

## SUPPORTING INFORMATION

# Asymmetric transfer hydrogenation of ketones catalyzed by rhodium complexes containing amino acid triazole ligands

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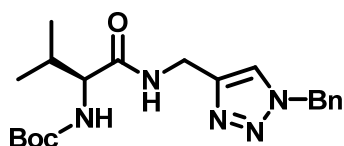
## EXPERIMENTAL

### General considerations.

Characterizations were made by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. NMR spectra were recorded on Bruker Avance II ( $^1\text{H}$ , 400 MHz;  $^{13}\text{C}$ , 100 MHz) and were referenced internally with  $\text{CDCl}_3$  ( $\delta\text{H}$  7.26,  $\delta\text{C}$  77.16 ppm). High resolution mass spectrometry was performed on a Bruker micrOTOF/ESI. Benzylazide<sup>1</sup>, 1-(azidomethyl)naphthalene<sup>1</sup>, 9-(azidomethyl)anthracene<sup>1</sup>, (R)-(1-azidoethyl)benzene<sup>2</sup>, Azidobenzene<sup>3</sup>, 1-azido-4-methoxybenzene<sup>3</sup> and 1-azido-4-nitrobenzene<sup>3</sup> were prepared according to literature procedures.

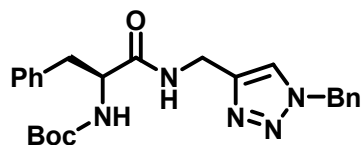
### General procedure for the preparation of triazole substituted amide ligands

NMM (1.2 eq) was slowly added to a solution of the Boc-protected amino acid (1.0 eq) at  $-15^\circ\text{C}$ . Isobutyl chloroformate (1.1 eq) was added dropwise and the reaction mixture was stirred for 1 h. Propargylamine was added and the reaction mixture was stirred at r.t. for 3 h after which it was filtered through a plug of silica (4 x 4 cm) and eluted with EtOAc. The solvent was removed under reduced pressure and the crude was purified by recrystallization from dichloromethane:pentane unless otherwise stated. The triazoles were prepared according to literature procedure<sup>4</sup>



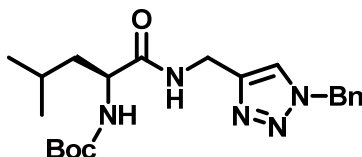
### (S)-tert-butyl 1-((1-benzyl-1H-1,2,3-triazol-4-yl)methylamino)-3-methyl-1-oxobutan-2-ylcarbamate (5a)

Boc-L-Val was reacted on a 10.0 mmol scale and the pure product was obtained as a pale grey solid in 77 % yield.  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (s, 1 H),  $\delta$  7.37-7.22 (m, 5 H),  $\delta$  6.83 (m, 1 H),  $\delta$  5.47 (s, 2 H),  $\delta$  5.00 (m, 1 H),  $\delta$  4.48 (d,  $J = 5.81$  Hz, 2 H),  $\delta$  3.92 (m, 1 H),  $\delta$  2.15-2.05 (m, 1 H),  $\delta$  1.39 (s, 9 H),  $\delta$  0.87 (d,  $J = 6.85$  Hz, 3 H),  $\delta$  0.81 (d,  $J = 6.85$  Hz, 3 H).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.75, 145.06, 134.56, 129.15, 128.80, 128.07, 123.54, 122.19, 79.98, 59.89, 54.23, 34.94, 30.88, 28.32, 19.27, 17.56.



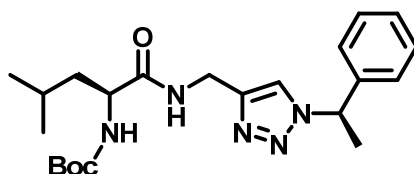
**(S)-tert-butyl 1-((1-benzyl-1H-1,2,3-triazol-4-yl)methylamino)-1-oxo-3-phenylpropan-2-ylcarbamate (5b)**

Boc-L-PhGly was reacted on a 5.0 mmol scale and the product was obtained as a brown solid in 76 % yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.44 (bs, 1 H), δ 7.41-7.09 (m, 10 H), δ 6.89 (bs, 1 H), δ 5.45 (s, 2 H), δ 5.14 (m, 1H), δ 4.44 (m, 1 H), δ 4.40 (m, 2 H), δ 3.02 (m, 2 H), δ 1.34 (s, 9 H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 171.47, 155.41, 136.68, 134.60, 129.38, 129.20, 128.89, 128.62, 128.18, 126.93, 80.21, 55.83, 54.43, 38.68, 34.97, 28.33.



**(S)-tert-butyl 1-((1-benzyl-1H-1,2,3-triazol-4-yl)methylamino)-4-methyl-1-oxopentan-2-ylcarbamate (5c)**

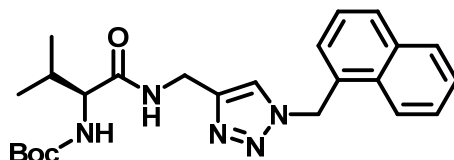
Boc-L-Leu was reacted on a 8.65 mmol scale and the product was obtained as a white solid in 72 % yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.54 (s, 1 H), δ 7.41-7.31 (m, 3 H), δ 7.27-7.24 (m, 2 H), δ 6.75 (s, 1 H), δ 5.49 (s, 2 H), δ 4.82 (s, 1 H), δ 4.51 (s, 1 H), δ 4.08 (s, 1 H) δ 1.63 (m, 3 H), δ 1.39 (s, 9 H), δ 0.90 (m, 6 H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 172.82, 147.31, 134.56, 129.27, 128.98, 128.96, 128.36, 128.24, 80.29, 69.37, 41.39, 35.14, 31.37, 28.41, 24.88, 23.12, 21.95.



**tert-butyl (S)-4-methyl-1-oxo-1-((1-((R)-1-phenylethyl)-1H-1,2,3-triazol-4-yl)methylamino)pentan-2-ylcarbamate (5f)**

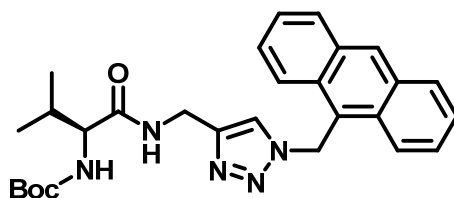
Boc-L-Leu was reacted on a 8.65 mmol scale and the product was obtained as a white solid in 19 % yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.44 (s, 1 H), δ 7.37-7.30 (m, 3 H), δ 7.26-7.23 (m,

2 H),  $\delta$  6.81 (bs, 1 H),  $\delta$  5.77 (q,  $J$  = 7.11 Hz, 1 H),  $\delta$  4.87 (bs, 1 H),  $\delta$  4.48 (d,  $J$  = 5.76 Hz, 2 H),  $\delta$  4.09 (bs, 1 H),  $\delta$  1.95 (d,  $J$  = 7.08 Hz, 3 H),  $\delta$  1.62 (m, 2 H),  $\delta$  1.43 (m, 1 H),  $\delta$  1.39 (s, 9 H),  $\delta$  0.89 (m, 6 H).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.83, 155.77, 144.66, 139.87, 129.16, 128.69, 126.60, 121.11, 80.19, 60.49, 53.32, 49.49, 35.08, 28.40, 24.86, 23.10, 21.95, 21.41



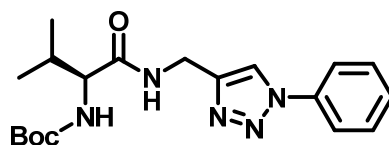
**(S)-tert-butyl 3-methyl-1-((1-(naphthalen-1-ylmethyl)-1H-1,2,3-triazol-4-yl)methylamino)-1-oxobutan-2-ylcarbamate (5d)**

Boc-L-Val was reacted on a 10.0 mmol scale and the pure product was obtained as a pale brown solid in 85 % yield.  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98-7.84 (m, 3 H),  $\delta$  7.55-7.38 (5 H),  $\delta$  6.63 (s, 1 H),  $\delta$  5.94 (s, 2 H),  $\delta$  4.96 (m, 1 H),  $\delta$  4.46 (s, 2 H),  $\delta$  3.89 (s, 1 H),  $\delta$  2.07 (m, 1 H),  $\delta$  1.39 (s, 9 H),  $\delta$  0.83 (d,  $J$  = 6.76 Hz, 3 H),  $\delta$  0.75 (d,  $J$  = 6.76 Hz, 3 H).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.81, 155.90, 134.01, 131.21, 130.14, 129.84, 129.03, 127.96, 126.83, 126.80, 126.45, 125.44, 123.57, 122.90, 79.89, 59.76, 52.47, 34.88, 31.05, 28.36, 19.24, 17.60.



