg, 59%. Pale yellow liquid oil. R_f = 0.6 (EtOAc/*n*-hexane, 1:2).

^{1}H NMR (400 MHz, CDCl$_3$) δ 9.81 (s, 1H), 7.24 (t, *J* = 7.9 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 2H), 6.94 (d, *J* = 7.6 Hz, 1H), 5.90 (d, *J* = 7.3 Hz, 1H), 5.77 (t, *J* = 7.6 Hz, 2H), 4.60 – 4.47 (m, 2H), 4.15 – 4.00 (m, 1H), 3.74 (s, 3H), 3.28 (q, *J* = 19.2, 16.2 Hz, 2H), 3.12 – 2.84 (m, 5H), 2.72 (q, *J* = 12.6 Hz, 1H), 2.61 (dd, *J* = 17.3, 6.2 Hz, 1H), 1.99 – 1.83 (m, 2H), 1.80 – 1.61 (m, 4H), 1.48 – 1.44 (m, 18H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 202.1, 172.3, 171.3, 170.8, 169.2, 155.5, 145.0, 141.8, 133.1, 130.0, 129.2, 128.7, 123.9, 121.2, 81.7, 80.3, 52.4, 52.2, 50.6, 47.7, 46.2, 37.4, 31.9, 31.5, 28.3, 28.0, 27.2, 22.7, 22.5.

HRMS (ESI, m/z) calcd for $C_{33}H_{48}N_3O_9$ $[M + H]^+$: 630.3385, found: 630.3378.



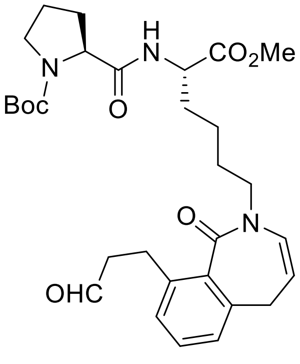
3w

Following general procedure, **1w** (0.1 mmol, 54.2 mg) and **2a** (0.3 mmol, 20 μL) were used to give product **3w**. 36.0 mg, 57%. Pale yellow liquid oil. R_f = 0.6 (EtOAc/*n*-hexane, 1:2).

^{1}H NMR (400 MHz, CDCl$_3$) δ 9.79 (s, 1H), 7.33 (d, *J* = 8.6 Hz, 5H), 7.27 – 7.21 (m, 1H), 7.13 (d, *J* = 7.7 Hz, 2H), 6.94 (d, *J* = 7.5 Hz, 1H), 5.85 (d, *J* = 7.5 Hz, 1H), 5.80 – 5.70 (m, 1H), 5.47 (s, 1H), 4.61 (d, *J* = 7.9 Hz, 1H), 4.57 (s, 2H), 4.32 (s, 1H), 4.04 (s, 1H), 3.92 (s, 1H), 3.74 (s, 3H), 3.62 – 3.56 (m, 1H), 3.23 (d, *J* = 30.9 Hz, 2H), 3.01 (t, *J* = 23.2 Hz, 4H), 2.71 (s, 1H), 1.92 (s, 1H), 1.67 (s, 3H), 1.47 (d, *J* = 2.7 Hz, 9H), 1.38 (d, *J* = 7.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.1, 172.3, 170.2, 169.2, 145.0, 141.7, 137.4, 133.0, 129.9, 129.2, 128.7, 128.4, 127.9, 127.7, 123.9, 121.2, 80.2, 73.4, 69.9, 53.8, 52.3, 52.2, 47.5, 46.1, 32.0, 31.4, 28.2, 28.0, 27.1, 22.4.

HRMS (ESI, m/z) calcd for $C_{35}H_{46}N_3O_8$ $[M + H]^+$: 636.3280, found: 636.3278.



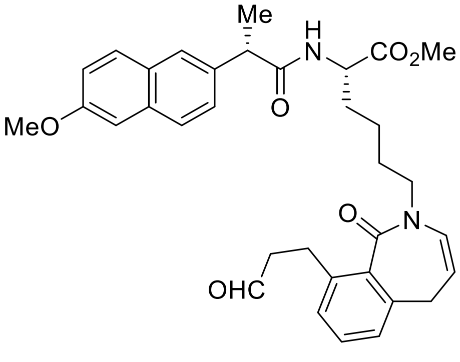
3x

Following general procedure, **1x** (0.1 mmol, 46.1 mg) and **2a** (0.3 mmol, 20 μL) were used to give product **3x**. 42.0 mg, 76%. Pale yellow liquid oil. R_f = 0.5 (EtOAc/*n*-hexane, 1:2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.24 (t, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 7.7 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 5.89 (d, *J* = 7.4 Hz, 1H), 5.76 (q, *J* = 7.4 Hz, 1H), 4.57 (s, 1H), 4.30 (s, 1H), 4.07 (s, 1H), 3.74 (s, 3H), 3.53 – 3.39 (m, 2H), 3.30 (d, *J* = 17.5 Hz, 2H), 3.14 – 2.89 (m, 4H), 2.72 (s, 1H), 2.09 (m, 1H), 1.99 – 1.87 (m, 3H), 1.80 – 1.57 (m, 4H), 1.47 (s, 11H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 167.2, 163.9, 139.7, 136.4, 127.8, 124.7, 123.9, 123.4, 118.6, 115.9, 75.1, 55.7, 47.0, 46.7, 42.3, 41.8, 40.8, 32.7, 26.8, 26.2, 23.0, 22.8, 21.8, 17.3, 16.3.

HRMS (ESI, m/z) calcd for $C_{30}H_{42}N_3O_7$ $[M + H]^+$: 556.3018, found: 556.3012.



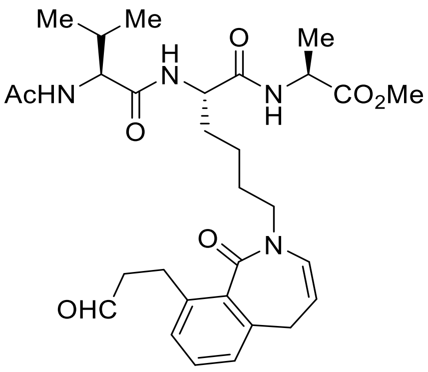
3y

Following general procedure, **1y** (0.1 mmol, 47.6 mg) and **2a** (0.3 mmol, 20 μL) were used to give product **3y**. 42.8 mg, 75%. Pale yellow liquid oil. R_f = 0.5 (EtOAc/*n*-hexane, 1:2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (s, 1H), 7.69 (dd, *J* = 20.3, 10.7 Hz, 3H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.15 (d, *J* = 15.9 Hz, 3H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.29 – 6.06 (m, 1H), 5.86 (d, *J* = 7.5 Hz, 1H), 5.76 (d, *J* = 7.6 Hz, 1H), 4.56 (s, 1H), 4.10 (d, *J* = 40.0 Hz, 1H), 3.93 (s, 3H), 3.75 (d, *J* = 10.7 Hz, 1H), 3.64 (s, 3H), 3.25 (d, *J* = 15.2 Hz, 2H), 3.10 (d, *J* = 10.9 Hz, 1H), 3.05 – 2.86 (m, 3H), 2.70 (s, 1H), 1.88 (s, 1H), 1.73 – 1.57 (m, 4H), 1.52 (d, *J* = 6.6 Hz, 1H), 1.40 – 1.24 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 174.2, 172.6, 169.4, 157.6, 145.0, 141.7, 136.1, 133.7, 133.1, 130.0, 129.2, 129.0, 128.9, 128.7, 127.3, 126.2, 126.1, 123.9, 121.5, 119.0, 105.6, 55.3, 52.2, 47.4, 46.7, 46.0, 31.4, 29.3, 27.9, 27.1, 22.4, 18.5.

HRMS (ESI, m/z) calcd for $C_{34}H_{39}N_2O_6$ $[M + H]^+$: 571.2803, found: 571.2795.



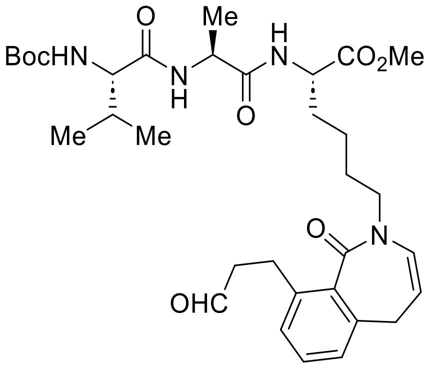
3z

Following general procedure, **1z** (0.1 mmol, 47.6 mg) and **2a** (0.3 mmol, 20 μL) were used to give product **3z**. 26.2 mg, 46%. Pale yellow solid. R_f = 0.5 (MeOH/Dichloromethane, 1:15).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.78 (s, 1H), 7.41 – 7.29 (m, 2H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 6.94 (dd, *J* = 7.7, 3.9 Hz, 1H), 6.84 – 6.67 (m, 1H), 5.89 (d, *J* = 7.3 Hz, 1H), 5.76 (q, *J* = 7.3 Hz, 1H), 4.62 – 4.33 (m, 3H), 4.11 (s, 1H), 3.72 (s, 3H), 3.29 (s, 2H), 3.14 (d, *J* = 12.8 Hz, 1H), 3.02 – 2.89 (m, 3H), 2.70 (d, *J* = 16.8 Hz, 1H), 2.10 (s, 1H), 2.04 – 1.98 (m, 4H), 1.96 – 1.90 (m, 1H), 1.88 – 1.79 (m, 1H), 1.68 - 1.60 (m, 1H), 1.48 – 1.42 (m, 2H), 1.38 (d, *J* = 7.1 Hz, 3H), 0.90 – 0.83 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.3, 173.1, 171.6, 171.2, 170.3, 145.1, 141.4, 133.0, 129.9, 129.0, 128.5, 124.0, 121.6, 58.1, 52.7, 52.3, 48.1, 47.2, 45.9, 31.9, 31.5, 27.9, 27.0, 23.0, 22.2, 19.0, 18.2, 17.8.

HRMS (ESI, m/z) calcd for $C_{30}H_{43}N_4O_7$ $[M + H]^+$: 571.3126, found: 571.3117



3aa

Following general procedure, **1aa** (0.1 mmol, 53.4 mg) and **2a** (0.3 mmol, 20 μL) were used to give product **3aa**. 38.4 mg, 61%. Pale yellow liquid oil. R_f = 0.5 (EtOAc/*n*-hexane, 4:1).

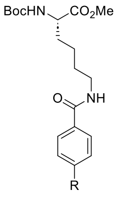
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.09 – 6.97 (m, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 6.81 (d, *J* = 7.3 Hz, 1H), 5.89 (d, *J* = 7.2 Hz, 1H), 5.78 (q, *J* = 7.4 Hz, 1H), 5.18 (d, *J* = 8.5 Hz, 1H), 4.58 – 4.42 (m, 2H), 4.11 (d, *J* = 19.1 Hz, 1H), 3.95 (s, 1H), 3.74 (s, 3H), 3.29 (d, *J* = 14.4 Hz, 2H), 3.13 – 2.89 (m, 4H), 2.73 (t, *J* = 11.6 Hz, 1H), 2.14 (s, 1H), 2.09 – 1.98 (m, 1H), 1.91 (s, 1H), 1.73 –1.59 (m, 2H), 1.49 – 1.40 (m, 11H), 1.34 (d, *J* = 7.0 Hz, 3H), 0.96 (d, *J* = 6.3 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2, 172.4, 172.0, 171.4, 169.6, 155.9, 145.0, 141.7, 133.0, 130.0, 129.1, 128.7, 124.0, 121.6, 79.9, 59.8, 52.4, 52.2, 48.7, 47.3, 46.1, 31.5, 31.4, 30.9, 28.3, 28.0, 27.1, 22.7, 19.3, 18.2, 17.6.

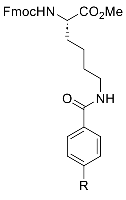
HRMS (ESI, m/z) calcd for $C_{33}H_{49}N_4O_8$ $[M + H]^+$: 629.3545, found: 629.3548

3、Substrate Preparation

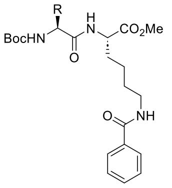
Peptides and amino acids **1a**, **1b**, **1d**, **1h** and **1p**, **1u**, **1v-1aa** were all prepared according to the previous reports[1-2]. **2a-2c**, **2g** and **2h** were commercially available aldehydes. The Aldehyde compounds **2d**,[3] **2e**[4] and **2f**[5] were prepared using reported methods.



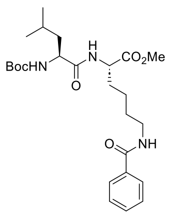
R = H, **1a**
R = Me, **1b**
R = OMe, **1d**
R = tBu, **1e**
R = Cl, **1g**
R = Br, **1h**



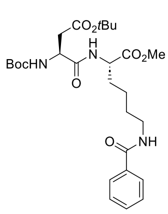
R = Et, **1c**
R = F, **1f**



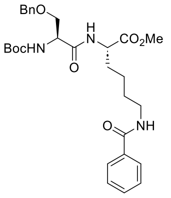
R = Me, **1p**
R = iPr, **1q**
R = H, **1s**
R = Ph, **1t**
R = Bn, **1u**



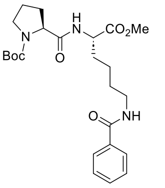
1r



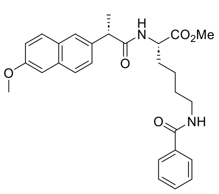
1v



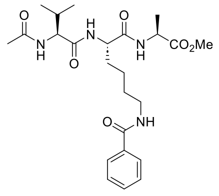
1w



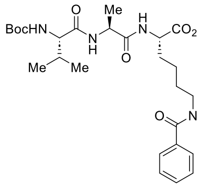
1x



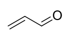
1y



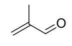
1z



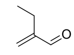
1aa



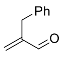
2a



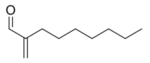
2b



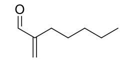
2c



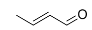
2d



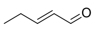
2e



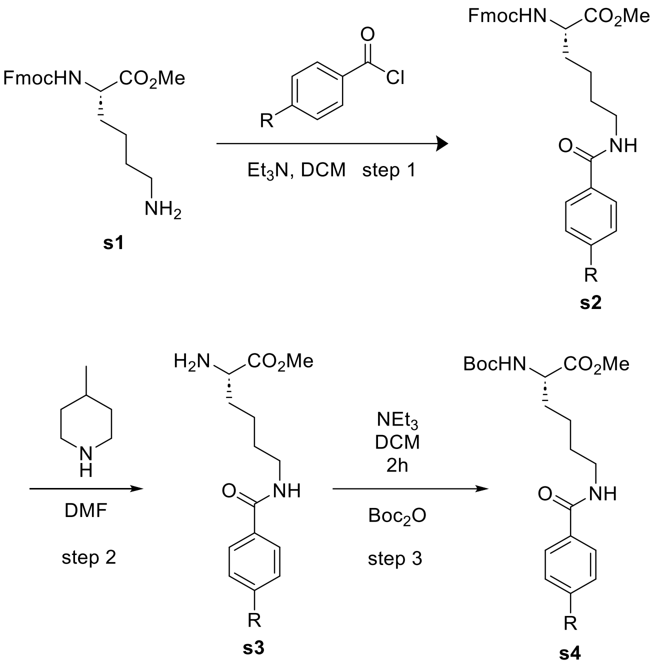
2f



2g



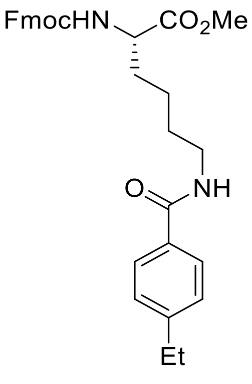
2h



Step 1: The **s1** was prepared using reported method.[6] The **s1** (1.5 mmol, 573.3 mg) was dissolved in DCM (3 mL) in a flask equipped with a magnetic stirring bar. Et_3N (3 mmol, 0.42 mL) was added to the solution and the mixture was cooled to 0 °C. Acid chloride (1.5 mmol, 1 equiv.) was added dropwise at 0 °C and the mixture was stirred at r.t for 2 h. The solvent was removed under reduced pressure and the reaction crude was purified by a silica gel column chromatography (EtOAc/*n*-hexane) to afford the products **s2**

Step 2: The **s2** (0.5 mmol, 1 equiv.) was dissolved in DMF (1 mL) in a flask equipped with a magnetic stirring bar. 4-Methylpiperidine (0.25 mL) was added to the solution and the mixture was stirred at r.t for 2 h. Then the mixture was concentrated in vacuo to remove the DMF and extracted with EA, the solvent was removed under reduced pressure and the resulted mixture was purified by a silica gel column chromatography (MeOH/Dichloromethane, 1:15) to yield the product **s3**.

Step 3: The **s3** (0.5 mmol) was dissolved in DCM (1 mL) in a flask equipped with a magnetic stirring bar. Et_3N (1 mmol, 208 μL) and $(Boc)_2O$ (1.5 mmol, 230 μL) were added to the solution and the mixture was stirred at r.t for 2 h. The solvent was removed under reduced pressure and the reaction crude was purified by a silica gel column chromatography (EtOAc/*n*-hexane) to afford the products **s4**.



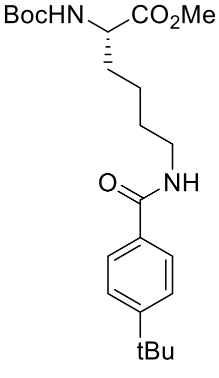
1c

Following step 1, **1c** was obtained as white solid. 163.3 mg, 21%. $R_f = 0.4$ (EtOAc/*n*-hexane, 1:1).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.78 (d, *J* = 7.6 Hz, 2H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 6.27 (s, 1H), 5.53 (d, *J* = 8.2 Hz, 1H), 4.42 (d, *J* = 8.3 Hz, 2H), 4.36 (t, *J* = 9.3 Hz, 1H), 4.23 (t, *J* = 7.2 Hz, 1H), 3.77 (s, 3H), 3.48 (q, *J* = 6.8 Hz, 2H), 2.66 (q, *J* = 7.8 Hz, 2H), 1.93 (d, *J* = 9.6 Hz, 1H), 1.79 (t, *J* = 7.2 Hz, 1H), 1.69 (s, 2H), 1.54 – 1.41 (m, 2H), 1.23 (t, *J* = 7.7 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 173.0, 167.7, 156.2, 148.1, 143.9, 143.7, 141.3, 131.9, 128.0, 127.7, 127.1, 127.0, 125.1, 120.0, 67.1, 53.6, 52.5, 47.2, 39.4, 32.3, 29.0, 28.7, 22.5, 15.3.

HRMS (ESI, m/z) calcd for $C_{31}H_{35}N_2O_5$ $[M + H]^+$: 515.2541, found: 515.2536



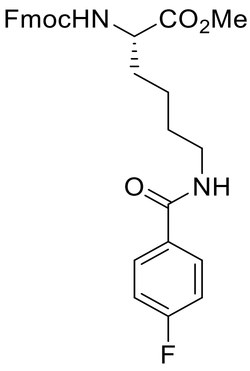
1e

Following steps 1-3, **1e** was obtained as white solid. 187.1 mg, 89% (from step 3). R_f = 0.4 (EtOAc/*n*-hexane, 1:1).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.76 – 7.68 (m, 2H), 7.45 – 7.39 (m, 2H), 6.45 (t, *J* = 5.9 Hz, 1H), 5.20 (d, *J* = 8.3 Hz, 1H), 4.36 – 4.20 (m, 1H), 3.72 (s, 3H), 3.48 – 3.39 (m, 2H), 1.89 – 1.77 (m, 1H), 1.73 – 1.57 (m, 3H), 1.48 – 1.37 (m, 11H), 1.32 (s, 9H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 173.2, 167.6, 155.5, 154.7, 131.7, 126.7, 125.3, 79.8, 53.1, 52.2, 39.4, 34.8, 32.2, 31.1, 29.0, 28.2, 22.5.

HRMS (ESI, m/z) calcd for $C_{23}H_{37}N_2O_5$ $[M + H]^+$: 421.2697, found: 421.2693.



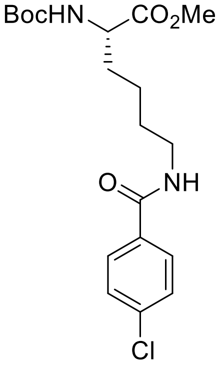
1f

Following step 1, **1f** was obtained as white solid. 205.6 mg, 27%. R_f = 0.4 (EtOAc/*n*-hexane, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 6.9 Hz, 4H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.03 (t, *J* = 8.5 Hz, 2H), 6.41 (s, 1H), 5.57 (d, *J* = 8.2 Hz, 1H), 4.41 (t, *J* = 8.5 Hz, 2H), 4.34 (t, *J* = 9.0 Hz, 1H), 4.22 (t, *J* = 7.2 Hz, 1H), 3.77 (s, 3H), 3.46 (q, *J* = 6.7 Hz, 2H), 1.96 – 1.86 (m, 1H), 1.76 (q, *J* = 7.8, 7.3 Hz, 1H), 1.68 (q, *J* = 7.8 Hz, 2H), 1.53 – 1.42 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 166.7, 164.6 (d, *J* = 251.6 Hz), 156.2, 143.7 (d, *J* = 15.9 Hz), 141.3, 130.7, 130.7, 129.3 (d, *J* = 8.9 Hz), 127.8, 127.1, 125.1, 125.1, 120.0, 115.5 (d, *J* = 21.8 Hz), 67.1, 53.5, 52.5, 47.1, 39.6, 32.4, 28.8, 22.5.

HRMS (ESI, m/z) calcd for $C_{29}H_{30}FN_2O_5$ $[M + H]^+$: 505.2134, found: 505.2126



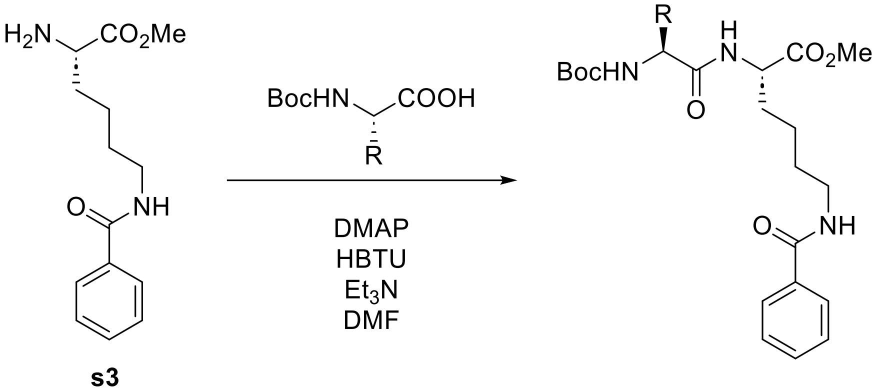
1g

Following steps 1-3, **1g** was obtained as white solid. 141.3 mg, 71% (from step 3). R_f = 0.5 (EtOAc/*n*-hexane, 1:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 6.53 (s, 1H), 5.19 (d, *J* = 8.3 Hz, 1H), 4.28 (d, *J* = 6.6 Hz, 1H), 3.73 (s, 3H), 3.43 (q, *J* = 6.6 Hz, 2H), 1.88 – 1.75 (m, 1H), 1.71 – 1.57 (m, 3H), 1.52 – 1.38 (m, 11H).

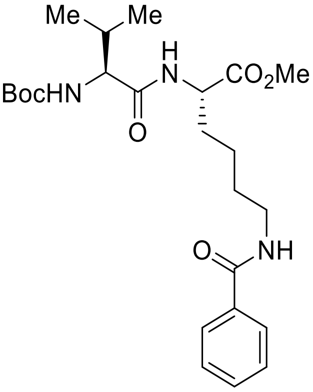
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 166.6, 155.5, 137.5, 133.0, 128.7, 128.4, 79.9, 53.1, 52.3, 39.6, 32.4, 28.8, 28.2, 22.6.

HRMS (ESI, m/z) calcd for $C_{19}H_{28}ClN_2O_5$ $[M + H]^+$: 399.1681, found: 399.1678.



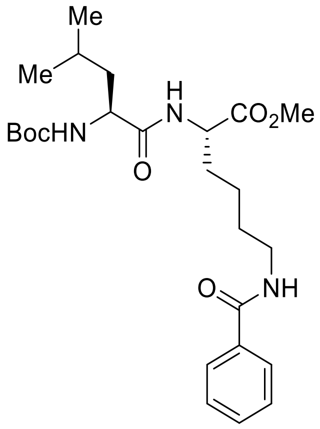
s3

The obtained **s3** (1 mmol, 264.1 mg) from above procedure was dissolved in DMF (2.0 mL) in a flask equipped with a magnetic stirring bar. The carboxylic acid (1.1 mmol, 1.1 equiv.) and NEt_3 (2 mmol, 278µL) were added and the mixture was cooled to 0 °C. Then HBTU (1.1 mmol, 417.2 mg) was added portion-wise and the mixture was stirred at room temperature. Then DMAP (0.1 mmol, 12.2 mg) was added and the reaction was stirred for 12 h. The reaction mixture was poured over 5% aqueous HCl (40 mL) under vigorous stirring. Extractions with ethyl acetate (10 mL × 3) followed. The organic layers were combined, washed with saturated aqueous $NaHCO_3$ (10 mL × 3), brine (10 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the reaction crude was purified by a silica gel column chromatography (EtOAc/*n*-hexane) to afford the products **1q-1t**.



1q

1q was obtained as white solid. 361.4 mg, 78%. $R_f = 0.5$ (EtOAc/*n*-hexane, 1:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.5 Hz, 2H), 7.50 – 7.44 (m, 1H), 7.40 (dd, *J* = 8.3, 6.6 Hz, 2H), 7.03 (d, *J* = 7.1 Hz, 2H), 5.09 (d, *J* = 9.0 Hz, 1H), 4.55 – 4.44 (m, 1H), 4.07 – 3.94 (m, 1H), 3.70 (s, 3H), 3.53 – 3.42 (m, 1H), 3.40 – 3.25 (m, 1H), 2.14 – 2.00 (m, 1H), 1.90 – 1.79 (m, 1H), 1.78 – 1.67 (m, 1H), 1.67 – 1.53 (m, 2H), 1.48 – 1.32 (m, 11H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.85 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 172.1, 167.8, 155.9, 134.5, 131.2, 128.3, 127.1, 79.8, 59.6, 52.2, 52.1, 39.3, 31.5, 30.8, 28.8, 28.2, 22.7, 19.1, 17.4.
HRMS (ESI, m/z) calcd for $C_{24}H_{38}N_3O_6$ $[M + H]^+$: 464.2755, found: 464.2760.



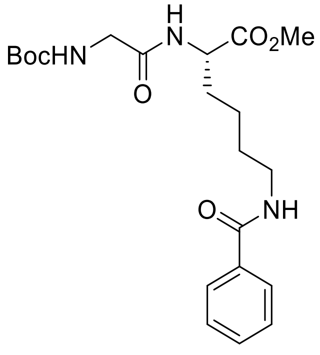
1r

1r was obtained as white solid. 439.1 mg, 92%. $R_f = 0.5$ (EtOAc/*n*-hexane, 1:1).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85 (d, *J* = 7.6 Hz, 2H), 7.52 – 7.46 (m, 1H), 7.42 (dd, *J* = 8.2, 6.6 Hz, 2H), 7.01 – 6.79 (m, 2H), 4.87 (d, *J* = 8.3 Hz, 1H), 4.62 – 4.50 (m, 1H), 4.15 (s, 1H), 3.73 (s, 3H), 3.55 – 3.45 (m, 1H), 3.44 – 3.32 (m, 1H), 2.12 - 1.96 (m, 1H), 1.92 – 1.81 (m, 1H), 1.76 – 1.57 (m, 5H), 1.44 – 1.37 (m, 11H), 0.89 (d, *J* = 6.2 Hz, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 173.0, 172.5, 167.8, 155.7, 134.6, 131.3, 128.4, 127.1, 80.0, 53.0, 52.3, 51.8, 41.0, 39.4, 31.9, 28.6, 28.2, 24.6, 22.9, 22.5, 21.7.

HRMS (ESI, m/z) calcd for $C_{25}H_{40}N_3O_6$ $[M + H]^+$: 478.2912, found: 478.2908.



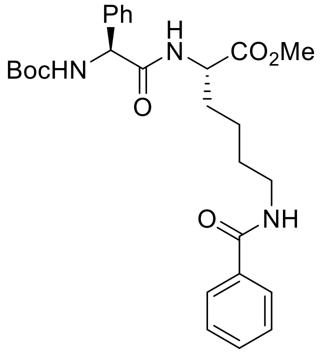
1s

1s was obtained as white solid. 328.6 mg, 78%. $R_f = 0.5$ (EtOAc/*n*-hexane, 1:1).

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.75 – 7.68 (m, 2H), 7.41 – 7.35 (m, 1H), 7.32 (t, *J* = 7.5 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.74 (t, *J* = 5.9 Hz, 1H), 5.41 (s, 1H), 4.61 – 4.34 (m, 1H), 3.70 (d, *J* = 4.9 Hz, 2H), 3.62 (s, 3H), 3.37 – 3.27 (m, 2H), 1.85 – 1.74 (m, 1H), 1.67 – 1.58 (m, 1H), 1.58 – 1.47 (m, 2H), 1.38 – 1.29 (m, 11H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 172.5, 169.7, 167.8, 156.1, 134.4, 131.2, 128.3, 126.9, 80.0, 52.3, 51.7, 44.0, 39.3, 31.6, 28.7, 28.1, 22.3.

HRMS (ESI, m/z) calcd for $C_{21}H_{32}N_3O_6$ $[M + H]^+$: 422.2286, found: 422.2281.



1t

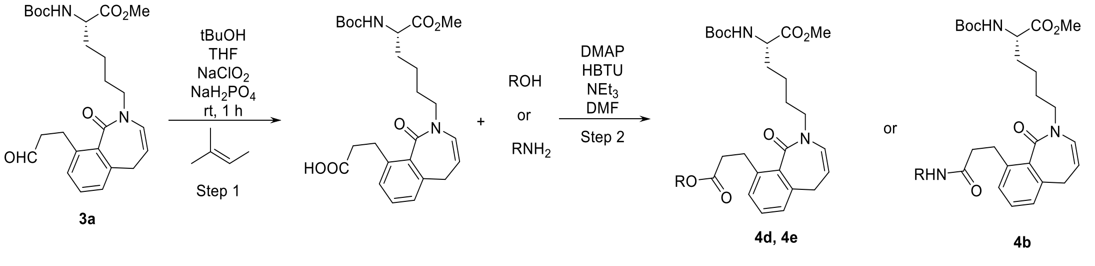
1t was obtained as white solid. 397.8 mg, 80%. *R*$_f$ = 0.5 (EtOAc/*n*-hexane, 1:1). Mixture of rotamers (4:1)

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 10.5, 7.5 Hz, 2H), 7.49 – 7.43 (m, 1H), 7.38 (q, *J* = 7.9, 7.3 Hz, 4H), 7.30 (d, *J* = 8.8 Hz, 1H), 7.26 (d, *J* = 14.1 Hz, 2H), 7.11 – 6.97 (m, 1H), 5.79 (dd, *J* = 11.0, 6.7 Hz, 1H), 5.36 – 5.17 (m, 1H), 4.59 – 4.42 (m, 1H), [3.68 (s), 3.59 (s), 3H], 3.47 – 3.19 (m, 2H), 1.89 – 1.76 (m, 1H), 1.75 – 1.64 (m, 1H), 1.63 – 1.49 (m, 2H), 1.45 – 1.28 (m, 11H).

^{13}**C NMR** (151 MHz, $CDCl_3$) δ 172.4, 172.1, 170.5, 167.8, 167.7, 155.1, 134.5, 131.3, 128.7, 128.4, 128.2, 127.2, 127.0, 126.9, 80.0, 58.4, 52.4, 52.3, 52.2, 51.8, 39.2, 31.5, 28.8, 28.2, 22.5, 22.1.

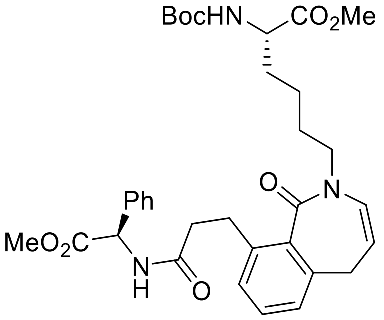
HRMS (ESI, m/z) calcd for $C_{27}H_{36}N_3O_6$ $[M + H]^+$: 498.2599, found: 498.2592.

4、Application Expansion



Step 1: **3a** (45.8 mg, 0.1 mmol), *tert*-butyl alcohol (1.2 mL), 2-methyl-2-butene (0.24 mmol, 0.25 mL), and THF (1.2 mL) were added to a round-bottom flask. $NaClO_2$ (0.13 mmol, 11.5 mg) and NaH_2PO_4 (0.26 mmol, 31.2 mg) dissolved in water were gradually added over a period of 10 min and the resulting mixture was stirred for 1 h at room temperature. After the removal of *tert*-butyl alcohol, 2-methyl-2-butene, and THF under reduced pressure, 2 M HCl was added to the reaction mixture to acidify it (pH = 2). The solution was then extracted with ethyl acetate. The organic phase was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude carboxylic acid did not require further purification and was used directly for the next step.

Step 2: The obtained carboxylic acid (0.1 mmol, 1 equiv.) was dissolved in DMF (0.2 mL) in a flask equipped with a magnetic stirring bar. The alcohol or amine (0.11 mmol, 1.1 equiv.) and NEt_3 (0.2 mmol, 28μL) were added and the mixture was cooled to 0 °C. Then HBTU (0.11 mmol, 41.7 mg) was added portion-wise and the mixture was stirred at room temperature. Then DMAP (0.01 mmol, 1.2 mg) was added and the reaction was stirred for 12 h. The reaction mixture was poured over 5% aqueous HCl (4 mL) under vigorous stirring. Extractions with ethyl acetate (1 mL × 3) followed. The organic layers were combined, washed with saturated aqueous $NaHCO_3$ (1 mL × 3), brine (1 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the reaction crude was purified by a silica gel column chromatography (EtOAc/*n*-hexane) to afford the products **4b**, **4d** and **4e**.



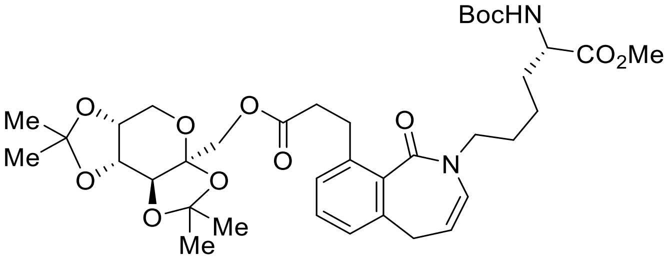
4b

4b was obtained as pale yellow liquid oil. 40.6 mg, 65%. R_f = 0.6 (EtOAc/*n*-hexane, 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 5H), 7.20 (s, 1H), 7.12 (s, 1H), 6.93 (d, *J* = 7.4 Hz, 1H), 5.88 (d, *J* = 7.4 Hz, 1H), 5.75 (q, *J* = 7.2 Hz, 1H), 5.58 (d, *J* = 7.6 Hz, 1H), 5.17 (d, *J* = 8.2 Hz, 1H), 4.29 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 1H), 3.72 (s, 6H), 3.28 (s, 2H), 3.14 – 2.86 (m, 3H), 2.81 (s, 2H), 2.56 (s, 1H), 2.06 (s, 1H), 1.76 – 1.61 (m, 3H), 1.47 – 1.37 (m, 11H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 172.5, 171.4, 169.6, 155.4, 144.9, 142.0, 136.6, 132.5, 130.1, 129.0, 128.8, 128.3, 127.3, 123.9, 121.4, 79.8, 56.4, 53.3, 52.6, 52.2, 47.5, 38.6, 32.1, 31.5, 31.0, 28.3, 28.1, 22.6.

HRMS (ESI, m/z) calcd for $C_{34}H_{44}N_3O_8$ $[M + H]^+$: 622.3123, found: 622.3115.



4d

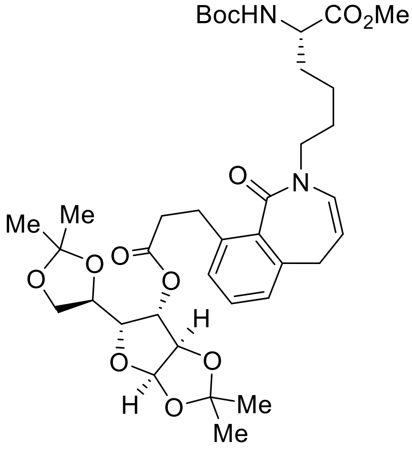
4d was obtained as pale yellow liquid oil. 37.9 mg, 53%. R_f = 0.6 (EtOAc/*n*-hexane, 1:1). Mixture of rotamers (7:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 1H), 6.96 – 6.90 (m, 1H), 5.89 (d, *J* = 7.4 Hz, 1H), 5.75 (q, *J* = 7.2 Hz, 1H), 5.13 (s, 1H), 4.61 (dd, *J* = 7.9, 2.6 Hz, 1H), 4.41 (d, *J* = 11.7 Hz, 1H), 4.31 (d, *J* = 2.7 Hz, 2H), 4.25 (dd, *J* = 7.9, 1.7 Hz, 1H), 4.13 (s, 1H), 4.03 (d, *J* = 11.7 Hz, 1H), 3.92 (dd, *J* = 13.0, 1.9 Hz, 1H), [3.79 (s), 3.71 (s), 4H], 3.31 (d, *J* = 17.1 Hz, 2H), 3.12 (q, *J* = 7.2 Hz, 1H), 2.94

(d, J = 26.2 Hz, 3H), 2.72 – 2.56 (m, 1H), 1.87 (s, 1H), 1.77 – 1.65 (m, 3H), 1.54 (s, 3H), 1.49 (s, 3H), 1.47 – 1.39 (m, 11H), 1.37 (d, J = 11.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 172.5, 155.3, 144.9, 141.7, 133.2, 129.9, 128.7, 123.9, 121.2, 109.1, 108.8, 101.6, 79.8, 70.8, 70.3, 70.1, 64.9, 61.2, 53.3, 52.3, 36.1, 31.5, 29.6, 28.3, 26.5, 25.9, 25.3, 24.1.

HRMS (ESI, m/z) calcd for $C_{37}H_{53}N_2O_{12}$ $[M + H]^+$:717.3593, found:717.3587.



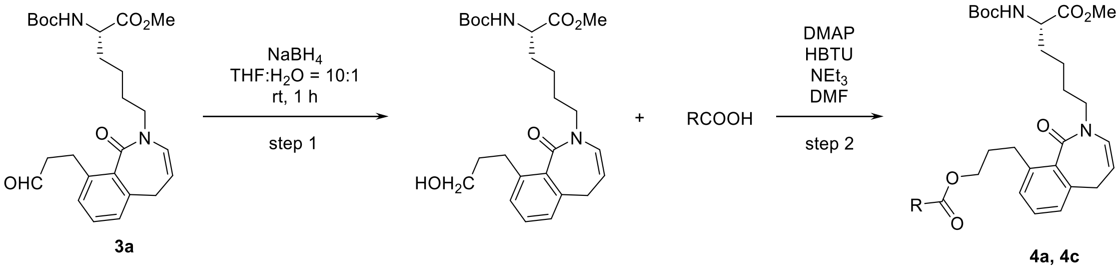
4e

4e was obtained as pale yellow liquid oil. 55.3 mg, 77%. R_f = 0.5 (EtOAc/*n*-hexane, 1:2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, J = 7.6 Hz, 1H), 7.14 (d, J = 7.8 Hz, 1H), 6.93 (d, J = 7.4 Hz, 1H), 5.93 (d, J = 3.6 Hz, 1H), 5.89 (d, J = 7.4 Hz, 1H), 5.75 (q, J = 7.1 Hz, 2H), 5.21 – 5.13 (m, 1H), 4.53 (d, J = 3.6 Hz, 1H), 4.37 – 4.31 (m, 2H), 4.21 (dd, J = 7.4, 2.9 Hz, 1H), 4.17 – 4.13 (m, 1H), 4.07 (dd, J = 7.6, 2.8 Hz, 1H), 4.02 – 3.96 (m, 2H), 3.73 (s, 3H), 3.28 (s, 2H), 3.14 (s, 1H), 2.96 (s, 2H), 2.81 (d, J = 4.9 Hz, 1H), 2.63 (s, 1H), 1.88 (d, J = 18.5 Hz, 2H), 1.75 – 1.64 (m, 3H), 1.50 (s, 2H), 1.44 – 1.40 (m, 12H), 1.36 (s, 2H), 1.31 (d, J = 3.6 Hz, 3H), 1.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 171.9, 169.2, 155.4, 145.0, 141.3, 133.1, 129.8, 129.2, 128.7, 124.0, 121.1, 112.1, 109.2, 105.0, 83.2, 79.7, 76.0, 72.4, 67.0, 53.3, 52.2, 47.7, 36.0, 32.3, 31.5, 28.3, 28.1, 26.73, 26.66, 26.2, 25.2, 22.6.

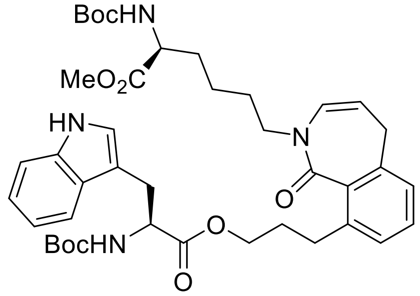
HRMS (ESI, m/z) calcd for $C_{37}H_{53}N_2O_{12}$ $[M + H]^+$:717.3593, found:717.3590.



Step 1: **3a** (0.1 mmol, 45.8 mg), THF (0.3 mL) and H_2O (0.03 mL) were added to a round-bottom flask. The solution and the mixture were cooled to 0 °C. Sodium borohydride (0.15 mmol, 5.7mg) was added slowly at 0 °C and the mixture was stirred at r.t for 1 h. The solution was then extracted with dichloromethane. The organic phase

was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude alcohol did not require further purification and was used directly for the next step.

Step 2: The obtained alcohol (0.1 mmol, 1 equiv.) was dissolved in DMF (0.2 mL) in a flask equipped with a magnetic stirring bar. The carboxylic acid (0.11 mmol, 1.1 equiv.) and NEt_3 (0.2 mmol, 28μL) were added and the mixture was cooled to 0 °C. Then HBTU (0.11 mmol, 41.7 mg) was added portion-wise and the mixture was stirred at room temperature. Then DMAP (0.01 mmol, 1.2 mg) was added and the reaction was stirred for 12 h. The reaction mixture was poured over 5% aqueous HCl (4 mL) under vigorous stirring. Extractions with ethyl acetate (1 mL × 3) followed. The organic layers were combined, washed with saturated aqueous $NaHCO_3$ (1 mL × 3), brine (1 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the reaction crude was purified by a silica gel column chromatography (EtOAc/*n*-hexane) to afford the products **4a** and **4c**.



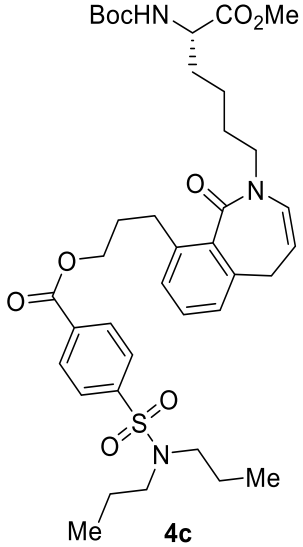
4a

4a was obtained as pale yellow liquid oil. 35.3 mg, 47%. R_f = 0.4 (EtOAc/*n*-hexane, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 25.6 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.24 – 7.15 (m, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.03 (t, *J* = 6.9 Hz, 2H), 6.92 (d, *J* = 7.4 Hz, 1H), 5.87 (d, *J* = 7.4 Hz, 1H), 5.76 (q, *J* = 7.2 Hz, 1H), 5.29 – 5.05 (m, 2H), 4.65 (q, *J* = 6.3 Hz, 1H), 4.29 (s, 1H), 4.11 (d, *J* = 17.3 Hz, 3H), 3.73 (s, 3H), 3.37 – 3.13 (m, 4H), 3.03 – 2.82 (m, 2H), 2.61 (s, 1H), 2.00 (s, 1H), 1.83 (s, 2H), 1.75 – 1.61 (m, 3H), 1.52 – 1.35 (m, 20H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 172.3, 169.4, 155.5, 155.2, 144.9, 142.3, 136.1, 132.9, 129.7, 129.1, 128.6, 127.8, 123.6, 122.9, 122.0, 121.4, 119.4, 118.7, 111.2, 110.1, 79.8, 79.6, 65.1, 54.3, 53.3, 52.2, 47.6, 47.1, 32.3, 31.9, 31.5, 30.5, 30.2, 28.3, 28.1, 22.6.

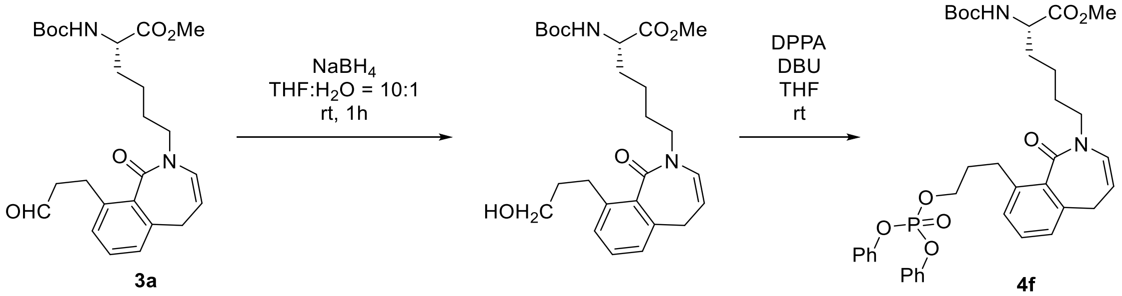
HRMS (ESI, m/z) calcd for $C_{41}H_{55}N_4O_9$ $[M + H]^+$: 747.3964, found: 747.3957.



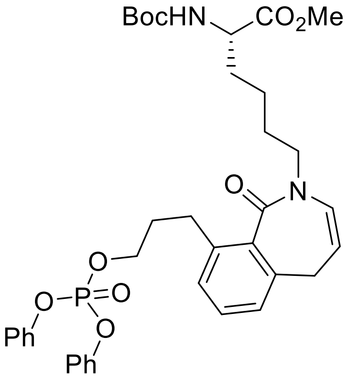
4c

4c was obtained as pale yellow liquid oil. 30.8 mg, 42%. R_f = 0.5 (EtOAc/*n*-hexane, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 8.7, 2.6 Hz, 2H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 6.92 (d, *J* = 7.4 Hz, 1H), 5.87 (d, *J* = 7.3 Hz, 1H), 5.73 (q, *J* = 7.2 Hz, 1H), 5.15 (s, 1H), 4.41 – 4.24 (m, 3H), 4.12 (d, *J* = 10.0 Hz, 1H), 3.74 (s, 3H), 3.35 – 3.19 (m, 2H), 3.14 – 3.01 (m, 5H), 2.99 (d, *J* = 9.2 Hz, 1H), 2.79 (d, *J* = 7.7 Hz, 1H), 2.21 (s, 1H), 2.05 (d, *J* = 3.6 Hz, 1H), 1.85 (s, 1H), 1.78 – 1.65 (m, 3H), 1.62 – 1.50 (m, 6H), 1.46 – 1.39 (m, 9H), 0.88 (t, *J* = 7.4 Hz, 6H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 173.2, 169.4, 165.3, 155.5, 145.1, 144.1, 142.4, 133.8, 133.0, 130.4, 130.3, 130.2, 129.8, 129.2, 128.7, 126.9, 123.7, 121.4, 79.8, 65.5, 53.3, 52.3, 49.9, 47.7, 32.4, 32.1, 31.5, 30.9, 30.5, 28.3, 22.7, 21.9, 11.2.
HRMS (ESI, m/z) calcd for $C_{38}H_{54}N_3O_9S$ $[M + H]^+$: 728.3576, found: 728.3581.



According to above procedure, **3a** (0.1 mmol, 45.8 mg) was converted into the crude alcohol. The crude alcohol was dissolved in THF (0.5 mL) in a flask equipped with a magnetic stirring bar. The mixture was sealed and placed under N_2 atmosphere, then DBU (0.12 mmol, 26μL) and DPPA (0.03 mmol, 20μL) were added. The mixture was stirred at room temperature for 4 h. The reaction mixture was quenched with 1M HCl under vigorous stirring. Extractions with ethyl acetate followed. The organic layers were combined, washed with saturated aqueous $NaHCO_3$, brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the reaction crude was purified by a silica gel column chromatography (EtOAc/*n*-hexane) to afford the product **4f**.



