CHEMISTRY
A European Journal

Supporting Information

α-Amino Acid-Isosteric α-Amino Tetrazoles

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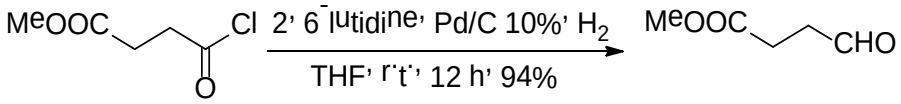
Supporting Information

Contents

1. Experimental Procedure and Characterization of Uncommercially Avaiable Starting Materials

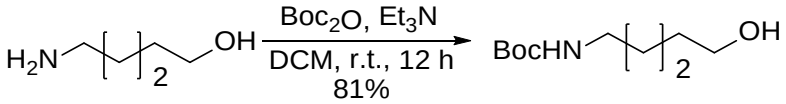
Methyl 4-oxobutanoate (10)



9 **10**

Methyl 4-chloro-4oxobutyrate (**9**) (4.2 ml, 33.2 mmol) was dissolved in THF (82 ml) and was degassed with N_2 for 5 min. Then 2, 6-lutidine (3.9 ml, 33.5 mmol) and 10% palladium on carbon (350 mg) were added. The reaction mixture stirred for overnight under H_2. The reaction mixture was filtered through a Celite pad. The filtrate was concentrated under reduced pressure. The product was yellow liquid (3.2 g, 94%). It was used directly in the next step without further purification.

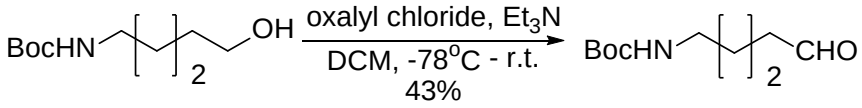
tert-Butyl (5-hydroxypentyl)carbamate (12)



11 **12**

5-Aminopentan-1-ol (**11**) (2 g, 19 mmol) was dissolved in 15 ml CH_2Cl_2 in a 100 ml round-bottomed flask equipped with a magnetic stirring egg and a pressure equalizing addition funnel and was cooled down to 0°C under ice and water bath. Di-*tert*-butyl dicarbonate (4.6 g, 21 mmol) in CH_2Cl_2 (15 ml) was added dropwise over 30 min. After the addition, the ice and water bath was removed. The reaction mixture continued to stir for overnight at room temperature. The reaction mixture was washed with saturated $NaHCO_3$ (15 ml), was dried with brine (25 ml × 2) and dried over $MgSO_4$, filtered. The filtrate was concentrated under the reduced pressure to give the product as an light yellow oil (3.17 g, 81%).

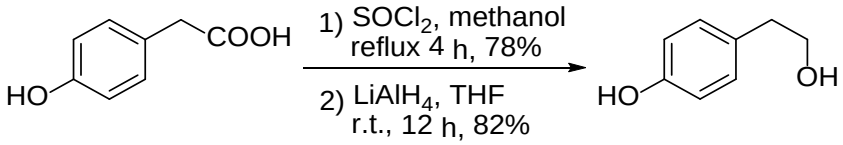
***tert*-Butyl (5-oxopentyl)carbamate (13)**



12 **13**

Oxalyl chloride (1 ml, 12 mmol) was dissolved in CH_2Cl_2 in a 250 ml round-bottomed flask. Then it was cooled down to -78°C. DMSO (1.5 ml) in CH_2Cl_2 was added dropwise. The reaction mixture reacted for 15 min at -78°C. Then *tert*-butyl (5-hydroxypentyl)carbamate (**12**) (3 g, 15 mmol) in 30 ml CH_2Cl_2 and was added dropwise. After the addition, the reaction mixture stirred for 25 min at -78°C. The cooling bath was removed, the reaction mixture was warmed to room temperature. Then it was poured into ice and water mixture, extracted with CH_2Cl_2 (50 ml × 2). The organic layer was separated and was washed with water (25 ml × 2), dried with brine (25 ml × 2), dried over $MgSO_4$, filtered. The filtration was concentrated under the reduced pressure to give the crude product as a yellow oil. It was purified using combiflash machine to give the product as a white solid (0.86 g, 43%).

4-(2-Hydroxyethyl)phenol (17)

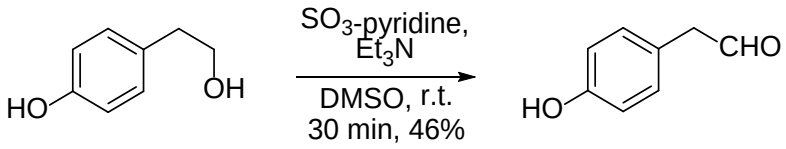


16 **17**

2-(4-Hydroxyphenyl)acetic acid (**16**) (1.5 g, 10 mmol) was dissolved in methanol (20 ml) and was cooled down to 0°C under ice and water bath. A few drops of $SOCl_2$ was added. Then the cooling bath was removed and refluxed for overnight. The solvent was removed under reduced pressure. It was used directly in the next step without further purification. Lithium aluminum hydride (2.2 g, 60 mmol) was suspended in a round-bottomed flask containing THF (90 ml) under ice and water bath. Methyl 2-(4-hydroxyphenyl)acetate (3.3 g, 20 mmol) added drop wise. The reaction mixture stirred for overnight at room temperature. Then it was quenched with 20% sodium hydroxide (10 ml). The reaction mixture was concentrated under reduced pressure. The residue was extracted with EtOAc (50ml × 3), separated. The organic phase was washed with

brine (50 ml × 2), dried with $MgSO_4$, filtered, concentrated. It was purified using combiflash machine to obtain the product as a yellowish solid (2.3 g, 82%).

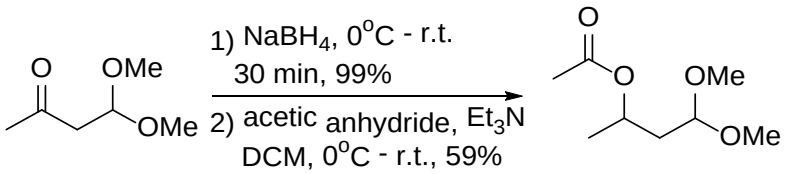
2-(4-Hydroxyphenyl)acetaldehyde (18)



17 **18**

4-(2-Hydroxyethyl)phenol (**17**) (0.7 g, 5.2 mmol) was dissolved in DMSO (6.9 ml) containing triethylamine (1.4 ml, 10 mmol). Then SO_3·Pyridine complex in DMSO (5 ml) was added dropwise very slowly. Then the reaction mixture stirred for 1 h at room temperature. Then the reaction was quenched with cold water (50 ml), the reaction mixture continued to stir for 5 min at room temperature. Then the reaction mixture was extracted with CH_2Cl_2 (50 ml × 3). The organic phase was washed with water, dried with brine (25 ml × 2), dried over $MgSO_4$, filtered, concentrated to obtain the product as a yellow oil (295 mg, 46%). It was used directly in the next step without further purification.

1,1-Dimethoxypropan-2-ol (20)

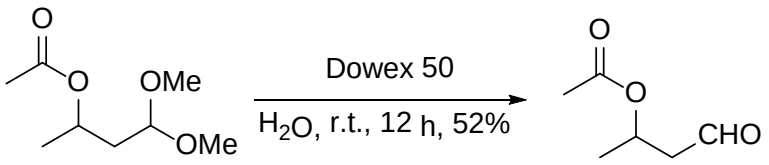


19 **20**

1, 1-Dimethoxypropan-2-one (**19**) (12 ml, 100 mmol) was dissolved in a round-bottomed flask containing a mixture of methanol/THF = 1/1 (100 ml). The mixture was cooled down to 0°C under ice and water bath. Then sodium borohydride (3.8 g, 100 mmol) was added. The reaction mixture stirred for 30 min at room temperature. Then the reaction mixture was neutralized with 1N HCl to pH = 6. Then the reaction mixture was extracted with ether (100 ml × 3), the organic phase was separated and washed with brine (100 ml × 2), dried with $MgSO_4$, filtered. The

solvent was removed under reduced pressure to obtain the product as a light yellow oil with a quantitative yield. 1,1-dimethoxypropan-2-ol (0.8 g, 6.9 mmol) was dissolved in a round-bottomed flask containing CH_2Cl_2 (3 ml). Then triethyl amine (1.9 ml, 14 mmol) and DMAP (39 mg, 0.32 mmol) were added. The reaction mixture was cooled down to 0°C under ice and water bath. Acetic anhydride (0.7 ml, 7.5 mmol) in CH_2Cl_2 (2 ml) was added drop wise. It stirred for 2h. Then the reaction mixture was extracted with CH_2Cl_2. The organic phase was separated and washed with water (25 ml × 2), 0.1N HCl (10 ml × 2), was dried with brine (25 ml × 2), dried over $MgSO_4$, filtered, was purified using combiflash machine to obtain the colorless solid as a product (735 mg, 59%).

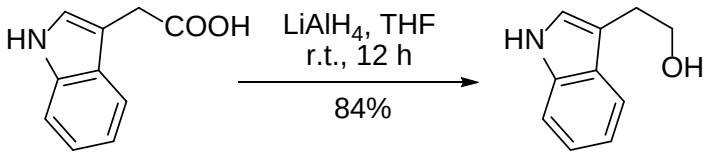
4-Oxopropan-2-yl acetate (21)



20 **21**

1,1-Dimethoxypropan-2-yl acetate (**20**) (0.96 g, 5.9 mmol) was dissolved in a round-bottomed flask containing water (5 ml). Then Dowex 50 (544 mg) were added. The reaction mixture stirred for overnight at room temperature. The reaction mixture was filtered and extracted with EtOAc (25 ml × 2), dried with brine (25 ml × 2), dried over $MgSO_4$, filtered, concentrated. The product was obtained as a colorless oil (354 mg, 52%).

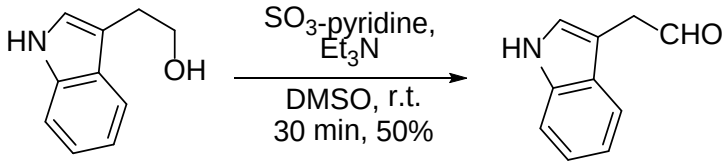
2-(1H-Indol-3-yl)ethanol (23)



22 **23**

Lithium aluminum hydride (1.6 g, 43 mmol) was suspended in a round-bottomed flask containing THF (90 ml) under ice and water bath. 2-(1H-indol-3-yl)acetic acid (**22**) (2.4 g, 13.8 mmol) added in portions. The reaction mixture stirred for overnight at room temperature. Then it was quenched with sodium hydroxide (20%). The reaction mixture was concentrated under reduced pressure. The residue was extracted with EtOAc (50 ml × 3), separated. The organic phase was washed with brine (25 ml × 2), dried with $MgSO_4$, filtered, concentrated. It was purified using combiflash machine to obtain the product as a grey solid (1.9 g, 84%).

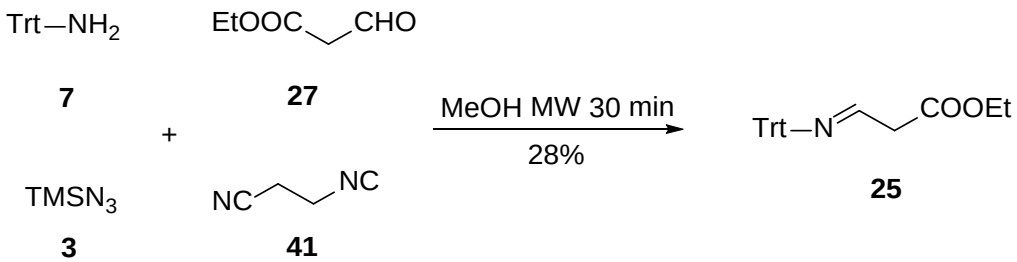
2-(1H-Indol-3-yl)acetaldehyde (24)



23 **24**

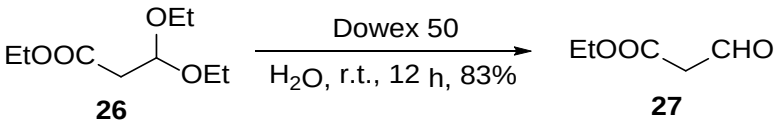
2-(1H-indol-3-yl)ethanol (**23**) (0.3 g, 2 mmol) was dissolved in DMSO (5 ml) containing triethylamine (1.4 ml, 10 mmol). Then SO_3·Pyridine complex (1 g) in DMSO (3 ml) was added dropwise very slowly. Then the reaction mixture stirred for 30 min at 0°C. Then the reaction was quenched with cold water (50 ml), the reaction mixture continued to stir for 5 min at room temperature. Then the reaction mixture was extracted with CH_2Cl_2 (50 ml × 4). The organic phase was washed with water (25 ml × 2), dried with brine (25 ml × 2), dried over $MgSO_4$, filtered, concentrated to obtain the product as a yellow oil (160 mg, 50%). It was used directly in the next step without further purification.

Ethyl 3-(tritylimino)propanoate (25)



Ethyl 3-oxopropanoate (116.2mg, 1 mmol) and tritylamine (260.1mg, 1 mmol) were suspended in MeOH (1 mL) in a sealed vial with a magnetic stirring bar. The reaction was heated at 100°C for 15 minutes using microwave irradiation. Then isocyanide (81.2mg, 1 mmol) and azidotrimethylsilane (135 µL, 1 mmol) were added into the reaction mixture and further heated at 100°C for 15 minutes using microwave irradiation. The solvent was removed under reduced pressure and the residue was purified using flash chromatography.

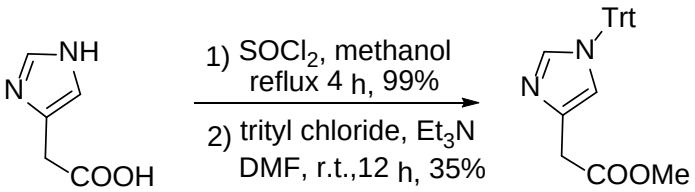
Ethyl 3-oxopropanoate (27)



26 **27**

Ethyl 3, 3-dietoxypropanoate (**26**) (390 µl, 2 mmol) was dissolved in a 50 ml round-bottomed flask. Then Dowex 50 was added. The reaction mixture stirred for 24 h at room temperature. The reaction mixture was filtered and the aqueous phase was extracted with CH_2Cl_2 for several times. The organic phases were combined and dried with brine (25 ml × 2), dried over $MgSO_4$, concentrated under the reduced pressure to give the product as a colorless liquid (194 mg, 83%).

Methyl 2-(1-trityl-1H-imidazol-4-yl)acetate (29)

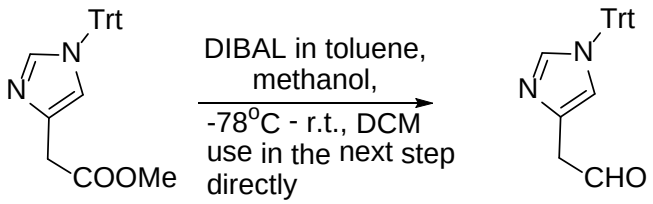


28 **29**

2-(1H-imidazol-4-yl)acetic acid (**28**) (0.8 g, 5 mmol) was dissolved in methanol (30 ml) and was cooled down to 0°C under ice and water bath. A few drops of thionyl chloride was added. Then the cooling bath was removed and refluxed for overnight. The solvent was removed under reduced pressure. It was used directly in the next step without further purification. Methyl 2-(1H-imidazol-4-yl)acetate hydrochloride (1.8 g, 10 mmol) was dissolved in DMF (8.4 ml) and triethylamine (4 ml, 29 mmol) was added. The reaction mixture stirred for 1h at room

temperature. Then trityl chloride (2.8 g, 10 mmol) was added. The reaction mixture continued to stir for overnight at room temperature. The solvent was coevaporated with hexane for several times. Then the reside was purified using combiflash machine to give the product as a white solid (2.5 g, 65%).

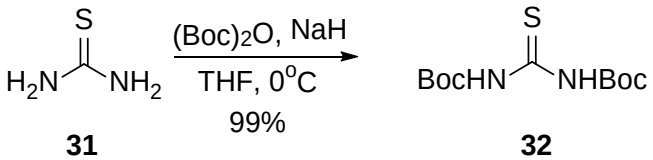
2-(1-Trityl-1H-imidazol-4-yl)acetaldehyde (30)



29 **30**

Methyl 2-(1-trityl-1H-imidazol-4-yl)acetate (**29**) (0.4 g, 1mmol) was dissolved in CH_2Cl_2 and was cooled down to -78°C. DIBAL (1.7 M in toluene, 0.6 ml) was added drop wise. During the addition, the temperature was kept below -78°C. After the addtion, the reaction mixture stirred for 1.5 h, 0.3 ml DIBAL was added. After stirring 3 h at -78°C, 0.3 ml DIBAL was added again. 10 min later, 1.5 ml methanol was added drop wise to quench the reaction. Then the reaction mixture was warmed up slowly to room temperature. The reaction mixture was filtered and concentrated under the reduced pressure. The residue was used in the next step directly without further purification.

Di-*tert*-butyl sulfinyldicarbamate (32)

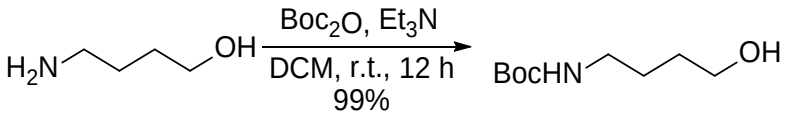


31 **32**

To a stirred colorless solution of thiourea (**30**) (0.57 g, 7.5 mmol) in THF (150 ml) under N_2 at 0°C was added heptane washed NaH (1.4 g, 1.35 mmol). After 5 min, the 0°C bath was removed

and the reaction mixture was allowed to stir at room temperature for 10 min. The reaction mixture was cooled to 0°C and di-*tert*-butyl dicarbonate (3.6 g, 16.5 mmol) was added neat. After 30 min, the 0°C bath was removed. A slurry formed within 30 min. The reaction mixture was stirred for another 2 h at room temperature and was then quenched with an aqueous solution of saturated $NaHCO_3$(10 ml). The reaction mixture was poured into water (150 ml) and extracted with ethyl acetate (70 ml × 3). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced vaccum, 2.03 g (99% as an off-white solid which was used without further purification.

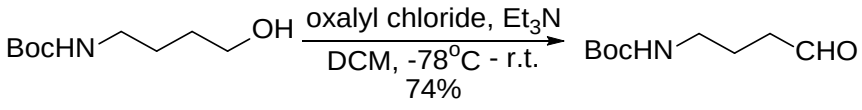
***tert*-Butyl (4-hydroxybutyl)carbamate (34)**



33 **34**

4-Aminobutan-1-ol (**32**) (900 mg, 10 mmol) was dissolved in THF in a 100 ml round-bottomed flask equipped with a magnetic stirring egg and a pressure equalizing addition funnel and was cooled down to 0°C under ice and water bath. Di-*tert*-butyl dicarbonate (2.4 g, 10 mmol) in THF was added drop wise over 30 min. After the addition, the ice and water bath was removed. The reaction mixture continued to stir for overnight at room temperature. The reaction mixture was washed with saturated $NaHCO_3$ (50 ml), was dried with brine (50 ml × 2) and dried over $MgSO_4$, filtered. The filtrate was concentrated under the reduced pressure to give the product as a light yellow oil (3.8 g, 99%).

***tert*-Butyl (4-oxobutyl)carbamate (35)**



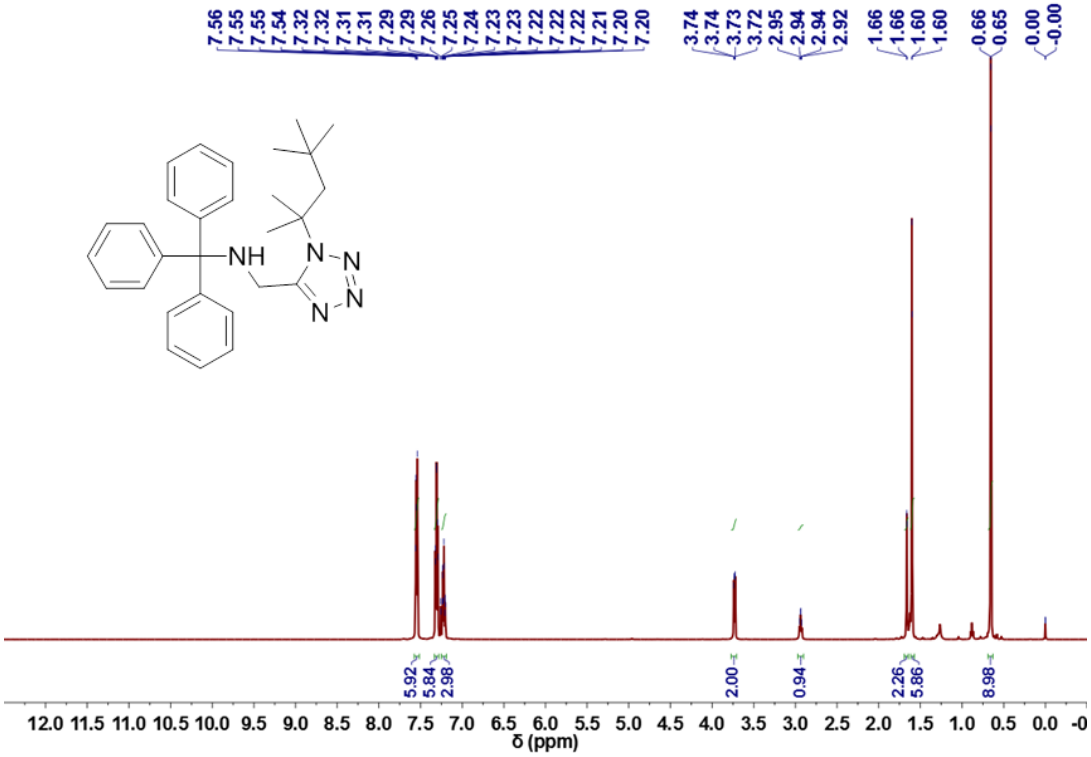
34 **35**

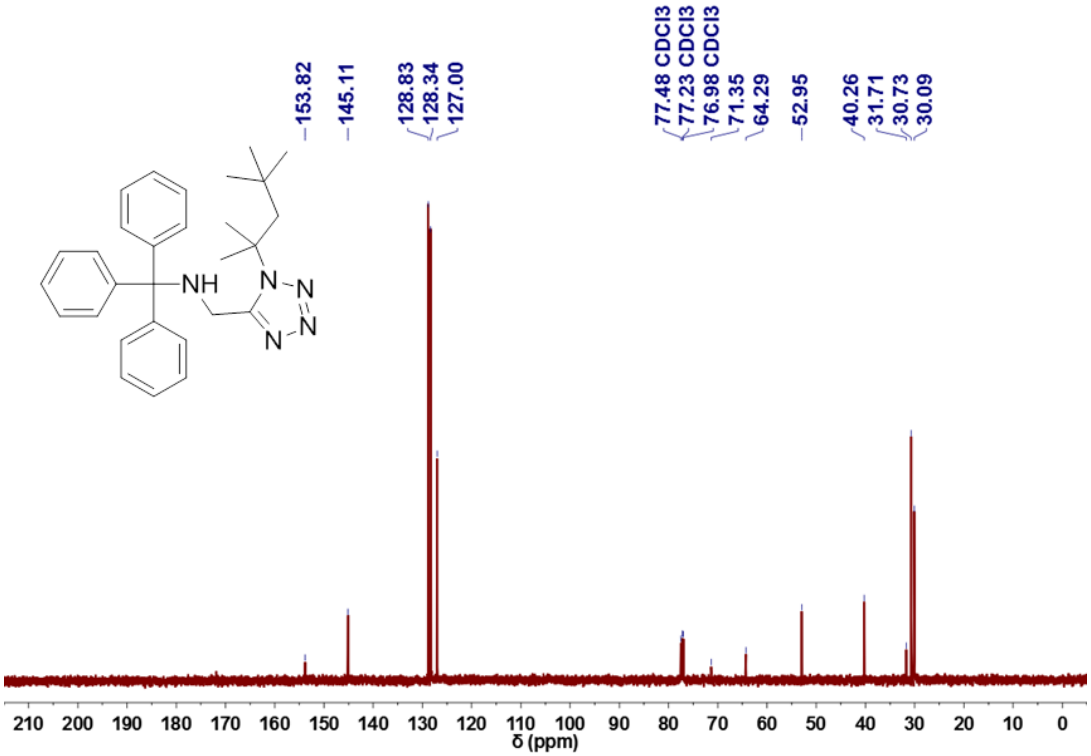
Oxalyl chloride (450 µl, 5 mmol) was dissolved in CH_2Cl_2 in a 3-necked round-bottomed flask. Then it was cooled down to -78°C. DMSO (0.72 ml) in CH_2Cl_2 was added dropwise. The

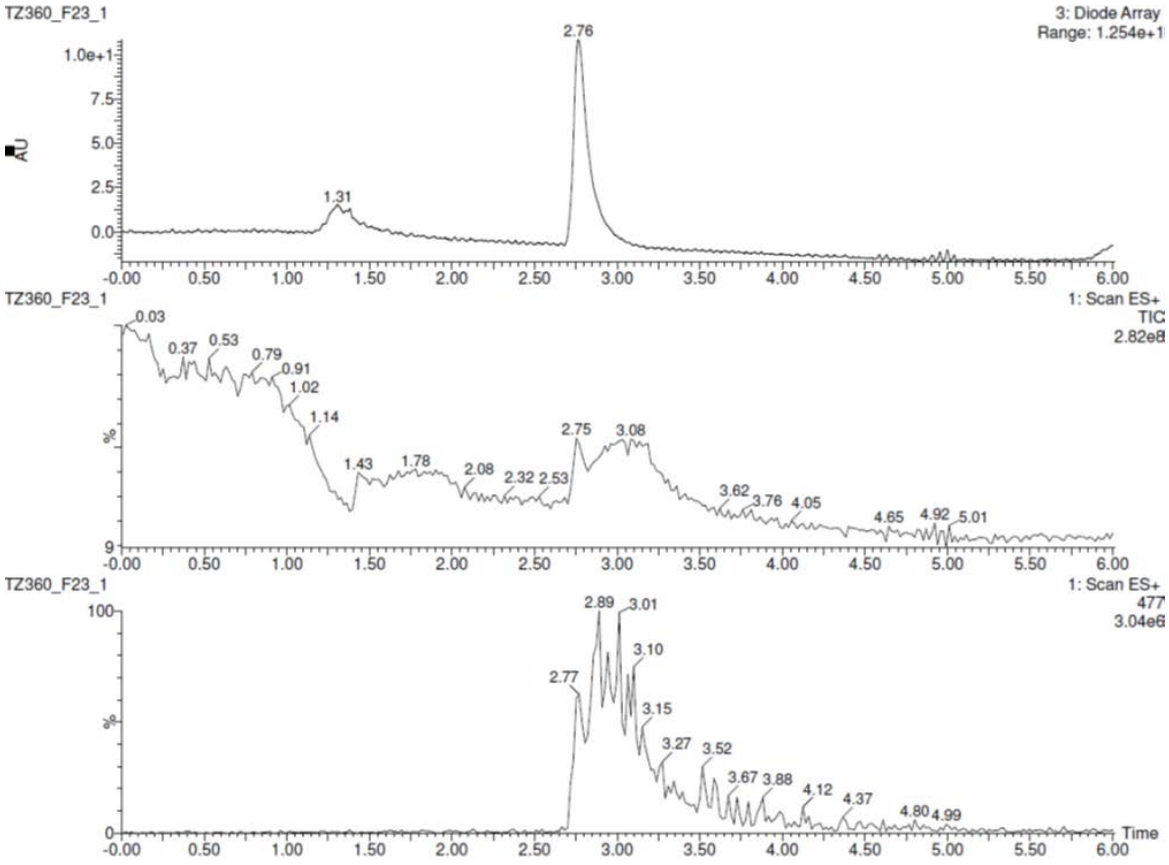
reaction mixture reacted for 15 min at -78^{o}C. Then *tert*-butyl (5-hydroxypentyl)carbamate (**33**) (0.9 g, 5 mmol) in CH_2Cl_2 and was added dropwise. After the addition, the reaction mixture stirred for 25 min at -78^{o}C. The cooling bath was removed, the reaction mixture was warmed to room temperature. Then it was poured into ice and water mixture, extracted with CH_2Cl_2 (30 ml × 3). The organic layer was separated and was washed with water (30 ml × 2), dried with brine, dried over $MgSO_4$, filtered. The filtration was concentrated under the reduced pressure to give the product as a yellow oil. It was purified using combiflash machine to give the product (879 mg, 74%).

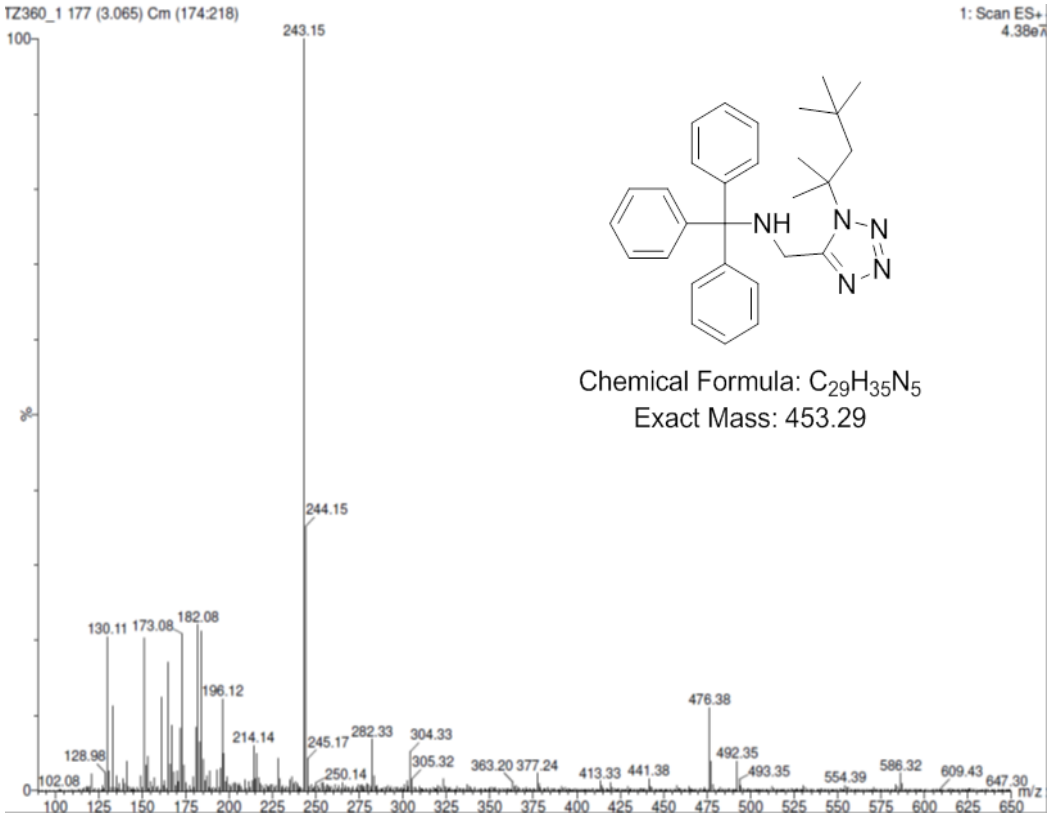
2. Spectra of Products (^{1}H NMR, ^{13}C NMR Spectra and MS)

1,1,1-Triphenyl-N-((1-(2,4,4-trimethylpentan-2-yl)-1H-tetrazol-5-yl)methyl)methanamine (5a)



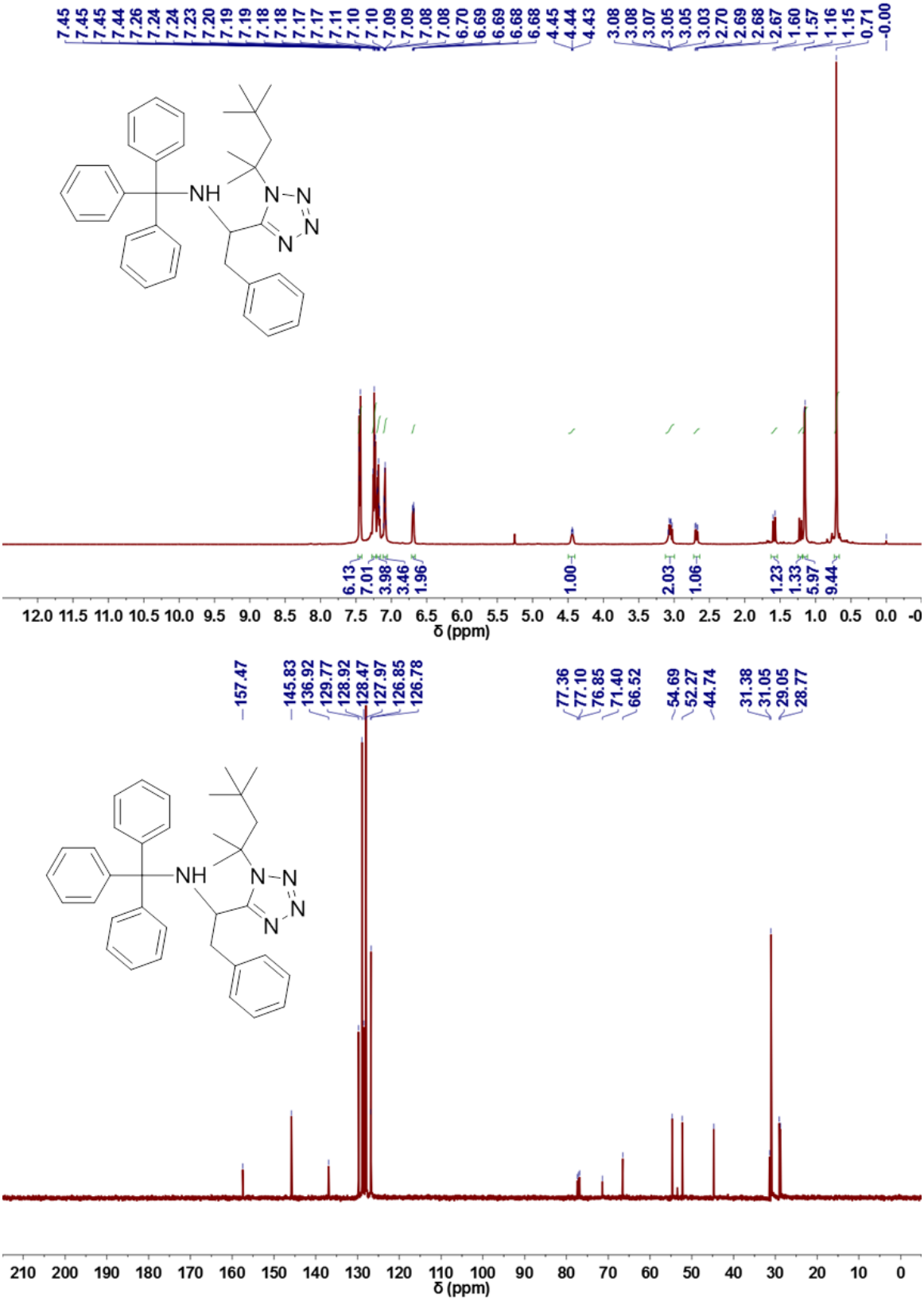


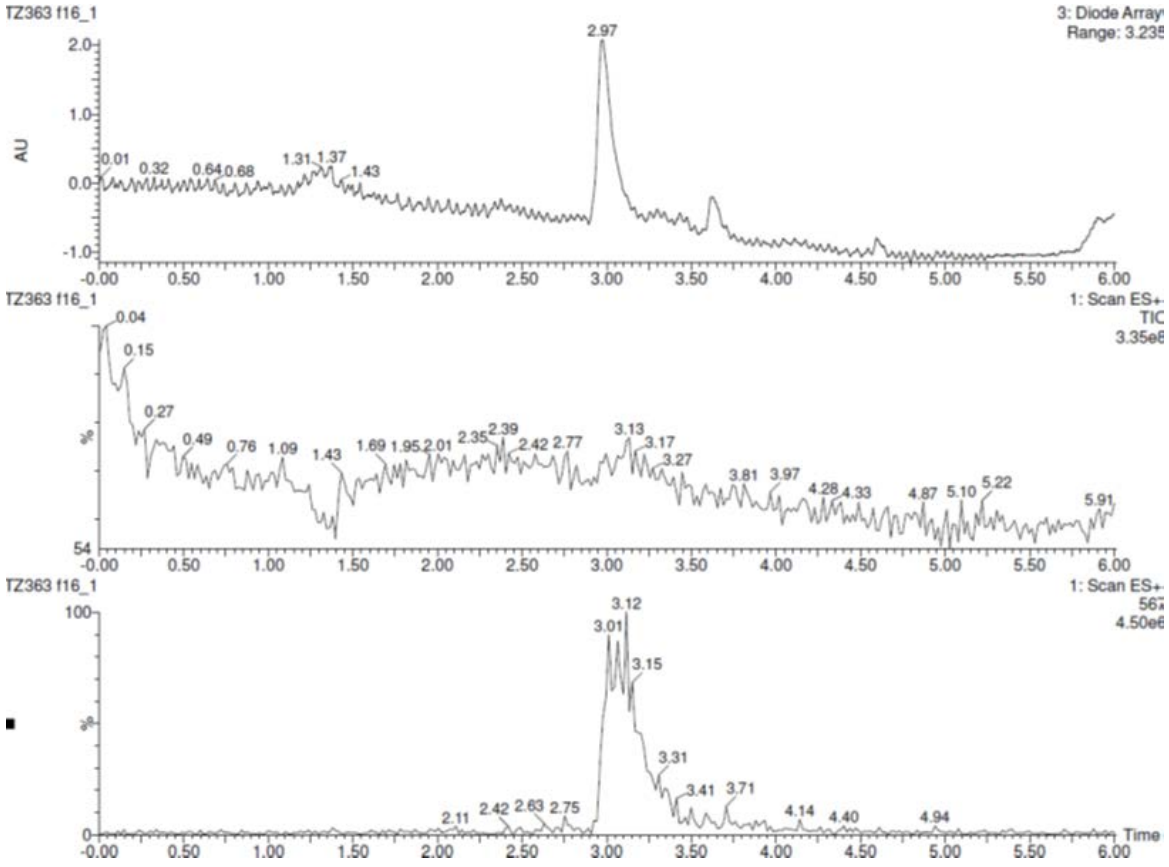


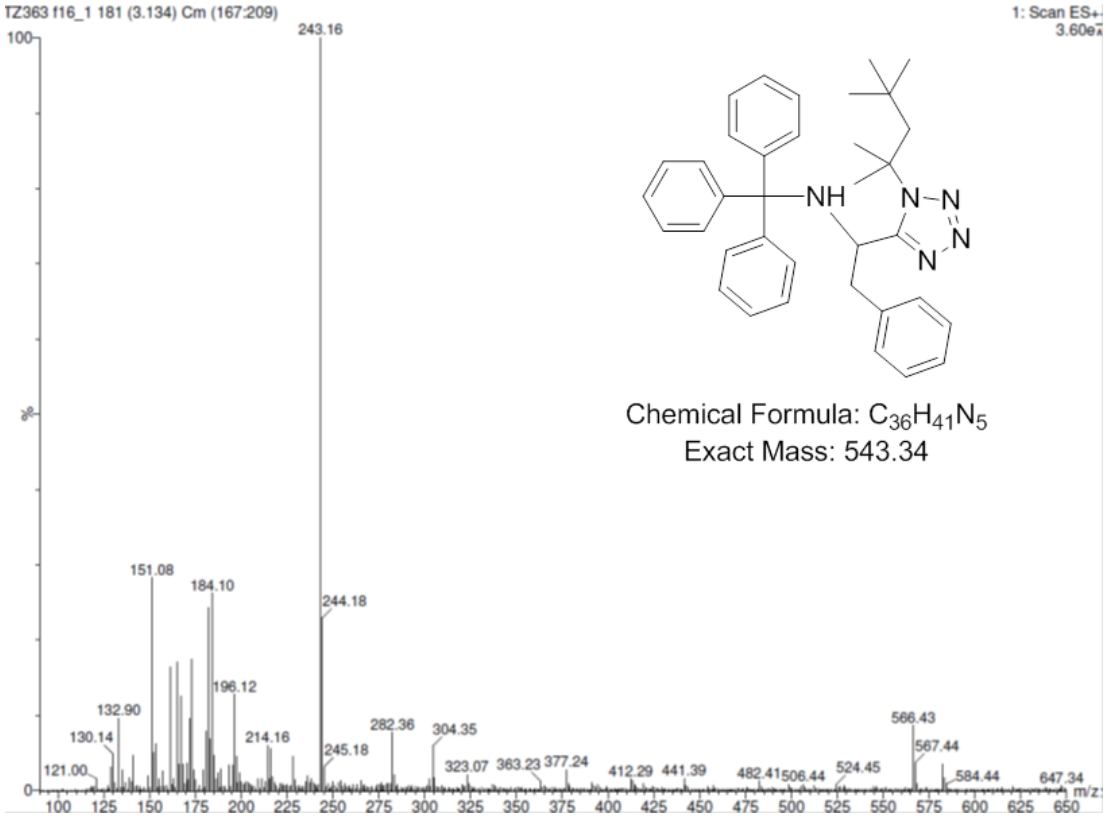


Chemical Formula: $C_{29}H_{35}N_5$
Exact Mass: 453.29

1-(1-(2,4,4-Trimethylpentan-2-yl)-1H-tetrazol-5-yl)-N-tritylethanamine (5b)







Chemical Formula: $C_{36}H_{41}N_5$
Exact Mass: 543.34

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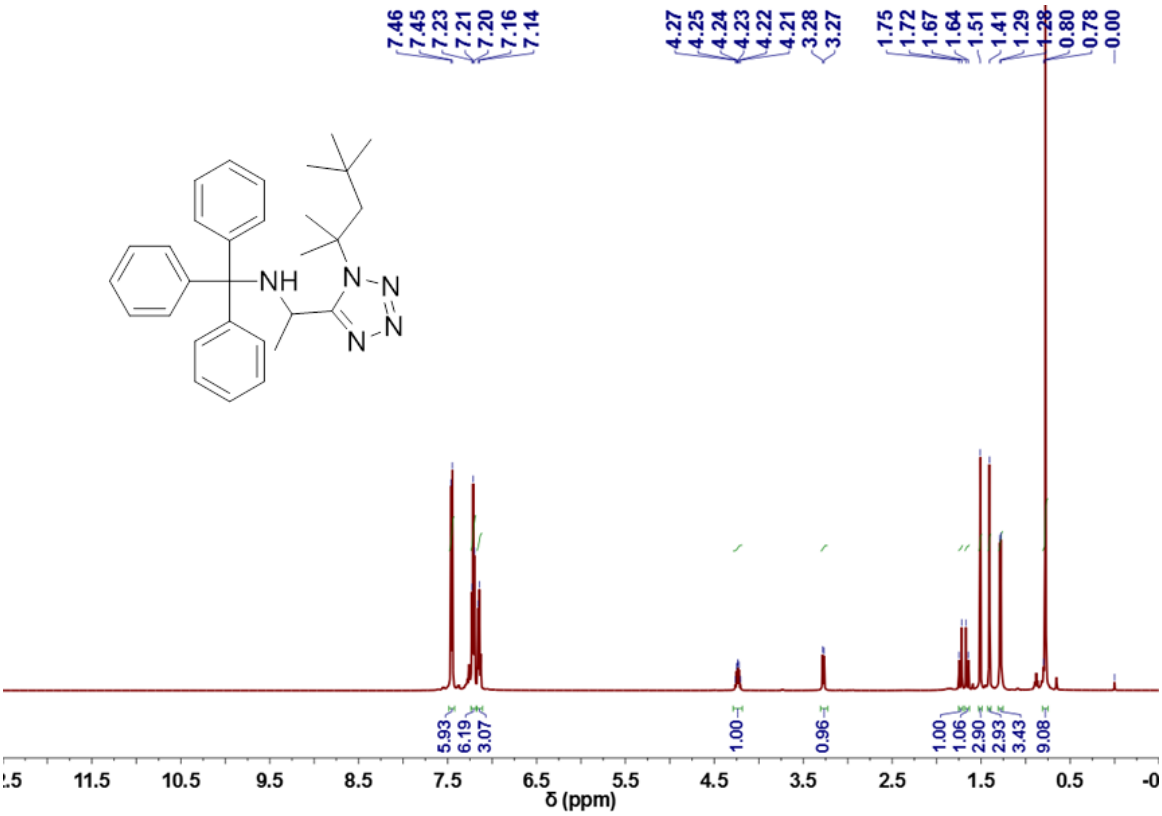

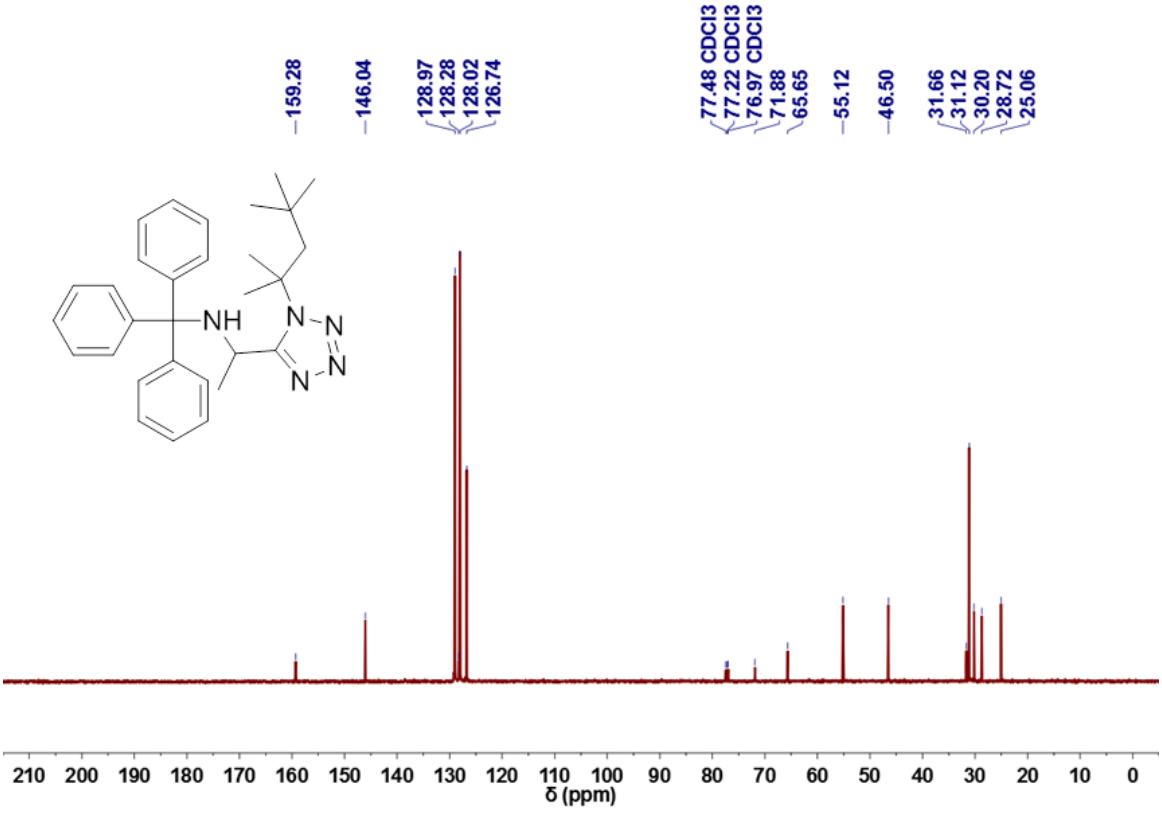

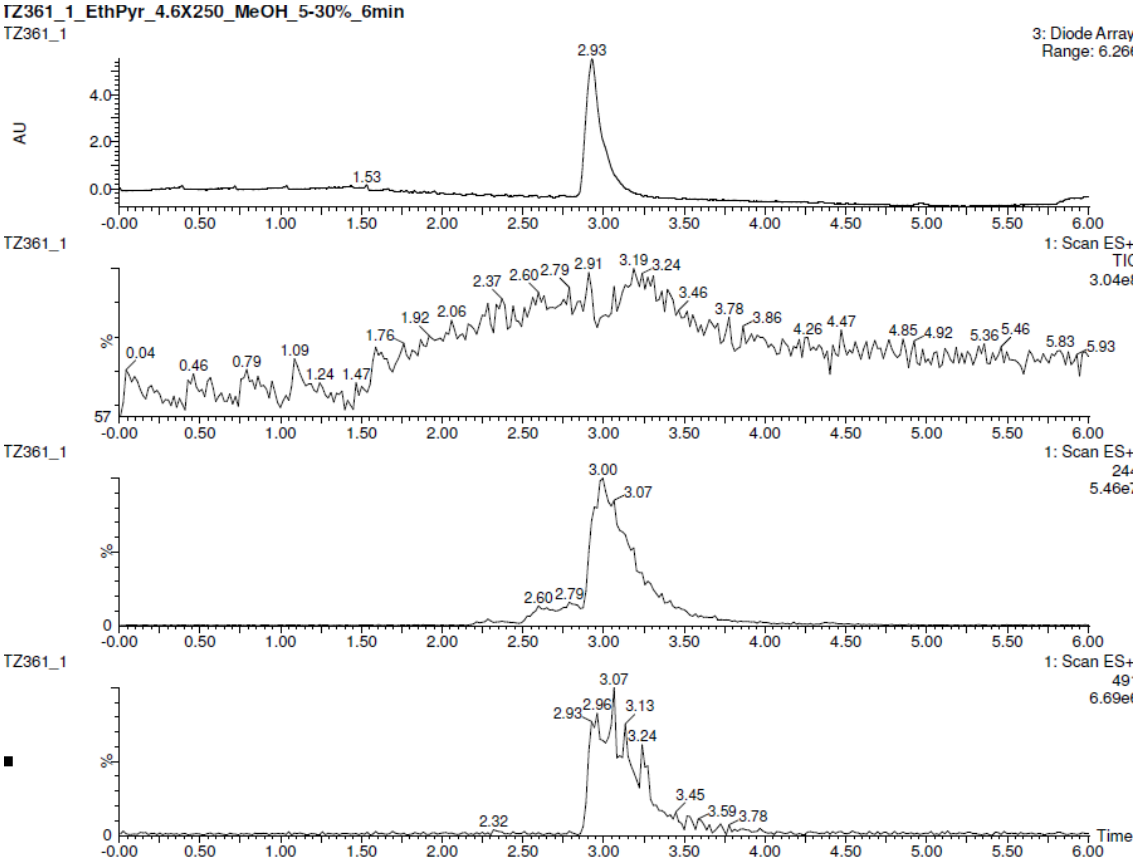
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2.06
2.37
2.60
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5.46
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5.93
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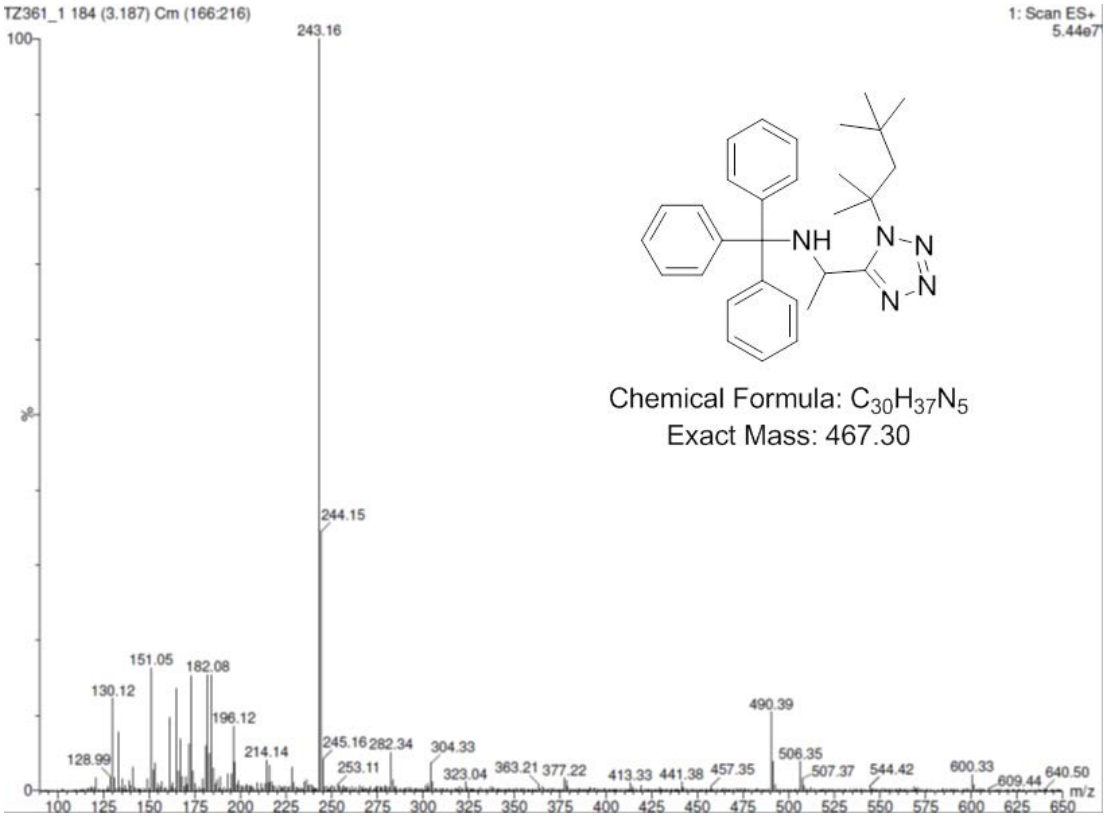
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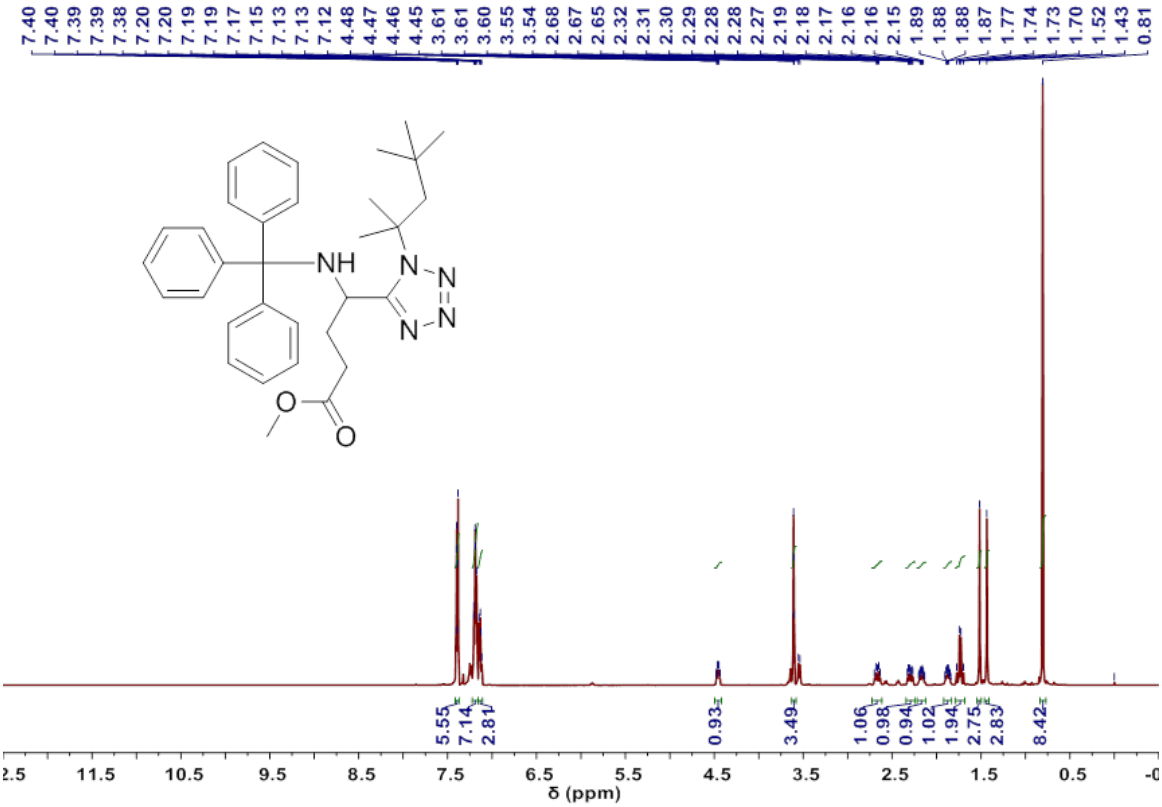
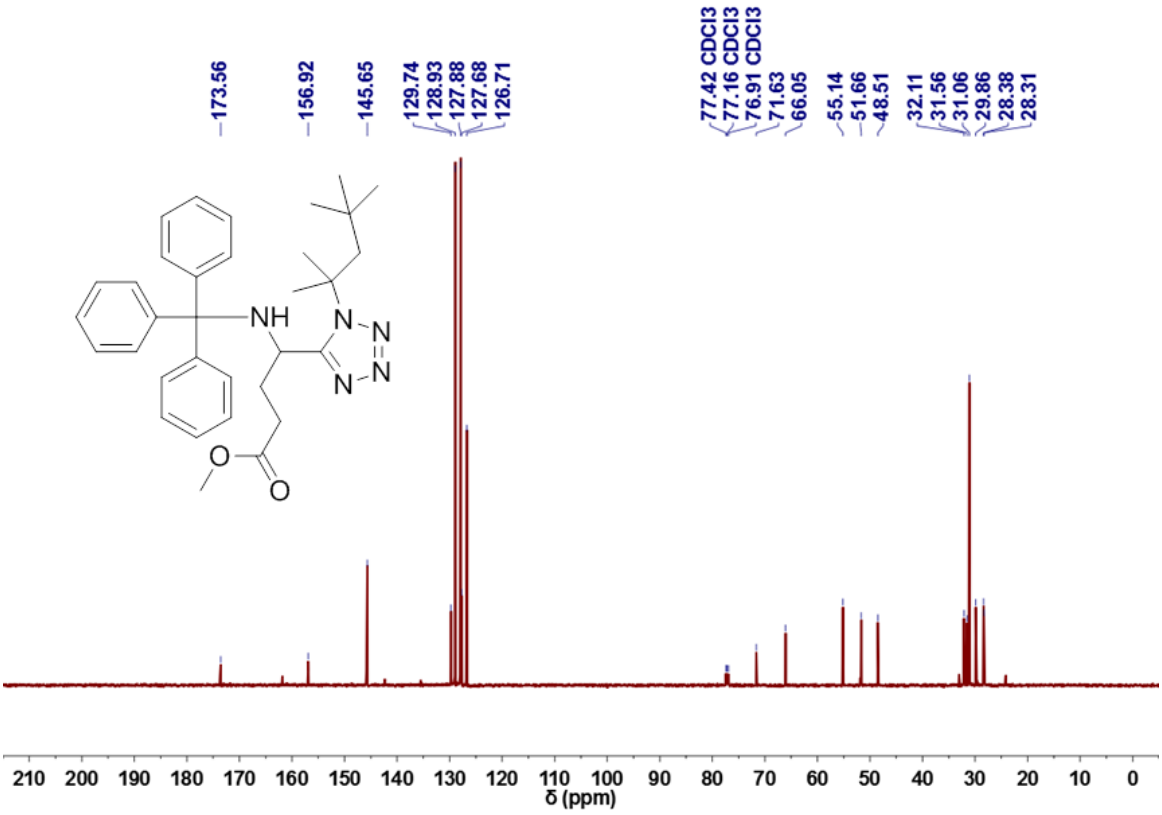
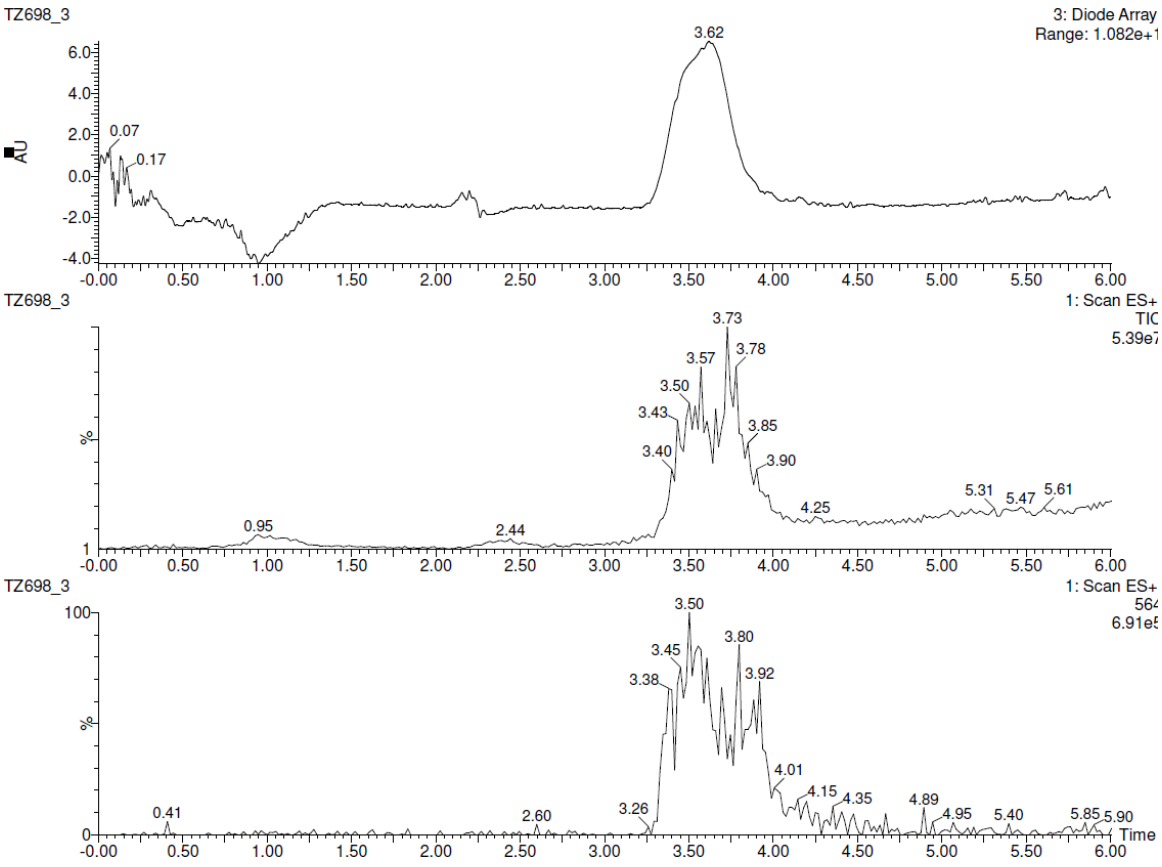
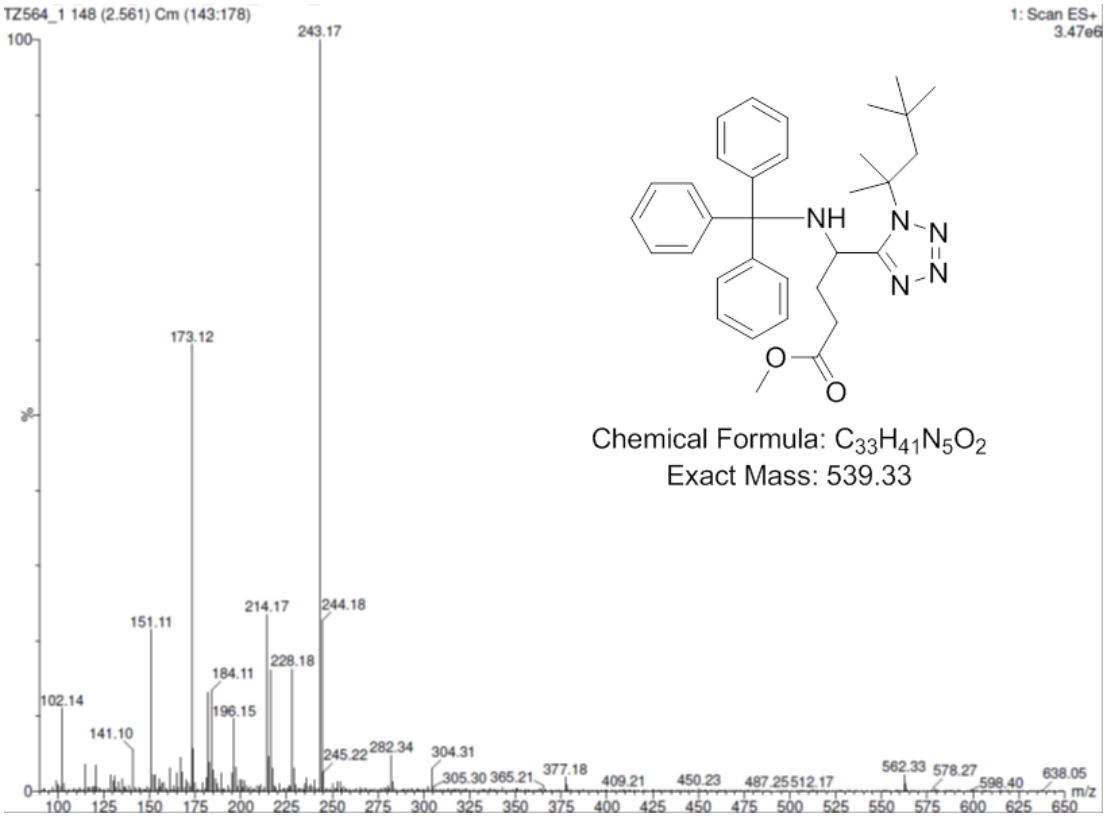
N
N
Chemical Formula: C30H37N5
Exact Mass: 467.30

