Supporting Information for

Original artical

Extensive expanding the chemical diversity of fusidane-type antibiotics using a stochastic combinational strategy

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Supporting Methods

Detailed purification procedure of compounds

*Purification of **5***

The culture medium extract (1.0 g) from the 5 L culture of AOS1 was subjected to ODS column chromatography on MPLC and eluted stepwise using MeOH–H_2O gradient (35:65, 80:20 and 100:0, *v*/*v*). Fraction 2 was further purified by reverse-phase semi-preparative HPLC (70% CH_3CN–H_2O containing 0.1% formic acid, 3 mL/min) to yield **5** (43.5 mg).

*Purification of **6***

The culture medium extract (0.31 g) from the 2 L culture of AOS2 was subjected to ODS column chromatography on MPLC and eluted stepwise using MeOH–H_2O gradient (35:65, 80:20 and 100:0, *v*/*v*). Fraction 2 was further purified by reverse-phase semi-preparative HPLC (80% CH_3CN–H_2O containing 0.1% formic acid, 3 mL/min) to yield **6** (4.3 mg).

*Purification of **9–11***

The culture medium extract (0.41 g) from the 2 L culture of AOS3 was subjected to ODS column chromatography on MPLC and eluted stepwise using MeOH–H_2O gradient (35:65, 70:30 and 100:0, *v*/*v*). Fraction 2 was further purified by reverse-phase semi-preparative HPLC (90% CH_3CN–H_2O containing 0.1% formic acid, 3 mL/min) to yield **9** (2.1 mg), **10** (1.2 mg) and **11** (5.0 mg).

*Purification of **12–15***

The culture medium extract (0.6 g) from the 3.5 L culture of AOS4 was subjected to ODS column chromatography on MPLC and eluted stepwise using MeOH–H_2O gradient (35:65, 60:40 and 100:0, *v*/*v*). Fraction 2 was further purified by reverse-phase semi-preparative HPLC (55% CH_3CN–H_2O containing 0.1% formic acid, 3 mL/min) to yield **12** (27.5 mg), **13** (3.6 mg), **14** (8.1 mg) and **15** (15.3 mg).

*Purification of **17–22***

The culture medium extract (1.03 g) from the 5 L culture of AOS5 was subjected to ODS column chromatography on MPLC and eluted stepwise using MeOH–H_2O gradient (30:70, 60:40 and 100:0, *v*/*v*). Fraction 2 was further purified by reverse-phase semi-preparative HPLC (45% CH_3CN–H_2O containing 0.1% formic acid, 3 mL/min) to yield **17** (28.0 mg), **18** (17 mg), **19** (7.0 mg), **20** (98.0 mg), **21** (20.0 mg) and **22** (10.0 mg).

*Purification of **23–25***

The culture medium extract (0.52 g) from the 2.5 L culture of AOS6 was subjected to ODS column chromatography on MPLC and eluted stepwise using MeOH–H_2O gradient (35:75, 70:30 and 100:0, *v*/*v*). Fraction 2 was further purified by reverse-phase semi-preparative

HPLC (70% $CH_3CN–H_2O$ containing 0.1% formic acid, 3 mL/min) to yield **23** (47.0 mg), **24** (4.0 mg) and **25** (1.5 mg).

*Purification of **26***

The culture medium extract (0.8 g) from the 3 L culture of AOS7 was subjected to ODS column chromatography on MPLC and eluted stepwise using $MeOH–H_2O$ gradient (35:65, 70:30 and 100:0, *v*/*v*). Fraction 2 was further purified by reverse-phase semi-preparative HPLC (70% $CH_3CN–H_2O$ containing 0.1% formic acid, 3 mL/min) to yield **26** (47.0 mg).

*Purification of **29***

The culture medium extract (0.55 g) from the 3 L culture of AOS8 was subjected to ODS column chromatography on MPLC and eluted stepwise using $MeOH–H_2O$ gradient (40:60, 70:30 and 100:0, *v*/*v*). Fraction 2 was further purified by reverse-phase semi-preparative HPLC (70% $CH_3CN–H_2O$ containing 0.1% formic acid, 3 mL/min) to yield **29** (14.0 mg).

*Purification of **30–34***

The culture medium extract (0.67 g) from 4 L culture of AOS9 was subjected to ODS column chromatography on MPLC and eluted stepwise using $MeOH–H_2O$ gradient (40:60, 70:30 and 100:0, *v*/*v*). Fraction 2 was further purified by reverse-phase semi-preparative HPLC (80% $MeOH–H_2O$ containing 0.1% formic acid, 3 mL/min) to yield **30** (1.8 mg), **31** (12.0 mg), **32** (2.0 mg), **33** (5.0 mg) and **34** (6.4 mg).

*Purification of **35–40***

The culture medium extract (1.05 g) from the 5 L culture of AOS10 was subjected to ODS column chromatography on MPLC and eluted stepwise using $MeOH–H_2O$ gradient (40:60, 60:40, 70:30 and 100:0, *v*/*v*). Fractions 2 and 3 were further purified by reverse-phase semi-preparative HPLC (42% $CH_3CN–H_2O$ containing 0.1% formic acid, 3 mL/min) to yield **35** (3.1 mg), **36** (7.7 mg), **37** (7.0 mg), **38** (3.0 mg), **39** (1.4 mg) and **40** (25.0 mg).

*Purification of **41–43***

The culture medium extract (0.83 g) from the 4 L culture of AOS11 was subjected to ODS column chromatography on MPLC and eluted stepwise using $MeOH–H_2O$ gradient (35:65, 50:50, 70:30 and 100:0, *v*/*v*). Fraction 3 was further purified by reverse-phase semi-preparative HPLC (60% $CH_3CN–H_2O$ containing 0.1% formic acid, 3 mL/min) to yield **41** (2.0 mg), **42** (1.1 mg) and **43** (3.0 mg).

*Purification of **44–46***

The culture medium extract (0.93 g) from 4 L culture of AOS12 was subjected to ODS column chromatography on MPLC and eluted stepwise using $MeOH–H_2O$ gradient (35:65, 55:45, 70:30 and 100:0, *v*/*v*). Fraction 3 was further purified by reverse-phase semi-preparative HPLC (60% CH_3CN–H_2O containing 0.1% formic acid, 3 mL/min) to yield **44** (3.0 mg), **45** (1.1 mg) and **46** (5.0 mg).

*Purification of **47–49***

The culture medium extract (0.82 g) from the 3.5 L culture of AOS13 was subjected to ODS column chromatography on MPLC and eluted stepwise using MeOH–H_2O gradient (35:65, 70:30 and 100:0, *v*/*v*). Fraction 2 was further purified by reverse-phase semi-preparative HPLC (37% CH_3CN–H_2O containing 0.1% formic acid, 3 mL/min) to yield **47** (12.0 mg), **48** (38.0 mg) and **49** (11.0 mg).

*Purification of **50–52***

The culture medium extract (0.91 g) from the 5 L culture of AOS14 was subjected to ODS column chromatography on MPLC and eluted stepwise using MeOH–H_2O gradient (45:55, 55:45, 65:35, 75:25 and 100:0, *v*/*v*). Fractions 3 and 4 were further purified by reverse-phase semi-preparative HPLC (42% CH_3CN–H_2O containing 0.1% formic acid, 3 mL/min) to yield **50** (6.3 mg), **51** (10.4 mg) and **52** (3.5 mg).

*Purification of **55–57***

The culture medium extract (0.88 g) from the 5 L culture of AOS15 was subjected to ODS column chromatography on MPLC and eluted stepwise using MeOH–H_2O gradient (40:60, 60:40, 70:30 and 100:0, *v*/*v*). Fraction 3 was further purified by reverse-phase semi-preparative HPLC (40% CH_3CN–H_2O containing 0.1% formic acid, 3 mL/min) to yield **55** (15.3 mg), **56** (13.0 mg) and **57** (6.3 mg).

*Purification of **58** and **59***

The culture medium extract (0.83 g) from the 5 L culture of AOS16 was subjected to ODS column chromatography on MPLC and eluted stepwise using MeOH–H_2O gradient (50:50, 60:40, 70:30 and 100:0, *v*/*v*). Fractions 2 and 3 were further purified by reverse-phase semi-preparative HPLC (50% CH_3CN–H_2O containing 0.1% formic acid, 3 mL/min) to yield **58** (33.5 mg) and **59** (7.5 mg).

*Purification of **60***

The culture medium extract (1.0 g) from the 5 L culture of AOS17 was subjected to ODS column chromatography on MPLC and eluted stepwise using MeOH–H_2O gradient (50:50, 70:30 and 100:0, *v*/*v*). Fraction 2 was further purified by reverse-phase semi-preparative HPLC (60% CH_3CN–H_2O containing 0.1% formic acid, 3 mL/min) to yield **60** (80.0 mg).

*Purification of **61***

The culture medium extract (1.1 g) from the 5 L culture of AOS18 was subjected to ODS column chromatography on MPLC and eluted stepwise using MeOH–H_2O gradient (35:65, 50:50, 70:30 and 100:0, *v*/*v*). Fraction 3 was further purified by reverse-phase semi-preparative HPLC (75% CH_3CN–H_2O containing 0.1% formic acid, 3 mL/min) to yield **61** (35.0 mg).

Purification of ***37****,* ***38*** *and* ***62***

The culture medium extract (1.04 g) from the 4 L culture of AOS19 was subjected to ODS column chromatography on MPLC and eluted stepwise using MeOH–H_2O gradient (35:65, 50:50, 60:40, 70:30 and 100:0, *v*/*v*). Fraction 3 was further purified by reverse-phase semi-preparative HPLC (40% CH_3CN–H_2O containing 0.1% formic acid, 3 mL/min) to yield **37** (7.0 mg), **38** (3.0 mg) and **62** (1.2 mg).

Purification of ***63***

The culture medium extract (1.04 g) from the 4 L culture of AOS20 was subjected to ODS column chromatography on MPLC and eluted stepwise using MeOH–H_2O gradient (50:50, 60:40, 70:30, 80:20 and 100:0, *v*/*v*). Fraction 4 was further purified by reverse-phase semi-preparative HPLC (60% CH_3CN–H_2O containing 0.1% formic acid, 3 mL/min) to yield **63** (6.0 mg).

Purification of ***64–66***

The culture medium extract (1.2 g) from the 10 L culture of AOS23 was subjected to ODS column chromatography on MPLC and eluted stepwise using MeOH–H_2O gradient (50:50, 60:40, 70:30 and 100:0, *v*/*v*). Fraction 3 was further purified by reverse-phase semi-preparative HPLC (60% CH_3CN–H_2O containing 0.1% formic acid, 3 mL/min) to yield **64** (3.4 mg), **65** (3.8 mg) and **66** (10.0 mg).

Purification of ***67***

The culture medium extract (0.89 g) from the 5 L culture of AOS24 was subjected to ODS column chromatography on MPLC and eluted stepwise using MeOH–H_2O gradient (50:50, 70:30 and 100:0, *v*/*v*). Fraction 2 was further purified by reverse-phase semi-preparative HPLC (45% CH_3CN–H_2O containing 0.1% formic acid, 3 mL/min) to yield **67** (10.0 mg).

Purification of ***68*** *and* ***69***

The culture medium extract (1.03 g) from 5 L culture of AOS26 was subjected to MPLC on ODS column chromatography and eluted stepwise using MeOH–H_2O gradient (50:50, 70:30 and 100:0, *v*/*v*). Fraction 2 was further purified by reverse-phase semi-preparative HPLC (45% CH_3CN–H_2O containing 0.1% formic acid, 3 mL/min) to yield **68** (10.0 mg) and **69** (1.2 mg).

Structural characterization

Compound **5**: white powder; $[\alpha]_D^{27}$ +7.80 (*c* 5.67, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 206 nm (4.09); IR (KBr) ν_{max} 3437, 2971, 2949, 2871, 1716, 1666, 1440, 1374, 1254, 1019 cm^{-1};

HRESIMS (positive) *m/z* 513.3212 $[M + H]^+$ (Calcd. for $C_{31}H_{45}O_6$, 513.3216), see Fig. S3A; NMR spectra, see Fig. S3B–H; NMR data, see Table S3; **5** is identified as 16*β*-acetyloxy-11*α*-hydroxy-29-norprotosta-1,17(20)*Z*,24-trien-3-one-21-oic acid.

Compound **6**: white powder; $[\alpha]_D^{22}$ +54.9 (*c* 0.59, CH_3OH); UV (CH_3OH) λ_{max} (log *ε*) 204 nm (3.78); IR (KBr) ν_{max} 3370, 3026, 2970, 2923, 2866, 1711, 1453, 1379, 1265, 1106 cm^{-1}. HRESIMS (positive) *m/z* 439.3209 $[M + H – CH_3COOH]^+$ (Calcd. for $C_{29}H_{43}O_3$, 439.3212), see Fig. S4A; NMR spectra, see Fig. S4B–H; NMR data, see Table S4; **6** is identified as 16*β*-acetyloxy-3*α*-hydroxy-29-norprotosta-1,17(20)*Z*,24-trien-21-oic acid.

Compound **9**: white powder, $[\alpha]_D^{26}$ +56.3 (*c* 0.77, CH_2Cl_2); UV (CH_3OH) λ_{max} (log *ε*) 205 nm (4.32); IR (KBr) ν_{max} 3503, 2955, 2921, 2852, 1716, 1672, 1554, 1542, 1456, 1374, 1252, 1030 cm^{-1}; HRESIMS (positive) *m/z* 551.2975 $[M + Na]^+$ (Calcd. for $C_{31}H_{44}O_7Na$, 551.2985), see Fig. S5A; NMR spectra, see Fig. S5B–H; NMR data, see Table S5; **9** is identified as 16*β*-acetyloxy-6*α*,7*β*-dihydroxy-29-norprotosta-1,17(20)*Z*,24-trien-3-one-21-oic acid.

Compound **10**: white powder; $[\alpha]_D^{26}$ +42.6 (*c* 0.47, CH_3OH); UV (CH_3OH) λ_{max} (log *ε*) 204 nm (3.75); IR (KBr) ν_{max} 3446, 2921, 2853, 1719, 1671, 1454, 1375, 1250, 1028 cm^{-1}; HRESIMS (positive) *m/z* 513.3224 $[M + H]^+$ (Calcd. for $C_{31}H_{45}O_6$, 513.3216), see Fig. S6A; NMR spectra, see Fig. S6B–H; NMR data, see Table S6; **10** is identified as 16*β*-acetyloxy-6*α*-hydroxy-29-norprotosta-1,17(20)*Z*,24-trien-3-one-21-oic acid.

Compound **11**: white powder; $[\alpha]_D^{26}$ +31.0 (*c* 0.98, CH_3OH); UV (CH_3OH) λ_{max} (log *ε*) 204 nm (4.44); IR (KBr) ν_{max} 3423, 2973, 2938, 2876, 1715, 1669, 1453, 1376, 1254, 1141, 1028 cm^{-1}; HRESIMS (positive) *m/z* 513.3211 $[M + H]^+$ (Calcd. for $C_{31}H_{45}O_6$, 513.3216), see Fig. S7A; NMR spectra, see Fig. S7B–H; NMR data, see Table S7; **11** is identified as 16*β*-acetyloxy-7*β*-hydroxy-29-norprotosta-1,17(20)*Z*,24-trien-3-one-21-oic acid.

Compound **12**: white powder; $[\alpha]_D^{22}$ +56.3 (*c* 1.82, CH_3OH); UV (CH_3OH) λ_{max} (log *ε*) 205 nm (3.89); IR (KBr) ν_{max} 3484, 2968, 2941, 2886, 1711, 1454, 1379, 1263, 1182, 1153, 1106, 1031 cm^{-1}; HRESIMS (positive) *m/z* 569.3099 $[M + Na]^+$ (Calcd. for $C_{31}H_{46}O_8Na$, 569.3090), see Fig. S8A; NMR spectra, see Fig. S8B–H; NMR data, see Table S8; **12** is identified as 16*β*-acetyloxy-6*α*,7*β*,11*α*-trihydroxy-29-norprotosta-17(20)*Z*,24-dien-3-one-21-oic acid.

Compound **13**: white powder; $[\alpha]_D^{23}$ +15.7 (*c* 0.54, CH_3OH); UV (CH_3OH) λ_{max} (log *ε*) 204 nm (3.91); IR (KBr) ν_{max} 3450, 2940, 2876, 1714, 1551, 1447, 1378, 1263, 1184, 1151, 1026 cm^{-1}; HRESIMS (positive) *m/z* 555.3290 $[M + Na]^+$ (Calcd. for $C_{31}H_{48}O_7Na$, 555.3298), see Fig. S9A; NMR spectra, see Fig. S9B–H; NMR data, see Table S9; **13** is identified as

16β-acetyloxy-3β,7β,11α-trihydroxy-29-norprotosta-17(20)*Z*,24-dien-21-oic acid.

Compound **14**: white powder; $[\alpha]_D^{23}$ +48.6 (*c* 0.37, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 205 nm (3.97); IR (KBr) ν_{max} 3441, 2970, 2939, 2883, 1703, 1649, 1383, 1261, 1019 cm^{-1}; HRESIMS (positive) *m*/*z* 553.3136 [M + Na]$^+$ (Calcd. for $C_{31}H_{46}O_7Na$, 553.3141), see Fig. S10A; NMR spectra, see Fig. S10B–H; NMR data, see Table S10; **14** is identified as 16β-acetyloxy-6α,11α-dihydroxy-29-norprotosta-17(20)*Z*,24-dien-3-one-21-oic acid.

Compound **15**: white powder; $[\alpha]_D^{23}$ +22.4 (*c* 0.62, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 204 nm (3.88); IR (KBr) ν_{max} 3500, 2966, 2941, 2880, 1703, 1557, 1452, 1378, 1262, 1194, 1150, 1105, 1031 cm^{-1}; HRESIMS (positive) *m*/*z* 553.3130 [M + Na]$^+$ (Calcd. for $C_{31}H_{46}O_7Na$, 553.3141), see Fig. S11A; NMR spectra, see Fig. S11B–H; NMR data, see Table S11; **15** is identified as 16β-acetyloxy-7β,11α-dihydroxy-29-norprotosta-17(20)*Z*,24-dien-3-one-21-oic acid.

Compound **17**: white powder; $[\alpha]_D^{24}$ –38.5 (*c* 0.55, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 204 nm (3.90); IR (KBr) ν_{max} 3444, 2980, 2936, 2871, 1712, 1650, 1454, 1440, 1377, 1263, 1182, 1153, 1101, 1033 cm^{-1}; HRESIMS (positive) *m*/*z* 569.3085 [M + Na]$^+$ (Calcd. for $C_{31}H_{46}O_8Na$, 569.3090), see Fig. S12A; NMR spectra, see Fig. S12B–H; NMR data, see Table S12; **17** is identified as 16β-acetyloxy-3β,6β,11α-trihydroxy-29-norprotosta-17(20)*Z*,24-dien-7-one-21-oic acid.

