

SUPPORTING INFORMATION

Synthesis of New Fluorinated Tebufenpyrad Analogs with Acaricidal Activity through Regioselective Pyrazole Formation.

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General methods.

All reactions were carried out under nitrogen atmosphere. The solvents were purified prior to use: THF was distilled from sodium/benzophenone; CH₂Cl₂ was distilled from calcium hydride. The reactions were monitored with the aid of thin-layer chromatography (TLC) on 0.25-mm precoated silica gel plates. Visualization was carried out with UV light. Flash column chromatography was performed on silica gel 60 (particle size 0.040-0.063 mm) with the solvents indicated in each case. Melting points are uncorrected. Chemical shifts are given in ppm (δ), referenced to the residual proton resonances of the solvents or fluorotrichloromethane in ¹⁹F NMR experiments. Coupling constants (J) are given in Hertz (Hz). The letters m, s, d, t, and q stand for multiplet, singlet, doublet, triplet, and quartet respectively. The letters br indicate that the signal is broad.

3-(1-Fluoroethyl)-1-methyl-1H-pyrazole-5-carboxylic acid (17).

Pale yellow solid from *n*-hexane-ethyl acetate (77% yield); mp 136-8 °C. ¹H NMR (300 MHz, CDCl₃): δ 1.65 (dd, $J_1^{\text{HF}} = 24.0$ Hz, $J_2^{\text{HF}} = 6.5$, 3H; CH₃), 4.13 (s, 3H; CH₃), 5.65 (dq, $J_1^{\text{HF}} = 48.3$ Hz, $J_2^{\text{HF}} = 6.5$ Hz, 1H; CH), 6.94 (d, $J = 1.5$ Hz, 1H; CH) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ 20.8 (d, $^2J_{\text{CF}} = 24.7$ Hz), 39.7, 85.8 (d, $^1J_{\text{CF}} = 162.1$ Hz), 109.4 (d, $^3J_{\text{CF}} = 2.9$ Hz), 134.2 (d, $^4J_{\text{CF}} = 1.1$ Hz), 151.0 (d, $^2J_{\text{CF}} = 23.6$ Hz), 160.7 ppm. ¹⁹F NMR (CDCl₃, 282.4 MHz): δ -166.9 (dq, $J_1^{\text{FH}} = 48.3$ Hz, $J_2^{\text{FH}} = 24.0$ Hz, 1F; CF) ppm. HRMS: calcd for C₇H₉FN₂O₂ (M⁺) 172.0648; found 172.0616.

3-(2,2,2-Trifluoroethyl)-1-methyl-1H-pyrazole-5-carboxylic acid (19).

Pale yellow solid from *n*-hexane-ethyl acetate (60% yield); mp 133-5 °C. ¹H NMR (300 MHz, CDCl₃): δ 3.46 (q, $J_{\text{HF}} = 11.2$ Hz, 2H; CH₂), 3.98 (s, 3H; CH₃), 6.74 (s, 1H; CH) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ 32.6 (q, $^2J_{\text{CF}} = 30.8$ Hz), 38.7, 111.1, 125.8 (q, $^1J_{\text{CF}} = 275.1$ Hz), 133.8, 140.3, 159.9 ppm. ¹⁹F NMR (CDCl₃, 282.4 MHz): δ -69.1 (t, $J_{\text{FH}} = 11.2$ Hz, 3F; CF₃) ppm. HRMS: calcd for C₇H₇N₂O₂F₃ (M⁺) 208.0459; found 208.0454.

3-(2,2-Difluoroethyl)-1-methyl-1H-pyrazole-5-carboxylic acid (20).

Flash chromatography [*n*-hexane-EtOAc (8:1)] ($R_f = 0.40$) afforded **20** as a pale yellow solid (65% yield); mp 198-200 °C. ¹H NMR (300 MHz, CDCl₃): δ 3.22 (td, $J_1^{\text{HF}} = 17.7$ Hz, $J_2 = 4.5$, 2H; CH₂), 4.13 (s, 3H; CH₃), 6.23 (tt, $J_1^{\text{HF}} = 56.7$ Hz, $J_2 = 4.5$ Hz, 1H; CH), 6.85 (s, 1H; CH) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ 33.6 (t, $^2J_{\text{CF}} = 23.0$ Hz), 39.0, 111.3, 116.7 (t, $^1J_{\text{CF}} = 239.2$ Hz), 133.8, 142.9, 160.4 ppm. ¹⁹F NMR

(CDCl₃, 282.4 MHz): δ -126.9 (dt, $J_1^{\text{FH}} = 56.7$ Hz, $J_2^{\text{FH}} = 17.7$ Hz, 2F; CF₂) ppm. HRMS: calcd for C₇H₈N₂O₂F₂ (M⁺) 190.0517; found 190.0554.

3-(2-Fluoroethyl)-1-methyl-1H-pyrazole-5-carboxylic acid (21).

Pale yellow solid from *n*-hexane-ethyl acetate (75% yield); mp 172-4 °C. ¹H NMR (300 MHz, CDCl₃): δ 3.02 (dt, $J_1^{\text{HF}} = 23.7$ Hz, $J_2 = 6.4$ Hz, 2H; CH₂), 4.11 (s, 3H; CH₃), 4.72 (dt, $J_1^{\text{HF}} = 47.1$ Hz, $J_2 = 6.4$ Hz, 2H; CH₂), 6.80 (s, 1H) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ 30.0, 38.9, 82.9 (d, $^1J_{\text{CF}} = 166.4$ Hz), 110.5, 133.4, 147.0 (d, $^3J_{\text{CF}} = 6.3$ Hz), 160.5 ppm. ¹⁹F NMR (CDCl₃, 282.4 MHz): δ -217.9 (tt, $J_1^{\text{FH}} = 47.1$ Hz, $J_2^{\text{FH}} = 23.7$ Hz, 1F; CF) ppm. HRMS: calcd for C₇H₉FN₂O₂ (M⁺) 172.0648; found 172.0628.

3-Ethoxycarbonyl-1 methyl-1H-pyrazole-5-carboxylic acid (25).

Flash chromatography [*n*-hexane-EtOAc (2:1)] (R_f = 0.20) afforded **25** as a white solid (90% yield); mp 198-9 °C. ¹H NMR (300 MHz, CDCl₃): δ 1.21 (t, $J = 7.1$ Hz, 3H; CH₃), 4.07 (s, 3H; CH₃), 4.18 (q, $J = 7.1$ Hz, 2H; CH₂), 7.11 (s, 1H; CH) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ 13.9, 39.9, 60.5, 113.6, 125.4, 134.4, 141.8, 161.3 ppm. HRMS: calcd for C₈H₁₀N₂O₄ (M⁺) 198.0641; found 198.0628.

4-Chloro-3-ethoxycarbonyl-1 methyl-1H-pyrazole-5-carboxylic acid (26).

Flash chromatography [*n*-hexane-EtOAc (2:1)] (R_f = 0.20) afforded **26** as a white solid (60% yield); mp 180-2 °C. ¹H NMR (300 MHz, CDCl₃): δ 1.22 (t, $J = 7.2$ Hz, 3H; CH₃), 4.06 (s, 3H; CH₃), 4.21 (q, $J = 7.2$ Hz, 2H; CH₂) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ 14.9, 41.7, 60.9, 116.6, 132.3, 138.4, 159.6, 160.4 ppm. HRMS: calcd for C₈H₉ClN₂O₄ (M⁺) 232.0251; found 232.0243.

***N*-(4-*tert*-Butylbenzyl)-4-chloro-3-(2,2,2-trifluoroethyl)-1-methyl-1H-pyrazole-5-carboxamide (24).**

Flash chromatography [*n*-hexane-EtOAc (8:1)] (R_f = 0.40) afforded **24** as a yellow oil (45% yield, two steps). ¹H NMR (300 MHz, CDCl₃): δ 1.25 (s, 9H; (CH₃)₃), 3.37 (q, $J_{\text{HF}} = 10.2$ Hz, 2H; CH₂), 4.12 (s, 3H), 4.54 (d, $J = 5.3$ Hz, 2H; CH₂), 6.88 (broad, 1H; NH), 7.21 (d, $J = 8.3$ Hz, 2H; Ar-H), 7.32 (d, $J = 8.3$ Hz, 2H; Ar-H) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ 31.5 (q, $^2J_{\text{CF}} = 32.4$ Hz), 31.7, 34.9, 41.6, 43.7, 110.2, 125.3 (q, $^1J_{\text{CF}} = 277.3$ Hz), 126.2, 127.8, 132.3, 134.5, 138.3 (q, $^3J_{\text{CF}} = 3.4$ Hz), 151.3, 158.3 ppm. ¹⁹F NMR (282.4 MHz, CDCl₃): δ -65.6 (t, $J_{\text{FH}} = 10.2$ Hz, 3F; CF₃) ppm. HRMS: calcd for C₁₈H₂₁ClF₃N₃O (M⁺) 387.1325; found 387.1326.

***N*-(4-*tert*-Butylbenzyl)-4-chloro-3-ethoxycarbonyl-1-methyl-1*H*-pyrazole-5-carboxamide (27).**

Flash chromatography [*n*-hexane-EtOAc (6:1)] (*R*_f = 0.40) afforded **27** as a pale yellow oil (92% yield). ¹H NMR (300 MHz, CDCl₃): δ 1.23 (s, 9H; C(CH₃)₃), 1.31 (t, *J* = 7.2 Hz, 3H; CH₃), 4.16 (s, 3H; CH₃), 4.33 (q, *J* = 7.2 Hz, 2H; CH₂), 4.53 (d, *J* = 5.4 Hz, 2H; CH₂), 7.08 (t, *J* = 5.4 Hz, 1H; NH), 7.20 (d, *J* = 8.3 Hz, 2H; Ar-*H*), 7.30 (d, *J* = 8.3 Hz, 2H; Ar-*H*) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ 14.7, 31.7, 34.9, 42.3, 43.7, 61.8, 112.5, 126.2, 127.8, 133.6, 134.4, 138.0, 151.2, 158.0, 160.7 ppm. HRMS: calcd for C₁₉H₂₄ClN₃O₃ (M⁺) 377.1506; found 377.1517.

***N*-(4-*tert*-Butylbenzyl)-4-chloro-3-formyl-1-methyl-1*H*-pyrazole-5-carboxamide (28).**

Flash chromatography [*n*-hexane-EtOAc (6:1)] (*R*_f = 0.40) afforded **28** as a pale yellow oil (86% yield). ¹H NMR (300 MHz, CDCl₃): δ 1.25 (s, 9H; C(CH₃)₃), 4.22 (s, 3H; CH₃), 4.55 (d, *J* = 5.6 Hz, 2H; CH₂), 6.97 (broad, 1H; NH), 7.21 (d, *J* = 8.3 Hz, 2H; Ar-*H*), 7.32 (d, *J* = 8.3 Hz, 2H; Ar-*H*), 9.90 (s, 1H; CH) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ 31.6, 34.9, 42.6, 43.8, 111.0, 126.2, 127.8, 133.8, 134.2, 144.2, 151.3, 157.8, 184.6 ppm. HRMS: calcd for C₁₇H₂₀ClN₃O₂ (M⁺) 333.1244; found 333.1243.

***N*-(4-*tert*-Butylbenzyl)-4-chloro-3-(1-hydroxyethyl)-1-methyl-1*H*-pyrazole-5-carboxamide (29).**

Flash chromatography [*n*-hexane-EtOAc (2:1)] (*R*_f = 0.30) afforded **29** as a pale yellow oil (65% yield). ¹H NMR (300 MHz, CDCl₃): δ 1.24 (s, 9H; C(CH₃)₃), 1.48 (d, *J* = 6.2 Hz, 3H; CH₃), 2.46 (broad, 1H; OH), 4.07 (s, 3H; CH₃), 4.53 (d, *J* = 5.7 Hz, 2H; CH₂), 4.89 (q, *J* = 6.2 Hz, 1H; CH), 6.91 (broad, 1H; NH), 7.20 (d, *J* = 8.3 Hz, 2H; Ar-*H*), 7.32 (d, *J* = 8.3 Hz, 2H; Ar-*H*) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ 22.8, 31.6, 34.9, 41.2, 43.6, 63.5, 106.7, 126.1, 127.7, 132.2, 134.6, 150.5, 151.1, 158.5 ppm. HRMS: calcd for C₁₈H₂₄ClN₃O₂ (M⁺) 349.1557; found 349.1550.

***N*-(4-*tert*-Butylbenzyl)-4-chloro-3-(1-fluoroethyl)-1-methyl-1*H*-pyrazole-5-carboxamide (30).**

Flash chromatography [*n*-hexane-EtOAc (6:1)] (*R*_f = 0.30) afforded **30** as a pale yellow oil (88% yield). ¹H NMR (300 MHz, CDCl₃): δ 1.26 (s, 9H; C(CH₃)₃), 1.69 (dd, *J*₁^{HF} = 23.3 Hz, *J*₂ = 6.8 Hz, 3H; CH₃), 4.12 (s, 3H; CH₃), 4.56 (d, *J* = 5.6 Hz, 2H; CH₂), 5.65 (dq, *J*₁^{HF} = 48.0 Hz, *J*₂ = 6.8 Hz, 1H; CH), 6.92 (broad, 1H; NH), 7.23 (d, *J* = 8.3 Hz, 2H; Ar-*H*), 7.33 (d, *J* = 8.3 Hz, 2H; Ar-*H*) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ 19.5 (d, ²*J*_{CF} = 25.3 Hz), 31.6, 34.9, 41.5, 43.6, 83.6 (d, ¹*J*_{CF} = 164.4 Hz), 108.6 (d, ³*J*_{CF} = 2.3 Hz), 126.1, 127.7, 132.4, 134.5, 146.3 (d, ²*J*_{CF} = 22.4 Hz), 151.1, 158.4 ppm. ¹⁹F NMR (282.4 MHz,

CDCl₃): δ -167.9 (dq, $J_1^{\text{FH}} = 48.0$ Hz, $J_2^{\text{FH}} = 23.3$ Hz, 1F; CF) ppm. HRMS: calcd for C₁₈H₂₃ClFN₃O (M⁺) 351.1514; found 351.1502.

***N*-(4-*tert*-Butylbenzyl)-3-(1-fluoroethyl)-1-methyl-1*H*-pyrazole-5-carboxamide (30').**

Flash chromatography [*n*-hexane-EtOAc (8:1)] ($R_f = 0.40$) afforded **30'** as a pale yellow oil (83% yield). ¹H NMR (300 MHz, CDCl₃): δ 1.24 (s, 9H; C(CH₃)₃), 1.57 (dd, $J_1^{\text{HF}} = 23.7$ Hz, $J_2 = 6.6$ Hz, 3H; CH₃), 4.07 (d, $J = 1.1$, 3H; CH₃), 4.45 (d, $J = 5.6$ Hz, 2H; CH₂), 5.54 (dq, $J_1^{\text{HF}} = 47.8$ Hz, $J_2 = 6.6$ Hz, 1H; CH), 6.33 (broad, 1H; NH), 6.47 (d, $J = 0.8$ Hz, 1H; CH), 7.18 (d, $J = 8.3$ Hz, 2H; Ar-H), 7.30 (d, $J = 8.3$ Hz, 2H; Ar-H) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ 21.3 (d, $^2J_{\text{CF}} = 24.2$ Hz), 34.9, 31.7, 39.7, 43.7, 85.9 (d, $^1J_{\text{CF}} = 162.5$ Hz), 104.1 (d, $^3J_{\text{CF}} = 2.8$ Hz), 126.2, 128.1, 134.9, 136.5, 150.1 (d, $^2J_{\text{CF}} = 25.3$ Hz), 151.3, 159.9 ppm. ¹⁹F NMR (282.4 MHz, CDCl₃): δ -165.2 (dq, $J_1^{\text{FH}} = 47.8$ Hz, $J_2^{\text{FH}} = 23.7$ Hz, 1F; CF) ppm. HRMS: calcd for C₁₈H₂₄FN₃O (M⁺) 317.1903; found 317.1911.

***N*-(4-*tert*-Butylbenzyl)-3-(2,2-difluoroethyl)-1-methyl-1*H*-pyrazole-5-carboxamide (32').**

Flash chromatography [*n*-hexane-EtOAc (8:1)] ($R_f = 0.40$) afforded **32'** as a yellow oil (73% yield). ¹H NMR (300 MHz, CDCl₃): δ 1.24 (s, 9H; C(CH₃)₃), 3.06 (td, $J_1^{\text{HF}} = 17.3$ Hz, $J_2^{\text{HF}} = 4.5$ Hz, 2H; CH₂), 4.07 (s, 3H; CH₃), 4.46 (d, $J = 5.7$ Hz, 2H; CH₂), 5.88 (tt, $J_1^{\text{HF}} = 56.5$ Hz, $J_2 = 4.5$ Hz, 1H; CH), 6.24 (broad, 1H; NH), 7.19 (d, $J = 8.3$ Hz, 2H; Ar-H), 7.31 (d, $J = 8.3$, 2H; Ar-H) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ 31.7, 34.1 (t, $^2J_{\text{CF}} = 23.0$ Hz), 34.9, 39.6, 43.7, 106.7, 116.1 (t, $^1J_{\text{CF}} = 240.9$ Hz), 126.2, 128.1, 134.8, 136.6, 142.6, 151.3, 159.9 ppm. ¹⁹F NMR (282.4 MHz, CDCl₃): δ -115.7 (dt, $J_1^{\text{FH}} = 56.5$ Hz, $J_2^{\text{FH}} = 17.3$ Hz, 2F; CF₂) ppm. HRMS: calcd for C₁₈H₂₃F₂N₃O (M⁺) 335.1809; found 335.1804.

***N*-(4-*tert*-Butylbenzyl)-4-chloro-3-(2-oxoethyl)-1-methyl-1*H*-pyrazole-5-carboxamide (31).**

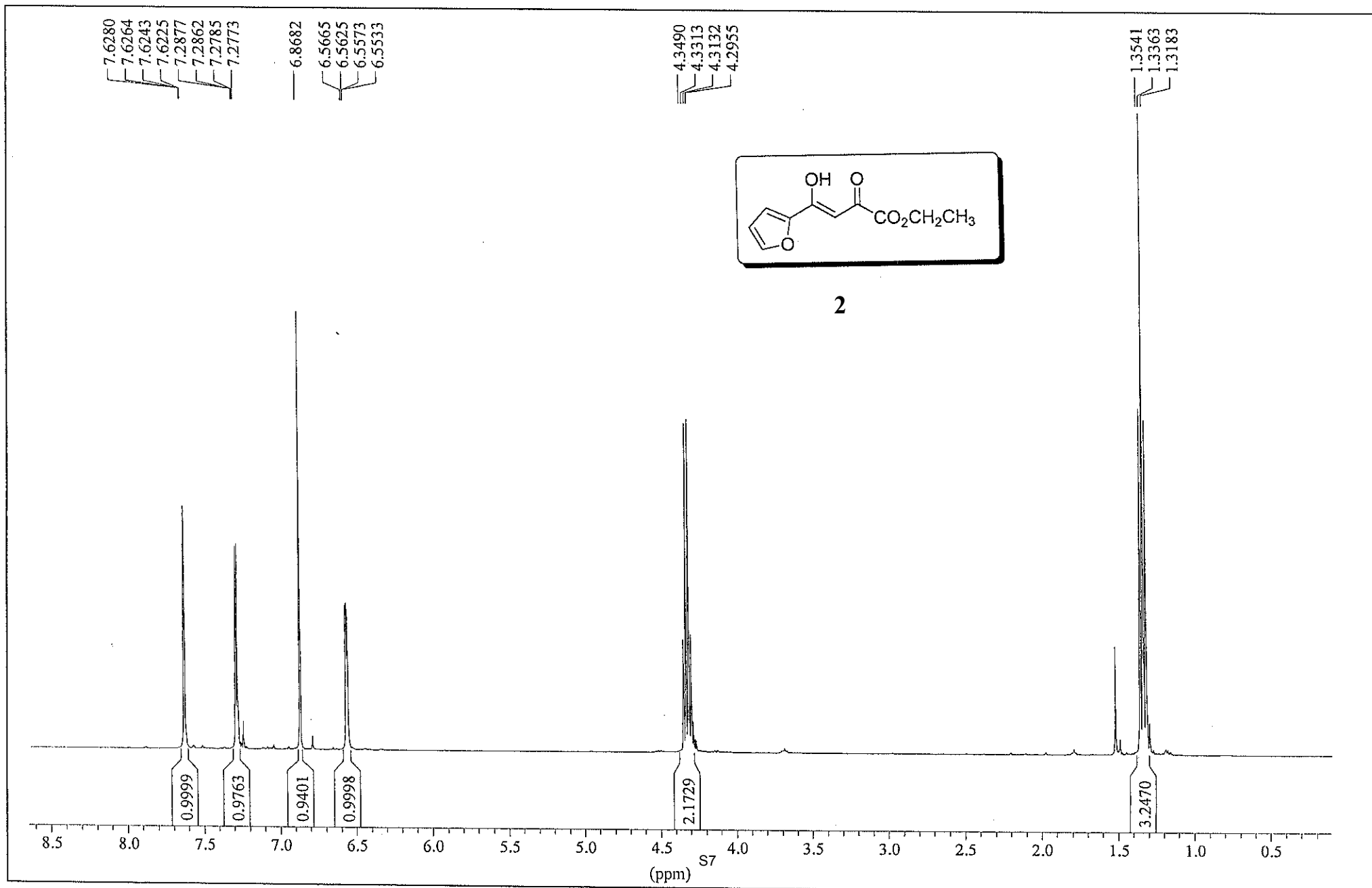
This compound was not purified, as it decomposed quickly when column chromatography was performed on silica gel. Yellow oil (83% yield). ¹H NMR (300 MHz, CDCl₃): δ 1.25 (s, 9H; C(CH₃)₃), 3.65 (d, $J = 1.5$ Hz, 2H; CH₂), 4.11 (s, 3H; CH₃), 4.54 (d, $J = 5.6$ Hz, 2H; CH₂), 6.88 (broad, 1H; NH), 7.21 (d, $J = 8.3$ Hz, 2H; Ar-H), 7.32 (d, $J = 8.3$ Hz, 2H; Ar-H), 9.67 (t, $J = 1.5$ Hz, 1H; CH) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ 30.3, 33.5, 39.6, 39.9, 42.3, 108.2, 124.8, 126.4, 130.8, 133.1, 139.1, 149.8, 157.0, 195.8 ppm. HRMS: calcd for C₁₈H₂₂ClN₃O₂ (M⁺) 347.1401; found 347.1403.

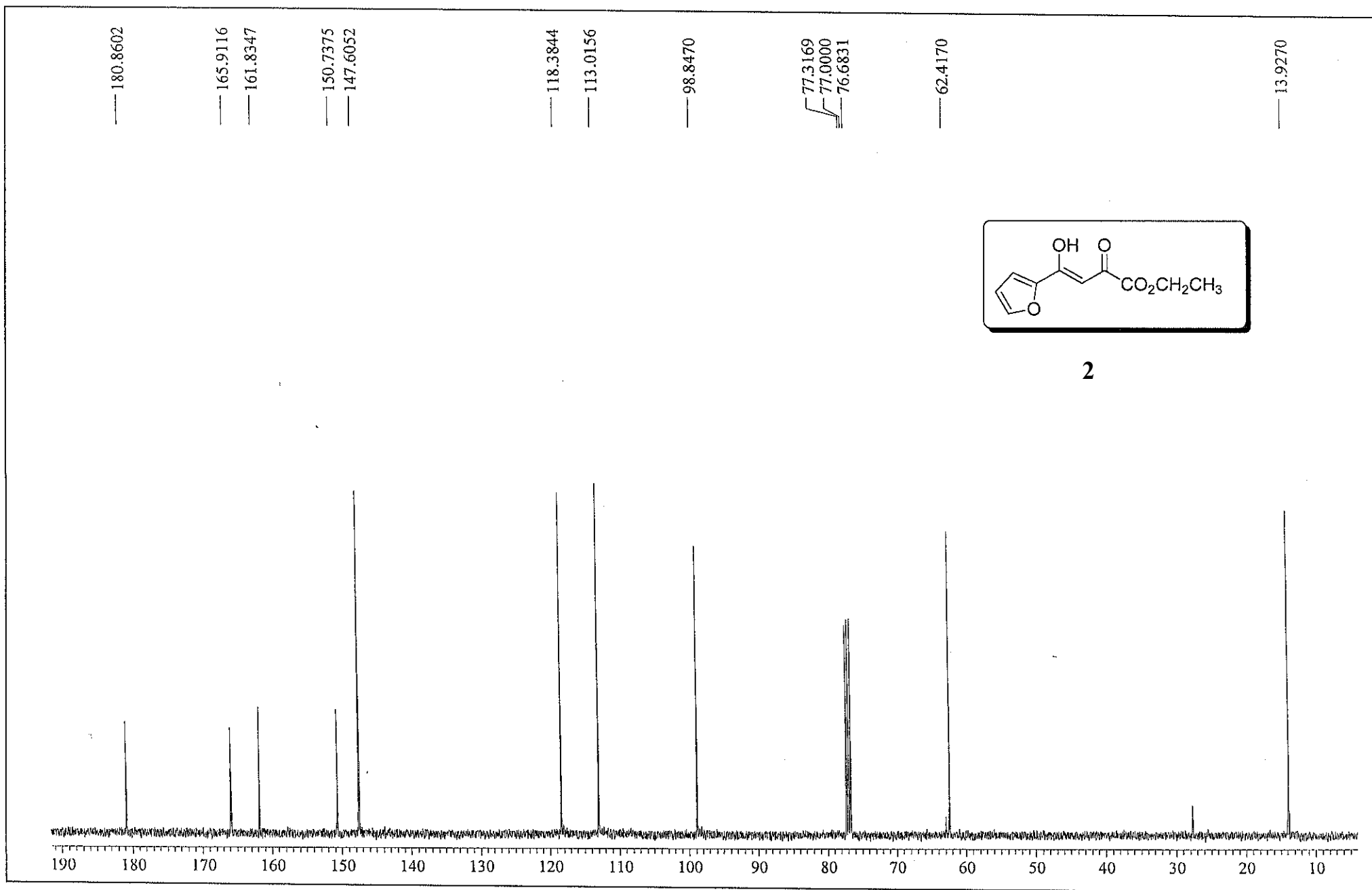
***N*-(4-*tert*-Butylbenzyl)-4-chloro-3-(2,2-difluoroethyl)-1-methyl-1*H*-pyrazole-5-carboxamide (32).**

Flash chromatography [*n*-hexane-EtOAc (8:1)] (*R*_f = 0.30) afforded **32** as a yellow oil (58% yield, two steps). ¹H NMR (300 MHz, CDCl₃): δ 1.26 (s, 9H; C(CH₃)₃), 3.12 (td, *J*₁^{HF} = 15.8 Hz, *J*₂ = 4.7 Hz, 2H; CH₂), 4.11 (s, 3H; CH₃), 4.55 (d, *J* = 5.6 Hz, 2H; CH₂), 5.99 (tt, *J*₁^{HF} = 56.0 Hz, *J*₂ = 4.7 Hz, 1H; CH), 6.89 (broad, 1H; NH), 7.22 (d, *J* = 8.2 Hz, 2H; Ar-*H*), 7.33 (d, *J* = 8.2 Hz, 2H; Ar-*H*) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ 31.3, 31.4 (t, ²*J*_{CF} = 24.7 Hz), 34.6, 41.0, 43.3, 109.2, 115.1 (t, ¹*J*_{CF} = 242.2 Hz), 125.8, 127.4, 131.7, 134.2, 140.1, 150.8, 158.0 ppm. ¹⁹F NMR (282.4 MHz, CDCl₃): δ -115.1 (dt, *J*₁^{FH} = 56.0 Hz, *J*₂^{FH} = 15.8 Hz, 2F; CF₂). HRMS: calcd for C₁₈H₂₂ClF₂N₃O (M⁺) 369.1419; found 369.1416.

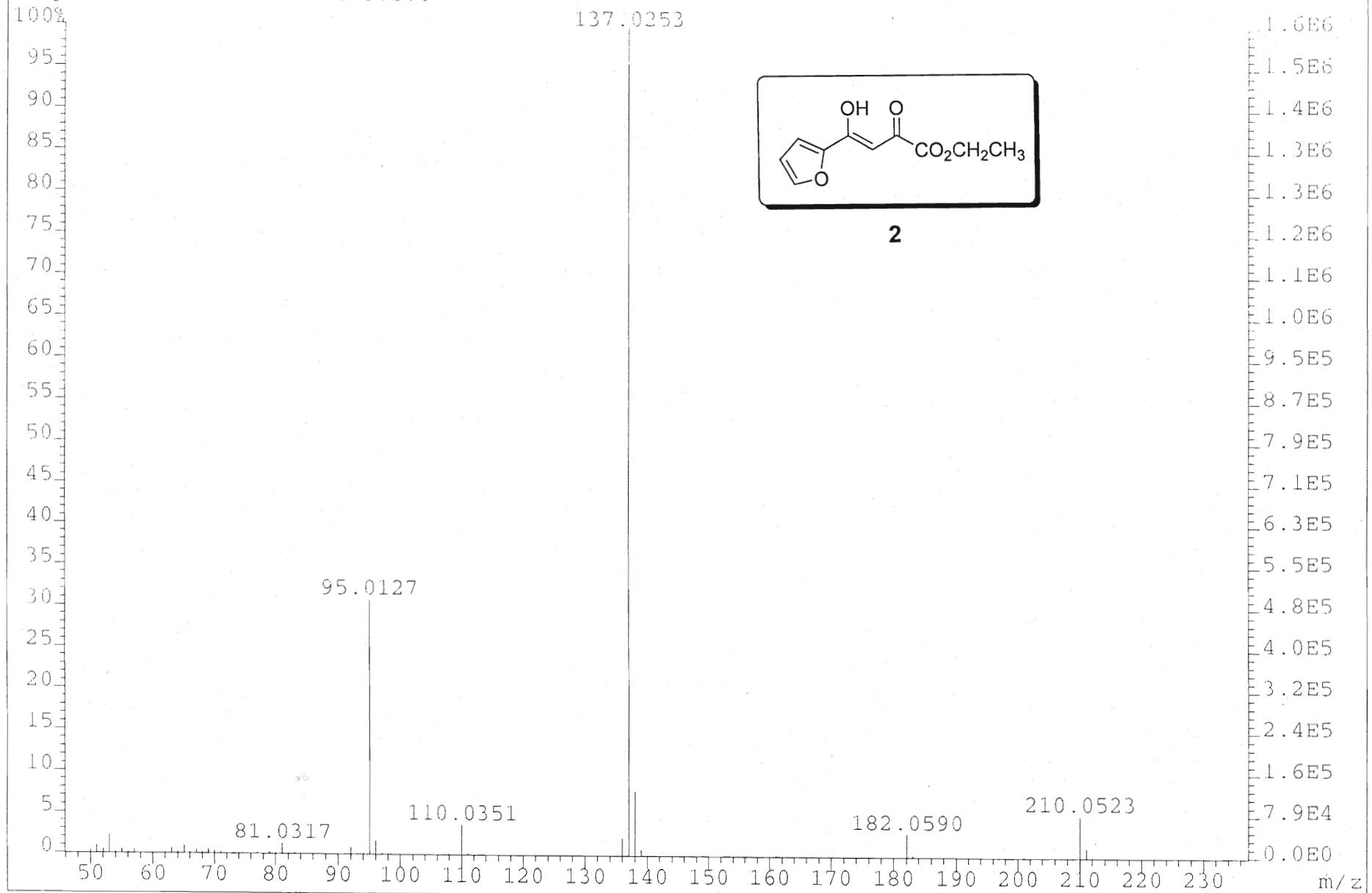
***N*-(4-*tert*-Butylbenzyl)-4-chloro-3-(2-fluoroethyl)-1-methyl-1*H*-pyrazole-5-carboxamide (33).**

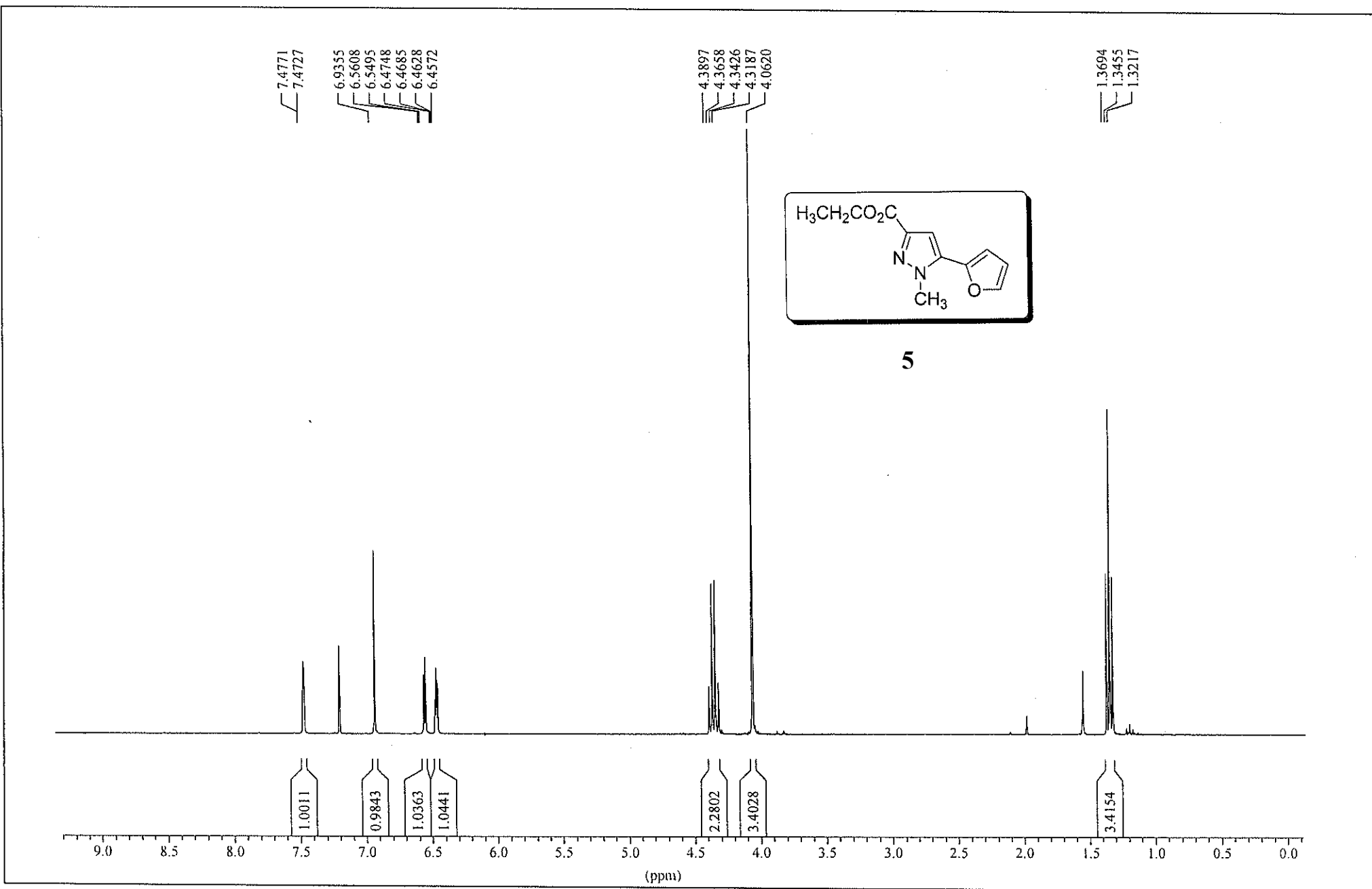
Flash chromatography [*n*-hexane-EtOAc (2:1)] (*R*_f = 0.30) afforded **33** as a pale yellow oil (65% yield). ¹H NMR (300 MHz, CDCl₃): δ 1.26 (s, 9H; C(CH₃)₃), 2.97 (dt, *J*₁^{HF} = 21.7 Hz, *J*₂ = 6.6 Hz, 2H; CH₂), 4.10 (s, 3H; CH₃), 4.55 (d, *J* = 5.6 Hz, 2H; CH₂), 4.65 (dt, *J*₁^{HF} = 56.5 Hz, *J*₂ = 6.6 Hz, 2H; CH₂), 6.91 (broad, 1H; NH), 7.22 (d, *J* = 8.2 Hz, 2H; Ar-*H*), 7.33 (d, *J* = 8.2 Hz, 2H; Ar-*H*) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ 27.2 (d, ²*J*_{CF} = 22.5 Hz), 31.3, 34.6, 40.9, 43.2, 81.7 (d, ¹*J*_{CF} = 169.1 Hz), 108.6, 125.8, 127.4, 131.4, 134.3, 143.6 (d, ³*J*_{CF} = 7.7 Hz), 150.8, 158.2 ppm. ¹⁹F NMR (282.4 MHz, CDCl₃): δ -217.0 (tt, *J*₁^{FH} = 56.5 Hz, *J*₂^{FH} = 21.7 Hz, 1F; CF). HRMS: calcd for C₁₈H₂₃ClFN₃O (M⁺) 351.1514; found 351.1503.

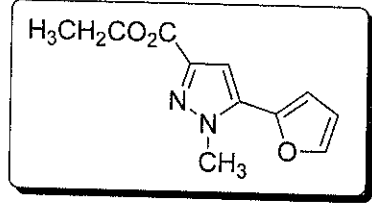
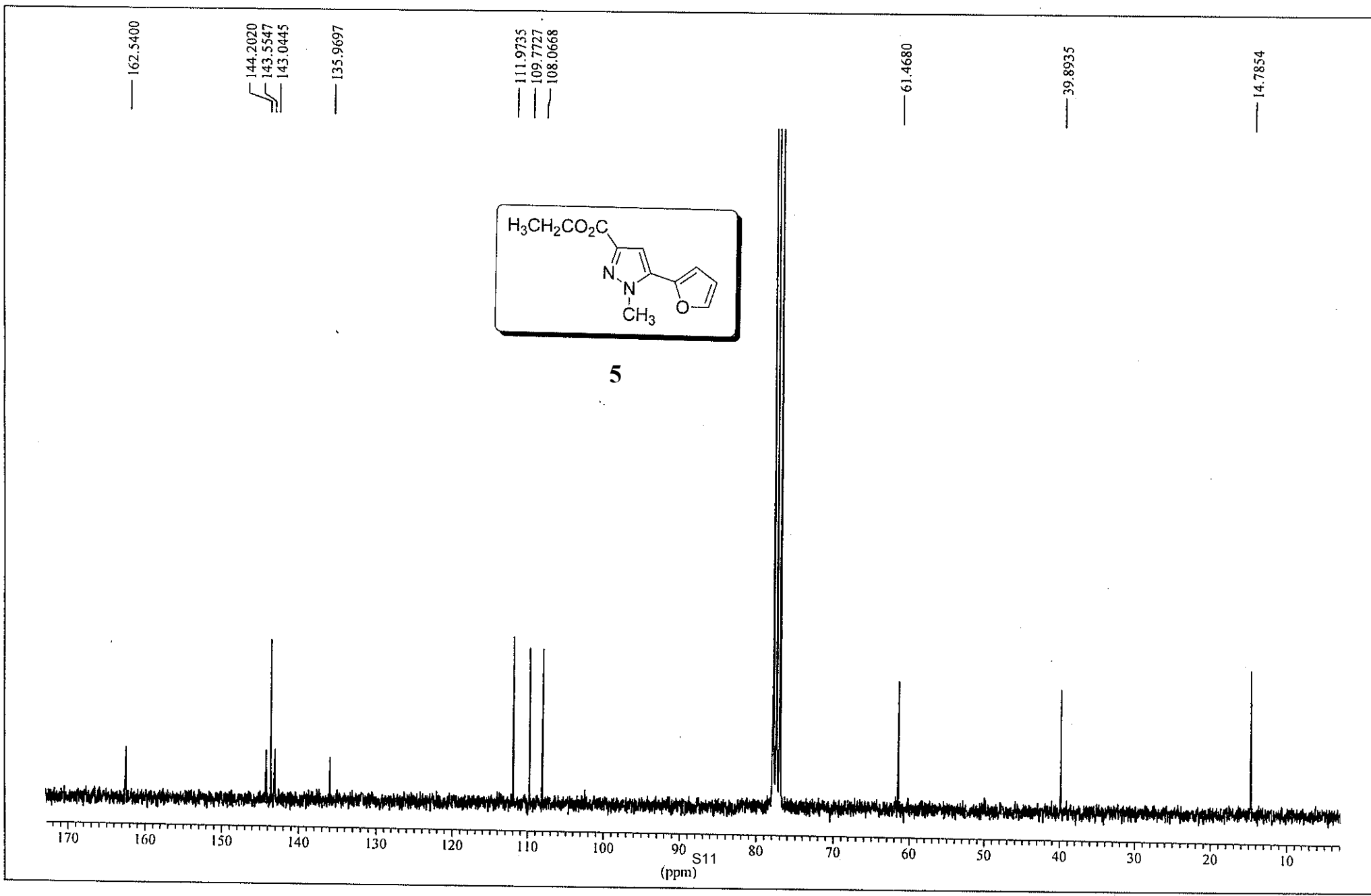




File:EI_4_9_3 Ident:17-4_9 Win 200PPM FILT(EXCL,ALL) Acq: 4-SEP-2008 09:51:53 Cal:EI_4_9_3
AutoSpecE EI+ Magnet BpM:137 BpI:1585664 TIC:2863306 Flags:NORM
Sample Text:test File Text:SV0



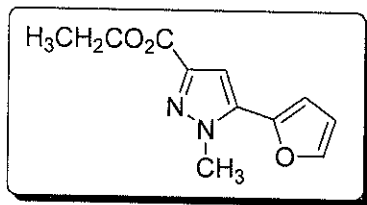
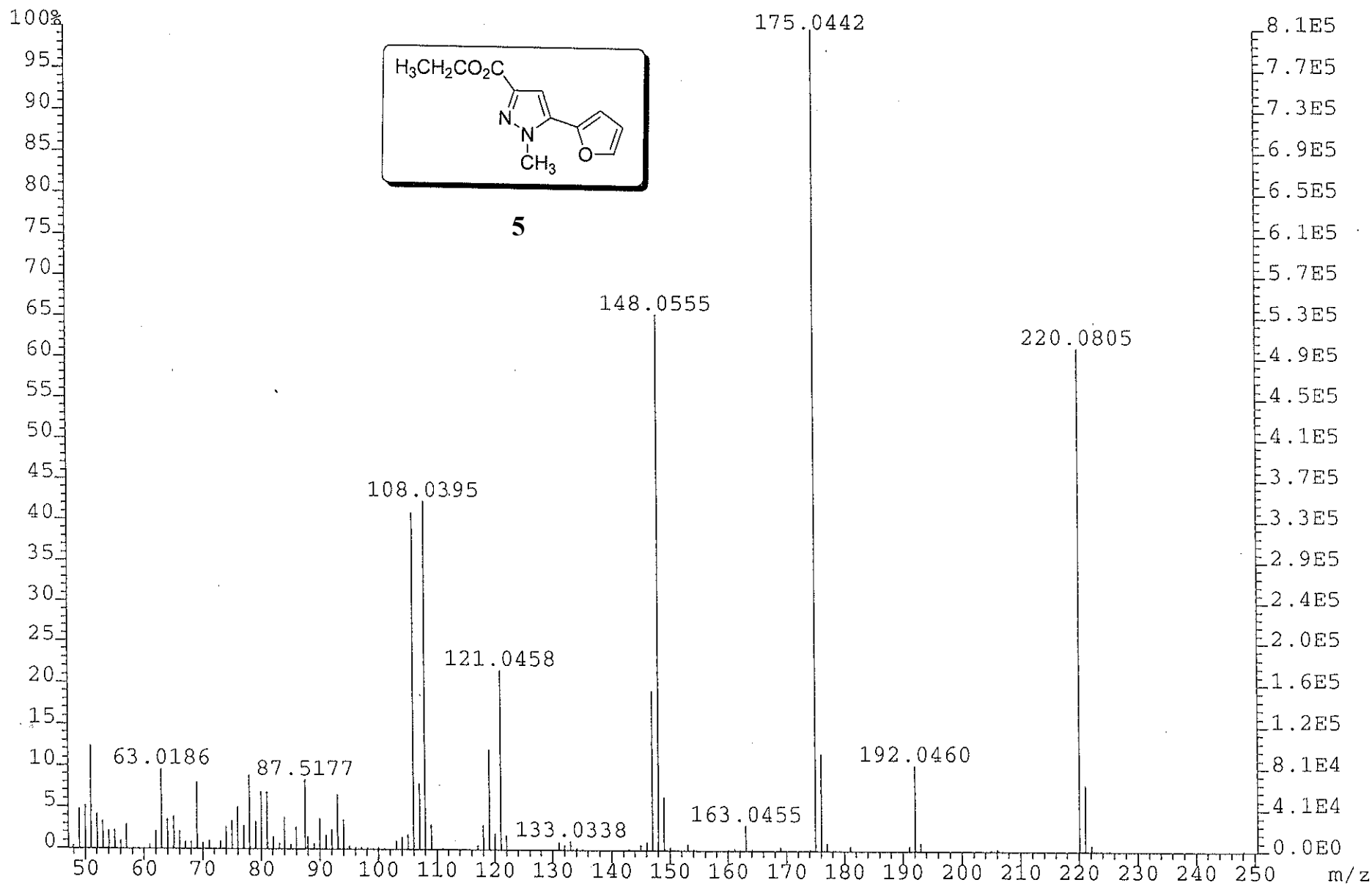




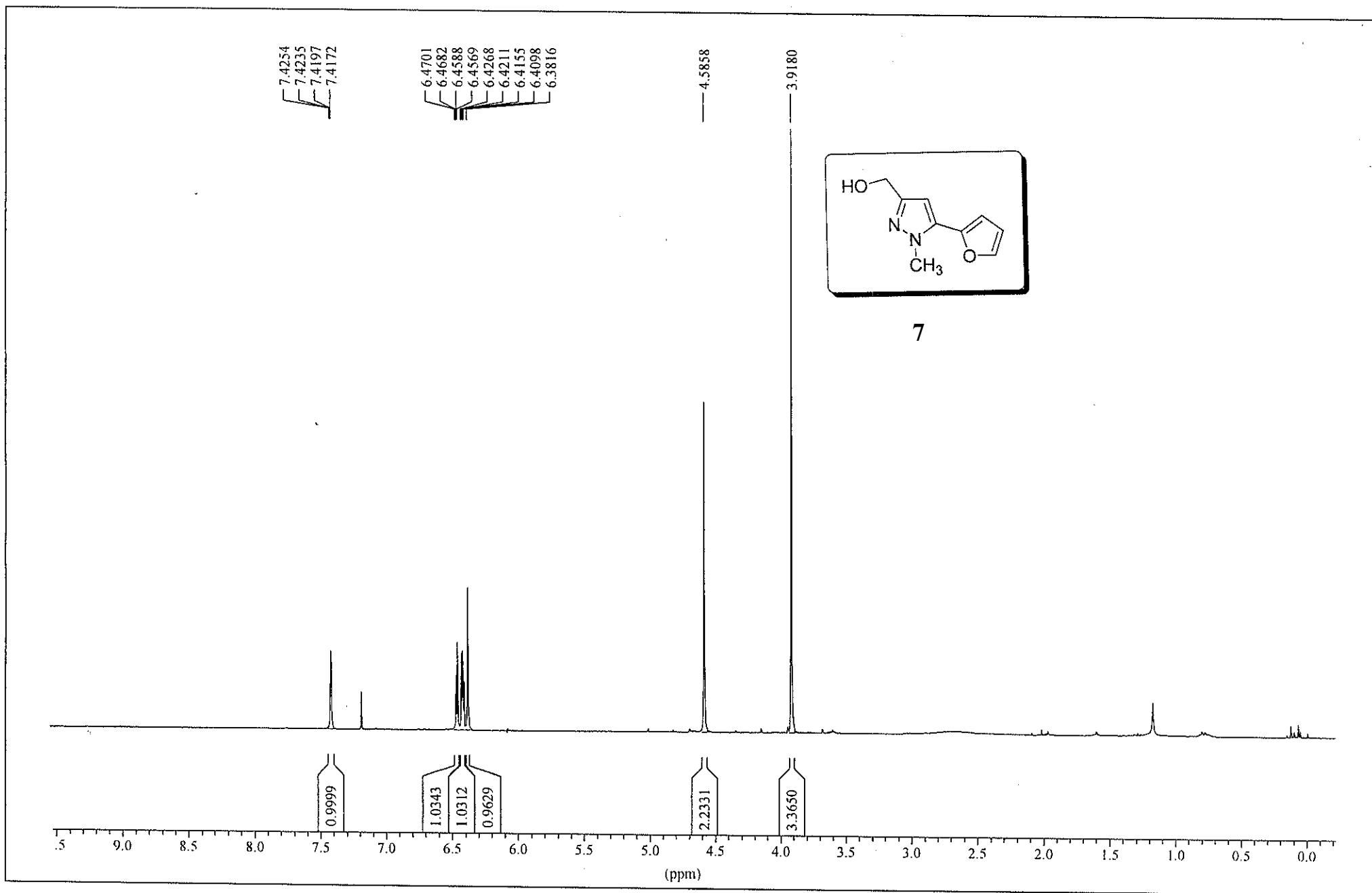
5

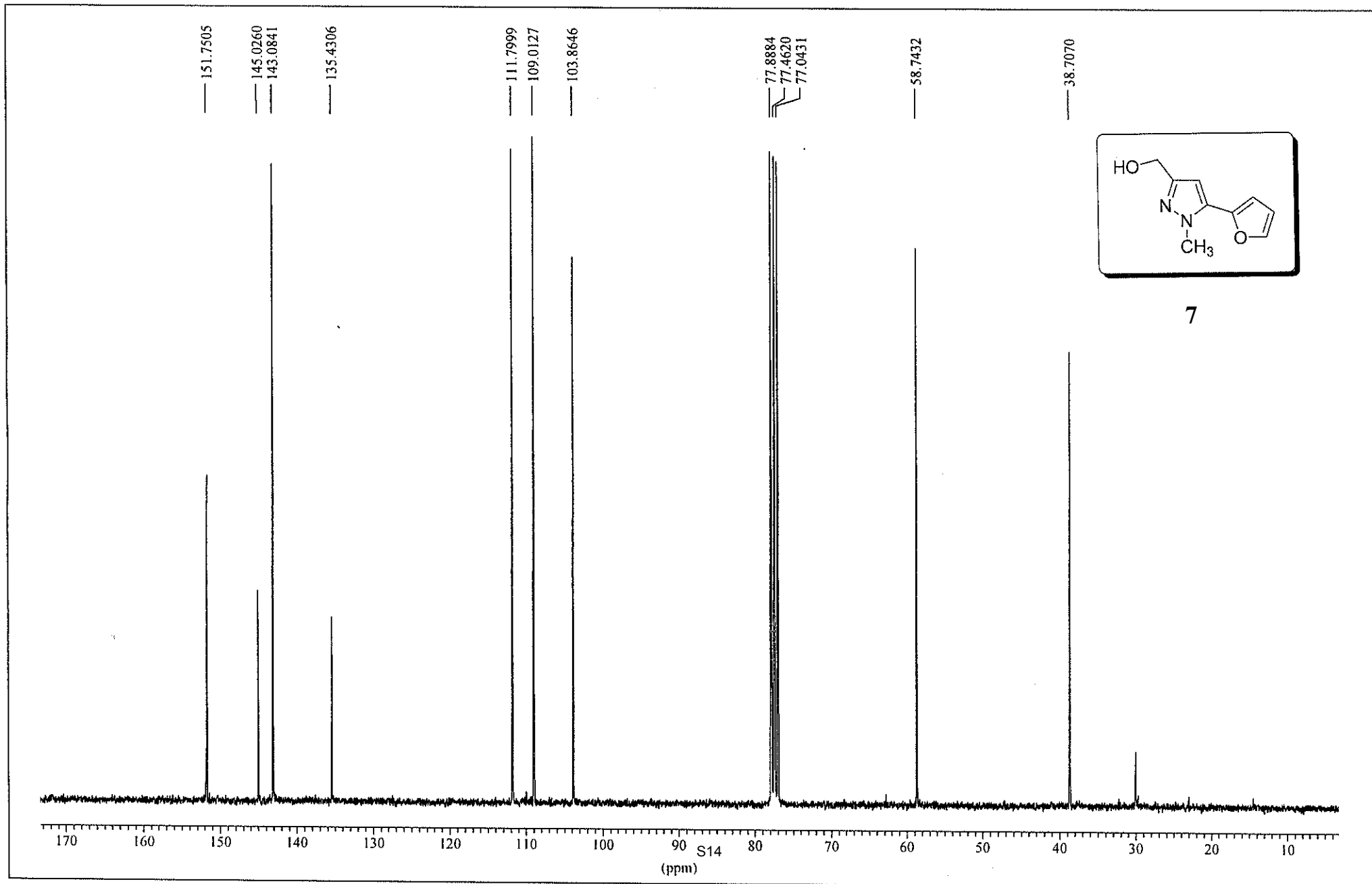
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

S11

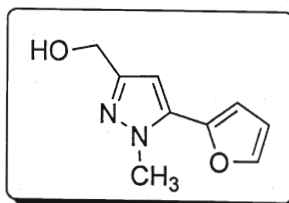
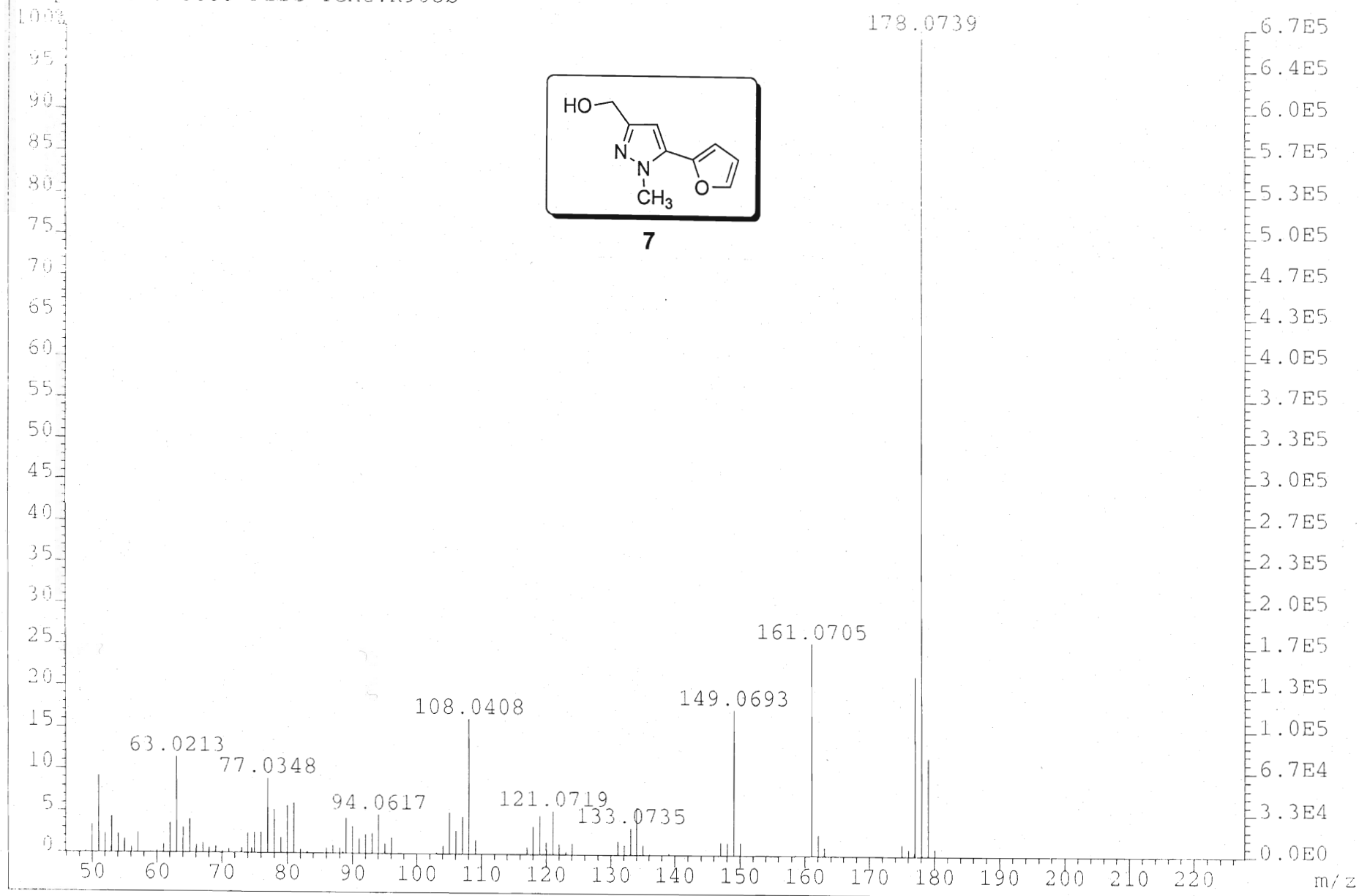


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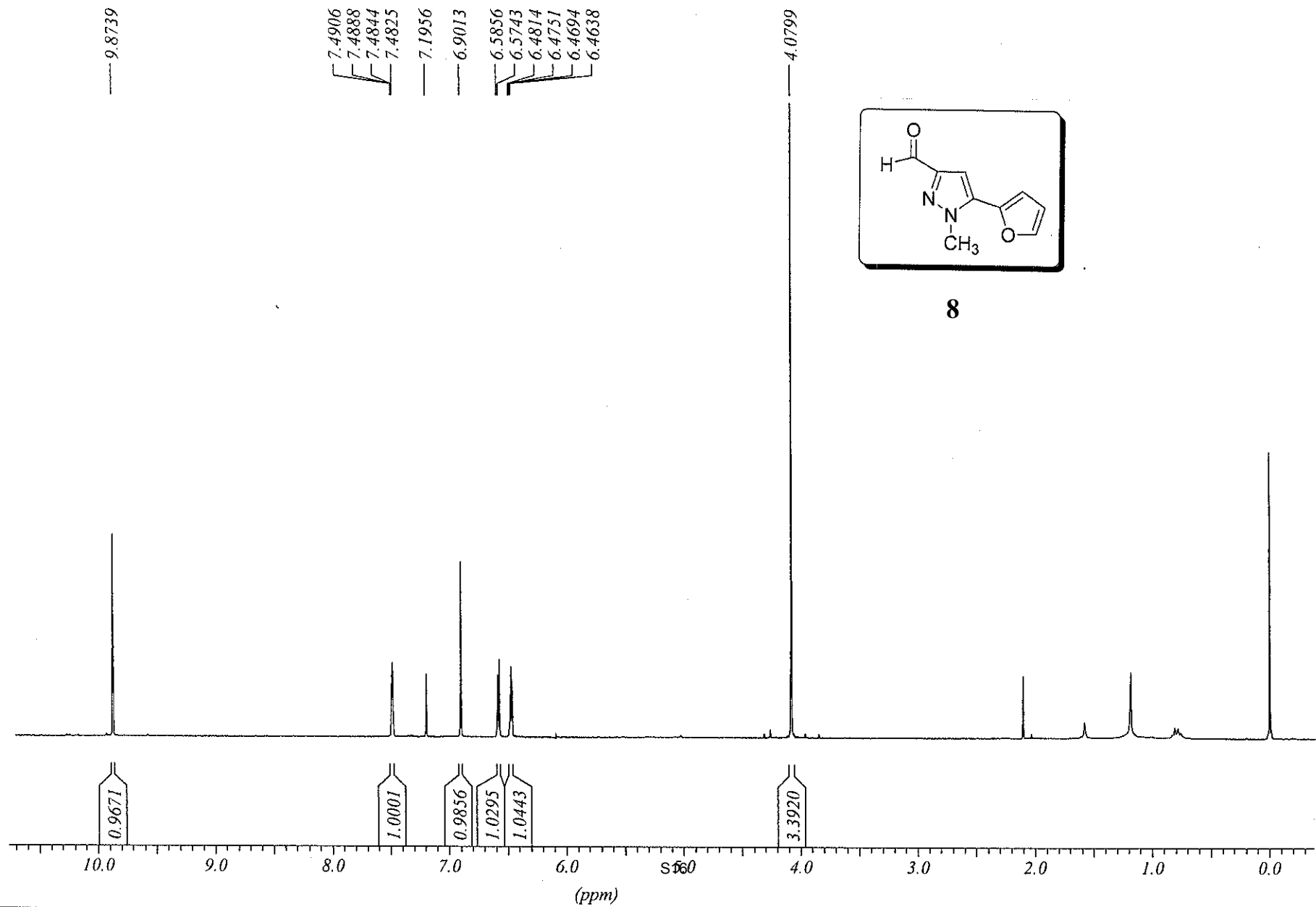