Methyl 4-(1-(2,4,4-trimethylpentan-2-yl)-1H-tetrazol-5-yl)-4-(tritylamino)butanoate (5d)





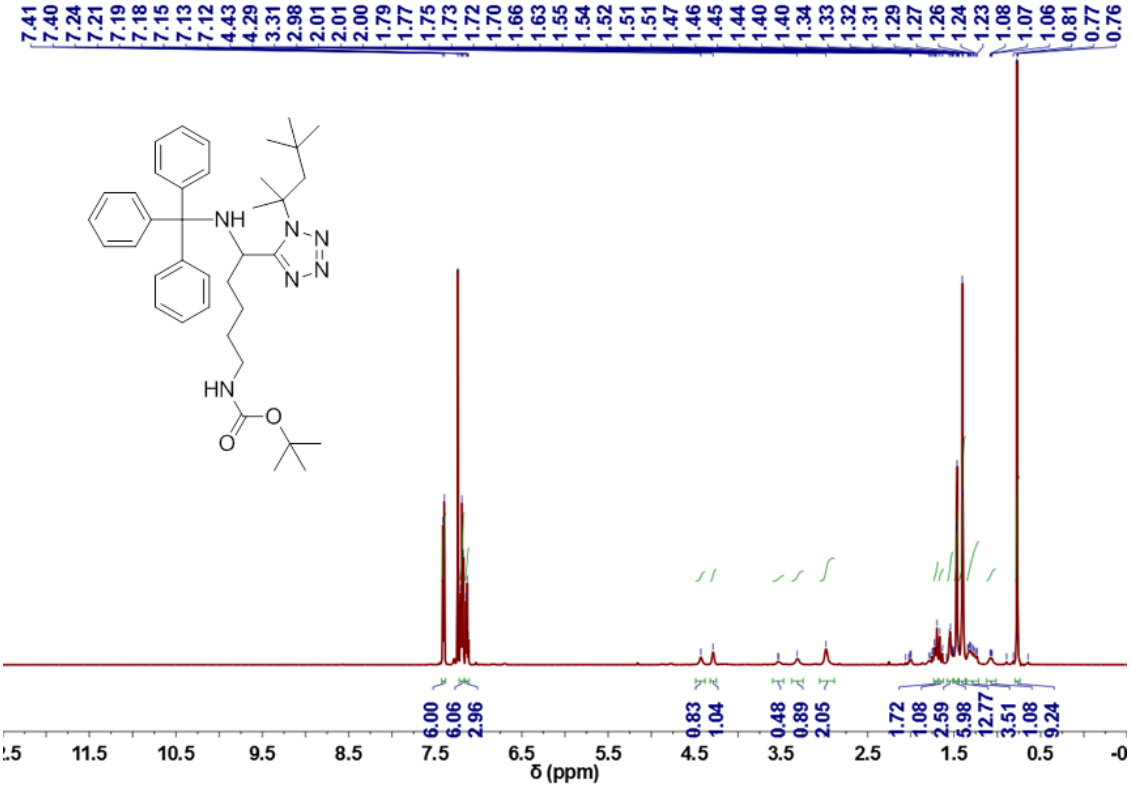


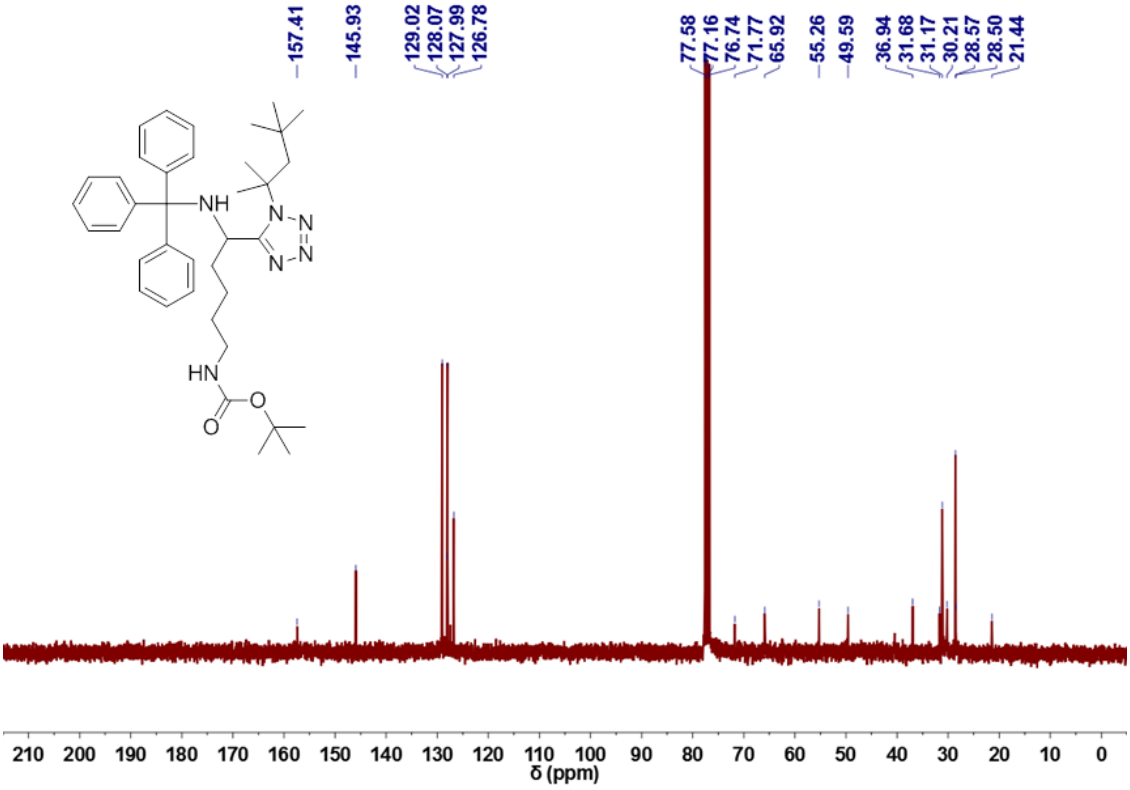


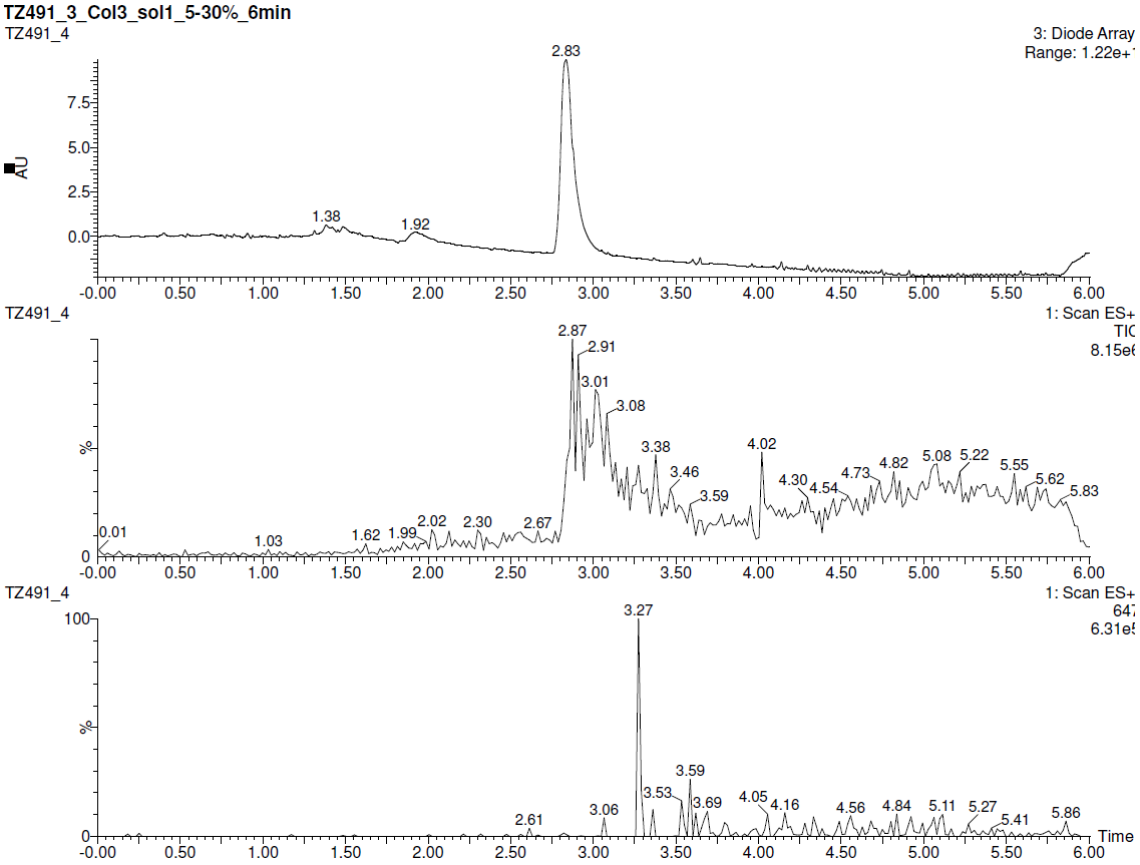
Chemical Formula: $C_{33}H_{41}N_5O_2$

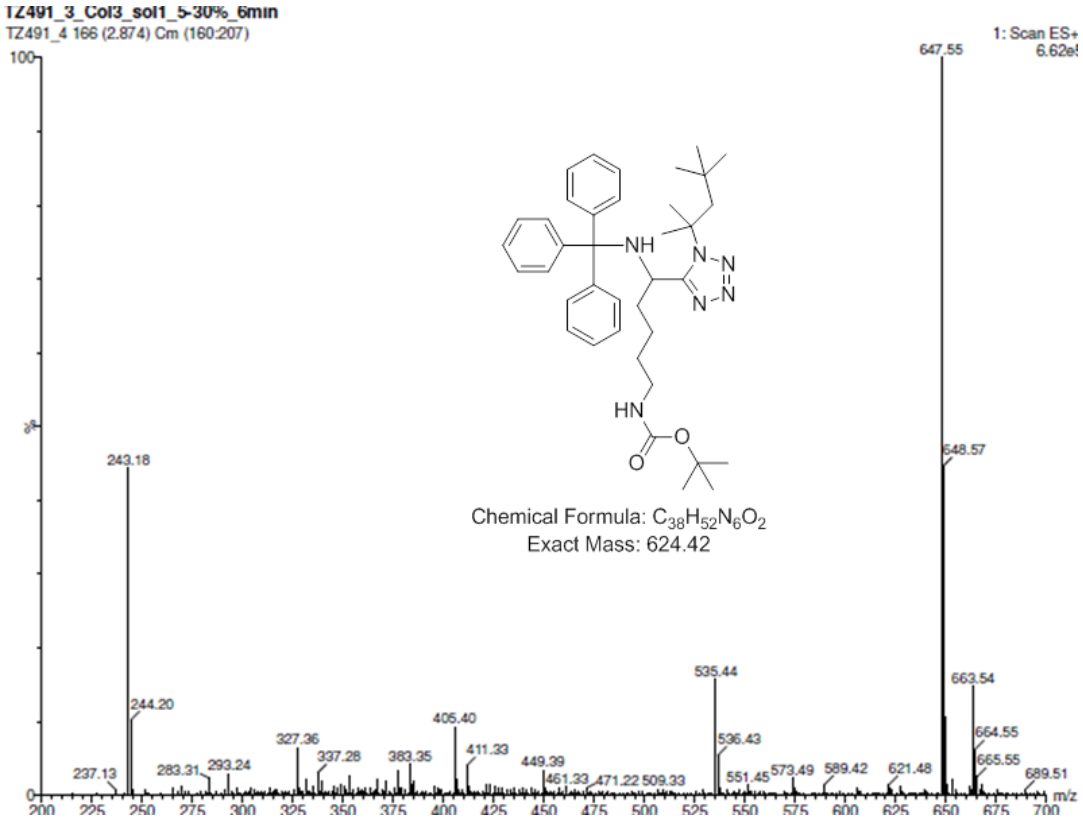
Exact Mass: 539.33

***tert*-Butyl (5-(1-(2,4,4-trimethylpentan-2-yl)-1H-tetrazol-5-yl)-5-(tritylamino)pentyl)carbamate (5e)**

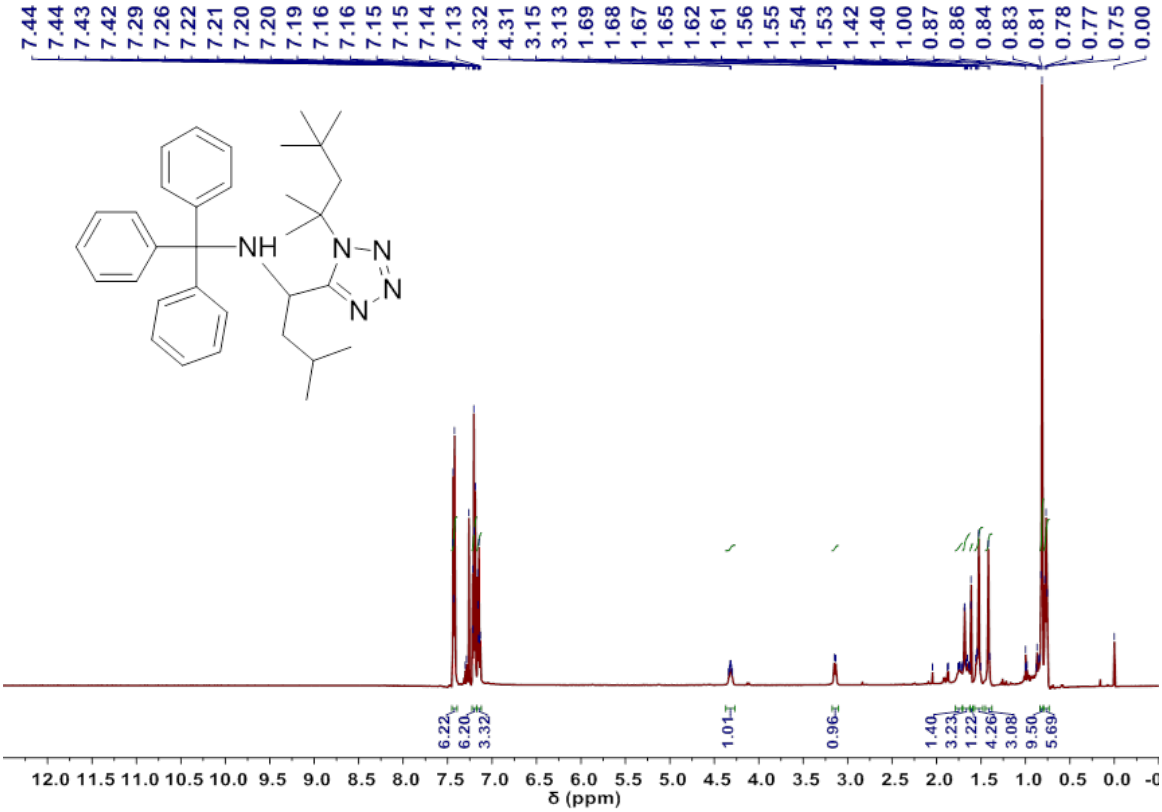


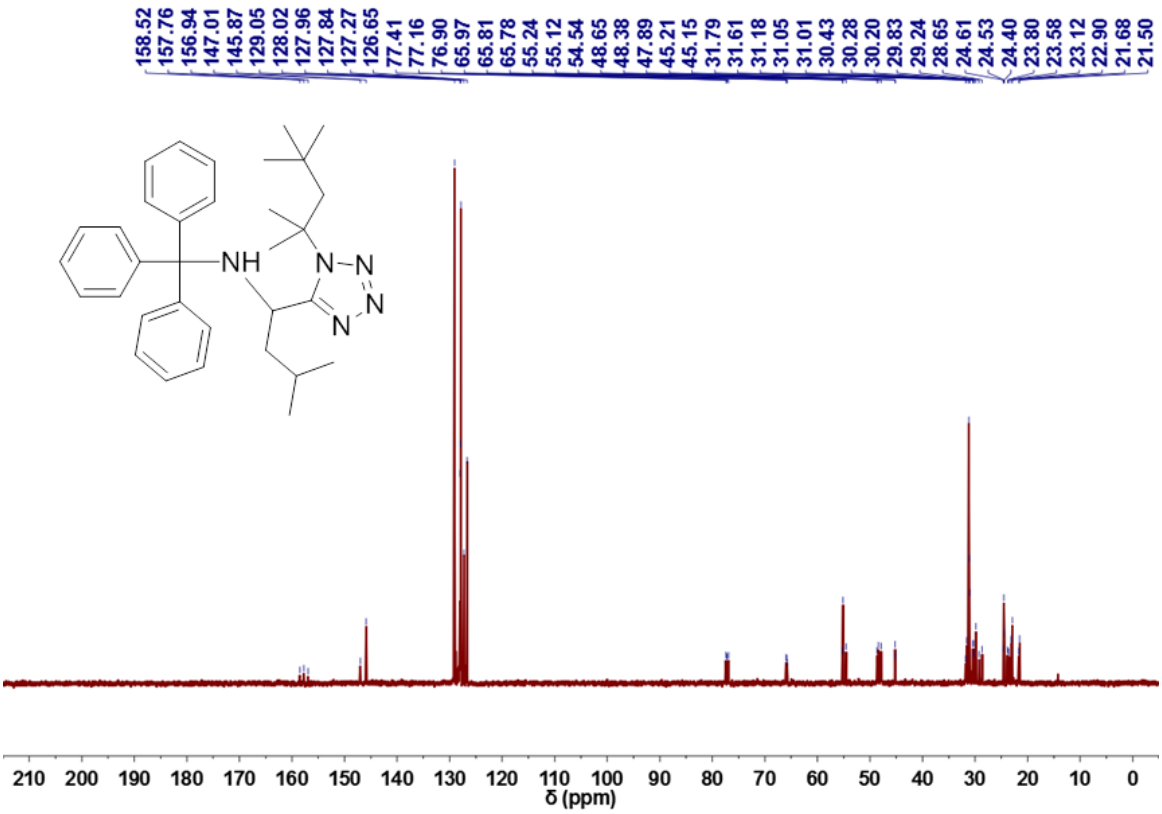


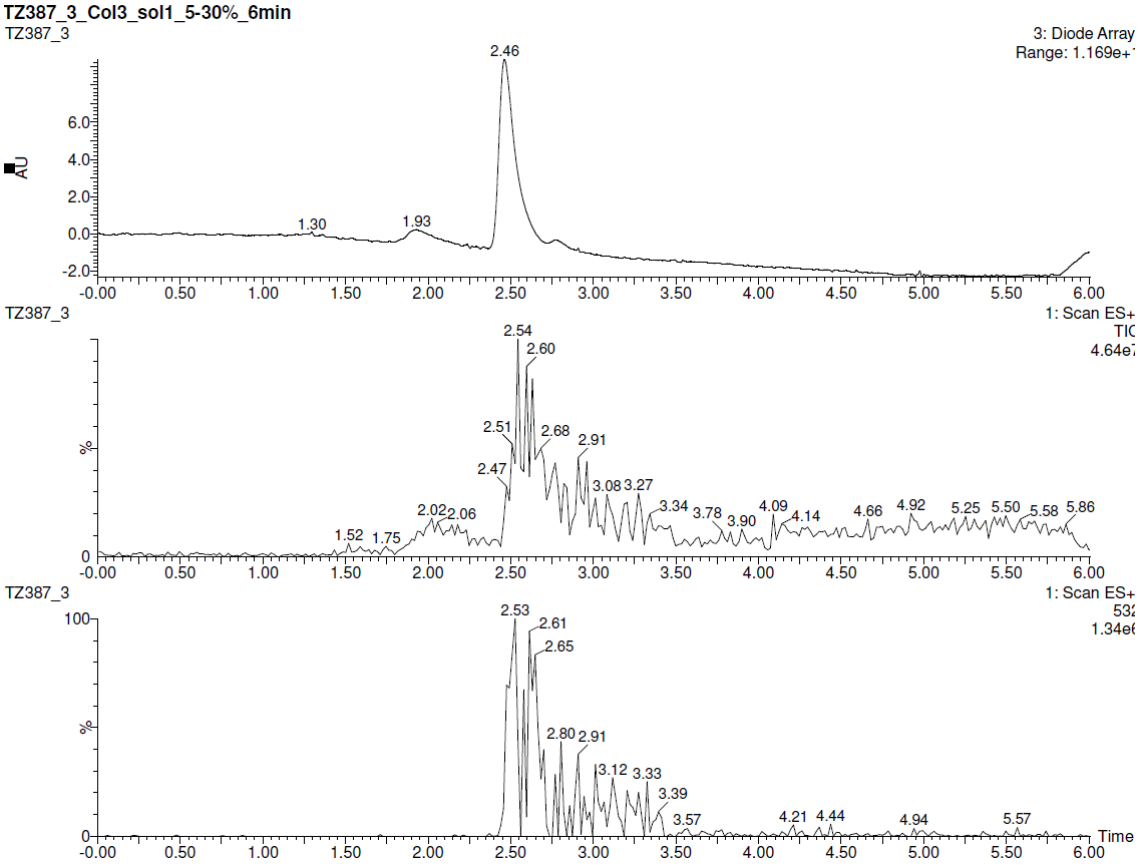

TZ491_3_Col3_sol1_5-30%_6min
TZ491_4
3: Diode Array
Range: 1.22e+
AU
2.83
1.38
1.92
TZ491_4
1: Scan ES+
TIC
8.15e
%
2.87
2.91
3.01
3.08
3.38
4.02
3.46
3.59
4.30
4.54
4.73
4.82
5.08
5.22
5.55
5.62
5.83
0.01
1.03
1.62
1.99
2.02
2.30
2.67
TZ491_4
1: Scan ES+
6.31e
%
3.27
3.59
3.53
3.69
4.05
4.16
4.56
4.84
5.11
5.27
5.41
5.86
2.61
3.06
Time

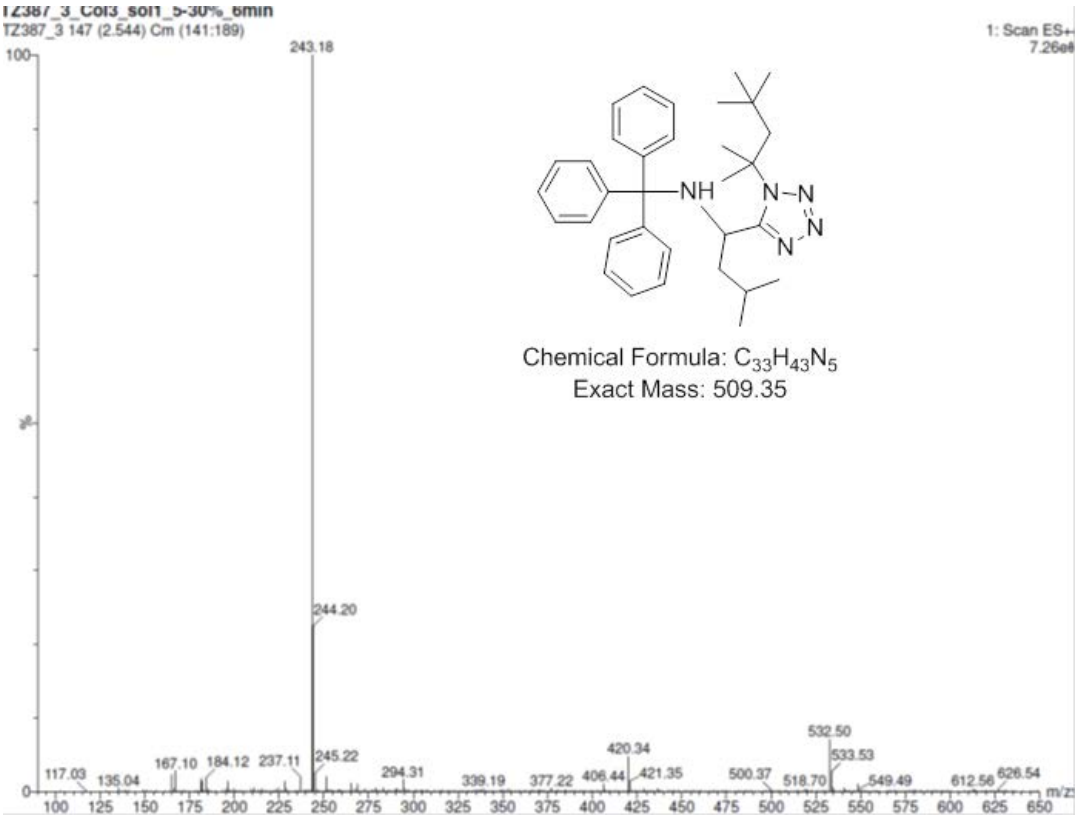

TZ491_3_Col3_sol1_5-30%_6min
TZ491_4 166 (2.874) Cm (160:207)
1: Scan ES+
6.62e
647.55
%
243.18
244.20
648.57
535.44
663.54
405.40
327.36
536.43
664.55
337.28
411.33
383.35
665.55
237.13
283.31
293.24
449.39
551.45
573.49
589.42
621.48
689.51
m/z
NH
N
N
N
HN
O
O
Chemical Formula: C38H52N6O2
Exact Mass: 624.42

3-Methyl-1-(1-(2,4,4-trimethylpentan-2-yl)-1H-tetrazol-5-yl)-N-tritylbutan-1-amine (5f)

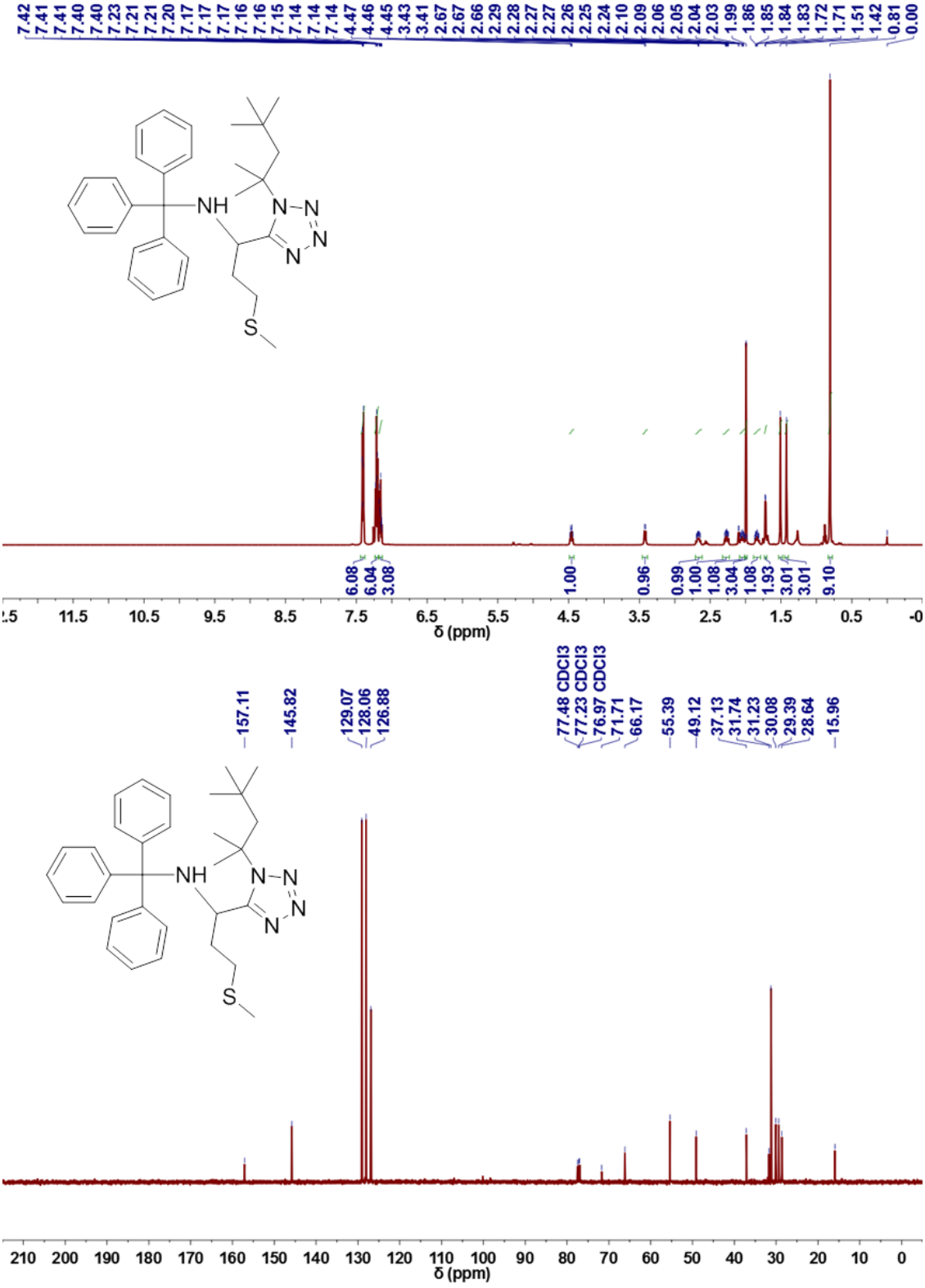


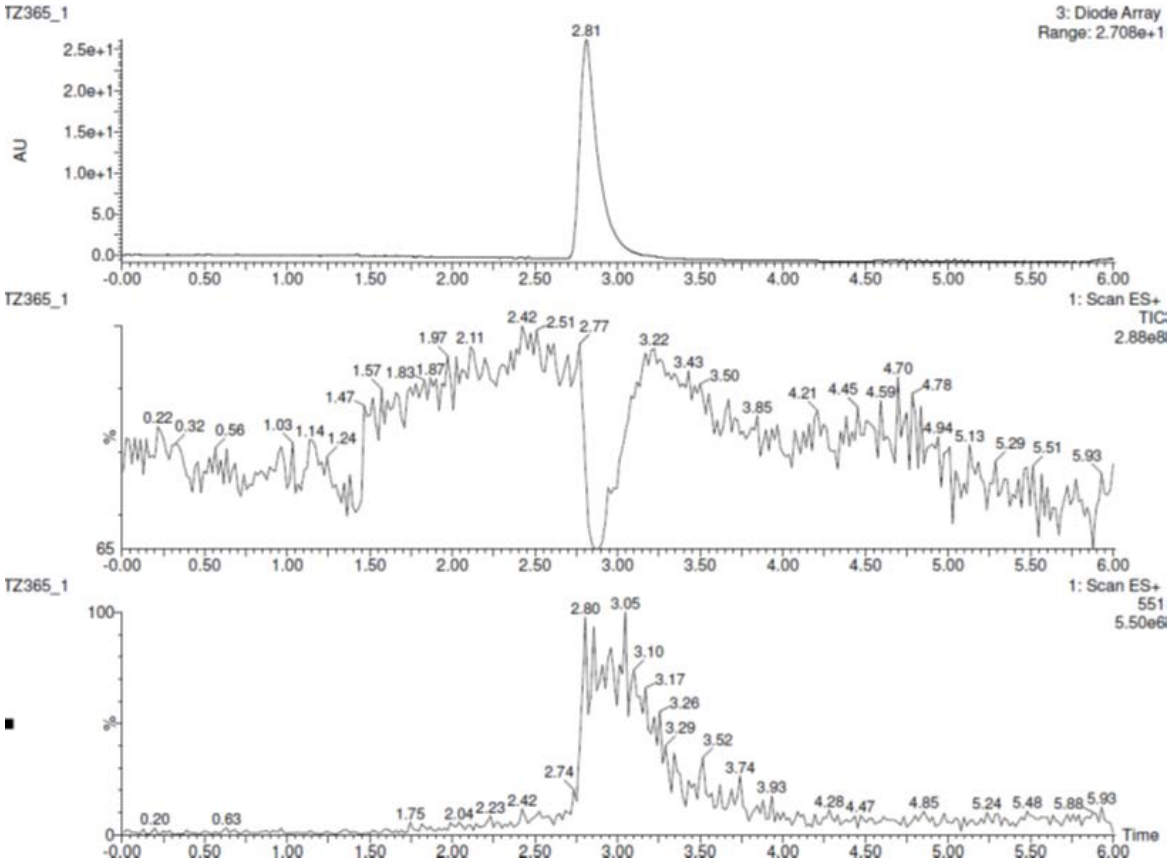


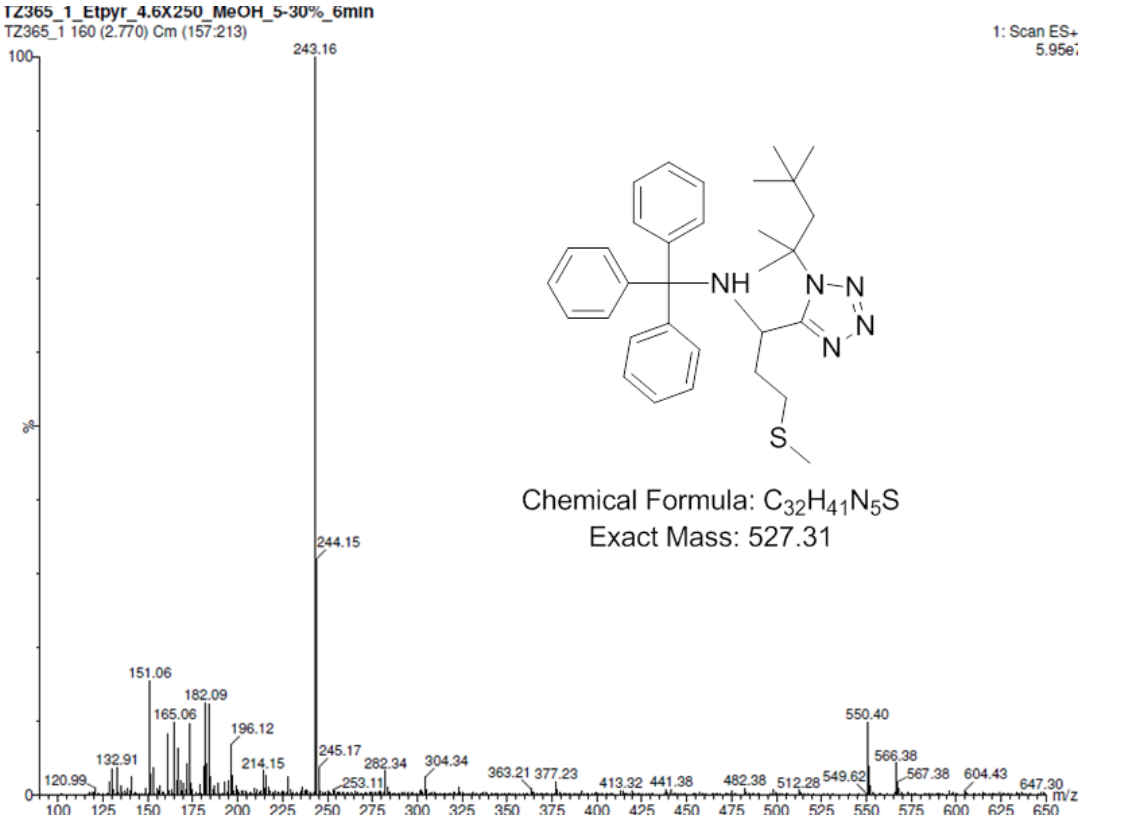

TZ387_3_Col3_sol1_5-30%_6min
TZ387_3
3: Diode Array
Range: 1.169e+
AU
2.46
1.30
1.93
TZ387_3
1: Scan ES+
TIC
4.64e7
%
2.54
2.60
2.51
2.68
2.91
2.47
3.08
3.27
2.02
2.06
3.34
3.78
3.90
4.09
4.14
4.66
4.92
5.25
5.50
5.58
5.86
1.52
1.75
TZ387_3
1: Scan ES+
1.34e6
%
2.53
2.61
2.65
2.80
2.91
3.12
3.33
3.39
3.57
4.21
4.44
4.94
5.57
Time


TZ387_3_Col3_sol1_5-30%_6min
TZ387_3 147 (2.544) Cm (141:189)
1: Scan ES+
7.26e6
%
243.18
244.20
245.22
117.03
135.04
167.10
184.12
237.11
294.31
339.19
377.22
406.44
420.34
421.35
500.37
518.70
532.50
533.53
549.49
612.56
626.54
m/z
NH
N–N
N
N
Chemical Formula: C33H43N5
Exact Mass: 509.35

3-(Methylthio)-1-(1-(2,4,4-trimethylpentan-2-yl)-1H-tetrazol-5-yl)-N-tritylpropan-1-amine (5g)

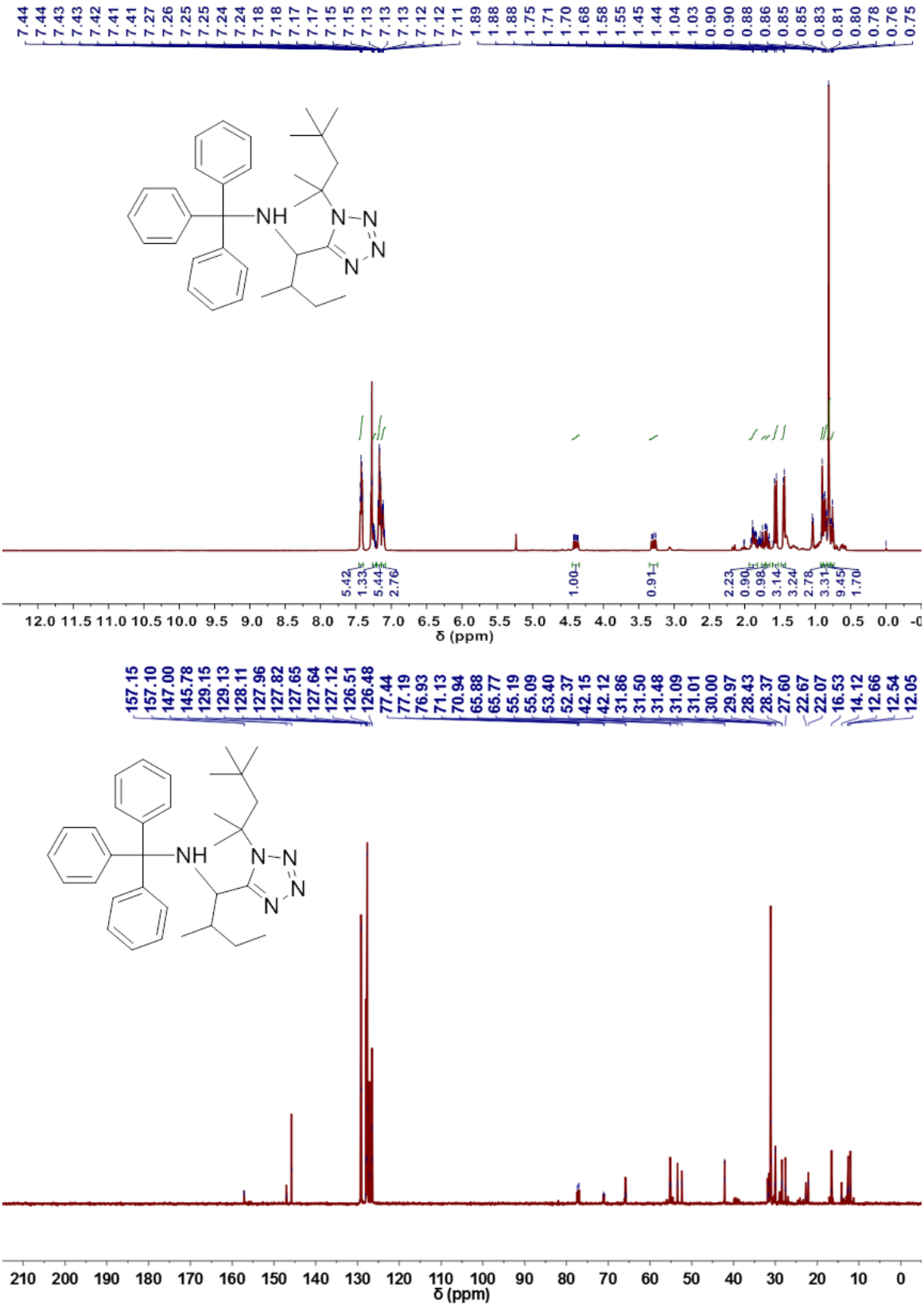


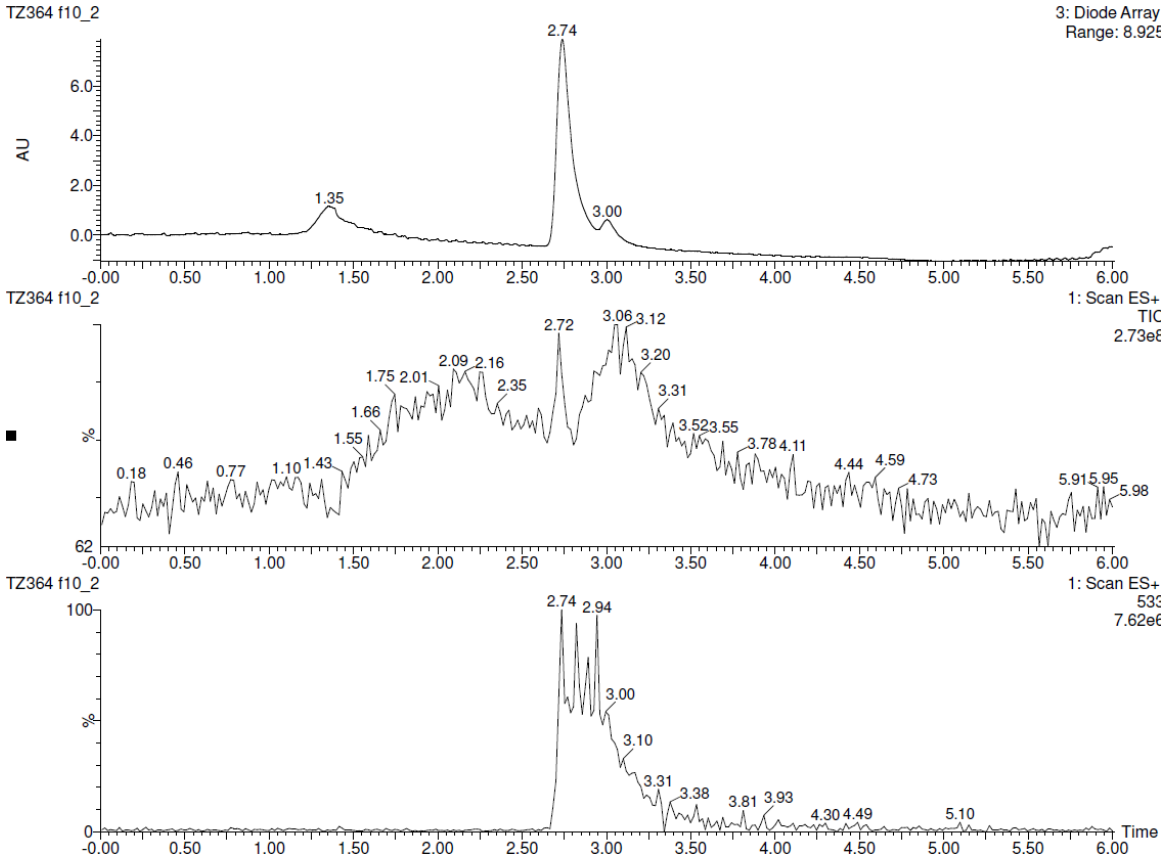


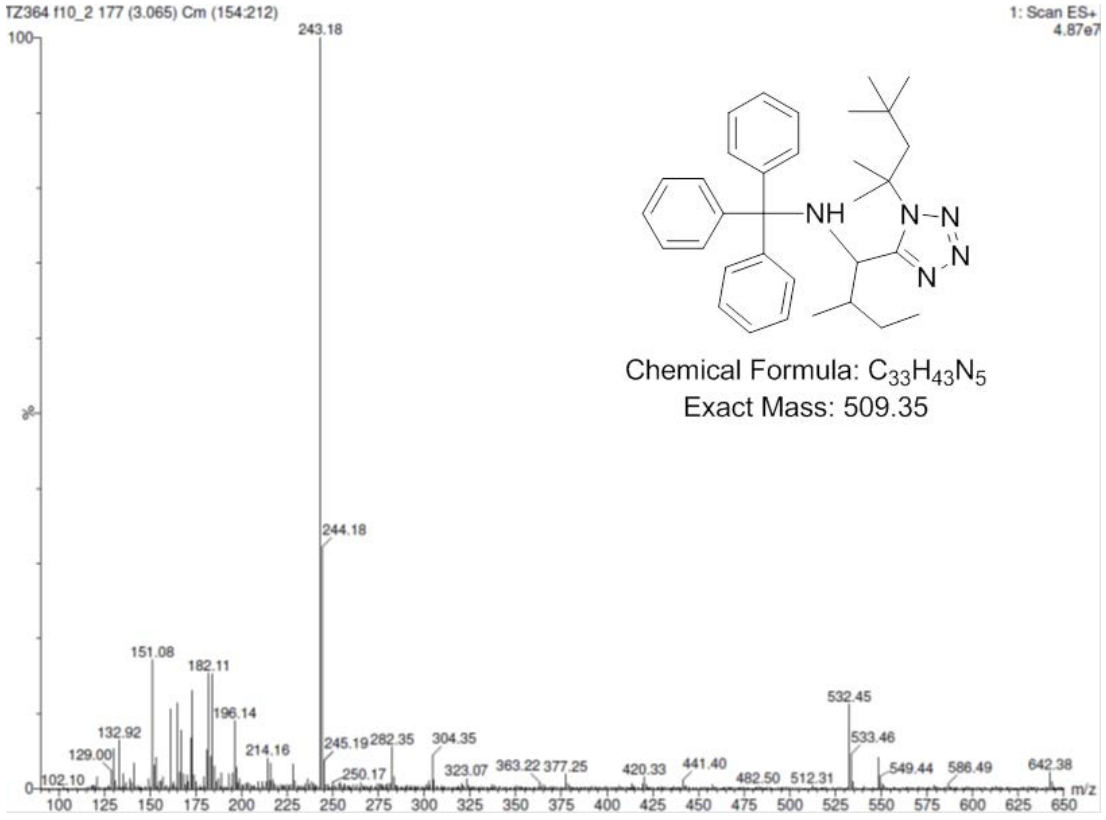


Chemical Formula: $C_{32}H_{41}N_5S$
Exact Mass: 527.31

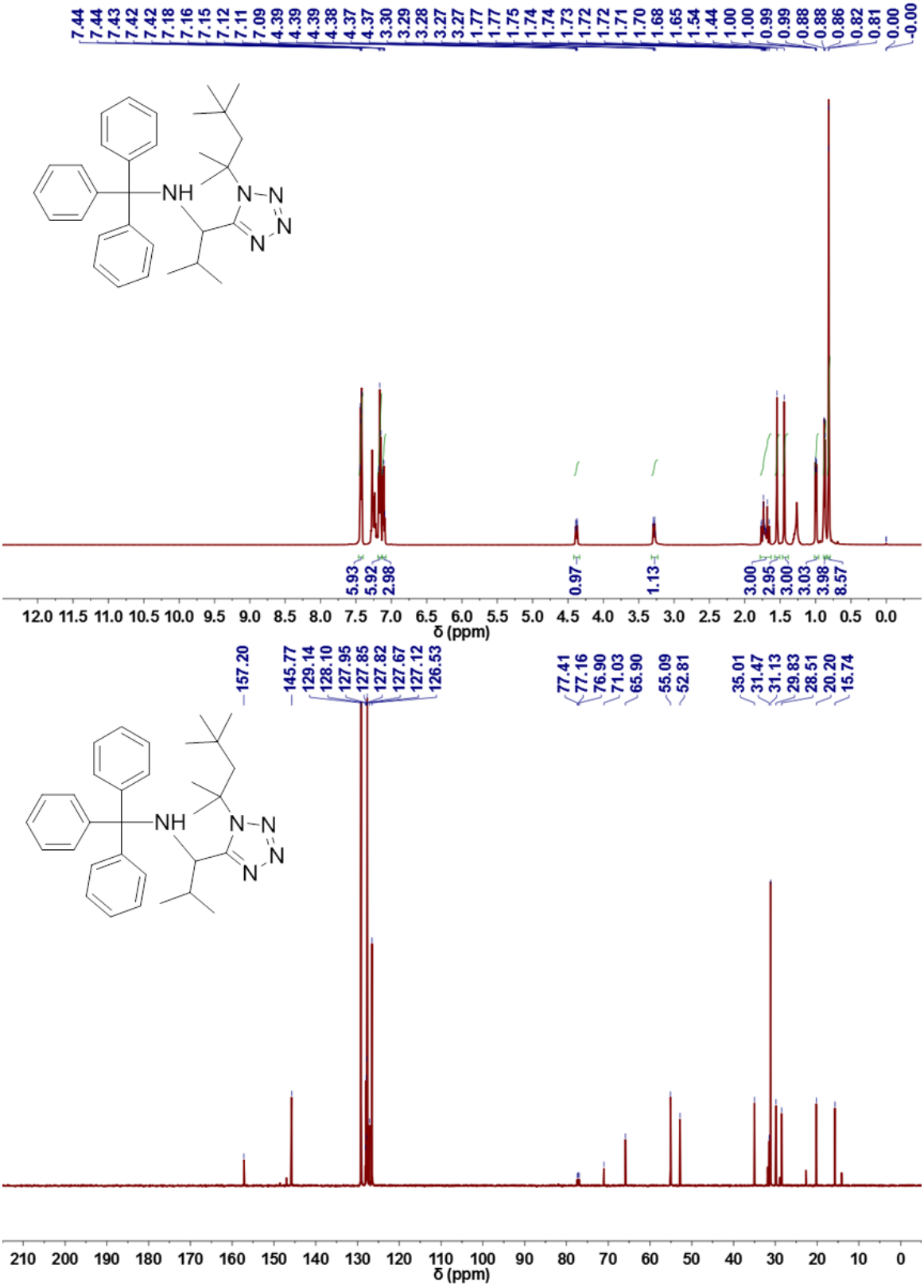
2-Methyl-1-(1-(2, 4, 4-trimethylpentan-2-yl)-1H-tetrazol-5-yl)-N-tritylbutan-1-amine (5h)

