Supporting Information

for

Zirconocene-Mediated Highly Regio- and Stereoselective Synthesis of Multisubstituted Olefins Starting from 1-Alkynylboronates

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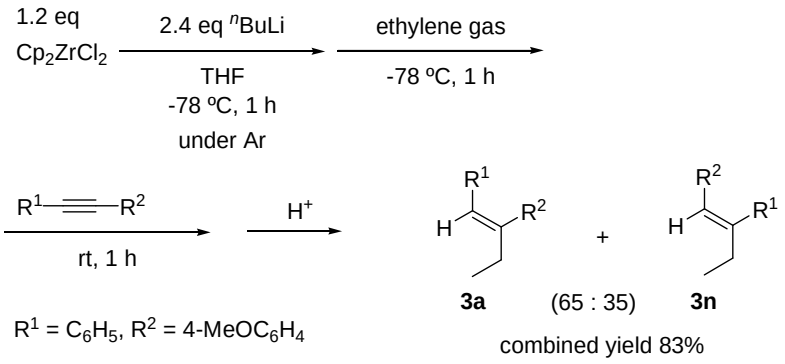
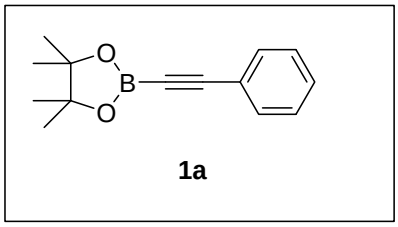
1. General. All the reactions were carried out under an Ar atmosphere using standard Schlenk techniques. Glassware was dried in an oven (130 °C) and heated under reduced pressure before use. Dehydrated toluene, dichloromethane, hexane, and diethyl ether were purchased from Kanto Chemicals Co., Ltd. For thin layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. Silica gel column chromatography was carried out using Silica gel 60 N (spherical, neutral, 40-100 □m) from Kanto Chemicals Co., Ltd. NMR spectra (^1H, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$, and $^{19}F\{^1H\}$) were recorded on Varian INOVA-600 (600 MHz) or Mercury-300 (300 MHz) spectrometers. Peak positions of the $^{11}B\{^1H\}$ NMR spectra were referenced to an external BF_3 OEt_2. Infrared spectra were recorded on a Shimadzu IRPrestige-21 spectrophotometer. GC analyses were performed on a Shimadzu GC-14A equipped with a flame ionization detector using Shimadzu Capillary Column (CBP1-M25-025) and Shimadzu C-R6A-Chromatopac integrator. Melting Points were measured on a Yanagimoto micromelting point apparatus and are uncorrected. The GC yields were determined using suitable hydrocarbon internal standards. GC/MS analyses were carried out on a SHIMADZU GC-17A equipped with a SHIMADZU QP-5050 GC-MS system. Elemental analyses were carried out with a Perkin-Elmer 2400 CHN elemental analyzer at Osaka City University.

2. Experimental procedures and Spectroscopic Data for New Compounds



Regioselectivity upon Formation of Zirconacyclopentene using Unsymmetrical Diarylethyne. To a solution of zirconocene dichloride (702 mg, 2.4 mmol) in THF (12 mL) was added dropwise butyllithium (3 mL, 4.8 mmol, 1.6 M hexane solution) at -78 °C. The reaction mixture was stirred for 1 h at -78 °C and then atmospheric ethylene gas was introduced into a vessel at -78 °C. The reaction mixture was warmed to room temperature and 1-(methoxyphenyl)-2-phenylethyne (417 mg, 2.0 mmol) was added. The reaction mixture was stirred for 1 h, quenched with 1.0 M HCl, and extracted with diethyl ether. Organic layer was separated and the

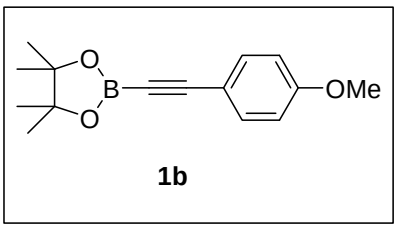
aqueous layer was extracted with diethyl ether. The combined ethereal layers were washed with brine, and dried over $MgSO_4$. Filtration and concentration under vacuum, followed by purification with bulb to bulb distillation (180 ºC/2 Torr) gave a mixture of **3a** and **3n** (combined yield was 83%, **3a**: **3n** = 65:35 determined by ^{1}H NMR and GC measurements). Regio- and stereochemistry of the synthesized compounds **3a** and **3n** was determined by comparison of spectroscopic data of authentic samples obtained in this paper.



1a

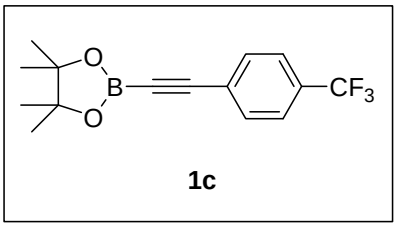
General Procedure for 1-Alkynyldioxaborolanes 1: Synthesis of 4,4,5,5-Tetramethyl-2-(phenylethynyl)-1,3,2-dioxaborolane (1a).[1] To a solution of phenylacetylene (1.32 mL, 12 mmol) in THF (30 mL) in a 50 mL of Schlenk tube -78 °C under an Ar atmosphere were added dropwise n-BuLi (7.5 mL, 1.6 M hexane solution, 12 mmol). The reaction mixture was stirred for 1 h at -78 °C. The resulting reaction mixture was then added to a solution of 4,4,5,5-tetramethyl-2-(1-methylethoxy)-1,3,2-dioxaborolane (2.04 mL, 10 mmol) in THF (30 mL) -78 °C. After being stirred for 2 h at -78 °C, the reaction mixture was quenched with 1.0 M HCl/Et_2O (12.6 mL, 12.6 mmol), and the mixture was warmed to room temperature with additional 1 h stirring. Filtration and evaporation afforded a pale yellow oil. Bulb to bulb distillation (160 ºC/2 Torr) gave **1a** (2.22 g, 9.72 mmol, 97% yield) as white solid. Mp. 58-60 ºC. FT-IR (neat, cm^{-1}): 2981 (m), 2195 (ν(C≡C), w), 1461 (m), 1388 (m), 1372 (m), 1130 (m), 692 (s). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 1.33 (s, 12H), 7.26-7.36 (m, 3H), 7.51-7.54 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, rt): δ 24.6, 84.4, 101.7, 121.8, 128.2, 129.4, 132.5. The carbon signal attached to B was not observed due to low intensity; ^{11}B NMR ($CDCl_3$, 96 MHz, rt) δ 24.05. MS (EI, m/z (relative intensity)): 228 (M^+, 34), 213 (23), 170 (33), 155 (18), 143 (74), 129 (100), 124 (13), 102 (12), 85 (16), 77 (28).

(1) Gandon, V.; Leca, D.; Aechtner, T.; Vollhardt, K. P. C.; Malacria, M.; Aubert, C. *Org. Lett.* **2004**, *6*, 3405-3407.



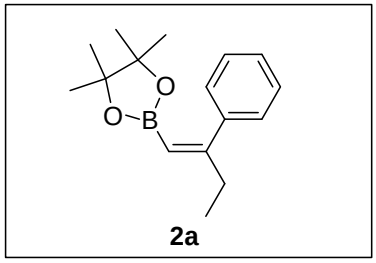
1b

2-[(4-Methoxyphenyl)ethynyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1b). White solid. Yield: 89% (2.29 g, 8.88 mmol). Bp. 190 ºC/2 Torr. Mp. 72-74 ºC. FT-IR (neat, cm^{-1}): 2976 (m), 2184 (ν(C≡C), w), 1383 (m), 1249 (s), 1140 (m), 845 (s). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 1.31 (s, 12H), 3.80 (s, 3H), 6.82 (d, J = 9.9, 2H), 7.47 (d, J = 9.9, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz, rt): δ 24.6, 55.2, 84.3, 102.1, 113.8, 113.9, 134.2, 160.4. The carbon signal attached to B was not observed due to low intensity; ^{11}B NMR ($CDCl_3$, 96 MHz, rt) δ 23.94. MS (EI, m/z (relative intensity)): 258 (M^+, 80), 243 (18), 199 (14), 173 (83), 158 (100), 143 (13), 128 (12), 115 (28), 89 (10), 85 (12). HRMS Calcd for $C_{15}H_{19}BO_3$: 258.1427. Found: M^+, 258.1422.



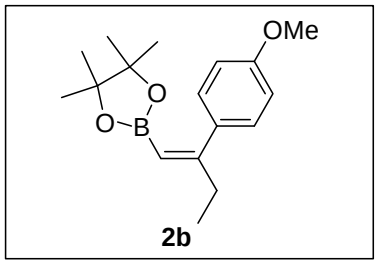
1c

2-[(4-Trifluoromethylphenyl)ethynyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1c). White solid. Yield: 66% (1.96 g, 6.63 mmol). Bp. 150 ºC/2 Torr. Mp. 113-114 ºC. FT-IR (neat, cm^{-1}): 2988 (m), 2199 (ν(C≡C), w), 1382 (m), 1376 (m), 1138 (m), 841 (s). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 1.33 (s, 12H), 7.58 (d, J = 8.4, 2H), 7.63 (d, J = 8.4, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz, rt): δ 24.6, 84.7, 99.8, 123.7 (q, J = 270.6 Hz), 125.2 (q, J = 3.7 Hz), 125.6, 131.0 (q, J = 32.5 Hz), 132.6. The carbon signal attached to B was not observed due to low intensity; ^{11}B NMR ($CDCl_3$, 96 MHz, rt) δ 23.89; ^{19}F NMR ($CDCl_3$, 282 MHz, rt) -63.52. MS (EI, m/z (relative intensity)): 296 (M^+, 28), 281 (39), 238 (23), 211 (56), 197 (100), 177 (25), 169 (27), 141 (13), 124 (27), 85 (29). Anal. Calcd for $C_{15}H_{16}F_3BO_2$: C, 60.85; H, 5.45%. Found: C, 60.65; H, 5.43%.



2a

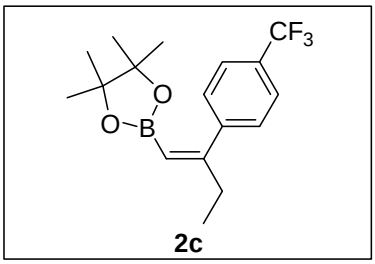
General Procedure for Zirconocene-Mediated Regio- and Stereoselective Ethylation of 1a-1c: Formation of (*Z*)-4,4,5,5-Tetramethyl-2-(2-phenyl-1-buten-1-yl)-1,3,2-dioxaborolane (2a). To a solution zirconocene dichloride (7.02 g, 24 mmol) in THF (120 mL) in a 300 mL of two-necked flask under an Ar atmosphere were added dropwise n-BuLi (30 mL, 48 mmol, 1.6 M hexane solution) at -78 ºC. After the reaction mixture was stirred for 1 h at -78 ºC, atmospheric ethylene gas was introduced into the vessel for 1 h at -78 ºC. The reaction mixture was warmed to room temperature and 4,4,5,5-tetramethyl-2-(phenylethynyl)-1,3,2-dioxaborolane (**1a**) was added. The mixture was stirred for 1 h, quenched with 1 M hydrochloric acid (50 mL), and extracted with diethyl ether (25 mL x 2). The combined ethereal layer was washed with brine and dried over $MgSO_4$. Filtration and evaporation afforded yellow oil. Bulb to bulb distillation (150 ºC/2 Torr) gave **3a** (4.21 g, 16.3 mmol, 80% yield) as pale yellow oil. FT-IR (neat, cm^{-1}): 2933 (m), 1628 (w), 1461 (m), 1379 (m), 1371 (m), 1146 (m), 740 (s), 698 (s). ^{1}H NMR ($CDCl_3$, 300 MHz, rt): δ 1.04 (t, J = 7.4 Hz, 3H), 1.12 (s, 12H), 2.49 (q, J = 7.4 Hz, 2H), 5.45 (s, 1H), 7.24-7.28 (m, 5H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, rt): δ 12.5, 24.5, 24.8, 33.3, 82.9, 127.1, 127.5, 127.8, 143.1, 163.6; ^{11}B NMR ($CDCl_3$, 96 MHz, rt) δ 30.02. MS (EI, m/z (relative intensity)): 258 (M^+, 51), 201 (39), 172 (17), 158 (69), 143 (100), 129 (25), 117 (24), 115 (16), 105 (51), 101 (24). Anal. Calcd for $C_{16}H_{23}BO_2$: C, 74.44; H, 8.98%. Found: C, 74.11; H, 8.98%.



2b

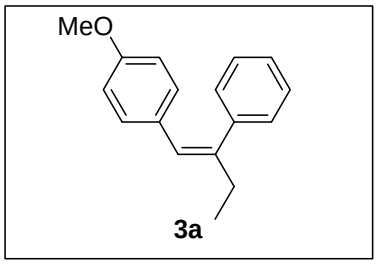
(*Z*)-4,4,5,5-Tetramethyl-2-[2-(4-methoxyphenyl)-1-buten-1-yl]-1,3,2-dioxaborolane (**2b**). Yellow solid, Yield: 72% (4.15 g, 14.4 mmol). Bp. 180 ºC/2 Torr. Mp. 42-43 ºC. FT-IR ($CHCl_3$, cm^{-1}): 2979 (m), 2935 (m), 2837 (m), 1622 (w), 1381 (m), 1372 (m), 1246 (s), 1109 (m), 835 (s). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ

1.03 (t, J = 7.2 Hz, 3H), 1.11 (s, 12H), 2.47 (q, J = 7.4 Hz, 2H), 3.81 (s, 3H), 5.38 (s, 1H), 6.81 (d, J = 8.7 Hz, 2H), 7.20 (d, J = 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz, rt) δ 12.7, 24.6, 24.8, 33.3, 55.2, 82.9, 112.9, 129.0, 135.4, 159.0, 163.2; ^{11}B NMR ($CDCl_3$, 96 MHz, rt) δ 30.18; ^{19}F NMR ($CDCl_3$, 282 MHz, rt) δ -62.9. MS (EI, m/z (relative intensity)): 288 (M^+, 55), 231 (11), 188 (18), 172 (100), 160 (10), 147 (15), 135 (22), 129 (7), 101 (11), 83 (6). Anal. Calcd for $C_{17}H_{25}BO_3$: C, 70.85; H, 8.74%. Found: C, 70.65; H, 8.78%.



2c

(*Z*)-4,4,5,5-Tetramethyl-2-[2-(4-trifluoromethyphenyl)-1-buten-1-yl]-1,3,2-dioxaborolane (**2c**)**.** Pale yellow oil. Yield: 68% (4.44 g , 13.6 mmol). Bp. 140 ºC/2 Torr. FT-IR (neat, cm^{-1}): 2978 (m), 2935 (m), 1631 (w), 1380 (m), 1371 (m), 1126 (m). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 1.04 (t, J = 7.4 Hz, 3H), 1.10 (s, 12H), 2.47 (q, J = 7.4 Hz, 2H), 5.53 (s, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.54 (d, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz, rt) δ 12.3, 24.5, 33.4, 83.1, 124.3 (q, J = 270.4 Hz), 124.4 (q, J = 3.8 Hz), 128.2, 129.2, (q, J = 32.0 Hz), 143.8, 146.9, 162.6; ^{11}B NMR ($CDCl_3$, 96 MHz, rt) δ 29.81; ^{19}F NMR ($CDCl_3$, 282 MHz, rt) -62.89. MS (EI, m/z (relative intensity)): 326 (M^+, 49), 311 (22), 269 (20), 240 (47), 226 (35), 211 (100), 207 (50), 173 (22), 101 (45), 85 (19). Anal. Calcd for $C_{17}H_{22}BF_3O_2$: C, 62.60; H, 6.80%. Found: C, 62.59; H, 6.81%.

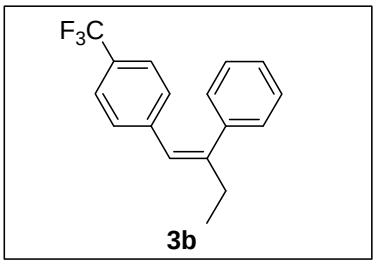


3a

General Procedure for Suzuki-Miyaura Cross-Coupling Reaction of 2a-2c with Aryl Iodides: Formation of (*Z*)-1-(4-Methoxyphenyl)-2-phenyl-1-butene (3a). To a solution of bis(dibenzylidene)palladium ($Pd(dba)_2$) (115 mg, 0.20 mmol, 10 mol %), P^tBu_3 (4 mL, 0.1 M hexane solution,

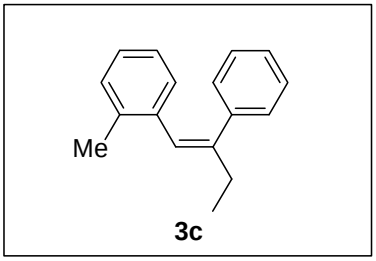
0.40 mmol, 20 mol %), and (*Z*)-4,4,5,5-tetramethyl-2-(2-phenyl-1-buten-1-yl)-1,3,2-dioxaborolane (**2a**) (516 mg, 2.0 mmol) in THF (20 mL) in a 50 mL of Schlenk tube under an Ar atmosphere were added 4-iodoanisole (515 mg, 2.2 mmol) and KOH aqueous solution (2 mL, 3.0 M solution, 6.0 mmol) at room temperature. The reaction mixture was stirred for 12 h at room temperature, quenched with ammonium chloride, and extracted with diethyl ether (25 mL x 2). The combined ethereal layer was washed with $NaHCO_3$ aq., brine and dried over $MgSO_4$. Filtration and evaporation afforded a brown oil. Bulb to bulb distillation (190 ºC/2 Torr) gave **3a** (448 mg, 1.62 mmol, 81% yield) as a colorless liquid. R_f = 0.40 (hexane). FT-IR (neat, cm^{-1}): 2964 (m), 2933 (m), 1608 (w), 1251 (s), 826 (s), 701 (s). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 1.09 (t, J = 7.2 Hz, 3H), 2.52 (q, J = 7.2 Hz, 2H), 3.74 (s, 3H), 6.40 (s, 1H), 6.66 (d, J = 8.1 Hz, 2H), 6.88 (d, J = 8.1 Hz, 2H), 7.18-7.37 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz, rt) δ 12.9, 33.3, 55.0, 113.1, 124.4, 126.6, 128.5, 128.6, 130.0, 130.1, 141.7, 143.0, 157.8. MS (EI, m/z (relative intensity)): 238 (M^+, 100), 223 (57), 208 (10), 178 (12), 165 (19), 145 (21), 129 (10), 121 (19), 115 (43), 91 (18). Anal. Calcd for $C_{17}H_{18}O_2$: C, 85.67; H, 7.61%. Found: C, 85.60; H, 7.61%.

Preparation of **3b-3q** were carried out analogously to **3a.**



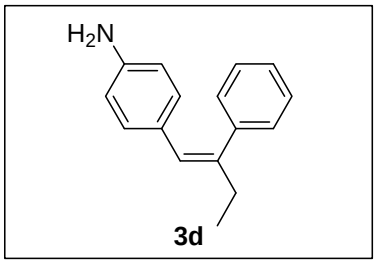
3b

(*Z*)-1-(4-Trifluoromethylphenyl)-2-phenyl-1-butene (3b). Colorless liquid. Isolated yield was 83% (459 mg, 1.66 mmol). Bp. 150 ºC/2 Torr. R_f = 0.50 (hexane). FT-IR (neat, cm^{-1}): 2970 (m), 2934 (m), 1615 (w), 1123 (m), 759 (s), 701 (s). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 1.10 (t, J = 7.4 Hz, 3H), 2.55 (q, J = 7.3 Hz, 2H), 6.45 (s, 1H), 7.01 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 7.28-7.36 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz, rt) δ 12.7, 33.6, 123.8, 124.2 (q, J = 270.0 Hz), 124.7 (q, J = 3.8 Hz), 127.2, 127.8 (q, J = 31.9 Hz), 128.3, 128.6, 129,0, 140.8, 141.2, 147.7; ^{19}F NMR ($CDCl_3$, 282 MHz, rt) -62.95. MS (EI, m/z (relative intensity)): 276 (M^+, 100), 261 (38), 247 (30), 207 (17), 183 (30), 178 (20), 129 (29), 117 (51), 115 (57), 91 (43). Anal. Calcd for $C_{17}H_{15}F_3$: C, 73.90; H, 5.47%. Found: C, 73.93; H, 5.55%.



3c

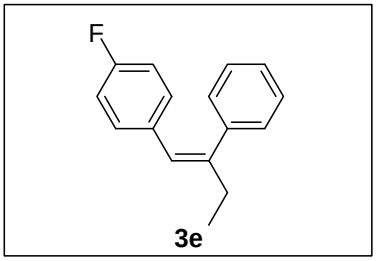
(*Z*)-1-(2-Methylphenyl)-2-phenyl-1-butene (3c).[2] Colorless liquid. Isolated yield was 83% (369 mg, 1.66 mmol). Bp. 180 ºC/2 Torr. R_f = 0.70 (hexane). FT-IR (neat, cm^{-1}): 2966 (m), 2932 (m), 1600 (w), 1459 (m), 732 (s), 698 (s). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 1.14 (t, J = 7.4 Hz, 3H), 2.33 (s, 3H), 2.61 (q, J = 7.4 Hz, 2H), 6.53 (s, 1H), 6.76 (d, J = 7.4 Hz, 1H), 6.86 (t, J = 7.2 Hz, 1H), 7.01-7.22 (m, 7H); ^{13}C NMR ($CDCl_3$, 75 MHz, rt) δ 13.3, 20.0, 32.4, 124.1, 125.1, 126.1, 126.5, 127.9, 128.7, 129.5, 129.8, 136.2, 137.2, 141.0, 144.8. MS (EI, m/z (relative intensity)): 222 (M^+, 100), 207 (33), 193 (48), 179 (28), 165 (16), 129 (44), 117 (10), 115 (50), 105 (10), 91 (27).



3d

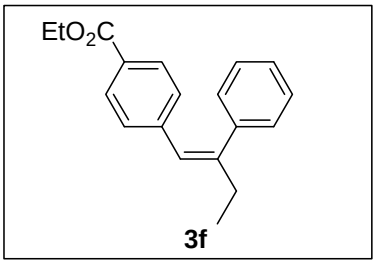
(*Z*)-1-(4-Aminophenyl)-2-phenyl-1-butene (3d). Colorless liquid. Isolated yield was 80% (357 mg, 1.60 mmol). Bp. 180 ºC/2 Torr. R_f = 0.10 (hexane/ethyl acetate = 10/1). FT-IR ($CHCl_3$, cm^{-1}): 3458 (m), 3376 (m), 2964 (m), 2930 (m), 1620 (m), 826 (m), 763 (s), 701 (s). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 1.05 (t, J = 7.2 Hz, 3H), 2.47 (q, J = 7.2 Hz, 2H), 3.56 (s, 2H), 6.32 (s, 1H), 6.48 (d, J = 8.7 Hz, 2H), 6.74 (d, J = 8.7 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 7.24-7.33 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, rt) δ 13.0, 33.5, 114.8, 124.7, 124.7, 126.5, 128.4, 128.6, 129.9, 141.86, 141.94, 143.8. MS (EI, m/z (relative intensity)): 223 (M^+, 100), 208 (66), 193 (22), 165 (13), 130 (43), 115 (69), 106 (55), 96 (12), 91 (41), 77 (17). Anal. Calcd for $C_{16}H_{17}N$: C, 86.05; H, 7.67; N, 6.27%. Found: C, 85.69; H, 7.74; N, 6.15%.

(2) James, B. G.; Pattenden, G. *J. Chem. Soc., Perkin Trans. 1,* **1974**, 1204-1208.



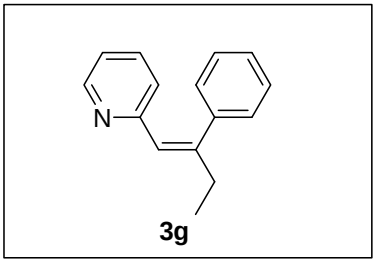
3e

(*Z*)-1-(4-Fluorophenyl)-2-phenyl-1-butene (3e). Colorless liquid. Isolated yield was 55% (249 mg, 1.10 mmol). Bp. 140 ºC/2 Torr. R_f = 0.40 (hexane). FT-IR (neat, cm^{-1}): 2968 (m), 2933 (m), 1602 (m), 1229 (s), 828 (m), 762 (s), 700 (s). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 1.09 (t, J = 7.5 Hz, 3H), 2.52 (q, J = 7.5 Hz, 2H), 6.41 (s, 1H), 6.78 (t, J = 7.5 Hz, 2H), 6.90 (t, J = 8.1 Hz, 2H), 7.15 (d, J = 7.8, 2H), 7.26-7.35 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, rt) δ 12.8, 33.4, 114.6 (d, J = 21.0 Hz), 123.9, 127.0, 128.5 (d, J = 4.0 Hz), 130.4 (d, J = 7.7 Hz), 133.6 (d, J = 3.4 Hz), 141.2, 144.8, 159.5, 162.7; ^{19}F NMR ($CDCl_3$, 282 MHz, rt) -116.75. MS (EI, m/z (relative intensity)): 226 (M^+, 100), 210 (58), 196 (41), 183 (12), 133 (62), 117 (36), 115 (83), 109 (31), 98 (12), 91 (41). Anal. Calcd for $C_{16}H_{15}F$: C, 84.92; H, 6.68%. Found: C, 84.95; H, 6.78%.



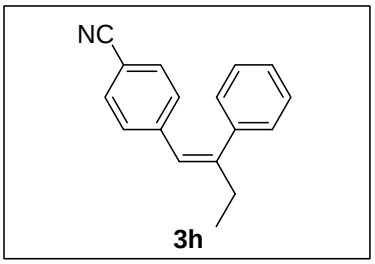
3f

(*Z*)-1-(4-Ethoxycarbonylphenyl)-2-phenyl-1-butene (3f). Colorless liquid. Isolated yield was 82% (473 mg, 1.64 mmol). Bp. 200 ºC/2 Torr. R_f = 0.10 (hexane). FT-IR (neat, cm^{-1}): 2969 (m), 2934 (m), 1717 (s), 160 6(w), 1367 (m), 701 (s). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 1.09 (t, J = 7.3 Hz, 3H), 1.34 (t, J = 7.2 Hz, 3H), 2.54 (q, J = 7.4 Hz, 2H), 4.31 (q, J = 7.2 Hz, 2H), 6.46 (s, 1H), 6.97 (d, J = 8.1 Hz, 2H), 7.11-7.15 (m, 2H), 7.26-7.31 (m, 3H), 7.61 (d, J = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz, rt) δ 12.7, 14.3, 33.6, 60.7, 124.4, 127.1, 127.8, 128.3, 128.6, 128.8, 129.1, 141.0, 142.3, 147.6, 166.5. MS (EI, m/z (relative intensity)): 280 (M^+, 100), 235 (19), 207 (36), 191 (18), 179 (35), 165 (16), 129 (35), 117 (13), 115 (32), 91 (22). Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19%. Found: C, 81.26; H, 7.19%.



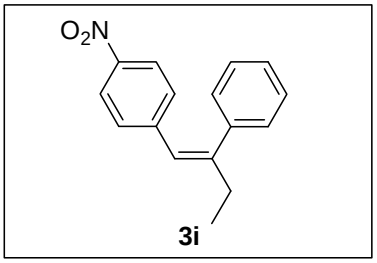
3g

(*Z*)-1-(2-Pyridyl)-2-phenyl-1-butene (3g). Colorless liquid. Isolated yield was 79% (331 mg, 1.58 mmol). Bp. 140 ºC/2 Torr. R_f = 0.10 (hexane/ethyl acetate = 10/1). FT-IR (neat, cm^{-1}): 2967 (m), 2932 (m), 1636 (w), 1585 (m), 772 (s), 701 (s). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 1.10 (t, J = 7.5 Hz, 3H), 2.55 (q, J = 7.2 Hz, 2H), 6.58 (d, J = 8.1 Hz, 1H), 6.63 (s, 1H), 6.94 (t, J = 6.9 Hz, 1H), 7.12-7.15 (m, 2H), 7.20-7.32 (m, 4H), 8.48 (d, J = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz, rt) δ 12.5, 33.4, 120.8, 123.5, 125.8, 127.2, 128.1, 128.6, 135.4, 140.9, 148.6, 149.2, 156.5. MS (EI, m/z (relative intensity)): 209 (M^+, 35), 208 (100), 193 (27), 180 (17), 117 (10), 115 (8), 93 (13), 90 (14), 84 (10), 78 (16). HRMS Calcd for $C_{15}H_{15}N$: 209.1204. Found: M^+, 209.1216.



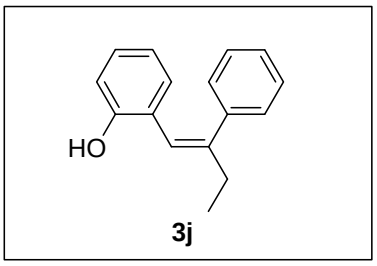
3h

(*Z*)-1-(4-Cyanophenyl)-2-phenyl-1-butene (3h). Colorless liquid. Isolated yield was 86% (401 mg, 1.72 mmol). Bp. 170 ºC/2 Torr. R_f = 0.10 (hexane). FT-IR ($CHCl_3$, cm^{-1}): 2968 (m), 2933 (m), 2224 (s, νCN), 1603 (m), 828 (m), 773 (s), 701 (s). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 1.08 (t, J = 7.5 Hz, 3H), 2.54 (q, J = 7.5 Hz, 2H), 6.42 (s, 1H), 6.98 (d, J = 8.4 Hz, 2H), 7.09-7.13 (m, 2H), 7.28-7.36 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz, rt) δ 12.6, 33.6, 109.1, 119.1, 123.6, 127.4, 128.1, 128.7, 129.4, 131.5, 140.4, 142.4, 149.1. MS (EI, m/z (relative intensity)): 233 (M^+, 100), 218 (63), 204 (48), 190 (11), 155 (16), 140 (40), 117 (43), 115 (45), 91 (27), 77 (12). Anal. Calcd for $C_{15}H_{17}N$: C, 87.52; H, 6.48; N, 6.00%. Found: C, 87.24; H, 6.57; N, 5.93%.



3i

(*Z*)-1-(4-Nitrophenyl)-2-phenyl-1-butene (3i). Yellow solid. Isolated yield was 92% (411 mg, 1.84 mmol). Bp. 180 ºC/2 Torr. R_f = 0.15 (hexane). Mp. 30-32 ºC. FT-IR ($CHCl_3$, cm^{-1}: 2970 (m), 2934 (m), 1593 (s), 1517 (s), 1341 (s), 830 (w), 753 (s), 702 (s). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 1.10 (t, J = 7.2 Hz, 3H), 2.56 (q, J = 7.5 Hz, 2H), 6.48 (s, 1H), 7.03 (d, J = 9.0 Hz, 2H), 7.12 (d, J = 7.8 Hz, 2H), 7.29-7.35 (m, 3H), 7.93 (d, J = 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz, rt) δ 12.6, 33.6, 123.1, 123.3, 127.6, 128.1, 128.8, 129.4, 140.3, 144.5, 145.6, 150.0. MS (EI, m/z (relative intensity)): 253 (M^+, 100), 238 (17), 223 (14), 207 (28), 192 (41), 178 (37), 93 (46), 165 (22), 152 (11), 129 (10), 115 (31), 91 (25). HRMS Calcd for $C_{16}H_{15}NO_2$: 253.1103. Found: M^+, 253.1101.



3j

(*Z*)-1-(2-Hydroxyphenyl)-2-phenyl-1-butene (3j).[3] White solid. Isolated yield was 58% (260 mg, 1.16 mmol). Bp. 150 ºC/2 Torr. R_f = 0.20 (hexane/ethyl acetate = 10/1). Mp. 41-43 ºC. FT-IR ($CHCl_3$, cm^{-1}): 3545 (w), 3420 (w), 2969 (m), 2934 (m), 754 (s), 668 (s). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 1.15 (t, J = 7.5 Hz, 3H), 2.66 (q, J = 7.5 Hz, 2H), 5.04 (s, 1H), 6.53 (s, 1H), 6.74 (t, J = 7.5 Hz, 2H), 6.95 (d, J = 7.5 Hz, 1H), 7.06 (d, J = 7.5 Hz, 1H), 7.17-7.30 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz, rt) δ 13.1, 32.2, 115.4, 119.6, 120.2, 124.3, 127.4, 128.0, 128.2, 128.4, 130.4, 139.9, 147.2, 152.5. MS (EI, m/z (relative intensity)): 224 (M^+, 47), 195 (100), 178 (9), 167 (59), 152 (15), 131 (13), 115 (32), 105 (14), 91 (23), 77 (17). Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19%. Found: C, 85.36; H, 7.34%.

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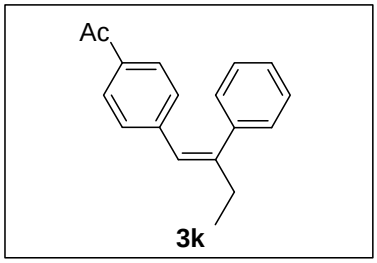
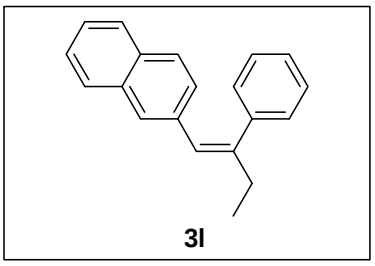
(3) Nishimae, S.; Inoue, R.; Shinokubo, H.; Oshima, K. *Chem. Lett.* **1998**, 785-786.



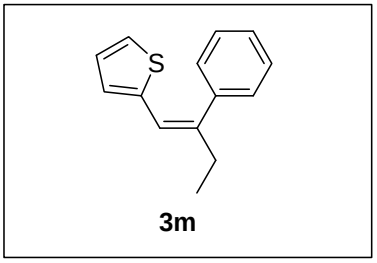
3k

(*Z*)-1-(4-Acetylphenyl)-2-phenyl-1-butene (3k). Yellow liquid. Isolated yield was 56% (280 mg, 1.12 mmol). Bp. 190 ºC/2 Torr. R_f = 0.10 (hexane). FT-IR (neat, cm^{-1}): 2971 (m), 2935 (m), 1684 (s), 1601 (w), 1268 (m), 872 (m), 826 (s), 764 (s), 701 (s). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 1.09 (t, J = 7.2 Hz, 3H), 2.50 (s, 3H), 2.54 (q, J = 7.5 Hz, 2H), 6.46 (s, 1H), 6.84 (d, J = 8.4 Hz, 2H), 7.12-7.15 (m, 2H), 7.29-7.32 (m, 3H), 7.68 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz, rt) δ 12.7, 26.4, 33.6, 124.2, 127.2, 127.9, 128.3, 128.6, 128.9, 134.5, 140.9, 142.6, 148.0, 197.6. MS (EI, m/z (relative intensity)): 250 (M^+, 100), 235 (68), 207 (14), 191 (13), 178 (29), 165 (18), 129 (25), 115 (18), 110 (11), 91 (20). Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25%. Found: C, 86.06; H, 7.23%.



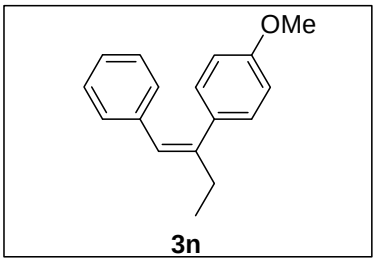
3l

(*Z*)-1-(1-Naphthyl)-2-phenyl-1-butene (3l). Colorless liquid. Isolated yield was 94% (486 mg, 1.88 mmol). Bp. 195 ºC/2 Torr. R_f = 0.40 (hexane). FT-IR (neat, cm^{-1}): 2965 (m), 2931 (m), 1636 (w), 800 (s), 779 (s), 773 (s), 699 (s). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 1.26 (t, J = 7.2 Hz, 3H), 2.75 (q, J = 7.5 Hz, 2H), 6.98-7.03 (m, 2H), 7.09-7.21 (m, 6H), 7.49-7.56 (m, 2H), 7.65 (d, J = 8.1 Hz, 1H) 7.86 (d, J = 7.2 Hz, 1H) 8.21 (d, J = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz, rt) δ 13.3, 32.4, 123.2, 124.7, 125.3, 125.5, 125.7, 126.5, 126.5, 127.7, 127.9, 128.4, 128.6, 132.3, 133.4, 135.3, 140.9, 146.5. MS (EI, m/z (relative intensity)): 258 (M^+, 90), 243 (24), 229 (100), 215 (9), 202 (7), 165 (44), 152 (10), 141 (12), 115 (28), 91 (34). Anal. Calcd for $C_{18}H_{20}$: C, 92.98; H, 7.02%. Found: C, 92.88; H, 7.08%.



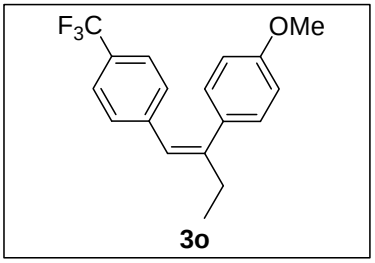
3m

(*Z*)-1-(2-Thienyl)-2-phenyl-1-butene (3m). Colorless liquid. Isolated yield was 85% (364 mg, 1.70 mmol). Bp. 170 ºC/2 Torr. R_f = 0.20 (hexane). FT-IR (neat, cm^{-1}): 3050 (m), 2966 (m), 2931 (m), 740 (s), 699 (s). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 1.11 (t, J = 7.2 Hz, 3H), 2.48 (q, J = 7.4 Hz, 2H), 6.63 (s, 1H), 6.76 (d, J = 3.5 Hz, 1H), 6.81-6.84 (m, 1H), 6.96 (d, J = 3.5 Hz, 1H), 7.21-7.25 (m, 2H), 7.38-7.47 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, rt) δ 12.7, 33.6, 118.7, 124.7, 125.9, 126.8, 127.4, 128.7, 128.9, 141.1, 141.1, 143.6. MS (EI, m/z (relative intensity)): 214 (M^+, 100), 199 (48), 185 (20), 165 (41), 152 (11), 129 (8), 115 (61), 97 (22), 91 (16), 77 (9). Anal. Calcd for $C_{14}H_{14}S$: C, 78.46; H, 6.58%. Found: C, 78.40; H, 6.61%.



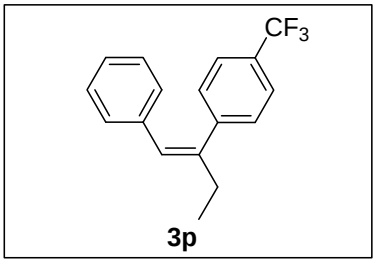
3n

(*Z*)-1-Phenyl-2-(4-methoxyphenyl)-1-butene (3n). Colorless liquid. Isolated yield was 85% (405 mg, 1.70 mmol). Bp. 180 ºC/2 Torr. R_f = 0.40 (hexane). FT-IR (neat, cm^{-1}): 2964 (m), 2933 (m), 1607 (w), 1245 (m), 832 (s). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 1.09 (t, J = 7.2 Hz, 3H), 2.52 (q, J = 7.2 Hz, 2H), 3.83 (s, 3H), 6.43 (s, 1H), 6.83-6.87 (m, 2H), 6.88-7.00 (m, 2H), 6.88-7.13 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz, rt) δ 12.9, 33.5, 55.1, 113.8, 124.8, 125.9, 127.8, 128.9, 129.6, 133.5, 137.8, 144.4, 158.4. MS (EI, m/z (relative intensity)): 238 (M^+, 100), 223 (18), 209 (23), 194 (11), 178 (13), 165 (24), 147 (20), 129 (13), 115 (33), 91 (20). Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61%. Found: C, 85.44; H, 7.73%.



