Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

# Supporting Information

# KI-catalyzed arylation of benzothiazoles from the coupling of aryl aldehydes with benzothiazoles in neat water

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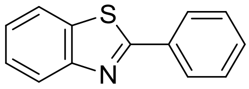
## General Information:

All experiments were conducted under $N_2$ atmosphere. Flash column chromatography was performed over silica gel 48-75 μm. All melting points were determined on a Beijing Science Instrument Dianguang Instrument Factory XT4B melting point apparatus and are uncorrected. $^1$H-NMR spectra were recorded on Bruker AVIII-400 Hz spectrometers. Chemical shifts(in ppm): were referenced to tetramethylsilane($\delta$ = 0 ppm) in $CDCl_3$ as an internal standard. $^{13}$C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$($\delta$ = 77.00 ppm):. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

## Catalytic general procedure: 2-phenylbenzothiazole(3aa):

An oven-dried reaction tube (5 mL) was charged with benzothiazole (**1a**, 68 mg, 0.5 mmol), benzaldehyde (2a, 80 mg, 0.75 mmol), 70% TBHP in water (207 μL, 1.5 mmol), KI (17 mg, 0.01 mmol) and water 1 mL. The resulting solution was stirring at 100 $^o$C under $N_2$ for 8 h(monitored by TLC). Upon completion of the reaction, the mixture was extracted with ethyl acetate (10 mL × 3). The organic layers were combined, washed with saturated $Na_2S_2O_3$ aqueous solution, saturated $NaHCO_3$ aqueous solution, dried over anhydrous $Na_2SO_4$, and filtered. The solvents were removed via rotary evaporator and the residue was purified with flash chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give **3aa** as white solid; yield: 76.1 mg (72%).

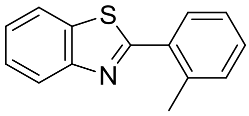
## 2-phenylbenzothiazole (3aa, CAS: 883-93-2)[1]



$^1$H-NMR(400 MHz, $CDCl_3$, ppm): $\delta$ 8.09 (m, 3H), 7.90 (d, $J$ = 8.0 Hz, 1H), 7.51-7.47 (m, 4H), 7.38 (t, $J$ = 7.6 Hz, 1H), 2.66 (s, 3H); $^{13}$C-NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 168.0, 154.1, 135.1, 133.6, 131.0, 129.0, 127.5, 126.3, 125.2, 123.2, 121.6; mp: 110-112 $^o$C (lit. 112-114 $^o$C).

## 2-(2-Methylphenyl) benzothiazole (3ab, CAS: 15903-58-9)[2]

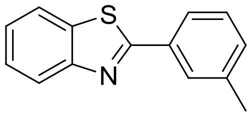
The product was isolated as white solid in 58% yield (65.1mg).



$^1$H-NMR (400 MHz, $CDCl_3$, ppm): *δ* 8.06 (d, *J* = 8.1 Hz, 1H), 7.94 (s, 1H), 7.42-7.24 (m, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.33 (m, 4H); $^{13}$C-NMR (100 MHz, $CDCl_3$, ppm): *δ* 168.0, 153.8, 137.3, 135.6, 133.1, 131.5, 130.5, 130.0, 126.1, 126.1, 125.1, 123.4, 121.4, 21.3; mp: 52-54 °C (lit. 53-54 °C).

## 2-(3-Methylphenyl) benzothiazole (3ac, CAS: 1211-32-1)[2]

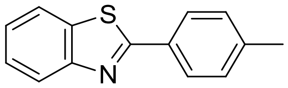
The product was isolated as white solid in 54% yield (60.9 mg).



$^1$H-NMR (400 MHz, $CDCl_3$, ppm): *δ* 8.10 (d, *J* = 8.1 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.88 (m, 2H), 7.48 (t, *J* = 7.0 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 1H), 2.45 (s, 3H); $^{13}$C-NMR (100 MHz, $CDCl_3$, ppm): *δ* 168.3, 154.1, 138.9, 135.0, 133.5, 131.8, 128.9, 128.0, 126.2, 125.1, 124.8, 123.2, 121.6, 21.3; mp: 67-68 °C (lit. 67-68 °C).

## 2-(4-Methylphenyl) benzothiazole (3ad, CAS: 16112-21-3)[1]

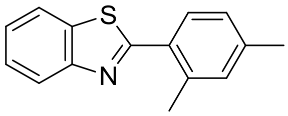
The product was isolated as white solid in 62% yield (70 mg).



$^1$H-NMR (400 MHz, $CDCl_3$, ppm): *δ* 8.05 (d, *J* = 8.1 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.9Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H); $^{13}$C-NMR (100 MHz, $CDCl_3$, ppm): *δ* 168.2, 154.2, 141.4, 135.0, 130.9, 129.7, 127.5, 126.2, 125.0, 123.0, 121.5, 21.5; mp: 85-86 °C (lit. 84-86 °C).

## 2-(2, 4-Dimethylphenyl) benzothiazole (3ae, CAS: 902086-26-4)[9]

The product was isolated as white solid in 49% yield (59 mg).

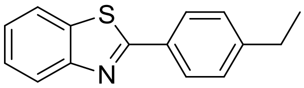


$^1$H-NMR (400 MHz, $CDCl_3$, ppm): *δ* 8.08 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.0 Hz, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.15 (s, 1H), 7.11 (d, *J* =

8.0, 1H), 2.64 (s, 3H), 2.38 (s, 3H); $^{13}$C-NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 168.2, 153.8, 140.2, 137.1, 135.5, 132.3, 130.5, 130.3, 126.8, 126.0, 124.9, 123.2, 121.3, 21.3, 21.3; mp: 111-113 °C (lit. 111-113 °C).

**2-(2-Ethylphenyl) benzothiazole (3af, CAS: 50685-15-9)[4]**

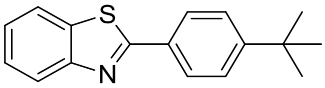
The product was isolated as yellow solid in 59% yield (70 mg).



$^1$H-NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.05 (d, J= 8.2 Hz, 1H), 8.00 (d, $J$ = 8.0 Hz, 2H), 7.87 (d, $J$ =7.8 Hz, 1H), 7.47 (t, $J$ = 7.6 Hz, 1H), 7.36 (t, $J$ = 7.5 Hz, 1H), 7.31 (d, $J$ = 8.0 Hz, 2H), 2.71 (q, $J$ = 7.6 Hz, 2H), 1.28 (t, $J$ =7.6 Hz, 3H); $^{13}$C-NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 168.2, 154.2, 147.6, 134.9, 131.2, 128.5, 127.6, 126.2, 125.0, 123.0, 121.5, 28.8, 15.3; mp: 85-87 °C.

**2-(4-tert-Butylphenyl) benzothiazole (3ag, CAS: 56048-52-3) [4]**

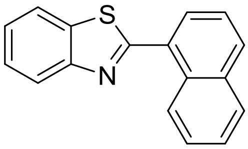
The product was isolated as white solid in 57% yield (75.7 mg).



$^1$H-NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.06 (d, $J$ = 8.6 Hz, 1H), 8.02 (d, $J$ = 8.6 Hz), 7.88 (d, $J$ = 7.8 Hz, 1H), 7.52-7.45 (m, 3H), 7.36 (t, $J$ = 7.2 Hz, 1H), 1.36 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 168.1, 154.5, 154.2, 135.0, 130.9, 127.3, 126.2, 126.0, 125.0, 123.1, 121.5, 35.0, 31.2; mp: 107-108 °C (lit. 107-108 °C).

**2-(Naphthalen-1-yl) benzothiazole (3ah, CAS: 56048-50-1)[6]**

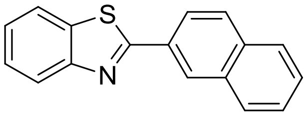
The product was isolated as yellow oil in 60% yield (100.7 mg).



$^1$H-NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.93 (d, $J$ = 8.6 Hz, 1H), 8.19 (d, $J$ = 8.2 Hz, 1H), 7.99-7.91 (m, 4H), 7.63-7.52 (m, 4H), 7.44 (t, $J$ = 7.6 Hz, 1H); $^{13}$C-NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 167.6, 154.1, 135.4, 134.0, 131.1, 130.8, 129.4, 128.4, 127.6, 126.5, 126.3, 125.9, 125.3, 125.0, 123.5, 121.4.

### 2-(Naphthalen-2-yl) benzothiazole (3ai, CAS: 56048-51-2) [8]

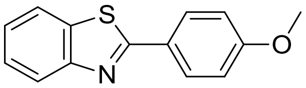
The product was isolated as white solid in 47 % yield (79.3 mg).



$^1$H-NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.56 (d, J= 1.2 Hz, 1H), 8.20 (dd, *J* = 8.7 Hz, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 7.98-7.86 (m, 4H), 7.56-7.49 (m, 3H), 7.40 (t, *J* = 7.6 Hz, 1H); $^{13}$C-NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 168.1, 154.2, 135.1, 134.6, 133.2, 131.0, 128.9, 128.8, 127.9, 127.6, 127.4, 126.9, 126.4, 125.2, 124.4, 123.2, 121.6; mp: 125-127 $^o$C (lit. 125-127 $^o$C).

### 2-(4-Methoxyphenyl) benzothiazole (3aj, CAS: 6265-92-5) [2]

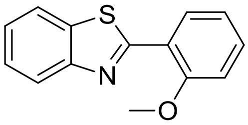
The product was isolated as white solid in 46% yield (55.7 mg).



$^1$H-NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.02 (d, *J* = 8.7 Hz, 3H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 8.7 Hz, 2H), 3.86 (s, 3H); $^{13}$C-NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 167.8, 161.9, 154.2, 134.8, 129.1, 126.4, 126.2, 124.7, 122.8,121.5, 114.3, 55.4; mp: 123-125 $^o$C (lit. 122-124 $^o$C).

### 2-(2-Methoxyphenyl) benzothiazole (3ak, CAS: 6269-47-2) [3]

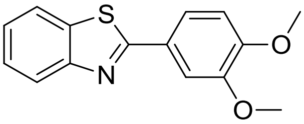
The product was isolated as white solid in 46% yield (55 mg).



$^1$H-NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.53 (dd, *J* = 7.9 Hz, 1H), 8.08 (d, *J* = 7.9 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.50-7.43 (m, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 8.7 Hz, 1H), 4.04 (s, 3H); $^{13}$C-NMR(100 MHz, $CDCl_3$, ppm): $\delta$ 163.1, 157.2, 152.1, 136.1, 131.7, 129.5, 125.8, 124.5, 122.8, 122.3, 121.2, 121.1, 111.7, 55.7; mp: 105-106 $^o$C (lit. 103-105 $^o$C).

### 2-(3, 4-Dimethoxyphenyl) benzothiazole (3al, CAS: 6638-45-5)[7]

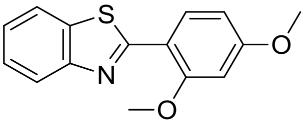
The product was isolated as white solid in 55% yield (74.9 mg).



$^1$H-NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.03 (d, $J$ = 8.0 Hz, 1H), 7.86 (d, $J$ = 8.0 Hz, 1H), 7.70 (d, $J$ = 2 Hz, 1H), 7.58 (dd, $J$ = 8.3 Hz, 1H), 7.34 (t, $J$ = 3.5 Hz, 1H), 6.92 (d, $J$ = 8.4 Hz, 1H), 4.01 (s, 3H), 3.93(s, 3H); $^{13}$C-NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 167.8, 154.1, 151.5, 149.3, 134.8, 126.6, 126.2, 124.8, 122.8, 121.4, 121.1, 111.0, 109.7, 56.1, 56.0; mp: 130-131 $^o$C (lit. 130-131 $^o$C).

## 2-(2, 4-Dimethoxyphenyl) benzothiazole (3am, CAS: 56048-59-0) [5]

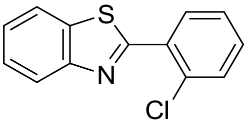
The product was isolated as light purple solid in 45% yield (61.4 mg).



$^1$H-NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.46 (d, $J$ = 8.8 Hz, 1H), 8.03 (d, $J$ = 8.2 Hz, 1H), 7.87 (d, $J$ = 7.8 Hz, 1H), 7.44 (t, $J$ = 7.2Hz, 1H), 7.31 (t, $J$ = 7.4 Hz, 1H), 6.65 (dd, $J$ = 8.8 Hz ,1H), 6.53 (d, $J$ = 2.4 Hz, 1H), 3.98 (s, 3H), 3.84 (s, 3H) ; $^{13}$C-NMR(100 MHz, $CDCl_3$, ppm): $\delta$ 163.2, 162.8, 158.5, 152.2, 135.6, 130.7, 125.7, 124.1, 122.3, 121.0, 115.6, 105.9, 98.4, 55.6, 55.4; mp: 125-127 $^o$C (lit. 125-127 $^o$C).

## 2-(4-Chlorophenyl) benzothiazole (3an, CAS: 6269-46-1)[3]

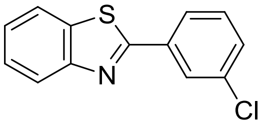
The product was isolated as white solid in 72% yield (88.7 mg).



$^1$H-NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.22-8.20(m, 1H), 8.13 (d, $J$ = 8.2 Hz, 1H), 7.54-7.50 (m, 2H), 7.44-7.39 (m, 3H); $^{13}$C-NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 164.1, 152.5, 136.1, 132.7, 132.3, 131.7, 131.1, 130.8, 127.1, 126.3, 125.4, 123.4, 121.4; mp: 83-84 $^o$C (lit. 84-85 $^o$C).

## 2-(3-Chlorophenyl) benzothiazole (3ao, CAS: 22868-31-1)[3]

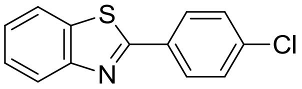
The product was isolated as white solid in 61% yield (74.7 mg).



$^1$H-NMR (400 MHz, $CDCl_3$, ppm): *δ* 8.12 (s, 1H), 8.08 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 7.4 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 7.4 Hz, 1H), 7.49-7.39 (m, 3H); $^{13}$C-NMR (100 MHz, $CDCl_3$, ppm): *δ* 166.2, 154.0, 135.3, 135.1, 135.1, 130.8, 130.2, 127.4, 126.5, 125.7, 125.5, 123.4, 121.7; mp: 97-99 °C (lit. 97-98 °C).

**2-(4-Chlorophenyl) benzothiazole (3ap, CAS: 6265-91-4)[1]**

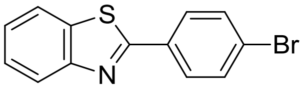
The product was isolated as white solid in 73% yield (89.5 mg).



$^1$H-NMR (400 MHz, $CDCl_3$, ppm): *δ* 8.06 (d, *J* = 8.2 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.52-7.46 (m, 3H), 7.40 (t, *J* = 7.4 Hz, 1H) ; $^{13}$C-NMR (100 MHz, $CDCl_3$, ppm): *δ* 166.6, 154.1, 137.0, 135.1, 132.1, 129.3, 128.7, 126.5, 125.4, 123.3, 121.6; mp: 115-117 °C (lit. 115-117 °C).

**2-(4-Bromophenyl) benzothiazole (3aq, CAS: 19654-19-4)[1]**

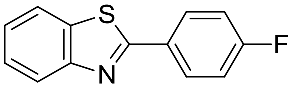
The product was isolated as white solid in 65% yield (94.2 mg).



$^1$H-NMR (400 MHz, $CDCl_3$, ppm): *δ* 8.06 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.6 Hz, 2H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.64-7.60 (m, 2H), 7.50(t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H); $^{13}$C-NMR(100 MHz, $CDCl_3$, ppm): *δ* 166.7, 154.1, 135.0, 132.5, 132.2, 128.9, 126.5, 125.4, 125.4, 123.3, 121.6; mp: 129-131 °C (lit. 131-132 °C).

**2-(4-Fluorophenyl) benzothiazole (3ar, CAS: 1629-26-1)[1]**

The product was isolated as white solid in 40% yield (45.8 mg).

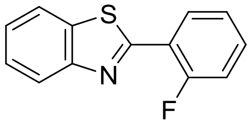


$^1$H-NMR (400 MHz, $CDCl_3$, ppm): *δ* 8.09-8.04 (m, 3H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.20-7.14 (m, 2H); $^{13}$C-NMR (100 MHz, $CDCl_3$, ppm):

*δ* 166.2 (d, *J* = 101.9 Hz), 163.2, 154.1, 135.0, 130.0 (d, *J* = 3.1 Hz), 129.5 (d, *J* = 8.6 Hz), 126.4, 125.2, 123.2, 121.6, 116.1 (d, *J* = 22.0 Hz); mp: 98-100 °C (lit. 99-100 °C).

**2-(2-Fluorophenyl) benzothiazole (3as, CAS: 1747-46-2)[3]**

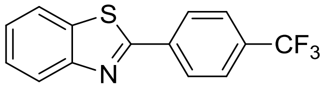
The product was isolated as white solid in 42% yield (48.4 mg).



$^1$H-NMR (400 MHz, $CDCl_3$, ppm): *δ* 8.41 (t, *J* = 7.6Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H),7.46 (m, 3H), 7.30 (t, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H); $^{13}$C-NMR (100 MHz, $CDCl_3$, ppm): *δ* 162.0, 160.2 (d, *J* = 180.7 Hz), 152.5, 135.7 (d, *J* = 7.9 Hz), 132.1 (d, *J* = 8.7 Hz), 129.7 (d, *J* = 2.1 Hz), 126.3, 125.3, 124.7,124.6, 123.3, 121.4, 116.4 (d, *J* = 21.8 Hz); mp: 67-68 °C (lit. 67-68 °C).

**2-(4-Trifluoromethylphenyl) benzothiazole(3at, CAS: 134384-31-9) [2]**

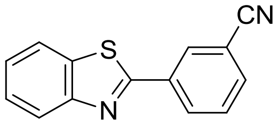
The product was isolated as white solid in 65% yield (90.7 mg).



$^1$H-NMR (400 MHz, $CDCl_3$, ppm): *δ* 8.21 (d, *J* = 8.3 Hz, 2H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H); $^{13}$C-NMR (100 MHz, $CDCl_3$, ppm): *δ* 166.0, 154.0, 136.8, 135.2, 132.3 (q, *J* = 32.6 Hz), 127.8, 126.7, 126.0 (q, *J* = 3.7 Hz), 123.7(q, *J* = 270.8 Hz), 123.6, 121.7; mp: 160-161 °C (lit. 160-161 °C).

**2-(3-Cyanophenyl) benzothiazole (3au, CAS: 67362-99-6) [8]**

The product was isolated as white solid in 62% yield (72.9 mg).

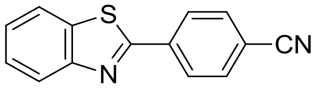


$^1$H-NMR (400 MHz, $CDCl_3$, ppm): *δ* 8.40 (s, 1H), 8.29 (d, *J* = 7.9 Hz, 2H), 8.10 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.9 Hz, 1H), 7.53 (t, *J*

= 7.6 Hz, 1H), 7.44(t, *J* = 7.4 Hz, 1H); $^{13}$C-NMR (100 MHz, CDCl$_3$, ppm): *δ* 165.0, 153.9, 135.1, 134.8, 133.8, 131.4, 130.8, 129.9, 126.8, 125.9, 123.6, 121.8, 118.0, 113.5; mp: 156-158 °C (lit. 158°C).

### 2-(4-Cyanophenyl) benzothiazole (3av, CAS: 17930-02-8) [6]

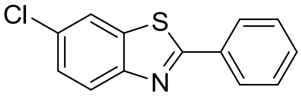
The product was isolated as white solid in 70% yield (82.8 mg).



$^1$H-NMR (400 MHz, CDCl$_3$, ppm): *δ* 8.19 (d, *J* = 8.2 Hz, 2H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.54 (t, *J* = 7.0 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H); $^{13}$C-NMR (100 MHz, CDCl$_3$, ppm): *δ* 165.3, 154.0, 137.4, 135.3, 132.7, 127.9, 126.8, 126.0, 123.8, 121.8, 118.2, 114.1; mp: 165-167 °C (lit. 165-166 °C).

### 6-Chloro-2-phenylbenzothiazole (3ba, CAS: 952-16-9) [12]

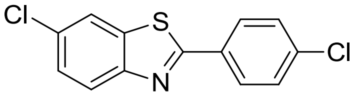
The product was isolated as white solid in 75% yield (91.7 mg).



$^1$H-NMR (400 MHz, CDCl$_3$, ppm): *δ* 8.07-8.04 (m, 3H), 7.98 (d, *J*= 8.6 Hz, 1H), 7.50-7.48 (m, 3H), 7.34 (dd, *J* = 8.7 Hz, 1H); $^{13}$C-NMR (100 MHz, CDCl$_3$, ppm): *δ* 169.9, 155.0, 133.3, 133.2, 132.3, 131.3, 129.1, 127.6, 125.6, 123.0, 122.3; mp: 139-141 °C (lit. 138-140 °C).

### 6-Chloro-2-(4-chlorophenyl) benzothiazole (3bp, CAS: 15952-14-4) [10]

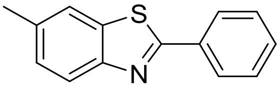
The product was isolated as white solid in 58% yield (81.8 mg).



$^1$H-NMR (400 MHz, CDCl$_3$, ppm): *δ* 8.03 (d, *J* =2 Hz, 1H), 8.01-7.98 (m, 2H), 7.79 (d, *J* = 8.6 Hz, 1H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.36 (dd, *J* = 8.4 Hz, 1H); $^{13}$C-NMR (100 MHz, CDCl$_3$, ppm): *δ* 168.4, 154.9, 137.5, 133.3, 132.5, 131.7, 129.3, 128.7, 125.9, 123.1, 122.3; mp: 140-142 °C (lit. 140-142 °C).

### 6-methyl-2-phenylbenzothiazole (3ca, CAS: 10205-58-0) [11]

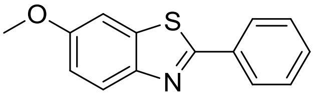
This product was isolated as white solid in 79% yield (88.5 mg).



