Supplementary Data

Mechanistic Considerations in the Synthesis of 2-Aryl-Indole Analogues under Bischler-Mohlau Conditions

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Experimental Procedures

CH_2Cl_2, THF, EtOH, and Et_2O were used in their anhydrous forms as obtained from the chemical suppliers. Reactions were performed under an inert atmosphere using nitrogen gas, unless specified otherwise. Thin-layer chromatography (TLC) plates (precoated glass plates with silica gel 60 F254, 0.25 mm thickness) were used to monitor reactions. Purification of intermediates and products was carried out with a flash purification system (Biotage Isolera 1 or 4) using silica gel (200-400 mesh, 60 Å) prepacked columns. Intermediates and products synthesized were characterized on the basis of their ^1H NMR (500 MHz), ^{13}C NMR (125 MHz), and DEPT ^{13}C NMR (125 MHz) spectroscopic data using a Varian VNMRS 500 MHz instrument. Spectra were recorded in $CDCl_3$. All of the chemical shifts are expressed in ppm (δ), coupling constants (*J*) are presented in Hz, and peak patterns are reported as broad (br), singlet (s), doublet (d), double doublet (dd), quartet of doublets (qd) quartet (q), and multiplet (m). ^{13}C-labeled atoms have their ^{13}C-NMR chemical shift values denoted with bold text in each appropriate experimental write-up.

3-(tert-Butyldimethylsilyloxy)-4-methoxybenzaldehyde ***11***

To a clean dry round bottom flask 3-hydroxy-4-methoxybenaldehyde **10** (5.02 g, 32.9 mmol) was dissolved in CH_2Cl_2 (100 mL). The solution was cooled to 0 ^oC and Et_3N (5.04 mL, 36.2 mmol) was added followed by the addition of *N*,*N*-dimethylaminopyridine (DMAP) (0.402 g, 3.29 mmol). The reaction mixture was stirred for 10 min and *tert*-butyldimethylsilyl chloride (TBSCl) (5.29 g, 36.2 mmol) was added gradually. The solution was allowed to warm to room temperature and was stirred for 12 hours. The reaction was diluted with water (50 mL), transferred to a separatory funnel, and was extracted with CH_2Cl_2. The organic extracts were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The TBS benzaldehyde product **11** (9.24 g, 34.7 mmol) was isolated quantitatively as a yellow oil and was taken to the next step without further purification.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.80 (s, 1H, C$\underline{H}$O), 7.45 (dd, J = 8.5, 2.0 Hz, 1H, Ar$\underline{H}$), 7.35 (d, J = 2.0 Hz, 1H, Ar$\underline{H}$), 6.93 (d, J = 8.5 Hz, 1H, Ar$\underline{H}$), 3.87 (s, 3H, OC$\underline{H}_3$), 0.99 (s, 9H, C(C$\underline{H}_3$)$_3$), 0.16 (s, 6H, Si(C$\underline{H}_3$)$_2$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 190.2, 156.2, 145.2, 130.0, 126.0, 119.4, 110.9, 55.1, 25.3, 18.0, -5.0.

3-tert-Butyldimethylsilyloxy-1-(1'-hydroxyethyl)-4-methoxybenzene ***12***

To a solution of magnesium turnings (0.40 g, 17 mmol) in diethyl ether (Et_2O) was added ^{13}C-labeled methyl iodide (1.00 mL, 16.0 mmol). The solution was refluxed for 30 minutes until the turnings were dissolved. The solution was cooled to room temperature and TBS benzaldehyde **11** (1.92 g, 7.20 mmol) in Et_2O was added dropwise. The reaction mixture was stirred for 5 hours. Upon completion the reaction mixture was slowly quenched with 0.1 M HCl and extracted with Et_2O. The organic extracts were washed sequentially with saturated $NaHCO_3$ solution and water. The organic layer was further dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture was subjected to flash chromatography using a prepacked 50 g silica column [solvent A, EtOAc, solvent B, hexanes; gradient, 7%A / 93%B (1 CV), 7%A / 93%B → 60%A / 40%B (10 CV), 60%A / 40%B (2 CV); flow rate, 40 mL/min; monitored at 254 and 280 nm] to yield ^{13}C-labeled alcohol **12** (1.54 g, 5.45 mmol, 75%, R_f = 0.47 (70:30 hexanes:EtOAc)) as a yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.90 (dd, *J* = 8.2, 2.2 Hz, 1H, Ar$\underline{H}$), 6.88 (d, *J* = 2.2 Hz, 1H, Ar$\underline{H}$), 6.81 (d, *J* = 8.2 Hz, 1H, Ar$\underline{H}$), 4.79 (qd, *J* = 6.4, 2.0 Hz, 1H, C$\underline{H}$), 3.79 (s, 3H, O$C\underline{H}_3$), 1.79 (s, 1H, O$\underline{H}$), 1.45 (dd, *J* = 6.4 Hz, $J_{C\text{-}H}$ = 126.6 Hz, 3H, $C\underline{H}_3$), 1.00 (s, 9H, $C(C\underline{H}_3)_3$), 0.16 (s, 6H, $Si(C\underline{H}_3)_2$).

^{13}C NMR ($CDCl_3$, 500 MHz): δ 150.30, 145.02, 138.64, 118.50 (d, *J* = 1.9 Hz), 118.27 (d, *J* = 1.6 Hz), 111.96, 69.96 (d, *J* = 38.6 Hz), 55.56, 25.73, **24.96**, 18.45, -4.59 (d, *J* = 1.4 Hz).

HRMS $[M+Na]^+$: 306.1578 (calcd for $[C_{14}{}^{13}CH_{26}NaO_3Si]^+$, 306.1577).

*3-tert-Butyldimethylsilyloxy-4-methoxyacetophenone **13***

The crude alcohol **12** (1.76 g, 6.23 mmol) was dissolved in CH_2Cl_2 (50 mL). Celite (1.5 g) was added and the solution was cooled to 0 °C. Pyridinium chlorochromate (PCC) (1.48 g, 6.86 mmol) was added in small increments allowing 10 minutes of stirring between each addition. The reaction was allowed to warm to room temperature and stirred for 12 hours. The reaction mixture was filtered through a 50/50 mixture of silica gel/celite rinsing well with CH_2Cl_2. The filtrate was concentrated under reduced pressure providing the desired ^{13}C-labeled acetophenone **13** (1.48 g, 5.28 mmol, 85%) as a pale yellow solid.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.58 (dd, *J* = 8.5, 2.1 Hz, 1H, Ar$\underline{H}$), 7.47 (d, *J* = 1.9 Hz, 1H, Ar$\underline{H}$), 6.87 (d, *J* = 8.3 Hz, 1H, Ar$\underline{H}$), 3.87 (s, 3H, $OC\underline{H}_3$), 2.53 (d, *J* = 127.3 Hz, 3H, $C\underline{H}_3$), 1.01 (s, 9H, , $C(C\underline{H}_3)_3$), 0.17 (s, 6H, $Si(C\underline{H}_3)_2$).

^{13}C NMR ($CDCl_3$, 500 MHz): δ 196.71 (d, *J* = 42.7 Hz), 155.31 , 144.83 , 130.59 (d, *J* = 13.9 Hz), 123.50 , 120.47 , 110.78 , 55.48 , **26.30** , 25.68 , 18.44 , -4.63 .

HRMS $[M+H]^+$: 282.1603 (calcd for $[C_{14}{}^{13}CH_{25}O_3Si]^+$, 282.1601).

1-(3-tert-Butyldimethylsilyloxy-4-methoxyphenyl)-1-trimethylsilylethene ***14***

To a solution of diisopropylamine (1.1 mL, 7.0 mmol) in THF (30 mL) at 0 °C was added *n*-butyllithium (3.2 mL, 7.9 mmol) dropwise. The LDA solution was allowed to stir for 15 minutes and a solution of TBS acetophenone **13** (1.48 g, 5.26 mmol) in THF (5 mL) was added dropwise. The solution was stirred for 10 min and TMSCl (1.0 mL, 7.9 mmol) was added dropwise and the reaction was allowed to warm to room temperature. The solution was stirred for 12 hours and was quenched using 10% $NaHCO_3$ (100 mL). The reaction mixture was extracted with Et_2O, dried over Na_2SO_4, and concentrated under reduced pressure resulting in ^{13}C-labeled TMS enol ether **14**

(1.95 g, 5.51 mmol) quantitatively as a dark yellow oil which was taken to the next step without purification.

^{1}HNMR ($CDCl_3$, 500 MHz): δ 7.23 (dd, J = 8.5, 2.0 Hz, 1H Ar$\underline{H}$), 7.18 (d, J = 2.0 Hz, 1H, Ar$\underline{H}$), 6.82 (d, J = 8.5 Hz, 1H, Ar$\underline{H}$), 4.83 (dd, J = 1.5 Hz, $J_{C\text{-}H}$ = 159.5 Hz, 1H, $C\underline{H}_2$), 4.38 (dd, J = 1.5 Hz, $J_{C\text{-}H}$ = 159.0 Hz, 1H, $C\underline{H}_2$), 3.83 (s, 3H, $OC\underline{H}_3$), 1.08 (s, 9H, $C(C\underline{H}_3)_3$), 0.32 (s, 9H, $Si(C\underline{H}_3)_3$), 0.23 (s, 6H, $Si(C\underline{H}_3)_2$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 155.4 (d, J = 82.0 Hz), 151.3, 144.6, 130.8 (d, J = 6.9 Hz), 118.9 (d, J = 2.4 Hz), 118.2 (d, J = 2.3 Hz), 111.3 (d, J = 42.6 Hz), **89.6**, 55.5, 25.9, 18.6, 0.2, -4.5.

*3'-(tert-Butyldimethylsilyloxy)-4'-methoxy-2-bromoacetophenone **15***

A solution of crude **14** (1.95 g, 5.51 mmol) in CH_2Cl_2 (30 mL) and K_2CO_3 (0.033 g, 0.239 mmol) was cooled to 0 °C. Bromine (0.17 mL, 3.3 mmol) was added dropwise and the solution was allowed to stir for 30 minutes. The reaction was quenched with 10 % sodium thiosulfate solution, transferred to a separatory funnel, and extracted with CH_2Cl_2. The organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was subjected to flash chromatography using a prepacked 100 g silica column [solvent A, EtOAc, solvent B, hexanes; gradient, 2%A / 98%B (4 CV), 2%A / 98%B → 20%A / 80%B (10 CV), 20%A / 80%B (2 CV); flow rate, 50 mL/min; monitored at 254 and 280 nm] to yield ^{13}C-labeled bromoacetophenone **15** as a tan solid (1.16 g, 3.22 mmol, 58%, $R_f = 0.29$ (80:20 hexanes:EtOAc)).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.62 (dd, *J* = 8.5, 2.2 Hz, 1H, Ar<u>H</u>), 7.49 (d, J = 2.2 Hz, 1H, Ar<u>H</u>), 6.89 (d, *J* = 8.5 Hz, 1H, Ar<u>H</u>), 4.38 (d, $J_{C\text{-}H}$ = 150.9 Hz, 2H, $C\underline{H}_2$), 3.89 (s, 3H, $OC\underline{H}_3$), 1.01 (s, 9H, $C(C\underline{H}_3)_3$), 0.18 (s, 6H, $Si(C\underline{H}_3)_2$).

^{13}C NMR ($CDCl_3$, 500 MHz): δ 189.89 (d, *J* = 43.8 Hz), 156.10 , 145.13 , 127.12 (d, *J* = 17.2 Hz), 124.21 , 121.10 , 111.00 , 55.55 , **30.69** , 25.65 , 18.43 , -4.61 .

HRMS $[M+Na]^+$: 382.0533 (calcd for $[C_{14}{}^{13}CH_{23}BrNaO_3Si]^+$, 382.0526).

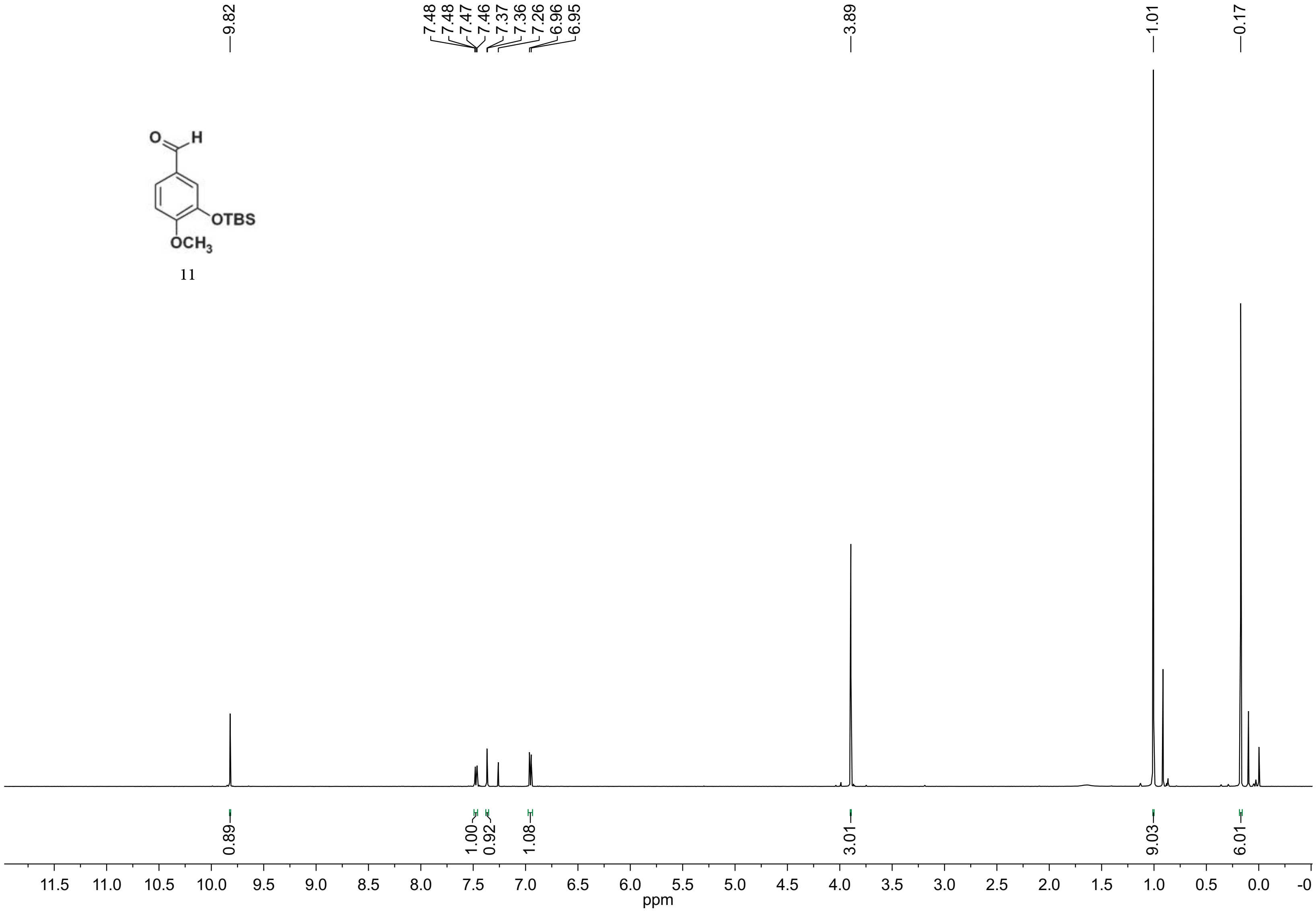
2-(3'-tert-Butyldimethylsilyloxy-4'-methoxyphenyl)-6-methoxyindole ***16***

A solution of *m*-anisidine (0.41 mL, 3.7 mmol) was dissolved in *N,N*-dimethylaniline (10 mL) and was heated to reflux at 170 °C. A solution of **15** (0.40 g, 1.1 mmol) in EtOAc (1 mL) was added dropwise. The reaction mixture was stirred at 170° C for 12 hours. The reaction mixture was allowed to cool to room temperature and was extracted with EtOAc (3 x 50 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash chromatography using a prepacked 50 g silica column [solvent A, EtOAc, solvent B, hexanes; gradient, 2%A / 98%B (1 CV), 2%A / 98%B → 25%A / 75%B (10 CV), 25%A / 75%B (2 CV); flow rate, 40 mL/min; monitored at 254 and 280 nm] resulted in the desired ^{13}C-labeled phenylindole **16** (0.312 g, 0.81 mmol, 73%, $R_f = 0.48$ (50:50 hexanes:EtOAc)) as a light tan solid. A portion of compound **16** was recrystallized from hexane and dichloromethane to obtain the analytical data.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.14 (br s, 1H, N$\underline{H}$), 7.48 (dd, *J* = 8.6 Hz, 2.9 Hz, 1H, Ar$\underline{H}$), 7.16 (m, 2H, Ar$\underline{H}$), 6.90 (m, 2H, Ar$\underline{H}$), 6.83 – 6.40 (m, 2H, Ar$\underline{H}$), 3.87 (s, 3H, OC$\underline{H}_3$), 3.85 (s, 3H, OC$\underline{H}_3$), 1.06 (s, 9H, C(C$\underline{H}_3$)$_3$), 0.22 (s, 6H, Si(C$\underline{H}_3$)$_2$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 156.36 , 150.57 , 145.39 , 137.37 (d, *J* = 3.3 Hz), 136.85, 125.77 (d, *J* = 3.6 Hz), 123.68 (d, *J* = 56.5 Hz), 120.89 (d, *J* = 2.4 Hz), 118.18 (d, *J* = 2.9 Hz), 117.81 (d, *J* = 2.5 Hz), 112.36 , 109.89 (d, *J* = 4.6 Hz), **98.68**, 94.46 (d, *J* = 2.4 Hz), 55.68 , 55.53 , 25.75 , 18.49 , -4.57 .

