Electronic Supplementary Material (ESI) for RSC Advances

Stereoselectivity of A-ring contraction for 3-oxotriterpenoids

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Supplementary Information

1. Experimental

NMR spectra (300 or 500 MHz ^{1}H NMR and 75 or 125 MHz ^{13}C NMR) were recorded using Varian Unity Inova 300 and Varian 500 with Auto-Tuner. ^{1}H and ^{13}C NMR chemical shifts are reported in parts per million (ppm) and referenced to tetramethylsilane as internal standard. GC/MS spectra were recorded using Hewlett-Packard 5890 gas chromatograph (Alltech AT^{TM}-35 column, (35% phenyl)-65% methylpolysiloxane, length 10 m, id 0.18 mm, d_f 0.20 μm) and Hewlett-Packard 5970A mass selection detector. CD spectra were recorded using Olis DSM 17 CD digital subtractive method circular dichrometer with a Cary prism and grating monochromator. Optical rotations were measured using Jasco P-1010 polarimeter.

2-Hydroxylup-1,20-dien-3-one (6)

Lupenone (**1**) (0.60 g, 1.41 mmol) was mixed with potassium *tert*-butoxide (0.60 g, 5.35 mmol) in *tert*-butanol (25 ml). Suspension was stirred at 40 °C. Dry oxygen was constantly introduced in for 55 min. 1 N hydrochloric acid (100 ml) was added to the reaction solution. Precipitate was filtered, washed with water (3x50 ml) and hot water (70 °C, 3x30 ml) and dried in vacuum. Titled compound (**6**) was obtained as white solid (0.58 g, 94%). The product was purified on silica (hexane/ethyl ether, 95/5), m.p. 151-154 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.46 (s, 1H), 5.91 (s, 1H), 4.72 (s, 1H), 4.61 (s, 1H), 2.41 (m, 1H), 2.02-0.82 (m, 41H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 201.48, 150.92, 144.10, 129.23, 109.78, 54.21, 48.40, 48.17, 48.16, 45.85, 44.20, 43.41, 43.25, 41.92, 40.21, 38.88, 35.75, 34.16, 30.03, 27.58, 27.35, 25.23, 21.85, 21.41, 20.41, 19.53, 18.99, 18.29, 16.72, 14.68. HRMS (ESI): *m/z* 461.3389 ([M+Na$^+$] $C_{30}H_{46}NaO_2^+$ requires 461.3390).

2,28-Dihydroxylup-1,20-dien-3-one (7)

Betulone (**2**) (2.00 g, 4.54 mmol) was mixed with potassium *tert*-butoxide (2.00 g, 17.82 mmol) in *tert*-butanol (60 ml). Suspension was stirred at 40 °C. Dry oxygen was constantly introduced in for 55 min. 1 N hydrochloric acid (100 ml) was added to the reaction solution. Precipitate was filtered, washed with water (3x50 ml) and hot water (70 °C, 3x30 ml) and dried in vacuum. Titled compound (**7**) was obtained as yellow solid (1.90 g, 92%). The product was purified on silica (hexane/ethyl ether, 95/5), m.p. 174-178 °C decomp. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.45 (s, 1H), 5.91 (s, 1H), 4.71 (s, 1H), 4.62 (s, 1H), 3.81 (d, 1H), 3.37 (d, 1H), 2.41 (m, 1H), 2.02-0.82 (m, 38H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 201.55, 150.52, 144.21, 129.22, 110.26, 60.88, 54.27, 48.92, 48.09, 48.08, 45.88, 44.30, 43.35, 42.07, 38.94, 37.69, 34.27, 34.18, 30.00, 29.42, 27.44, 27.25, 25.35, 21.94, 21.38, 20.49, 19.40, 19.05, 16.79, 14.97. HRMS (ESI): *m/z* 447.3349 ([M+Na$^+$] $C_{30}H_{46}NaO_3^+$ requires 477.3339).

2-Hydroxy-3-oxolup-1,20-dien-28-oic acid (8)

Betulonic acid (**3**) (0.56 g, 1.23 mmol) was mixed with potassium *tert*-butoxide (0.55 g, 4.90 mmol) in *tert*-butanol (25 ml). Suspension was stirred at 40 °C. Dry oxygen was constantly introduced in for 1 hr. 1 N hydrochloric acid (100 ml) was added to the reaction solution. Precipitate was filtered, washed with water (3x50 ml) and hot water (70 °C, 3x30 ml) and dried in vacuum. Titled compound (**8**) was obtained as white solid (0.54 g, 93%), m.p. 177-184 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.48 (s, 1H), 5.95 (s, 1H), 4.72 (s, 1H), 4.65 (s, 1H), 3.08 (m, 1H), 2.26 (m, 2H), 2.00 (m, 2H), 1.80-0.72 (m, 34H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 201.46, 150.32, 144.14, 129.21, 110.17, 56.72, 56.58, 54.23, 49.36, 47.11, 45.92, 44.22, 43.00, 41.77, 38.90, 37.29, 34.19, 32.33, 30.75, 29.79, 27.35, 25.57, 21.82, 21.32, 20.41, 19.57, 18.95, 16.68, 14.82. HRMS (ESI): *m/z* 491.3139 ([M+Na$^+$] $C_{30}H_{44}NaO_4^+$ requires 491.3132).

2-Hydroxy-19β,28-epoxy-18α-olean-1-en-3-one (9)

Allobetulone (**4**) (2.02 g, 4.58 mmol) was mixed with potassium *tert*-butoxide (2.06 g, 18.36 mmol) in *tert*-butanol (100 ml). Suspension was stirred at 40 °C. Dry oxygen was constantly introduced in for 1 hr. 1 N hydrochloric acid (150 ml) was added to the reaction solution. Precipitate was filtered, washed with water (3x60 ml) and hot water (70 °C, 3x30 ml) and dried in vacuum. Titled compound (**9**) was obtained as white solid. The product was purified on silica (hexane/ethyl ether, 90/10) (2.04 g, 95%), m.p. 143-146 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ

6.51 (s, 1H), 5.94 (s, 1H), 3.80 (d, 1H), 3.57 (s, 1H), 3.48 (d, 1H), 1.77-0.72 (m, 41H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 201.17, 144.20, 129.39, 88.21, 71.54, 54.50, 47.01, 46.48, 44.33, 41.78, 41.76, 41.33, 39.01, 36.65, 37.01, 34.55, 33.85, 32.99, 29.13, 27.42, 26.63, 26.53, 24.87, 21.92, 21.54, 20.88, 19.00, 16.52, 13.66. HRMS (ESI): *m/z* 477.3349 ([M+Na$^+$] $C_{30}H_{46}NaO_3^+$ requires 477.3339).

2-Hydroxy-3-oxo-18α-olean-1-en-28,19β-olide (10)

28-Oxoallobetulone (**5**) (1.01 g, 2.22 mmol) was mixed with potassium *tert*-butoxide (1.03 g, 9.18 mmol) in tert-butanol (50 ml). Suspension was stirred at 40 °C. Dry oxygen was constantly introduced in for 2 hr until solution was formed. 1 N hydrochloric acid (60 ml) was added to the reaction solution. Precipitate was filtered, washed with water (3x50 ml) and hot water (70 °C, 3x30 ml) and dried in vacuum. Titled compound (**10**) was obtained as white solid (0.96 g, 92%). Crystallization from methanol gave colorless crystals, m.p. 313-316 °C decomp. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.47 (s, 1H), 5.92 (s, 1H), 3.96 (s, 1H), 1.92-0.88 (m, 41H). ^{1}H NMR (300 MHz, Py-d_5): δ 10.09 (s, 1H), 6.70 (s, 1H), 4.08 (s, 1H), 2.03-0.82 (m, 41H). ^{13}C NMR (75 MHz, Py-d_5): δ 201.17, 179.49, 146.62, 129.87, 85.76, 54.28, 46.72, 46.72, 46.19, 44.79, 41.41, 40.44, 38.71, 36.58, 33.71, 33.57, 32.72, 32.01, 28.78, 28.13, 27.82, 26.40, 25.97, 23.61, 21.89, 21.36, 21.04, 19.01, 15.84, 13.50. HRMS (ESI): *m/z* 491.3143 ([M+Na$^+$] $C_{30}H_{44}NaO_4^+$ requires 491.3132).

3β-Hydroxy-1(2→3)-abeolup-20-en-2-oic acid (11)

2-Hydroxylup-1,20-dien-3-one (**6**) (1.00 g, 2.28 mmol) was mixed with potassium hydroxide powder (0.64 g, 11.40 mmol) in *tert*-butanol (40 ml) containing water (2 ml). Resulting mixture was stirred at 75 °C for 11 hr. Reaction mixture was poured in 1 N hydrochloric acid (150 ml). White precipitate was filtered, washed with water (4x50 ml) and dried to give titled compound (**11**) (0.90 g, 87%). Crystallization from benzene gave white crystals, m.p. 248-251 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.71 (s, 1H), 4.59 (s, 1H), 2.40 (m, 1H), 2.10(d, 1H), 1.94 (m, 1H), 1.80-0.81 (m, 41H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.99, 151.19, 109.62, 87.35, 62.19, 53.98, 50.68, 48.79, 48.55, 48.28, 44.12, 43.22, 43.20, 41.94, 40.28, 38.46, 35.88, 34.56, 30.08, 27.91, 27.38, 25.12, 23.84, 21.05, 19.55, 19.07, 18.25, 16.94, 16.43, 15.00. HRMS (ESI): *m/z* 479.3509 ([M+Na$^+$] $C_{30}H_{48}NaO_3^+$ requires 479.3496).

3β,28-Dihydroxy-1(2→3)-abeolup-20-en-2-oic acid (12)

2,28-Dihydroxylup-1,20-dien-3-one (**7**) (1.00 g, 2.20 mmol) was mixed with potassium hydroxide powder (0.62 g, 11.00 mmol) in *tert*-butanol (40 ml) containing water (2 ml). Resulting mixture was stirred at 75 °C for 24 hr. Reaction mixture was poured in 1 N hydrochloric acid (150 ml). White precipitate was filtered, washed with water (4x50 ml) and dried to give titled compound (**12**) (0.78 g, 75%). Crystallization from benzene gave white crystals, m.p. 251-254 °C. ^{1}H NMR (300 MHz, CD_3OD): δ 4.71 (s, 1H), 4.60 (s, 1H), 3.77(d, 1H), 3.33 (d, 1H), 2.44 (m, 1H), 2.11 (d, 1H), 2.04-0.92 (m, 39H). ^{13}C NMR (75 MHz, CD_3OD): δ 179.91, 151.86, 110.26, 88.09, 63.25, 60.32, 55.00, 51.85, 50.01, 48.95, 48.60, 48.20, 44.80, 43.91, 43.00, 38.87, 35.60, 35.10, 30.80, 30.41, 28.40, 27.80, 26.40, 24.60, 21.11, 19.86, 19.40, 17.39, 16.74, 15.33. HRMS (ESI): *m/z* 495.3547 ([M+Na$^+$] $C_{30}H_{48}NaO_4^+$ requires 495.3445).

3β-Hydroxy-1(2→3)-abeolup-20-ene-2,28-dioic acid (13)

2-Hydroxy-3-oxolup-1,20-dien-28-oic acid (**8**) (1.00 g, 2.13 mmol) was mixed with potassium hydroxide powder (0.60 g, 10.65 mmol) in *tert*-butanol (40 ml) containing water (2 ml). Resulting mixture was stirred at 75 °C for 24 hr. Reaction mixture was poured in 1 N hydrochloric acid (100 ml). White precipitate was filtered, washed with water (4x50 ml) and dried to give titled compound (**13**) (0.82 g, 79%). Crystallization from methanol gave white crystals, m.p. 210-217 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.75 (s, 1H), 4.63 (s, 1H), 3.00 (m, 1H), 2.40-1.90 (m, 4H), 1.80-0.75 (m, 36H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 183.18, 182.43, 150.55, 110.02, 87.28, 62.24, 56.65, 50.75, 49.49, 48.75, 47.21, 44.10, 42.80, 41.80, 38.84, 37.37, 34.62, 32.45, 30.81, 29.87, 27.36, 25.52, 23.71, 21.07, 19.61, 19.35, 19.00, 16.87, 16.40, 15.16. HRMS (ESI): *m/z* 509.3251 ([M+Na$^+$] $C_{30}H_{46}NaO_5^+$ requires 509.3238).

19β,28-Epoxy-3β-hydroxy-1(2→3)-abeo-18α-oleanan-2-oic acid (14)

Method A. 2-Hydroxy-19β,28-epoxy-18α-olean-1-en-3-one (**9**) (1.00 g, 2.20 mmol) was mixed with potassium hydroxide powder (0.62 g, 11.00 mmol) in *tert*-butanol (40 ml) containing water (2.0 ml). Resulting mixture was stirred at 75 °C for 11 hr. Reaction mixture was poured in 1 N hydrochloric acid (200 ml). White precipitate was filtered off, washed with water (4x50 ml), dried and crystallized from toluene to give titled compound (**14**) (0.87 g, 84%), m.p. 299-304 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.62 (d, 1H), 3.50 (s, 1H), 3.32 (d, 1H), 2.15 (d, 1H), 1.78 (d, 1H), 1.72-0.62 (m, 41H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 178.49, 87.50, 86.63, 70.96, 62.37, 54.56, 51.33, 47.66, 43.90, 41.63, 41.04, 36.78, 36.63, 34.58, 34.22, 34.02, 33.15, 29.52, 27.96, 26.88, 26.53, 26.48, 26.32, 24.94, 24.04, 21.38, 19.00, 17.48, 16.21, 14.16. HRMS (ESI): *m/z* 473.3627 ([M+H$^+$] $C_{30}H_{49}O_4^+$ requires 473.3625).

Method B ("one pot" synthesis). Oxygen was constantly introduced into the vigorously stirred mixture of allobetulone (**4**) (0.10 g, 0.22 mmol) and potassium *tert*-butoxide (0.10 g, 0.89 mmol) in *tert*-butanol (7 ml) at 40 ºC for 1 hr. Then water (0.7 ml) was added and reaction mixture was stirred at 70-75 ºC for 24 hr, cooled to room temperature, diluted with 1 N hydrochloric acid (80 ml), stirred at room temperature for 1 hr, filtered, washed with water, dried and crystallized from toluene to give titled compound (**14**) (0.08 g, 80%).

19β,28-Epoxy-3β-hydroxy-28-oxo-1(2→3)-abeo-18α-oleanan-2-oic acid (15)

2-Hydroxy-3-oxo-18α-olean-1-en-28,19β-olide (**10**) (0.55 g, 1.17 mmol) was mixed with potassium hydroxide powder (0.33 g, 5.87 mmol) in *tert*-butanol (21.4 ml) containing water (1.06 ml). Resulting mixture was stirred at 80 °C for 22 hr. Reaction mixture was poured in 1 N hydrochloric acid (100 ml). White precipitate was filtered, washed with water (4x50 ml) and dried to give titled compound (**15**) (0.55 g, 96%). Crystallization from methanol gave colorless crystals, m.p. 284-286 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.94 (s, 1H), 2.12 (d, 1H), 1.89-0.90 (m, 42H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.86, 179.91, 87.12, 86.12, 62.11, 54.11, 51.17, 48.52, 46.76, 46.13, 43.88, 41.42, 40.07, 36.13, 33.71, 33.55, 32.30, 31.96, 28.75, 28.15, 27.09, 26.29, 25.53, 23.96, 23.57, 20.63, 18.64, 17.15, 15.57, 13.84. HRMS (ESI): *m/z* 509.3239 ([M+Na$^+$] $C_{30}H_{46}NaO_5^+$ requires 509.3238).

Methyl 3β-hydroxy-1(2→3)-abeolup-20-en-2-oate (16) and methyl 3α-hydroxy-1(2→3)-abeolup-20-en-2-oate (16')

Method A. 3β-Hydroxy-1(2→3)-abeolup-20-en-2-oic acid (**11**) (50.5 mg, 110.6 μmol) was dissolved in ethyl ether (3 ml). Ethereal diazomethane (2 ml, ~0.02 g/ml) was added to form yellow solution. Mixture was stirred for 30 min. Reaction solution was flashed with dry nitrogen[1] to remove diazomethane excess and evaporated in vacuum to give methyl 3β-hydroxy-1(2→3)-abeolup-20-en-2-oate (**16**) as white solid (51.0 mg, 98%).

Method B. 2-Hydroxylup-1,20-dien-3-one (**6**) (0.40 g, 0.91 mmol) was added to a solution of potassium methoxide (0.06 g, 0.91 mmol) in dry methanol (30 ml). Reaction mixture was kept at 60 °C in closed vial for 3 days. Then it was cooled to room temperature, diluted with water (100 ml) and acidified with 3% hydrochloric acid. Precipitate was filtered, washed with water and dried to give mixture of isomers **16**/**16'** (78/22 ratio, 0.41 g, 95%). It was separated on silica (hexanes/ethyl ether, 95/5). Methyl 3β-hydroxy-1(2→3)-abeolup-20-en-2-oate (**16**) was isolated with the first fraction, R_f = 0.33. Methyl 3α-hydroxy-1(2→3)-abeolup-20-en-2-oate (**16'**) was isolated with the second fraction, R_f = 0.25.

Methyl 3β-hydroxy-1(2→3)-abeolup-20-en-2-oate (**16**), m.p. 159-162 ºC, $[\alpha]_D$ +35.6º (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.70 (s, 1H), 4.58 (s, 1H), 3.78 (s, 3H), 3.23 (s, 1H), 2.39 (m, 1H), 2.04-0.81 (m, 43H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.70, 151.16, 109.61, 87.38, 62.22, 53.52, 52.44, 50.65, 48.89, 48.57, 48.56, 48.26, 44.11, 43.23, 41.92, 40.28, 38.45, 35.89, 34.57, 30.08, 27.91, 27.29, 25.14, 23.83, 21.15, 19.57, 19.06, 18.25, 16.68, 16.44, 15.03. HRMS (ESI): *m/z* 493.3646 ([M+Na$^+$] $C_{31}H_{50}NaO_3^+$ requires 493.3652).

Methyl 3α-hydroxy-1(2→3)-abeolup-20-en-2-oate (**16'**), m.p. 223-226 ºC, $[\alpha]_D$ +13.7º (ethanol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.62 (s, 1H), 4.50 (s, 1H), 3.67 (s, 3H), 3.00 (s, 1H), 2.47 (d, 1H), 2.30 (m, 1H), 1.84 (m, 1H), 1.70-0.69 (m, 41H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 176.13, 151.22, 109.60, 87.06, 59.94, 54.44, 52.22, 51.52, 48.79, 48.56, 48.31, 43.69, 43.24, 43.22, 42.25, 40.29, 38.52, 35.88, 34.61, 30.12, 27.92, 25.19, 24.83, 23.78, 21.30, 19.56, 18.62, 18.24, 18.07, 16.30, 15.01. HRMS (ESI): *m/z* 493.3649 ([M+Na$^+$] $C_{31}H_{50}NaO_3^+$ requires 493.3652).

Methyl 3β,28-dihydroxy-1(2→3)-abeolup-20-en-2-oate (17)

[1] Nitrogen-overflow passed through 3% hydrochloric acid for diazomethane detoxification.

3β,28-Dihydroxy-1(2→3)-abeolup-20-en-2-oic acid (**12**) (51.0 mg, 107.9 μmol) was dissolved in ethyl ether (3 ml). Ethereal diazomethane (2 ml, ~0.02 g/ml) was added to form yellow solution. Mixture was stirred for 30 min. Reaction solution was flashed with dry nitrogen[1] to remove diazomethane excess and evaporated in vacuum to give titled compound (**17**) as white solid (52.0 mg, 99%), m.p. 167-169 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.68 (s, 1H), 4.58 (s, 1H), 3.80 (d, 1H), 3.77 (s, 3H), 3.34 (d, 1H), 3.24 (s, 1H), 2.39 (m, 1H), 2.07-0.81 (m, 40H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.64, 150.68, 109.95, 87.38, 62.20, 60.70, 53.50, 52.45, 50.62, 49.00, 48.87, 48.05, 47.99, 44.06, 43.09, 42.00, 37.69, 34.53, 34.24, 30.00, 29.97, 27.50, 27.27, 25.22, 23.72, 21.11, 19.34, 19.03, 16.67, 16.44, 15.25. HRMS (ESI): *m/z* 509.3613 ([M+Na$^+$] $C_{31}H_{50}NaO_4^+$ requires 509.3601).

Dimethyl 3β-hydroxy-1(2→3)-abeolup-20-ene-2,28-dioate (18)

3β-Hydroxy-1(2→3)-abeolup-20-ene-2,28-dioic acid (**13**) (51.0 mg, 104.8 μmol) was dissolved in diethyl ether (3 ml). Ethereal diazomethane (2 ml, ~0.02 g/ml) was added to form yellow solution. Mixture was stirred for 30 min. Reaction solution was flashed with dry nitrogen[1] to remove diazomethane excess and evaporated in vacuum to give titled compound (**18**) as white solid (53.0 mg, 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.75 (s, 1H), 4.62 (s, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.20 (s, 1H), 3.00 (m, 1H), 2.12-2.29 (m, 2H), 2.08 (d, 1H), 1.70-1.90 (m, 2H), 1.80-0.70 (m, 34H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.66, 176.91, 150.79, 109.84, 87.37, 62.26, 56.77, 53.54, 52.45, 51.55, 50.78, 49.73, 48.88, 47.27, 44.10, 42.78, 41.76, 38.70, 37.27, 34.61, 32.51, 30.86, 30.12, 27.28, 25.55, 23.78, 21.13, 19.65, 19.04, 16.67, 16.40, 15.21. HRMS (ESI): *m/z* 537.3549 ([M+Na$^+$] $C_{32}H_{50}NaO_5^+$ requires 537.3551).

Methyl 19β,28-epoxy-3β-hydroxy-1(2→3)-abeo-18α-oleanan-2-oate (19)

19β,28-Epoxy-3β-hydroxy-1(2→3)-abeo-18α-oleanan-2-oic acid (**14**) (50.0 mg, 105.8 μmol) was dissolved in ethyl ether (3 ml). Ethereal diazomethane (2 ml, ~0.02 g/ml) was added to form yellow solution. Mixture was stirred for 30 min. Reaction solution was flashed with dry nitrogen[1] to remove diazomethane excess and evaporated in vacuum to give titled compound (**19**) as white solid (50.0 mg, 97%), m.p. 225-229 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.80 (s, 3H), 3.79 (d, 1H), 3.55 (s, 1H), 3.47 (d, 1H), 3.20 (s, 1H), 2.08 (d, 1H), 1.80 (d, 1H), 1.70-0.70 (m, 40H). ^{13}C NMR (75 MHz, CD_3OD): δ 179.07, 90.27, 89.14, 72.92, 63.91, 55.70, 53.34, 52.94, 50.03, 48.68, 45.52, 43.28, 42.62, 38.29, 37.90, 36.26, 35.70, 34.36, 30.11, 28.40, 28.01, 27.80, 25.84, 25.80, 25.49, 21.81, 20.42, 18.54, 17.21, 15.13. HRMS (ESI): *m/z* 509.3613 ([M+Na$^+$] $C_{31}H_{50}NaO_4^+$ requires 509.3601).

Methyl 19β,28-epoxy-3β-hydroxy-28-oxo-1(2→3)-abeo-18α-oleanan-2-oate (20)

19β,28-Epoxy-3β-hydroxy-28-oxo-1(2→3)-abeo-18α-oleanan-2-oic acid (**15**) (33.7 mg, 69.2 μmol) was dissolved in tetrahydrofuran (2.5 ml). Ethereal diazomethane (2 ml, ~0.02 g/ml) was added to form yellow solution. Mixture was stirred for 30 min. Reaction solution was flashed with dry nitrogen[1] to remove diazomethane excess and evaporated in vacuum to give titled compound (**20**) as white solid (34.3 mg, 99%), m.p. 273-276 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.94 (s, 1H), 3.78 (s, 3H), 3.17 (s, 1H), 2.06 (d, 1H), 1.89-0.88 (m, 42H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 179.82, 177.16, 87.17, 86.07, 62.15, 53.56, 52.22, 51.16, 48.60, 46.77, 46.09, 43.82, 41.39, 40.07, 36.12, 33.74, 33.54, 32.30, 31.97, 28.75, 28.14, 26.98, 26.31, 25.55, 23.95, 23.55, 20.73, 18.63, 16.85, 15.58, 13.88. HRMS (ESI): *m/z* 523.3391 ([M+Na$^+$] $C_{31}H_{48}NaO_5^+$ requires 523.3394).

Potassium 1-oxo-1,3-seco-2-norlup-20-en-3-oate (21)

Potassium hydroxide powder (0.0218 g, 0.3885 mmol) was dissolved in methanol (5 ml). 1α-Hydroxy-2-oxa-2-norlup-20-en-3-one (**31**) (0.1720 g, 0.3885 mmol) was added to the solution. Resulting mixture was stirred and refluxed for 2 hr. Reaction mixture was evaporated in vacuum. Solid product was dried in vacuum (0.1 torr, 90 °C) to give titled compound (**21**) as white powder (0.1851 g, 99%). ^{1}H NMR (300 MHz, CD_3OD, 1wt% KOH): δ 9.19 (s, 1H), 4.70 (s, 1H), 4.58 (s, 1H), 2.40 (m, 1H), 2.10 (m, 1H), 2.06-0.71 (m, 40H). ^{13}C NMR (300 MHz, CD_3OD, 1wt% KOH): δ 206.98, 184.93, 150.49, 109.18, 54.52, 48.48, 48.16, 47.83, 47.03, 43.29, 42.99, 40.97, 39.73, 39.30, 38.71, 35.39, 33.21, 30.08, 29.73, 27.47, 26.65, 25.04, 23.12, 19.79, 18.53, 17.38, 15.33, 13.85, 11.26. HRMS (ESI): *m/z* 503.2891 ([M+Na$^+$] $C_{29}H_{45}KNaO_3^+$ requires 503.2898).

Potassium 28-hydroxy-1-oxo-1,3-seco-2-norlup-20-en-3-oate (22)

Potassium hydroxide powder (0.0252 g, 0.4491 mmol) was dissolved in methanol (5 ml). 1α,28-Dihydroxy-2-oxa-2-norlup-20-en-3-one (**32**) (0.2060 g, 0.4491 mmol) was added to the solution. Resulting mixture was stirred and refluxed for 2 hr. Reaction mixture was evaporated in vacuum. Solid product was dried in vacuum (0.1 torr, 90 °C) to give titled compound (**22**) as white powder (0.2215 g, 99%). ^{1}H NMR (300 MHz, CD_3OD, 1wt% KOH): δ 9.22 (s, 1H), 4.68 (s, 1H), 4.57 (s, 1H), 3.74 (d, 1H), 3.29 (d, 1H), 2.42 (m, 1H), 2.20 (m, 1H), 2.06-0.71 (m, 37H). ^{13}C NMR (300 MHz, CD_3OD, 1wt% KOH): δ 207.30, 185.10, 150.54, 109.18, 59.13, 54.43, 48.65, 48.32, 47.95, 47.81, 47.67, 43.16, 39.82, 39.12, 37.89, 33.91, 33.10, 29.68, 29.05, 27.02, 25.13, 25.07, 24.18, 22.88, 20.27, 18.25, 15.16, 13.99, 11.35. HRMS (ESI): *m/z* 519.2852 ([M+Na$^+$] $C_{29}H_{45}KNaO_4^+$ requires 519.2847).

Potassium 1-oxo-1,3-seco-2-norlup-20-en-3,28-dioate (23)

Potassium hydroxide powder (0.0223 g, 0.3974 mmol) was dissolved in methanol (5 ml). 1α-Hydroxy-2-oxa-3-oxo-2-norlup-20-en-28-oic acid (**33**) (0.0939 g, 0.1987 mmol) was added to the solution. Resulting mixture was stirred and refluxed for 2 hr. Reaction mixture was evaporated in vacuum. Solid product was dried in vacuum (0.1 torr, 90 °C) to give titled compound (**23**) as white powder (0.1081 g, 99%). ^{1}H NMR (300 MHz, CD_3OD, 1wt% KOH): δ 9.21 (s, 1H), 4.69 (s, 1H), 4.55 (s, 1H), 3.20 (m, 1H), 2.80-2.55 (m, 2H), 2.34-0.72 (m, 36H). ^{13}C NMR (300 MHz, CD_3OD, 1wt% KOH): δ 207.37, 185.11, 183.47, 151.93, 108.29, 57.85, 54.60, 49.52, 48.50, 47.80, 47.29, 42.96, 39.64, 39.54, 38.52, 37.99, 33.40, 31.05, 30.06, 26.01, 25.67, 25.50, 23.47, 23.21, 19.99, 18.57, 15.60, 13.87, 11.30. HRMS (ESI): *m/z* 571.2185 ([M+Na$^+$] $C_{29}H_{42}K_2NaO_5^+$ requires 571.2199).

Potassium 19β,28-epoxy-1-oxo-2-nor-18α-oleanan-3-oate (24)

Potassium hydroxide powder (0.0202 g, 0.3600 mmol) was dissolved in methanol (5 ml). 19β,28-Epoxy-1α-hydroxy-2-oxa-2-nor-18α-oleanan-3-one (**34**) (0.1651 g, 0.3600 mmol) was added to the solution. Resulting mixture was stirred and refluxed for 2 hr. Reaction mixture was evaporated in vacuum. Solid product was dried in vacuum (0.1 torr, 90 °C) to give titled compound (**24**) as white powder (0.1773 g, 99%). ^{1}H NMR (300 MHz, CD_3OD, 1wt% KOH): δ 9.28 (s, 1H), 3.82 (d, 1H), 3.57 (s, 1H), 3.51 (d, 1H), 2.25 (m, 1H), 1.96 (m, 1H), 1.70-0.90 (m, 39H). ^{13}C NMR (300 MHz, CD_3OD, 1wt% KOH): δ 208.40, 186.28, 89.51, 72.19, 55.65, 48.88, 47.89, 42.70, 42.31, 40.78, 40.61, 37.52, 37.21, 36.04, 33.85, 33.76, 29.24, 27.61, 27.10, 27.03, 26.08, 25.40, 24.84, 24.15, 21.46, 16.14, 13.86, 12.79. HRMS (ESI): *m/z* 519.2841 ([M+Na$^+$] $C_{29}H_{45}KNaO_4^+$ requires 519.2847).

Potassium 19β,28-epoxy-1,28-dioxo-1,3-seco-2-nor-18α-oleanan-3-oate (25)

Potassium hydroxide powder (0.0182 g, 0.3243 mmol) was dissolved in methanol (5 ml). 1α-Hydroxy-2-oxa-3-oxo-2-nor-18α-oleanan-28,19β-olide (**35**) (0.1533 g, 0.3243 mmol) was added to the solution. Resulting suspension was stirred and refluxed for 2 hr. Reaction mixture was evaporated in vacuum. Solid product was dried in vacuum (0.1 torr, 90 °C) to give titled compound (**25**) as white powder (0.1632 g, 99%), m.p. 464-465 °C decomp. ^{1}H NMR (300 MHz, CD_3OD, 1wt% KOH): δ 9.24 (s, 1H), 4.01 (s, 1H), 2.22-0.89 (m, 41H). ^{13}C NMR (75 MHz, CD_3OD, 1wt% KOH): δ 208.26, 186.21, 182.18, 87.71, 55.67, 47.67, 47.63, 41.51, 40.97, 40.54, 37.99, 34.55, 33.69, 33.52, 32.72, 29.13, 29.10, 26.97, 26.48, 26.46, 25.12, 24.04, 21.27, 15.89, 13.96, 12.77. HRMS (ESI): *m/z* 533.2636 ([M+Na$^+$] $C_{29}H_{43}KNaO_5^+$ requires 533.2640).

1α-Hydroxy-2-oxa-2-norlup-20-en-3-one (31)

Lupenone (**1**) (0.50 g, 1.18 mmol) was mixed with potassium *tert*-butoxide (0.50 g, 4.45 mmol) in *tert*-butanol (20 ml). Suspension was stirred and heated at 40 °C. Dry oxygen was bubbled in for 26 hr. Reaction suspension was evaporated in vacuum. Solid residue was washed with dichloromethane (2x40 ml) at room temperature. Precipitate was filtered and dried. It was suspended in water (20 ml) and treated with 1 N hydrochloric acid (20 ml). White precipitate was filtered, washed with water (5x30 ml) and dried. The product was purified on silica (ethyl ether eluent) to give white solid product (0.45 g, 87%), m.p. 146-148 °C.[2] ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.27 (s, 0.84H),

[2] The chemical structure for products **31-35/26-30** was assigned after ^{1}H NMR analysis in solutions where they consisted of two tautomeric forms**.** The chemical structure for these products in a solid state could be different but was not studied.

4.67 (s, 1H), 4.54 (s, 1H), 2.36 (m, 1H), 2.30-0.80 (m, 41H), contains 16% of 1-oxo-2-nor-2,3-secolupan-3-oic acid (**26**) (δ 9.23 (s, 0.16H)). ^{13}C NMR (75 MHz, $CDCl_3$): δ 179.45, 151.08, 109.77, 100.99, 48.40, 48.24, 43.44, 43.21, 42.61, 40.61, 40.50, 40.21, 39.61, 38.29, 35.74, 32.86, 29.99, 28.89, 27.66, 24.89, 23.79, 21.23, 19.50, 19.10, 18.27, 16.00, 14.78, 14.09. HRMS (ESI): *m/z* 465.3337 ([M+Na$^+$] $C_{29}H_{46}NaO_3^+$ requires 465.3339).

1α,28-Dihydroxy-2-oxa-2-norlup-20-en-3-one (32)

Betulone (**2**) (1.00 g, 2.27 mmol) was mixed with potassium *tert*-butoxide (1.00 g, 8.87 mmol) in *tert*-butanol (40 ml). Suspension was stirred and heated at 40 °C. Dry oxygen was bubbled in for 30 hr. Reaction mixture was evaporated in vacuum. Solid residue was washed with dichloromethane (2x40 ml) at room temperature. Precipitate was filtered and dried. It was suspended in water (20 ml) and treated with 1 N hydrochloric acid (20 ml). White precipitate was filtered, washed with water (5x30 ml) and dried. The product was purified on silica (ethyl ether eluent) to give white solid product (0.80 g, 77%), m.p. 154-157 °C.[2] ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.29 (s, 0.78H), 4.68 (s, 1H), 4.58 (s, 1H), 3.81 (d, 1H), 3.36 (d, 1H), 2.40 (m, 1H), 1.97-0.79 (m, 38H), contains 21% of 1-oxo-28-hydroxy-1,3-seco-2-norlupan-3-oic acid (**27**) (δ 9.26 (s, 0.21H)). ^{13}C NMR (75 MHz, $CDCl_3$): δ 179.37, 150.55, 110.11, 100.93, 60.75, 48.84, 48.03, 47.96, 43.31, 42.60, 40.59, 40.19, 39.58, 37.56, 34.19, 32.82, 29.88, 29.32, 28.87, 27.24, 24.97, 23.76, 21.12, 19.26, 19.05, 15.97, 14.97, 14.06. HRMS (ESI): *m/z* 481.3289 ([M+Na$^+$] $C_{29}H_{46}NaO_4^+$ requires 481.3288).

1α-Hydroxy-2-oxa-3-oxo-2-norlup-20-en-28-oic acid (33)

Betulonic acid (**3**) (1.00 g, 2.20 mmol) was mixed with potassium *tert*-butoxide (1.00 g, 8.90 mmol) in *tert*-butanol (40 ml). Suspension was stirred and heated at 40 °C. Dry oxygen was bubbled in for 26 hr. Reaction mixture was evaporated in vacuum. Solid residue was washed with dichloromethane (2x40 ml) at room temperature. Precipitate was filtered and dried. It was suspended in water (40 ml) and treated with 1 N hydrochloric acid (20 ml). White precipitate was filtered, washed with water (5x30 ml) and dried to give white solid product (0.80 g, 77%), m.p. 190-208 °C.[2] ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.29 (s, 0.85H), 4.75 (s, 1H), 4.63 (s, 1H), 3.00 (m, 1H), 2.50-0.70 (m, 38H), contains 15% of 1-oxo-1,3-seco-2-norlup-20-en-3,28-dioic acid (**28**) (δ 9.35 (s, 0.15H)). ^{13}C NMR (75 MHz, DMSO-d_6): δ 179.38, 177.93, 151.01, 110.39, 100.78, 56.05, 54.39, 49.10, 47.30, 46.43, 43.01, 42.58, 40.99, 40.28, 39.58, 38.25, 37.00, 33.03, 32.34, 30.71, 29.83, 29.23, 25.49, 24.58, 24.04, 19.63, 16.05, 15.00, 14.65. HRMS (ESI): *m/z* 495.3093 ([M+Na$^+$] $C_{29}H_{44}NaO_5^+$ requires 495.3081).

19β,28-Epoxy-1α-hydroxy-2-oxa-2-nor-18α-oleanan-3-one (34)

Allobetulone (**4**) (0.53 g, 1.20 mmol) was mixed with potassium *tert*-butoxide (0.50 g, 4.45 mmol) in *tert*-butanol (20 ml). Suspension was stirred and heated at 40 °C. Dry oxygen was bubbled in for 26 hr. Reaction mixture was evaporated in vacuum. Solid residue was washed with dichloromethane (2x40 ml) at room temperature. Precipitate was filtered and dried. It was suspended in water (20 ml) and treated with 1 N hydrochloric acid (20 ml). White precipitate was filtered, washed with water (5x30 ml) and dried to give white solid product (0.45 g, 82%), m.p. 236-245 °C.[2] ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.29 (s, 1H), 3.75 (d, 1H), 3.52 (s, 1H), 3.47 (d, 1H), 2.50-1.70 (m, 2H), 1.70-0.70 (m, 39H). HRMS (ESI): *m/z* 481.3287 ([M+Na$^+$] $C_{29}H_{46}NaO_4^+$ requires 481.3288).

1α-Hydroxy-2-oxa-3-oxo-2-nor-18α-oleanan-28,19β-olide (35)

28-Oxoallobetulone (**5**) (1.01 g, 2.22 mmol) was mixed with potassium *tert*-butoxide (1.00 g, 8.87 mmol) in *tert*-butanol (50 ml). Suspension was stirred and heated at 50 °C. Dry oxygen was bubbled in for 50 hr. Reaction suspension was evaporated in vacuum. Solid residue was washed with dichloromethane (2x40 ml) at room temperature. Precipitate was filtered and dried. It was suspended in water (20 ml) and treated with 1 N hydrochloric acid (20 ml). White precipitate was filtered, washed with water (5x30 ml) and dried. Product was refluxed with methanol (10 ml). Precipitate was hot filtered, washed with methanol (10 ml) and dried to give white solid product (0.78 g, 74%), m.p. 351-353 °C decomp.[2] ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.33 (s, 1H), 3.93 (s, 1H), 2.20-0.92 (m, 41H). ^{1}H NMR (300 MHz, Py-d_5): δ 5.67 (s, 0.6H), 4.04 (m, 1H), 2.51-0.83 (m, 41H), contains 40% of 19β,28-epoxy-1,28-dioxo-1,3-seco-2-nor-18α-oleanan-3-oic acid (**30**) (δ 9.58 (s, 0.4H)). ^{13}C NMR (75 MHz, $CDCl_3$): δ 179.73, 178.54, 100.43, 85.95, 46.64, 46.10, 42.51, 40.68, 40.39, 40.26, 40.03, 39.44, 36.03, 33.56, 32.29, 32.12,

31.91, 29.71, 28.72, 27.85, 26.02, 25.46, 23.93, 23.44, 20.95, 18.67, 15.33, 14.17, 13.67. HRMS (ESI): *m/z* 495.3093 ([M+Na^+] $C_{29}H_{44}NaO_5^+$ requires 495.3081).