4f

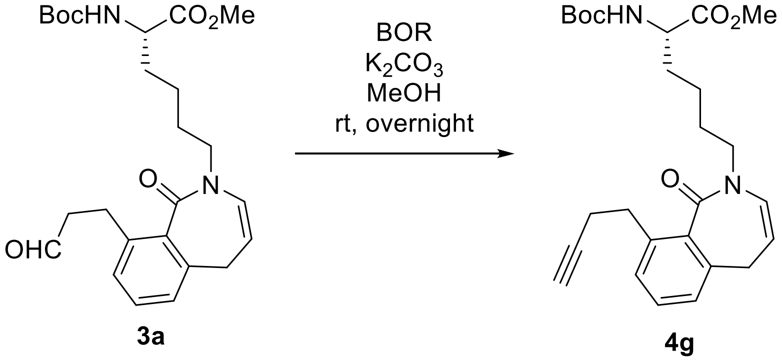
4f was obtained as pale yellow liquid oil. 23.5 mg, 34%. *R*f = 0.6 (EtOAc/*n*-hexane, 1:1).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.41 – 7.32 (m, 4H), 7.30 – 7.17 (m, 7H), 7.05 (d, *J* = 7.7 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 5.87 (dd, *J* = 7.4, 1.9 Hz, 1H), 5.80 – 5.70 (m, 1H), 5.12 (d, *J* = 16.2 Hz, 1H), 4.40 – 4.21 (m, 3H), 4.12 (s, 1H), 3.74 (s,3H), 3.35 – 3.13 (m, 2H), 3.06 – 2.89 (m, 2H), 2.67 (d, *J* = 10.1 Hz, 1H), 2.15 (s, 1H), 2.05 – 1.94 (m, 1H), 1.87 (d, *J* = 9.9 Hz, 1H), 1.74 – 1.61 (m, 3H), 1.49 – 1.36 (m, 11H)

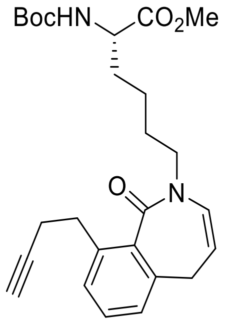
^{13}C NMR (151 MHz, CDCl$_3$) δ 173.7, 169.3, 150.6, 145.0, 142.4, 133.0, 129.7, 129.2, 128.8, 125.2, 123.7, 121.3, 120.1, 120.0, 79.7, 69.0, 53.5, 52.2, 47.7, 32.1, 32.0, 31.5, 30.1, 28.3, 22.5.

^{31}P NMR (162 MHz, CDCl$_3$) δ -11.9.

HRMS (ESI, m/z) calcd for $C_{37}H_{46}N_2O_9P$ $[M + H]^+$: 693.2936, found: 693.2927.



The alkynylation reaction was conveniently carried out in methanol by **3a** (0.1 mmol, 45.8 mg) with the Bestmann–Ohira reagent (0.12 mmol, 18μL) in the presence of K_2CO_3 (0.2 mmol, 27.6 mg) overnight at rt and concentrated in vacuum; the crude product **4g** was purified by a silica gel column chromatography (EtOAc/*n*-hexane).



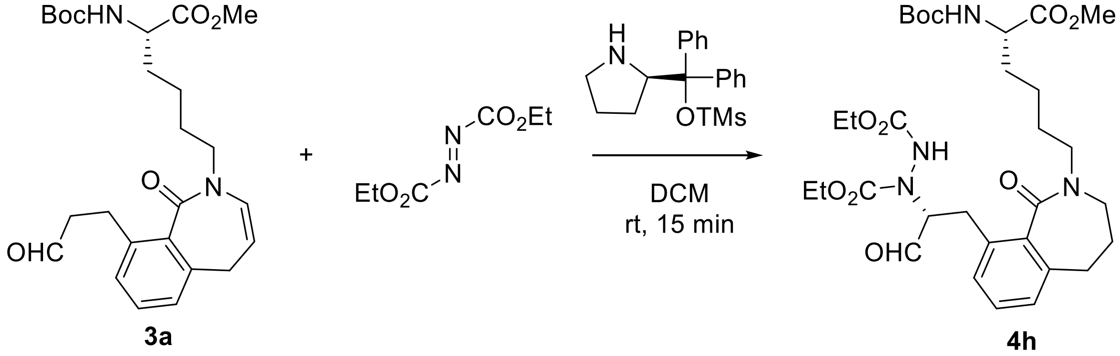
4g

4g was obtained as pale yellow liquid oil. 26.2 mg, 58%. R_f = 0.5 (EtOAc/*n*-hexane, 1:2).

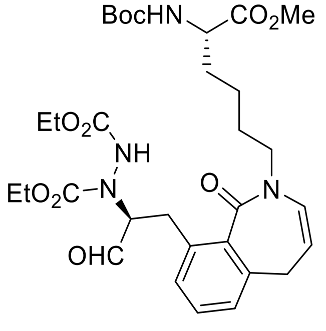
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.5 Hz, 1H), 7.23 – 7.19 (m, 1H), 6.95 (dd, *J* = 7.2, 1.5 Hz, 1H), 5.89 (d, *J* = 7.4 Hz, 1H), 5.76 (q, *J* = 7.2 Hz, 1H), 5.12 (s, 1H), 4.31 (s, 1H), 4.12 (s, 1H), 3.75 (s, 3H), 3.30 (s, 2H), 3.10 – 2.94 (m, 2H), 2.89 (d, *J* = 7.7 Hz, 1H), 2.63 (s, 1H), 2.49 (s, 1H), 1.97 (t, *J* = 2.7 Hz, 1H), 1.88 (s, 1H), 1.73 (d, *J* = 13.7 Hz, 3H), 1.50 – 1.39 (m, 11H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.3, 172.5, 154.2, 144.0, 140.7, 133.0, 129.7, 129.2, 128.9, 124.0, 121.2, 85.1, 79.7, 68.8, 53.3, 52.3, 47.7, 33.3, 32.4, 31.5, 28.3, 22.6, 20.6.

HRMS (ESI, m/z) calcd for $C_{26}H_{35}N_2O_5$ $[M + H]^+$: 455.2541, found: 455.2542.



The **3a** (0.12 mmol, 55 mg) and (*R*)-2-(diphenyl(trimethylsilyloxy)methyl)pyrrolidine (0.01 mmol, 3.25 mg) was dissolved DCM (0.1 mL) in a flask equipped with a magnetic stirring bar. Then diethylazodicarboxylate (0.1 mmol, 16μL) was added. The solvent was removed under reduced pressure and the reaction crude was purified by a silica gel column chromatography (EtOAc/*n*-hexane) to afford the product **4h**.



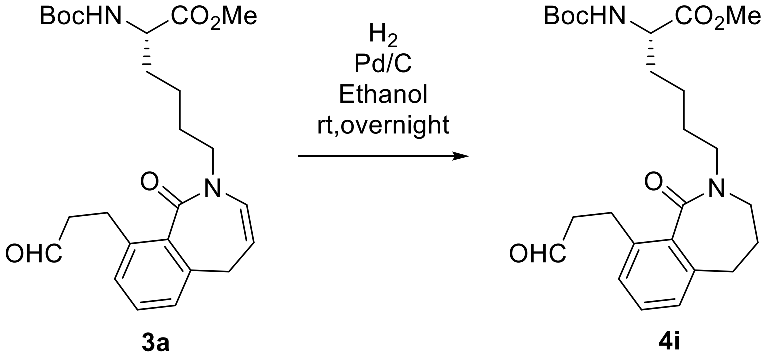
4h

4h was obtained as pale yellow liquid oil. 55.9 mg, 88%. R_f = 0.5 (EtOAc/*n*-hexane, 1:1).

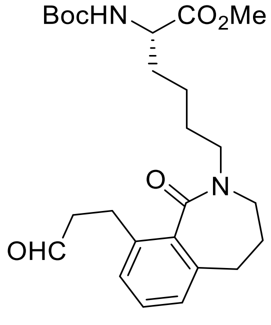
^{1}H NMR (600 MHz, CDCl$_3$) δ 9.94 – 9.72 (m, 1H), 7.27 (d, *J* = 7.4 Hz, 2H), 6.97 (d, *J* = 28.5 Hz, 1H), 5.89 (d, *J* = 7.3 Hz, 1H), 5.79 (q, *J* = 7.3 Hz, 1H), 5.11 (s, 1H), 4.94 (s, 1H), 4.32 (s, 1H), 4.28 – 3.93 (m, 6H), 3.76 (s, 3H), 3.28 (s, 3H), 2.99 (d, *J* = 18.8 Hz, 2H), 1.88 (s, 1H), 1.71 (s, 3H), 1.47 – 1.42 (m, 11H), 1.35 – 1.21 (m, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 199.9, 173.1, 169.1, 156.3, 155.3, 145.0, 130.0, 129.0, 124.5, 124.0, 121.5, 79.8, 62.7, 61.9, 53.2, 52.2, 47.5, 32.4, 32.2, 31.5, 28.2, 22.5, 14.4, 14.1.

HRMS (ESI, m/z) calcd for $C_{31}H_{45}N_4O_{10}$ $[M + H]^+$: 633.3130, found: 633.3127.



A solution of **3a** (0.1mmol, 45.8 mg) in ethanol (1 mL) containing Pd (0.005 mmol, 5.3 mg, 10 % on C; 30 wt.-%) was hydrogenated at 1 atm at 30 °C overnight. The Pd/C was removed by filtration through filter paper, and the solvent was removed under reduced pressure, the crude product **4i** was purified by a silica gel column chromatography (EtOAc/*n*-hexane).



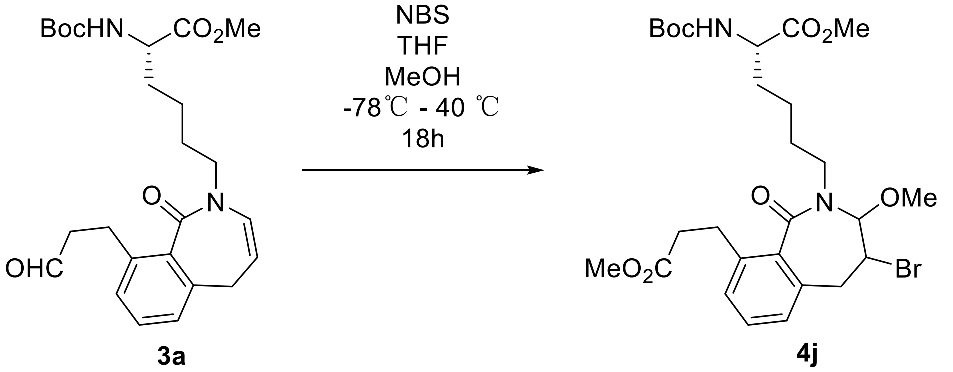
4i

4i was obtained as pale yellow liquid oil. 26.0 mg, 56%. R_f = 0.5 (EtOAc/*n*-hexane, 1:1).

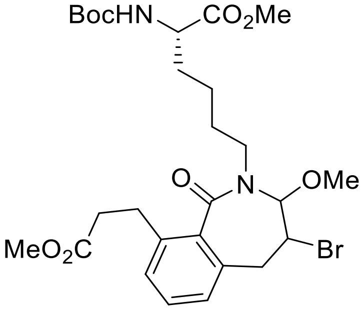
^{1}H NMR (400 MHz, CDCl$_3$) δ 9.79 (d, *J* = 1.8 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.18 – 7.13 (m, 1H), 7.03 – 6.97 (m, 1H), 5.17 (s, 1H), 4.40 – 4.19 (m, 1H), 3.75 (s, 3H), 3.64 (s, 1H), 3.48 (s, 1H), 3.18 (dd, *J* = 20.8, 11.3 Hz, 3H), 2.94 (d, *J* = 6.9 Hz, 2H), 2.77 – 2.69 (m, 3H), 2.20 (s, 1H), 1.87 (d, *J* = 8.9 Hz, 1H), 1.76 – 1.67 (m, 4H), 1.48 – 1.38 (m, 11H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 202.1, 173.2, 169.7, 155.4, 139.5, 136.9, 135.0, 129.9, 128.6, 126.2, 79.8, 53.2, 52.2, 46.1, 45.8, 32.3, 32.1, 30.2, 29.3, 28.3, 26.4, 22.6.

HRMS (ESI, m/z) calcd for $C_{25}H_{37}N_2O_6$ $[M + H]^+$: 461.2646, found: 461.2643.



At −78 °C, a solution of NBS (0.1 mmol, 18 mg) in THF (0.5 mL) was added dropwise to a solution of compound **3a** (0.1 mmol, 45.8 mg) in methanol (1.5 mL); the reaction mixture was allowed to reach 40 °C and stirred overnight and concentrated in vacuum; the crude product **4j** was purified by a silica gel column chromatography (EtOAc/*n*-hexane).



4j

4j was obtained as pale yellow liquid oil. 28.8 mg, 48%. R_f = 0.5 (EtOAc/*n*-hexane, 1:2). Dr = 1.2:1.

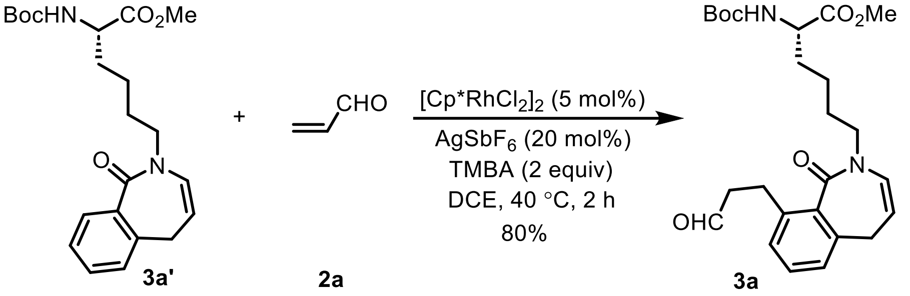
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 5.11 (d, *J* = 8.0 Hz, 1H), 4.36 (q, *J* = 9.3, 8.0 Hz, 3H), 3.77 (d, *J* = 5.1 Hz, 5H), [3.70 – 3.67 (m), 3.61 (s), 3H], [3.43 (d, *J* = 3.3 Hz), 3.40 – 3.38 (m), 3H], 3.32 – 3.26 (m, 2H), [3.11 (s), 2.99 – 2.92 (m), 2H], 2.81 – 2.73 (m, 1H), 2.67 – 2.60 (m, 1H), 1.88 (s, 1H), 1.75 (d, *J* = 11.2 Hz, 3H), 1.48 – 1.44 (m, 11H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 168.4, 155.4, 139.8, 134.4, 132.2, 130.3, 129.8, 128.4, 93.0, 79.9, 59.4, 59.4, 54.2, 53.3, 52.3, 51.5, 39.3, 35.5, 32.3, 32.2, 29.4, 29.3, 28.7, 28.3, 23.1.

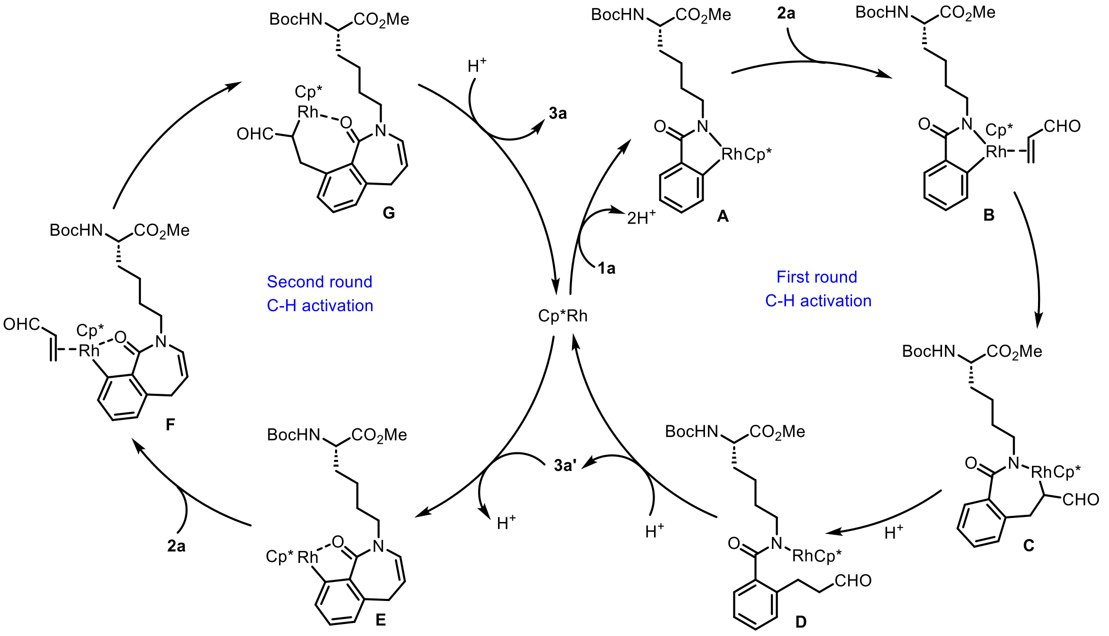
HRMS (ESI, m/z) calcd for $C_{27}H_{40}BrN_2O_8$ $[M + H]^+$: 599.1963, found: 599.1960.

5、Reaction Mechanism

In a seal capped flask equipped with a stirring bar, **3a'** (0.025 mmol, 10.5 mg), **2a** (0.075 mmol, 5 μL), $[RhCp^*Cl_2]_2$ (0.00125 mmol, 0.8 mg), $AgSbF_6$ (0.005 mmol, 1.7 mg), TMBA (0.05 mmol, 8.2 mg) and DCE (0.25 mL, 0.1 M) were added. The reaction mixture was put in an oil bath and heated at 40 °C for 2 h, cooled to room temperature. The solvent was removed in vacuo and the remaining residue was purified by a silica gel column chromatography (EtOAc/*n*-hexane from 1:20 to 1:2, then EtOAc/*n*-hexane 1:2) to afford the product **3a**. 9.2 mg, 80%.



Based on our experimental results, we proposed the reaction mechanism (**Scheme S1**). Firstly, Rh(III)-catalyzed C-H activation of **1a** affords five-membered rhodacycle **A**, followed by the coordination of Rh(III) center with alkene giving intermediate **B**. Subsequent alkene insertion into the C-Rh bond generates seven-membered rhodacycle **C**, which undergoes protonation to produce intermediate **D**. Intramolecular cyclization and dehydration of intermediate **D** deliver intermediate **3a′** and regenerate the active Rh(III) species. Then Rh(III)-catalyzed C-H activation of **3a′** gives five-membered rhodacycle **E**, followed by the coordination with second alkene affording intermediate **F**. Subsequent alkene insertion and protonation deliver the desired product **3a** and regenerate the Rh(III) catalyst.



Scheme S1. Proposed reaction mechanism.

6、In Vitro Antifungal Activities.

Each target compound was dissolved in DMSO to prepare the stock solution (10.0 g/L). The stock solution was added into the PDA medium, and the concentration of target compound in the medium was 50.0 mg/L. Pure DMSO without the target compound was utilized as the blank control, and boscalid was coassayed as the reference compound. Fresh dishes with a diameter of 5 mm were taken from the edge of the PDA-cultured fungi colonies and inoculated on the above three PDA media. Each treatment was tested for three replicates, and the antifungal effect was averaged. The relative inhibitory rate I (%) of all the tested compounds was calculated through the equation: I (%) = [(C − T)/(C − 5)] × 100. In this equation, I is the inhibitory rate and C and T are the colony diameter of the blank control (mm) and treatment (mm), respectively.

Mycelia growth of four crop pathogenic fungi and a forest pathogenic fungus after treating with the target compounds on PDA medium as illustrated in the figures (**Figure S1**) below.

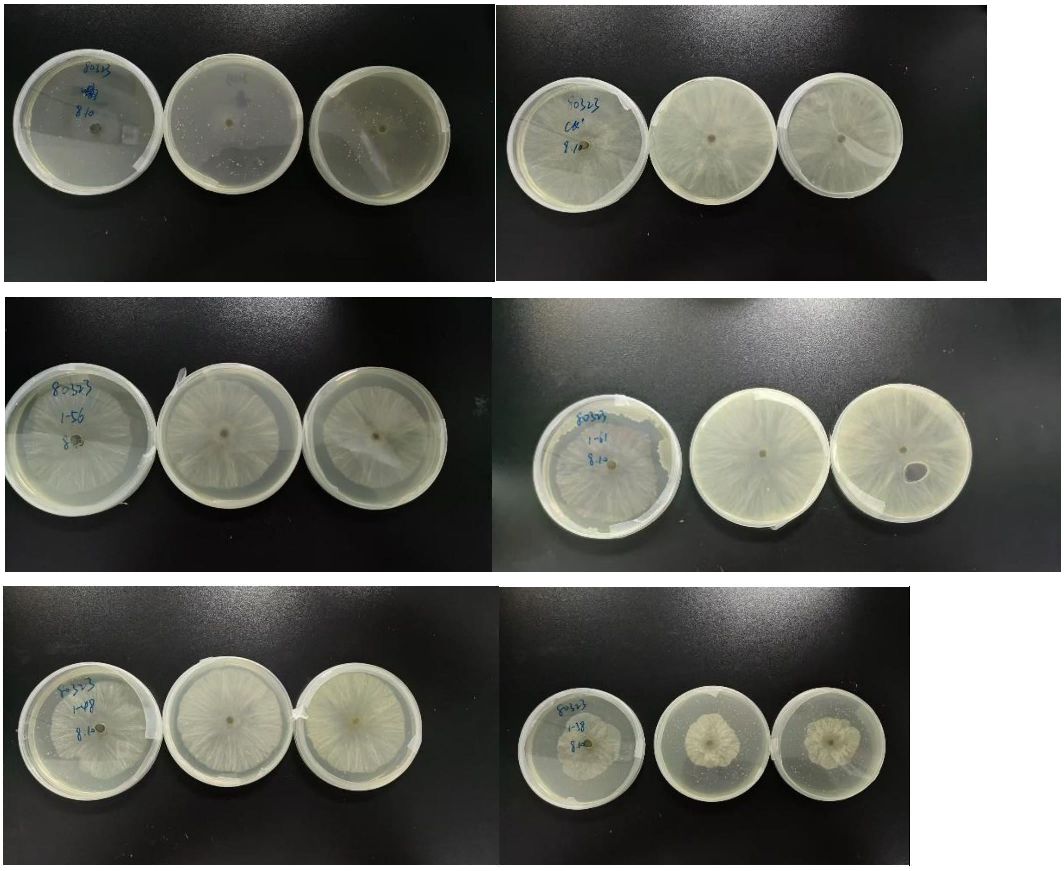


Figure S1-1. *C. chrysosperma*

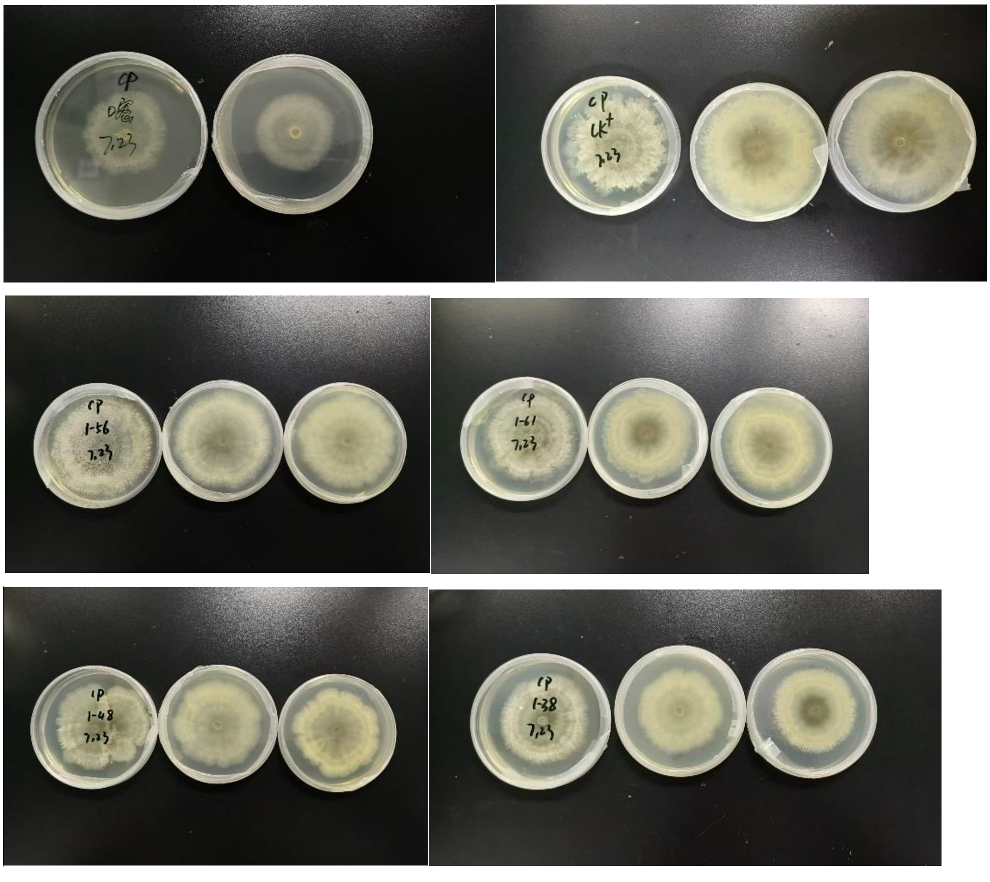


Figure S1-2 *C. paradoxa*

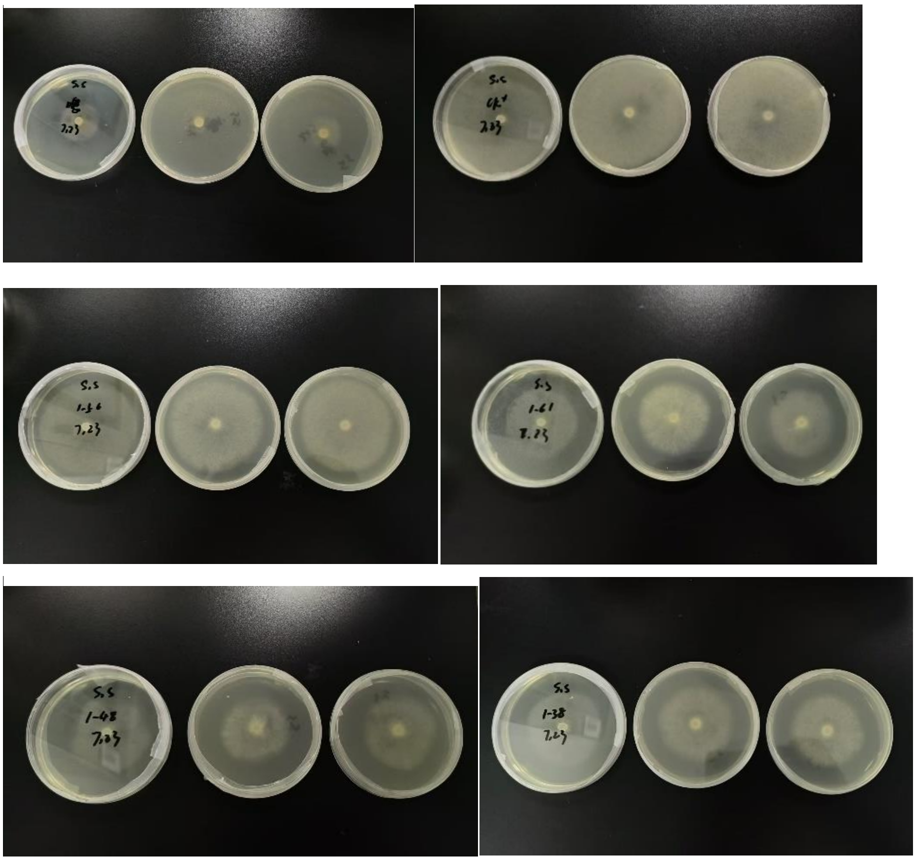


Figure S1-3 *S. sclerotiorum*

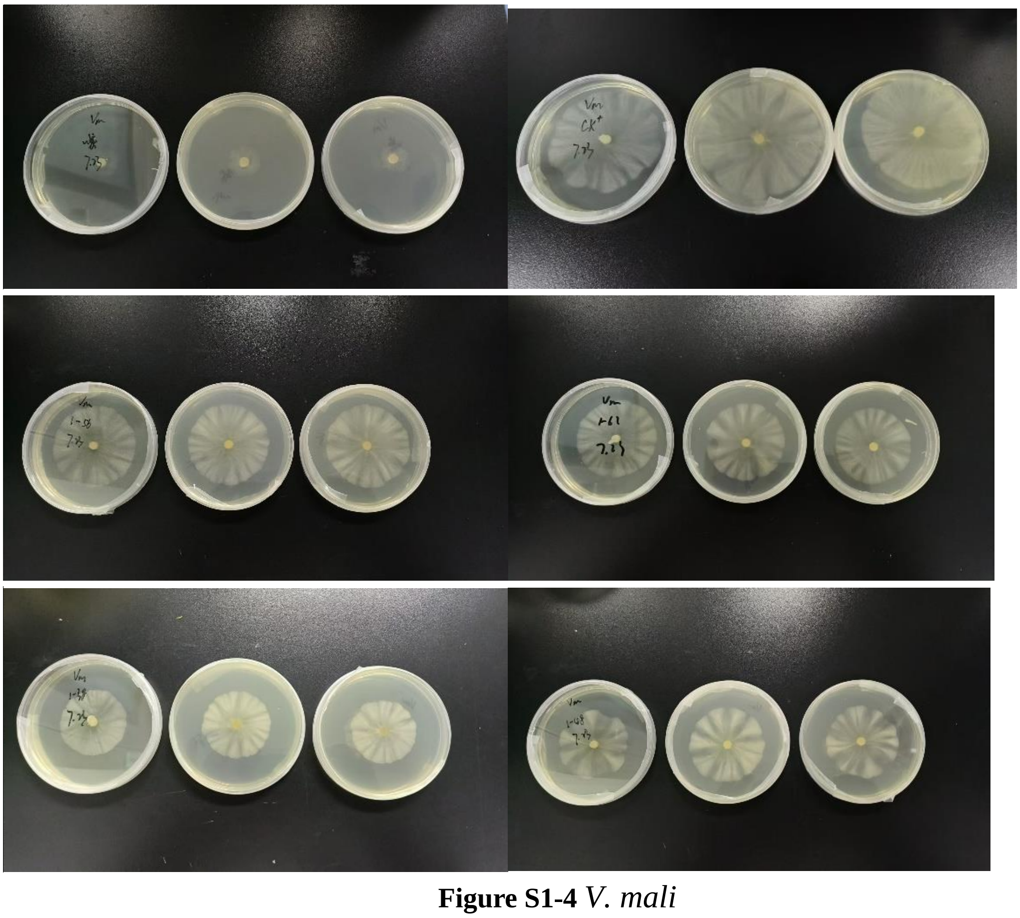
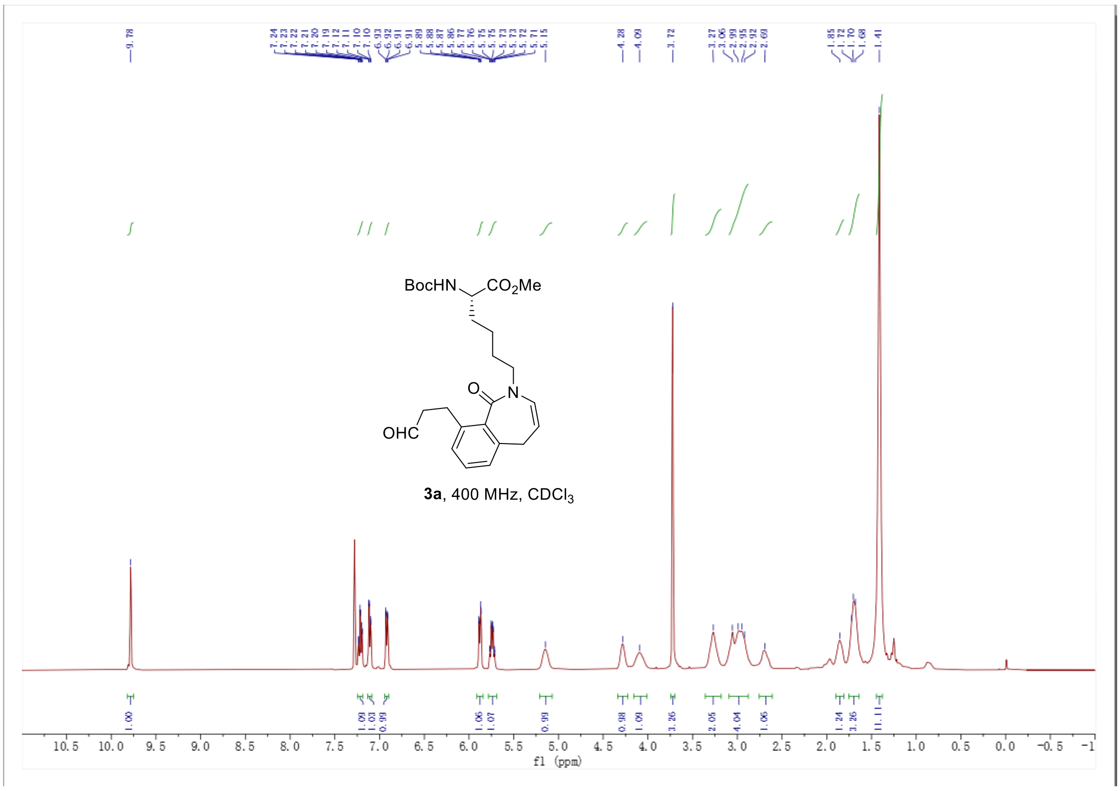
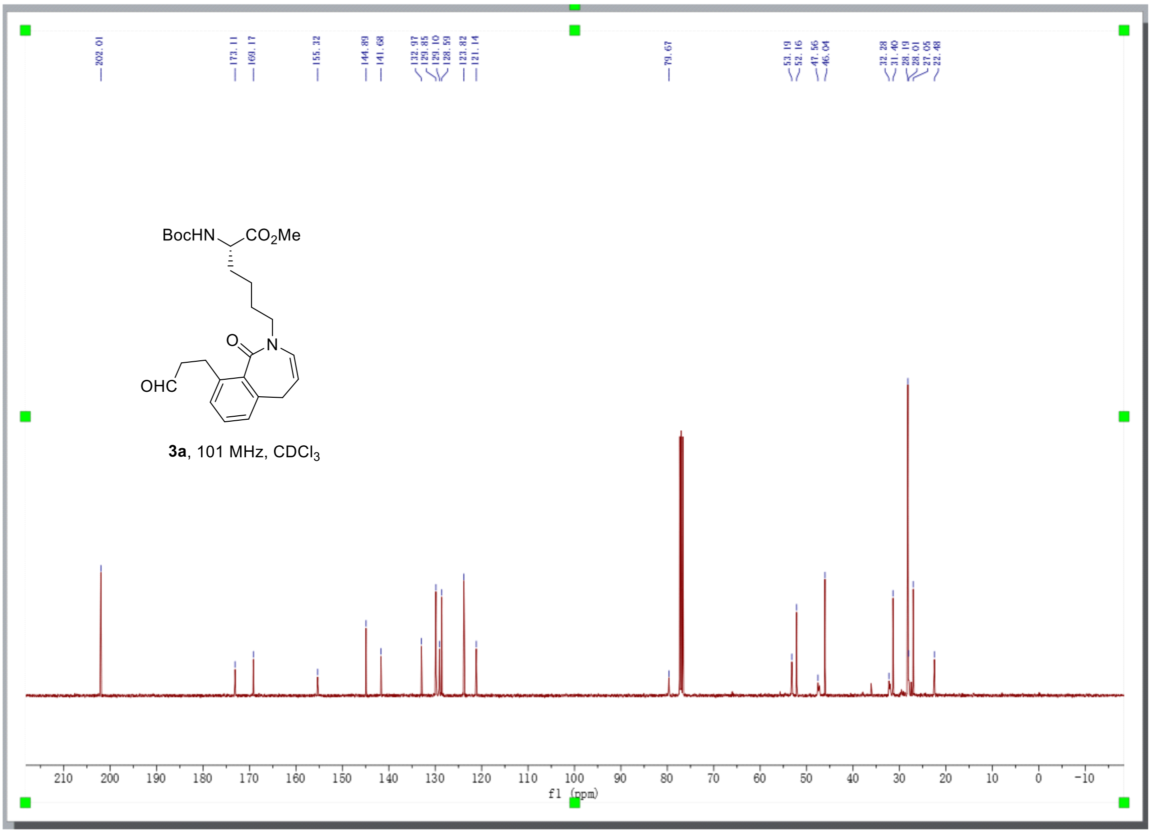


Figure S1-4 *V. mali*

7、Spectra


9.78
7.24 7.23 7.22 7.21 7.20 7.19 7.12 7.11 7.10 7.10 6.93 6.92 6.91 6.91 5.89 5.88 5.87 5.86 5.77 5.76 5.75 5.75 5.73 5.73 5.72 5.71 5.15
4.28 4.09 3.72 3.27 3.06 2.99 2.95 2.92 2.69 1.85 1.72 1.70 1.68 1.41
BocHN
CO$_2$Me
O
N
OHC
3a, 400 MHz, CDCl$_3$
1.00 1.09 1.03 0.99 1.06 1.07 0.99 0.98 1.09 3.26 2.05 4.04 1.06 1.24 3.26 11.11
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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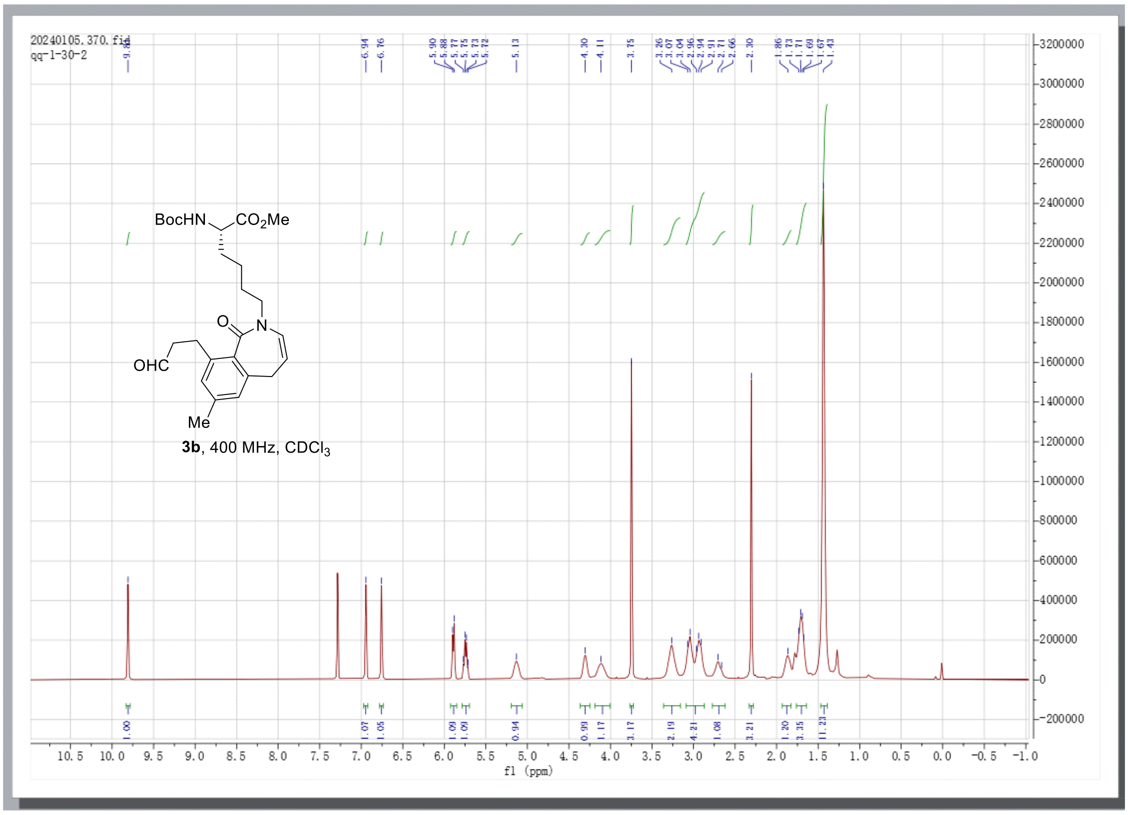
155.32
144.89 141.68
132.97 129.85 129.10 128.59 123.82 121.14
79.67
53.19 52.16 47.56 46.04
32.28 31.40 28.19 28.01 27.05 22.48
BocHN
CO$_2$Me
O
N
OHC
3a, 101 MHz, CDCl$_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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3.04
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2.94
2.91
2.71
2.66
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1.73
1.71
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1.67
1.43
BocHN
CO2Me
O
N
OHC
Me
3b, 400 MHz, CDCl3
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1.05
1.09
1.09
0.94
0.99
1.17
3.17
2.19
4.21
1.08
3.21
1.20
3.15
11.23
10.5
10.0
9.5
9.0
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8.0
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4.5
4.0
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2.5
2.0
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f1 (ppm)
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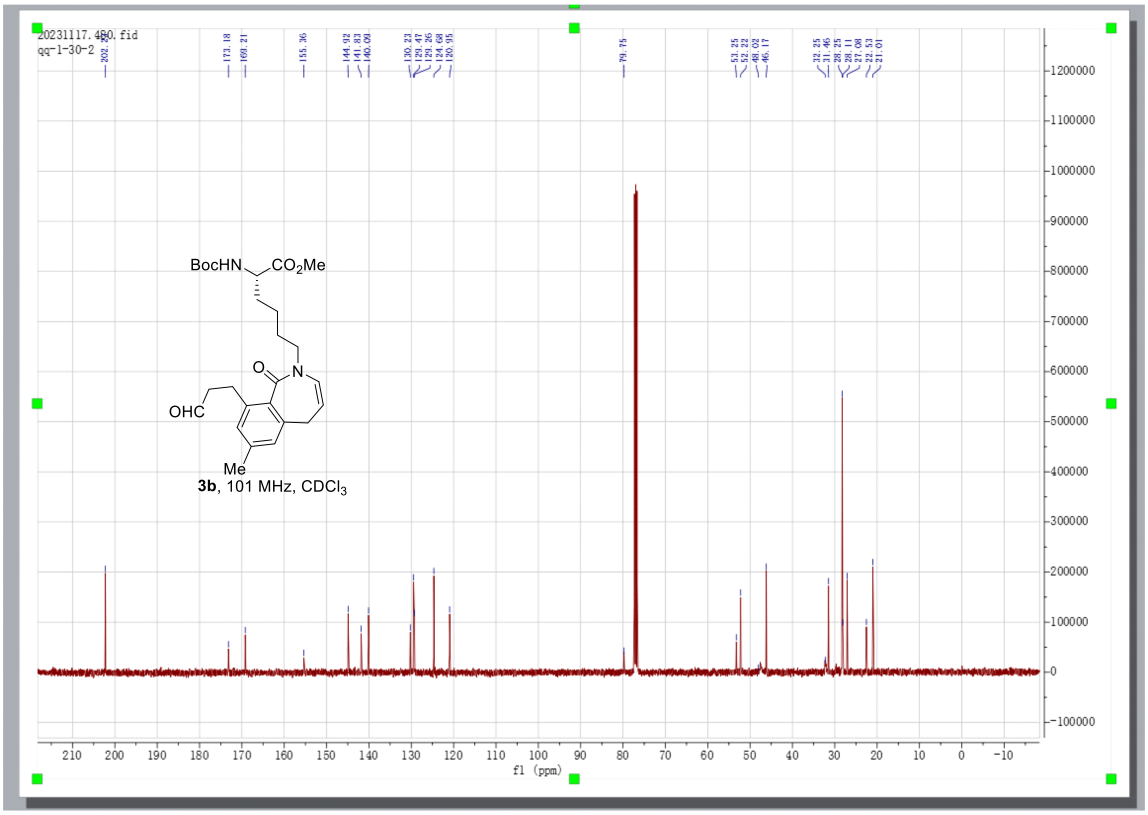
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53.25
52.22
48.02
46.17
32.25
31.46
28.25
28.11
27.08
22.51
21.01
BocHN
CO2Me
O
N
OHC
Me
3b, 101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
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400000
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200000
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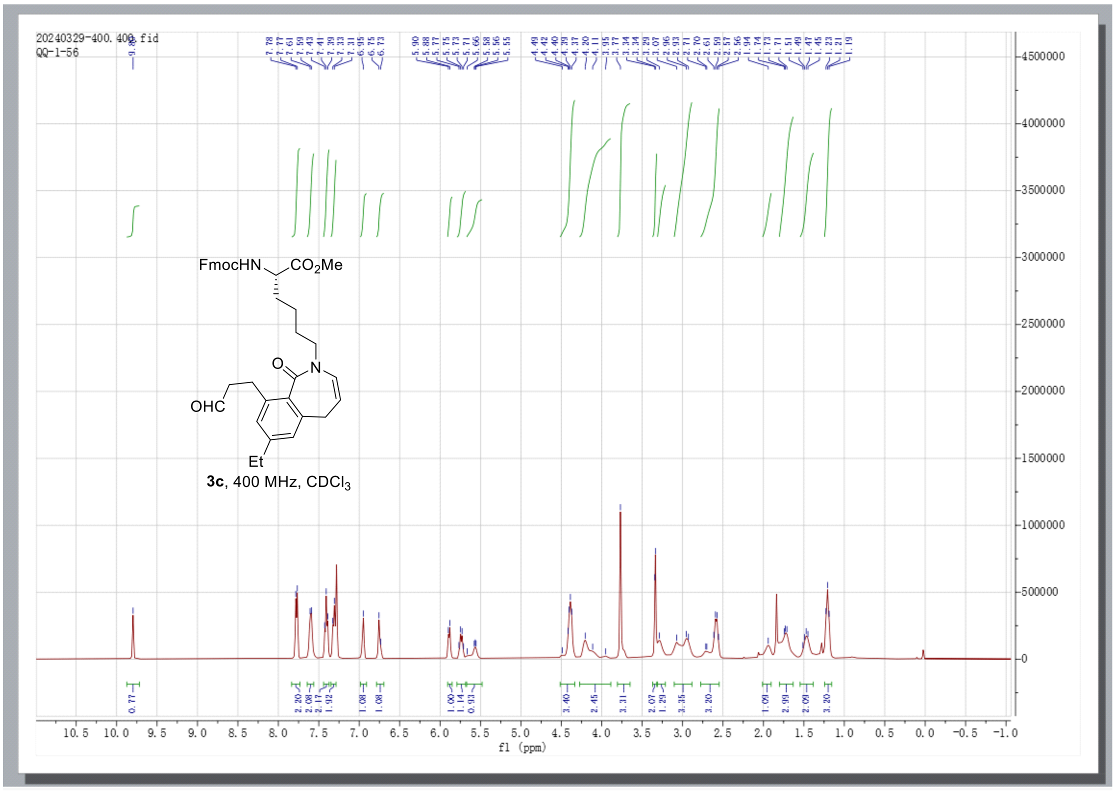
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5.75
5.73
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4.37
4.20
4.11
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3.29
3.07
2.96
2.93
2.71
2.70
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2.59
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1.47
1.45
1.23
1.21
1.19
FmocHN
CO2Me
O
N
OHC
Et
3c, 400 MHz, CDCl3
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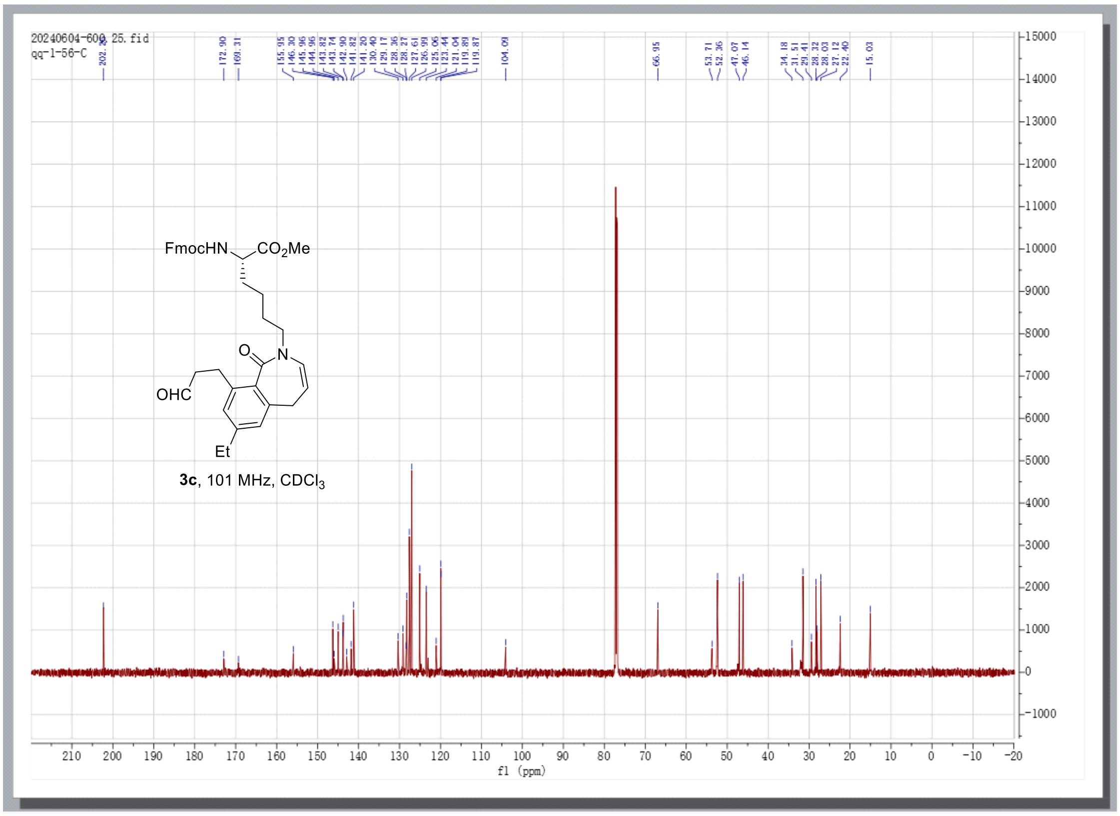
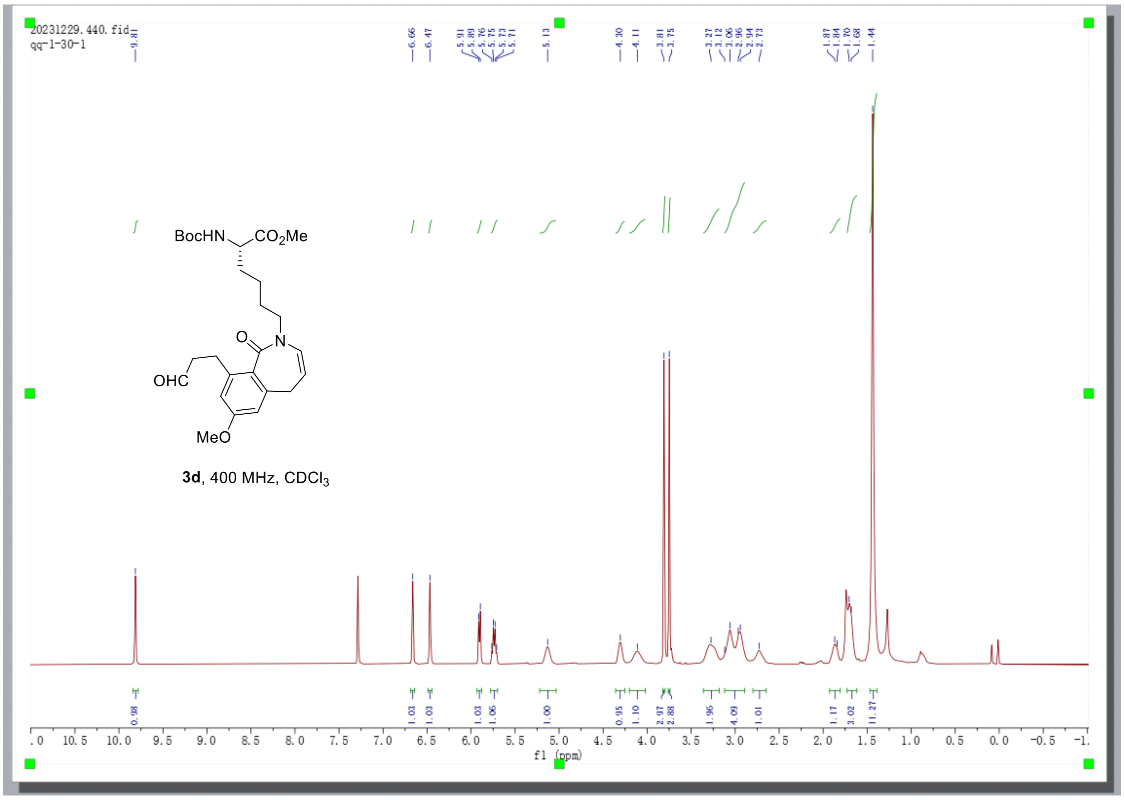
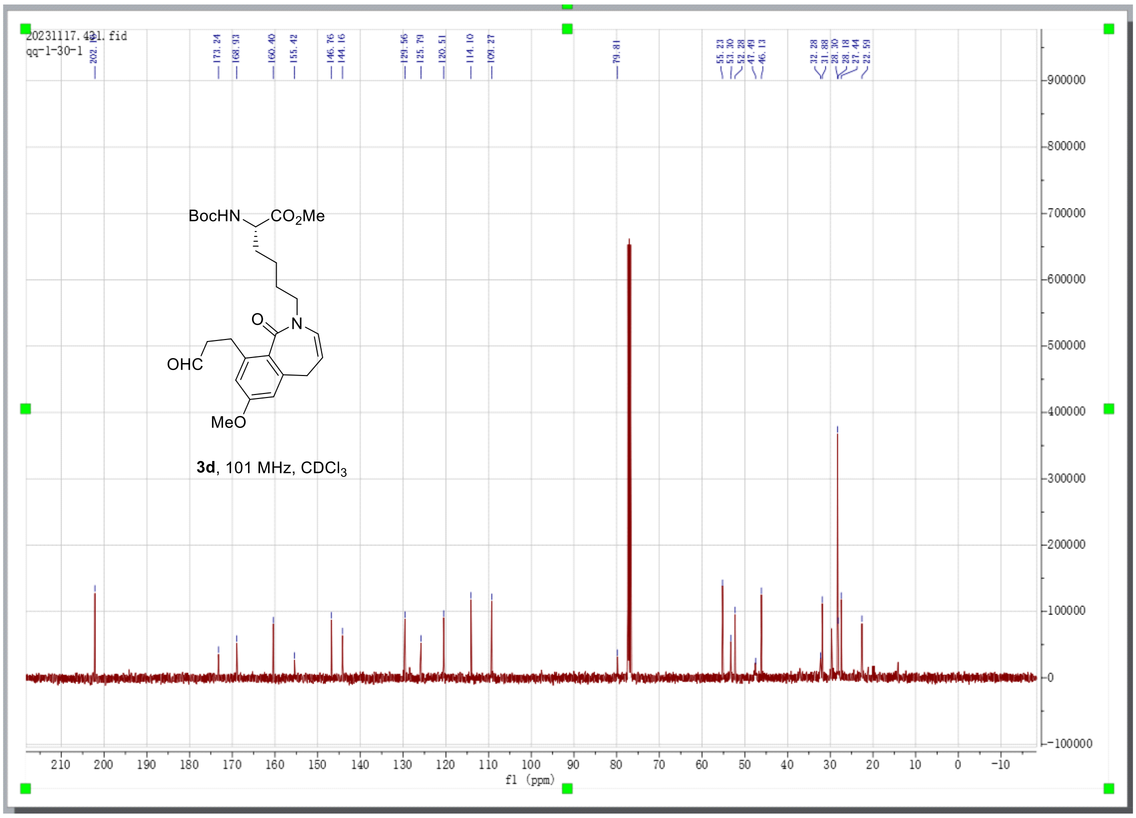
2.20
2.08
2.17
1.92
1.08
1.08
1.00
1.14
0.93
3.40
2.45
3.31
2.07
1.29
3.35
3.20
1.09
2.99
2.09
3.20
f1 (ppm)

