

## **Cu(II)-Alginate-Based Superporous Hydrogel Catalyst for Click Chemistry Azide-Alkyne Cycloaddition Type Reactions in Water**

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<sup>b</sup> *Laboratoire de Chimie Analytique et Moléculaire, LCAM, Faculté Polydisciplinaire de Safi, Université Cadi Ayyad, 4162 Safi, Morocco.*

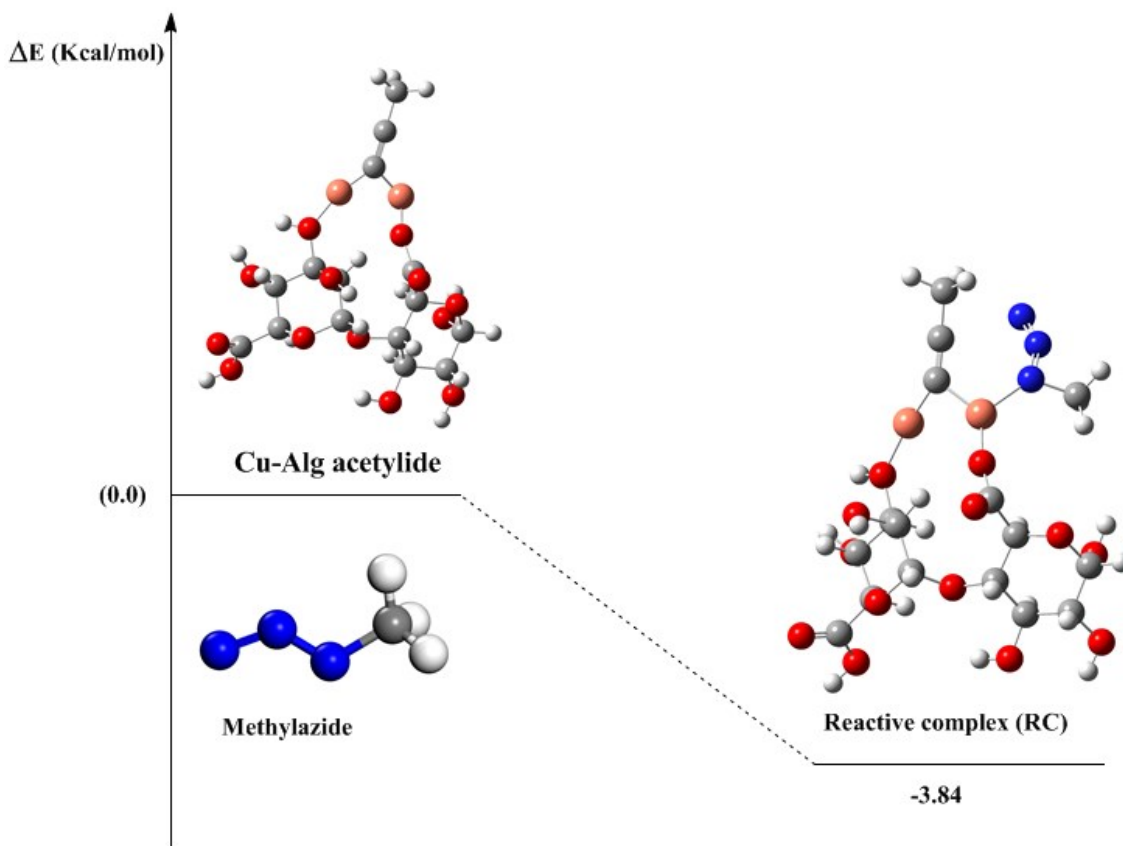
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***Electronic Supporting Information***

## 1. Theoretical studies



**Figure S1.** Calculated of reactive complex (RC) forming in aqueous phase

## 2. Characterization data of the 1,2,3-triazole products

**1-Benzyl-4-phenyl-1H-1,2,3-triazole (3a):** White solid.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 5.59 (s, 2H,  $\text{CH}_2$ ), 7.31-7.44 (m, 8H,  $\text{CH}_{\text{Ar}}$ ), 7.69 (s, 1H,  $\text{CH}_{\text{triazole}}$ ), 7.81-7.83 (s, 2H,  $\text{CH}_{\text{Ar}}$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 54.6 ( $\text{CH}_2$ ), 119.95 ( $\text{CH}_{\text{Ar}}$ ), 126.1 ( $\text{CH}_{\text{Ar}}$ ), 128.5 (2 $\text{CH}_{\text{Ar}}$ ), 128.6 (2 $\text{CH}_{\text{Ar}}$ ), 129.2 ( $\text{C}_{\text{Ar}}$ ), 129.56 ( $\text{CH}_{\text{triazole}}$ ), 130.9 ( $\text{C}_{\text{Ar}}$ ), 135.1 ( $\text{C}_{\text{Ar}}$ ). HRMS (ESI) [ $\text{M} + \text{H}$ ] $^+$  found  $m/z = 236.1183$ . Calcd value for  $\text{C}_{15}\text{H}_{13}\text{N}_3 = 236.1182$ .

**Methyl 4-(1-benzyl-1H-1,2,3-triazol-4-yl)benzoate (3b):** White solid.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 3.94 (s, 3H,  $\text{CH}_3$ ), 5.61 (s, 2H,  $\text{CH}_2$ ), 7.33-7.36 (m, 2H,  $\text{CH}_{\text{Ar}}$ ), 7.40-7.43 (m,

3H, CH<sub>ar</sub>), 7.76 (s, 1H, CH<sub>triazole</sub>), 7.88-7.91 (d, *J* = 9 Hz, 2H, CH<sub>ar</sub>), 8.08-8.11 (d, *J* = 9 Hz, 2H, CH<sub>ar</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ ppm): 52.5 (CH<sub>2</sub>), 54.8 (CH<sub>2</sub>), 120.73 (CH<sub>ar</sub>), 125.9 (CH<sub>ar</sub>), 128.5 (2CH<sub>ar</sub>), 129.3 (2CH<sub>ar</sub>), 129.6 (2CH<sub>ar</sub>), 130.0 (CH<sub>ar</sub>), 130.6 (CH<sub>triazole</sub>), 134.8 (C<sub>ar</sub>), 135.2 (C<sub>ar</sub>), 148.1 (C<sub>triazole</sub>), 156.25 (C<sub>ar</sub>), 167.2 (C<sub>carbonyl</sub>). HRMS (ESI) [M + H]<sup>+</sup> found *m/z* = 294.1242. Calcd value for C<sub>17</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub> = 294.1237.

**1-benzyl-4-(phoxymethyl)-1H-1,2,3-triazole (3c):** White solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ ppm): 5.21 (s, 2H, CH<sub>2</sub>), 5.55 (s, 2H, OCH<sub>2</sub>), 6.96-7.00 (q, 3H, CH<sub>ar</sub>), 7.28-7.33 (q, 4H, CH<sub>ar</sub>), 7.37-7.41 (m, 3H, CH<sub>ar</sub>), 7.57 (s, 1H, CH<sub>triazole</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ ppm): 54.70 (CH<sub>2</sub>), 62.5 (CH<sub>2</sub>), 115.2 (2CH<sub>ar</sub>), 121.6 (CH<sub>triazole</sub>), 128.5 (2CH<sub>ar</sub>), 129.2 (2CH<sub>ar</sub>), 129.5 (4CH<sub>ar</sub>), 129.92 (C<sub>ar</sub>), 134.9 (C<sub>triazole</sub>), 158.6 (C<sub>ar</sub>). HRMS (ESI) [M + H]<sup>+</sup> found *m/z* = 266.1289. Calcd value for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>O = 266.1288.

**Methyl 1-benzyl-1H-1,2,3-triazole-4-carboxylate (3d):** White solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ ppm): 3.94 (s, 3H, OCH<sub>3</sub>), 5.59 (s, 2H, CH<sub>2</sub>), 7.29-7.32 (q, 2H, CH<sub>ar</sub>), 7.39-7.43 (m, 3H, CH<sub>ar</sub>), 8.01 (s, 1H, CH<sub>triazole</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ ppm): 52.6 (CH<sub>3</sub>), 54.9 (CH<sub>2</sub>), 127.6 (CH<sub>triazole</sub>), 128.7 (CH<sub>ar</sub>), 129.6 (2CH<sub>ar</sub>), 129.7 (2CH<sub>ar</sub>), 131.8 (C<sub>ar</sub>), 134 (C<sub>triazole</sub>), 161.5 (C<sub>carbonyl</sub>). HRMS (ESI) [M + H]<sup>+</sup> found *m/z* = 218.0921, Calcd value for C<sub>11</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub> = 218.0924.

**1-benzyl-4-(4-methoxyphenyl)-1H-1,2,3-triazole (3e):** White solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ ppm): 3.85 (s, 3H, OCH<sub>3</sub>), 5.58 (s, 2H, CH<sub>2</sub>), 6.94-6.97 (d, 2H, CH<sub>ar</sub>), 7.31-7.41 (m, 5H, CH<sub>ar</sub>), 7.60 (s, 1H, CH<sub>triazole</sub>), 7.73-7.76 (d, 2H, CH<sub>ar</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ ppm): 54.6 (OCH<sub>3</sub>), 55.7 (CH<sub>2</sub>), 114.6 (2CH<sub>ar</sub>), 119.1 (C<sub>ar</sub>), 123.6 (2CH<sub>ar</sub>), 127.4 (C<sub>ar</sub>),

128.45 (3CH<sub>ar</sub>), 129.15 (2CH<sub>ar</sub>), 129.54 (CH<sub>triazole</sub>), 135.17 (C<sub>ar</sub>), 148.62 (C<sub>triazole</sub>), 160.01 (C<sub>ar</sub>). HRMS (ESI) [M + H]<sup>+</sup> found *m/z* = 266.1284. Calcd value for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>O = 266.1287.

**1-(4-fluorobenzyl)-4-phenyl-1H-1,2,3-triazole (3f):** White solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ ppm): 5.57 (s, 2H, CH<sub>2</sub>), 7.07-7.13 (dd, 2H, CH<sub>ar</sub>), 7.31-7.45 (m, 5H, CH<sub>ar</sub>), 7.73 (s, 1H, CH<sub>triazole</sub>), 7.82-7.85 (d, 2H, CH<sub>ar</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ ppm): 54.0 (CH<sub>2</sub>), 116.4 (CH<sub>ar</sub>), 116.7 (CH<sub>ar</sub>), 126.1 (2CH<sub>ar</sub>), 128.7 (CH<sub>ar</sub>), 129.3 (2CH<sub>ar</sub>), 130.3 (CH<sub>triazole</sub>), 130.4 (2CH<sub>ar</sub>), 130.6 (C<sub>ar</sub>), 130.8 (C<sub>ar</sub>), 161.7 (C<sub>triazole</sub>), 165.0 (C<sub>ar</sub>). HRMS (ESI) [M + H]<sup>+</sup> found *m/z* = 254.1094. Calcd value for C<sub>15</sub>H<sub>12</sub>N<sub>3</sub>F = 254.1088.

**4-((4-phenyl-1H-1,2,3-triazol-1-yl)methyl)pyridine (3g):** White solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ ppm): 5.73 (s, 2H, CH<sub>2</sub>); 7.25-7.36 (m, 2H, CH<sub>Ar</sub>); 7.41-7.46 (m, 3H, CH<sub>Ar</sub>); 7.69-7.75 (m, 1H, CH<sub>Ar</sub>); 7.83-7.87 (m, 1H, CH<sub>Ar</sub>); 7.96 (s, 1H, CH<sub>Triazole</sub>); 8.64 (s, 2H, CH<sub>Ar</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ ppm): 56.1 (CH<sub>2</sub>); 120.6 (2 CH<sub>Ar</sub>); 124.0 (2 CH<sub>Ar</sub>); 126.1 (CH<sub>Ar</sub>); 128.6 (2 CH<sub>Ar</sub>); 129.2 (C<sub>Ar</sub>); 130.9 (CH<sub>Triazole</sub>); 137.8 (C<sub>Ar</sub>); 150.1 (C<sub>Triazole</sub>); 154.9 (2 CH<sub>Ar</sub>). HRMS (ESI) [M + H]<sup>+</sup> found *m/z* = 237.1132. Calcd value for C<sub>14</sub>H<sub>12</sub>N<sub>4</sub> = 237.1134.

**1-(4-methoxyphenyl)-4-(phenoxyethyl)-1H-1,2,3-triazole (3h):** White solid. <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>, δ ppm): 3.78 (s, 3H, CH<sub>3</sub>); 5.21 (s, 2H, CH<sub>2</sub>); 6.88-6.96 (q, 5H, CH<sub>Ar</sub>); 7.23-7.26 (d, 2H, CH<sub>Ar</sub>); 7.54 (s, 1H, CH<sub>Ar</sub>); 7.57 (s, 1H, CH<sub>Ar</sub>); 7.96 (s, 1H, CH<sub>Triazole</sub>). <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>, δ ppm): 56.0 (CH<sub>3</sub>); 62.4 (CH<sub>2</sub>); 115.2 (2CH<sub>Ar</sub>); 115.22 (2CH<sub>Ar</sub>); 121 (CH<sub>Triazole</sub>); 121.7 (CH<sub>Ar</sub>); 130.0 (2 CH<sub>Ar</sub>); 130.2 (2 CH<sub>Ar</sub>); 130.68 (2 CH<sub>Ar</sub>); 131.1 (C<sub>Ar</sub>); 144.94 (C<sub>Triazole</sub>); 158.6 (C<sub>Ar</sub>); 160.3 (C<sub>Ar</sub>). HRMS (ESI) [M + H]<sup>+</sup> found *m/z* = 282.1242. Calcd value for C<sub>16</sub>H<sub>16</sub>N<sub>3</sub> = 282.1237.

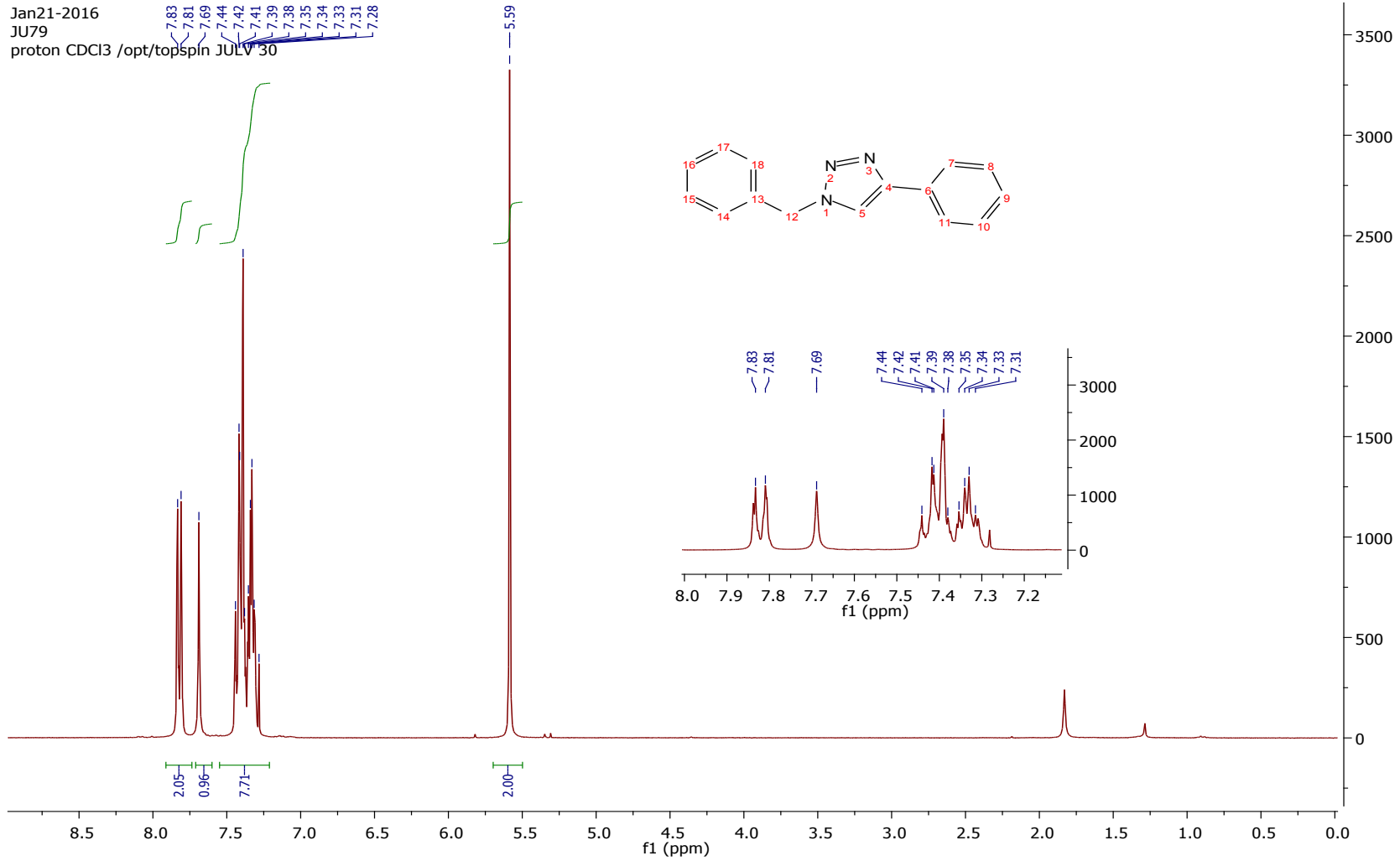
**1-(4-methoxyphenyl)-4-phenyl-1H-1,2,3-triazole (3i):** White solid.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 3.87 (s, 3H,  $\text{OCH}_3$ ), 7.05-7.08 (d, 2H,  $\text{CH}_{\text{ar}}$ ), 7.37- 7.42 (dd, 1H,  $\text{CH}_{\text{ar}}$ ), 7.47-7.51 (d, 2H,  $\text{CH}_{\text{ar}}$ ), 7.71-7.74 (d, 2H,  $\text{CH}_{\text{ar}}$ ), 7.97 (s, 2H,  $\text{CH}_{\text{ar}}$ ), 8.26 (s, 1H,  $\text{CH}_{\text{triazole}}$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 56.1 ( $\text{CH}_3$ ), 115.0 ( $\text{CH}_{\text{ar}}$ ), 115.3 ( $\text{C}_{\text{ar}}$ ), 122.7 ( $2\text{CH}_{\text{ar}}$ ), 126.3 ( $\text{CH}_{\text{ar}}$ ), 126.6 ( $2\text{CH}_{\text{ar}}$ ), 127 ( $2\text{CH}_{\text{ar}}$ ), 129 ( $\text{CH}_{\text{triazole}}$ ), 129.4 ( $\text{C}_{\text{ar}}$ ), 146.1 ( $\text{C}_{\text{triazole}}$ ), 160.5 ( $\text{C}_{\text{ar}}$ ). HRMS (ESI)  $[\text{M} + \text{H}]^+$  found  $m/z = 252.1133$ . Calcd value for  $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O} = 252.1131$ .

