Supporting Information For

Catalytic, Metal-free Alkylheteroarylation of Alkenes via Distal Heteroaryl *ipso*-Migration

Yonghui He,[a] Yaqi Wang,[a] Jun Gao,[a] Liang Zeng,[a] Shusheng Li[a], Wei Wang,[a] Xiaohui Zheng,[b] Shengyong Zhang,[c] Lijun Gu[a*] and Ganpeng Li[a*]

[a] Key Laboratory of Chemistry in Ethnic Medicinal Resources, State Ethnic Affairs Commission & Ministry of Education, Yunnan Minzu University, Kunming, Yunnan Province, 650500, P. R. China

[b] College of Life Science, Northwest University, Xi'an, Shanxi Province, 710069, P. R. China

[c] Department of Chemistry, School of Pharmacy, Fourth Military Medical University, Xi'an, Shanxi Province, 710032, P. R. China

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(A) Materials and equipment

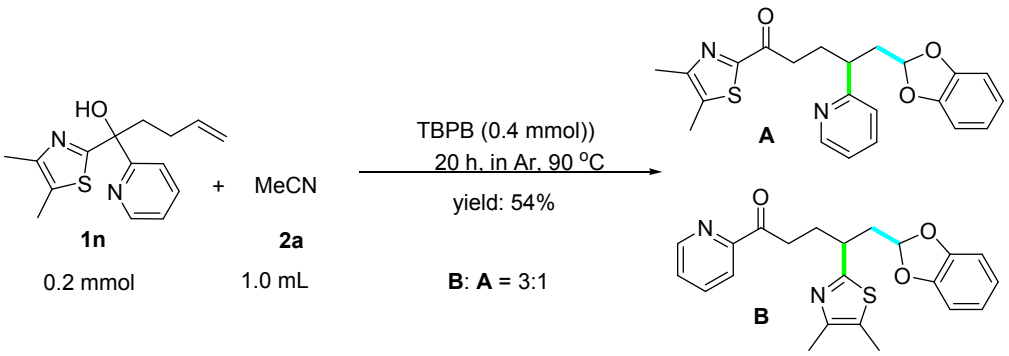
Reagents were obtained commercially and used as received. ^{1}H NMR spectra were recorded on a Bruker-400 NMR spectrometer using TMS as an internal standard. Chemical shift values (δ) are given in ppm. Coupling constants (J) were measured in Hz. High Resolution mass spectrometer (HRMS) spectra were recorded on a Bruker micrOTOF-Q II analyzer. 200-300 mesh silica gel was used for column chromatography.

(B) Typical experimental procedure for the difunctionalization of olefins

To a Schlenk tube were added Tertiary alcohol **1** (0.2 mmol, 1 equiv), MeCN **2** (1.0 mL), TBPB (0.8 mmol, 4 equvi). Then the tube was charged with argon, and was stirred at 90 ℃ for 20 h. After the reaction was finished, the reaction mixture was diluted in 30 mL ethyl acetate, washed with a saturated solution of brine (8 mL), saturated $NaHCO_3$ (10 mL), a saturated solution of brine (8 mL), dried ($MgSO_4$) and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to give the product **3**.

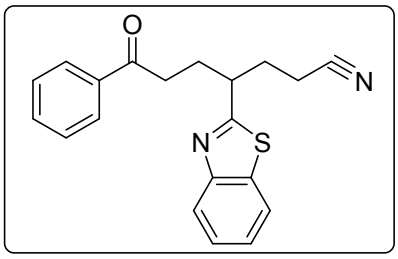
(C) Experimental for migratory efficiency

To a Schlenk tube were added benzothiazole-substituted tertiary alcohol **1m** (0.2 mmol), TBPB (0.8 mmol, 4 equvi), MeCN (1.0 mL). Then the tube was charged with argon, and was stirred at 90 ℃ for 20 h. After the reaction was finished, the reaction mixture was diluted in 30 mL ethyl acetate, washed with a saturated solution of brine (8 mL), saturated $NaHCO_3$ (10 mL), a saturated solution of brine (8 mL), dried ($MgSO_4$) and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to give the products **A** and **B**.



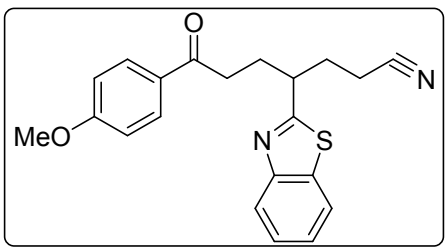
(D) Characterization data of compounds

4-(Benzo[d]thiazol-2-yl)-7-oxo-7-phenylheptanenitrile (3aa)：



Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$), δ: 8.02 (d, J = 8.0 Hz, 1H), 8.00-7.88 (m, 3H), 7.57-7.50 (m, 2H), 7.46-7.40 (m, 3H), 3.49-3.42 (m,1H), 3.09-2.99 (m, 2H), 2.47-2.42 (m,2H), 2.38-2.21 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ: 198.8, 172.5, 153.0, 136.5, 134.5, 133.2, 128.6, 127.9, 126.3, 125.3, 122.9, 121.8, 119.0, 43.1, 35.6, 31.5, 29.7, 15.3; LRMS (EI 70 ev) m/z (%): 334 (M^+, 100); HRMS m/z (ESI) calcd for $C_{20}H_{19}N_2OS$ $[M+H]^+$ 335.1213, found 335.1218.

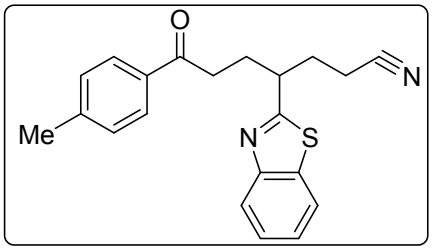
4-(benzo[d]thiazol-2-yl)-7-(4-methoxyphenyl)-7-oxoheptanenitrile (3ab):



Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 (d, J = 8.0 Hz, 1H), 7.88-7.83 (m, 3H), 7.50 (t, J = 8.0 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 6.88 (d, J = 8 Hz, 2H), 3.83 (s, 3H), 3.45-3.36(m, 1H), 2.98-2.93 (m, 2H), 2.44-2.39 (m, 2H), 2.33-2.21 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ: 197.4, 172.7, 163.5, 153.0, 134.6, 130.2, 129.6, 126.2, 125.2, 122.9, 121.7, 119.0, 113.7, 55.4, 43.2, 35.2, 31.5, 29.8, 15.3.; LRMS (EI 70 ev)

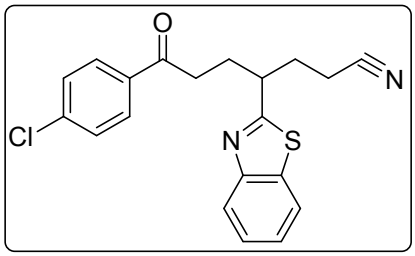
m/z (%): 364 (M^+, 100); HRMS m/z (ESI) calcd for $C_{21}H_{21}N_2O_2S$ $[M+H]^+$ 365.1318, found 365.1325.

4-(benzo[d]thiazol-2-yl)-7-oxo-7-(p-tolyl)heptanenitrile (3ac):



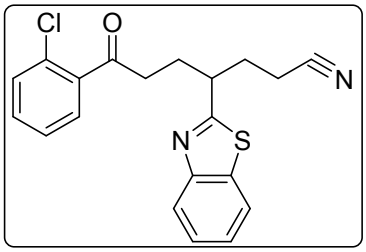
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 (d, J = 9.0 Hz, 2H), 7.80 (d, J = 8.8 Hz, 1H), 7.60 (t, J = 7.6 Hz, 2H), 7.47-7.43 (m, 2H), 7.39-7.35 (m, 2H); 3.45-3.38 (m, 1H), 3.02-2.90 (m, 2H), 2.43-2.34 (m, 2H), 2.31-2.20 (m, 4H), 2.03 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ: 197.5, 172.2, 164.5, 139.5, 134.4, 133.3, 130.8, 129.0, 128.5, 125.2, 122.9, 121.7, 118.9, 42.9, 35.5, 31.4, 29.5, 20.9, 15.2; LRMS (EI 70 ev) m/z (%): 348 (M^+, 100); HRMS m/z (ESI) calcd for $C_{21}H_{21}N_2OS[M+H]^+$ 349.1369, found 349.1360.

4-(benzo[d]thiazol-2-yl)-7-(4-chlorophenyl)-7-oxoheptanenitrile (3ad):



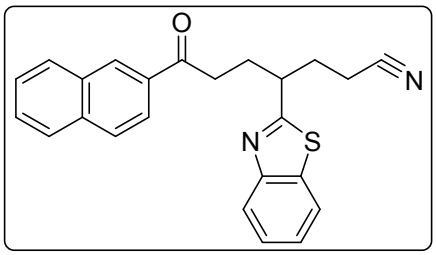
Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 8.0 Hz, 2H), 7.42-7.37 (m, 4H), 3.46-3.38 (m, 1H), 3.00-2.95(m, 2H), 2.44-2.39 (m, 2H), 2.35-2.20 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ: 197.6, 172.3, 153.0, 134.8, 134.5, 129.3, 128.9, 127.8, 126.3, 125.6, 125.3, 123.0, 121.8, 43.1, 35.6, 31.5, 26.9, 15.3.; LRMS (EI 70 ev) m/z (%): 368 (M^+, 100); HRMS m/z (ESI) calcd for $C_{20}H_{18}ClN_2OS$ $[M+H]^+$ 369.0822, found 369.0824.

4-(benzo[d]thiazol-2-yl)-7-(2-chlorophenyl)-7-oxoheptanenitrile (3ae):



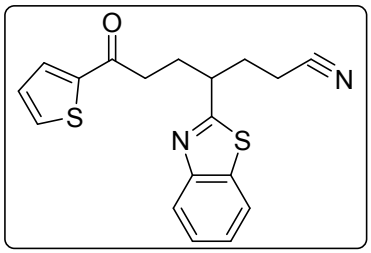
Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.54-7.47 (m, 5H), 3.48-3.43 (m, 1H), 3.38-3.29(m, 2H), 2.44-2.27 (m, 6H); ^{13}C NMR (100MHz, $CDCl_3$) δ: 194.1, 172.2, 165.7, 153.3, 137.1, 134.5, 130.9, 127.7, 127.0, 126.2, 125.4, 122.9, 122.4, 121.7, 119.0, 42.9, 35.8, 31.2, 29.4, 15.2.; LRMS (EI 70 ev) m/z (%): 368 (M^+, 100); HRMS m/z (ESI) calcd for $C_{20}H_{18}ClN_2OS$ $[M+H]^+$ 369.0822, found 369.0824.

4-(benzo[d]thiazol-2-yl)-7-(naphthalen-2-yl)-7-oxoheptanenitrile (3af):



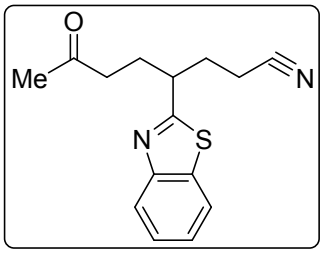
White oil, (1:1 dr); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.98 (t, *J* = 6.4 Hz, 1H), 7.83 (t, *J* = 8.6 Hz, 3H), 7.49-7.45 (m, 2H), 7.37-7.31 (m, 3H), 3.61-3.52 (m, 0.5H), 3.50-3.44 (m, 0.5H), 3.01-2.88(m, 2H), 2.84-2.76 (m, 1H), 2.36-2.22 (m, 4H), 2.19-1.99 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 198.59, 198.50, 172.5, 172.0, 153.0, 152.9, 136.3, 136.2, 134.3, 132.93, 132.91, 128.3, 127.6, 125.9, 124.9, 122.66, 122.62, 121.5, 120.19, 120.12, 42.4, 41.3, 41.2, 37.4, 37.2, 35.3, 35.2, 34.3, 34.1, 31.2, 28.9, 28.7; LRMS (EI 70 ev) m/z (%): 384 (M^+, 100); HRMS m/z (ESI) calcd for $C_{24}H_{21}N_2OS$ $[M+H]^+$ 385.1369, found 385.1365.

4-(benzo[d]thiazol-2-yl)-7-oxo-7-(thiophen-2-yl)heptanenitrile (3ag):



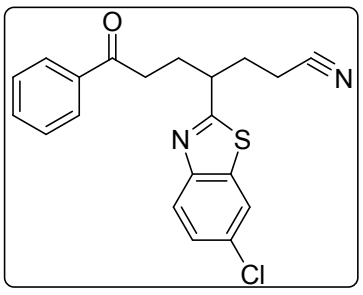
Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 4.0 Hz, 2H), 7.49 (t, *J*=4.0 Hz, 1H), 7.39 (t, *J* = 8 Hz, 1H),7.06 (t, *J* = 4 Hz, 1H), 3.45-3.36 (m, 1H), 2.97-2.93(m, 2H), 2.43-2.38 (m, 2H), 2.34-2.20 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ: 191.7, 172.4, 153.1, 143.8, 134.6, 133.7, 131.9, 128.0, 126.3, 125.3, 122.9, 121.7, 118.9, 43.1, 36.3, 31.4, 29.8, 15.2; LRMS (EI 70 ev) m/z (%): 340 (M^+, 100); HRMS m/z (ESI) calcd for $C_{18}H_{17}N_2OS_2$ $[M+H]^+$ 341.0776, found 341.0775.

4-(benzo[d]thiazol-2-yl)-7-oxooctanenitrile (3ah):



White oil;^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.0Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 3.34-3.26(m, 1H), 2.48-2.44 (m, 2H), 2.40-2.35 (m, 2H), 2.33-2.14 (m, 4H), 2.08 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ: 207.3, 172.4, 153.0, 134.5, 129.1, 126.2, 125.3, 122.9, 121.7, 118.9, 42.8, 40.5, 31.3, 30.0, 29.1, 15.3; LRMS (EI 70 ev) m/z (%): 272 (M^+, 100); HRMS m/z (ESI) calcd for $C_{15}H_{17}N_2OS$ $[M+H]^+$ 273.1056, found 273.1063.

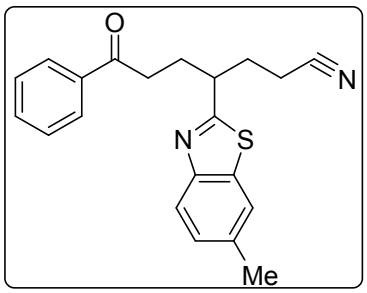
4-(6-chlorobenzo[d]thiazol-2-yl)-7-oxo-7-phenylheptanenitrile (3ai):



Brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98-7.96 (m, 1H), 7.91-7.86 (m, 3H), 7.47-7.42 (m, 4H), 3.47-3.40 (m, 1H), 3.05-3.01 (m, 2H), 2.47-2.41 (m, 2H); 2.36-2.22 (m, 4H); ^{13}C NMR (100MHz, CDCl3) δ: 198.7, 173.1, 151.7, 136.5, 133.4, 133.3, 131.3, 129.1,128.6, 127.9, 127.1, 123.7, 121.4, 43.1, 35.6, 31.3, 29.6, 26.3, 15.3. LRMS (EI 70 ev) m/z (%): 368 (M^+, 79); HRMS m/z (ESI) calcd for

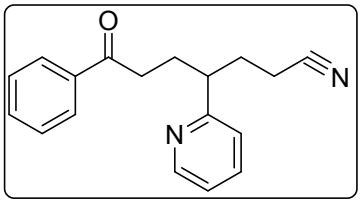
$C_{20}H_{18}ClN_2OS$ $[M+H]^+$ 369.0822, found 369.0824.

4-(6-methylbenzo[d]thiazol-2-yl)-7-oxo-7-phenylheptanenitrile (3aj):



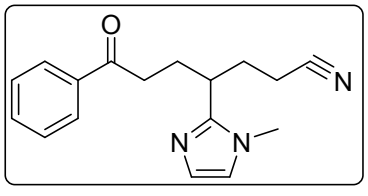
Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89-7.87 (m, 3H), 7.68 (s, 1H), 7.55 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.43 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.33 (d, *J* = 4.4 Hz, 1H), 3.45-3.38 (m, 1H), 3.05-3.00 (m, 2H), 2.50 (s, 3H); 2.46-2.41 (m, 2H), 2.36-2.25 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ: 198.9, 171.4, 151.2, 136.6, 135.4, 134.7, 133.2, 128.5, 127.9, 127.8, 122.4, 121.5, 119.0, 43.1, 35.7, 31.5, 29.7, 21.4, 15.3; LRMS (EI 70 ev) m/z (%): 348 (M^+ , 100); HRMS m/z (ESI) calcd for $C_{21}H_{21}N_2OS$ $[M+H]^+$ 349.1369, found 349.1360.

7-oxo-7-phenyl-4-(pyridin-2-yl)heptanenitrile (3ak):



Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.63(d, *J* = 3.6 Hz, 1H), 8.00-7.94 (m, 2H), 7.82-7.78 (m, 1H), 7.73-7.71 (t, *J* = 8.8 Hz, 1H), 7.59-7.52 (m, 2H), 7.47-7.42 (m, 2H), 3.25-3.17(m, 1H), 3.00-2.92 (m, 1H), 2.27-2.25 (m, 5H), 2.07-2.01 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ: 200.4, 161.6, 149.0, 137.0, 136.8, 131.3, 129.4, 128.9, 128.6, 119.6, 45.4, 35.7, 30.9, 29.6, 15.1; LRMS (EI 70 ev) m/z (%): 278 (M^+ , 100); HRMS m/z (ESI) calcd for $C_{18}H_{19}N_2O[M+H]^+$ 279.1491, found 279.1484.

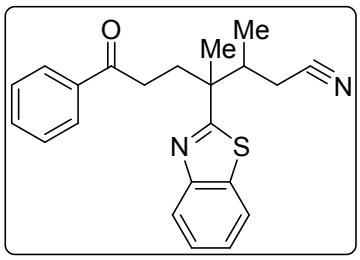
4-(1-methyl-1H-imidazol-2-yl)-7-oxo-7-phenylheptanenitrile (3al):



Pale yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.96 (d, *J* = 6.0 Hz, 2H), 7.54-749 (m,

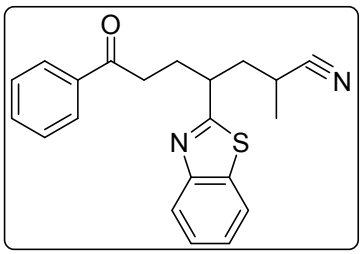
1H), 7.39-7.33 (m, 2H), 7.00 (d, J = 7.6 Hz, 1H), 6.79 (d, J = 7.6 Hz, 1H), 3.93 (s, 3H), 3.50-3.43 (m, 1H), 3.06-3.00 (m, 2H), 2.46-2.40 (m, 2H), 2.38-2.26 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.1, 148.3 136.0, 132.6, 128.7, 128.0, 127.4, 119.9, 119.0, 42.8, 35.7, 31.4, 29.9, 29.0, 15.7; LRMS (EI 70 ev) m/z (%): 281 (M^+ , 100); HRMS m/z (ESI) calcd for $C_{17}H_{20}N_3O[M+H]^+$ 282.1600, found 282.1605.

4-(benzo[d]thiazol-2-yl)-3,4-dimethyl-7-oxo-7-phenylheptanenitrile (3am):



Yellow oil, (1:1.1 dr); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, J = 8.0 Hz, 1H), 7.90-7.81 (m, 1H), 7.52-7.47 (m, 2H), 7.42-7.36, 2.95-2.90 (m, 1H), 2.87-2.63 (m, 2H), 2.43-2.35 (m, 2H), 2.31-2.18 (m, 2H), 1.54 (m, 1.4H), 1.50 (m, 1.6H), 1.29 (d, J = 6.8 Hz, 1.6H), 1.15 (d, J = 6.8 Hz, 1.4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.3, 199.1, 177.1,176.5, 152.8, 136.5, 133.2, 133.1, 128.5, 128.0, 127.9, 126.2, 126.1, 125.3, 125.2, 123.1, 123.0, 121.7, 121.6, 119.2, 46.8, 46.6, 41.0, 39.9, 35.0, 33.7, 33.4, 32.6, 21.0, 20.7, 20.3, 19.1, 15.2, 14.3. LRMS (EI 70 ev) m/z (%): 362 (M^+ , 100); HRMS m/z (ESI) calcd for $C_{22}H_{23}N_2OS$ $[M+H]^+$ 363.1525, found 363.1529.