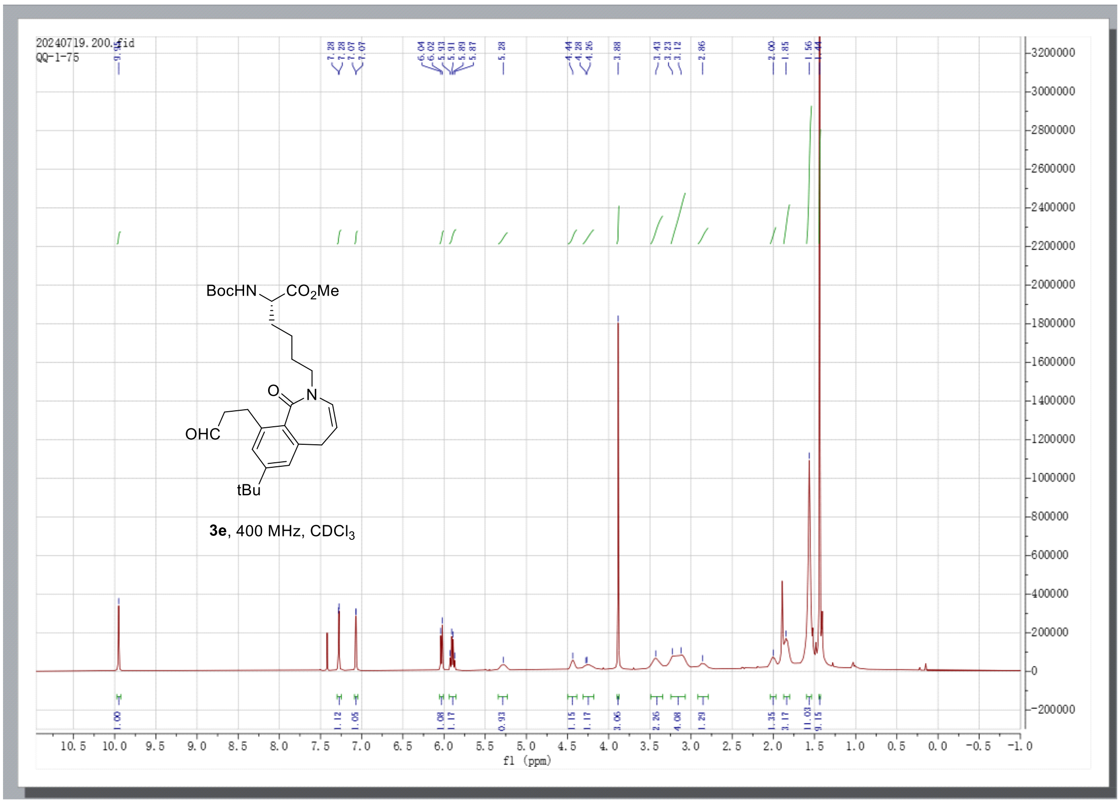

20240604-600.25.fid
qq-1-56-C
202.
172.90
169.31
155.95
146.30
145.96
144.96
143.82
143.74
142.90
141.82
141.20
130.40
129.17
128.36
128.27
127.61
126.99
125.06
123.44
121.04
119.89
119.87
104.09
66.95
53.71
52.36
47.07
46.14
34.18
31.51
29.41
28.12
28.03
27.12
22.40
15.03
FmocHN
CO2Me
O
N
OHC
Et
3c, 101 MHz, CDCl3
f1 (ppm)

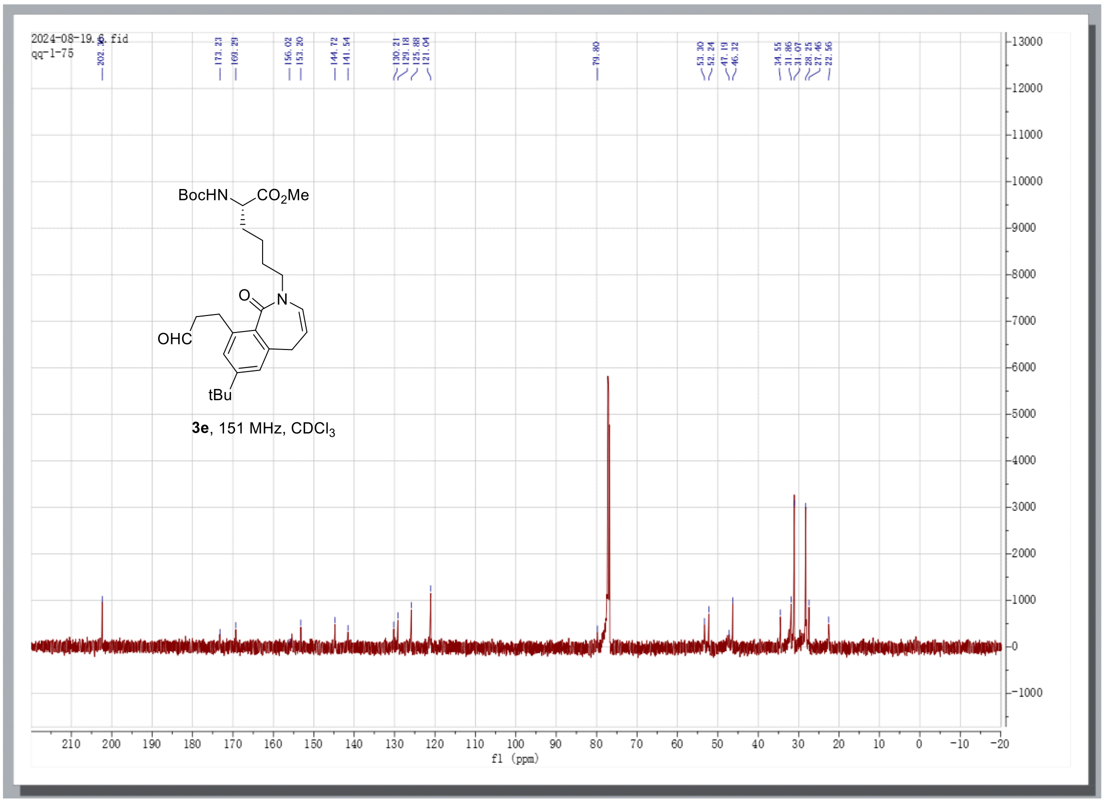


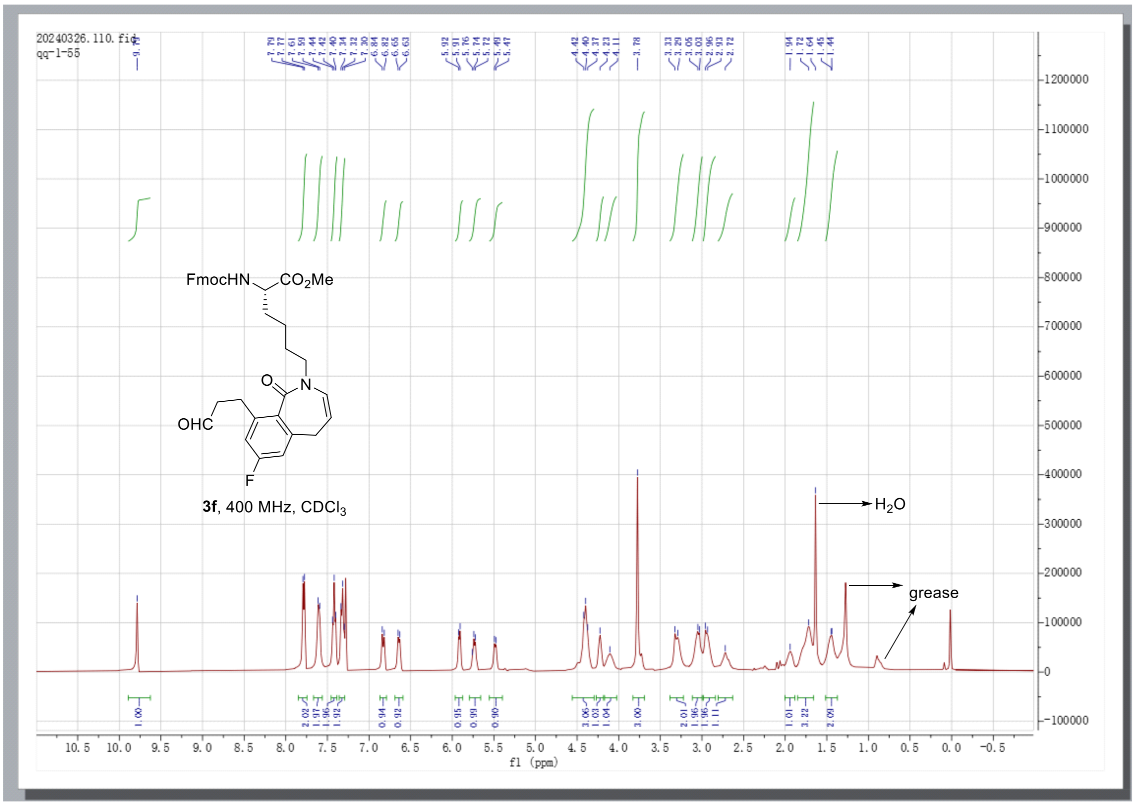
3d, 400 MHz, $CDCl_3$



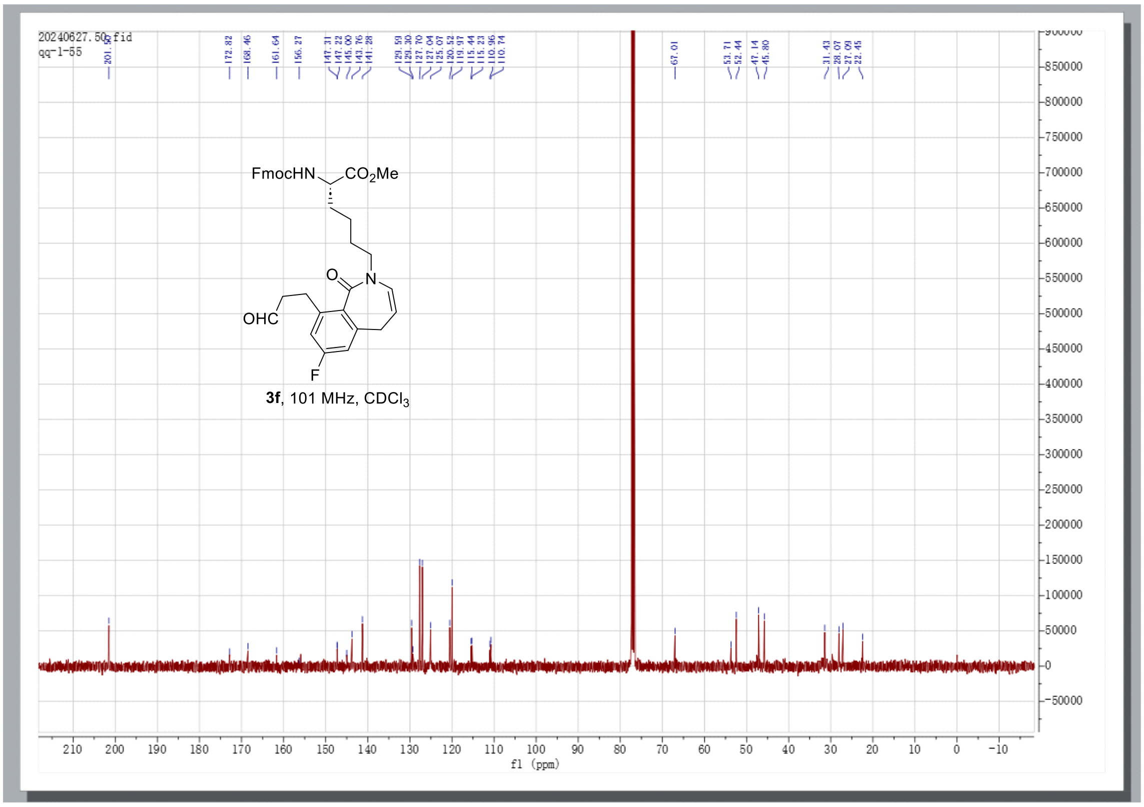
3d, 101 MHz, $CDCl_3$


20240719.200.fid
QQ-1-75
9.95
7.28
7.28
7.07
7.07
6.04
6.02
5.93
5.91
5.89
5.87
5.28
4.44
4.28
4.26
3.88
3.43
3.23
3.12
2.86
2.00
1.85
1.56
1.44
BocHN
CO2Me
O
N
OHC
tBu
3e, 400 MHz, CDCl3
1.00
1.12
1.05
1.08
1.17
0.93
1.15
1.17
3.06
2.26
4.08
1.29
1.35
3.17
11.03
9.15
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)
3200000
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
−200000

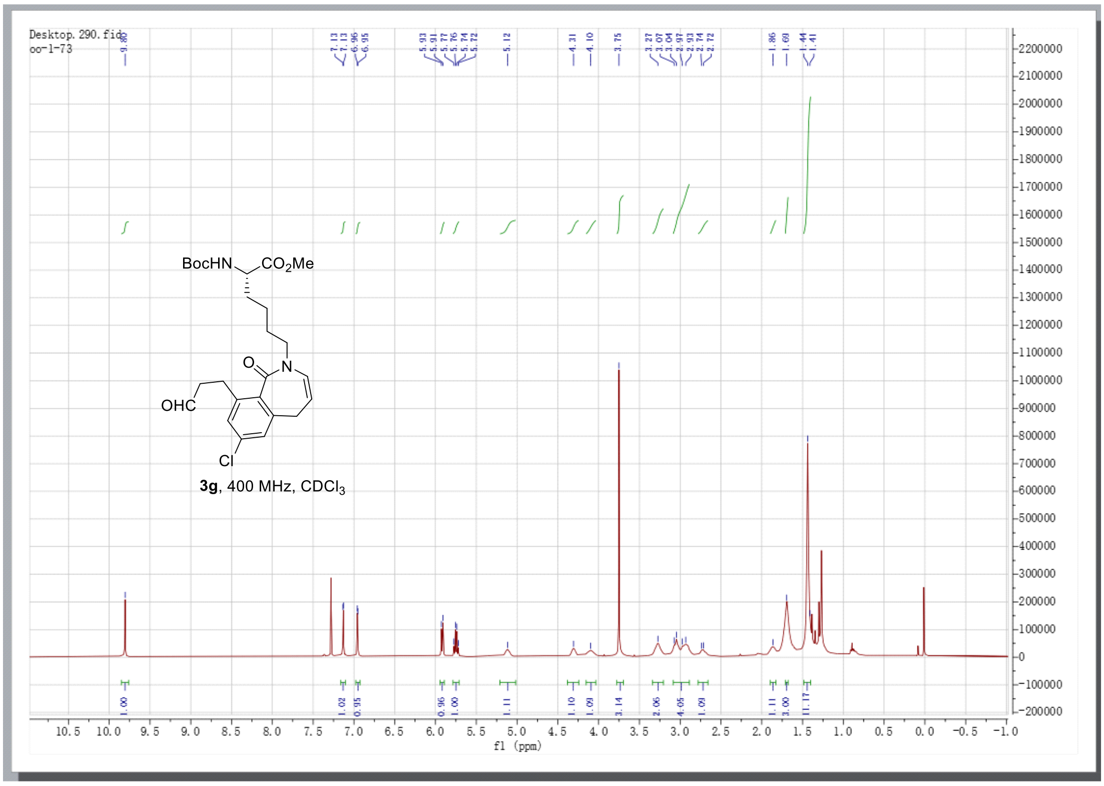

2024-08-19.6.fid
qq-1-75
202.3
173.23
169.29
156.02
153.20
144.72
141.54
130.21
129.18
125.88
121.04
79.80
53.30
52.24
47.19
46.32
34.55
31.86
31.07
28.25
27.46
22.56
BocHN
CO2Me
O
N
OHC
tBu
3e, 151 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000



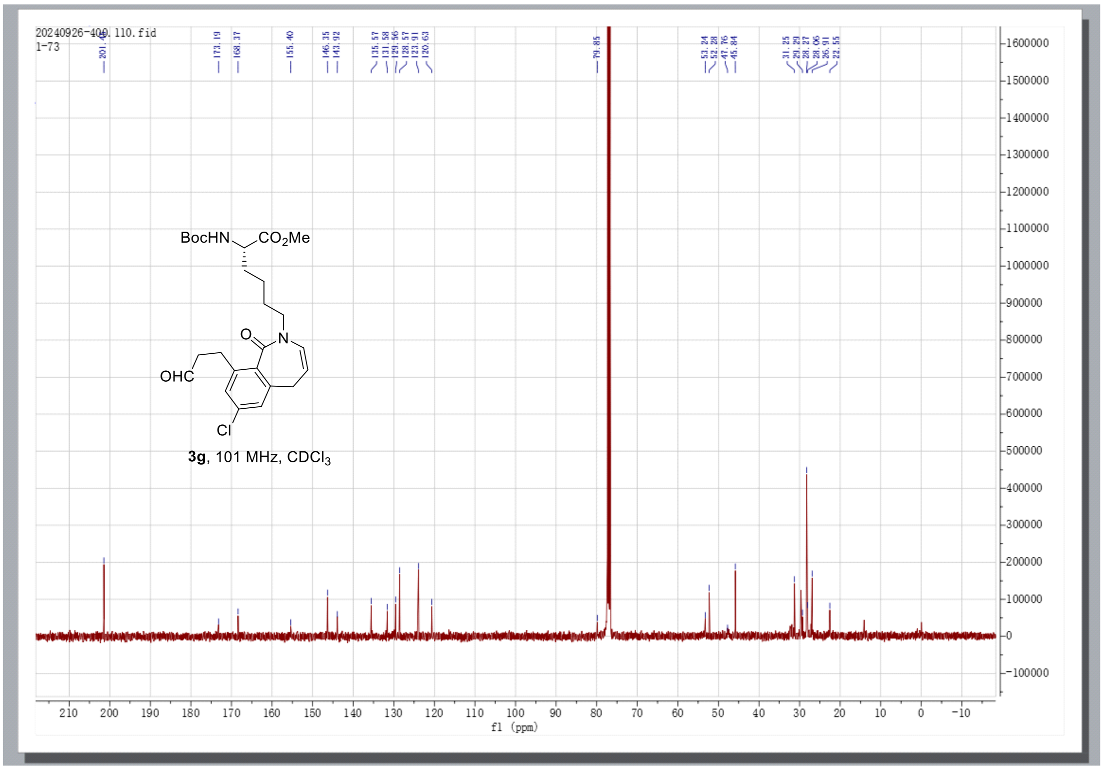
3f, 400 MHz, $CDCl_3$



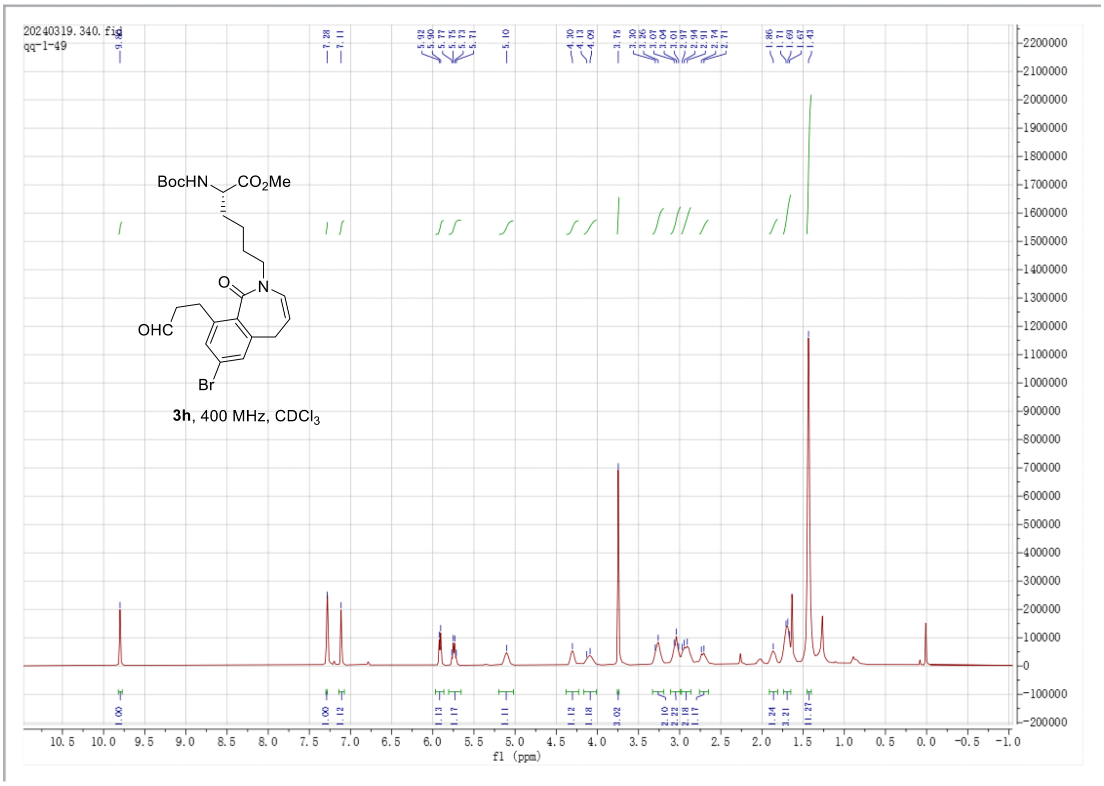
3f, 101 MHz, $CDCl_3$

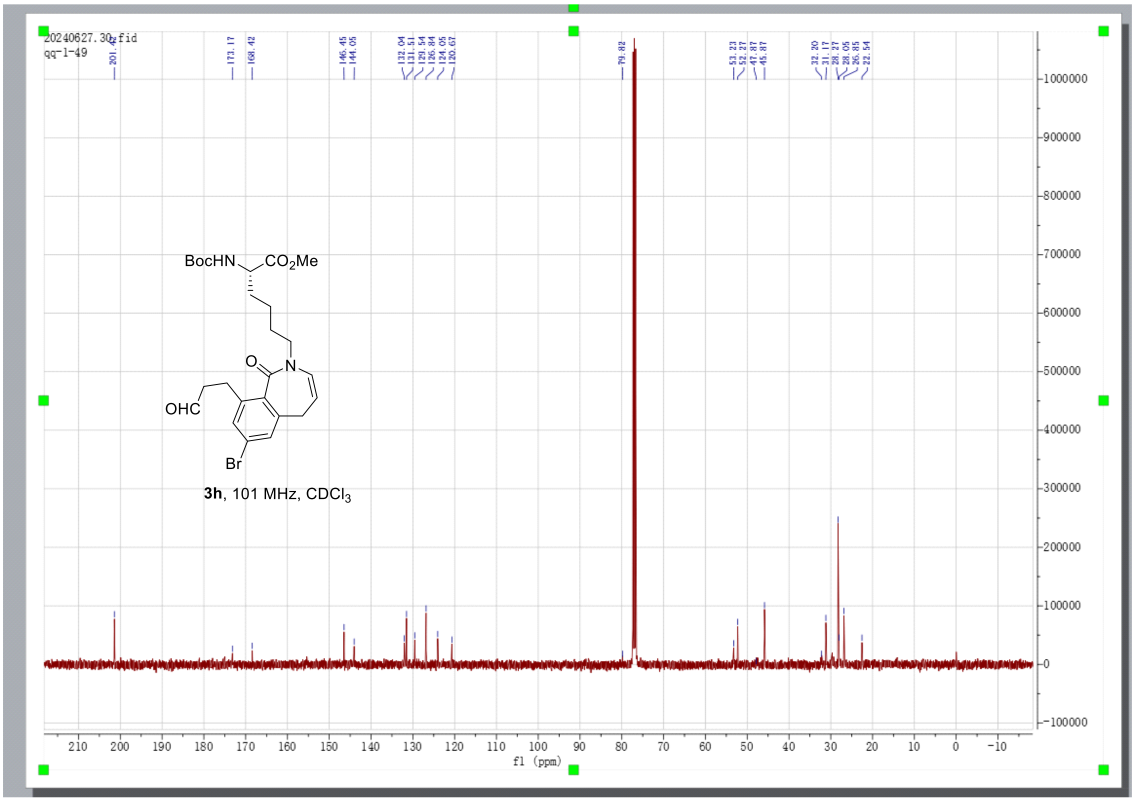


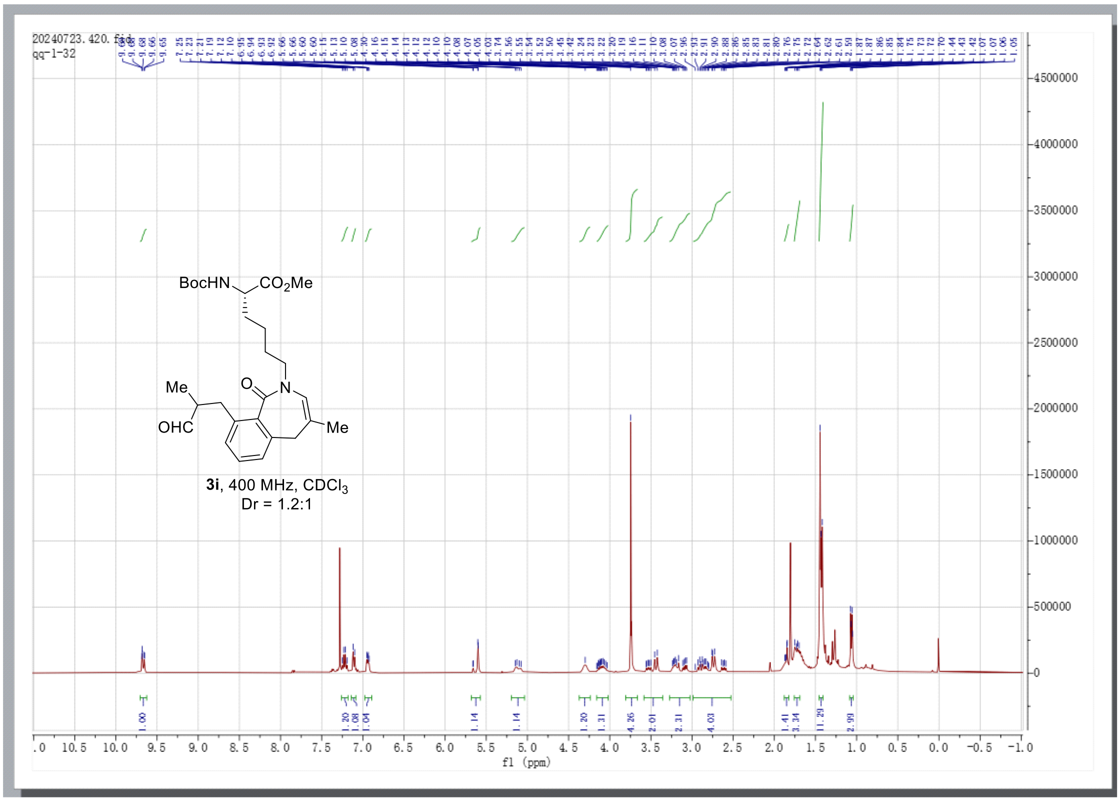
3g, 400 MHz, $CDCl_3$

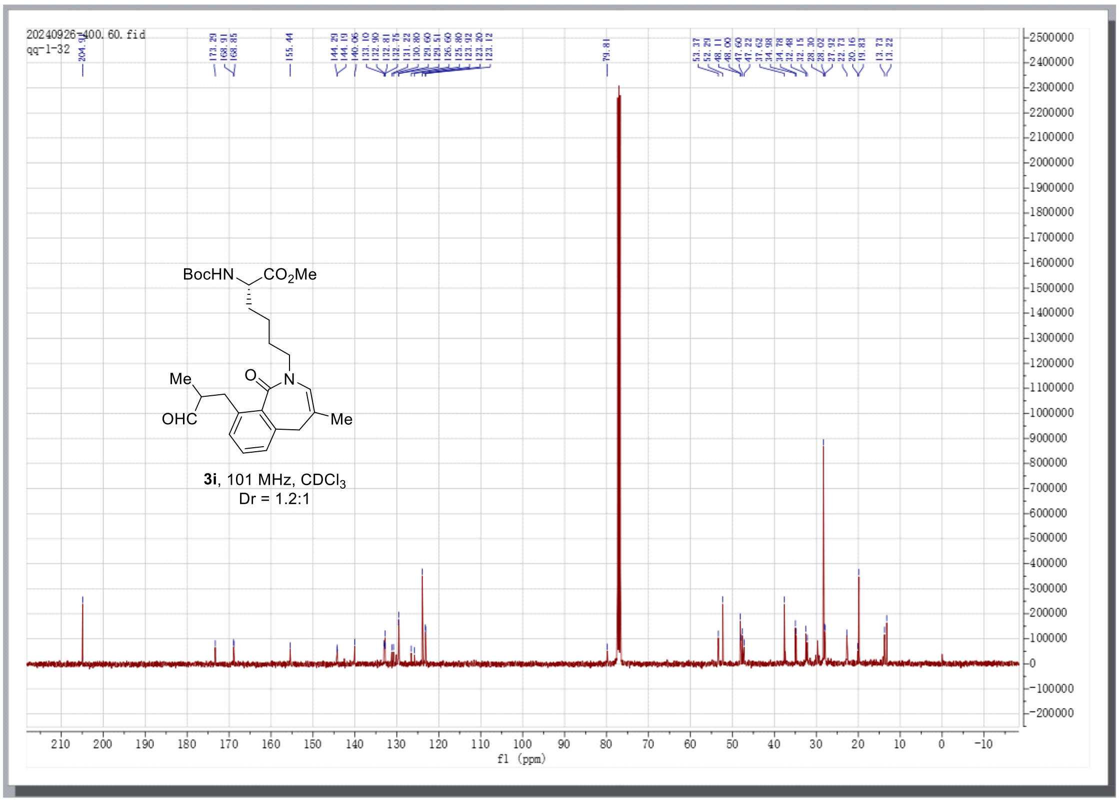


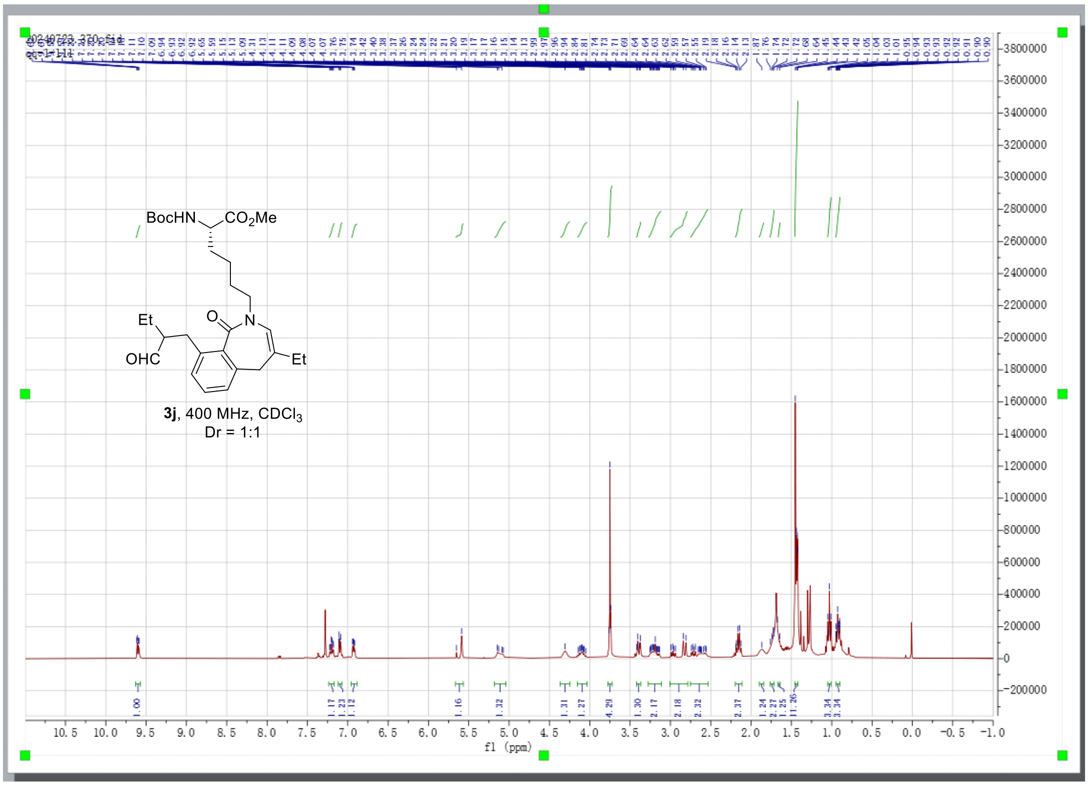
3g, 101 MHz, $CDCl_3$

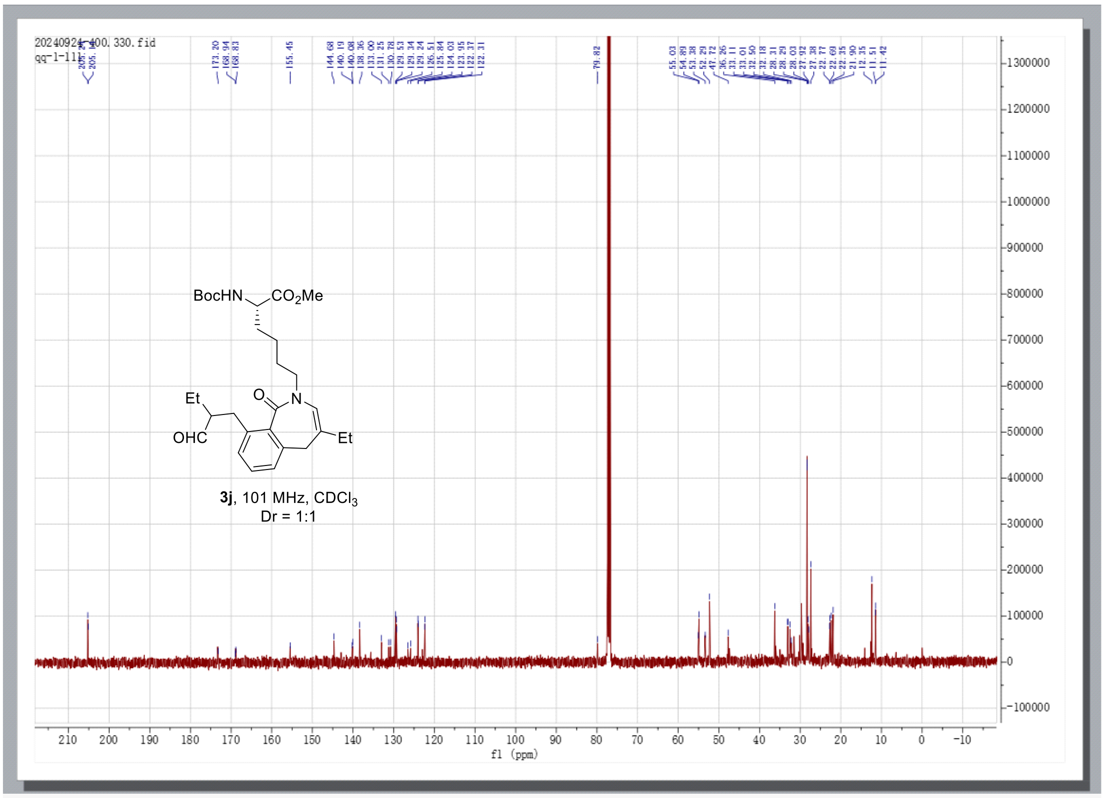

20240319.340.fid
qq-1-49
9.80
7.28
7.11
5.92
5.90
5.77
5.75
5.73
5.71
5.10
4.30
4.13
4.09
3.75
3.30
3.26
3.07
3.04
3.01
2.97
2.94
2.91
2.74
2.71
1.86
1.71
1.69
1.67
1.43
BocHN
CO2Me
O
N
OHC
Br
3h, 400 MHz, CDCl3
1.00
1.00
1.12
1.13
1.17
1.11
1.12
1.18
3.02
2.10
2.22
2.18
1.17
1.24
3.21
11.27
f1 (ppm)

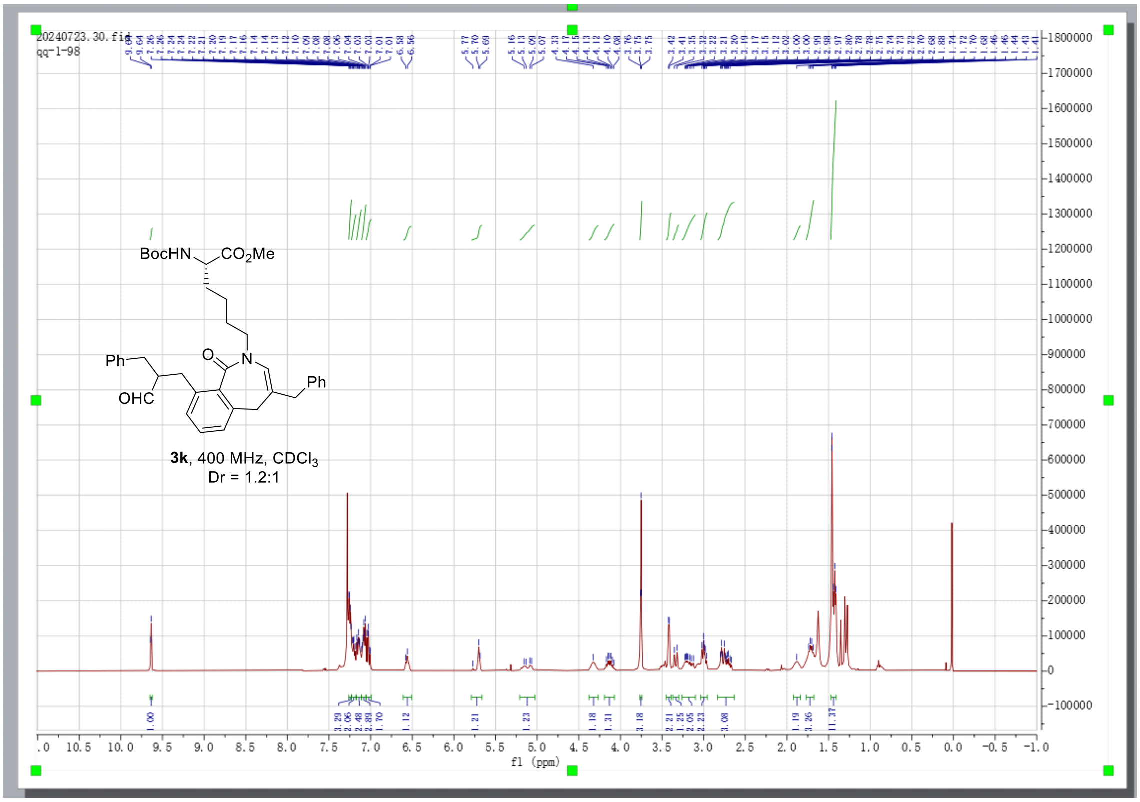

20240627.30.fid
qq-1-49
201.42
173.17
168.42
146.45
144.05
132.04
131.51
129.54
126.84
124.05
120.67
79.82
53.23
52.27
47.87
45.87
32.20
31.17
28.27
28.05
26.85
22.54
BocHN
CO2Me
O
N
OHC
Br
3h, 101 MHz, CDCl3
f1 (ppm)

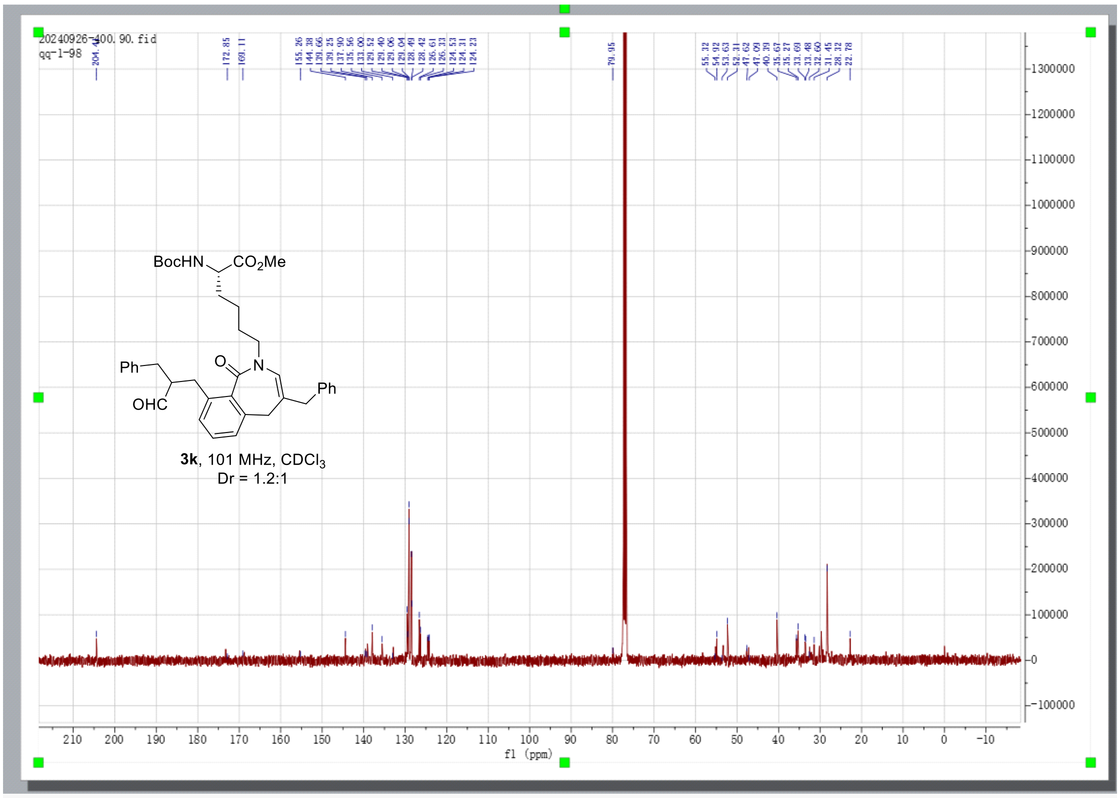

20240723.420.fid
qq-1-32
9.69 9.68 9.68 9.66 9.65 7.25 7.23 7.21 7.19 7.12 7.10 6.95 6.94 6.93 6.92 5.66 5.66 5.60 5.60 5.15 5.13 5.10 5.08 4.30 4.16 4.15 4.14 4.13 4.12 4.12 4.10 4.10 4.08 4.07 4.05 4.03 3.74 3.56 3.55 3.54 3.52 3.50 3.45 3.42 3.24 3.23 3.22 3.20 3.19 3.16 3.11 3.10 3.08 3.07 2.96 2.93 2.91 2.90 2.88 2.86 2.85 2.83 2.81 2.80 2.76 2.75 2.72 2.64 2.62 2.61 2.59 1.87 1.87 1.86 1.85 1.84 1.75 1.73 1.72 1.70 1.44 1.43 1.42 1.07 1.07 1.06 1.05
BocHN
CO2Me
Me
O
N
OHC
Me
3i, 400 MHz, CDCl3
Dr = 1.2:1
1.00 1.20 1.08 1.04 1.14 1.14 1.20 1.31 4.26 2.01 2.31 4.03 1.41 3.34 11.29 2.99
4500000 4000000 3500000 3000000 2500000 2000000 1500000 1000000 500000 0
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

