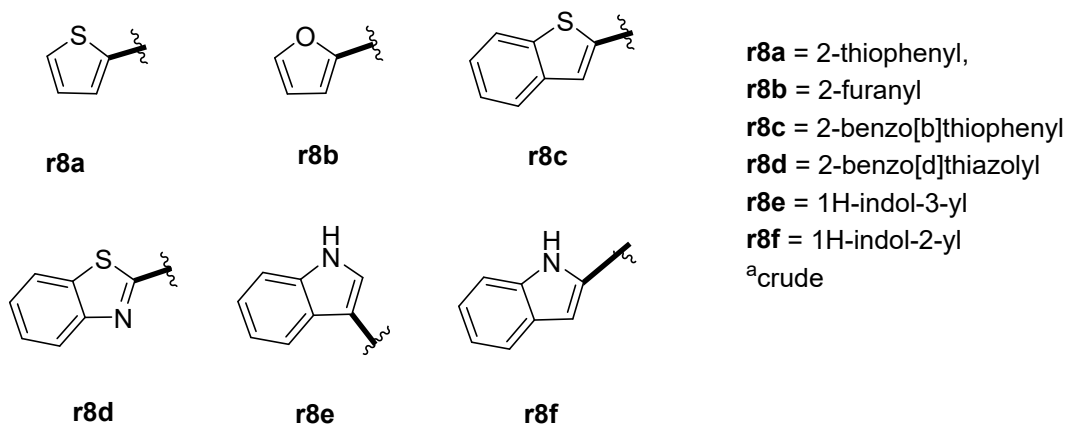
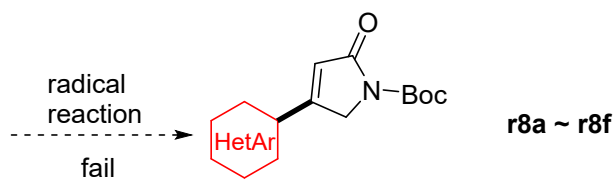
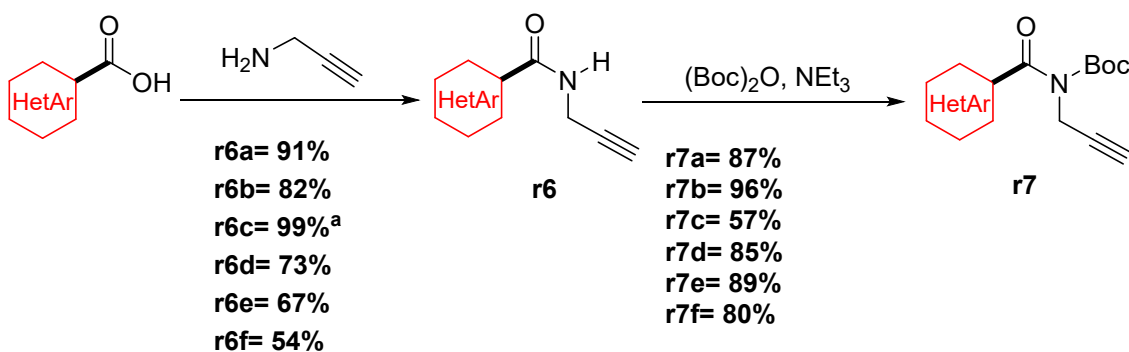


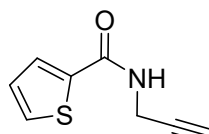
## Supporting Information

Unsuccessful examples:

heteroaryl groups (2-thiophenyl, 2-thiazolyl, 2-furanyl, 2-benzo[b]thiophenyl, 2-methylbenzo[d]thiazolyl, 1H-indol-3-yl, 1H-indol-2-yl)



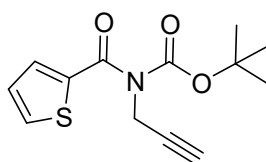
***N*-(Prop-2-yn-1-yl)thiophene-2-carboxamide (r6a)**



**r6a**

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 (d,  $J = 3.6$  Hz, 1H), 7.46 (d,  $J = 5.1$  Hz, 1H), 7.04 (t,  $J = 4.4$  Hz, 1H), 6.37 (br s, amide N-H, 1H), 4.20 (dd,  $J = 5.4$ , 2.4 Hz, 1H), 2.24 (t,  $J = 2.4$  Hz, 1H,  $\text{C}\equiv\text{C}-\underline{\text{H}}$ )

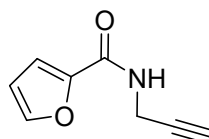
***tert*-Butyl prop-2-yn-1-yl(thiophene-2-carbonyl)carbamate (r7a)**



**r7a**

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (dd,  $J = 4.8$ , 1.2 Hz, 1H), 7.48 (dd,  $J = 3.9$ , 1.2 Hz, 1H), 7.04 (dd,  $J = 5.1$ , 3.9 Hz, 1H), 4.46 (d,  $J = 2.4$  Hz, 2H), 2.22 (t,  $J = 2.4$  Hz, 1H,  $\text{C}\equiv\text{C}-\underline{\text{H}}$ ), 1.34 (s, 9H).

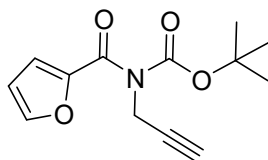
***N*-(Prop-2-yn-1-yl)furan-2-carboxamide (r6b)**



**r6b**

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44–7.43 (dd,  $J = 1.8$ , 0.6 Hz, 1H), 7.13 (dd,  $J = 3.6$ , 0.6 Hz, 1H), 6.58–6.46 (br s, amide N-H overlapped with one dd at 6.49,  $J = 3.6$ , 1.8 Hz, 2H), 4.21 (dd,  $J = 5.6$ , 2.6 Hz, 2H), 2.26 (t,  $J = 2.6$  Hz, 1H,  $\text{C}\equiv\text{C}-\underline{\text{H}}$ );  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  157.9 (C), 147.4 (C), 144.2 (CH), 114.8 (CH), 112.2 (CH), 79.2 (CH), 71.9 (CH), 28.9 ( $\text{CH}_2$ ).

***tert*-Butyl (furan-2-carbonyl)(prop-2-yn-1-yl)carbamate (r7b)**

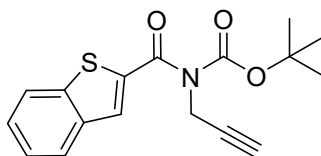


**r7b**

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (t,  $J = 0.8$  Hz, 1H), 7.06 (dd,  $J = 3.6$ , 0.6 Hz, 1H), 6.47 (dd,  $J = 3.6$ , 1.8 Hz, 1H), 6.41 (d,  $J = 2.4$  Hz, 2H), 2.18 (t,  $J = 0.8$  Hz, 1H,  $\text{C}\equiv\text{C}-\underline{\text{H}}$ ), 1.32 (s, 9H);  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  161.4 (C), 152.0 (C), 148.4 (C), 144.5 (CH), 117.3 (CH), 112.2 (CH), 83.6 (C), 78.8 (C,  $\underline{\text{C}}\equiv\text{C}-\text{H}$ ), 71.2 (CH,  $\text{C}\equiv\text{C}-\underline{\text{H}}$ ), 34.9 ( $\text{CH}_2$ ), 27.6 ( $\text{CH}_3 \times 3$ ).

***tert*-Butyl(benzo[b]thiophene-2-carbonyl)(prop-2-yn-1-yl)carbamate**

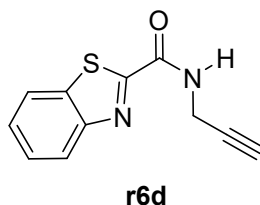
**(r7c)**



**r7c**

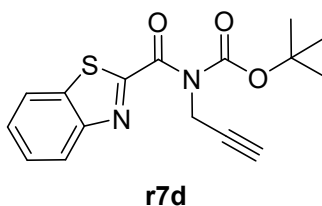
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (t,  $J = 6.2$  Hz, 2H), 7.71 (s, 1H), 7.47–7.36 (m, 2H), 4.53 (d,  $J = 2.1$  Hz, 2H), 2.27 (t,  $J = 2.4$  Hz, 1H,  $\text{C}\equiv\text{C}-\underline{\text{H}}$ ), 1.31 (s, 9H);  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  166.5 (C), 152.4 (C), 141.3 (C), 138.5 (C), 138.2 (C), 128.3 (CH), 126.7 (CH), 125.3 (CH), 125.0 (CH), 122.6 (CH), 84.2 (C,  $\text{O}-\underline{\text{C}}(\text{CH}_3)_3$ ), 78.8 (C,  $\underline{\text{C}}\equiv\text{C}-\text{H}$ ), 71.4 (CH,  $\text{C}\equiv\text{C}-\underline{\text{H}}$ ), 35.5 ( $\text{CH}_2$ ), 27.6 ( $\text{CH}_3 \times 3$ ).

***N*-(Prop-2-yn-1-yl)benzo[d]thiazole-2-carboxamide (r6d)**



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (d,  $J = 7.2$  Hz, 1H), 7.96 (d,  $J = 7.5$ , 1H), 7.63 (br s, 1H, amide N-H), 7.55 (td,  $J = 7.2$ , 1.2 Hz, 1H), 7.49 (td, 7.5, 1.4 Hz, 1H), 4.30 (dd,  $J = 5.4$ , 2.4 Hz, 2H), 2.31 (t,  $J = 2.6$  Hz, 1H,  $\text{C}\equiv\text{C}-\underline{\text{H}}$ ), 1.22 (s, 9H).

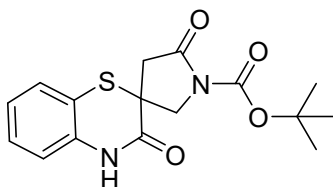
***tert*-Butyl(benzo[d]thiazole-2-carbonyl)(prop-2-yn-1-yl)carbamate (r7d)**



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 (dd,  $J = 7.5$ , 1.2 Hz, 1H), 7.98 (dd,  $J = 7.5$ , 1.5 Hz 1H), 7.61–7.49 (m, 2H), 4.63 (d,  $J = 2.4$  Hz, 2H), 2.30 (t,  $J = 2.7$  Hz, 1H,  $\text{C}\equiv\text{C}-\underline{\text{H}}$ ), 1.22 (s, 9H);  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  164.6 (C), 162.1 (C), 152.1 (C), 151.1 (C), 135.9 (C), 127.0 (CH $\times$ 2), 124.6 (CH), 122.1 (CH), 84.7 (C, O- $\underline{\text{C}}$ ( $\text{CH}_3$ ) $_3$ ), 78.1 (C,  $\underline{\text{C}}\equiv\text{C}-\text{H}$ ), 71.7 (CH,  $\text{C}\equiv\text{C}-\underline{\text{H}}$ ),

35.2 (CH<sub>2</sub>), 27.4 (CH<sub>3</sub> × 3).

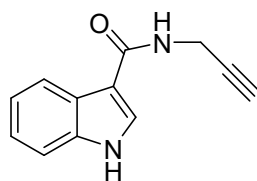
***tert*-Butyl-3,5'-dioxo-3,4-dihydrospiro[benzo[b][1,4]thiazine-2,3'-pyrrolidine]-1'-carboxylate (r8d)**



**r8d** (obtained)

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.48 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.23 (t, *J* = 6.9 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 7.2 Hz, 1H), 6.72 (br s, 1H, NH), 4.16 (s, 2H), 3.56 (s, 2H), 1.55 (s, 9H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>) δ 165.6 (C), 149.2 (C), 146.2 (C), 135.4 (CH), 129.8 (C), 129.4 (CH), 123.8 (C), 121.9 (CH), 120.2 (CH), 119.4 (C), 83.4 (C, O-C(CH<sub>3</sub>)<sub>3</sub>), 77.3 (C), 50.0 (CH<sub>2</sub>), 32.5 (CH<sub>2</sub>), 28.1 (CH<sub>3</sub> × 3).

***N*-(Prop-2-yn-1-yl)-1H-indole-3-carboxamide (r6e)**

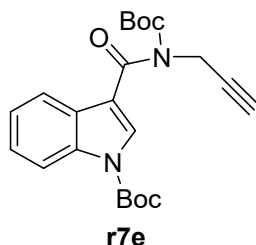


**r6e**

r5

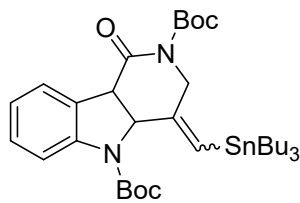
$^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  8.09–7.99 (m, 1H), 7.86–7.77 (m, 1H), 7.40–7.29 (m, 1H), 7.17–7.01 (m, 2H), 4.11 (t,  $J = 2.4$  Hz, 2H), 2.55–2.48 (m, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $(\text{CD})_3\text{CO}$ )  $\delta$  164.4 (C), 136.6 (C), 127.4 (CH), 127.3 (CH), 122.2 (CH), 121.3 (CH), 120.6 (CH), 111.7 (CH), 81.4 (C), 70.6 (C), 27.8 ( $\text{CH}_2$ ).