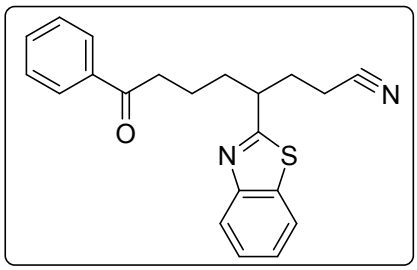
4-(benzo[d]thiazol-2-yl)-2-methyl-7-oxo-7-phenylheptanenitrile (3ba):



Yellow oil; (1:1 dr); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.99 (dd, J = 4.0 Hz, J = 4.0 Hz, 1H), 7.86 (t, J = 3.6 Hz, 2H), 7.51-7.45 (m, 3H), 7.41(t, J = 6.0 Hz, 2H), 3.58-3.51 (m, 0.5H), 3.49-3.44 (m, 0.5H), 3.06-2.92 (m, 2H), 2.73-2.69 (m, 0.5H), 2.59-2.55 (m, 0.5H), 2.33-2.28 (m, 2H), 2.20-2.15 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.8, 198.7, 172.9 172.7, 153.1, 136.4, 134.4, 133.14, 133.11, 129.2, 128.6, 128.4, 127.8,

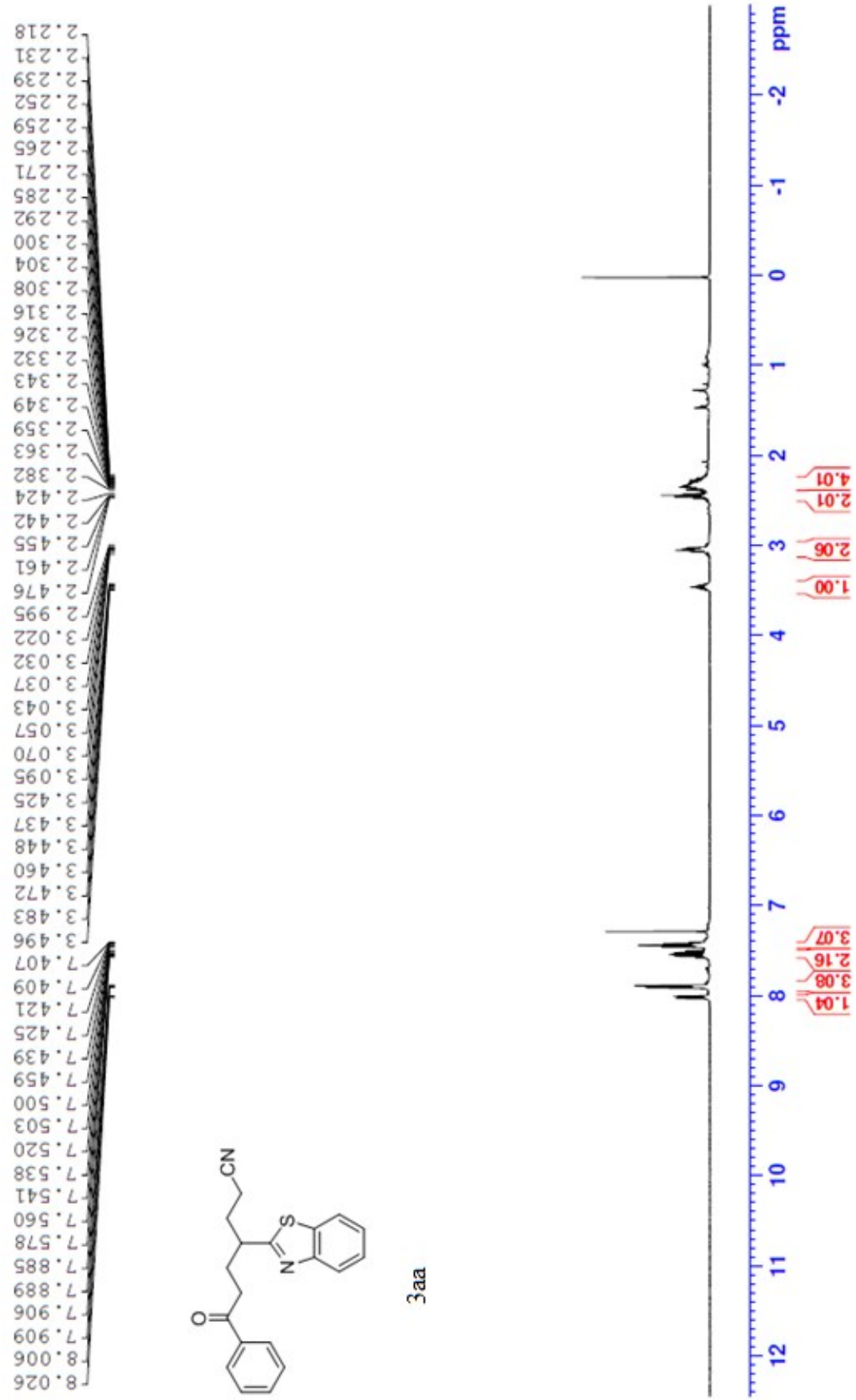
126.1, 125.19, 125.14, 122.8, 122.2, 121.7, 121.6, 42.2, 41.4, 40.1, 39.7, 35.6, 35.5, 30.8, 30.3, 23.9, 23.0, 18.3, 17.5; LRMS (EI 70 ev) m/z (%): 348 (M^+ , 100); HRMS m/z (ESI) calcd for $C_{22}H_{21}N_2OS[M+H]^+$ 349.1369, found 349.1365.

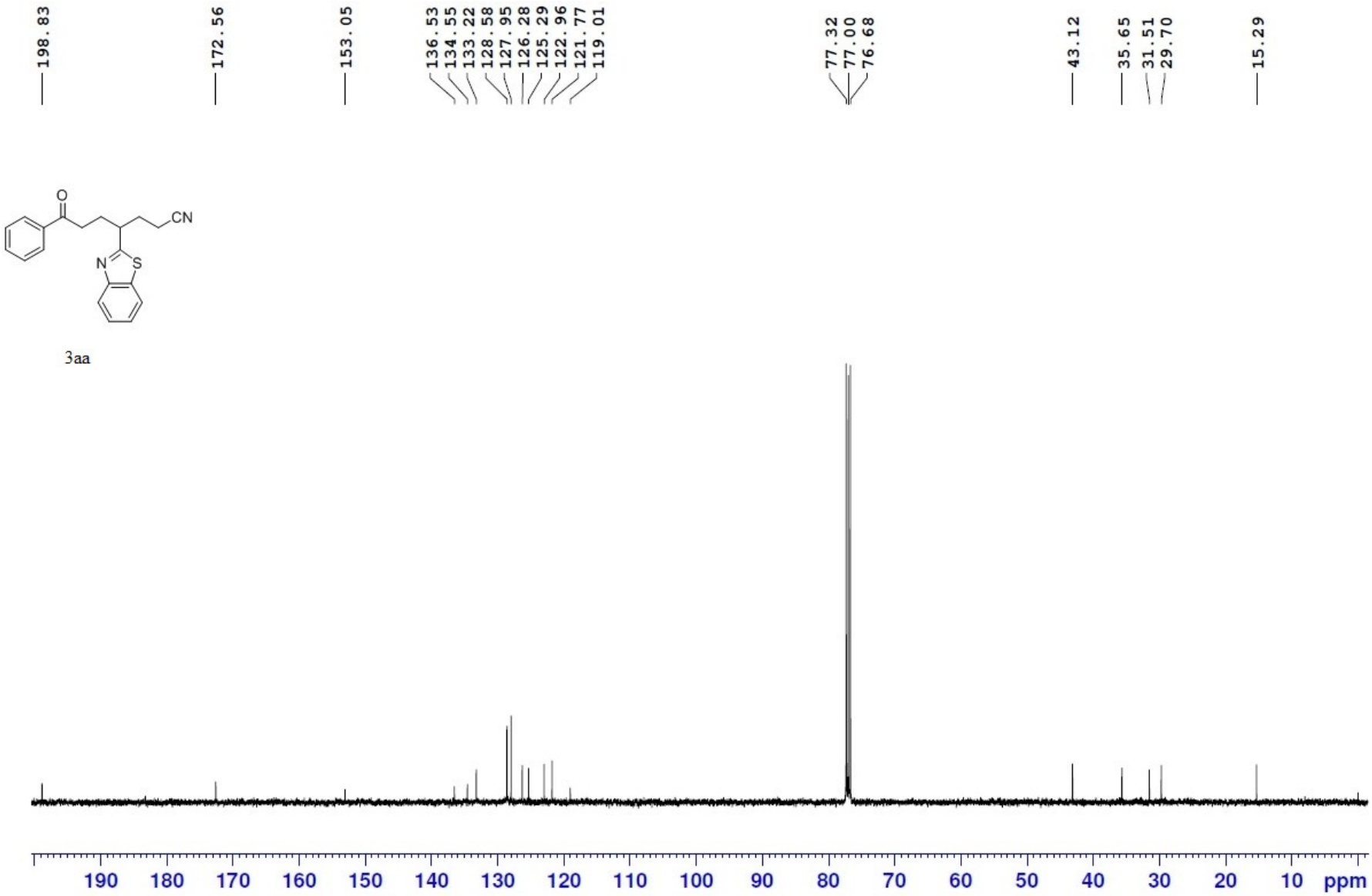
4-(benzo[d]thiazol-2-yl)-8-oxo-8-phenyloctanenitrile (5aa):



Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (d, *J*=8.0, 1H), 7.90-7.84 (m, 3H), 7.46-7.35 (m, 5H), 3.38-3.31 (m, 1H), 3.05-2.91 (m, 2H), 2.43-2.33 (m, 2H), 2.25-2.18 (m, 2H), 1.93-1.78(m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ: 199.4, 171.1, 153.0, 136.7, 134.5, 133.0, 128.5, 127.9,126.1, 125.1, 122.8, 121.7, 119.1, 43.6, 37.8, 35.1, 31.0, 21.5, 14.1; LRMS (EI 70 ev) m/z (%): 348 (M^+ , 100); HRMS m/z (ESI) calcd for $C_{21}H_{21}N_2OS[M+H]^+$ 349.1369, found 349.1365.

(E) Copies of ^{1}H and ^{13}C NMR Spectra

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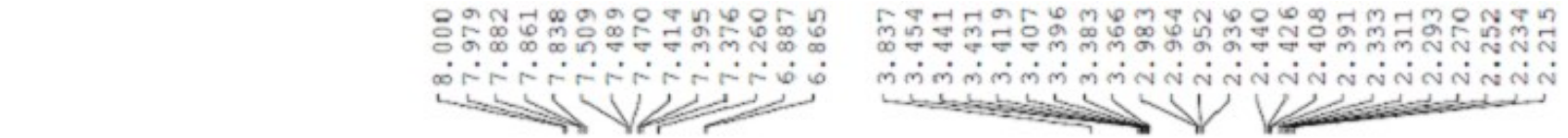
134.55
133.22
128.58
127.95
126.28
125.29
122.96
121.77
119.01
77.32
77.00
76.68
43.12
35.65
31.51
29.70
15.29
O
CN
N
S
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

3aa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7.470
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7.395
7.376
7.260
6.887
6.865
3.837
3.454
3.441
3.431
3.419
3.407
3.396
3.383
3.366
2.983
2.964
2.952
2.936
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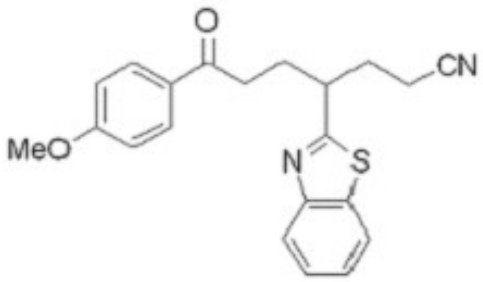
2.408
2.391
2.333
2.311
2.293
2.270
2.252
2.234
2.215


O
CN
MeO
N
S

3ab

12
11
10
9
8
7
6
5
4
3
2
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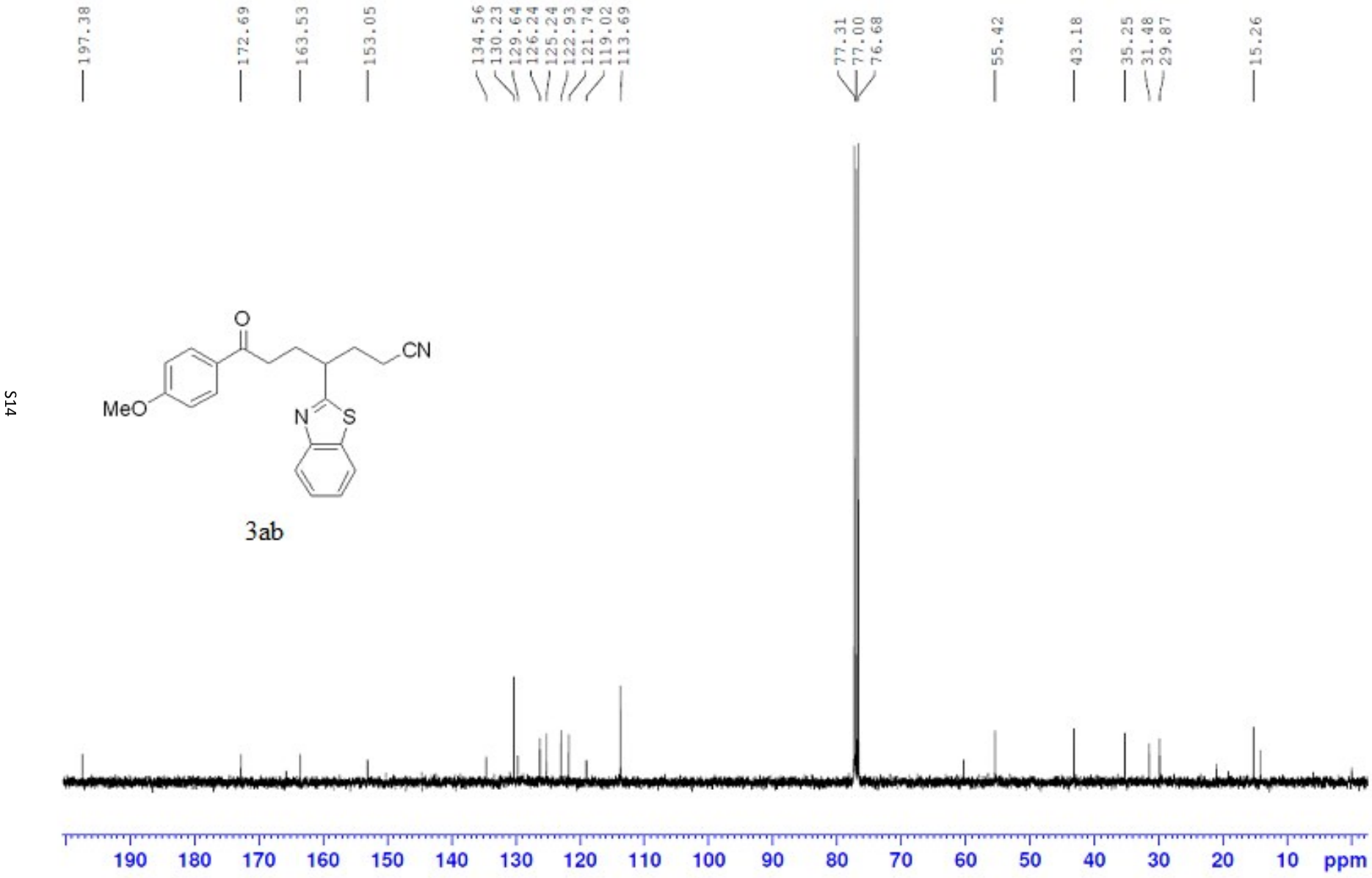
0
ppm
1.02
3.01
1.05
1.10
2.03
3.05
1.00
2.10
2.01
4.01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126.24
125.24
122.93
121.74
119.02
113.69
77.31
77.00
76.68
55.42
43.18
35.25
31.48
29.87
15.26
O
CN
MeO
N
S
3ab
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150
140
130
120
110
100
90
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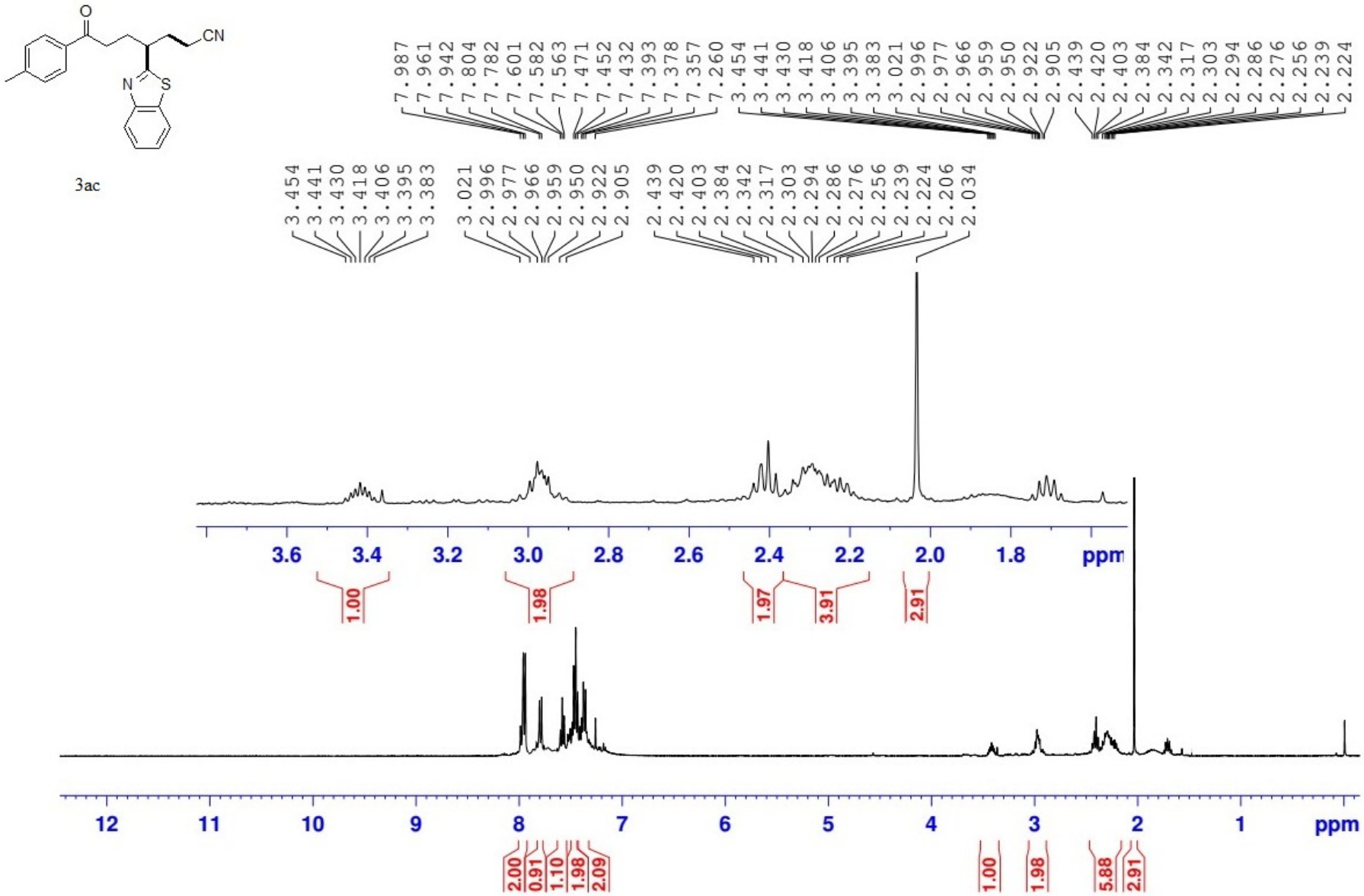
70
60
50
40
30
20
10
ppm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CN
N
S
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7.582
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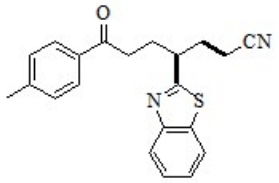
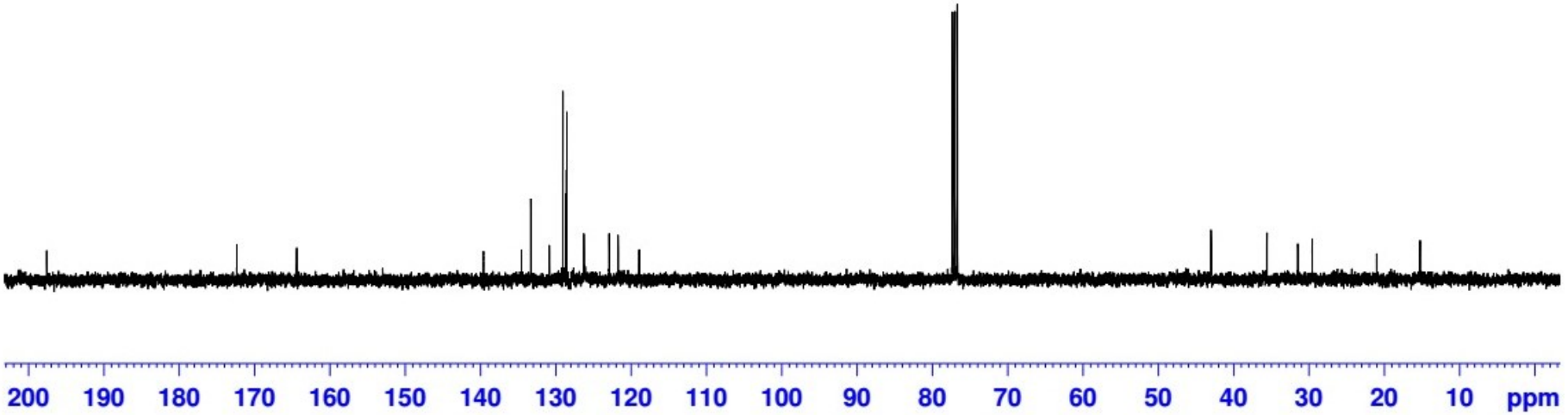
7.471
7.452
7.432
7.393
7.378
7.357
7.260
3.454
3.441
3.430
3.418
3.406
3.395
3.383
3.021
2.996
2.977
2.966
2.959
2.950
2.922
2.905
2.439
2.420
2.403
2.384
2.342
2.317
2.303
2.294
2.286
2.276
2.256
2.239
2.224
2.206
2.034
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
ppm
1.00
1.98
1.97
3.91
2.91
12
11
10
9
8
7
6
5
4
3
2
1
ppm
2.00
0.91
1.10
1.98
2.09
1.00
1.98
5.88
2.91


