SUPPORTING INFORMATION

Domino reaction of pyrrolidinium ylides: Michael addition – [1,2]-Stevens rearrangement

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1. Reactions optimization

Table S1. Optimization of reaction of salt **1** with methyl acrylate (**2d**)

Entry	Salt	**2d/1**[a] [mol/mol]	DMSO [mL]	Composition of the reaction mixture [%][b]	
1	**1a**	10	1.25	**4da**, 26	**3a**,3
2	**1a**	10	0.9	**4da**, 48	**3a**,5
3	**1a**	5	0.9	**4da**, 57	**3a**,4
4	**1a**	2	0.9	**4da**, 65	**3a**,5
5	**1a**	1.5	0.9	**4da**, 64	**3a**,5
6	**1a**	**2**	**0.5**	**4da**, **77**	**3a**,4
7	**1a**	2	0.25	**4da**, 72	**3a**,4
8	**1b**	**2**	**0.5**	**4db, 75**	**3b**, 1
9	**1c**	**2**	**0.5**	**4dc, 78**	**3c**, 2

[a] Reaction conditions: a mixture of salt **1** (0.25 mmol), **2d** (excess given in table), DMSO (volume given in table) and K_2CO_3 (10 eq) was stirred for 17 h.

[b] Determined by GC.

Table S2. Optimization of reaction of salt **1** with *t*-butyl acrylate (**2c**)

Entry	**Salt** [mmol]	**2c/1** [mol/mol]	Solvent [mL]	Base	Time [h]	Content of products **4** and **3** in the reaction mixture [%][a]	
1	**1a**, 0.7	10	CH_2Cl_2, 5	50% NaOH[b]	6	**4ca**, 37	**3a**, 39
2	**1a**, 0.7	20	CH_2Cl_2, 5	50% NaOH[b]	6	**4ca**, 19	**3a**, 35
3	**1a**, 0.25	2	DMSO, 1.8	K_2CO_3[c]	17	**4ca**, 60	**3a**, 8
4	**1a**, 0.25	**2**	DMSO, 0.5	K_2CO_3[c]	17	**4ca**, **76**	**3a**, 4
5	**1b**, 0.25	**2**	DMSO, 0.5	K_2CO_3[c]	17	**4cb**, **74**	**3b**, 5
6	**1c**, 0.25	**2**	DMSO, 0.5	K_2CO_3[c]	17	**4cc**, **79**	**3c**, 3

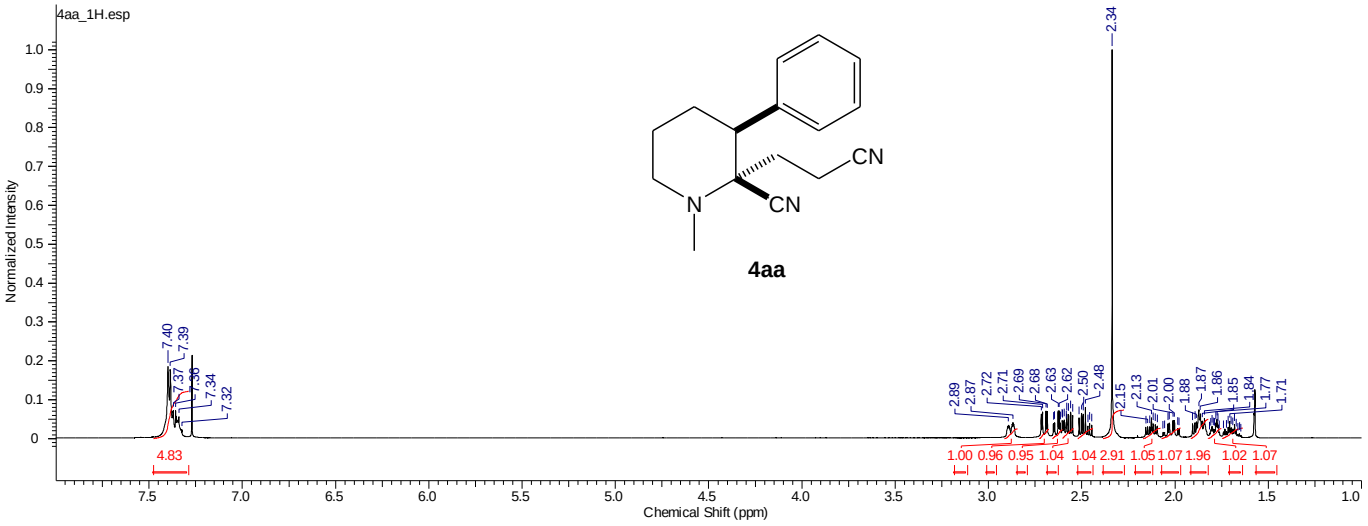
[a] Determined by GC.

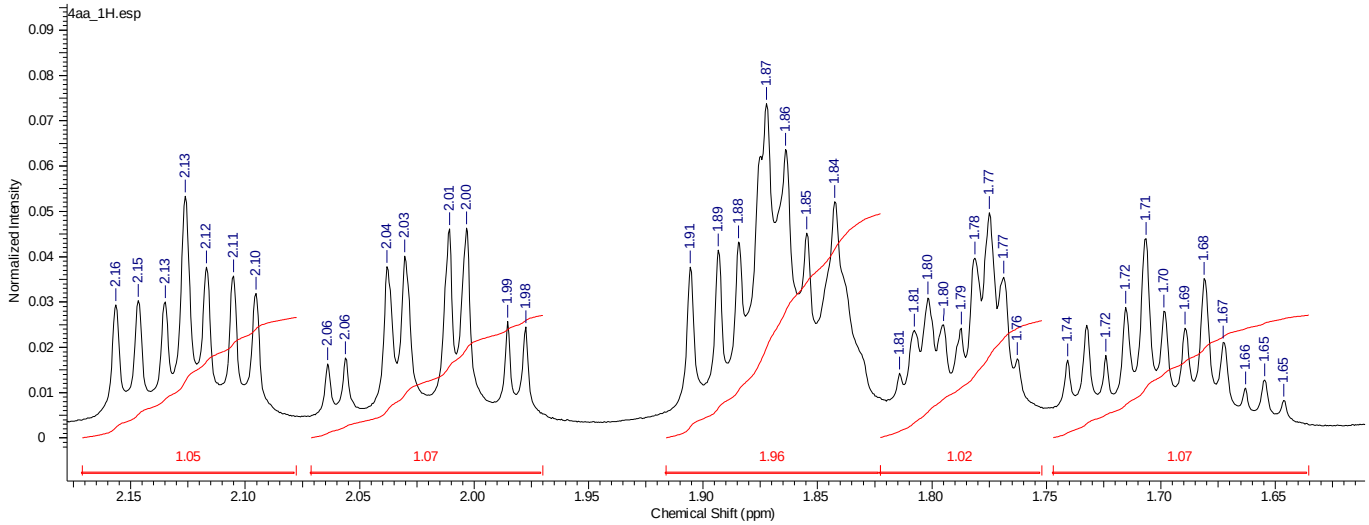
[b] 1.5 mL

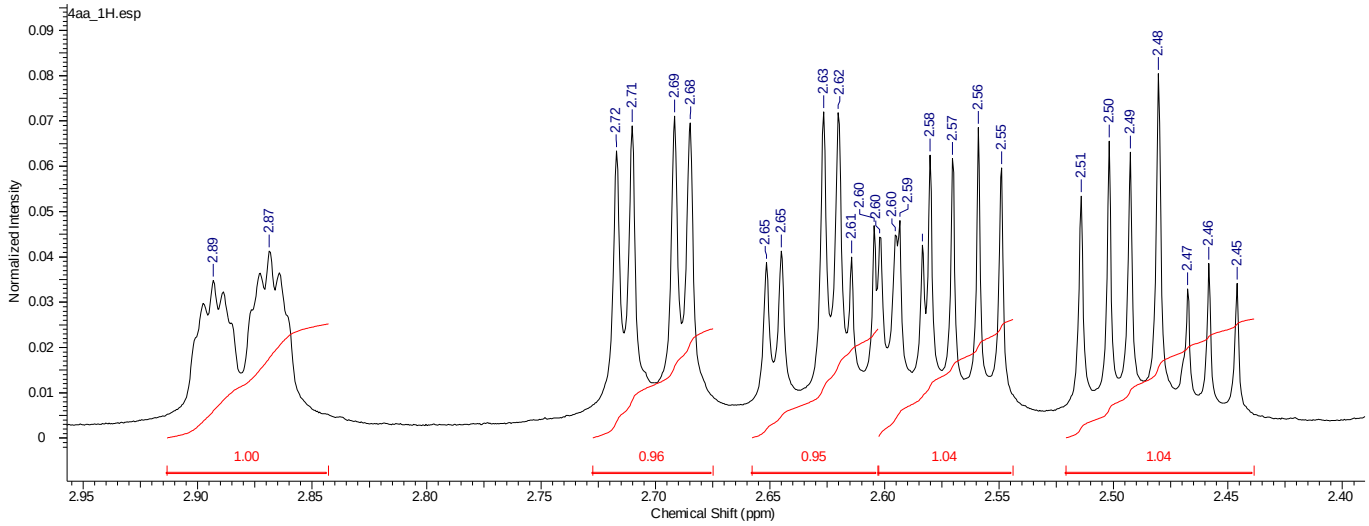
[c] 10 equivalents

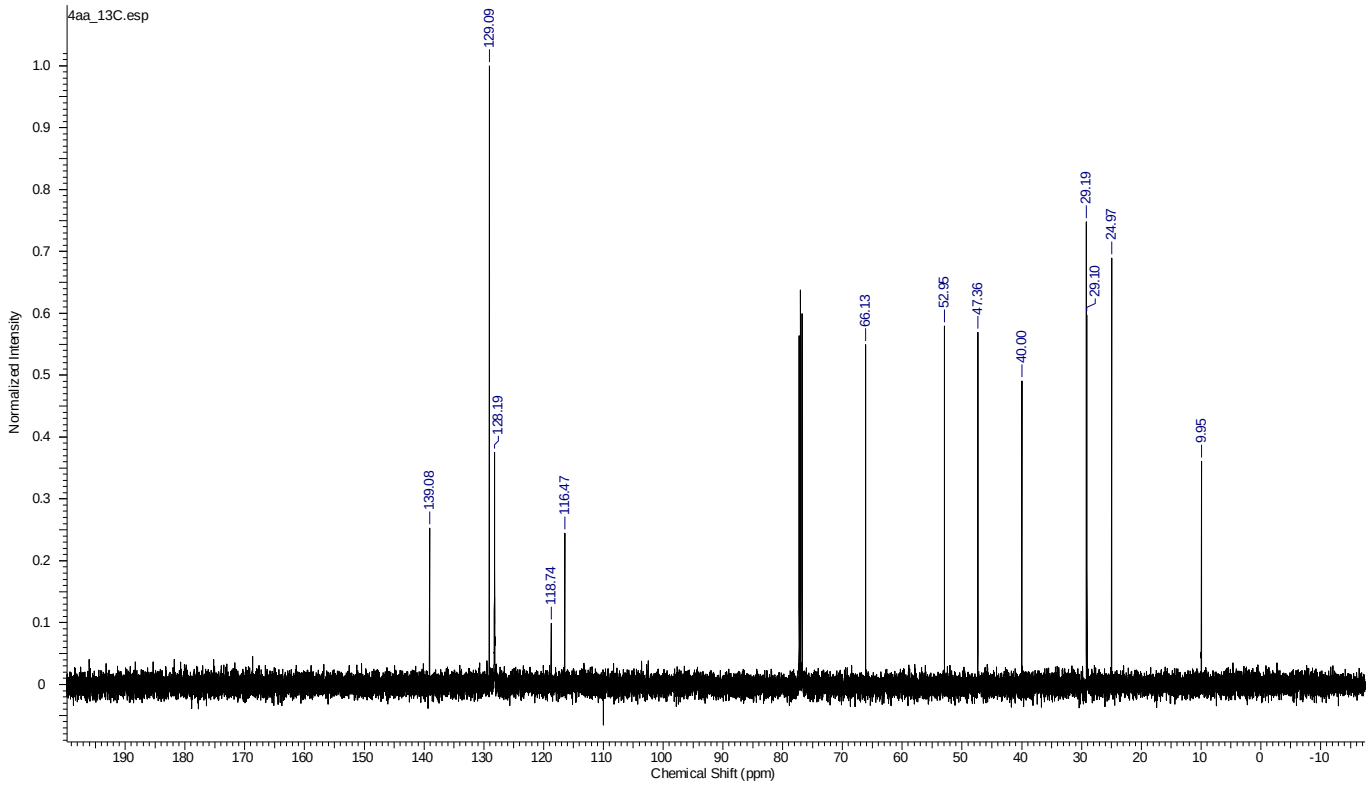
2. ^{1}H and ^{13}C spectra of compounds 4

2-cyano-2-(2-cyanoethyl)-1-methyl-3-phenylpiperidine (4aa)









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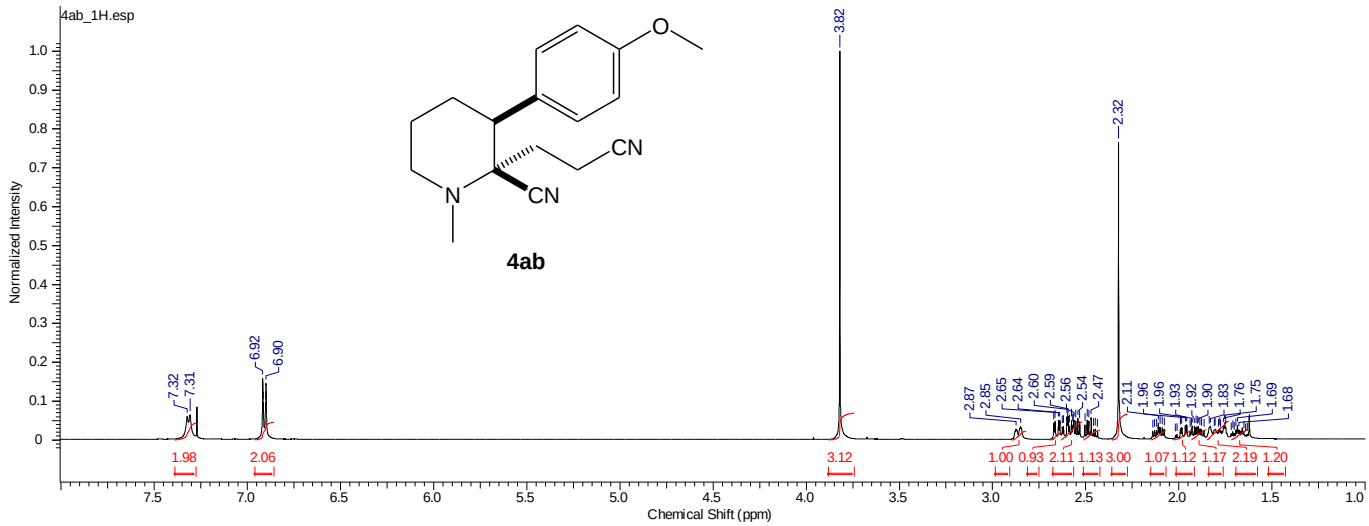

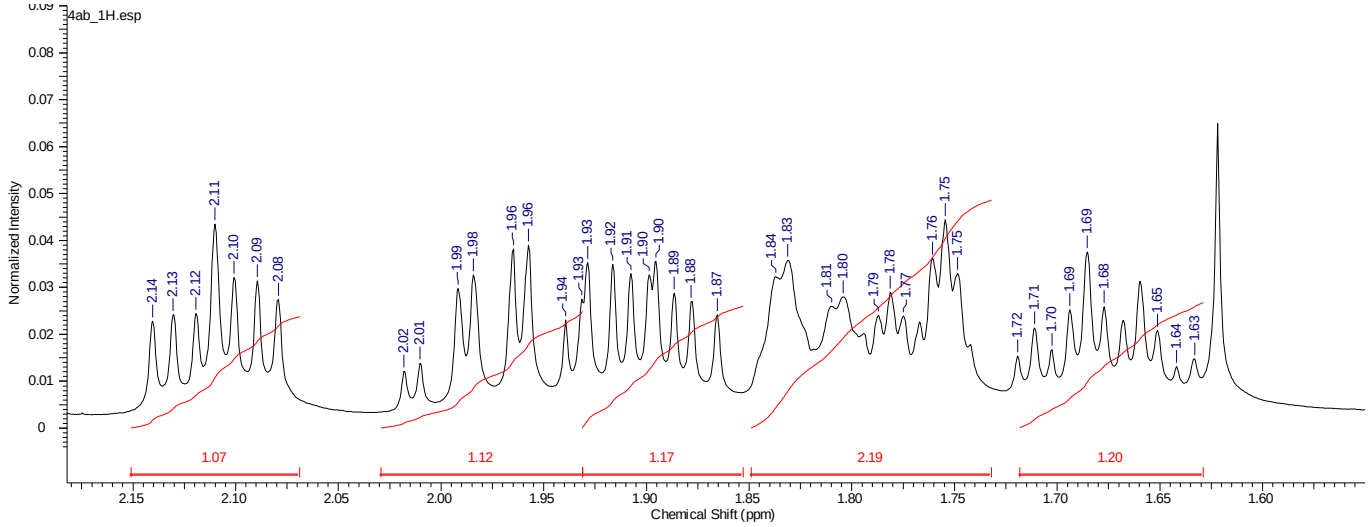
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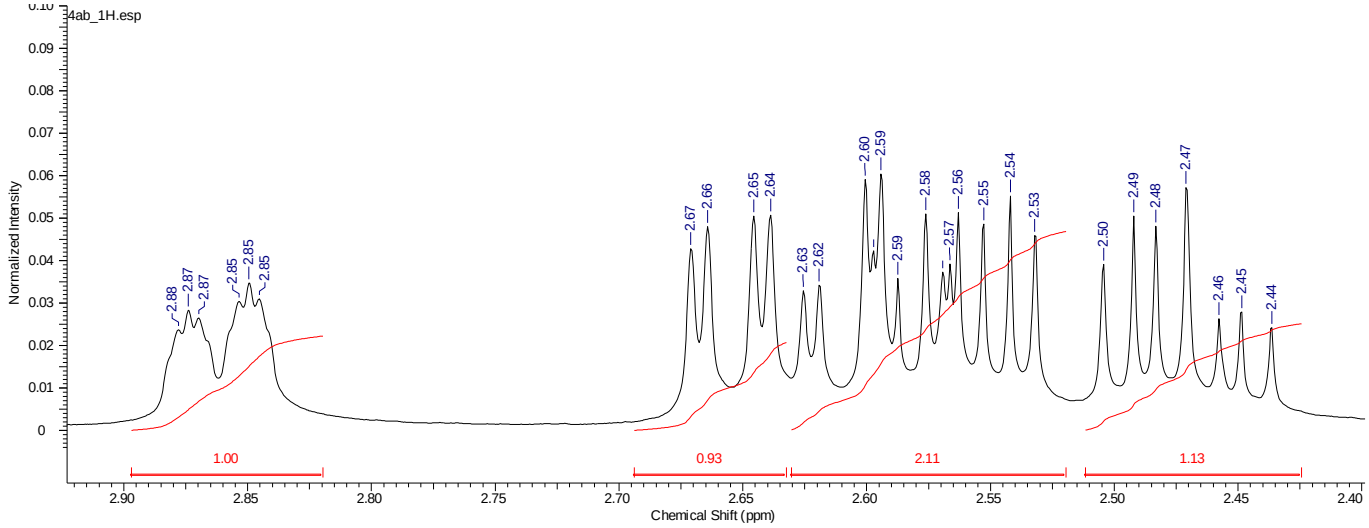
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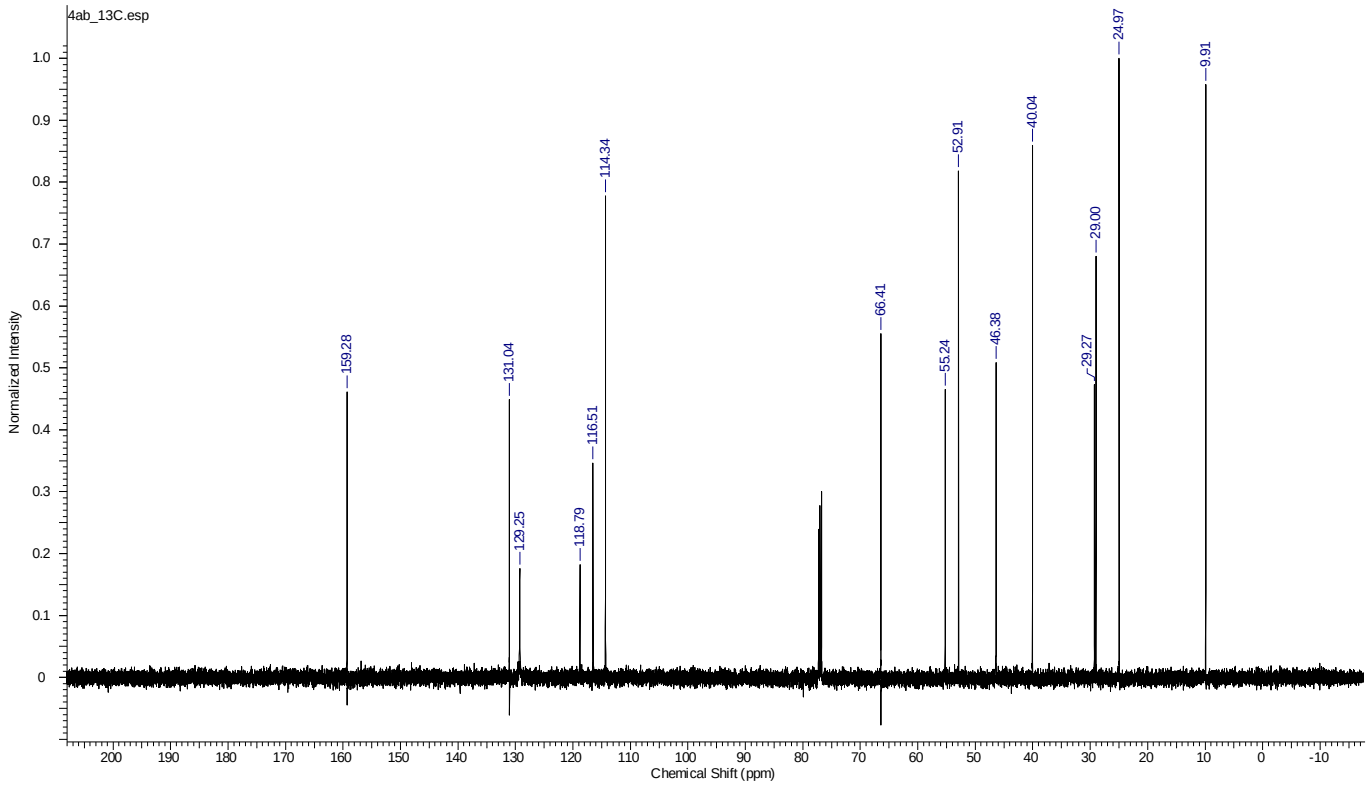

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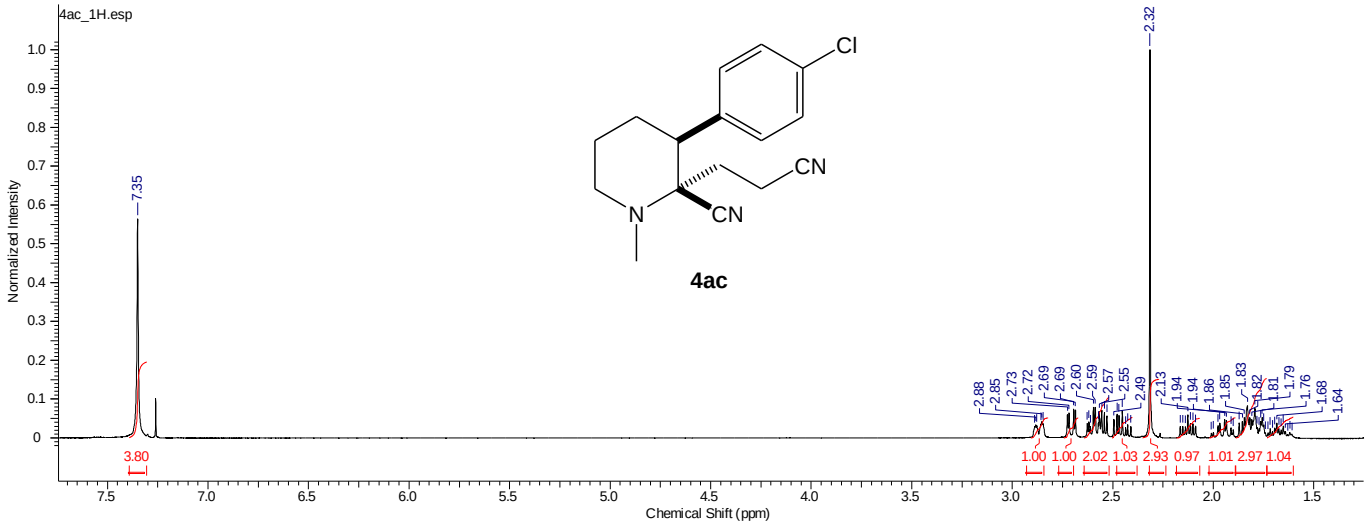