***tert*-Butyl 3-((*tert*-butoxycarbonyl)(prop-2-yn-1-yl)carbamoyl)-1H-indole-1-carboxylate (r7e)**



$^1\text{H}$  NMR (300 MHz,  $(\text{CD})_3\text{CO}$ )  $\delta$  8.21 (d,  $J = 7.5$  Hz, 1H), 8.06 (s, 1H), 7.82 (d,  $J = 8.1$  Hz, 1H), 7.41–7.34 (m, 2H), 4.57 (d,  $J = 2.4$  Hz), 2.76 (t,  $J = 2.4$  Hz, 1H), 1.70 (s, 9H), 1.23 (s, 9H);  $^{13}\text{C}$  NMR (75 MHz,  $(\text{CD})_3\text{CO}$ )  $\delta$  166.1 (C), 152.3 (C), 148.9 (C), 134.9 (C), 129.7 (CH), 127.7 (C), 125.0 (CH), 123.6 (CH), 120.5 (CH), 117.7 (C), 115.2 (CH), 84.9 (C), 82.9 (C), 79.7 (C), 71.5 (CH), 34.4 ( $\text{CH}_2$ ), 27.2( $\text{CH}_3 \times 3$ ), 26.8 ( $\text{CH}_3 \times 3$ ).

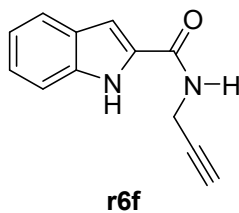
**Di-*tert*-butyl 1-oxo-4-((tributylstannyl)methylene)-3,4,4a,9b-tetrahydro-1H-pyrido[4,3-b]indole-2,5-dicarboxylate (r8e)**



**r8e**

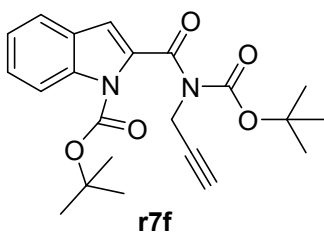
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95–7.62 (m, 2H), 7.39 (d,  $J = 7.5$  Hz, 1.5 H,  $\text{H}_{\text{major}}$ ), 7.32 (t,  $J = 7.8$  Hz, 0.5 H,  $\text{H}_{\text{minor}}$ ), 7.28–7.19 (m, 2H), 7.07–6.94 (m, 2H), 6.22 (d,  $J = 0.6$  Hz, 1H,  $\text{H}_{\text{major}}$ ), 6.12 (t,  $J = 0.9$  Hz, 0.5H), 5.11 (d,  $J = 9.9$  Hz, 1.5 H), 4.49 (d,  $J = 10.2$  Hz, 1.5 H), 4.17 (d,  $J = 13.5$  Hz, 2H), 3.98–3.87 (m, 2H), 1.57–1.18 (m, Bu and  $9\text{H}_{\text{Boc}}$ ), 0.97–0.79 (m, Bu and  $9\text{H}_{\text{Boc}}$ ) ;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  168.4 (C, major), 168.3 (C, minor), 152.0 (C), 151.2 (C, major), 151.15 (C, minor), 143.9 (C), 142.5 (C), 133.7 (C, major), 132.0 (CH, minor), 130.4 (CH, minor), 129.1 (CH, major), 127.1 (CH, minor), 126.8 (C, major), 125.0 (CH, major), 123.3 (CH, minor), 123.26 (CH, major), 123.0 (C, minor), 115.2 (CH, minor), 115.1 (CH, major), 83.5 (C, minor), 83.4 (C, major), 81.5 (C), 77.2 (CH, minor), 64.9 (CH, major), 51.7 (CH), 49.3 ( $\text{CH}_2$ , minor), 48.8 ( $\text{CH}_2$ , major), 40.0 (C), 29.0 ( $\text{CH}_2 \times 3$ , Bu), 28.4 ( $\text{CH}_3 \times 3$ , major), 28.3 ( $\text{CH}_3 \times 3$ , major), 27.4 ( $\text{CH}_2 \times 3$ , Bu), 22.8 ( $\text{CH}_3 \times 3$ , minor), 22.5 ( $\text{CH}_3 \times 3$ , minor), 13.6 ( $\text{CH}_3 \times 3$ , Bu), 10.3 ( $\text{CH}_2 \times 3$ , Bu) ; MS (ESI $^+$ ) :  $m/z$  calcd for  $\text{C}_{34}\text{H}_{54}\text{N}_2\text{O}_5\text{Sn}$   $[\text{M}+\text{Na}]^+$  : 713.30 ; found: 713.30.

***N*-(Prop-2-yn-1-yl)-1H-indole-2-carboxamide (r6f)**



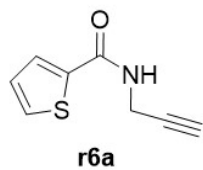
$^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  7.60 (d,  $J = 8.1$  Hz, 1H), 7.44 (d,  $J = 8.4$  Hz, 1H), 7.22 (td,  $J = 7.7, 0.9$  Hz, 1H), 7.08–7.03 (s, one s overlapped with one td at 7.06,  $J = 7.5, 0.6$  Hz, 2H), 4.17 (d,  $J = 2.4$  Hz, 2H), 2.62 (t,  $J = 2.6$  Hz, 1H).

***tert*-Butyl 2-((*tert*-butoxycarbonyl)(prop-2-yn-1-yl)carbamoyl)-1H-indole-2-carboxylate (r7f)**

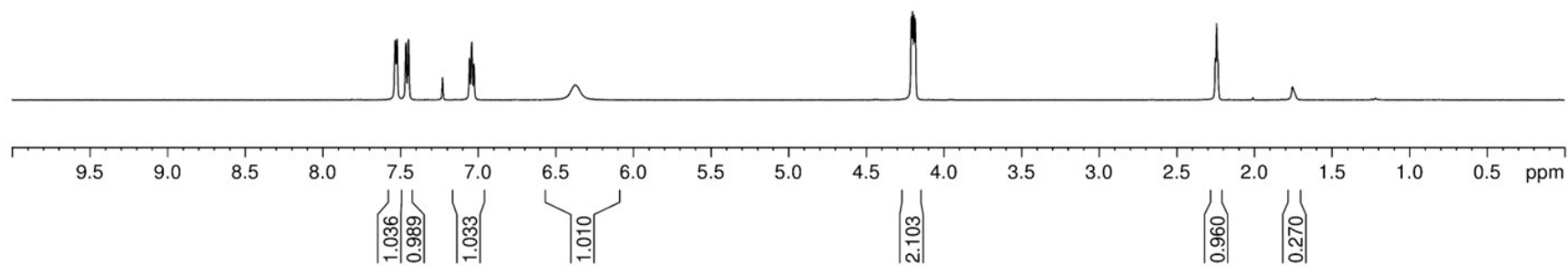


$^1\text{H}$  NMR (300 MHz,  $(\text{CD})_3\text{CO}$ )  $\delta$  8.16 (d,  $J = 8.1$  Hz, 1H), 7.56 (d,  $J = 7.8$  Hz, 1H), 7.38 (td,  $J = 7.8, 1.2$  Hz, 1H), 7.27 (td,  $J = 7.8, 0.6$  Hz, 1H), 6.65 (s, 1H), 4.66 (d,  $J = 2.4$  Hz, 2H), 2.26 (t,  $J = 2.4$  Hz, 1H), 1.63 (s, 9H), 1.19 (s, 9H).

YYL1006-B-20230804

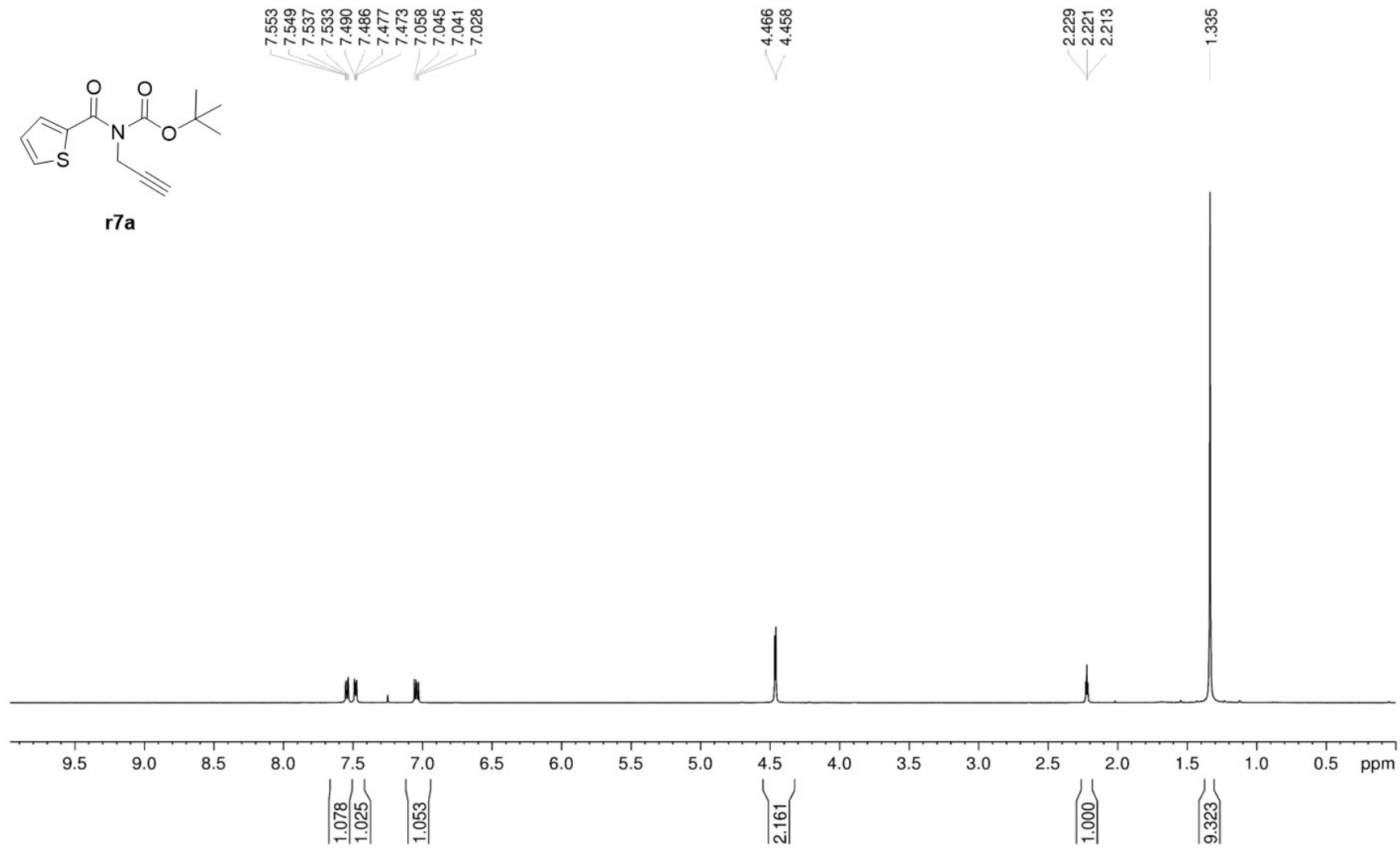
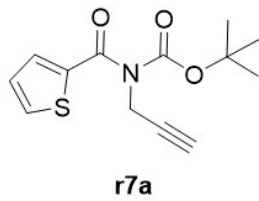


7.534  
7.522  
7.465  
7.448  
7.229  
7.055  
7.041  
7.026  
6.372  
4.209  
4.201  
4.191  
4.183  
2.249  
2.241  
2.233  
1.753