Methyl 1-oxo-1,3-seco-2-norlupan-3-oate (36)

1α-Hydroxy-2-oxa-2-norlup-20-en-3-one (**31**) (50.0 mg, 113.0 mmol) was dissolved ethyl ether (3 ml). Ethereal diazomethane (3 ml, ~0.02 g/ml) was added to form yellow solution. Mixture was stirred at room temperature for 1 hr. Reaction solution was flashed with dry nitrogen[1] to remove diazomethane excess and evaporated in vacuum. Product was crystallized from benzene to give a titled compound (**36**) as a white solid (50.6 mg, 98%), m.p. 135-138 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.15 (s, 1H), 4.68 (s, 1H), 4.58 (s, 1H), 3.61 (s, 3H), 2.38 (m, 1H), 2.07 (d, 1H), 1.98-0.74 (m, 40H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.93, 178.38, 150.76, 109.83, 54.56, 51.96, 48.94, 48.30, 48.07, 46.64, 43.52, 43.24, 40.13, 39.86, 39.55, 38.61, 35.60, 33.25, 29.98, 27.64, 25.47, 25.02, 24.15, 23.24, 20.37, 19.51, 18.25, 15.99, 14.72, 11.88. HRMS (ESI): *m/z* 479.3511 ([M+Na^+] $C_{30}H_{48}NaO_3^+$ requires 479.3496).

Methyl 1-oxo-28-hydroxy-1,3-seco-2-norlupan-3-oate (37)

1α,28-Dihydroxy-2-oxa-2-norlup-20-en-3-one (**32**) (50.0 mg, 109.0 mmol) was dissolved ethyl ether (3 ml). Ethereal diazomethane (3 ml, ~0.02 g/ml) was added to form yellow solution. Mixture was stirred at room temperature for 1 hr. Reaction solution was flashed with dry nitrogen[1] to remove diazomethane excess and evaporated in vacuum to give titled compound (**37**) as a white solid (50.5 mg, 98%), m.p. 136-139 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.14 (s, 1H), 4.67 (s, 1H), 4.58 (s, 1H), 3.81 (d, 1H), 3.61 (s, 3H), 3.35 (d, 1H), 2.38 (m, 1H), 2.07-0.80 (m, 38H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.60, 178.09, 150.02, 109.92, 60.42, 54.26, 51.71, 48.69, 48.49, 47.74, 47.63, 46.37, 43.13, 39.69, 39.27, 37.61, 33.90, 32.94, 29.63, 28.93, 26.99, 25.22, 24.83, 23.90, 22.88, 20.09, 19.03, 15.73, 14.67, 11.62. HRMS (ESI): *m/z* 495.3459 ([M+Na^+] $C_{30}H_{48}NaO_4^+$ requires 495.3445).

Dimethyl 1-oxo-1,3-seco-2-norlup-20-en-3,28-dioate (38)

1α-Hydroxy-2-oxa-3-oxo-2-norlup-20-en-28-oic acid (**33**) (50.0 mg, 105.8 mmol) was dissolved in ethyl ether (3 ml). Ethereal diazomethane (3 ml, ~0.02 g/ml) was added to form yellow solution. Mixture was stirred at room temperature for 1 hr. Reaction solution was flashed with dry nitrogen[1] to remove diazomethane excess and evaporated in vacuum to give titled compound (**38**) as a white solid (51.9 mg, 98%), m.p. 179-182 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.15 (s, 1H), 4.72 (s, 1H), 4.59 (s, 1H), 3.65 (s, 3H), 3.62 (s, 3H), 3.0 (m, 1H), 2.35-2.17 (m, 2H), 2.08-0.70 (m, 36H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.71, 178.13, 176.52, 150.13, 109.79, 56.47, 54.27, 51.73, 51.35, 49.11, 48.63, 46.36, 42.74, 39.42, 39.41, 38.43, 36.83, 33.00, 31.88, 30.43, 29.60, 25.12, 23.90, 22.94, 20.09, 19.30, 15.67, 14.58, 11.64. HRMS (ESI): *m/z* 523.3388 ([M+Na^+] $C_{31}H_{48}NaO_5^+$ requires 523.3394).

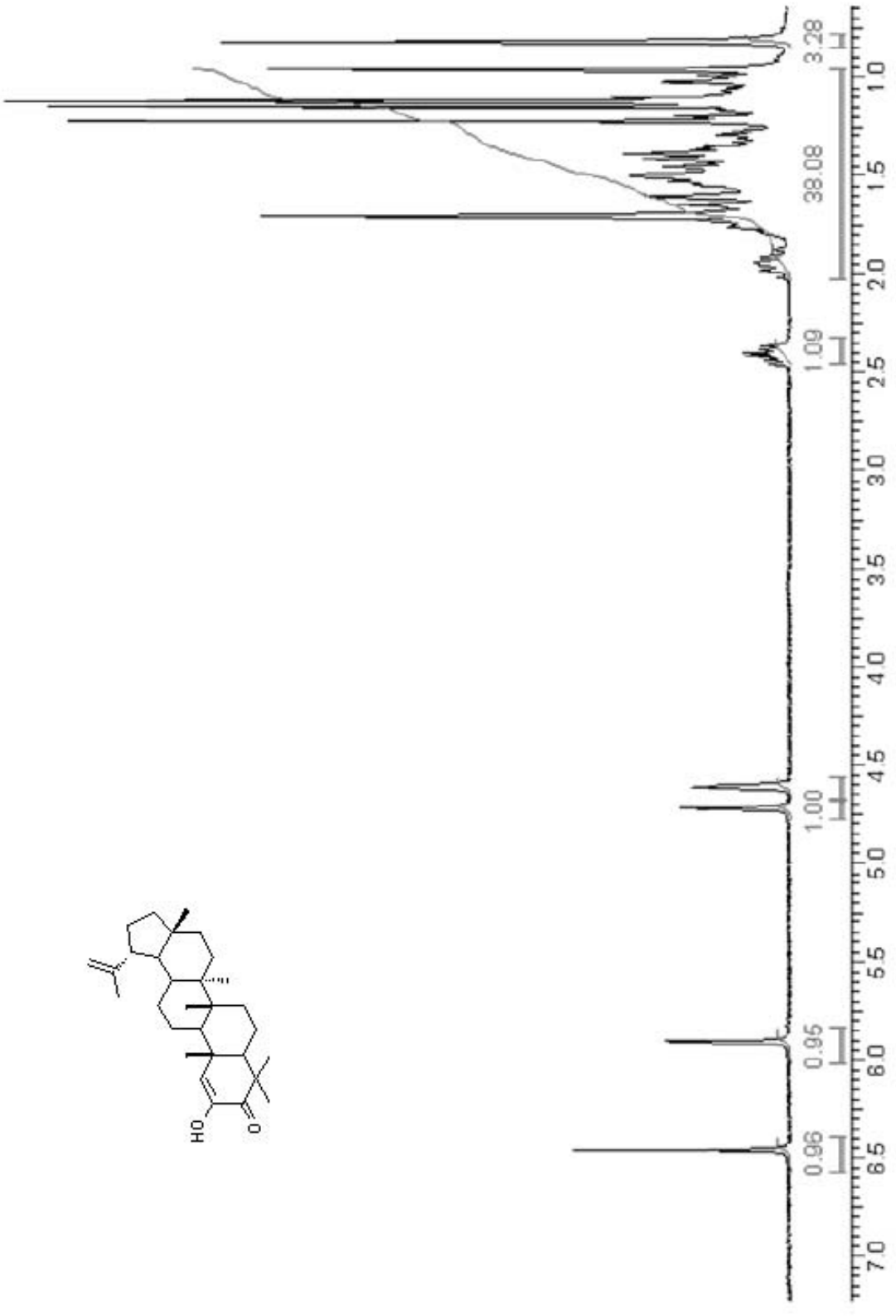
Methyl 1-oxo-19β,28-epoxy-1,3-seco-2-nor-18a-oleanan-3-oate (39)

19β,28-Epoxy-1α-hydroxy-2-oxa-2-nor-18α-oleanan-3-one (**34**) (50.0 g, 109.0 mmol) was dissolved in ethyl ether (3 ml). Ethereal diazomethane (3 ml, ~0.02 g/ml) was added to form yellow solution. Mixture was stirred at room temperature for 1 hr. Reaction solution was flashed with dry nitrogen to remove diazomethane excess and evaporated in vacuum to give titled compound (**39**) as white solid (50.5 g, 98%), m.p. 118-122 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.15 (s, 1H), 3.72 (d, 1H), 3.59 (s, 3H), 3.45 (s, 1H), 3.41 (d, 1H), 2.08 (d, 1H), 1.76 (d, 1H), 1.70-0.70 (m, 39H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.93, 178.34, 88.06, 71.45, 54.59, 51.88, 49.05, 46.84, 46.62, 41.72, 41.70, 39.61, 39.59, 36.53, 36.51, 34.75, 32.84, 28.99, 26.68, 26.67, 26.66, 26.36, 26.36, 24.77, 22.89, 24.55, 20.33, 15.86, 13.70, 12.18. HRMS (ESI): *m/z* 495.3449 ([M+Na^+] $C_{30}H_{48}NaO_4^+$ requires 495.3445).

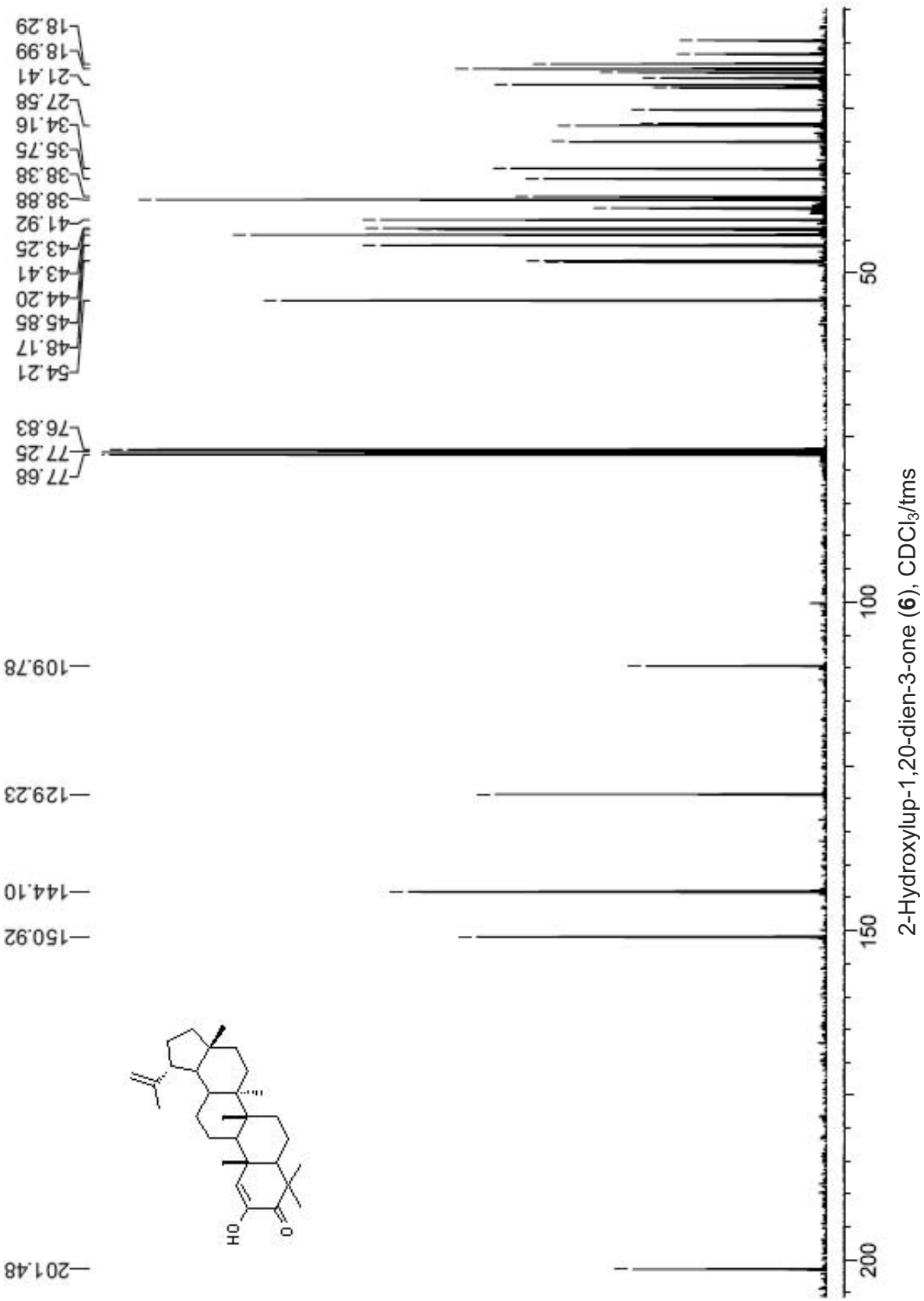
Methyl 19β,28-epoxy-1,28-dioxo-1,3-seco-2-nor-18α-oleanan-3-oate (40)

1α-Hydroxy-2-oxa-3-oxo-2-nor-18α-oleanan-28,19β-olide (**35**) (0.21 g, 0.44 mmol) was suspended in chloroform (9 ml). Ethereal diazomethane (15 ml, ~0.02 g/ml) was added to form yellow solution. Mixture was stirred at room temperature for 1 hr. Reaction solution was flashed with dry nitrogen[1] to remove diazomethane excess and evaporated in vacuum to give titled compound (**40**) as white solid (0.20 g, 91%), m.p. 276-279 °C decomp. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.17 (s, 1H), 3.91 (s, 1H), 3.60 (s, 3H), 2.09-0.94 (m, 41H). ^{13}C NMR

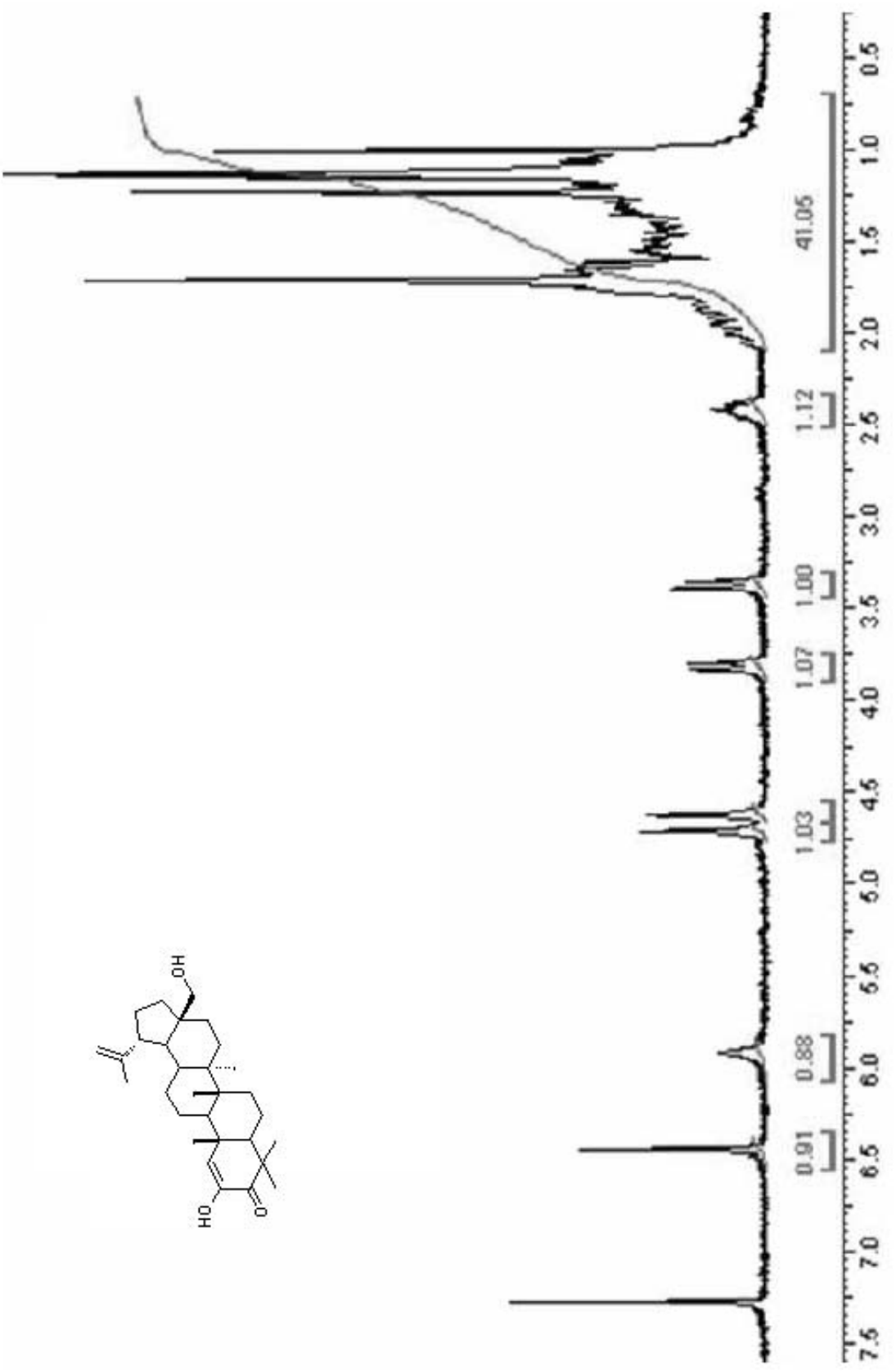
(75 MHz, $CDCl_3$): δ 202.52, 179.59, 178.01, 85.78, 54.28, 51.72, 48.80, 46.47, 46.31, 46.11, 40.29, 39.95, 39.29, 36.33, 33.55, 32.39, 32.27, 31.85, 28.67, 27.85, 25.96, 25.39, 25.32, 23.90, 23.81, 22.73, 19.95, 15.43, 13.56, 11.95. HRMS (ESI): *m/z* 509.3249 ([$M+Na^+$] $C_{30}H_{46}NaO_5^+$ requires 509.3238).



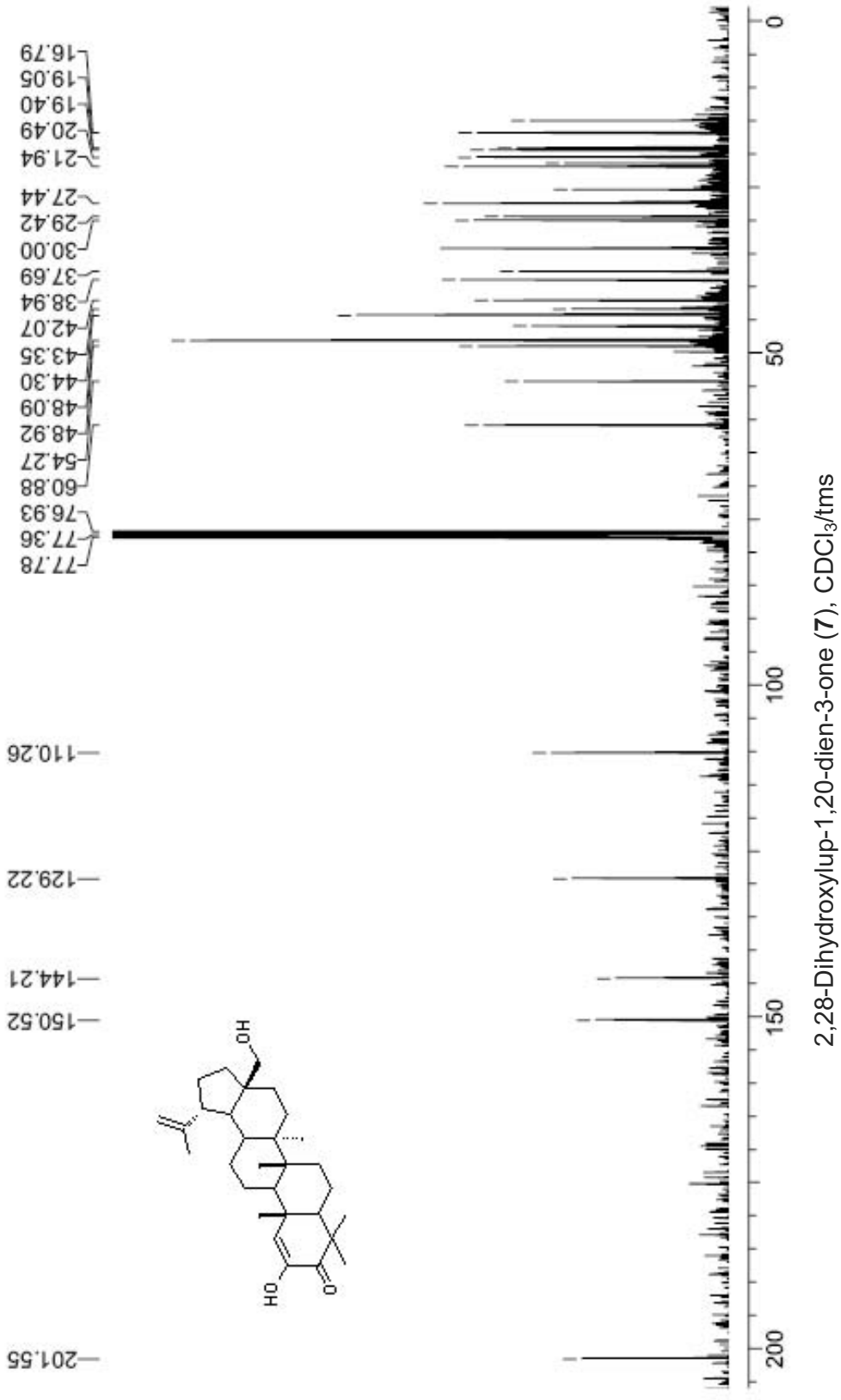
2-Hydroxylup-1,20-dien-3-one (**6**), $CDCl_3$/tms



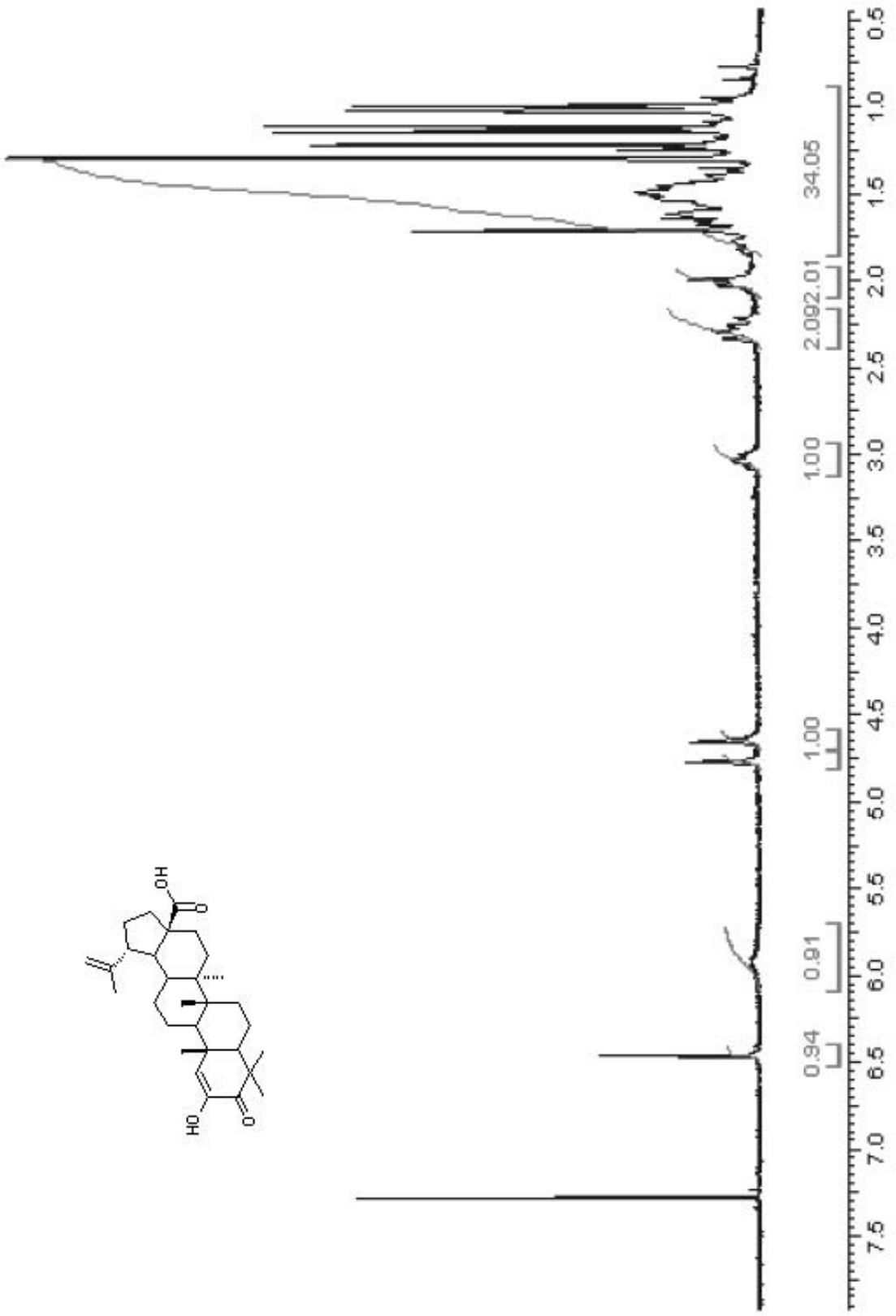
2-Hydroxylup-1,20-dien-3-one (**6**), $CDCl_3$/tms



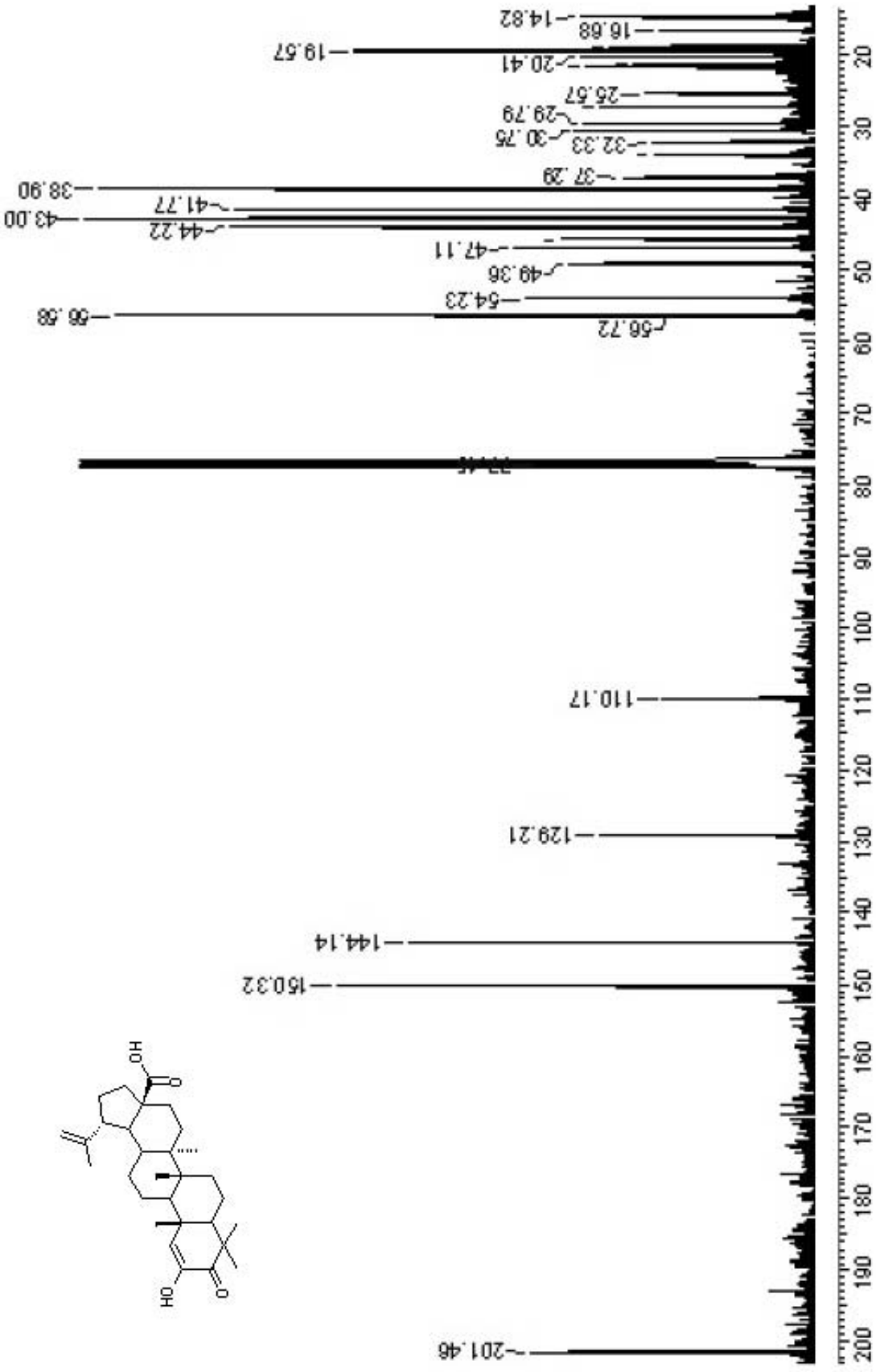
2,28-Dihydroxylup-1,20-dien-3-one (**7**), $CDCl_3$/tms



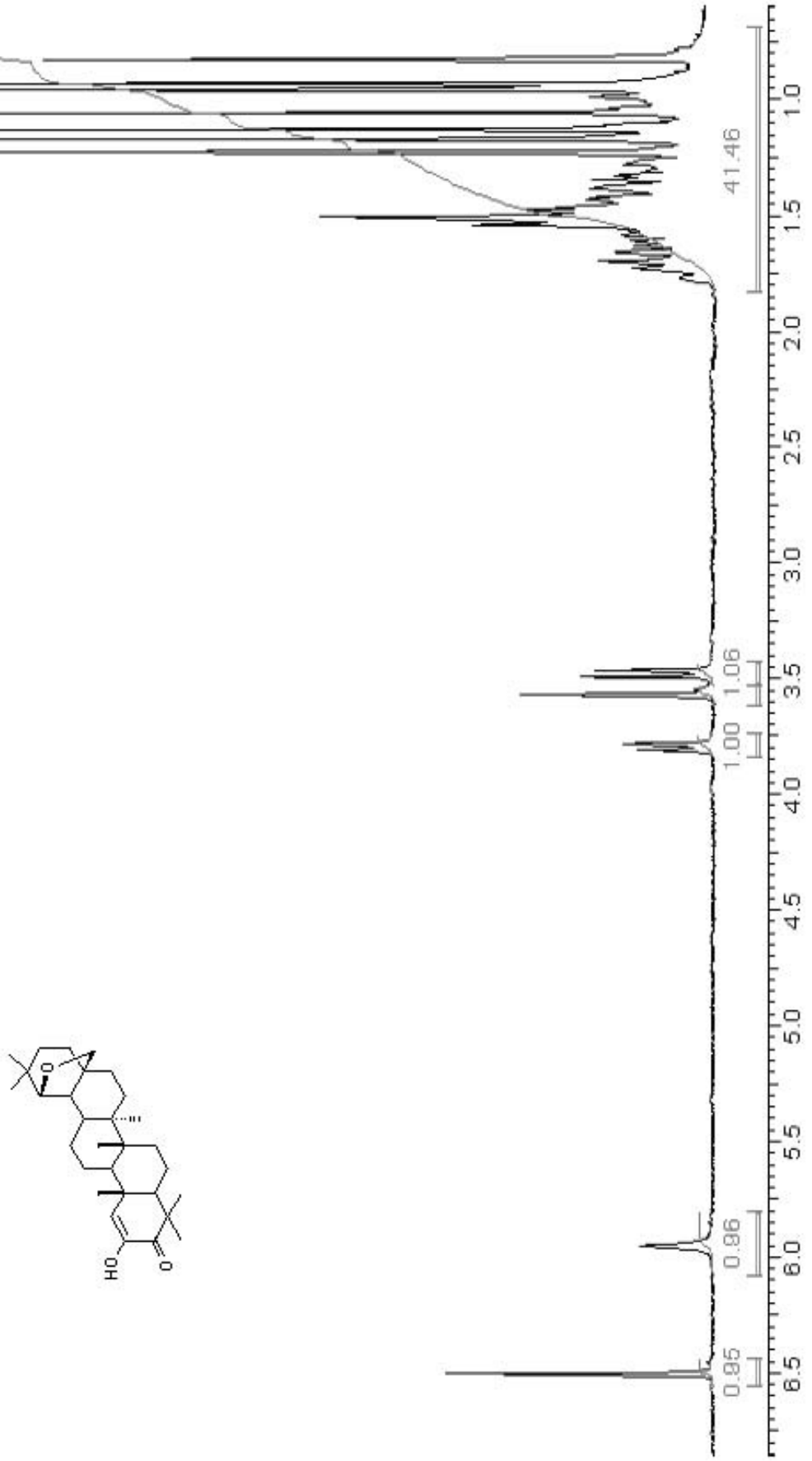
2,28-Dihydroxylup-1,20-dien-3-one (**7**), $CDCl_3$/tms



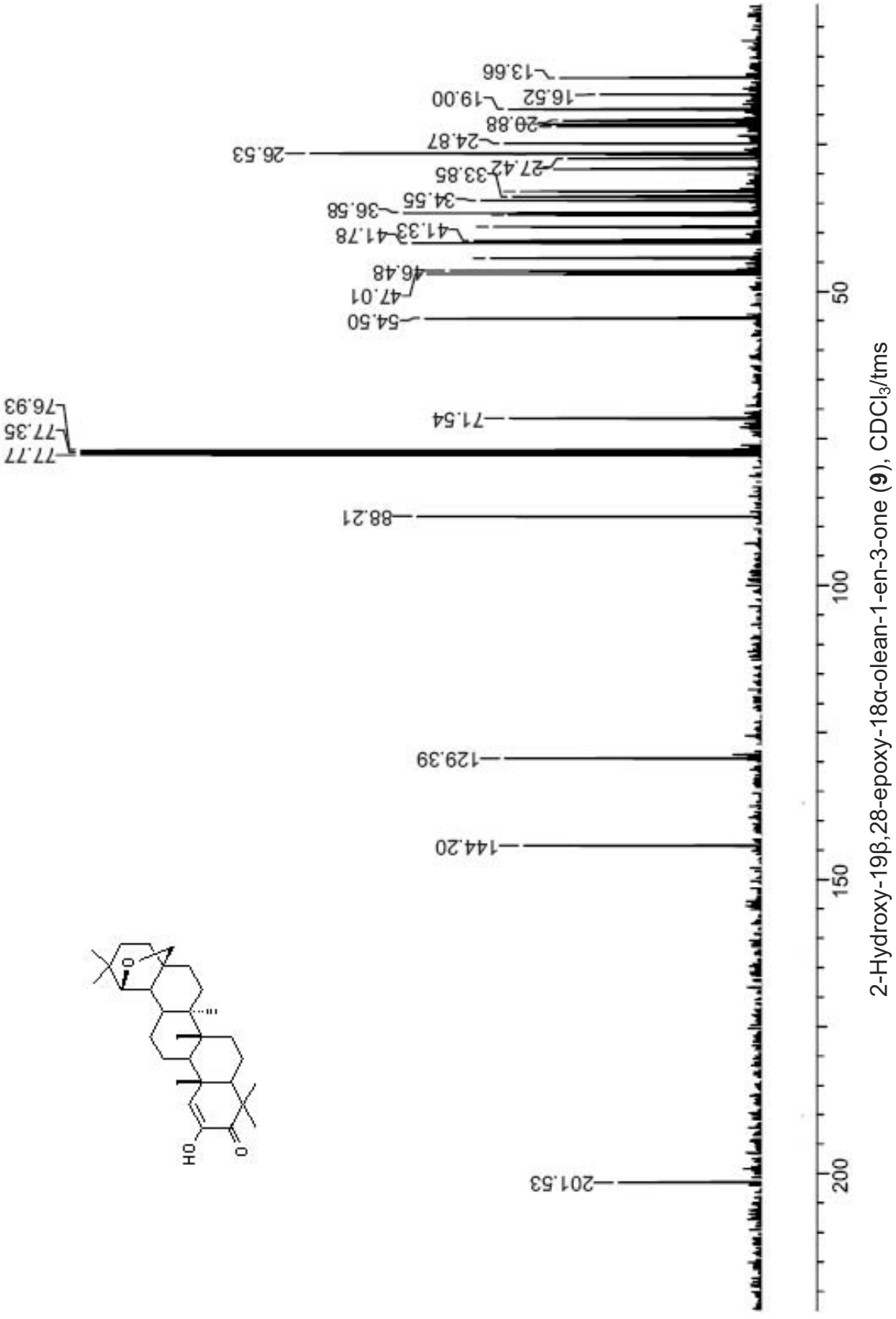
2-Hydroxy-3-oxolup-1,20-dien-28-oic acid (**8**), $CDCl_3$/tms