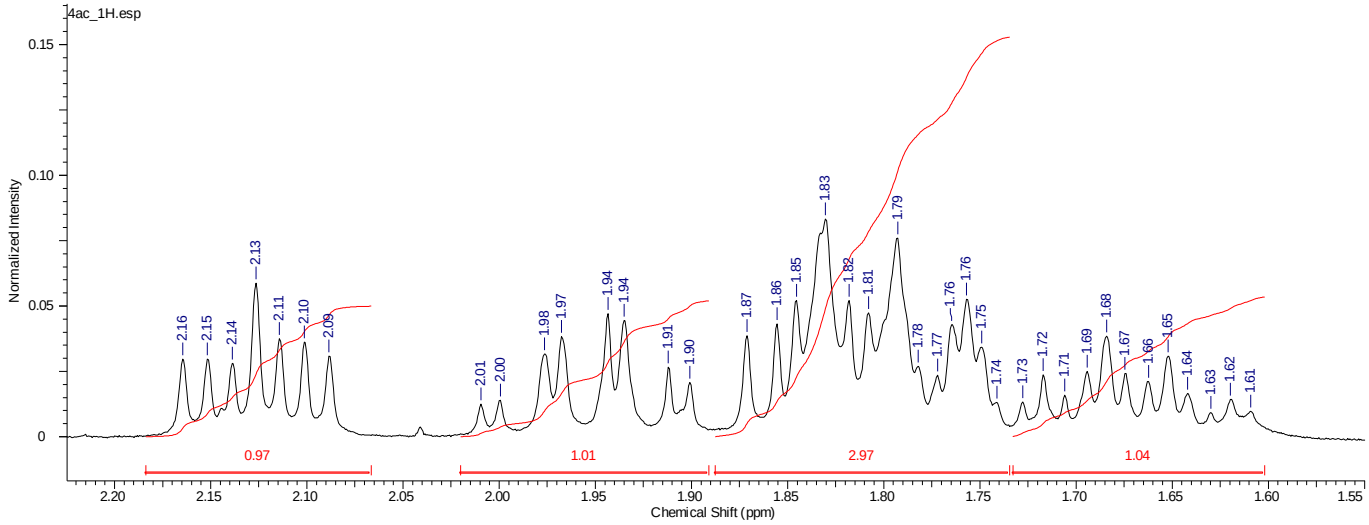
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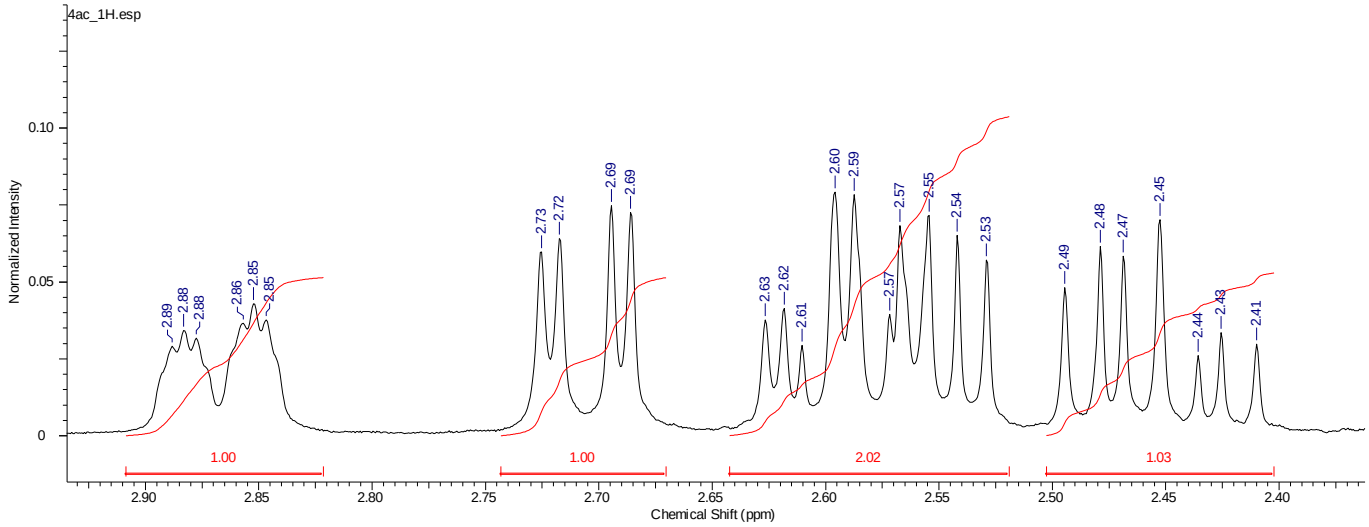
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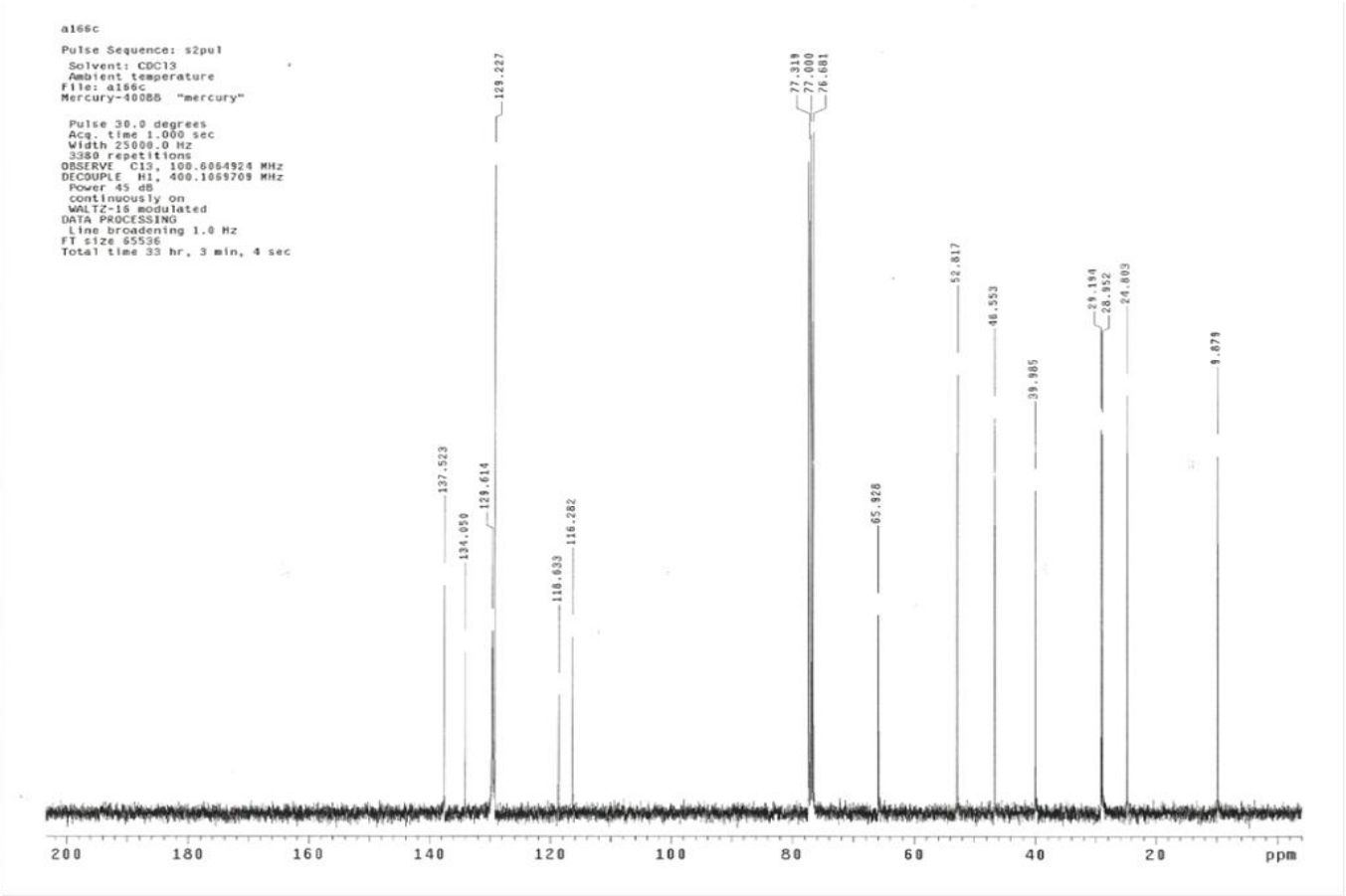
1.03



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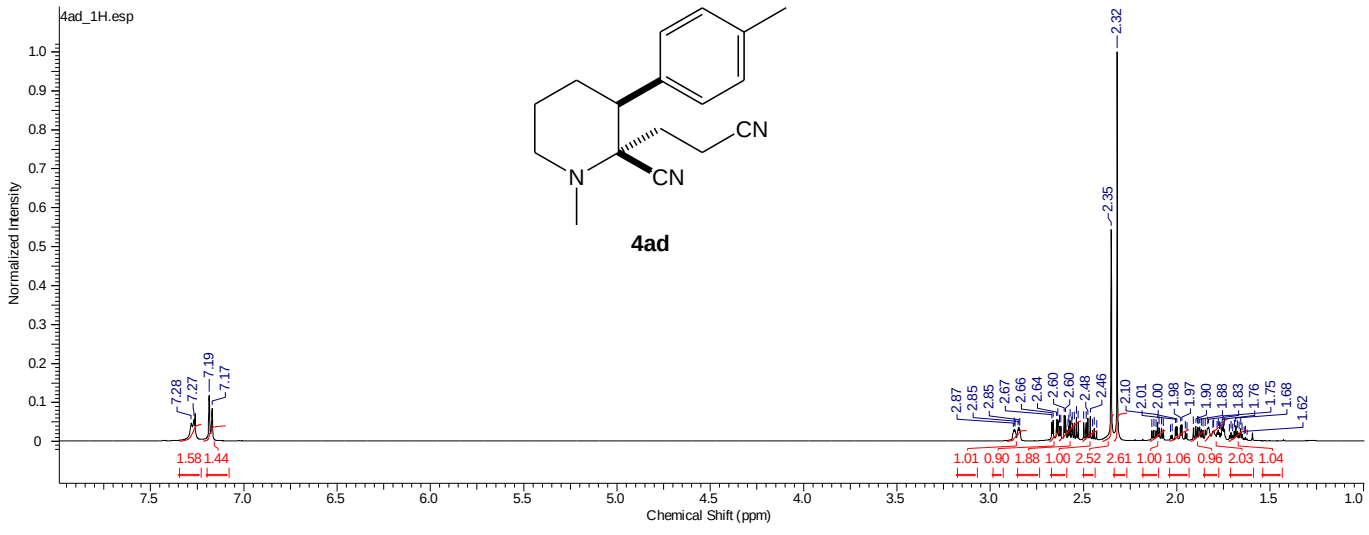

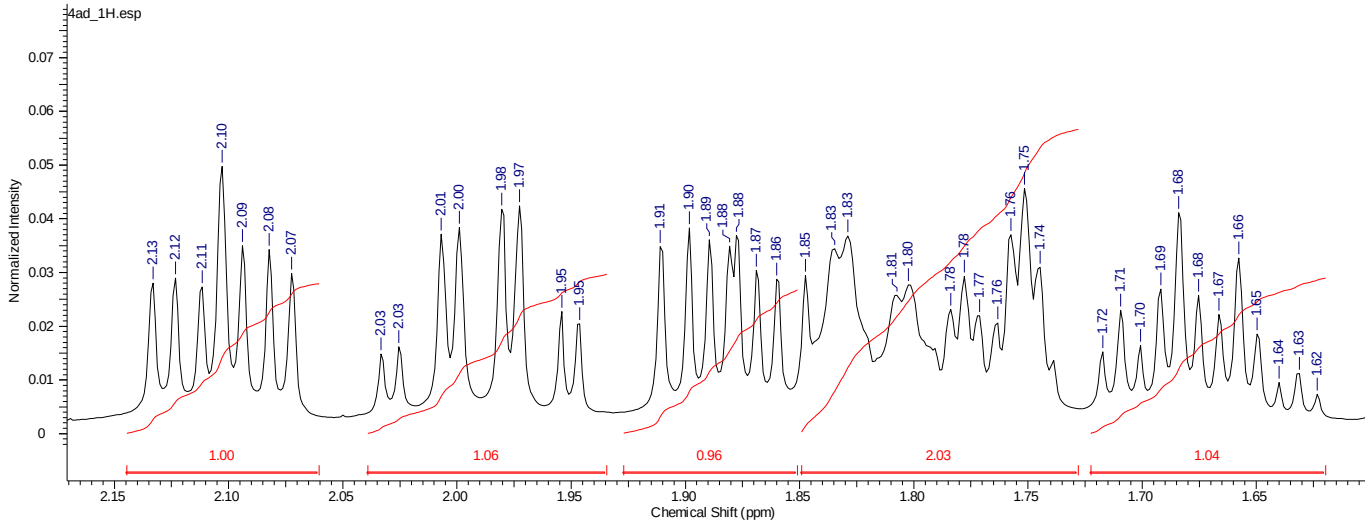
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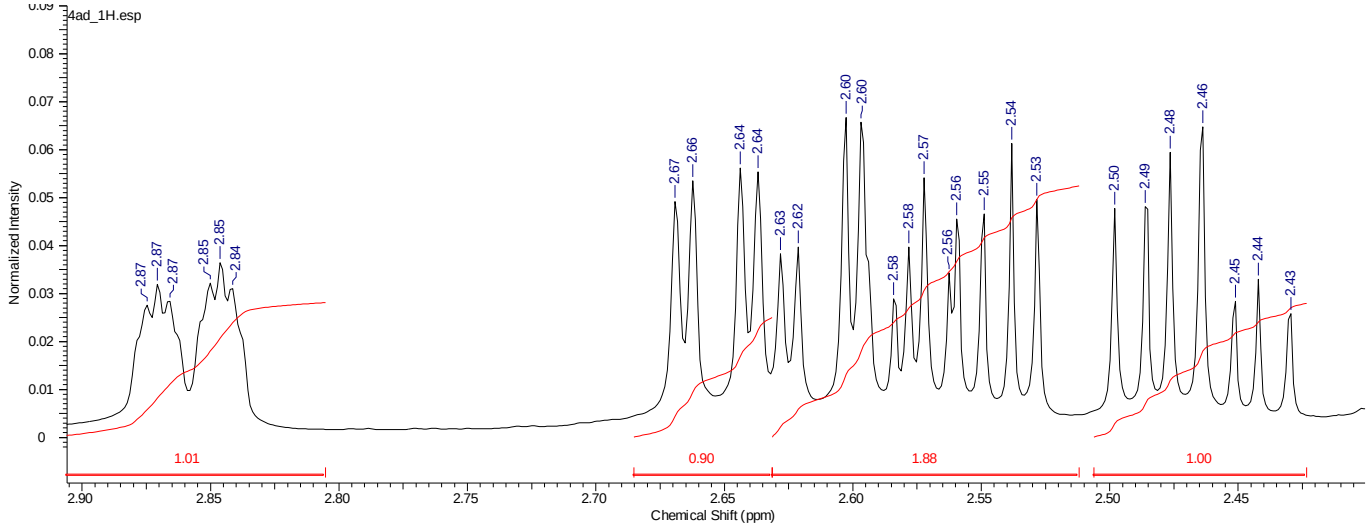
1.04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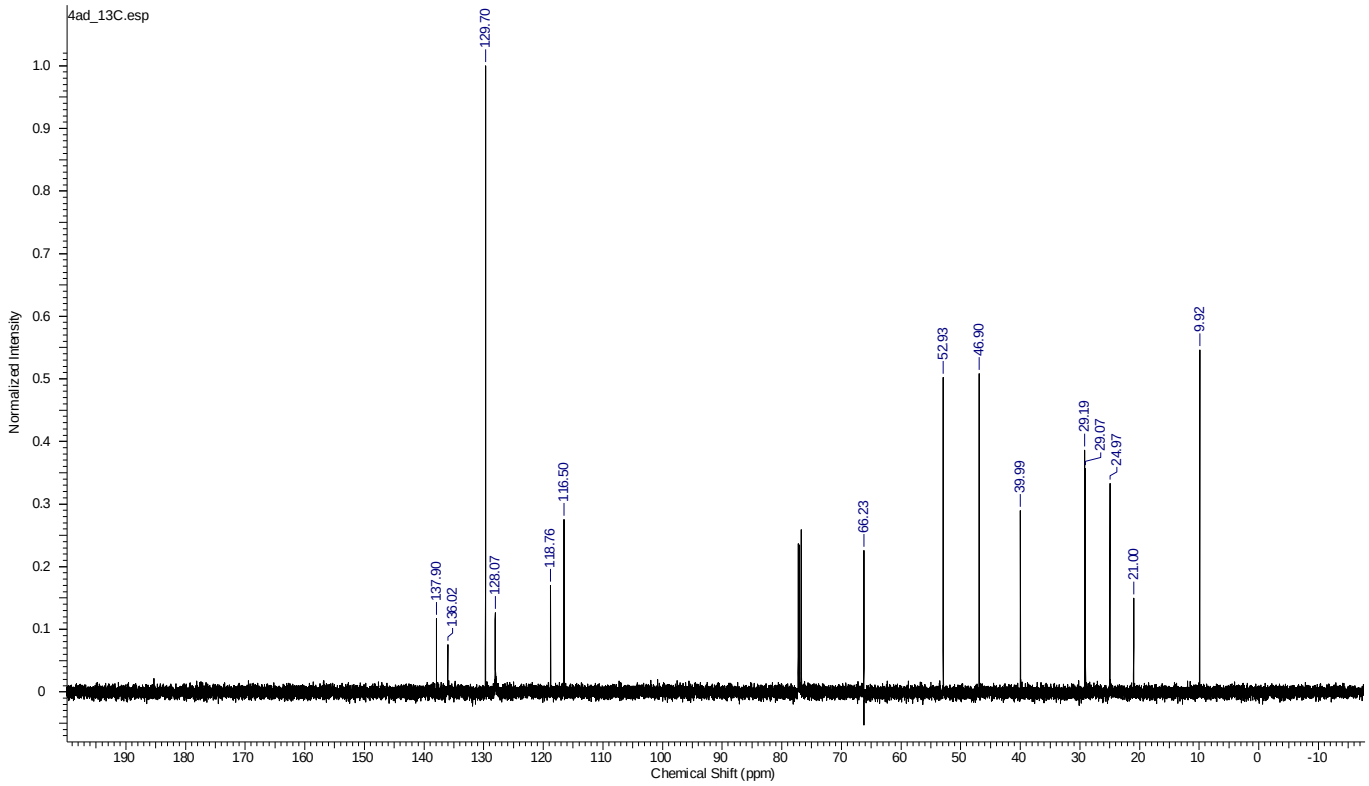
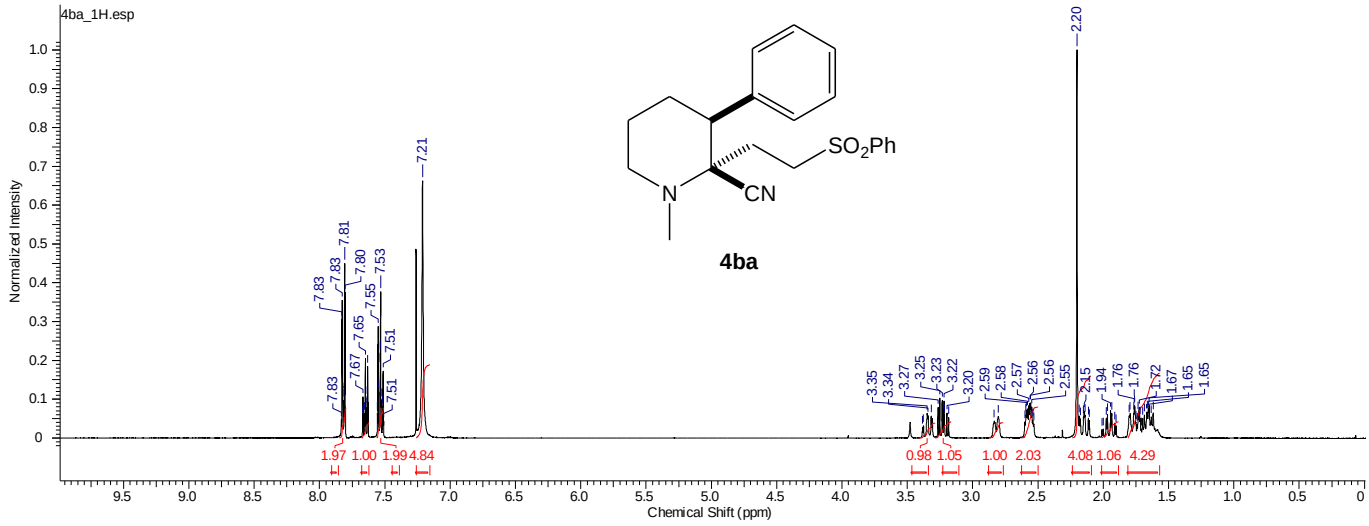
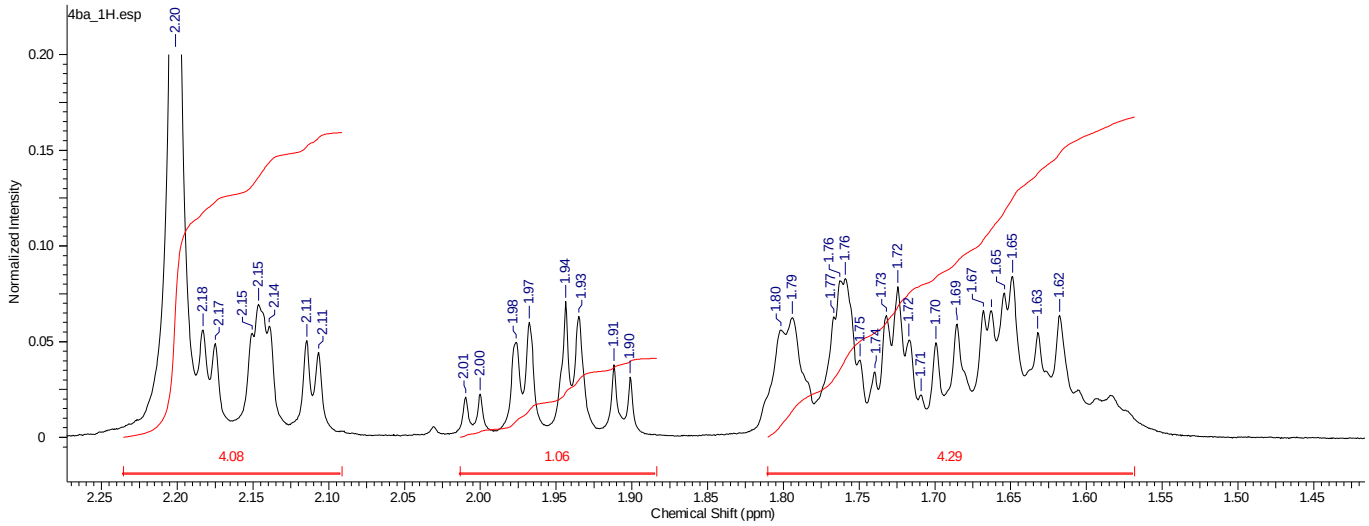


2-cyano-1-methyl-3-phenyl-2-(2-phenylsulfonylethyl)piperidine (4ba)