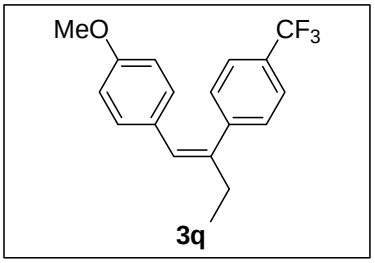
3o

(*Z*)-1-(4-Trifluoromethylphenyl)-2-(4-methoxypheny)-1-butene (3o). Colorless liquid. Isolated yield was 72% (441 mg, 1.44 mmol). Bp. 170 ºC/2 Torr. R_f = 0.20 (hexane). FT-IR (neat, cm^{-1}): 2968 (m), 2936 (m), 1609 (w), 1246 (m), 1124 (m), 833 (s). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 1.08 (t, J = 7.4 Hz, 3H), 2.52 (q, J = 7.2 Hz, 2H), 3.82 (s, 3H), 6.42 (s, 1H), 6.84-6.88 (m, 2H), 7.03-7.08 (m, 4H), 7.35 (d, J = 7.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz, rt) δ 12.8, 33.5, 55.1, 114.0, 123.5, 124.3 (q, J = 270.1 Hz), 124.7 (q, J = 3.8 Hz), 127.6 (q, J = 32.2 Hz), 130.2, 131.8, 132.8, 141.5, 147.2, 158.8; ^{19}F NMR ($CDCl_3$, 282 MHz, rt) -62.91. MS (EI, m/z (relative intensity)): 306 (M^+, 100), 291 (12), 277 (24), 262 (11), 183 (14), 178 (8), 165 (14), 147 (26), 121 (8), 108 (16), 91 (11). Anal. Calcd for $C_{18}H_{17}F_3O$: C, 70.58; H, 5.59%. Found: C, 70.63; H, 5.59%.

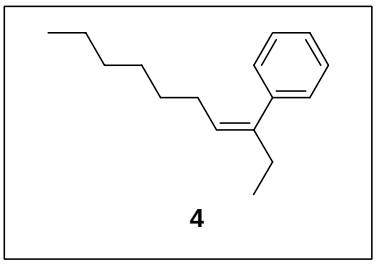


3p

(*Z*)-1-Phenyl-2-(4-trifluoromethylphenyl)-1-butene (3p). Colorless liquid. Isolated yield was 85% (470 mg, 1.70 mmol). Bp. 150 ºC/2 Torr. R_f = 0.50 (hexane). FT-IR (neat, cm^{-1}): 2970 (m), 2935 (m), 1615 (w), 1128 (m), 756 (s), 696 (s). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 1.07 (t, J = 7.8 Hz, 3H), 2.52 (q, J = 7.8 Hz, 2H), 6.52 (s, 1H), 6.90-6.91 (m, 2H), 7.09-7.13 (m, 3H), 7.27-7.28 (m, 2H), 7.55 (d, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz, rt) δ 12.8, 33.1, 124.3 (q, J = 270.4 Hz), 125.4 (q, J = 3.7 Hz), 126.3, 126.4, 128.0, 128.9 (q, J = 32.0 Hz), 129.0, 129.1, 136.9, 143.3, 145.4; ^{19}F NMR ($CDCl_3$, 282 MHz, rt) -62.90. MS (EI, m/z (relative intensity)): 276 (M^+, 100), 261 (52), 247 (22), 207 (16), 183 (29), 178 (17), 165 (15), 129 (33), 115 (85), 105 (18), 91 (96). Anal. Calcd for $C_{17}H_{15}F_3$: C, 73.90; H, 5.47%. Found: C, 74.06; H, 5.62%.

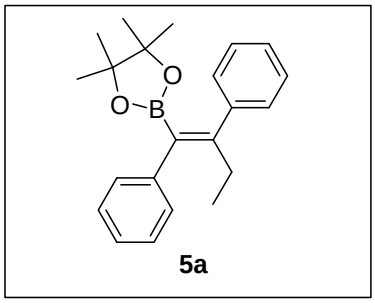


(*Z*)-1-(4-Methoxypheny)-2-(4-trifluoromethylphenyl)-1-butene (3q). Colorless liquid. Isolated yield was 75% (459.5 mg, 1.50 mmol). Bp. 170 ºC/2 Torr. R_f = 0.20 (hexane). FT-IR (neat, cm^{-1}): 2967 (m), 2935 (m), 1608 (w), 1253 (m), 1126 (m), 827 (s). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 1.05 (t, J = 7.8 Hz, 3H), 2.50 (q, J = 7.8 Hz, 2H), 3.74 (s, 3H), 6.44 (s, 1H), 6.65 (d, J = 7.8 Hz, 2H), 6.83 (d, J = 8.4 Hz, 2H), 7.27-7.28 (m, 2H), 7.55 (d, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz, rt) δ 12.9, 33.1, 55.1, 113.4, 124.3 (q, J = 270.3 Hz), 125.4 (q, J = 3.7 Hz), 126.8, 128.3 (q, J = 32.5 Hz), 129.1, 129.5, 130.1, 141.4, 145.6, 158.1; ^{19}F NMR ($CDCl_3$, 282 MHz, rt) -62.86. MS (EI, m/z (relative intensity)): 306 (M^+, 100), 291 (68), 276 (8), 251 (7), 183 (28), 178 (10), 165 (10), 145 (13), 121 (56), 115 (14), 108 (12), 91 (19). Anal. Calcd for $C_{18}H_{17}F_3O$: C, 70.58; H, 5.59%. Found: C, 70.72; H, 5.66%.



[(*1Z*)-1-Ethyl-1-octenyl]benzene (4). Under an Ar atmosphere, $Ni(cod)_2$ (22.4 mg, 0.080 mmol), bathophenanthroline (53 mg, 0.16 mmol), (*Z*)-4,4,5,5-tetramethyl-2-(2-phenyl-1-buten-1-yl)-1,3,2-dioxaborolane (**2a**) (619.6 mg, 2.4 mmol), and KO^{t}Bu (360 mg, 3.2 mmol) were placed in a 50 mL Schlenk tube equipped with a stirring bar. Then 2-butanol (12 mL) as a solvent was added and the reaction mixture was stirred for 10 minutes at room temperature. To the resulting dark purple mixture, 1-iodohexane (295 μL, 2.0 mmol) was then added by syringe, and the reaction mixture was heated at 60 ºC (oil bath) for 5 h. The resulting white suspension was allowed to cool to room temperature, and then it was filtered through a short pad of silica gel. The filtrate was concentrated under vacuum, and the product was isolated by bulb to bulb distillation (120 ºC/2 Torr) as a colorless oil. Isolated yield was 44% (190 mg, 0.88 mmol). Bp. 120 ºC/2 Torr.

R_f = 0.60 (hexane). FT-IR (neat, cm^{-1}): 2960 (m), 2925 (m), 2855 (m), 2360 (m), 2337 (m), 1461 (m), 1456 (m), 767 (s), 700 (s). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 0.86 (t, J = 7.2 Hz, 3H), 0.96 (t, J = 7.2 Hz, 3H), 1.17-1.34 (m, 8H), 1.91 (q, J = 7.2 Hz, 2H), 2.34 (q, J = 7.2 Hz, 2H), 5.43 (t, J = 7.5 Hz, 1H), 7.11-7.15 (m, 2H), 7.20-7.26 (m, 1H), 7.30-7.36 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz, rt) δ 13.1, 14.1, 22.6, 28.8, 28.9, 30.1, 31.7, 32.1, 126.1, 126.2, 127.9, 128.4, 141.7, 142.4. MS (EI, m/z (relative intensity)): 216 (M^+, 11), 187 (17), 145 (48), 132 (32), 129 (14), 117 (100), 115 (28), 105 (28), 91 (72), 77 (7). HRMS Calcd for $C_{16}H_{24}$: 216.1878. Found: M^+, 216.1879. Synthesis of (*E*)-isomer has been reported.[4]



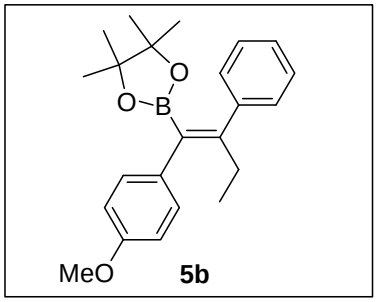
5a

2-[(1*E*)-1,2-Diphenyl-1-butenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5a). [865999-25-3][5] To a solution zirconocene dichloride (1.05 g, 3.6 mmol) in THF (18 mL) in a 25 mL of Schlenk tube under an Ar atmosphere were added dropwise n-BuLi (4.5 mL, 7.2 mmol, 1.6 M hexane solution) at -78 ºC. After the reaction mixture was stirred for 1 h at -78 °C, atmospheric ethylene gas was introduced into the vessel for 1 h at -78 ºC. The reaction mixture was warmed to room temperature and 4,4,5,5-tetramethyl-2-(phenylethynyl)-1,3,2-dioxaborolane (**1a**; 682 mg, 3 mmol) was added. After 1 h, ^{i}PrOH (185 µL, 2.4 mmol) was added and the reaction mixture was stirred for additional 1 h. To the mixture were added $Pd(PPh_3)_4$ (336 mg, 0.3 mmol), PhI (330 µL, 3 mmol), CuCl (300 mg, 3 mmol). The mixture was stirred for 1 h at room temperature and quenched with 1 M hydrochloric acid (10 mL), and extracted with diethyl ether (10 mL x 2). The combined ethereal layer was washed with brine and dried over $MgSO_4$. Filtration, evaporation, and column chromatography on silica gel (R_f= 0.2; hexane/AcOEt = 19:1) gave **5a** (431 mg, 1.4 mmol, 47% yield) as yellow solid. Mp. 37-38 ºC. FT-IR (KBr, cm^{-1}): 2977 (m), 2932 (m), 2857 (m), 1598 (m), 1492 (m), 1356 (m), 1299 (m), 1269 (m),

(4) Shi, J.-c.; Negishi, E.-i. *J. Organomet. Chem.* **2003**, 687, 518-524.

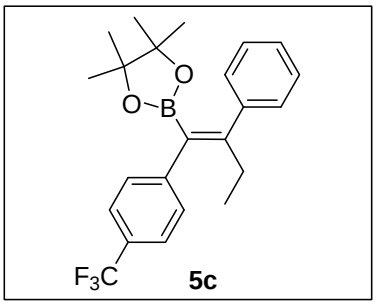
(5) Shimizu, M,; Nakamaki, C,; Shimono, K,; Schelper, M,; Kurahashi, T,; Hiyama, T. *J. Am. Chem. Soc.,***2005,** *127,* 12506-12507.

1214 (m), 1104 (m), 975 (s), 904 (s), 854 (s), 702 (s). ^{1}H NMR (300 MHz, $CDCl_3$, rt) δ 0.87 (t, J = 7.5 Hz, 3H), 1.00 (s, 12H), 2.43 (q, J = 7.5 Hz, 2H), 7.23-7.35 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$, rt) δ 13.6, 24.3, 27.1, 83.3, 125.9, 127.0, 127.9, 128.1, 128.3, 128.4, 141.4, 143.6, 153.8. The carbon signal attached to B was not observed due to low intensity; ^{11}B NMR ($CDCl_3$, 96 MHz, rt) δ 30.16. MS (EI, m/z (relative intensity)): 334 (M^+, 70), 277 (100), 234 (51), 218 (32), 130 (78).



5b

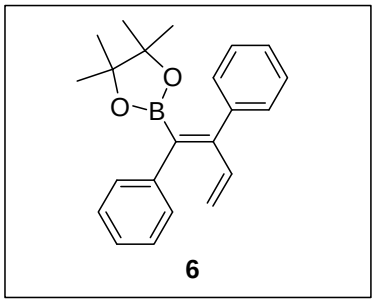
2-[(1*E*)-1-(4-Methoxyphenyl)-2-phenyl-1-butenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5b). [865999-30-0][5] White solid. Isolated yield was 62% (677 mg, 1.86 mmol). R_f = 0.40 (hexane/AcOEt = 9:1). Mp. 63-64 ºC. FT-IR (KBr, cm^{-1}): 2972 (m), 2830 (m), 2874 (m), 1604 (w), 1509 (m), 1462 (m), 1440 (m), 1353 (m), 1283 (m), 1245 (m), 1142 (m), 1033 (s), 854 (s), 703 (s). ^{1}H NMR (300 MHz, $CDCl_3$, rt) δ 0.86 (t, J = 7.5 Hz, 3H), 1.00 (s, 12H), 2.44 (q, J = 7.5 Hz, 2H), 3.82 (s, 3H), 6.89 (d, J = 8.7 Hz, 2H), 7.16 (d, J = 8.7 Hz, 2H), 7.27-7.36 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, rt) δ 13.3, 24.4, 27.0, 55.1, 83.2, 113.6, 126.9, 127.8, 128.4, 129.5, 133.8, 143.7, 153.4, 157.8. The carbon signal attached to B was not observed due to low intensity; ^{11}B NMR ($CDCl_3$, 96 MHz, rt) δ 30.01. MS (EI, m/z (relative intensity)): 364 (M^+, 100), 307 (35), 264 (33), 249 (35), 160 (46).



5c

4,4,5,5-Tetramethyl-2-[(1*E*)-2-phenyl-1-[4-(trifluoromethyl)phenyl]-1-butenyl]-1,3,2-dioxaborolane (5c). [865999-27-5][5] White solid. Isolated yield was 40% (481 mg, 1.20 mmol). R_f = 0.45 (hexane/AcOEt =

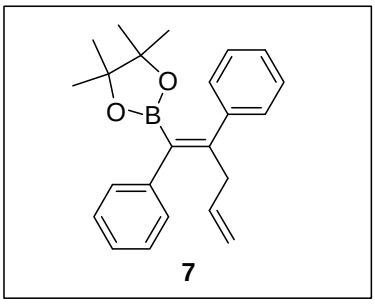
9:1). Mp. 77-79 ºC. FT-IR (KBr, cm^{-1}): 2978 (m), 2932 (m), 2874 (m), 1613 (w), 1351 (m), 1325 (m), 1145 (m), 1105 (m), 1066 (m), 856 (s), 701 (s). ^{1}H NMR (300 MHz, $CDCl_3$, rt) δ 0.85 (t, J = 7.5 Hz, 3H), 1.00 (s, 12H), 2.38 (q, J = 7.5 Hz 2H), 7.28-7.36 (m, 7H), 7.60 (d, J = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, rt) δ 13.1, 24.3, 27.3, 83.5, 124.4 (q, J = 270.1 Hz), 125.1 (q, J = 3.7 Hz), 127.3, 127.9, 128.0 (q, J = 32.0 Hz), 128.3, 128.7, 143.1, 145.4, 155.4. The carbon signal attached to B was not observed due to low intensity; ^{11}B NMR ($CDCl_3$, 96 MHz, rt) δ 30.07; ^{19}F NMR ($CDCl_3$, 282 MHz, rt) δ -62.74. MS (EI, m/z (relative intensity)): 402 (M^+, 27), 345 (73), 302 (20), 286 (17), 101 (100).



6

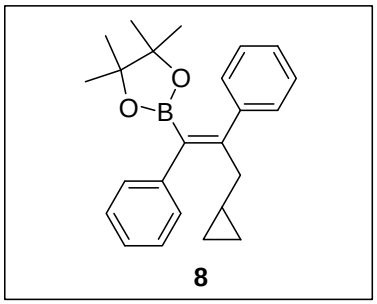
2-[(1*E*)-1,2-Diphenyl-1,3-butadienyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6). A 50 mL Schlenk tube under argon was charged with Cp_2ZrCl_2 (1.05g, 3.6 mmol) and 18 mL of THF. The mixture was cooled to -78 ºC, and then 2 equiv of n-BuLi (4.5 mL, 7.2 mmol, 1.6 M THF solution) was added dropwise via syringe. After the reaction mixture was stirred at -78 ºC for 1 h under argon, ethylene gas was introduced for 1h, and **1a** (682 mg, 3 mmol) was added at -78 ºC. The resulting mixture was gradually warmed to room temperature and stirred for 1 h. To this was added vinyl ethyl ether (0.640 mL, 4.5 mmol) at room temperature. After the mixture was stirred for 20 h at 50 ºC. CuCl (300 mg, 3 mmol), DMPU (0.544 mL, 4.5 mmol), $Pd(PPh_3)_4$ (336 mg, 0.3 mmol,), and iodobenzene (0.369 mL, 3.3 mmol) was added successively at room temperature, and the mixture was stirred for 3 h at 50 ºC The reaction mixture was quenched with 3 M HCl, extracted two times with diethyl ether. Extract was dried over $MgSO_4$ and concentrated. Purification with column chromatography on silica gel (R_f= 0.2; hexane/Et_2O = 19:1) afforded the title compound as colorless liquid. Isolated yield was 26% (259 mg, 0.78 mmol). FT-IR (KBr, cm^{-1}): 2978 (m), 2930 (m), 1559 (w), 1492 (m), 1442 (m), 1362 (m), 1306 (m), 1268 (m), 1215 (m), 1141 (m), 972 (m), 911 (s), 854 (s), 701 (s). ^{1}H NMR (300 MHz, $CDCl_3$, rt) δ 0.98 (s, 12H), 4.87 (d, J = 18.9 Hz 1H), 5.17 (d, J = 12.3 Hz 1H), 6.74 (q, J = 9.1Hz 1H),7.25-7.36 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$, rt) δ 24.3, 83.4, 119.4, 126.4, 127.2, 127.7, 128.0, 129.2, 130.1, 136.3, 140.1; 141.1, 148.5. The carbon signal attached to B was not observed due to their low intensity; ^{11}B NMR ($CDCl_3$,

96 MHz, rt) δ 30.09. MS (EI, m/z (relative intensity)): 332 (M^+, 21), 275 (17), 232 (41), 213 (41), 207 (77), 204 (100), 84 (68). HRMS Calcd for $C_{22}H_{25}BO_2$: 332.1948. Found: M^+, 332.1945.



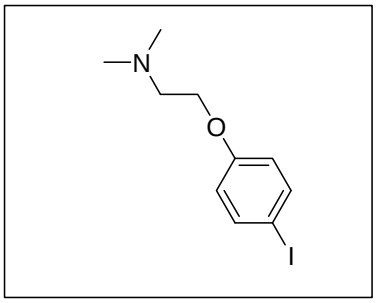
7

2-[(1*E*)-1,2-Diphenyl-1,4-pentadienyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7). A 50 mL Schlenk tube under argon was charged with Cp_2ZrCl_2 (1.05g, 3.6 mmol) and 18 mL of THF. The mixture was cooled to -78 ºC, and then 2 equiv of n-BuLi (4.5 mL, 7.2 mmol, 1.6 M THF solution) was added dropwise via syringe. After the reaction mixture was stirred at -78 ºC for 1 h under argon, ethylene gas (1 atm) was introduced for 1h, and **1a** (682 mg, 3 mmol) was added at -78 ºC. The resulting mixture was gradually warmed to room temperature and stirred for 1 h. To this was added allyloxytrimethylsilane (0.743 mL, 4.5 mmol) at room temperature. After the mixture was stirred for 20 h at 50 ºC, CuCl (300 mg, 3 mmol), DMPU (0.544 mL, 4.5 mmol), $Pd(PPh_3)_4$ (336 mg, 0.3 mmol,), and iodobenzene (0.369 mL, 3.3 mmol) was added successively at room temperature, and the mixture was stirred for 3 h at 50 ºC. The reaction mixture was quenched with 3 M HCl, extracted two times with diethyl ether. Extract was dried over $MgSO_4$ and concentrated. Purification with column chromatography on silica gel (R_f= 0.2; hexane/Et_2O = 19:1) afforded the title compound as white solid. Isolated yield was 43% (450 mg, 1.3 mmol). R_f = 0.20 (hexane/Et_2O = 19:1). Mp. 50-52 ºC. FT-IR (KBr, cm^{-1}): 2976 (m), 2927 (m), 1596 (w), 1493 (m), 1443 (m), 1355 (m), 1302 (m), 1265 (m), 1219 (m), 1141 (m), 978 (m), 906 (s), 854 (s), 701 (s). ^{1}H NMR (300 MHz, $CDCl_3$, rt) δ 1.02 (s, 12H), 3.18 (m, 2H), 4.88 (m, 2H), 5.63 (m, 1H),7.21-7.40 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$, rt) δ 24.3, 38.6, 83.4, 115.9, 126.1, 127.2, 127.8, 128.1, 128.3, 128.4, 135.8, 141.2; 143.5, 149.2. The carbon signal attached to B was not observed due to their low intensity; ^{11}B NMR ($CDCl_3$, 96 MHz, rt) δ 30.24. MS (EI, m/z (relative intensity)): 346 (M^+, 11), 247 (18), 246 (100), 218 (39), 207 (21), 142 (23), 84 (16). Anal. Calcd for $C_{23}H_{27}BO_2$: C, 79.78; H, 7.86%. Found: C, 79.54; H, 7.89%.

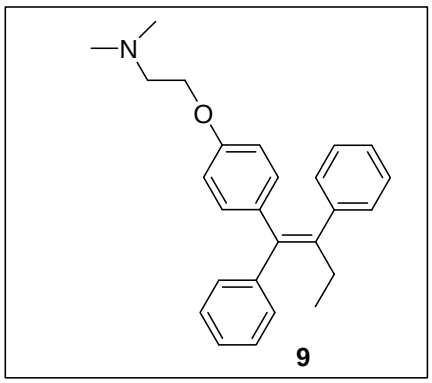


8

2-[(1*E*)-1,2-Diphenyl-3-cyclopropyl-1-propenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8). A 50 mL Schlenk tube under argon was charged with Cp_2ZrCl_2 (1.05g, 3.6 mmol) and 18 mL of THF. The mixture was cooled to -78 ºC, and then 2 equiv of n-BuLi (4.5 mL, 7.2 mmol, 1.6 M THF solution) was added dropwise via syringe. After the reaction mixture was stirred at -78 ºC for 1 h under argon, ethylene gas (1 atm) was introduced for 1h, and **1a** (682 mg, 3 mmol) was added at -78 ºC. The resulting mixture was gradually warmed to room temperature and stirred for 1 h. To this was added 4-bromo-1-butene (0.456 mL, 4.5 mmol) at room temperature. After the mixture was stirred for 20 h at 50 ºC, CuCl (300 mg, 3 mmol), DMPU (0.544 mL, 4.5 mmol), $Pd(PPh_3)_4$ (336 mg, 0.3 mmol,), and iodobenzene (0.369 mL, 3.3 mmol) was added successively at room temperature, and the mixture was stirred for 3 h at 50 ºC. The reaction mixture was quenched with 3 M HCl, extracted two times with diethyl ether. Extract was dried over $MgSO_4$ and concentrated. Purification with column chromatography on silica gel (R_f= 0.35; hexane/Et_2O = 9:1) afforded the title compound. Isolated yield was 54% (584 mg, 1.62 mmol). White solid. Isolated yield was 54% (584mg,1.62 mmol). R_f= 0.35 (hexane:Et_2O = 9:1). Mp. 56-58 ºC. FT-IR (KBr, cm^{-1}): 3003 (m), 2978 (m), 1599 (w), 1386 (m), 1370 (m), 1356 (m), 1303 (m), 1264 (m), 1212 (m), 1143 (m), 1020 (m), 969 (m), 855 (s), 764 (s), 705 (s). ^{1}H NMR (300 MHz, $CDCl_3$, rt) δ -0.20 (q, J = 5 Hz, 2H), 0.23 (dt, J = 7.5, 7.5Hz, 2H), 0.56 (quin, J = 13.5 Hz, 1H), 0.99 (s, 12H), 2.31 (d, J = 11.5Hz, 2H), 7.19-7.42 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$, rt) δ 4.6, 10.0, 24.3, 38.2, 83.2, 125.8, 126.8, 127.7, 128.0, 128.51, 128.54, 141.2, 144.2, 151.8. The carbon signal attached to B was not observed due to their low intensity; ^{11}B NMR ($CDCl_3$, 96 MHz, rt) δ 30.01. MS (EI, m/z (relative intensity)): 360 (M^+, 43), 260 (44), 232 (94), 143 (100), 101 (61). Anal. Calcd for $C_{24}H_{29}BO_2$: C, 80.01; H, 8.11%. Found: C, 79.59; H, 8.17%.



Preparation of *N*-[2-(4-Iodophenoxy)ethyl]-*N*,*N*-dimethylamine.[6] Potassium hydroxide (226 mg, 4 mmol) was added to a solution of 4-iodophenol (888 mg, 4 mmol) in ethanol (10 mL) at room temperature. The reaction was stirred for 3 h and the solvent evaporated to afford 4-iodophenoxide salt as a yellow oil. Sodium hydroxide (200 mg, 5 mmol) in water (1 mL) was added to a cold solution of 2-dimethylaminoethylchloride hydrochloride (600 mg, 4.2 mmol) in water (2 mL) at 0 °C. The reaction mixture was saturated with solid NaCl and extracted with toluene (5 × 3 mL). The combined toluene extracts were dried over KOH and filtered. The resulting solution was added to the 4-iodophenoxide salt and refluxed for 12 h. The reaction was cooled to room temperature and filtered. The filtrate was washed with saturated aqueous NaOH (3 × 10 mL) and brine (5 mL). The organic phase was dried, filtered, and purified by bulb to bulb distillation (160-170 °C/2.8 Torr) to give 703 mg (2.4 mmol, 60%) of the title compound as a brown oil. ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 2.33 (s, 6H), 2.72 (t, J = 5.7 Hz, 2H), 4.02 (d, J = 5.7 Hz, 2H), 6.66-6.70 (m, 2H), 7.52-7.56 (m, 2H). ^{1}H NMR spectrum in agreement with literature.



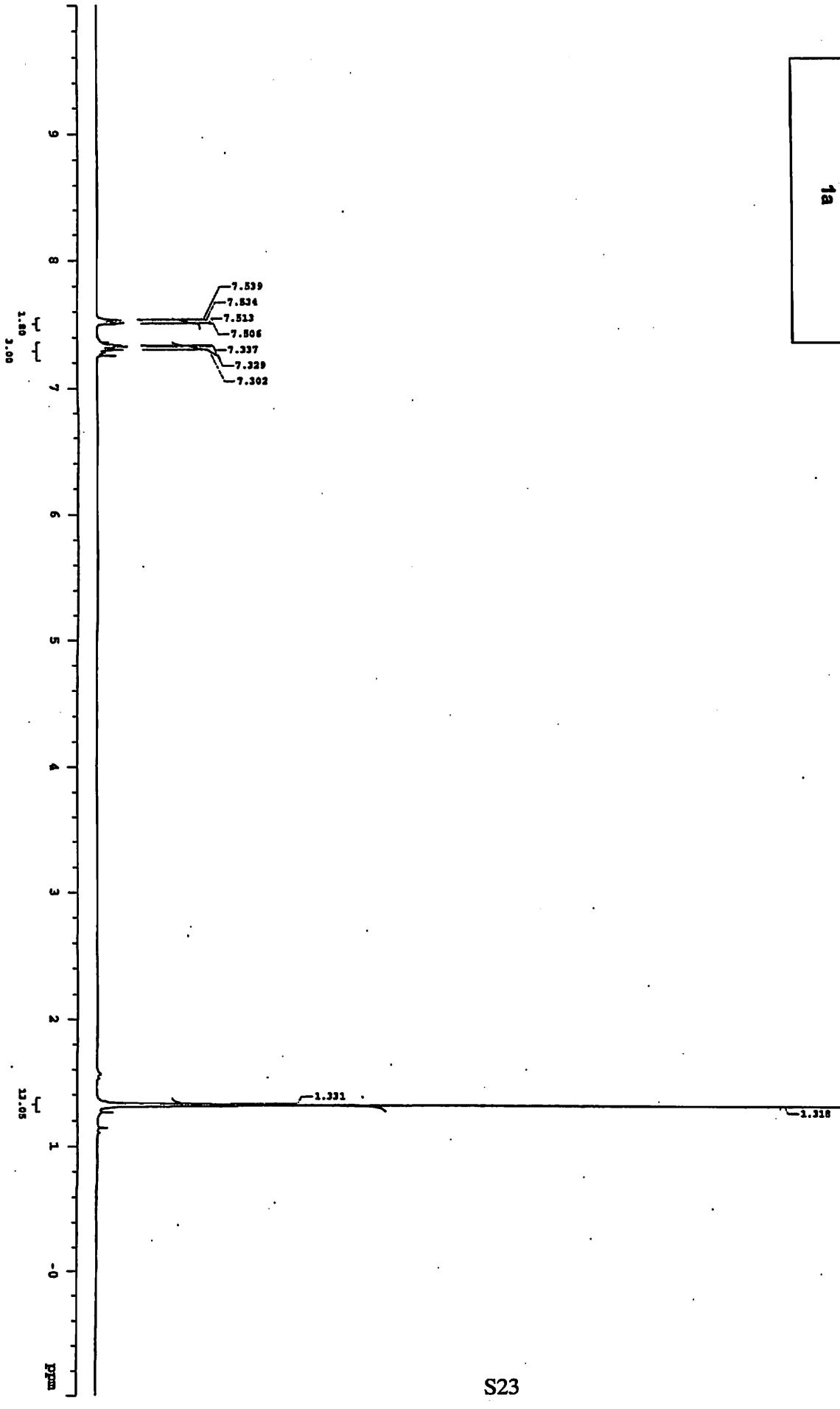
9

(Z)-Tamoxifen ((*Z*)-2-[4-(1,2-Diphenyl-1-butenyl)phenoxy]-*N*,*N*-dimethylethanamine) (9). [10540-29-

(6) Tessier, P. E.; Penwell, A. J.; Souza, F. E. S.; Fallis, A. G. *Org.Lett.* **2003**, *5*, 2989-2992.

1][7] A mixture of **5a** (18 mg, 0.054 mmol), *N*-[2-(4-iodophenoxy)ethyl]-*N*,*N*-dimethylamine (70 mg, 0.24 mmol), $Pd(dba)_2$ (12 mg, 0.02 mmol), 0.1 M P^tBu_3/hexane (400 μl, 0.04 mmol), and 3 M NaOH aqueous solution (300 μL, 0.9 mmol) in THF (2 mL) was stirred at 60 °C for 48 h. The reaction mixture was quenched with saturated aq. NH_4Cl (1 mL). The resulting mixture was diluted with chloroform (10 mL) and washed with water (3 mL). The organic layer was separated, dried over anhydrous magnesium sulfate, and concentrated under vacuum. The crude product was purified by column chromatography ($CHCl_3$/MeOH/Et_3N = 100:10:1) to give **9** as pale yellow solid (52 mg, 0.14 mmol, 70% yield). FT-IR (KBr, cm^{-1}): 3021 (m), 2930 (m), 2761 (m), 1610 (w), 1512 (m), 1247 (m). ^1H NMR (300 MHz, $CDCl_3$, rt) δ 0.93 (t, J = 7.5 Hz, 3H), 2.33 (s, 6H), 2.46 (q, J = 7.5Hz, 2H), 2.69 (t, J = 5.7 Hz, 2H), 3.95 (t, J = 5.7 Hz, 2H), 6.56 (d, J = 8.7 Hz, 2H), 6.77 (d, J = 8.7 Hz, 2H), 7.11-7.37 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$, rt) δ 13.6, 29.0, 45.7, 58.2, 65.4, 113.3, 126.0, 126.5, 127.8, 128.1, 129.4, 129.7, 131.8, 135.6, 138.1, 141.3, 142.4, 143.8, 156.6. MS (EI, m/z (relative intensity)): 371 (M^+, 23), 252 (5), 165 (5), 152 (4), 129 (4), 72 (100).