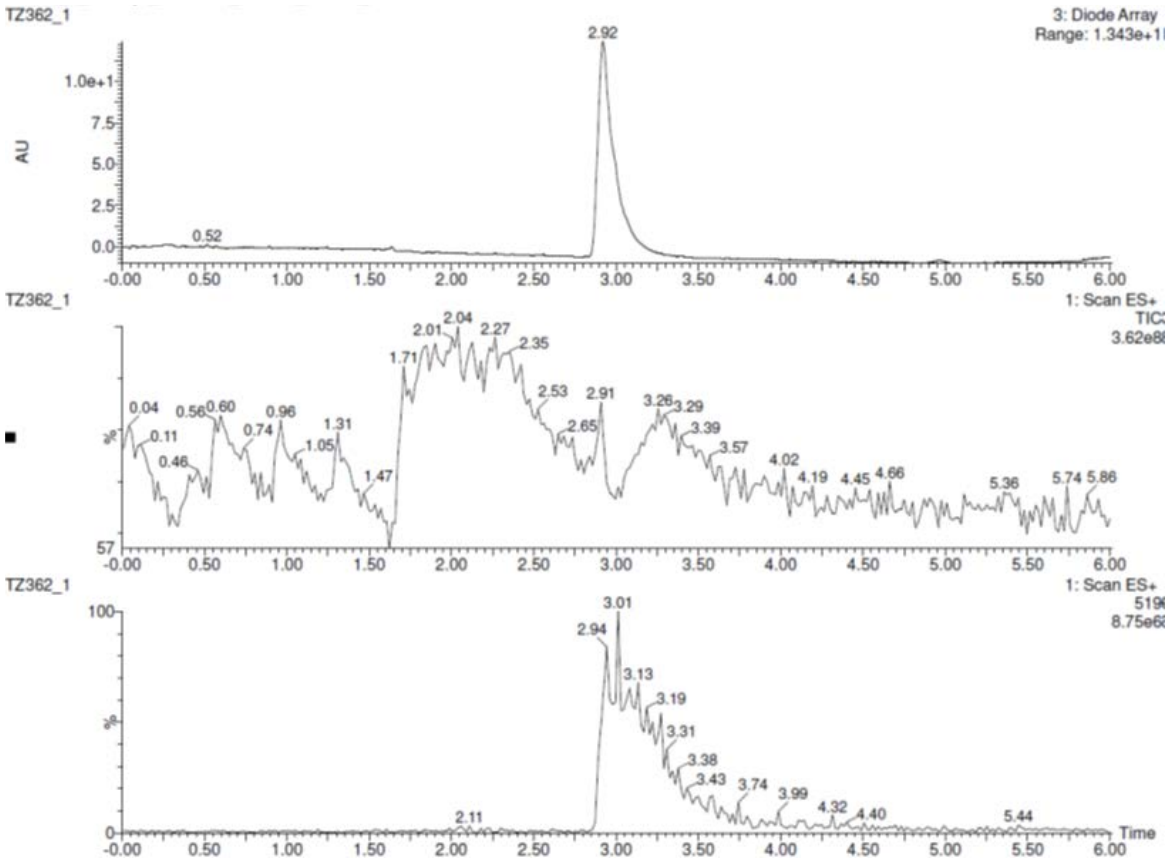


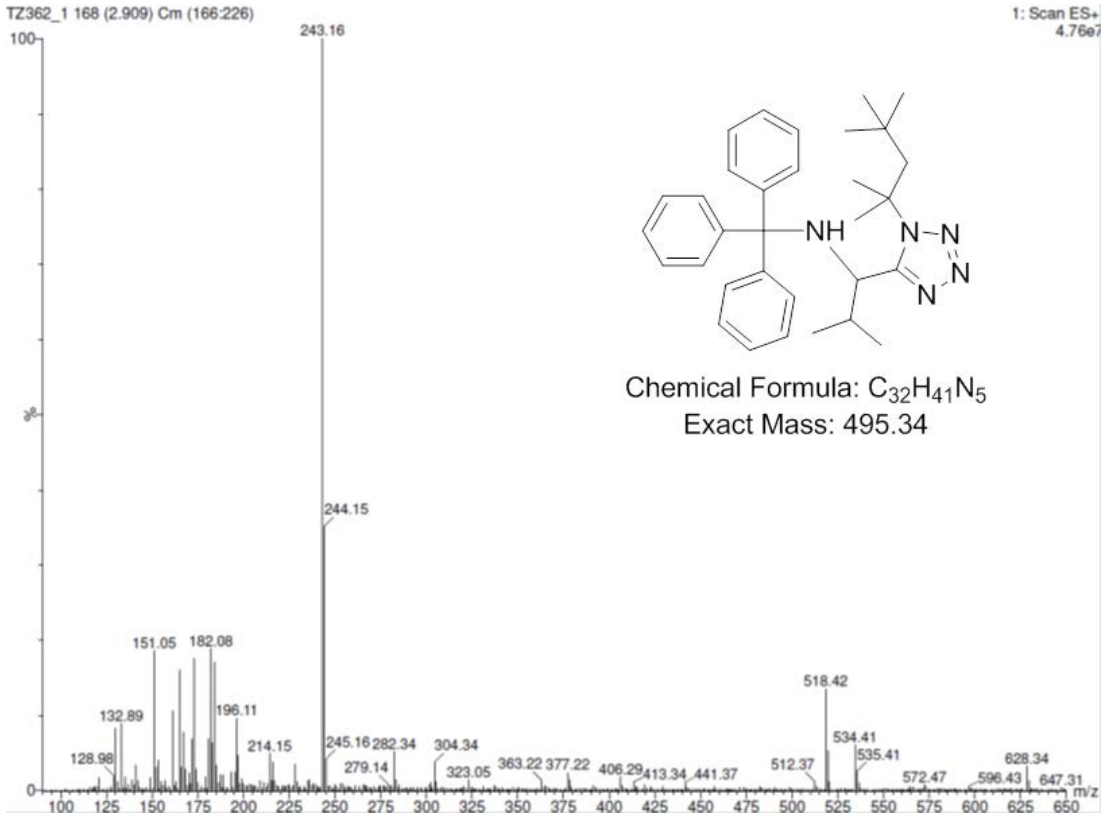

TZ364 f10_2
3: Diode Array
Range: 8.925
AU
2.74
1.35
3.00
TZ364 f10_2
1: Scan ES+
TIC
2.73e8
%
2.72
3.06
3.12
3.20
3.31
3.52
3.55
3.78
4.11
2.09
2.16
2.35
1.75
2.01
1.66
1.55
1.43
1.10
0.77
0.46
0.18
4.44
4.59
4.73
5.91
5.95
5.98
TZ364 f10_2
1: Scan ES+
533
7.62e6
2.74
2.94
3.00
3.10
3.31
3.38
3.81
3.93
4.30
4.49
5.10
Time


TZ364 f10_2 177 (3.065) Cm (154:212)
1: Scan ES+
4.87e7
243.18
244.18
151.08
182.11
196.14
132.92
129.00
214.16
102.10
245.19
282.35
304.35
250.17
323.07
363.22
377.25
420.33
441.40
482.50
512.31
532.45
533.46
549.44
586.49
642.38
m/z
NH
N
N
N
Chemical Formula: C33H43N5
Exact Mass: 509.35

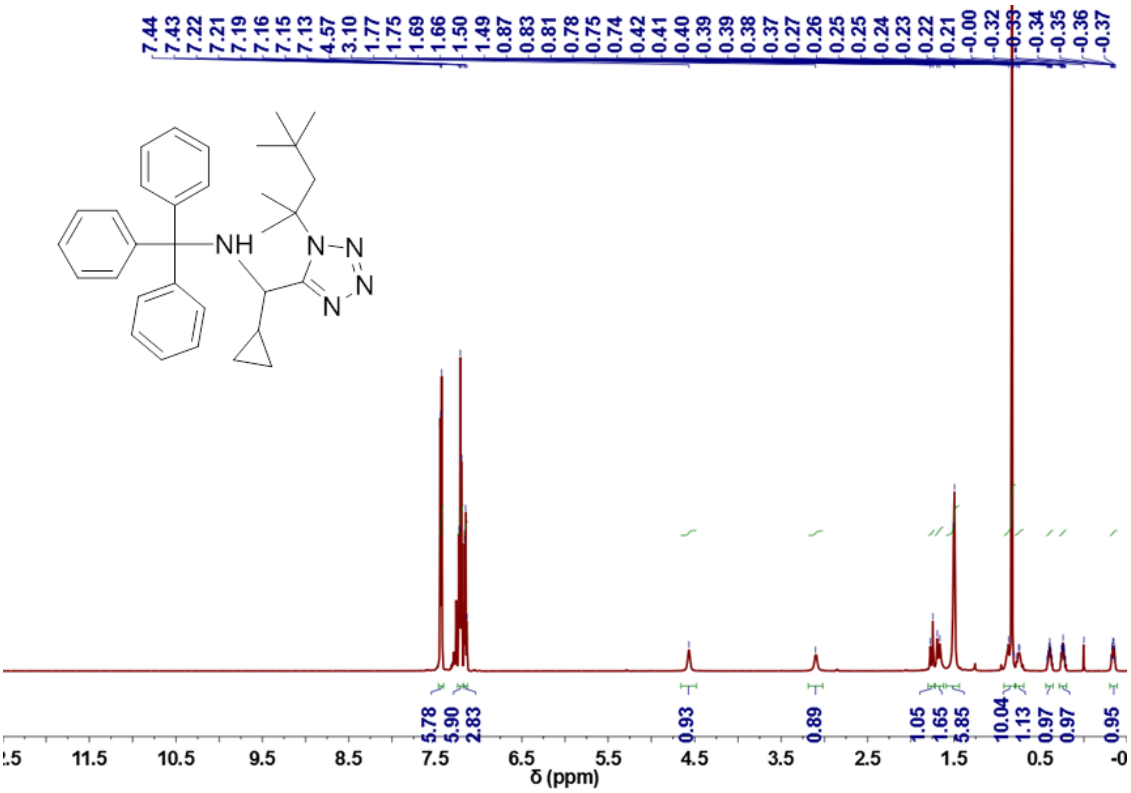
2-Methyl-1-(1-(2,4,4-trimethylpentan-2-yl)-1H-tetrazol-5-yl)-N-tritylpropan-1-amine (5i)

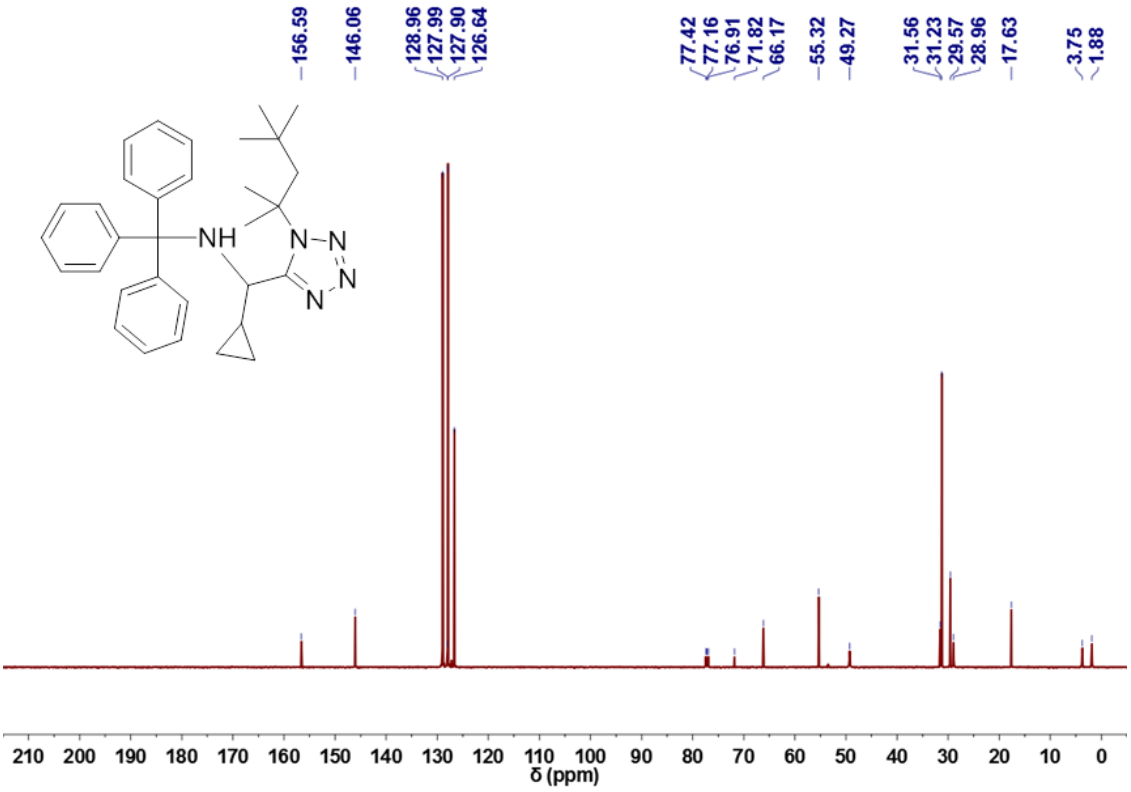


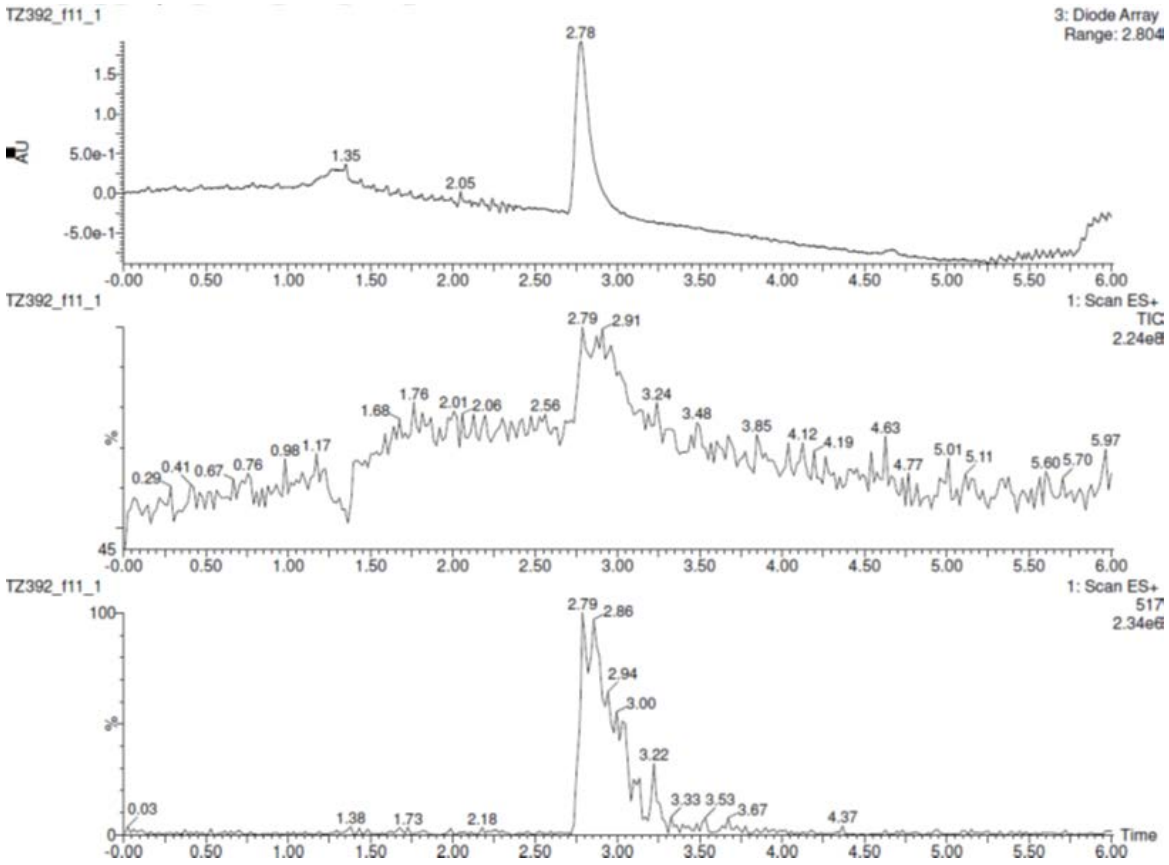

TZ362_1
3: Diode Array
Range: 1.343e+1
AU
2.92
0.52
TZ362_1
1: Scan ES+
TIC
3.62e8
%
2.01
2.04
2.27
1.71
2.35
2.53
2.91
3.26
3.29
3.39
3.57
4.02
4.19
4.45
4.66
5.36
5.74
5.86
0.04
0.56
0.60
0.96
0.74
1.31
1.05
0.11
0.46
1.47
TZ362_1
1: Scan ES+
8.75e6
3.01
2.94
3.13
3.19
3.31
3.38
3.43
3.74
3.99
4.32
4.40
5.44
2.11
Time

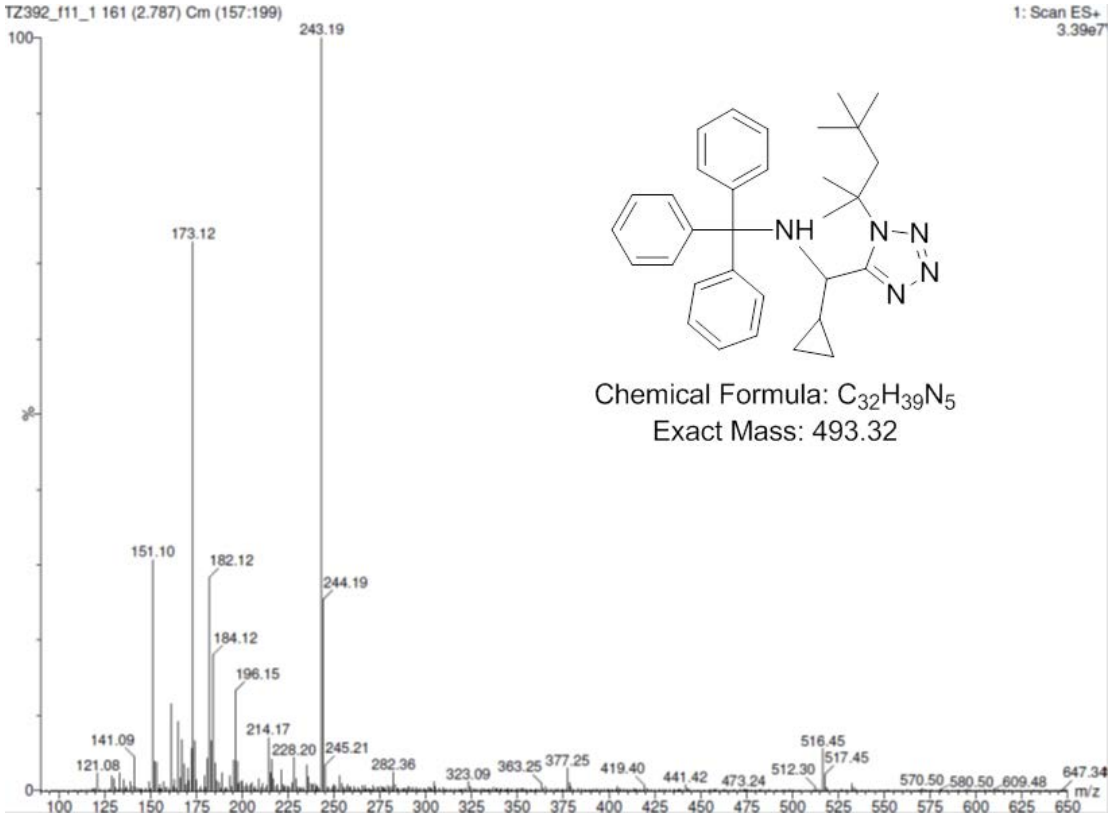

TZ362_1 168 (2.909) Cm (166:226)
1: Scan ES+
4.76e7
%
243.16
244.15
151.05
182.08
132.89
196.11
214.15
128.98
245.16
282.34
279.14
304.34
323.05
363.22
377.22
406.29
413.34
441.37
512.37
518.42
534.41
535.41
572.47
596.43
628.34
647.31
m/z
NH
N
N
N
Chemical Formula: C32H41N5
Exact Mass: 495.34

***N*-(Cyclopropyl(1-(2,4,4-trimethylpentan-2-yl)-1H-tetrazol-5-yl)methyl)-1,1,1 triphenylmethanamine (5j)**



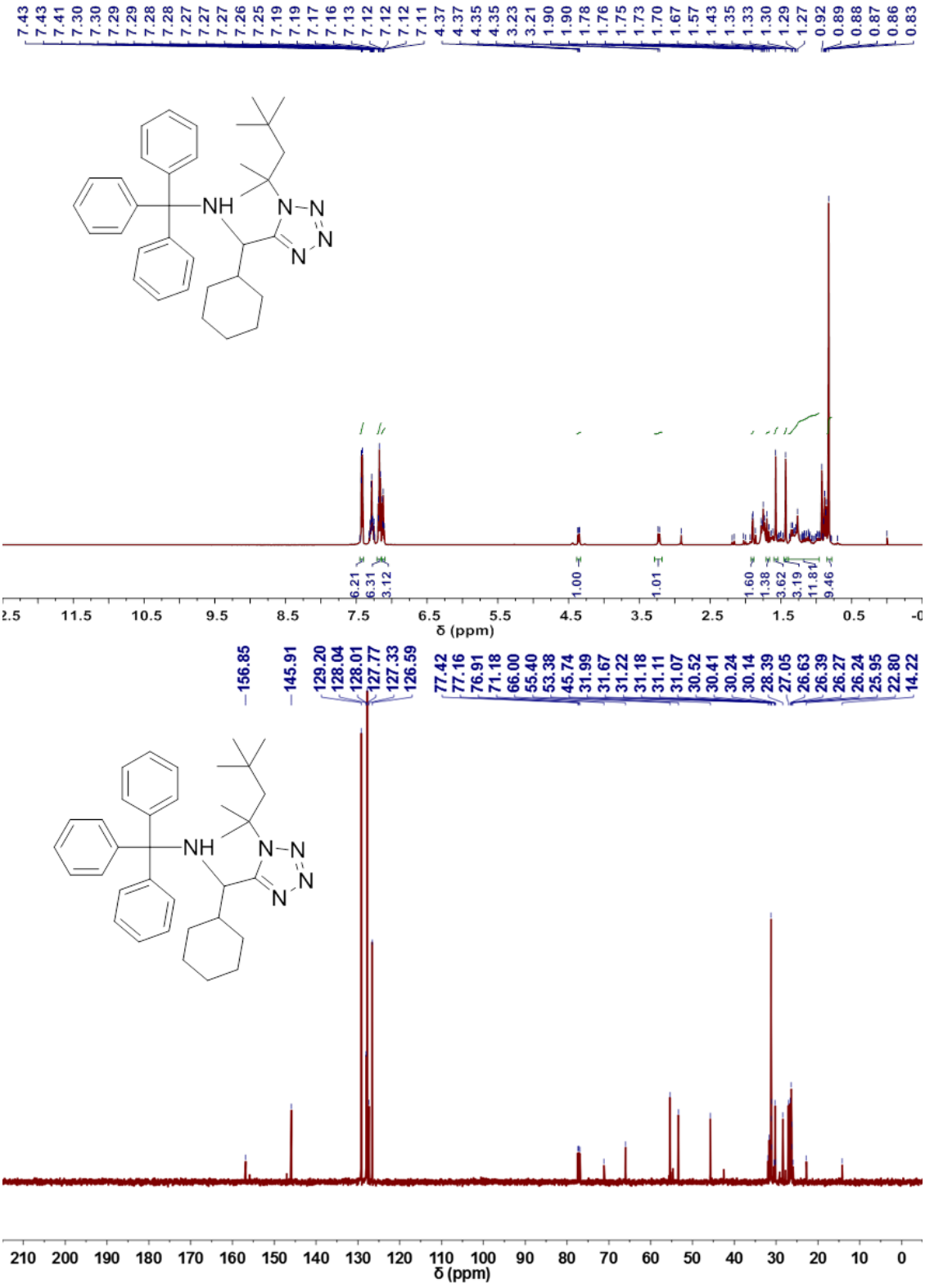


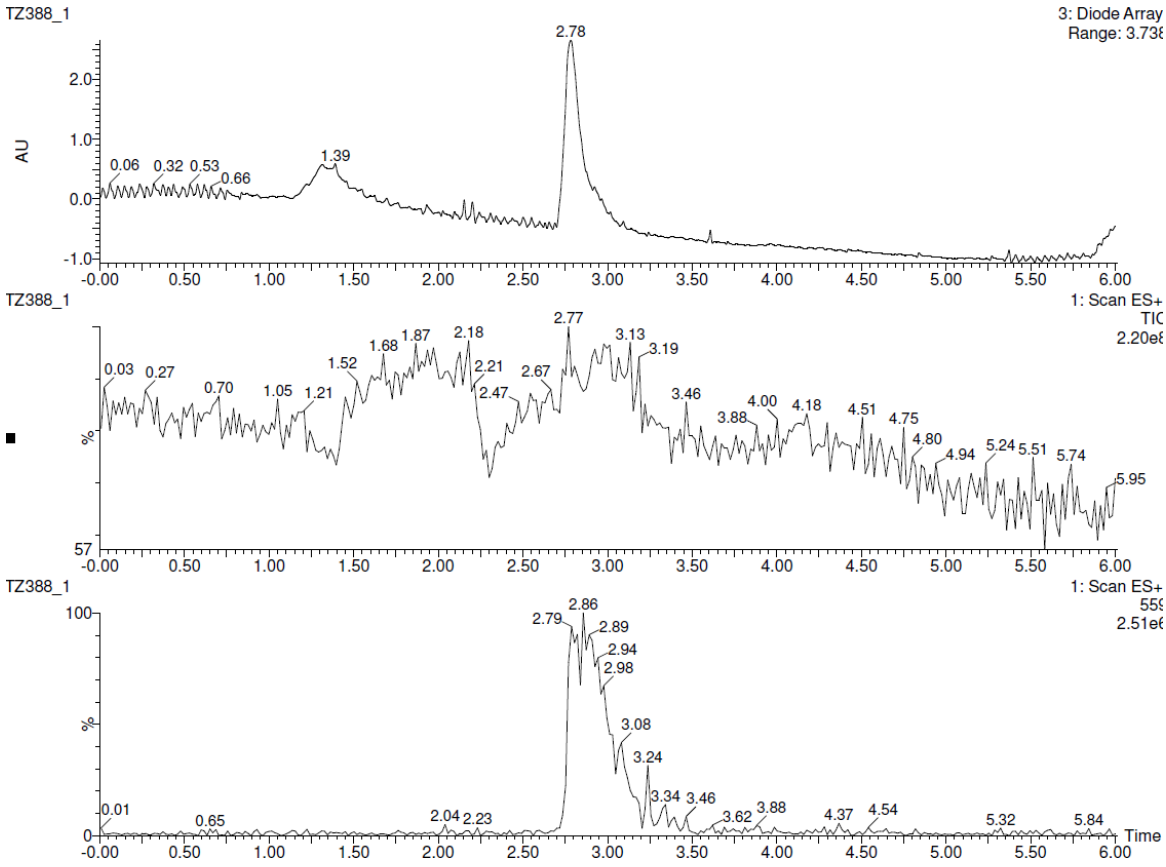


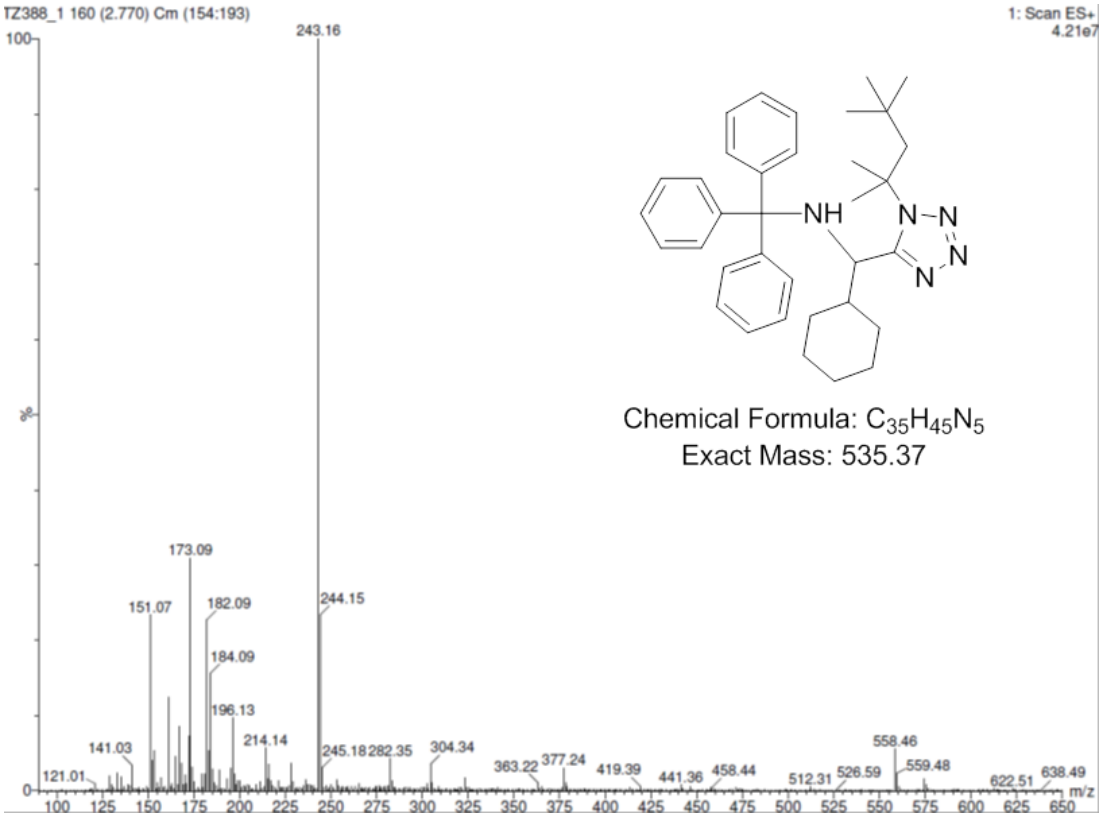


Chemical Formula: $C_{32}H_{39}N_5$
Exact Mass: 493.32

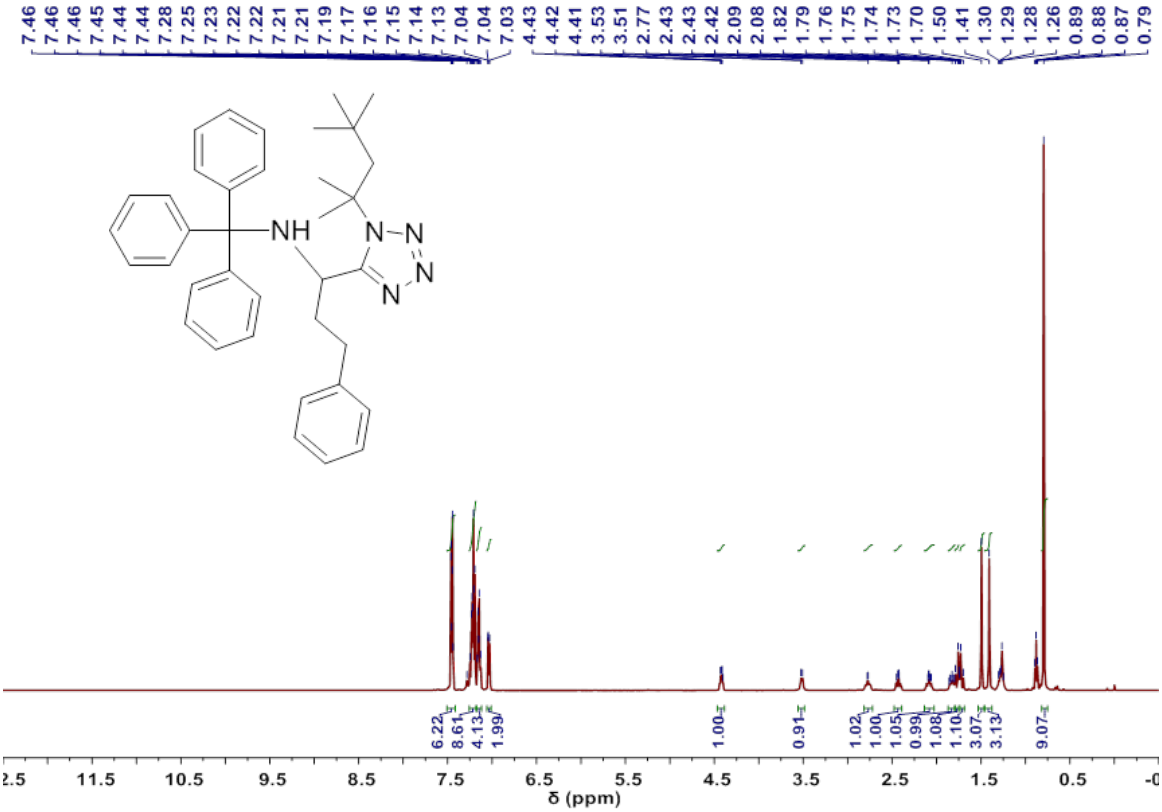
***N*-(Cyclohexyl(1-(2,4,4-trimethylpentan-2-yl)-1H-tetrazol-5-yl)methyl)-1,1,1-triphenylmethanamine (5k)**

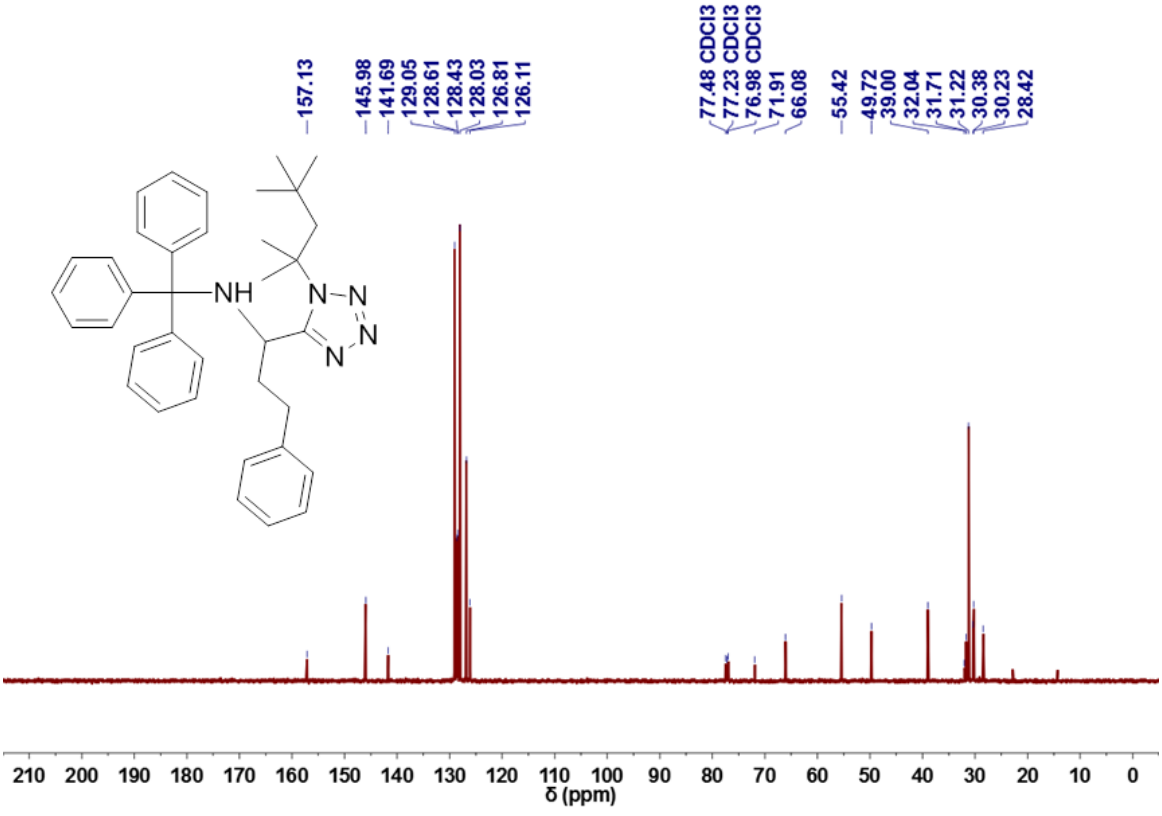


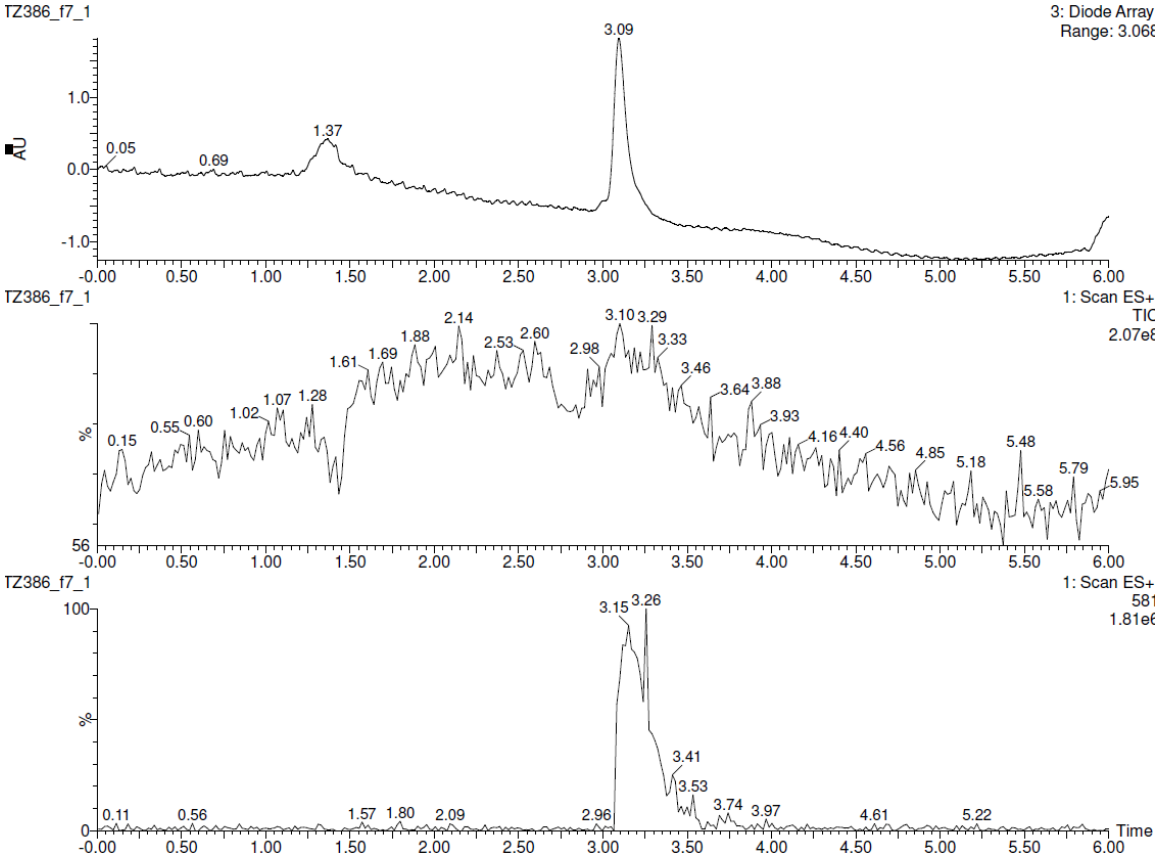

TZ388_1
3: Diode Array
Range: 3.73
AU
2.78
1.39
0.06
0.32
0.53
0.66
TZ388_1
1: Scan ES+
TIC
2.20e8
%
2.77
3.13
3.19
2.18
1.87
1.68
1.52
2.21
2.67
2.47
1.21
1.05
0.70
0.27
0.03
3.46
4.00
3.88
4.18
4.51
4.75
4.80
4.94
5.24
5.51
5.74
5.95
57
TZ388_1
1: Scan ES+
2.51e6
100
%
2.86
2.79
2.89
2.94
2.98
3.08
3.24
3.34
3.46
3.62
3.88
4.37
4.54
5.32
5.84
0.01
0.65
2.04
2.23
0
Time

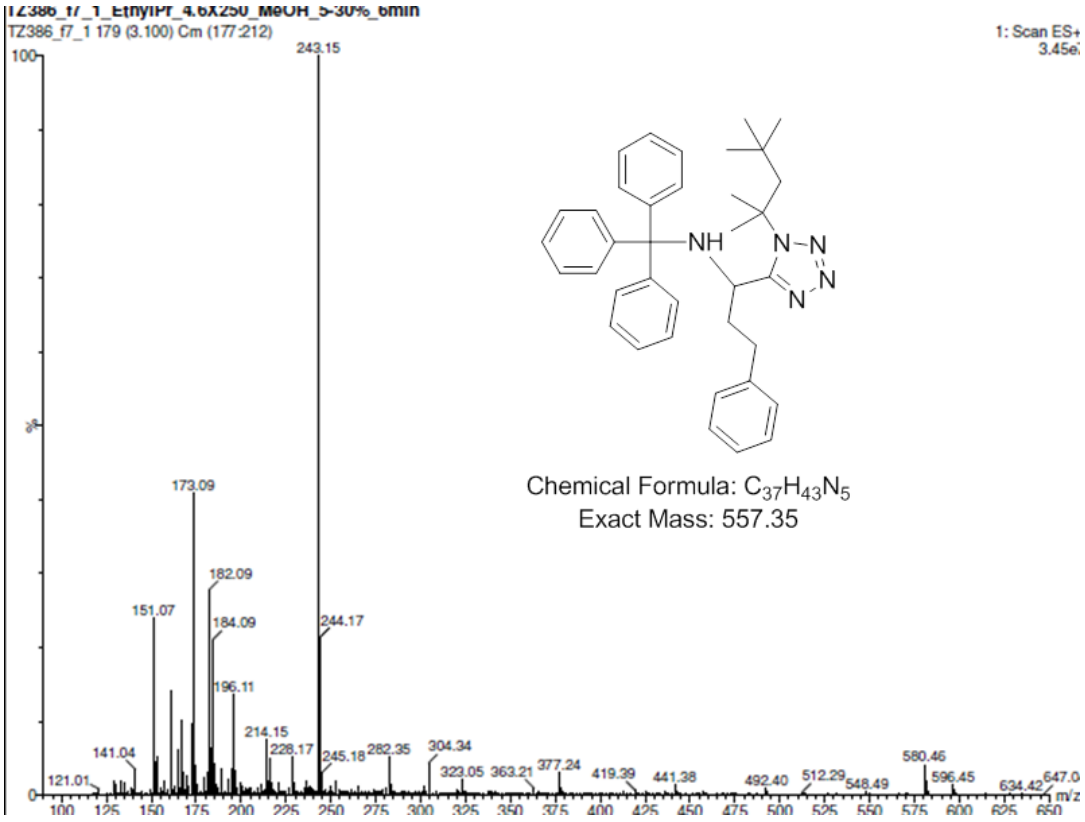

TZ388_1 160 (2.770) Cm (154:193)
1: Scan ES+
4.21e7
100
%
243.16
173.09
151.07
182.09
244.15
184.09
196.13
214.14
141.03
245.18
282.35
304.34
121.01
363.22
377.24
419.39
441.36
458.44
512.31
526.59
558.46
559.48
622.51
638.49
0
m/z
NH
N
N
N
Chemical Formula: C35H45N5
Exact Mass: 535.37

3-Phenyl-1-(1-(2,4,4-trimethylpentan-2-yl)-1H-tetrazol-5-yl)-N-tritylpropan-1-amine (5l)



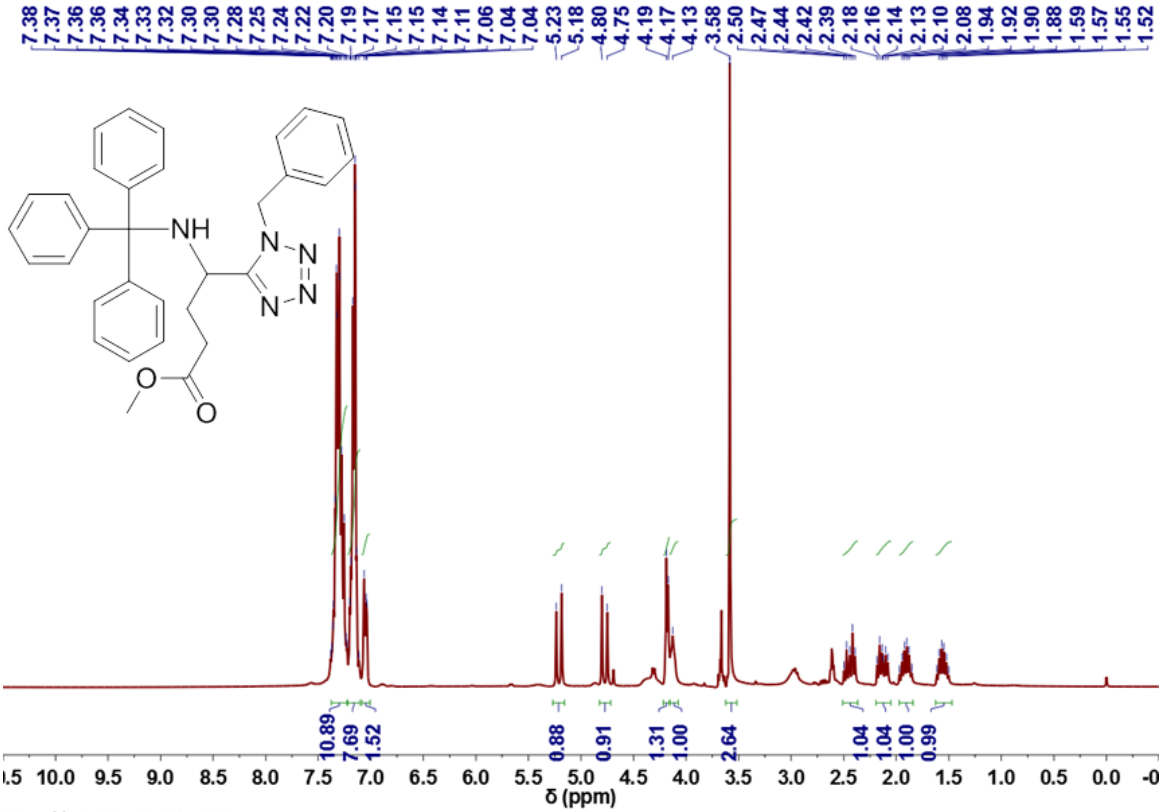


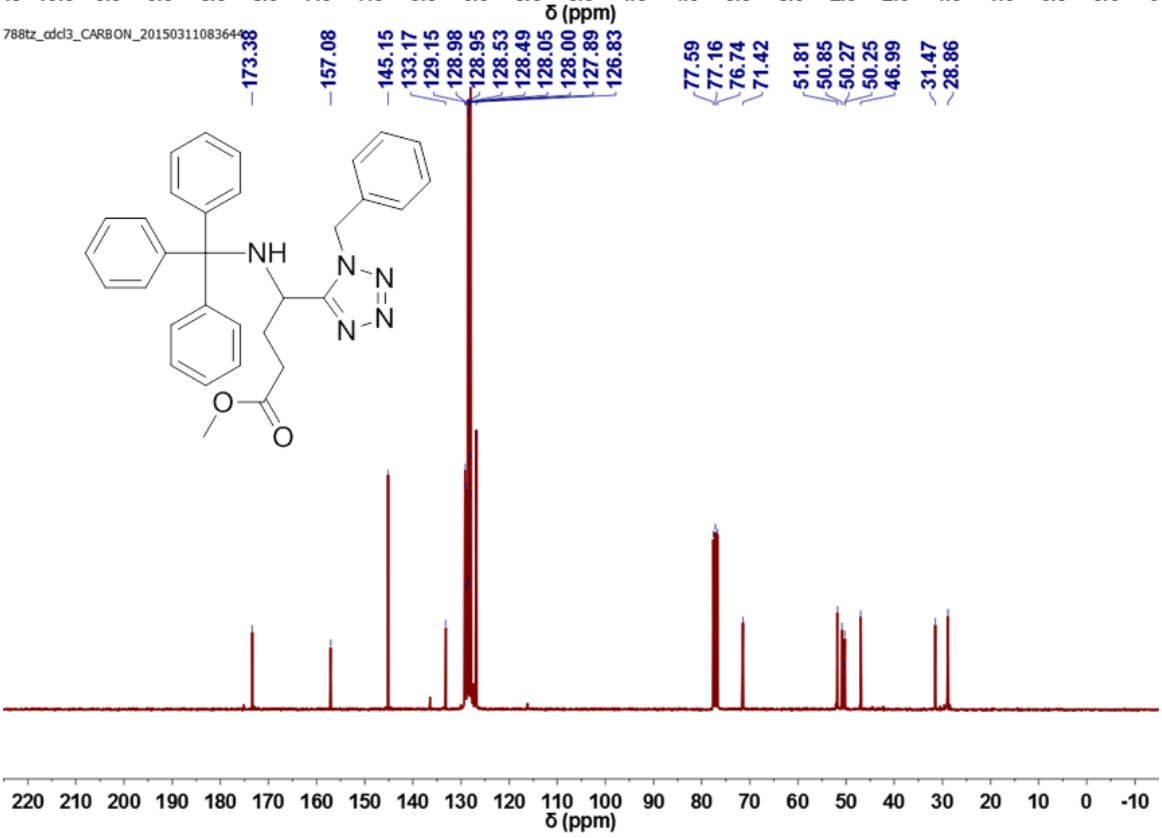


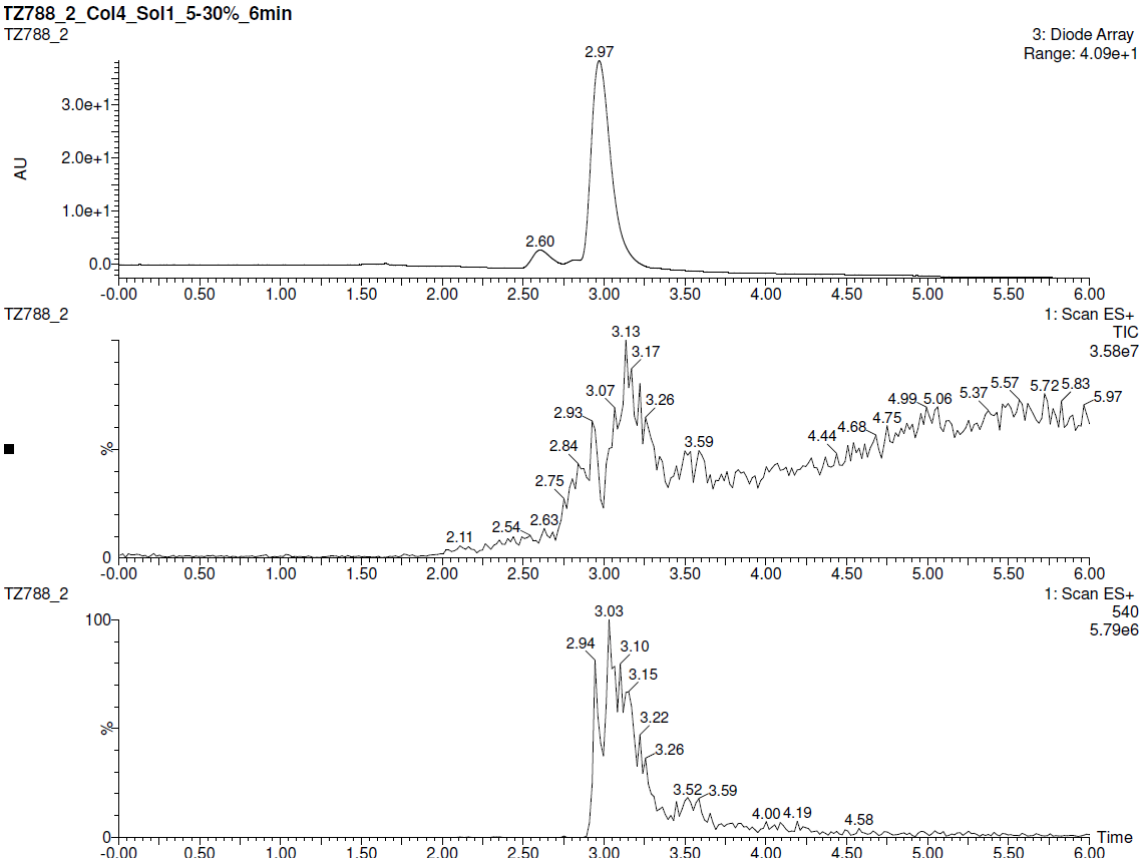


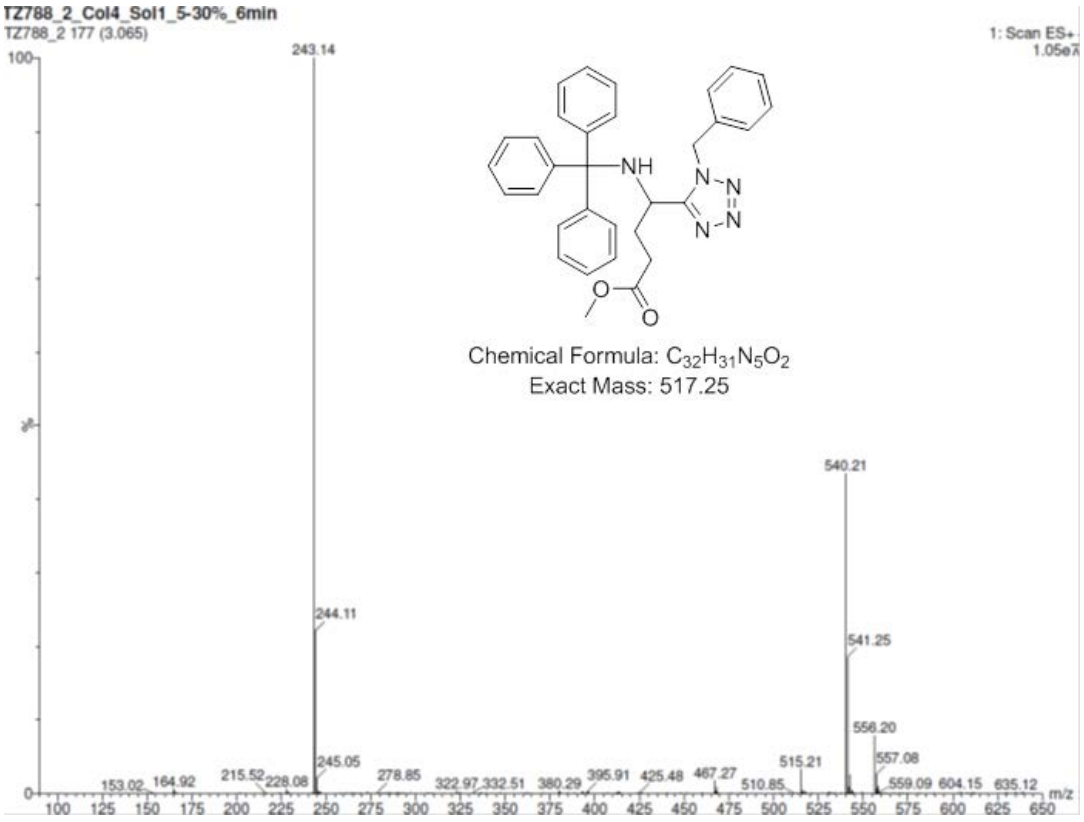
Chemical Formula: $C_{37}H_{43}N_5$
Exact Mass: 557.35

Methyl 4-(1-benzyl-1H-tetrazol-5-yl)-4-(tritylamino)butanoate (5m)

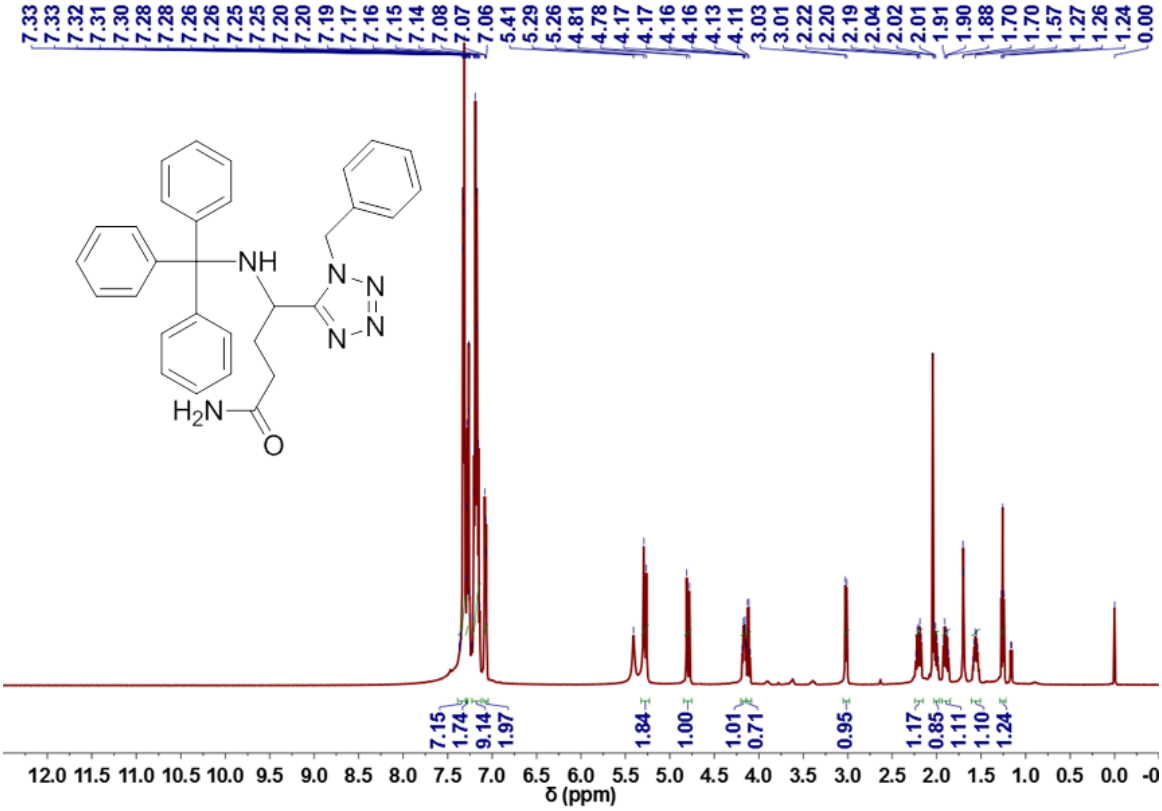


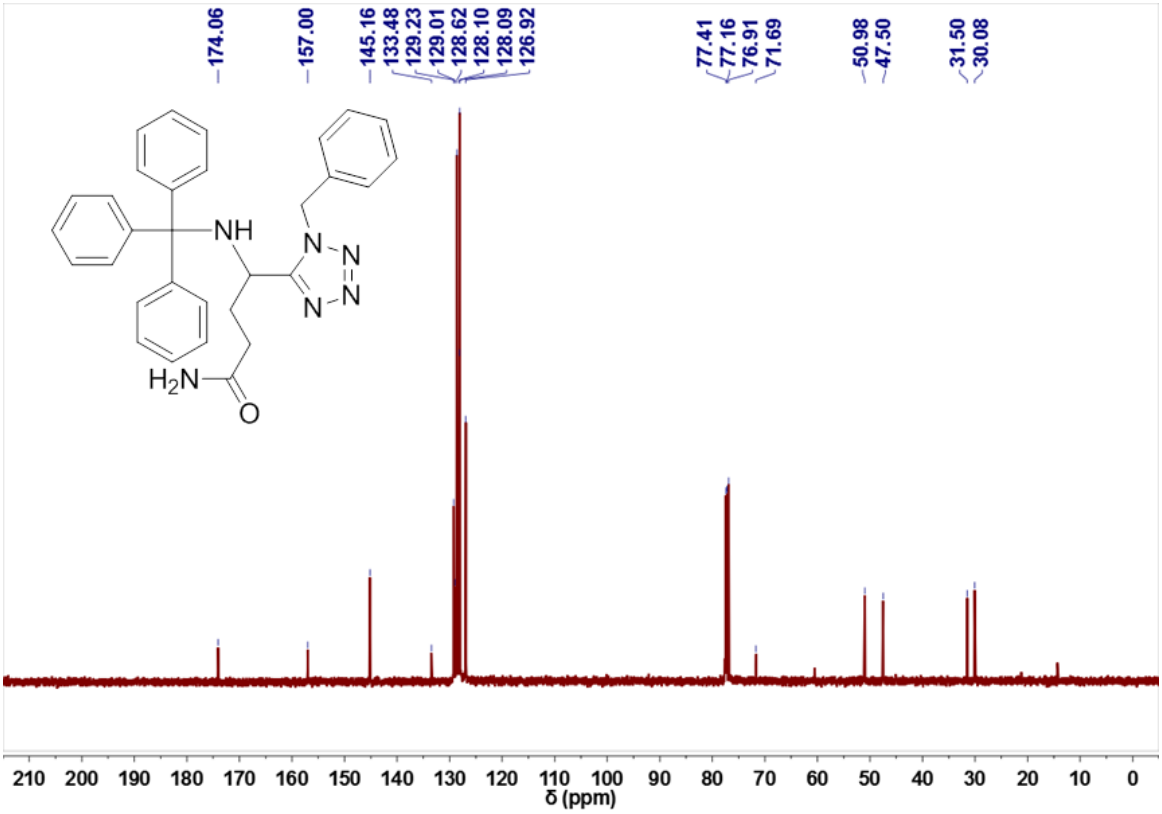


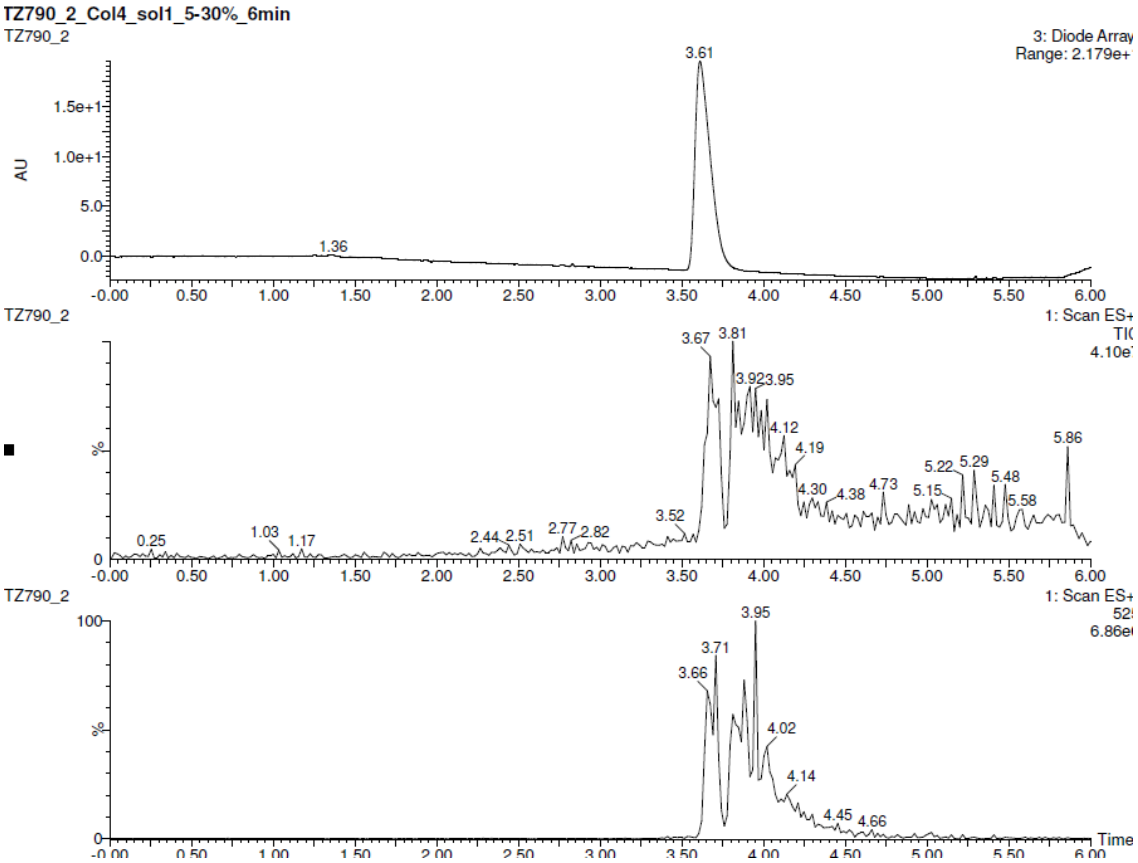

TZ788_2_Col4_Sol1_5-30%_6min
TZ788_2
3: Diode Array
Range: 4.09e+1
AU
2.97
2.60
TZ788_2
1: Scan ES+
TIC
3.58e7
%
3.13
3.17
3.07
3.26
2.93
2.84
3.59
2.75
2.63
2.54
2.11
4.44
4.68
4.75
4.99
5.06
5.37
5.57
5.72
5.83
5.97
TZ788_2
1: Scan ES+
540
5.79e6
100
%
3.03
2.94
3.10
3.15
3.22
3.26
3.52
3.59
4.00
4.19
4.58
Time