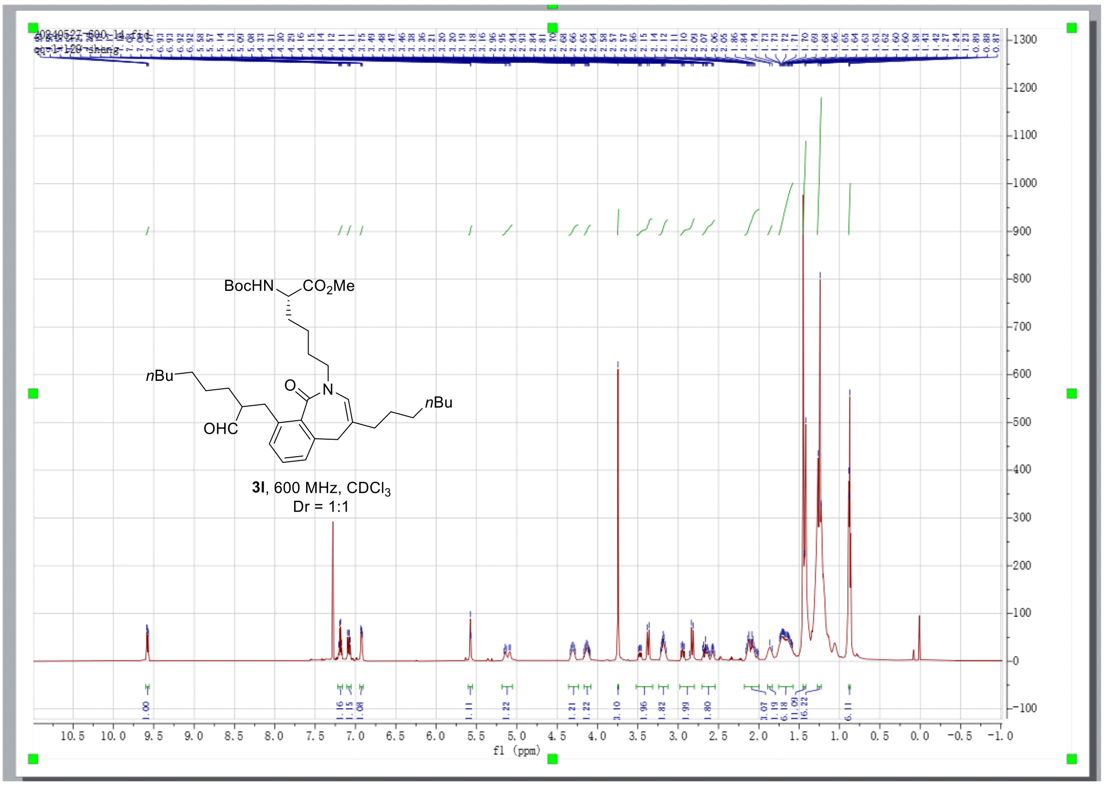

20240926-400.60.fid
qq-1-32
204.9
173.29 168.91 168.85
155.44
144.29 144.19 140.06 133.10 132.90 132.81 132.75 131.22 130.80 129.60 129.51 126.60 125.80 123.92 123.20 123.12
79.81
53.37 52.29 48.11 48.00 47.60 47.22 37.62 34.98 34.78 32.48 32.15 28.30 28.02 27.92 22.73 20.16 19.83 13.73 13.22
BocHN
CO2Me
Me
O
N
OHC
Me
3i, 101 MHz, CDCl3
Dr = 1.2:1
2500000 2400000 2300000 2200000 2100000 2000000 1900000 1800000 1700000 1600000 1500000 1400000 1300000 1200000 1100000 1000000 900000 800000 700000 600000 500000 400000 300000 200000 100000 0 −100000 −200000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

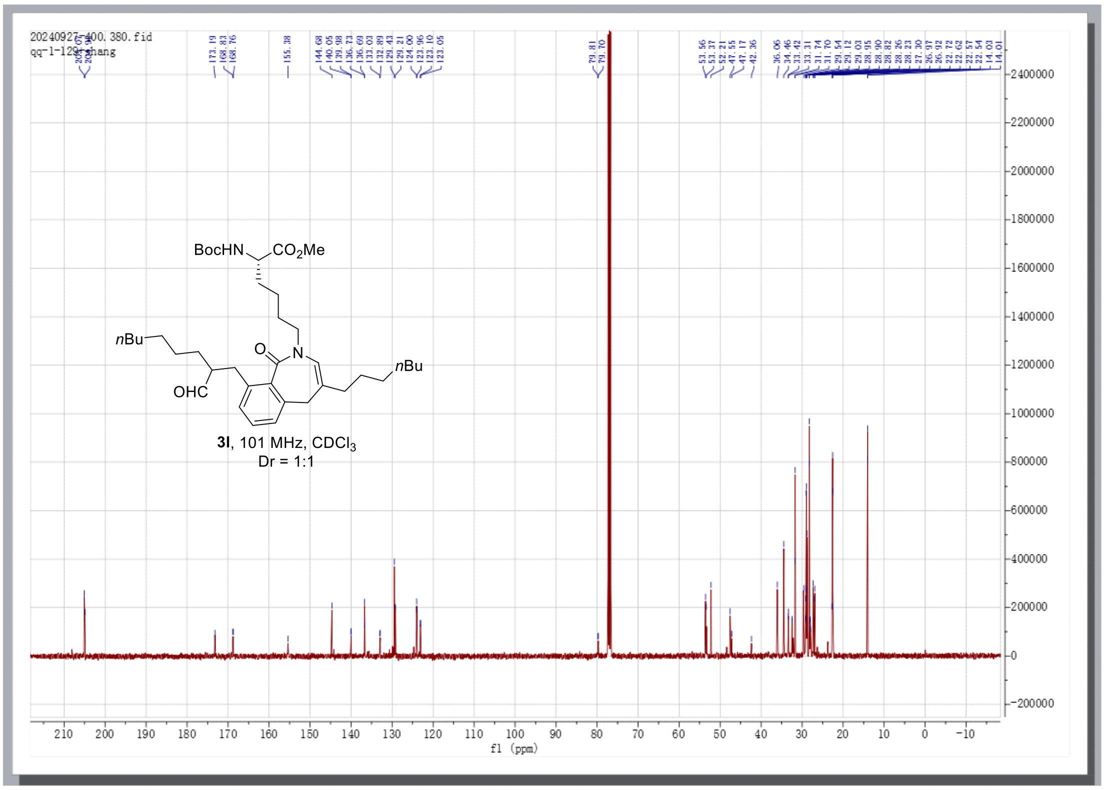

20240723_370.fid
qq-1-111
BocHN
CO2Me
Et
O
N
OHC
Et
3j, 400 MHz, CDCl3
Dr = 1:1
1.00
1.17
1.23
1.12
1.16
1.32
1.31
1.27
4.29
1.30
2.17
2.18
2.32
2.37
1.24
2.27
1.25
11.26
3.34
3.34
f1 (ppm)

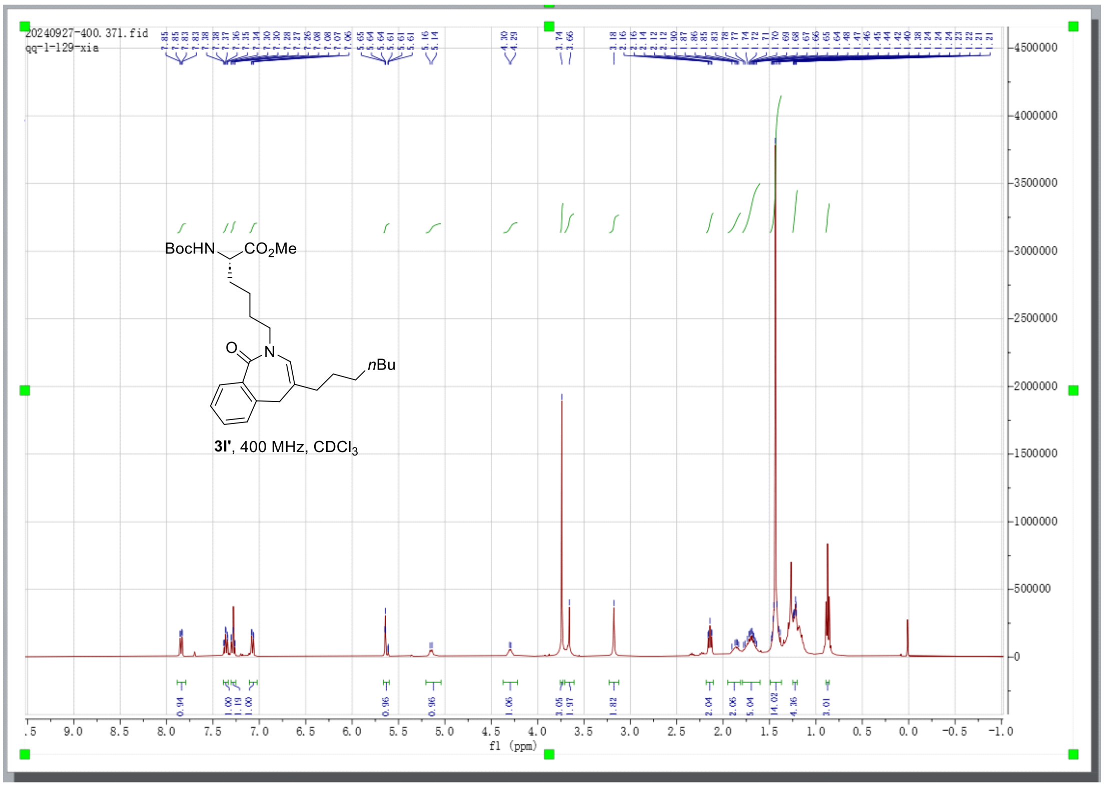

20240924_400.330.fid
qq-1-111
205.
205.
173.20
168.94
168.83
155.45
144.68
140.19
140.08
138.36
133.00
131.25
130.28
129.53
129.34
129.24
126.51
125.84
124.03
123.95
122.37
122.31
79.82
55.03
54.89
53.38
52.29
47.72
36.26
33.11
33.01
32.50
32.18
28.31
28.29
28.03
27.92
27.38
22.77
22.69
22.35
21.90
12.35
11.51
11.42
BocHN
CO2Me
Et
O
N
OHC
Et
3j, 101 MHz, CDCl3
Dr = 1:1
f1 (ppm)

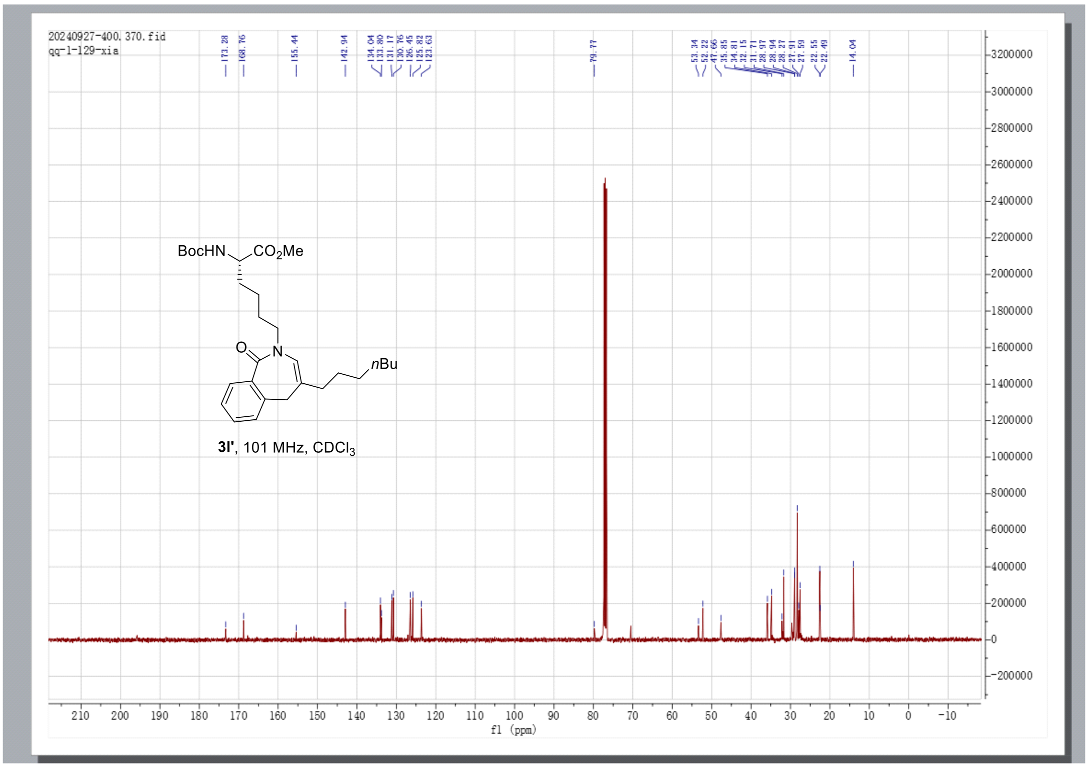

20240723.30.fid
qq-1-98
9.65 9.64 7.26 7.26 7.24 7.24 7.22 7.21 7.20 7.19 7.17 7.16 7.14 7.14 7.13 7.12 7.10 7.09 7.08 7.08 7.06 7.04 7.03 7.03 7.01 7.01 6.58 6.56 5.77 5.70 5.69 5.16 5.13 5.09 5.07 4.33 4.17 4.15 4.13 4.12 4.10 4.08 3.76 3.75 3.75 3.42 3.41 3.35 3.32 3.22 3.21 3.20 3.19 3.17 3.15 3.12 3.02 3.00 3.00 2.99 2.98 2.97 2.80 2.78 2.78 2.75 2.74 2.73 2.72 2.70 2.68 1.88 1.74 1.72 1.70 1.68 1.46 1.44 1.43 1.41
BocHN
CO2Me
Ph
OHC
O
N
Ph
3k, 400 MHz, CDCl3
Dr = 1.2:1
1.00 3.29 2.06 2.48 2.89 1.70 1.12 1.21 1.23 1.18 1.31 3.18 2.21 1.25 2.05 2.23 3.08 1.19 3.26 11.37
f1 (ppm)

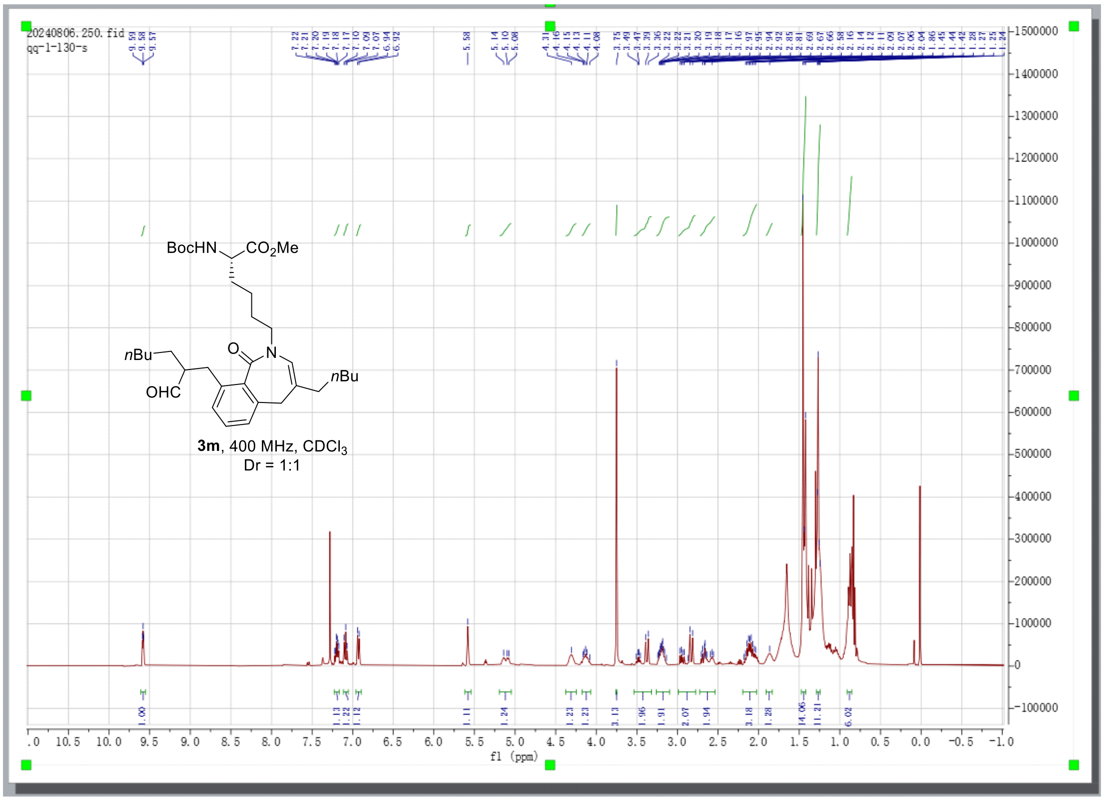

20240926-400.90.fid
qq-1-98
204.4
172.85 169.11
155.26 144.38 139.66 139.25 137.90 135.56 133.00 129.52 129.40 129.06 129.04 128.49 128.42 126.61 126.33 124.53 124.31 124.23
79.95
55.32 54.92 53.63 52.31 47.62 47.09 40.39 35.67 35.27 33.69 33.48 32.60 31.45 28.32 22.78
BocHN
CO2Me
Ph
OHC
O
N
Ph
3k, 101 MHz, CDCl3
Dr = 1.2:1
f1 (ppm)


20240927-600_14.fid
qq-1-129-zhang
BocHN
CO2Me
nBu
O
N
OHC
nBu
3l, 600 MHz, CDCl3
Dr = 1:1
1.00
1.16
1.15
1.08
1.11
1.22
1.21
1.22
3.10
1.96
1.82
1.99
1.80
3.07
1.19
6.18
11.09
16.22
6.11
f1 (ppm)

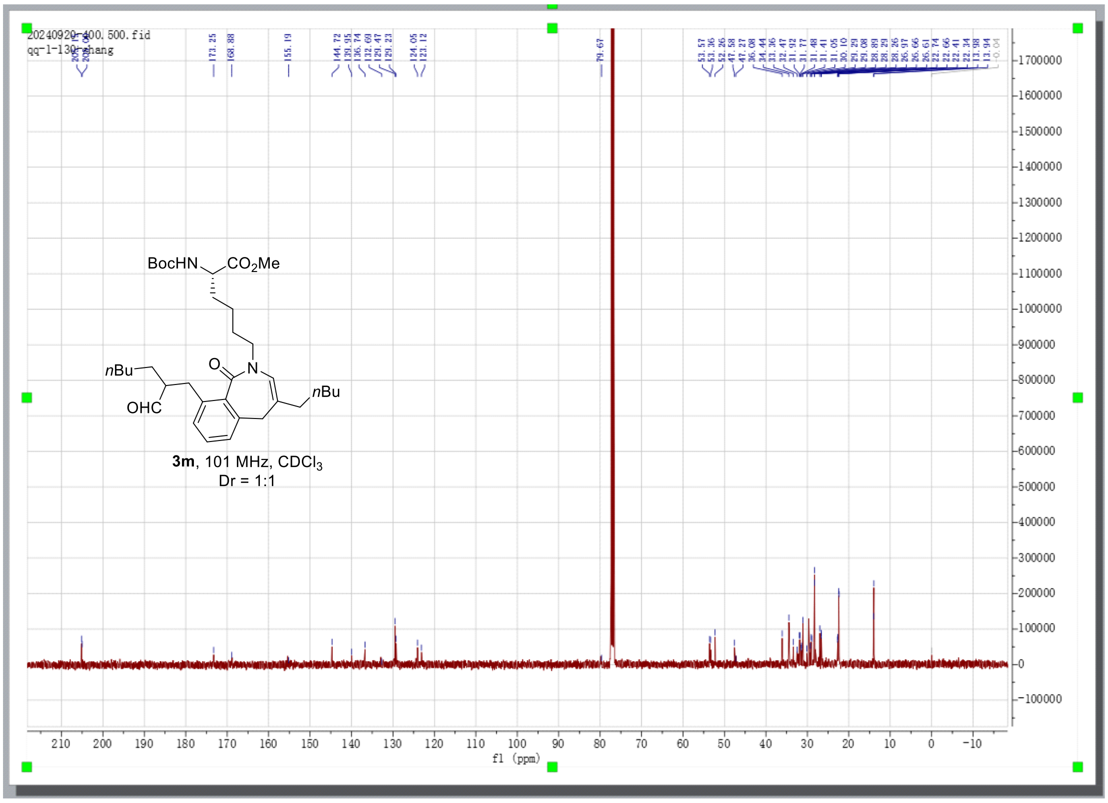

20240927-400, 380.fid
qq-1-129-zhang
BocHN
CO2Me
nBu
O
N
OHC
nBu
3l, 101 MHz, CDCl3
Dr = 1:1
f1 (ppm)


20240927-400. 371. fid
qq-1-129-xia
7.85 7.85 7.83 7.83 7.38 7.38 7.37 7.36 7.35 7.34 7.30 7.30 7.28 7.27 7.26 7.08 7.08 7.07 7.06 5.65 5.64 5.64 5.61 5.61 5.61 5.16 5.14 4.30 4.29 3.74 3.66 3.18 2.16 2.16 2.14 2.12 2.12 1.90 1.87 1.86 1.85 1.83 1.78 1.77 1.74 1.72 1.71 1.70 1.69 1.68 1.67 1.66 1.65 1.64 1.48 1.47 1.46 1.45 1.44 1.42 1.40 1.38 1.24 1.24 1.24 1.23 1.22 1.21 1.21
BocHN
CO2Me
O
N
nBu
3l', 400 MHz, CDCl3
0.94
1.00
1.19
1.00
0.96
0.96
1.06
3.05
1.97
1.82
2.04
2.06
5.04
14.02
4.36
3.01
f1 (ppm)

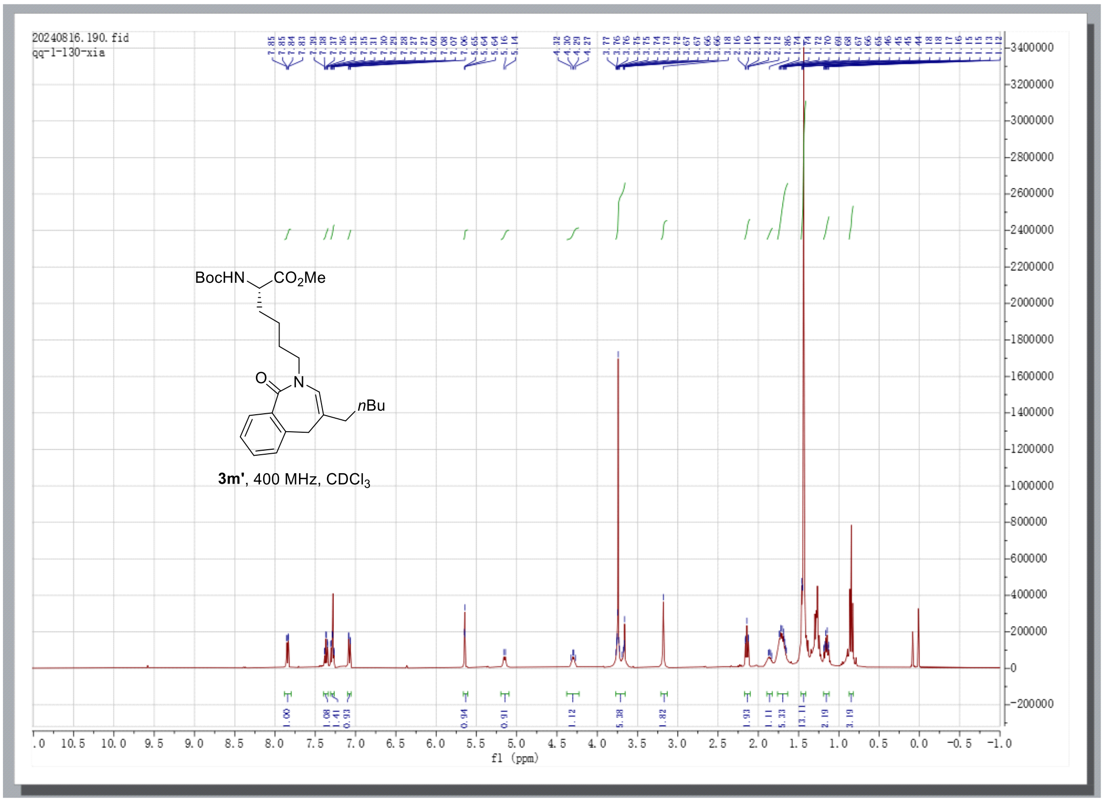

20240927-400. 370. fid
qq-1-129-xia
173.28 168.76 155.44 142.94 134.04 133.80 131.17 130.76 126.45 125.82 123.63 79.77 53.34 52.22 47.66 35.85 34.81 32.15 31.71 28.97 28.94 28.27 27.91 27.59 22.55 22.49 14.04
BocHN
CO2Me
O
N
nBu
3l', 101 MHz, CDCl3
f1 (ppm)



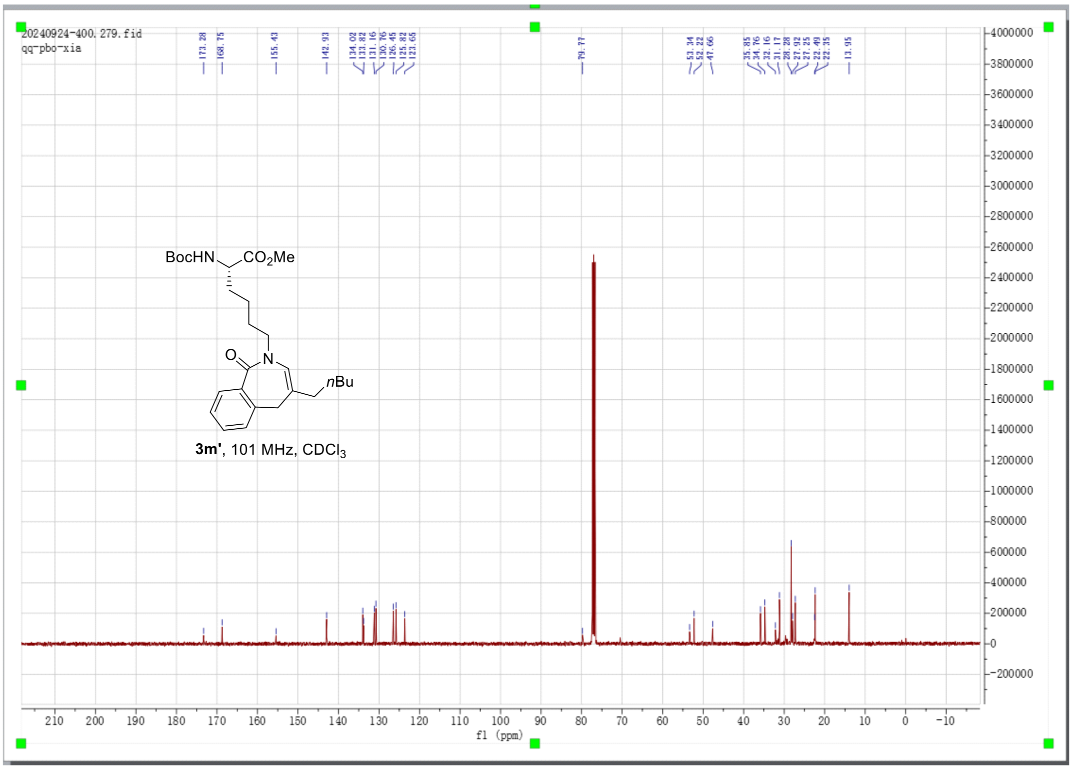
3m, 400 MHz, CDCl$_3$
Dr = 1:1



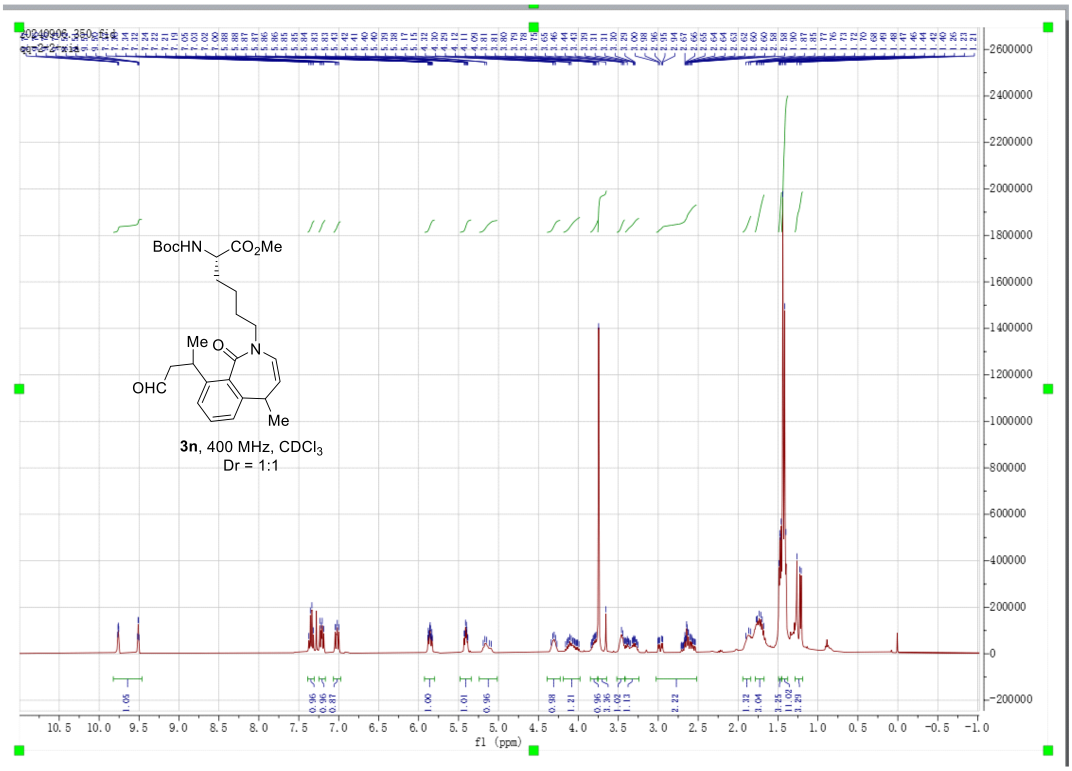
3m, 101 MHz, CDCl$_3$
Dr = 1:1

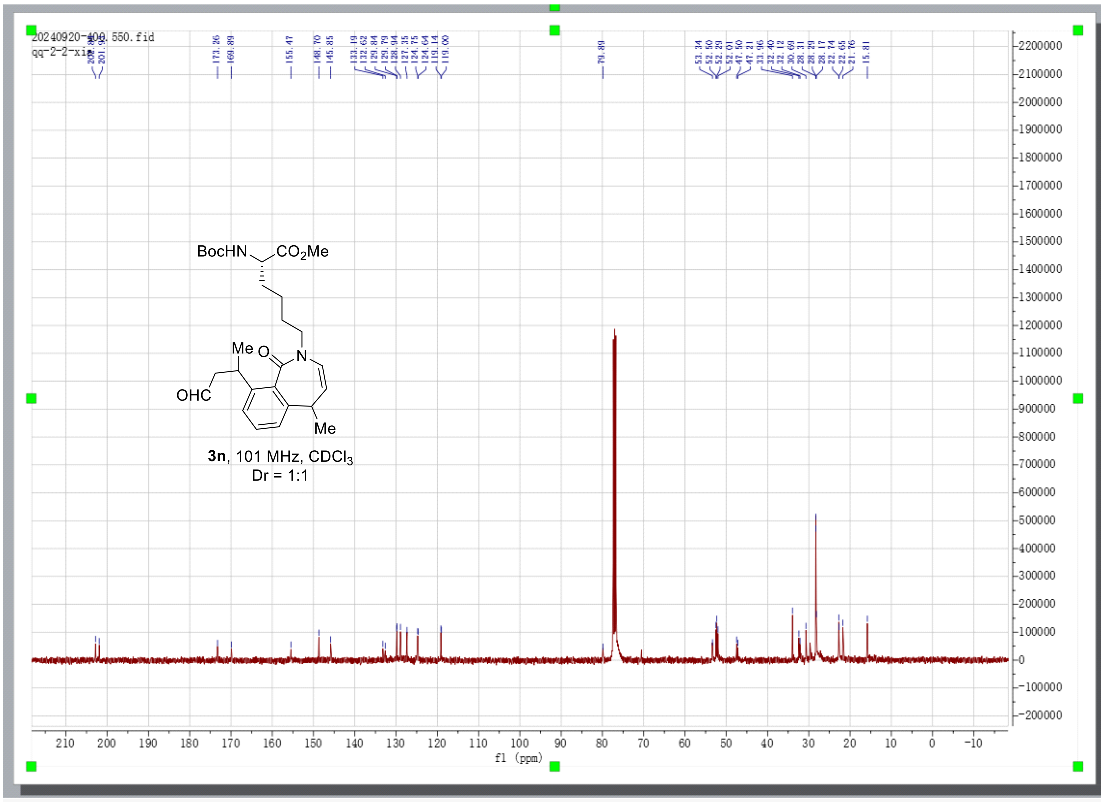


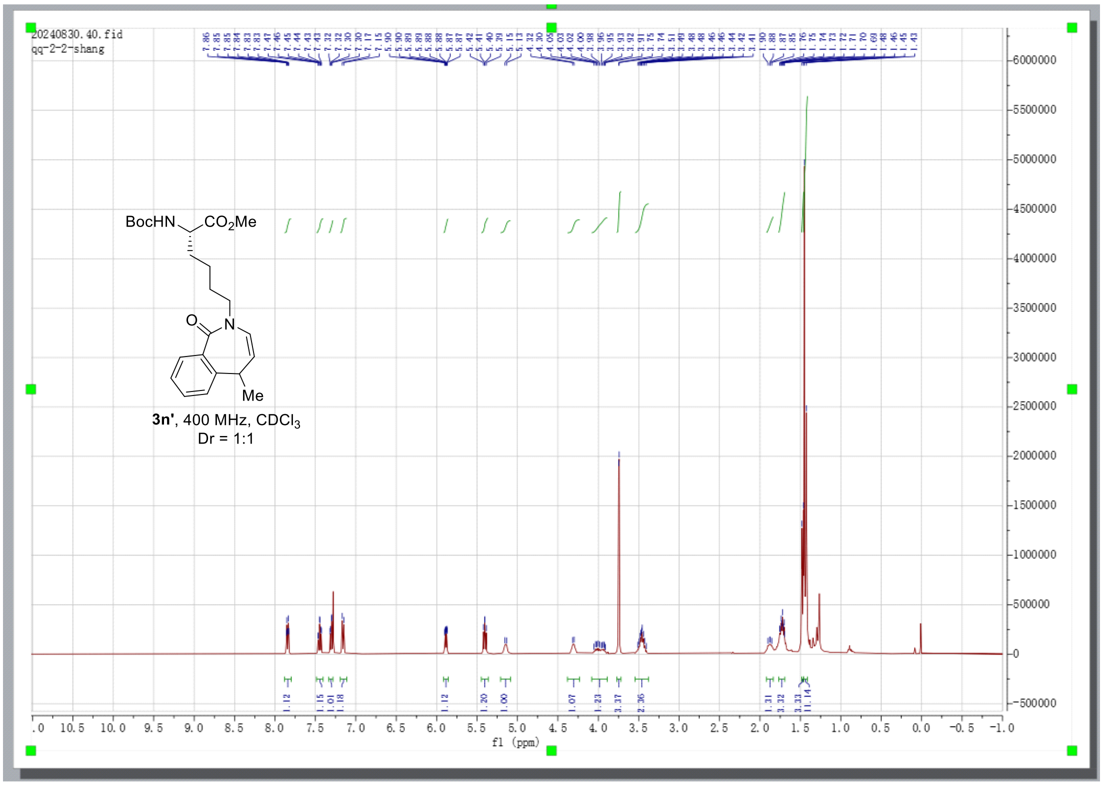
3m', 400 MHz, $CDCl_3$

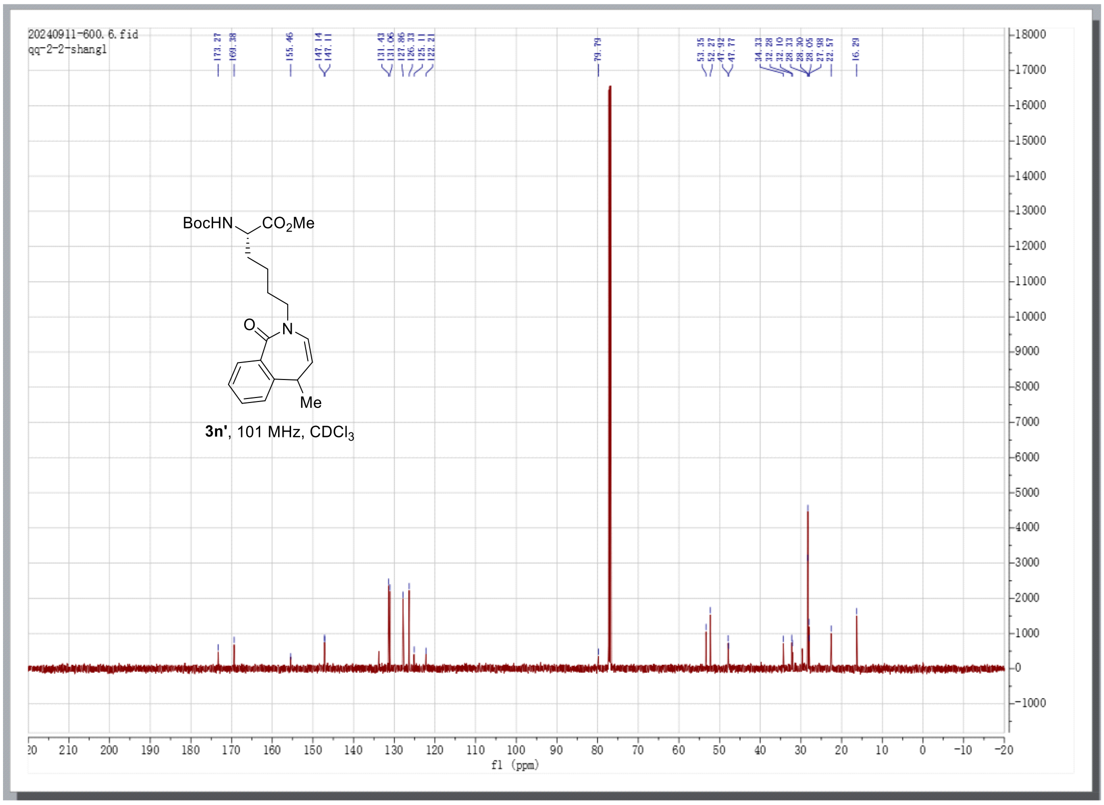


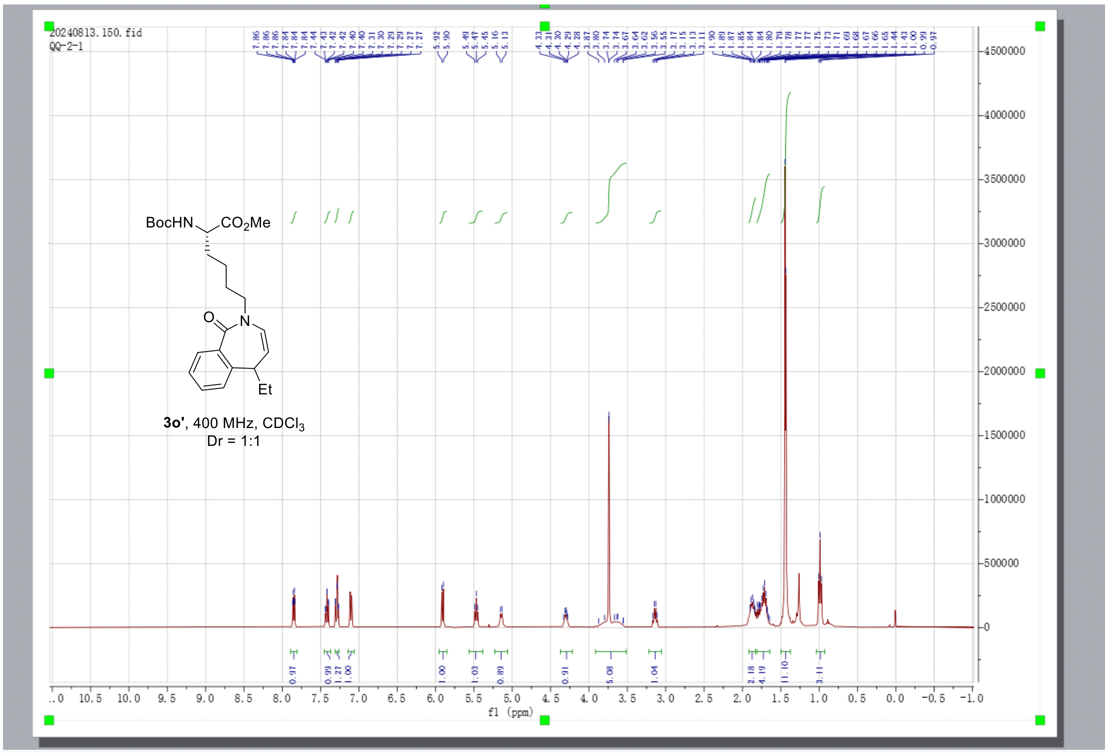
3m', 101 MHz, $CDCl_3$

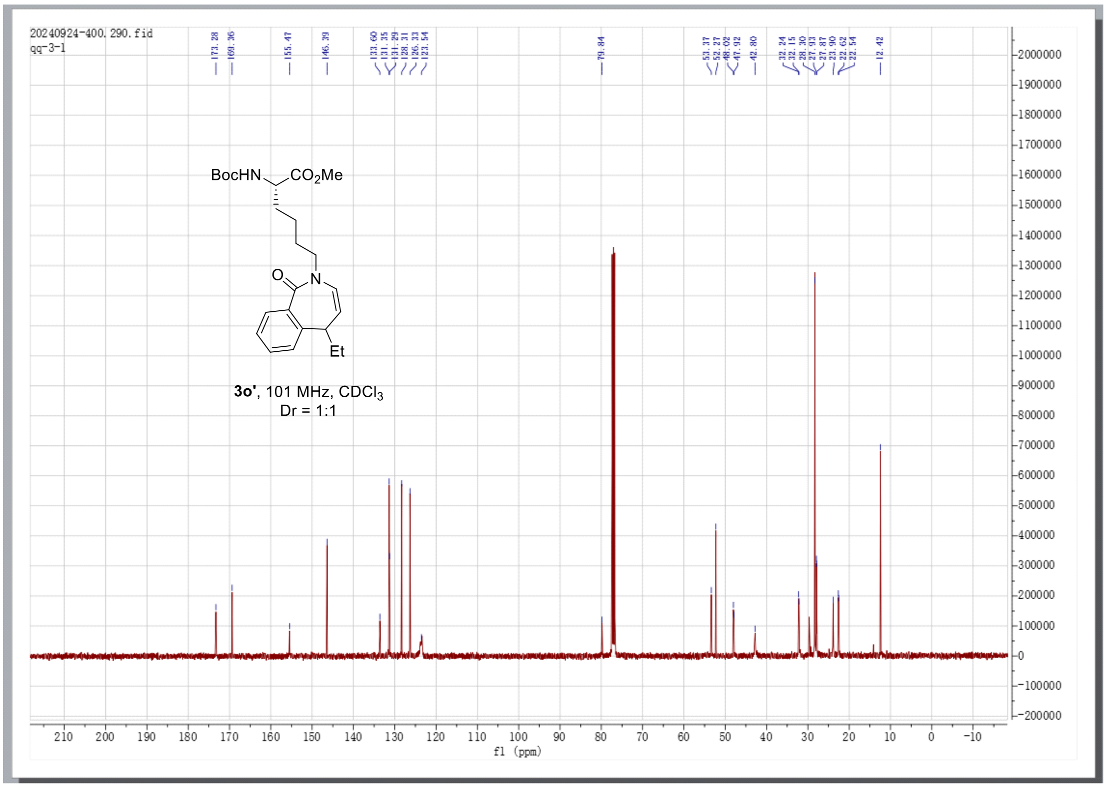

20240906-350.fid
qq-2-2-xia
7.34 7.32 7.24 7.22 7.21 7.19 7.05 7.03 7.02 7.00 5.88 5.88 5.87 5.86 5.86 5.85 5.85 5.84 5.83 5.83 5.43 5.42 5.41 5.40 5.40 5.39 5.38 5.17 5.15 4.32 4.30 4.29 4.12 4.11 4.09 3.81 3.81 3.80 3.79 3.78 3.75 3.65 3.46 3.44 3.43 3.39 3.31 3.31 3.30 3.29 3.00 2.98 2.96 2.95 2.94 2.67 2.66 2.65 2.64 2.64 2.63 2.62 2.60 2.60 2.58 2.58 1.90 1.87 1.85 1.77 1.76 1.73 1.72 1.70 1.68 1.49 1.48 1.47 1.46 1.44 1.42 1.40 1.26 1.23 1.21
BocHN
CO2Me
Me
O
N
OHC
Me
3n, 400 MHz, CDCl3
Dr = 1:1
1.05
0.96
0.96
0.87
1.00
1.01
0.96
0.98
1.21
0.96
3.36
1.02
1.13
2.22
1.32
3.04
3.25
11.02
3.29
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)
2600000 2400000 2200000 2000000 1800000 1600000 1400000 1200000 1000000 800000 600000 400000 200000 0 −200000


20240920-400.550.fid
qq-2-2-xia
201.9
173.26
169.89
155.47
148.70
145.85
133.19
132.62
129.84
129.79
128.94
127.35
124.75
124.64
119.14
119.00
79.89
53.34
52.50
52.29
52.01
47.50
47.21
33.96
32.40
32.12
30.69
28.31
28.29
28.17
22.74
22.65
21.76
15.81
BocHN
CO2Me
Me
O
N
OHC
Me
3n, 101 MHz, CDCl3
Dr = 1:1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
2200000 2100000 2000000 1900000 1800000 1700000 1600000 1500000 1400000 1300000 1200000 1100000 1000000 900000 800000 700000 600000 500000 400000 300000 200000 100000 0 −100000 −200000

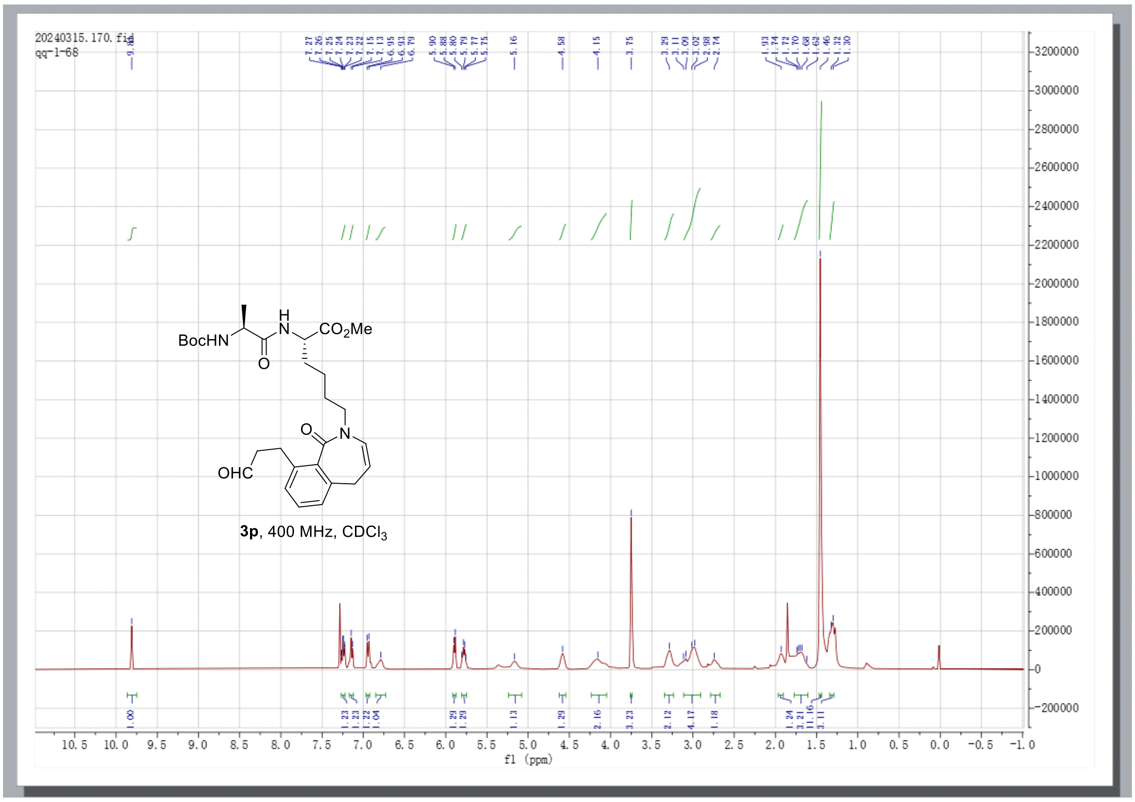

20240830.40.fid
qq-2-2-shang
7.86 7.85 7.85 7.84 7.83 7.83 7.47 7.46 7.45 7.44 7.43 7.43 7.32 7.32 7.30 7.30 7.17 7.15 5.90 5.90 5.89 5.89 5.88 5.88 5.87 5.87 5.42 5.41 5.40 5.39 5.15 5.13 4.32 4.30 4.05 4.03 4.02 4.00 3.98 3.96 3.95 3.93 3.92 3.91 3.75 3.74 3.51 3.49 3.48 3.48 3.46 3.46 3.44 3.42 3.41 1.90 1.88 1.87 1.85 1.76 1.75 1.74 1.73 1.72 1.71 1.70 1.69 1.48 1.46 1.45 1.43
BocHN
CO_2Me
O
N
Me
3n', 400 MHz, $CDCl_3$
Dr = 1:1
1.12 1.15 1.01 1.18 1.12 1.20 1.00 1.07 1.23 3.37 2.36 1.31 3.32 3.33 11.14
f1 (ppm)