HRMS $[M+H]^+$: 385.2031 (calcd for $[C_{21}{}^{13}CH_{30}NO_3Si]^+$, 385.2023).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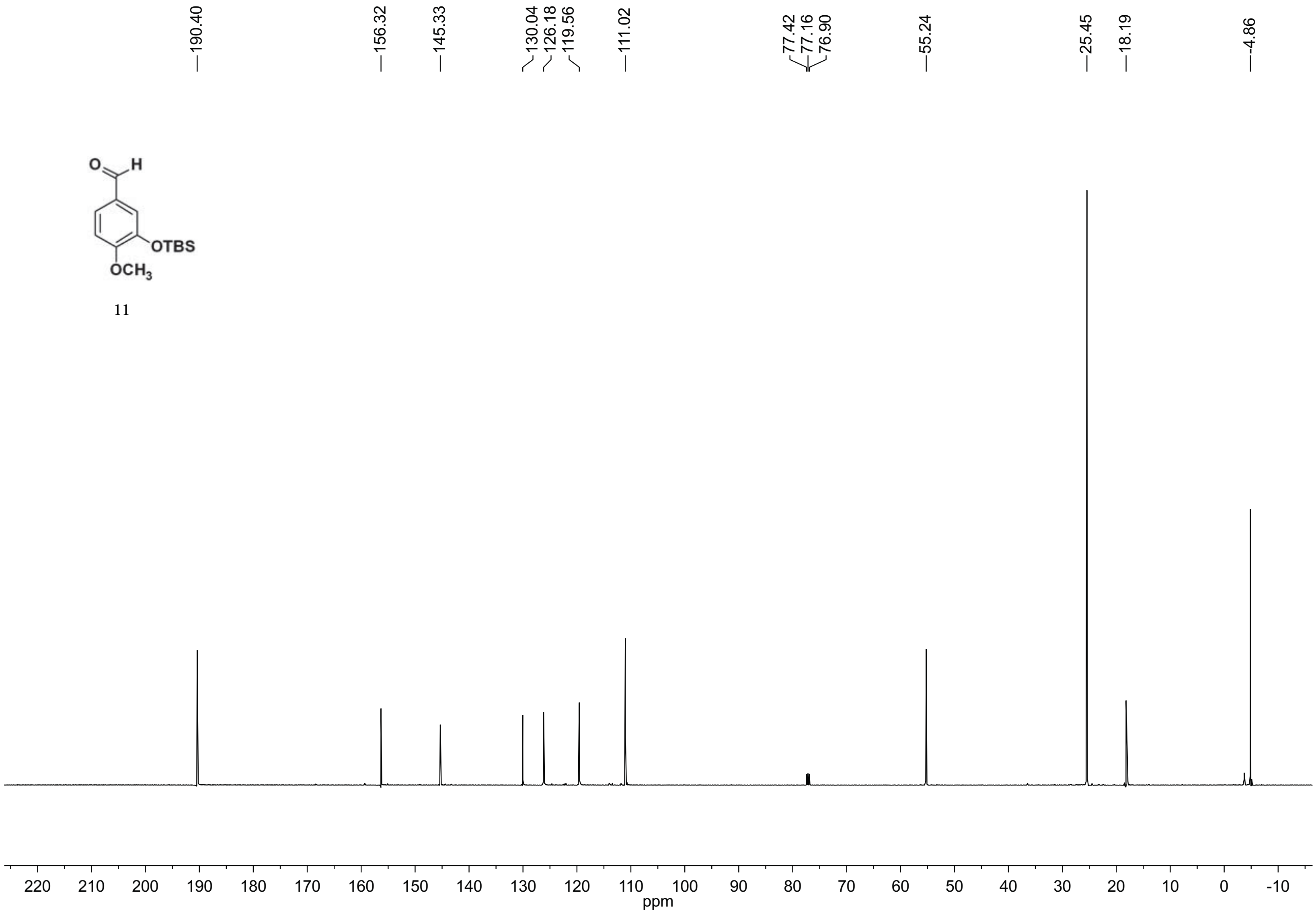
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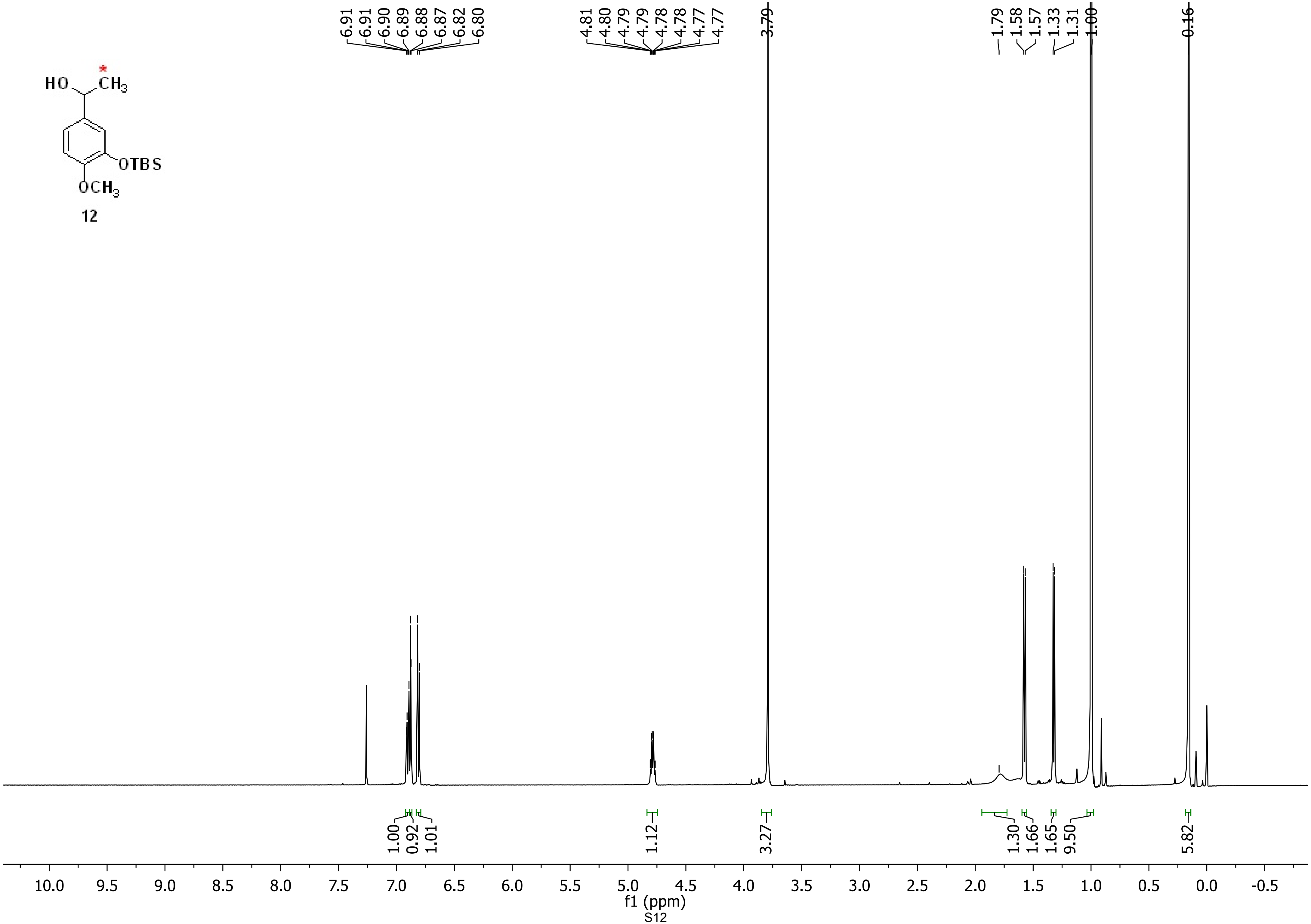
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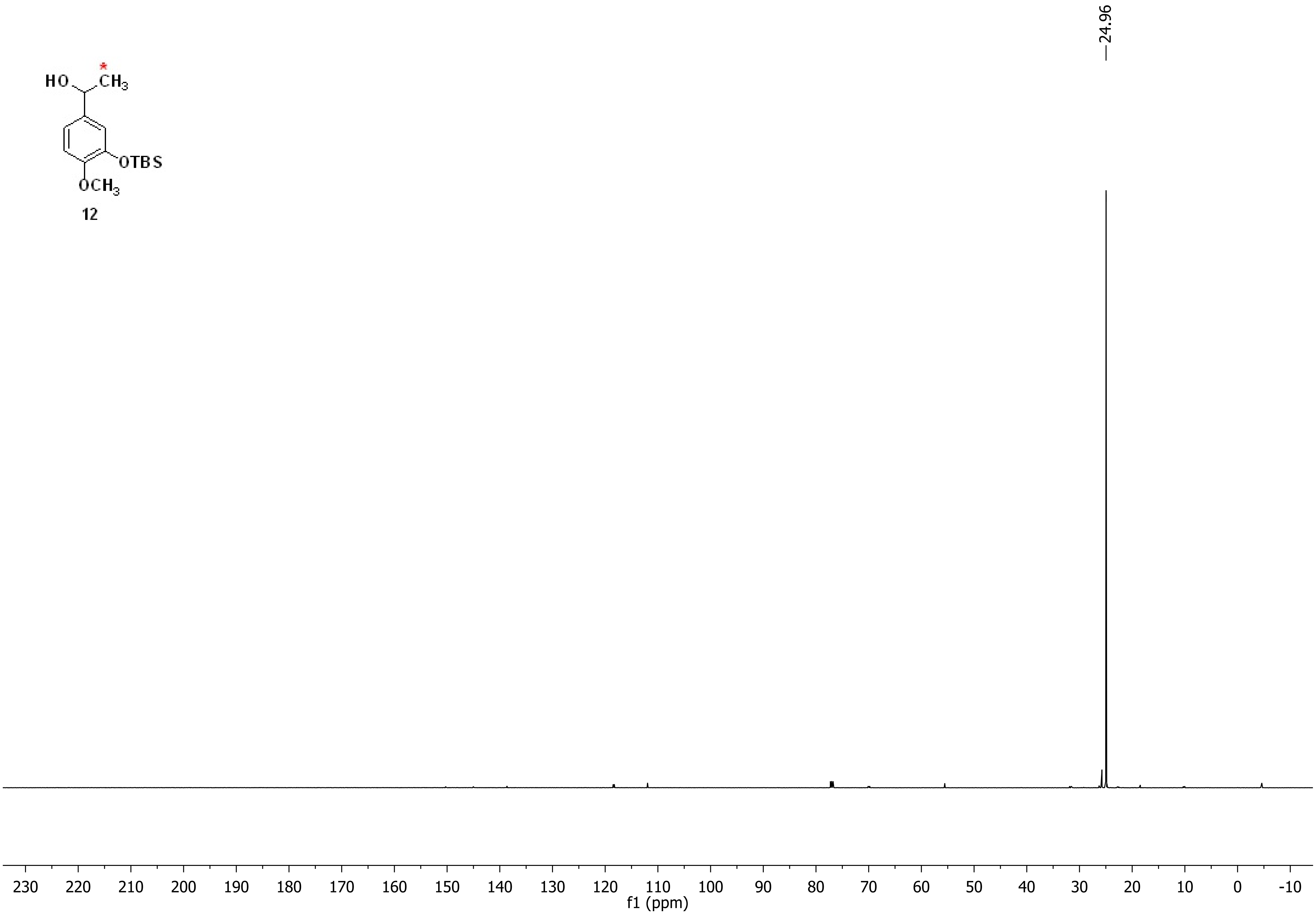

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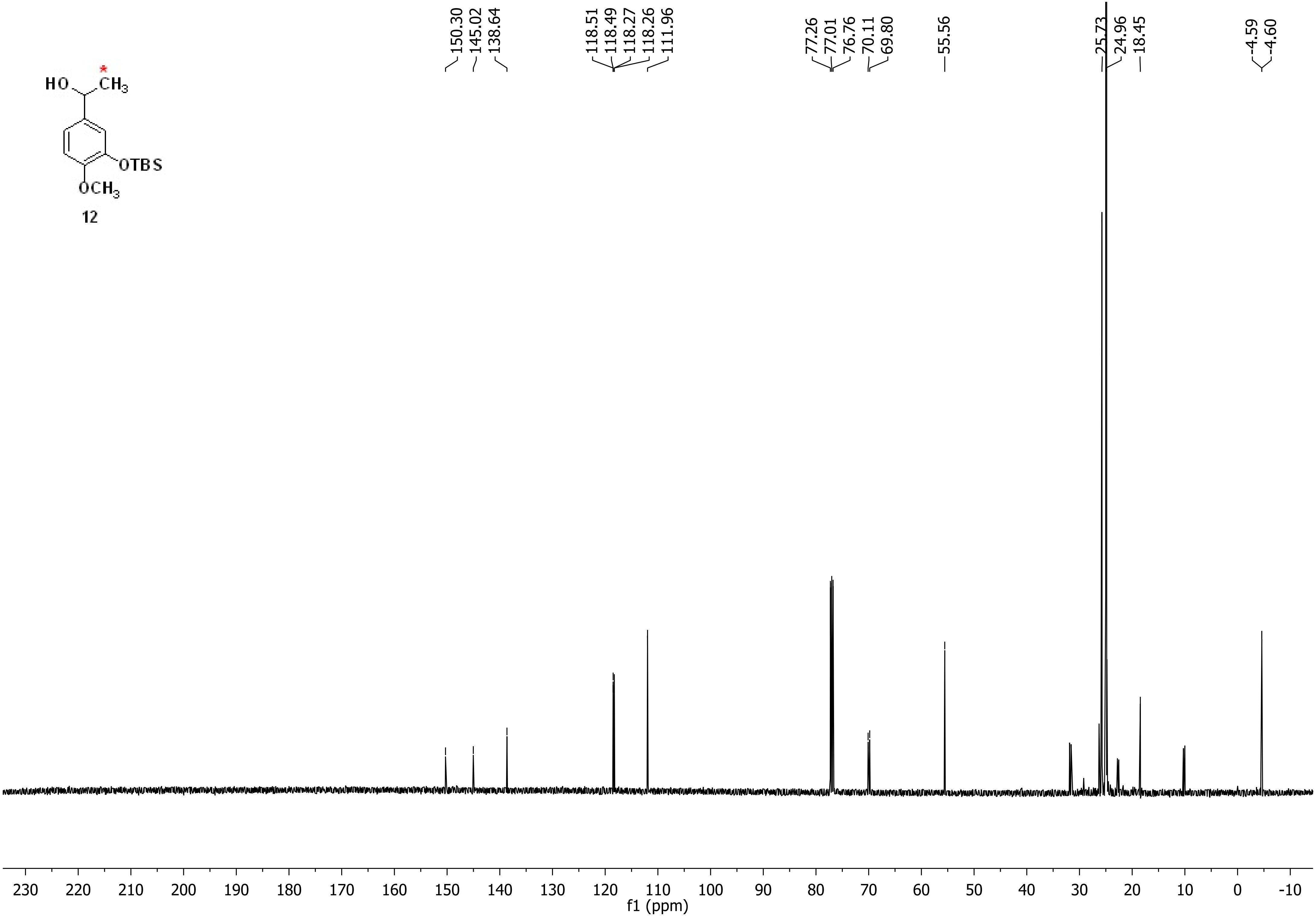
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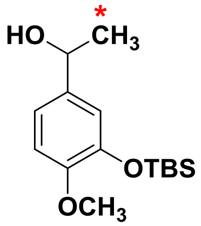