197.560
172.250
164.514
139.596
134.487
133.304
130.864
129.063
128.568
125.295
122.910
121.735
118.928
77.317
77.000
76.682
42.994
35.573
31.452
29.564
20.985
15.231


O
CN
N
S

3ac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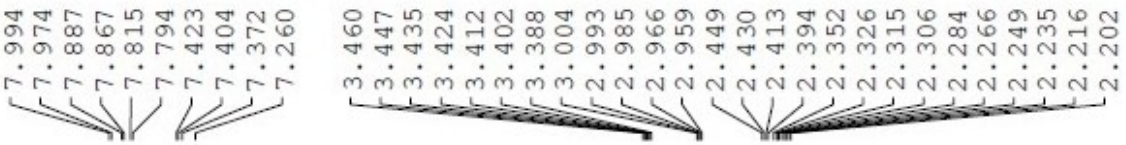
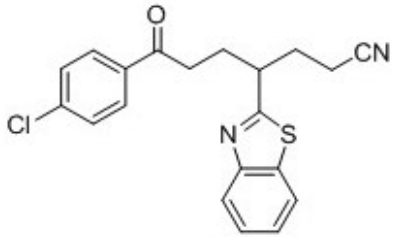
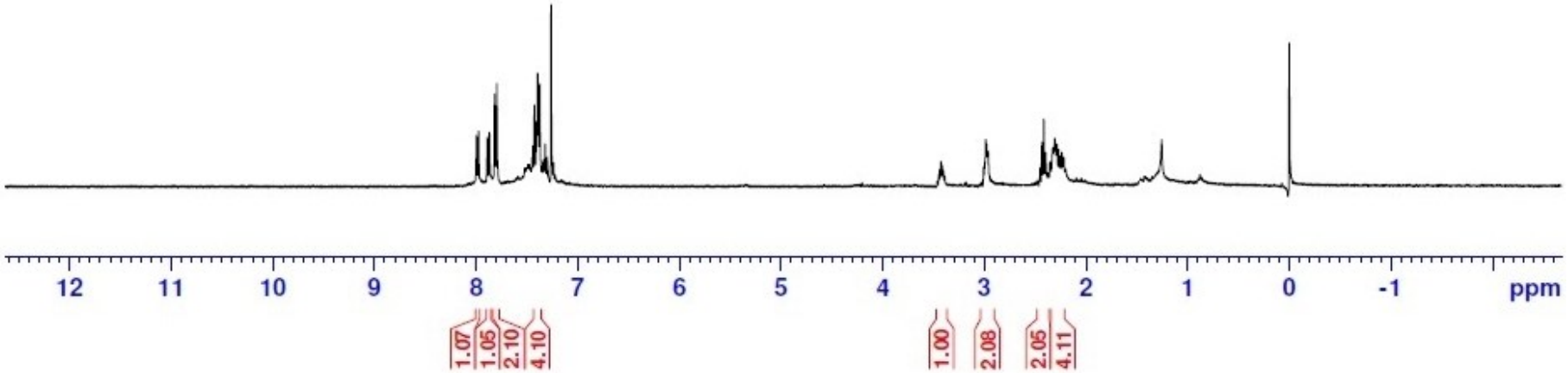
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.994
7.974
7.887
7.867
7.815
7.794
7.423
7.404
7.372
7.260
3.460
3.447
3.435
3.424
3.412
3.402
3.388
3.004
2.993
2.985
2.966
2.959
2.449
2.430
2.413
2.394
2.352
2.326
2.315
2.306
2.284
2.266
2.249
2.235
2.216
2.202


O
CN
Cl
N
S

3ad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10
9
8
7
6
5
4
3
2
1
0
-1
ppm
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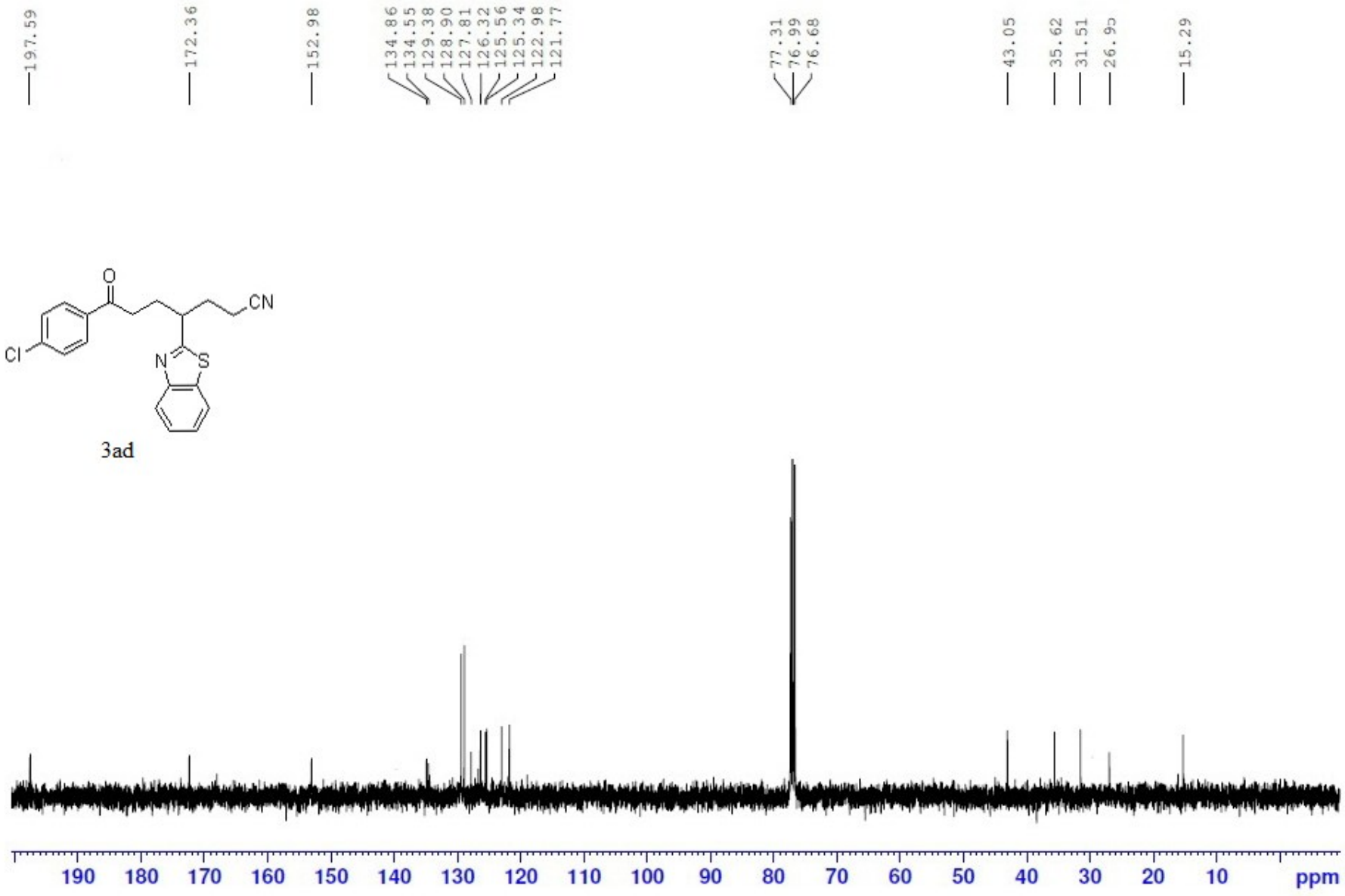
1.05
2.10
4.10
1.00
2.08
2.05
4.11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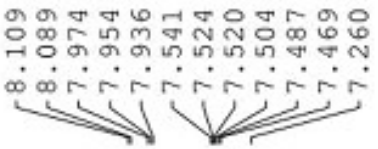
129.38
128.90
127.81
126.32
125.56
125.34
122.98
121.77
77.31
76.99
76.68
43.05
35.62
31.51
26.95
15.29
O
CN
Cl
N
S
3ad
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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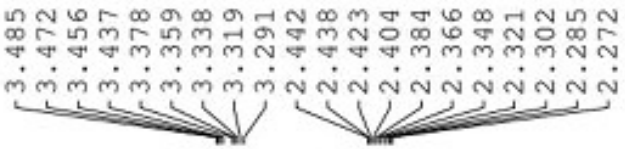
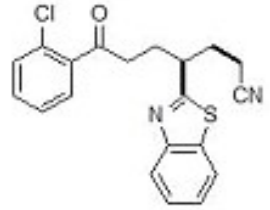
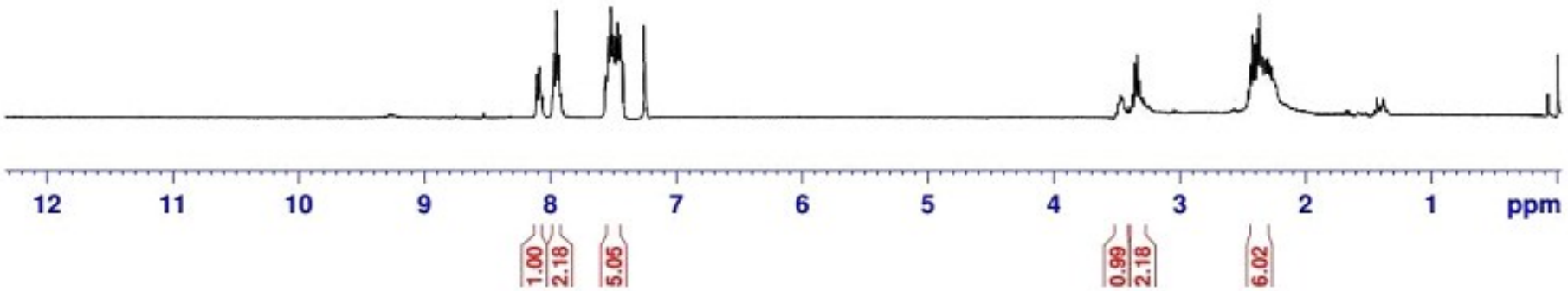
7.954
7.936
7.541
7.524
7.520
7.504
7.487
7.469
7.260

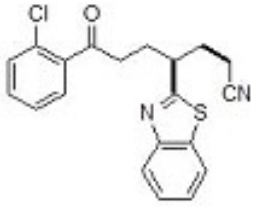

3.485
3.472
3.456
3.437
3.378
3.359
3.338
3.319
3.291
2.442
2.438
2.423
2.404
2.384
2.366
2.348
2.321
2.302
2.285
2.272


Cl
O
CN
N
S

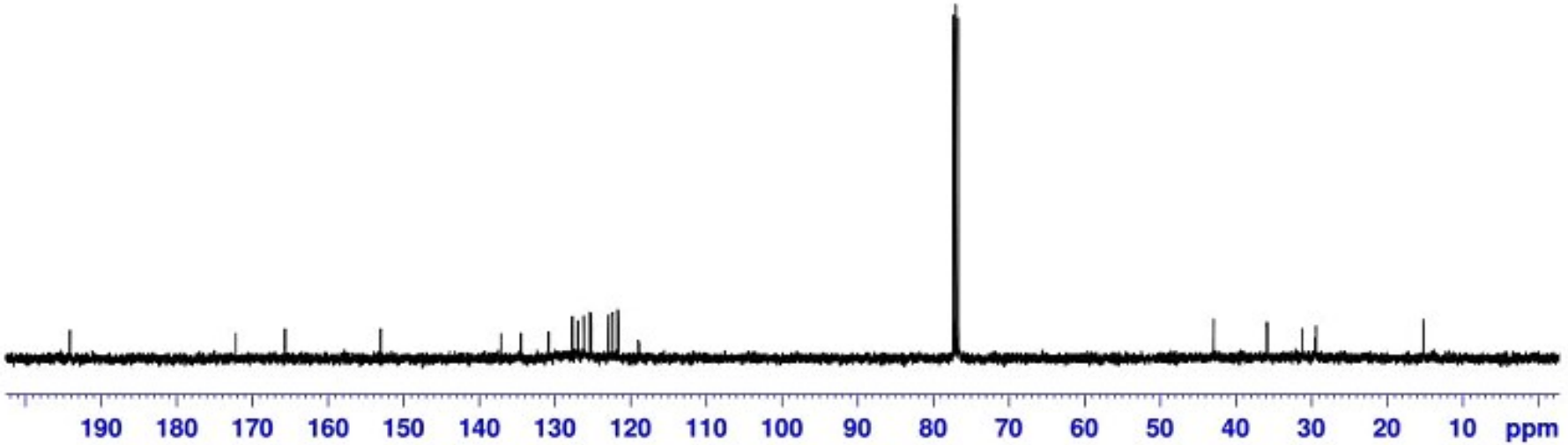
3ae


12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.18
5.05
0.99
2.18
6.02


194.105
172.164
165.676
153.346
137.142
134.541
130.870
127.712
126.967
126.209
125.369
122.921
122.358
121.688
118.974
77.319
77.001
76.683
42.908
35.847
31.176
29.384
15.199


Cl
O
CN
N
S

3ae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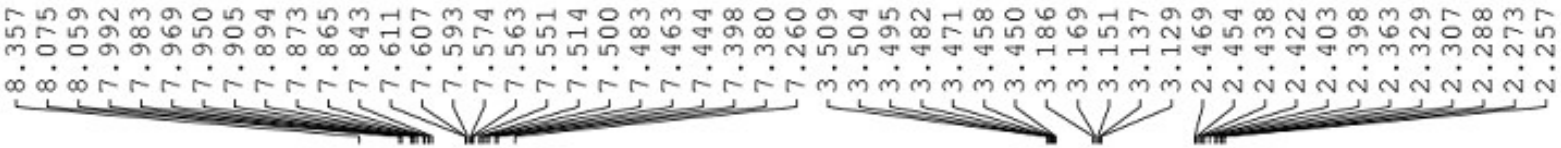
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.905
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7.873
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7.843
7.611
7.607
7.593
7.574
7.563
7.551
7.514
7.500
7.483
7.463
7.444
7.398
7.380
7.260
3.509
3.504
3.495
3.482
3.471
3.458
3.450
3.186
3.169
3.151
3.137
3.129
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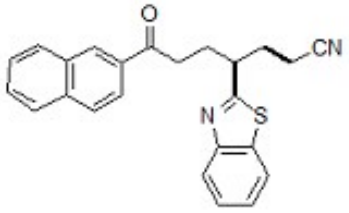
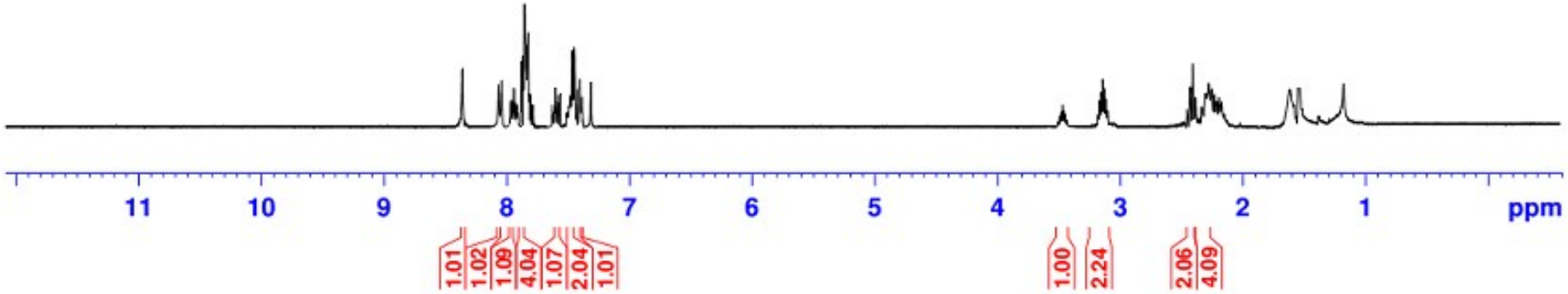
2.454
2.438
2.422
2.403
2.398
2.363
2.329
2.307
2.288
2.273
2.257


O
CN
N
S

3af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9
8
7
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5
4
3
2
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1.09
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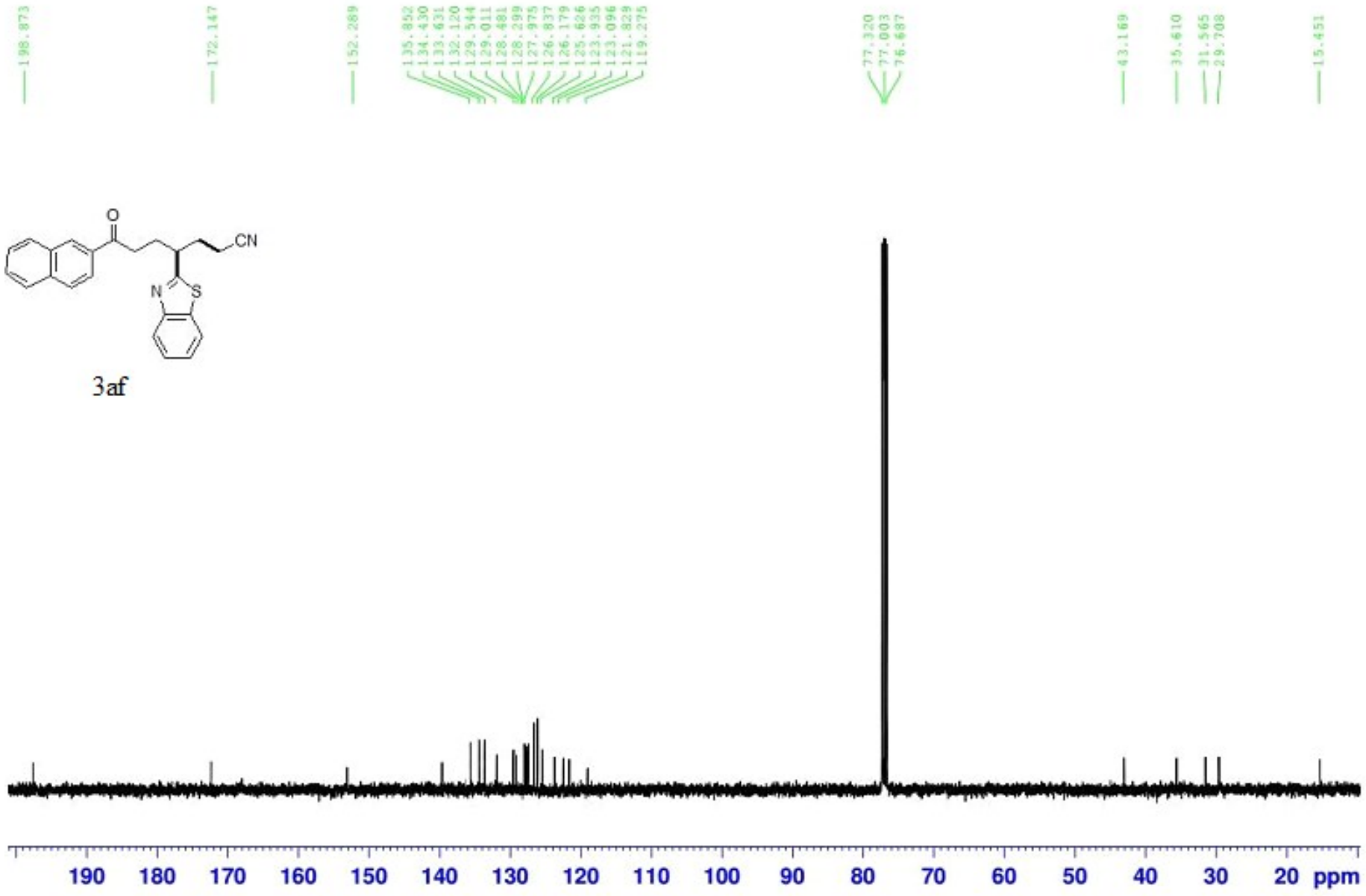
1.07
2.04
1.01
1.00
2.24
2.06
4.09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129.344
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128.299
127.975
126.837
126.179
125.626
123.935
123.096
121.829
119.275
77.320
77.003
76.687
43.169
35.610
31.565
29.708
15.451
O
CN
N
S
190
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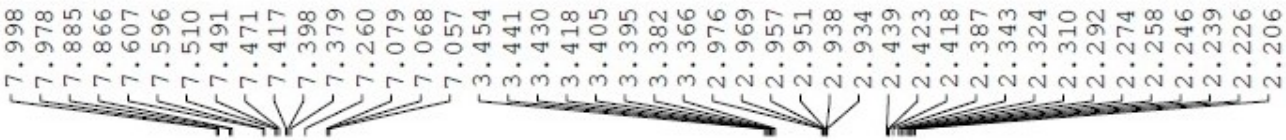
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