(7) Itami, K.; Kamei, T.; Yoshida, J.-i. *J. Am. Chem. Soc.* **2003**, *125*, 14670-14671.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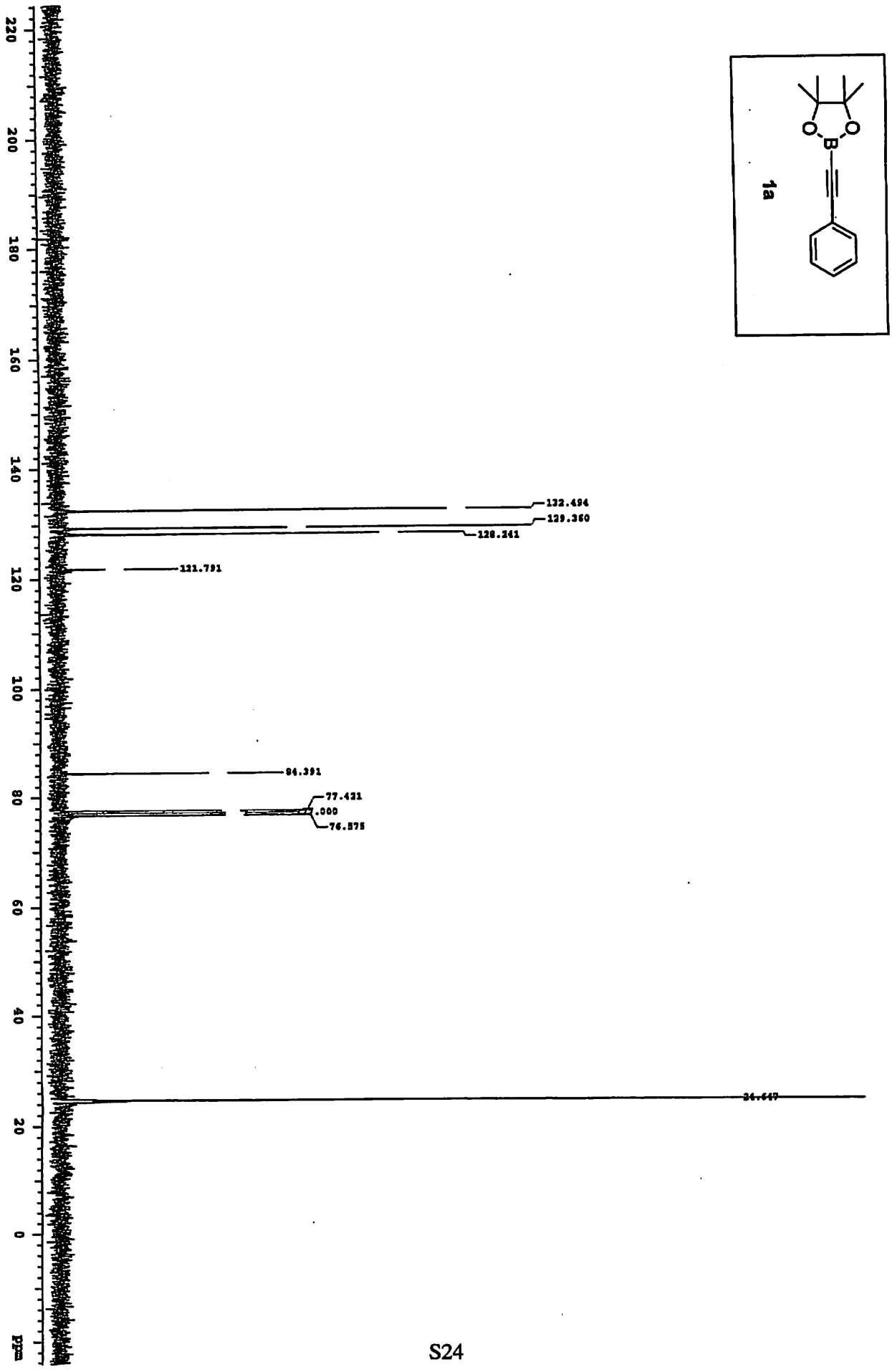
1a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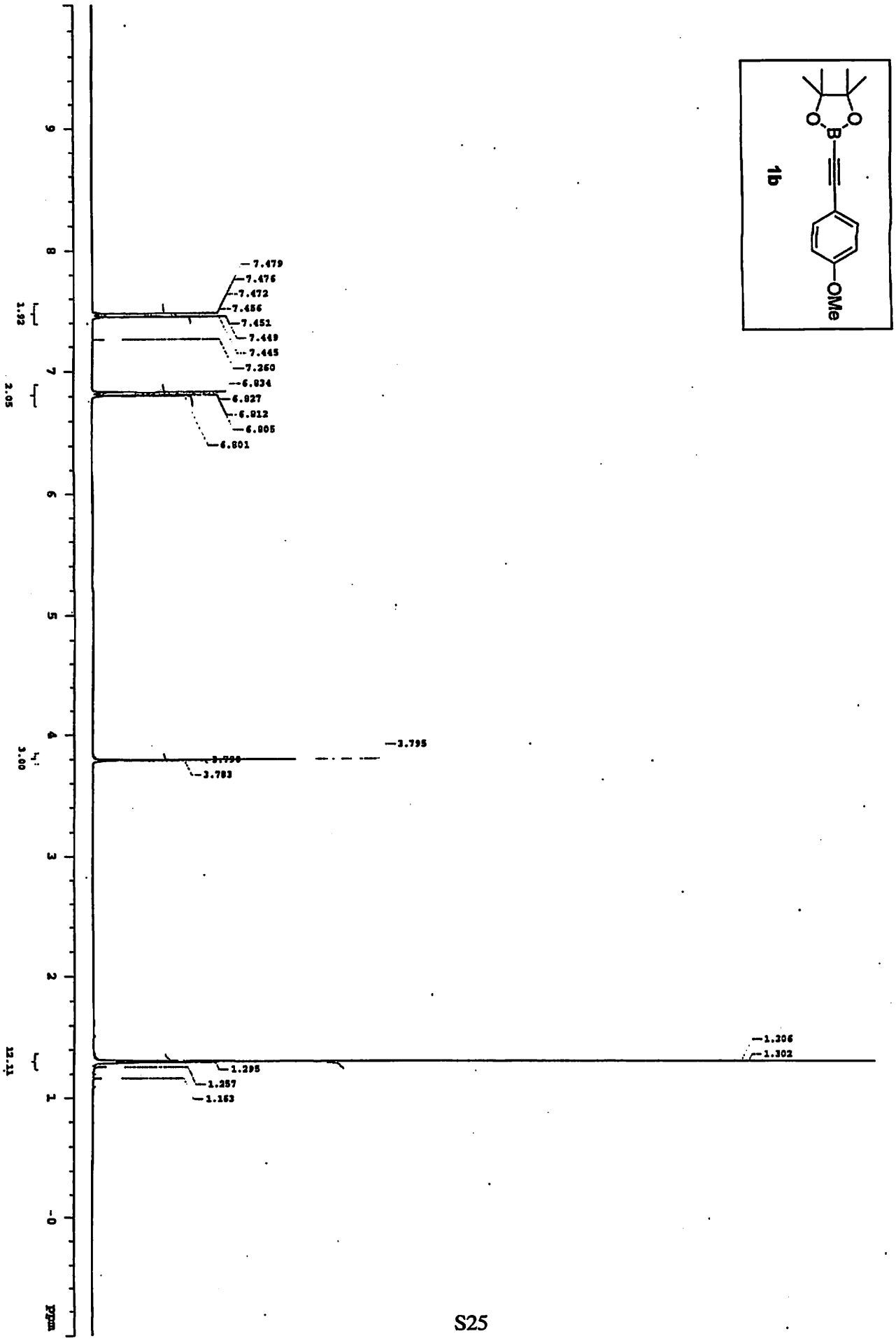
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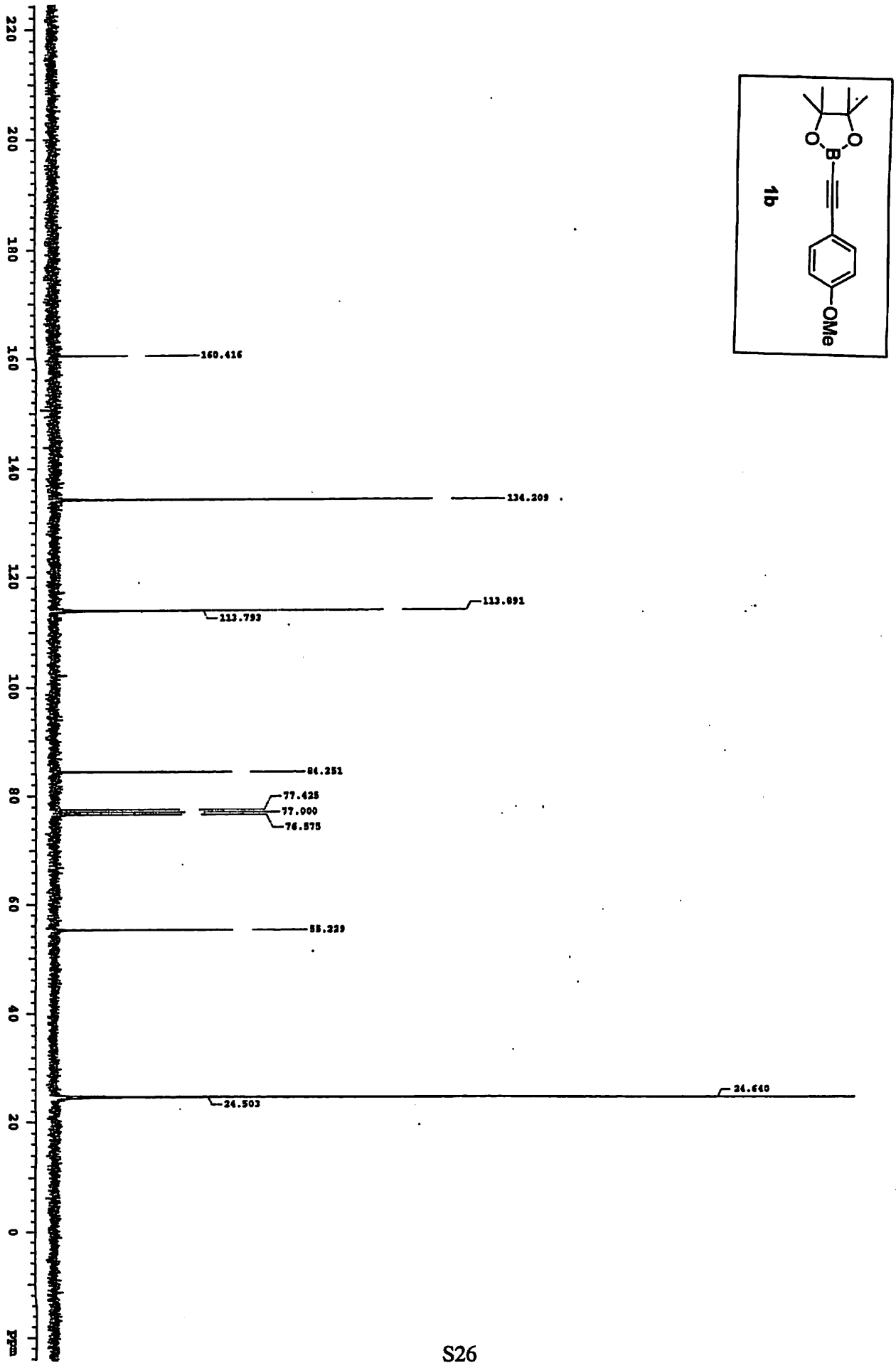
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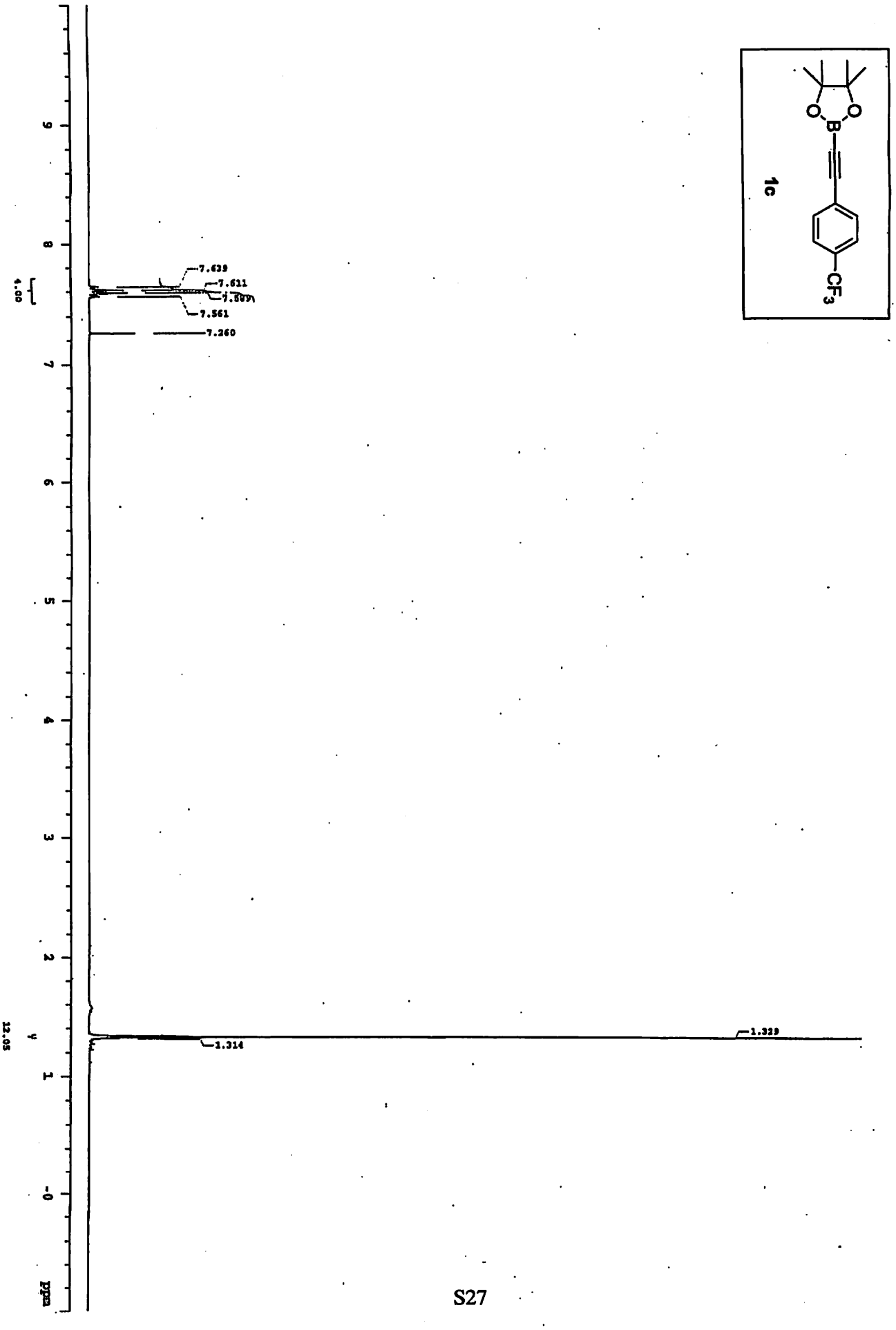
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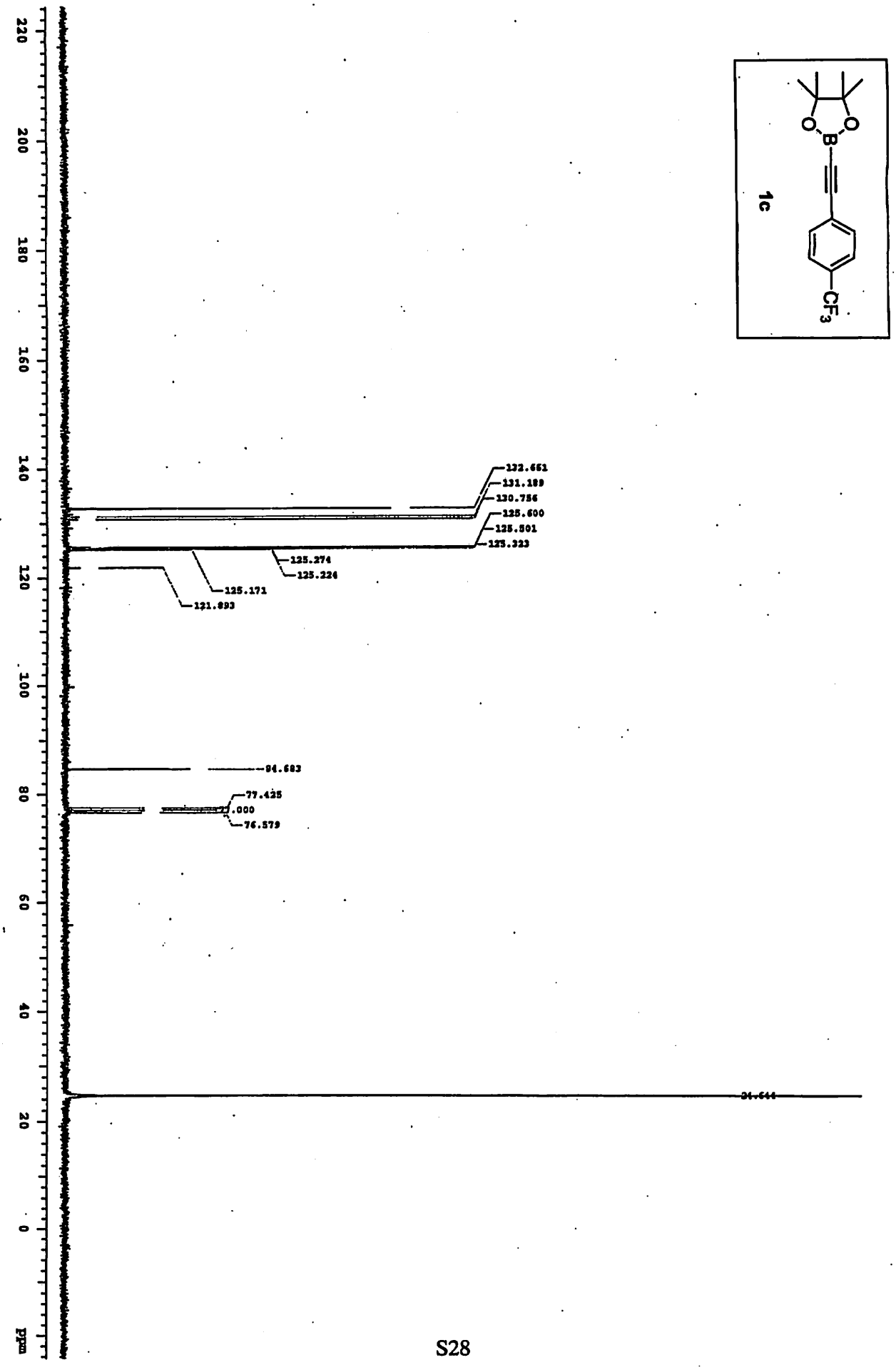
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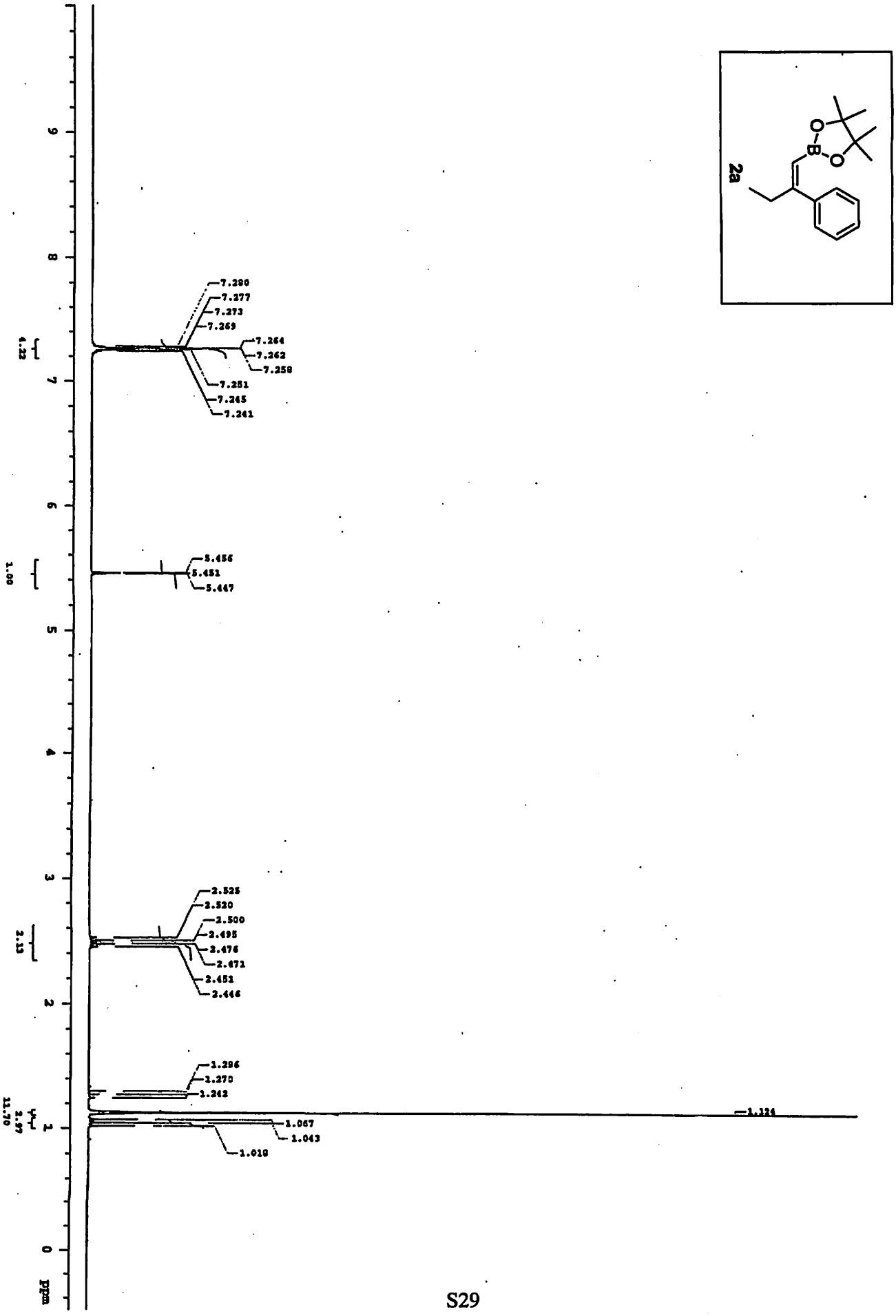
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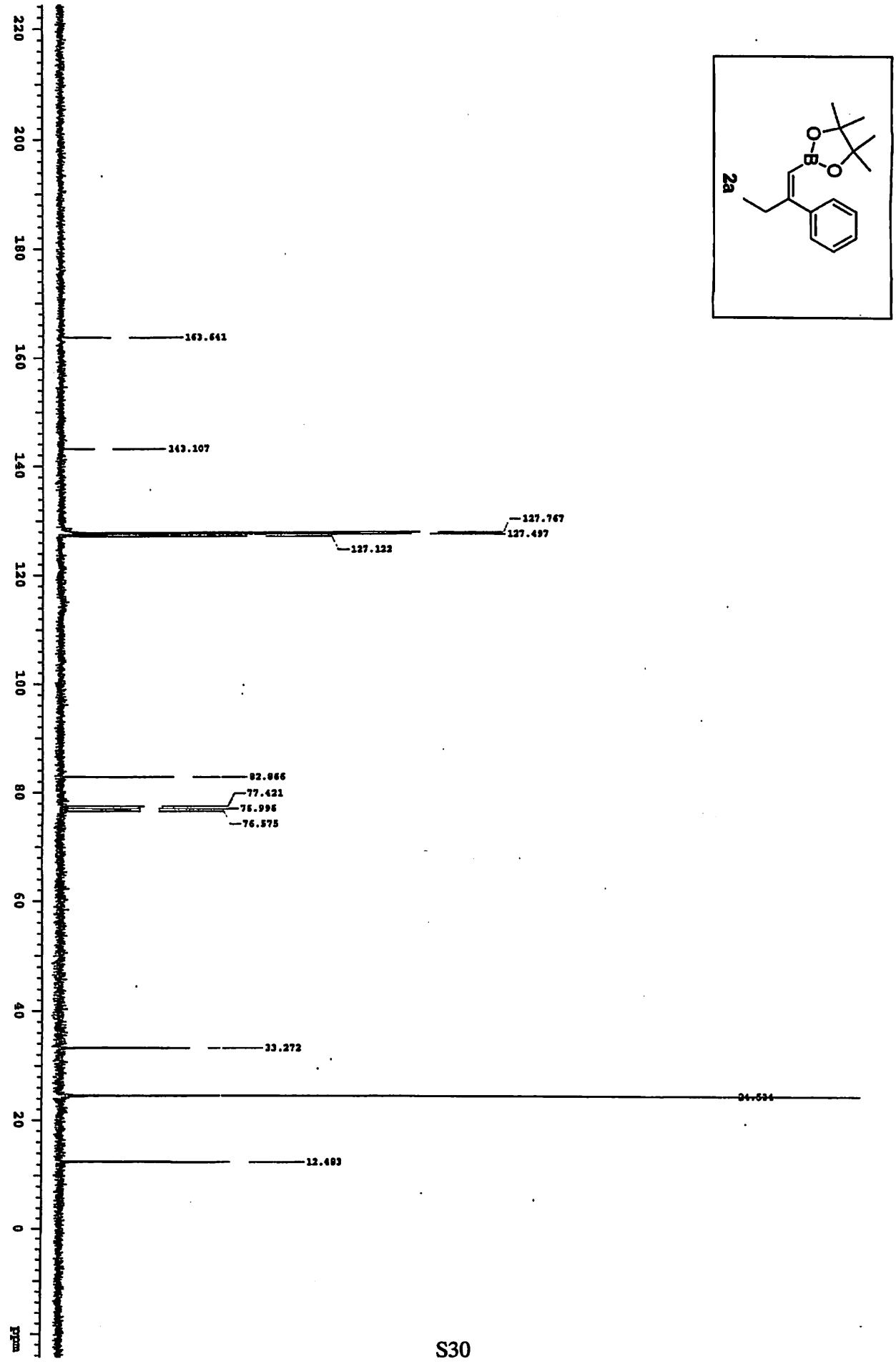
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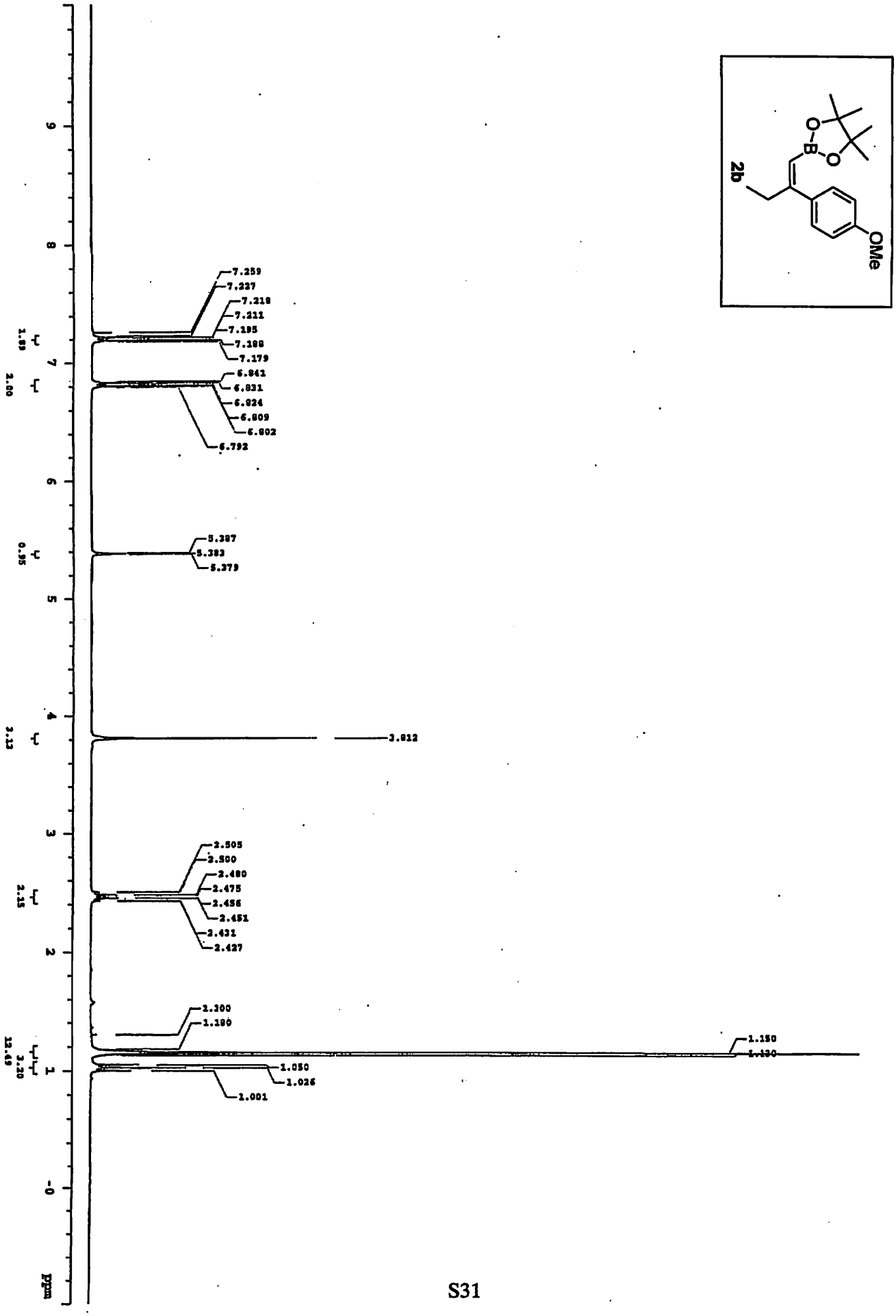
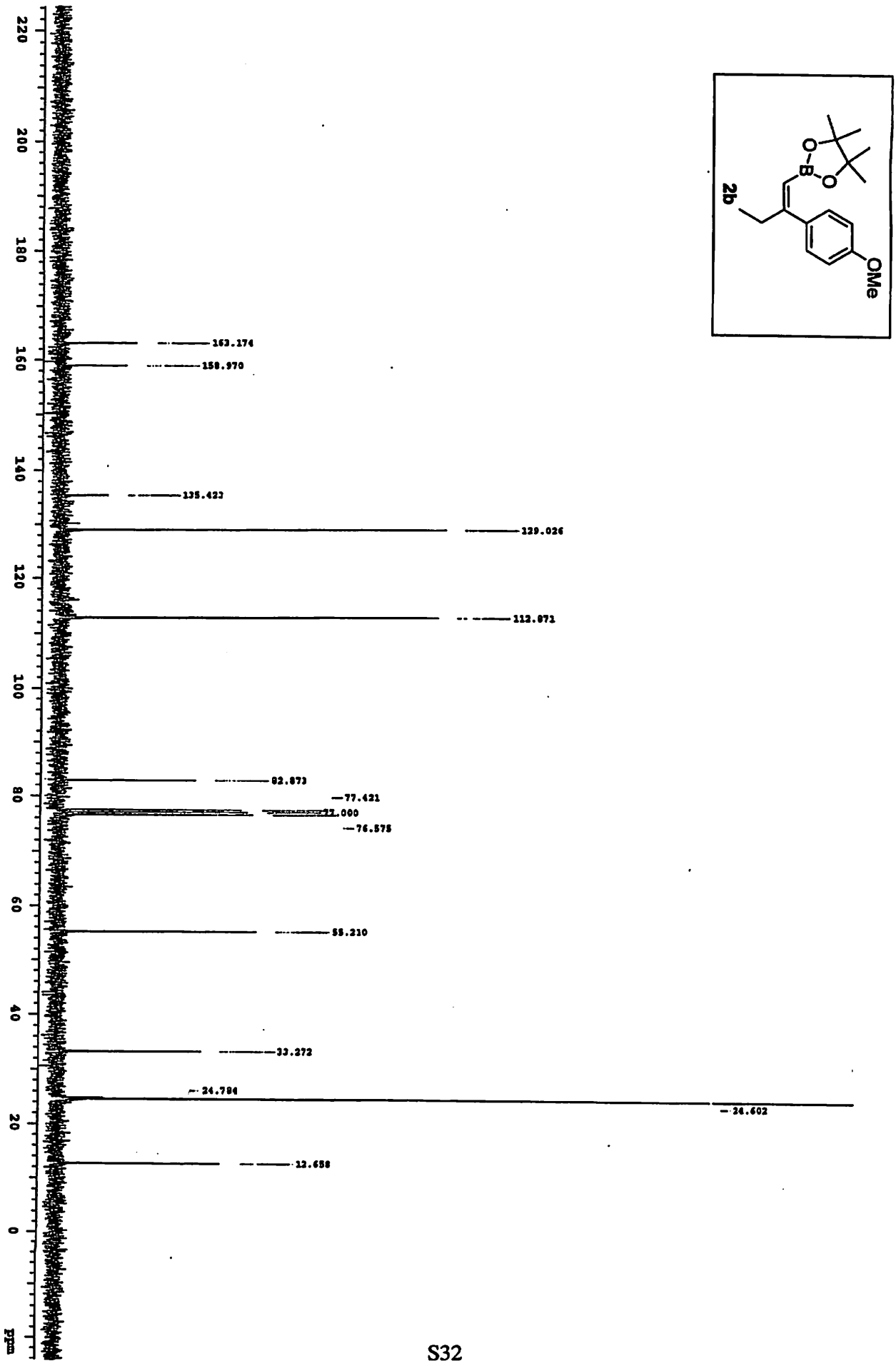
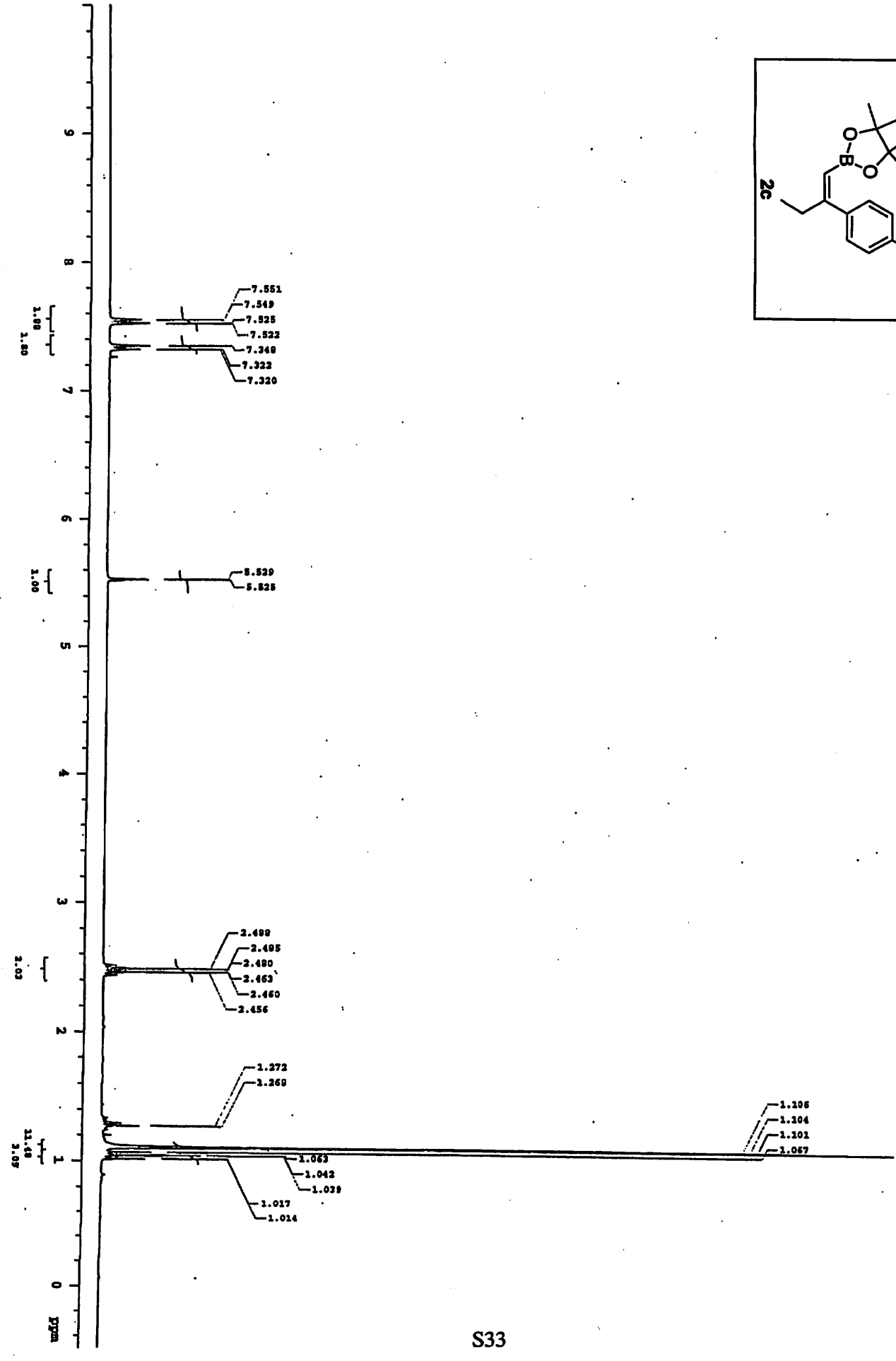
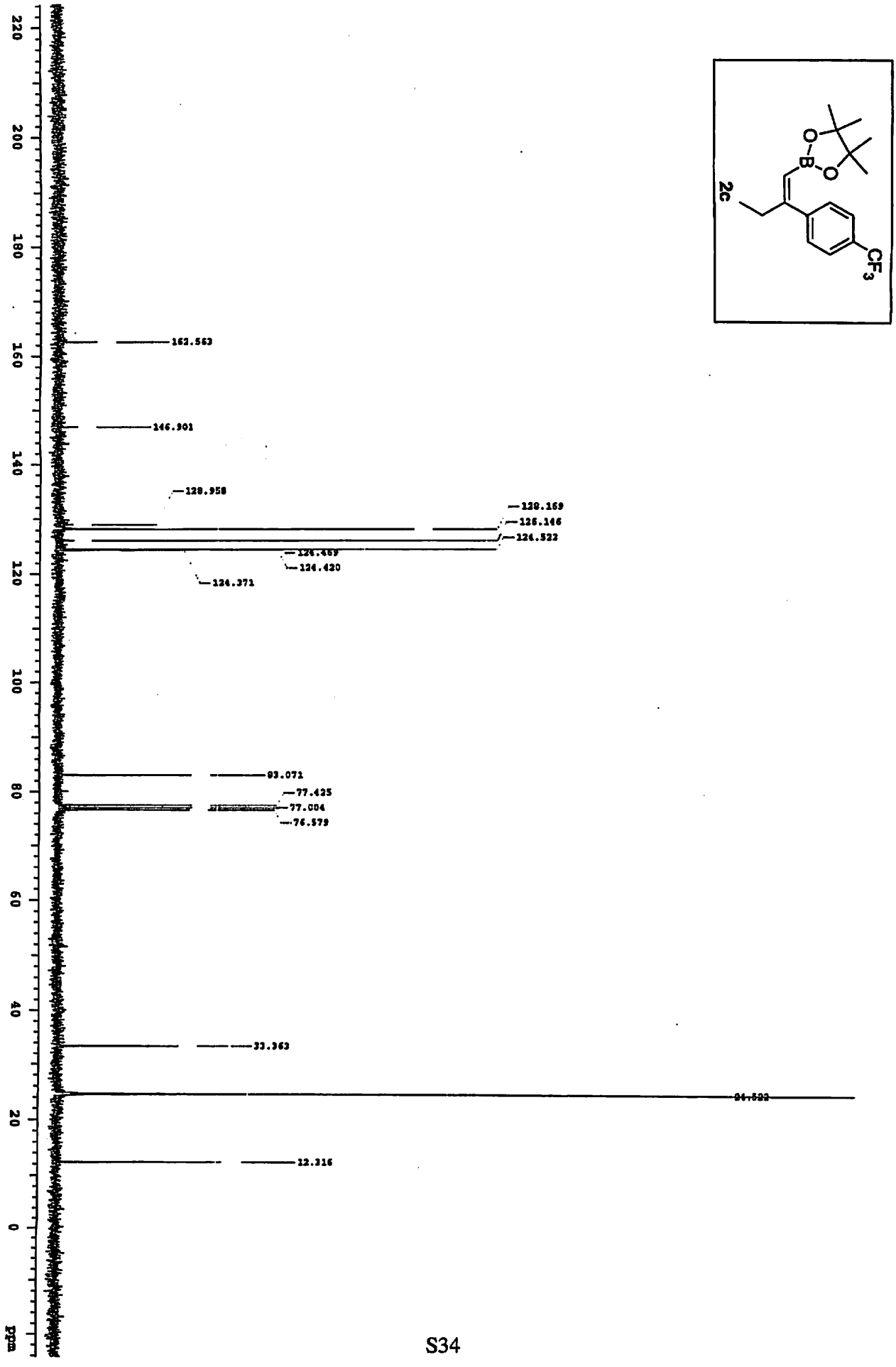
ppm

2a

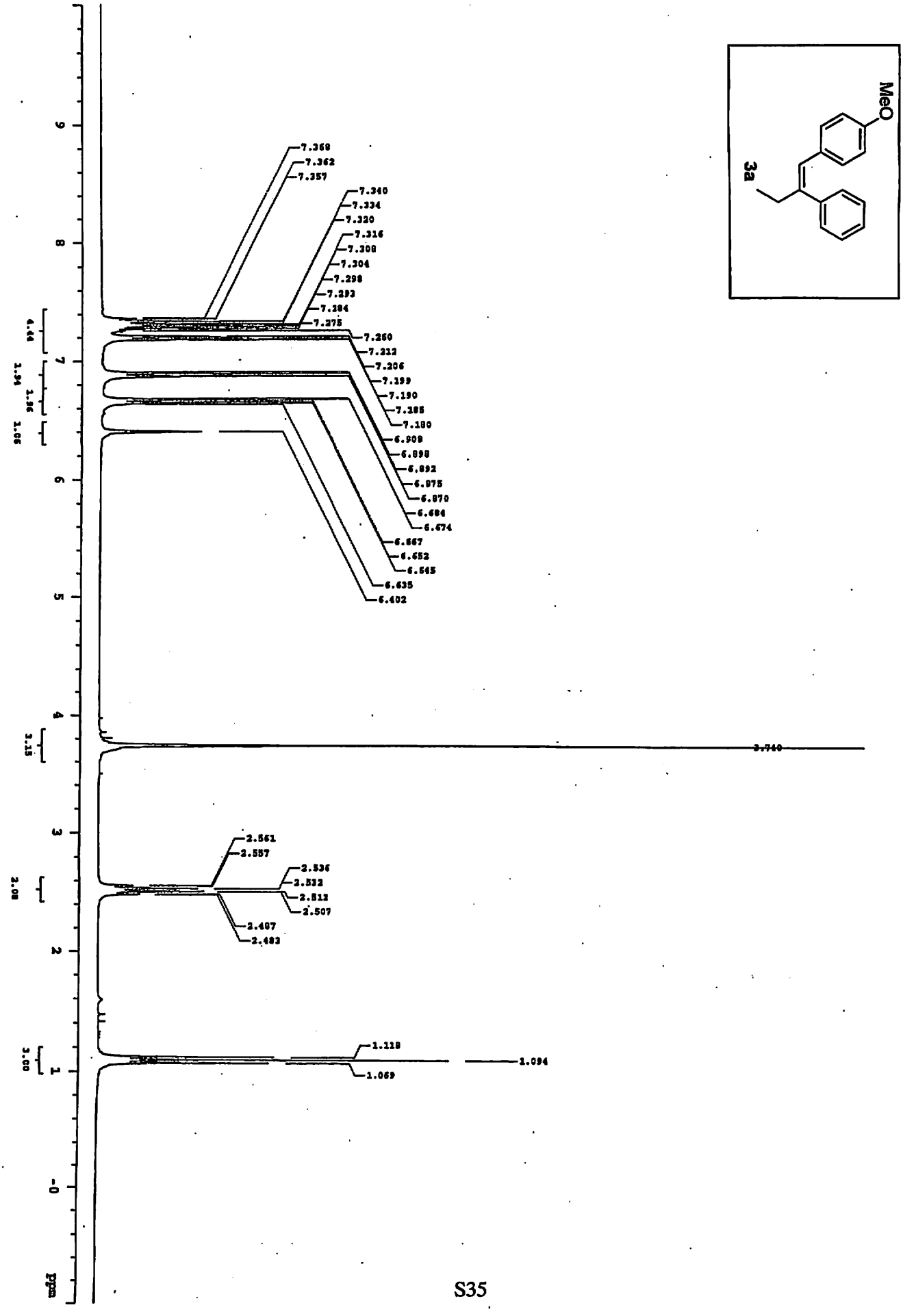

2b
OMe
7.259
7.227
7.218
7.211
7.195
7.188
7.179
6.841
6.831
6.824
6.809
6.802
6.792
5.387
5.383
5.379
3.812
2.505
2.500
2.480
2.475
2.456
2.451
2.431
2.427
1.300
1.190
1.150
1.130
1.050
1.026
1.001
1.89
2.00
0.95
3.13
2.35
12.49
3.20
ppm

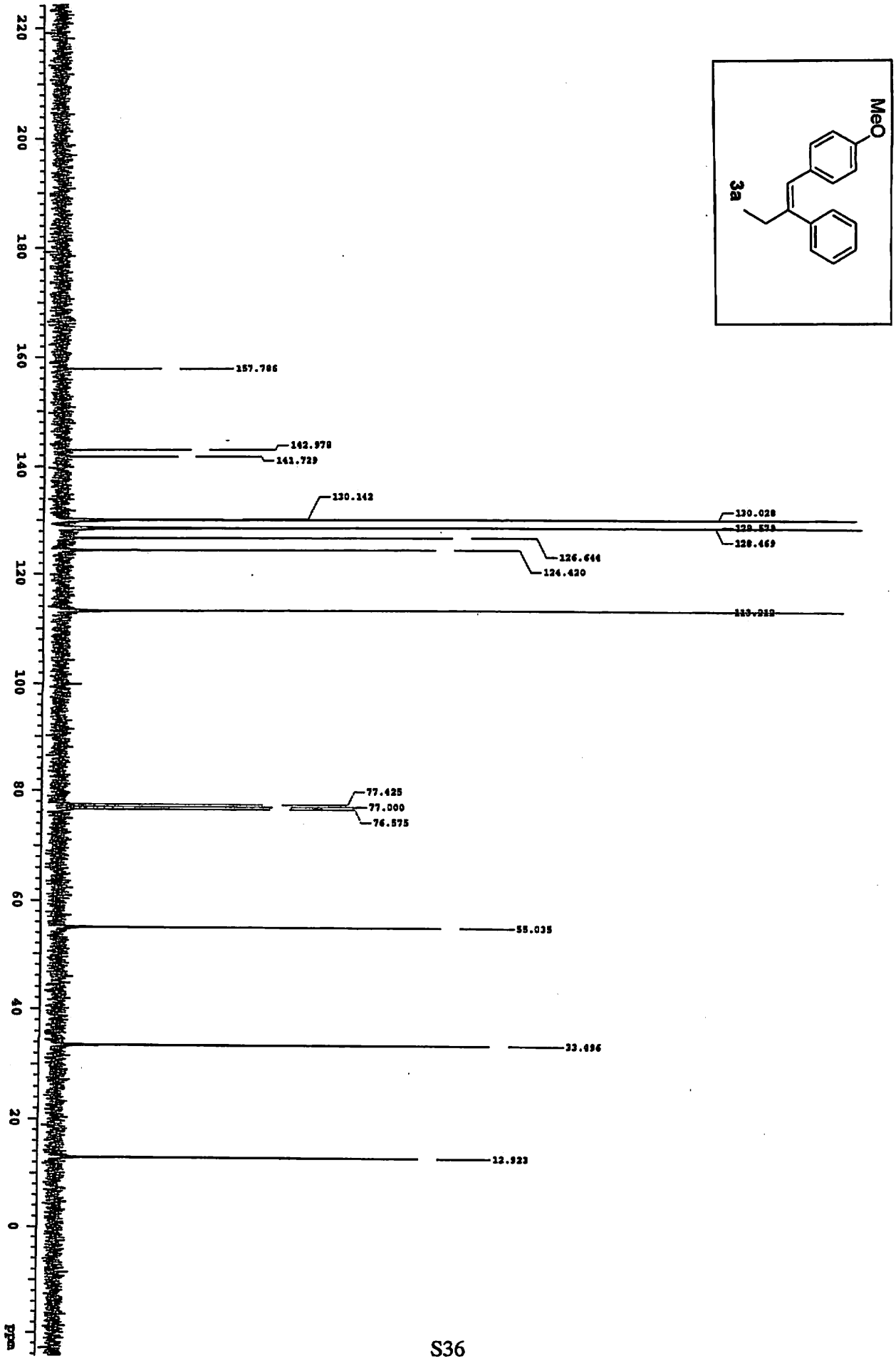

2b
OMe
163.174
158.970
135.423
129.026
112.871
82.873
77.421
77.000
76.575
55.210
33.272
24.784
24.602
12.658
ppm