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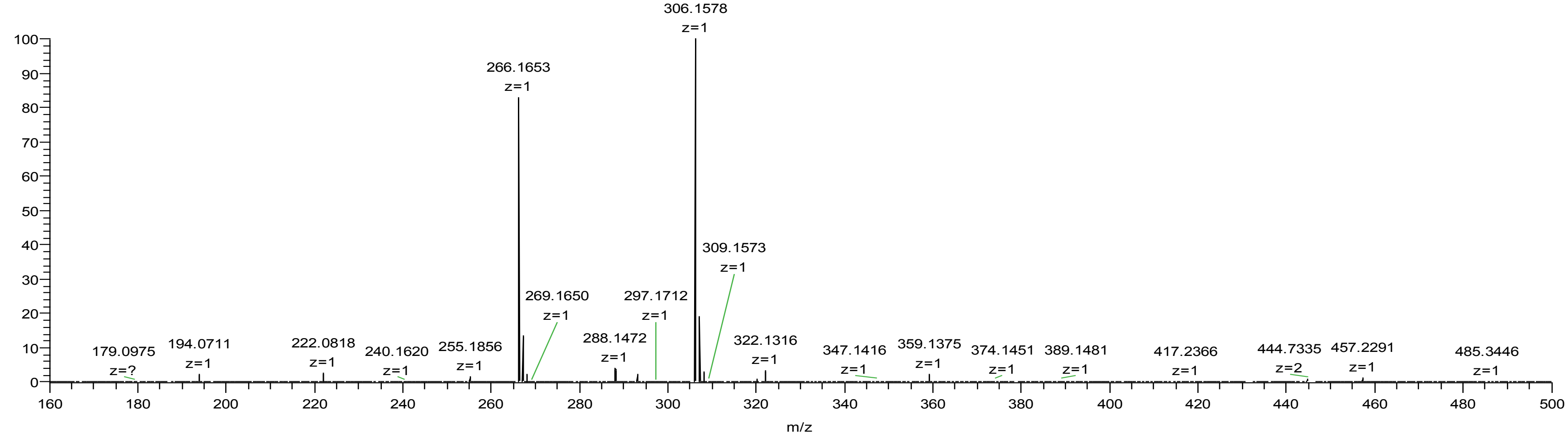

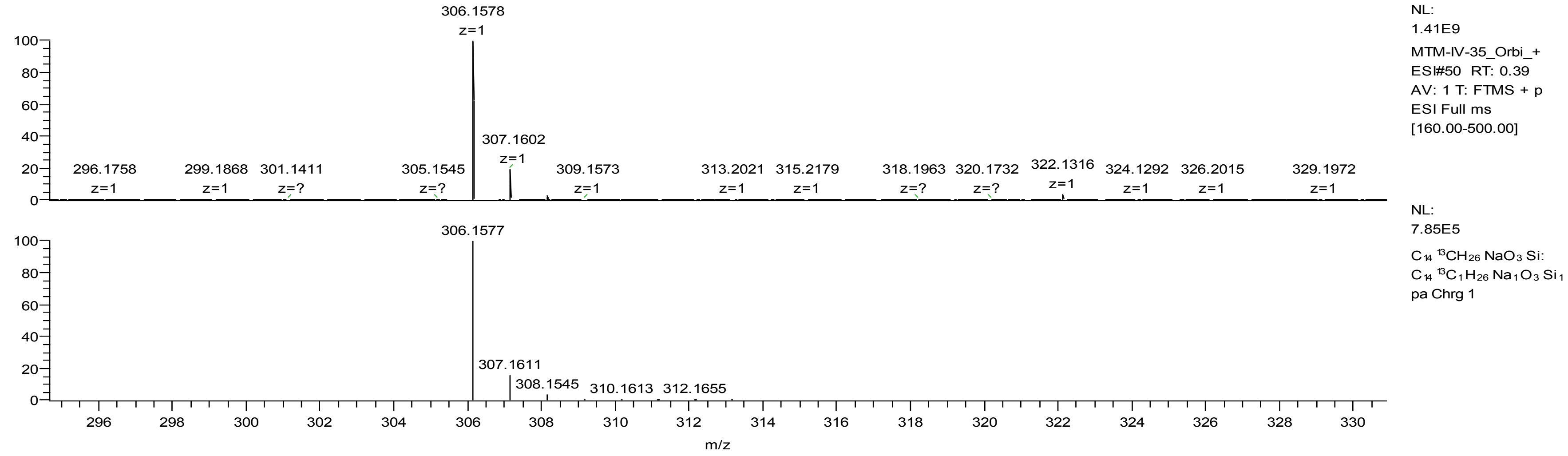

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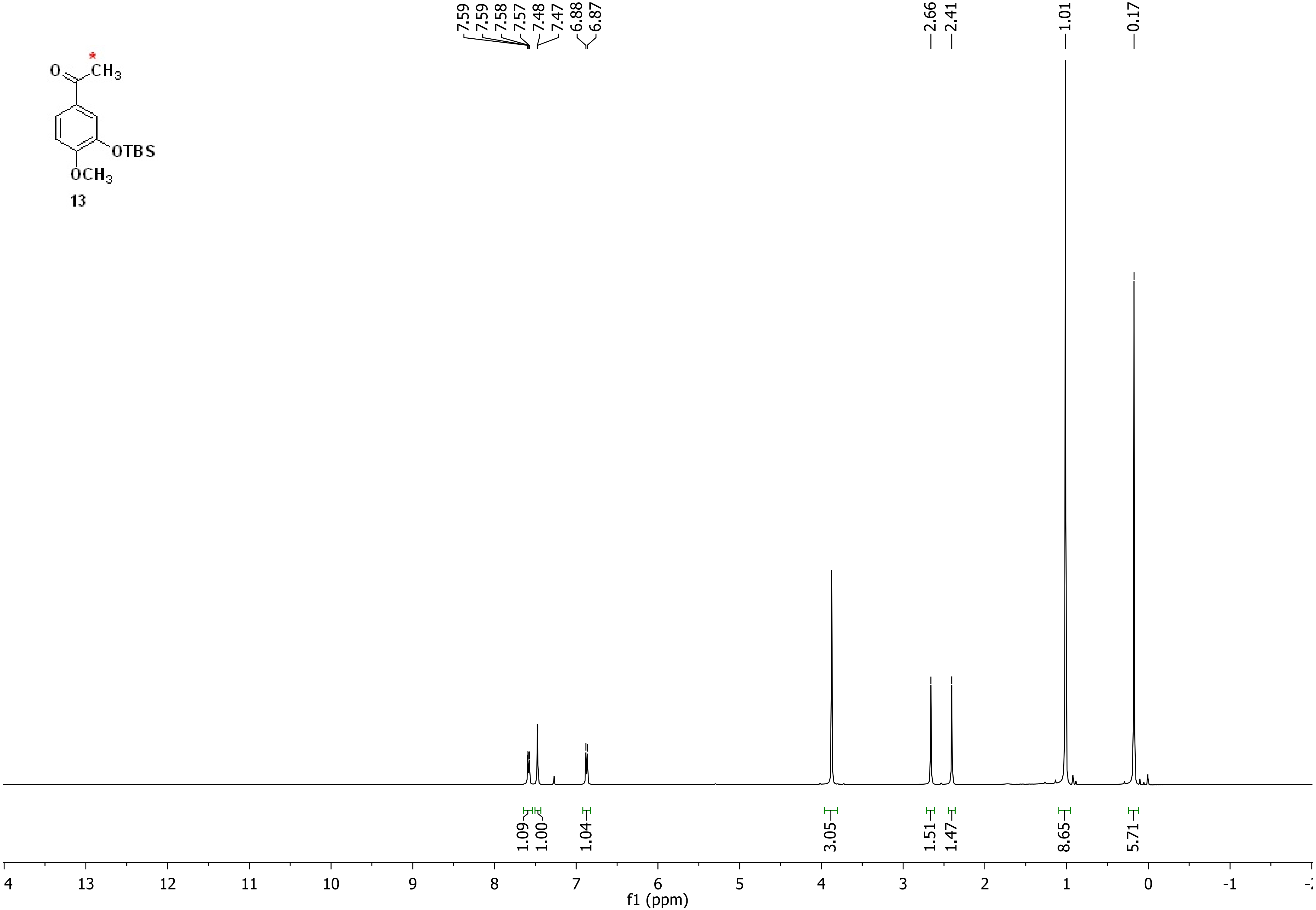

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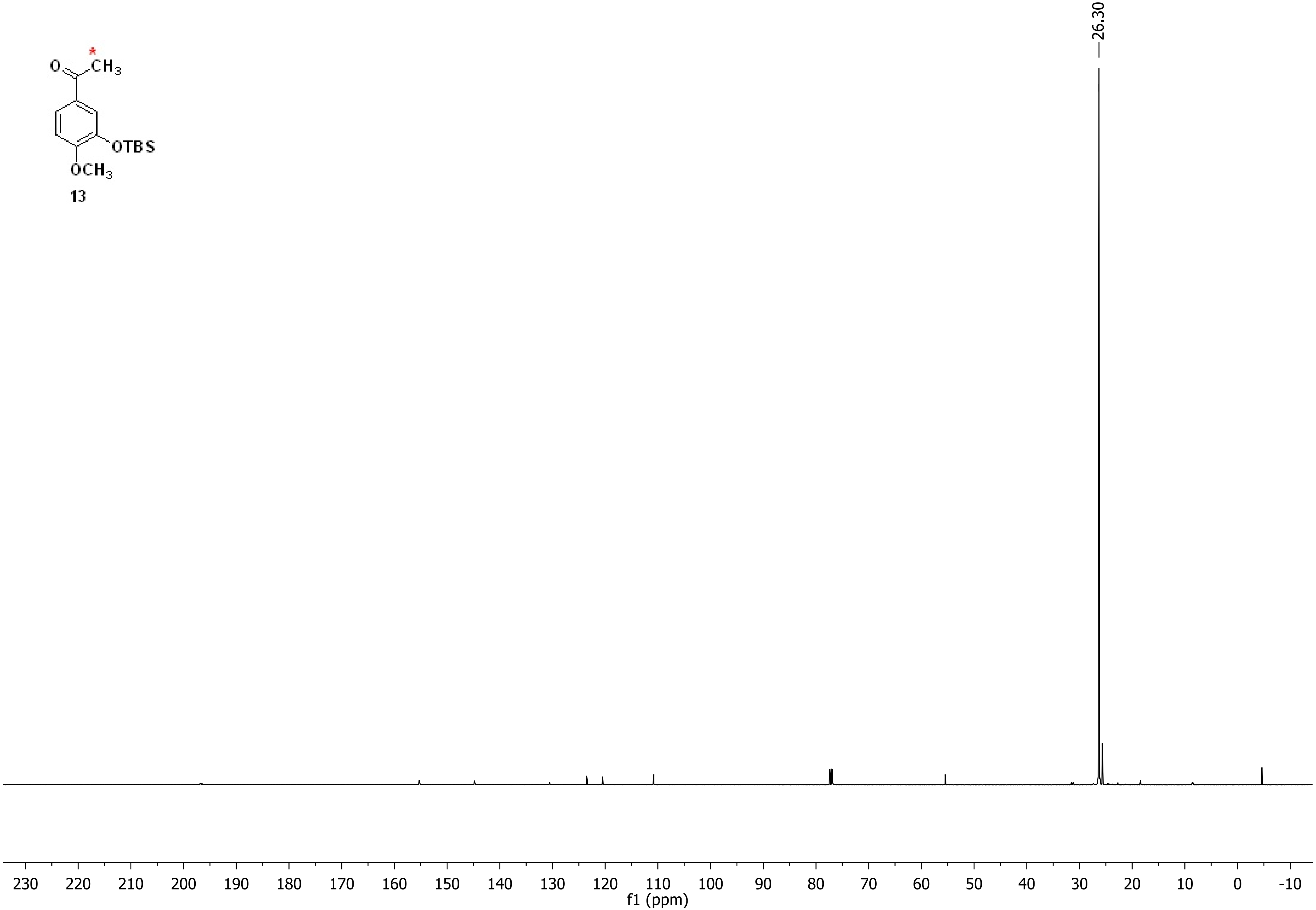
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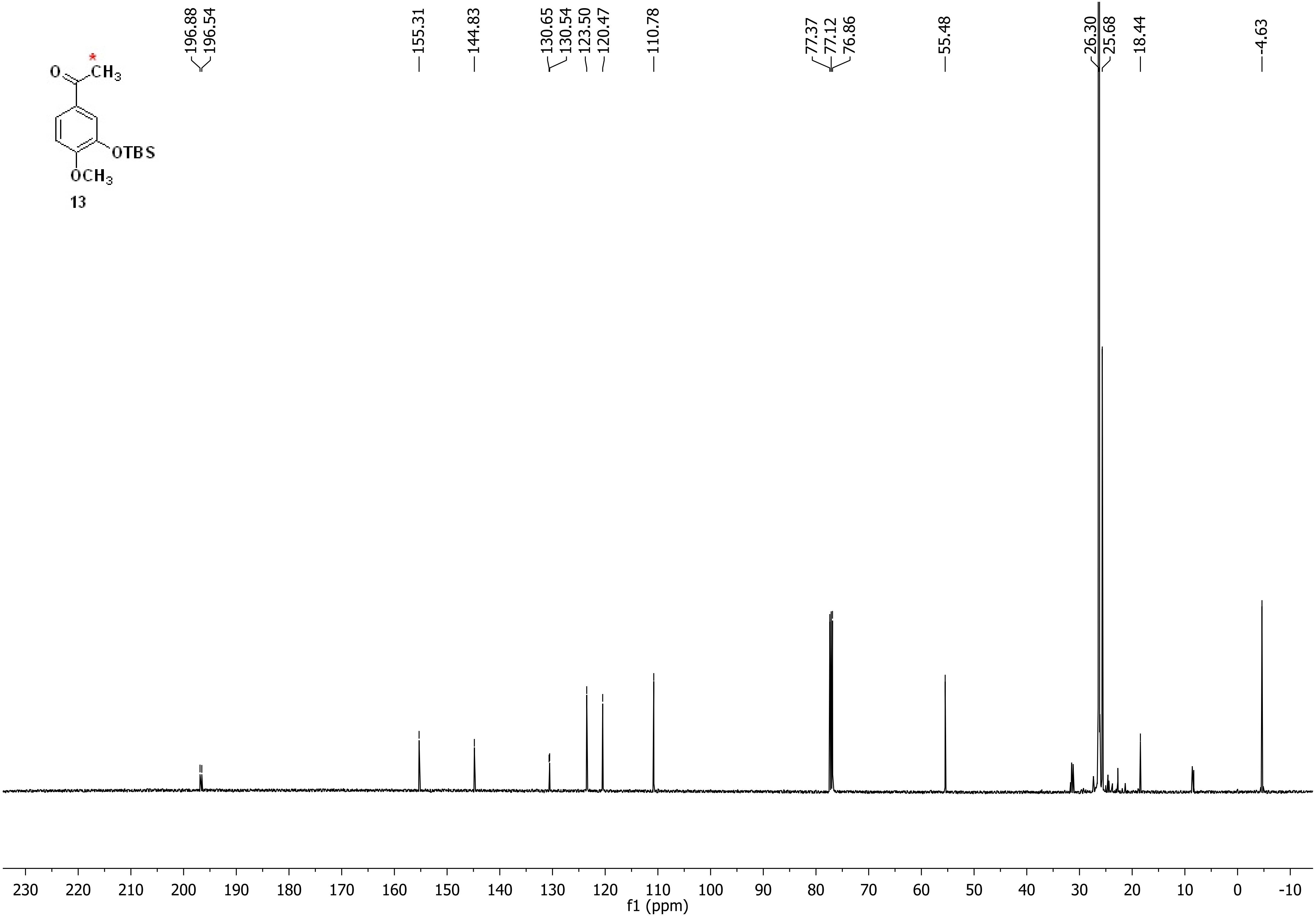
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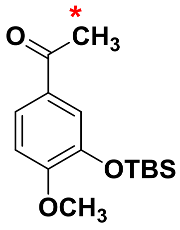

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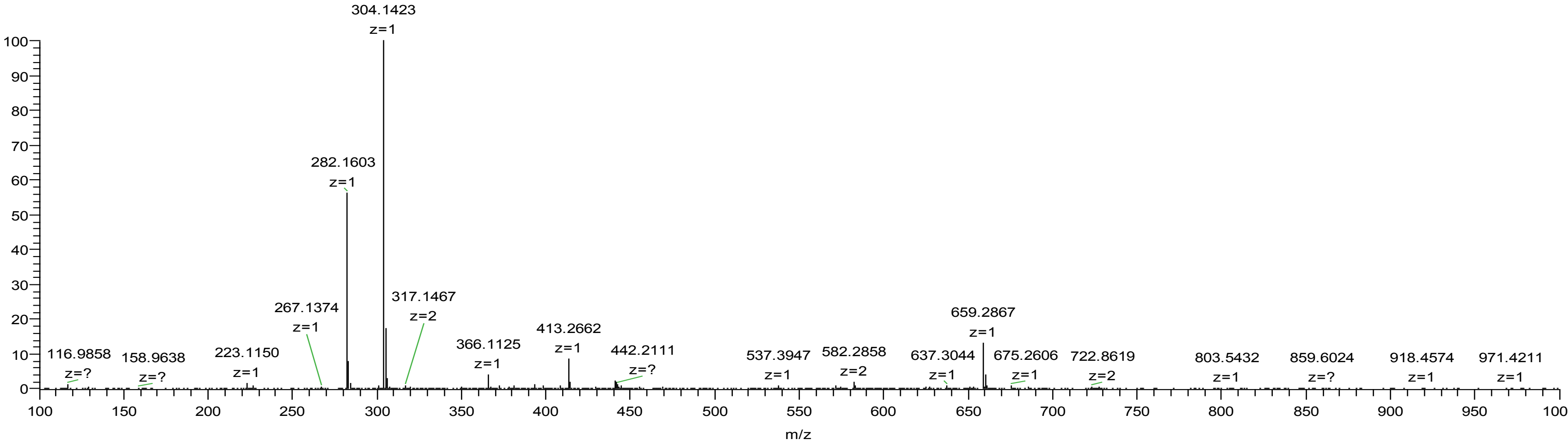