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) of **r6a**

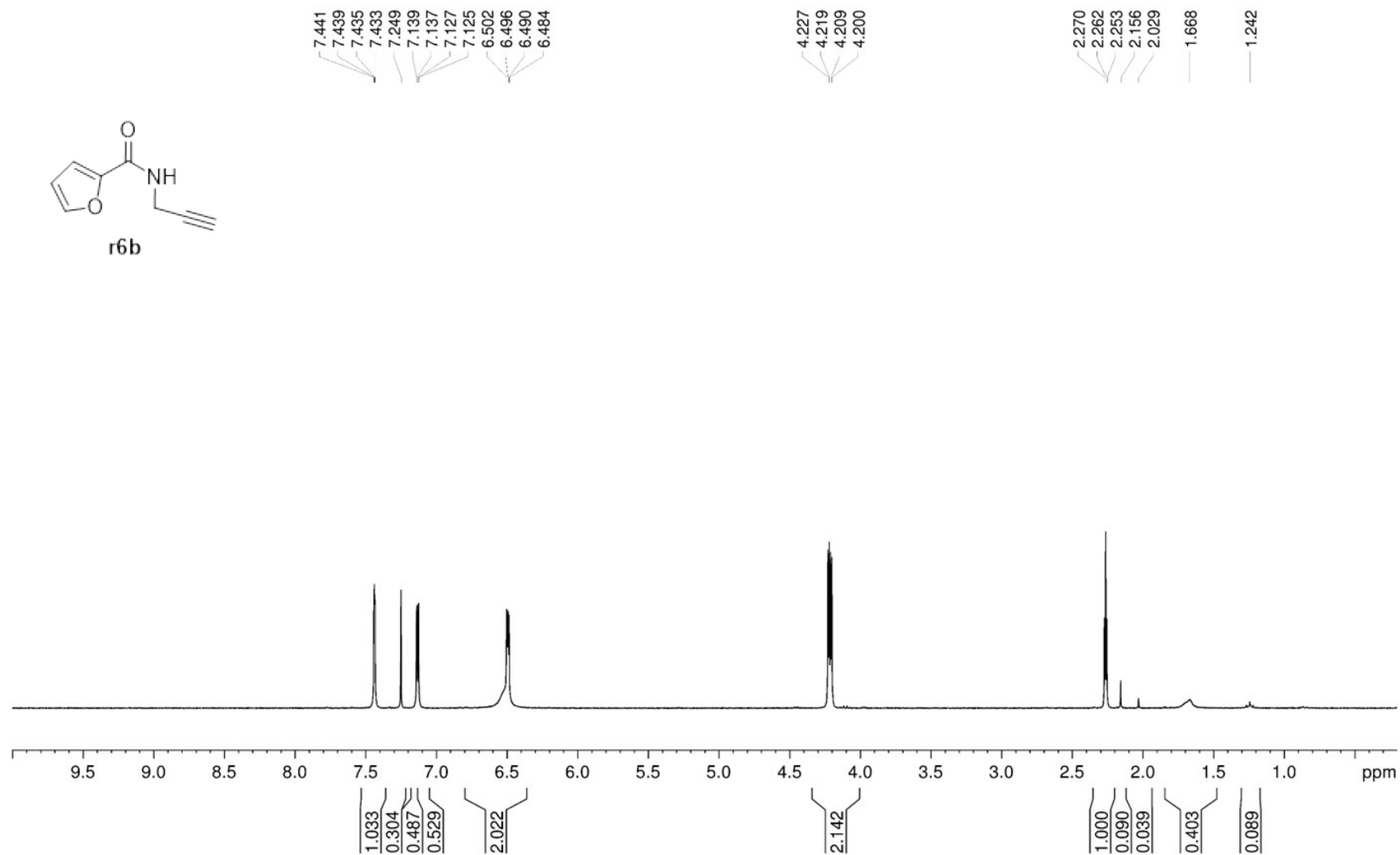
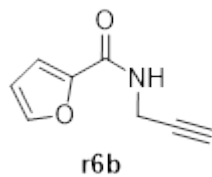
YYL1007-B-20230810



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) of **r7a**

r10

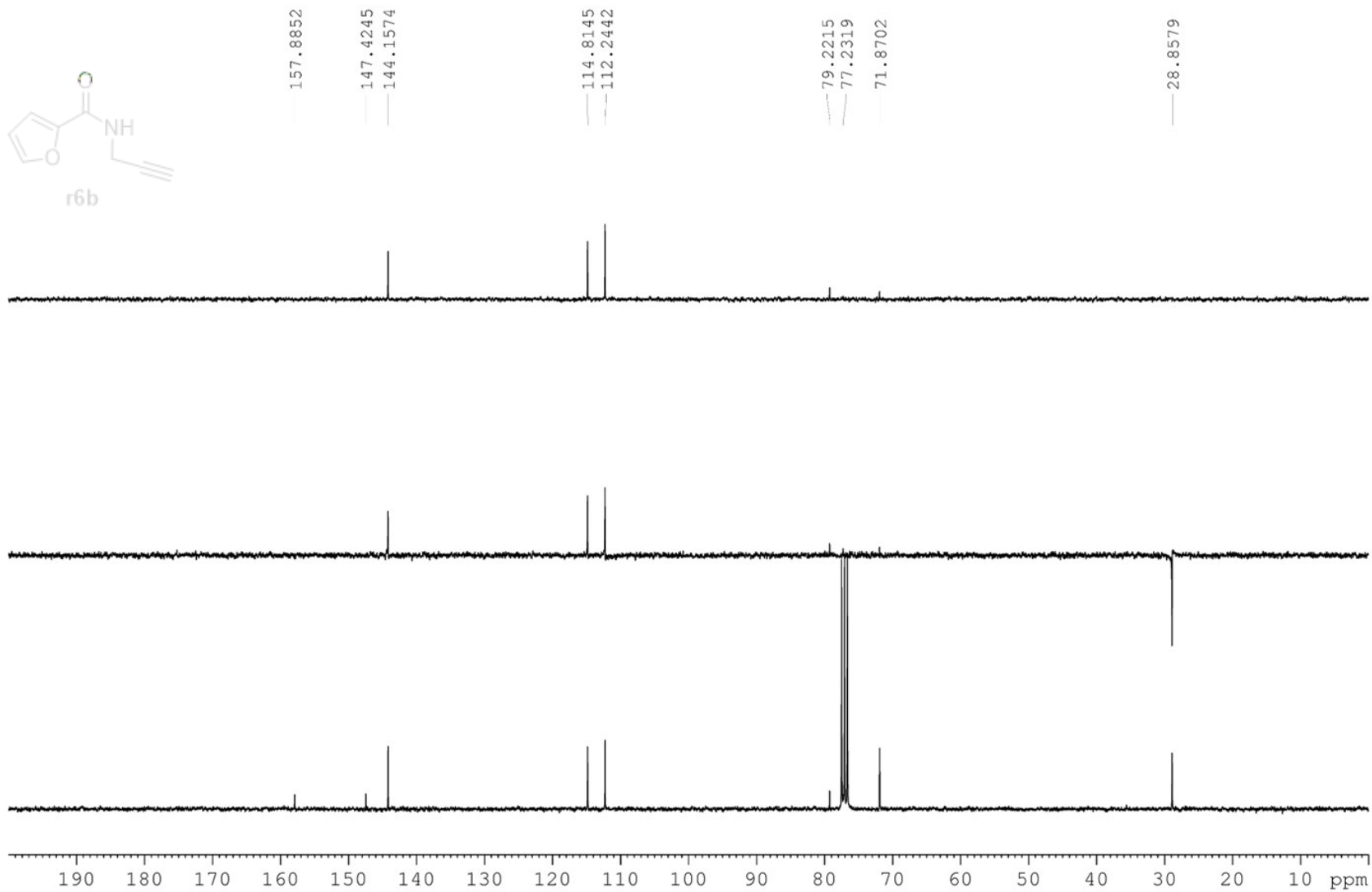
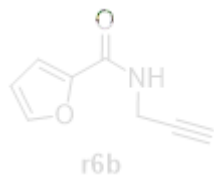
YTH1012-B-20230706(C13)



<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) of **r6b** (trace of impurity)

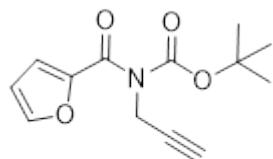
r11

YTH1012-B-20230706 (C13)

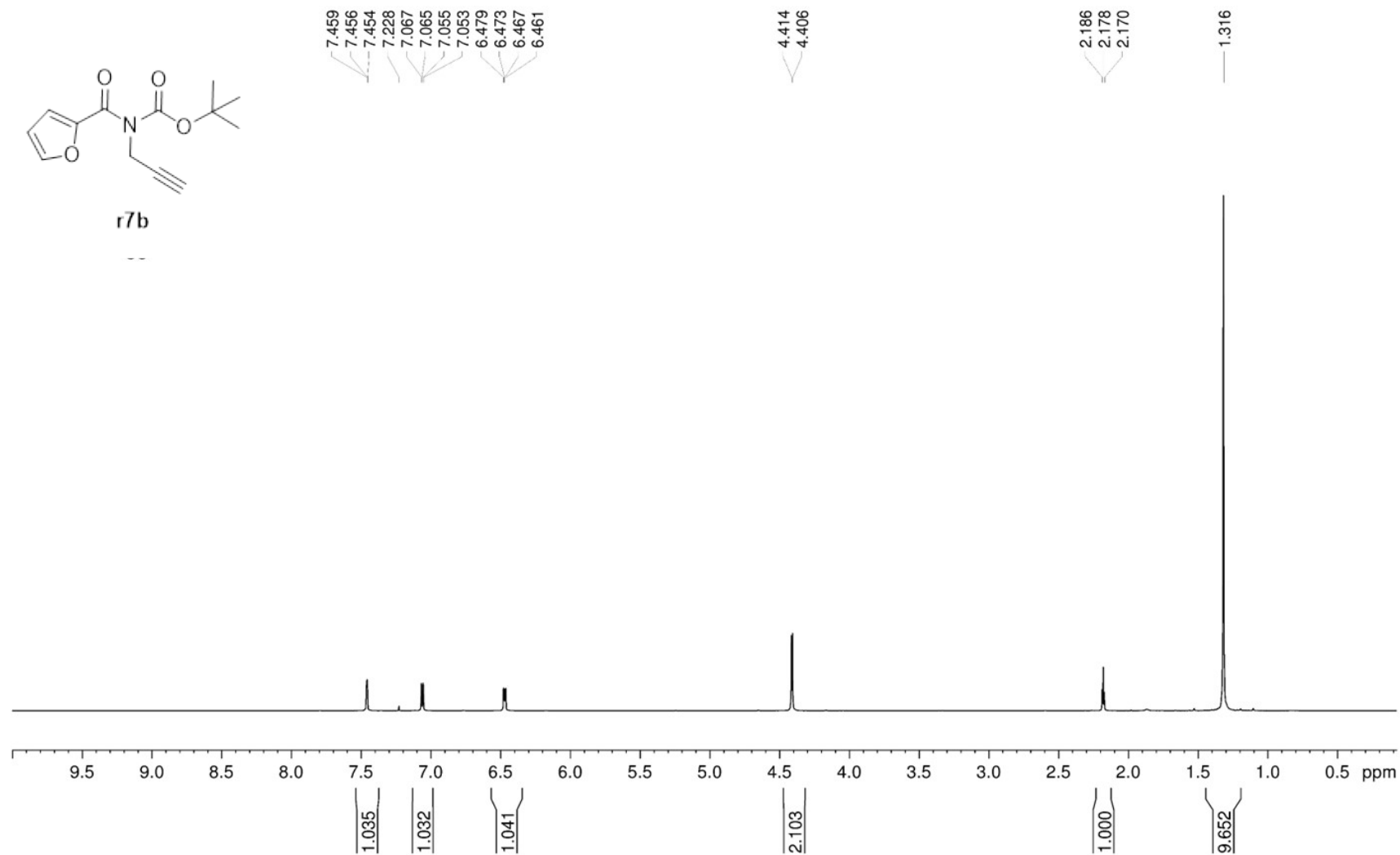


$^{13}\text{C}\{^1\text{H}\}$ -DEPT NMR (75 MHz,  $\text{CDCl}_3$ ) of r6b  
r12

YTH2023-B-20230731



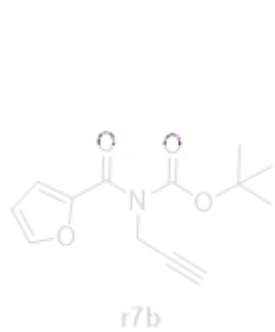
r7b



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) of r7b

r13

YTH2023-B-20231009 (C13)