3af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7.510
7.491
7.471
7.417
7.398
7.379
7.260
7.079
7.068
7.057
3.454
3.441
3.430
3.418
3.405
3.395
3.382
3.366
2.976
2.969
2.957
2.951
2.938
2.934
2.439
2.423
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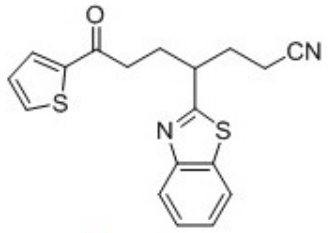
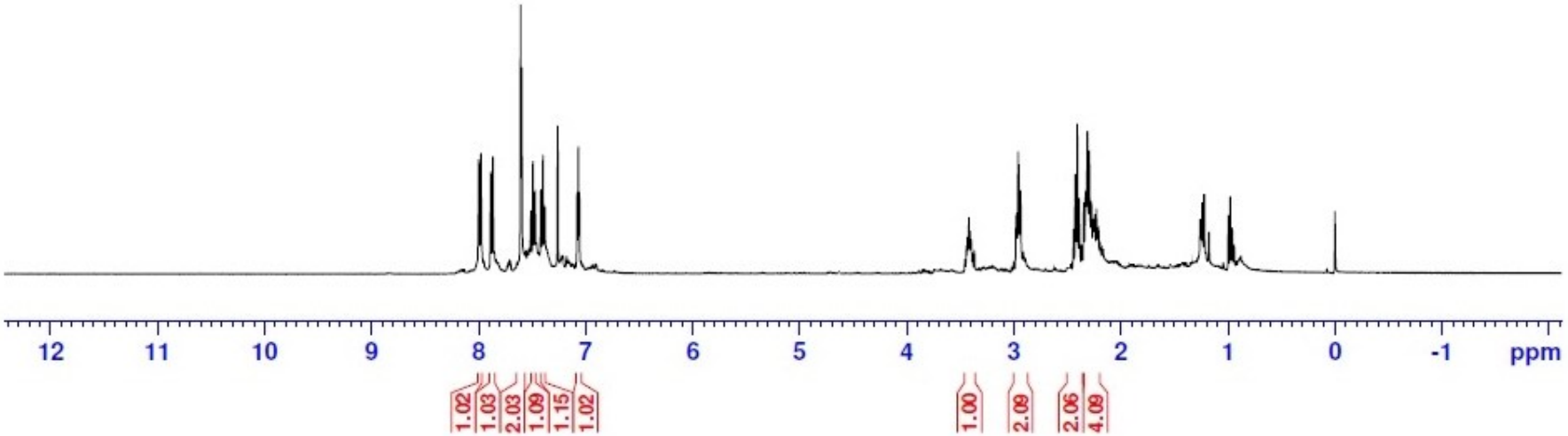
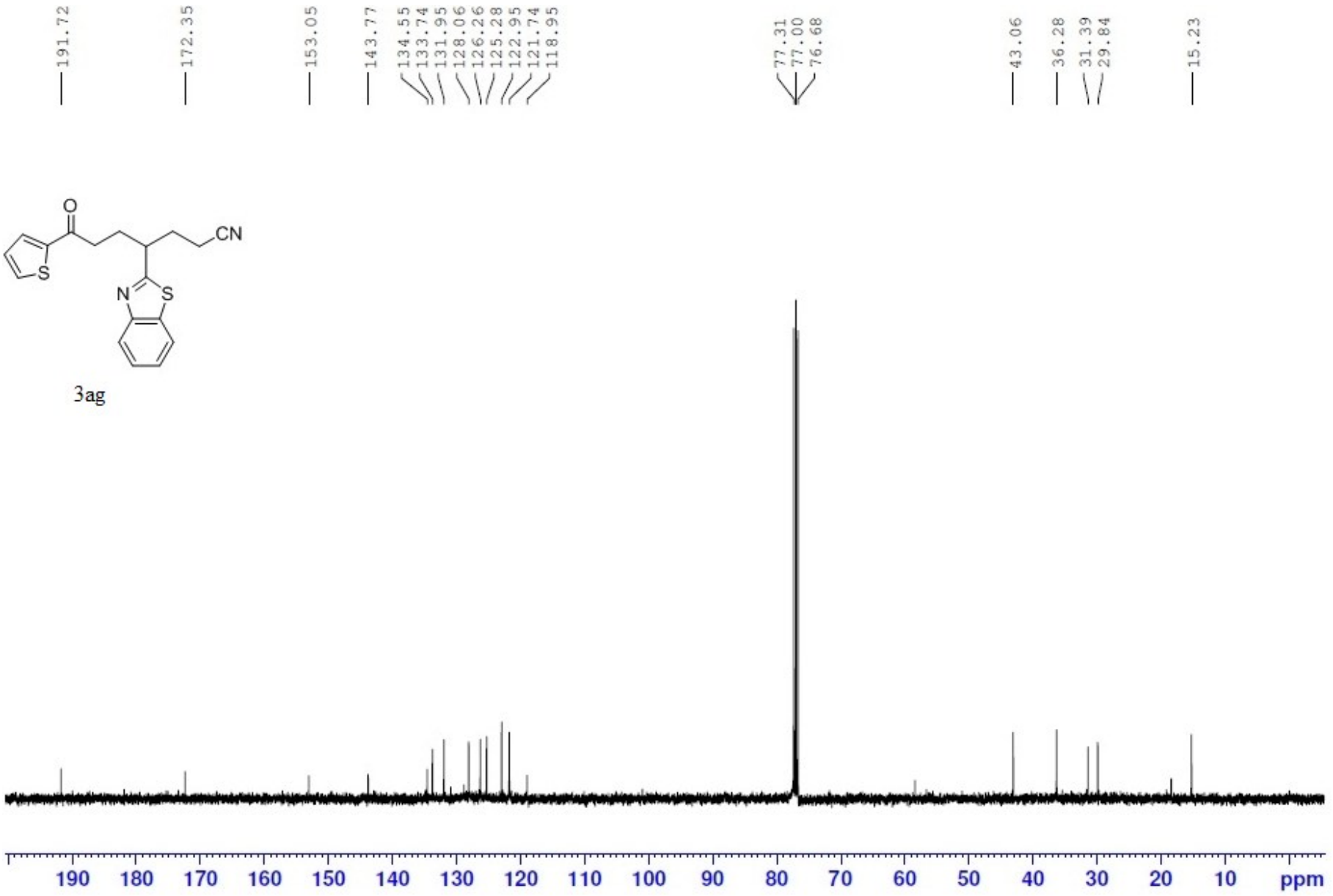
2.206


O
CN
S
N
S

3ag


12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.02
1.03
2.03
1.09
1.15
1.02
1.00
2.09
2.06
4.09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133.74
131.95
128.06
126.26
125.28
122.95
121.74
118.95
77.31
77.00
76.68
43.06
36.28
31.39
29.84
15.23
O
CN
S
N
S
3ag
190
180
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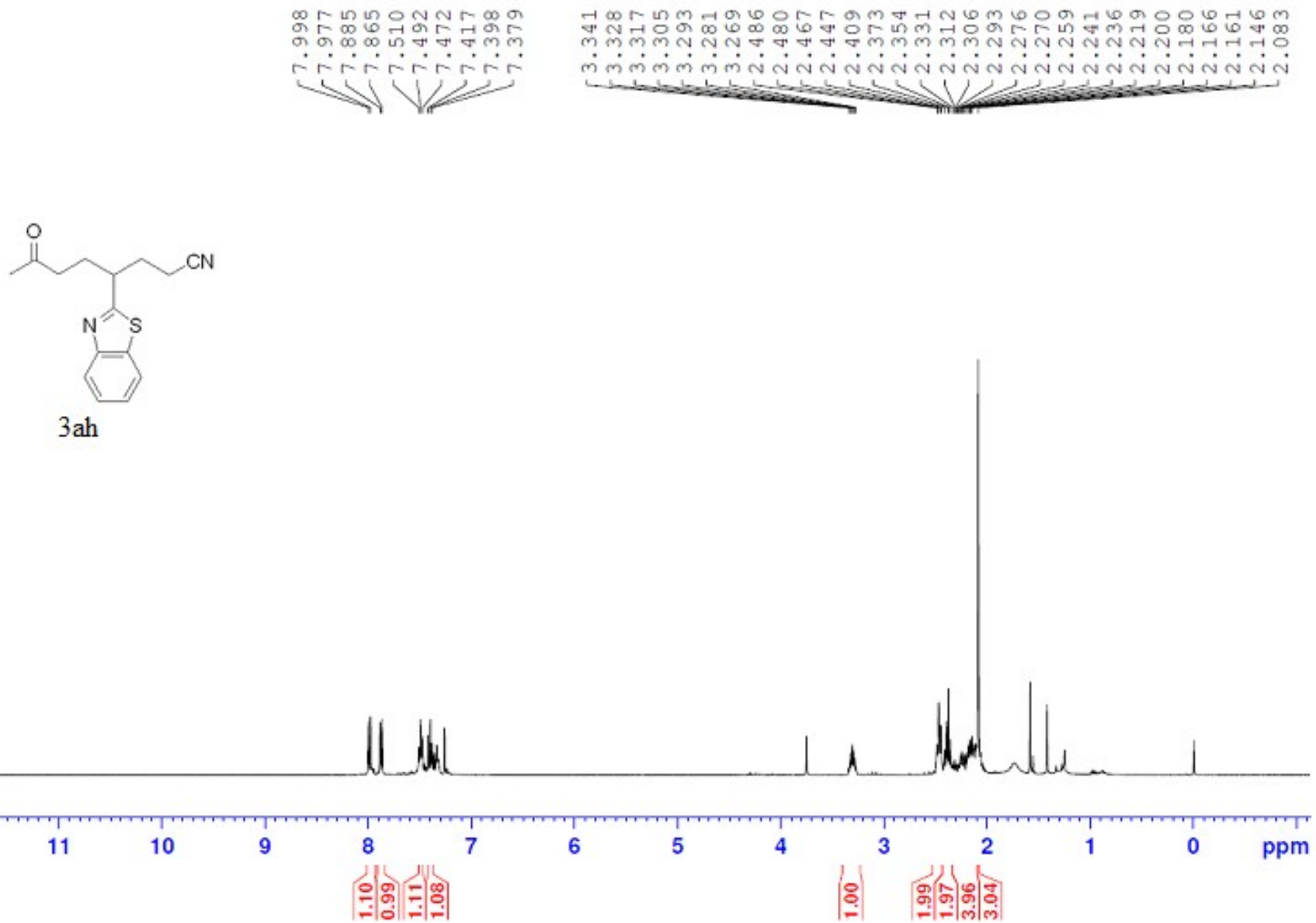
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.379
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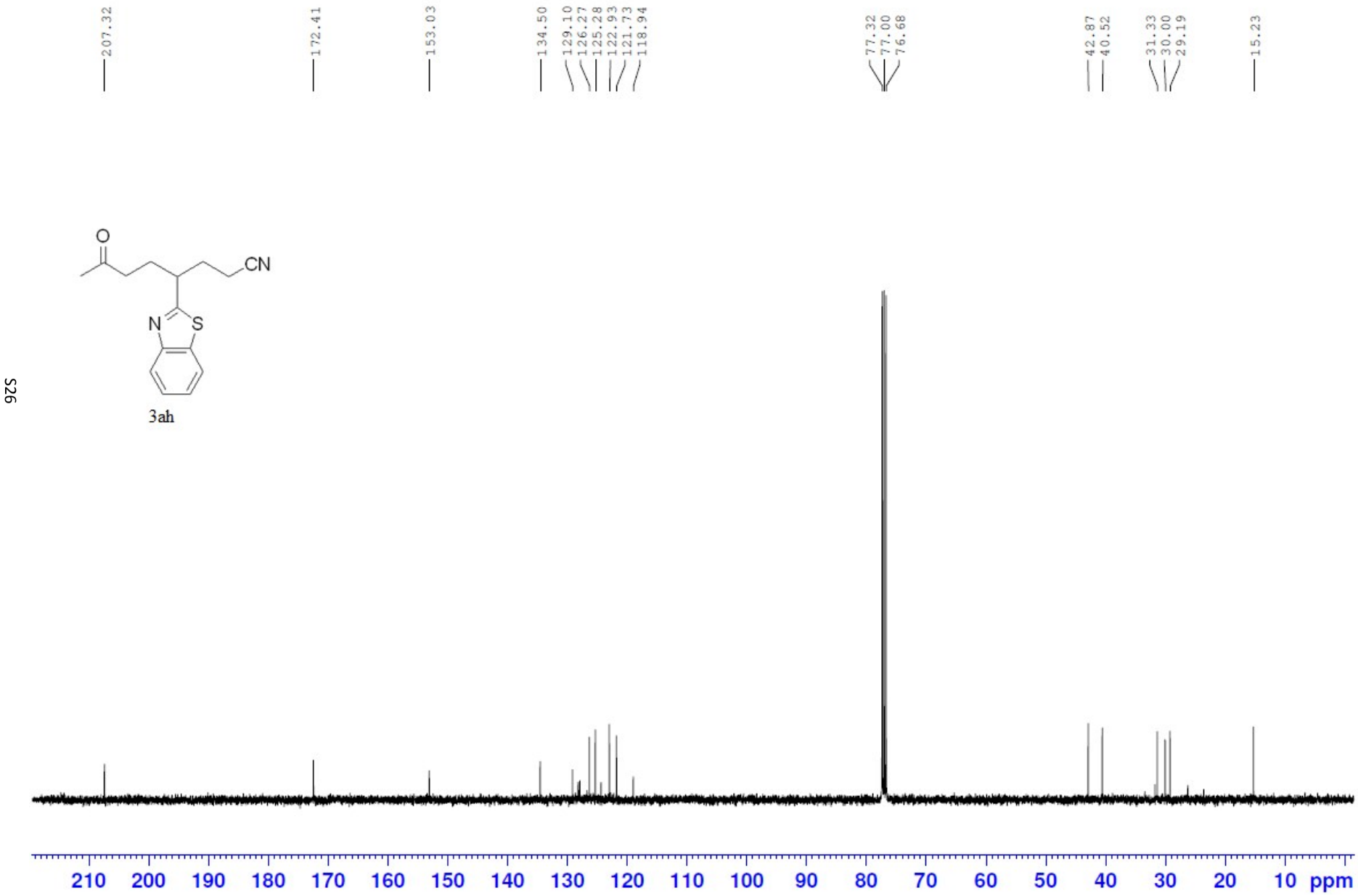
3.328
3.317
3.305
3.293
3.281
3.269
2.486
2.480
2.467
2.447
2.409
2.373
2.354
2.331
2.312
2.306
2.293
2.276
2.270
2.259
2.241
2.236
2.219
2.200
2.180
2.166
2.161
2.146
2.083
O
CN
N
S
3ah
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.10
0.99
1.11
1.08
1.00
1.99
1.97
3.96
3.04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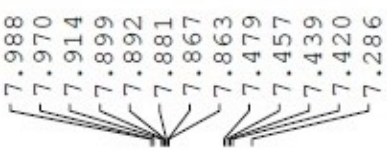
134.50
129.10
126.27
125.28
122.93
121.73
118.94
77.32
77.00
76.68
42.87
40.52
31.33
30.00
29.19
15.23
O
CN
N
S
3ah
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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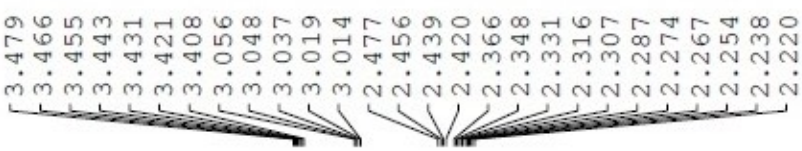
7.286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3.421
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3.056
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3.037
3.019
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2.477
2.456
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2.366
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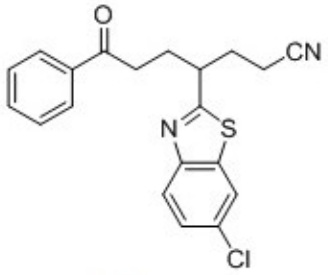
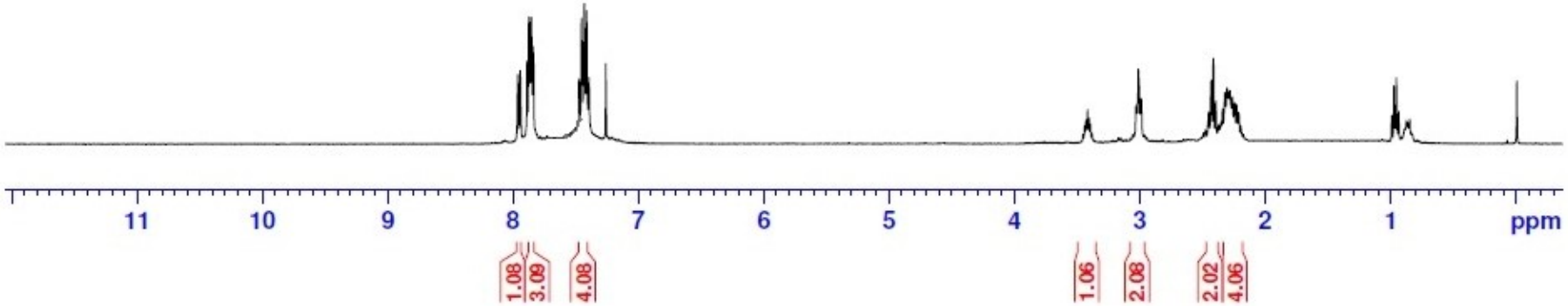
2.287
2.274
2.267
2.254
2.238
2.220