Compound **18**: white powder; $[\alpha]_D^{25}$ –10.4 (*c* 5.08, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 204 nm (3.99); IR (KBr) ν_{max} 3451, 2961, 2934, 2869, 1716, 1444, 1377, 1264, 1175, 1137, 1062, 1038 cm^{-1}; HRESIMS (positive) *m*/*z* 555.3280 [M + Na]$^+$ (Calcd. for $C_{31}H_{48}O_7Na$, 555.3298), see Fig. S13A; NMR spectra, see Fig. S13B–H; NMR data, see Table S13; **18** is identified as 16β-acetyloxy-3β,7α,11α-trihydroxy-29-norprotosta-17(20)*Z*,24-dien-21-oic acid.

Compound 1**9**: white powder; $[\alpha]_D^{22}$ –24.3 (*c* 0.45, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 204 nm (3.86); IR (KBr) ν_{max} 3439, 2952, 2930, 2871, 1707, 1557, 1438, 1425, 1378, 1266, 1188, 1144, 1078, 1054, 1022 cm^{-1}; HRESIMS (positive) *m*/*z* 553.3141 [M + Na]$^+$ (Calcd. for $C_{31}H_{46}O_7Na$, 553.3141), see Fig. S14A; NMR spectra, see Fig. S14B–H; NMR data, see Table S14; **19** is identified as 16β-acetyloxy-3β,11α-dihydroxy-29-norprotosta-17(20)*Z*,24-dien-7-one-21-oic acid.

Compound **20**: white powder; $[\alpha]_D^{22}$ –29.1 (*c* 0.40, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 205 nm (3.96); IR (KBr) ν_{max} 3472, 2973, 1697, 1457, 1375, 1263, 1185, 1048, 1107, 1069, 1035 cm^{-1}; HRESIMS (positive) *m*/*z* 567.2930 [M + Na]$^+$ (Calcd. for $C_{31}H_{44}O_8Na$, 567.2934), see Fig. S15A; NMR spectra, see Fig. S15B–H; NMR data, see Table S15; **20** is identified as

16β-acetyloxy-6β,11α-dihydroxy-29-norprotosta-17(20)Z,24-dien-3,7-dione-21-oic acid.

Compound **21**: white powder; $[\alpha]_{D}^{22}$ –12.0 (c 1.37, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 206 nm (3.80); IR (KBr) ν_{max} 3502, 2969, 2938, 2886, 1703, 1444, 1378, 1260, 1177, 1147, 1066, 1036, 1010 cm^{-1}; HRESIMS (positive) m/z 553.3130 $[M + Na]^+$, (Calcd. for $C_{31}H_{46}O_7Na$, 553.3141), see Fig. S16A; NMR spectra, see Fig. S16B–H; NMR data, see Table S16; **21** is identified as 16β-acetyloxy-7α,11α-dihydroxy-29-norprotosta-17(20)Z,24-dien-3-one-21-oic acid.

Compound **22**: white powder; $[\alpha]_{D}^{28}$ –20.7 (c 5.08, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 207 nm (3.93); IR (KBr) ν_{max} 3464, 2972, 1708, 1455, 1378, 1258, 1196, 1147, 1071, 1038 cm^{-1}; HRESIMS (positive) m/z 551.2984 $[M + Na]^+$, (Calcd. for $C_{31}H_{44}O_7Na$, 551.2985), see Fig. S17A; NMR spectra, see Fig. S17B–H; NMR data, see Table S17; **22** is identified as 16β-acetyloxy-11α-hydroxy-29-norprotosta-17(20)Z,24-dien-3,7-dione-21-oic acid.

Compound **23**: white powder; $[\alpha]_{D}^{24}$ –50.5 (c 0.60, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 205 nm (3.83); IR (KBr) ν_{max} 3445, 2975, 2938, 2874, 1714, 1467, 1376, 1259, 1158, 1074, 1030, 1000 cm^{-1}; HRESIMS (positive) m/z 553.3129 $[M + Na]^+$ (Calcd. for $C_{31}H_{46}O_7Na$, 553.3141), see Fig. S18A; NMR spectra, see Fig. S18B–H; NMR data, see Table S18; **23** is identified as 16β-acetyloxy-3α,6β-dihydroxy-29-norprotosta-17(20)Z,24-dien-7-one-21-oic acid.

Compound **24**: white powder; $[\alpha]_{D}^{26}$ –26.5 (c 0.17, CH_2Cl_2); UV (CH_3OH) λ_{max} (log ε) 204 nm (4.52); IR (KBr) ν_{max} 3121, 2951, 2870, 1713, 1447, 1399, 1265, 1140 cm^{-1}; HRESIMS (positive) m/z 539.3366 $[M + Na]^+$, (Calcd. for $C_{31}H_{48}O_6Na$, 539.3349), see Fig. S19A; NMR spectra, see Fig. S19B–H; NMR data, see Table S19; **24** is identified as 16β-acetyloxy-3α,7α-dihydroxy-29-norprotosta-17(20)Z,24-dien-21-oic acid.

Compound **25**: white powder; $[\alpha]_{D}^{26}$ –30.8 (c 0.50, CH_2Cl_2); UV (CH_3OH) λ_{max} (log ε) 204 nm (3.75); IR (KBr) ν_{max} 3404, 2980, 2963, 2934, 2872, 1741, 1700, 1678,1443, 1376, 1245, 1177, 1145, 1028 cm^{-1}; HRESIMS (positive) m/z 537.3196 $[M + Na]^+$, (Calcd. for $C_{31}H_{46}O_6Na$, 537.3192), see Fig. S20A; NMR spectra, see Fig. S20B–H; NMR data, see Table S20; **25** is identified as 16β-acetyloxy-3α-hydroxy-29-norprotosta-17(20)Z,24-dien-7-one-21-oic acid

Compound **26**: white powder; $[\alpha]_{D}^{26}$ –47.1 (c 1.25, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 204 nm (3.97), 232 nm (3.99); IR (KBr) ν_{max} 3447, 2971, 2928, 2855, 1712, 1666, 1456, 1377, 1257, 1034 cm^{-1}; HRESIMS (positive) m/z 543.2949 $[M + H]^+$ (Calcd. for $C_{31}H_{43}O_8$, 543.2958), see Fig. S21A; NMR spectra, see Fig. S21B–H; NMR data, see Table S21; **26** is identified as 16β-acetyloxy-6β,11α-dihydroxy-29-norprotosta-1,17(20)Z,24-trien-3,7-dione-21-oic acid.

Compound **29**: white powder; $[\alpha]_D^{26}$ –96.0 (*c* 0.32, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 204 nm (4.13); IR (KBr) ν_{max} 3550, 3024, 2970, 2955, 2929, 2897, 2871, 1723, 1457, 1376, 1254, 1175, 1152, 1109, 1087, 1059, 1033 cm^{-1}; HRESIMS (positive) *m*/*z* 497.3270 $[M + H - H_2O]^+$ (Calcd. for $C_{31}H_{45}O_5$, 497.3267), see Fig. S22A; NMR spectra, see Fig. S22B–H; NMR data, see Table S22; **29** is identified as 16*β*-acetyloxy-3*α*,11*α*-dihydroxy-29-norprotosta-1,17(20)*Z*,24-trien-21-oic acid.

Compound **30**: white powder; $[\alpha]_D^{26}$ –117.7 (*c* 0.23, CH_2Cl_2); UV (CH_3OH) λ_{max} (log ε) 204 nm (3.88); IR (KBr) ν_{max} 3417, 2959, 2931, 2876, 1712, 1453, 1377, 1258, 1205, 1142, 1035 cm^{-1}; HRESIMS (positive) *m*/*z* 551.2980 $[M + Na]^+$ (Calcd. for $C_{31}H_{44}O_7Na$, 551.2985), see Fig. S23A; NMR spectra, see Fig. S23B–H; NMR data, see Table S23; **30** is identified as 16*β*-acetyloxy-3*α*,6*β*-dihydroxy-29-norprotosta-1,17(20)*Z*,24-trien-7-one-21-oic acid.

Compound **31**: white powder; HRESIMS (positive) *m*/*z* 513.3204 $[M + H]^+$ (Calcd. for $C_{31}H_{45}O_6$, 513.3216), see Fig. S24A; NMR spectra, see Fig. S24 B–H; NMR data, see Table S24; **31** is identified as 16*β*-acetyloxy-7*α*-hydroxy-29-norprotosta-1,17(20)*Z*,24-trien-3-one-21-oic acid (Maunakeanolic acid A).

Compound **32**: white powder; $[\alpha]_D^{26}$–36.9 (*c* 0.42, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 204 nm (3.95); IR (KBr) ν_{max} 3443, 2965, 2932, 2867, 1718, 1451, 1376, 1261, 1036 cm^{-1}; HRESIMS (positive) *m*/*z* 537.3209 $[M + Na]^+$ (Calcd. for $C_{31}H_{46}O_6Na$, 537.3192), see Fig. S25A; NMR spectra, see Fig. S25B–H; NMR data, see Table S25; **32** is identified as 16*β*-acetyloxy-3*α*,7*α*-dihydroxy-29-norprotosta-1,17(20)*Z*,24-trien-21-oic acid.

Compound **33**: white powder; $[\alpha]_D^{26}$ +39.2 (*c* 0.53, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 204 nm (4.11), 231 nm (4.14); IR (KBr) ν_{max} 3423, 2976, 2929, 2870, 1731, 1704, 1669, 1445, 1400, 1380, 1244, 1190, 1143, 1030 cm^{-1}; HRESIMS (positive) *m*/*z* 533.2862 $[M + Na]^+$ (Calcd. for $C_{31}H_{42}O_6Na$, 533.2879), see Fig. S26A; NMR spectra, see Fig. S26B–H; NMR data, see Table S26; **33** is identified as 16*β*-acetyloxy-29-norprotosta-1,17(20)*Z*,24-trien-3,7-dione-21-oic acid.

Compound **34**: white powder; $[\alpha]_D^{26}$ –100.1 (*c* 0.13, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 204 nm (3.90); IR (KBr) ν_{max} 3396, 2972, 2929, 2870, 1742, 1703, 1454, 1374, 1257, 1146, 1028 cm^{-1}; HRESIMS (positive) *m*/*z* 535.3053 $[M + Na]^+$ (Calcd. for $C_{31}H_{44}O_6Na$, 535.3036), see Fig. S27A; NMR spectra, see Fig. S27B–H; NMR data, see Table S27; **34** is identified as 16*β*-acetyloxy-3*α*-hydroxy-29-norprotosta-1,17(20)*Z*,24-trien-7-one-21-oic acid.

Compound **35**: white powder; $[\alpha]_D^{29}$ +121.7 (*c* 1.0, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 205 nm

(4.50); IR (KBr) ν_{max} 3353, 2967, 2932, 2873, 1714, 1542, 1456, 1433, 1382, 1267, 1077, 1033, 1017 cm^{-1}; HRESIMS (positive) *m/z* 545.3113 [M + H – H_2O]$^+$, (Calcd. for $C_{31}H_{45}O_8$, 545.3114), see Fig. S28A; NMR spectra, see Fig. S28B–H; NMR data, see Table S28; **35** is identified as 16*β*-acetyloxy-1*α*,6*α*,7*β*,11*α*-tetrahydroxy-29-norprotosta-17(20)*Z*,24-dien-3-one-21-oic acid.

Compound **36**: white powder; $[\alpha]_D^{29}$ +29.6 (*c* 0.7, CH_3OH); UV (CH_3OH) λ_{max} (log *ε*) 196 nm (4.88); IR (KBr) ν_{max} 3398, 2969, 2935, 2873, 1713, 1663, 1554, 1442, 1381, 1266, 1028 cm^{-1}; HRESIMS (positive) *m/z* 529.3177 [M + H]$^+$ (Calcd. for $C_{31}H_{45}O_7$, 529.3165), see Fig. S29A; NMR spectra, see Fig. S29B–H; NMR data, see Table S29; **36** is identified as 16*β*-acetyloxy-6*α*,11*α*-dihydroxy-29-norprotosta-1,17(20)*Z*,24-trien-3-one-21-oic acid.

Compound **37**: white powder; $[\alpha]_D^{29}$ +30.4 (*c* 2.57, CH_3OH); UV (CH_3OH) λ_{max} (log *ε*) 210 nm (4.02), 227 nm (4.01); IR (KBr) ν_{max} 2967, 2929, 2870, 1715, 1666, 1438, 1376, 1036, 1007; HRESIMS (positive) *m/z* 529.3165 [M + H]$^+$ (Calcd. for $C_{31}H_{45}O_7$, 529.3165), see Fig. S30A; NMR spectra, see Fig. S30B–H; NMR data, see Table S30; **37** is identified as 16*β*-acetyloxy-7*α*,11*α*-dihydroxy-29-norprotosta-1,17(20)*Z*,24-trien-3-one-21-oic acid.

Compound **38**: white powder; $[\alpha]_D^{29}$ +75.2 (*c* 0.93, CH_3OH); UV (CH_3OH) λ_{max} (log *ε*) 205 nm (3.96); IR (KBr) ν_{max} 3442, 2962, 2929, 2870, 1712, 1546, 1440, 1381, 1265, 1038, 1007; HRESIMS (positive) *m/z* 469.2958 [M + H – H_2O – CH_3COOH]$^+$ (Calcd. for $C_{29}H_{41}O_5$, 469.2954), see Fig. S31A; NMR spectra, see Fig. S31B–H; NMR data, see Table S31; **38** is identified as 16*β*-acetyloxy-1*α*,7*α*,11*α*-trihydroxy-29-norprotosta-17(20)*Z*,24-dien-3-one-21-oic acid.

Compound **39**: white powder; $[\alpha]_D^{29}$ –53.4 (*c* 0.47, CH_3OH); UV (CH_3OH) λ_{max} (log *ε*) 204 nm (4.35), 231 nm (4.21); IR (KBr) ν_{max} 3299, 2972, 2919, 2851, 1714, 1671, 1542, 1457, 1436, 1419, 1384, 1264, 1035 cm^{-1}; HRESIMS (positive) *m/z* 467.2789 [M + H – CH_3COOH]$^+$ (Calcd. for $C_{29}H_{39}O_5$, 467.2797), see Fig. S32A; NMR spectra, see Fig. S32B–H; NMR data, see Table S32; **39** is identified as 16*β*-acetyloxy-11*α*-hydroxy-29-norprotosta-1,17(20)*Z*,24-trien-3,7-dione-21-oic acid.

Compound **40**: white powder; $[\alpha]_D^{29}$ +13.1 (*c* 1.7, CH_3OH); UV (CH_3OH) λ_{max} (log *ε*) 206 nm (3.83); IR (KBr) ν_{max} 3485, 2968, 2932, 2870, 1713, 1455, 1379, 1260, 1165, 1029 cm^{-1}; HRESIMS (positive) *m/z* 469.2954 [M + H – H_2O – CH_3COOH]$^+$ (Calcd. for $C_{29}H_{41}O_5$, 469.2954), see Fig. S33A; NMR spectra, see Fig. S33B–H; NMR data, see Table S33; **40** is identified as 16*β*-acetyloxy-1*α*,7*β*,11*α*-trihydroxy-29-norprotosta-17(20)*Z*,24-dien-3-one-21-oic acid.

Compound **41**: white powder; $[\alpha]_{D}^{29}$ –7.9 (*c* 1.13, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 203 nm (4.05); IR (KBr) ν_{max} 2918, 2874, 2848, 1715, 1596, 1543, 1454, 1383, 1359, 1272, 1032 cm^{-1}; HRESIMS (positive) *m/z* 553.3124 $[M + Na]^+$ (Calcd. for $C_{31}H_{46}O_7Na$, 553.3141), see Fig. S34A; NMR spectra, see Fig. S34B–H; NMR data, see Table S34; **41** is identified as 16*β*-acetyloxy-3*α*,6*α*,7*β*-trihydroxy-29-norprotosta-1,17(20)*Z*,24-trien-21-oic acid.

Compound **42**: white powder; $[\alpha]_{D}^{27}$ –26.1 (*c* 0.67, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 203 nm (4.17); IR (KBr) ν_{max} 3439, 2952, 2933, 2871, 1714, 1649, 1442, 1377, 1268, 1021 cm^{-1}; HRESIMS (positive) *m/z* 495.3103 $[M + H – H_2O]^+$ (Calcd. for $C_{31}H_{43}O_5$, 495.3110), see Fig. S35A; NMR spectra, see Fig. S35B–H; NMR data, see Table S35; **42** is identified as 16*β*-acetyloxy-3*α*-hydroxy-29-norprotosta-1,17(20)*Z*,24-trien-6-one-21-oic acid.

Compound **43**: white powder; $[\alpha]_{D}^{29}$ –8.2 (*c* 1.67, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 203 nm (5.05); IR (KBr) ν_{max} 3515, 2942, 2870, 1713, 1450, 1379, 1269, 1026 cm^{-1}; HRESIMS (positive) *m/z* 537.3190 $[M + Na]^+$ (Calcd. for $C_{31}H_{46}O_6Na$, 537.3192), see Fig. S36A; NMR spectra, see Fig. S36B–H; NMR data, see Table S36; **43** is identified as 16*β*-acetyloxy-3α,7*β*-dihydroxy-29-norprotosta-1,17(20)*Z*,24-trien-21-oic acid.

Compound **44**: white powder; $[\alpha]_{D}^{26}$ +9.3 (*c* 1.23, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 206 nm (4.10), 231 nm (4.13); IR (KBr) ν_{max} 3449, 2963, 2933, 2877, 1731, 1675, 1564, 1455, 1376, 1251, 1034 cm^{-1}; HRESIMS (positive) *m/z* 593.3098 $[M + Na]^+$ (Calcd. for $C_{33}H_{46}O_8Na$, 593.3090), see Fig. S37A; NMR spectra, see Fig. S37B–H; NMR data, see Table S37; **44** is identified as 6*α*,16*β*-diacetyloxy-7*β*-hydroxy-29-norprotosta-1,17(20)*Z*,24-trien-3-one-21-oic acid.

Compound **45**: white powder; $[\alpha]_{D}^{26}$ +19.9 (*c* 7.3, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 204 nm (4.03), 230 nm (3.99); IR (KBr) ν_{max} 3463.5, 2959, 2932, 2876, 1730, 1676, 1454, 1375, 1249, 1141, 1029 cm^{-1}; HRESIMS (positive) *m/z* 593.3080 $[M + Na]^+$ (Calcd. for $C_{33}H_{46}O_8Na$, 593.3090), see Fig. S38A; NMR spectra, see Fig. S38B–H; NMR data, see Table S38; **45** is identified as 7*β*,16*β*-diacetyloxy-6*α*-hydroxy-29-norprotosta-1,17(20)*Z*,24-trien-3-one-21-oic acid.