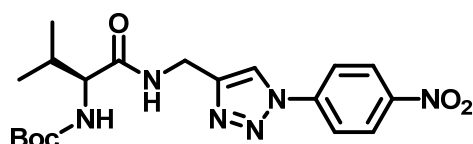
**(S)-tert-butyl 1-((1-(anthracen-9-ylmethyl)-1H-1,2,3-triazol-4-yl)methylamino)-3-methyl-1-oxobutan-2-ylcarbamate (5e)**

Boc-L-Val was reacted on a 10.0 mmol scale and the pure product was obtained as a pale grey solid in 84 % yield.  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.54 (s, 1 H),  $\delta$  8.25 (d,  $J$  = 8.64 Hz, 2 H),  $\delta$  8.04 (d,  $J$  = 8.16, 2 H),  $\delta$  7.58-7.48 (m, 4 H),  $\delta$  7.14 (bs, 1 H),  $\delta$  6.87 (bs, 1 H),  $\delta$  6.44 (s, 2 H),  $\delta$  5.03 (m, 1 H),  $\delta$  4.32 (s, 2 H),  $\delta$  3.85 (m, 1 H),  $\delta$  1.96 (m, 1 H),  $\delta$  1.35 (s, 9 H),  $\delta$  0.74 (d,  $J$  = 6.44 Hz, 3 H),  $\delta$  0.67 (d,  $J$  = 6.84 Hz, 3 H).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.52, 155.90, 134.42, 131.55, 130.94, 130.16, 129.68, 127.88, 125.54, 123.72, 123.33, 122.97, 80.02, 59.77, 46.84, 34.81, 30.93, 28.38, 19.22, 17.48.



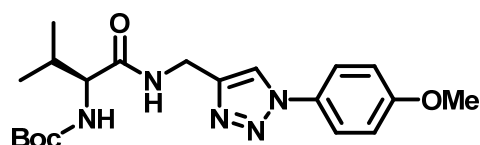
**(S)-tert-butyl 3-methyl-1-oxo-1-((1-phenyl-1H-1,2,3-triazol-4-yl)methylamino)butan-2-ylcarbamate (5g)**

Boc-L-Val was reacted on a 10.0 mmol scale and the pure product was obtained as a beige solid in 79 % yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03, (s, 1 H), δ 7.72-7.69 (m, 2 H), δ 7.52-7.48 (m, 2 H), δ 7.44-7.40 (m, 1 H), δ 7.03 (s, 1 H), δ 5.11 (m, 1 H), δ 4.62 (d, *J* = 5.85 Hz, 2 H), δ 3.98 (m, 1 H), δ 2.16 (m, 1 H), δ 1.40 (s, 9 H), δ 0.94 (d, *J* = 6.76 Hz, 3 H), δ 0.88 (d, *J* = 6.84 Hz, 3 H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 172.12, 156.03, 137.12, 129.87, 129.84, 128.92, 120.77, 120.64, 80.13, 60.17, 35.05, 30.96, 28.42, 19.46, 17.81.



**(S)-tert-butyl 3-methyl-1-oxo-1-((1-(4-nitrophenyl)-1H-1,2,3-triazol-4-yl)methylamino)-1-oxobutan-2-ylcarbamate (5h)**

Boc-L-Val was reacted on a 10.0 mmol scale and the pure product was obtained as a pale yellow solid in 78 % yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 8.42-8.39 (m, 2 H), δ 8.18 (s, 1 H), δ 7.99-7.95 (m, 2 H), δ 6.82 (bs, 1 H), δ 5.00 (bs, 1 H), δ 4.64 (d, *J* = 5.99 Hz, 2 H), δ 3.94 (m, 1 H), δ 2.18 (m, 1 H), δ 1.41 (s, 9 H), δ 0.96 (d, *J* = 6.63 Hz, 3 H), δ 0.91 (d, *J* = 6.87 Hz, 3 H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 172.33, 156.23, 147.39, 146.74, 141.23, 125.77, 120.81, 120.57, 80.38, 60.41, 35.01, 30.71, 28.43, 19.49, 17.88.

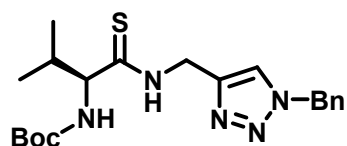


**(S)-tert-butyl 1-((1-(4-methoxyphenyl)-1H-1,2,3-triazol-4-yl)methylamino)-3-methyl-1-oxobutan-2-ylcarbamate (5i)**

Boc-L-Val was reacted on a 10.0 mmol scale and the pure product was obtained as a pale grey solid in 71 % yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (s, 1 H),  $\delta$  7.62-7.58 (m, 2 H),  $\delta$  7.02-6.98 (m, 2 H),  $\delta$  6.79 (bs, 1 H),  $\delta$  5.02 (m, 1 H),  $\delta$  4.61 (d,  $J = 5.57$  Hz, 2 H),  $\delta$  3.96 (m, 1 H),  $\delta$  3.86 (s, 3 H),  $\delta$  2.18 (m, 1 H),  $\delta$  1.41 (s, 9 H),  $\delta$  0.94 (d,  $J = 6.83$  Hz, 3 H),  $\delta$  0.89 (d,  $J = 6.83$  Hz, 3 H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.01, 160.02, 156.05, 141.81, 130.99, 129.00, 122.39, 114.97, 80.21, 60.20, 55.78, 34.99, 30.87, 28.44, 19.48, 17.77

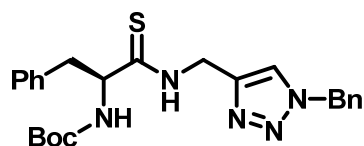
### General procedure for the preparation of triazole substituted thioamide ligands

The triazole substituted amide ligand (1.0 eq) and Lawesson's reagent (0.85 eq) were added to dry THF, heated to 65 °C and stirred over night. The solution was filtered through a plug of silica (4 x 4 cm), eluted with EtOAc and concentrated under reduced pressure. The crude product was purified with column chromatography using silica column.



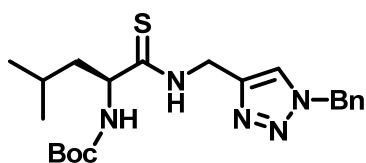
### (S)-tert-butyl 1-((1-benzyl-1H-1,2,3-triazol-4-yl)methylamino)-3-methyl-1-thioxobutan-2-ylcarbamate (2a)

Compound **5a** was reacted on a 0.31 mmol scale to produce the ligand as a white solid in 82 % yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.57 (m, 1 H),  $\delta$  7.65 (s, 1 H),  $\delta$  7.35-7.29 (m, 3 H),  $\delta$  7.24-7.20 (m, 2 H),  $\delta$  5.46 (m, 2 H),  $\delta$  5.42 (m, 1 H),  $\delta$  4.91 (m, 2 H),  $\delta$  4.22 ( $t_{\text{app}}$ ,  $J = 8.00$  Hz, 1 H),  $\delta$  2.12 (m, 1 H),  $\delta$  1.34 (s, 9 H),  $\delta$  0.86-0.80 (m, 6 H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  204.70, 155.71, 143.03, 134.52, 129.14, 128.80, 128.04, 123.24, 79.90, 66.04, 54.25, 40.42, 33.79, 28.34, 19.56, 17.98. HRMS  $m/z$   $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{20}\text{H}_{29}\text{N}_5\text{O}_2\text{S}$ : 426.1934; found 426.1933.