2c
CF3
7.551
7.549
7.525
7.522
7.348
7.322
7.320
5.529
5.525
2.499
2.495
2.490
2.483
2.460
2.456
1.272
1.269
1.106
1.104
1.101
1.067
1.063
1.042
1.039
1.017
1.014
1.89
1.89
1.00
2.03
11.48
3.07
ppm


162.563
146.901
129.958
129.169
126.146
126.522
126.469
126.420
124.371
93.071
77.425
77.004
76.579
33.363
24.522
12.316
ppm

2c
O
B
O
CF3


MeO
3a
7.368
7.362
7.357
7.340
7.334
7.320
7.316
7.308
7.304
7.298
7.293
7.284
7.275
7.260
7.212
7.206
7.199
7.190
7.185
7.180
6.909
6.898
6.892
6.875
6.870
6.684
6.674
6.667
6.652
6.645
6.635
6.402
3.740
2.561
2.557
2.536
2.532
2.512
2.507
2.487
2.483
1.118
1.094
1.069
4.44
1.94
1.95
1.05
3.15
2.08
3.00
ppm


MeO
3a
157.786
142.978
141.729
130.142
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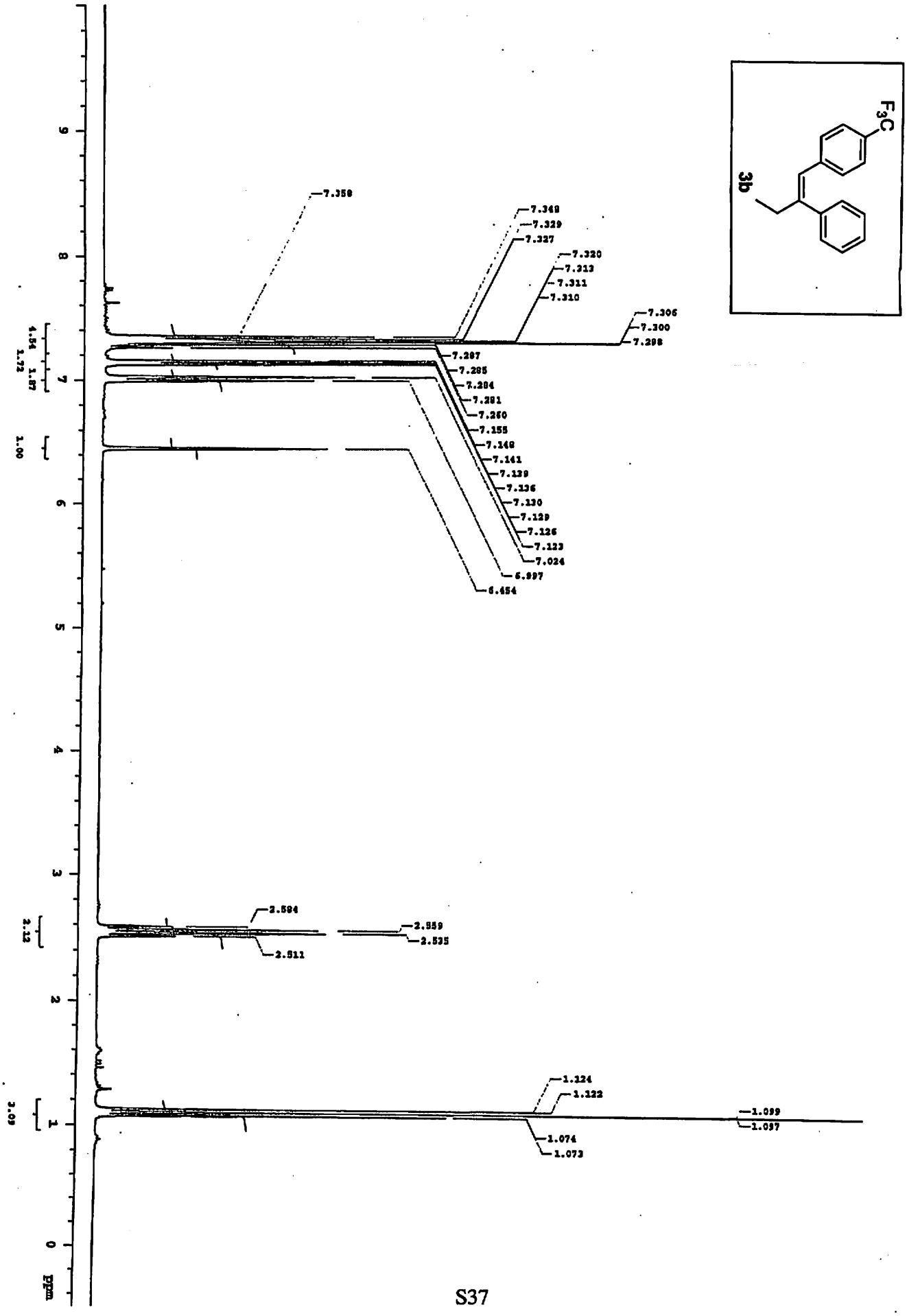
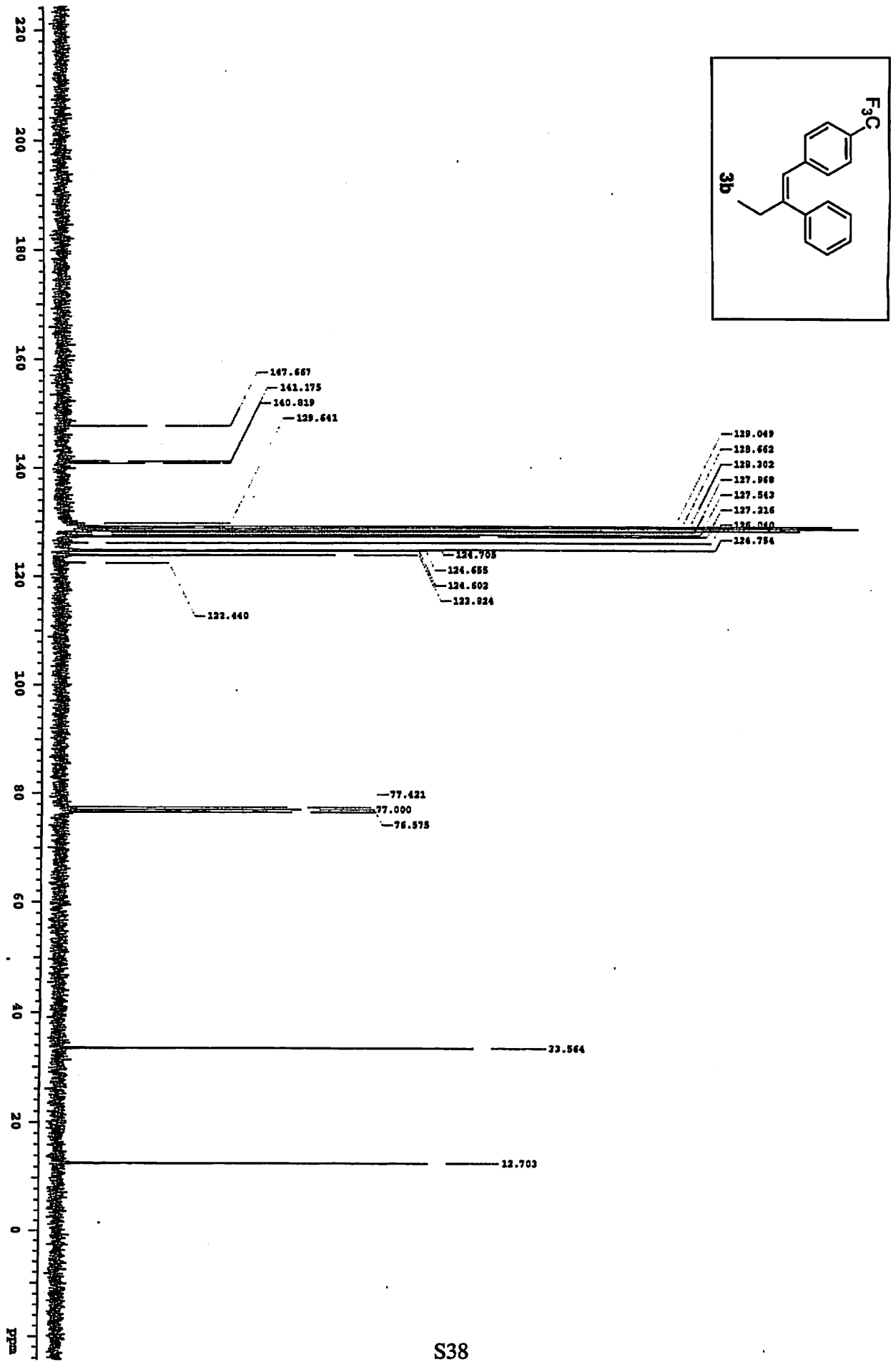
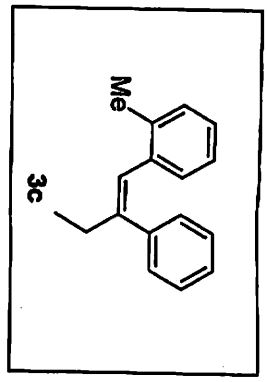
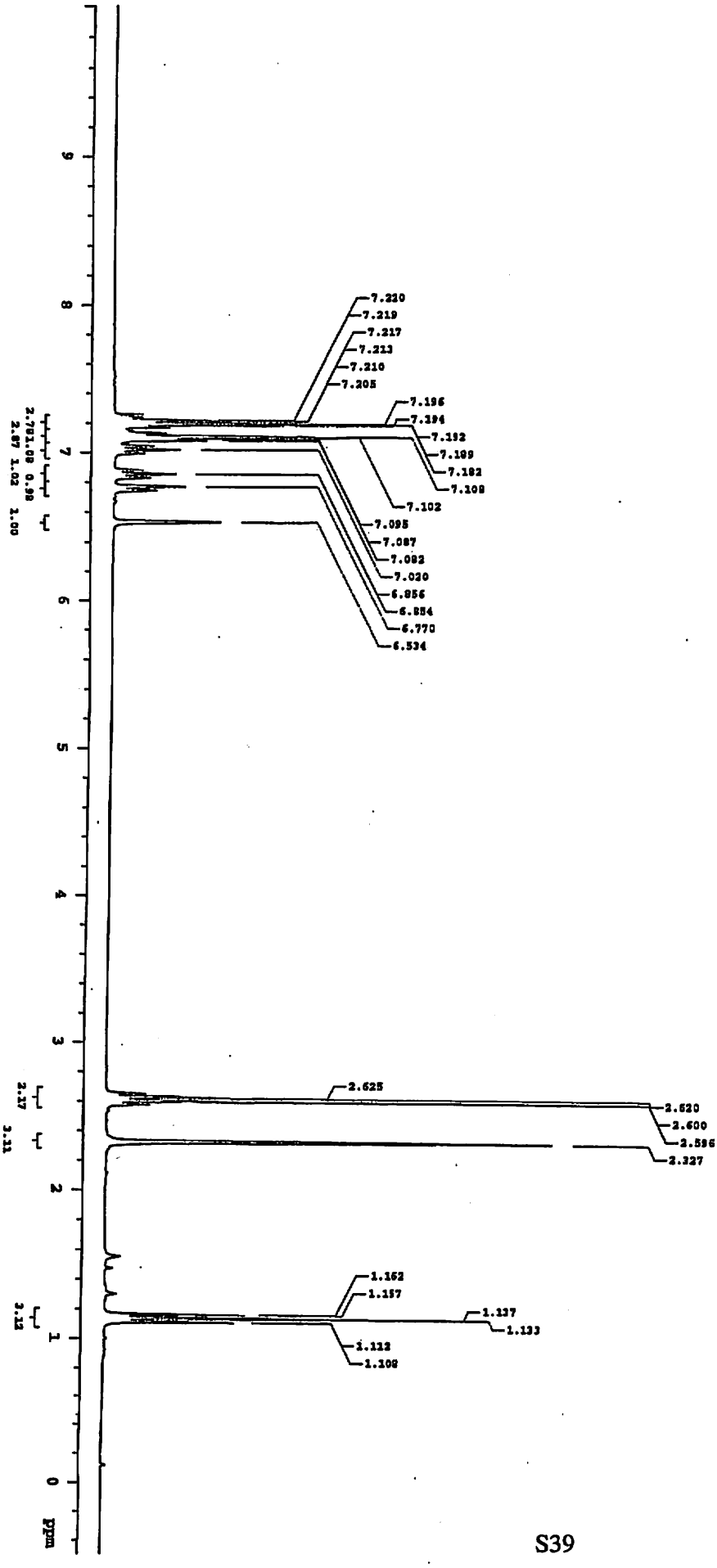
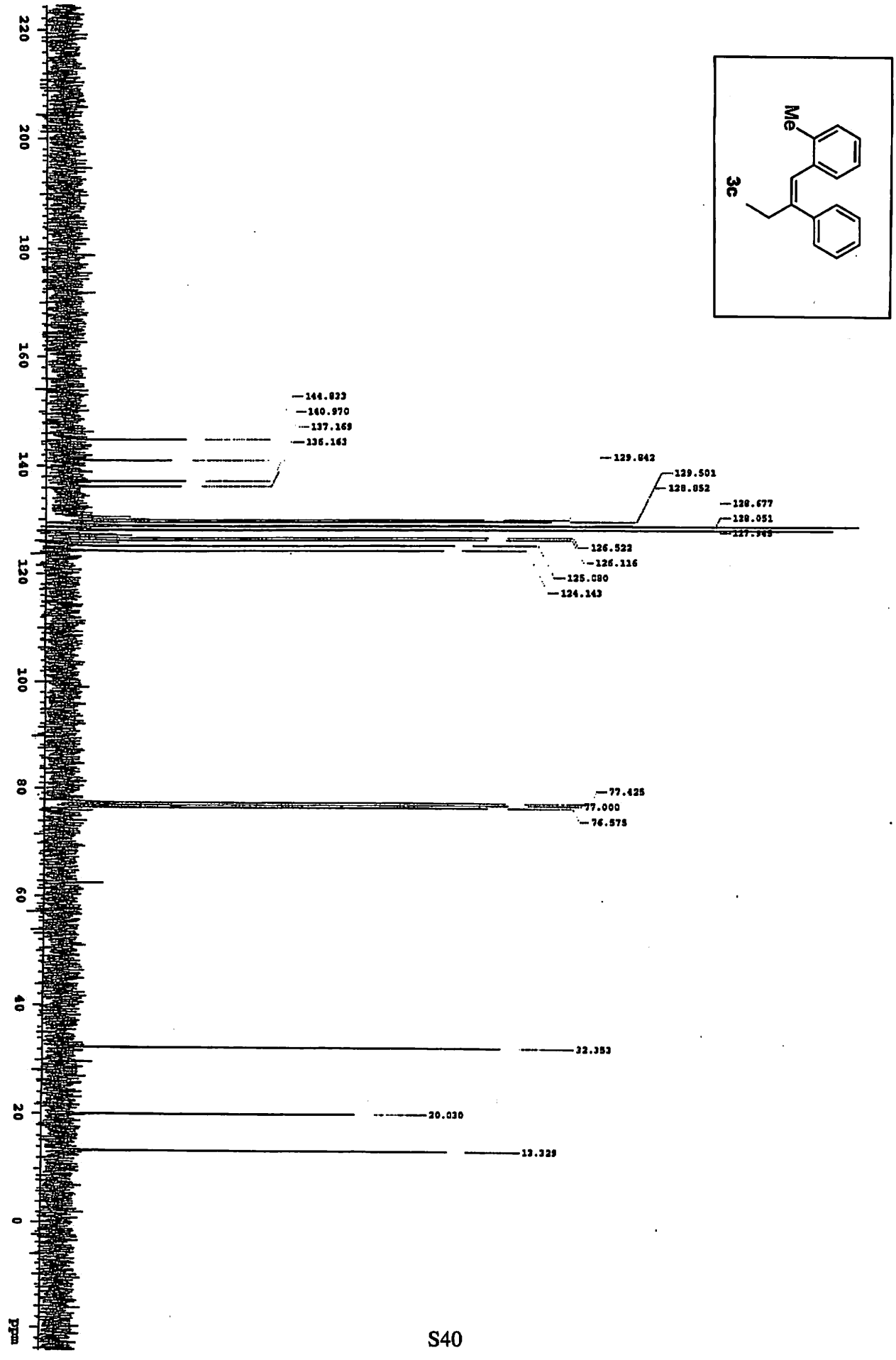
128.469
126.644
124.420
77.425
77.000
76.575
55.035
33.496
12.923
ppm

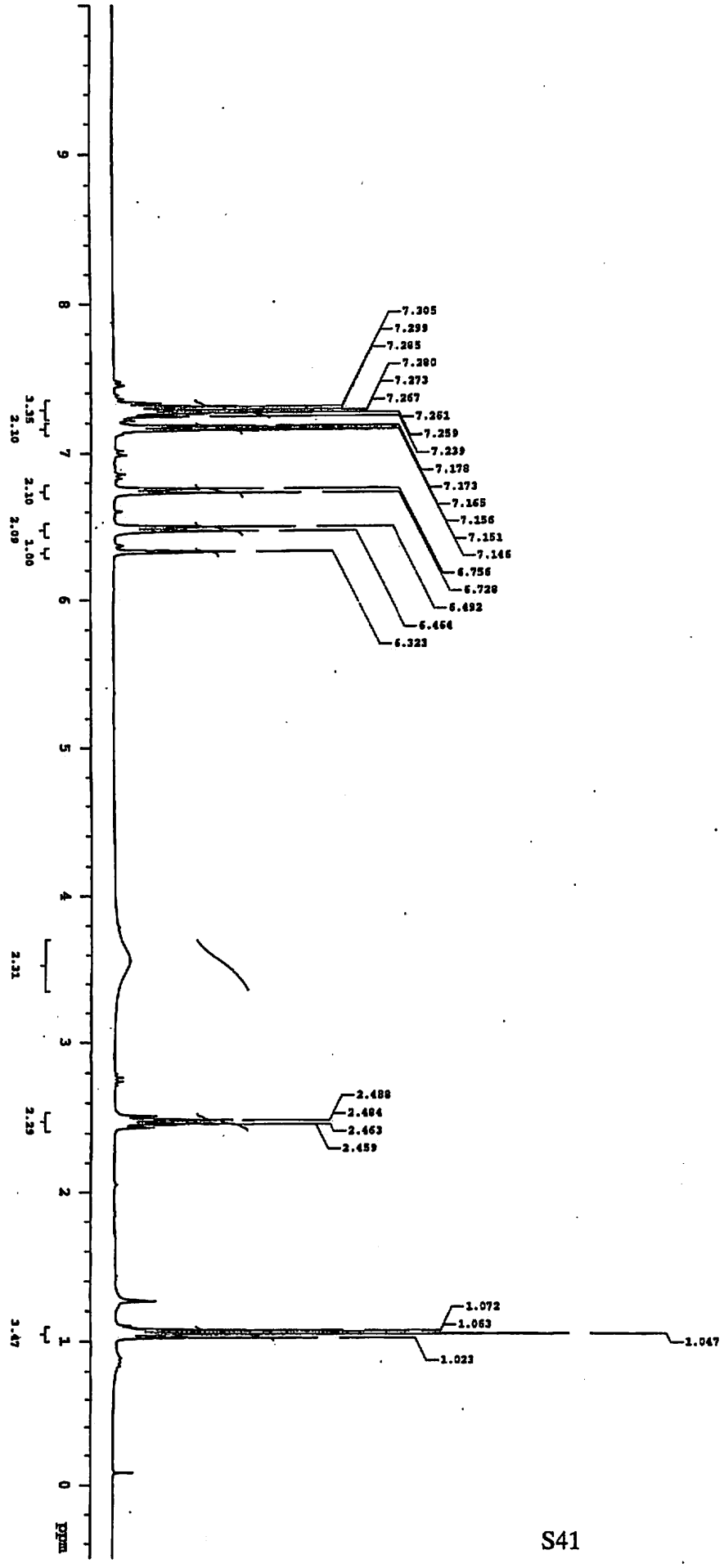

3b
F3C
7.359
7.349
7.329
7.327
7.320
7.313
7.311
7.310
7.306
7.300
7.298
7.287
7.285
7.284
7.281
7.260
7.155
7.148
7.141
7.139
7.136
7.130
7.129
7.126
7.123
7.024
6.997
6.454
2.594
2.559
2.535
2.511
1.124
1.122
1.099
1.097
1.074
1.073
4.54
1.87
1.72
1.00
2.13
3.09
ppm

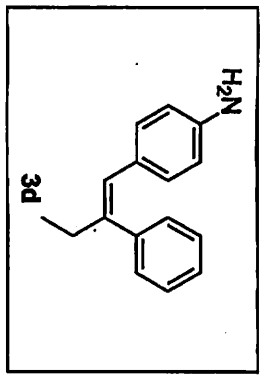

3b
F3C
147.667
141.175
140.819
129.641
129.049
128.662
128.302
127.968
127.563
127.216
126.040
124.754
124.705
124.655
124.602
123.924
122.440
77.421
77.000
76.575
33.564
12.703
ppm

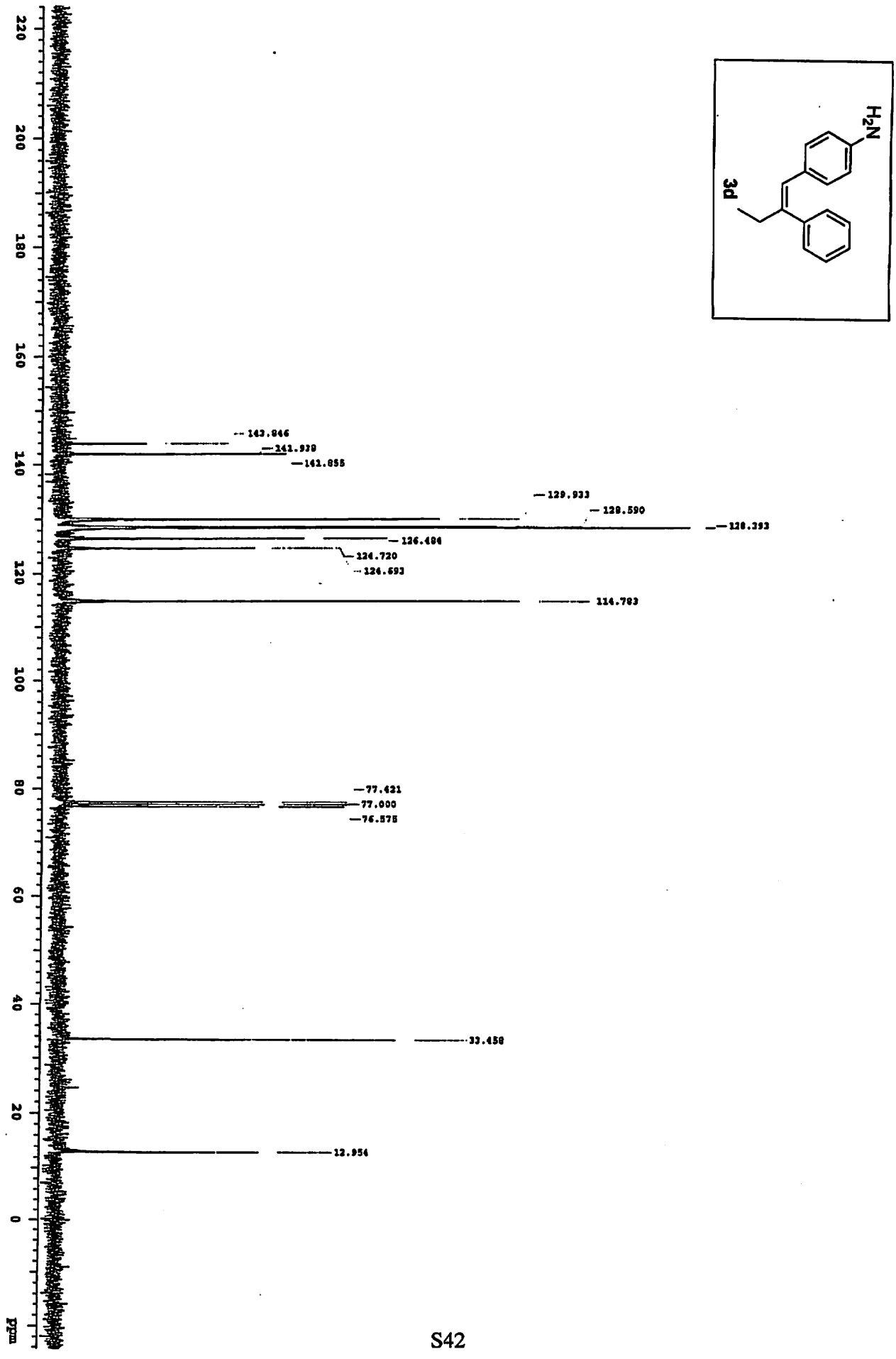

Me
3c

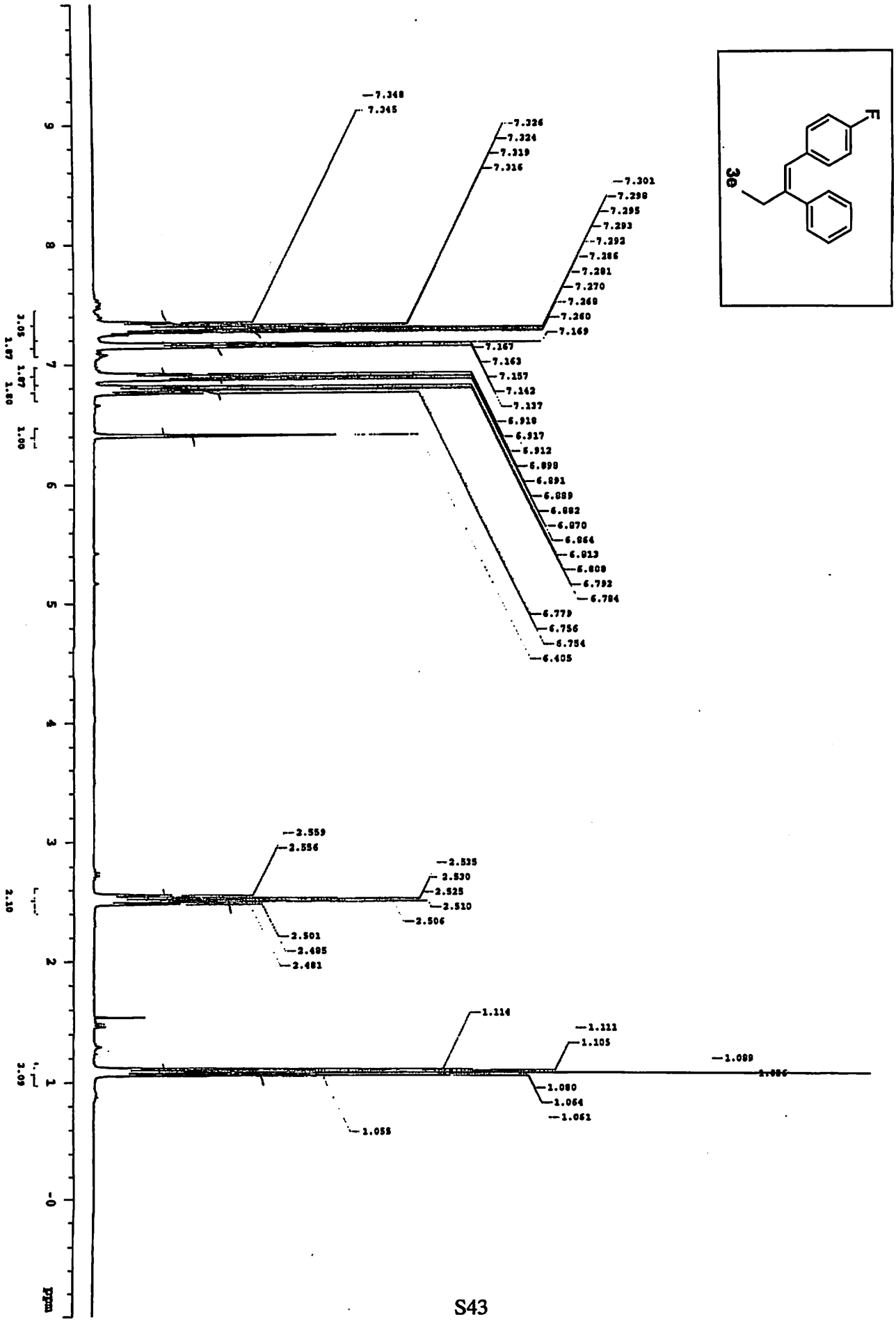

7.220
7.219
7.217
7.213
7.210
7.205
7.196
7.194
7.192
7.189
7.182
7.108
7.102
7.095
7.087
7.082
7.020
6.856
6.854
6.770
6.534
2.625
2.620
2.600
2.596
2.327
1.162
1.157
1.137
1.133
1.112
1.108
2.781.08 0.98
2.67 1.02 1.00
2.17
3.31
3.12
ppm


Me
3c
144.833
140.970
137.169
136.163
129.842
129.501
128.852
128.677
128.051
126.522
126.116
125.080
124.143
77.425
77.000
76.575
32.353
20.030
13.329
220
200
180
160
140
120
100
80
60
40
20
0
ppm


7.305
7.299
7.285
7.280
7.273
7.267
7.261
7.259
7.239
7.178
7.173
7.165
7.156
7.151
7.146
6.756
6.728
6.492
6.464
6.323
2.488
2.484
2.463
2.459
1.072
1.063
1.047
1.023
3.35
2.10
2.10
2.09
1.00
2.31
2.29
3.47
ppm


H2N
3d


143.946
141.939
141.855
129.933
129.590
128.393
126.484
124.720
124.693
114.783
77.421
77.000
76.575
33.458
12.956
ppm
3d
H2N


7.348
7.345
7.326
7.324
7.319
7.316
7.301
7.298
7.295
7.293
7.292
7.286
7.281
7.270
7.269
7.260
7.169
7.167
7.163
7.157
7.142
7.137
6.918
6.917
6.912
6.898
6.891
6.889
6.882
6.870
6.864
6.813
6.808
6.792
6.784
6.779
6.756
6.754
6.405
2.559
2.556
2.535
2.530
2.525
2.510
2.506
2.501
2.495
2.481
1.114
1.111
1.105
1.089
1.080
1.064
1.061
1.055
3.05
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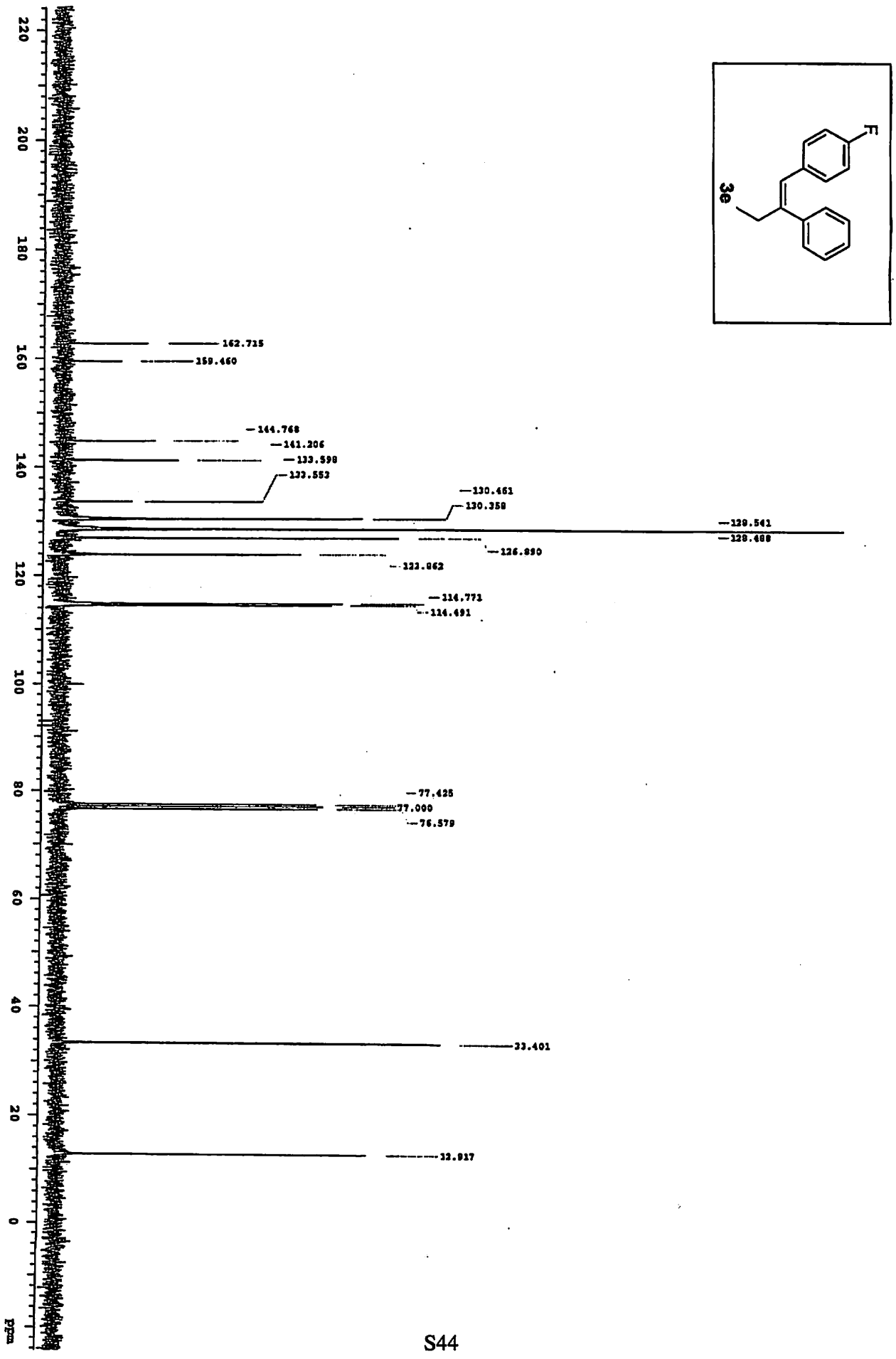
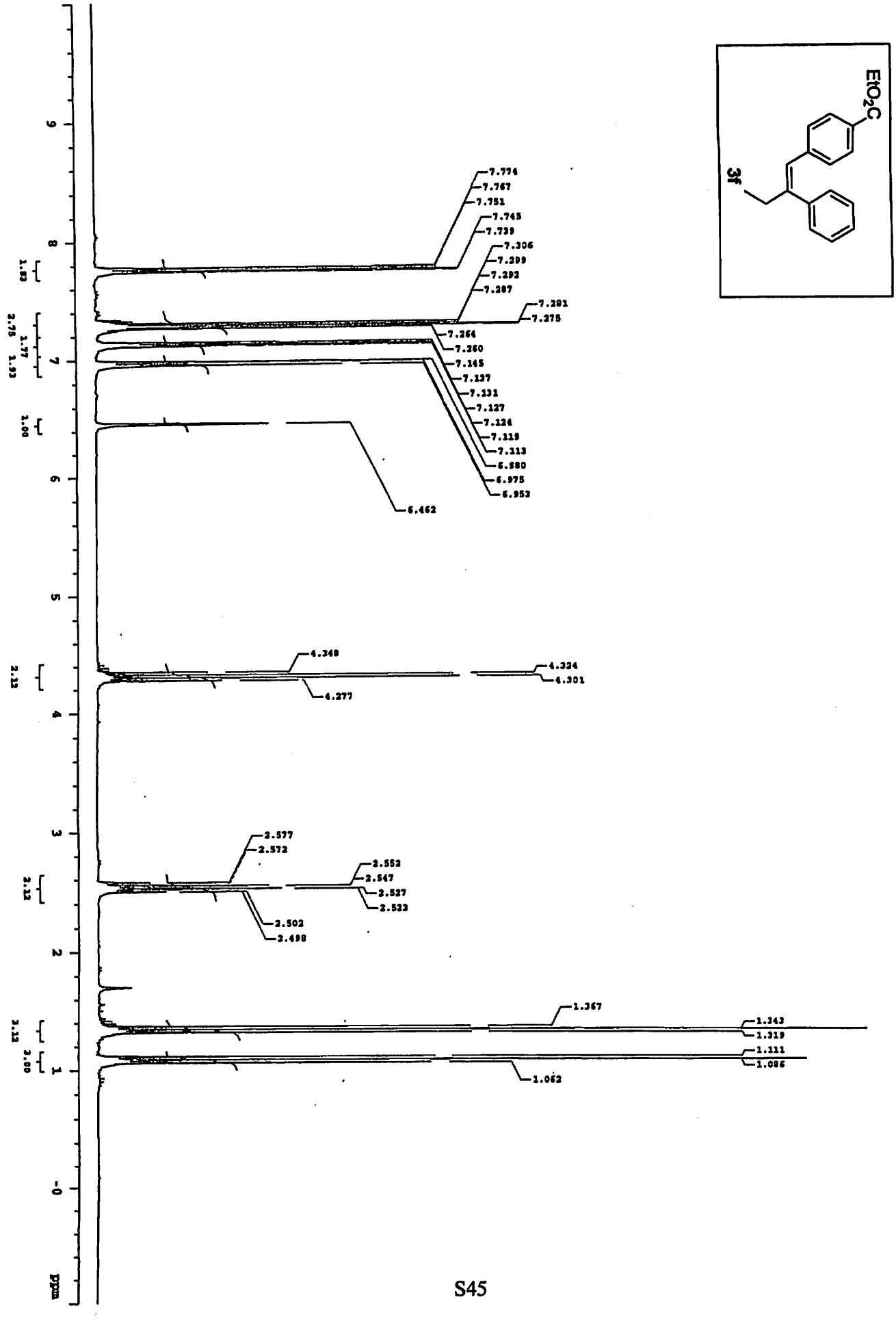
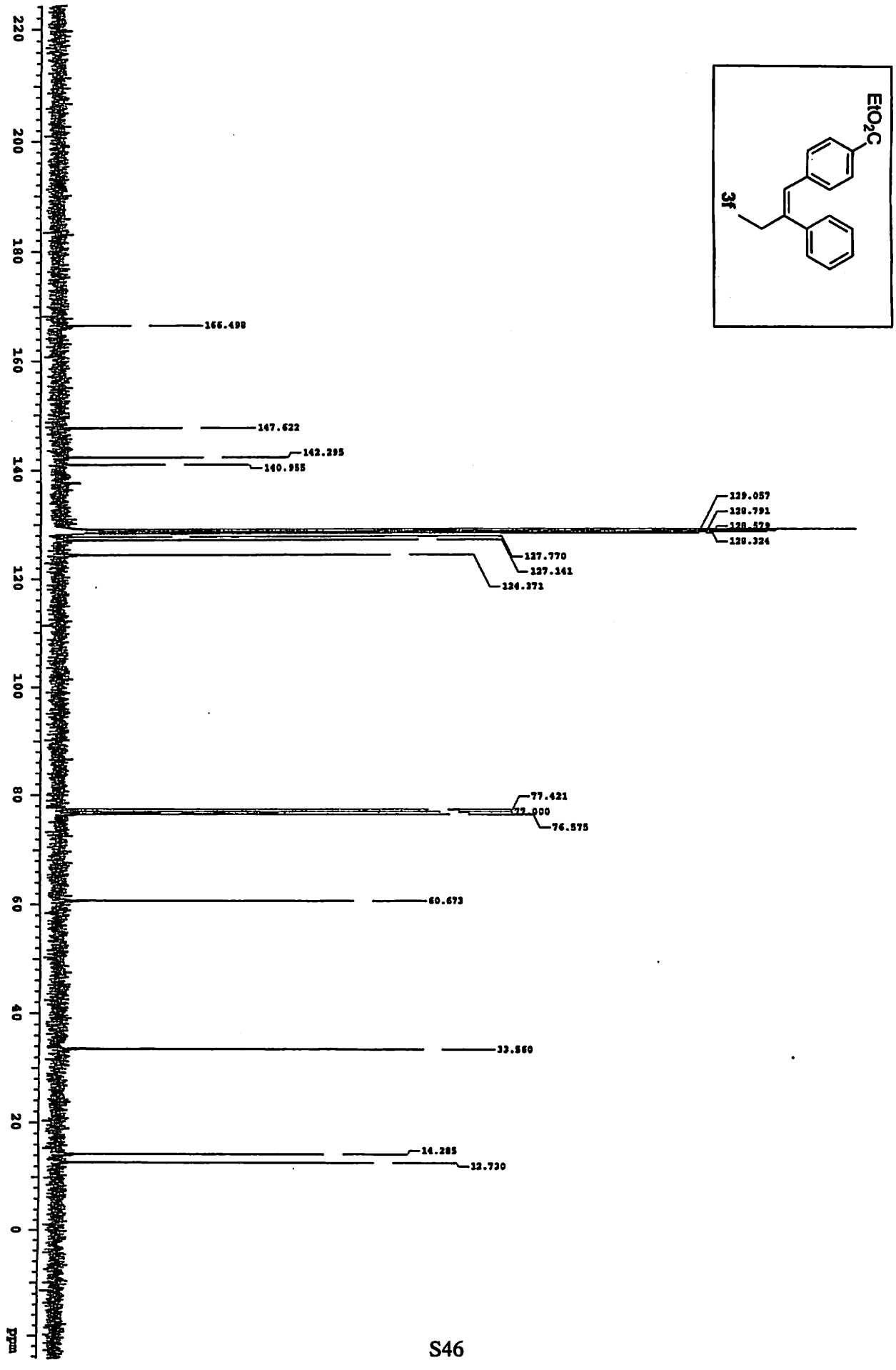
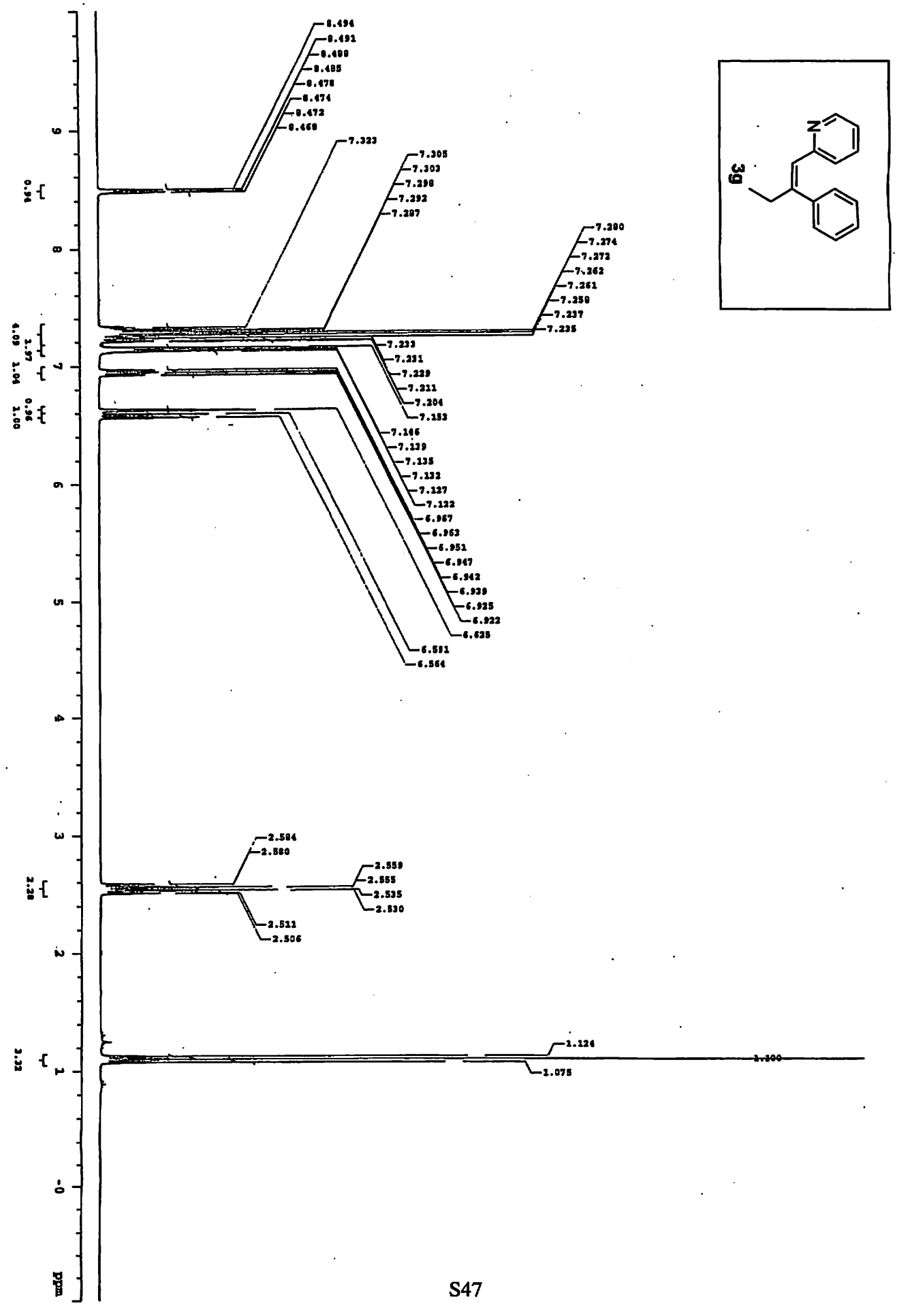
1.87
1.80
1.00
2.10
3.09
ppm
F
3e