# 1-Benzyl-4-phenyl-1H-1,2,3-triazole (3a)

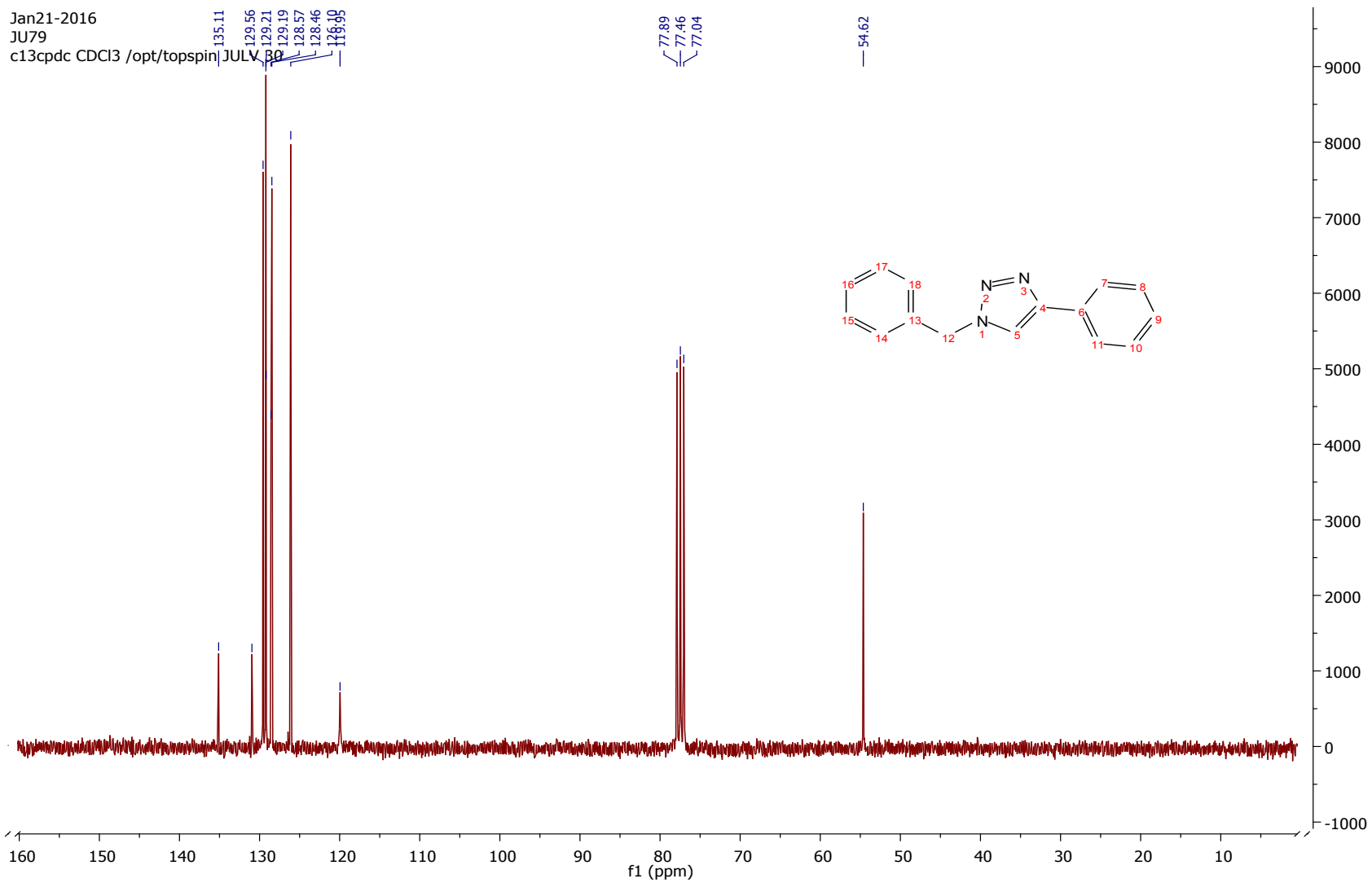
Jan21-2016

JU79

proton CDCl3 /opt/topspin JULY 30



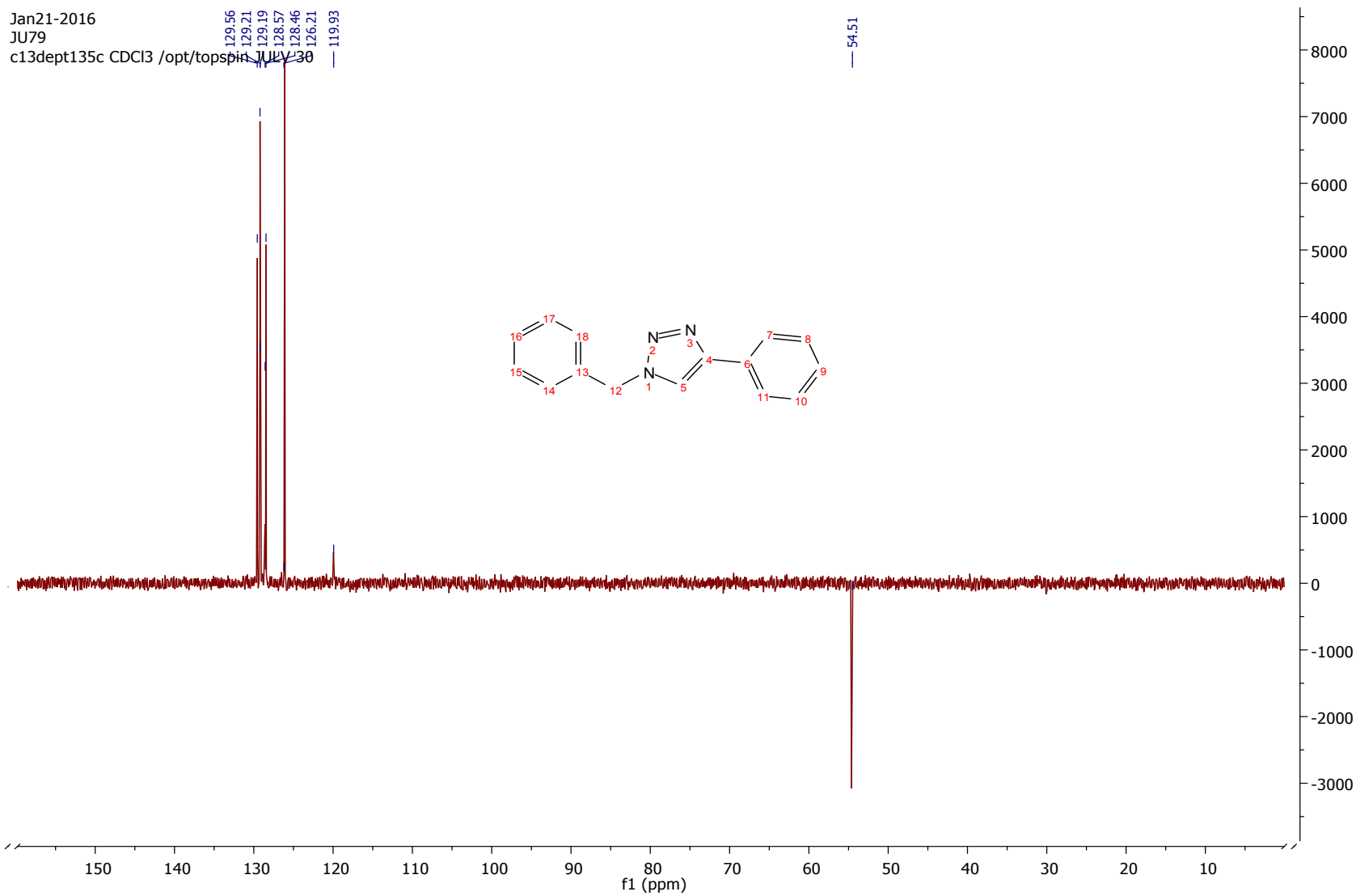
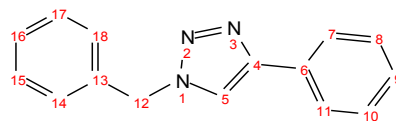
Jan21-2016  
JU79  
c13cpdc CDCl3 /opt/topspin| JULY 30



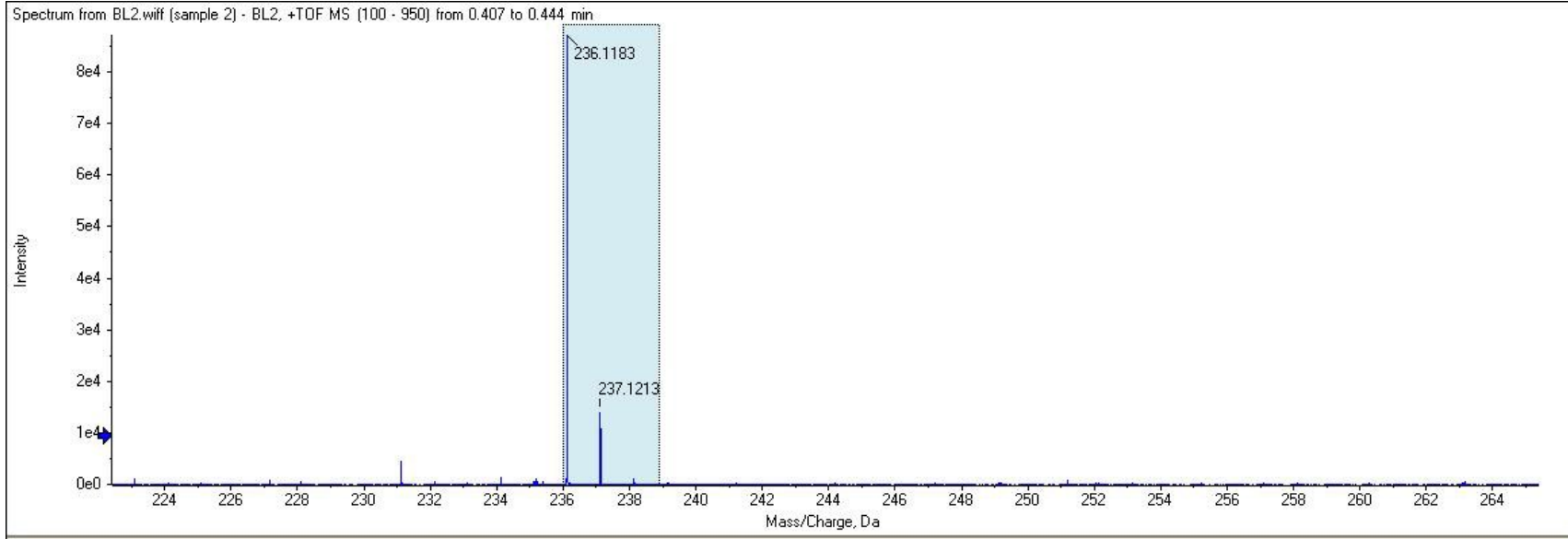
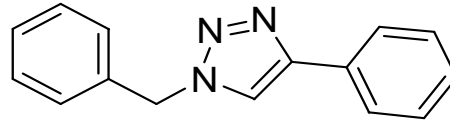
Jan21-2016  
JU79  
c13dept135c CDCl3 /opt/topspin/

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129.21  
129.19  
128.57  
128.46  
126.21  
119.93