161.3632

152.0467

148.3539

144.4757

117.2907

112.1799

83.6162

78.8253

77.5325

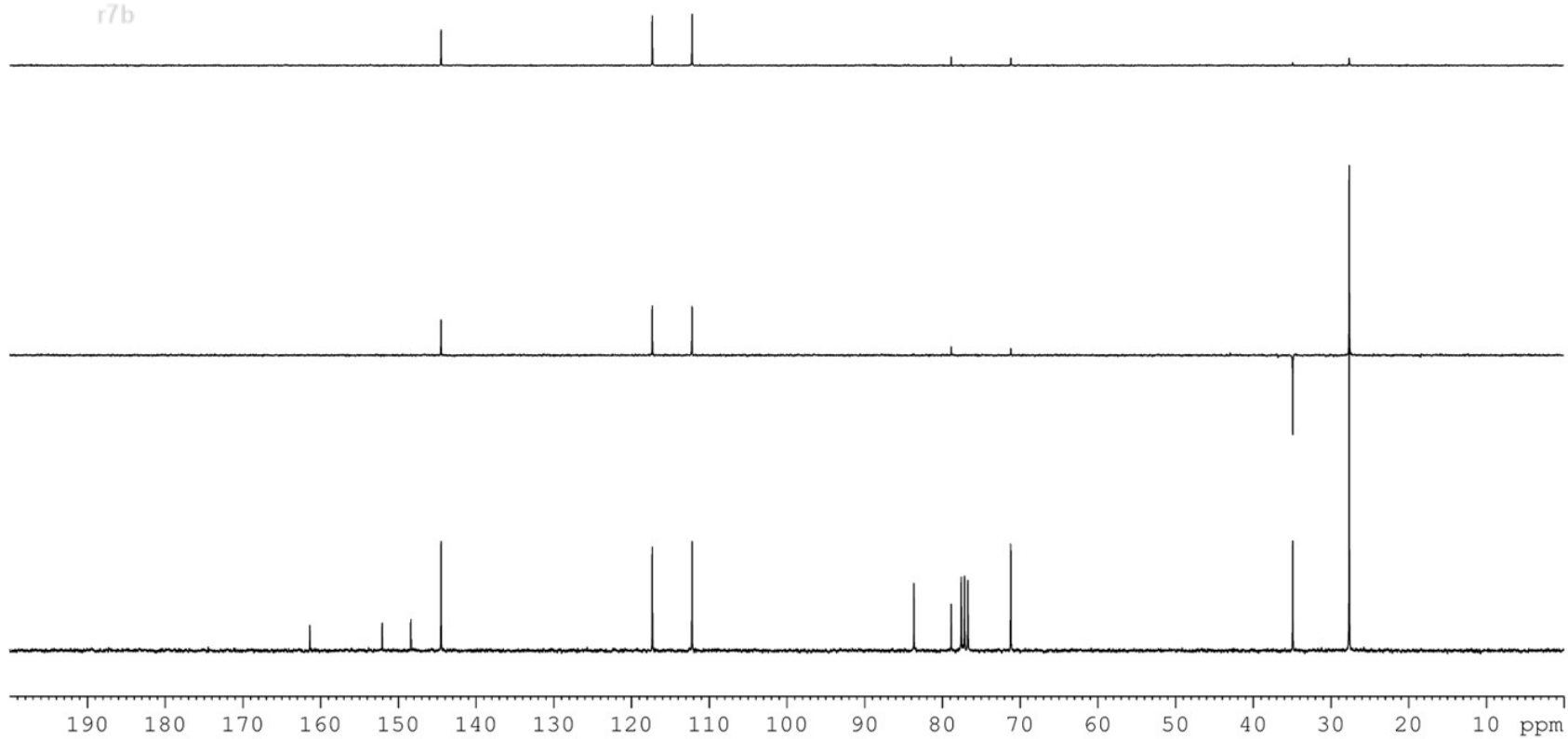
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76.6837

71.1668

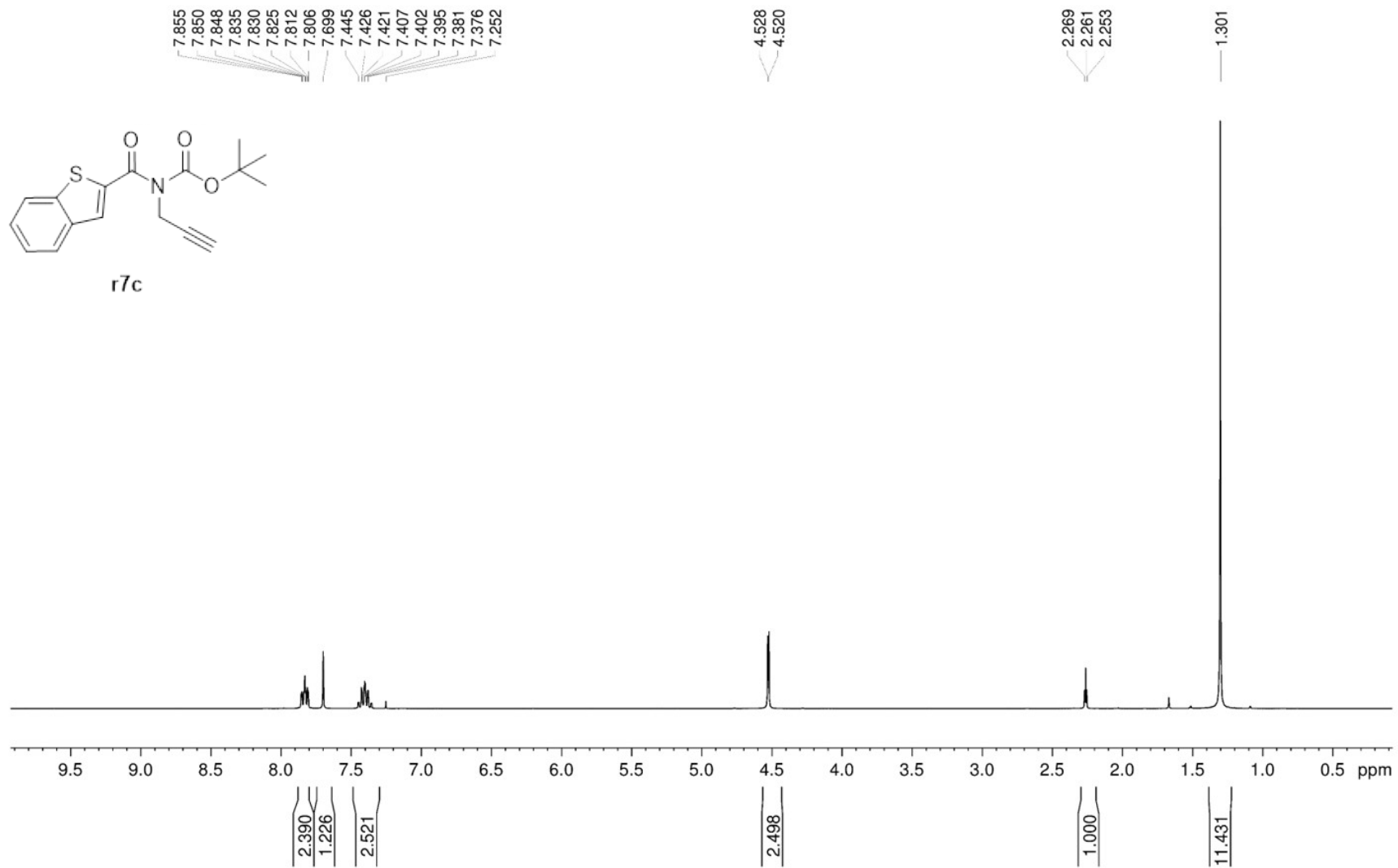
34.8770

27.6055



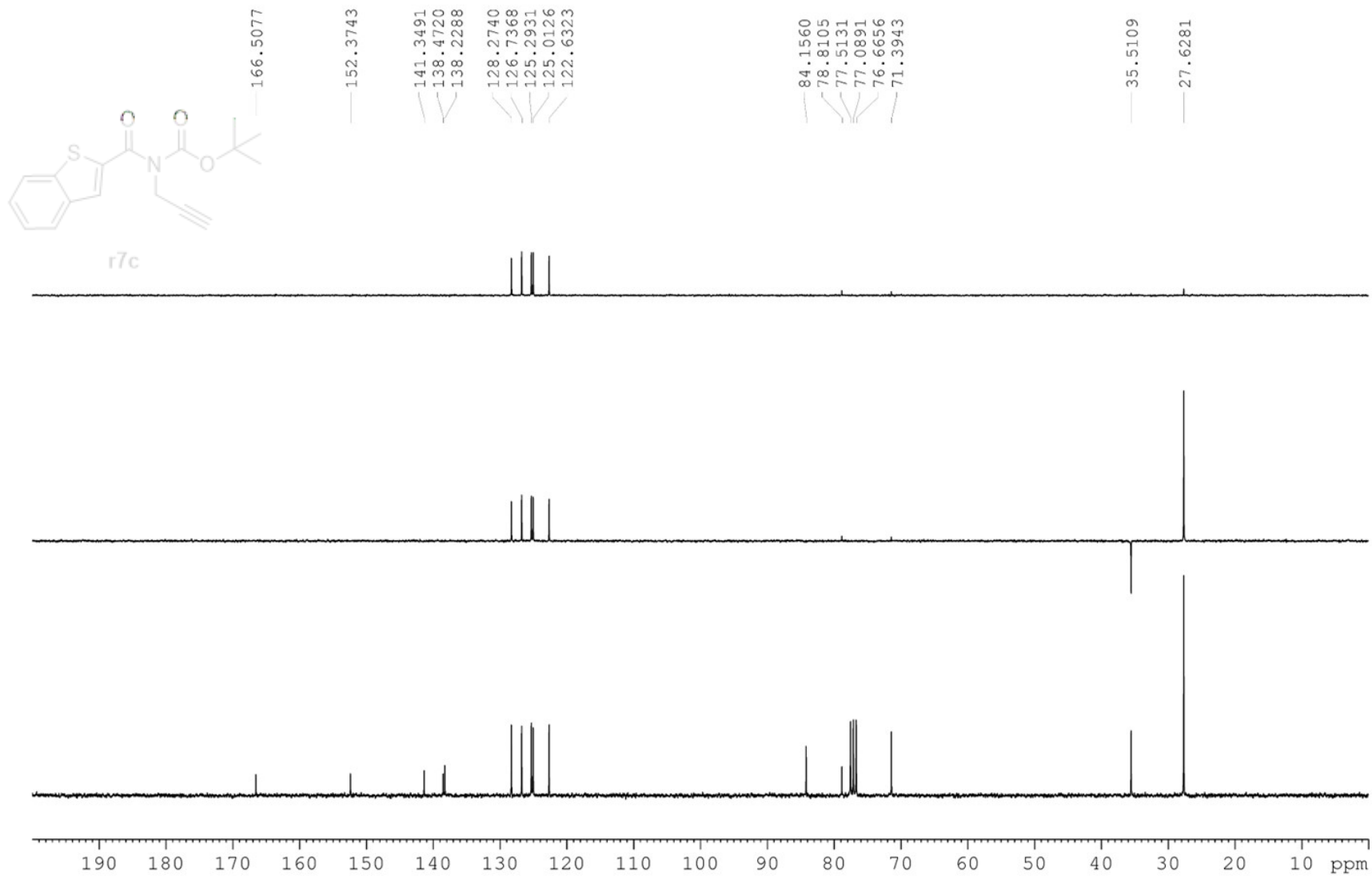
$^{13}\text{C}\{^1\text{H}\}$ -DEPT NMR (75 MHz,  $\text{CDCl}_3$ ) of **r7b**  
r14

YTH1017-B-20231017(C13)



**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) of r7c**  
r15

YTH1017-B-20231017 (C13)



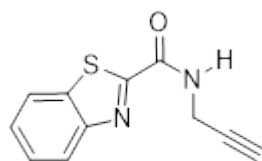
$^{13}\text{C}\{^1\text{H}\}$ -DEPT NMR (75 MHz,  $\text{CDCl}_3$ ) of **r7c**  
r16

YTH2003-B-20230630

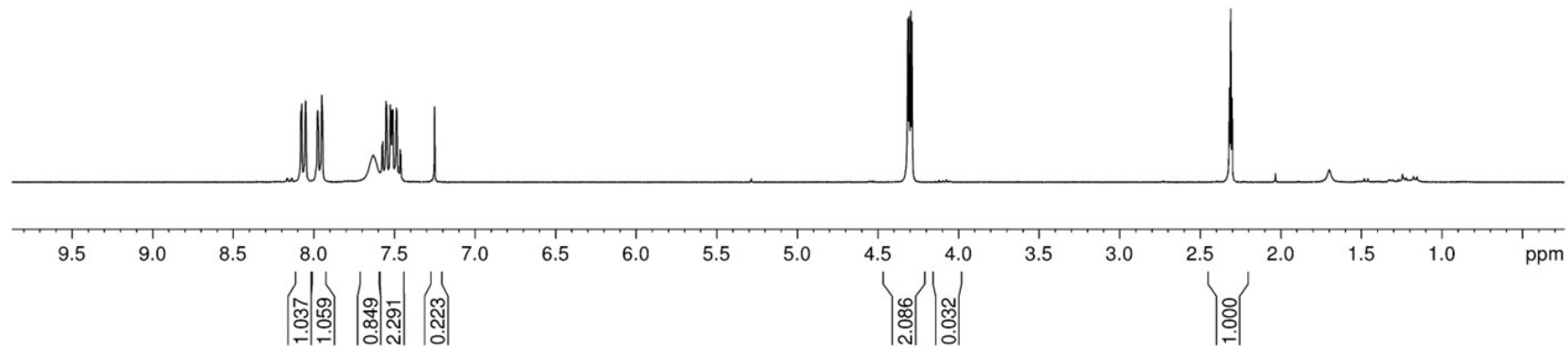
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7.571  
7.551  
7.547  
7.525  
7.520  
7.513  
7.508  
7.487  
7.483  
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7.249