Compound **46**: white powder; $[\alpha]_{D}^{26}$ +35.1 (*c* 0.87, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 204 nm (4.31), 229 nm (4.20); IR (KBr) ν_{max} 3418, 2959, 2934, 2870, 1731, 1676, 1454, 1245, 1029 cm^{-1}; HRESIMS (positive) *m/z* 577.3149 $[M + Na]^+$ (Calcd. for $C_{33}H_{46}O_7Na$, 577.3141), see Fig. S39A; NMR spectra, see Fig. S39B–H; NMR data, see Table S39; **46** is identified as 7*β*,16*β*-diacetyloxy-29-norprotosta-1,17(20)*Z*,24-trien-3-one-21-oic acid**.**

Compound **47**: white powder; $[\alpha]_{D}^{21}$ +19.3 (*c* 0.44, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 204 nm

(4.08); IR (KBr) ν_{max} 2961, 2934, 2877, 1716, 1653, 1635, 1558, 1454, 1377, 1266, 1179, 1147, 1024 cm^{-1}; HRESIMS (positive) *m*/*z* 571.3237 [M+ Na]$^+$ (Calcd. for $C_{31}H_{48}O_8Na$, 571.3247), see Fig. S40A; NMR spectra, see Fig. S40B–H; NMR data, see Table S40; **47** is identified as 16*β*-acetyloxy-3*α*,6*α*,7*β*,11*α*-tetrahydroxy-29-norprotosta-17(20)*Z*,24-dien-21-oic acid.

Compound **48**: white powder; $[\alpha]_D^{21}$ +10.3 (*c* 0.28, CH_3OH); UV (CH_3OH) λ_{max} (log *ε*) 204 nm (3.94); IR (KBr) ν_{max} 3454, 2971, 2935, 2879, 1718, 1446, 1380, 1260, 1145, 1060, 1022 cm^{-1}; HRESIMS (positive) *m*/*z* 533.3484 [M + H]$^+$ (Calcd. for $C_{31}H_{49}O_7$, 533.3478), see Fig. S41A; NMR spectra, see Fig. S41B–H; NMR data, see Table S41; **48** is identified as 16*β*-acetyloxy-3*α*,6*α*,11*α*-trihydroxy-29-norprotosta-17(20)*Z*,24-dien-21-oic acid.

Compound **49**: white powder, $[\alpha]_D^{21}$ 14.7 (*c* 0.19, CH_3OH); UV (CH_3OH) λ_{max} (log *ε*) 204 (3.54); IR (KBr) ν_{max} 3446, 2952, 2929, 2874, 1716, 1654, 1558, 1541, 1457, 1377, 1267, 1144, 1105, 1025, 973 cm^{-1}; HRESIMS (positive) *m*/*z* 533.3497 [M + H]$^+$ (Calcd. for $C_{31}H_{49}O_7$, 533.3478), see Fig. S42A; NMR spectra, see Fig. S42B–H; NMR data, see Table S42, **49** is identified as 16*β*-Acetyloxy-3*α*,7*β*,11*α*-trihydroxy-29-norprotosta-17(20)*Z*,24-dien-21-oic acid.

Compound **50**: white powder; $[\alpha]_D^{21}$ +20.9 (*c* 0.63, CH_2Cl_2); UV (CH_3OH) λ_{max} (log *ε*) 204 nm (4.09); IR (KBr) ν_{max} 3501, 2968, 2938, 2886, 1715, 1453, 1376, 1256, 1146, 1107, 1032 cm^{-1}; HRESIMS (positive) *m*/*z* 611.3185 [M + Na]$^+$ (Calcd. for $C_{33}H_{48}O_9Na$, 611.3196), see Fig. S43A; NMR spectra, see Fig. S43B–H; NMR data, see Table S43; **50** is identified as 7*β*,16*β*-diacetyloxy-6*α*,11*α*-dihydroxy-29-norprotosta-17(20)*Z*,24-dien-3-one-21-oic acid.

Compound **51**: white powder; $[\alpha]_D^{21}$ +65.2 (*c* 0.45, CH_3OH); UV (CH_3OH) λ_{max} (log *ε*) 205 nm (4.27); IR (KBr) ν_{max} 3484, 2969, 2943, 2886, 1713, 1456, 1440, 1377, 1257, 1032 cm^{-1}; HRESIMS (positive) *m*/*z* 611.3174 [M + Na]$^+$ (Calcd. for $C_{33}H_{48}O_9Na$, 611.3196), see Fig. S44A; NMR spectra, see Fig. S44B–H; NMR data, see Table S44; **51** is identified as 6*α*,16*β*-diacetyloxy-7*β*,11*α*-dihydroxy-29-norprotosta-17(20)*Z*,24-dien-3-one-21-oic acid.

Compound **52**: white powder; $[\alpha]_D^{21}$ +40.6 (*c* 0.42, CH_3OH); UV (CH_3OH) λ_{max} (log *ε*) 201 nm (3.99); IR (KBr) ν_{max} 3525, 2957, 2938, 2883, 1715, 1457, 1377, 1253, 1142, 1028 cm^{-1}; HRESIMS (positive) *m*/*z* 595.3248 [M + Na]$^+$ (Calcd. for $C_{33}H_{48}O_8Na$, 595.3247), see Fig. S45A; NMR spectra, see Fig. S45B–H; NMR data, see Table S45; **52** is identified as 6*α*,16*β*-diacetyloxy-11*α*-hydroxy-29-norprotosta-17(20)*Z*,24-dien-3-one-21-oic acid.

Compound **55**: white powder; HRESIMS (positive) *m*/*z* 569.3071 [M + Na]$^+$ (Calcd. for $C_{31}H_{46}O_8Na$, 569.3090), see Fig. S46A; NMR spectra, see Fig. S46B–H; NMR data, see

Table S46; **55** is identified as 16*β*-acetyloxy-3*α*,6*β*,11*α*-trihydroxy-29-norprotosta-17(20)*Z*,24-dien-7-one-21-oic acid (CAS Registry Number: 779980-64-2).

Compound **56**: white powder; HRESIMS (positive) *m*/*z* 533.3490 $[M + H]^+$ (Calcd. for $C_{31}H_{49}O_7$, 533.3478), see Fig. S47A; NMR spectra, see Fig. S47B–H; NMR data, see Table S47; **56** is identified as 16*β*-acetyloxy-3*α*,7*α*,11*α*-trihydroxy-29-norprotosta-17(20)*Z*,24-dien-21-oic acid (CAS Registry Number: 35805-38-0).

Compound **57**: white powder; HRESIMS (positive) *m*/*z* 531.3325 $[M + H]^+$ (Calcd. for $C_{31}H_{47}O_7$, 531.3322), see Fig. S48A; NMR spectra, see Fig. S48B–H; NMR data, see Table S48; **57** is identified as 16*β*-acetyloxy-3*α*,11*α*-dihydroxy-29-norprotosta-17(20)*Z*,24-dien-7-one-21-oic acid (CAS Registry Number: 764590-42-3).

Compound **58**: white powder; $[\alpha]_D^{26}$ –66.3 (*c* 2.67, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 204 nm (3.65); IR (KBr) ν_{max} 3445, 2950, 2930, 2870, 1718, 1652, 1455, 1442, 1375, 1261, 1233, 1154, 1032 cm^{-1}; HRESIMS (positive) *m*/*z* 609.3043 $[M + Na]^+$ (Calcd. for $C_{33}H_{46}O_9Na$, 609.3040), see Fig. S49A; NMR spectra, see Fig. S49B–H; NMR data, see Table S49; **58** is identified as 6*β*,16*β*-diacetyloxy-11*α*-hydroxy-29-norprotosta-17(20)Z,24-dien-3,7-dione-21-oic acid.

Compound **59**: white powder, $[\alpha]_D^{26}$ –85.6 (*c* 0.92, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 204 nm (4.07); IR (KBr) ν_{max} 3502, 2975, 2935, 2864, 1746, 1713, 1459, 1438, 1375, 1224, 1150, 1060, 1028 cm^{-1}; HRESIMS (positive) *m*/*z* 611.3185 $[M + Na]^+$ (Calcd. for $C_{33}H_{48}O_9Na$, 611.3196), see Fig. S50A; NMR spectra, see Fig. S50B–H; NMR data, see Table S50; **59** is identified as 6*β*,16*β*-diacetyloxy-3*β*,11*α*-dihydroxy-29-norprotosta-17(20)Z,24-dien-7-one-21-oic acid.

Compound **60**: white powder; $[\alpha]_D^{25}$ –74.7 (*c* 1.33, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 204 nm (3.95); IR (KBr) ν_{max} 3395, 2952, 2924, 2852, 1750, 1716, 1652, 1458, 1376, 1255, 1226, 1021 cm^{-1}; HRESIMS (positive) *m*/*z* 595.3240 $[M + Na]^+$ (Calcd. for $C_{33}H_{48}O_8Na$, 595.3247), see Fig. S51A; NMR spectra, see Fig. S51B–H; NMR data, see Table S51; **60** is identified as 6*β*,16*β*-diacetyloxy-3*α*-hydroxy-29-norprotosta-17(20)*Z*,24-dien-7-one-21-oic acid.

Compound **61**: white powder; $[\alpha]_D^{27}$ –89.0 (*c* 2.33,CH_3OH); UV (CH_3OH) λ_{max} (log ε) 204 nm (4.07), 231 nm (4.08); IR (KBr) ν_{max} 3546, 3468, 2977, 2941, 2883, 1752, 1725, 1699, 1663, 1457, 1374, 1252, 1214, 1033 cm^{-1}; HRESIMS (positive) *m*/*z* 585.3038 $[M + H]^+$ (Calcd. for

$C_{33}H_{45}O_9$, 585.3064), see Fig. S52A; NMR spectra, see Fig. S52B–H; NMR data, see Table S52; **61** is identified as 6*β*,16*β*-diacetyloxy-11*α*-hydroxy-29-norprotosta-1,17(20)Z,24-trien-3,7-dione-21-oic acid.

Compound **62**: white powder; $[\alpha]_D^{25}$ –41.3 (*c* 0.40, CH_3OH); UV (CH_3OH) λ_{max} (log *ε*) 201 nm (3.98); IR (KBr) ν_{max} 3315, 2964, 2929, 2879, 1711, 1593, 1456, 1433, 1382, 1266, 1034 cm^{-1}; HRESIMS (positive) *m*/*z* 567.2936 $[M + Na]^+$ (Calcd. for $C_{31}H_{44}O_8Na$, 567.2934), see Fig. S53A; NMR spectra, see Fig. S53B–H; NMR data, see Table S53; **62** is identified as 16*β*-acetyloxy-3*α*,6*β*,11*α*-trihydroxy-29-norprotosta-1,17(20)*Z*,24-trien-7-one-21-oic acid.

Compound **63**: white powder; $[\alpha]_D^{21}$ –148.3 (*c* 0.47, CH_3OH); UV (CH_3OH) λ_{max} (log *ε*) 203 nm (4.06); IR (KBr) ν_{max} 32970, 2925, 2882, 1751, 1712, 1454, 1374, 1226, 1036 cm^{-1}; HRESIMS (positive) *m*/*z* 571.3270 $[M + H]^+$ (Calcd. for $C_{33}H_{47}O_8$, 571.3271), see Fig. S54A; NMR spectra, see Figs. S54B–K and S61; NMR data, see Table S54; **63** is identified as 6*β*,16*β*-diacetyloxy-3*α*-hydroxy-29-norprotosta-1,17(20)*Z*,24-trien-7-one-21-oic acid.

Compound **64**: white powder; $[\alpha]_D^{21}$ –21.7 (*c* 1.27, CH_3OH); UV (CH_3OH) λ_{max} (log *ε*) 203 nm (4.00); IR (KBr) ν_{max} 3419, 2962, 2932, 2873, 1721, 1652, 1438, 1377, 1256, 1026 cm^{-1}; HRESIMS (positive) *m*/*z* 513.3210 $[M + H – CH_3COOH]^+$ (Calcd. for $C_{31}H_{45}O_6$, 513.3216), see Fig. S55A; NMR spectra, see Fig. S55B–H; NMR data, see Table S55; **64** is identified as 7*β*,16*β*-diacetyloxy-3*α*,6*α*-dihydroxy-29-norprotosta-1,17(20)*Z*,24-trien-21-oic acid.

Compound **65**: white powder; $[\alpha]_D^{27}$ +18.0 (*c* 2.13, CH_3OH); UV (CH_3OH) λ_{max} (log *ε*) 203 nm (4.08); IR (KBr) ν_{max} 3412, 2960, 2939, 2871, 1731, 1652, 1439, 1375, 1251, 1019 cm^{-1}; HRESIMS (positive) *m*/*z* 579.3308 $[M + Na]^+$ (Calcd. for $C_{33}H_{48}O_7Na$, 579.3298), see Fig. S56A; NMR spectra, see Fig. S56B–H; NMR data, see Table S56; **65** is identified as 6*α*,16*β*-diacetyloxy-3*α*-hydroxy-29-norprotosta-1,17(20)*Z*,24-trien-21-oic acid.

Compound **66**: white powder; $[\alpha]_D^{21}$ +41.2 (*c* 1.13, CH_3OH); UV (CH_3OH) λ_{max} (log *ε*) 205 nm (4.07), 231 nm (4.12); IR (KBr) ν_{max} 3444, 2977, 2936, 2873, 1734, 1674, 1439, 1375, 1250, 1025 cm^{-1}; HRESIMS (positive) *m*/*z* 555.3330 $[M + H]^+$ (Calcd. for $C_{33}H_{47}O_7$, 555.3322), see Fig. S57A; NMR spectra, see Fig. S57B–H; NMR data, see Table S57; **66** is identified as 6*α*,16*β*-diacetyloxy-29-norprotosta-1,17(20)*Z*,24-trien-3-one-3-one-21-oic acid.

Compound **67**: white powder; $[\alpha]_D^{29}$+27.6 (*c* 3.8, CH_3OH); UV (CH_3OH) λ_{max} (log *ε*) 206 nm (4.10); IR (KBr) ν_{max} 3485, 2952, 2936, 2885, 1719, 1441, 1378, 1261, 1141, 1025 cm^{-1}; HRESIMS (positive) *m*/*z* 597.3405 $[M + Na]^+$ (Calcd. for $C_{33}H_{50}O_8Na$, 597.3403), see Fig. S58A; NMR spectra, see Fig. S58B–H; NMR data, see Table S58; **67** is identified as 6*α*,16*β*-diacetyloxy-3*α*,11*α*-dihydroxy-29-norprotosta-17(20)Z,24-dien-21-oic acid.

Compound **68**: white powder; $[\alpha]_D^{26}$ –92.9 (*c* 0.38, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 204 nm (4.02); IR (KBr) ν_{max} 3482, 2958, 2935, 2883, 1719, 1440, 1376, 1230, 1144, 1066, 1023 cm^{-1}; HRESIMS (positive) *m*/*z* 611.3179 $[M + Na]^+$ (Calcd. for $C_{33}H_{48}O_9Na$, 611.3196), see Fig. S59A; NMR spectra, see Fig. S59B–H; NMR data, see Table S59; **68** is identified as 6*β*,16*β*-diacetyloxy-3*α*,11*α*-dihydroxy-29-norprotosta-17(20)*Z*,24-dien-7-one-21-oic acid.

Compound **69**: white powder; $[\alpha]_D^{26}$ –58.0 (*c* 0.8, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 203 nm (4.08); IR (KBr) ν_{max} 3413, 2960, 2929, 2879, 1717, 1648, 1436, 1383, 1263, 1232, 1057, 1019 cm^{-1}; HRESIMS (positive) *m*/*z* 609.3029 $[M + Na]^+$ (Calcd. for $C_{33}H_{46}O_9Na$, 609.3040), see Fig. S60A; NMR spectra, see Fig. S60B–H; NMR data, see Table S60; **69** is identified as 6*β*,16*β*-diacetyloxy-3*α*,11*α*-dihydroxy-29-norprotosta-1,17(20)*Z*,24-trien-7-one-21-oic acid.

Compound **81**: white powder; $[\alpha]_D^{28}$ +63.0 (*c* 4.3, CH_3OH); UV (CH_3OH) λ_{max} (log ε) 204 nm (4.10); IR (KBr) ν_{max} 3451.0, 3023, 2959, 2933, 2870, 1717, 1648, 1591, 1443, 1374, 1261, 1029, 1006 cm^{-1}; HRESIMS (positive) *m*/*z* 521.3245 $[M + Na]^+$ (Calcd. for $C_{31}H_{46}O_5Na$, 521.3243), see Fig. S61A; NMR spectra, see Fig. S61B–H; NMR data, see Table S61; **81** is identified as 16*β*-acetyloxy-3*β*-hydroxy-29-norprotosta-1,17(20)*Z*,24-trien-21-oic acid.

*Absolute configuration determination of **35**, **38** and **40***

As the relative configuration of C-1 of **35**, **38** and **40** cannot be determined *via* ROESY analysis, quantum chemical calculation of NMR shifts was employed. The flexible side chain of fusidane-type antibiotics can lead to more conformations, which has less impact on NMR shifts. Therefore, **35** was simplified as (1*S**,4*S**,5*S**,6*R**,7*R**,8*S**,9*S**,10*S**,11*R**,13*R**,14*S**,16*S**)-**35**-**A** and (1*R**,4*S**,5*S**,6*R**,7*R**,8*S**,9*S**,10*S**,11*R**,13*R**,14*S**,16*S**)-**35**-**B** (Fig. S63). The molecules of **35**-**A** and **35**-**B** were converted into SIMILES codes before their initial 3D structure were generated with CORINA version 3.4. Conformer databases were generated in CONFLEX version 7.0 using the MMFF94s force-field, with an energy window for acceptable conformers (ewindow) of 5 kcal/mol above the ground state, a maximum number of conformations per molecule (maxconfs) of 100, and an RMSD cutoff (rmsd) of 0.5 Å. Then each conformer of the acceptable conformers was optimized with the HF/6-31G(d) method in Gaussian09. Further optimization at the B3LYP/6-31G(d) level determined the dihedral angles. The optimized conformers (Table S63) were used for ^{13}C NMR shifts calculation, which was performed with Gaussian09 (mPW1PW91/6-31+G(d,p)). The solvent effect was taken into account by the polarizable-conductor calculation model (PCM, CD_3OD as the solvent). Computed chemical shifts were scaled empirically according to $\delta_{corr.} = \delta_{calcd.} \times$ slope

+ intercept, where $\delta_{calcd.}$ is the calculated chemical shift, and slope and intercept are the slope and intercept resulting from a regression calculation on a plot of $\delta_{calcd.}$ against $\delta_{exptl.}$[1]. The comparison was judged by R square (R^2) analysis, mean absolute error (MAE) and DP4+ probability[2] (Table S68). Finally, the relative configuration of **35** was determined as 1*S**,4*S**,5*S**,6*R**,7*R**,8*S**,9*S**,10*S**,11*R**,13*R**,14*S**,16*S**, and the absolute configuration was assigned as 1*S*,4*S*,5*S*,6*R*,7*R*,8*S*,9*S*,10*S*,11*R*,13*R*,14*S*,16*S*. Likewise, the optimized conformers (Table S64) were used for ^{13}C NMR shifts calculation, which was performed with Gaussian09 (mPW1PW91/6-311+G(d,p)) for **38**. The absolute configuration of **38** was assigned as 1*S*,4*S*,5*S*,7*R*,8*S*,9*S*,10*S*,11*R*,13*R*, 14*S*, 16*S* (Fig. S64, Tables S64 and S68). On the basis of comparision of ^{13}C chemical shifts between **38** and **40** (Table S66), the relative configuration of **40** was determined, and the absolute configuration of **40** was assigned as 1*S*,4*S*,5*S*,7*S*,8*S*,9*S*,10*S*,11*R*,13*R*,14*S*,16*S*.