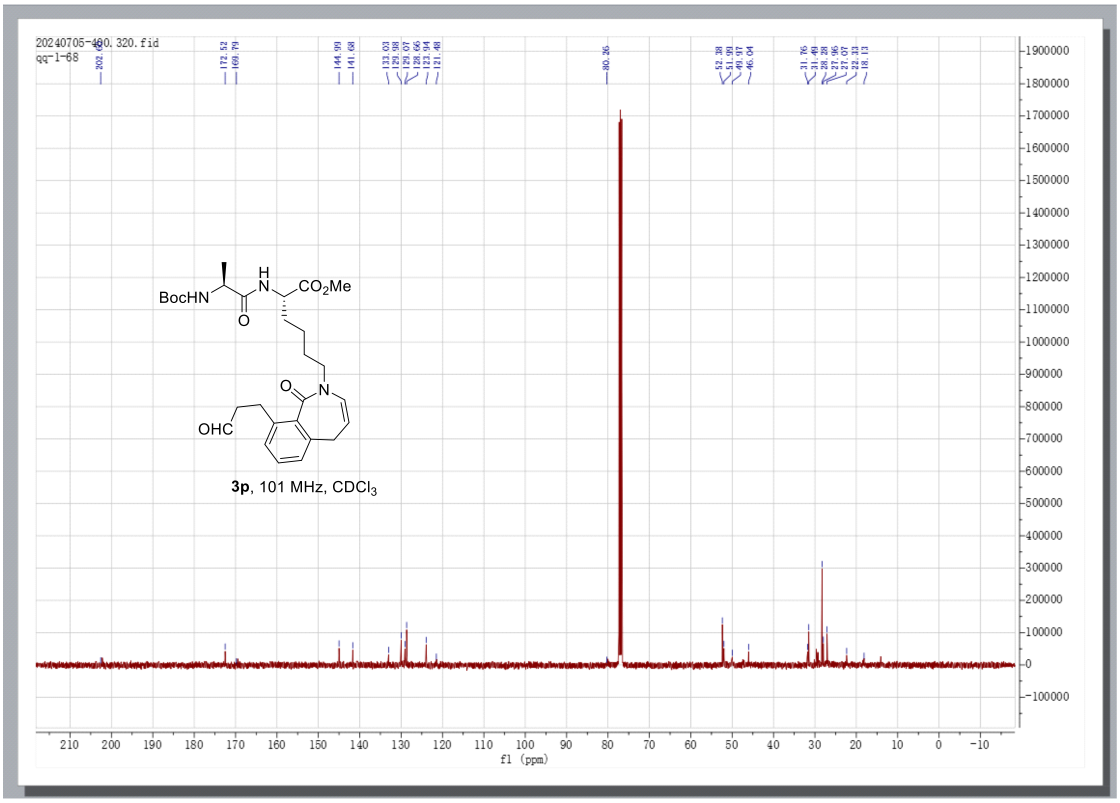

20240911-600.6.fid
qq-2-2-shang1
173.27 169.38 155.46 147.14 147.11 131.43 131.06 127.86 126.33 125.11 122.21 79.79 53.35 52.27 47.92 47.77 34.23 32.28 32.10 28.33 28.30 28.05 27.98 22.57 16.29
BocHN
CO_2Me
O
N
Me
3n', 101 MHz, $CDCl_3$
f1 (ppm)

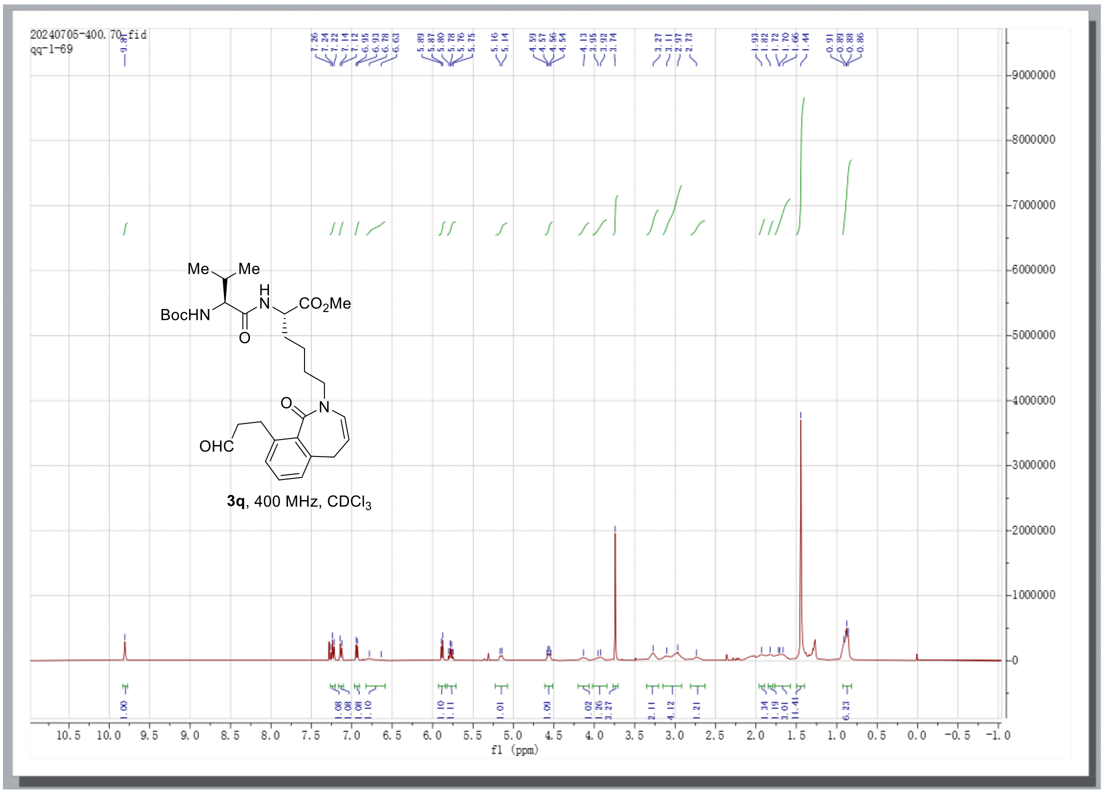

20240813.150.fid
QQ-2-1
7.86 7.86 7.84 7.84 7.44 7.43 7.42 7.42 7.40 7.40 7.31 7.30 7.29 7.27 7.27 5.92 5.90 5.49 5.47 5.45 5.16 5.13 4.33 4.31 4.30 4.29 4.28 3.87 3.80 3.74 3.74 3.67 3.64 3.62 3.56 3.55 3.17 3.15 3.13 3.11 1.90 1.89 1.87 1.85 1.84 1.84 1.80 1.79 1.78 1.77 1.77 1.75 1.73 1.71 1.69 1.68 1.67 1.66 1.65 1.44 1.00 0.99 0.97
BocHN
CO2Me
O
N
Et
3o', 400 MHz, CDCl3
Dr = 1:1
0.97 0.99 1.27 1.00 1.00 1.03 0.89 0.91 5.08 1.04 2.18 4.19 11.10 3.11
f1 (ppm)


20240924-400.290.fid
qq-3-1
173.28 169.36 155.47 146.39 133.60 131.35 131.29 128.31 126.31 123.54 79.84 53.37 52.27 48.02 47.92 42.80 32.24 32.15 28.30 27.93 27.87 23.90 22.62 22.54 12.42
BocHN
CO2Me
O
N
Et
3o', 101 MHz, CDCl3
Dr = 1:1
f1 (ppm)

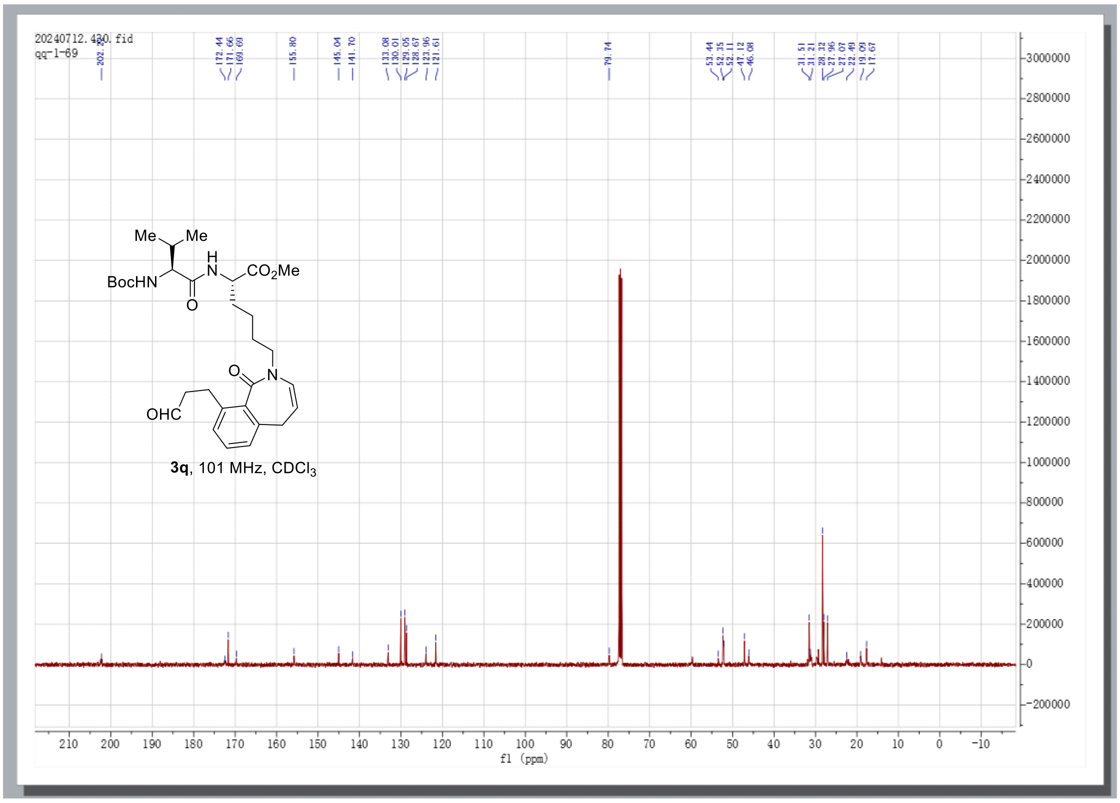
f


20240315.170.fid
qq-1-68
9.80
7.27 7.26 7.25 7.24 7.23 7.22 7.15 7.13 6.95 6.93 6.79
5.90 5.88 5.80 5.79 5.77 5.75
5.16
4.58
4.15
3.75
3.29 3.11 3.09 3.02 2.98 2.74
1.93 1.74 1.72 1.70 1.68 1.62 1.46 1.32 1.30
BocHN
H
N
CO2Me
O
O
N
OHC
3p, 400 MHz, CDCl3
1.00 1.23 1.23 1.22 1.04 1.29 1.29 1.13 1.29 2.16 3.23 2.12 4.17 1.18 1.24 3.21 1.16 3.11
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
3200000 3000000 2800000 2600000 2400000 2200000 2000000 1800000 1600000 1400000 1200000 1000000 800000 600000 400000 200000 0 -200000

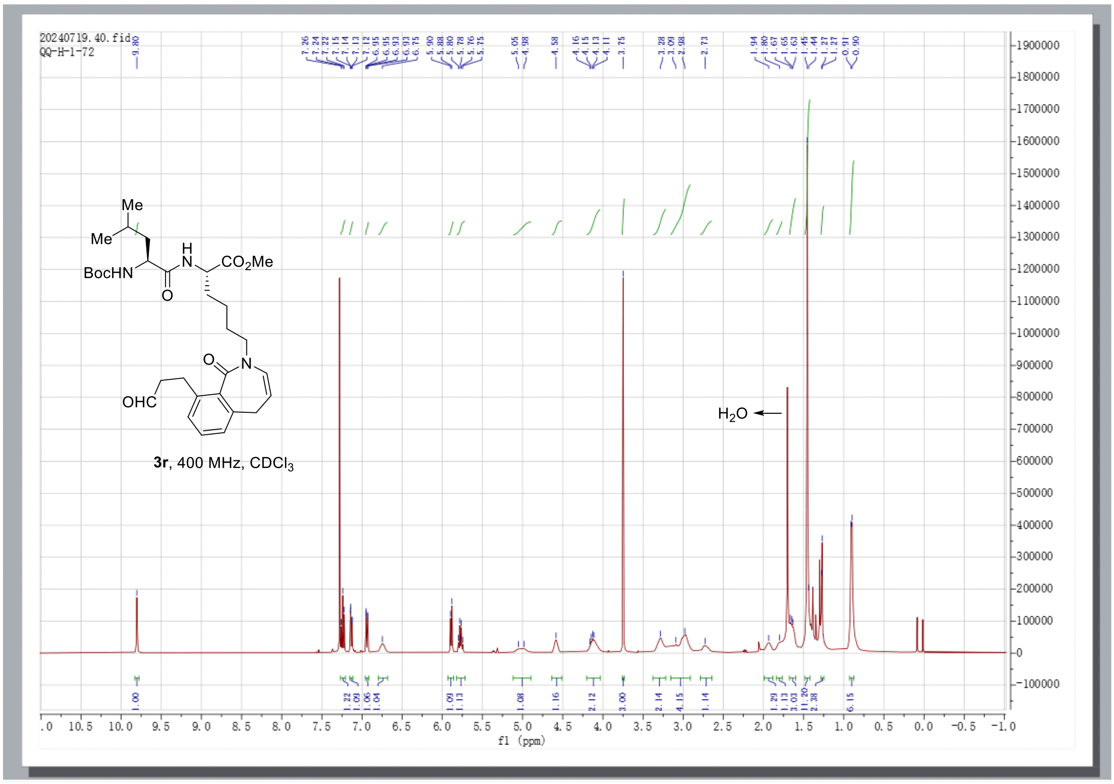

20240705-400.320.fid
qq-1-68
202.63
172.52 169.79
144.99 141.68
133.03 129.98 129.07 128.66 123.94 121.48
80.26
52.38 51.99 49.97 46.04
31.76 31.49 28.28 27.96 27.07 22.33 18.13
BocHN
H
N
CO2Me
O
O
N
OHC
3p, 101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
1900000 1800000 1700000 1600000 1500000 1400000 1300000 1200000 1100000 1000000 900000 800000 700000 600000 500000 400000 300000 200000 100000 0 -100000

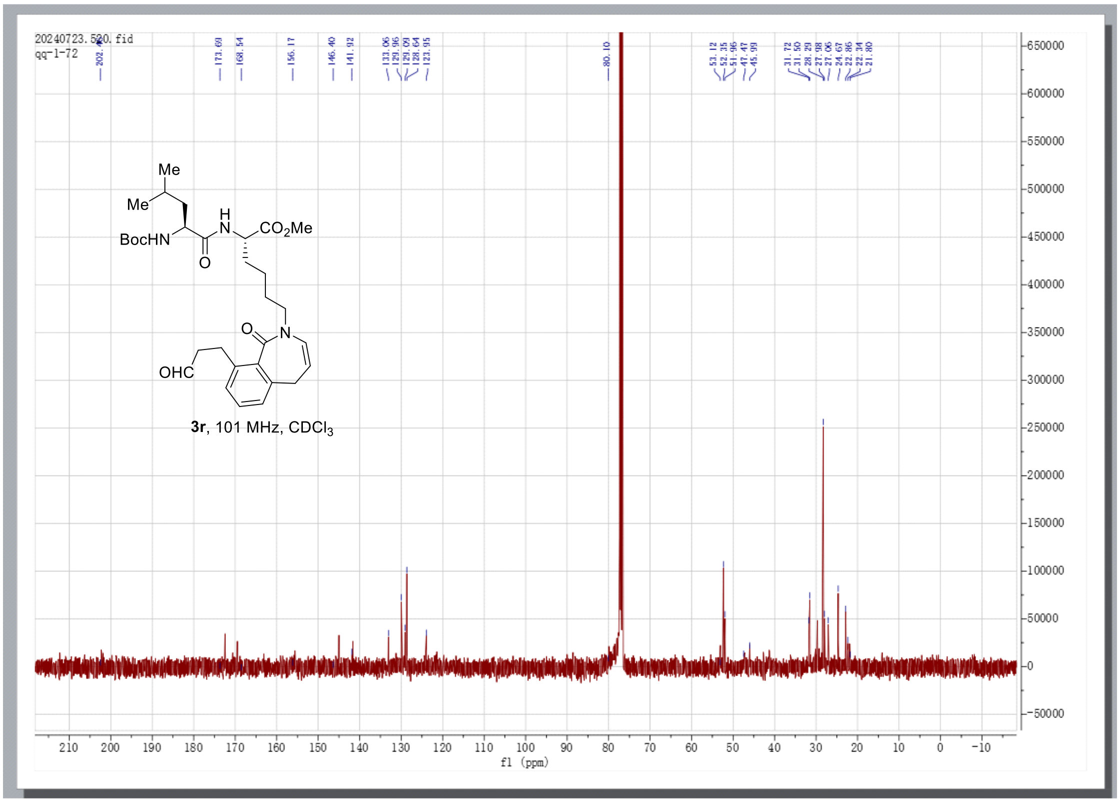


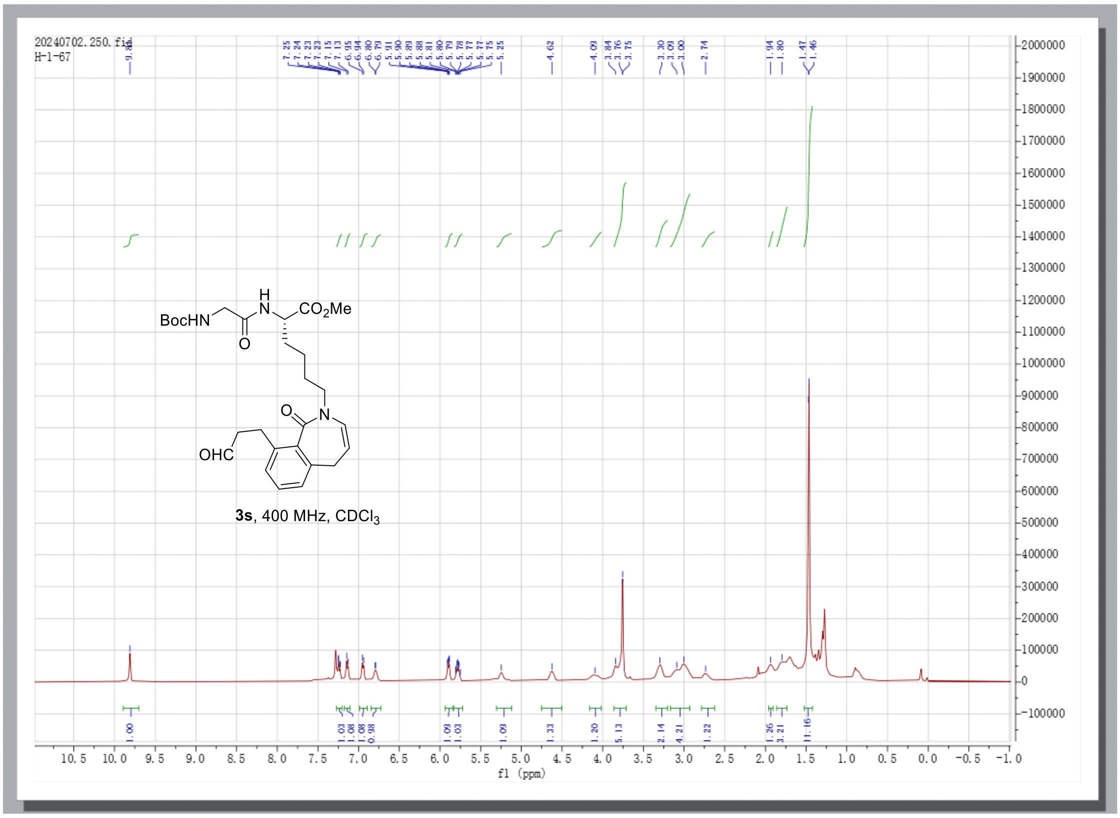
3q, 400 MHz, $CDCl_3$



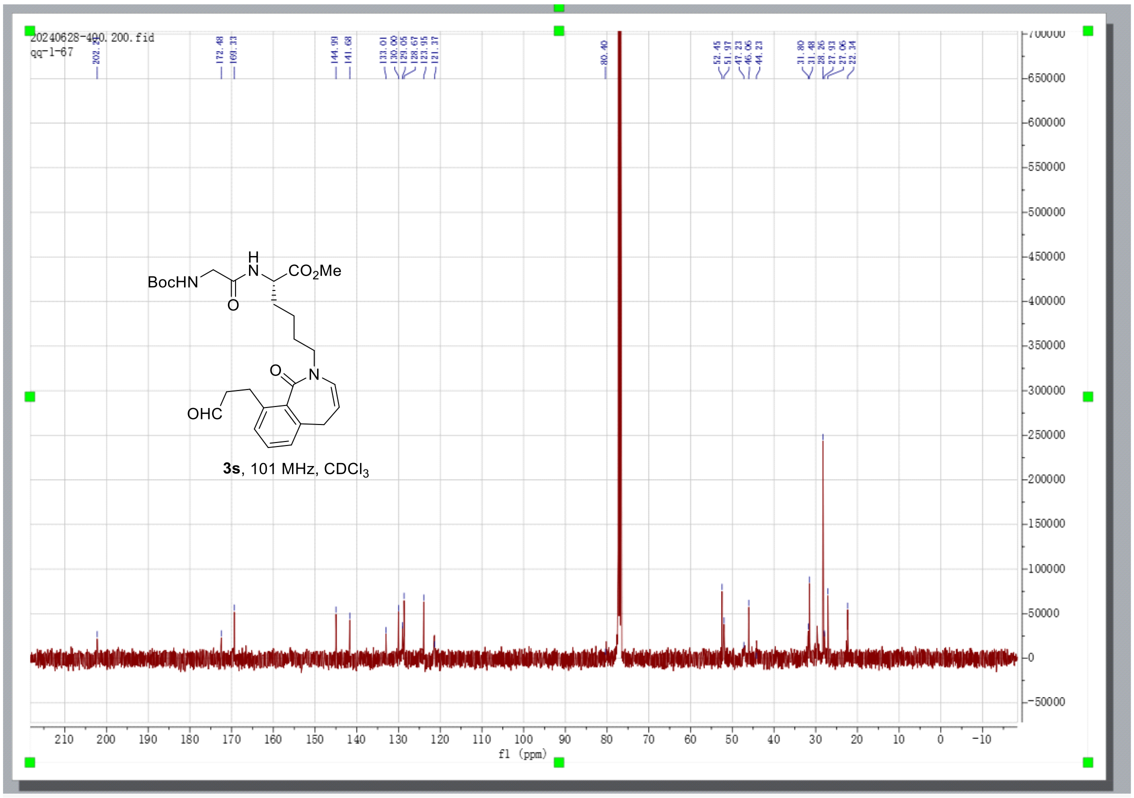
3q, 101 MHz, $CDCl_3$


20240719.40.fid
QQ-H-1-72
9.80
7.26 7.24 7.22 7.15 7.14 7.13 7.12 6.95 6.93 6.93 6.75
5.90 5.88 5.80 5.78 5.76 5.75
5.05 4.98
4.58
4.16 4.15 4.13 4.11
3.75
3.28 3.09 2.98
2.73
1.94 1.80 1.67 1.65 1.63 1.45 1.44 1.27 1.27 0.91 0.90
1.00
1.22 1.09 1.06 1.04
1.09 1.13
1.08
1.16
2.12
3.00
2.14
4.15
1.14
1.29 1.13 3.03 11.20 2.38
6.15
H2O
Me
Me
BocHN
H
N
CO2Me
O
O
N
OHC
3r, 400 MHz, CDCl3
f1 (ppm)

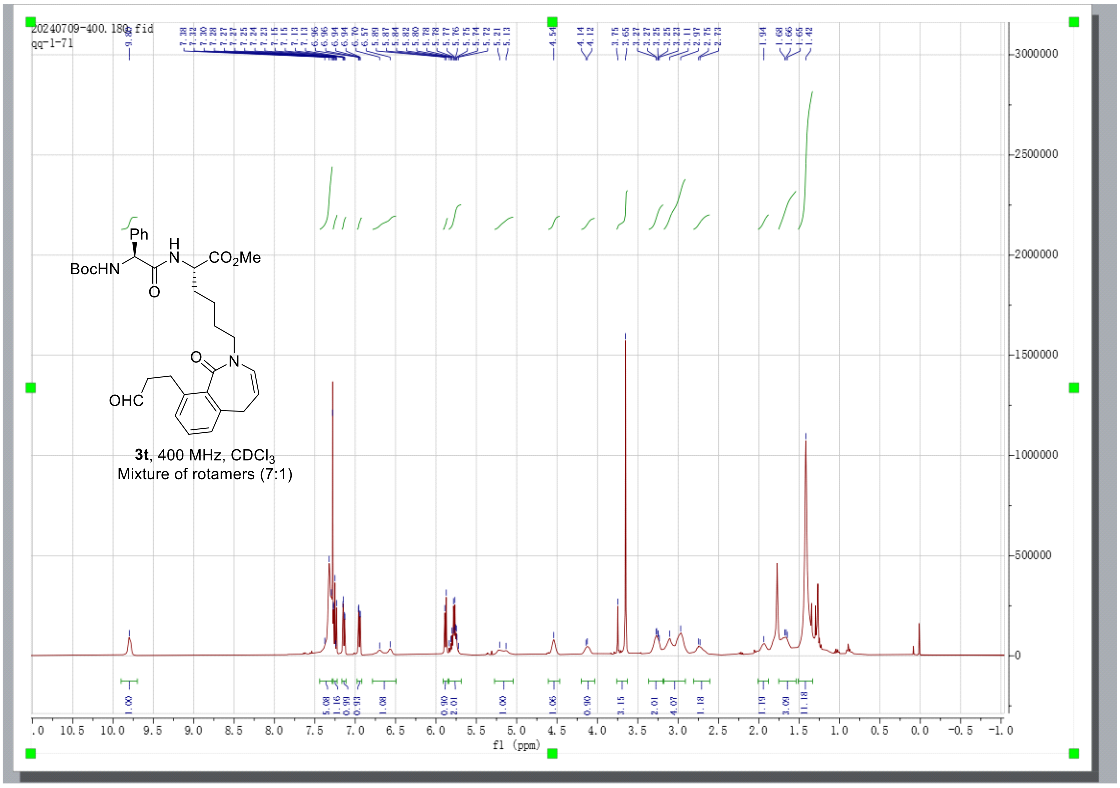

20240723.520.fid
qq-1-72
202.
171.69
168.54
156.17
146.40
141.92
133.06 129.96 129.09 128.64 123.95
80.10
53.12 52.35 51.96 47.47 45.99
31.72 31.50 28.29 27.98 27.06 24.67 22.86 22.34 21.80
Me
Me
BocHN
H
N
CO2Me
O
O
N
OHC
3r, 101 MHz, CDCl3
f1 (ppm)

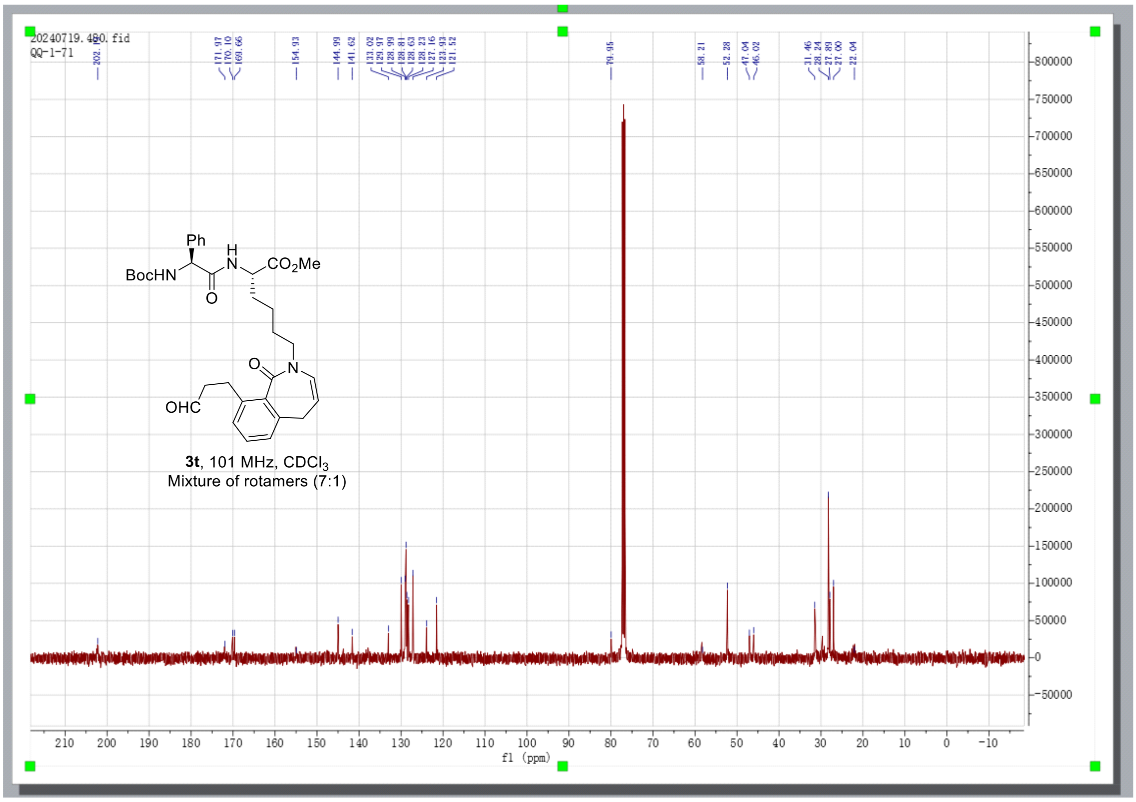


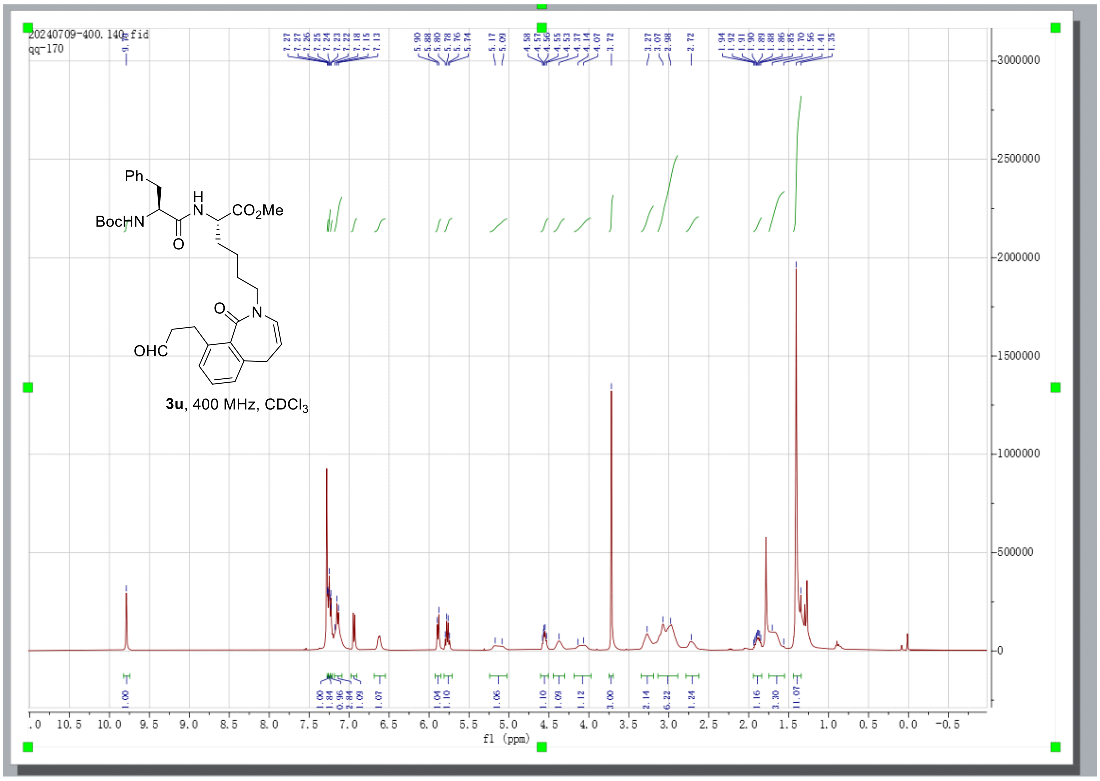
3s, 400 MHz, $CDCl_3$

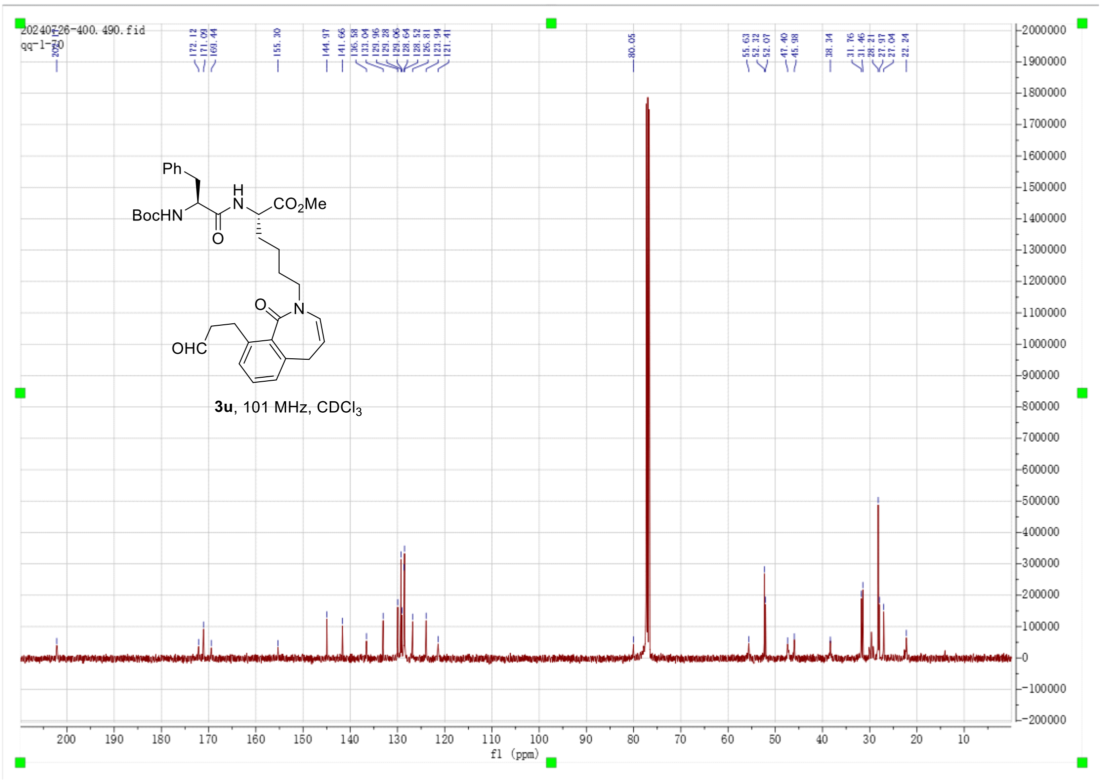


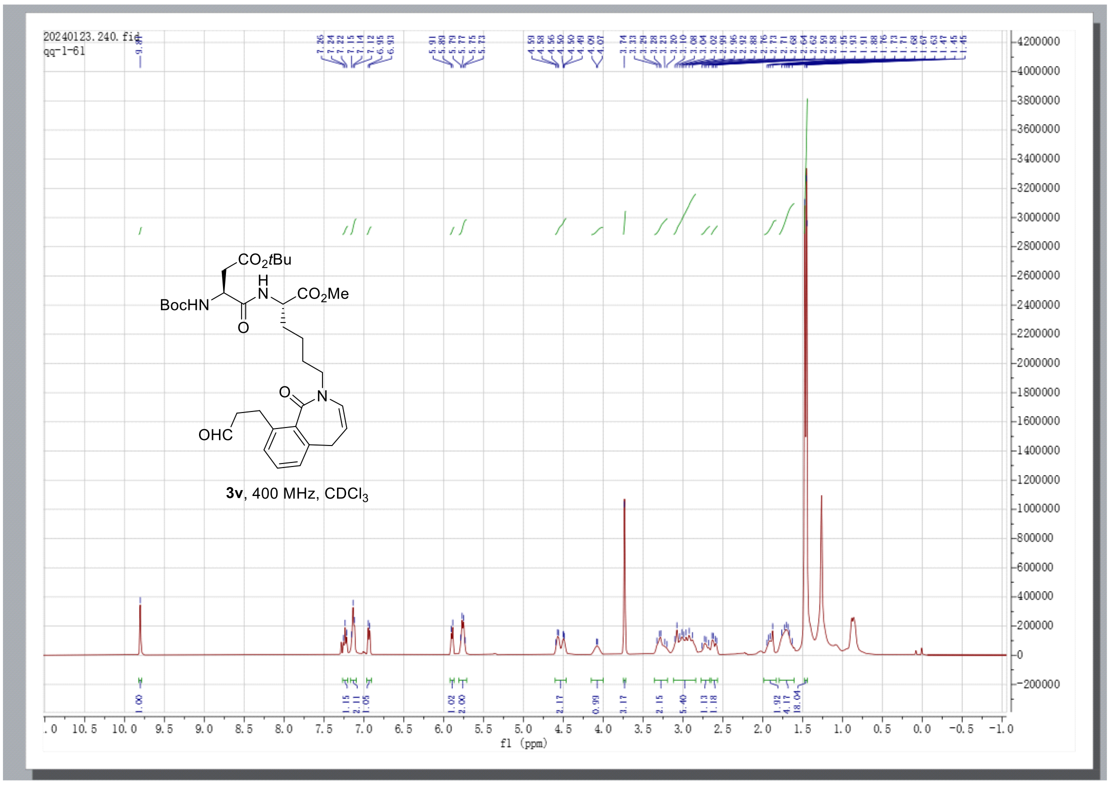
3s, 101 MHz, $CDCl_3$

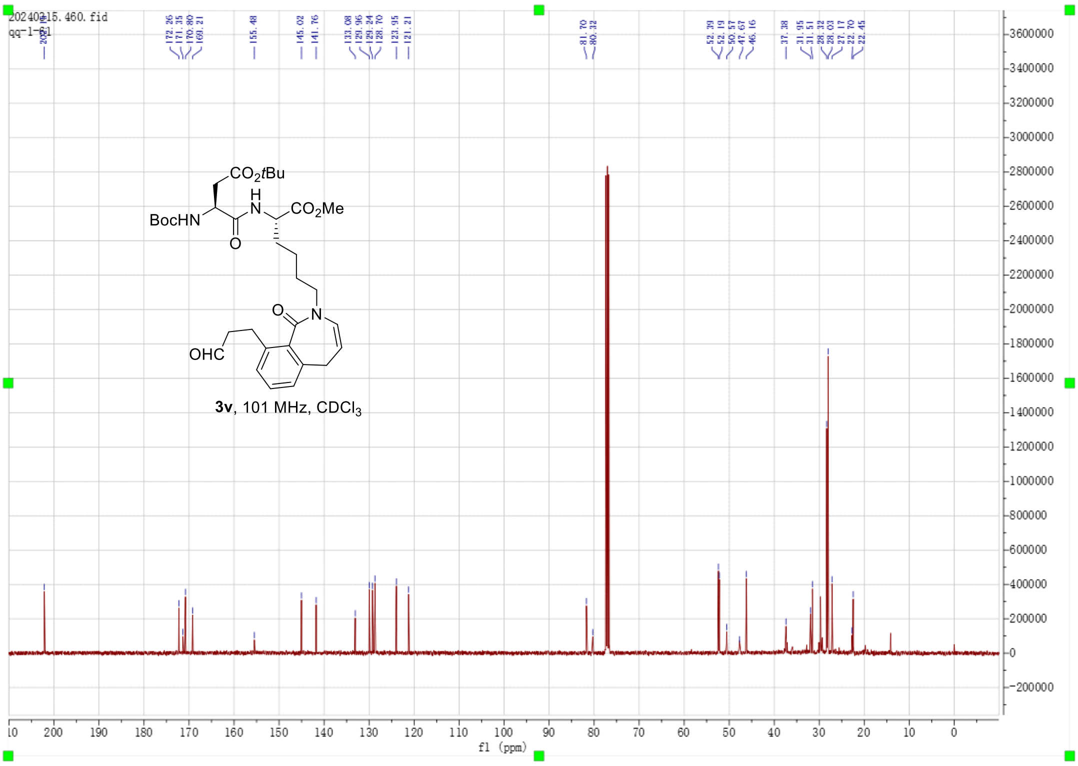

20240709-400.180.fid
qq-1-71
9.80
7.38 7.32 7.30 7.28 7.27 7.27 7.25 7.24 7.23 7.15 7.15 7.13 7.13 6.96 6.96 6.94 6.94 6.70 6.57 5.89 5.87 5.84 5.82 5.80 5.78 5.78 5.77 5.76 5.75 5.74 5.72 5.21 5.13
4.54 4.14 4.12
3.75 3.65 3.27 3.27 3.25 3.25 3.23 3.11 2.97 2.75 2.73
1.94 1.68 1.66 1.65 1.42
Ph
H
N
BocHN
CO_2Me
O
O
N
OHC
3t, 400 MHz, $CDCl_3$
Mixture of rotamers (7:1)
1.00
5.08 1.16 0.99 0.93 1.08
0.90 2.01 1.00 1.06 0.90 3.15 2.01 4.07 1.18 1.19 3.09 11.18
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
3000000
2500000
2000000
1500000
1000000
500000
0

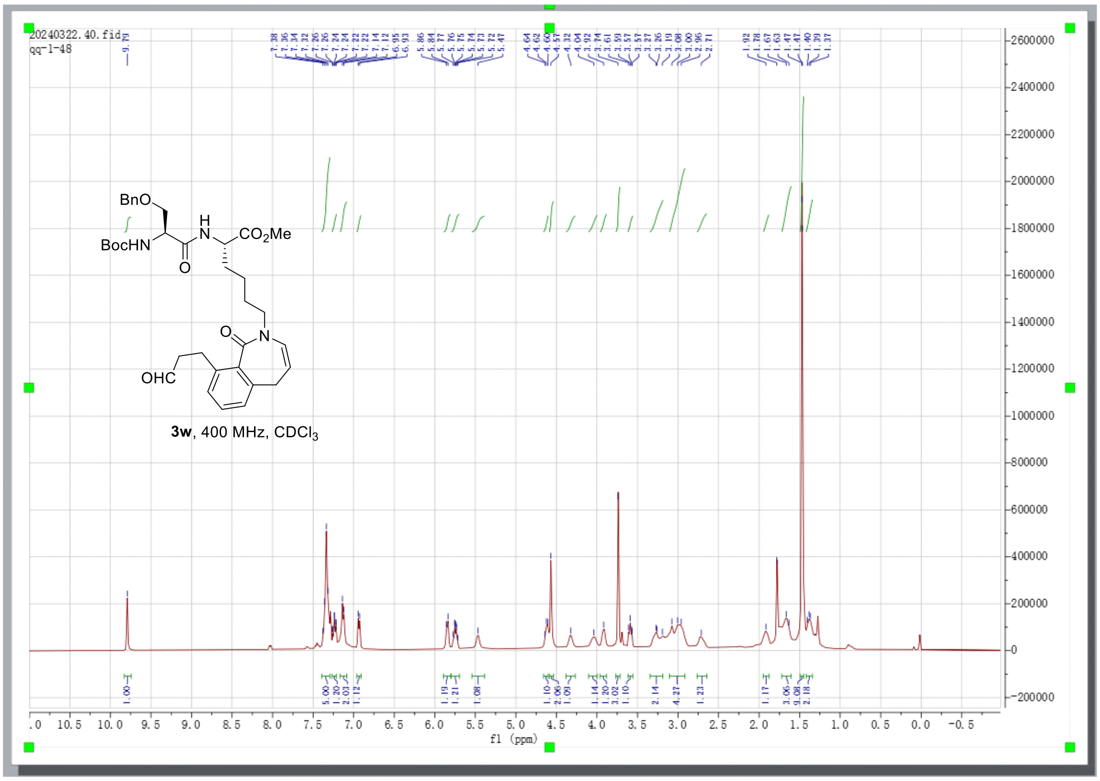

20240719.480.fid
QQ-1-71
202.10
171.97 170.10 169.66
154.93
144.99 141.62
133.02 129.97 128.99 128.81 128.63 128.23 127.16 123.93 121.52
79.95
58.21 52.28 47.04 46.02
31.46 28.24 27.89 27.00 22.04
Ph
H
N
BocHN
CO_2Me
O
O
N
OHC
3t, 101 MHz, $CDCl_3$
Mixture of rotamers (7:1)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
800000
750000
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000

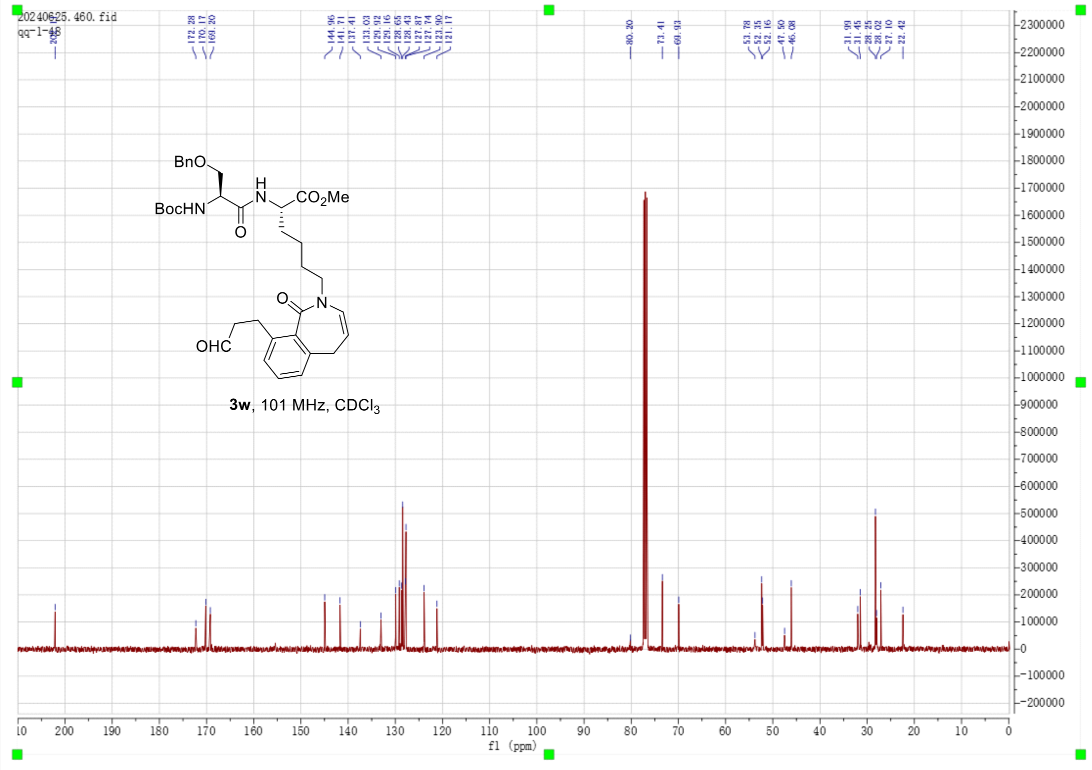

20240709-400.140.fid
qq-170
9.78
7.27 7.27 7.26 7.25 7.24 7.23 7.22 7.18 7.15 7.13
5.90 5.88 5.80 5.78 5.76 5.74
5.17 5.09
4.58 4.57 4.56 4.55 4.53 4.37 4.14 4.07
3.72
3.27 3.07 2.98
2.72
1.94 1.92 1.91 1.90 1.89 1.88 1.86 1.85 1.70 1.56 1.41 1.35
Ph
BocHN
H
N
CO2Me
O
O
N
OHC
3u, 400 MHz, CDCl3
1.00 1.00 1.84 0.96 2.04 1.09 1.07 1.04 1.10 1.06 1.10 1.09 1.12 3.00 2.14 6.22 1.24 1.16 3.30 11.07
3000000
2500000
2000000
1500000
1000000
500000
0
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