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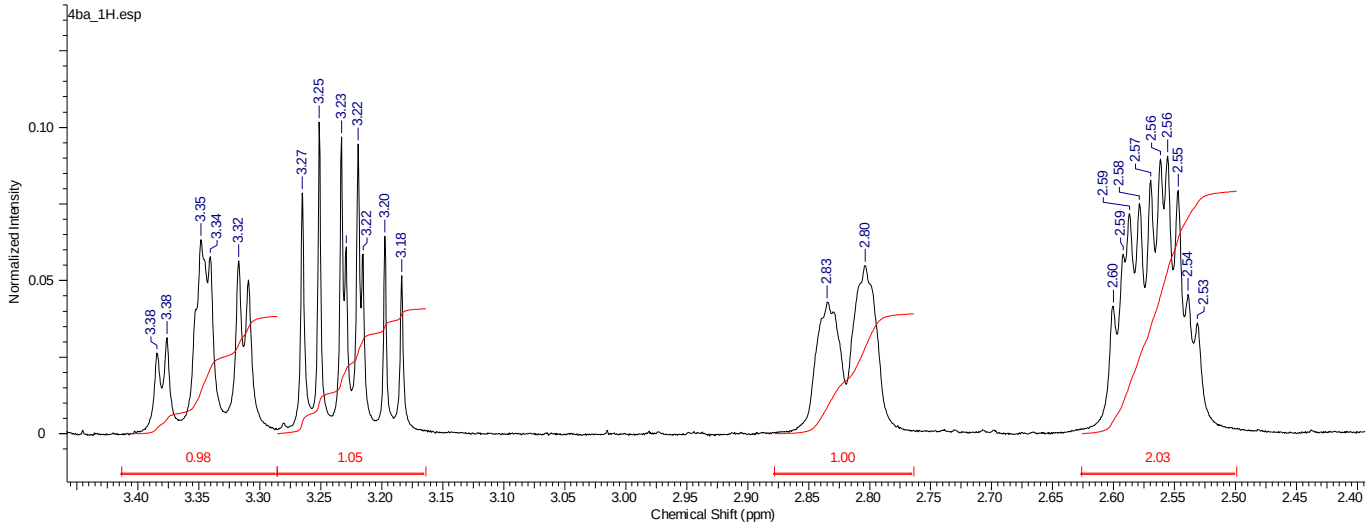
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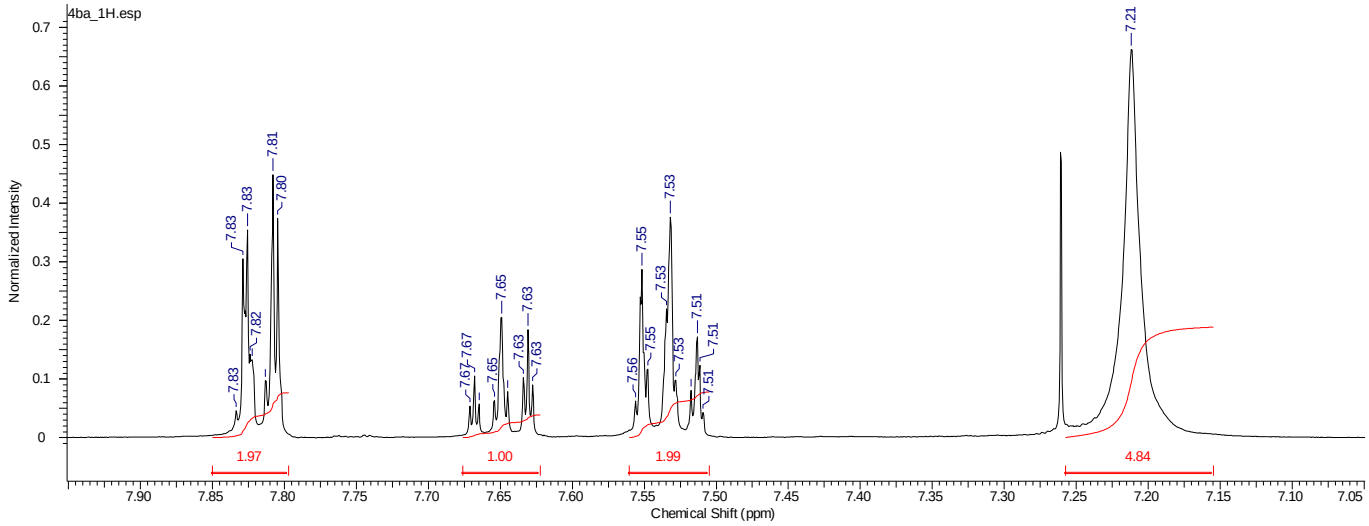
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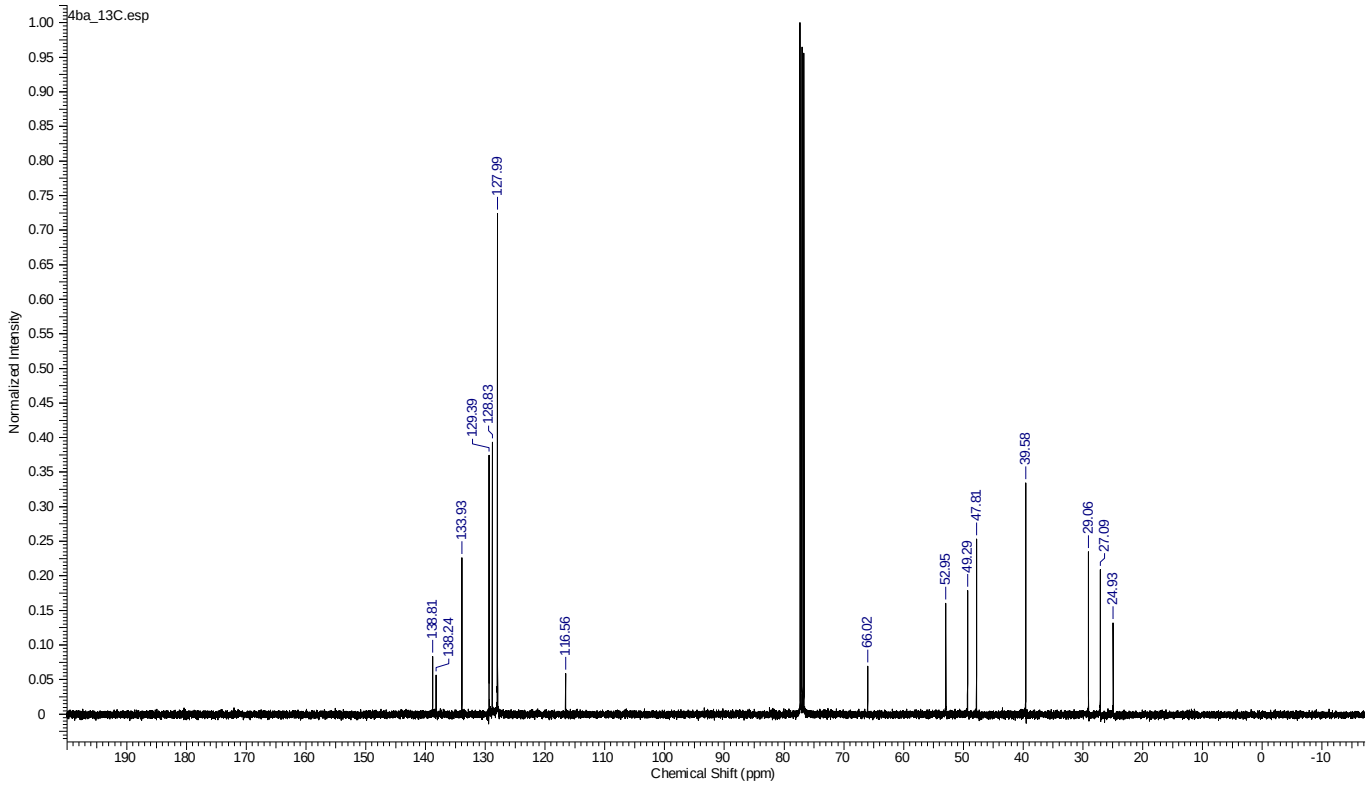
4.84



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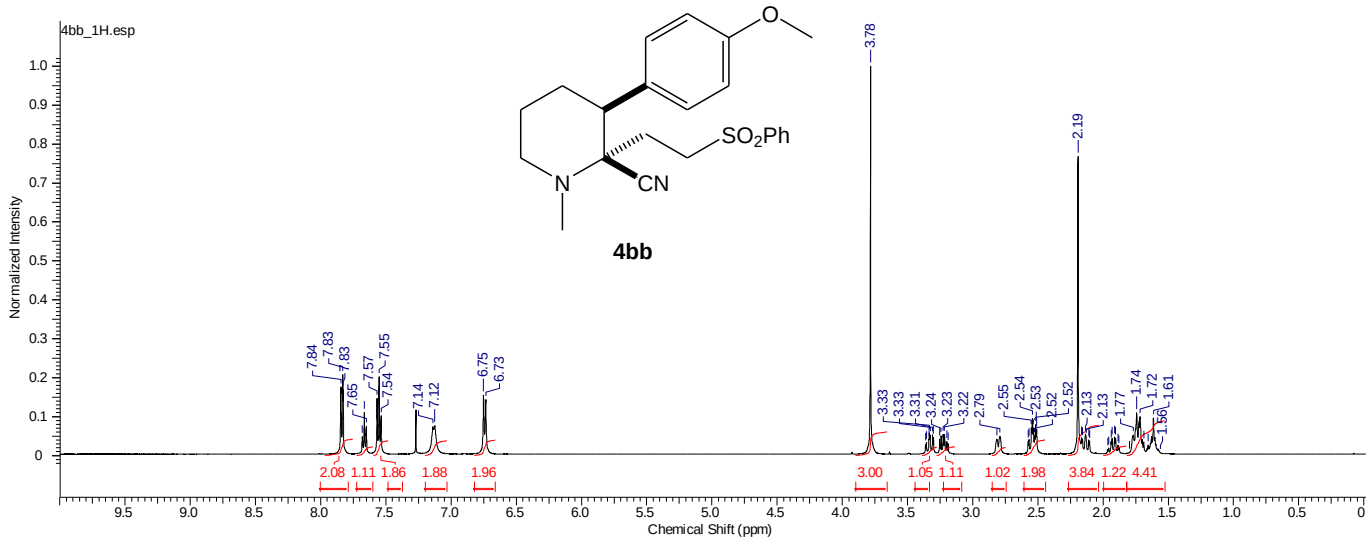

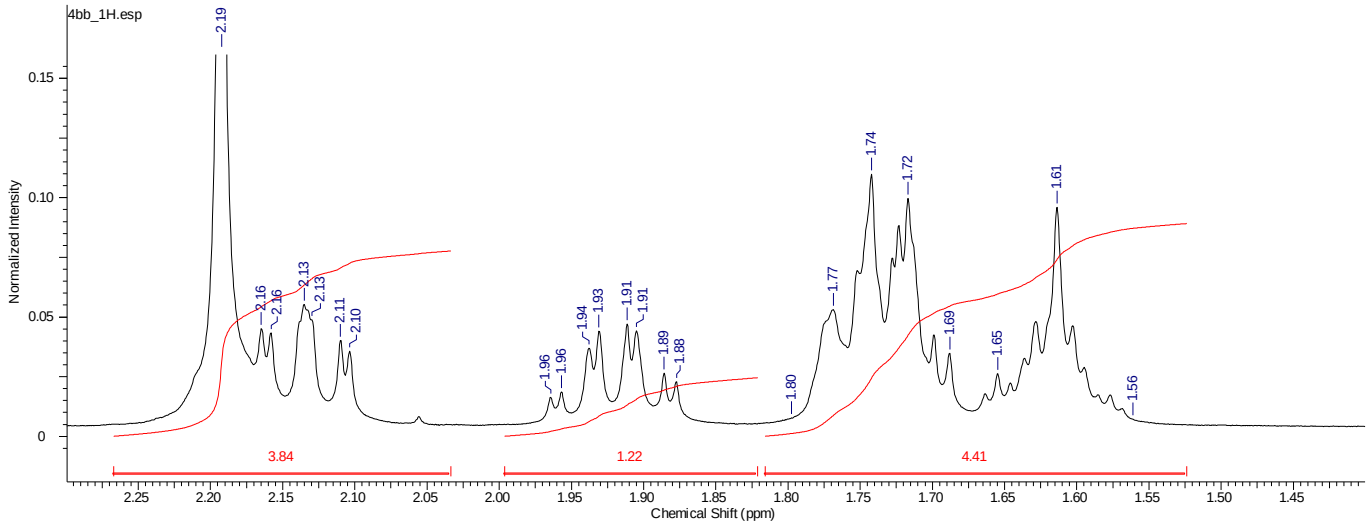
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2.13
2.13
2.11
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1.96
1.96
1.94
1.93
1.91
1.91
1.89
1.88
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1.61
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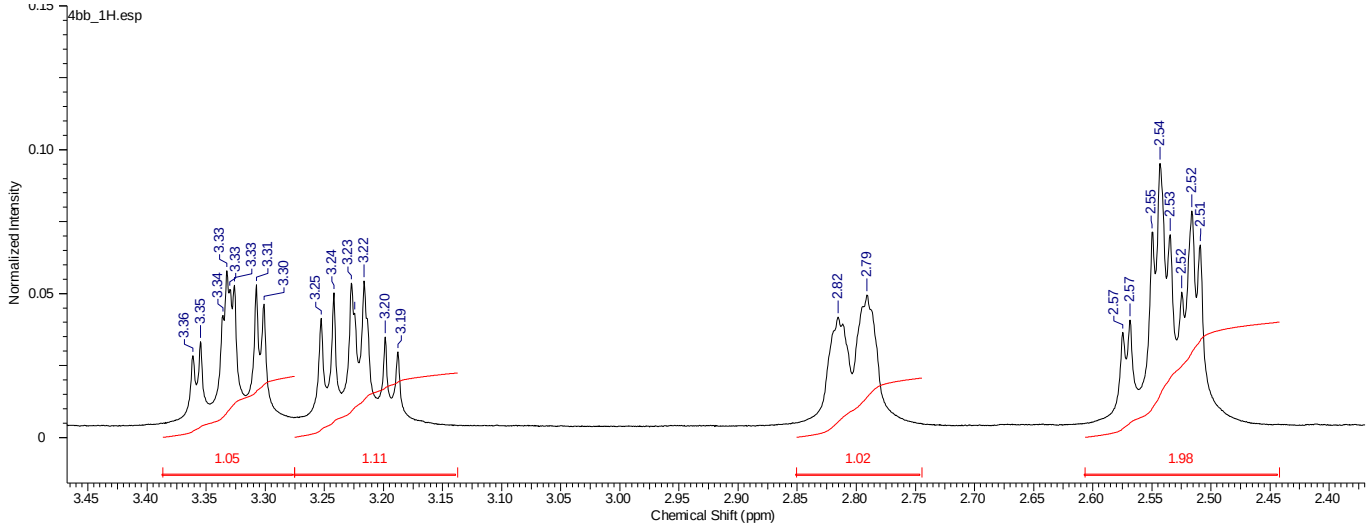
1.22
4.41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3.23
3.22
3.20
3.19
2.82
2.79
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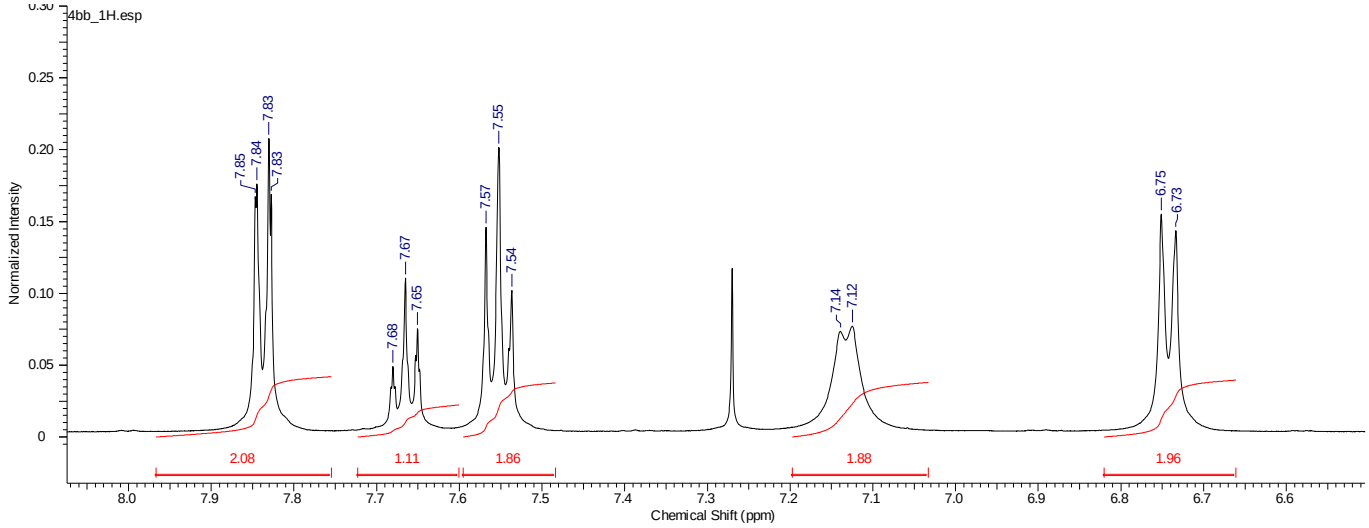
1.11
1.02
1.98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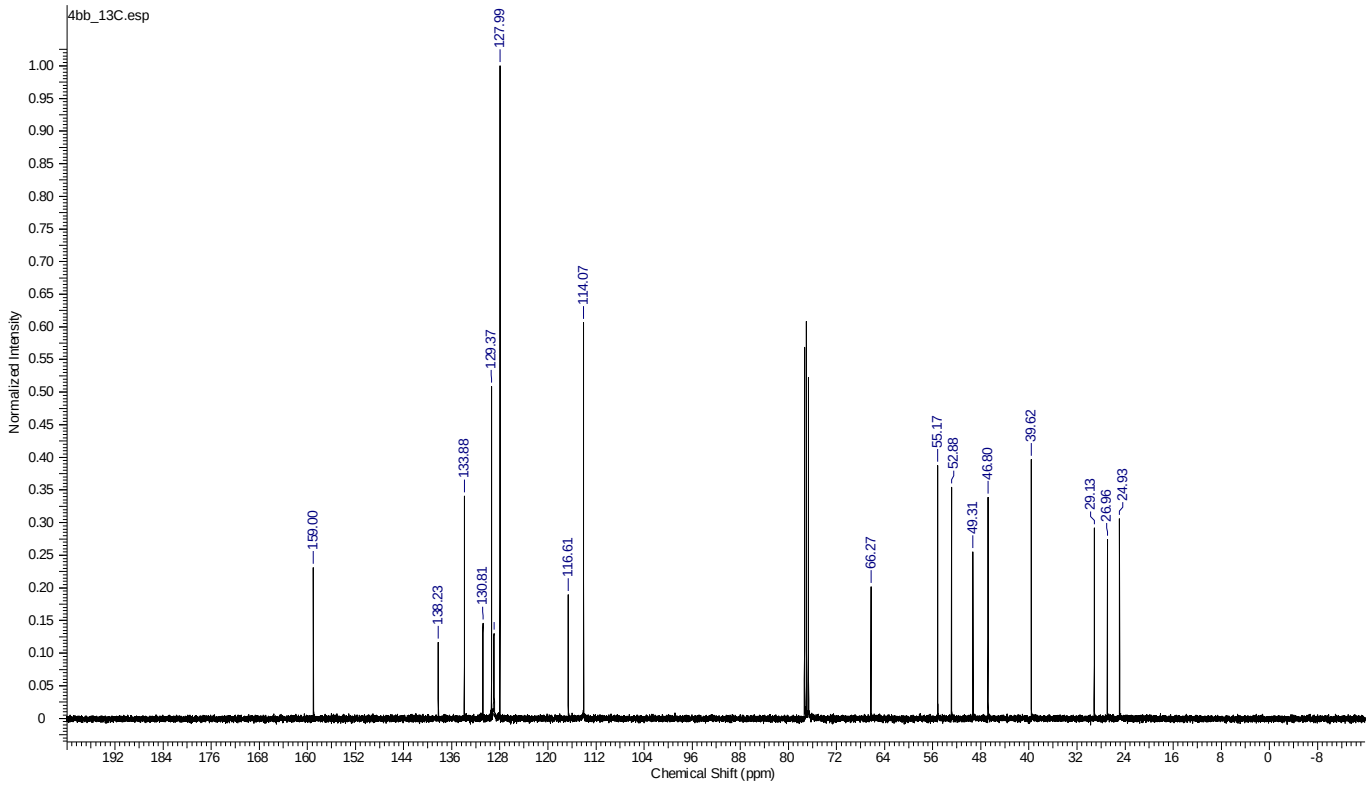
1.88
1.96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133.88
130.81
129.37
127.99
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52.88
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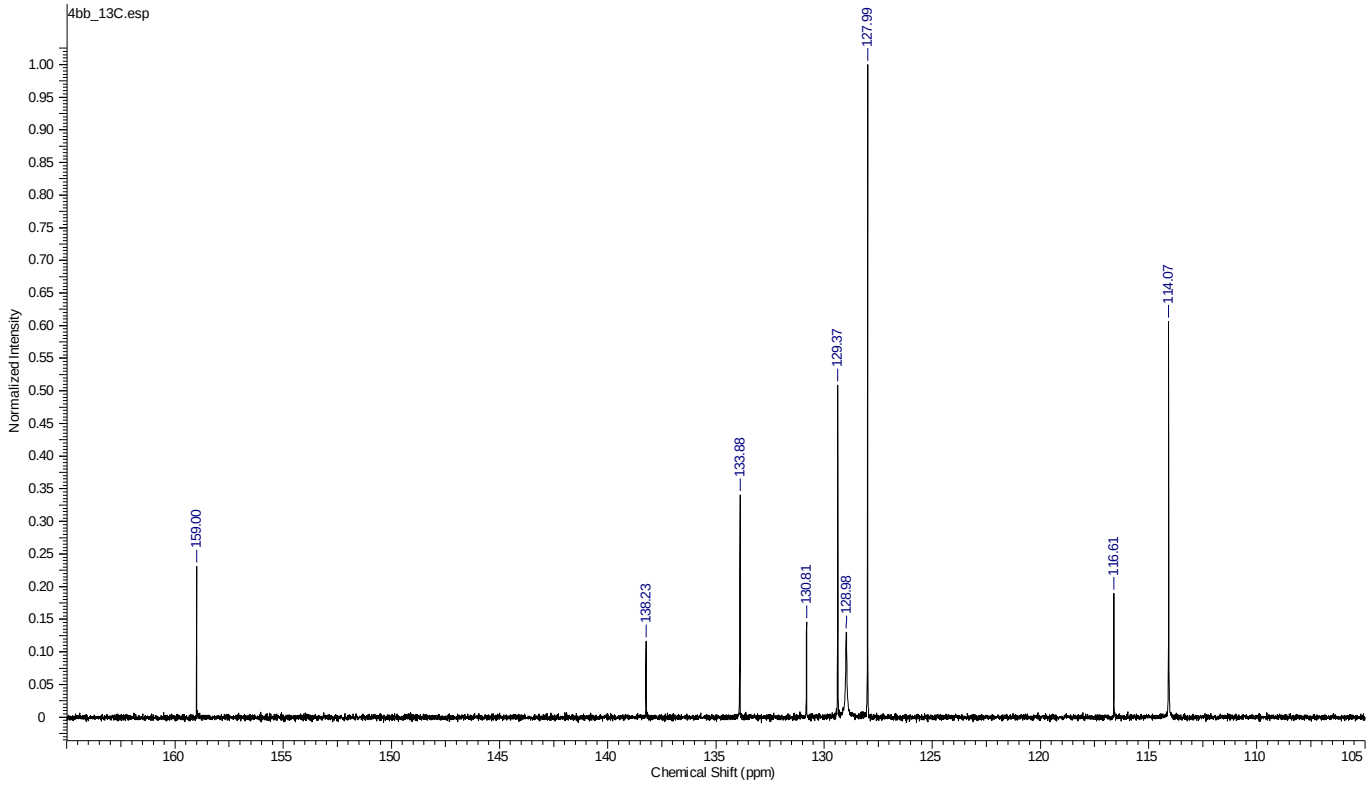
46.80
39.62
29.13
26.96
24.93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Chemical Shift (ppm)
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133.88
130.81
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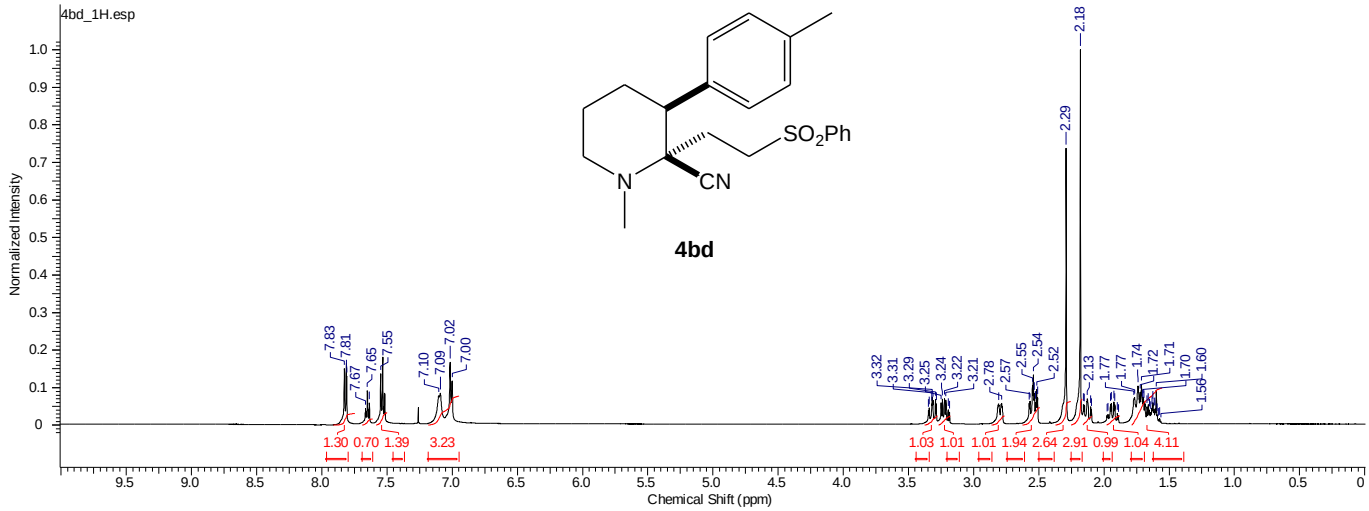
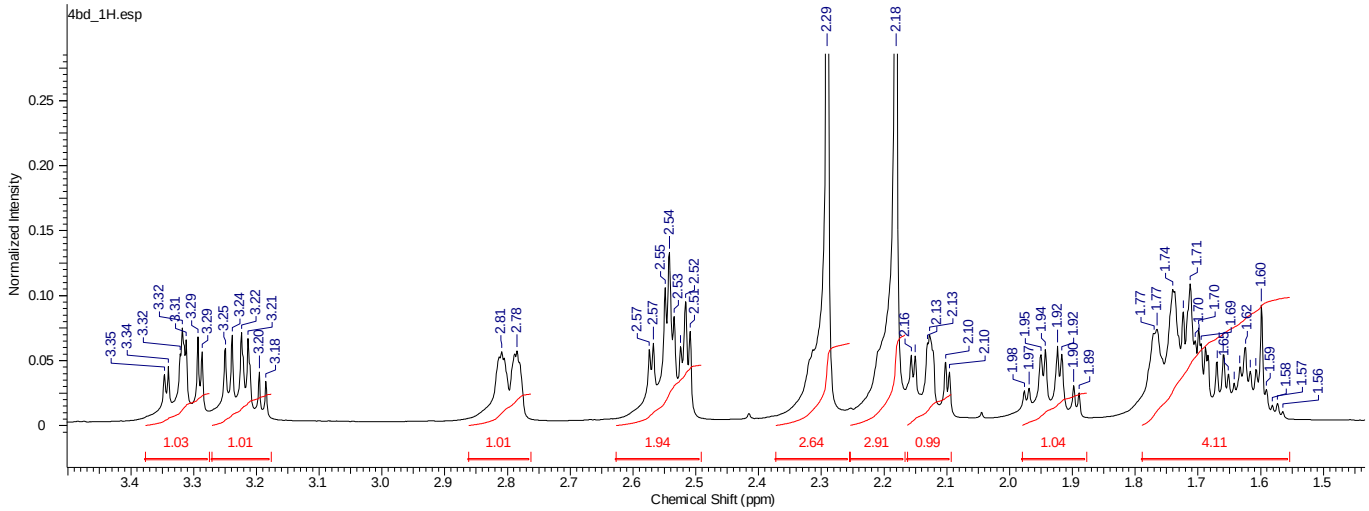
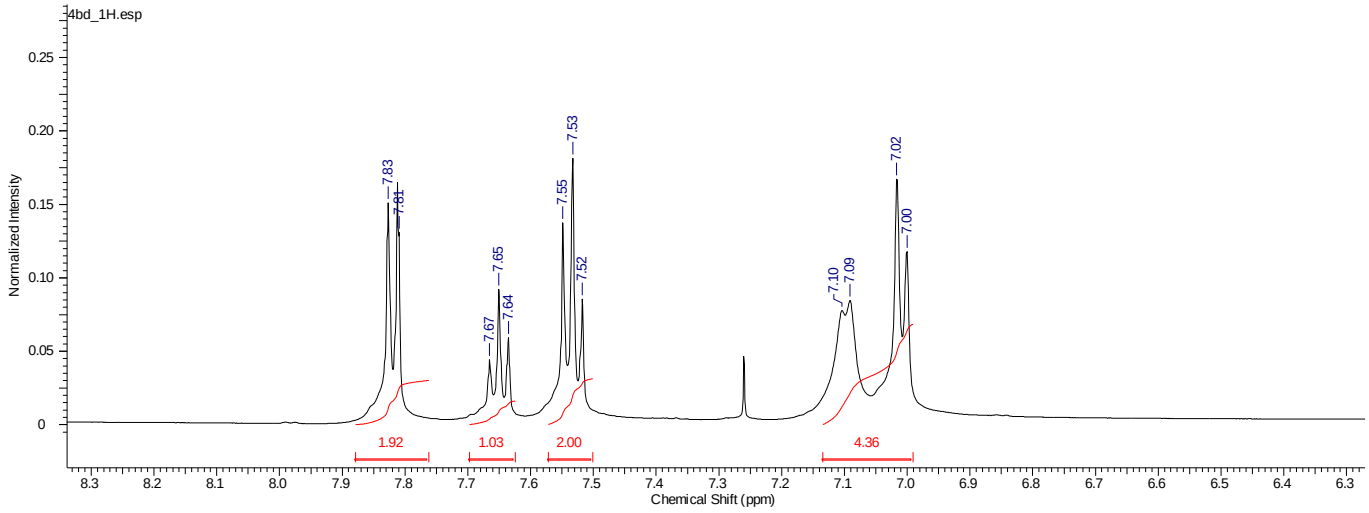
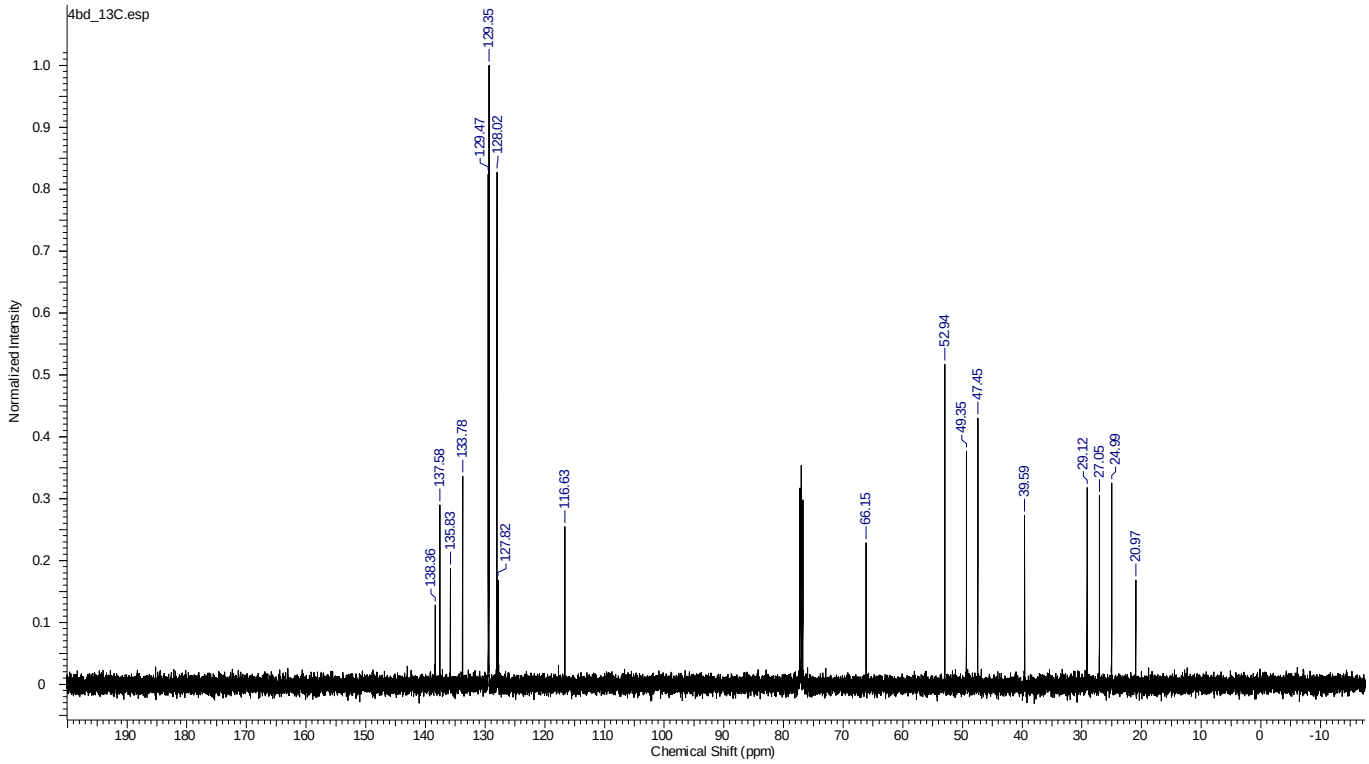
127.99
116.61
114.07