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4.295  
4.286

2.317  
2.308  
2.300

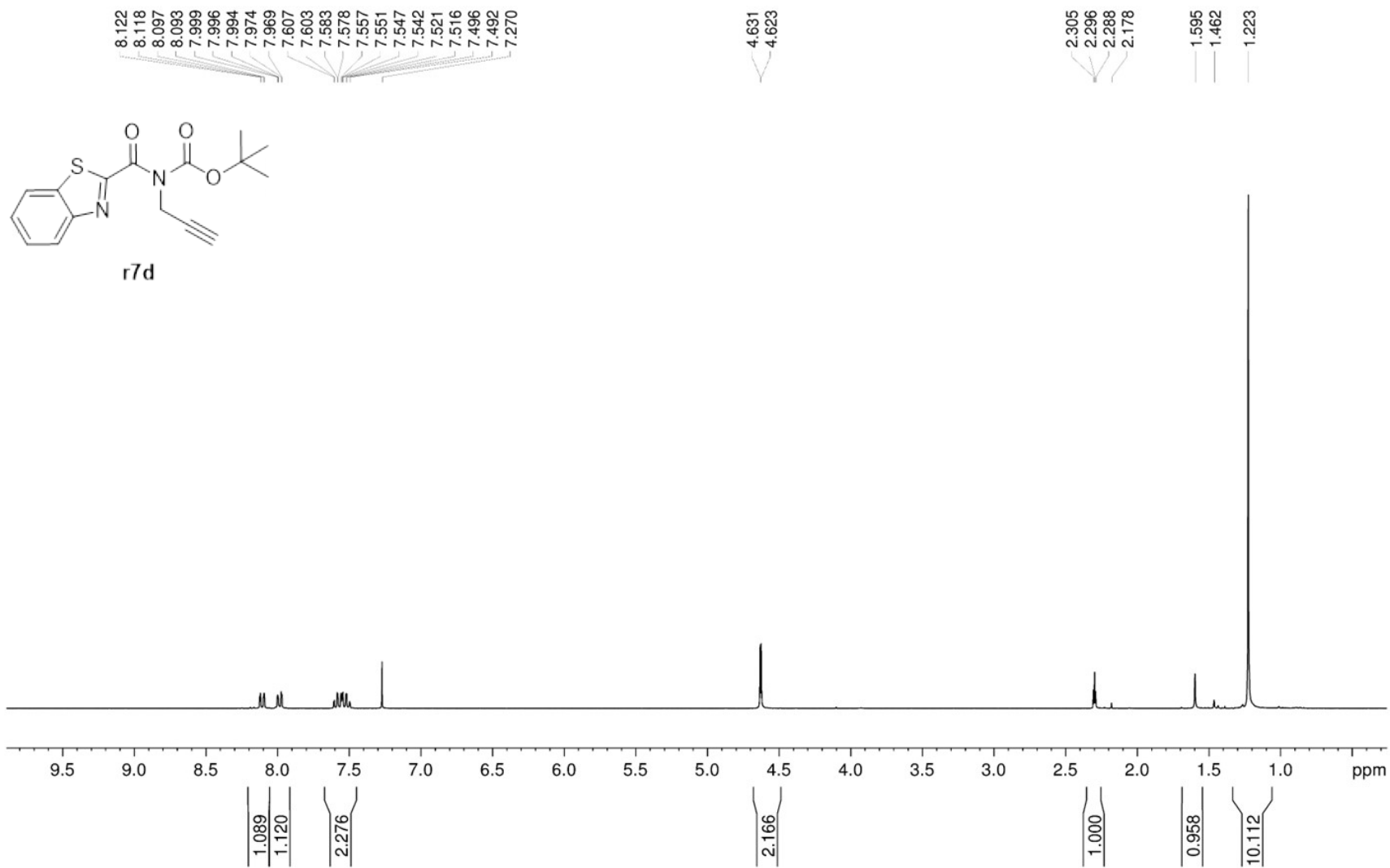


r6d



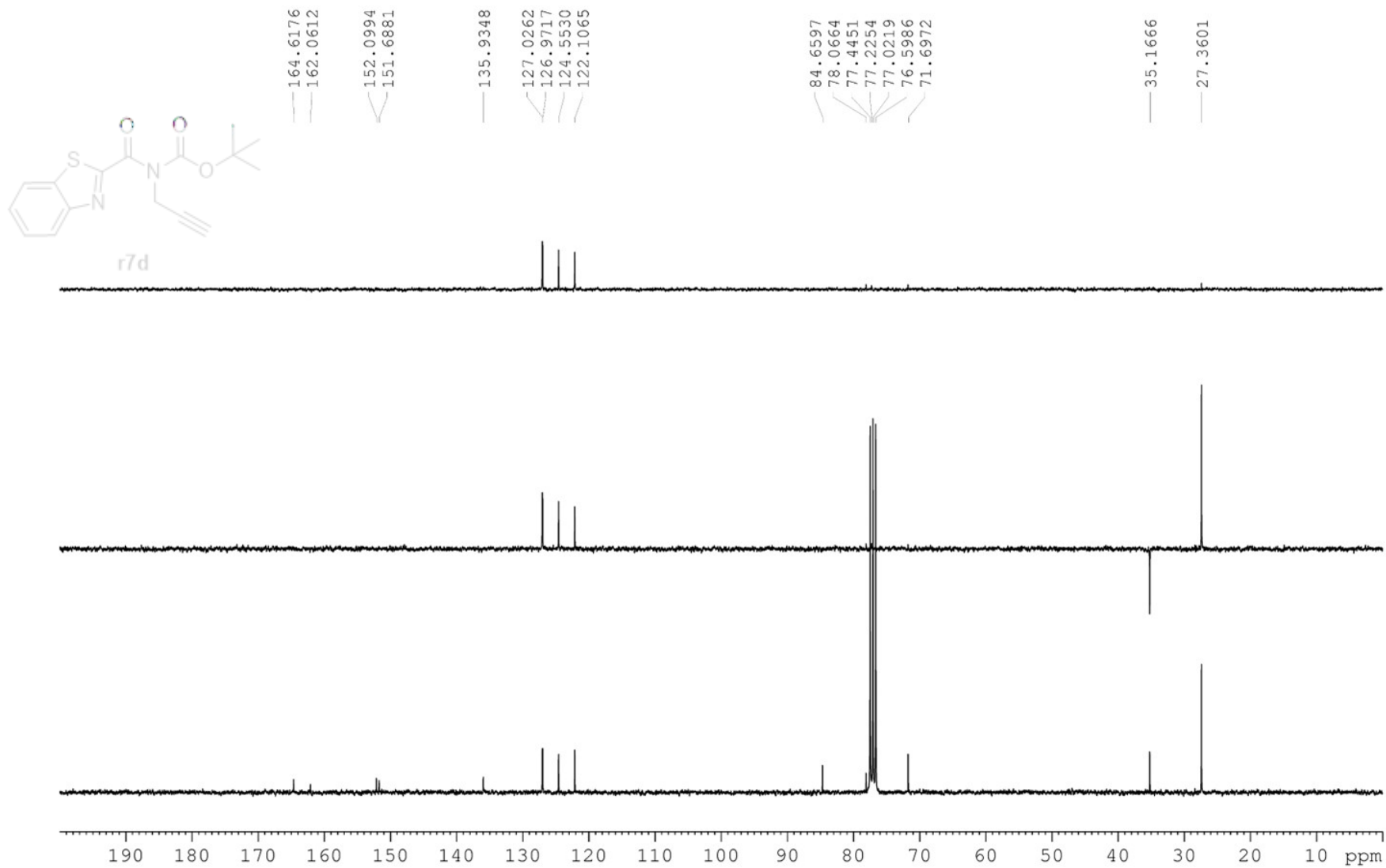
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) of r6d (trace of impurity)

YTH2004-B2-20230718(C13)



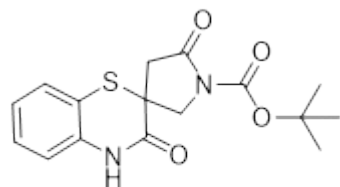
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) of **r7d** (water at around 1.6 ppm)  
r18

YTH2004-B2-20230718 (C13)



$^{13}\text{C}\{^1\text{H}\}$ -DEPT NMR (75 MHz,  $\text{CDCl}_3$ ) of **r7d**  
r19

YTH2021-B3-20230808(C13)



**r8d** (obtained)

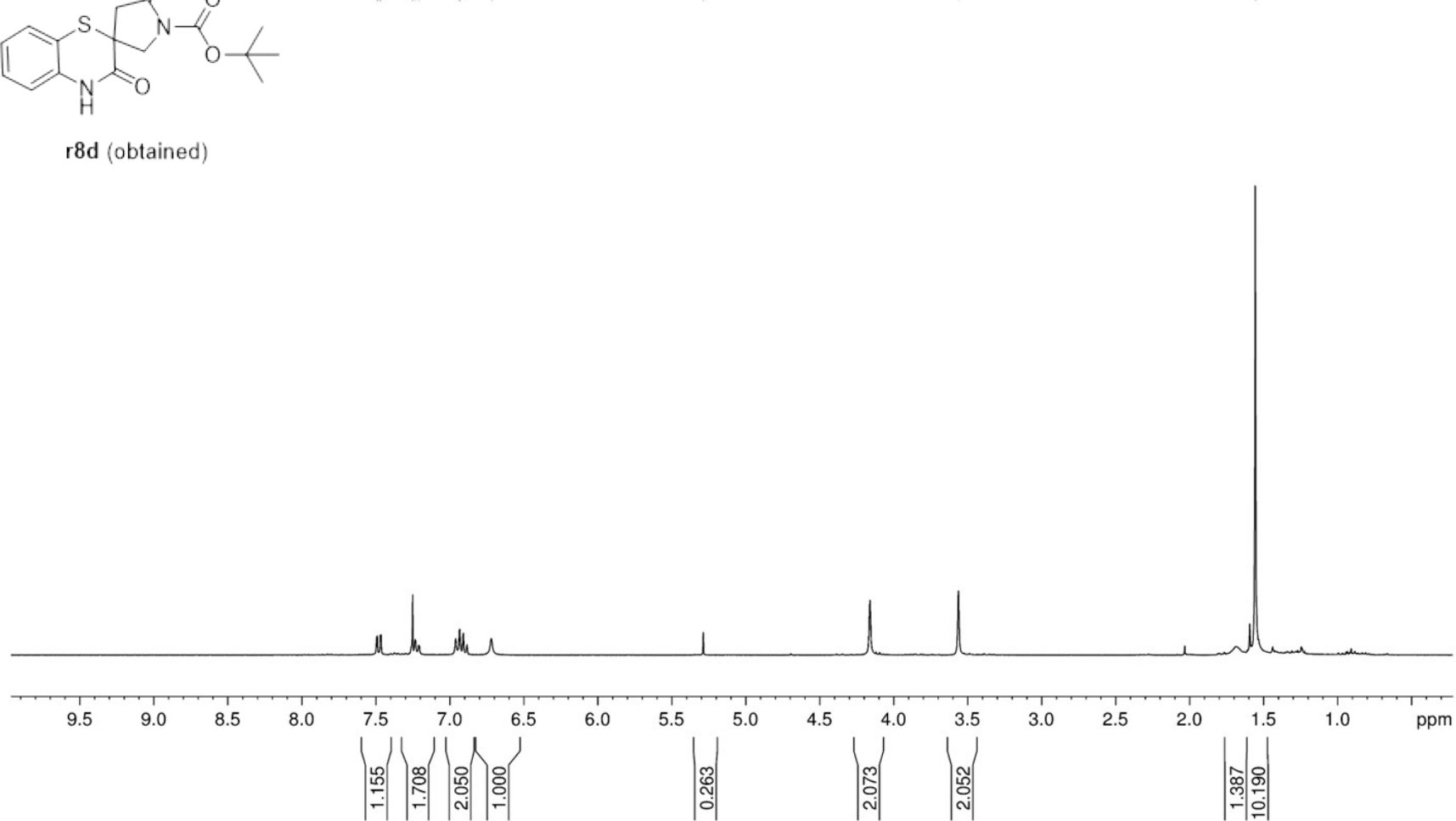
7.493  
7.489  
7.468  
7.463  
7.249  
7.232  
7.209  
6.958  
6.932  
6.907  
6.883  
6.718