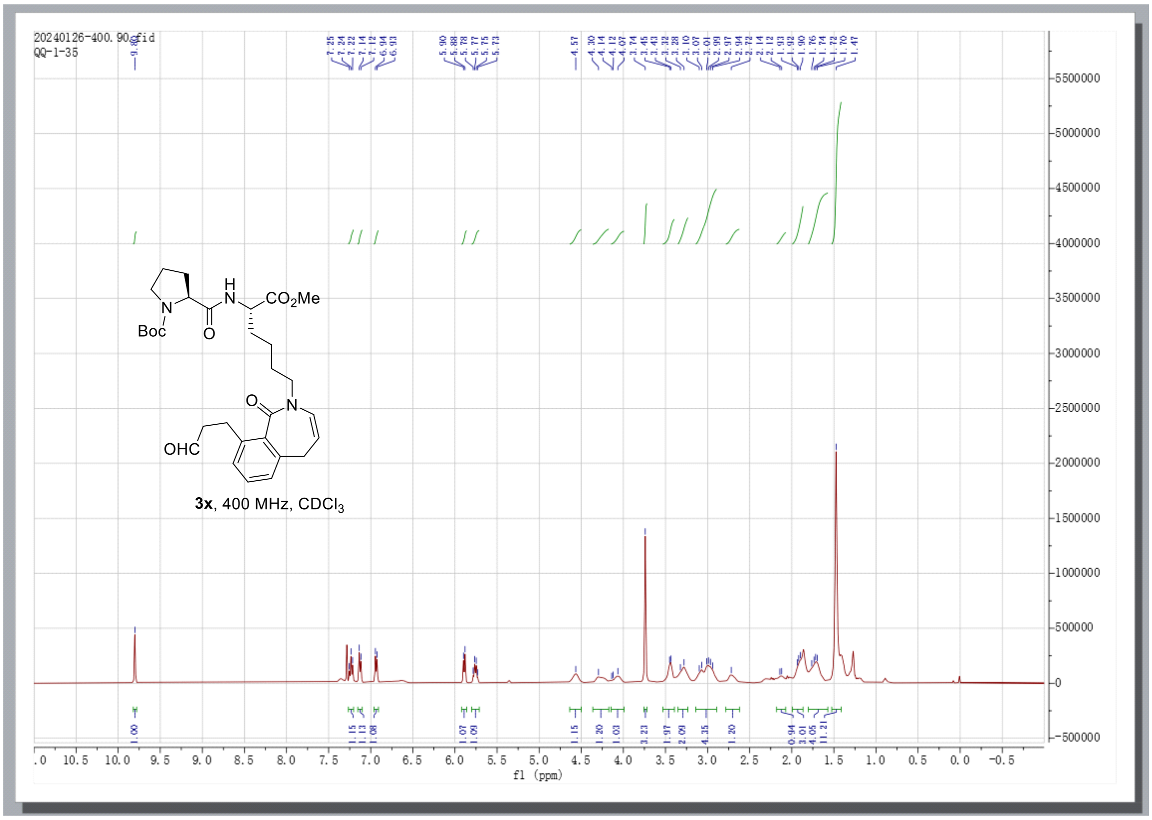

20240726-400.490.fid
qq-1-70
201.71
172.12 171.09 169.44
155.30
144.97 141.66 136.58 133.04 129.96 129.28 129.06 128.64 128.52 126.81 123.94 121.41
80.05
55.63 52.32 52.07
47.40 45.98
38.34
31.76 31.46 28.21 27.97 27.04
22.24
Ph
BocHN
H
N
CO2Me
O
O
N
OHC
3u, 101 MHz, CDCl3
2000000
1900000
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
-200000
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

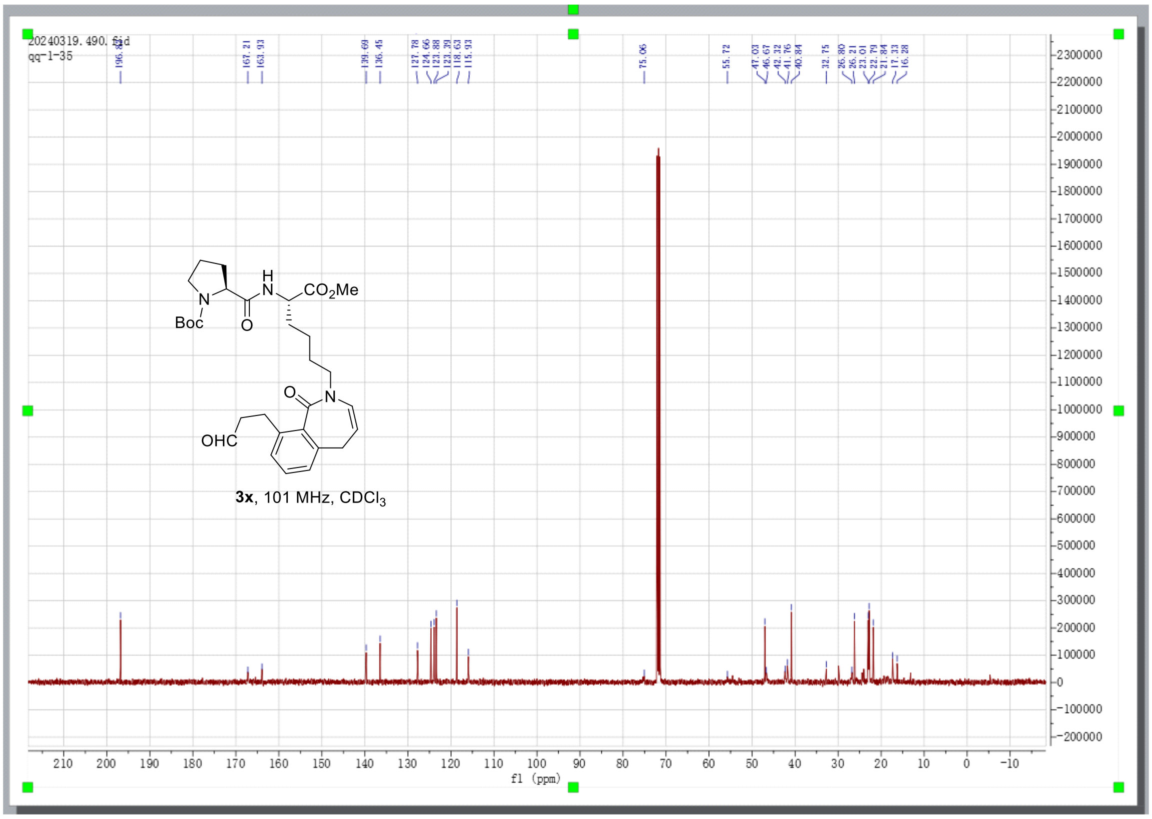

3v, 400 MHz, $CDCl_3$

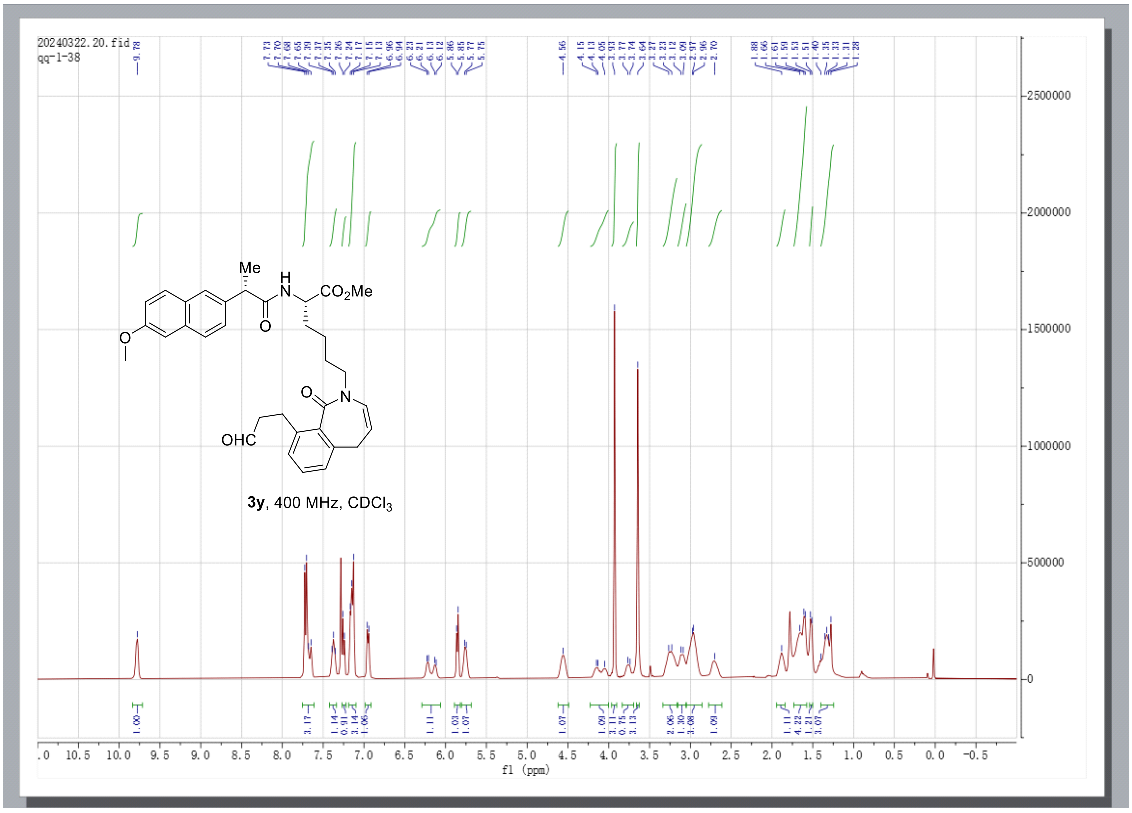

3v, 101 MHz, $CDCl_3$

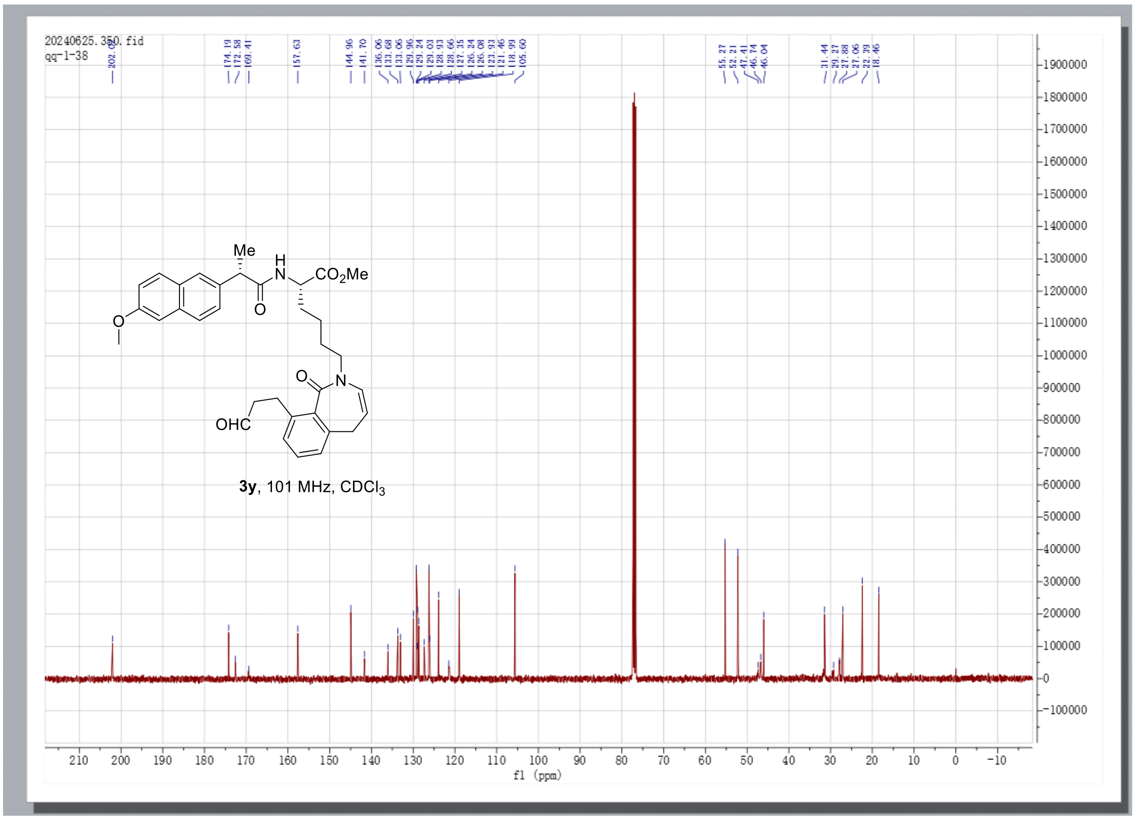

20240322.40.fid
qq-1-48
9.79
7.38 7.36 7.34 7.32 7.26 7.26 7.24 7.24 7.22 7.22 7.14 7.12 6.95 6.93
5.86 5.84 5.77 5.76 5.75 5.74 5.73 5.72 5.47
4.64 4.62 4.60 4.57 4.32 4.04 3.92 3.74 3.61 3.59 3.57 3.57 3.27 3.26 3.19 3.08 3.00 2.96 2.71
1.92 1.78 1.67 1.63 1.47 1.47 1.40 1.39 1.37
BnO
H
N
CO$_2$Me
BocHN
O
O
N
OHC
3w, 400 MHz, CDCl$_3$
1.00
5.00 1.20 2.01 1.12
1.19 1.21 1.08
1.10 2.06 1.09 1.14 1.20 3.02 1.10 2.14 4.27 1.23
1.17 3.06 9.08 2.18
2600000 2400000 2200000 2000000 1800000 1600000 1400000 1200000 1000000 800000 600000 400000 200000 0 −200000
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

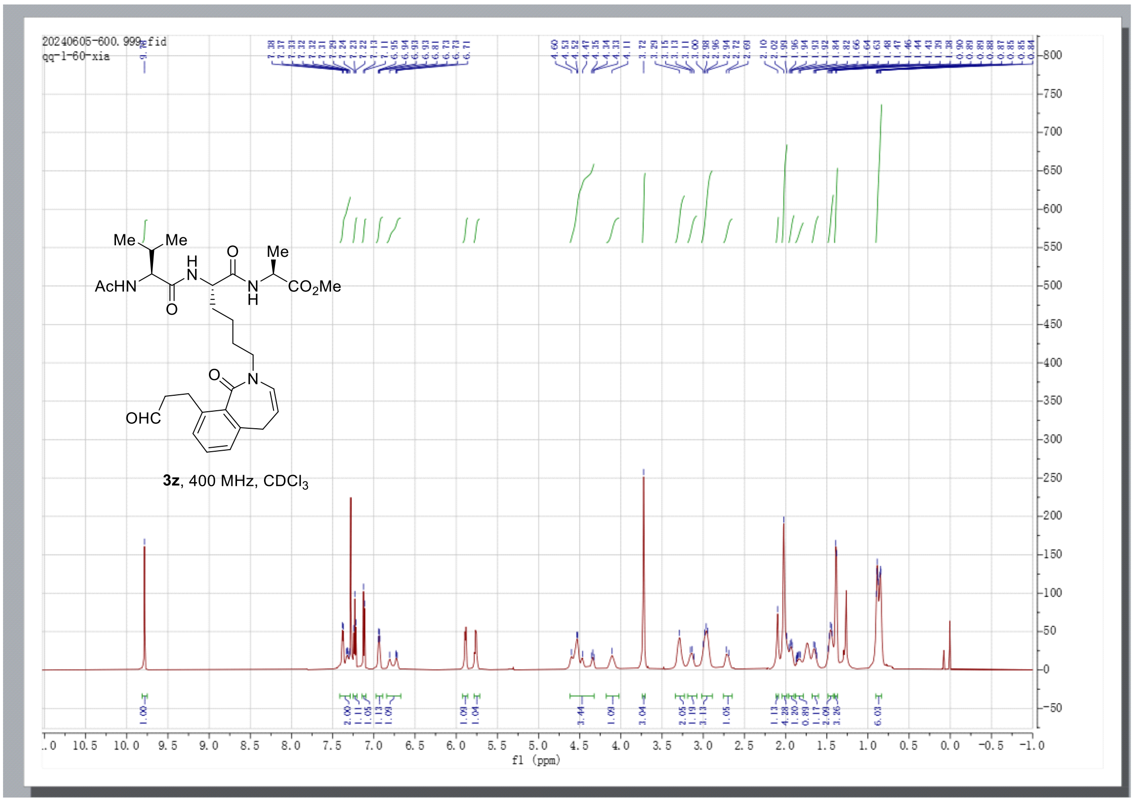

20240625.460.fid
qq-1-48
201.92
172.28 170.17 169.20
144.96 141.71 137.41 133.03 129.92 129.16 128.65 128.43 127.87 127.74 123.90 121.17
80.20
73.41
69.93
53.78 52.35 52.16 47.50 46.08
31.99 31.45 28.25 28.02 27.10 22.42
BnO
H
N
CO$_2$Me
BocHN
O
O
N
OHC
3w, 101 MHz, CDCl$_3$
2300000 2200000 2100000 2000000 1900000 1800000 1700000 1600000 1500000 1400000 1300000 1200000 1100000 1000000 900000 800000 700000 600000 500000 400000 300000 200000 100000 0 −100000 −200000
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


20240126-400.90.fid
QQ-1-35
9.80
7.25 7.24 7.22 7.14 7.12 6.94 6.93
5.90 5.88 5.78 5.77 5.75 5.73
4.57 4.30 4.14 4.12 4.07 3.74 3.45 3.43 3.32 3.28 3.10 3.07 3.01 2.99 2.97 2.94 2.72 2.14 2.12 1.93 1.92 1.90 1.76 1.74 1.72 1.70 1.47
1.00 1.15 1.13 1.08 1.07 1.09 1.15 1.20 1.03 3.23 1.97 2.09 4.15 1.20 0.94 3.01 4.05 11.21
N
Boc
O
H
N
CO2Me
O
N
OHC
3x, 400 MHz, CDCl3
f1 (ppm)
5500000 5000000 4500000 4000000 3500000 3000000 2500000 2000000 1500000 1000000 500000 0 −500000

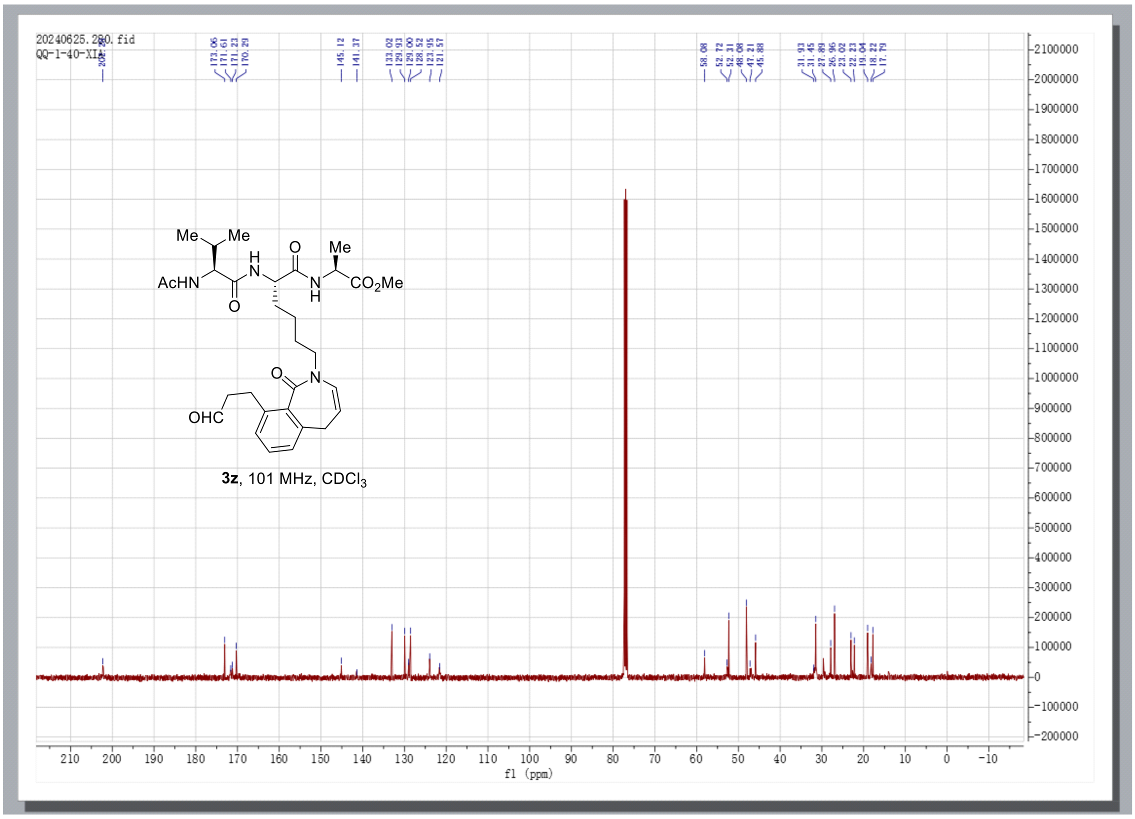

20240319.490.fid
qq-1-35
196.80
167.21 163.93
139.69 136.45
127.78 124.66 123.88 123.39 118.63 115.93
75.06
55.72
47.03 46.67 42.32 41.76 40.84
32.75
26.80 26.21 23.01 22.79 21.84 17.33 16.28
N
Boc
O
H
N
CO2Me
O
N
OHC
3x, 101 MHz, CDCl3
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
2300000 2200000 2100000 2000000 1900000 1800000 1700000 1600000 1500000 1400000 1300000 1200000 1100000 1000000 900000 800000 700000 600000 500000 400000 300000 200000 100000 0 −100000 −200000


20240322.20.fid
qq-1-38
9.78
7.73 7.70 7.68 7.65 7.39 7.37 7.35 7.26 7.24 7.17 7.15 7.13 6.96 6.94
6.23 6.21 6.13 6.12 5.86 5.85 5.77 5.75
4.56 4.15 4.13 4.05 3.93 3.77 3.74 3.64 3.27 3.23 3.12 3.09 2.97 2.96 2.70
1.88 1.66 1.61 1.59 1.53 1.51 1.40 1.35 1.33 1.31 1.28
1.00 3.17 1.14 0.91 3.14 1.06 1.11 1.03 1.07 1.07 1.09 3.11 0.75 3.13 2.06 1.30 3.08 1.09 1.11 4.22 1.21 3.07
Me
H
N
CO2Me
O
O
N
O
OHC
3y, 400 MHz, CDCl3
2500000
2000000
1500000
1000000
500000
0
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

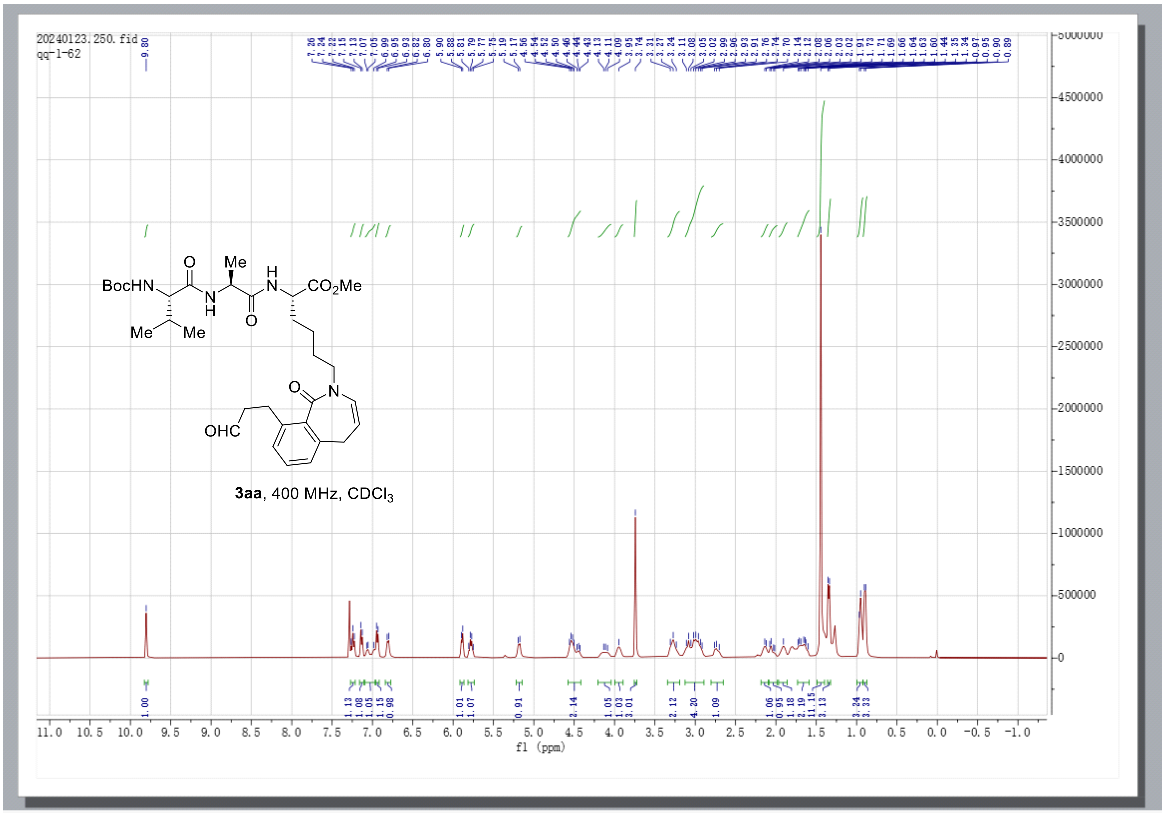

20240625.350.fid
qq-1-38
202.05
174.19 172.58 169.41
157.63
144.96 141.70 136.06 133.68 133.06 129.96 129.24 129.03 128.93 128.66 127.35 126.24 126.08 123.93 121.46 118.99 105.60
55.27 52.21 47.41 46.74 46.04
31.44 29.27 27.88 27.06 22.39 18.46
Me
H
N
CO2Me
O
O
N
O
OHC
3y, 101 MHz, CDCl3
1900000
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

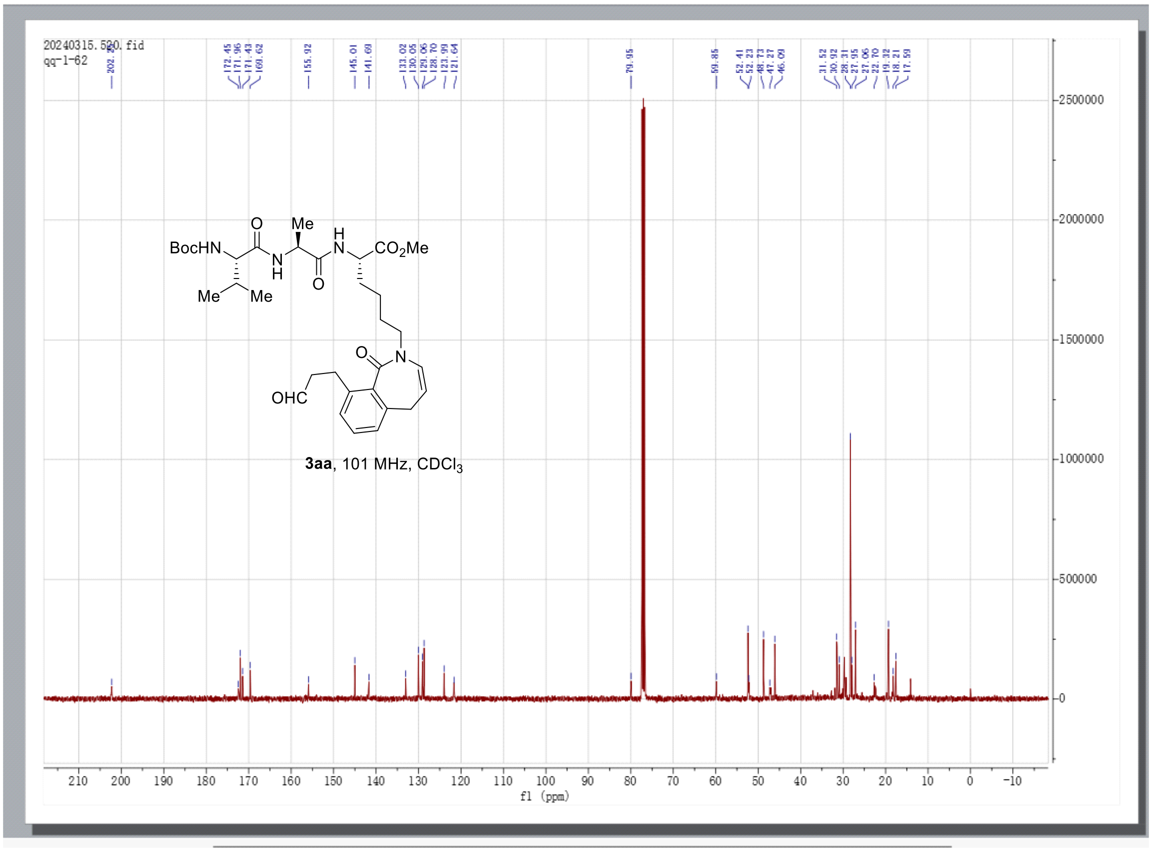


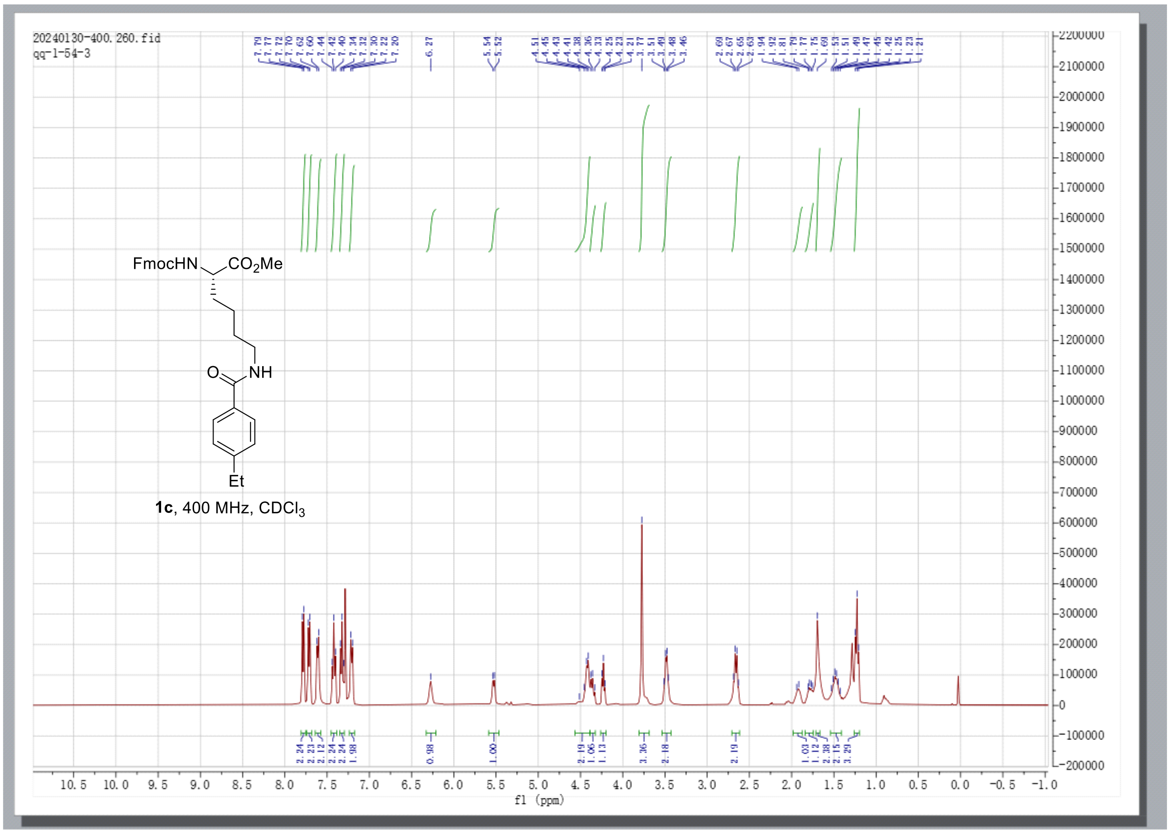
3z, 400 MHz, $CDCl_3$



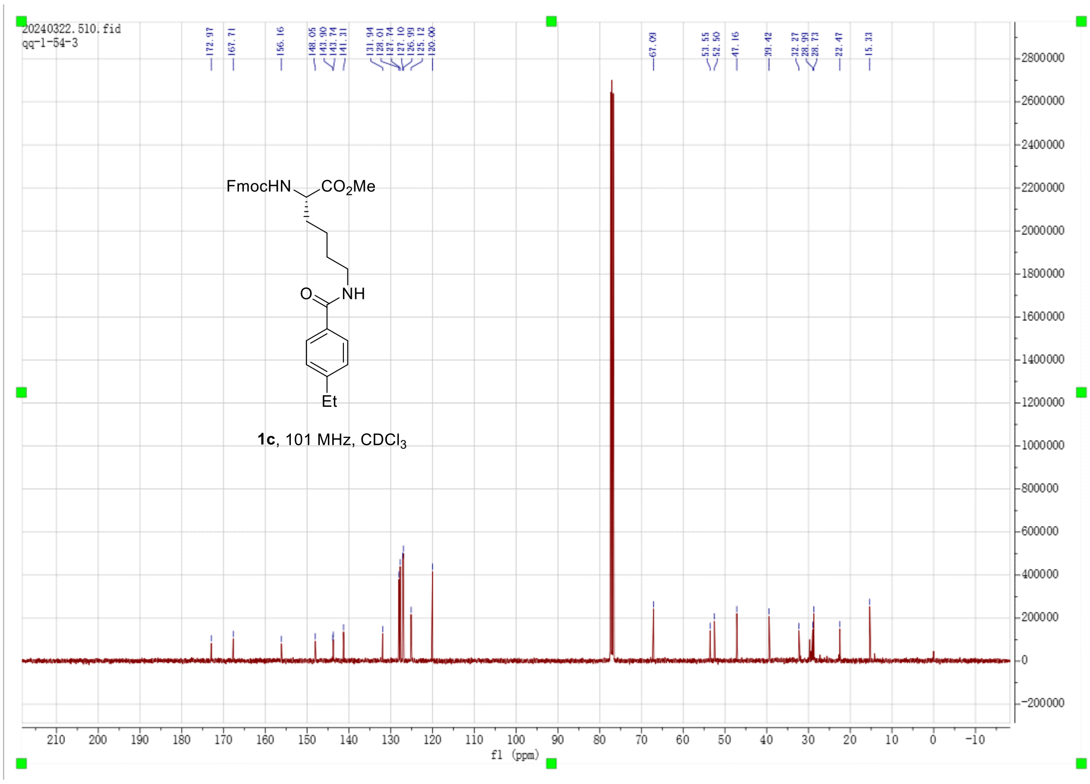
3z, 101 MHz, $CDCl_3$


20240123.250.fid
qq-1-62
9.80
7.26 7.24 7.22 7.15 7.13 7.07 7.05 6.99 6.95 6.93 6.82 6.80 5.90 5.88 5.81 5.79 5.77 5.75 5.19 5.17 4.56 4.54 4.52 4.50 4.46 4.44 4.43 4.13 4.11 4.09 3.95 3.74 3.31 3.27 3.24 3.11 3.08 3.05 3.02 2.99 2.96 2.93 2.91 2.76 2.74 2.70 2.14 2.12 2.08 2.06 2.03 2.02 1.91 1.73 1.71 1.69 1.66 1.64 1.63 1.60 1.44 1.35 1.34 0.97 0.95 0.90 0.89
BocHN
O
Me
H
N
CO2Me
N
H
O
Me
Me
O
N
OHC
3aa, 400 MHz, CDCl3
1.00 1.13 1.08 1.05 1.15 0.98 1.01 1.07 0.91 2.14 1.05 1.03 3.01 2.12 4.20 1.09 1.06 0.95 1.18 2.19 11.15 2.13 2.24 2.33
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
5000000 4500000 4000000 3500000 3000000 2500000 2000000 1500000 1000000 500000 0

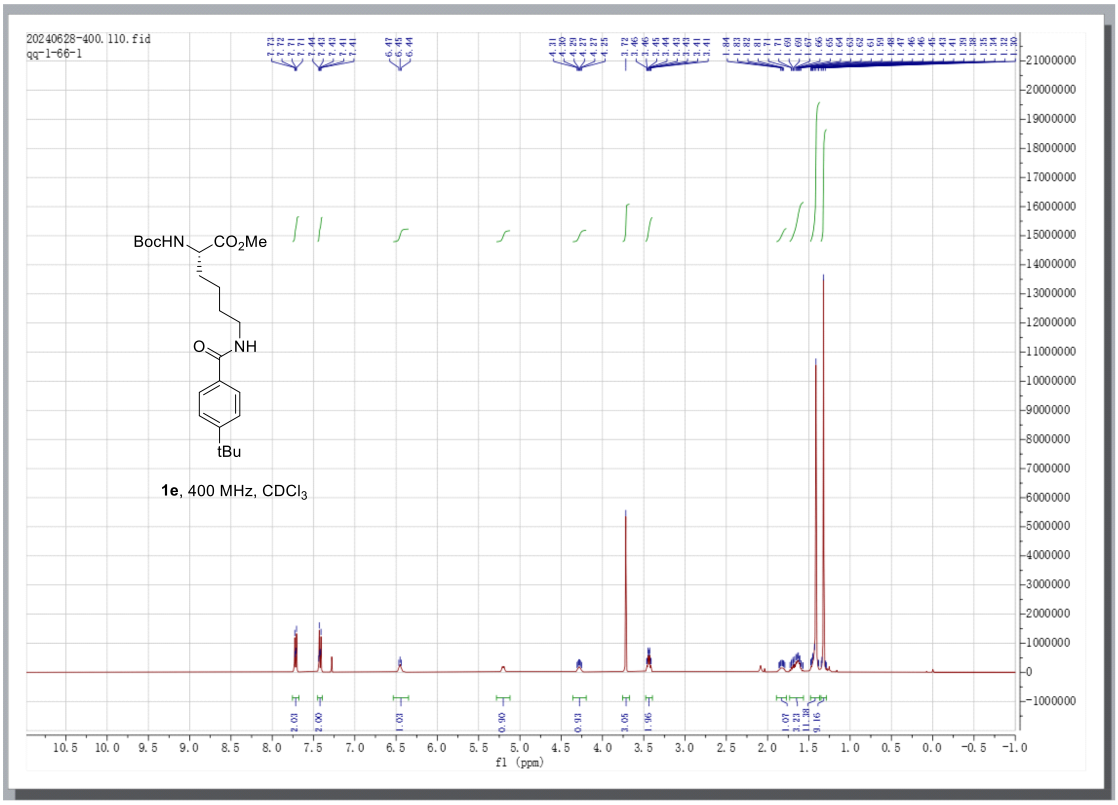

20240315.520.fid
qq-1-62
202.
172.45 171.96 171.43 169.62
155.92
145.01 141.69
133.02 130.05 129.06 128.70 123.99 121.64
79.95
59.85
52.41 52.23 48.73 47.27 46.09
31.52 30.92 28.31 27.95 27.06 22.70 19.32 18.21 17.59
BocHN
O
Me
H
N
CO2Me
N
H
O
Me
Me
O
N
OHC
3aa, 101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
2500000 2000000 1500000 1000000 500000 0



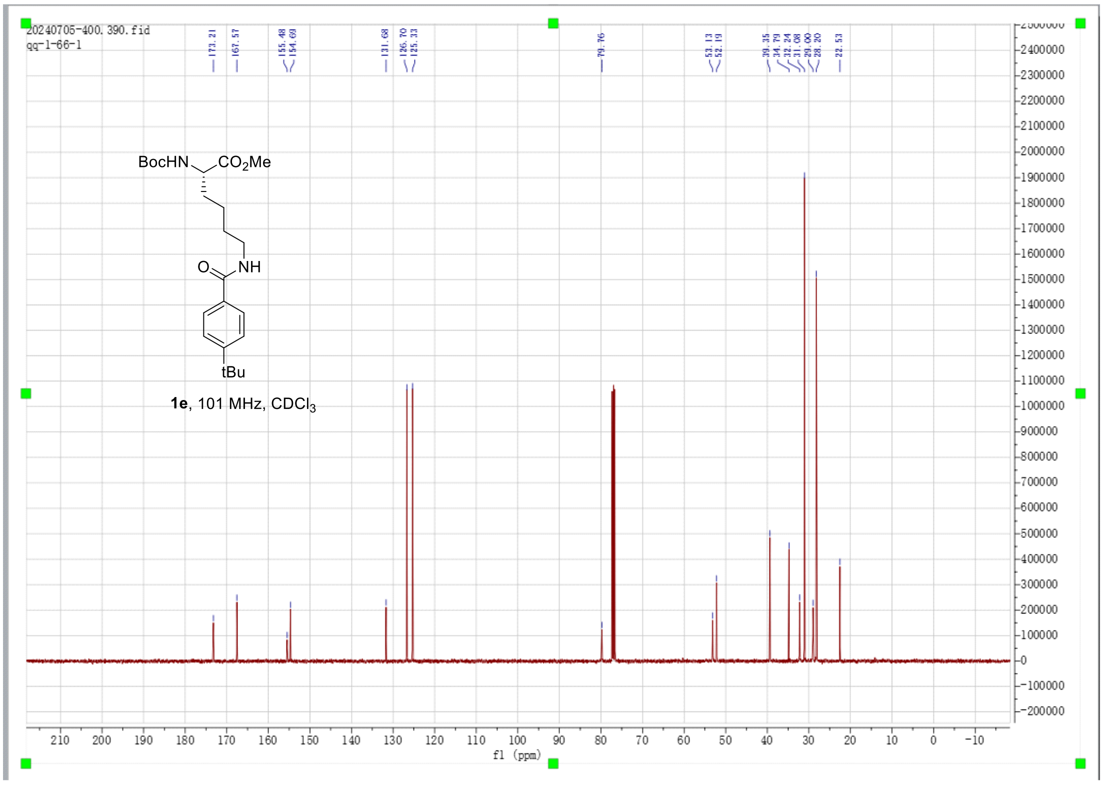
1c, 400 MHz, CDCl$_3$



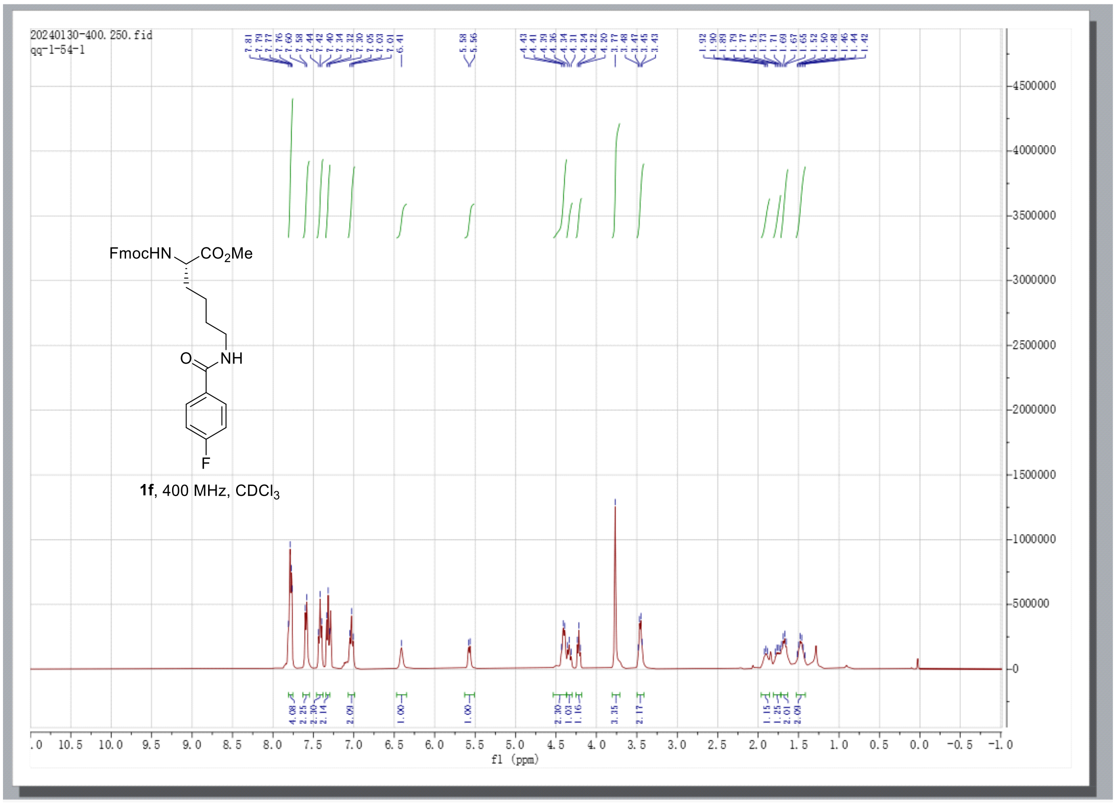
1c, 101 MHz, CDCl$_3$

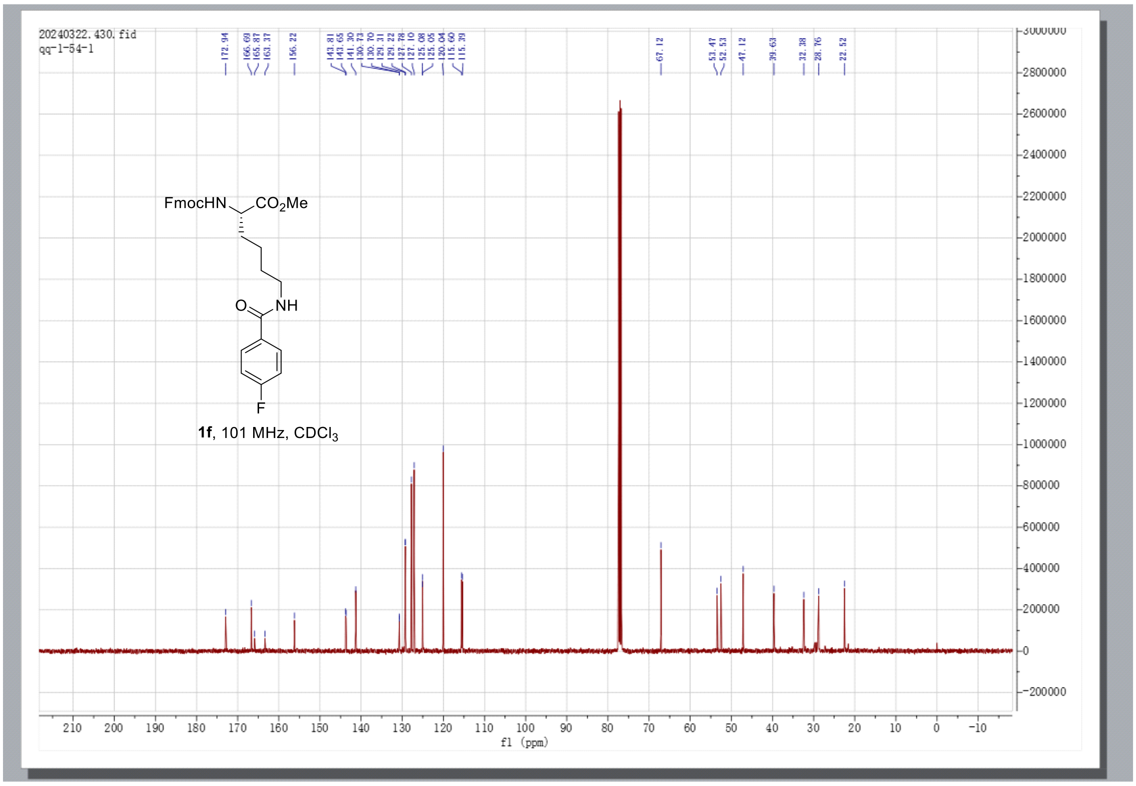


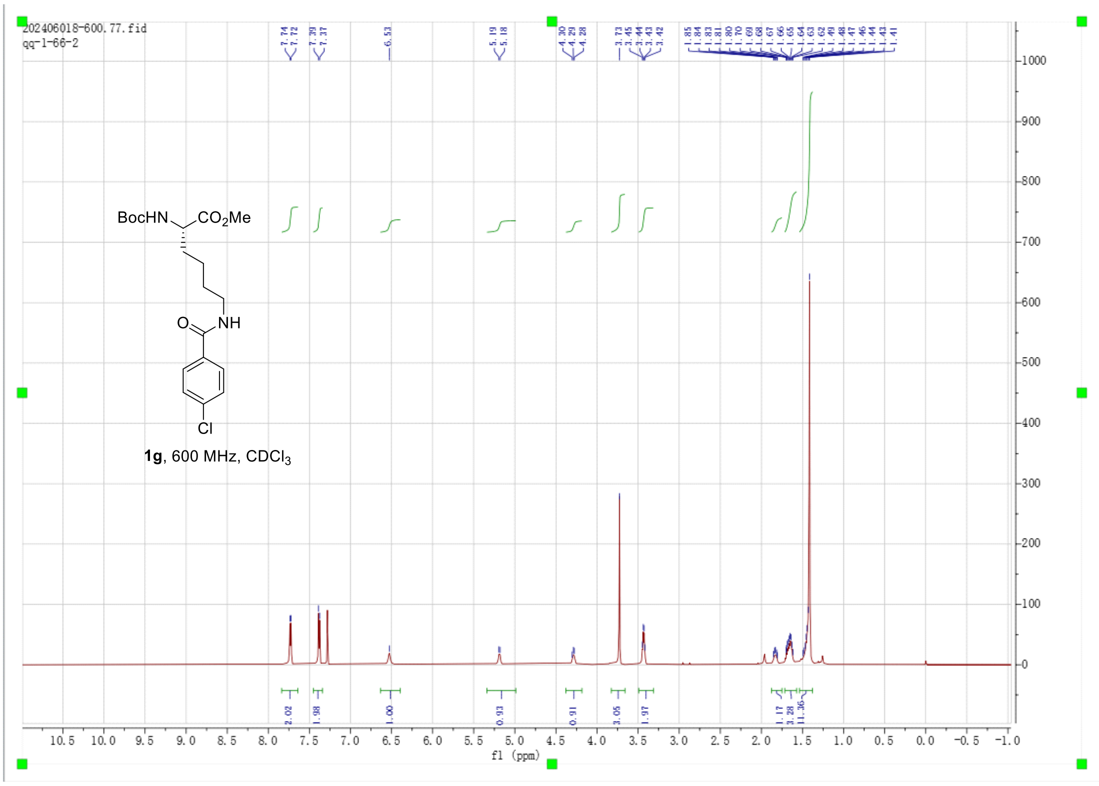
1e, 400 MHz, $CDCl_3$

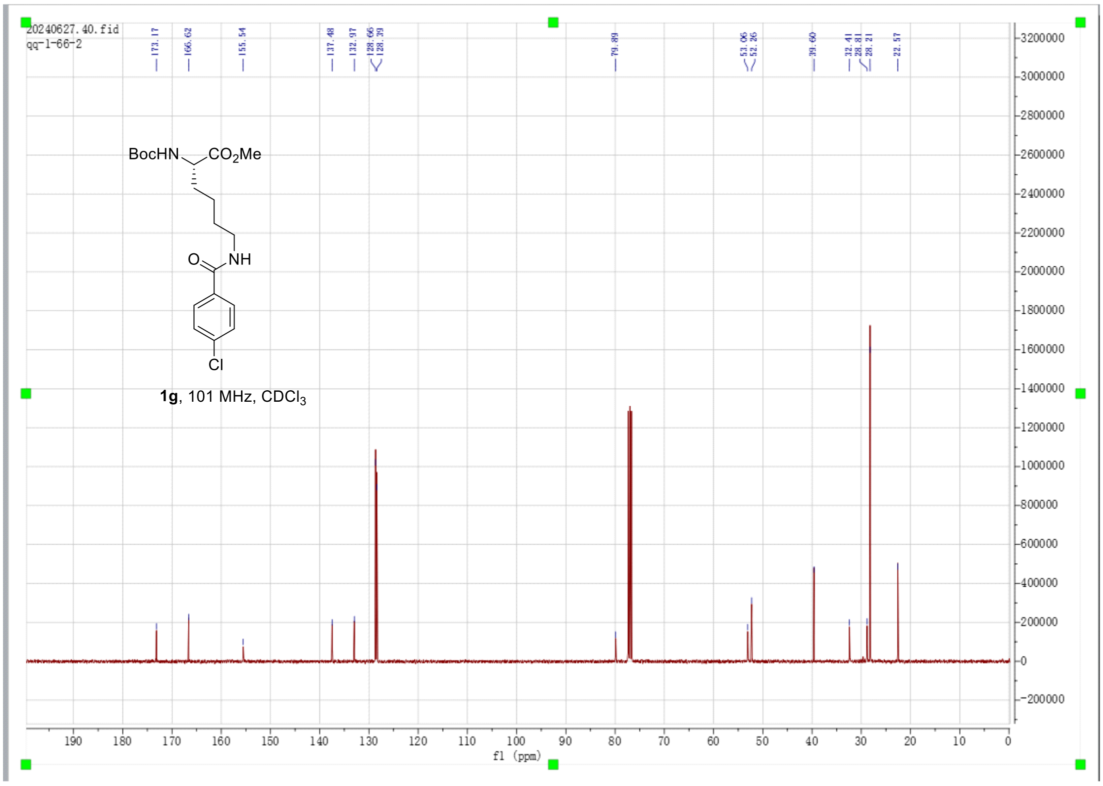


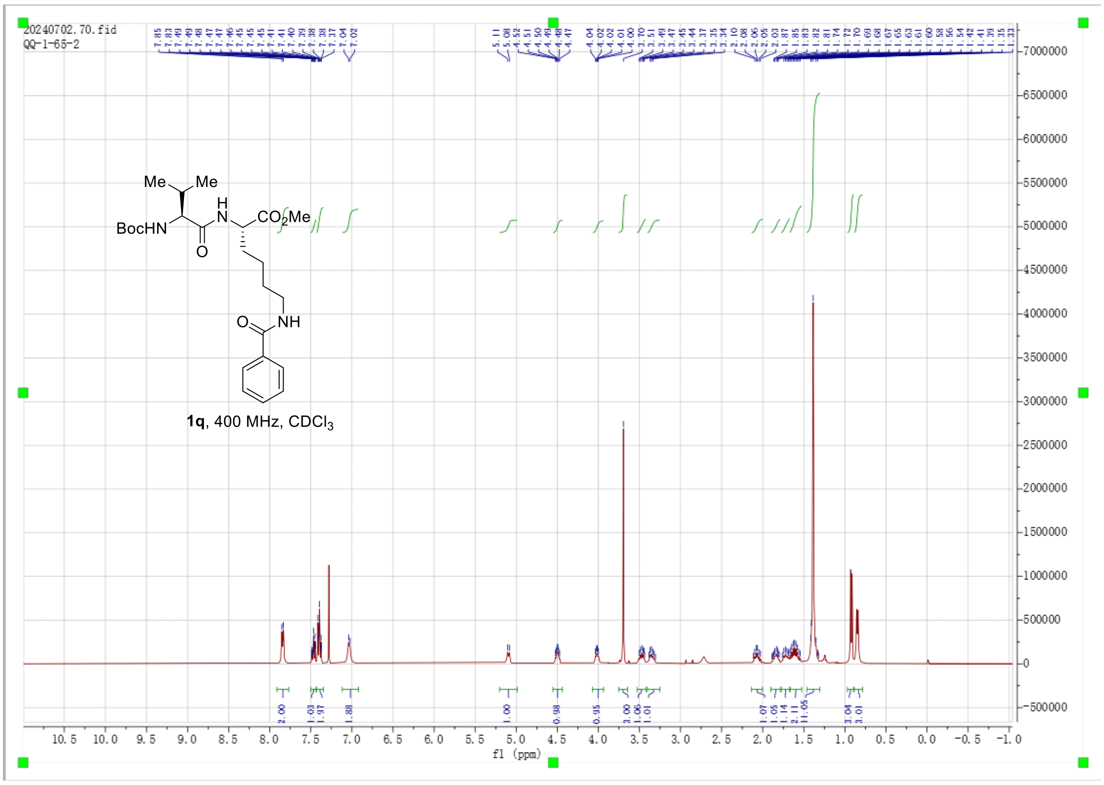
1e, 101 MHz, $CDCl_3$


20240130-400.250.fid
qq-1-54-1
7.81
7.79
7.77
7.76
7.60
7.58
7.44
7.42
7.40
7.34
7.32
7.30
7.05
7.03
7.01
6.41
5.58
5.56
4.43
4.41
4.39
4.36
4.34
4.31
4.24
4.22
4.20
3.77
3.48
3.47
3.45
3.43
1.92
1.90
1.89
1.79
1.77
1.75
1.73
1.71
1.69
1.67
1.65
1.52
1.50
1.48
1.46
1.44
1.42
FmocHN
CO2Me
O
NH
F
1f, 400 MHz, CDCl3
4.08
2.25
2.30
2.14
2.09
1.00
1.00
2.30
1.03
1.16
3.35
2.17
1.15
1.25
2.01
2.09
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