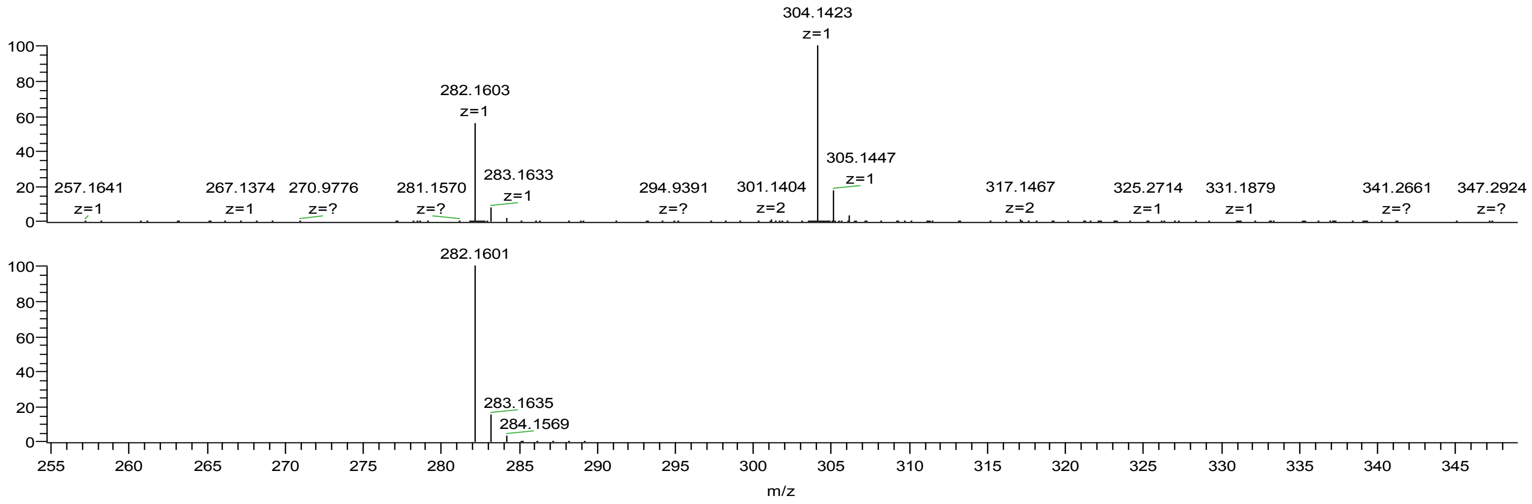

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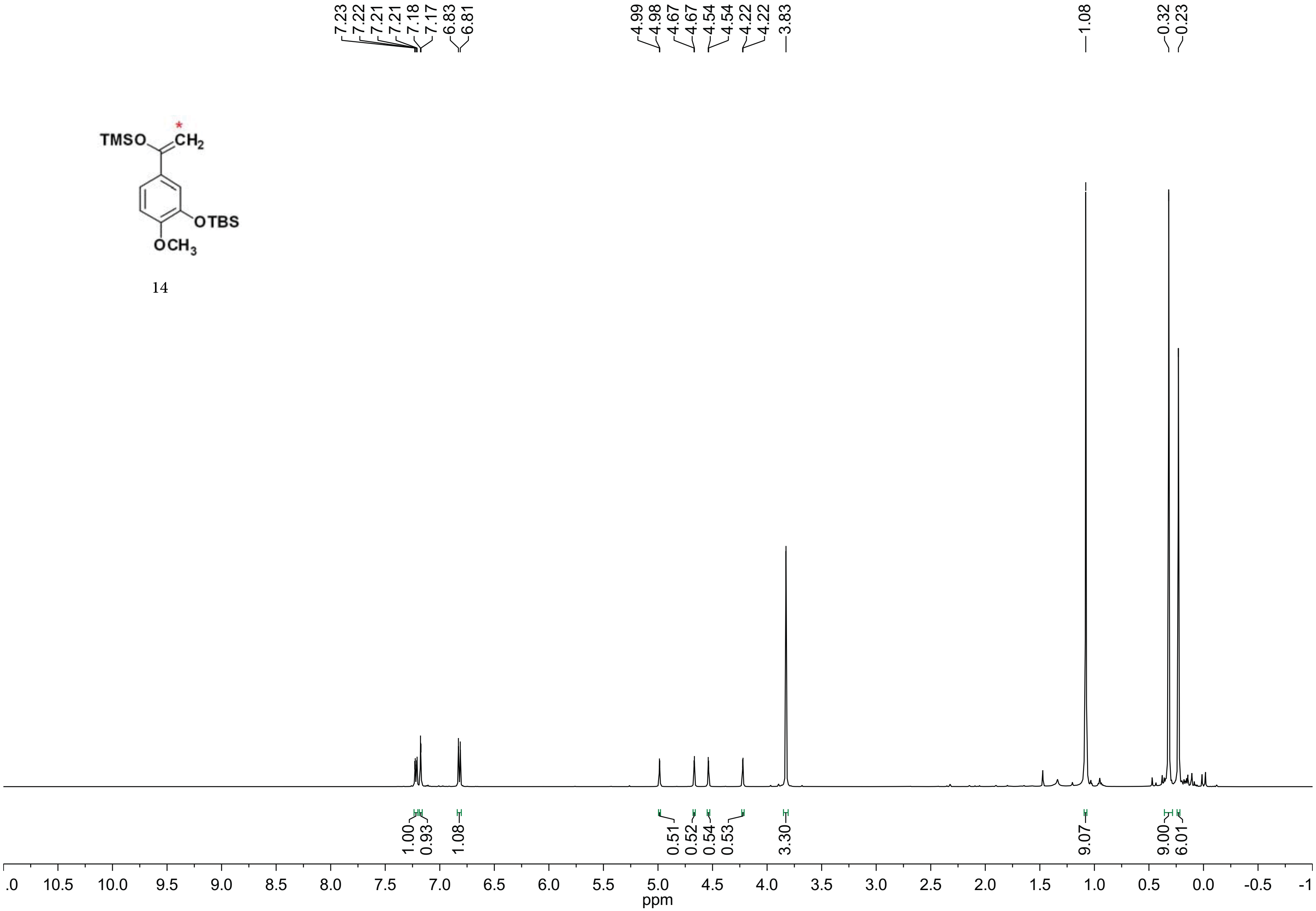
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4.22
3.83
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0.23
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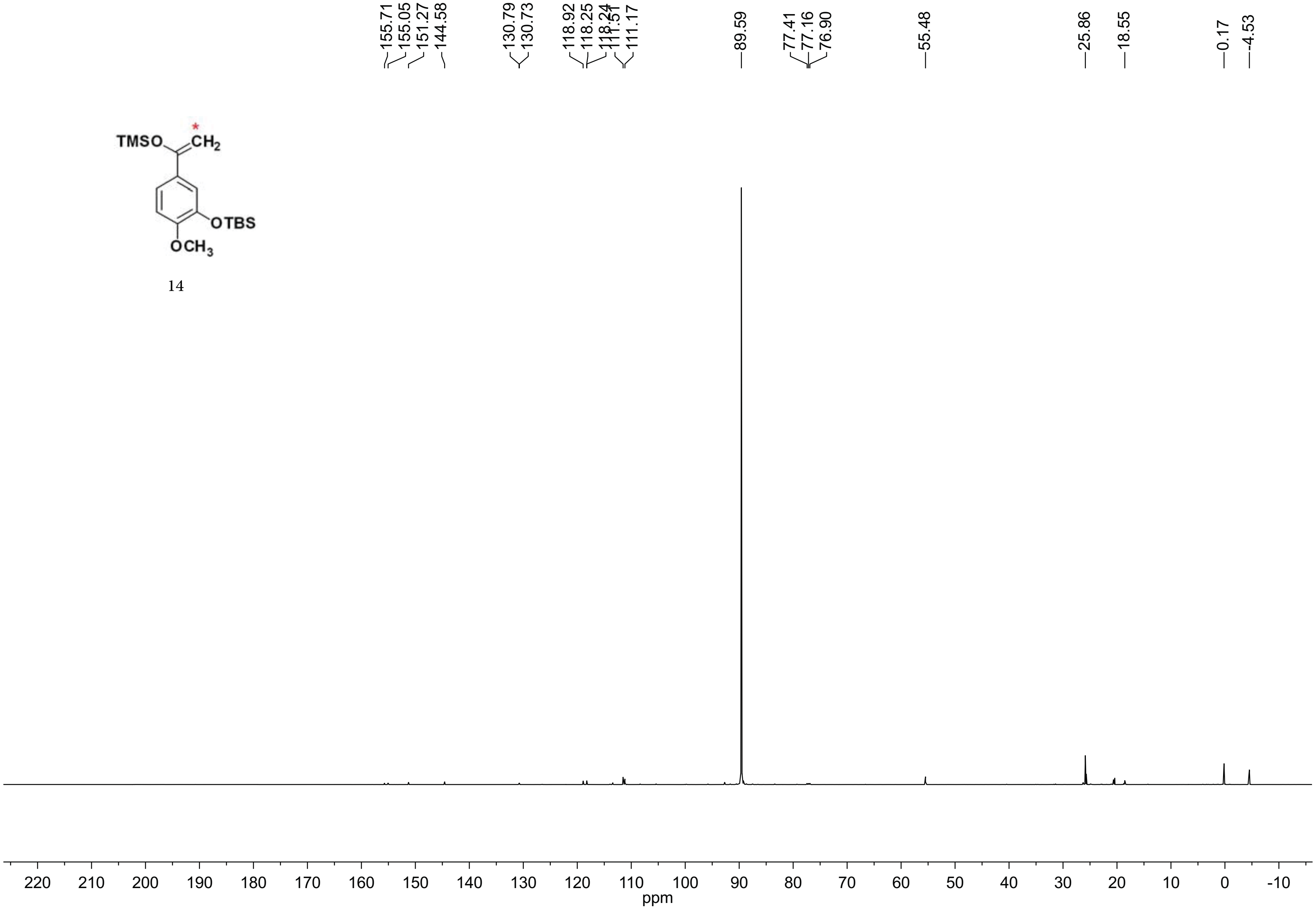
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CH_2
OTBS
OCH_3

14

155.71
155.05
151.27
144.58
130.79
130.73
118.92
118.25
118.24
111.51
111.17
89.59
77.41
77.16
76.90
55.48
25.86
18.55
0.17
-4.53
220
210
200
190
180
170
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110
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90
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40
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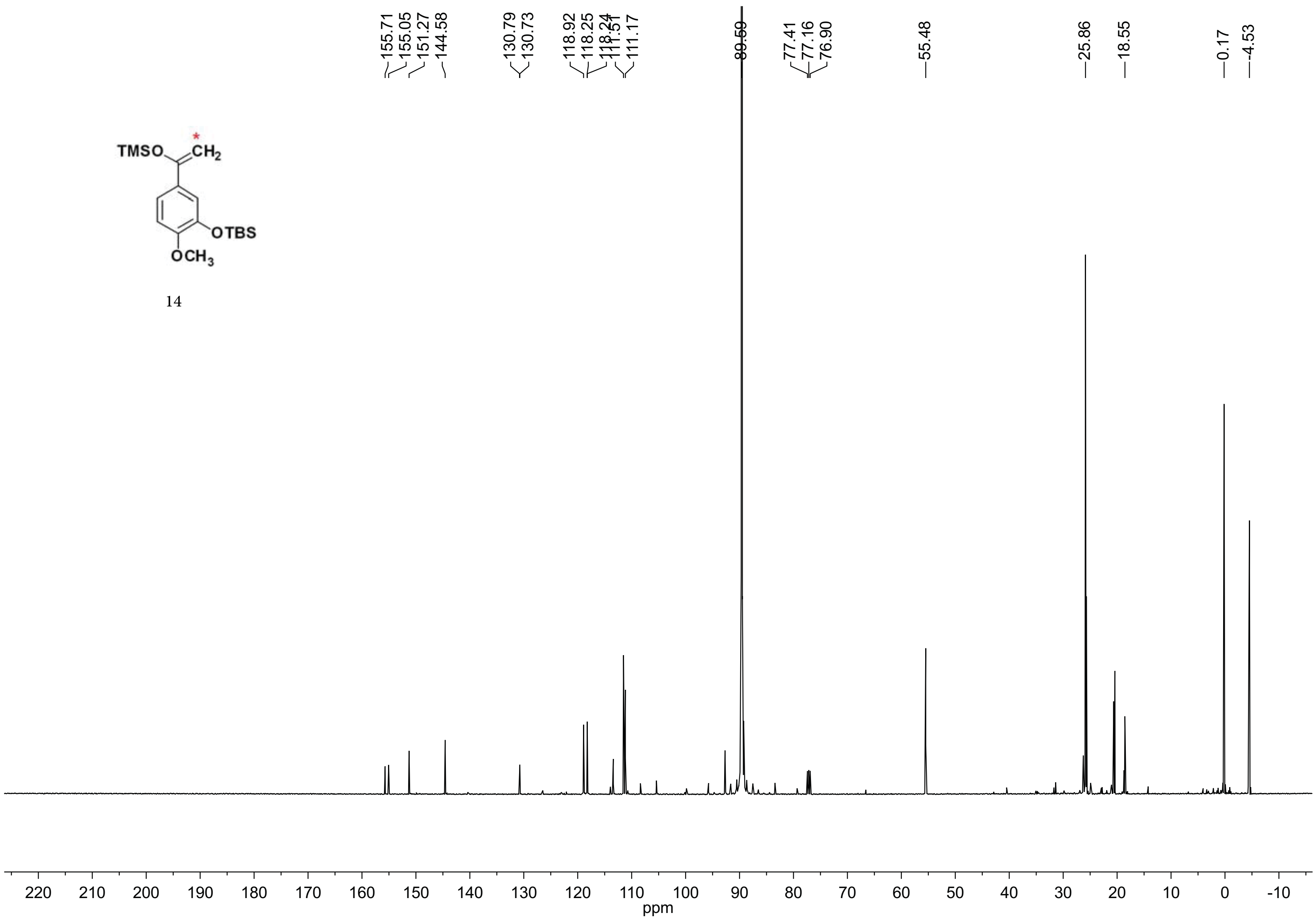
-10
ppm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118.92
118.25
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111.17
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77.41
77.16
76.90
55.48
25.86
18.55
0.17
-4.53
TMSO
*
CH$_2$
OTBS
OCH$_3$
14
220
210
200
190
180
170
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100
90
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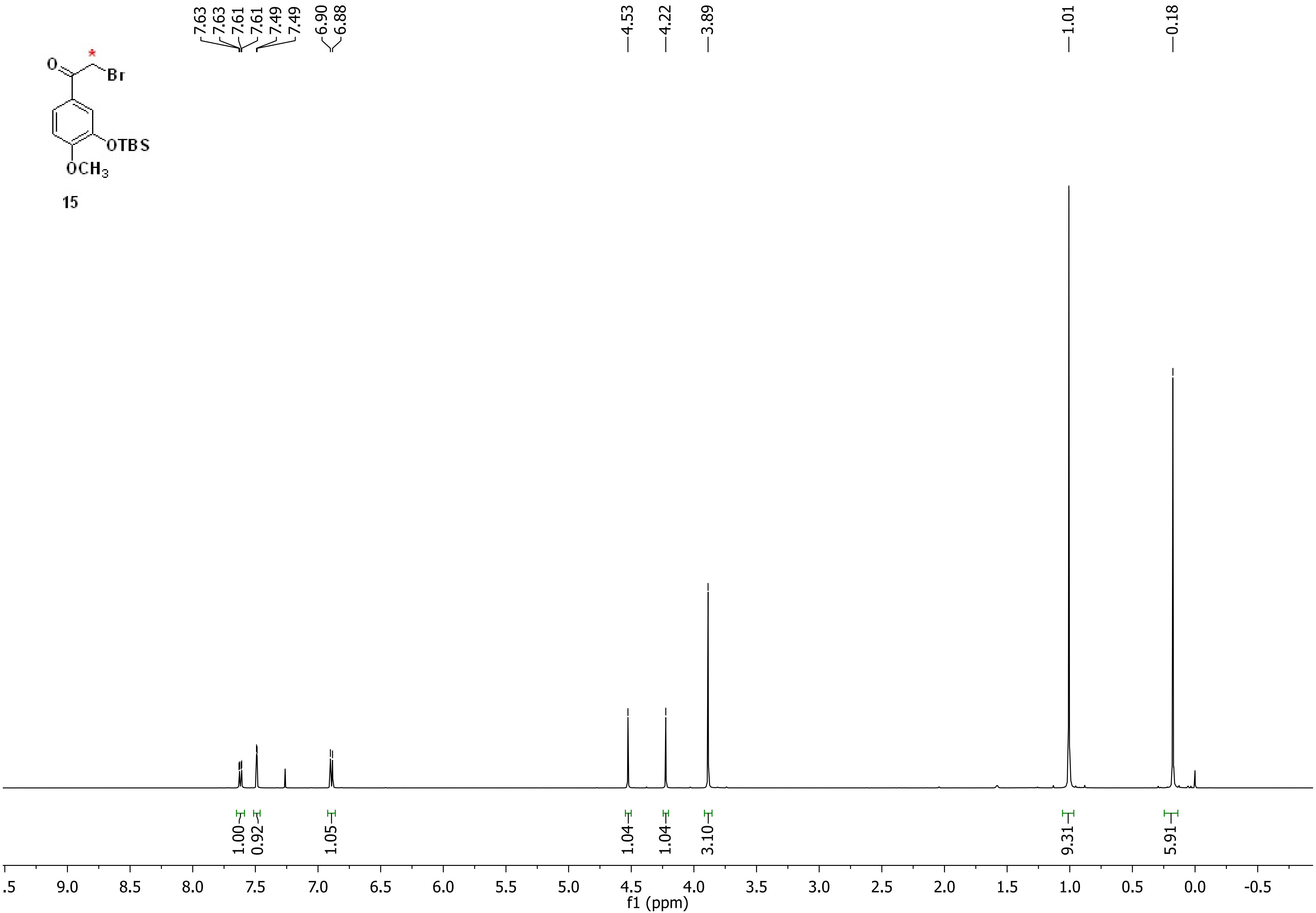
ppm