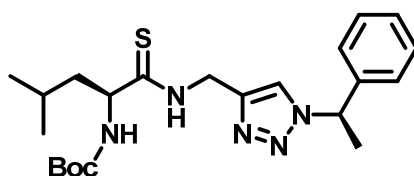
### (S)-tert-butyl 1-((1-benzyl-1H-1,2,3-triazol-4-yl)methylamino)-3-phenyl-1-thioxopropan-2-ylcarbamate (2b)

Compound **5b** was reacted on a 1.86 mmol scale and the thioamide was obtained as a white solid after column chromatography using EtOAc:n-pentane 1:3 as eluent in 83 % yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 9.40 (s, 1 H), δ 7.45 (s, 1 H), δ 7.37-7.30 (m, 3 H), δ 7.25-7.23 (m, 2 H), δ 7.08 (s, 5 H), δ 5.61 (s, 1 H), δ 5.43 (s, 2 H), δ 4.75 (m, 3 H), δ 3.10 (m, 2 H), δ 1.29 (s, 9 H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 203.53, 154.88, 142.64, 136.51, 134.33, 129.18, 128.99, 128.67, 128.19, 127.92, 126.58, 123.02, 79.88, 61.68, 54.03, 42.02, 40.17, 28.10. HRMS *m/z* [M + Na]<sup>+</sup> calculated for C<sub>24</sub>H<sub>29</sub>N<sub>5</sub>O<sub>2</sub>S: 474.1934; found 474.1935.



**(S)-tert-butyl 1-((1-benzyl-1H-1,2,3-triazol-4-yl)methylamino)-4-methyl-1-thioxopentan-2-ylcarbamate (2c)**

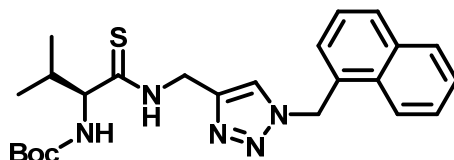
Compound **5c** was reacted on a 1.86 mmol scale and the thioamide was obtained as a white solid after column chromatography using EtOAc:n-pentane 1:2 as eluent in 62 % yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 8.96 (s, 1 H), δ 7.59 (s, 1 H), δ 7.39-7.32 (m, 3 H), δ 7.26-7.24 (m, 2 H), δ 5.49 (s, 2 H), δ 5.18 (s, 1 H), δ 4.91 (d, *J* = 5.40 Hz, 2 H), δ 4.43 (m, 1 H), δ 1.74-1.52 (m, 3 H), δ 1.36 (s, 9 H), δ 0.90 (d, *J* = 6.29 Hz, 6 H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 205.90, 155.62, 143.03, 134.50, 129.25, 128.93, 128.17, 123.01, 80.25, 59.61, 54.36, 44.88, 40.72, 28.36, 25.03, 23.14, 21.93. HRMS *m/z* [M + Na]<sup>+</sup> calculated for C<sub>21</sub>H<sub>31</sub>N<sub>5</sub>O<sub>2</sub>S: 440.2111; 440.2091.



**tert-butyl (S)-4-methyl-1-((1-((R)-1-phenylethyl)-1H-1,2,3-triazol-4-yl)methylamino)-1-thioxopentan-2-ylcarbamate (2f)**

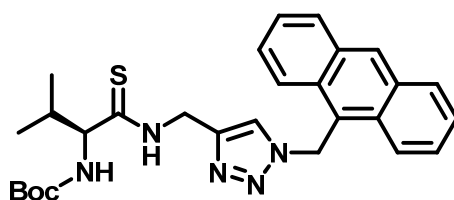
Compound **5f** was reacted on a 0.38 mmol scale and the thioamide was obtained as a white solid after column chromatography using EtOAc:n-pentane 1:2 as eluent in 40 % yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 8.98 (s, 1 H), δ 7.58 (s, 1 H), δ 7.38-7.29 (m, 3 H), δ 7.26-7.23 (m, 2 H), δ 5.77 (q, *J* = 7.10 Hz, 1 H), δ 5.19 (d, *J* = 7.99 Hz, 1 H), δ 4.90 (dd, *J* = 5.28, 3.16 Hz,

2 H),  $\delta$  4.43 (m, 1 H),  $\delta$  1.96 (d,  $J$  = 7.15 Hz, 3 H),  $\delta$  1.74-1.52 (m, 3 H),  $\delta$  1.36 (s, 9 H),  $\delta$  6.34 (d,  $J$  = 6.34 Hz, 6 H).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  205.83, 155.55, 142.60, 139.80, 129.13, 128.70, 126.54, 121.97, 80.11, 60.58, 59.58, 44.91, 40.68, 28.35, 25.00, 23.12, 21.92, 21.43. HRMS  $m/z$   $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{22}\text{H}_{33}\text{N}_5\text{O}_2\text{S}$ : 454.2270; 454.2247



**(S)-tert-butyl-3-methyl-1-((1-(naphthalen-1-ylmethyl)-1H-1,2,3-triazol-4-yl)methylamino)-1-thioxobutan-2-ylcarbamate (2d)**

Compound **5d** was reacted on a 1.98 mmol scale to give the thioamide as a white solid after column chromatography using toluene:EtOAc 1:1 as the eluent in 40 % yield.  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.09 (m, 1 H),  $\delta$  7.95-7.79(m, 3 H),  $\delta$  7.53-7.37 (m, 5 H),  $\delta$  5.93 (d,  $J$  = 3.02 Hz, 2 H),  $\delta$  5.29 (m, 1 H),  $\delta$  4.86 (m, 2 H),  $\delta$  4.17-4.13 (m, 1 H),  $\delta$  2.17 (m, 1 H),  $\delta$  1.35 (s, 9 H),  $\delta$  0.81 (m, 6 H).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  204.51, 155.71, 142.81, 134.04, 131.18, 130.20, 129.76, 129.08, 127.90, 127.41, 126.51, 125.48, 123.08, 122.87, 80.06, 65.95, 52.52, 40.52, 33.67, 28.38, 19.64, 17.82. HRMS  $m/z$   $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{24}\text{H}_{31}\text{N}_5\text{O}_2\text{S}$ : 476.2091; found 476.2087.

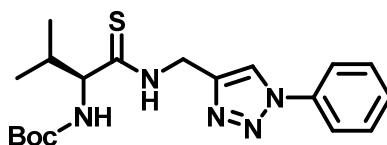


**(S)-tert-butyl-1-((1-(anthracen-9-ylmethyl)-1H-1,2,3-triazol-4-yl)methylamino)-3-methyl-1-thioxobutan-2-ylcarbamate (2e)**

Compound **5e** was reacted on a 2.05 mmol scale to give the thioamide as a yellow solid after column chromatography using toluene:EtOAc 1:1 as the eluent in 24 % yield.  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.77 (bs, 1 H),  $\delta$  8.55 (s, 1 H),  $\delta$  8.26 (d,  $J$  = 8.82 Hz, 2 H),  $\delta$  8.05 (d,  $J$  = 8.47 Hz, 2 H),  $\delta$  7.60-7.49 (m, 4 H),  $\delta$  7.26 (m, 1 H),  $\delta$  6.47 (s, 2 H),  $\delta$  5.21 (m, 1 H),  $\delta$  4.81-4.67 (m, 2 H),  $\delta$  4.08 ( $t_{\text{app}}$ ,  $J$  = 7.72 Hz, 1 H),  $\delta$  2.16 (bs, 1 H),  $\delta$  1.33 (s, 9 H),  $\delta$  0.78-0.76 ( $m_{\text{app}}$ , 6 H).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  204.18, 155.65, 142.52, 131.56, 130.88, 130.14, 129.65,

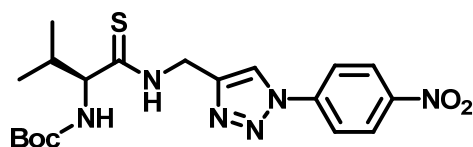


127.88, 125.56, 123.62, 122.97, 122.33, 80.11, 66.40, 46.66, 40.66, 33.58, 28.36, 19.65, 17.70. HRMS  $m/z$   $[M + Na]^+$  calculated for  $C_{28}H_{33}N_5O_2S$ : 526.2247; found 526.2240.