$^1$H-NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.07 (s, 1H), 7.95 (d, $J$ = 8.2 Hz, 1H), 7.69 (s, 1H), 7.48 (s, 3H), 7.30 (d, $J$ =8.0 Hz, 1H), 2.50 (s, 3H); $^{13}$C-NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 167.0, 152.3, 135.4, 135.2, 133.8, 130.7, 129.0, 128.0, 127.4, 122.7, 121.4, 21.5; mp: 125-127 °C (lit. 124-126 °C).

## 6-methoxy-2-phenylbenzothiazole (3da, CAS: 10205-69-3) [12]

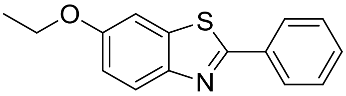
This product was isolated as white solid in 63% yield (75.9 mg).



$^1$H-NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.04-8.02 (m, 2H), 7.94 (d, $J$ = 8.9 Hz, 1H), 7.48-7.45 (m, 3H), 7.33 (d, $J$ = 2.8 Hz, 1H), 7.08 (dd, $J$ =8.9 Hz, 1H), 3.88 (s, 3H); $^{13}$C-NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 165.5, 157.8, 148.7, 136.4, 133.8, 130.5, 128.9, 127.2, 123.7, 115.6, 104.2, 55.8; mp: 112-114 °C (lit. 112-112 °C) .

## 6-ethoxy-2-phenylbenzothiazole (3ea, CAS: 101096-95-1) [13]

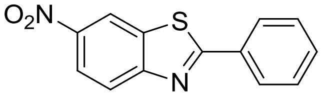
This product was isolated as white solid in 54% yield (64.2 mg).



$^1$H-NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.03 (d, $J$ = 8.0 Hz, 2H), 7.93 (d, $J$ = 8.9 Hz, 1H), 7.48-7.45 (m, 3H), 7.33 (d, $J$ = 2.5 Hz, 1H), 7.07 (dd, $J$ = 9.0 Hz, 1H), 4.09 (q, $J$ = 7.0 Hz, 2H), 1.45 (t, $J$ = 7.0 Hz, 3H); $^{13}$C-NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 165.4, 157.1, 148.6, 136.4, 133.8, 130.5, 128.9, 127.2, 123.7, 116.0, 104.9, 64.1, 14.8; mp: 113-115 °C (lit. 112-114 °C).

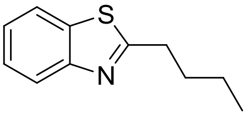
## 6-nitro-2-phenylbenzothiazole (3fa, CAS: 38338-23-7) [12]

This product was isolated as yellow solid in 36% (46.4 mg).



$^1$H-NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.83 (d, $J$ = 2.2 Hz, 1H), 8.36 (dd, $J$ = 9.0 Hz, 1H), 8.14-8.10 (m, 3H), 7.57-7.51(m, 3H); $^{13}$C-NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 173.8, 157.8, 145.0, 135.3, 132.7, 132.2, 129.3, 127.9, 123.3, 121.9, 118.2; mp: 188-190 $^{o}$C (lit. 191-192 $^{o}$C).

**2-Butylbenzothiazole (3aw, CAS: 54798-95-7)** [14]

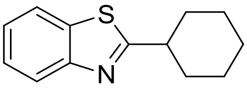


An oven-dried reaction tube(5 mL) was charged with benzothiazole (**1a**, 68 mg, 0.5 mmol), pentanal (**2v**, 64.5 mg, 0.75 mmol), 70% TBHP in water (207 μL, 1. 5 mmol), KI (17 mg, 0.01 mmol) and water 1 mL. The resulting solution was stirring at 100 $^{o}$C under $N_2$. After 4h, additional penanal (64.5 mg, 0.75 mmol), 70% TBHP in water (207 μL, 1.5 mmol), KI (17 mg, 0.01 mmol) was added into the reaction solution. The resulting solution was stirring at 100 $^{o}$C under $N_2$ for another 4h. Upon completion of the reaction, the mixture was extracted with ethyl acetate (10 mL × 3). The organic layers were combined, washed with saturated $Na_2S_2O_3$ aqueous solution, saturated $NaHCO_3$ aqueous solution, dried over anhydrous $Na_2SO_4$, and filtered. The solvents were removed via rotary evaporator and the residue was purified with flash chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give 3aw as yellow oil; yield: 44.8 mg (47%).

$^{1}$H-NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.96 (d, $J$ = 8.0 Hz 1H), 7.84 (d, $J$ = 8.0 Hz, 1H), 7.44 (t, $J$ = 7.5 Hz, 1H), 7.34 (t, $J$ = 7.3 Hz, 1H), 3.12 (t, $J$ = 7.6 Hz, 2H), 1.91-1.83 (m, 2H), 1.48 (t, $J$ = 7.6 Hz, 2H), 0.98 (t, $J$ = 7.6 Hz, 3H); $^{13}$C-NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 177.6, 153.1, 134.6, 125.8, 124.5, 122.6, 121.5, 34.1, 31.8, 22.3, 13.8.

**2-Butylbenzothiazole (3ax, CAS: 40115-03-5)** [15]

The product was isolated as yellow oil in 46% yield (49.7 mg).



$^{1}$H-NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.97 (d, $J$ = 8.1 Hz, 1H), 7.84 (d, $J$ = 7.9 Hz, 1H), 7.44 (t, $J$ = 7.6 Hz, 3H), 7.33 (t, $J$ = 7.5 Hz, 1H), 3.10 (m, 1H), 2.20 (d, $J$ = 12 Hz, 2H), 1.91-1.87 (m, 2H), 1.78-1.59 (m, 4H), 1.50-1.26 (m, 4H); $^{13}$C-NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 177.6, 153.1, 134.5, 125.8, 124.5, 122.5, 121.5, 43.4, 33.4, 26.0, 25.8.

### The $^{13}$C benzaldehyde labeled experiments

The isotope reagents was purchased from J&K. Benzaldehyde(α-$^{13}$C, 99%) was used without further purification.

$^{13}$C Enrichments of afforded product was calculated from the integrated resonances detected by inverse gated decoupling $^{13}$C NMR. Carbon resonances were integrated and standardized to three different positions (C(154.2 ppm), C(126.3 ppm), C(125.2 ppm)). The ratio of the integrated signal form the labeled sample to unlabeled product was determined, and then the three sets were averaged. This quotient was multiplied by the natural abundance of $^{13}$C (1.1%) to give the percent $^{13}$C incorporations at the position of $^{13}$C-**3aa**.

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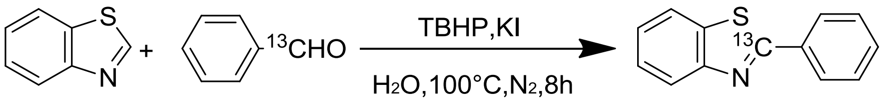
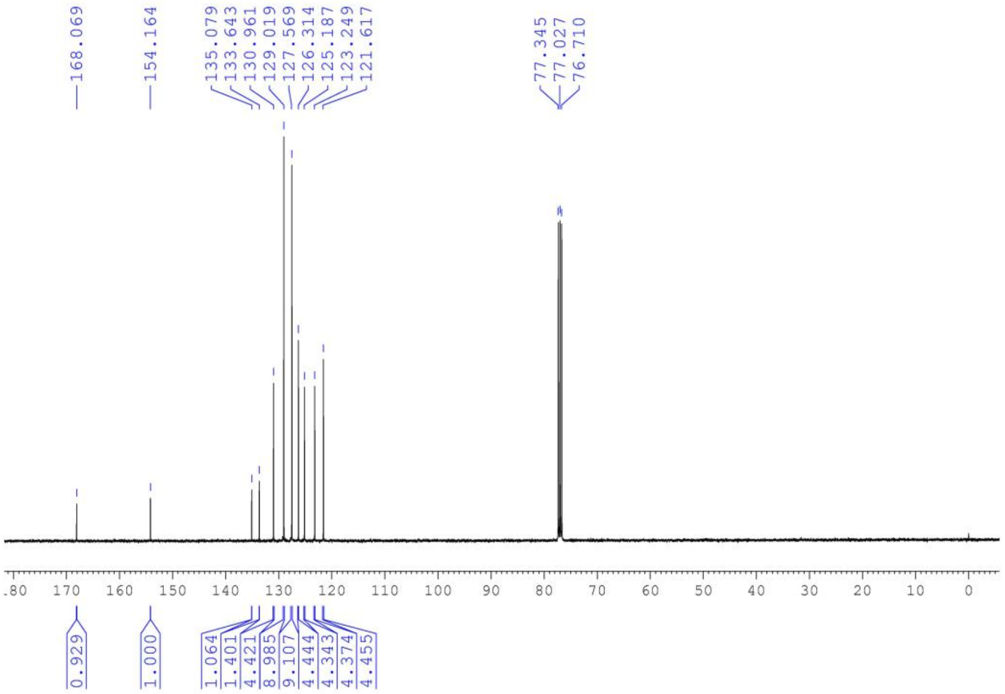


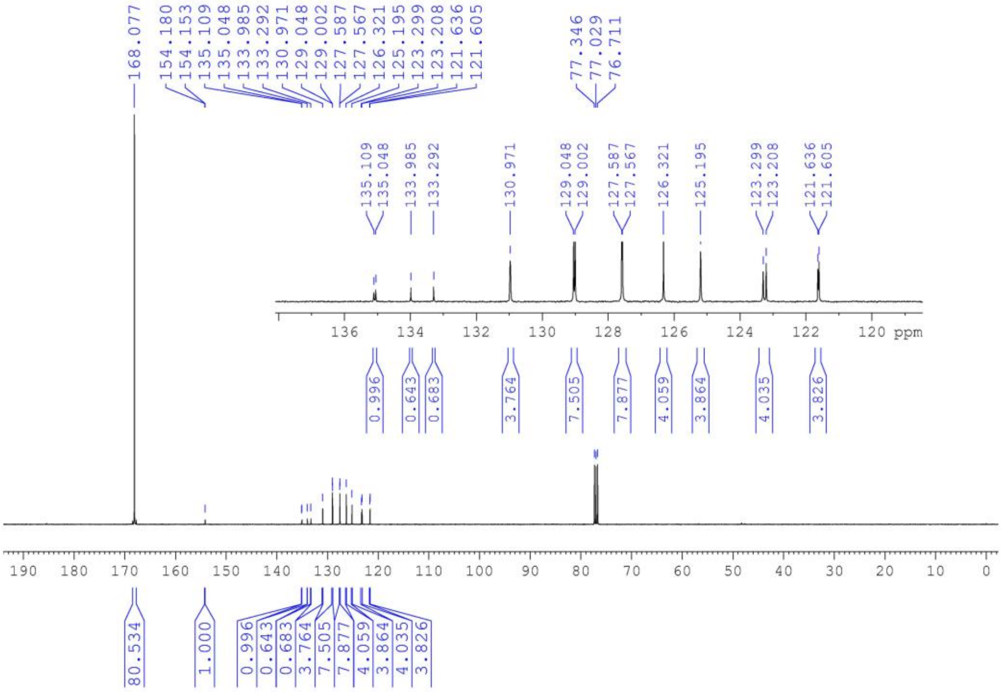
### 2-phenylbenzothiazole (3aa)

Inverse gated decoupling $^{13}$C NMR: (100 MHz, $CDCl_3$) $\delta$ 168.1 (int. = 0.93), 154.2 (int. = 1.00), 135.1, 133.6, 131.0, 129.0, 127.6, 126.3(int. = 4.44), 125.2(int. = 4.34), 123.2, 121.6.



**2-phenylbenzothiazole ($^{13}$C-3aa)**

Inverse gated decoupling $^{13}$C NMR: (100 MHz, $CDCl_3$) $\delta$ 168.1 (int. = 80.53), 154.2 (int. = 1.00), 135.1, 133.6, 131.0, 129.0, 127.6, 126.3 (int. = 4.06), 125.2 (int. = 3.86), 123.3, 121.6.



| Authentic $\delta$ (ppm): | | 168.07 |
|---|---|---|
| Labeled $\delta$ (ppm): | | 168.08 |
| C(154.2 ppm): | Ratio Labeled | 80.53 |
| | Ratio Unlabeled | 0.93 |
| | Labeled / Unlabeled | 87.53 |
| C(126.3 ppm): | Ratio Labeled | 19.83 |
| | Ratio Unlabeled | 0.22 |
| | Labeled / Unlabeled | 90.14 |
| C(125.2 ppm): | Ratio Labeled | 20.86 |
| | Ratio Unlabeled | 0.23 |
| | Labeled / Unlabeled | 90.70 |
| Average Labeled / Unlabeled | | 89.46 |
| Absolute Abundance (%) | | 97.42 |

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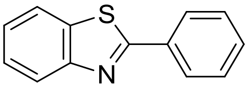
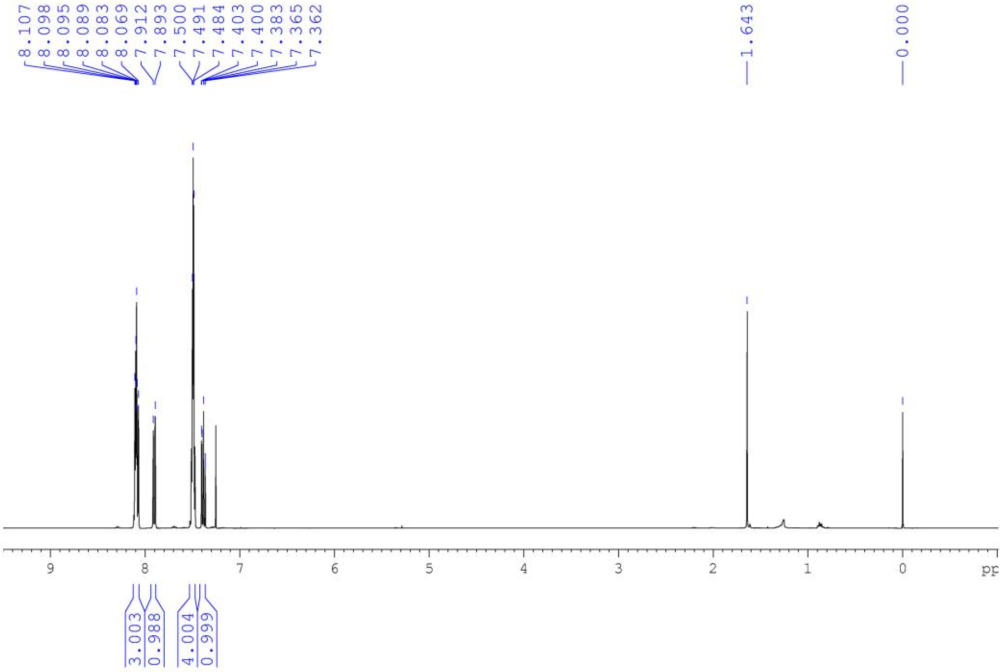
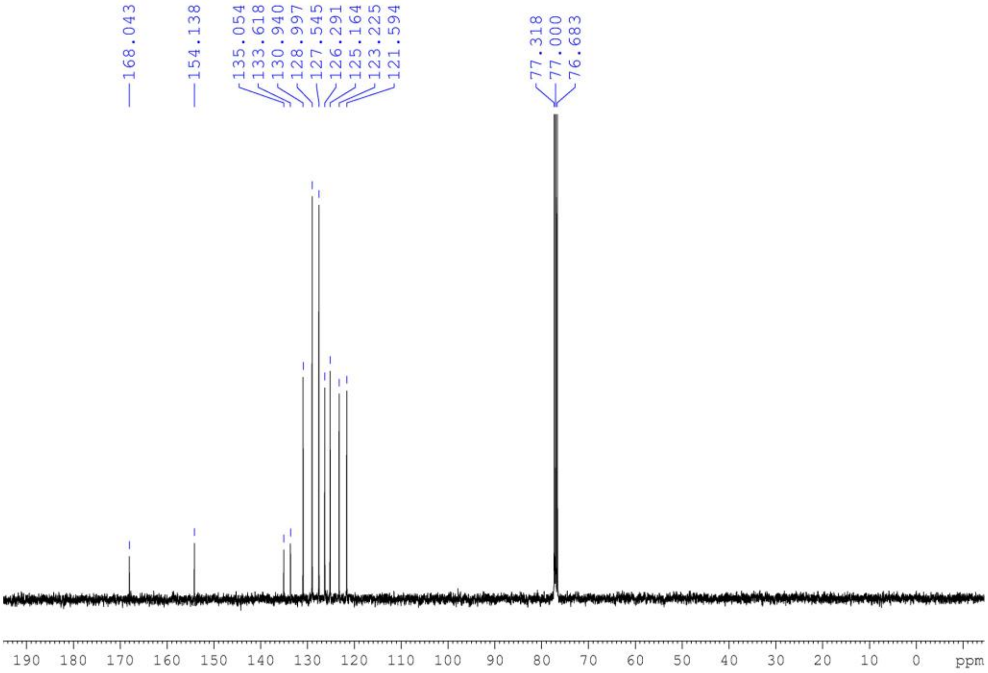
# 1H NMR and 13C NMR spectra of products