15

OTBS
OCH3
Br
O
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7.63
7.61
7.61
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6.90
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4.53
4.22
3.89
1.01
0.18
1.00
0.92
1.05
1.04
1.04
3.10
9.31
5.91
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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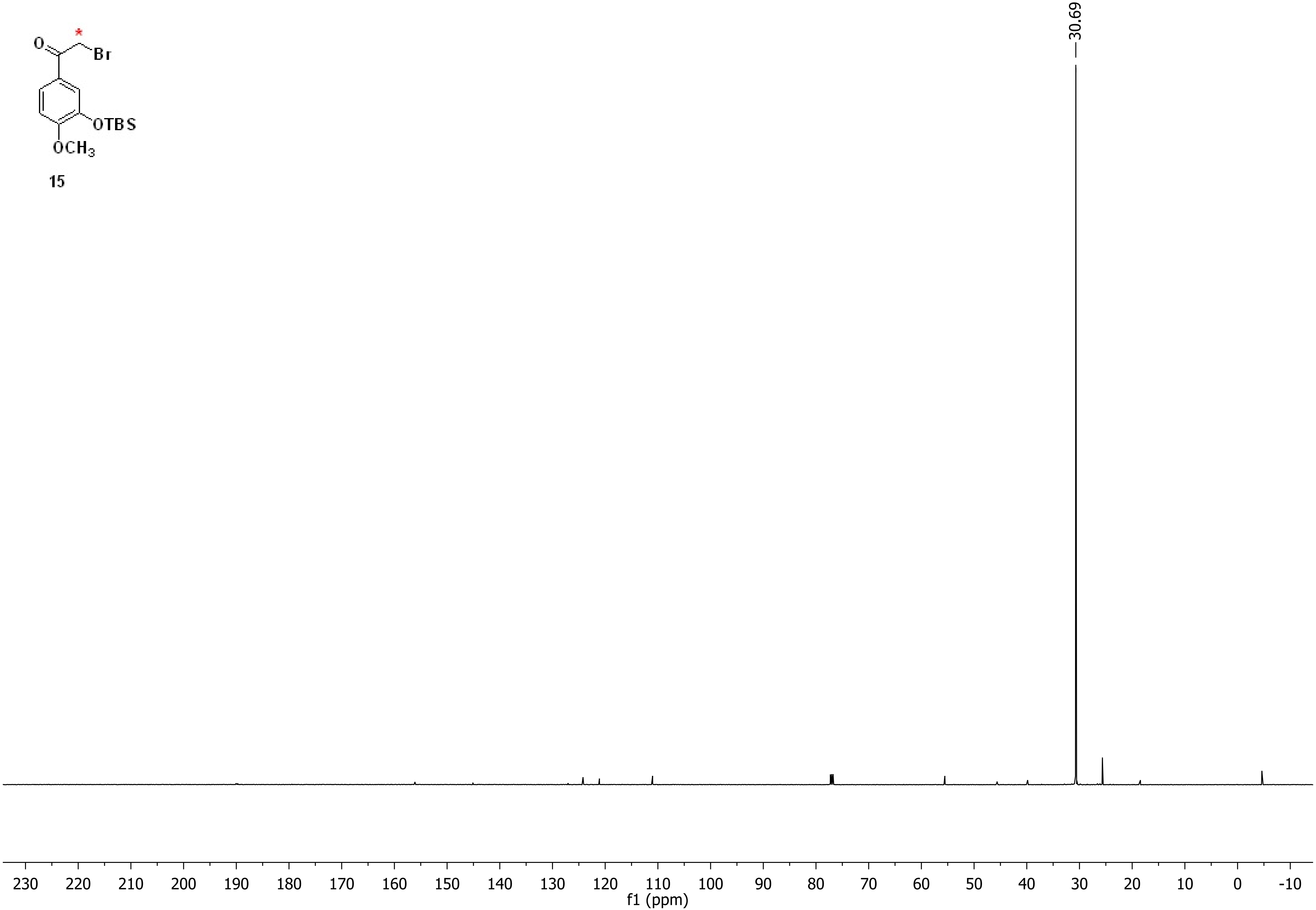
f1 (ppm)



15

O
Br
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100
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80
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60
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40
30
20
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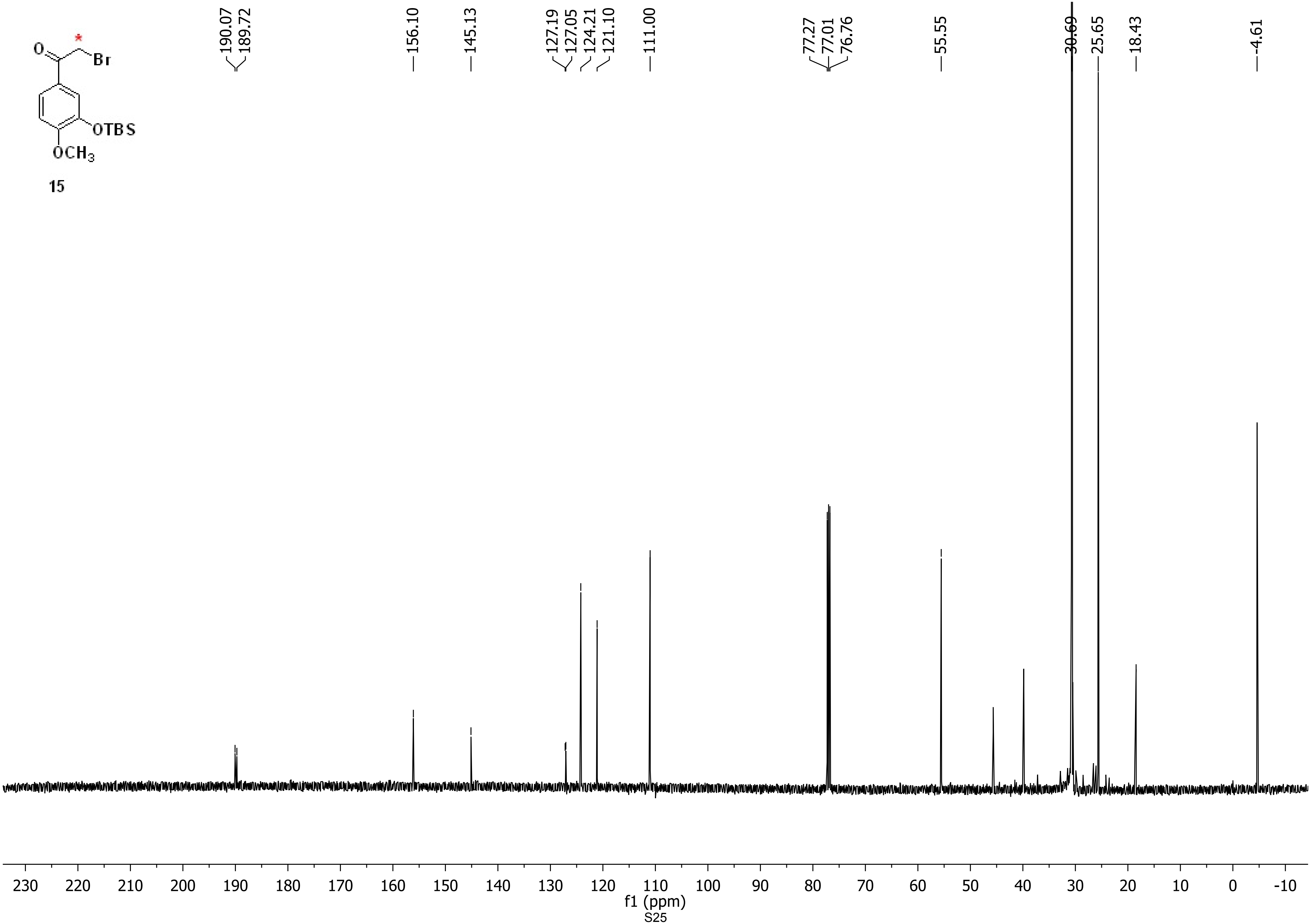
0
-10
f1 (ppm)


*
O
Br
OTBS
OCH3

15

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127.05
124.21
121.10
111.00
77.27
77.01
76.76
55.55
30.69
25.65
18.43
-4.61
230
220
210
200
190
180
170
160
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40
30
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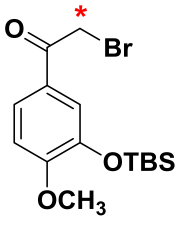
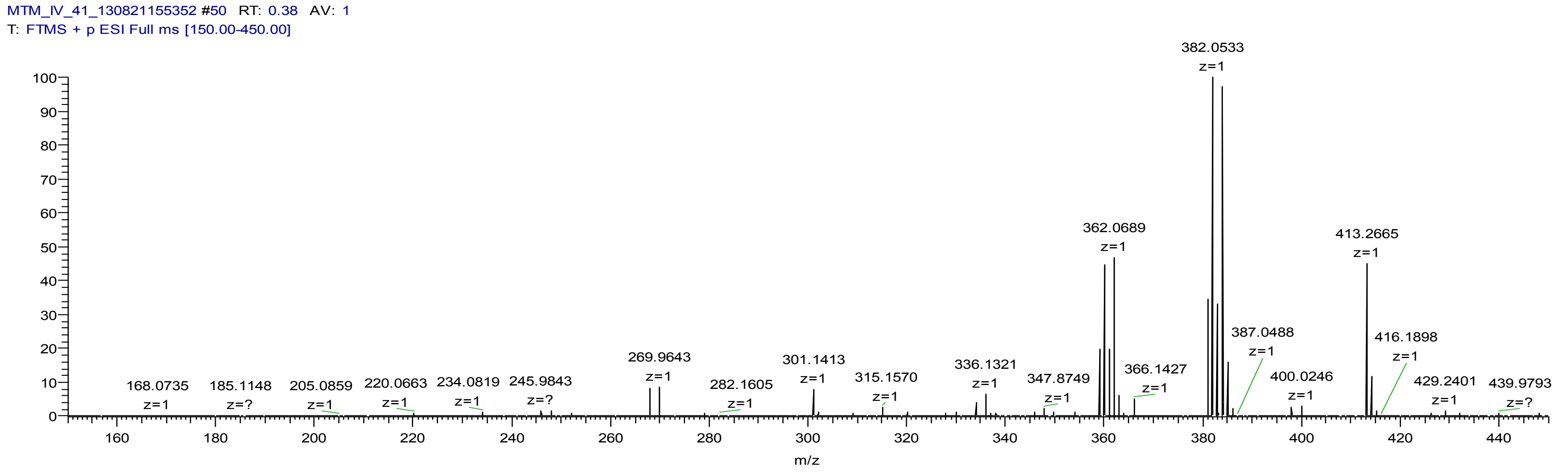
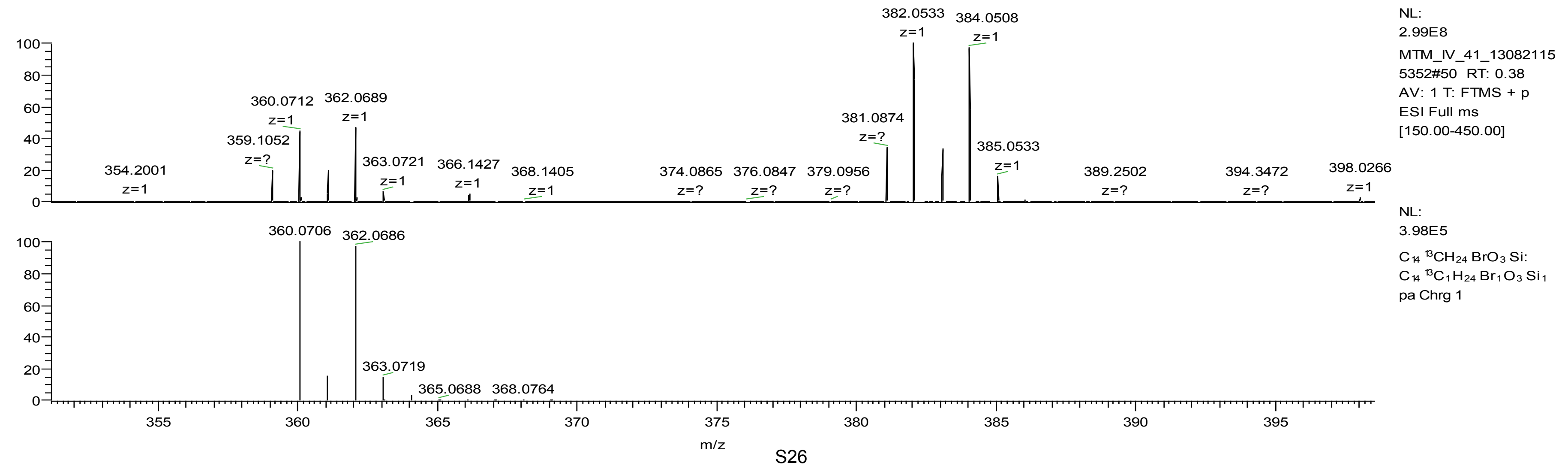
10
0
-10
f1 (ppm)