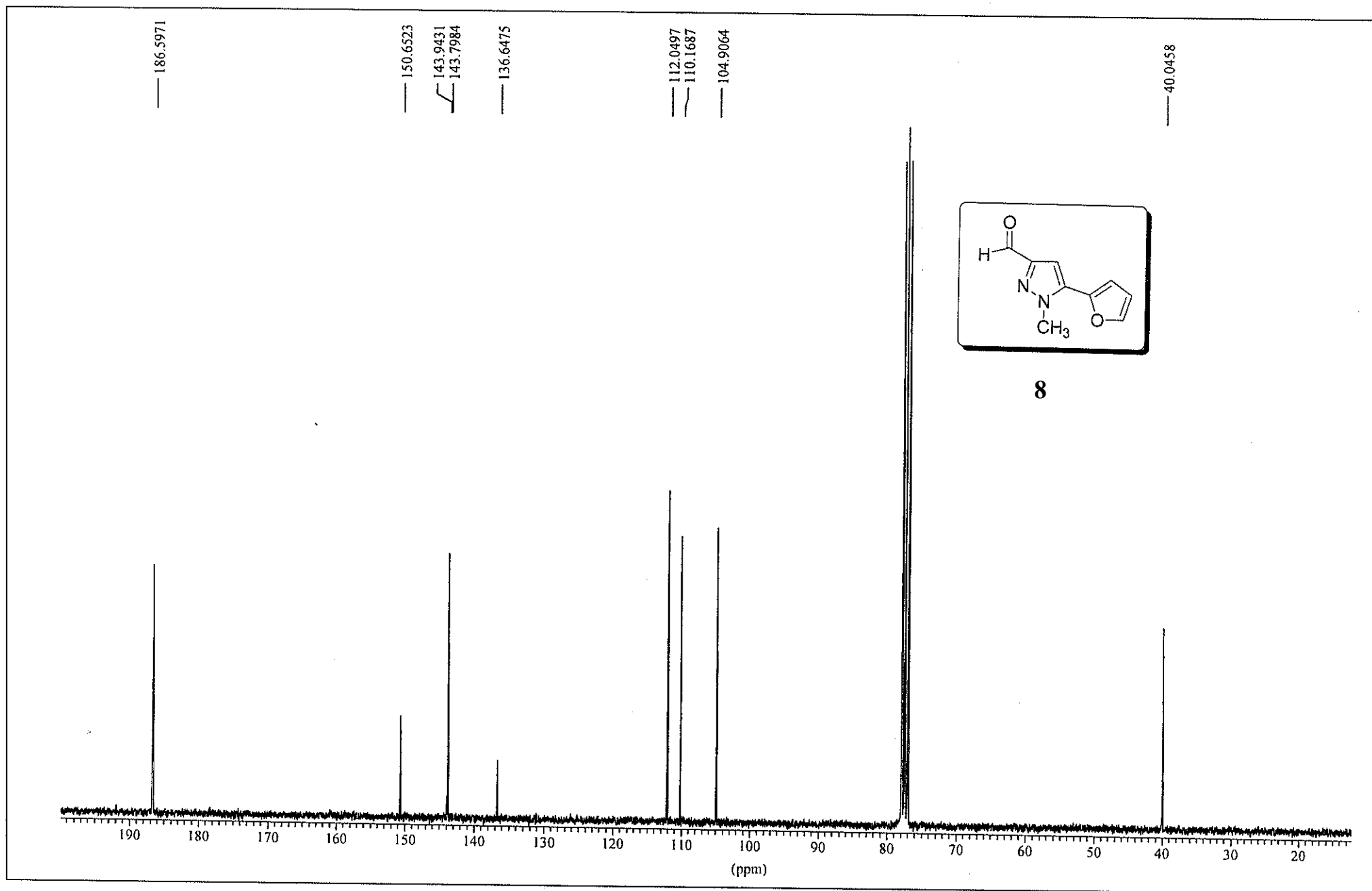


File:EI_4_9_1 Ident:17-3_7 Win 200PPM FILT(EXCL,ALL) Acq: 4-SEP-2008 08:21:48 Cal:EI_4_9_1
AutoSpecE EI+ Magnet BpM:178 BpI:668672 TIC:2679848 Flags:NORM
Sample Text:test File Text:R908b

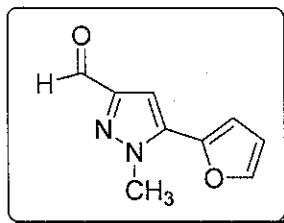
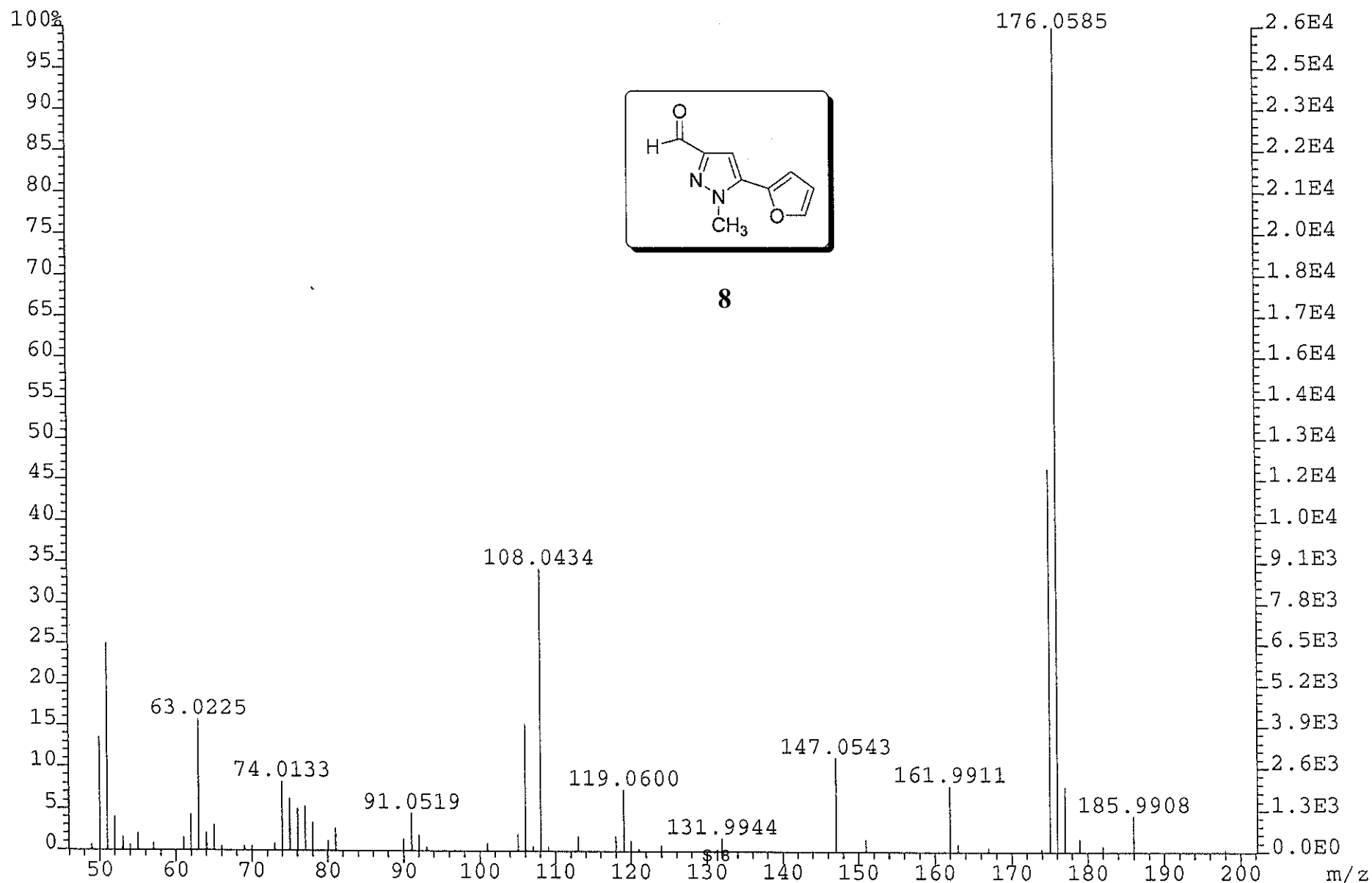


7

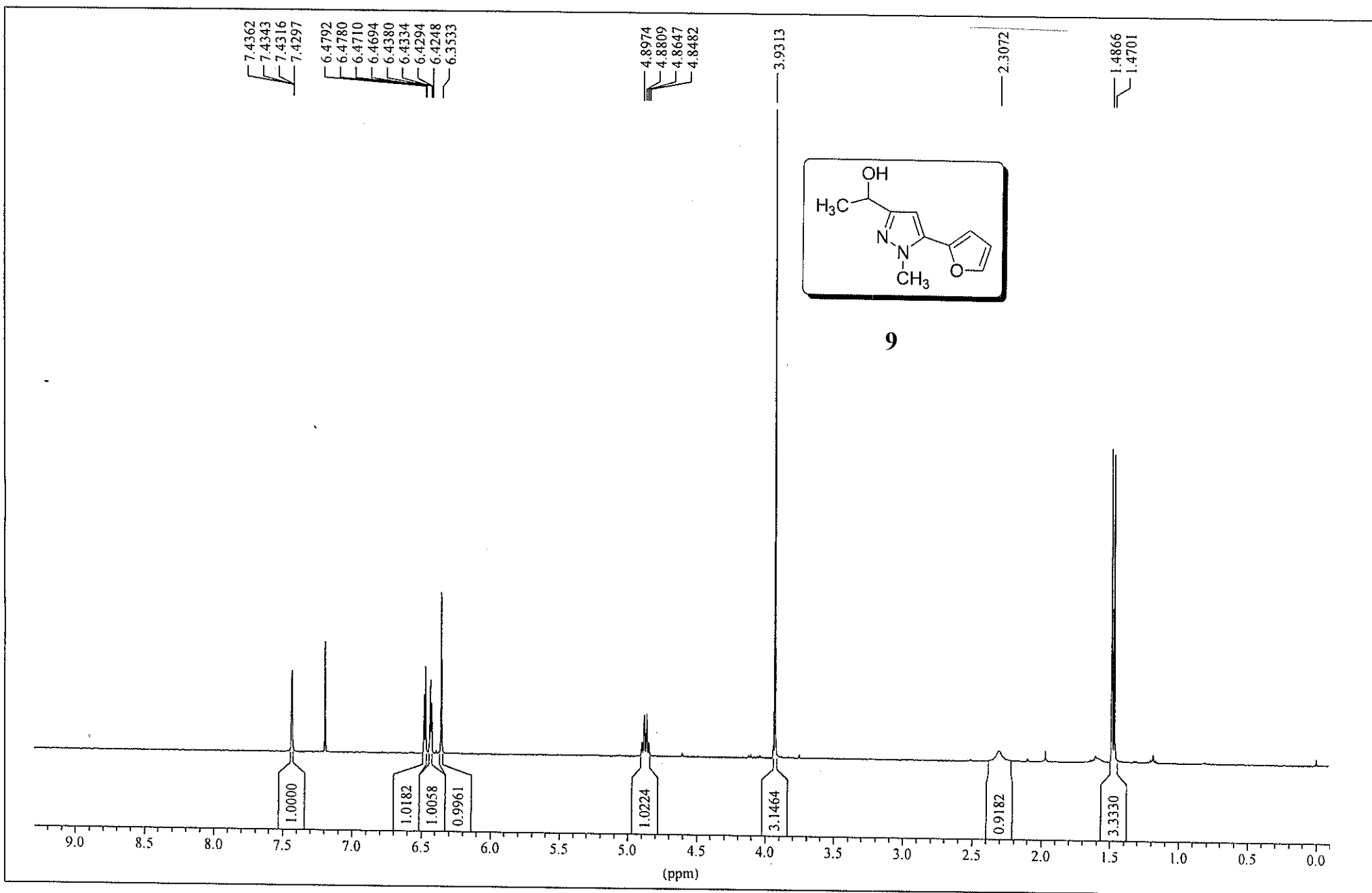


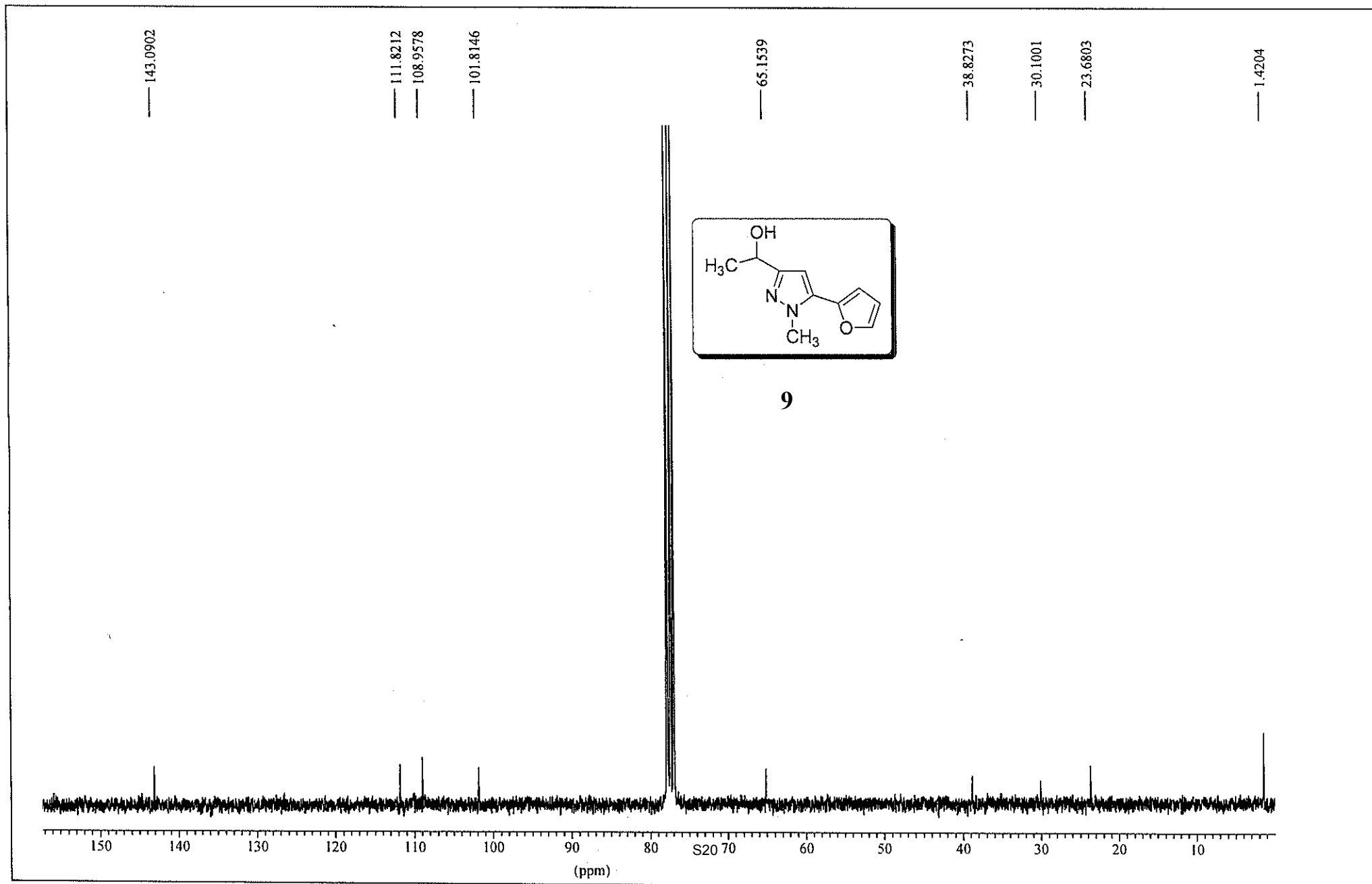


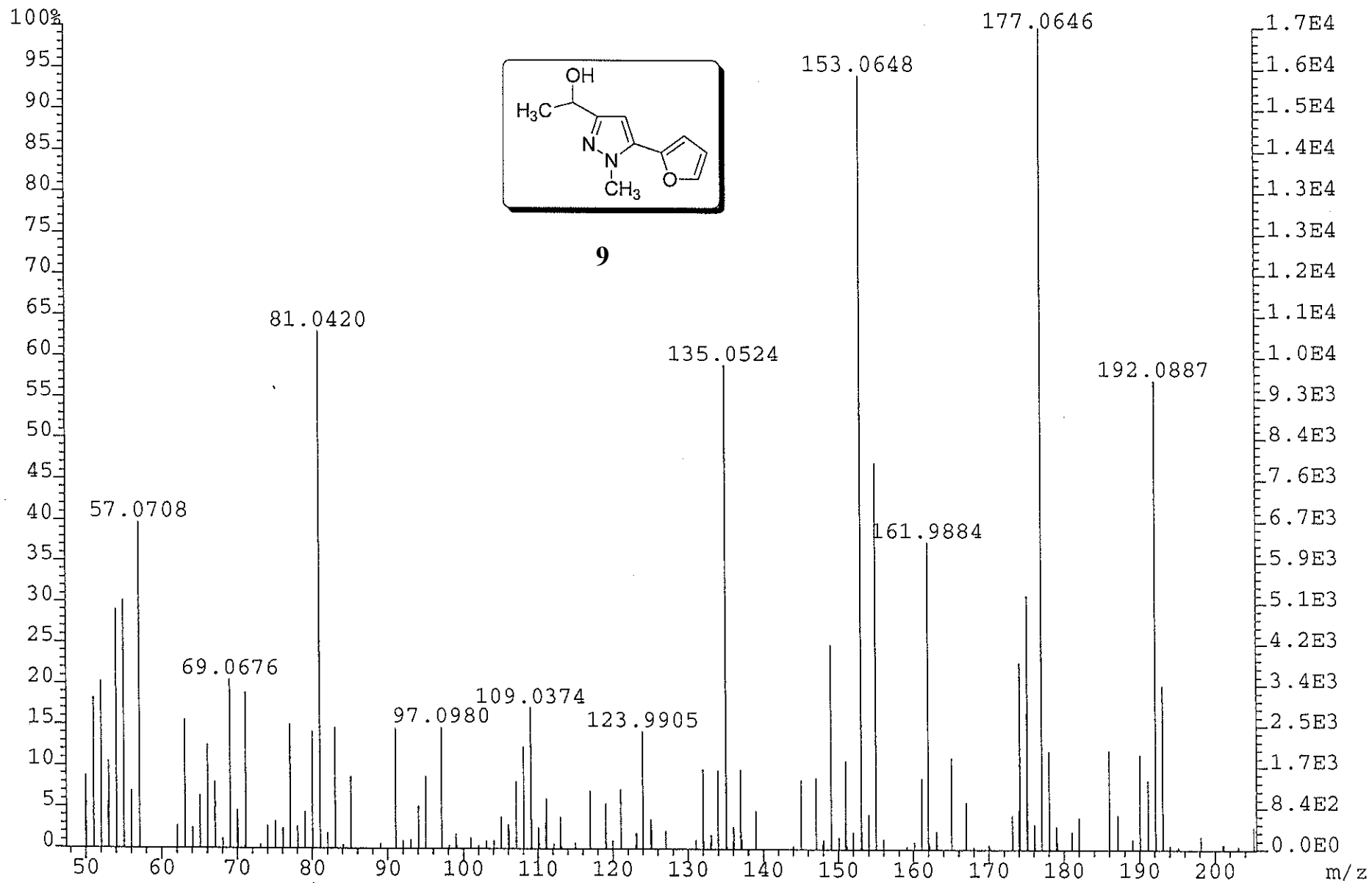
AutoSpecE EI+ Magnet BpM:176 BpI:26074 TIC:179871 Flags:NORM

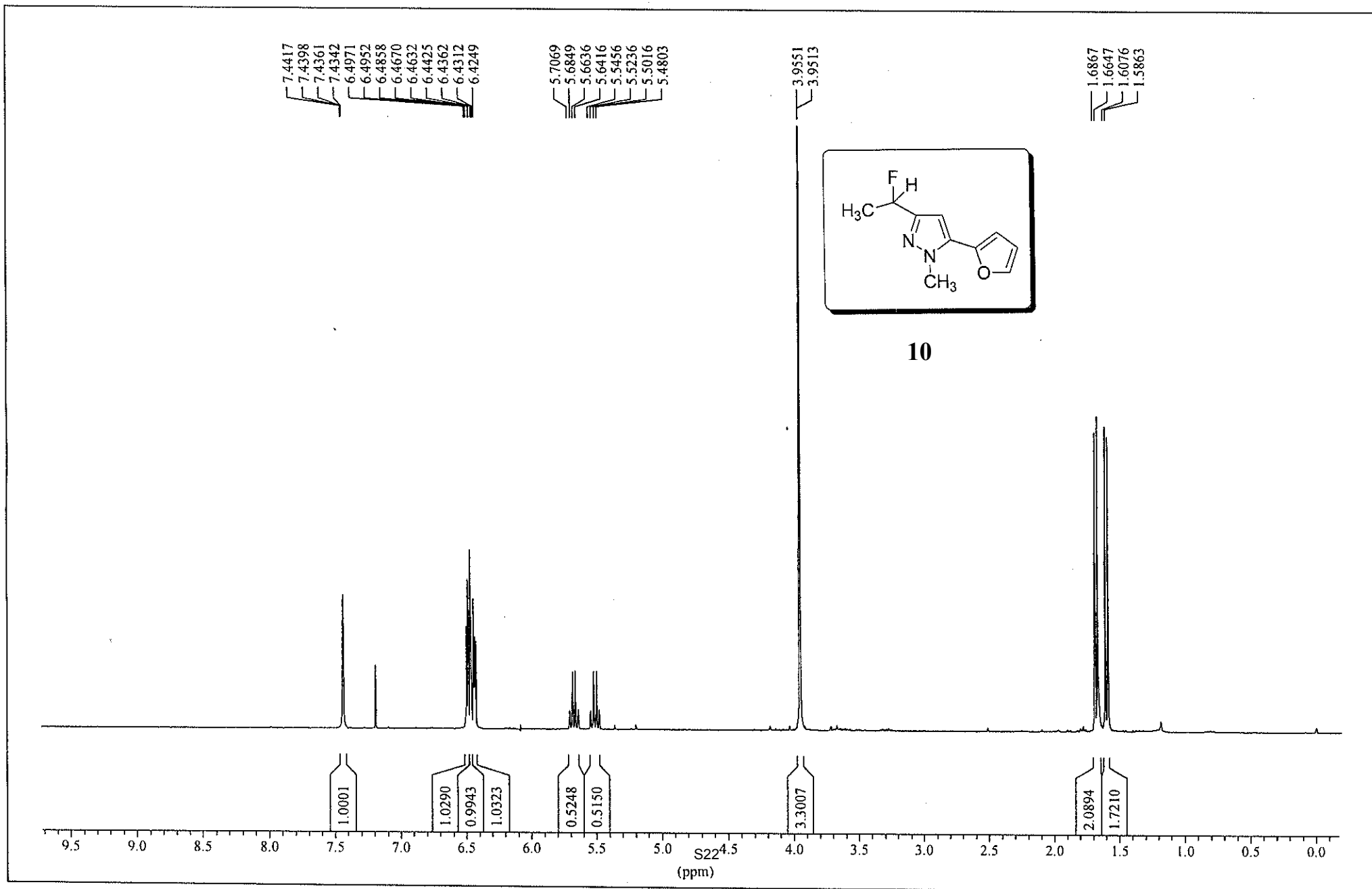


8

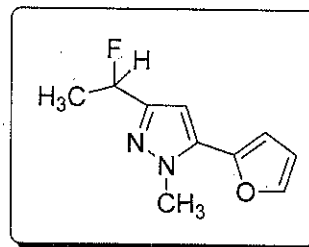




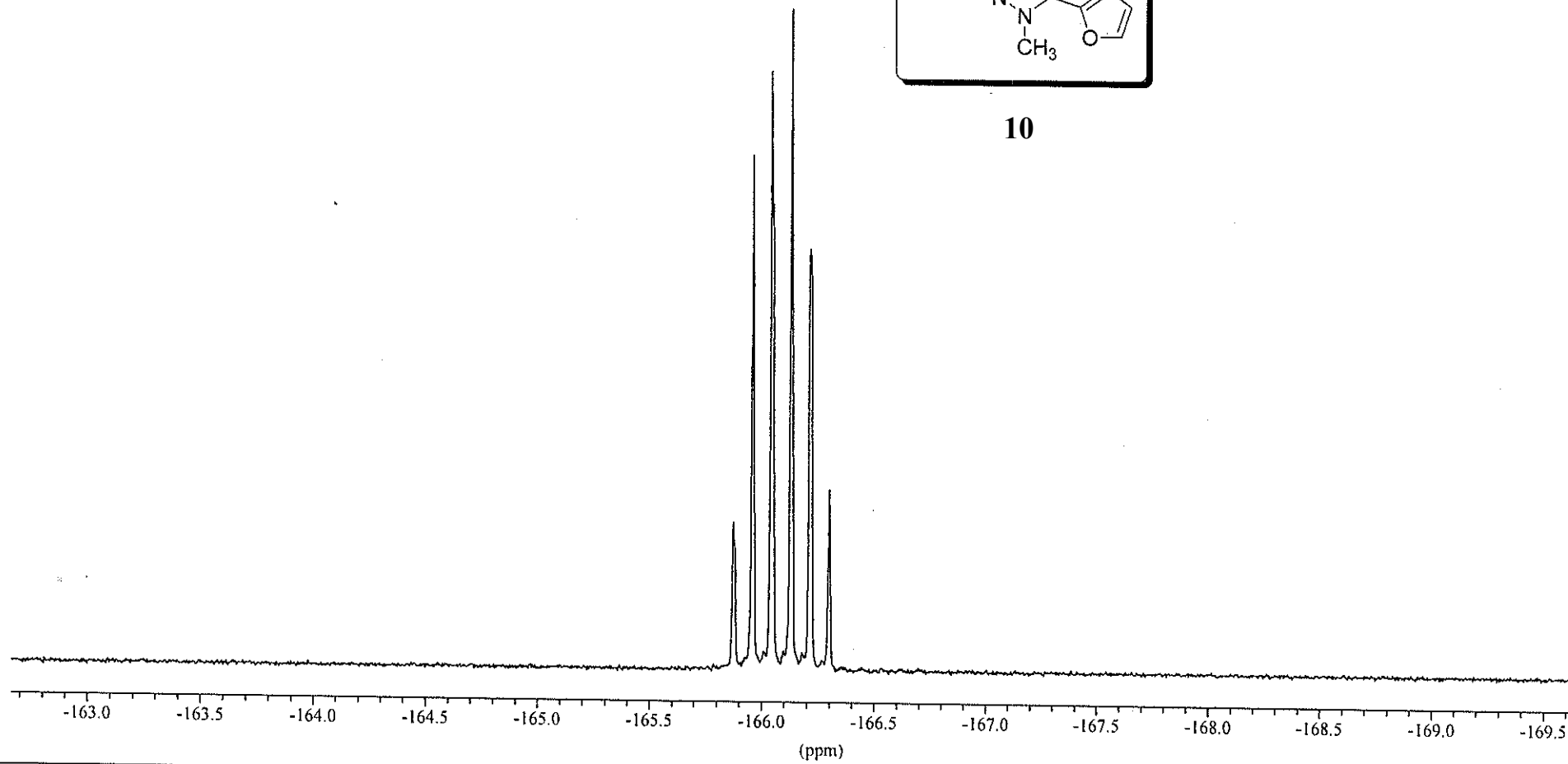


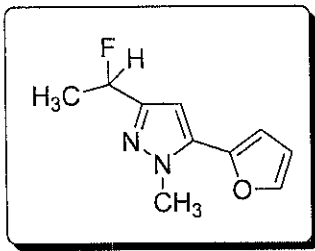


-165.8748
-165.9603
-166.0427
-166.0488
-166.1312
-166.2136
-166.2991

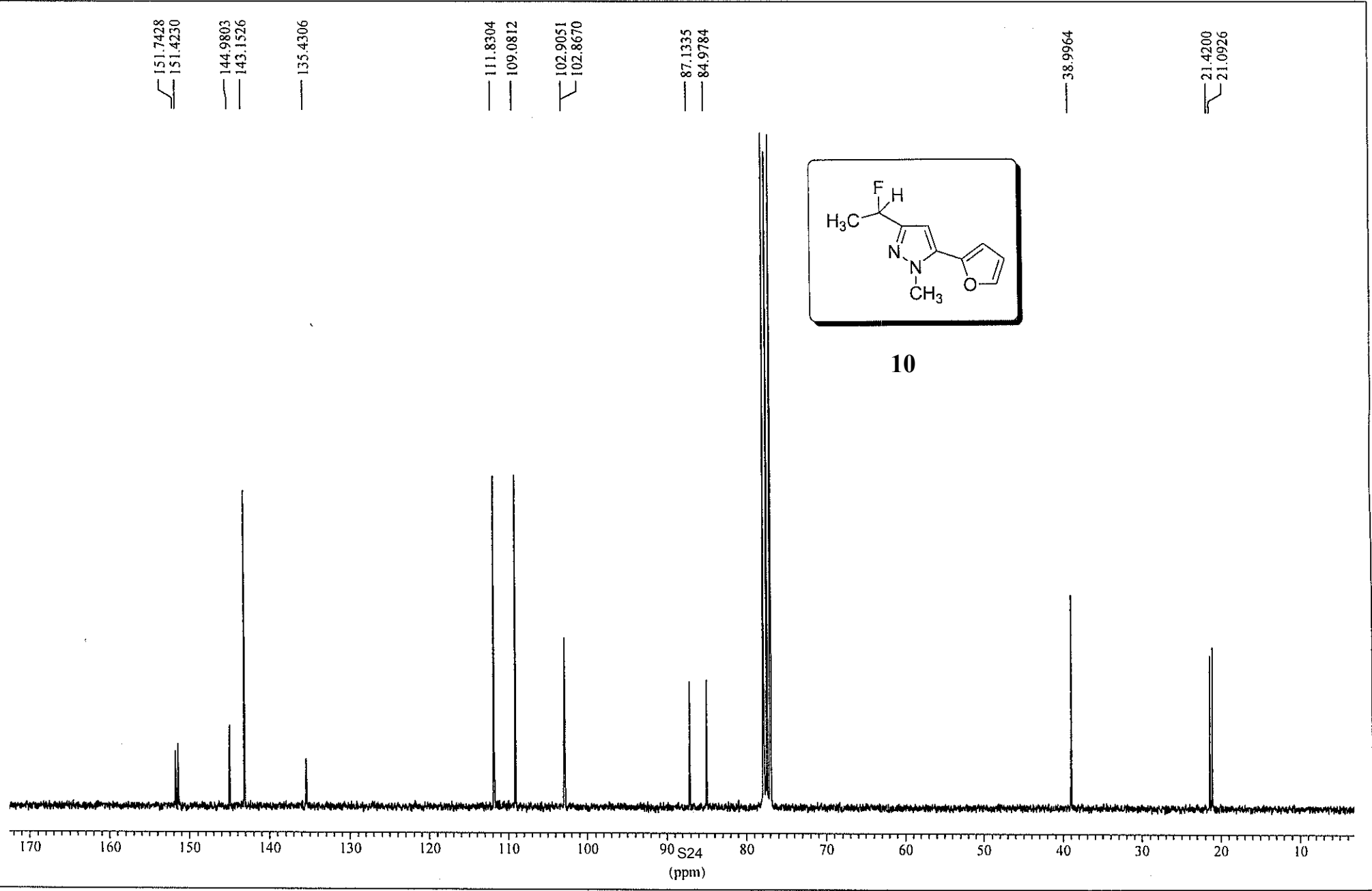


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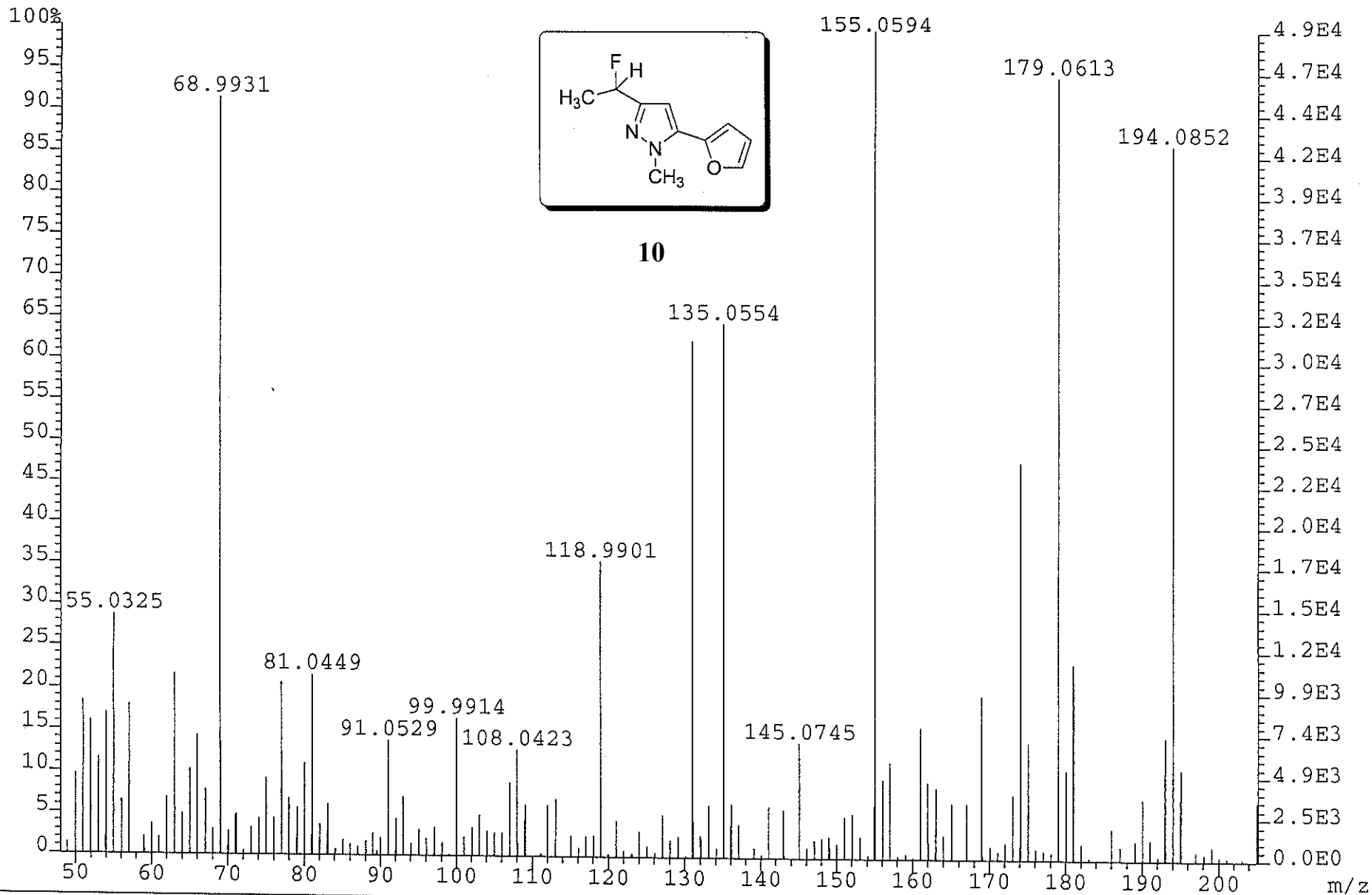


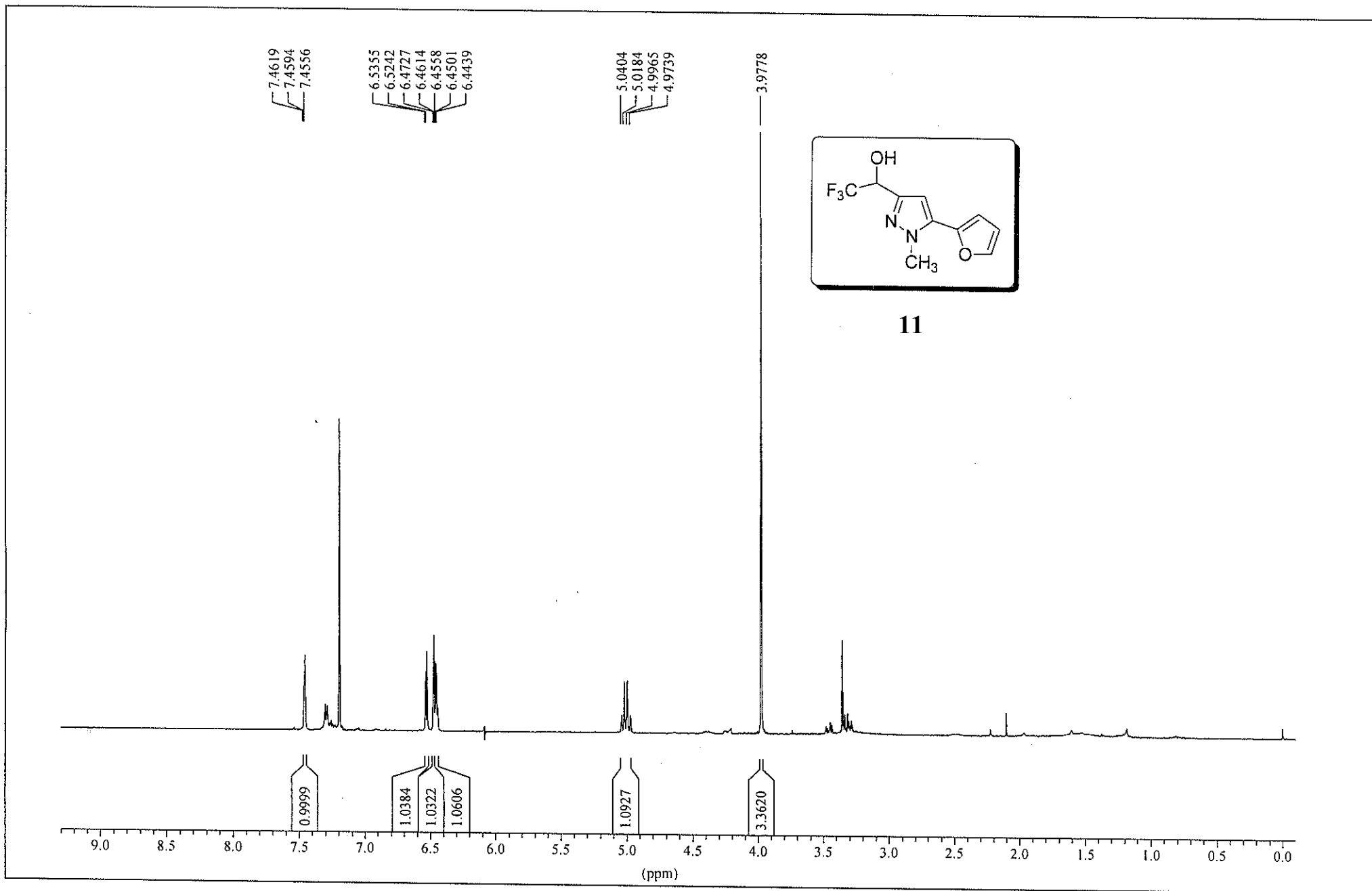


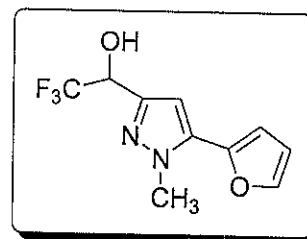
10



AutoSpecE EI+ Magnet BpM:155 BpI:49369 TIC:853261 Flags:NORM

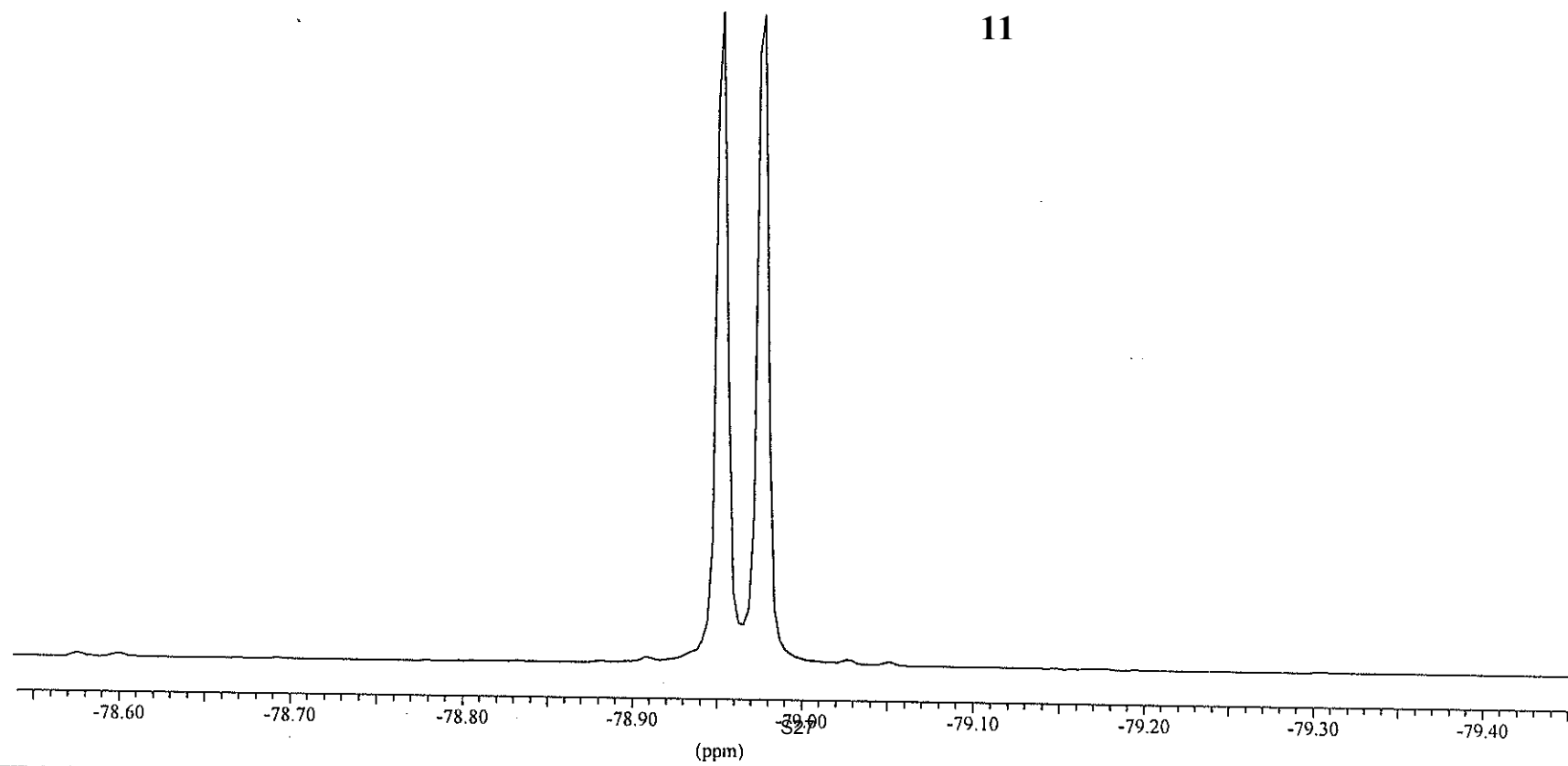


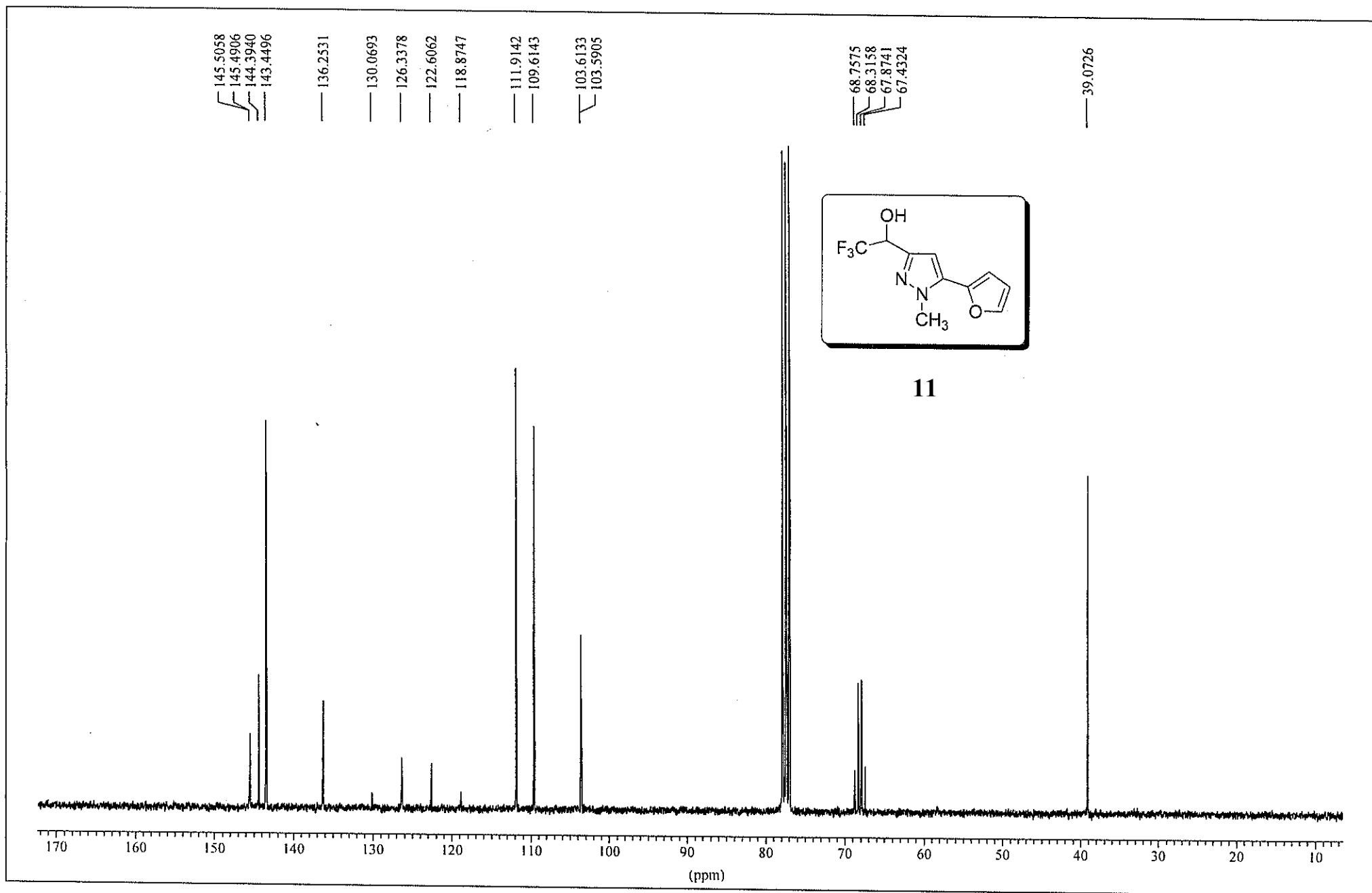




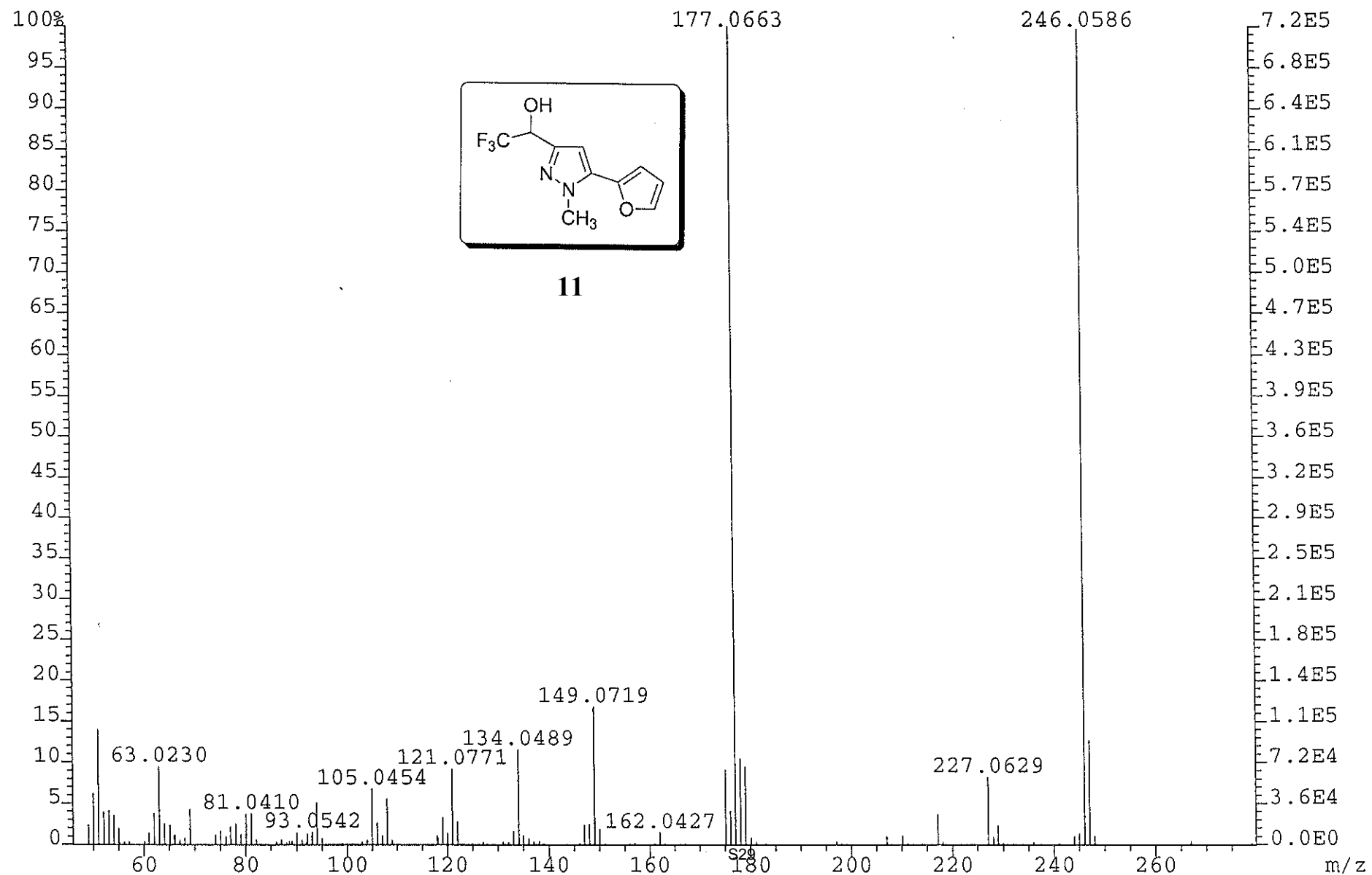
11

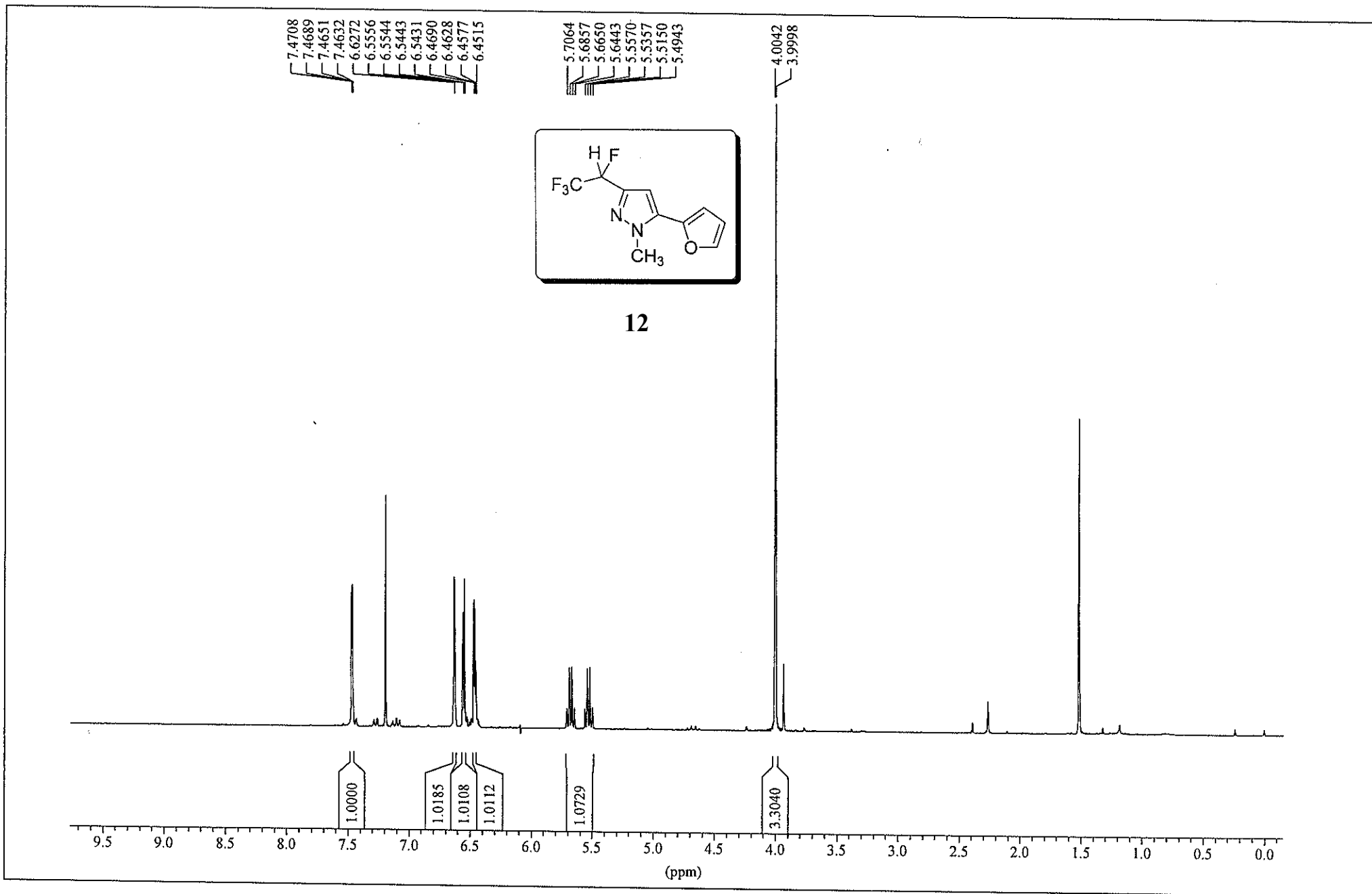
— -78.9534
— -78.9778



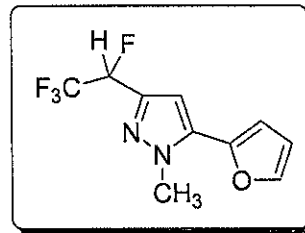
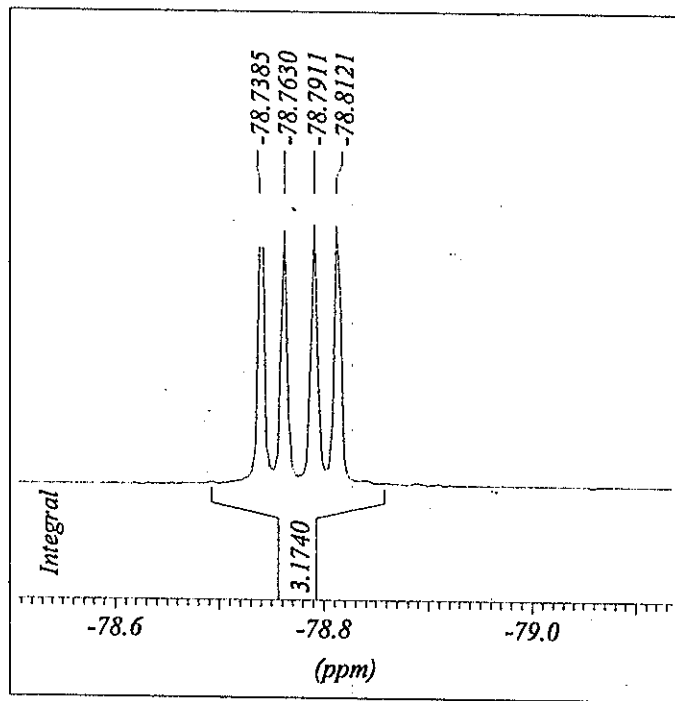


AutoSpecE EI+ Magnet BpM:177 BpI:716032 TIC:3437247 Flags:NORM



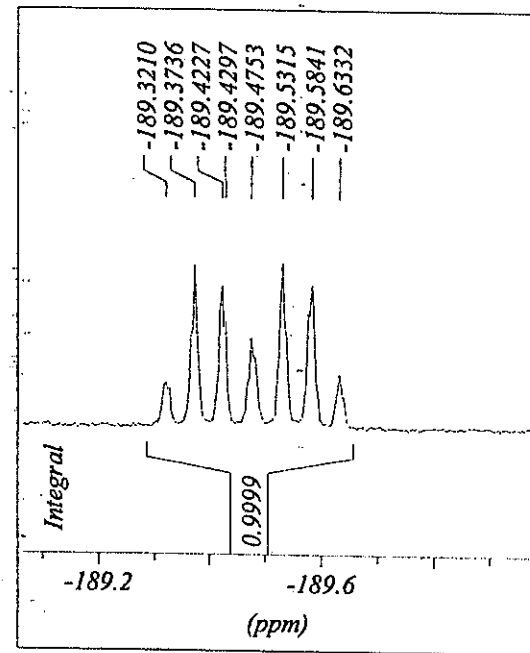


-78.7385
-78.7630
-78.7911
-78.8121



12

-189.3210
-189.3736
-189.4227
-189.4297
-189.4753
-189.5315
-189.5841
-189.6332

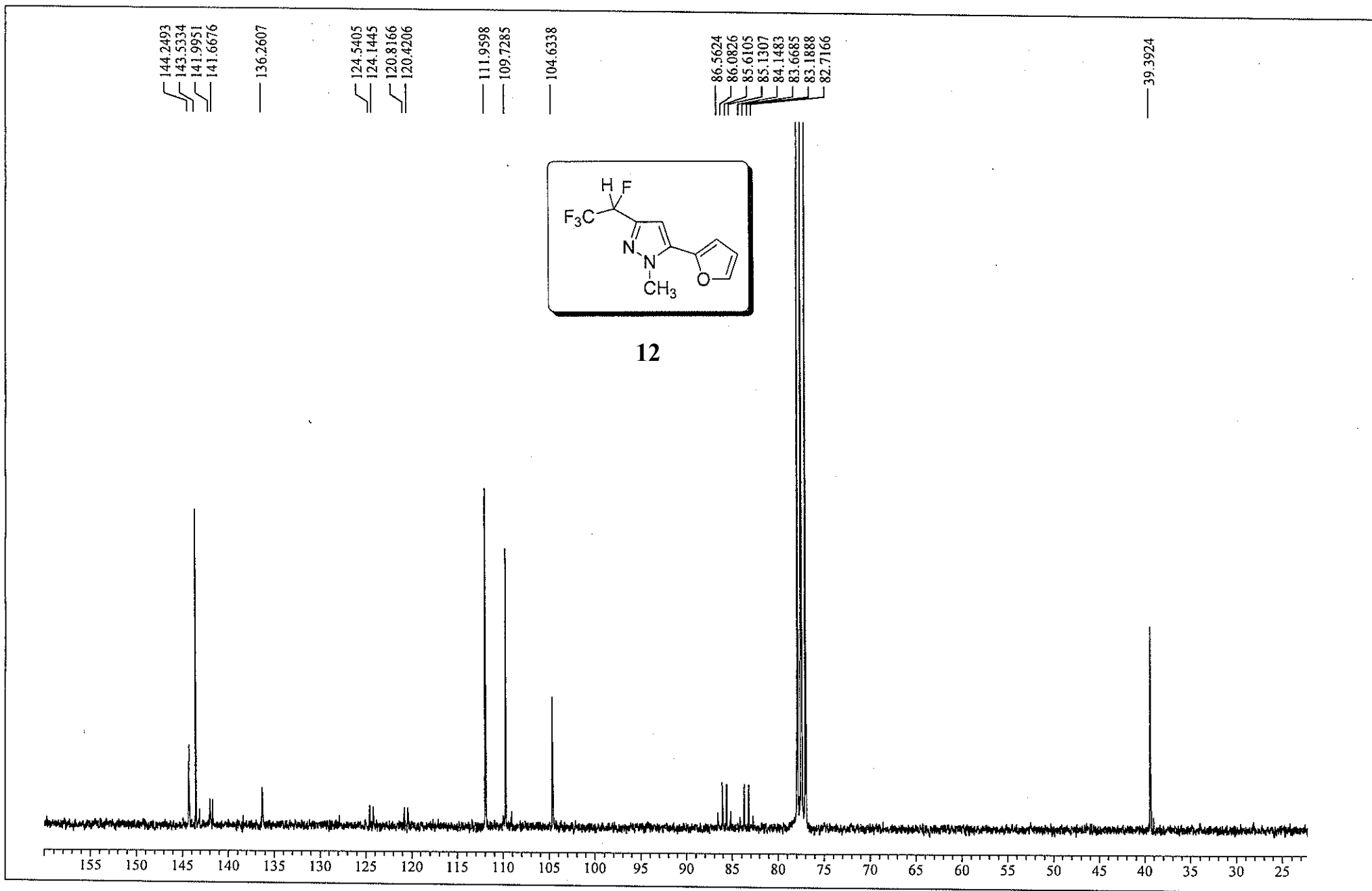


3.1740

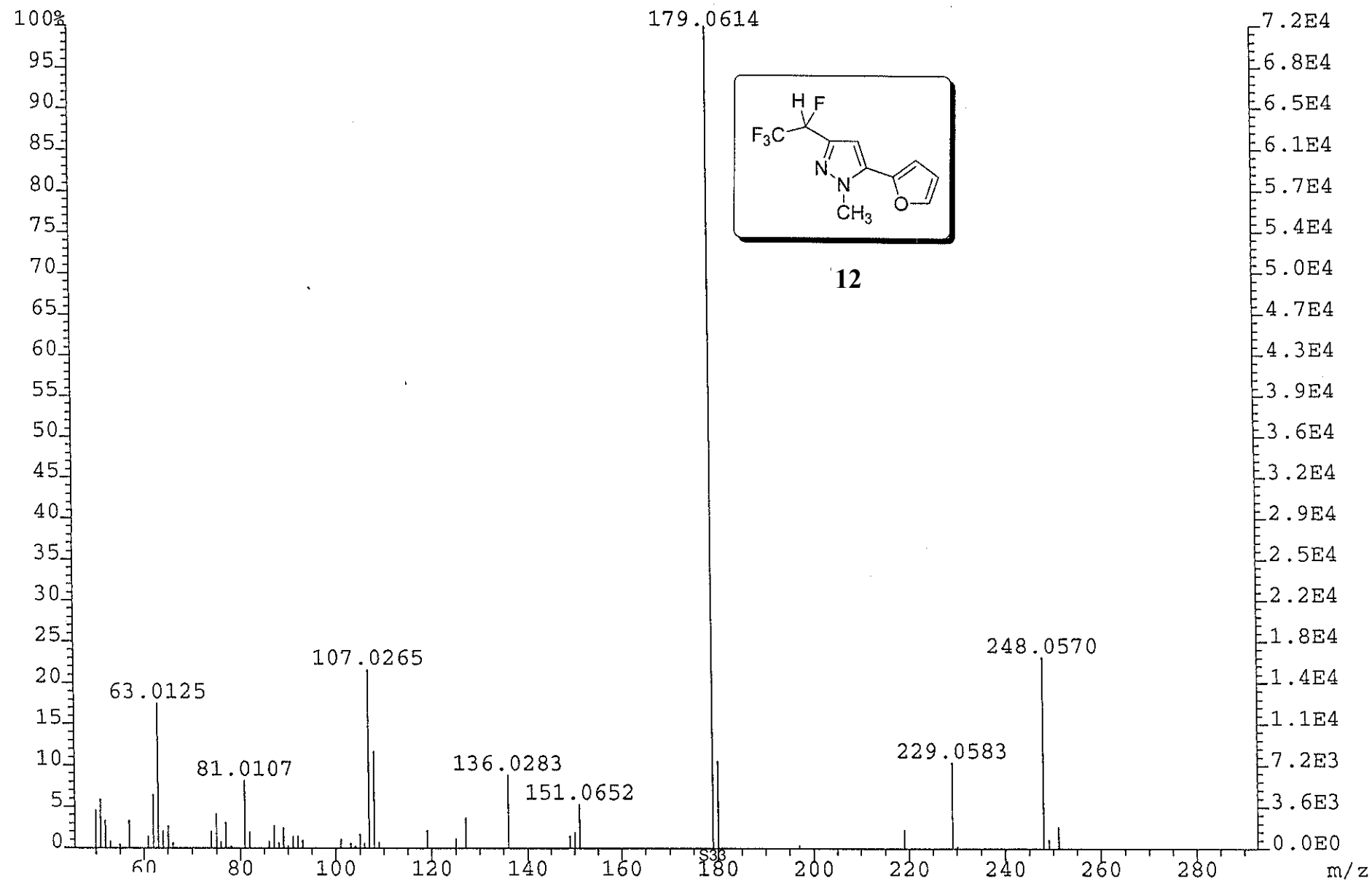
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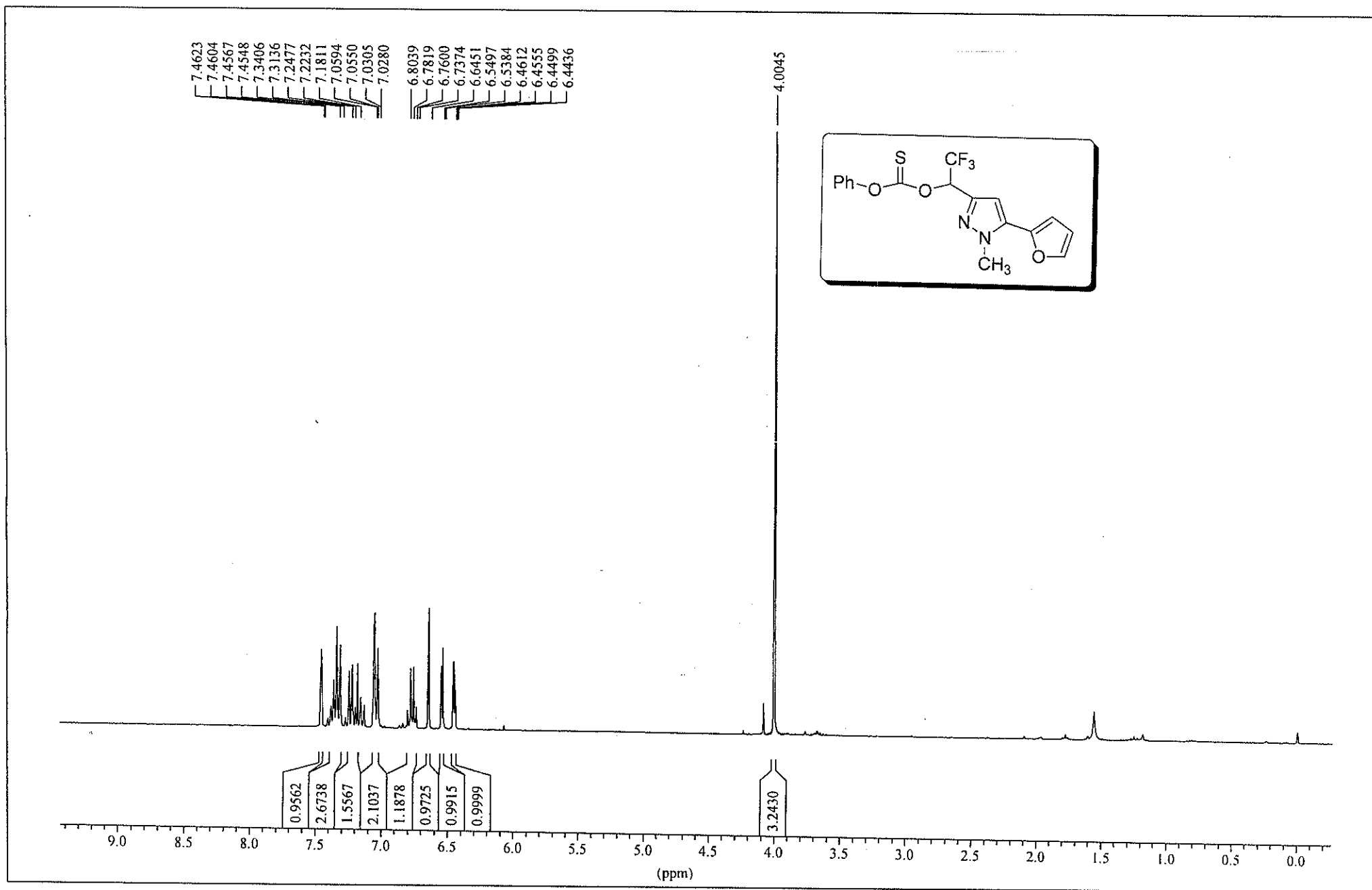
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S31

