Electrochemical C-H functionalization and subsequent C-S and C-N bond formation: Paired electrosynthesis of 3-amino-2-thiocyanato α,β-unsaturated carbonyl derivatives mediated by bromide ion

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1. Experimental

1.1 Instruments and reagents

All melting points are uncorrected. IR spectra were recorded as KBr pellets. All the material **1a-1n** and solvents were commercially available and used without further purification.

1.2 Typical procedure for the synthesis of 3-amino-2-thiocyanato-2-butenoate 3 by constant current electrolysis.

A 50 mL beaker-type cell was equipped with a Pt anode and a Pt plate cathode and connected to a DC regulated power supply. To the cell was added ethyl acetoacetate **1** (1 mmol), amine **2** (1.5 mmol) and NH_4Br (50 mol%) dissolved in 15 mL of CH_3CN. The mixture was electrolyzed using constant current conditions (~5 mA/cm^2) at 40 ^oC while stirring. The electrolysis was terminated when the starting material **1** was consumed as determined by TLC. After the electrolysis, the solvent was removed under reduced pressure and extraction was carried out using ethyl acetate (3×15 mL); the combined organic layers were washed with a saturated aqueous Na_2CO_3 solution, and dried over $MgSO_4$. Purified product was obtained after column chromatography on silica gel using a solvent mixture of petroleum ether and ethyl acetate.

1.3 Cyclic voltammetry experiments

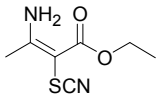
Cyclic voltammograms were recorded at room temperature using a Princeton Applied Research Model 273A Potentiostat/Galvanostat equipped with electrochemical analysis software and a conventional three-electrode cell. A glassy carbon (GC) disk electrode (ca. ϕ = 3 mm) or a Pt disk electrode (ca. ϕ = 1 mm) was used as the working electrode and a Pt wire as the counter electrode. $Ag/AgNO_3$ (0.1 M in CH_3CN) was used as a reference electrode. All electrodes for CV experiments were purchased from CH Instruments, Inc. USA.

The working electrodes were carefully polished on a polishing pad before each experiment using a fine mesh alumina slurry, and then ultrasonically rinsed with

acetone. All solutions were degassed by sparging dry nitrogen through the solution for 10 min prior to conducting each electrochemical experiment; a nitrogen atmosphere was maintained throughout. In each measurement, the three electrodes were fixed in place, and were not allowed to be disturbed in any manner.

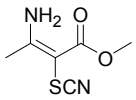
2. Spectroscopic Data

(*E*)-3-Amino-2-thiocyanato-but-2-enoic acid ethyl ester (3a)[1]



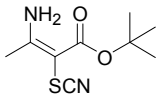
White solid; m.p. 111 - 113 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.37 (t, J = 7.2 Hz, 3H), 2.42 (s, 3H), 4.25 (q, J = 7.2 Hz, 2H), 5.56 (s, 1H), 9.32 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 14.4, 23.2, 60.75, 75.5, 113.7, 168.4, 168.6; **IR** (KBr) (cm^{-1}): υ 3417, 2986, 2142, 1622, 1269; **HRMS** calcd for $C_7H_9N_2O_2S$: 185.0385, found: 185.0355.

(*E*)-3-Amino-2-thiocyanato-but-2-enoic acid methyl ester (3b)[2]



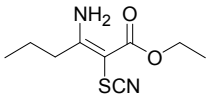
White solid; m.p. 90 - 93 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.43 (s, 3H), 3.81 (s, 3H), 5.60 (s, 1H), 9.31 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 23.4, 52.0, 76.0, 113.3, 128.8, 168.5, 168.8; **IR** (KBr) (cm^{-1}): υ 3427, 3329, 2950, 2146, 1633, 1276; **HRMS** calcd for $C_6H_9N_2O_2S$: 173.0385, found: 173.0381.

(*E*)-3-Amino-2-thiocyanato-but-2-enoic acid tert-butyl ester (3c)[3]



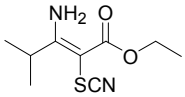
Pale yellow solid; m.p. 82 - 84 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.56 (s, 9H), 2.37 (s, 3H), 5.42 (s, 1H), 9.25 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 23.5, 28.3, 81.2, 113.6, 167.3, 168.0; **IR** (KBr) (cm^{-1}): υ 3292, 3101, 1597, 1527, 1430; **HRMS** calcd for $C_9H_{15}N_2O_2S$: 215.0854, found: 215.0847.

(*E*)-3-Amino-2-thiocyanato-hex-2-enoic acid ethyl ester (3d)[1]



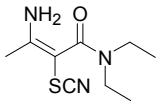
Pale yellow solid; m.p. 121 - 123 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.07 (t, J = 7.6 Hz, 3H), 1.38 (t, J = 6.8 Hz, 3H), 1.69-1.78 (m, 2H), 2.68-2.71 (m, 2H), 4.26 (q, J = 6.8 Hz, 2H), 5.54 (s, 1H), 9.41 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.7, 14.4, 21.3, 38.1, 60.8, 75.7, 113.7, 168.7, 171.8; **IR** (KBr) (cm^{-1}): υ 3410, 3295, 2965, 2146, 1621, 1266; **HRMS** calcd for $C_9H_{13}N_2O_2S$: 213.0698, found: 213.0707.

(*E*)-3-Amino-4-methyl-2-thiocyanato-pent-2-enoic acid ethyl ester (3e)



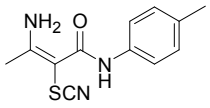
Brown oil; liquid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.23 (d, J = 6.8 Hz, 6H), 1.35 (t, J = 6.8 Hz, 3H), 3.64-3.71 (m, 1H), 4.24 (q, J = 7.2 Hz, 2H), 5.73 (s, 1H), 9.55 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 14.4, 20.3, 32.5, 60.8, 74.3, 113.9, 168.4, 176.5; **IR** (KBr) (cm^{-1}): υ 3424, 2982, 2143, 1668, 1612, 1161; **HRMS** calcd for $C_9H_{13}N_2O_2S$: 213.0698, found: 213.0707.

(*E*)-3-Amino-2-thiocyanato-but-2-enoic acid diethylamide (3g)



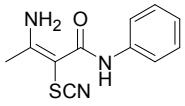
Pale yellow solid; m.p. 135 - 136 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.19 (t, J = 6.8 Hz, 6H), 2.23 (s, 3H), 3.47 (q, J = 7.2 Hz, 4H), 5.34 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.6, 16.3, 41.6, 113.6, 148.7, 163.8, 167.2; **IR** (KBr) (cm^{-1}): υ 3293, 3144, 2149, 1592, 1272; **HRMS** calcd for $C_9H_{16}N_3OS$: 214.1014, found: 214.1010.

(*E*)-3-Amino-2-thiocyanato-but-2-enoic acid p-tolylamide (3h)



Pale yellow solid; m.p. 123 - 125 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.35 (s, 3H), 2.44 (s, 3H), 5.60 (s, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 8.25 (s, 1H), 10.15 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 20.9, 24.0, 75.4, 111.7, 121.1, 129.5, 134.1, 135.1, 166.8, 167.8; **IR** (KBr) (cm^{-1}): υ 3330, 2156, 1592, 1503, 1231, 803; **HRMS** calcd for $C_{12}H_{14}N_3OS$: 248.0858, found: 248.0853.

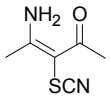
(*E*)-3-Amino-2-thiocyanato-but-2-enoic acid phenylamide (3i)



Pale yellow solid; m.p. 139 - 140 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.46 (s, 3H), 5.61 (s, 1H), 7.15 (t, J = 7.2 Hz, 1H), 7.35-7.39 (m, 2H), 7.52 (d, J = 7.6 Hz, 2H), 8.32 (s, 1H), 10.17 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 24.0, 75.4, 111.7, 120.9, 124.4, 129.0, 137.8, 166.9, 168.0; **IR** (KBr) (cm^{-1}): υ 3387, 3335, 2152, 1529, 1230,

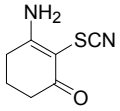
751; **HRMS** calcd for $C_{11}H_{12}N_3OS$: 234.0701, found: 234.0695.

(*E*)-4-Amino-3-thiocyanato-pent-3-en-2-one (3j)[3]



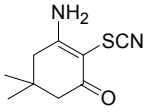
Pale yellow solid; m.p. 122 - 123 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.43 (s, 3H), 2.51 (s, 3H), 5.98 (s, 1H), 10.97 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 24.0, 29.0, 87.0, 113.0, 169.5, 198.1; **IR** (KBr) (cm^{-1}): υ 3419, 2978, 2150, 1612, 1255; **HRMS** calcd for $C_6H_7N_2OS$: 155.0279, found: 155.0289.

(*E*)-3-Amino-2-thiocyanato-cyclohex-2-enone (3k)[4]



Deep green solid; m.p. 96 - 100 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ 1.78-1.84 (m, 2H), 2.31 (t, J = 6.4 Hz, 2H), 2.61 (t, J = 6.0 Hz, 2H), 7.79 (s, 1H), 8.19 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ 20.6, 30.3, 37.2, 86.7, 112.9, 171.6, 190.3; **IR** (KBr) (cm^{-1}): υ 3396, 3311, 3193, 2148, 1615, 1522, 1297; **HRMS** calcd for $C_7H_7N_2OS$: 167.0279, found: 167.0285.

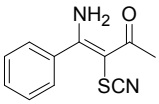
(*E*)-3-Amino-5,5-dimethyl-2-thiocyanato-cyclohex-2-enone (3l)[4]



Pale yellow solid; m.p. 149 - 151 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.11 (s, 6H), 2.41 (s, 2H), 2.52 (s, 2H), 5.47 (s, 1H), 6.08 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6):

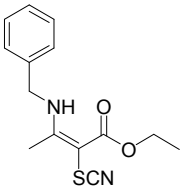
δ 27.8, 31.8, 43.4, 50.6, 85.4, 112.9, 170.0, 189.8; **IR** (KBr) (cm^{-1}): υ 3392, 3311, 3182, 2964, 2145, 1622, 1527, 1318; **HRMS** calcd for $C_9H_{11}N_2OS$: 195.0592, found: 195.0600.

(*E*)-3-Amino-1-phenyl-2-thiocyanato-but-2-en-1-one (3m)



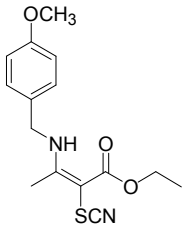
Pale yellow solid; m.p. 141 - 144 ^oC; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.54 (s, 3H), 6.29 (s, 1H), 7.45-7.47 (m, 3H), 7.52-7.54 (m, 2H), 11.22 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 24.4, 86.7, 113.6, 126.8, 128.1, 129.9, 141.0, 171.9, 196.3; **IR** (KBr) (cm^{-1}): υ 782, 729, 699, 658, 540; **HRMS** calcd for $C_{11}H_9N_2OS$: 217.0436, found: 217.0444.

(*E*)-ethyl-3-(benzylamino)-2-thiocyanatobut-2-enoate (3o)



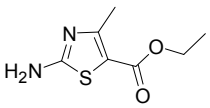
Pale yellow oil; liquid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.35 (t, J = 7.2 Hz, 3H), 2.44 (s, 3H), 4.22 (q, J = 7.2 Hz, 2H), 4.53 (d, J = 5.6 Hz, 2H), 7.25-7.40 (m, 5H), 10.57 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 14.4, 17.9, 48.4, 60.7, 74.8, 113.8, 126.9, 128.0, 129.1, 136.6, 169.3, 169.5; **IR** (KBr) (cm^{-1}): υ 2981, 2147, 1575, 1455, 1235, 1069; **HRMS** calcd for $C_{14}H_{15}N_2O_2S$: 275.0854, found: 275.0792.

(*E*)-ethyl 3-(4-methoxybenzylamino)-2-thiocyanatobut-2-enoate (3p)



White solid; m.p. 64 - 66 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.36 (t, J = 7.2 Hz, 3H), 2.47 (s, 3H), 3.83 (s, 3H), 4.22 (q, J = 7.2 Hz, 2H), 4.47 (d, J = 5.6 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H),10.48 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 14.4, 17.9, 48.0, 55.3, 60.7, 74.6, 113.9, 114.5, 128.4, 128.4, 159.4, 169.3, 169.3. **IR** (KBr) (cm^{-1}): υ 3447, 2148, 1635, 1576, 1516, 1252; **HRMS** calcd for $C_{15}H_{17}N_2O_3S$: 305.0960, found: 305.0965.

Ethyl 2-amino-4-methylthiazole-5-carboxylate (4a)[5]

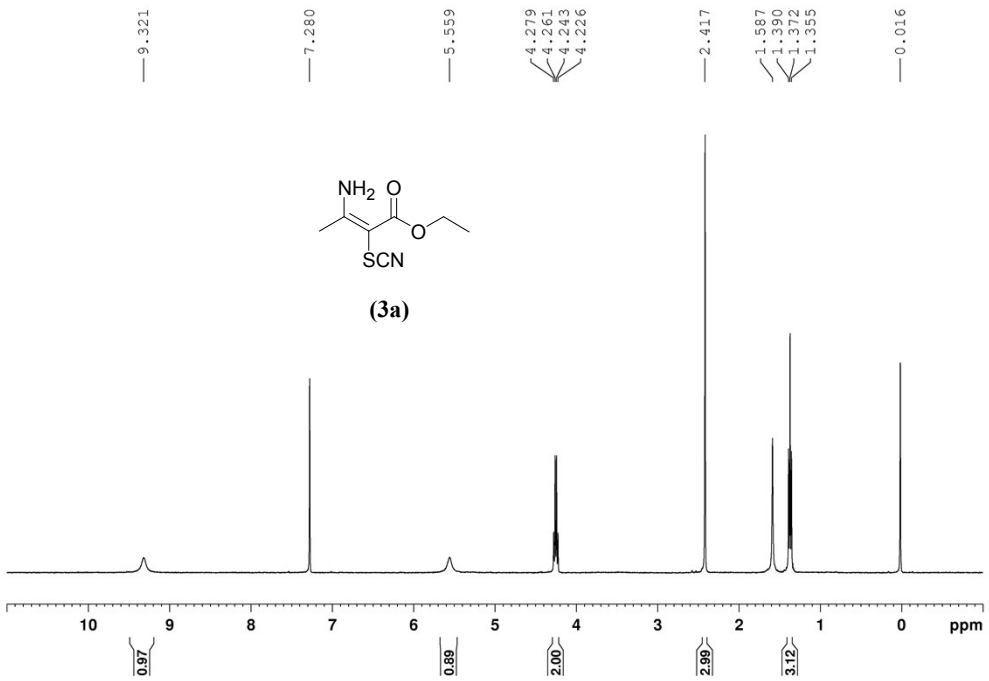


White solid; m.p. 173 - 175 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.35 (t, J = 7.2 Hz, 3H), 2.55 (s, 3H), 4.28 (q, J = 7.2 Hz, 2H), 5.39 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 14.4, 17.2, 60.6, 111.5, 160.0, 162.5, 169.2.

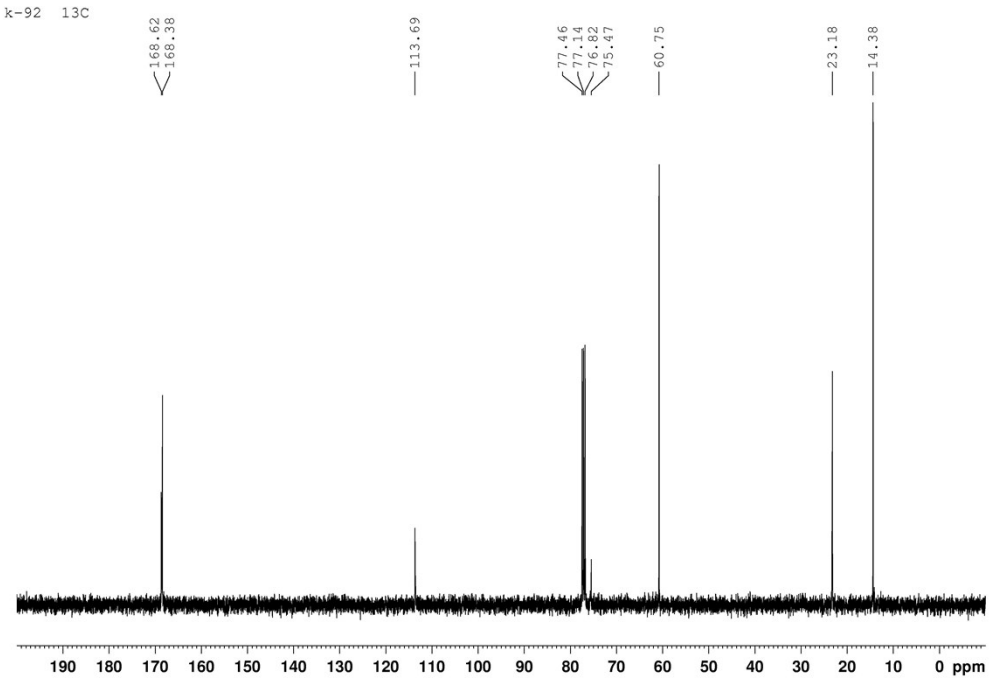
References

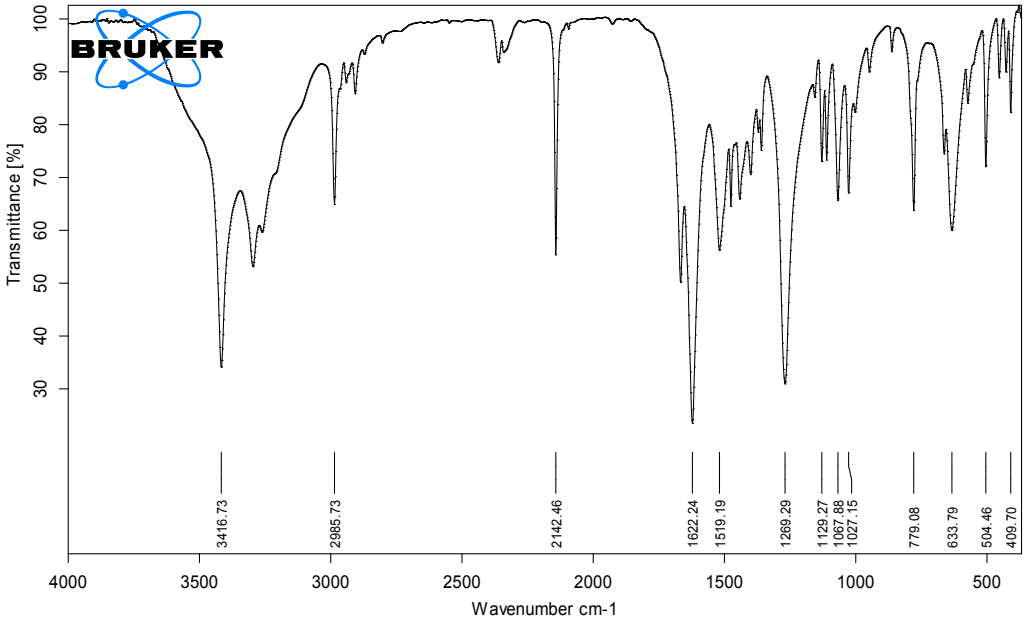
[1] Y. S. Park and K. Kim, *Tetrahedron Lett.,* 1999, **40**, 6439.
[2] J. M. Chen and X. Huang, *Synlett*., 2004, **3**, 552.
[3] Chandler, C. *Sci. Synth.*, 2008, **32**, 385.
[4] M. V. Stasevych, *Heteroat Chem*., 2005, **16**, 205.
[5] N. Azizi, *Comptes Rendus Chimie,* 2015*,* **18***,* 626.