Absolute configuration determination of ***6, 29, 30, 32, 34, 41–43, 63–65*** *and* ***69***

For compounds **6**, **29**, **30**, **32**, **34**, **41**–**43**, **63**–**65** and **69**, the relative configuration of C-3 cannot be determined *via* NOESY or coupling constants analysis. Therefore, we planned to perform chemical derivatization to obtain analogues bearing 3*α*-OH/the C1–C2 double bond and 3*β*-OH/the C1–C2 double bond. We added **7** (10.0 mg) to a stirred solution of $NaBH_4$ (5.0 mg) in Et_2O (10 mL) in an ice and water bath. Then the mixture was stirred in the dark at room temperature for 24 h. The solvent was removed under reduced pressure, and the residue was further purified by semi-preparative HPLC with isocratic elution of 80% CH_3CN–H_2O to give **6** (0.5 mg) and **81** (4.1 mg). According to ROESY analysis, the relative configuration of **81** was determined as 3*S**,4*S**,5*S**,8*S**,9*S**,10*S**,13*R**,14*S**,16*S**, and the absolute configuration of **81** was assigned as 3*S*,4*S*,5*S*,8*S*,9*S*,10*S*,13*R*,14*S*,16*S*. Therefore, the absolute configuration of **6**, the epimer of **81** at C-3, was assigned as 3*R*,4*S*,5*S*,8*S*,9*S*,10*S*,13*R*,14*S*,16*S*. And based on the coupling constants ($^3J_{H\text{-}3,\,H\text{-}4}$ = 4.4 Hz for 3*α*-OH, and $^3J_{H\text{-}3,\,H\text{-}4}$ = 7.9 Hz for 3*β*-OH), we determined that 3-OH in compounds **29**, **30**, **32**, **34**, **41**–**43**, **63**–**65** and **69** was *α*-oriented (Table. S69). Additionally, we also performed quantum chemical calculation of NMR shifts for **34** (CD_3OD as the solvent) and **42** ($CDCl_3$ as the solvent)[1,2], and the optimized conformers (Tables S62 and S65) were used for ^{13}C NMR shifts calculation, which was performed with Gaussian09 (mPW1PW91/6-31+G(d,p)). The results indicated that 3-OH in **34** and **42** was indeed *α*-oriented (Figs. S62 and S65, Table S67).

Supporting Figures

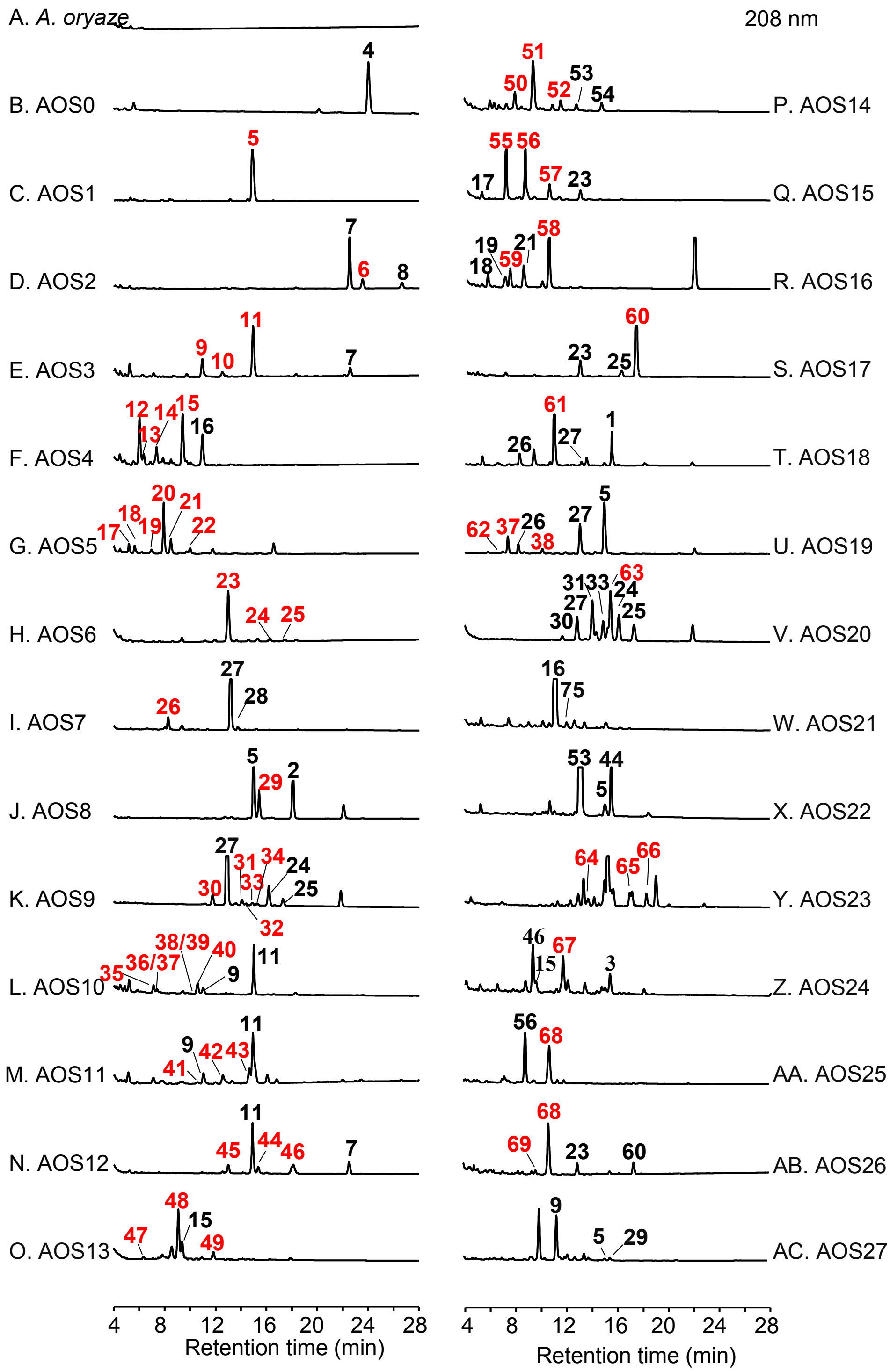
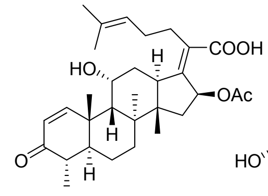


Figure S1 HPLC analysis of metabolites from *A. oryzae* transformants.

(A) *A. oryzae* NSAR1; (B) *A. oryzae* harboring *helA*, *helB1*, *helB2*, *helC*, *helB4* and *helD2* (AOS0); (C) AOS0 harboring *helE* and *fusB1* (AOS1); (D) AOS0 harboring *helE* and *fusC1* (AOS2); (E) AOS0 harboring *helE* and *cepB4* (AOS3); (F) AOS0 harboring *fusB1* and *cepB4* (AOS4); (G) AOS0 harboring *helB3* and *fusB1* (AOS5); (H) AOS0 harboring *helB3* and *fusC1* (AOS6); (I) AOS0 harboring *helE*, *fusB1* and *helB3* (AOS7); (J) AOS0 harboring *helE*, *fusB1* and *fusC1* (AOS8); (K) AOS0 harboring *helE*, *fusC1* and *helB3* (AOS9); (L) AOS0 harboring *helE*, *fusB1* and *cepB4* (AOS10); (M) AOS0 harboring *helE*, *fusC1* and *cepB4* (AOS11); (N) AOS0 harboring *helE*, *cepB4* and *cepD2* (AOS12); (O) AOS0 harboring *fusB1*, *cepB4* and *fusC1* (AOS13); (P) AOS0 harboring *fusB1*, *cepB4* and *cepD2* (AOS14); (Q) AOS0 harboring *helB3*, *fusB1* and *fusC1* (AOS15); (R)AOS0 harboring *helB3*, *fusB1* and *helD1* (AOS16); (S) AOS0 harboring *helB3*, *fusC1* and *helD1* (AOS17); (T) AOS0 harboring *helE*, *fusB1*, *helB3* and *helD1* (AOS18); (U) AOS0 harboring *helE*, *fusB1*, *helB3* and *fusC1* (AOS19); (V) AOS0 harboring *helE*, *fusC1*, *helB3* and *helD1* (AOS20); (W) AOS0 harboring *helE*, *fusB1*, *cepB4* and *fusC1* (AOS21); (X) AOS0 harboring *helE*, *fusB1*, *cepB4* and *cepD2* (AOS22); (Y) AOS0 harboring *helE*, *cepB4*, *cepD2* and *fusC1* (AOS23); (Z) AOS0 harboring *fusB1*, *fusC1*, *cepB4* and *cepD2* (AOS24); (AA) AOS0 harboring *fusB1*, *fusC1*, *helB3* and *helD1* (AOS25). (AB) AOS0 harboring *helE*, *fusB1*, *fusC1*, *helB3* and *helD1* (AOS26); (AC) AOS0 harboring *helE*, *fusB1*, *fusC1*, *cepB4* and *cepD2* (AOS27).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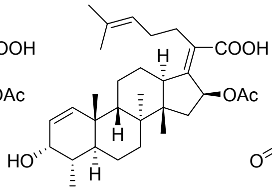
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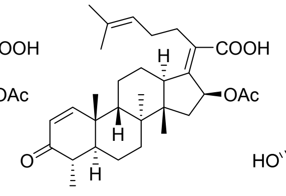
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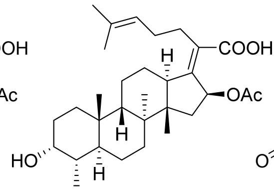
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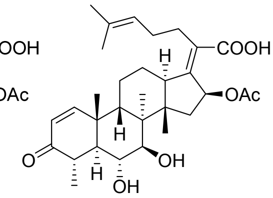
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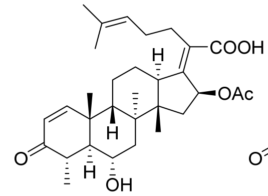
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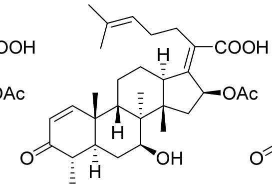
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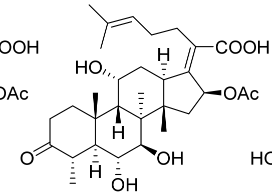
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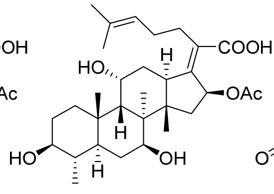
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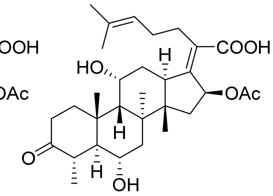
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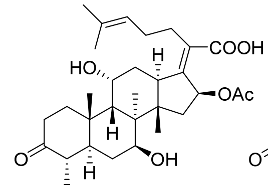
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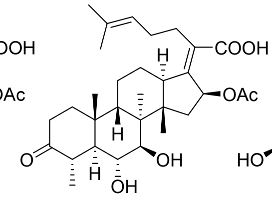
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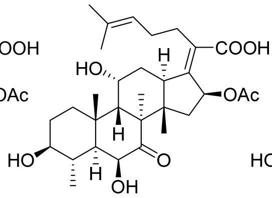
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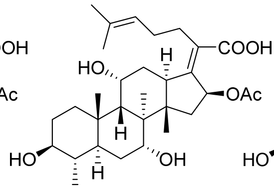
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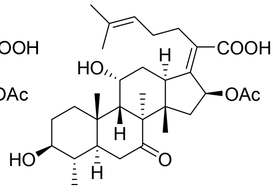
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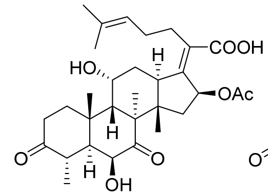
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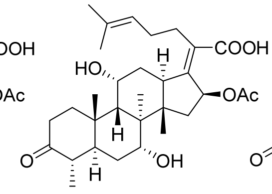
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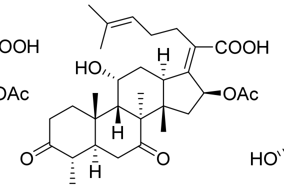
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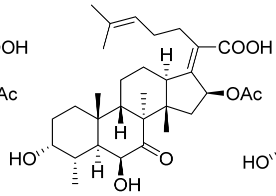
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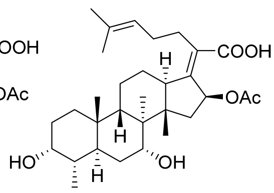
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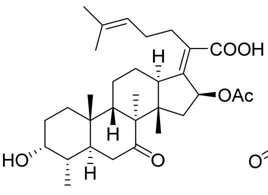
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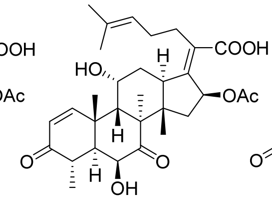
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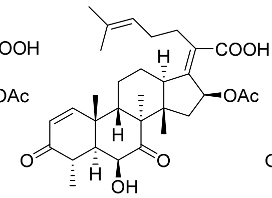
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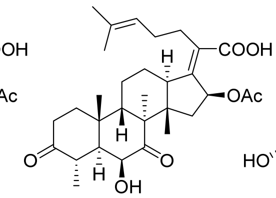
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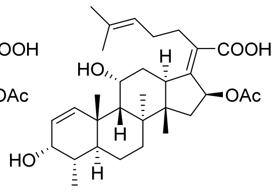
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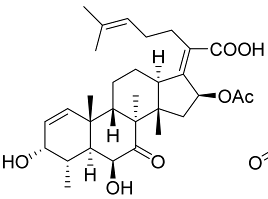
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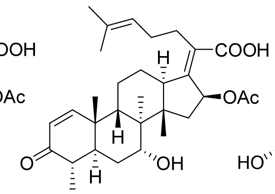
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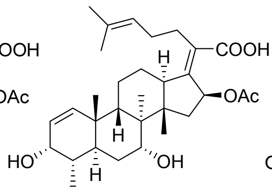
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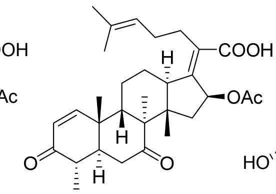
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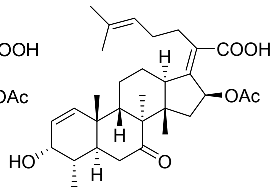
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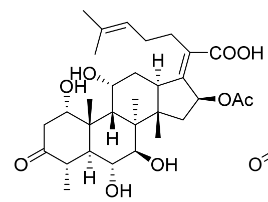
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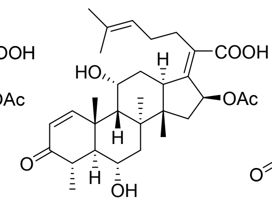
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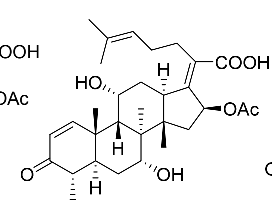
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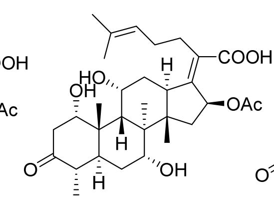
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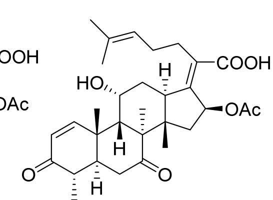
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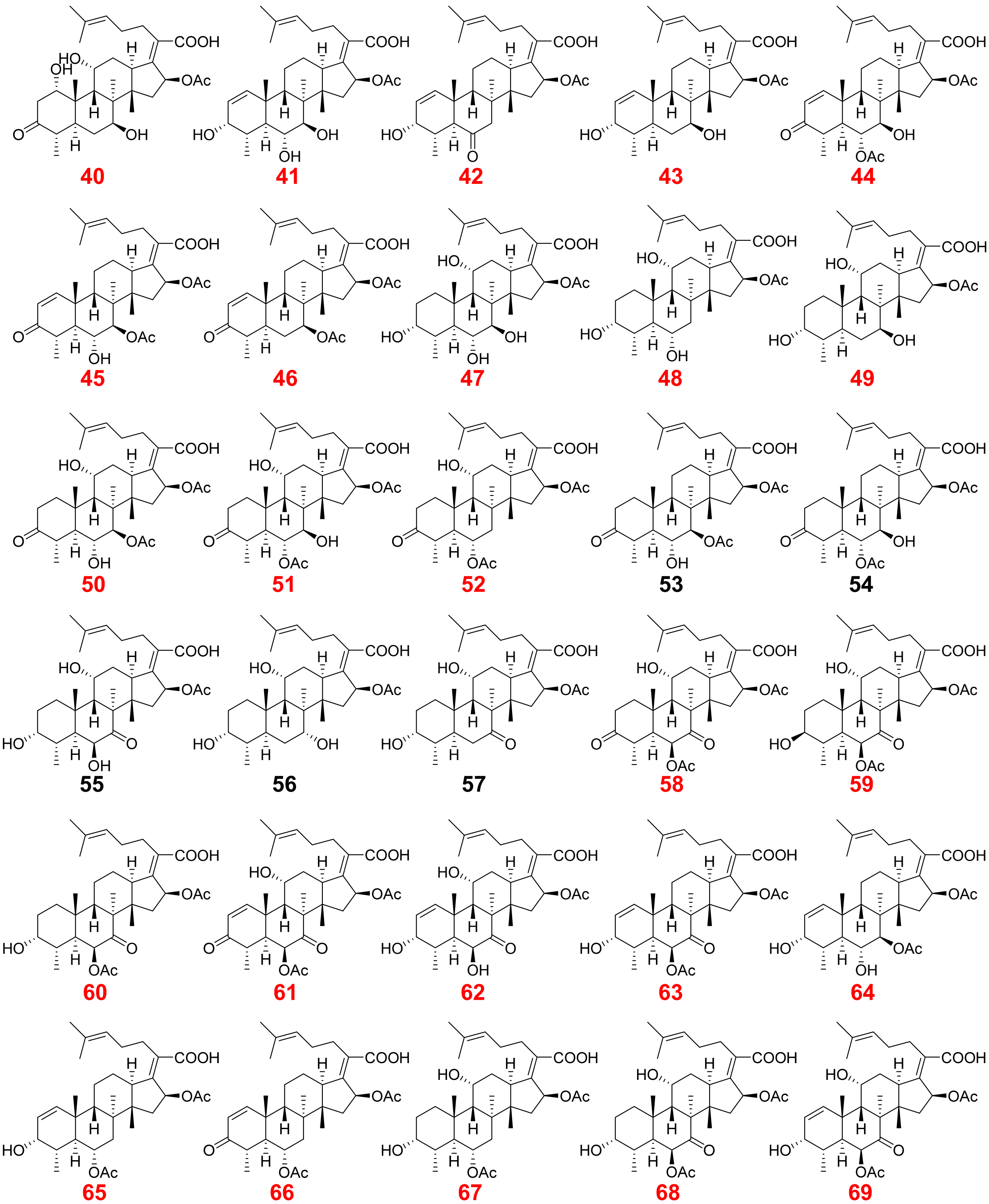
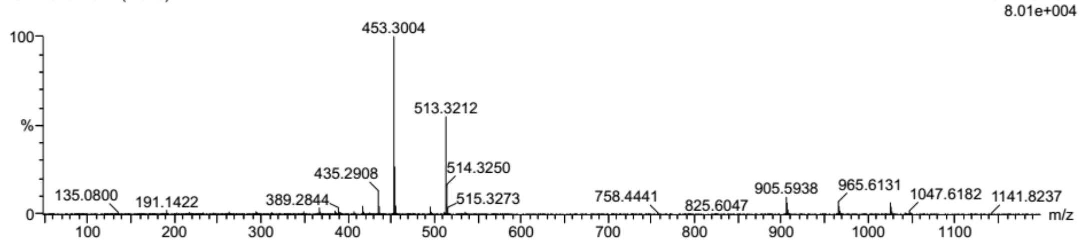


Figure S2 Fusidane-type antibiotics produced *via* the stochastic combinational strategy.