2-cyano-1-methyl-3-(4-methylphenyl)-2-(2-phenylsulfonylethyl)piperidine (4bd)





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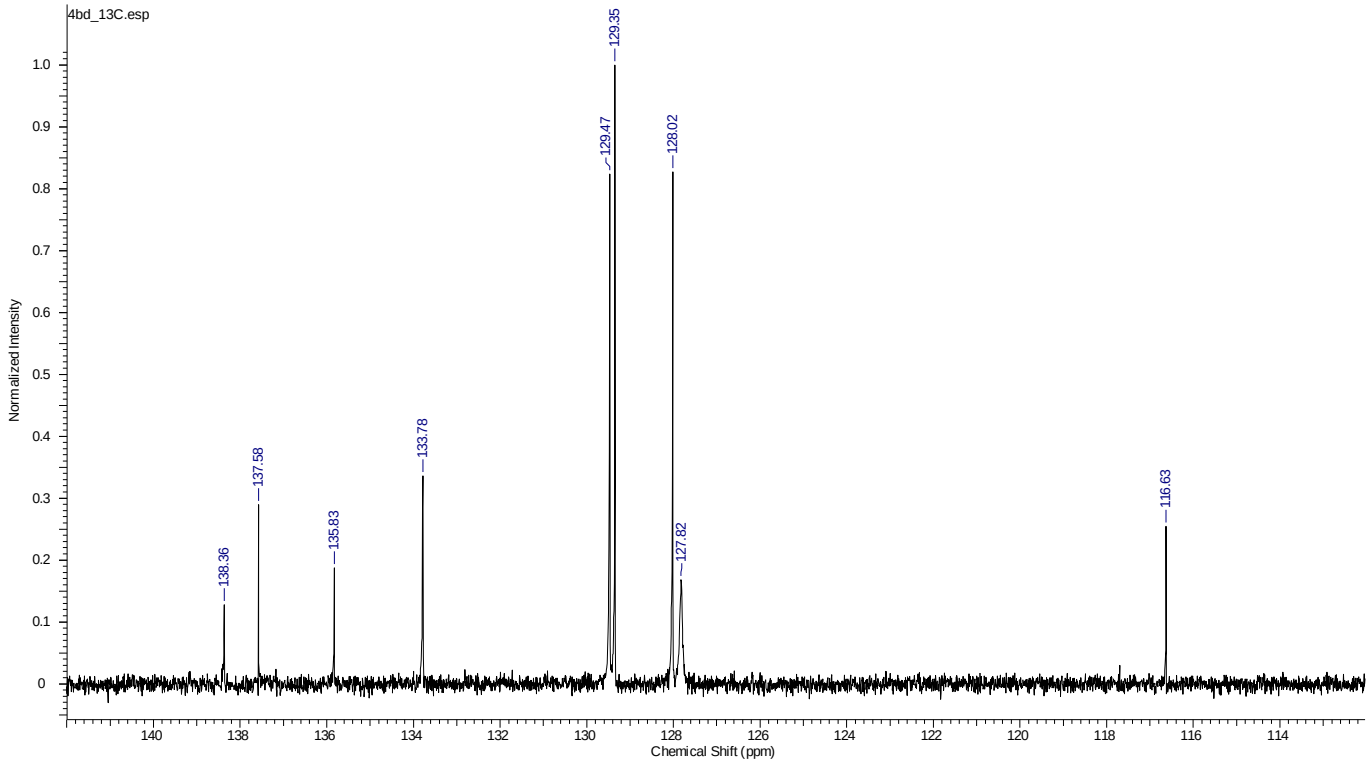
24.99
20.97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Normalized Intensity
Chemical Shift (ppm)
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129.47
128.02
137.58
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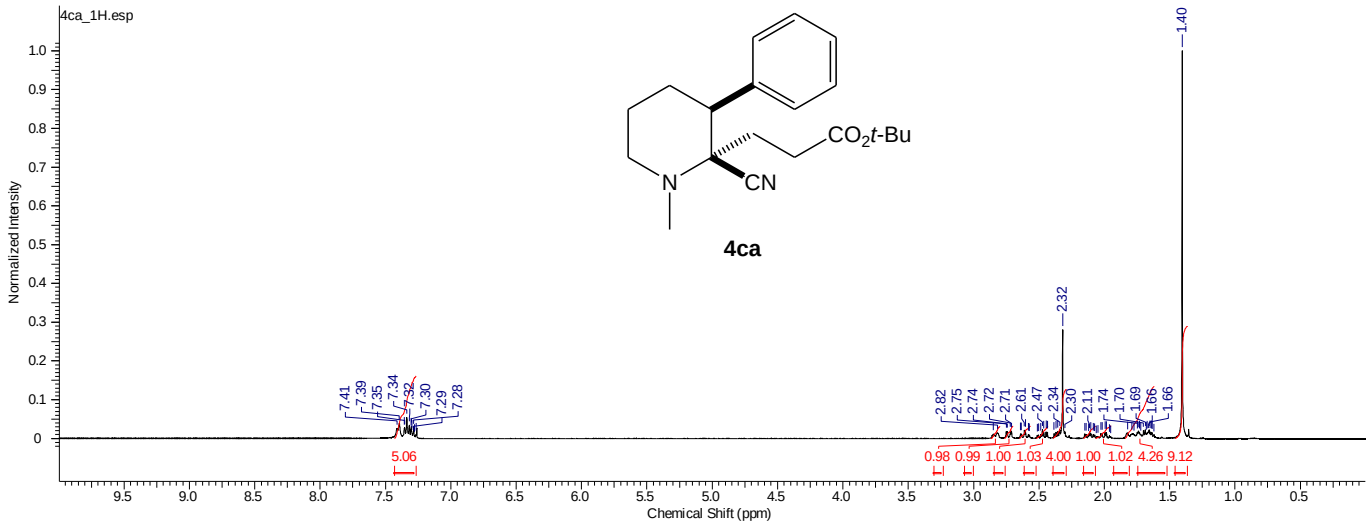
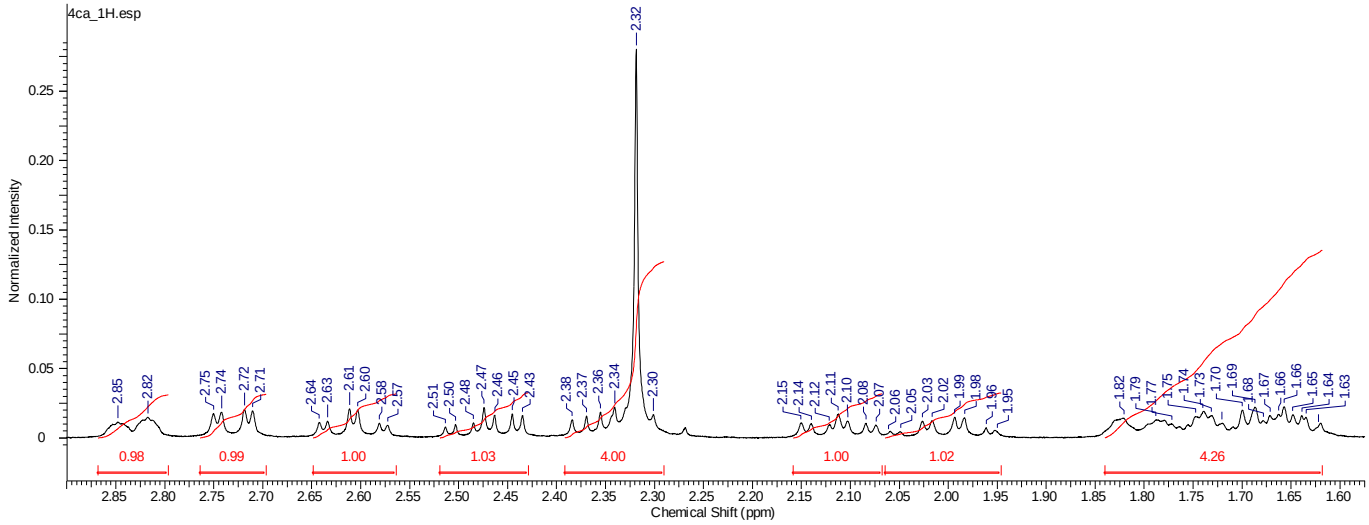
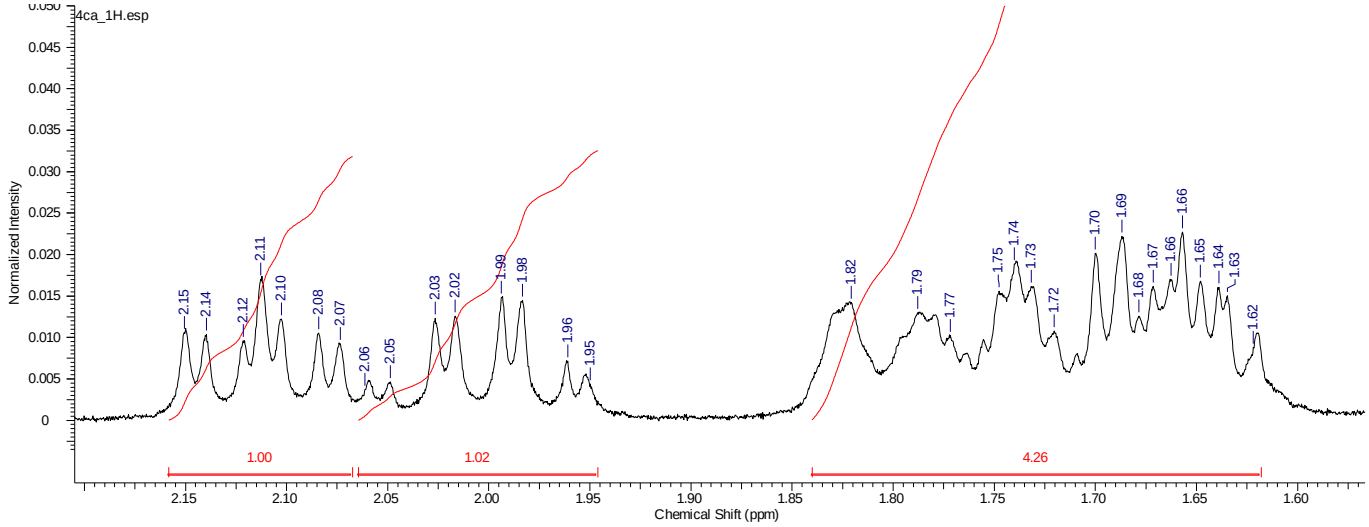
127.82
116.63

2-(2-*tert*-butoxycarbonylethyl)-2-cyano-1-methyl-3-phenylpiperidine (4ca)