5.285

4.158

3.560

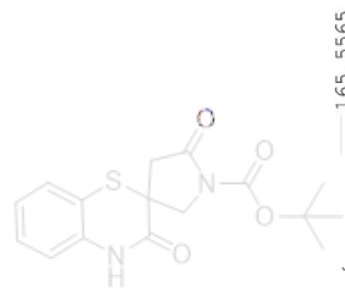
1.554



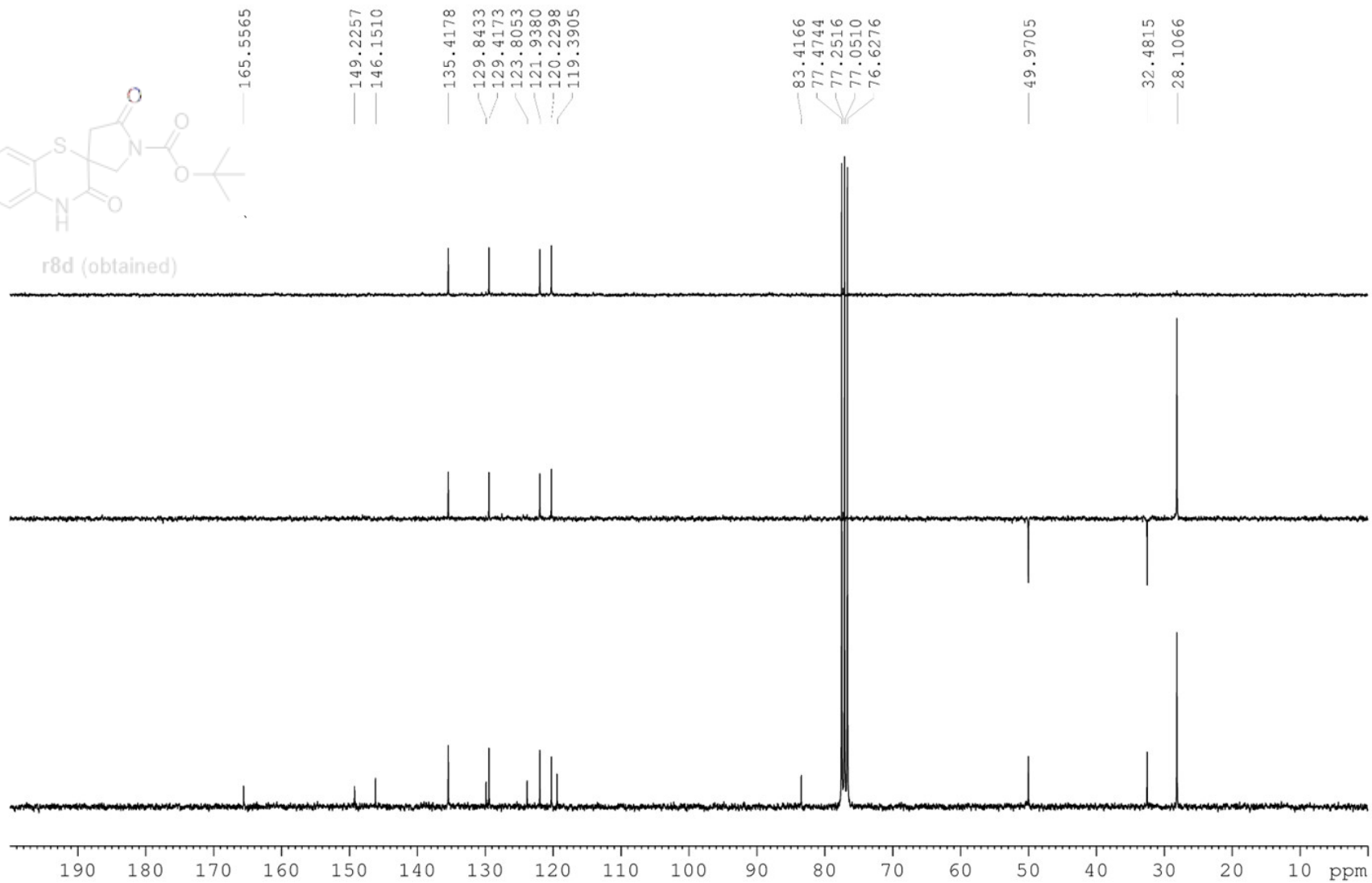
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) of **r8d** (contaminated with tin residue)

r20

YTH2021-B3-20230808 (C13)

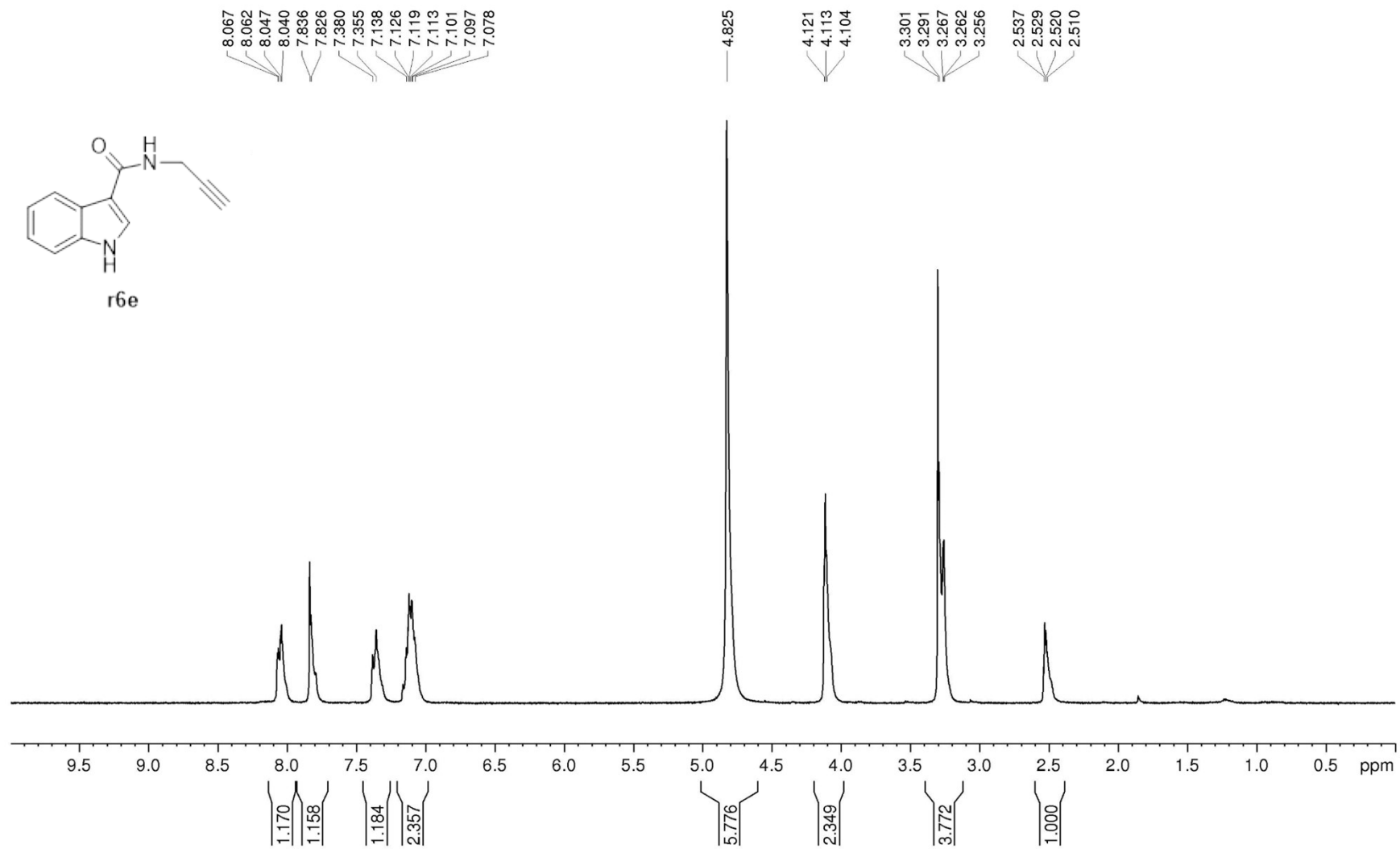


r8d (obtained)



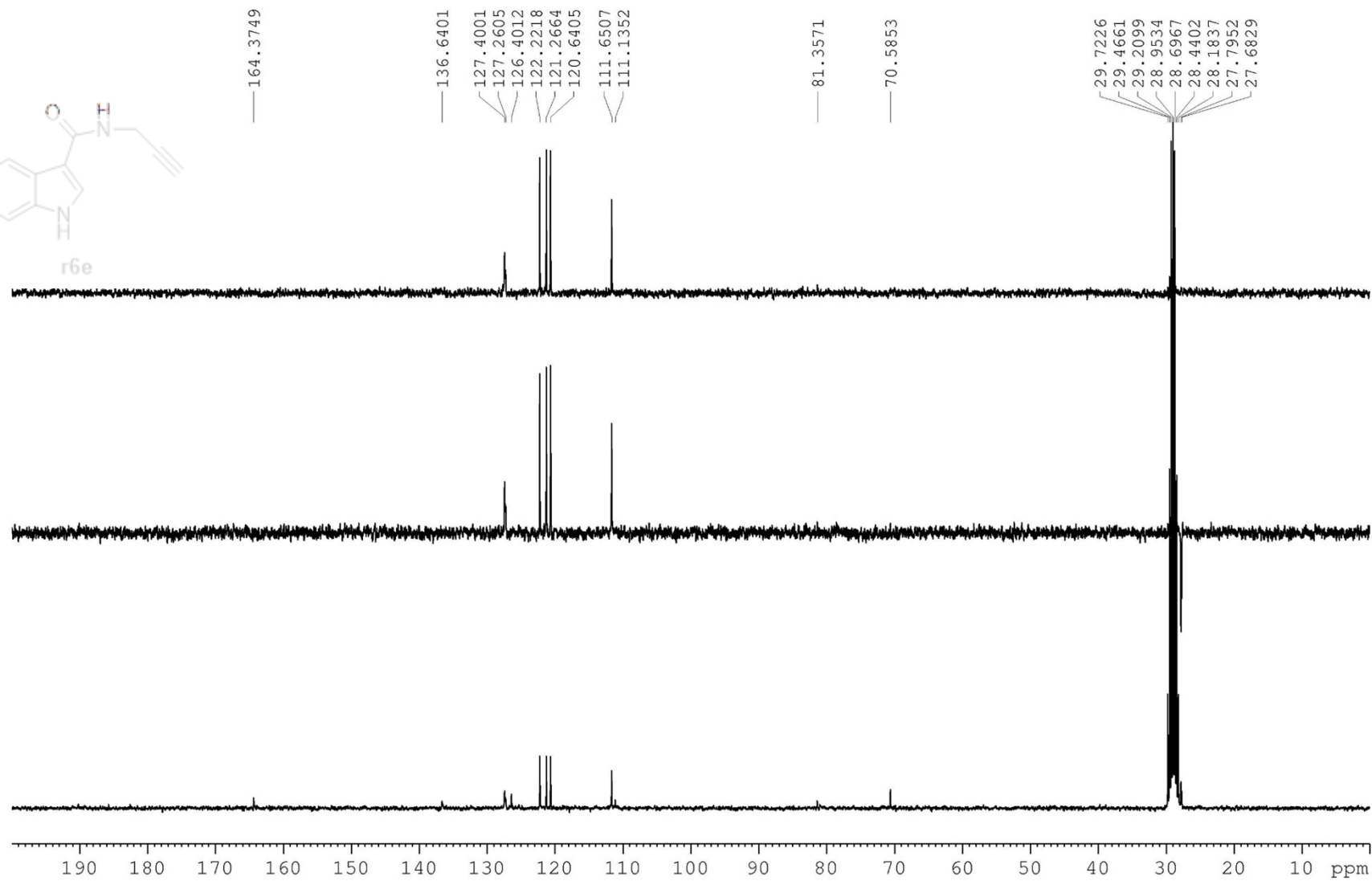
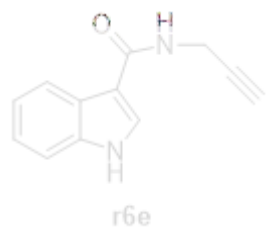
$^{13}\text{C}\{^1\text{H}\}$ -DEPT NMR (75 MHz,  $\text{CDCl}_3$ ) of **r8d**  
r21