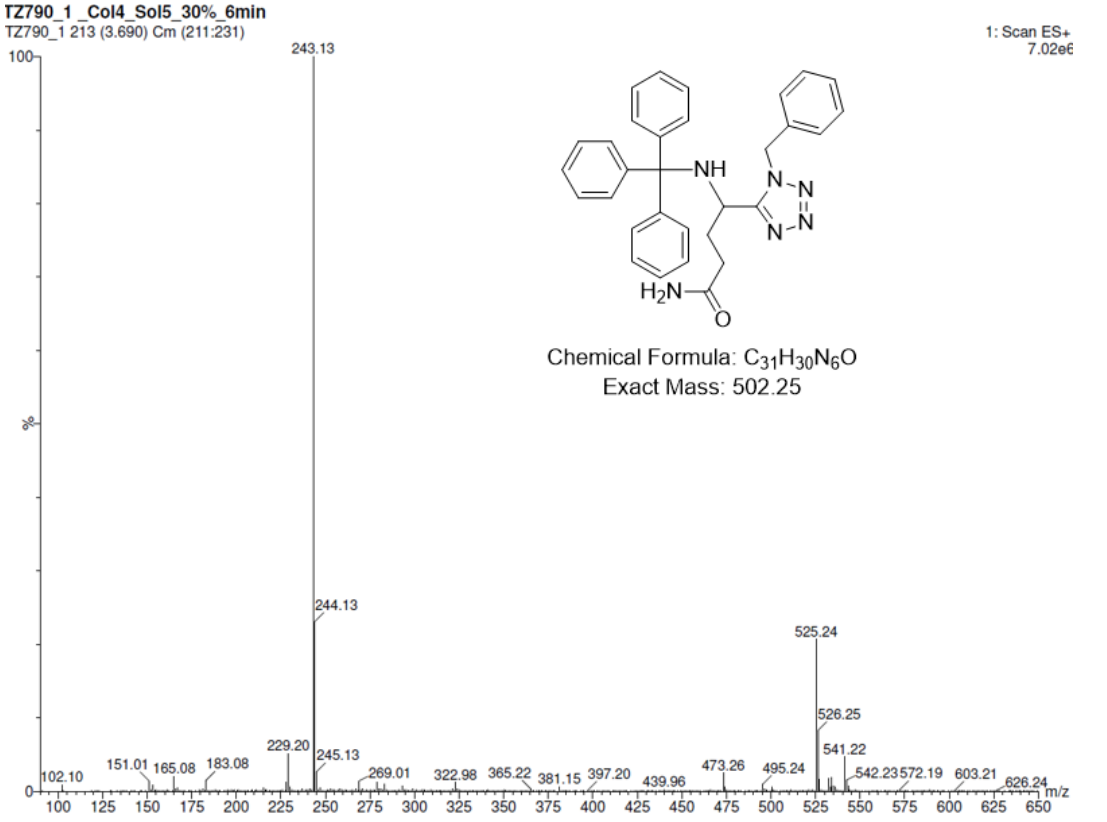

TZ788_2_Col4_Sol1_5-30%_6min
TZ788_2 177 (3.065)
1: Scan ES+
100
%
243.14
244.11
245.05
540.21
541.25
556.20
557.08
515.21
153.02
164.92
215.52
228.08
278.85
322.97
332.51
380.29
395.91
425.48
467.27
510.85
559.09
604.15
635.12
m/z
NH
N
N
N
O
O
Chemical Formula: C32H31N5O2
Exact Mass: 517.25

4-(1-Benzyl-1H-tetrazol-5-yl)-4-(tritylamino)butanamide (5m')

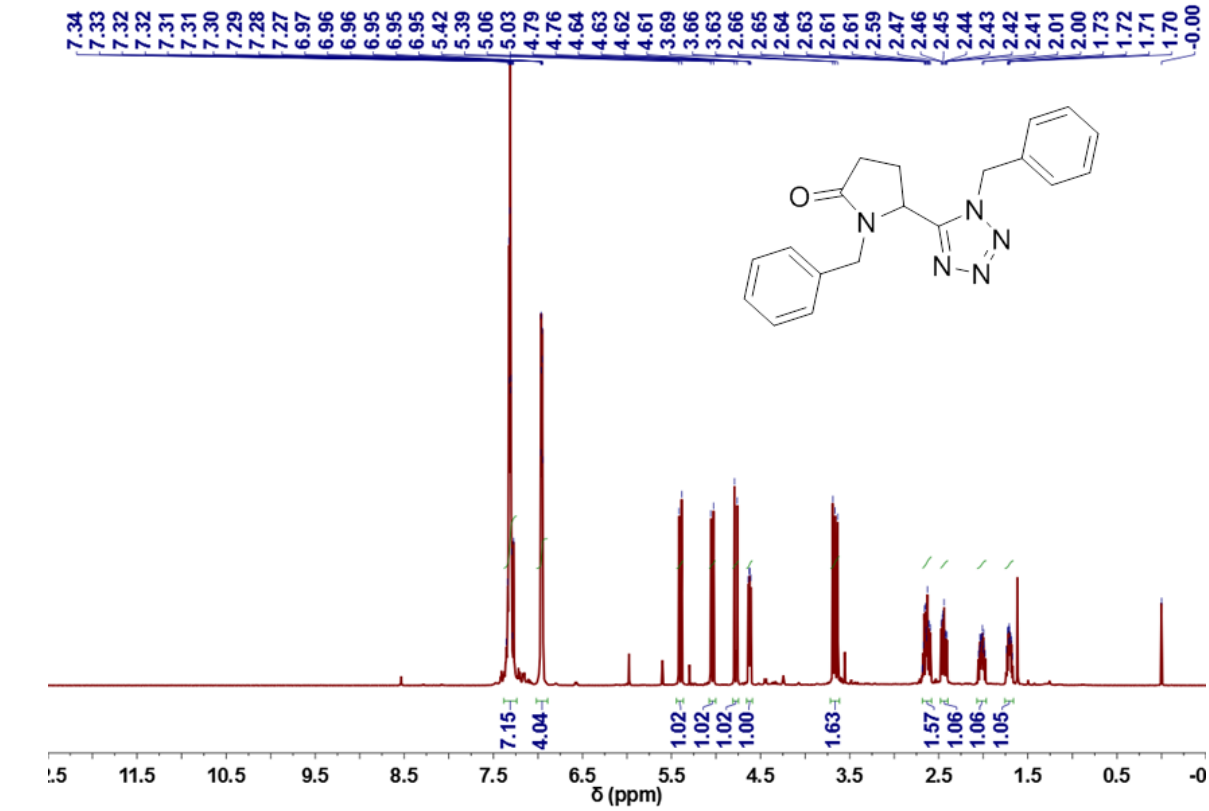


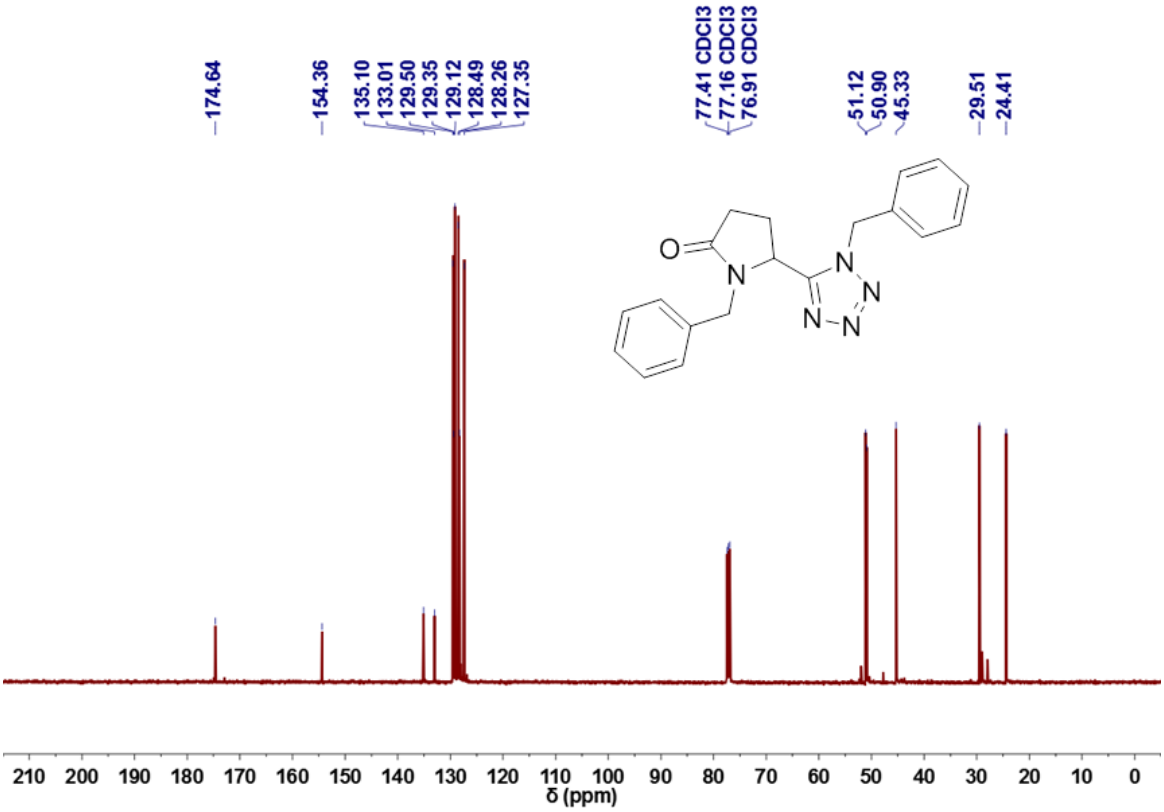


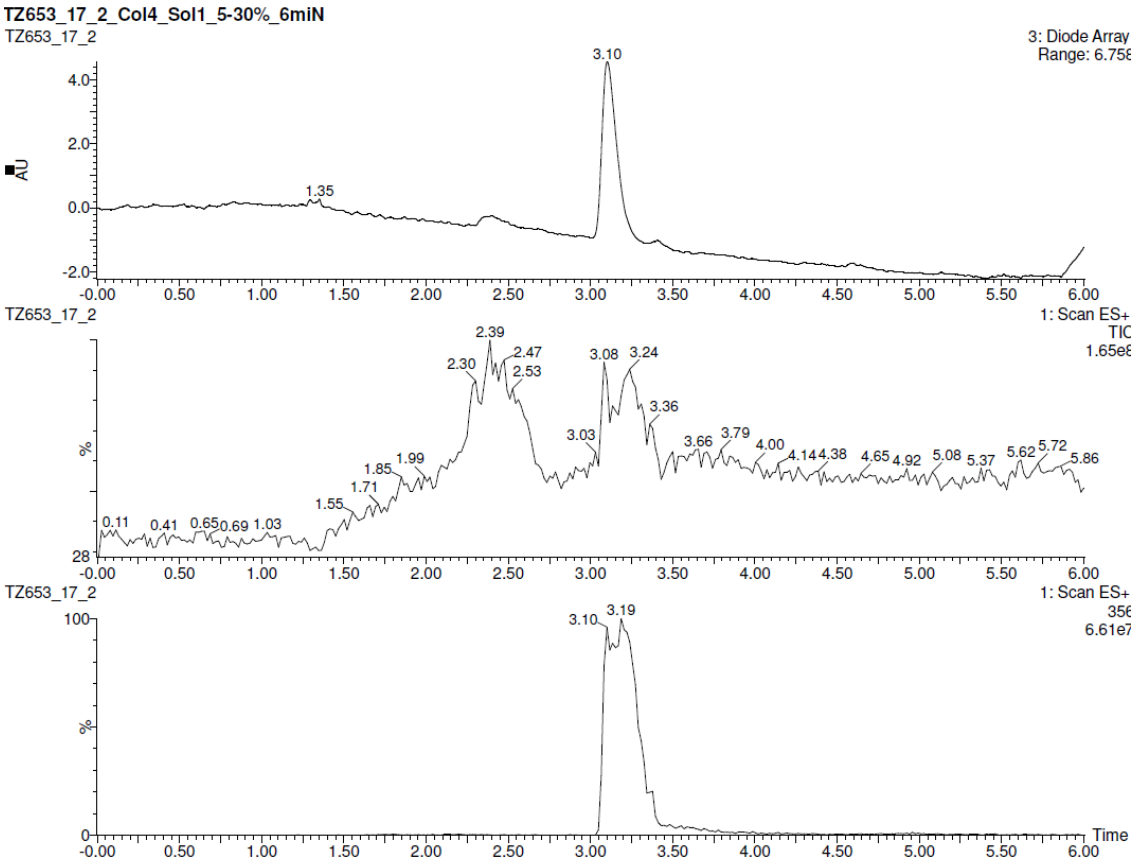

TZ790_2_Col4_sol1_5-30%_6min
TZ790_2
3: Diode Array
Range: 2.179e+
AU
3.61
1.36
TZ790_2
1: Scan ES+
TI
4.10e
%
3.67
3.81
3.92
3.95
4.12
4.19
5.86
5.22
5.29
5.48
4.30
4.38
4.73
5.15
5.58
3.52
0.25
1.03
1.17
2.44
2.51
2.77
2.82
TZ790_2
1: Scan ES+
52
6.86e
3.95
3.71
3.66
4.02
4.14
4.45
4.66
Time

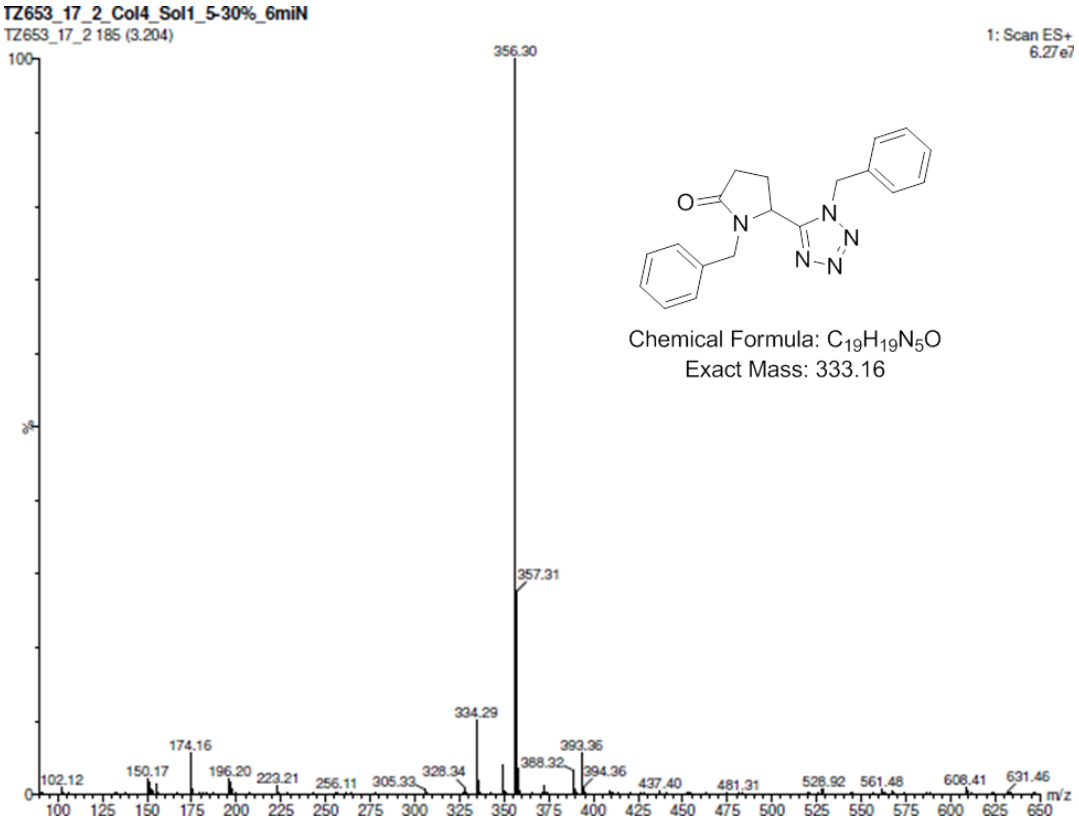

TZ790_1 _Col4_Sol5_30%_6min
TZ790_1 213 (3.690) Cm (211:231)
1: Scan ES+
7.02e6
%
243.13
244.13
525.24
526.25
541.22
229.20
245.13
102.10
151.01
165.08
183.08
269.01
322.98
365.22
381.15
397.20
439.96
473.26
495.24
542.23
572.19
603.21
626.24
m/z
NH
N
N
N
N
H2N
O
Chemical Formula: C31H30N6O
Exact Mass: 502.25

1-Benzyl-5-(1-benzyl-1H-tetrazol-5-yl)pyrrolidin-2-one (5m'')



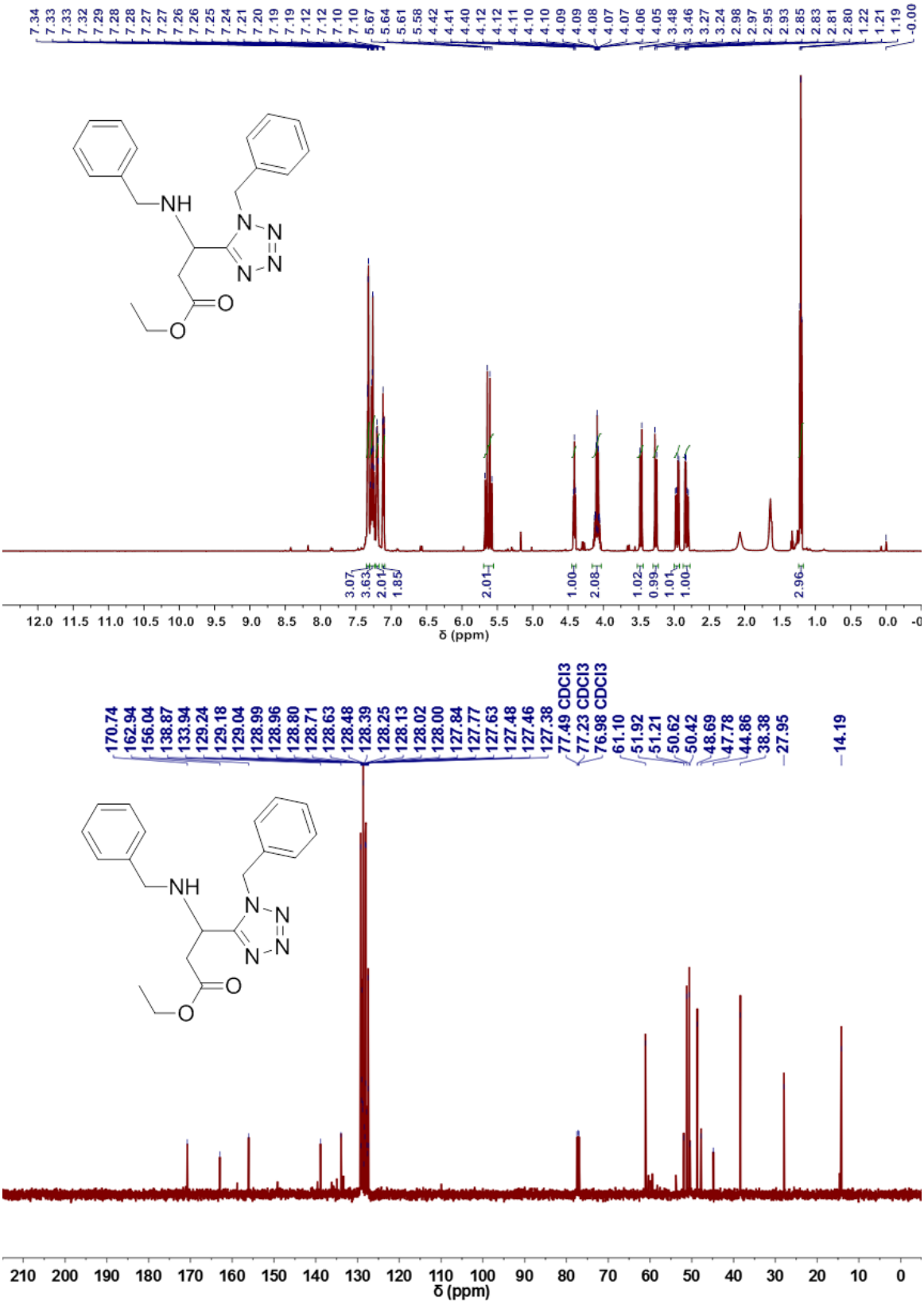


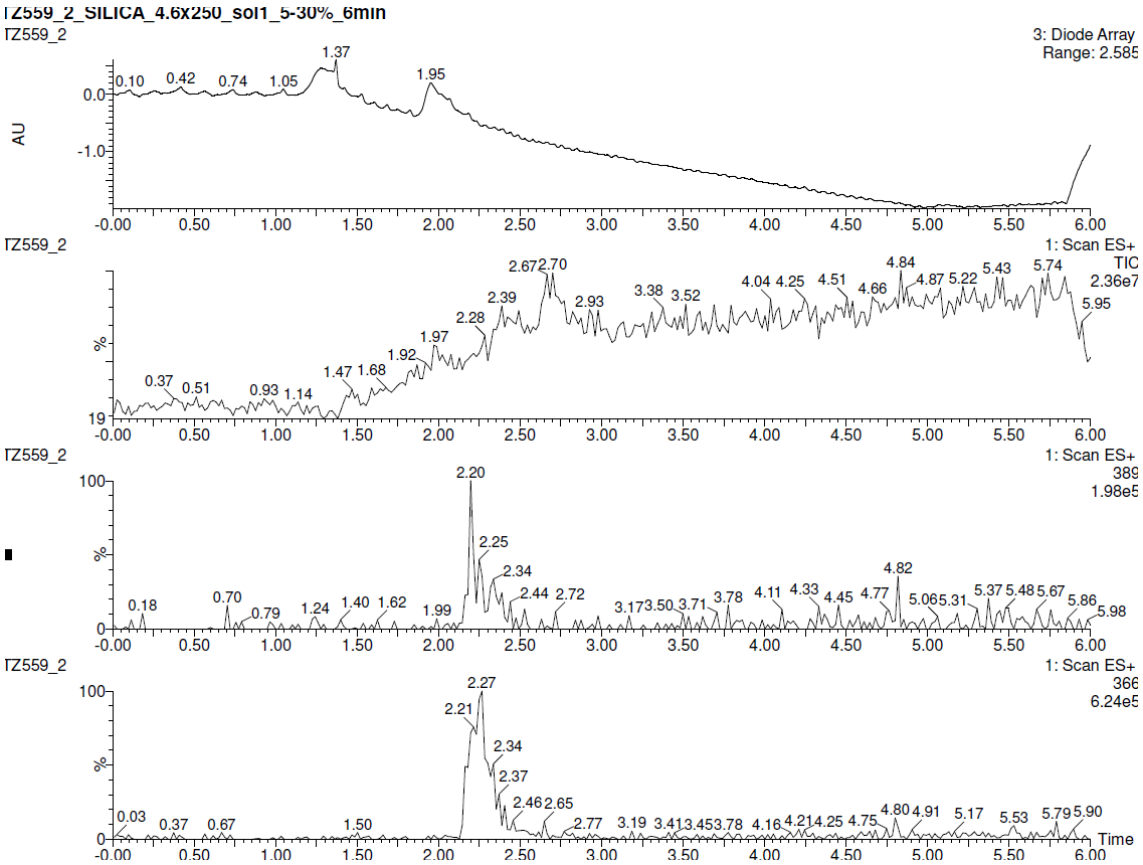


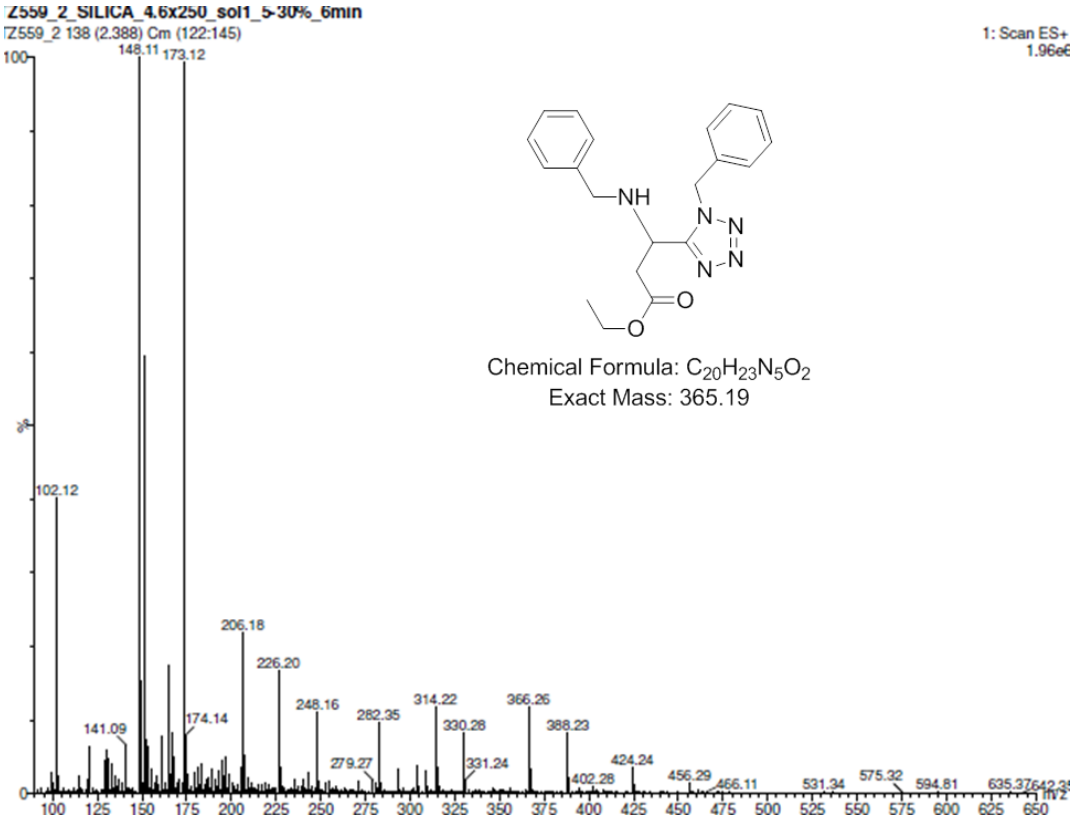


Chemical Formula: $C_{19}H_{19}N_5O$
Exact Mass: 333.16

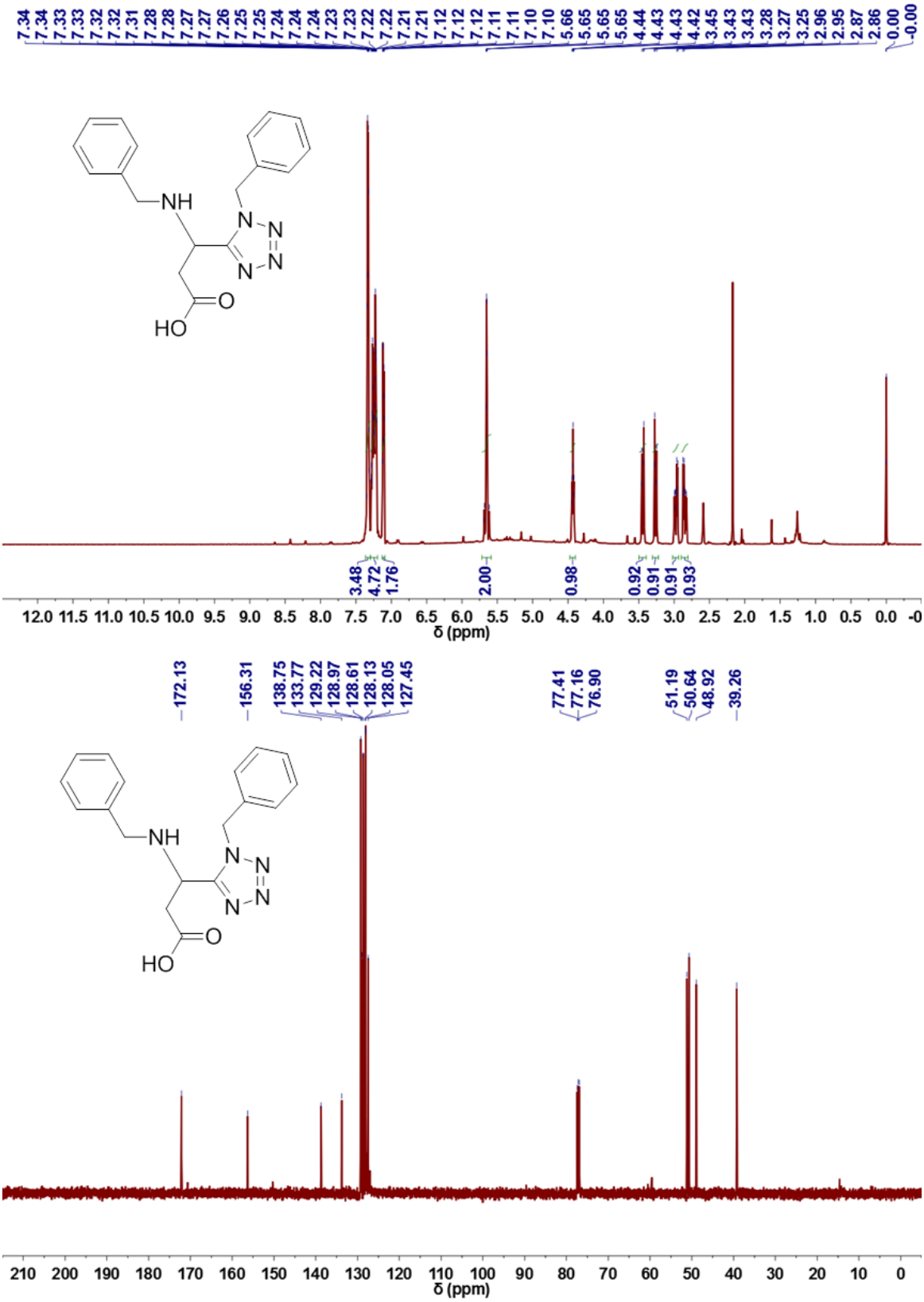
Ethyl 3-(1-benzyl-1H-tetrazol-5-yl)-3-(benzylamino)propanoate (5n)

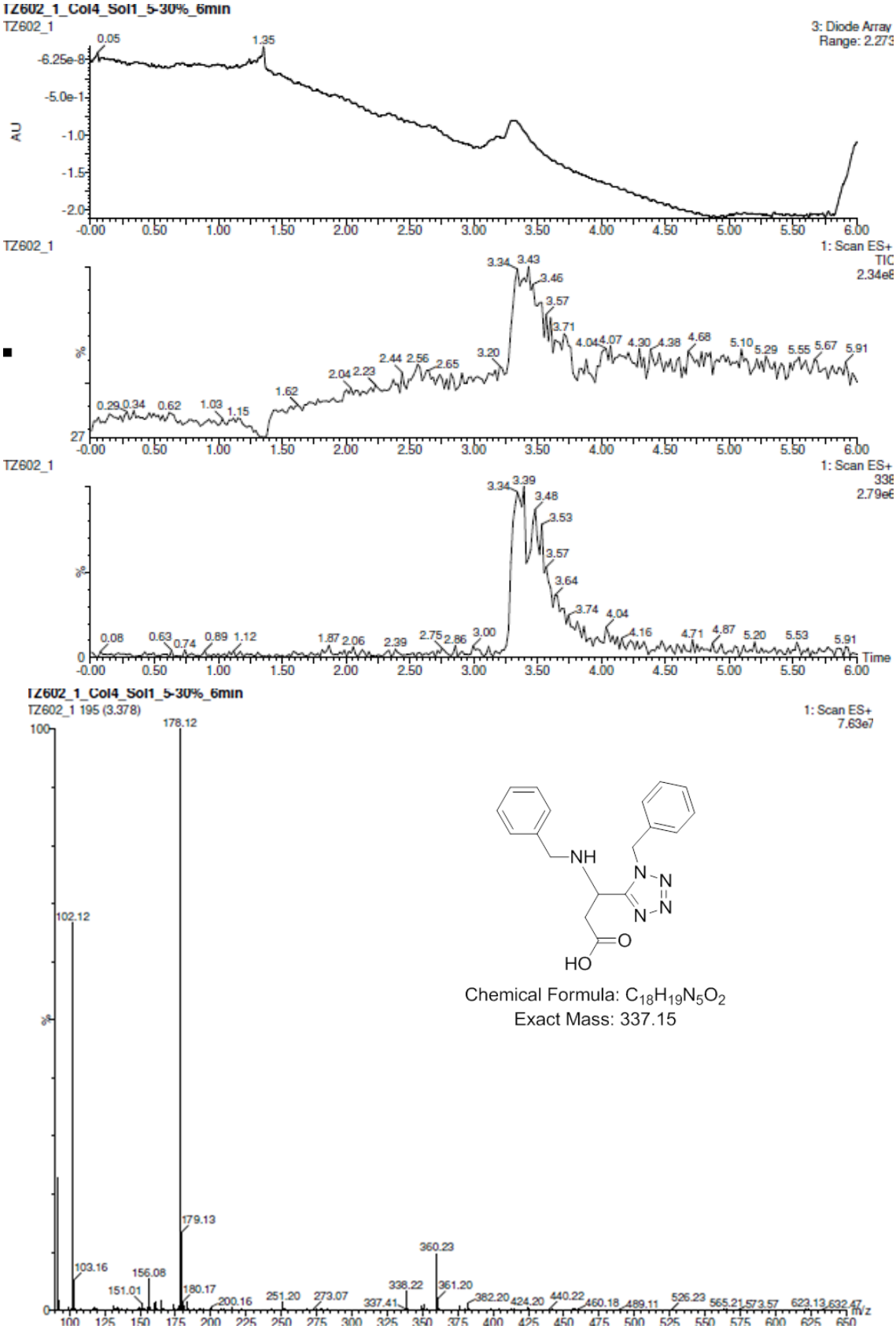



TZ559_2_SILICA_4.6x250_sol1_5-30%_6min
TZ559_2
3: Diode Array
Range: 2.585
AU
TZ559_2
1: Scan ES+
TIC
2.36e7
%
TZ559_2
1: Scan ES+
389
1.98e5
%
TZ559_2
1: Scan ES+
366
6.24e5
%
Time


TZ559_2_SILICA_4.6x250_sol1_5-30%_6min
TZ559_2 138 (2.388) Cm (122:145)
1: Scan ES+
1.96e6
%
NH
N
N
N
O
O
Chemical Formula: C20H23N5O2
Exact Mass: 365.19

3-(1-Benzyl-1H-tetrazol-5-yl)-3-(benzylamino)propanoic acid (5n')

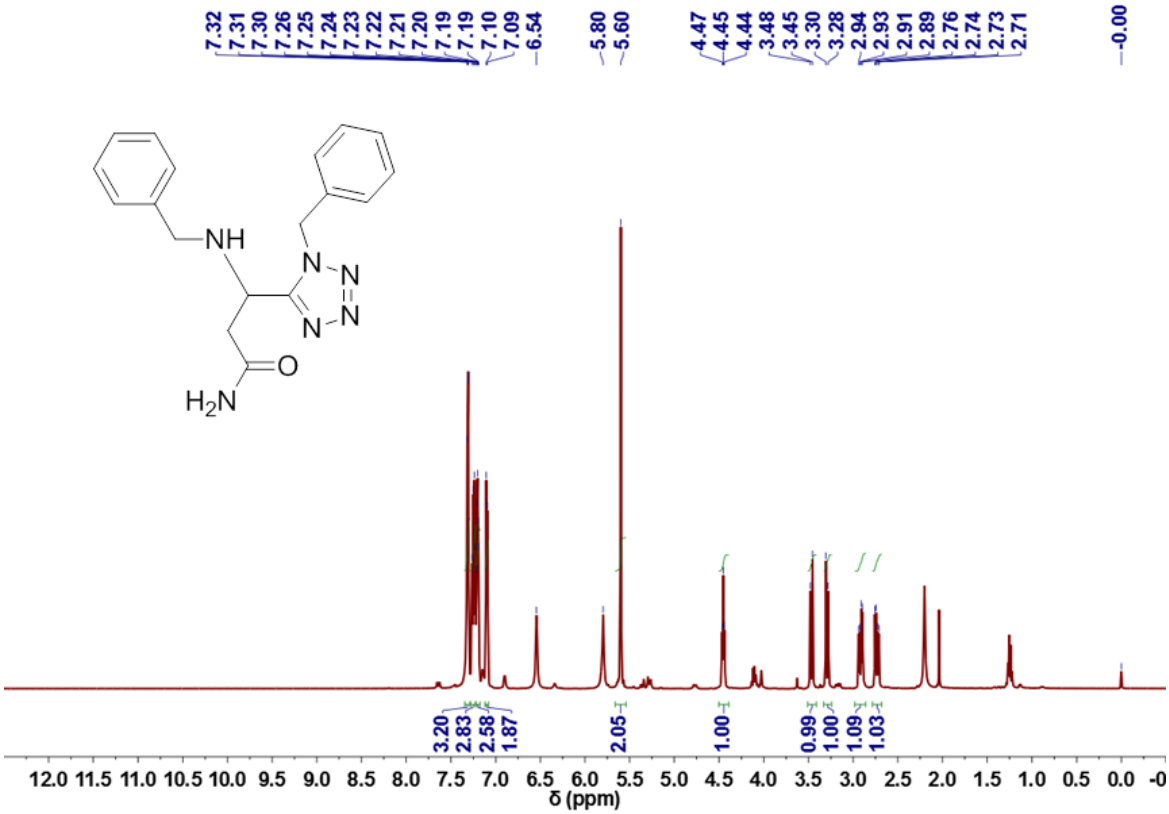


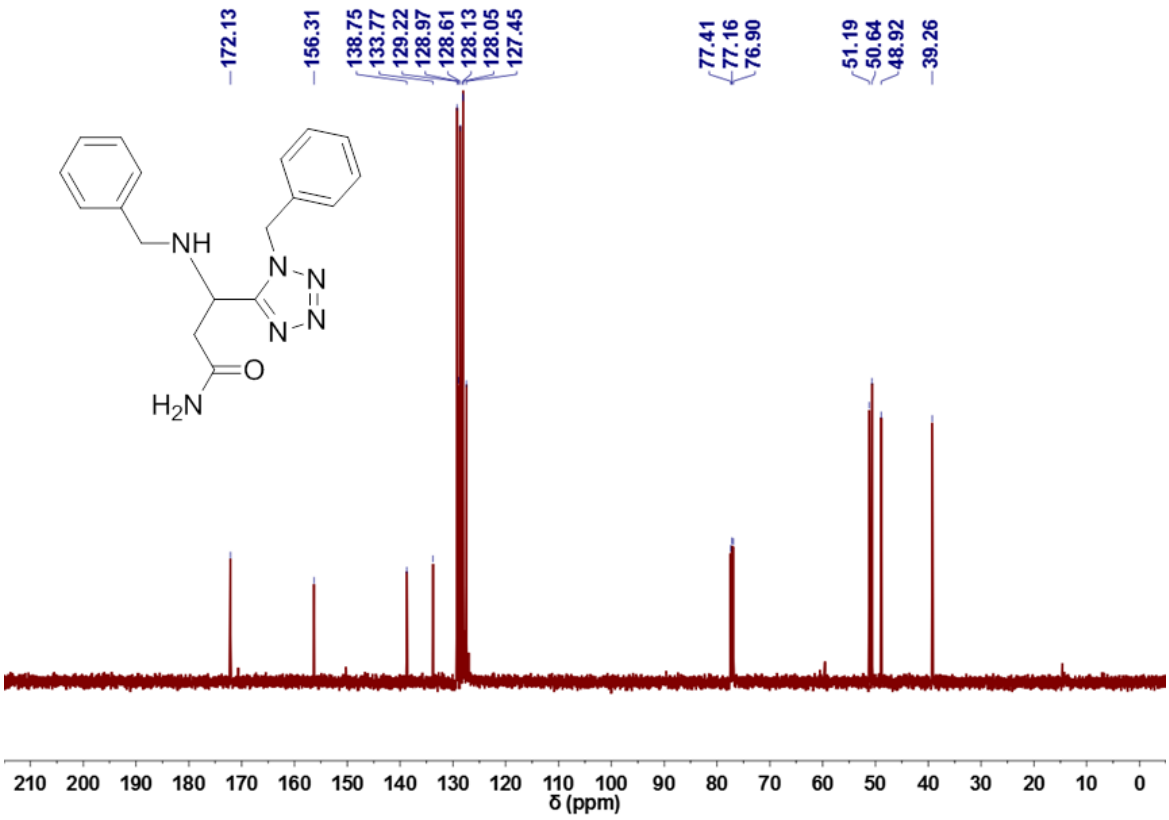


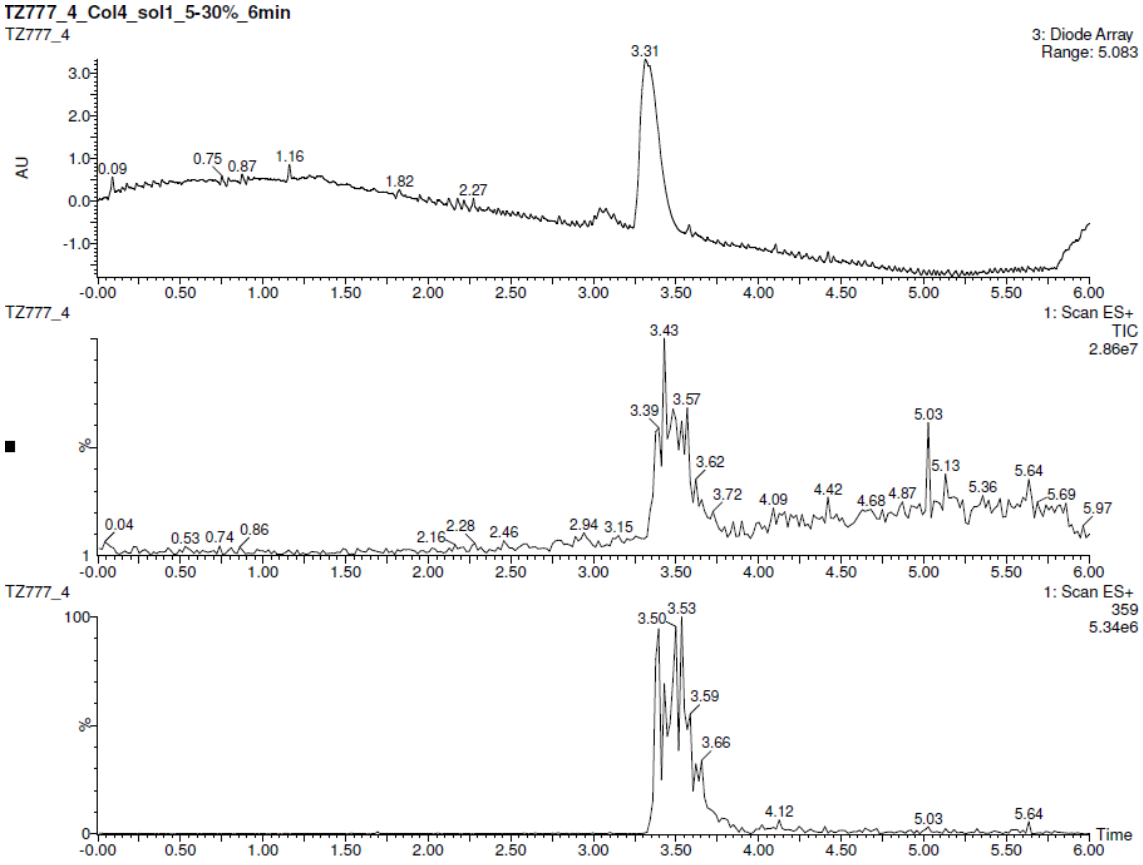
Chemical Formula: $C_{18}H_{19}N_5O_2$

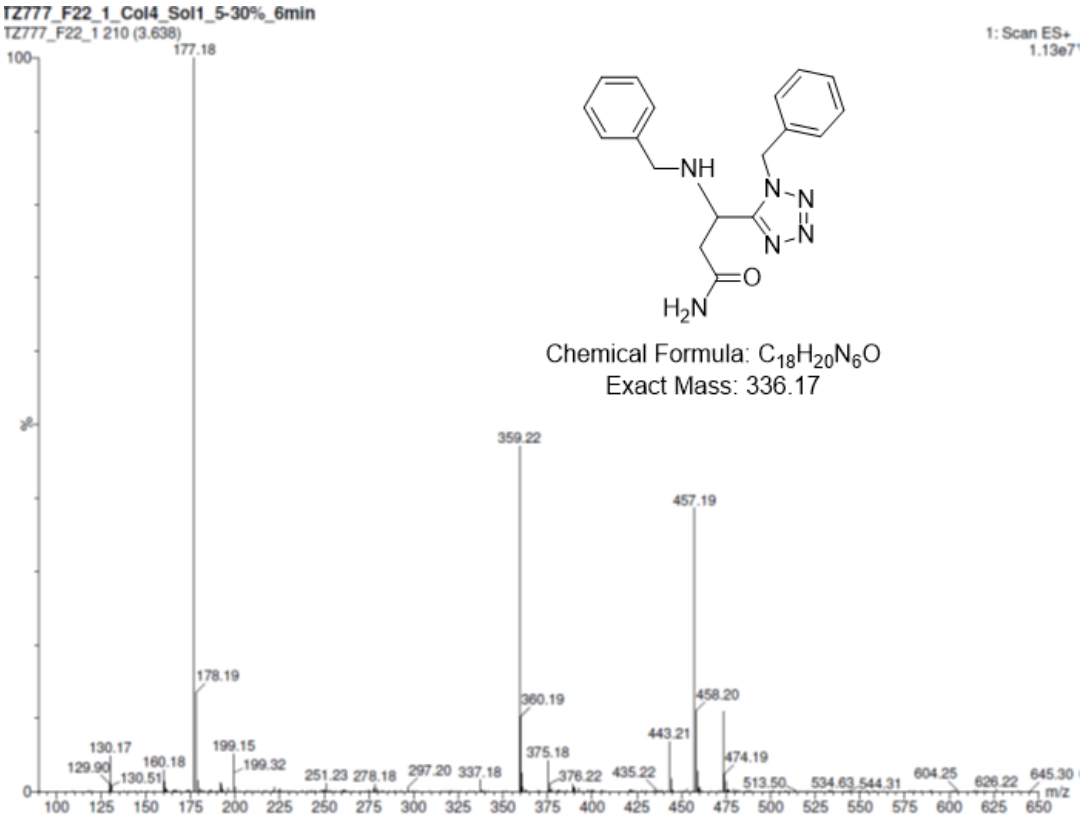
Exact Mass: 337.15

3-(1-Benzyl-1H-tetrazol-5-yl)-3-(benzylamino)propanamide (5o')

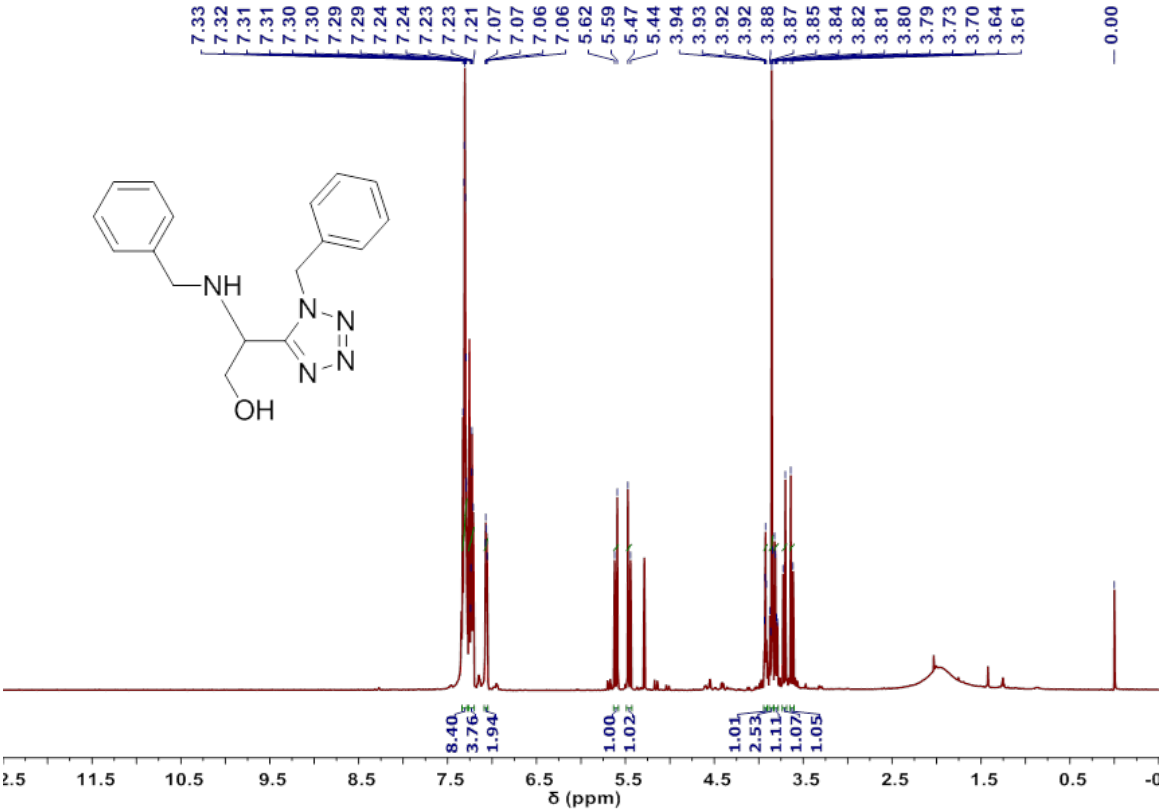


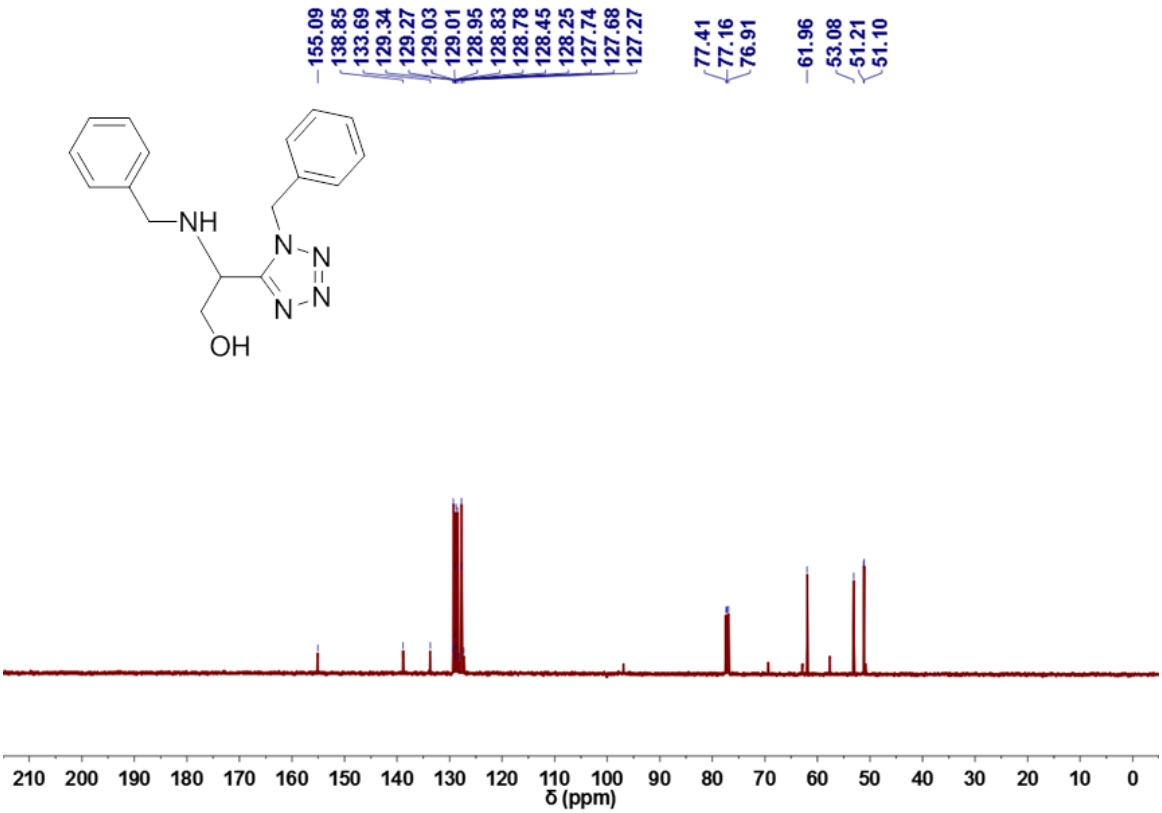


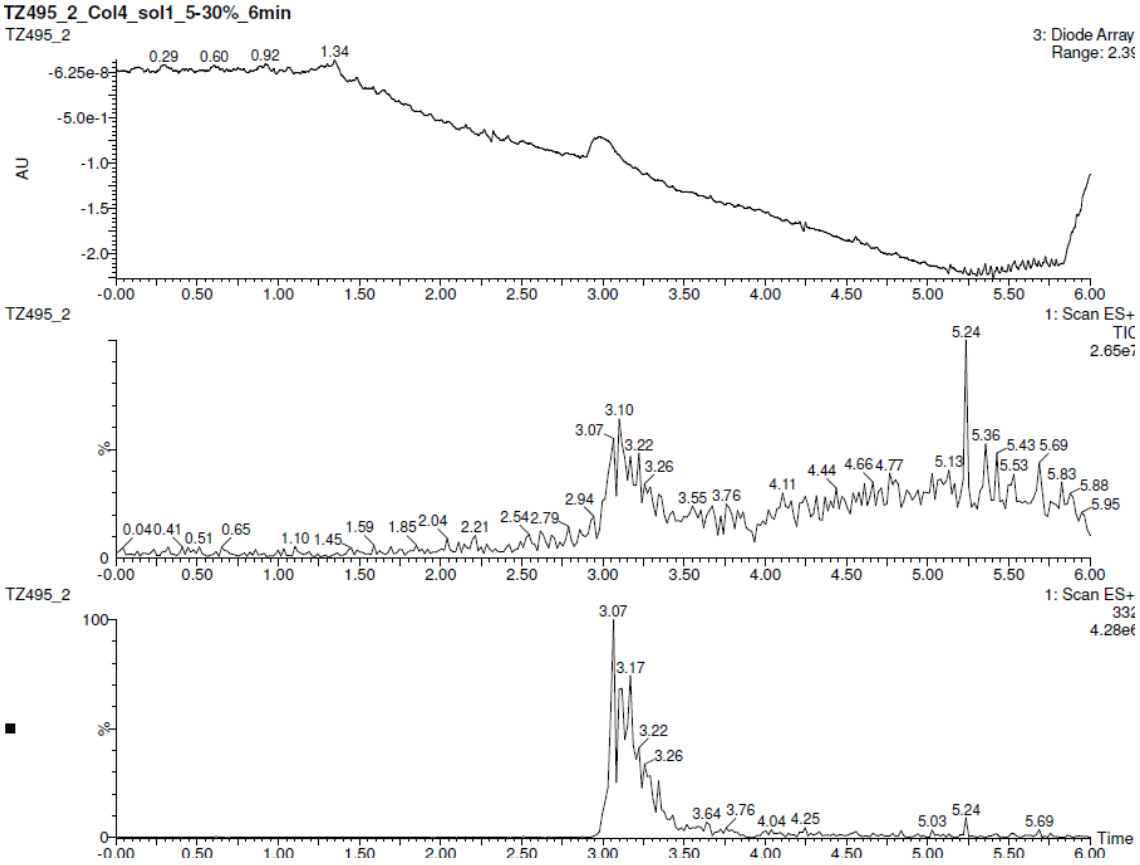

TZ777_4_Col4_sol1_5-30%_6min
TZ777_4
3: Diode Array
Range: 5.083
AU
3.31
0.09
0.75
0.87
1.16
1.82
2.27
TZ777_4
1: Scan ES+
TIC
2.86e7
%
3.43
3.39
3.57
3.62
3.72
4.09
4.42
4.68
4.87
5.03
5.13
5.36
5.64
5.69
5.97
0.04
0.53
0.74
0.86
2.16
2.28
2.46
2.94
3.15
TZ777_4
1: Scan ES+
359
5.34e6
100
%
3.50
3.53
3.59
3.66
4.12
5.03
5.64
0
Time