3. Spectroscopy



(3a)




BRUKER
Transmittance [%]
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90
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70
60
50
40
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2985.73
2142.46
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1519.19
1269.29
1129.27
1067.88
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409.70
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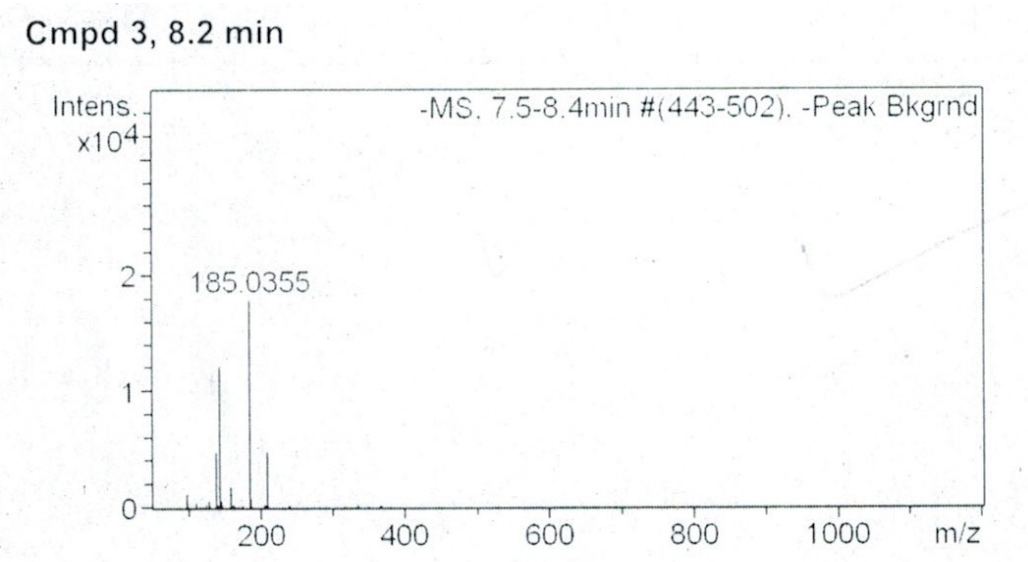
3000
2500
2000
1500
1000
500
Wavenumber cm-1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Intens.
x10^4
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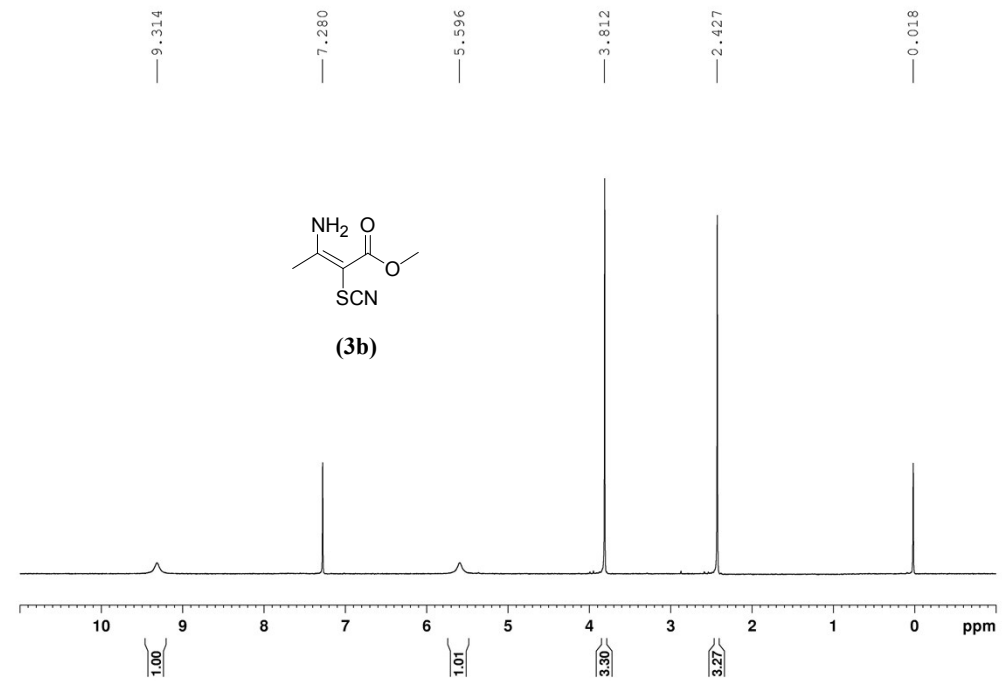
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5
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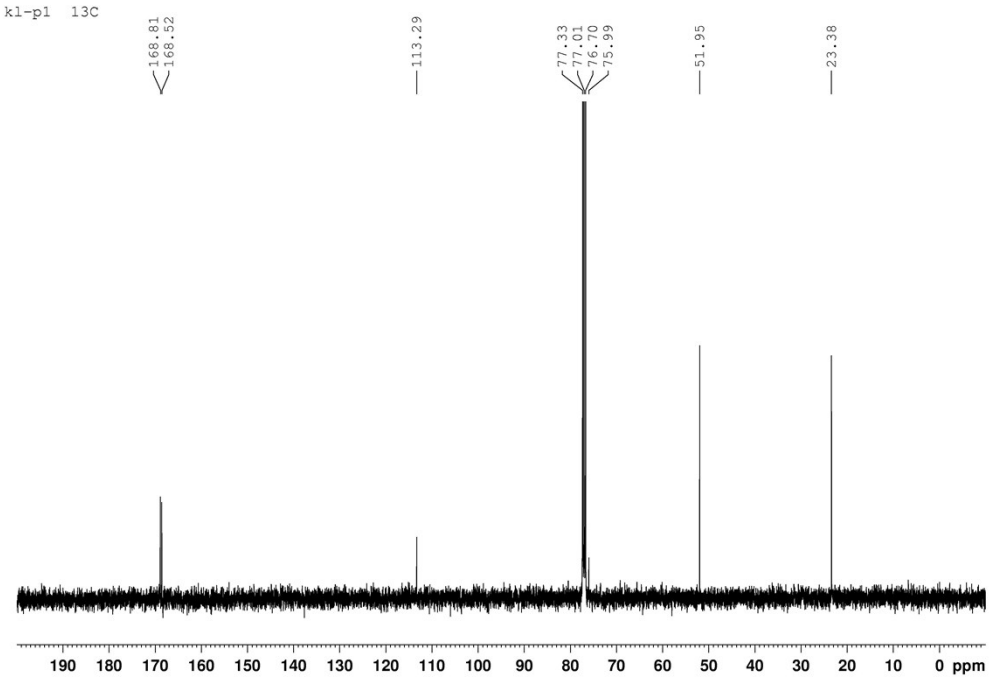
(3b)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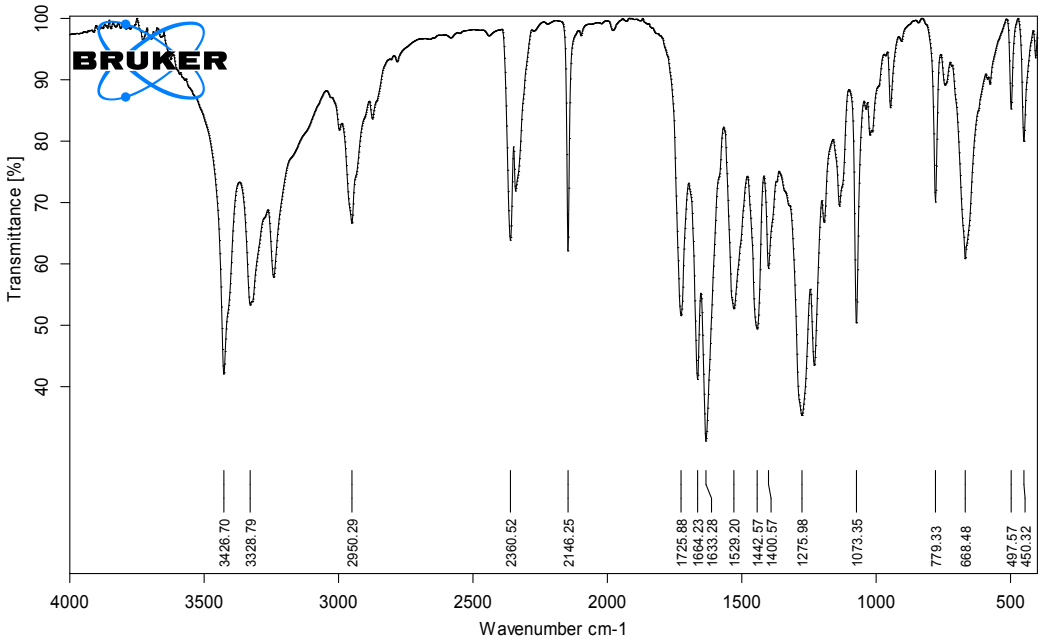
BRUKER
Transmittance [%]
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1633.28
1529.20
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1073.35
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3000
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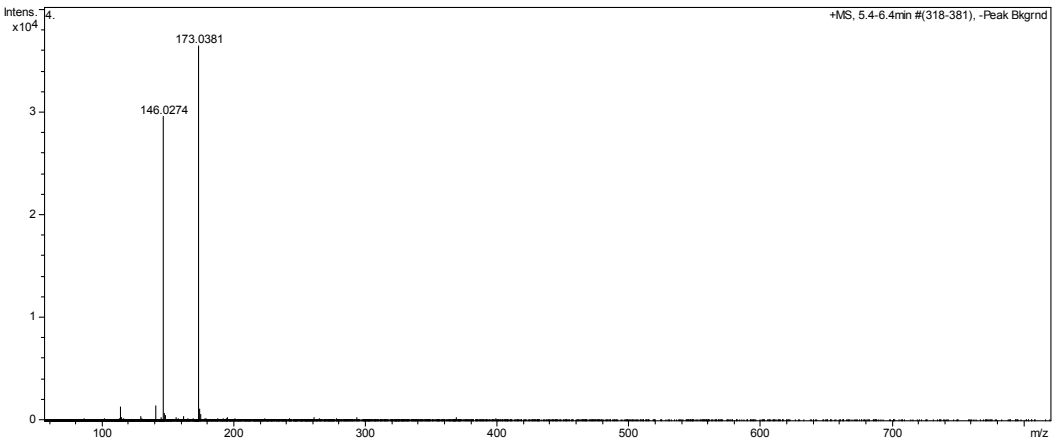
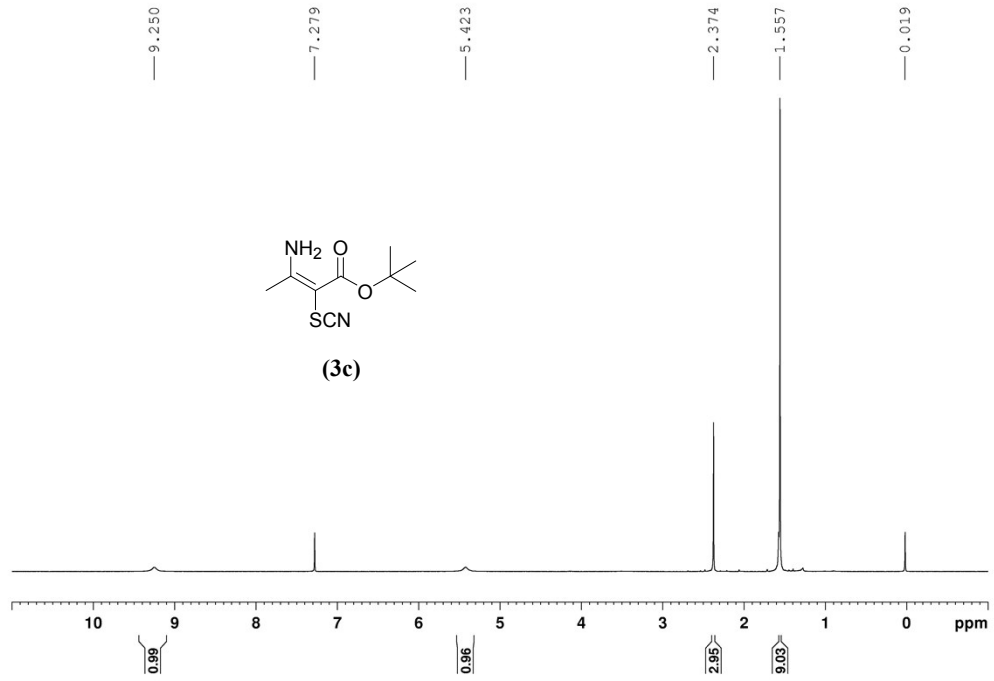
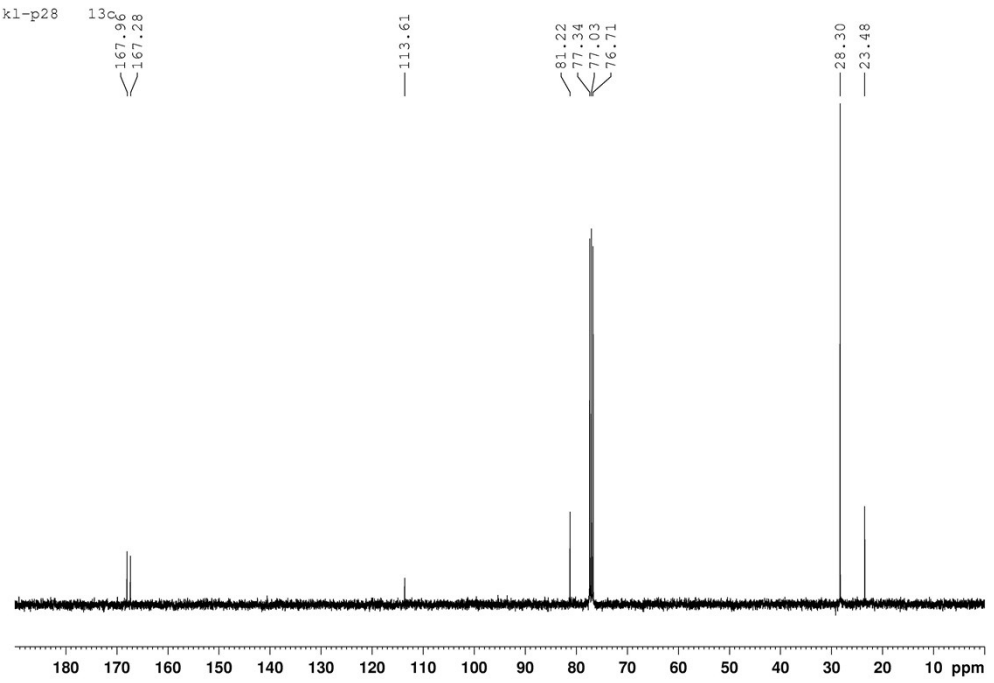
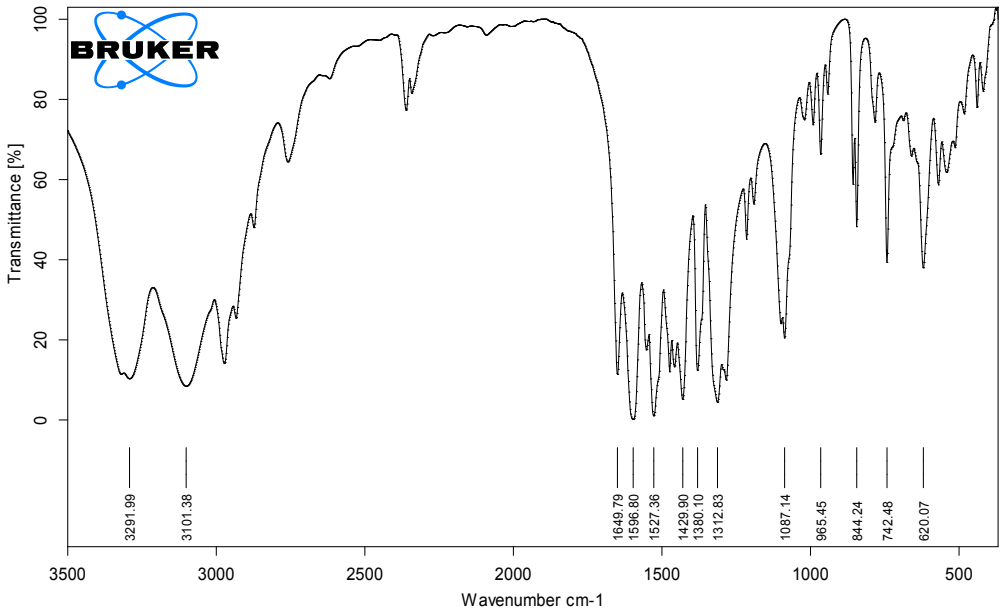
2000
1500
1000
500
Wavenumber cm-1