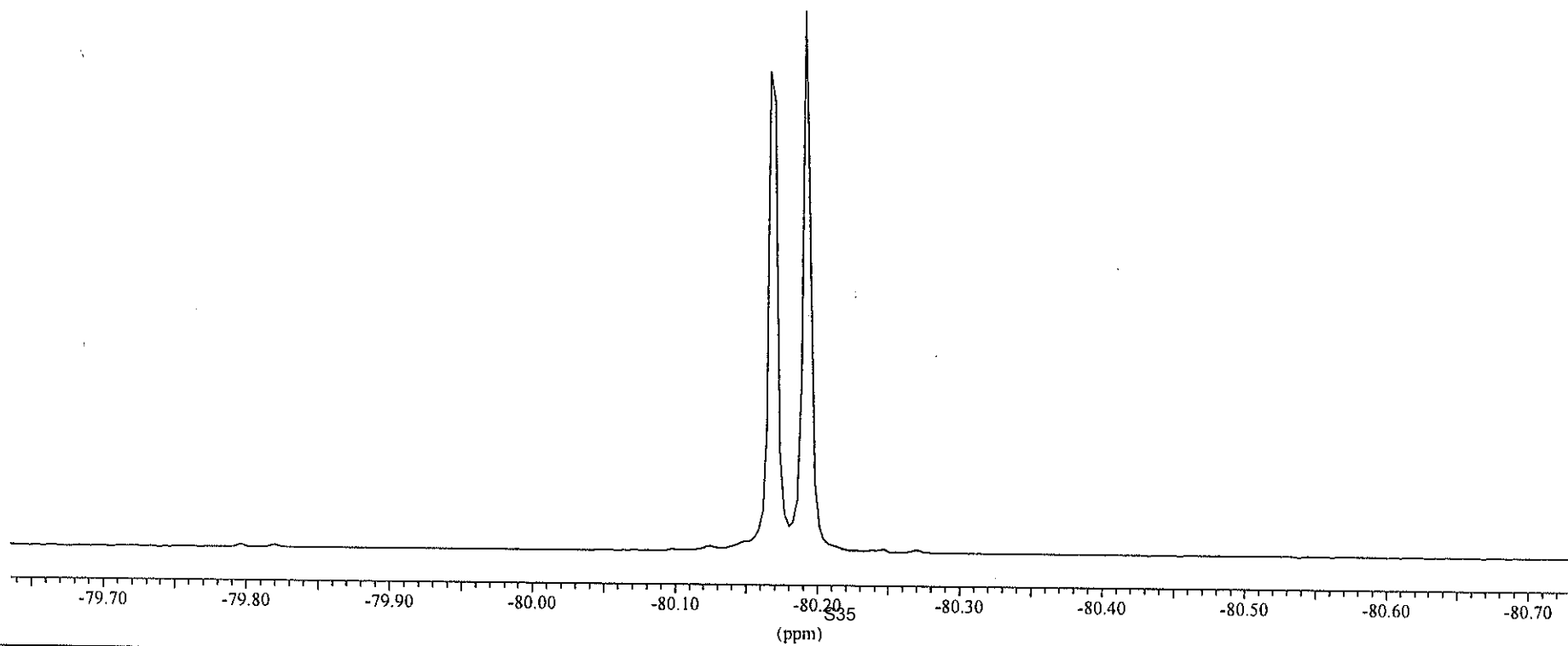
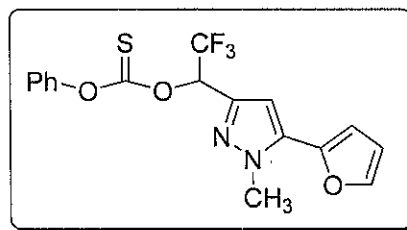


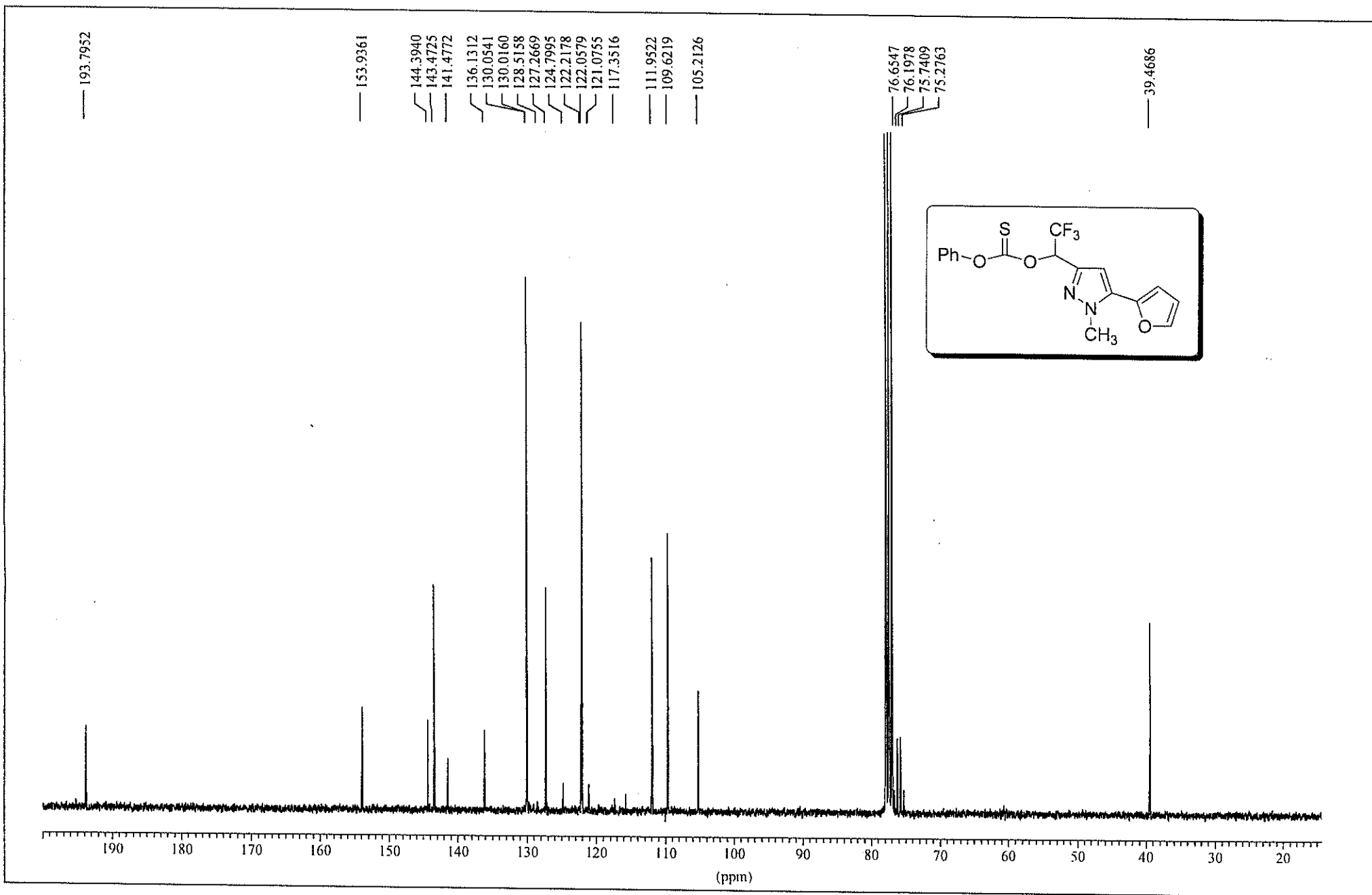
AutoSpecE EI+ Magnet BpM:179 BpI:71776 TIC:217577 Flags:NORM



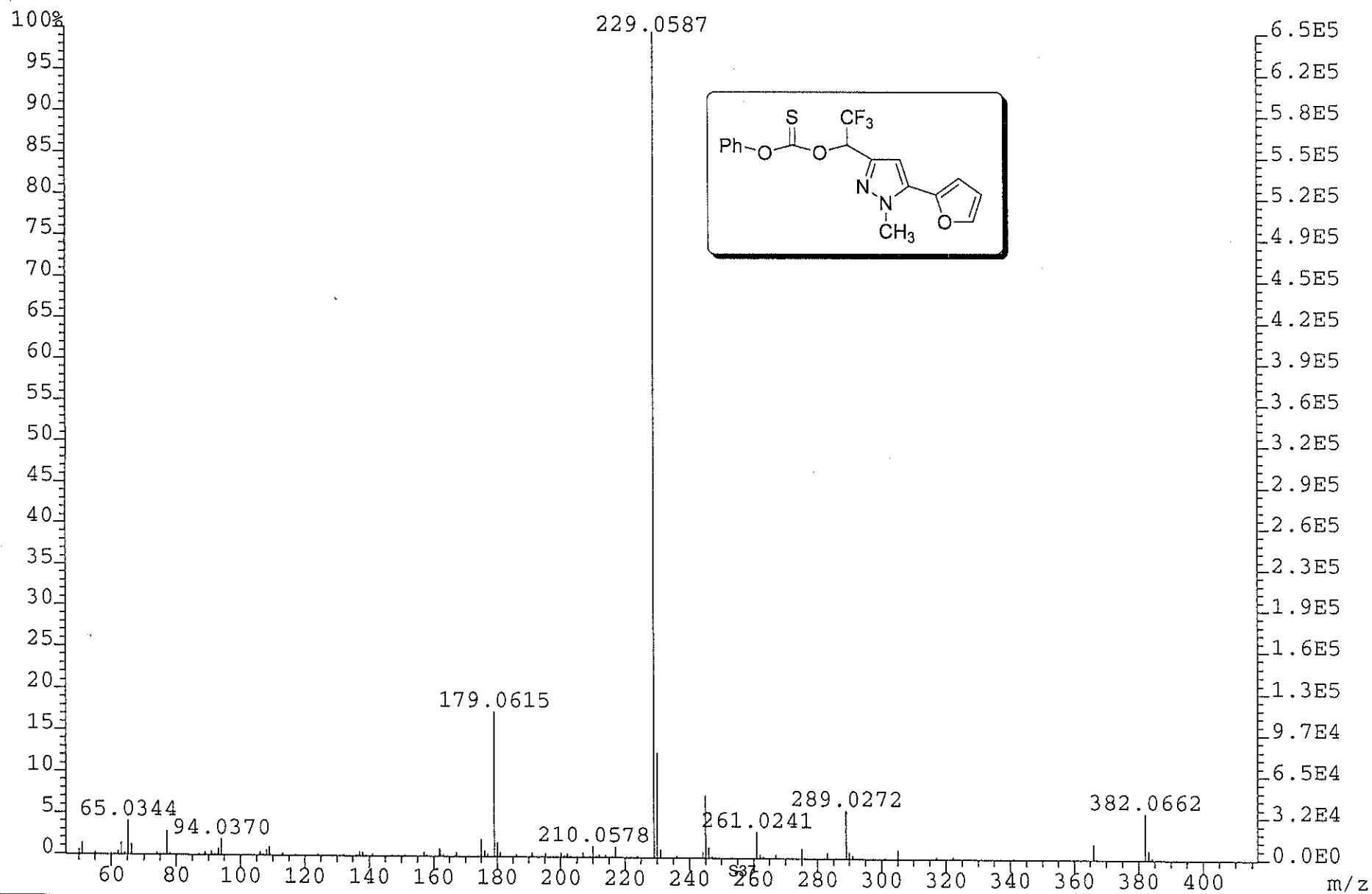


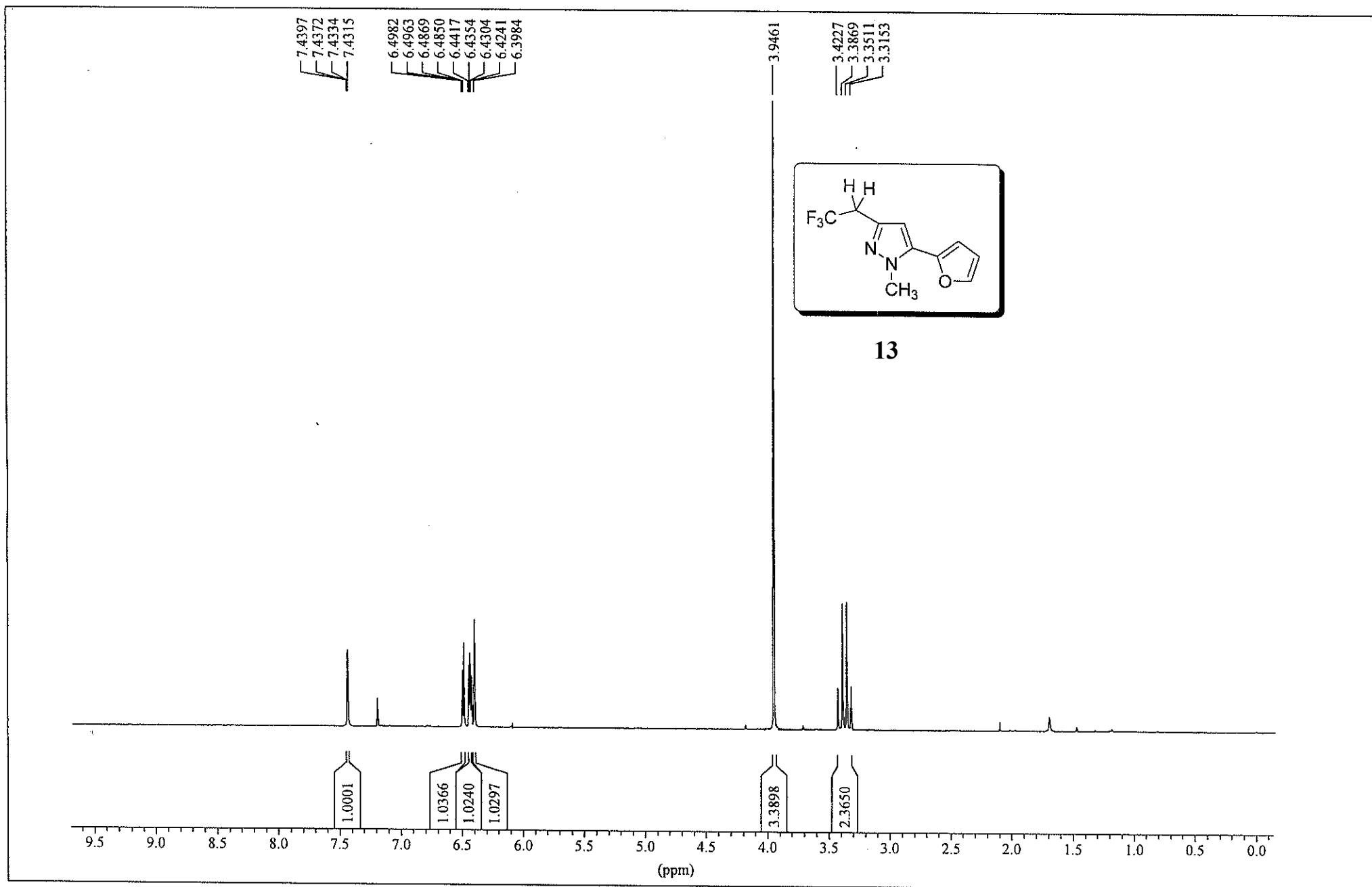
-80.1679
-80.1923



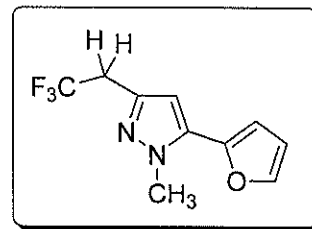


AutoSpecE EI+ Magnet BpM:229 BpI:648704 TIC:1484092 Flags:NORM

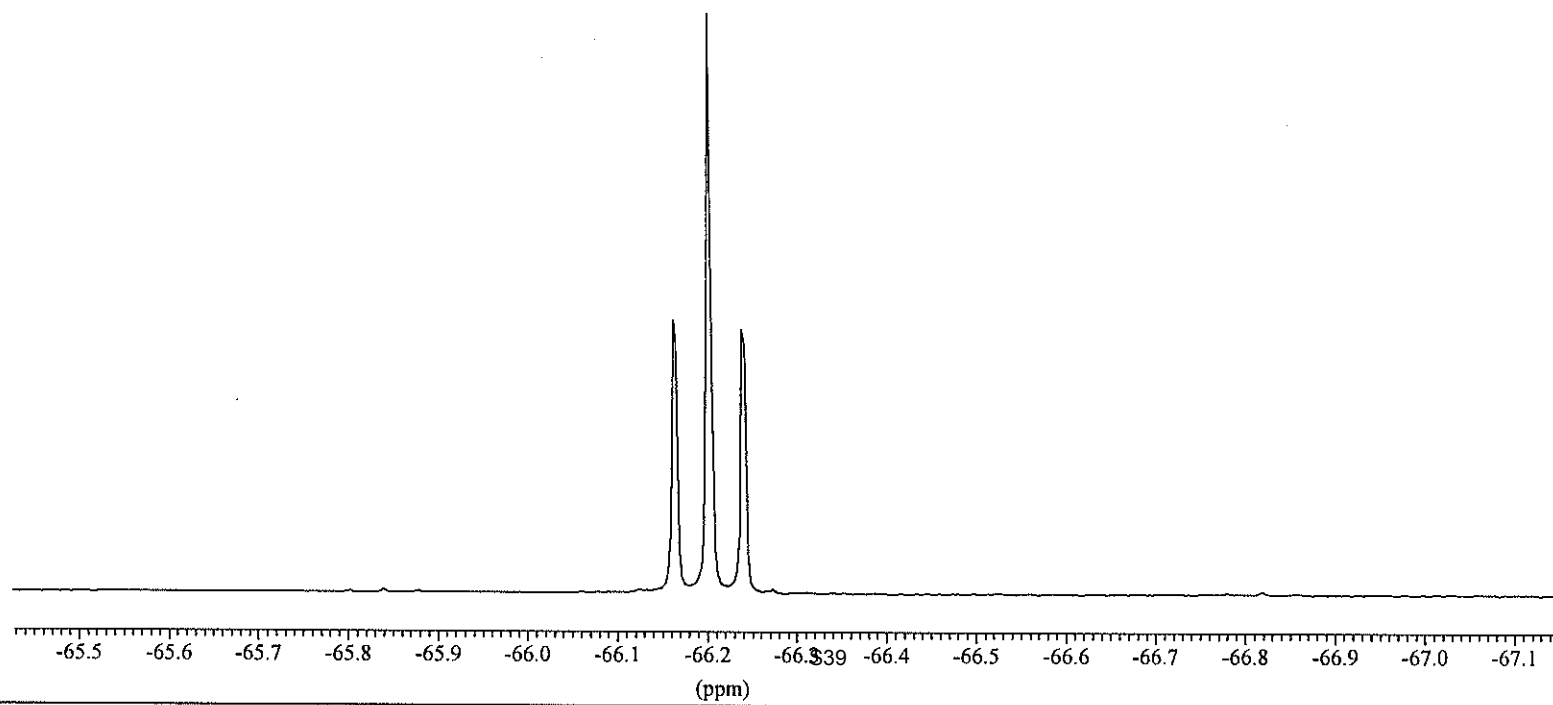


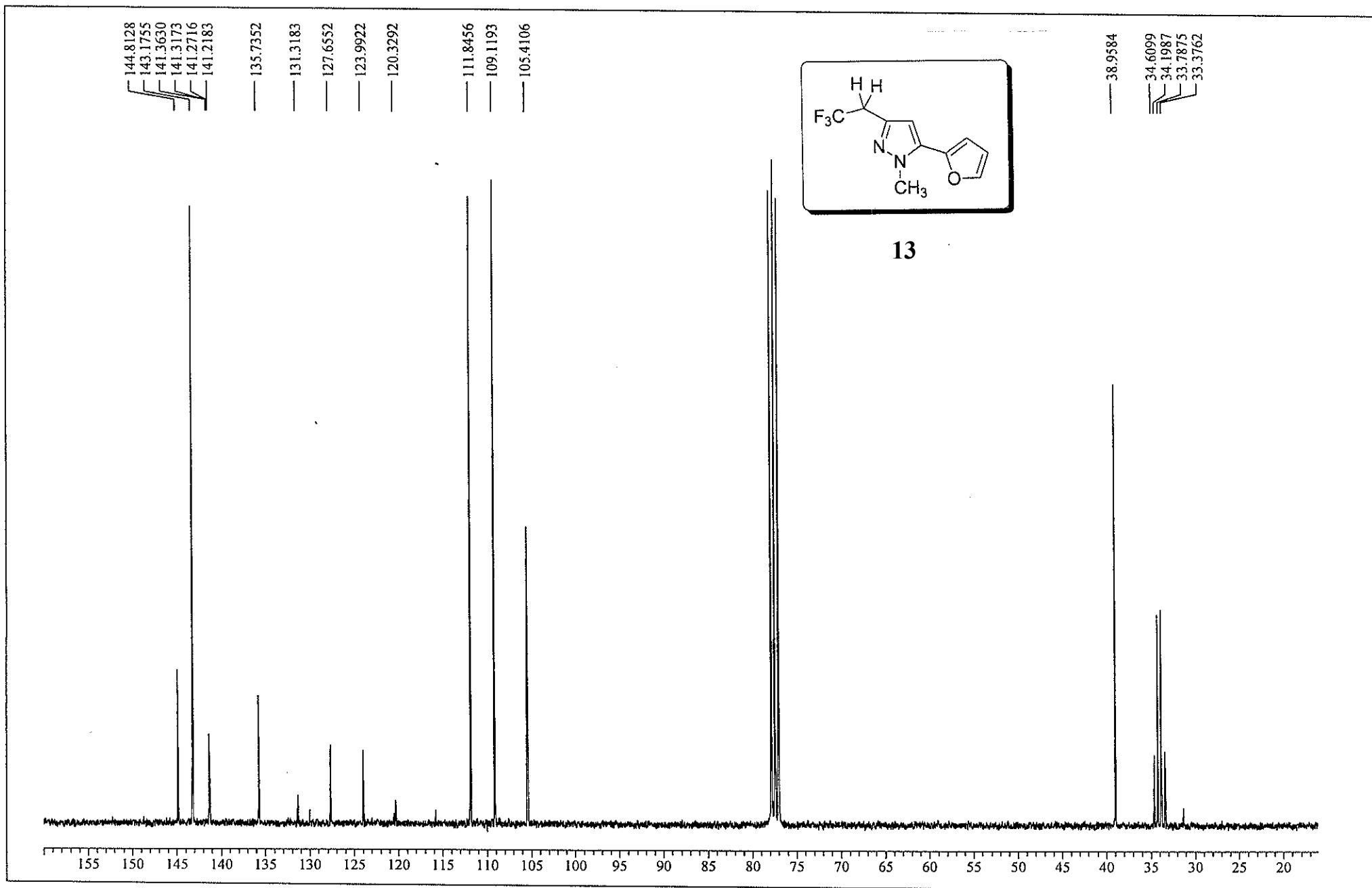


-66.1629
-66.2026
-66.2392

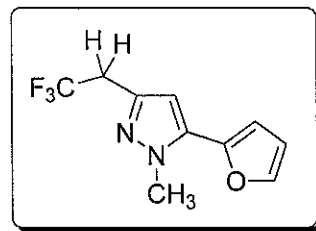
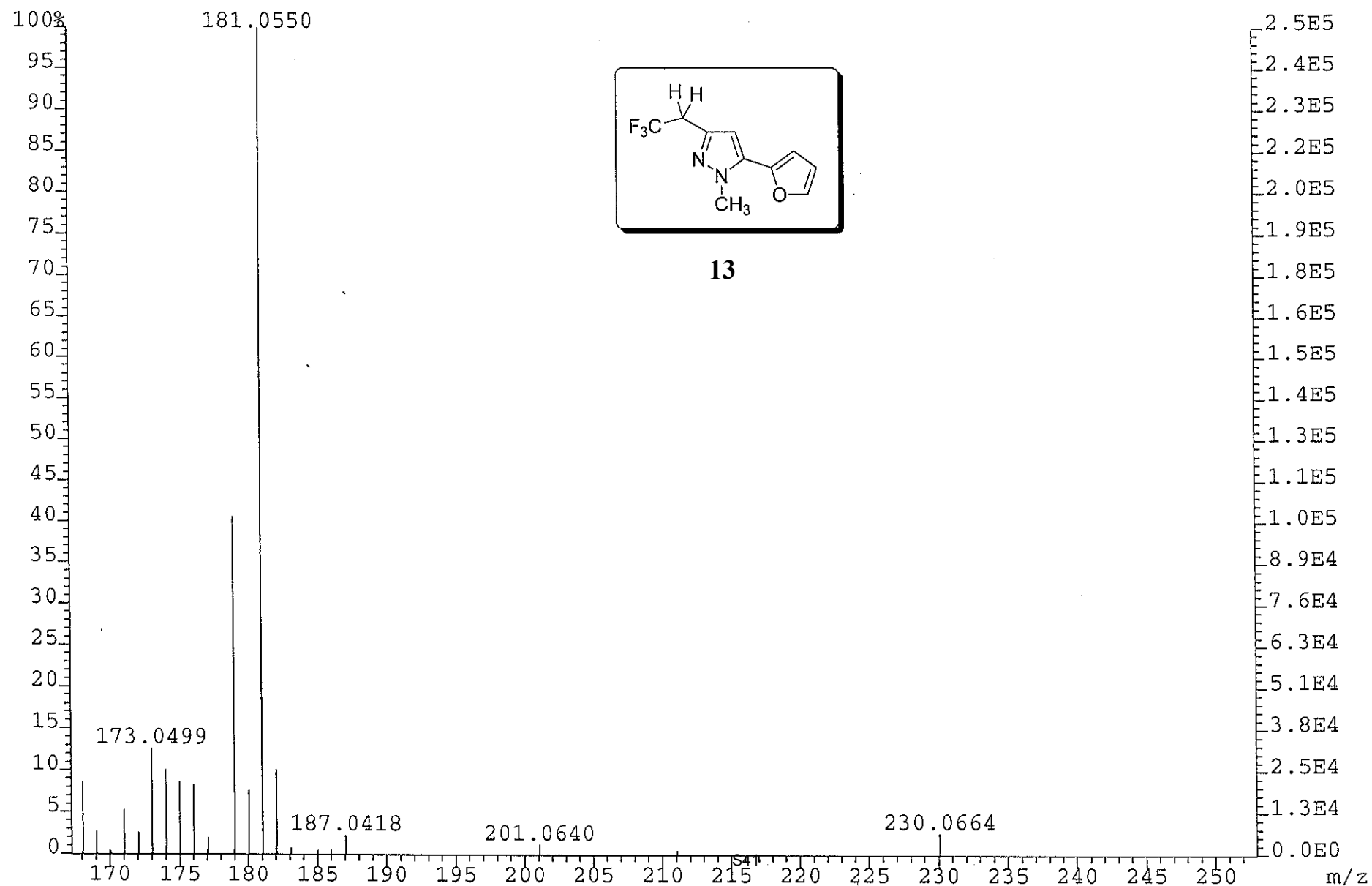


13

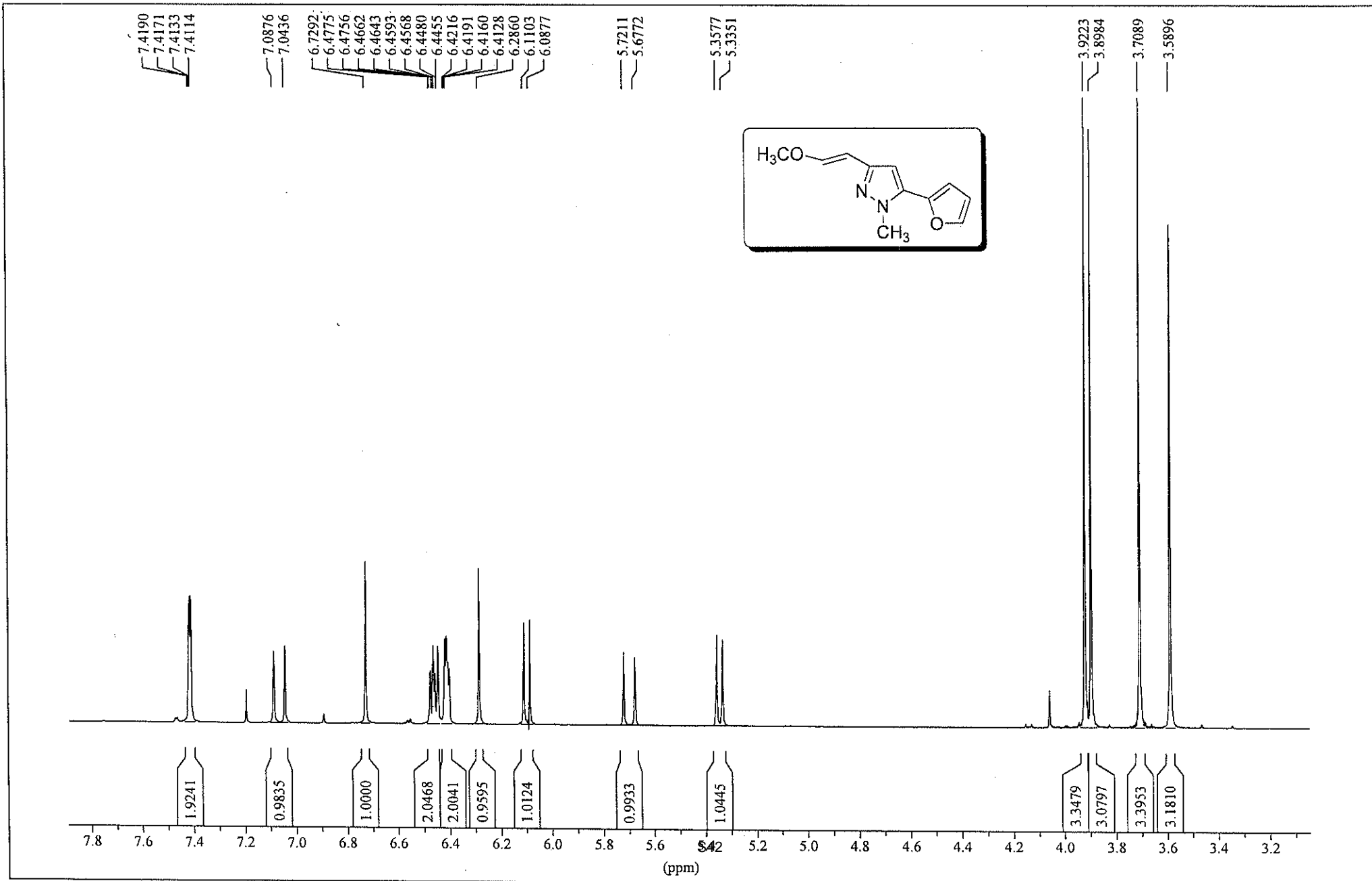


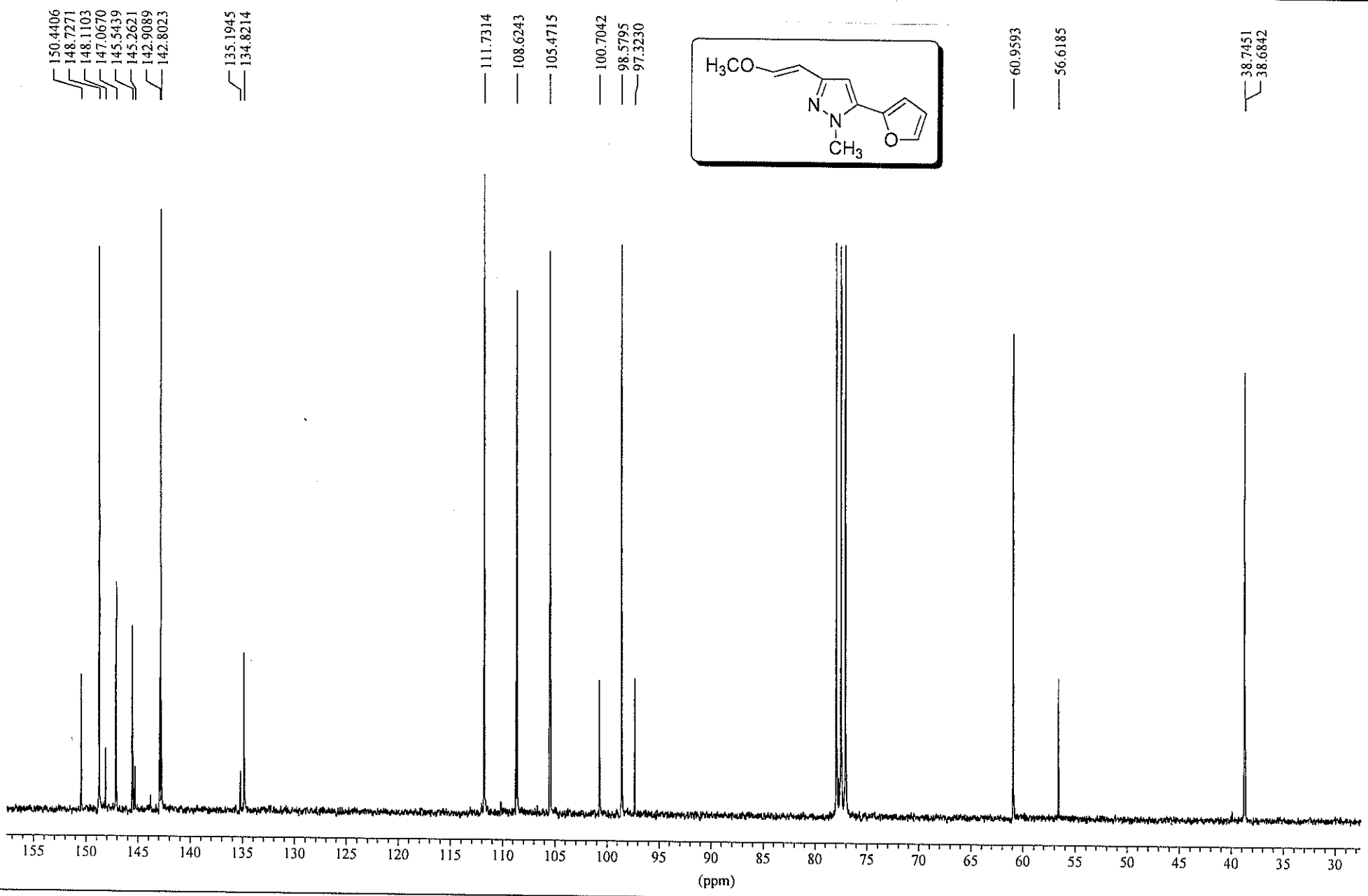
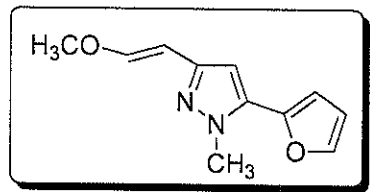


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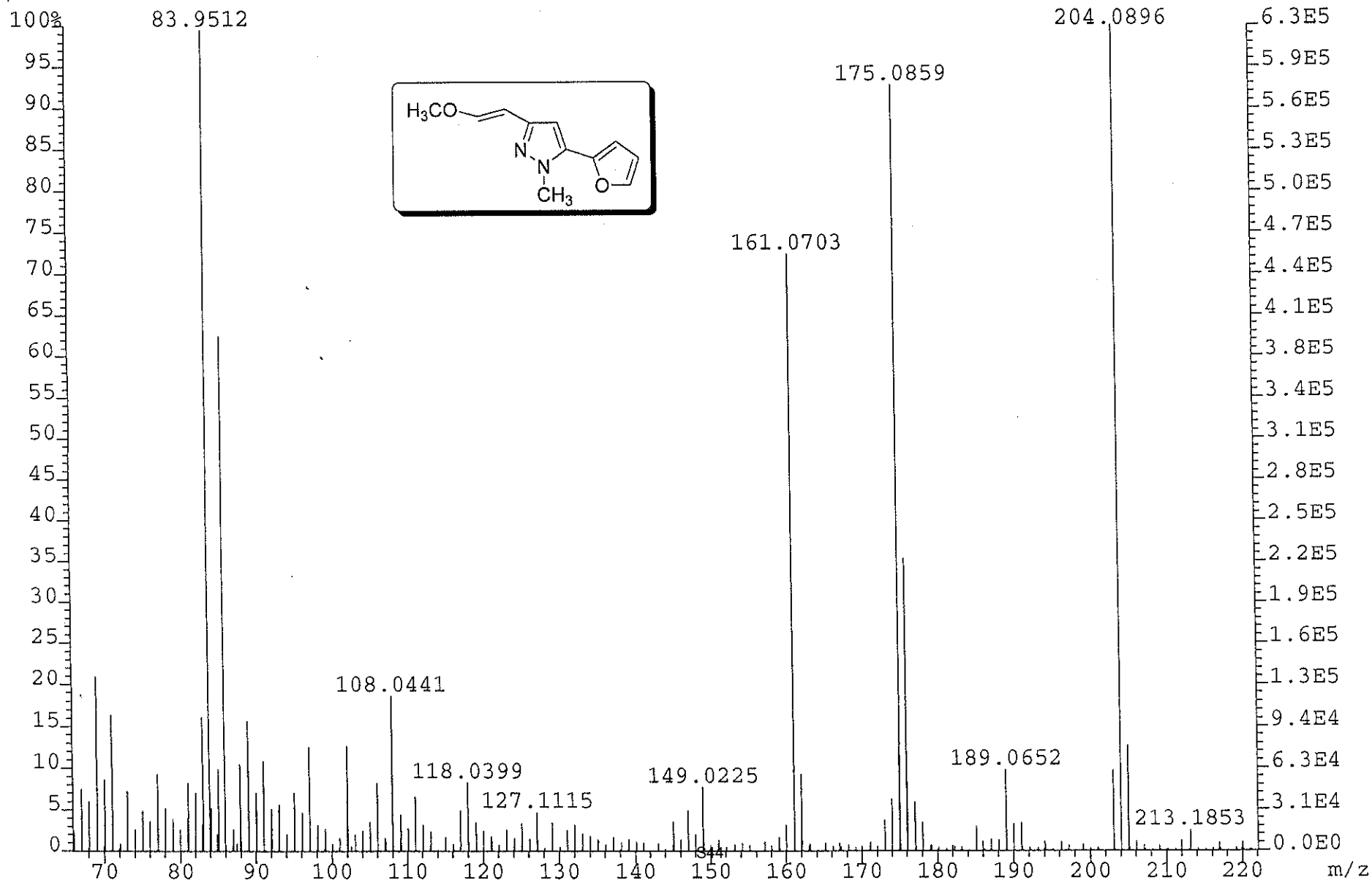


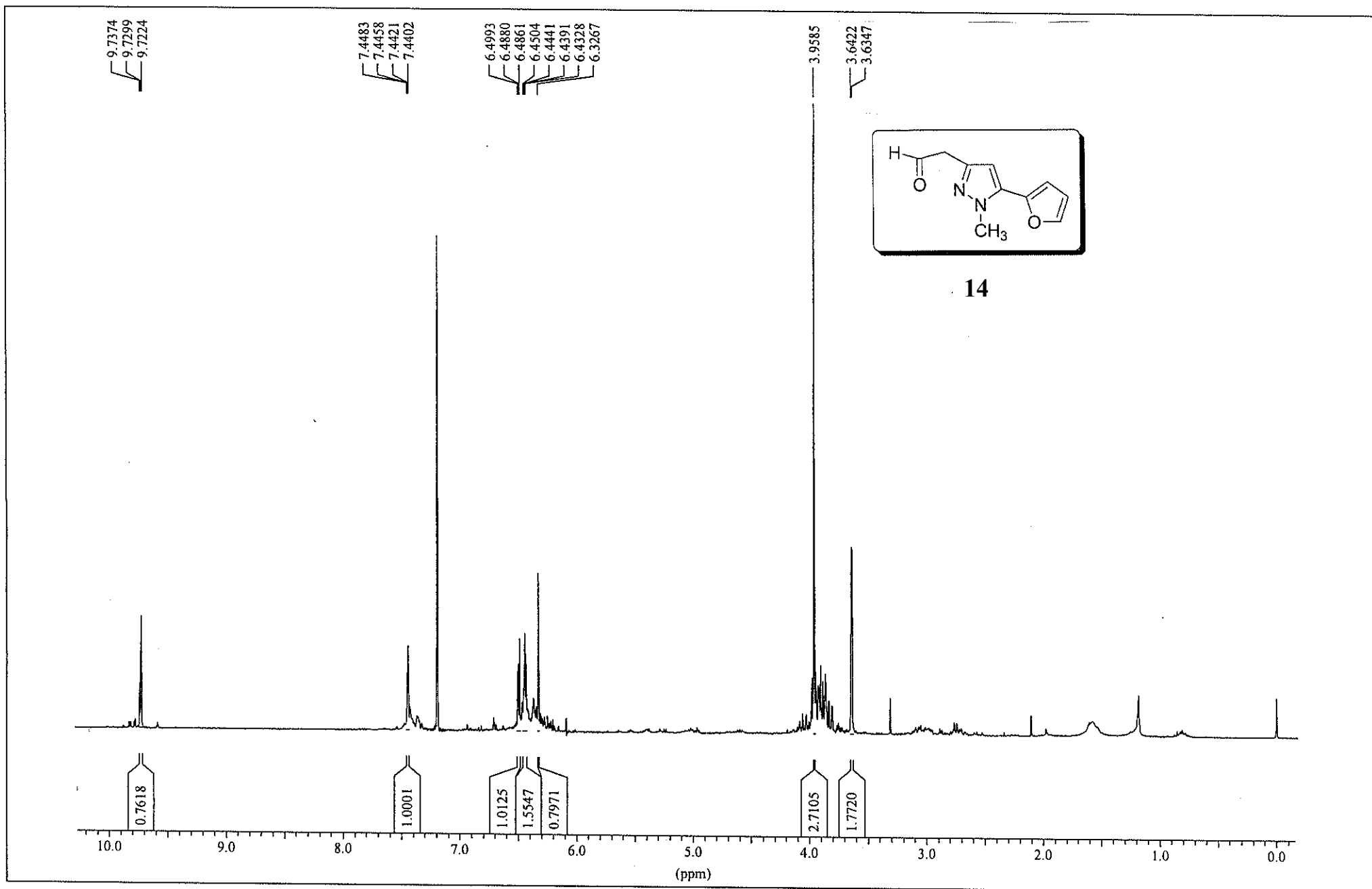
13

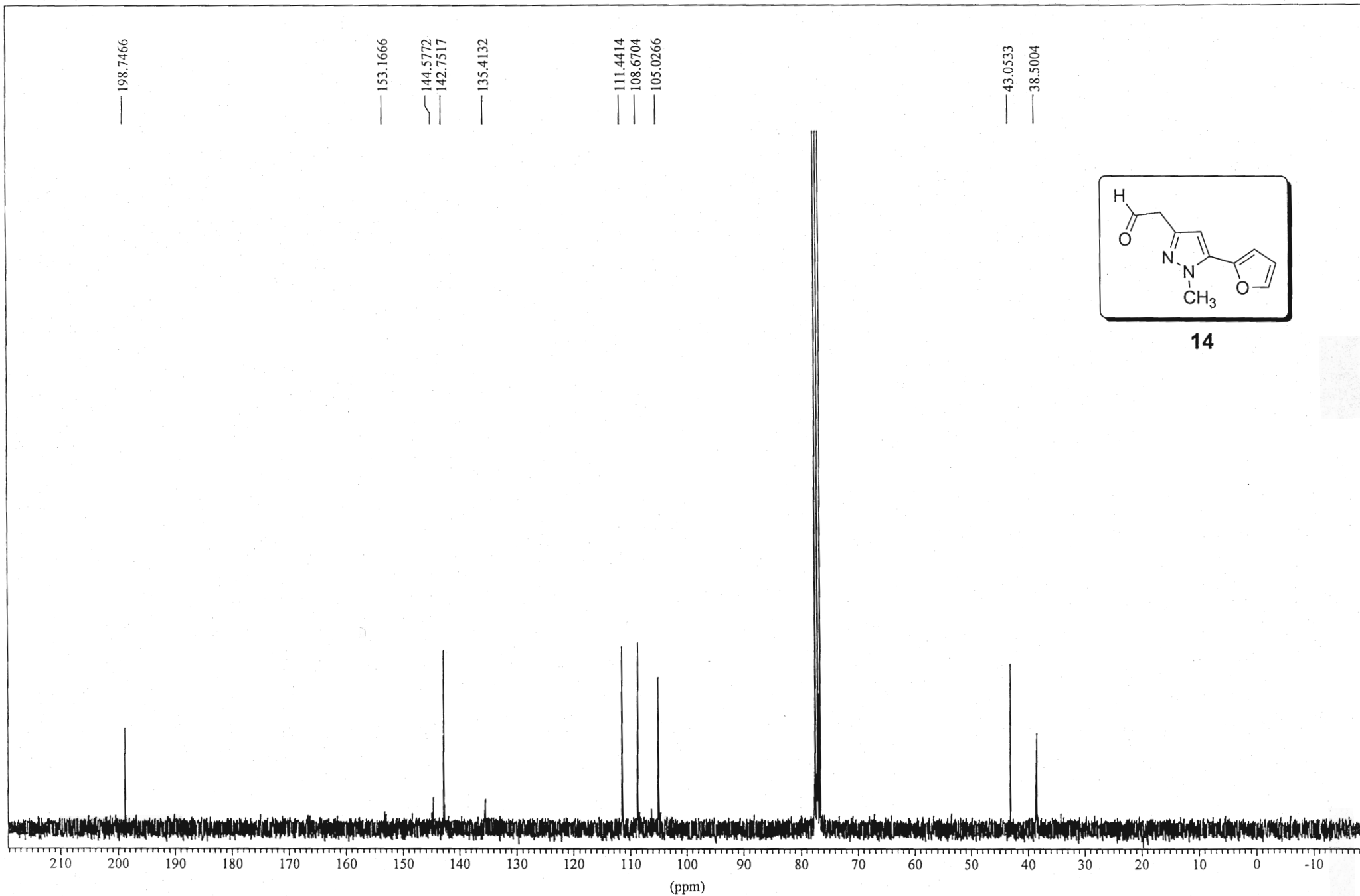




AutoSpecE EI+ Magnet BpM:49 BpI:978688 TIC:11763232 Flags:NORM

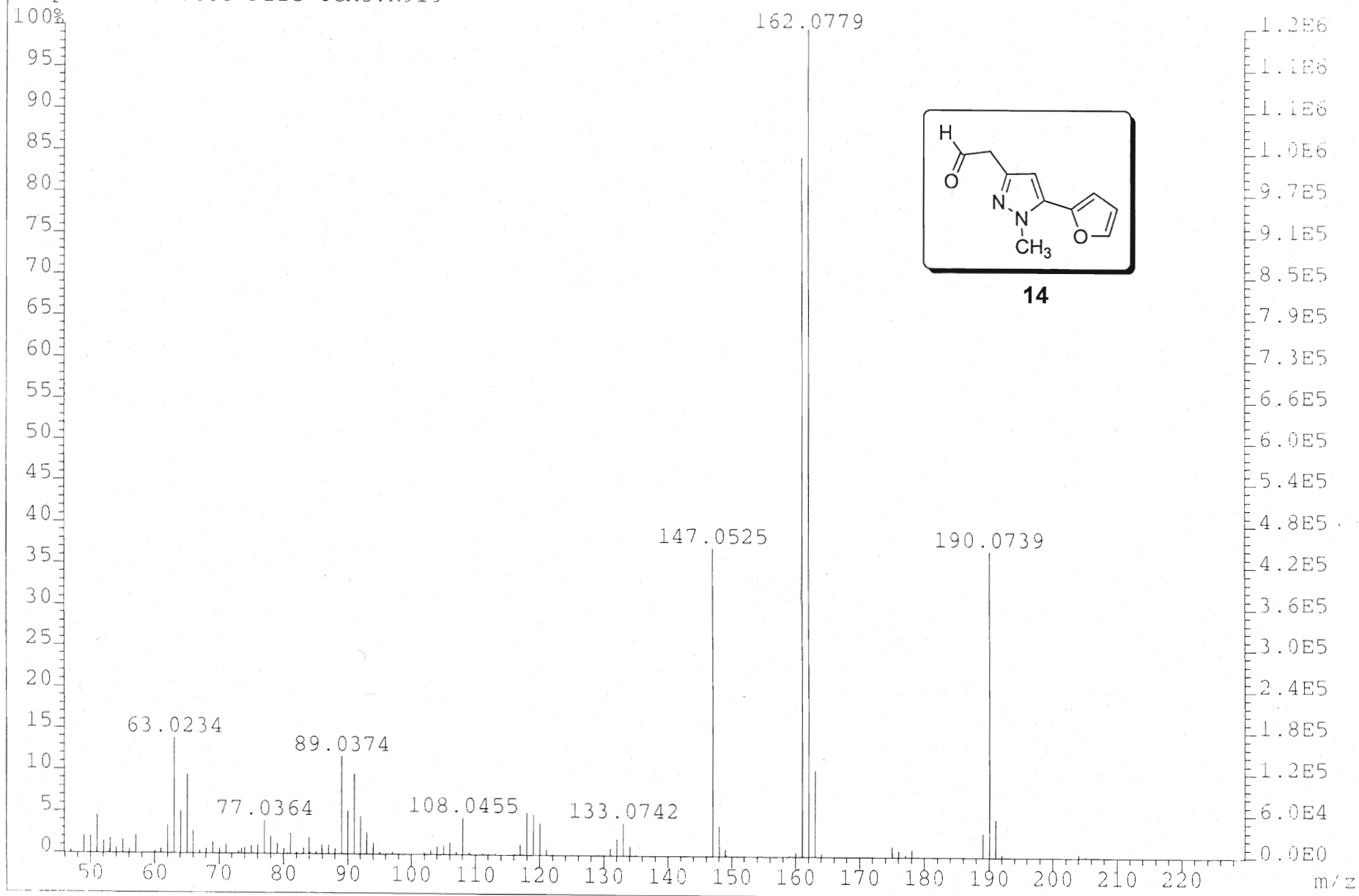


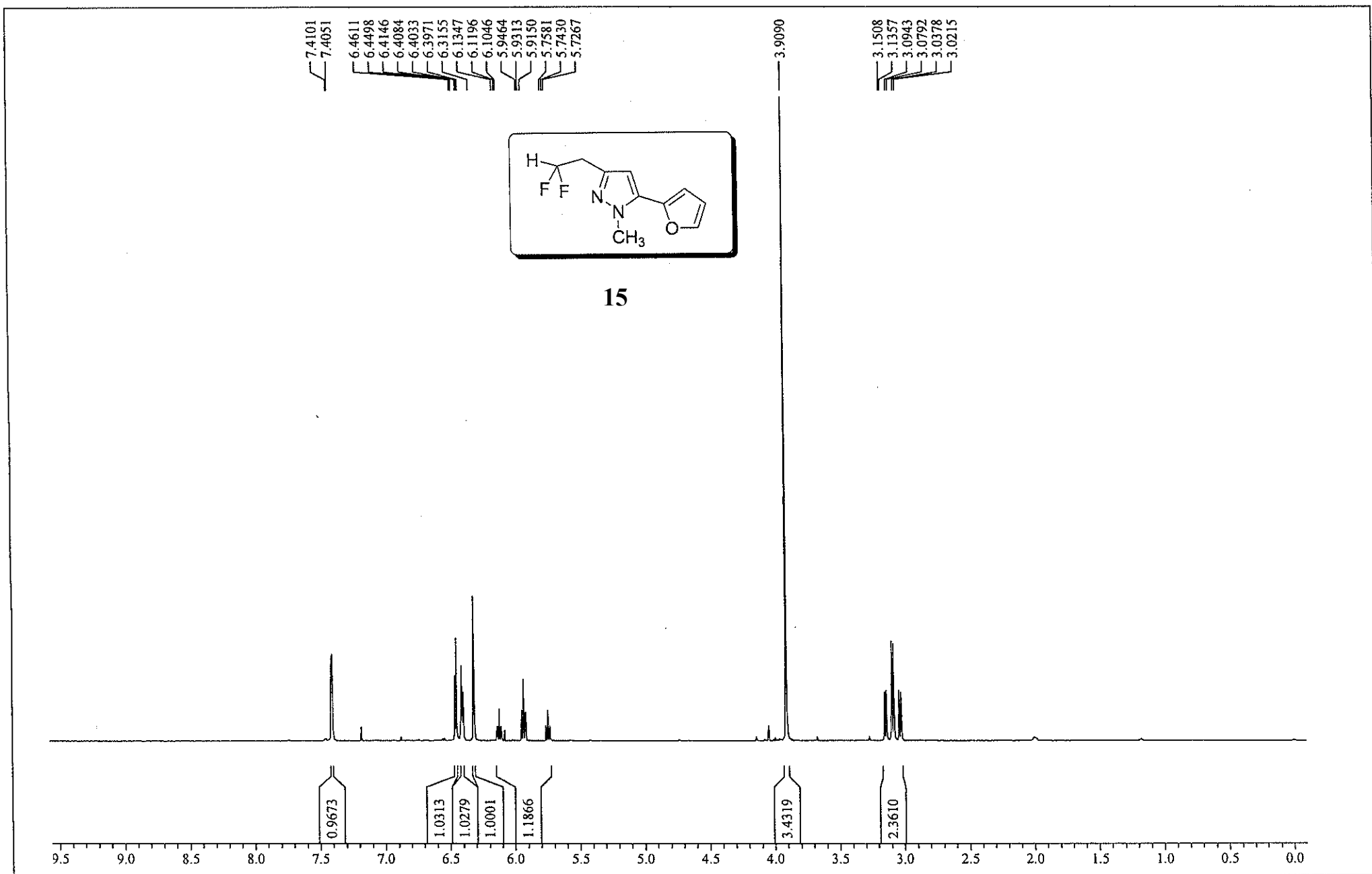


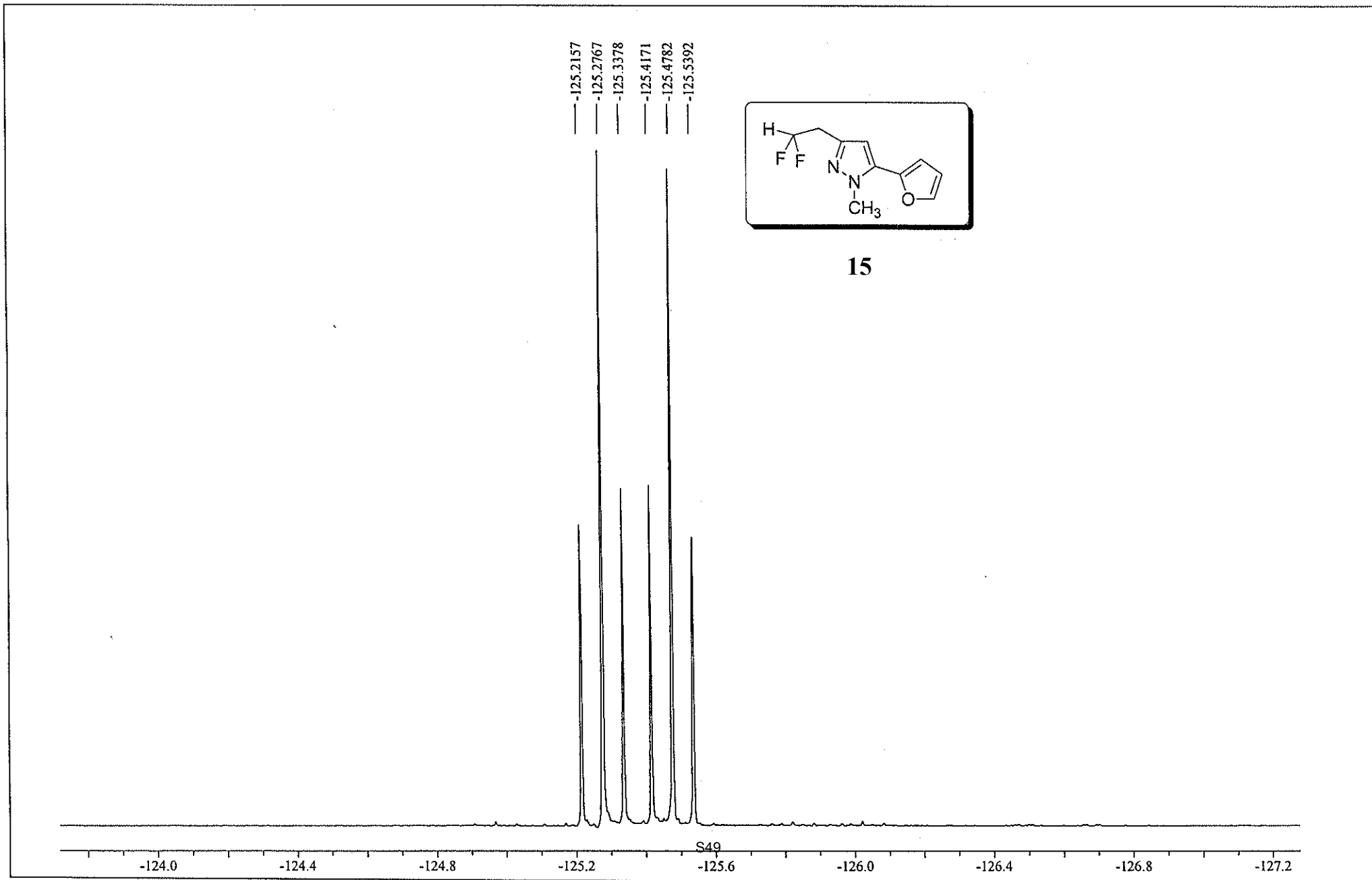


14

File:EI_9_9_7 Ident:16-5_8 Win 200PPM FILT(EXCL,ALL) Acq: 9-SEP-2008 10:55:57 Cal:EI_9_9_7
AutoSpecE EI+ Magnet BpM:162 BpI:1208832 TIC:5464108 Flags:NORM
Sample Text:test File Text:R913