**3aa**







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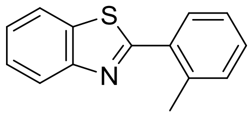
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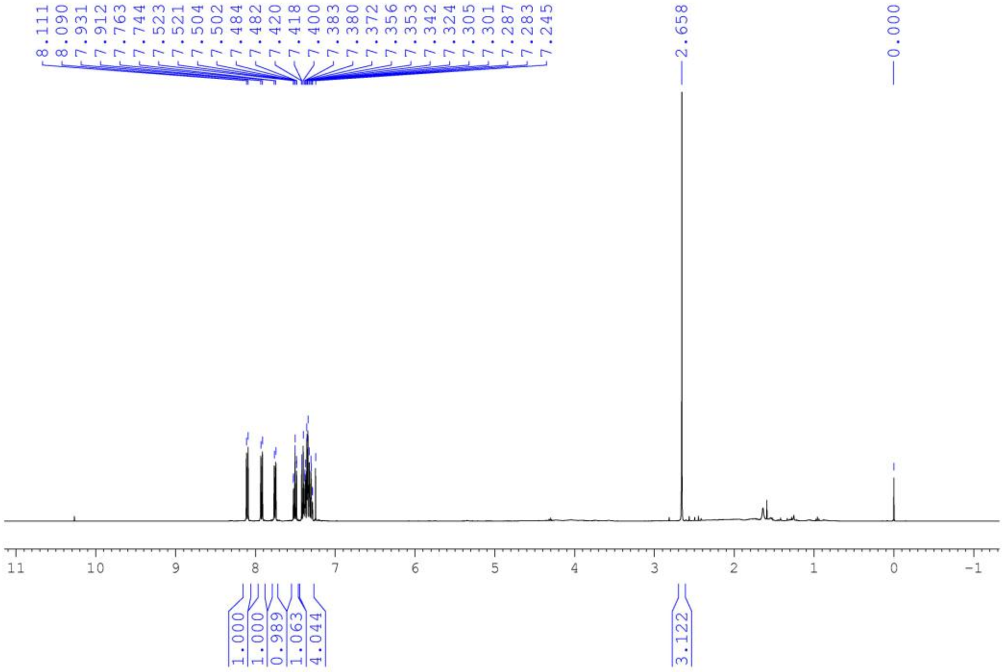
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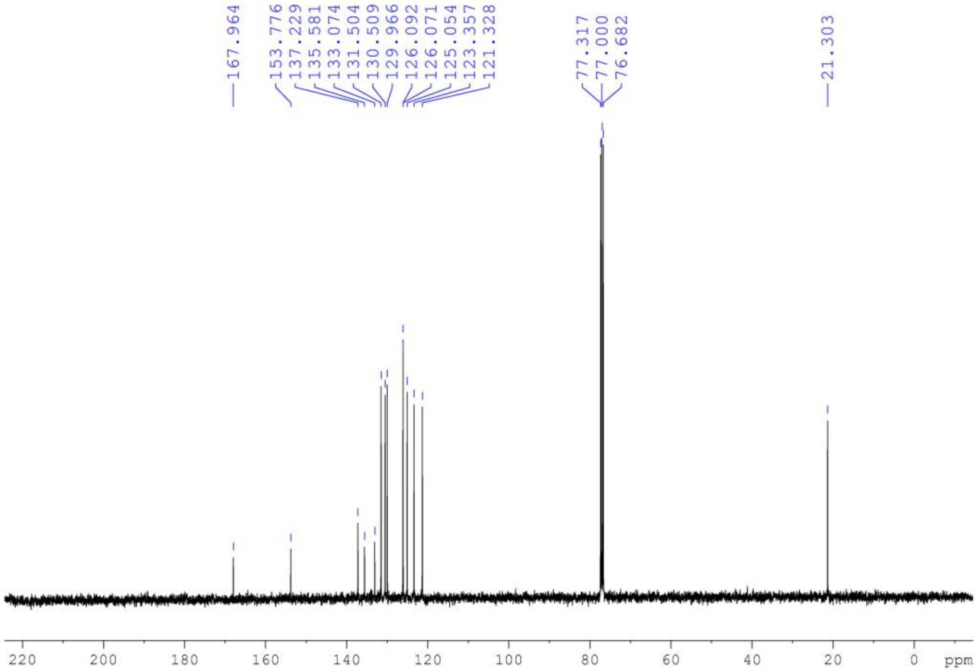
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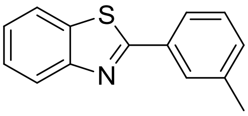
**3ac**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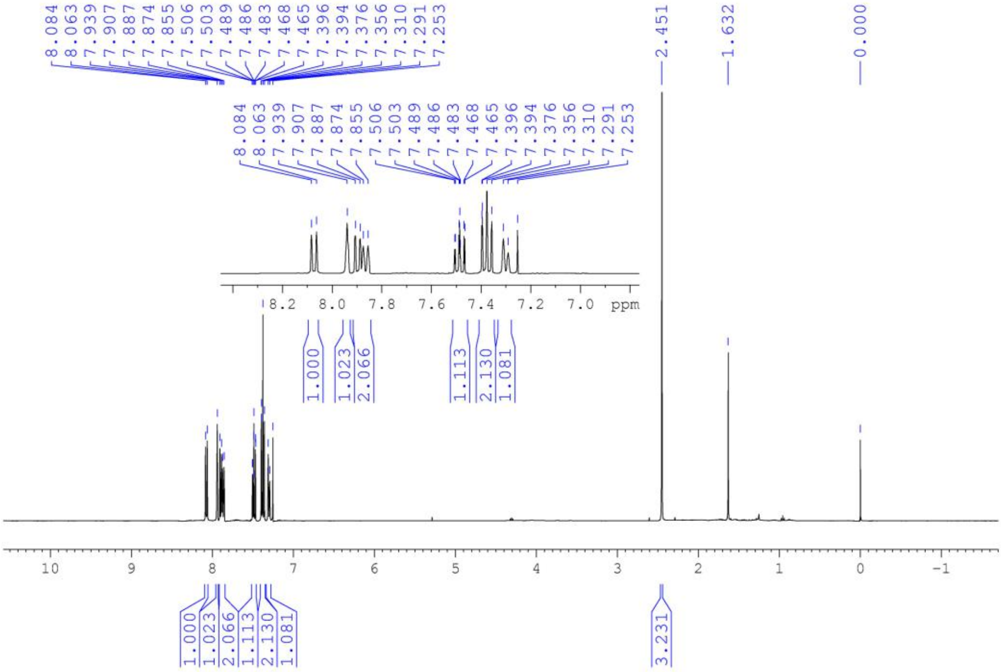
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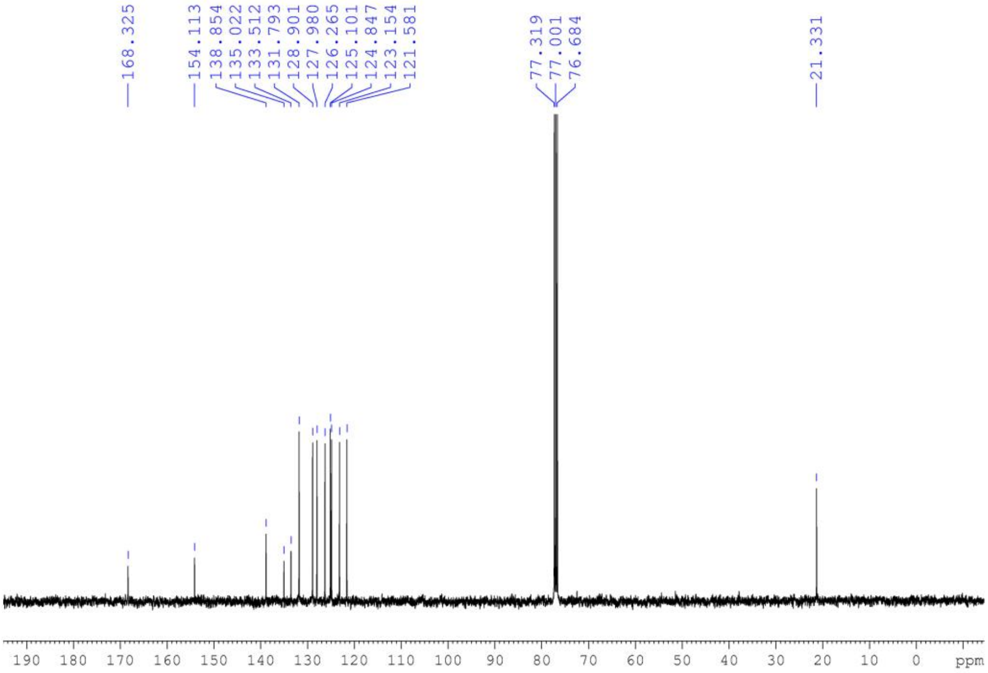
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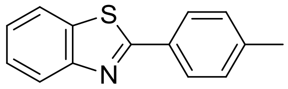
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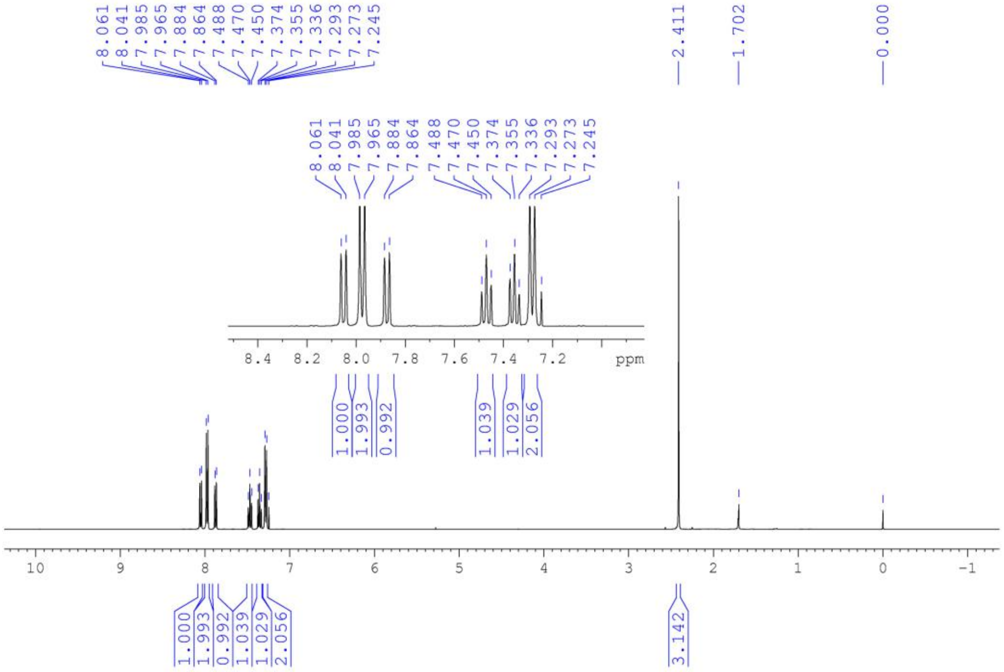
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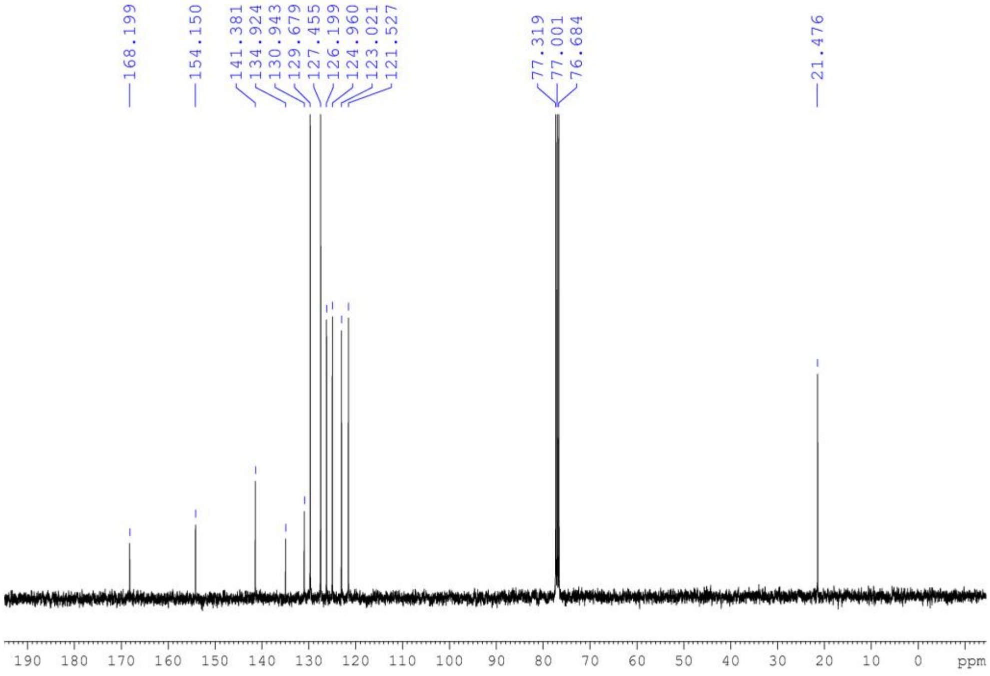
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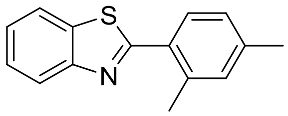
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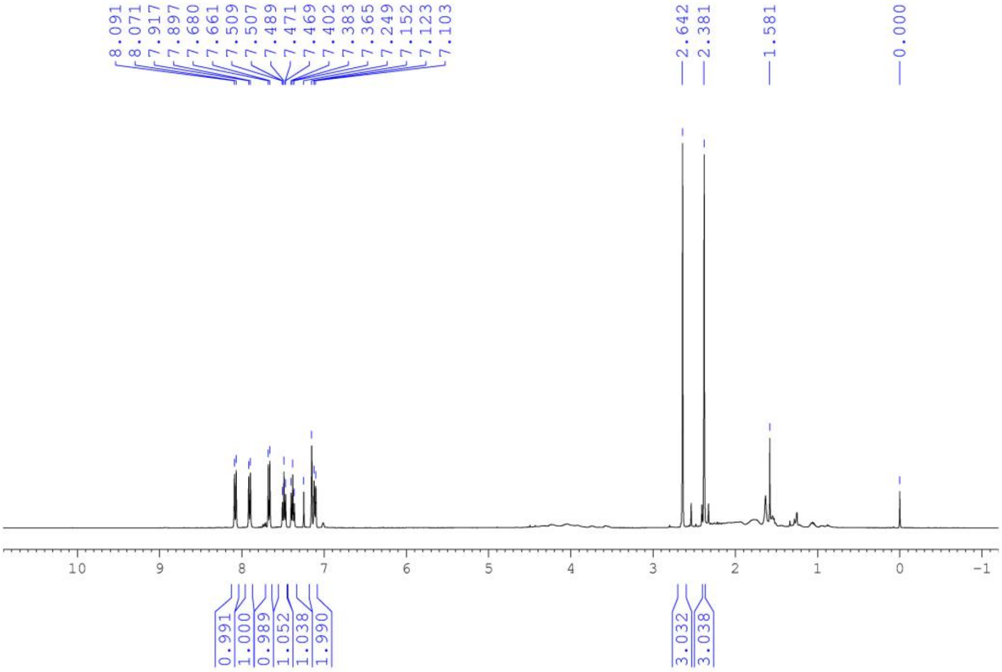
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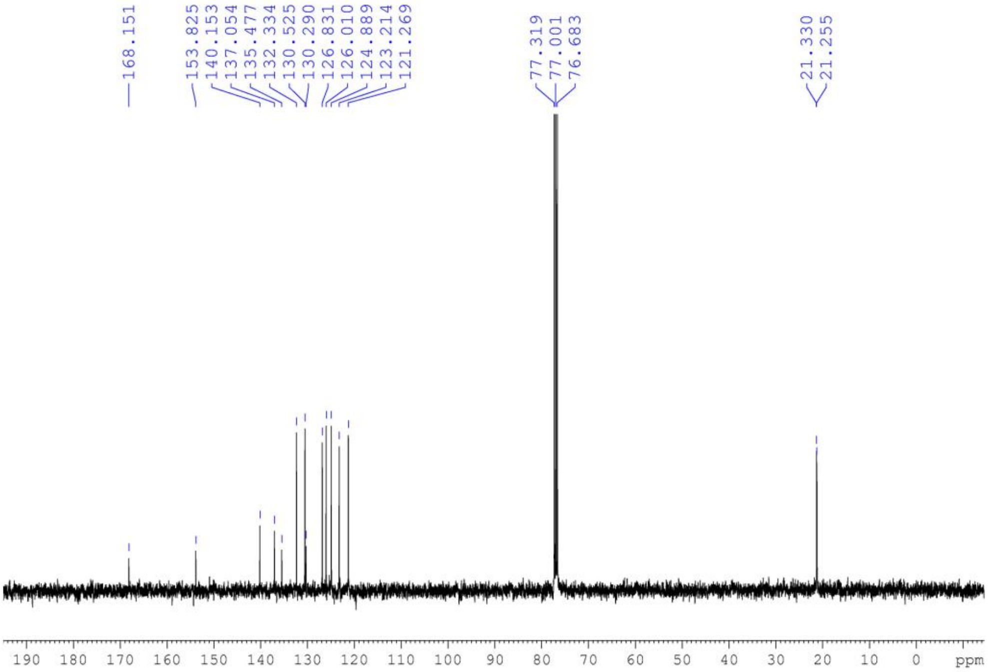
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130.290
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126.010
124.889
123.214
121.269
77.319
77.001
76.683
21.330
21.255
190
180
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120
110
100
90
80
70
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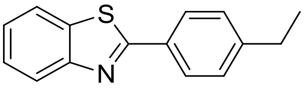
0
ppm

**3af**


S
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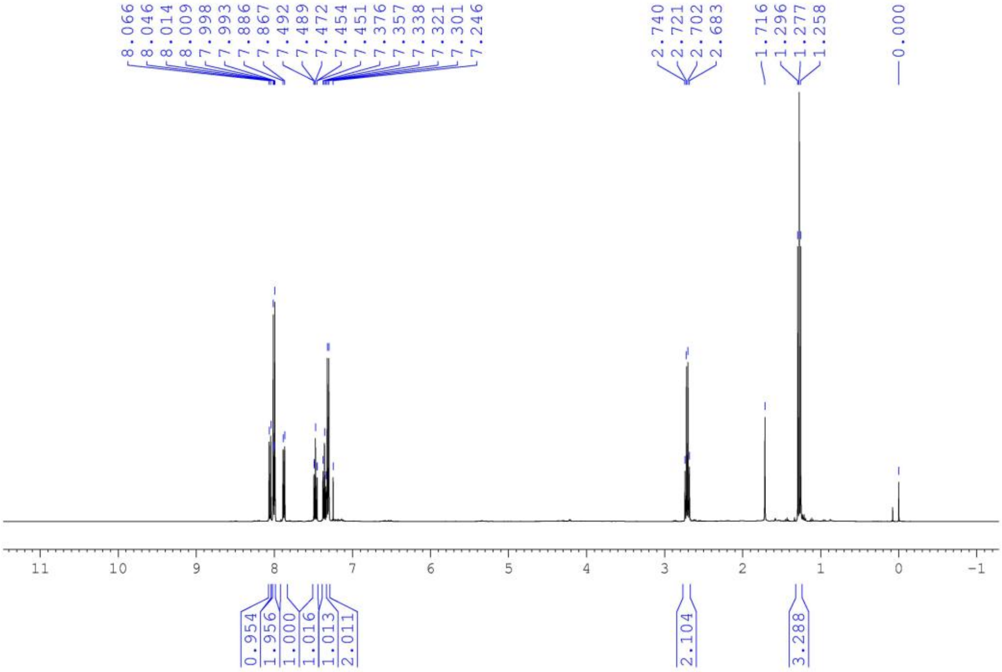
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8.009
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7.993
7.886
7.867
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7.489
7.472
7.454
7.451
7.376
7.357
7.338
7.321
7.301
7.246
2.740
2.721
2.702
2.683
1.716
1.296
1.277
1.258
0.000
11
10
9
8
7
6
5
4
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1.016
1.013
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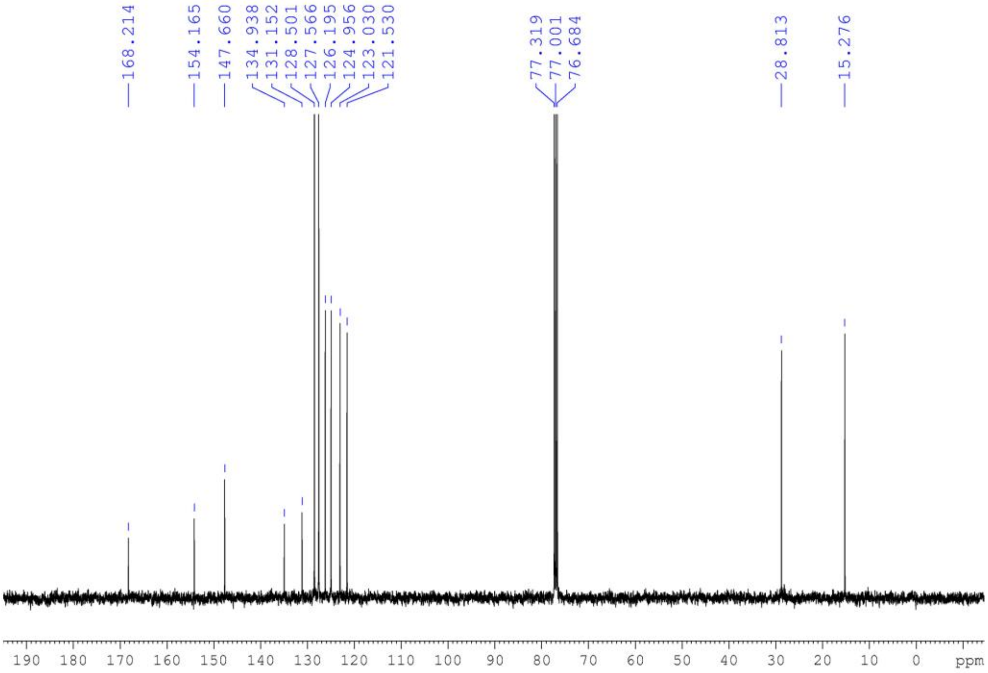
2.104
3.288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147.660
134.938
131.152
128.501
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126.195
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123.030
121.530
77.319
77.001
76.684
28.813
15.276
190
180
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80
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40
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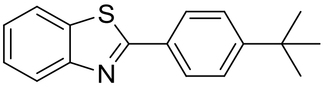
0
ppm