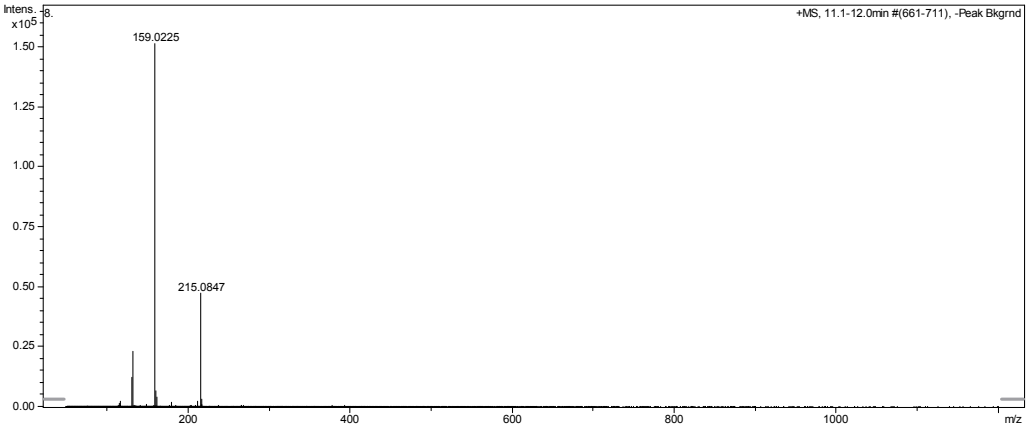

Intens.
x10^4
4.
+MS, 5.4-6.4min #(318-381), -Peak Bkgrnd
173.0381
146.0274
3
2
1
0
100
200
300
400
500
600
700
m/z

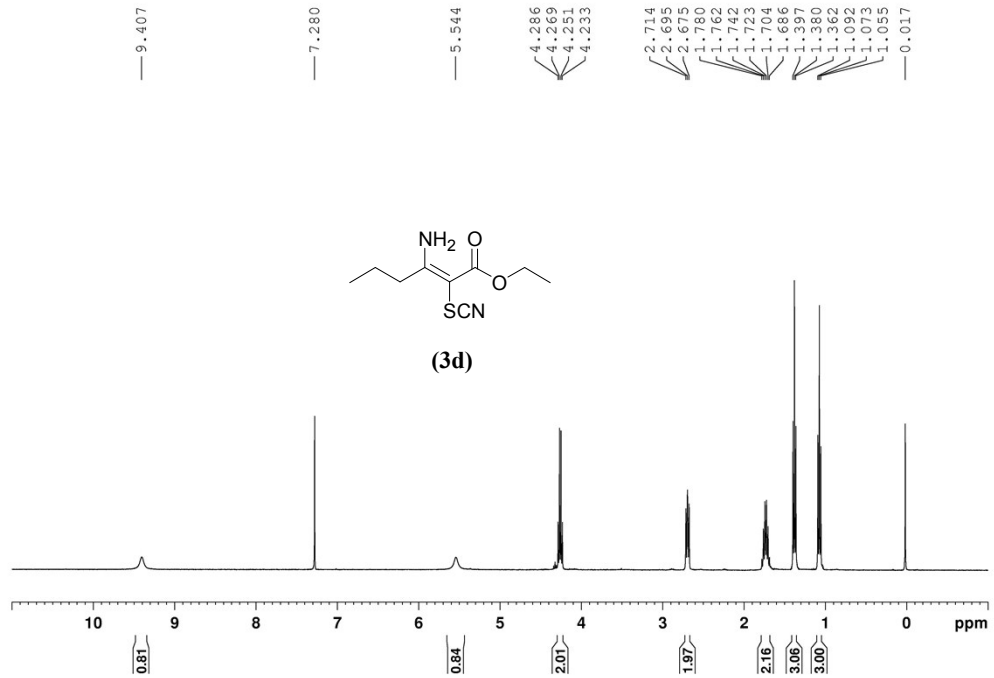

9.250
7.279
5.423
2.374
1.557
0.019
NH2
O
O
SCN
10
9
8
7
6
5
4
3
2
1
0
ppm
0.99
0.96
2.95
9.03

(3c)

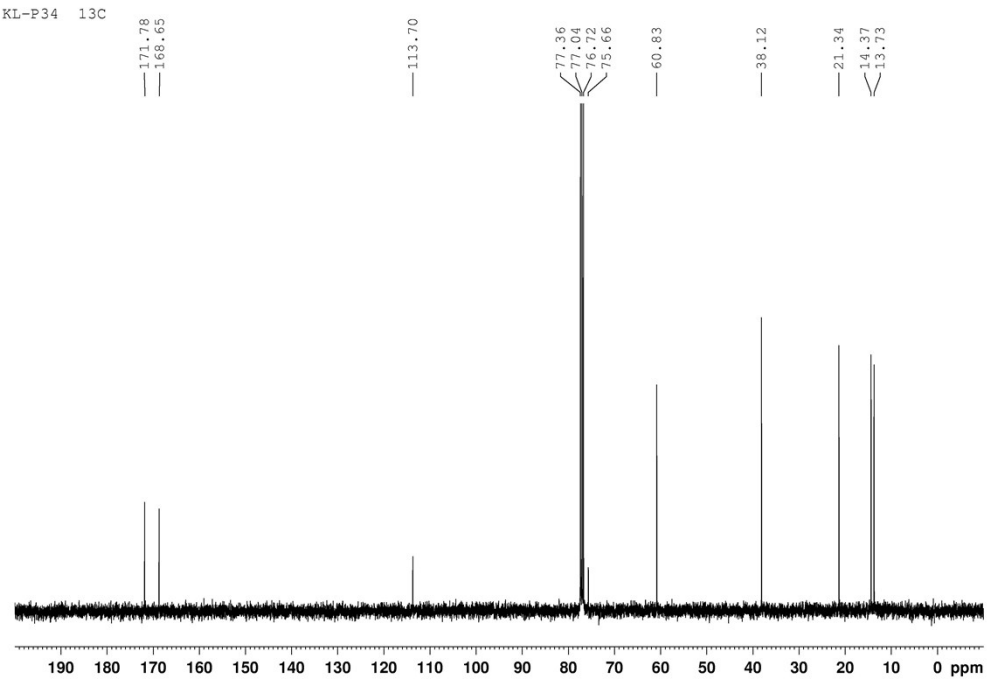

kl-p28
13c
167.96
167.28
113.61
81.22
77.34
77.03
76.71
28.30
23.48
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

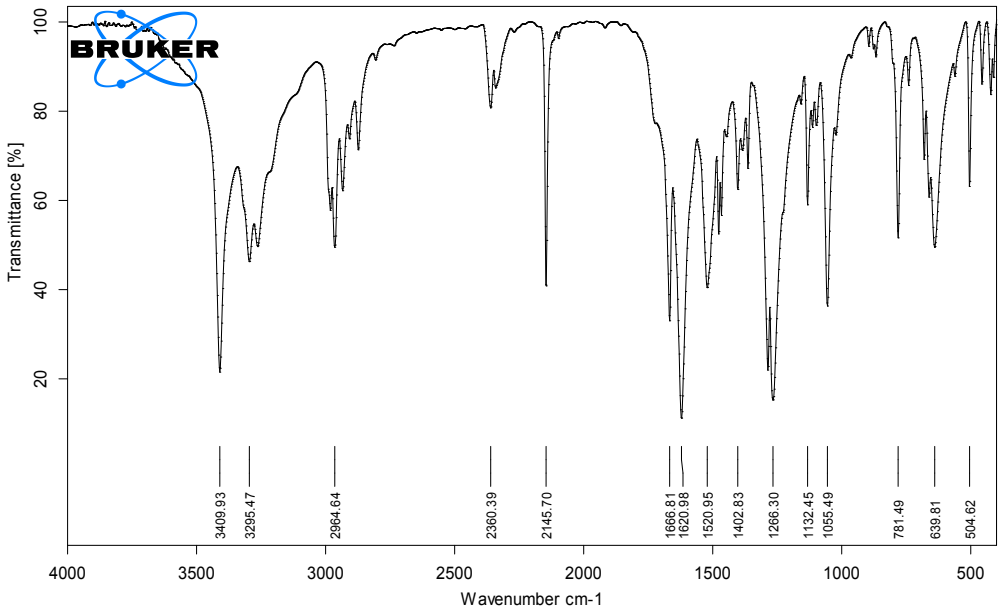

BRUKER
Transmittance [%]
100
80
60
40
20
0
3291.99
3101.38
1649.79
1596.80
1527.36
1429.90
1380.10
1312.83
1087.14
965.45
844.24
742.48
620.07
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

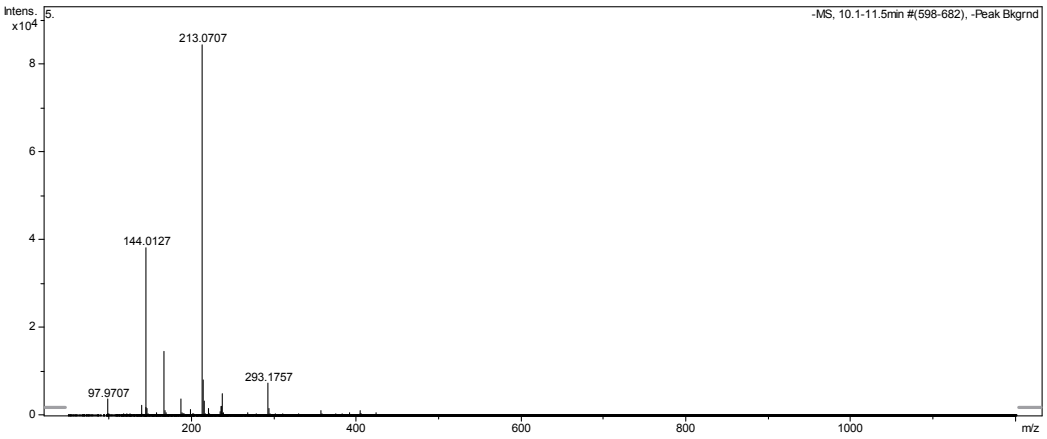

Intens.
x10^5
+MS, 11.1-12.0min #(661-711), -Peak Bkgrnd
159.0225
215.0847
1.50
1.25
1.00
0.75
0.50
0.25
0.00
200
400
600
800
1000
m/z

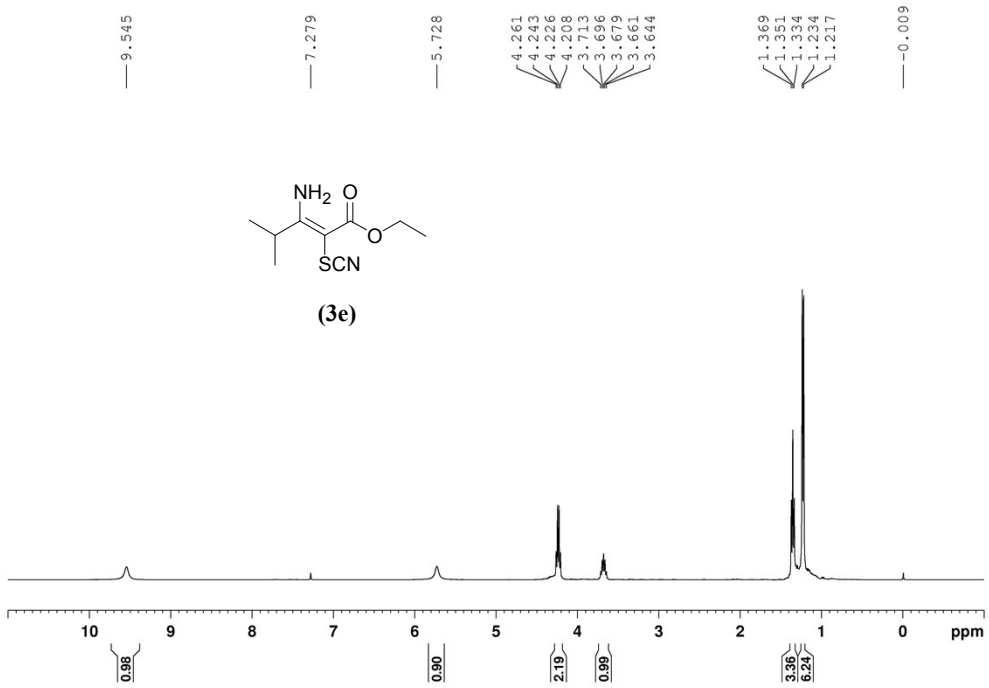

9.407
7.280
5.544
4.286
4.269
4.251
4.233
2.714
2.695
2.675
1.780
1.762
1.742
1.723
1.704
1.686
1.397
1.380
1.362
1.092
1.073
1.055
0.017
NH2
O
O
SCN
10
9
8
7
6
5
4
3
2
1
0
ppm
0.81
0.84
2.01
1.97
2.16
3.06
3.00

(3d)

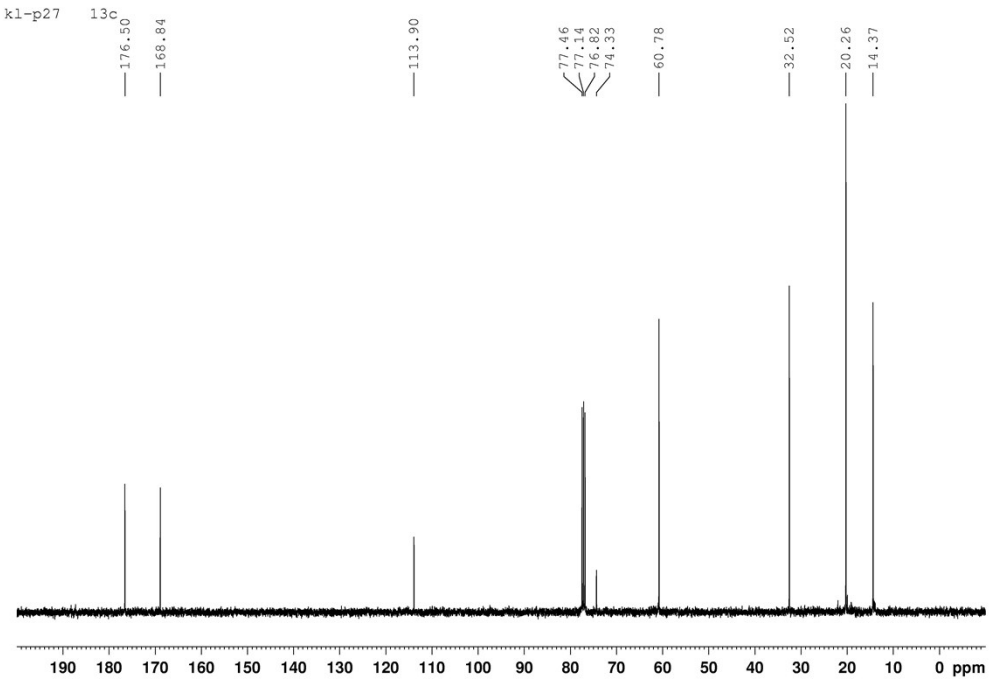

KL-P34 13C
171.78
168.65
113.70
77.36
77.04
76.72
75.66
60.83
38.12
21.34
14.37
13.73
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

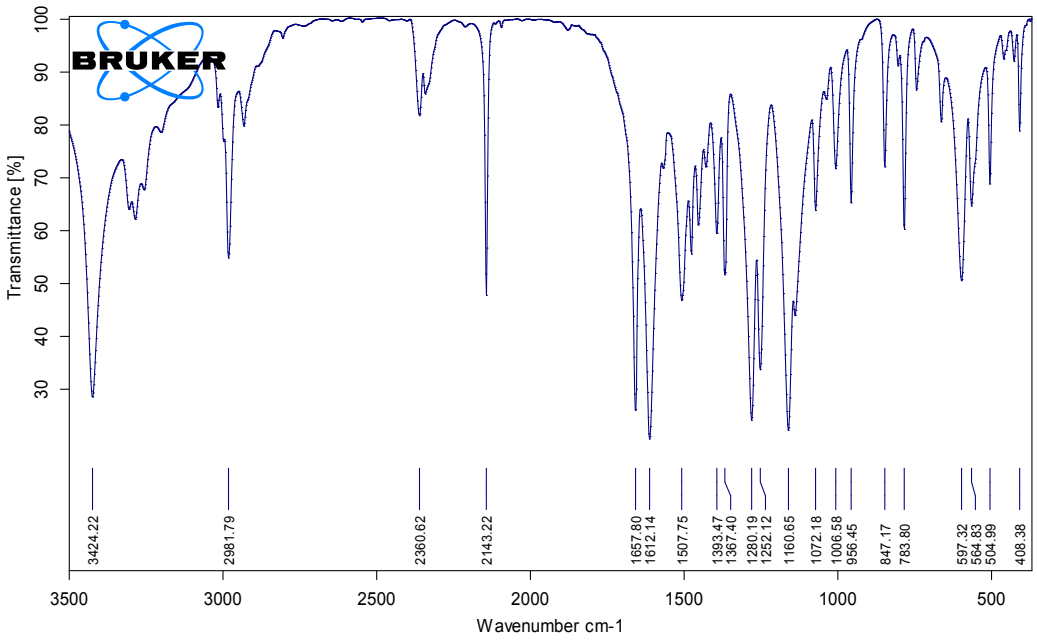

BRUKER
Transmittance [%]
100
80
60
40
20
3409.93
3295.47
2964.64
2360.39
2145.70
1666.81
1620.98
1520.95
1402.83
1266.30
1132.45
1055.49
781.49
639.81
504.62
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

