

Intermolecular Radical Carboaminohydroxylation of Olefins with Aryl Diazonium Salts and TEMPO

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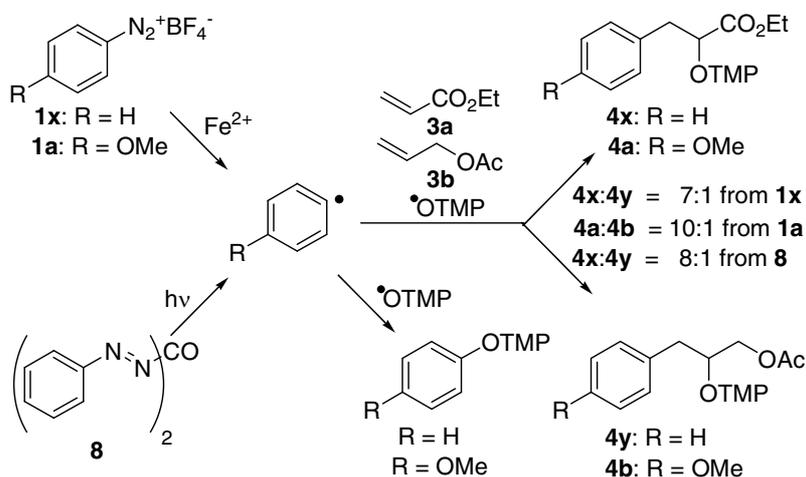
General experimental

Solvents and reagents were degassed with argon prior to use in radical reactions. Infra-red spectra were recorded on a Fourier transform IR spectrometer. ¹H NMR spectra were recorded on 250, 360 and 500 MHz spectrometers using CDCl₃, CD₃OD, CD₃CN and C₆D₆ as solvents referenced to TMS (0 ppm), CHCl₃ (7.26 ppm), CHD₂OD (3.31 ppm), CHD₂CN (1.94 ppm) or C₆HD₅ (7.15 ppm). Chemical shifts are reported in parts per million (ppm). Coupling constants are in Hertz (*J* Hz). The following abbreviations are used for the description of signals: s (singlet), d (doublet), dd (double doublet), t (triplet), q (quadruplet), m (multiplet). ¹³C NMR spectra were recorded at 62.9 and 90.6 MHz in CDCl₃, CD₃OD, CD₃CN and C₆D₆ using CDCl₃ (77.0 ppm), CD₃OD (49.5 ppm), CD₃CN (1.24 ppm) and C₆D₆ (128.0 ppm) as standard. Chemical shifts are given in parts per million (ppm). ¹⁹F NMR spectra were recorded at 235.3 MHz using CFCl₃ (0 ppm) as standard. Mass spectra were recorded using electron impact (EI). Analytical TLC was carried out on Merck silica gel plates using short wave (254 nm) UV light and KMnO₄ to visualise components. Silica gel (Kieselgel 60, 40-63 μm, Merck) was used for flash column chromatography.

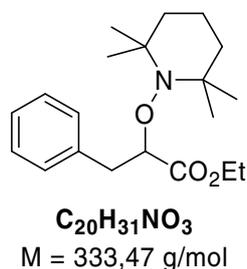
Competition experiments

In the competition experiments, the aryl diazonium salt (1mmol) was decomposed with $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ (3 mmol) in the presence of ethyl acrylate (10 mmol), allyl acetate (10 mmol) and TEMPO (3 mmol) in DMSO/water (5:1). After addition of ascorbic acid, aqueous work-up and removal of excess olefin under reduced pressure, the product mixture was analyzed by $^1\text{H-NMR}$.

Similar results were obtained from the photochemical decomposition of bisphenyl carbodiazone (**8**) (1 mmol) in the presence of ethyl acrylate (10 mmol), allyl acetate (10 mmol) and TEMPO (3 mmol) in CH_2Cl_2 (5 mL), although TEMPO-trapping of the aryl radical occurred to an increased extent.



3-Phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-propionic acid ethyl ester (**4x**)



Light brown oil.

R_f : 0.70 (100% CH_2Cl_2)

$^1\text{H-NMR}$: (360 MHz, CDCl_3): $\delta = 1.02$ (t, $^3J = 7.2$ Hz, 3H), 1.00–1.10 (m, 2H), 1.13 (s, 6H), 1.25 (s, 6H), 1.35–1.58 (m, 4H), 2.99 (dd, $^3J = 10.4$ Hz, $^2J = 13.0$

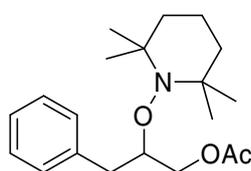
Hz, 1H), 3.27 (dd, $^3J = 5.4$ Hz, $^2J = 13.0$ Hz, 1H), 3.94 (q, $^3J = 7.2$ Hz, 2H), 4.45 (dd, $^3J = 5.4$ Hz, $^3J = 10.4$ Hz, 1H), 7.13–7.26 (m, 5H).

$^{13}\text{C-NMR}$: (90.6 MHz, CDCl_3): $\delta = 13.8$ (CH_3), 17.1 (CH_2), 20.1 (CH_3), 20.2 (CH_3), 33.0 (CH_3), 33.6 (CH_3), 39.8 (CH_2), 40.3 (CH_2), 59.3 (C_q), 60.0 (CH_2), 60.7 (C_q), 86.7 (CH), 126.5 (CH), 128.2 ($2\times\text{CH}$), 129.4 ($2\times\text{CH}$), 136.1 (C_q), 172.7 (C_q).

ESI-MS: $m/z = 334$ [$\text{M}^+ + \text{H}$].

HR-ESI-MS: $\text{C}_{20}\text{H}_{32}\text{NO}_3$ [$\text{M}^+ + \text{H}$] calcd.: 334.2377, found.: 334.2368.

Acetic acid 3-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-propyl ester (4y)



$\text{C}_{20}\text{H}_{31}\text{NO}_3$
M = 333,47 g/mol

Colorless oil.

R_f : 0.50 (100% CH_2Cl_2)

$^1\text{H-NMR}$: (360 MHz, CDCl_3): $\delta = 1.03$ (s, 3H), 1.10 (s, 9H), 1.20–1.60 (m, 6H), 2.06 (s, 3H), 2.76 (dd, $^3J = 7.2$ Hz, $^2J = 13.3$ Hz, 1H), 3.13 (dd, $^3J = 5.0$ Hz, $^2J = 13.3$ Hz, 1H), 4.09–4.20 (m, 3H), 7.18–7.29 (m, 5H).

$^{13}\text{C-NMR}$: (90.6 MHz, CDCl_3): $\delta = 14.4$ (CH_2), 17.5 (CH_3), 17.7 (CH_3), 18.2 (CH_3), 30.9 (CH_3), 31.4 (CH_3), 34.5 (CH), 37.5 ($2\times\text{CH}_2$), 57.0 (C_q), 57.4 (C_q), 61.3 (CH_2), 77.9 (CH), 123.3 (CH), 125.4 ($2\times\text{CH}$), 126.7 ($2\times\text{CH}$), 135.7 (C_q), 168.0 (C_q).

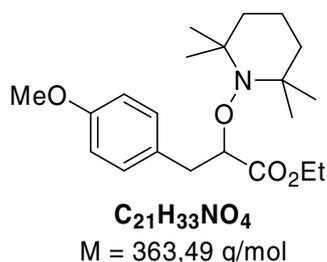
APCI-MS: $m/z = 334$ [$\text{M}^+ + \text{H}$].

HR-APCI-MS: $\text{C}_{20}\text{H}_{32}\text{NO}_3$ [$\text{M}^+ + \text{H}$] calcd.: 334.2377, found.: 334.2374.

General procedure

To a degassed 2:1 mixture of DMSO and water (3 mL) under argon were added the olefin (3 mmol for activated, 10 mmol for nonactivated substrates), $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ (834 mg, 3 mmol) and TEMPO (313 mg, 2 mmol). A solution of the arenediazonium salt (1 mmol) in 2:1 DMSO-water (1 mL) was added dropwise over a period of 10 to 15 min and the resulting mixture was left to stir at r.t. for another 10 min before ascorbic acid (528 mg, 3 mmol) was added. After 10 more min, the mixture was diluted with water (50 mL) and extracted with Et_2O (3×30 mL). The combined organic phases were washed with satd. NaCl and dried over Na_2SO_4 . Concentration and purification by column chromatography furnished the carboaminohydroxylation products. Solvent mixtures for purification are given with the R_f values. Products were obtained as light brown oils or solids.

3-(4-Methoxy-phenyl)-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-propionic acid ethyl ester (4a)



Light brown solid.

m.p.: 65-66 °C

R_f: 0.50 (100% CH₂Cl₂)

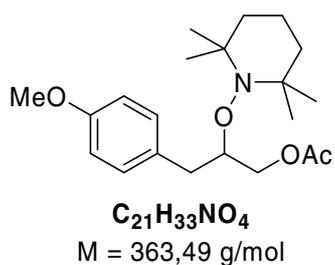
¹H-NMR: (360 MHz, CDCl₃): δ = 1.04 (s, 3H), 1.05 (t, ³J = 7.2 Hz, 3H), 1.13 (s, 6H), 1.20–1.55 (m, 6H), 1.25 (s, 3H), 2.93 (dd, ³J = 10.4 Hz, ²J = 13.3 Hz, 1H), 3.20 (dd, ³J = 5.3 Hz, ²J = 13.3 Hz, 1H), 3.76 (s, 3H), 3.95 (dq, J = 0.8 Hz, ³J = 7.2 Hz, 2H), 4.39 (dd, ³J = 5.3 Hz, ³J = 10.4 Hz, 1H), 6.78 (d, ³J = 8.8 Hz, 2H), 7.07 (d, ³J = 8.8 Hz, 2H).

¹³C-NMR: (90.6 MHz, CDCl₃): δ = 13.9 (CH₃), 17.1 (CH₂), 20.0 (CH₃), 20.2 (CH₃), 33.0 (CH₃), 33.5 (CH₃), 37.7 (CH₂), 40.3 (2×CH₂), 55.2 (CH₃), 59.4 (C_q), 60.0 (CH₂), 60.4 (C_q), 86.8 (CH), 113.7 (2×CH), 128.0 (C_q), 130.4 (2×CH), 158.3 (C_q), 172.8 (C_q).

ESI-MS: *m/z* = 364 [M⁺+H].

HR-ESI-MS: C₂₁H₃₄NO₄ [M⁺+H] calcd.: 364.2482, found.: 364.2472.

Acetic acid 3-(4-methoxy-phenyl)-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-propyl ester (4b)



Light brown oil.

R_f: 0.35 (100% CH₂Cl₂)

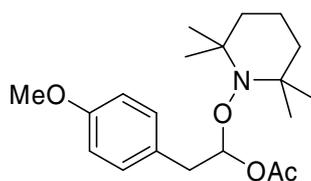
¹H-NMR: (500 MHz, CDCl₃): δ = 1.03 (s, 3H), 1.11 (s, 6H), 1.14 (s, 3H), 1.25–1.35 (m, 1H), 1.35–1.60 (m, 5H), 2.07 (s, 3H), 2.71 (dd, ³*J* = 7.8 Hz, ²*J* = 13.8 Hz, 1H), 3.07 (dd, ³*J* = 5.3 Hz, ²*J* = 13.8 Hz, 1H), 3.77 (s, 3H), 4.10–4.19 (m, 3H), 6.81 (d, ³*J* = 8.8 Hz, 2H), 7.11 (d, ³*J* = 8.8 Hz, 2H).

¹³C-NMR: (90.6 MHz, CDCl₃): δ = 17.0 (CH₂), 20.1 (CH₃), 20.3 (CH₃), 20.7 (CH₃), 33.5 (CH₃), 34.0 (CH₃), 36.1 (CH₂), 40.1 (2×CH₂), 55.0 (CH₃), 59.6 (C_q), 60.1 (C_q), 63.9 (CH₂), 80.7 (CH), 113.5 (2×CH), 130.2 (C_q), 130.2 (2×CH), 157.8 (C_q), 170.7 (C_q).

APCI-MS: *m/z* = 364 [M⁺+H].

HR-APCI-MS: C₂₁H₃₄NO₄ [M⁺+H] calcd.: 364.2482, found.: 334.2477.

Acetic acid 2-(4-methoxy-phenyl)-1-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester (4c)



C₂₀H₃₁NO₄
M = 349,46 g/mol

Light yellow oil.

R_f: 0.50 (100% CH₂Cl₂)

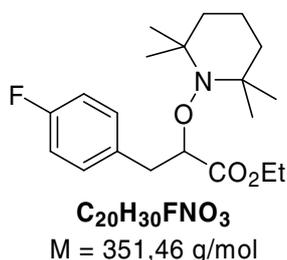
¹H-NMR: (360 MHz, CDCl₃): δ = 1.00 (s, 3H), 1.04 (s, 3H), 1.08 (s, 3H), 1.12 (s, 3H), 1.22–1.63 (m, 6H), 1.96 (s, 3H), 2.90 (dd, ³*J* = 5.4 Hz, ²*J* = 14.0 Hz, 1H), 2.99 (dd, ³*J* = 5.4 Hz, ²*J* = 14.0 Hz, 1H), 3.78 (s, 3H), 6.29 („t“, ³*J* = 5.4 Hz, 1H), 6.81 (d, ³*J* = 7.2 Hz, 2H), 7.16 (d, ³*J* = 7.2 Hz, 2H).

¹³C-NMR: (90.6 MHz, CDCl₃): δ = 17.6 (CH₂), 20.1 (CH₃), 20.4 (CH₃), 21.3 (CH₃), 32.9 (CH₃), 33.7 (CH₃), 39.1 (CH₂), 40.0 (CH₂), 40.2 (CH₂), 55.2 (CH₃), 59.1 (C_q), 60.8 (C_q), 101.2 (CH), 113.5 (2×CH), 127.7 (C_q), 131.0 (2×CH), 158.3 (C_q), 169.9 (C_q).

APCI-MS: *m/z* = 350 [M⁺+H].

HR-APCI-MS: C₂₀H₃₂NO₄ [M⁺+H] calcd.: 350.2325, found.: 350.2319.

**3-(4-Fluoro-phenyl)-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-propionic acid ethyl ester
(4d)**



Light brown solid.

m.p.: 60-61 °C

R_f: 0.70 (100% CH₂Cl₂)

¹H-NMR: (250 MHz, CDCl₃): δ = 1.03 (s, 3H), 1.04 (t, ³*J* = 7.3 Hz, 3H), 1.12 (s, 6H), 1.20–1.55 (m, 6H), 1.23 (s, 3H), 2.96 (dd, ³*J* = 10.3 Hz, ²*J* = 13.3 Hz, 1H), 3.22 (dd, ³*J* = 5.5 Hz, ²*J* = 13.3 Hz, 1H), 3.95 (q, ³*J* = 7.3 Hz, 2H), 4.40 (dd, ³*J* = 5.5 Hz, ³*J* = 10.3 Hz, 1H), 6.93 (dd, ³*J*_{HF} = 8.8 Hz, ³*J* = 8.8 Hz, 2H), 7.11 (dd, ⁴*J*_{HF} = 5.5 Hz, ³*J* = 8.8 Hz, 2H).