**3ag**


S
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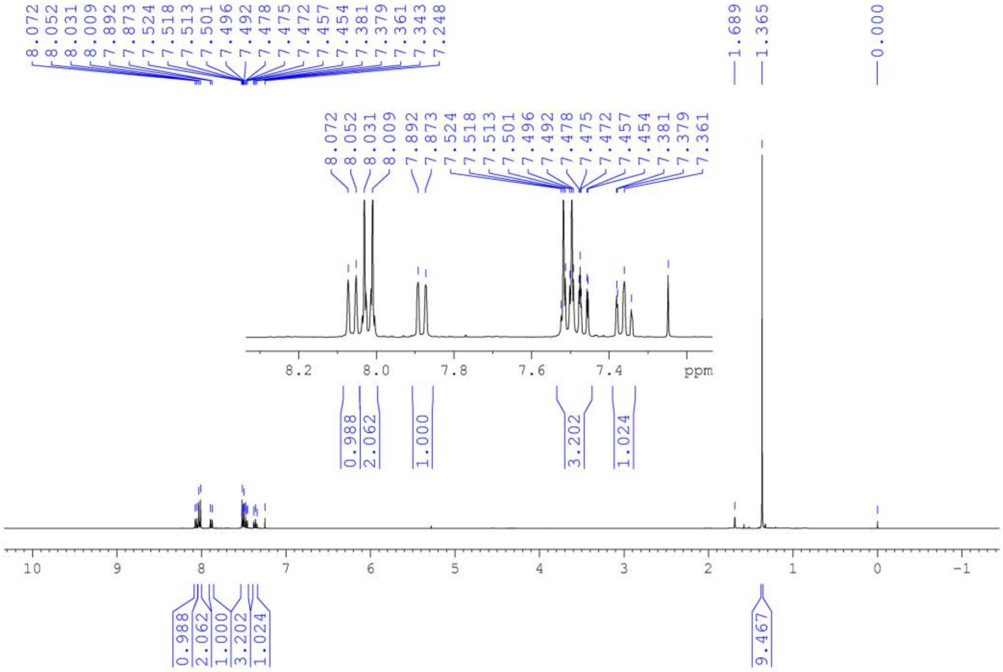
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7.518
7.513
7.501
7.496
7.492
7.478
7.475
7.472
7.457
7.454
7.381
7.379
7.361
7.343
7.248
1.689
1.365
0.000
8.2
8.0
7.8
7.6
7.4
ppm
0.988
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1.024
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5
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2
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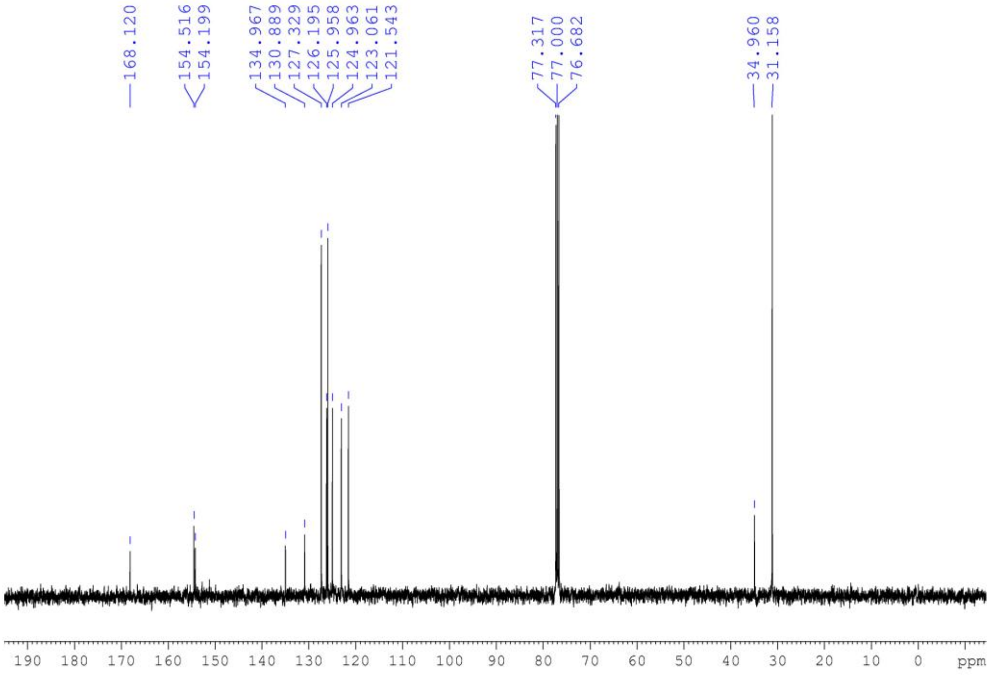
-1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126.195
125.958
124.963
123.061
121.543
77.317
77.000
76.682
34.960
31.158
190
180
170
160
150
140
130
120
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50
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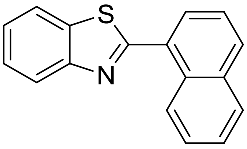
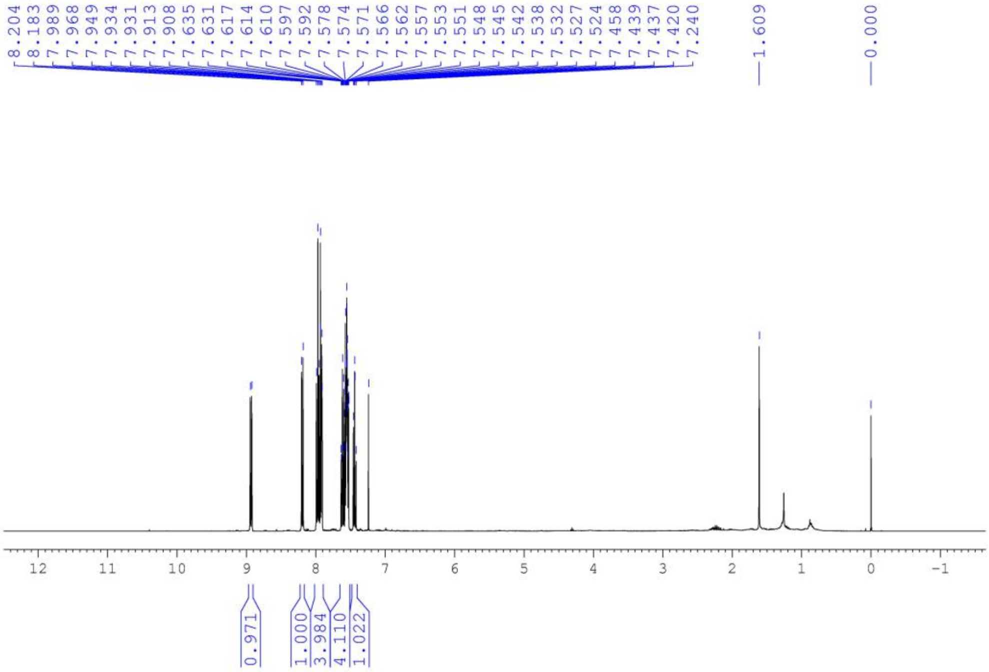
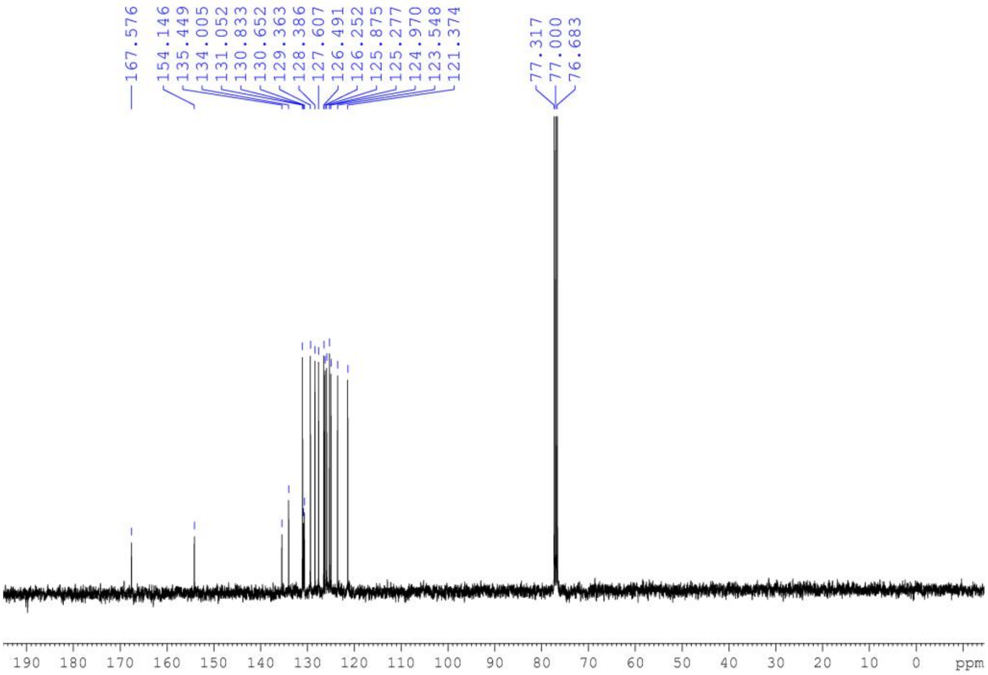
30
20
10
0
ppm

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

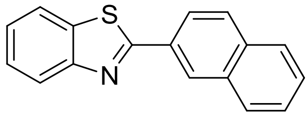
**3ah**







**3ai**


S
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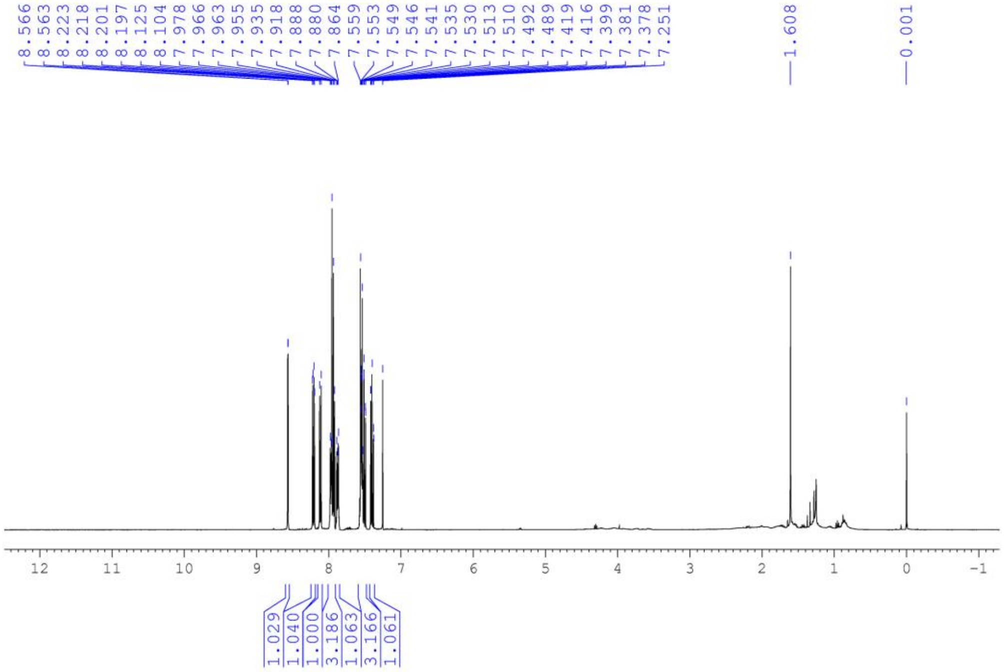
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8.197
8.125
8.104
7.978
7.966
7.963
7.955
7.935
7.918
7.888
7.880
7.864
7.559
7.553
7.549
7.546
7.541
7.535
7.530
7.513
7.510
7.492
7.489
7.419
7.416
7.399
7.381
7.378
7.251
1.608
0.001
12
11
10
9
8
7
6
5
4
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2
1
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1.029
1.040
1.000
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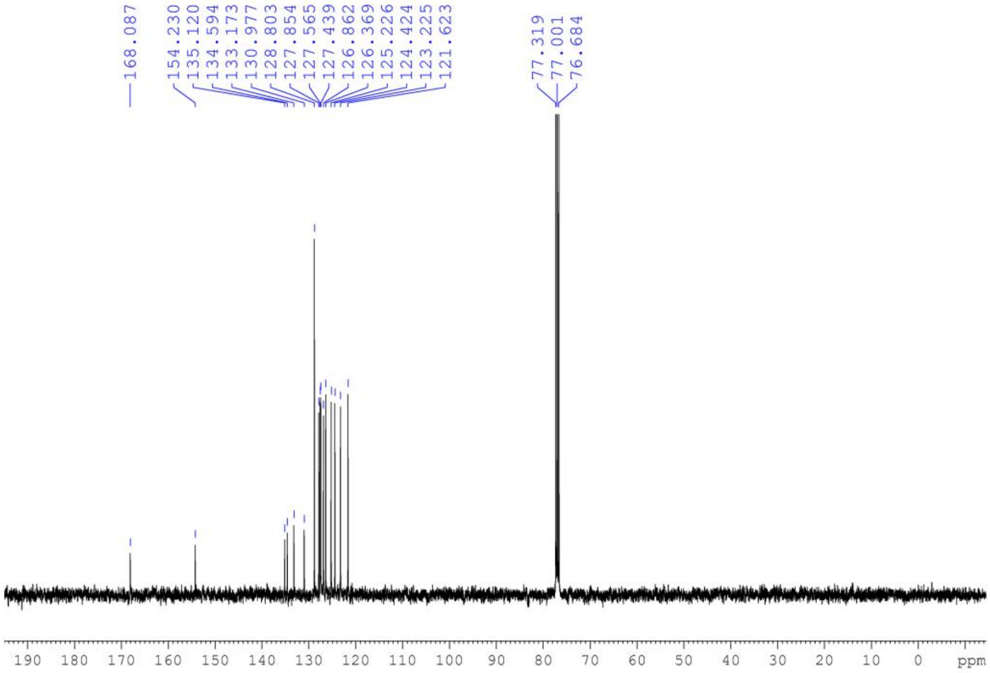
1.063
3.166
1.061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127.854
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127.439
126.862
126.369
125.226
124.424
123.225
121.623
77.319
77.001
76.684
190
180
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150
140
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120
110
100
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80
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20
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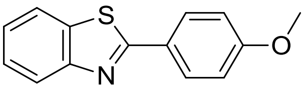
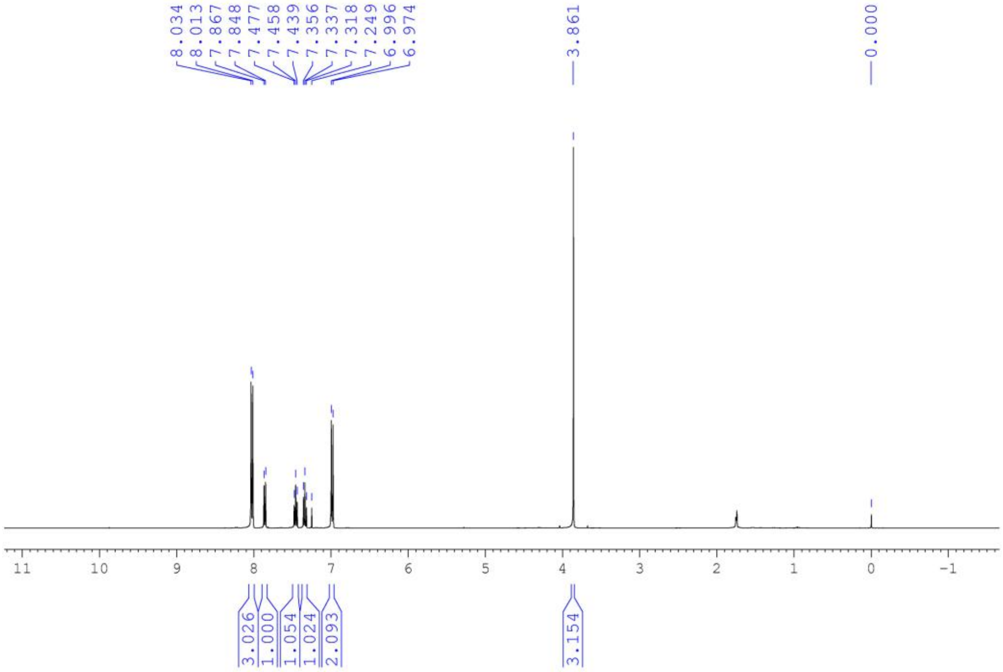
0
ppm

**3aj**


S
N
O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7.477
7.458
7.439
7.356
7.337
7.318
7.249
6.996
6.974
3.861
0.000
11
10
9
8
7
6
5
4
3
2
1
0
-1
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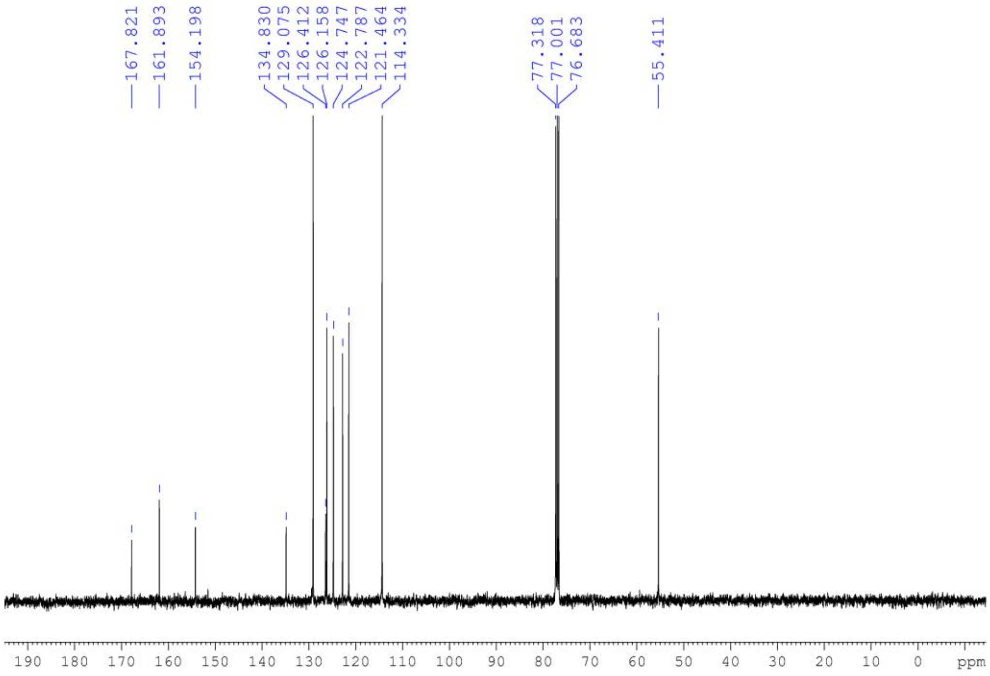
1.000
1.054
1.024
2.093
3.154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126.158
124.747
122.787
121.464
114.334
77.318
77.001
76.683
55.411
190
180
170
160
150
140
130
120
110
100
90
80
70
60
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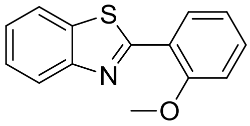
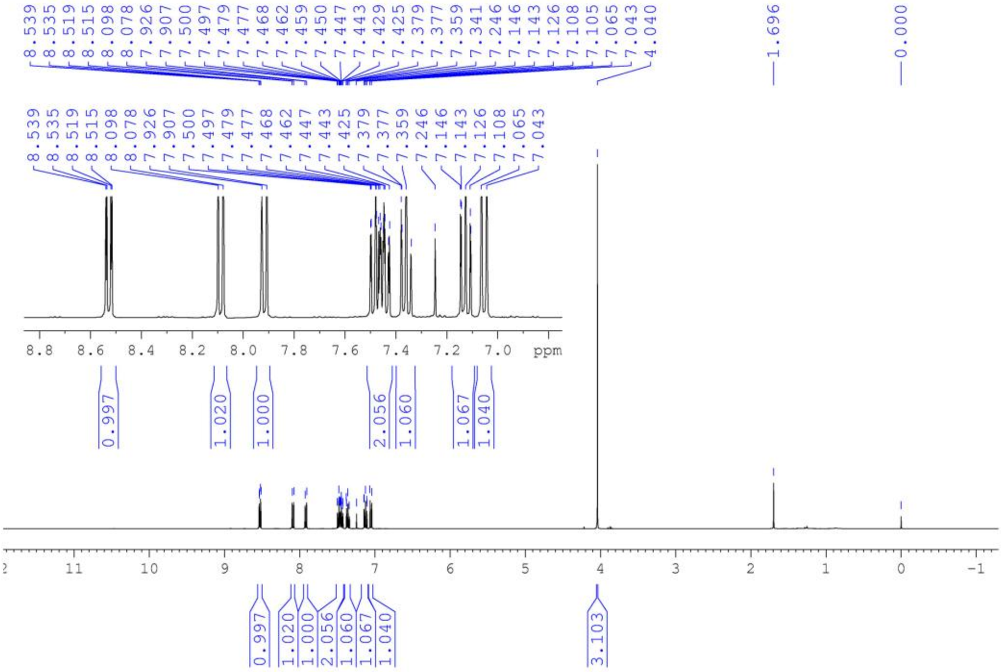
40
30
20
10
0
ppm

**3ak**


S
N
O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7.907
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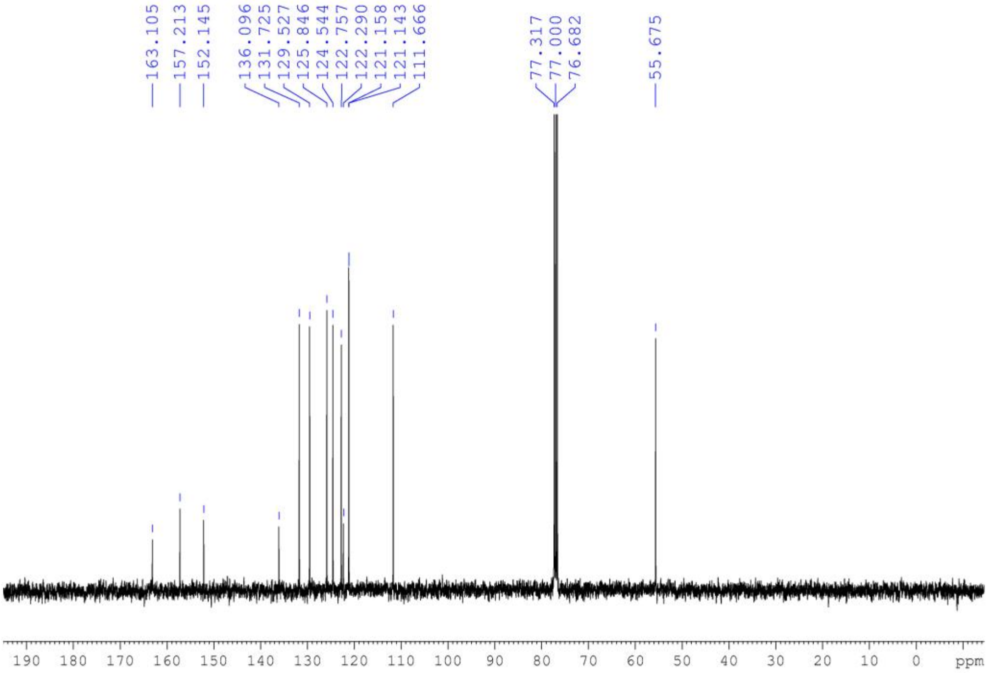
7.497
7.479
7.477
7.468
7.462
7.459
7.450
7.447
7.443
7.429
7.425
7.379
7.377
7.359
7.341
7.246
7.146
7.143
7.126
7.108
7.105
7.065
7.043
4.040
1.696
0.000
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
ppm
0.997
1.020
1.000
2.056
1.060
1.067
1.040
11
10
9
8
7
6
5
4
3
2
1
0
-1
3.103


163.105
157.213
152.145
136.096
131.725
129.527
125.846
124.544
122.757
122.290
121.158
121.143
111.666
77.317
77.000
76.682
55.675
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
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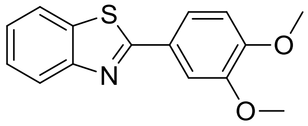
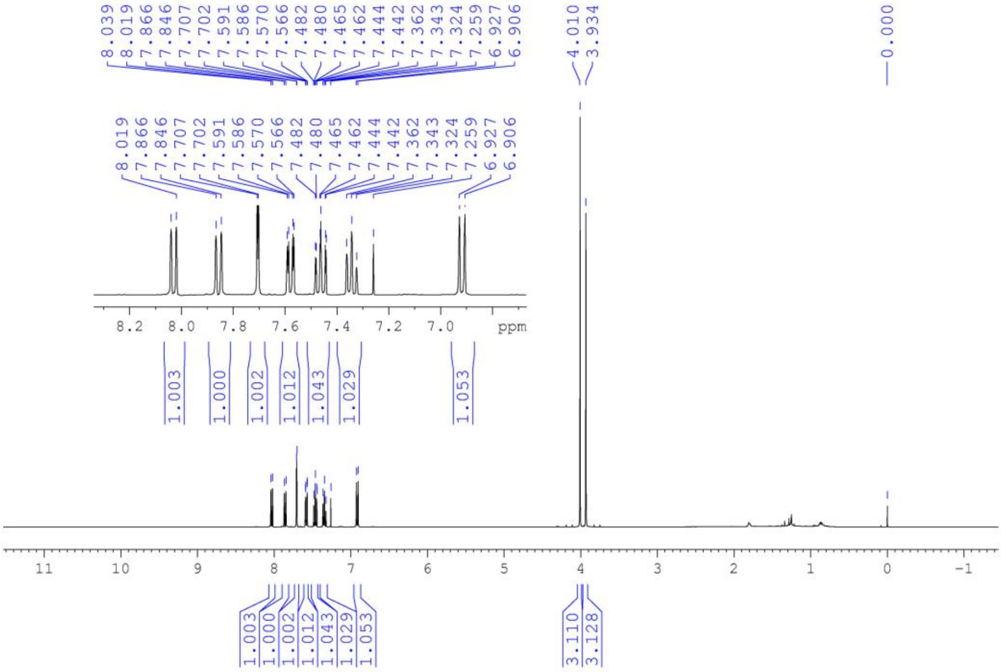
0
ppm