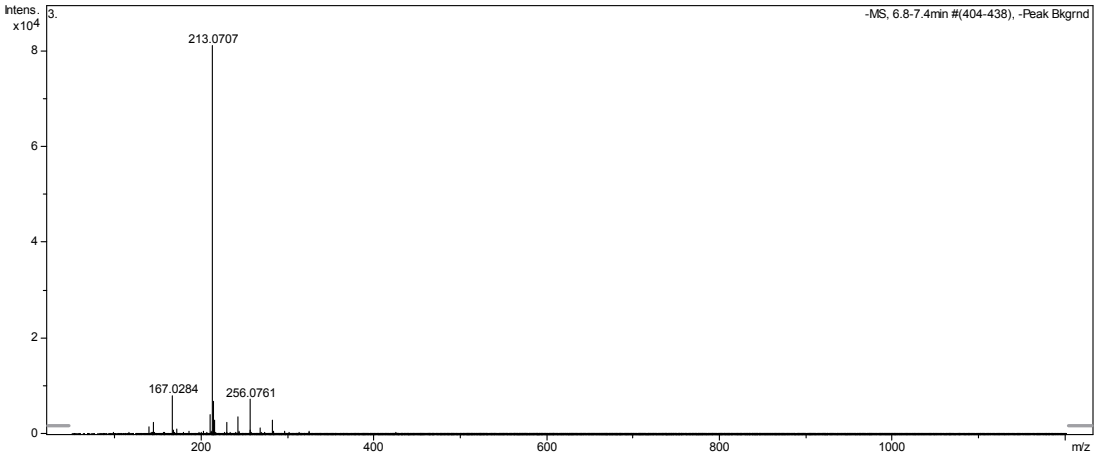

Intens.
x10^4
-MS, 10.1-11.5min #(598-682), -Peak Bkgrnd
213.0707
144.0127
293.1757
97.9707
8
6
4
2
0
200
400
600
800
1000
m/z

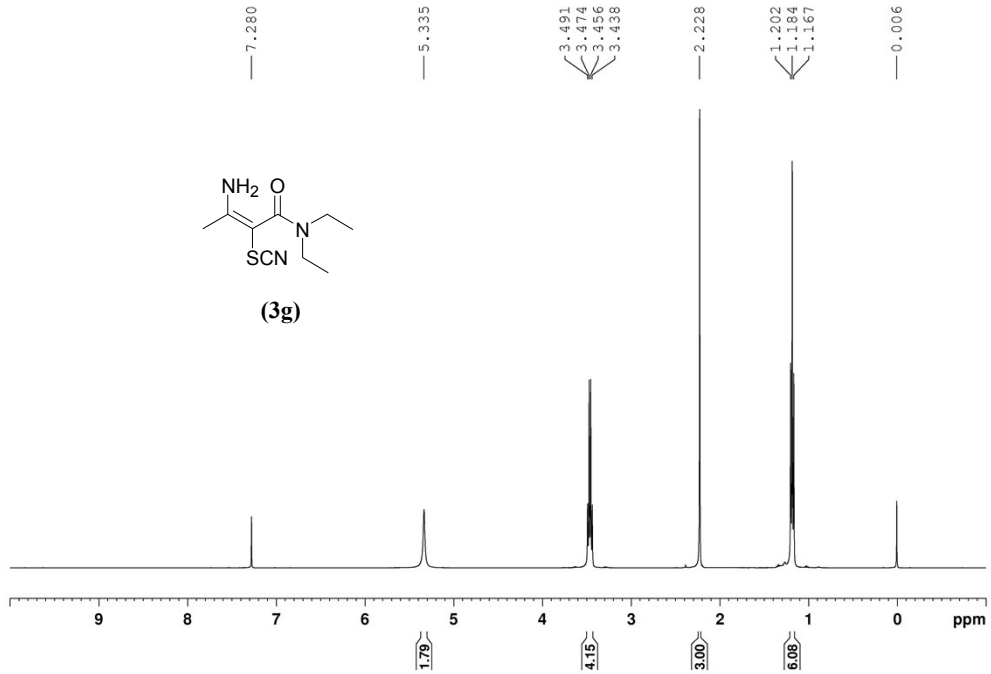

9.545
7.279
5.728
4.261
4.243
4.226
4.208
3.713
3.696
3.679
3.661
3.644
1.369
1.351
1.334
1.234
1.217
0.009
NH2
O
O
SCN
10
9
8
7
6
5
4
3
2
1
0
ppm
0.98
0.90
2.19
0.99
3.36
6.24

(3e)

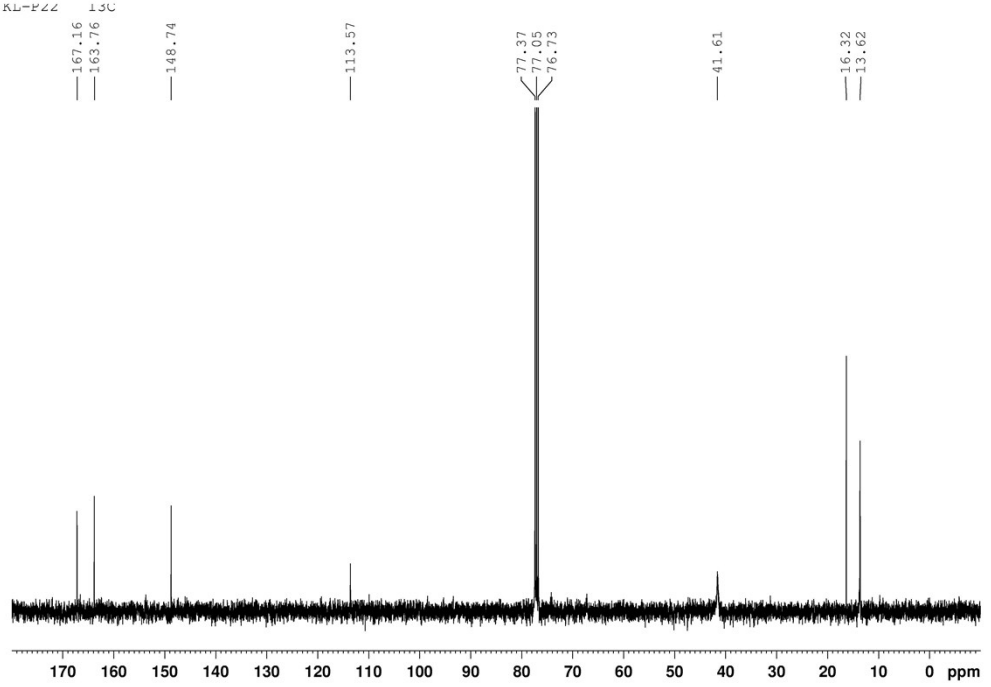

kl-p27 13c
176.50
168.84
113.90
77.46
77.14
76.82
74.33
60.78
32.52
20.26
14.37
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

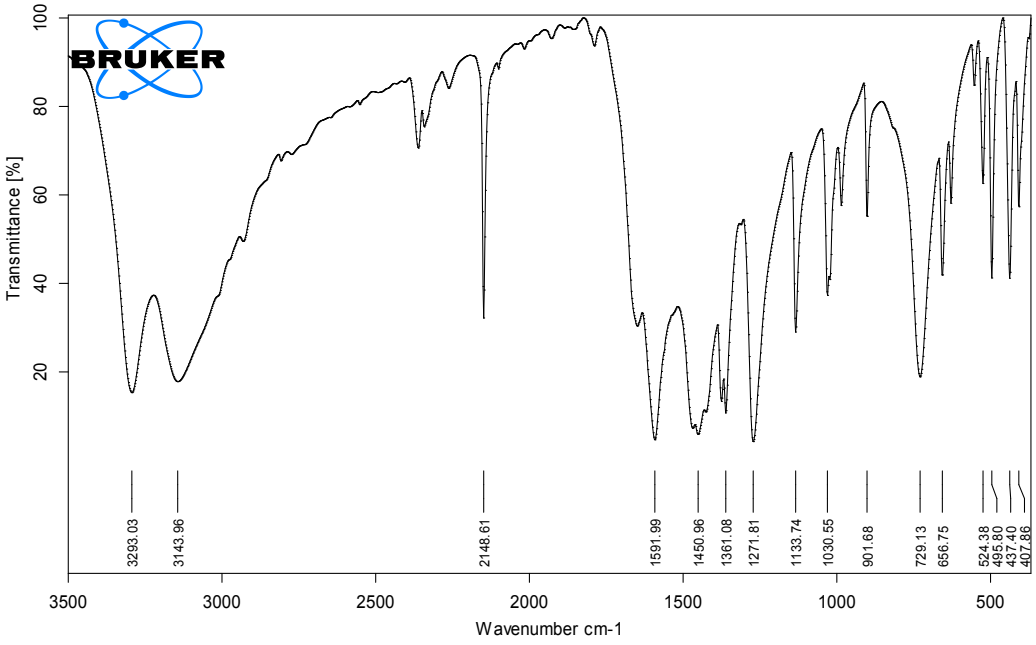

BRUKER
Transmittance [%]
100
90
80
70
60
50
40
30
3424.22
2981.79
2360.62
2143.22
1657.80
1612.14
1507.75
1393.47
1367.40
1280.19
1252.12
1160.65
1072.18
1006.58
956.45
847.17
783.80
597.32
564.83
504.99
408.38
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

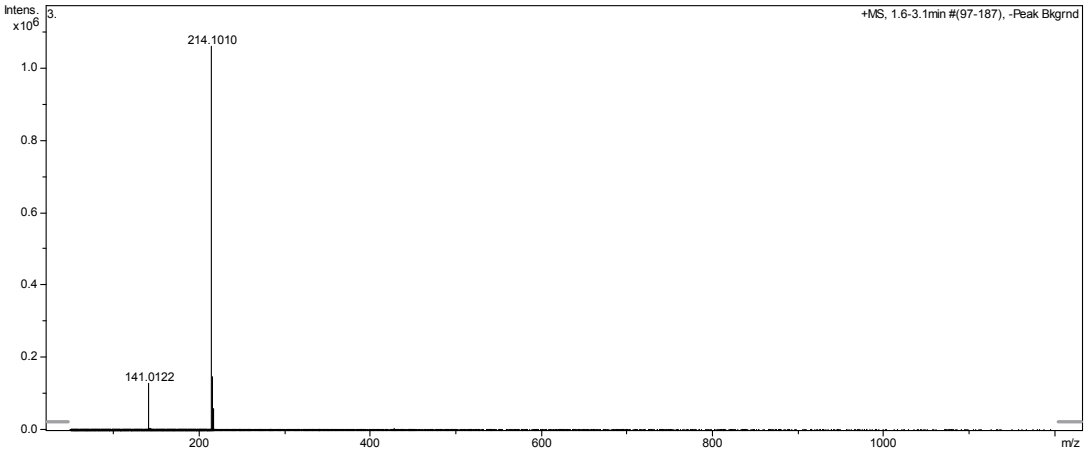

Intens.
x10^4
3.
-MS, 6.8-7.4min #(404-438), -Peak Bkgrnd
213.0707
167.0284
256.0761
8
6
4
2
0
200
400
600
800
1000
m/z

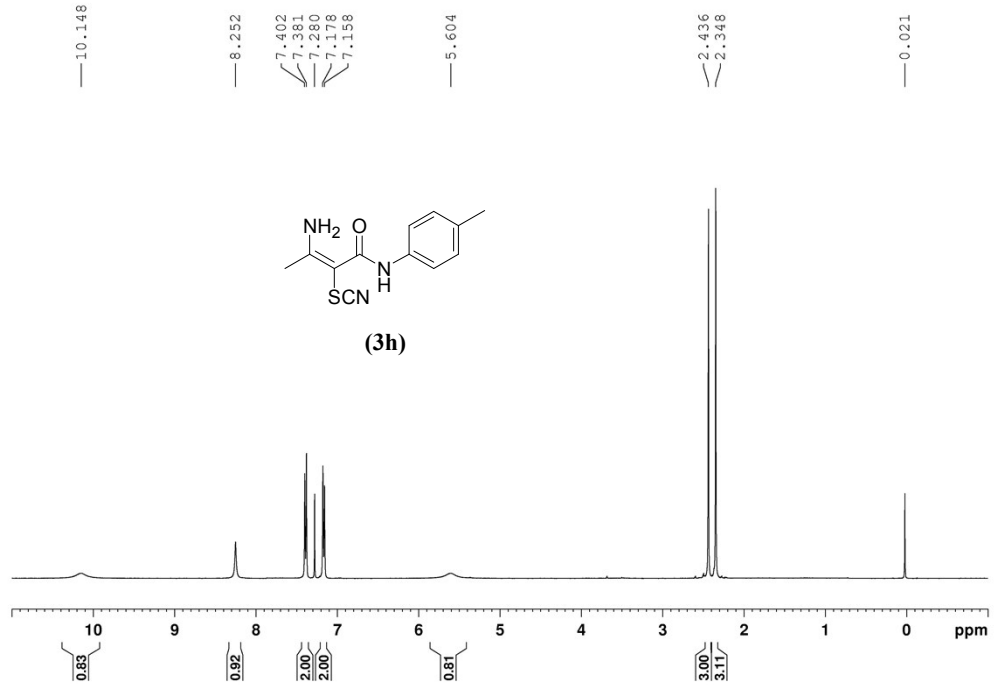

7.280
5.335
3.491
3.474
3.456
3.438
2.228
1.202
1.184
1.167
0.006
NH2
O
N
SCN
9
8
7
6
5
4
3
2
1
0
ppm
1.79
4.15
3.00
6.08

(3g)

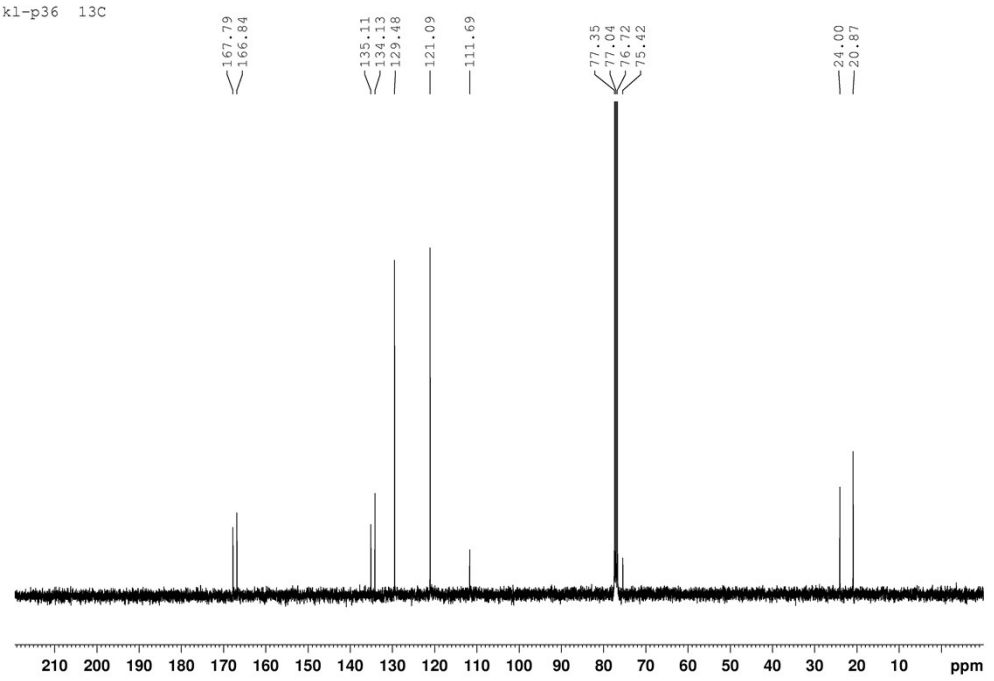

167.16
163.76
148.74
113.57
77.37
77.05
76.73
41.61
16.32
13.62
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

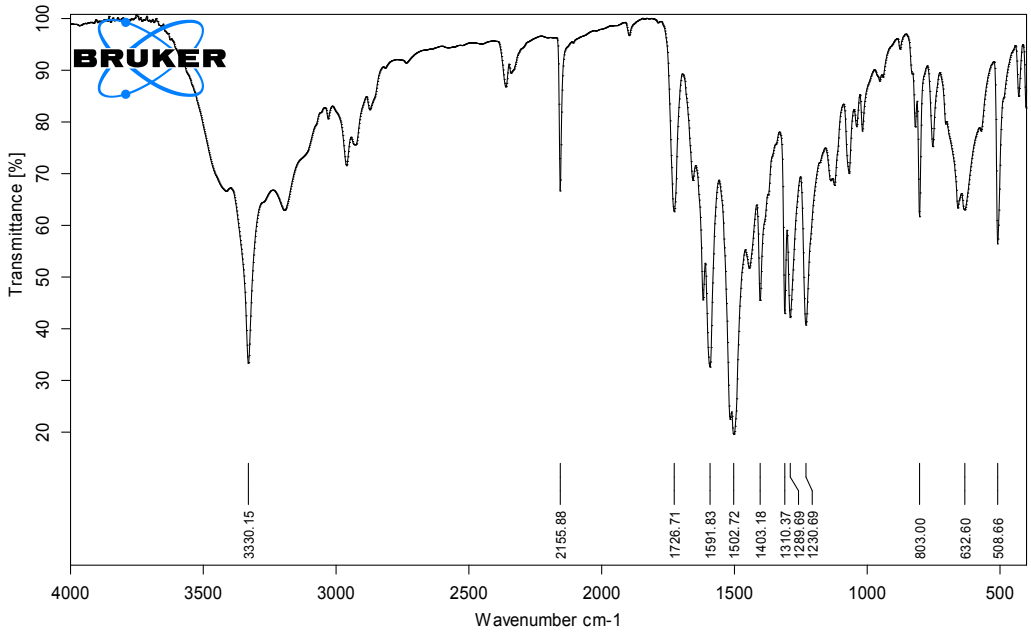

BRUKER
Transmittance [%]
100
80
60
40
20
3293.03
3143.96
2148.61
1591.99
1450.96
1361.08
1271.81
1133.74
1030.55
901.68
729.13
656.75
524.38
495.80
437.40
407.86
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