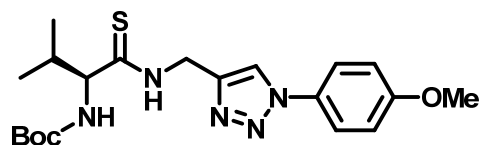
**(S)-tert-butyl 3-methyl-1-((1-phenyl-1H-1,2,3-triazol-4-yl)methylamino)-1-thioxobutan-2-ylcarbamate (2g)**

Compound **5g** was reacted on a 1.60 mmol scale and the thioamide was obtained as a white solid after column chromatography using EtOAc:n-pentane 1:3 as eluent in 63 % yield.  $^1H$ -NMR (400 MHz,  $CDCl_3$ )  $\delta$  9.35 (s, 1 H),  $\delta$  8.19 (s, 1 H),  $\delta$  7.70 (m, 2 H),  $\delta$  7.51 (m, 2 H),  $\delta$  7.44 (m, 1 H),  $\delta$  5.37 (d,  $J = 8.60$  Hz, 1 H),  $\delta$  5.06 (m, 2 H),  $\delta$  4.25 ( $t_{app}$ ,  $J = 7.79$  Hz, 1 H),  $\delta$  2.25 (s, 1 H),  $\delta$  1.37 (s, 9 H),  $\delta$  0.91 (m, 6 H).  $^{13}C$ -NMR (100 MHz,  $CDCl_3$ )  $\delta$  204.99, 155.86, 143.38, 136.95, 129.90, 129.05, 121.57, 120.67, 80.18, 66.56, 40.51, 33.64, 28.40, 19.77, 18.00. HRMS  $m/z$   $[M + Na]^+$  calculated for  $C_{19}H_{27}N_5O_2S$ : 412.1778; found 412.1779.



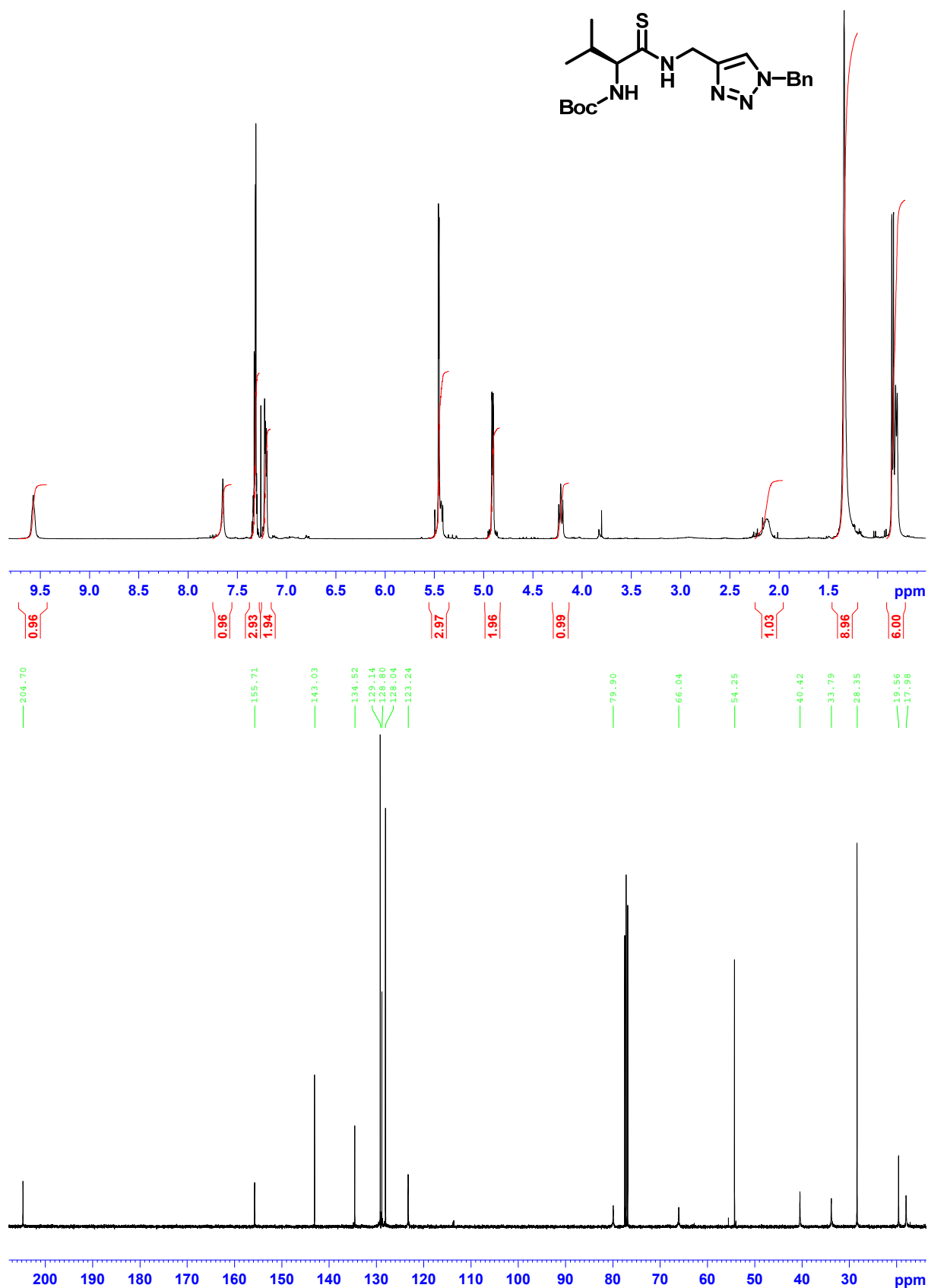
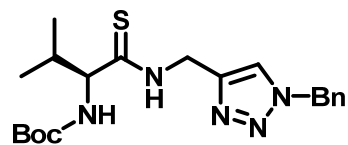
**(S)-tert-butyl 3-methyl-1-((1-(4-nitrophenyl)-1H-1,2,3-triazol-4-yl)methylamino)-1-thioxobutan-2-ylcarbamate (2h)**