O
CN
N
S
Cl

3ai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9
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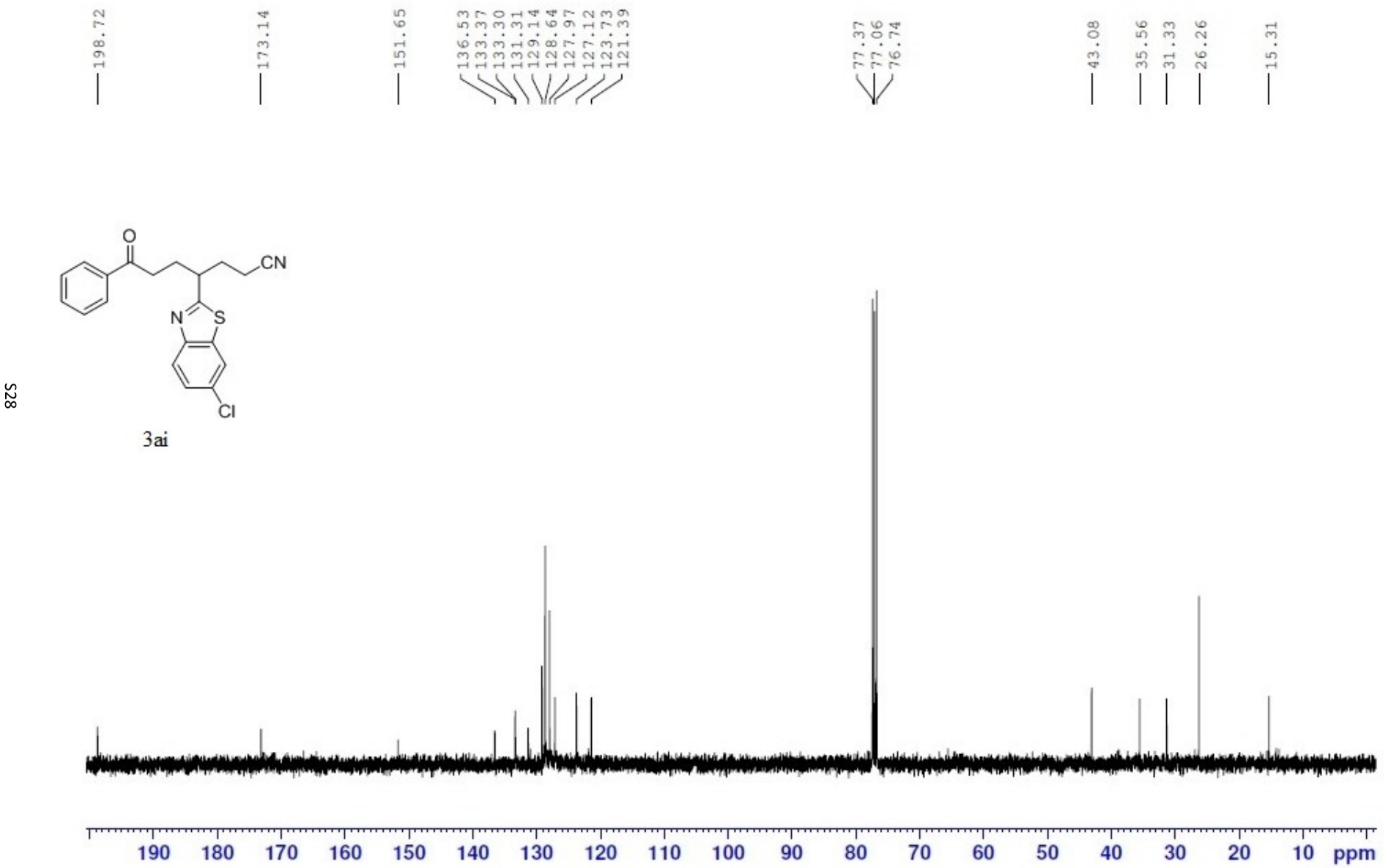
ppm
1.08
3.09
4.08
1.06
2.08
2.02
4.06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173.14
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133.37
133.30
131.31
129.14
128.64
127.97
127.12
123.73
121.39
77.37
77.06
76.74
43.08
35.56
31.33
26.26
15.31
O
CN
N
S
Cl
3ai
190
180
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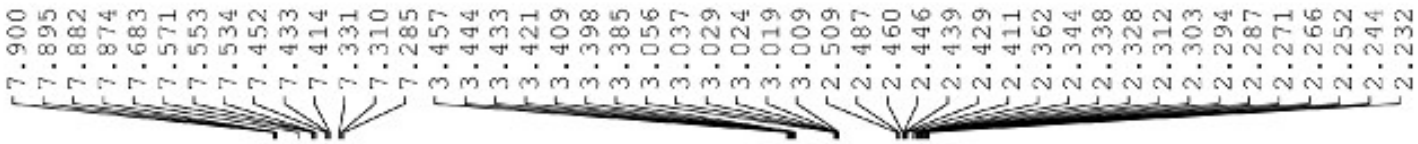
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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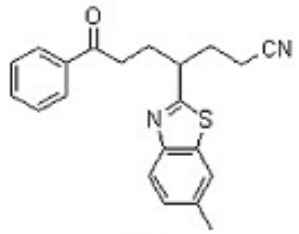
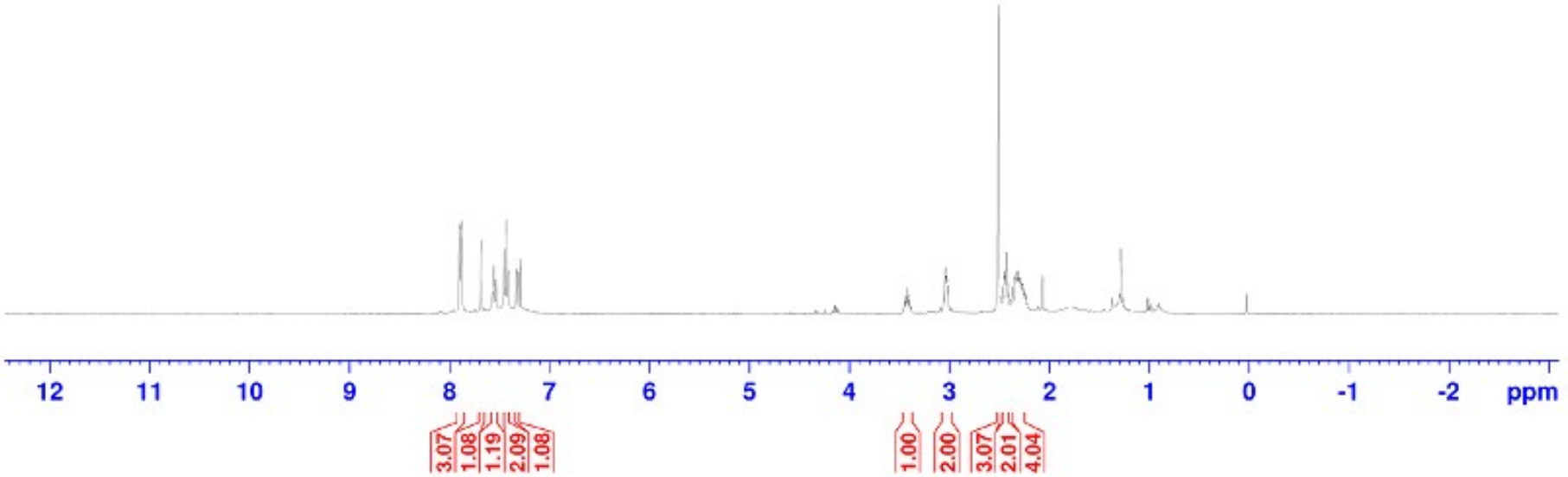
7.553
7.534
7.452
7.433
7.414
7.331
7.310
7.285
3.457
3.444
3.433
3.421
3.409
3.398
3.385
3.056
3.037
3.029
3.024
3.019
3.009
2.509
2.487
2.460
2.446
2.439
2.429
2.411
2.362
2.344
2.338
2.328
2.312
2.303
2.294
2.287
2.271
2.266
2.252
2.244
2.232


O
CN
N
S

3aj


12
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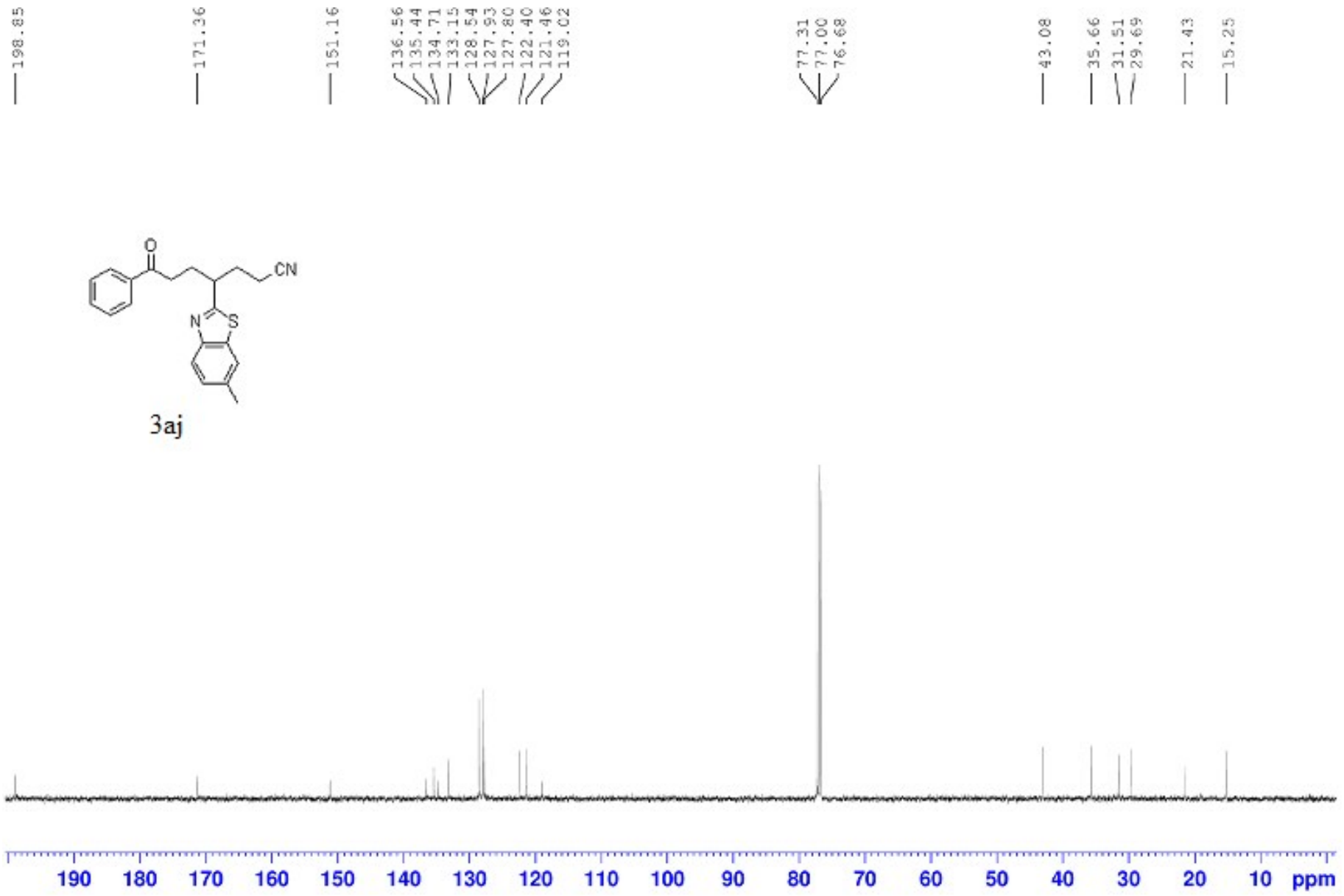
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm
3.07
1.08
1.19
2.09
1.08
1.00
2.00
3.07
2.01
4.04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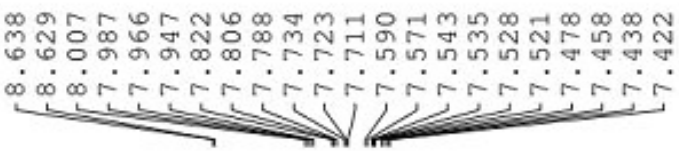
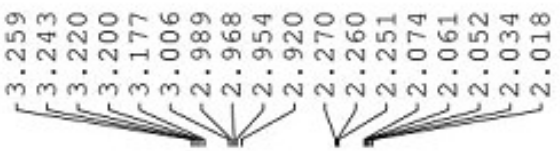
171.36
151.16
136.56
135.44
134.71
133.15
128.54
127.93
127.80
122.40
121.46
119.02
77.31
77.00
76.68
43.08
35.66
31.51
29.69
21.43
15.25
O
CN
N
S
3aj
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.638
8.629
8.007
7.987
7.966
7.947
7.822
7.806
7.788
7.734
7.723
7.711
7.590
7.571
7.543
7.535
7.528
7.521
7.478
7.458
7.438
7.422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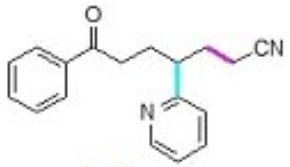
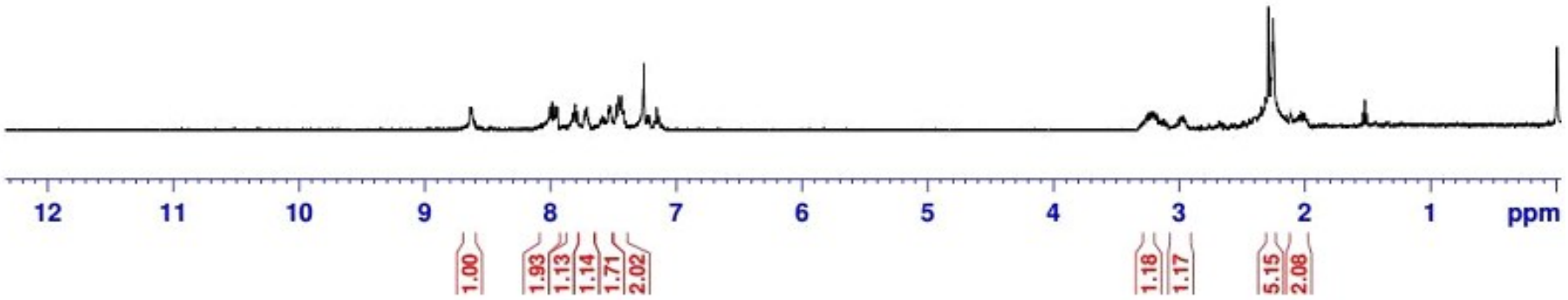
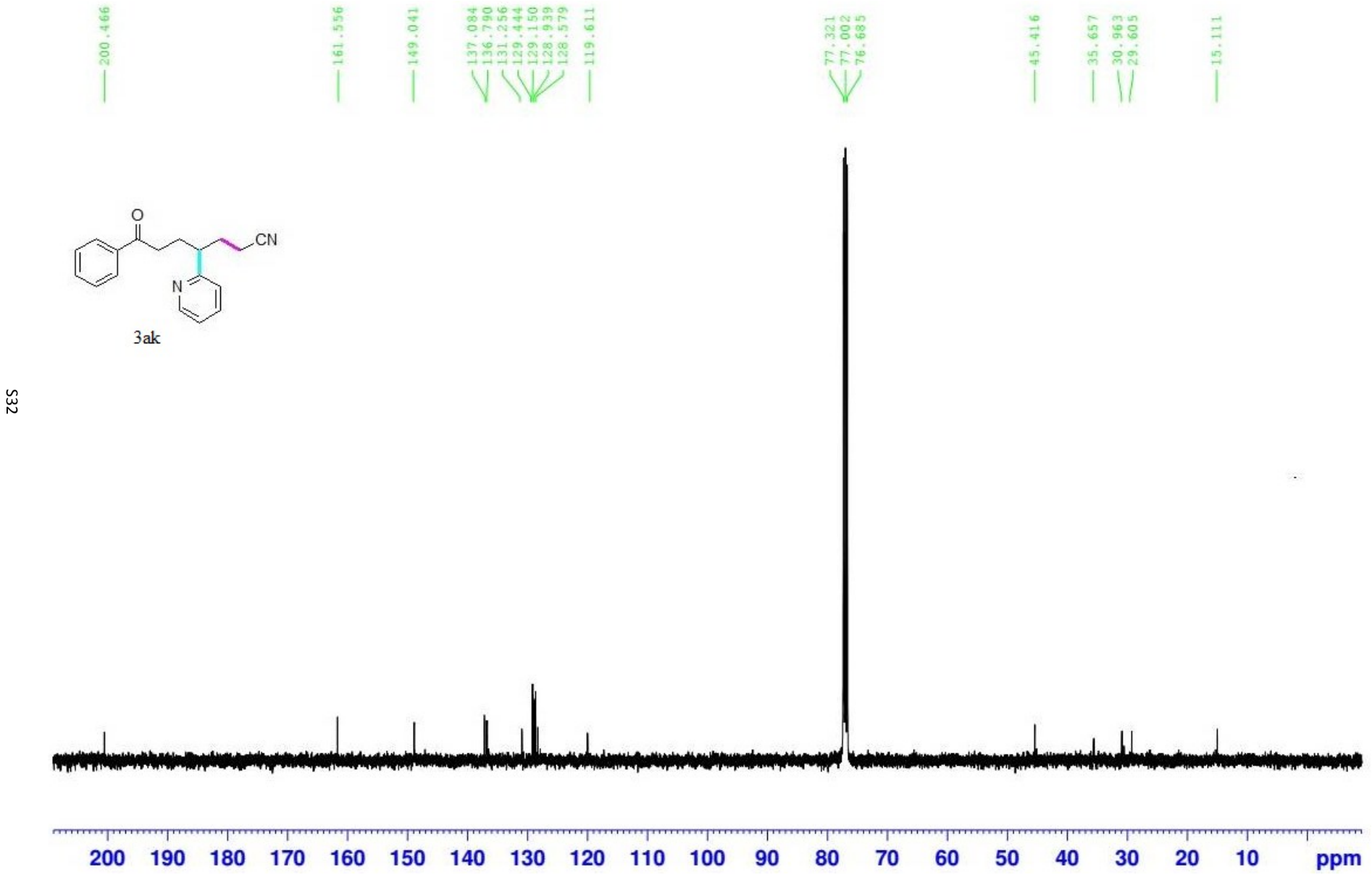
3.243
3.220
3.200
3.177
3.006
2.989
2.968
2.954
2.920
2.270
2.260
2.251
2.074
2.061
2.052
2.034
2.018


O
CN
N

3ak


12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.93
1.13
1.14
1.71
2.02
1.18
1.17
5.15
2.08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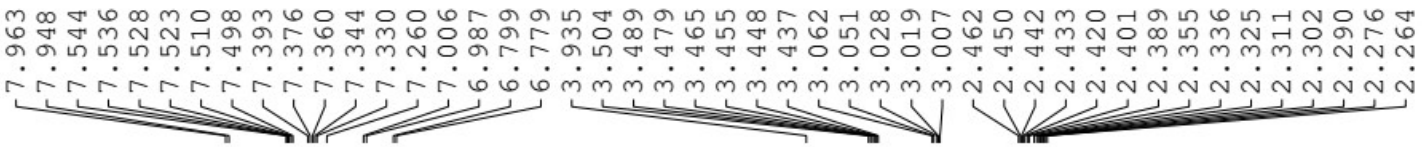
161.556
149.041
137.084
136.790
131.256
129.444
129.150
128.939
128.579
119.611
77.321
77.002
76.685
45.416
35.657
30.963
29.605
15.111
O
CN
N
3ak
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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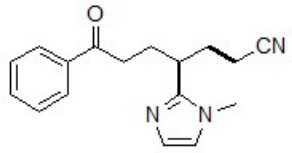
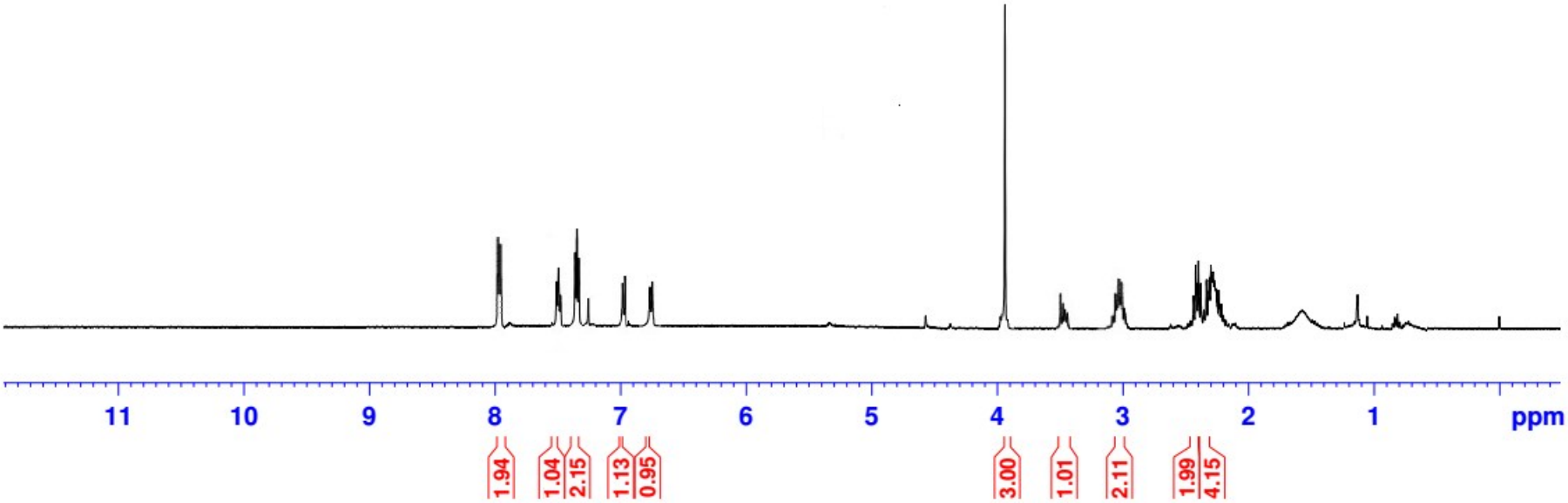
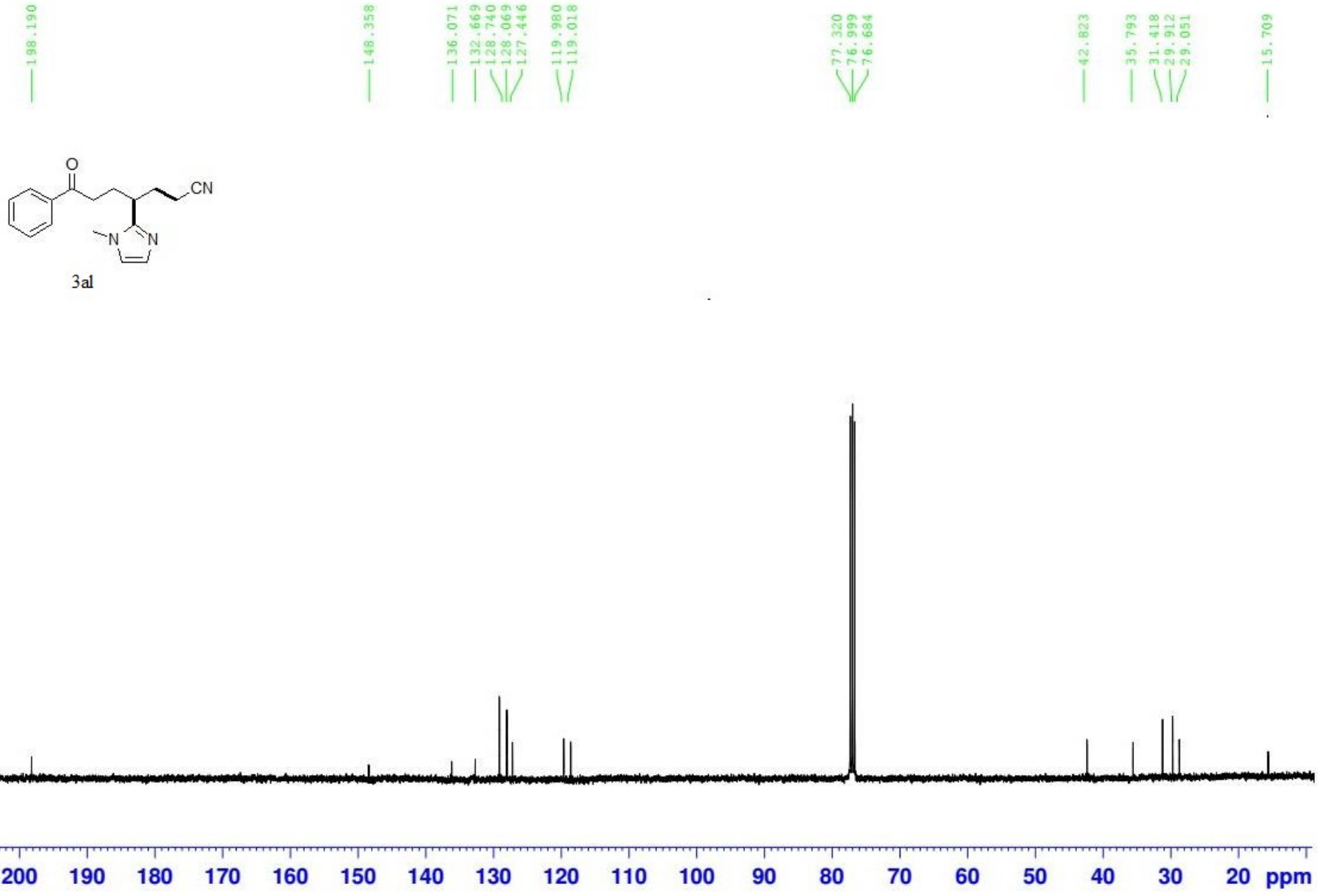
7.948
7.544
7.536
7.528
7.523
7.510
7.498
7.393
7.376
7.360
7.344
7.330
7.260
7.006
6.987
6.799
6.779
3.935
3.504
3.489
3.479
3.465
3.455
3.448
3.437
3.062
3.051
3.028
3.019
3.007
2.462
2.450
2.442
2.433
2.420
2.401
2.389
2.355
2.336
2.325
2.311
2.302
2.290
2.276
2.264