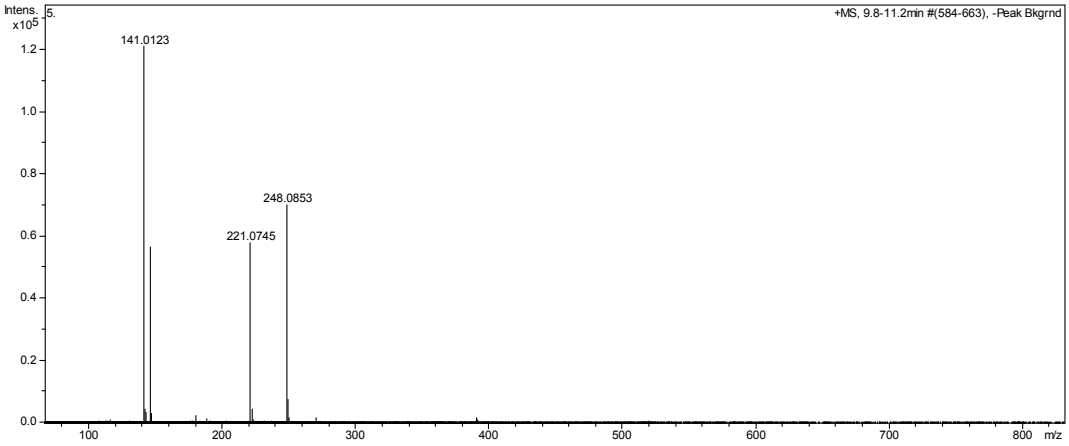

Intens.
x10^6
3.
+MS, 1.6-3.1min #(97-187), -Peak Bkgrnd
214.1010
141.0122
1.0
0.8
0.6
0.4
0.2
0.0
200
400
600
800
1000
m/z

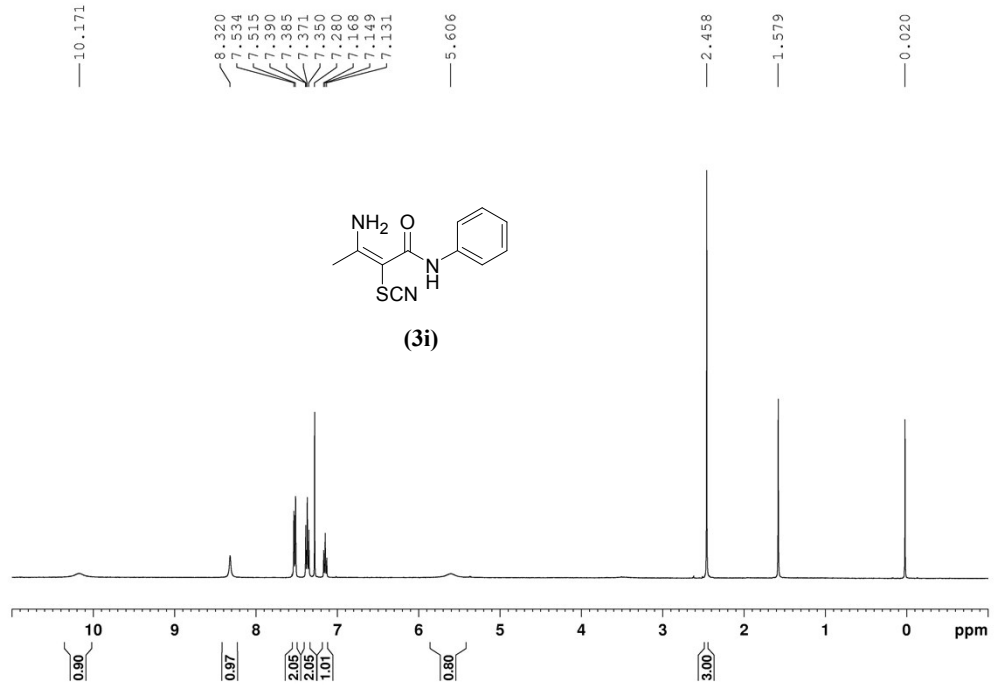

10.148
8.252
7.402
7.381
7.280
7.178
7.158
5.604
2.436
2.348
0.021
NH2
O
N
H
SCN
10
9
8
7
6
5
4
3
2
1
0
ppm
0.83
0.92
2.00
2.00
0.81
3.00
3.11

(3h)

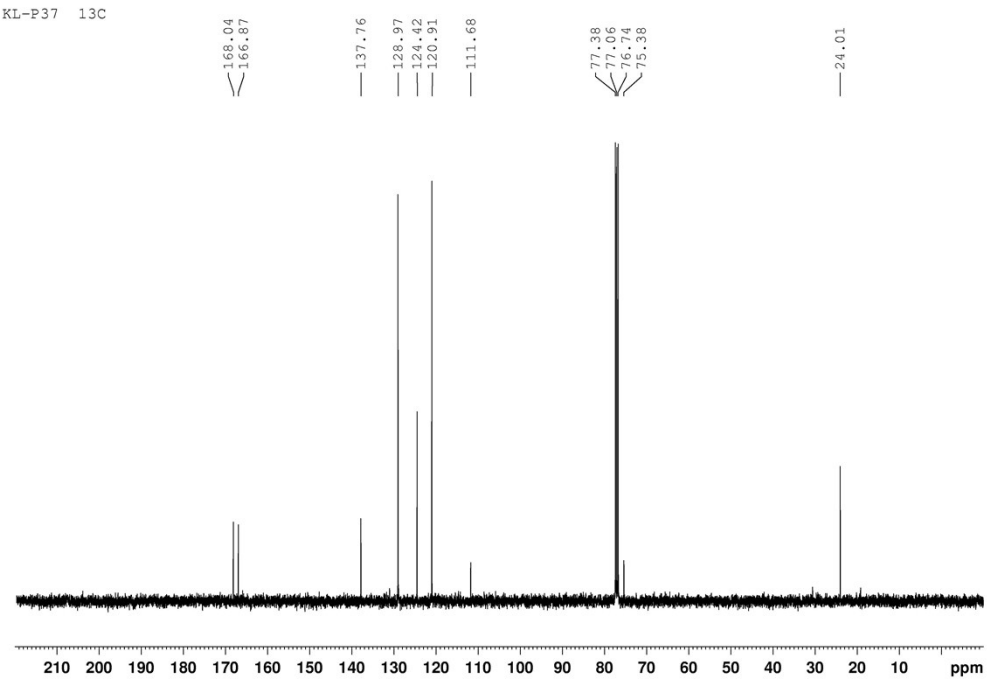

kl-p36 13C
167.79
166.84
135.11
134.13
129.48
121.09
111.69
77.35
77.04
76.72
75.42
24.00
20.87
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

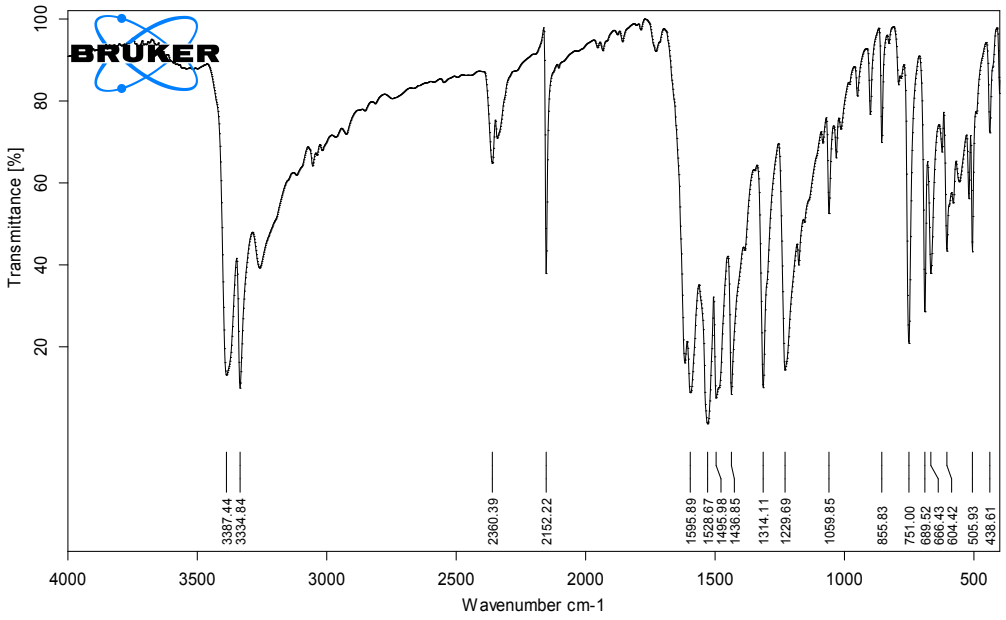

BRUKER
Transmittance [%]
100
90
80
70
60
50
40
30
20
3330.15
2155.88
1726.71
1591.83
1502.72
1403.18
1310.37
1289.69
1230.69
803.00
632.60
508.66
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

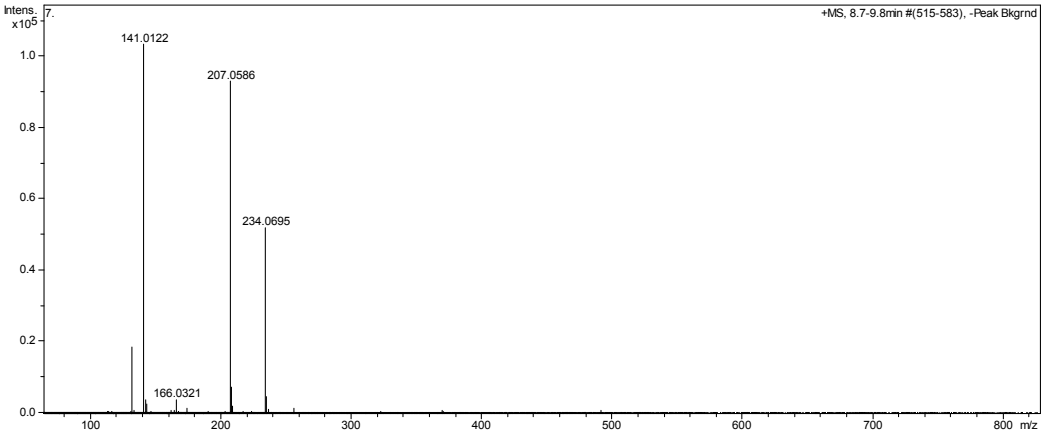

Intens.
x10^5
+MS, 9.8-11.2min #(584-663), -Peak Bkgrnd
141.0123
248.0853
221.0745
1.2
1.0
0.8
0.6
0.4
0.2
0.0
100
200
300
400
500
600
700
800
m/z

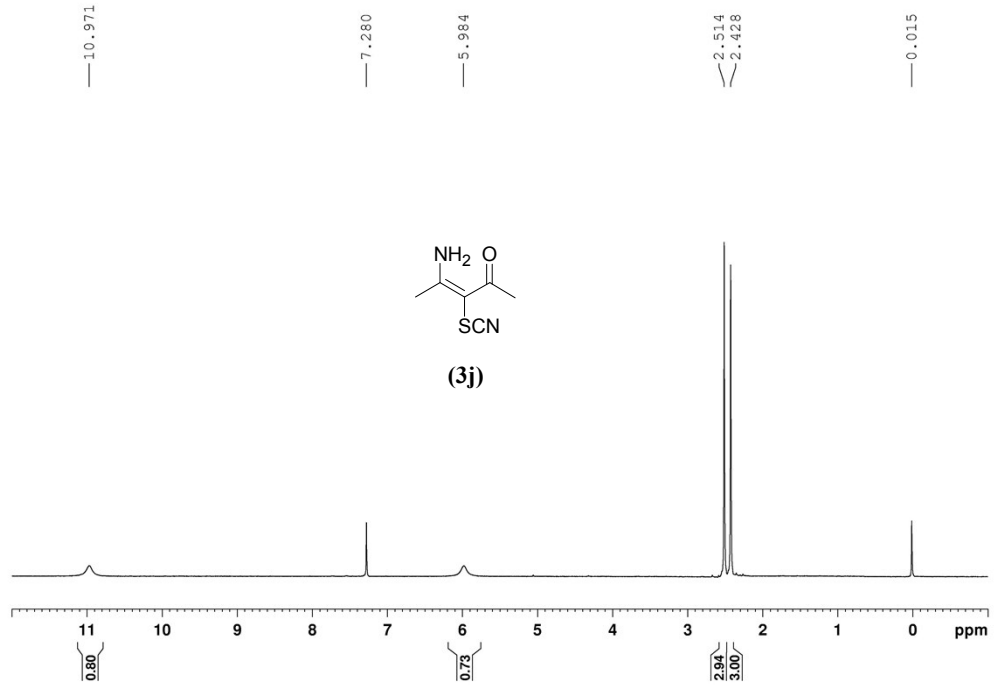

10.171
8.320
7.534
7.515
7.390
7.385
7.371
7.350
7.280
7.168
7.149
7.131
5.606
2.458
1.579
0.020
NH2
O
N
H
SCN
10
9
8
7
6
5
4
3
2
1
0
ppm
0.90
0.97
2.05
2.05
1.01
0.80
3.00

(3i)

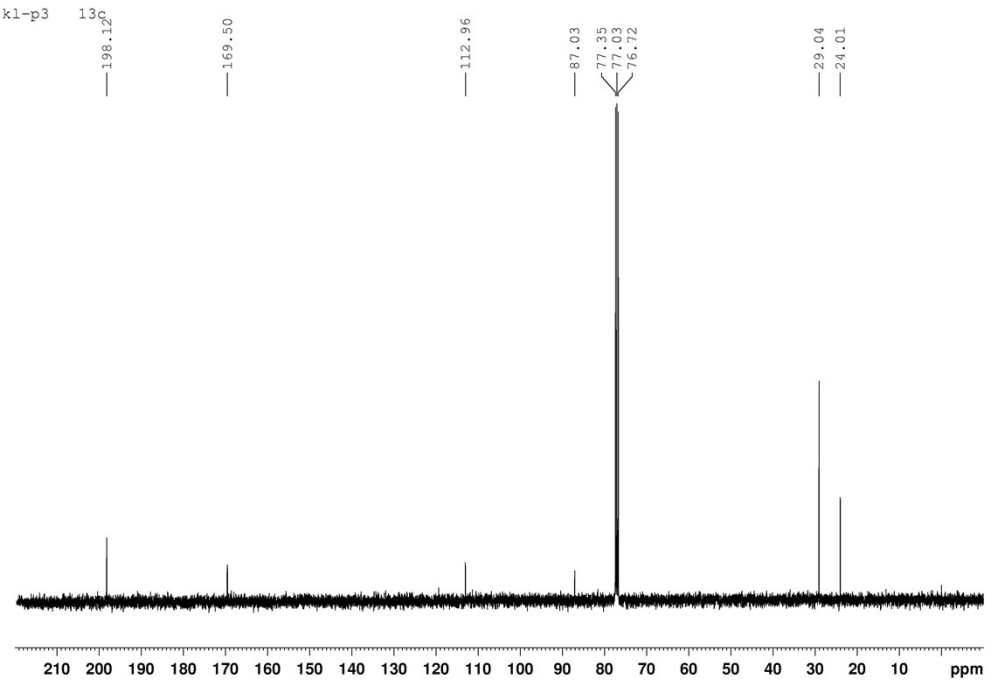

KL-P37 13C
168.04
166.87
137.76
128.97
124.42
120.91
111.68
77.38
77.06
76.74
75.38
24.01
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

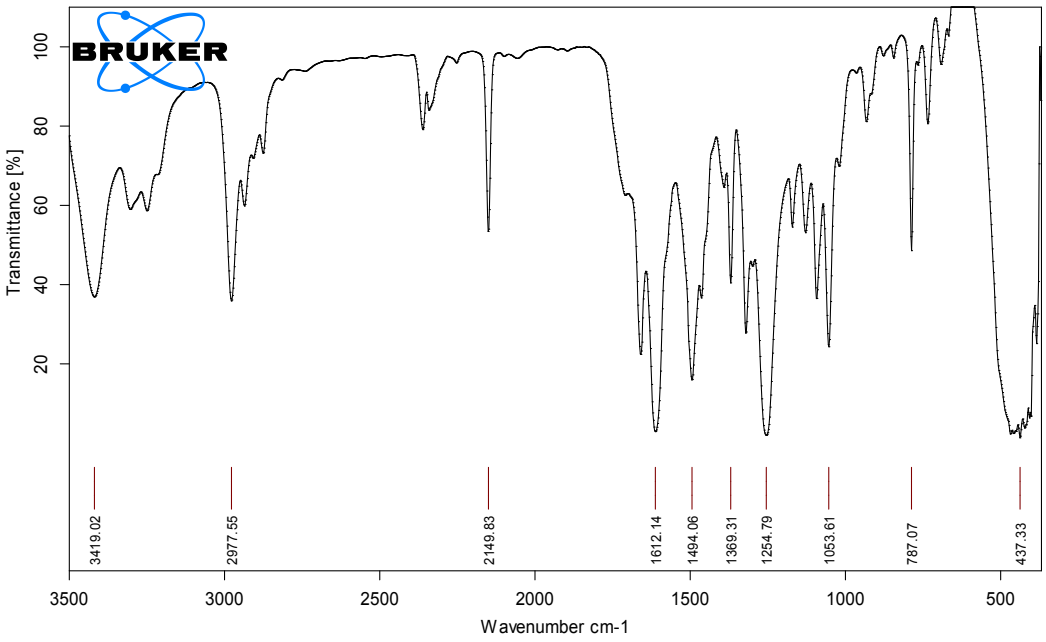

Transmittance [%]
100
80
60
40
20
3387.44
3334.84
2360.39
2152.22
1595.89
1528.67
1495.98
1436.85
1314.11
1229.69
1059.85
855.83
751.00
689.52
666.43
604.42
505.93
438.61
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