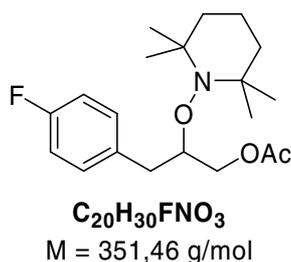
¹³C-NMR: (62.9 MHz, CDCl₃): δ = 13.9 (CH₃), 17.0 (CH₂), 20.0 (CH₃), 20.2 (CH₃), 33.0 (CH₃), 33.6 (CH₃), 37.7 (CH₂), 40.2 (2×CH₂), 59.4 (C_q), 60.1 (CH₂), 60.4 (C_q), 86.5 (d, ⁵*J*_{CF} = 1.3 Hz, CH), 115.0 (d, ²*J*_{CF} = 21.3 Hz, 2×CH), 130.9 (d, ³*J*_{CF} = 7.9 Hz, 2×CH), 131.8 (d, ⁴*J*_{CF} = 3.3 Hz, C_q), 161.7 (d, ¹*J*_{CF} = 244.6 Hz, C_q), 172.6 (C_q).

¹⁹F-NMR: (235.3 MHz, CDCl₃): δ = - 116.9.

ESI-MS: *m/z* = 352 [M⁺+H].

HR-ESI-MS: C₂₀H₃₁FNO₃ [M⁺+H] calcd.: 352.2282, found.: 352.2273.

**Acetic acid 3-(4-fluoro-phenyl)-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-propyl ester
(4e)**



Light brown oil.

R_f : 0.50 (100% CH_2Cl_2)

$^1\text{H-NMR}$: (250 MHz, CDCl_3): δ = 1.01 (s, 3H), 1.07 (s, 3H), 1.09 (s, 6H), 1.20–1.60 (m, 6H), 2.07 (s, 3H), 2.75 (dd, 3J = 6.8 Hz, 2J = 13.8 Hz, 1H), 3.05 (dd, 3J = 5.5 Hz, 2J = 13.8 Hz, 1H), 4.06–4.25 (m, 3H), 6.96 (dd, $^3J_{\text{HF}}$ = 8.8 Hz, 3J = 8.8 Hz, 2H), 7.16 (dd, $^4J_{\text{HF}}$ = 5.5 Hz, 3J = 8.8 Hz, 2H).

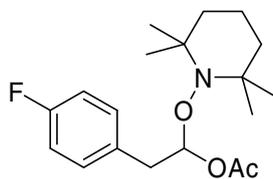
$^{13}\text{C-NMR}$: (62.9 MHz, CDCl_3): δ = 17.2 (CH_2), 20.3 (CH_3), 20.5 (CH_3), 20.9 (CH_3), 33.7 (CH_3), 34.2 (CH_3), 36.6 (CH_2), 40.3 ($2\times\text{CH}_2$), 59.8 (C_q), 60.4 (C_q), 64.0 (CH_2), 80.5 (d, $^5J_{\text{CF}}$ = 1.3 Hz, CH), 115.0 (d, $^2J_{\text{CF}}$ = 21.1 Hz, $2\times\text{CH}$), 130.9 (d, $^3J_{\text{CF}}$ = 7.8 Hz, $2\times\text{CH}$), 134.1 (d, $^4J_{\text{CF}}$ = 3.2 Hz, C_q), 161.5 (d, $^1J_{\text{CF}}$ = 243.9 Hz, C_q), 170.8 (C_q).

$^{19}\text{F-NMR}$: (235.3 MHz, CDCl_3): δ = - 117.7.

APCI-MS: m/z = 352 [$\text{M}^+\text{+H}$].

HR-APCI-MS: $\text{C}_{20}\text{H}_{31}\text{FNO}_3$ [$\text{M}^+\text{+H}$] calcd.: 352.2282, found.: 352.2276.

Acetic acid 2-(4-fluoro-phenyl)-1-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester (4f)



$\text{C}_{19}\text{H}_{28}\text{FNO}_3$

$M = 337,43 \text{ g/mol}$

Light brown oil.

R_f : 0.60 (100% CH_2Cl_2)

$^1\text{H-NMR}$: (250 MHz, CDCl_3): δ = 0.99 (s, 3H), 1.02 (s, 3H), 1.07 (s, 3H), 1.11 (s, 3H), 1.20–1.60 (m, 6H), 1.96 (s, 3H), 2.93 (dd, 3J = 5.5 Hz, 2J = 14.1 Hz, 1H), 3.01 (dd, 3J = 5.5 Hz, 2J = 14.1 Hz, 1H), 6.29 (,t“, 3J = 5.5 Hz, 1H), 6.96 (dd, $^3J_{\text{HF}}$ = 8.8 Hz, 3J = 8.8 Hz, 2H), 7.21 (dd, $^4J_{\text{HF}}$ = 5.5 Hz, 3J = 8.8 Hz, 2H).

$^{13}\text{C-NMR}$: (62.9 MHz, CDCl_3): δ = 17.0 (CH_2), 20.1 (CH_3), 20.4 (CH_3), 21.3 (CH_3), 32.9 (CH_3), 33.8 (CH_3), 39.2 (CH_2), 40.0 (CH_2), 40.2 (CH_2), 59.2 (C_q), 60.8 (C_q), 100.8 (d, $^5J_{\text{CF}}$ = 1.3 Hz, CH), 114.9 (d, $^2J_{\text{CF}}$ = 21.2 Hz, $2\times\text{CH}$), 131.4

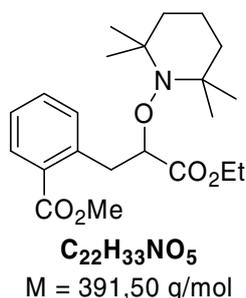
(d, $^4J_{CF} = 3.3$ Hz, C_q), 131.5 (d, $^3J_{CF} = 7.9$ Hz, $2\times CH$), 161.8 (d, $^1J_{CF} = 244.4$ Hz, C_q), 169.9 (C_q).

^{19}F -NMR: (235.3 MHz, $CDCl_3$): $\delta = -117.0$.

EI-MS: m/z (%) = 337 (0.5) [M^+], 199 (22), 184 (25), 157 (84), 142 (100), 109 (18), 83 (17), 69 (15), 55 (21).

HR-ESI-MS: $C_{19}H_{29}FNO_3$ [$M^+ + H$] calcd.: 338.2126, found.: 338.2118.

2-[2-Ethoxycarbonyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl]-benzoic acid methyl ester (4g)



Light yellow oil.

R_f : 0.50 (1:100 acetone- CH_2Cl_2)

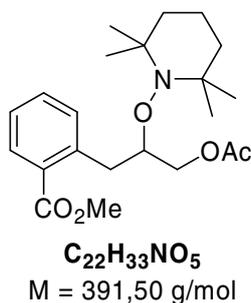
1H -NMR: (250 MHz, $CDCl_3$): $\delta = 1.00$ (t, $^3J = 7.1$ Hz, 3H), 1.03 (s, 3H), 1.04 (s, 3H), 1.11 (s, 6H), 1.20–1.55 (m, 6H), 3.18 (dd, $^3J = 8.6$ Hz, $^2J = 12.9$ Hz, 1H), 3.70–3.95 (m, 3H), 3.88 (s, 3H), 4.59 (dd, $^3J = 7.2$ Hz, $^3J = 8.6$ Hz, 1H), 7.22–7.29 (m, 2H), 7.35–7.42 (m, 1H), 7.84–7.87 (m, 1H).

^{13}C -NMR: (90.6 MHz, $CDCl_3$): $\delta = 13.8$ (CH_3), 17.1 (CH_2), 20.1 (CH_3), 20.2 (CH_3), 33.0 (CH_3), 33.5 (CH_3), 37.1 (CH_2), 40.3 ($2\times CH_2$), 52.0 (CH_3), 59.4 (C_q), 59.9 (CH_2), 60.3 (C_q), 85.4 (CH), 126.7 (CH), 130.4 (C_q), 130.6 (CH), 131.6 (CH), 132.7 (CH), 137.8 (C_q), 167.7 (C_q), 172.7 (C_q).

ESI-MS: $m/z = 392$ [$M^+ + H$].

HR-ESI-MS: $C_{22}H_{34}NO_5$ [$M^+ + H$] calcd.: 392.2431, found.: 392.2418.

**2-[3-Acetoxy-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-propyl]-benzoic acid methyl ester
(4h)**



Light brown oil.

R_f: 0.35 (1:100 acetone–CH₂Cl₂)

¹H-NMR: (500 MHz, CDCl₃): δ = 0.80 (s, 3H), 0.85 (s, 3H), 1.05 (s, 3H), 1.09 (s, 3H), 1.20–1.27 (m, 2H), 1.36–1.52 (m, 4H), 2.03 (s, 3H), 3.21 (dd, ³*J* = 8.0 Hz, ²*J* = 13.3 Hz, 1H), 3.30 (dd, ³*J* = 5.2 Hz, ²*J* = 13.3 Hz, 1H), 3.84 (s, 3H), 4.16 (dd, ³*J* = 5.0 Hz, ²*J* = 11.0 Hz, 1H), 4.22–4.27 (m, 1H), 4.30 (dd, ³*J* = 3.5 Hz, ³*J* = 11.0 Hz, 1H), 7.22 („t“, ³*J* = 7.5 Hz, 1H), 7.32 (d, ³*J* = 7.5 Hz, 1H), 7.38 („t“, ³*J* = 7.5 Hz, 1H), 7.83 (d, ³*J* = 7.5 Hz, 1H).

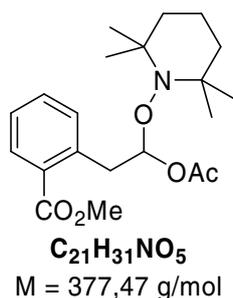
¹³C-NMR: (62.9 MHz, CDCl₃): δ = 17.0 (CH₂), 20.0 (CH₃), 20.3 (CH₃), 20.8 (CH₃), 33.2 (CH₃), 33.9 (CH₃), 35.7 (CH₂), 40.1 (CH₂), 40.3 (CH₂), 51.6 (CH₃), 59.3 (C_q), 60.2 (C_q), 64.7 (CH₂), 79.8 (CH), 126.0 (CH), 130.0 (C_q), 130.3 (CH), 131.2 (CH), 132.5 (CH), 140.3 (C_q), 167.8 (C_q), 170.7 (C_q).

EI-MS: *m/z* (%) = 391 (0.5) [M⁺+H], 236 (11), 235 (74), 176 (11), 175 (100), 161 (12), 157 (12), 156 (7), 143 (13), 142 (64), 131 (26), 114 (8), 91 (10), 83 (10).

ESI-MS: *m/z* = 392 [M⁺+H].

HR-ESI-MS: C₂₂H₃₄NO₅ [M⁺+H] calcd.: 392.2431, found.: 392.2418.

**2-[2-Acetoxy-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl]-benzoic acid methyl ester
(4i)**



Light yellow oil.

R_f : 0.5 (1:4 EtOAc–pentane)

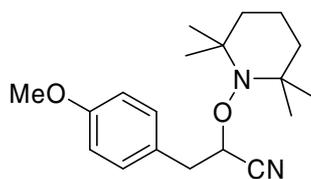
$^1\text{H-NMR}$: (250 MHz, CDCl_3): δ = 0.98 (s, 3H), 1.02 (s, 3H), 1.09 (s, 3H), 1.13 (s, 3H), 1.25–1.25 (m, 6H), 1.95 (s, 3H), 3.34 (dd, $^3J = 5.9$ Hz, $^2J = 13.3$ Hz, 1H), 3.62 (dd, $^3J = 5.9$ Hz, $^2J = 13.3$ Hz, 1H), 3.93 (s, 3H), 6.48 („t“, $^3J = 5.9$ Hz, 1H), 7.28–7.49 (m, 3H), 7.90 (dd, $^4J = 1.5$ Hz, $^3J = 7.8$ Hz, 1H).

$^{13}\text{C-NMR}$: (62.9 MHz, CDCl_3): δ = 17.0 (CH_2), 19.9 (CH_3), 20.2 (CH_3), 21.2 (CH_3), 32.7 (CH_3), 33.7 (CH_3), 37.6 (CH_2), 39.9 (CH_2), 40.1 (CH_2), 51.9 (CH_3), 59.0 (C_q), 60.5 (C_q), 99.7 (CH), 126.6 (CH), 130.3 (CH), 130.8 (C_q), 131.3 (CH), 133.0 (CH), 136.7 (C_q), 167.9 (C_q), 169.6 (C_q).

ESI-MS: $m/z = 378$ [$\text{M}^+\text{+H}$].

HR-ESI-MS: $\text{C}_{21}\text{H}_{32}\text{NO}_5$ [$\text{M}^+\text{+H}$] calcd.: 378.2275, found.: 378.2265.

3-(4-Methoxy-phenyl)-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-propionitrile (4j)



$\text{C}_{19}\text{H}_{28}\text{N}_2\text{O}_2$
M = 316,44 g/mol

Light yellow oil.

R_f : 0.70 (100% CH_2Cl_2)

$^1\text{H-NMR}$: (250 MHz, CDCl_3): δ = 1.09 (s, 6H), 1.13 (s, 3H), 1.20–1.60 (m, 6H), 1.27 (s, 3H), 3.06 (dd, $^3J = 7.2$ Hz, $^2J = 13.9$ Hz, 1H), 3.12 (dd, $^3J = 6.2$ Hz, $^2J = 13.9$ Hz, 1H), 3.80 (s, 3H), 4.74 (dd, $^3J = 6.2$ Hz, $^3J = 7.2$ Hz, 1H), 6.86 (d, $^3J = 8.8$ Hz, 2H), 7.22 (d, $^3J = 8.8$ Hz, 2H).

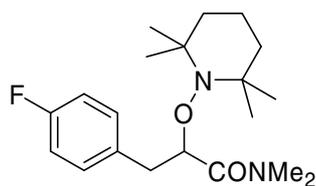
$^{13}\text{C-NMR}$: (62.9 MHz, CDCl_3): δ = 17.0 (CH_2), 20.3 (CH_3), 20.5 (CH_3), 33.6 (CH_3), 34.0 (CH_3), 38.5 (CH_2), 39.9 (CH_2), 40.0 (CH_2), 55.2 (CH_3), 59.9 (C_q), 61.0 (C_q), 75.3 (CH), 113.9 (2 \times CH), 119.3 (C_q), 126.7 (C_q), 130.8 (2 \times CH), 158.9 (C_q).

EI-MS: m/z (%) = 316 (1) [$\text{M}^+\text{+H}$], 301 (3), 160 (52), 159 (43), 156 (100), 144 (10), 123 (20), 121 (11), 116 (12), 89 (9), 69 (17).

ESI-MS: $m/z = 317 [M^+ + H]$.

HR-ESI-MS: $C_{19}H_{29}N_2O_2 [M^+ + H]$ calcd.: 317.2224, found.: 317.2216.

3-(4-Fluoro-phenyl)-*N,N*-dimethyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-propionamide (4k)



$C_{20}H_{31}FN_2O_2$
M= 350,47 g/mol

Light brown solid.

m.p.: 84-85°C

R_f : 0.70 (20:1 CH_2Cl_2 -MeOH)

1H -NMR: (360 MHz, $CDCl_3$): $\delta = 0.99$ (s, 3H), 1.11 (s, 3H), 1.13 (s, 3H), 1.20–1.60 (m, 6H), 1.24 (s, 3H), 2.77 (s, 3H), 2.78 (s, 3H), 3.06 (dd, $^3J = 10.1$ Hz, $^2J = 13.0$ Hz, 1H), 3.17 (dd, $^3J = 5.0$ Hz, $^2J = 13.0$ Hz, 1H), 4.75 (dd, $^3J = 5.0$ Hz, $^2J = 10.1$ Hz, 1H), 6.92 (dd, $^3J_{HF} = 8.6$ Hz, $^3J = 8.6$ Hz, 2H), 7.14 (dd, $^4J_{HF} = 5.4$ Hz, $^3J = 8.6$ Hz, 2H).