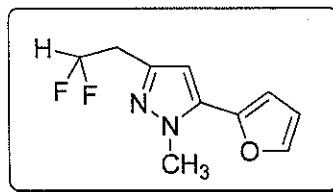


144.9864
143.5243
143.4329
143.3415
143.0978
143.0826

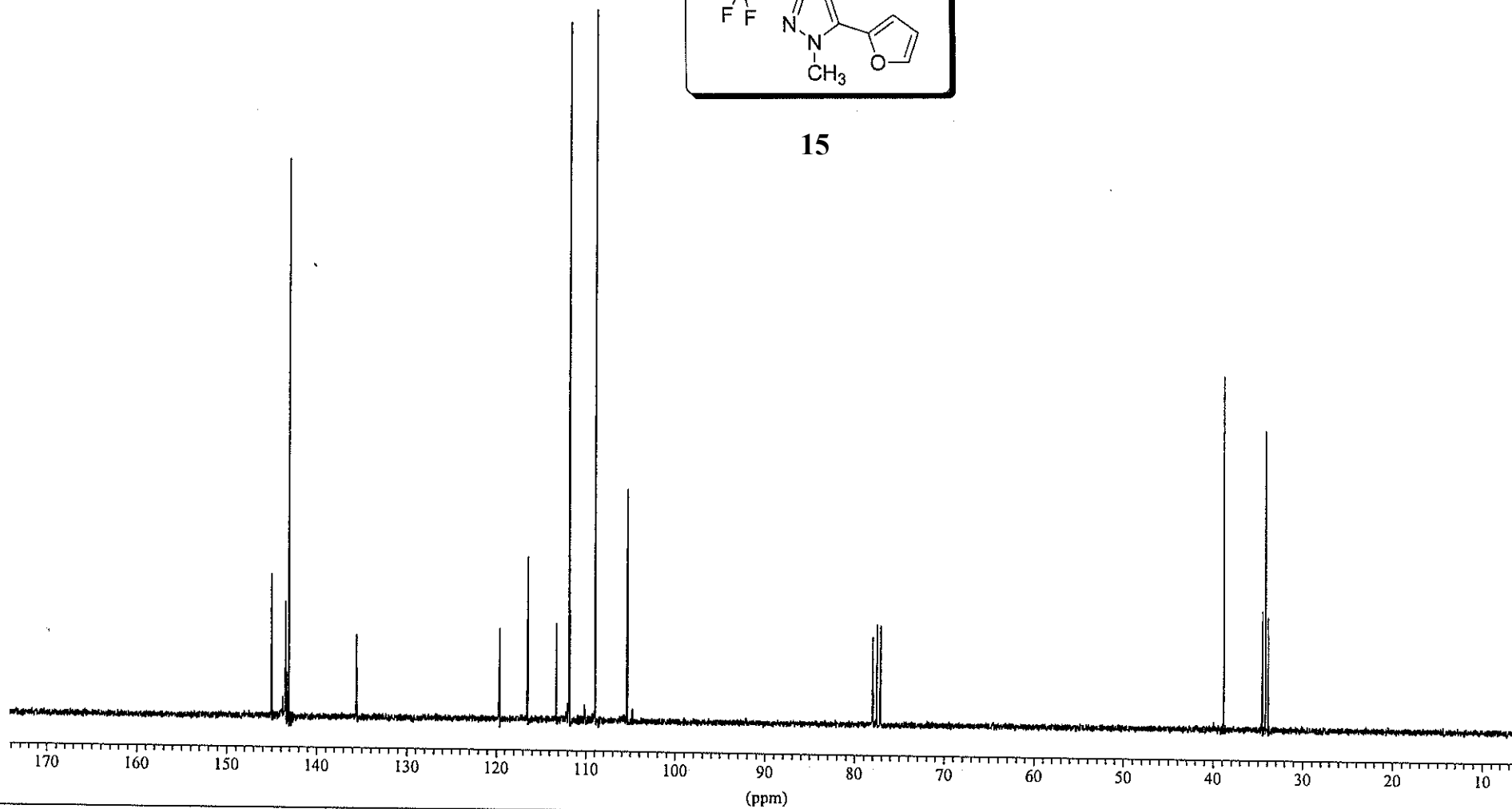
135.5509

119.6347
116.4514
113.2605
111.8136
108.9502
105.3557

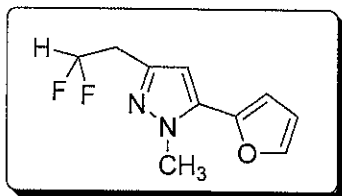
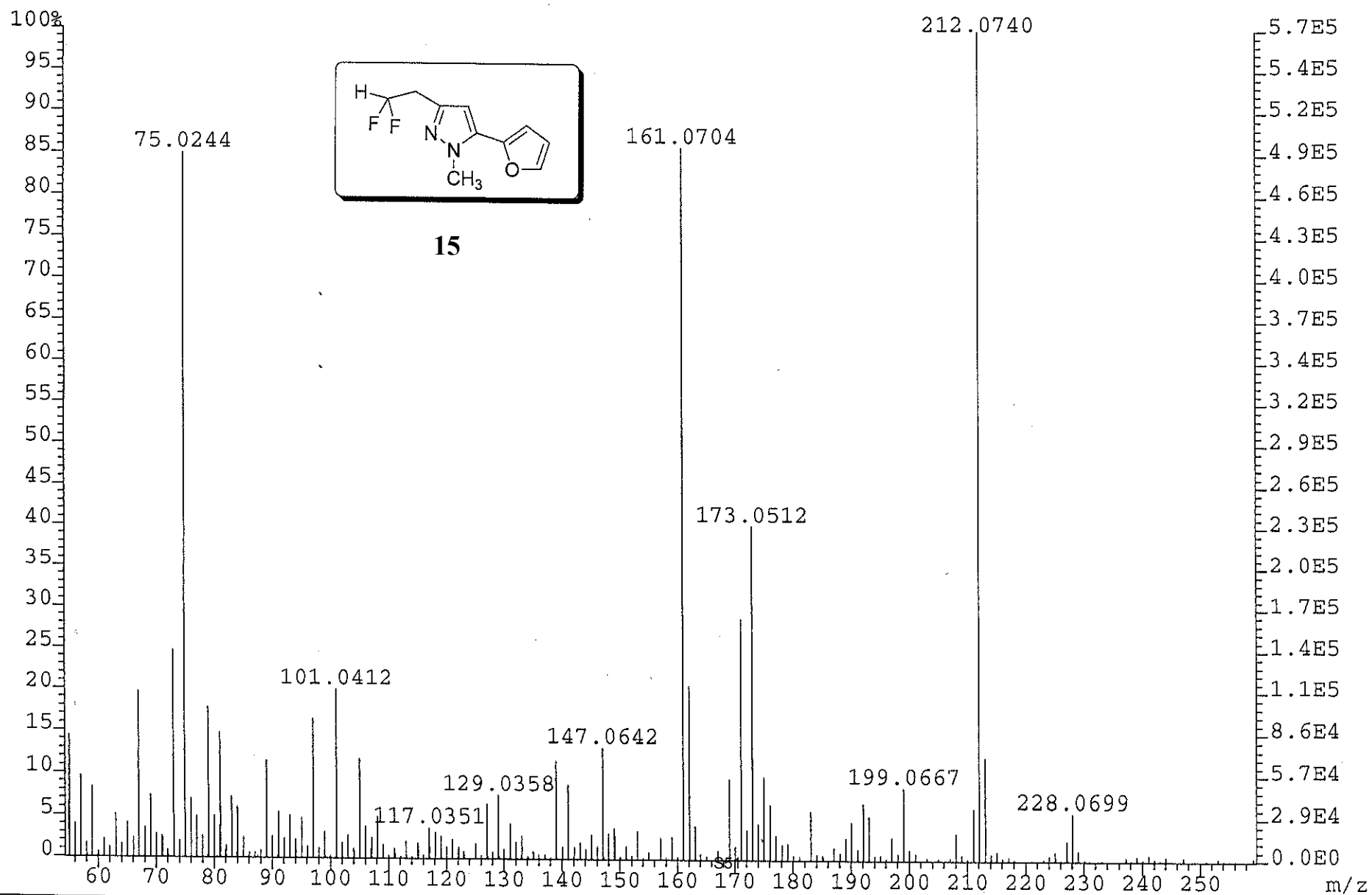
38.7969
34.4866
34.1819
33.8773



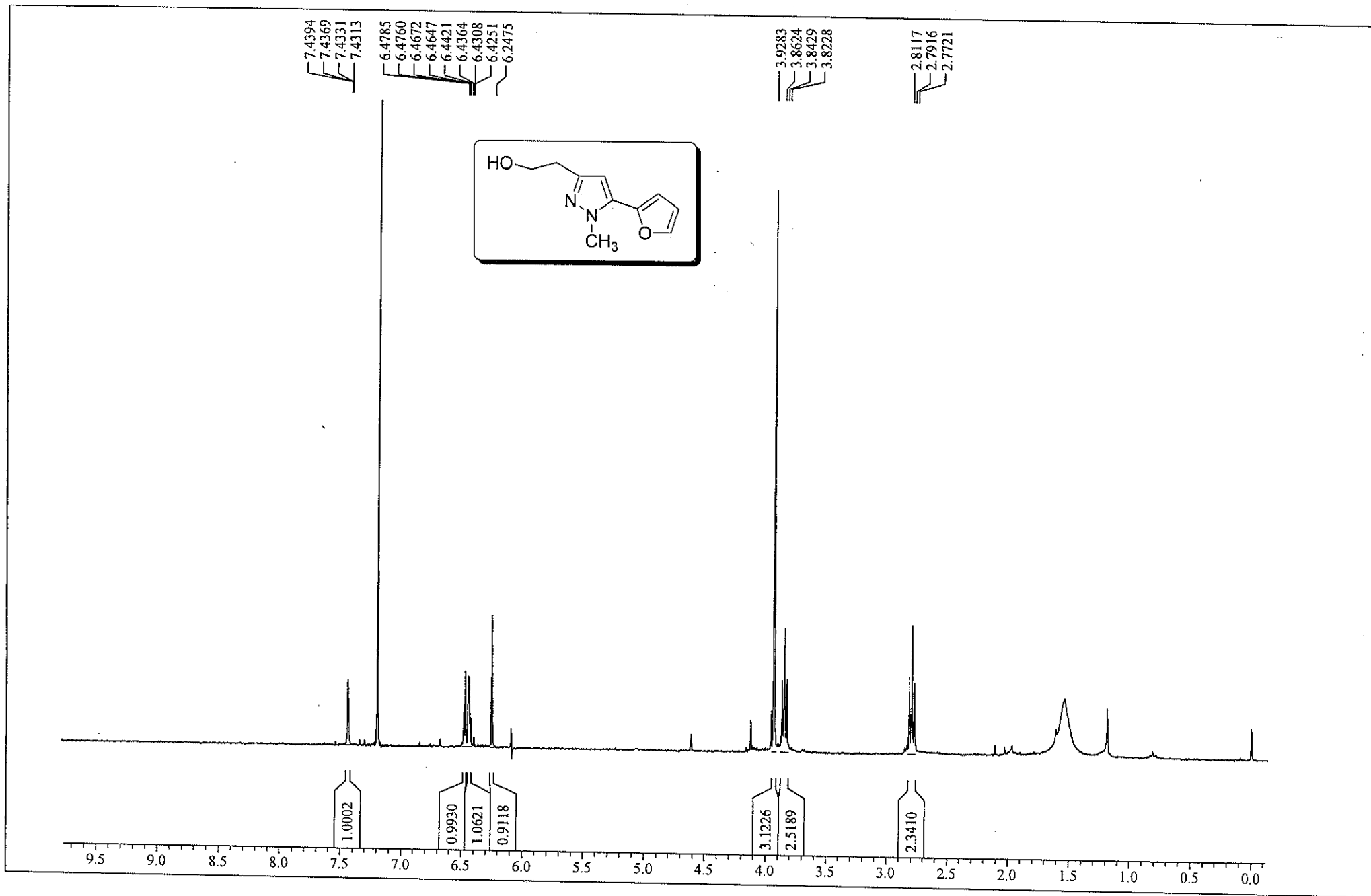
15

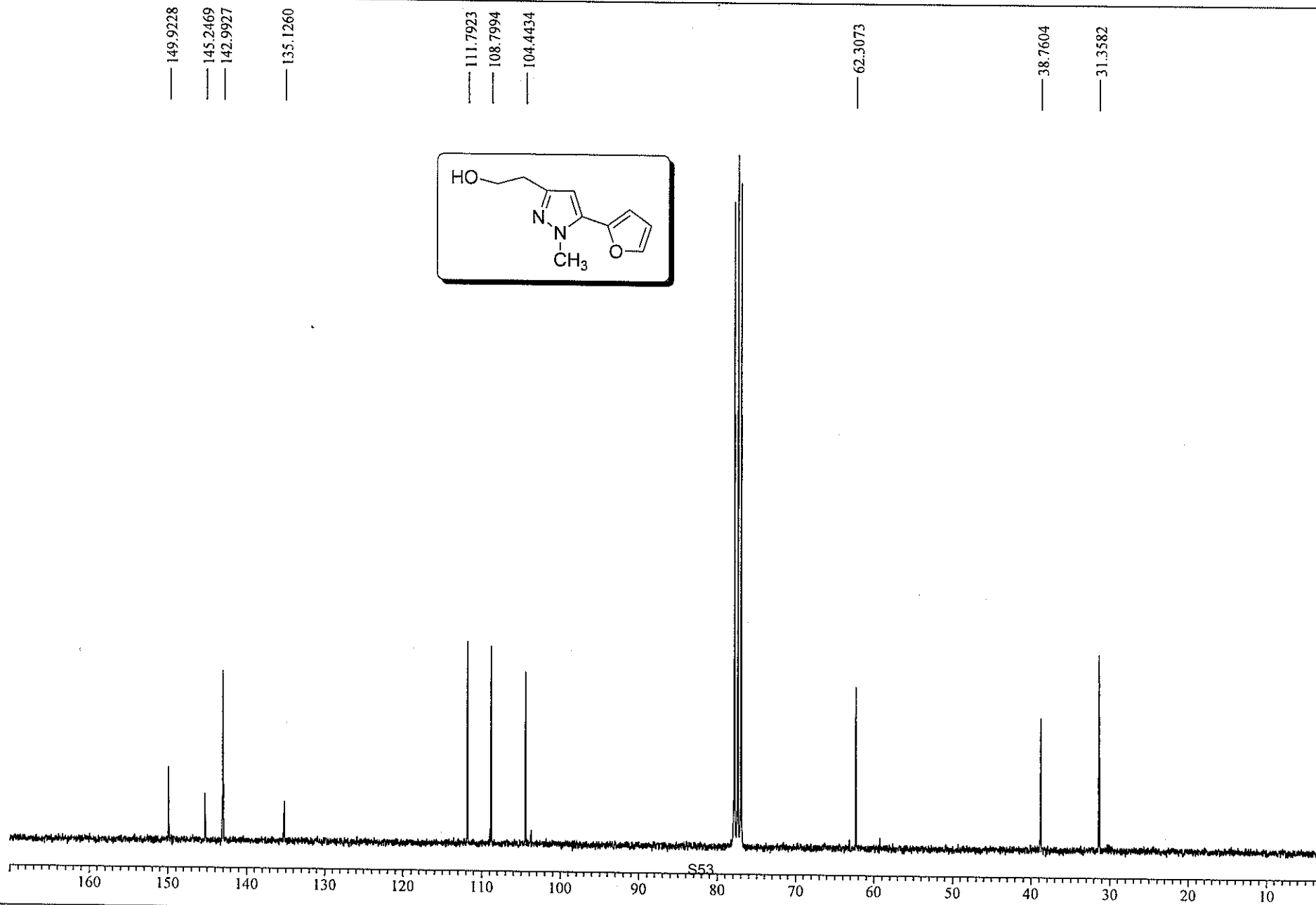
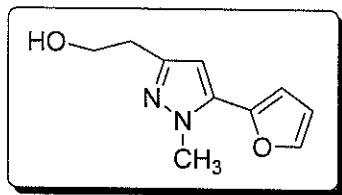


AutoSpecE EI+ Magnet BpM:212 BpI:573440 TIC:5997909 Flags:NORM

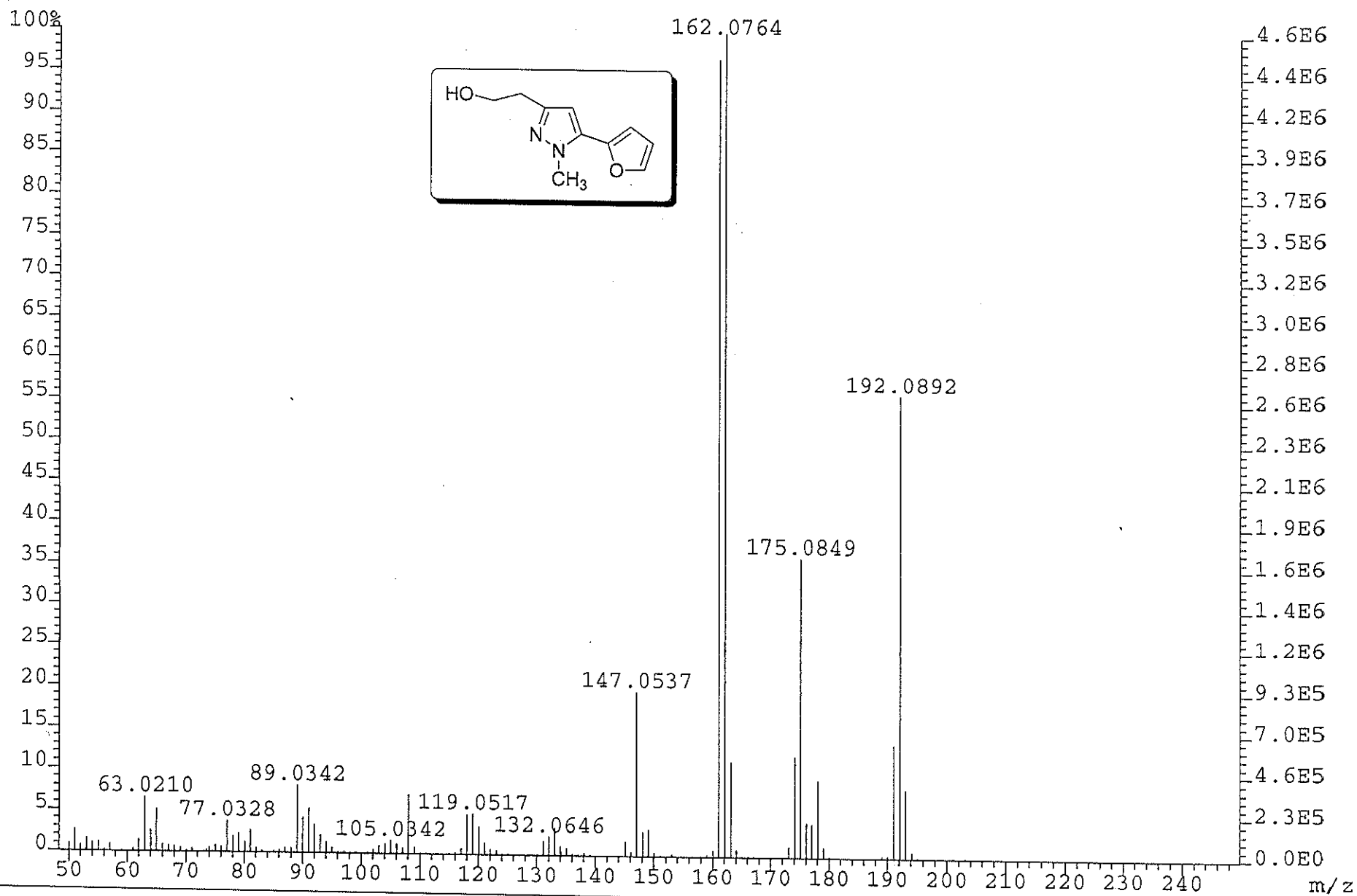


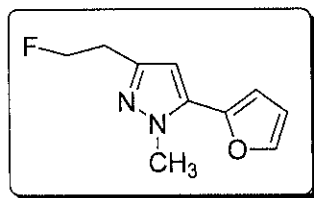
15



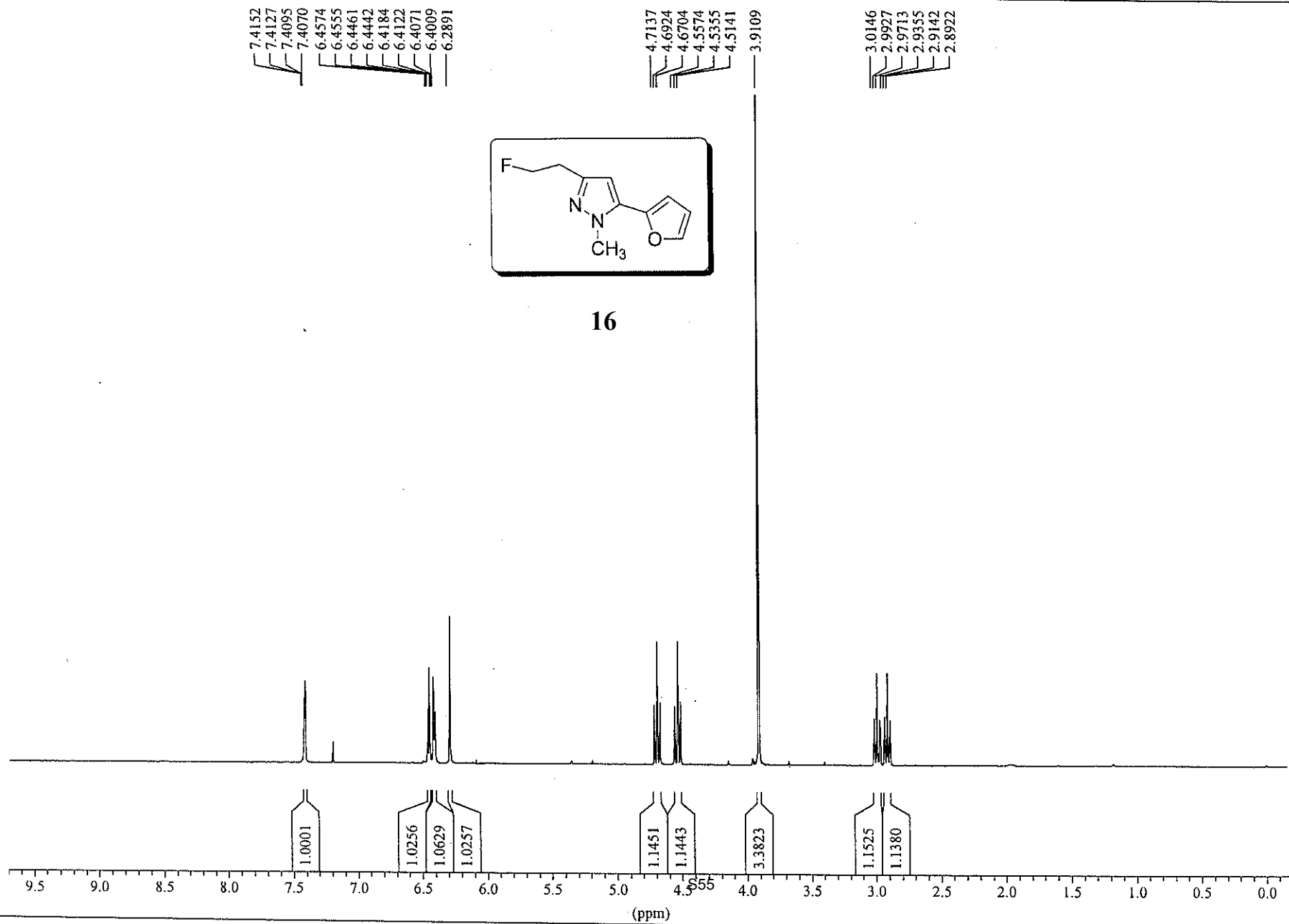


AutoSpecE EI+ Magnet BpM:162 BpI:4638720 TIC:24345260 Flags:NORM

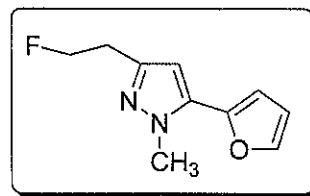




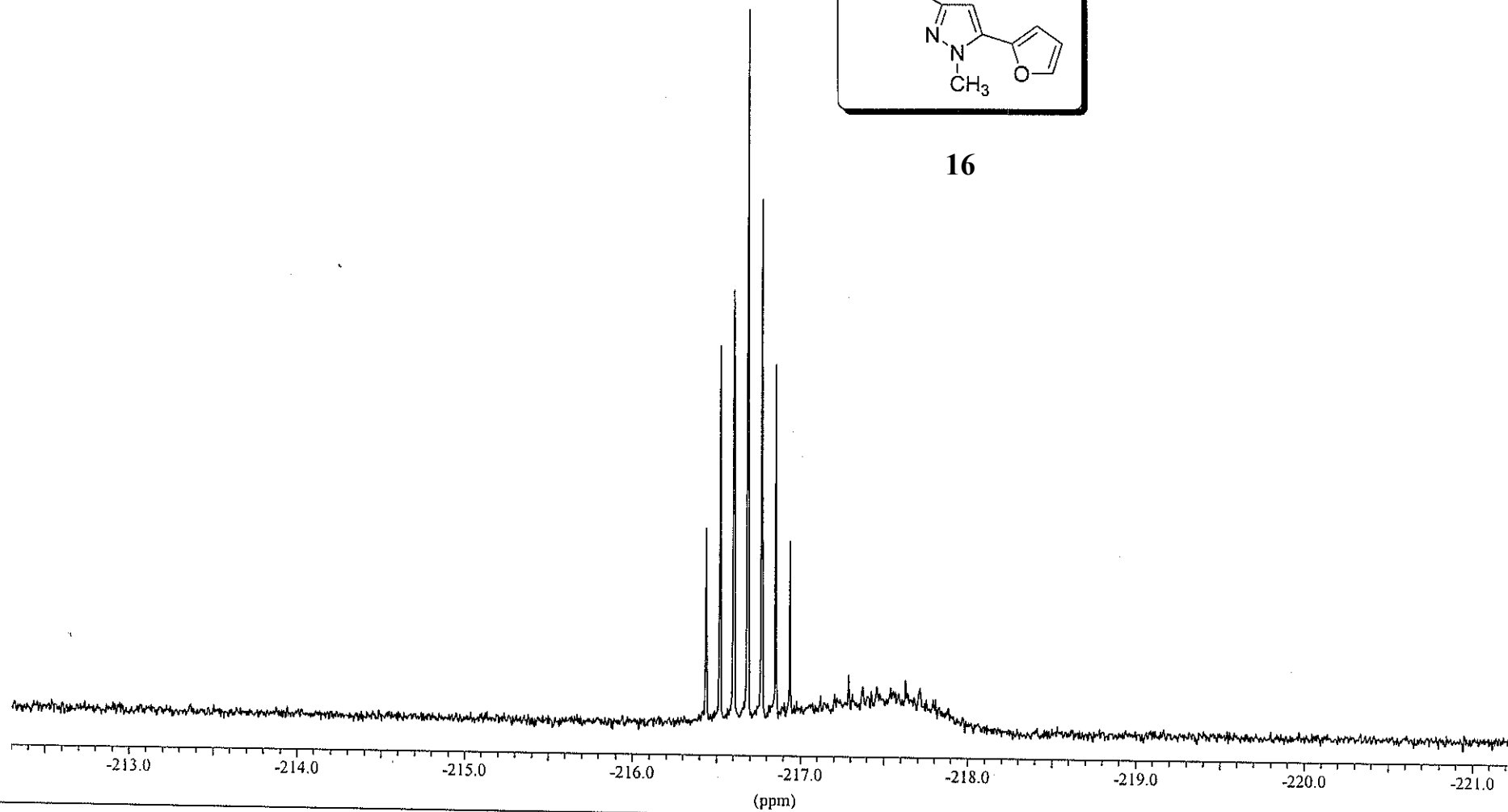
16



-216.4404
-216.5246
-216.6053
-216.6895
-216.7737
-216.8580
-216.9422



16



147.7676
147.6762

145.1326
143.0460

135.3621

111.8075

108.9137

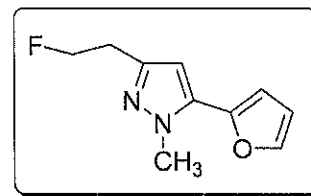
104.6795

84.5138

82.2901

38.6690

29.9798
29.6980

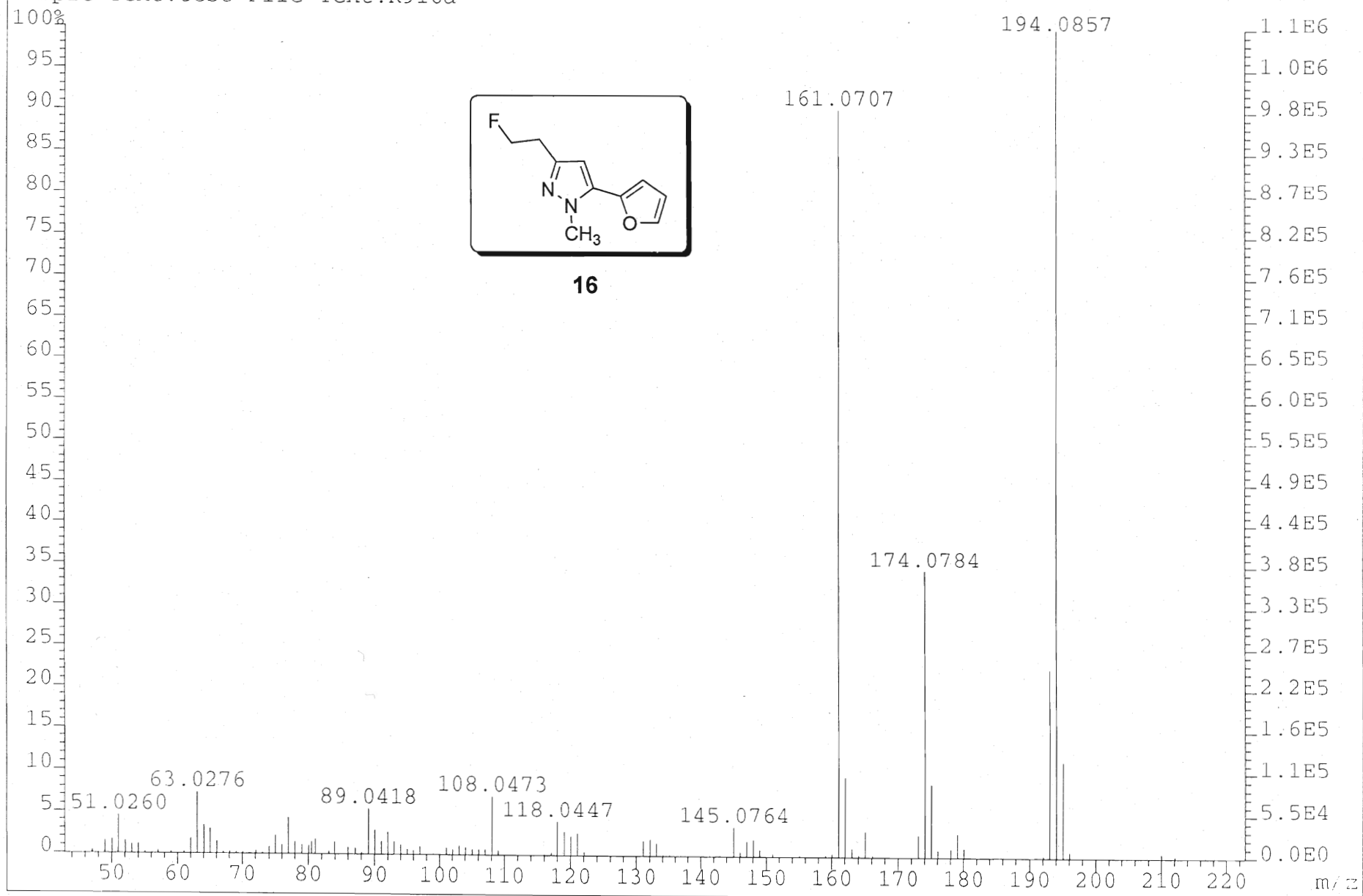


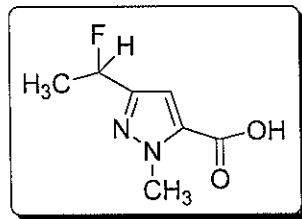
16

155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25

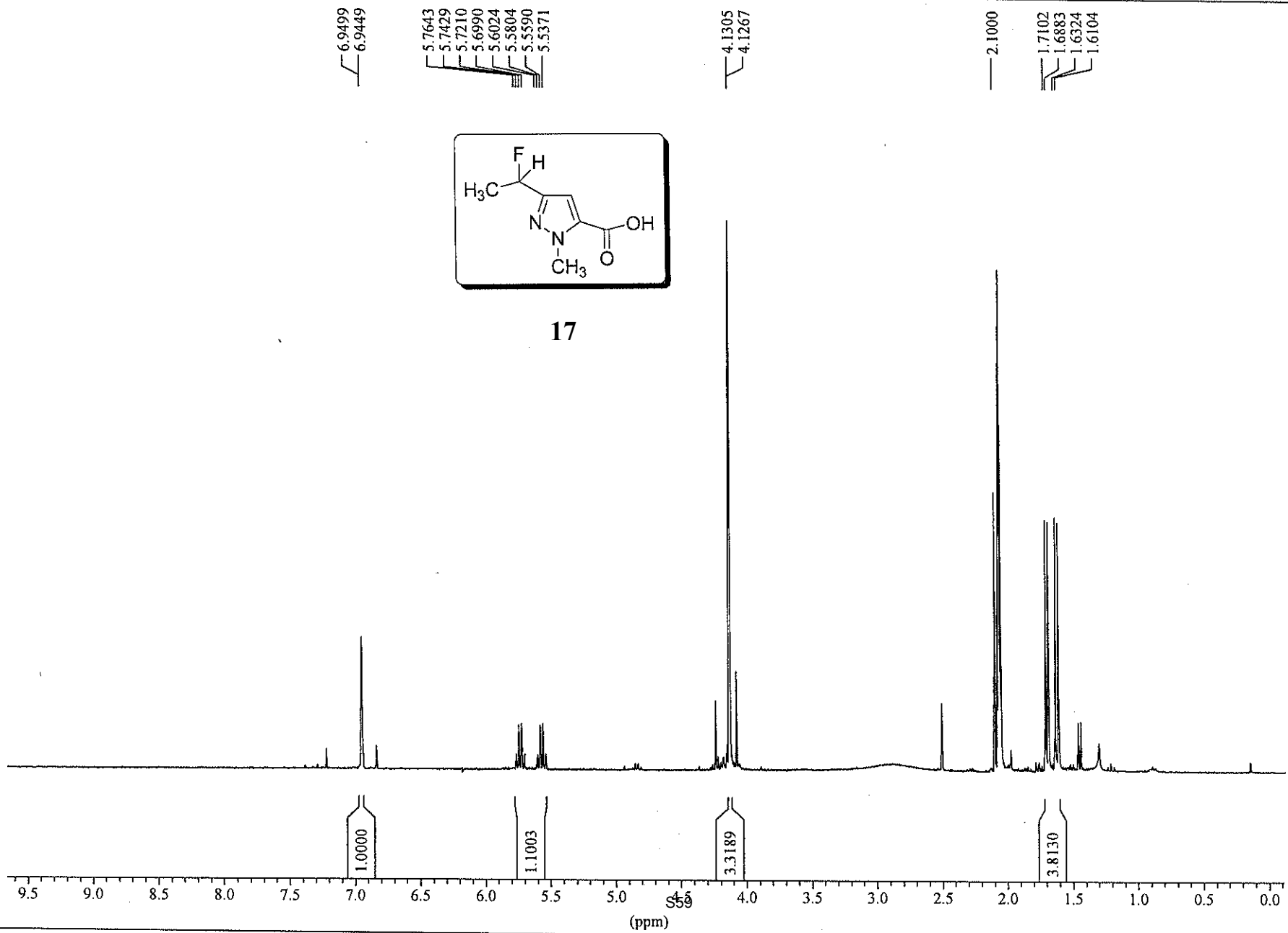
(ppm)

File:EI_10_9_2 Ident:16_17-6_9 Win 200PPM FILT(EXCL,ALL) Acq:10-SEP-2008 12:48:25 +1:49 Cal:EI_>
AutoSpecE EI+ Magnet BpM:194 BpI:1091456 TIC:4473207 Flags:NORM
Sample Text:test File Text:R916a

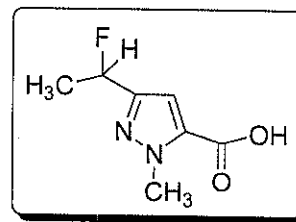




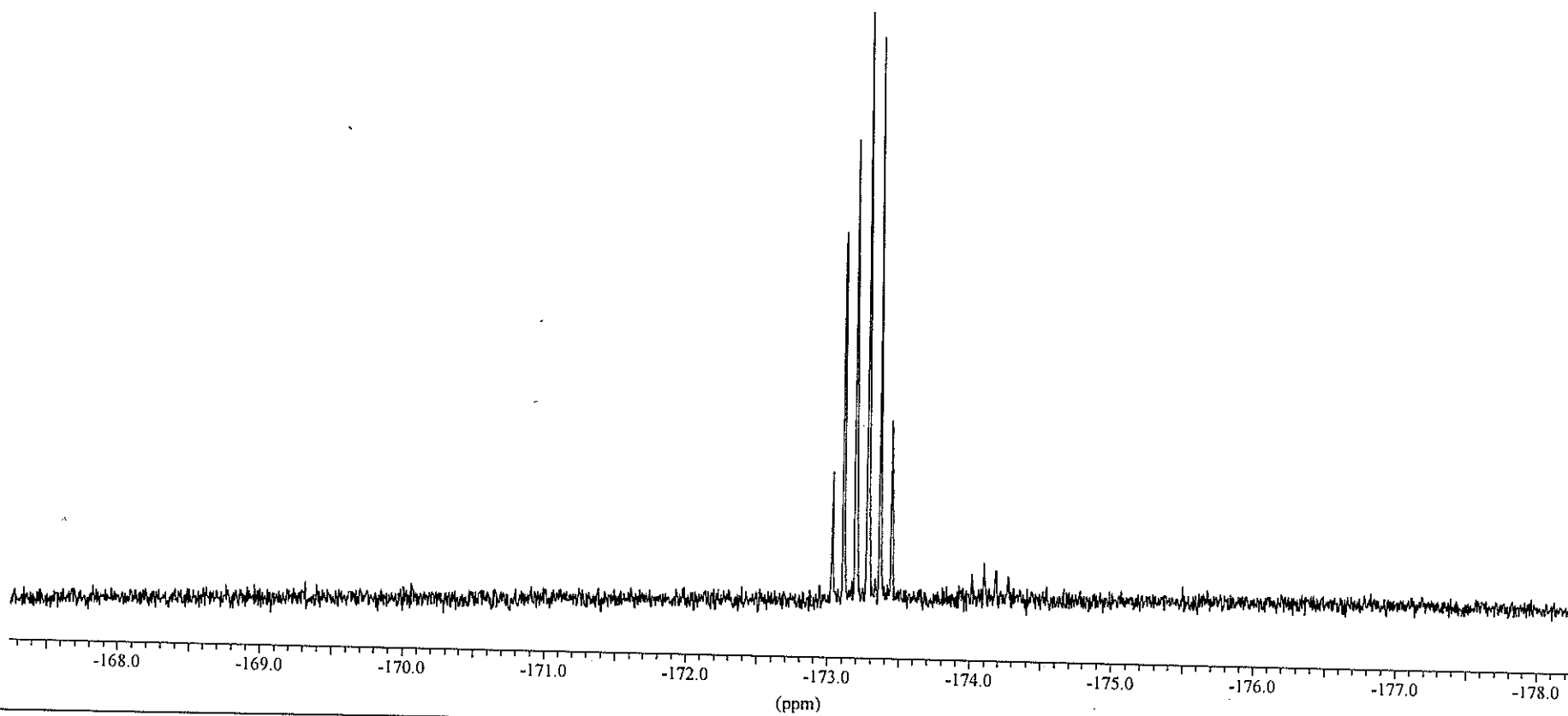
17

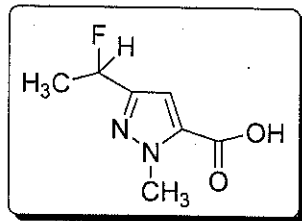


-173.0261
-173.0352
-173.1085
-173.1176
-173.1970
-173.2855
-173.3680
-173.4504

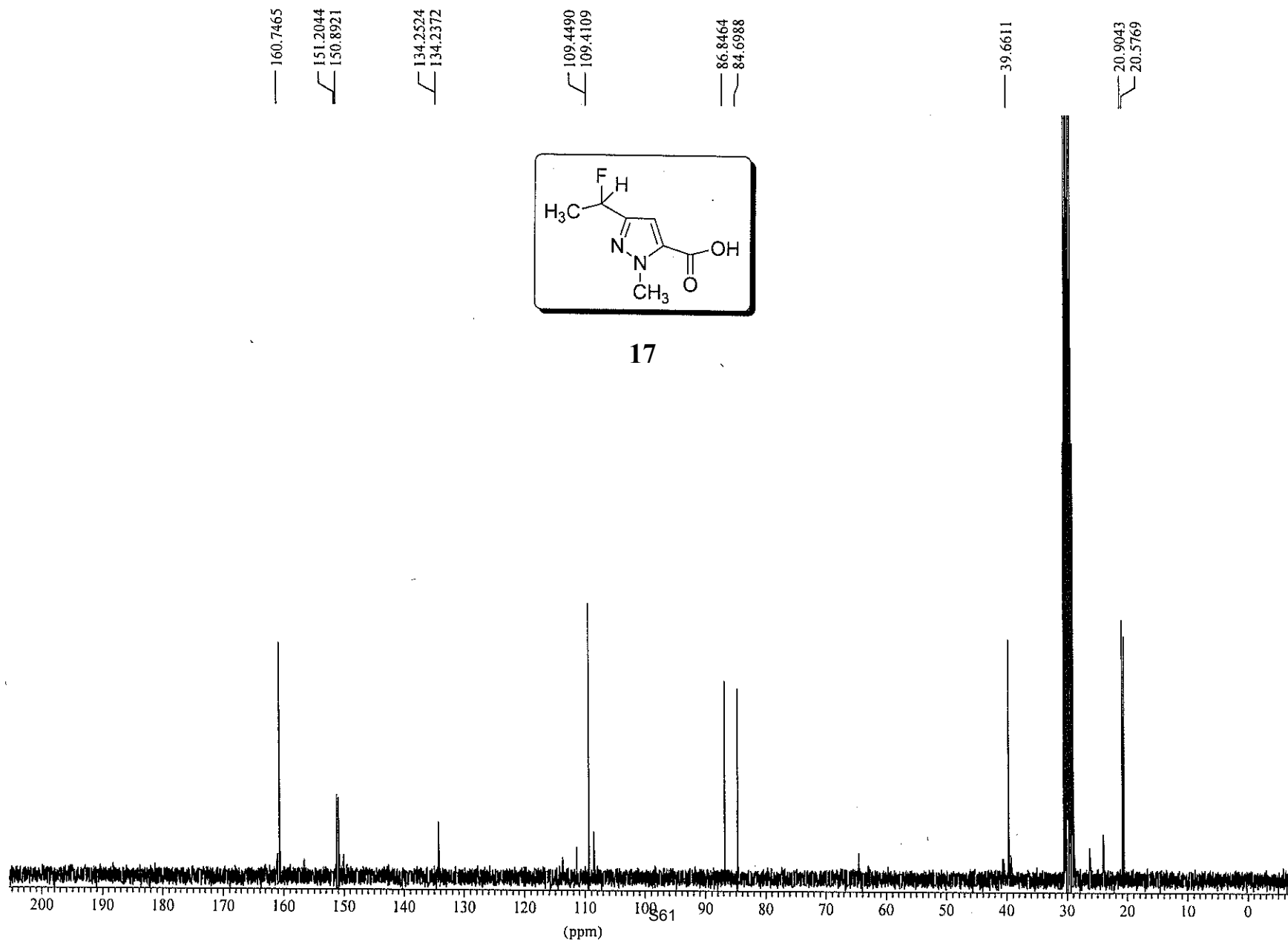


17

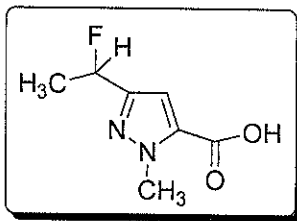
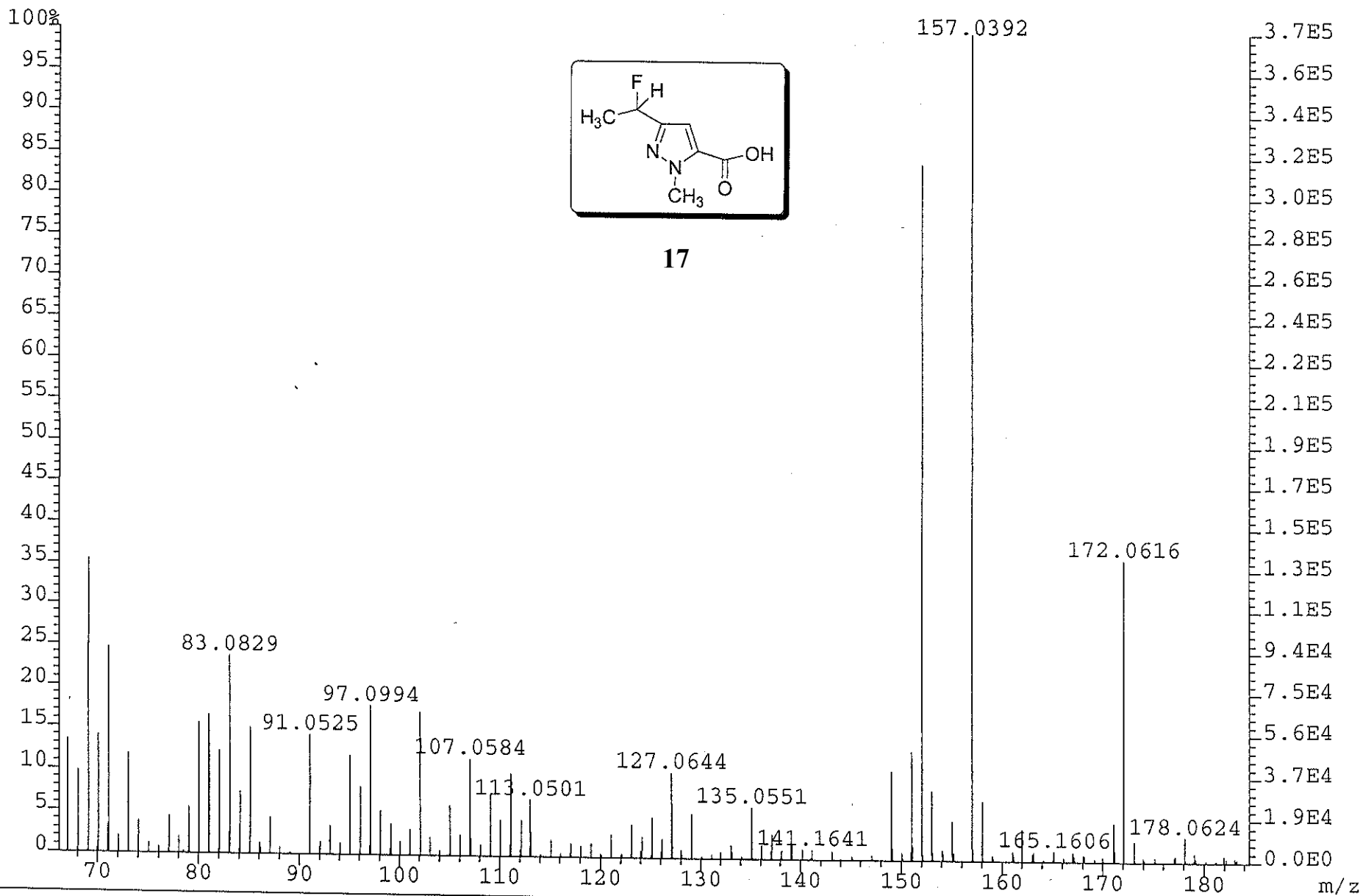




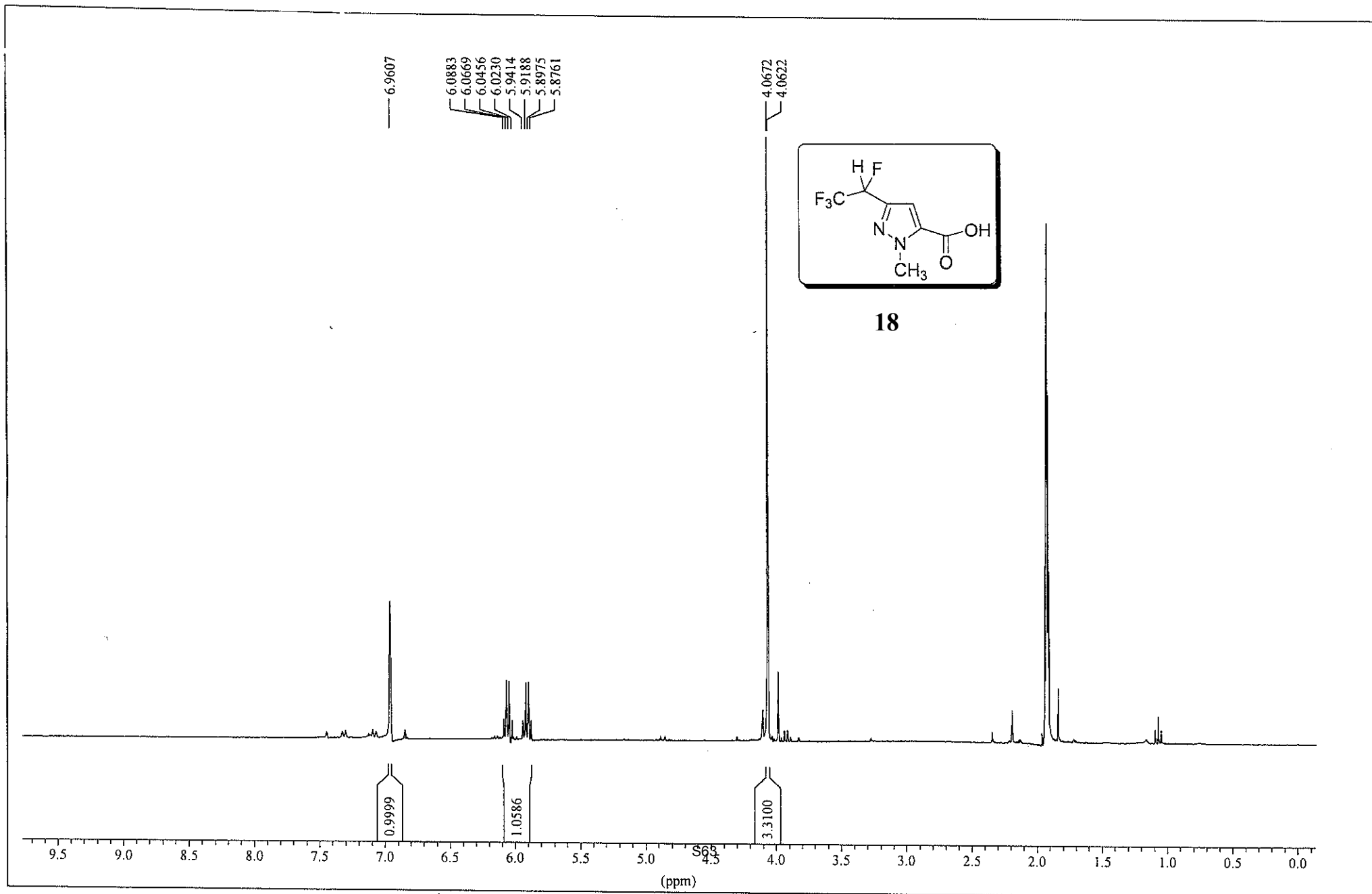
17

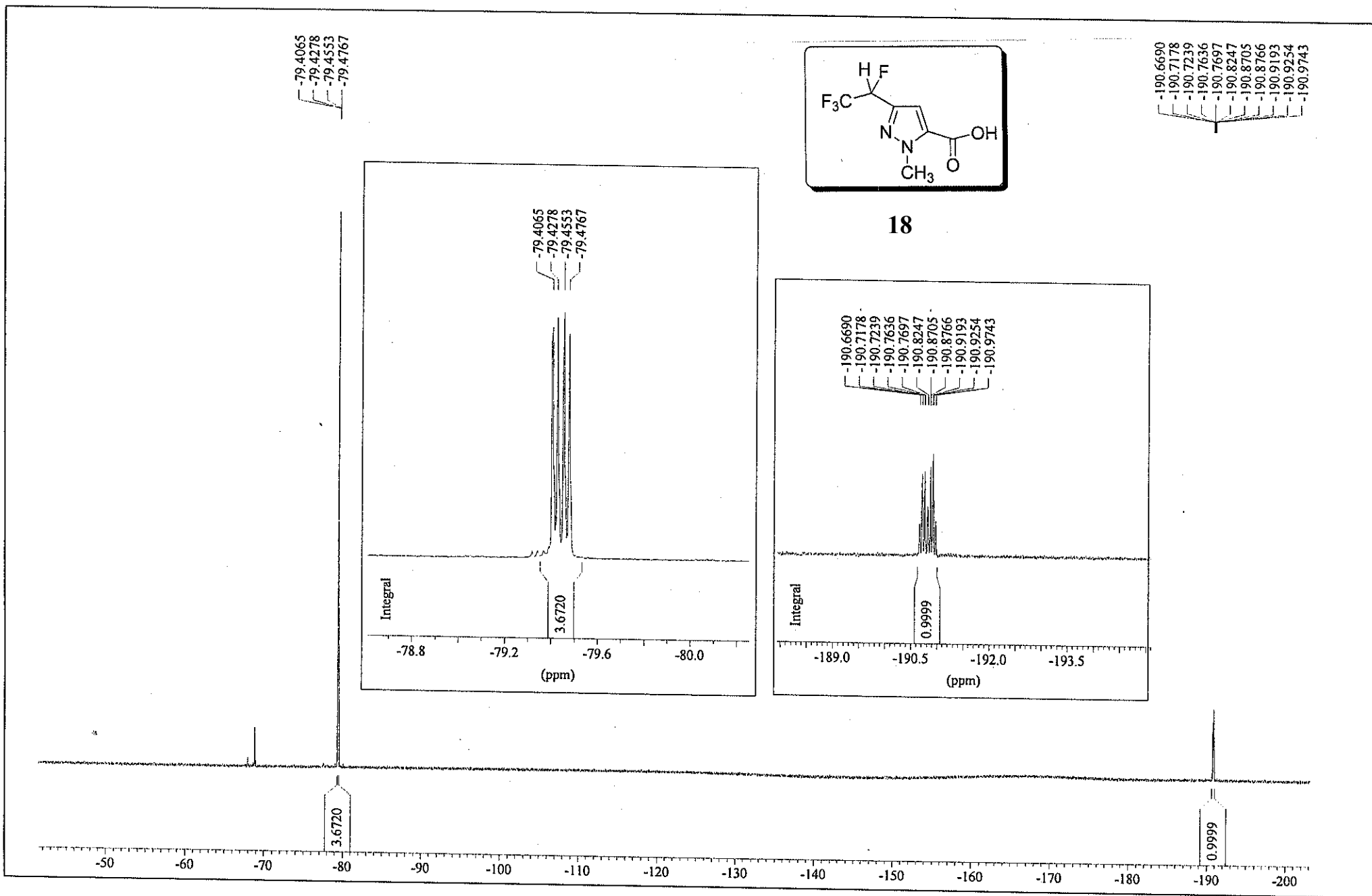


AutoSpecE EI+ Magnet BpM:157 BpI:374656 TIC:5733716 Flags:NORM



17





160.5333

141.7536
141.7384
141.7156
141.4262

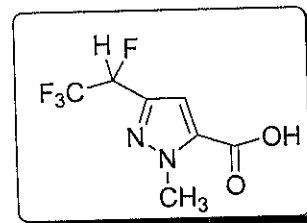
135.6308

125.5328
125.1444
121.8241
121.4357

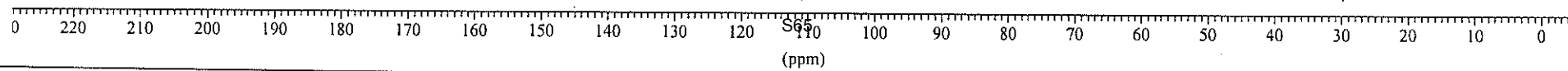
111.5128
111.4899
111.4671
111.4518

86.7702
86.2981
85.8259
85.3537
84.3866
83.9144
83.4423
82.9625

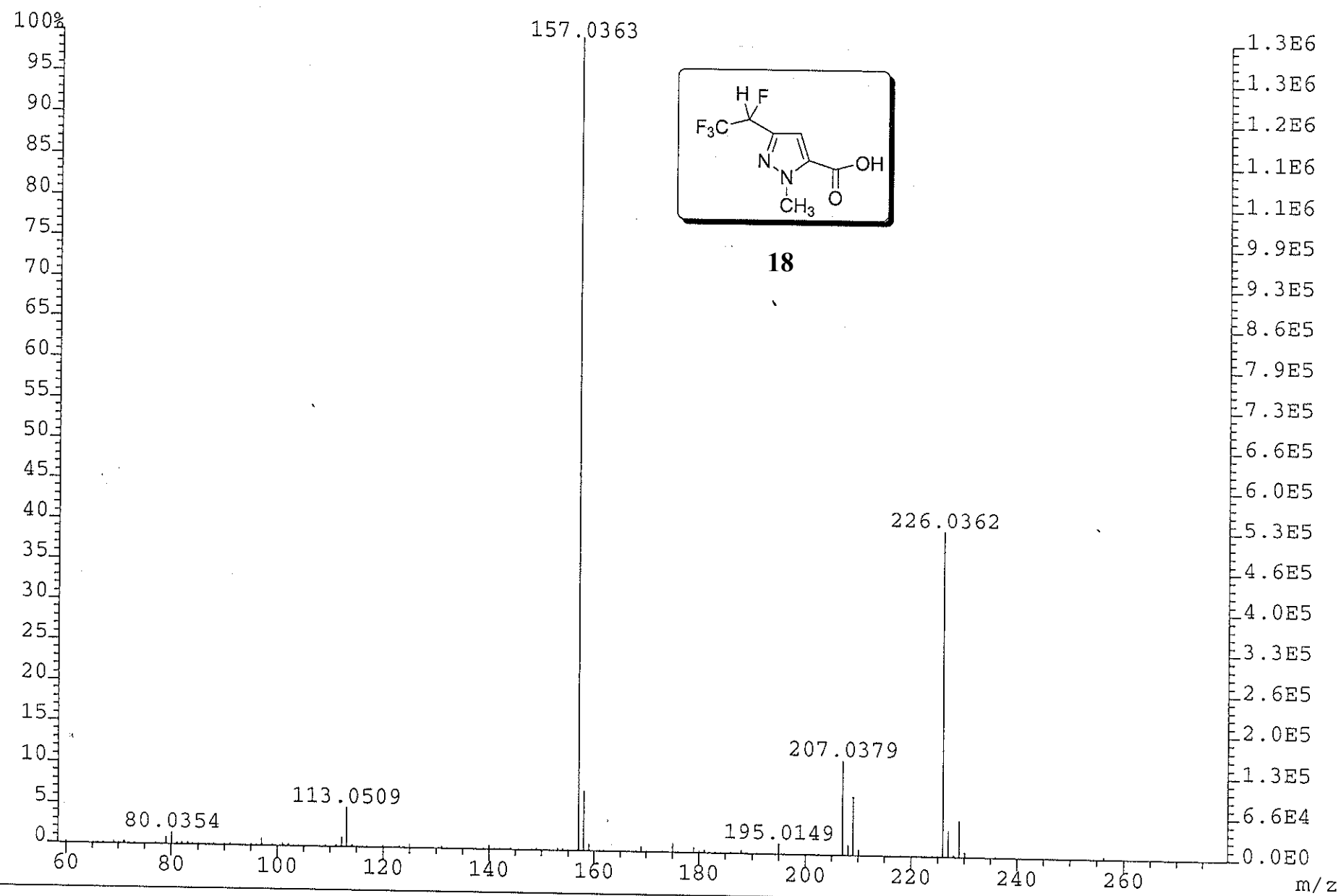
40.4227

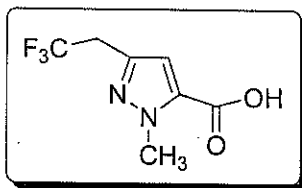


18

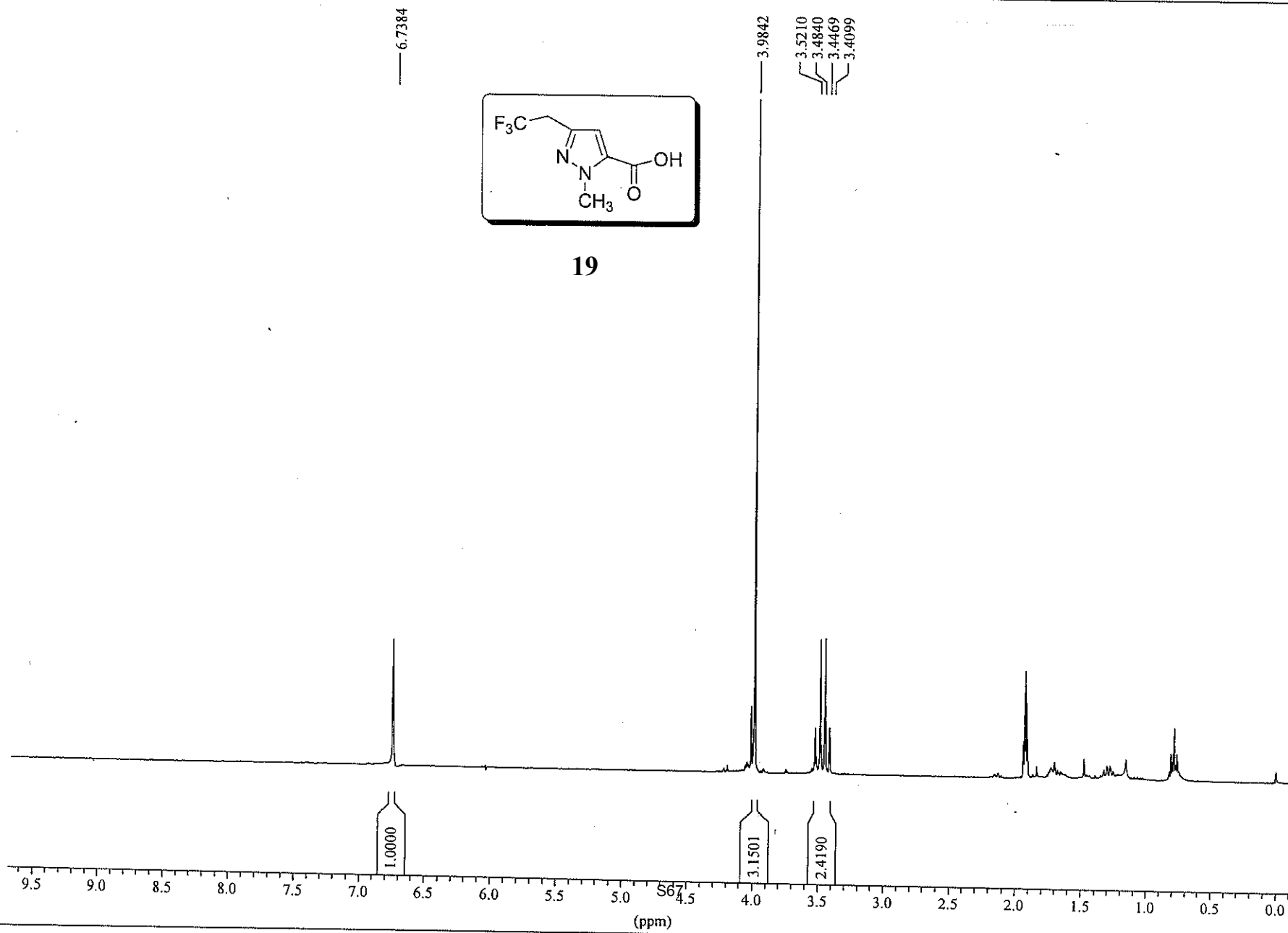


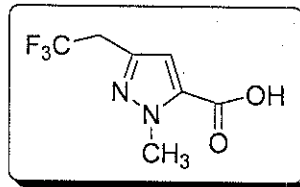
AutoSpecE EI+ Magnet BpM:157 BpI:1324544 TIC:2900089 Flags:NORM