**3al**


S
N
O
O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7.586
7.570
7.566
7.482
7.480
7.465
7.462
7.444
7.442
7.362
7.343
7.324
7.259
6.927
6.906
4.010
3.934
0.000
8.2
8.0
7.8
7.6
7.4
7.2
7.0
ppm
1.003
1.000
1.002
1.012
1.043
1.029
1.053
11
10
9
8
7
6
5
4
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2
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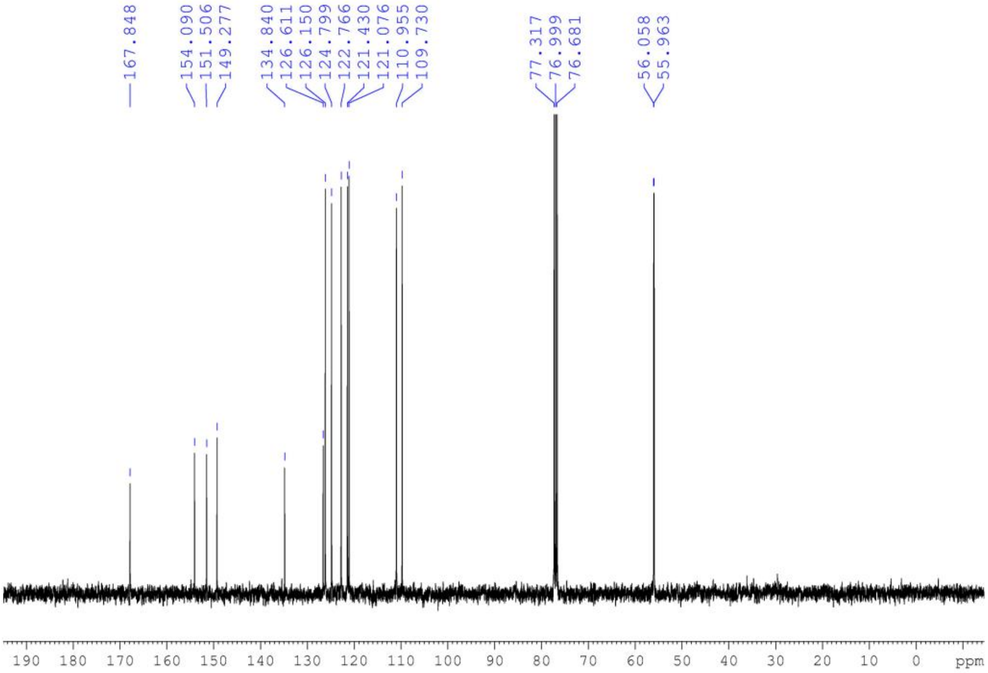
-1
3.110
3.128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126.150
124.799
122.766
121.430
121.076
110.955
109.730
77.317
76.999
76.681
56.058
55.963
190
180
170
160
150
140
130
120
110
100
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80
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60
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40
30
20
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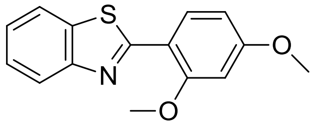
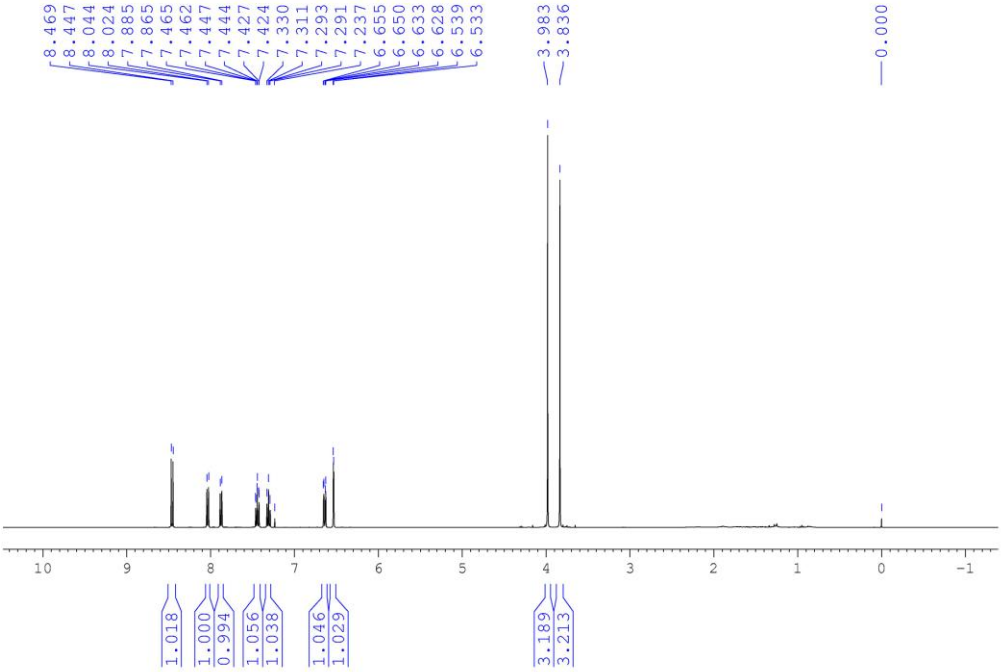
0
ppm

**3am**


S
N
O
O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8.024
7.885
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7.462
7.447
7.444
7.427
7.424
7.330
7.311
7.293
7.291
7.237
6.655
6.650
6.633
6.628
6.539
6.533
3.983
3.836
0.000
10
9
8
7
6
5
4
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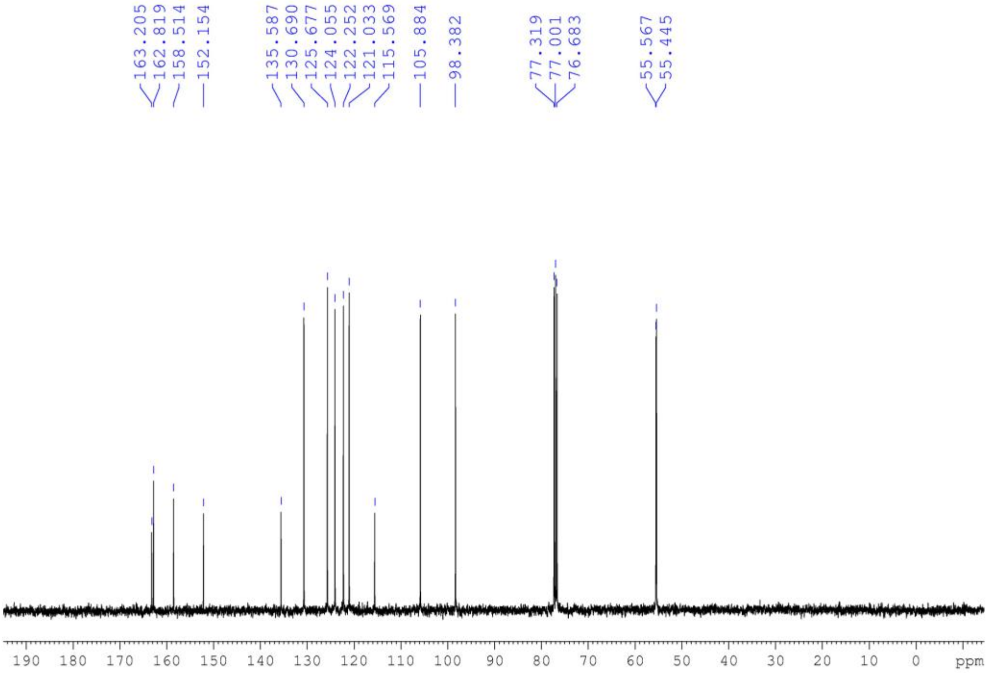
3.213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162.819
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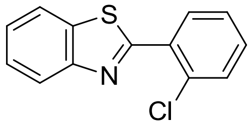
125.677
124.055
122.252
121.033
115.569
105.884
98.382
77.319
77.001
76.683
55.567
55.445
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

**3an**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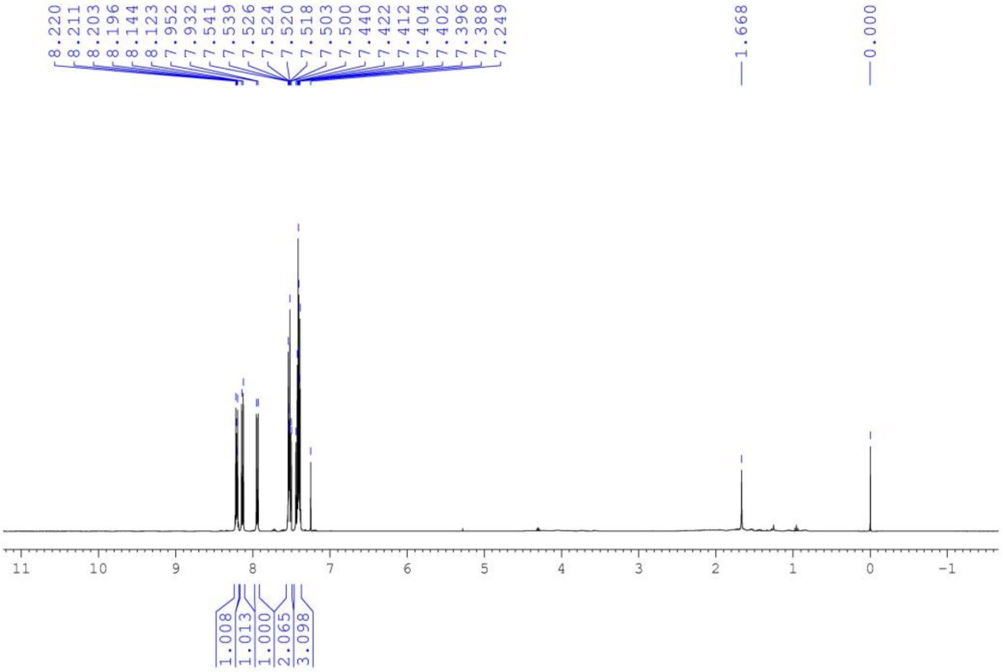
Cl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8.203
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8.144
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7.932
7.541
7.539
7.526
7.524
7.520
7.518
7.503
7.500
7.440
7.422
7.412
7.404
7.402
7.396
7.388
7.249
1.668
0.000
11
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5
4
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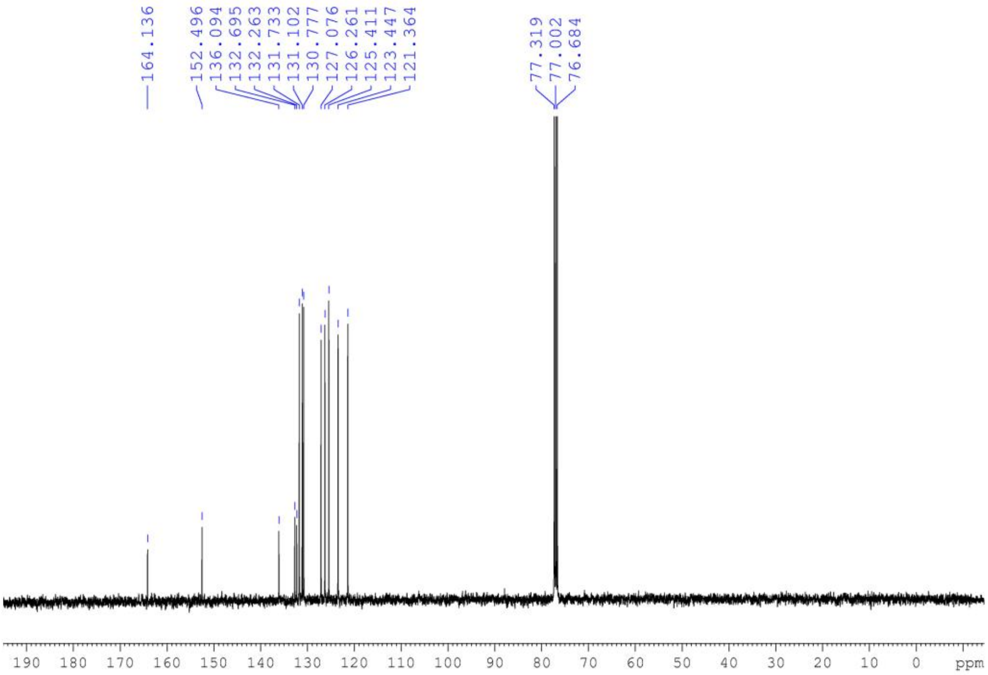
1.000
2.065
3.098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132.695
132.263
131.733
131.102
130.777
127.076
126.261
125.411
123.447
121.364
77.319
77.002
76.684
190
180
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120
110
100
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40
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20
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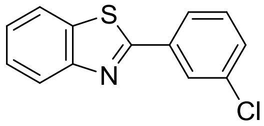
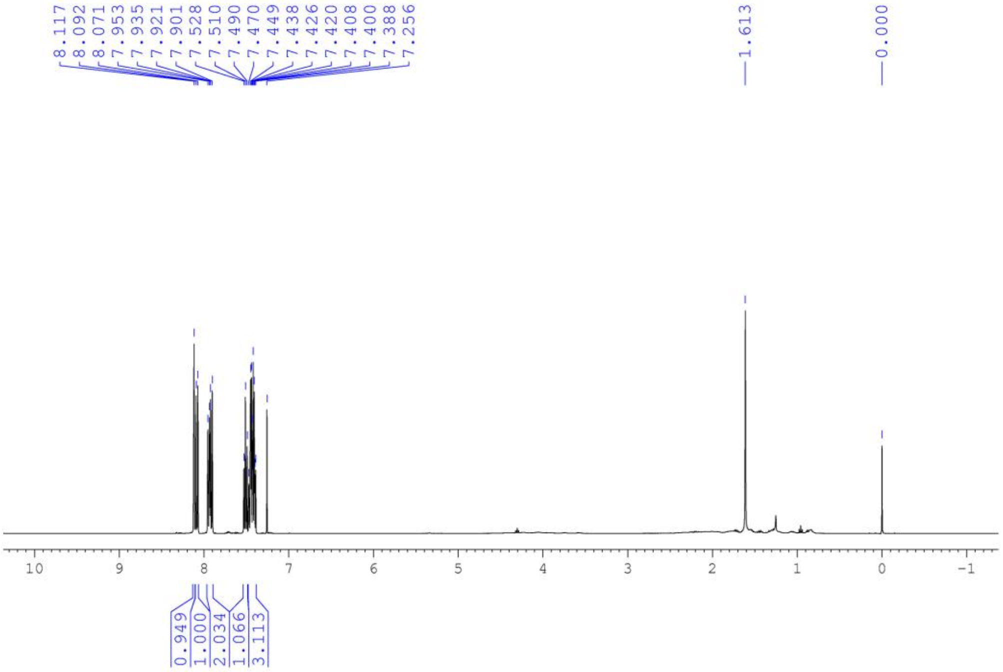
0
ppm

**3ao**


S
N
Cl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7.490
7.470
7.449
7.438
7.426
7.420
7.408
7.400
7.388
7.256
1.613
0.000
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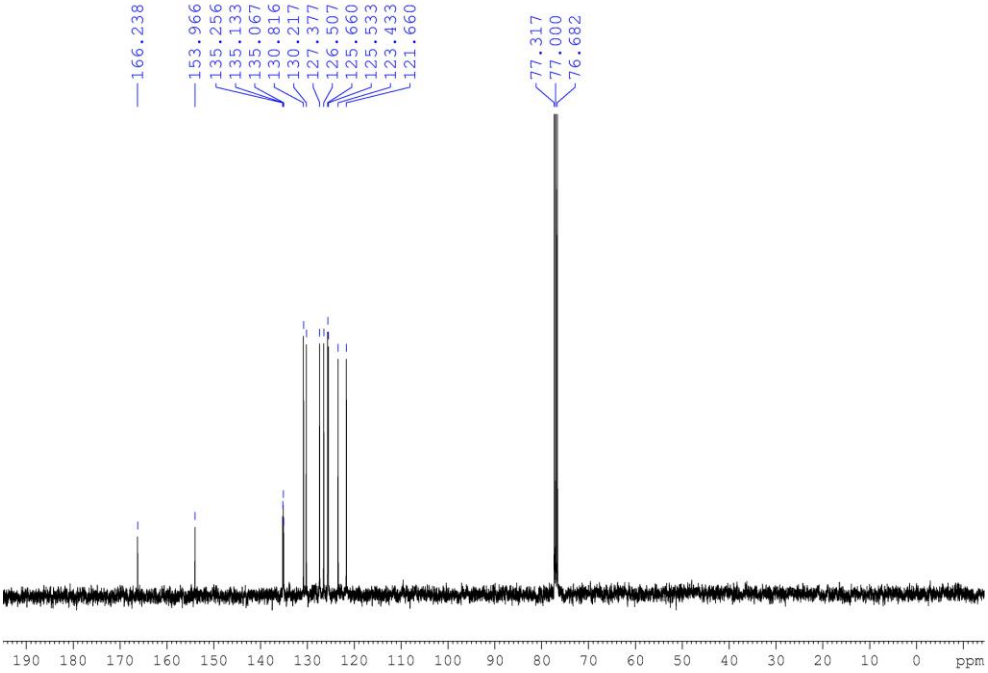
3.113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125.660
125.533
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77.317
77.000
76.682
190
180
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120
110
100
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80
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50
40
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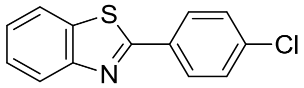
0
ppm

**3ap**


S
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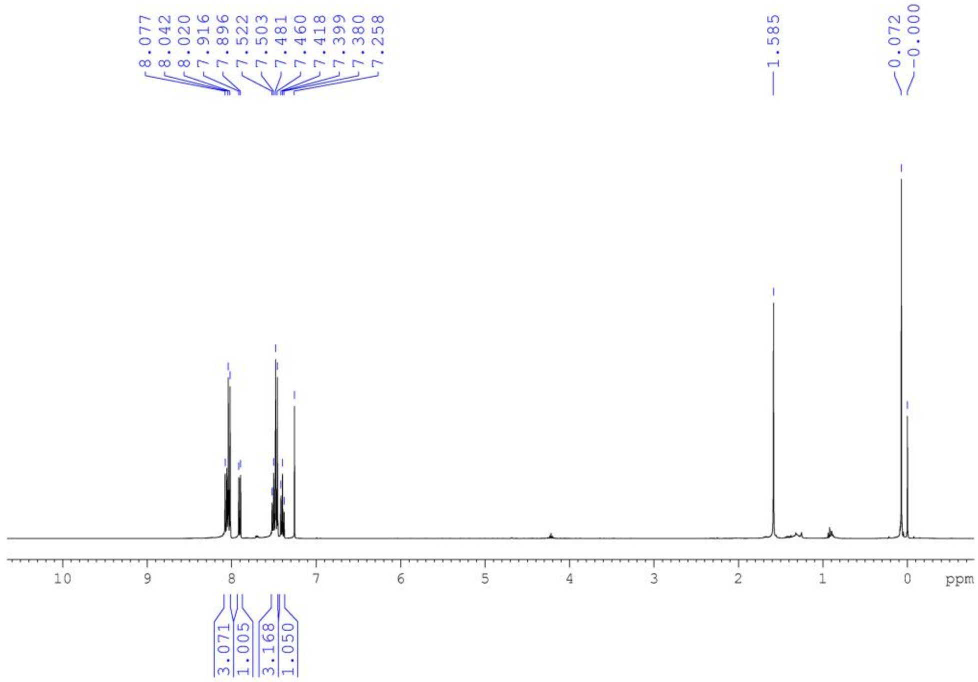
Cl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7.522
7.503
7.481
7.460
7.418
7.399
7.380
7.258
1.585
0.072
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6
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4
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ppm
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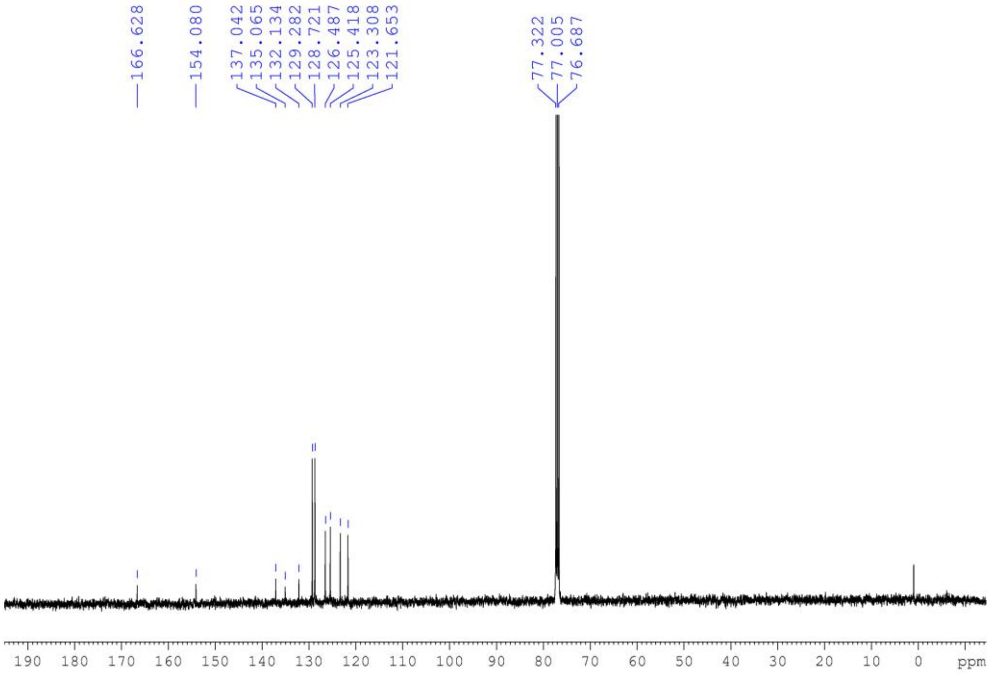
1.050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125.418
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121.653
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76.687
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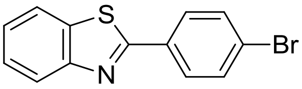
ppm