3e
F
162.725
159.460
144.768
141.206
133.598
133.553
130.461
130.358
129.541
129.488
126.890
123.862
116.771
116.491
77.425
77.000
76.579
33.401
32.917
ppm


EtO2C
3f
7.774
7.767
7.751
7.745
7.739
7.306
7.299
7.292
7.287
7.281
7.275
7.264
7.260
7.145
7.137
7.131
7.127
7.124
7.118
7.113
6.980
6.975
6.953
6.462
4.348
4.324
4.301
4.277
2.577
2.572
2.552
2.547
2.527
2.523
2.502
2.498
1.367
1.343
1.319
1.111
1.086
1.062
ppm


EtO2C
3f
166.498
147.622
142.295
140.955
129.057
128.791
128.579
128.324
127.770
127.141
124.371
77.421
77.000
76.575
60.673
33.560
14.285
12.730
ppm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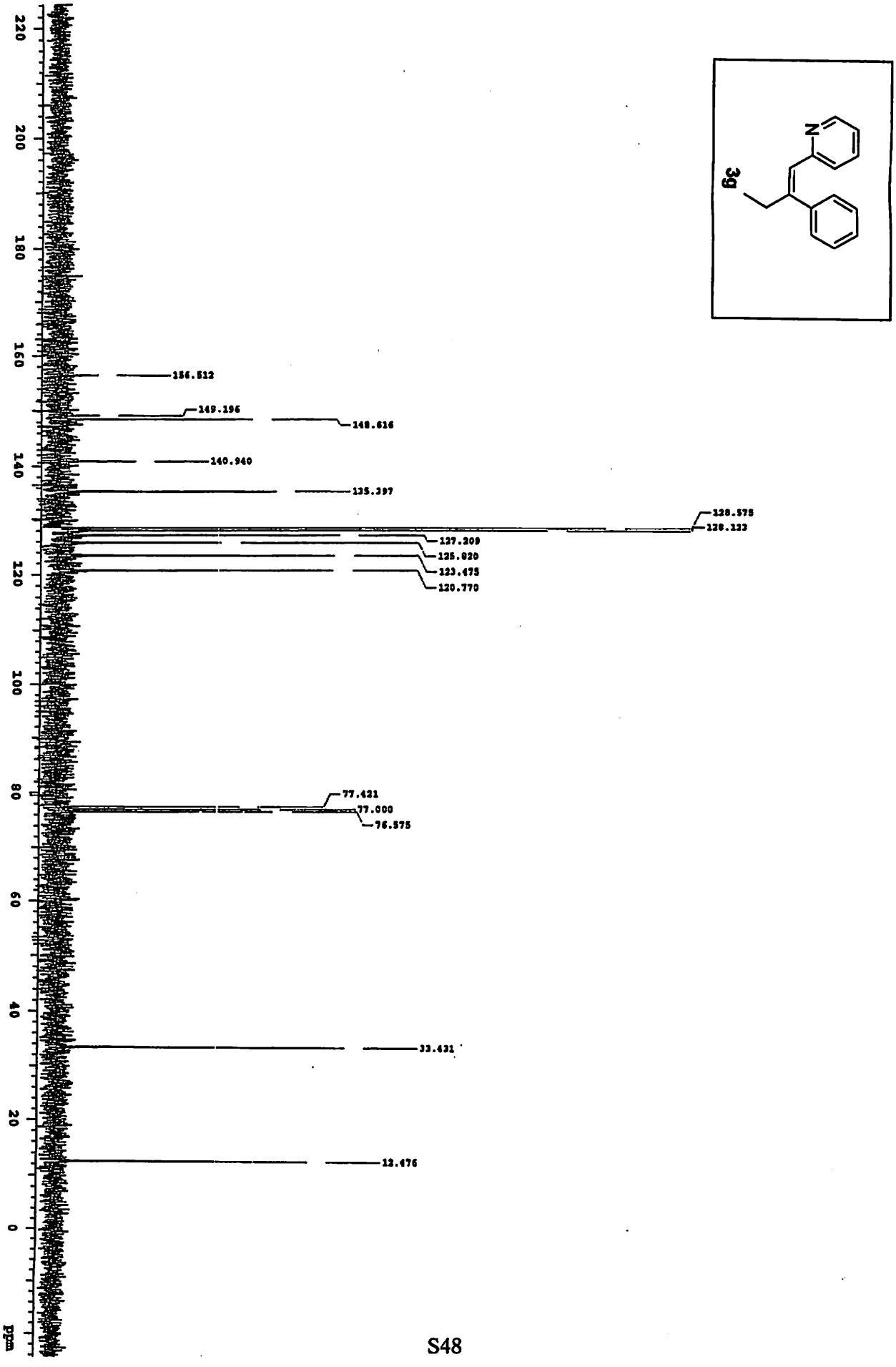
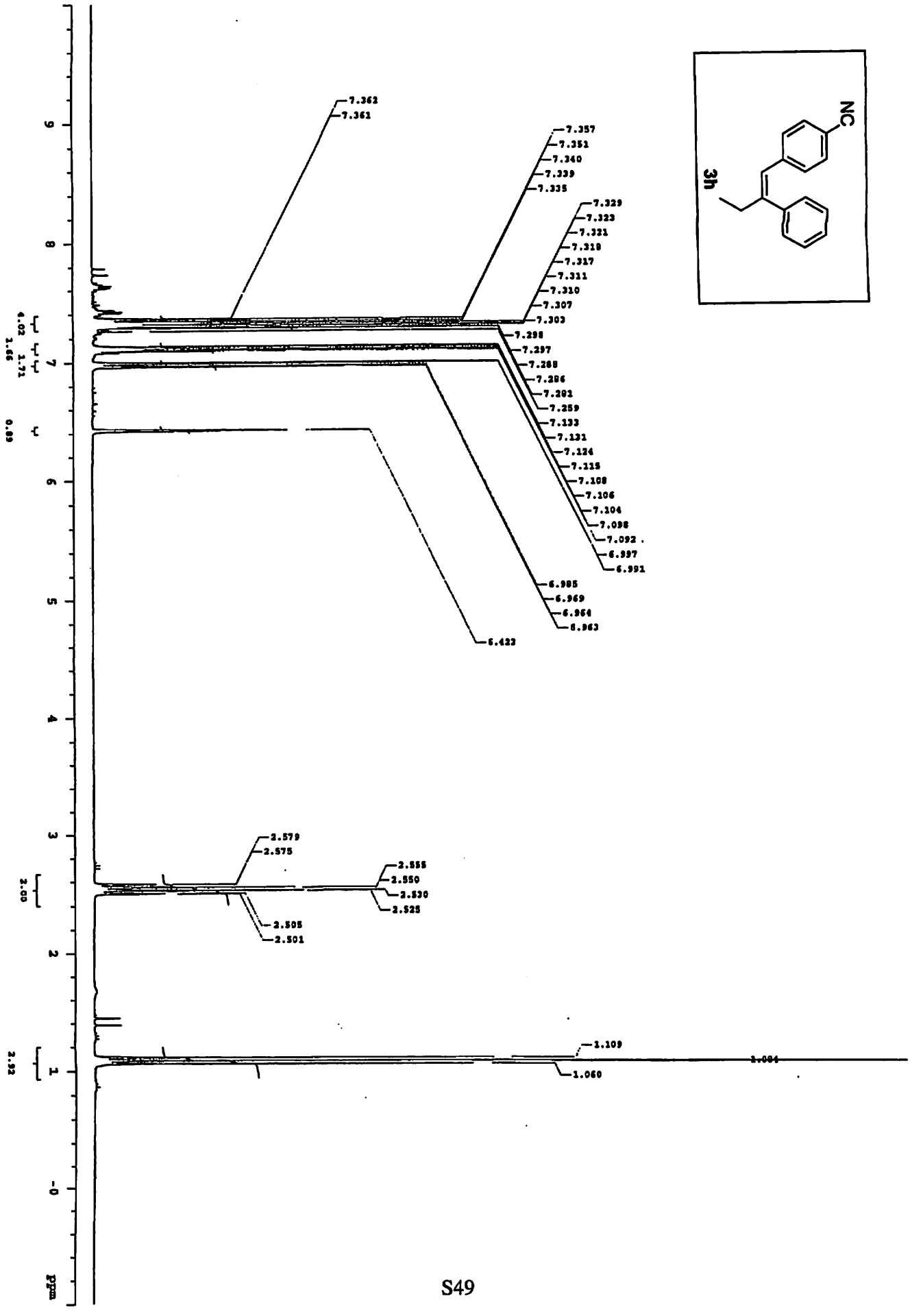
8.488
8.485
8.478
8.474
8.472
8.469
7.323
7.305
7.303
7.298
7.292
7.287
7.280
7.274
7.272
7.262
7.261
7.259
7.237
7.235
7.233
7.231
7.229
7.211
7.204
7.153
7.146
7.139
7.135
7.133
7.127
7.122
6.967
6.963
6.951
6.947
6.942
6.939
6.925
6.922
6.625
6.591
6.564
2.584
2.580
2.559
2.555
2.535
2.530
2.511
2.506
1.124
1.100
1.075
3g
N
ppm


3g
N
156.512
149.196
148.616
140.940
135.397
128.575
128.133
127.309
125.920
123.475
120.770
77.421
77.000
76.575
33.431
12.476
ppm


3h
NC
7.362
7.361
7.357
7.351
7.340
7.339
7.335
7.329
7.323
7.321
7.319
7.317
7.311
7.310
7.307
7.303
7.298
7.297
7.288
7.286
7.281
7.259
7.133
7.131
7.124
7.115
7.108
7.106
7.104
7.098
7.092
6.997
6.991
6.985
6.969
6.964
6.963
6.423
2.579
2.575
2.555
2.550
2.530
2.525
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1.109
1.084
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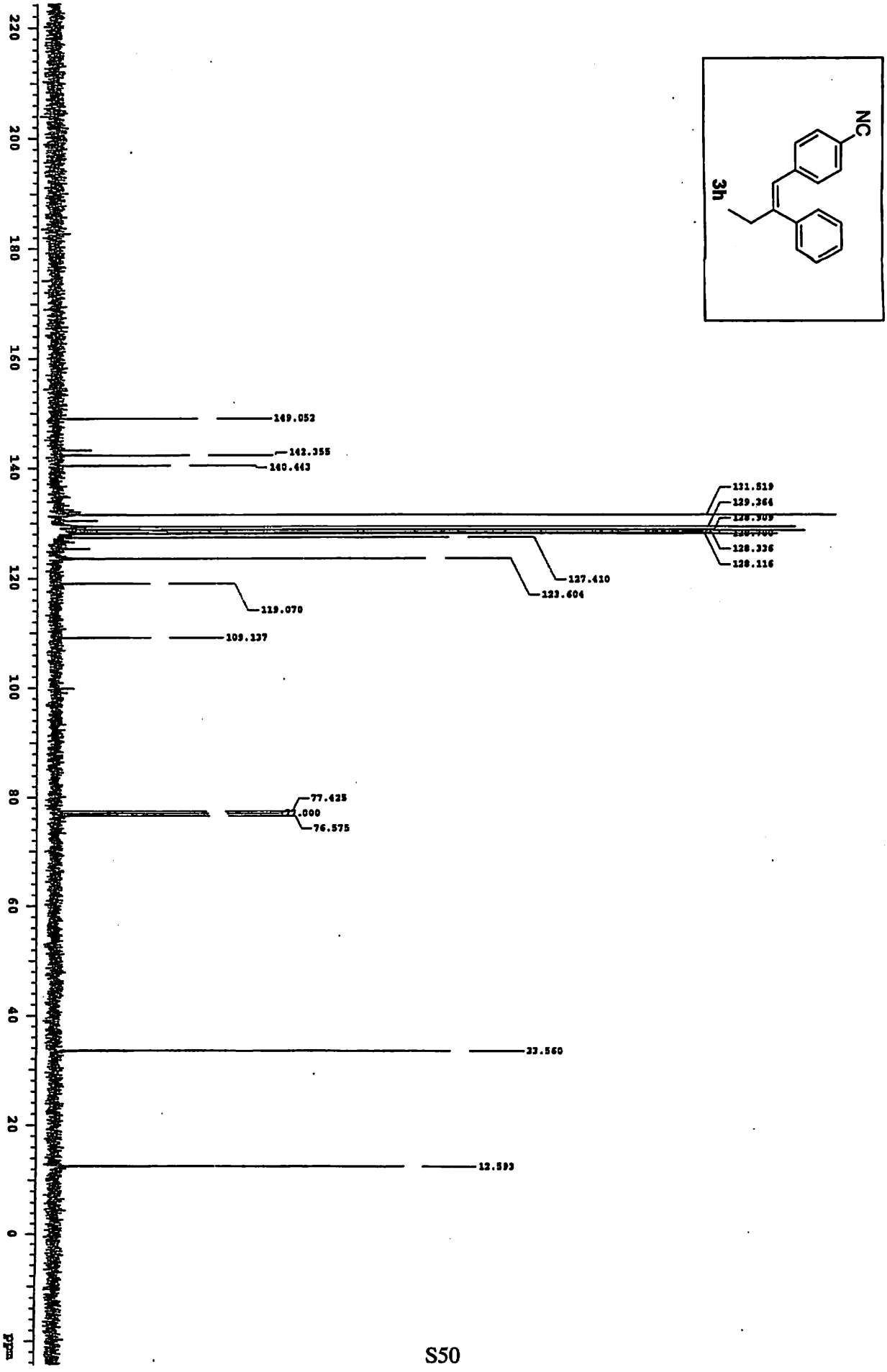
1.71
0.89
2.00
2.92
ppm


NC
3h
149.052
142.355
140.443
131.519
129.364
128.309
128.336
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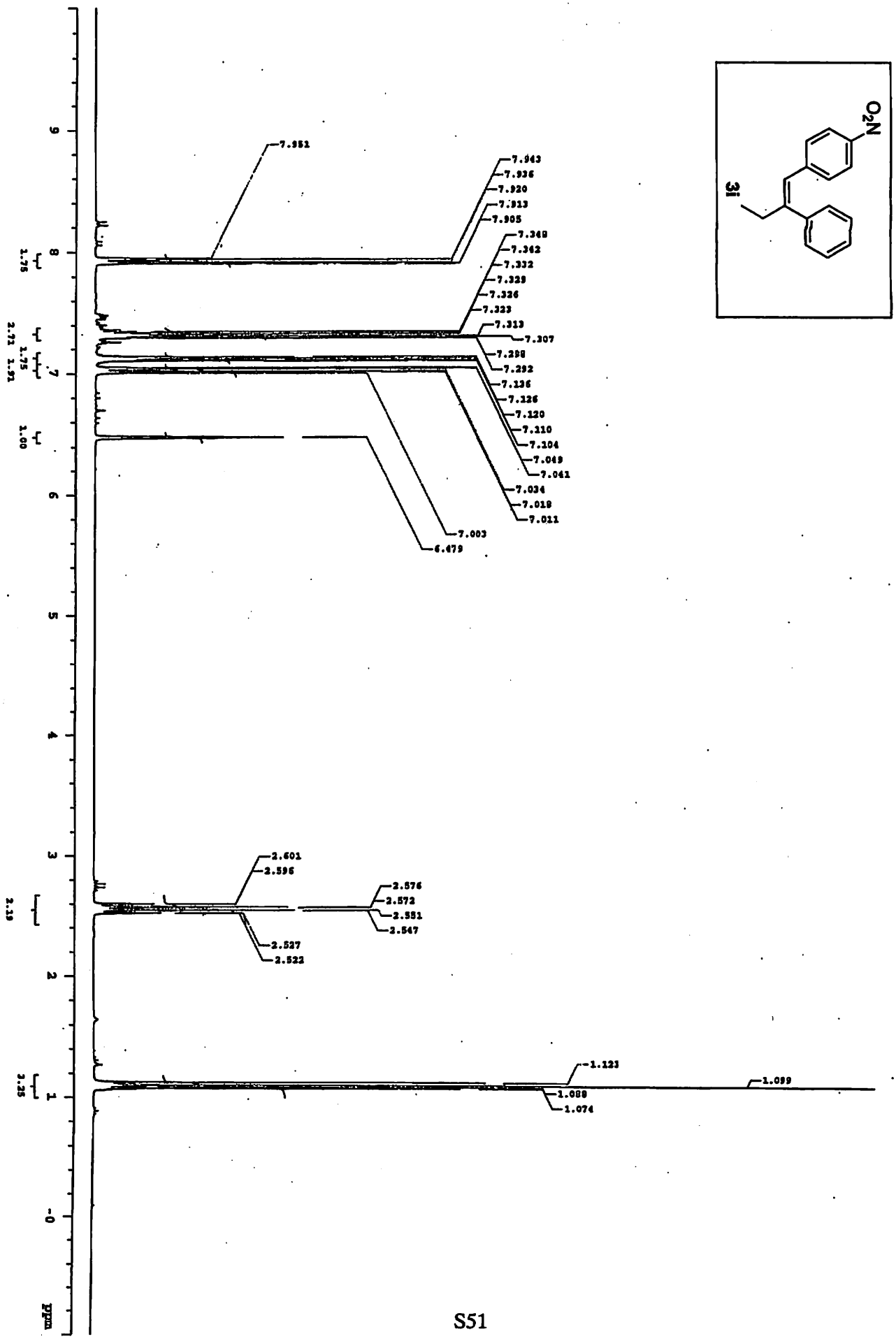
127.410
123.604
119.070
109.137
77.425
77.000
76.575
33.560
12.593
ppm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7.905
7.369
7.362
7.332
7.329
7.326
7.323
7.313
7.307
7.298
7.292
7.136
7.126
7.120
7.110
7.104
7.049
7.041
7.034
7.018
7.011
7.003
6.479
2.601
2.596
2.576
2.572
2.551
2.547
2.527
2.522
1.123
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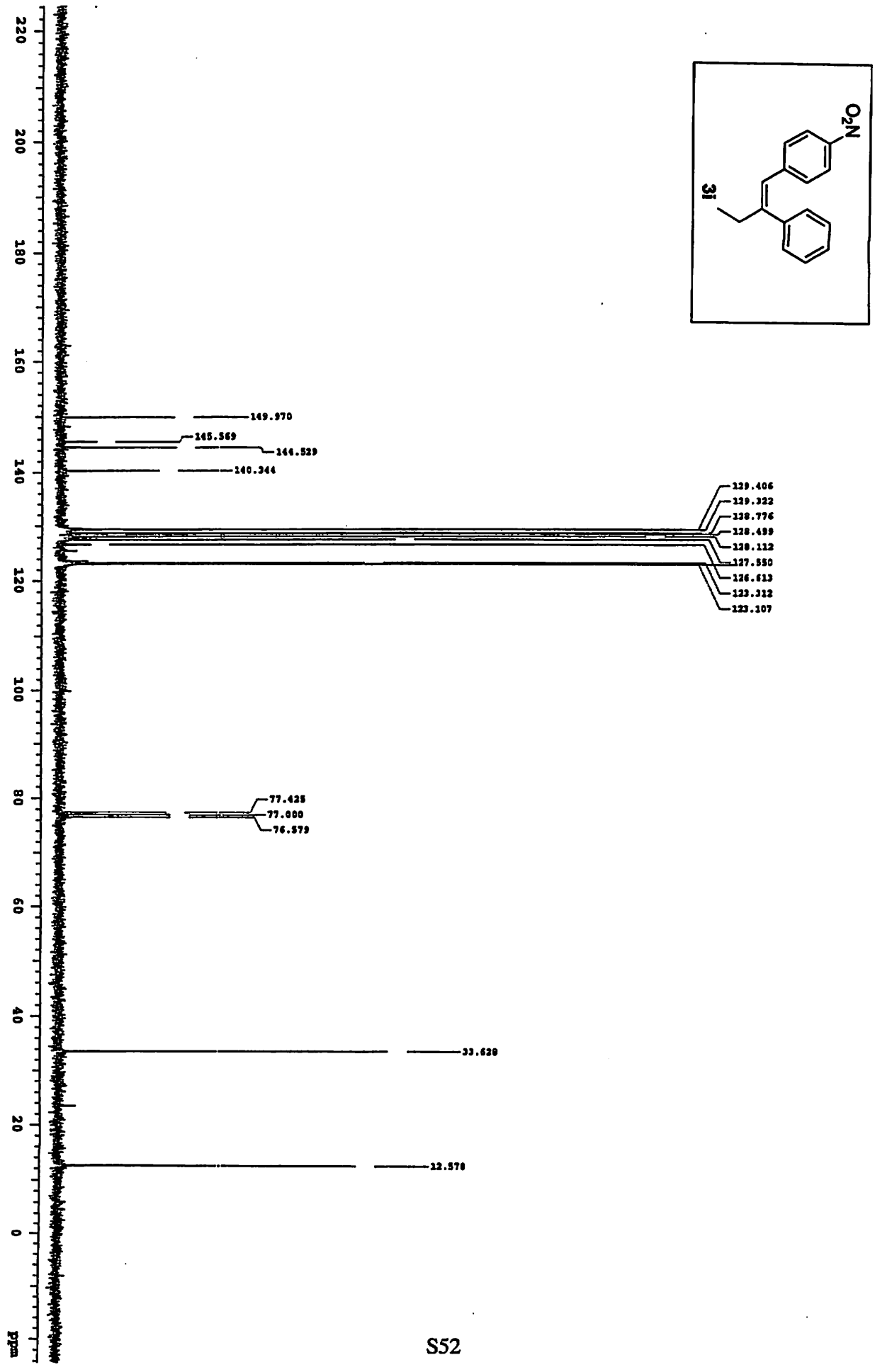
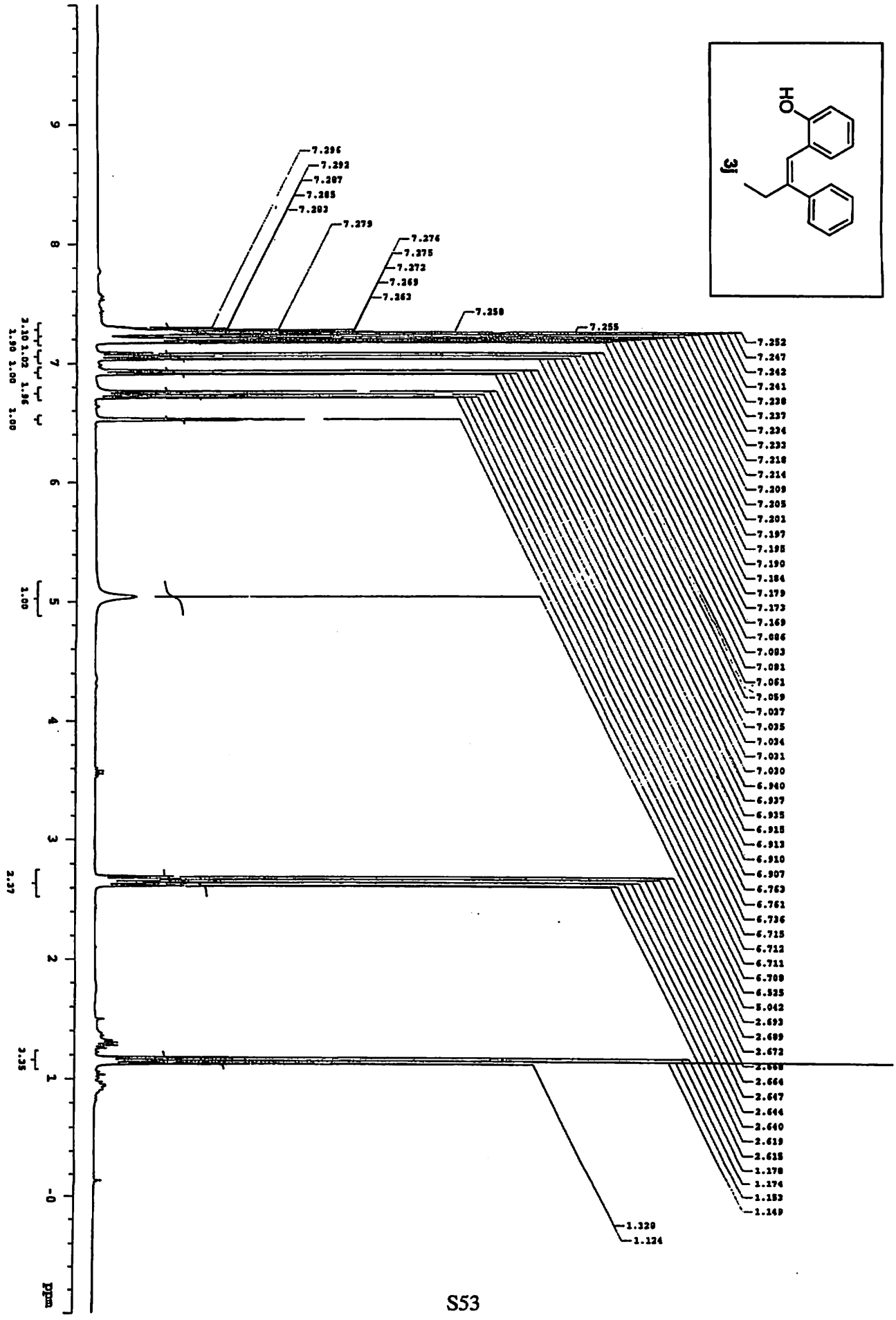
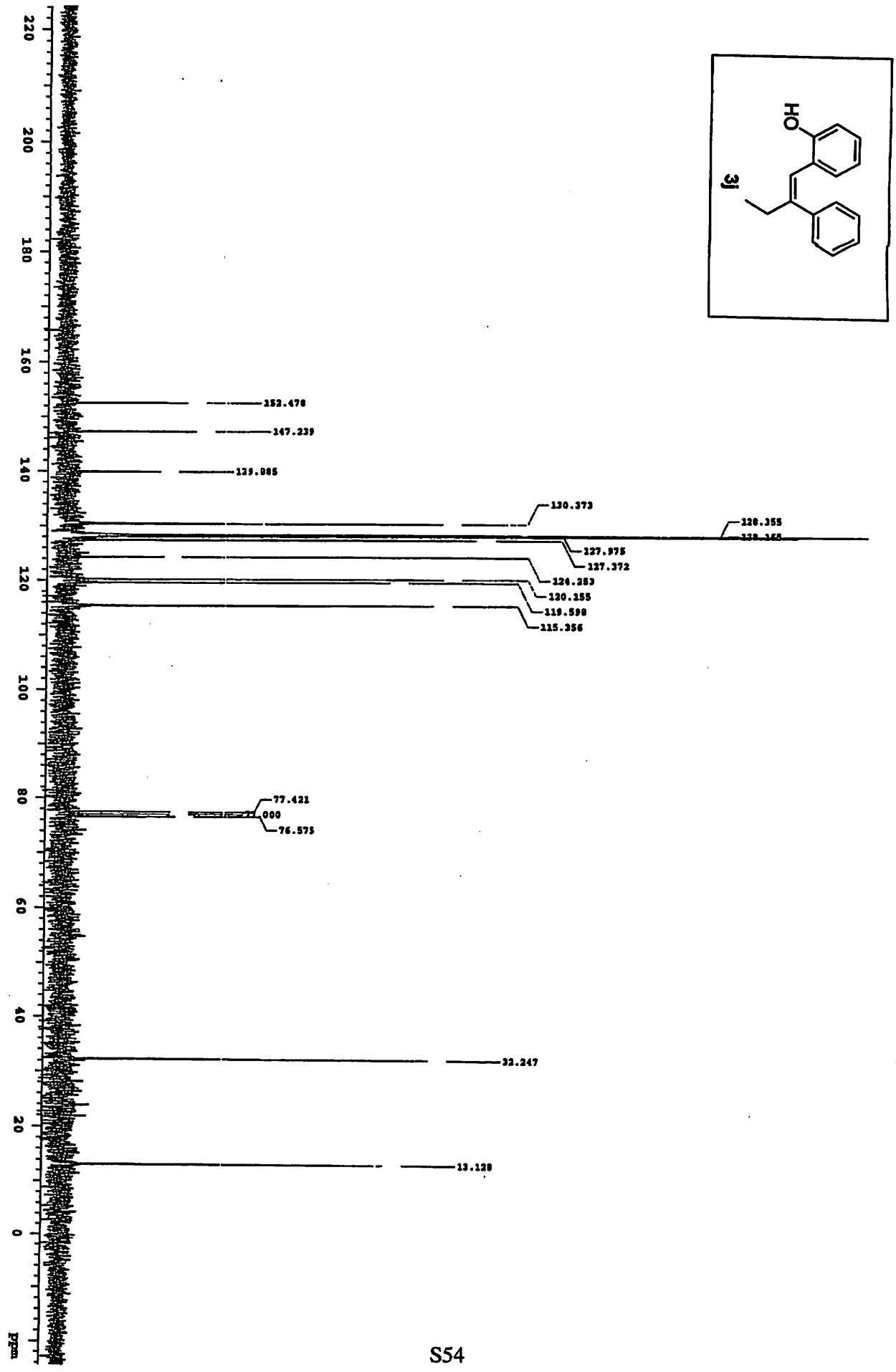
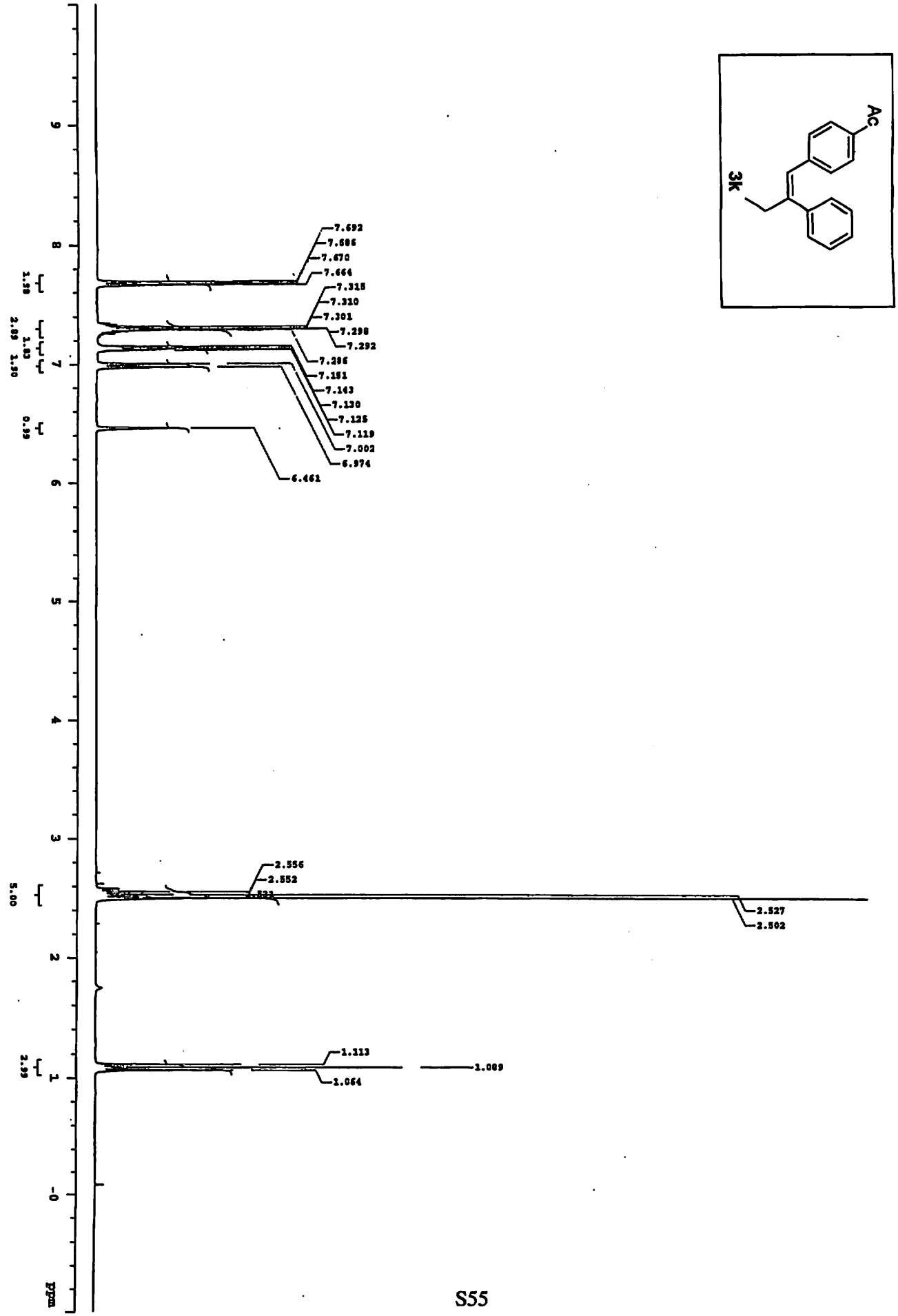
1.75
2.71
1.75
1.91
1.00
2.19
3.25
ppm
O2N
3i