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1.96
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1.72
1.70
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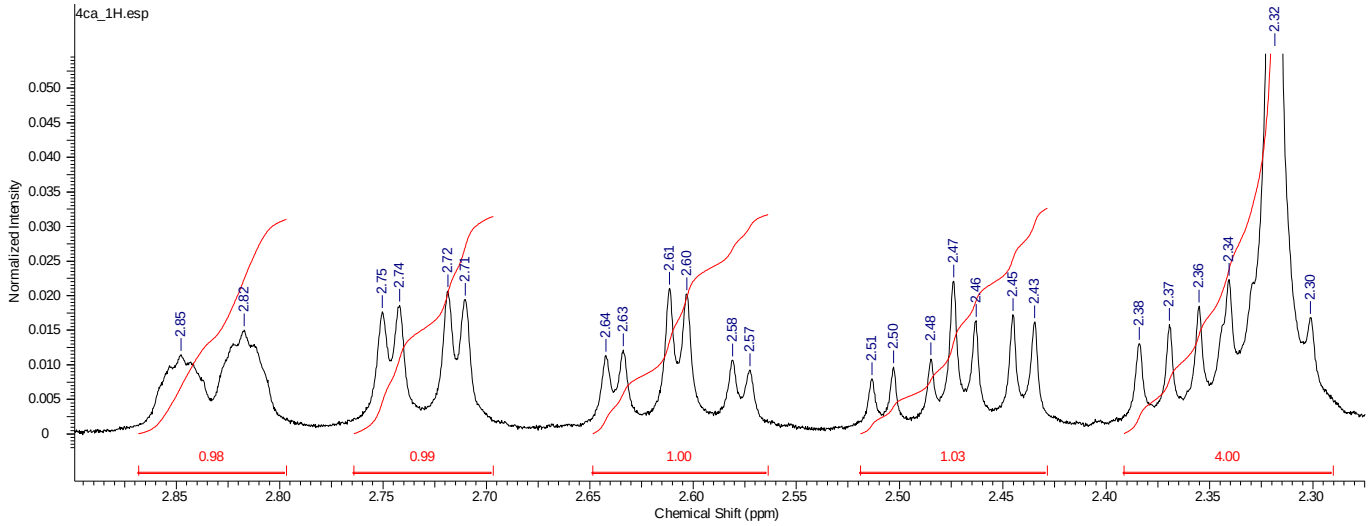
1.62
1.00
1.02
4.26
Chemical Shift (ppm)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2.58
2.57
2.51
2.50
2.48
2.47
2.46
2.45
2.43
2.38
2.37
2.36
2.34
2.32
2.30
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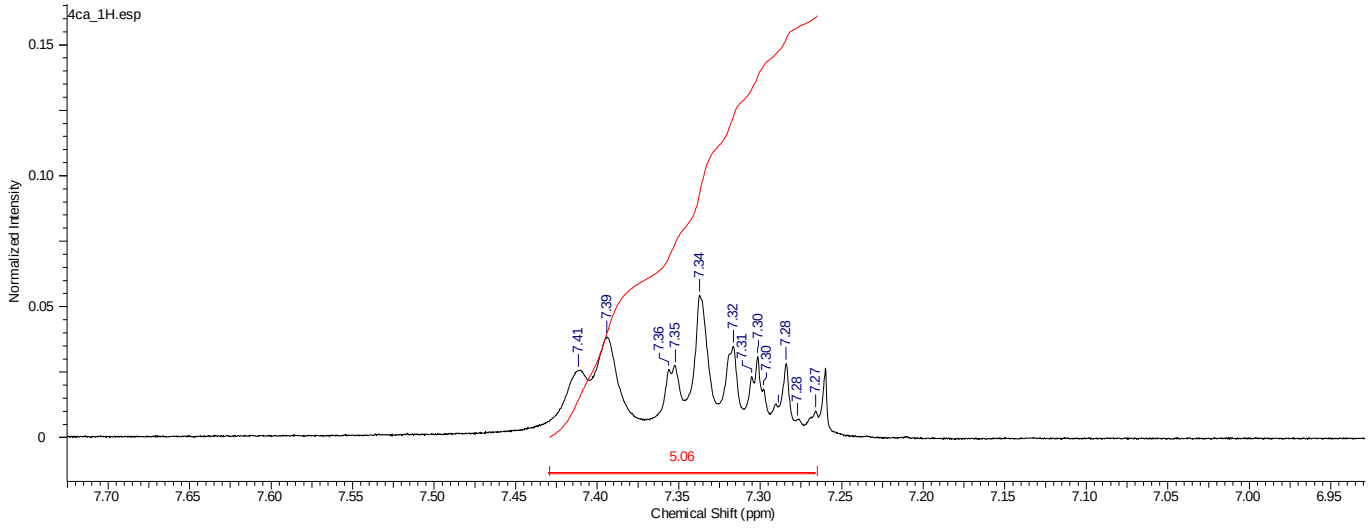
0.99
1.00
1.03
4.00
Chemical Shift (ppm)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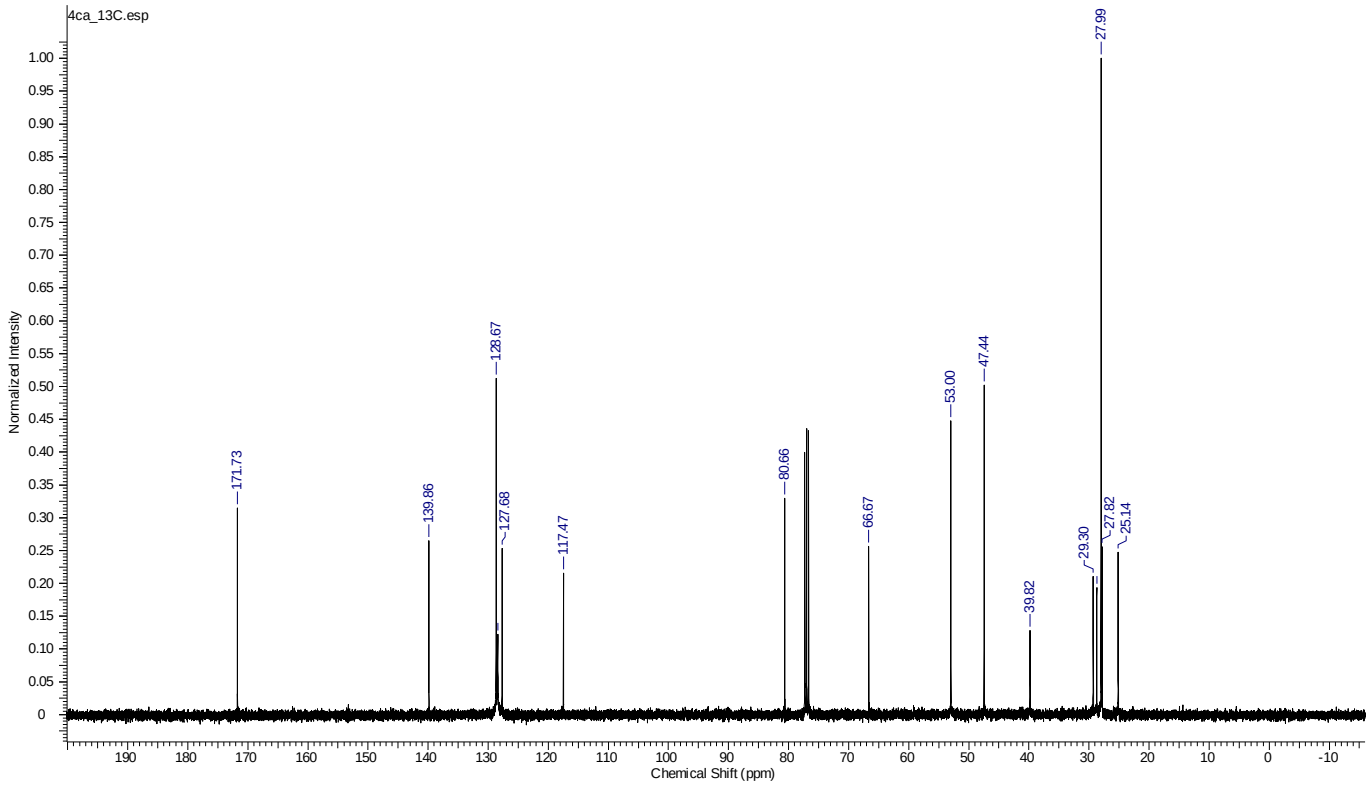
7.31
7.30
7.30
7.28
7.28
7.27
5.06
Chemical Shift (ppm)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Normalized Intensity
Chemical Shift (ppm)
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127.68
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66.67
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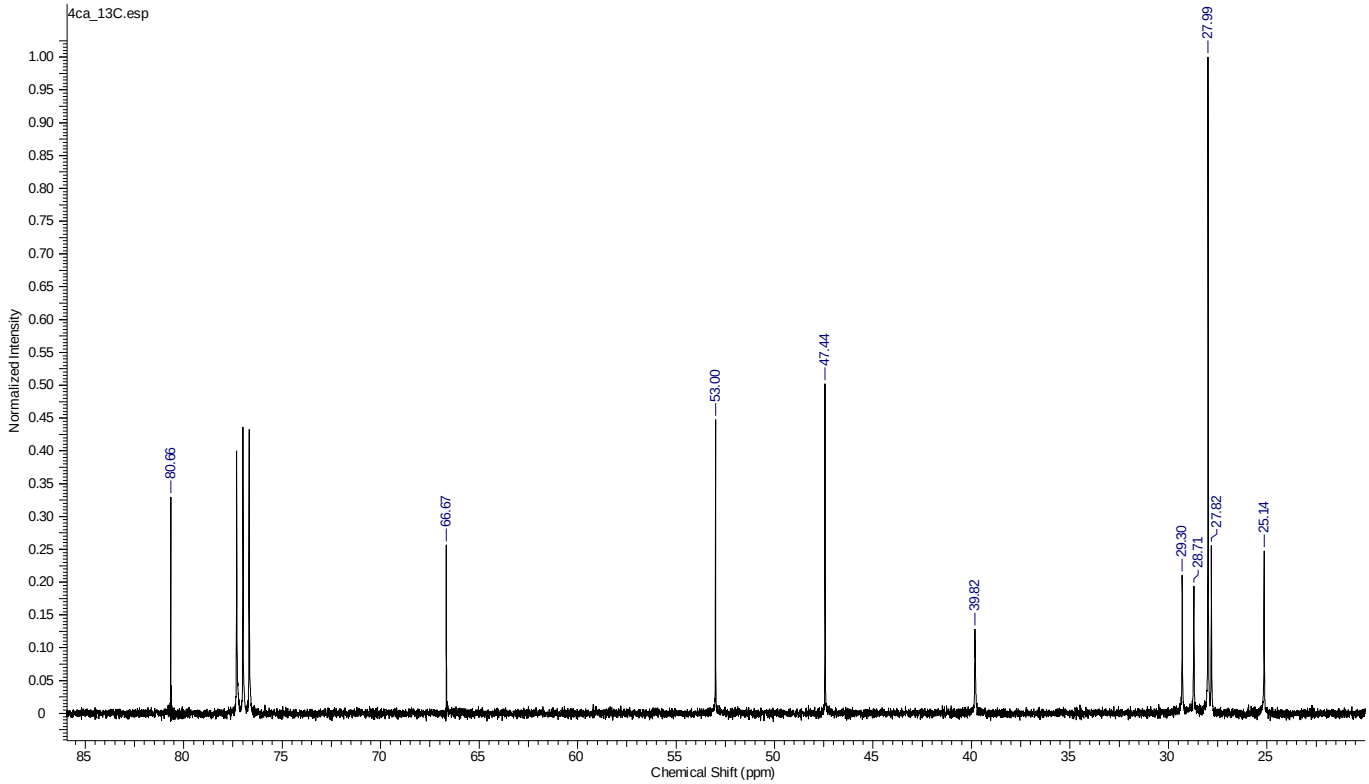
47.44
39.82
29.30
27.82
25.14
27.99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Normalized Intensity
Chemical Shift (ppm)
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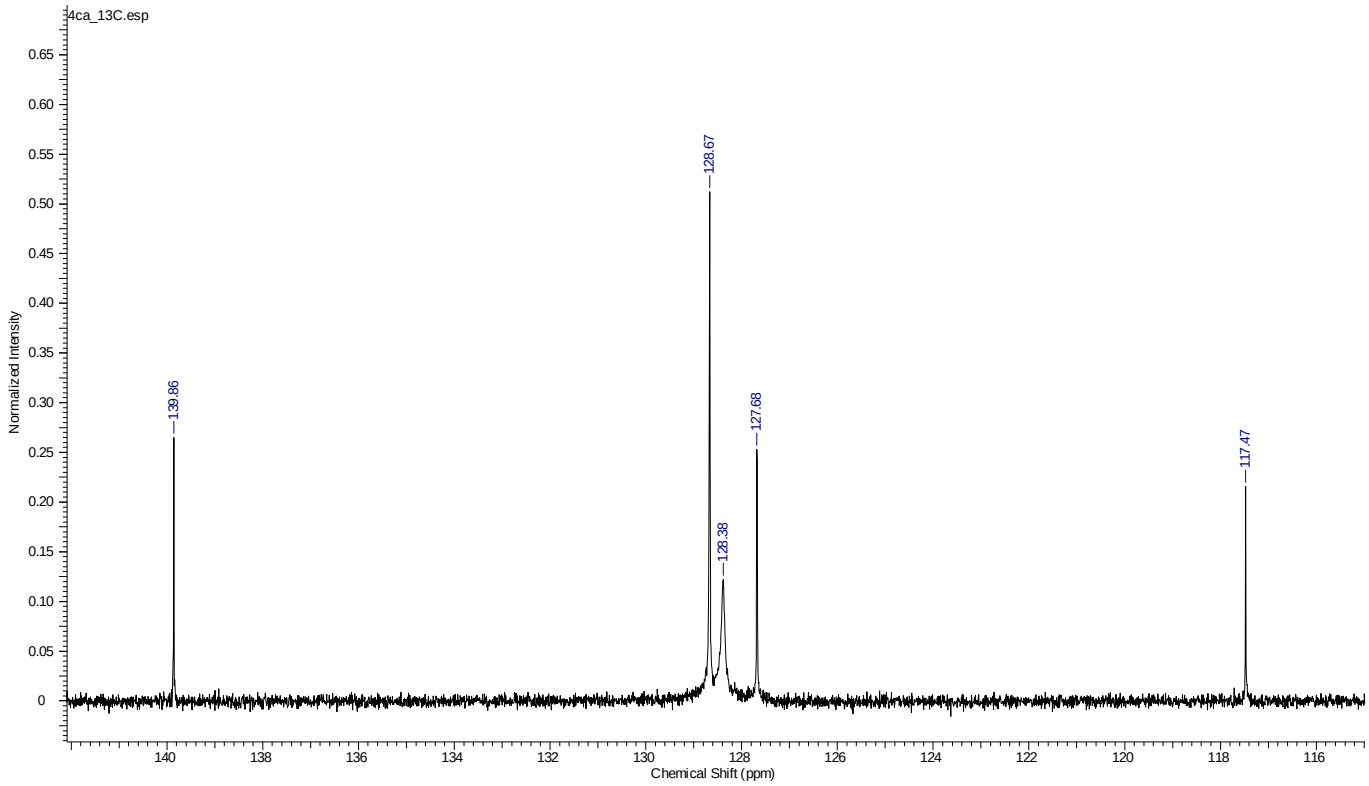
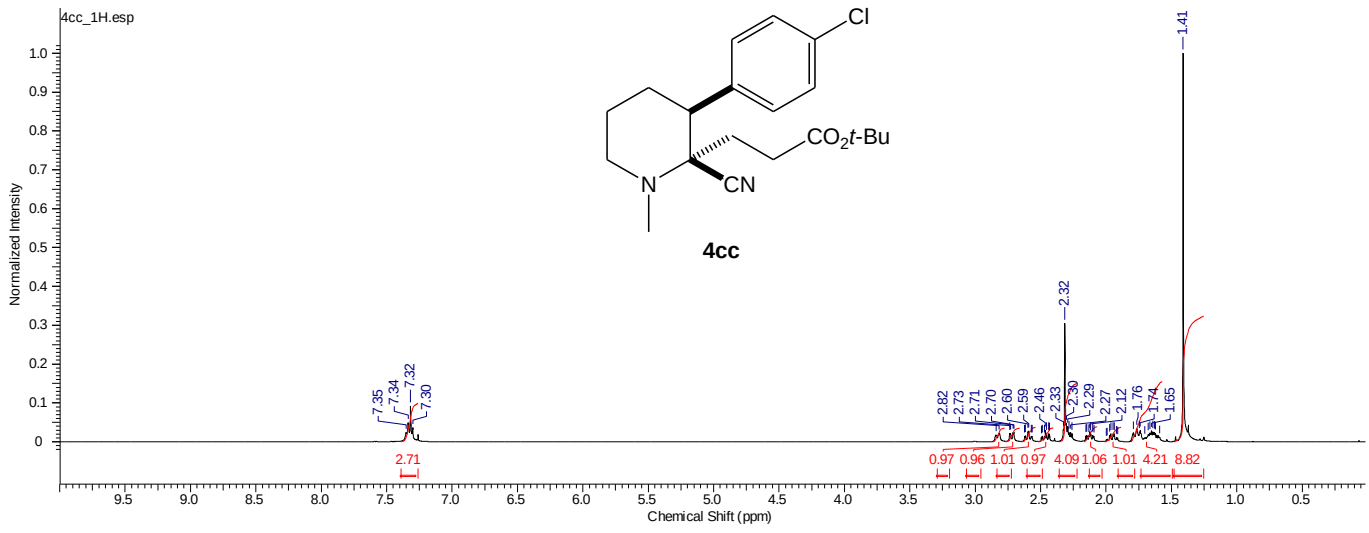
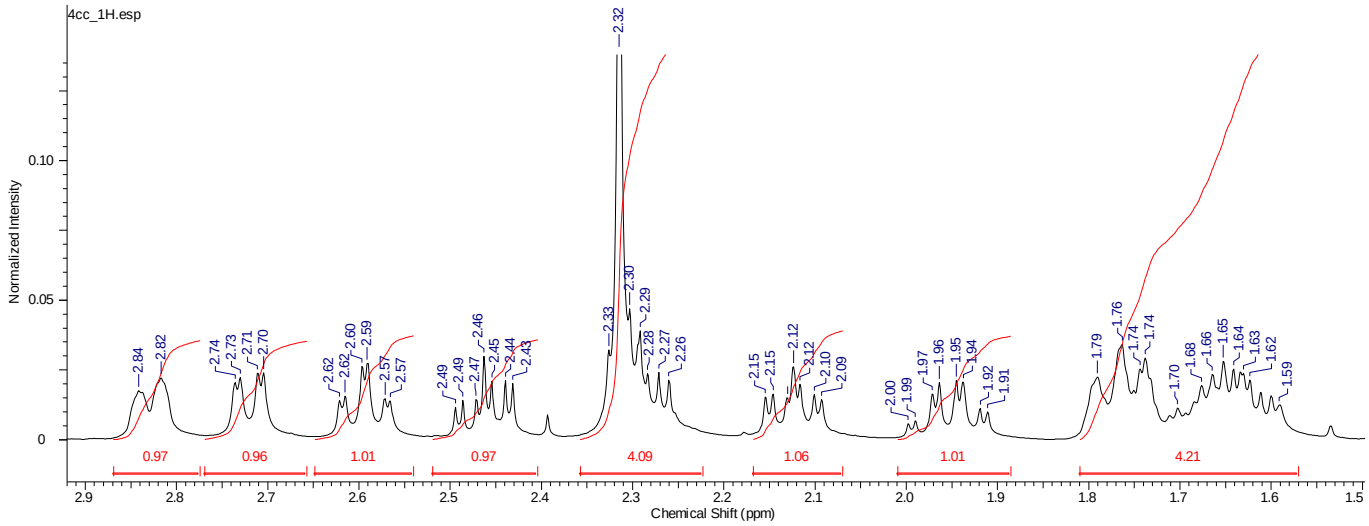
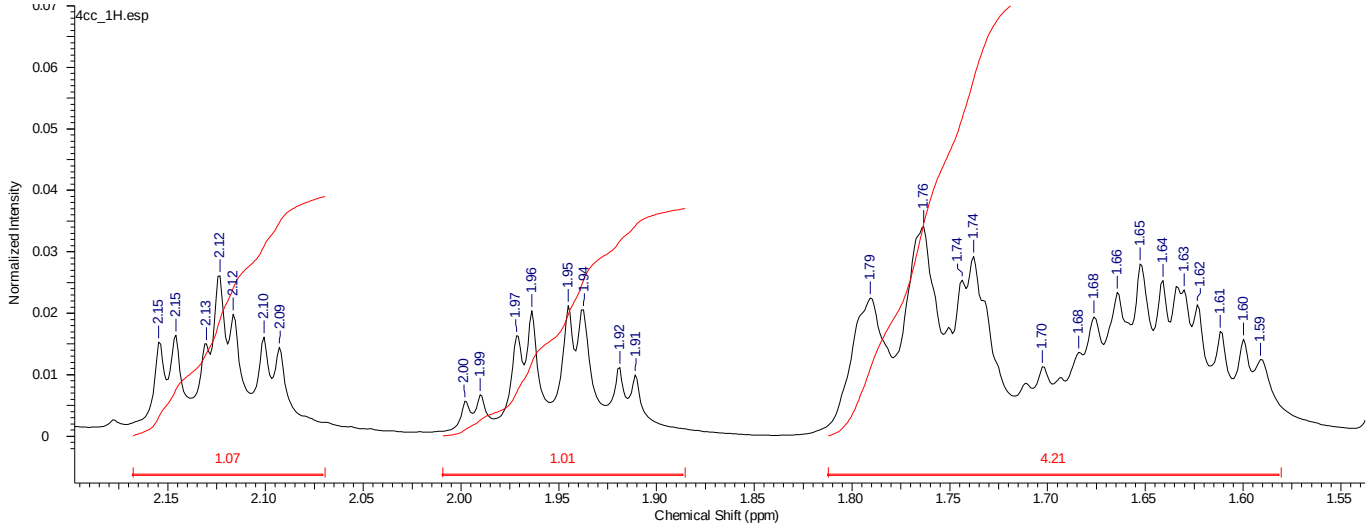
53.00
47.44
39.82
29.30
28.71
27.82
25.14
27.99

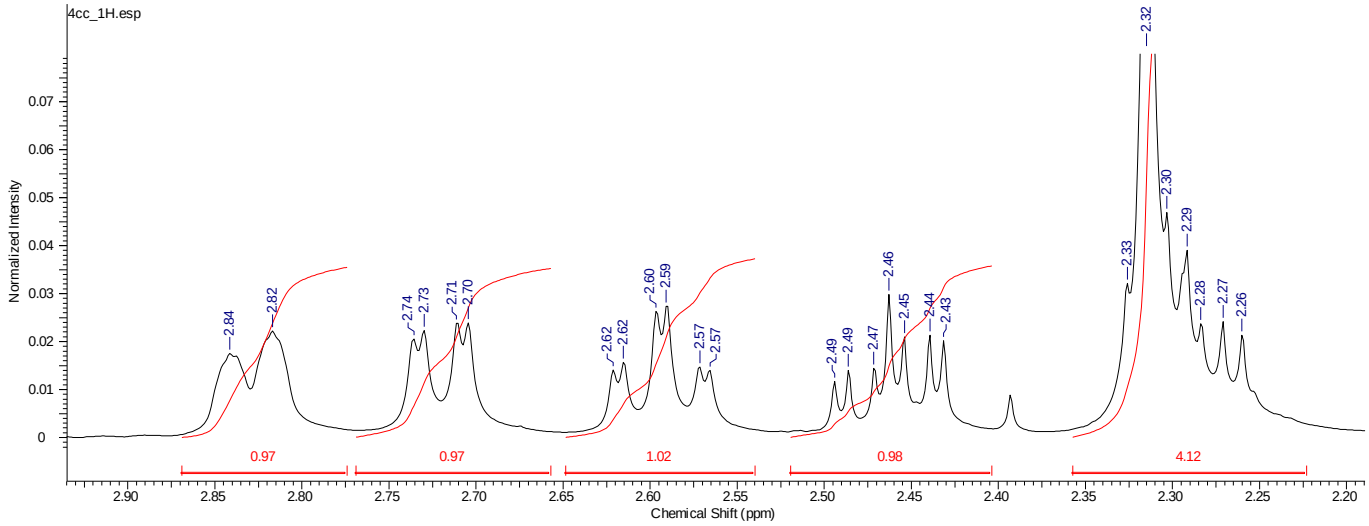


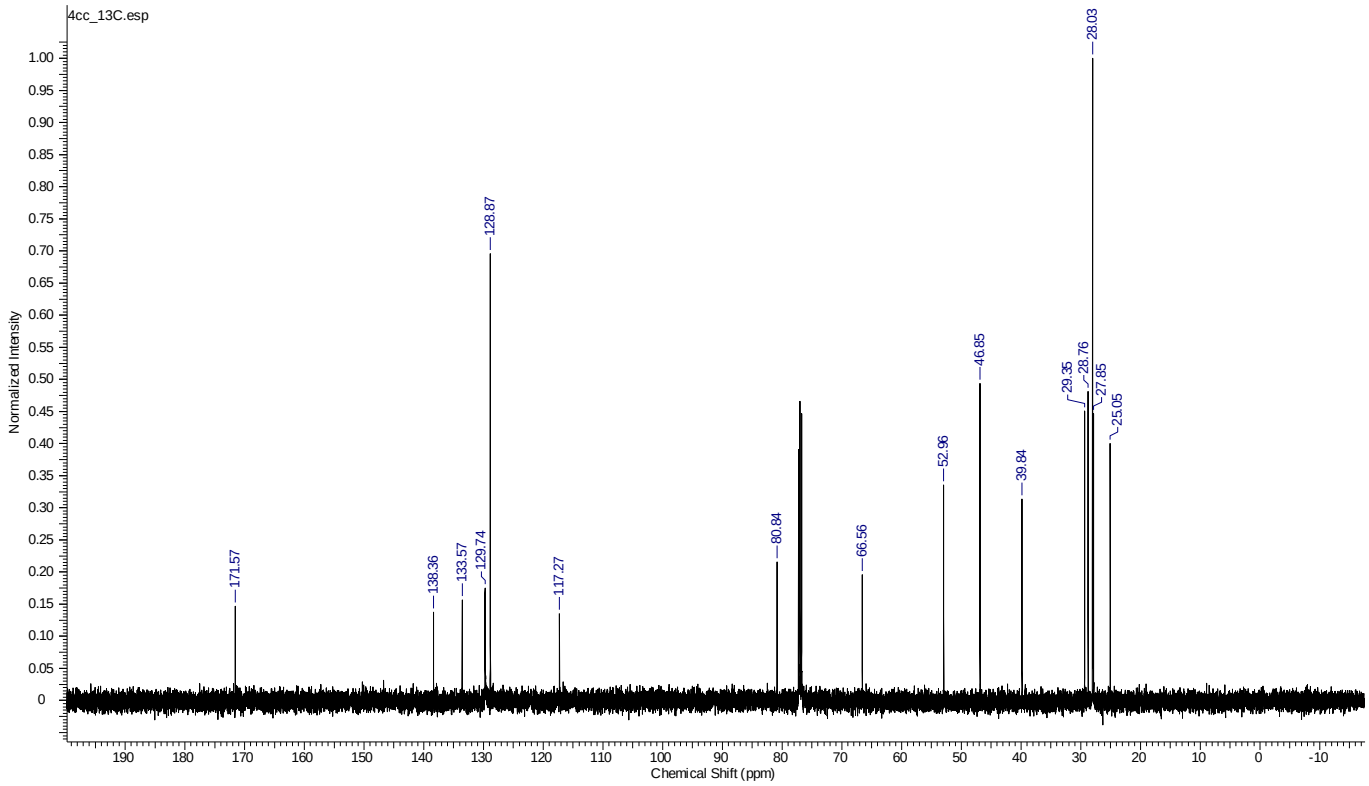
2-(2-*tert*-butoxycarbonylethyl)-3-(4-chlorophenyl)-2-cyano-1-methylpiperidine (4cc)



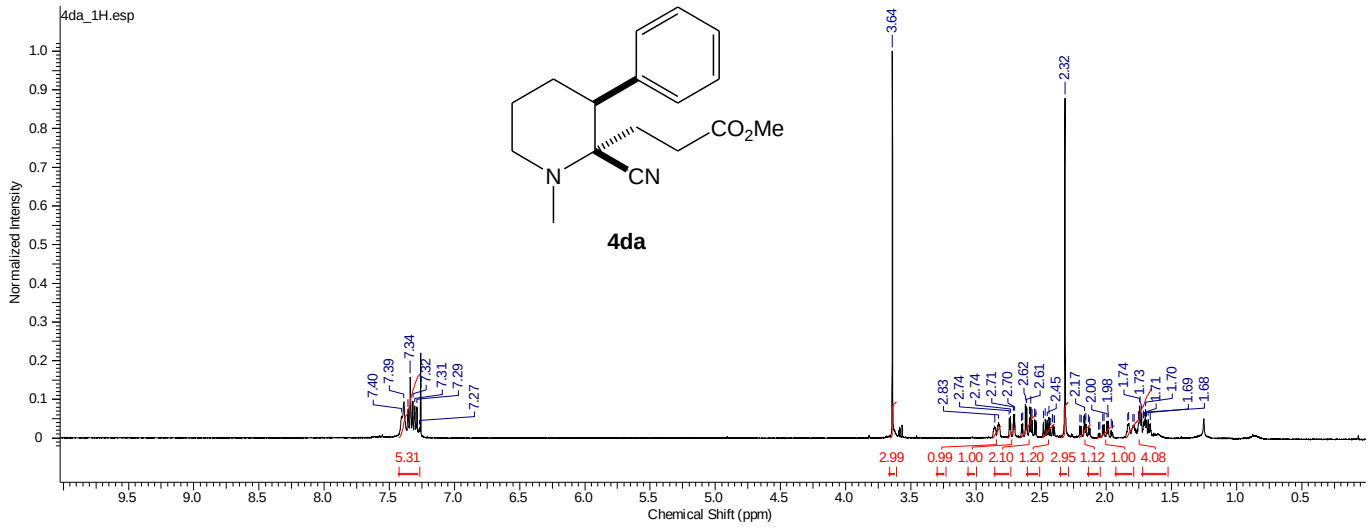

4cc_1H.esp
Normalized Intensity
Chemical Shift (ppm)
0.97
0.96
1.01
0.97
4.09
1.06
1.01
4.21