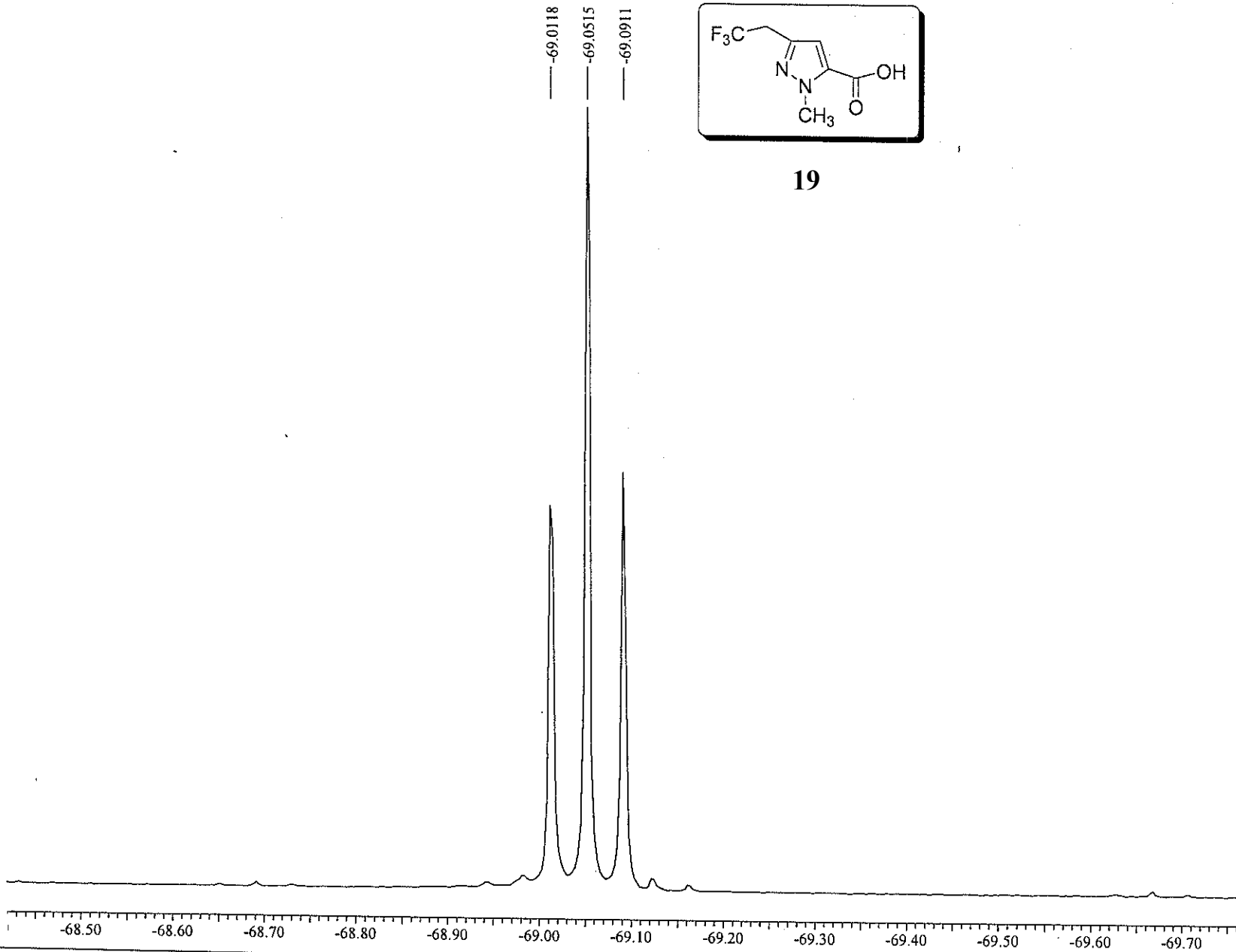


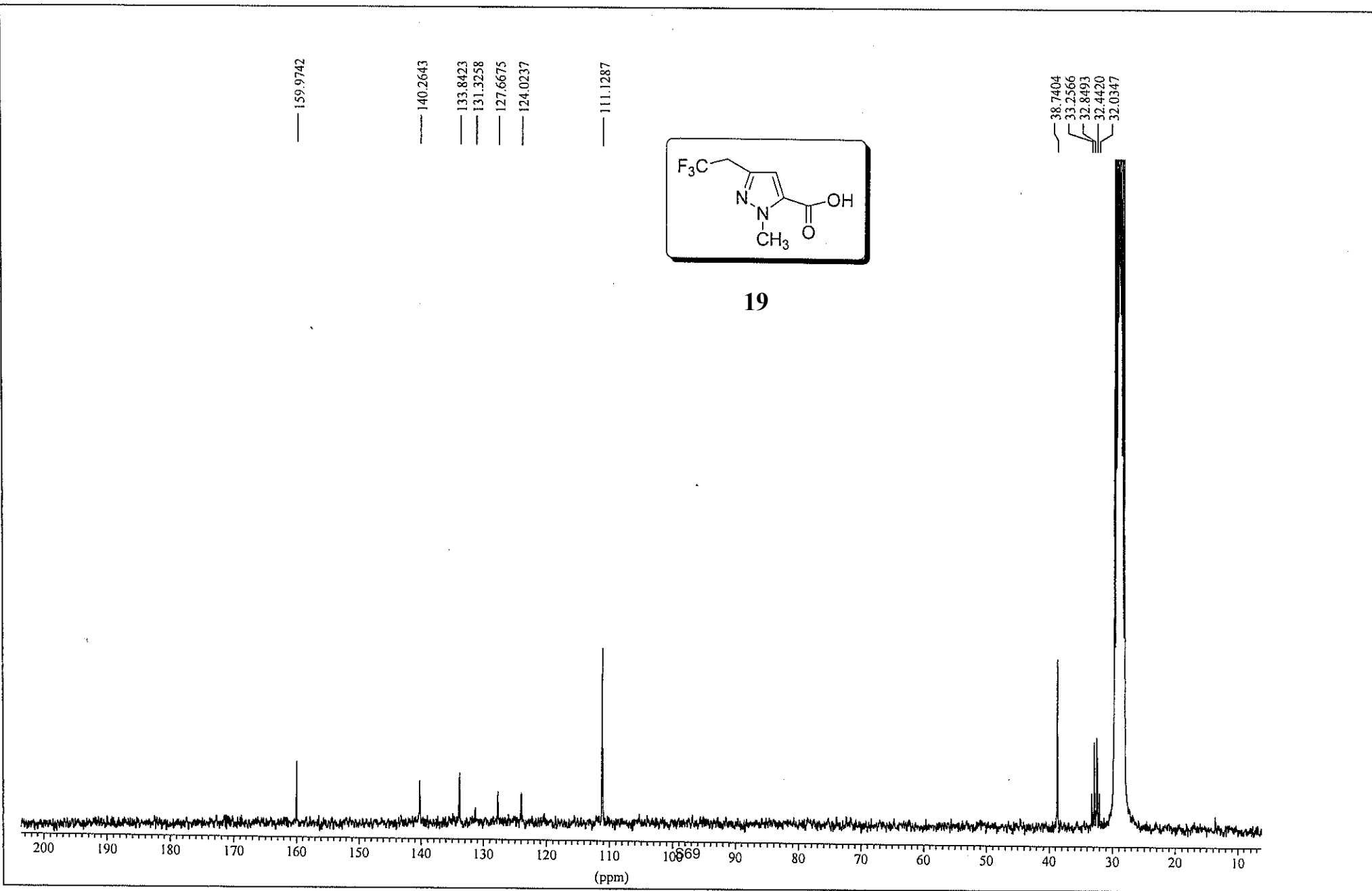
19



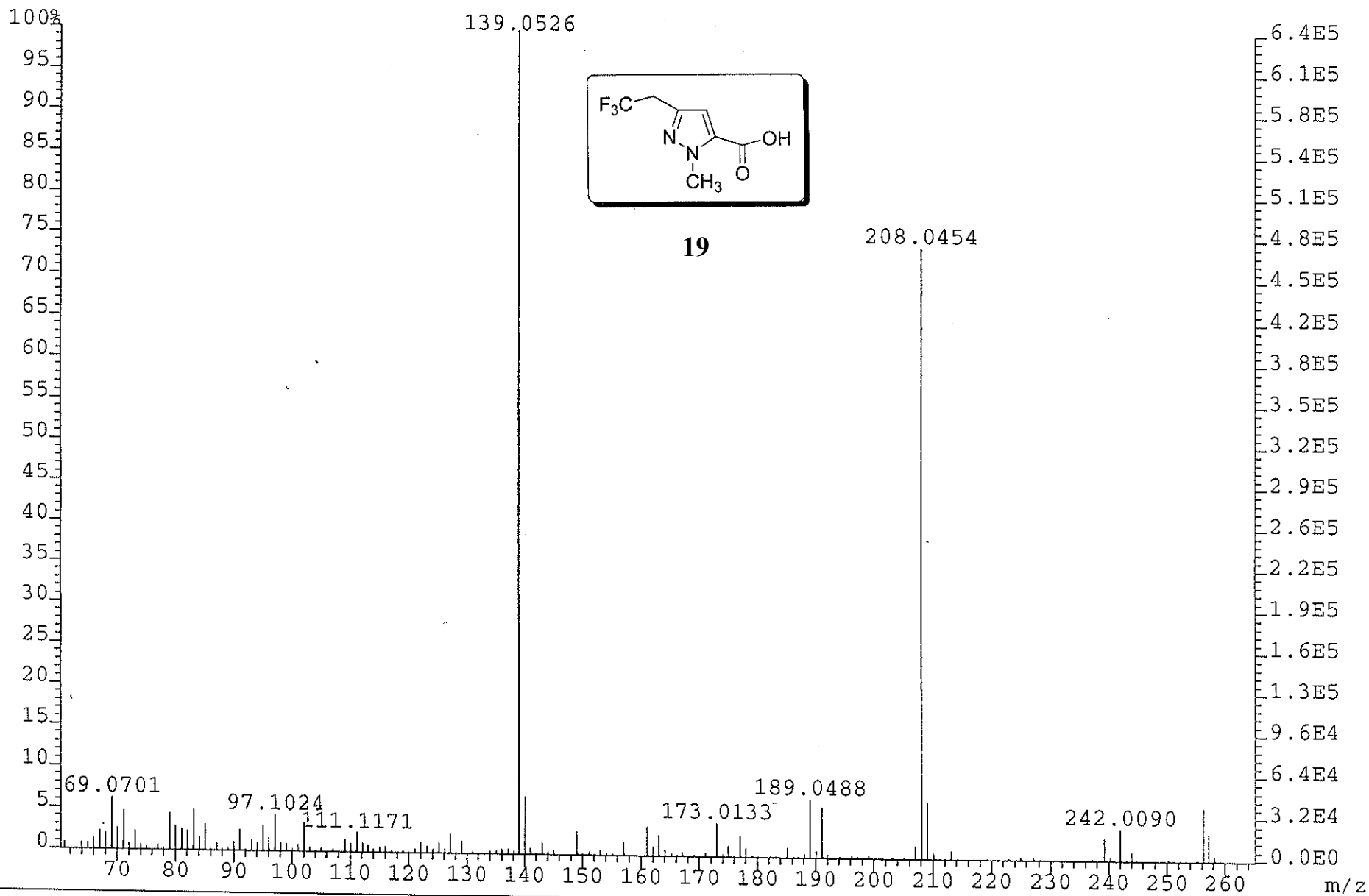


19





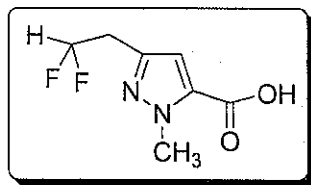
AutoSpecE EI+ Magnet BpM:139 BpI:639147 TIC:2935689 Flags:NORM



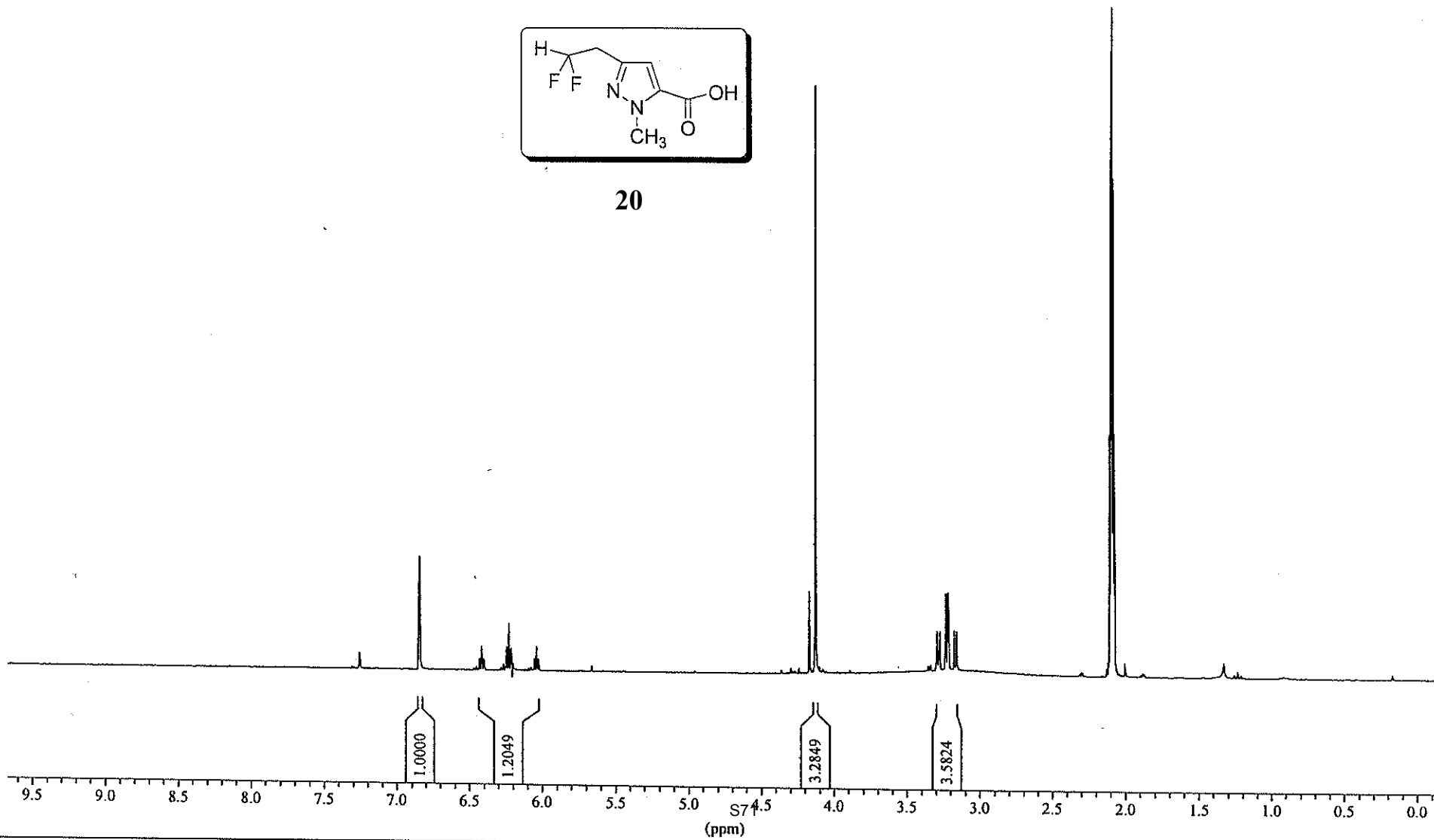
6.8464
6.4322
6.4171
6.4020
6.2439
6.2288
6.2137
6.0556
6.0405
6.0254

4.1286

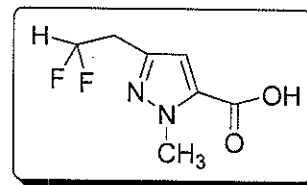
3.2913
3.2763
3.2336
3.2185
3.1759
3.1608



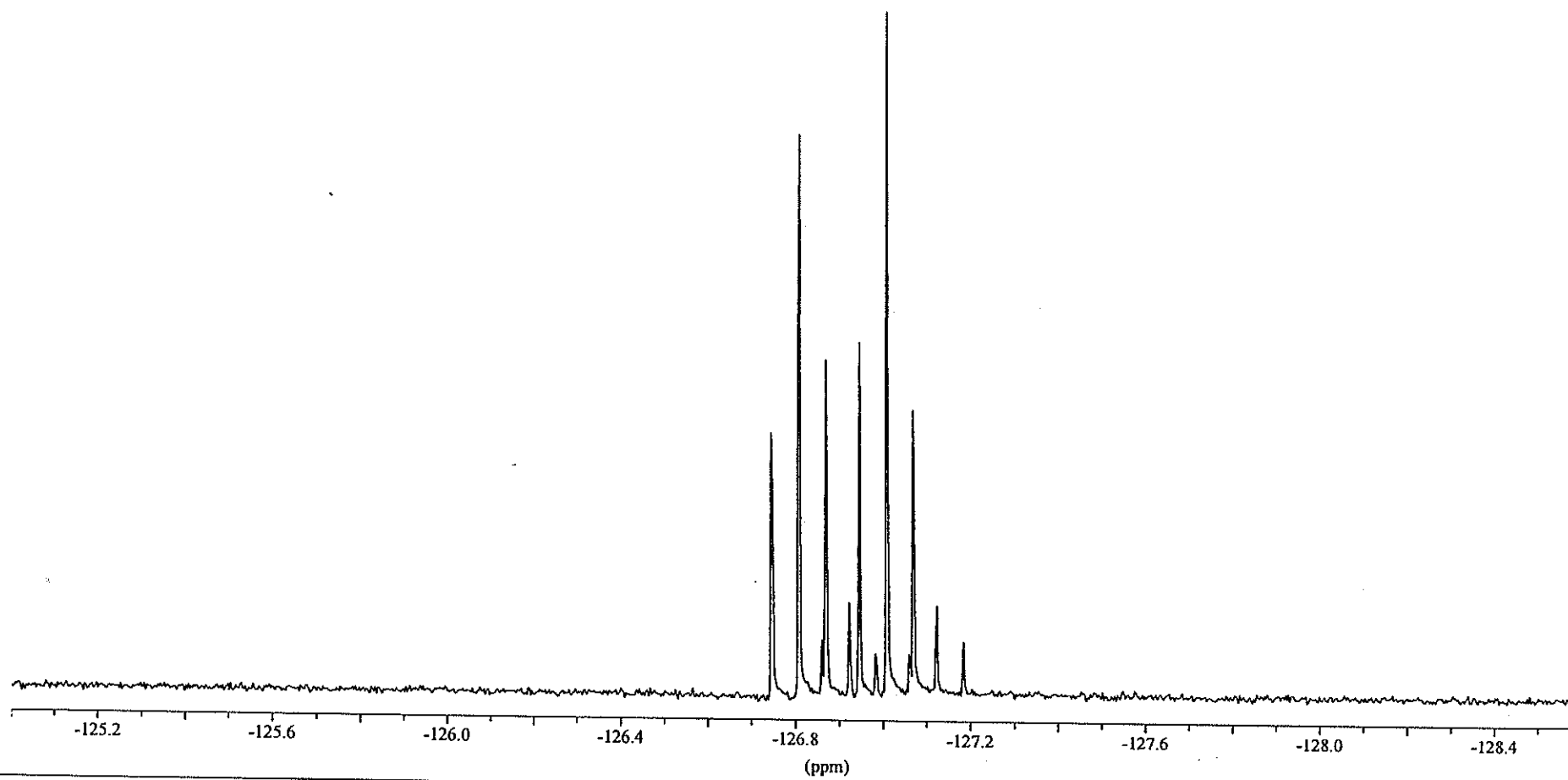
20

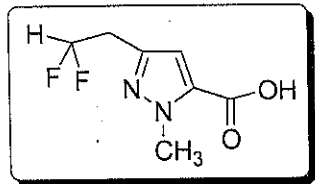


-126.7450
-126.8091
-126.8702
-126.9465
-127.0076
-127.0686

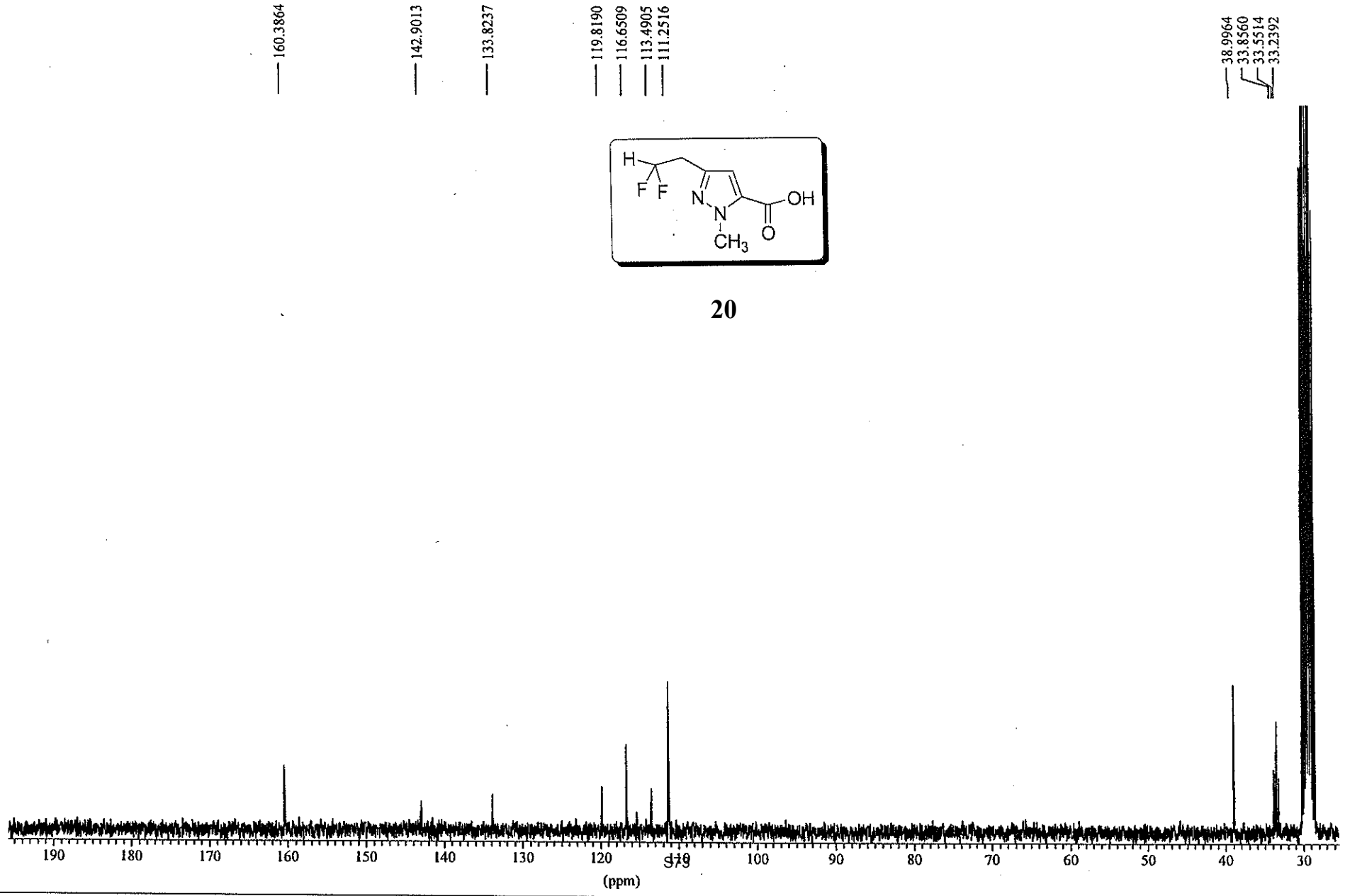


20

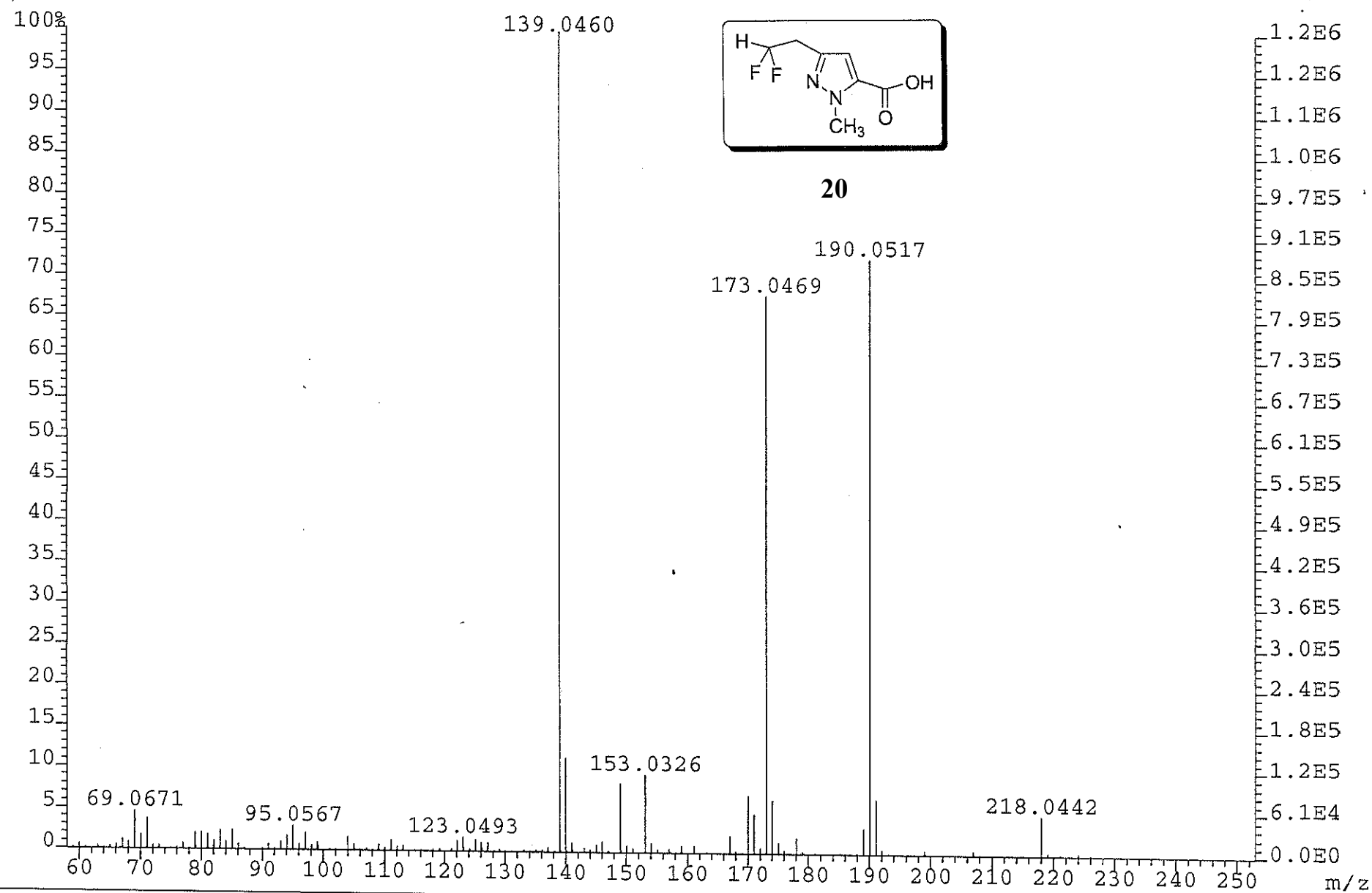


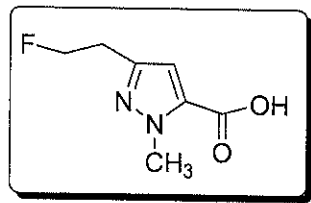


20

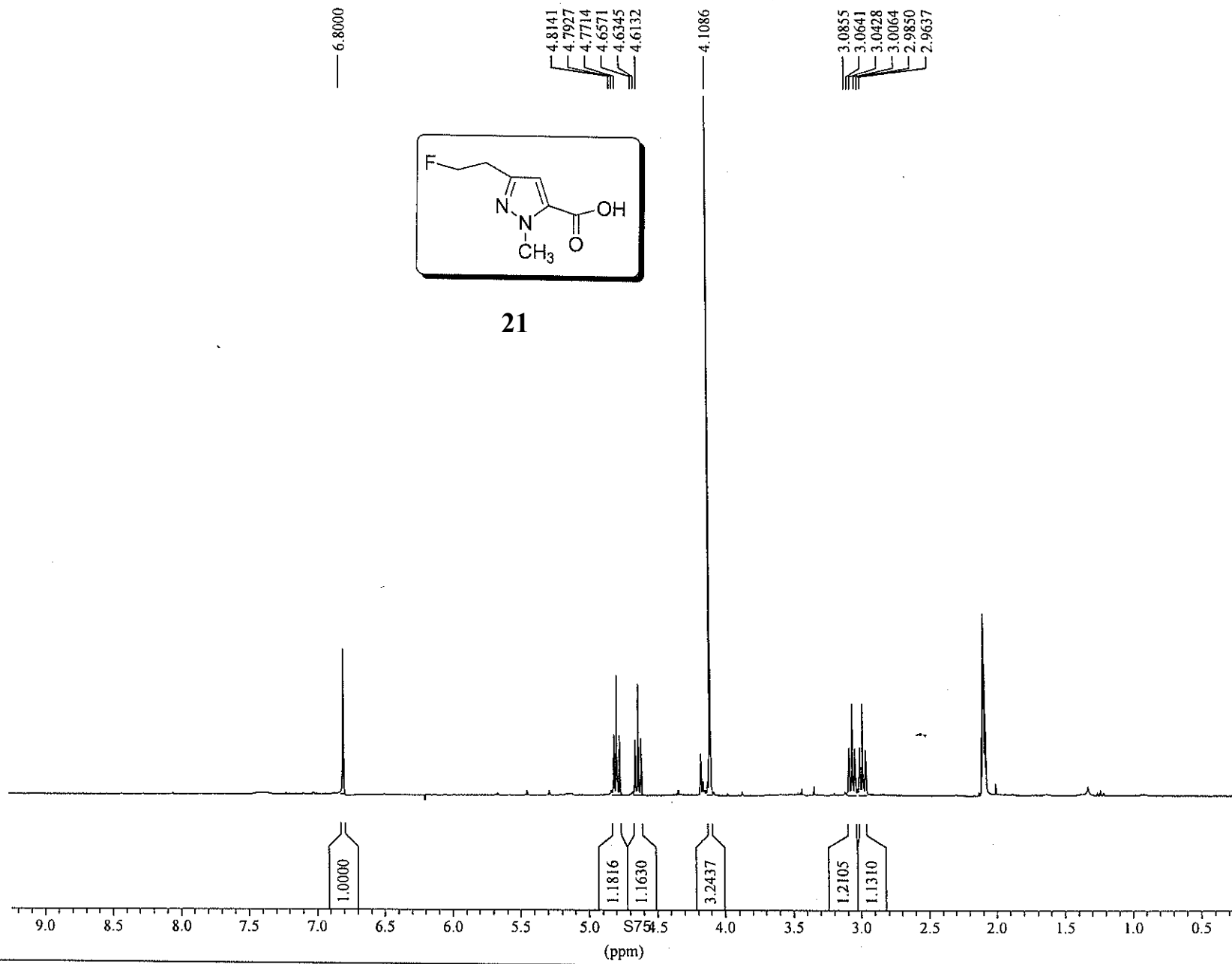


AutoSpecE EI+ Magnet BpM:139 BpI:1213952 TIC:5120405 Flags:NORM

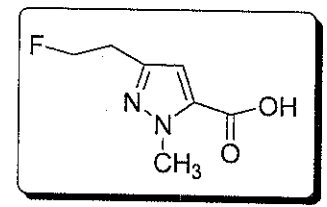




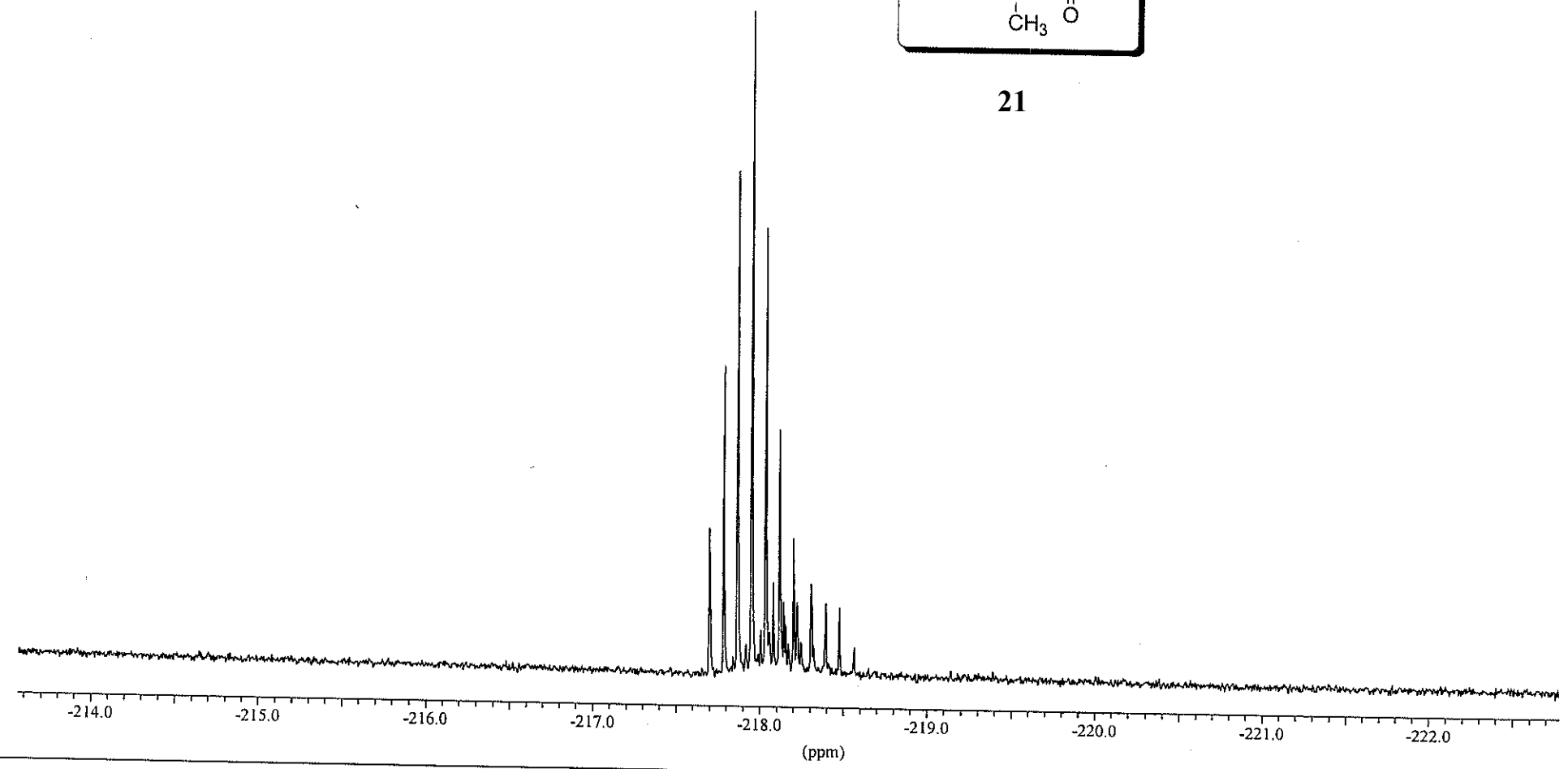
21

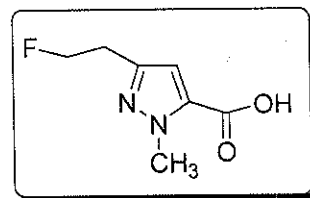


-217.6965
-217.7807
-217.8649
-217.9491
-218.0333
-218.1140
-218.1982

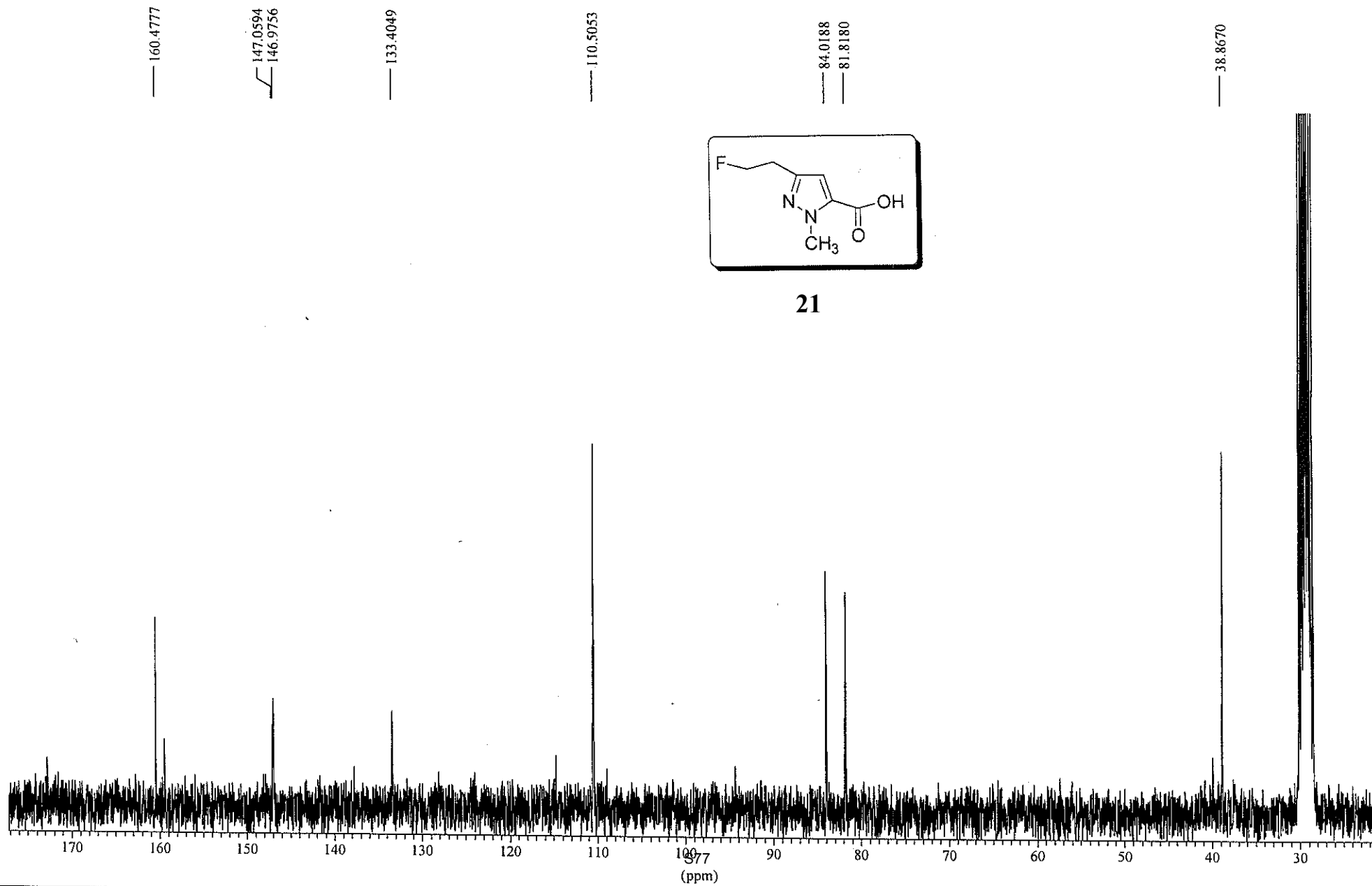


21

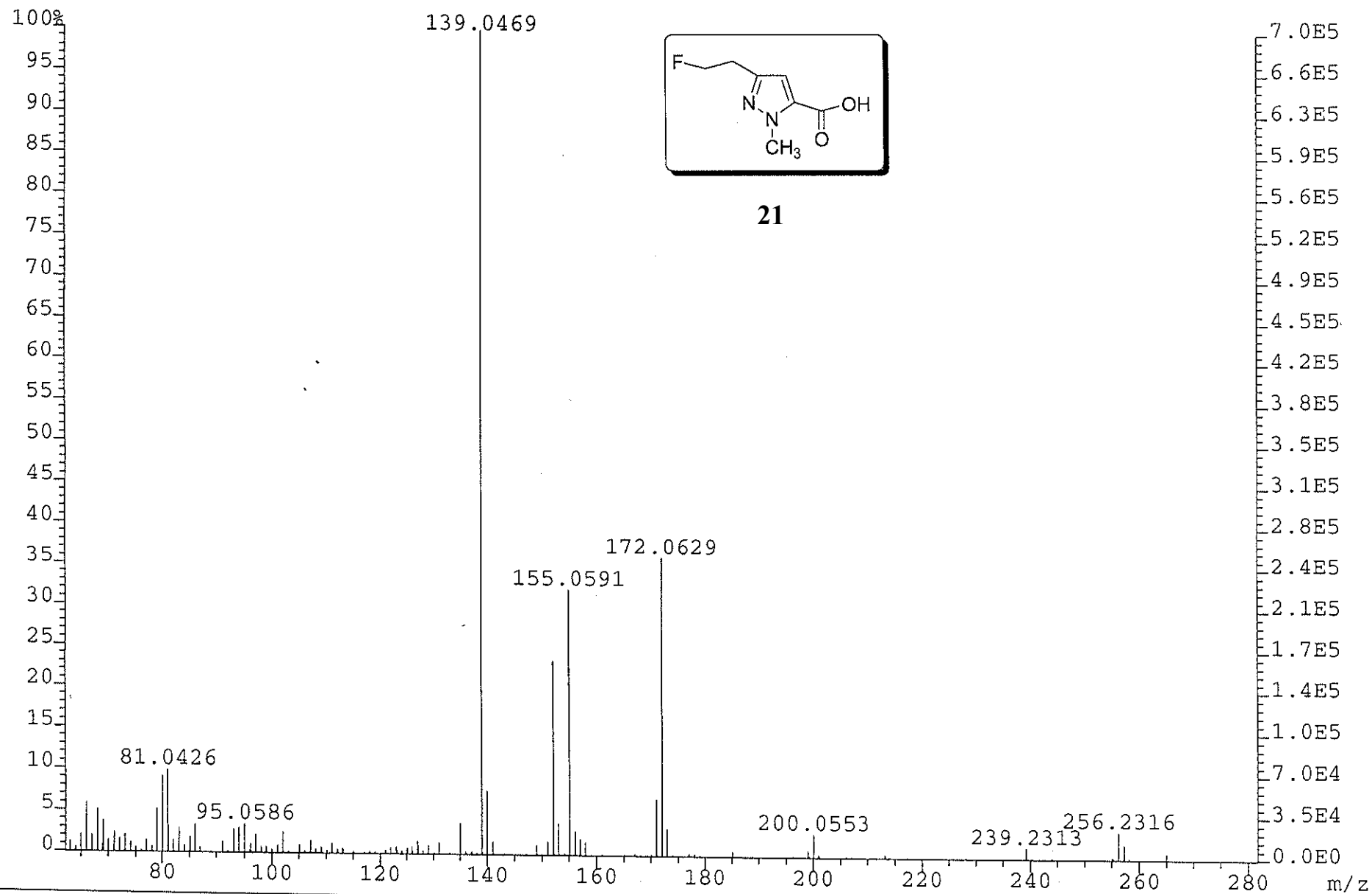




21

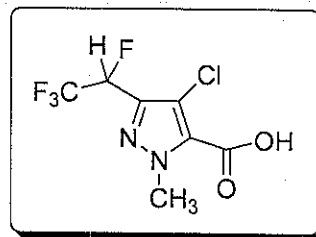


AutoSpecE EI+ Magnet BpM:139 BpI:695808 TIC:3656655 Flags:NORM

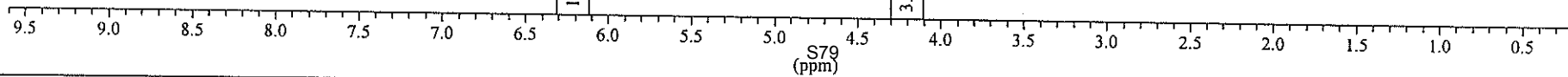


6.3168
6.2955
6.2742
6.2516
6.1725
6.1511
6.1285
6.1072

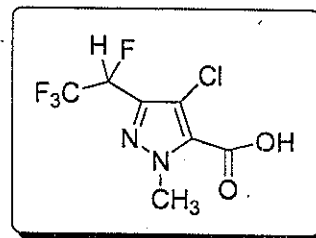
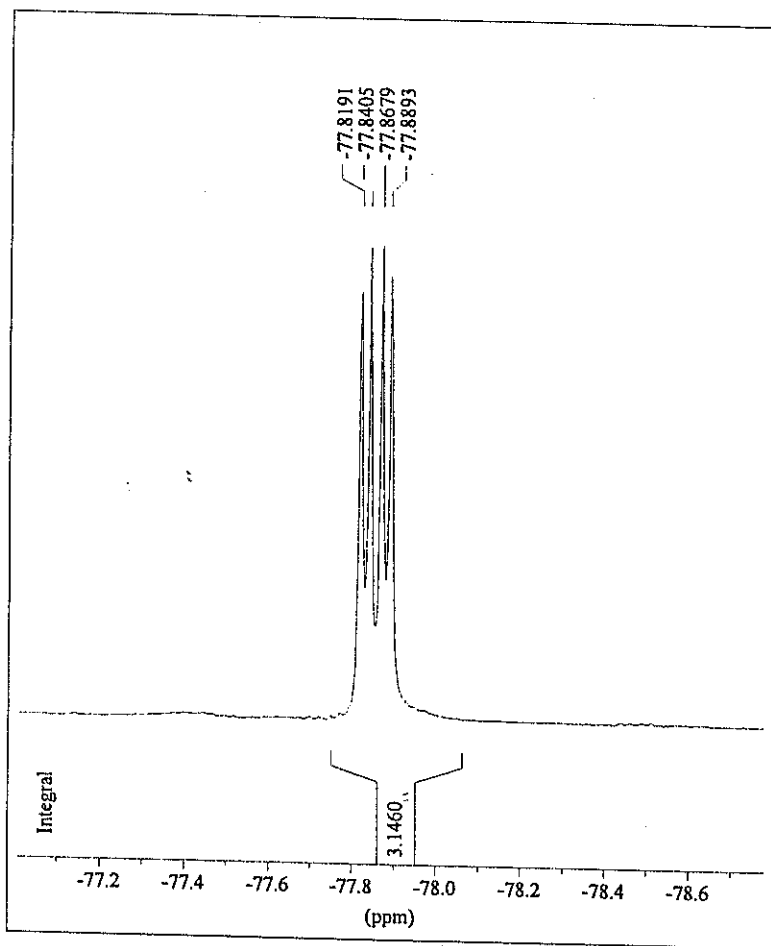
4.2092
4.2066



22

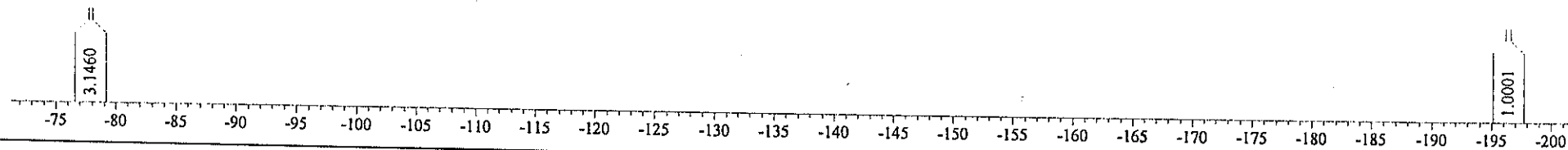
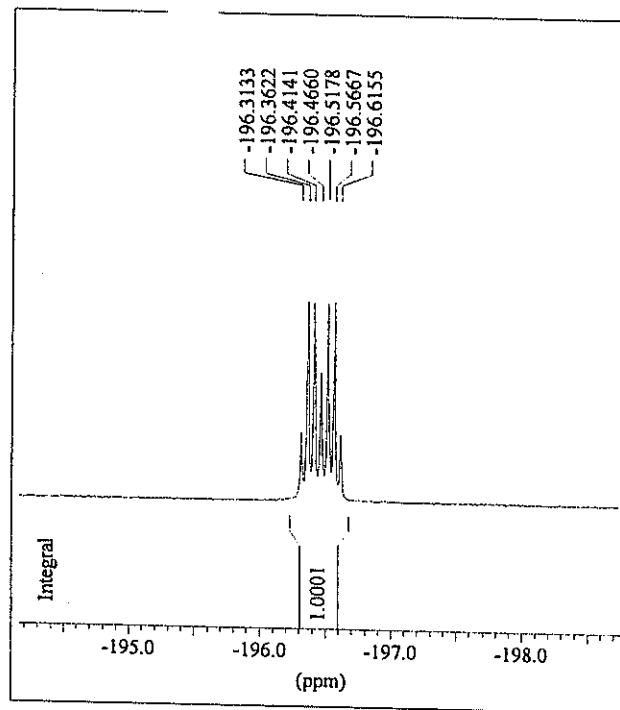