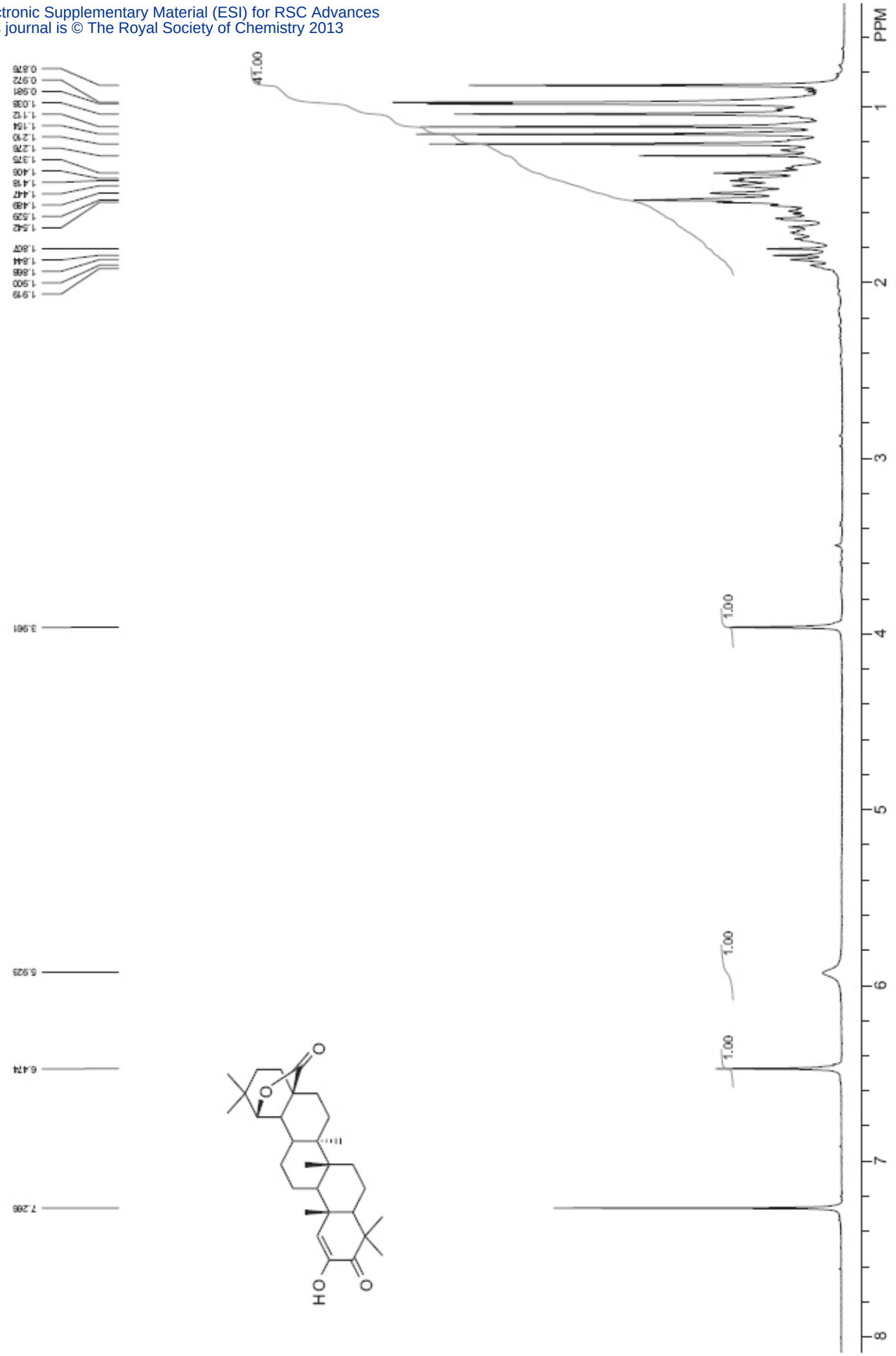
2-Hydroxy-3-oxolup-1,20-dien-28-oic acid (**8**), $CDCl_3$/tms



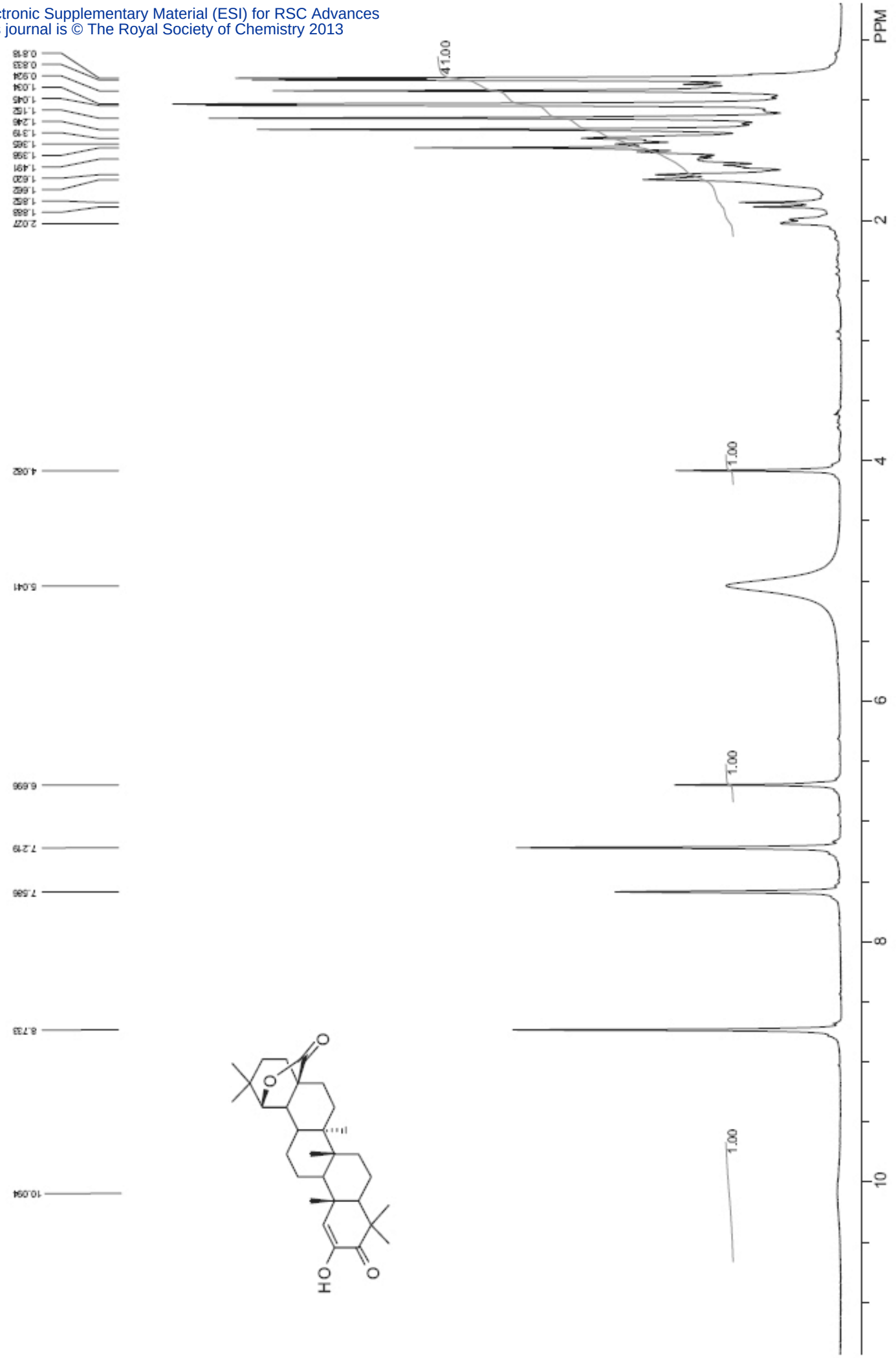
2-Hydroxy-19β,28-epoxy-18α-olean-1-en-3-one (**9**), $CDCl_3$/tms



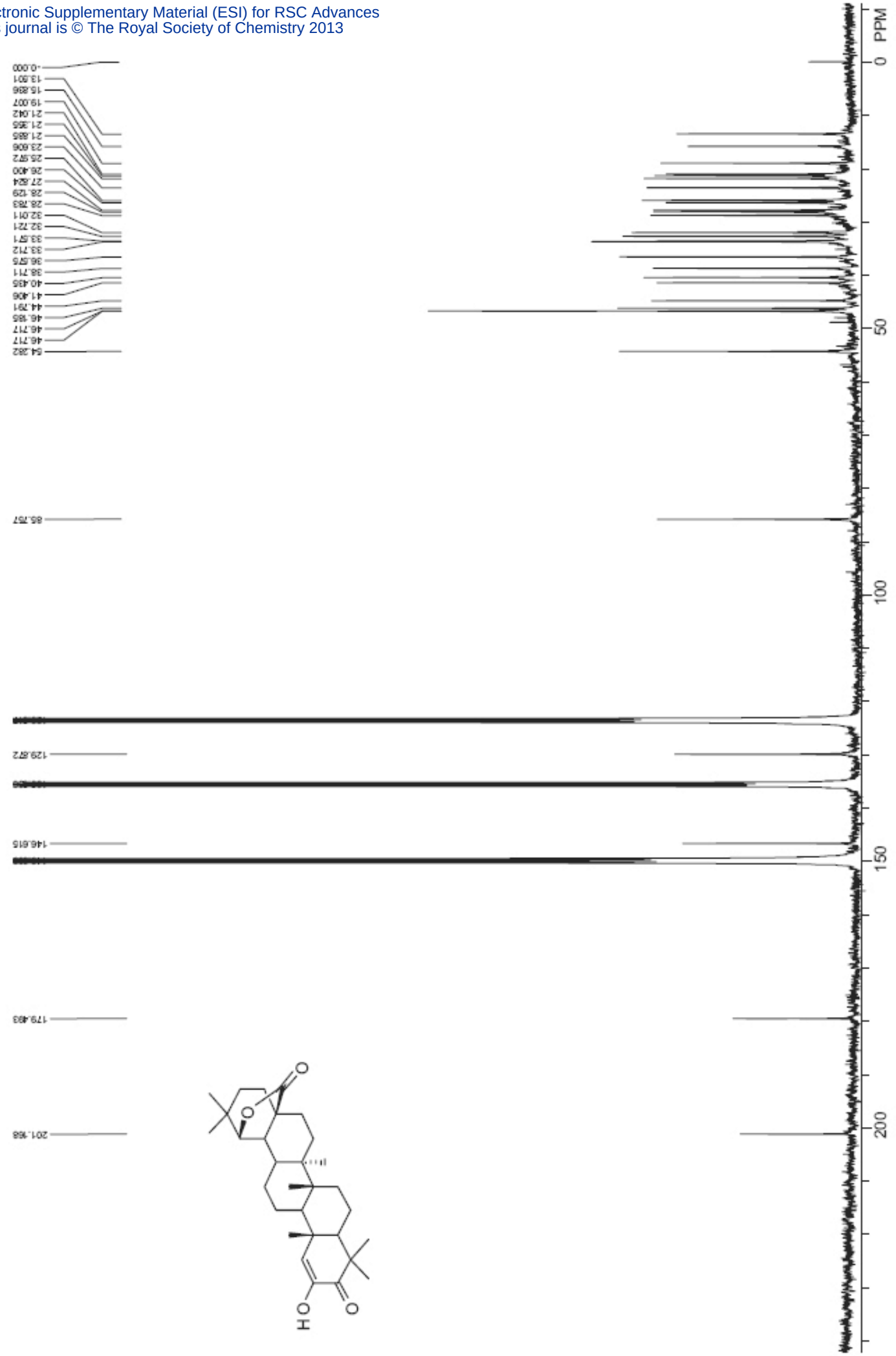
2-Hydroxy-19β,28-epoxy-18α-olean-1-en-3-one (**9**), $CDCl_3$/tms



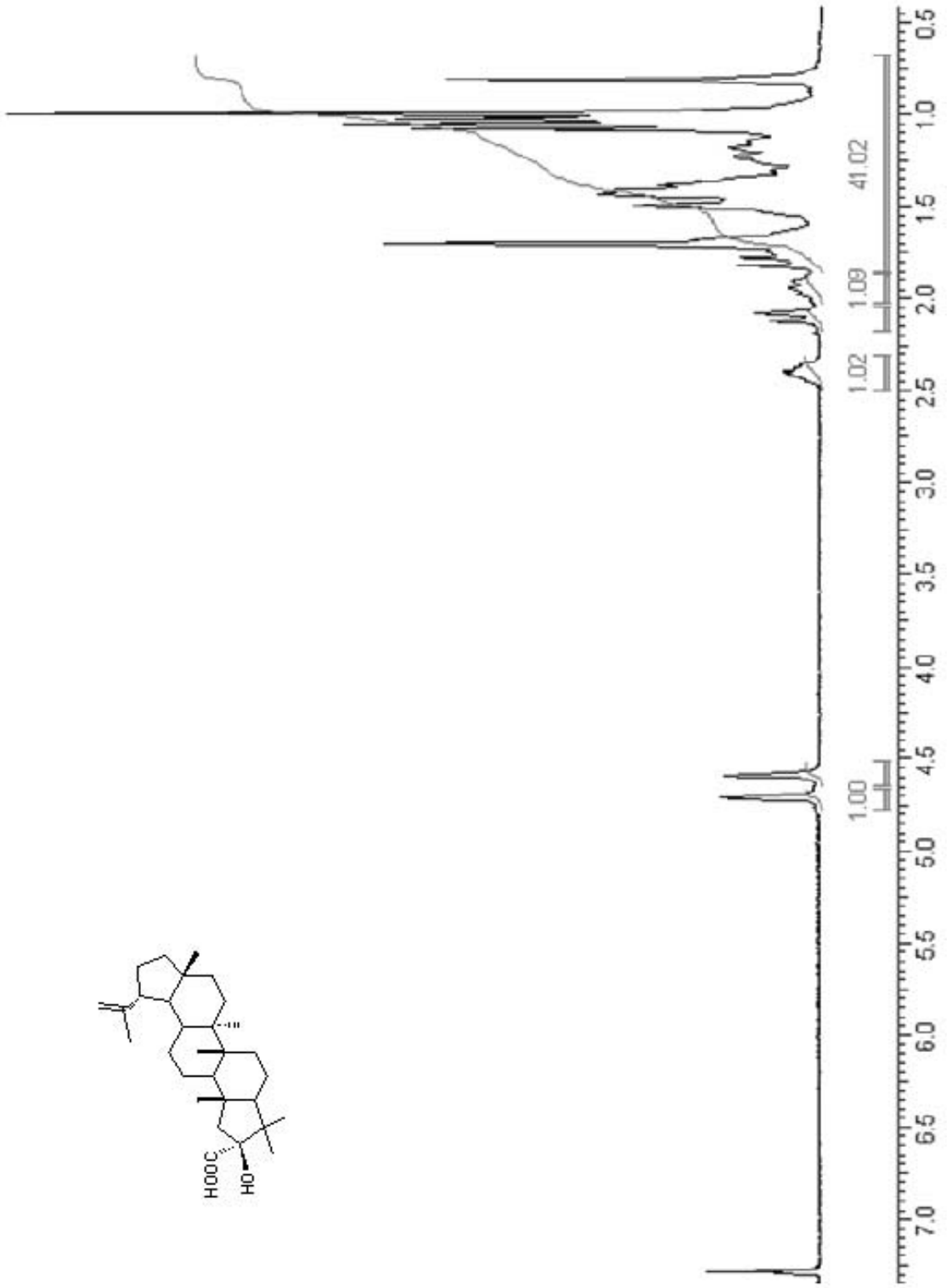
2-Hydroxy-3-oxo-18α-olean-1-en-28,19β-olide (**10**), $CDCl_3$/tms



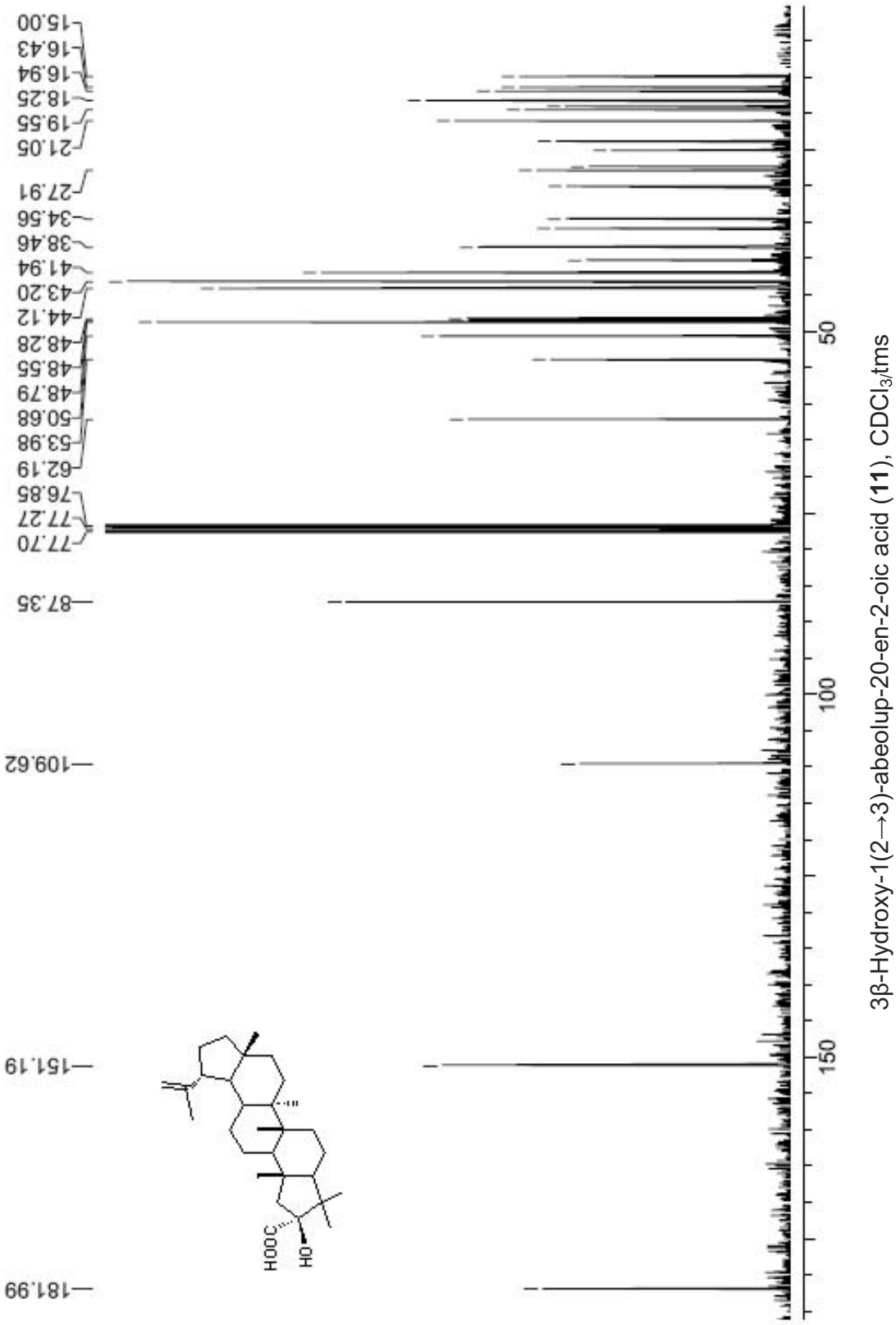
2-Hydroxy-3-oxo-18α-olean-1-en-28,19β-olide (**10**), Py-d_5/tms



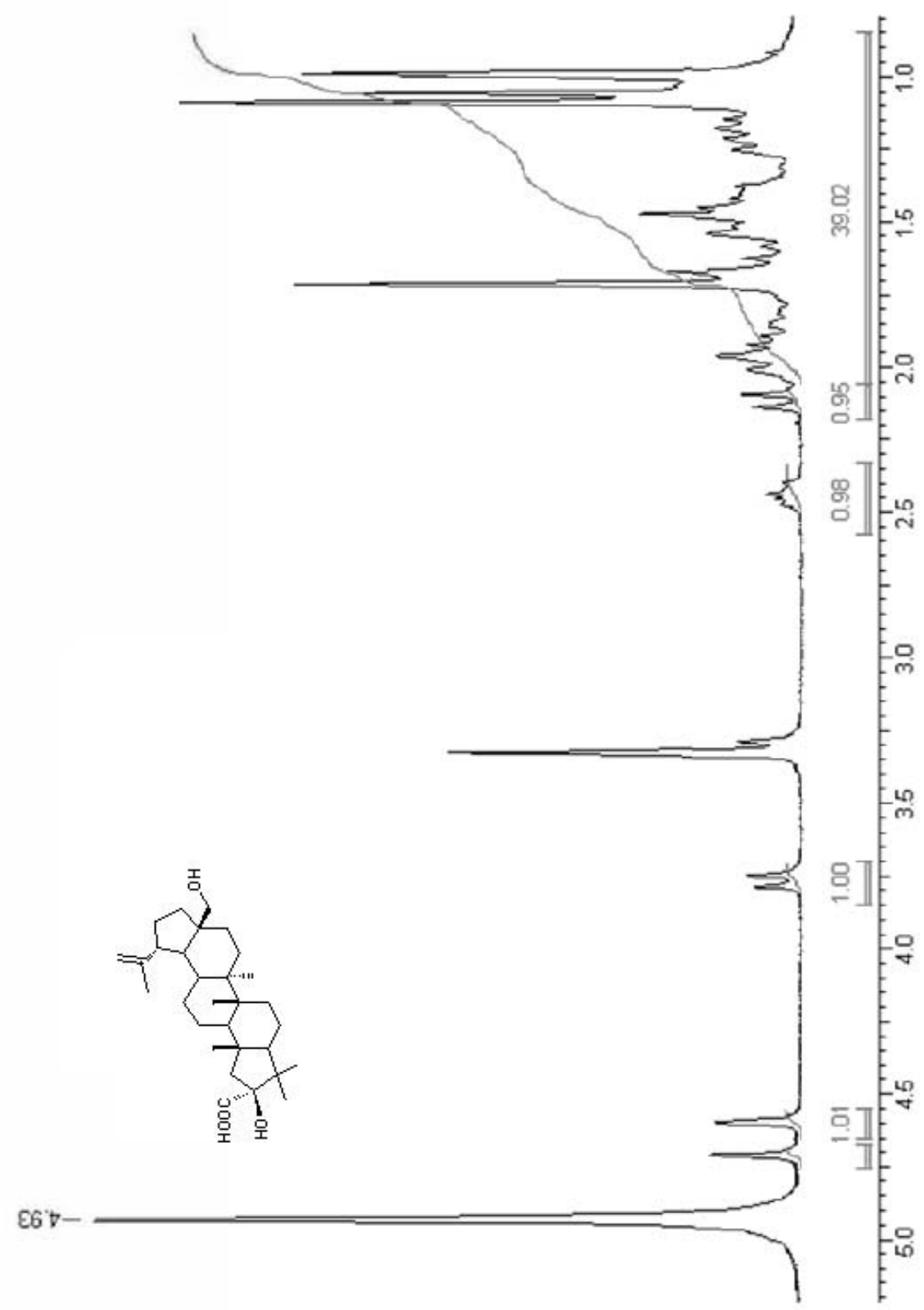
2-Hydroxy-3-oxo-18α-olean-1-en-28,19β-olide (**10**), Py-d_5/tms



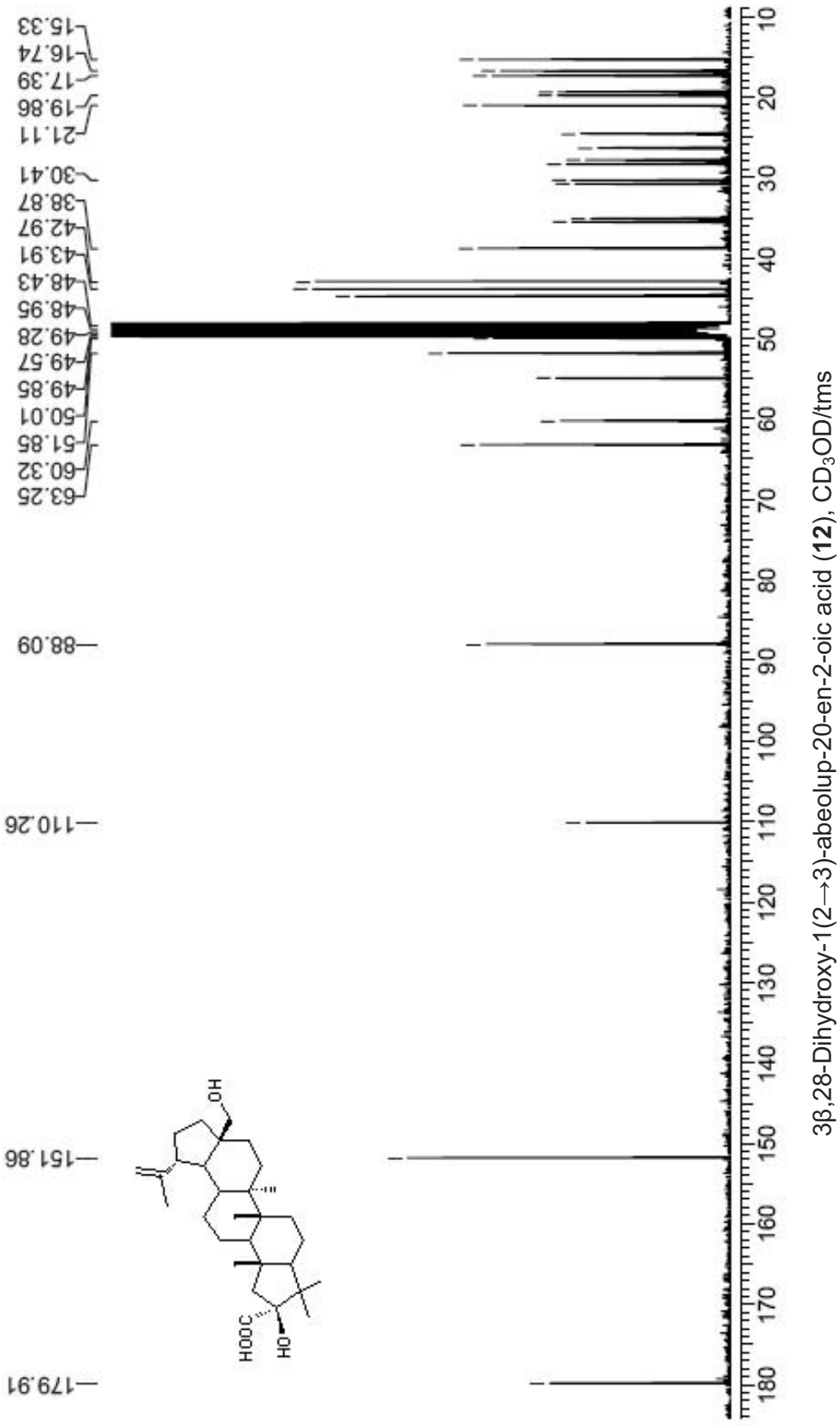
3β-Hydroxy-1(2→3)-abeolup-20-en-2-oic acid (**11**), $CDCl_3$/tms



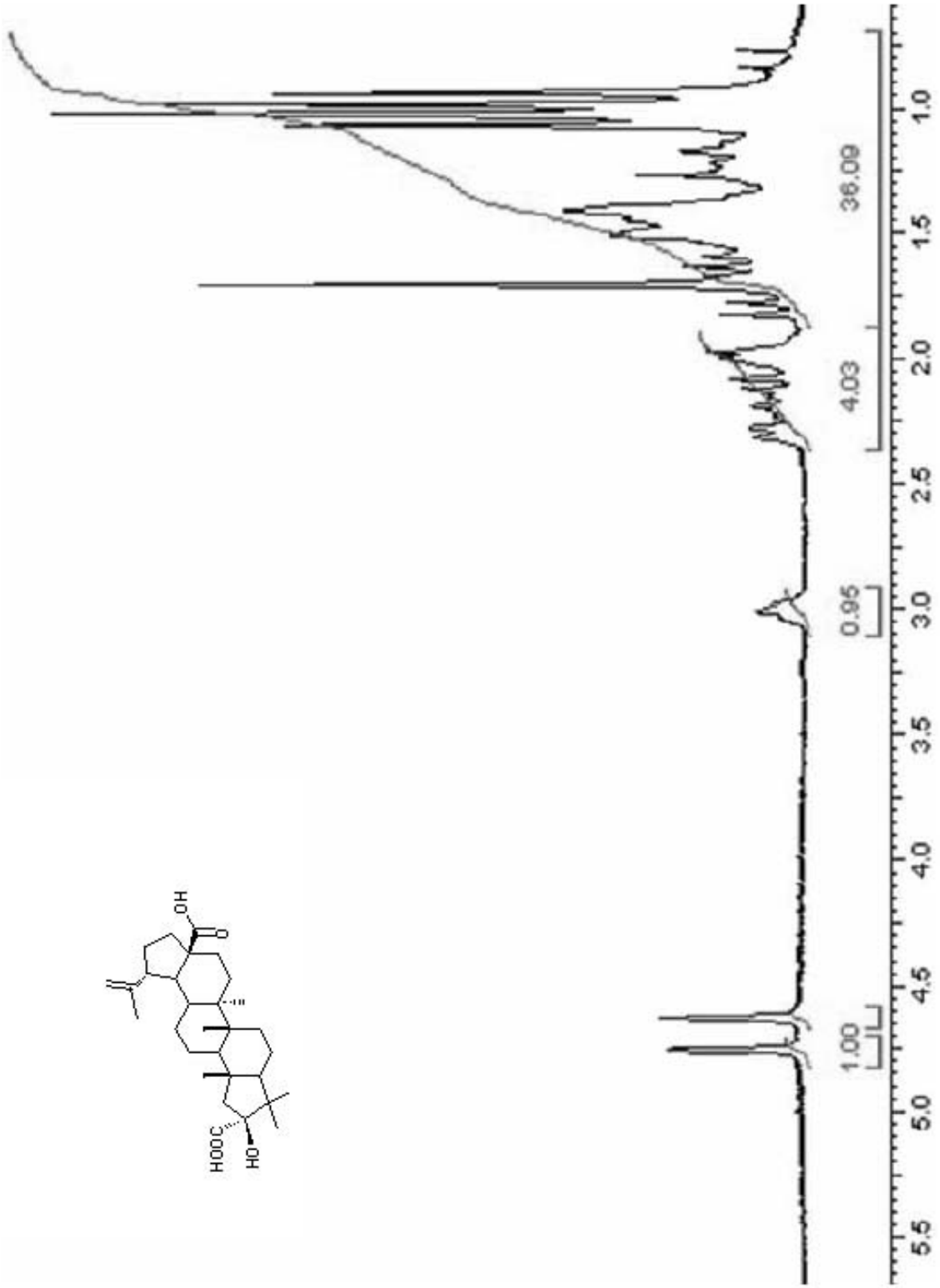
3β-Hydroxy-1(2→3)-abeolup-20-en-2-oic acid (**11**), $CDCl_3$/tms



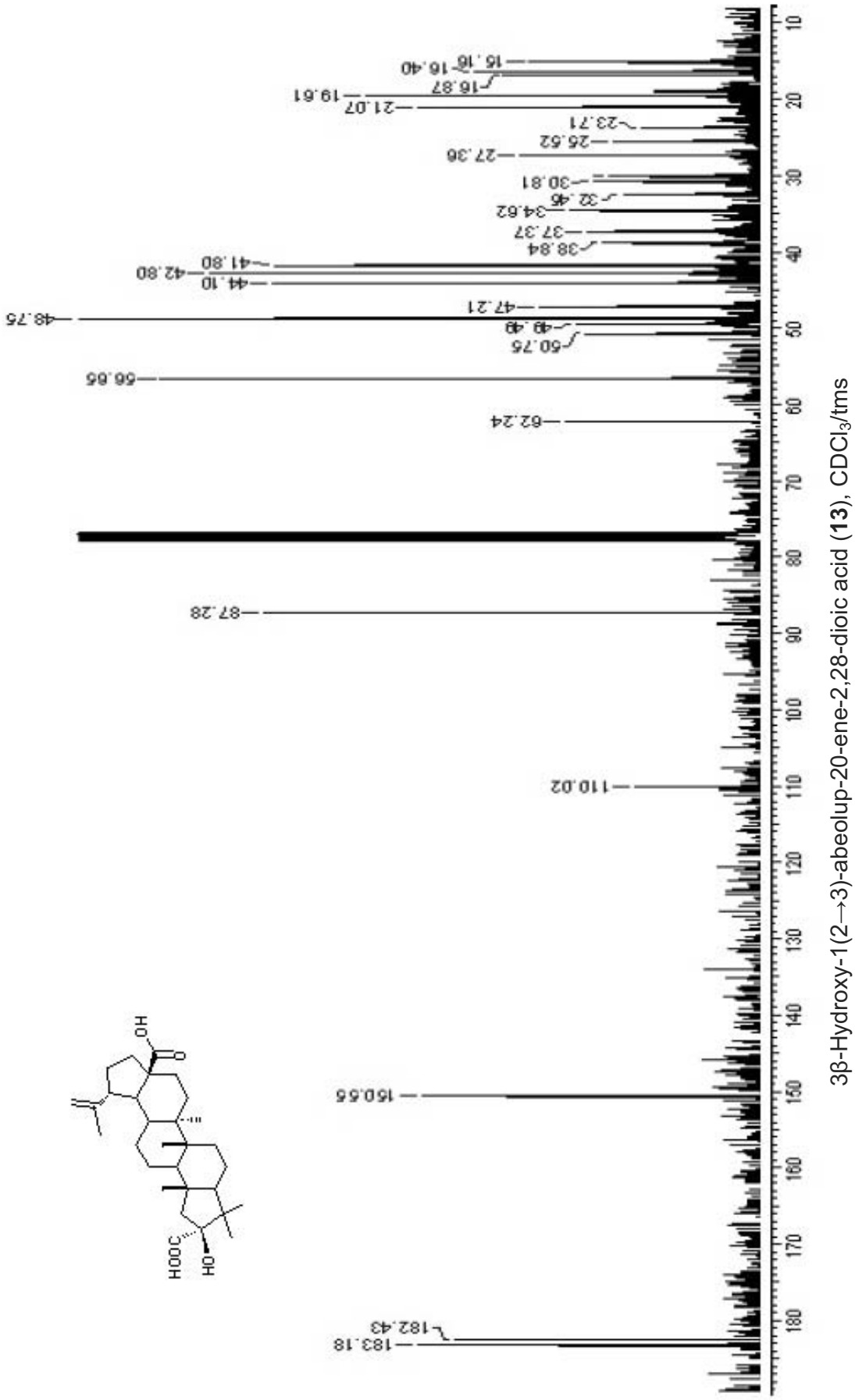
3β,28-Dihydroxy-1(2→3)-abeolup-20-en-2-oic acid (**12**), CD_3OD/tms



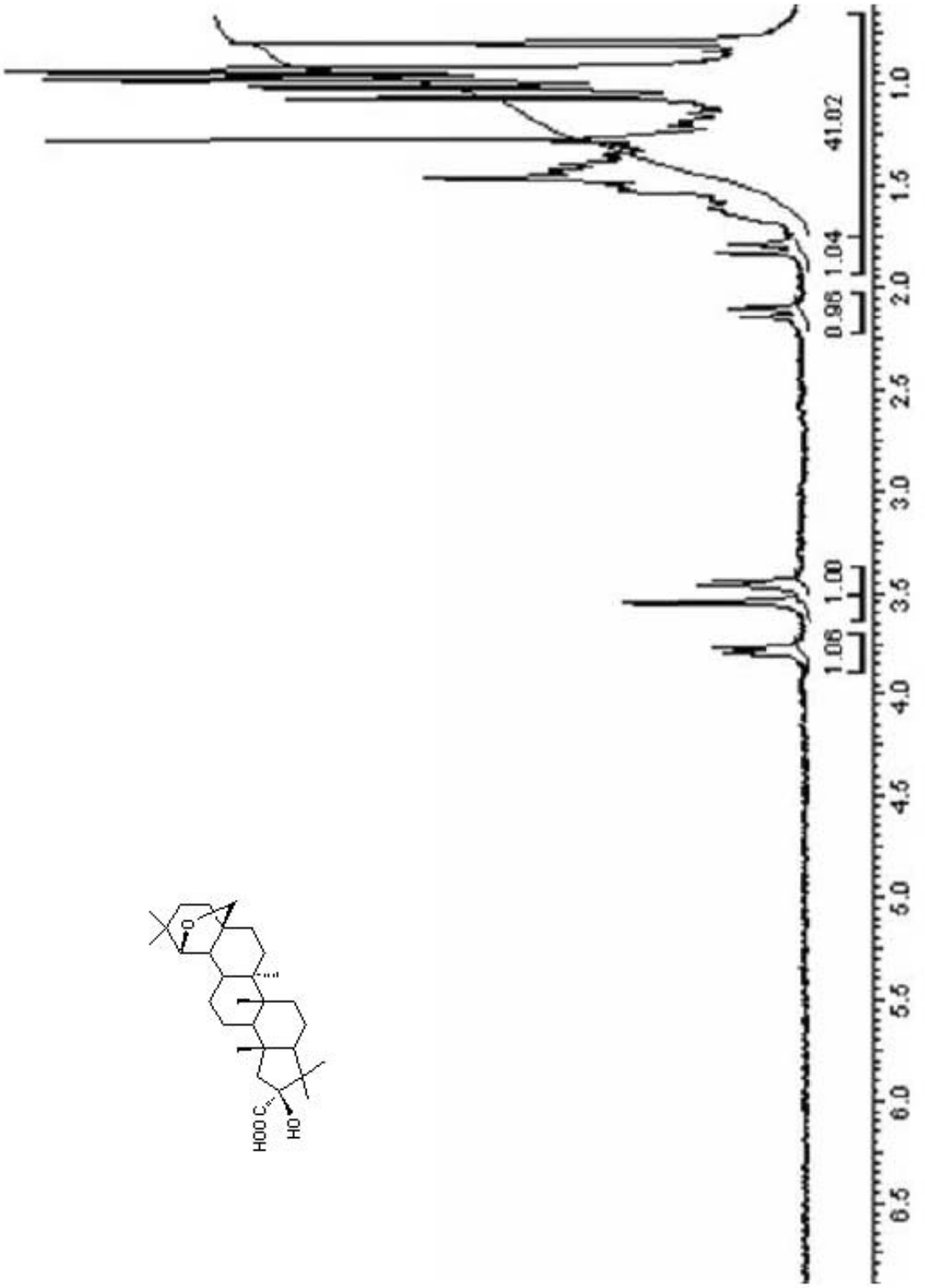
3β,28-Dihydroxy-1(2→3)-abeolup-20-en-2-oic acid (**12**), CD_3OD/tms