CCL2005-B-20220707



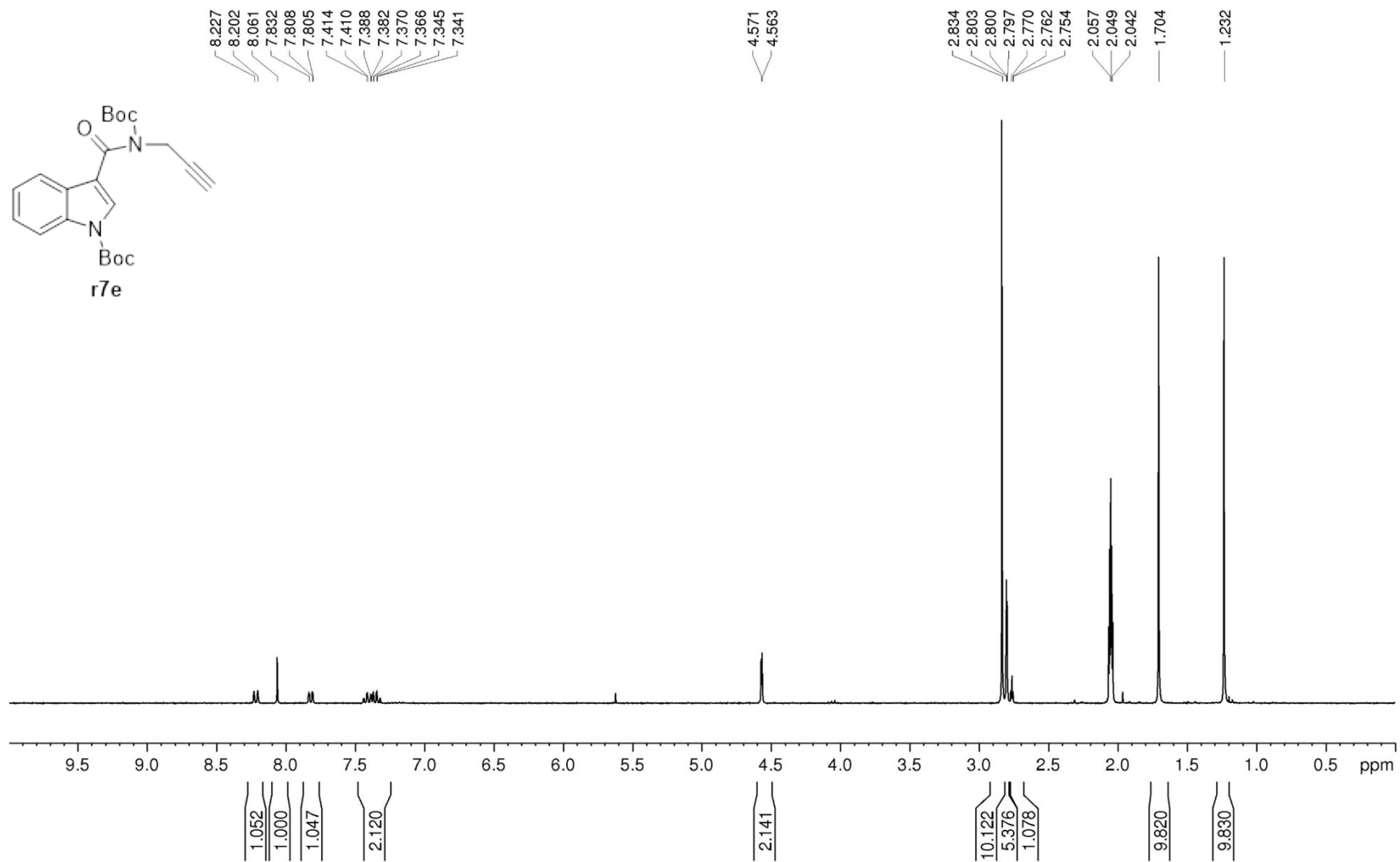
<sup>1</sup>H NMR (300 MHz, (CD)<sub>3</sub>CO) of **r6e**

CCL2005-B-20220929 (C13)



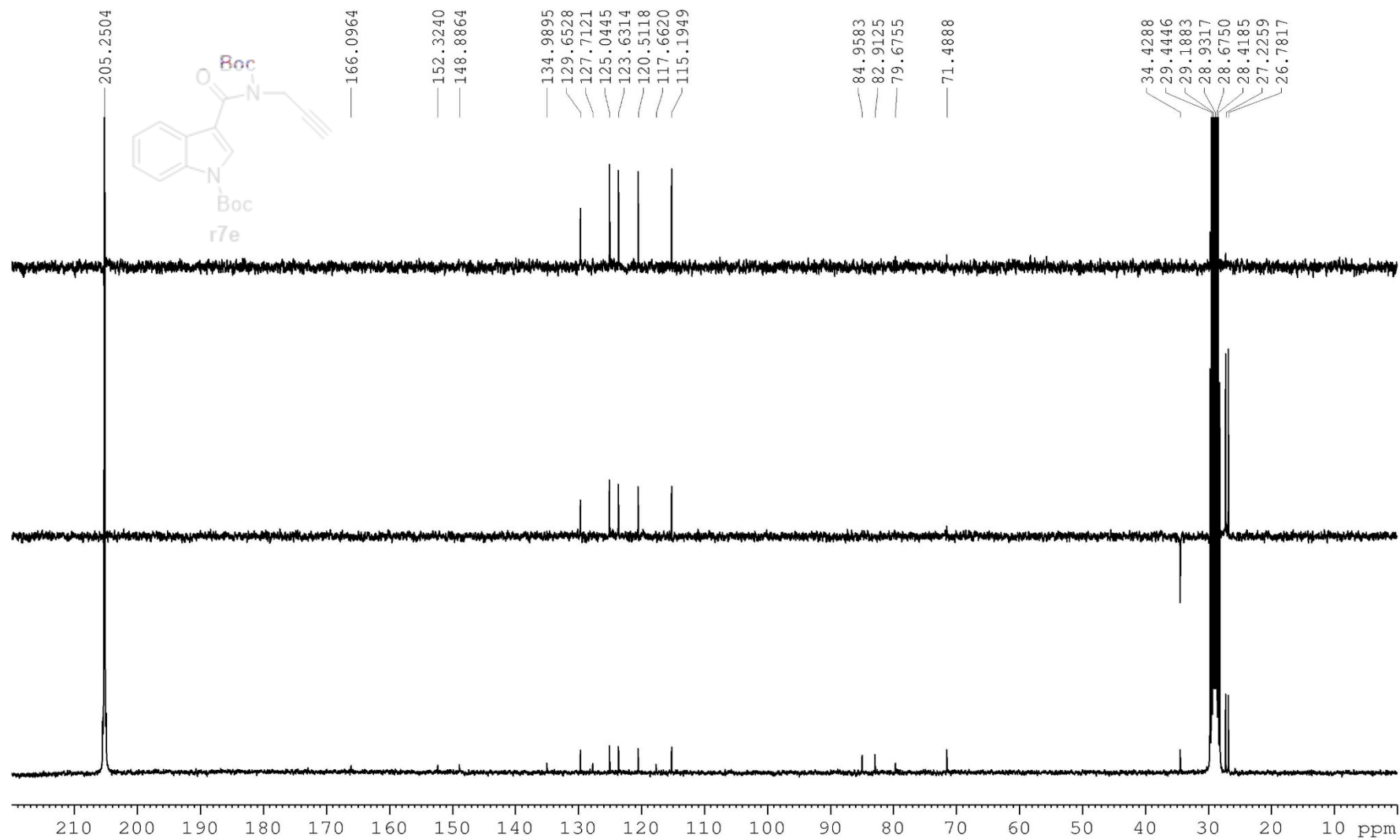
$^{13}\text{C}\{^1\text{H}\}$ -DEPT NMR (75 MHz,  $(\text{CD})_3\text{CO}$ ) of r6e

CCL2011-B-20220906(C13)



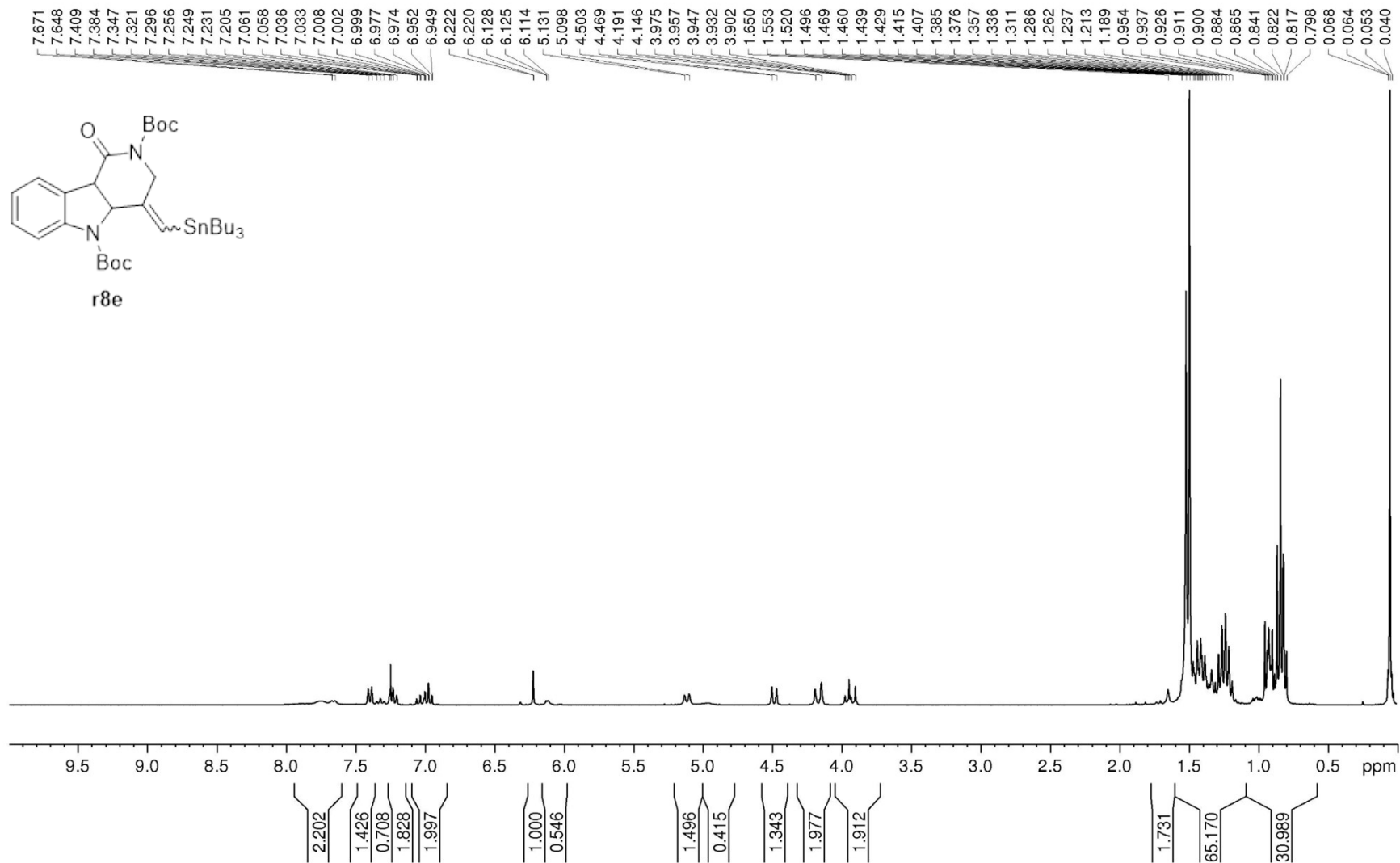
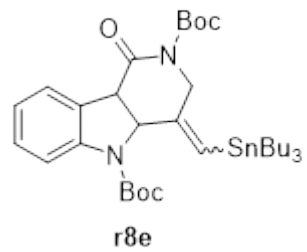
<sup>1</sup>H NMR (300 MHz, (CD)<sub>3</sub>CO) of r7e

CCL2011-B-20220906 (C13)



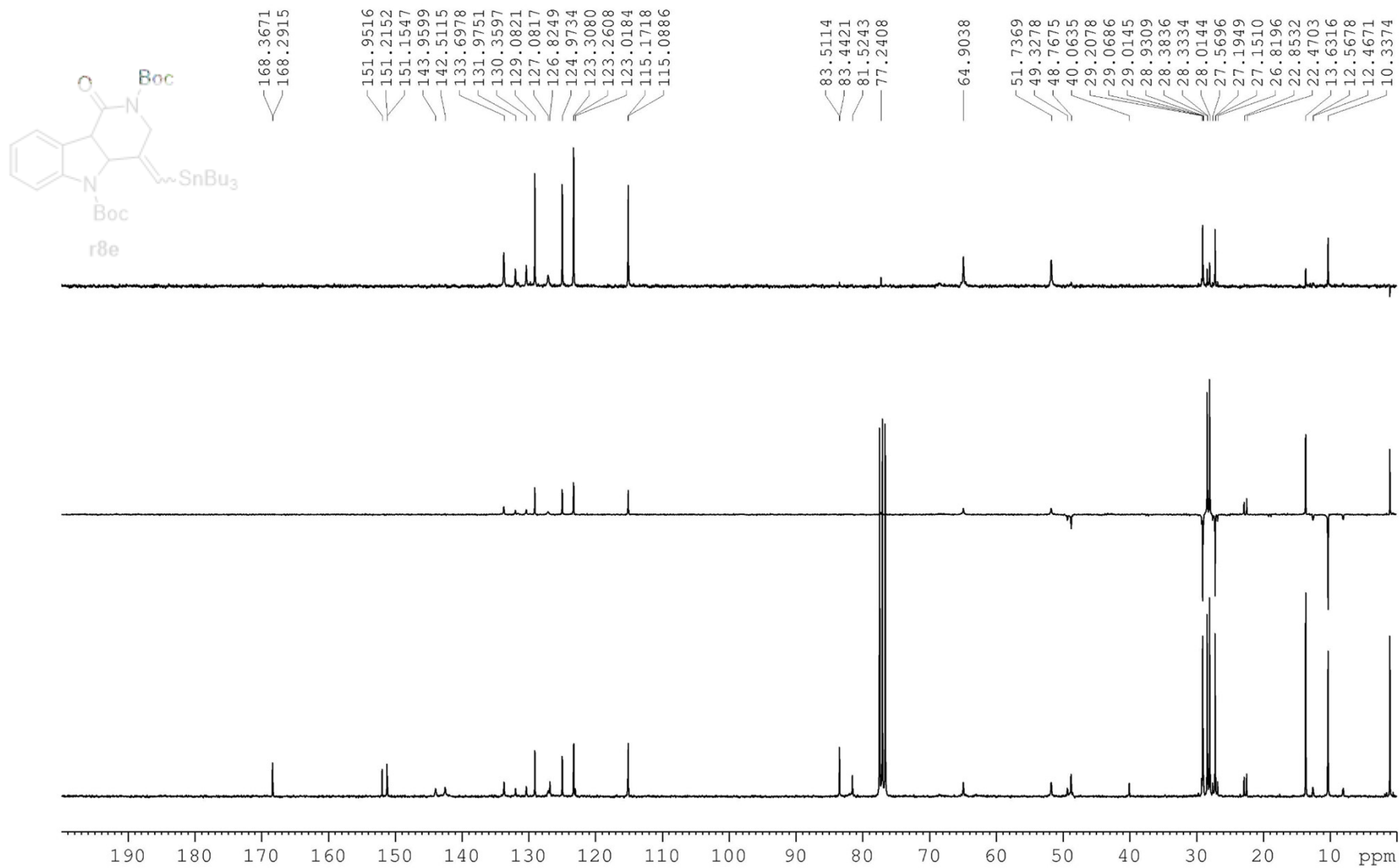
$^{13}\text{C}\{^1\text{H}\}$ -DEPT NMR (75 MHz,  $(\text{CD})_3\text{CO}$ ) of **r7e**