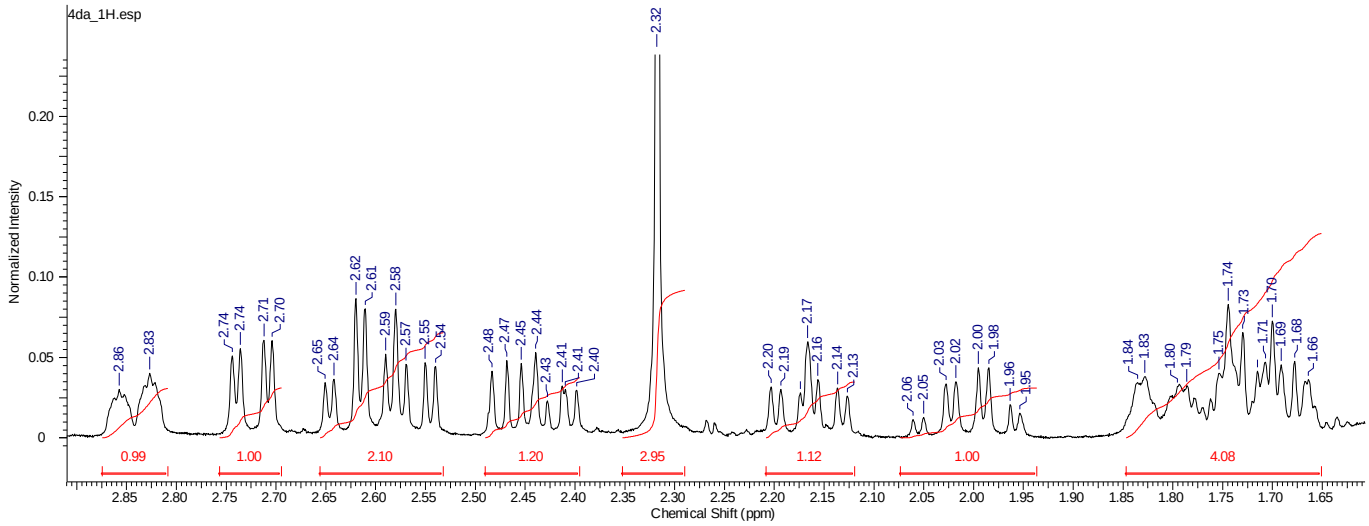

4cc_1H.esp
Normalized Intensity
Chemical Shift (ppm)
1.07
1.01
4.21

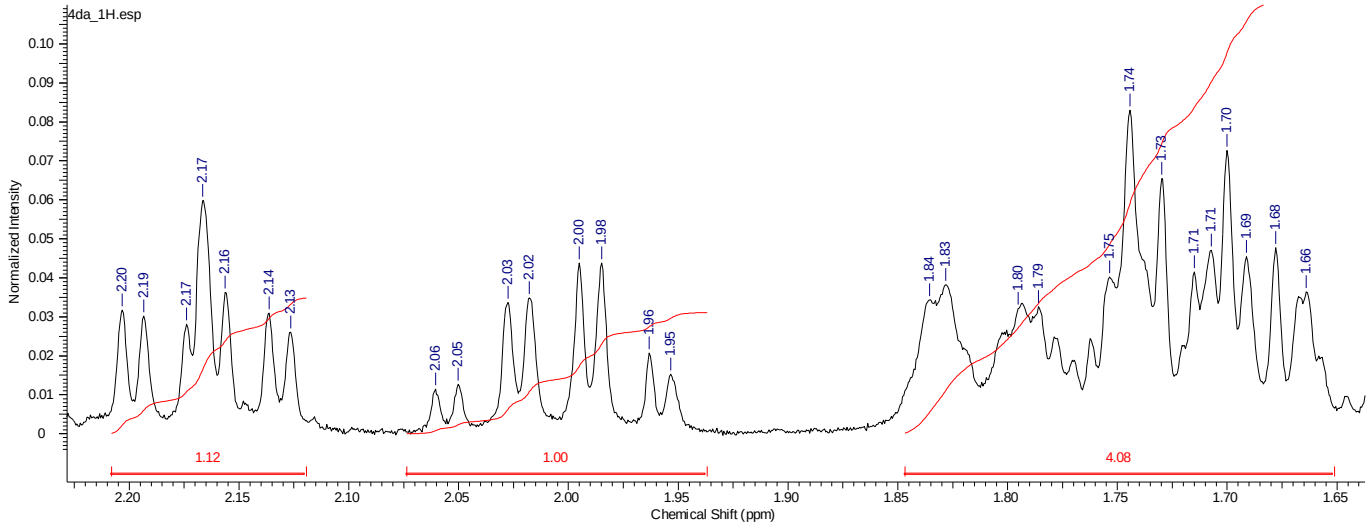

4cc_1H.esp
Normalized Intensity
Chemical Shift (ppm)
0.97
0.97
1.02
0.98
4.12

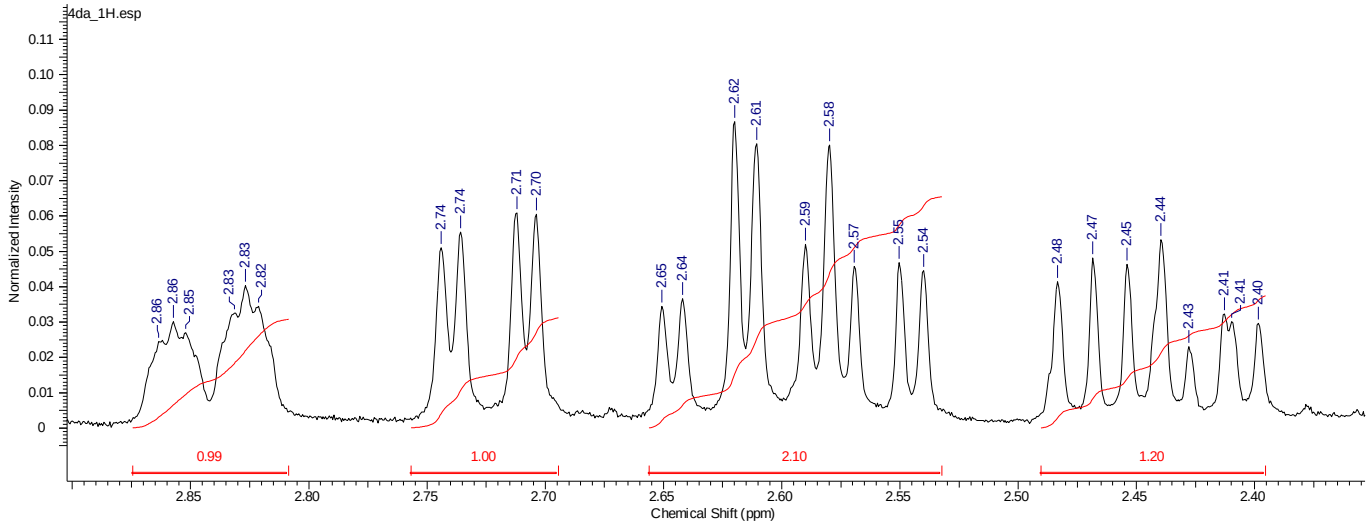


2-cyano-2-(2-methoxycarbonylethyl)-1-methyl-3-phenylpiperidine (4da)




4da_1H.esp
Normalized Intensity
Chemical Shift (ppm)
0.99
1.00
2.10
1.20
2.95
1.12
1.00
4.08


4da_1H.esp
Normalized Intensity
Chemical Shift (ppm)
1.12
1.00
4.08


4da_1H.esp
Normalized Intensity
Chemical Shift (ppm)
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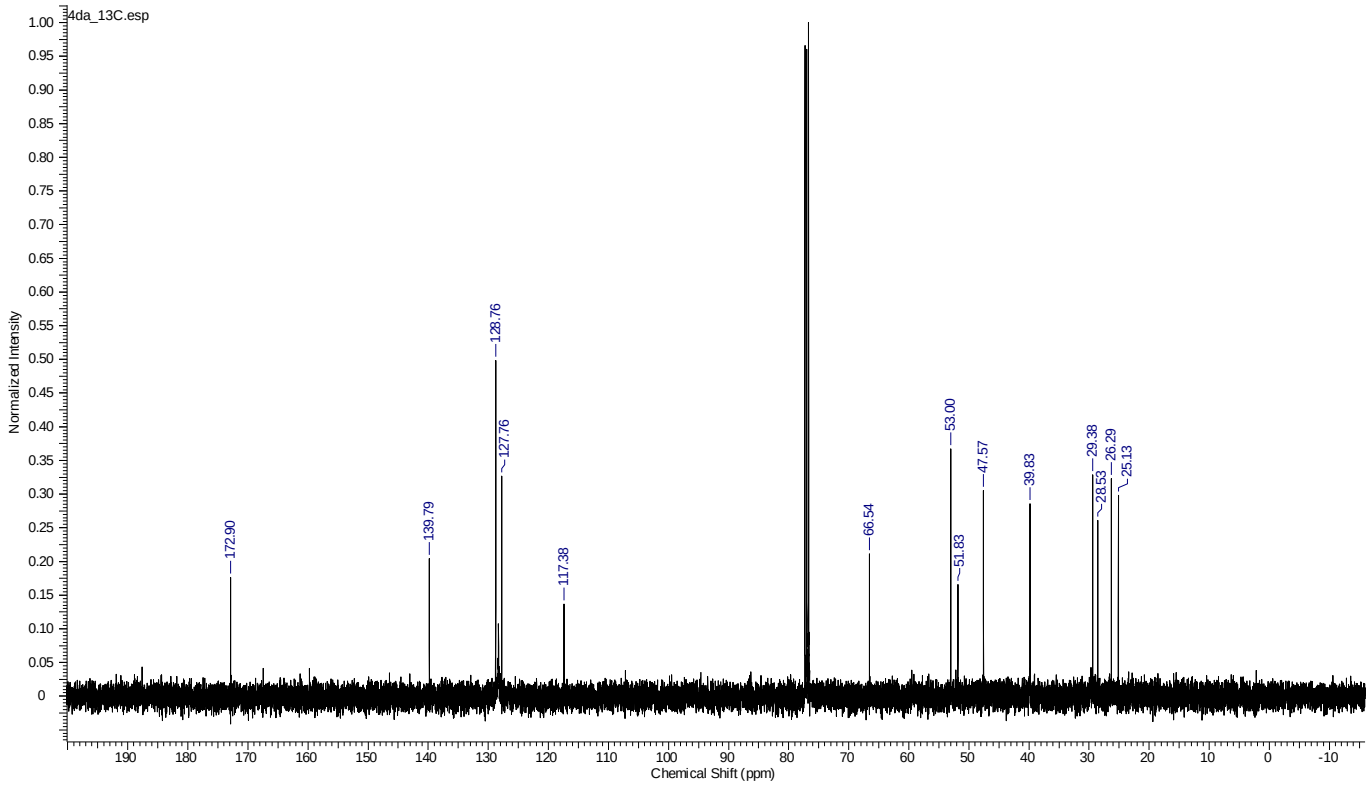
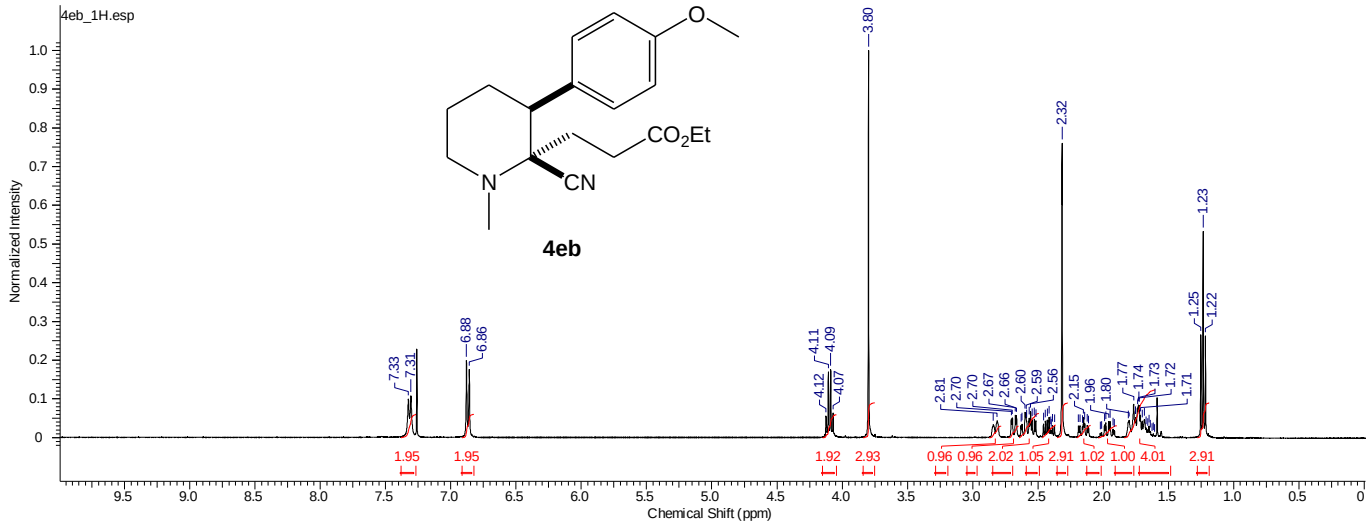
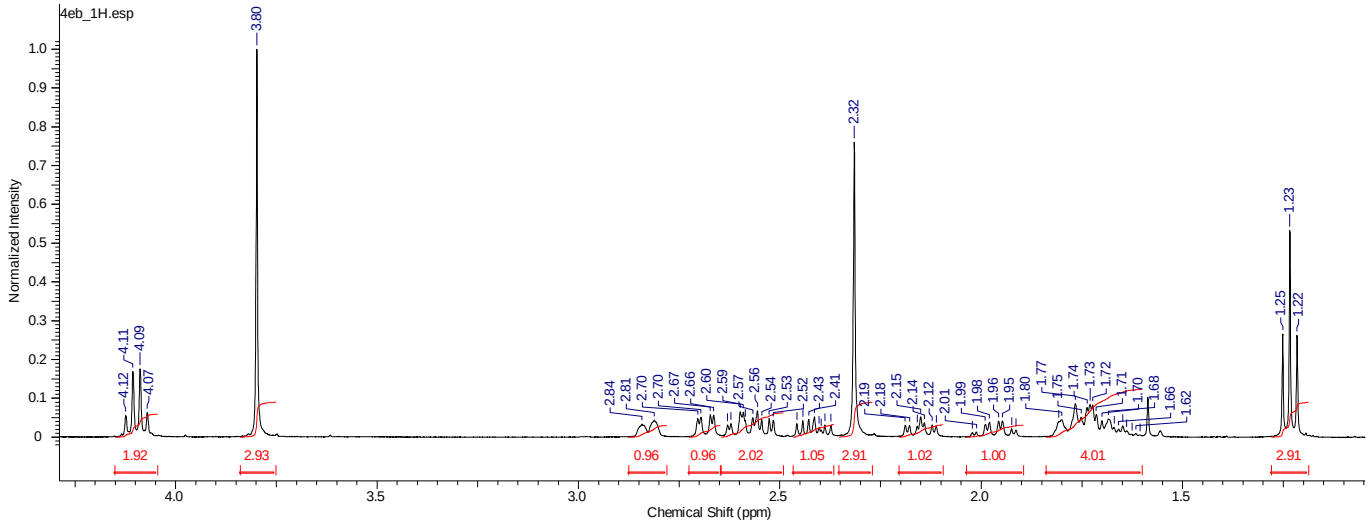
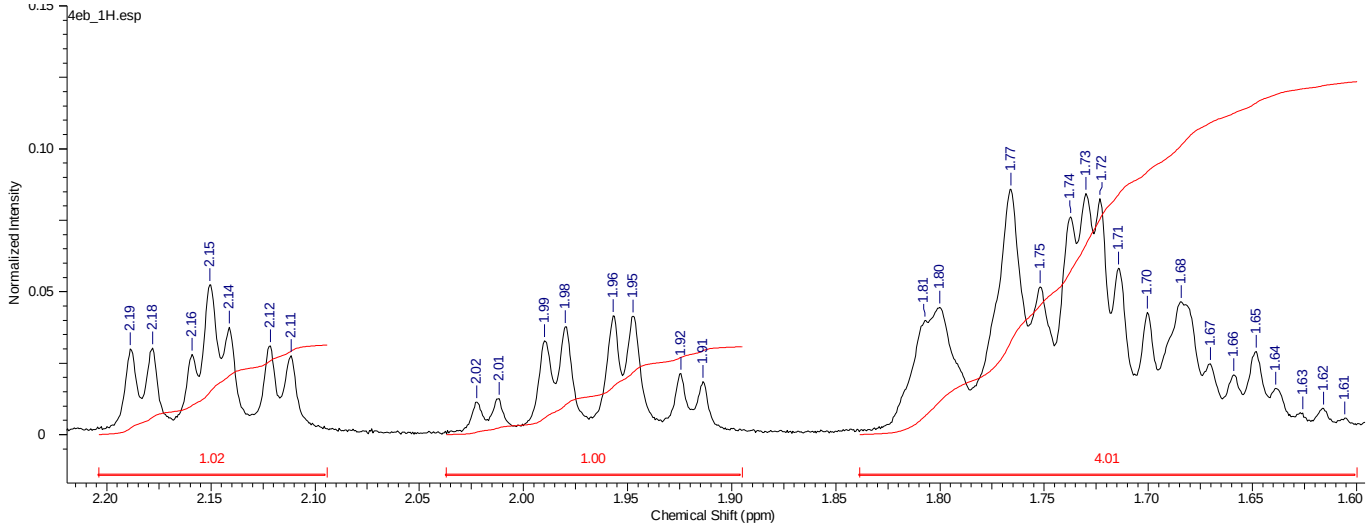
1.00
2.10
1.20



2-cyano-2-(2-ethoxycarbonylethyl)-3-(4-methoxyphenyl)-1-methylpiperidine (4eb)




4eb_1H.esp
Normalized Intensity
Chemical Shift (ppm)
3.80
2.32
1.23
1.25
1.22
4.11
4.09
4.12
4.07
1.92
2.93
0.96
0.96
2.02
1.05
2.91
1.02
1.00
4.01
2.91


4eb_1H.esp
Normalized Intensity
Chemical Shift (ppm)
2.19
2.18
2.16
2.15
2.14
2.12
2.11
2.02
2.01
1.99
1.98
1.96
1.95
1.92
1.91
1.81
1.80
1.77
1.75
1.74
1.73
1.72
1.71
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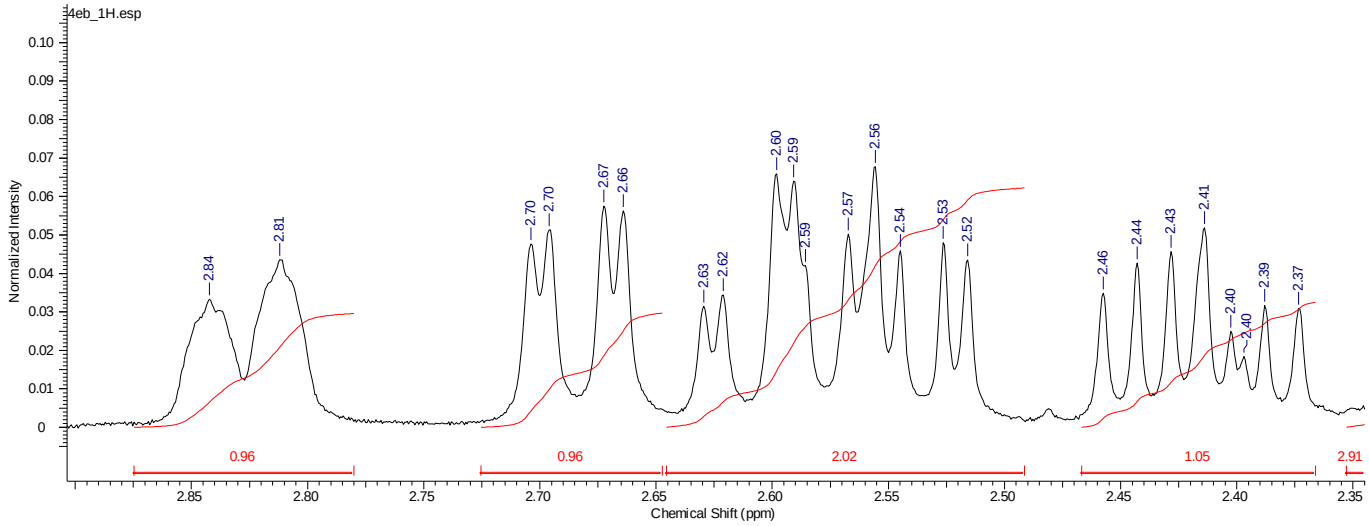
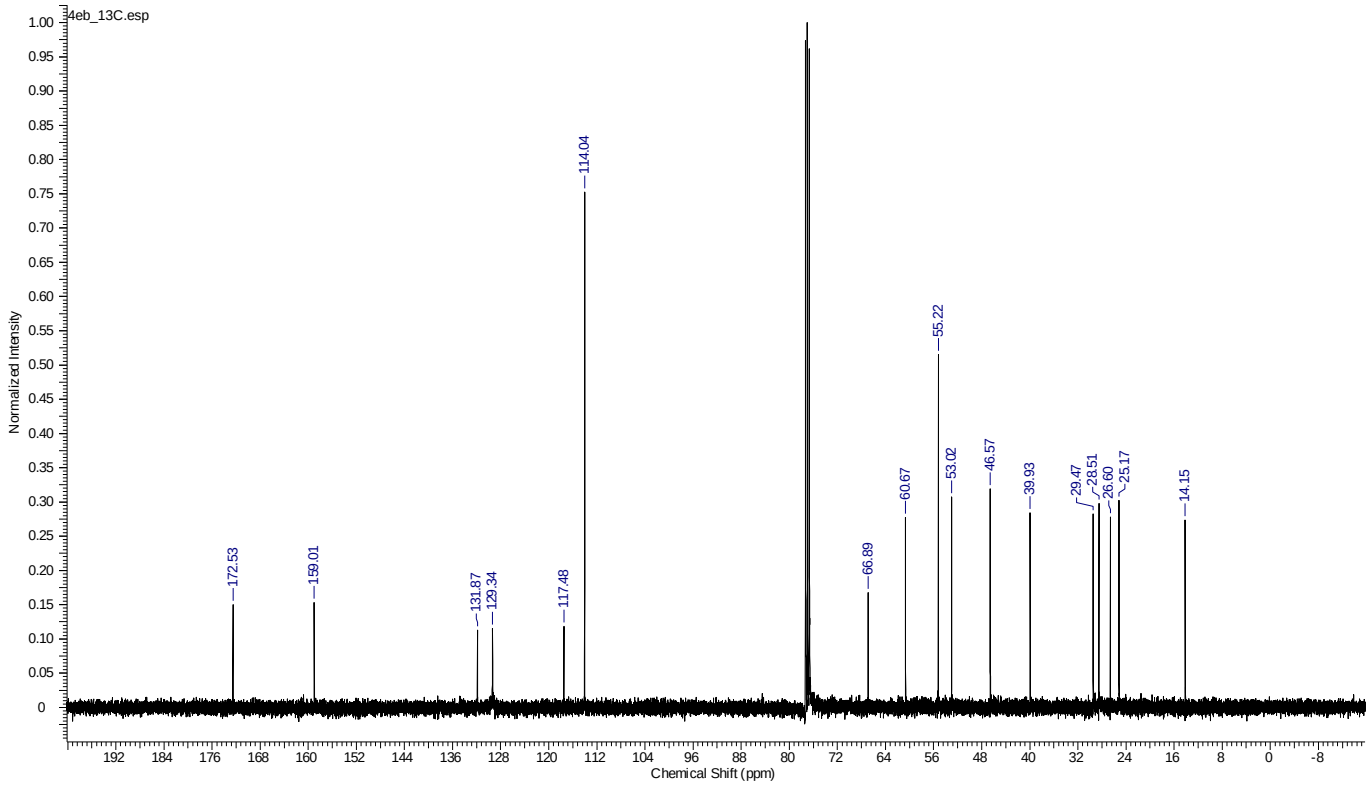
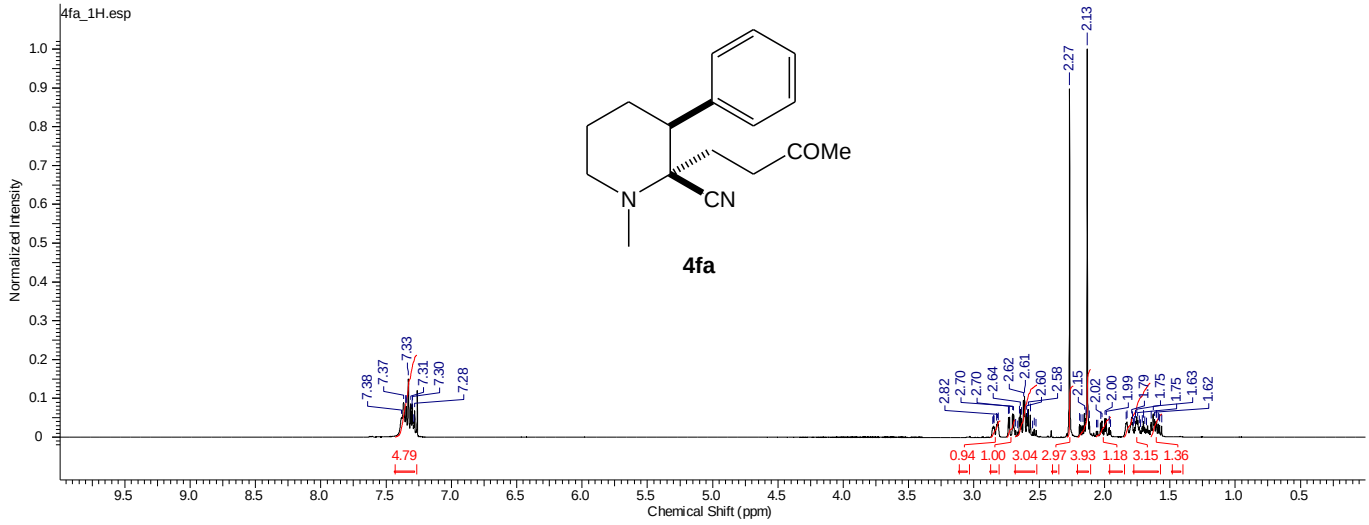
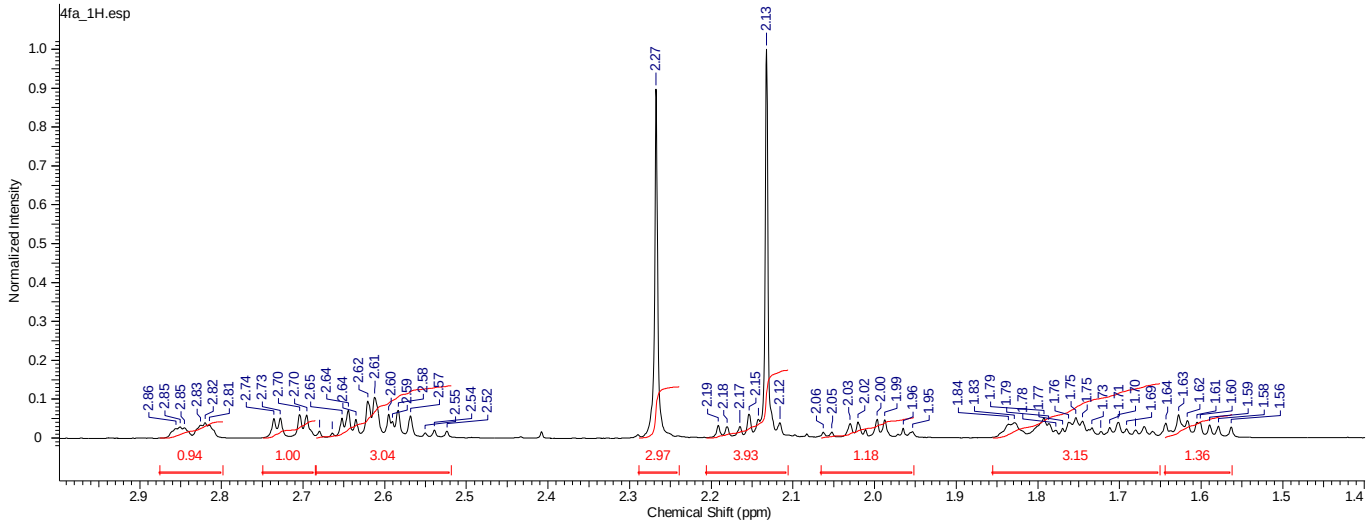
1.63
1.62
1.61
1.02
1.00
4.01