New compounds are marked in red. And compounds **7**, **8**, **16**, **27**, **28**, **53** and **54** were identified by comparison with standards or mass spectrometry analysis.

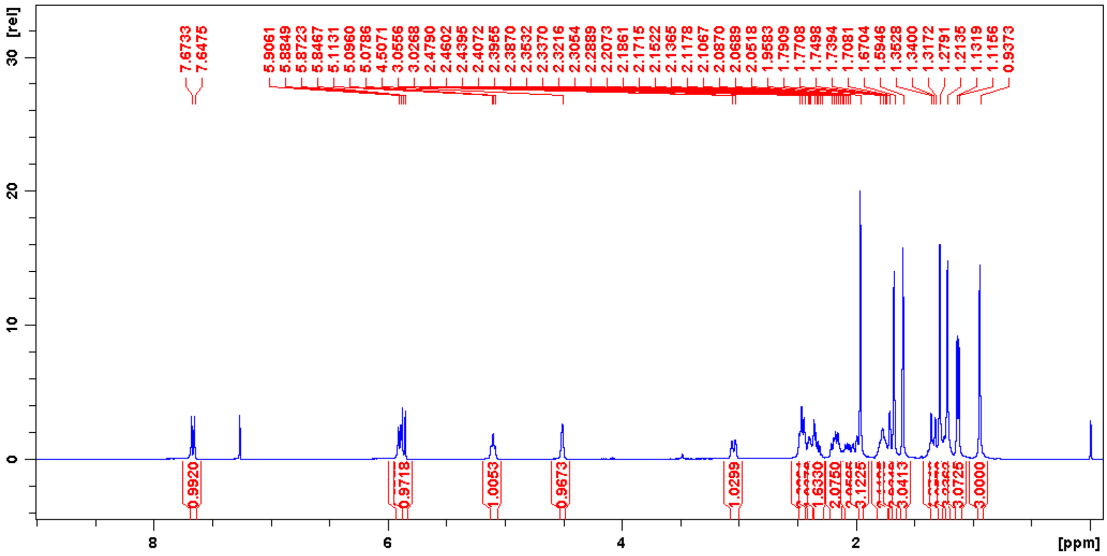
A

Monoisotopic Mass, Even Electron Ions
248 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
1J
20171028-4 314 (2.528)

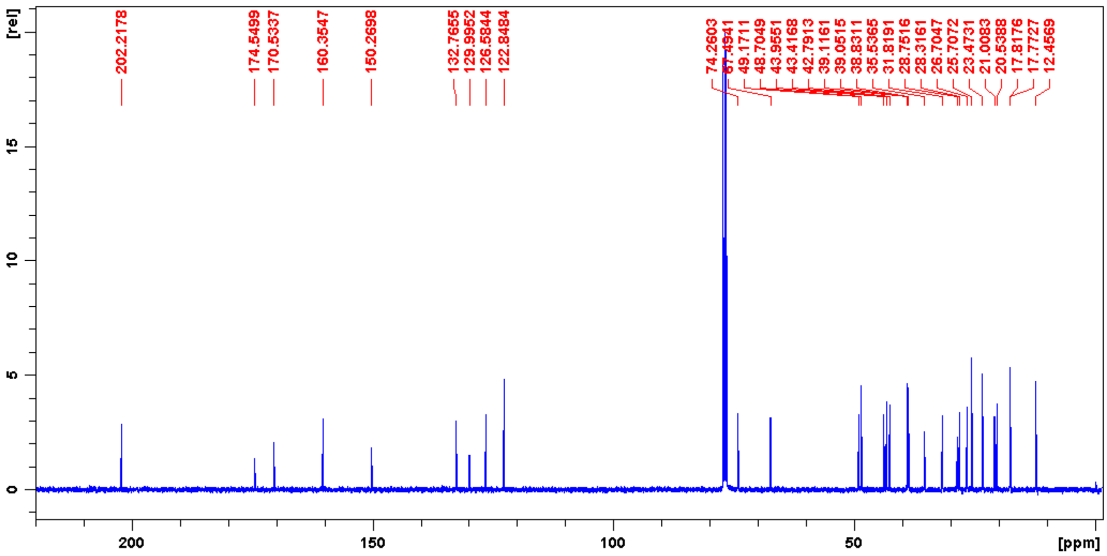


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
513.3212	513.3216	-0.4	-0.8	9.5	97.3	0.908	40.32	C31 H45 O6
	513.3192	2.0	3.9	6.5	96.9	0.516	59.68	C29 H46 O6 Na

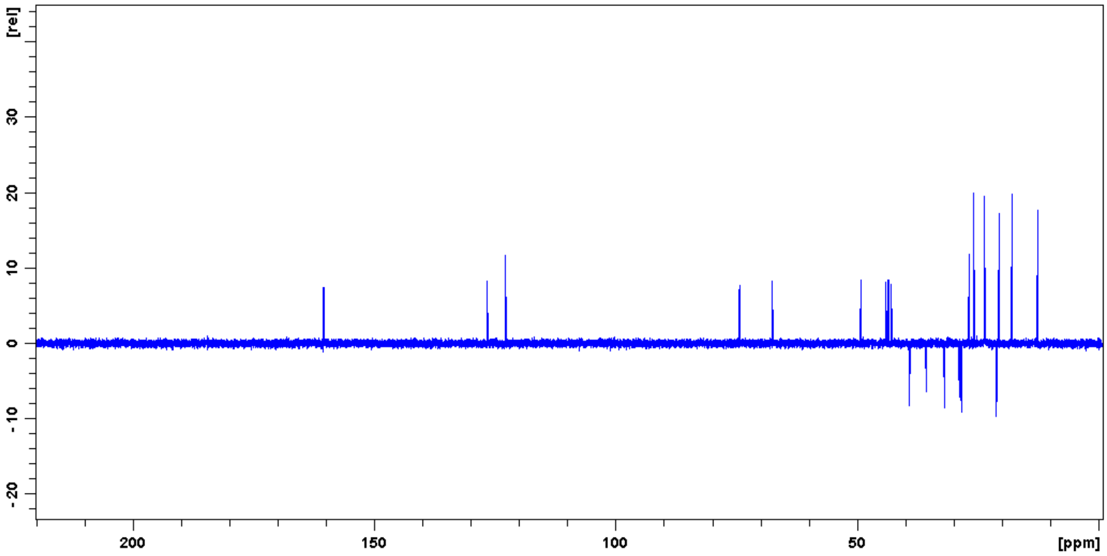
B



C



D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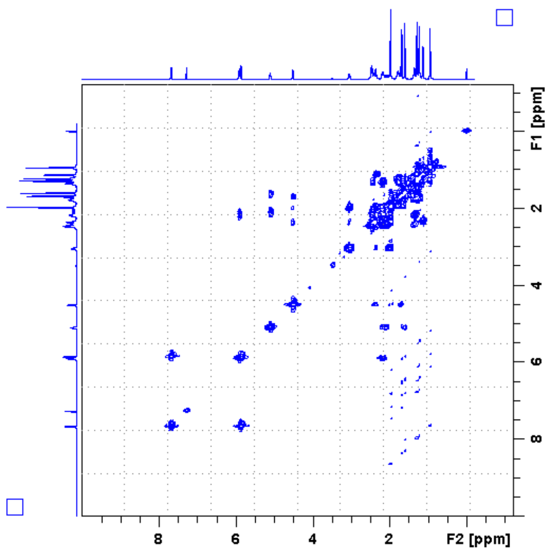
[ppm]

E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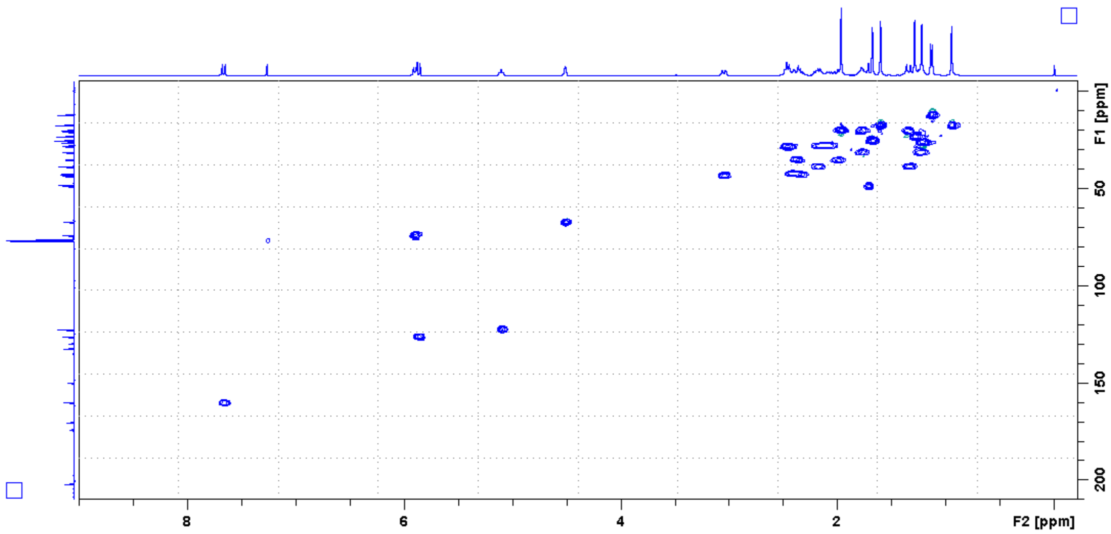
4
6
8
F2 [ppm]

F


F1 [ppm]
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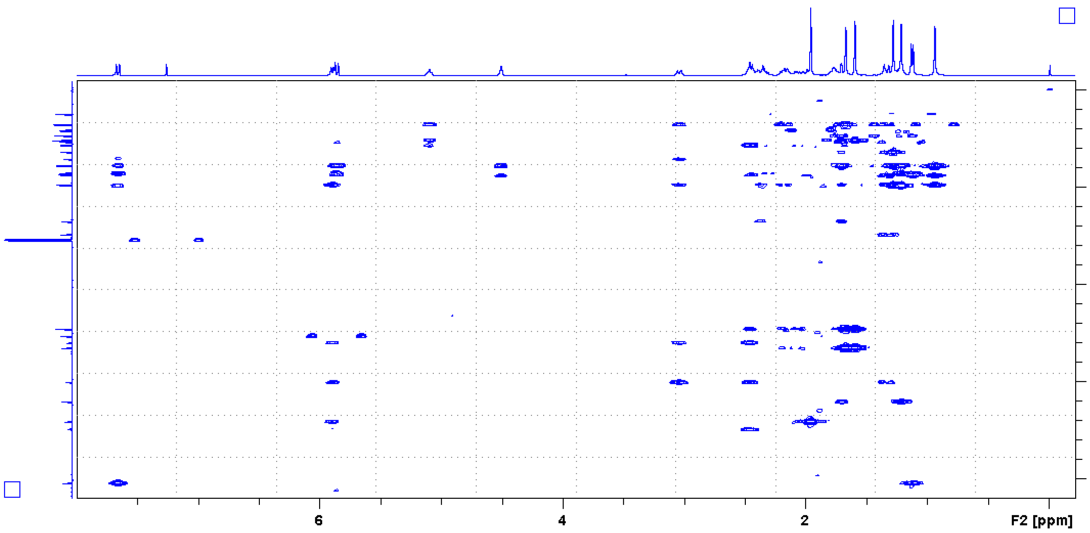
150
200
8
6
4
2
F2 [ppm]

G



H

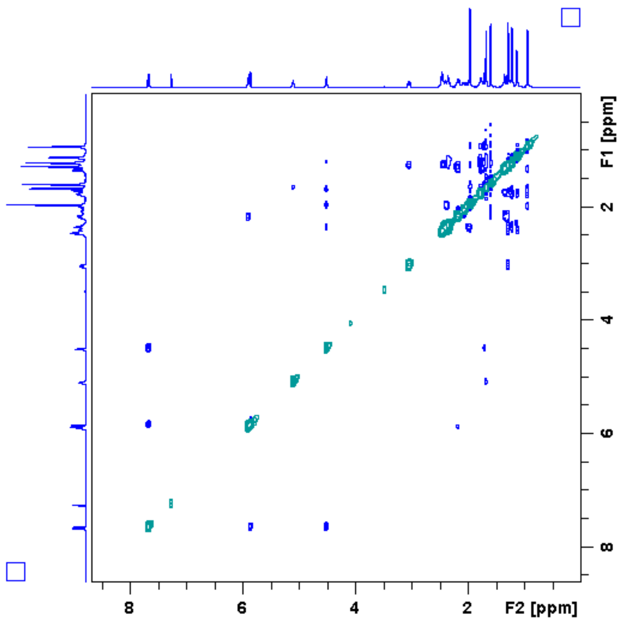
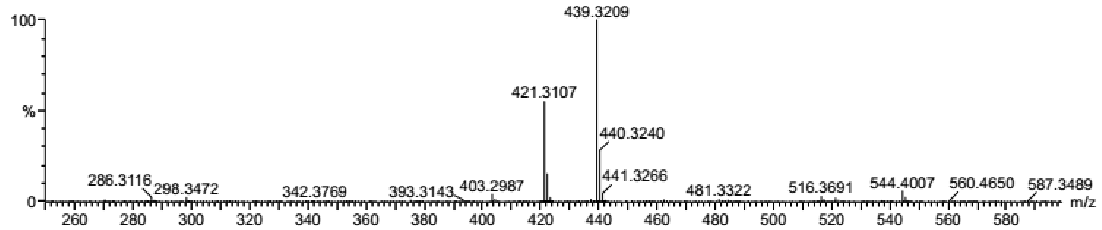


Figure S3 HRESIMS and NMR spectra of **5**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 400 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 100 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 100 MHz; (E) ^{1}H–^{1}H COSY spectrum in $CDCl_3$ at 400 MHz; (F) HSQC spectrum in $CDCl_3$ at 400 MHz; (G) HMBC spectrum in $CDCl_3$ at 400 MHz; (H) ROESY spectrum in $CDCl_3$ at 400 MHz.

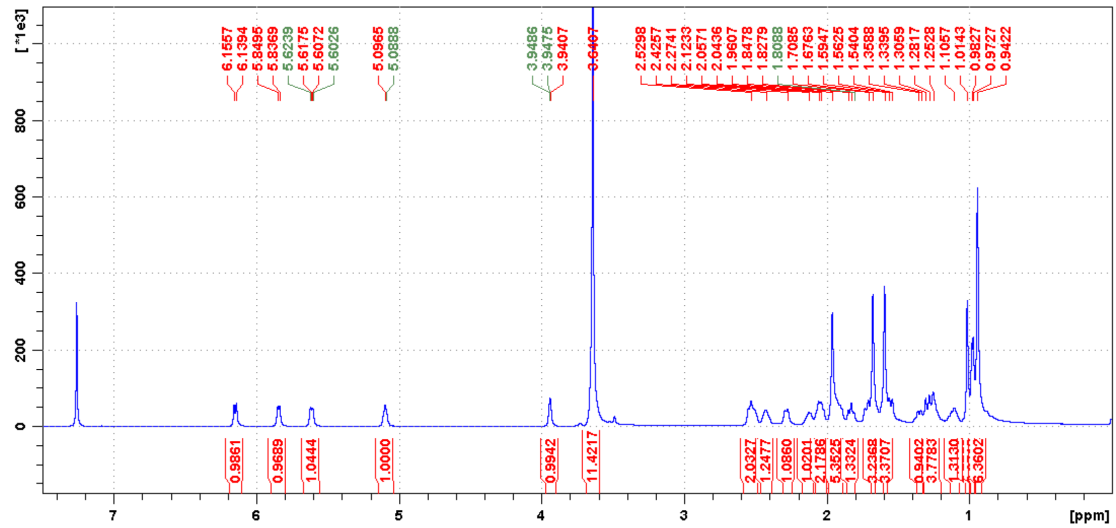
A

Monoisotopic Mass, Even Electron Ions
198 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
52
20190107_57 270 (2.177)

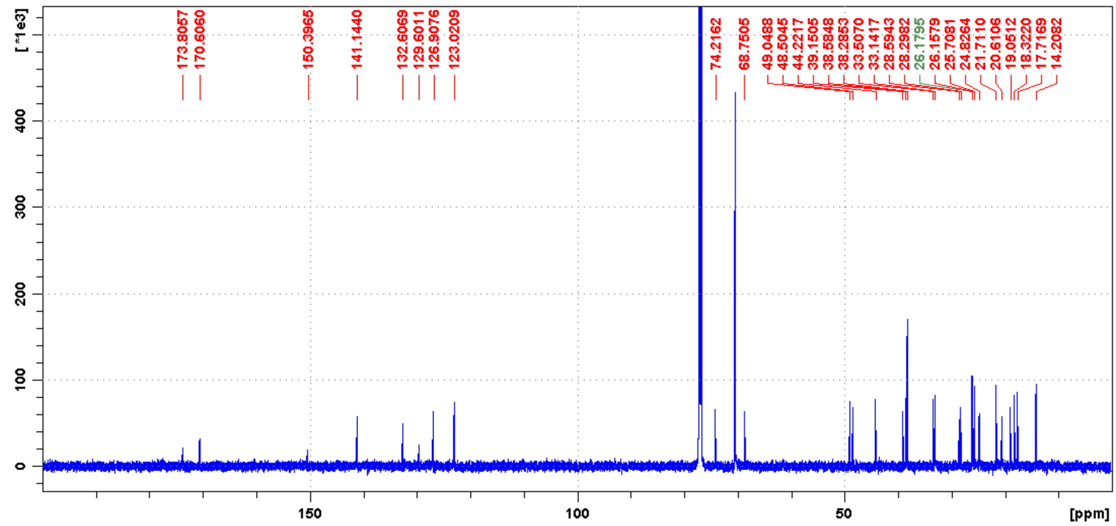


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
439.3209	439.3212	-0.3	-0.7	8.5	272.4	1.575	20.70	C29 H43 O3
	439.3188	2.1	4.8	5.5	271.1	0.232	79.30	C27 H44 O3 Na