CCL2015-B-20220726(C13)



<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) of **r8e**

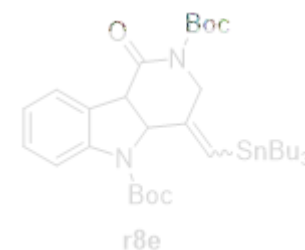
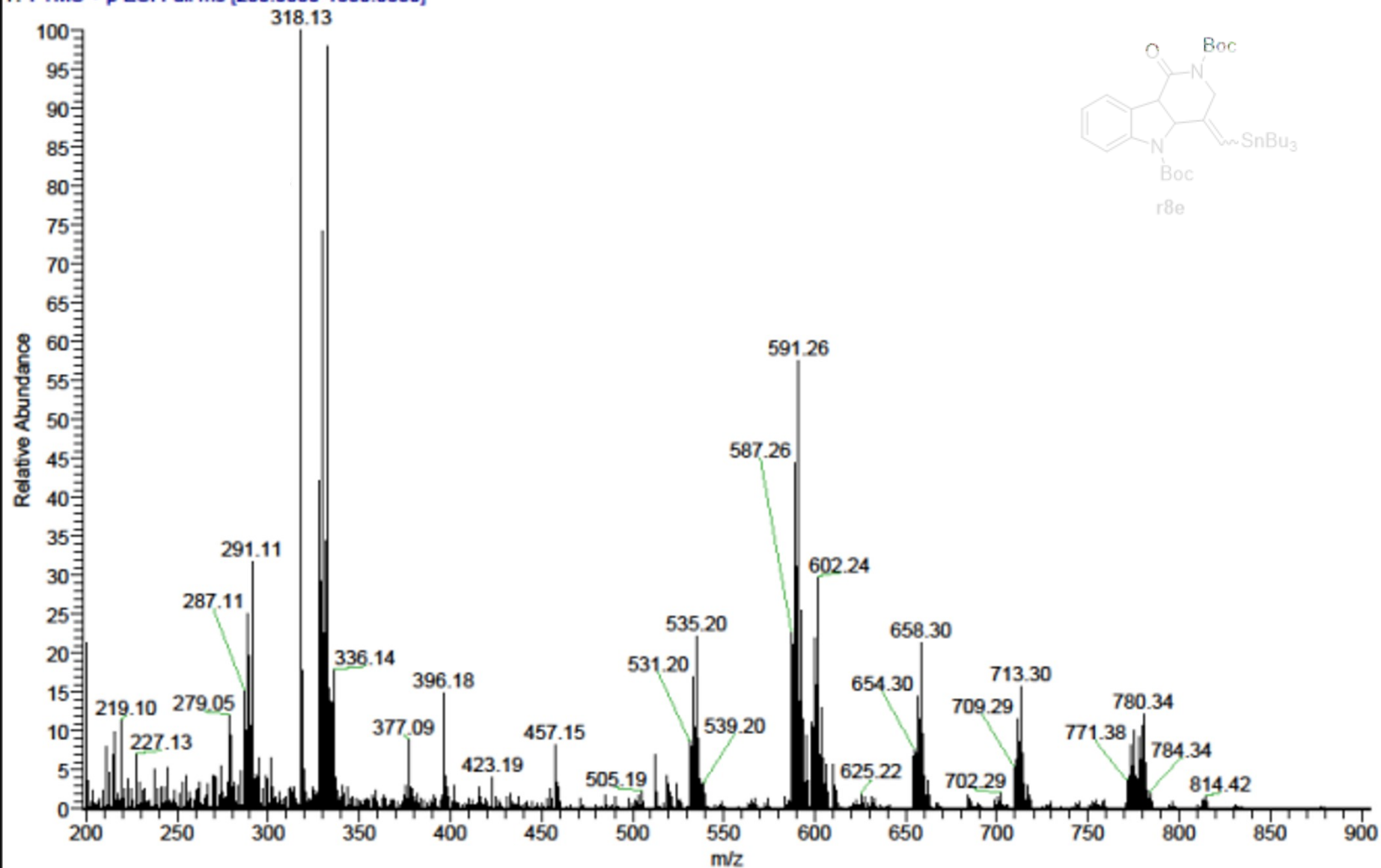
CCL2015-B-20220726 (C13)



$^{13}\text{C}\{^1\text{H}\}$ -DEPT NMR (75 MHz,  $\text{CDCl}_3$ ) of **r8e**

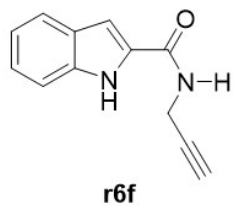
data11 #6-15 RT: 0.05-0.11 AV: 5 NL: 2.74E7

T: FTMS + p ESI Full ms [200.0000-1000.0000]

MS (ESI<sup>+</sup>) of r8e

r28

JYX1009-B-20230112



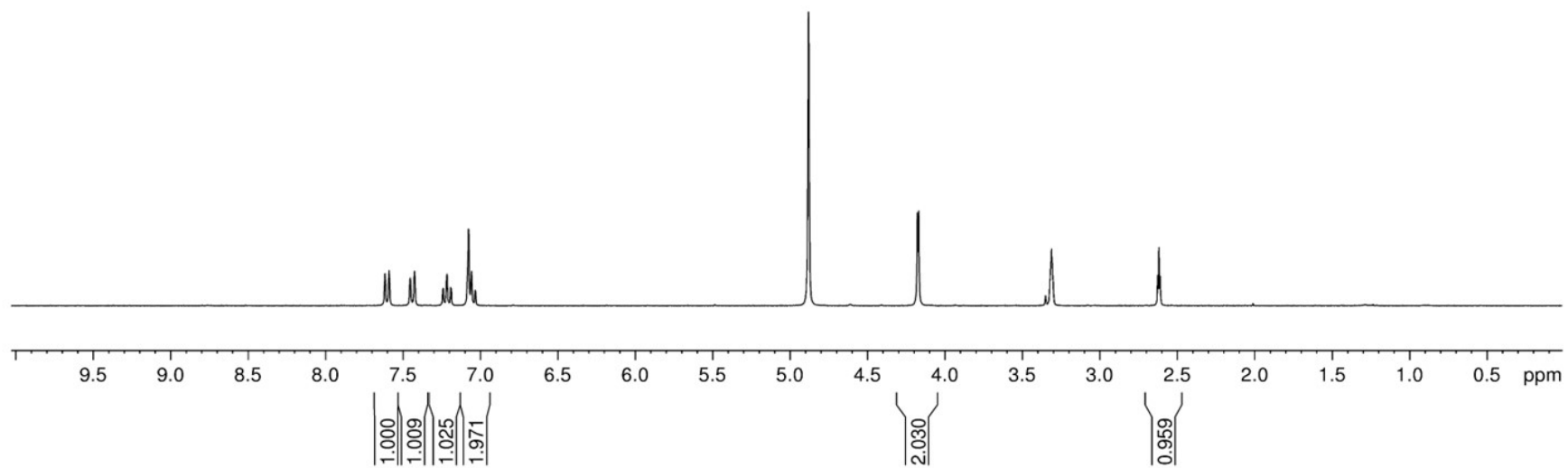
7.616  
7.589  
7.452  
7.424  
7.242  
7.239  
7.215  
7.191  
7.188  
7.076  
7.057  
7.033  
7.031

4.880

4.177  
4.169

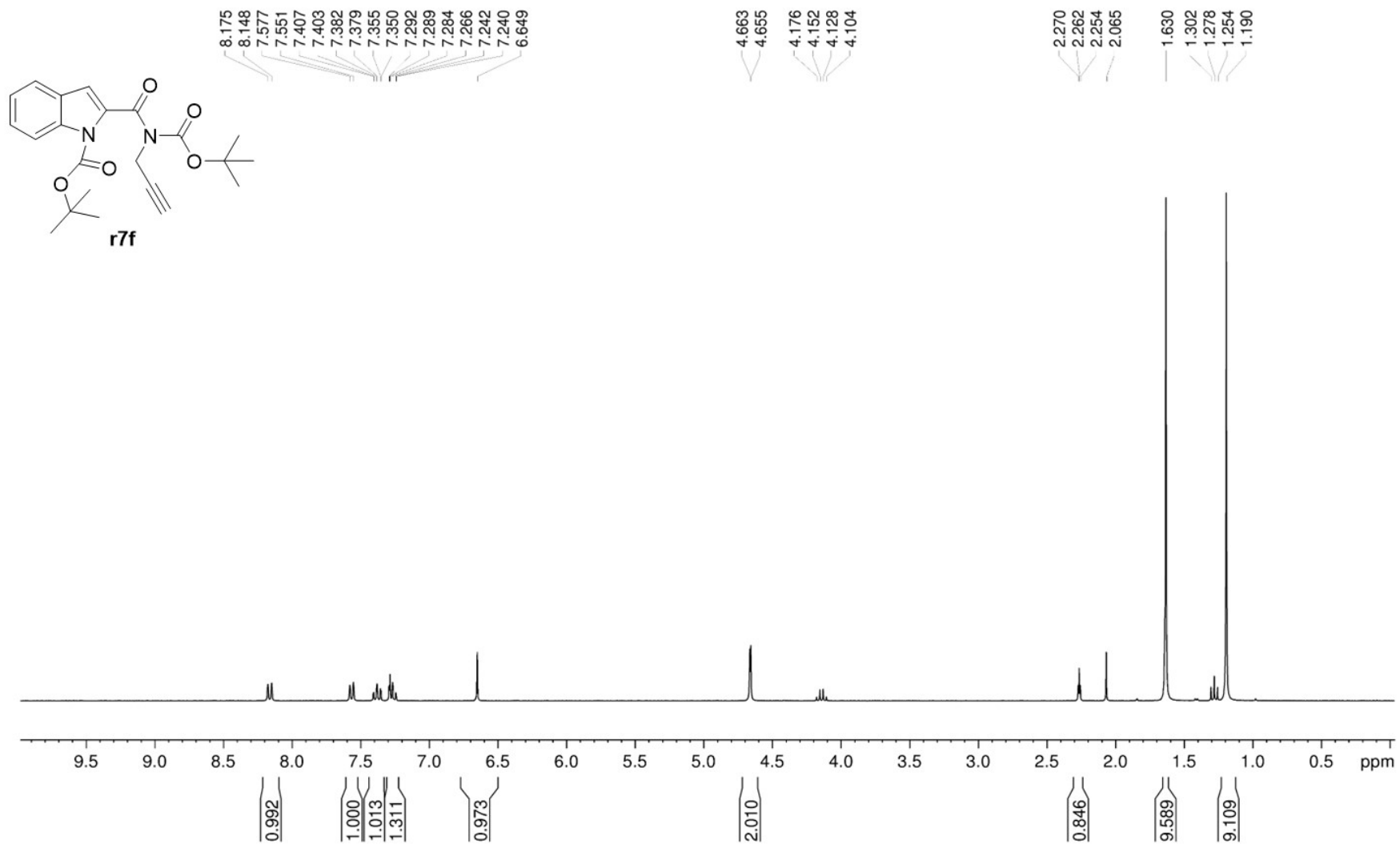
3.349  
3.311

2.625  
2.617  
2.608



$^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{OD}$ ) of **r6f**

JYX1013-B-20230206



$^{13}\text{C}\{^1\text{H}\}$ -DEPT NMR (75 MHz,  $\text{CDCl}_3$ ) of **r7f** (contaminated with EtOAc)  
r30