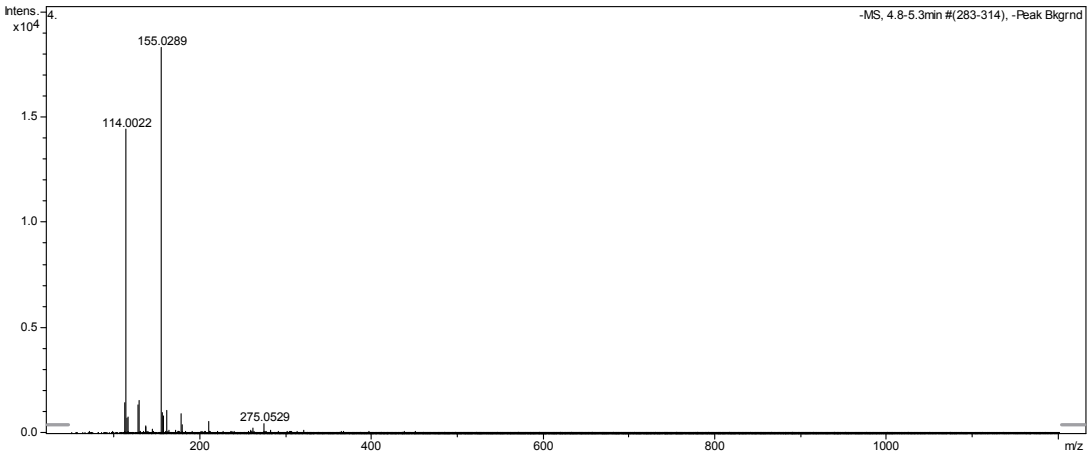

Intens.
x10^5
+MS, 8.7-9.8min #(515-583), -Peak Bkgrnd
141.0122
207.0586
234.0695
166.0321
1.0
0.8
0.6
0.4
0.2
0.0
100
200
300
400
500
600
700
800
m/z

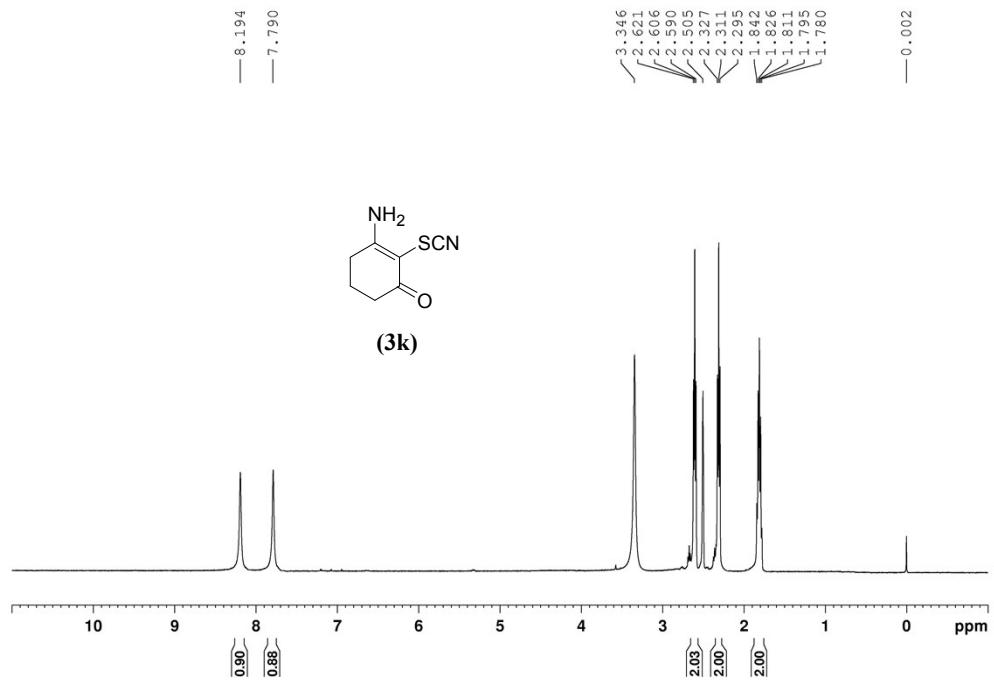

10.971
7.280
5.984
2.514
2.428
0.015
NH2
O
SCN
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.80
0.73
2.94
3.00

(3j)

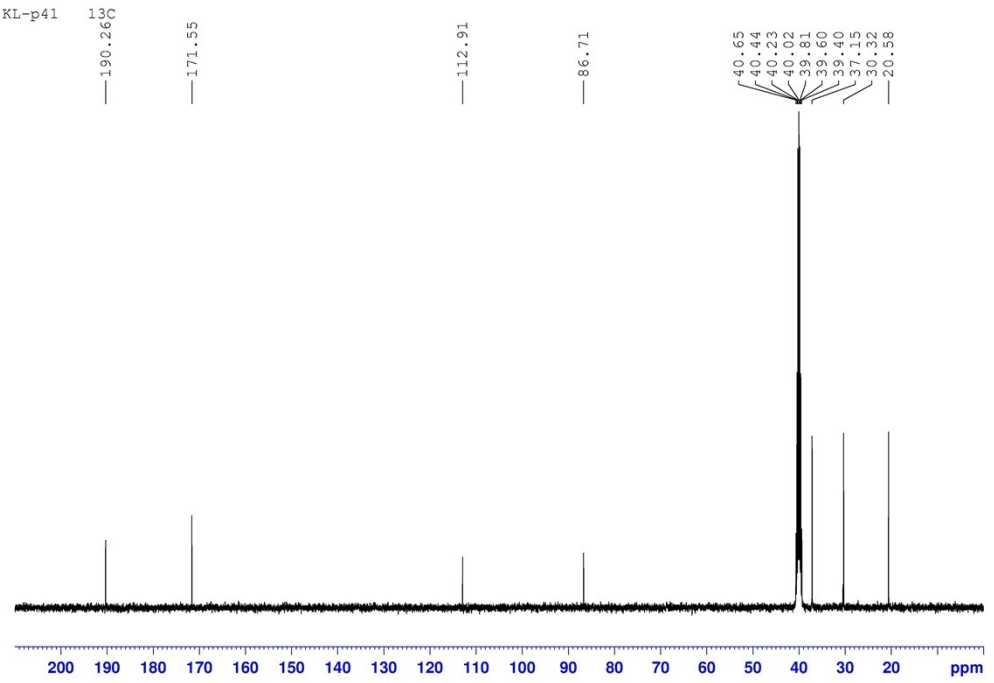

k1-p3 13c
198.12
169.50
112.96
87.03
77.35
77.03
76.72
29.04
24.01
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

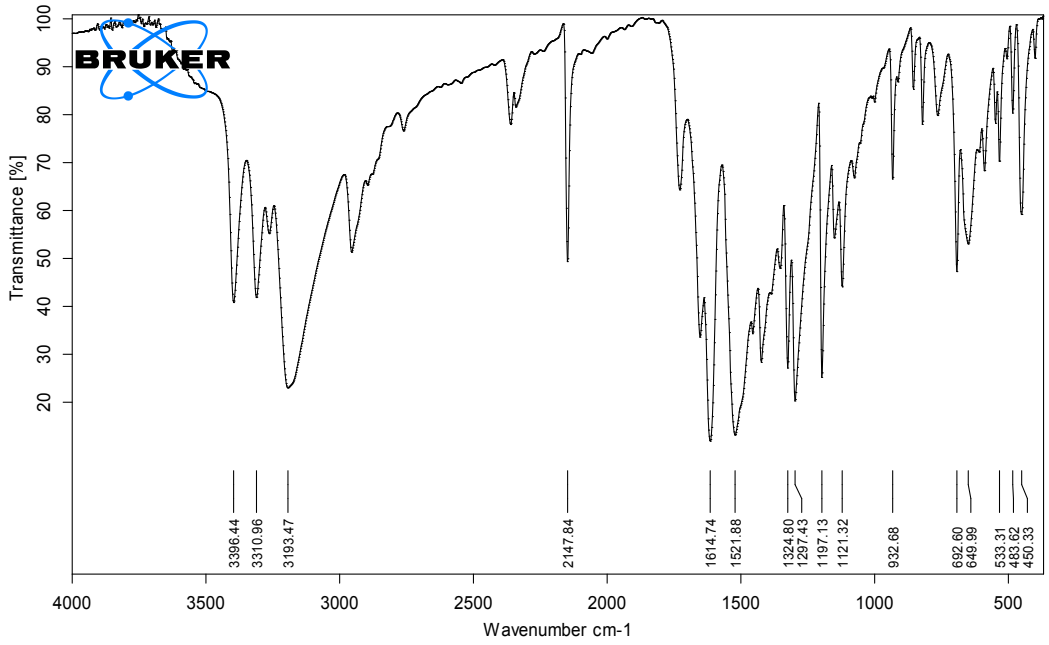

BRUKER
Transmittance [%]
100
80
60
40
20
3419.02
2977.55
2149.83
1612.14
1494.06
1369.31
1254.79
1053.61
787.07
437.33
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

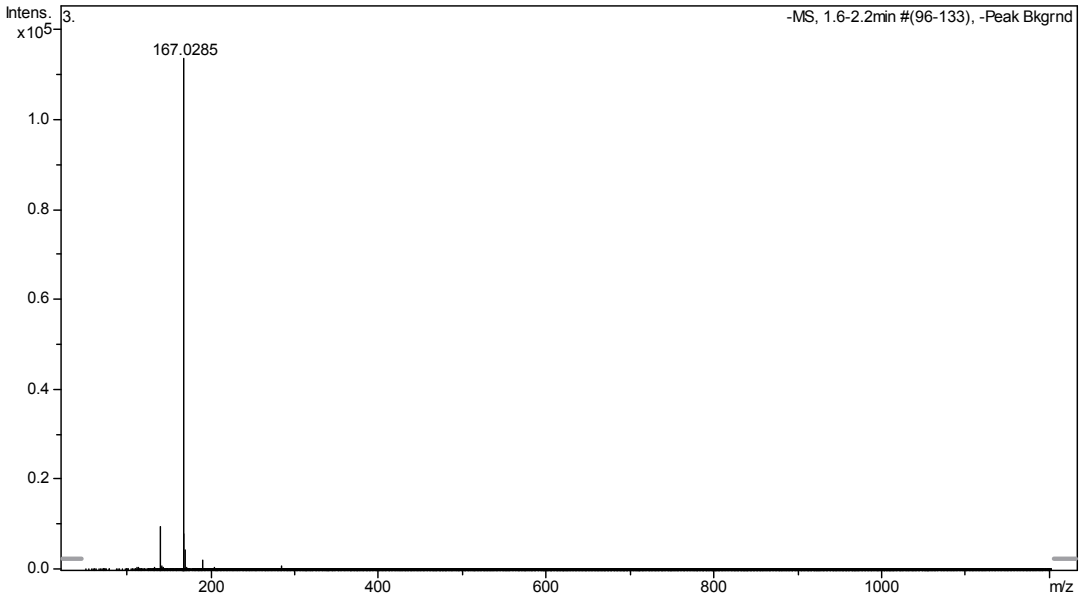

Intens.
x10^4
-MS, 4.8-5.3min #(283-314), -Peak Bkgrnd
155.0289
114.0022
275.0529
1.5
1.0
0.5
0.0
200
400
600
800
1000
m/z

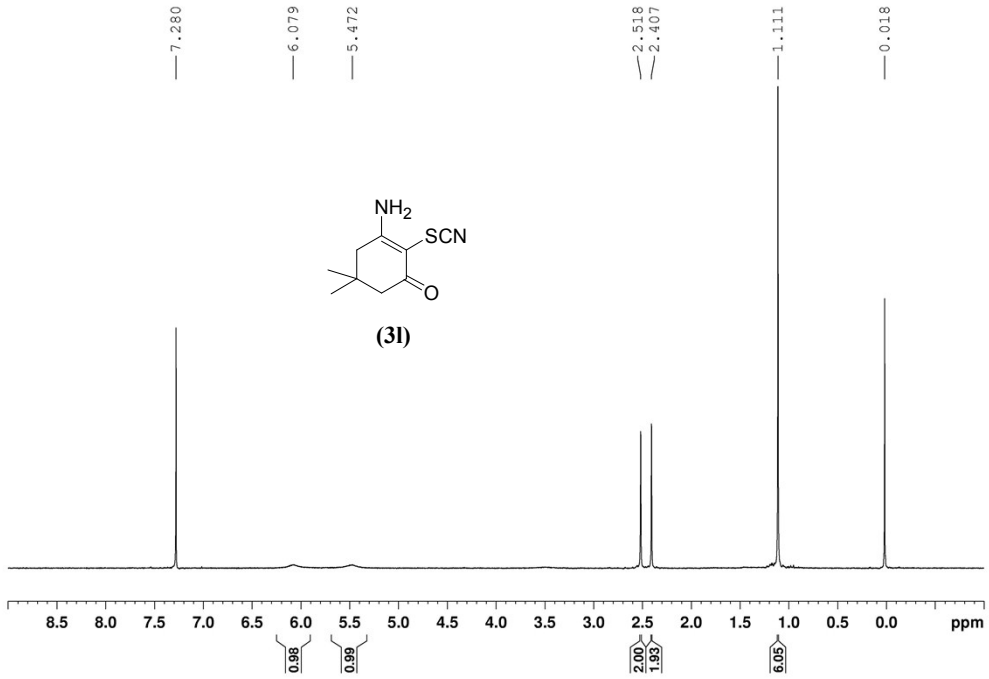

8.194
7.790
3.346
2.621
2.606
2.590
2.505
2.327
2.311
2.295
1.842
1.826
1.811
1.795
1.780
0.002
NH2
SCN
O
10
9
8
7
6
5
4
3
2
1
0
ppm
0.90
0.88
2.03
2.00
2.00

(3k)

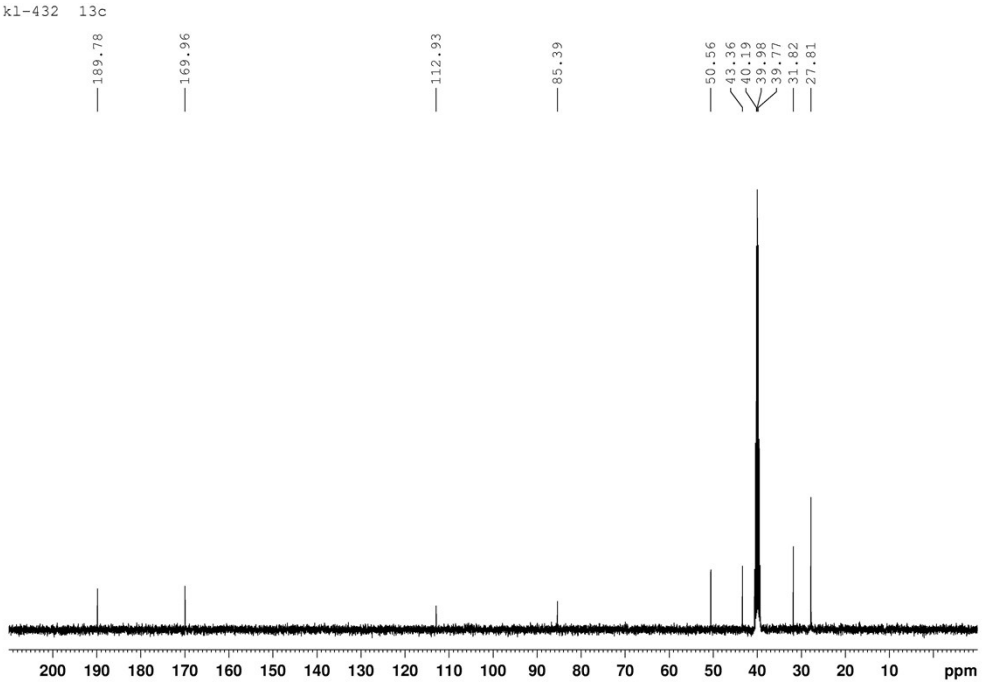

KL-p41 13C
190.26
171.55
112.91
86.71
40.65
40.44
40.23
40.02
39.81
39.60
39.40
37.15
30.32
20.58
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

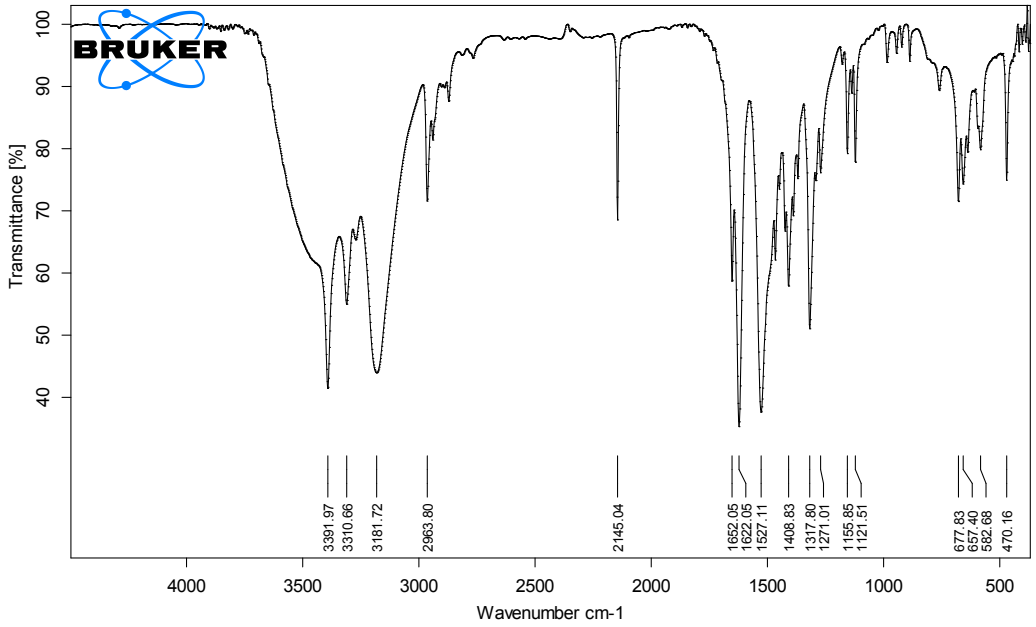

BRUKER
Transmittance [%]
100
90
80
70
60
50
40
30
20
3396.44
3310.96
3193.47
2147.84
1614.74
1521.88
1324.80
1297.43
1197.13
1121.32
932.68
692.60
649.99
533.31
483.62
450.33
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