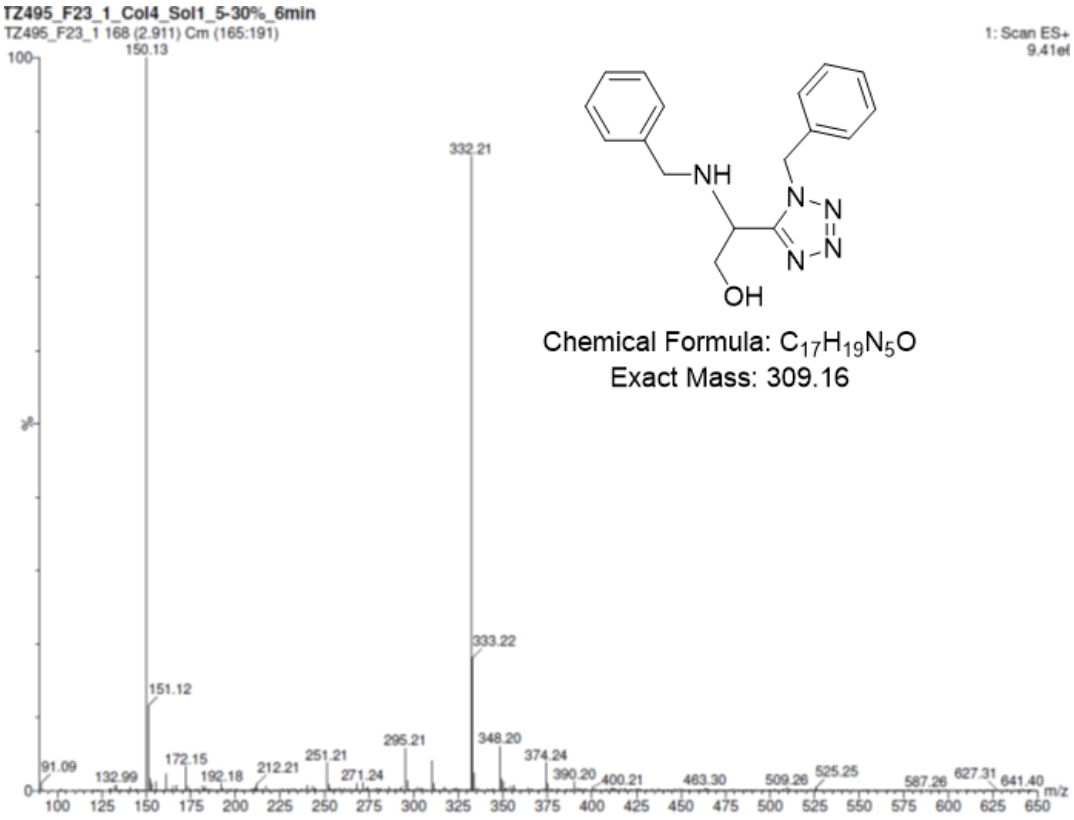

TZ777_F22_1_Col4_Sol1_5-30%_6min
TZ777_F22_1 210 (3.638)
1: Scan ES+
1.13e7
100
177.18
%
359.22
457.19
178.19
360.19
458.20
443.21
474.19
130.17
129.90
160.18
130.51
199.15
199.32
375.18
376.22
435.22
513.50
534.63
544.31
604.25
626.22
645.30
251.23
278.18
297.20
337.18
0
m/z
NH
N
N
N
N
O
H2N
Chemical Formula: C18H20N6O
Exact Mass: 336.17

2-(1-Benzyl-1H-tetrazol-5-yl)-2-(benzylamino)ethan-1-ol (5p)

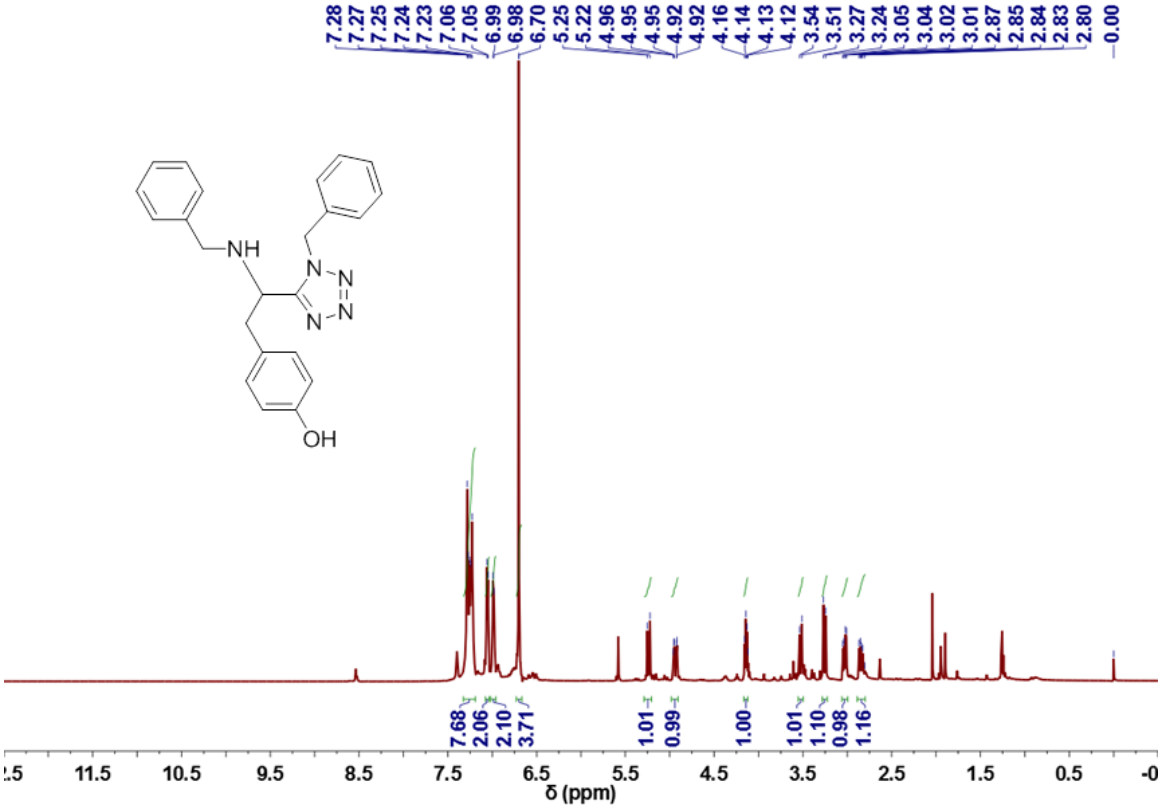


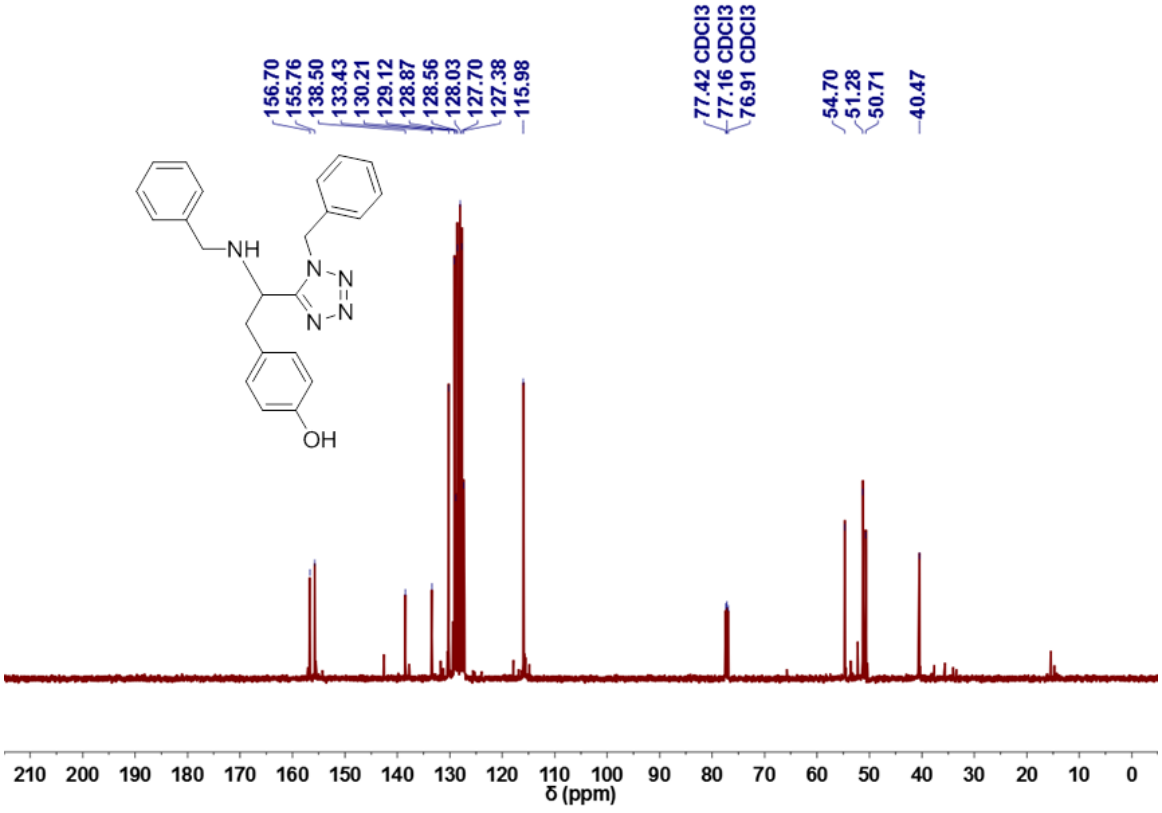


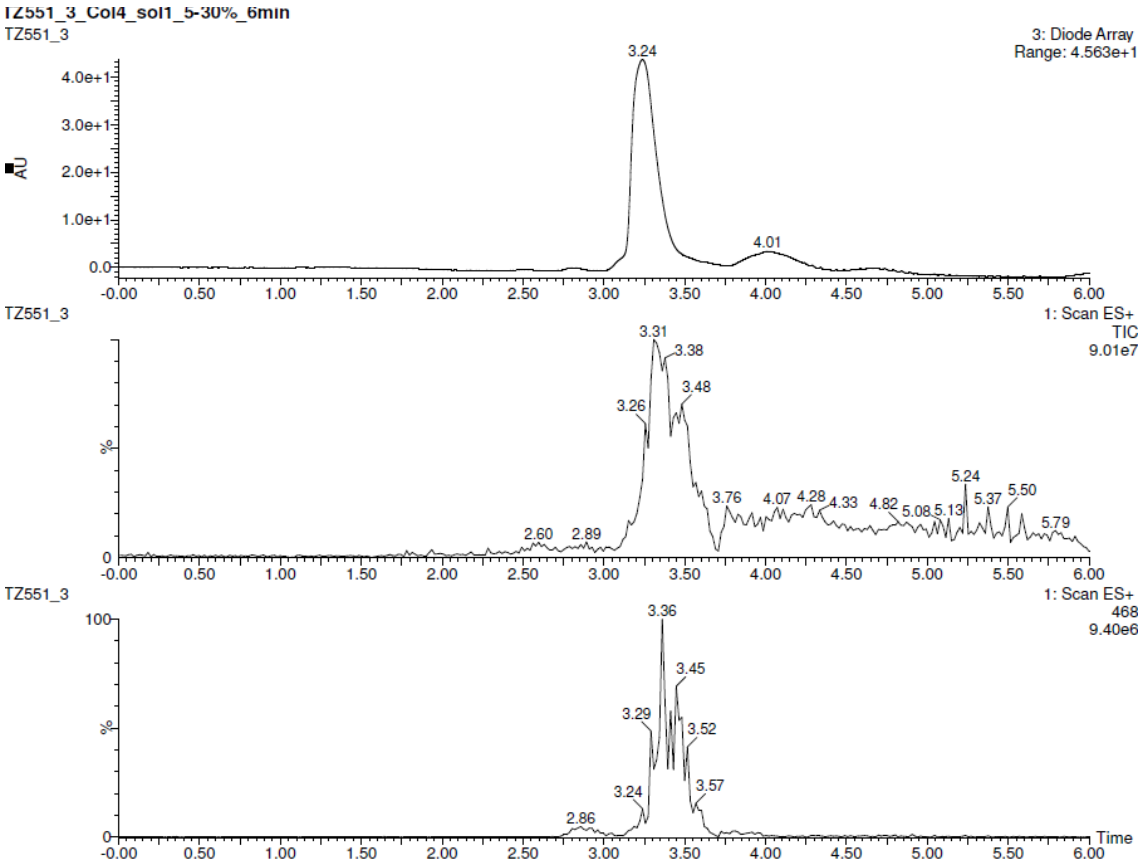

TZ495_2_Col4_sol1_5-30%_6min
TZ495_2
3: Diode Array
AU
TZ495_2
1: Scan ES+
TIC
TZ495_2
1: Scan ES+
Time

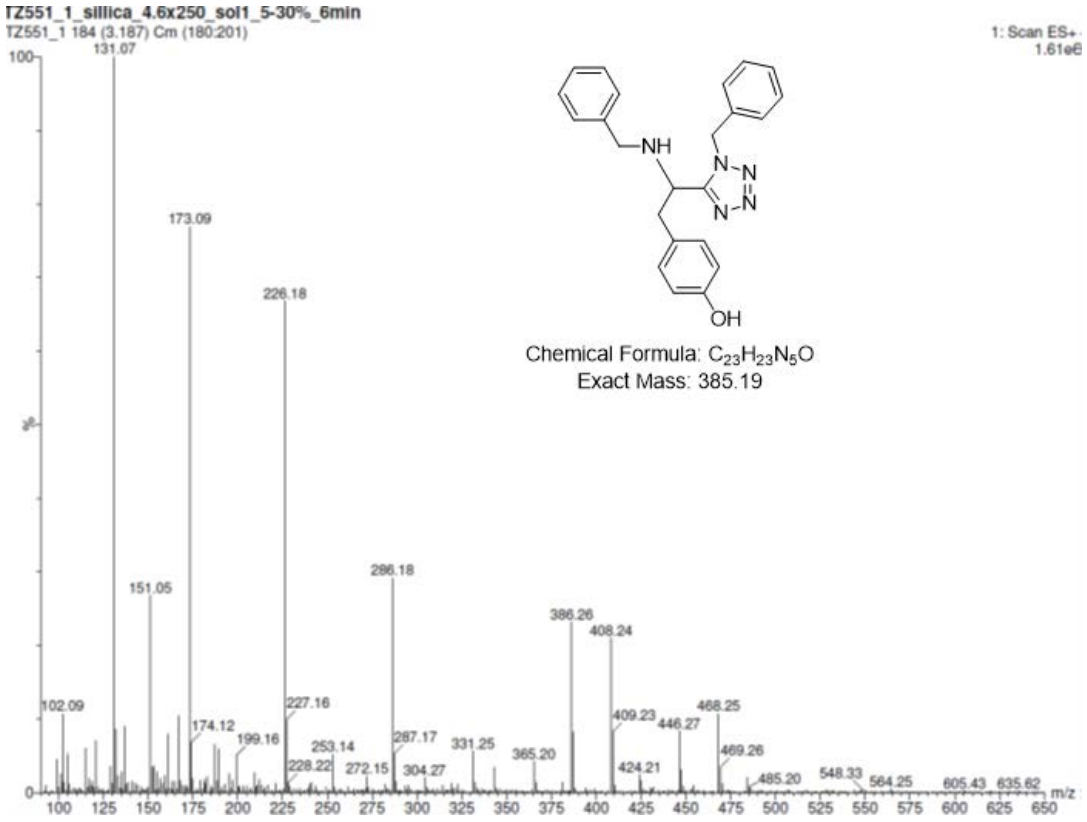

TZ495_F23_1_Col4_Sol1_5-30%_6min
TZ495_F23_1 168 (2.911) Cm (165:191)
1: Scan ES+
NH
N
N
N
OH
Chemical Formula: C17H19N5O
Exact Mass: 309.16
m/z

4-(2-(1-Benzyl-1H-tetrazol-5-yl)-2-(benzylamino)ethyl)phenol (5q)

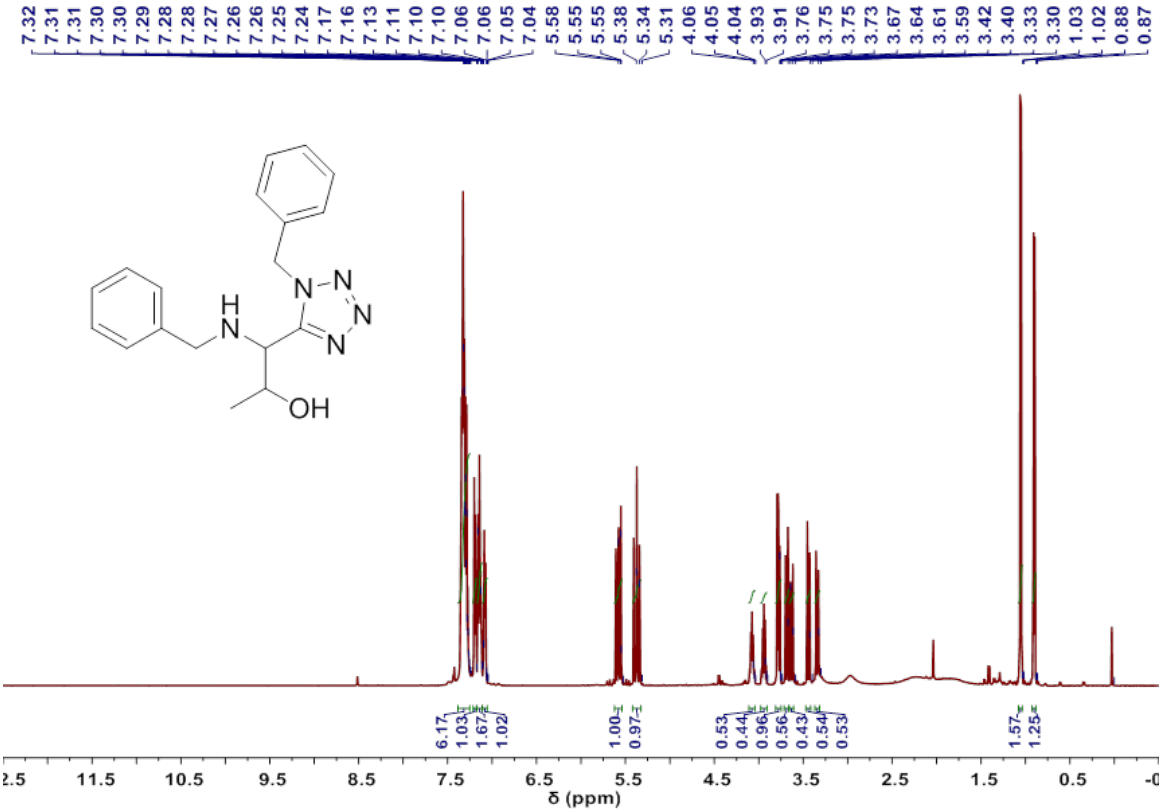


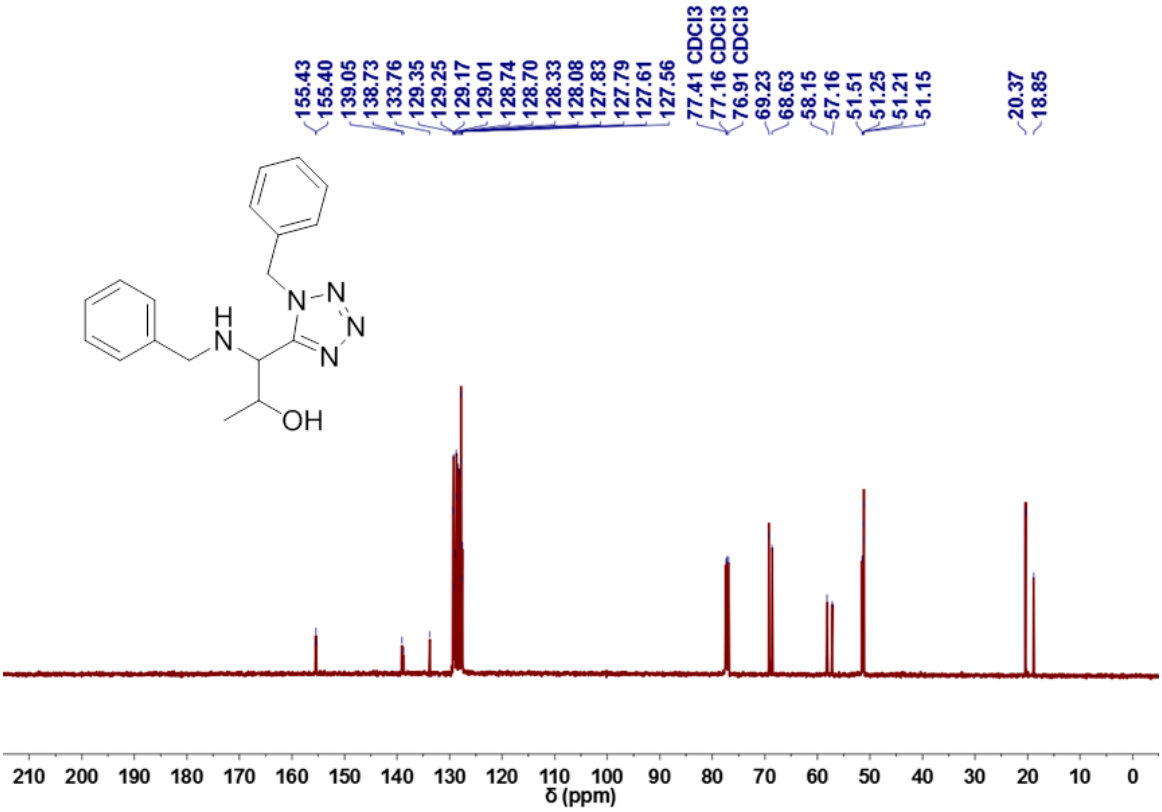


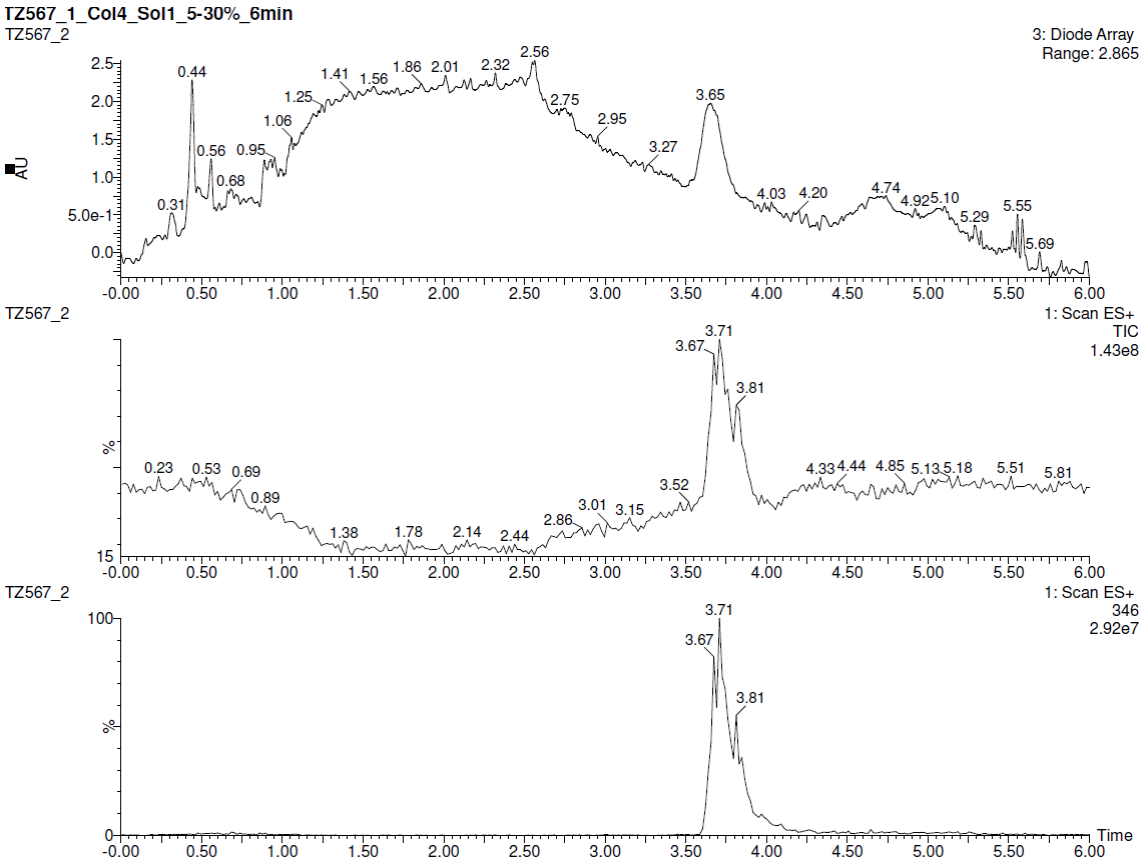

TZ551_3_Col4_sol1_5-30%_6min
TZ551_3
3: Diode Array
Range: 4.563e+1
AU
3.24
4.01
TZ551_3
1: Scan ES+
TIC
9.01e7
%
3.31
3.38
3.48
3.26
2.60
2.89
3.76
4.07
4.28
4.33
4.82
5.08
5.13
5.24
5.37
5.50
5.79
TZ551_3
1: Scan ES+
468
9.40e6
%
3.36
3.45
3.29
3.52
3.24
3.57
2.86
Time

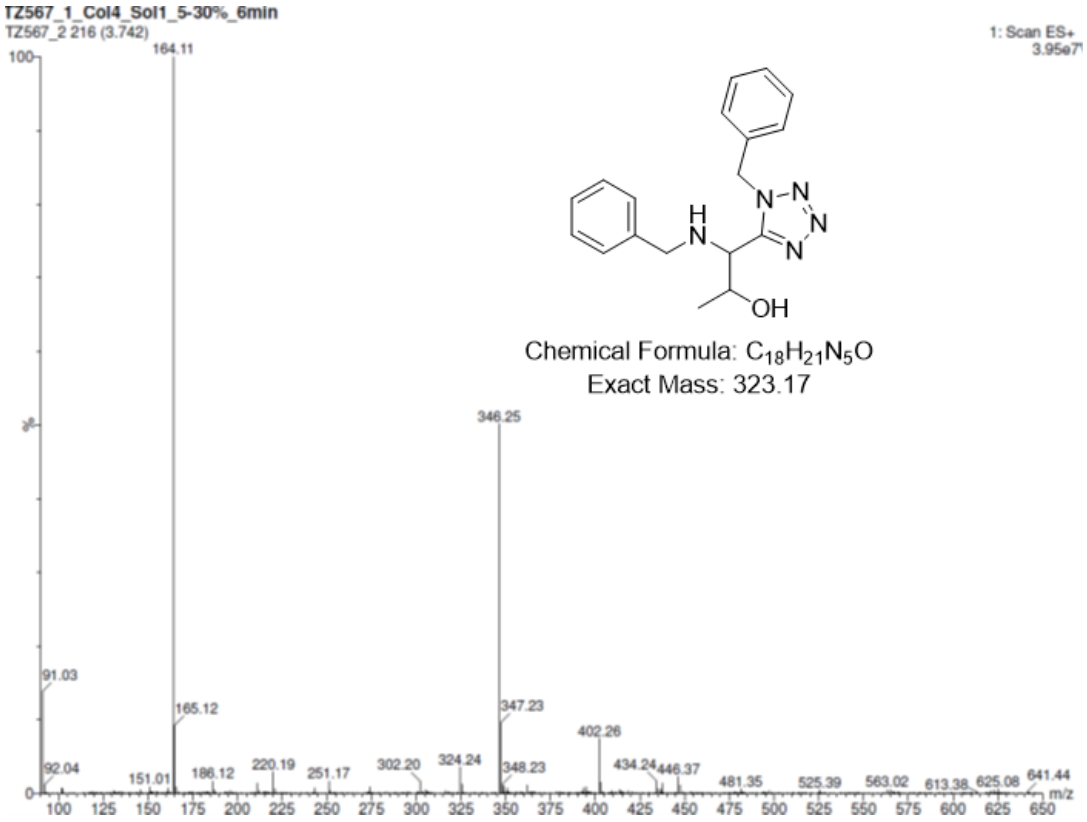

TZ551_1_sillica_4.6x250_sol1_5-30%_6min
TZ551_1 184 (3.187) Cm (180:201)
1: Scan ES+
1.61e6
131.07
173.09
226.18
151.05
286.18
386.26
408.24
102.09
227.16
174.12
199.16
253.14
287.17
331.25
365.20
409.23
446.27
468.25
469.26
228.22
272.15
304.27
424.21
485.20
548.33
564.25
605.43
635.62
m/z
NH
N
N
N
OH
Chemical Formula: C23H23N5O
Exact Mass: 385.19

1-(1-Benzyl-1H-tetrazol-5-yl)-1-(benzylamino)propan-2-ol (5r)





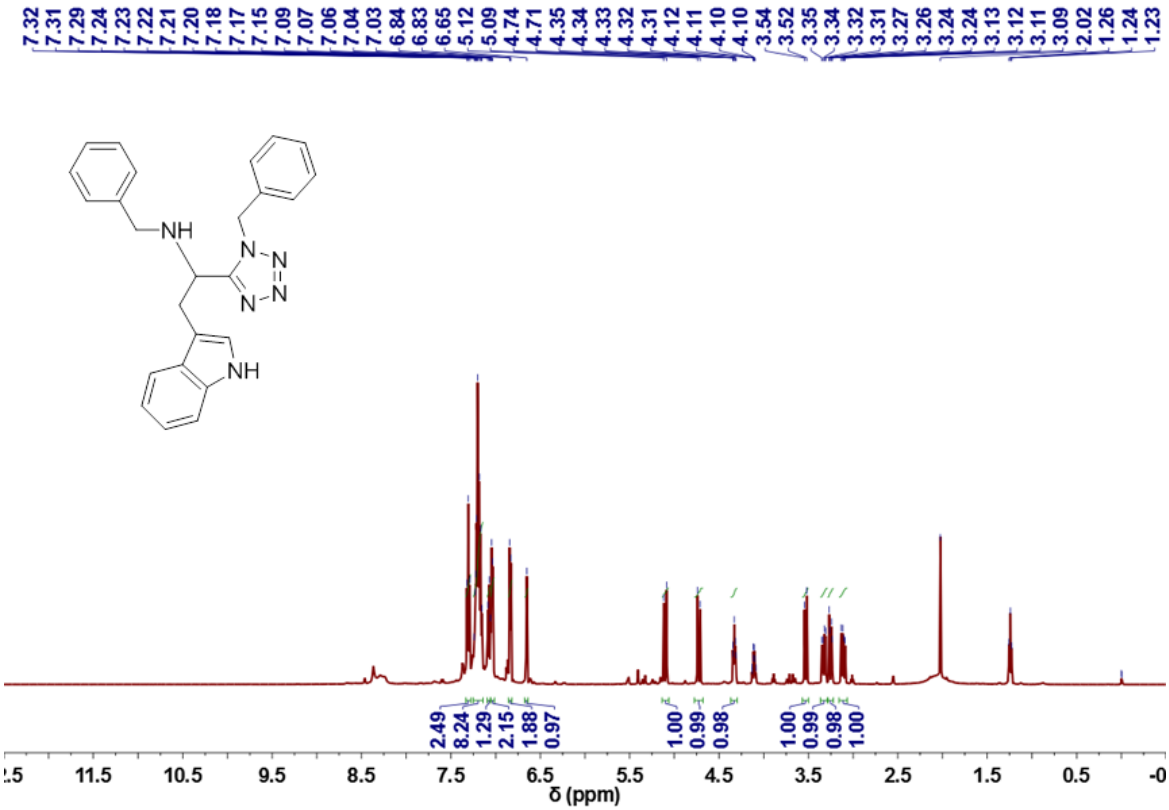


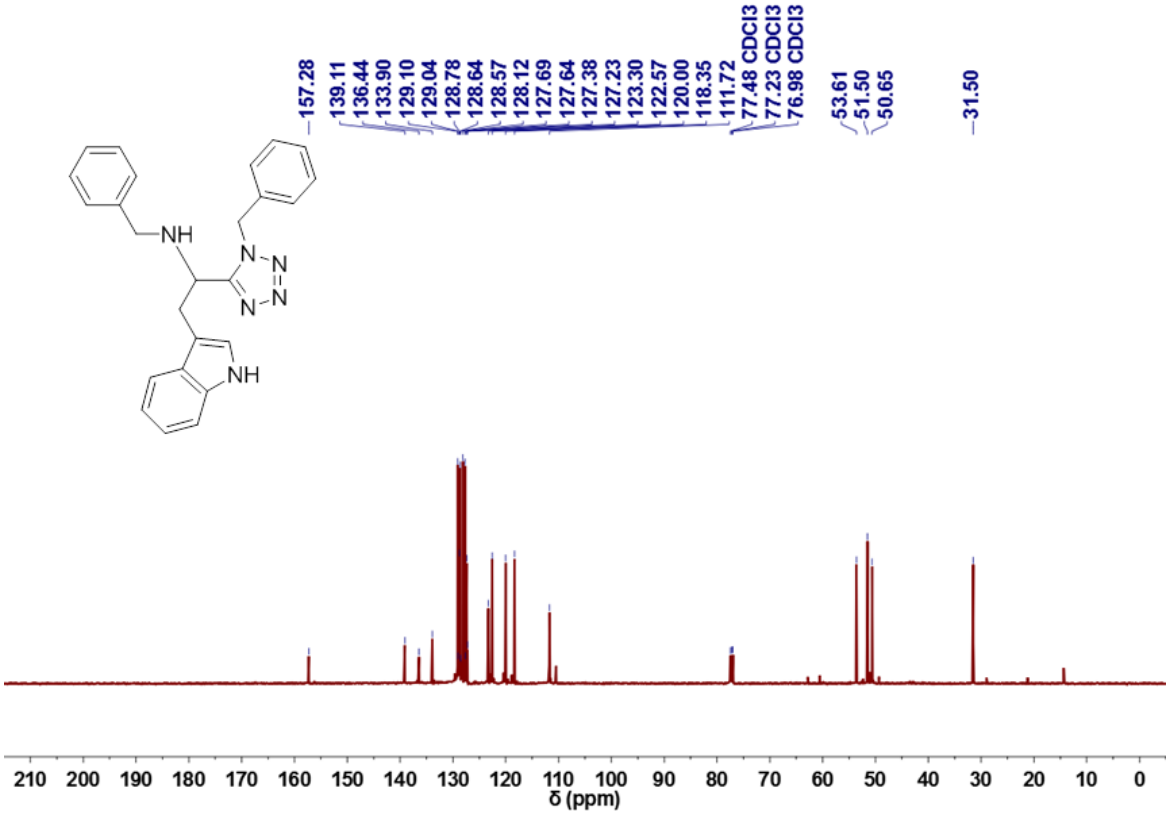


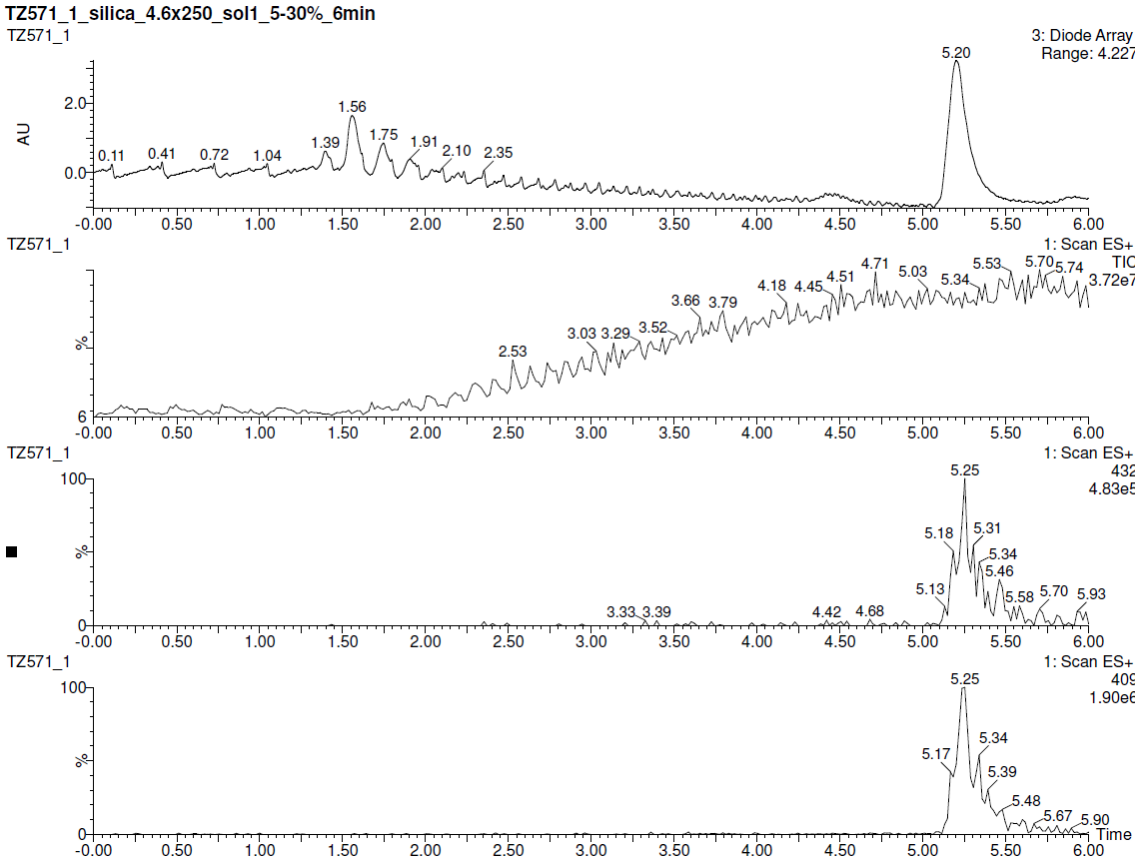
Chemical Formula: $C_{18}H_{21}N_5O$

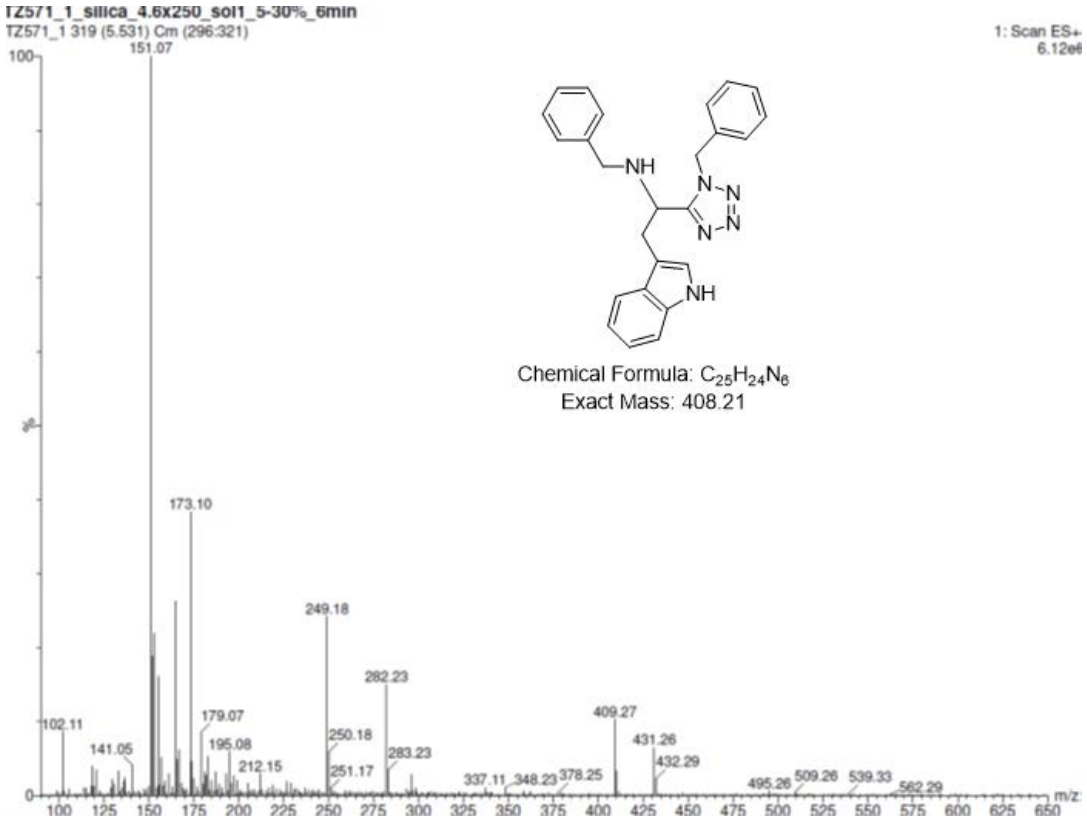
Exact Mass: 323.17

***N*-Benzyl-1-(1-benzyl-1H-tetrazol-5-yl)-2-(1H-indol-3-yl)ethanamine (5s)**

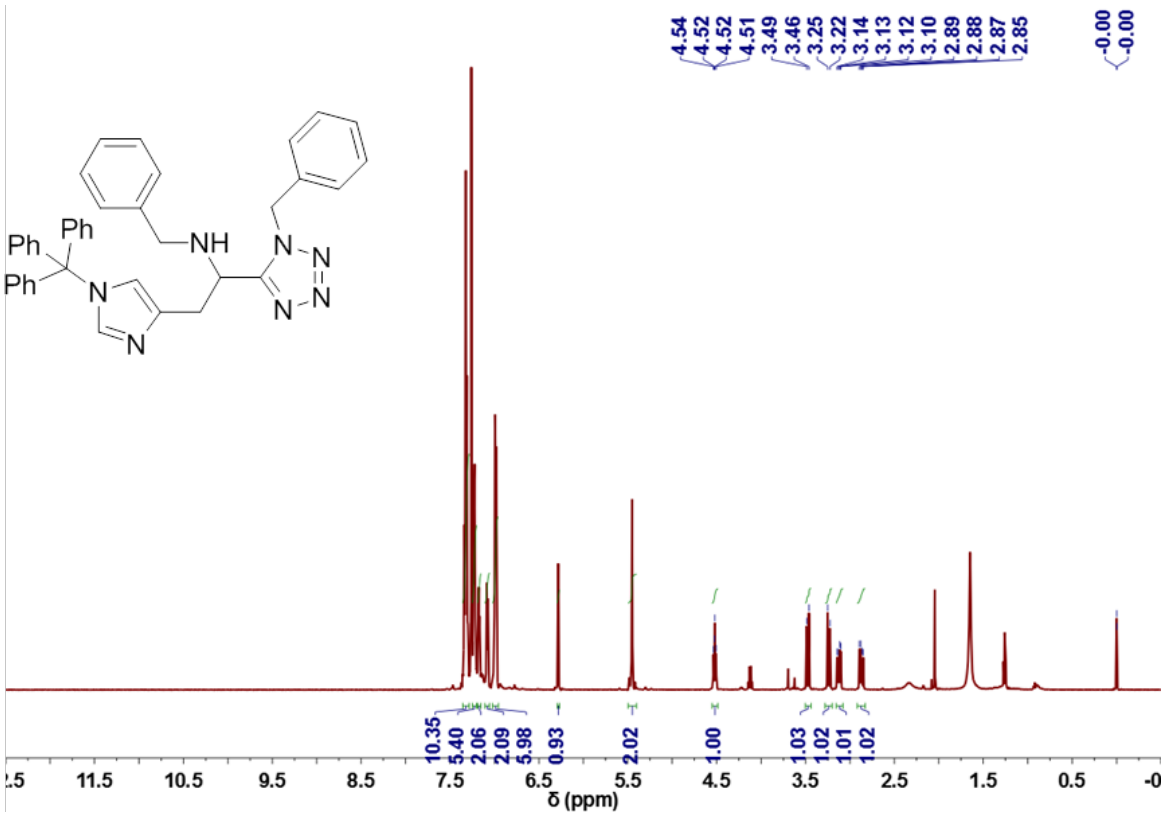


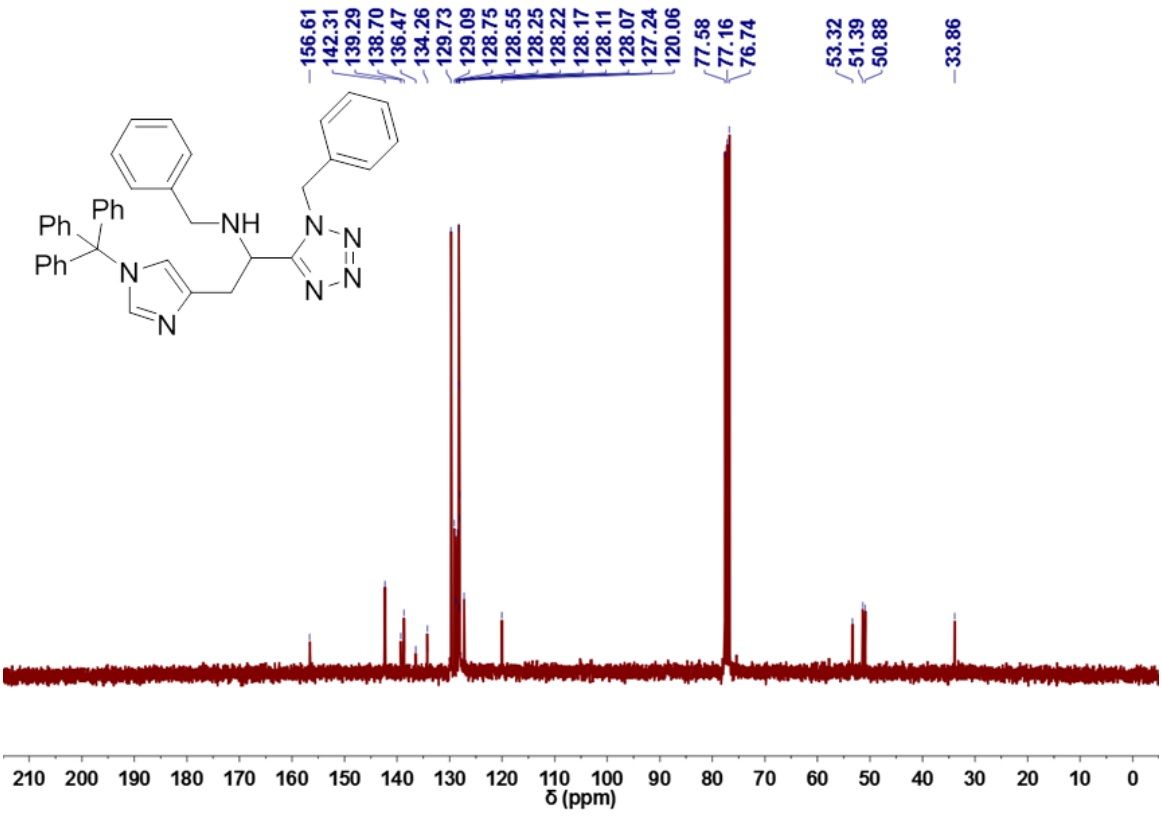


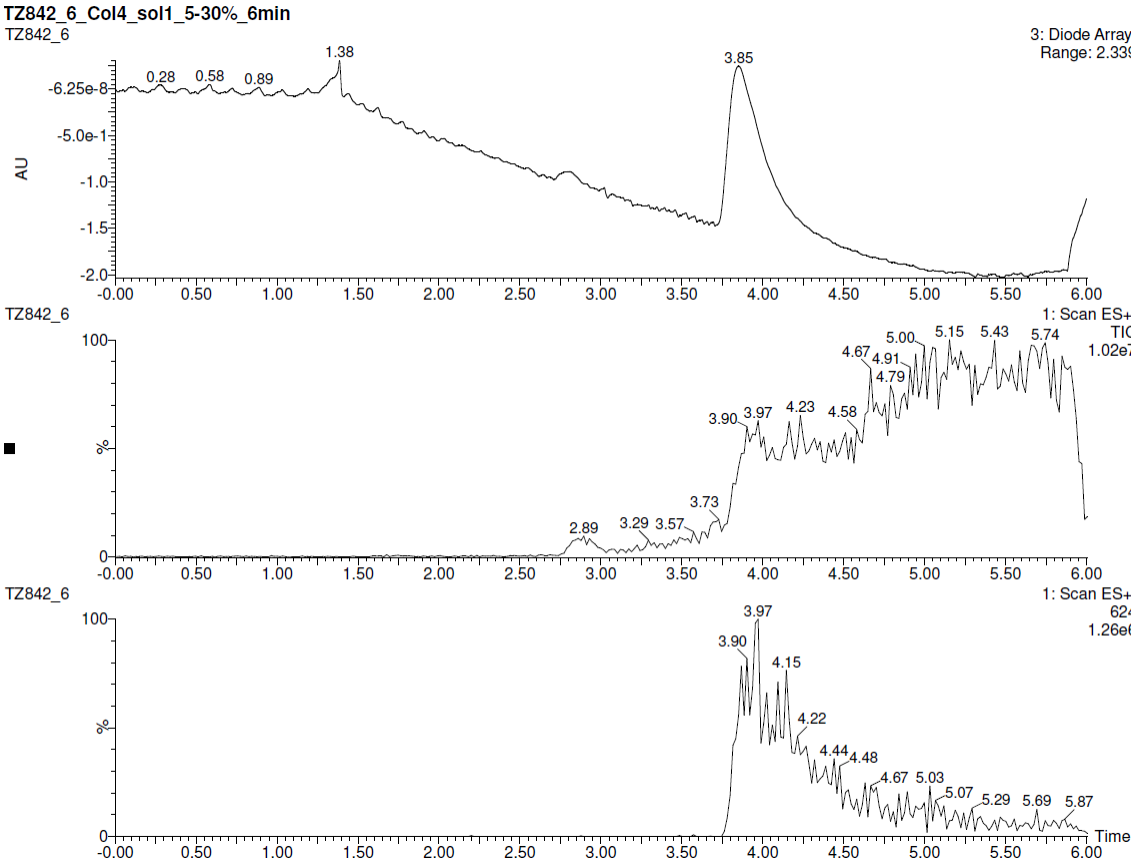

TZ571_1_silica_4.6x250_sol1_5-30%_6min
TZ571_1
3: Diode Array
Range: 4.227
AU
5.20
1.56
1.75
1.91
1.39
2.10
2.35
0.11
0.41
0.72
1.04
TZ571_1
1: Scan ES+
TIC
3.72e7
%
2.53
3.03
3.29
3.52
3.66
3.79
4.18
4.45
4.51
4.71
5.03
5.34
5.53
5.70
5.74
TZ571_1
1: Scan ES+
4.83e5
%
5.25
5.18
5.31
5.34
5.46
5.13
5.58
5.70
5.93
3.33
3.39
4.42
4.68
TZ571_1
1: Scan ES+
1.90e6
%
5.25
5.17
5.34
5.39
5.48
5.67
5.90
Time

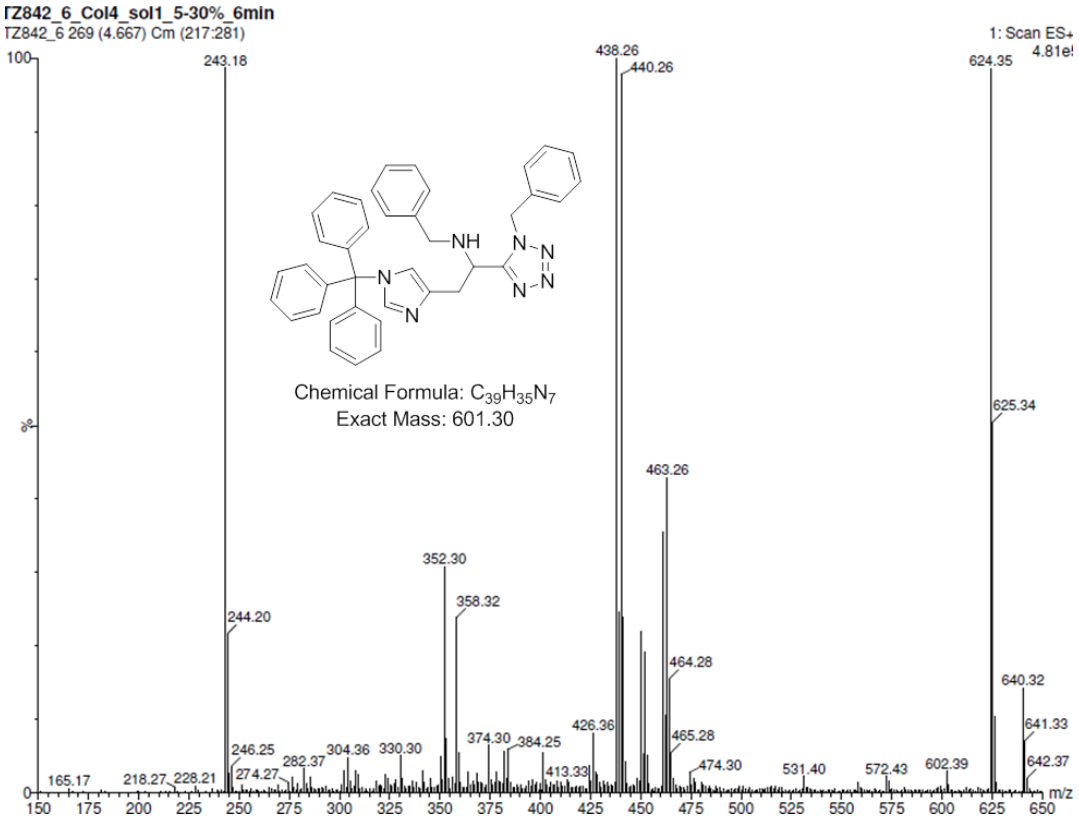

TZ571_1_silica_4.6x250_sol1_5-30%_6min
TZ571_1 319 (5.531) Cm (296:321)
1: Scan ES+
6.12e6
%
151.07
173.10
249.18
282.23
102.11
141.05
179.07
195.08
212.15
250.18
251.17
283.23
337.11
348.23
378.25
409.27
431.26
432.29
495.26
509.26
539.33
562.29
m/z
NH
N
N
N
NH
Chemical Formula: C25H24N6
Exact Mass: 408.21