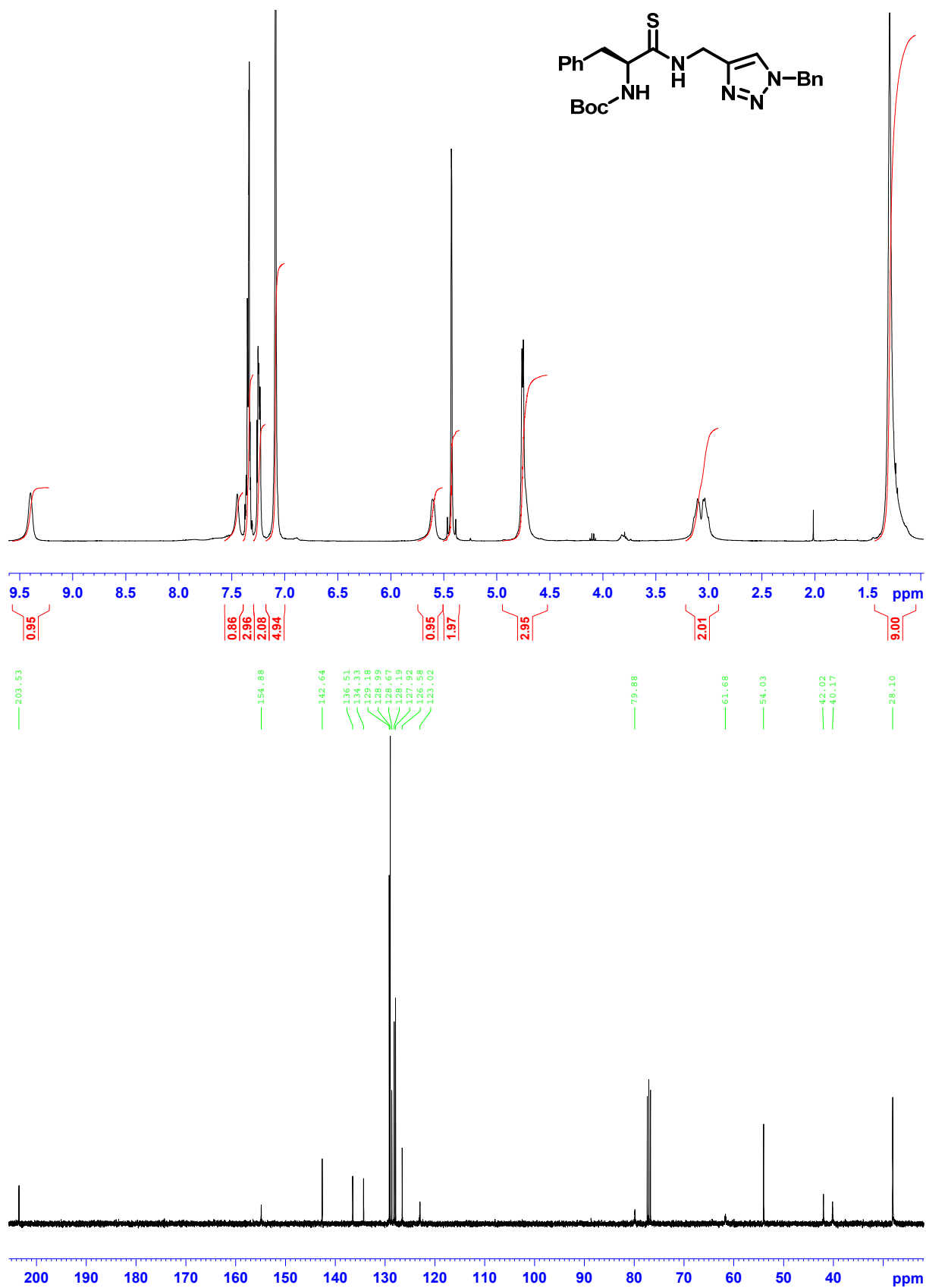
Compound **5h** was reacted on a 1.69 mmol scale and the thioamide was obtained as a yellow solid after column chromatography using EtOAc:n-pentane 1:2 as eluent in 44 % yield.  $^1H$ -NMR (400 MHz,  $CDCl_3$ )  $\delta$  9.10 (s, 1 H),  $\delta$  8.42-8.39 (m, 2 H),  $\delta$  8.33 (s, 1 H),  $\delta$  8.00-7.96 (m, 2 H),  $\delta$  5.28 (m, 1 H),  $\delta$  5.08 (d,  $J = 5.58$  Hz, 2 H),  $\delta$  4.21 (m, 1 H),  $\delta$  2.25 (m, 1 H),  $\delta$  1.37 (s, 9 H),  $\delta$  0.91 (m, 6 H).  $^{13}C$ -NMR (100 MHz,  $CDCl_3$ )  $\delta$  205.40, 156.02, 147.46, 144.29, 141.09, 125.67, 121.49, 120.69, 80.50, 66.89, 40.39, 33.47, 28.41, 19.79, 18.07. HRMS  $m/z$   $[M + Na]^+$  calculated for  $C_{19}H_{26}N_6O_4S$ : 457.1628; found 457.1644.