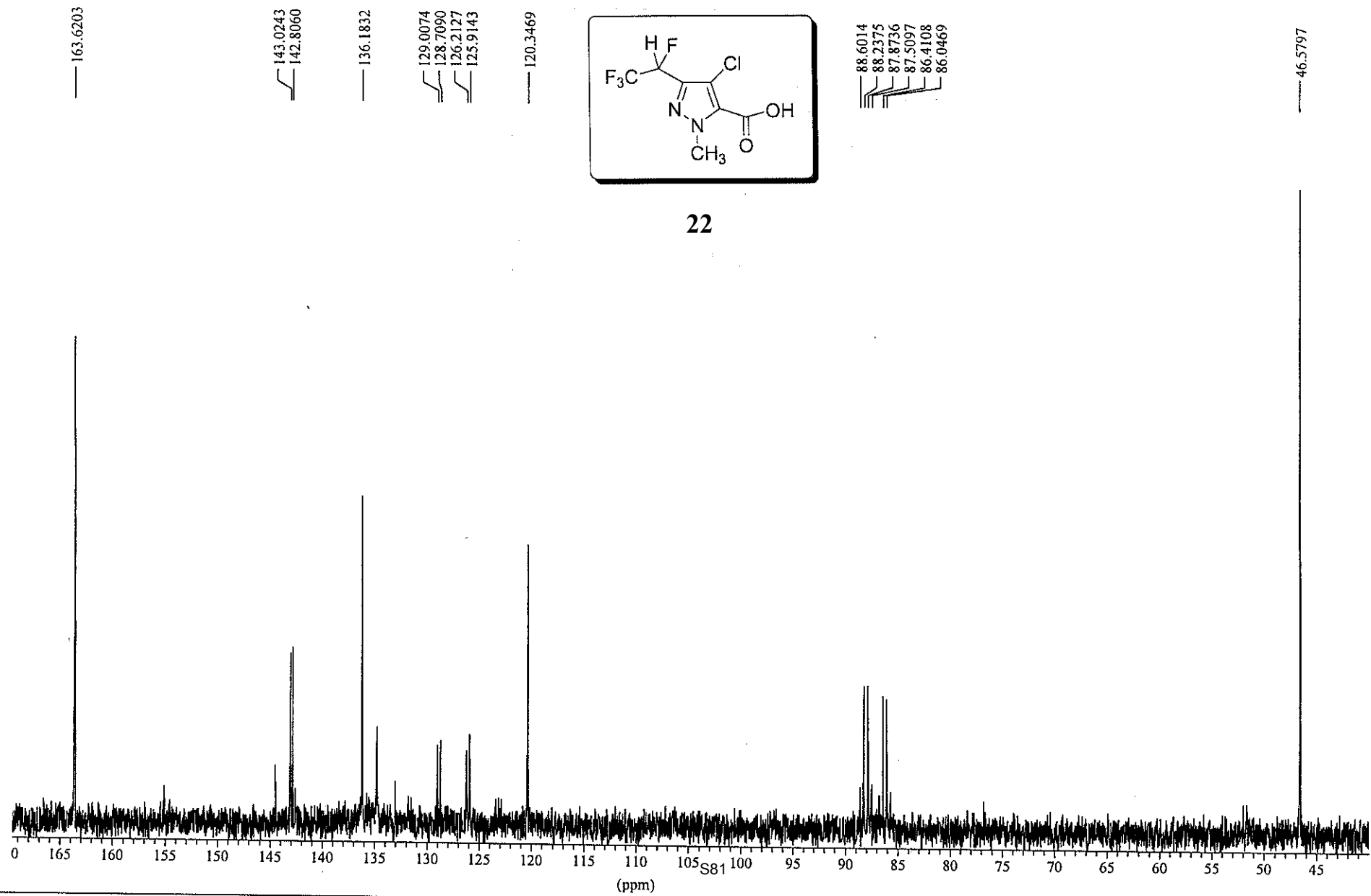
-77.8191
-77.8405
-77.8679
-77.8893

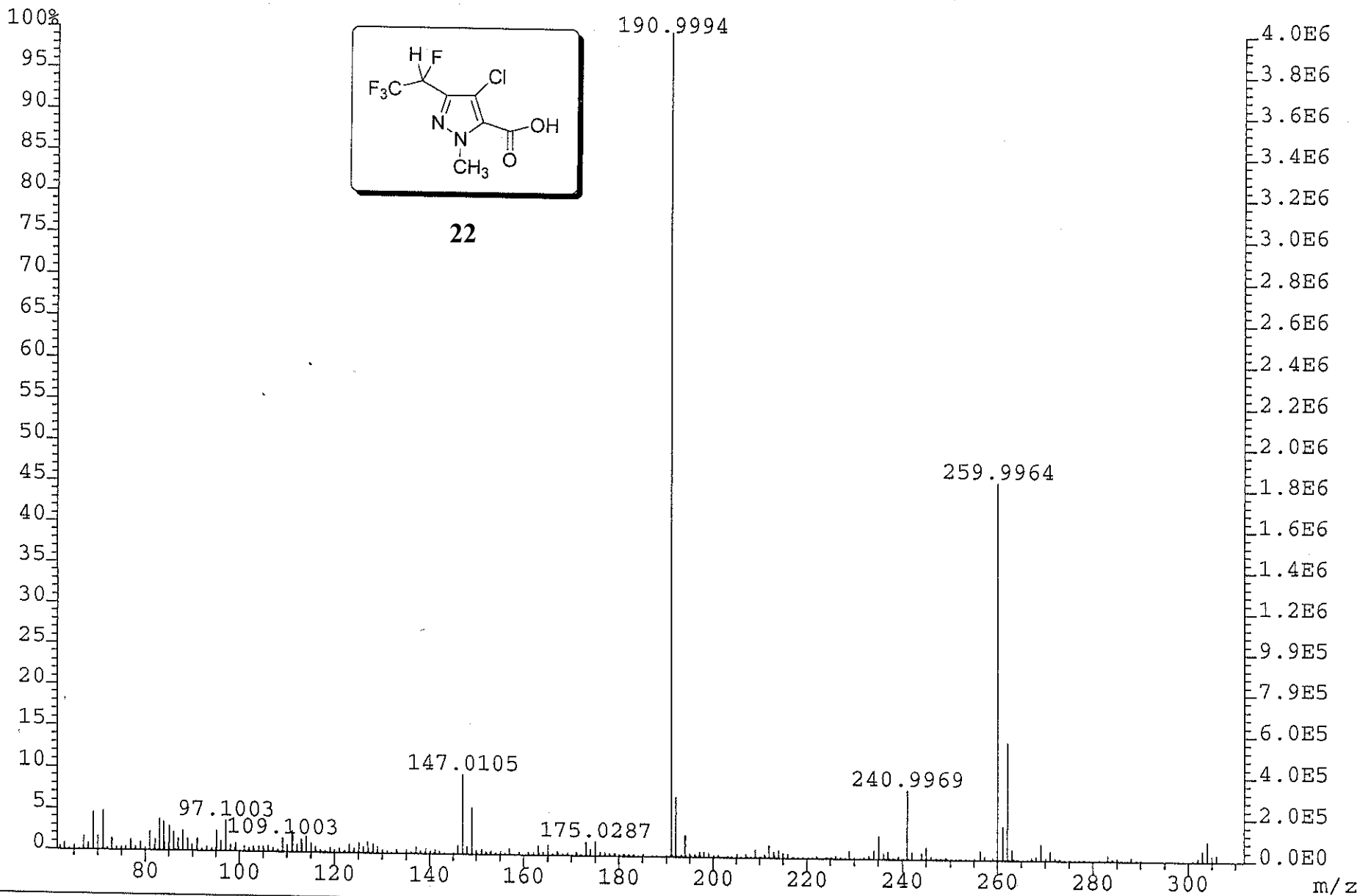


22

-196.3133
-196.3622
-196.4141
-196.4660
-196.5178
-196.5667
-196.6155







7.3582
7.3306
7.2439
7.2163

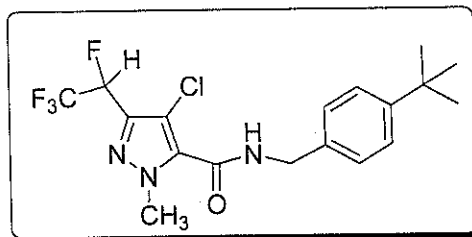
6.8774

5.7928
5.7727
5.7514
5.7300
5.6472
5.6258
5.6057
5.5844

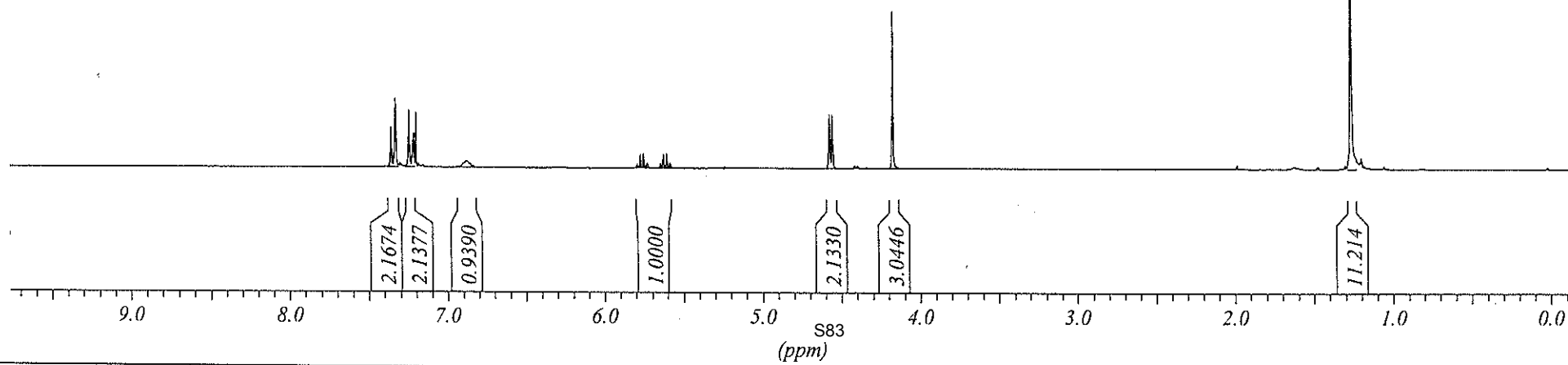
4.5739
4.5550

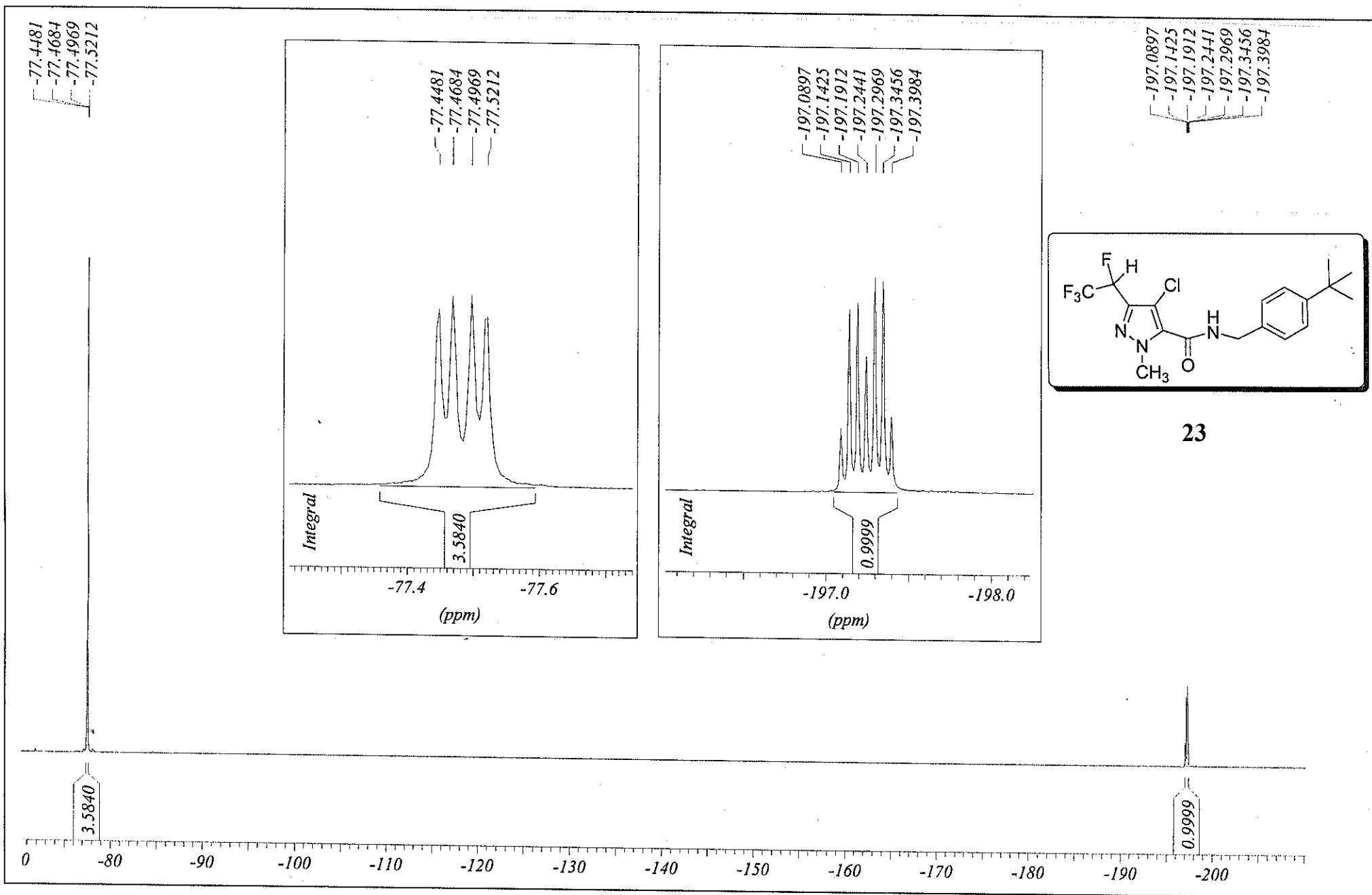
4.1734
4.1709

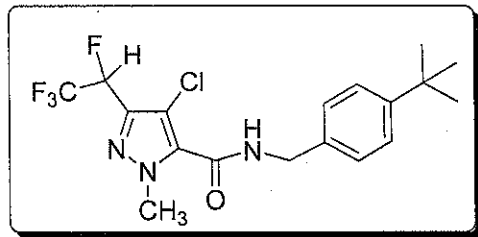
1.2648



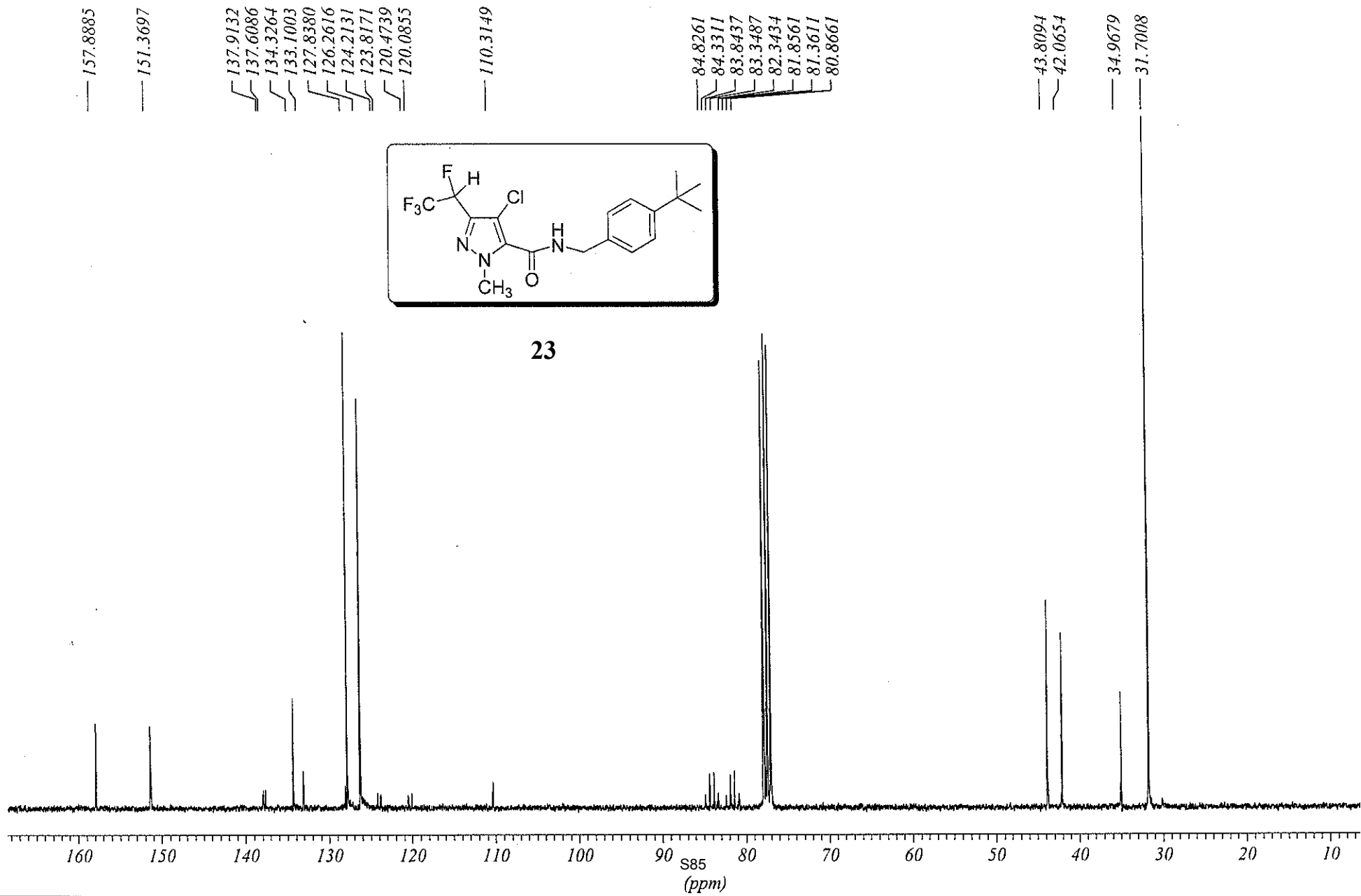
23

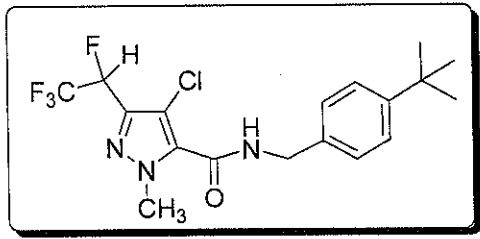




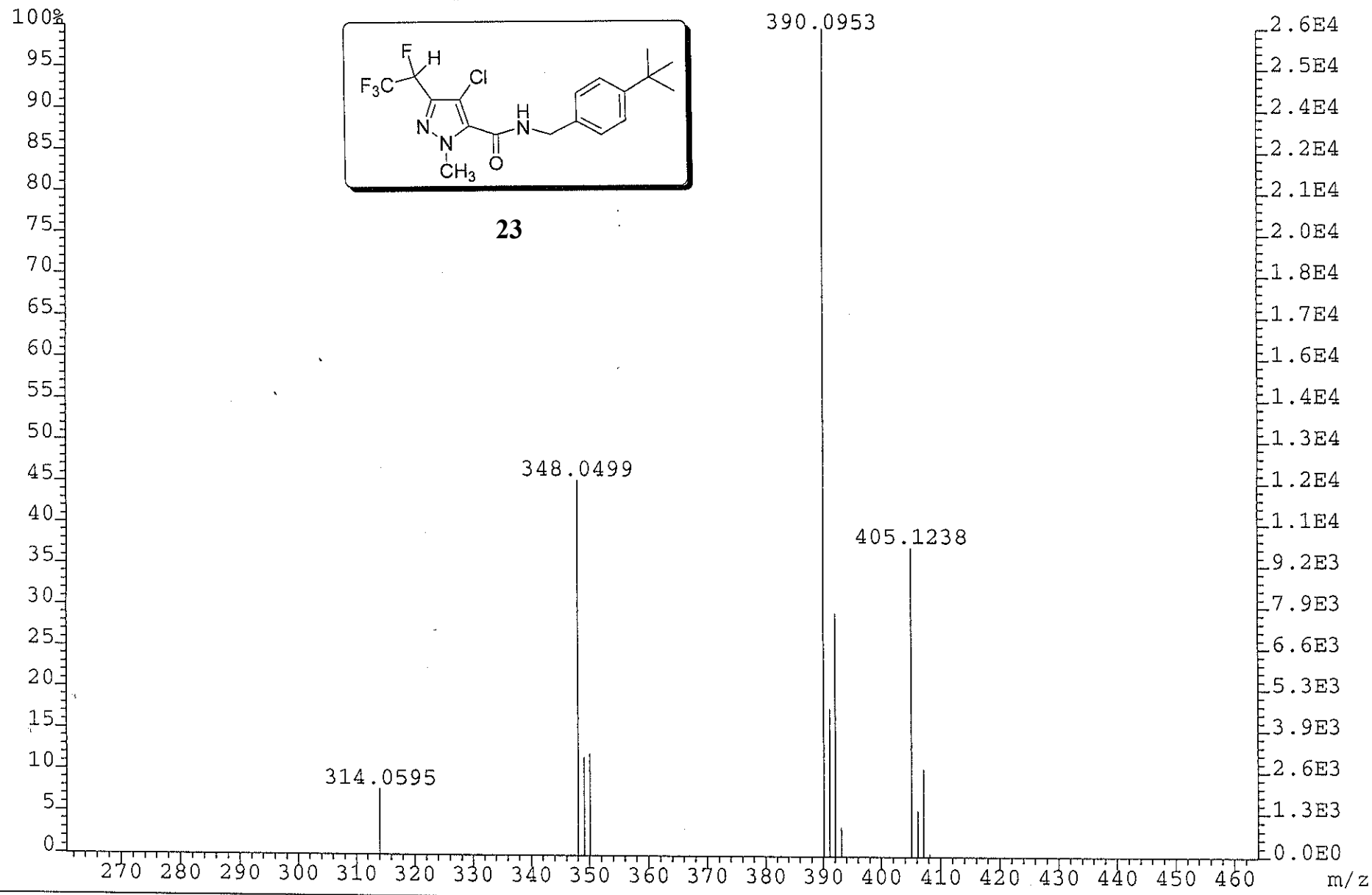


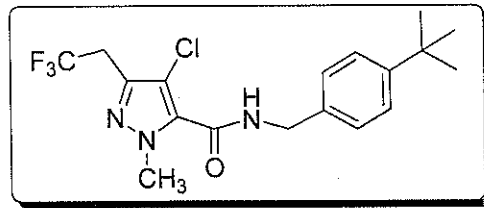
23



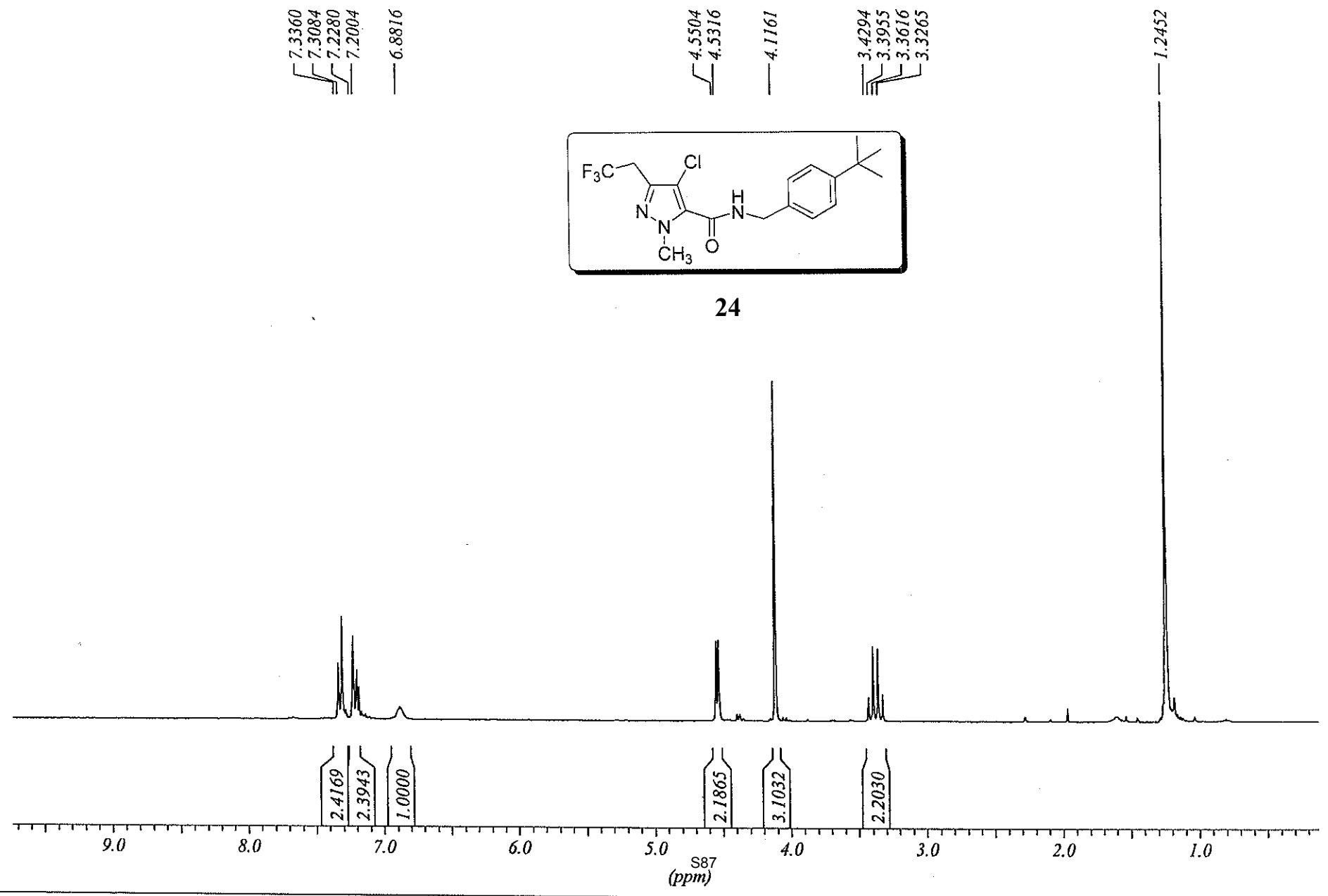


23

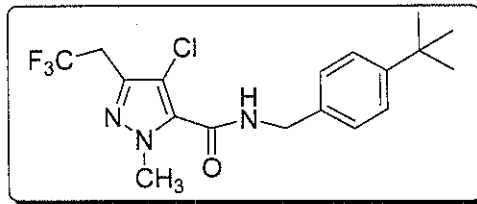




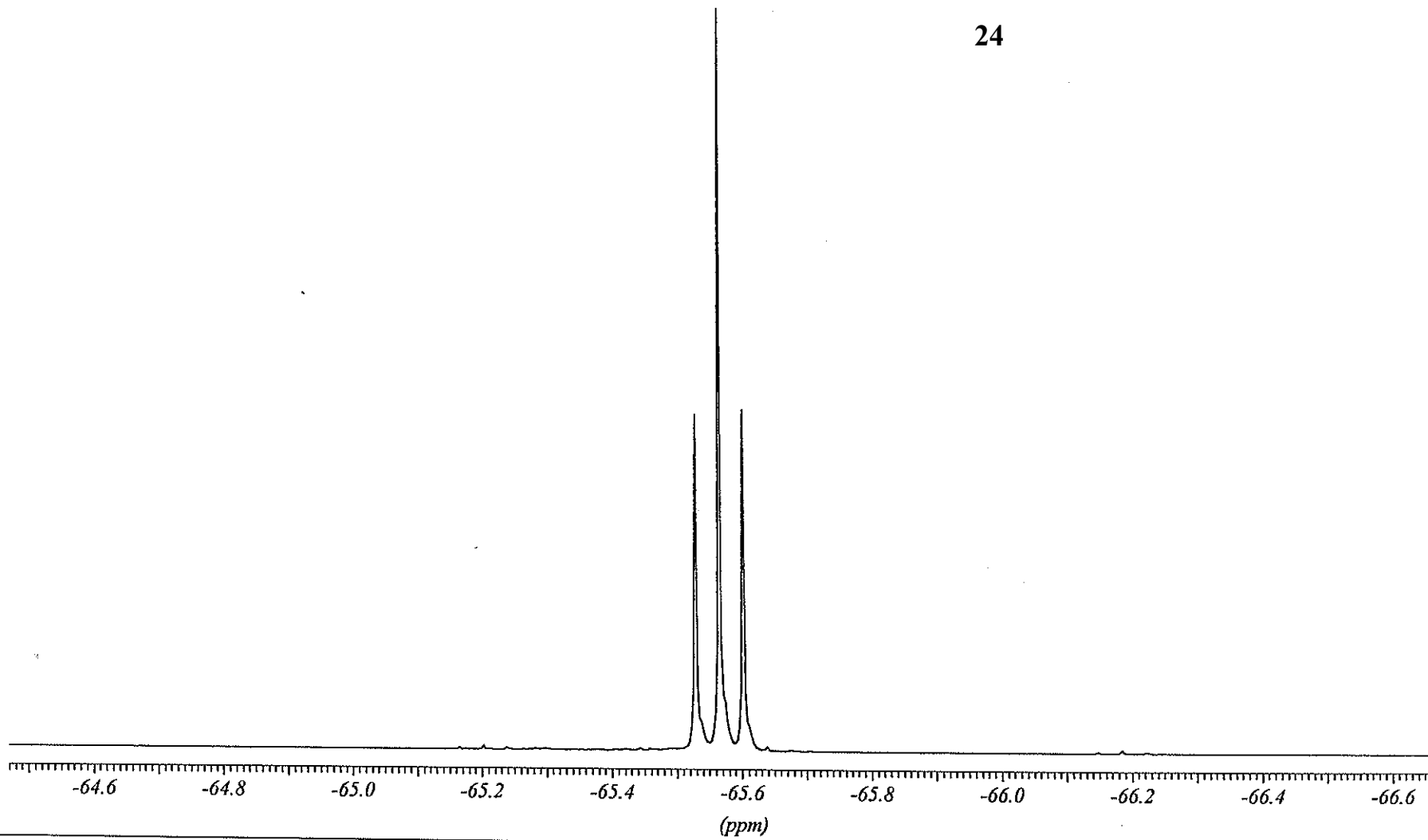
24



-65.5286
-65.5652
-65.6018



24



— 158.3150

— 151.2555

— 138.3549

— 138.3092

— 138.2635

— 138.2178

— 134.5244

— 132.2854

— 130.7471

— 127.8152

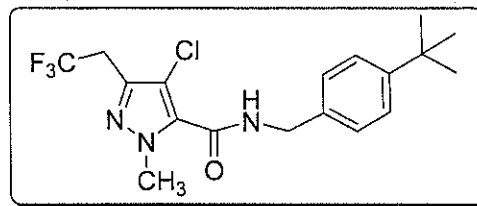
— 127.0689

— 126.2235

— 123.3906

— 119.7200

— 110.2007



24

— 43.6951

— 41.5704

— 34.9526

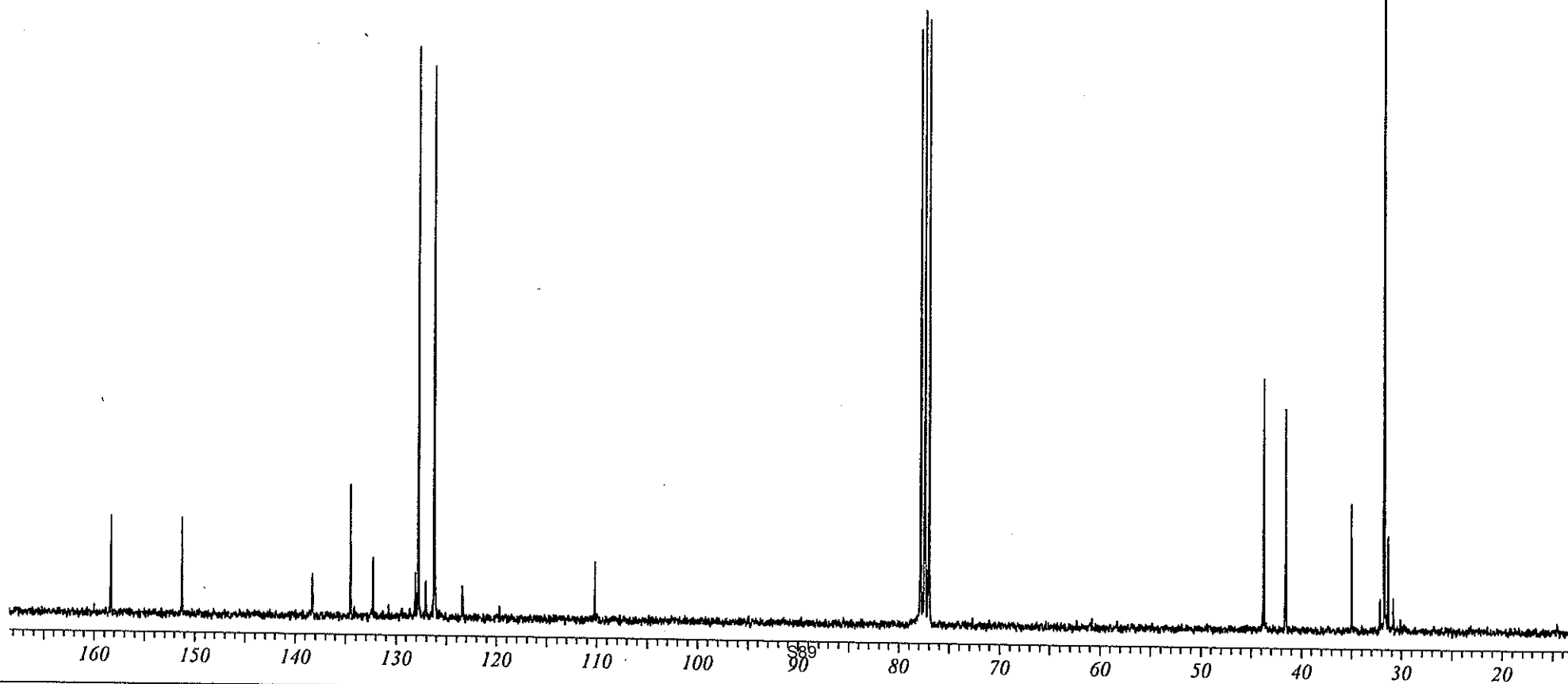
— 32.1425

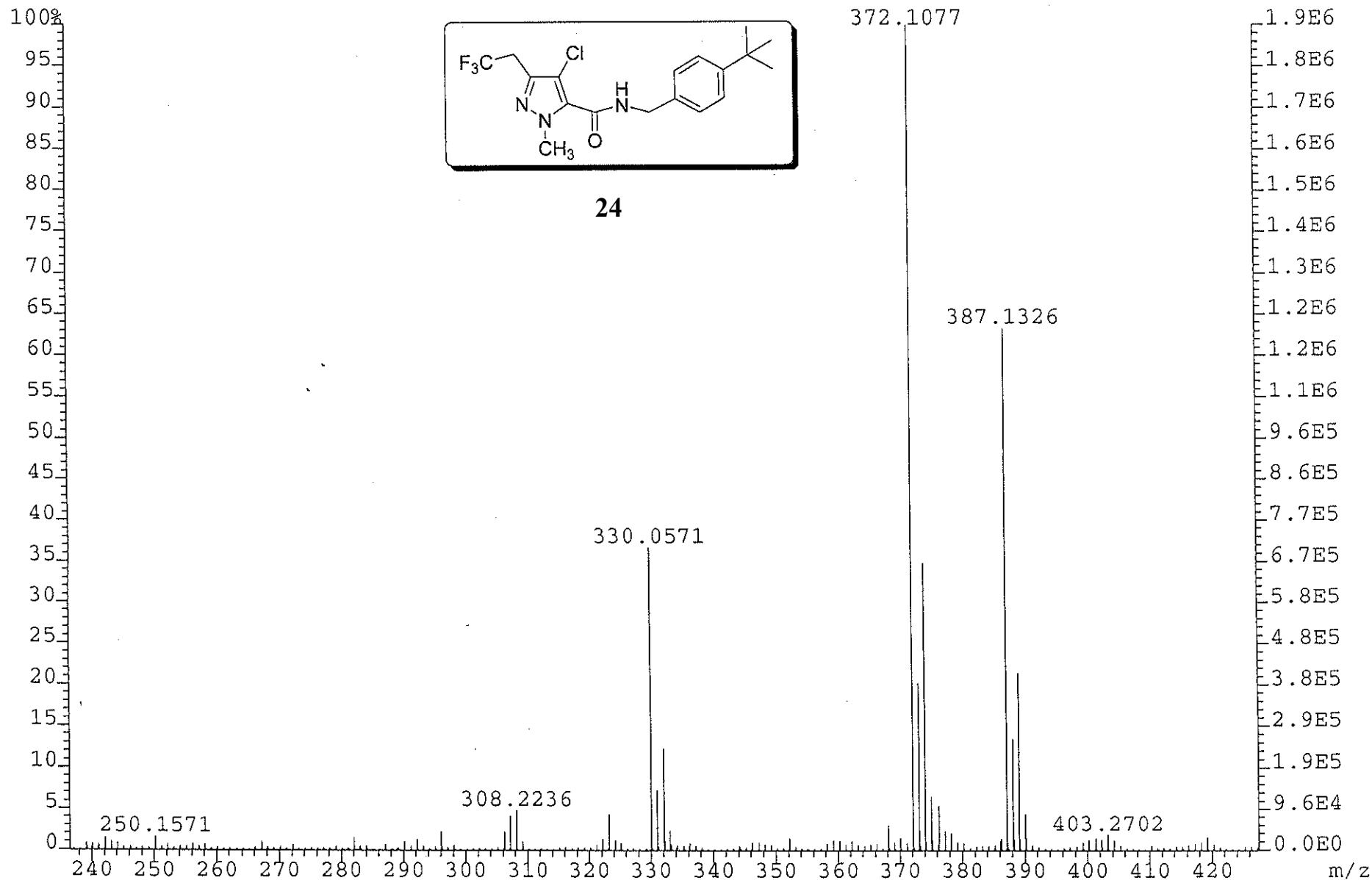
— 31.7008

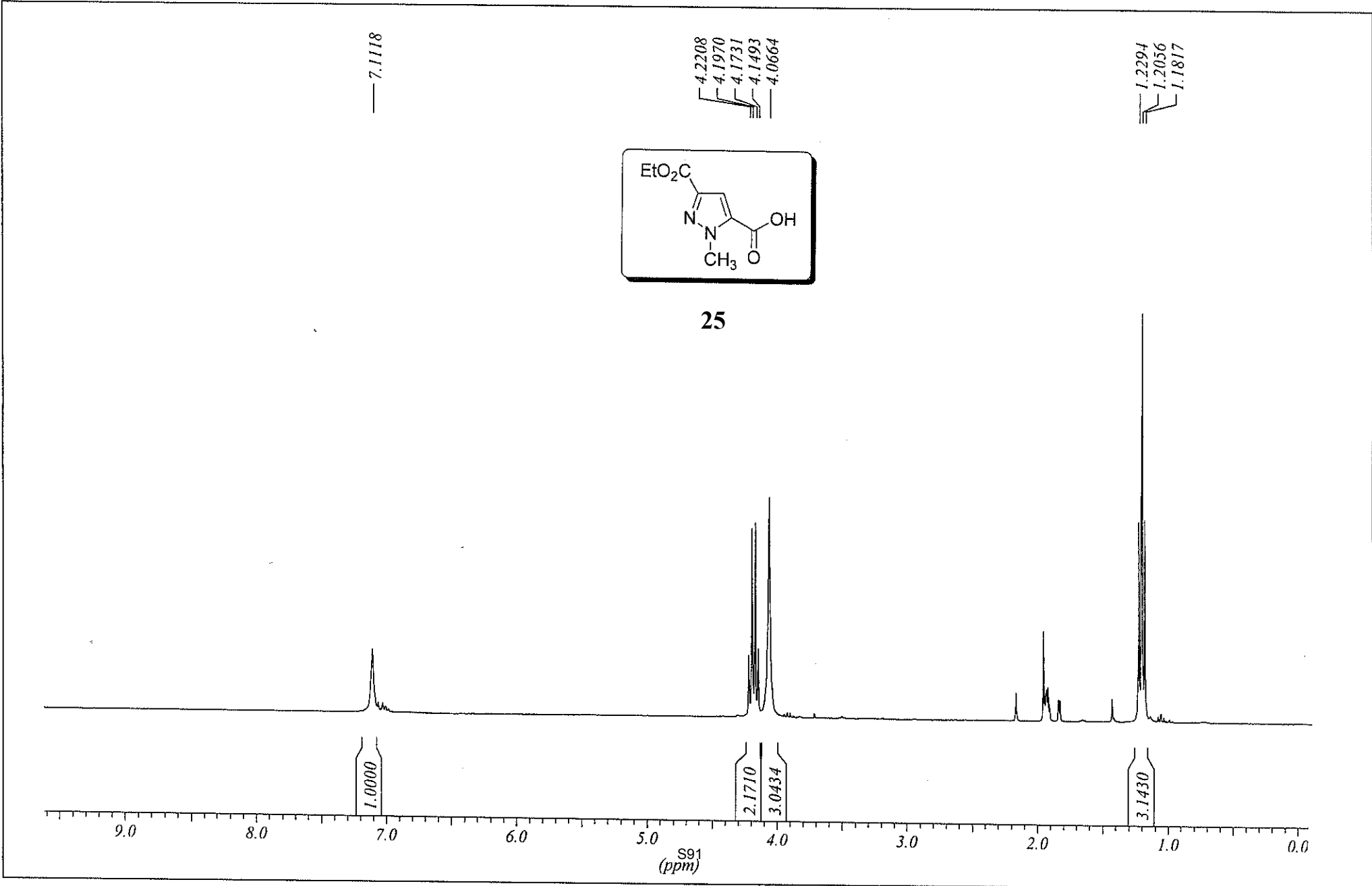
— 31.4419

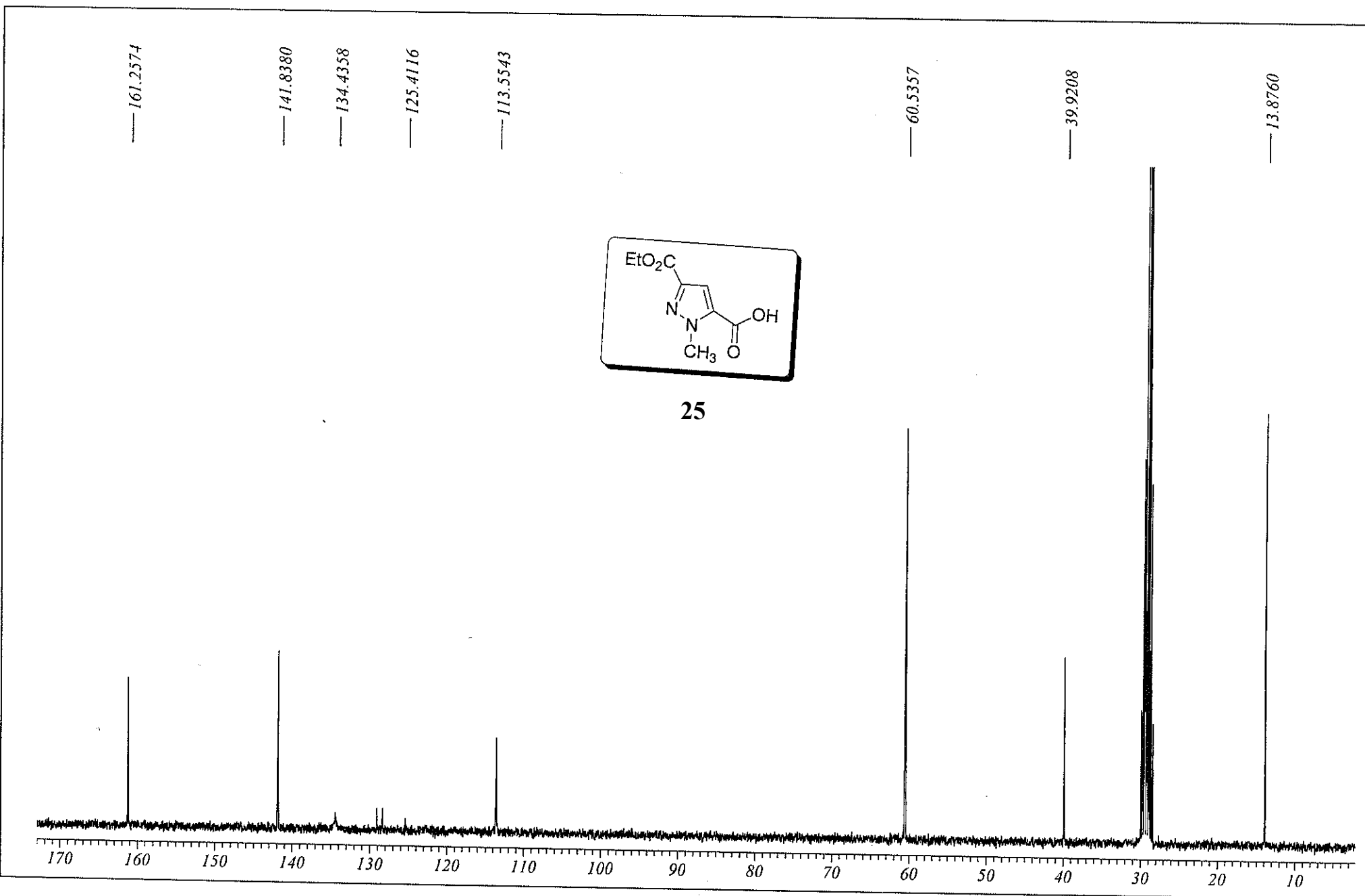
— 31.2896

— 30.8632

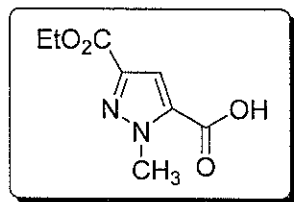
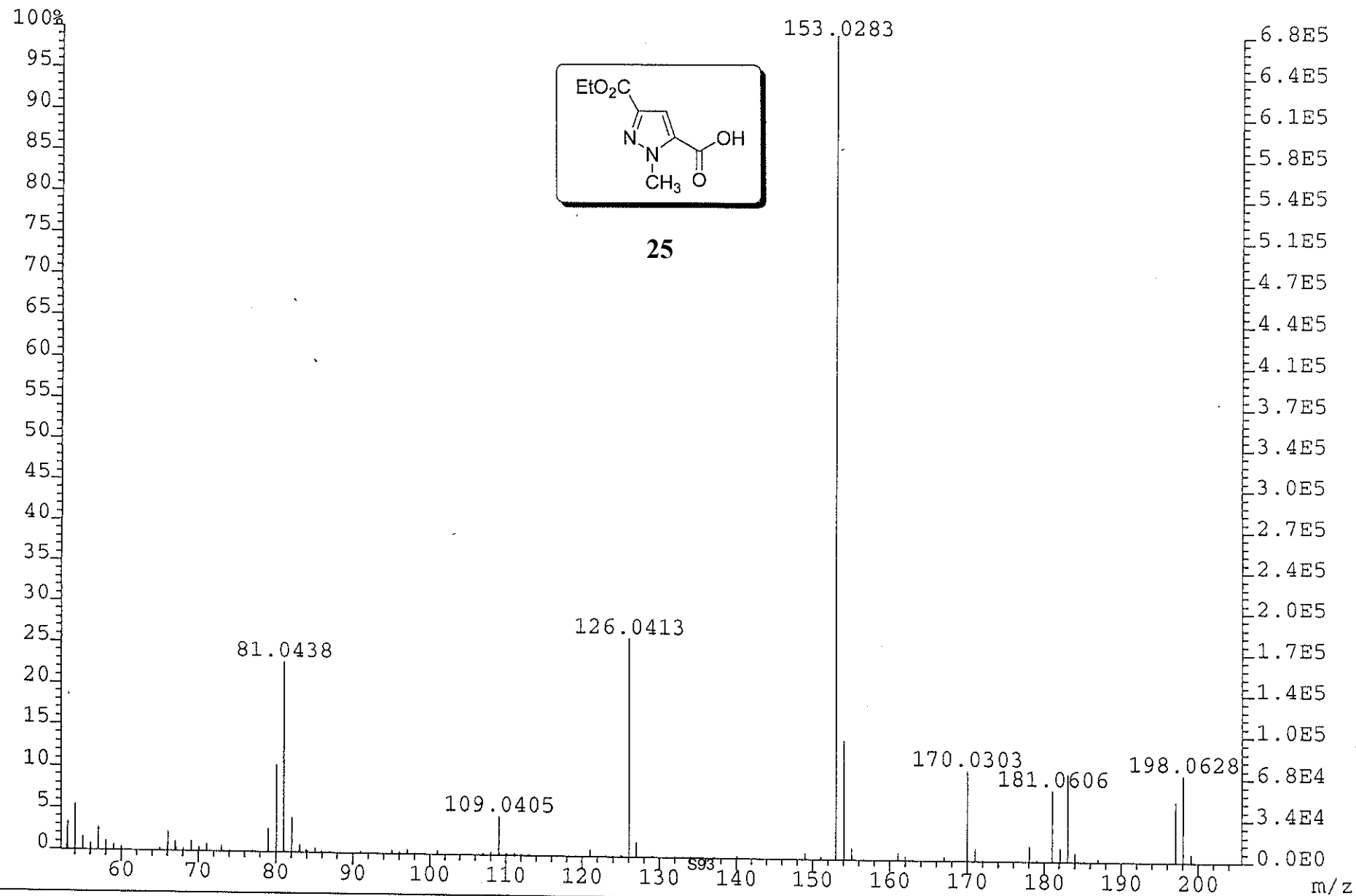




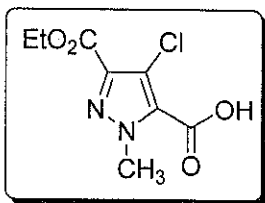




AutoSpecE EI+ Magnet BpM:153 BpI:677632 TIC:2113290 Flags:NORM



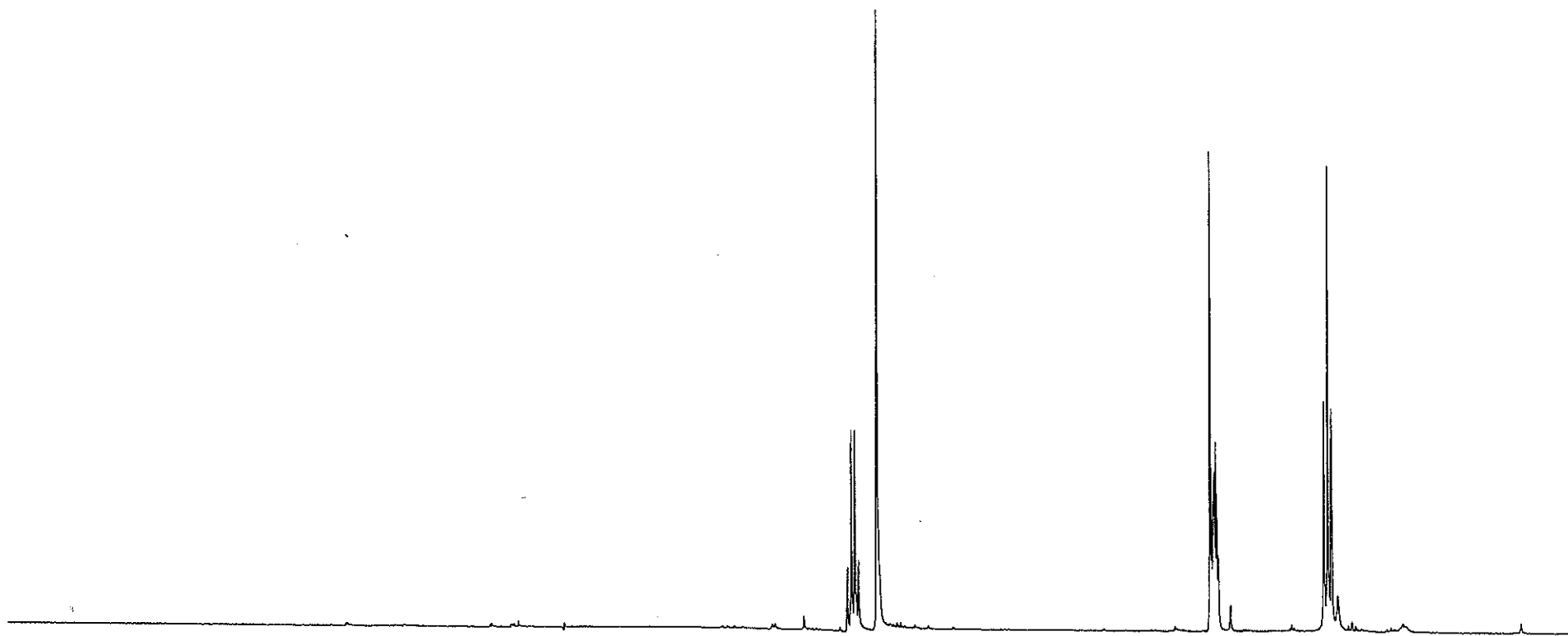
25



26

4.2475
4.2236
4.1998
4.1772
4.0592

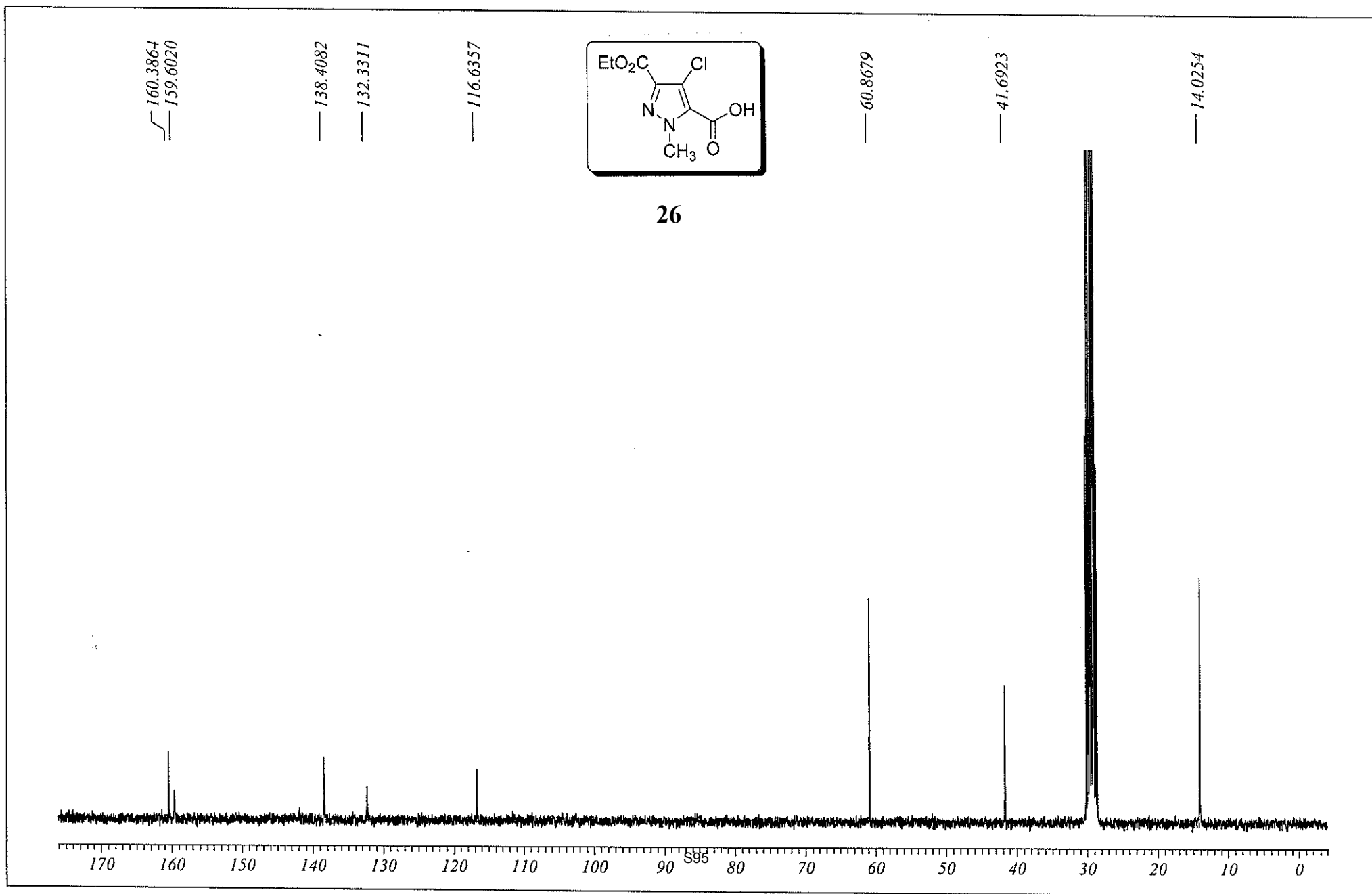
1.2435
1.2196
1.1958



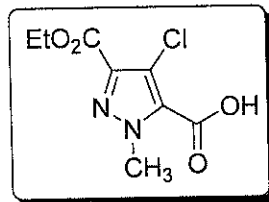
1.0000
1.7180

1.6240

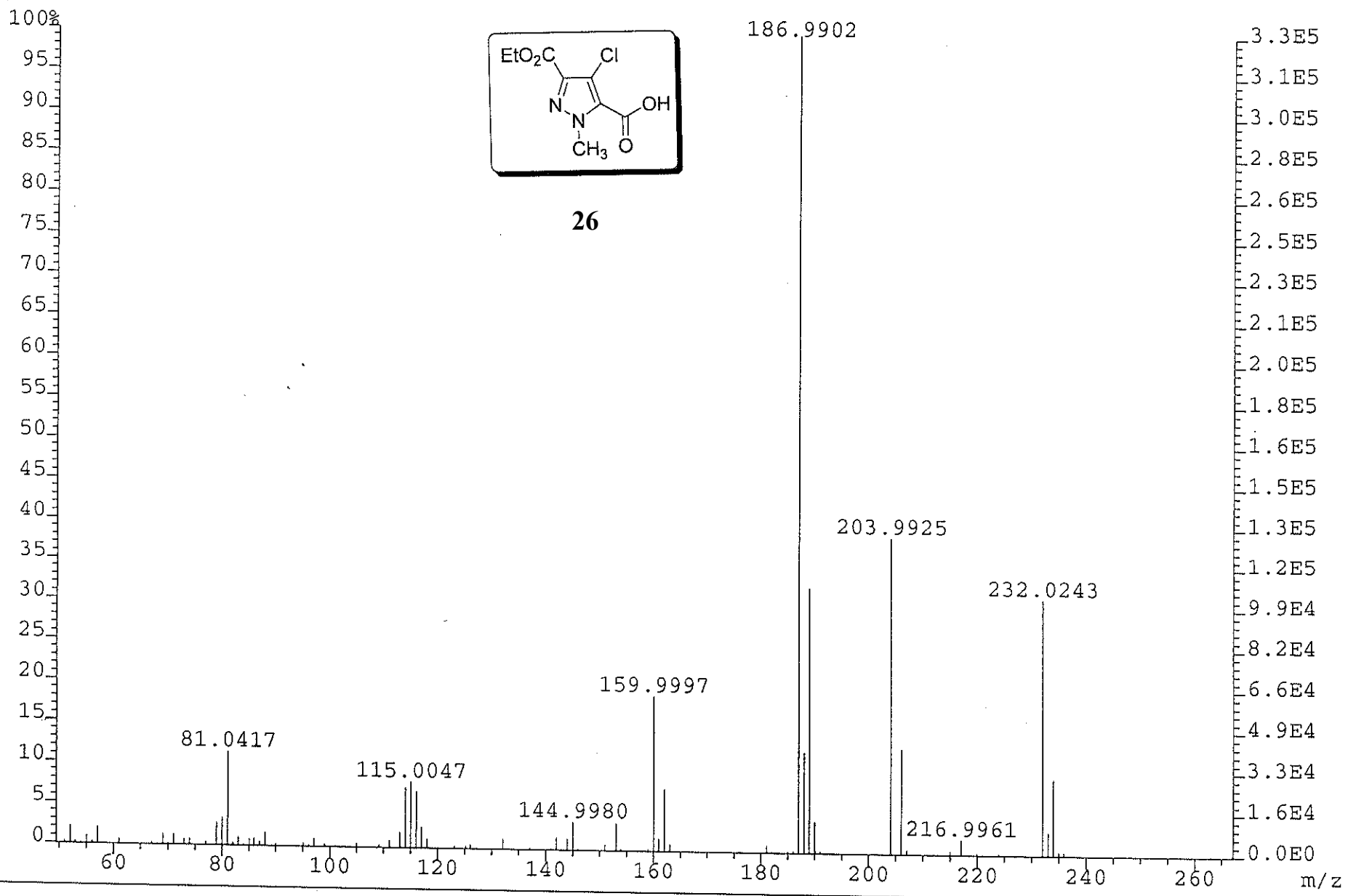
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0