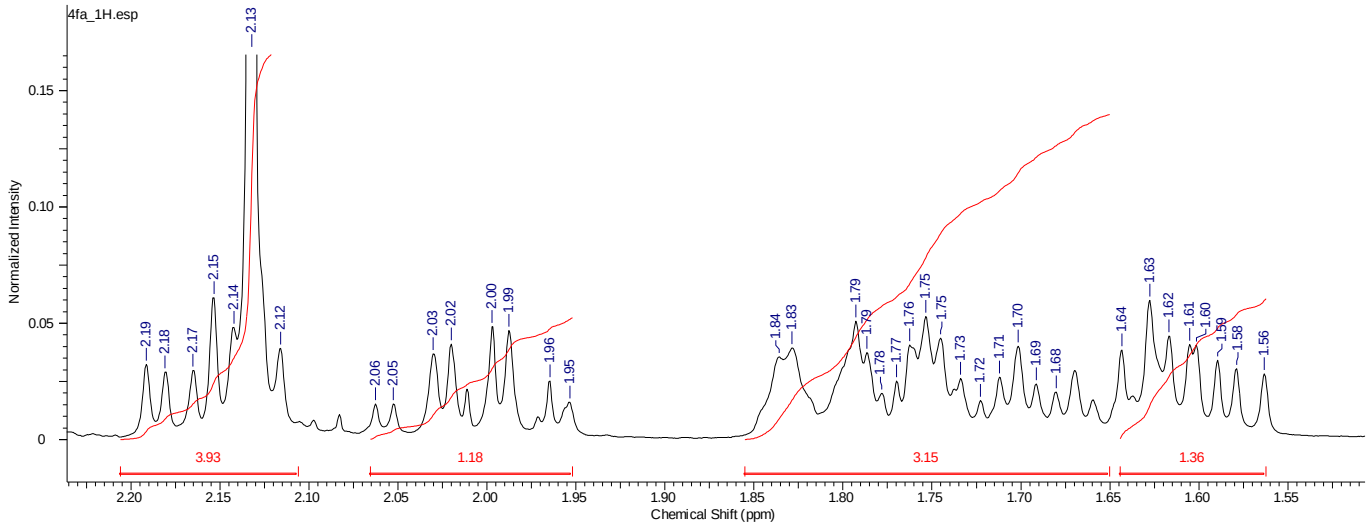

4eb_1H.esp
Normalized Intensity
Chemical Shift (ppm)
2.84
2.81
2.70
2.70
2.67
2.66
2.63
2.62
2.60
2.59
2.59
2.57
2.56
2.54
2.53
2.52
2.46
2.44
2.43
2.41
2.40
2.40
2.39
2.37
0.96
0.96
2.02
1.05
2.91

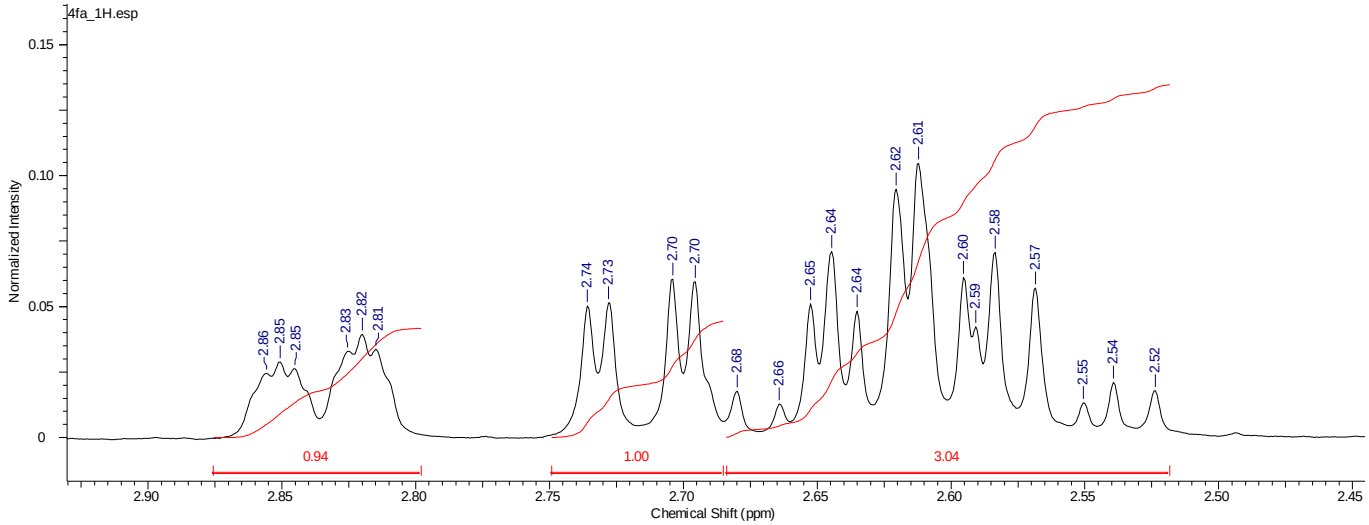


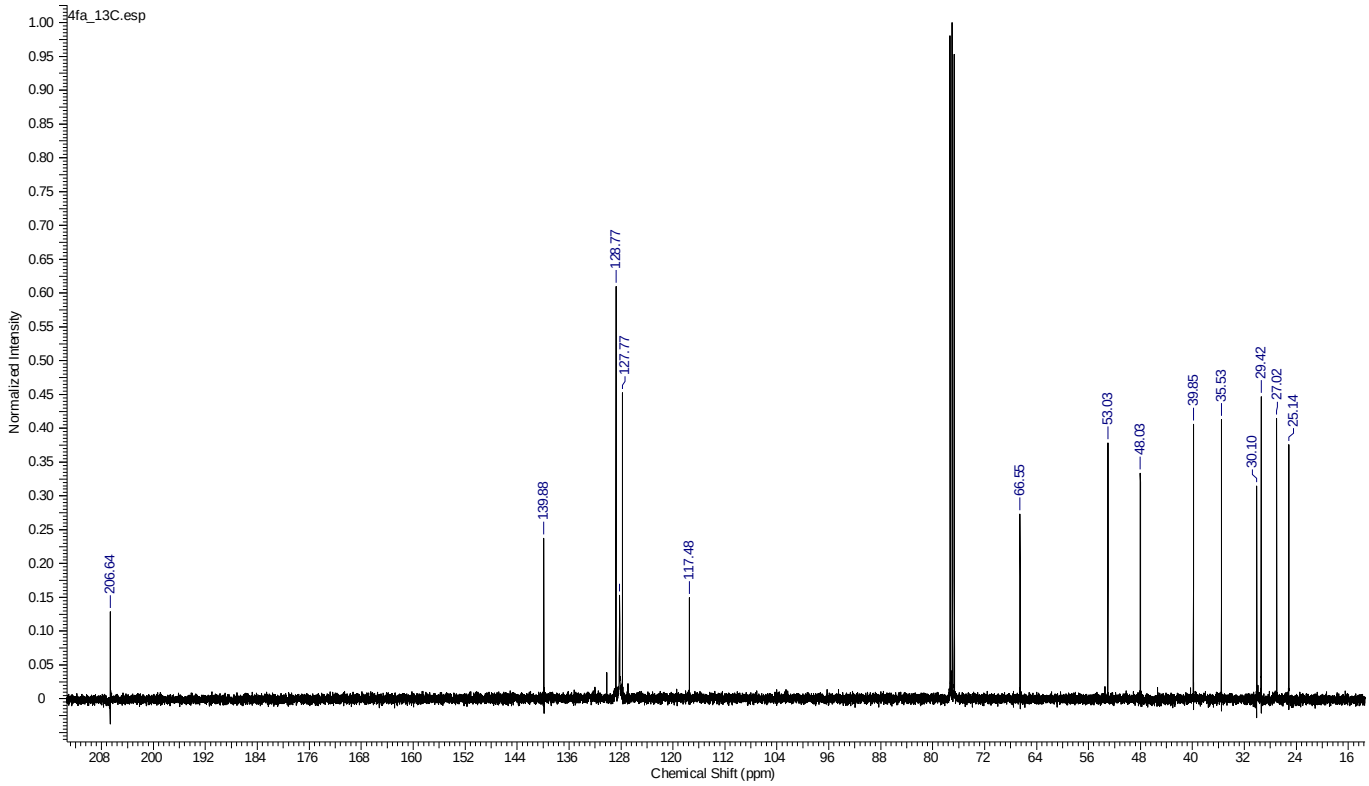
2-cyano-1-methyl-2-(3-oxobutyl)-3-phenylpiperidine (4fa)



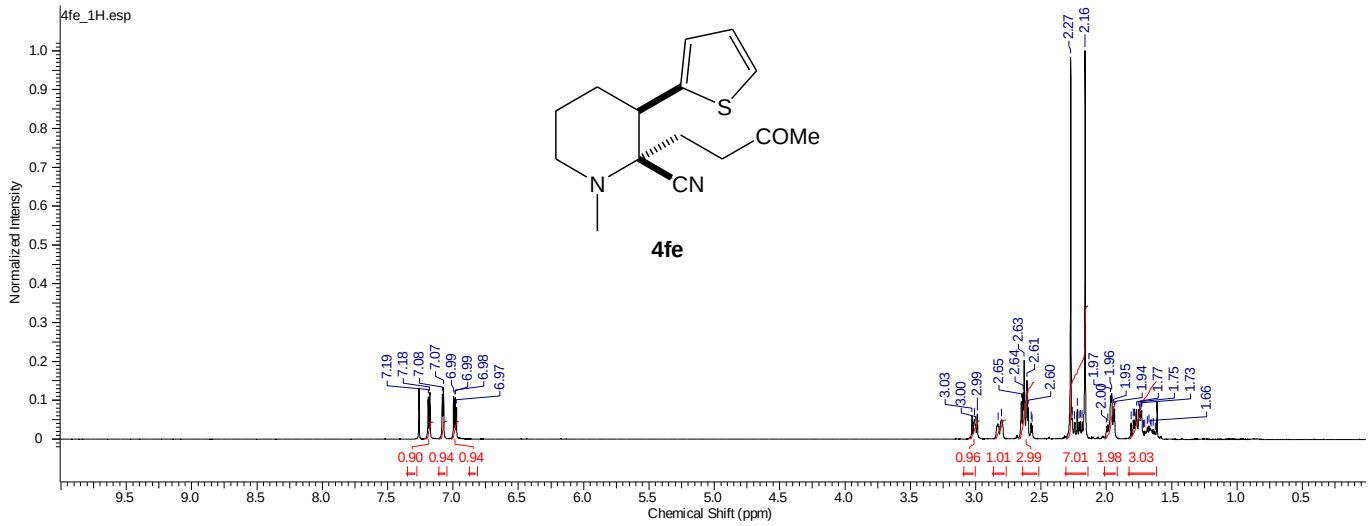

4fa_1H.esp
Normalized Intensity
Chemical Shift (ppm)
0.94
1.00
3.04
2.97
3.93
1.18
3.15
1.36

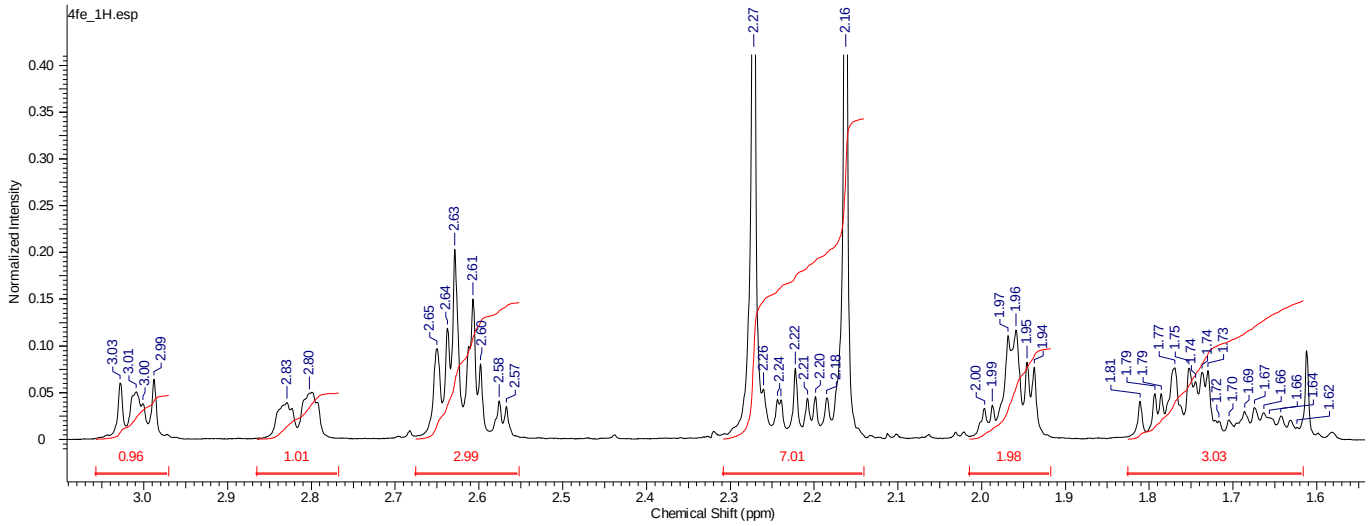

4fa_1H.esp
Normalized Intensity
Chemical Shift (ppm)
3.93
1.18
3.15
1.36

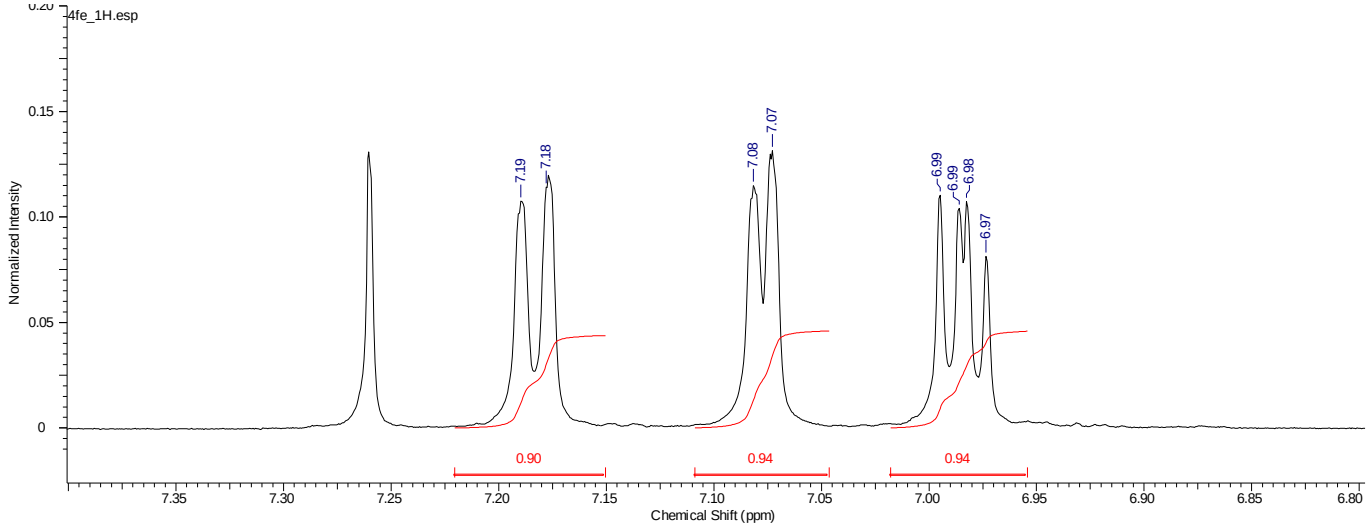

4fa_1H.esp
Normalized Intensity
Chemical Shift (ppm)
0.94
1.00
3.04

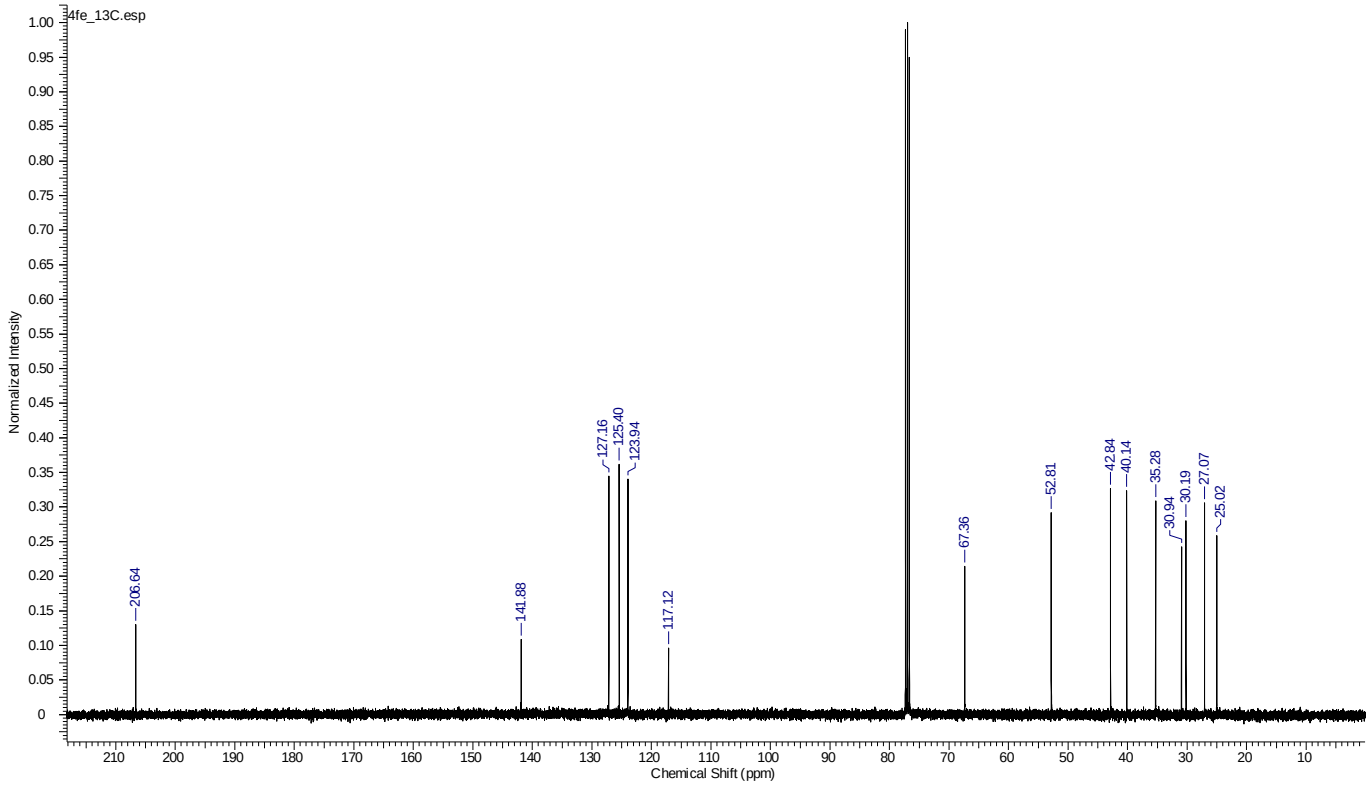


2-cyano-1-methyl-2-(3-oxobutyl)-3-(thiophen-2-yl)piperidine (4fe)