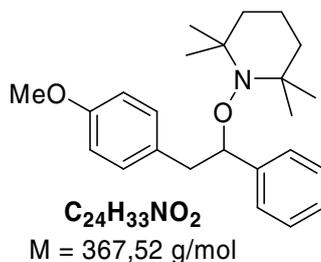
^{13}C -NMR: (90.6 MHz, $CDCl_3$): $\delta = 16.9$ (CH_2), 19.9 (CH_3), 20.2 (CH_3), 32.5 (CH_3), 33.3 (CH_3), 35.3 (CH_3), 37.0 (CH_3), 37.5 (CH_2), 40.1 (CH_2), 40.3 (CH_2), 59.2 (C_q), 60.4 (C_q), 80.0 (d, $^5J_{CF} = 1.3$ Hz, CH), 114.8 (d, $^2J_{CF} = 23.3$ Hz, 2 \times CH), 130.8 (d, $^3J_{CF} = 7.9$ Hz, 2 \times CH), 132.5 (d, $^4J_{CF} = 3.3$ Hz, C_q), 161.4 (d, $^1J_{CF} = 244.4$ Hz, C_q), 172.0 (C_q).

^{19}F -NMR: (235.3 MHz, $CDCl_3$): $\delta = -117.1$.

ESI-MS: $m/z = 351 [M^+ + H]$.

HR-ESI-MS: $C_{20}H_{32}FN_2O_2 [M^+ + H]$ calcd.: 351.2443, found.: 351.2435.

1-[2-(4-Methoxy-phenyl)-1-phenyl-ethoxy]-2,2,6,6-tetramethyl-piperidine (4l)



Light brown oil.

R_f: 0.70 (100% CH₂Cl₂)

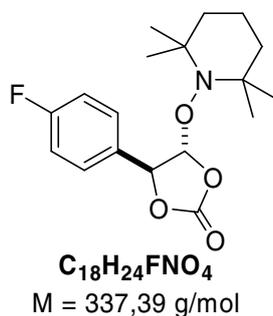
¹H-NMR: (360 MHz, CDCl₃): δ = 0.61 (s, 3H), 1.04 (s, 3H), 1.20 (s, 3H), 1.20–1.60 (m, 6H), 1.38 (s, 3H), 2.85 (dd, ³*J* = 10.1 Hz, ²*J* = 13.0 Hz, 1H), 3.55 (dd, ³*J* = 4.3 Hz, ²*J* = 13.0 Hz, 1H), 3.73 (s, 3H), 4.75 (dd, ³*J* = 4.3 Hz, ³*J* = 10.1 Hz, 1H), 6.66 (d, ³*J* = 8.6 Hz, 2H), 7.22 (d, ³*J* = 8.6 Hz, 2H), 7.07–7.10 (m, 2H), 7.16–7.22 (m, 3H).

¹³C-NMR: (90.6 MHz, CDCl₃): δ = 17.0 (CH₂), 20.4 (br, 2×CH₃), 34.3 (CH₃), 34.4 (CH₃), 40.5 (2×CH₂), 42.1 (CH₂), 55.1 (CH₃), 59.8 (br, 2×C_q), 88.8 (CH), 113.3 (2×CH), 126.9 (CH), 127.5 (2×CH), 128.1 (2×CH), 130.5 (C_q), 130.6 (2×CH), 142.8 (C_q), 157.7 (C_q).

ESI-MS: *m/z* = 368 [M⁺+H].

HR-ESI-MS: C₂₄H₃₄NO₂ [M⁺+H] calcd.: 368.2584, found.: 368.2574.

***trans*-4-(4-Methoxy-phenyl)-5-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-[1,3]dioxolan-2-one (4m)**



Colorless oil.

R_f: 0.70 (100% CH₂Cl₂)

¹H-NMR: (360 MHz, CDCl₃): δ = 0.87 (s, 3H), 1.13 (s, 6H), 1.20–1.60 (m, 6H), 1.27 (s, 3H), 3.06 (d, ³J = 3.2 Hz, 1H), 5.79 (d, ³J = 3.2 Hz, 1H), 7.12 (dd, ³J_{HF} = 8.6 Hz, ³J = 8.6 Hz, 2H), 7.32 (d, ⁴J_{HF} = 5.0 Hz, ³J = 8.6 Hz, 2H).

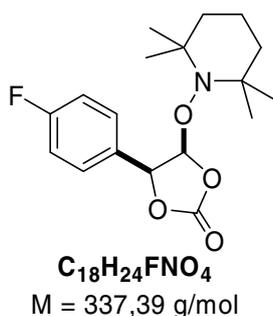
¹³C-NMR: (90.6 MHz, CDCl₃): δ = 16.8 (CH₂), 20.2 (CH₃), 20.4 (CH₃), 32.9 (CH₃), 33.7 (CH₃), 39.6 (CH₂), 40.1 (CH₂), 59.8 (C_q), 60.9 (C_q), 82.6 (CH), 110.4 (CH), 116.3 (d, ²J_{CF} = 23.3 Hz, 2×CH), 128.4 (d, ³J_{CF} = 8.7 Hz, 2×CH), 130.7 (d, ⁴J_{CF} = 3.4 Hz, C_q), 153.1 (C_q), 163.4 (d, ¹J_{CF} = 250.1 Hz, C_q).

¹⁹F-NMR: (235.3 MHz, CDCl₃): δ = - 111.1.

ESI-MS: *m/z* = 338 [M⁺+H].

HR-ESI-MS: C₁₈H₂₅FNO₄ [M⁺+H] calcd.: 338.1762, found.: 338.1758.

***cis*-4-(4-Methoxy-phenyl)-5-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-[1,3]dioxolan-2-one (4m')**



Colorless oil.

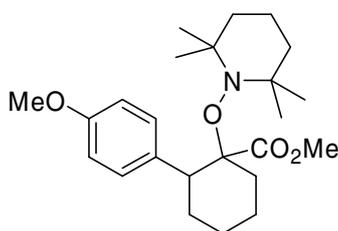
*R*_f: 0.45 (100% CH₂Cl₂)

¹H-NMR: (250 MHz, CDCl₃): δ = 0.42 (s, 3H), 0.82 (s, 3H), 0.97 (s, 3H) 1.20–1.60 (m, 6H), 1.25 (s, 3H), 5.65 (d, ³J = 6.3 Hz, 1H), 6.02 (d, ³J = 6.3 Hz, 1H), 7.11 (dd, ³J_{HF} = 8.8 Hz, ³J = 8.8 Hz, 2H), 7.40 (d, ⁴J_{HF} = 5.3 Hz, ³J = 8.8 Hz, 2H).

¹³C-NMR: (90.6 MHz, CDCl₃): δ = 16.8 (CH₂), 19.6 (CH₃), 20.7 (CH₃), 32.3 (CH₃), 34.0 (CH₃), 39.6 (CH₂), 40.0 (CH₂), 59.7 (C_q), 61.1 (C_q), 81.1 (CH), 104.7 (CH), 116.3 (d, ²J_{CF} = 22.0 Hz, 2×CH), 127.6 (d, ⁴J_{CF} = 3.4 Hz, C_q), 130.0 (d, ³J_{CF} = 8.5 Hz, 2×CH), 153.5 (C_q), 163.4 (d, ¹J_{CF} = 249.0 Hz, C_q).

¹⁹F-NMR: (235.3 MHz, CDCl₃): δ = - 111.9.

2-(4-Methoxy-phenyl)-1-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-cyclohexanecarboxylic acid methyl ester (4n)



C₂₄H₃₇NO₄
M = 403,55 g/mol

Colorless solid.

m.p. 123–124°C

R_f: 0.50 (1:1 CH₂Cl₂–pentane)

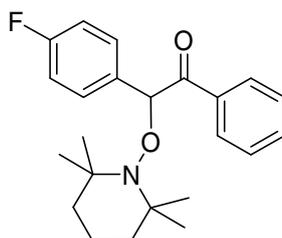
¹H-NMR: (360 MHz, CDCl₃): δ = 0.85 (s, 3H), 0.99 (s, 3H), 1.22 (s, 3H), 1.25–1.60 (m, 8H), 1.37 (s, 3H), 1.62–1.70 (m, 1H), 1.74–1.98 (m, 4H), 2.17–2.32 (m, 2H), 3.09 (dd, ³J = 3.2 Hz, ²J = 13.0 Hz, 1H), 3.41 (s, 3H), 3.80 (s, 3H), 6.78 (d, ³J = 8.8 Hz, 2H), 7.09 (d, ³J = 8.8 Hz, 2H).

¹³C-NMR: (90.6 MHz, CDCl₃): δ = 16.9 (CH₂), 20.2 (CH₃), 21.2 (CH₃), 24.1 (CH₂), 26.1 (CH₂), 30.0 (CH₂), 32.1 (CH₂), 33.0 (CH₃), 34.6 (CH₃), 40.9 (CH₂), 41.5 (CH₂), 50.1 (CH₃), 51.3 (CH), 55.1 (CH₃), 59.9 (C_q), 60.0 (C_q), 85.5 (C_q), 112.3 (2×CH), 129.8 (2×CH), 134.7 (C_q), 158.0 (C_q), 174.4 (C_q).

ESI-MS: *m/z* = 404 [M⁺+H].

HR-ESI -MS: C₂₄H₃₈NO₄ [M⁺+H] calcd.: 404.2796, found.: 404.2787.

2-(4-Fluoro-phenyl)-1-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethanone (5)



C₂₃H₂₈FNO₂
M = 369,47 g/mol

Light brown oil.

R_f: 0.50 (1:20 EtOAc–pentane)

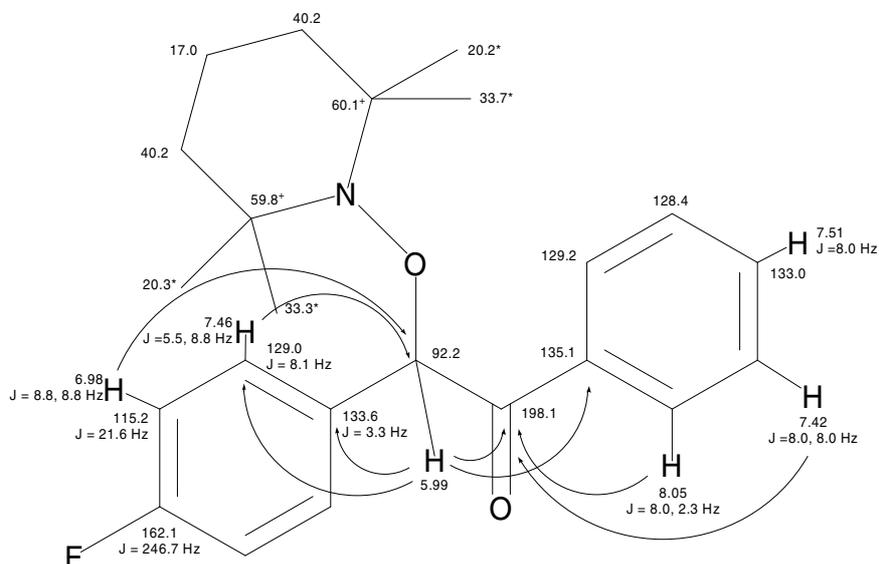
¹H-NMR: (250 MHz, CDCl₃): δ = 0.79 (s, 3H), 0.99 (s, 3H), 1.17 (s, 6H), 1.20–1.60 (m, 6H), 5.99 (s, 1H), 6.97 (dd, ³J_{HF} = 8.8 Hz, ³J = 8.8 Hz, 2H), 7.38–7.51 (m, 5H), 8.05 (dd, ⁴J_{HF} = 2.3 Hz, ³J = 8.8 Hz, 2H).

¹³C-NMR: (90.6 MHz, CDCl₃): δ = 16.9 (CH₂), 20.1 (CH₃), 20.2 (CH₃), 33.2 (CH₃), 33.6 (CH₃), 40.1 (2×CH₂), 59.6 (C_q), 60.0 (C_q), 92.0 (CH), 115.2 (d, ²J_{CF} = 21.6 Hz, 2×CH), 128.3 (2×CH), 128.8 (d, ³J_{CF} = 8.1 Hz, 2×CH), 129.0 (2×CH), 132.9 (C_q), 133.5 (d, ⁴J_{CF} = 3.3 Hz, C_q), 135.0 (C_q), 162.0 (d, ¹J_{CF} = 246.7 Hz, C_q), 198.1 (C_q).

¹⁹F-NMR: (235.3 MHz, CDCl₃): δ = – 115.0.

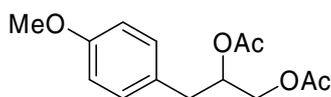
ESI-MS: *m/z* = 370 [M⁺+H].

Selected NOESY interactions for compound 5:



For NMR data of a related compound, see: *Tetrahedron Lett.* **1983**, 4075.

Acetic acid 1-acetoxymethyl-2-(4-methoxy-phenyl)-ethyl ester (6)



C₁₄H₁₈O₅
M = 266,29 g/mol

Compound **6** was prepared from **4b** (0.20 mmol) by treatment with Zn powder (500 mg) in AcOH (5 mL) and Ac₂O (3 mL) at 100 °C for 2 h.

Colorless oil.

R_f: 0.65 (1:2 EtOAc–pentane)

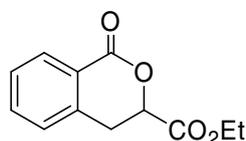
¹H-NMR: (250 MHz, CDCl₃): δ = 2.02 (s, 3H), 2.07 (s, 3H), 2.81 (dd, ³J = 7.0 Hz, ²J = 14.0 Hz, 1H), 2.88 (dd, ³J = 6.8 Hz, ²J = 14.0 Hz, 1H), 3.78 (s, 3H), 3.98 (dd, ³J = 6.3 Hz, ³J = 11.8 Hz, 1H), 4.22 (dd, ³J = 3.8 Hz, ³J = 11.8 Hz, 1H), 5.16–5.26 (m, 1H), 6.82 (d, ³J = 8.8 Hz, 2H), 7.11 (d, ³J = 8.8 Hz, 2H).

¹³C-NMR: (62.9 MHz, CDCl₃): δ = 20.8 (CH₃), 21.0 (CH₃), 36.1 (CH₂), 55.2 (CH₃), 64.2 (CH₂), 72.2 (CH), 113.9 (2×CH), 128.2 (C_q), 130.2 (2×CH), 158.5 (C_q), 170.3 (C_q), 170.7 (C_q).

EI-MS: *m/z* (%) = 266 (1) [M⁺], 206 (38), 165 (9), 164 (25), 163 (33), 147 (14), 135 (9), 121 (100), 108 (9), 91 (9).

HR-EI-MS: C₁₄H₁₈O₅ [M⁺] calcd.: 266.1154, found.: 266.1148.

1-Oxo-isochroman-3-carboxylic acid ethyl ester (7)



C₁₂H₁₂O₄
M = 220,22 g/mol

Compound **7** was prepared from **4g** (0.25 mmol) by treatment with Zn powder (500 mg) in AcOH (5 mL) at 100 °C for 2 h.