54.51

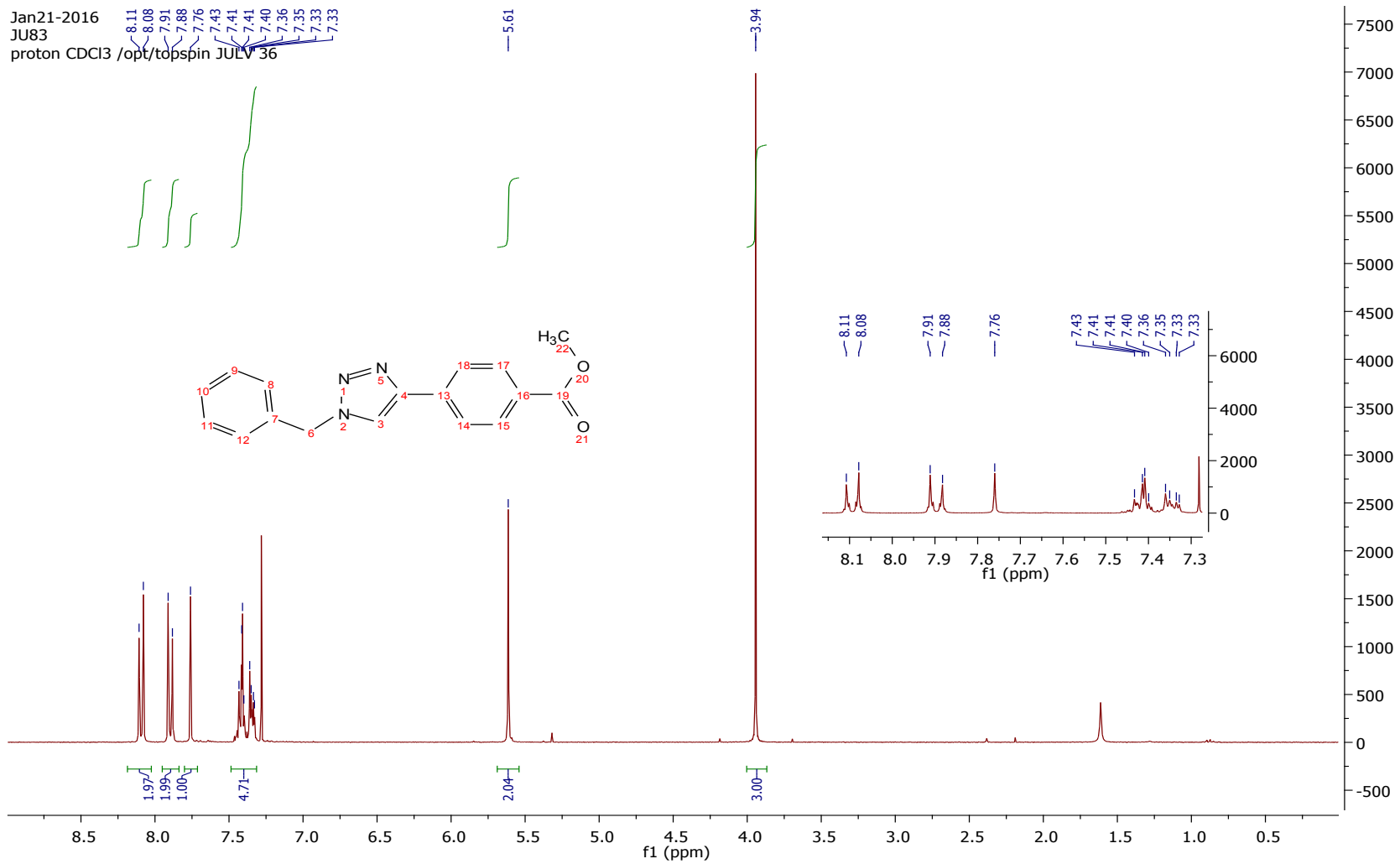






# Methyl 4-(1-benzyl-1H-1,2,3-triazol-4-yl)benzoate (3b)

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JU83  
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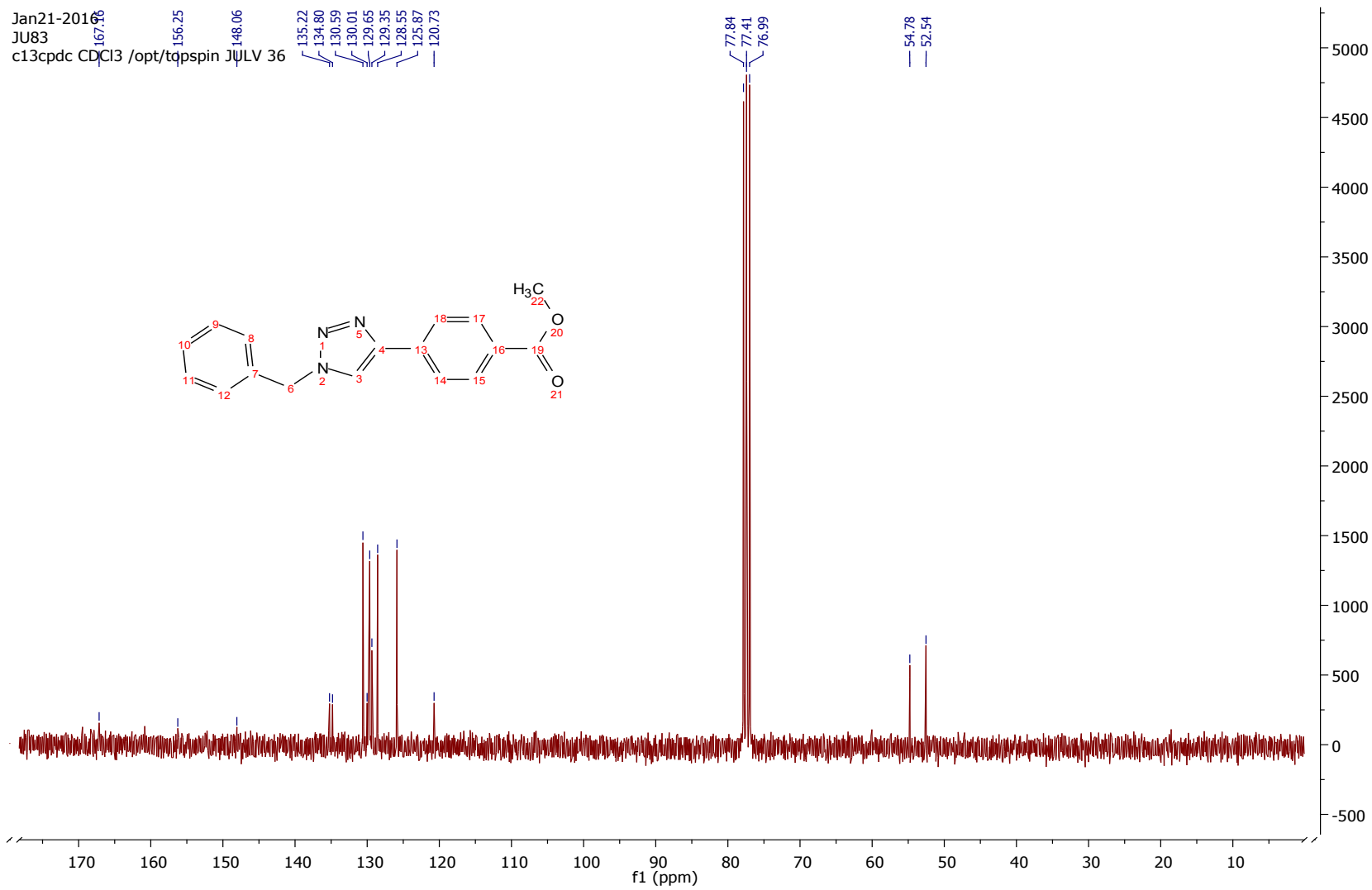
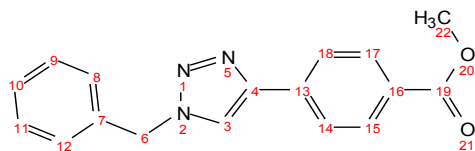


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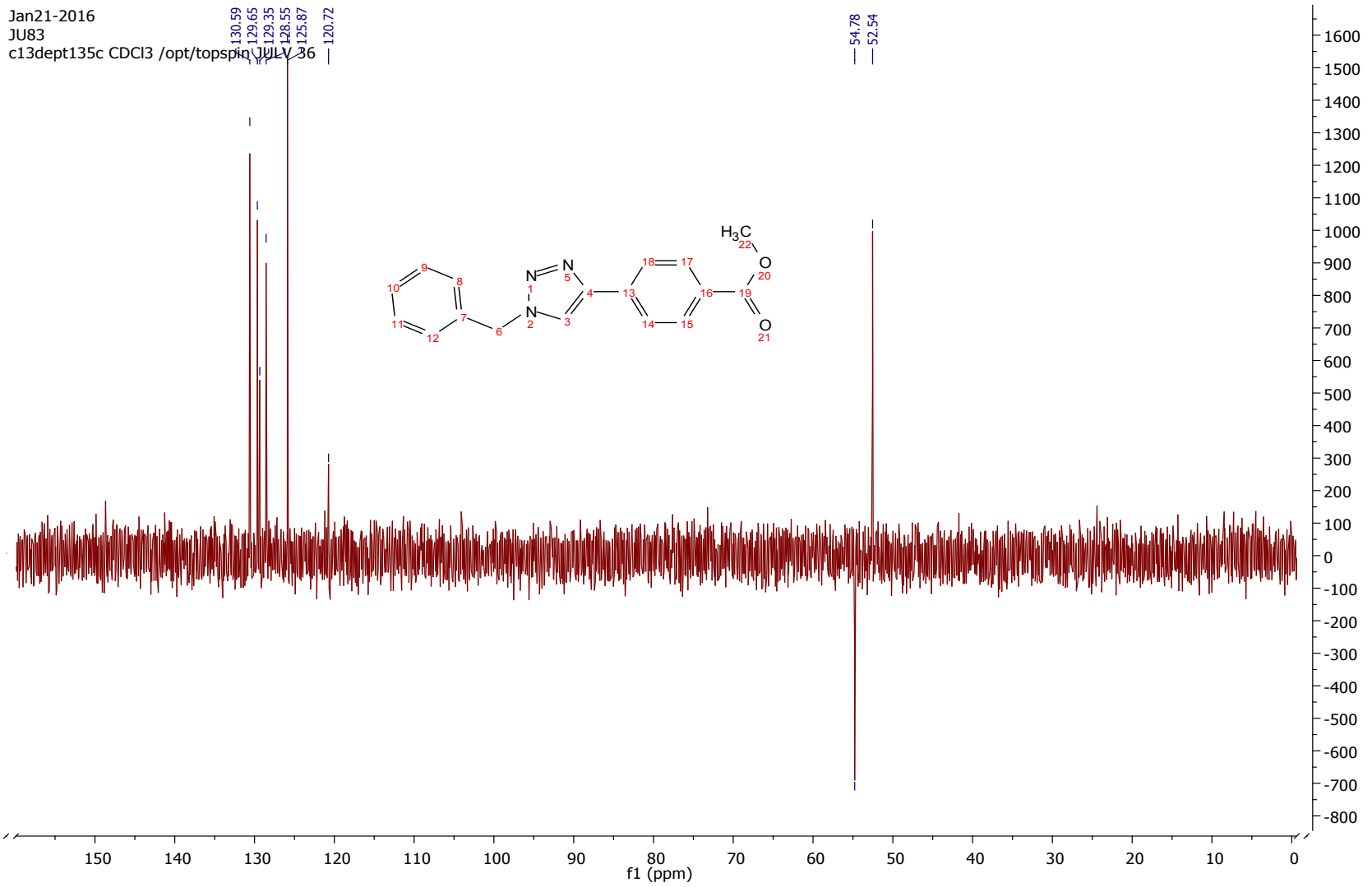
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156.25  
148.06  
135.22  
134.80  
130.59  
130.01  
129.65  
129.35  
128.55  
125.87  
120.73

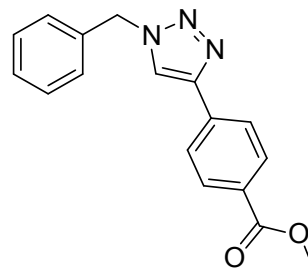
77.84  
77.41  
76.99

54.78  
52.54

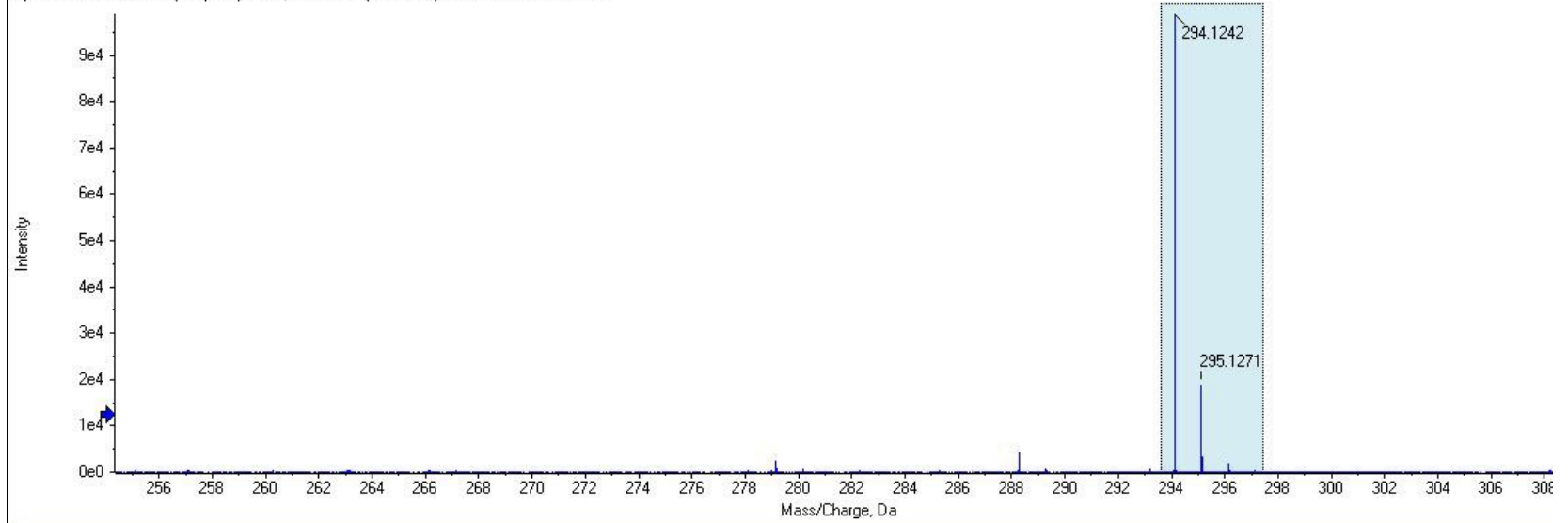


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JU83  
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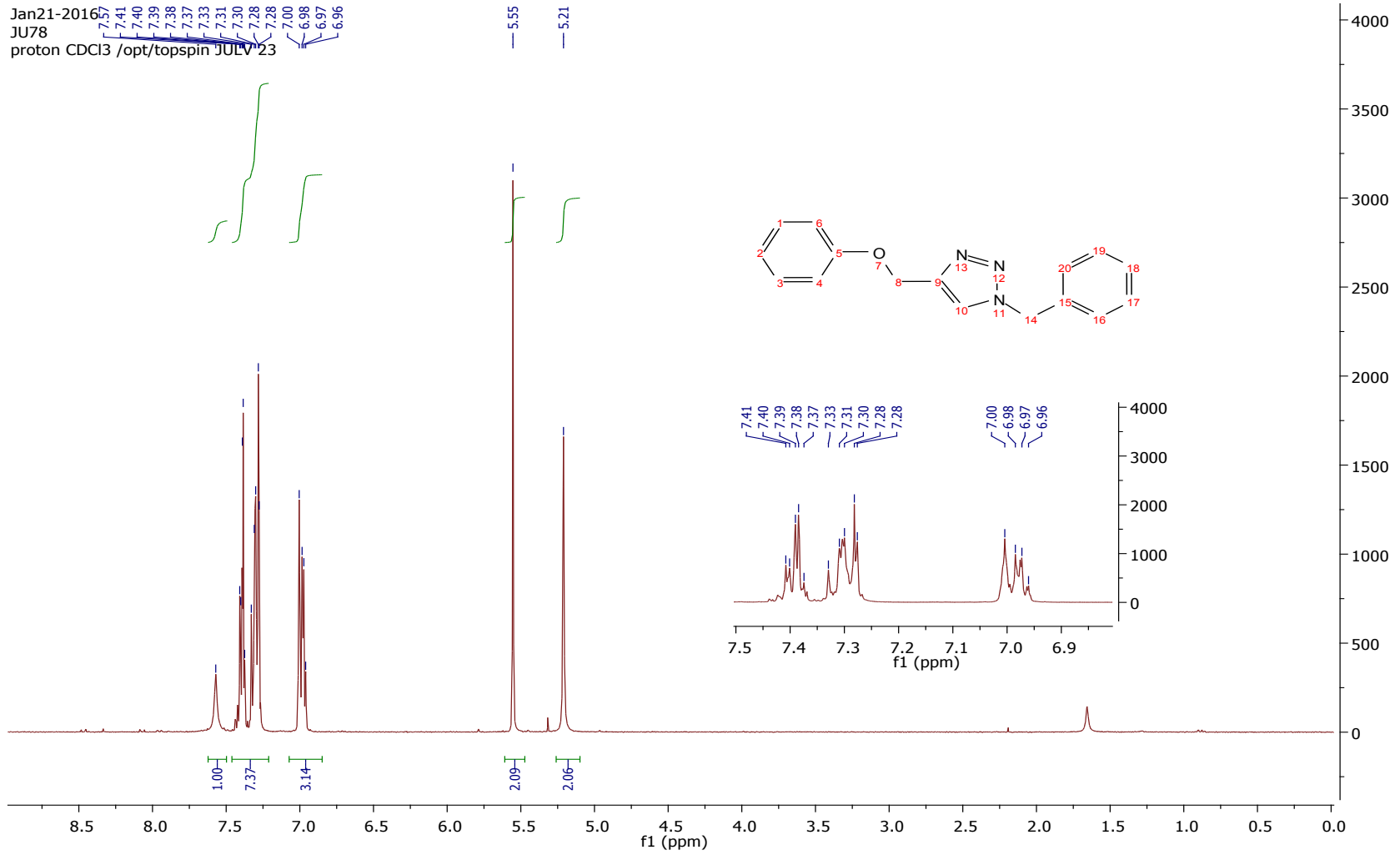


Spectrum from BL6.wiff (sample 1) - BL6, +TOF MS (100 - 950) from 0.551 to 0.597 min