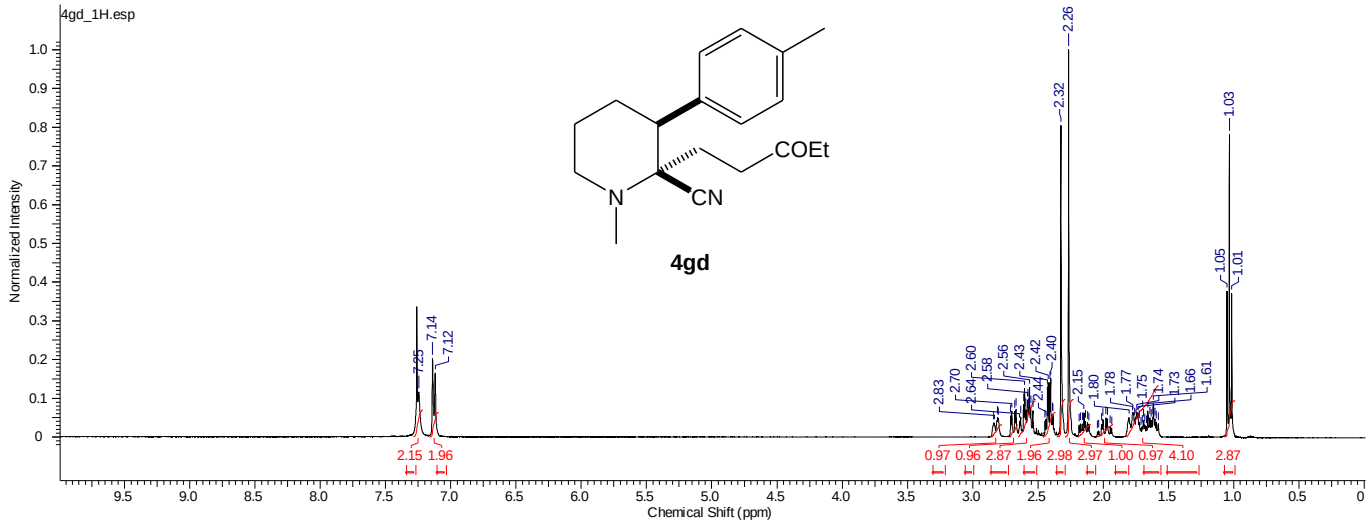


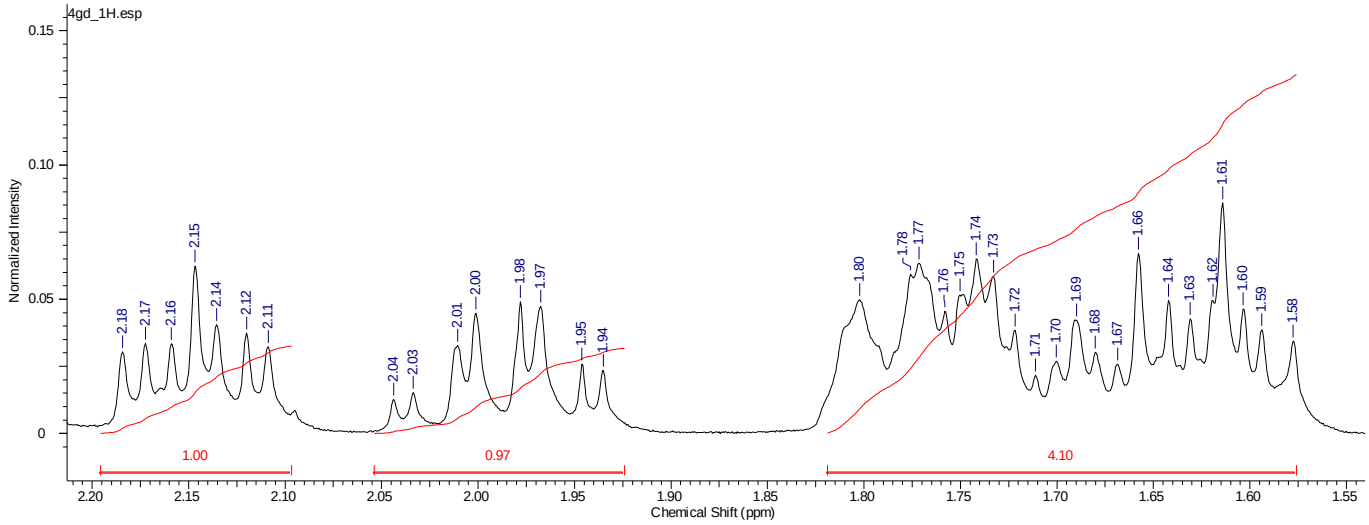

4fe_1H.esp
Normalized Intensity
Chemical Shift (ppm)
0.96
1.01
2.99
7.01
1.98
3.03

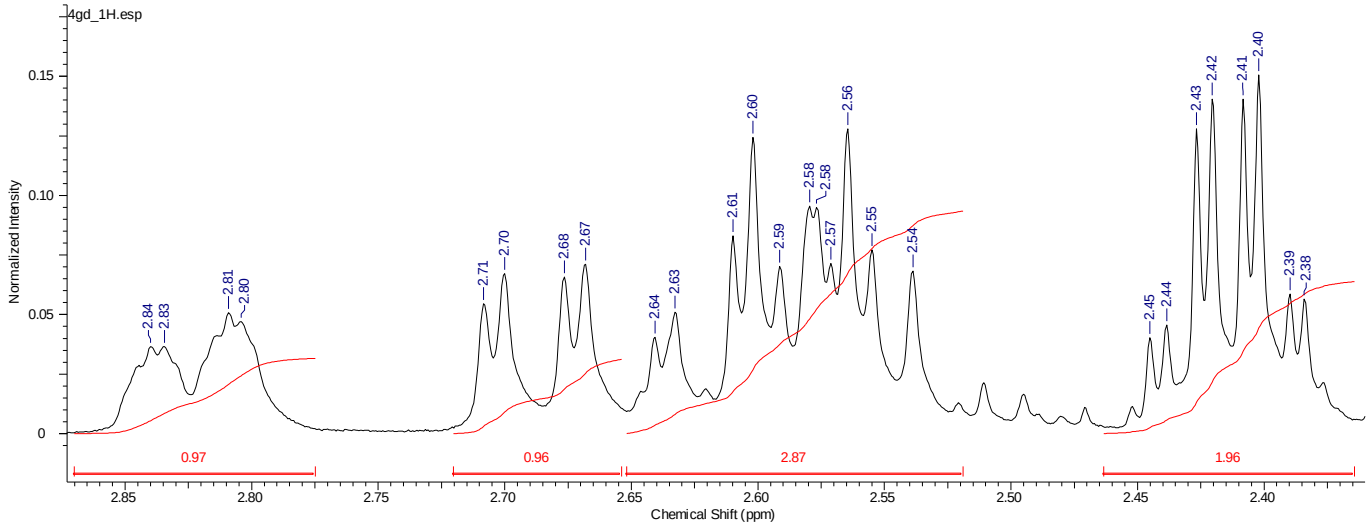

4fe_1H.esp
Normalized Intensity
Chemical Shift (ppm)
0.90
0.94
0.94

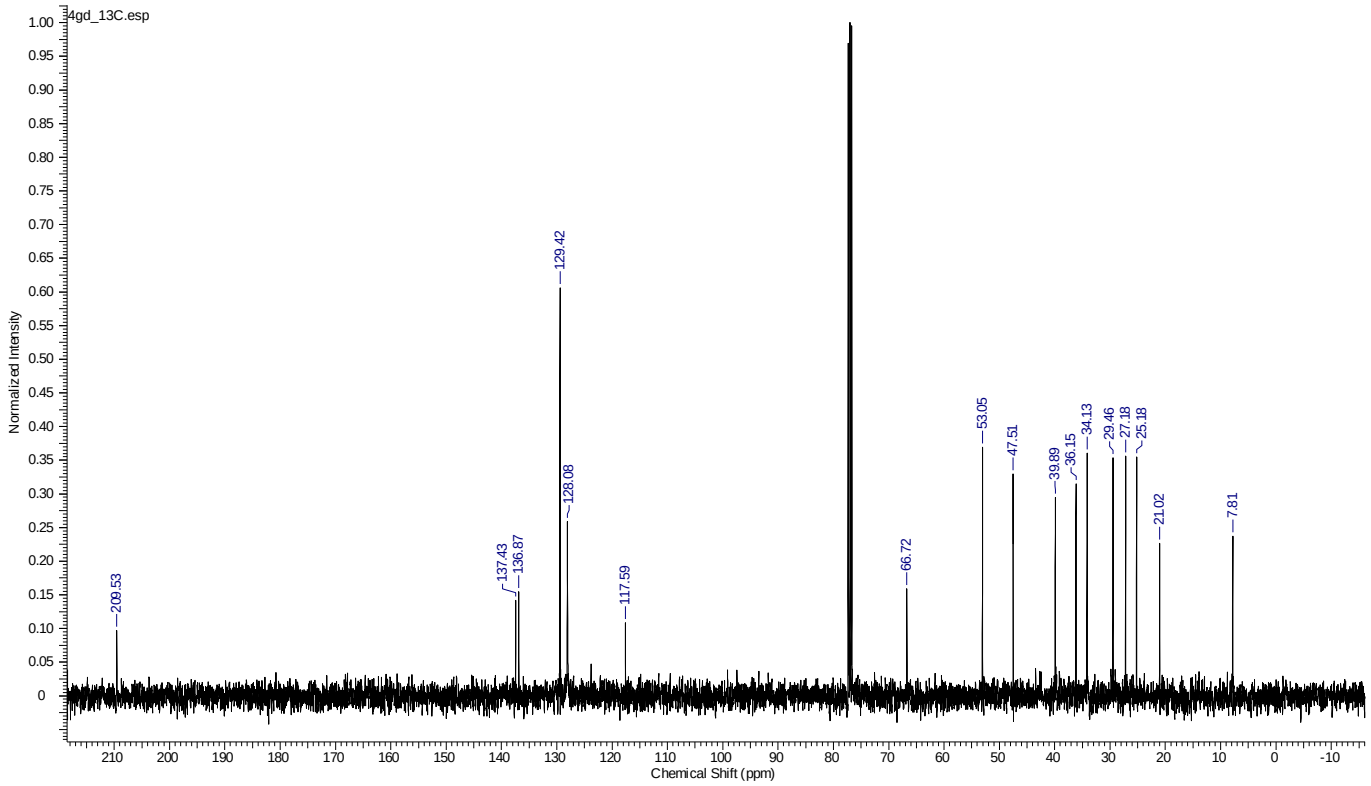


2-cyano-1-methyl-3-(4-methylphenyl)-2-(3-oxopentyl)piperidine (4gd)

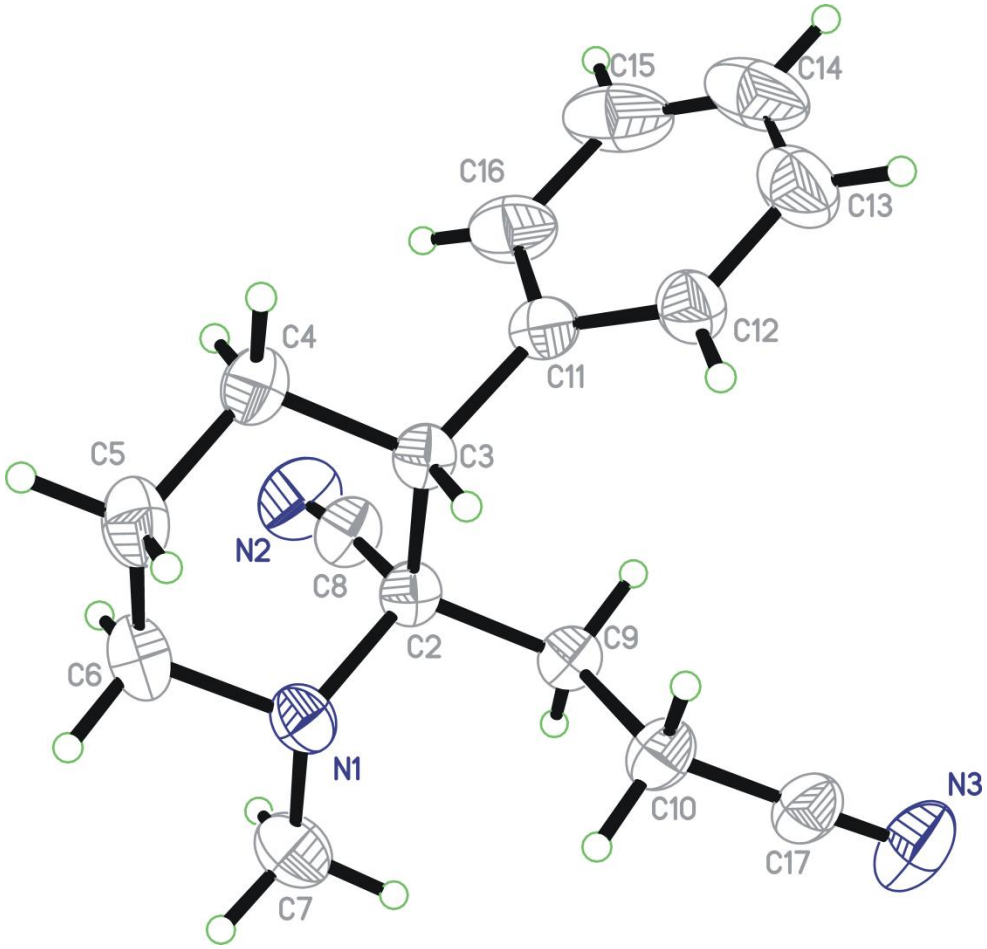


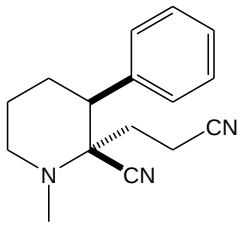

4gd_1H.esp
Normalized Intensity
Chemical Shift (ppm)
1.00
0.97
4.10


4gd_1H.esp
Normalized Intensity
Chemical Shift (ppm)
0.97
0.96
2.87
1.96


4gd_13C.esp
Normalized Intensity
Chemical Shift (ppm)
209.53
137.43
136.87
129.42
128.08
117.59
66.72
53.05
47.51
39.89
36.15
34.13
29.46
27.18
25.18
21.02
7.81

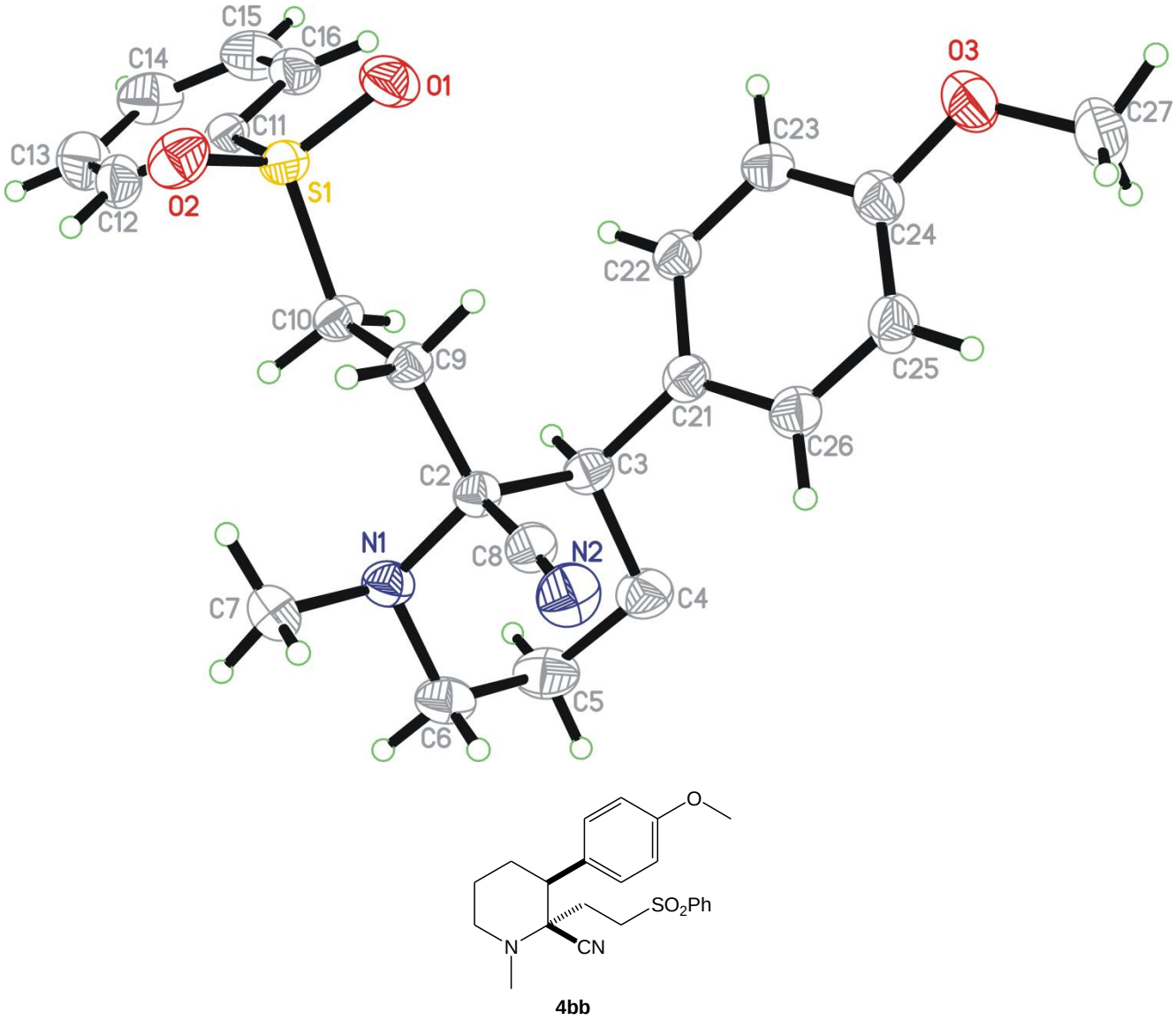
3. Crystallographic data of compounds 4aa, 4bb, 4ca





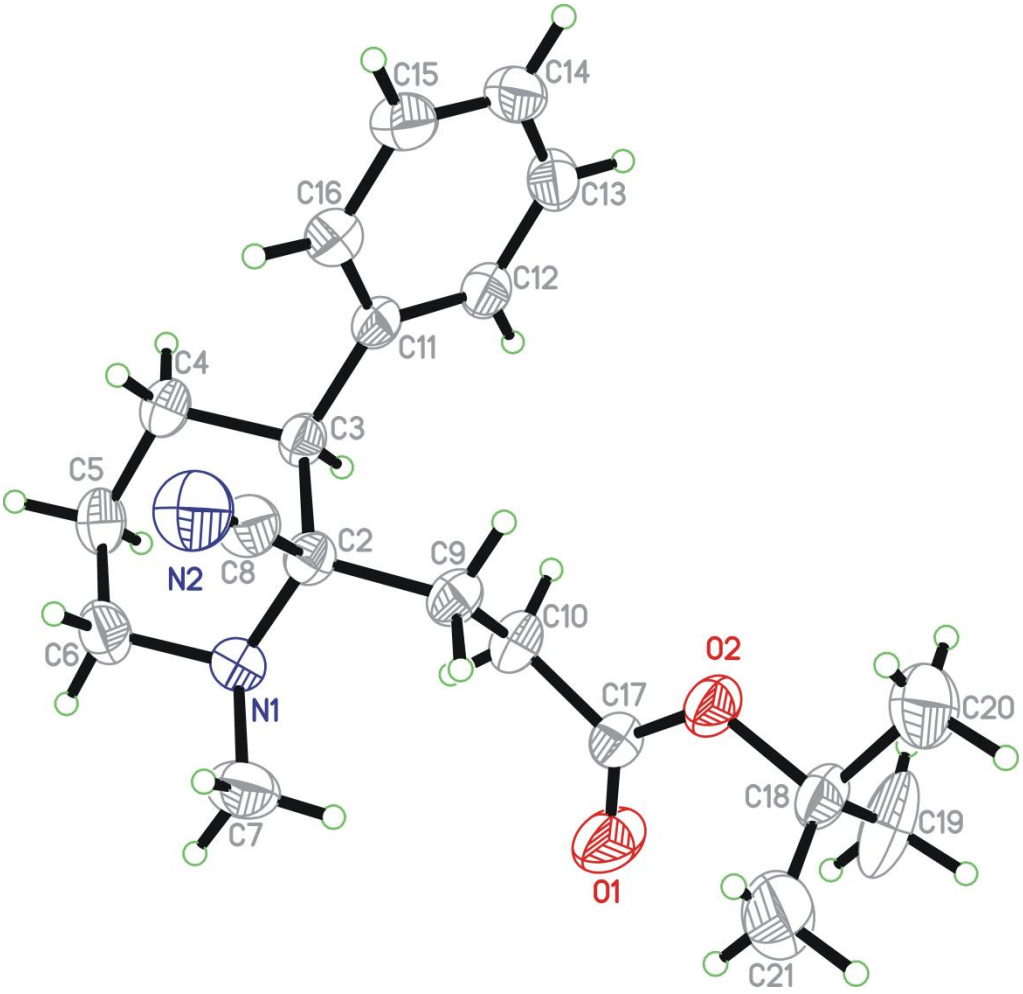
4aa

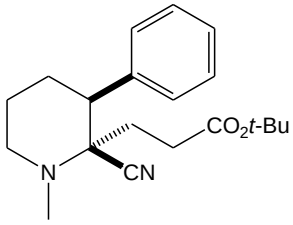
Figure 1. 2-cyano-2-(2-cyanoethyl)-1-methyl-3-phenylpiperidine (4aa)



4bb

Figure 2. 2-cyano-3-(4-methoxyphenyl)- 1-methyl -2-(2-phenylsulfonylethyl)piperidine (4bb)





4ca

Figure 3. 2-(2-*tert*-butoxycarbonylethyl)-2-cyano-1-methyl-3-phenylpiperidine (4ca)

Table S3. Crystallographic data for compounds **4aa**, **4bb**, **4ca**

CCDC number	1822278	1822279	1822280
Compound	**4aa**	**4bb**	**4ca**
Empirical formula	$C_{16}H_{19}N_3$	$C_{22}H_{24}N_2O_3S$	$C_{20}H_{28}N_2O_2$
Formula weight	253.34	396.49	328.44
Temperature	293(2) K	293(2) K	293(2) K
Wavelength	1.54184 Å	1.54184 Å	1.54184 Å
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P 2_1/n	P 21/n	P -1
Unit cell dimensions	a=7.12920(10) Å	a=10.90480(10) Å	a=7.8725(2) Å, α=95.609(2)°
	b=9.77300(10) Å, β=95.1770(10)°	b=11.17140(10) Å, β=95.5410(10)°	b=10.5460(3) Å, β=97.192(2)°
	c = 21.1929(2) Å	c=17.31320(10) Å	c=12.3593(2) Å, γ=108.834(2)°
Volume	1470.56(3) $Å^3$	2099.27(3) $Å^3$	953.04(4) $Å^3$
Z	4	4	2
Density (calculated)	1.144 Mg/m^3	1.255 Mg/m^3	1.145 Mg/m^3
Absorption coefficient	0.536 mm^{-1}	1.567 mm^{-1}	0.581 mm^{-1}
F(000)	544	840	356
Crystal size	0.498 x 0.313 x 0.137 mm^3	0.367 x 0.244 x 0.185 mm^3	0.446 x 0.228 x 0.165 mm^3
θ range for data collection	4.19 to 71.27°.	4.60 to 71.22°.	3.64 to 71.23°.
Index ranges	-8≤h≤8, -11≤k≤11, -25≤l≤26	-13≤h≤13, -13≤k≤13, -21≤l≤20	-9≤h≤9, -12≤k≤12, -15≤l≤15
Reflections collected	23250	37267	39962
Independent reflections	2845 [R(int) = 0.0302]	4060 [R(int) = 0.0367]	3675 [R(int) = 0.0269]
Completeness to θ = 71.27°	99.6 %	99.4 %	99.5 %
Absorption correction	Analytical	Analytical	Analytical
Max. and min. transmission	0.935 and 0.821	0.777 and 0.618	0.919 and 0.843
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2845 / 0 / 173	4060 / 0 / 253	3675 / 24 / 224
Goodness-of-fit on F^2	1.063	1.064	1.081
Final R indices [I>2σ(I)]	R1 = 0.0433, wR2 = 0.1249	R1 = 0.0444, wR2 = 0.1302	R1 = 0.0713, wR2 = 0.2206
R indices (all data)	R1 = 0.0483, wR2 = 0.1309	R1 = 0.0494, wR2 = 0.1368	R1 = 0.0759, wR2 = 0.2277
Extinction coefficient	0.0056(7)		
Largest diff. peak and hole	0.184 and -0.173 $e·Å^{-3}$	0.623 and -0.270 $e.Å^{-3}$	0.462 and -0.357 $e·Å^{-3}$