**3aq**


S
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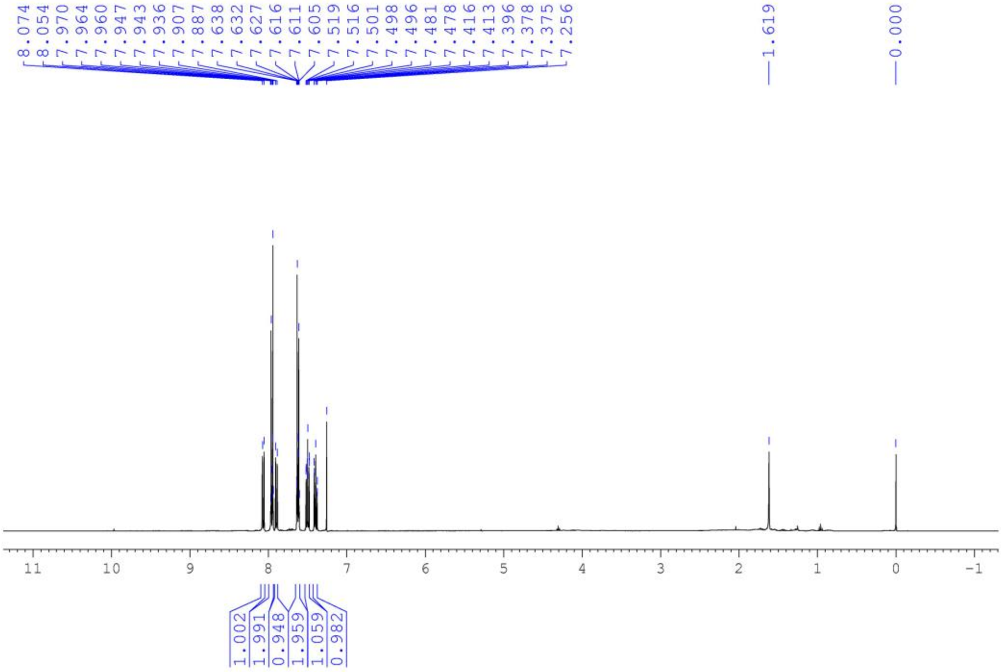
Br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7.632
7.627
7.616
7.611
7.605
7.519
7.516
7.501
7.498
7.496
7.481
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7.413
7.396
7.378
7.375
7.256
1.619
0.000
11
10
9
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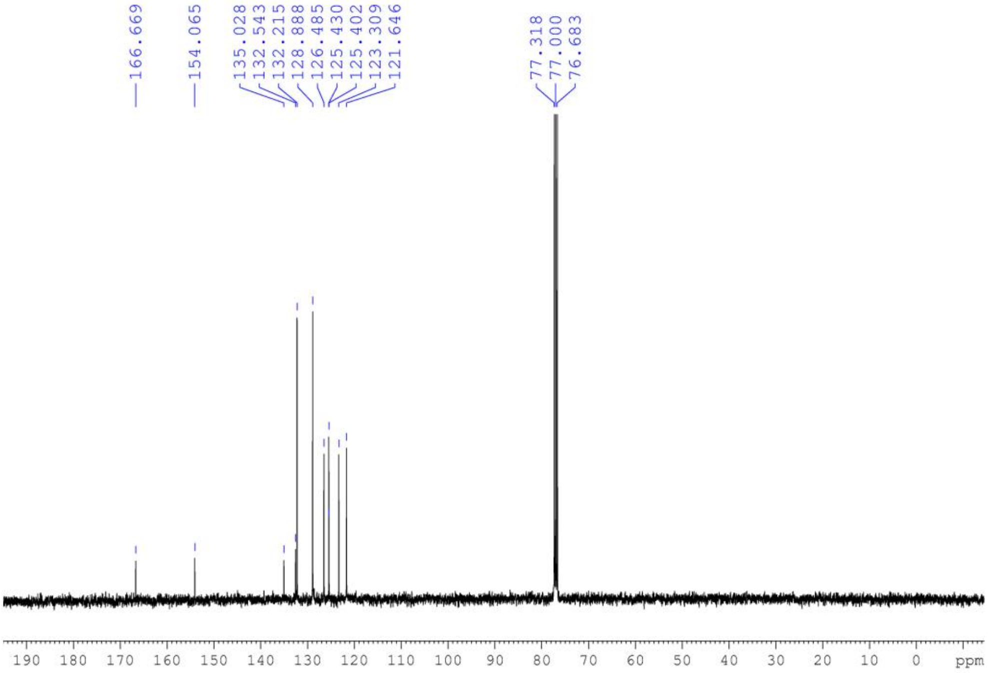
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77.000
76.683
190
180
170
160
150
140
130
120
110
100
90
80
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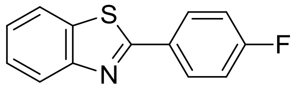
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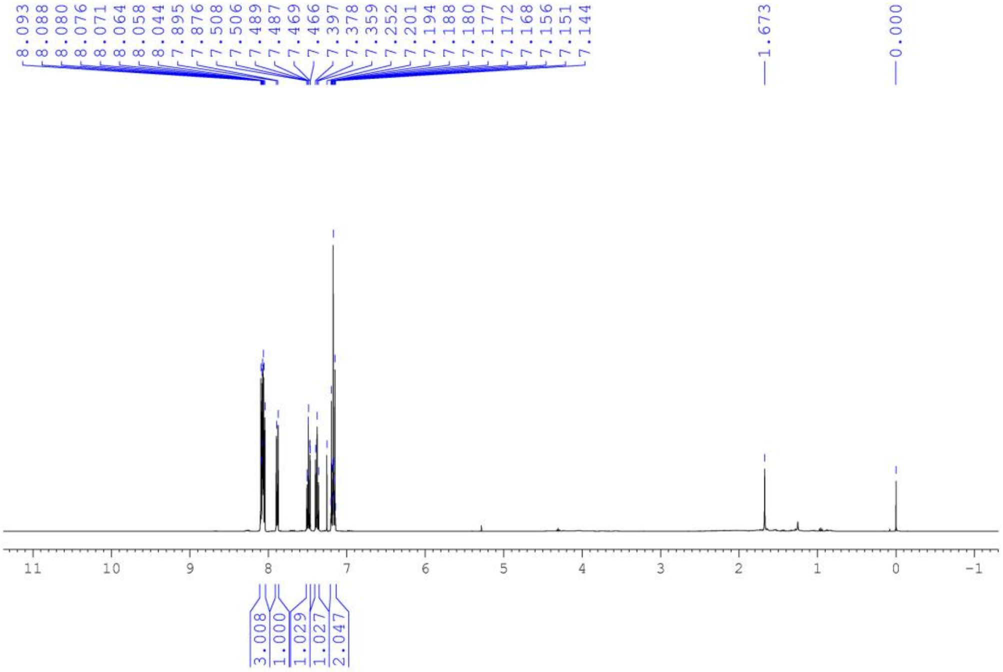
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7.876
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7.506
7.489
7.487
7.469
7.466
7.397
7.378
7.359
7.252
7.201
7.194
7.188
7.180
7.177
7.172
7.168
7.156
7.151
7.144
1.673
0.000
11
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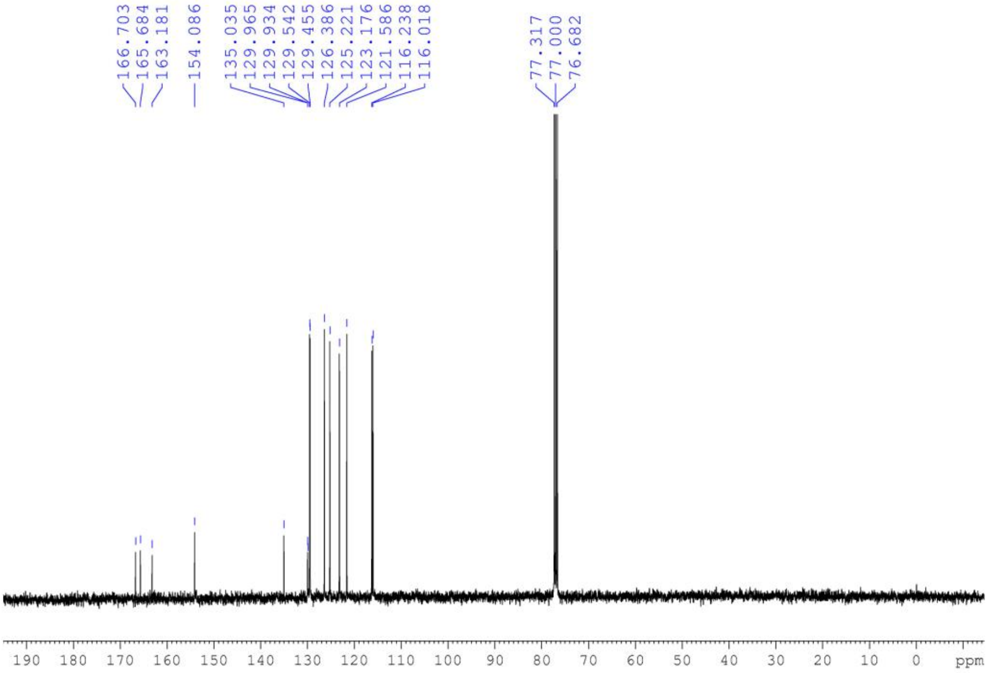
2.047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129.542
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125.221
123.176
121.586
116.238
116.018
77.317
77.000
76.682
190
180
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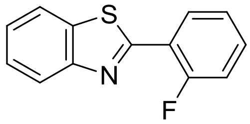
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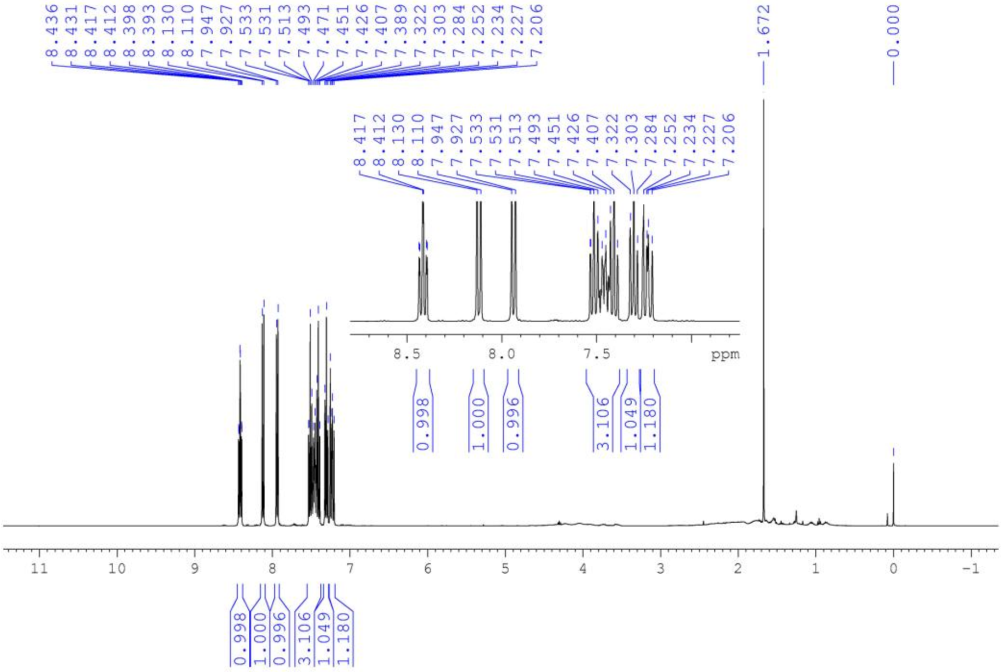
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8.130
8.110
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7.927
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7.531
7.513
7.493
7.471
7.451
7.426
7.407
7.389
7.322
7.303
7.284
7.252
7.234
7.227
7.206
1.672
0.000
8.417
8.412
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8.110
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7.426
7.407
7.322
7.303
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7.252
7.234
7.227
7.206
8.5
8.0
7.5
ppm
0.998
1.000
0.996
3.106
1.049
1.180
11
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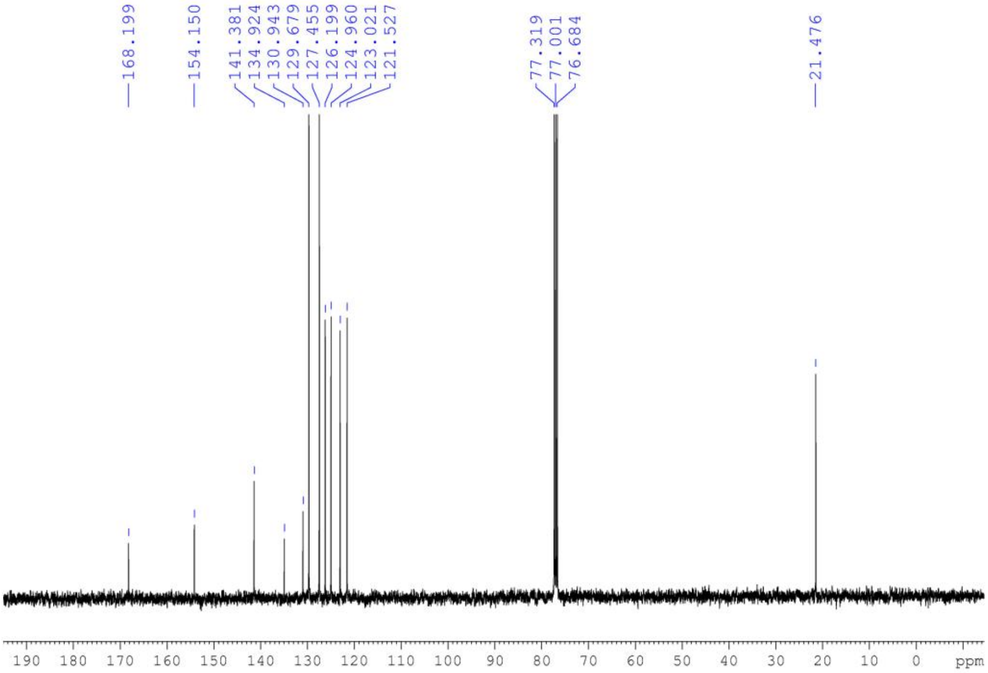
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123.021
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77.319
77.001
76.684
21.476
190
180
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120
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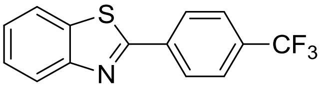
0
ppm