# 1-benzyl-4-(phenoxyethyl)-1H-1,2,3-triazole (3c)

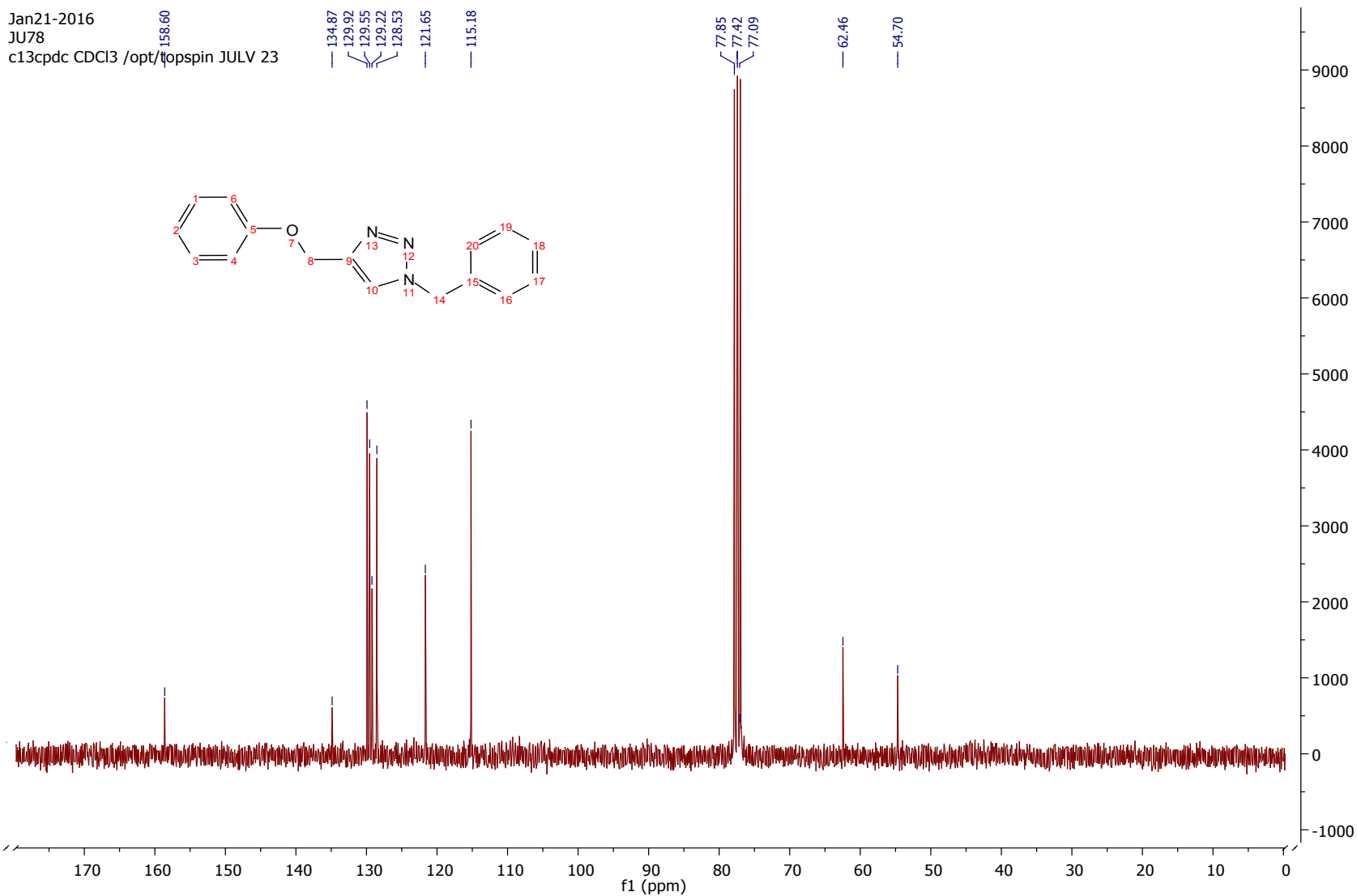
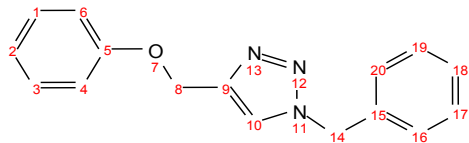
Jan21-2016  
JU78  
proton CDCl3 /opt/topspin JULY 23



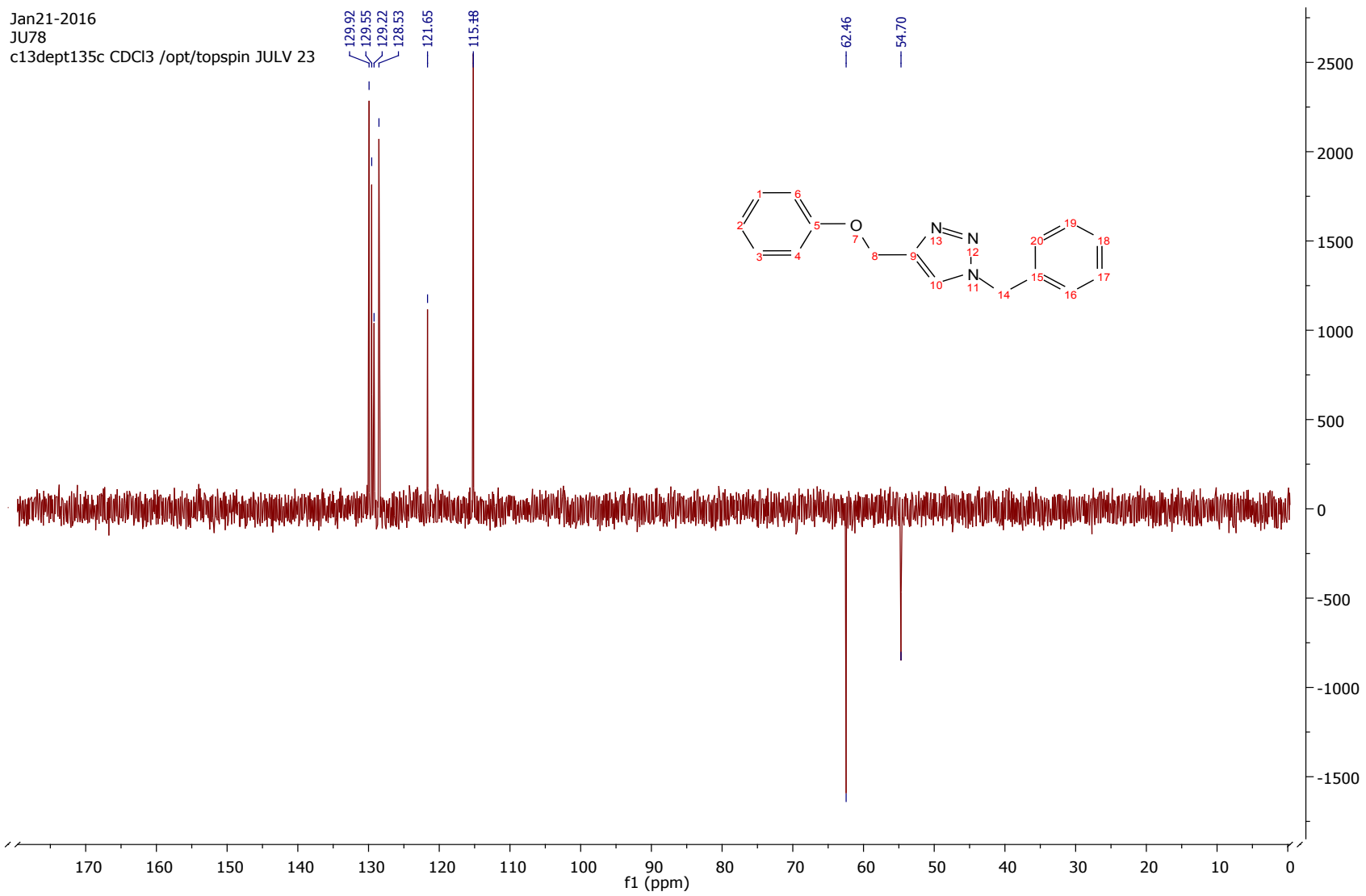
Jan21-2016  
JU78  
c13cpdc CDCl3 /opt/topspin JULV 23

158.60  
134.87  
129.92  
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128.53  
121.65  
115.18

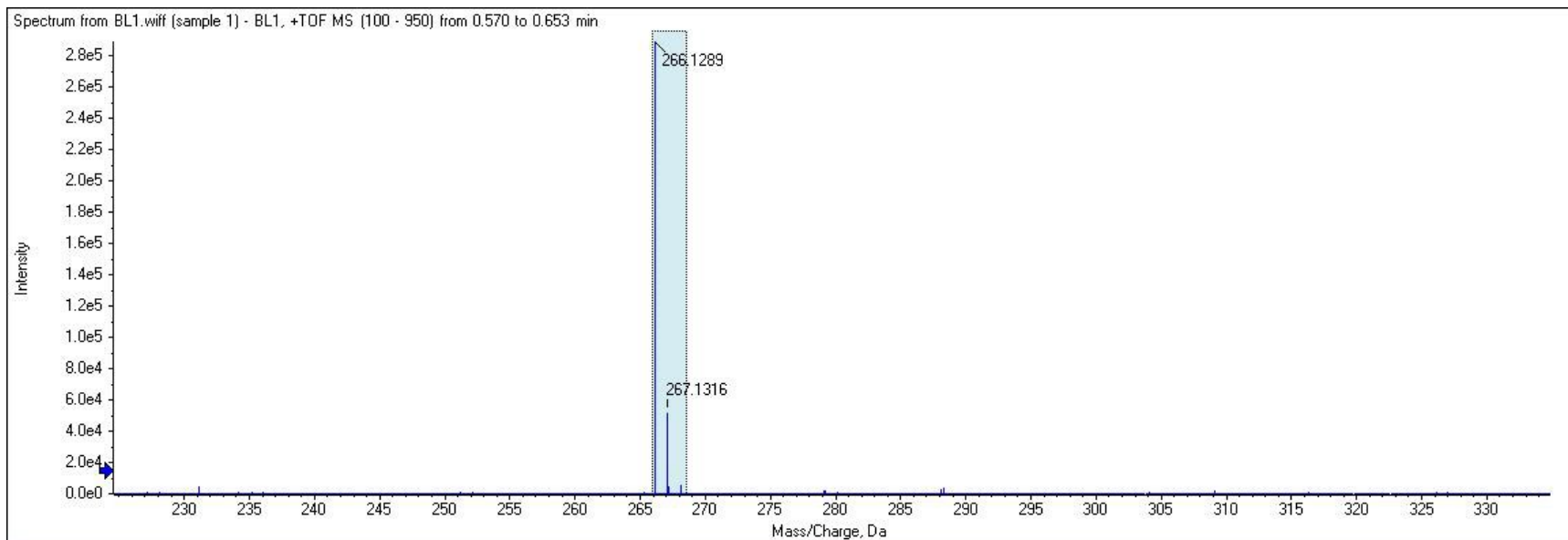
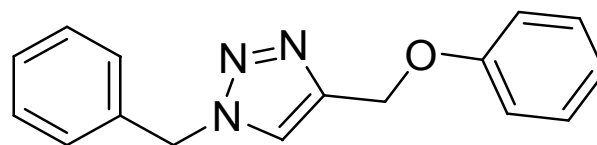
77.85  
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77.09  
62.46  
54.70



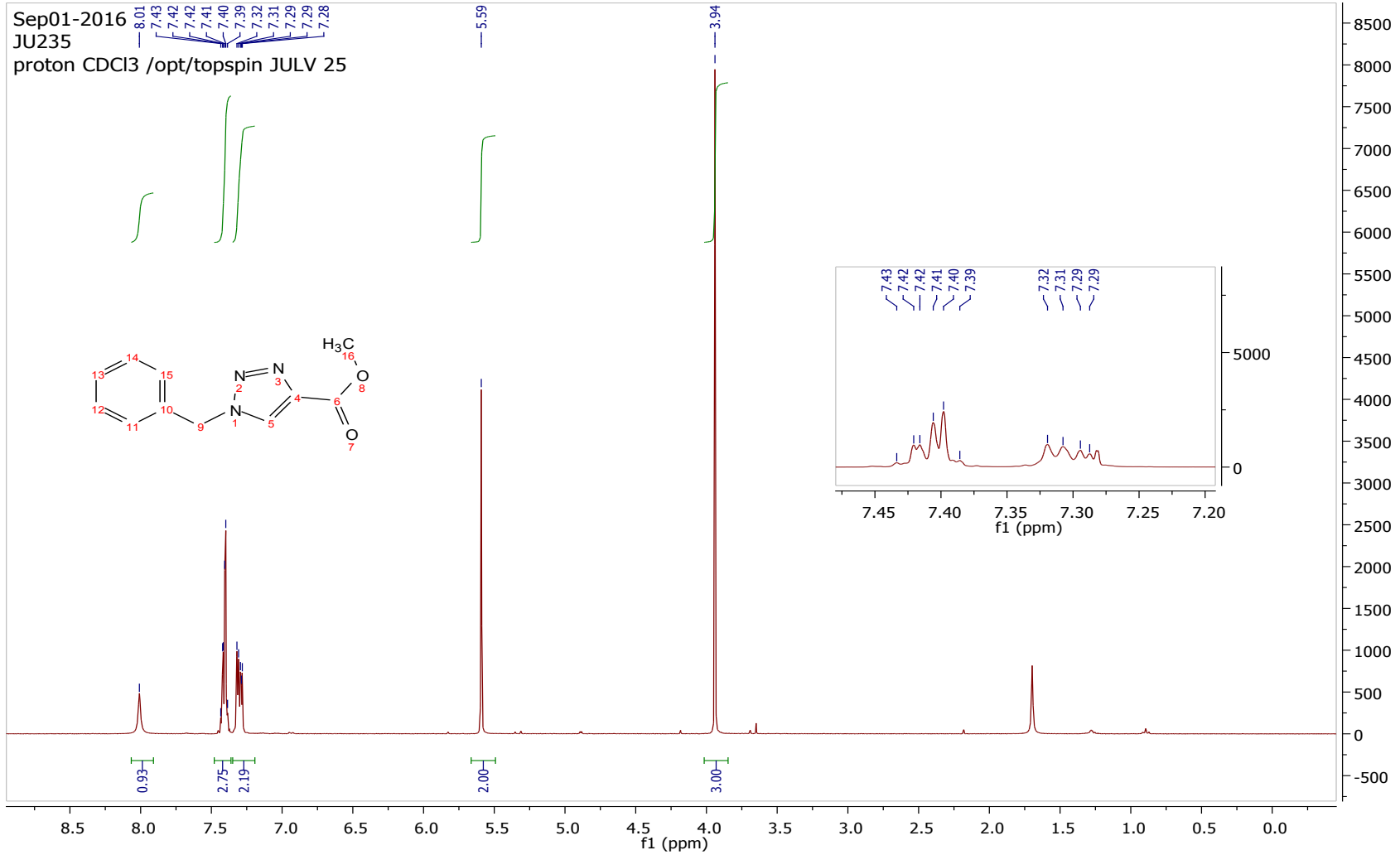
Jan21-2016  
JU78  
c13dept135c CDCl3 /opt/topspin JULV 23



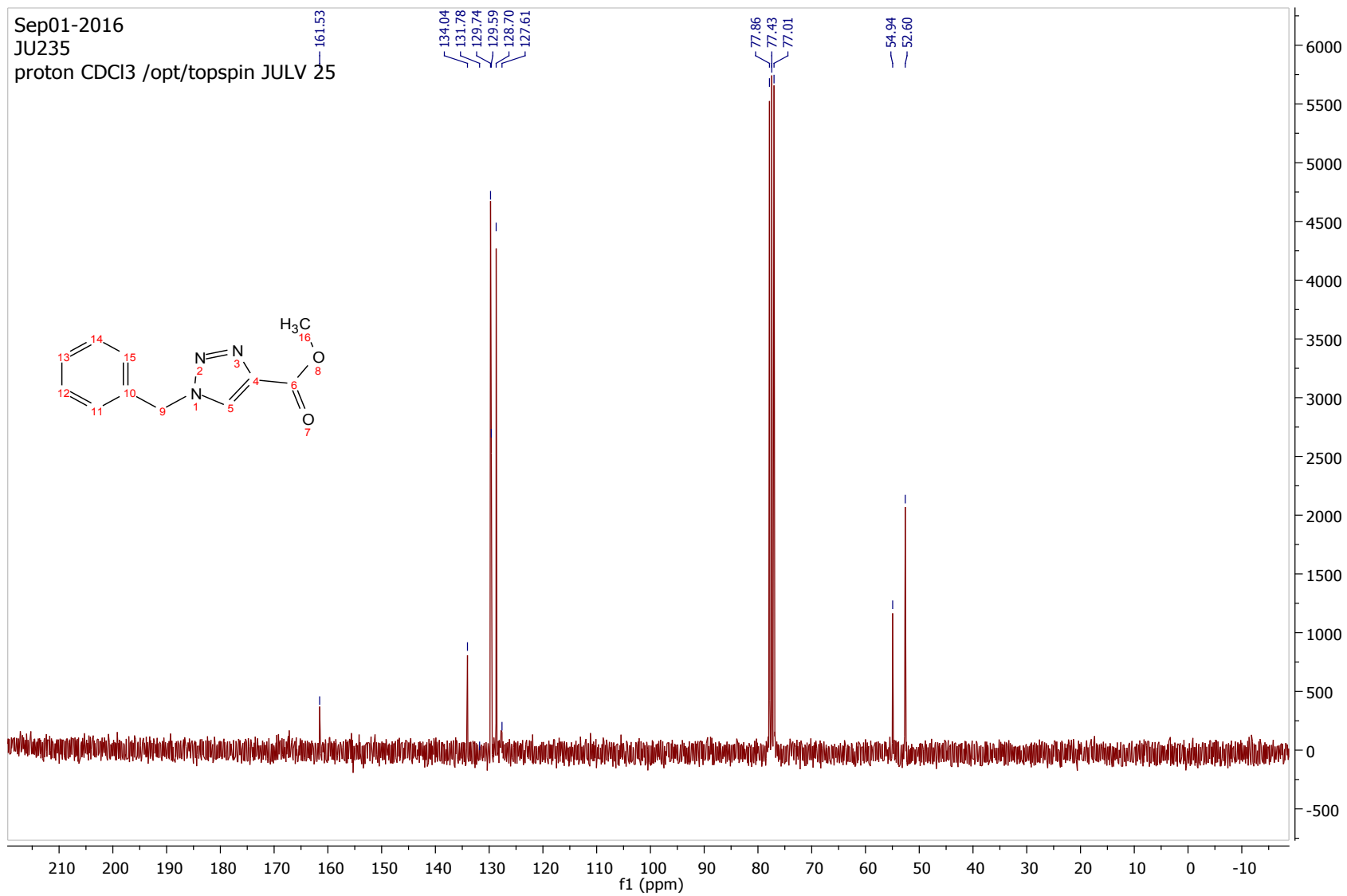
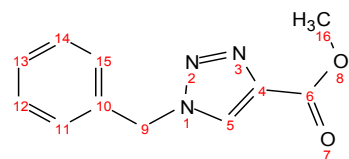