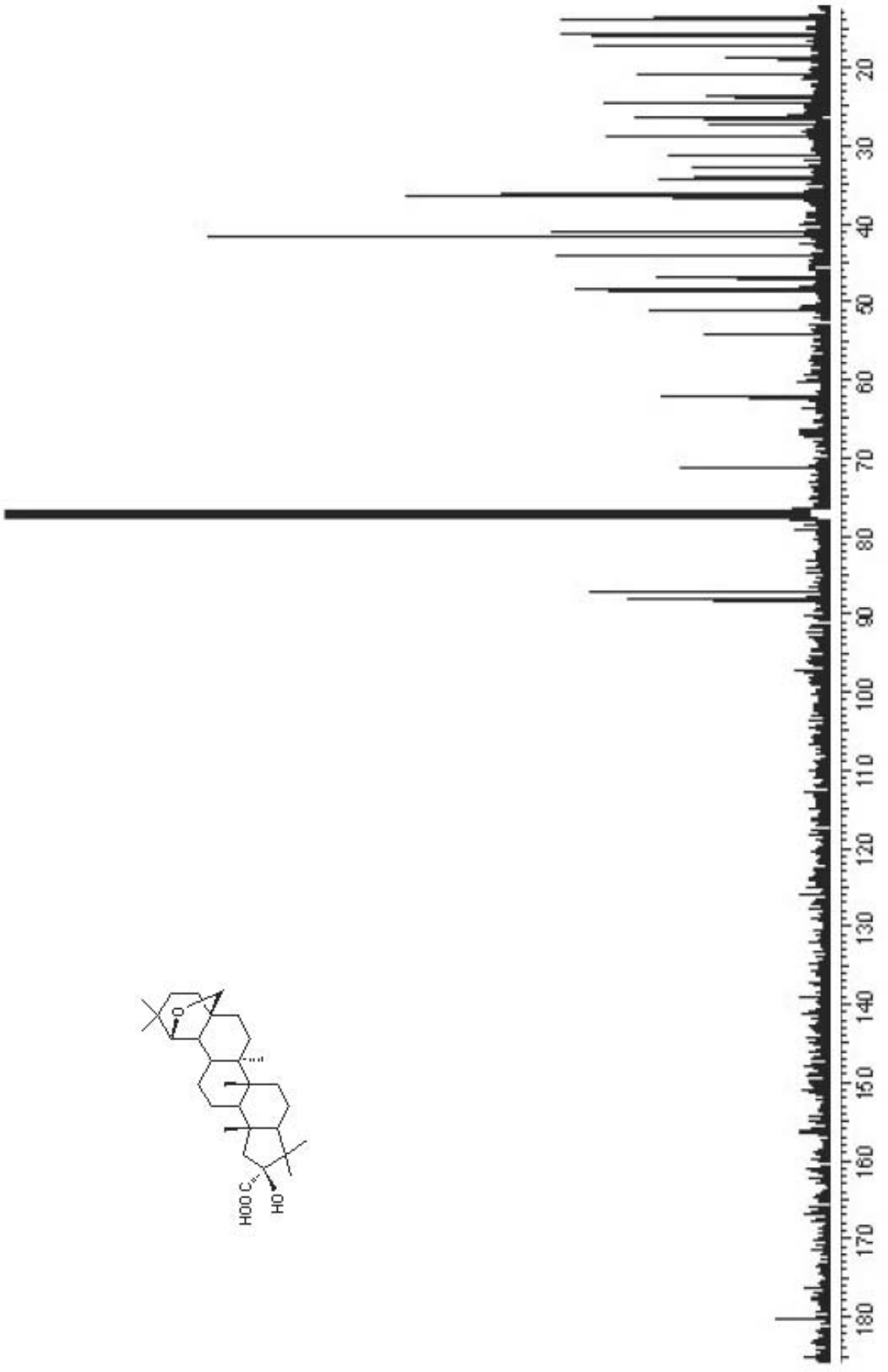
3β-Hydroxy-1(2→3)-abeolup-20-ene-2,28-dioic acid (**13**), $CDCl_3$/tms



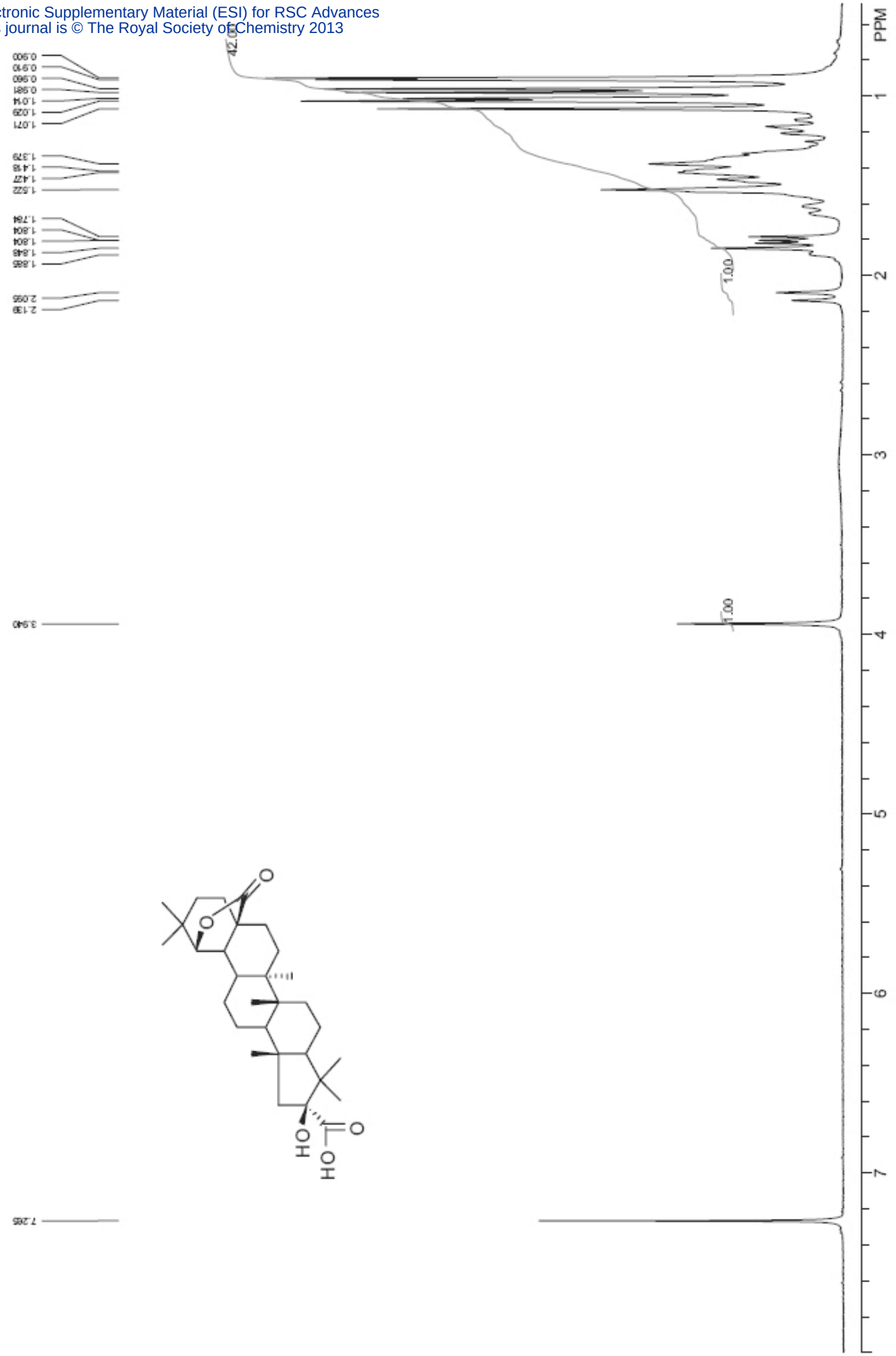
3β-Hydroxy-1(2→3)-abeolup-20-ene-2,28-dioic acid (**13**), $CDCl_3$/tms



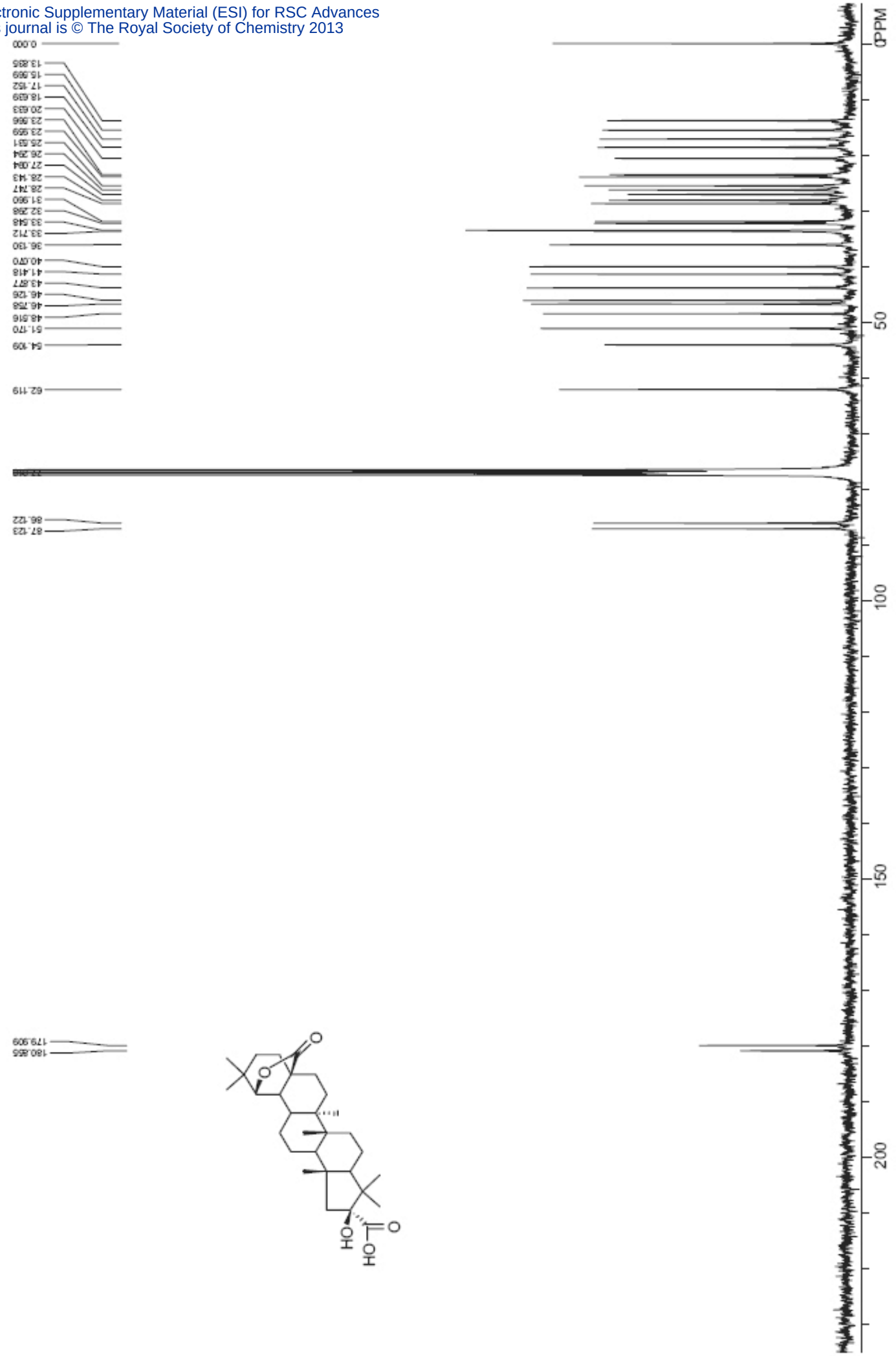
19β,28-Epoxy-3β-hydroxy-1(2→3)-abeo-18α-oleanan-2-oic acid (**14**), $CDCl_3$/tms



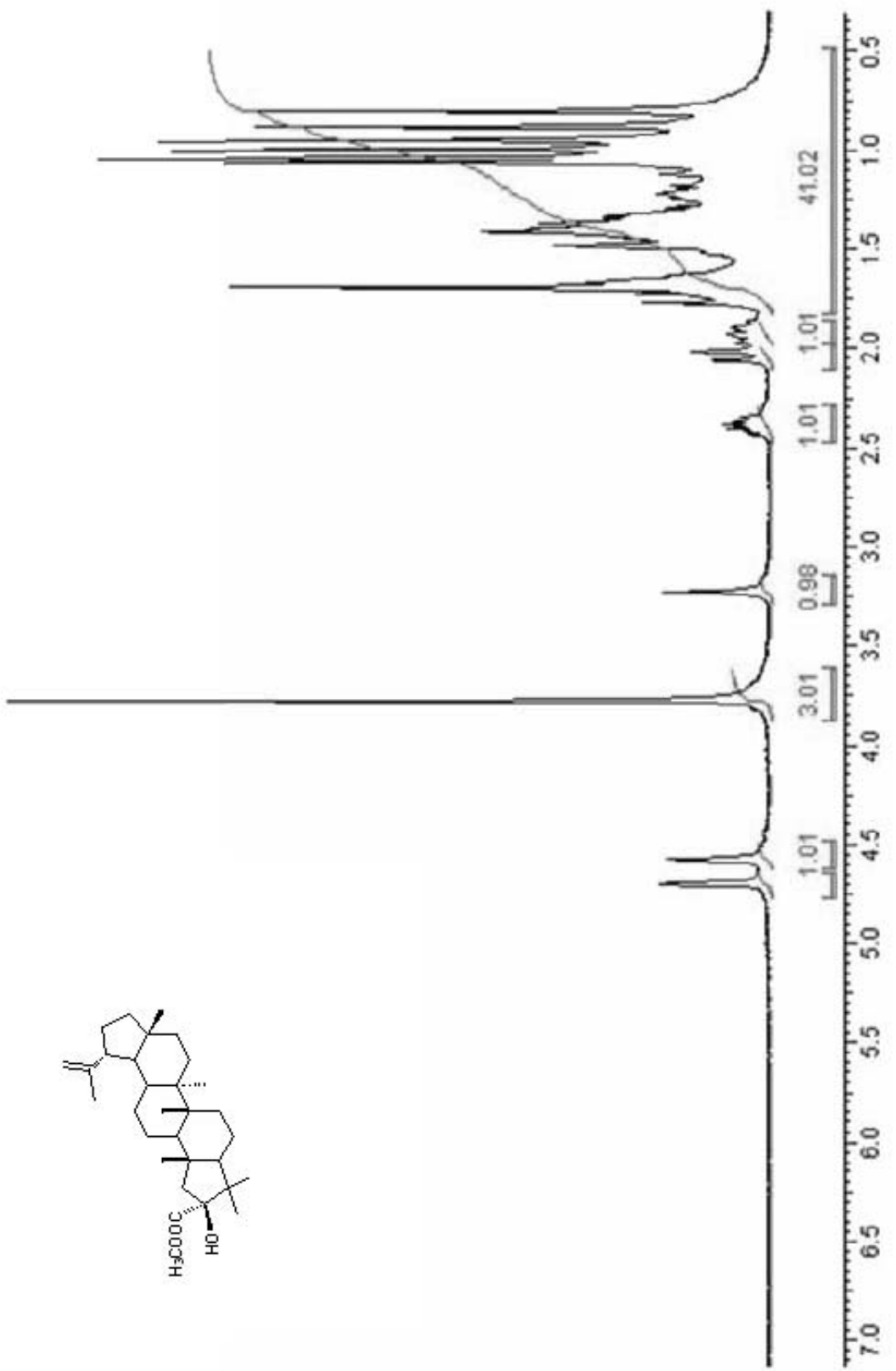
19β,28-Epoxy-3β-hydroxy-1(2→3)-abeo-18α-oleanan-2-oic acid (**14**), $CDCl_3$/tms



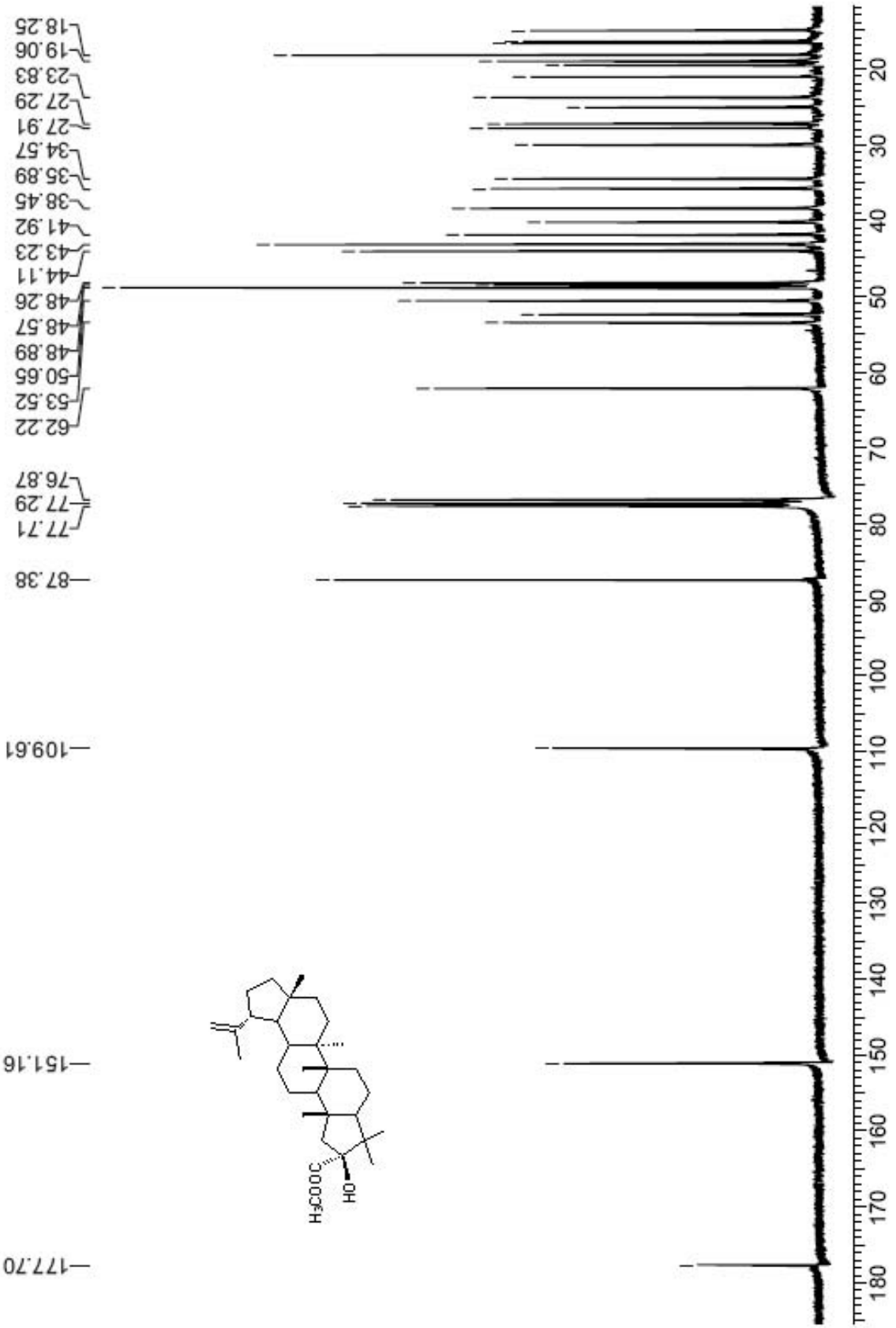
19β,28-Epoxy-3β-hydroxy-28-oxo-1(2→3)-abeo-18α-oleanan-2-oic acid (**15**), $CDCl_3$/tms



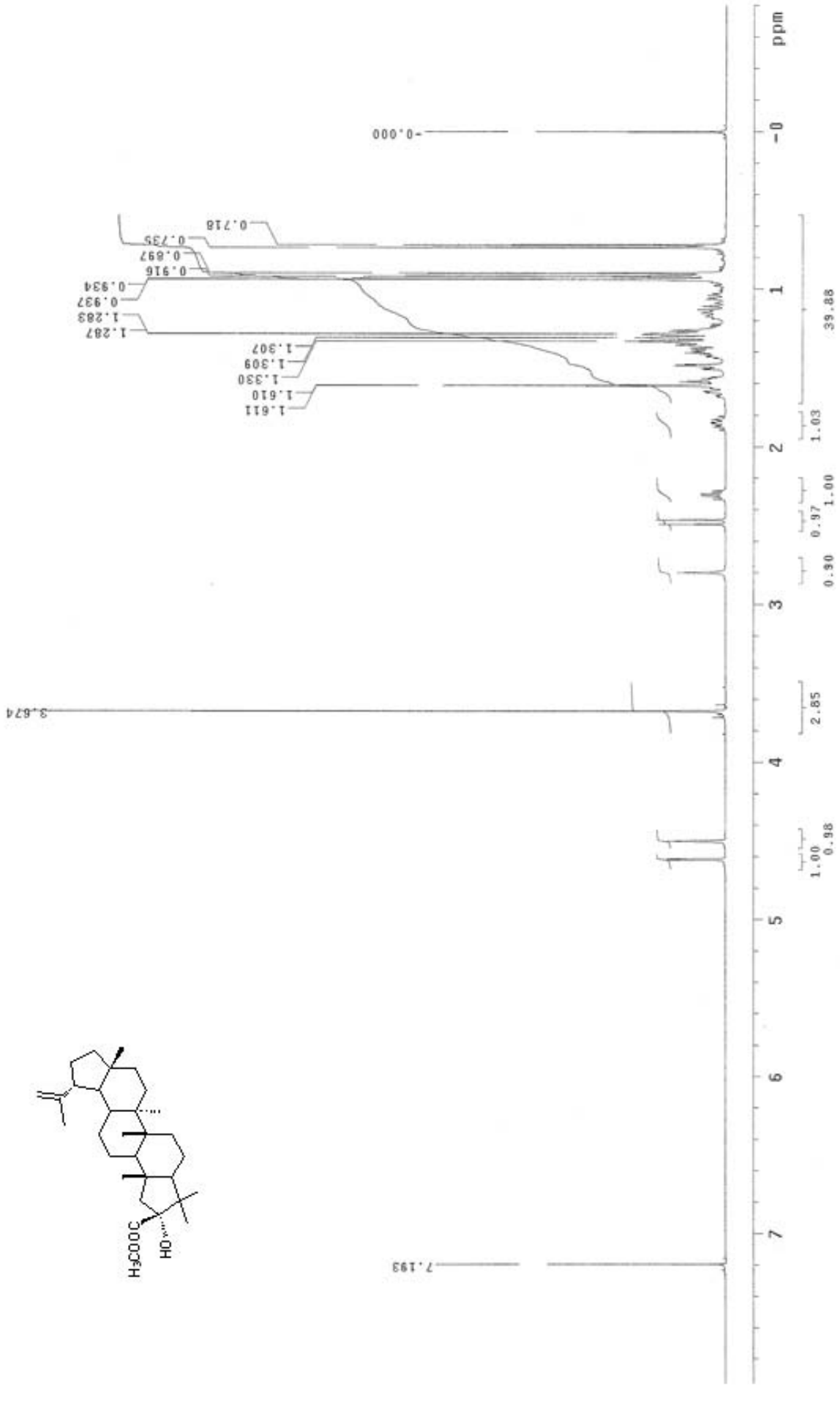
19β,28-Epoxy-3β-hydroxy-28-oxo-1(2→3)-abeo-18α-oleanan-2-oic acid (**15**), $CDCl_3$/tms



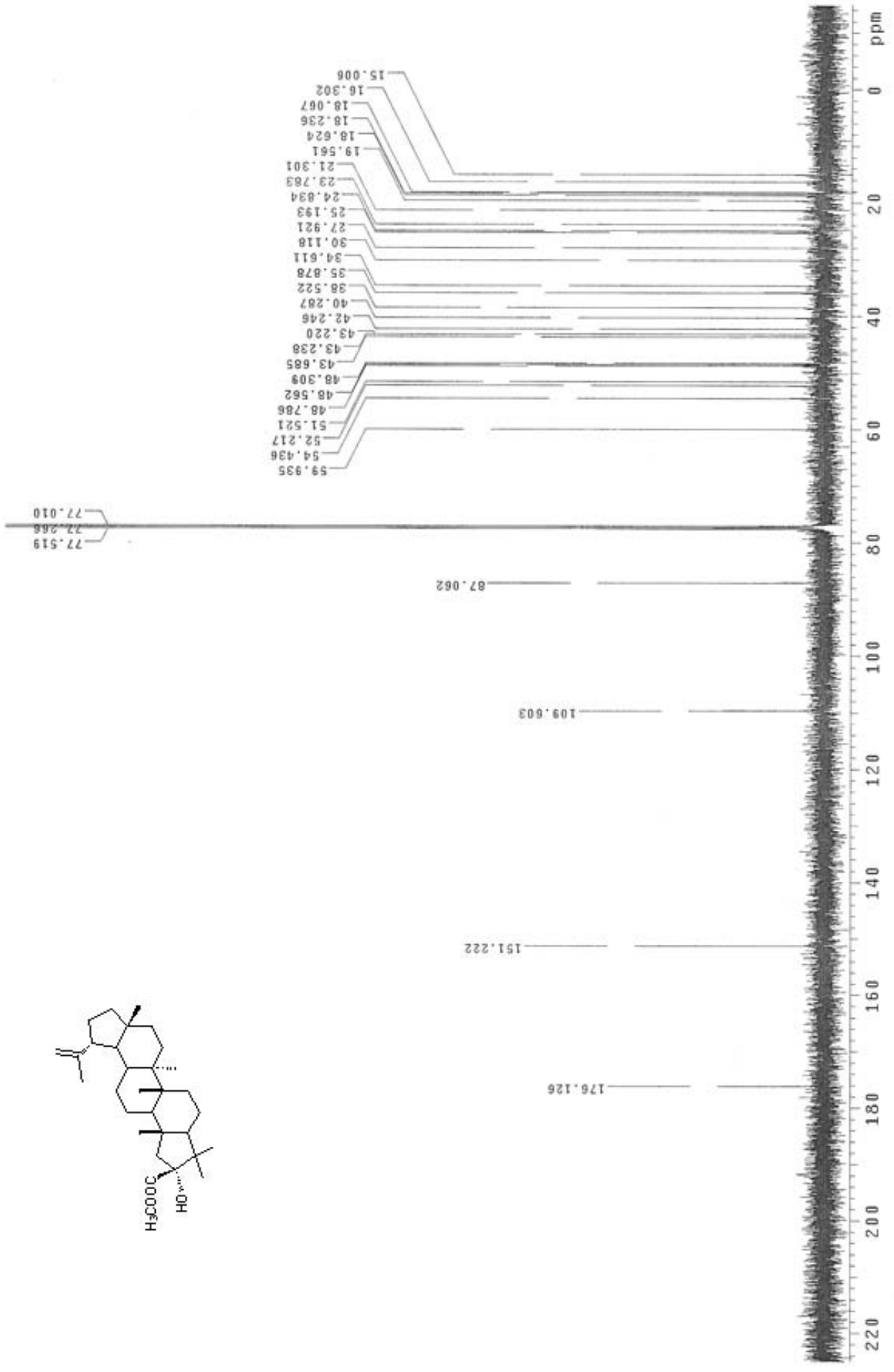
Methyl 3β-hydroxy-1(2→3)-abeolup-20-en-2-oate (**16**), $CDCl_3$/tms



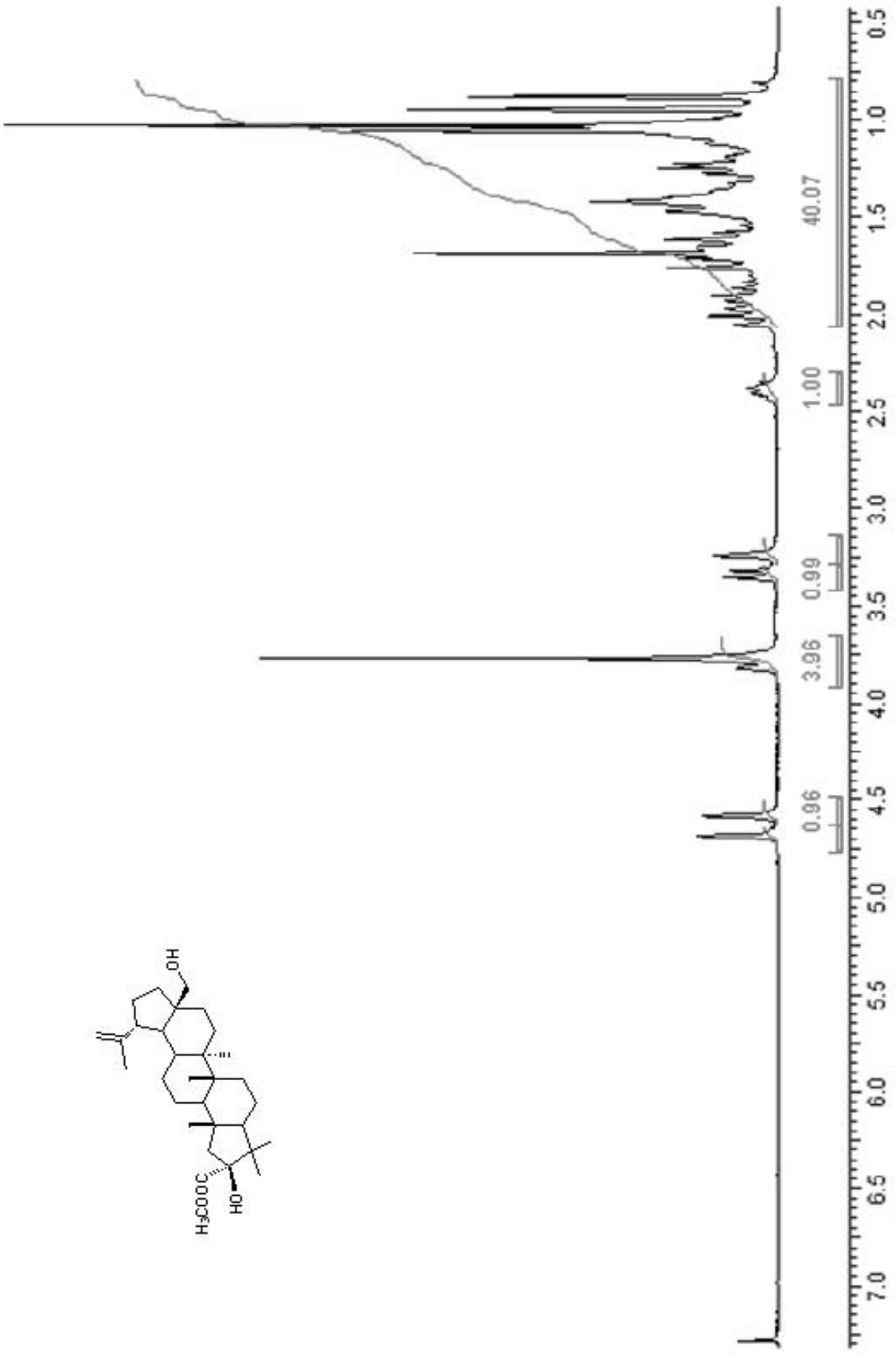
Methyl 3β-hydroxy-1(2→3)-abeolup-20-en-2-oate (**16**), $CDCl_3$/tms



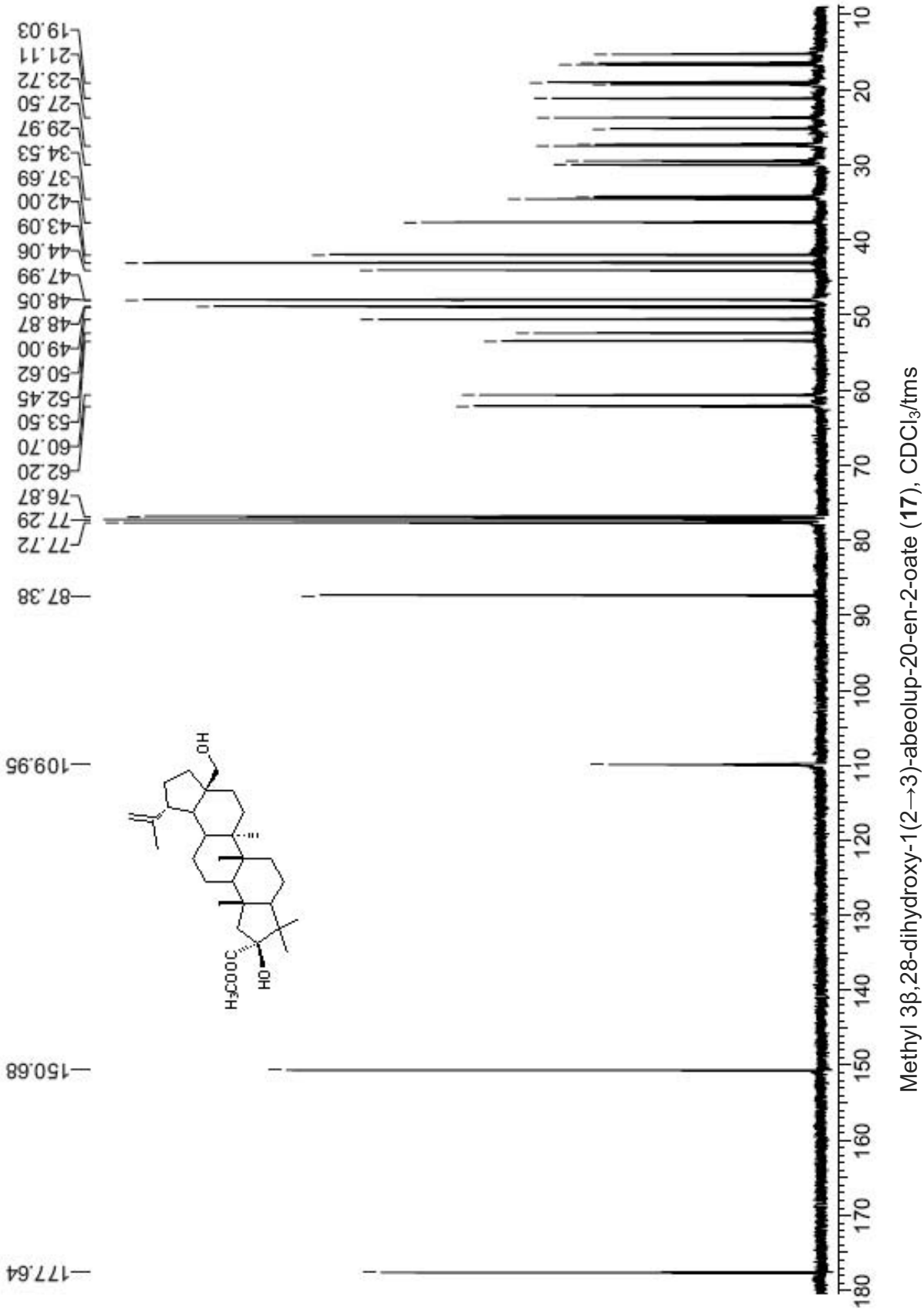
Methyl 3α-hydroxy-1(2→3)-abeolup-20-en-2-oate (**16'**), $CDCl_3$/tms



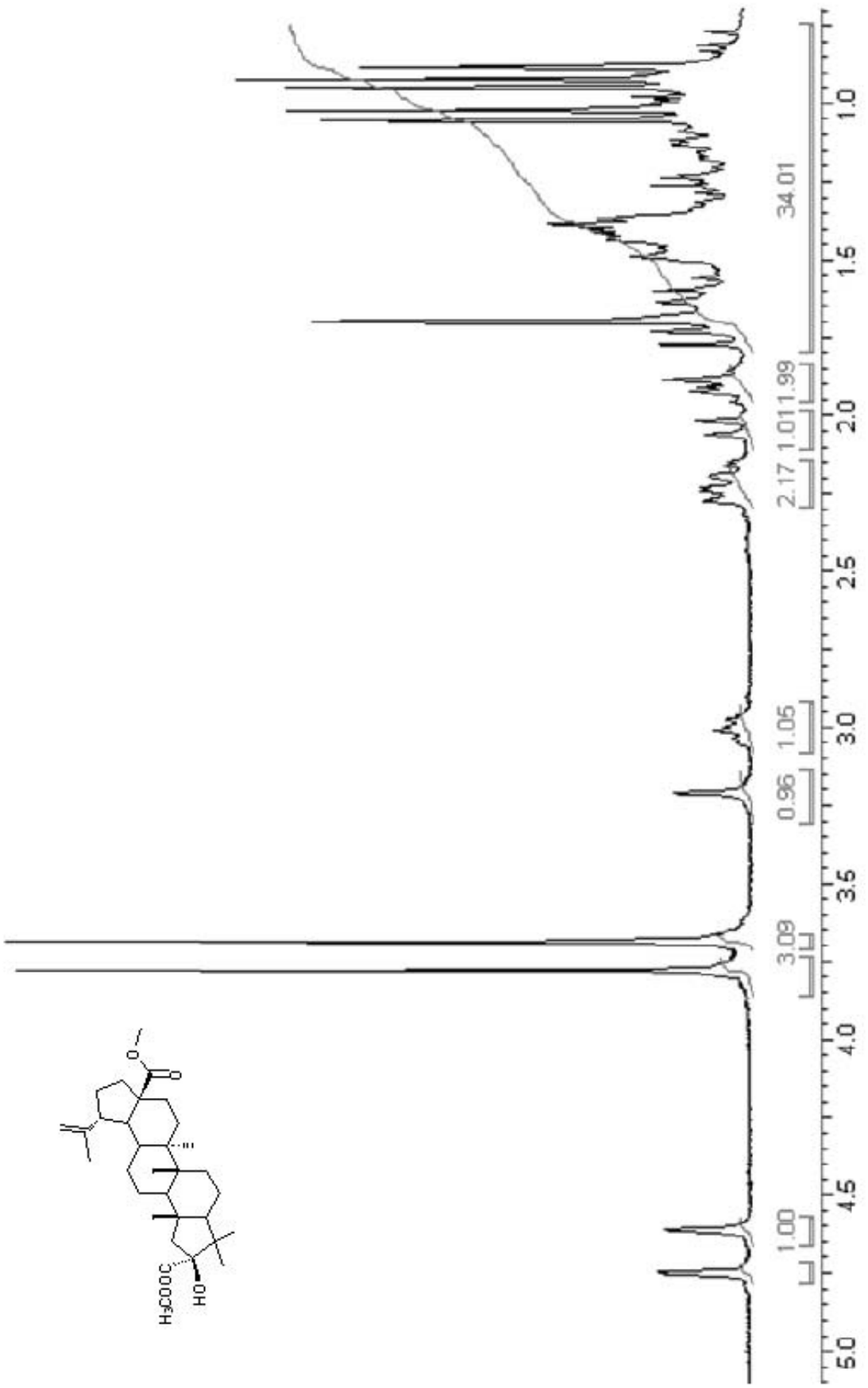
Methyl 3α-hydroxy-1(2→3)-abeolup-20-en-2-oate (**16'**), $CDCl_3$/tms