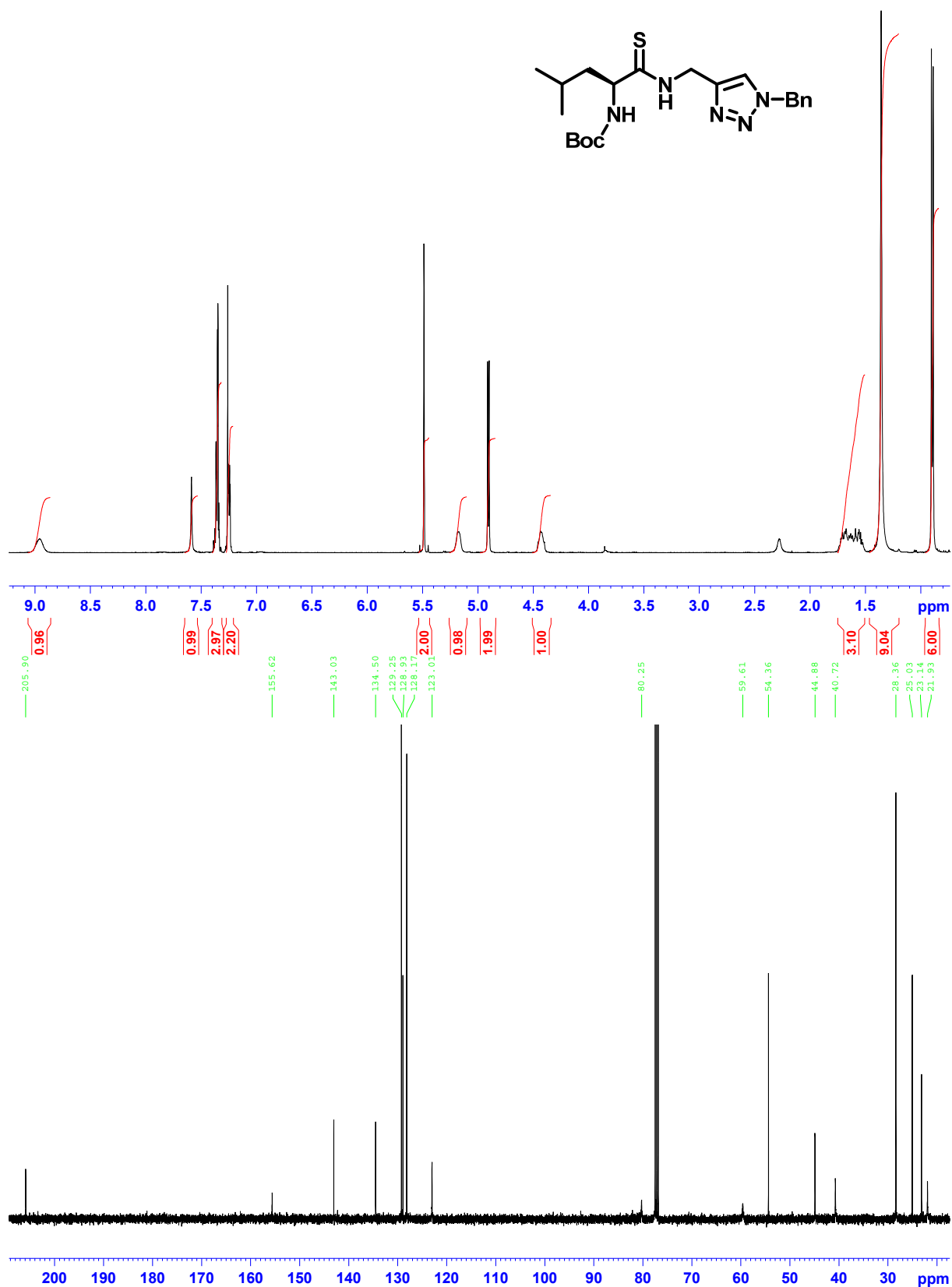


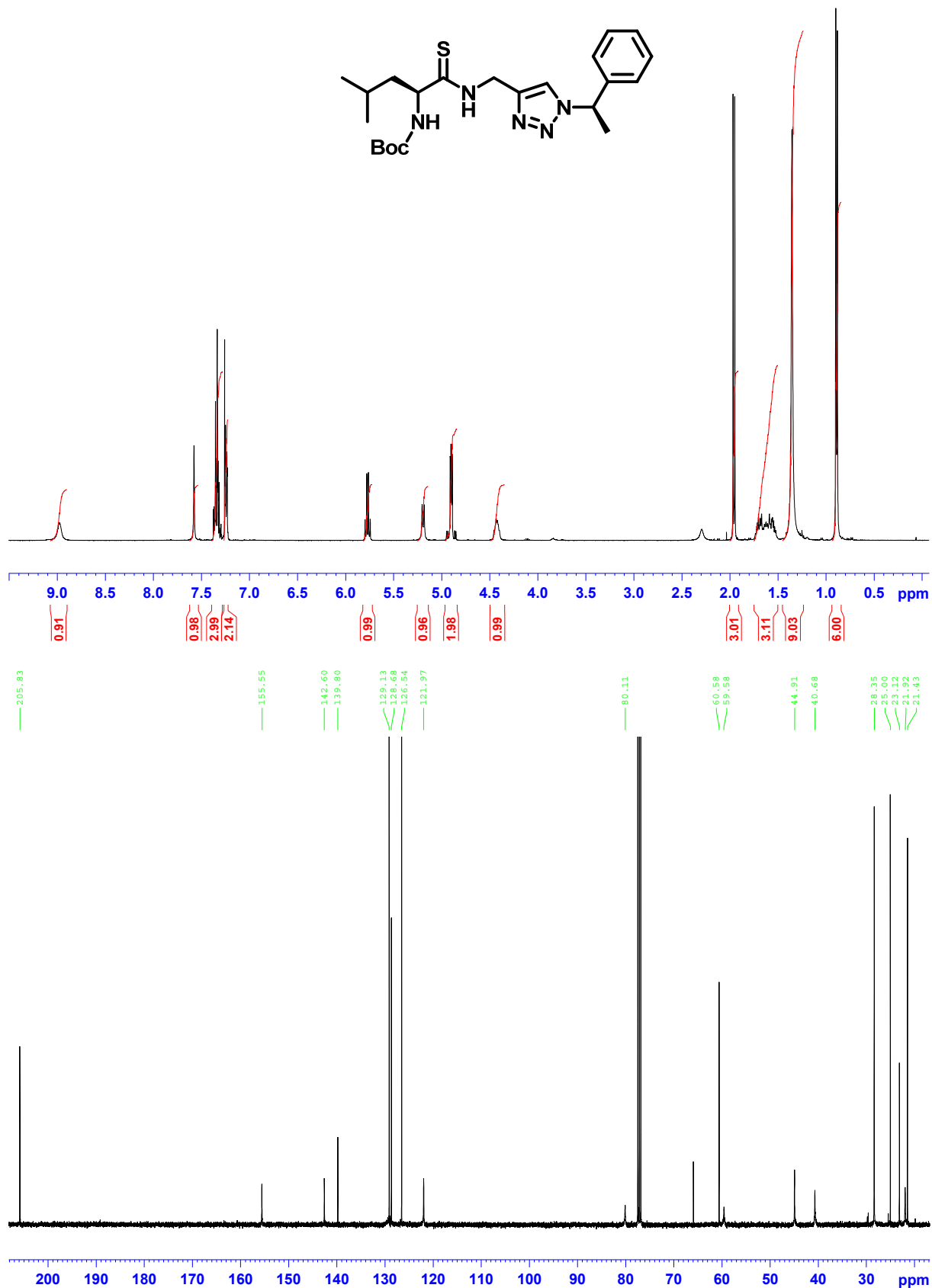
**(S)-tert-butyl 1-((1-(4-methoxyphenyl)-1H-1,2,3-triazol-4-yl)methylamino)-3-methyl-1-thioxobutan-2-ylcarbamate (2i)**

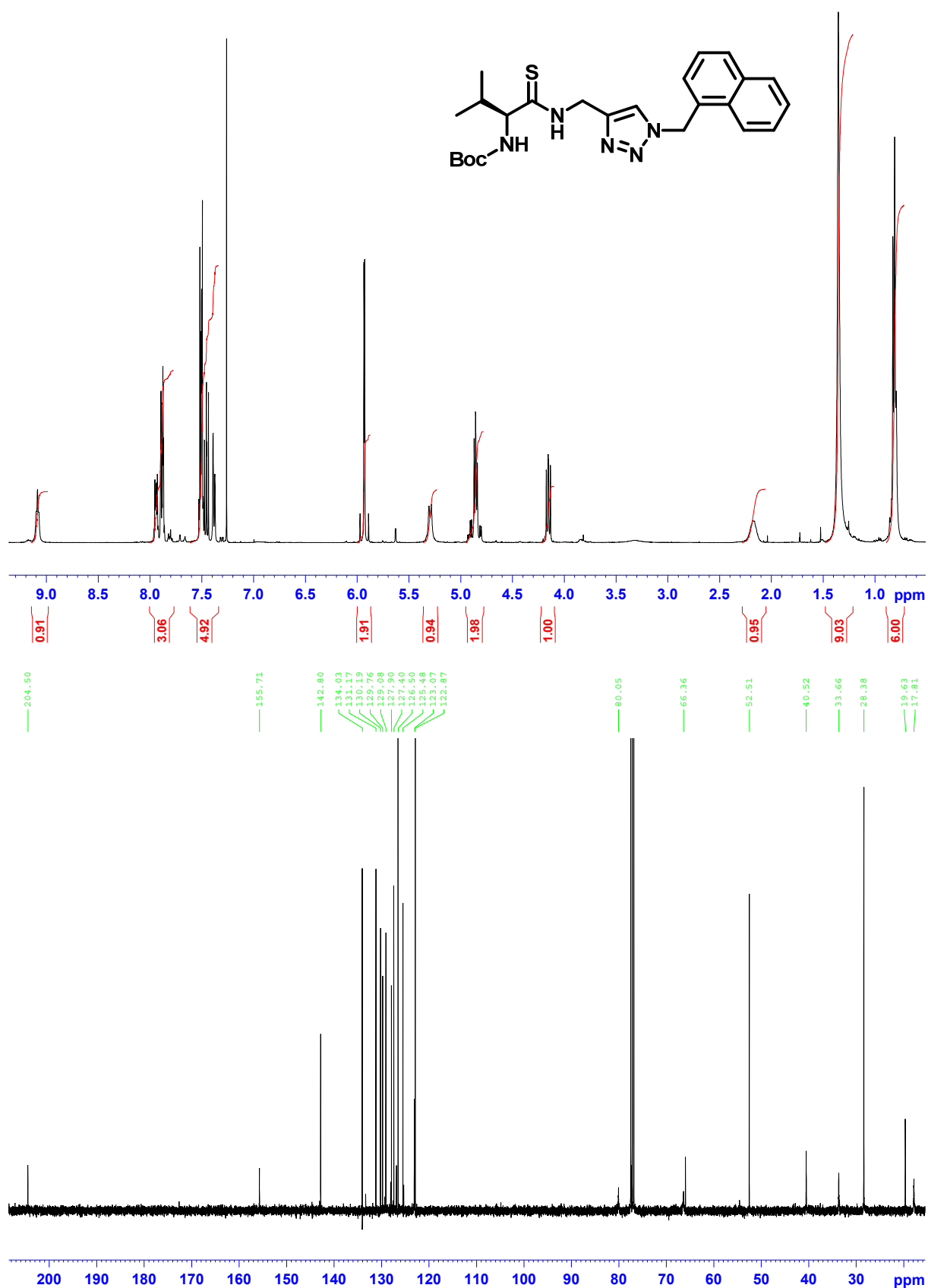
Compound **5i** was reacted on a 1.54 mmol scale and the thioamide was obtained as a white solid after column chromatography using EtOAc:n-pentane 1:1 as eluent in 67 % yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 9.23 (bs, 1 H), δ 8.08 (s, 1 H), δ 7.61-7.57 (m, 2 H), δ 7.01-6.98 (m, 2 H), δ 5.33 (m, 1 H), δ 5.09-5.00 (m, 2 H), δ 4.25-4.21 (m, 1 H), δ 3.86 (s, 3 H), δ 2.27 (m, 1 H), δ 1.37 (s, 9 H), δ 0.91-0.89 (m, 6 H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 204.84, 160.05, 155.81, 143.11, 130.38, 122.29, 121.59, 144.89, 80.16, 66.58, 55.75, 40.56, 33.60, 28.39, 19.78, 17.96. HRMS *m/z* [M + Na]<sup>+</sup> calculated for C<sub>20</sub>H<sub>29</sub>N<sub>5</sub>O<sub>3</sub>S: 442.1883; found 442.1870 .