Colorless solid.

m.p.: 86-87 °C

*R*_f: 0.40 (1:3 EtOAc–pentane)

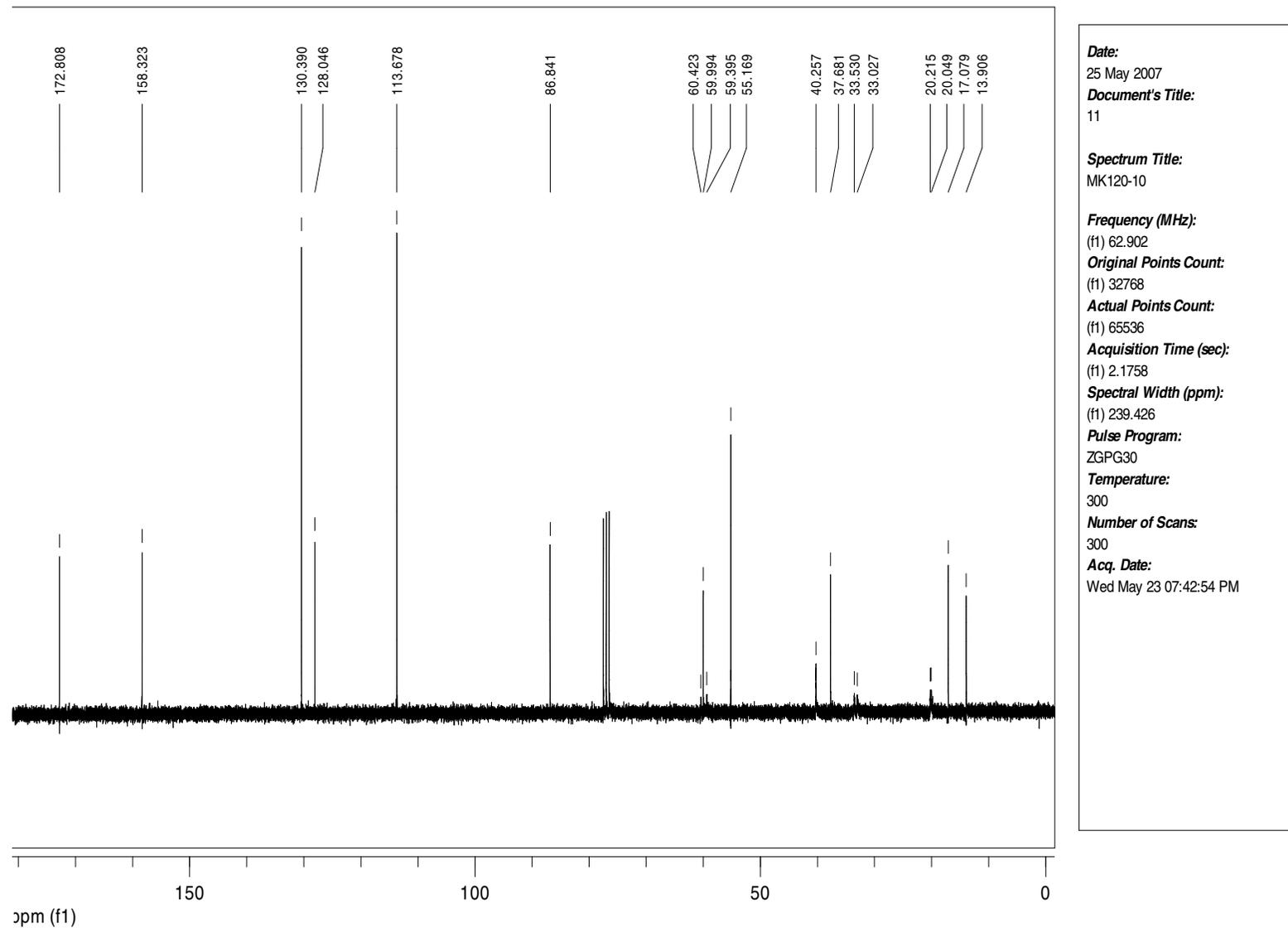
¹H-NMR: (250 MHz, CDCl₃): δ = 1.16 (t, ³*J* = 7.1 Hz, 3H), 3.27 (dd, ³*J* = 5.4 Hz, ²*J* = 16.5 Hz, 1H), 3.44 (dd, ³*J* = 5.4 Hz, ²*J* = 16.5 Hz, 1H), 4.16 (dd, ³*J* = 2.5 Hz, ³*J* = 7.1 Hz, 2H), 5.14 (t, ³*J* = 5.4 Hz, 1H), 7.24 (d, ³*J* = 7.5 Hz, 1H), 7.39 (t, ³*J* = 7.5 Hz, 1H), 7.53 (dt, ⁴*J* = 1.3 Hz, ³*J* = 7.5 Hz, 1H), 8.08 (d, ³*J* = 7.5 Hz, 1H).

¹³C-NMR: (90.6 MHz, CDCl₃): δ = 13.9 (CH₃), 30.2 (CH₂), 62.0 (CH₂), 74.9 (CH), 124.9 (C_q), 127.4 (CH), 128.1 (CH), 130.1 (CH), 133.9 (CH), 136.2 (C_q), 163.4 (C_q), 168.9 (C_q).

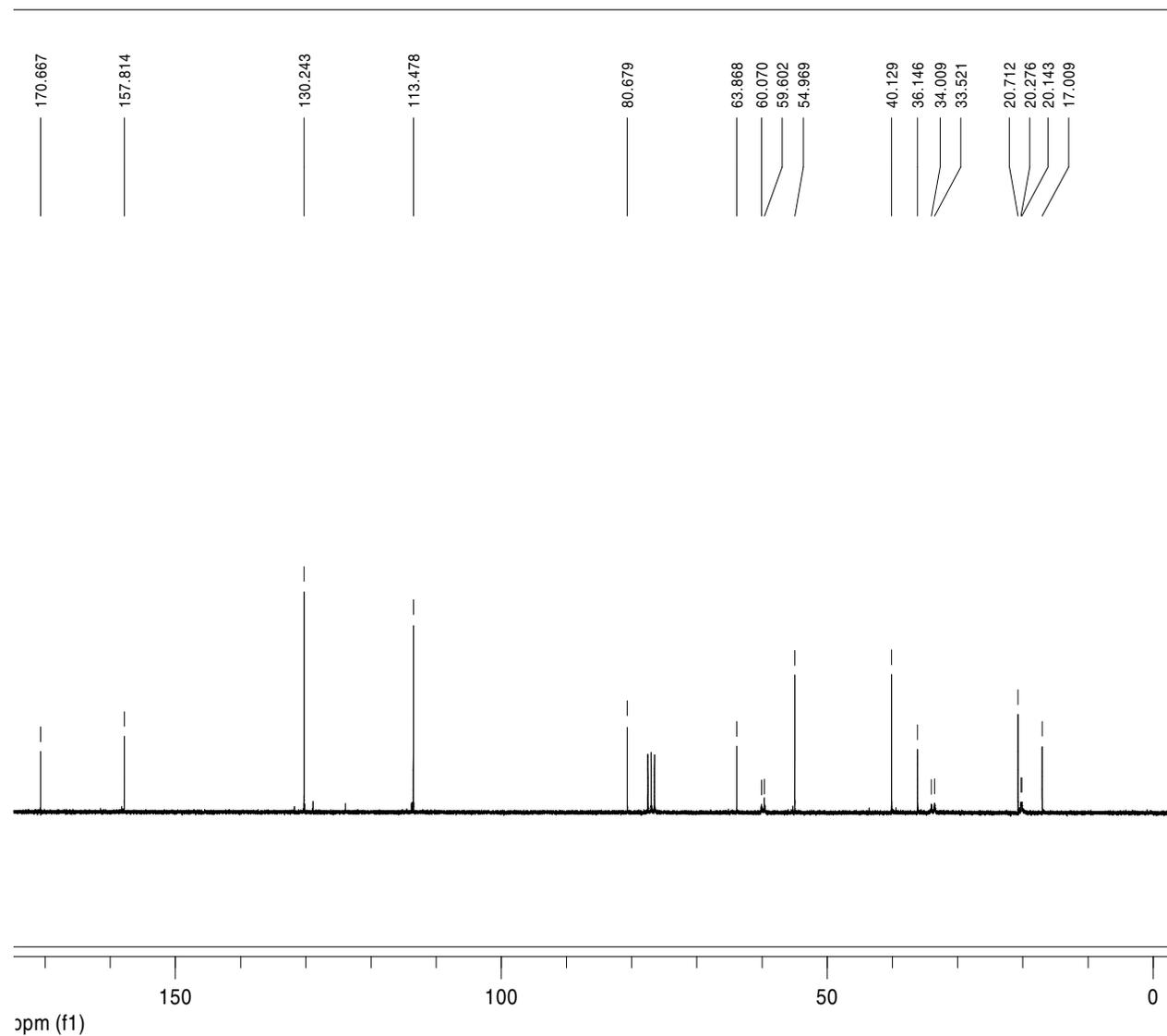
EI-MS: *m/z* (%) = 220 (12) [M⁺], 148 (9), 147 (100), 120 (6), 119 (83), 91 (55).

HR-EI-MS: C₁₂H₁₂O₄ [M⁺] calcd.: 220.0736, found.: 220.2736.

3-(4-Methoxy-phenyl)-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-propionic acid ethyl ester (4a)



Acetic acid 3-(4-methoxy-phenyl)-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-propyl ester (4b)



Date:

25 May 2007

Document's Title:

11

Spectrum Title:

MK119-10

Frequency (MHz):

(f1) 62.902

Original Points Count:

(f1) 32768

Actual Points Count:

(f1) 65536

Acquisition Time (sec):

(f1) 2.1758

Spectral Width (ppm):

(f1) 239.426

Pulse Program:

ZGPG30

Temperature:

300

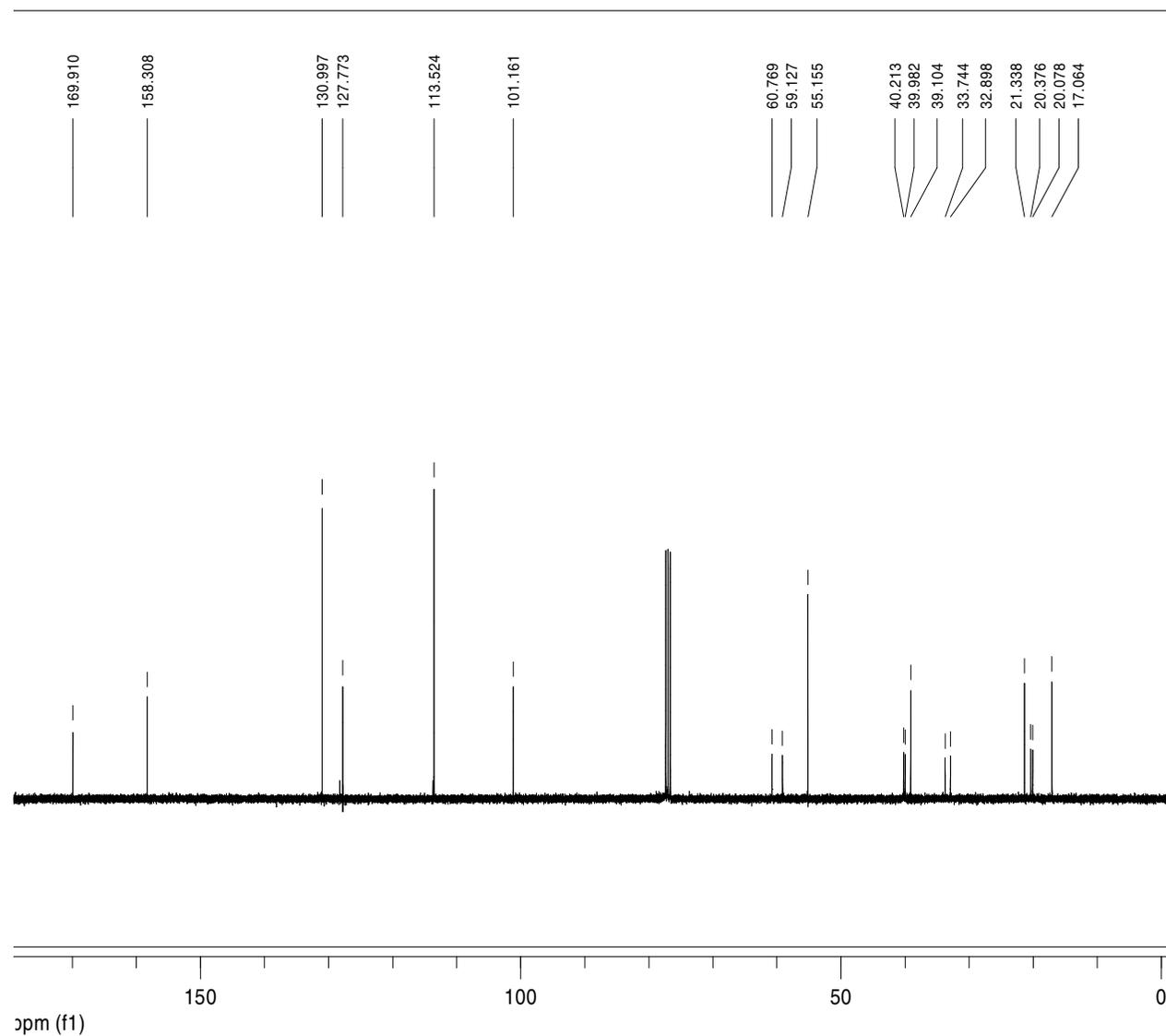
Number of Scans:

300

Acq. Date:

Wed May 23 12:04:26 AM

Acetic acid 2-(4-methoxy-phenyl)-1-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester (4c)



Date:

31 May 2007

Document's Title:

11

Spectrum Title:

MK121-20
C13CPD300 CDCl3 (C:\u) akbach 95

Frequency (MHz):

(f1) 90.564

Original Points Count:

(f1) 32768

Actual Points Count:

(f1) 65536

Acquisition Time (sec):

(f1) 1.5139

Spectral Width (ppm):

(f1) 239.003

Pulse Program:

ZGPG30

Temperature:

300

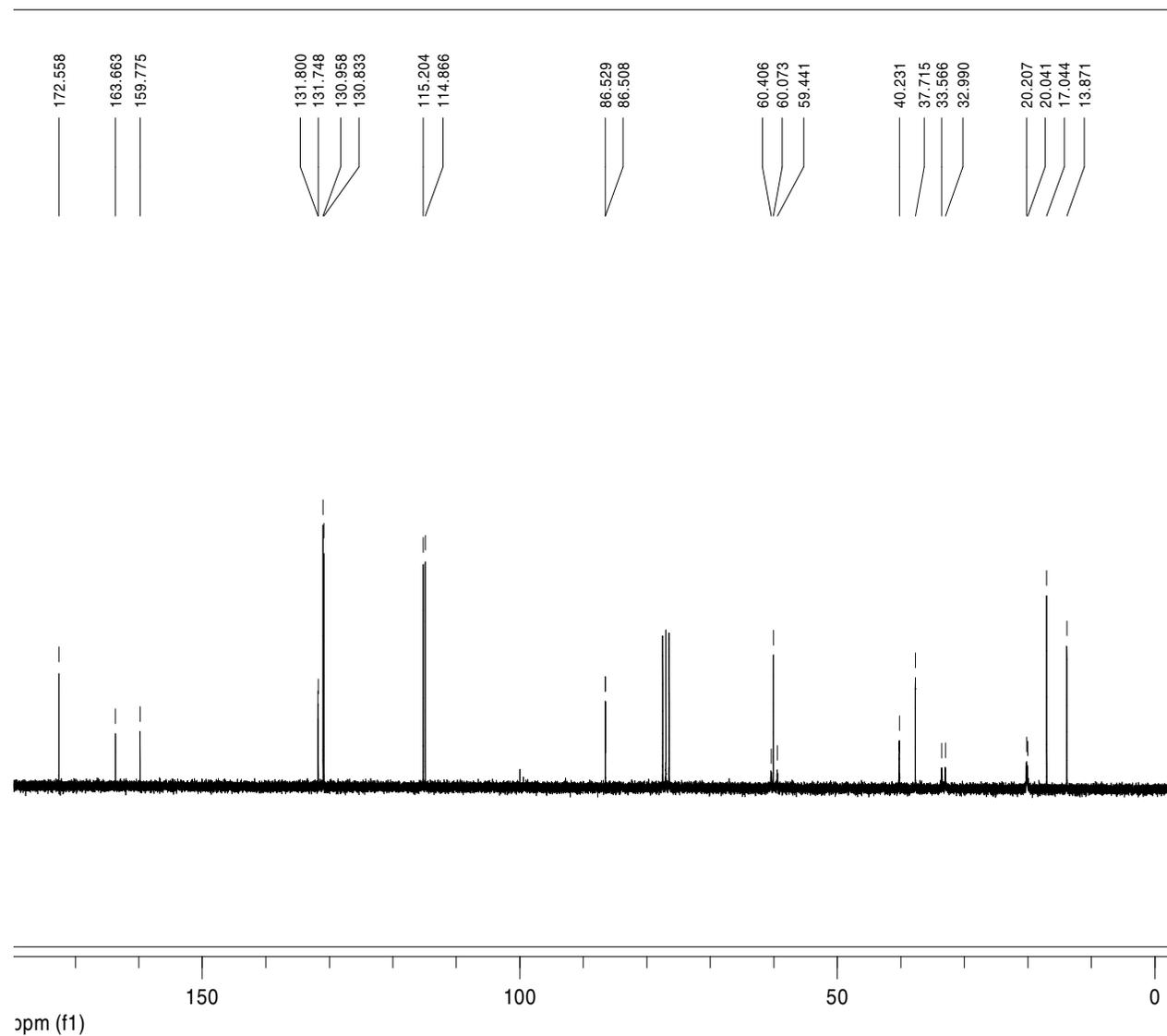
Number of Scans:

400

Acq. Date:

Thu May 31 02:13:57 PM

3-(4-Fluoro-phenyl)-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-propionic acid ethyl ester (4d)



Date:

25 May 2007

Document's Title:

11

Spectrum Title:

MK122-10

Frequency (MHz):

(f1) 62.902

Original Points Count:

(f1) 32768

Actual Points Count:

(f1) 65536

Acquisition Time (sec):

(f1) 2.1758

Spectral Width (ppm):

(f1) 239.426

Pulse Program:

ZGPG30

Temperature:

300

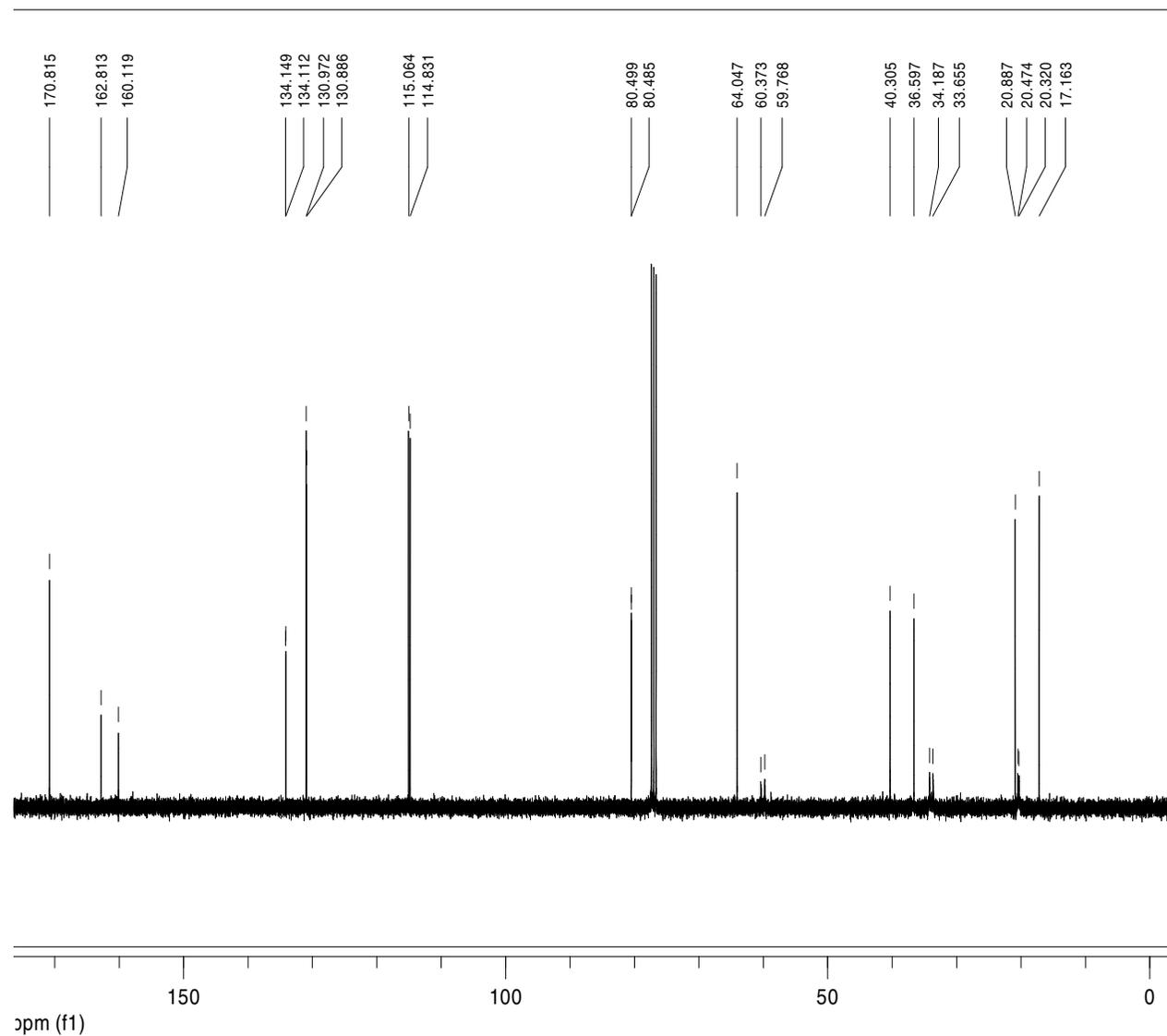
Number of Scans:

300

Acq. Date:

Thu May 24 01:30:09 PM

Acetic acid 3-(4-fluoro-phenyl)-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-propyl ester (4e)



Date:

25 May 2007

Document's Title:

11

Spectrum Title:

Mk123-10
C13CPD300 CDCl3 (C:\u) akbach 7

Frequency (MHz):

(f1) 90.564

Original Points Count:

(f1) 32768

Actual Points Count:

(f1) 65536

Acquisition Time (sec):

(f1) 1.5139

Spectral Width (ppm):

(f1) 239.003

Pulse Program:

ZGPG30

Temperature:

300

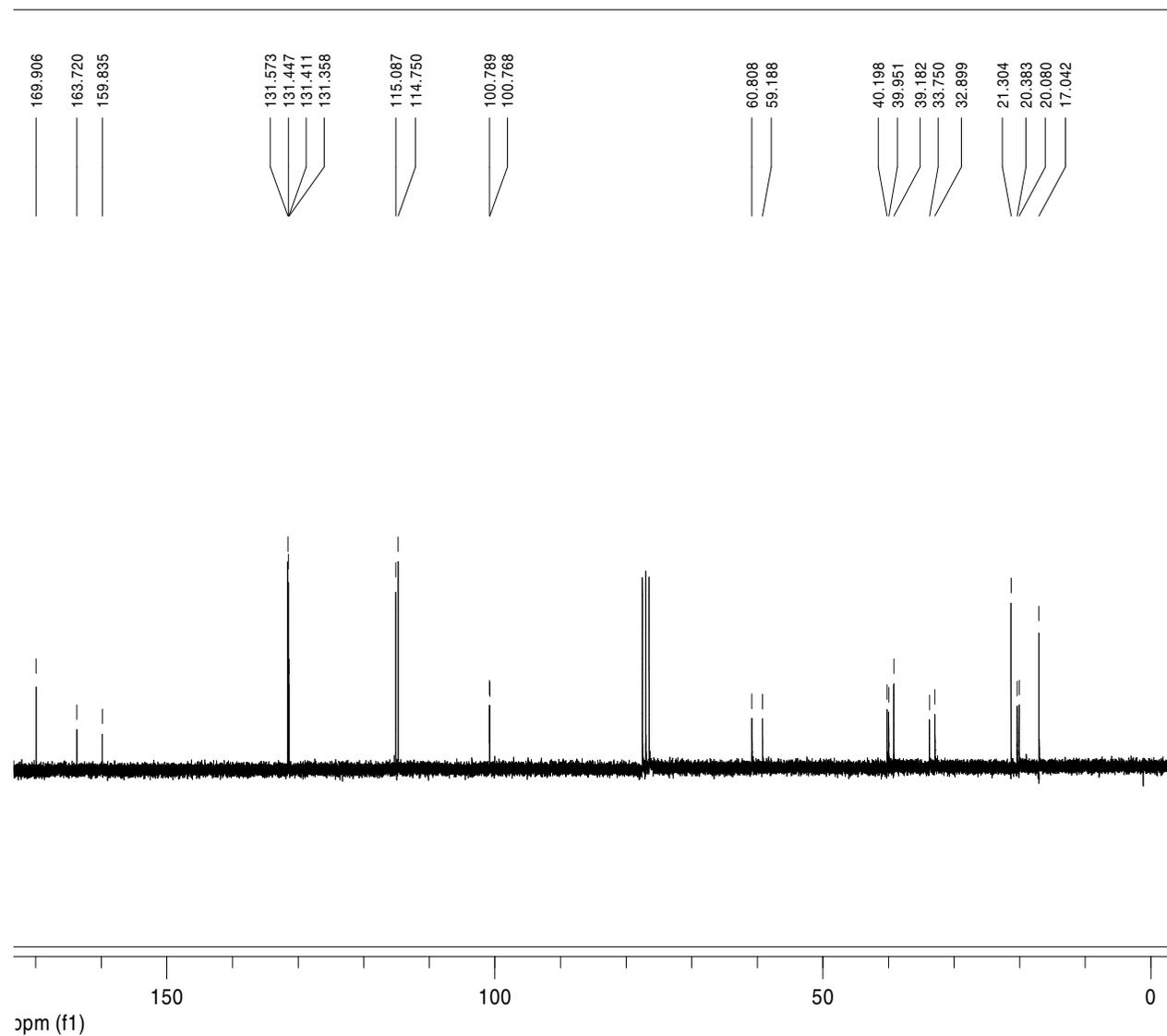
Number of Scans:

400

Acq. Date:

Fri May 25 01:35:35 PM

Acetic acid 2-(4-fluoro-phenyl)-1-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester (4f)



Date:

25 May 2007

Document's Title:

11

Spectrum Title:

MK124-10

Frequency (MHz):

(f1) 62.902

Original Points Count:

(f1) 32768

Actual Points Count:

(f1) 65536

Acquisition Time (sec):

(f1) 2.1758

Spectral Width (ppm):

(f1) 239.426

Pulse Program:

ZGPG30

Temperature:

300

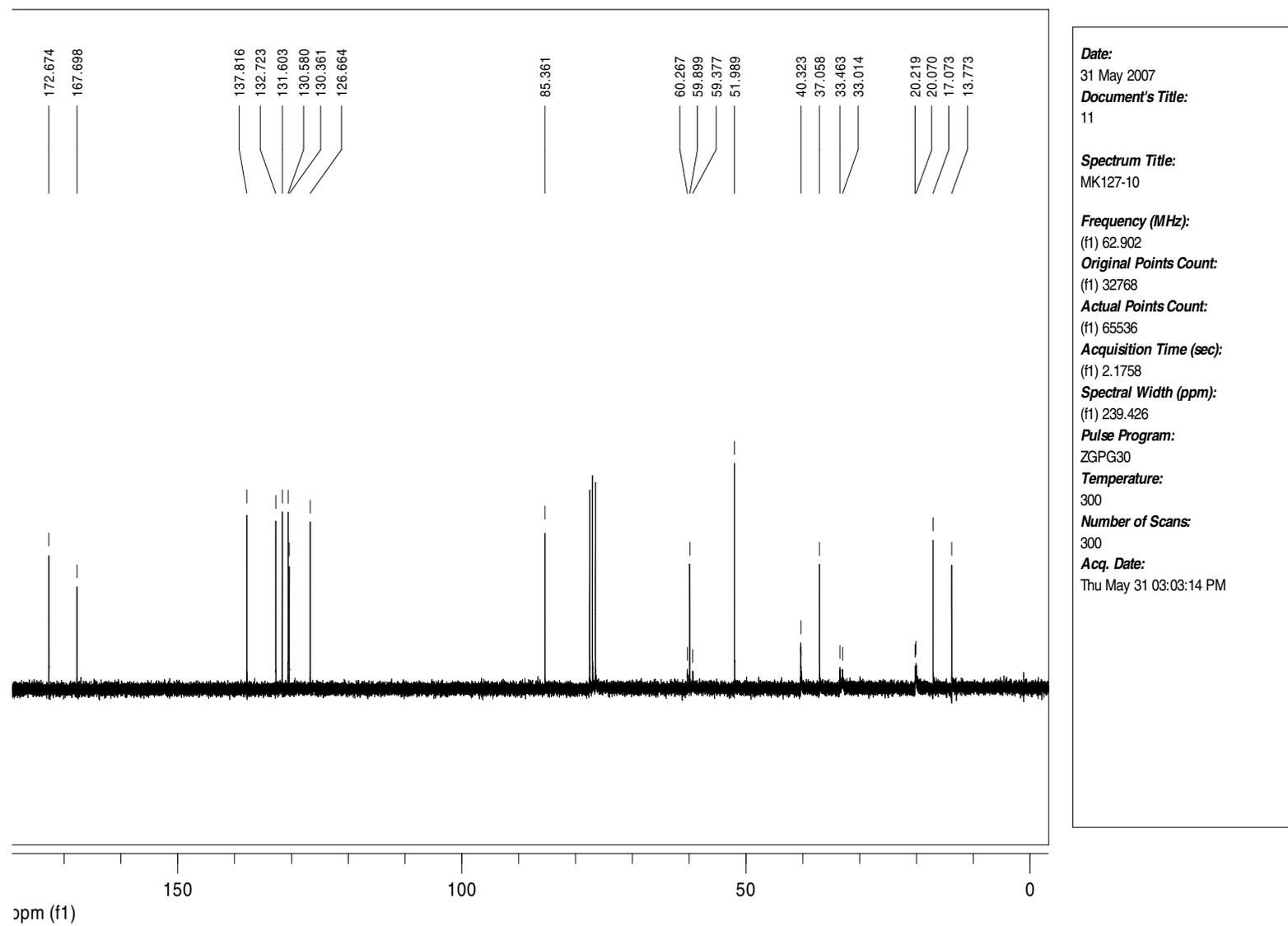
Number of Scans:

300

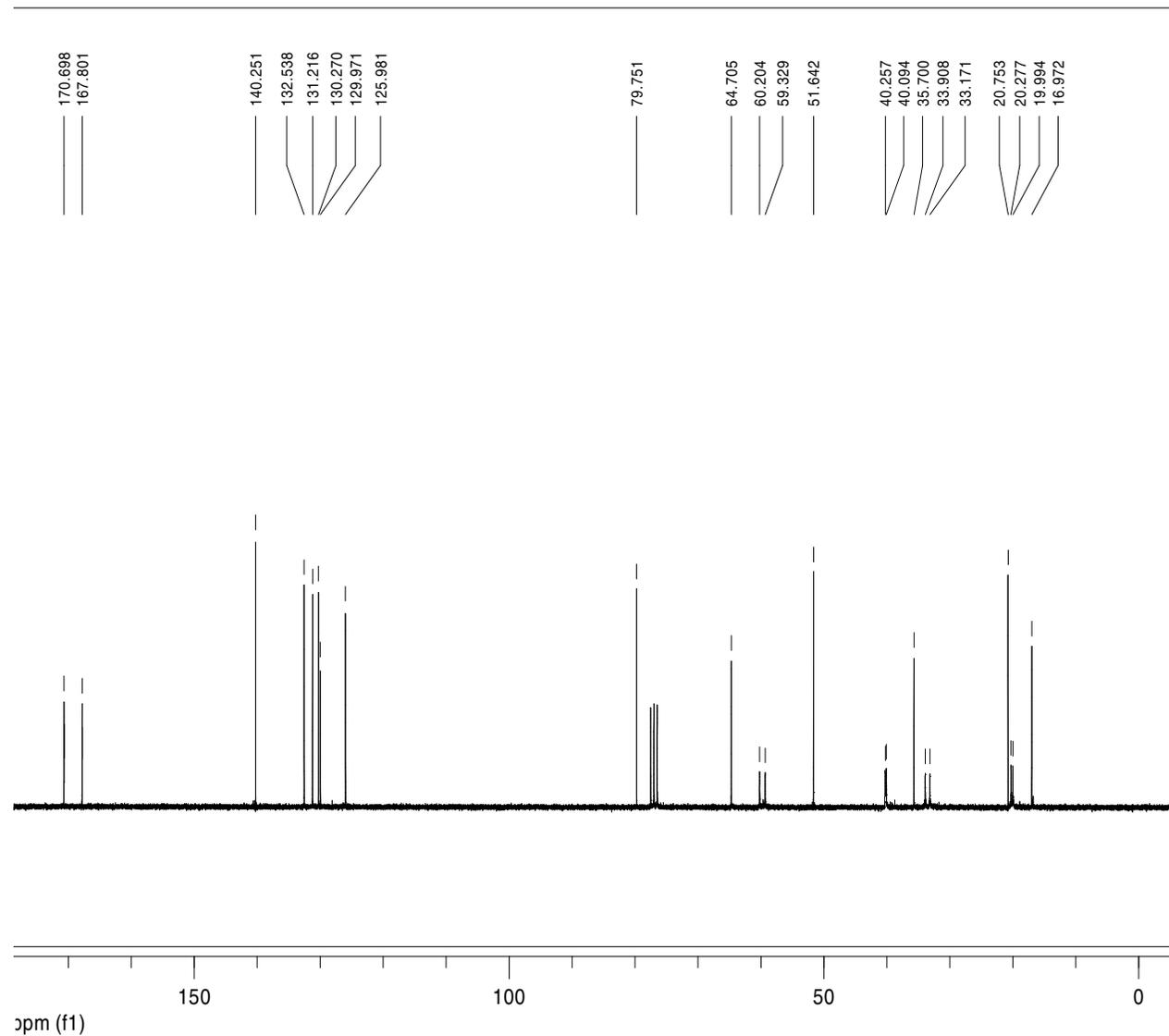
Acq. Date:

Fri May 25 04:02:13 PM

2-[2-Ethoxycarbonyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl]-benzoic acid methyl ester (4g)



2-[3-Acetoxy-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-propyl]-benzoic acid methyl ester (4h)



Date:

31 May 2007

Document's Title:

10

Spectrum Title:

MK126-10b

Frequency (MHz):

(f1) 62.902

Original Points Count:

(f1) 32768

Actual Points Count:

(f1) 65536

Acquisition Time (sec):

(f1) 2.1758

Spectral Width (ppm):

(f1) 239.426

Pulse Program:

ZGPG30

Temperature:

300

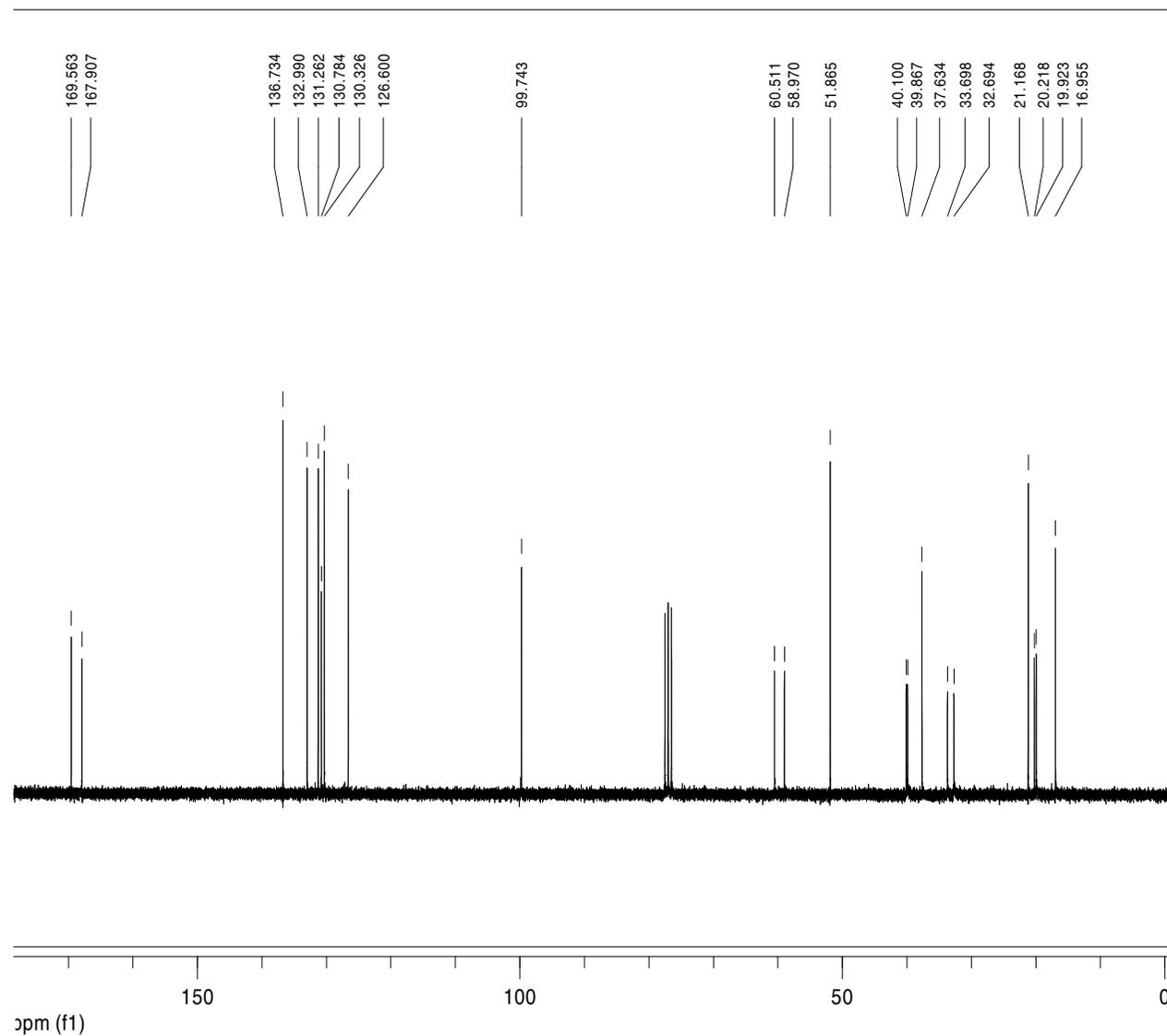
Number of Scans:

500

Acq. Date:

Thu May 31 12:20:25 AM

2-[2-Acetoxy-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl]-benzoic acid methyl ester (4i)



Date:

31 May 2007

Document's Title:

11

Spectrum Title:

MK128-10

Frequency (MHz):

(f1) 62.902

Original Points Count:

(f1) 32768

Actual Points Count:

(f1) 65536

Acquisition Time (sec):

(f1) 2.1758

Spectral Width (ppm):

(f1) 239.426

Pulse Program:

ZGPG30

Temperature:

300

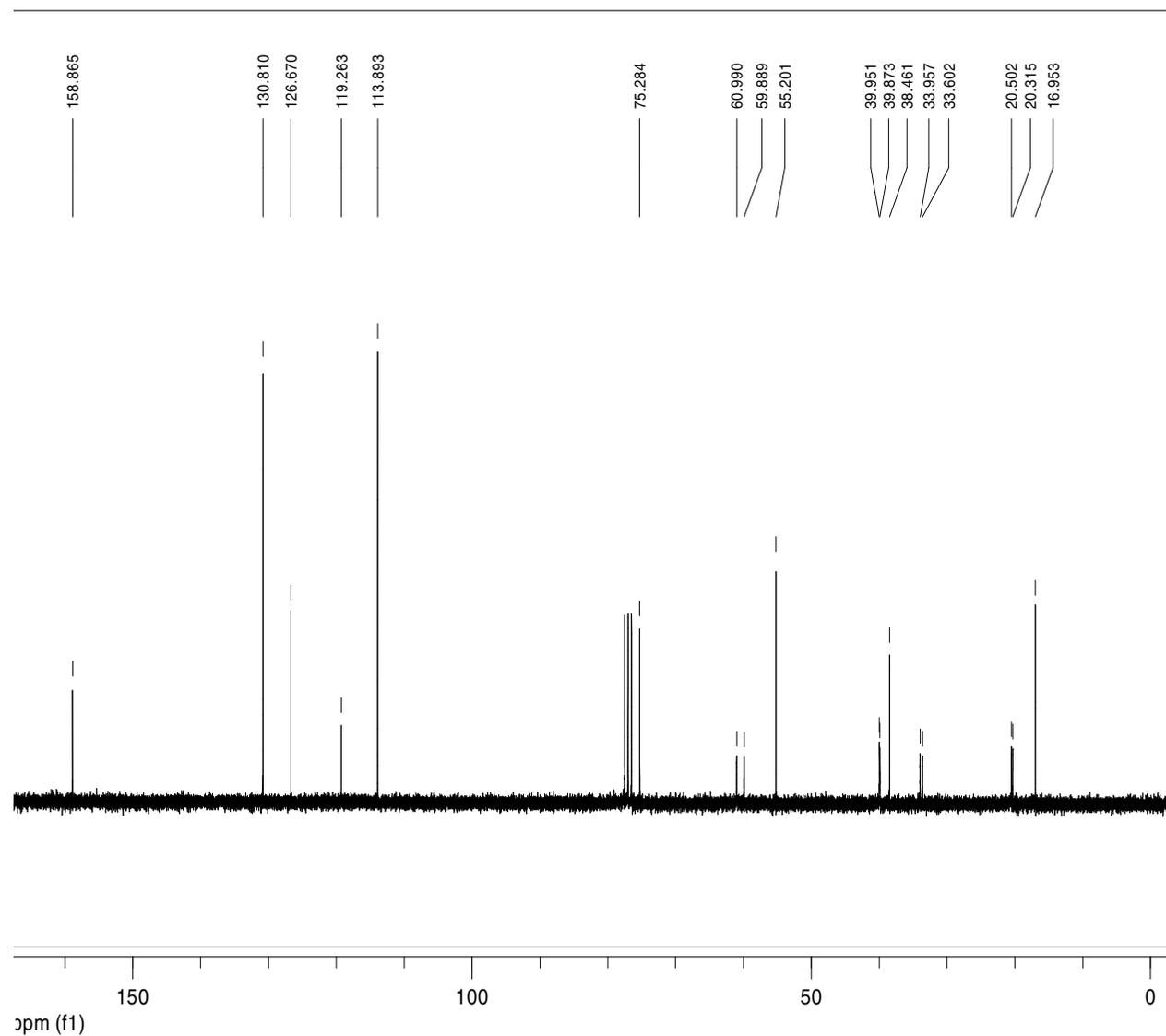
Number of Scans:

300

Acq. Date:

Thu May 31 06:10:33 PM

3-(4-Methoxy-phenyl)-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-propionitrile (4j)



Date:

13 Jun 2007

Document's Title:

11

Spectrum Title:

MK125-10

Frequency (MHz):

(f1) 62.902

Original Points Count:

(f1) 32768

Actual Points Count:

(f1) 65536

Acquisition Time (sec):

(f1) 2.1758

Spectral Width (ppm):

(f1) 239.426

Pulse Program:

ZGPG30

Temperature:

300

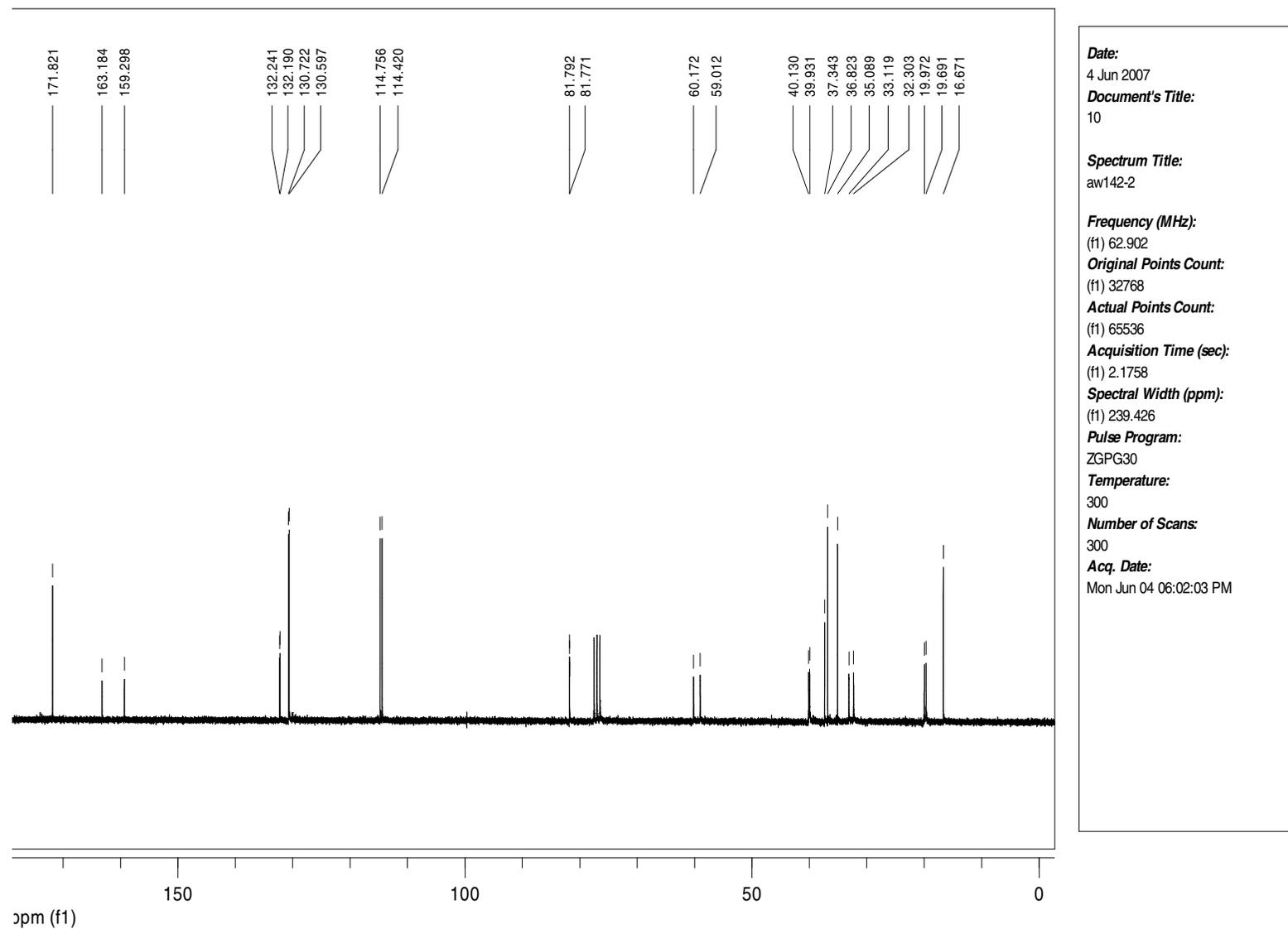
Number of Scans:

300

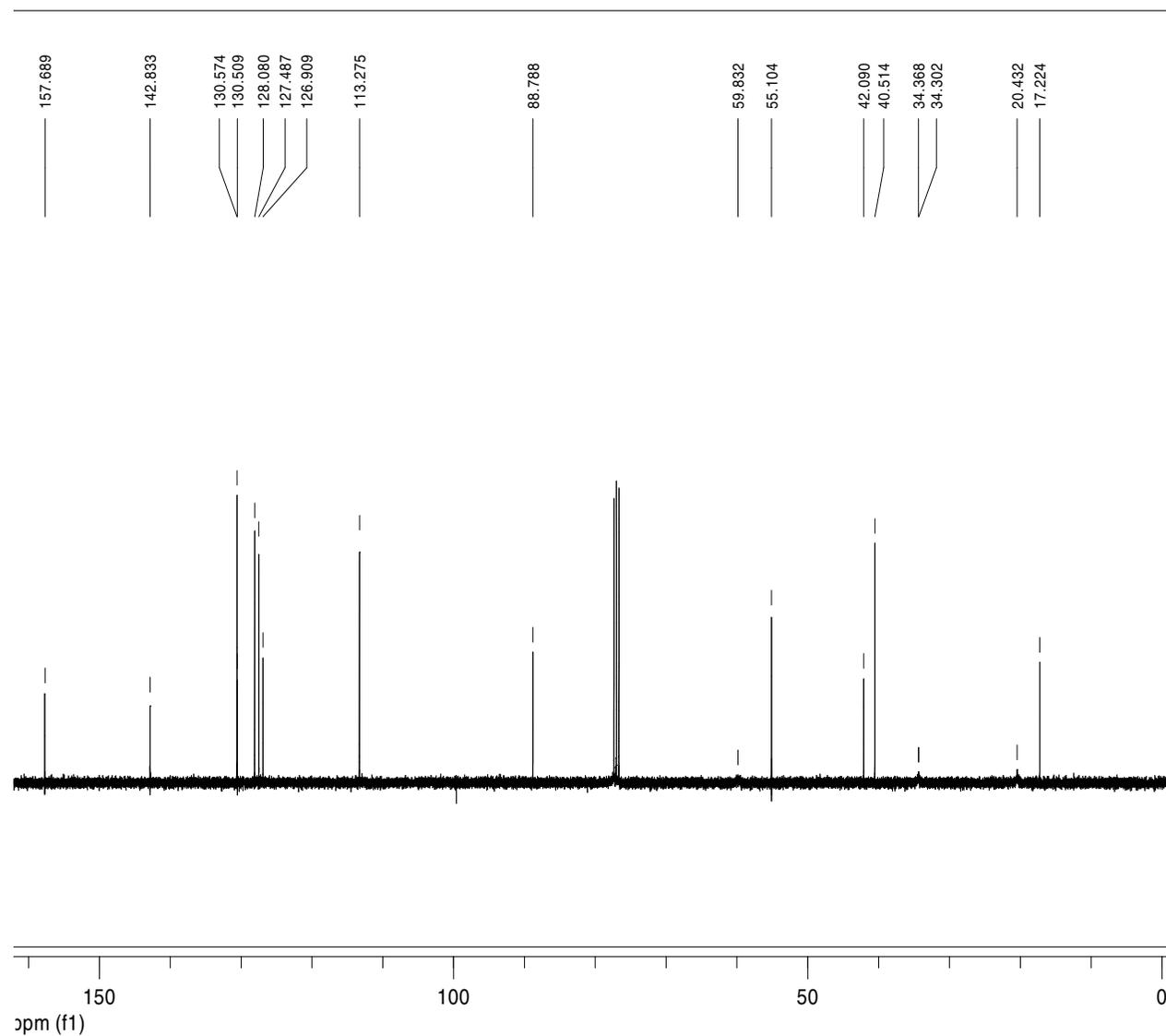
Acq. Date:

Tue May 29 06:22:35 PM

3-(4-Fluoro-phenyl)-N,N-dimethyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-propionamide (4k)



1-[2-(4-Methoxy-phenyl)-1-phenyl-ethoxy]-2,2,6,6-tetramethyl-piperidine (4I)



Date:

31 May 2007

Document's Title:

11

Spectrum Title:

AW141-2
C13CPD300 CDCl3 (C:\u) akbach 94

Frequency (MHz):

(f1) 90.564

Original Points Count:

(f1) 32768

Actual Points Count:

(f1) 65536

Acquisition Time (sec):

(f1) 1.5139

Spectral Width (ppm):

(f1) 239.003

Pulse Program:

ZGPG30

Temperature:

300

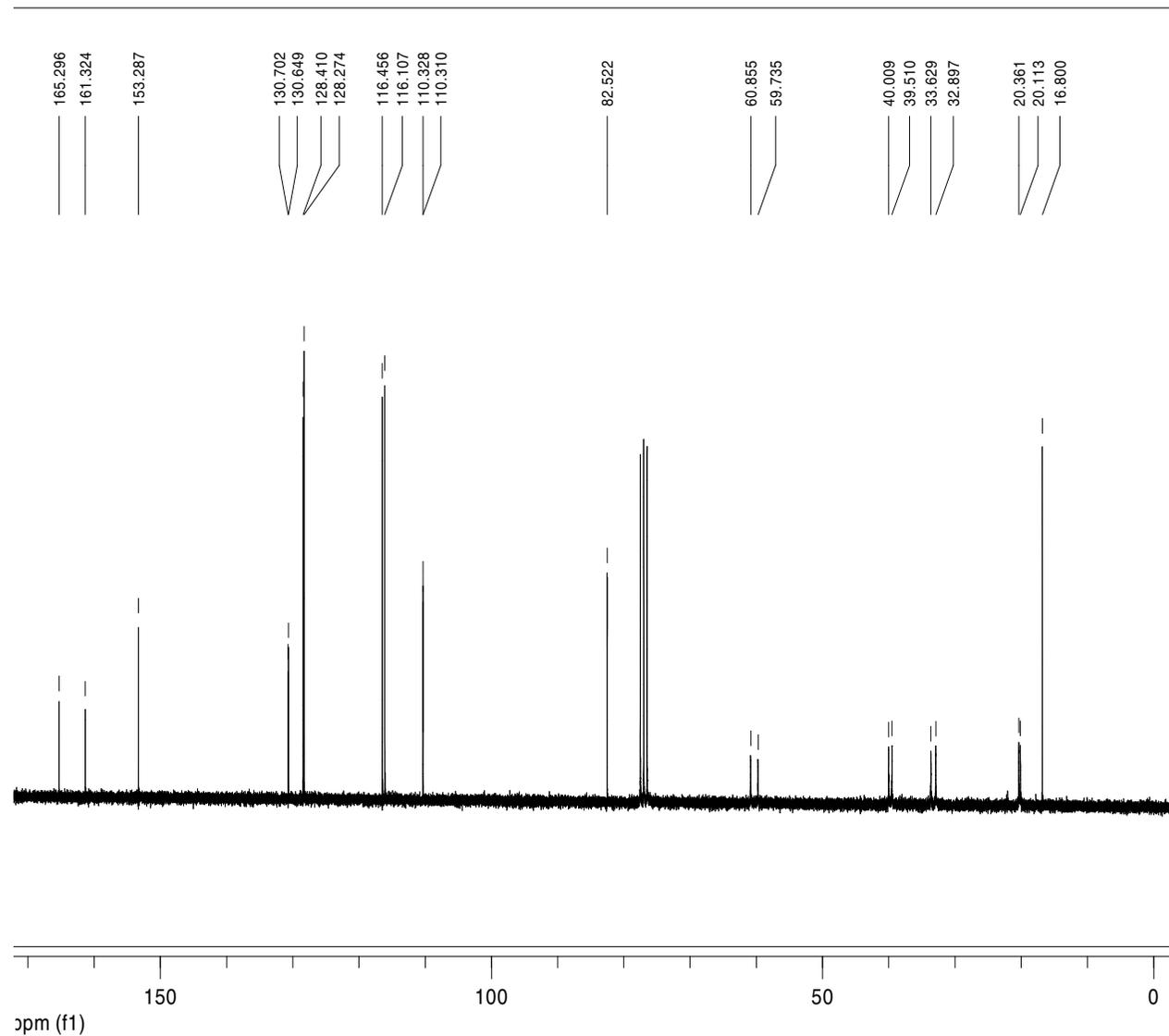
Number of Scans:

400

Acq. Date:

Thu May 31 01:41:22 PM

trans-4-(4-Methoxy-phenyl)-5-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-[1,3]dioxolan-2-one (4m)



Date:

14 Jun 2007

Document's Title:

11

Spectrum Title:

MK133-9

Frequency (MHz):

(f1) 62.902

Original Points Count:

(f1) 32768

Actual Points Count:

(f1) 65536

Acquisition Time (sec):

(f1) 2.1758

Spectral Width (ppm):

(f1) 239.426

Pulse Program:

ZGPG30

Temperature:

300

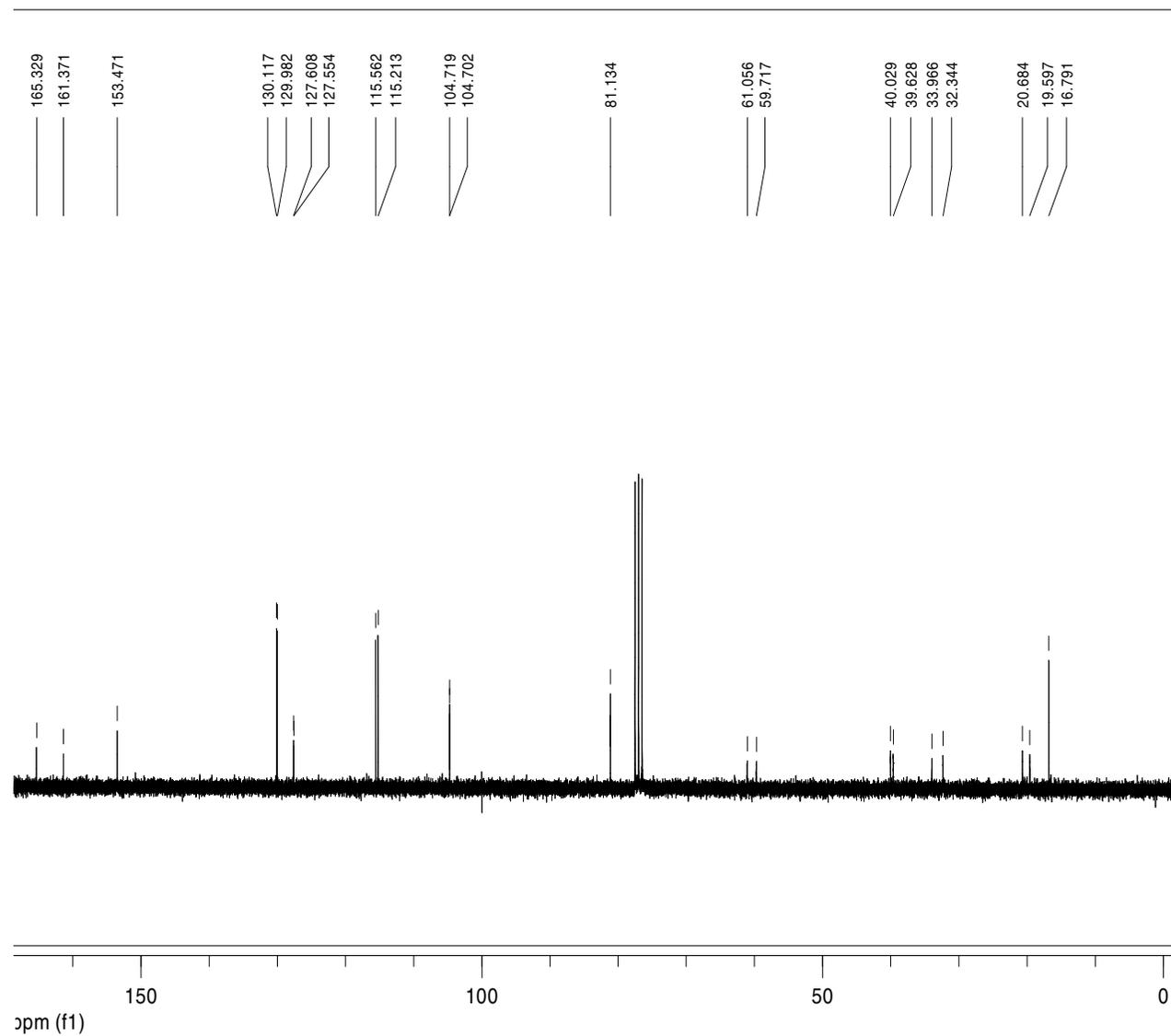
Number of Scans:

600

Acq. Date:

Thu Jun 14 10:31:40 AM

cis-4-(4-Methoxy-phenyl)-5-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-[1,3]dioxolan-2-one (4m')



Date:

13 Jun 2007

Document's Title:

10

Spectrum Title:

MK133-11b

Frequency (MHz):

(f1) 62.902

Original Points Count:

(f1) 32768

Actual Points Count:

(f1) 65536

Acquisition Time (sec):

(f1) 2.1758

Spectral Width (ppm):

(f1) 239.426

Pulse Program:

ZGPG30

Temperature:

300

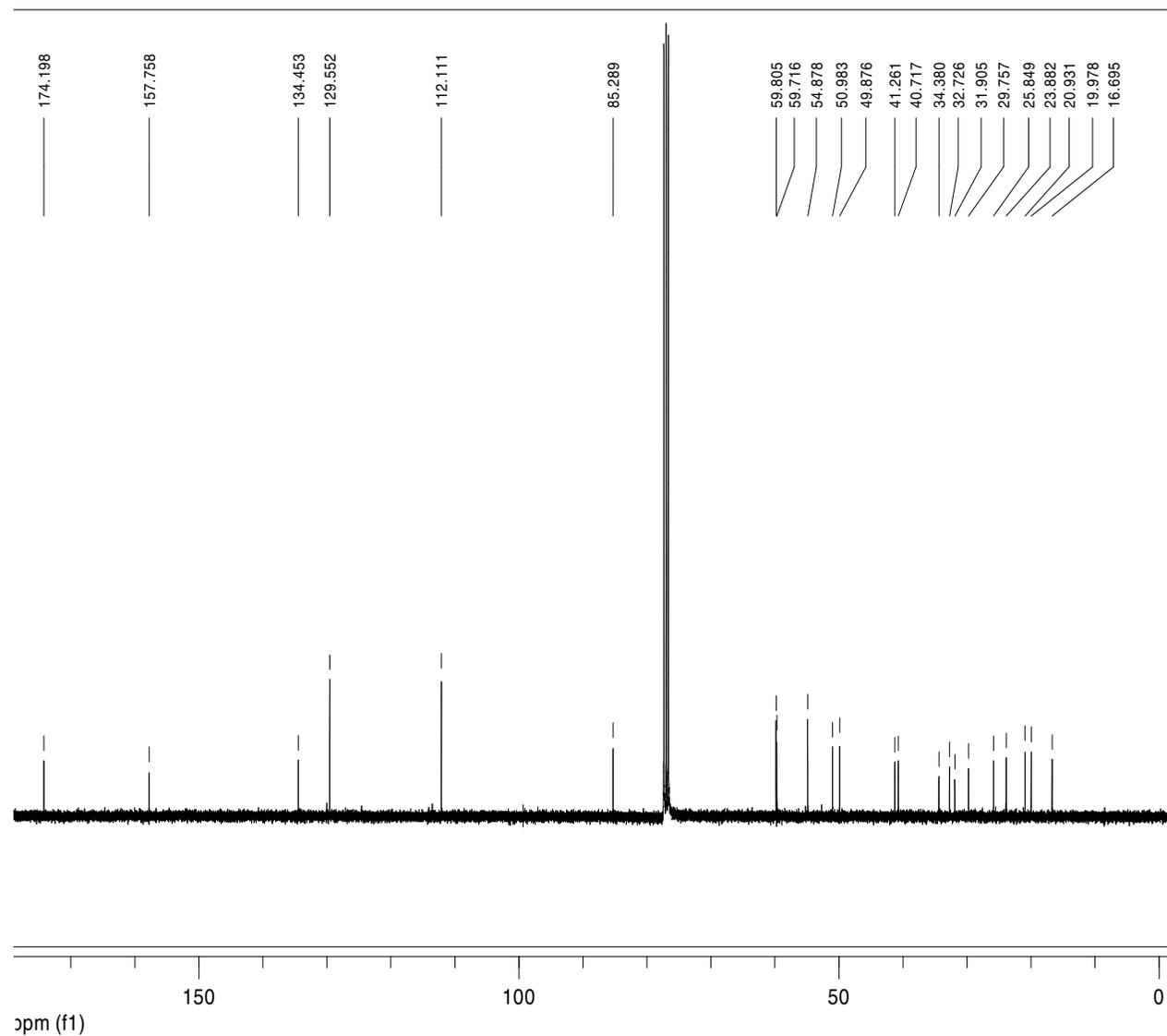
Number of Scans:

600

Acq. Date:

Wed Jun 13 04:02:45 PM

2-(4-Methoxy-phenyl)-1-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-cyclohexanecarboxylic acid methyl ester (4n)



Date:

6 Jun 2007

Document's Title:

10

Spectrum Title:

MK130-20b
C13CPD CDCl3 (C:\u) akbach 1

Frequency (MHz):

(f1) 90.564

Original Points Count:

(f1) 32768

Actual Points Count:

(f1) 65536

Acquisition Time (sec):

(f1) 1.5139

Spectral Width (ppm):

(f1) 239.003

Pulse Program:

ZGPG30

Temperature:

300

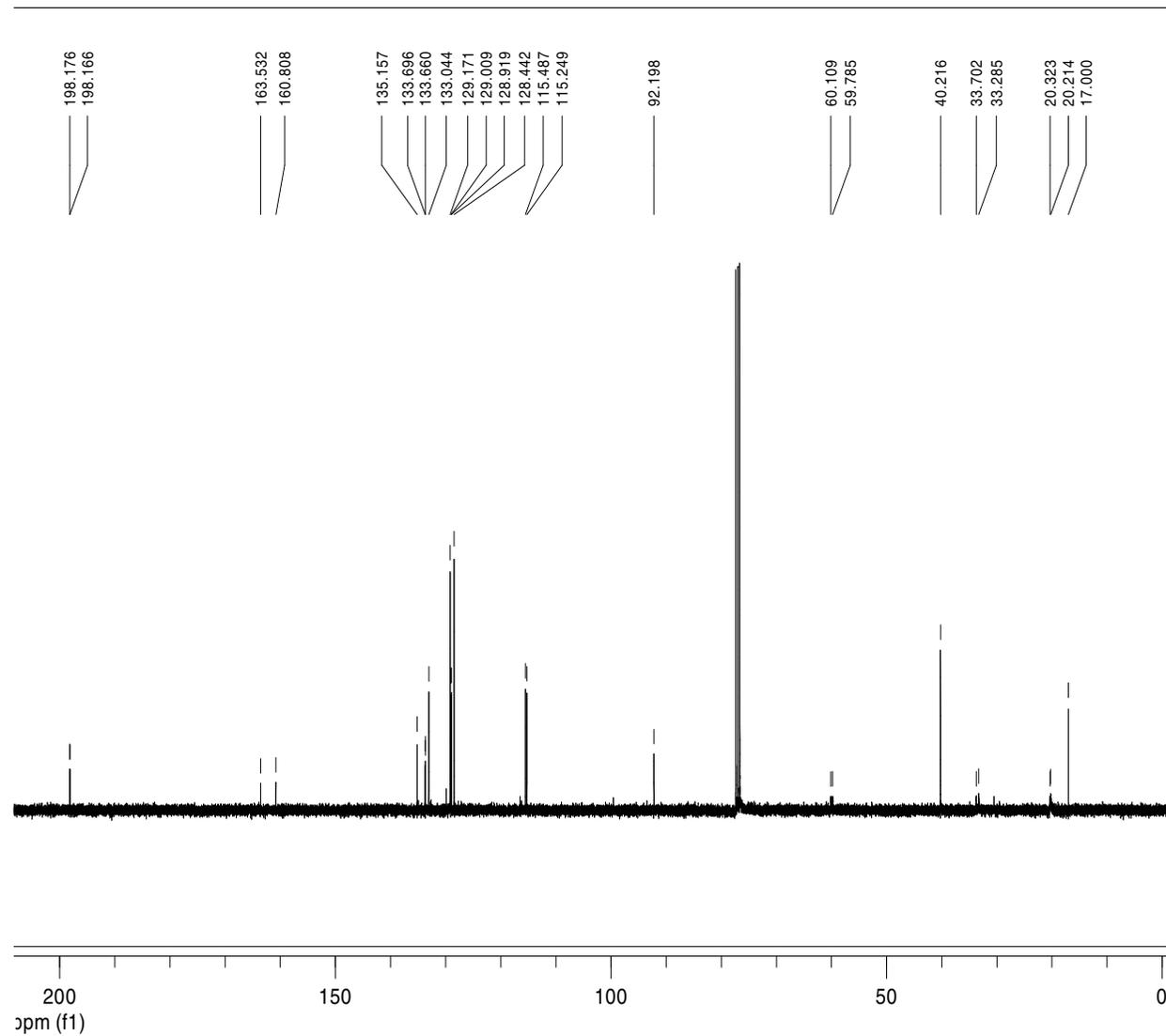
Number of Scans:

1024

Acq. Date:

Wed Jun 06 10:45:32 AM

2-(4-Fluoro-phenyl)-1-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethanone (5)



Date:

13 Jun 2007

Document's Title:

11

Spectrum Title:

AW144-30
C13CPD300 CDCl3 (C:\u) akbach 67

Frequency (MHz):

(f1) 90.564

Original Points Count:

(f1) 32768

Actual Points Count:

(f1) 65536

Acquisition Time (sec):

(f1) 1.5139

Spectral Width (ppm):

(f1) 239.003

Pulse Program:

ZGPG30

Temperature:

300

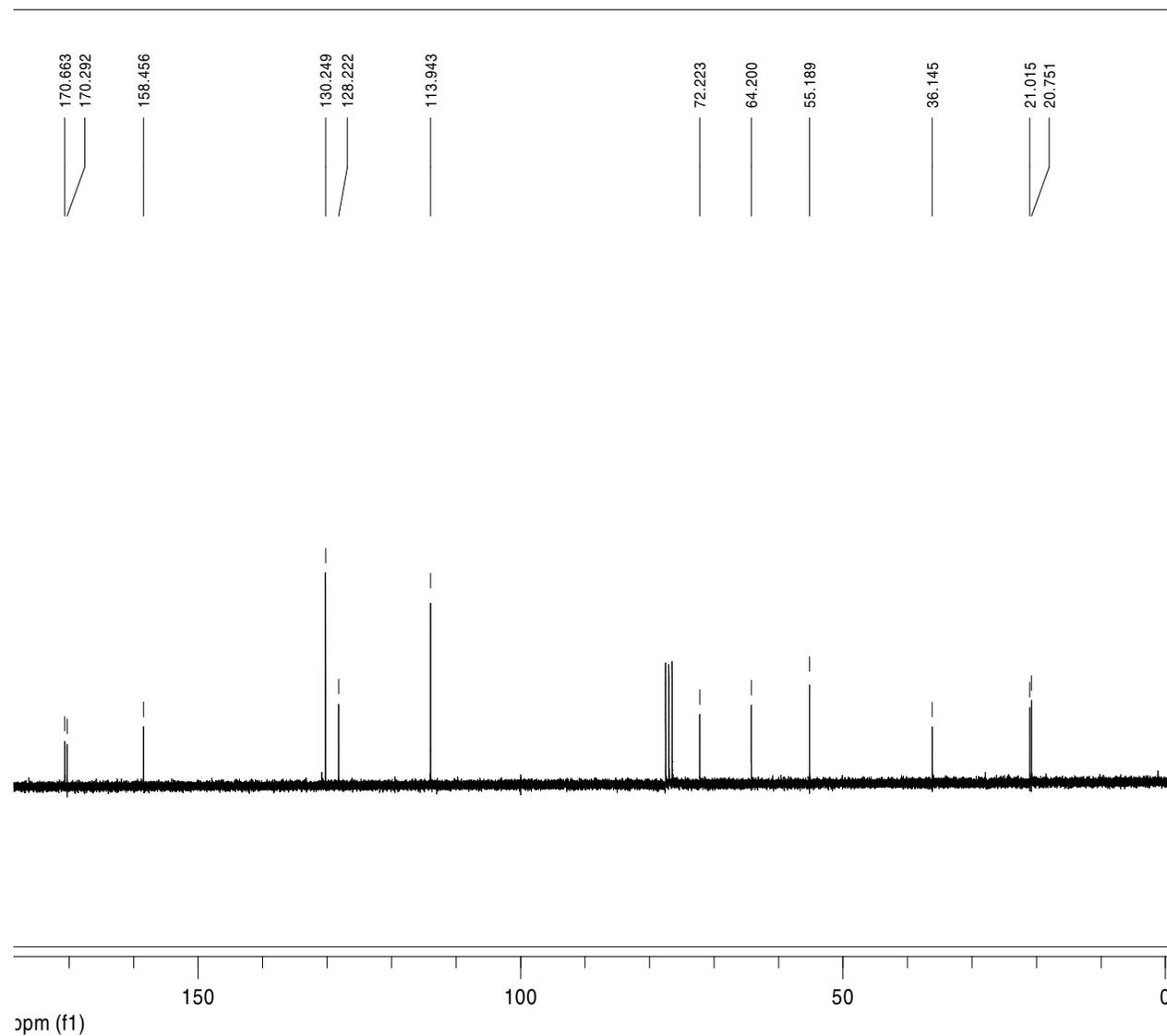
Number of Scans:

600

Acq. Date:

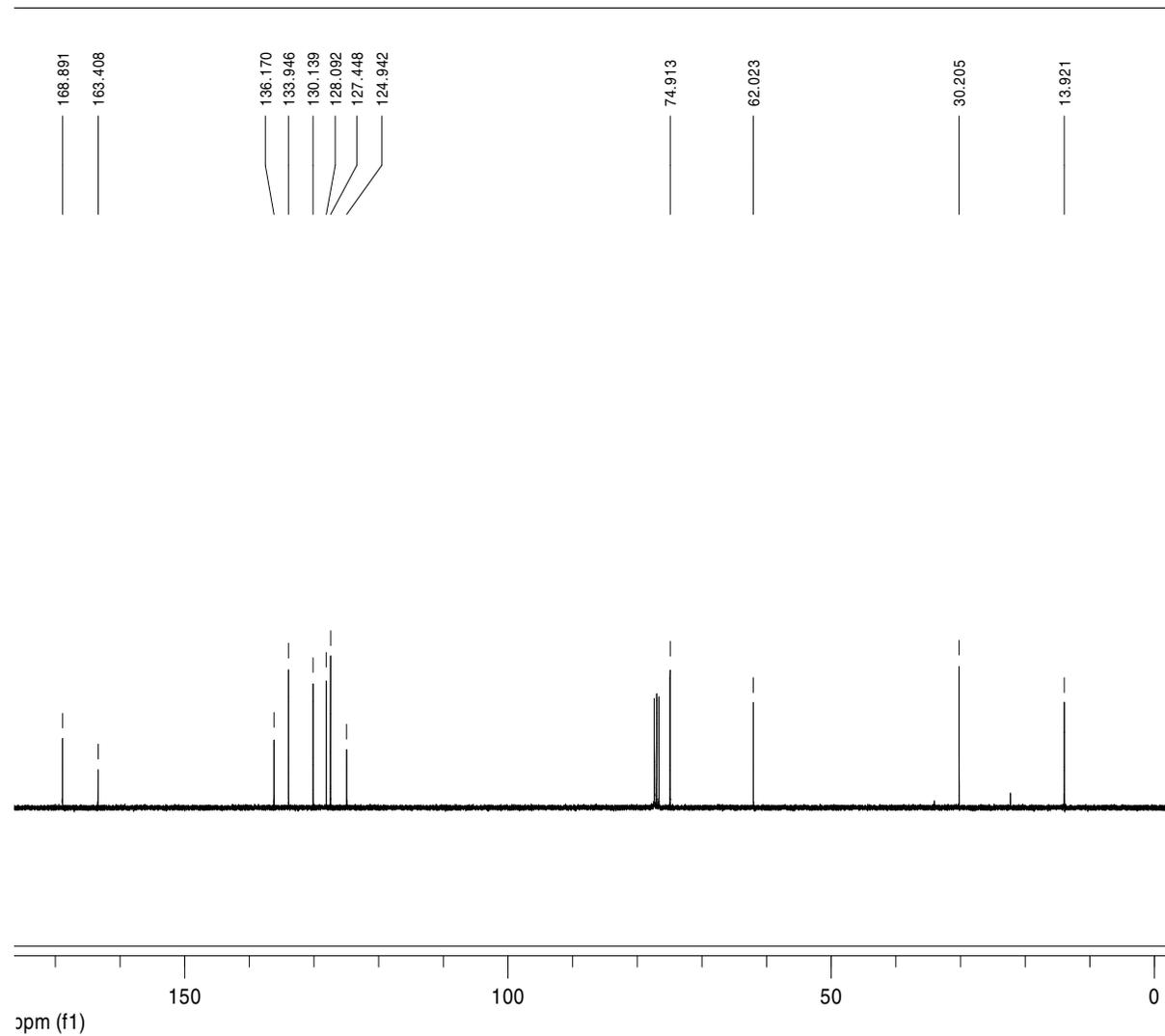
Mon Jun 11 06:31:50 PM

Acetic acid 1-acetoxymethyl-2-(4-methoxy-phenyl)-ethyl ester (6)



Date:
25 May 2007
Document's Title:
11
Spectrum Title:
DU61-11
Frequency (MHz):
(f1) 62.902
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 65536
Acquisition Time (sec):
(f1) 2.1758
Spectral Width (ppm):
(f1) 239.426
Pulse Program:
ZGPG30
Temperature:
300
Number of Scans:
300
Acq. Date:
Fri May 25 12:30:16 AM

1-Oxo-isochroman-3-carboxylic acid ethyl ester (7)



Date:

8 Jun 2007

Document's Title:

11

Spectrum Title:

MK132-11
C13CPD300 CDCl3 (C:\u) akbach 24

Frequency (MHz):

(f1) 90.564

Original Points Count:

(f1) 32768

Actual Points Count:

(f1) 65536

Acquisition Time (sec):

(f1) 1.5139

Spectral Width (ppm):

(f1) 239.003

Pulse Program:

ZGPG30

Temperature:

300

Number of Scans:

400

Acq. Date:

Wed Jun 06 11:19:54 PM