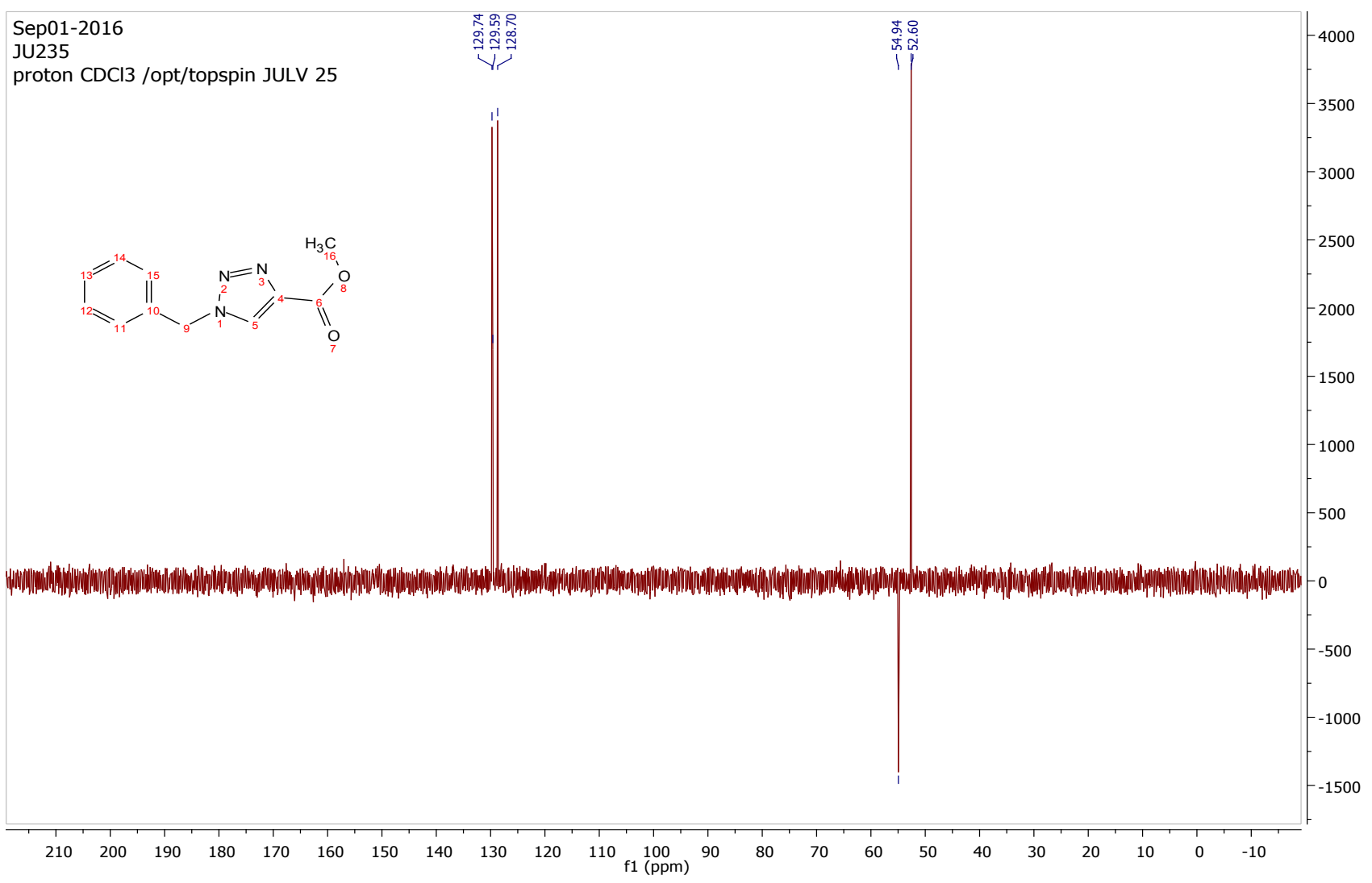
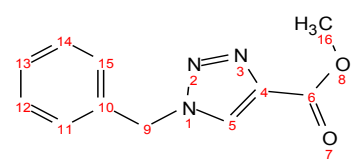
# Methyl 1-benzyl-1H-1,2,3-triazole-4-carboxylate (3d)

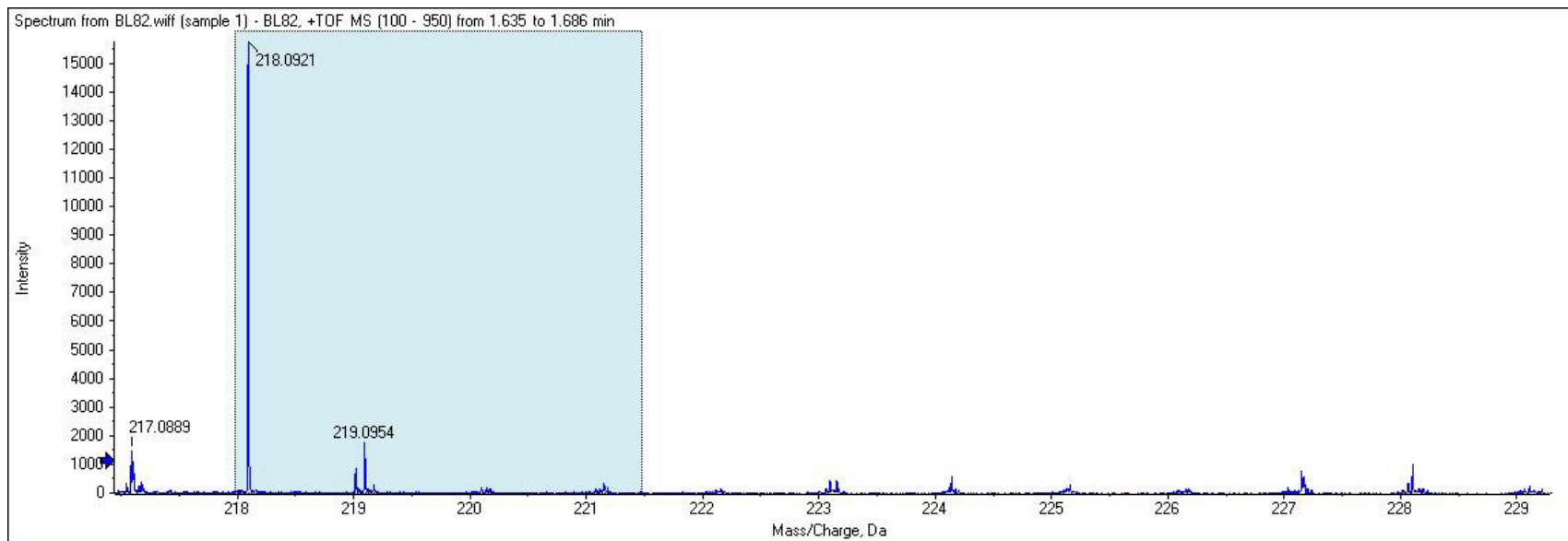
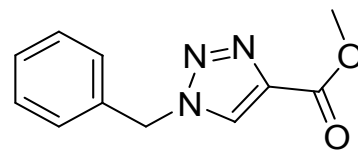


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JU235  
proton CDCl3 /opt/topspin JULV 25

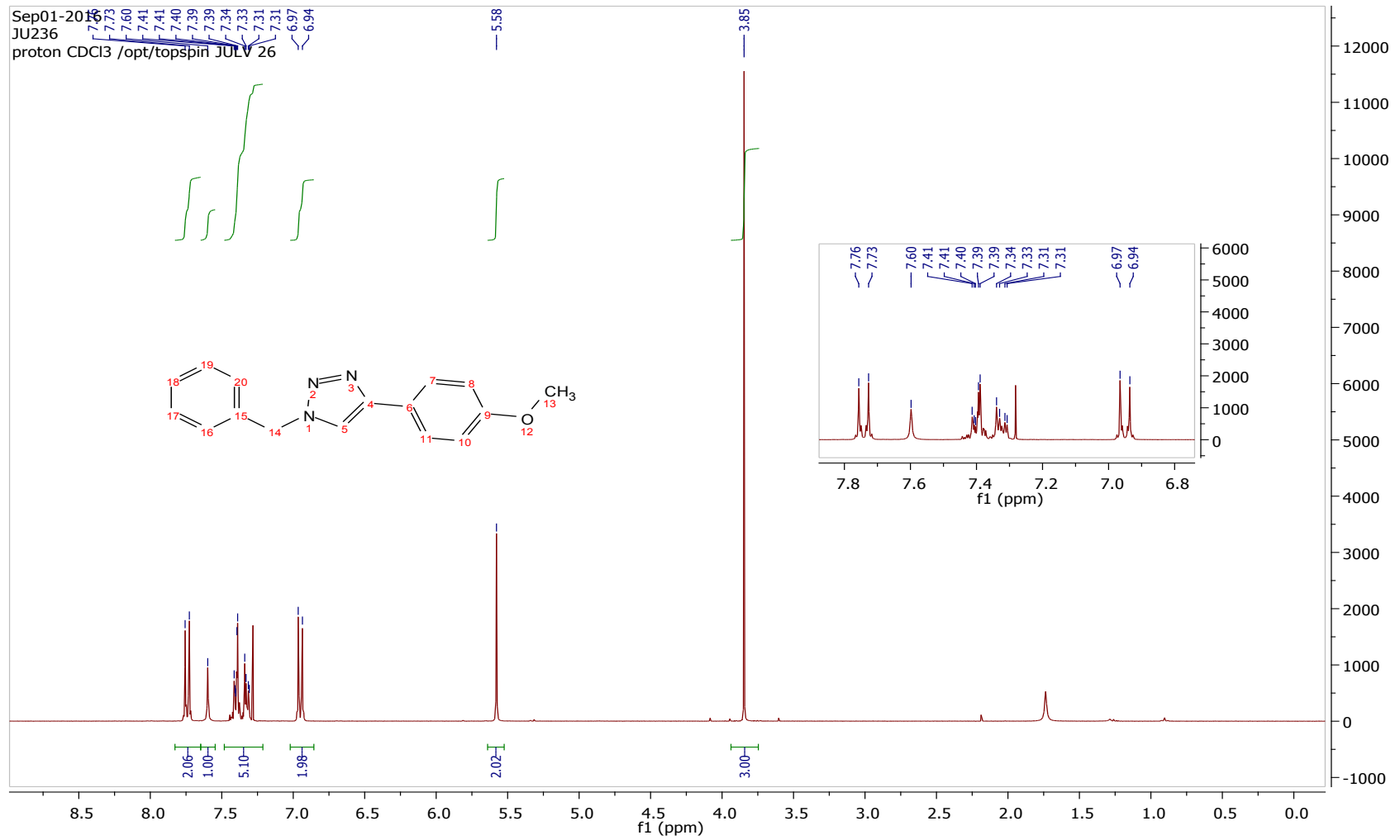


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JU235  
proton CDCl3 /opt/topspin JULV 25





# 1-benzyl-4-(4-methoxyphenyl)-1H-1,2,3-triazole (3e)

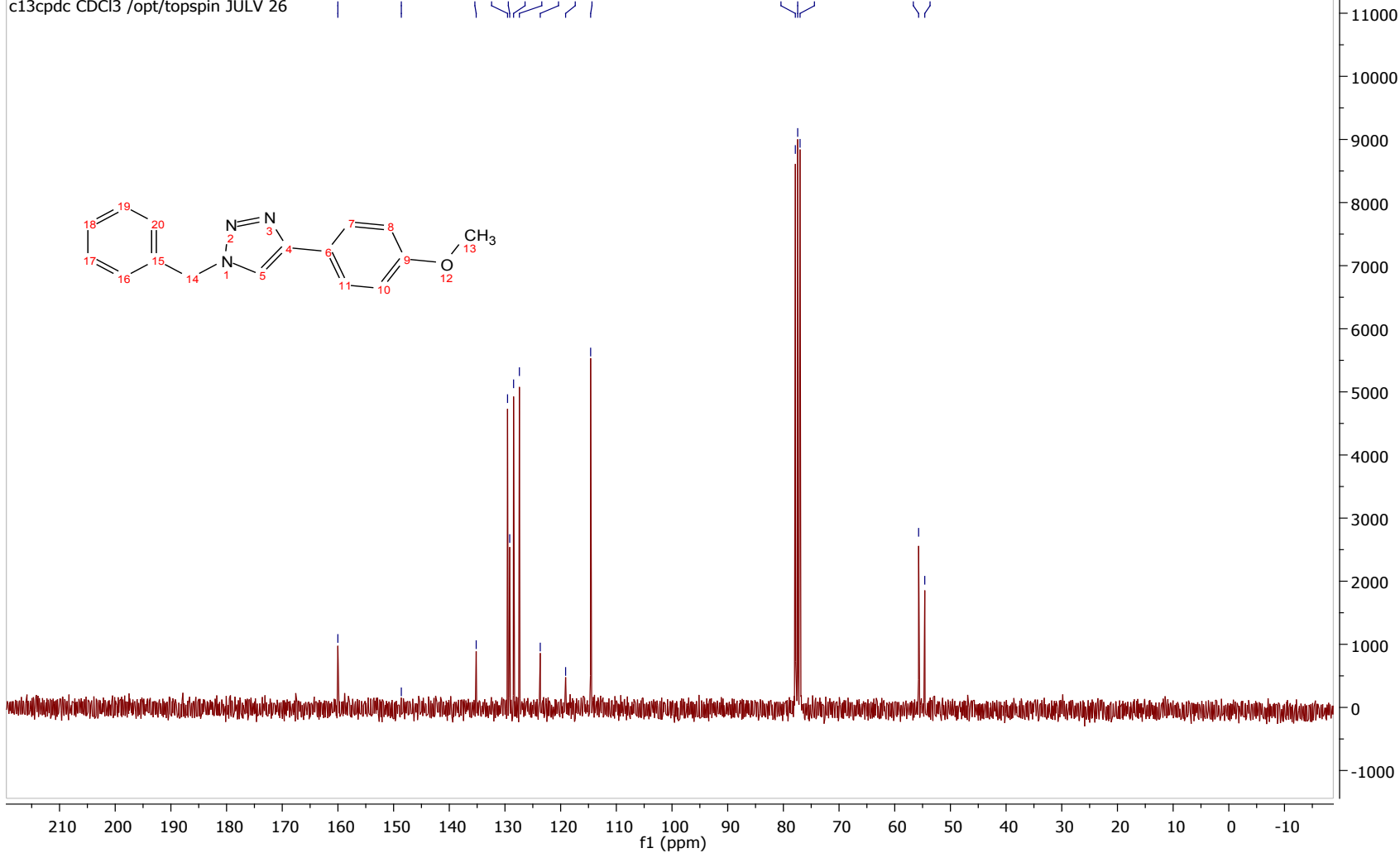
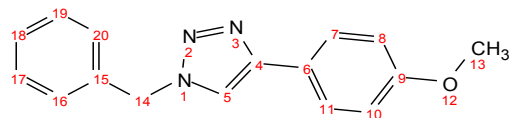