AutoSpecE EI+ Magnet BpM:187 BpI:328832 TIC:1359558 Flags:NORM



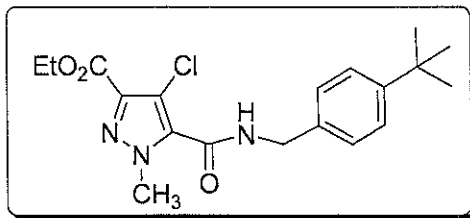
26



7.3160
7.2884
7.2131
7.1854
7.1013
7.0838
7.0674

4.5405
4.5217
4.3647
4.3409
4.3170
4.2944
4.1564

1.3382
1.3143
1.2904
1.2264

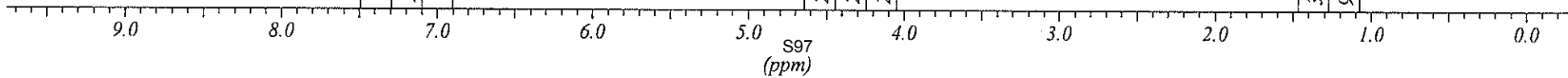


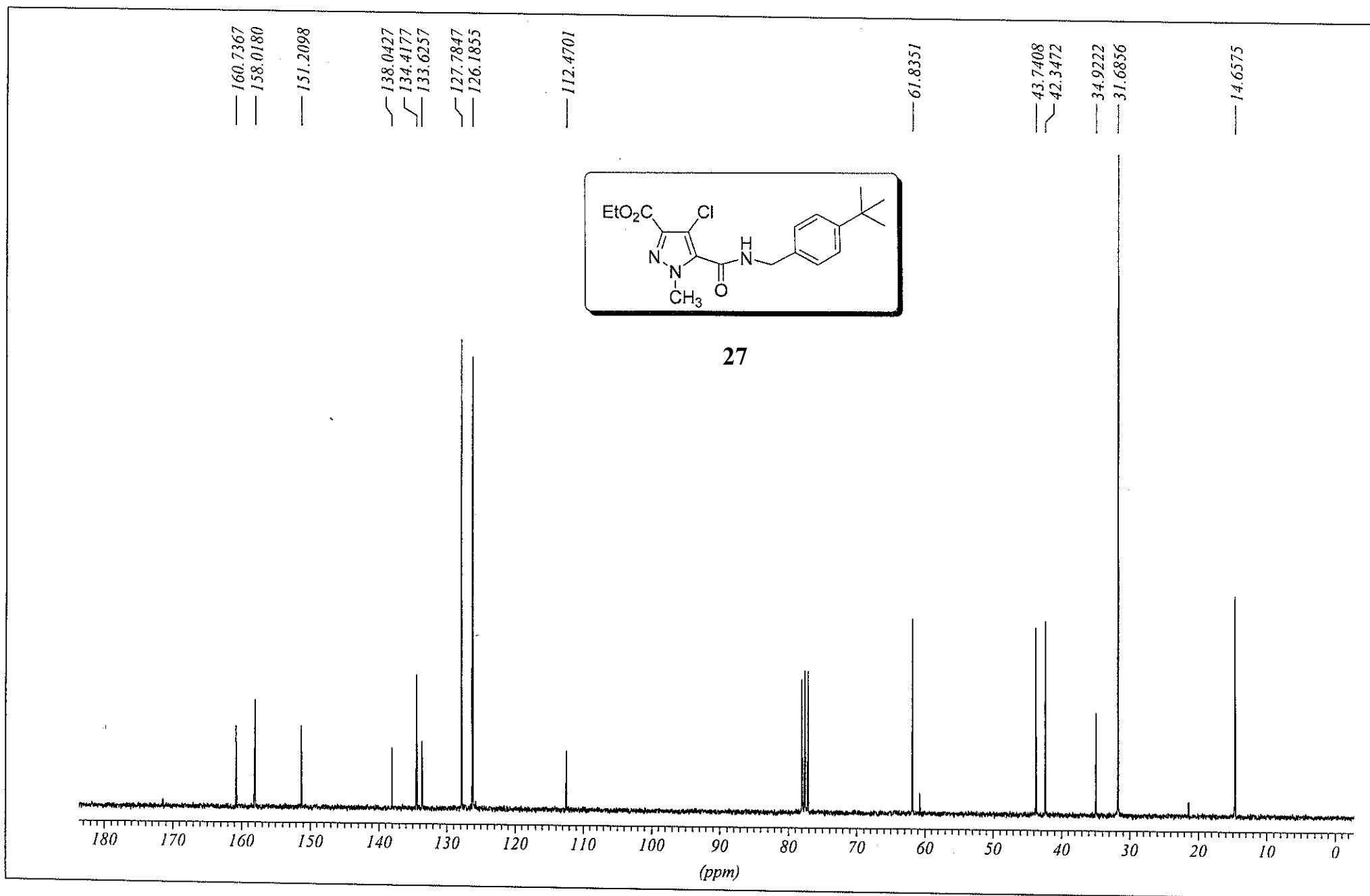
27

1.9949
2.0724
1.0000

2.0741
2.0631
2.9998

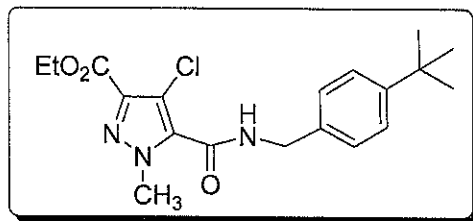
3.0221
9.4930





AutoSpecE EI+ Magnet BpM:316 BpI:383360 TIC:2432255 Flags:NORM

100%



27

316.0784

3.8E5

3.6E5

3.5E5

3.3E5

3.1E5

2.9E5

2.7E5

2.5E5

2.3E5

2.1E5

1.9E5

1.7E5

1.5E5

1.3E5

9.6E4

7.7E4

5.8E4

3.8E4

1.9E4

0.0E0

377.1517

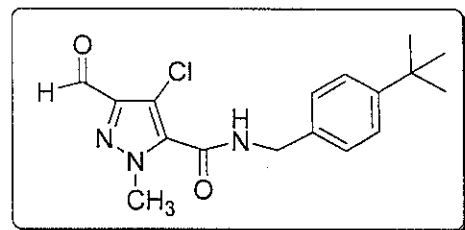
215.0221

85.9562

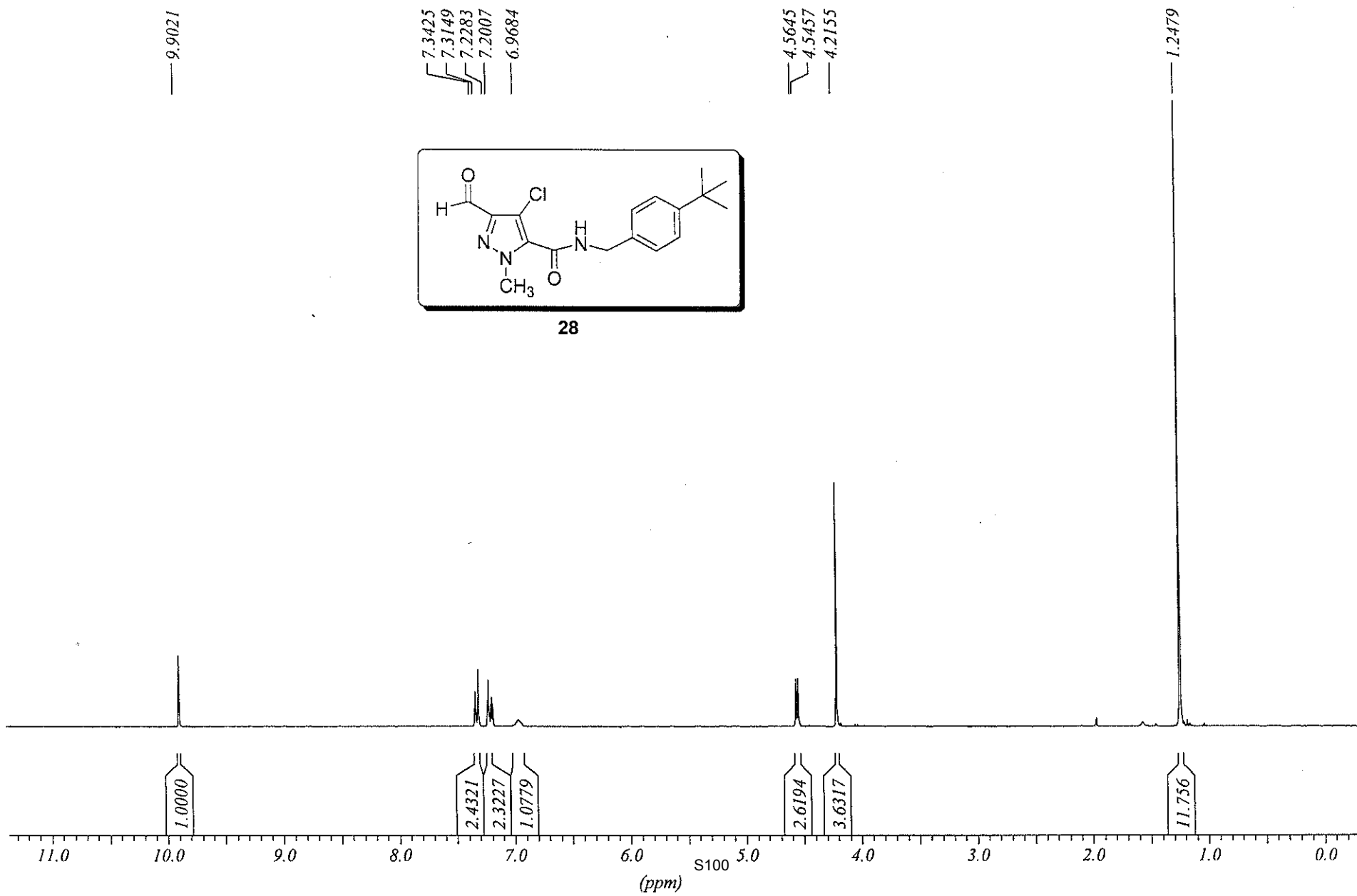
147.1134 186.9896

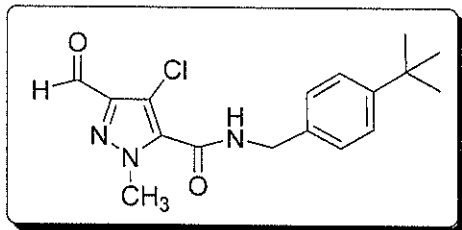
334 1140

60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 m/z

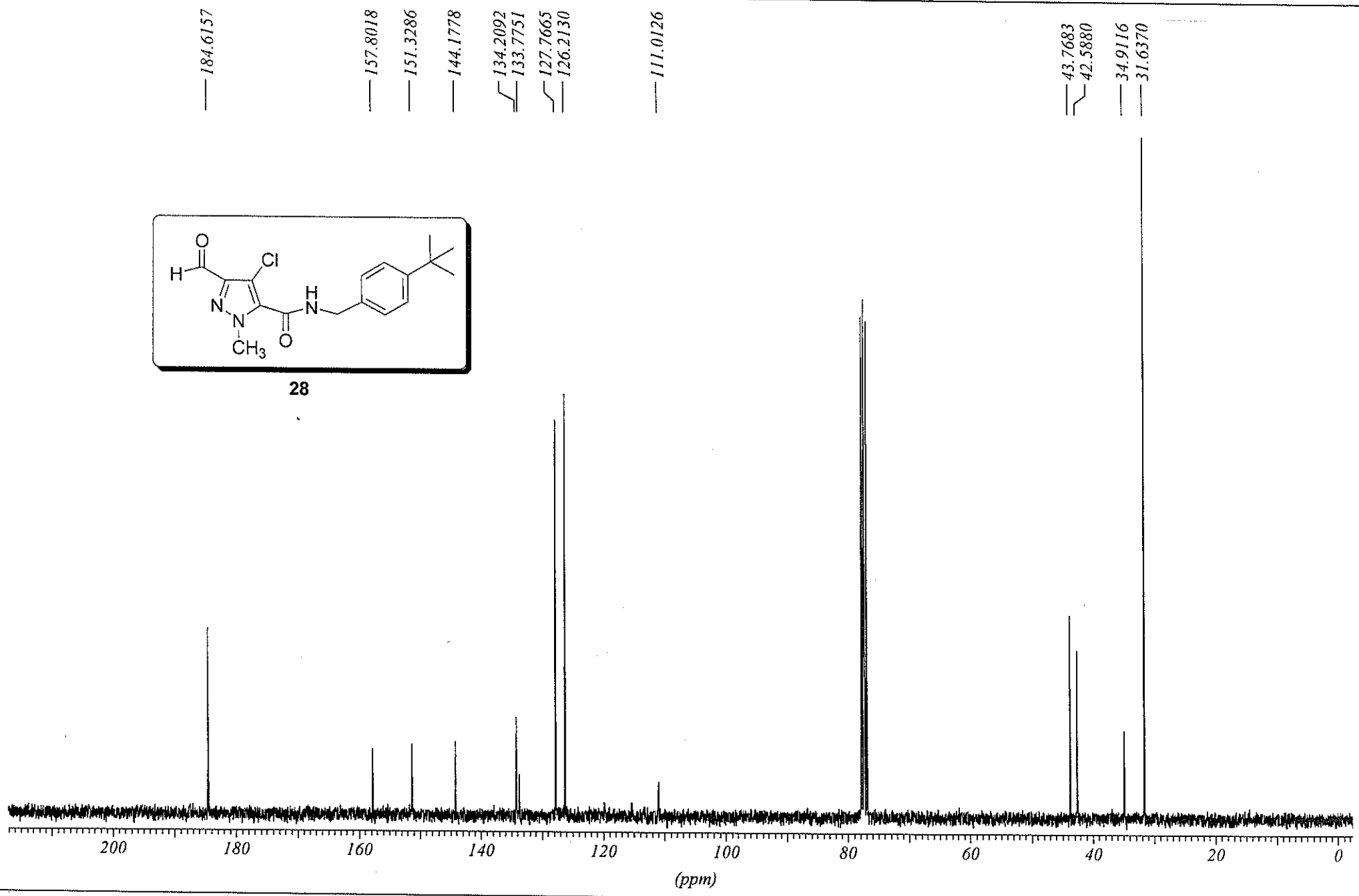


28





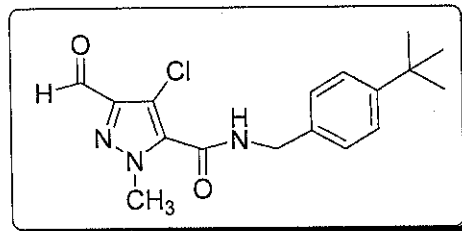
28



AutoSpecE EI+ Magnet BpM:318 BpI:690432 TIC:5266669 Flags:NORM

100%
59.0401

95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0



28

318.1029

276.0551

333.1243

131.0850

83.9520

170.9961

147.1187

194.0790

6.9E5

6.6E5

6.2E5

5.9E5

5.5E5

5.2E5

4.8E5

4.5E5

4.1E5

3.8E5

3.5E5

3.1E5

2.8E5

2.4E5

2.1E5

1.7E5

1.4E5

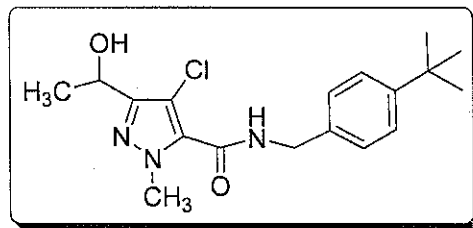
1.0E5

6.9E4

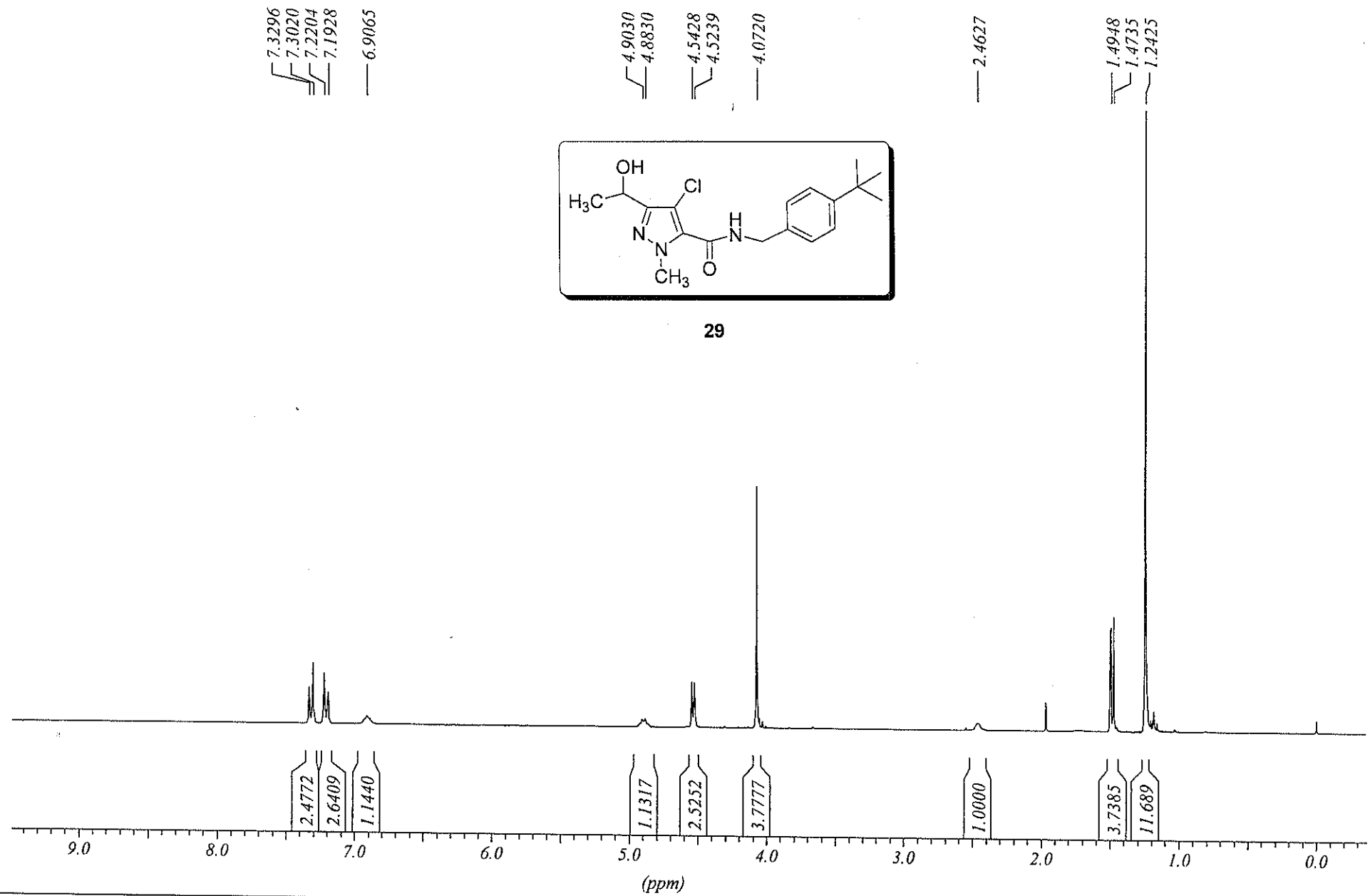
3.5E4

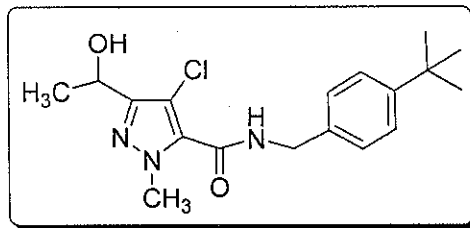
0.0E0

m/z

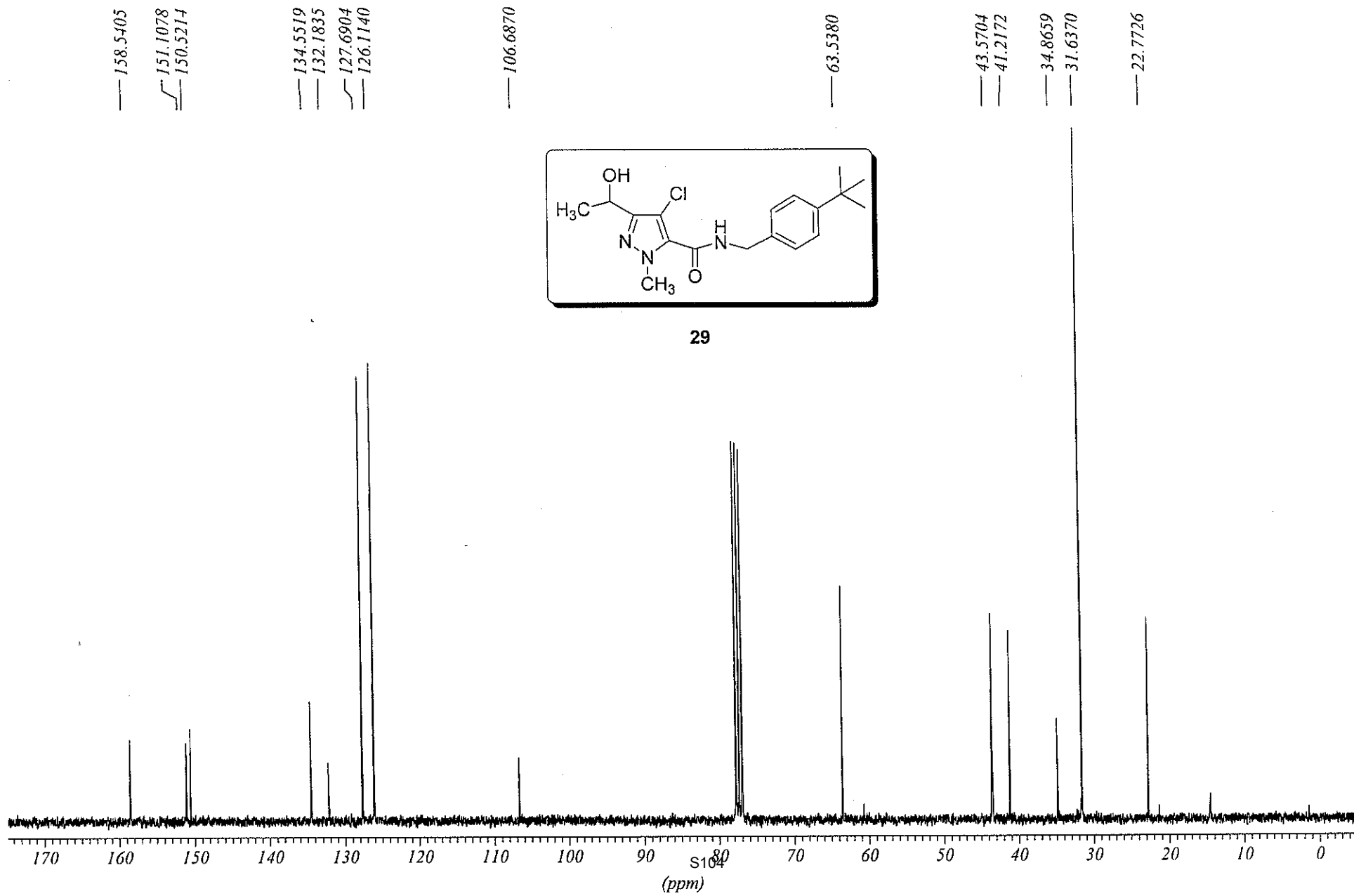


29

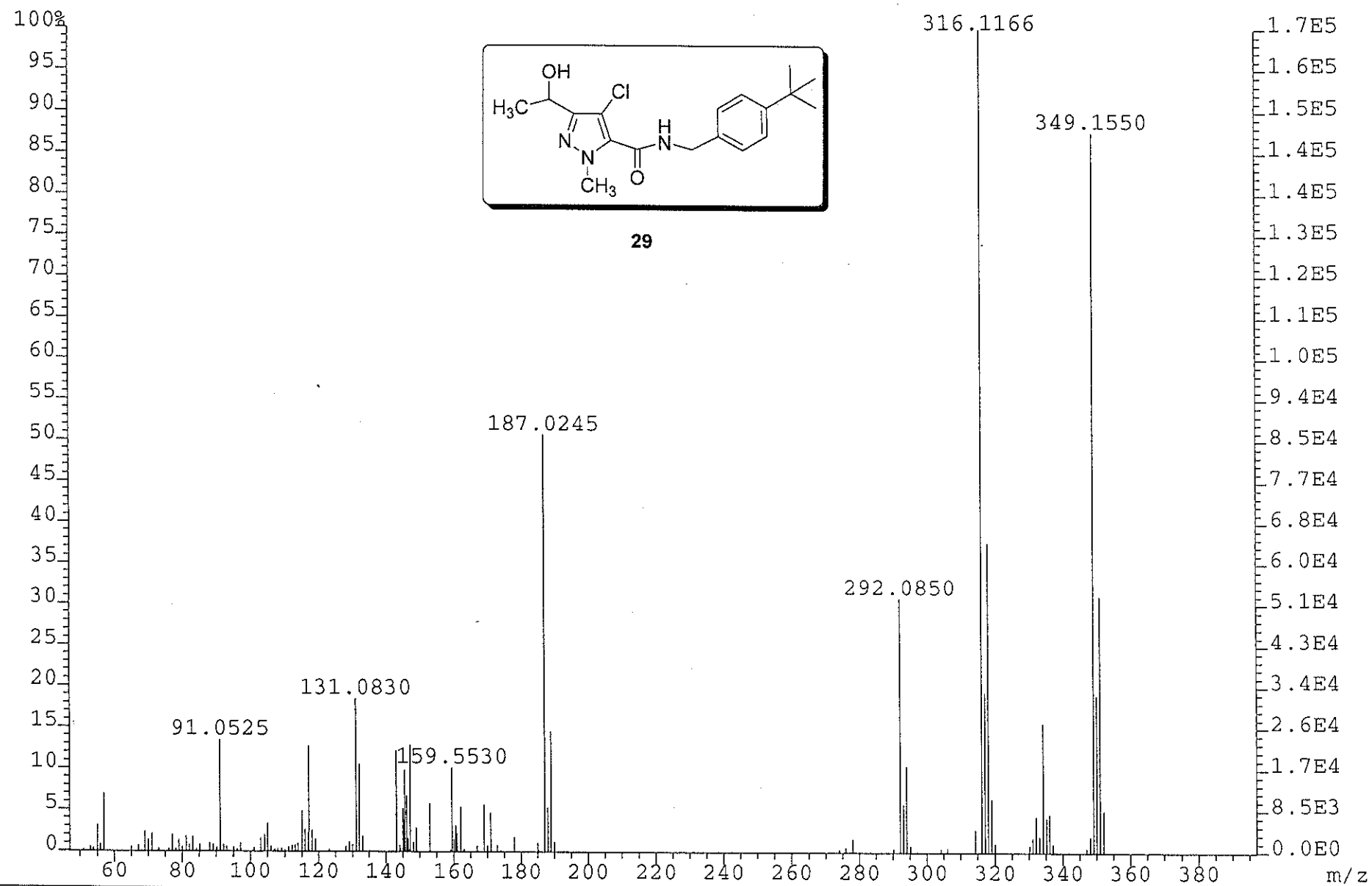


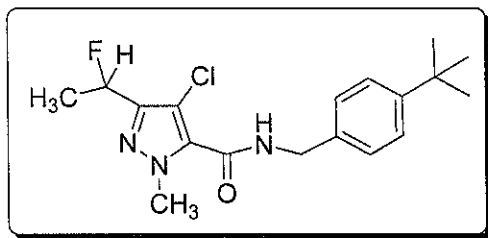


29

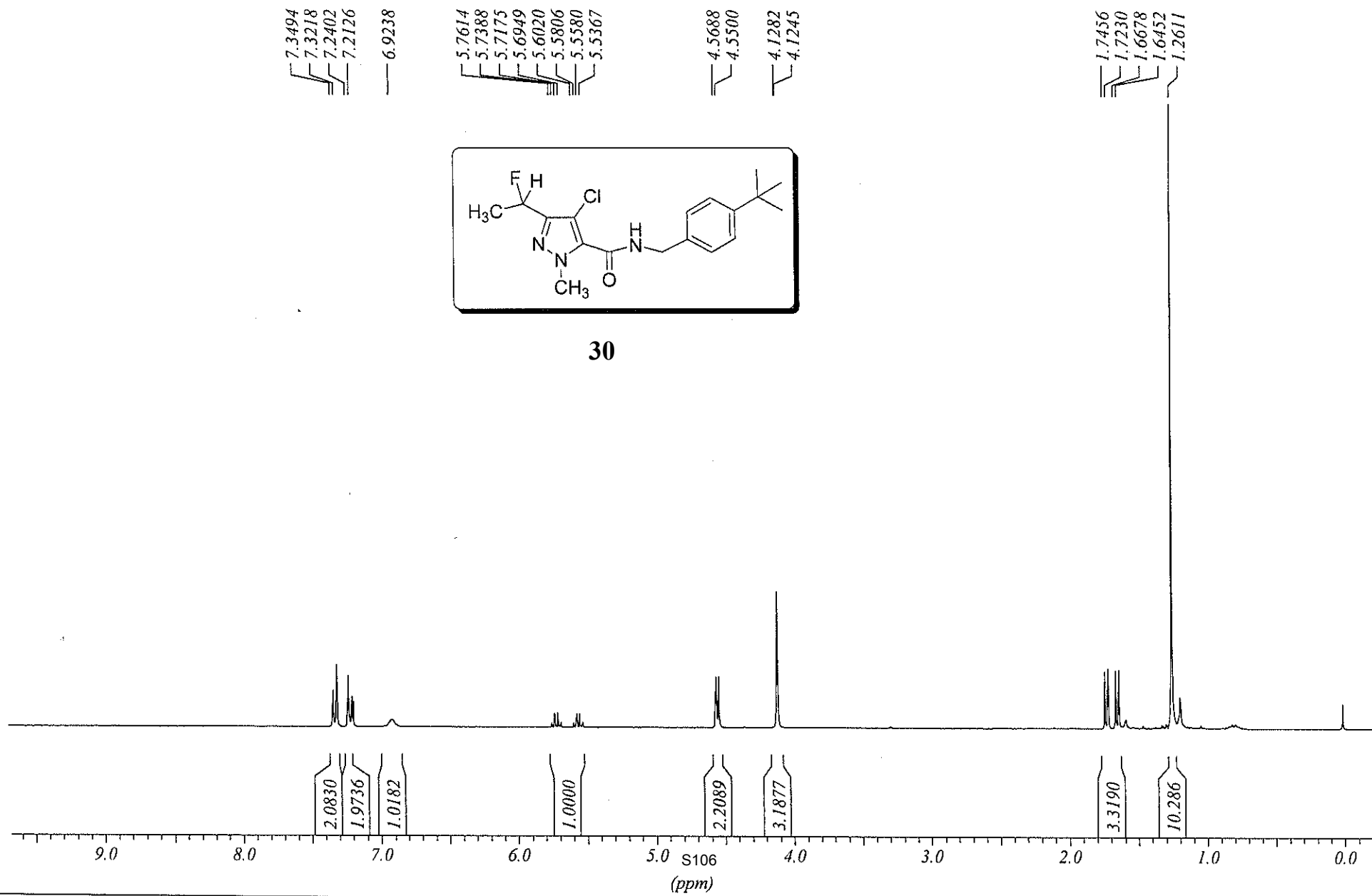


AutoSpecE EI+ Magnet BpM:316 BpI:170112 TIC:1204943 Flags:NORM

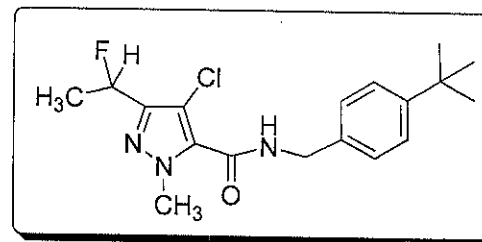




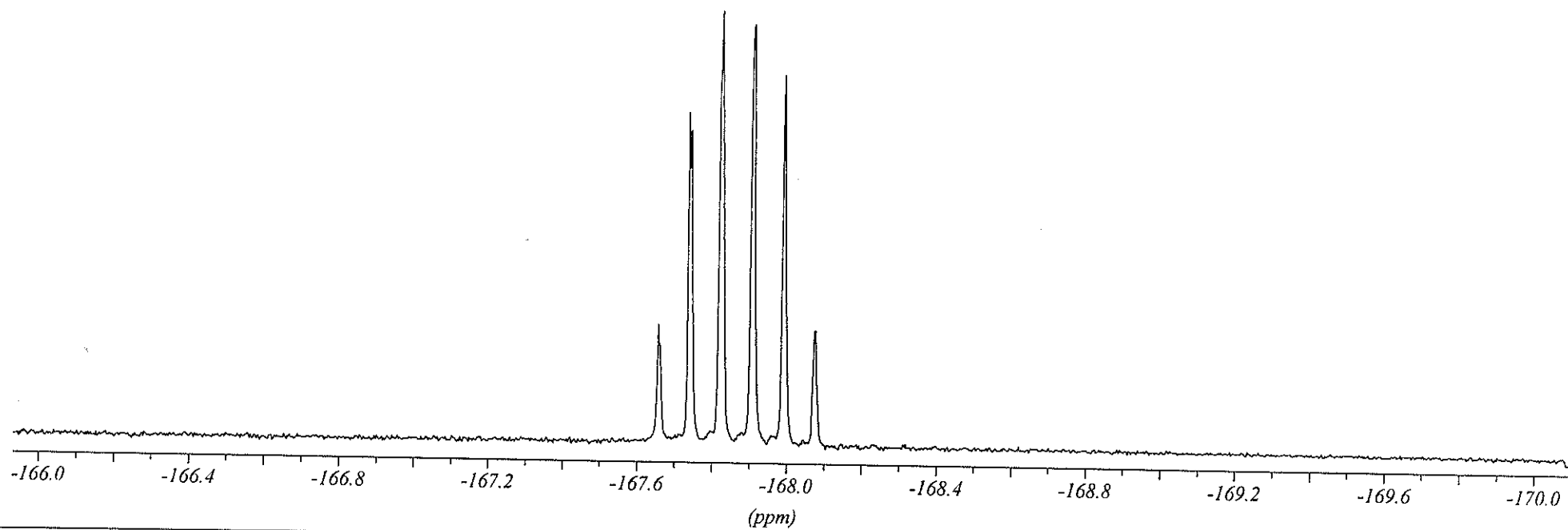
30

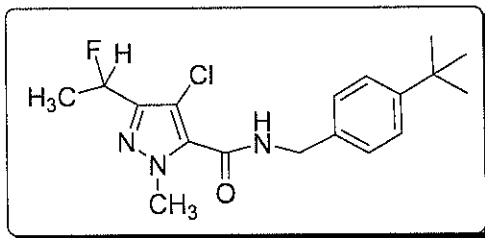


-167.6556
-167.7380
-167.7441
-167.8265
-167.9120
-167.9944
-168.0768

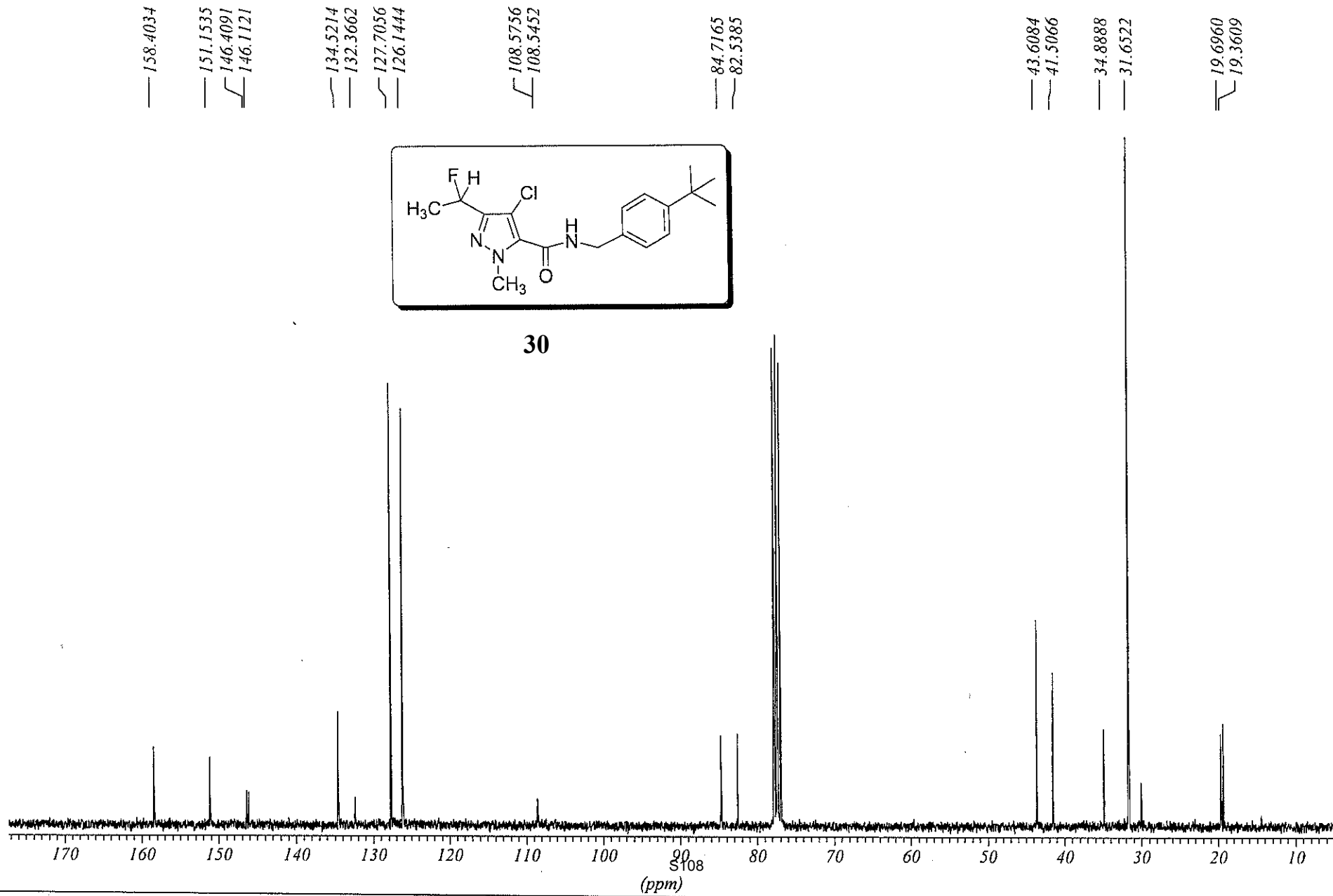


30

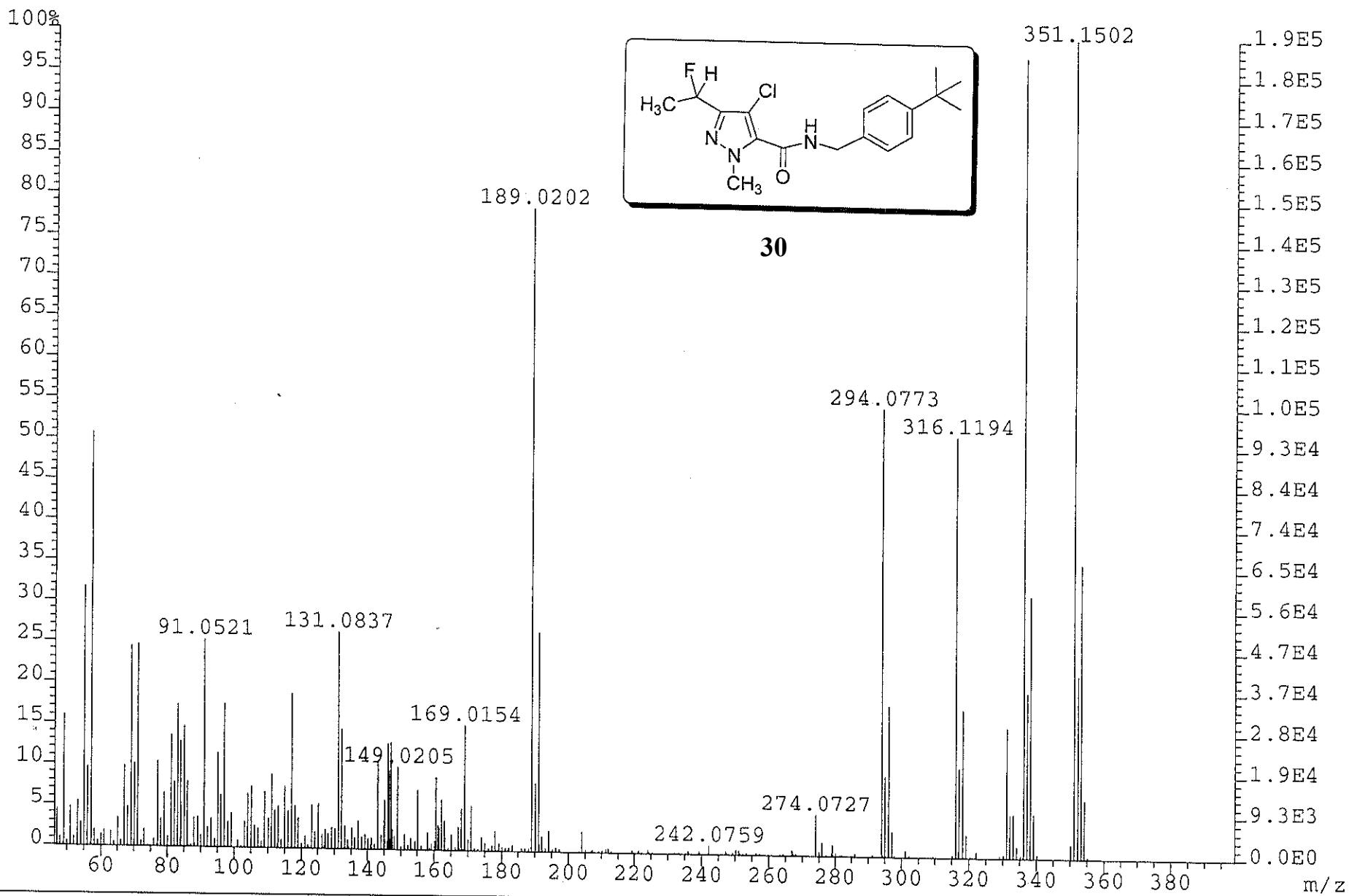


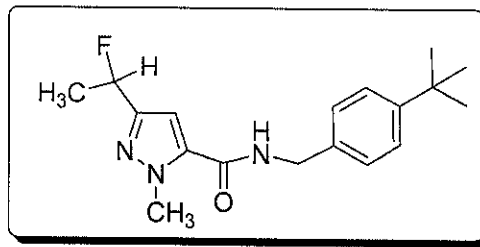


30

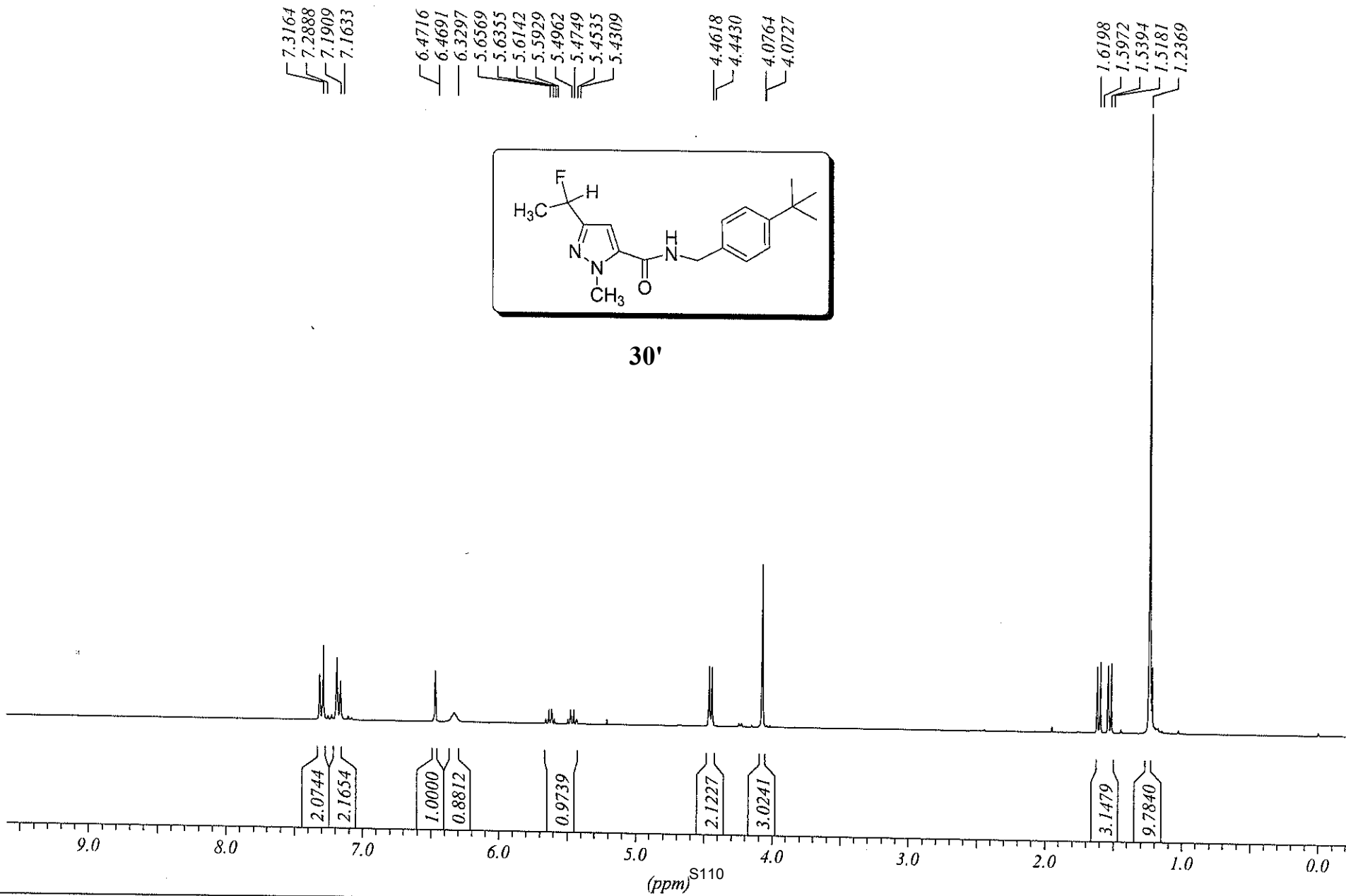


AutoSpecE EI+ Magnet BpM:351 BpI:186048 TIC:2857427 Flags:NORM

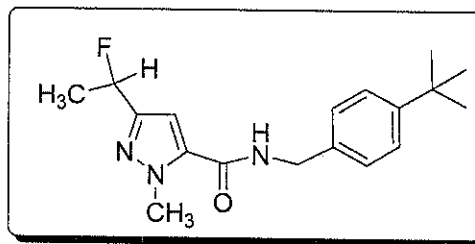




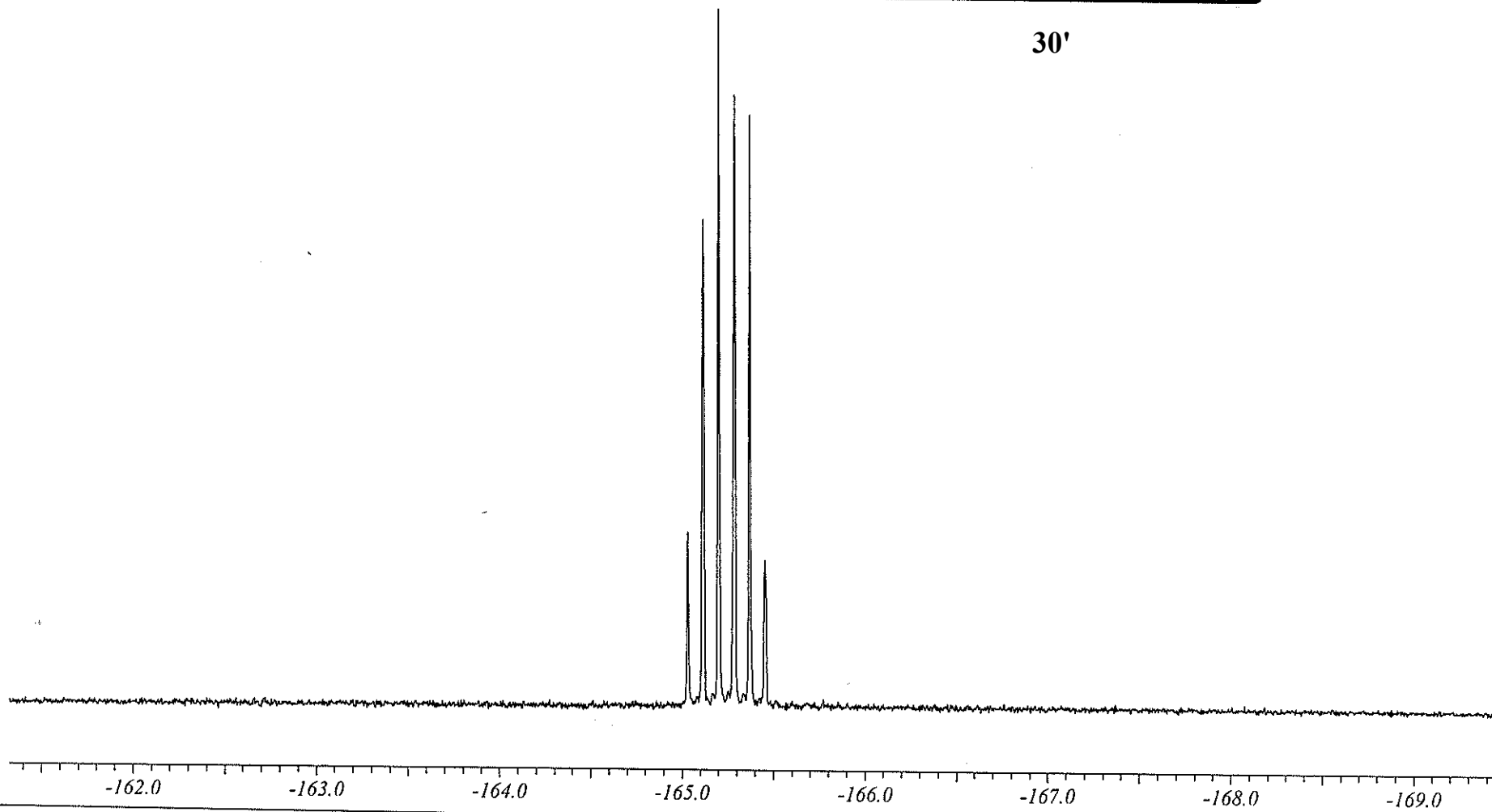
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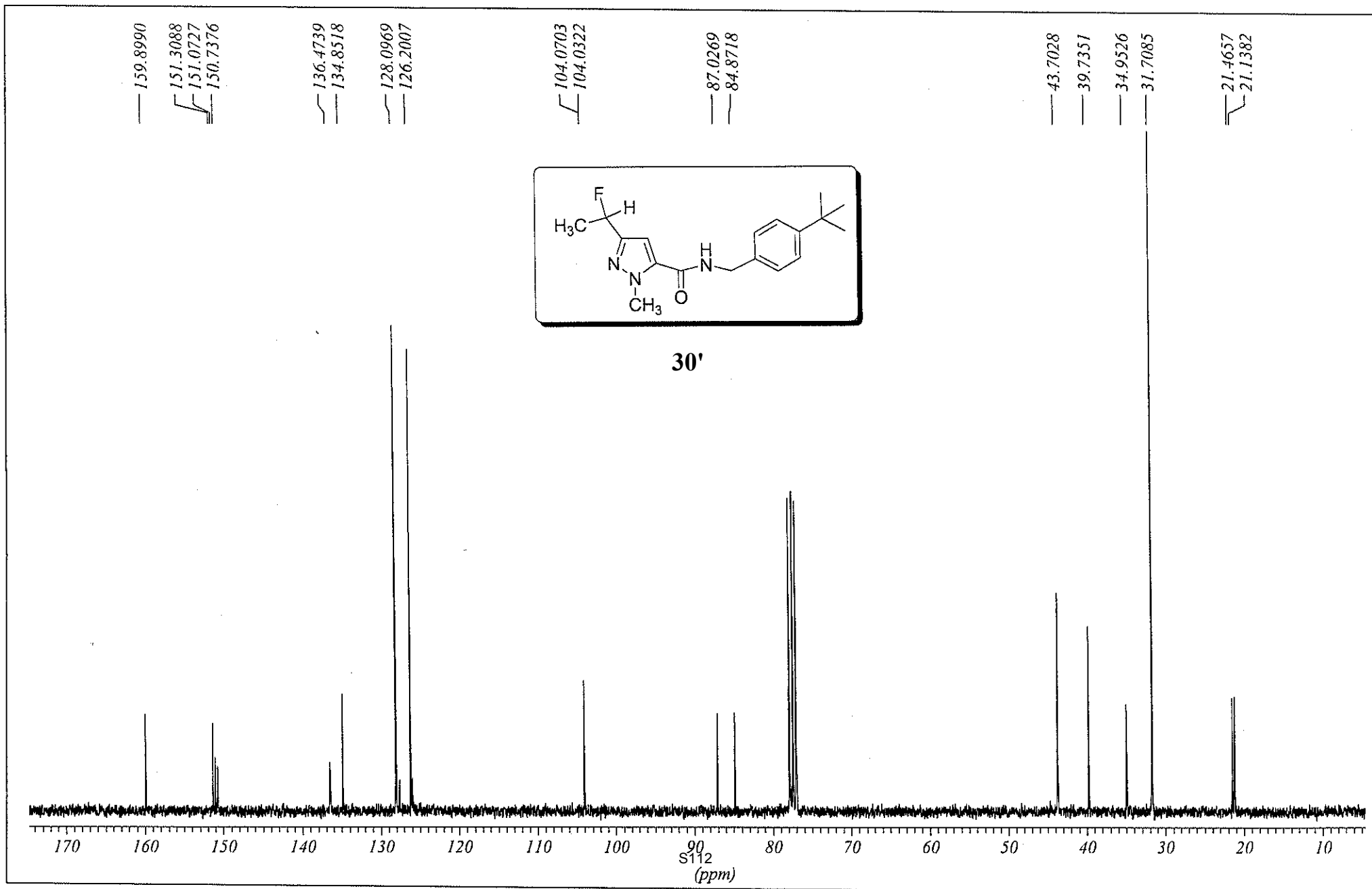


-165.0333
-165.1157
-165.2012
-165.2867
-165.3722
-165.4546

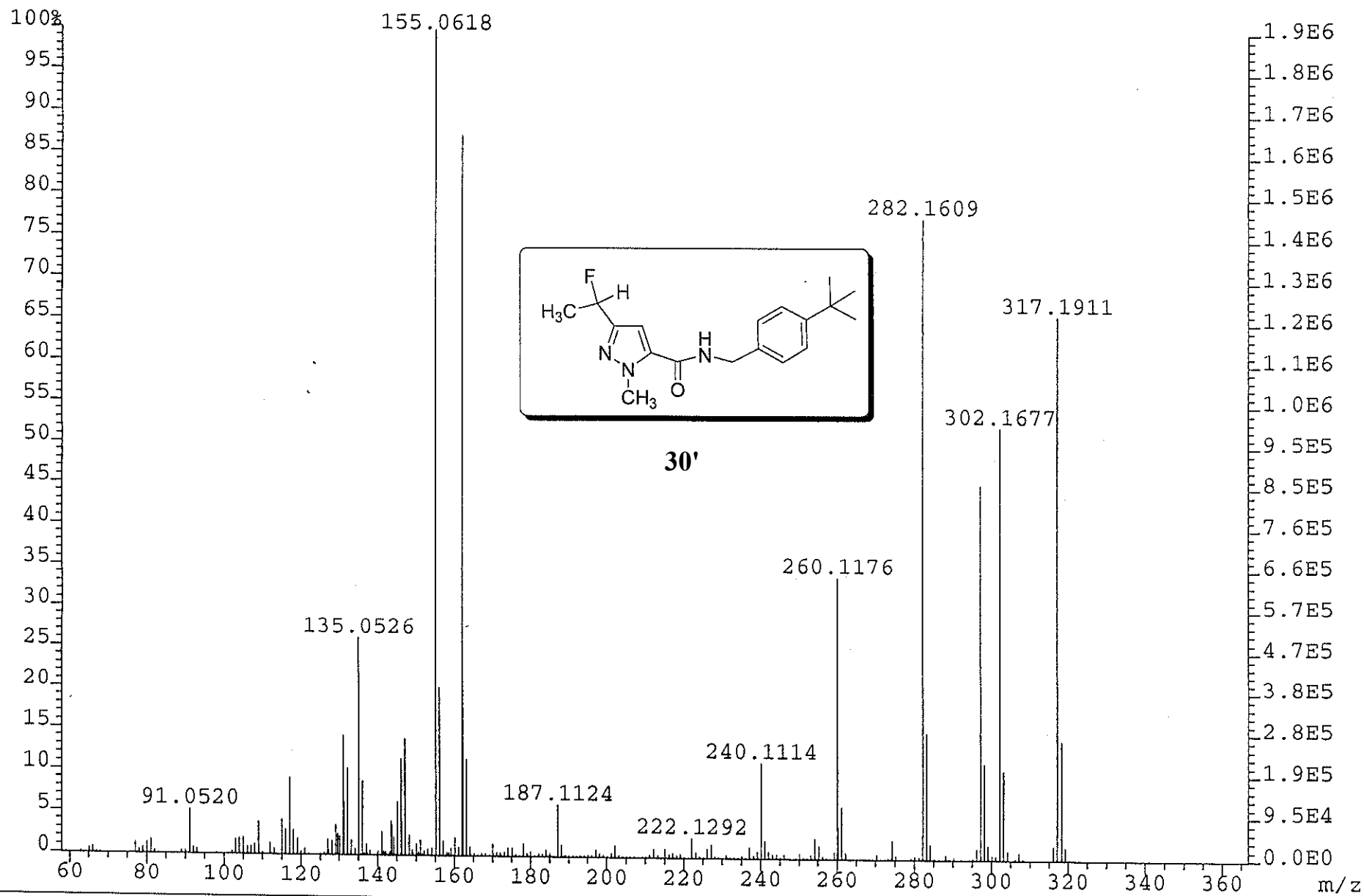


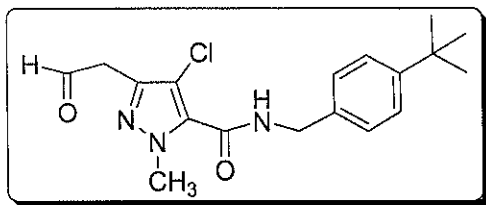
30'



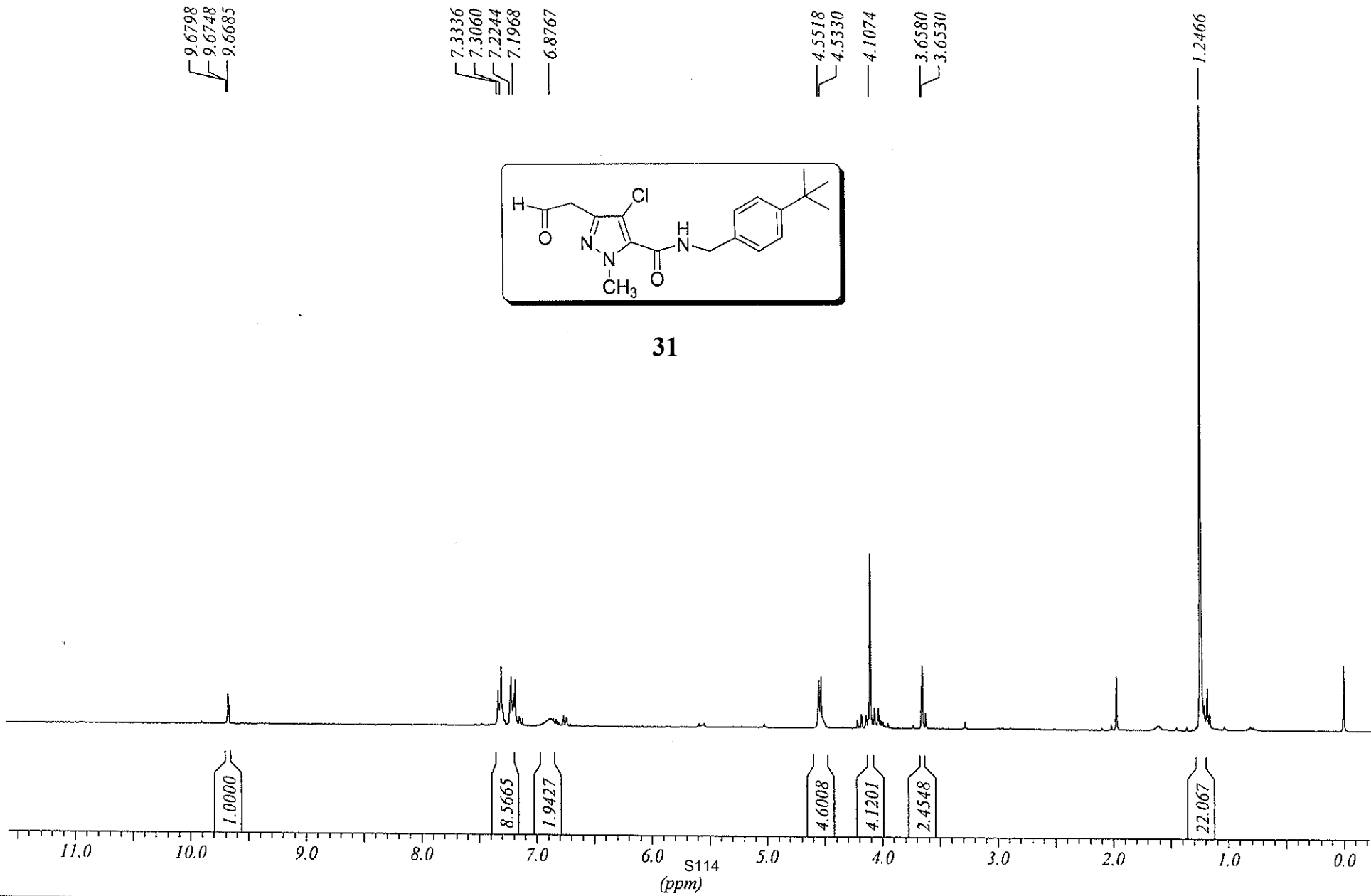


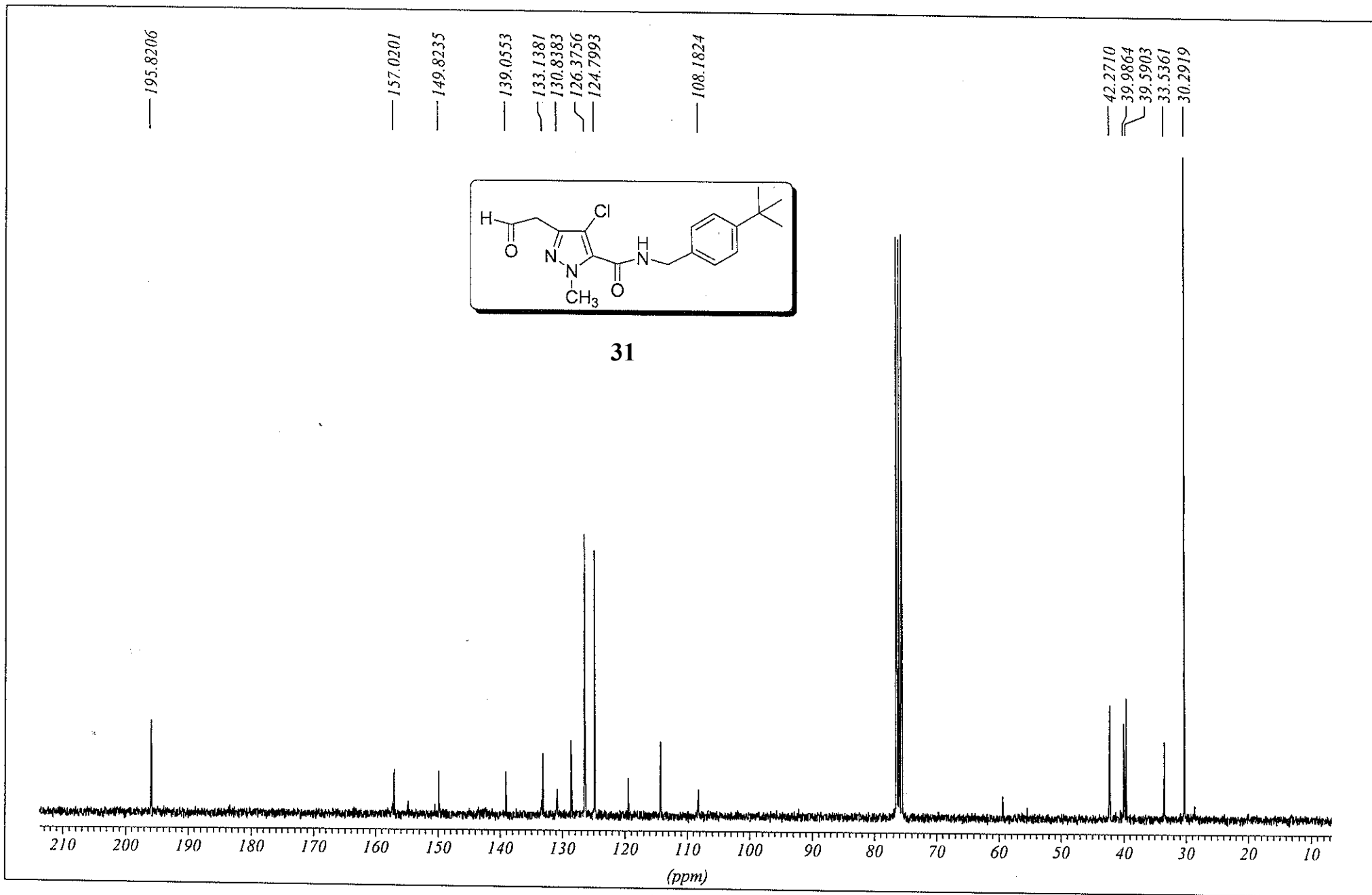
AutoSpecE EI+ Magnet BpM:155 BpI:1893888 TIC:18717220 Flags:NORM