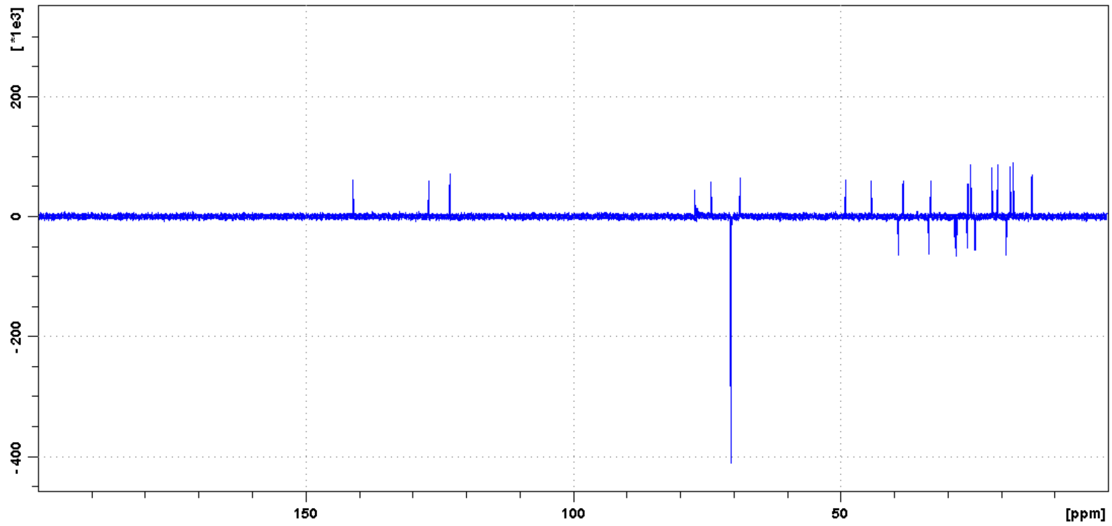
B



C



D



[*1e3]
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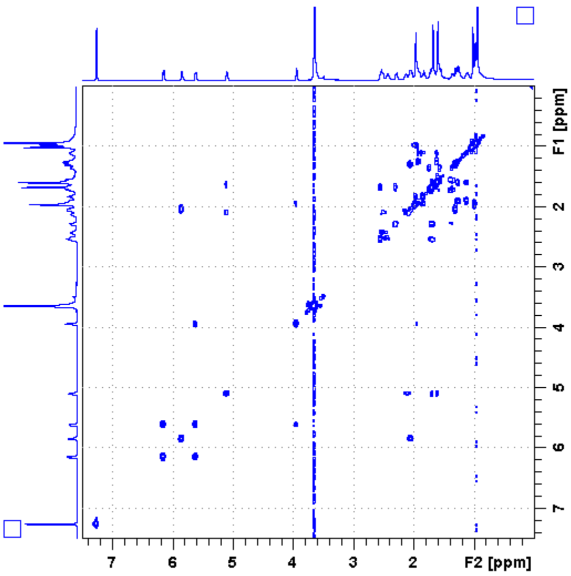
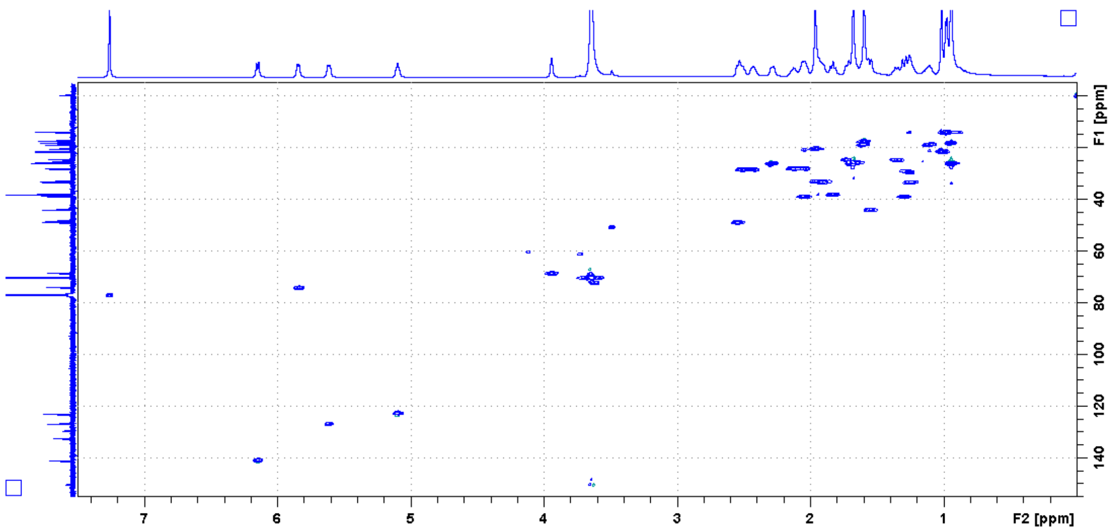
-200
-400
150
100
50
[ppm]

E



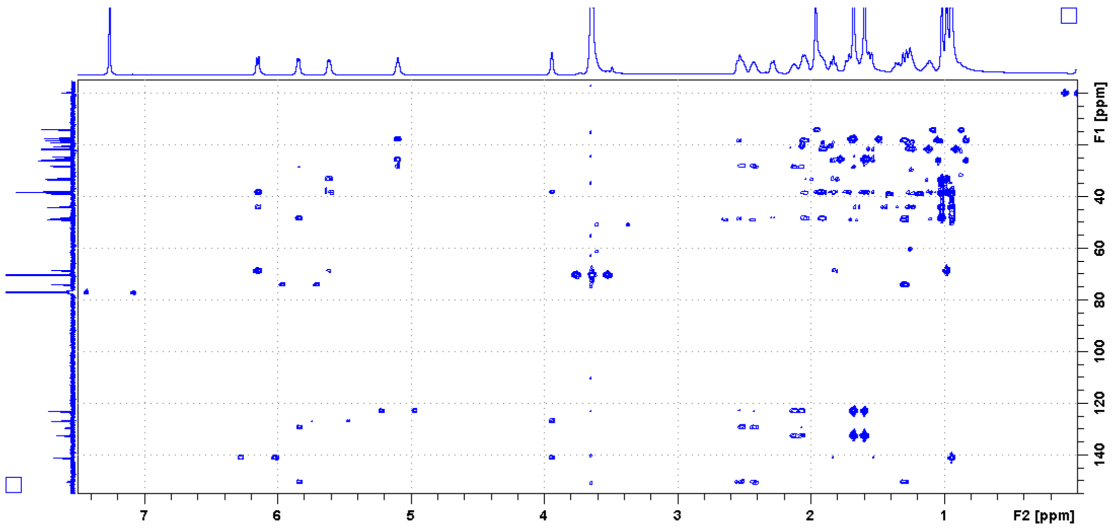
F1 [ppm]
2
3
4
5
6
7
F2 [ppm]

F

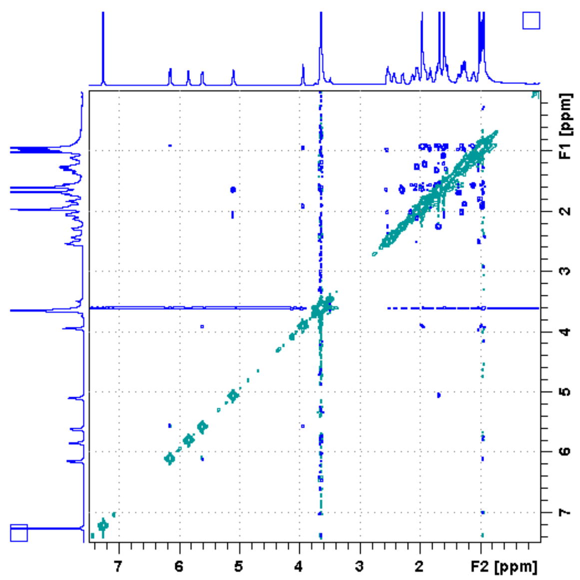


F1 [ppm]
40
60
80
100
120
140
7
6
5
4
3
2
1
F2 [ppm]

G



H



I

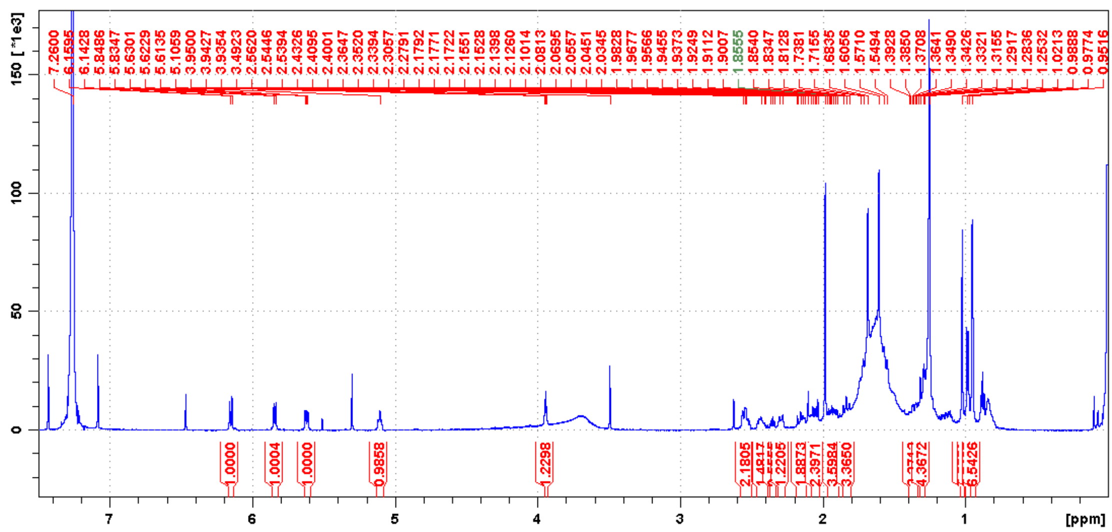
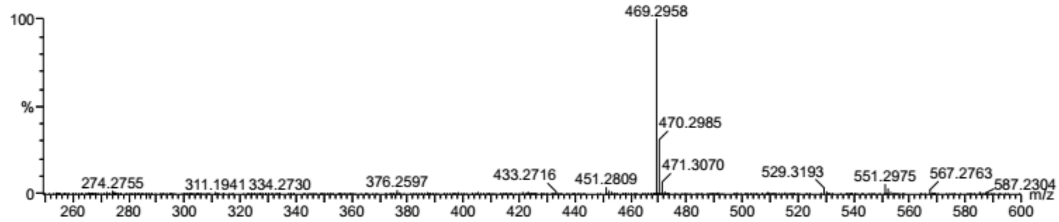


Figure S4 HRESIMS and NMR spectra of **6**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 600 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 150 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in $CDCl_3$ at 600 MHz; (F) HSQC spectrum in $CDCl_3$ at 600 MHz; (G) HMBC spectrum in $CDCl_3$ at 600 MHz; (H) NOESY spectrum in $CDCl_3$ at 600 MHz; (I) ^{1}H NMR spectrum of 6 obtained *via* chemical derivatization in $CDCl_3$ at 600 MHz.

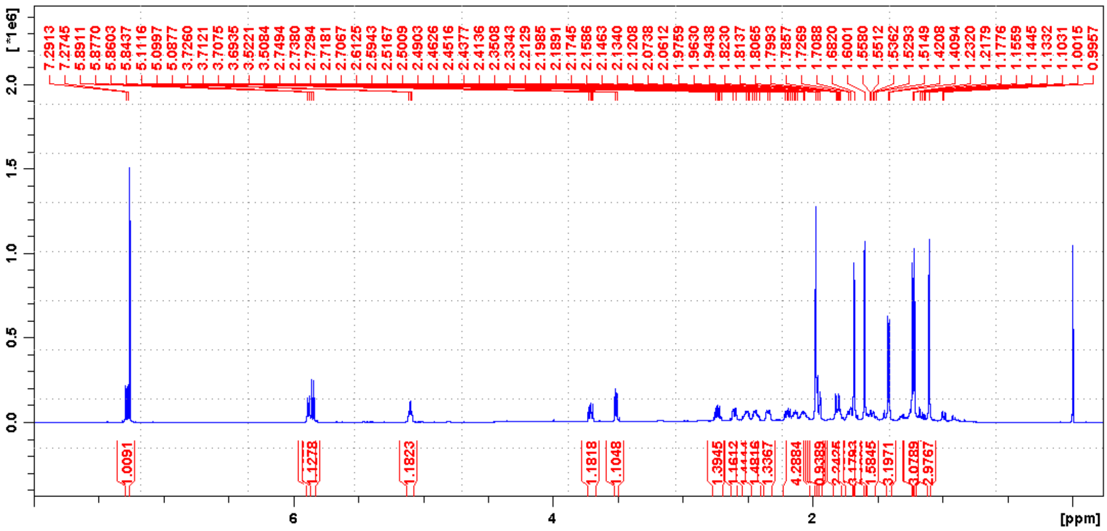
A

Monoisotopic Mass, Even Electron Ions
295 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
53
20190107_58 214 (1.724)

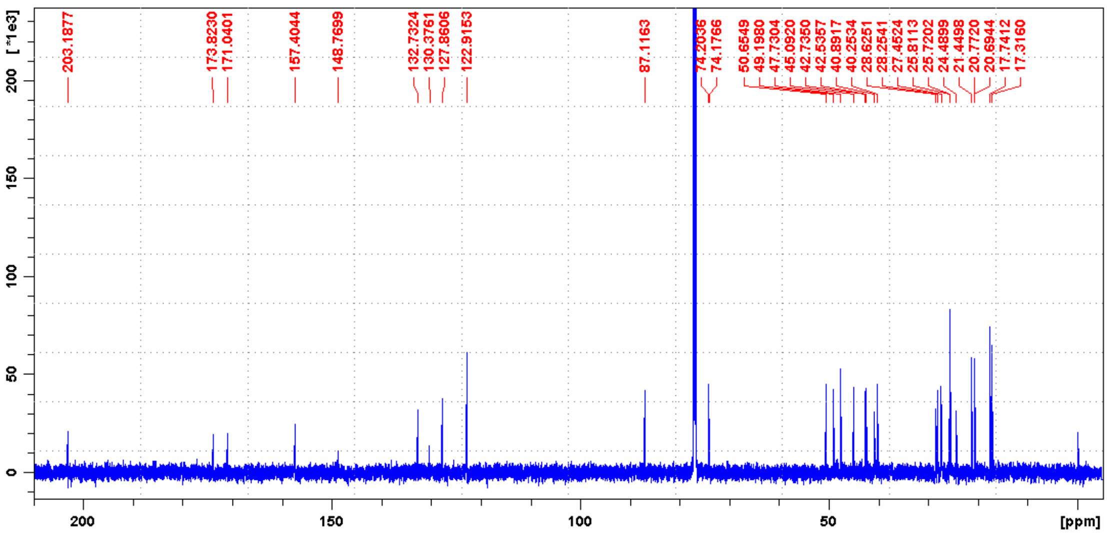


Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
551.2975	551.2985	-1.0	-1.8	9.5	33.3	1.067	34.42	C31 H44 O7 Na
	551.2950	2.5	4.5	21.5	32.6	0.422	65.58	C40 H39 O2

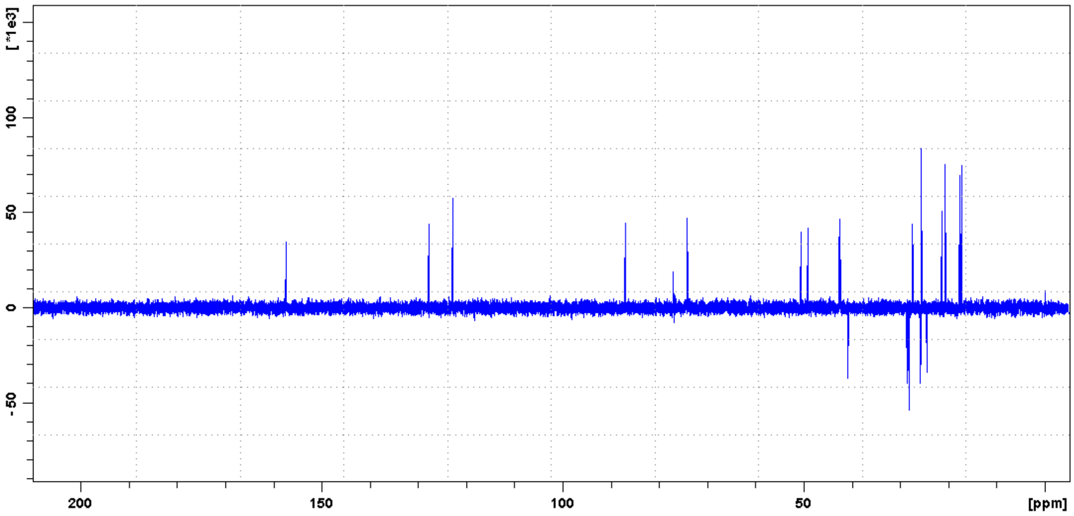
B



C



D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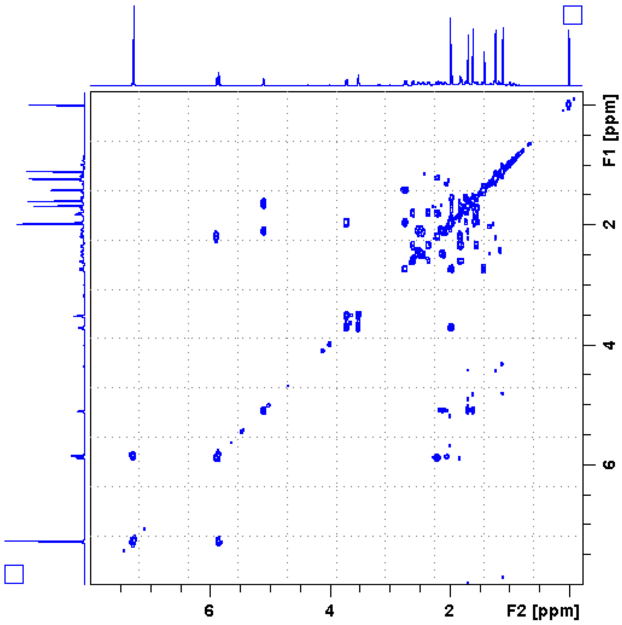
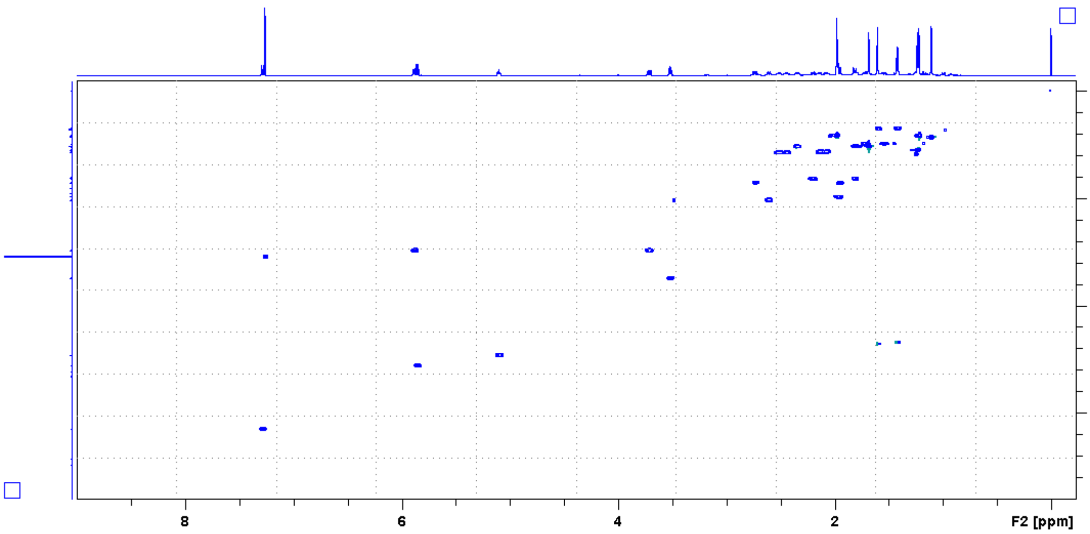
200
150
100
50
[ppm]