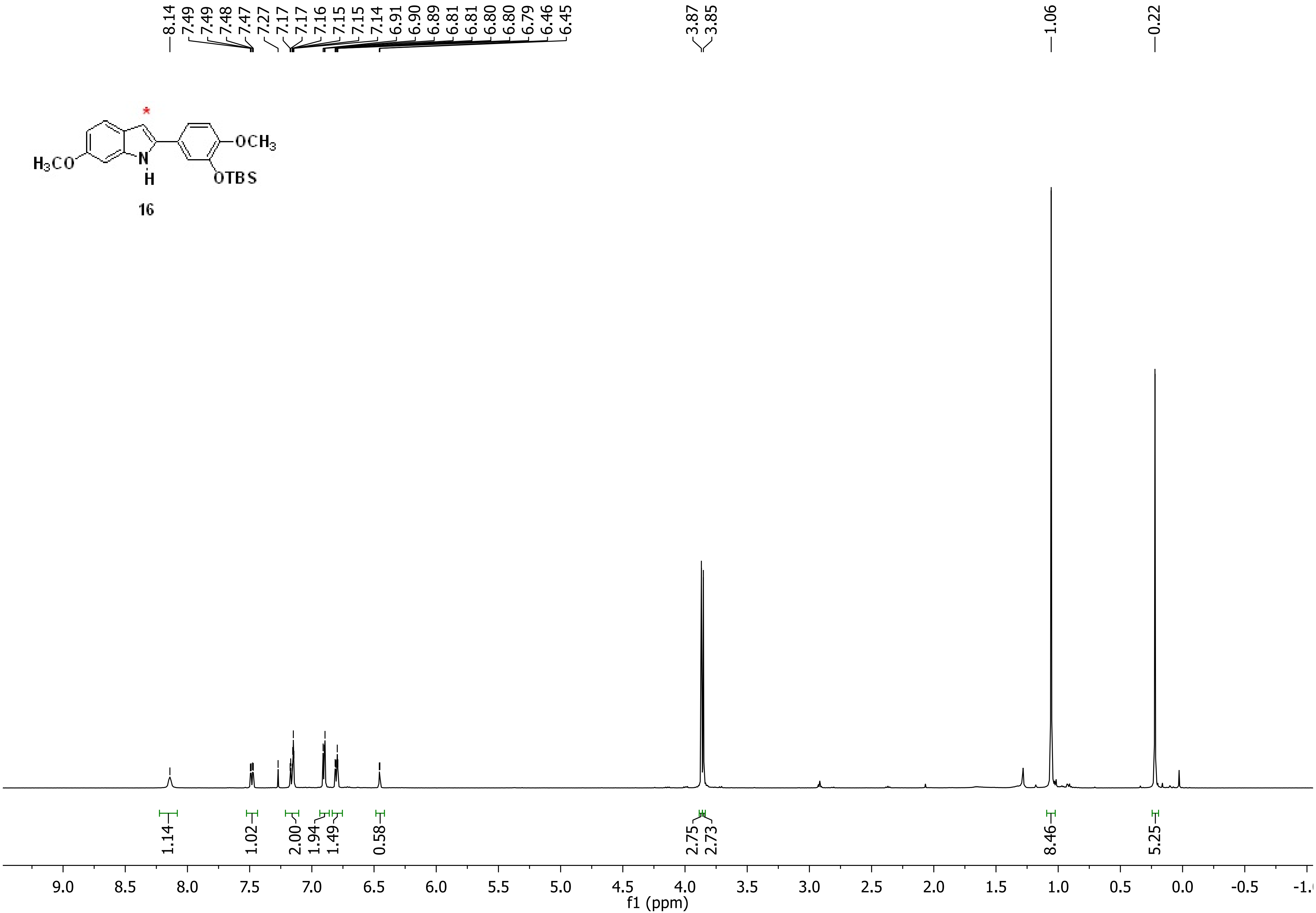


15

C:\Xcalibur\...\MTM_IV_41_130821155352 8/21/2013 3:53:52 PM MTM_IV_41



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6.90
6.89
6.81
6.81
6.80
6.80
6.79
6.46
6.45
3.87
3.85
1.06
0.22
*
H3CO
N
H
OCH3
OTBS
16
1.14
1.02
2.00
1.94
1.49
0.58
2.75
2.73
8.46
5.25
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.0
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0.0
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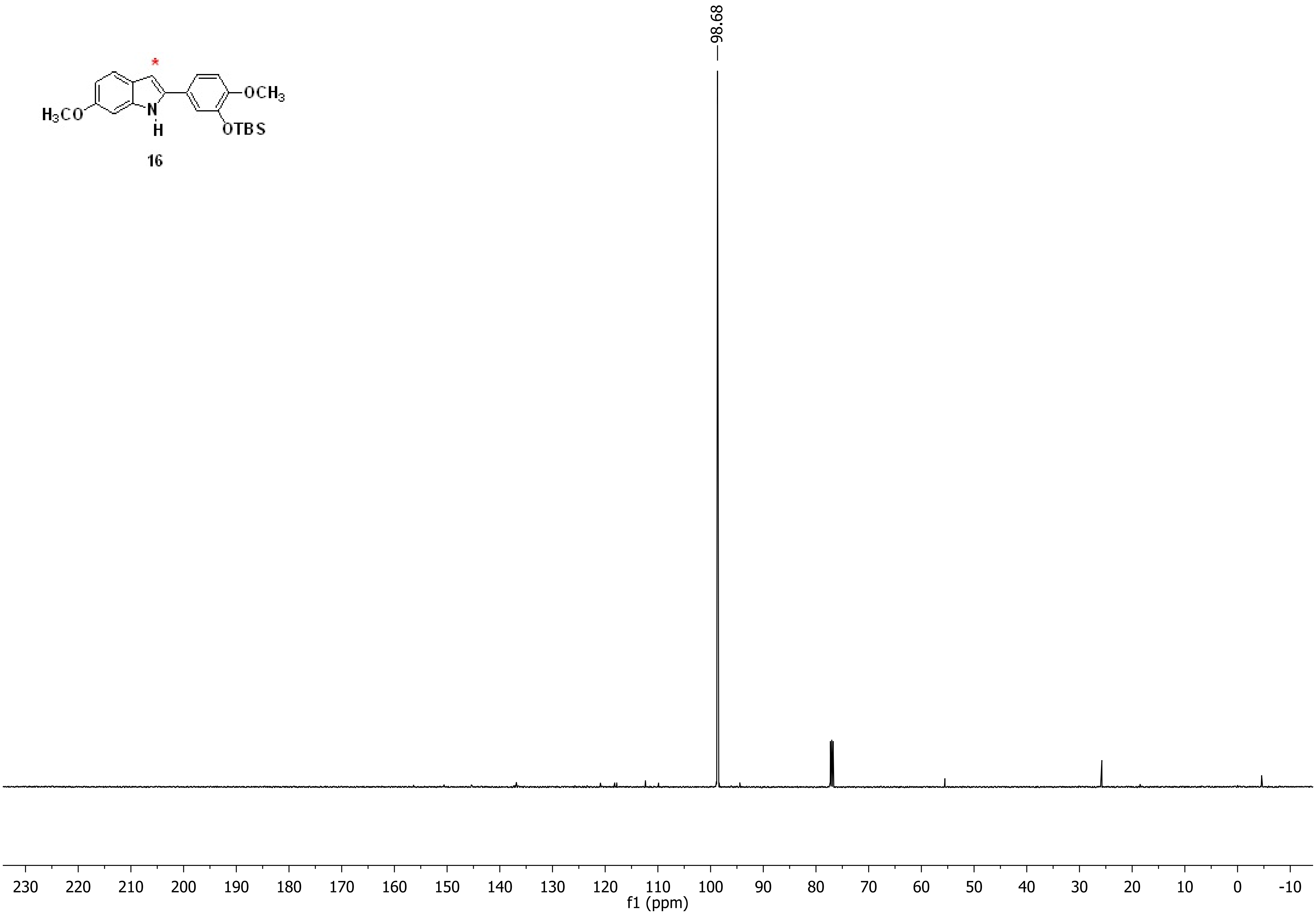
-1.
f1 (ppm)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H
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OTBS
*
16
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220
210
200
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180
170
160
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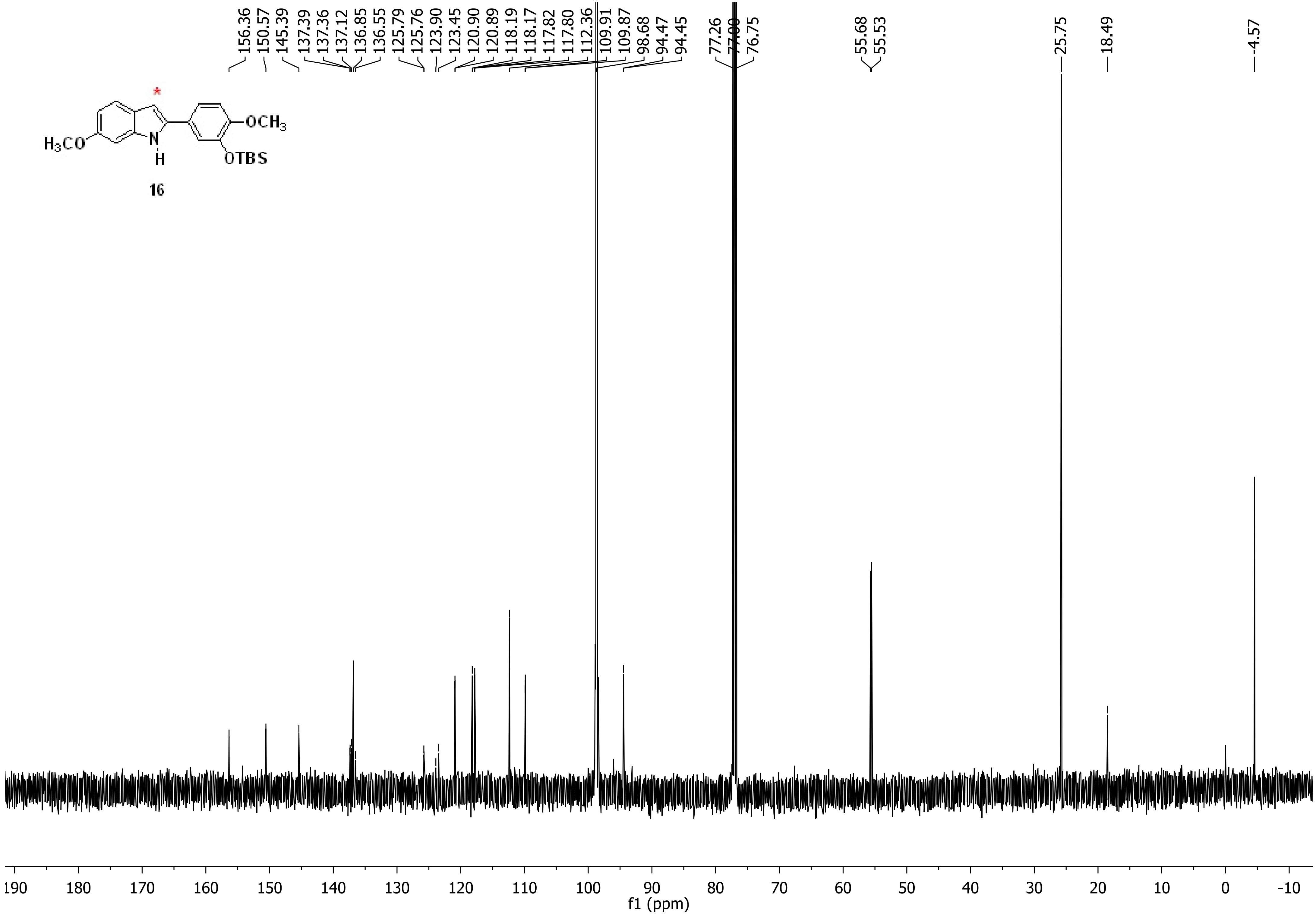
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


156.36
150.57
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137.36
137.12
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136.55
125.79
125.76
123.90
123.45
120.90
120.89
118.19
118.17
117.82
117.80
112.36
109.91
109.87
98.68
94.47
94.45
77.26
77.00
76.75
55.68
55.53
25.75
18.49
-4.57
*
H_3CO
N
H
OCH_3
OTBS
16
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

```
Data File C:\CHEM32\1\DATA\ZHE\141217ZS_II_394.D
Sample Name: C13indole

    =====================================================================
    Acq. Operator   : HAICHAN NIU
    Acq. Instrument : Instrument 1                Location :   -
    Injection Date  : 12/17/2014 1:24:43 PM
    Acq. Method     : C:\CHEM32\1\METHODS\GRAD 2 50-90 ACN.M
    Last changed    : 12/17/2014 1:22:13 PM by HAICHAN NIU
    Analysis Method : C:\CHEM32\1\DATA\ZHE\141217ZS_II_394.D\DA.M (GRAD 2 50-90 ACN.M)
    Last changed    : 12/30/2014 4:47:19 PM by ERICAP
    Sample Info     : GRAD 2 50 -90 ACN
                      C13indole
                      20141217
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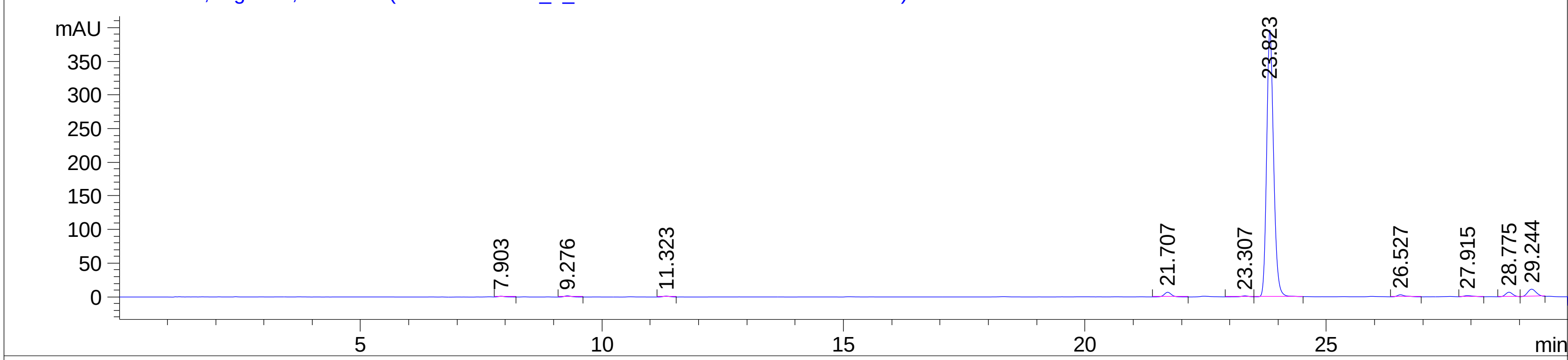
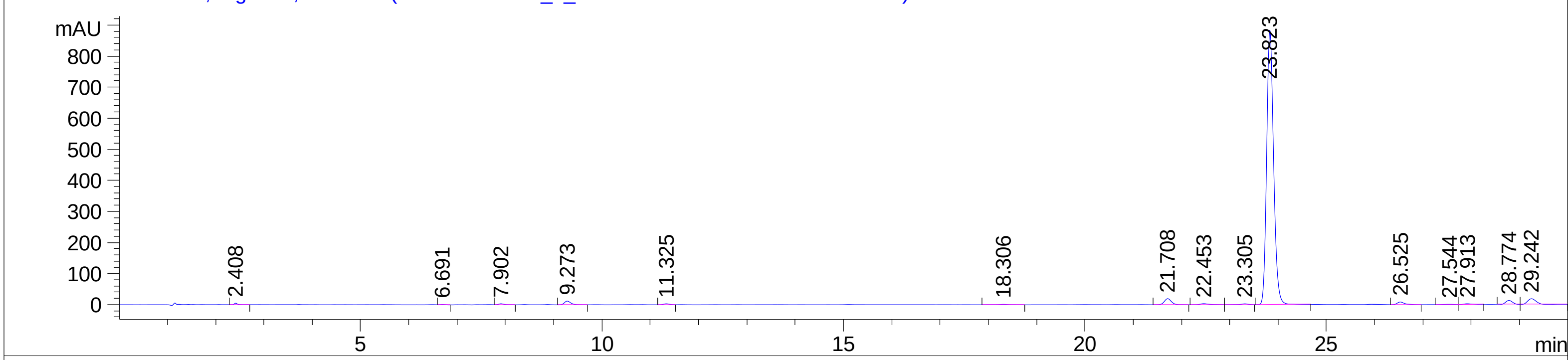
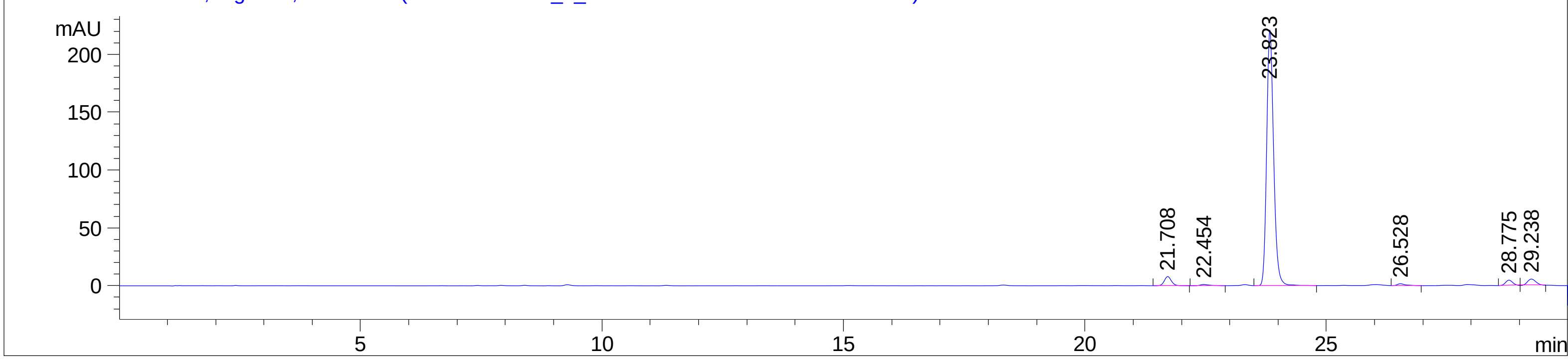
*DAD1 A, Sig=254,4 Ref=off (ZHE\141217ZS_II_394.D - ZHE\20141217BLANK03.D)

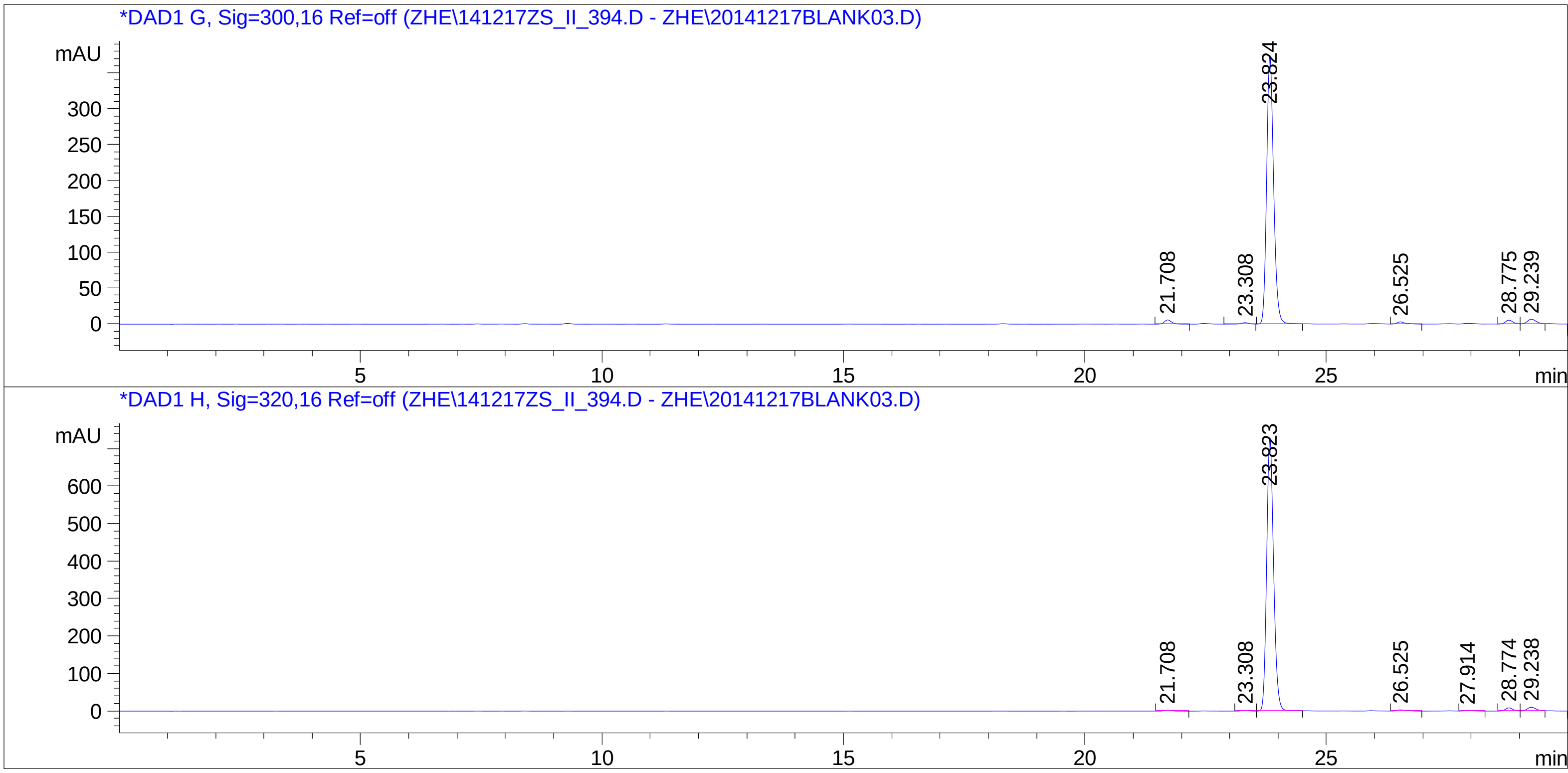


*DAD1 C, Sig=210,8 Ref=off (ZHE\141217ZS_II_394.D - ZHE\20141217BLANK03.D)



*DAD1 E, Sig=280,16 Ref=off (ZHE\141217ZS_II_394.D - ZHE\20141217BLANK03.D)