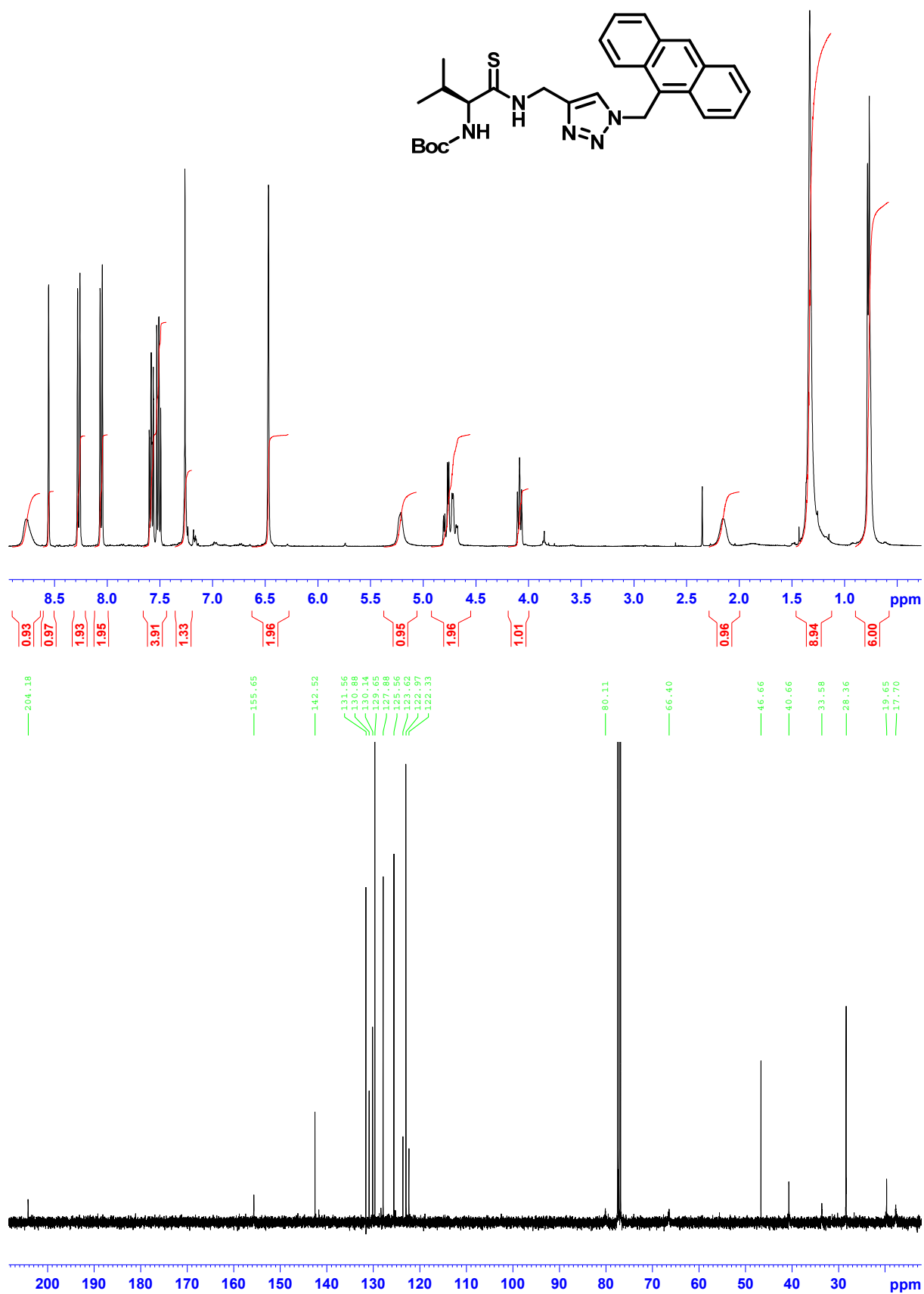




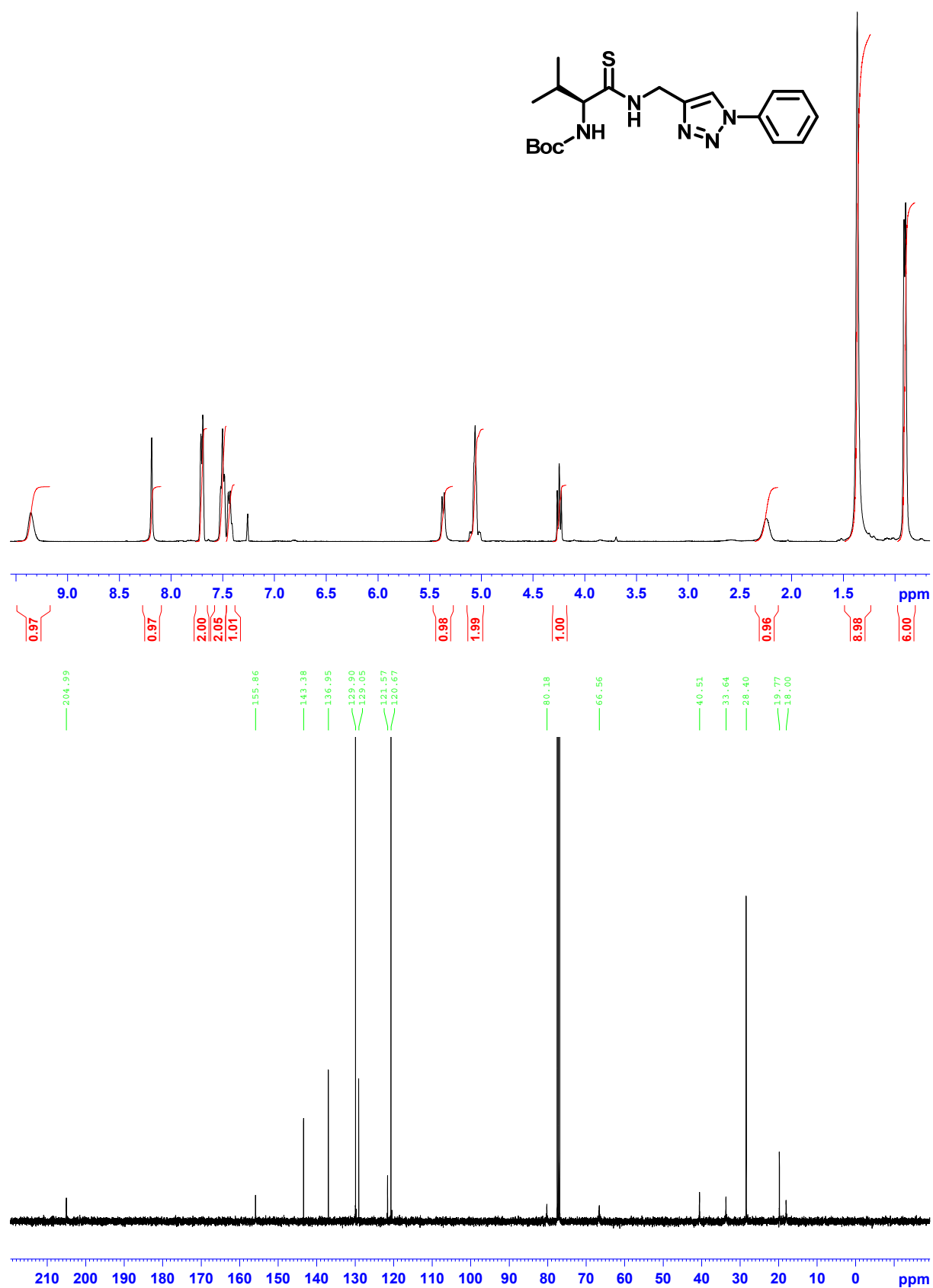


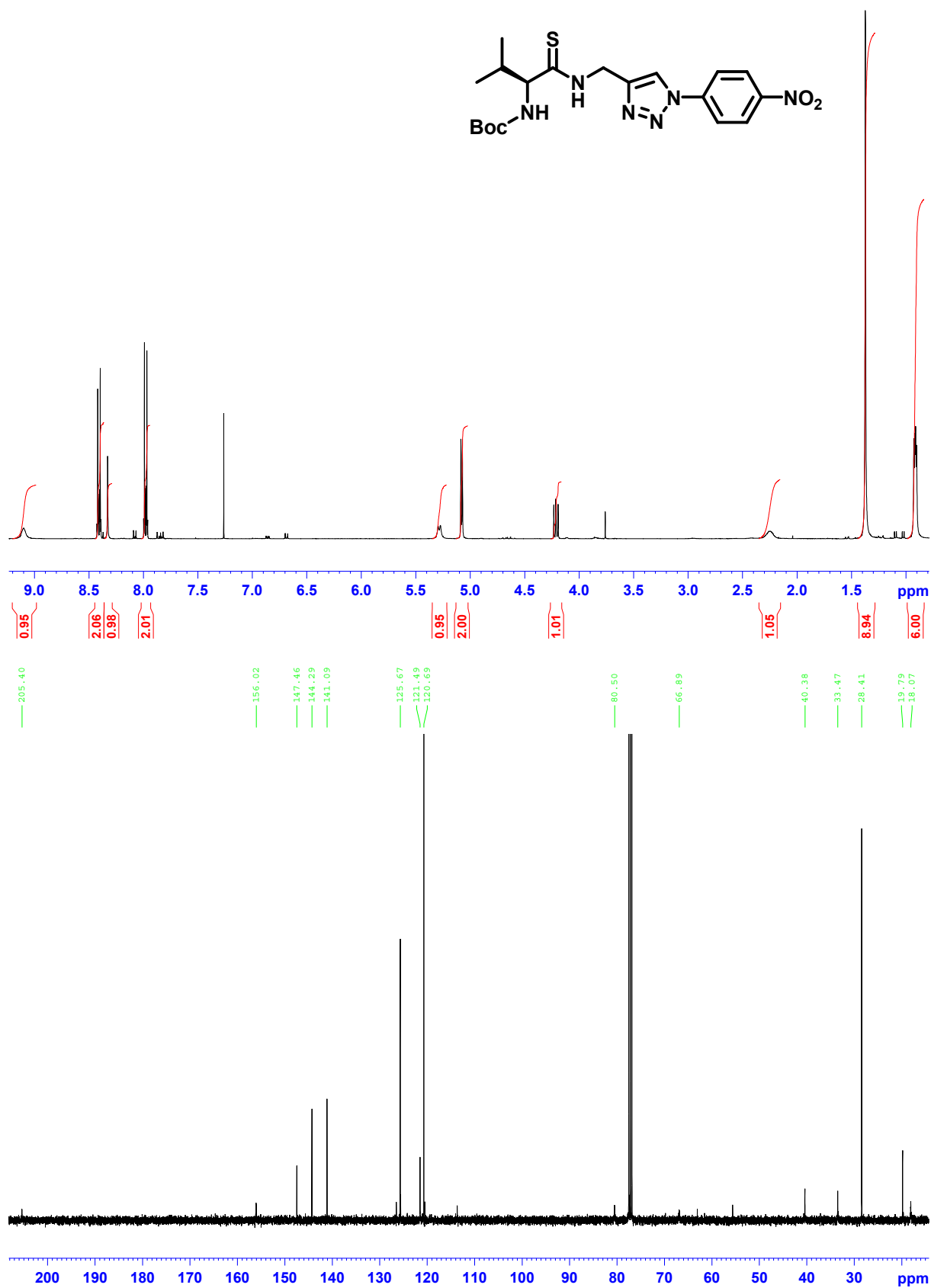