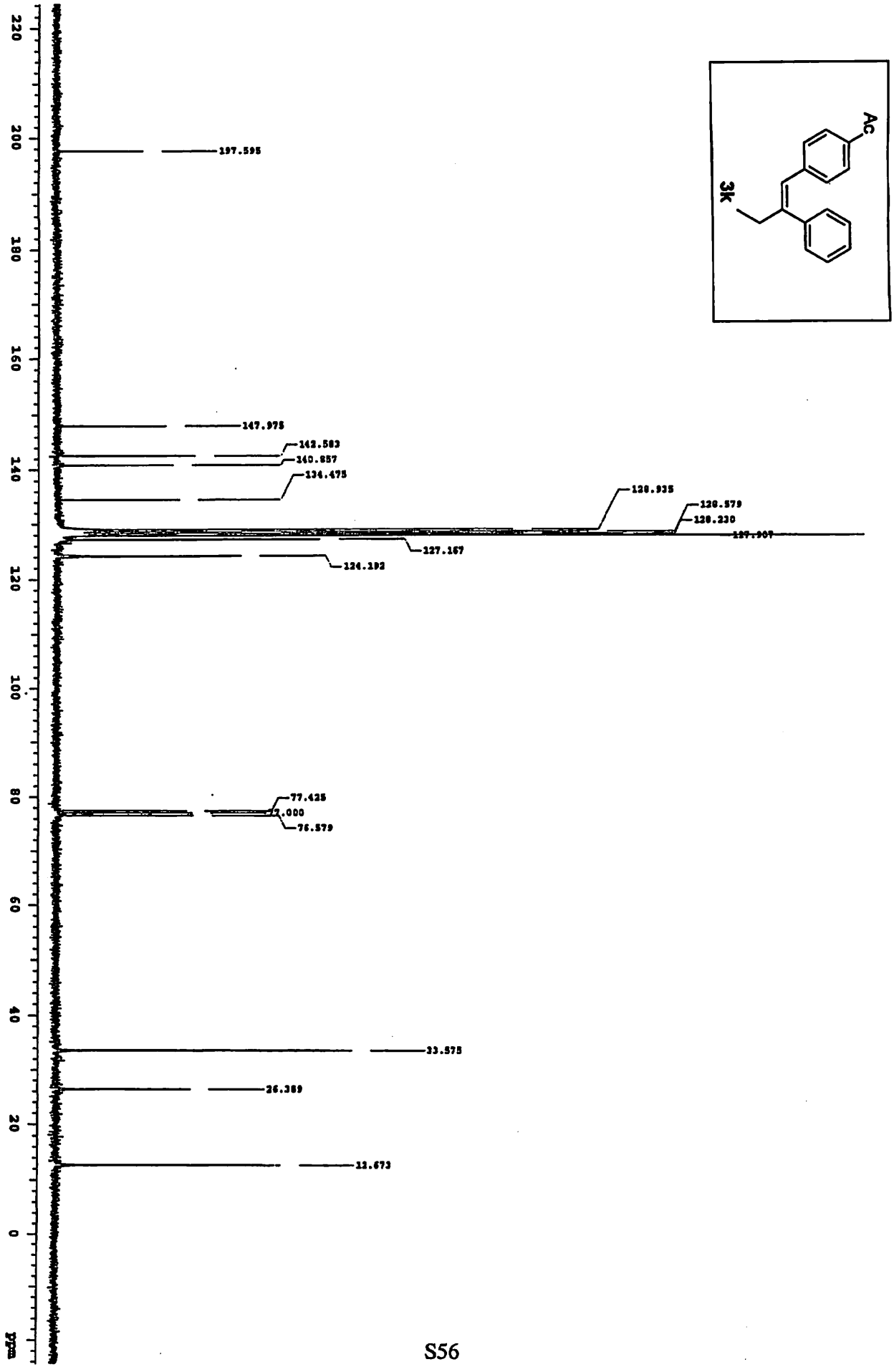

O2N
3l
149.970
145.569
144.529
140.344
129.406
129.322
128.776
128.499
128.112
127.550
126.613
123.312
123.107
77.425
77.000
76.579
33.628
12.578
ppm


3j
HO
7.296
7.292
7.287
7.285
7.283
7.279
7.276
7.275
7.272
7.269
7.263
7.250
7.255
7.252
7.247
7.242
7.241
7.238
7.237
7.234
7.233
7.218
7.214
7.209
7.205
7.201
7.197
7.195
7.190
7.184
7.179
7.173
7.169
7.086
7.083
7.081
7.061
7.059
7.037
7.035
7.034
7.031
7.030
6.940
6.937
6.935
6.918
6.913
6.910
6.907
6.763
6.761
6.736
6.715
6.712
6.711
6.709
6.525
5.042
2.693
2.689
2.672
2.666
2.647
2.644
2.640
2.619
2.615
1.178
1.174
1.153
1.149
1.329
1.124
2.10 1.02 1.96
1.99 1.00 1.00
1.00
2.37
2.35
ppm


HO
3j
152.478
147.239
139.085
130.373
128.355
128.165
127.975
127.372
126.283
120.155
119.598
115.356
77.421
000
76.575
32.247
13.128
ppm


7.692
7.686
7.670
7.664
7.318
7.310
7.301
7.298
7.292
7.286
7.151
7.143
7.130
7.125
7.119
7.002
6.974
6.461
2.556
2.552
2.527
2.502
1.313
1.089
1.064
1.98
2.09
1.03
1.90
0.99
5.00
2.99
ppm

Ac
3k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142.583
140.857
134.475
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128.579
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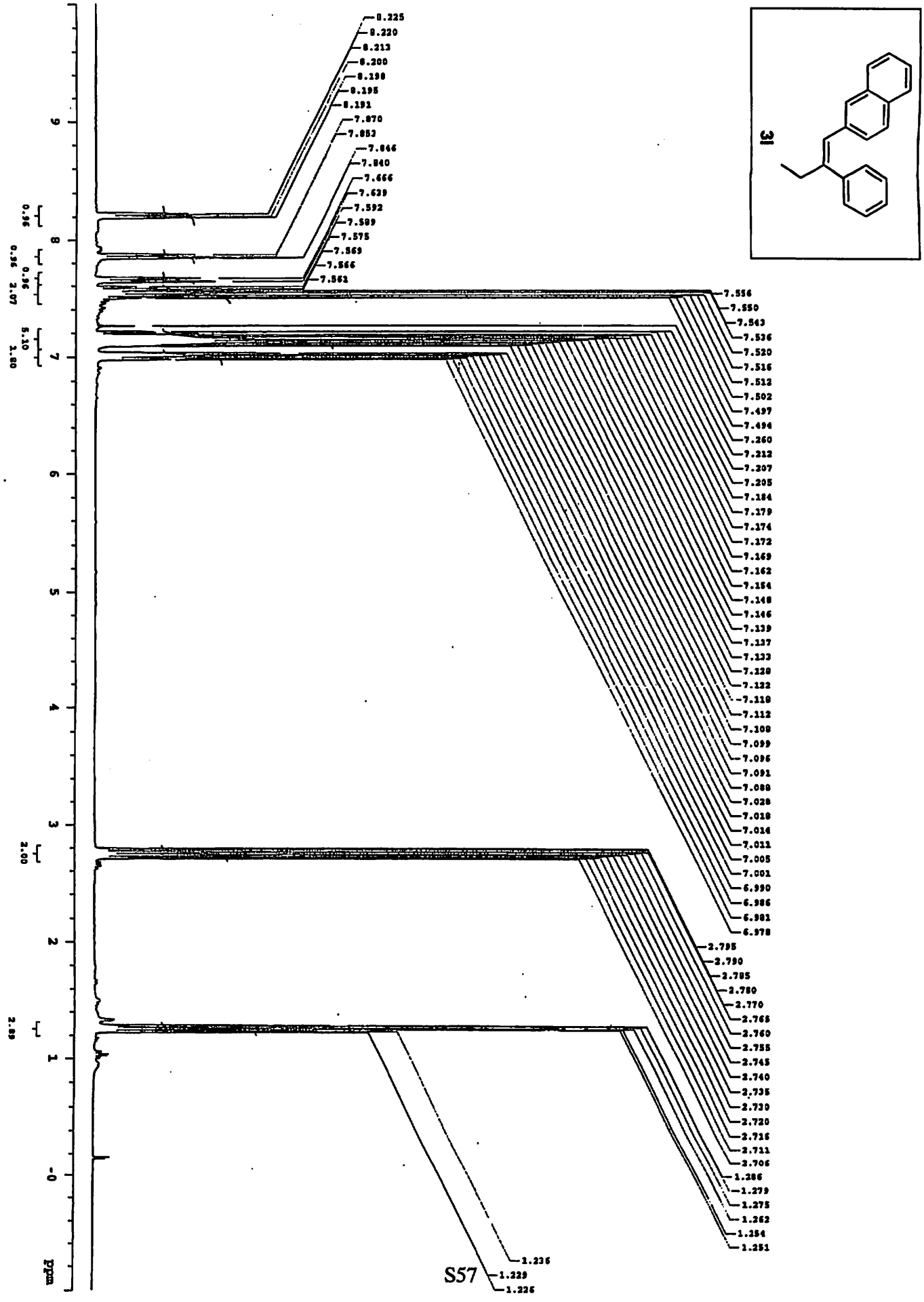
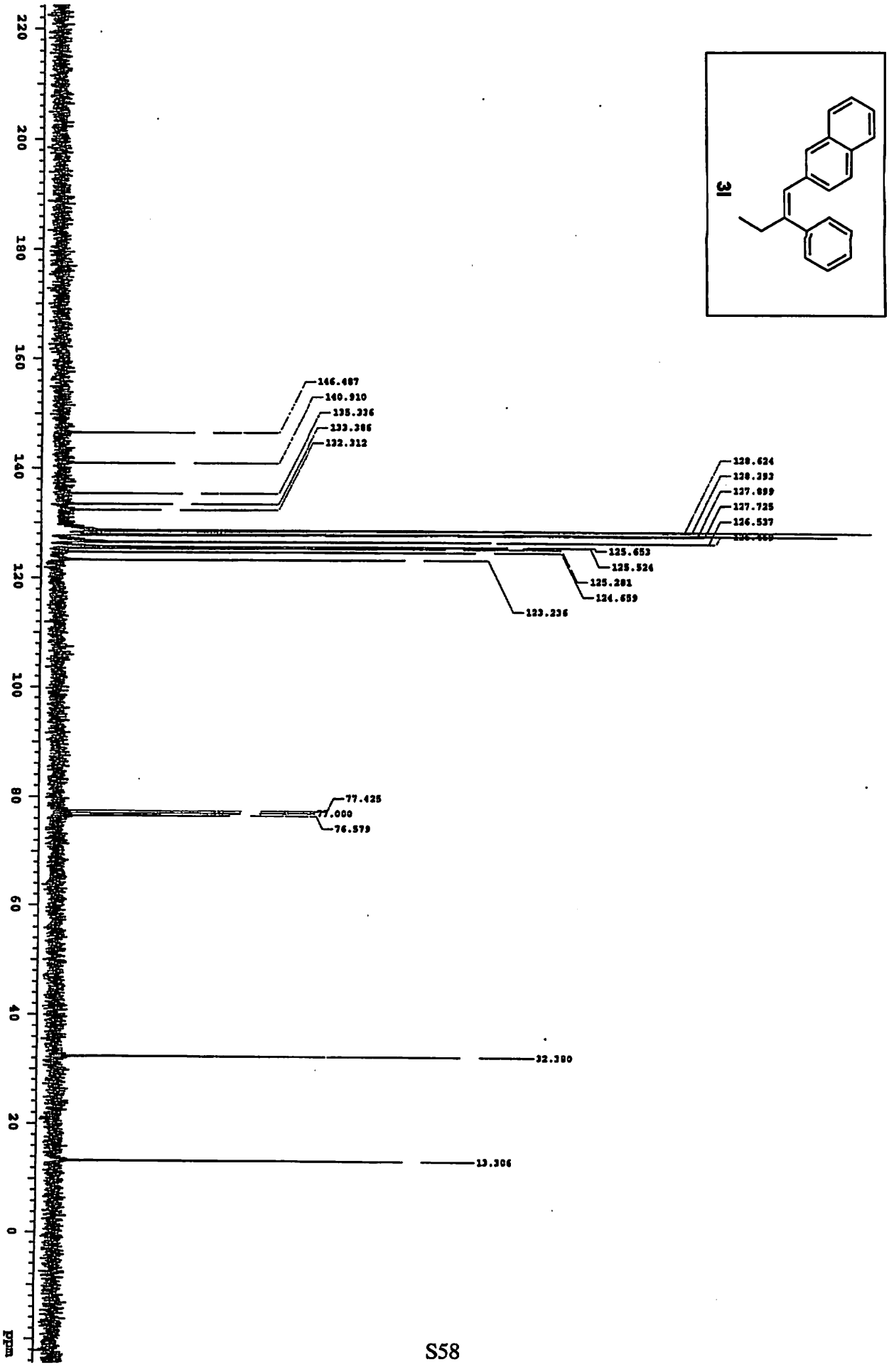
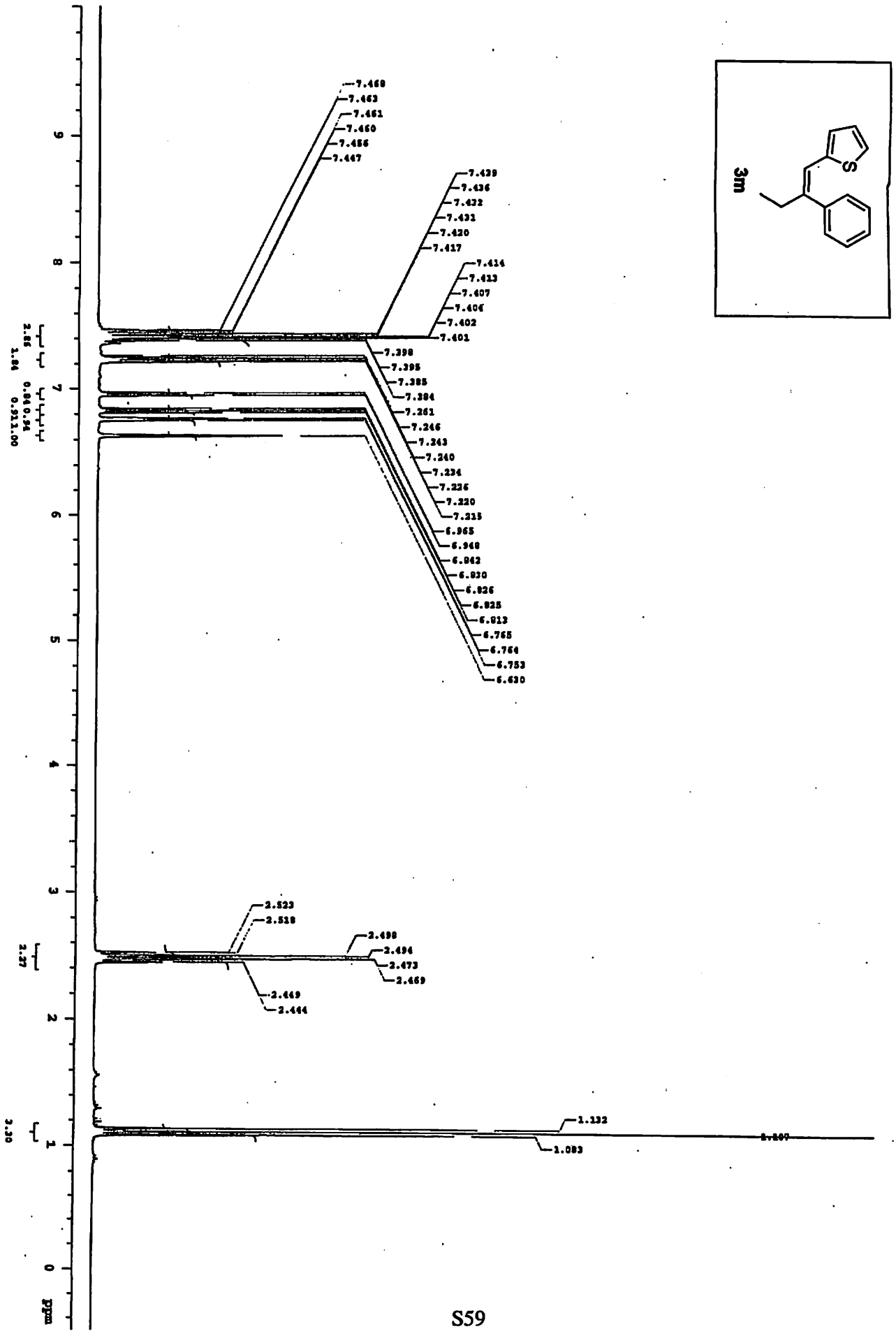
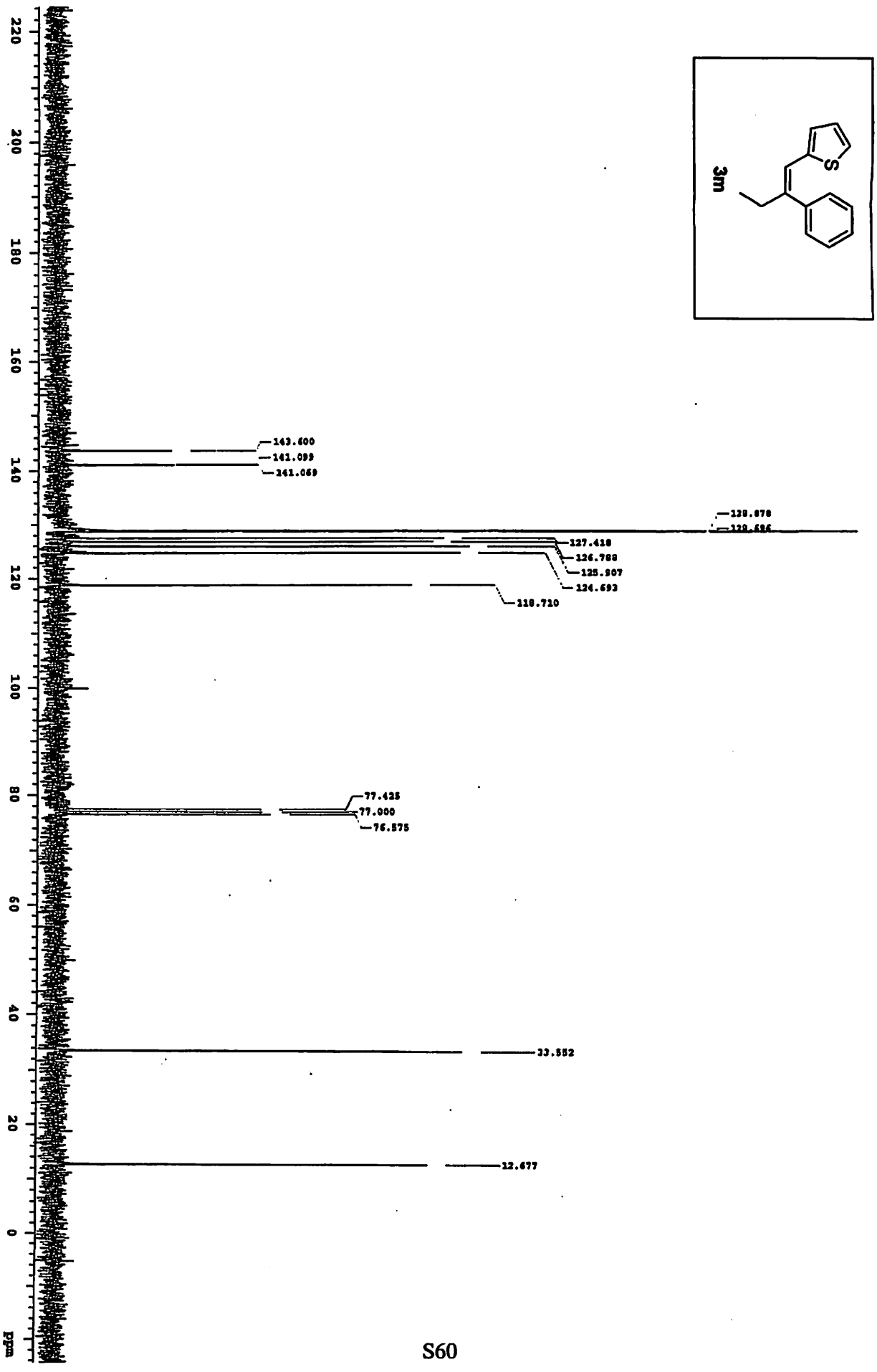
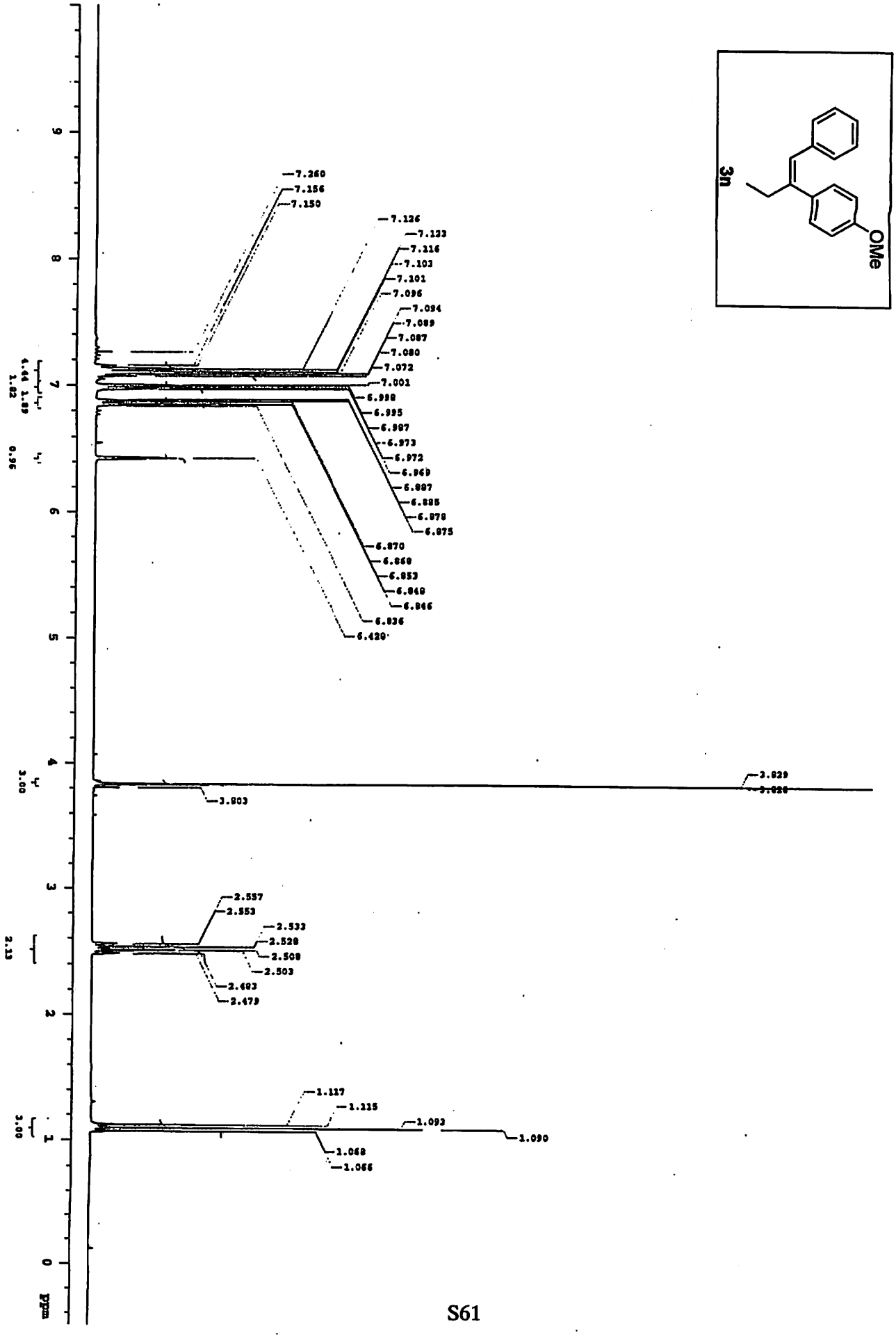
124.192
77.425
77.000
76.579
33.575
26.389
11.673
ppm
Ac
3k

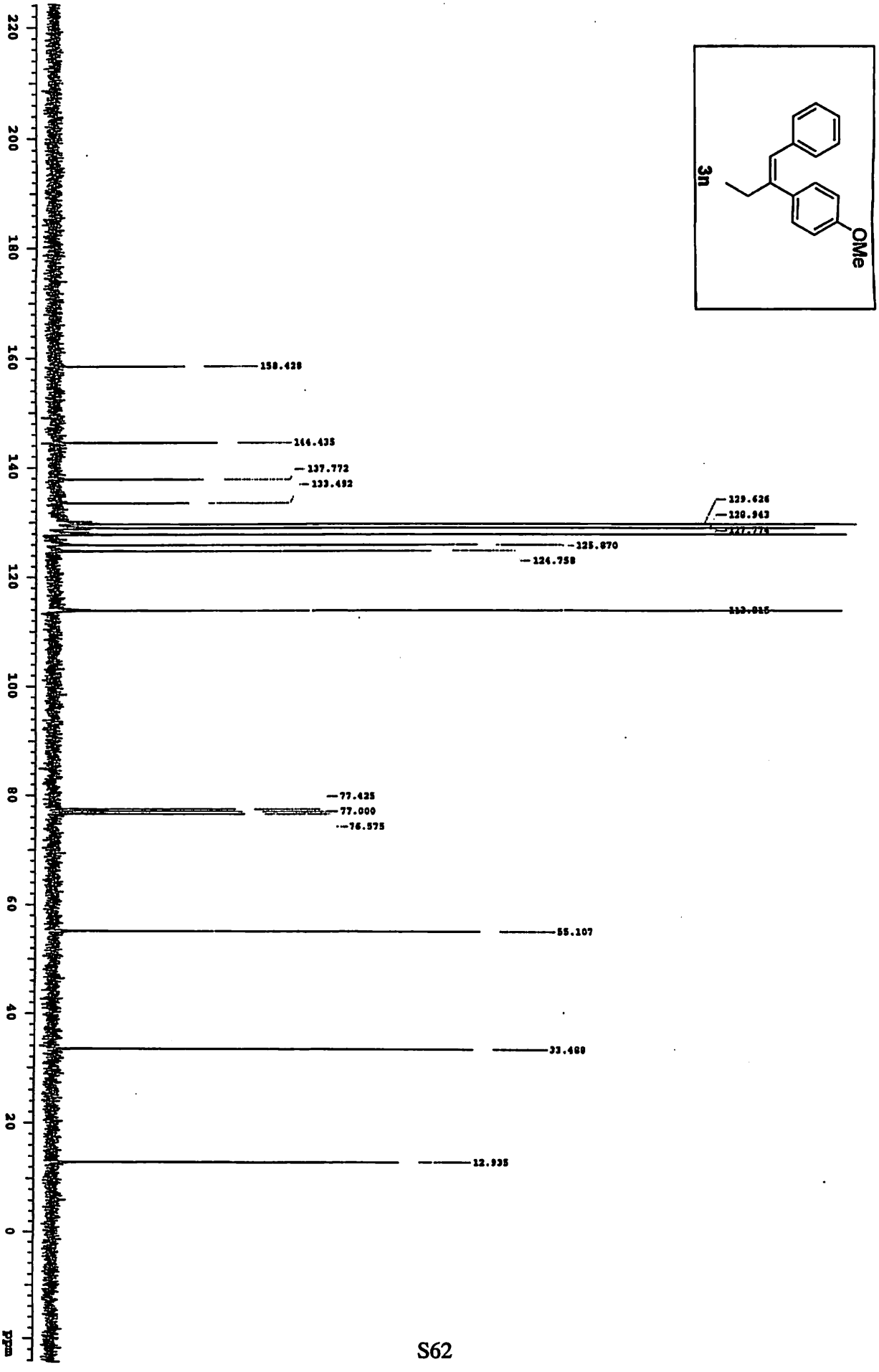

31
8.225
8.220
8.213
8.200
8.198
8.195
8.191
7.870
7.852
7.846
7.840
7.666
7.639
7.592
7.589
7.575
7.569
7.566
7.561
7.556
7.550
7.543
7.536
7.520
7.516
7.512
7.502
7.497
7.494
7.260
7.212
7.207
7.205
7.184
7.179
7.174
7.172
7.169
7.162
7.154
7.148
7.146
7.139
7.137
7.133
7.128
7.122
7.118
7.112
7.108
7.099
7.096
7.091
7.088
7.028
7.018
7.014
7.011
7.005
7.001
6.990
6.986
6.981
6.978
2.795
2.790
2.785
2.780
2.770
2.765
2.760
2.755
2.745
2.740
2.735
2.730
2.720
2.716
2.711
2.706
1.286
1.279
1.275
1.262
1.254
1.251
1.236
1.229
1.226
0.96
0.96
2.07
5.10
1.80
2.00
2.89
ppm

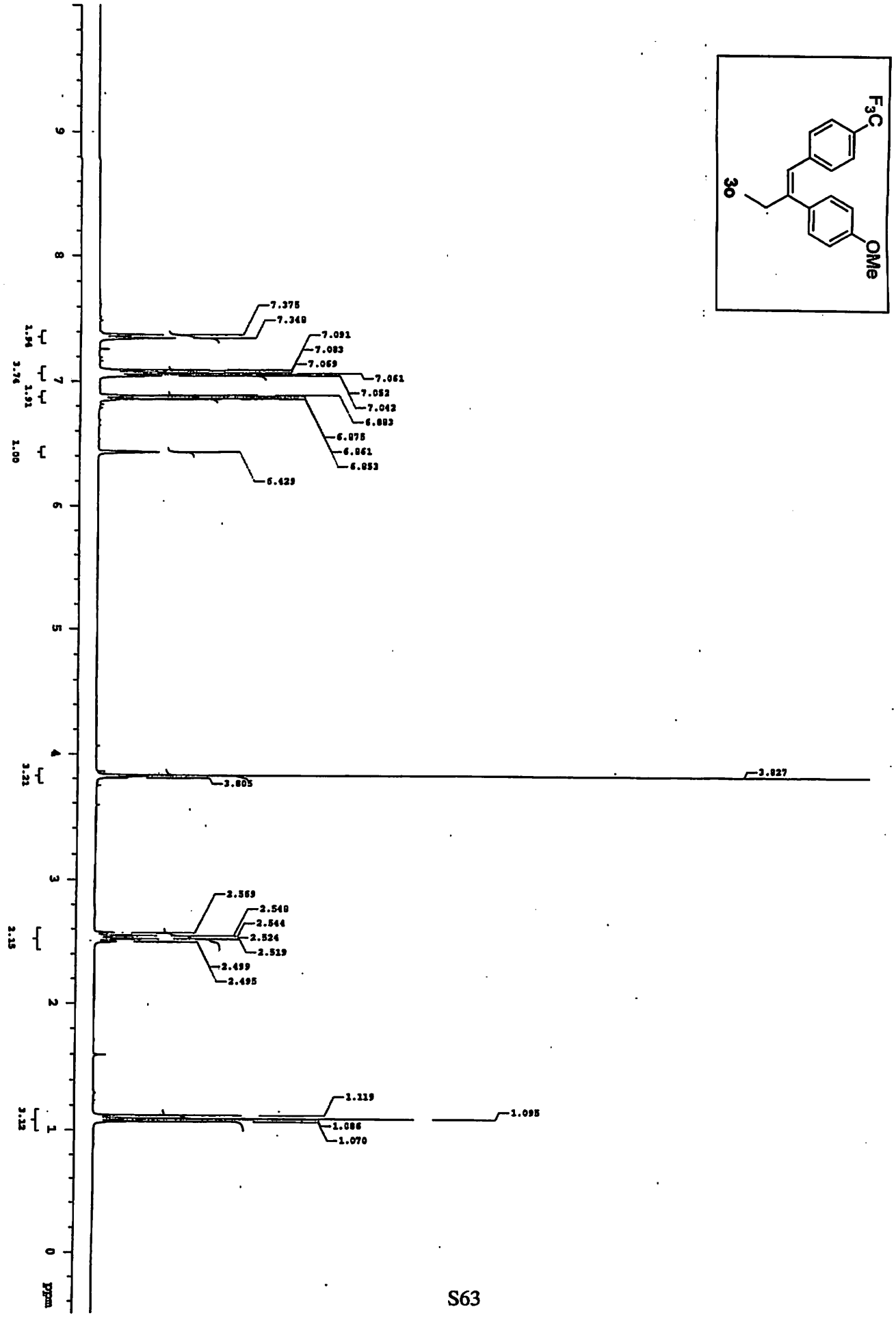

31
146.487
140.910
135.336
133.386
132.312
128.624
128.393
127.899
127.725
126.537
125.653
125.524
125.281
124.659
123.236
77.425
77.000
76.579
32.380
13.306
ppm

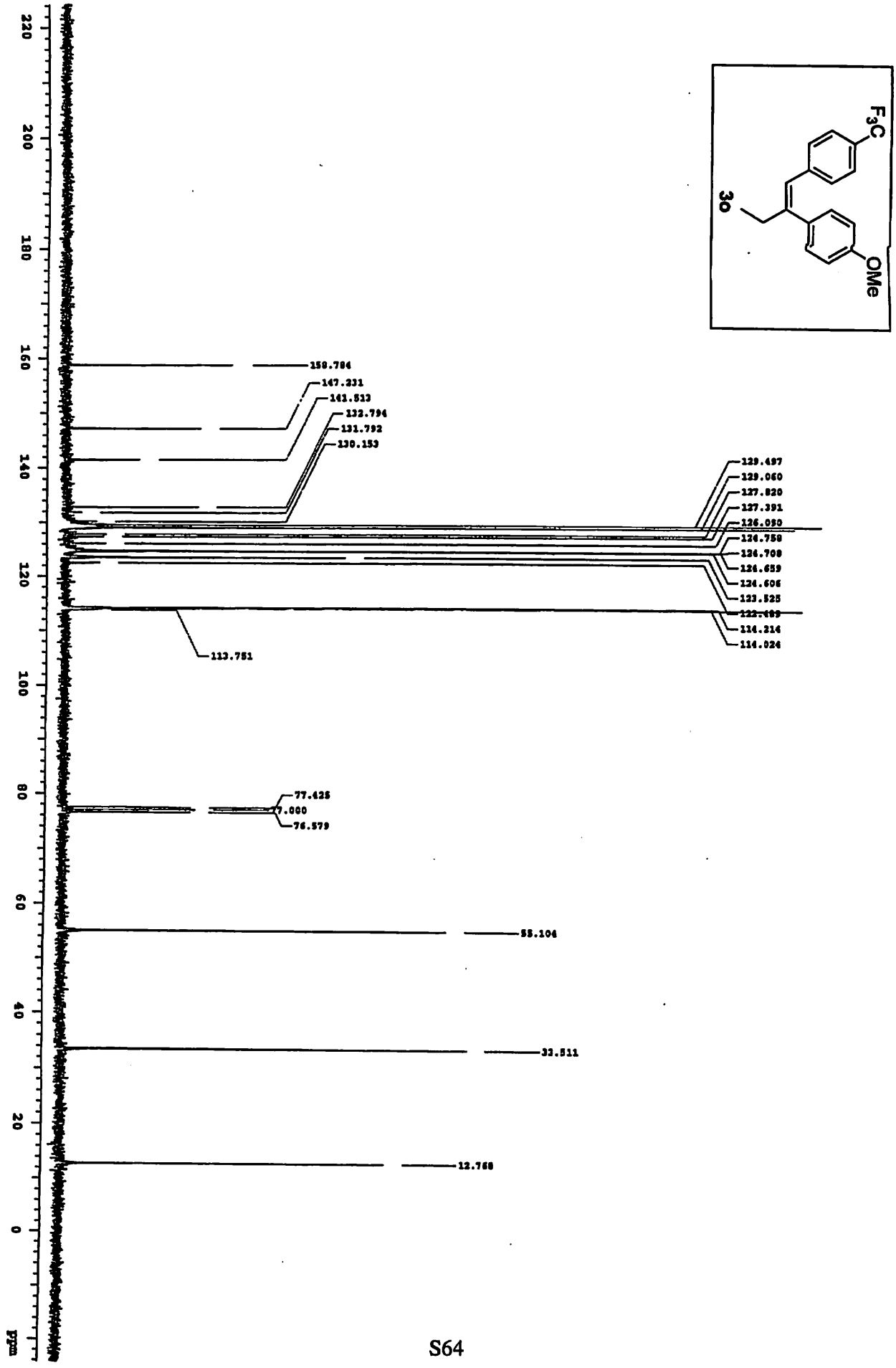

3m
S
7.469
7.463
7.461
7.460
7.456
7.447
7.439
7.436
7.432
7.431
7.420
7.417
7.414
7.413
7.407
7.406
7.402
7.401
7.398
7.395
7.385
7.384
7.261
7.246
7.243
7.240
7.234
7.226
7.220
7.215
6.965
6.960
6.942
6.930
6.926
6.925
6.913
6.765
6.764
6.753
6.630
2.523
2.518
2.498
2.494
2.473
2.469
2.449
2.444
1.132
1.083
2.85
1.84
0.86
0.94
0.91
1.00
2.27
3.30
ppm

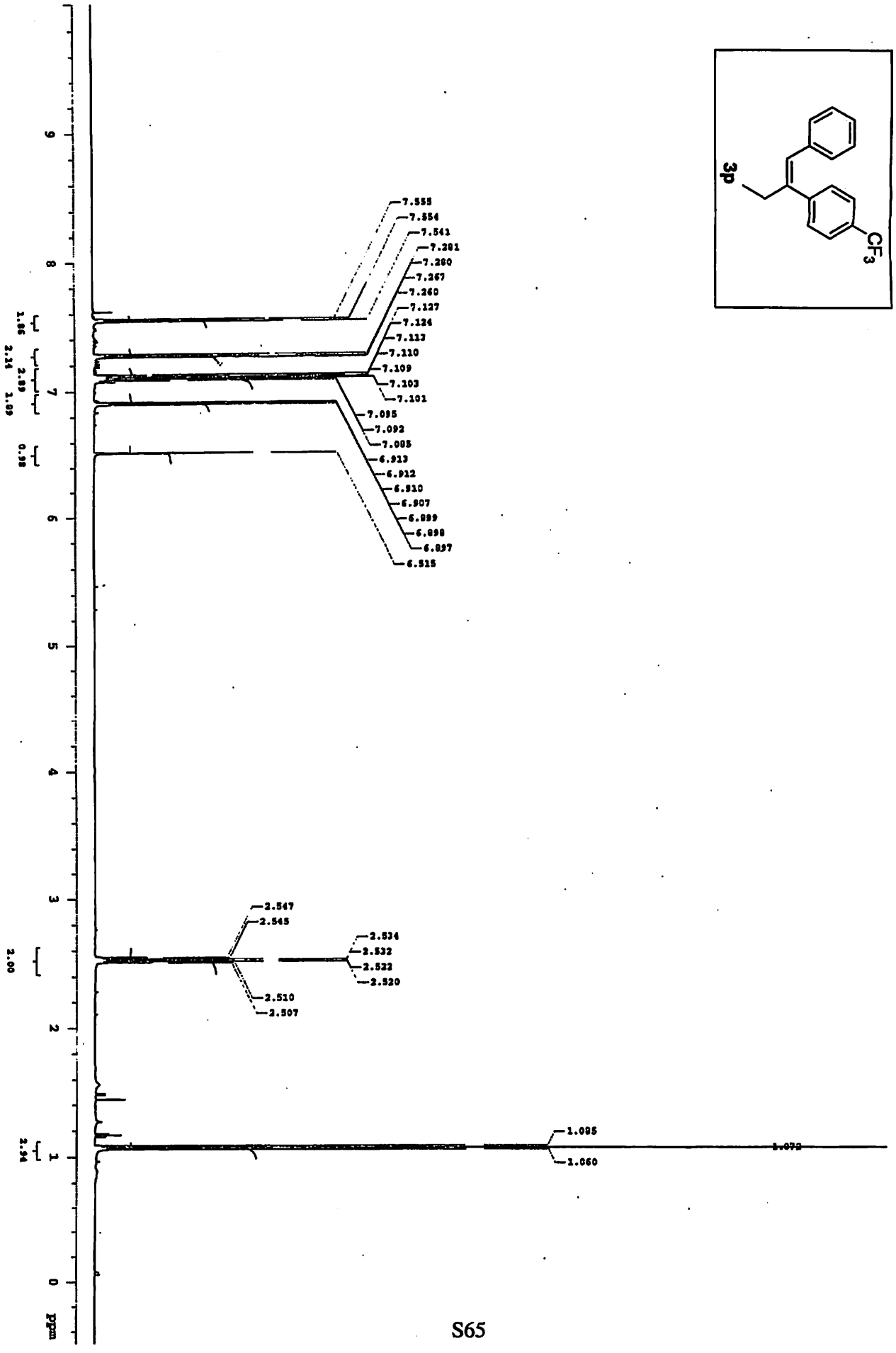

3m
S
143.600
141.093
141.069
128.878
129.686
127.418
126.788
125.907
124.693
118.710
77.425
77.000
76.575
33.552
12.677
ppm