```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   7.903 BB    0.1237    8.97274    1.09440   0.2070
   2   9.276 BB    0.1403   16.84550    1.81463   0.3886
   3  11.323 BB    0.1362   12.08191    1.35247   0.2787
   4  21.707 BB    0.1573   72.22176    6.94540   1.6662
   5  23.307 BB    0.1472   14.23725    1.49431   0.3285
   6  23.823 BB    0.1541 3944.59912  396.45770  91.0046
   7  26.527 BB    0.1736   37.00466    3.09254   0.8537
   8  27.915 BB    0.1954   23.40132    1.75668   0.5399
   9  28.775 BB    0.1618   70.08858    6.71465   1.6170
  10  29.244 BB    0.1943  135.05341   10.91752   3.1158

Totals :                  4334.50624  431.64030
```

```
   Signal 2: DAD1 C, Sig=210,8 Ref=off
    Signal has been modified after loading from rawdata file!

   Peak RetTime Type  Width     Area      Height     Area  
     #   [min]        [min]   [mAU*s]     [mAU]        %   
   ----|-------|----|-------|----------|----------|--------|
      1   2.408 BB    0.0683   22.30968    4.97948   0.2266
      2   6.691 VB    0.1052    8.28824    1.19031   0.0842
      3   7.902 BB    0.1218   25.92144    3.22458   0.2633
      4   9.273 BB    0.1402  112.41674   12.11774   1.1418
      5  11.325 BB    0.1379   28.51899    3.20380   0.2897
      6  18.306 BB    0.1813   17.94281    1.44024   0.1823
      7  21.708 BB    0.1557  202.23770   19.70864   2.0542
      8  22.453 BB    0.1920   45.83818    3.47165   0.4656
      9  23.305 BB    0.1578   29.30734    2.80739   0.2977
     10  23.823 BB    0.1541 8799.65332  884.17999  89.3806
     11  26.525 BB    0.1619   95.05730    8.80946   0.9655
     12  27.544 BV    0.2140   17.40180    1.16646   0.1768
     13  27.913 VB    0.1982   39.21973    2.89218   0.3984
     14  28.774 BV    0.1639  143.44379   13.50203   1.4570
     15  29.242 VB    0.2077  257.59482   19.05302   2.6165

   Totals :                  9845.15189  981.74698



   Signal 3: DAD1 E, Sig=280,16 Ref=off
    Signal has been modified after loading from rawdata file!

   Peak RetTime Type  Width     Area      Height     Area  
     #   [min]        [min]   [mAU*s]     [mAU]        %   
   ----|-------|----|-------|----------|----------|--------|
      1  21.708 BB    0.1556   81.35815    7.93701   3.3271
      2  22.454 BB    0.1947   14.99190    1.10235   0.6131
      3  23.823 BB    0.1549 2214.12866  221.04308  90.5459
      4  26.528 BB    0.1712   19.06033    1.62073   0.7795
      5  28.775 BB    0.1619   48.55169    4.64699   1.9855
      6  29.238 BB    0.1939   67.21884    5.44941   2.7489

   Totals :                  2445.30957  241.79956



   Signal 4: DAD1 G, Sig=300,16 Ref=off
    Signal has been modified after loading from rawdata file!

   Peak RetTime Type  Width     Area      Height     Area  
     #   [min]        [min]   [mAU*s]     [mAU]        %   
   ----|-------|----|-------|----------|----------|--------|
      1  21.708 BB    0.1539   59.15012    5.85095   1.4892
      2  23.308 BB    0.1493   18.53098    1.90773   0.4666
      3  23.824 BB    0.1539 3725.80444  375.04620  93.8063
```

```
   Peak RetTime Type  Width     Area      Height     Area
     #   [min]        [min]   [mAU*s]     [mAU]        %
   ----|-------|----|-------|----------|----------|--------|
      4  26.525 BB    0.1657   34.37233    3.04487   0.8654
      5  28.775 BB    0.1619   55.19741    5.28453   1.3897
      6  29.239 BB    0.1927   78.75215    6.43651   1.9828

   Totals :                  3971.80744  397.57080



   Signal 5: DAD1 H, Sig=320,16 Ref=off
    Signal has been modified after loading from rawdata file!

   Peak RetTime Type  Width     Area      Height     Area
     #   [min]        [min]   [mAU*s]     [mAU]        %
   ----|-------|----|-------|----------|----------|--------|
      1  21.708 BB    0.1544   23.81687    2.34698   0.3156
      2  23.308 BB    0.1461   19.31839    2.04754   0.2560
      3  23.823 BB    0.1537 7247.35693  730.59741  96.0400
      4  26.525 BB    0.1665   35.64434    3.13880   0.4723
      5  27.914 BB    0.1906   13.79213    1.09783   0.1828
      6  28.774 BB    0.1616   87.57129    8.40103   1.1605
      7  29.238 BB    0.1930  118.68315    9.68232   1.5728

   Totals :                  7546.18311  757.31191


   =====================================================================
                             *** End of Report ***
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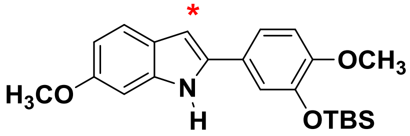
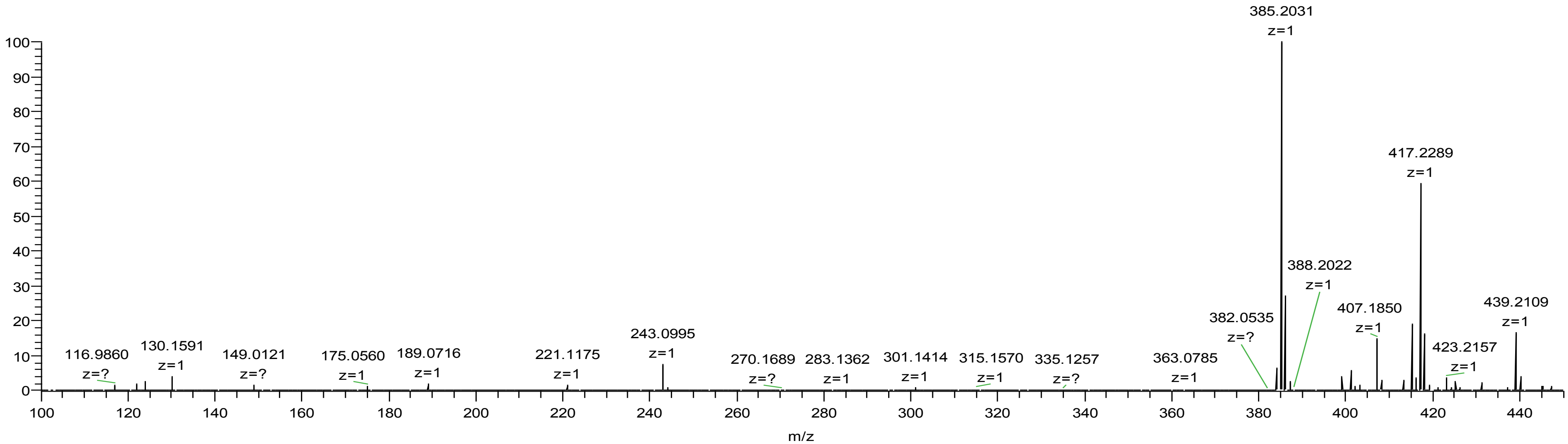
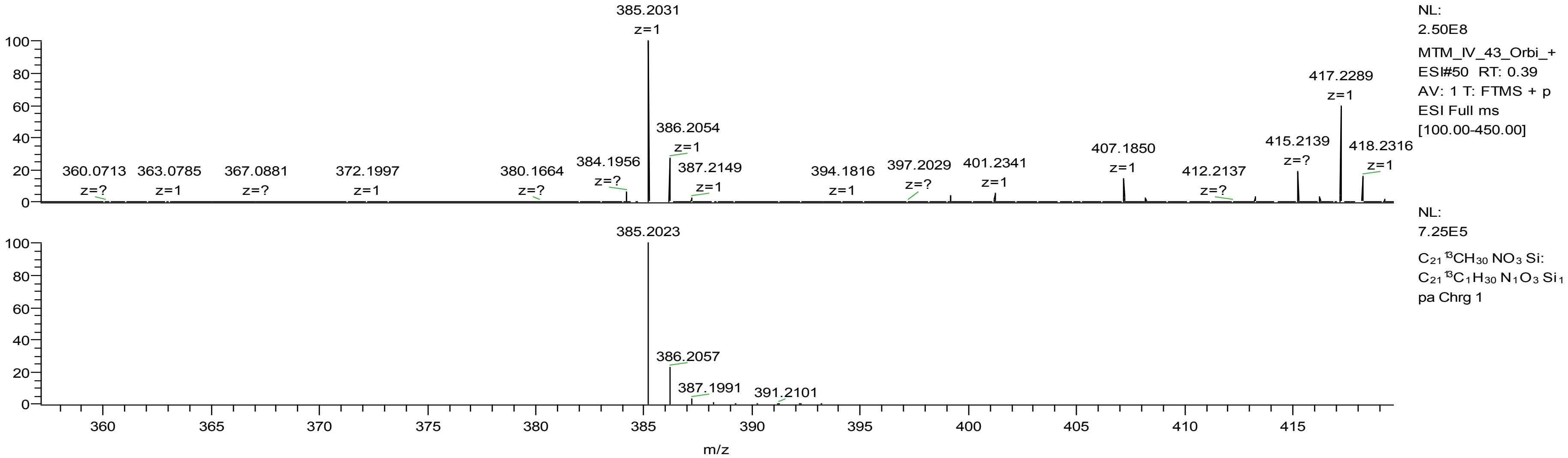


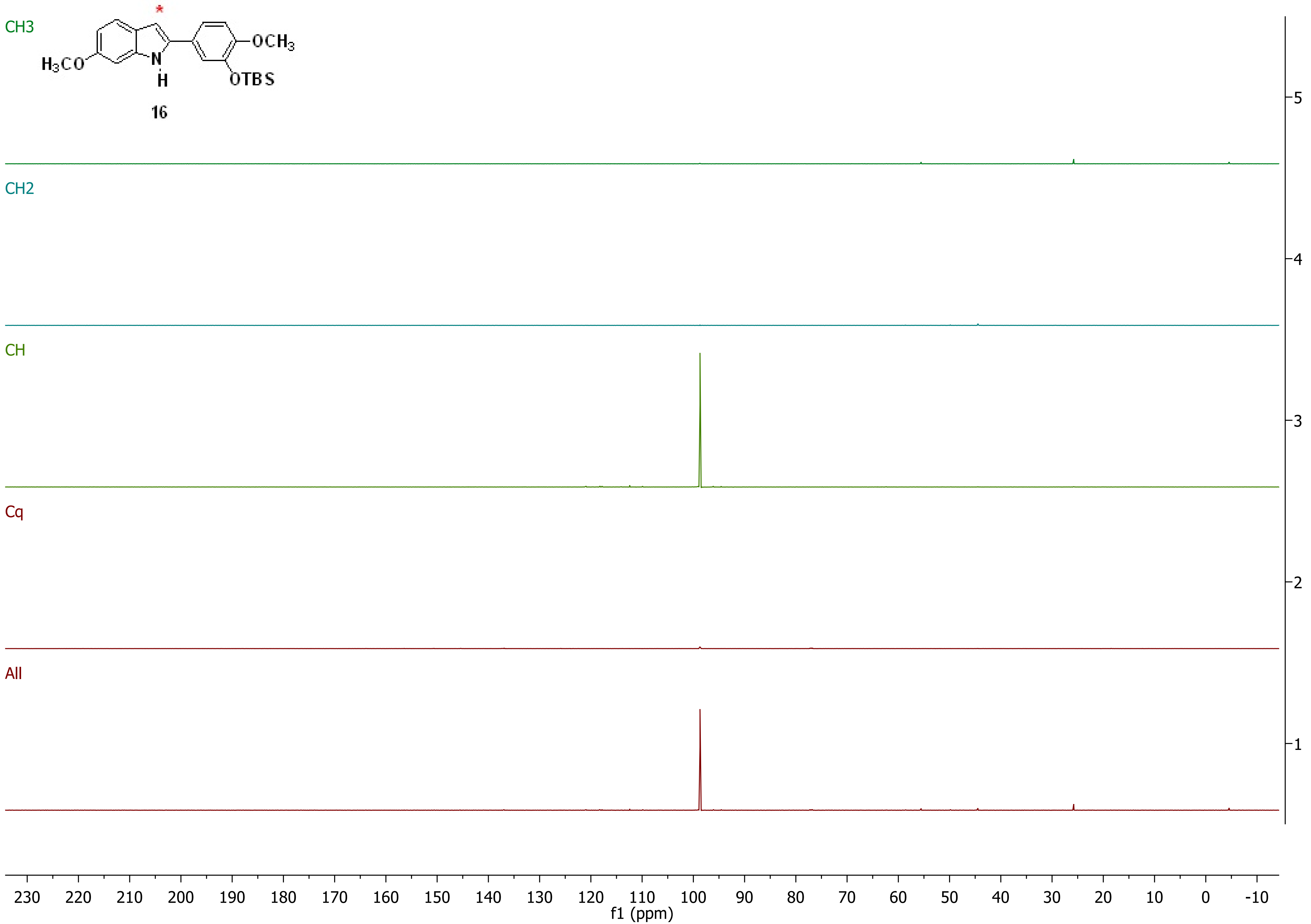
16

C:\Xcalibur\...\MTM_IV_43_Orbi_+ESI   8/21/2013 3:17:34 PM   MTM_IV_43

MTM_IV_43_Orbi_+ESI #50 RT: 0.39 AV: 1 NL
T: FTMS + p ESI Full ms [100.00-450.00]