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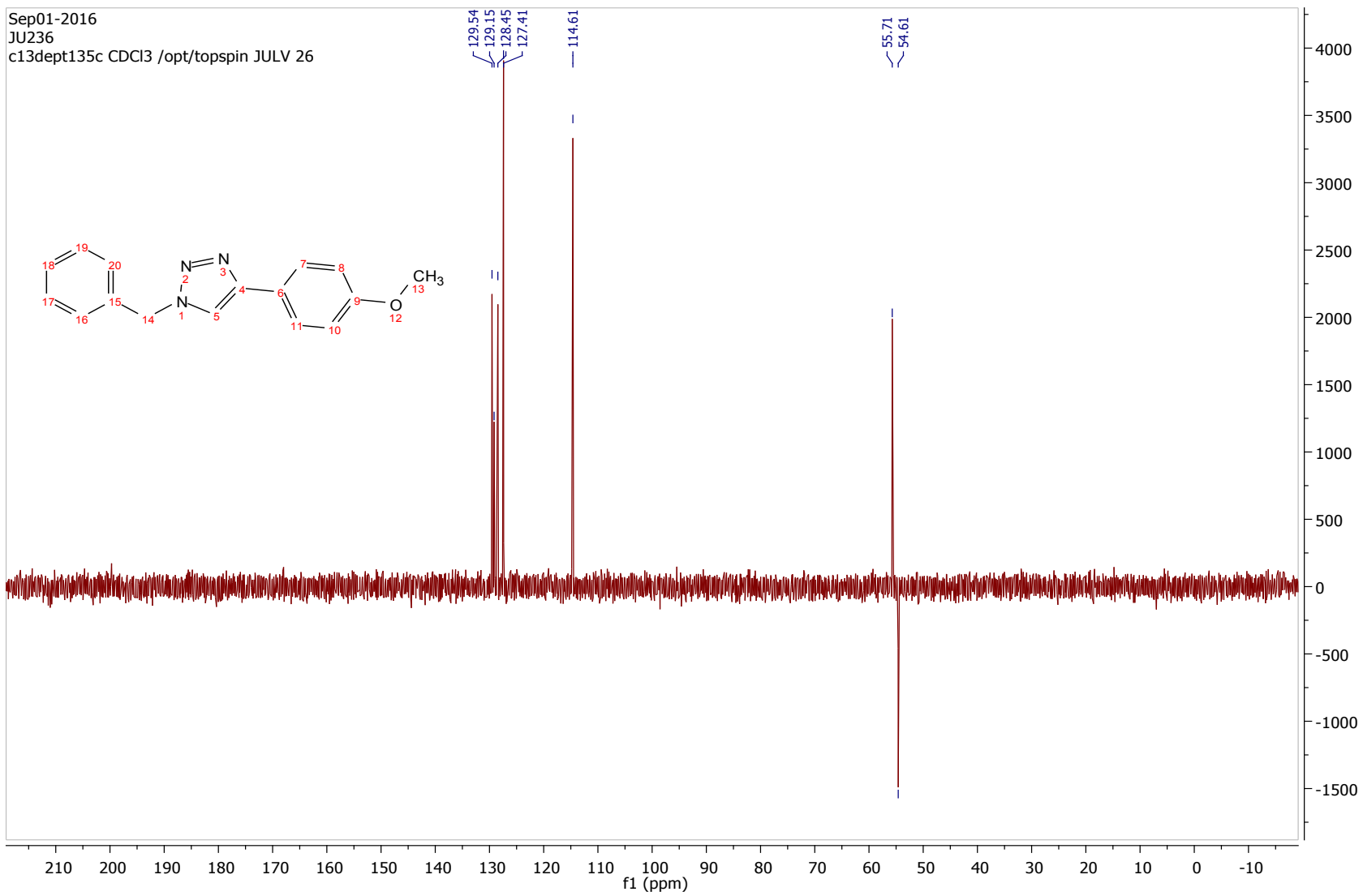
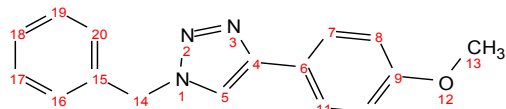
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123.66  
119.11  
114.61

77.85  
77.43  
77.00

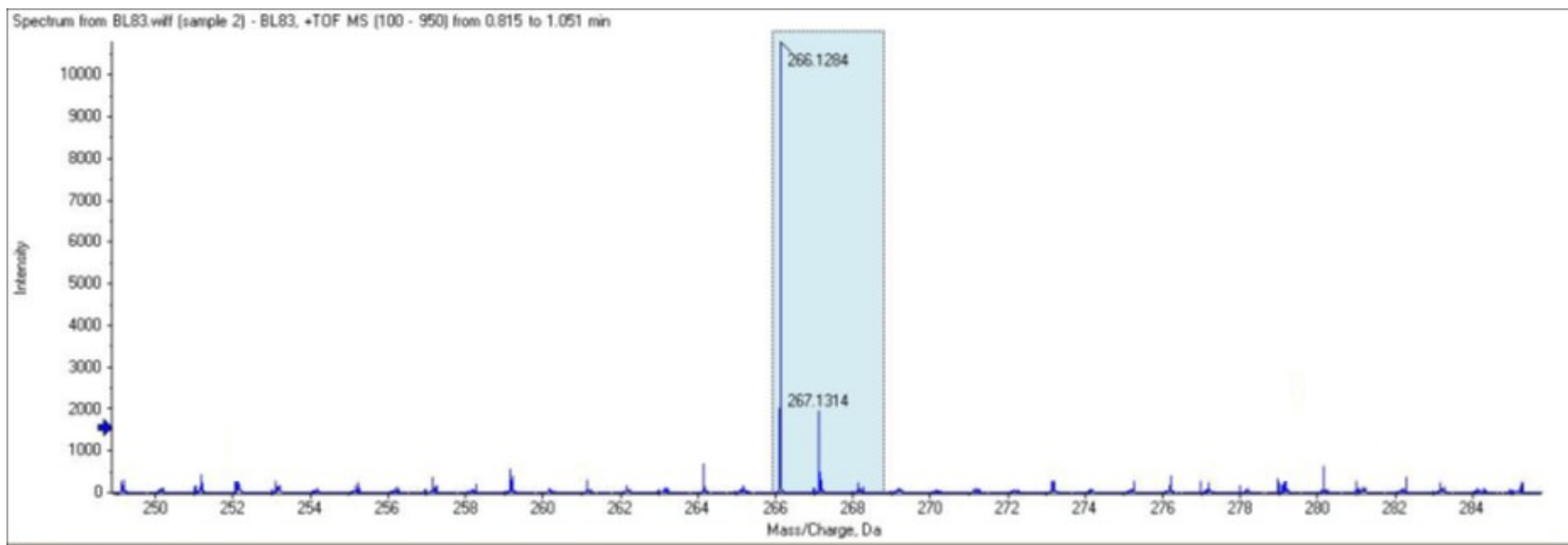
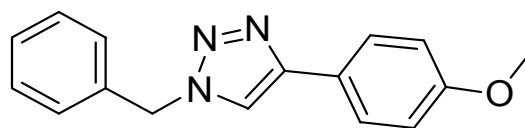
55.71  
54.61



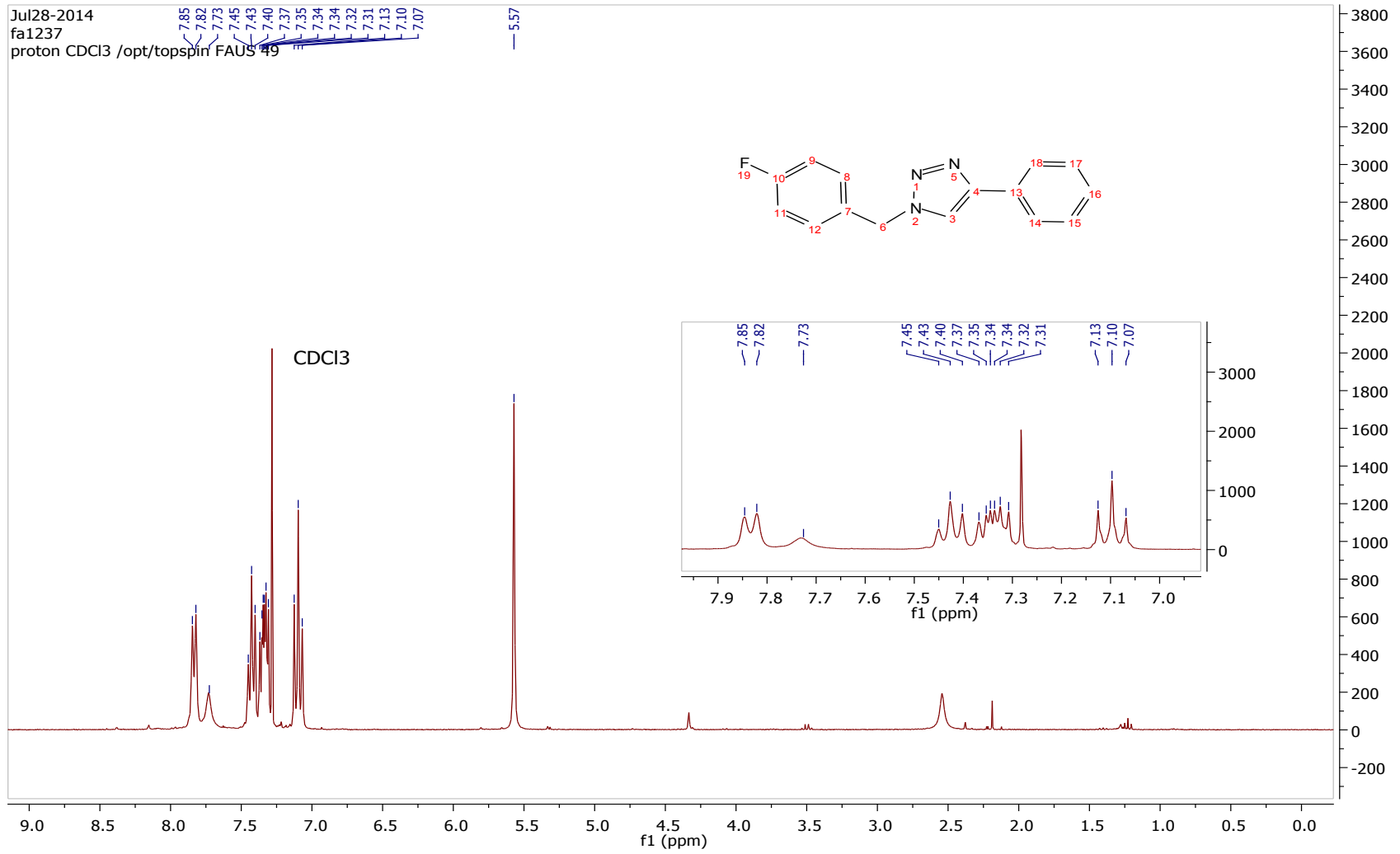
Sep01-2016  
JU236  
c13dept135c CDCl3 /opt/topspin JULV 26



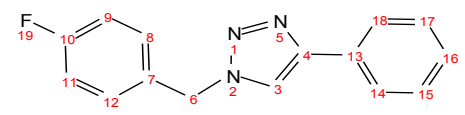
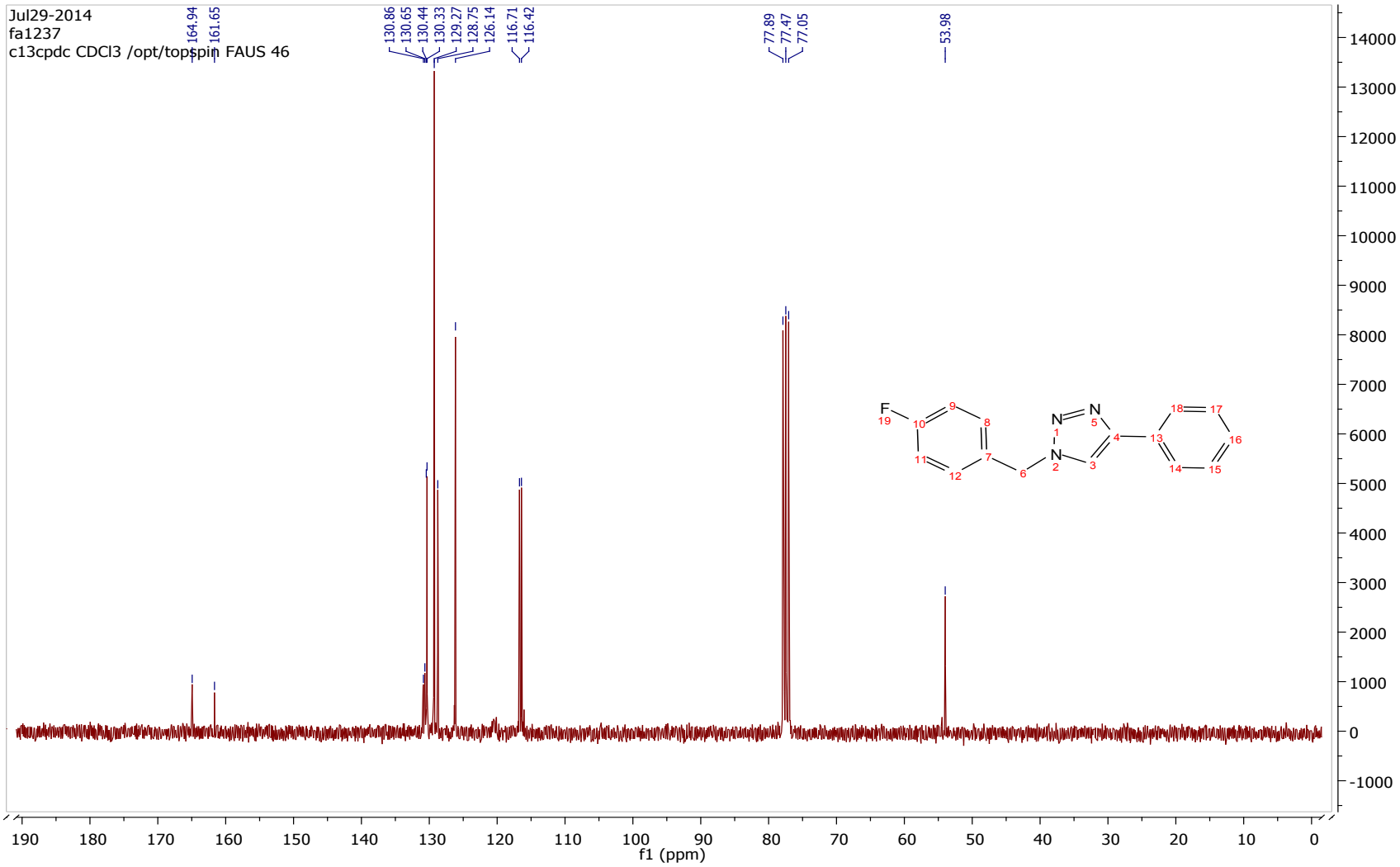