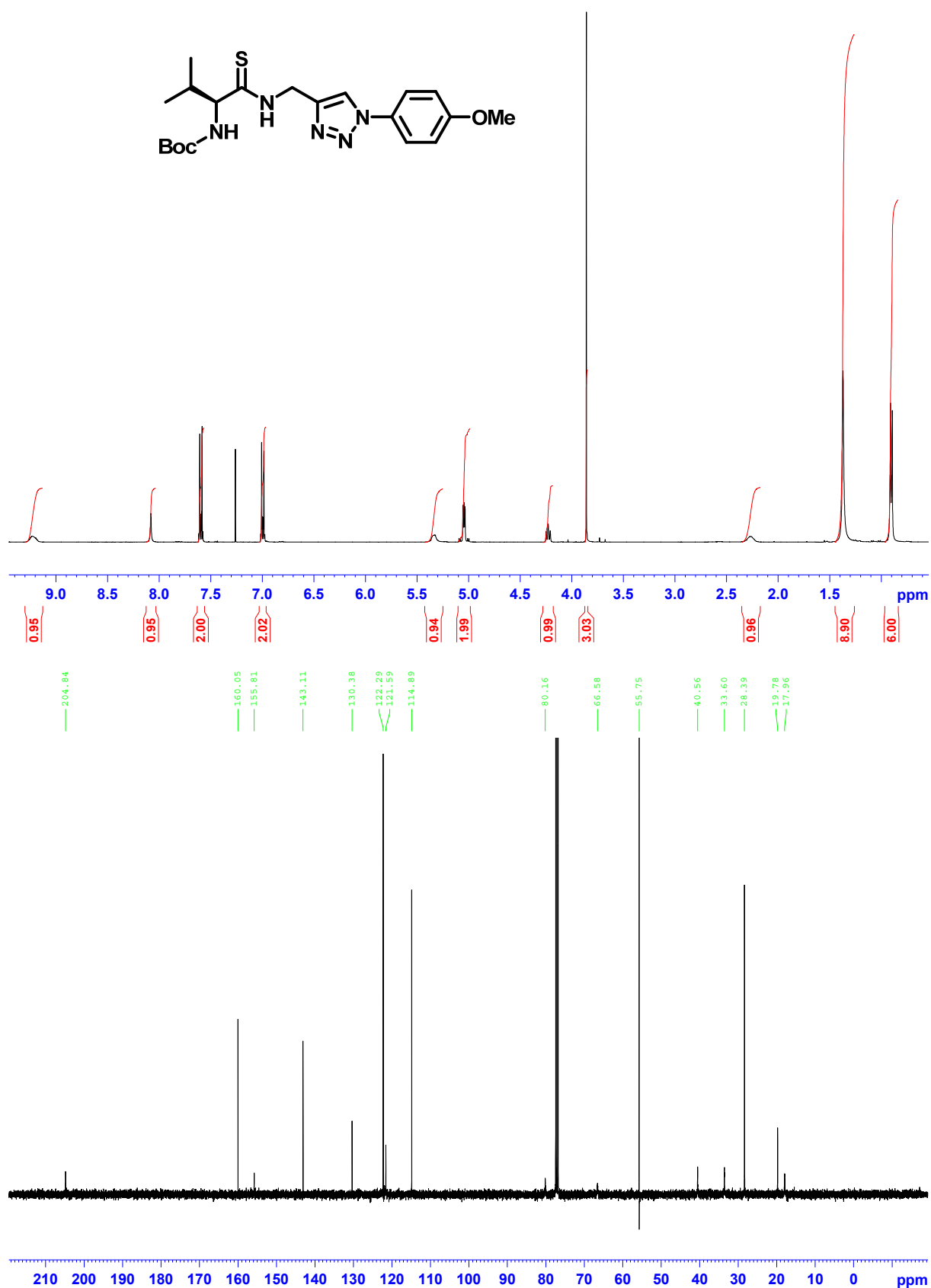












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