**3at**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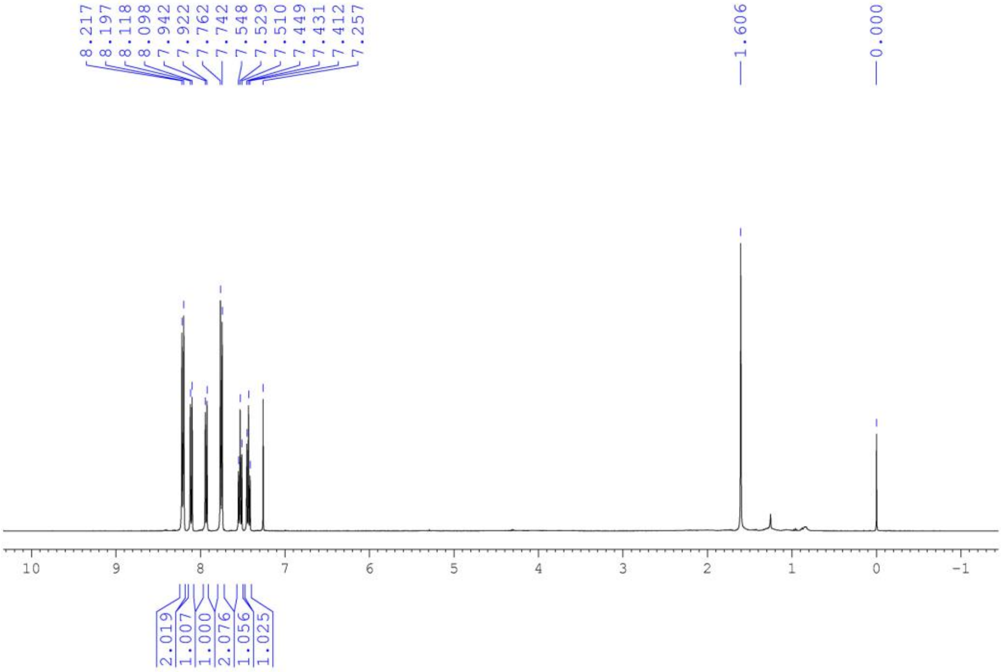
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7.922
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7.742
7.548
7.529
7.510
7.449
7.431
7.412
7.257
1.606
0.000
10
9
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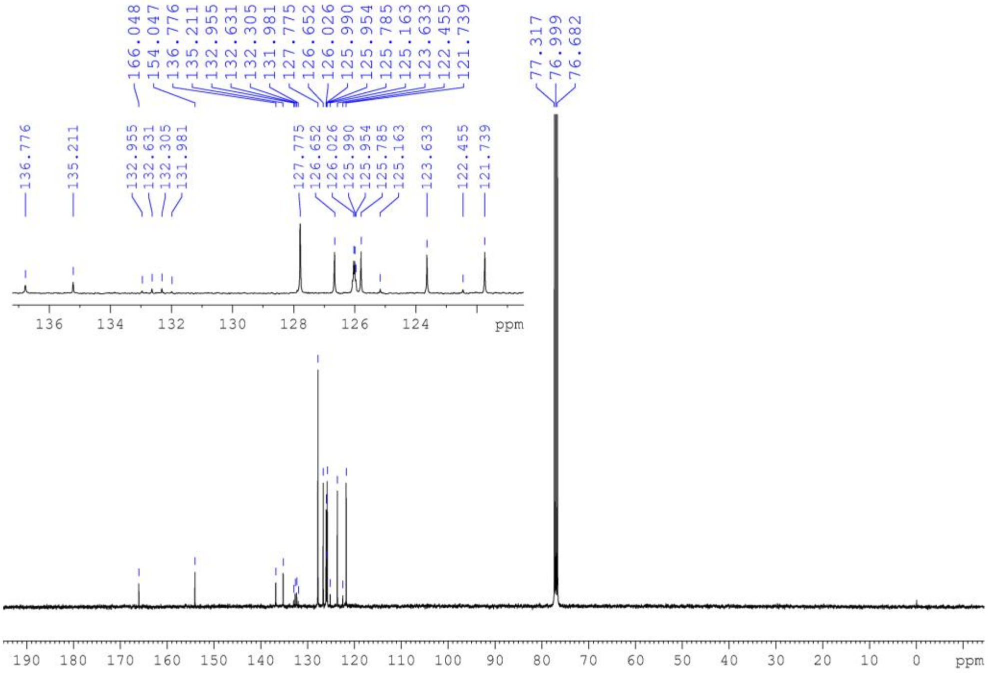
1.007
1.000
2.076
1.056
1.025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135.211
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132.631
132.305
131.981
127.775
126.652
126.026
125.990
125.954
125.785
125.163
123.633
122.455
121.739
77.317
76.999
76.682
136.776
135.211
132.955
132.631
132.305
131.981
127.775
126.652
126.026
125.990
125.954
125.785
125.163
123.633
122.455
121.739
136
134
132
130
128
126
124
ppm
190
180
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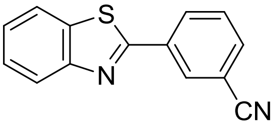
**3au**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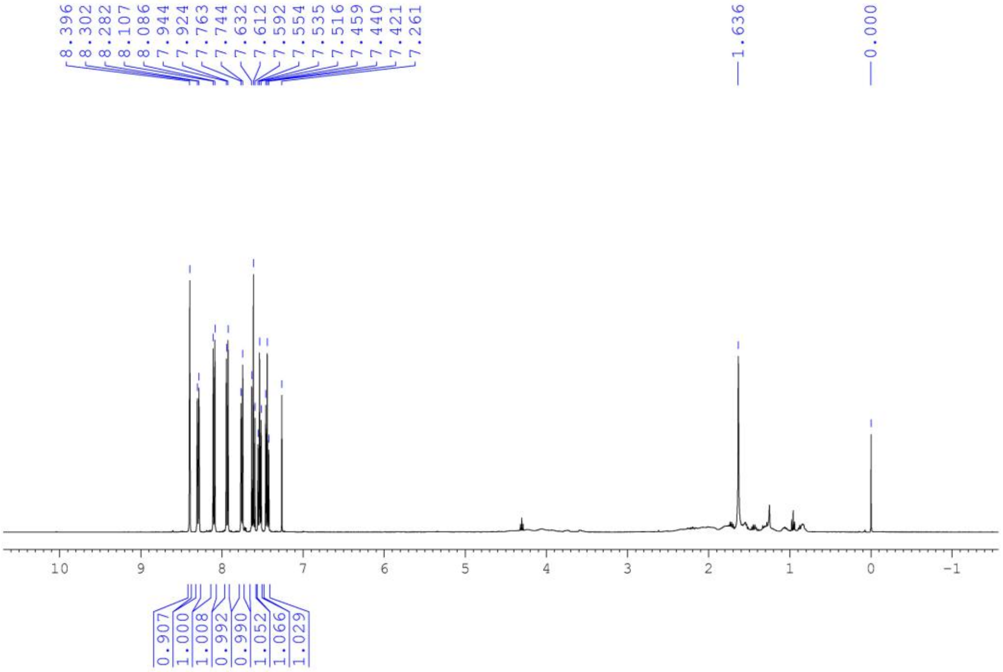
N
CN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8.107
8.086
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7.924
7.763
7.744
7.632
7.612
7.592
7.554
7.535
7.516
7.459
7.440
7.421
7.261
1.636
0.000
10
9
8
7
6
5
4
3
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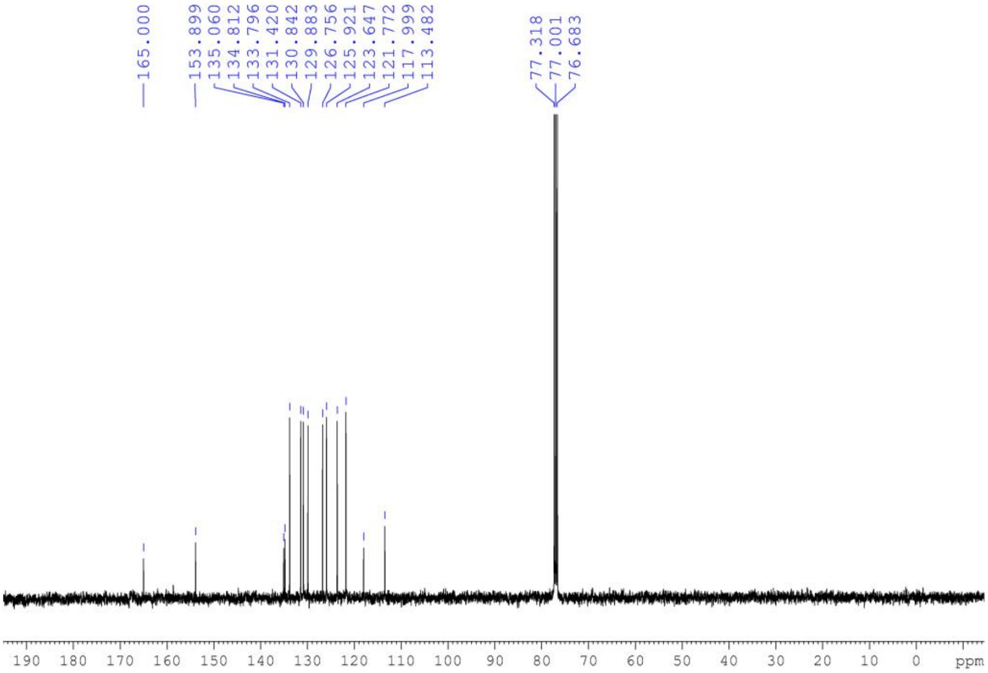
1
0
-1
0.907
1.000
1.008
0.992
0.990
1.052
1.066
1.029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131.420
130.842
129.883
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125.921
123.647
121.772
117.999
113.482
77.318
77.001
76.683
190
180
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120
110
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80
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60
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40
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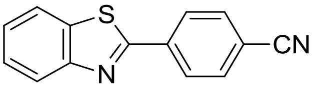
**3av**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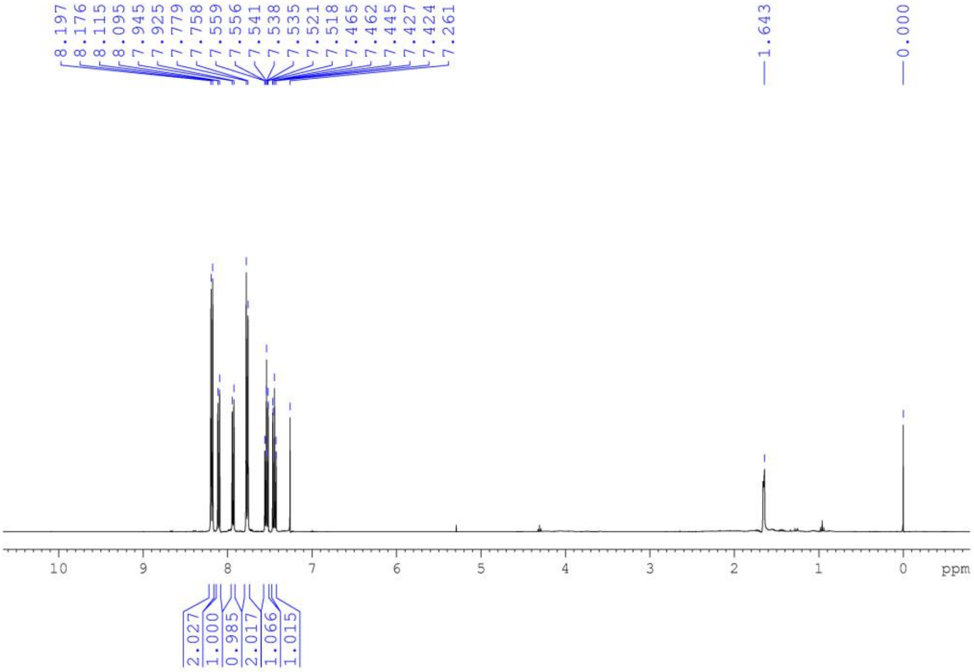
N
CN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7.925
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7.758
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7.556
7.541
7.538
7.535
7.521
7.518
7.465
7.462
7.445
7.427
7.424
7.261
1.643
0.000
10
9
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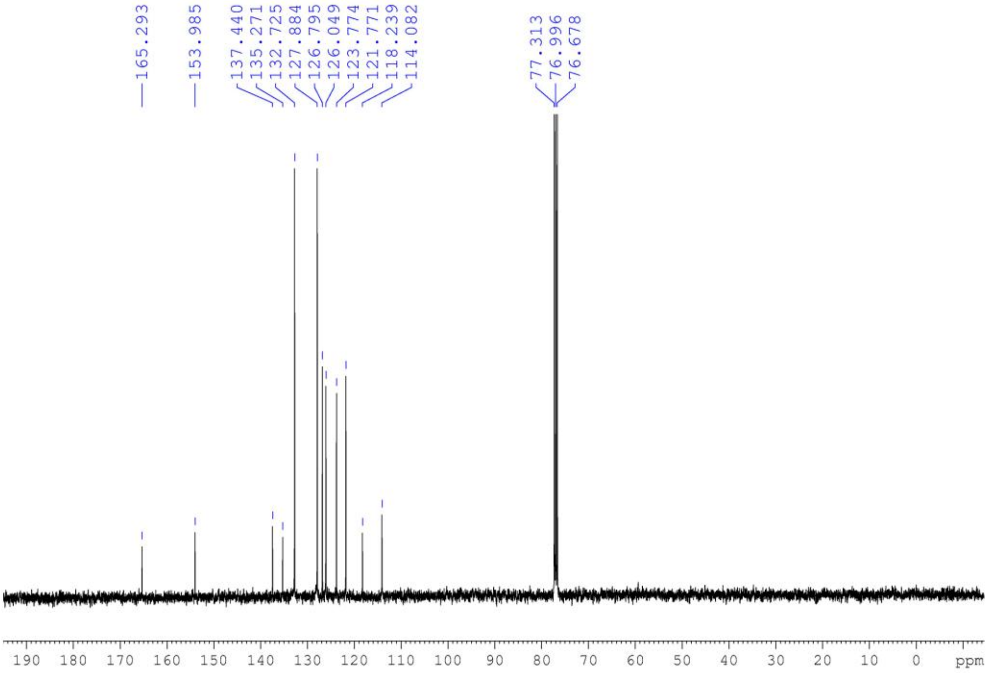
1.066
1.015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126.795
126.049
123.774
121.771
118.239
114.082
77.313
76.996
76.678
190
180
170
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150
140
130
120
110
100
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80
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40
30
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0
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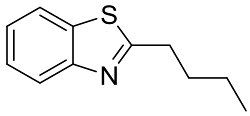
**3aw**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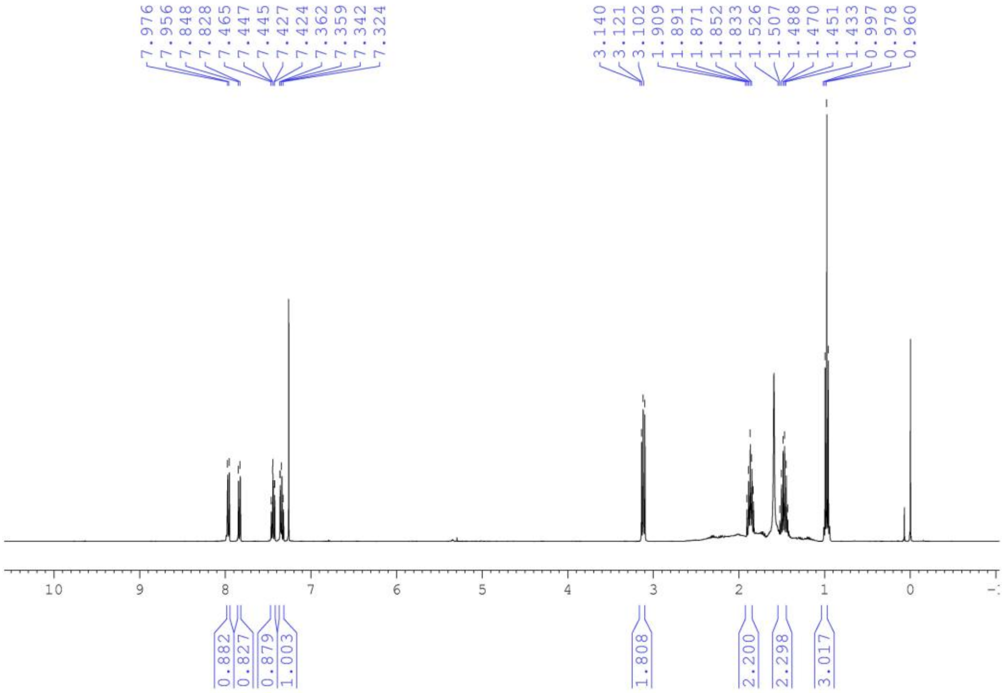
N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7.447
7.445
7.427
7.424
7.362
7.359
7.342
7.324
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3.121
3.102
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1.891
1.871
1.852
1.833
1.526
1.507
1.488
1.470
1.451
1.433
0.997
0.978
0.960
10
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7
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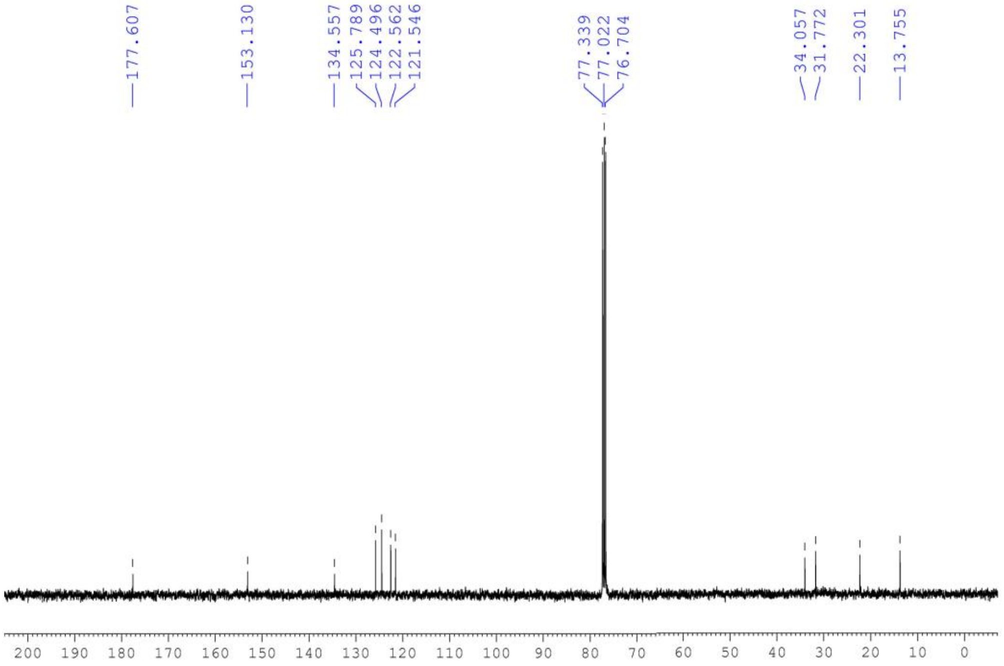
3.017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122.562
121.546
77.339
77.022
76.704
34.057
31.772
22.301
13.755
200
190
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120
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50
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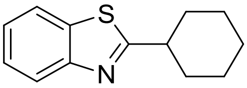
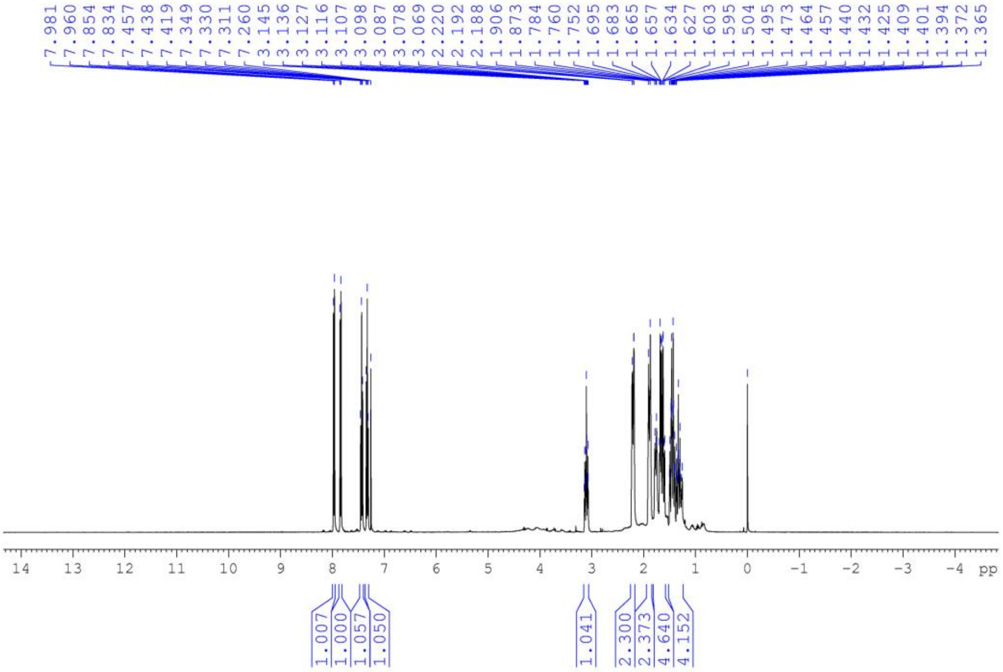
**3ax**


S
N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7.330
7.311
7.260
3.145
3.136
3.127
3.116
3.107
3.098
3.087
3.078
3.069
2.220
2.192
2.188
1.906
1.873
1.784
1.760
1.752
1.695
1.683
1.665
1.657
1.634
1.627
1.603
1.595
1.504
1.495
1.473
1.464
1.457
1.440
1.432
1.425
1.409
1.401
1.394
1.372
1.365
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10
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7
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1.041
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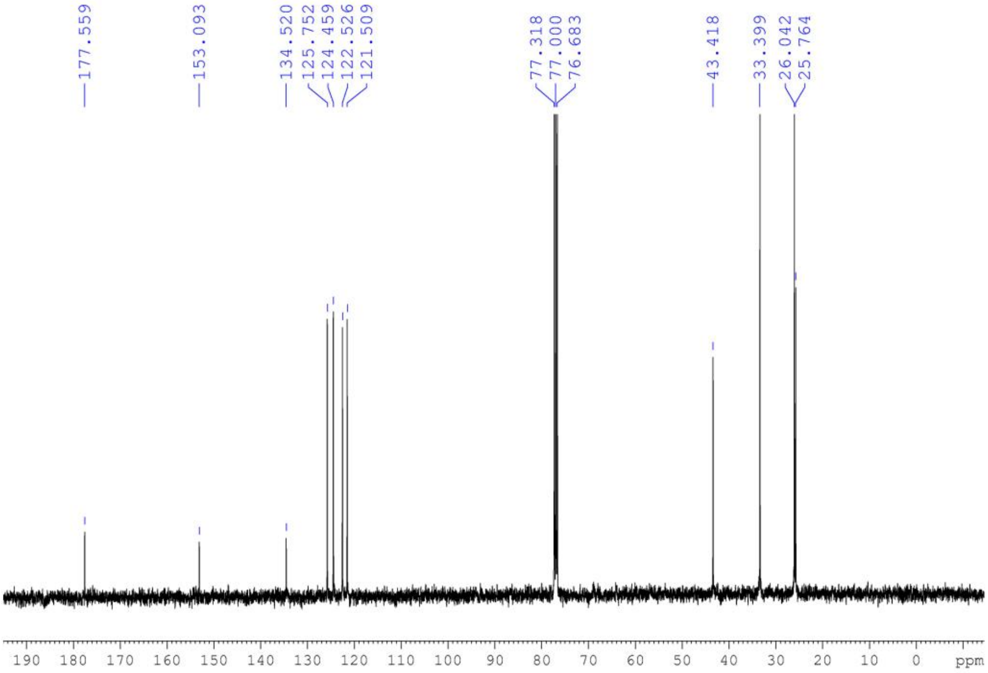
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77.318
77.000
76.683
43.418
33.399
26.042
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190
180
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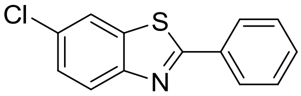
**3ba**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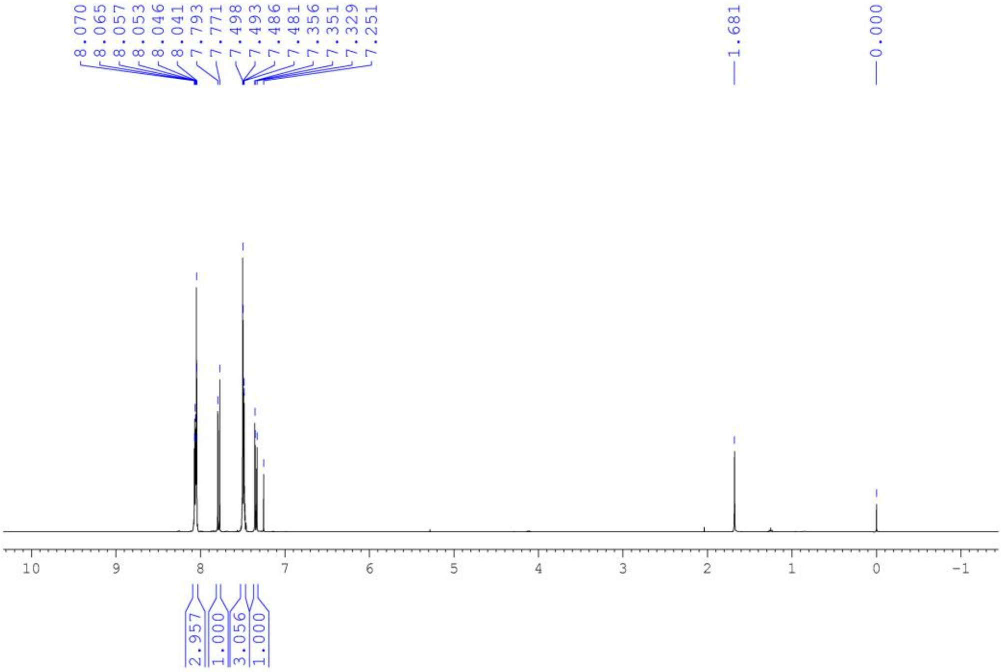
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7.771
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7.493
7.486
7.481
7.356
7.351
7.329
7.251
1.681
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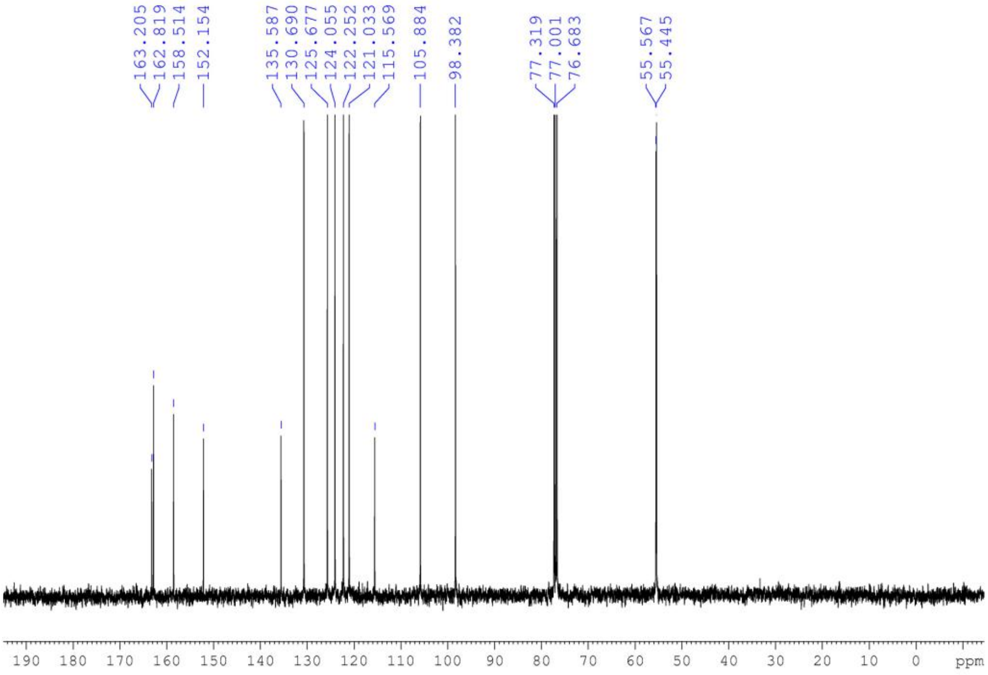
3.056
1.000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125.677
124.055
122.252
121.033
115.569
105.884
98.382
77.319
77.001
76.683
55.567
55.445
190
180
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120
110
100
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60
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40
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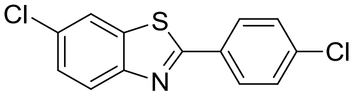
ppm