# 1-(4-fluorobenzyl)-4-phenyl-1H-1,2,3-triazole (3f)



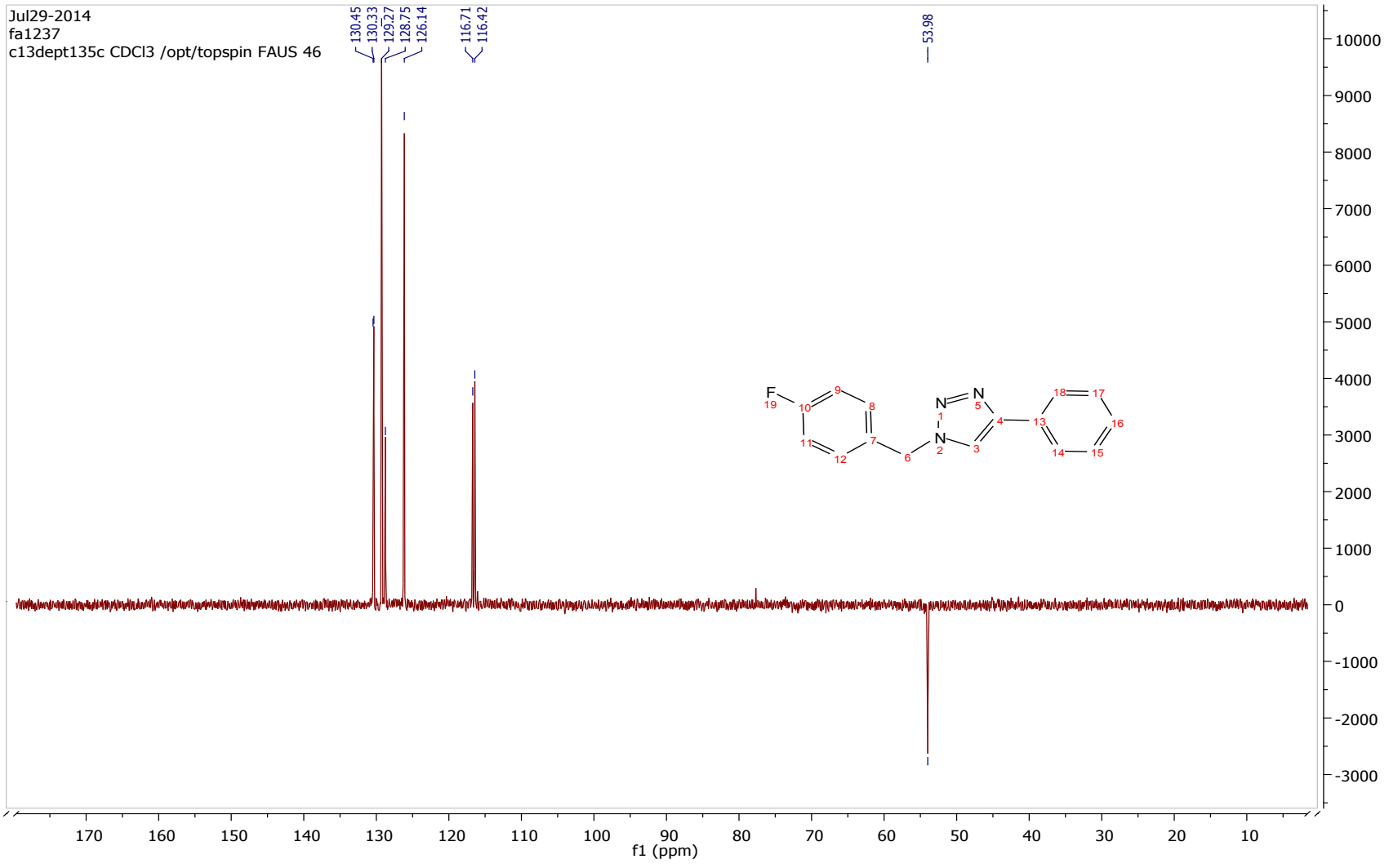
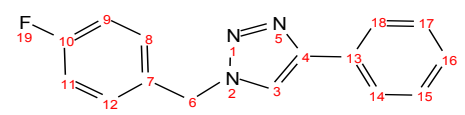
Jul29-2014  
fa1237  
c13cpdc CDCl3 /opt/topppii FAUS 46

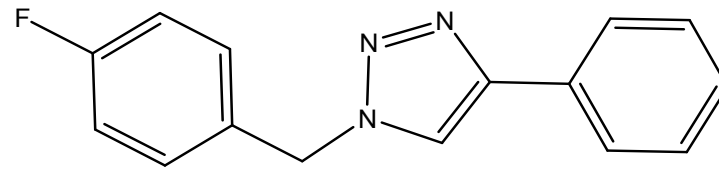


Jul29-2014  
fa1237  
c13dept135c CDCl3 /opt/topspin FAUS 46

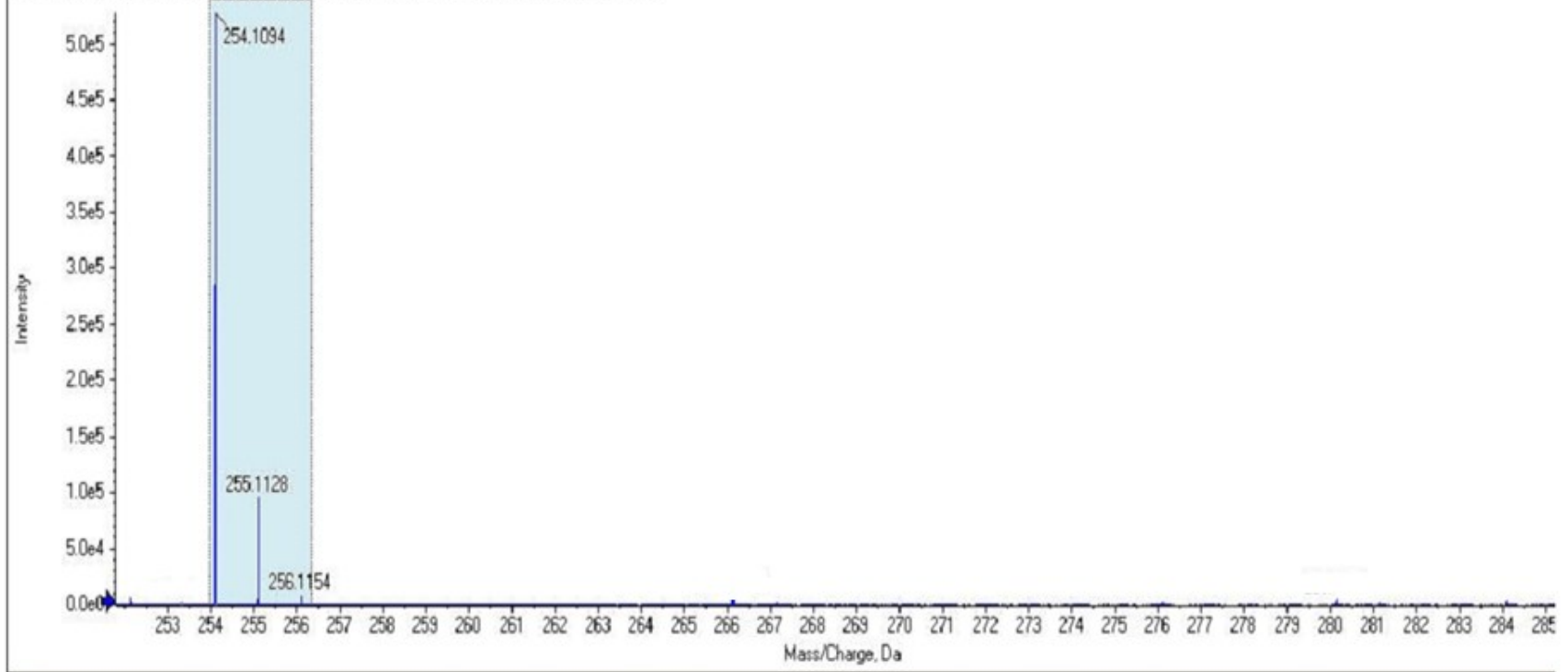
130.45  
130.33  
129.27  
128.75  
126.14  
116.71  
116.42

53.98





Spectrum from HB124.wiff (sample 1) - HB124, +TOF MS (100 - 1000) from 0.648 to 0.685 min

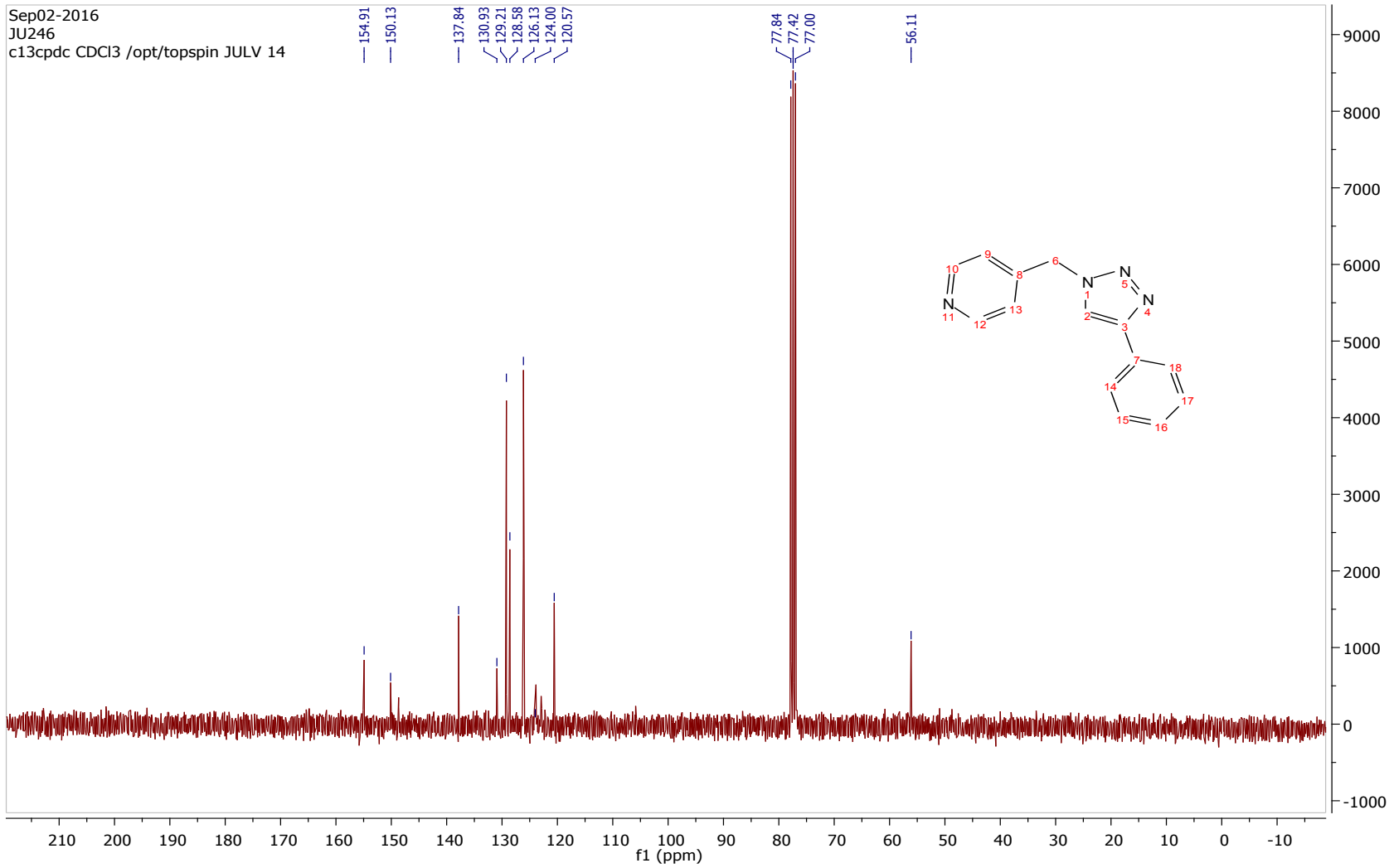




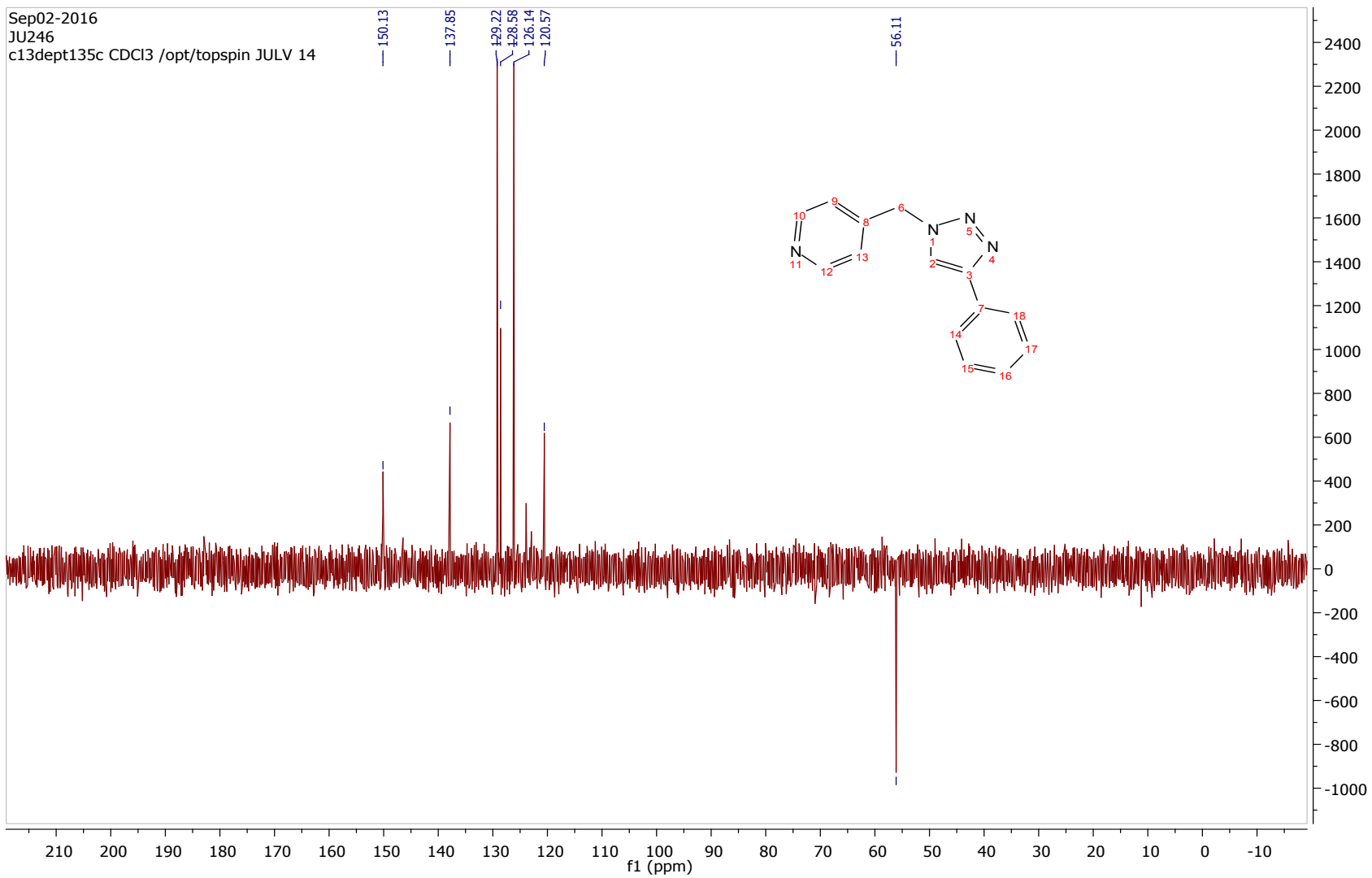
Sep02-2016  
JU246  
c13cpdc CDCl3 /opt/topspin JULV 14

154.91  
150.13  
137.84  
130.93  
129.21  
128.58  
126.13  
124.00  
120.57

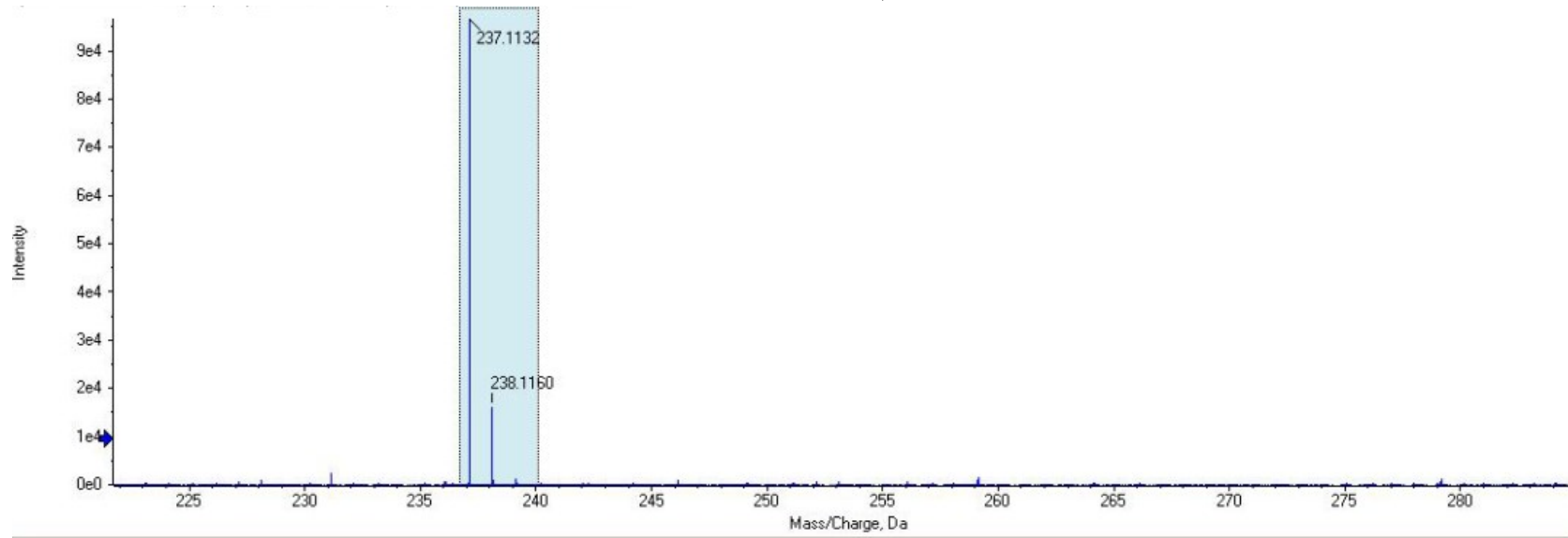
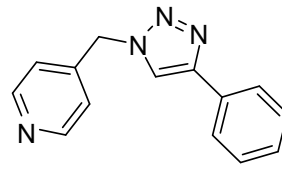
77.84  
77.42  
77.00  
56.11