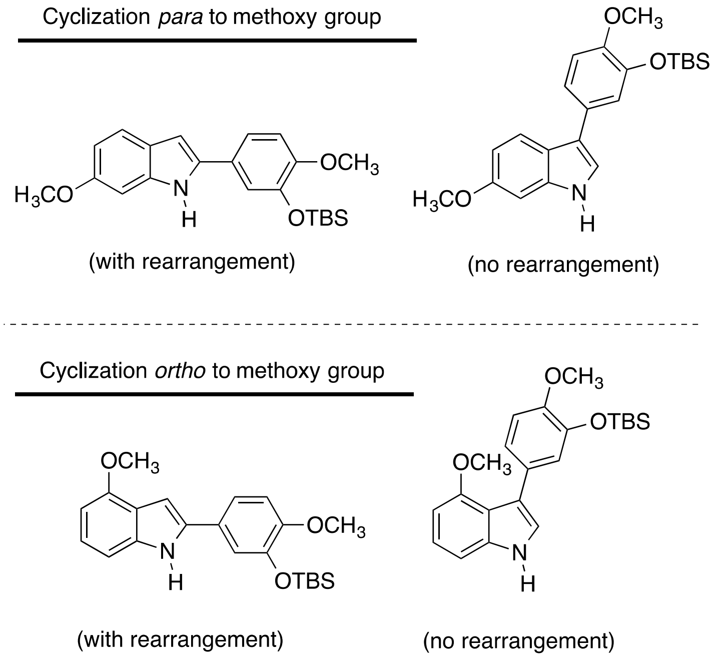




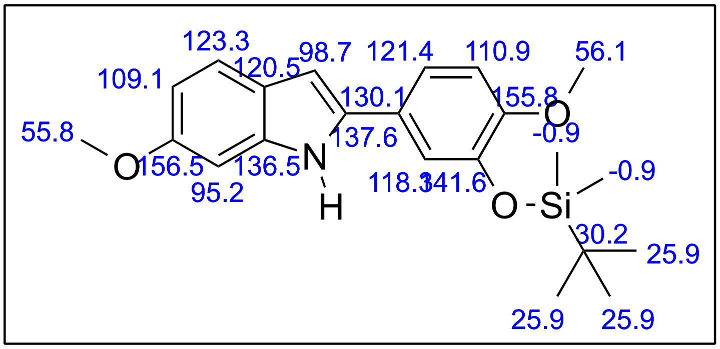

CH3
CH2
CH
Cq
All
*
H3CO
N
H
OCH3
OTBS
16
5
4
3
2
1
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

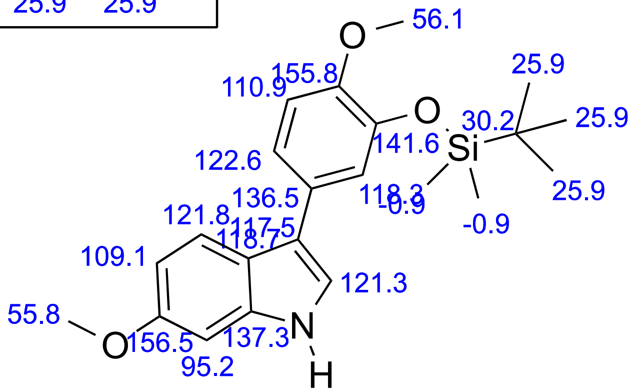
Predicted (ChemBioDraw, Version 13.0.2.3020) ^{13}C NMR Values for Possible Indole Regioisomers

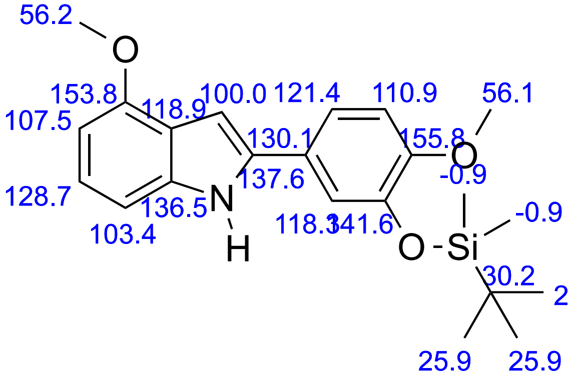
Indole Regioisomers as Possible Products Under Bischler-Mohlau Reaction Conditions

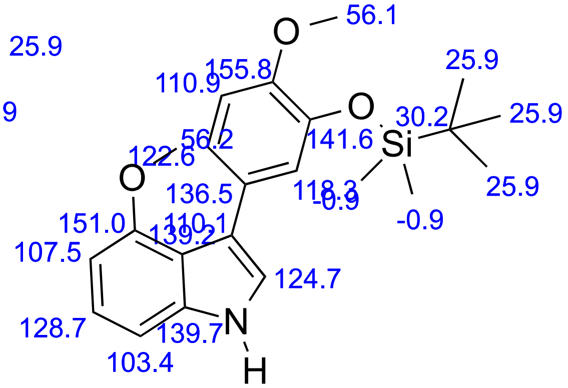


^{13}C-NMR Predicted (ChemBioDraw, Version 13.0.2.3020) Chemical Shifts for Possible Indole Regioisomers

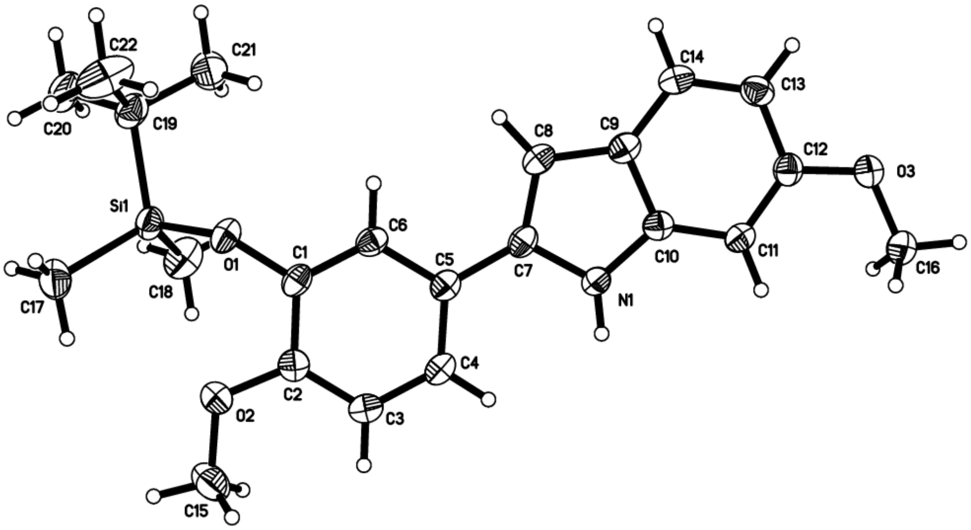








X-ray Crystallographic Data for ^{13}C Labeled Indole 16



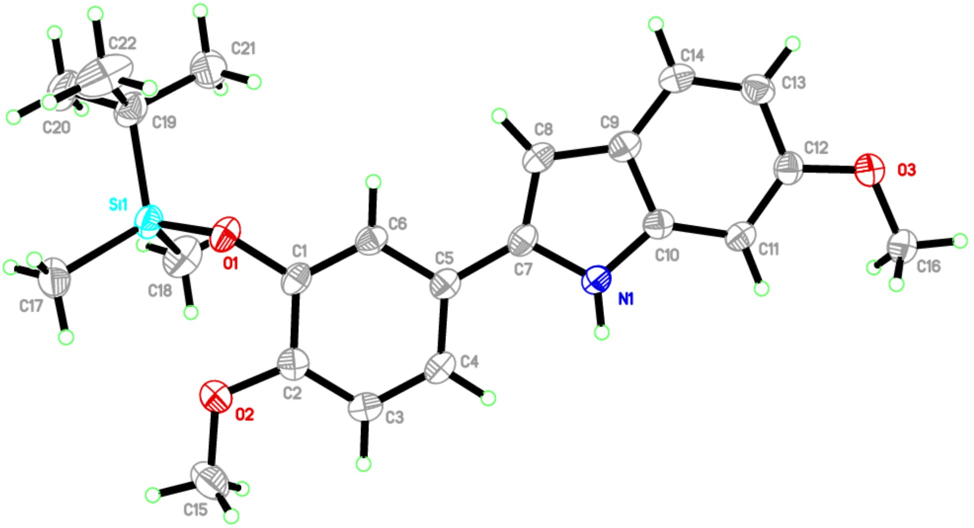


Table S1. Crystal data and structure refinement for Indole **16**.

Identification code	kp66	
Empirical formula	C22 H29 N O3 Si	
Formula weight	383.55	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 12.5182(6) Å	α= 90°.
	b = 23.1476(10) Å	β= 100.7843(17)°.
	c = 7.5208(3) Å	γ = 90°.
Volume	2140.79(16) Å^3	
Z	4	
Density (calculated)	1.190 Mg/m^3	
Absorption coefficient	0.130 mm^{-1}	
F(000)	824	
Crystal size	0.38 x 0.16 x 0.12 mm^3	
Theta range for data collection	2.42 to 26.85°.	
Index ranges	-15<=h<=15, -29<=k<=25, -9<=l<=9	
Reflections collected	25973	
Independent reflections	4565 [R(int) = 0.0410]	
Completeness to theta = 26.85°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9843 and 0.9526	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4565 / 0 / 251	
Goodness-of-fit on F^2	1.569	
Final R indices [I>2sigma(I)]	R1 = 0.0419, wR2 = 0.1071	
R indices (all data)	R1 = 0.0590, wR2 = 0.1115	
Largest diff. peak and hole	0.307 and -0.225 e.Å^{-3}	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for indole **16**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	-2359(1)	615(1)	10812(1)	28(1)
O(1)	-1718(1)	1161(1)	9999(1)	29(1)
O(2)	-1373(1)	1655(1)	13280(1)	33(1)
O(3)	5990(1)	2021(1)	6358(1)	33(1)
N(1)	2891(1)	1943(1)	9526(2)	25(1)
C(1)	-729(1)	1406(1)	10656(2)	25(1)
C(2)	-534(1)	1682(1)	12347(2)	25(1)
C(3)	451(1)	1958(1)	12936(2)	27(1)
C(4)	1238(1)	1962(1)	11862(2)	27(1)
C(5)	1069(1)	1687(1)	10190(2)	23(1)
C(6)	65(1)	1405(1)	9622(2)	25(1)
C(7)	1881(1)	1681(1)	9018(2)	24(1)
C(8)	1838(1)	1437(1)	7346(2)	26(1)
C(9)	2848(1)	1544(1)	6794(2)	25(1)
C(10)	3495(1)	1863(1)	8189(2)	24(1)
C(11)	4555(1)	2038(1)	8135(2)	25(1)
C(12)	4965(1)	1880(1)	6621(2)	26(1)
C(13)	4339(1)	1563(1)	5201(2)	29(1)
C(14)	3297(1)	1398(1)	5277(2)	29(1)
C(15)	-1193(1)	1901(1)	15046(2)	45(1)
C(16)	6666(1)	2332(1)	7773(2)	38(1)
C(17)	-3537(1)	901(1)	11724(2)	45(1)
C(18)	-1395(1)	230(1)	12588(2)	45(1)
C(19)	-2826(1)	149(1)	8766(2)	34(1)
C(20)	-3455(1)	-377(1)	9276(2)	43(1)
C(21)	-1833(2)	-63(1)	8029(3)	57(1)
C(22)	-3569(2)	496(1)	7300(3)	59(1)

Table S3. Bond lengths [Å] and angles [°] for indole **16**.

Si(1)-O(1)	1.6721(10)
Si(1)-C(18)	1.8536(16)
Si(1)-C(17)	1.8602(16)
Si(1)-C(19)	1.8804(16)
O(1)-C(1)	1.3674(16)
O(2)-C(2)	1.3690(17)
O(2)-C(15)	1.4236(18)
O(3)-C(12)	1.3744(17)
O(3)-C(16)	1.4253(17)
N(1)-C(10)	1.3785(17)
N(1)-C(7)	1.3892(17)
C(1)-C(6)	1.3717(19)
C(1)-C(2)	1.403(2)
C(2)-C(3)	1.386(2)
C(3)-C(4)	1.385(2)
C(4)-C(5)	1.3909(19)
C(5)-C(6)	1.4090(19)
C(5)-C(7)	1.4651(19)
C(7)-C(8)	1.3703(19)
C(8)-C(9)	1.4244(19)
C(9)-C(14)	1.404(2)
C(9)-C(10)	1.4078(19)
C(10)-C(11)	1.3953(19)
C(11)-C(12)	1.382(2)
C(12)-C(13)	1.4077(19)
C(13)-C(14)	1.371(2)
C(19)-C(22)	1.531(2)
C(19)-C(21)	1.533(2)
C(19)-C(20)	1.538(2)
O(1)-Si(1)-C(18)	109.52(6)
O(1)-Si(1)-C(17)	109.55(7)
C(18)-Si(1)-C(17)	111.09(8)
O(1)-Si(1)-C(19)	103.37(6)

C(18)-Si(1)-C(19)	111.97(8)
C(17)-Si(1)-C(19)	111.05(7)
C(1)-O(1)-Si(1)	130.24(9)
C(2)-O(2)-C(15)	117.18(12)
C(12)-O(3)-C(16)	116.89(11)
C(10)-N(1)-C(7)	109.62(12)
O(1)-C(1)-C(6)	119.82(12)
O(1)-C(1)-C(2)	120.58(13)
C(6)-C(1)-C(2)	119.54(13)
O(2)-C(2)-C(3)	125.42(13)
O(2)-C(2)-C(1)	115.06(12)
C(3)-C(2)-C(1)	119.52(14)
C(4)-C(3)-C(2)	120.28(14)
C(3)-C(4)-C(5)	121.31(13)
C(4)-C(5)-C(6)	117.51(13)
C(4)-C(5)-C(7)	122.88(13)
C(6)-C(5)-C(7)	119.61(12)
C(1)-C(6)-C(5)	121.83(13)
C(8)-C(7)-N(1)	108.04(12)
C(8)-C(7)-C(5)	130.01(13)
N(1)-C(7)-C(5)	121.95(12)
C(7)-C(8)-C(9)	108.10(12)
C(14)-C(9)-C(10)	118.06(13)
C(14)-C(9)-C(8)	134.94(13)
C(10)-C(9)-C(8)	106.99(12)
N(1)-C(10)-C(11)	129.53(13)
N(1)-C(10)-C(9)	107.25(12)
C(11)-C(10)-C(9)	123.21(13)
C(12)-C(11)-C(10)	116.66(13)
O(3)-C(12)-C(11)	123.82(13)
O(3)-C(12)-C(13)	114.63(12)
C(11)-C(12)-C(13)	121.54(13)
C(14)-C(13)-C(12)	120.84(13)
C(13)-C(14)-C(9)	119.67(13)
C(22)-C(19)-C(21)	109.39(15)
C(22)-C(19)-C(20)	108.96(13)

C(21)-C(19)-C(20)	108.91(13)
C(22)-C(19)-Si(1)	110.02(11)
C(21)-C(19)-Si(1)	109.30(11)
C(20)-C(19)-Si(1)	110.23(11)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2$x 10^3) for indole **16**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	24(1)	25(1)	35(1)	0(1)	7(1)	-4(1)
O(1)	25(1)	29(1)	32(1)	1(1)	2(1)	-7(1)
O(2)	31(1)	35(1)	35(1)	-7(1)	12(1)	-2(1)
O(3)	28(1)	38(1)	33(1)	-6(1)	10(1)	-6(1)
N(1)	26(1)	25(1)	24(1)	-2(1)	4(1)	-4(1)
C(1)	24(1)	18(1)	30(1)	3(1)	1(1)	-3(1)
C(2)	27(1)	22(1)	28(1)	2(1)	6(1)	1(1)
C(3)	30(1)	26(1)	25(1)	-2(1)	2(1)	0(1)
C(4)	24(1)	24(1)	30(1)	0(1)	-1(1)	-4(1)
C(5)	25(1)	19(1)	25(1)	4(1)	2(1)	-1(1)
C(6)	29(1)	20(1)	24(1)	1(1)	2(1)	-3(1)
C(7)	23(1)	19(1)	28(1)	3(1)	1(1)	-2(1)
C(8)	25(1)	21(1)	29(1)	-1(1)	-1(1)	-2(1)
C(9)	28(1)	19(1)	26(1)	1(1)	1(1)	0(1)
C(10)	29(1)	18(1)	24(1)	2(1)	4(1)	0(1)
C(11)	26(1)	22(1)	27(1)	-2(1)	2(1)	-2(1)
C(12)	28(1)	23(1)	29(1)	3(1)	6(1)	0(1)
C(13)	34(1)	26(1)	28(1)	-3(1)	9(1)	2(1)
C(14)	32(1)	25(1)	28(1)	-5(1)	1(1)	0(1)
C(15)	38(1)	67(1)	32(1)	-5(1)	10(1)	9(1)
C(16)	30(1)	45(1)	42(1)	-10(1)	12(1)	-10(1)
C(17)	36(1)	46(1)	58(1)	-10(1)	19(1)	-9(1)
C(18)	47(1)	36(1)	48(1)	10(1)	0(1)	-4(1)
C(19)	32(1)	26(1)	42(1)	-3(1)	6(1)	-7(1)
C(20)	35(1)	32(1)	60(1)	-4(1)	6(1)	-8(1)
C(21)	54(1)	50(1)	75(1)	-29(1)	29(1)	-18(1)
C(22)	77(2)	43(1)	48(1)	0(1)	-14(1)	-12(1)

NOTE:

Crystallographic data for ^{13}C labeled indole regioisomer **16** presented in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC deposition number 1041417). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.Uk).