***N*-Benzyl-1-(1-benzyl-1H-tetrazol-5-yl)-2-(1-trityl-1H-imidazol-4-yl)ethanamine (5t)**

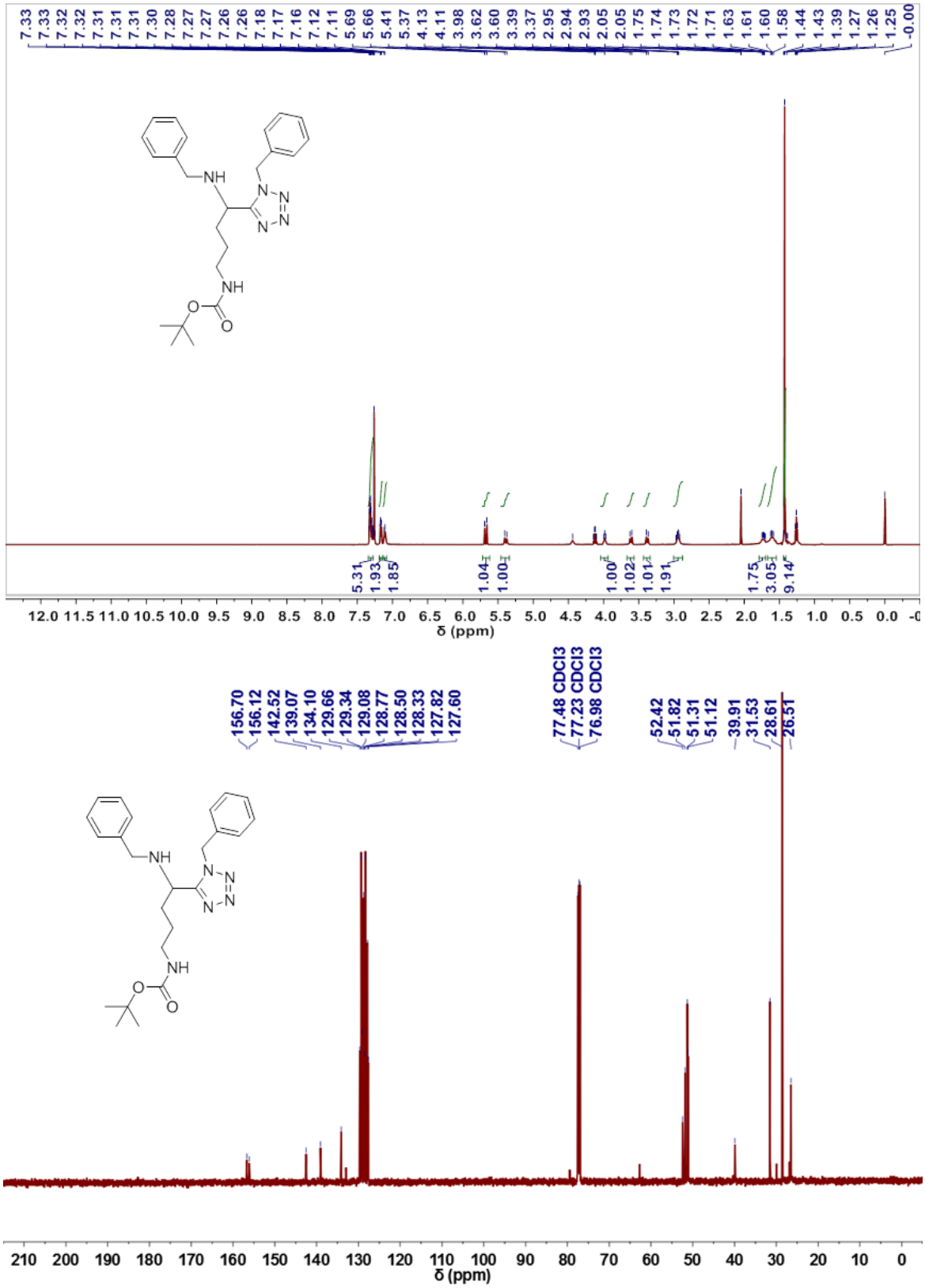


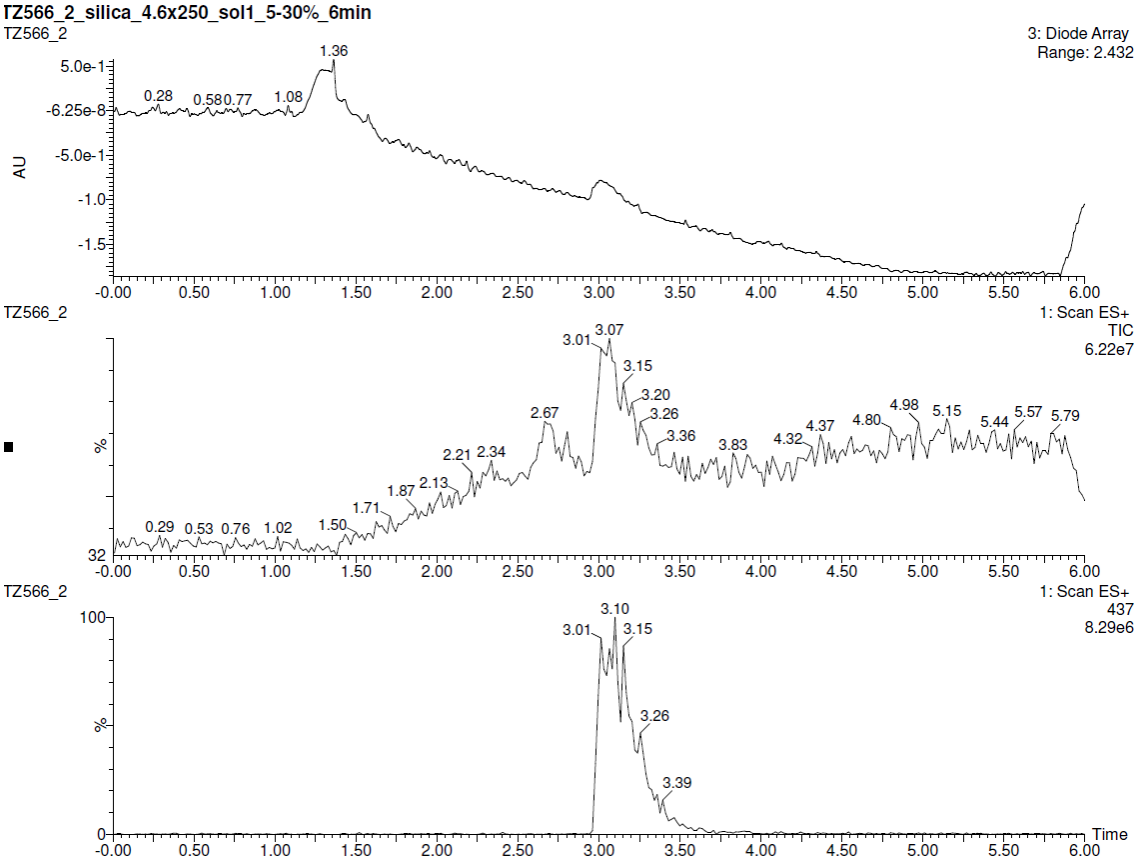


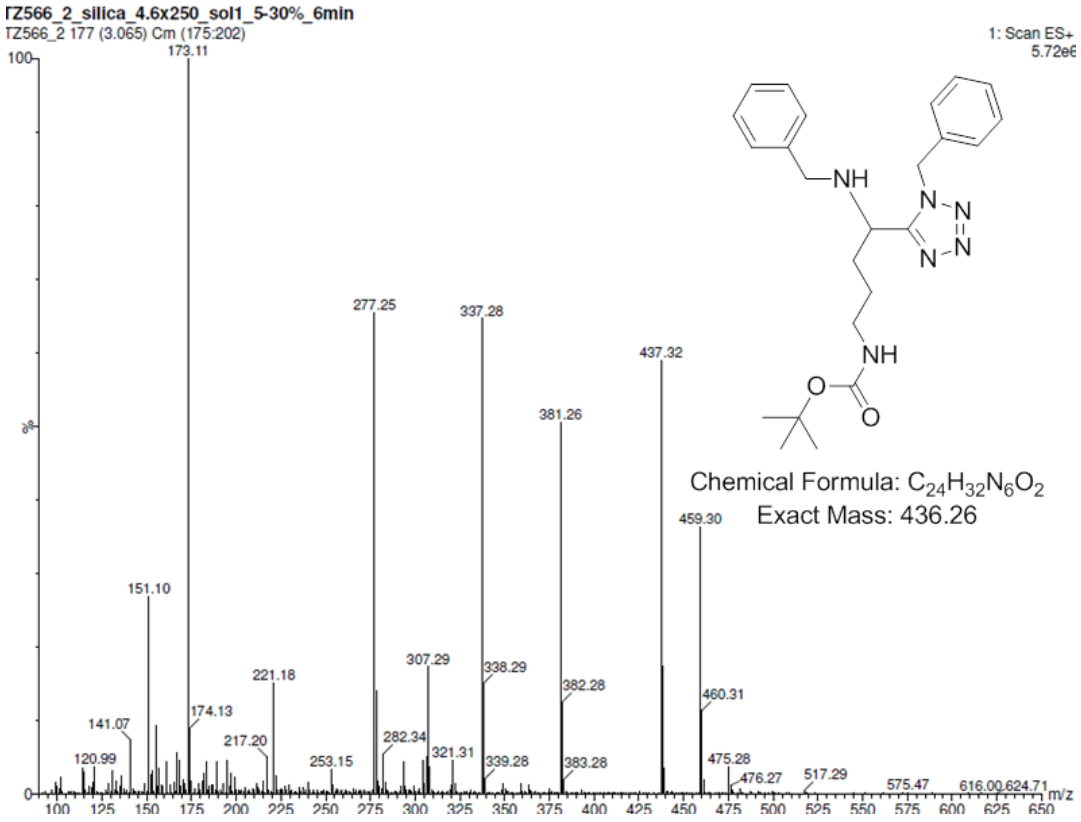

TZ842_6_Col4_sol1_5-30%_6min
TZ842_6
3: Diode Array
AU
TZ842_6
1: Scan ES+
%
TZ842_6
1: Scan ES+
%
Time


TZ842_6_Col4_sol1_5-30%_6min
TZ842_6 269 (4.667) Cm (217:281)
1: Scan ES+
%
Chemical Formula: C39H35N7
Exact Mass: 601.30
m/z

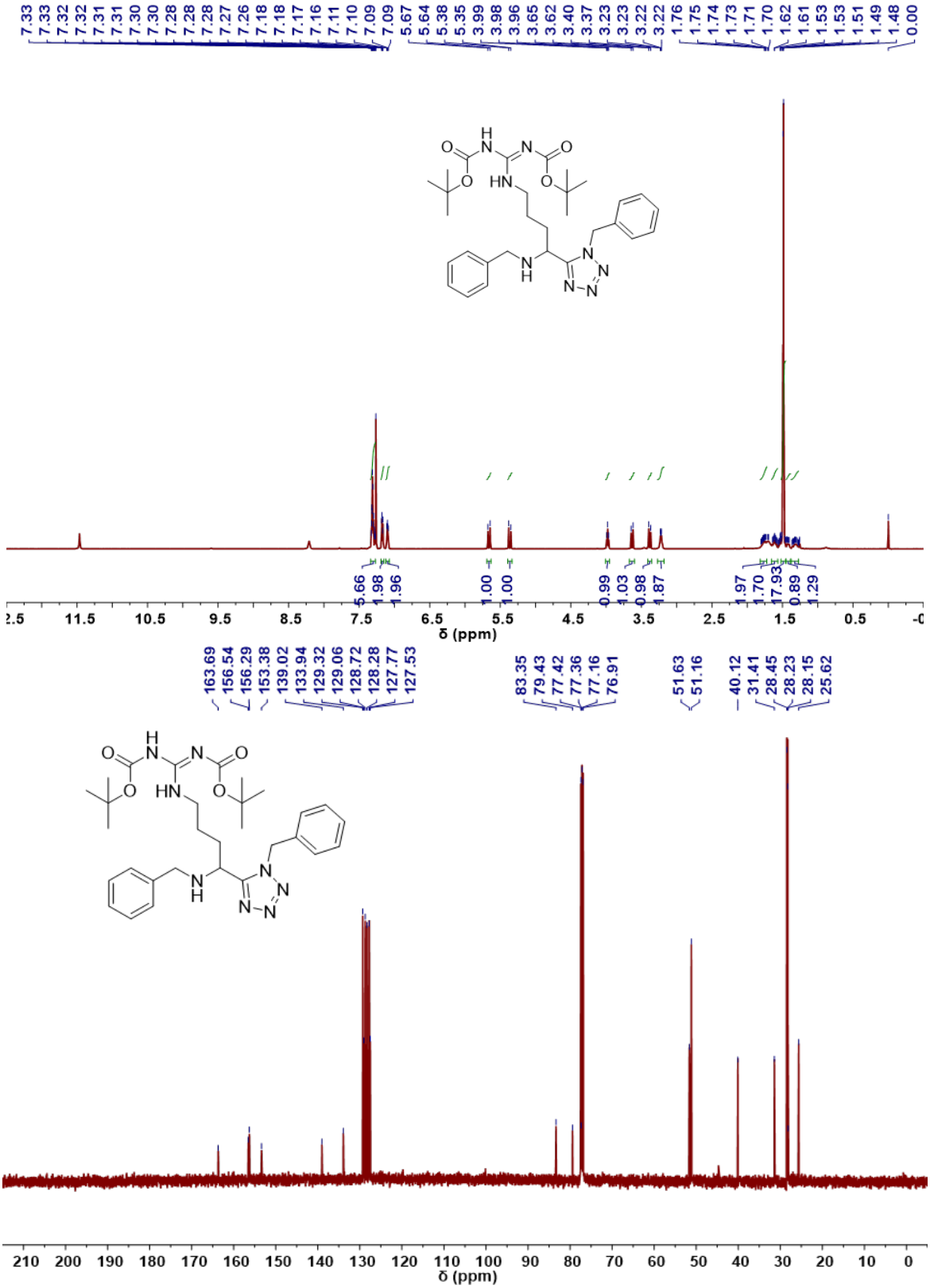
***tert*-Butyl (4-(1-benzyl-1H-tetrazol-5-yl)-4-(benzylamino)butyl)carbamate (5u)**



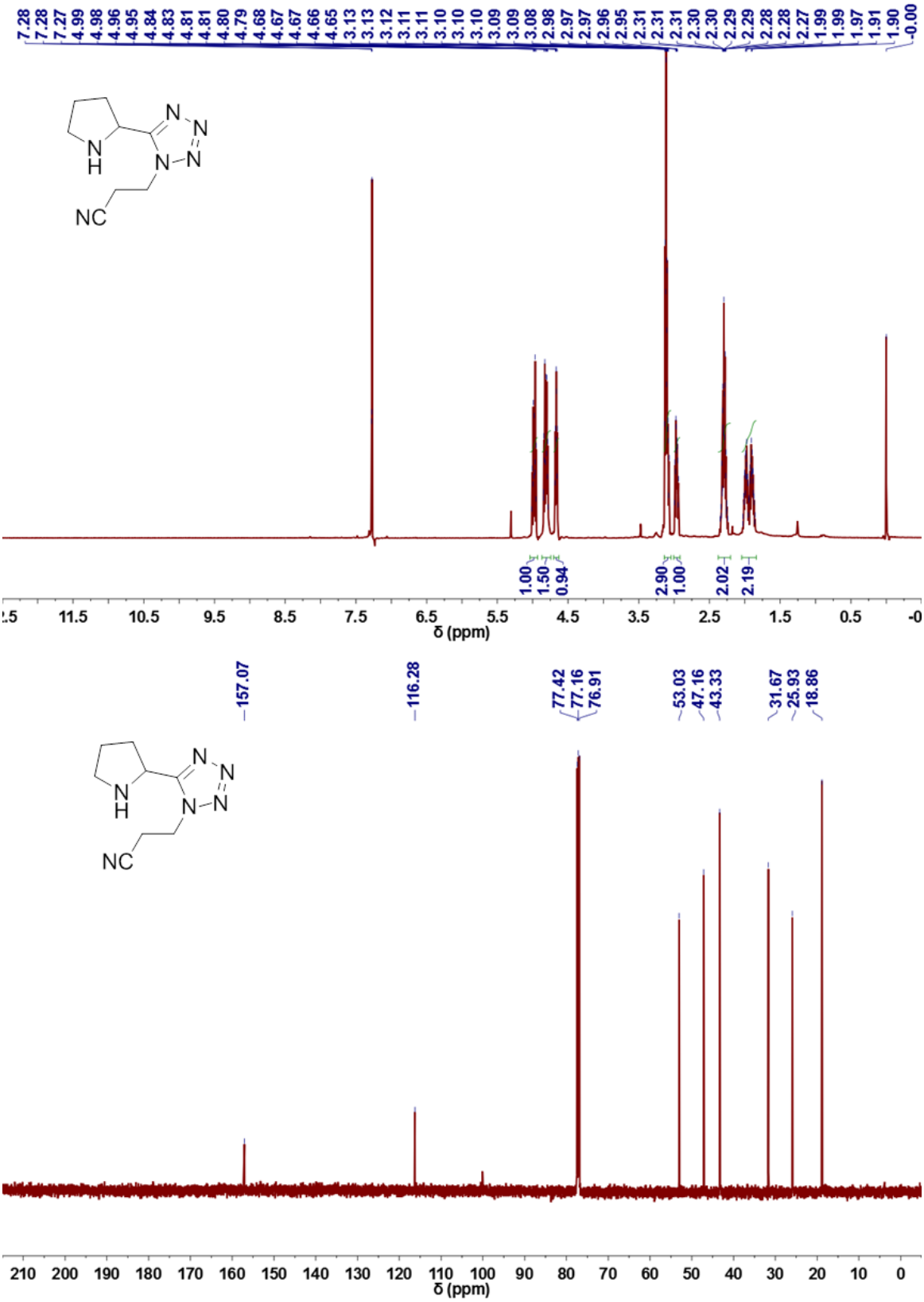

TZ566_2_silica_4.6x250_sol1_5-30%_6min
TZ566_2
3: Diode Array
Range: 2.432
AU
TZ566_2
1: Scan ES+
TIC
6.22e7
%
TZ566_2
1: Scan ES+
437
8.29e6
%
Time


TZ566_2_silica_4.6x250_sol1_5-30%_6min
TZ566_2 177 (3.065) Cm (175:202)
1: Scan ES+
5.72e6
%
m/z
NH
NH
O
O
Chemical Formula: C24H32N6O2
Exact Mass: 436.26

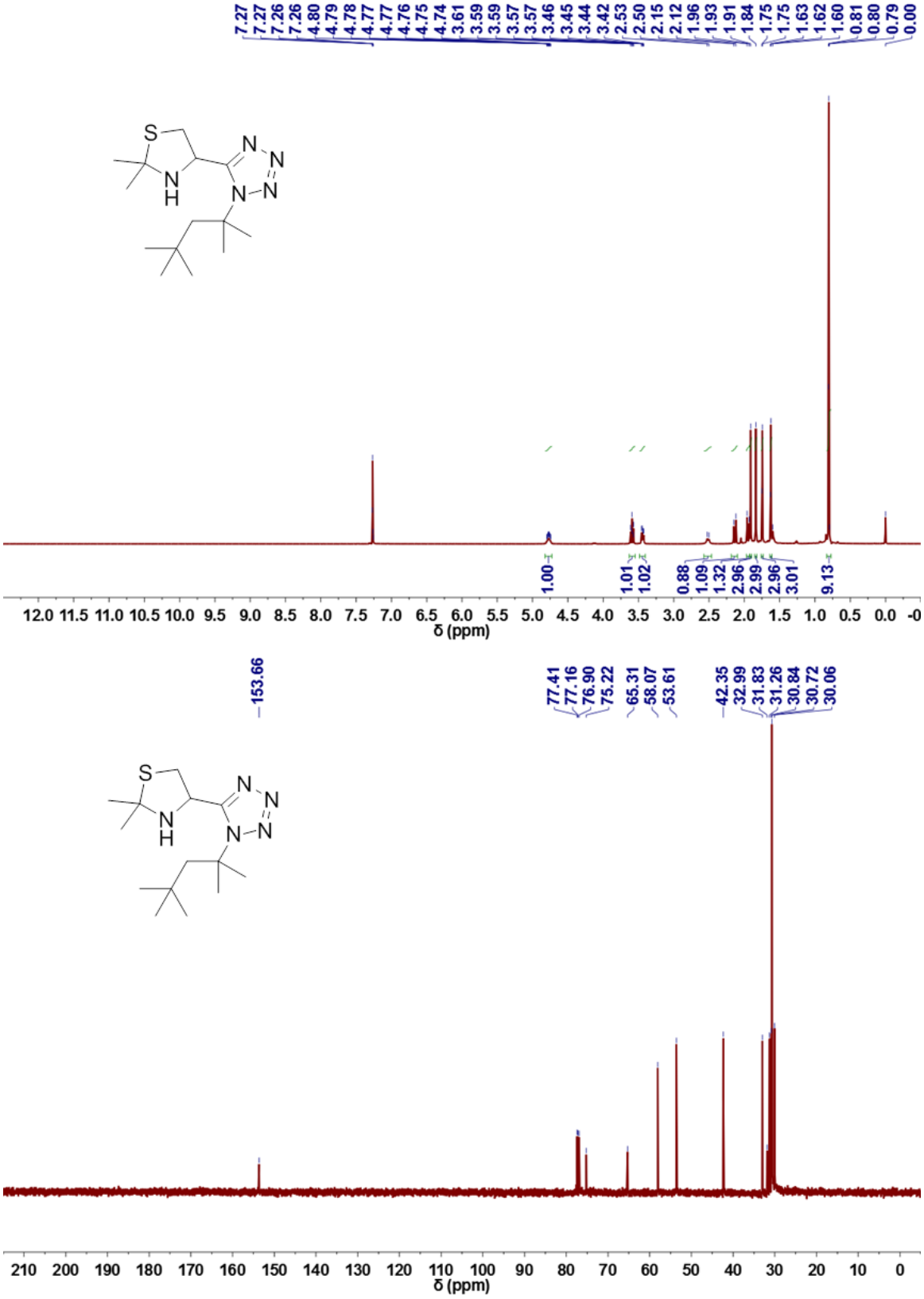
1-(4-Benzyl-amino-4-(1-benzyl-tetrazol-5-yl)butyl)diboc-guanidine (5u')

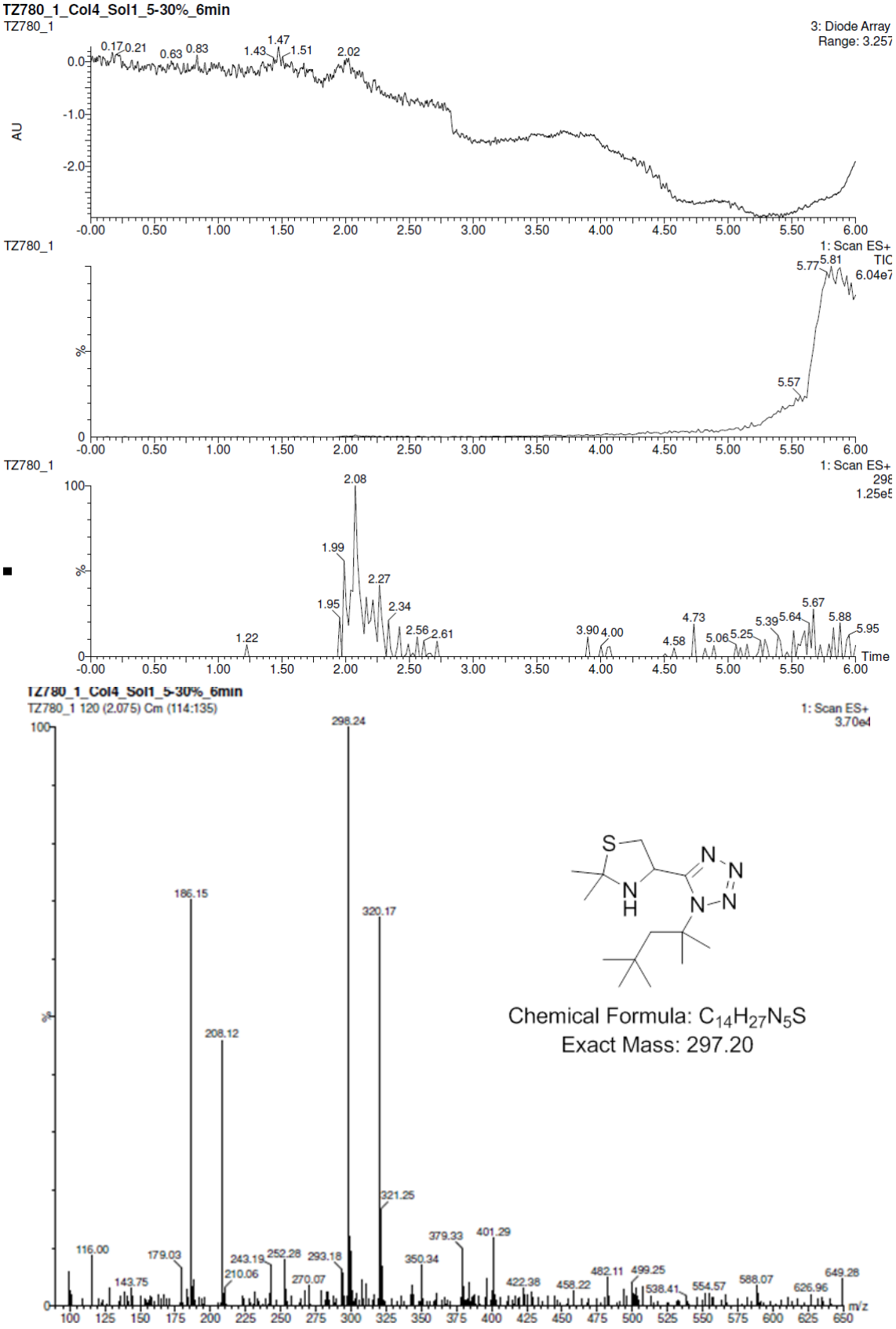


3-(5-(Pyrrolidin-2-yl)-1H-tetrazol-1-yl)propanenitrile (5v)

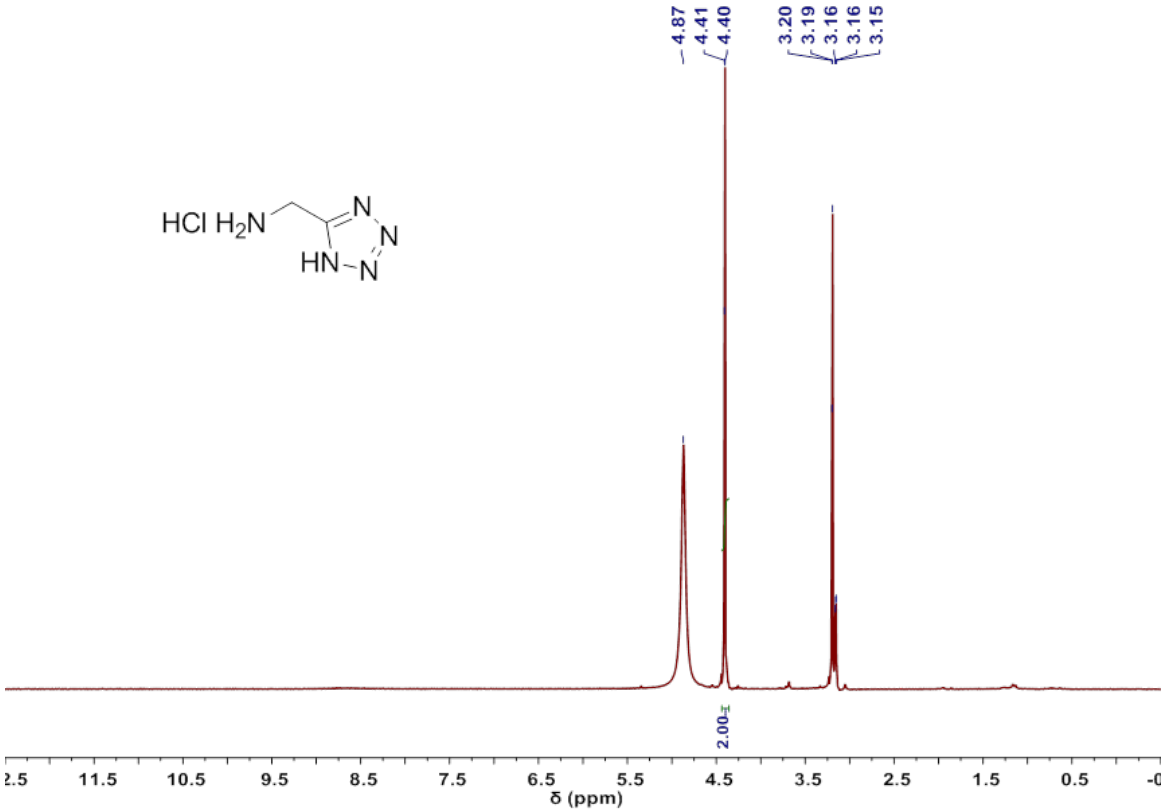


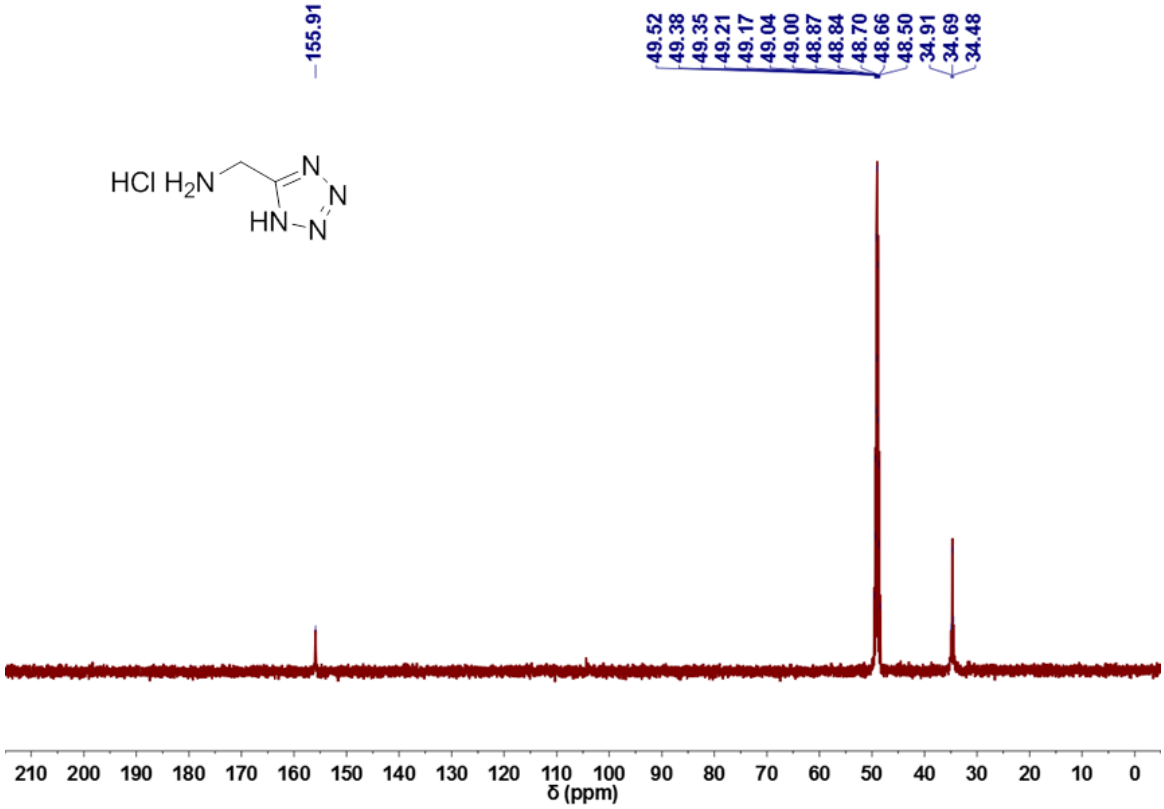
2,2-Dimethyl-4-(1-(2,4,4-trimethylpentan-2-yl)-1H-tetrazol-5-yl)thiazolidine (5w)



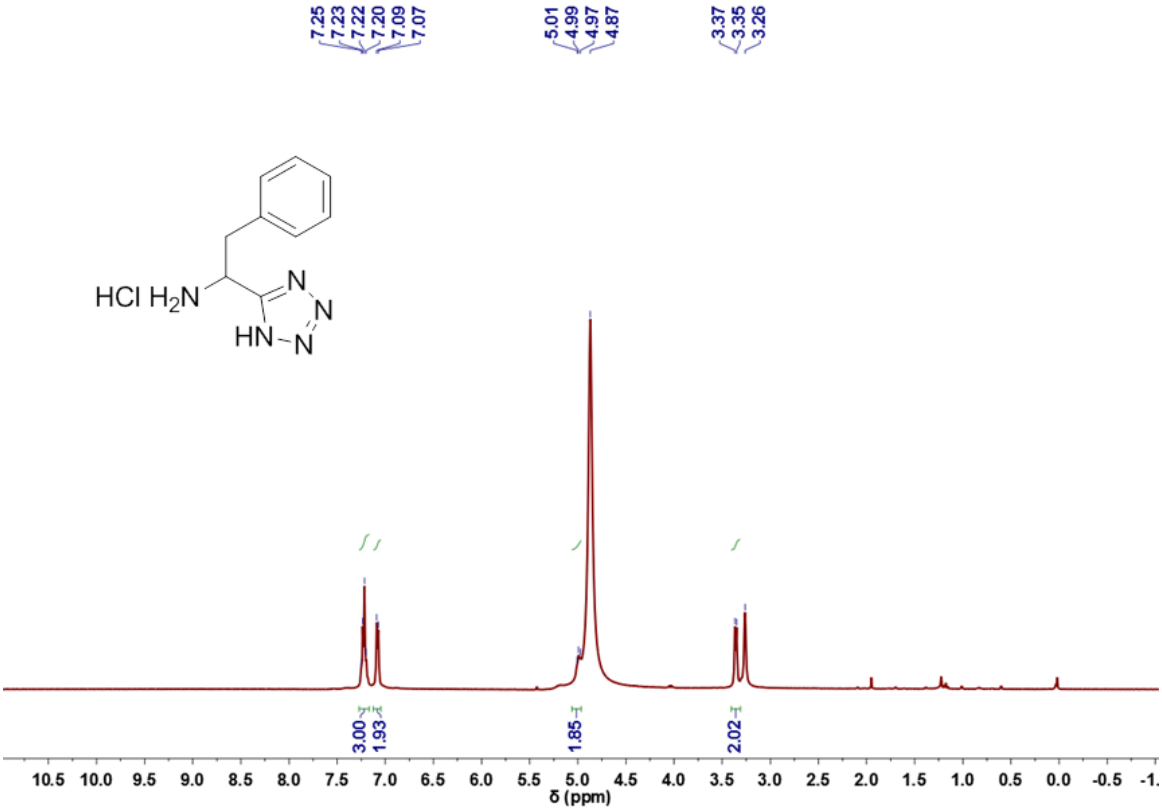

TZ780_1_Col4_Sol1_5-30%_6min
TZ780_1
3: Diode Array
Range: 3.257
AU
TZ780_1
1: Scan ES+
TIC
6.04e7
%
TZ780_1
1: Scan ES+
1.25e5
%
Time
TZ780_1_Col4_Sol1_5-30%_6min
TZ780_1 120 (2.075) Cm (114:135)
1: Scan ES+
3.70e4
%
m/z
Chemical Formula: C14H27N5S
Exact Mass: 297.20

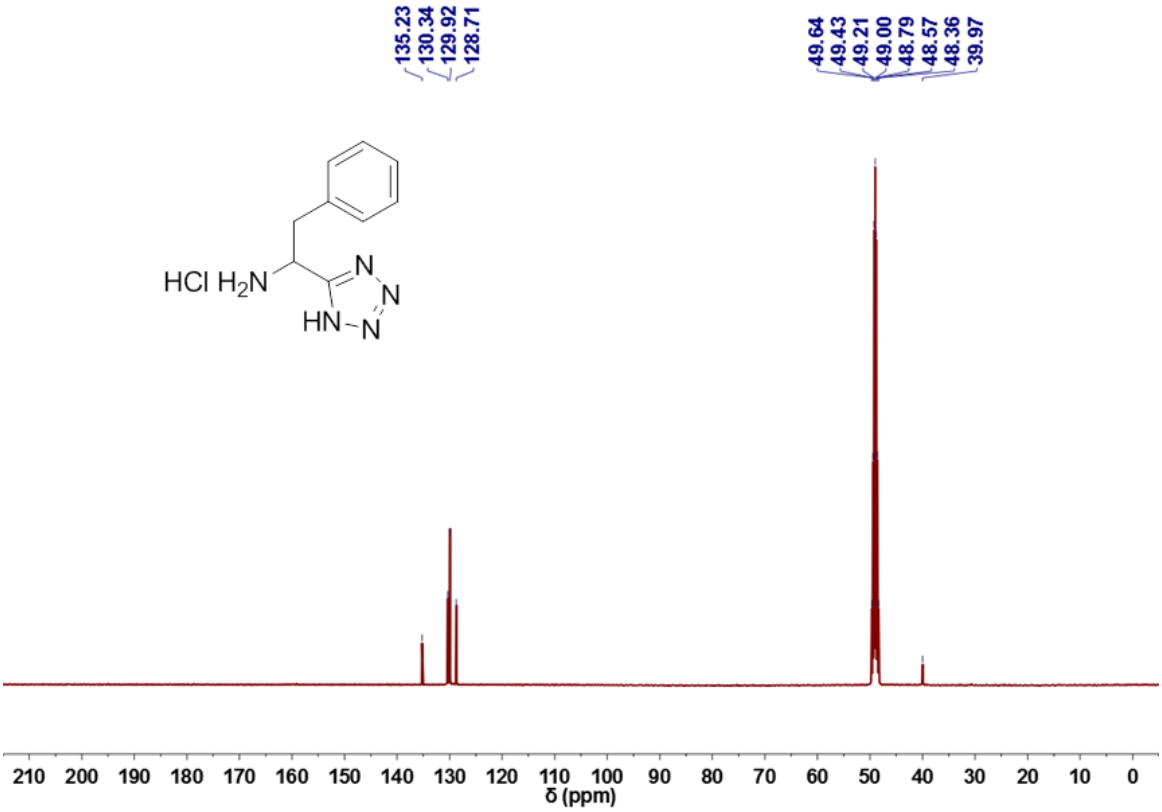
(1H-Tetrazol-5-yl)methanamine hydrogen chloride (6a)



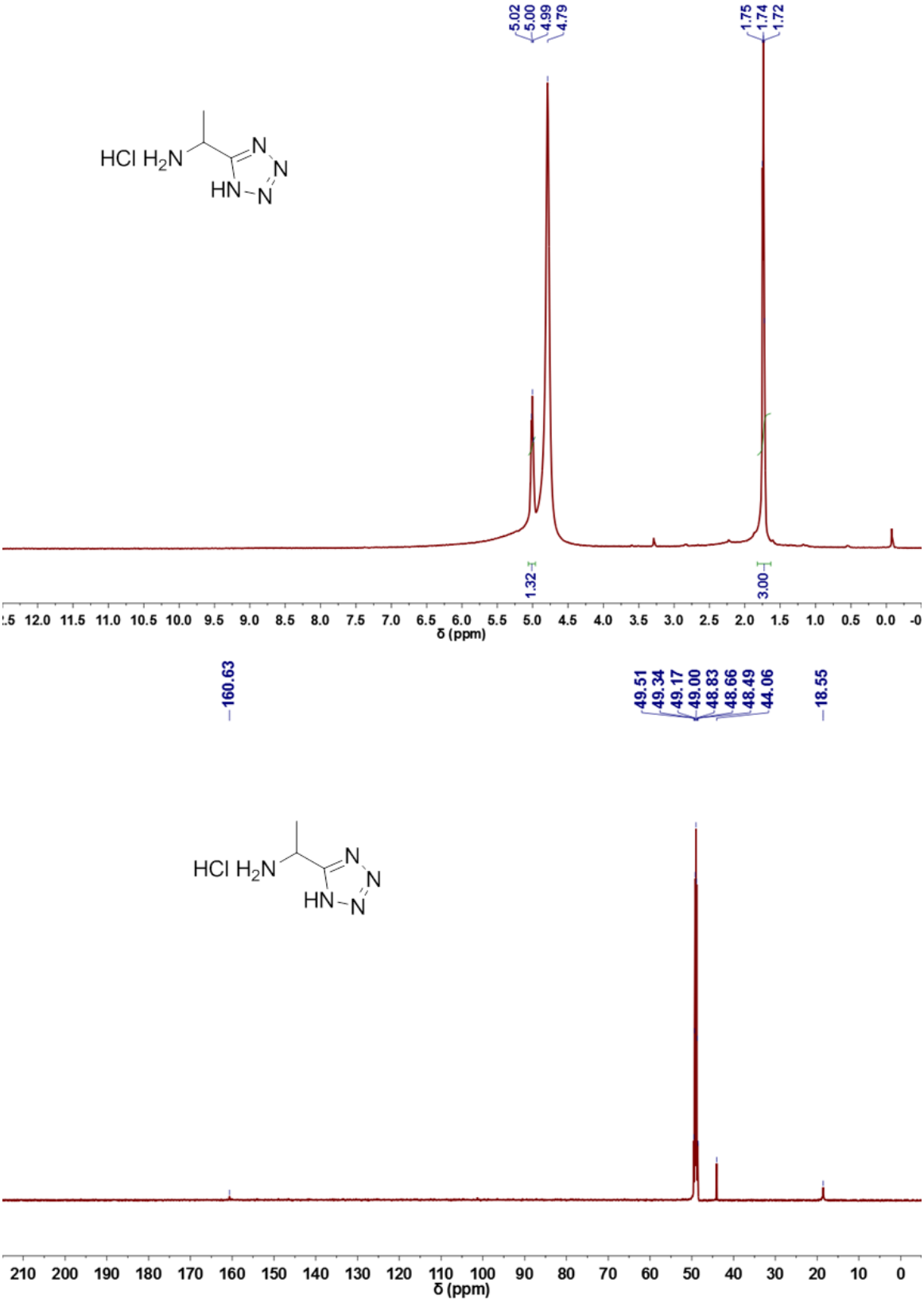


2-Phenyl-1-(1H-tetrazol-5-yl)ethanamine hydrogen chloride (6b)

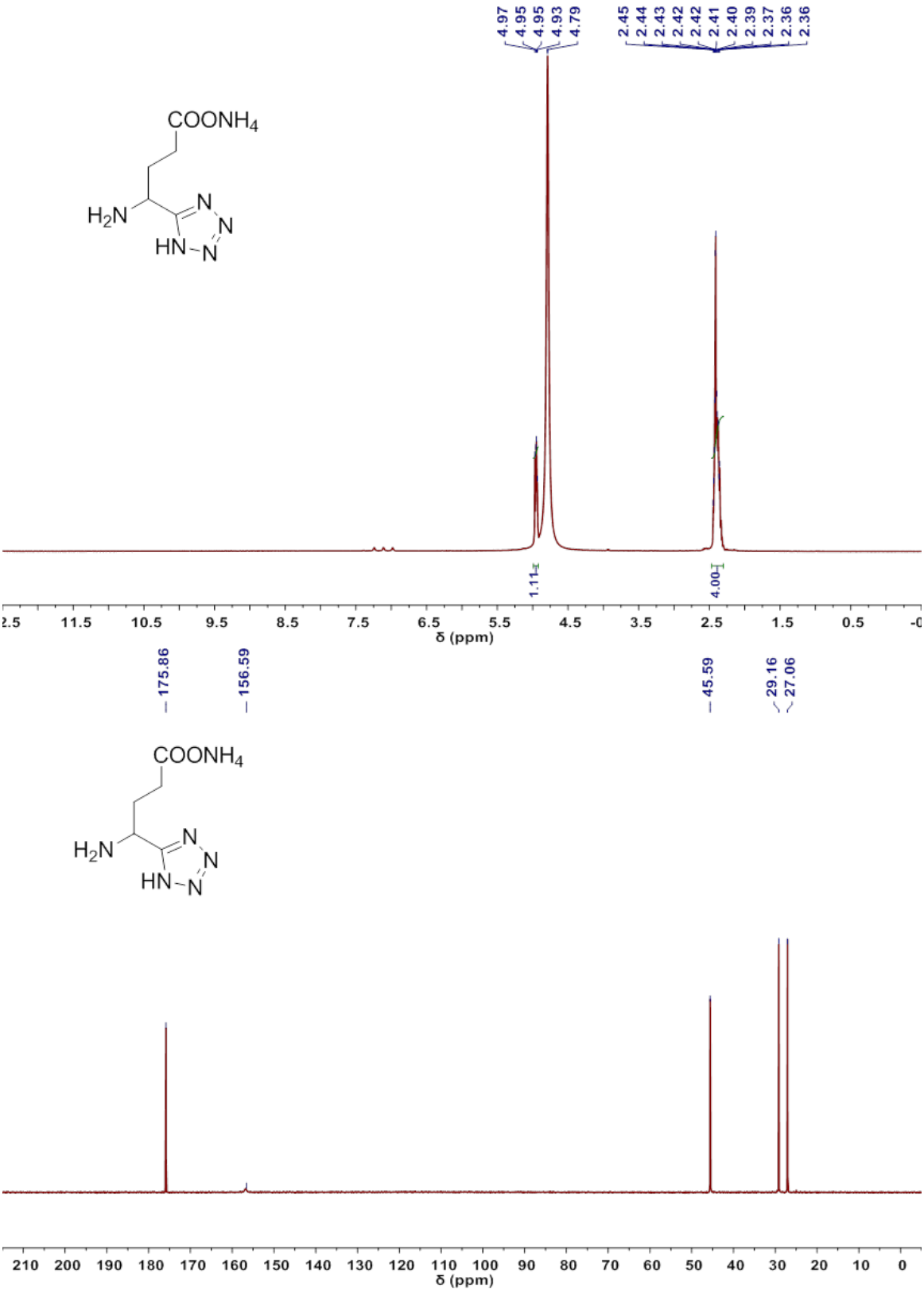




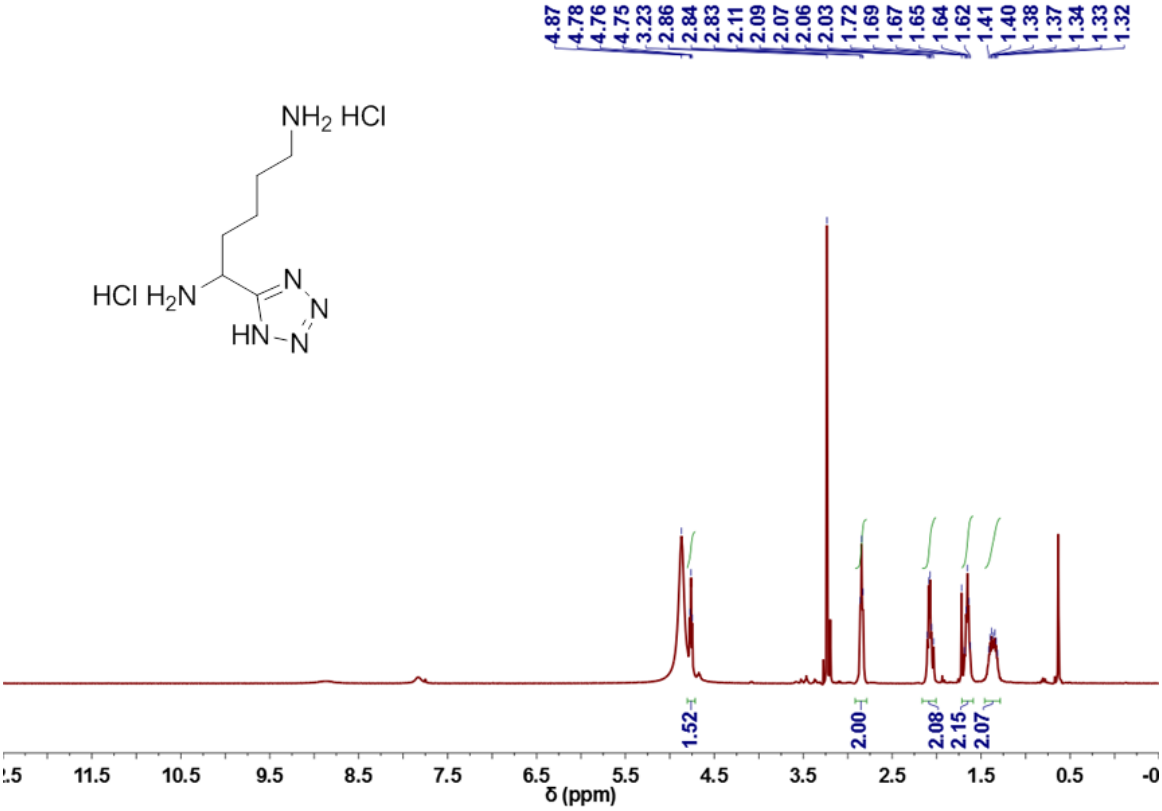
1-(1H-Tetrazol-5-yl)ethanamine hydrogen chloride (6c)

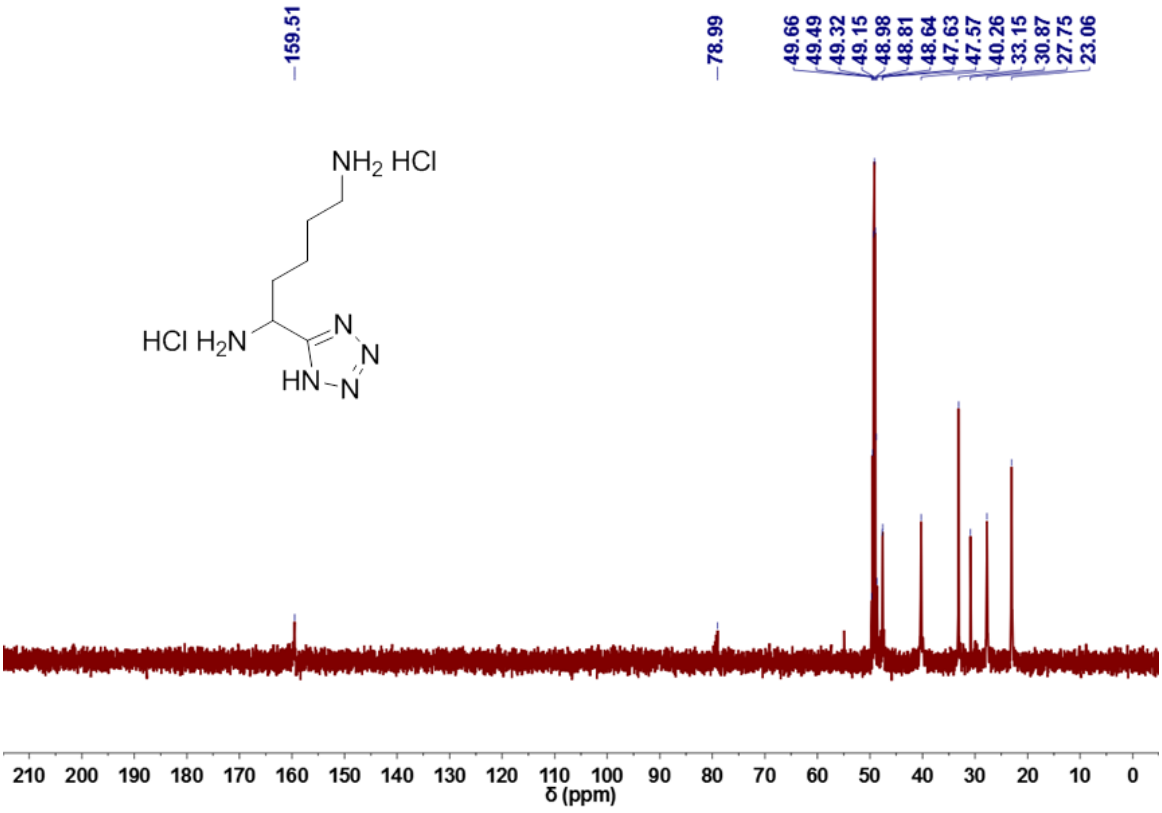


4-Amino-4-(1H-tetrazol-5-yl)butanoic acid (6d)

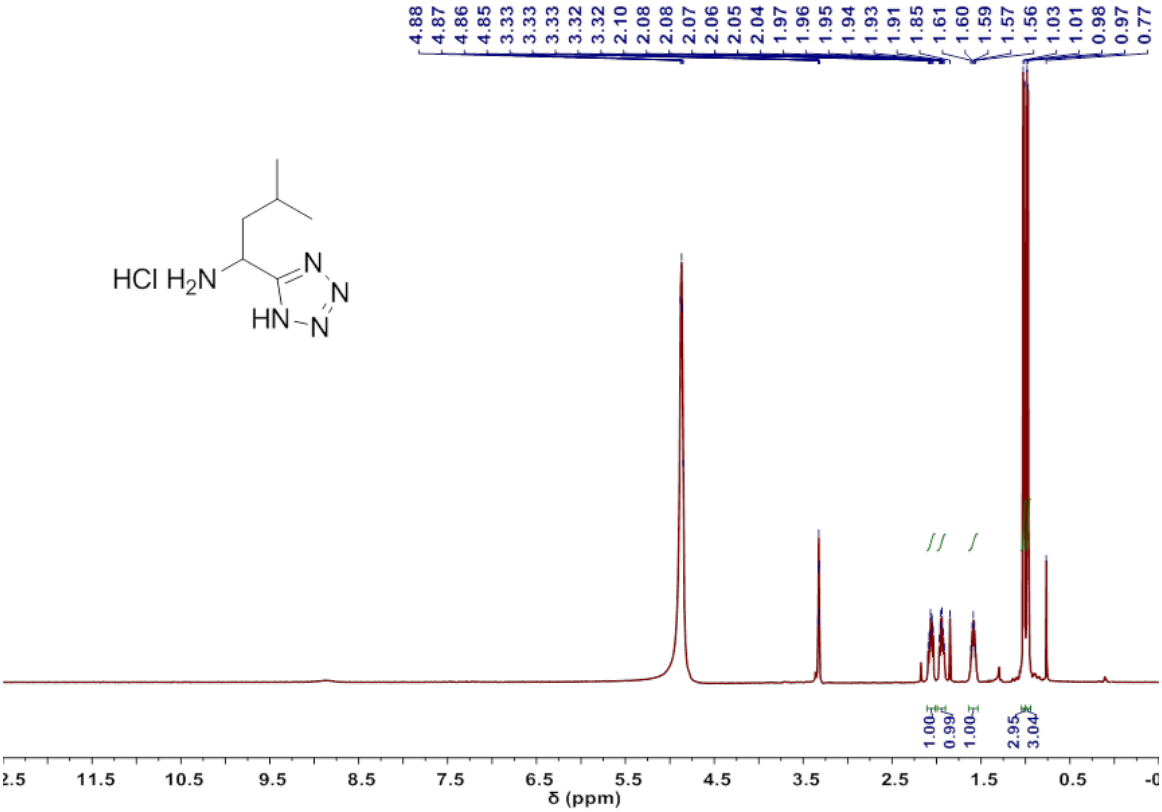


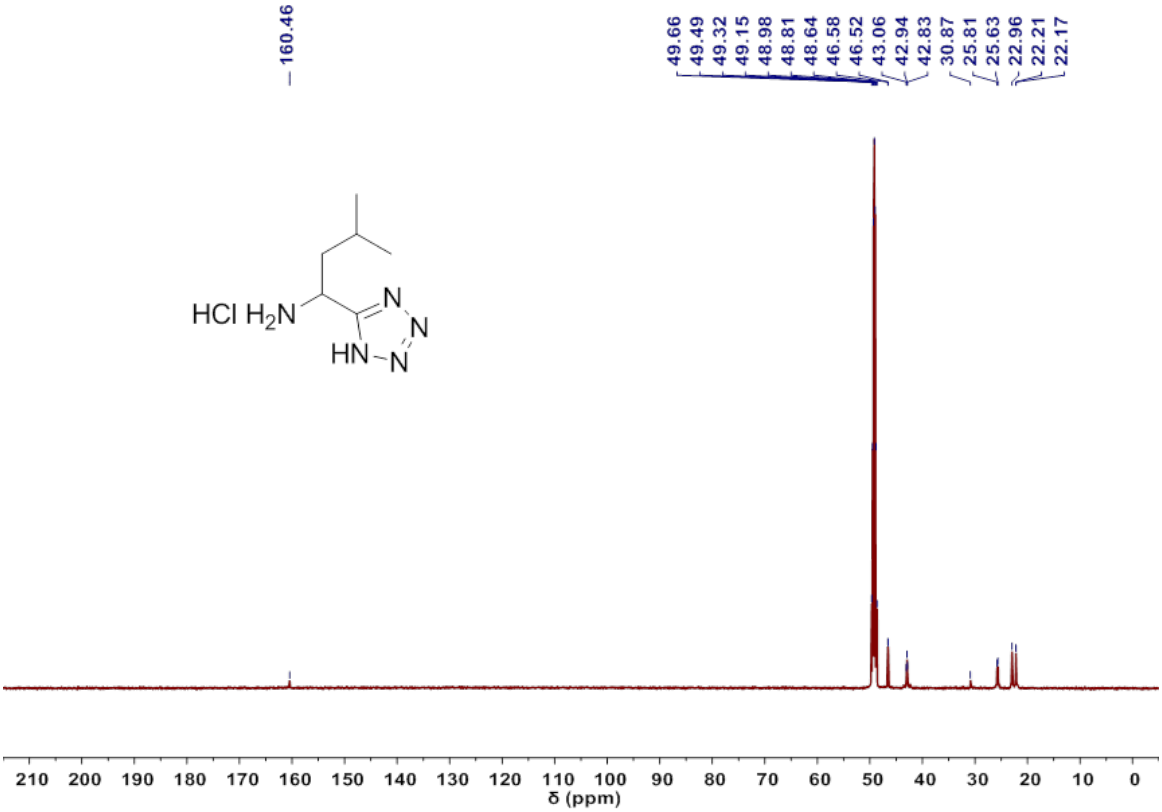
1-(1H-Tetrazol-5-yl)pentane-1,5-diamine dihydrochloride (6e)