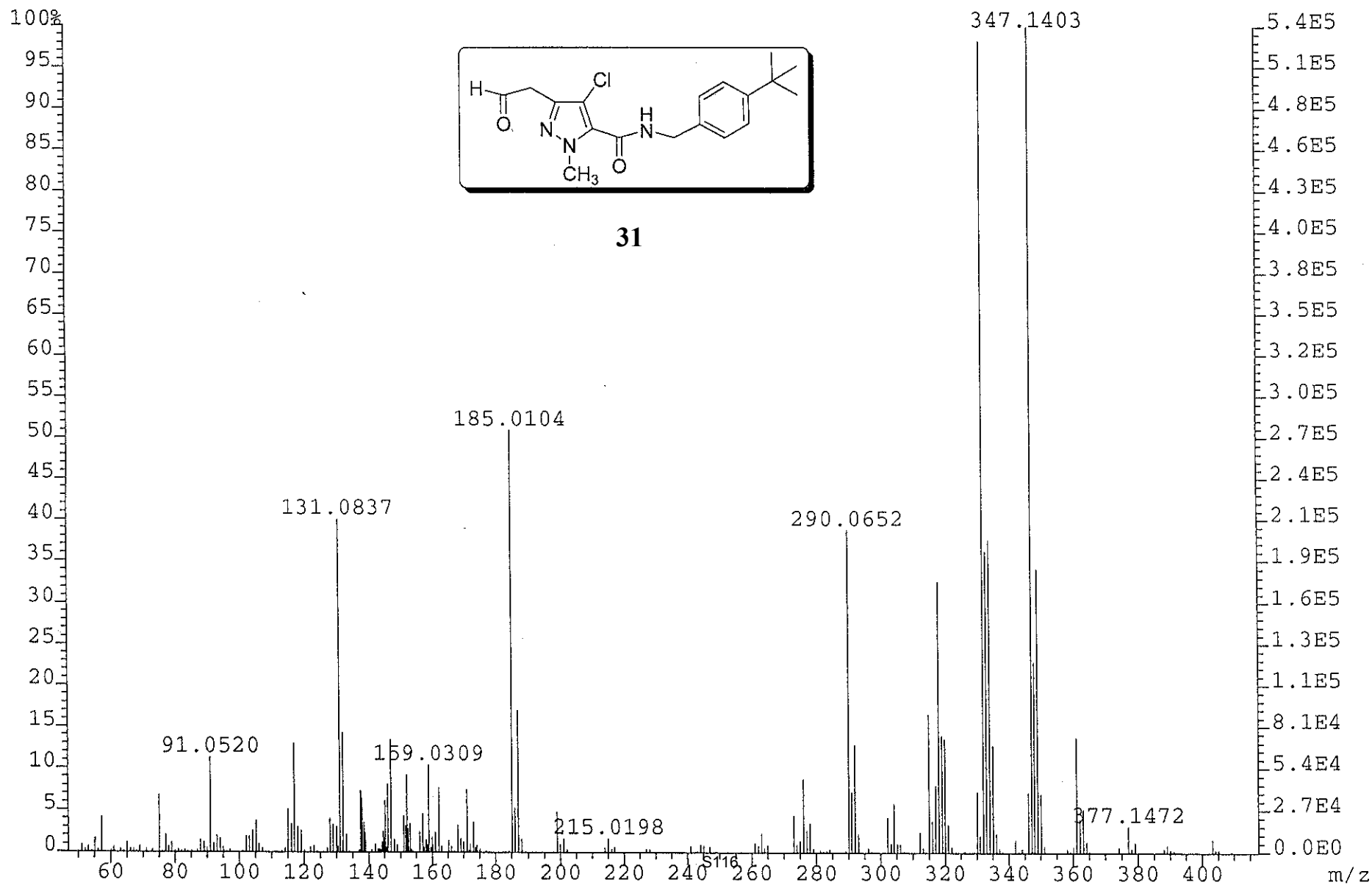


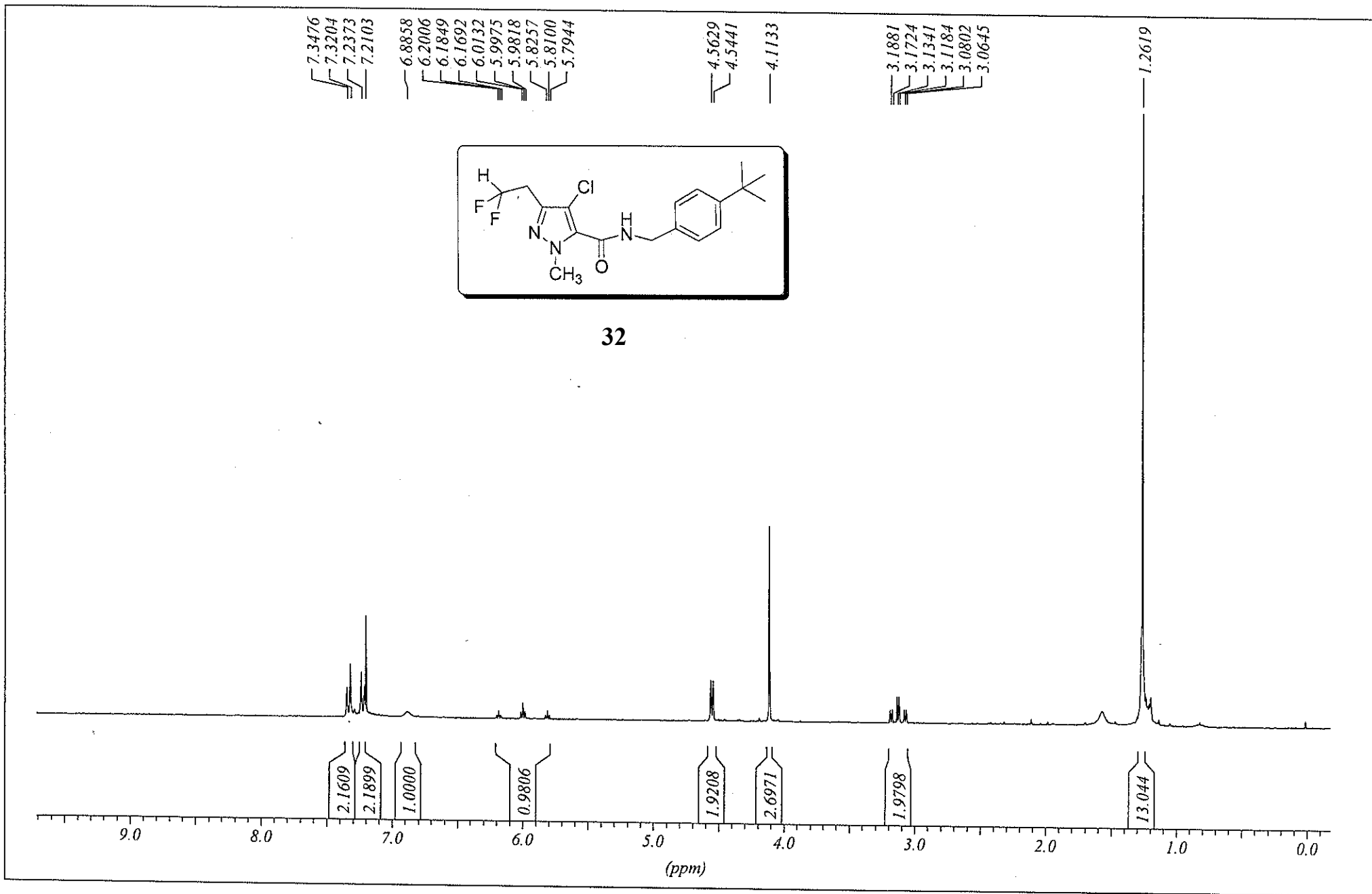
31



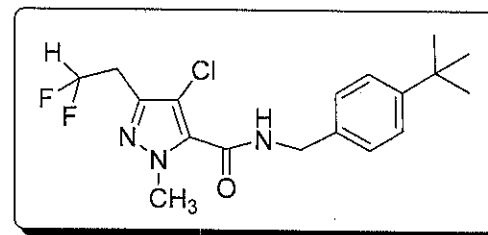


AutoSpecE EI+ Magnet BpM:347 BpI:537088 TIC:5435384 Flags:NORM

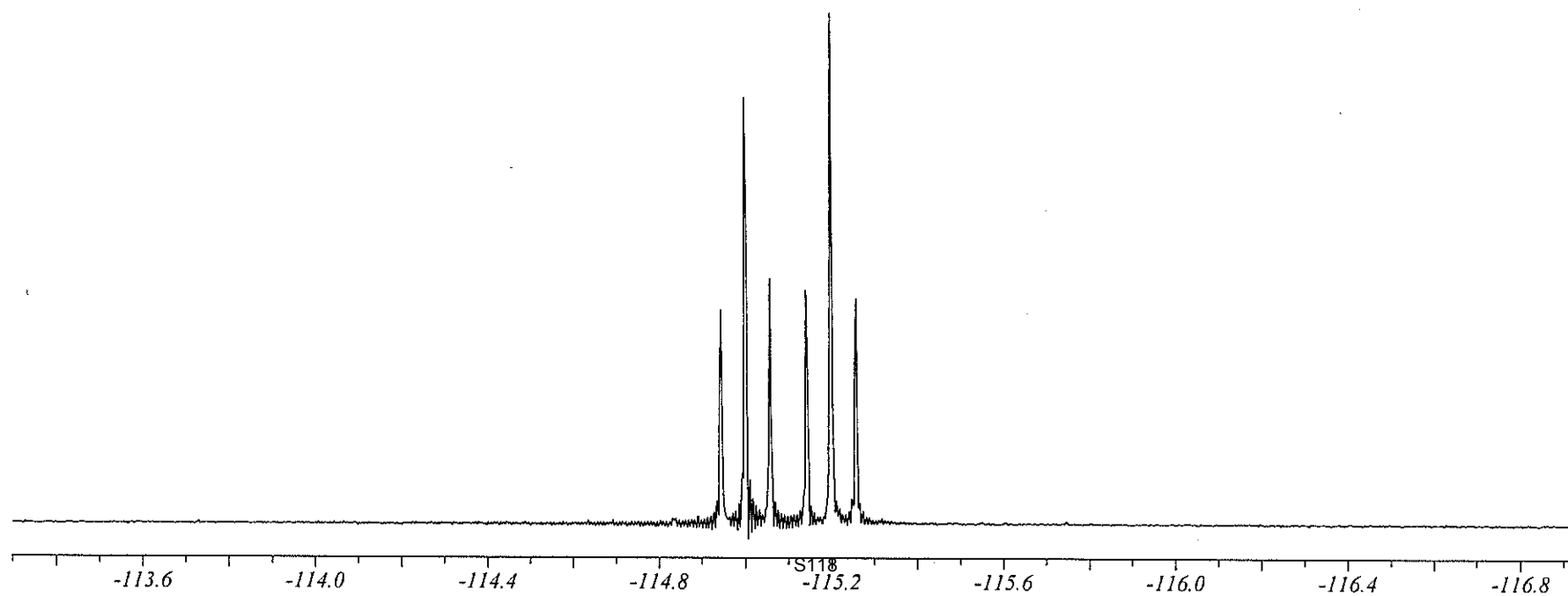


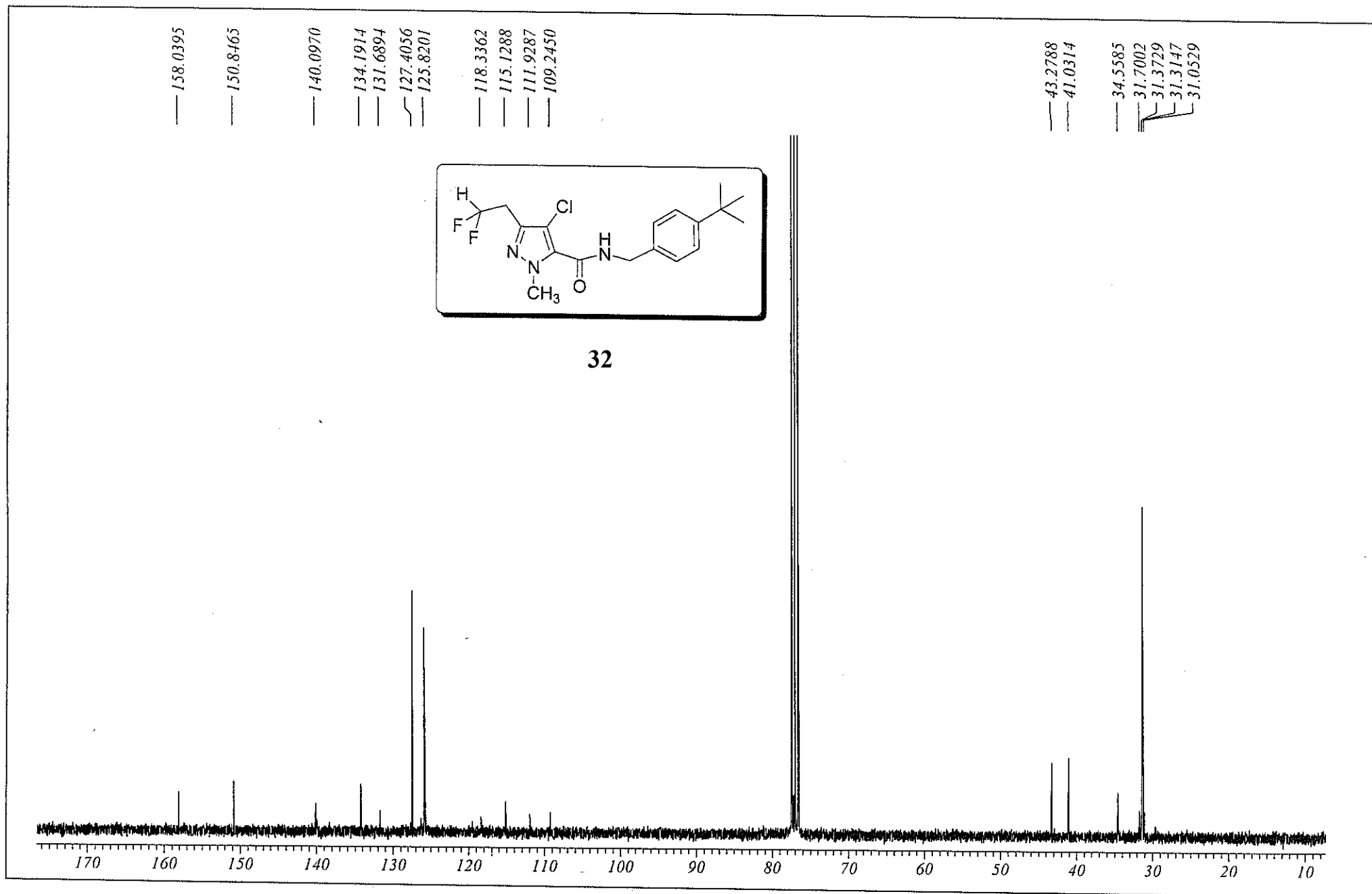


-114.9456
-115.0003
-115.0587
-115.1427
-115.2011
-115.2595

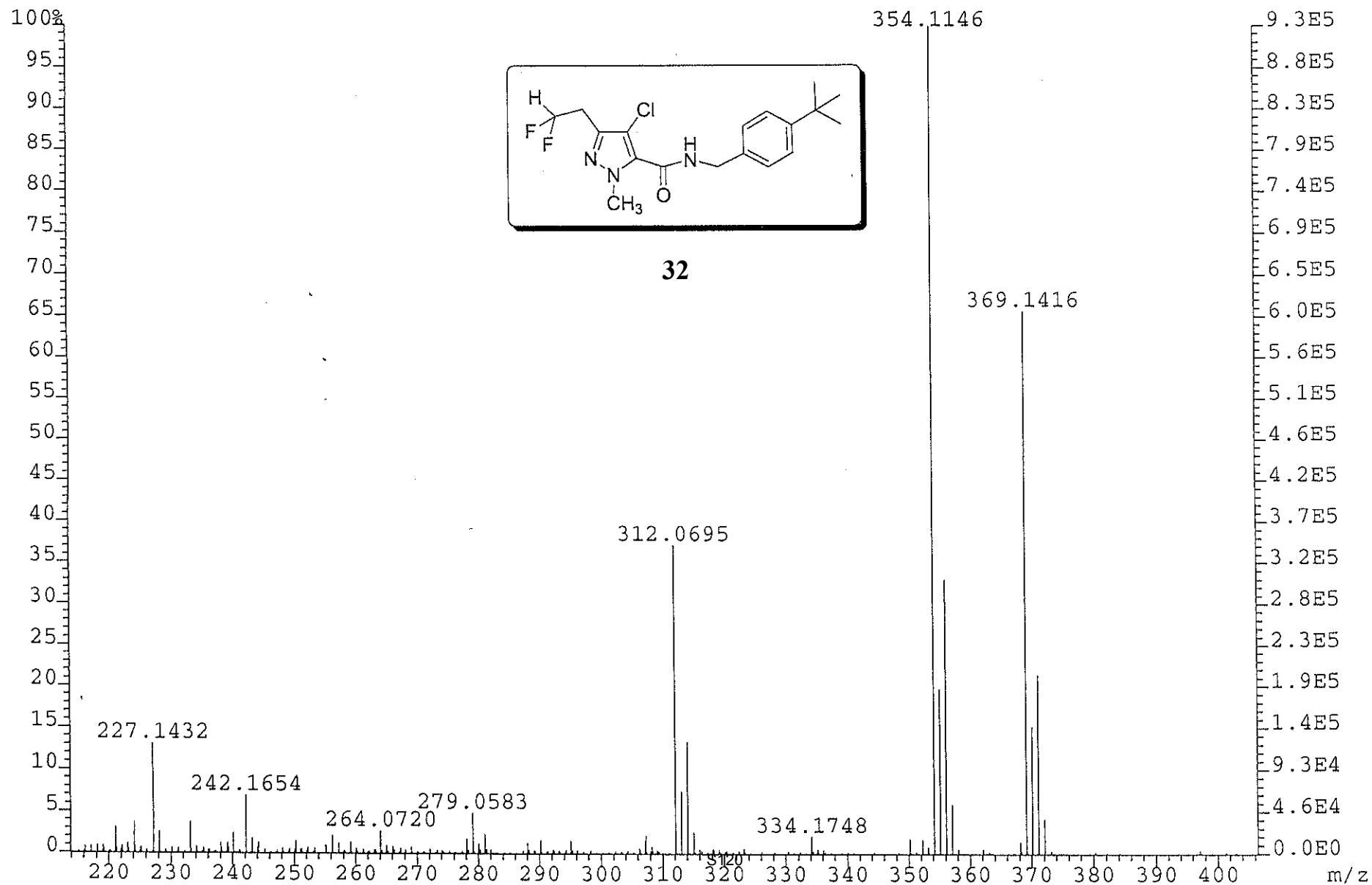


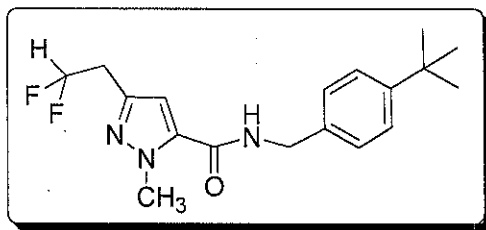
32



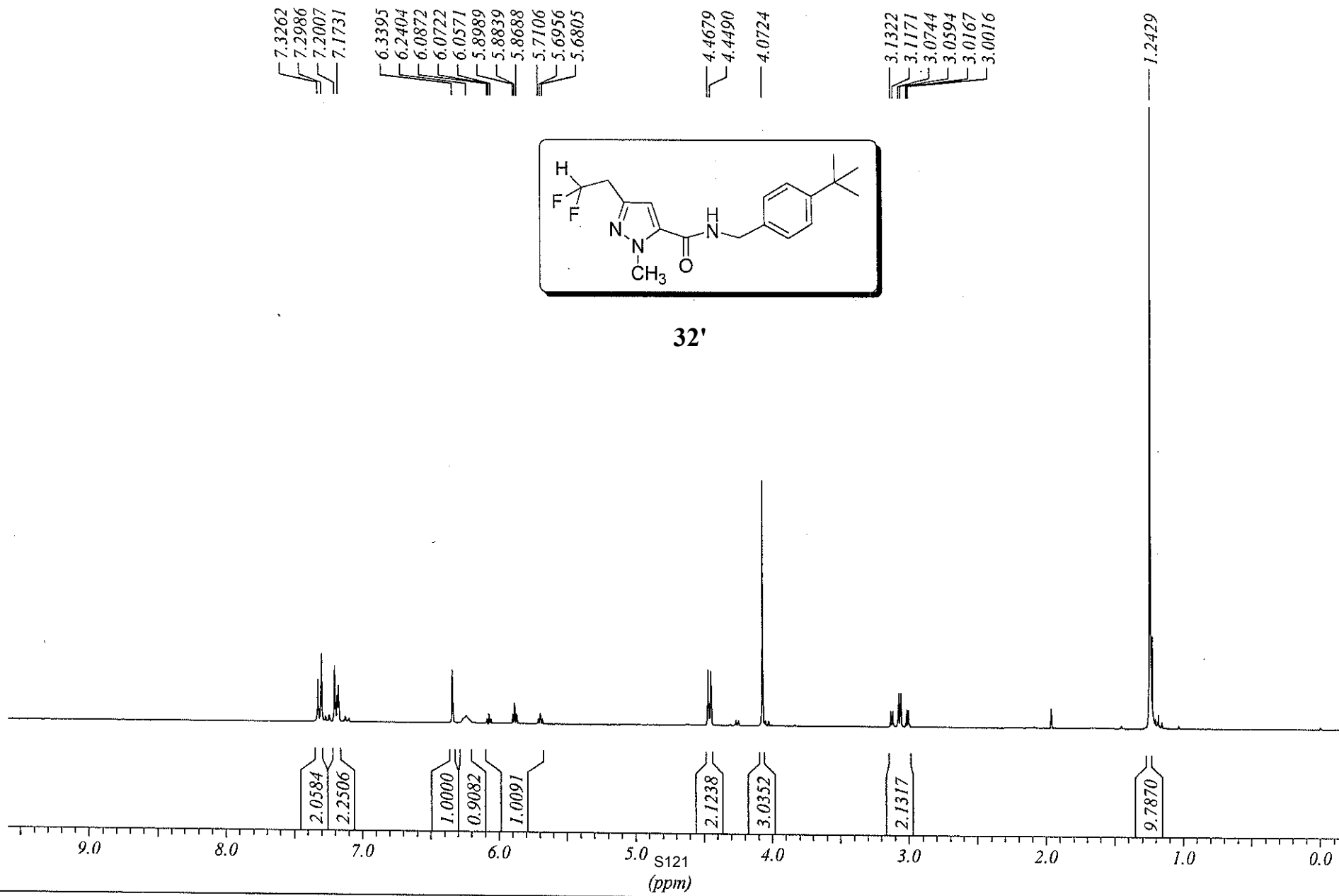


AutoSpecE EI+ Magnet BpM:207 BpI:1027072 TIC:20495702 Flags:NORM

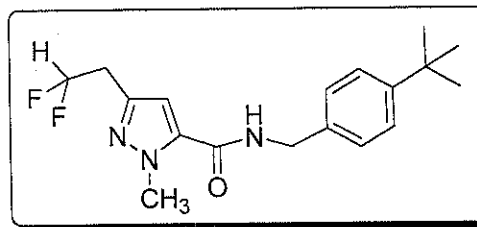




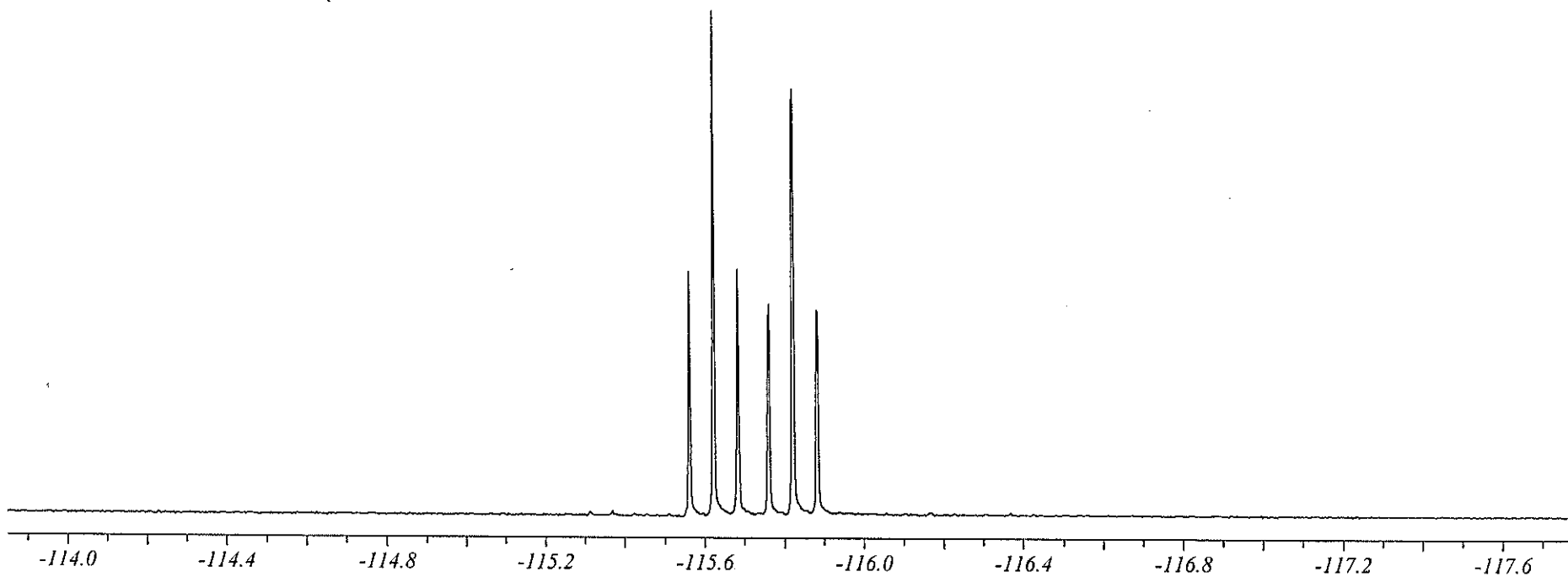
32'

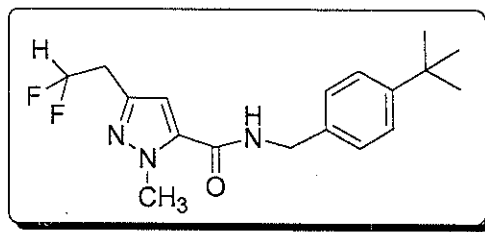


-115.5618
-115.6228
-115.6839
-115.7633
-115.8243
-115.8823



32'

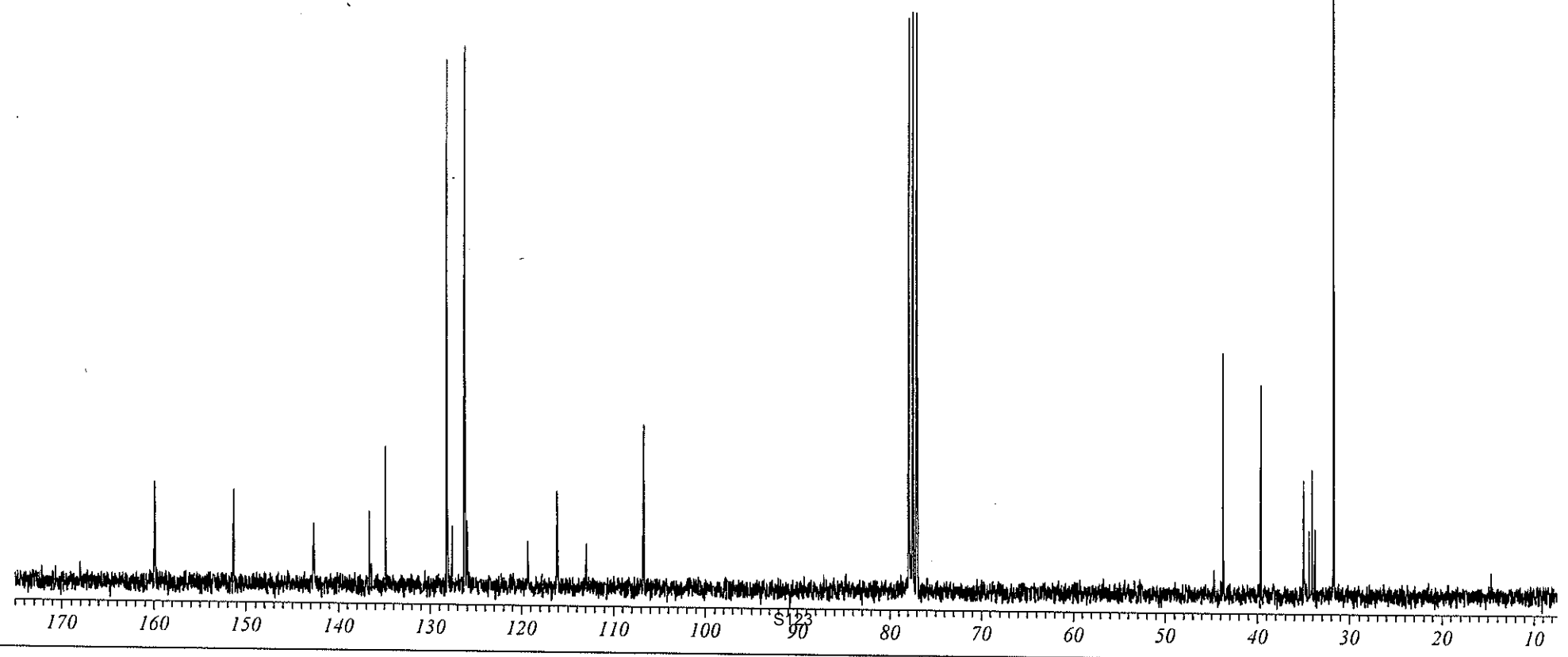




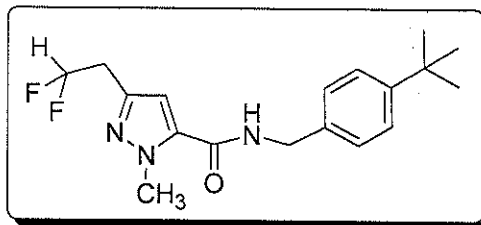
32'

- 159.8761
- 151.3392
- 142.6348
- 136.6034
- 134.8442
- 128.1426
- 126.2083
- 119.2935
- 116.1026
- 112.9118
- 106.6900

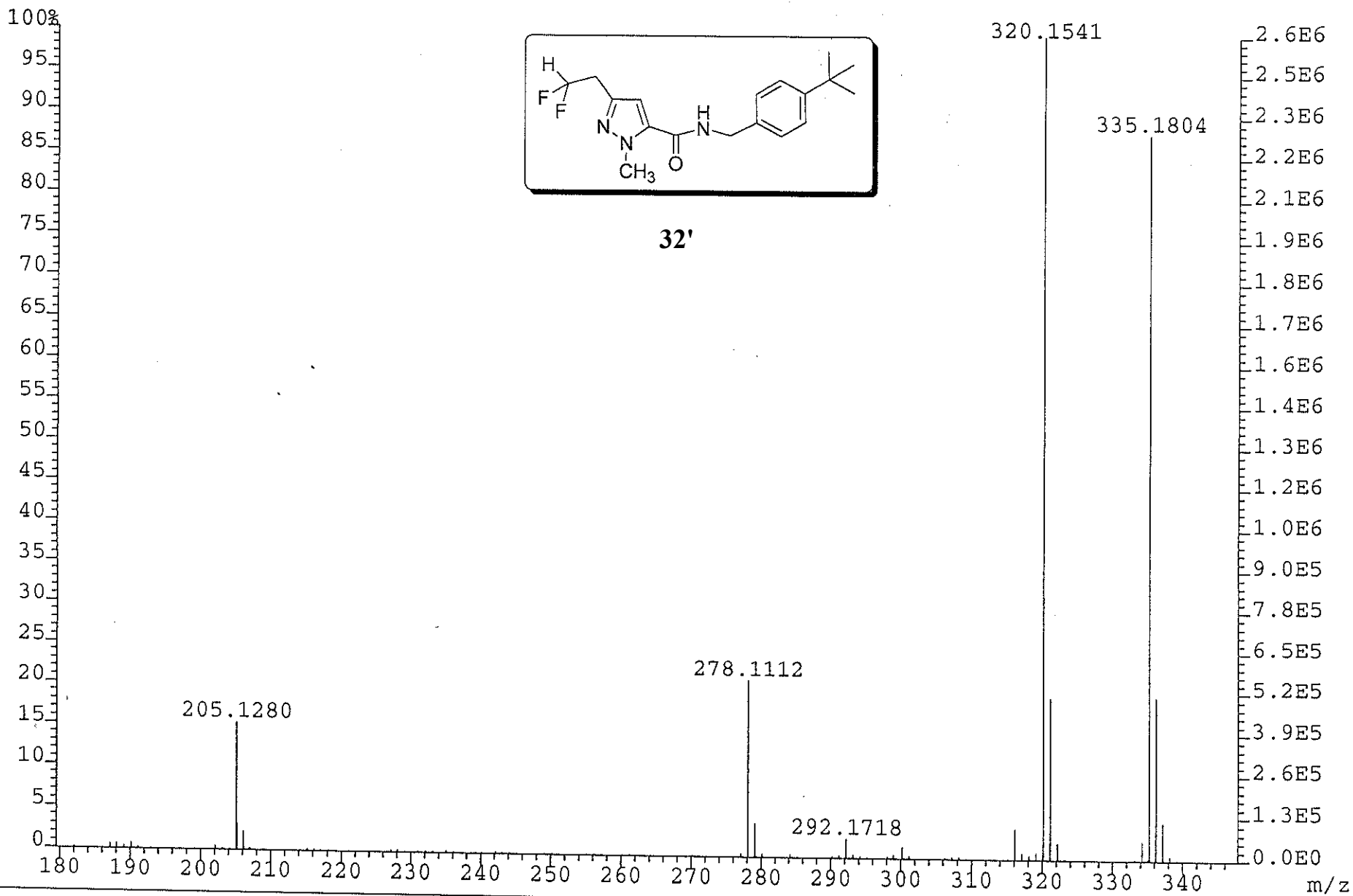
- 43.7028
- 39.5904
- 34.9603
- 34.3662
- 34.0616
- 33.7494
- 31.7085



AutoSpecE EI+ Magnet BpM:320 BpI:2584160 TIC:19574934 Flags:NORM



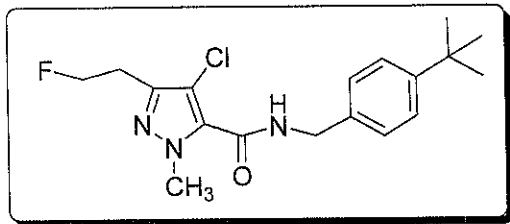
32'



7.3461
7.3180
7.2386
7.2101
— 6.9069

4.7248
4.7029
4.6810
4.5691
4.5616
4.5470
4.5431
4.5252
— 4.0981

3.0349
3.0128
2.9909
2.9626
2.9405
2.9186



33

1.2599

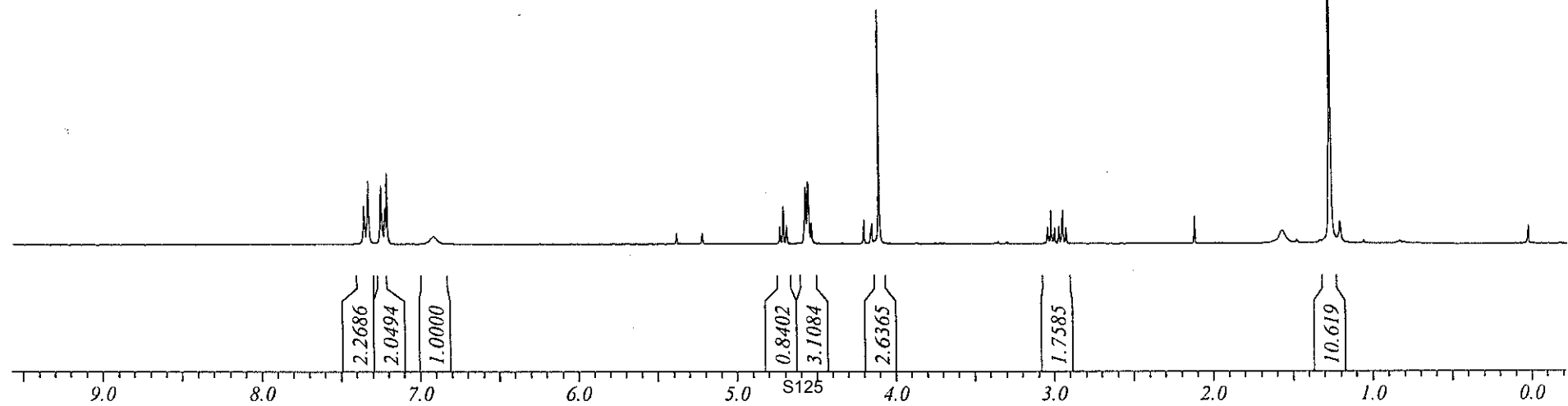
2.2686
2.0494
1.0000

0.8402
3.1084

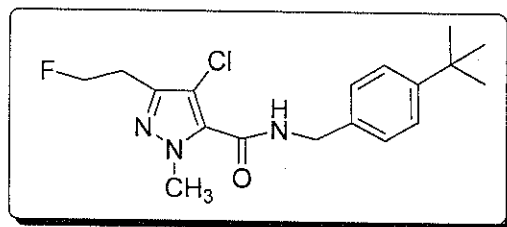
2.6365

1.7585

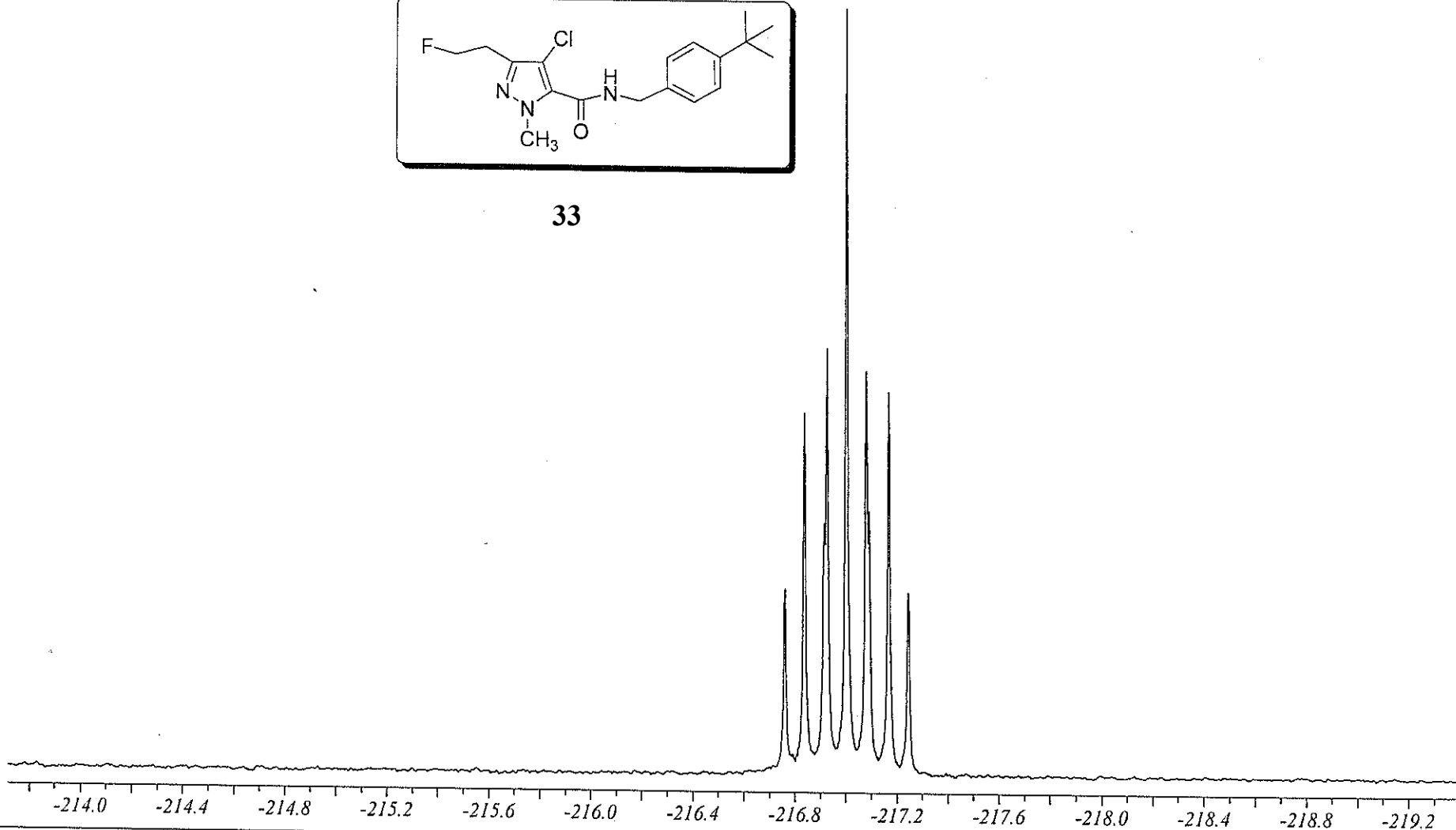
10.619

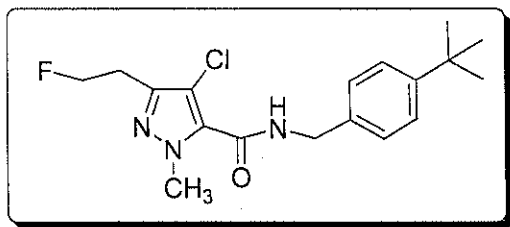


-216.7625
-216.8391
-216.9158
-216.9268
-217.0034
-217.0801
-217.0911
-217.1677
-217.2444

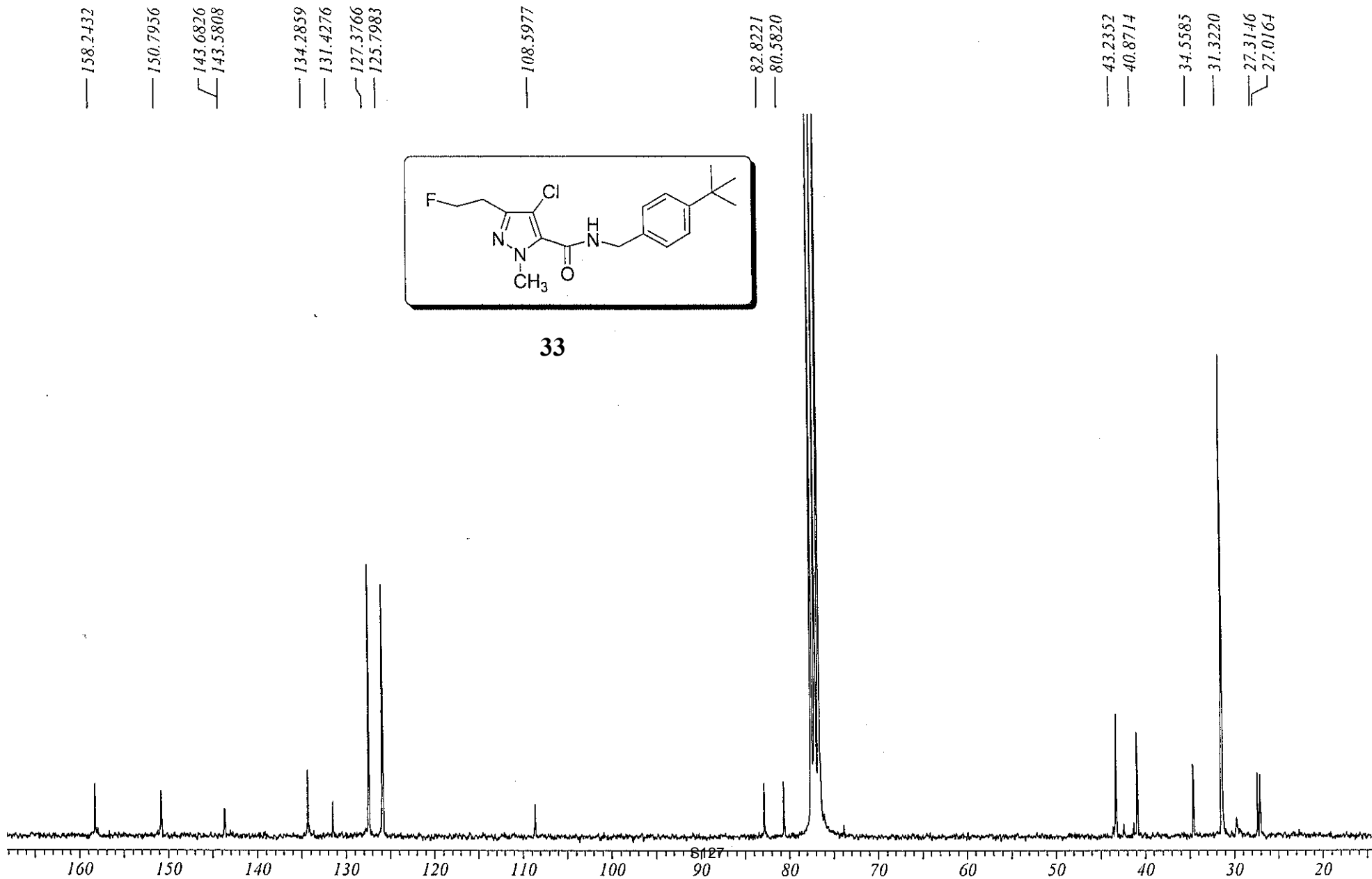


33

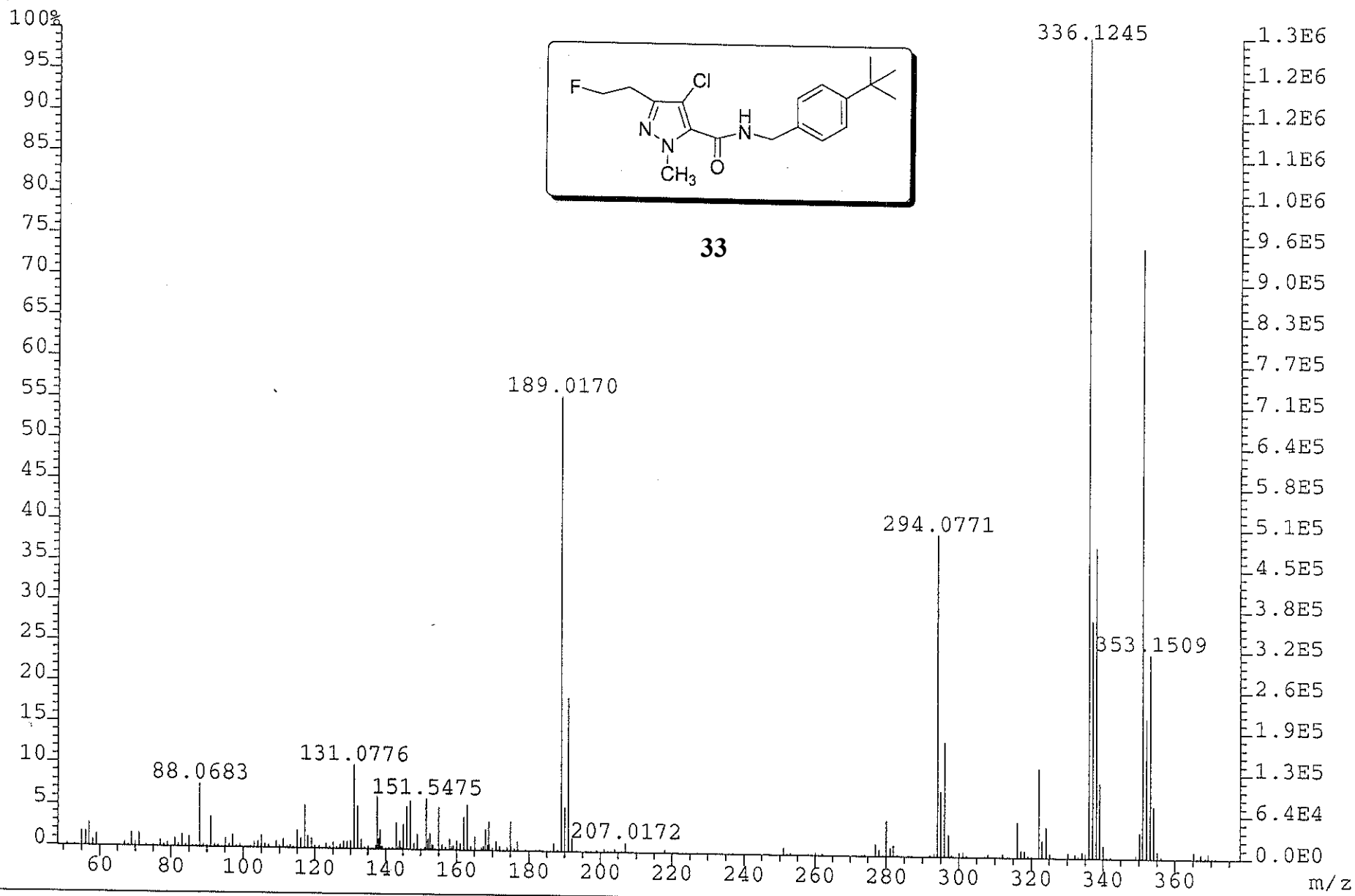




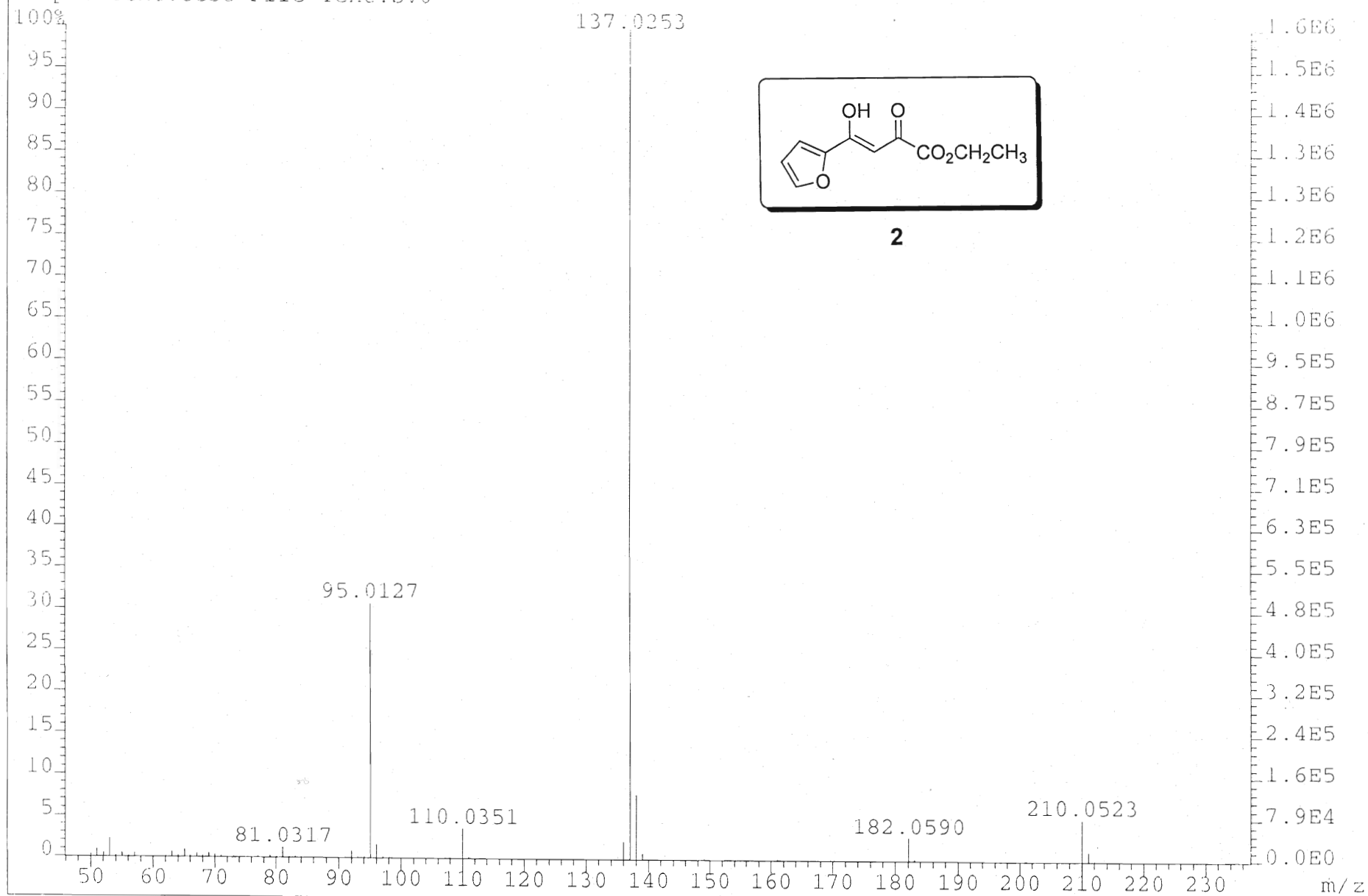
33



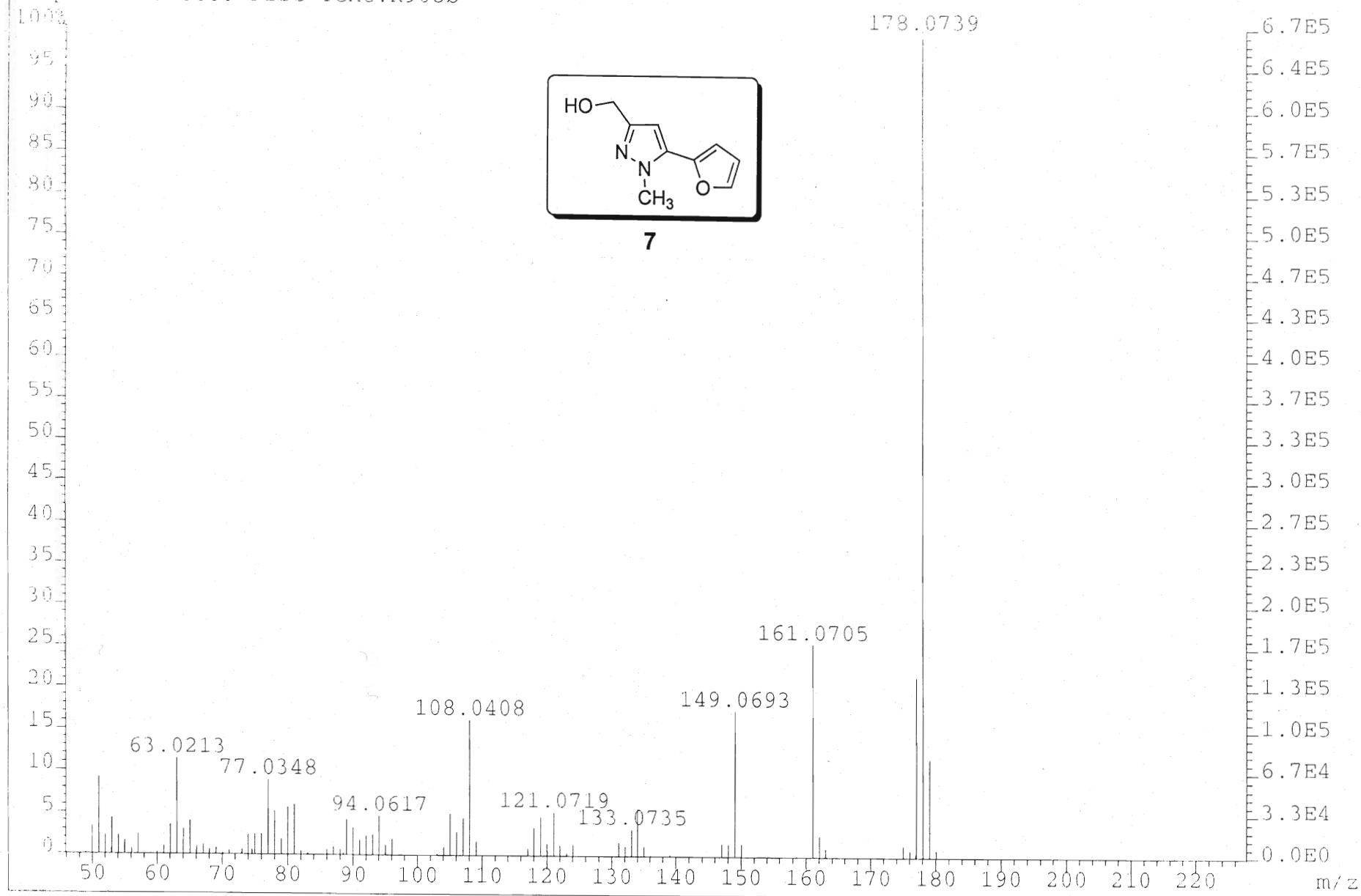
AutoSpecE EI+ Magnet BpM:336 BpI:1282048 TIC:8570642 Flags:NORM

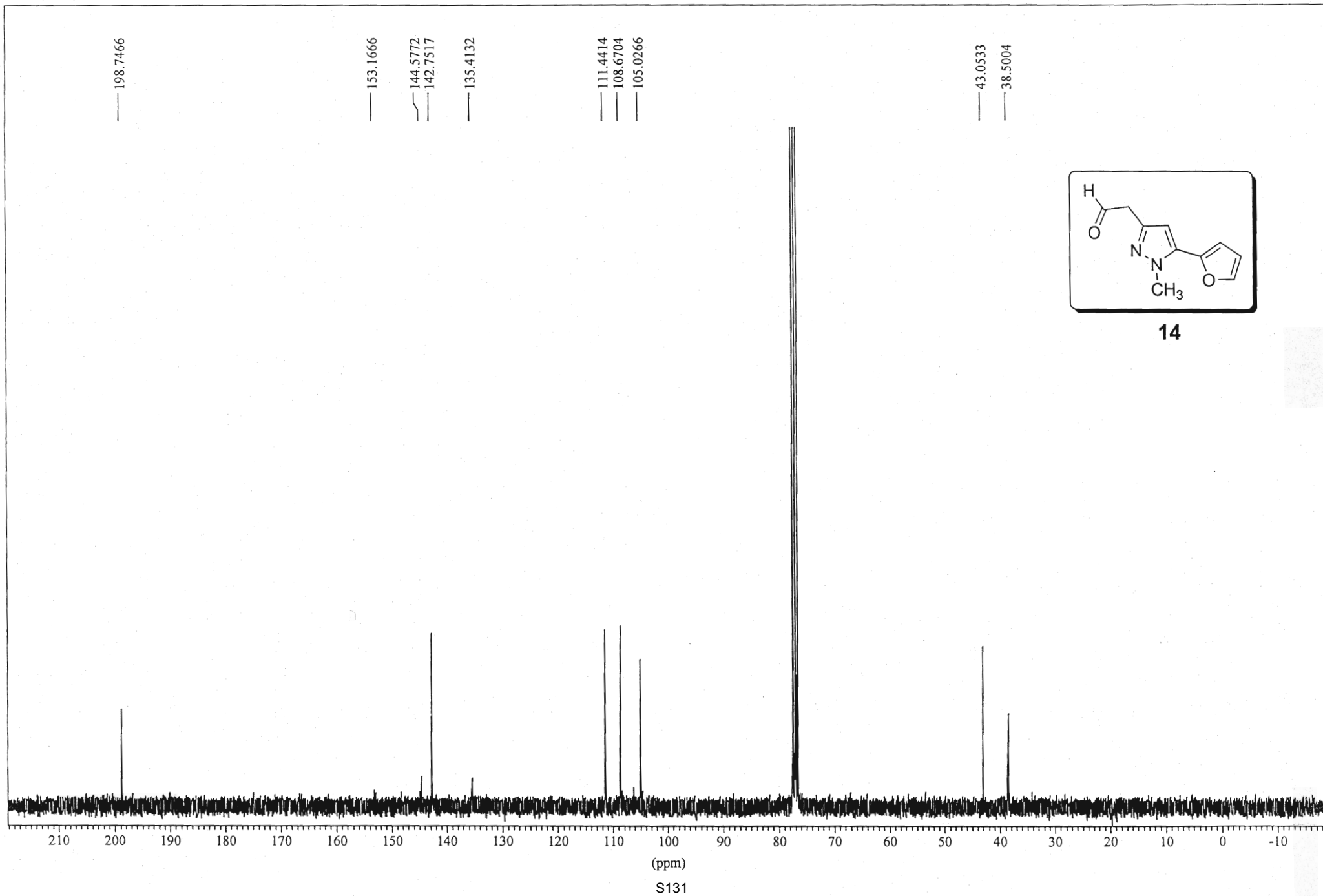


File:EI_4_9_3 Ident:17-4_9 Win 200PPM FILT(EXCL,ALL) Acq: 4-SEP-2008 09:51:53 Cal:EI_4_9_3
AutoSpecE EI+ Magnet BpM:137 BpI:1585664 TIC:2863306 Flags:NORM
Sample Text:test File Text:SV0



File:EI_4_9_1 Ident:17-3_7 Win 200PPM FILT(EXCL,ALL) Acq: 4-SEP-2008 08:21:48 Cal:EI_4_9_1
AutoSpecE EI+ Magnet BpM:178 BpI:668672 TIC:2679848 Flags:NORM
Sample Text:test File Text:R908b

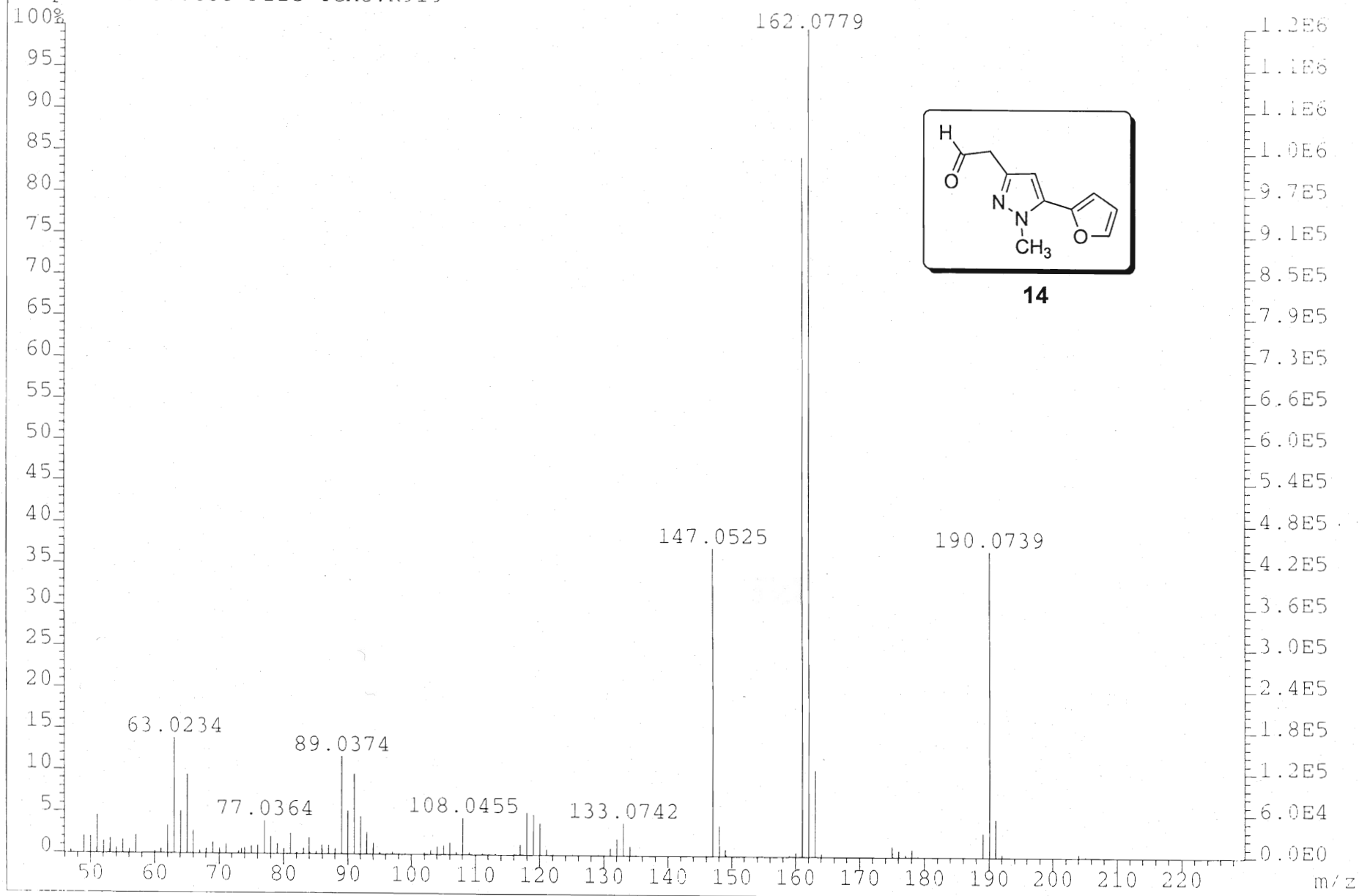




(ppm)

S131

File:EI_9_9_7 Ident:16-5_8 Win 200PPM FILT(EXCL,ALL) Acq: 9-SEP-2008 10:55:57 Cal:EI_9_9_7
AutoSpecE EI+ Magnet BpM:162 BpI:1208832 TIC:5464108 Flags:NORM
Sample Text:test File Text:R913



File:EI_10_9_2 Ident:16_17-6_9 Win 200PPM FILT(EXCL,ALL) Acq:10-SEP-2008 12:48:25 +1:49 Cal:EI_>
AutoSpecE EI+ Magnet BpM:194 BpI:1091456 TIC:4473207 Flags:NORM
Sample Text:test File Text:R916a