O
CN
N
N

3al


11
10
9
8
7
6
5
4
3
2
1
ppm
1.94
1.04
2.15
1.13
0.95
3.00
1.01
2.11
1.99
4.15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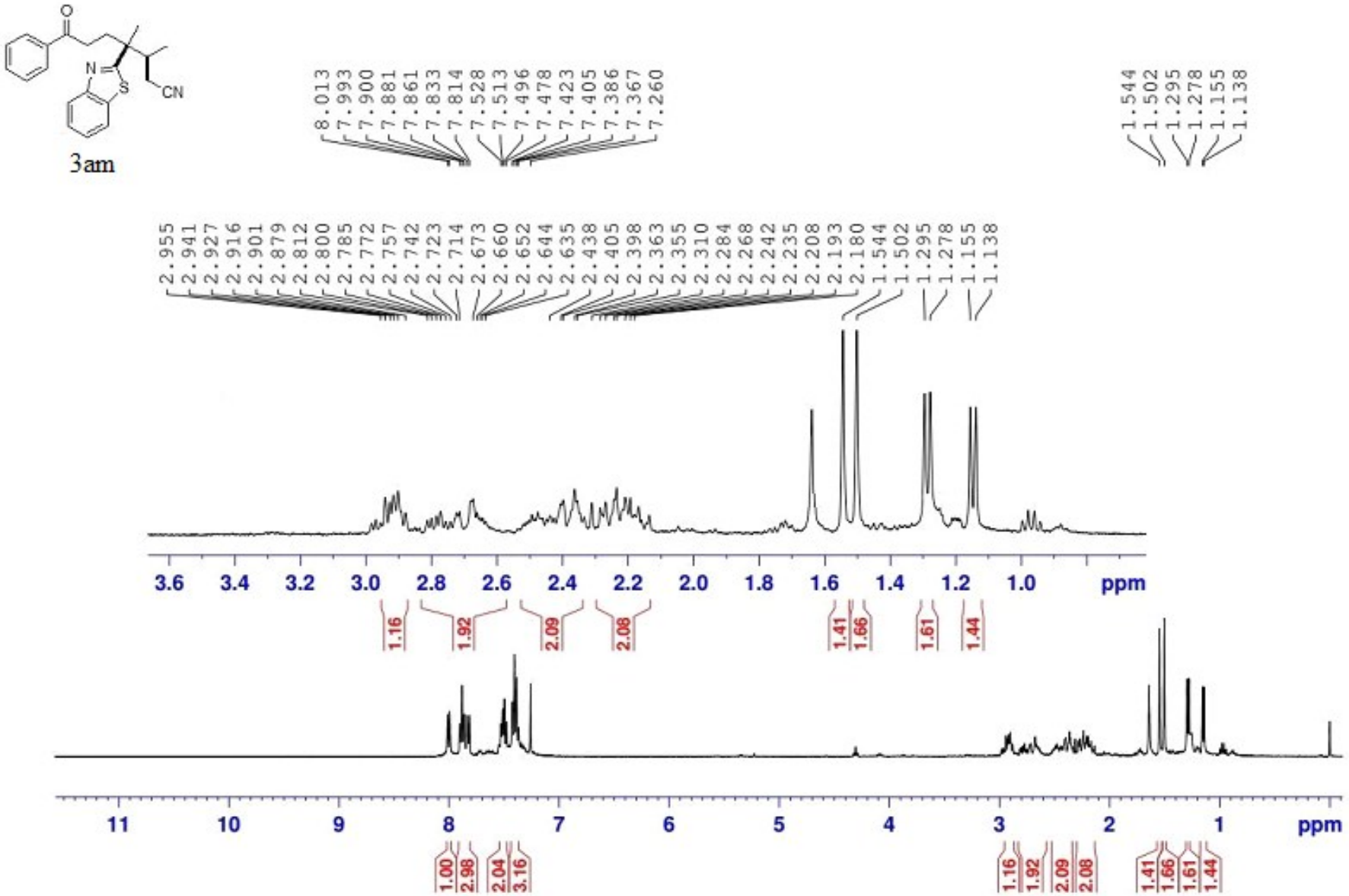
136.071
132.669
128.740
128.069
127.446
119.980
119.018
77.320
76.999
76.684
42.823
35.793
31.418
29.912
29.051
15.709
O
CN
N
N
3al
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


3am
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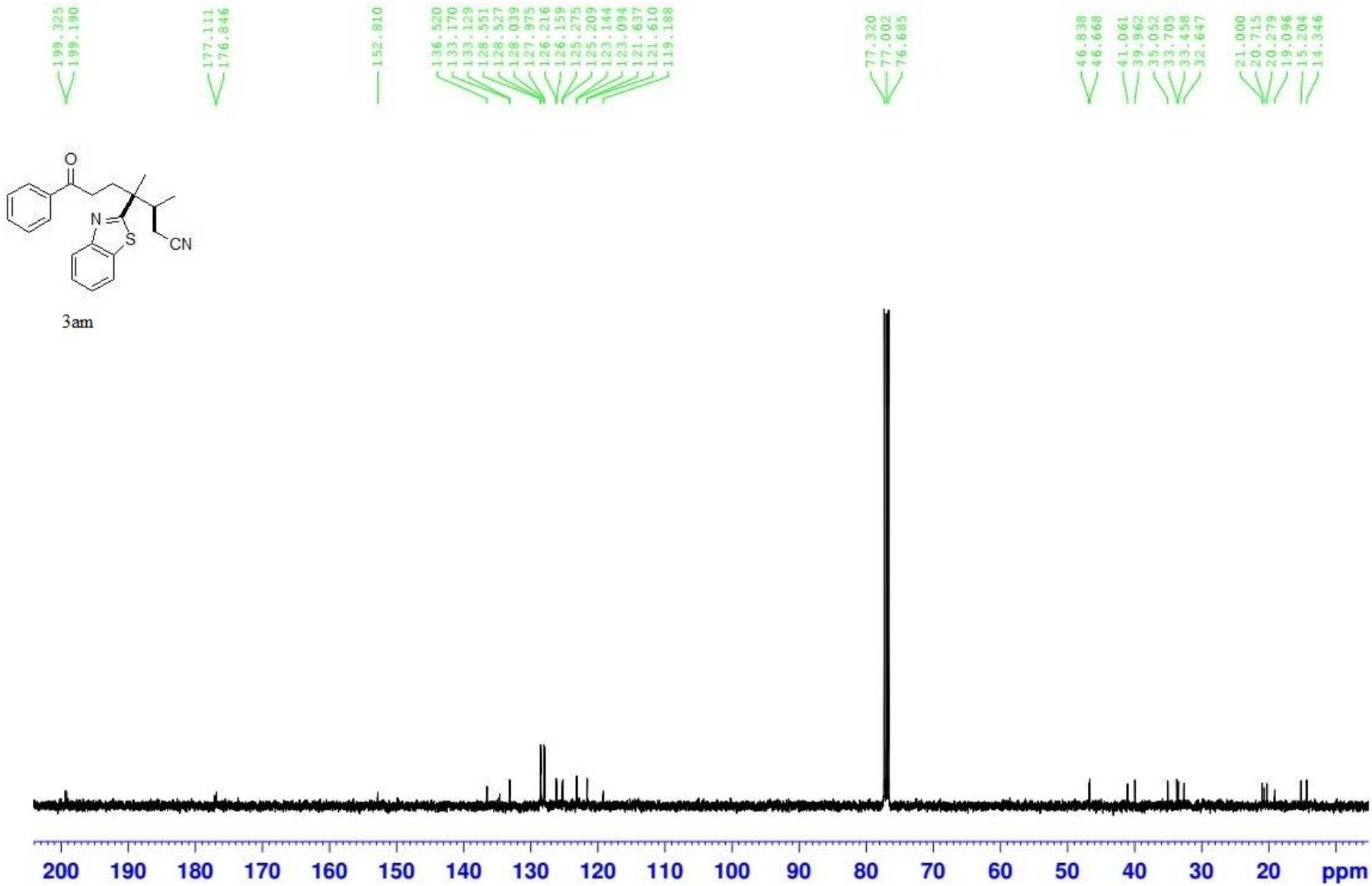
7.900
7.881
7.861
7.833
7.814
7.528
7.513
7.496
7.478
7.423
7.405
7.386
7.367
7.260
1.544
1.502
1.295
1.278
1.155
1.138
2.955
2.941
2.927
2.916
2.901
2.879
2.812
2.800
2.785
2.772
2.757
2.742
2.723
2.714
2.673
2.660
2.652
2.644
2.635
2.438
2.405
2.398
2.363
2.355
2.310
2.284
2.268
2.242
2.235
2.208
2.193
2.180
1.544
1.502
1.295
1.278
1.155
1.138
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
ppm
1.16
1.92
2.09
2.08
1.41
1.66
1.61
1.44
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.98
2.04
3.16
1.16
1.92
2.09
2.08
1.41
1.66
1.61
1.44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199.190
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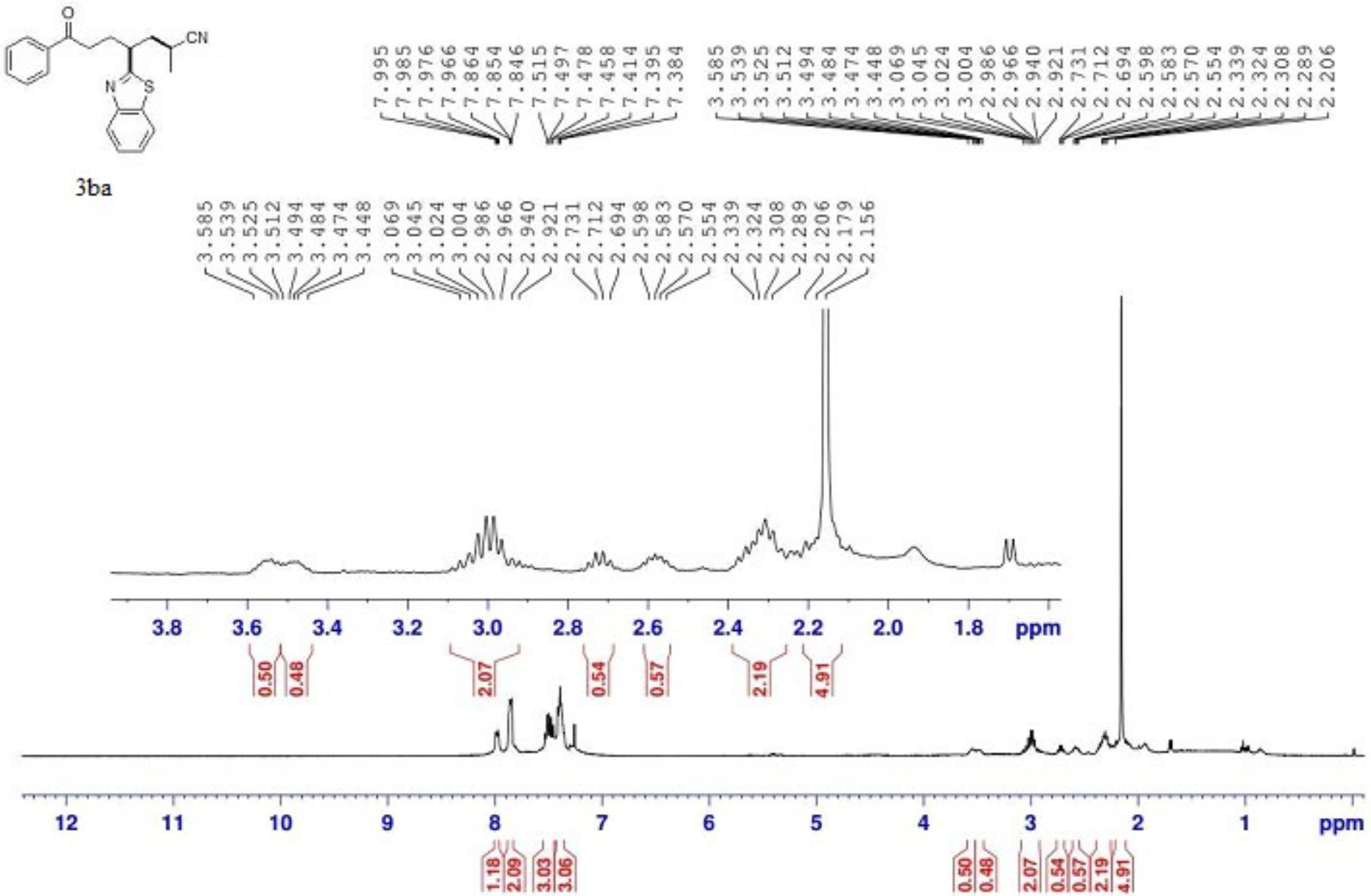
176.846
152.810
136.520
133.170
133.129
128.551
128.527
128.039
127.975
126.216
126.159
125.275
125.209
123.144
123.094
121.637
121.610
119.188
77.320
77.002
76.685
46.838
46.668
41.061
39.962
35.052
33.705
33.458
32.647
21.000
20.715
20.279
19.096
15.204
14.346
O
N
S
CN
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

3am


O
CN
N
S
3ba
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7.976
7.966
7.864
7.854
7.846
7.515
7.497
7.478
7.458
7.414
7.395
7.384
3.585
3.539
3.525
3.512
3.494
3.484
3.474
3.448
3.069
3.045
3.024
3.004
2.986
2.966
2.940
2.921
2.731
2.712
2.694
2.598
2.583
2.570
2.554
2.339
2.324
2.308
2.289
2.206
2.179
2.156
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
ppm
0.50
0.48
2.07
0.54
0.57
2.19
4.91
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.18
2.09
3.03
3.06
0.50
0.48
2.07
0.54
0.57
2.19
4.91


198.866
198.786
172.937
172.724
153.106
136.414
134.441
133.147
133.110
129.282
128.671
128.493
127.880
126.159
125.193
125.145
122.846
122.270
121.717
121.685
77.320
77.002
76.684
42.280
41.491
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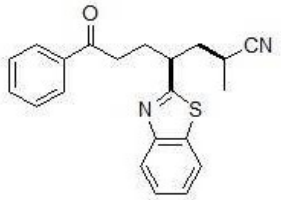
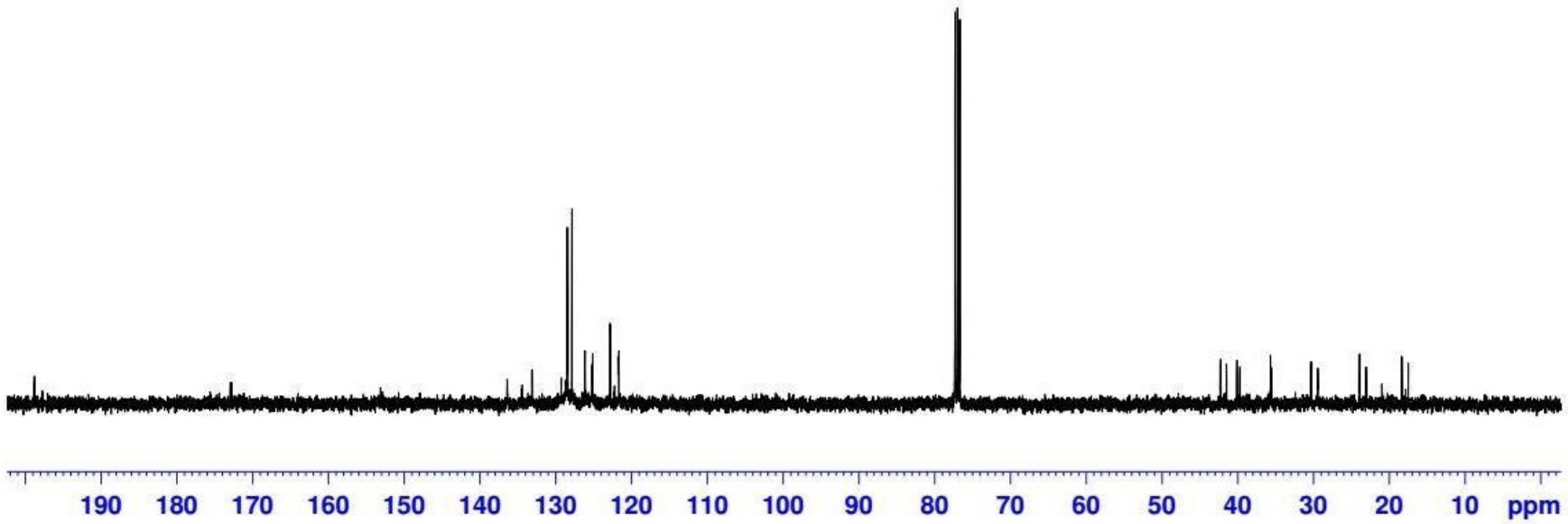
39.743
35.689
35.517
30.884
30.329
23.942
23.067
18.355
17.503