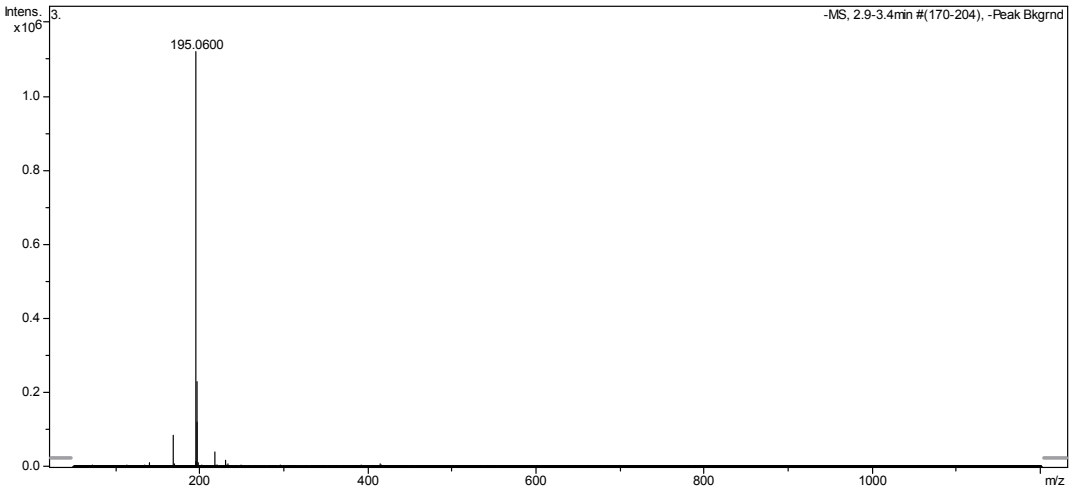

Intens.
x10^5
3.
-MS, 1.6-2.2min #(96-133), -Peak Bkgrnd
167.0285
1.0
0.8
0.6
0.4
0.2
0.0
200
400
600
800
1000
m/z

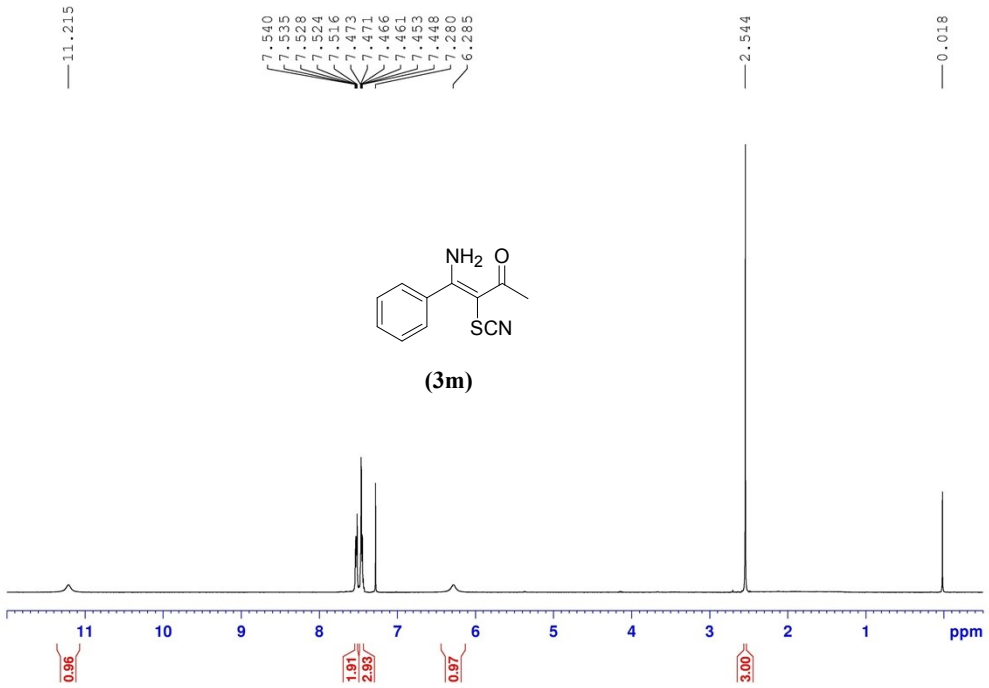

7.280
6.079
5.472
2.518
2.407
1.111
0.018
NH2
SCN
O
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.98
0.99
2.00
1.93
6.05

(3l)

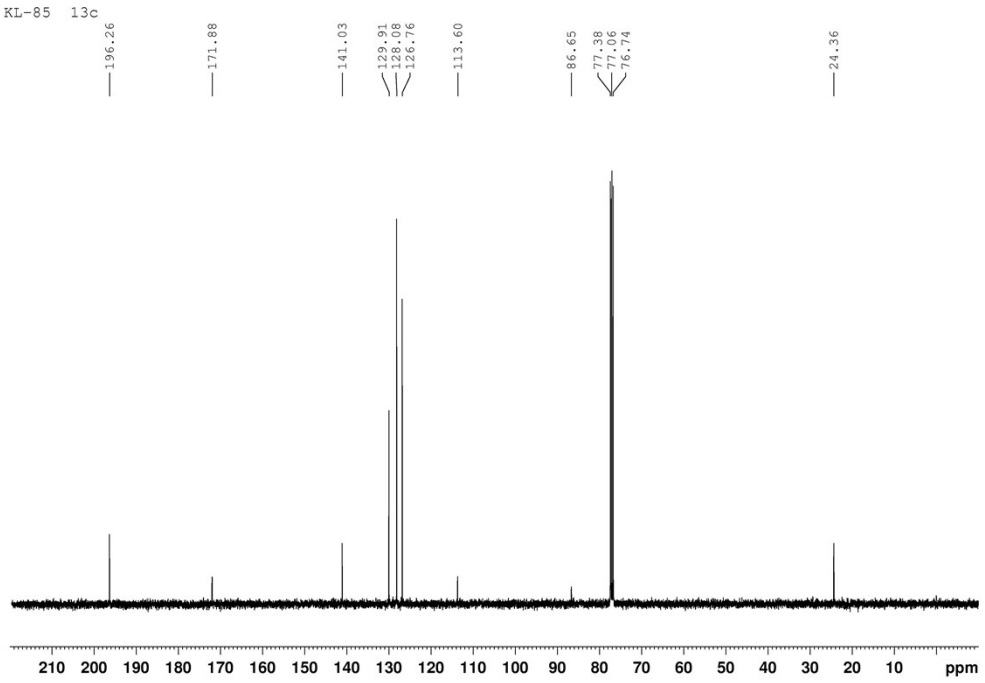

kl-432 13c
189.78
169.96
112.93
85.39
50.56
43.36
40.19
39.98
39.77
31.82
27.81
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

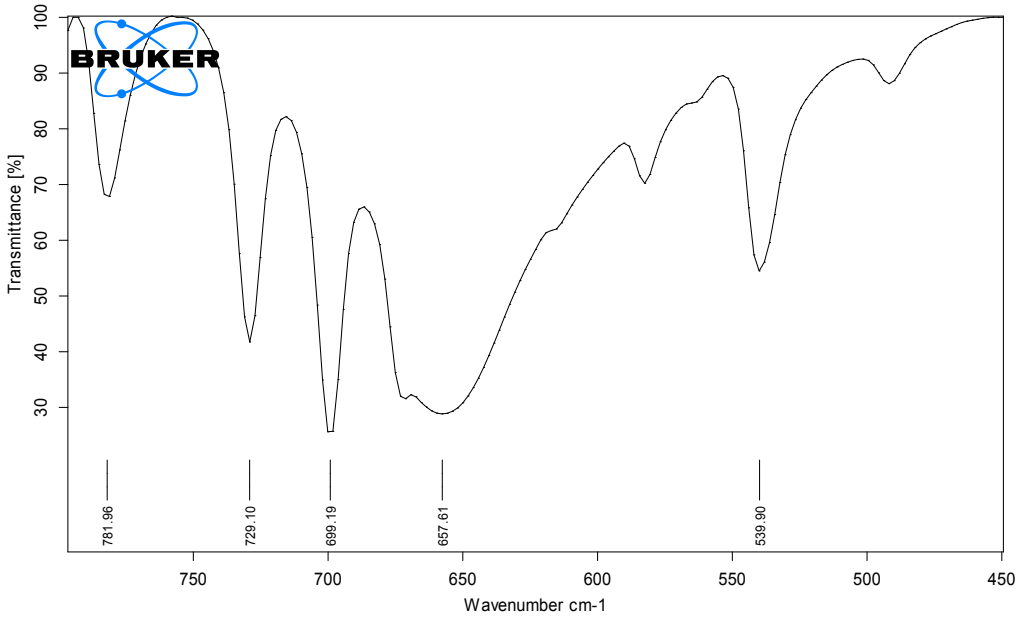

BRUKER
Transmittance [%]
100
90
80
70
60
50
40
3391.97
3310.66
3181.72
2963.80
2145.04
1652.05
1622.05
1527.11
1408.83
1317.80
1271.01
1155.85
1121.51
677.83
657.40
582.68
470.16
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

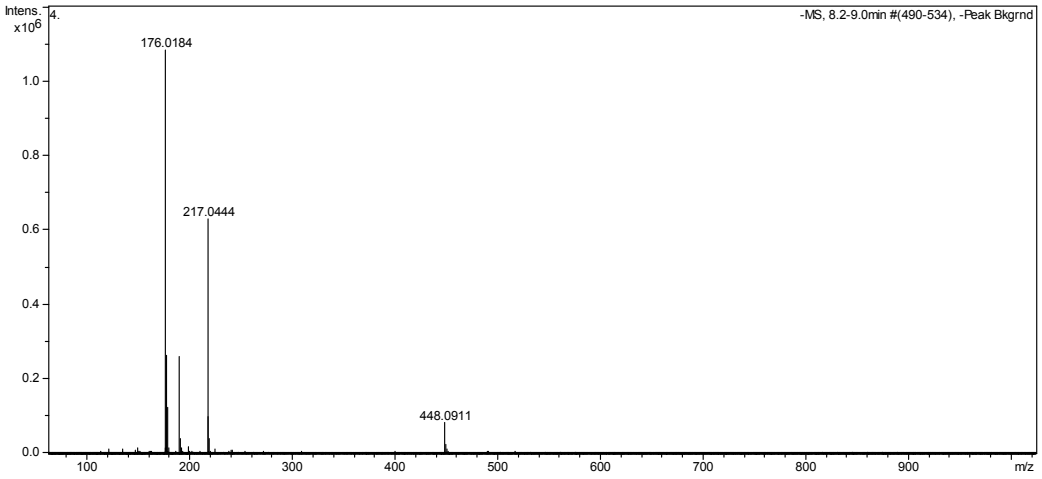

Intens.
x10^6
3.
-MS, 2.9-3.4min #(170-204), -Peak Bkgrnd
195.0600
1.0
0.8
0.6
0.4
0.2
0.0
200
400
600
800
1000
m/z

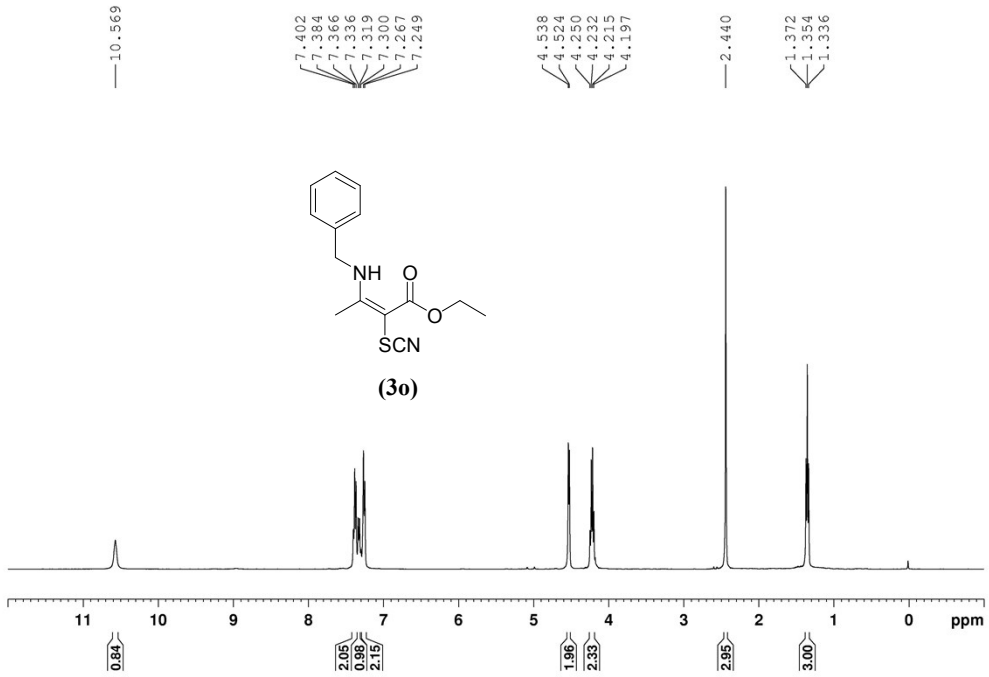

11.215
7.540
7.535
7.528
7.524
7.516
7.473
7.471
7.466
7.461
7.453
7.448
7.280
6.285
2.544
0.018
NH2
O
SCN
11
10
9
8
7
6
5
4
3
2
1
ppm
0.96
1.91
2.93
0.97
3.00

(3m)

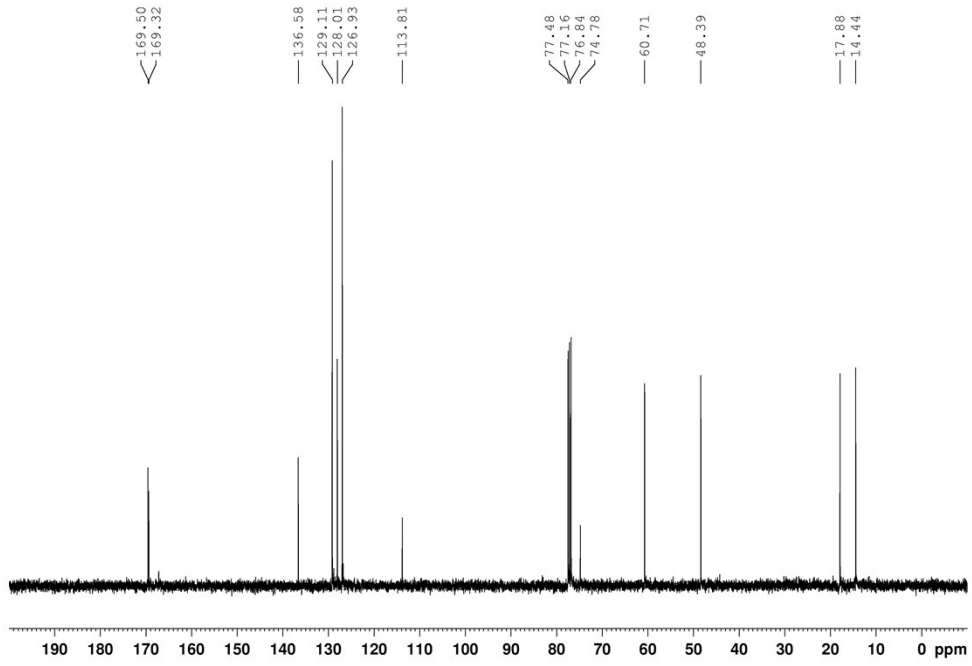

KL-85 13c
196.26
171.88
141.03
129.91
128.08
126.76
113.60
86.65
77.38
77.06
76.74
24.36
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

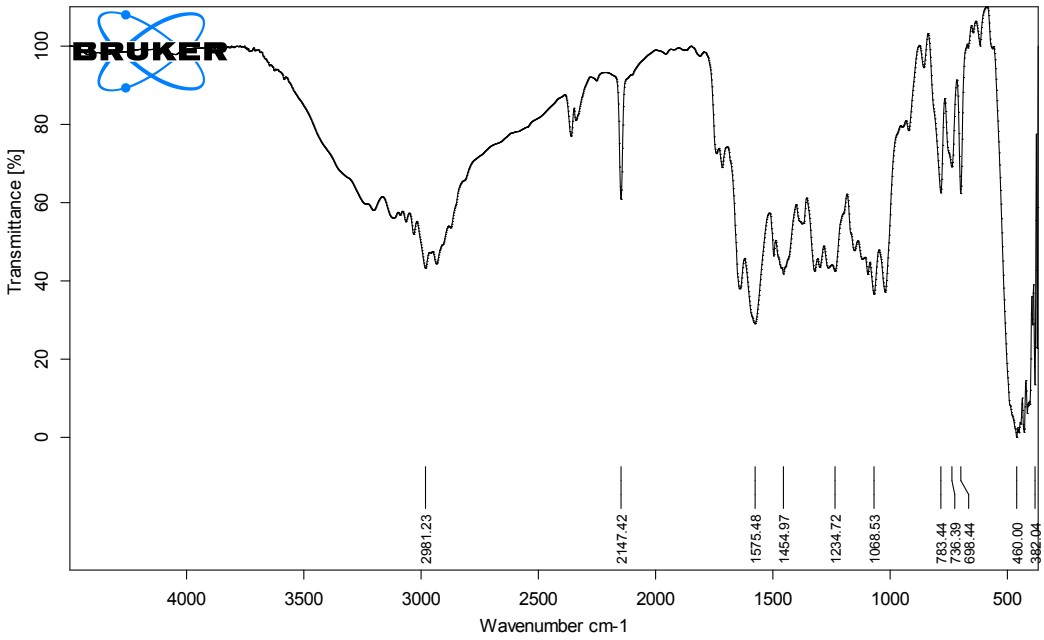

BRUKER
Transmittance [%]
100
90
80
70
60
50
40
30
781.96
729.10
699.19
657.61
539.90
750
700
650
600
550
500
450
Wavenumber cm-1