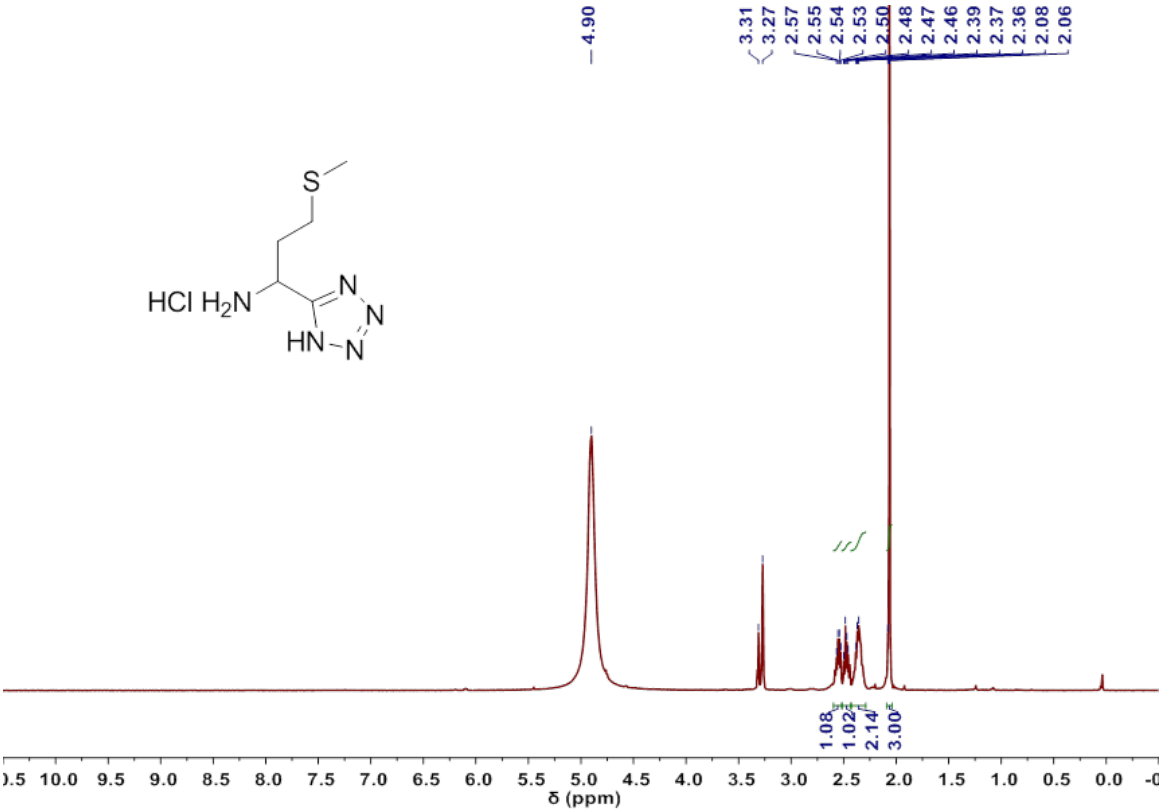


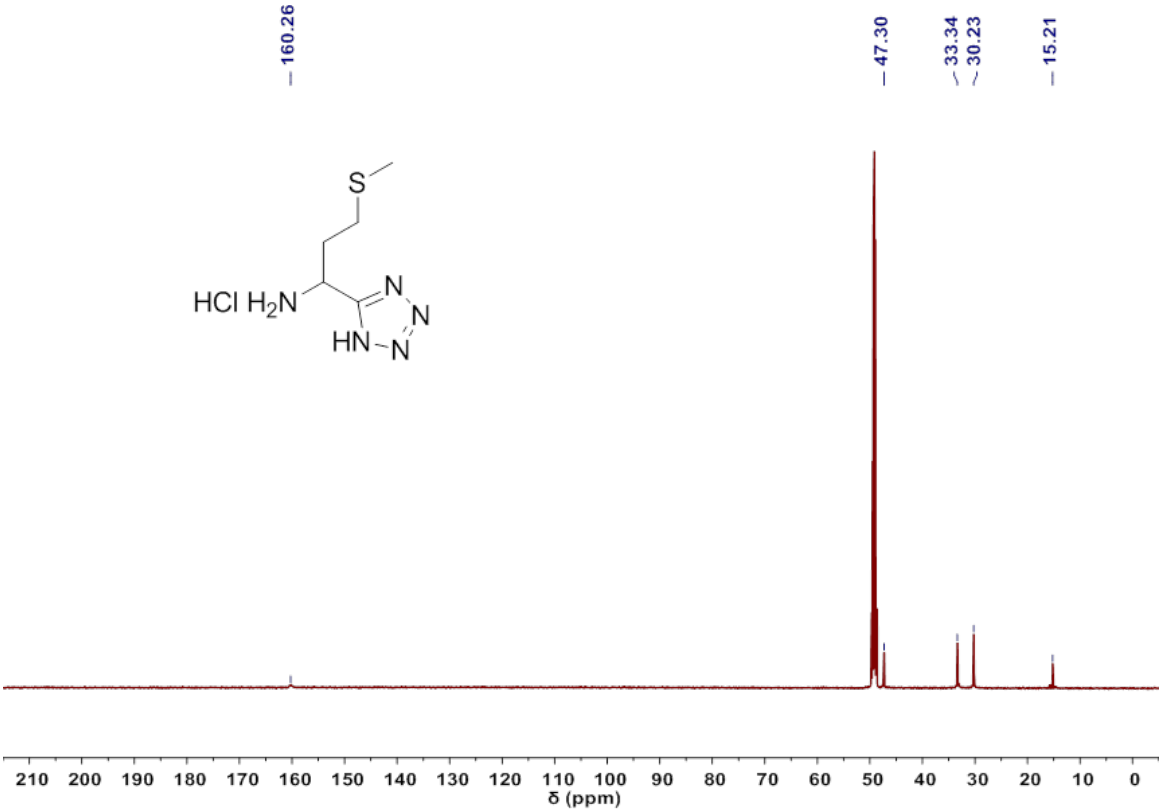
3-Methyl-1-(1H-tetrazol-5-yl)butan-1-amine hydrogen chloride (6f)



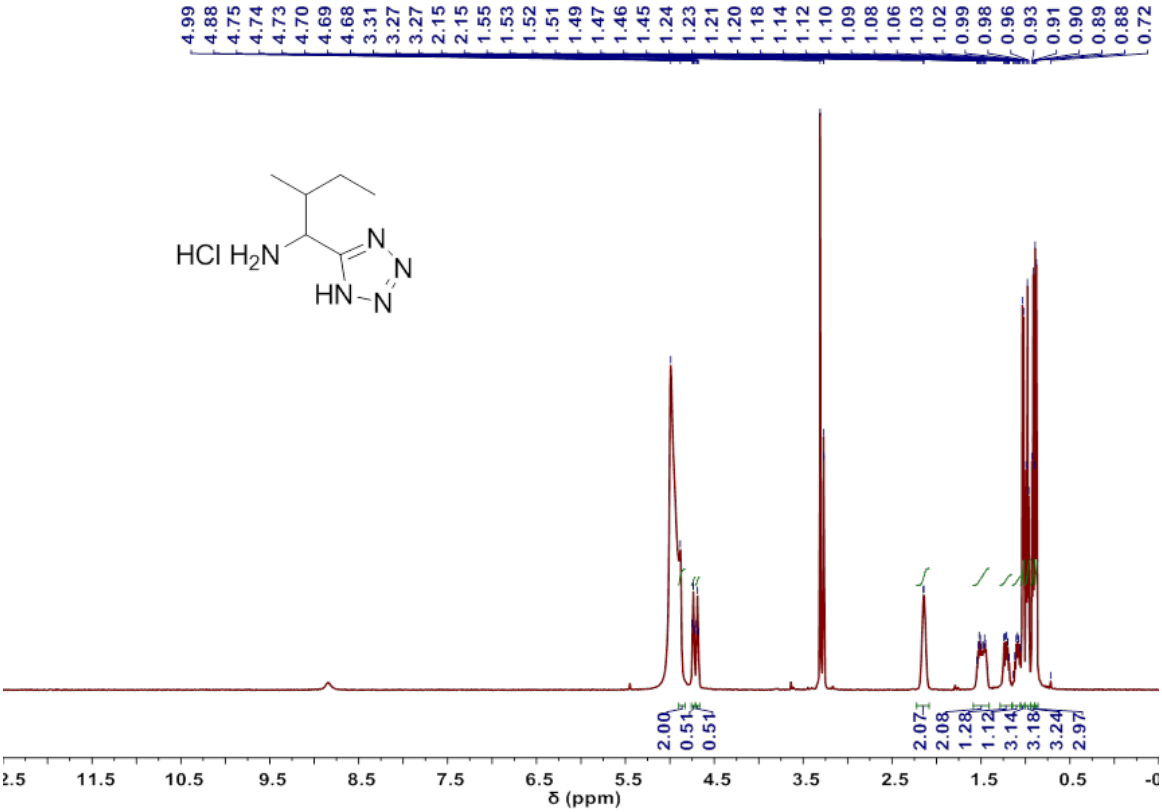


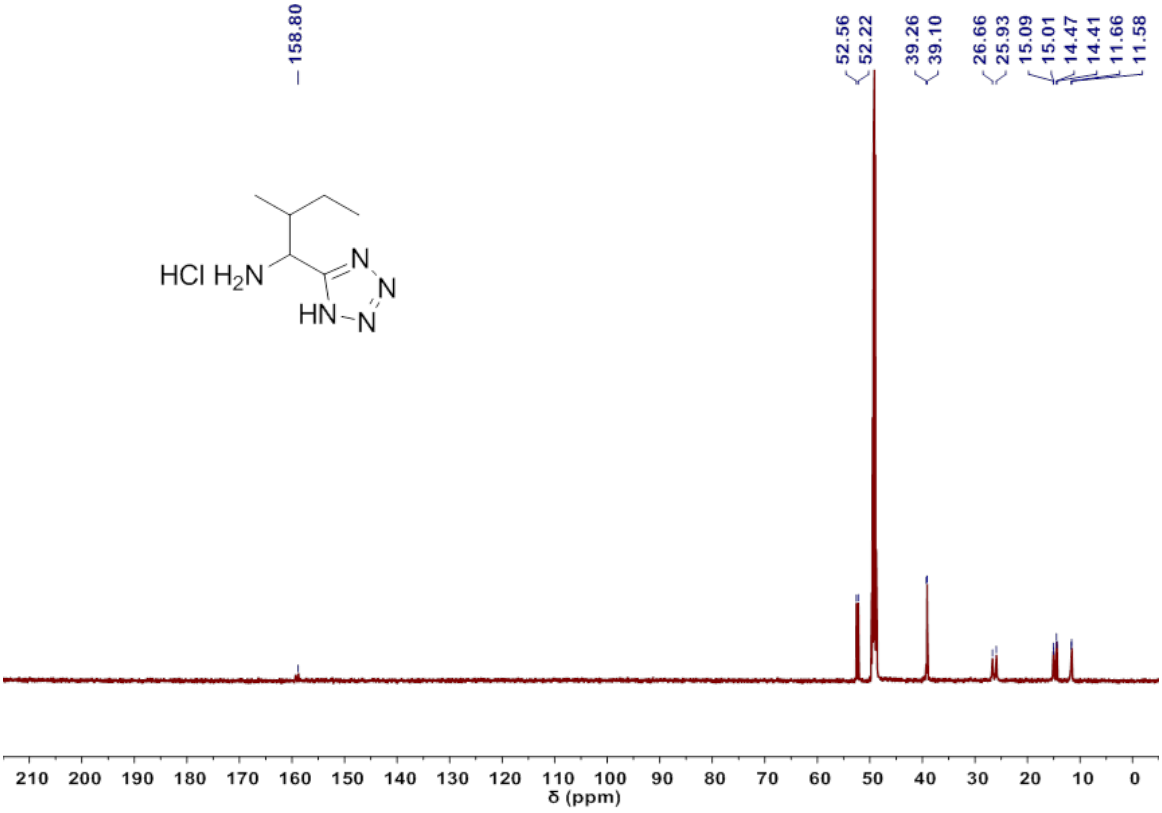
3-(Methylthio)-1-(1H-tetrazol-5-yl)propan-1-amine hydrochloride (6g)



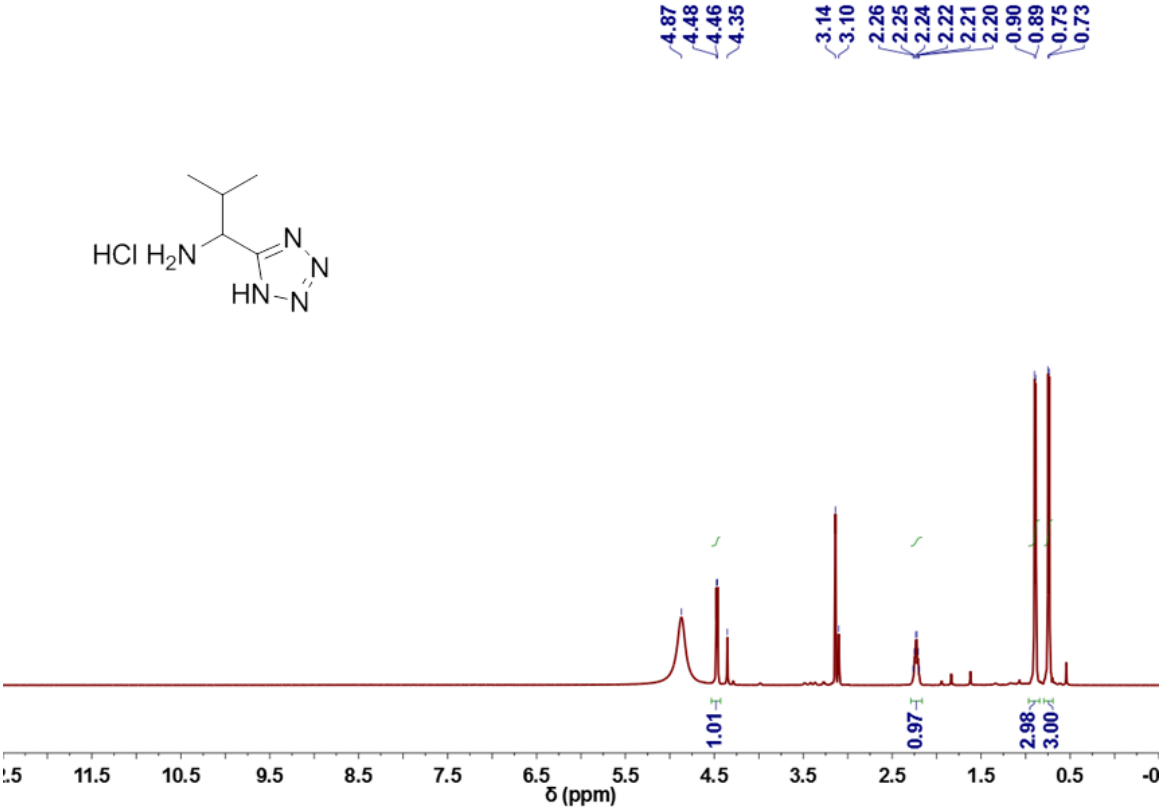


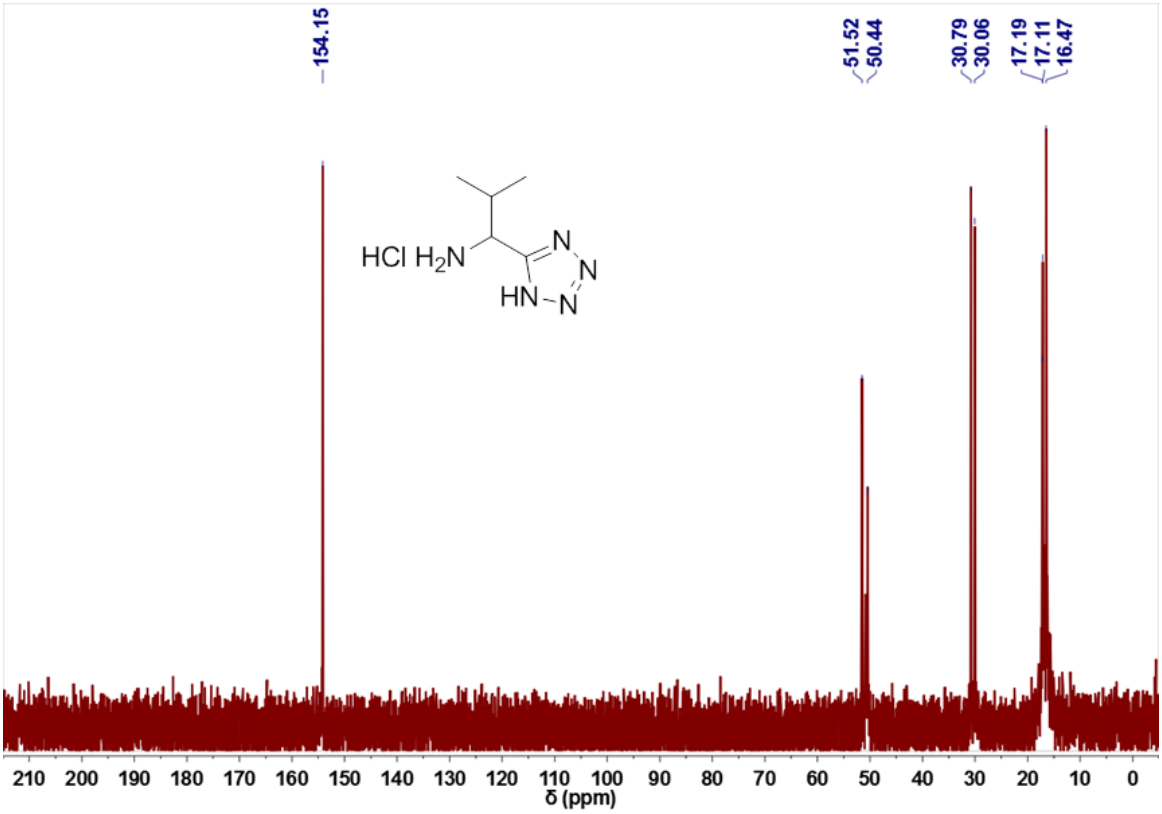
1-(1H-Tetrazol-5-yl)butan-1-amine hydrogen chloride (6h)



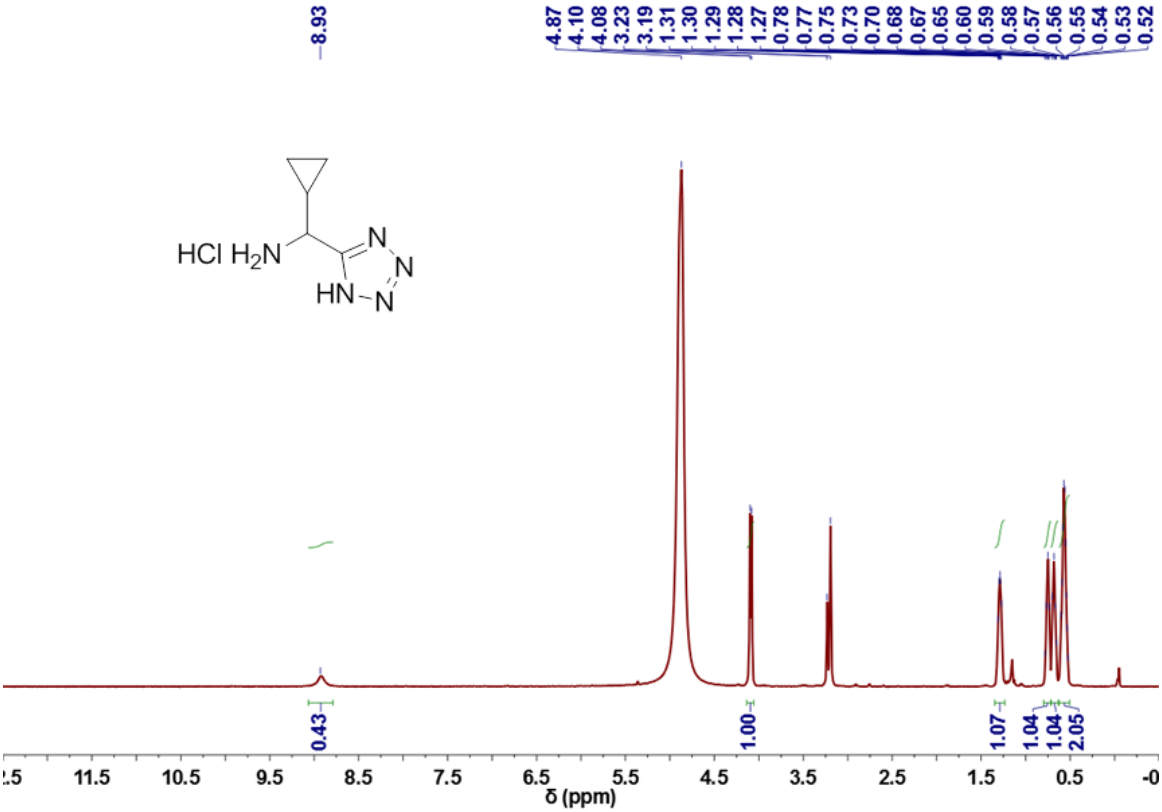


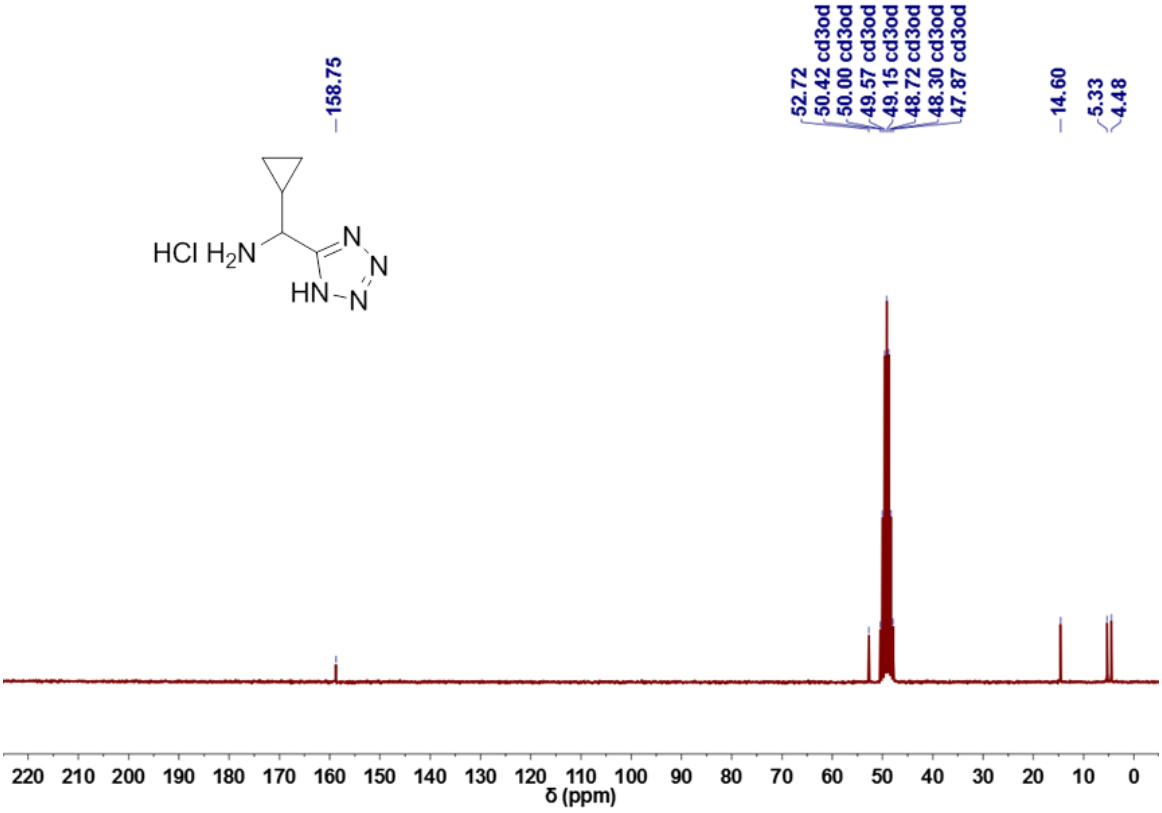
2-Methyl-1-(1H-tetrazol-5-yl)propan-1-amine hydrogen chloride (6i)



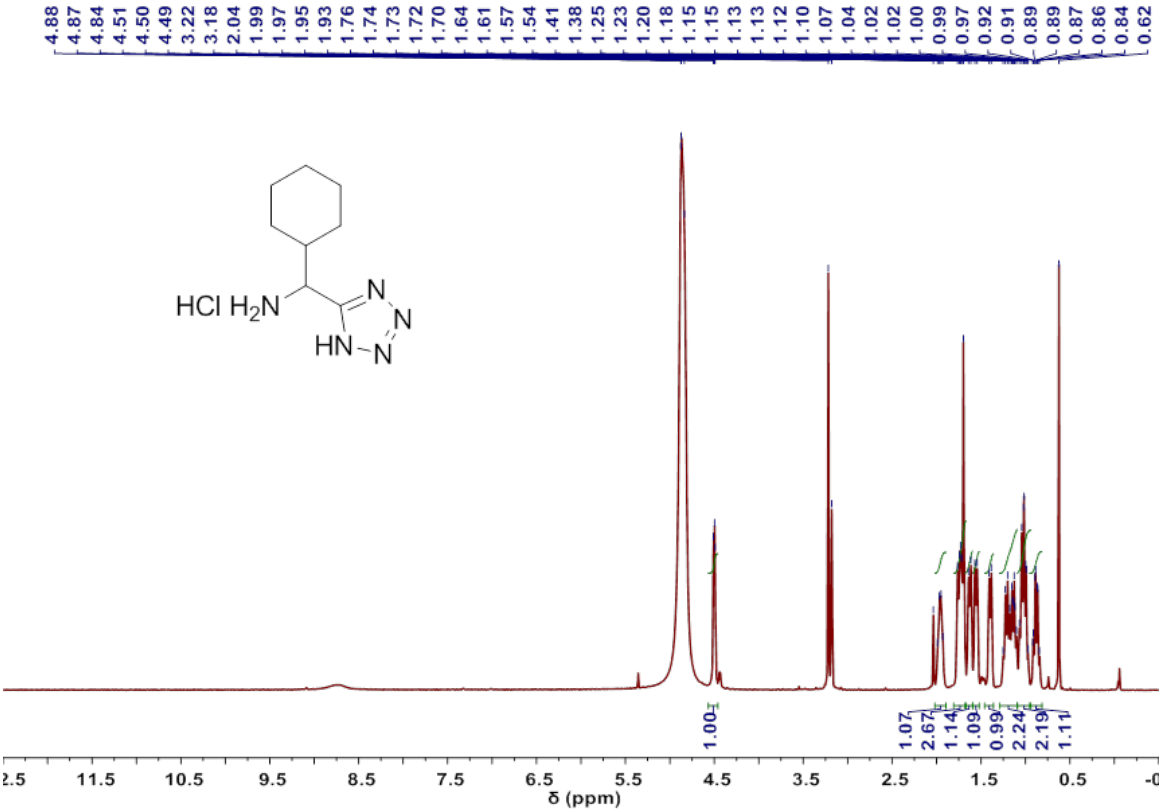


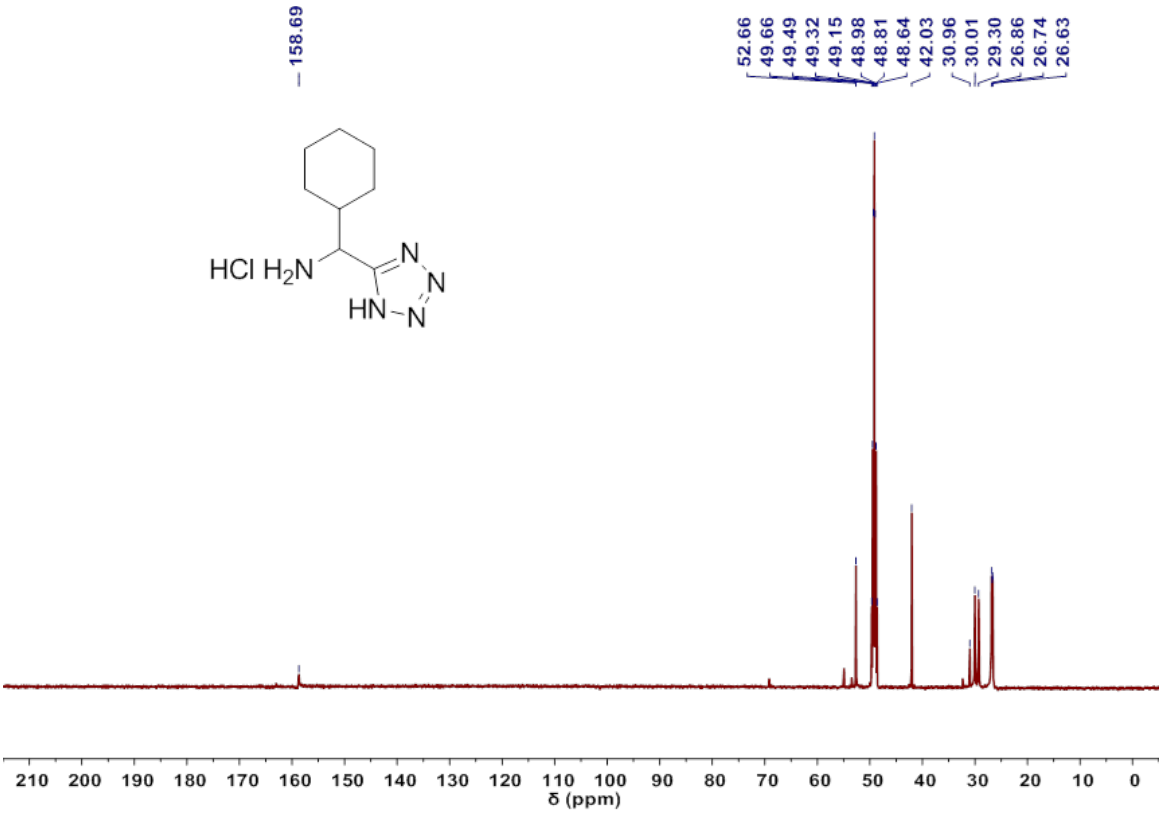
Cyclopropyl(1H-tetrazol-5-yl)methanamine hydrochloride (6j)



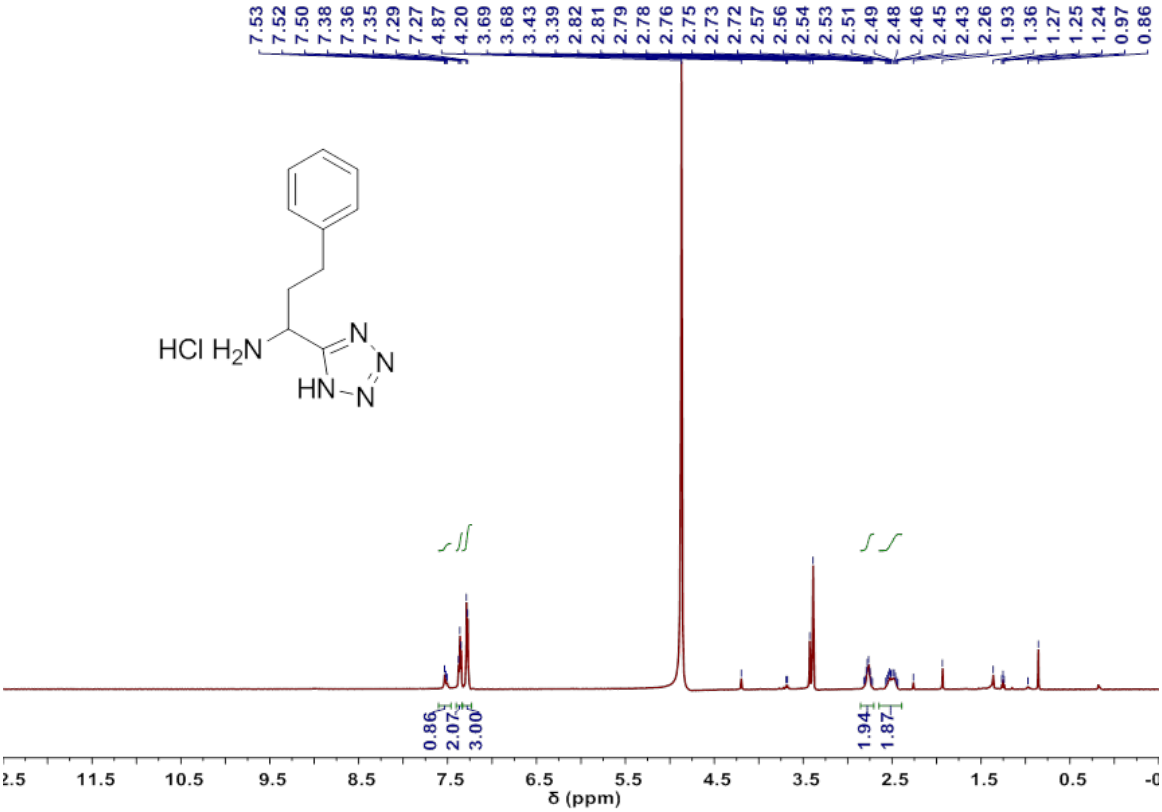


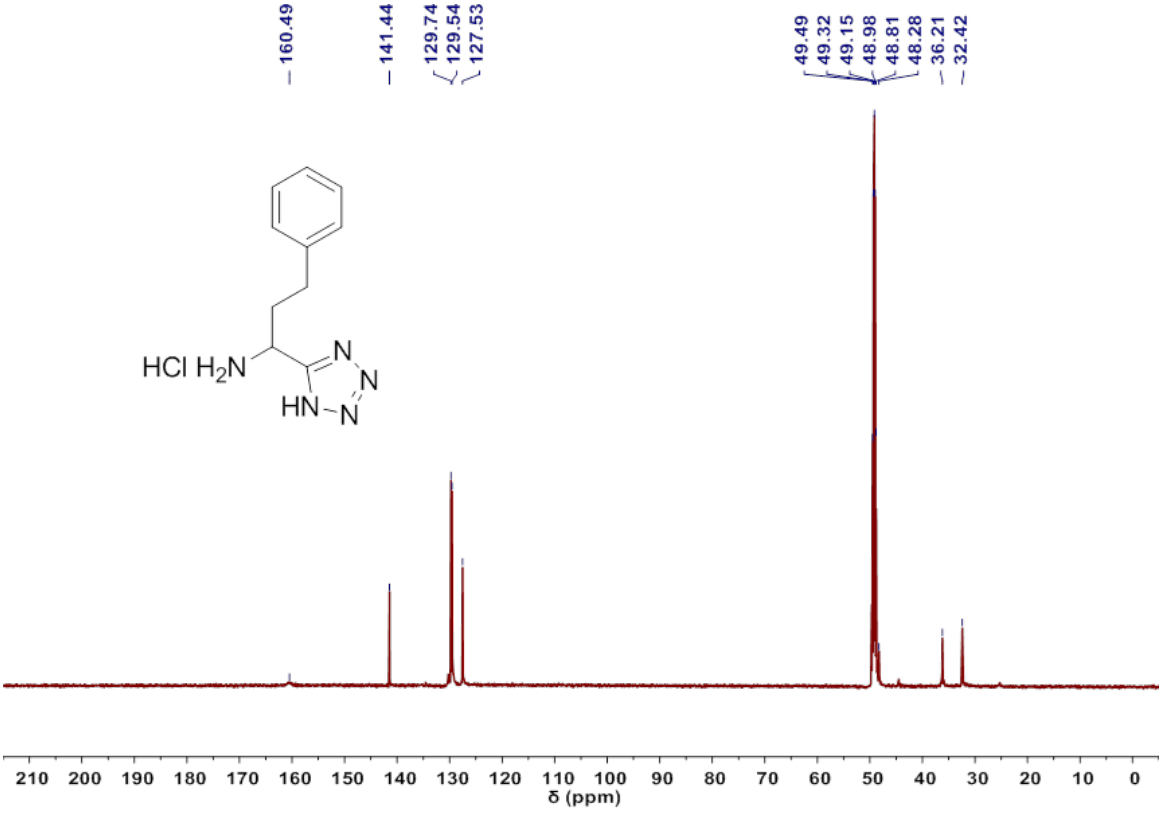
Cyclohexyl(1H-tetrazol-5-yl)methanamine hydrogen chloride (6k)



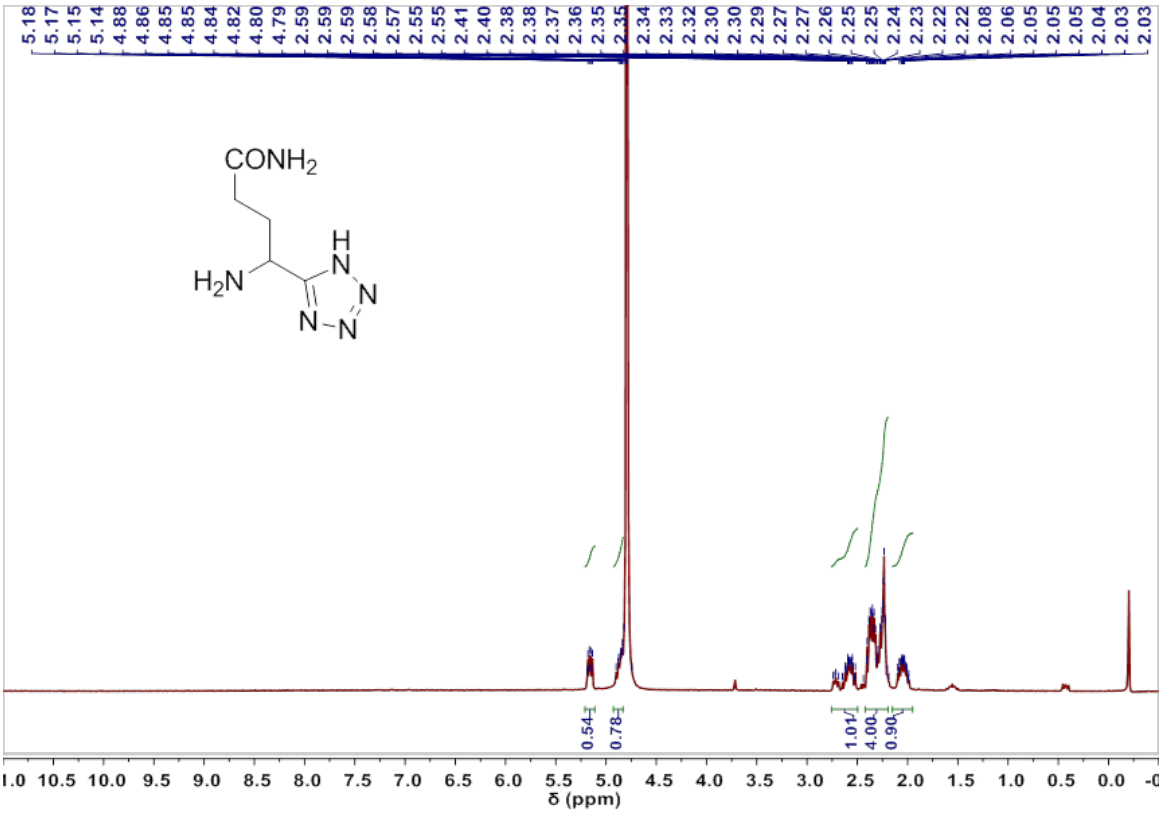


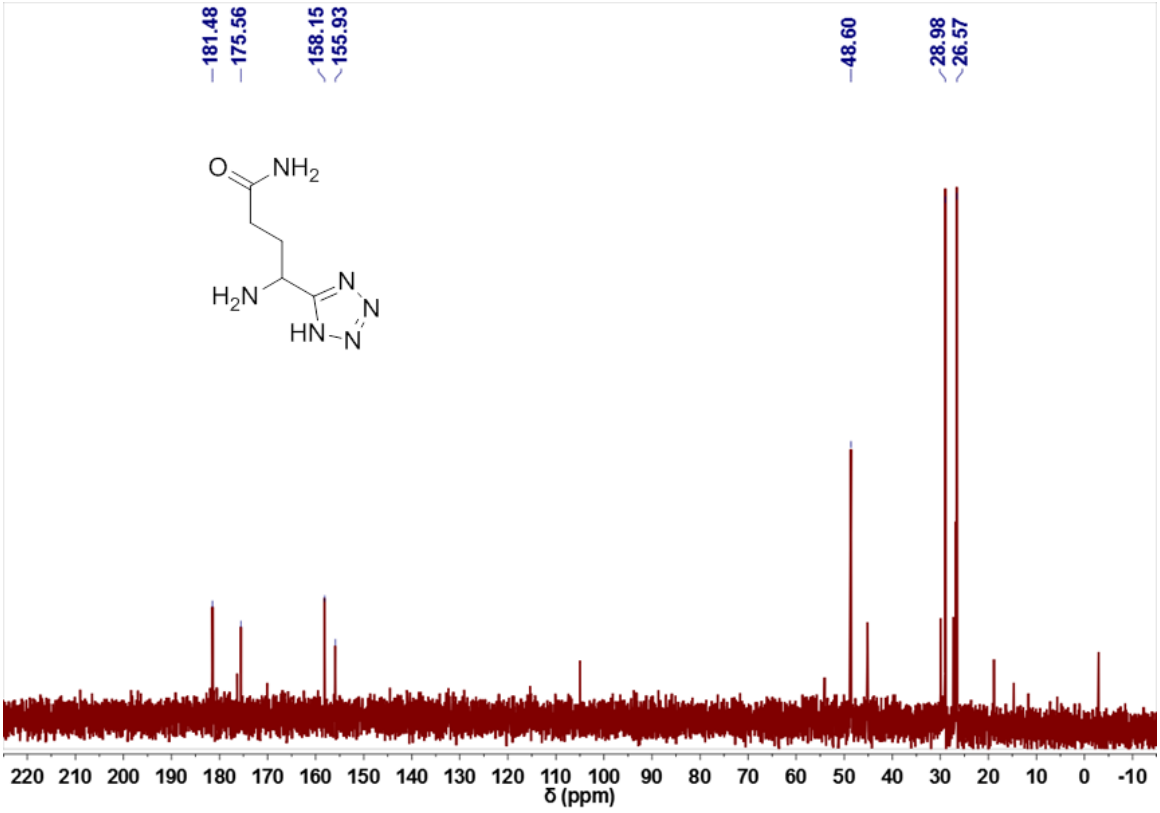
3-Phenyl-1-(1H-tetrazol-5-yl)propan-1-amine hydrogen chloride (6l)



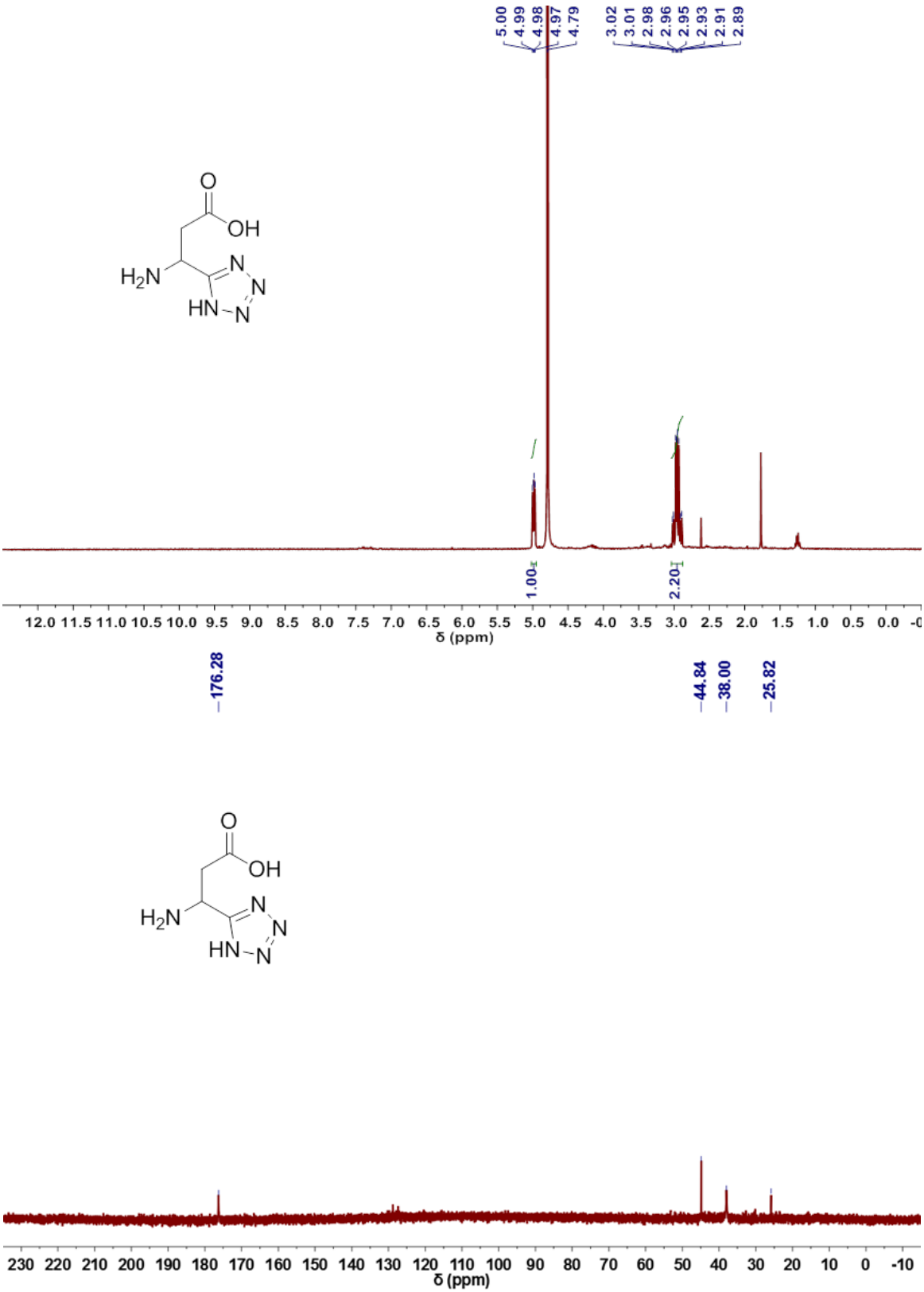


4-Amino-4-(1H-tetrazol-5-yl)butanamide (6m)

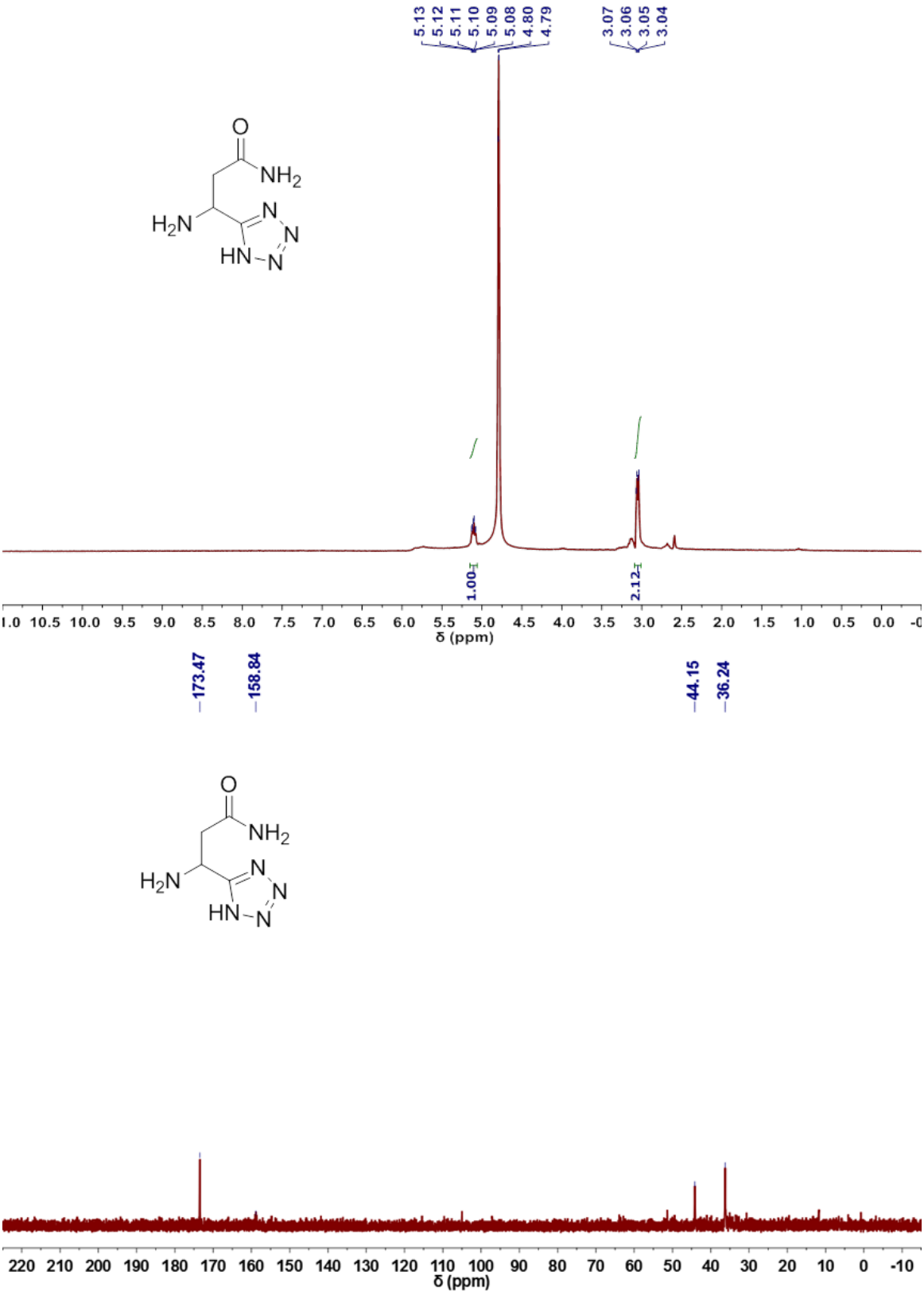




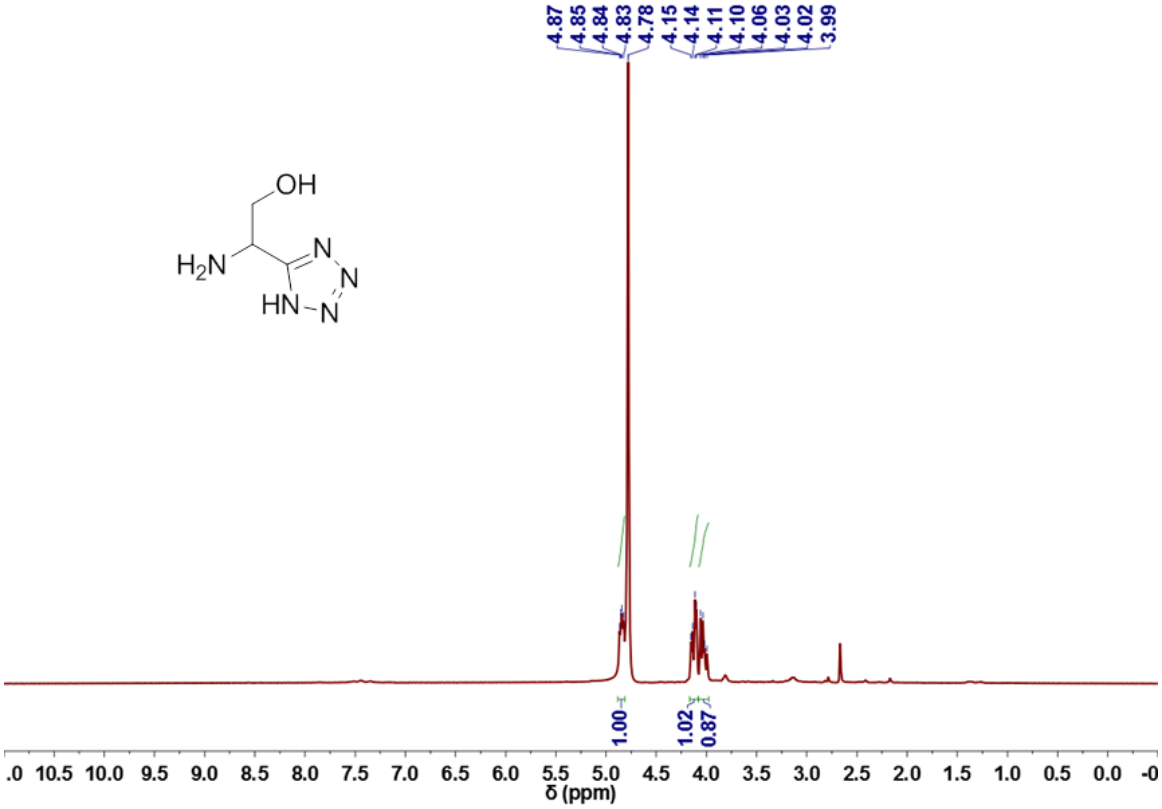
3-Amino-3-(1H-tetrazol-5-yl)propanoic acid (6n)

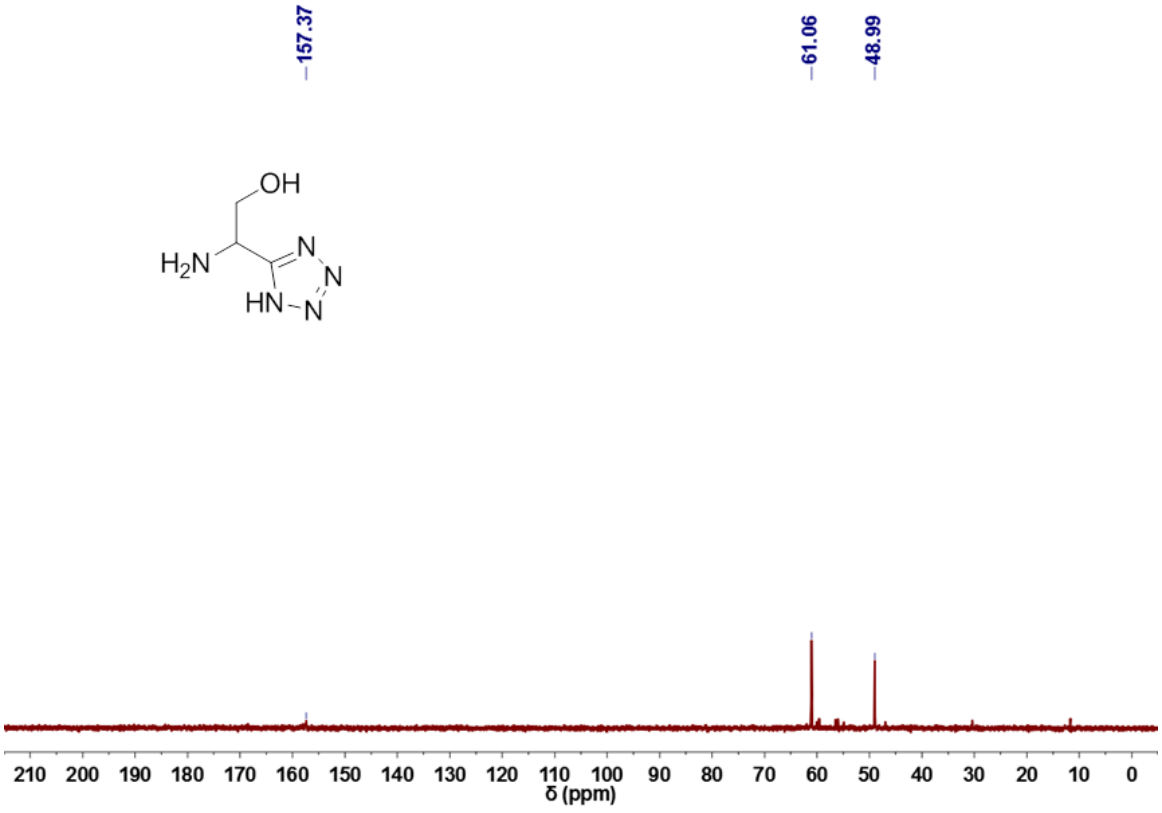


3-Amino-3-(1H-tetrazol-5-yl)propanamide (6o)

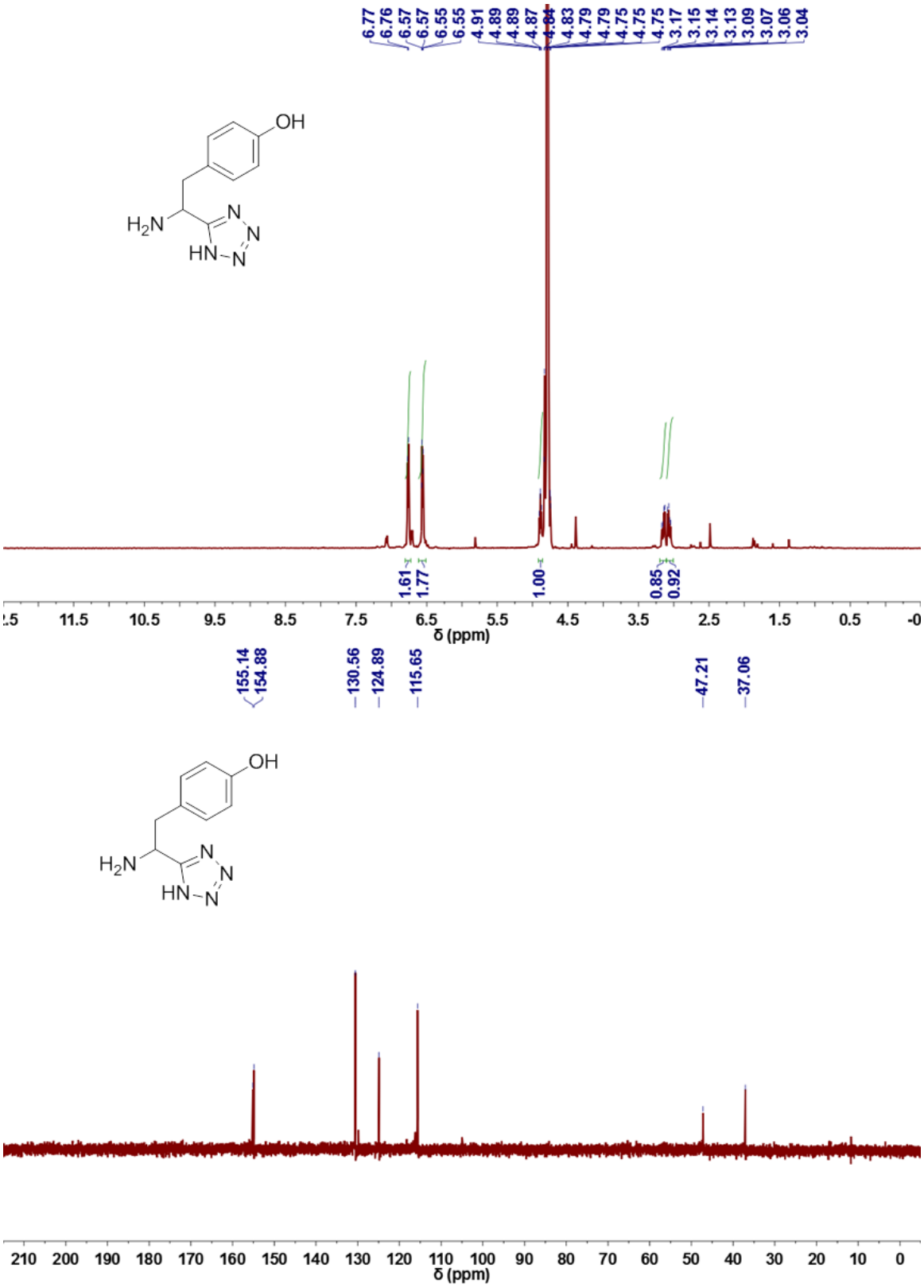


2-Amino-2-(1H-tetrazol-5-yl)ethanol (6p)