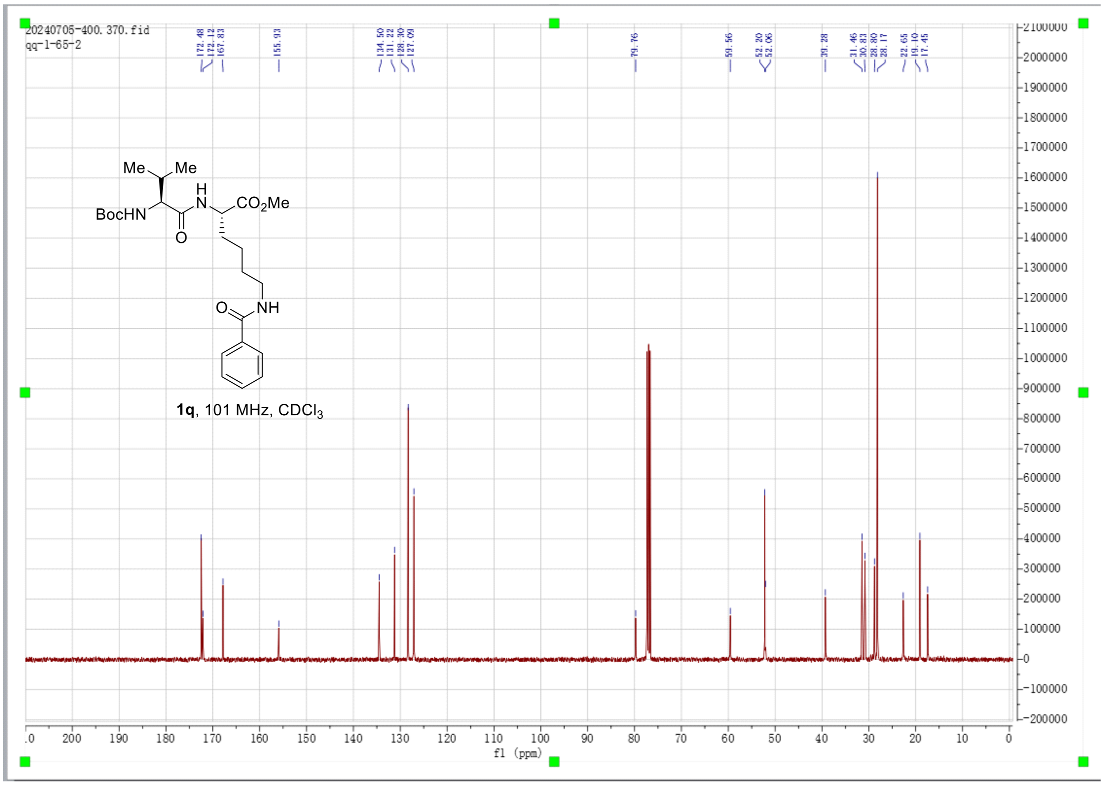

20240322.430.fid
qq-1-54-1
172.94
166.69
165.87
163.37
156.22
143.81
143.65
141.30
130.73
130.70
129.31
129.22
127.78
127.10
125.08
125.05
120.04
115.60
115.39
67.12
53.47
52.53
47.12
39.63
32.38
28.76
22.52
FmocHN
CO2Me
O
NH
F
1f, 101 MHz, CDCl3
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


202406018-600.77.fid
qq-1-66-2
7.74
7.72
7.39
7.37
6.53
5.19
5.18
4.30
4.29
4.28
3.73
3.45
3.44
3.43
3.42
1.85
1.84
1.83
1.81
1.80
1.70
1.69
1.68
1.67
1.66
1.65
1.64
1.63
1.62
1.49
1.48
1.47
1.46
1.44
1.43
1.41
BocHN
CO2Me
O
NH
Cl
1g, 600 MHz, CDCl3
2.02
1.98
1.00
0.93
0.91
3.05
1.97
1.17
3.28
11.36
f1 (ppm)
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
1000 900 800 700 600 500 400 300 200 100 0

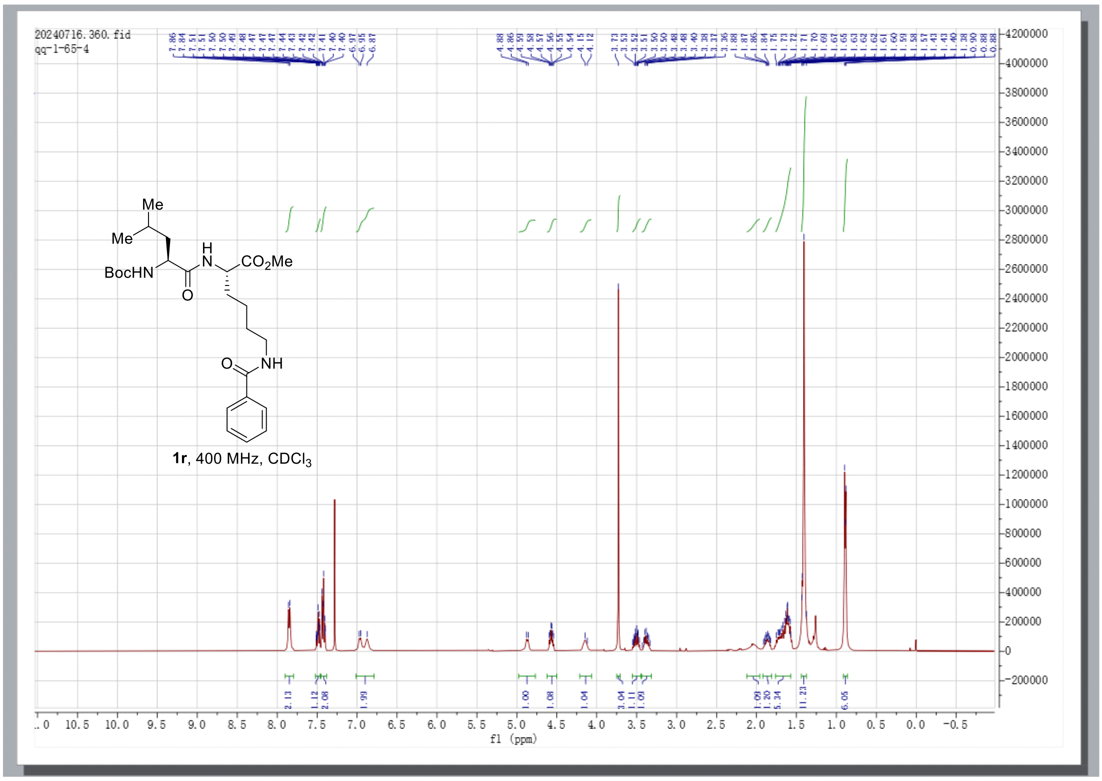

20240627.40.fid
qq-1-66-2
173.17
166.62
155.54
137.48
132.97
128.66
128.39
79.89
53.06
52.26
39.60
32.41
28.81
28.21
22.57
BocHN
CO2Me
O
NH
Cl
1g, 101 MHz, CDCl3
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
3200000 3000000 2800000 2600000 2400000 2200000 2000000 1800000 1600000 1400000 1200000 1000000 800000 600000 400000 200000 0 -200000

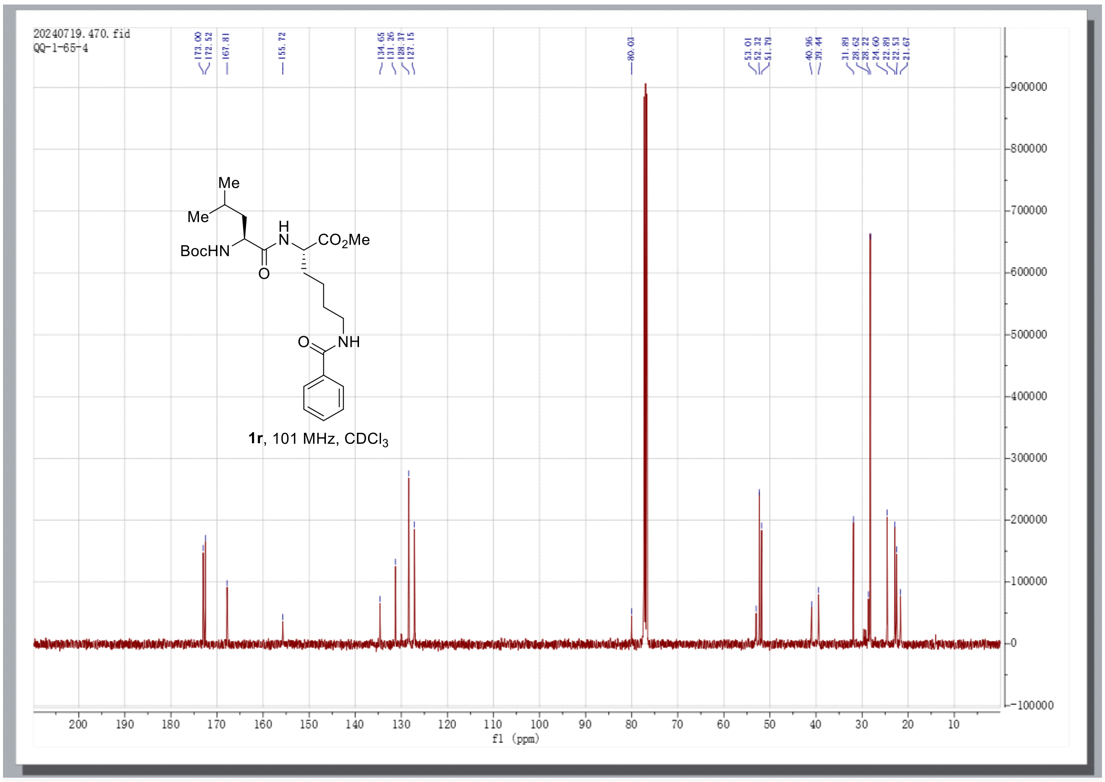


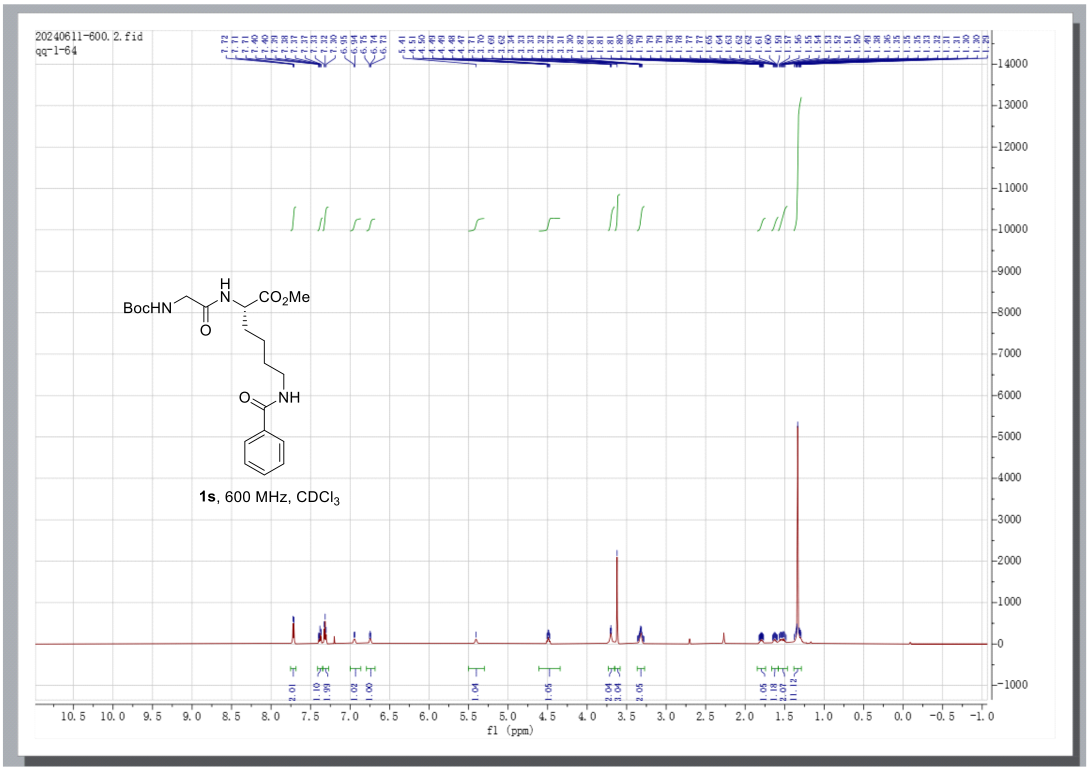
1q, 400 MHz, $CDCl_3$

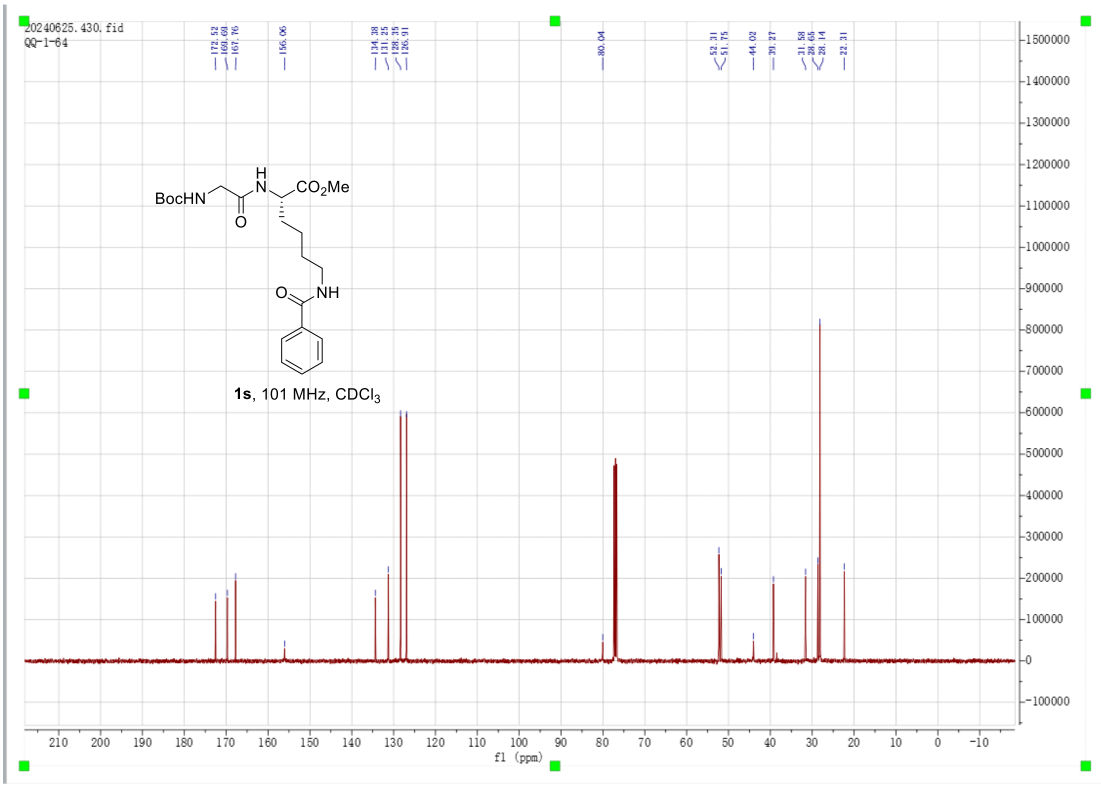


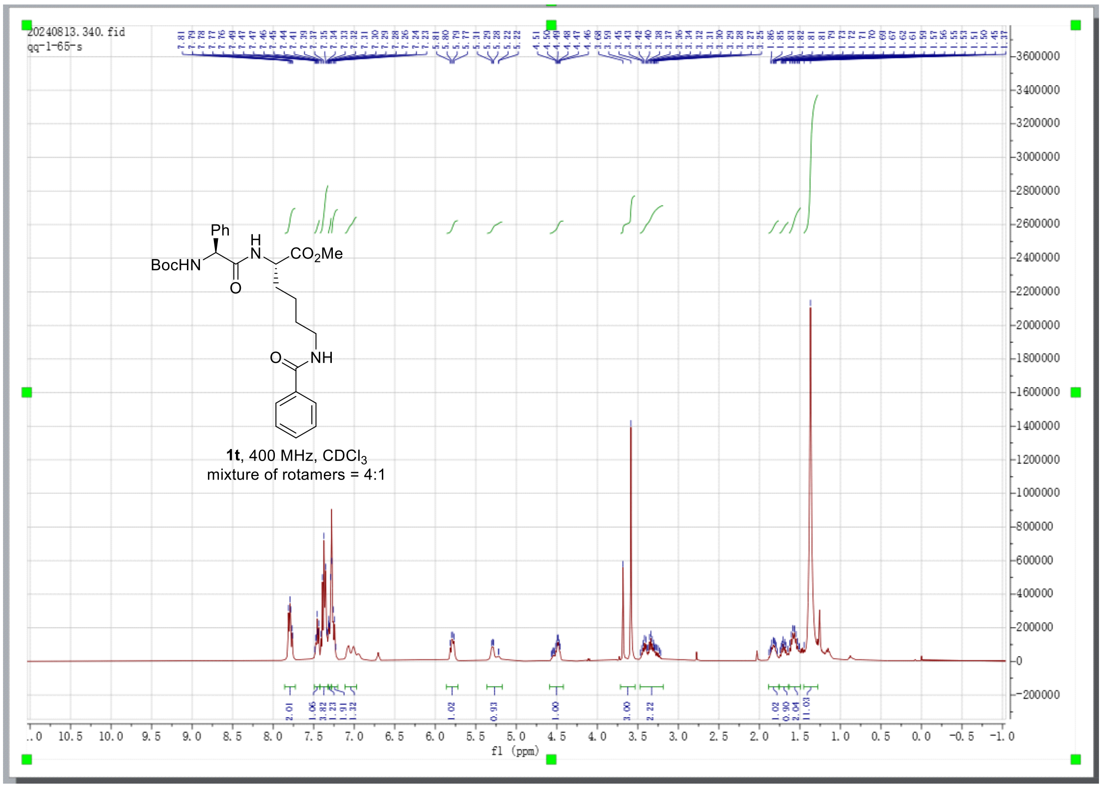
1q, 101 MHz, $CDCl_3$

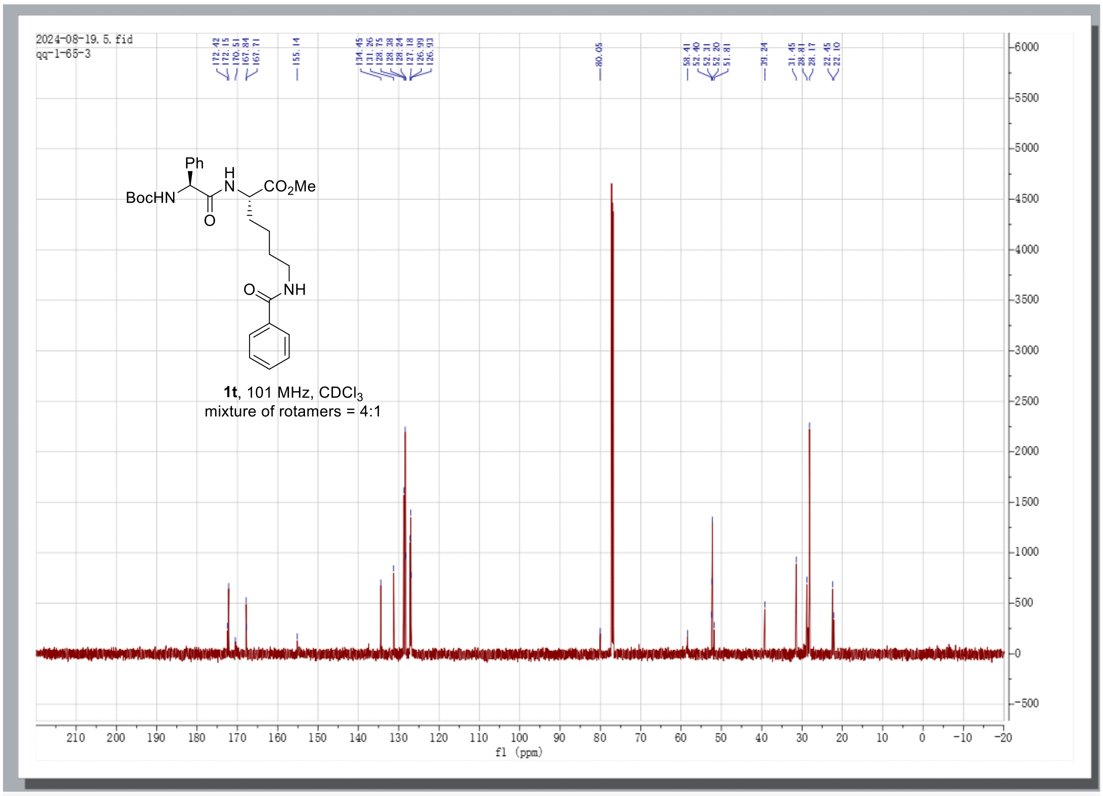

20240716.360.fid
qq-1-65-4
1r, 400 MHz, CDCl3
Me
Me
BocHN
H
N
CO2Me
O
O
NH
2.13
1.12
2.08
1.99
1.00
1.08
1.04
3.04
1.11
1.09
1.09
1.20
5.34
11.23
6.05
f1 (ppm)

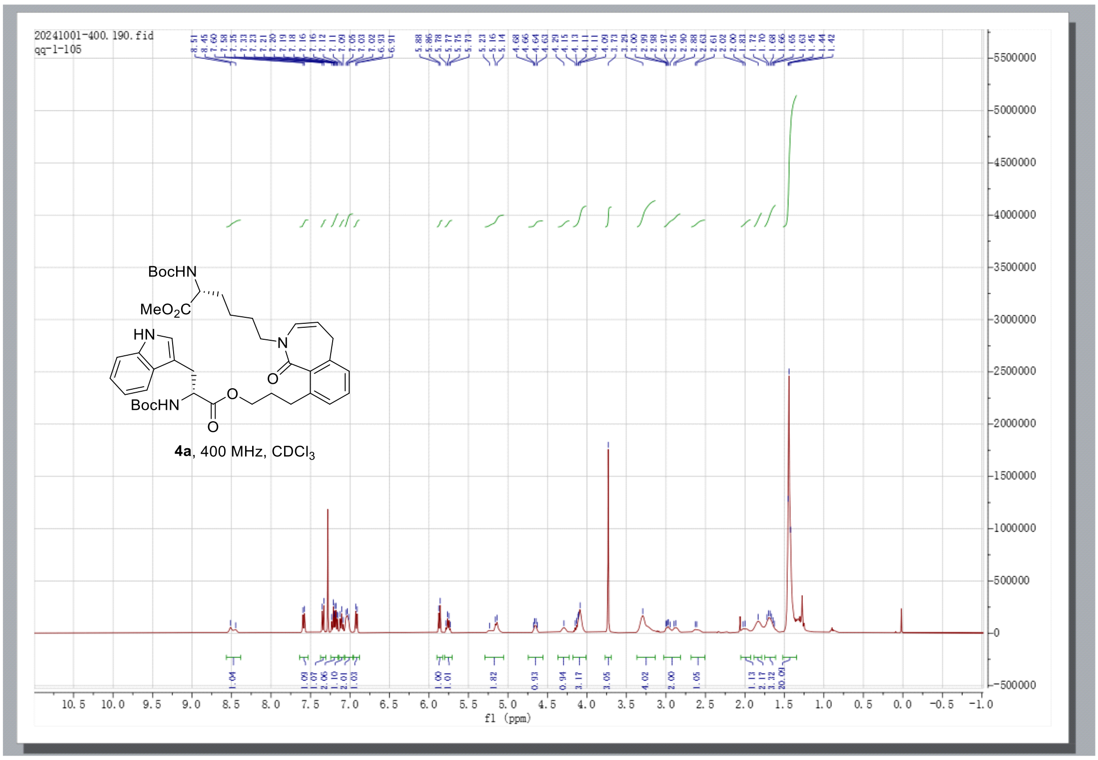

20240719.470.fid
QQ-1-65-4
173.00
172.52
167.81
155.72
134.65
131.26
128.37
127.15
80.03
53.01
52.12
51.79
40.96
39.44
31.89
28.62
28.22
24.60
22.89
22.53
21.67
1r, 101 MHz, CDCl3
Me
Me
BocHN
H
N
CO2Me
O
O
NH
f1 (ppm)

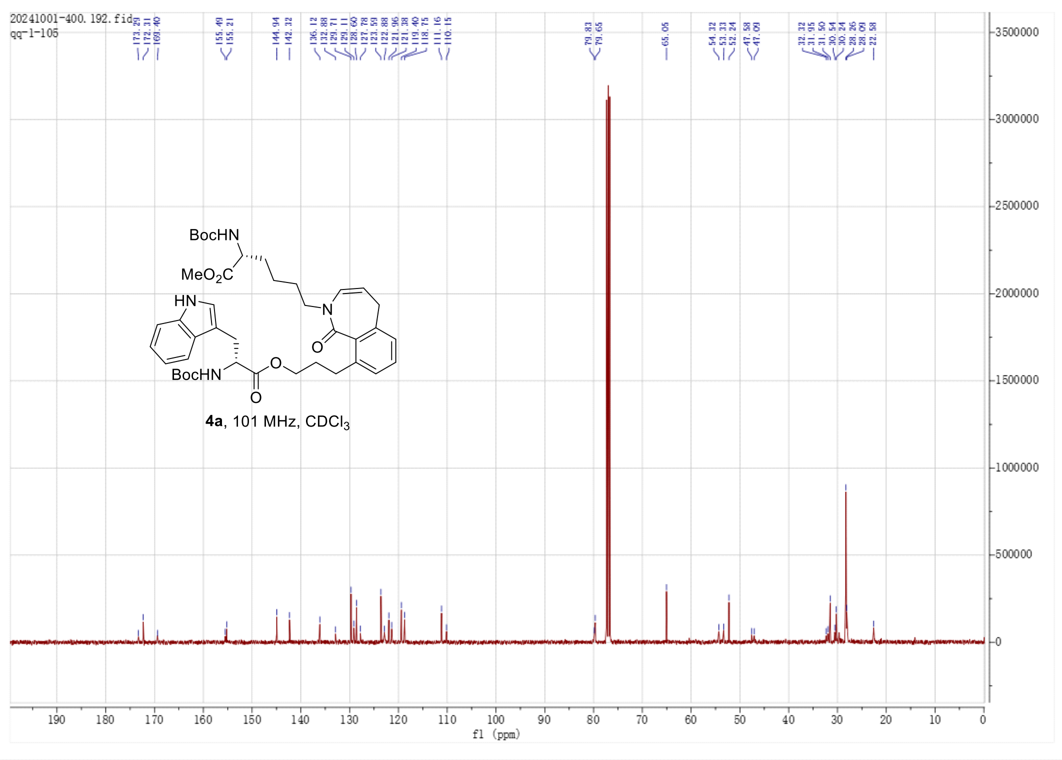

20240611-600.2.fid
qq-1-64
7.72 7.71 7.71 7.40 7.40 7.39 7.38 7.37 7.37 7.33 7.32 7.30 6.95 6.94 6.75 6.74 6.73 5.41 4.51 4.50 4.49 4.49 4.48 4.47 3.71 3.70 3.69 3.62 3.34 3.33 3.33 3.32 3.32 3.31 3.30 1.82 1.81 1.81 1.81 1.80 1.80 1.79 1.79 1.79 1.78 1.78 1.77 1.77 1.65 1.64 1.63 1.62 1.62 1.61 1.60 1.59 1.57 1.56 1.55 1.54 1.53 1.52 1.51 1.50 1.49 1.38 1.36 1.35 1.35 1.35 1.33 1.32 1.31 1.31 1.30 1.30 1.29
BocHN
H
N
CO2Me
O
O
NH
1s, 600 MHz, CDCl3
2.01
1.10
1.99
1.02
1.00
1.04
1.05
2.04
3.04
2.05
1.05
1.18
2.07
11.12
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)
14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 −1000

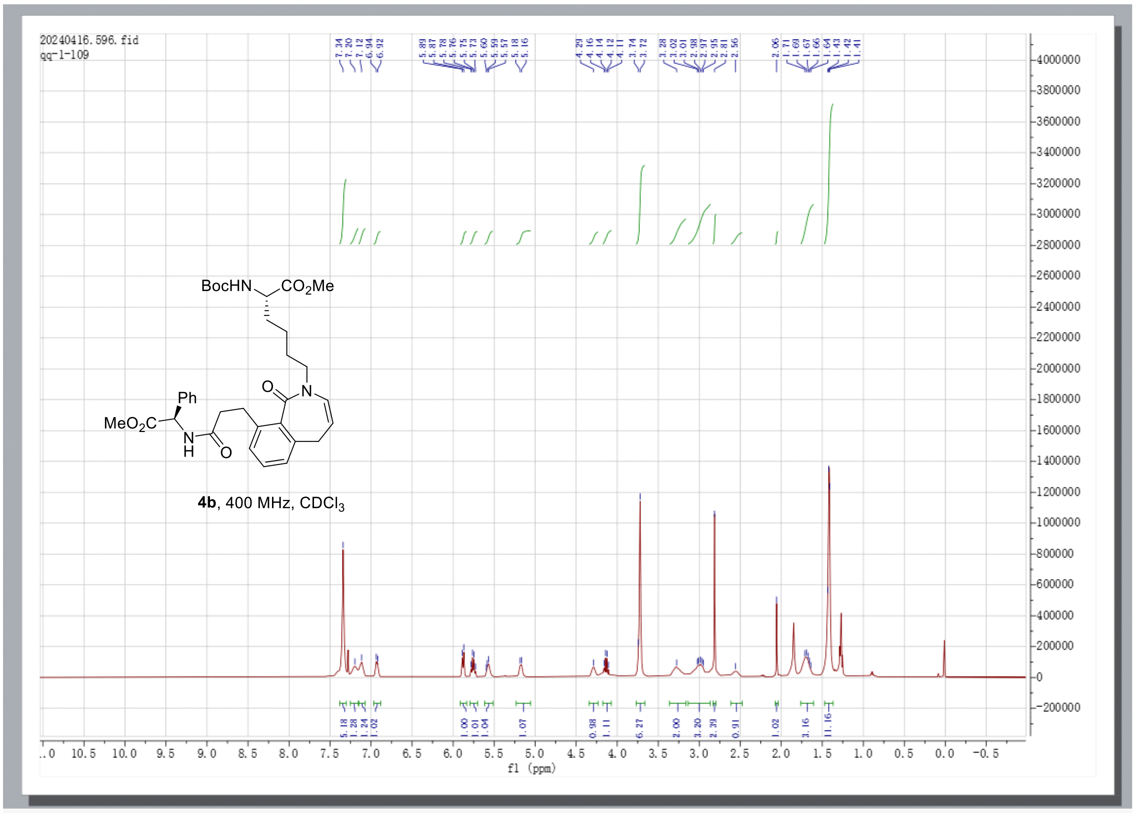

20240625.430.fid
QQ-1-64
172.52 169.69 167.76 156.06 134.38 131.25 128.35 126.91 80.04 52.31 51.75 44.02 39.27 31.58 28.65 28.14 22.31
BocHN
H
N
CO2Me
O
O
NH
1s, 101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)
1500000 1400000 1300000 1200000 1100000 1000000 900000 800000 700000 600000 500000 400000 300000 200000 100000 0 −100000


20240813.340.fid
qq-1-65-s
7.81 7.79 7.78 7.77 7.76 7.49 7.47 7.47 7.46 7.45 7.44 7.41 7.39 7.37 7.35 7.34 7.33 7.32 7.31 7.30 7.29 7.28 7.26 7.24 7.23 5.81 5.80 5.79 5.77 5.31 5.29 5.28 5.22 5.22 4.51 4.50 4.49 4.48 4.47 4.46 3.68 3.59 3.45 3.43 3.42 3.40 3.38 3.37 3.36 3.34 3.32 3.31 3.30 3.29 3.28 3.27 3.25 1.86 1.85 1.83 1.82 1.81 1.81 1.79 1.73 1.72 1.71 1.70 1.69 1.67 1.62 1.61 1.59 1.57 1.56 1.55 1.53 1.51 1.50 1.45 1.37
Ph
H
BocHN
N
CO2Me
O
O
NH
1t, 400 MHz, CDCl3
mixture of rotamers = 4:1
2.01 1.06 3.42 1.23 1.91 1.32 1.02 0.93 1.00 3.00 2.22 1.02 0.90 2.04 11.03
f1 (ppm)

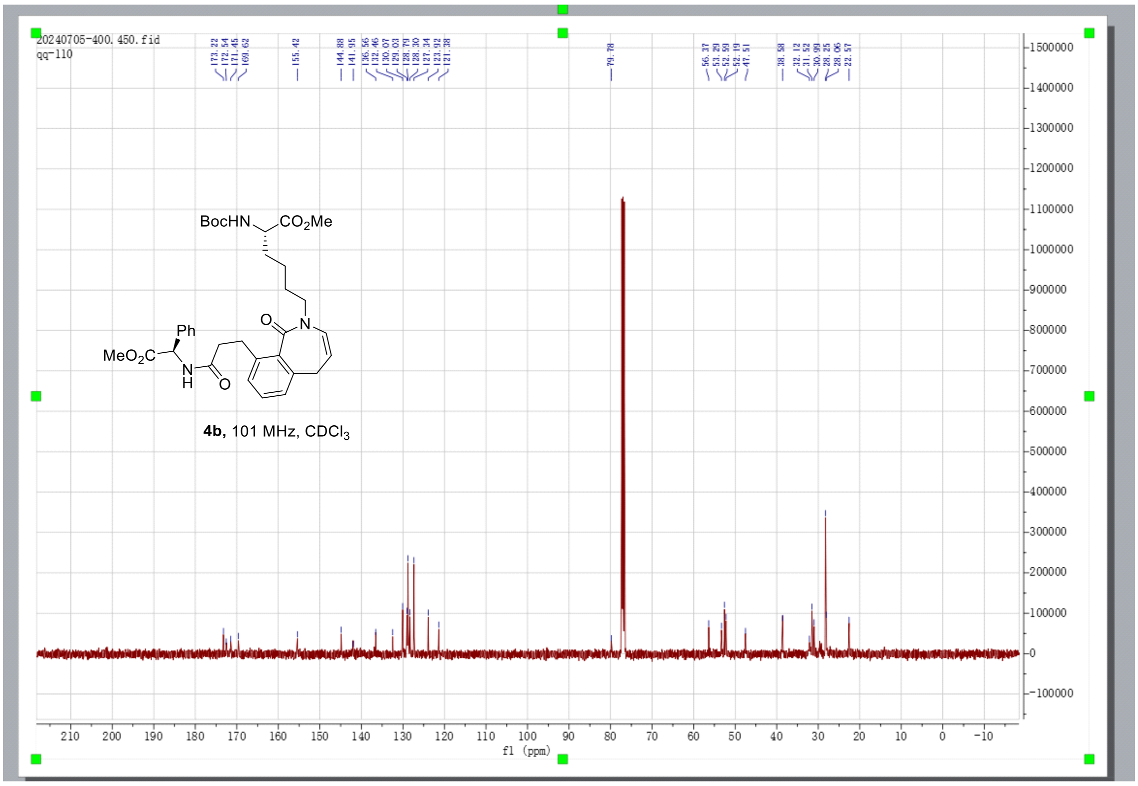

2024-08-19.5.fid
qq-1-65-3
172.42 172.15 170.51 167.84 167.71 155.14 134.45 131.26 128.75 128.38 128.24 127.18 126.99 126.93 80.05 58.41 52.40 52.31 52.20 51.81 39.24 31.45 28.81 28.17 22.45 22.10
Ph
H
BocHN
N
CO2Me
O
O
NH
1t, 101 MHz, CDCl3
mixture of rotamers = 4:1
f1 (ppm)


20241001-400.190.fid
qq-1-105
8.51 8.45 7.60 7.58 7.35 7.33 7.23 7.21 7.20 7.19 7.18 7.16 7.16 7.12 7.11 7.09 7.05 7.03 7.02 6.93 6.91
5.88 5.86 5.78 5.77 5.75 5.73 5.23 5.16 5.14 4.68 4.66 4.64 4.63 4.29 4.15 4.13 4.11 4.11 4.09 3.73
3.29 3.00 2.99 2.98 2.97 2.95 2.90 2.88 2.63 2.61 2.02 2.00 1.83 1.72 1.70 1.68 1.66 1.65 1.63 1.45 1.44 1.42
BocHN
MeO2C
HN
N
O
BocHN
O
O
4a, 400 MHz, CDCl3
1.04 1.09 1.07 2.06 1.10 2.01 1.03 1.00 1.01 1.82 0.93 0.94 3.17 3.05 4.02 2.00 1.05 1.13 2.17 3.32 20.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
5500000 5000000 4500000 4000000 3500000 3000000 2500000 2000000 1500000 1000000 500000 0 -500000

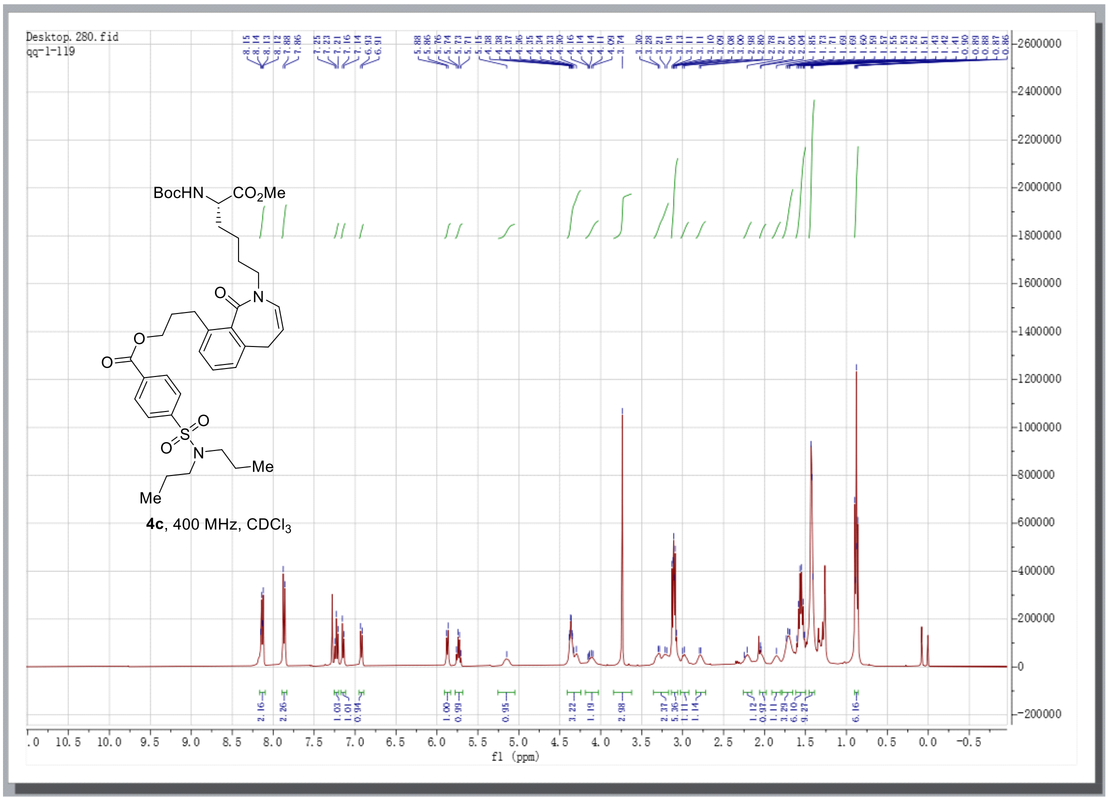

20241001-400.192.fid
qq-1-105
173.29 172.31 169.40 155.49 155.21 144.94 142.32 136.12 132.88 129.71 129.11 128.60 127.78 123.59 122.88 121.96 121.38 119.40 118.75 111.16 110.15
79.83 79.65 65.05 54.32 53.33 52.24 47.58 47.09 32.32 31.95 31.50 30.54 30.24 28.26 28.09 22.58
BocHN
MeO2C
HN
N
O
BocHN
O
O
4a, 101 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
3500000 3000000 2500000 2000000 1500000 1000000 500000 0