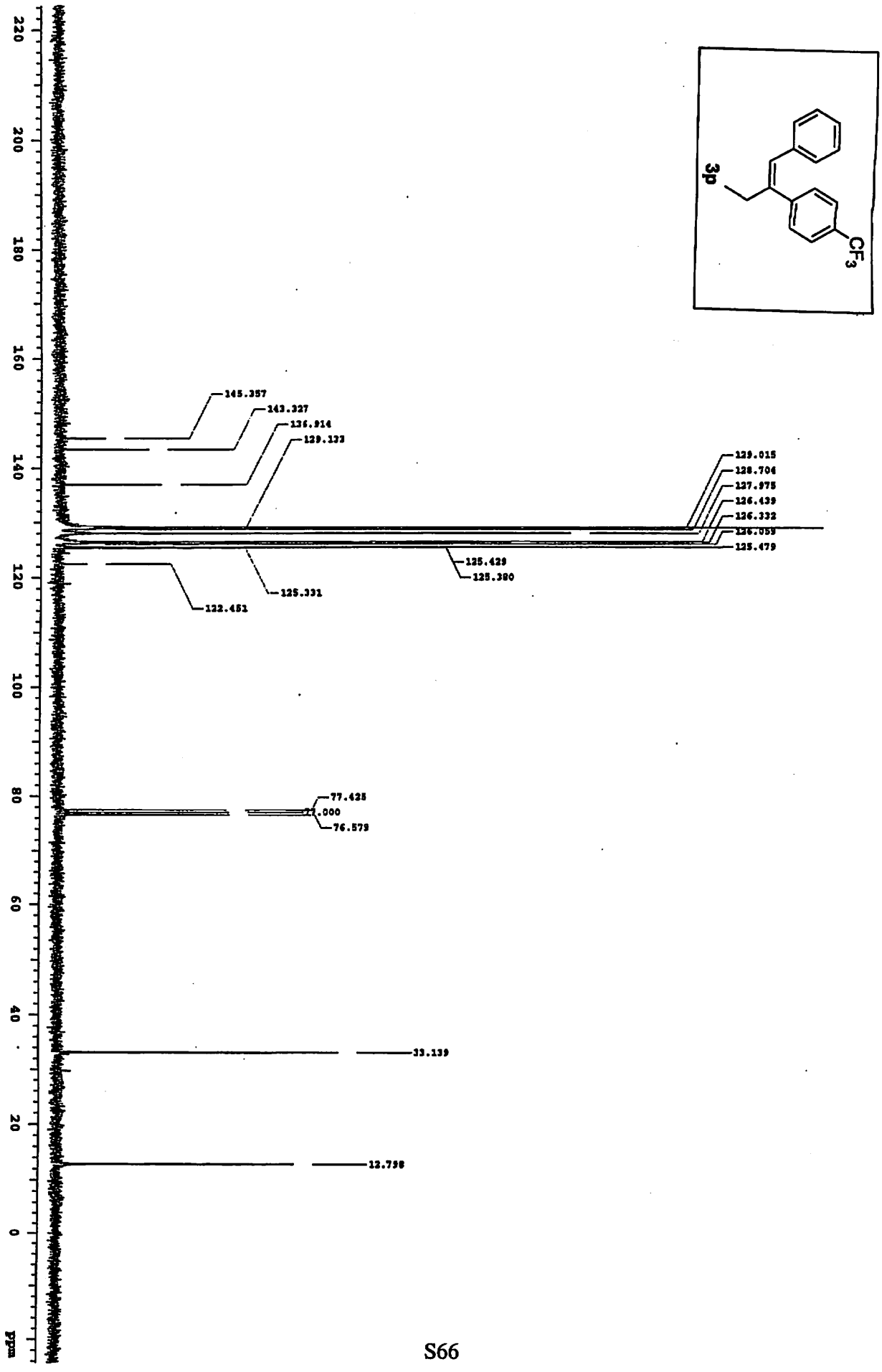

3n
OMe
7.260
7.156
7.150
7.126
7.123
7.116
7.103
7.101
7.096
7.094
7.089
7.087
7.080
7.072
7.001
6.998
6.995
6.987
6.973
6.972
6.969
6.887
6.885
6.878
6.875
6.870
6.860
6.853
6.849
6.846
6.836
6.429
3.829
3.803
2.557
2.553
2.533
2.528
2.508
2.503
2.483
2.479
1.117
1.115
1.093
1.090
1.068
1.066
ppm

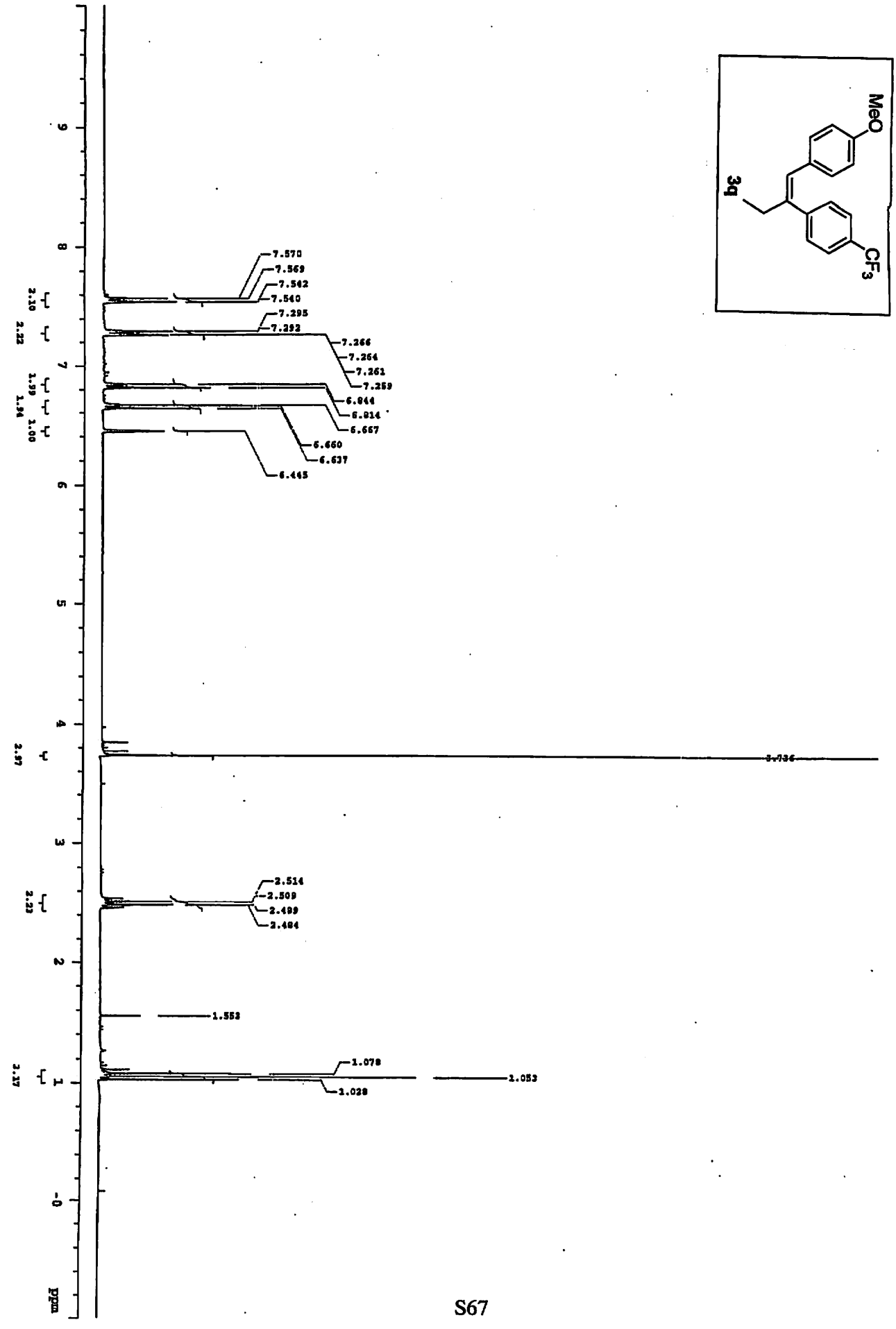

3n
OMe
158.428
144.435
137.772
133.492
129.626
128.943
125.870
124.758
77.425
77.000
76.575
55.107
33.468
12.935
ppm

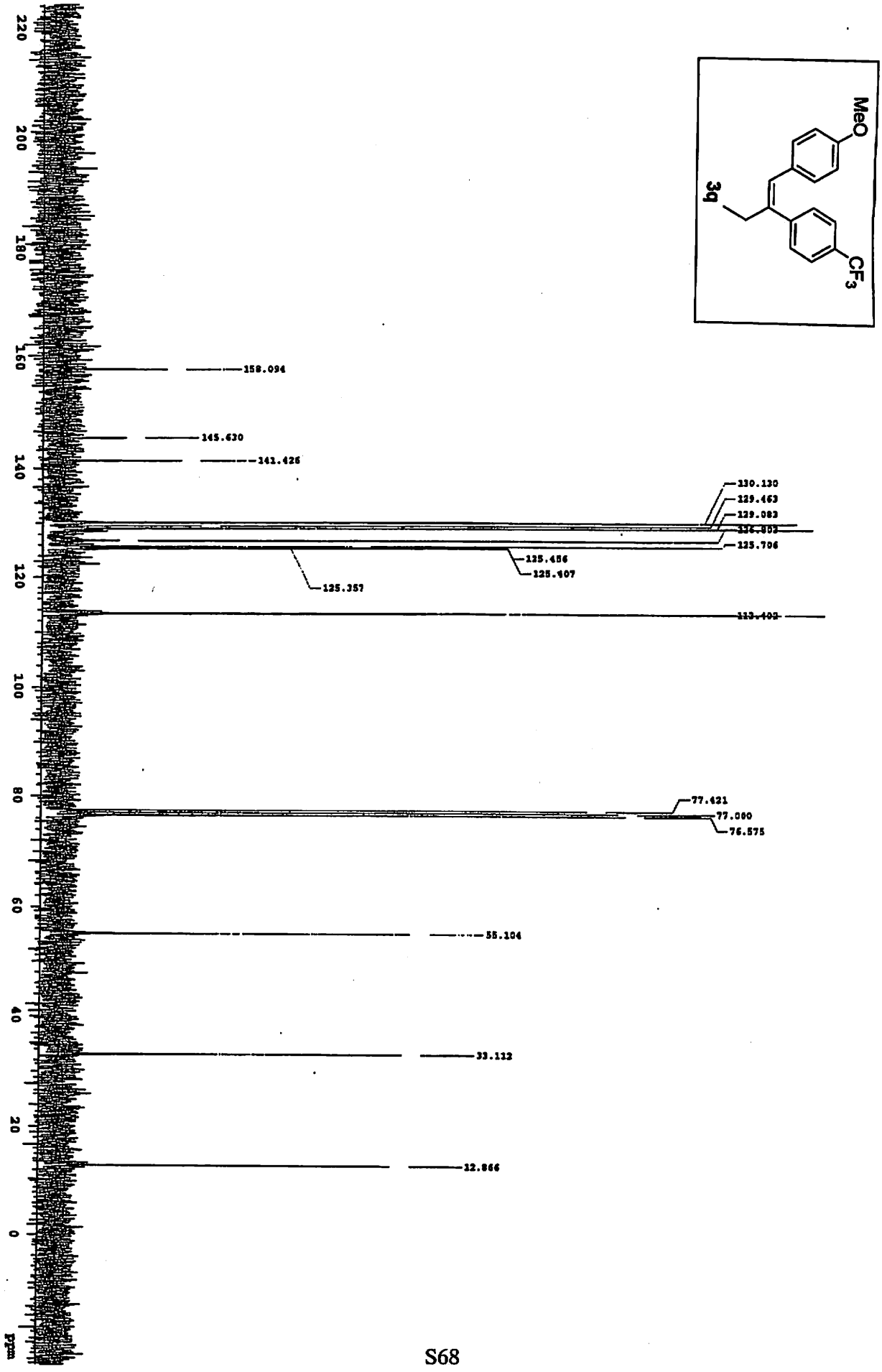

F3C
3o
OMe
7.375
7.369
7.091
7.083
7.069
7.061
7.052
7.042
6.883
6.875
6.861
6.853
6.429
3.827
3.805
2.569
2.548
2.544
2.524
2.519
2.499
2.495
1.119
1.095
1.086
1.070
ppm

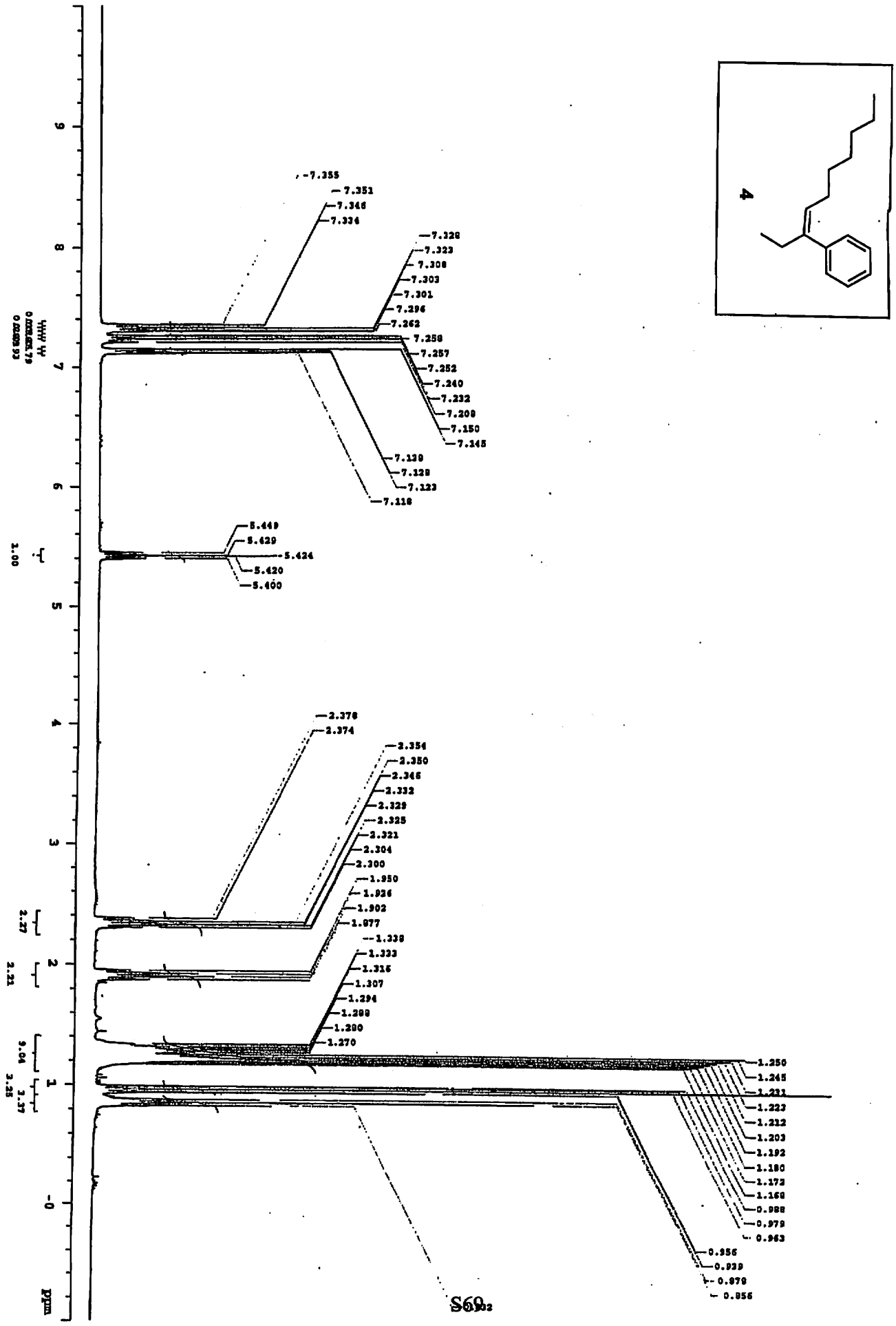

F3C
3o
OMe
159.784
147.231
141.513
132.794
131.792
130.153
129.497
129.060
127.820
127.391
126.050
126.758
126.708
126.659
126.606
123.525
122.489
114.214
114.024
113.751
77.425
7.000
76.579
55.106
33.511
12.768
ppm

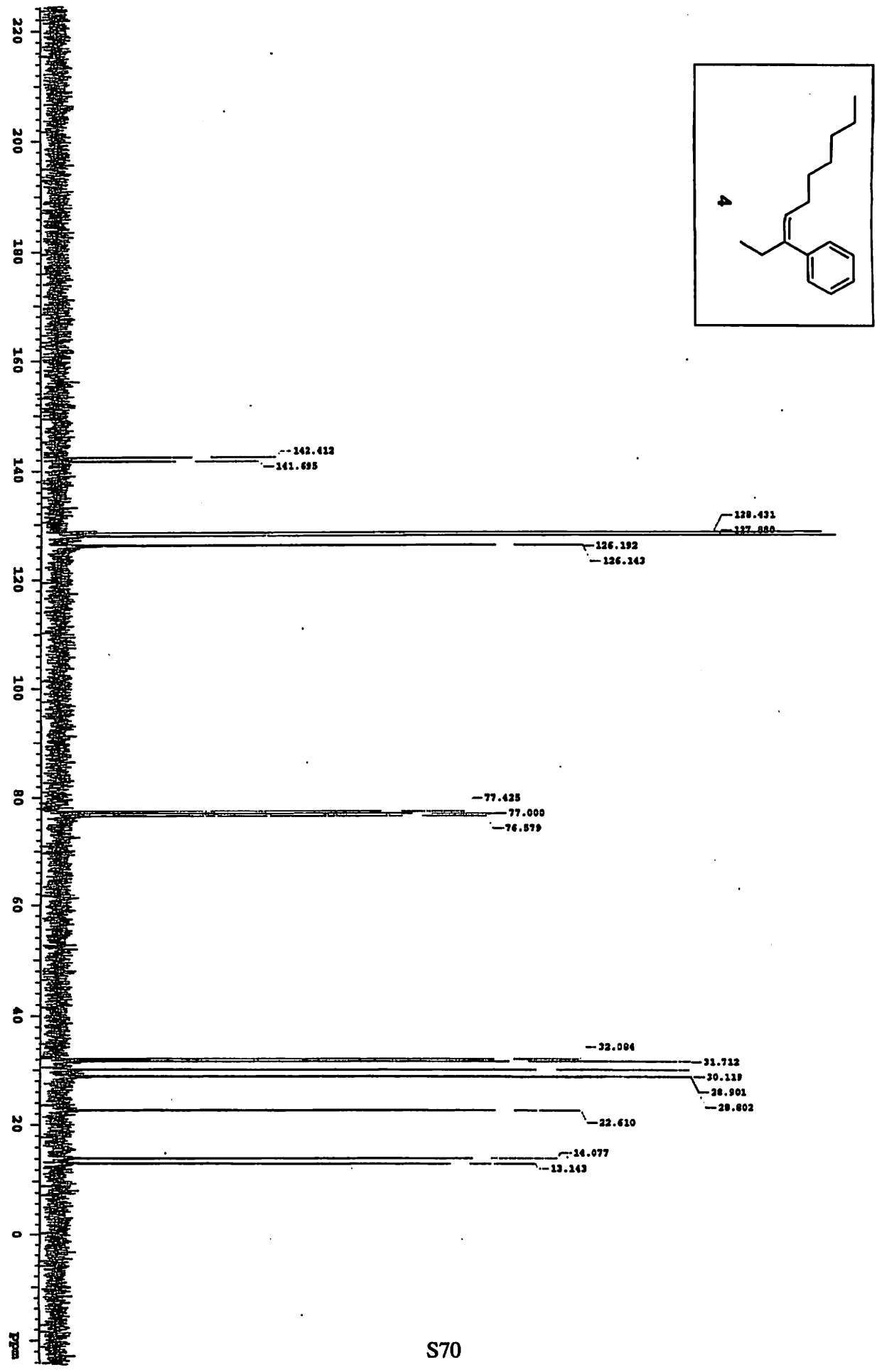

3p
CF3
7.555
7.554
7.541
7.281
7.280
7.267
7.260
7.127
7.124
7.113
7.110
7.109
7.103
7.101
7.095
7.092
7.085
6.913
6.912
6.910
6.907
6.899
6.898
6.897
6.515
2.547
2.545
2.534
2.532
2.522
2.520
2.510
2.507
1.095
1.060
1.00
2.14
2.89
1.89
1.86
0.98
2.00
2.94
ppm

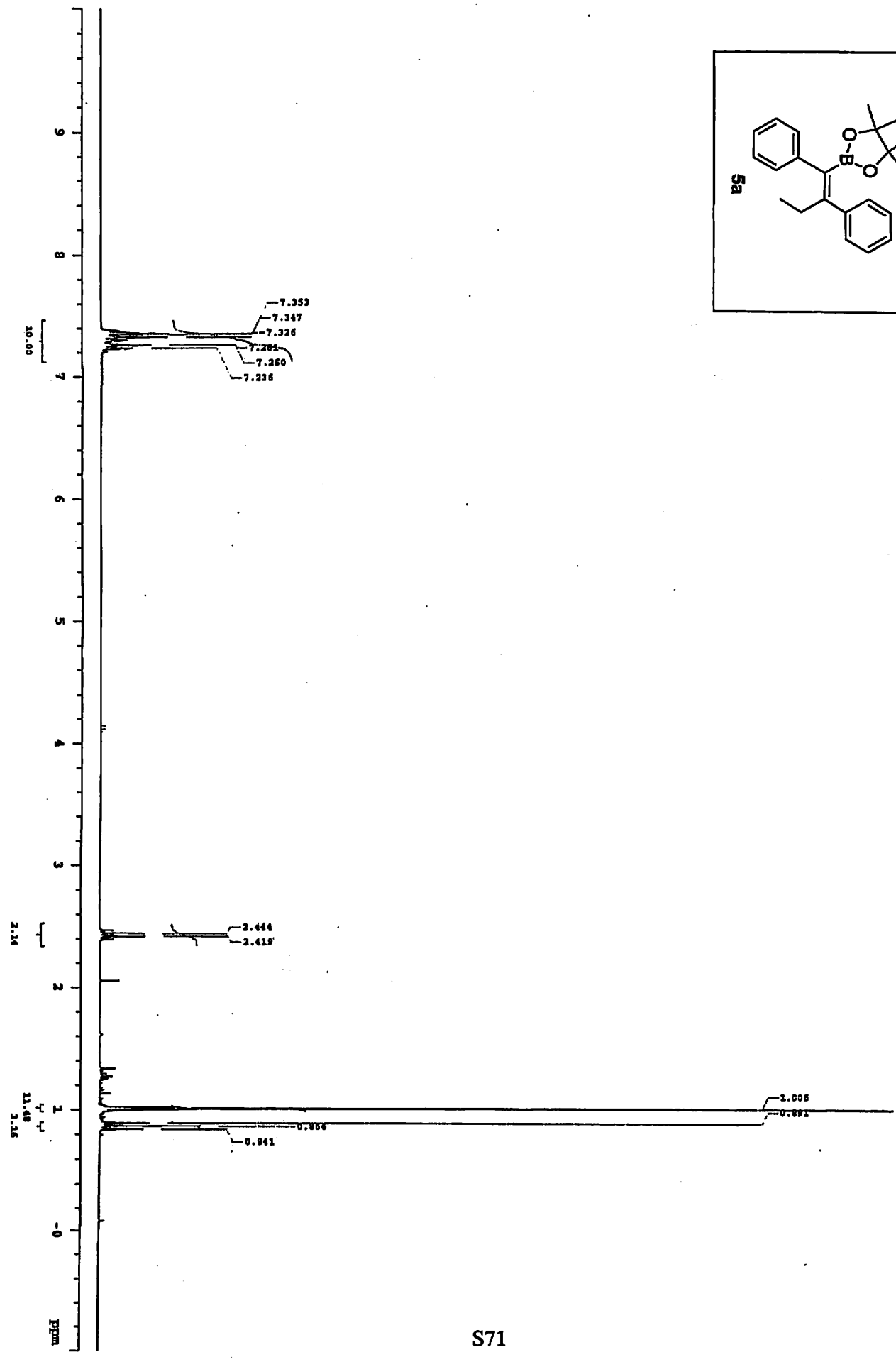

3p
CF3
145.357
143.327
136.914
129.133
129.015
128.704
127.975
126.439
126.332
126.059
125.479
125.429
125.380
125.331
122.451
77.425
77.000
76.579
33.139
12.798
ppm

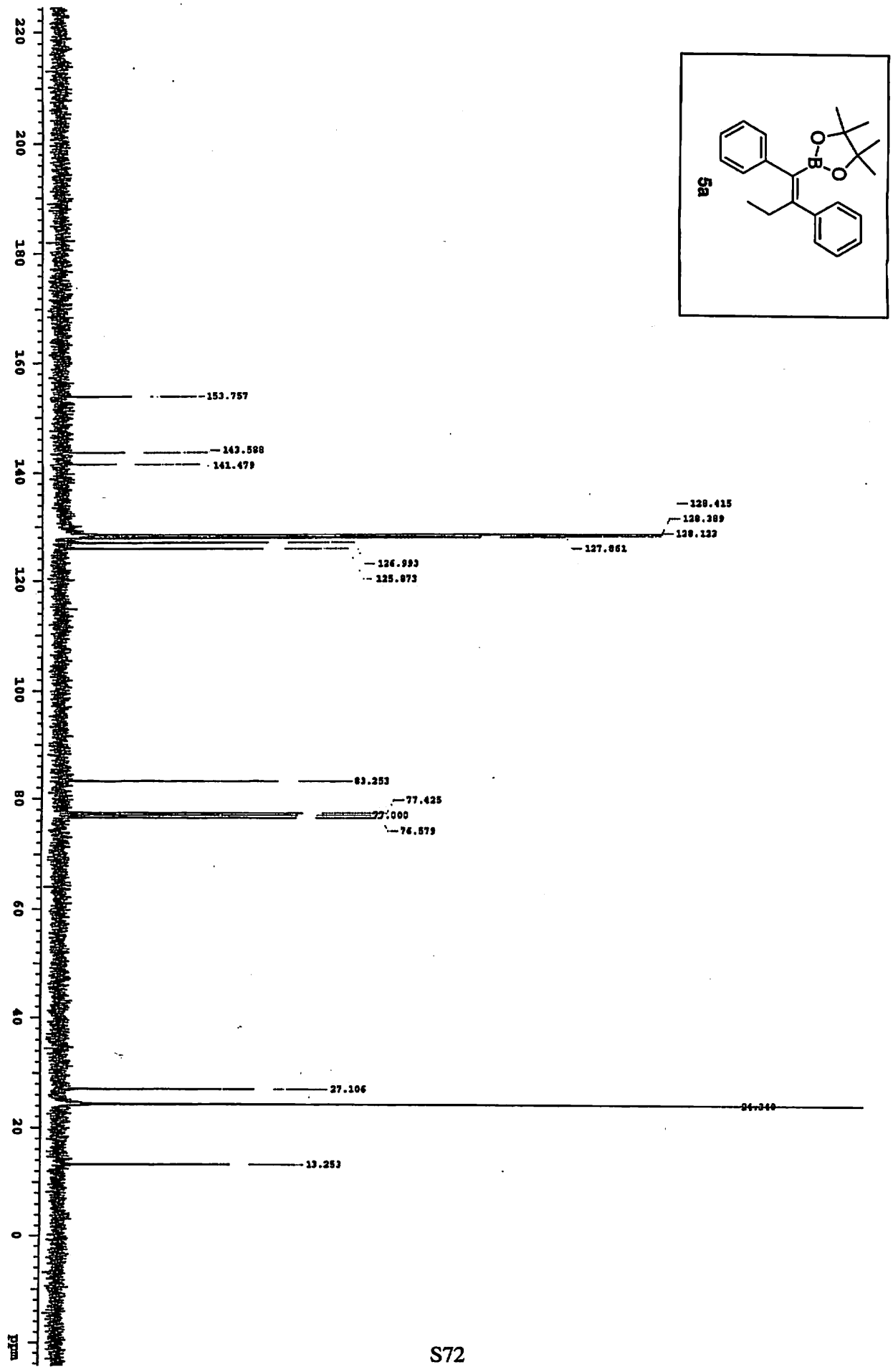

MeO
3q
CF3
7.570
7.569
7.562
7.560
7.295
7.292
7.266
7.264
7.261
7.259
6.944
6.814
6.667
6.660
6.637
6.445
3.836
2.514
2.509
2.499
2.494
1.553
1.078
1.053
1.028
ppm

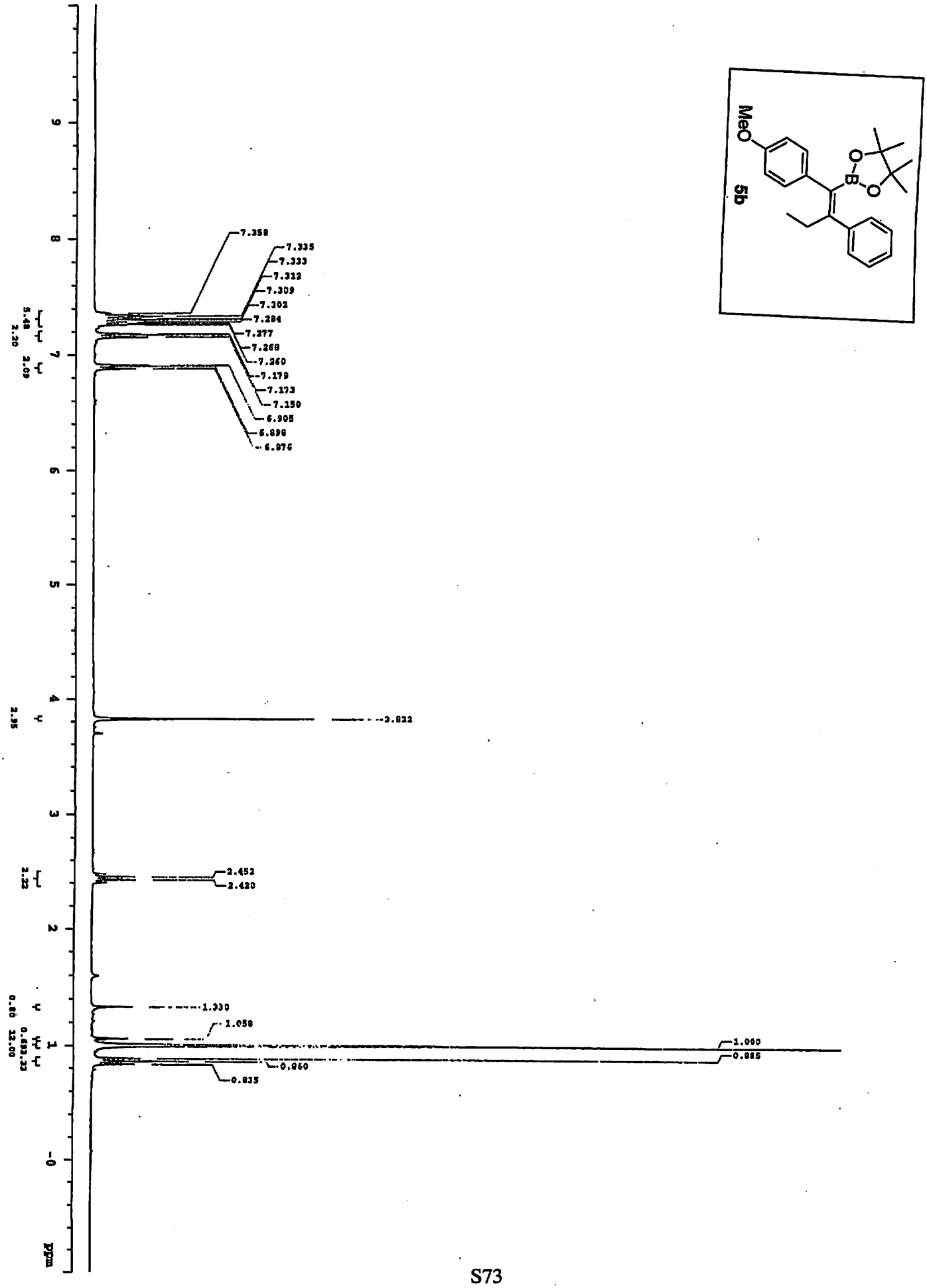

MeO
3q
CF3
158.094
145.630
141.426
130.130
129.463
129.083
125.706
125.456
125.407
125.357
113.402
77.421
77.000
76.575
55.104
33.112
12.866
ppm

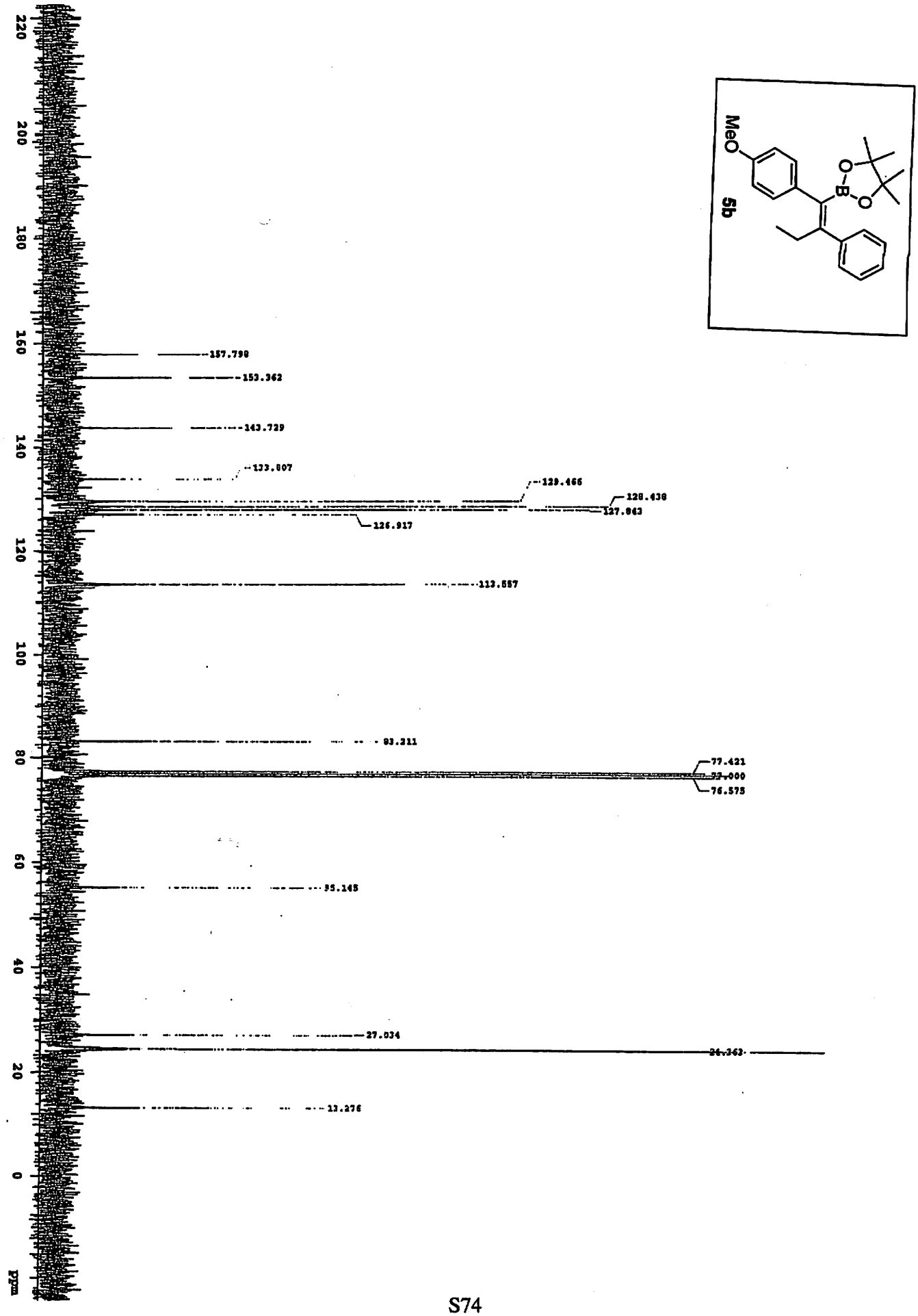

4
7.355
7.351
7.346
7.334
7.328
7.323
7.308
7.303
7.301
7.296
7.262
7.258
7.257
7.252
7.240
7.232
7.208
7.150
7.145
7.139
7.128
7.123
7.118
5.449
5.429
5.424
5.420
5.400
2.378
2.374
2.354
2.350
2.346
2.332
2.328
2.325
2.321
2.304
2.300
1.950
1.926
1.902
1.877
1.339
1.333
1.316
1.307
1.294
1.288
1.280
1.270
1.250
1.245
1.231
1.223
1.212
1.203
1.192
1.180
1.173
1.160
0.988
0.979
0.963
0.956
0.939
0.879
0.856
1.00
2.27
2.21
9.04
3.37
3.25
ppm