O
CN
N
S

3ba


190
180
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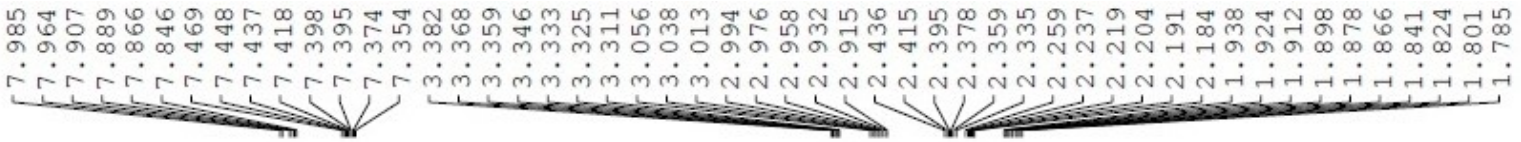
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.985
7.964
7.907
7.889
7.866
7.846
7.469
7.448
7.437
7.418
7.398
7.395
7.374
7.354
3.382
3.368
3.359
3.346
3.333
3.325
3.311
3.056
3.038
3.013
2.994
2.976
2.958
2.932
2.915
2.436
2.415
2.395
2.378
2.359
2.335
2.259
2.237
2.219
2.204
2.191
2.184
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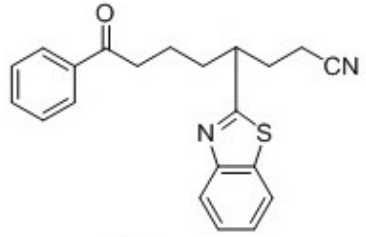
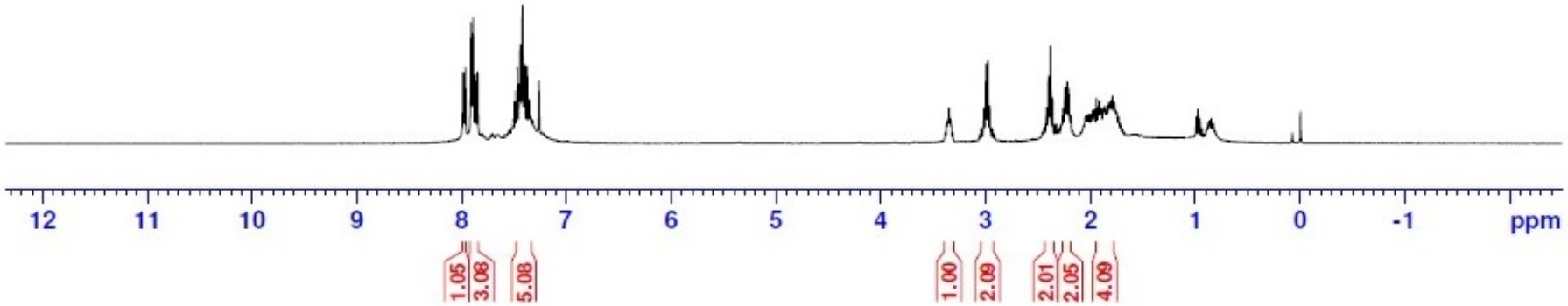
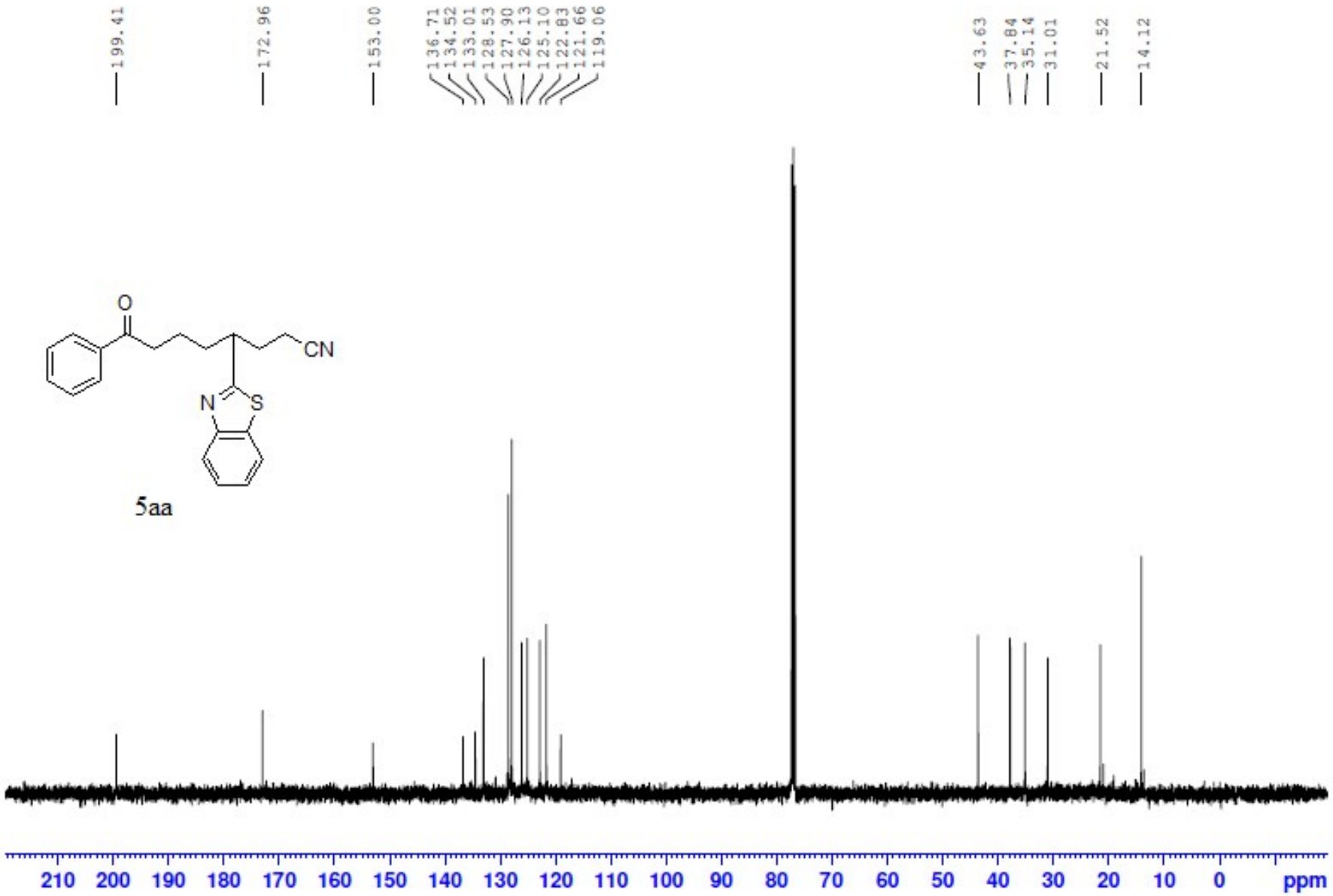
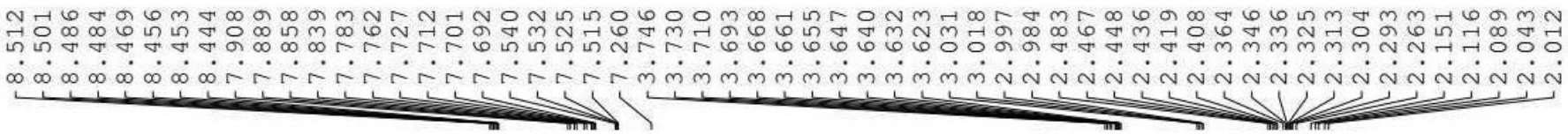
1.924
1.912
1.898
1.878
1.866
1.841
1.824
1.801
1.785


O
CN
N
S

5aa


12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.05
3.08
5.08
1.00
2.09
2.01
2.05
4.09


199.41
172.96
153.00
136.71
134.52
133.01
128.53
127.90
126.13
125.10
122.83
121.66
119.06
43.63
37.84
35.14
31.01
21.52
14.12
O
CN
N
S
5aa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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8.501
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8.484
8.469
8.456
8.453
8.444
7.908
7.889
7.858
7.839
7.783
7.762
7.727
7.712
7.701
7.692
7.540
7.532
7.525
7.515
7.260
3.746
3.730
3.710
3.693
3.668
3.661
3.655
3.647
3.640
3.632
3.623
3.031
3.018
2.997
2.984
2.483
2.467
2.448
2.436
2.419
2.408
2.364
2.346
2.336
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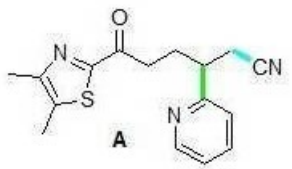
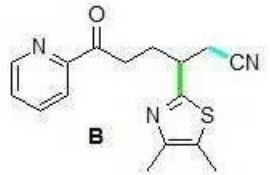
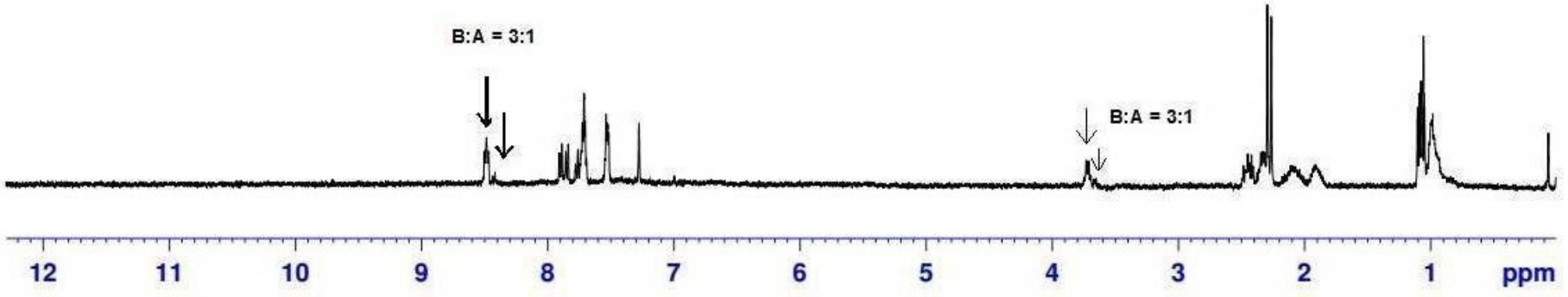
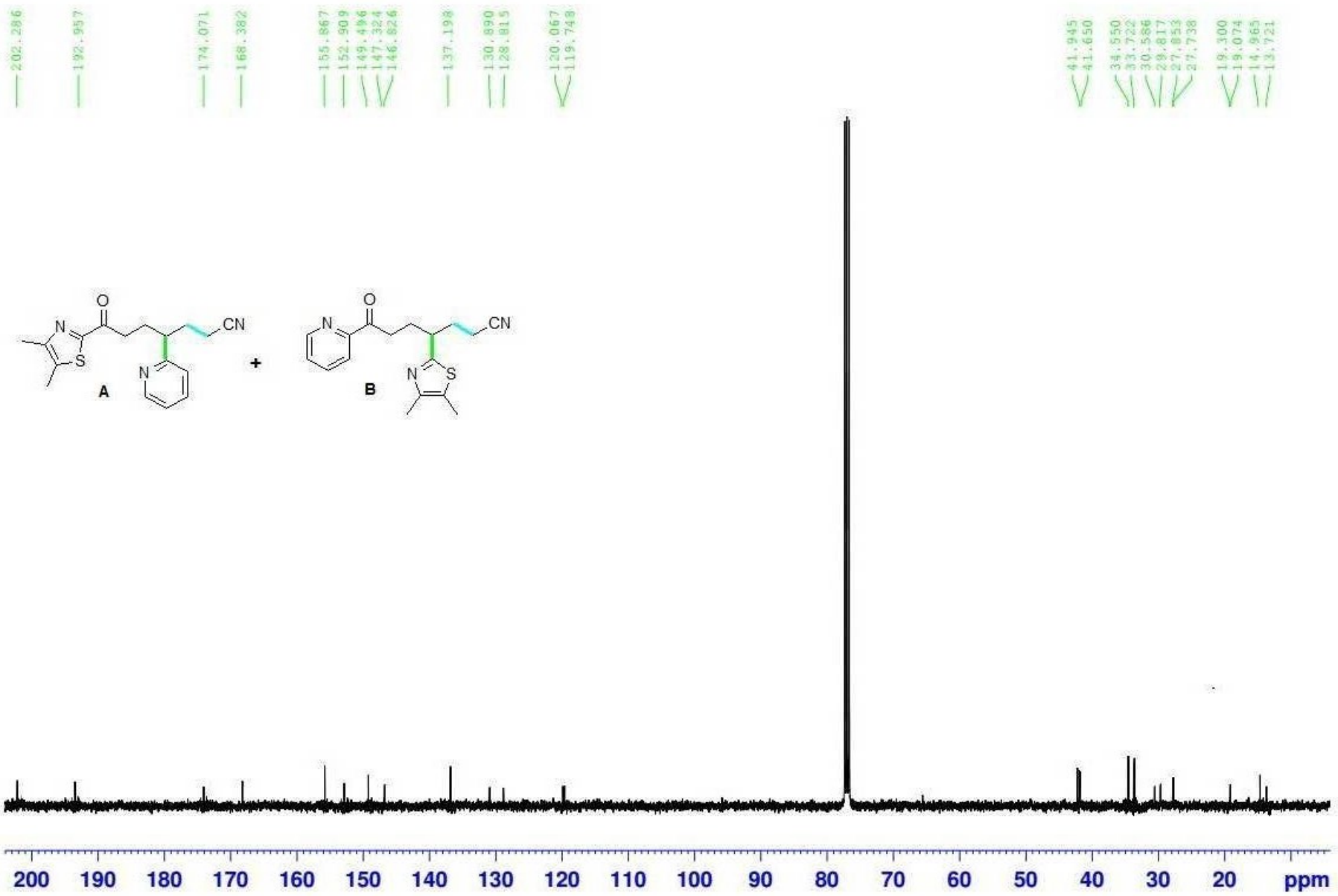
2.313
2.304
2.293
2.263
2.151
2.116
2.089
2.043
2.012


O
N
S
N
CN
A


O
N
CN
N
S
B


B:A = 3:1
B:A = 3:1
12
11
10
9
8
7
6
5
4
3
2
1
ppm


202.286
192.957
174.071
168.382
155.867
152.909
149.496
147.324
146.826
137.198
130.890
128.815
120.067
119.748
41.945
41.650
34.550
33.722
30.586
29.817
27.853
27.738
19.300
19.074
14.965
13.721
O
N
S
CN
N
A
+
O
N
CN
N
S
B
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

(F) Computational studies

1) Computational Methods

All structures were optimized at the level of M06-2X/def2-SVP [1] with solvent acetonitrile in the PCM solvent model. Vibrational analyses were performed on all optimized geometries, to ensure that the optimized structures corresponded to local minima [2]. And further single-point energies were obtained with def2-TZVP. Solvent effect was also considered using SMD model with CH_3CN as the solvent for the single-point energy calculation at larger basis set. The solution-phase Gibbs free energy was determined by adding the solvation single-point energy and the gas-phase thermal correction to the Gibbs free energy obtained from vibrational frequency calculation [3]. Unless otherwise specified, the solution-phase Gibbs free energy was used in the discussion. The Gaussian 09 suite of programs [4] was used throughout.

References

1. Zhao, Y.; Truhlar, D. G.*Theor. Chem. Acc.* **2008**, *120*, 215−241.
2. Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta.***1973**, *28*, 213-222.
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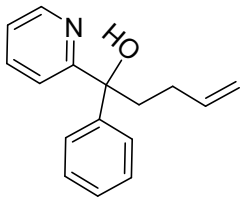
For example of 1k

The generated CH_2CN radical is ready to attack the terminal carbon of alkenyl moiety to afford intermediate **INT0 or INT0'** without transition states. Subsequently, the formed alkyl radical might undergo radical nucleophilic attack to either C of 2-pyridyl moiety (**path-I**) or C of phenyl moiety (**path-II**). Computational results show that the energy barriers for **path-I** and **path-II** are 52.9 and 58.4 kJ/mol, respectively, relative to **INT0 and INT0'**, suggesting that **path-I** is more favorable than **path-II** (Figure S1). Next, the formed radical addition intermediate (**INT1**) could undergo C-C bond cleavage to afford the heteroaryl ring migration intermediate **INT2**. The distance between cyano moiety and pyridyl group in INT1, TS2 and INT2 are 3.42 – 2.98 Å, suggesting there are pi-pi stacking interactions



1k

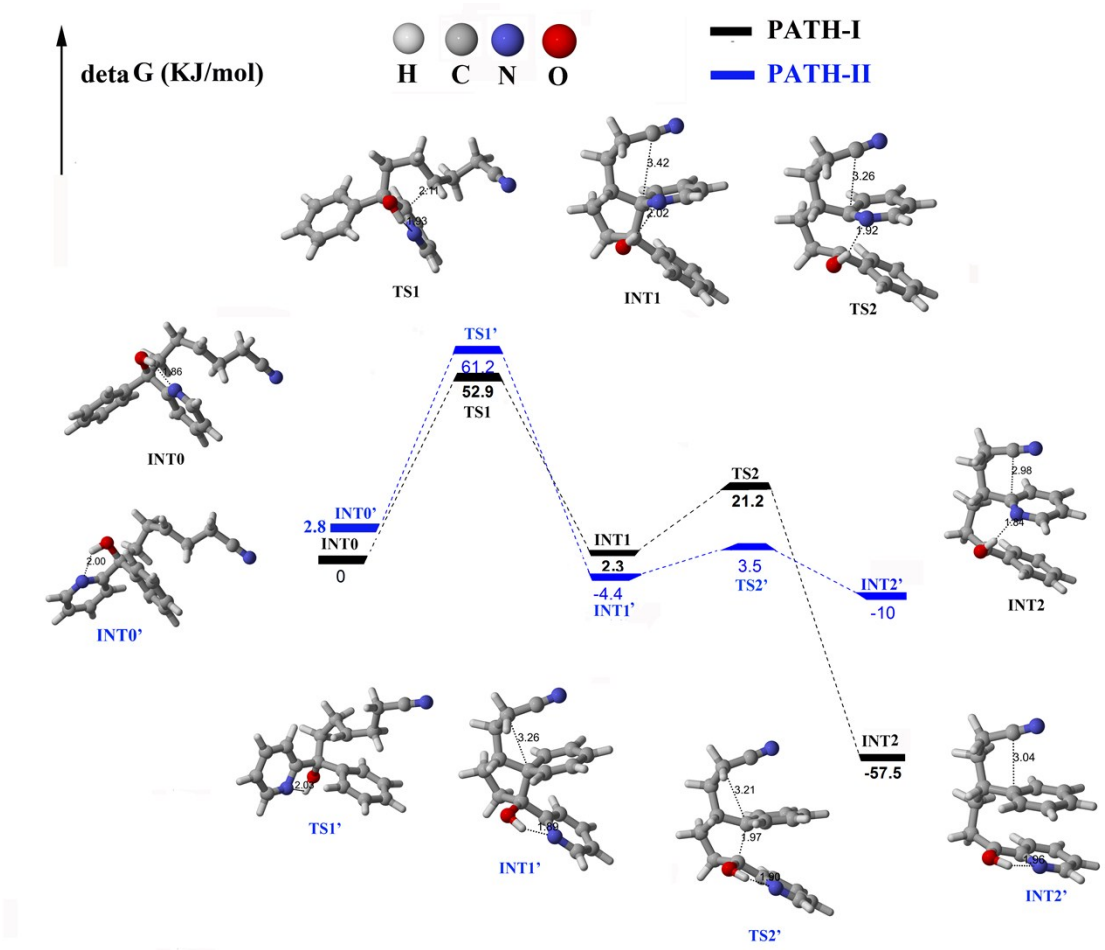


Figure S1. Energy profile (kJ/mol) for the CH_2CN radical attacking 1ab. Bond lengths are shown in Å.

2) **Cartesian Coordinates of Stationary Points**

1ab

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.891610	-1.817261	-0.300822
2	6	0	-1.683660	-2.340072	0.432956
3	6	0	-0.300203	-1.914692	-0.062291
4	6	0	0.225631	-0.619808	0.601532
5	1	0	-3.841444	-1.987254	0.219623
6	1	0	-1.747368	-3.441230	0.409939
7	1	0	-1.774731	-2.082066	1.499640
8	1	0	0.429275	-2.701377	0.182569
9	1	0	-0.297624	-1.810852	-1.157011
10	6	0	-2.933952	-1.232070	-1.498169
11	1	0	-3.886302	-0.928038	-1.937839

12	1	0	-2.035238	-1.025842	-2.084101
13	8	0	0.201000	-0.774974	1.999522
14	1	0	-0.582509	-0.274927	2.297576
15	6	0	1.661153	-0.294365	0.183625
16	6	0	2.382400	0.613962	0.970072
17	6	0	2.275845	-0.837505	-0.947570
18	6	0	3.682050	0.978014	0.629891
19	1	0	1.908917	1.026886	1.862258
20	6	0	3.581780	-0.474337	-1.290031
21	1	0	1.748295	-1.553539	-1.577841
22	6	0	4.287914	0.433524	-0.505387
23	1	0	4.228672	1.687234	1.253856
24	1	0	4.046553	-0.911120	-2.175442
25	1	0	5.307860	0.714588	-0.772706
26	6	0	-0.697109	0.551643	0.232630
27	6	0	-0.652097	1.189401	-1.010543
28	6	0	-2.485165	1.825369	0.910475
29	6	0	-1.592309	2.176407	-1.281202
30	1	0	0.103374	0.908914	-1.746493
31	6	0	-2.538402	2.497893	-0.306175
32	1	0	-3.195122	2.058685	1.708566
33	1	0	-1.590082	2.692713	-2.242490
34	1	0	-3.294796	3.263383	-0.478374
35	7	0	-1.581332	0.878144	1.169736

M06-2X/def2-TZVP/SMD//M06-2X/def2-SVP G=-748.7762193770

CH_2CN

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.001923	-1.201538	0.000000
2	1	0	-0.002117	-1.741079	0.946170
3	1	0	-0.002117	-1.741079	-0.946170
4	6	0	0.000000	0.195368	0.000000
5	7	0	0.002253	1.359882	0.000000

M06-2X/def2-TZVP/SMD//M06-2X/def2-SVP G= -132.0849274170

INT0

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	2.027783	-1.017279	-1.180308
2	6	0	1.027733	-2.118362	-1.041323
3	6	0	-0.183410	-1.786923	-0.155797
4	6	0	-0.985888	-0.565488	-0.653206
5	1	0	2.247330	-0.608158	-2.169011
6	1	0	1.510523	-3.013536	-0.604983
7	1	0	0.656033	-2.403213	-2.033449
8	1	0	-0.855113	-2.659094	-0.140190
9	1	0	0.139827	-1.619317	0.883101
10	6	0	2.848325	-0.537975	-0.029587
11	1	0	2.867341	0.565228	0.002350
12	1	0	2.414331	-0.876707	0.924604
13	6	0	4.304340	-1.047673	-0.121223
14	8	0	-1.137264	-0.643592	-2.045068
15	1	0	-0.690351	0.151516	-2.397511
16	6	0	-2.368715	-0.488994	0.007917
17	6	0	-3.404281	0.161140	-0.673455
18	6	0	-2.624489	-1.010181	1.280713
19	6	0	-4.665707	0.290367	-0.095225
20	1	0	-3.210992	0.555870	-1.671538
21	6	0	-3.887817	-0.879918	1.861707
22	1	0	-1.841948	-1.531380	1.834230
23	6	0	-4.912493	-0.229306	1.176645
24	1	0	-5.462345	0.798529	-0.641626
25	1	0	-4.068913	-1.295903	2.854262
26	1	0	-5.900254	-0.129467	1.629483
27	6	0	-0.243679	0.743206	-0.317561
28	6	0	0.057267	1.121850	0.995486
29	6	0	0.731213	2.646039	-1.166790
30	6	0	0.735744	2.317003	1.202155
31	1	0	-0.238422	0.495053	1.838167
32	6	0	1.088387	3.098318	0.099788
33	1	0	0.978032	3.229487	-2.057862
34	1	0	0.988934	2.638430	2.213612
35	1	0	1.621884	4.041108	0.217978
36	7	0	0.077925	1.498956	-1.362871
37	1	0	4.772203	-0.701188	-1.053901
38	1	0	4.327167	-2.146967	-0.132384
39	6	0	5.128126	-0.587318	0.999759
40	7	0	5.751819	-0.212184	1.895307