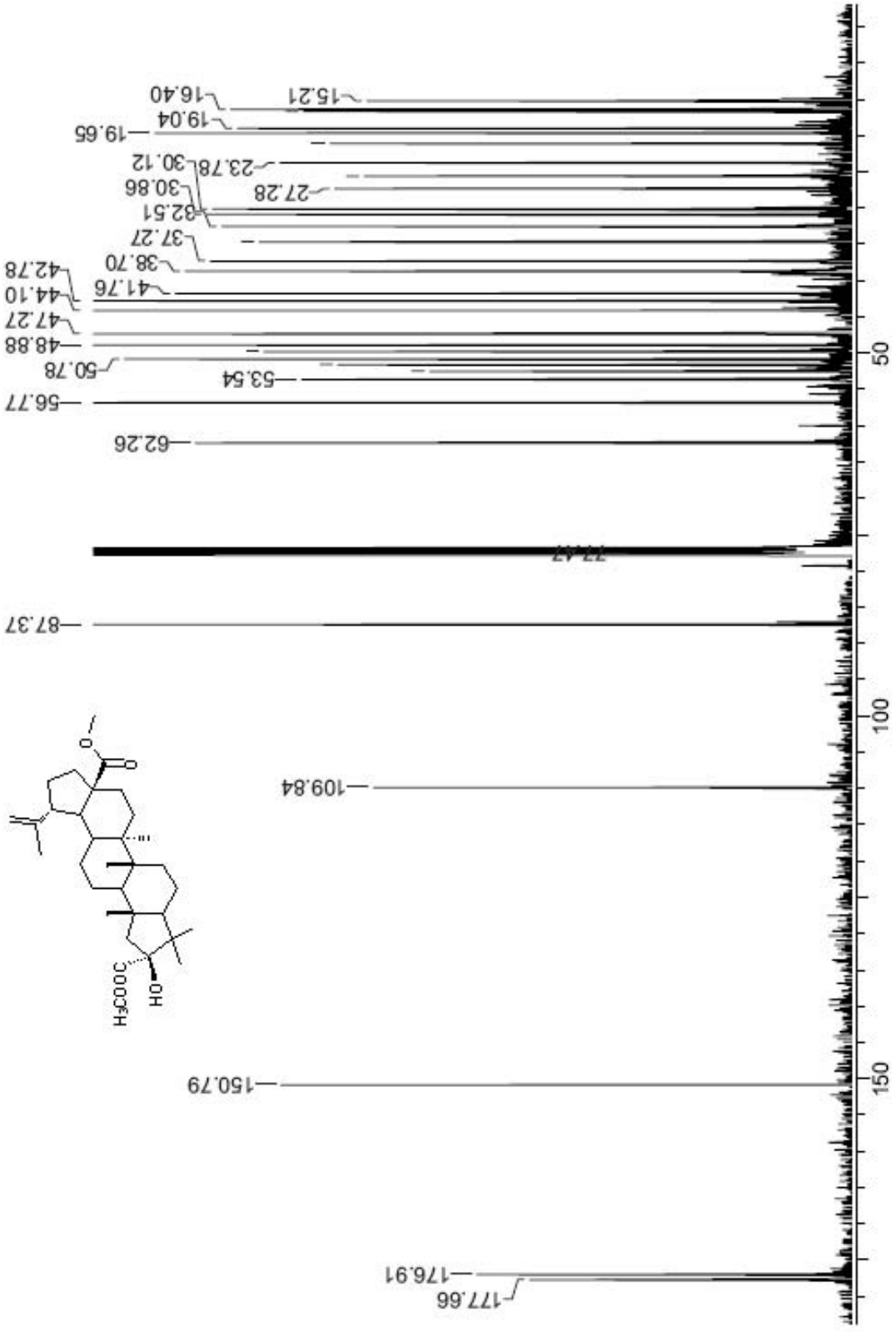
Methyl 3β,28-dihydroxy-1(2→3)-abeolup-20-en-2-oate (**17**), $CDCl_3$/tms



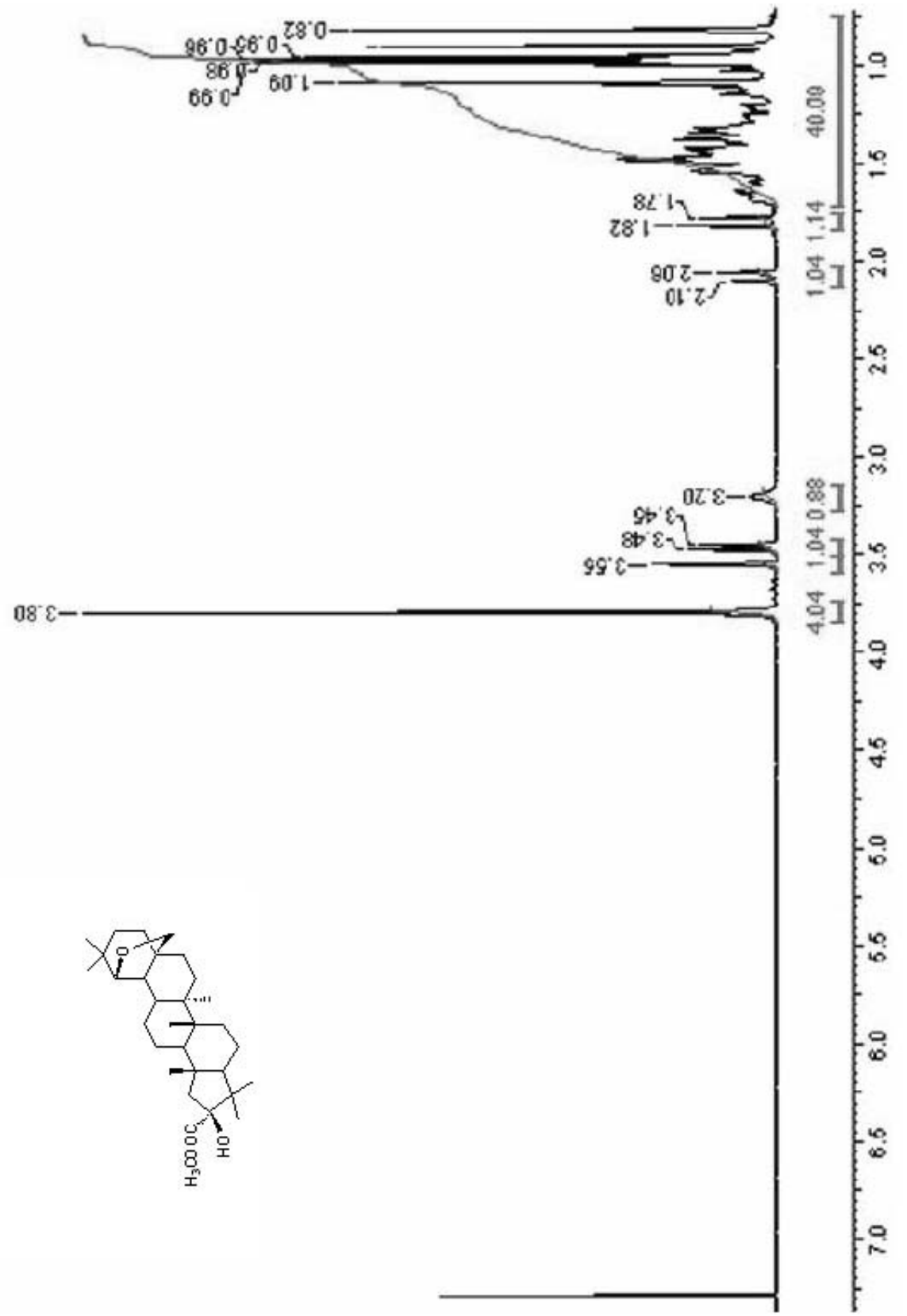
Methyl 3β,28-dihydroxy-1(2→3)-abeolup-20-en-2-oate (**17**), $CDCl_3$/tms



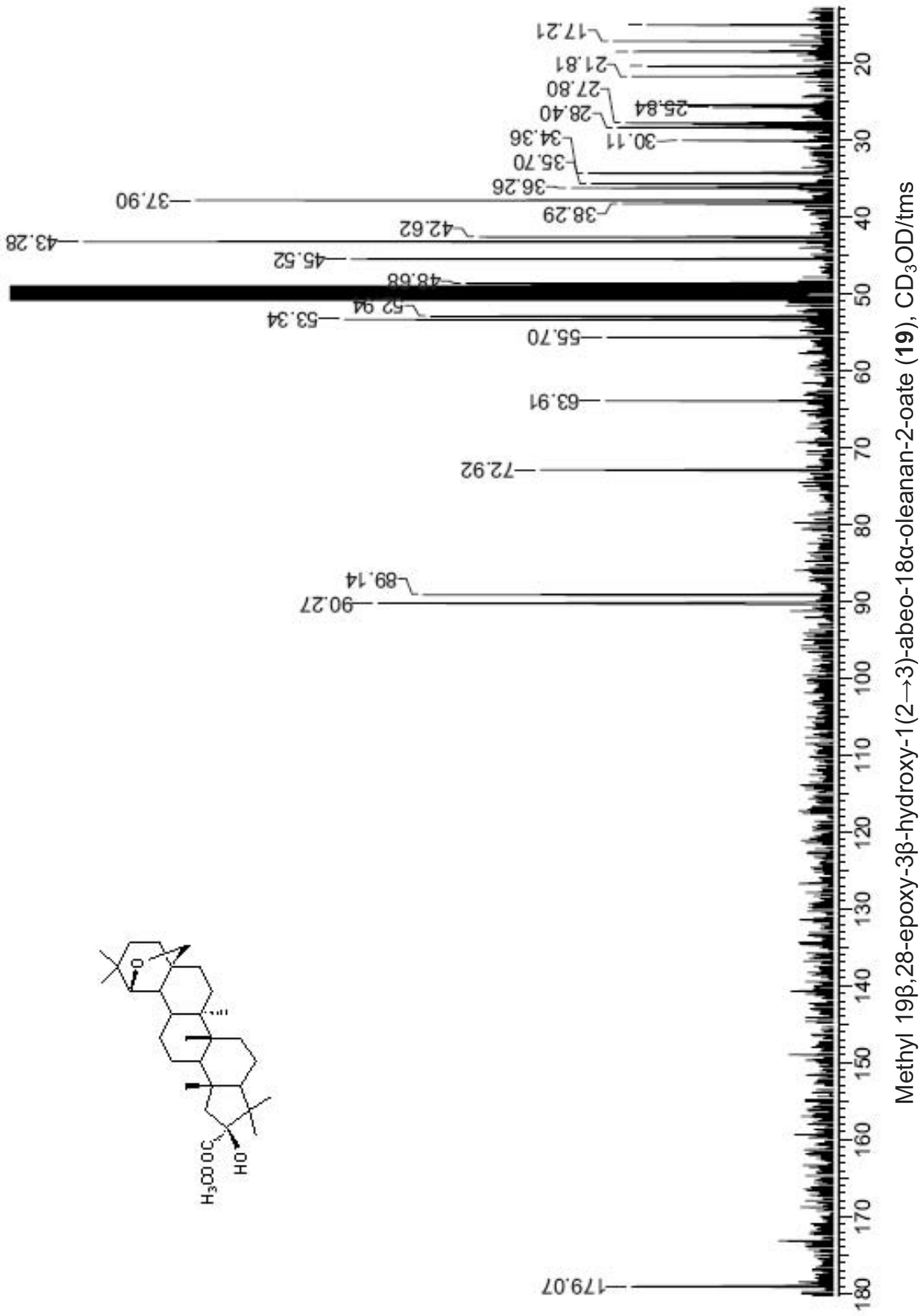
Dimethyl 3β-hydroxy-1(2→3)-abeolup-20-ene-2,28-dioate (**18**), $CDCl_3$/tms



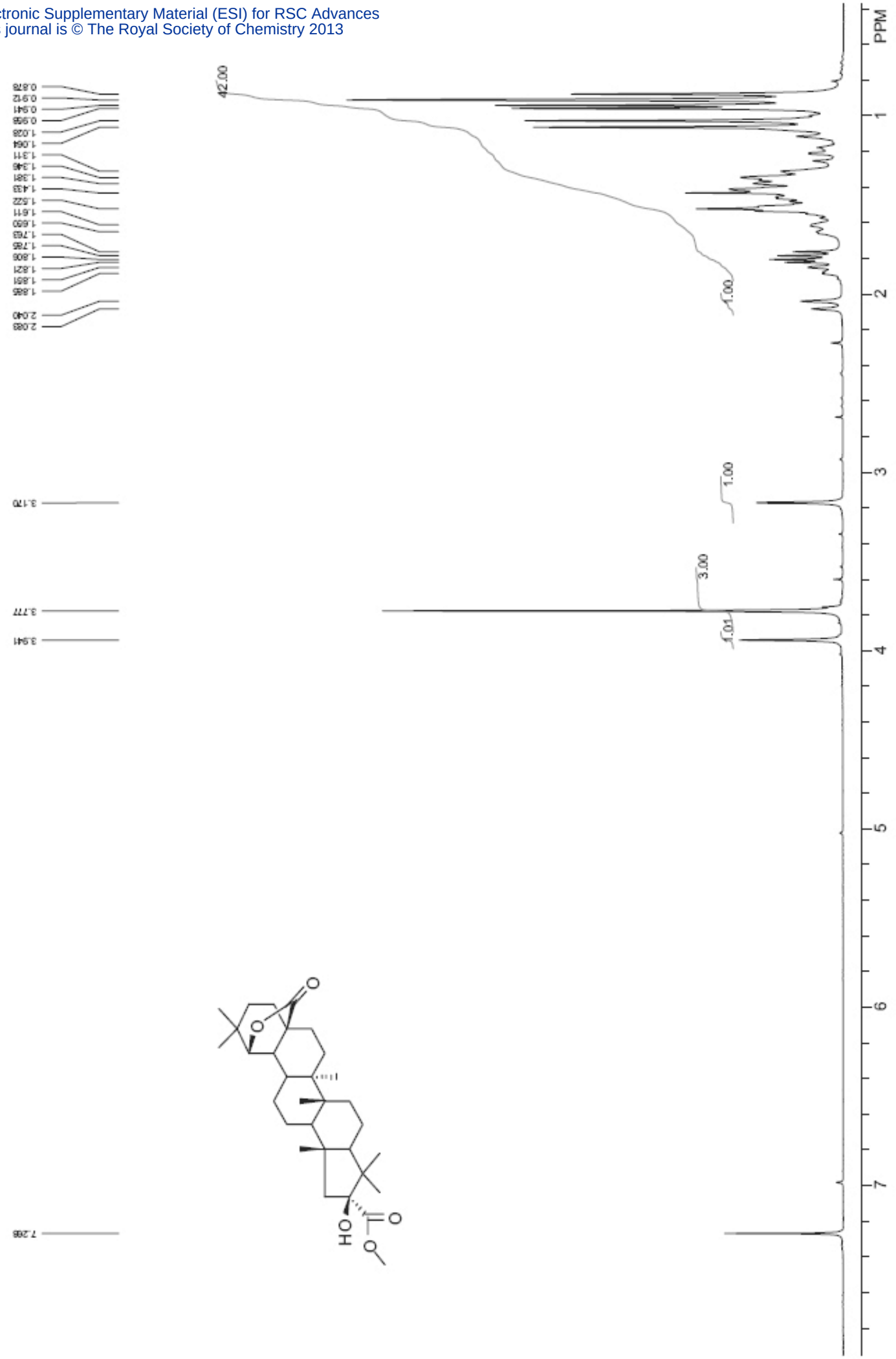
Dimethyl 3β-hydroxy-1(2→3)-abeolup-20-ene-2,28-dioate (**18**), $CDCl_3$/tms



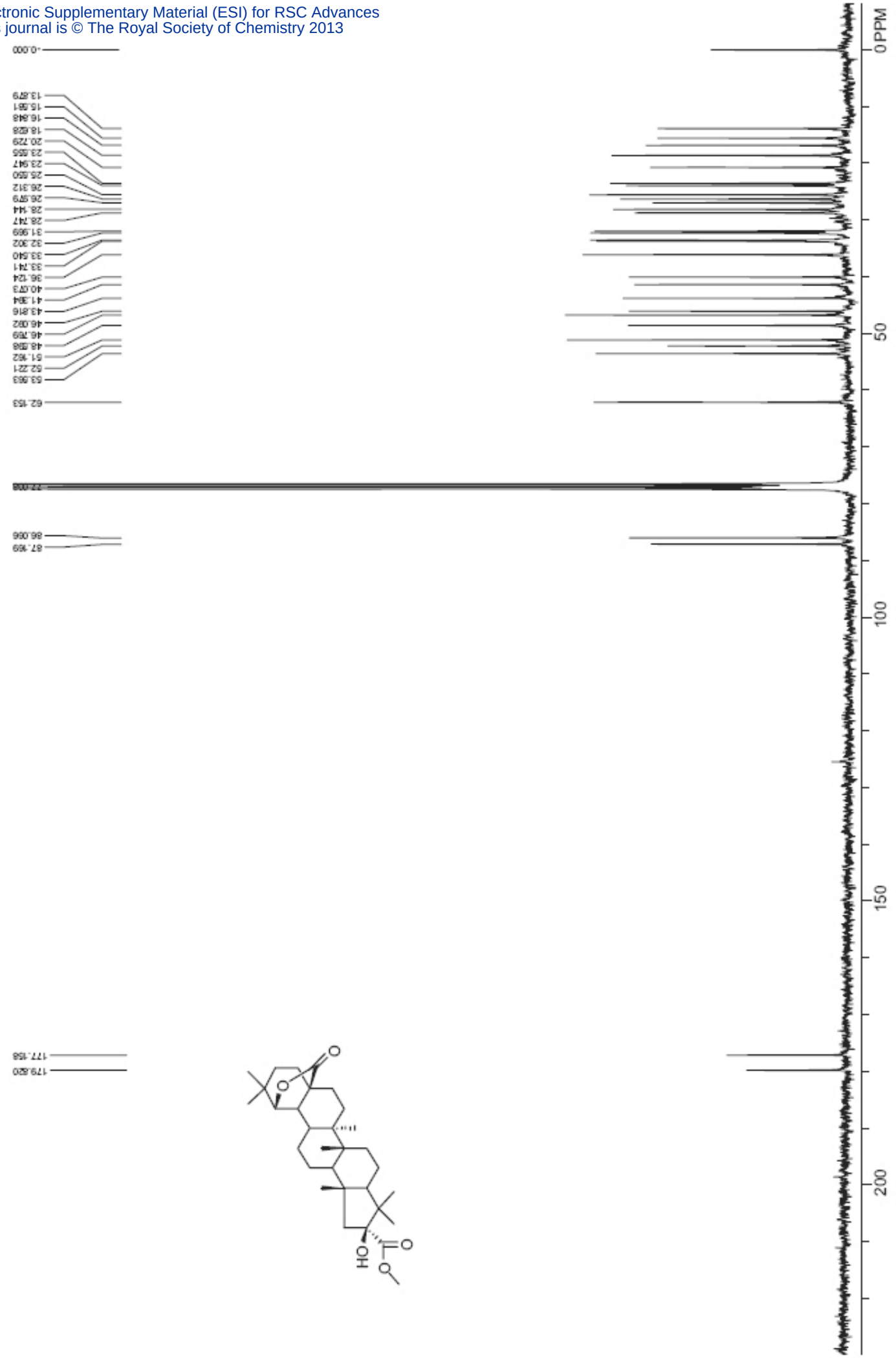
Methyl 19β,28-epoxy-3β-hydroxy-1(2→3)-abeo-18α-oleanan-2-oate (**19**), $CDCl_3$/tms



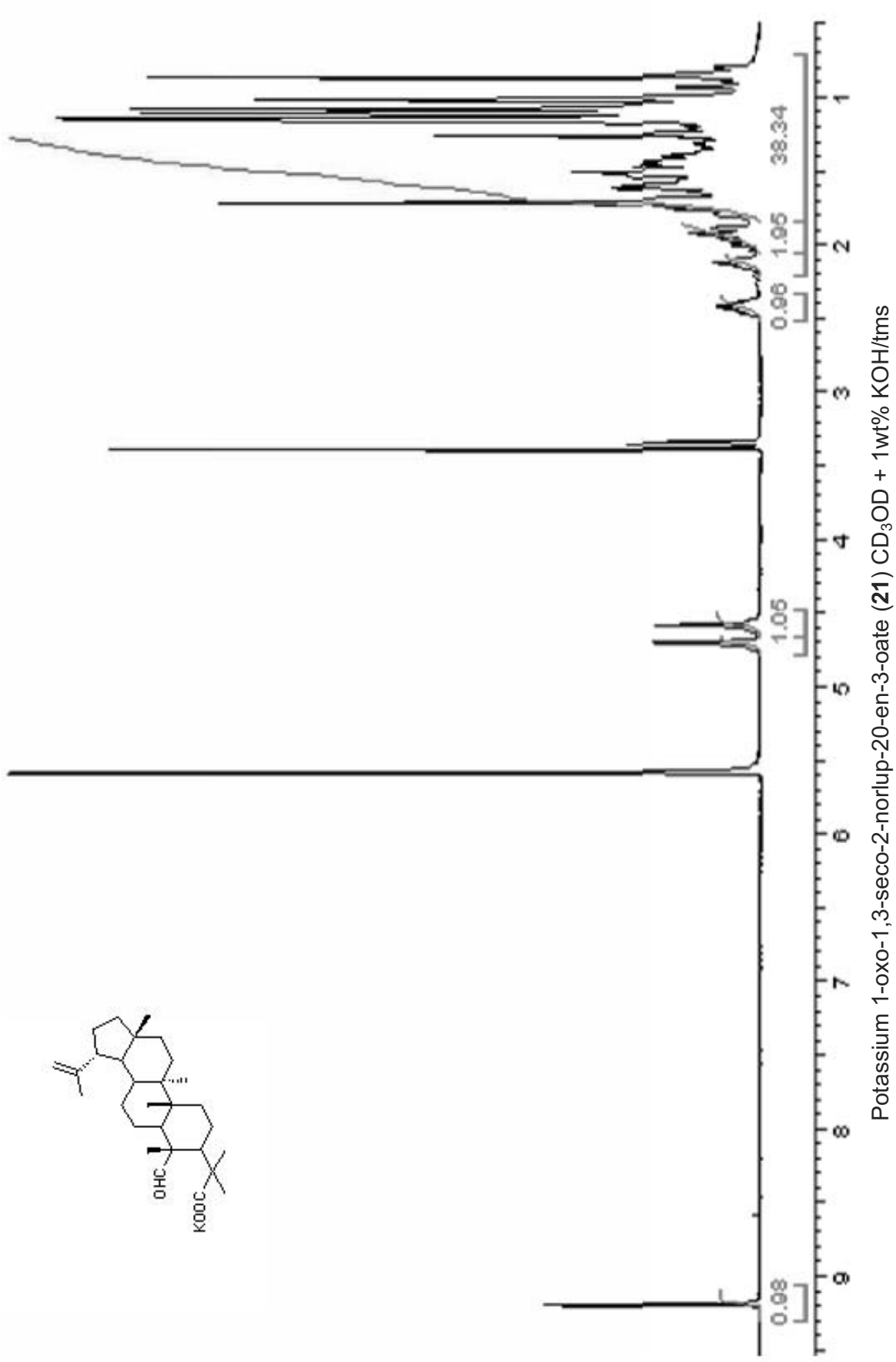
Methyl 19β,28-epoxy-3β-hydroxy-1(2→3)-abeo-18α-oleanan-2-oate (**19**), CD_3OD/tms



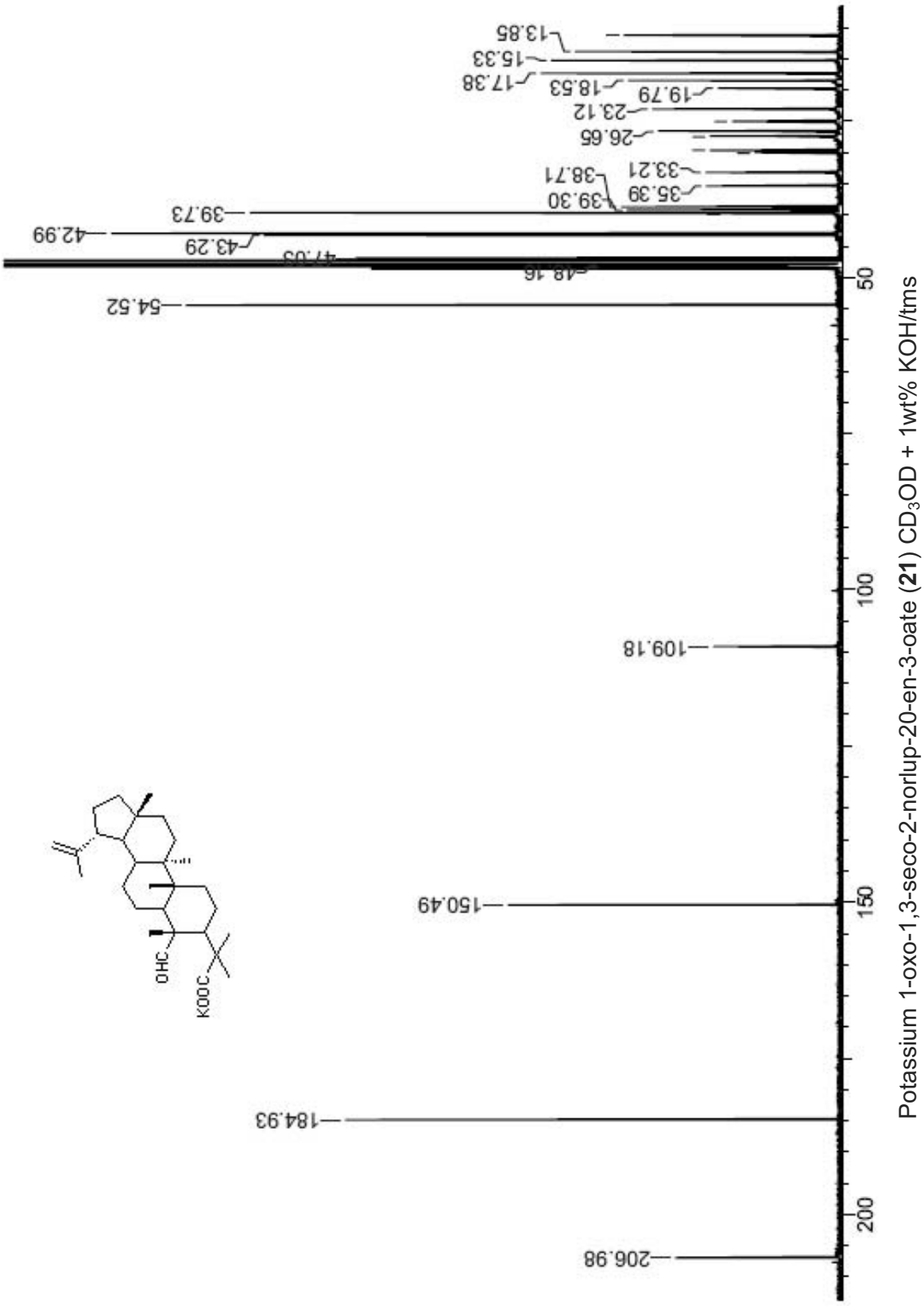
Methyl 19β,28-epoxy-3β-hydroxy-28-oxo-1(2→3)-abeo-18α-oleanan-2-oate (**20**),$CDCl_3$/tms



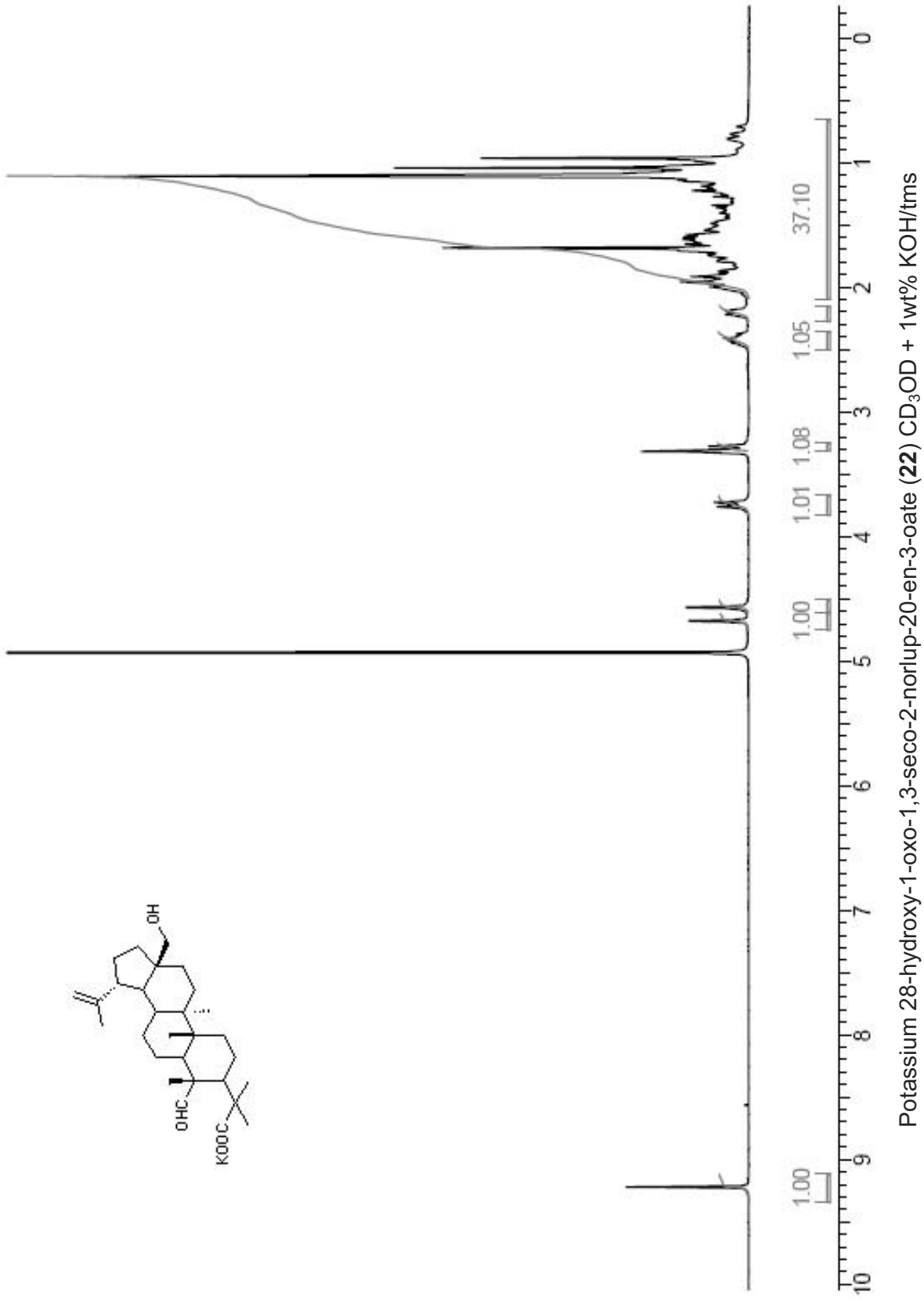
Methyl 19β,28-epoxy-3β-hydroxy-28-oxo-1(2→3)-abeo-18α-oleanan-2-oate (**20**),$CDCl_3$/tms



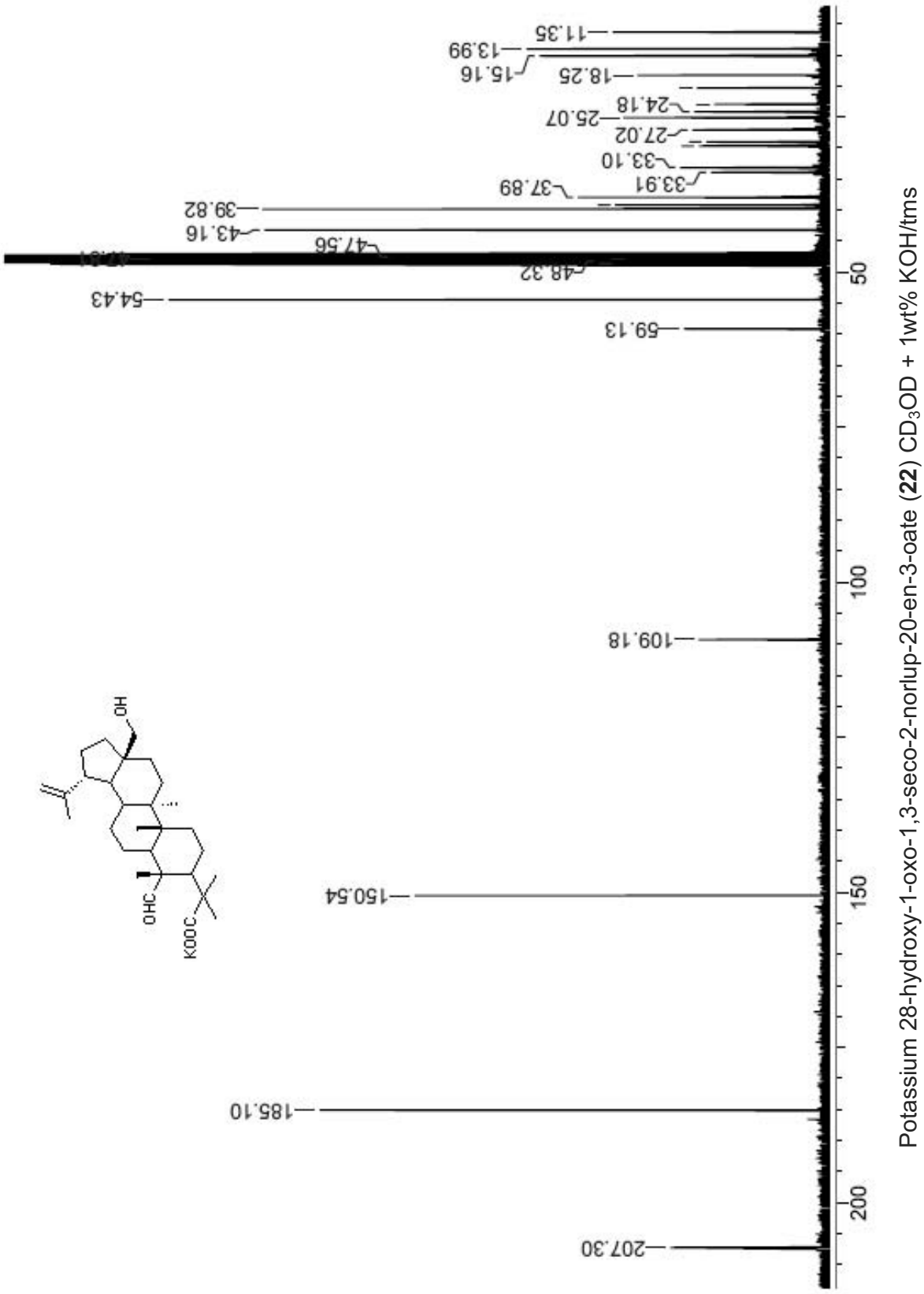
Potassium 1-oxo-1,3-seco-2-norlup-20-en-3-oate (**21**) CD_3OD + 1wt% KOH/tms



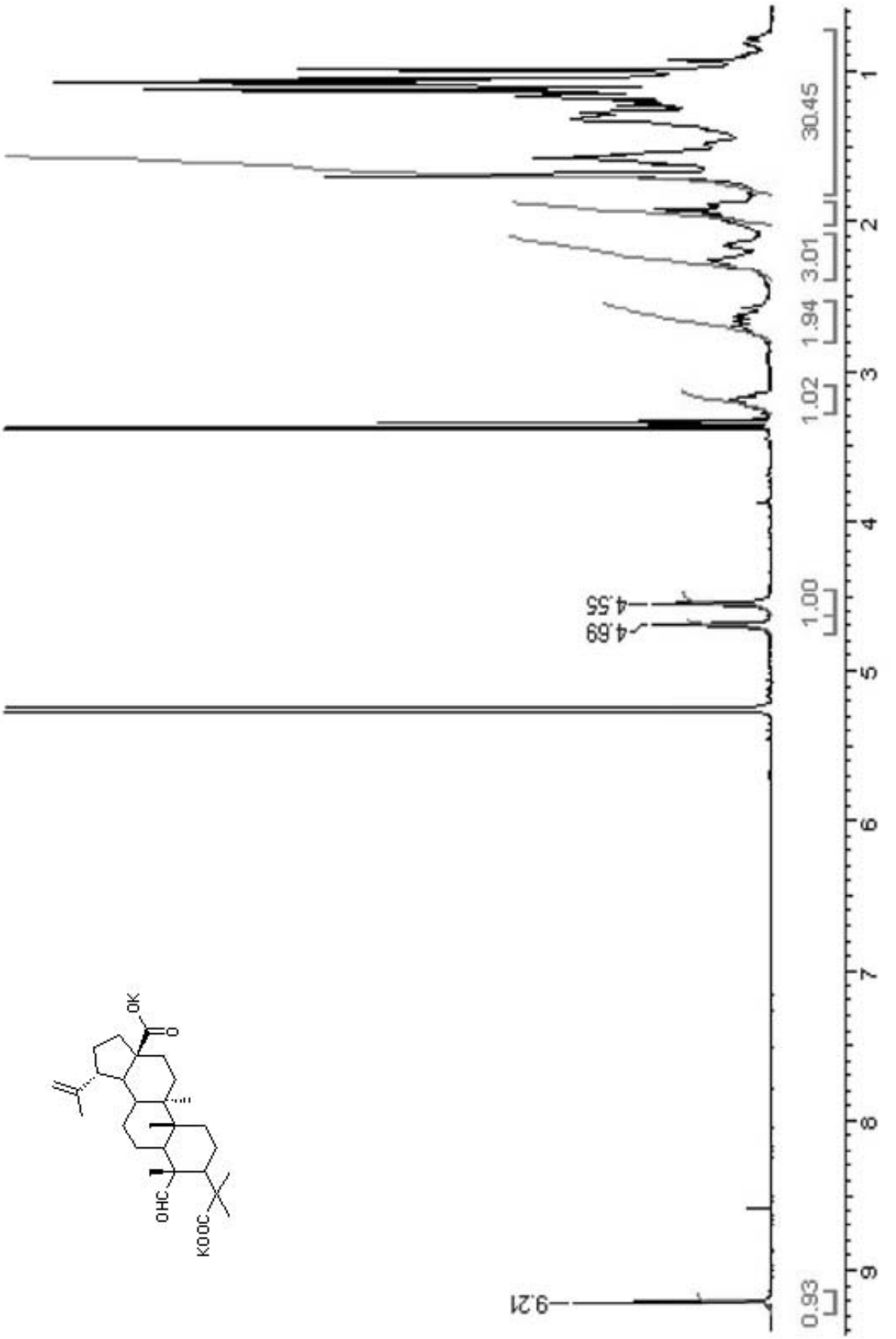
Potassium 1-oxo-1,3-seco-2-norlup-20-en-3-oate (**21**) CD_3OD + 1wt% KOH/tms



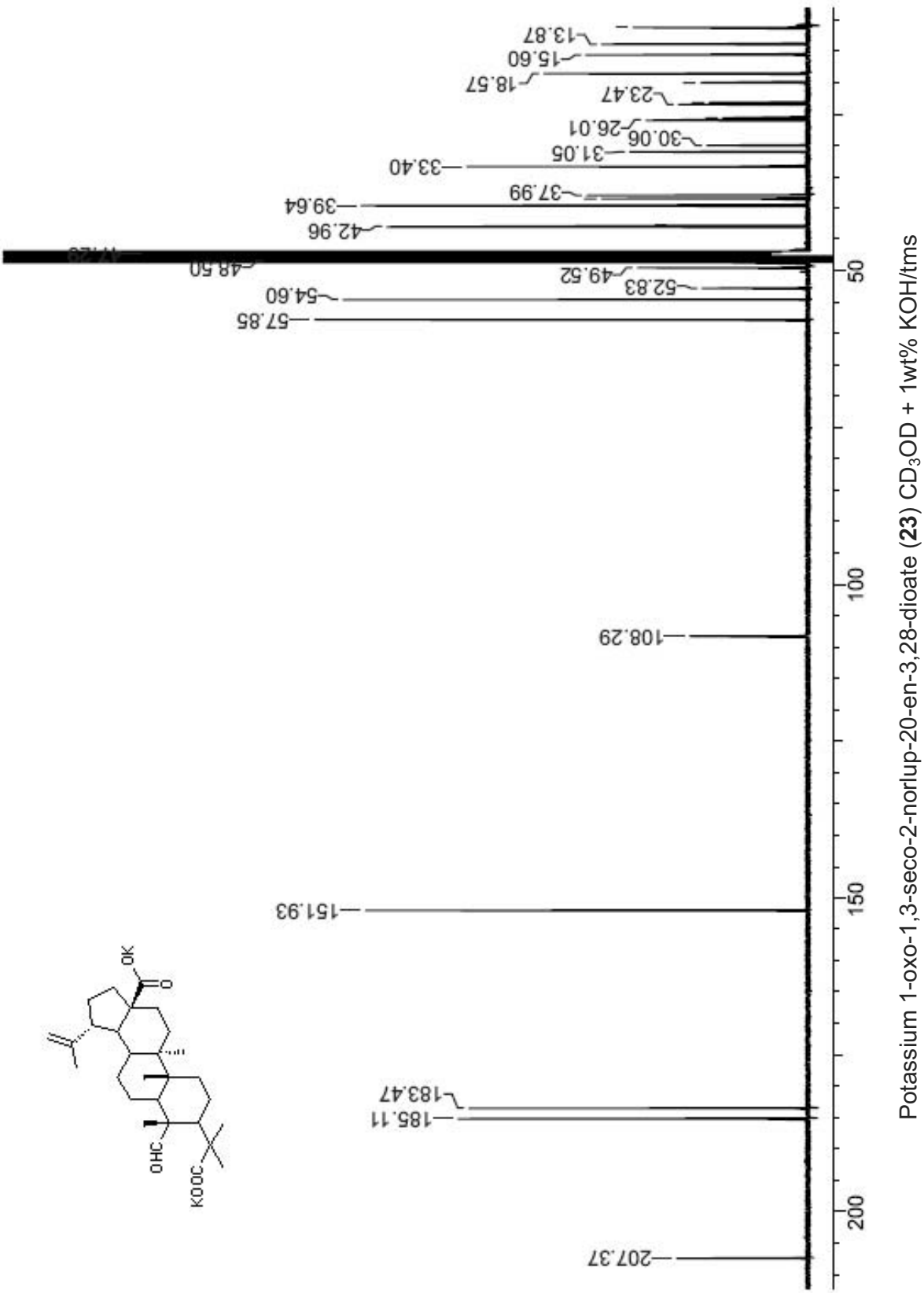
Potassium 28-hydroxy-1-oxo-1,3-seco-2-norlup-20-en-3-oate (**22**) CD_3OD + 1wt% KOH/tms



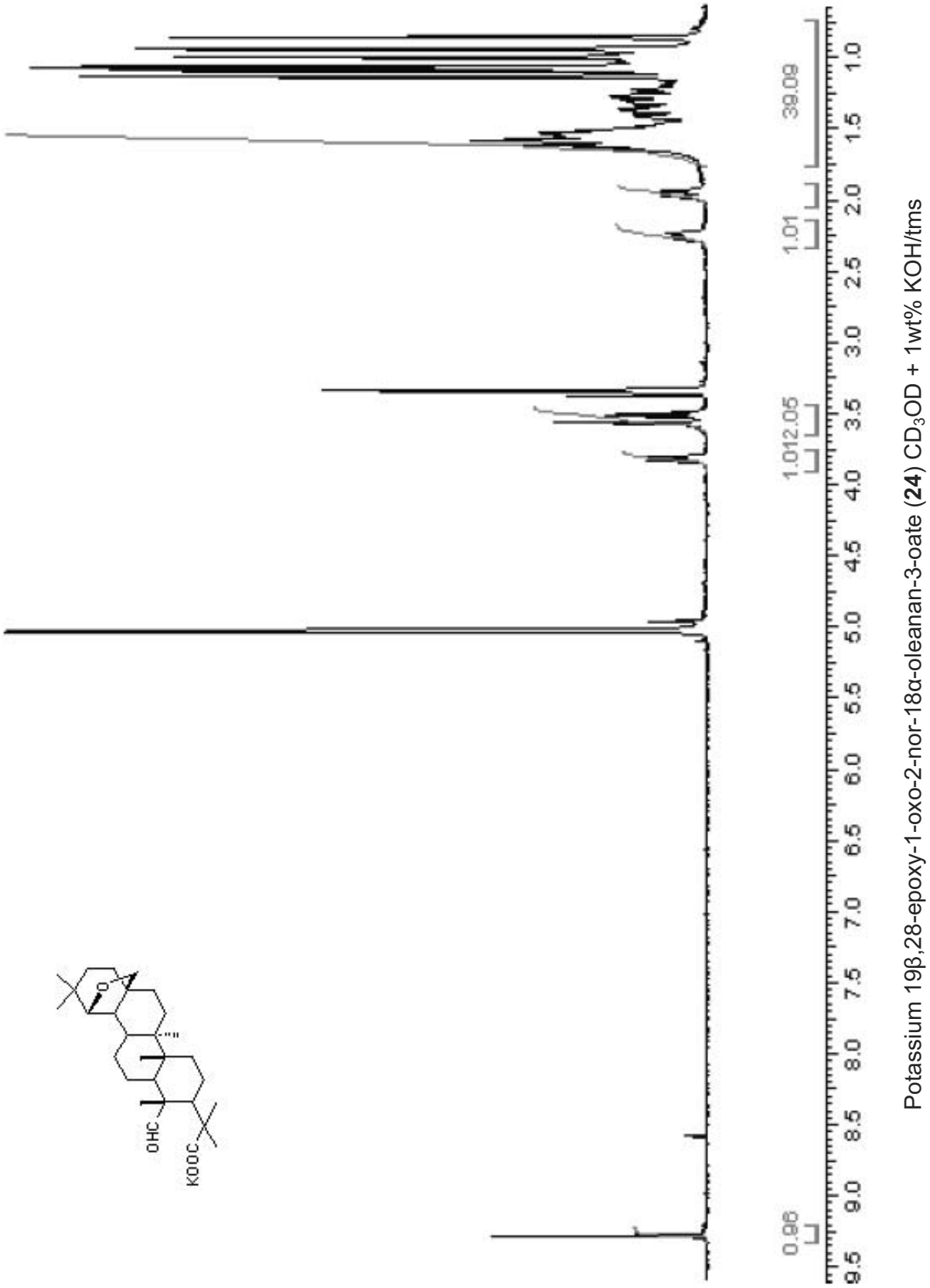
Potassium 28-hydroxy-1-oxo-1,3-seco-2-norlup-20-en-3-oate (**22**) CD_3OD + 1wt% KOH/tms



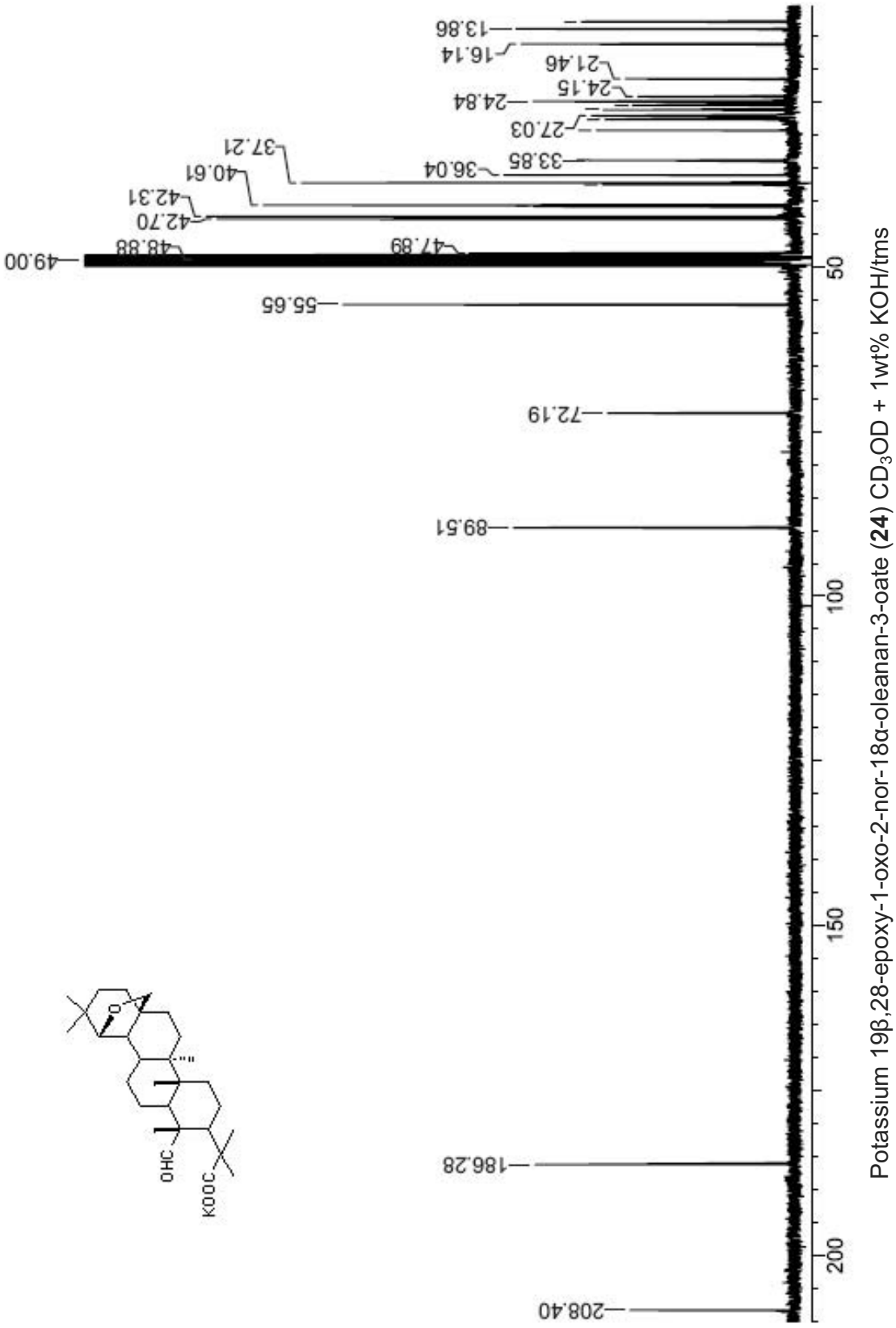
Potassium 1-oxo-1,3-seco-2-norlup-20-en-3,28-dioate (**23**) CD_3OD + 1wt% KOH/tms

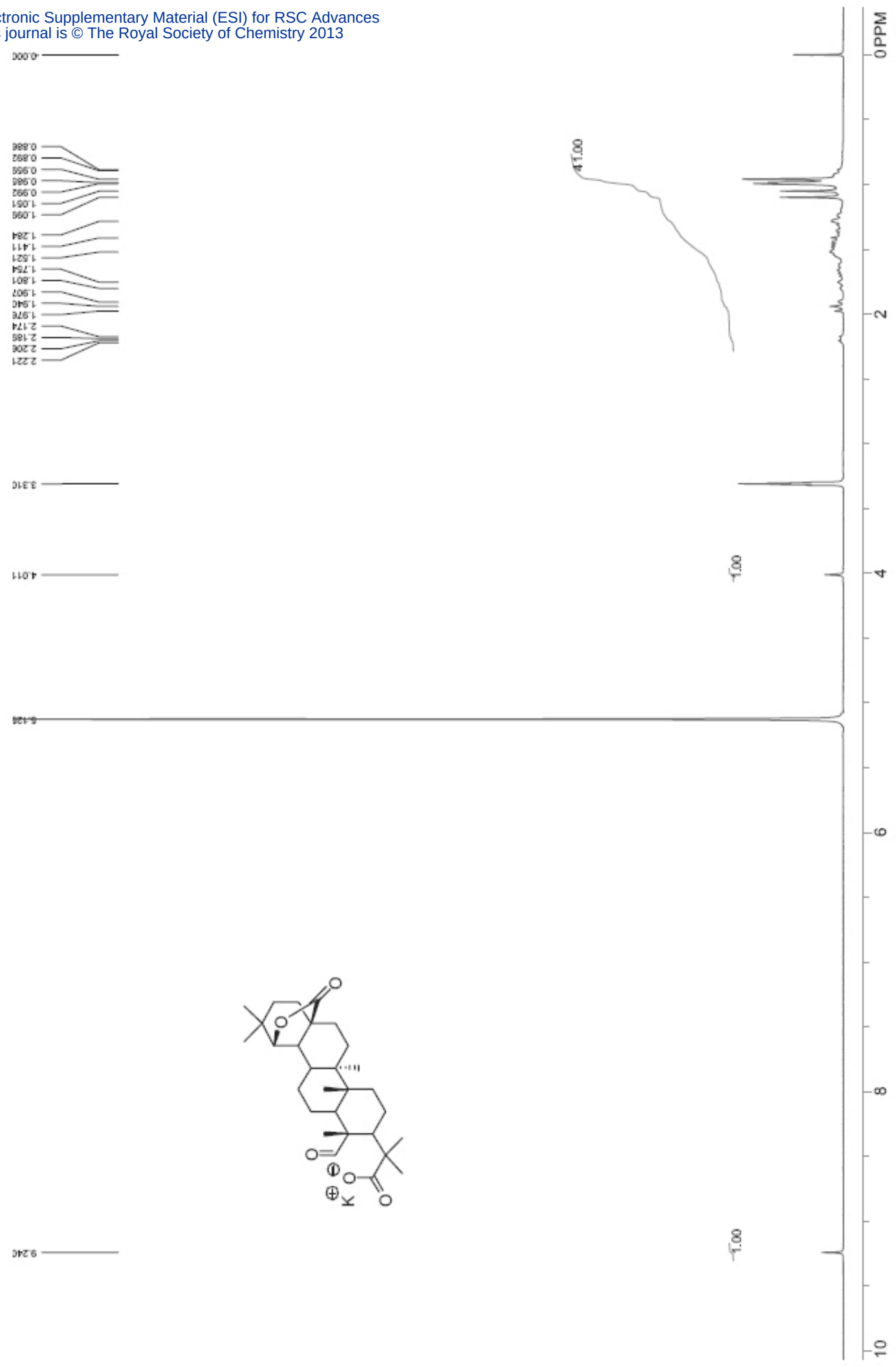


Potassium 1-oxo-1,3-seco-2-norlup-20-en-3,28-dioate (**23**) CD_3OD + 1wt% KOH/tms

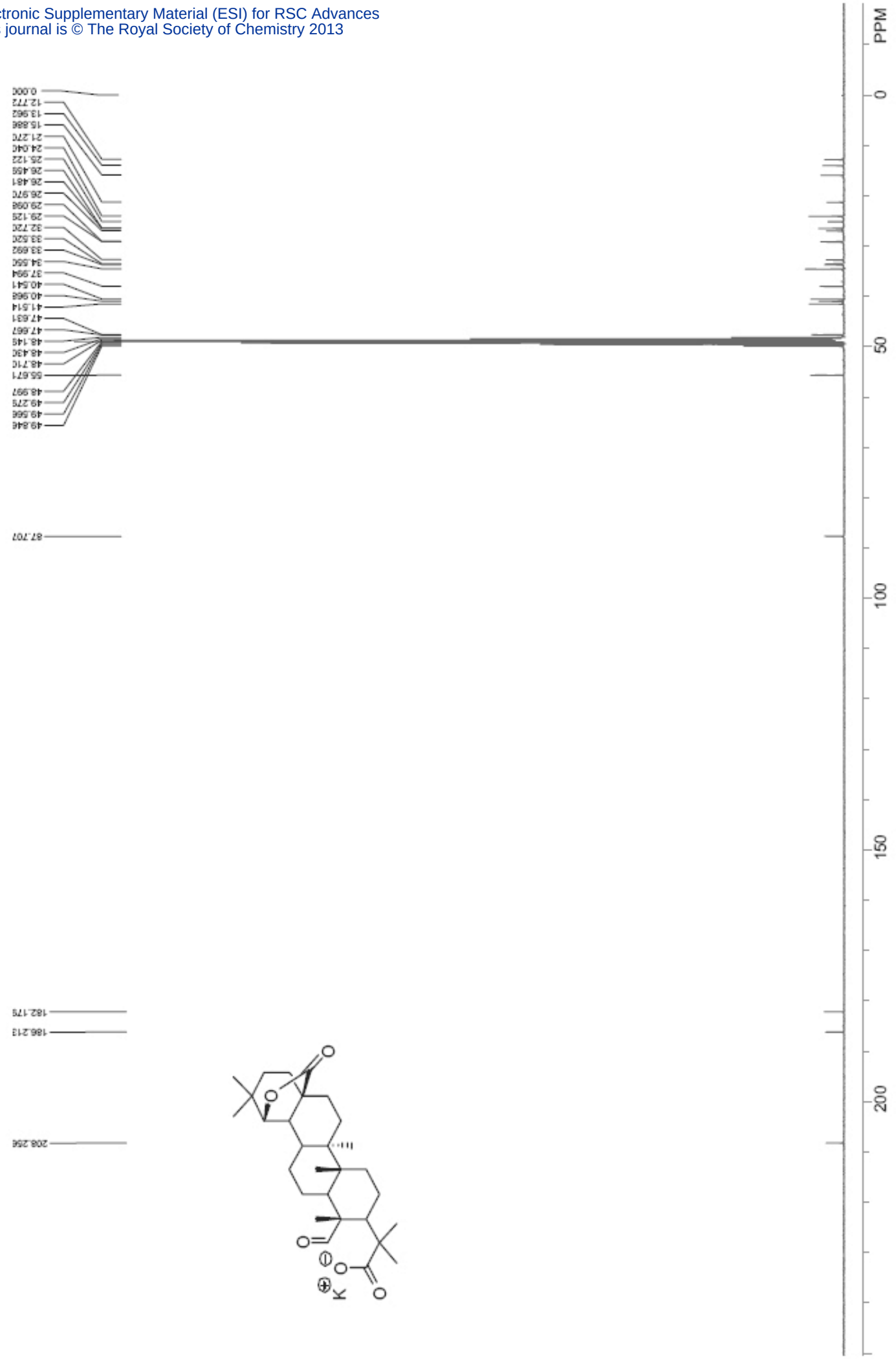


Potassium 19β,28-epoxy-1-oxo-2-nor-18α-oleanan-3-oate (**24**) CD_3OD + 1wt% KOH/tms

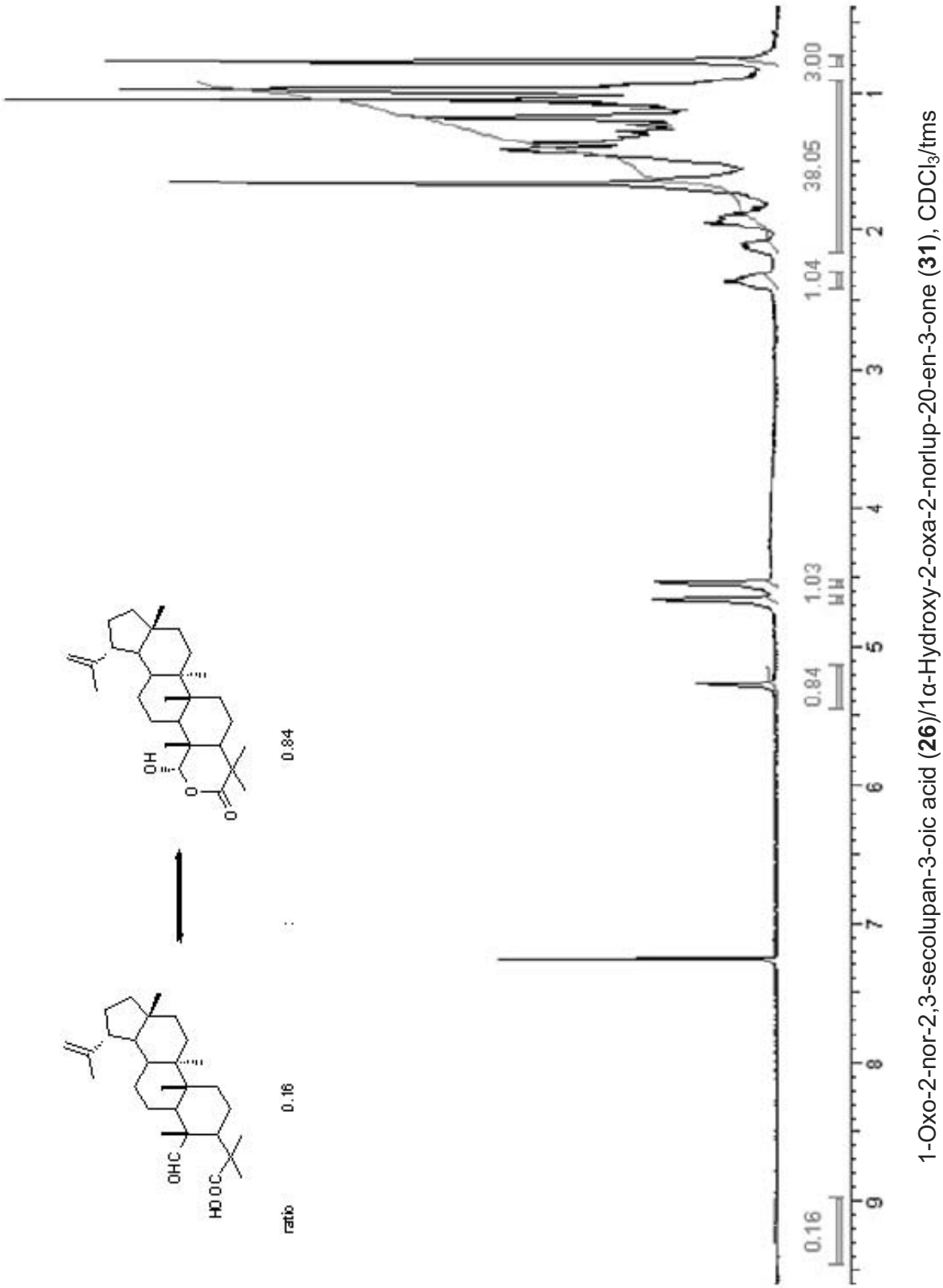




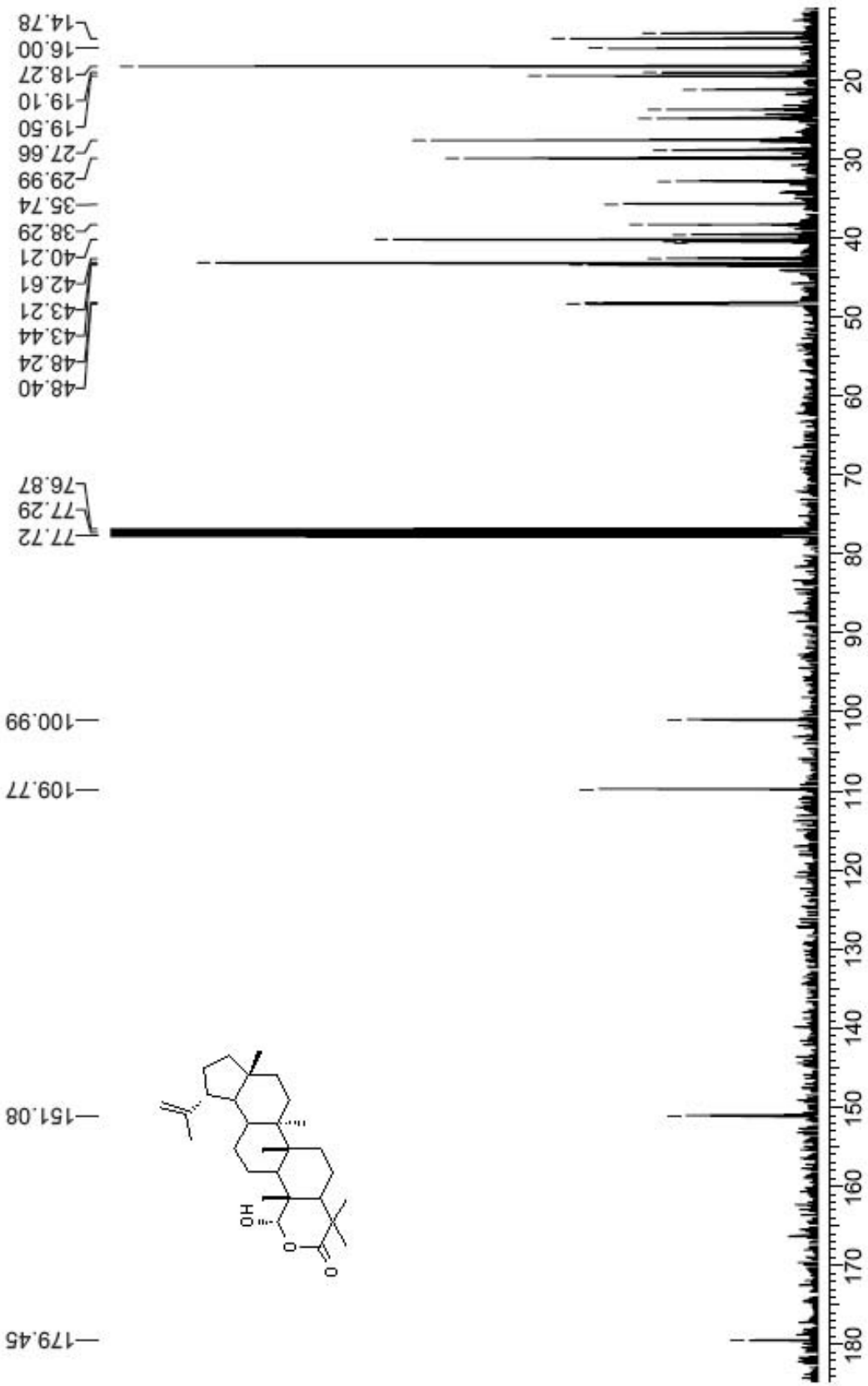
Potassium 19β,28-epoxy-1,28-dioxo-1,3-seco-2-nor-18α-oleanan-3-oate (**25**), CD_3OD+1wt%KOH/tms



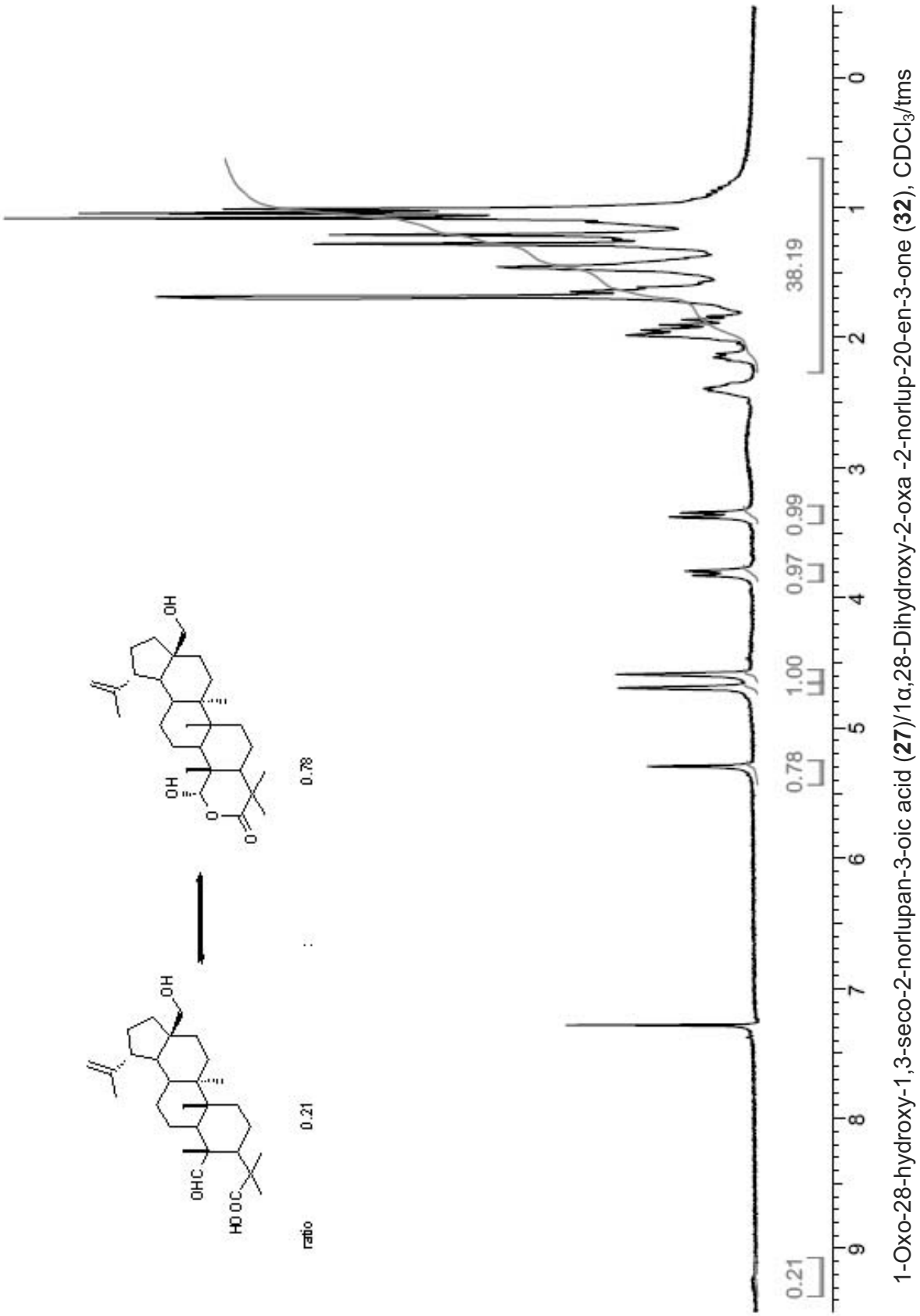
Potassium 19β,28-epoxy-1,28-dioxo-1,3-seco-2-nor-18α-oleanan-3-oate (**25**), CD_3OD+1wt%KOH/tms



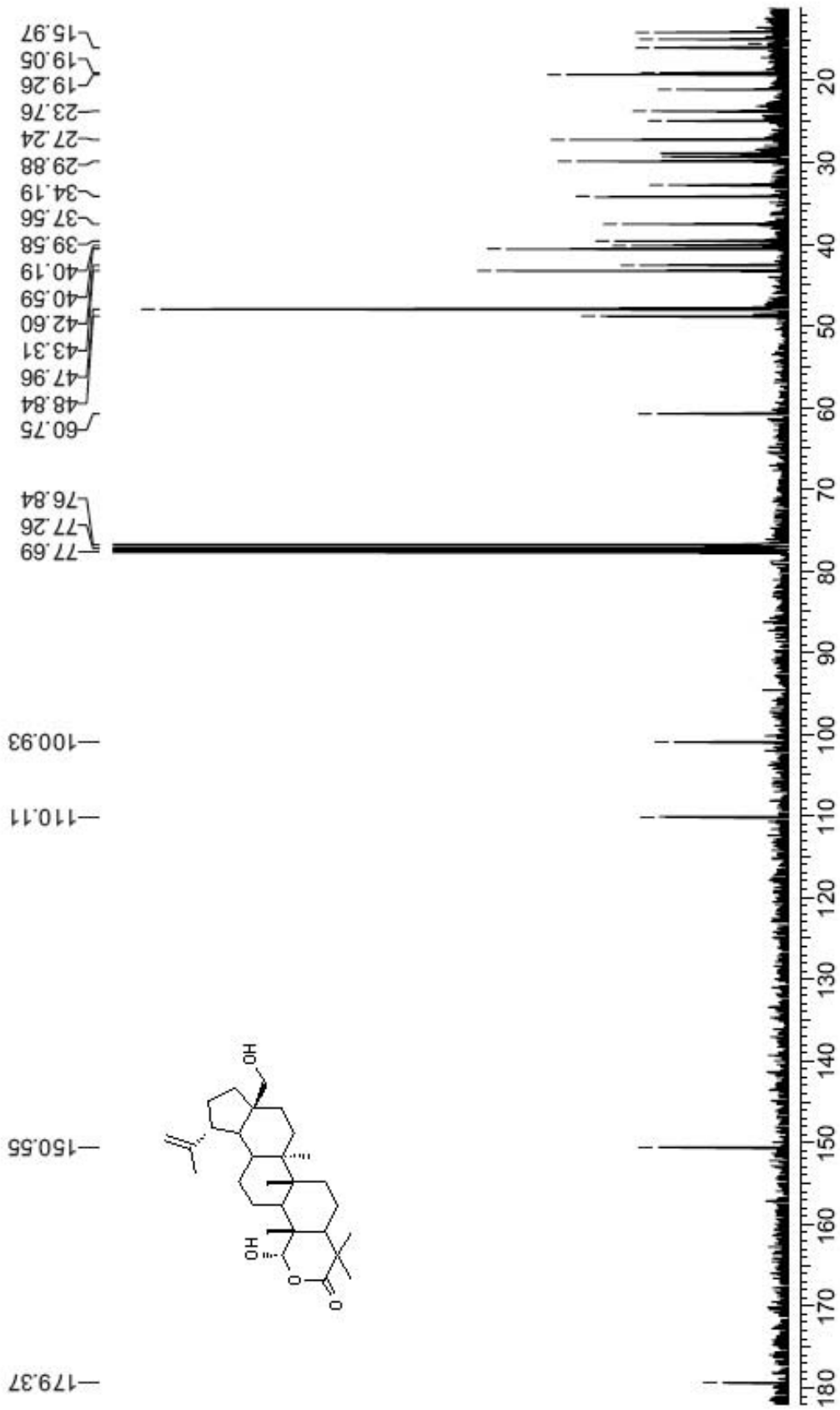
1-Oxo-2-nor-2,3-secolupan-3-oic acid (**26**)/1α-Hydroxy-2-oxa-2-norlup-20-en-3-one (**31**), $CDCl_3$/tms



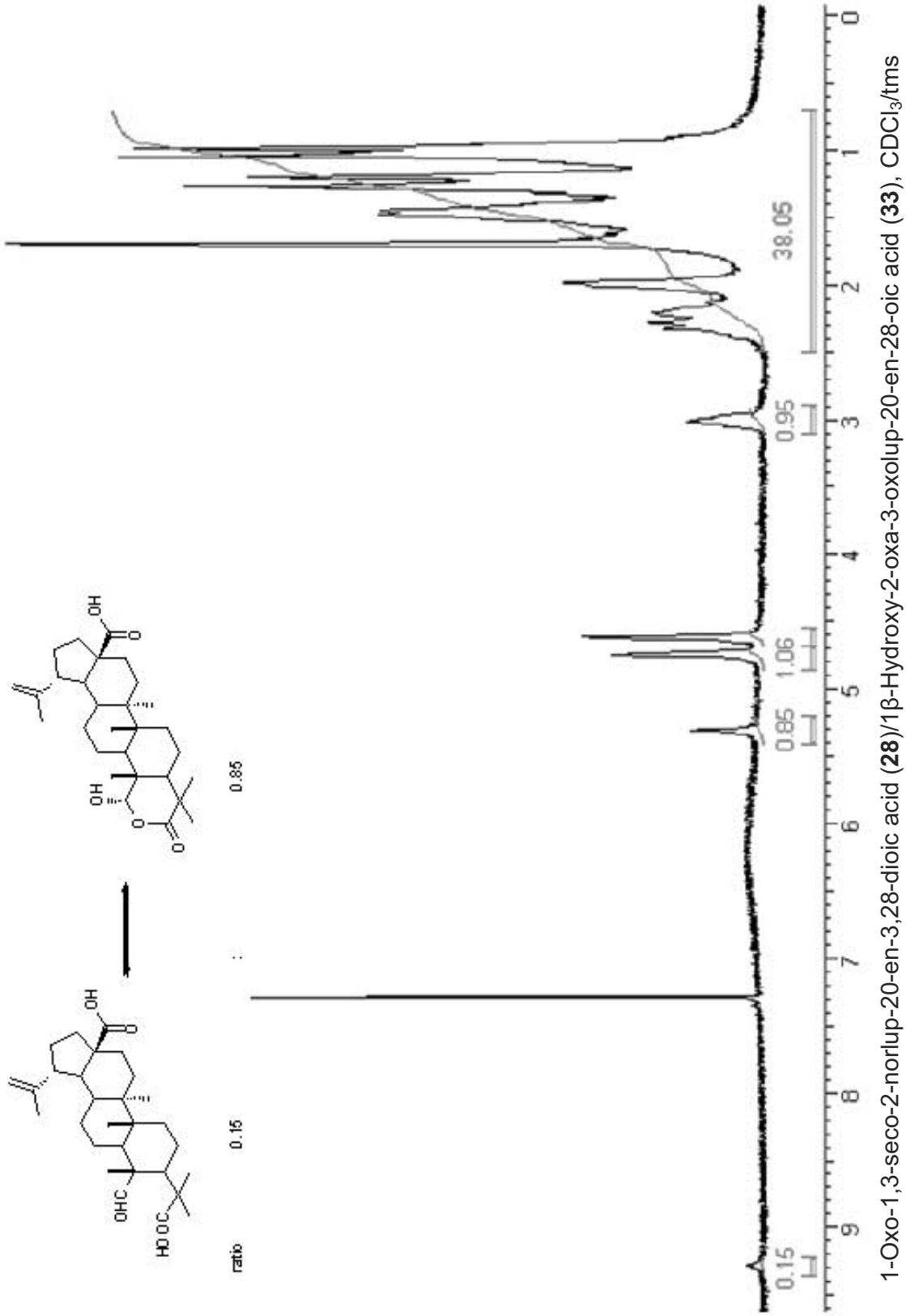
1α-Hydroxy-2-oxa-2-norlup-20-en-3-one (**31**), $CDCl_3$/tms



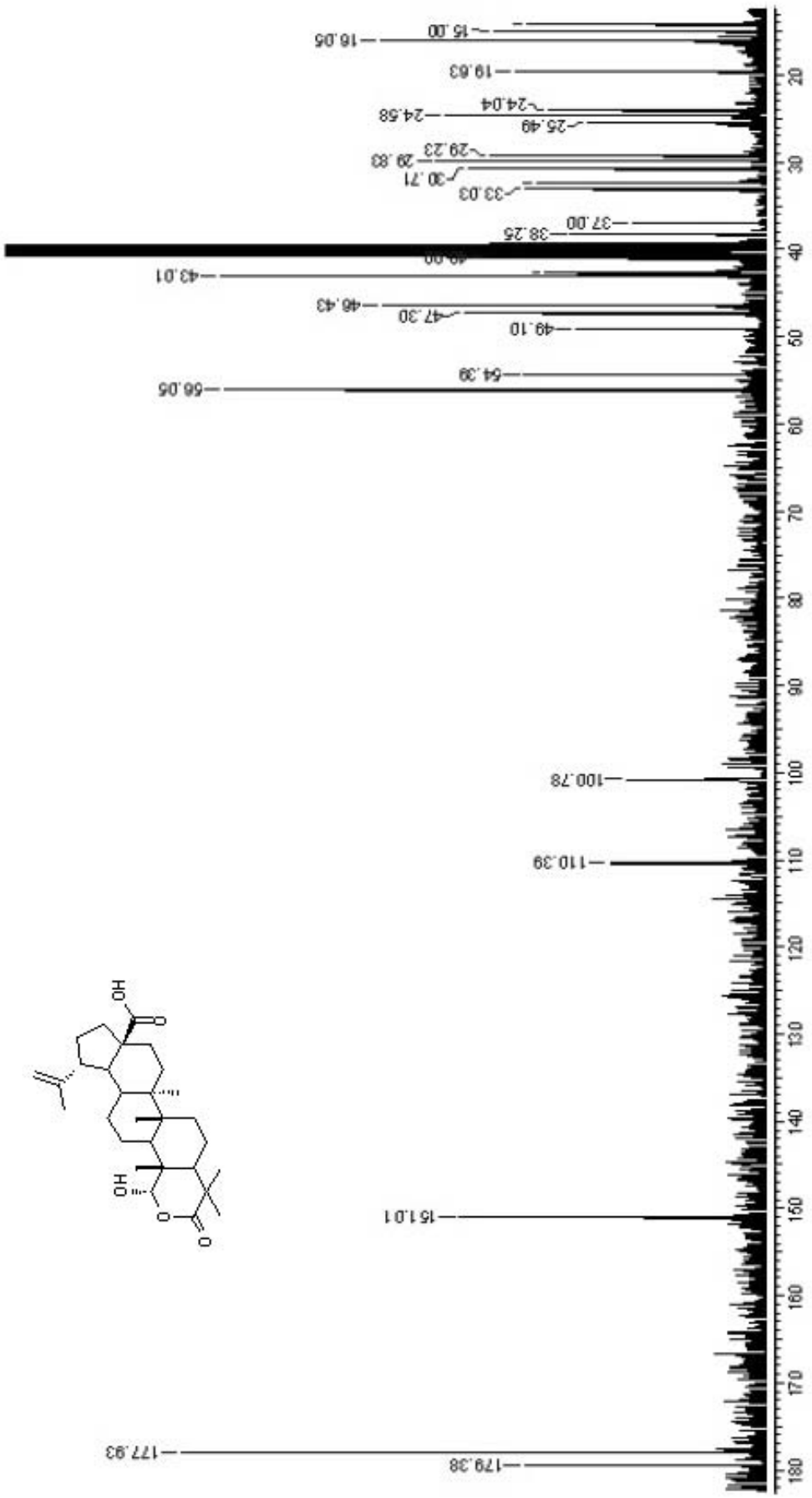
1-Oxo-28-hydroxy-1,3-seco-2-norlupan-3-oic acid (**27**)/1α,28-Dihydroxy-2-oxa -2-norlup-20-en-3-one (**32**), $CDCl_3$/tms



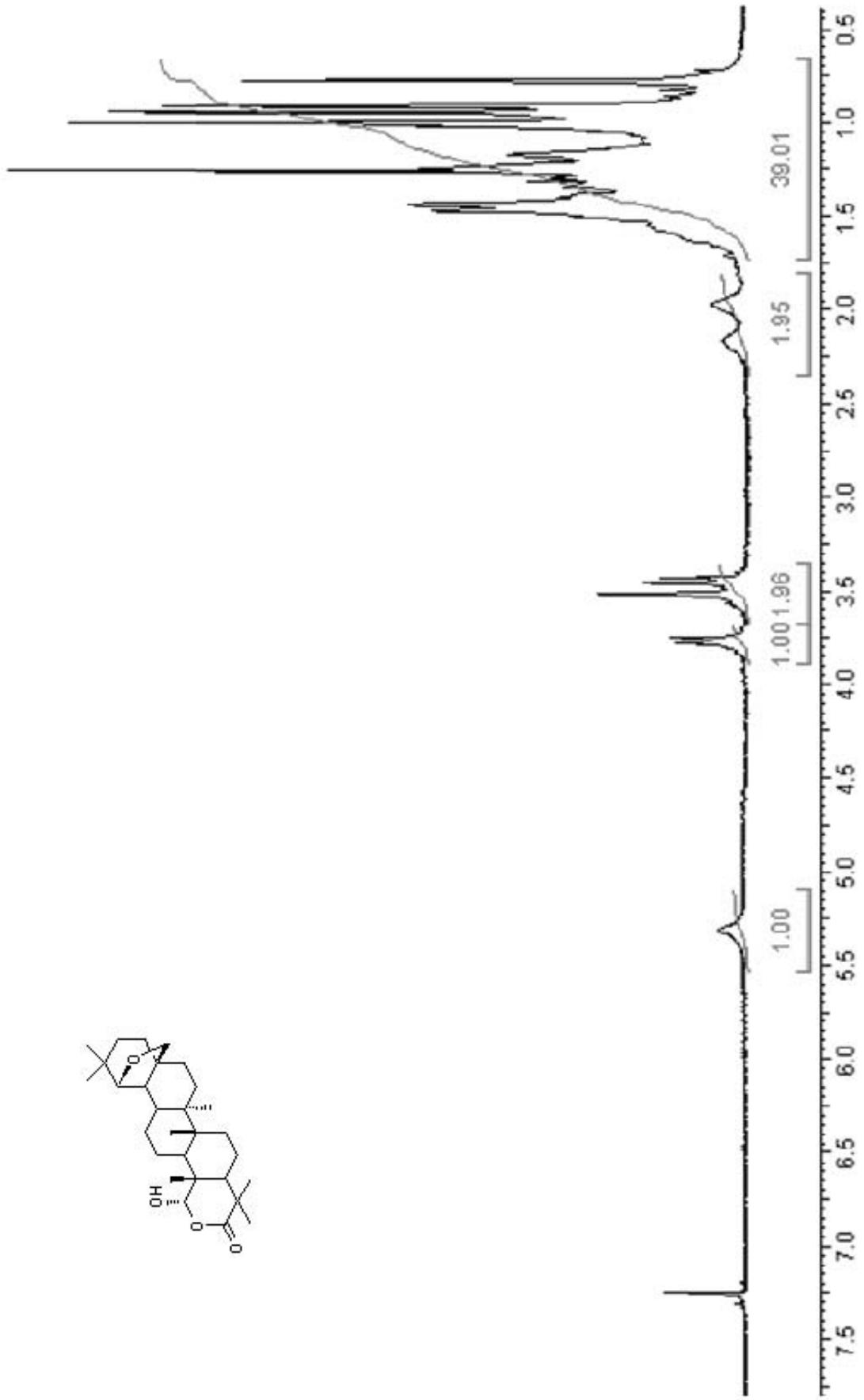
1α,28-Dihydroxy-2-oxa -2-norlup-20-en-3-one (**32**), $CDCl_3$/tms



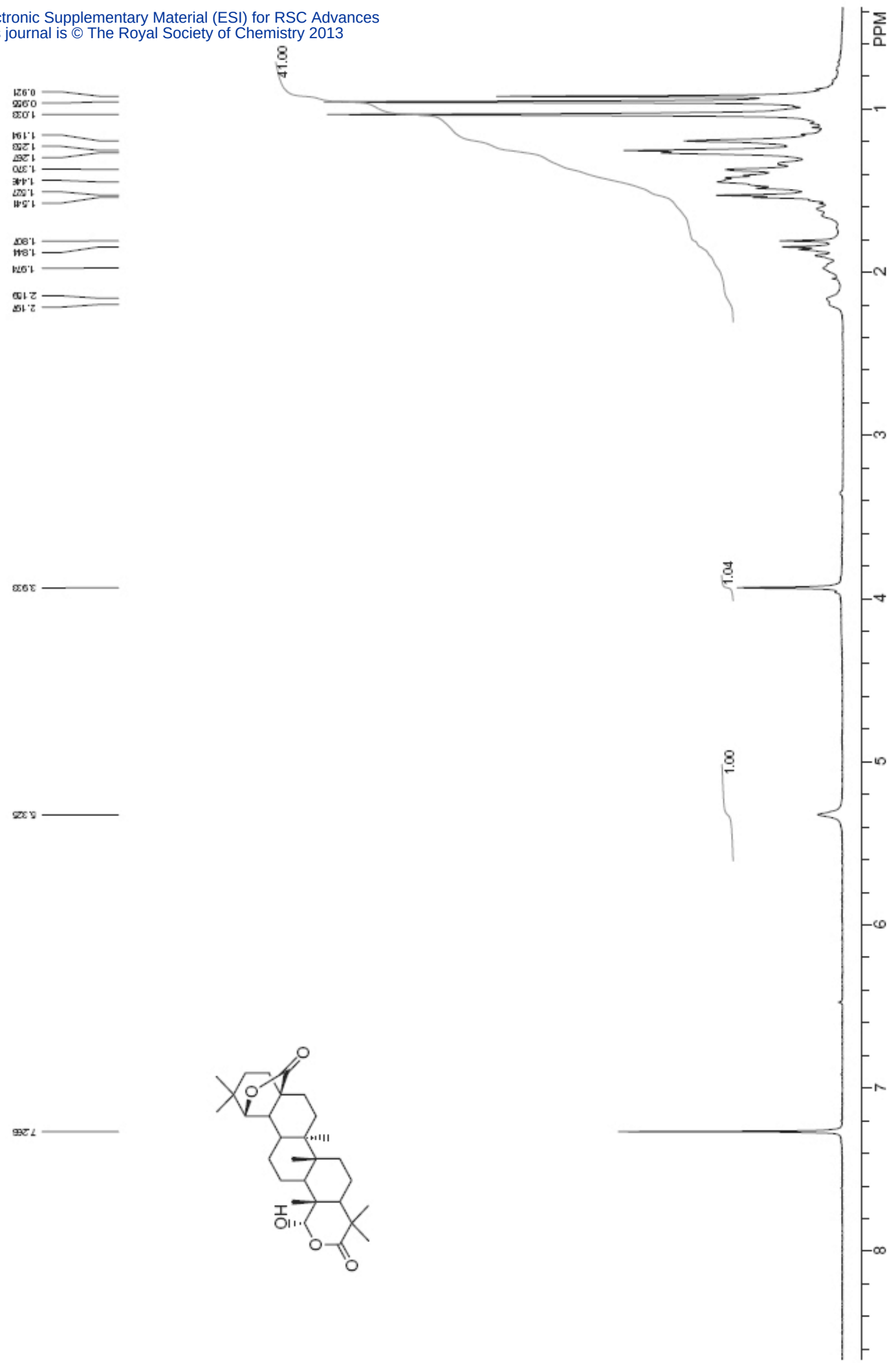
1-Oxo-1,3-seco-2-norlup-20-en-3,28-dioic acid (**28**)/1β-Hydroxy-2-oxa-3-oxolup-20-en-28-oic acid (**33**), $CDCl_3$/tms



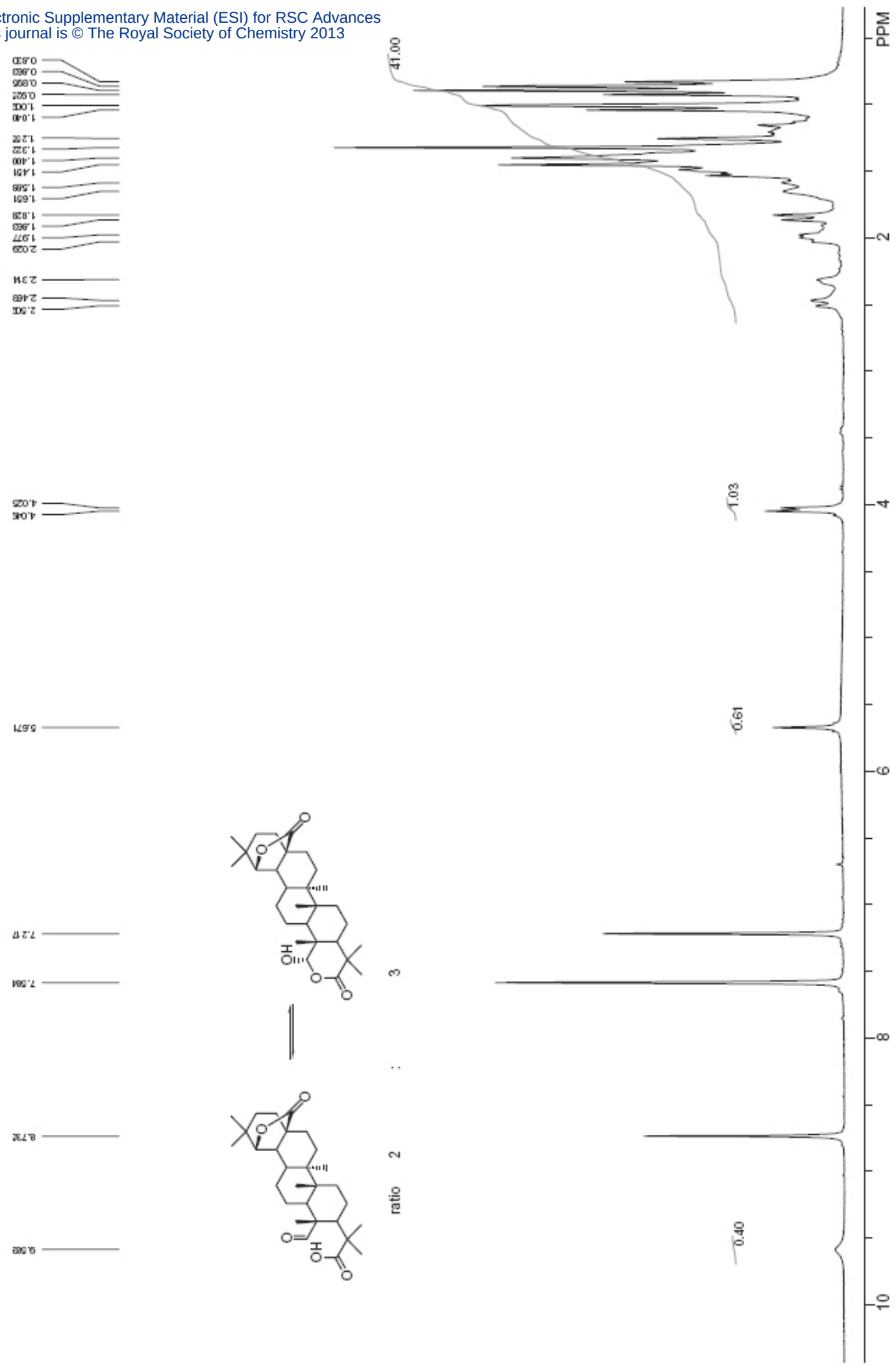
1β-Hydroxy-2-oxa-3-oxolup-20-en-28-oic acid (**33**), DMSO-d_6/tms



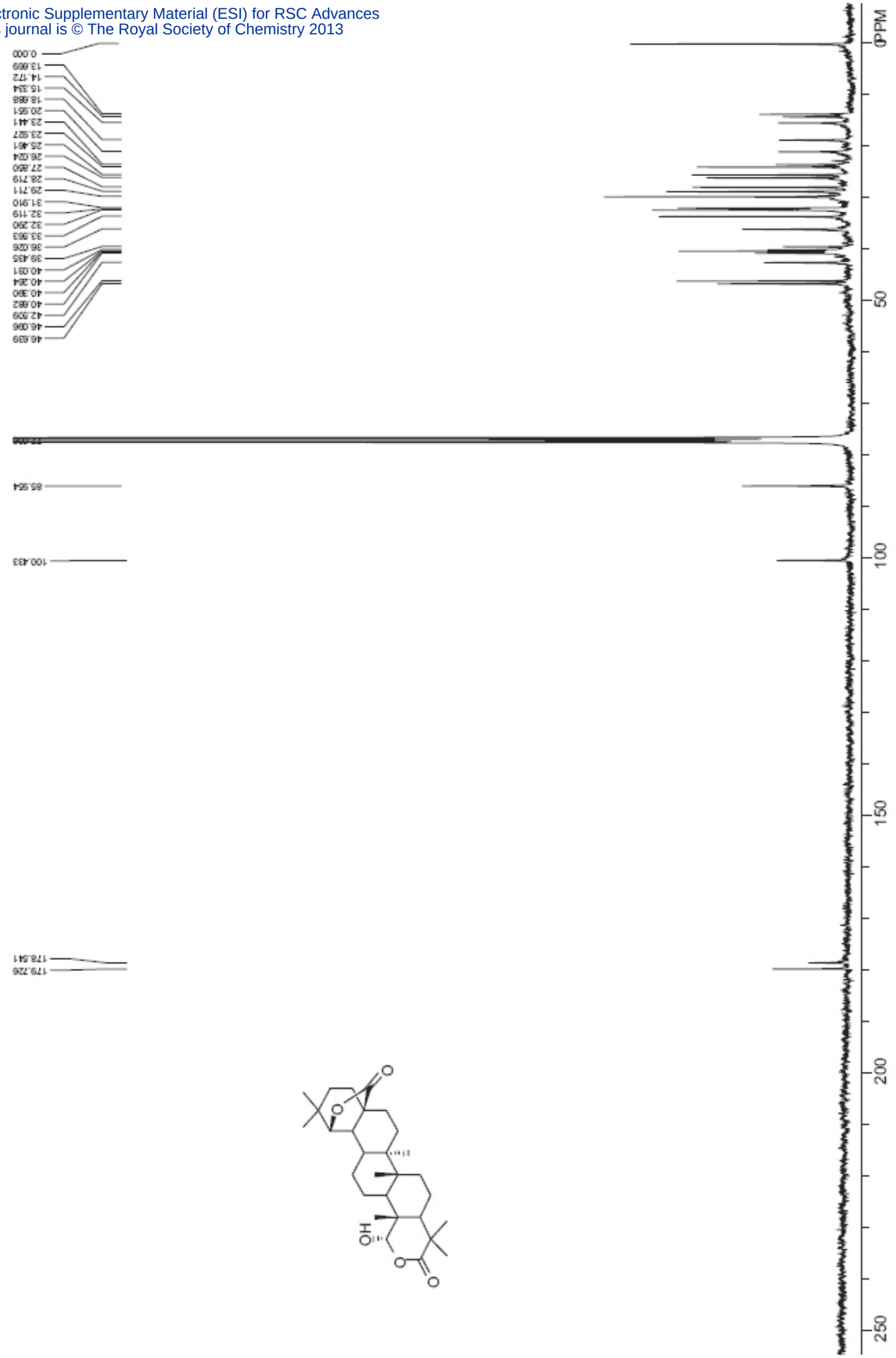
19β,28-Epoxy-1α-hydroxy-2-oxa-2-nor-18α-oleanan-3-one (**34**), $CDCl_3$/tms



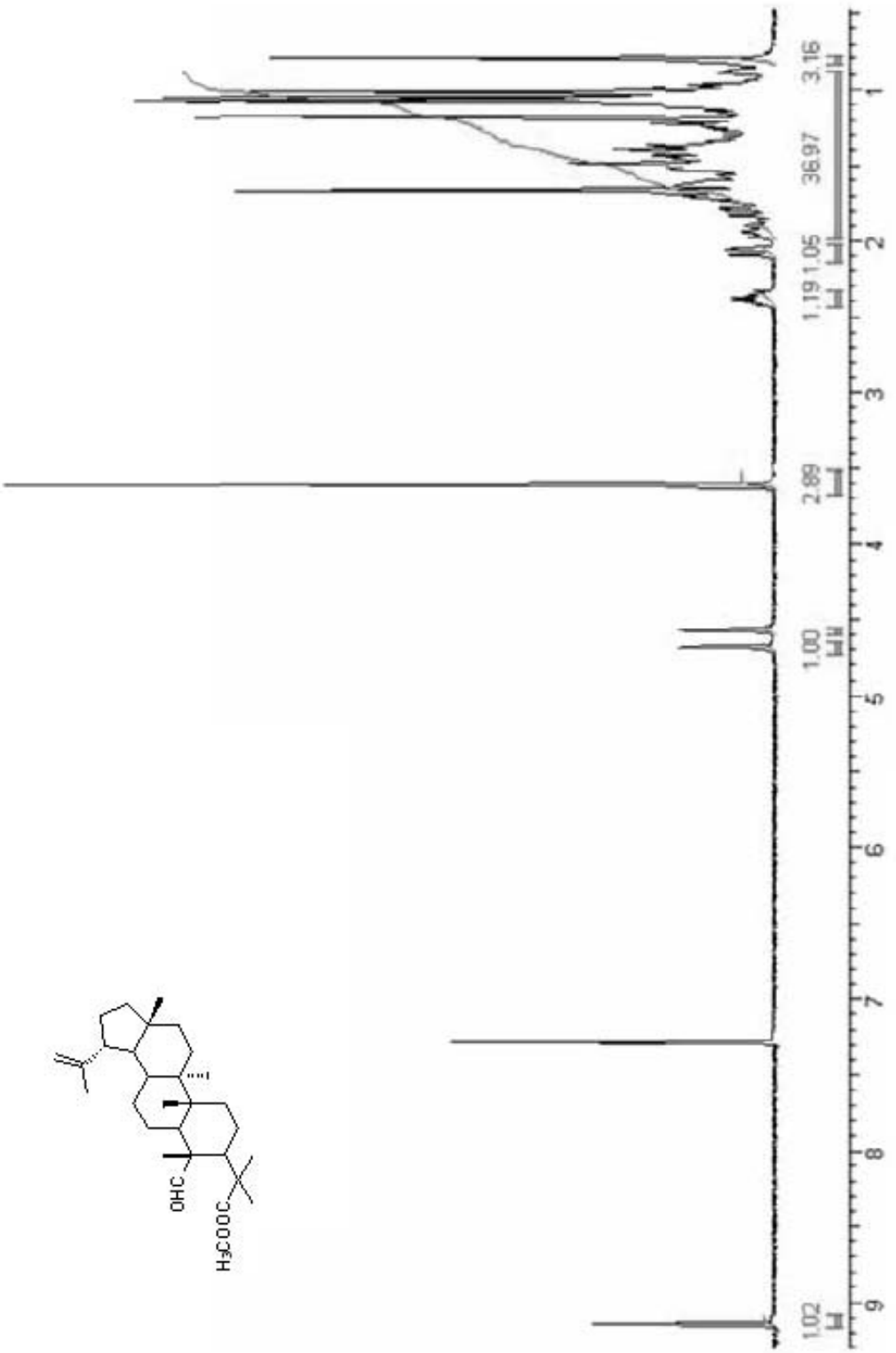
1-Hydroxy-2-oxa-3-oxo-2-nor-18α-oleanan-28,19β-olide (**35**), $CDCl_3$/tms



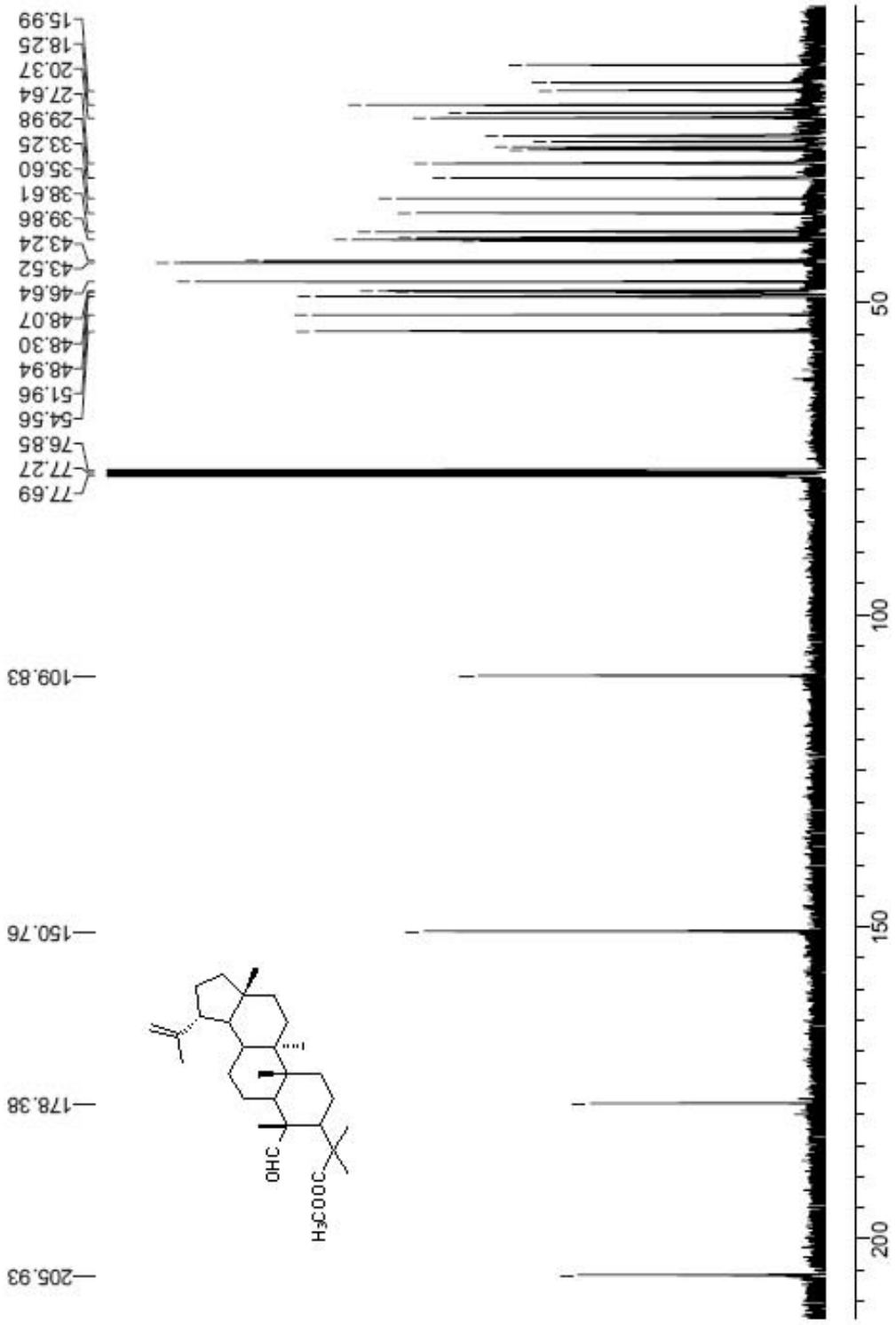
19β,28-Epoxy-1,28-dioxo-1,3-seco-2-nor-18α-oleanan-3-oic acid (**30**)/1-Hydroxy-2-oxa-3-oxo-2-nor-18α-oleanan-28,19β-olide (**35**), Py-d_5/tms



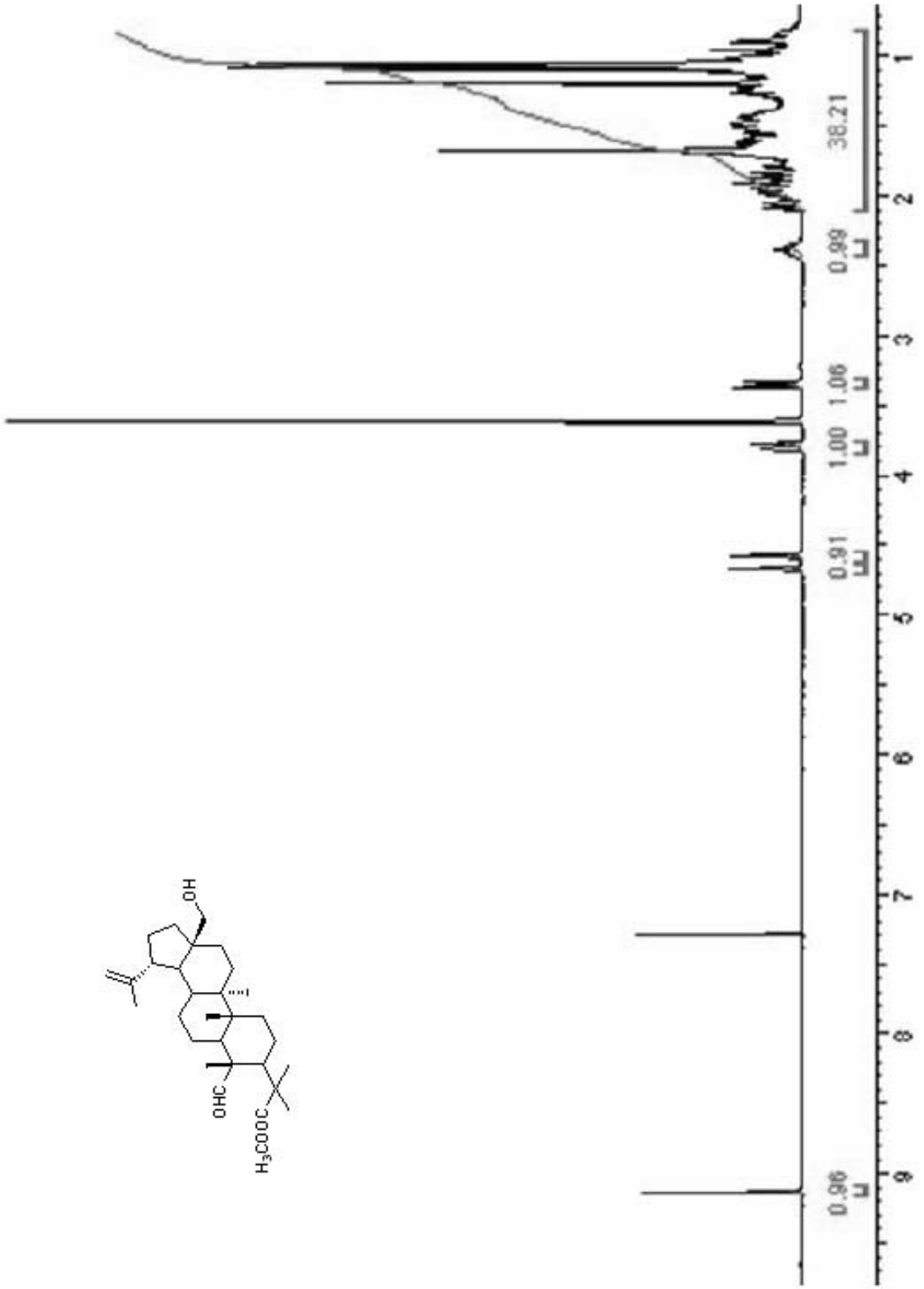
1-Hydroxy-2-oxa-3-oxo-2-nor-18α-oleanan-28,19β-olide (**35**), $CDCl_3$/tms



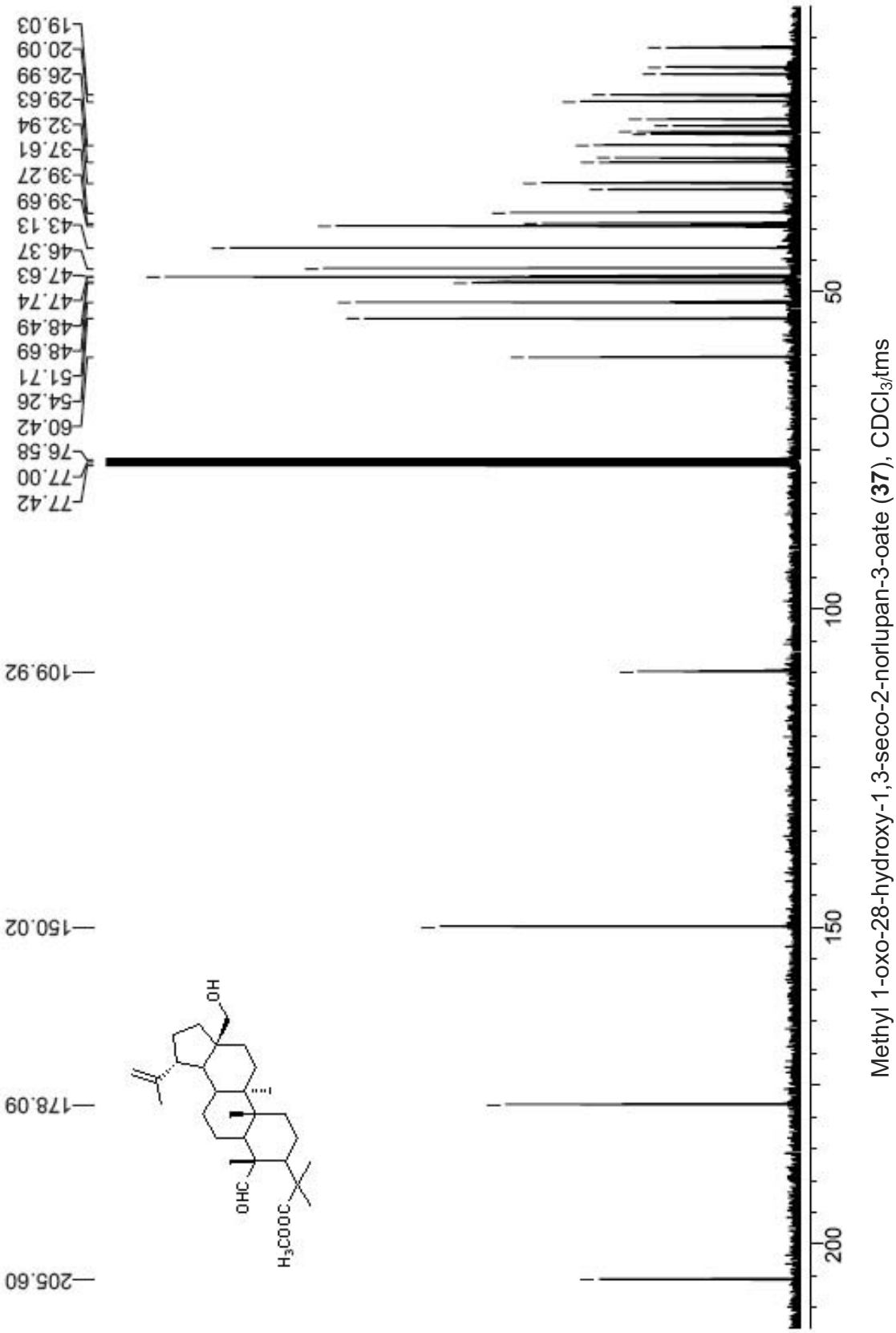
Methyl 1-oxo-2-nor-2,3-secolupan-3-oate (**36**), $CDCl_3$/tms



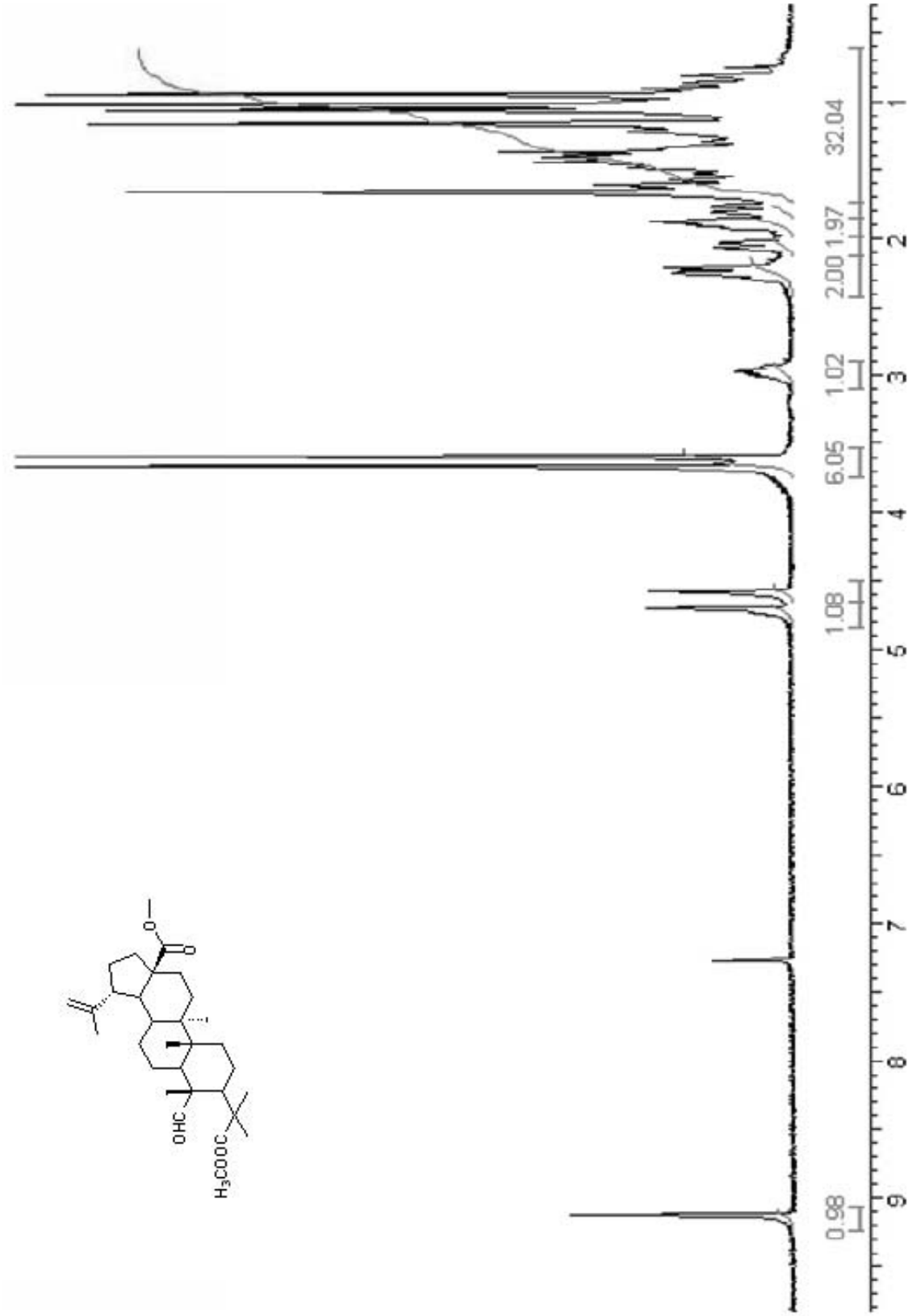
Methyl 1-oxo-2-nor-2,3-secolupan-3-oate (**36**), $CDCl_3$/tms



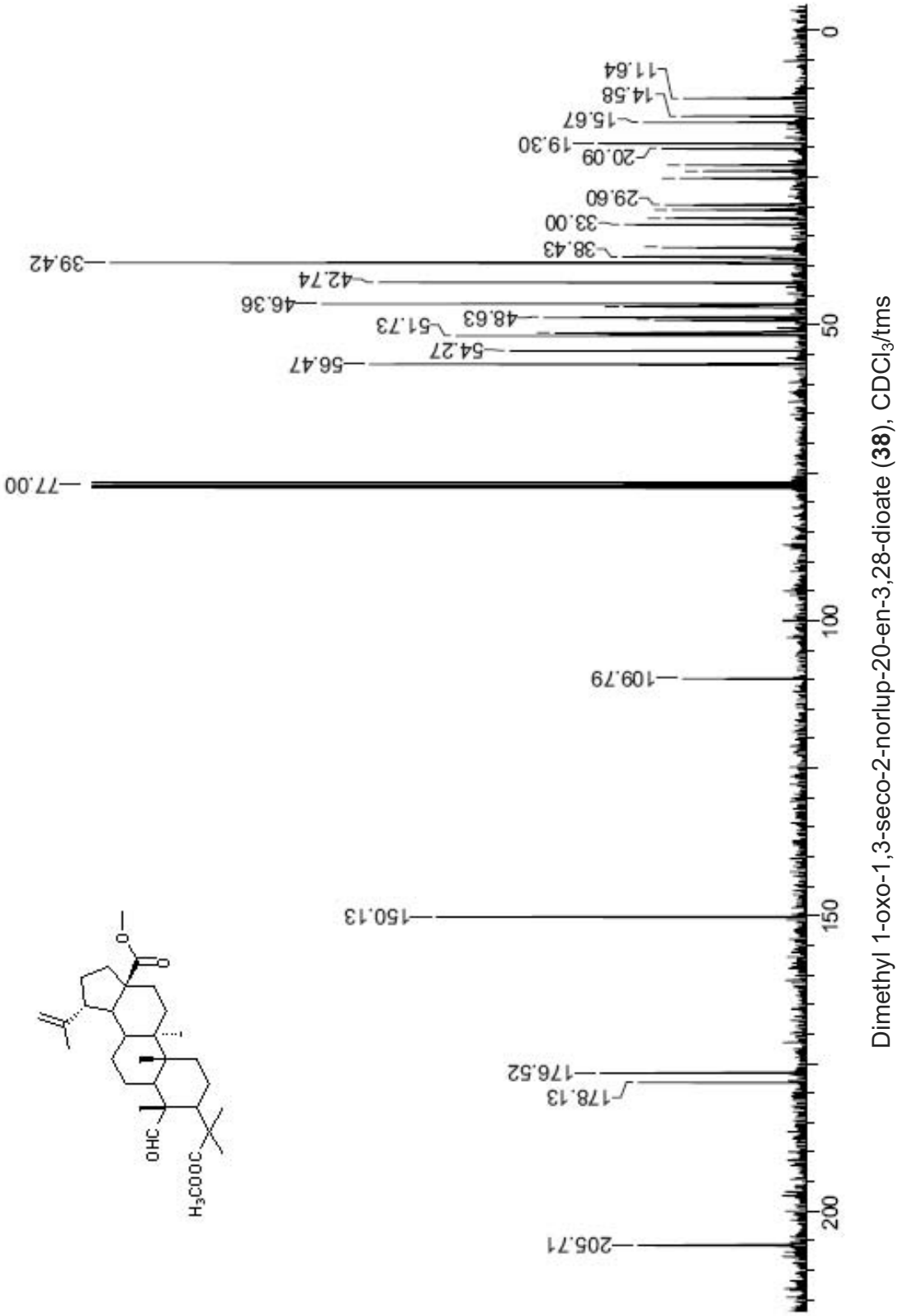
Methyl 1-oxo-28-hydroxy-1,3-seco-2-norlupan-3-oate (**37**), $CDCl_3$/tms



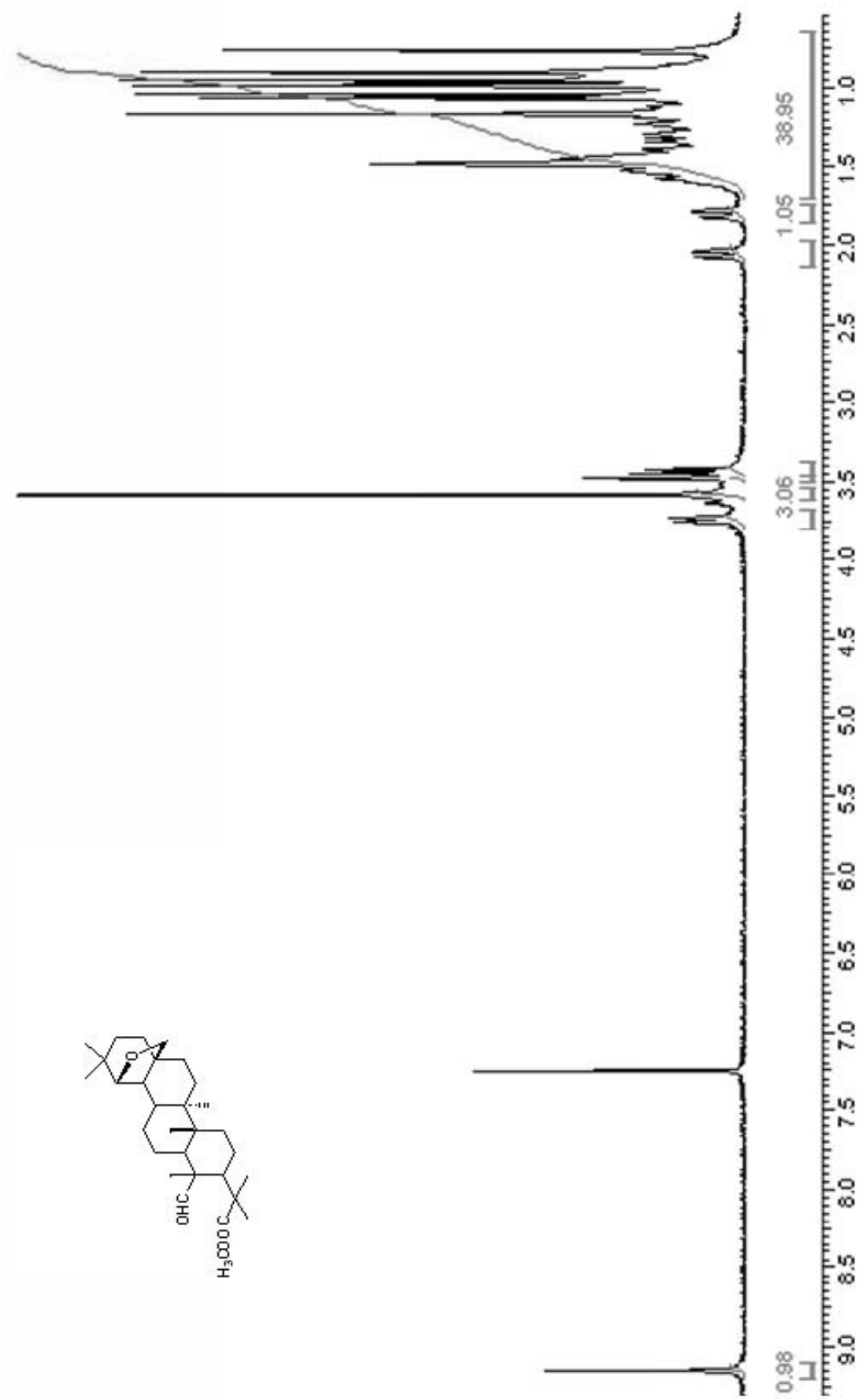
Methyl 1-oxo-28-hydroxy-1,3-seco-2-norlupan-3-oate (**37**), $CDCl_3$/tms



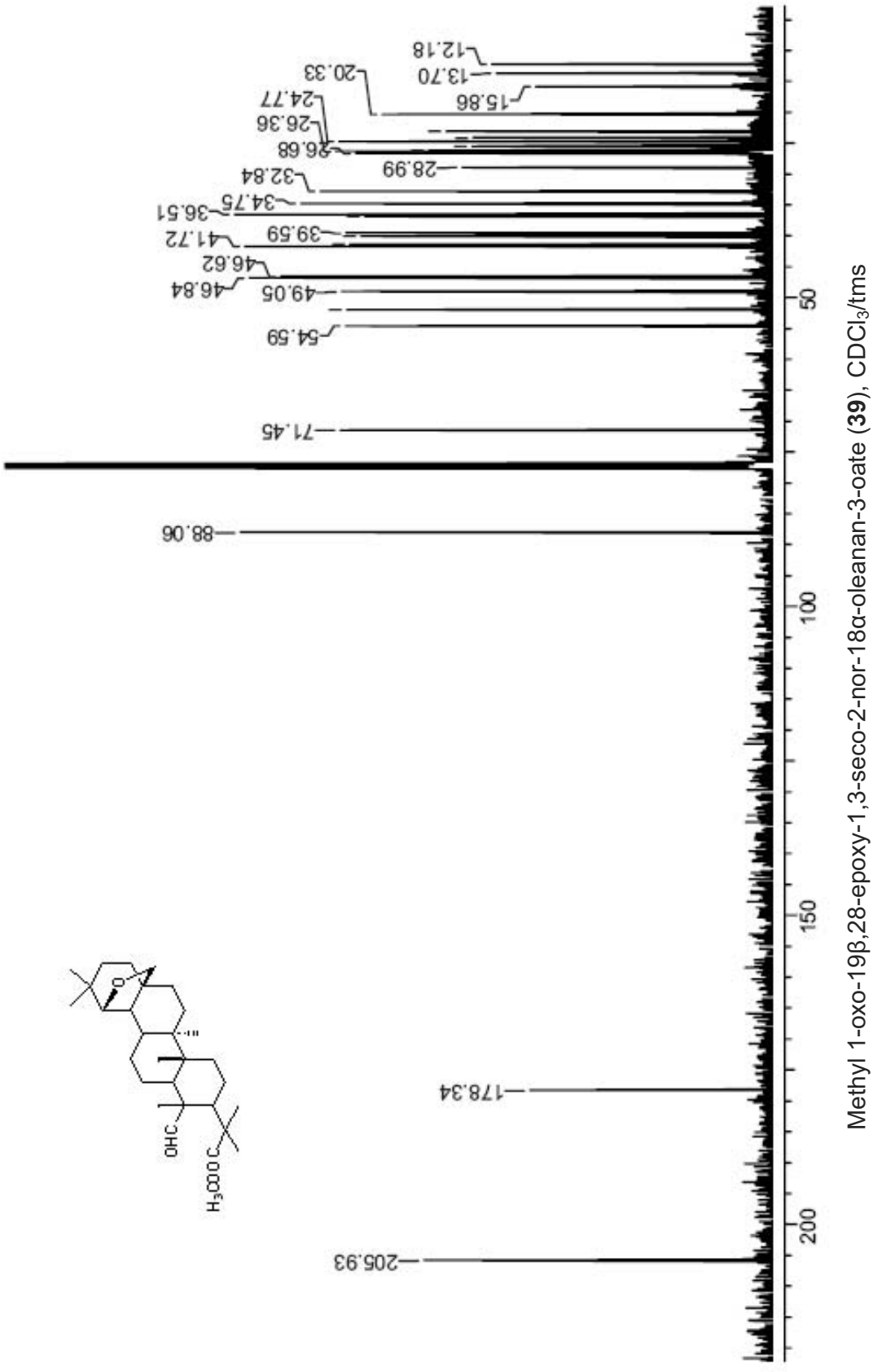
Dimethyl 1-oxo-1,3-seco-2-norlup-20-en-3,28-dioate (**38**), $CDCl_3$/tms



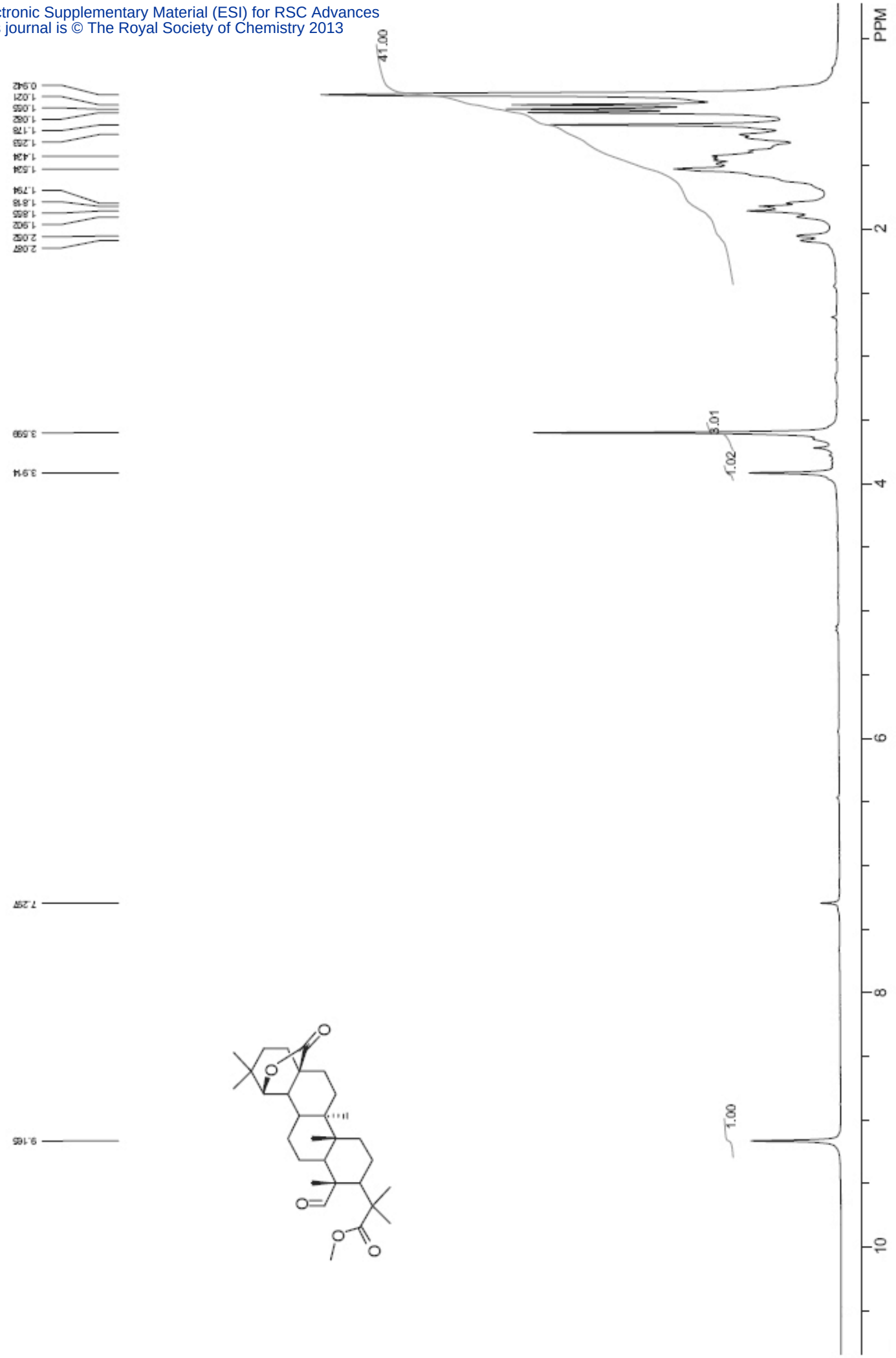
Dimethyl 1-oxo-1,3-seco-2-norlup-20-en-3,28-dioate (**38**), $CDCl_3$/tms



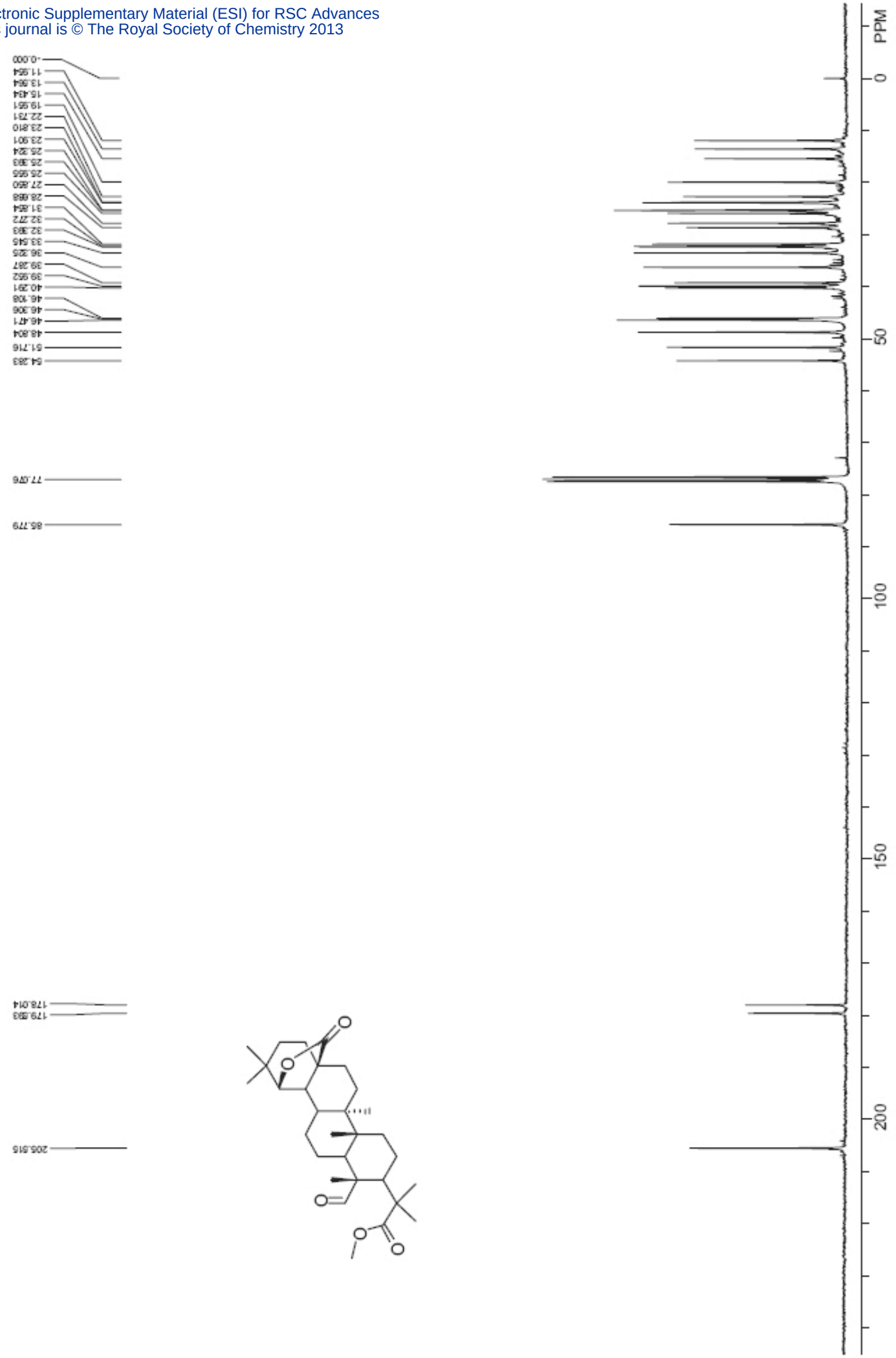
Methyl 1-oxo-19β,28-epoxy-1,3-seco-2-nor-18α-oleanan-3-oate (**39**), $CDCl_3$/tms



Methyl 1-oxo-19β,28-epoxy-1,3-seco-2-nor-18α-oleanan-3-oate (**39**), $CDCl_3$/tms



Methyl 19β,28-epoxy-1,28-dioxo-1,3-seco-2-nor-18α-oleanan-3-oate (**40**), $CDCl_3$/tms



Methyl 19β,28-epoxy-1,28-dioxo-1,3-seco-2-nor-18α-oleanan-3-oate (**40**), $CDCl_3$/tms

2. X-ray structural determination

Methyl 19β,28-epoxy-3β-hydroxy-1(2→3)-abeo-18α-oleanan-2-oate (**19**) crystals were obtained by slow evaporation of the chloroform solution at room temperature. X-ray intensity data were collected using a Rigaku AFC-7R diffractometer at room temperature with Mo K_α radiation and a graphite monochromator. A total of 3252 reflections were collected ($\theta = 2.5–27.5^o$); of these 3128 reflections were unique. The data were corrected for absorption using ψ-scan method. All raw data were processed using TeXsan 10.3b1 program.[3] The structures were solved by the direct method (Sir-92) and refined by full-matrix least-squares procedures on F^2 using the Crystals for Windows program.[4] The three-parameter Prince modified Chebychev polynomial weighting scheme incorporated in the program was used for the refinement. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were found in calculated positions and refined using the riding model. The position of O−H hydrogen was found using difference Fourier map. CCDC reference number is 721850. The important crystallographic data for compound **19** (Figure 1) are presented in Table 1, while selected bond distances and angles are listed in Table 2.

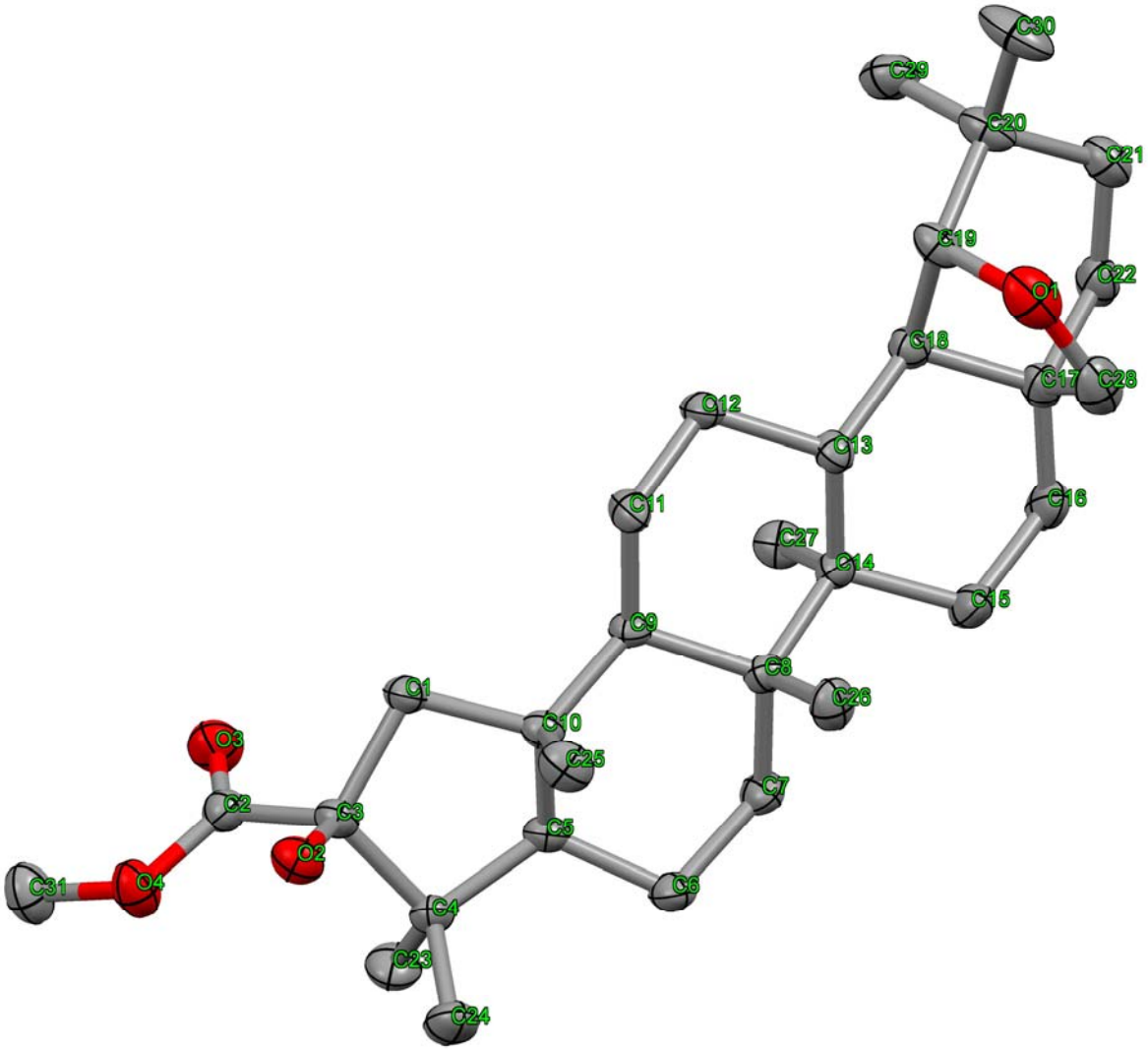


Figure 1 X-ray structure of methyl 19β,28-epoxy-3β-hydroxy-1(2→3)-abeo-18α-oleanan-2-oate (**19**) (ellipsoids are at 30% probability, all hydrogen atoms are omitted for clarity)

[3] TeXsan 10.3.b. Rigaku Inc. 1998.
[4] P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Cryst.*, 2003, **36**, 1487.

Table 1 Crystallographic data for compound **19**

Formula	$C_{31}H_{50}O_4$
Crystal class	Monoclinic
Space group	$P2_1$
Cell parameters:	
a, Å	7.4870(15)
b, Å	16.276(3)
c, Å	11.153(2)
β, ^{o}	90.01(3)
Volume Å^3	1359.1(4)
Z	2
Radiation type	Mo K_α
Crystal size (mm)	0.22x0.43x0.51
Reflection measured	3262
Independent reflections	3252
Reflection used	2542 ($\sigma \geq 3$)
2θ range	5 – 55
R_f	0.0781
R_w	0.1633
Number of parameters	317
Goodness of fit	0.8988

Table 2 Selected bond distances (Å) and angles (^{o}) for compound **19**

C28−O1	1.436(9)
C19−O1	1.450(7)
C3−O2	1.435(6)
C3−C2	1.538(8)
C2−O3	1.191(7)
C2−O4	1.341(7)
O4−C31	1.448(7)
O2−H−O1	2.442
O2−H−O4	2.571
C28−O1−C19	108.12
O2−C3−C2	108.91
C3−C2−O3	125.22
C3−C2−O4	111.86
C2−O4−C31	115.88

3. XYZ-coordinates of B3PW91/6-31G(d,p) optimized species

MIN1	**MIN2**	**MIN3**
HF=-657.6836693	HF=-657.6754739	HF=-657.675684
O -0.2812144 -0.3626100 -3.0889711	O -0.3141655 0.9246525 -2.8330571	O -0.7024420 -0.7389695 -2.9569879
C -0.0297110 -0.2226834 -1.8928601	C -0.1183285 0.2638980 -1.8345053	C -0.3129600 -0.2432859 -1.9199292
C 1.3951227 -0.2240895 -1.4965137	C 1.2614083 -0.4078080 -1.6504253	C 1.1965593 -0.0158461 -1.7190447
C -1.1240777 -0.0179616 -0.8468433	C -1.1827599 0.0285162 -0.7579249	C -1.2326331 0.1739415 -0.7666608
C -2.2510814 -1.0195389 -1.1698110	C -1.9899968 -1.1934531 -1.2633176	C -2.5848766 -0.5315357 -0.9459456
C 1.7993188 0.0180093 -0.2363458	H 1.9381692 -1.5359725 -0.0134992	H 1.5725709 -1.6537400 -0.4279892
H 2.8684118 0.0657676 -0.0306415	C 1.8057340 -0.4687113 -0.2430382	C 1.7246301 -0.5634227 -0.4219312
H -0.3565164 -1.3917940 0.5544305	H 2.8164442 -0.0394925 -0.2544204	H 2.8002044 -0.3681128 -0.3548722
C -0.5480749 -0.3058888 0.5696385	H -0.4306922 -1.4291239 0.6407093	H -0.6396361 -1.3442244 0.5954306
C -1.5278886 -0.0730447 1.7278243	C -0.5347767 -0.3313905 0.6285862	C -0.5732416 -0.2426962 0.5943584
C 0.8490189 0.2998999 0.8936835	C -1.4489025 0.0161656 1.8145229	C -1.3665946 0.2246680 1.8261110
C 0.8741616 1.8280608 1.1421733	C 0.9165569 0.1977079 0.8219054	C 0.9527308 0.0447575 0.7734165
C 1.3595313 -0.4181049 2.1702447	C 1.0248414 1.7271187 0.6959411	C 1.3314545 1.5356896 0.8807311
C -1.6883562 1.4059369 -1.0460991	C 1.4390190 -0.2537223 2.2056035	C 1.4093258 -0.6855084 2.0583129
O 2.2567281 -0.4411532 -2.5175736	C -2.1170491 1.2487918 -0.7296983	C -1.4574151 1.6968571 -0.9266131
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C 0.4115662 -0.2642760 3.3623818	H 1.5513115 -1.3480643 2.1923563	H 1.2760182 -1.7677212 1.9129153
H -1.6904371 1.0002889 1.8892304	C 0.5261024 0.1144819 3.3735365	C 0.6350784 -0.2566271 3.3051109
H -2.5080416 -0.4969992 1.4844357	H -1.6097468 1.1003125 1.8613933	H -1.2937628 1.3140606 1.9371763
H 0.7957834 -0.8415959 4.2121660	H -2.4375810 -0.4329570 1.6585897	H -2.4300019 0.0009787 1.6924326
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H 0.3924047 0.7827579 3.6916864	C -0.8736200 -0.4553663 3.1514429	C -0.8681676 -0.4521138 3.1071112
H -1.6890044 -0.5064436 3.8494332	H 0.4677303 1.2053741 3.4867903	H 0.8462841 0.7959268 3.5354281
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H -2.1347947 1.4848299 -2.0416461	H -1.6239983 2.1370384 -0.3250920	H -0.5318049 2.2750511 -0.9394546
H -3.1334684 -0.8258063 -0.5534618	H -2.4370927 1.4843104 -1.7471600	H -1.9832711 1.8924867 -1.8663781
H -2.5407688 -0.9276849 -2.2192235	H -2.7490281 -1.4679159 -0.5226784	H -3.3317502 -0.1314713 -0.2547915
H -1.9308496 -2.0526321 -0.9954754	H -2.4959011 -0.9601798 -2.2049338	H -2.9522916 -0.3865856 -1.9645300
H 1.6931023 -0.5334174 -3.3098180	H -1.3497866 -2.0677177 -1.4268330	H -2.4989872 -1.6102837 -0.7785264

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C -0.0840755 -0.4228540 -1.8052398	C 0.0828524 0.1637085 -1.7951261	C -0.2931669 -0.7946731 2.5615508
C 1.4066610 -0.3526120 -1.4577238	C 1.4076152 -0.4865564 -1.4219378	C -0.4706054 0.1356150 1.2993371
C -1.0013774 0.3763585 -0.8061459	C -1.0943451 -0.0944817 -0.7741282	C 0.9070212 0.4641598 0.5411190
C -2.4464347 -0.0527302 -1.1138347	C -1.8966015 -1.3486958 -1.1690739	C 2.1234534 -0.2621671 1.1393127
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C 1.7426074 -0.7499370 -0.0312453	C 1.8845534 -0.3069614 0.0134762	C -1.3617523 -0.5509395 0.2366865
H 2.8139458 -0.5818531 0.1413887	H 2.7900099 0.3138762 -0.0020982	H -2.4176344 -0.3455513 0.4477608
H -0.8233670 -1.1740918 0.5984365	H -0.3672666 -1.4514338 0.7091829	H 0.8712760 -1.1451320 -0.8327371
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C -1.4990504 0.4987800 1.7473578	C 0.8586396 0.2344036 1.0325435	C 1.4374224 0.4556078 -2.0838423
C 0.8960472 -0.0027786 1.0177745	H -1.2345849 -2.2126427 -1.2992594	C -0.8883473 -0.0309276 -1.1263208
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C 1.0793539 -0.7199171 2.3764984	C 0.8943068 1.7725601 1.0617769	C -1.1923488 -0.9395326 -2.3288621
C -0.8942675 1.8940640 -1.0300762	C 1.2600891 -0.3128704 2.4262353	C 1.2210562 1.9670909 0.5782050
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H 0.5149766 0.8887918 3.7143884	H -2.5324008 -0.5206435 1.5106122	H -0.7938980 0.4754679 -3.9202093
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H 1.6111517 1.8856734 0.1616228	H 1.8726689 2.1092331 1.4342094	H -1.4589396 1.9697924 -0.4604513
H 0.7851378 2.1011148 1.7052083	H 0.7525536 2.1469781 0.0417354	H -0.9718444 1.9255590 -2.1689337
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H -1.3568305 2.4636979 -0.2116065	H 2.2466649 0.0926603 2.6945716	H 2.1757790 2.1585023 0.0691171
H 0.1400564 2.2305642 -1.1376373	H -1.8764752 -0.3199673 3.9113308	H 0.4513881 2.5840992 0.1113346
H -1.4030613 2.1599783 -1.9607303	H -1.0746966 -1.6779093 3.1221770	H 1.3140045 2.3035873 1.6151061
H -3.1810333 0.5220726 -0.5343636	C 0.2450079 -0.0243481 3.5322253	H 3.0159664 -0.0735836 0.5249333
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MIN7	**TS1**	**TS2**
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O -2.0080620 1.9244840 1.0160324	O -0.0718029 0.1294556 3.2712289	O -2.0690763 -0.8275590 -1.4361975
C -2.3901399 0.9951590 0.2732828	C -0.1692300 -0.5666003 2.0526891	C -2.1033400 -0.3105657 -0.2819624
C -1.3007431 0.1431232 -0.4837660	C -1.3860213 -0.1611427 1.3164031	C -1.4314490 -0.8830577 0.9061728
C -0.5189808 -0.8681139 0.4889435	C 0.7647071 0.6834735 0.7235103	C -0.7203426 1.1319899 -0.1218940
C -0.9590776 -2.3154017 0.2307747	C 2.1568798 0.4141592 1.2682993	C -1.1909720 2.1537001 0.8974771
H -0.0916009 0.6472803 -2.1804373	H -1.2493782 -1.8852943 0.0900833	H 0.1784934 -2.0026960 1.6626443
C -0.2021025 1.0181780 -1.1531830	C -1.6206878 -0.8580793 -0.0043146	C -0.1596369 -1.6734193 0.6733175
H -0.5031292 2.0700703 -1.1984712	H -2.6987001 -0.8712589 -0.2072646	H -0.4162339 -2.5617046 0.0808876
H 1.0236734 -1.2233240 -0.9086284	H 0.9660923 -0.9772167 -0.5181137	H 0.7366137 0.6882997 1.3554037
C 0.9501357 -0.6677277 0.0435919	C 0.5962408 0.0516687 -0.6654345	C 0.6927502 0.6294643 0.2530733
C 1.1083096 0.8130018 -0.3762206	C 1.4668743 0.6635204 -1.7812783	C 0.9651275 -0.8722102 -0.0464199
H -0.8396503 -2.5931584 -0.8194502	C -0.8676738 -0.1441885 -1.1516990	H -1.3003910 1.7020504 1.8935730
H -2.0161891 -2.4499443 0.4848749	C -1.6199969 1.1558602 -1.4988138	H -2.1584539 2.5770641 0.6059903
C 1.1811018 1.8262588 0.7842194	C -0.8317741 -1.0546042 -2.3993571	C 0.9745000 -1.2220958 -1.5456973
C 2.3891183 0.9084461 -1.2236650	C 0.4105957 2.1486229 0.8880100	C 2.3290139 -1.2466529 0.5794230
C -0.7346233 -0.6003089 1.9884213	O -2.1410828 0.7460620 1.7342626	C -0.8580294 1.6815023 -1.5299413
O -1.9983435 -0.5614622 -1.5001023	H -0.8025164 0.7737519 3.2245531	O -1.8542825 -0.6783037 2.0632258
C 2.1084438 -1.1697547 0.9006515	H -1.8575526 -1.2340143 -2.7546946	C 1.8415371 1.5235471 -0.2508055
H -0.3709527 -3.0042217 0.8537973	H -0.4260696 -2.0333277 -2.1032246	H -0.4791538 2.9938523 0.9949350
H -0.1576429 -1.3235053 2.5813457	C 0.0291517 -0.4845319 -3.5313388	H -0.2494842 2.5903962 -1.6734171
H -0.4582646 0.4075575 2.2945128	H 1.1222231 1.6793032 -2.0235024	H -0.5812396 0.9470517 -2.2898027
H -1.7923192 -0.7282413 2.2432772	H 2.4989941 0.7692018 -1.4263447	H -1.9042361 1.9466417 -1.7187163
H -2.9323154 -0.3843704 -1.2136018	H 0.0476768 -1.1845596 -4.3788896	H -3.2763223 0.3351879 1.0616540
H 2.1641372 -0.6142369 1.8459236	C 1.4538362 -0.1993293 -3.0487267	H 1.8934586 1.4889753 -1.3471404
H 1.9670724 -2.2259785 1.1691218	H -0.4219048 0.4438053 -3.9095037	H 1.6314394 2.5694511 0.0106584
C 3.4212431 -1.0083183 0.1151681	H 2.0392946 0.2770474 -3.8489627	C 3.1940249 1.1081837 0.3368697
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H 0.1850188 1.9981257 1.2042599	H -1.0289097 1.8421938 -2.1135649	H -0.0439068 -1.1552696 -1.9422386
H 2.2665800 0.2944681 -2.1292200	H -2.5319097 0.9125085 -2.0618579	H 2.2548378 -1.1386538 1.6723512
H 2.5537113 1.9417049 -1.5619396	H 0.8860565 2.7853064 0.1210760	H 2.5403177 -2.3084833 0.3838655
H 4.2828227 -1.2853723 0.7392782	H -0.6673800 2.3444100 0.8614797	H 4.0017317 1.7321179 -0.0732717
H 3.4079850 -1.7165139 -0.7275082	H 0.7716430 2.5044266 1.8609583	H 3.1815327 1.2879853 1.4230854
C 3.6145485 0.4117162 -0.4398847	H 2.9397514 0.9391819 0.6933737	C 3.4856702 -0.3735158 0.0853795
H 4.5075855 0.4375335 -1.0804524	H 2.2258588 0.7536555 2.3079846	H 4.4192334 -0.6688375 0.5854997
H 3.8155983 1.1008569 0.3916390	H 2.3691163 -0.6612000 1.2619872	H 3.6454759 -0.5381315 -0.9891498