E


F1 [ppm]
2
4
6
6
4
2
F2 [ppm]

F


F1 [ppm]
50
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150
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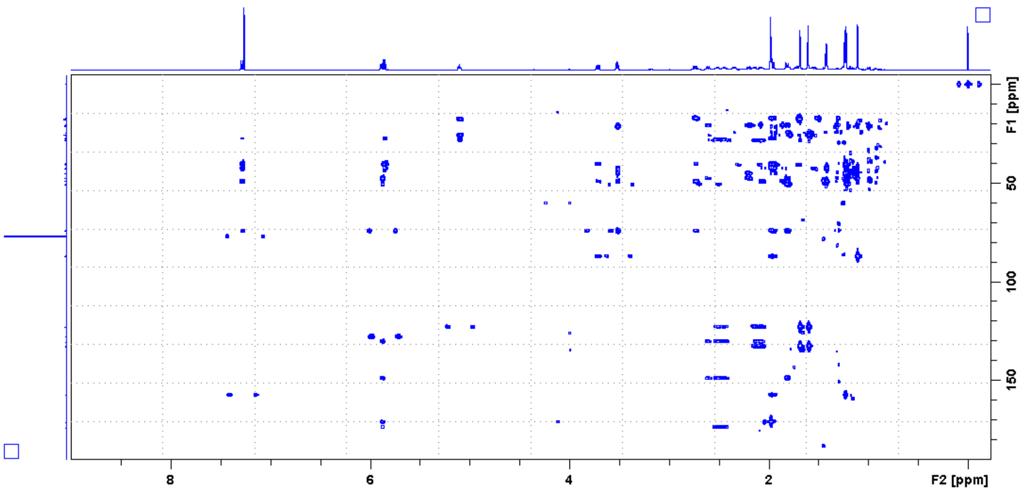
6
4
2
F2 [ppm]

G



H

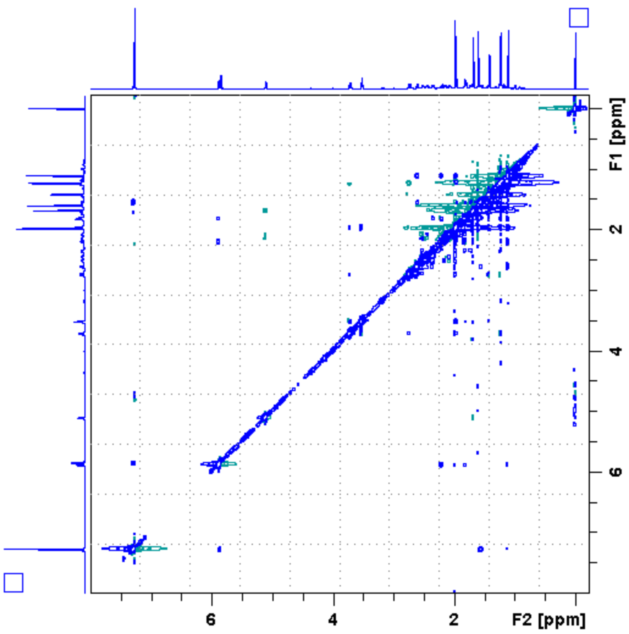
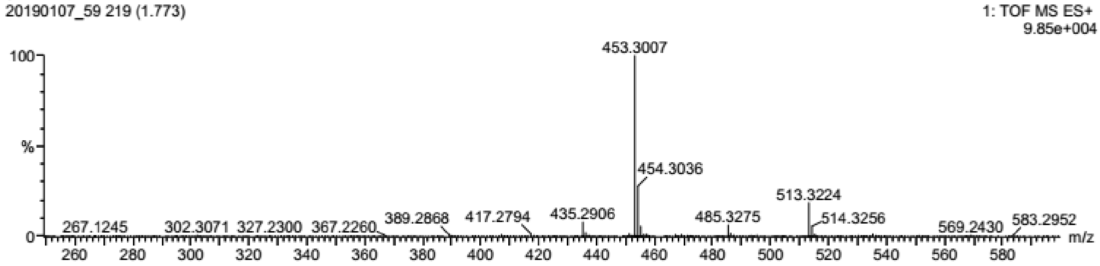


Figure S5 HRESIMS and NMR spectra of **9**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 600 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 150 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 150 MHz; (E) ^{1}H-^{1}H COSY spectrum in $CDCl_3$ at 600 MHz; (F) HSQC spectrum in $CDCl_3$ at 600 MHz; (G) HMBC spectrum in $CDCl_3$ at 600 MHz; (H) NOESY spectrum in $CDCl_3$ at 600 MHz.A

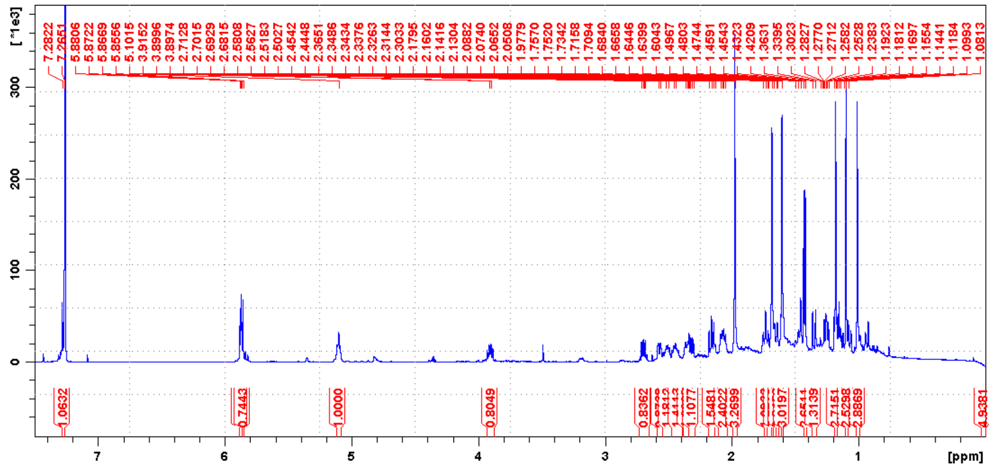
Monoisotopic Mass, Even Electron Ions
248 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
54
20190107_59 219 (1.773)



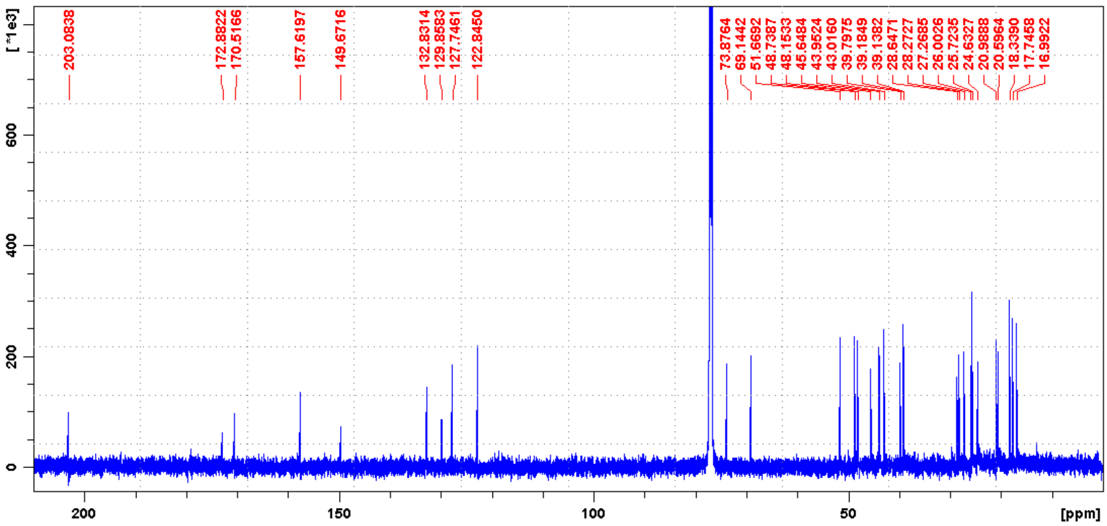
Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
513.3224	513.3216	0.8	1.6	9.5	143.4	n/a	n/a	C31 H45 O6

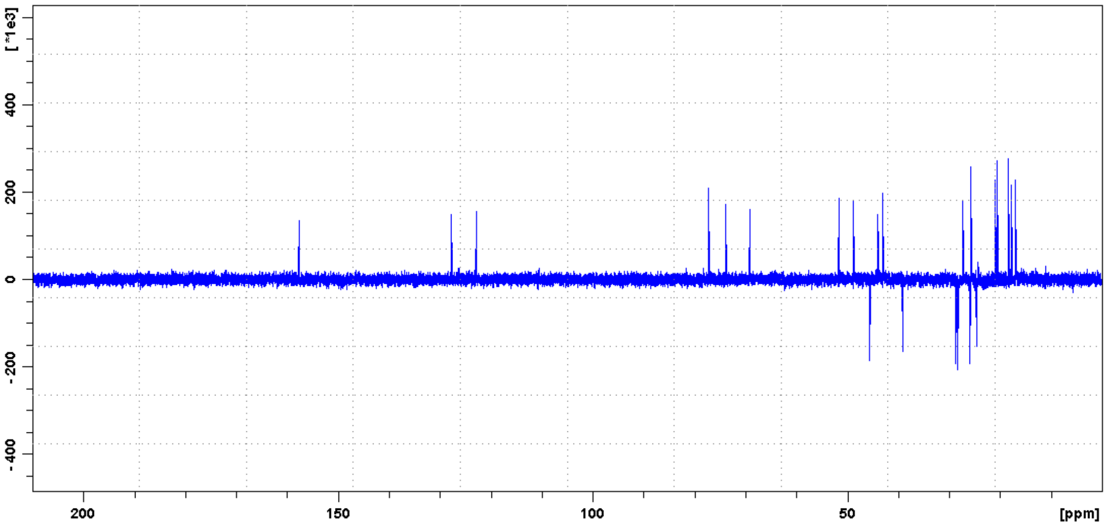
B



C



D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-400
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150
100
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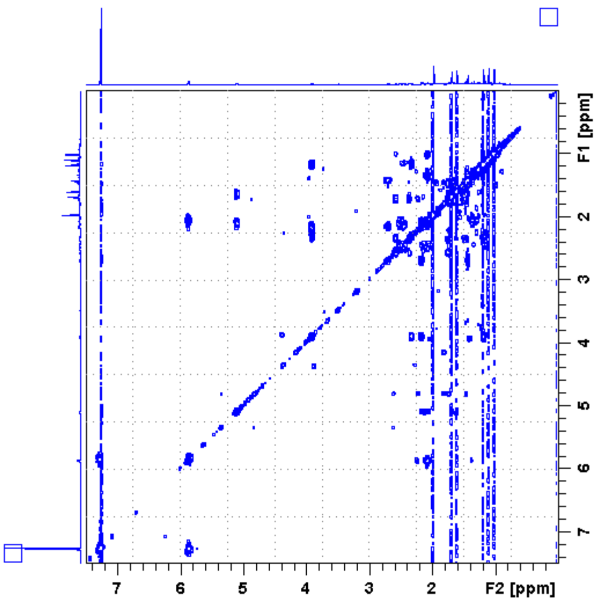
[ppm]

E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7
6
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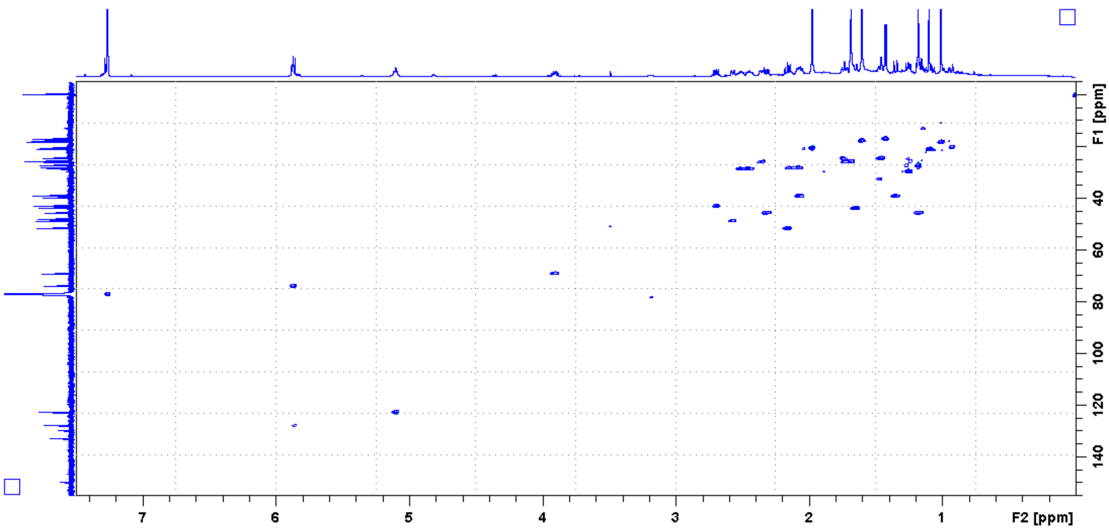
4
3
2
F2 [ppm]

F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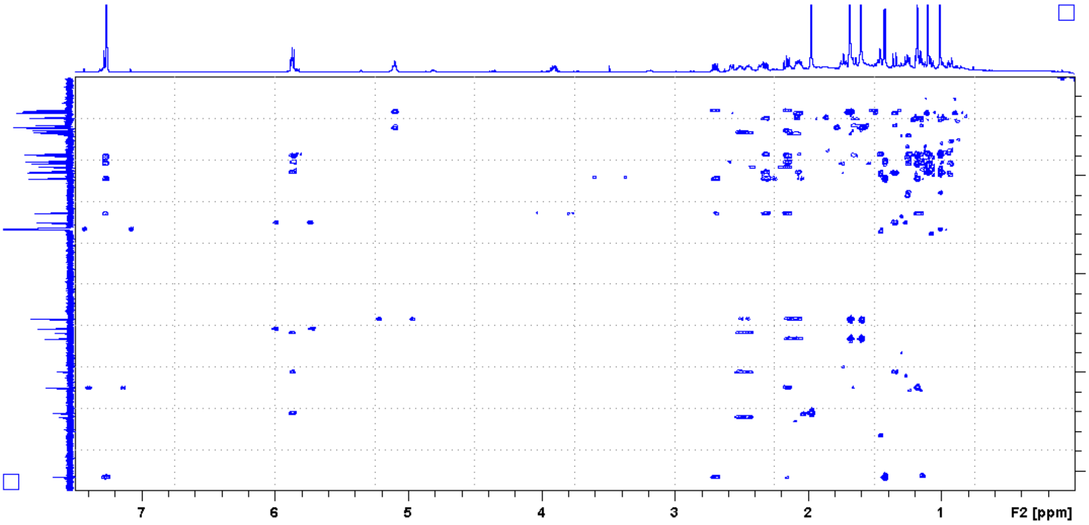
3
2
1
F2 [ppm]

G



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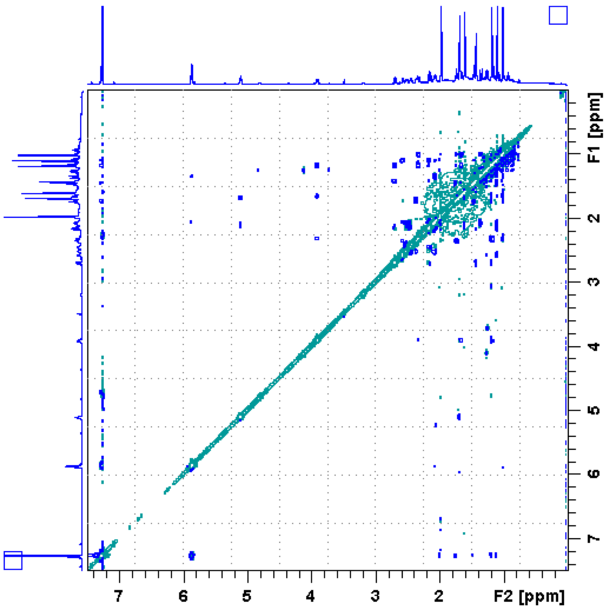
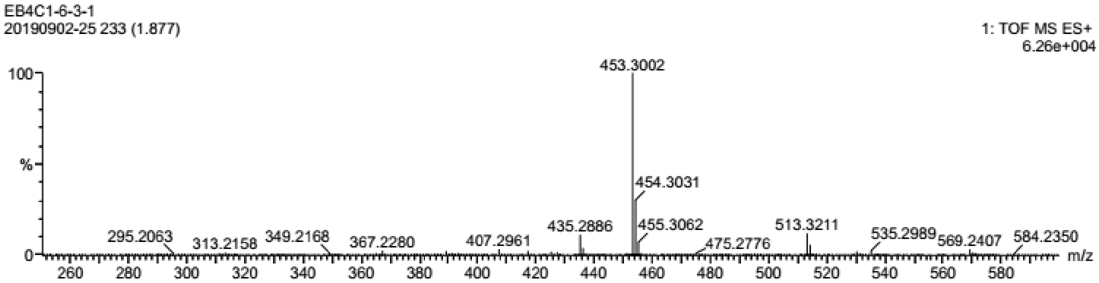


Figure S6 HRESIMS and NMR spectra of **10**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 600 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 150 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in $CDCl_3$ at 600 MHz; (F) HSQC spectrum in $CDCl_3$ at 600 MHz; (G) HMBC spectrum in $CDCl_3$ at 600 MHz; (H) NOESY spectrum in $CDCl_3$ at 600 MHz.