Sep02-2016  
JU246  
c13dept135c CDCl3 /opt/topspin JULV 14

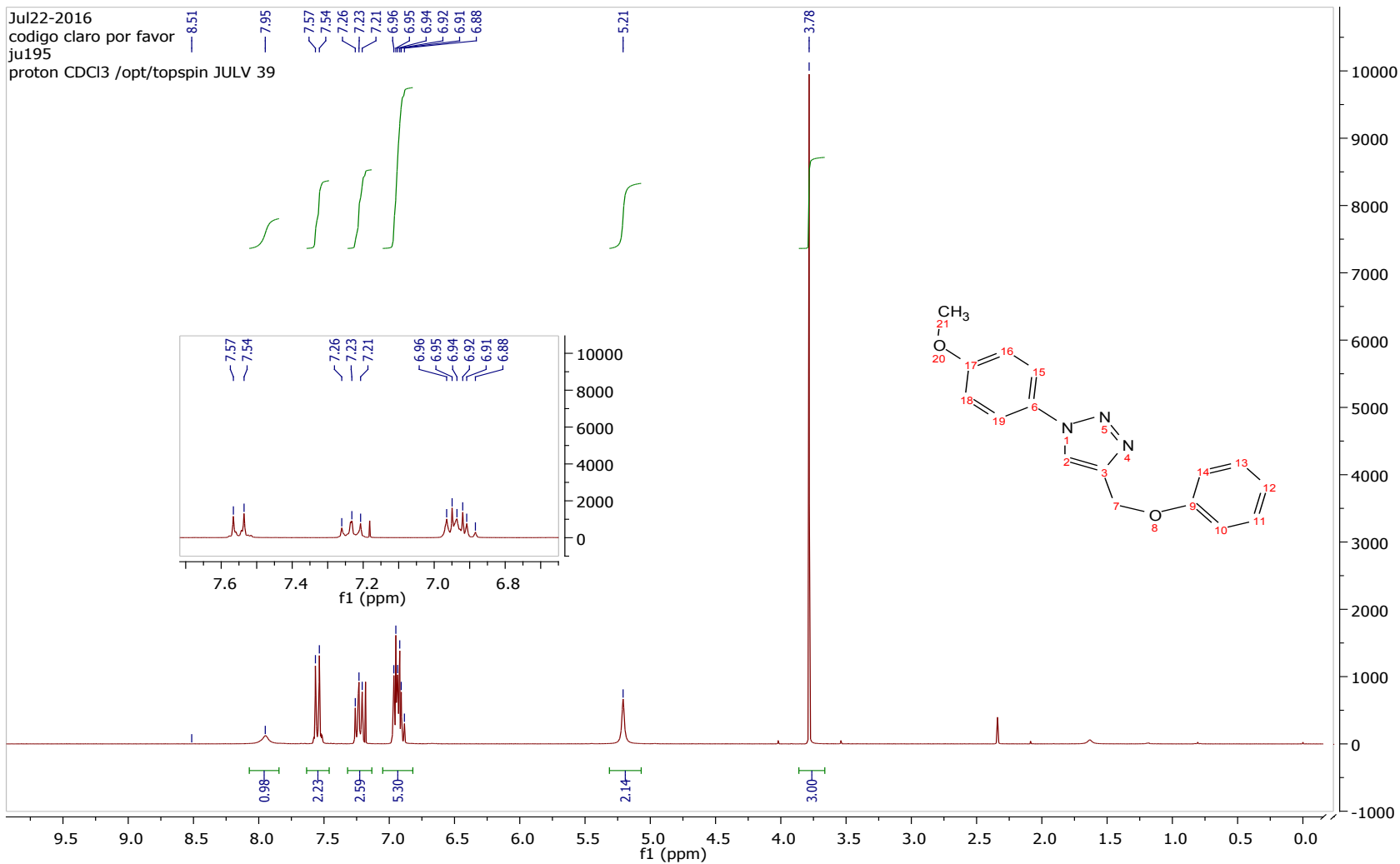




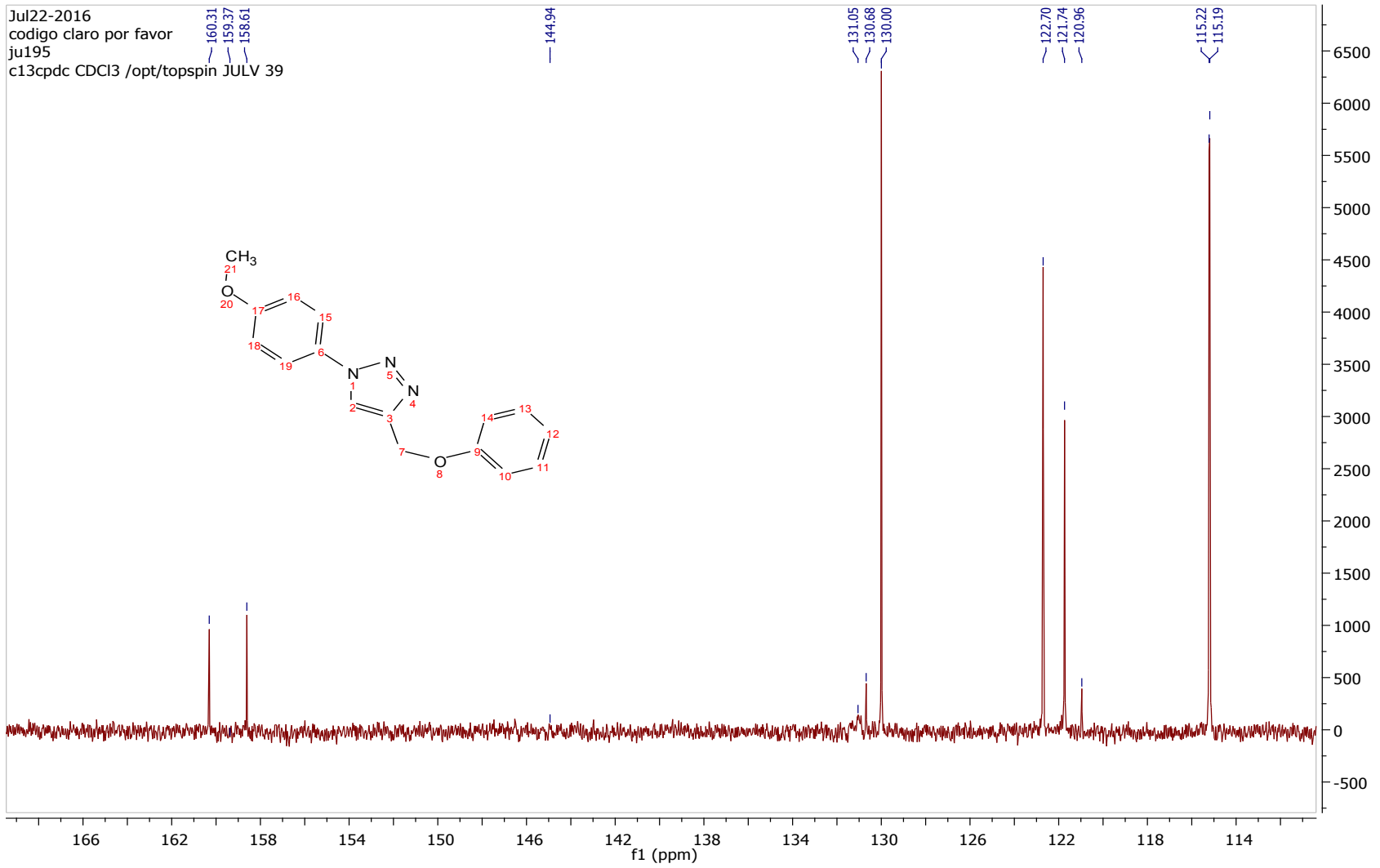
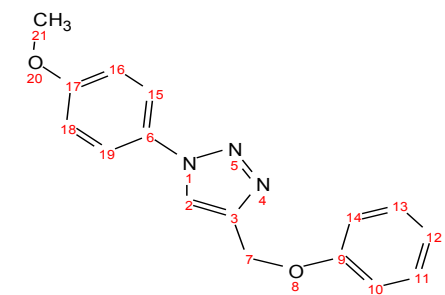


# 1-(4-methoxyphenyl)-4-(phenoxymethyl)-1H-1,2,3-triazole (3h)

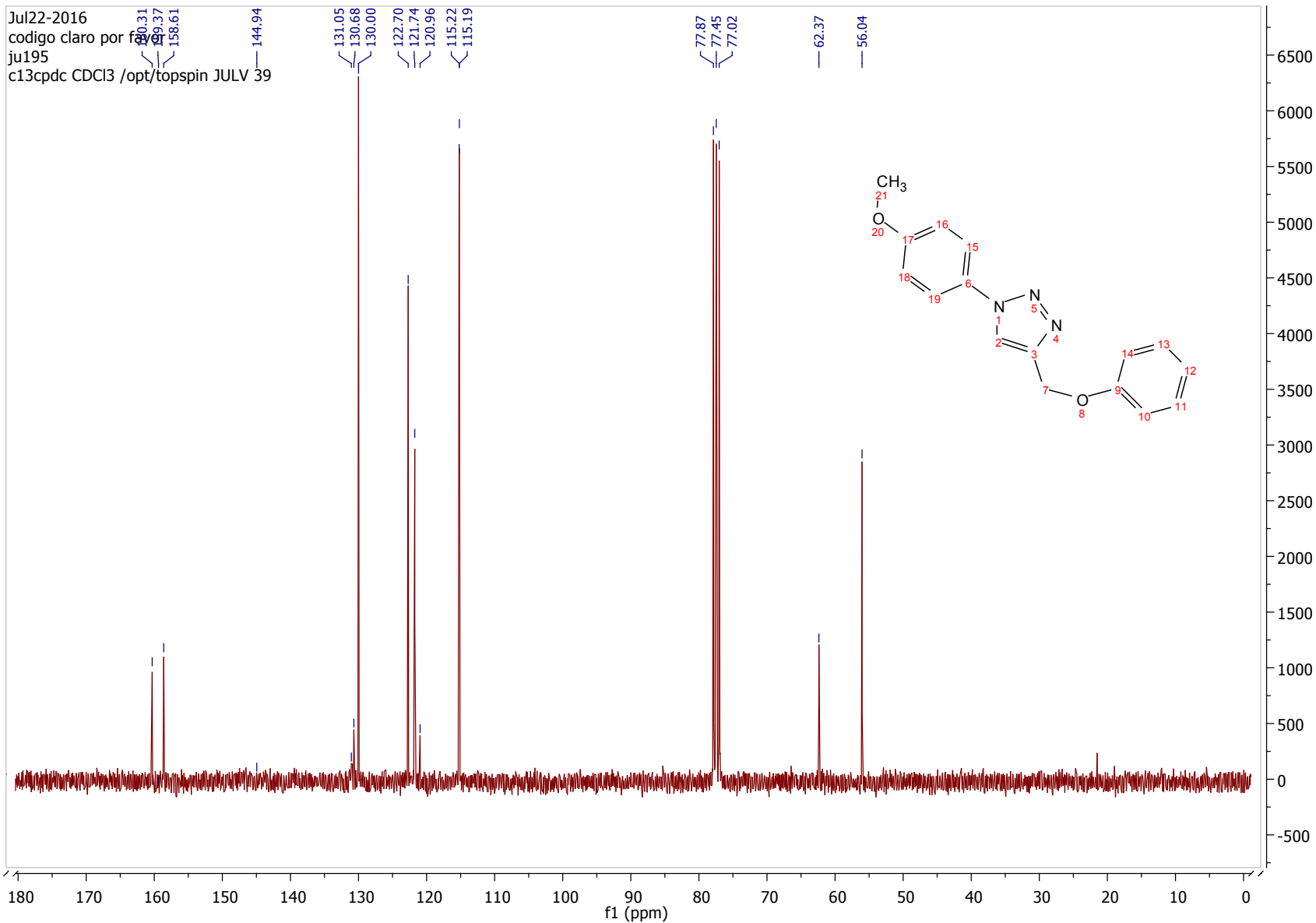
Jul22-2016  
codigo claro por favor  
ju195  
proton CDCl3 /opt/topspin JULV 39

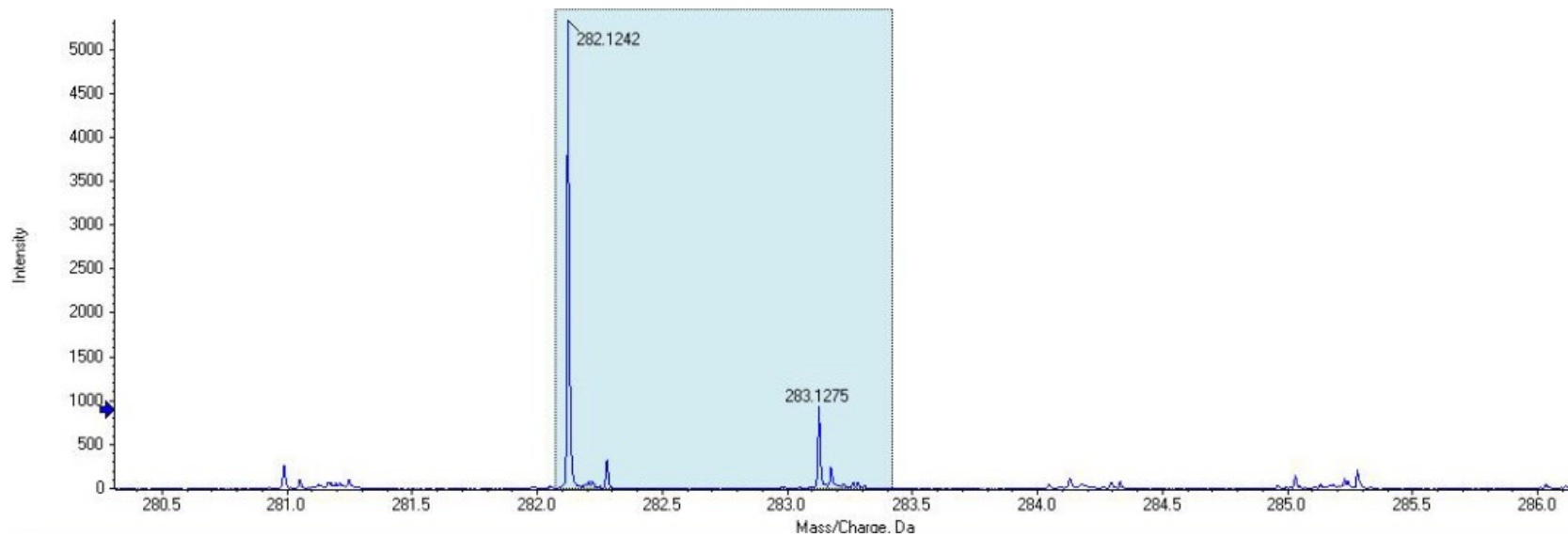
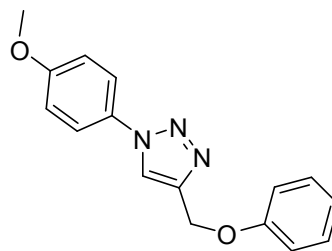


Jul22-2016  
codigo claro por favor  
ju195  
c13cpdc CDCl3 /opt/topspin JULV 39



Jul22-2016  
codigo claro por raver  
ju195  
c13cpdc CDCI3 /opt/topspin JULV 39





**1-(4-methoxyphenyl)-4-phenyl-1H-1,2,3-triazole (3i)**