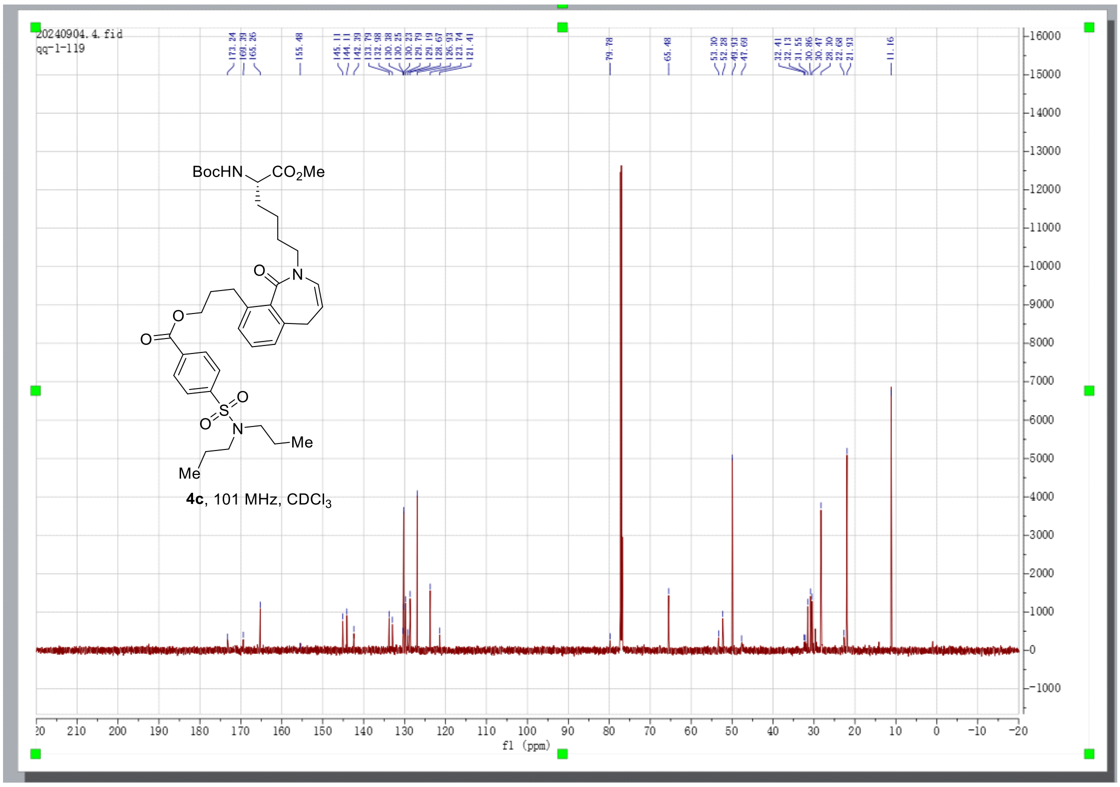
4b, 400 MHz, $CDCl_3$



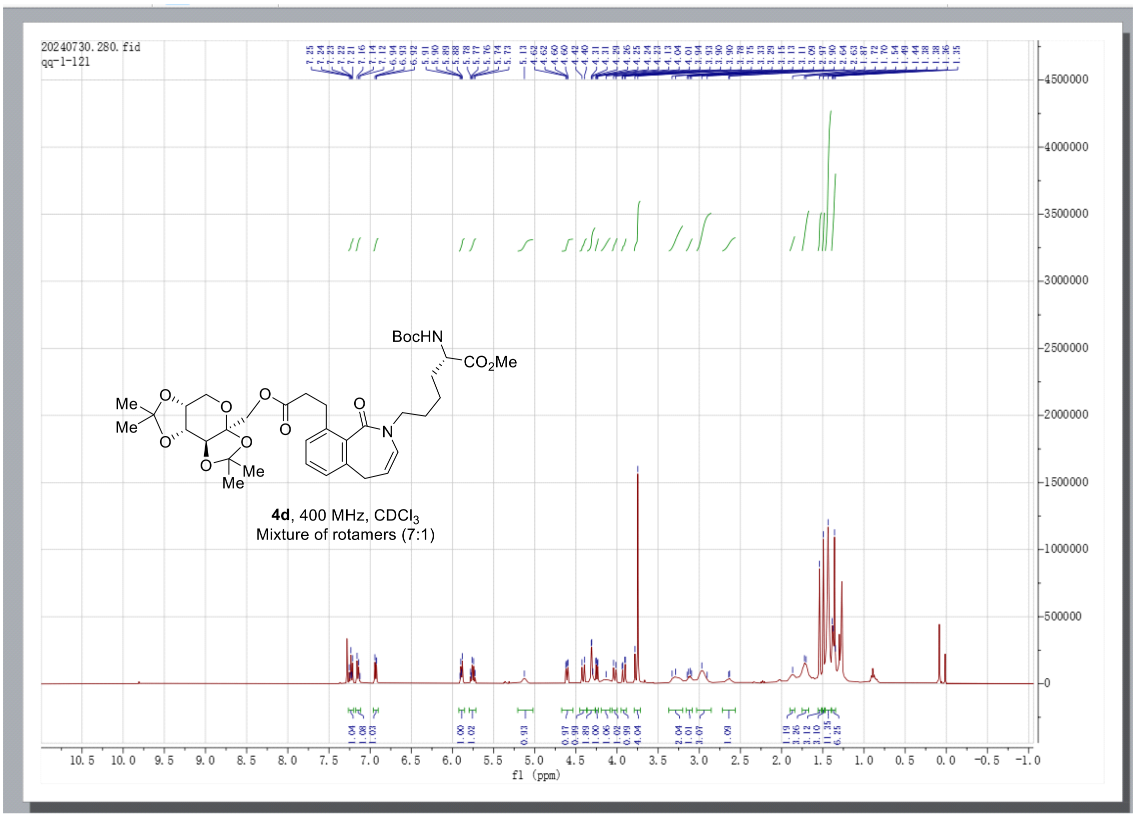
4b, 101 MHz, $CDCl_3$

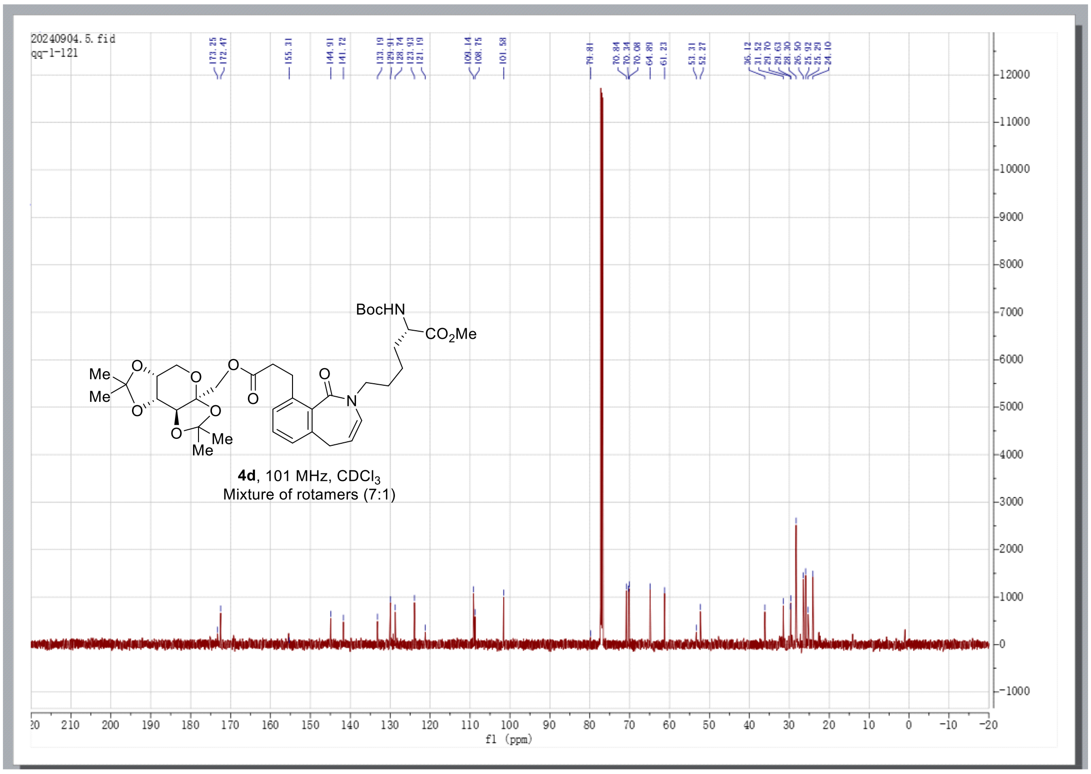


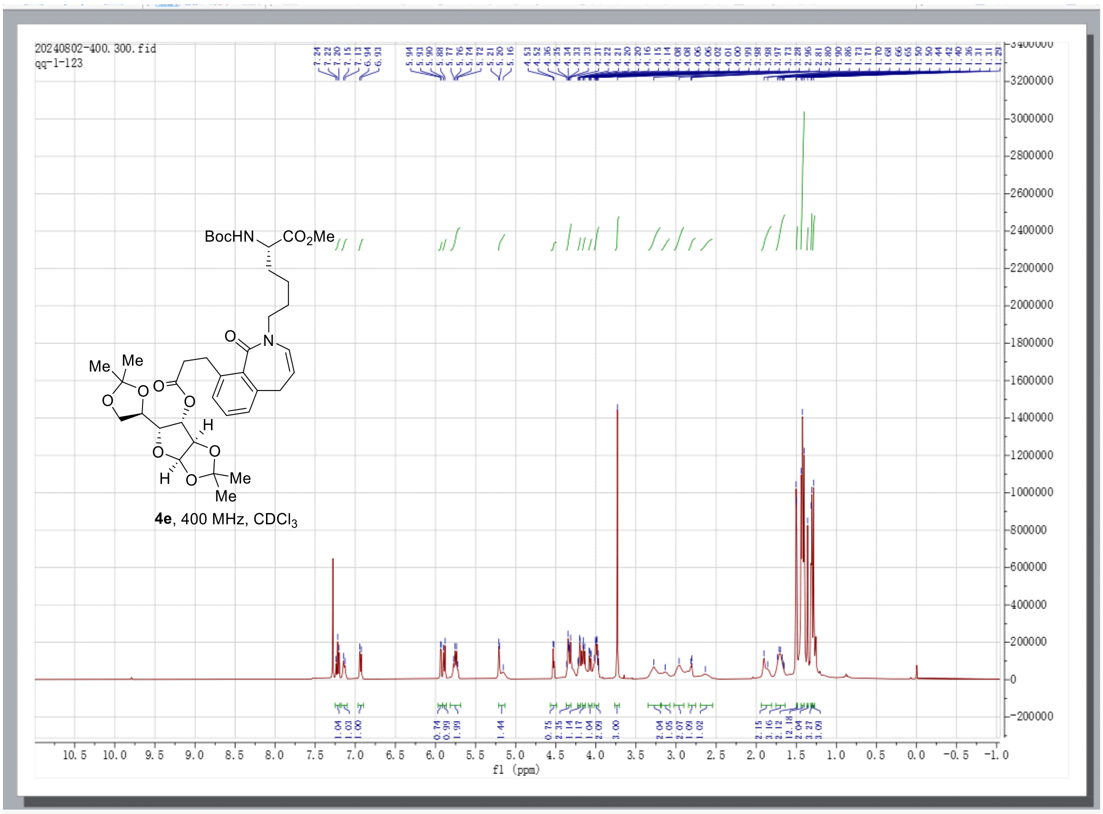
4c, 400 MHz, CDCl$_3$

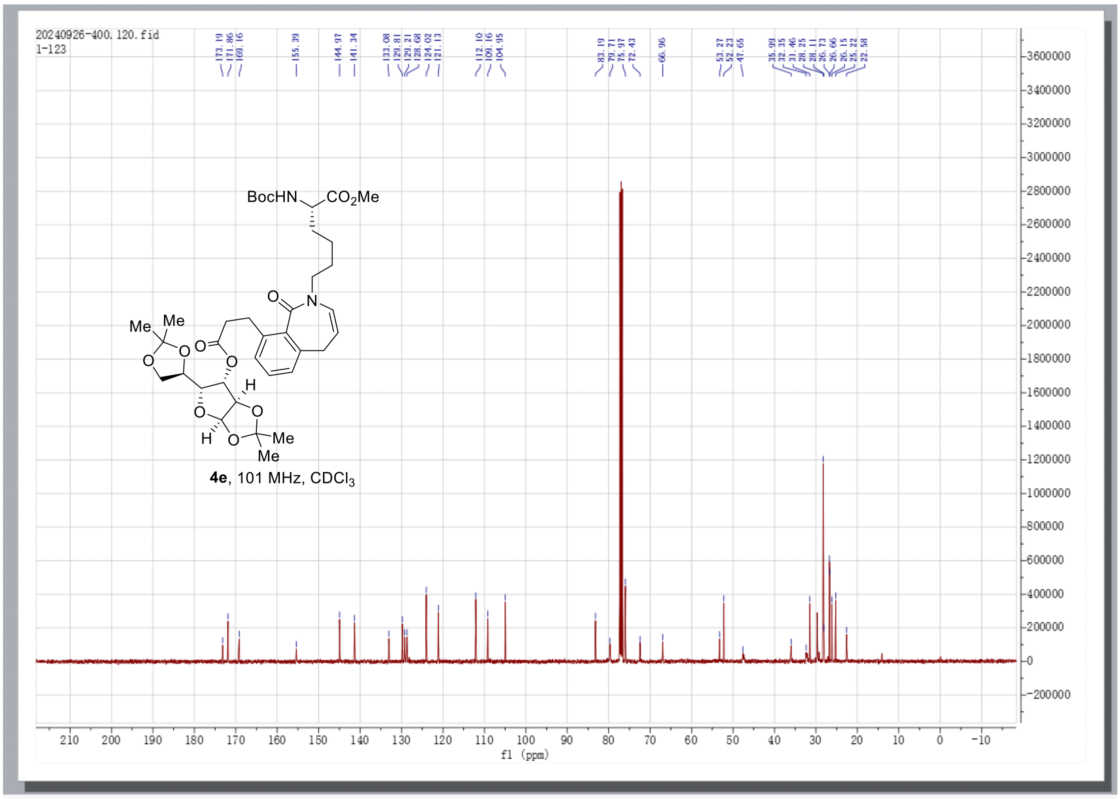


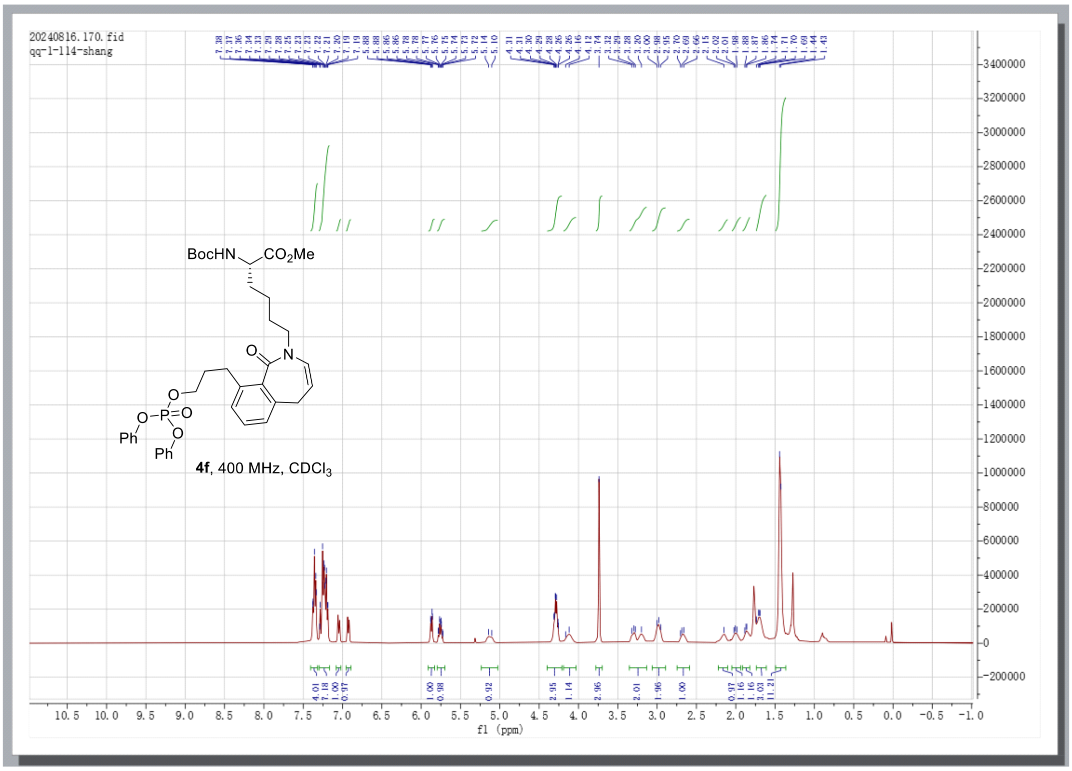
4c, 101 MHz, CDCl$_3$

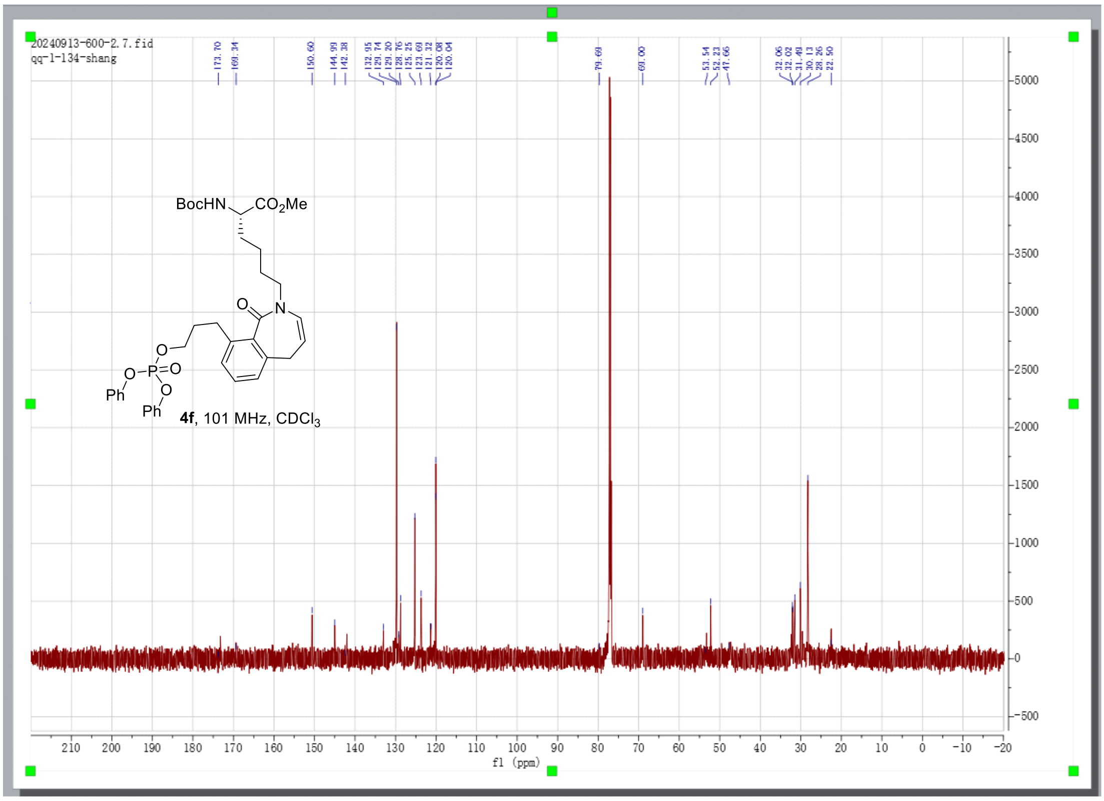

20240730.280.fid
qq-1-121
7.25 7.24 7.23 7.22 7.21 7.16 7.14 7.12 6.94 6.93 6.92 5.91 5.90 5.89 5.88 5.78 5.77 5.76 5.74 5.73 5.13 4.62 4.62 4.60 4.42 4.40 4.31 4.29 4.26 4.25 4.24 4.23 4.13 4.04 4.01 3.94 3.93 3.90 3.90 3.78 3.75 3.23 3.20 3.15 3.13 3.11 3.09 2.97 2.90 2.64 2.63 1.87 1.72 1.70 1.54 1.49 1.44 1.38 1.36 1.35
BocHN
CO2Me
Me
Me
O
O
O
O
O
Me
Me
O
O
O
N
4d, 400 MHz, CDCl3
Mixture of rotamers (7:1)
1.04 1.08 1.03 1.00 1.02 0.93 0.97 0.99 1.89 1.00 1.06 1.02 0.99 4.04 2.04 1.01 3.07 1.09 1.19 1.26 3.12 3.10 11.35 6.25
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

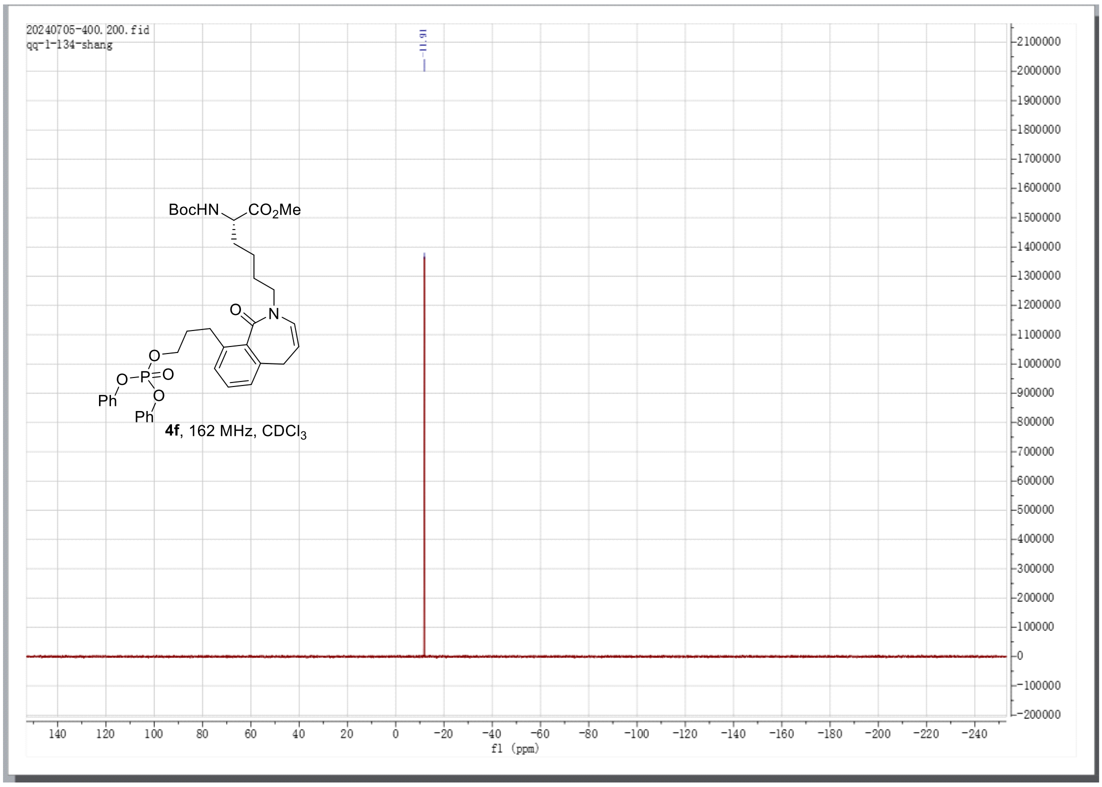

20240904.5.fid
qq-1-121
173.25 172.47 155.31 144.91 141.72 133.19 129.91 128.74 123.93 121.19 109.14 108.75 101.58 79.81 70.84 70.34 70.08 64.89 61.23 53.31 52.27 36.12 31.52 29.70 29.63 28.30 26.50 25.92 25.29 24.10
BocHN
CO2Me
Me
Me
O
O
O
O
O
Me
Me
O
O
O
N
4d, 101 MHz, CDCl3
Mixture of rotamers (7:1)
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

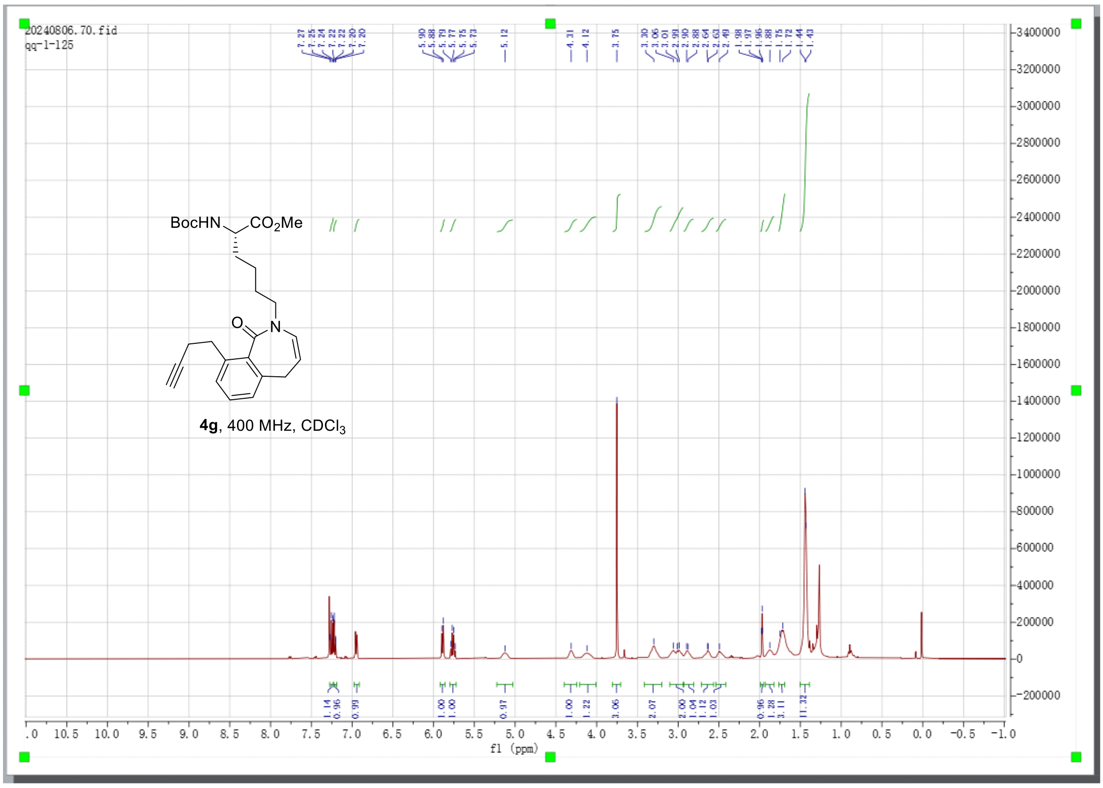

20240802-400.300.fid
qq-1-123
7.24 7.22 7.20 7.15 7.13 6.94 6.93 5.94 5.93 5.90 5.88 5.77 5.76 5.74 5.72 5.21 5.20 5.16 4.53 4.52 4.36 4.35 4.34 4.33 4.33 4.31 4.22 4.21 4.20 4.20 4.16 4.15 4.14 4.08 4.08 4.06 4.06 4.02 4.01 4.00 3.99 3.98 3.98 3.97 3.73 3.28 2.96 2.81 2.80 1.90 1.86 1.73 1.71 1.70 1.68 1.66 1.65 1.50 1.50 1.44 1.42 1.40 1.36 1.31 1.31 1.29
BocHN
CO2Me
O
N
Me
Me
O
O
O
O
H
O
O
H
O
Me
Me
4e, 400 MHz, CDCl3
1.04 1.03 1.00 0.74 0.99 1.99 1.44 0.75 2.35 1.14 1.17 1.04 2.09 3.00 2.04 1.05 2.07 1.09 1.02 2.15 3.16 2.12 12.18 2.04 3.27 3.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
3400000 3200000 3000000 2800000 2600000 2400000 2200000 2000000 1800000 1600000 1400000 1200000 1000000 800000 600000 400000 200000 0 -200000


20240926-400.120.fid
1-123
173.19 171.86 169.16 155.39 144.97 141.34 133.08 129.81 129.21 128.68 124.02 121.13 112.10 109.16 104.95 83.19 79.71 75.97 72.43 66.96 53.27 52.23 47.65 35.99 32.35 31.46 28.25 28.11 26.73 26.66 26.15 25.22 22.58
BocHN
CO2Me
O
N
Me
Me
O
O
O
O
H
O
O
H
O
Me
Me
4e, 101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
3600000 3400000 3200000 3000000 2800000 2600000 2400000 2200000 2000000 1800000 1600000 1400000 1200000 1000000 800000 600000 400000 200000 0 -200000

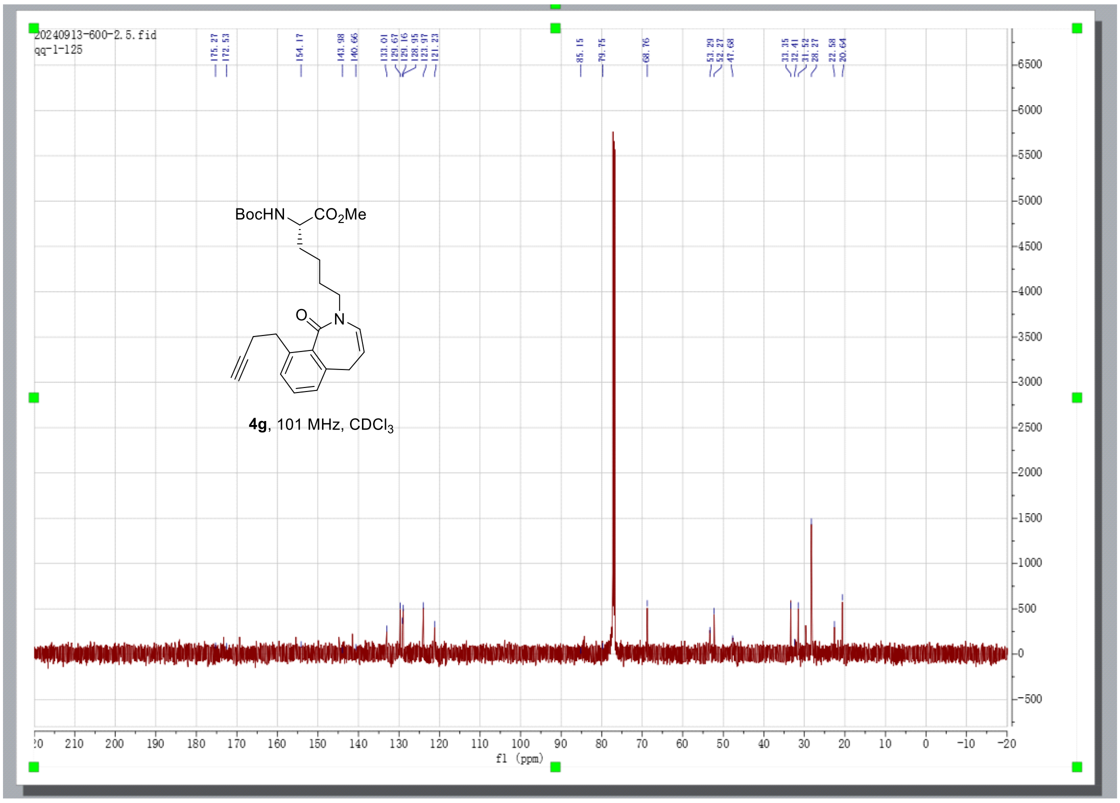

20240816.170.fid
qq-1-114-shang
7.38 7.37 7.36 7.34 7.33 7.29 7.28 7.25 7.23 7.23 7.22 7.21 7.20 7.19 7.19 5.88 5.88 5.86 5.86 5.78 5.78 5.77 5.76 5.75 5.74 5.73 5.72 5.14 5.10 4.31 4.31 4.30 4.29 4.28 4.26 4.26 4.25 4.16 4.12 3.74 3.32 3.29 3.28 3.20 3.00 2.98 2.95 2.70 2.69 2.66 2.15 2.02 2.01 1.98 1.88 1.87 1.86 1.74 1.71 1.70 1.69 1.44 1.43
BocHN
CO2Me
O
N
O
O-P=O
O
Ph
Ph
4f, 400 MHz, CDCl3
4.01 7.18 1.00 0.97 1.00 0.98 0.92 2.95 1.14 2.96 2.01 1.96 1.00 0.97 1.16 1.16 3.03 11.21
f1 (ppm)


20240913-600-2.7.fid
qq-1-134-shang
173.70 169.34 150.60 144.99 142.38 132.95 129.74 129.20 128.76 125.25 123.69 121.32 120.08 120.04 79.69 69.00 53.54 52.21 47.66 32.06 32.02 31.40 30.13 28.26 22.50
BocHN
CO2Me
O
N
O
O-P=O
O
Ph
Ph
4f, 101 MHz, CDCl3
f1 (ppm)

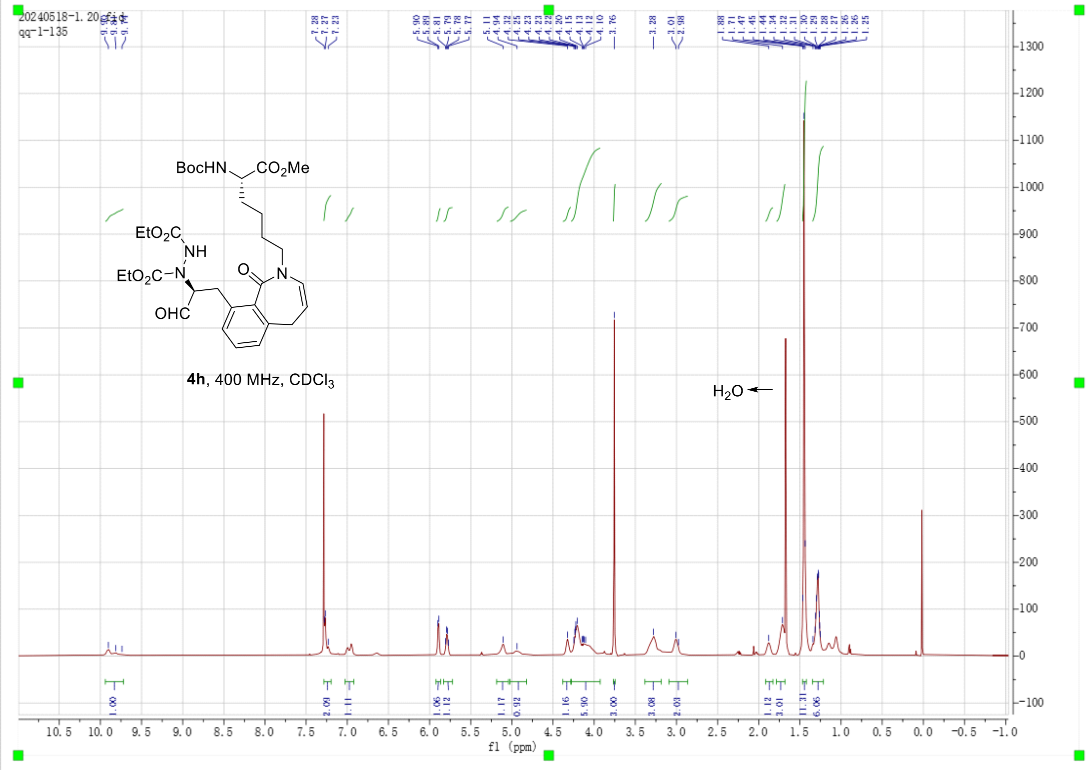

20240705-400.200.fid
qq-1-134-shang
-11.91
BocHN
CO2Me
O
N
O
O
P
O
O
Ph
Ph
4f, 162 MHz, CDCl3
2100000
2000000
1900000
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
-200000
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)



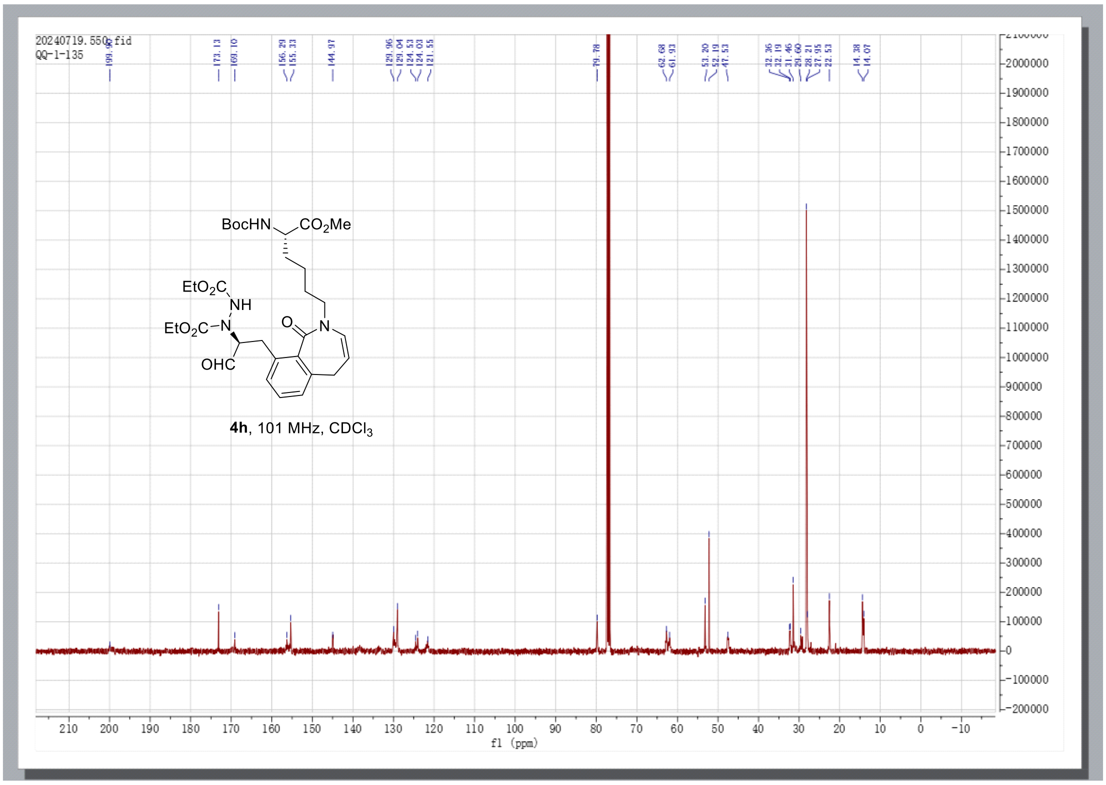
4g, 400 MHz, $CDCl_3$



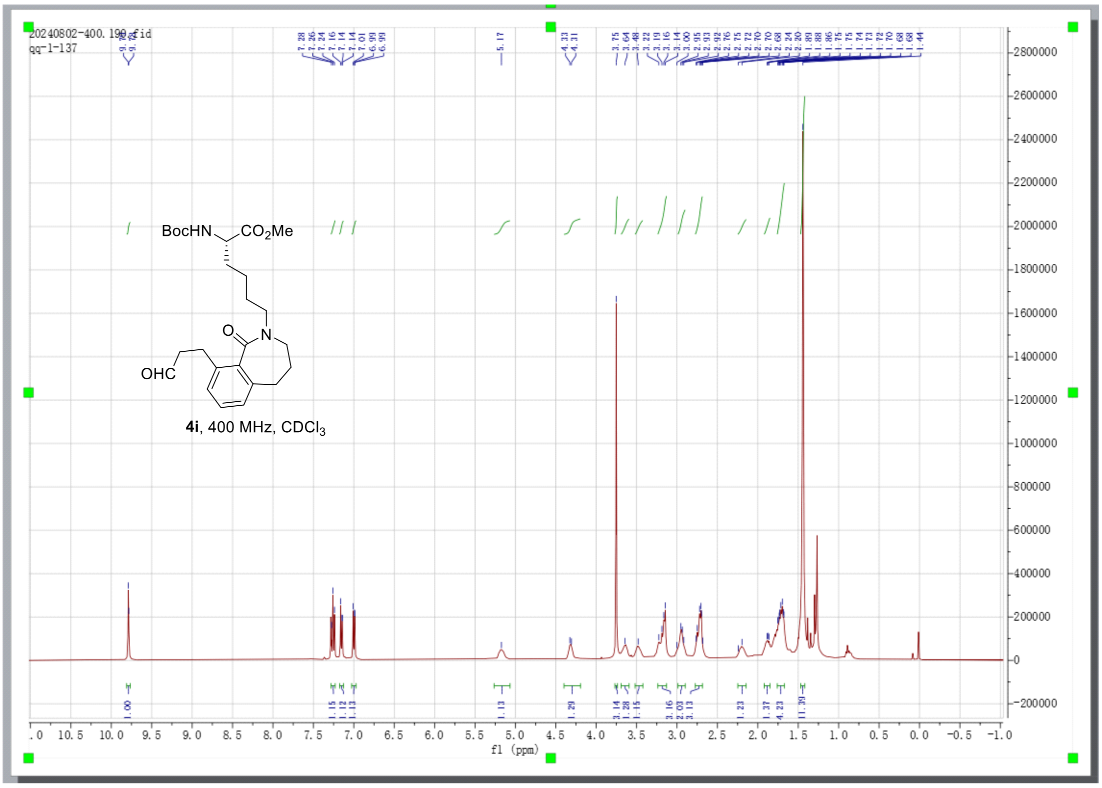
4g, 101 MHz, $CDCl_3$



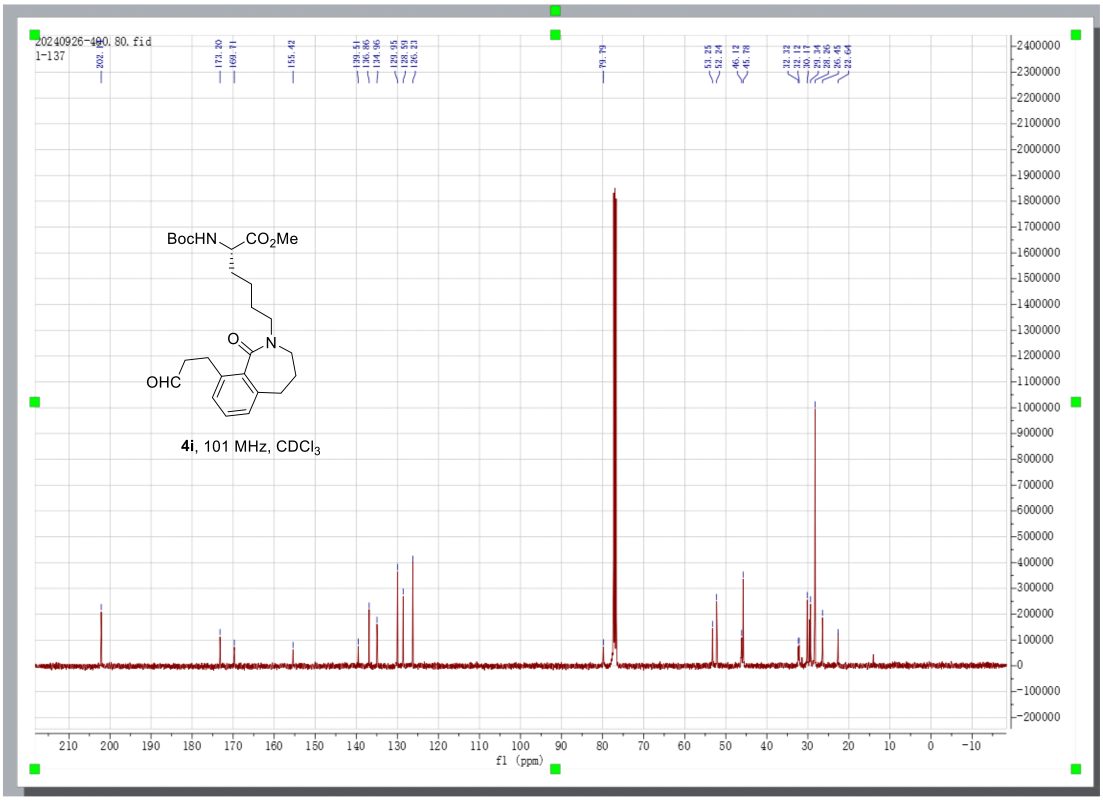
4h, 400 MHz, $CDCl_3$



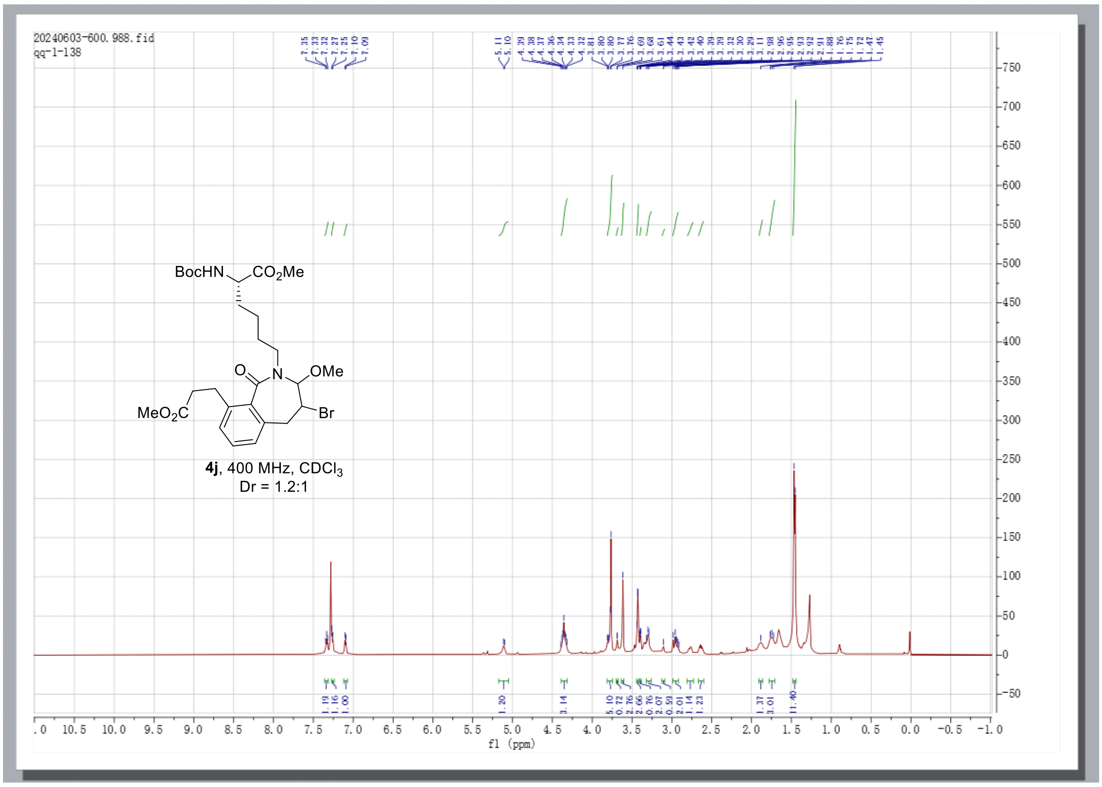
4h, 101 MHz, $CDCl_3$

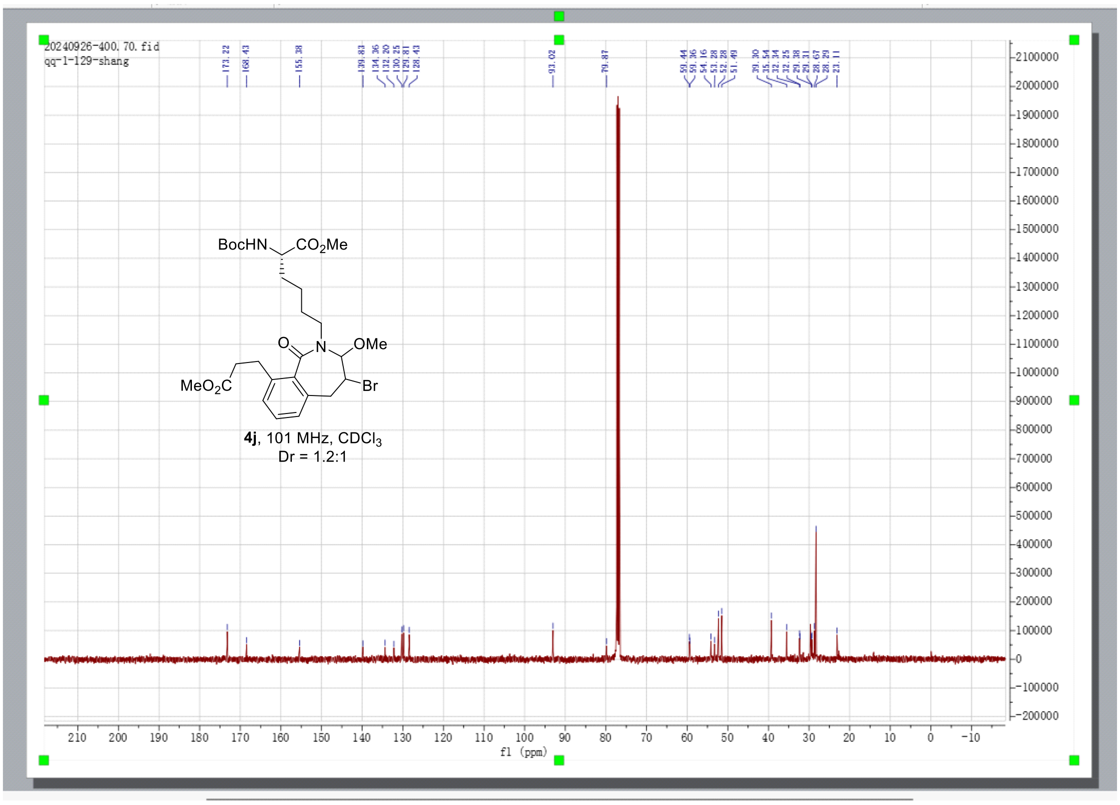


4i, 400 MHz, $CDCl_3$



4i, 101 MHz, $CDCl_3$


20240603-600.988.fid
qq-1-138
7.35 7.33 7.32 7.27 7.25 7.10 7.09
5.11 5.10
4.39 4.38 4.37 4.36 4.34 4.33 4.32 3.81 3.80 3.80 3.77 3.76 3.69 3.68 3.61 3.44 3.43 3.42 3.40 3.39 3.39 3.32 3.30 3.29 3.11 2.98 2.96 2.95 2.93 2.92 2.91 1.88 1.76 1.75 1.72 1.47 1.45
BocHN
CO$_2$Me
O
N
OMe
MeO$_2$C
Br
4j, 400 MHz, CDCl$_3$
Dr = 1.2:1
1.19 1.16 1.00
1.20
3.14
5.10 0.72 2.76 2.66 0.76 2.07 0.59 2.01 1.14 1.23
1.37 3.01
11.40
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
750 700 650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50


20240926-400.70.fid
qq-1-129-shang
173.22
168.43
155.38
139.83 134.36 132.20 130.25 129.81 128.41
93.02
79.87
59.44 59.36 54.16 53.28 52.28 51.49
39.30 35.54 32.25 29.38 29.31 28.67 28.29 23.11
BocHN
CO$_2$Me
O
N
OMe
MeO$_2$C
Br
4j, 101 MHz, CDCl$_3$
Dr = 1.2:1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
2100000 2000000 1900000 1800000 1700000 1600000 1500000 1400000 1300000 1200000 1100000 1000000 900000 800000 700000 600000 500000 400000 300000 200000 100000 0 -100000 -200000

8 、Reference

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