**3bp**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N
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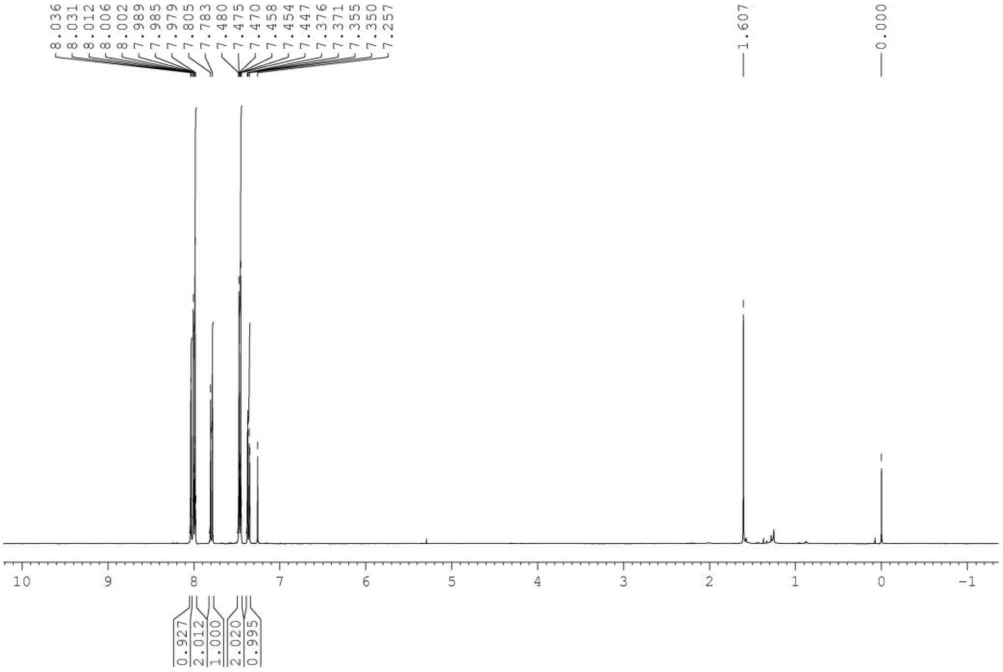
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7.783
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7.475
7.470
7.458
7.454
7.447
7.376
7.371
7.355
7.350
7.257
1.607
0.000
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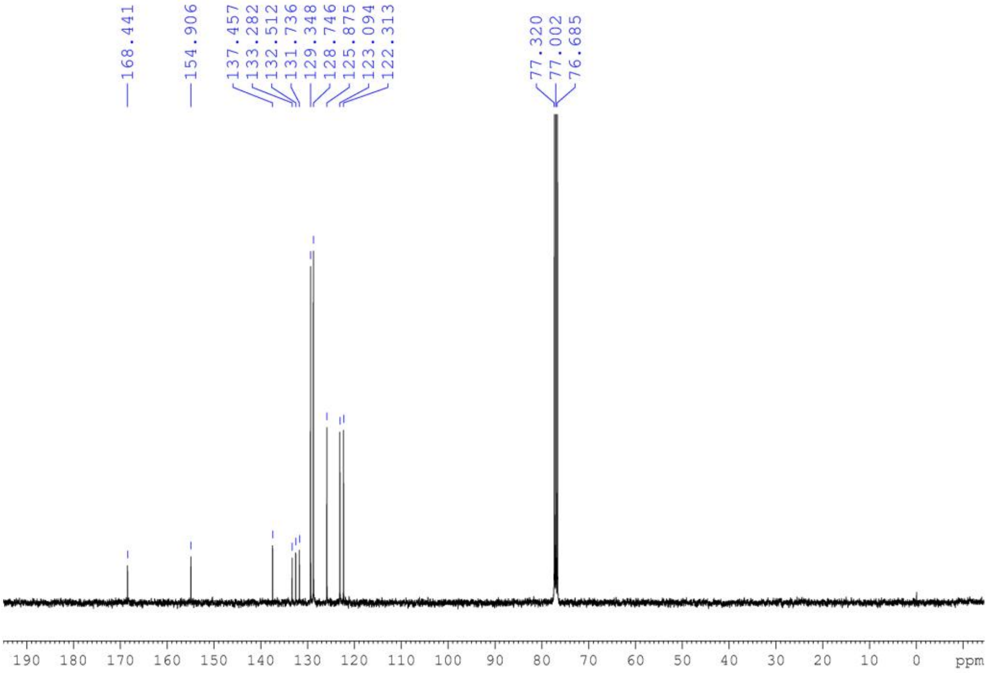
0.995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132.512
131.736
129.348
128.746
125.875
123.094
122.313
77.320
77.002
76.685
190
180
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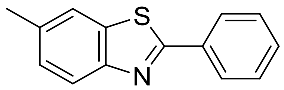
**3ca**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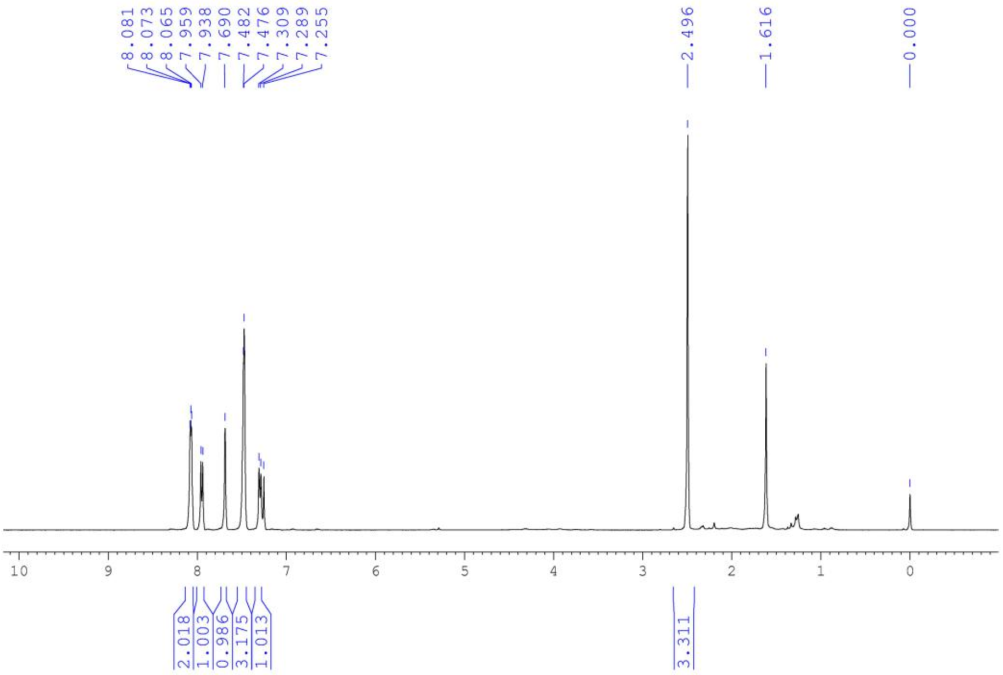
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7.255
2.496
1.616
0.000
10
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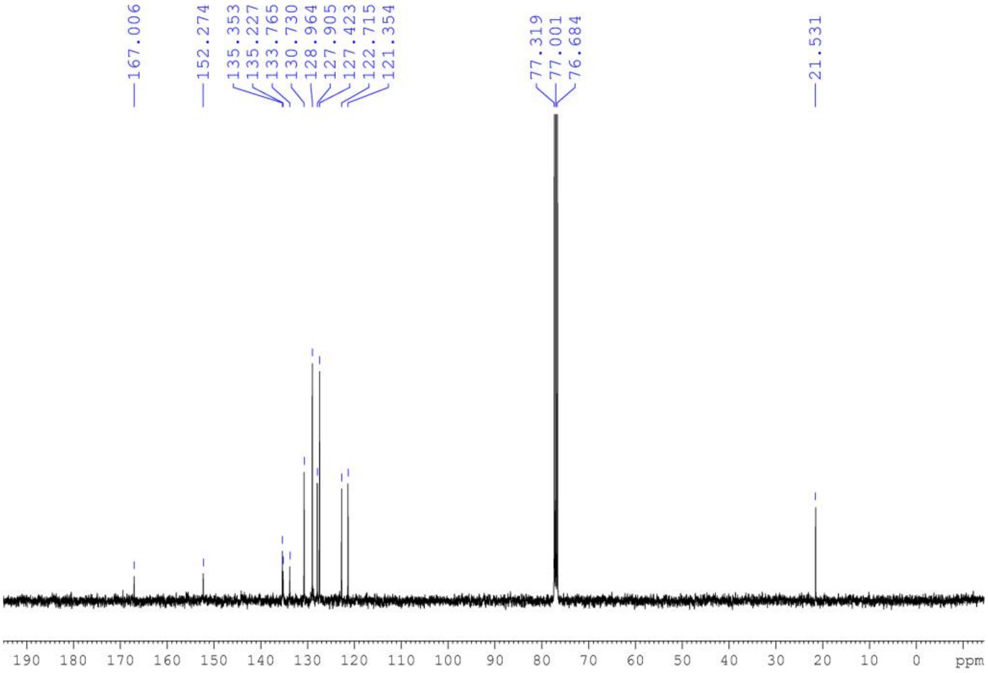
1.013
3.311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122.715
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77.001
76.684
21.531
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180
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120
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0
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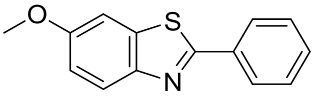
**3da**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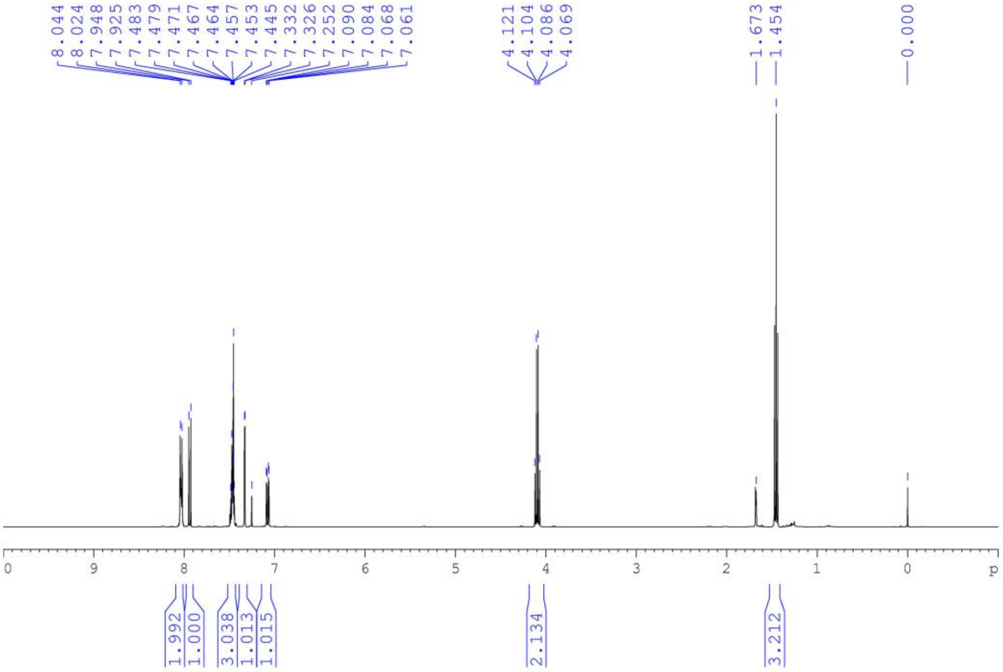
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7.457
7.453
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7.326
7.252
7.090
7.084
7.068
7.061
4.121
4.104
4.086
4.069
1.673
1.454
0.000
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1.015
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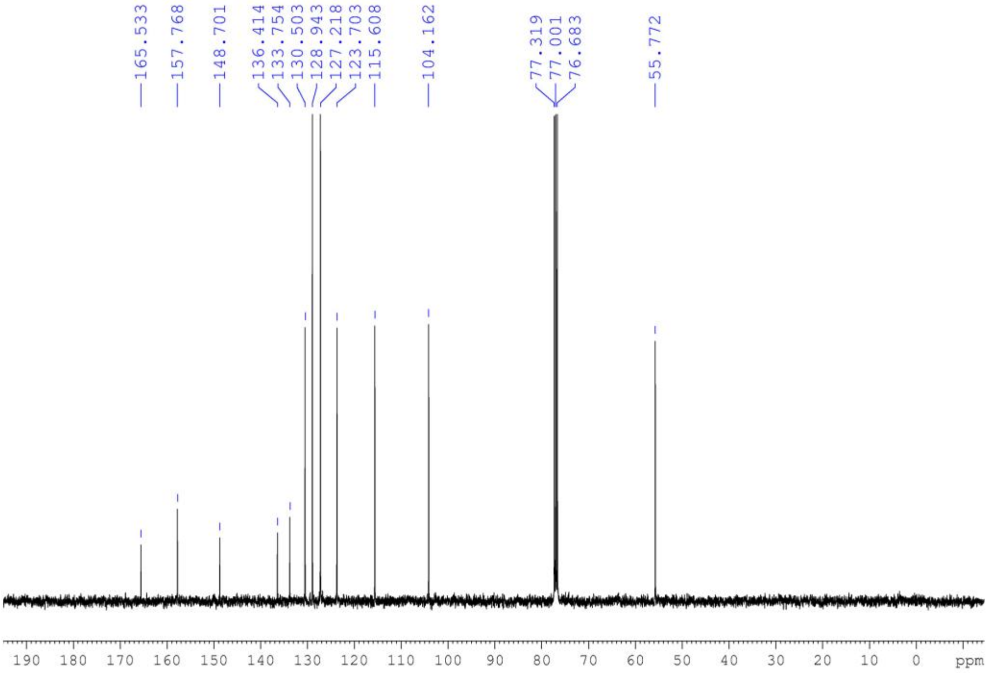
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130.503
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104.162
77.319
77.001
76.683
55.772
190
180
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110
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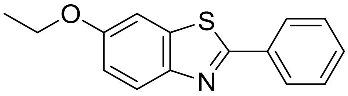
0
ppm

**3ea**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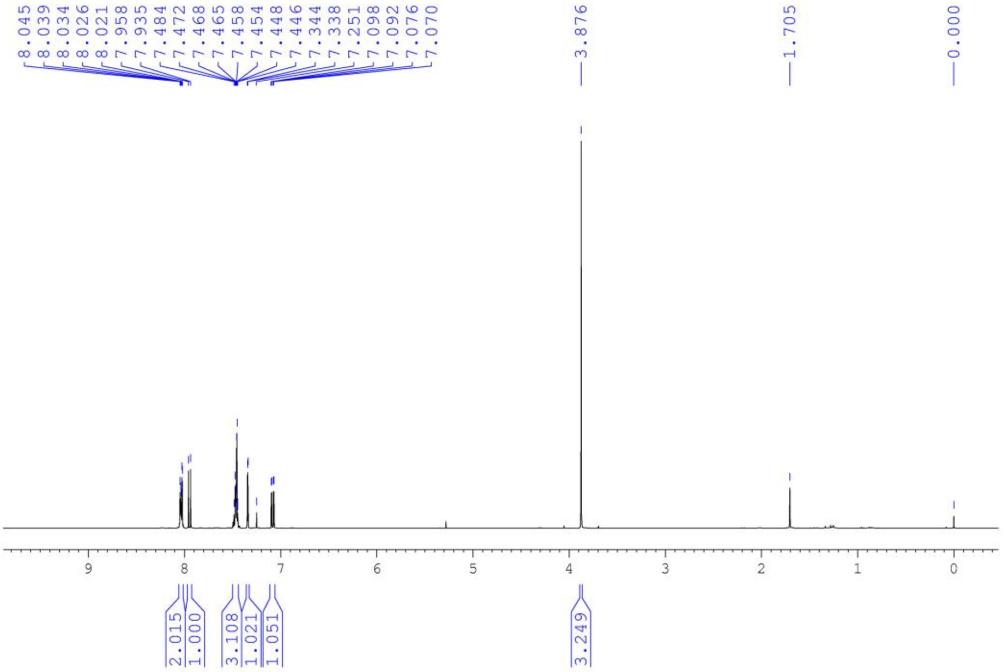
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7.454
7.448
7.446
7.344
7.338
7.251
7.098
7.092
7.076
7.070
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0.000
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8
7
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1.000
3.108
1.021
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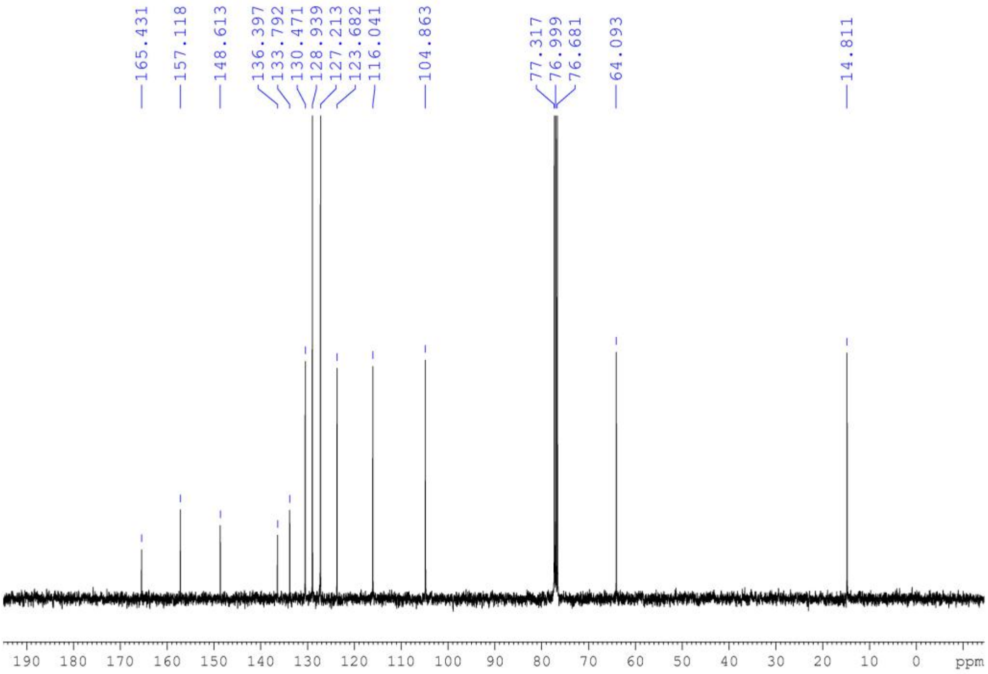
3.249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130.471
128.939
127.213
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116.041
104.863
77.317
76.999
76.681
64.093
14.811
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
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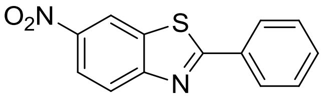
0
ppm

**3fa**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S
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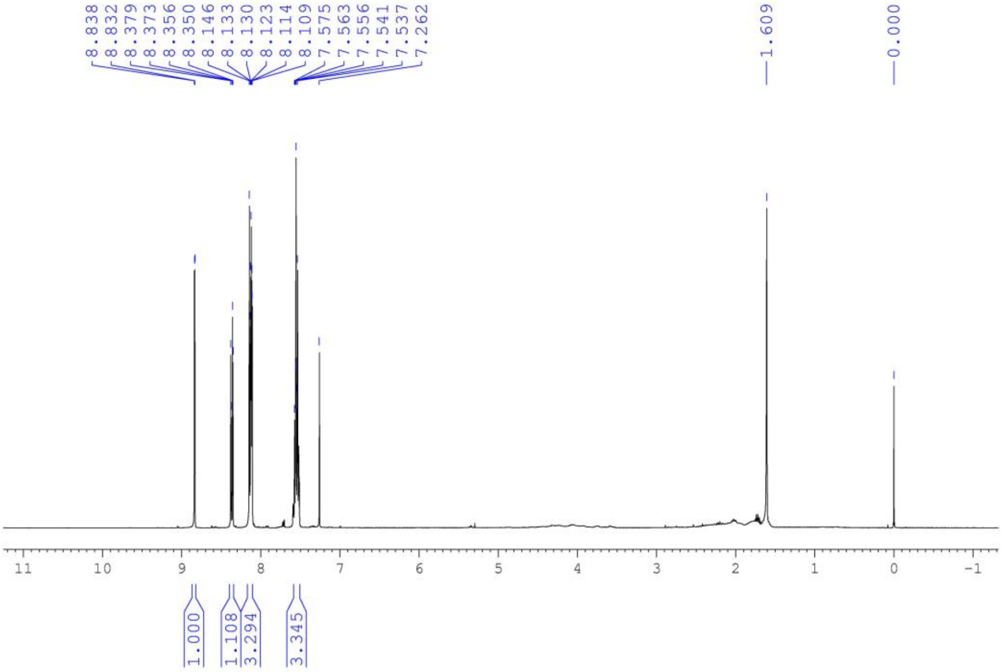
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8.350
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8.133
8.130
8.123
8.114
8.109
7.575
7.563
7.556
7.541
7.537
7.262
1.609
0.000
11
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4
3
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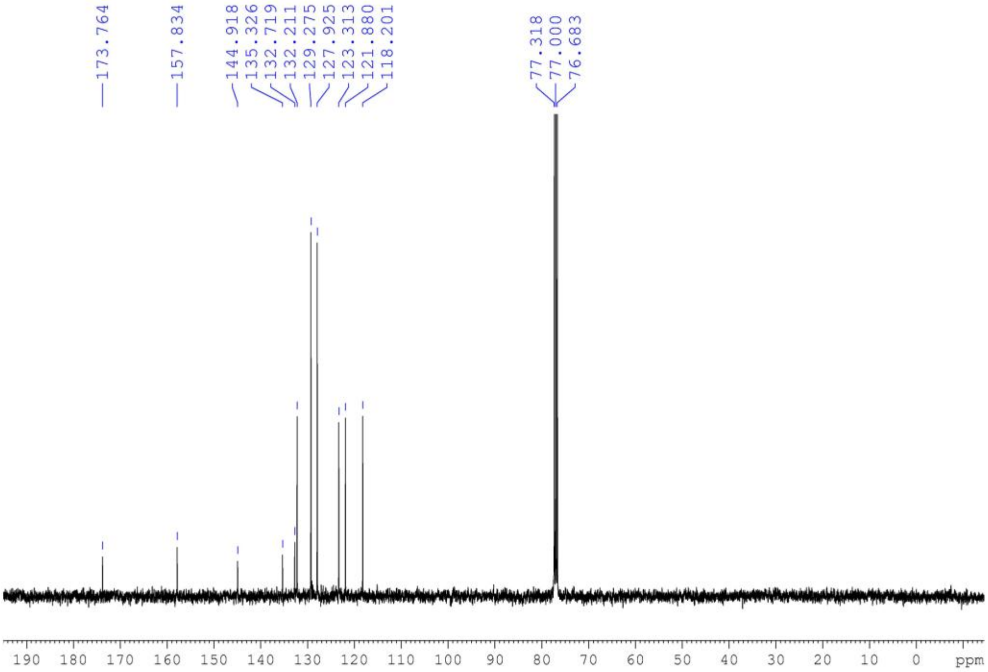
3.345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77.000
76.683
190
180
170
160
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140
130
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100
90
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50
40
30
20
10
0
ppm