M06-2X/def2-TZVP/SMD//M06-2X/def2-SVP G= -881.7156345060

INT0’

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.981223	-1.457872	-0.896717
2	6	0	0.889051	-2.410298	-0.535510
3	6	0	-0.288566	-1.810719	0.252372
4	6	0	-1.012018	-0.676797	-0.491154
5	1	0	2.201045	-1.262595	-1.948887
6	1	0	1.299877	-3.229171	0.085072
7	1	0	0.487998	-2.870426	-1.447461
8	1	0	-1.015462	-2.613956	0.450342
9	1	0	0.058293	-1.440493	1.229516
10	6	0	2.793164	-0.736377	0.125799
11	1	0	2.637420	0.355912	0.047733
12	1	0	2.482182	-1.026711	1.142180
13	6	0	4.299013	-1.022597	-0.043180
14	8	0	-1.188508	-1.078533	-1.825993
15	1	0	-1.983239	-0.606715	-2.131217
16	6	0	-2.402189	-0.406840	0.106922
17	6	0	-2.727624	-0.614161	1.449912
18	6	0	-4.517053	0.365561	-0.361772
19	6	0	-4.015482	-0.300063	1.878208
20	1	0	-1.996504	-1.022090	2.147832
21	6	0	-4.932514	0.203385	0.958666
22	1	0	-5.208436	0.748613	-1.117680
23	1	0	-4.299987	-0.453806	2.920262
24	1	0	-5.950605	0.459426	1.251230
25	6	0	-0.211958	0.635957	-0.414118
26	6	0	0.031941	1.255288	0.817858
27	6	0	1.045656	2.400058	-1.504354
28	6	0	0.777278	2.431121	0.890324
29	1	0	-0.363039	0.819383	1.738859
30	6	0	1.292095	3.006631	-0.272584
31	1	0	1.441919	2.843119	-2.419881
32	1	0	0.957464	2.898294	1.860022
33	1	0	1.879261	3.924769	-0.219157
34	1	0	4.632186	-0.728240	-1.049195
35	1	0	4.504728	-2.097081	0.067223
36	6	0	5.117002	-0.298843	0.933895
37	7	0	5.735388	0.281260	1.716708
38	6	0	0.294484	1.225646	-1.574502

39	1	0	0.110466	0.742424	-2.533777
40	7	0	-3.285177	0.069187	-0.771773

M06-2X/def2-TZVP/SMD//M06-2X/def2-SVP G= -881.7145952

TS1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.854622	-0.684636	-0.027057
2	6	0	-1.303638	-2.048459	-0.372805
3	6	0	0.202534	-1.941592	-0.653776
4	6	0	0.745356	-0.882738	0.300941
5	1	0	-2.104840	-0.534997	1.027947
6	1	0	-1.822999	-2.475409	-1.245189
7	1	0	-1.455826	-2.726407	0.476981
8	1	0	0.723776	-2.897371	-0.500494
9	1	0	0.371585	-1.636944	-1.695548
10	6	0	-2.784387	0.002576	-0.982706
11	1	0	-2.851977	1.074724	-0.742037
12	1	0	-2.406514	-0.078987	-2.012996
13	8	0	0.478853	-1.308575	1.613071
14	1	0	0.193817	-0.505100	2.089255
15	6	0	2.238483	-0.591638	0.121430
16	6	0	3.013204	-0.280427	1.244154
17	6	0	2.854137	-0.586512	-1.136799
18	6	0	4.366138	0.033513	1.115159
19	1	0	2.549044	-0.298748	2.229912
20	6	0	4.207614	-0.274754	-1.267588
21	1	0	2.285258	-0.832460	-2.034599
22	6	0	4.969387	0.038461	-0.141975
23	1	0	4.952310	0.272864	2.004224
24	1	0	4.668480	-0.281288	-2.256700
25	1	0	6.028354	0.280448	-0.244357
26	6	0	-0.057323	0.424598	0.062478
27	6	0	-0.011733	1.089038	-1.201959
28	6	0	-0.616232	2.416861	1.112200
29	6	0	-0.383076	2.416454	-1.278254
30	1	0	0.272186	0.541514	-2.101721
31	6	0	-0.728458	3.102315	-0.103854
32	1	0	-0.804016	2.942040	2.054292
33	1	0	-0.392299	2.930049	-2.241126
34	1	0	-1.025296	4.150327	-0.119862

35	7	0	-0.247581	1.150522	1.204286
36	6	0	-4.202010	-0.604139	-0.961672
37	1	0	-4.846882	-0.101882	-1.696531
38	1	0	-4.174403	-1.671639	-1.225717
39	6	0	-4.835883	-0.482086	0.354584
40	7	0	-5.310638	-0.373828	1.400669

M06-2X/def2-TZVP/SMD//M06-2X/def2-SVP G= -881.6945548010

TS1’

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.009299	-0.869664	0.301607
2	6	0	0.628871	-1.265123	1.704956
3	6	0	-0.587028	-0.453886	2.207706
4	6	0	-1.179120	0.431713	1.104514
5	1	0	0.437361	-1.348212	-0.502395
6	1	0	1.485307	-1.094187	2.374458
7	1	0	0.415808	-2.346664	1.752619
8	1	0	-1.376366	-1.092898	2.627673
9	1	0	-0.280951	0.227082	3.013650
10	6	0	2.439700	-0.604184	-0.043818
11	1	0	2.493970	-0.013724	-0.972978
12	1	0	2.918009	-0.011462	0.751084
13	8	0	-1.864868	1.483828	1.745253
14	1	0	-2.507501	1.806641	1.091523
15	6	0	-0.023091	1.025720	0.249881
16	6	0	0.876932	1.891164	0.941937
17	6	0	-0.145010	1.230944	-1.156065
18	6	0	1.719056	2.752310	0.258511
19	1	0	0.916258	1.852485	2.032714
20	6	0	0.703884	2.095750	-1.831754
21	1	0	-0.883801	0.660222	-1.721535
22	6	0	1.653580	2.855885	-1.137967
23	1	0	2.423370	3.371529	0.817626
24	1	0	0.614587	2.195018	-2.915332
25	1	0	2.312849	3.539524	-1.674082
26	6	0	-2.190499	-0.308022	0.223253
27	6	0	-2.177113	-1.686430	-0.002459
28	6	0	-4.042053	-0.041266	-1.119344
29	6	0	-3.147154	-2.238211	-0.837976
30	1	0	-1.432446	-2.325091	0.471748

31	6	0	-4.098631	-1.402724	-1.415941
32	1	0	-4.777993	0.649507	-1.540587
33	1	0	-3.160181	-3.312302	-1.028647
34	1	0	-4.874074	-1.792206	-2.075104
35	7	0	-3.114898	0.486067	-0.323592
36	6	0	3.229063	-1.916253	-0.234137
37	1	0	2.789538	-2.518901	-1.041951
38	1	0	3.197931	-2.524960	0.681750
39	6	0	4.635970	-1.672314	-0.563047
40	7	0	5.738802	-1.449564	-0.819750

M06-2X/def2-TZVP/SMD//M06-2X/def2-SVP G= -881.6880684

INT1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.736989	1.425453	0.064936
2	6	0	1.130995	2.581511	-0.749889
3	6	0	-0.402171	2.450877	-0.627270
4	6	0	-0.651591	1.264154	0.308325
5	1	0	1.810866	1.739009	1.115568
6	1	0	1.443388	2.507835	-1.803233
7	1	0	1.503157	3.546610	-0.380771
8	1	0	-0.873705	3.336982	-0.181674
9	1	0	-0.867352	2.289984	-1.607313
10	6	0	3.130229	1.028808	-0.407488
11	1	0	3.102855	0.665353	-1.446919
12	1	0	3.744847	1.941123	-0.415386
13	6	0	3.844740	0.004811	0.491909
14	8	0	-0.535468	1.741636	1.626925
15	1	0	-0.150451	1.012056	2.143448
16	6	0	-1.962415	0.516761	0.113176
17	6	0	-2.675601	0.064243	1.229592
18	6	0	-2.471635	0.225767	-1.160579
19	6	0	-3.855688	-0.665870	1.081096
20	1	0	-2.308716	0.299720	2.228247
21	6	0	-3.651797	-0.499761	-1.312067
22	1	0	-1.942016	0.558159	-2.054374
23	6	0	-4.348116	-0.952452	-0.190574
24	1	0	-4.394306	-1.006764	1.967043
25	1	0	-4.029614	-0.711464	-2.313738
26	1	0	-5.272958	-1.519395	-0.308777

27	6	0	0.639319	0.323484	0.049070
28	6	0	0.562741	-0.359329	-1.272995
29	6	0	0.454065	-1.806887	1.063130
30	6	0	0.308963	-1.700803	-1.361388
31	1	0	0.686538	0.241057	-2.177987
32	6	0	0.184883	-2.455203	-0.179824
33	1	0	0.460860	-2.414562	1.976588
34	1	0	0.217130	-2.183678	-2.335908
35	1	0	-0.041896	-3.519967	-0.198015
36	7	0	0.726025	-0.546414	1.198484
37	1	0	4.933615	0.147781	0.444413
38	1	0	3.544765	0.137273	1.542112
39	6	0	3.600915	-1.393531	0.128750
40	7	0	3.455086	-2.498215	-0.172226

M06-2X/def2-TZVP/SMD//M06-2X/def2-SVP G= -881.7147139390

INT1’

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.668756	1.476253	-0.101695
2	6	0	-1.076418	2.606384	0.766462
3	6	0	0.451274	2.394408	0.780405
4	6	0	0.711869	1.270330	-0.225216
5	1	0	-1.690810	1.819881	-1.147058
6	1	0	-1.485987	2.556814	1.787113
7	1	0	-1.357514	3.588281	0.362280
8	1	0	1.016244	3.282492	0.468562
9	1	0	0.800164	2.111515	1.781863
10	6	0	-3.090755	1.117320	0.315355
11	1	0	-3.104281	0.753512	1.354570
12	1	0	-3.678395	2.047294	0.306289
13	6	0	-3.813328	0.111359	-0.599733
14	8	0	0.698930	1.820321	-1.513403
15	1	0	1.349876	1.294765	-2.016675
16	6	0	1.997039	0.476781	-0.041685
17	6	0	2.490515	0.066097	1.201944
18	6	0	3.729096	-0.569075	-1.146329
19	6	0	3.654832	-0.694873	1.238926
20	1	0	1.973802	0.331378	2.122993
21	6	0	4.290845	-1.025375	0.042817
22	1	0	4.196839	-0.798223	-2.107835

23	1	0	4.062886	-1.027705	2.194605
24	1	0	5.204268	-1.619643	0.029541
25	6	0	-0.602808	0.340414	-0.058809
26	6	0	-0.603304	-0.363920	1.261541
27	6	0	-0.474499	-1.961153	-1.054036
28	6	0	-0.438389	-1.715386	1.376127
29	1	0	-0.712266	0.241154	2.166555
30	6	0	-0.324065	-2.540596	0.230426
31	1	0	-0.465359	-2.605451	-1.935861
32	1	0	-0.409166	-2.170846	2.368444
33	1	0	-0.180088	-3.615569	0.337580
34	1	0	-4.891344	0.326499	-0.623284
35	1	0	-3.450326	0.191314	-1.635444
36	6	0	-3.690901	-1.288008	-0.180791
37	7	0	-3.655570	-2.388585	0.165340
38	7	0	2.614560	0.160503	-1.181279
39	6	0	-0.660016	-0.616120	-1.204817
40	1	0	-0.776294	-0.182497	-2.200798

M06-2X/def2-TZVP/SMD//M06-2X/def2-SVP G= -881.71424

TS2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.776465	1.356546	0.030716
2	6	0	1.165263	2.488876	-0.785814
3	6	0	-0.332140	2.572337	-0.455887
4	6	0	-0.730915	1.406665	0.415551
5	1	0	1.850002	1.682473	1.083508
6	1	0	1.308057	2.285338	-1.863078
7	1	0	1.694561	3.435509	-0.590211
8	1	0	-0.565068	3.486082	0.117981
9	1	0	-0.942017	2.618375	-1.369668
10	6	0	3.181683	1.010404	-0.443777
11	1	0	3.168997	0.697493	-1.504125
12	1	0	3.781162	1.936359	-0.414286
13	8	0	-0.488088	1.678819	1.739644
14	1	0	-0.107984	0.858698	2.125237
15	6	0	-1.969487	0.648476	0.150813
16	6	0	-2.665459	0.048205	1.213531
17	6	0	-2.451925	0.444300	-1.154588
18	6	0	-3.788410	-0.740822	0.979990

19	1	0	-2.321327	0.215831	2.237418
20	6	0	-3.575409	-0.340730	-1.386389
21	1	0	-1.933695	0.895684	-2.006373
22	6	0	-4.245403	-0.944583	-0.320937
23	1	0	-4.313755	-1.198675	1.823523
24	1	0	-3.932333	-0.485157	-2.410434
25	1	0	-5.126962	-1.565158	-0.505895
26	6	0	0.785343	0.190505	0.026431
27	6	0	0.547504	-0.459662	-1.238080
28	6	0	0.286783	-1.808586	1.121242
29	6	0	0.088567	-1.757021	-1.274800
30	1	0	0.706879	0.096862	-2.168438
31	6	0	-0.080979	-2.455990	-0.072064
32	1	0	0.207147	-2.355166	2.072036
33	1	0	-0.122424	-2.242581	-2.232504
34	1	0	-0.450272	-3.483853	-0.051072
35	7	0	0.755650	-0.580465	1.186142
36	6	0	3.909280	-0.038389	0.400796
37	1	0	5.001171	0.084124	0.306454
38	1	0	3.674170	0.095015	1.471286
39	6	0	3.615336	-1.417659	0.041048
40	7	0	3.420325	-2.520255	-0.261170

M06-2X/def2-TZVP/SMD//M06-2X/def2-SVP G= -881.7071906900

TS2’

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.756842	1.354724	-0.073440
2	6	0	-1.212748	2.521506	0.753198
3	6	0	0.320077	2.476074	0.702551
4	6	0	0.752613	1.426044	-0.283591
5	1	0	-1.768548	1.665202	-1.134677
6	1	0	-1.565715	2.444418	1.797445
7	1	0	-1.616643	3.474164	0.372849
8	1	0	0.754730	3.441116	0.389783
9	1	0	0.736495	2.250969	1.695529
10	6	0	-3.189193	1.022720	0.324903
11	1	0	-3.226540	0.682828	1.376312
12	1	0	-3.768040	1.962085	0.294773
13	8	0	0.614029	1.848107	-1.573255
14	1	0	1.237574	1.285178	-2.082588

15	6	0	1.985709	0.637699	-0.087454
16	6	0	2.520301	0.301314	1.165091
17	6	0	3.604627	-0.592705	-1.176465
18	6	0	3.639159	-0.518848	1.211984
19	1	0	2.068723	0.674807	2.086921
20	6	0	4.192316	-0.991005	0.021566
21	1	0	4.019996	-0.929705	-2.134834
22	1	0	4.078928	-0.793187	2.174979
23	1	0	5.069150	-1.642541	0.018944
24	6	0	-3.908583	0.013608	-0.573977
25	1	0	-4.997254	0.189544	-0.546617
26	1	0	-3.608490	0.145057	-1.628433
27	6	0	-3.717879	-1.383326	-0.212531
28	7	0	-3.635200	-2.499972	0.090192
29	6	0	-0.760764	0.197442	0.011935
30	6	0	-0.673913	-0.716646	-1.107506
31	6	0	-0.578855	-0.413114	1.312999
32	6	0	-0.179800	-1.995277	-0.958788
33	1	0	-0.927640	-0.335924	-2.104122
34	6	0	-0.096196	-1.696485	1.446868
35	1	0	-0.787355	0.181748	2.211114
36	6	0	0.145105	-2.496454	0.313510
37	1	0	-0.060598	-2.635523	-1.838942
38	1	0	0.081811	-2.106853	2.446527
39	1	0	0.532766	-3.513193	0.426252
40	7	0	2.538572	0.198732	-1.230234

M06-2X/def2-TZVP/SMD//M06-2X/def2-SVP G= -881.7110438

INT2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.569452	1.296014	-0.122160
2	6	0	0.642727	2.271826	-0.871406
3	6	0	-0.532283	2.782362	-0.007532
4	6	0	-1.170420	1.698997	0.803821
5	1	0	1.670474	1.642057	0.918556
6	1	0	0.254132	1.781730	-1.778724
7	1	0	1.228209	3.139225	-1.212455
8	1	0	-0.149074	3.530262	0.702562
9	1	0	-1.263259	3.288542	-0.654531
10	6	0	2.974275	1.278383	-0.741884

11	1	0	2.934450	0.908206	-1.778446
12	1	0	3.341811	2.313244	-0.790673
13	6	0	4.006590	0.478044	0.064208
14	8	0	-0.651634	1.525182	2.046405
15	1	0	-0.151143	0.671652	2.066592
16	6	0	-2.129703	0.772320	0.298110
17	6	0	-2.632391	-0.269684	1.122094
18	6	0	-2.593904	0.833031	-1.043888
19	6	0	-3.533459	-1.201036	0.624177
20	1	0	-2.302356	-0.327672	2.160181
21	6	0	-3.494301	-0.105554	-1.527813
22	1	0	-2.230668	1.618237	-1.709070
23	6	0	-3.970700	-1.132400	-0.703299
24	1	0	-3.903574	-1.992757	1.278573
25	1	0	-3.831035	-0.040487	-2.564235
26	1	0	-4.677232	-1.867291	-1.091293
27	6	0	0.993789	-0.109691	-0.056403
28	6	0	0.750484	-0.837470	-1.228590
29	6	0	0.333905	-1.899412	1.240733
30	6	0	0.293906	-2.146056	-1.133301
31	1	0	0.927303	-0.382470	-2.204876
32	6	0	0.094549	-2.701239	0.130104
33	1	0	0.157071	-2.282917	2.249764
34	1	0	0.099744	-2.730282	-2.034331
35	1	0	-0.256628	-3.725290	0.254752
36	7	0	0.768311	-0.639486	1.152529
37	1	0	3.976657	0.776558	1.122993
38	1	0	5.019715	0.696999	-0.301785
39	6	0	3.847921	-0.980429	0.011196
40	7	0	3.755380	-2.130091	-0.031643

M06-2X/def2-TZVP/SMD//M06-2X/def2-SVP G= -881.7385246290

INT2’

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.579236	1.359291	-0.036635
2	6	0	0.605563	2.315886	-0.741212
3	6	0	-0.572832	2.782217	0.134793
4	6	0	-1.313910	1.675312	0.803594
5	1	0	1.771993	1.757956	0.974845
6	1	0	0.223617	1.839961	-1.658500

7	1	0	1.155553	3.212227	-1.067411
8	1	0	-0.195841	3.445251	0.927013
9	1	0	-1.258769	3.379314	-0.486439
10	6	0	2.923317	1.336480	-0.780626
11	1	0	2.774764	0.996624	-1.818285
12	1	0	3.307413	2.365291	-0.837166
13	6	0	4.006889	0.485859	-0.102884
14	8	0	-1.054282	1.481133	2.100163
15	6	0	-2.157227	0.727702	0.162181
16	6	0	-2.513128	0.789358	-1.210248
17	6	0	-3.342423	-1.234881	0.439220
18	6	0	-3.302337	-0.217449	-1.733732
19	1	0	-2.170223	1.615864	-1.833737
20	6	0	-3.729418	-1.264170	-0.902691
21	1	0	-3.664657	-2.031787	1.117646
22	1	0	-3.589646	-0.195893	-2.786600
23	1	0	-4.350536	-2.075589	-1.280152
24	6	0	1.023303	-0.045393	0.129903
25	6	0	0.555012	-0.769200	-0.974770
26	6	0	0.545289	-1.970907	1.534544
27	6	0	0.081211	-2.070766	-0.828097
28	1	0	0.555236	-0.311598	-1.967521
29	6	0	0.078210	-2.678518	0.428654
30	1	0	0.543929	-2.435367	2.522377
31	1	0	-0.285937	-2.615400	-1.700108
32	1	0	-0.293303	-3.698236	0.544454
33	1	0	4.010721	0.661876	0.983864
34	1	0	4.999539	0.776168	-0.475764
35	6	0	3.890639	-0.960640	-0.322845
36	7	0	3.851360	-2.098326	-0.512969
37	6	0	1.011660	-0.664300	1.383244
38	1	0	1.362656	-0.107617	2.255519
39	7	0	-2.587788	-0.280325	0.964782
40	1	0	-1.521573	0.647161	2.327607

M06-2X/def2-TZVP/SMD//M06-2X/def2-SVP G= -881.716457