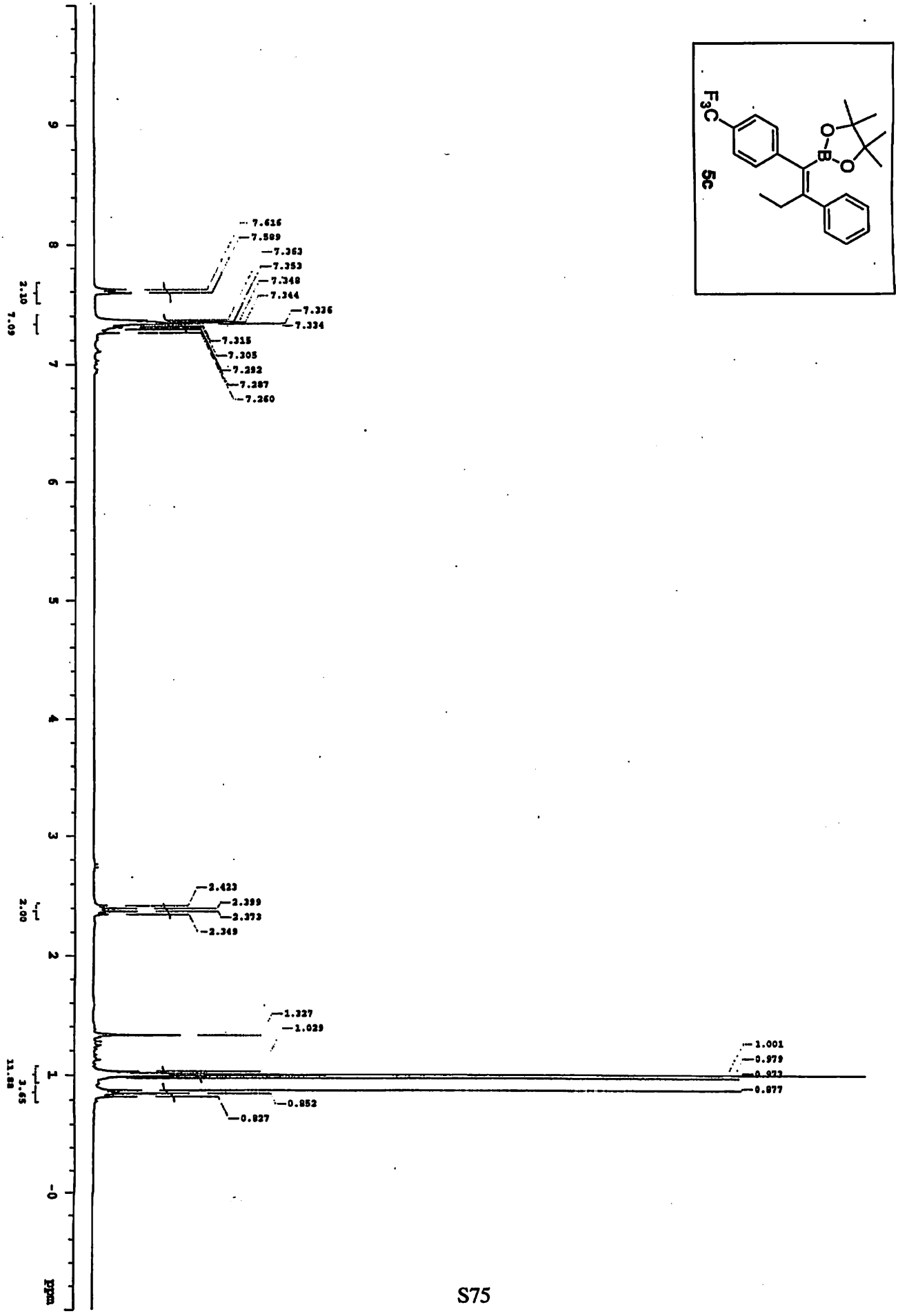

4
142.412
141.695
128.431
126.192
126.143
77.425
77.000
76.579
32.006
31.712
30.119
28.901
28.802
22.610
14.077
13.143
ppm

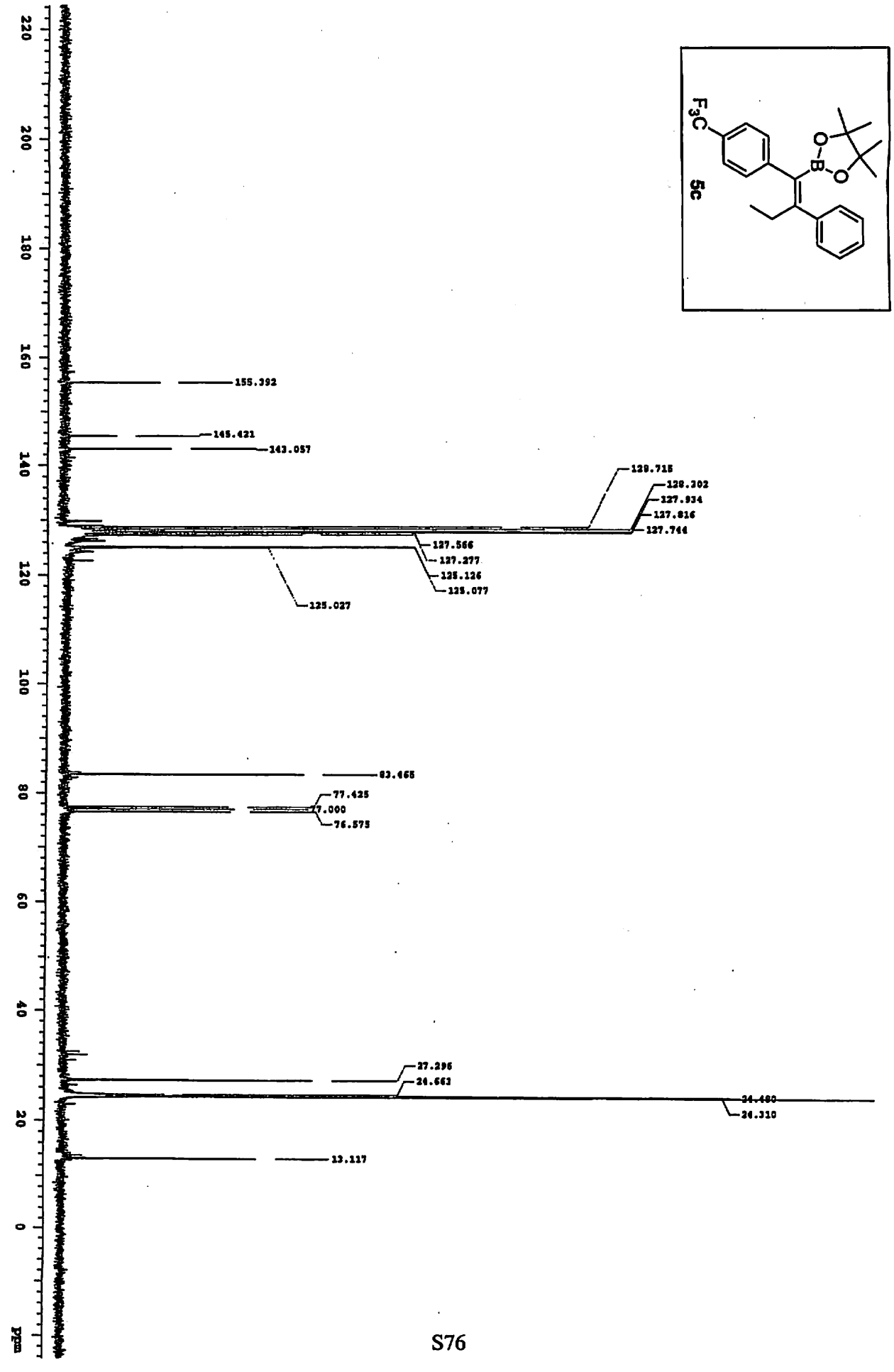

7.353
7.347
7.326
7.295
7.260
7.236
10.00
2.444
2.419
2.14
1.006
0.892
0.856
0.841
11.48
3.35
ppm
5a

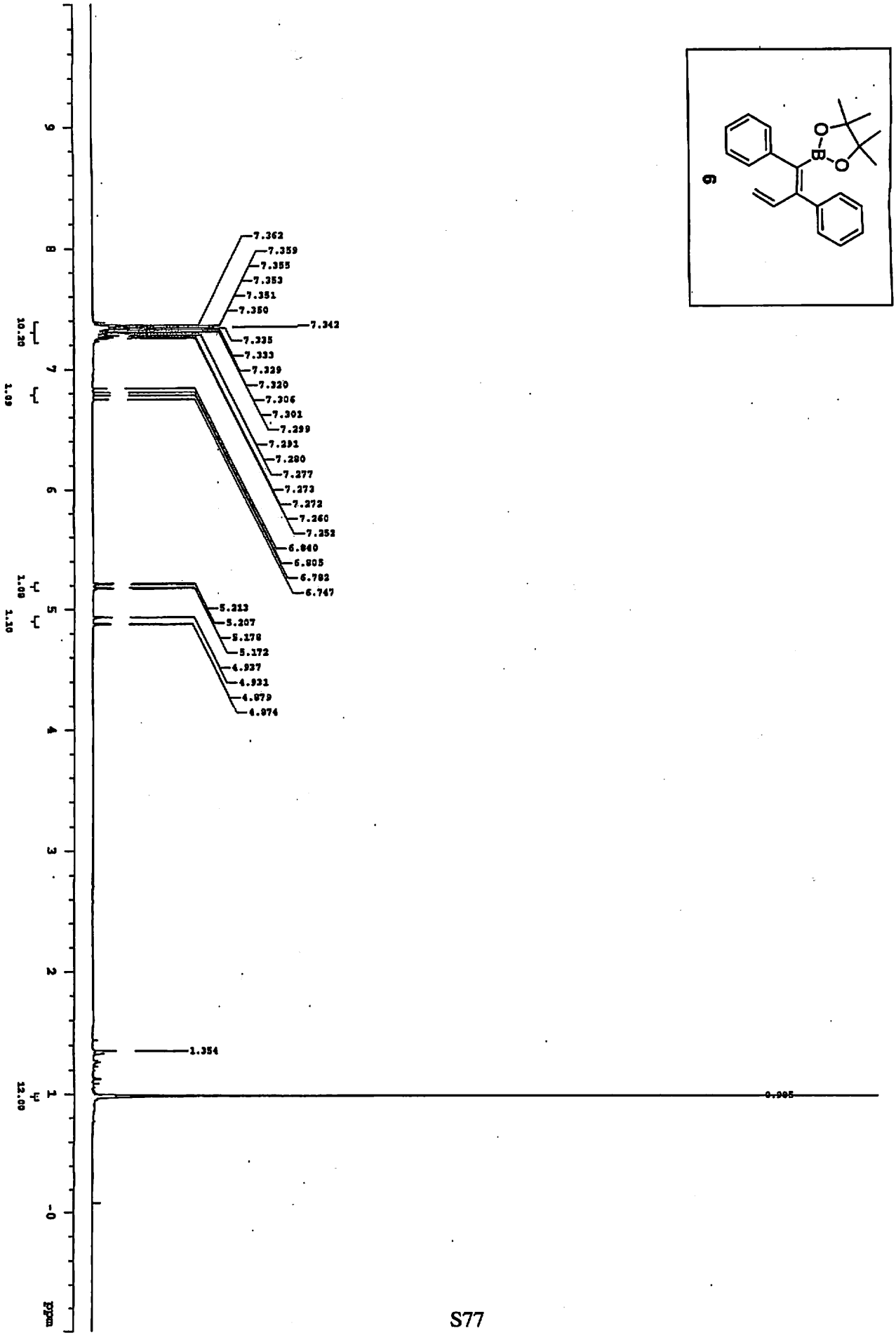

5a
153.757
143.588
141.479
128.415
128.389
128.133
127.861
126.993
125.873
83.253
77.425
77.000
76.579
27.106
24.340
13.253
ppm

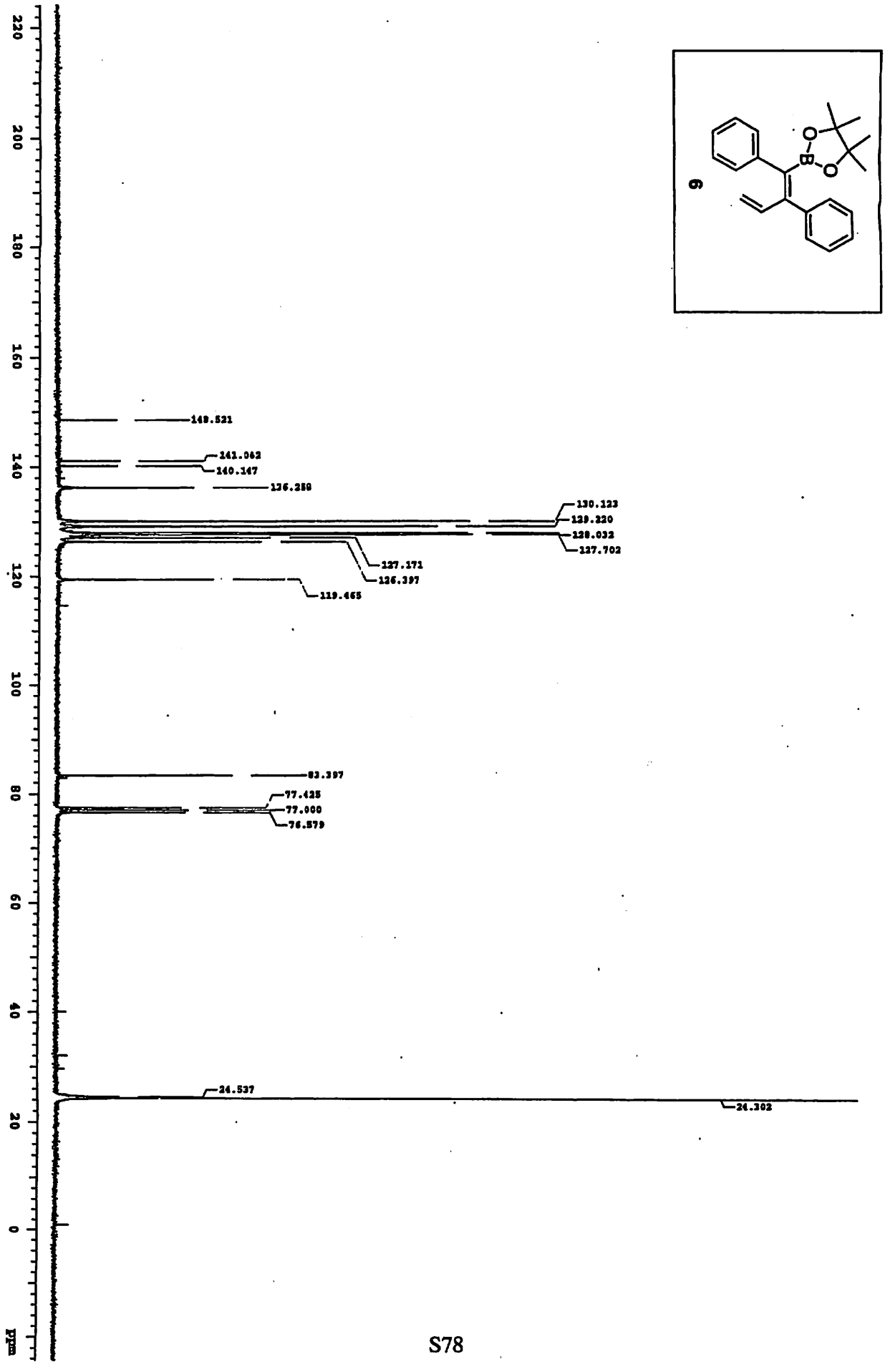

MeO
5b
7.358
7.335
7.333
7.312
7.309
7.302
7.284
7.277
7.269
7.260
7.179
7.173
7.150
6.905
6.898
6.876
3.822
2.452
2.420
1.330
1.058
1.000
0.885
0.860
0.835
ppm

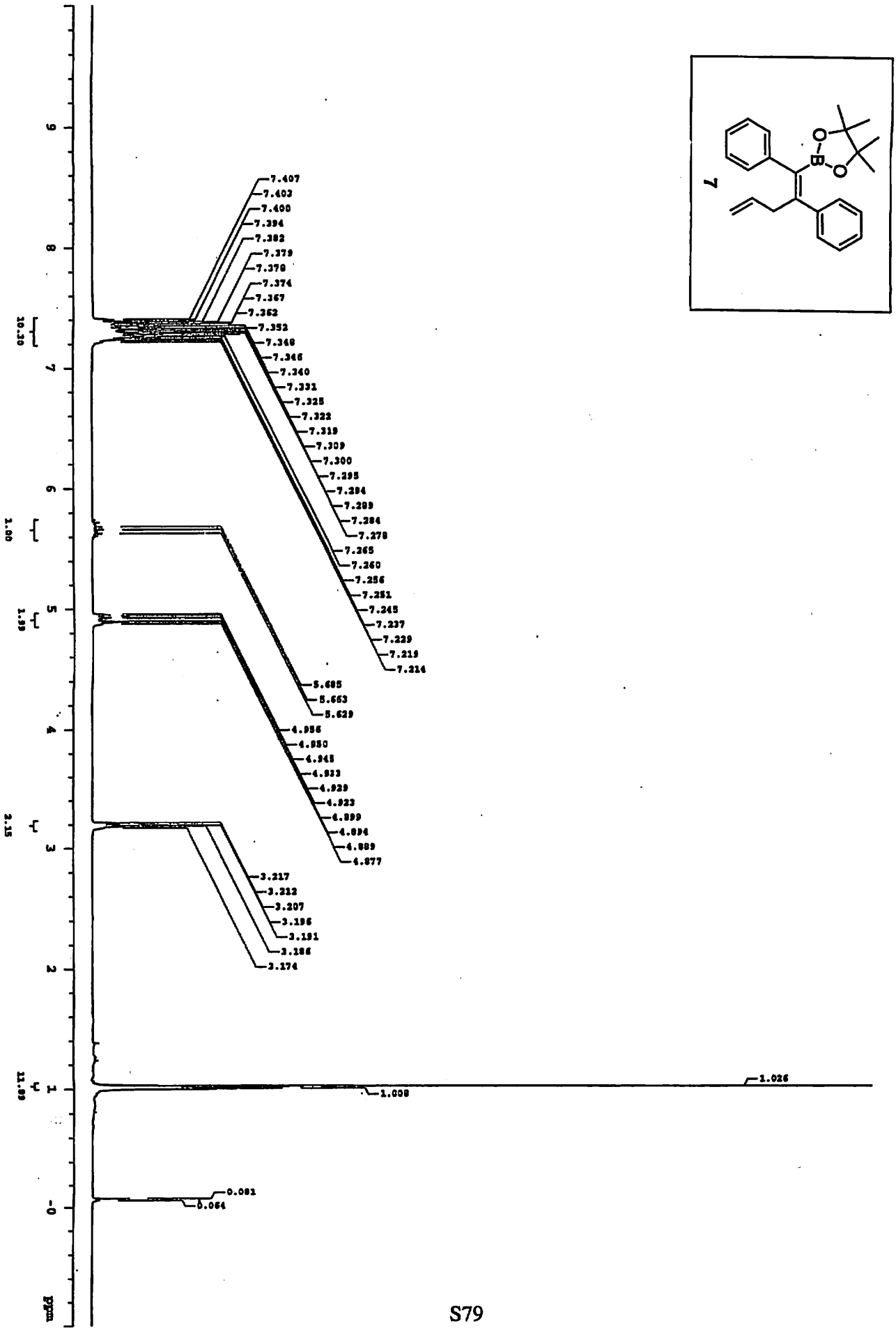

MeO
5b
157.798
153.362
143.729
133.807
129.466
128.438
127.863
126.917
113.557
93.211
77.421
77.000
76.575
55.145
27.034
24.362
13.276
220
200
180
160
140
120
100
80
60
40
20
0
ppm


F3C
5c
O
B
O
O
7.616
7.589
7.363
7.353
7.348
7.344
7.336
7.334
7.315
7.305
7.292
7.287
7.260
2.423
2.399
2.373
2.349
1.327
1.029
1.001
0.979
0.973
0.877
0.852
0.827
2.10
7.09
2.00
3.65
11.88
ppm


5c
155.392
145.421
143.057
129.715
128.302
127.934
127.816
127.744
127.566
127.277
125.126
125.077
125.027
83.465
77.425
77.000
76.575
27.296
24.663
24.480
24.310
13.117
ppm


9
7.362
7.359
7.355
7.353
7.351
7.350
7.342
7.335
7.333
7.329
7.320
7.306
7.301
7.299
7.291
7.280
7.277
7.273
7.272
7.260
7.252
6.840
6.805
6.782
6.747
5.213
5.207
5.178
5.172
4.937
4.931
4.879
4.874
1.354
0.995
10.20
1.09
1.00
1.10
12.00
ppm


9
149.521
141.062
140.147
136.259
130.123
129.220
128.032
127.702
127.171
126.397
119.465
83.397
77.425
77.000
76.579
24.537
24.302
ppm


7
7.407
7.403
7.400
7.394
7.382
7.379
7.378
7.374
7.367
7.362
7.352
7.348
7.346
7.340
7.331
7.325
7.322
7.319
7.309
7.300
7.295
7.294
7.289
7.284
7.278
7.265
7.260
7.256
7.251
7.245
7.237
7.229
7.219
7.214
5.695
5.663
5.629
4.956
4.950
4.948
4.933
4.929
4.923
4.899
4.894
4.889
4.877
3.217
3.212
3.207
3.196
3.191
3.186
3.174
1.026
1.000
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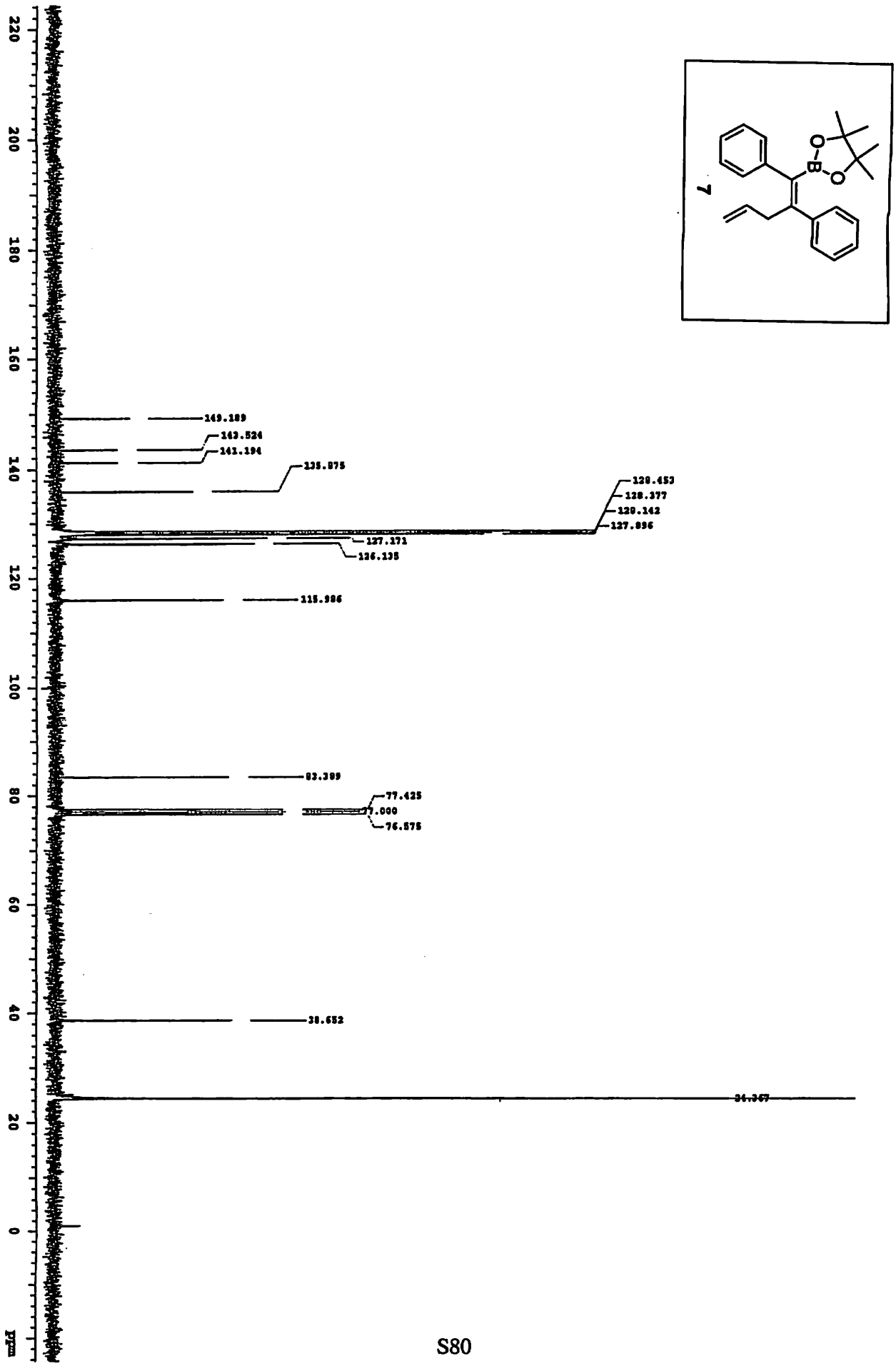
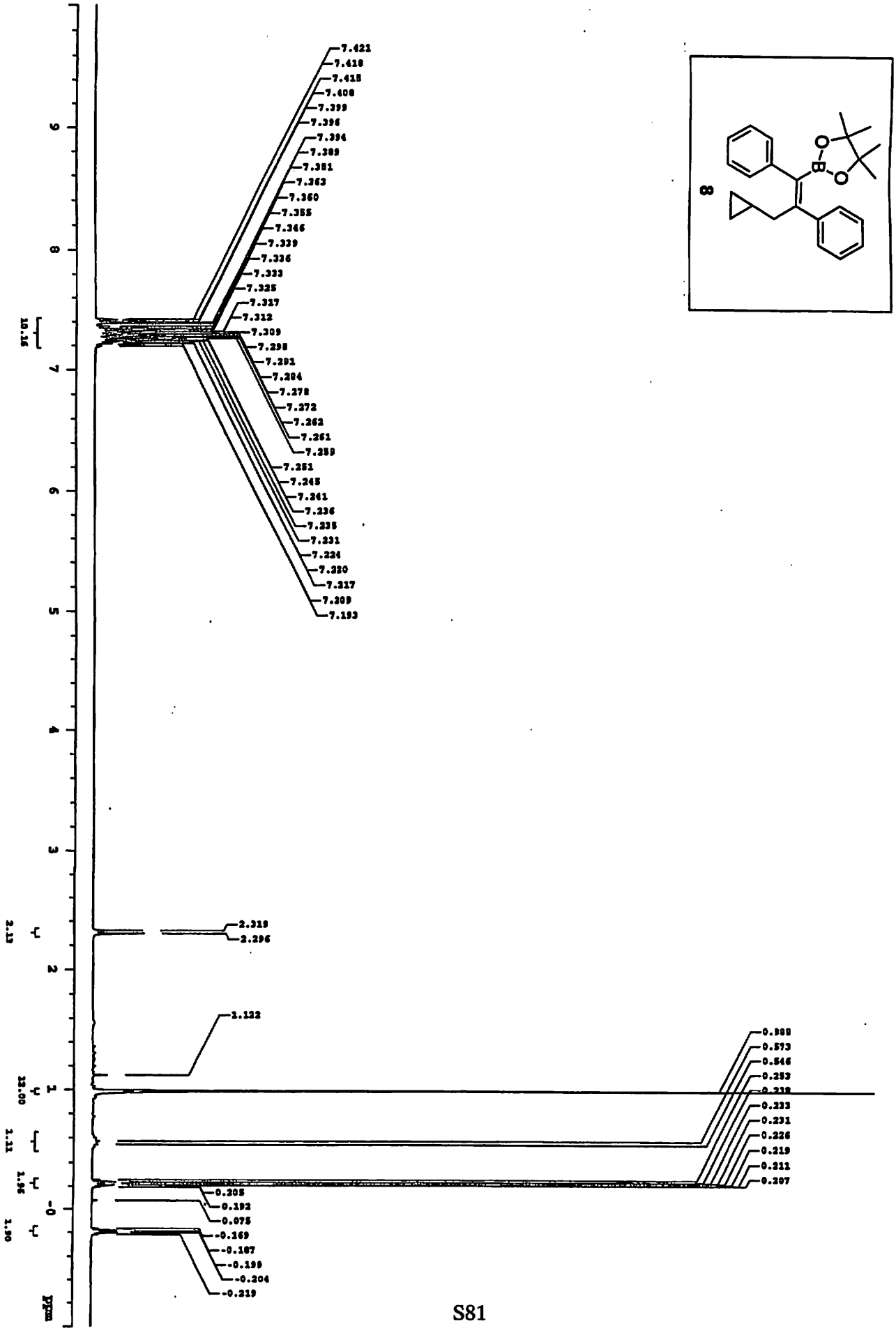
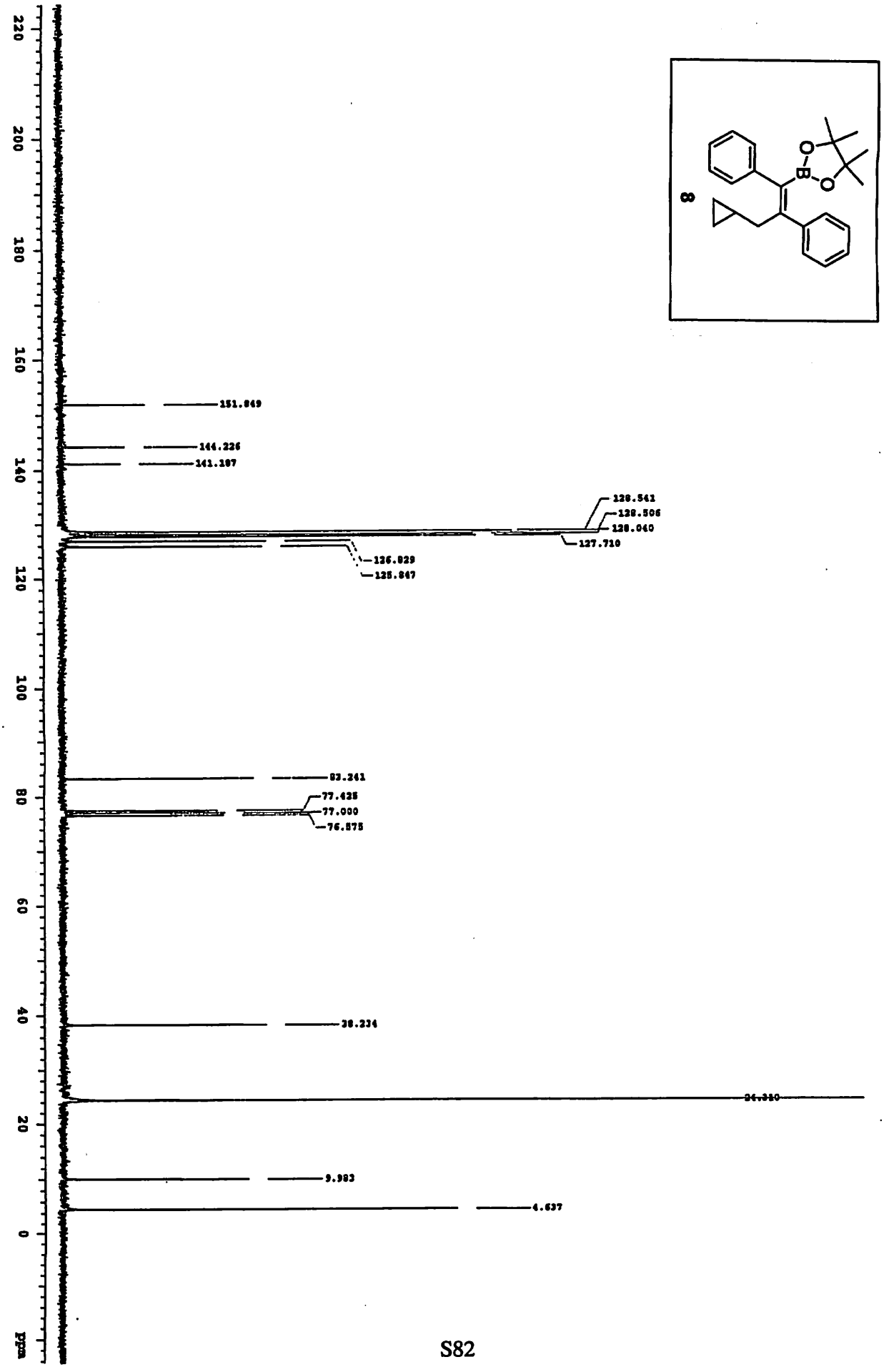
10.30
1.00
1.99
2.15
11.89
ppm


7
149.189
143.524
141.194
135.875
128.453
128.377
128.142
127.896
127.171
126.135
115.986
83.389
77.425
77.000
76.575
38.652
24.367
ppm


8
7.421
7.418
7.415
7.408
7.399
7.396
7.394
7.389
7.381
7.363
7.360
7.355
7.346
7.339
7.336
7.333
7.325
7.317
7.312
7.309
7.298
7.291
7.284
7.278
7.272
7.262
7.261
7.259
7.251
7.245
7.241
7.236
7.235
7.231
7.224
7.220
7.217
7.209
7.193
2.319
2.296
1.122
0.205
0.192
0.075
-0.169
-0.187
-0.199
-0.204
-0.219
ppm


8
151.849
144.226
141.197
128.541
128.506
128.040
127.710
126.829
125.847
83.241
77.425
77.000
76.575
38.234
24.310
9.983
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140
120
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80
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40
20
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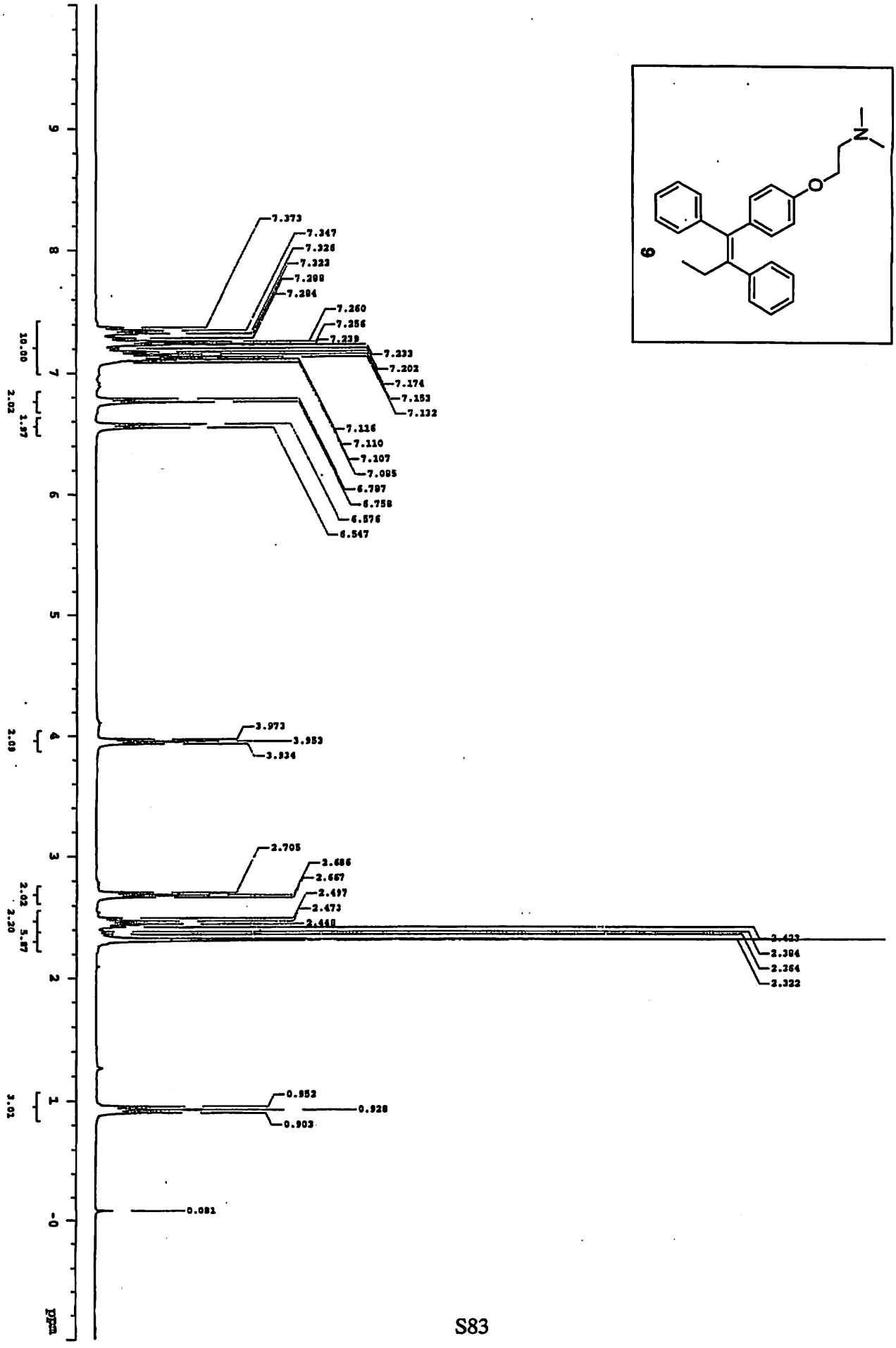
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7.323
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7.256
7.239
7.233
7.202
7.174
7.153
7.132
7.116
7.110
7.107
7.085
6.787
6.758
6.576
6.547
3.973
3.953
3.934
2.705
2.686
2.667
2.497
2.473
2.448
2.423
2.384
2.364
2.322
0.952
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2.09
2.03
2.20
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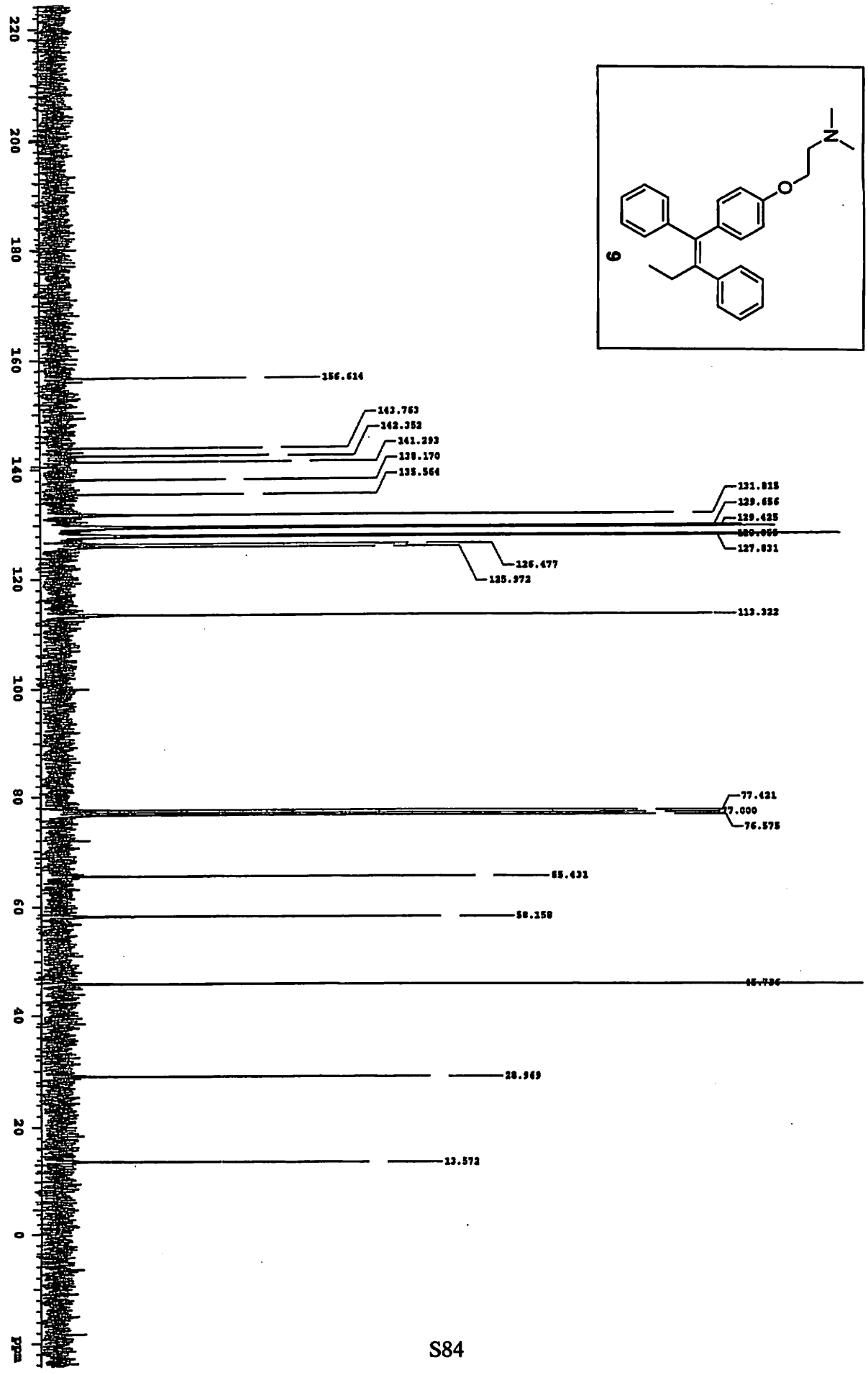
3.01
ppm


6
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113.322
77.421
77.000
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65.431
58.158
45.736
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ppm