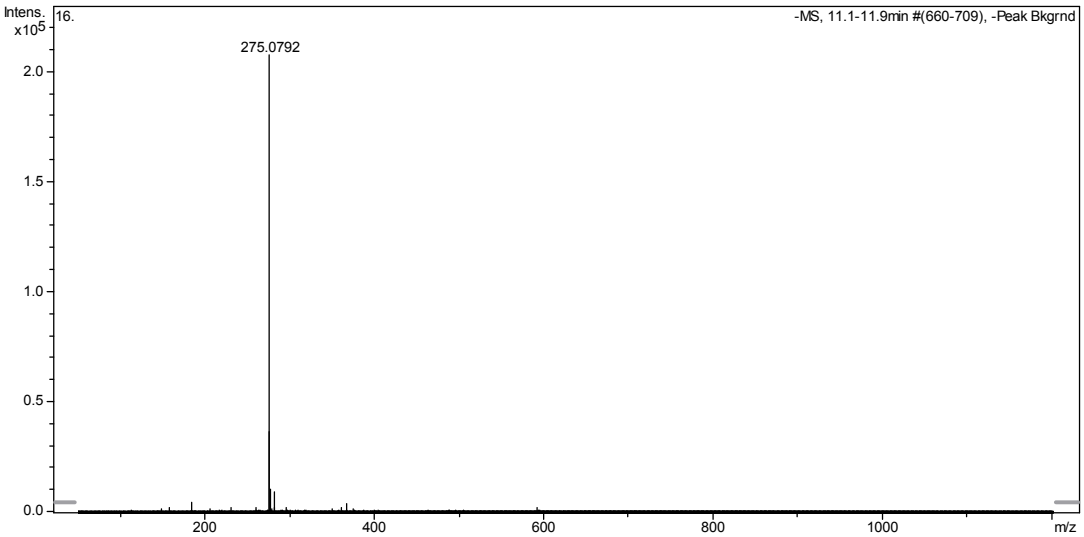

Intens.
x10^6
4.
-MS, 8.2-9.0min #(490-534), -Peak Bkgrnd
176.0184
217.0444
448.0911
1.0
0.8
0.6
0.4
0.2
0.0
100
200
300
400
500
600
700
800
900
m/z

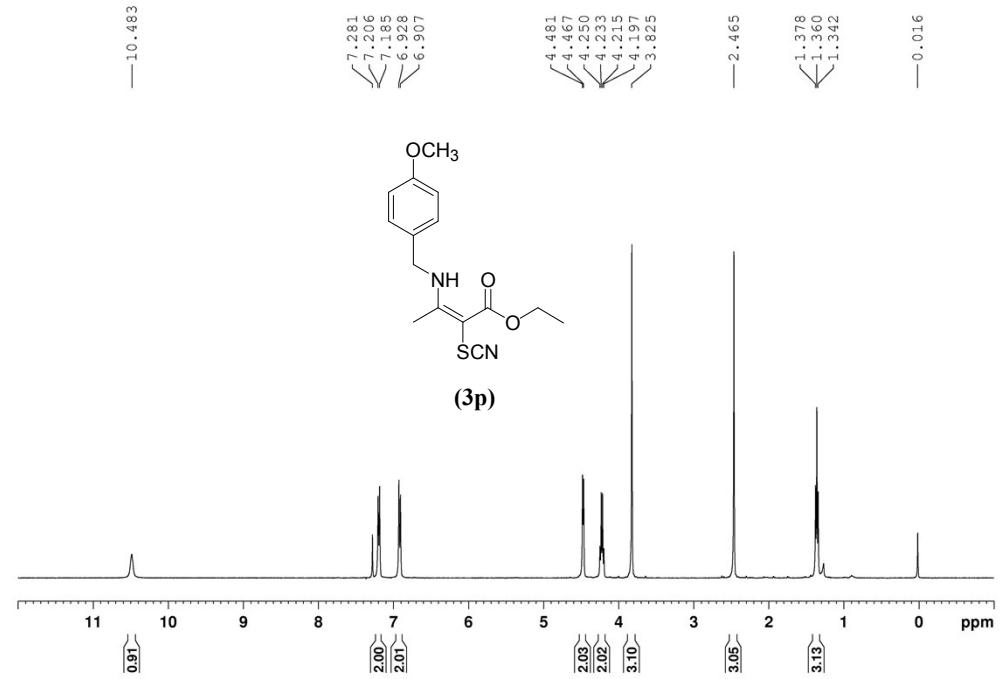

10.569
7.402
7.384
7.366
7.336
7.319
7.300
7.267
7.249
4.538
4.524
4.250
4.232
4.215
4.197
2.440
1.372
1.354
1.336
NH
O
O
SCN
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.84
2.05
0.98
2.15
1.96
2.33
2.95
3.00

(3o)

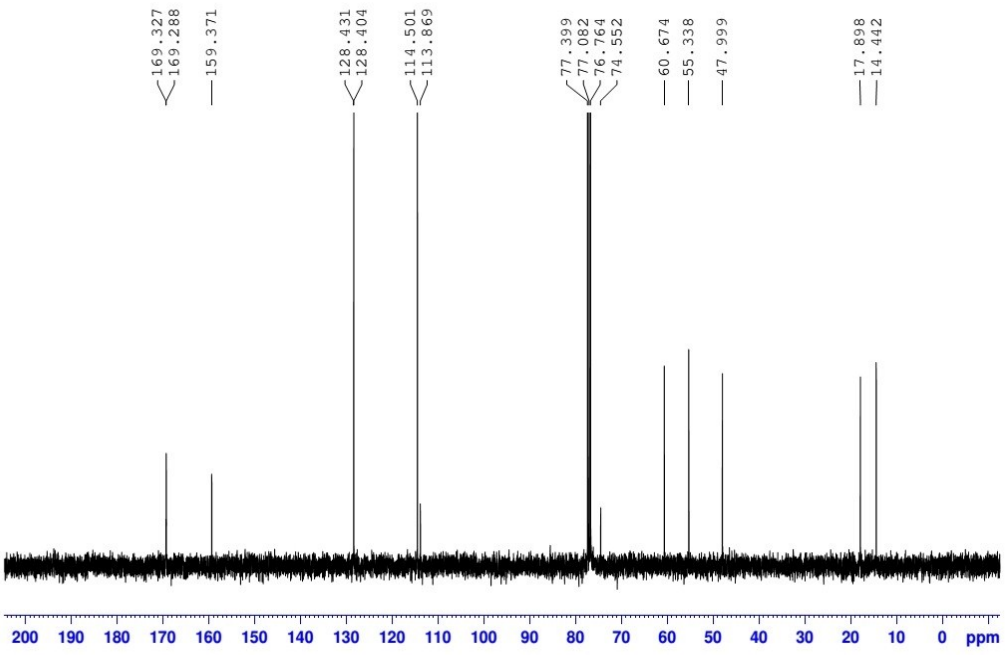

169.50
169.32
136.58
129.11
128.01
126.93
113.81
77.48
77.16
76.84
74.78
60.71
48.39
17.88
14.44
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

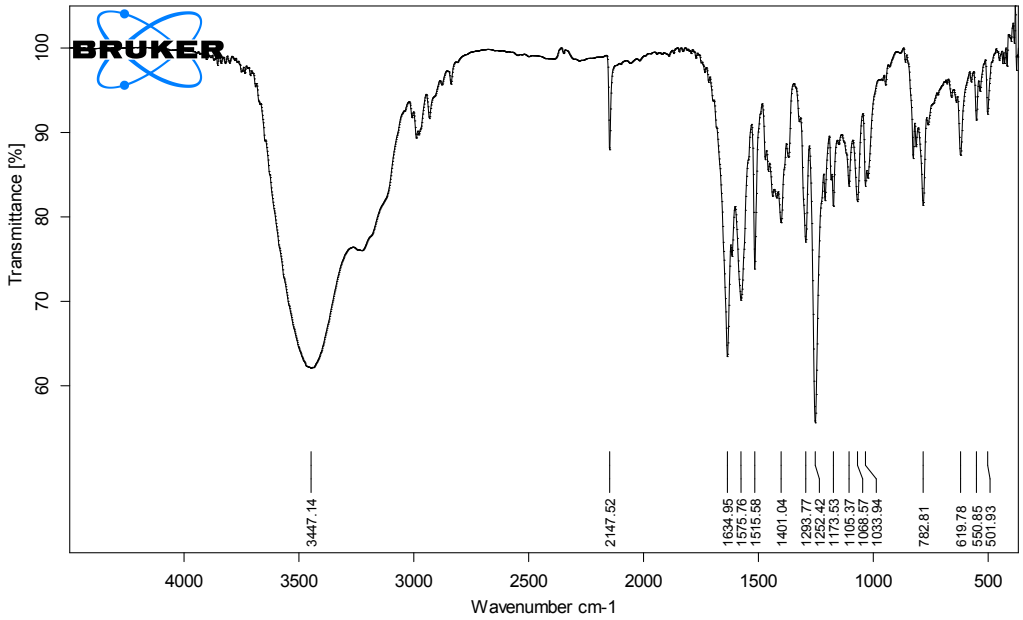

BRUKER
Transmittance [%]
0
20
40
60
80
100
2981.23
2147.42
1575.48
1454.97
1234.72
1068.53
783.44
736.39
698.44
460.00
382.04
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

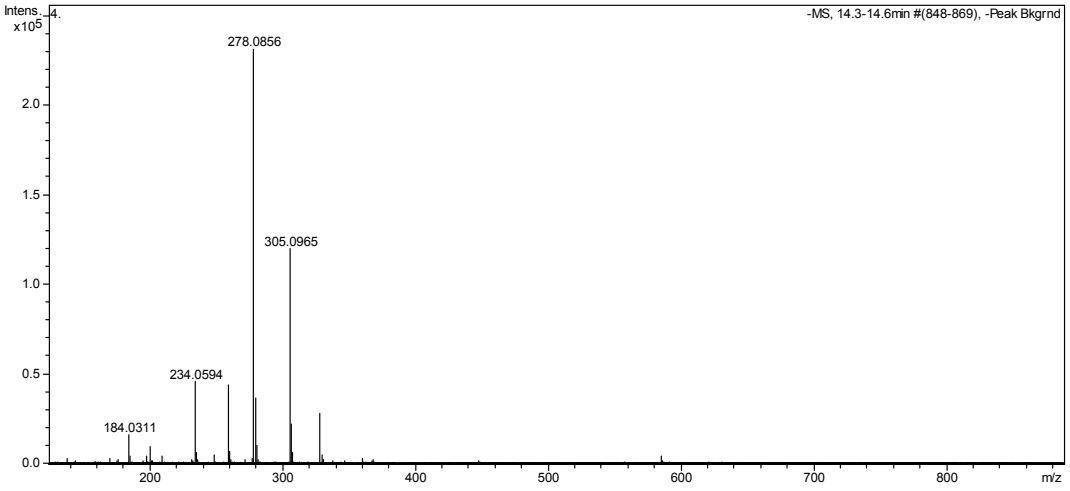

Intens.
x10^5
16.
-MS, 11.1-11.9min #(660-709), -Peak Bkgrnd
275.0792
2.0
1.5
1.0
0.5
0.0
200
400
600
800
1000
m/z

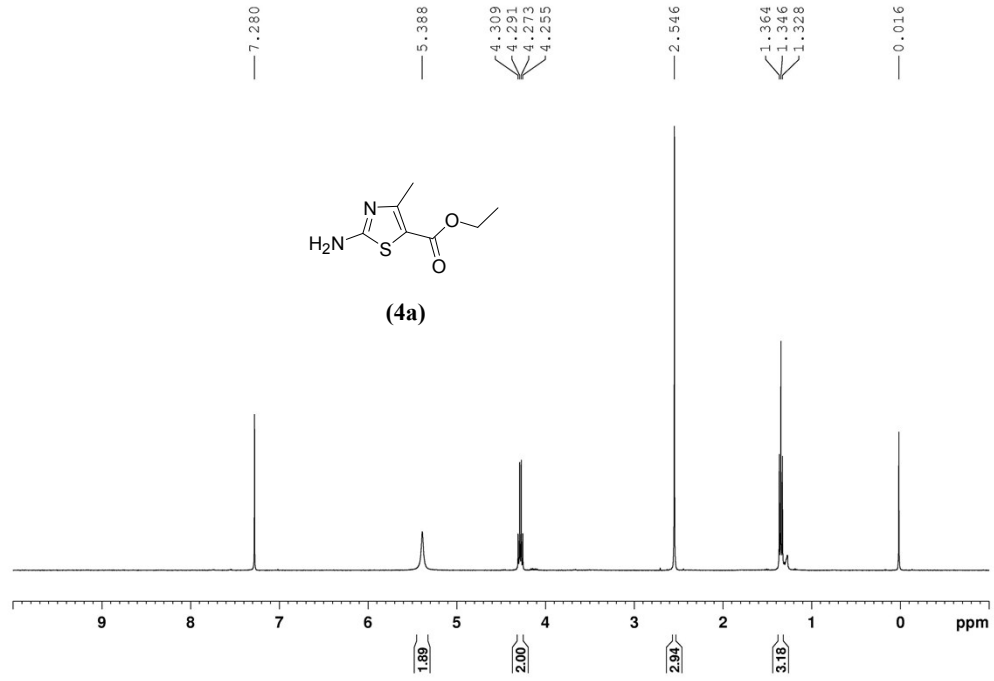

10.483
7.281
7.206
7.185
6.928
6.907
4.481
4.467
4.250
4.233
4.215
4.197
3.825
2.465
1.378
1.360
1.342
0.016
OCH3
NH
O
O
SCN
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.91
2.00
2.01
2.03
2.02
3.10
3.05
3.13

(3p)

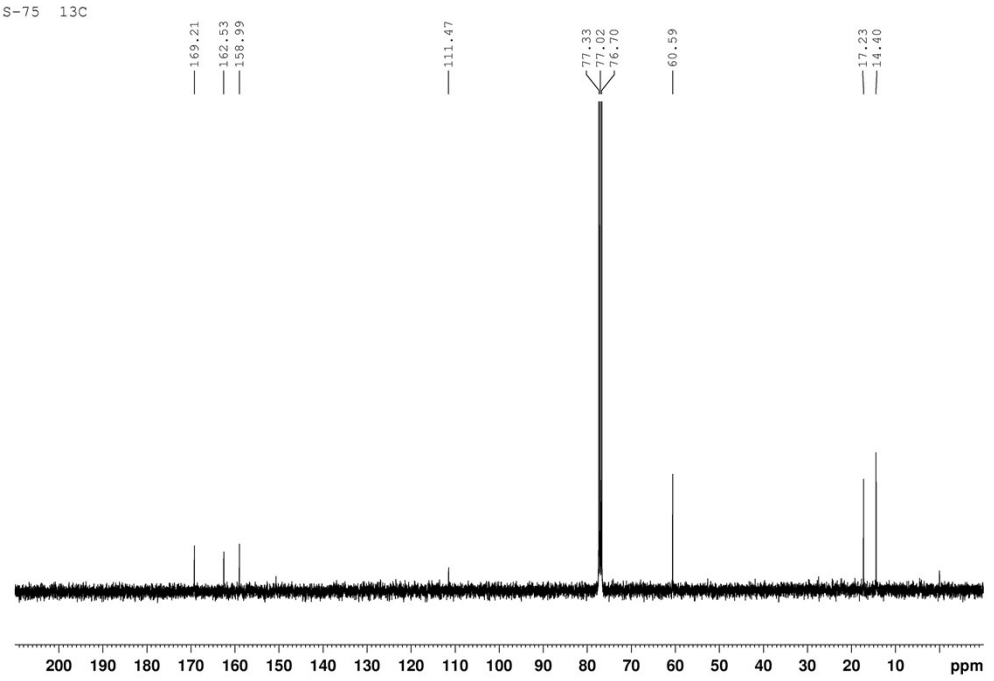

169.327
169.288
159.371
128.431
128.404
114.501
113.869
77.399
77.082
76.764
74.552
60.674
55.338
47.999
17.898
14.442
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


BRUKER
Transmittance [%]
100
90
80
70
60
3447.14
2147.52
1634.95
1575.76
1515.58
1401.04
1293.77
1252.42
1173.53
1105.37
1068.57
1033.94
782.81
619.78
550.85
501.93
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1


Intens.
x10^5
-MS, 14.3-14.6min #(848-869), -Peak Bkgrnd
278.0856
305.0965
234.0594
184.0311
2.0
1.5
1.0
0.5
0.0
200
300
400
500
600
700
800
m/z


7.280
5.388
4.309
4.291
4.273
4.255
2.546
1.364
1.346
1.328
0.016
N
O
H_2N
S
O
9
8
7
6
5
4
3
2
1
0
ppm
1.89
2.00
2.94
3.18

(4a)


S-75 13C
169.21
162.53
158.99
111.47
77.33
77.02
76.70
60.59
17.23
14.40
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm