

## Supporting Information

### **Pd/C-Catalyzed Deoxygenation of Phenol Derivatives Using Mg Metal in MeOH in the Presence of NH<sub>4</sub>OAc**

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## General

10% Pd/C was purchased from Aldrich, N.E. ChemCat, or Merck.

**General procedure for reductive cleavage of 3,4,5-trimethoxyphenyl triflate(1) using various metals and solvents (Table 1).** After two vacuum/Ar cycles to remove air from the reaction tube, the mixture of **1** (158.2 mg, 0.5 mmol), 10% Pd/C (15.9 mg, 10 wt % of **1**) and the metal (0.6 mmol) in solvent (2.0 mL) was stirred at ordinary pressure (balloon) and temperature (*ca.* 20°C) for 24 hours. The reaction mixture was filtrated using a membrane filter (Millipore, Millex<sup>®</sup>-LH, 0.45 µm) and the filtrate was partitioned between ether (10 mL) and water (10 mL). The aqueous layer was extracted with ether (10 mL × 3), and then combined organic layers were washed with brine (10 mL), dried with anhydrous MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The ratio of the substrate (**1**) and the product (**2**) was confirmed by <sup>1</sup>H NMR of the crude mixture in CDCl<sub>3</sub>.

**General procedure for reductive cleavage of 3,4,5-trimethoxyphenyl triflate(1) in the presence of various additives (Table 2)** After two vacuum/Ar cycles to remove air from the reaction tube, the mixture of **1** (158.2 mg, 0.5 mmol), 10% Pd/C (15.9 mg, 10 wt % of **1**), magnesium metal (14.6 mg, 0.6 mmol) and additive (0.5 mmol) in MeOH (2.0 mL) was stirred at ordinary pressure (balloon) and temperature (*ca.* 20°C) for appropriate time (see Table 3). The reaction mixture was filtrated using a membrane filter (Millipore, Millex<sup>®</sup>-LH, 0.45 µm) and the filtrate was partitioned between ether (10 mL) and water (10 mL). The aqueous layer was extracted with ether (10 mL × 3), and then combined organic layers were washed with brine (10 mL), dried with anhydrous MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The ratio of the substrate (**1**) and the product (**2**) was confirmed by <sup>1</sup>H NMR of the crude mixture in CDCl<sub>3</sub>.

**General procedure for reductive cleavage of various aryl triflates (Table 3).** After two vacuum/Ar cycles to remove air from the reaction tube, the mixture of the aryl triflate (0.5 mmol), 10% Pd/C (10 wt % of the aryl triflate), magnesium metal (14.6 mg, 0.6 mmol) and ammonium acetate (38.6 mg, 0.5 mmol) in MeOH (1 mL) was stirred at ordinary pressure (balloon) and at temperature (*ca.* 20°C) for the appropriate time (see Table 3). The reaction mixture was filtrated using a membrane filter (Millipore, Millex<sup>®</sup>-LH, 0.45 µm) and the filtrate was partitioned between ether (10 mL) and water (10 mL). The aqueous layer was extracted with ether (10 mL × 3), and then combined

organic layers were washed with brine (10 mL), dried with anhydrous MgSO<sub>4</sub>, filtered and concentrated under reduced pressure.

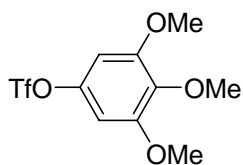
**General procedure for reductive cleavage of aryl mesylates or tosylate (Table 4).**

After two vacuum/Ar cycles to remove air from the reaction tube, the mixture of the aryl mesylate or tosylate (0.25 mmol), 10% Pd/C (10 wt % of the aryl mesylate or tosylate), magnesium metal (7.3 mg, 0.3 mmol) and ammonium acetate (0.25-7.5 mmol) in MeOH (1 mL) was stirred at ordinary pressure (balloon) and at temperature (*ca.* 20°C) for the appropriate time (see Table 4). The reaction mixture was filtrated using a membrane filter (Millipore, Millex<sup>®</sup>-LH, 0.45 µm) and the filtrate was partitioned between ether (10 mL) and water (10 mL). The aqueous layer was extracted with ether (10 mL × 3), and then combined organic layers were washed with brine (10 mL), dried with anhydrous MgSO<sub>4</sub>, filtered and concentrated under reduced pressure.

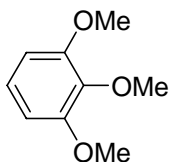
**General procedure for Table 5.** After two vacuum/Ar cycles to remove air from the reaction tube, the mixture of **1** (79.1 mg, 0.25 mmol), 10% Pd/C (8.0 mg, 10 wt % of **1**) and the magnesium metal (7.3 mg, 0.3 mmol) in deuterated methanol (1.0 mL) was stirred at ordinary pressure (balloon) and temperature (*ca.* 20°C) for 24 hours. The reaction mixture was filtrated using a membrane filter (Millipore, Millex<sup>®</sup>-LH, 0.45 µm) and the filtrate was partitioned between ether (10 mL) and water (10 mL). The aqueous layer was extracted with ether (10 mL × 3), and then combined organic layers were washed with brine (10 mL), dried with anhydrous MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The hydrogen source of the reaction was confirmed by <sup>1</sup>H NMR of the crude mixture in CDCl<sub>3</sub>.

**Preparation of 3,4,5- trimethoxyphenyl triflate<sup>1</sup>**

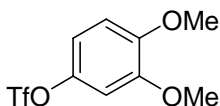
3,4,5-Trimethoxyphenol (**1**) (921 mg, 5.0 mmol) was dissolved in toluene(10 mL) and 30% K<sub>3</sub>PO<sub>4</sub> solution (10 mL) was added. The reaction mixture was cooled to 0 °C and triflic anhydride (1.0 mL, 6.0 mmol) was added slowly dropwise with stirring to maintain a reaction temperature of <10 °C. The reaction mixture was allowed to warm to room temperature and stirred for a further 30 minutes, then extracted with ethylacetate (10 mL × 2). The combined organic layers were washed with water (30 mL), dried over MgSO<sub>4</sub> and evaporated to give **1** (1.54 g, 97%) as a white solid.



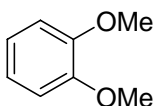
**3,4,5-trimethoxyphenyl triflate**<sup>2</sup> (Table 1, 2, 5 and Table 3 entry 2)



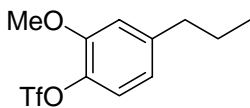
**1,2,3-trimethoxybenzene** (Table 1, 2, 5 and Table 3 entry 2, commercially available)



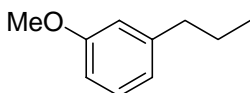
**3,4-dimethoxyphenyl triflate** (Table 3 entry 1) Colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 6.85 (d, *J*=2.4 Hz, 2H), 6.78 (d, *J*=2.2 Hz, 1H), 3.90 (s, 3H), 3.89 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 149.8, 148.9, 142.9, 120.4, 117.2, 112.9, 111.1, 105.4, 56.2. MS (EI) *m/z* 286 (M<sup>+</sup>, 28%), 153 (100), 125 (30). HRMS (EI) Calcd for C<sub>9</sub>H<sub>9</sub>O<sub>5</sub>F<sub>3</sub>S (M<sup>+</sup>) 286.0123. Found 286.0116.



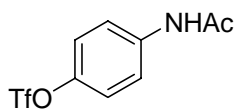
**1,2-dimethoxybenzene** (Table 3 entry 1, commercially available)



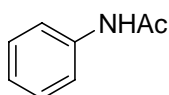
**2-methoxy-4-propylphenyl triflate**<sup>3</sup> (Table 3 entry 3)



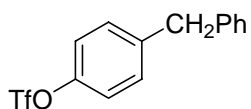
**1-methoxy-3-propylbenzene**<sup>3</sup> (Table 3 entry 3)



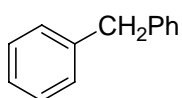
**4-acetamidophenyl triflate**<sup>4</sup> (Table 3 entry 4)



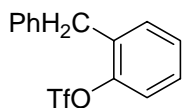
**N-phenylacetamide** (Table 3 entry 4, commercially available)



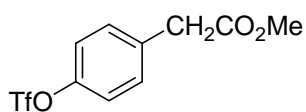
**4-benzylphenyl triflate**<sup>5</sup> (Table 3 entry 5)



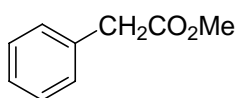
**diphenylmethane** (Table 3 entry 5, 6, Table 3 entries 7, 10, commercially available)



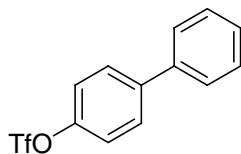
**2-benzylphenyl triflate**<sup>6</sup> (Table 3 entry 6)



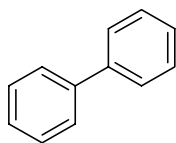
**4-[(methoxycarbonyl)methyl]phenyl triflate**<sup>8</sup> (Table 3 entry 7)



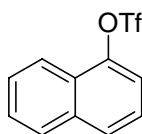
**methyl 2-phenylacetate** (Table 3 entry 7, Table 3 entries 3,4,5 commercially available)



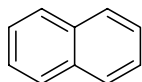
**4-phenylphenyl triflate** (Table 3 entry 8) White solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.64 (d,  $J=8.7$  Hz, 2H), 7.55 (d,  $J=7.2$  Hz, 2H), 7.46 (t,  $J=7.2$  Hz, 2H), 7.39 (t,  $J=7.2$  Hz, 1H), 7.34 (d,  $J=8.7$  Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  148.9, 141.7, 139.3, 129.0, 128.9, 128.1, 127.2, 121.6. MS (EI)  $m/z$  302 ( $\text{M}^+$ , 40%), 169 (100), 141 (46), 115 (28). HRMS (EI) Calcd for  $\text{C}_{13}\text{H}_9\text{O}_3\text{F}_3\text{S}$  ( $\text{M}^+$ ) 302.0225. Found 302.0213. Anal. Calcd for  $\text{C}_{13}\text{H}_9\text{O}_3\text{F}_3\text{S}$ : C, 51.66; H, 3.00. Found C, 51.44; H, 3.15.



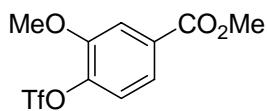
**biphenyl** (Table 3 entry 8, Table 3 entry 6, commercially available)



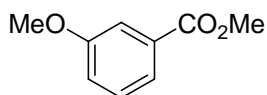
**naphthalene 5-yl triflate** (Table 3 entry 9, commercially available)



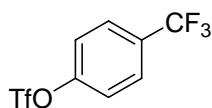
**naphthalene** (Table 3 entry 9, Table 3 entry 11, commercially available)



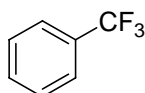
**4-(methoxycarbonyl)-2-methoxyphenyl triflate**<sup>9</sup> (Table 3 entry 10)



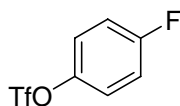
**methyl 3-methoxybenzoate** (Table 3 entry 10, commercially available)



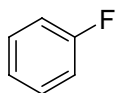
**4-(trifluoromethyl)phenyl triflate**<sup>10</sup> (Table 3 entry 11)



**trifluoromethylbenzene** (Table 3 entry 11, commercially available)

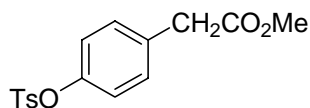


**4-fluorophenyl triflate** (Table 3 entry12) Colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.24 (td, *J*=5.0, 2.6 Hz, 2H), 7.12 (td, *J*=7.2, 2.1 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 123.2, 123.1, 123.1, 117.3, 117.2, 117.0, 117.0. MS (EI) *m/z* 244 (*M*<sup>+</sup>, 45%), 111 (100), 83 (78). HRMS (EI) Calcd for C<sub>7</sub>H<sub>4</sub>O<sub>3</sub>F<sub>4</sub>S (*M*<sup>+</sup>) 243.9817. Found 243.9812.



**fluorene** (Table 3 entry12, commercially available)

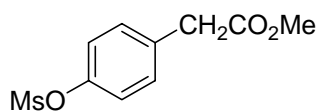
**Procedure for the preparation of 4-[(methoxycarbonyl)methyl]phenyl tosylate.** The mixture of methyl 2-(4-hydroxyphenyl) acetate (3.32 g, 20 mmol), *p*-toluenesulfonyl chloride (4.19 g, 22 mmol) and triethylamine (3.07 mL, 22mmol) in dry dichloromethane (50 mL) was stirred at room temperature for 10 hours. After evaporation of dichloromethane, the residue was partitioned between ethyl acetate (30 mL) and water (30 mL). The organic layer was washed with water (30 mL), sat. NaHCO<sub>3</sub> soln (30 mL), water (30 mL), dil. NaHSO<sub>4</sub> soln (30 mL), water (30 mL) and brine (30 mL) and dried over MgSO<sub>4</sub>. After filtration, the solvent was removed *in vacuo* and the oily residue was chromatographed on silica gel (ethyl acetate : hexane = 1 : 10 ~ 1 : 5) to give the pure product (5.77 g, 90%) as a clear oil.



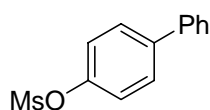
**4-[(methoxycarbonylmethyl)phenyl] phenyl tosylate** (Table 3 entries 1,2) Yellow oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.71 (d,  $J=8.3$  Hz, 2H), 7.31 (d,  $J=8.0$  Hz, 2H), 7.20 (d,  $J=8.8$ , 2H), 6.94 (d,  $J=8.5$ , 2H), 3.69 (s, 3H), 3.58 (s, 2H), 2.45 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  171.5, 148.7, 145.3, 132.9, 130.5, 129.7, 128.5, 122.4, 52.1, 40.4, 21.7. MS (EI)  $m/z$  320 ( $\text{M}^+$ , 90%), 155 (100), 91 (83). HRMS (EI) Calcd for  $\text{C}_{16}\text{H}_{16}\text{O}_5\text{S}$  ( $\text{M}^+$ ) 320.0718. Found 320.0724.

**Typical procedure for the preparation of 4-[(methoxycarbonylmethyl)phenyl] mesylate.**

Methyl 2-(4-hydroxyphenyl) acetate (1.66 g, 10 mmol) and triethylamine (1.67 mL, 12 mmol) were dissolved in dry dichloromethane (20 mL). The reaction mixture cooled to 0 °C and methanesulfonyl chloride (0.93 mL, 12 mmol) was added slowly dropwise with stirring to maintain a reaction temperature of <10 °C. The reaction mixture was allowed to warm to room temperature and stirred for a further 1 hour, then the reaction mixture was concentrated *in vacuo*. The residue was partitioned between ethyl acetate (20 mL) and water (20 mL). The organic layer was washed with aqueous saturated sodium hydrogen carbonate (10 mL), 10% aqueous sodium hydrogen sulfate (10 mL) and brine (20 mL), dried with anhydrous  $\text{MgSO}_4$ , filtered and concentrated under reduced pressure to give the corresponding mesylate (2.29 g, 94%) as a white solid.

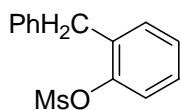


**4-[(methoxycarbonylmethyl)phenyl] mesylate** (Table 3 entries 3, 4, 5) White solid. mp 73-74°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.32 (d,  $J=8.6$  Hz, 2H), 7.23 (d,  $J=8.6$  Hz, 2H), 3.69 (s, 3H), 3.62 (s, 2H), 3.12 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  171.4, 148.33, 133.4, 131.0, 122.1, 52.2, 40.4, 37.3. MS (EI)  $m/z$  244 ( $\text{M}^+$ , 85%), 185 (75), 166 (42), 107 (100), 78 (34), 44 (30). HRMS (EI) Calcd for  $\text{C}_{10}\text{H}_{12}\text{O}_5\text{S}$  ( $\text{M}^+$ ) 244.0405. Found 244.0396. Anal. Calcd for  $\text{C}_{10}\text{H}_{12}\text{O}_5\text{S}$ : C, 49.17; H, 4.95. Found C, 49.08; H, 4.99.

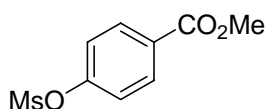


**4-phenylphenyl mesylate** (Table 3 entry 6, commercially available)

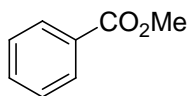




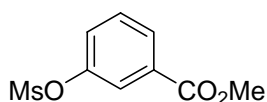
**2-benzylphenyl mesylate** (Table 3 entry 7) White solid. mp 56-58°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.39 (d,  $J=7.8$  Hz, 1H), 7.31-7.18 (m, 8H), 4.08 (s, 2H), 2.97 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  147.6, 139.5, 133.8, 131.6, 128.9, 128.5, 127.8, 127.2, 126.3, 121.7, 37.7, 36.2. MS (EI)  $m/z$  262 ( $\text{M}^+$ , 52%), 183 (100), 181 (85), 165 (50). HRMS (EI) Calcd for  $\text{C}_{14}\text{H}_{14}\text{O}_3\text{S}$  ( $\text{M}^+$ ) 262.0664. Found 262.0670. Anal. Calcd for  $\text{C}_{14}\text{H}_{14}\text{O}_3\text{S}$ : C, 64.10; H, 5.38. Found C, 64.00; H, 5.49.



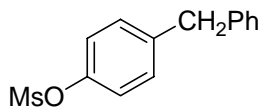
**4-(methoxycarbonyl) phenyl mesylate**<sup>11</sup> (Table 3 entry 8)



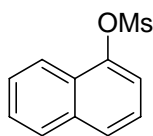
**methylbenzoate** (Table 3 entries 8, 9, commercially available)



**2-(methoxycarbonyl) phenyl mesylate**<sup>11</sup> (Table 3 entry 9)



**4-benzylphenyl mesylate** (Table 3 entry 10) White solid  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.32-7.16 (m, 9H), 3.98 (s, 2H), 3.11 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  147.6, 140.6, 140.2, 130.3, 128.9, 128.6, 126.4, 121.9, 41.3, 37.3. MS (EI)  $m/z$  262 ( $\text{M}^+$ , 100%), 183 (80), 155 (67). HRMS (EI) Calcd for  $\text{C}_{14}\text{H}_{14}\text{O}_3\text{S}$  ( $\text{M}^+$ ) 262.0664. Found 262.0660. Anal. Calcd for  $\text{C}_{14}\text{H}_{14}\text{O}_3\text{S}$ : C, 64.10; H, 5.38. Found C, 64.10; H, 5.40.

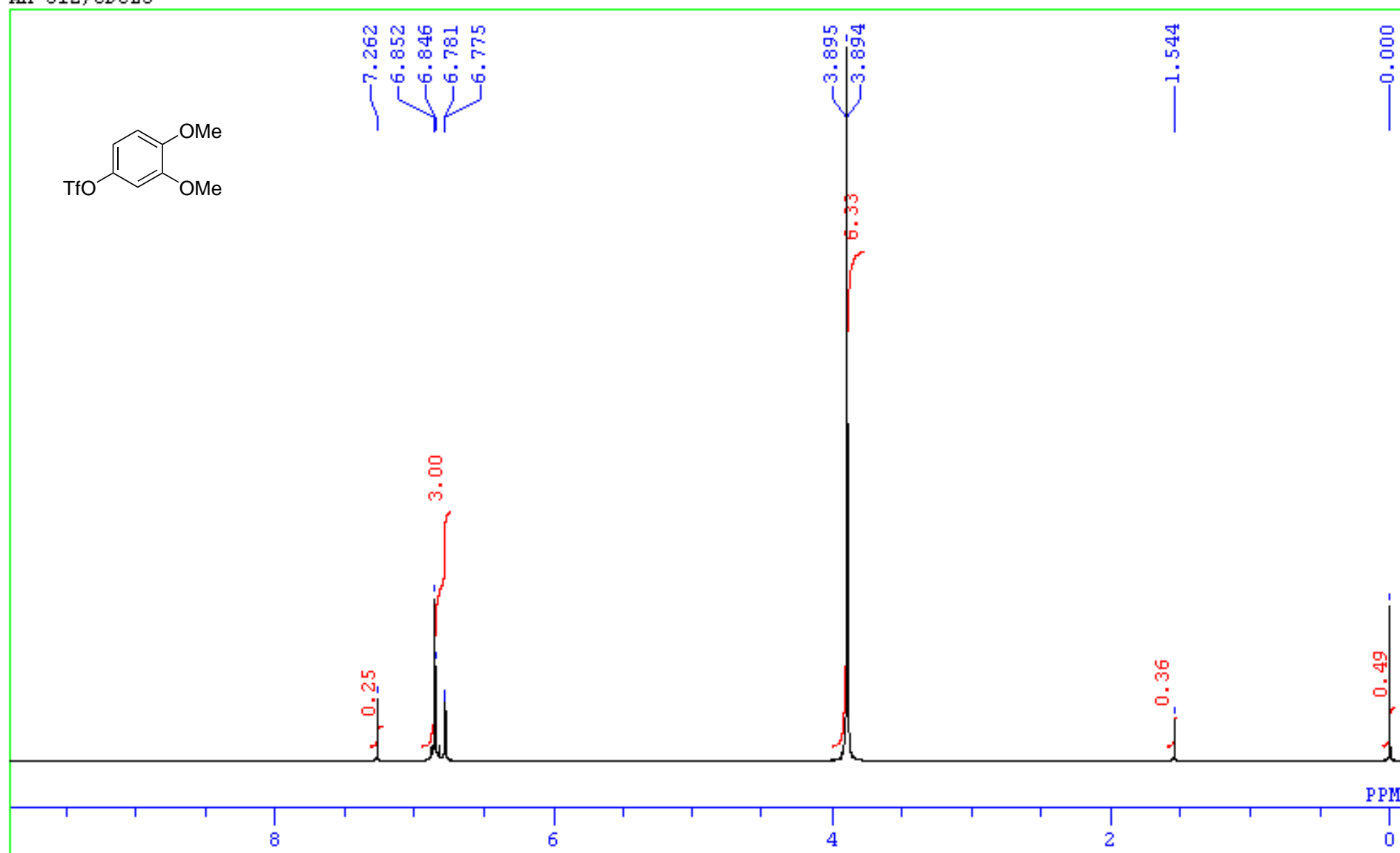


**naphthalene 5-yl mesylate** (Table 3 entry 11, commercially available)

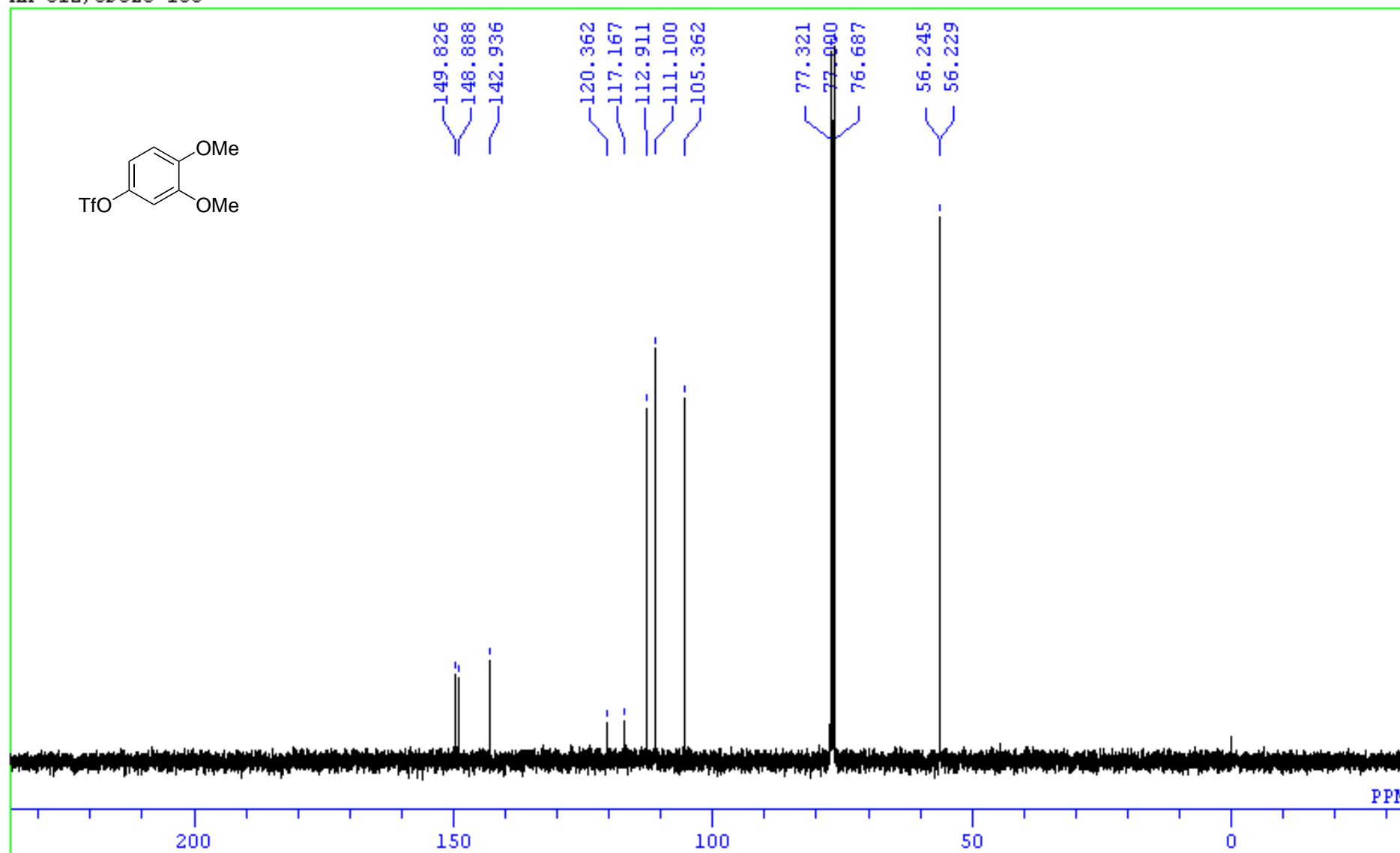
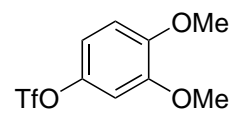
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AM-312/CDCL3



AM-312/CDCl<sub>3</sub>-13C



[ Mass Spectrum ]

Data : 8

Date : 04-Mar-03 15:56

Sample: AM-312-1

Note : M.Hosokawa

Inlet : Direct

Ion Mode : EI+

Spectrum Type : Regular [MF-Linear]

RT : 0.54 min

Scan# : 17

Temp : 0.0 deg.C

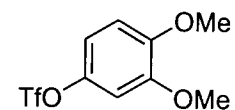
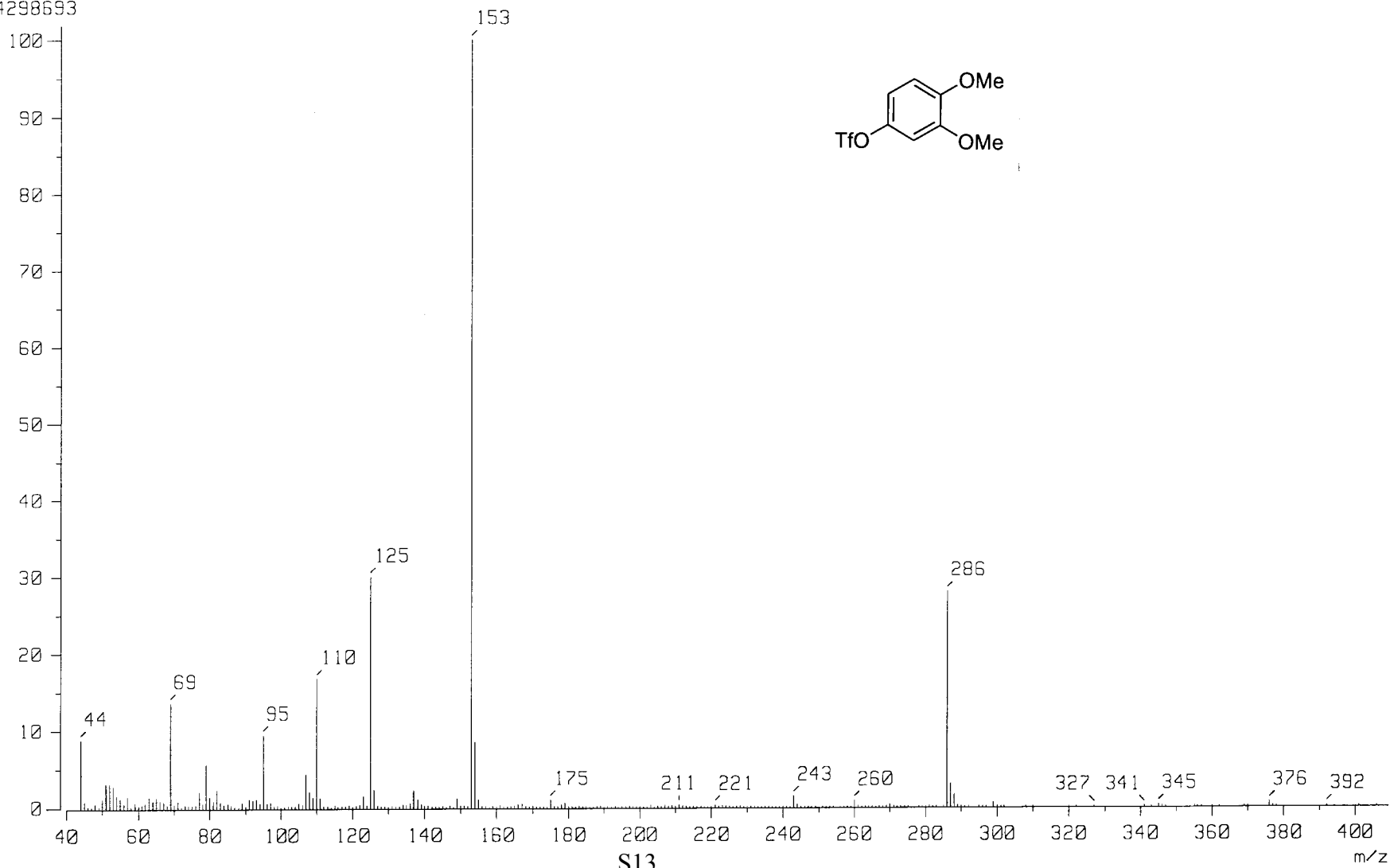
BP : m/z 153.0000

Int. : 1338.06

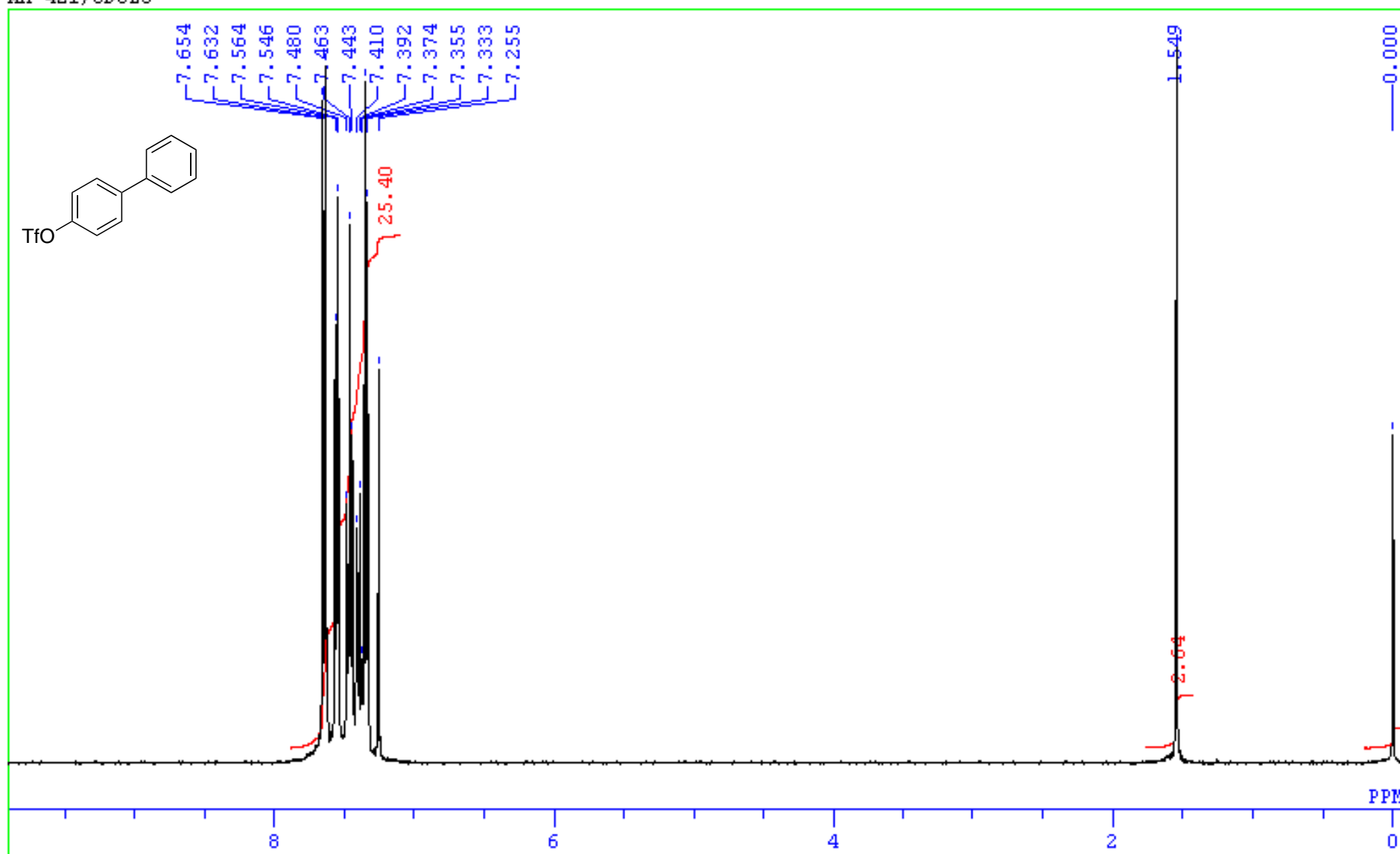
Output m/z range : 40.0000 to 409.2230

Cut Level : 0.00 %

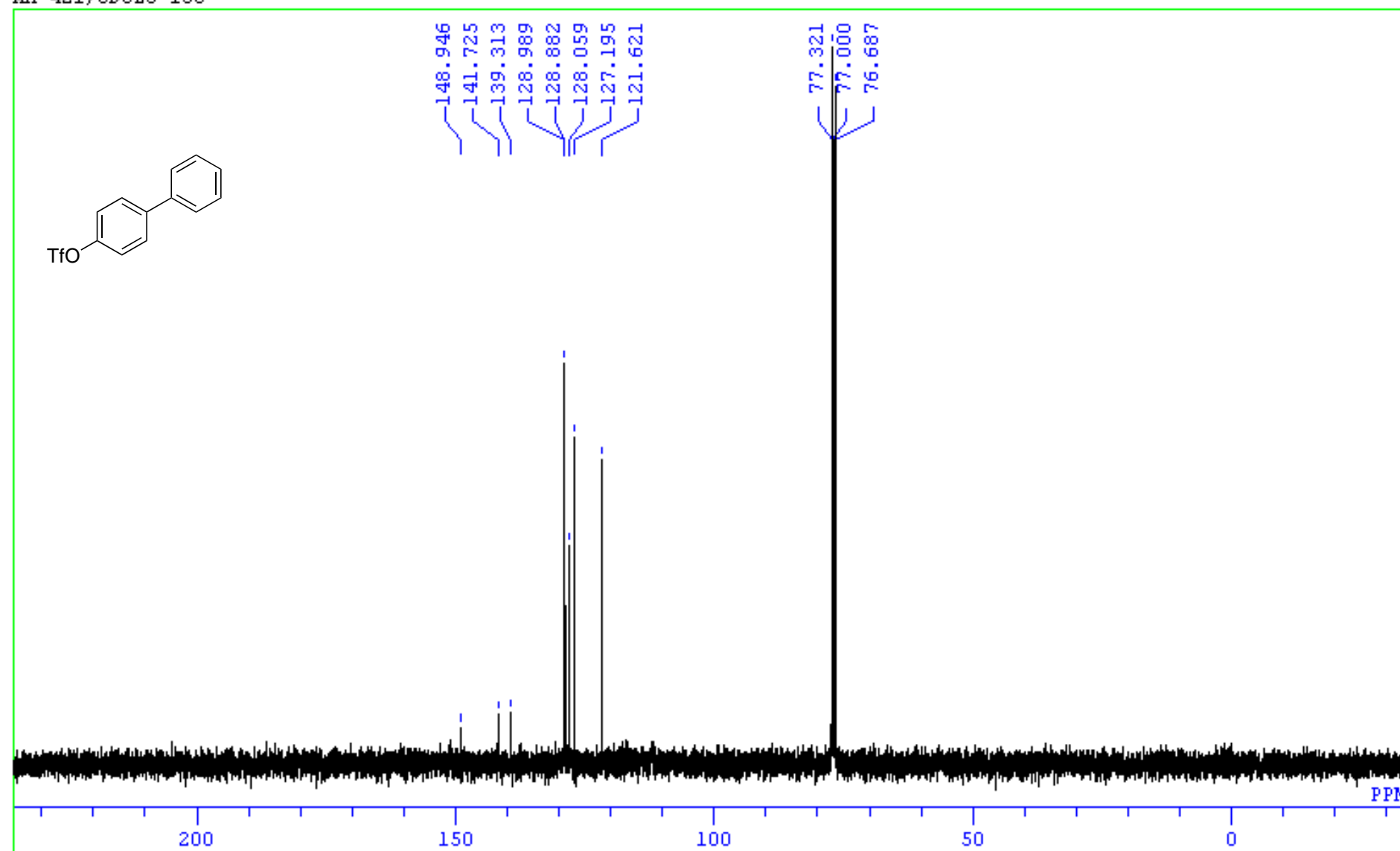
14298693



AM-421/CDCl<sub>3</sub>



AM-421/CDCL3-13C



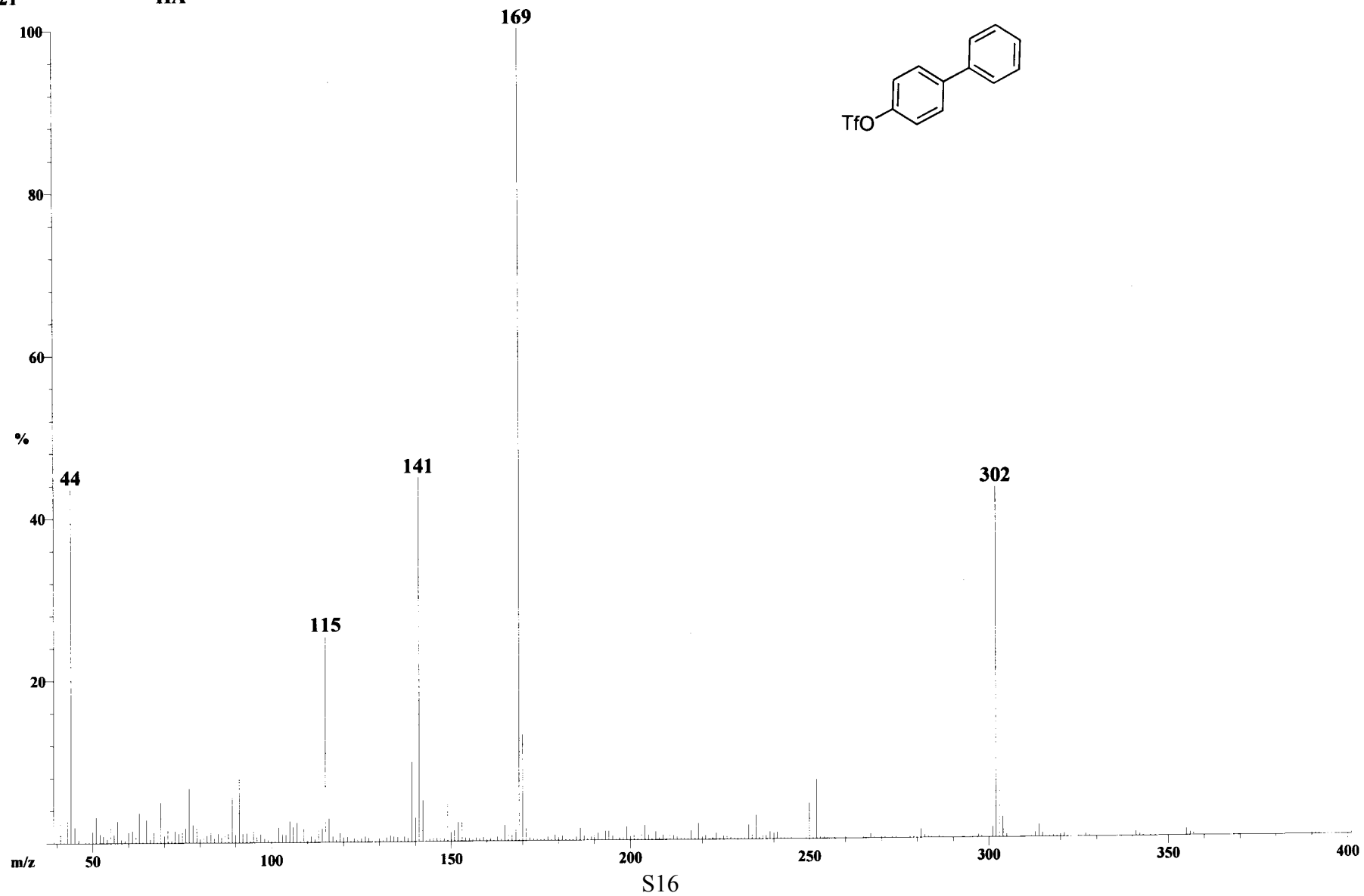
File: LR-05F039  
Instrument: SX102A

Date Run: 10-18-2005 (Time Run: 10:48:12)  
Ionization mode: EI+

Scan: 4  
Base: m/z 169; 88.2%FS TIC: 78441311  
AM-421 HA

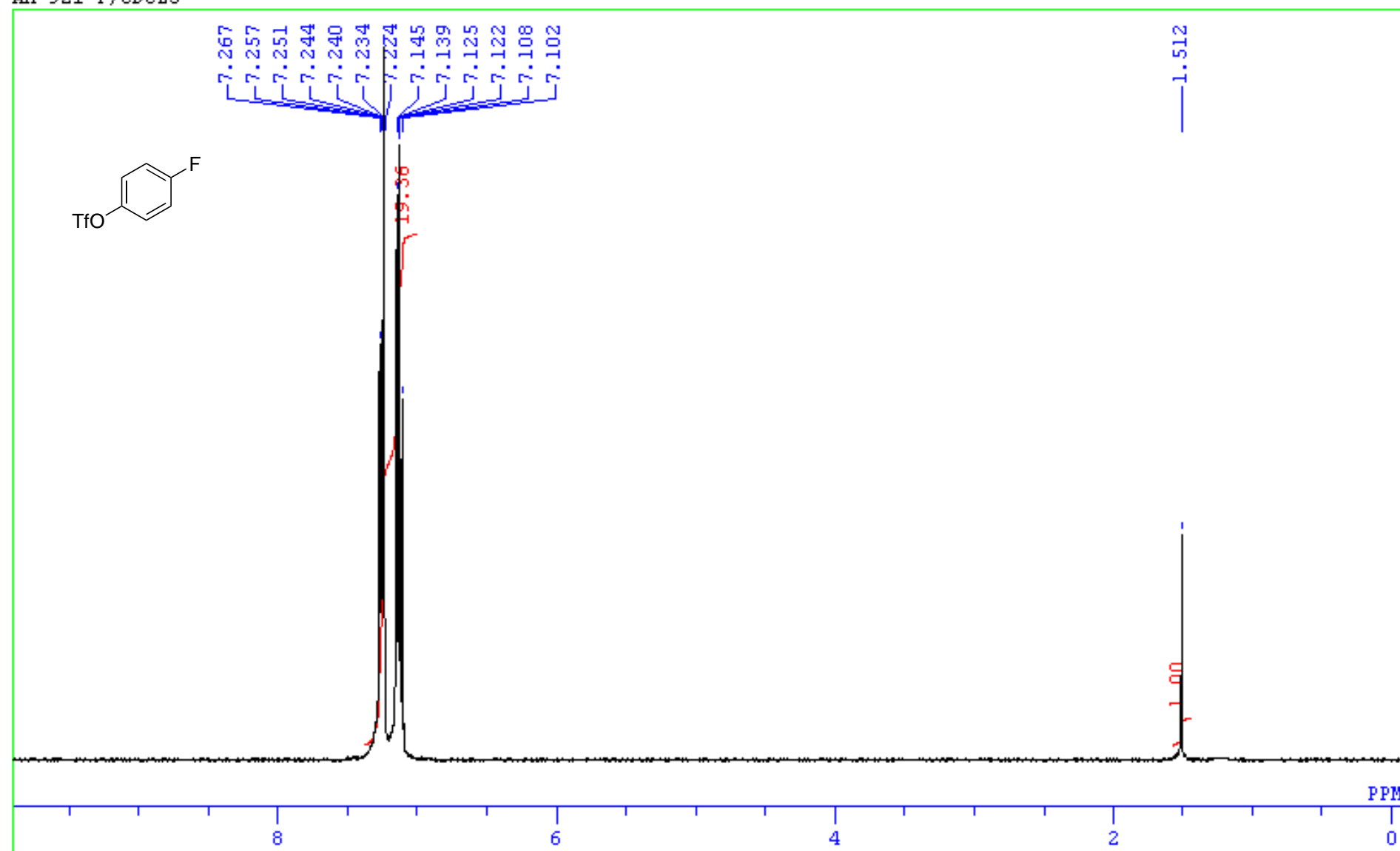
R.T.: .1

#Ions: 273

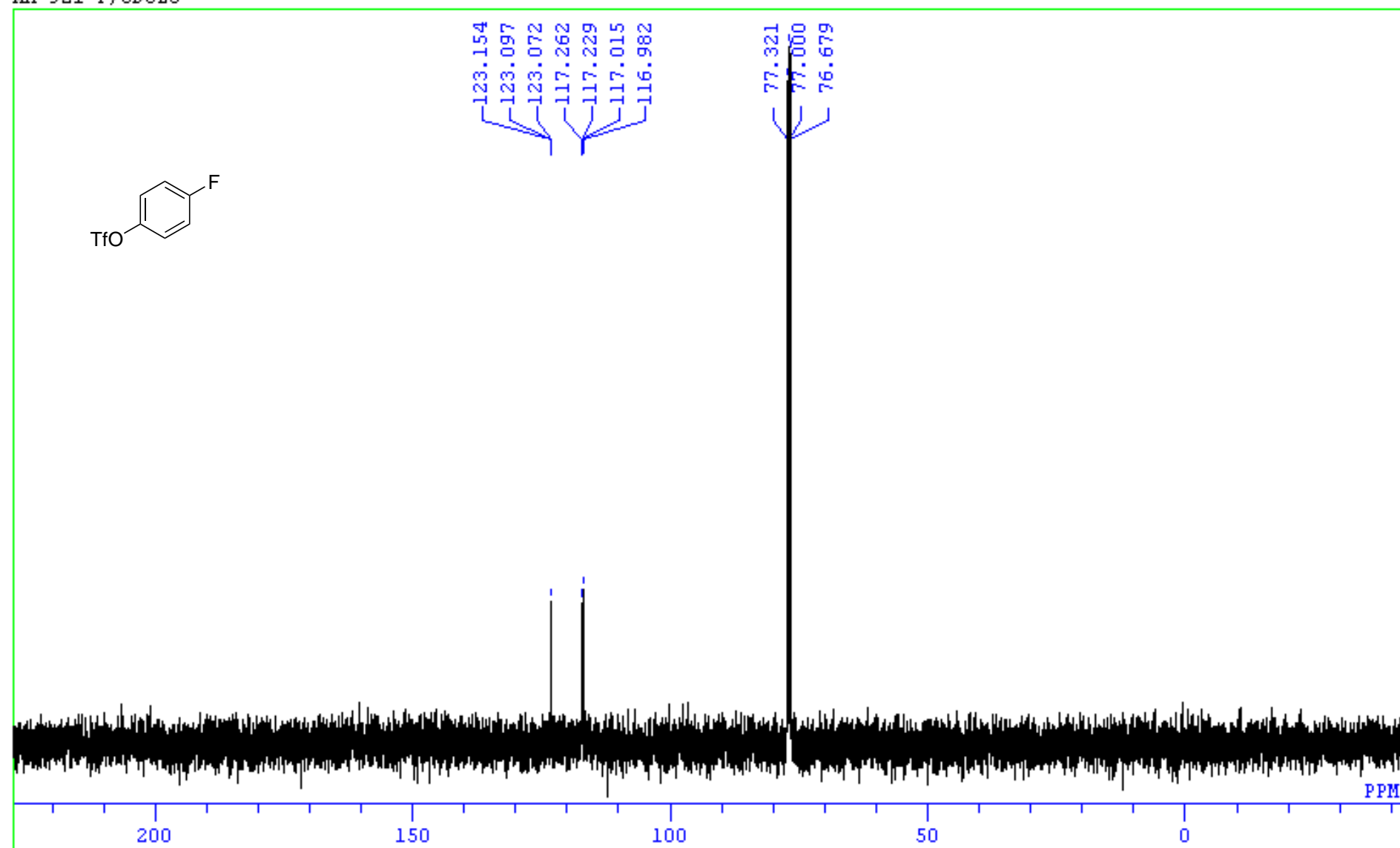




AM-921-P/CDCL<sub>3</sub>



AM-921-P/CDCL<sub>3</sub>



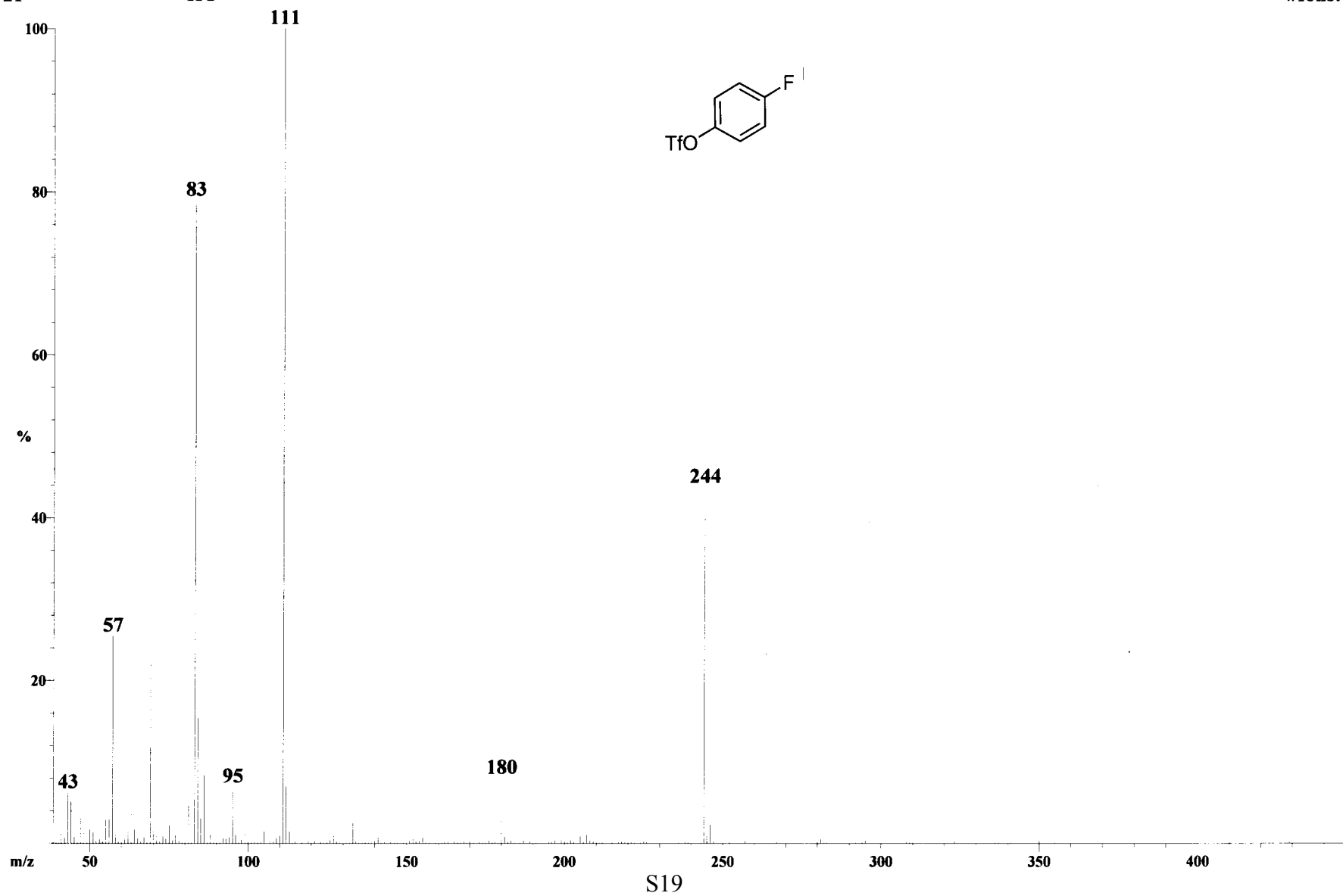
File: LR-OCT184  
Instrument: SX102A

Date Run: 10-14-2004 (Time Run: 08:57:17)  
Ionization mode: EI+

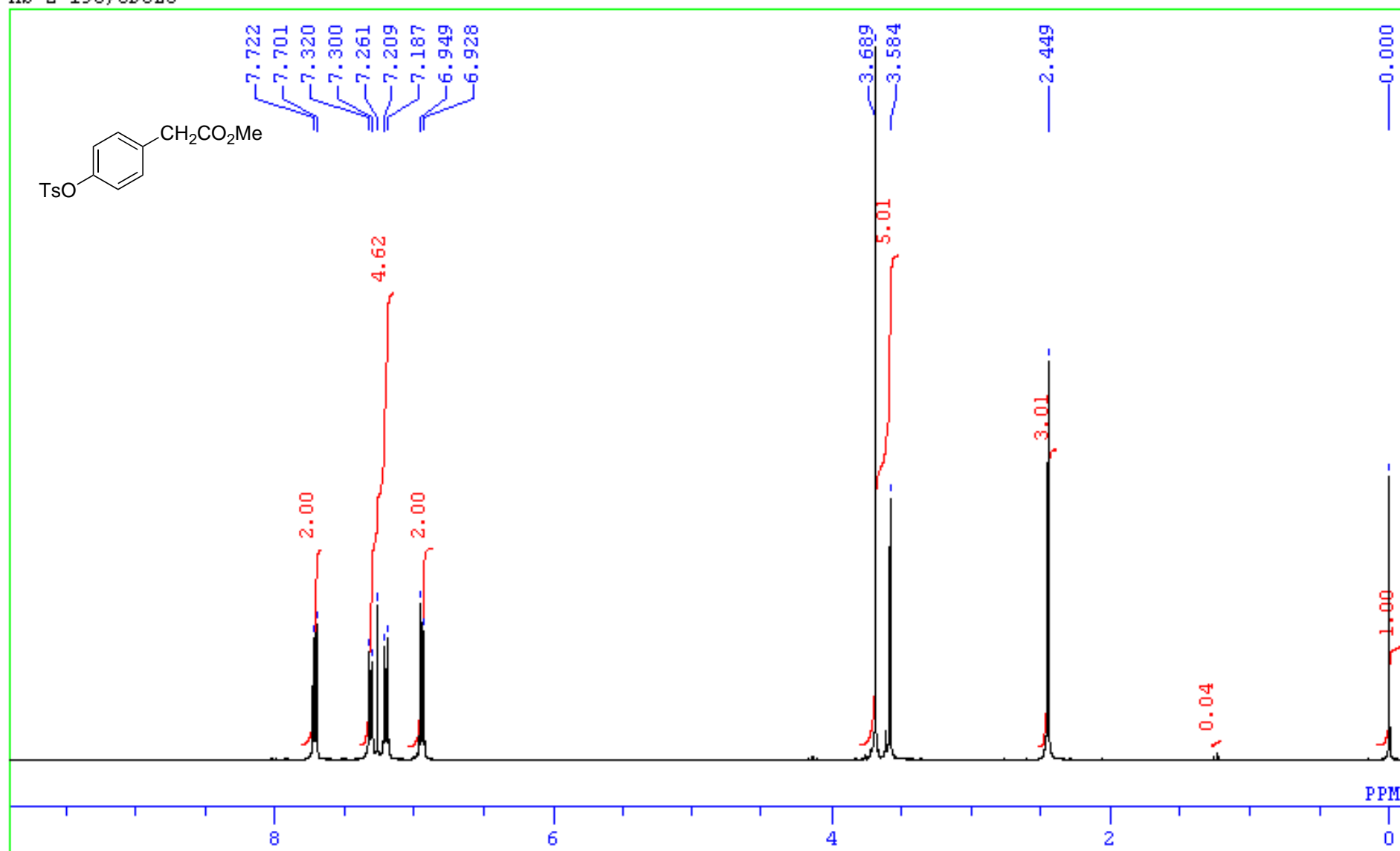
Scan: 20  
Base: m/z 111; 95.2%FS TIC: 72193592  
AM-921 HO

R.T.: .63

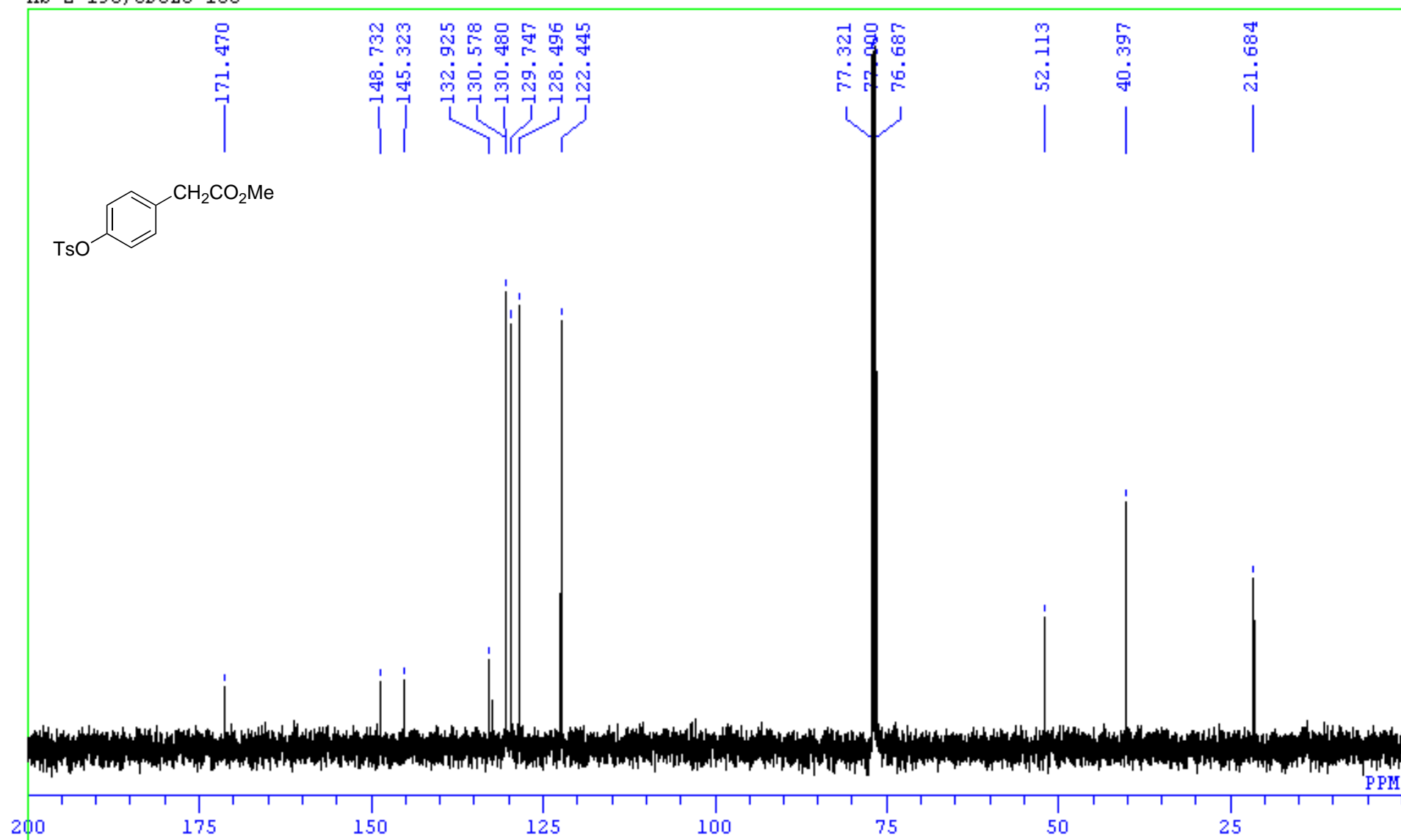
#Ions: 200



HS-2-190/CDCl<sub>3</sub>



HS-2-190/CDCL3-13C



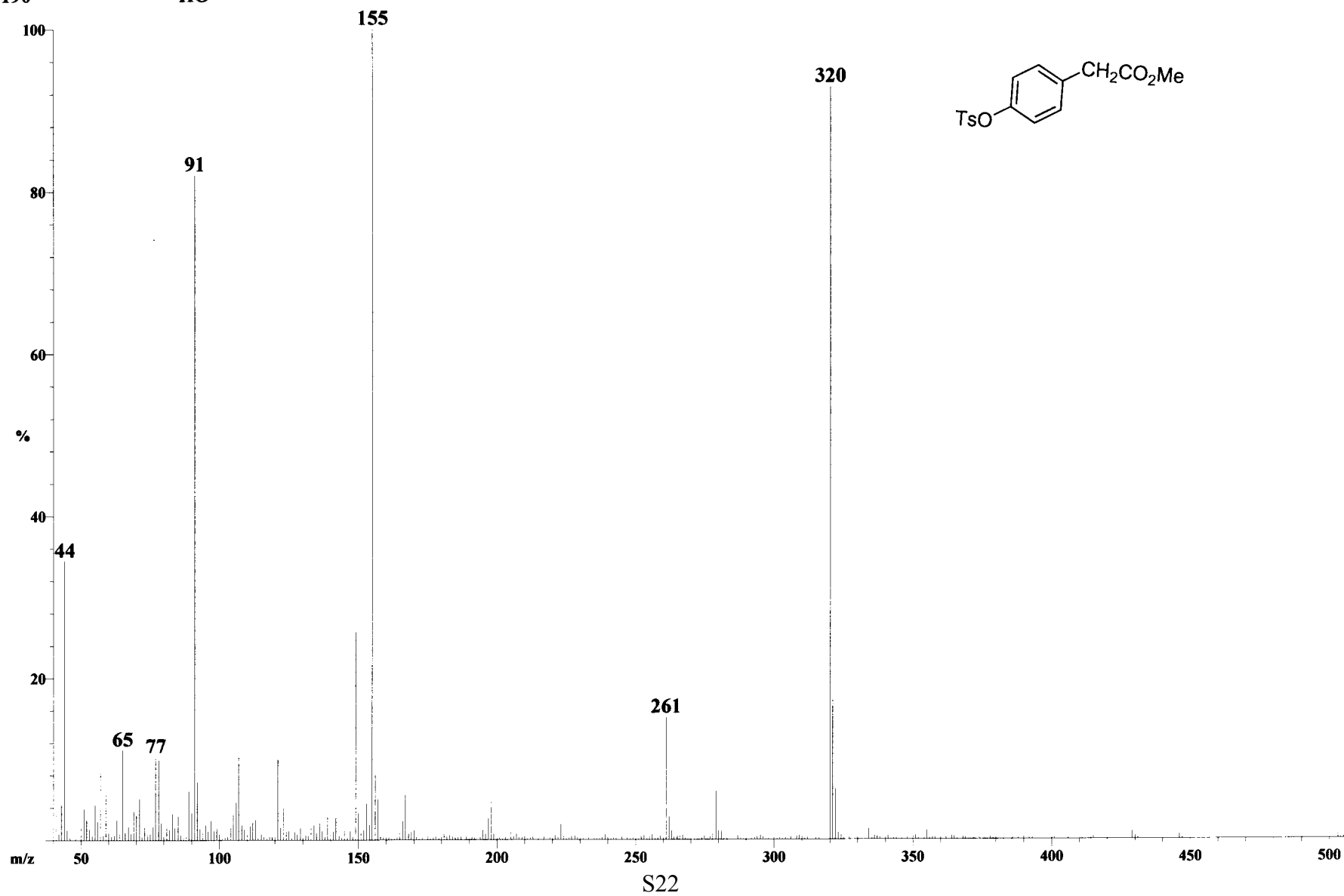
File: LR-05D670  
Instrument: SX102A

Date Run: 8-8-2005 (Time Run: 10:35:34)  
Ionization mode: EI+

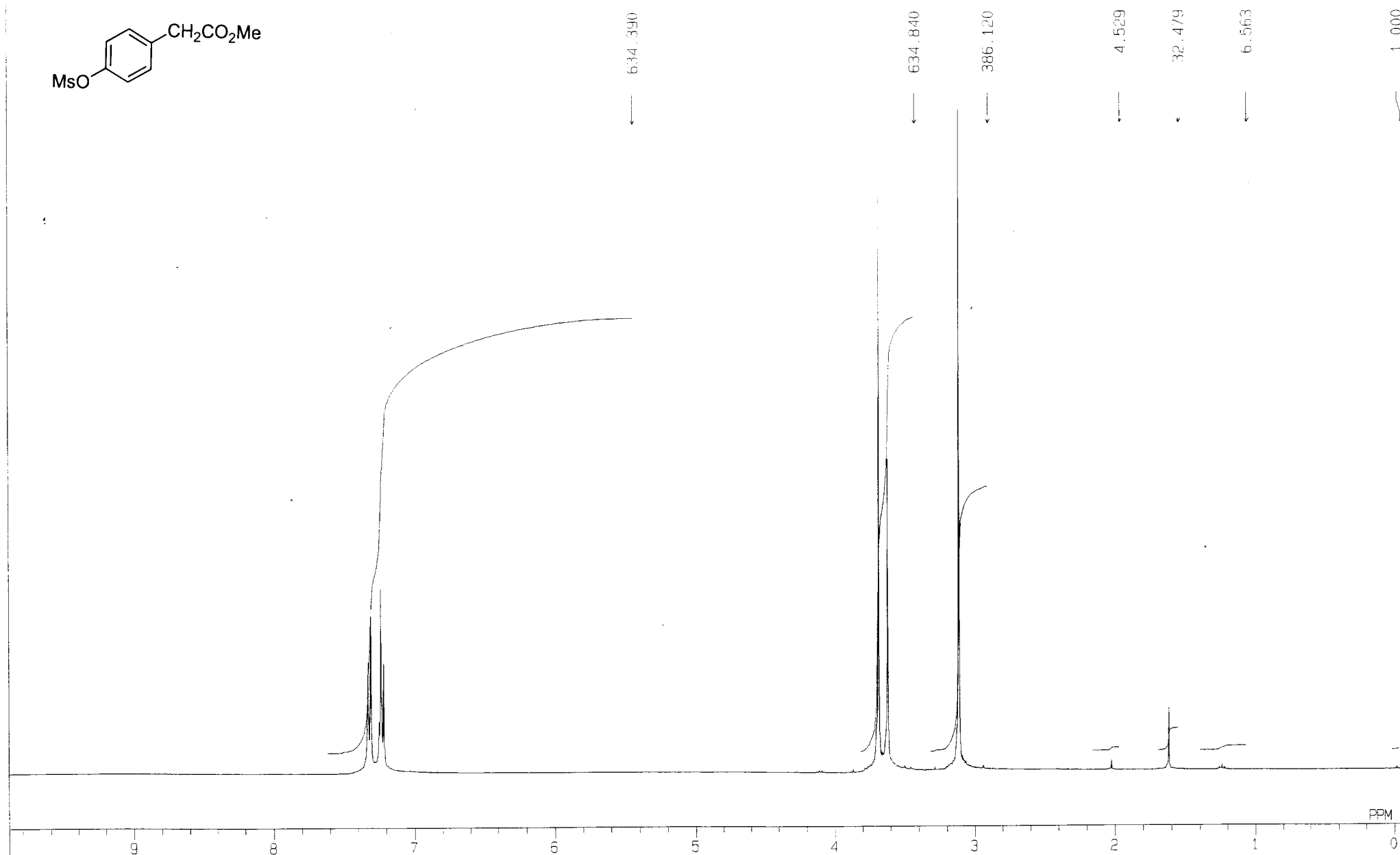
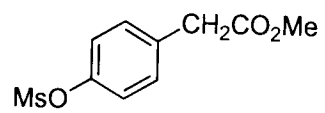
Scan: 45  
Base: m/z 155; 69.6%FS TIC: 84033236  
HS-2-190 HO

R.T.: 1.47

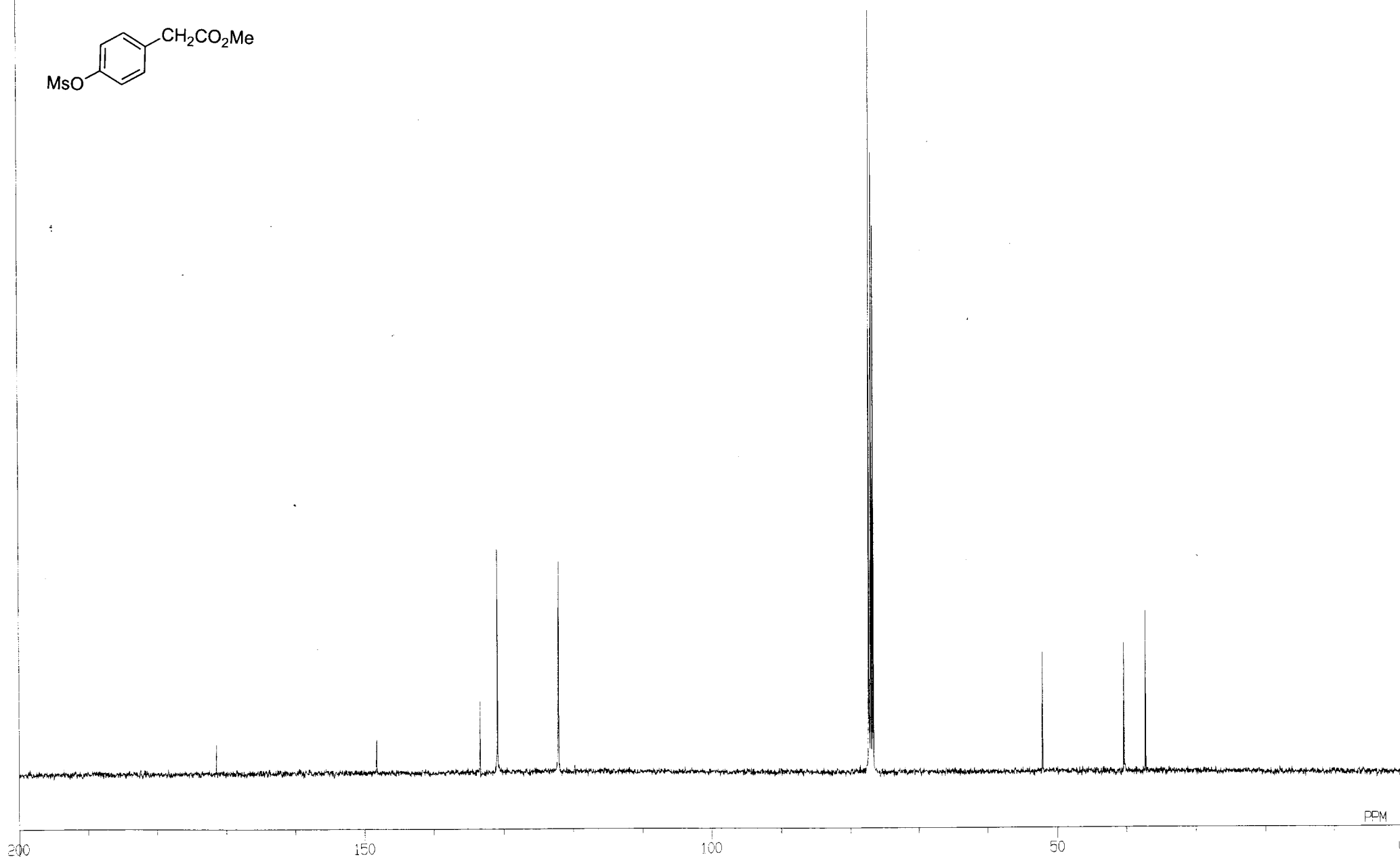
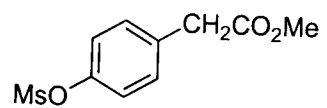
#Ions: 316



AM-29/CDCL<sub>3</sub>



AM-29/CDCL3





[ Mass Spectrum ]

Data : 8

Date : 25-Oct-.01 16:17

Sample: AM-29-2

Note : M.Hosokawa

Inlet : Direct

Ion Mode : EI+

Spectrum Type : Regular [MF-Linear]

RT : 0.67 min

Scan# : 21

Temp : 0.0 deg.C

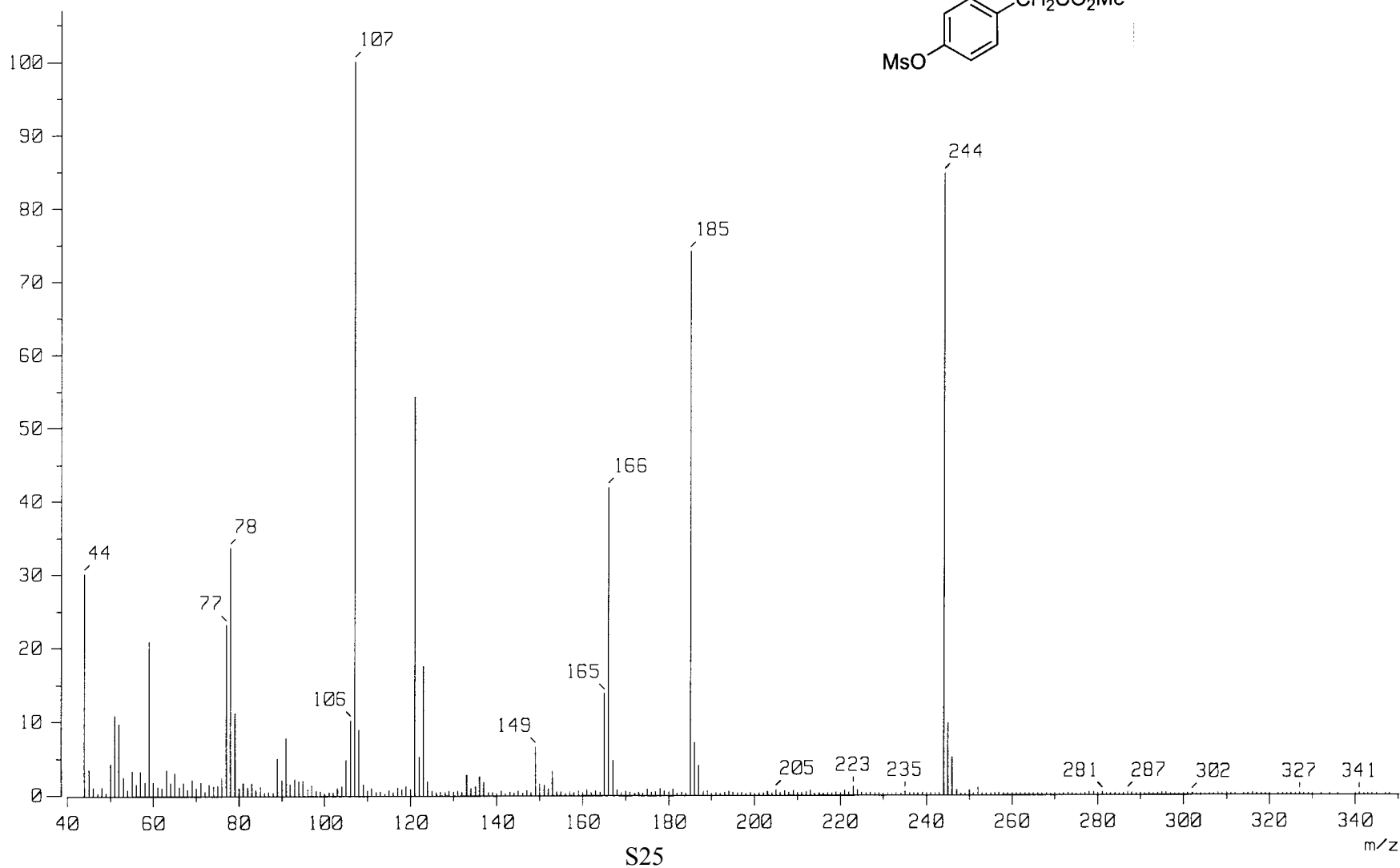
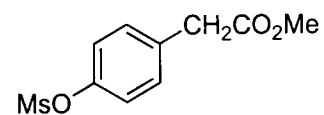
BP : m/z 107.0000

Int. : 1116.68

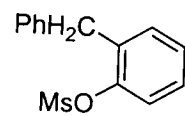
Output m/z range : 40.0000 to 350.1850

Cut Level : 0.00 %

12529570



AM-194P/CDCL3



209396.500

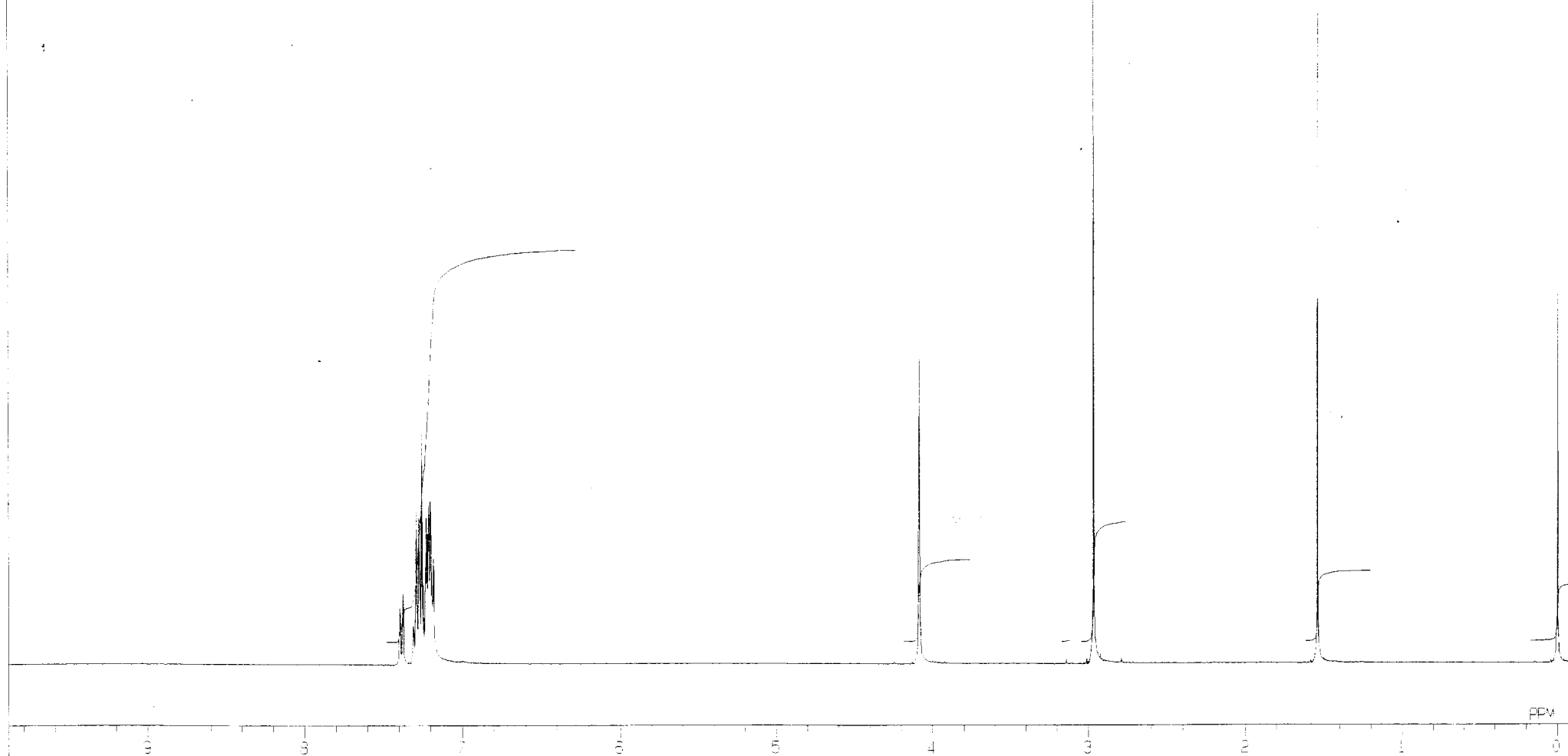
43507.290

251.830

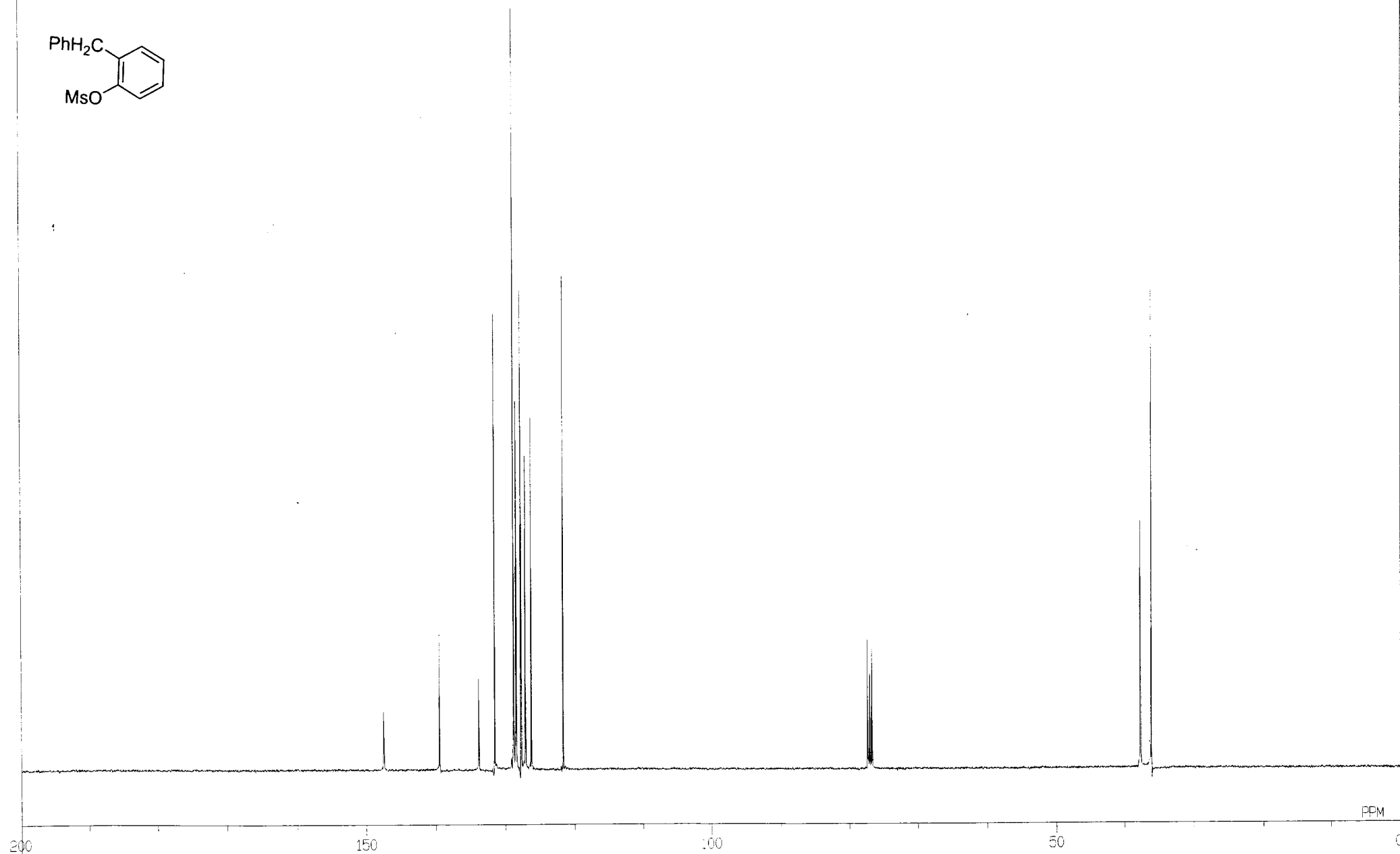
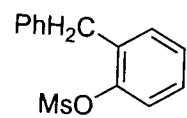
63433.030

37370.840

1.000



AM-194P/CDCL3



[ Mass Spectrum ]

Data : 3

Date : 10-Sep-02 09:47

Sample: AM-194

Note : M.Hosokawa

Inlet : Direct

Ion Mode : EI+

Spectrum Type : Regular [MF-Linear]

RT : 0.77 min

Scan# : 24

Temp : 0.0 deg.C

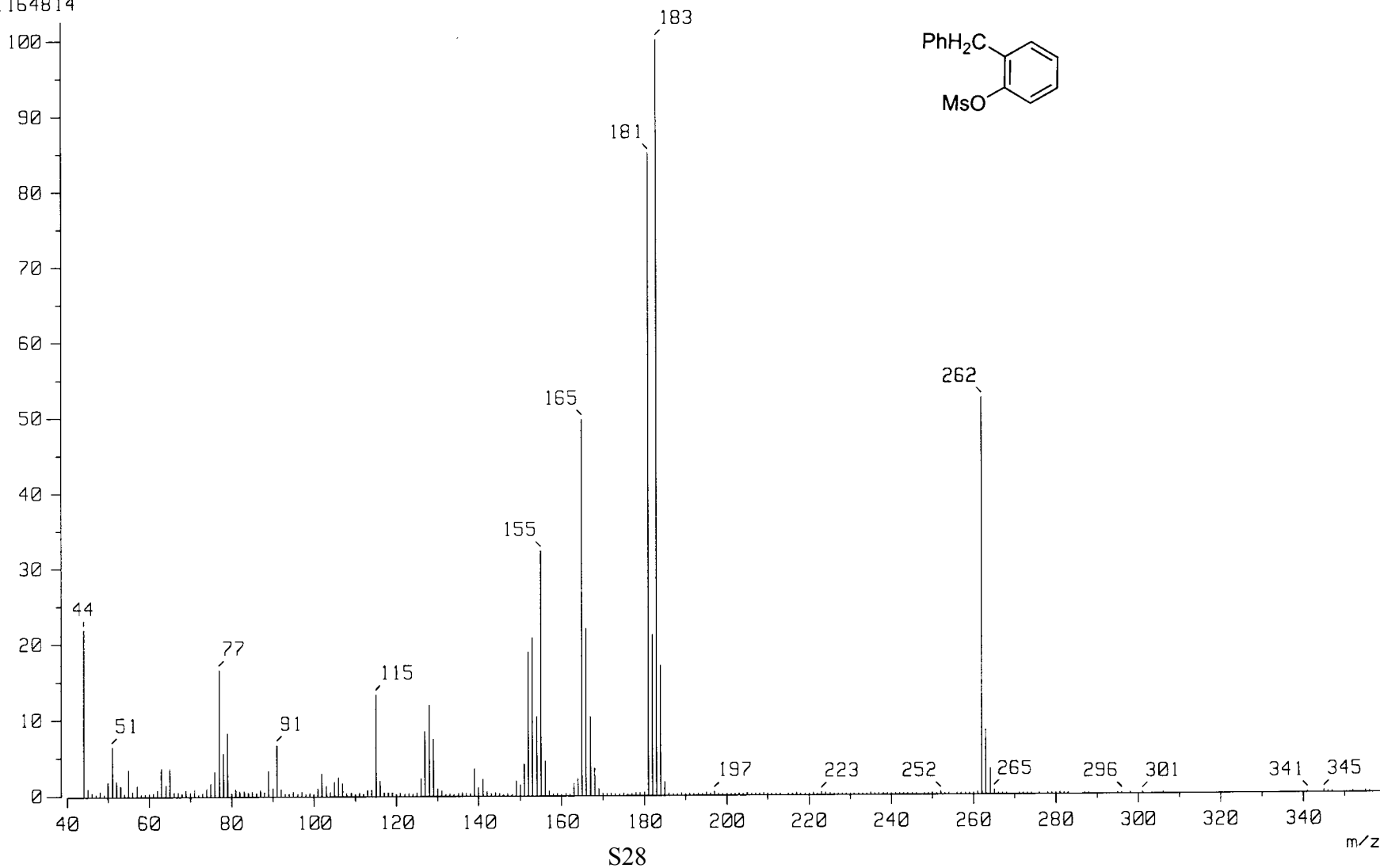
BP : m/z 183.0000

Int. : 1038.31

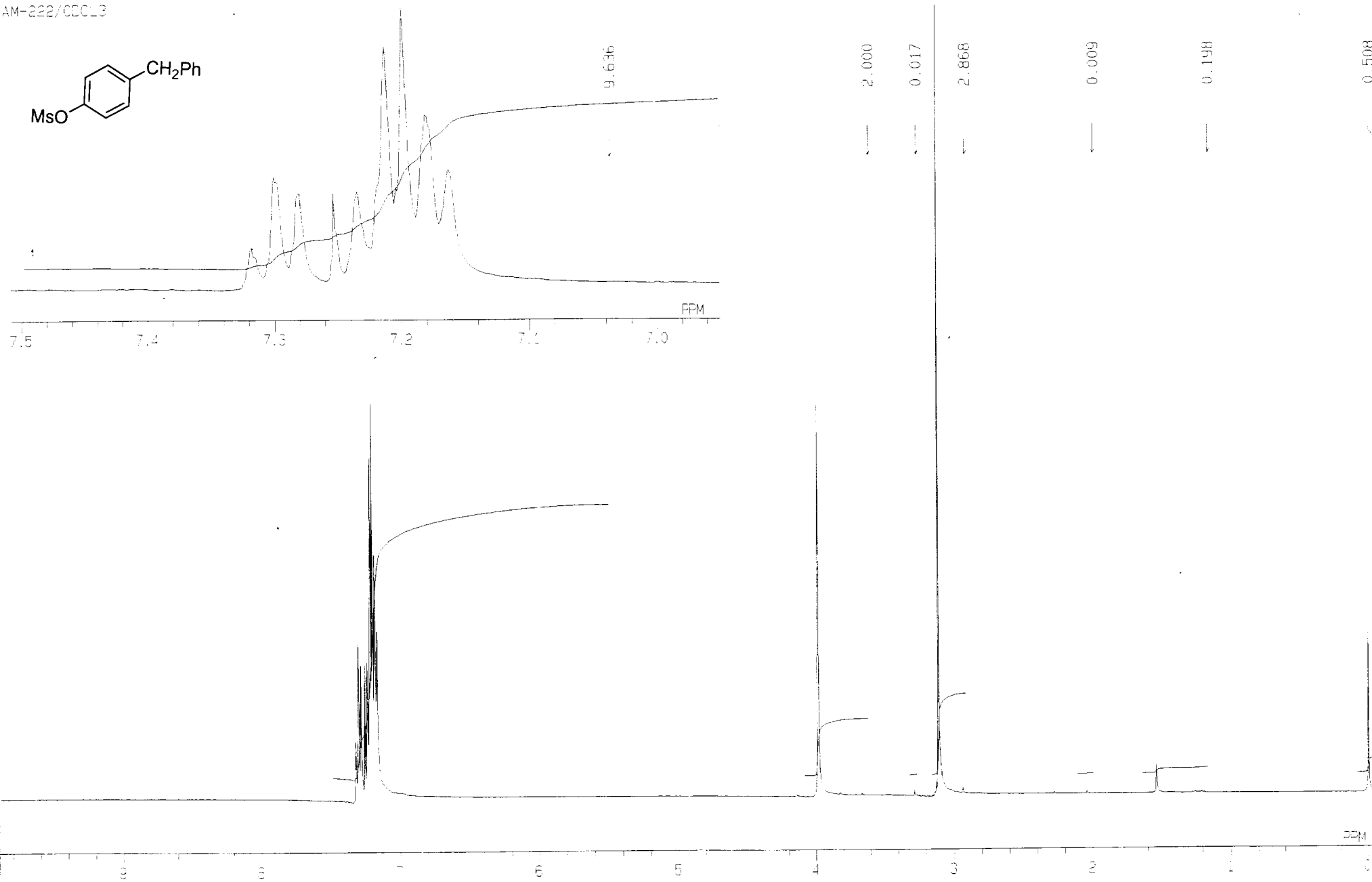
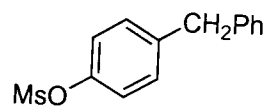
Output m/z range : 40.0000 to 358.6190

Cut Level : 0.00 %

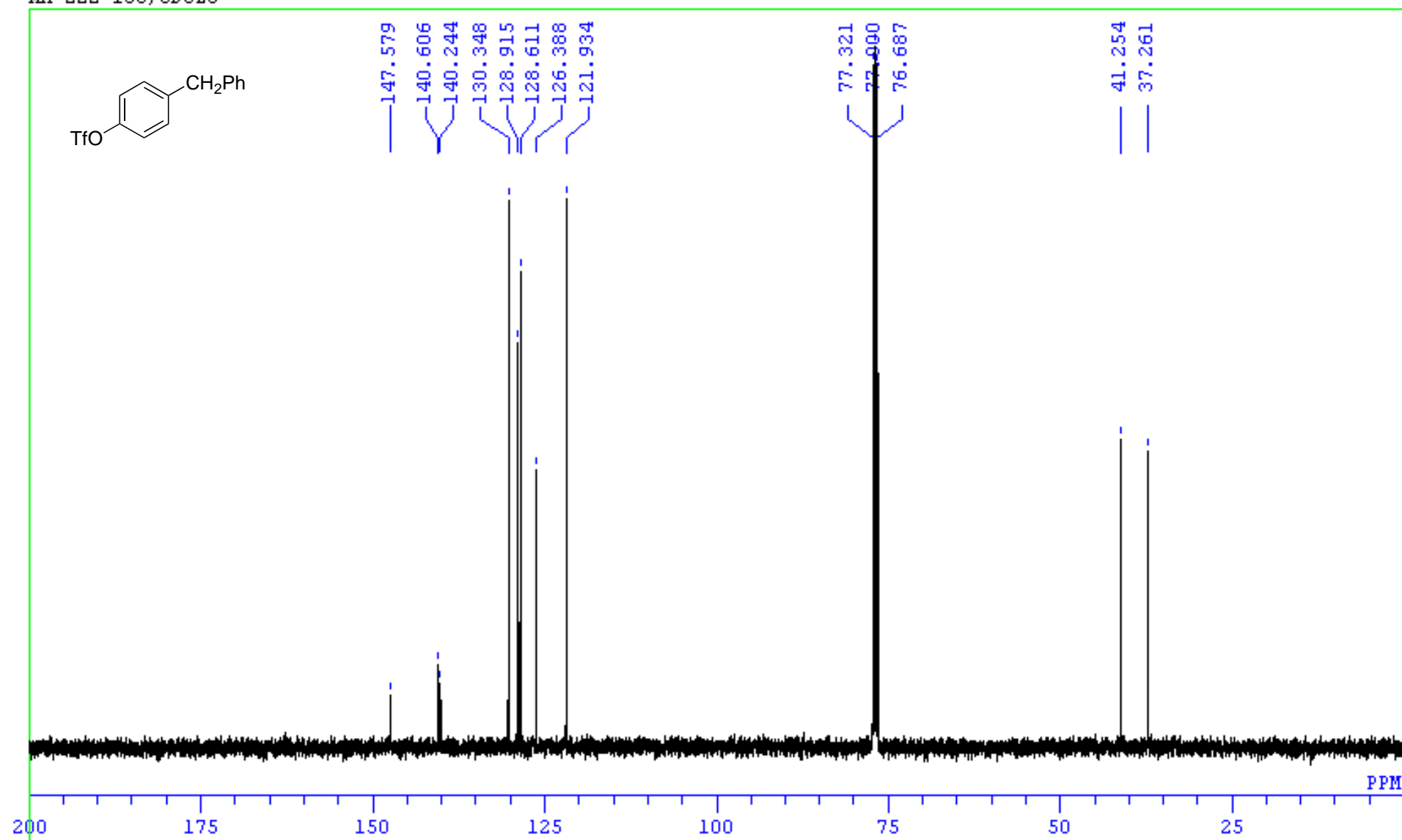
11164814



AM-222/CCCL3



AM-222-13C/CDCL3



[ Mass Spectrum ]

Data : 36

Date : 28-Oct- 02 17:33

Sample: AM-222

Note : M.Hayashi

Inlet : Direct

Ion Mode : EI+

Spectrum Type : Regular [MF-Linear]

RT : 0.07 min Scan# : 3

Temp : 0.0 deg.C

BP : m/z 262.0000 Int. : 1593.41

Output m/z range : 40.0000 to 300.5180

Cut Level : 0.00 %

17985150