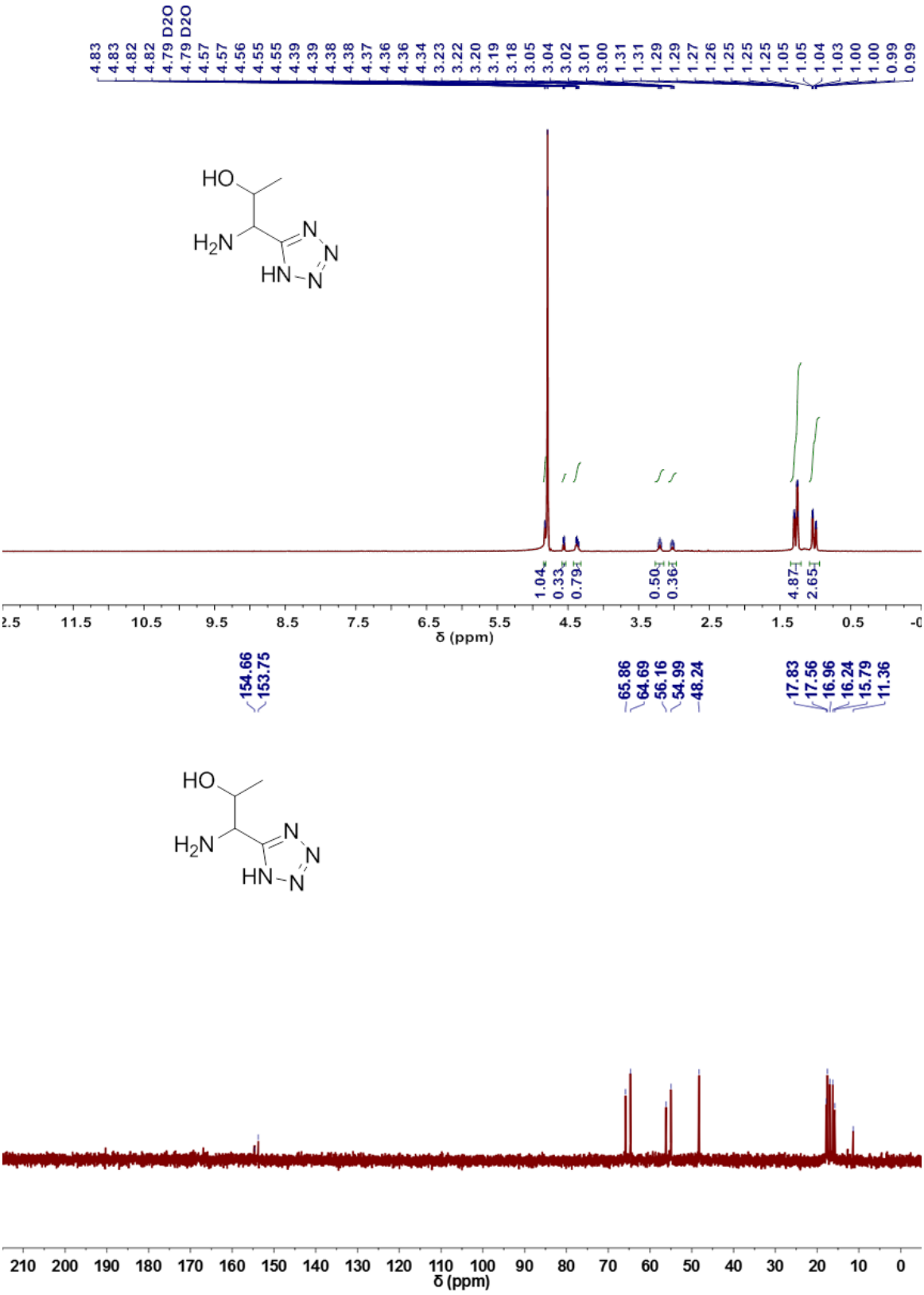




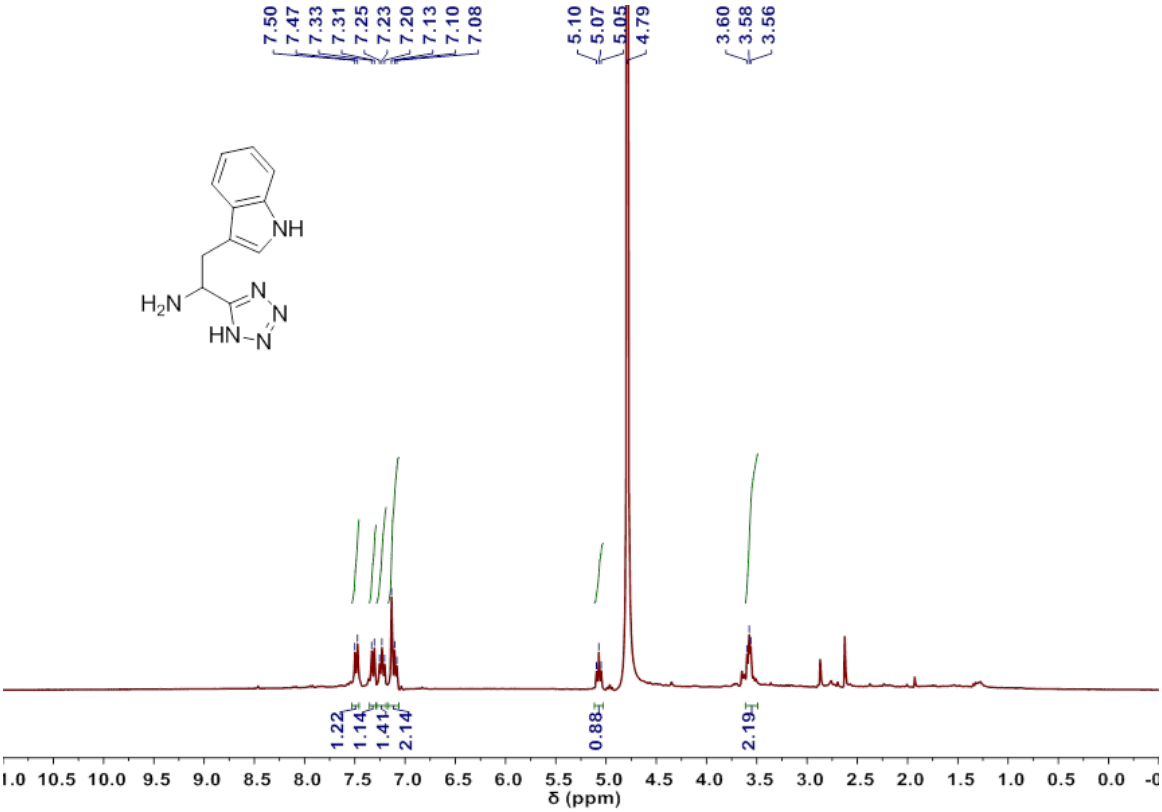
4-(2-Amino-2-(1H-tetrazol-5-yl)ethyl)phenol (6q)

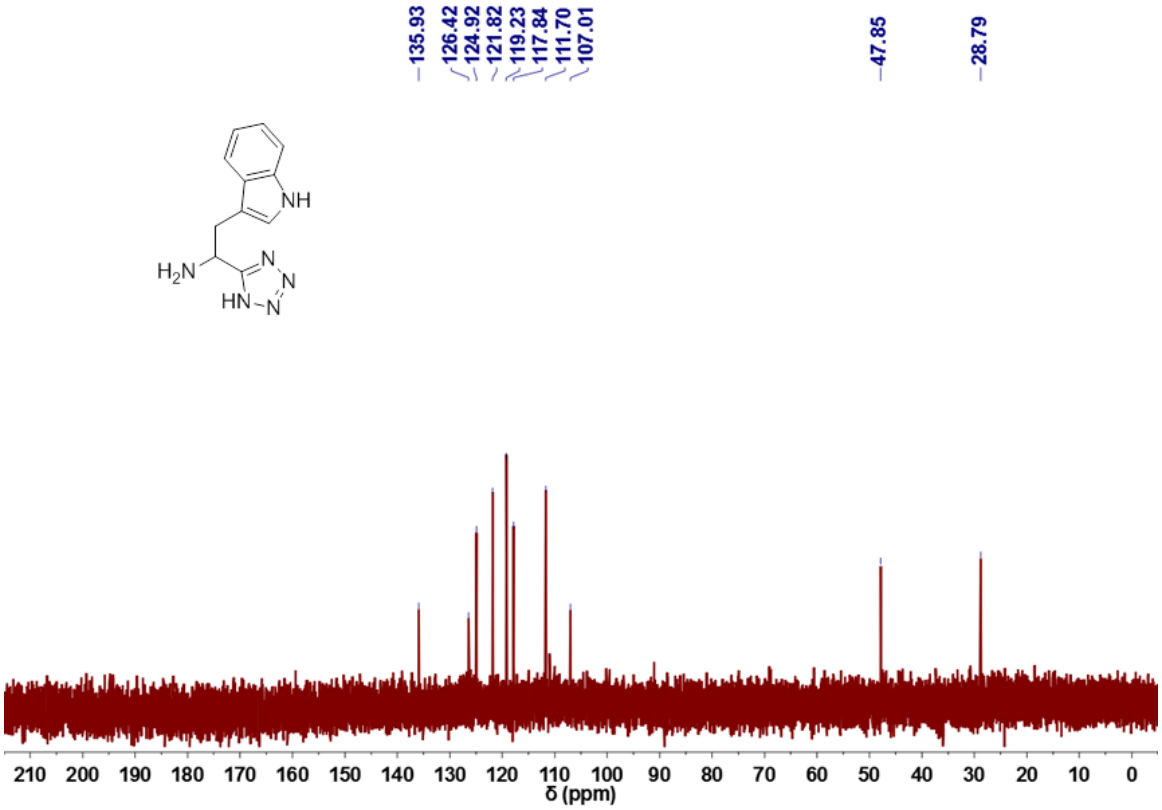


Amino-1-(1H-tetrazol-5-yl)propan-2-ol (6r)

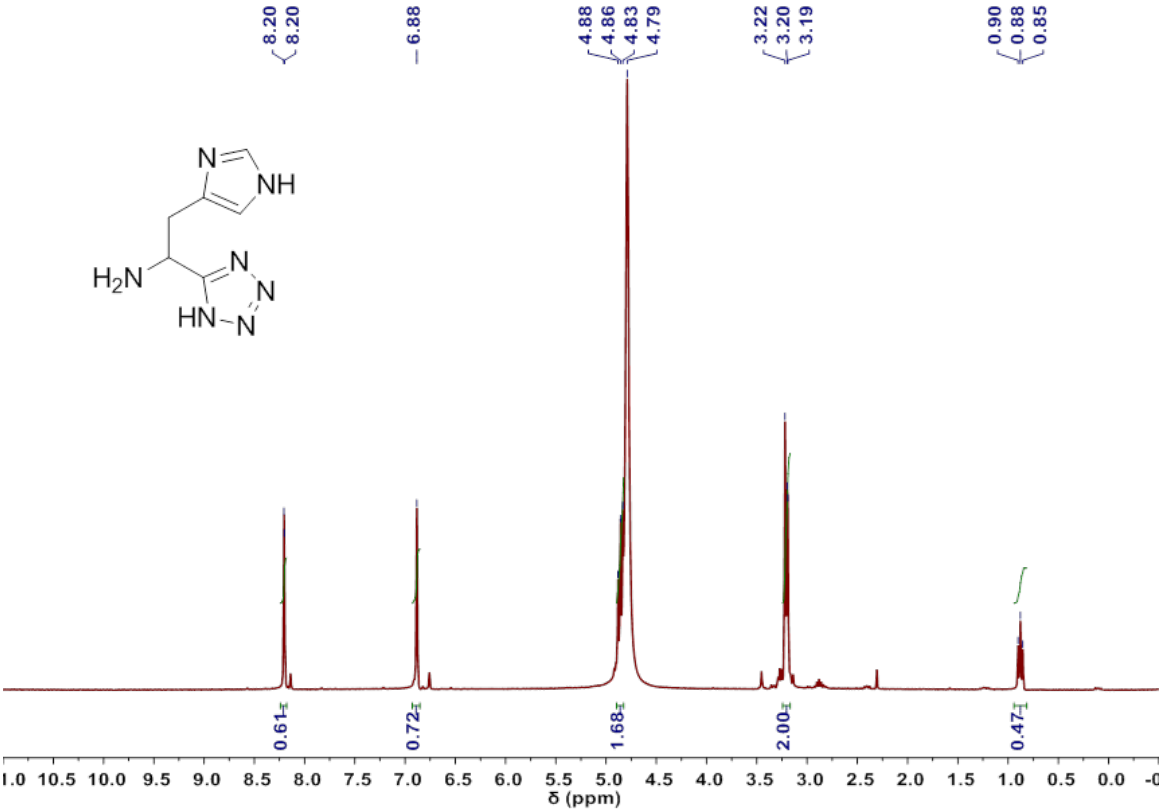


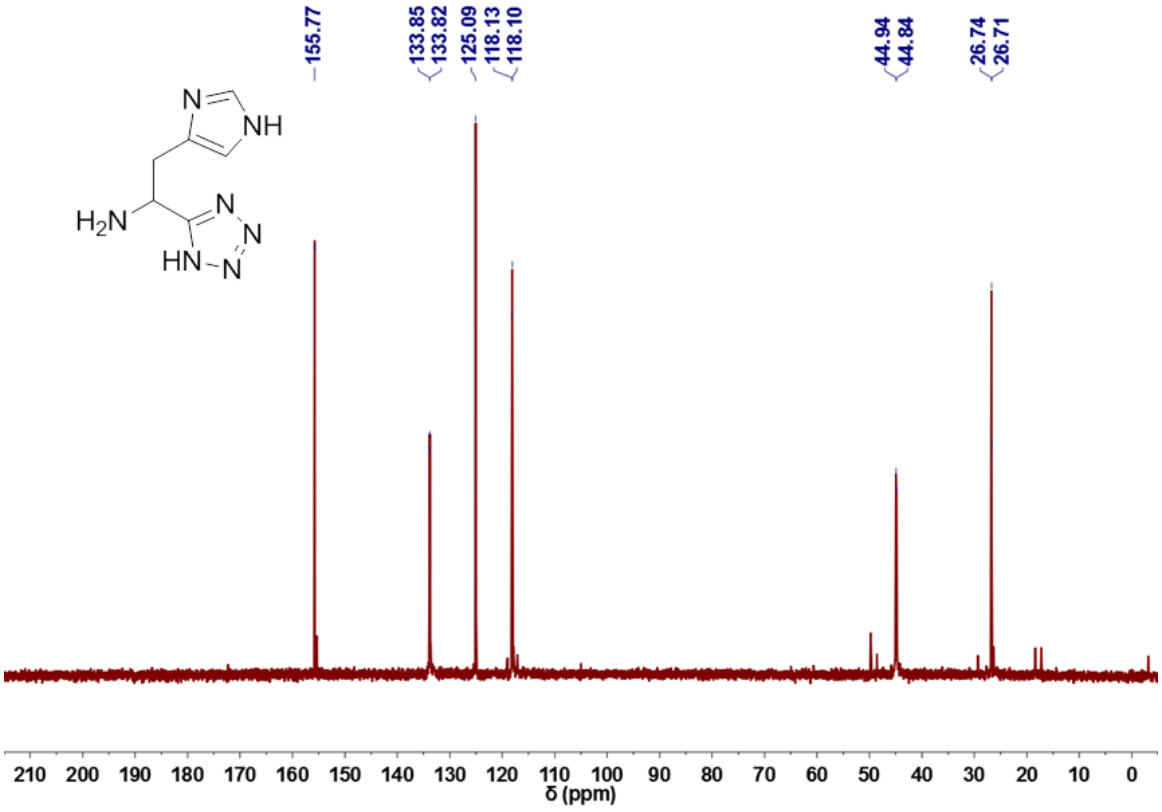
4-(2-Amino-2-(1H-tetrazol-5-yl)ethyl)phenol (6s)



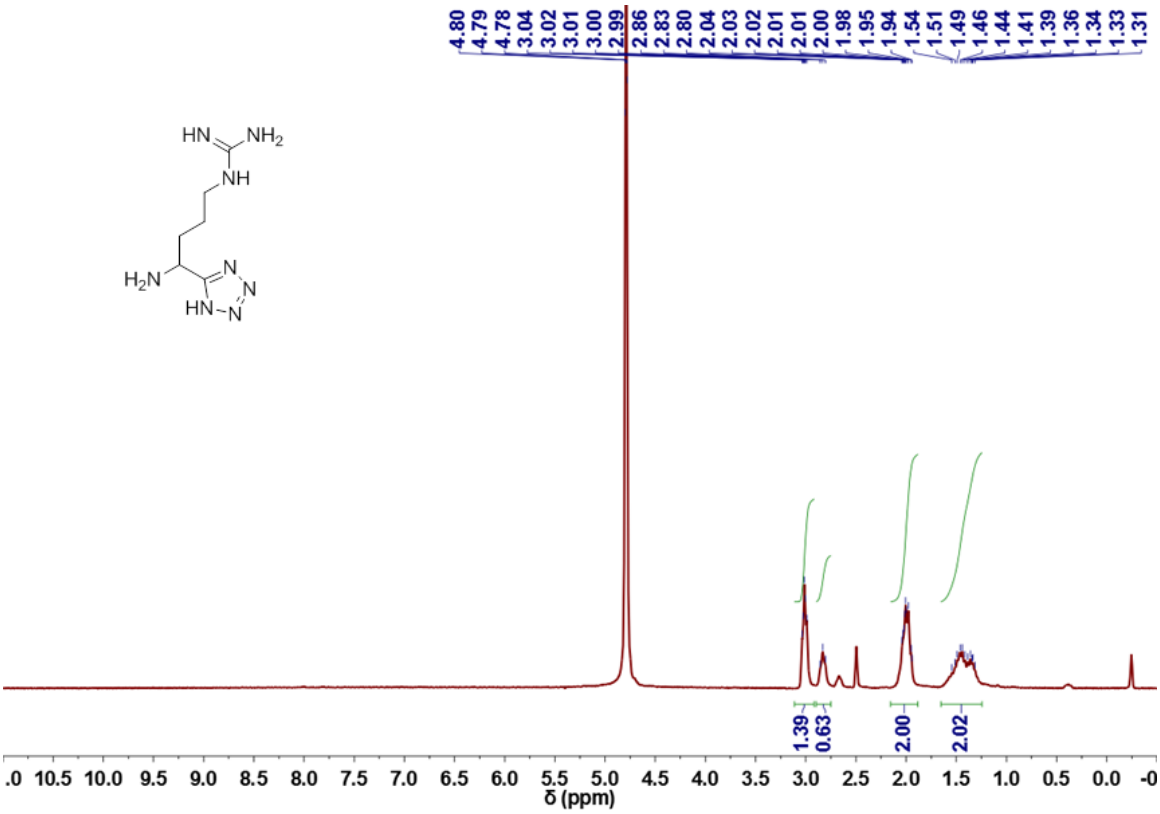


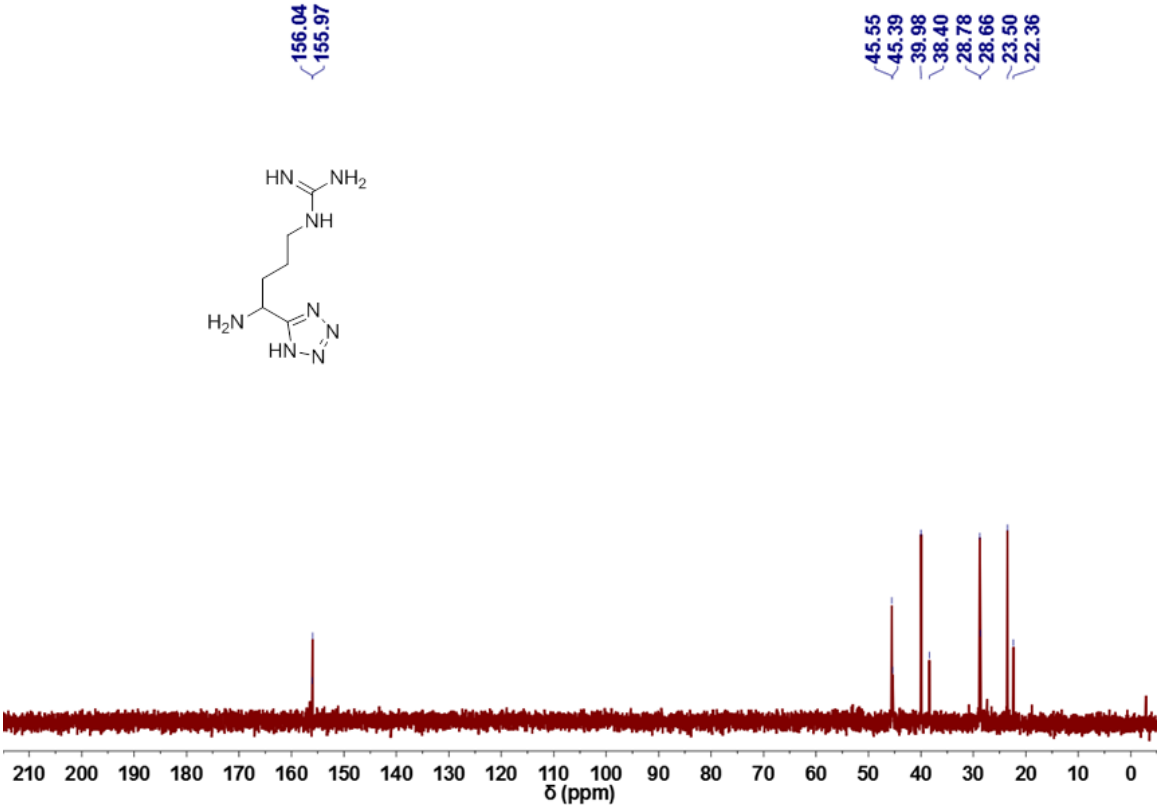
2-(1H-Imidazol-4-yl)-1-(1H-tetrazol-5-yl)ethanamine (6t)



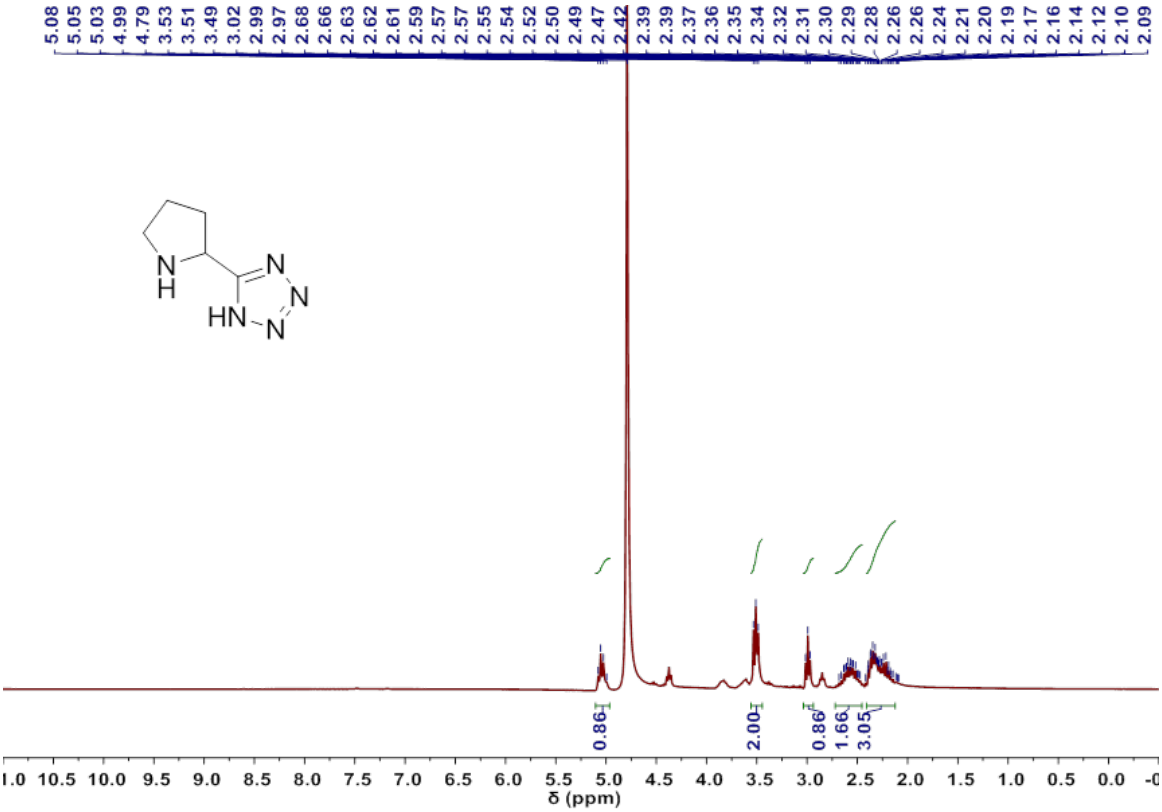


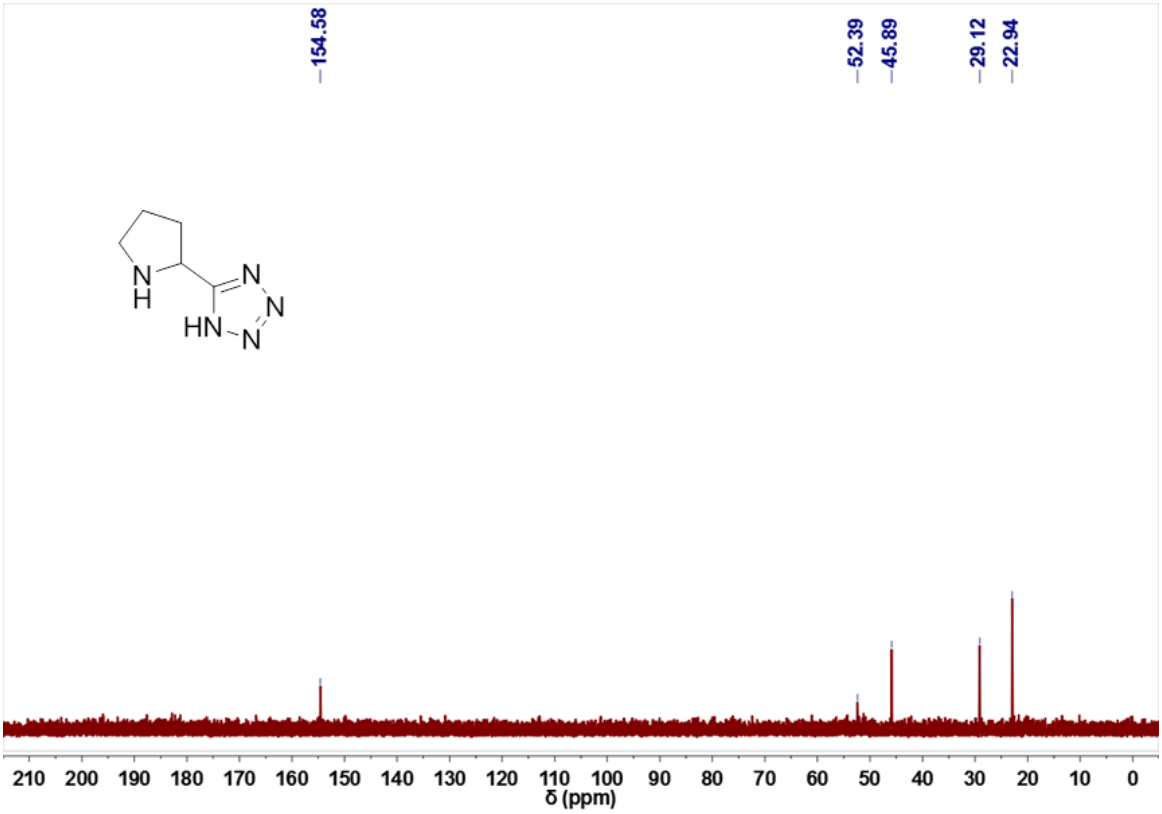
1-(4-Amino-4-(1H-tetrazol-5-yl)butyl)guanidine (6u)



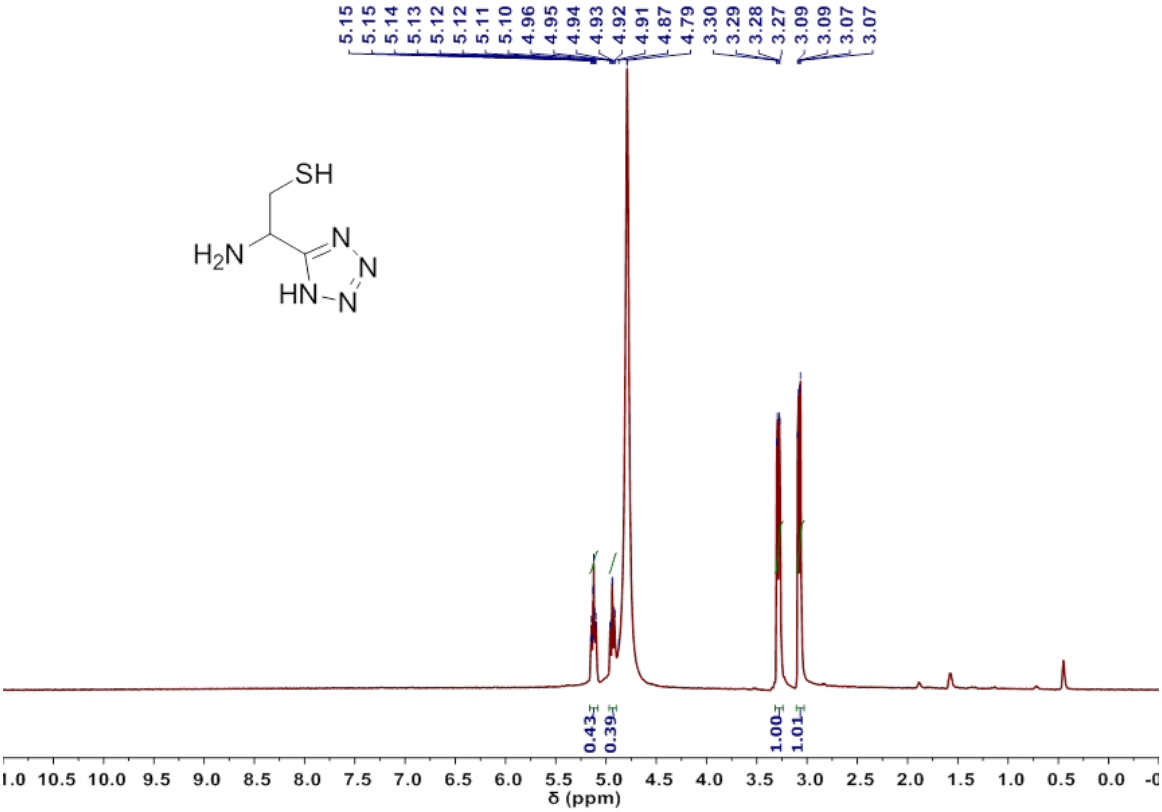


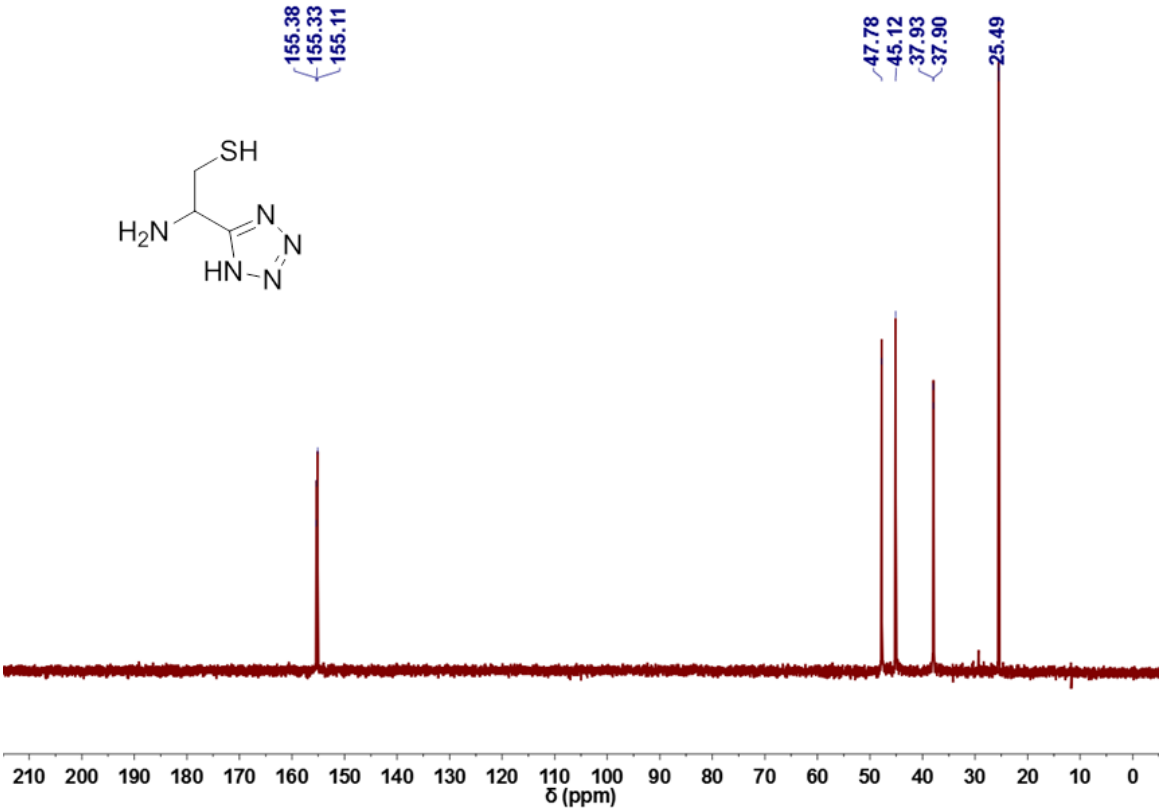
5-(Pyrrolidin-2-yl)-1H-tetrazole (6v)



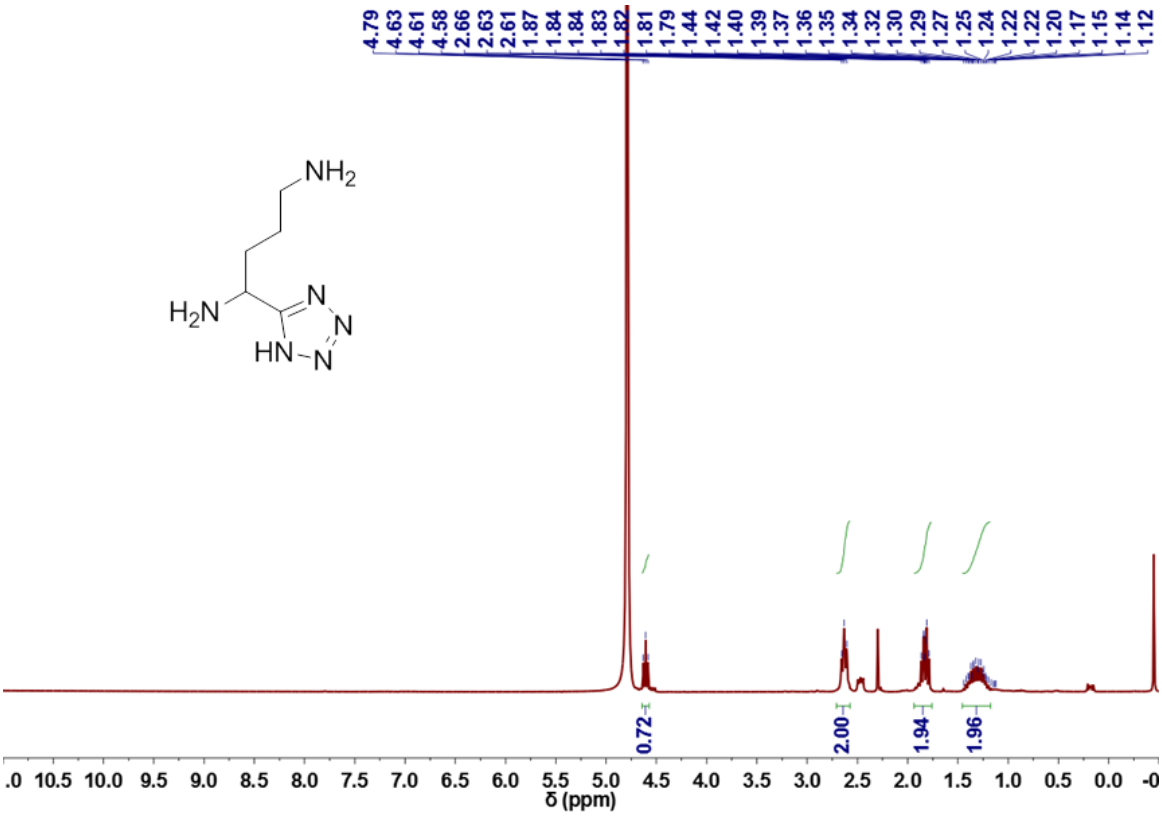


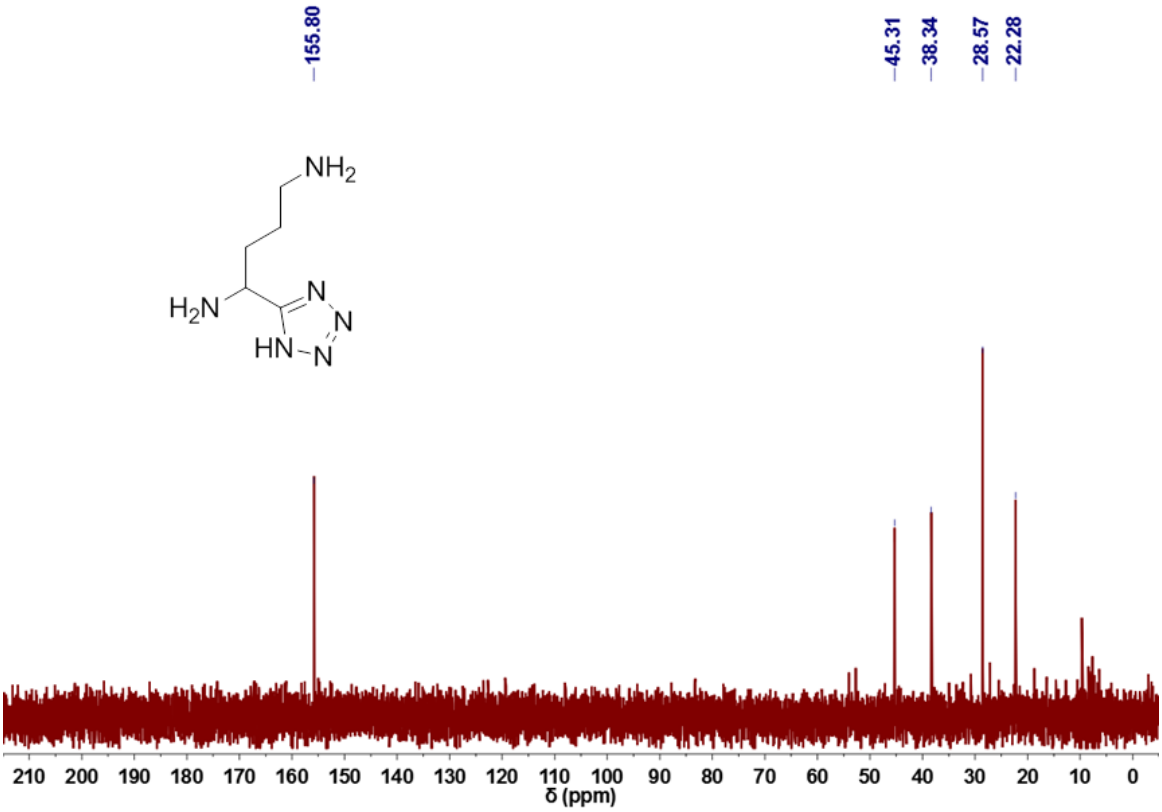
2-Amino-2-(1H-tetrazol-5-yl)ethanethiol (6w)



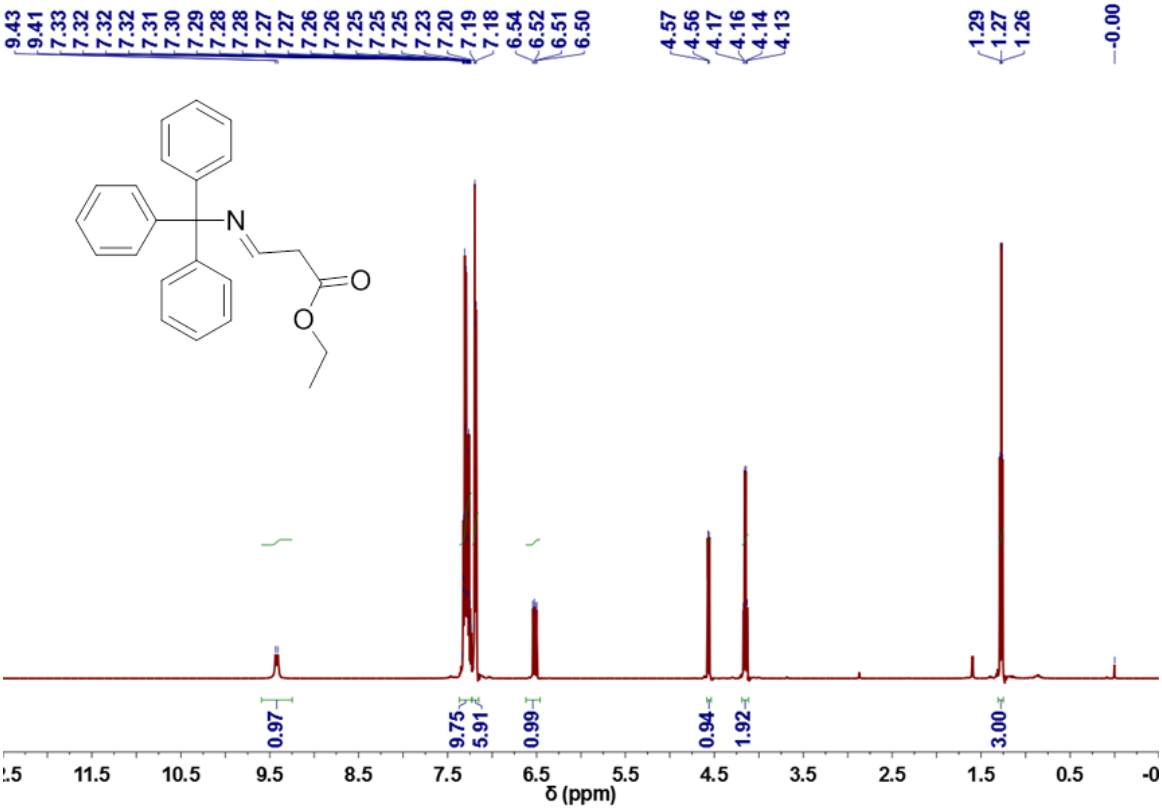


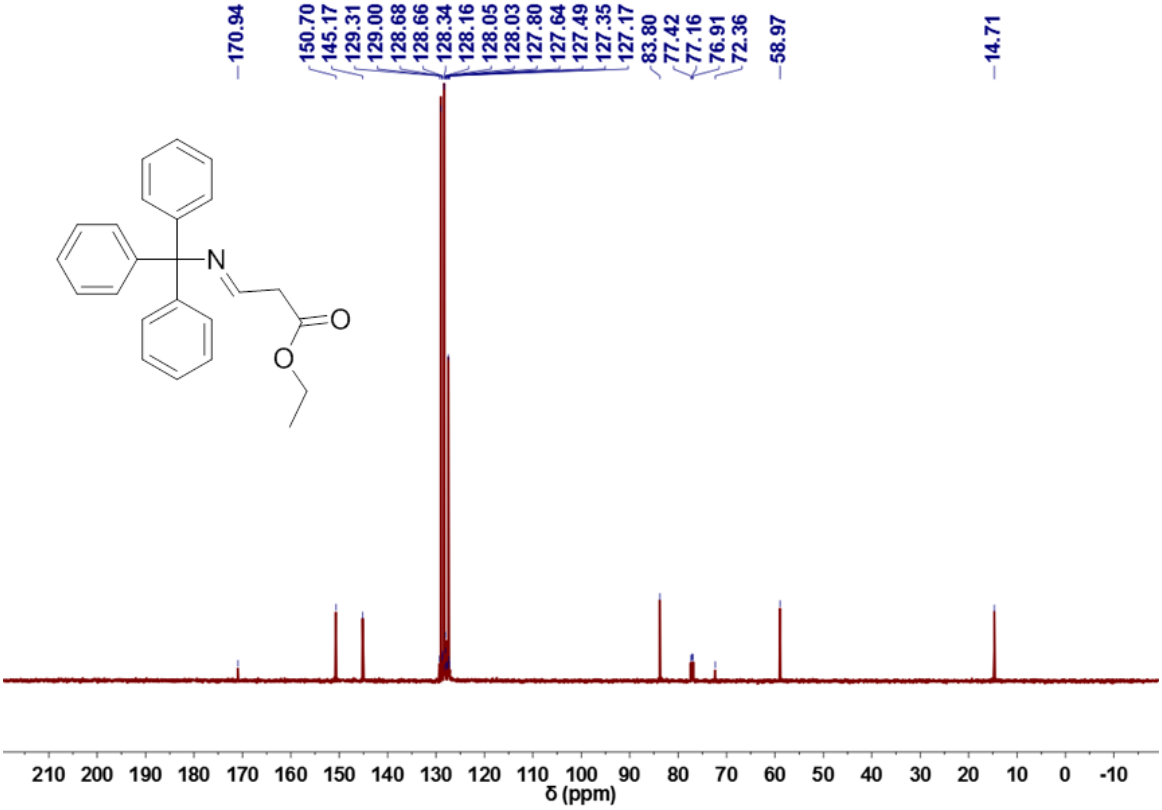
2-Amino-2-(1H-tetrazol-5-yl)ethanethiol (6x)





Ethyl 3-(tritylimino)propanoate (25)





3. Single Crystal X-Ray Structure Determination of Compounds 5a and 5j

Crystallographic data collection and structure refinement

The good quality single crystals of compounds **5a** and **5j**, suitable for X-ray diffraction experiment, were selected after crystallization process and mounted on Micro Mounts^{TM}. Intensity data were collected on the SuperNova diffractometer (*Rigaku - Oxford Diffraction*) equipped with Atlas detector and microfocus Mo Kα (λ = 0.71073 Å) radiation source at 120 K for crystals **5a** and **5j**. Data were processed using CRYSALIS^{Pro} [1]. The crystal data, details of data collection and structure refinement are summarized in Table 1.

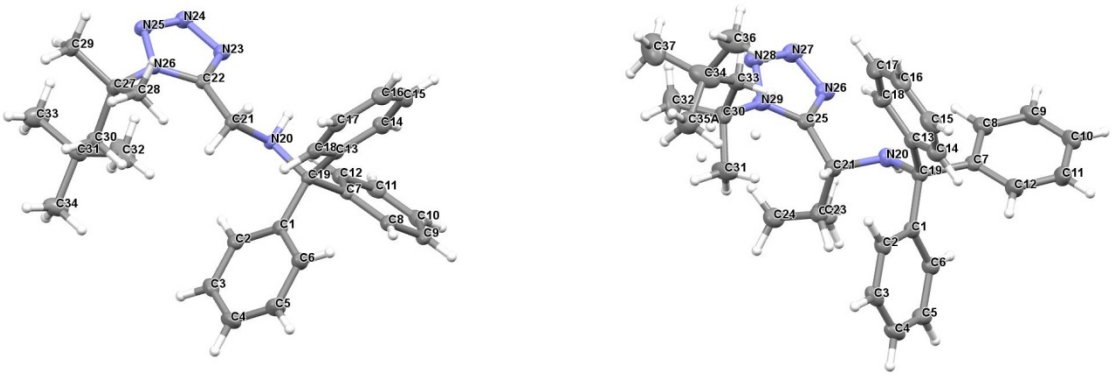
The phase problem was solved with SUPERFILP [2]. Non-hydrogen atoms were refined anisotropically. All hydrogen atoms bonded to carbon atoms were included in the structure factor calculations at idealized positions and refined using riding model with the isotropic displacement parameter U_{iso}[H] = 1.2 (or 1.5) U_{eq}[C]. The hydrogen atoms bounded to nitrogen or oxygen atoms were found on the difference Fourier map and refined with no restrains on displacement parameters. The structures were refined using weighted full-matrix least-squares on F^2 by SHELXL program [3]. Calculations were performed using WinGX integrated system (ver. 2013.2) [4]. Structural description graphics were performed with program Mercury 3.5 [5].

A local disorder of *tert*-butyl group is observed for structure **5j**, where two methyl groups required refinement of the disorder, according to high positive density on the difference Fourier map. Two alternative positions of methyl groups C35 and C37 in **5j** were refined of ca. 77% and 23%, occupancy, whereas for atom C36 the position of the disordered methyl was not clearly indicated on the difference map.

Crystallographic data for structures presented in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication: CCDC 1410965 (**5a**), CCDC 1410966 (**5j**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Table 1. Crystal data and structure refinement results of compounds **5a** and **5j**.

	5a	**5j**
Empirical moiety formula	C_{29} H_{35} N_5	C_{32} H_{39} N_5
Formula weight [g/mol]	453.62	493.68
Temperature [K]	120.0 (1)	120.0 (1)
Wavelength [Å]	0.71073	0.71073
Crystal system	Monoclinic	Orthorombic
Space group	$P2_1/c$	P*bca*
Unite cell dimensions	a = 8.8017(3) Å b = 27.2931(8) Å c = 11.1574(4) Å α=90° β= 107.933(4) ° γ=90°	a = 17.898(5) Å b = 14.928(5 Å c = 20.439(5 Å α=90° β=90° γ=90°
Volume [$Å^3$]	2550.08(15)	5461.00(3)
Z	4	8
D_{calc} [Mg/m^3]	1.182	1.201
μ [mm^{-1}]	0.071	0.072
F(000)	976	2128
Crystal size [mm^3]	0.4 x 0.4 x 0.2	0.6 x 0.5 x 0.5
Θ range	2.85° to 28.56°	2.95° to 28.61°
Index ranges	$-10 \leq h \leq 11$, $-34 \leq k \leq 34$, $-13 \leq l \leq 13$	$-15 \leq h \leq 23$, $-15 \leq k \leq 20$, $-26 \leq l \leq 24$
Refl. collected	13411	26165
Independent reflections	5246 [R(int) = 0.0245]	6487 [R(int) = 0.0360]
Completeness [%] to Θ	99.8 (Θ 26.3°)	99.7 (Θ 26.3°)
Absorption correction	Multi-scan	Multi-scan
Max. and min. transmission	0.933 and 1.000	0.514 and 1.000
Refinement method	Full-matrix least-squares on F2	Full-matrix least-squares on F^2
Data/ restraints/parameters	5246 / 0 / 317	6487 / 4 / 357
GooF on F2	1.034	1.030
Final R indices [I>2sigma(I)]	R1= 0.0417, wR2= 0.0946	R1= 0.0499, wR2= 0.1127
R indices (all data)	R1= 0.0538, wR2= 0.1021	R1= 0.0663, wR2= 0.1242
$\Delta\rho_{max}$, $\Delta\rho_{min}$ [$e \cdot Å^{-3}$]	0.27 and -0.19	0.41 and -0.59



5a **5j**

Figure 1. A view of a molecule of compounds **5a and 5j** in the crystal structure, showing the numbering scheme was employed. For the crystal structure of compound **5j**, the more abundant conformer is presented. Anisotropic atomic displacement ellipsoids for the non-hydrogen atoms are shown at the 50 % probability level and hydrogen atoms are displayed as spheres of arbitrary radius.

Acknowledgements

The research was carried out with the equipment purchased thanks to the financial support of the European Regional Development Fund in the framework of the Polish Innovation Economy Operational Program (contract no. POIG.02.01.00-12-023/08).

References

[1] Oxford Diffraction (2006). CrysAlisPro Oxford Diffraction Ltd, Abingdon, England, Version 1.171.36.20 (release 27-06-2012 CrysAlis171.NET)

[2] Palatinus, L. Chapuis, G., J. Appl. Cryst. 2007, 40, 786.

[3] Sheldrick, G. M. ActaCryst. 2008, A64, 112-122.

[4] Farrugia, L., J. J. Appl. Cryst. 1999, 32, 837-838.

[5] Macrae, C. F., Edgington, P.R., McCabe, P., Pidcock,, E., Shields G.P., Taylor, R., Towler, M., & van de Streek J., J. Appl. Cryst. 2006, 39, 453-457.

4. Single Crystal X-Ray Structure Determination of Compound 5l

Crystallographic data collection and structure refinement

Data were collected on an X-ray single crystal diffractometer equipped with a CCD detector (Bruker APEX II, κ–CCD), a fine-focus sealed tube (Bruker AXS, D8) (**5l**) with MoK$_\alpha$ radiation (λ = 0.71073 Å), and a graphite monochromator by using the SMART software package [1]. The measurements were performed on a single crystal coated with perfluorinated ether. The crystal was fixed on the top of a cactus prickle (Opuntia ficusindia) and transferred to the diffractometer. The crystal was frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using SAINT [2]. Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS [2]. Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structure. The structure was solved by direct methods with the aid of successive difference Fourier maps, and were refined against all data using WinGX [7] based on SIR-92 [3] in conjunction with SHELXL-97 [5]. Unless otherwise noticed non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms could be located in the difference Fourier maps and were allowed to refine freely. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2-F_c^2)^2$ with SHELXL-97 [5] weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography [4]. Images of the crystal structures were generated by PLATON [6]. CCDC 111111 (**5l**) contains the supplementary crystallographic data for this compound. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or via https://www.ccdc.cam.ac.uk/services/structure_deposit/

5l: Full refinement was possible without running into problems.

Compound 5l

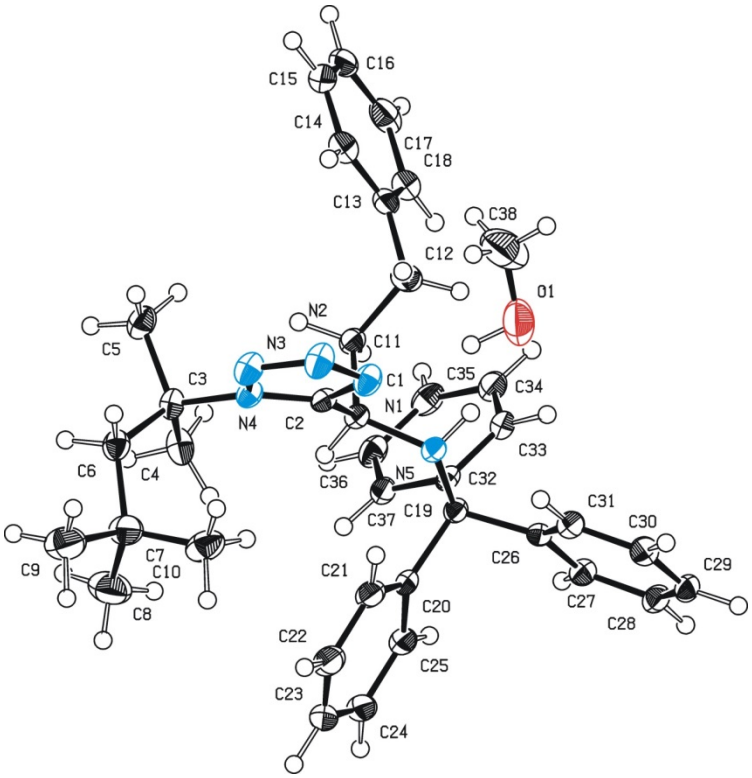


Figure 2. Ortep drawing of compound **5l** with 50% ellipsoids [6].

Operator:	*** Herdtweck ***
Molecular Formula:	C_{38} H_{47} N_5 O (C_{37} H_{43} N_5), (C H_4 O)
Crystal Color / Shape	Colorless fragment
Crystal Size	Approximate size of crystal fragment used for data collection: 0.20 × 0.46 × 0.46 mm
Molecular Weight:	589.81 a.m.u.
F_{000}:	1272
Systematic Absences:	h0l: h+l≠2n; 0k0: k≠2n
Space Group:	Monoclinic $P\ 2_1/n$ (I.T.-No.: 14)
Cell Constants:	Least-squares refinement of 9870 reflections with the programs "APEX suite" and "SAINT" [1,2]; theta range 1.83° < θ < 25.37°; Mo($K_{\bar{\alpha}}$); λ = 0.71073 Å a = 12.5284(4) Å b = 22.2553(7) Å β = 107.6692(9)° c = 12.7401(4) Å V = 3384.66(19)· Å^3; Z = 4; D_{calc} = 1.158 g cm^{-3}
Diffractometer:	Kappa APEX II (Area Diffraction System; BRUKER AXS); sealed tube; graphite monochromator; 50 kV; 30 mA; λ = 0.71073 Å; Mo($K_{\bar{\alpha}}$)
Temperature:	(-150±1) °C; (123±1) K

Measurement Range:	1.83° < θ < 25.37°; h: -15/15, k: -26/26, l: -15/15	
Measurement Time:	2 × 7.50 s per film	
Measurement Mode:	measured: 6 runs; 3249 films / scaled: 6 runs; 3249 films φ– and ω–movement; Increment: $\Delta\varphi/\Delta\omega$ = 0.50°; dx = 45.0 mm	
LP - Correction:	Yes [2]	
Intensity Correction	No/Yes; during scaling [2]	
Absorption Correction:	Multi-scan; during scaling; μ = 0.071 mm^{-1} [2]	
	Correction Factors: T_{min} = 0.6898 T_{max} = 0.7452	
Reflection Data:	69991	reflections were integrated and scaled
	1215	reflections systematic absent and rejected
	68776	reflections to be merged
	6206	independent reflections
	0.020	R_{int}: (basis F_o^2)
	6206	independent reflections (all) were used in refinements
	5558	independent reflections with $I_o > 2\sigma(I_o)$
	99.9 %	completeness of the data set
	585	parameter full-matrix refinement
	10.6	reflections per parameter
Solution:	Direct Methods [3, 7]; Difference Fourier syntheses	
Refinement Parameters:	In the asymmetric unit:	
	44	Non-hydrogen atoms with anisotropic displacement parameters
	47	Hydrogen atoms with isotropic displacement parameters
Hydrogen Atoms:	All hydrogen atom positions were found in the difference map calculated from the model containing all non-hydrogen atoms. The hydrogen positions were refined with individual isotropic displacement parameters.	
Atomic Form Factors:	For neutral atoms and anomalous dispersion [4, 5, 7]	
Extinction Correction:	no	
Weighting Scheme:	$w^{-1} = \sigma^2(F_o^2)+(a*P)^2+b*P$ with a: 0.0411; b: 1.1344; P: [Maximum(0 or F_o^2)+2$*F_c^2$]/3	
Shift/Err:	Less than 0.001 in the last cycle of refinement	
Resid. Electron Density:	+0.21 $e_{0;}^-/Å^3$; -0.21 $e_{0;}^-/Å^3$	
R1:	$\Sigma(\|\|F_o\|-\|F_c\|\|)/\Sigma\|F_o\|$	
[$F_o > 4\sigma(F_o)$; N=5558]:		= 0.0344
[all reflctns; N=6206]:		= 0.0390
wR2:	$[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$	
[$F_o > 4\sigma(F_o)$; N=5558]:		= 0.0837
[all reflctns; N=6206]:		= 0.0874
Goodness of fit:	$[\Sigma w(F_o^2-F_c^2)^2/(NO-NV)]^{1/2}$	= 1.026
Remarks:	Refinement expression $\Sigma w(F_o^2-F_c^2)^2$	

References

[1] APEX suite of crystallographic software. APEX 2 Version 2008.4. Bruker AXS Inc., Madison, Wisconsin, USA (2008).

[2] SAINT, Version 7.56a and SADABS Version 2008/1. Bruker AXS Inc., Madison, Wisconsin, USA (2008).

[3] Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli M. "**SIR92**", *J. Appl. Cryst.* **1994**, *27*, 435-436.

[4] International Tables for Crystallography, Vol. C, Tables 6.1.1.4 (pp. 500-502), 4.2.6.8 (pp. 219-222), and 4.2.4.2 (pp. 193-199), Wilson, A. J. C., Ed., Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992.

[5] Sheldrick, G. M. "**SHELXL-97**", University of Göttingen, Göttingen, Germany, (1998).

[6] Spek, A. L. "**PLATON**", A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, (2010).

[7] L. J. Farrugia, "**WinGX** (Version 1.70.01 January 2005) ", *J. Appl. Cryst.* **1999**, *32*, 837-838.