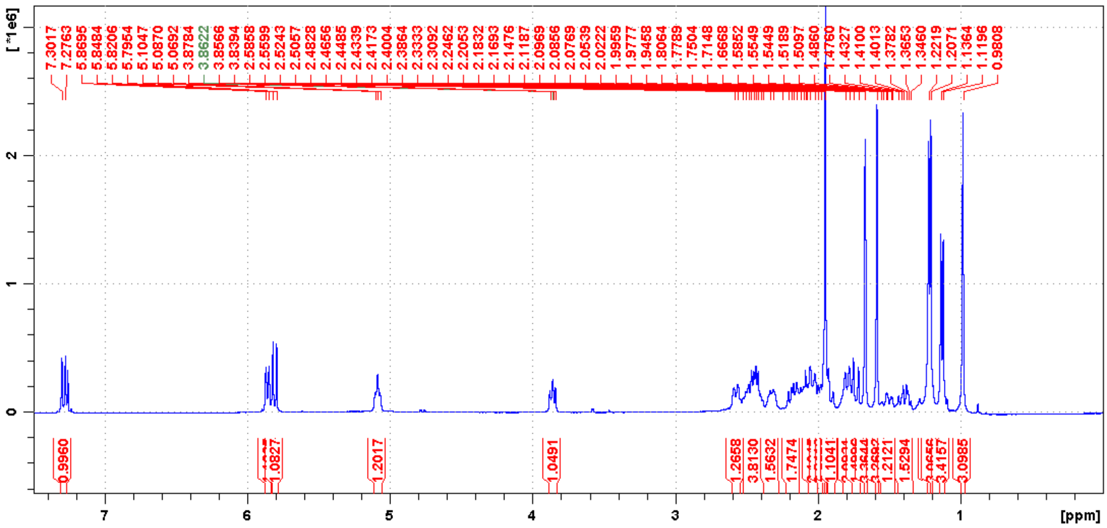
A

Monoisotopic Mass, Even Electron Ions
248 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1

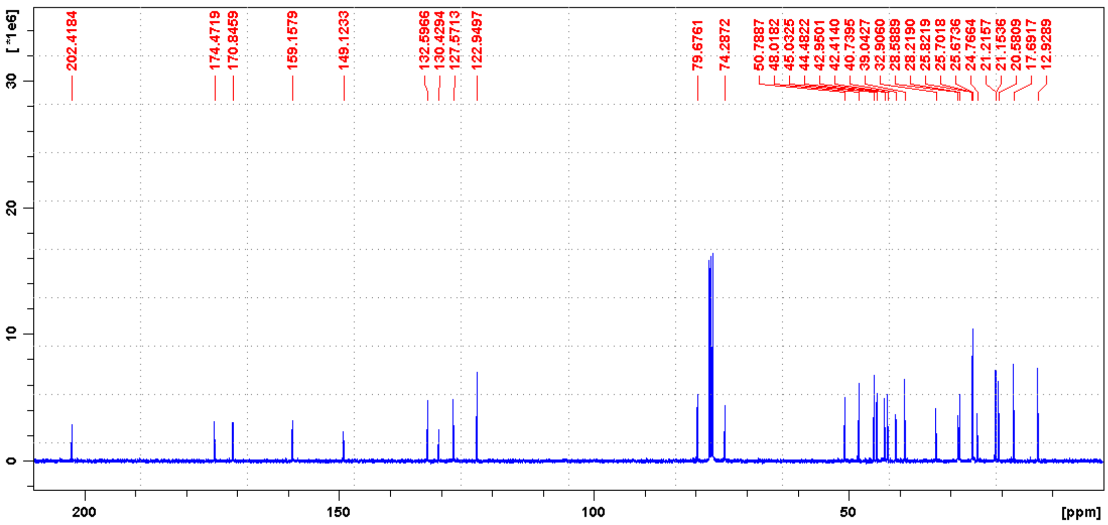


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
513.3211	513.3216	-0.5	-1.0	9.5	133.1	0.429	65.13	C31 H45 O6
	513.3192	1.9	3.7	6.5	133.7	1.053	34.87	C29 H46 O6 Na

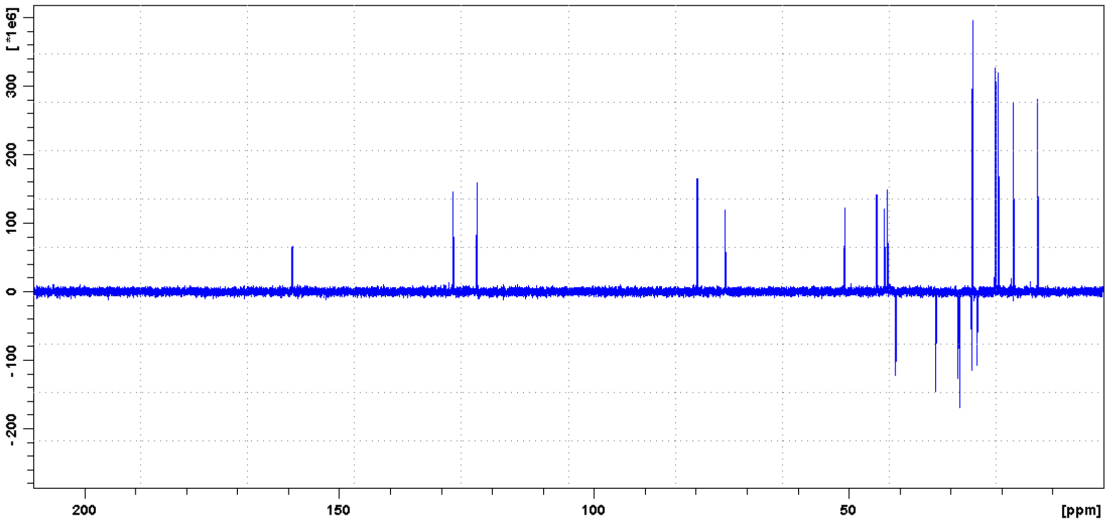
B



C



D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-100
-200
200
150
100
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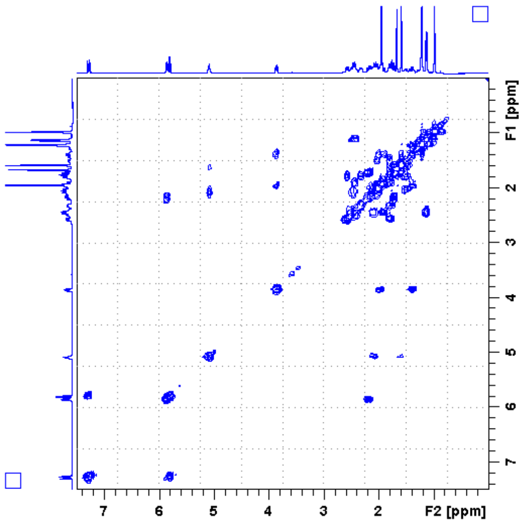
[ppm]

E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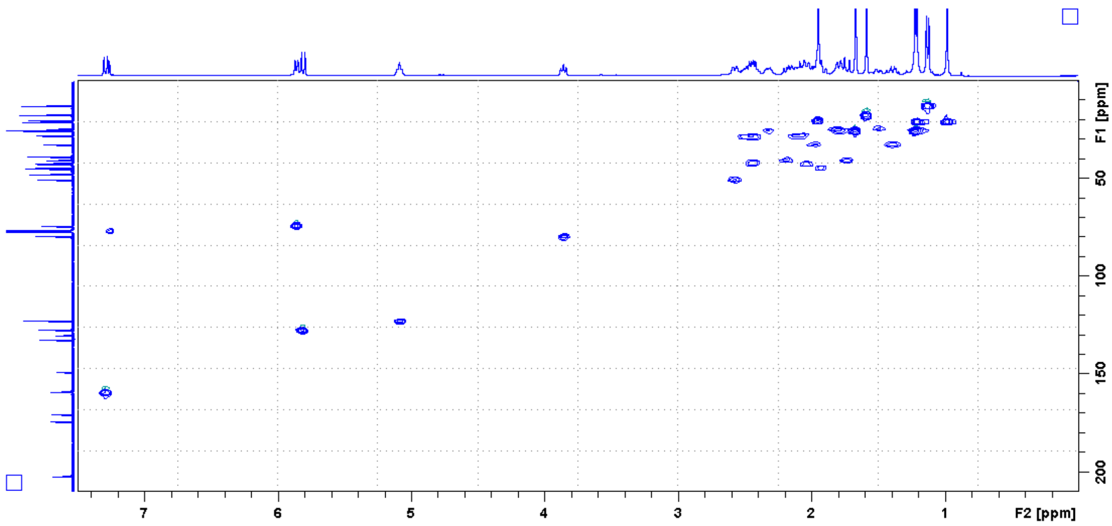
7
F2 [ppm]

F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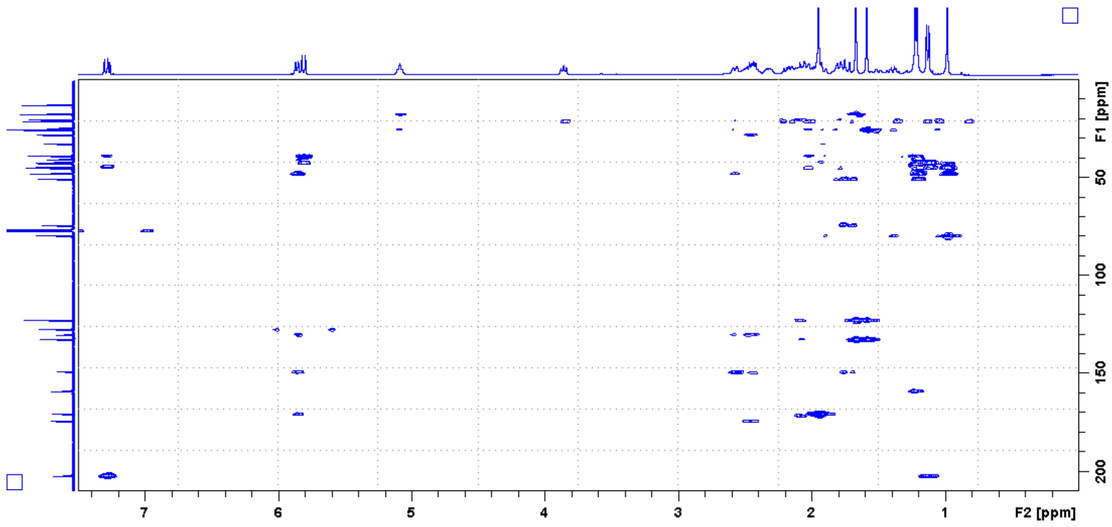
F2 [ppm]

G



H

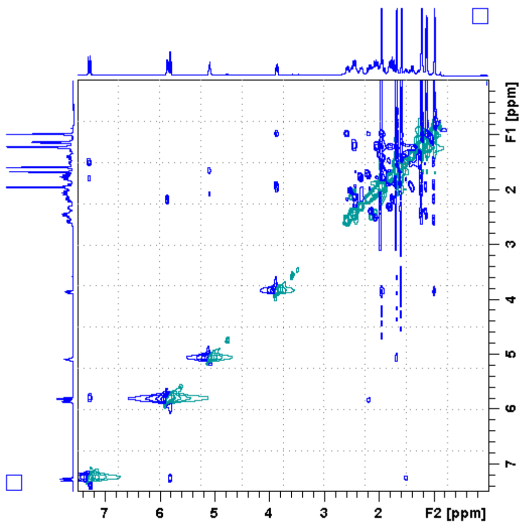
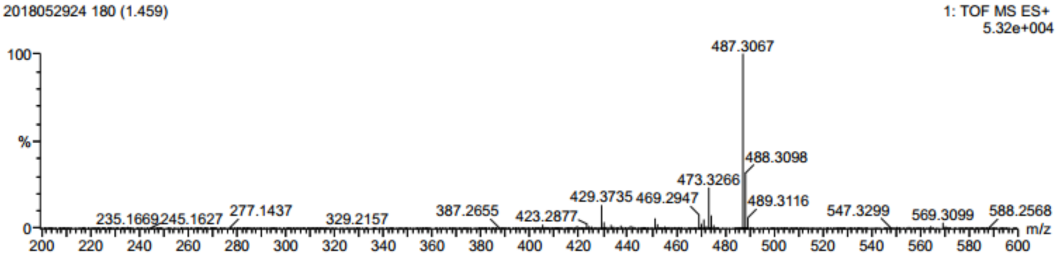


Figure S7 HRESIMS and NMR spectra of **11**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 400 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 100 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 100 MHz; (E) ^{1}H–^{1}H COSY spectrum in $CDCl_3$ at 400 MHz; (F) HSQC spectrum in $CDCl_3$ at 400 MHz; (G) HMBC spectrum in $CDCl_3$ at 400 MHz; (H) ROESY spectrum in $CDCl_3$ at 400 MHz.

A

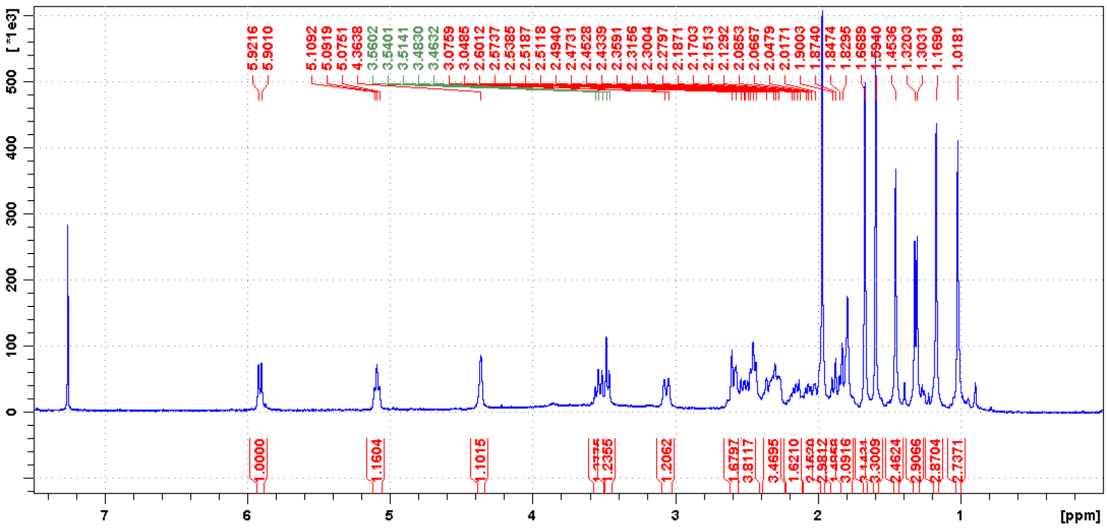
Monoisotopic Mass, Even Electron Ions
300 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
B1B4-1-2
2018052924 180 (1.459)



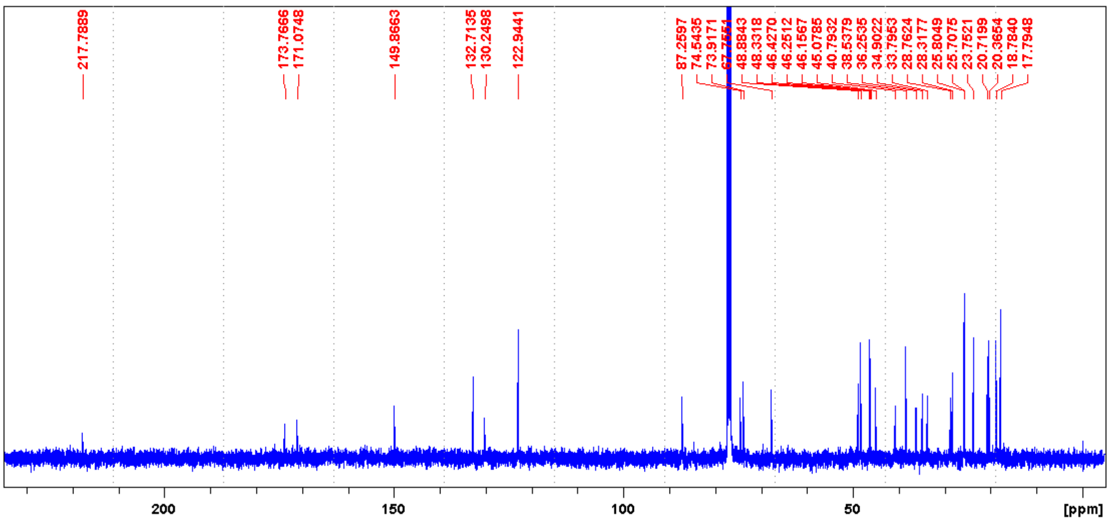
Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
569.3099	569.3090	0.9	1.6	8.5	65.8	0.592	55.32	C31 H46 O8 Na
	569.3114	-1.5	-2.6	11.5	66.0	0.806	44.68	C33 H45 O8

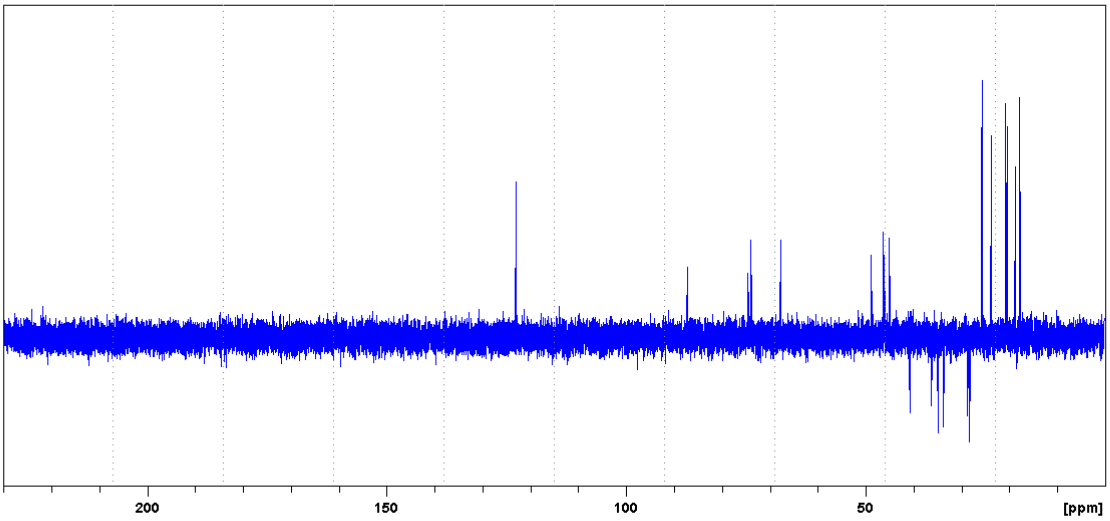
B



C



D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150
100
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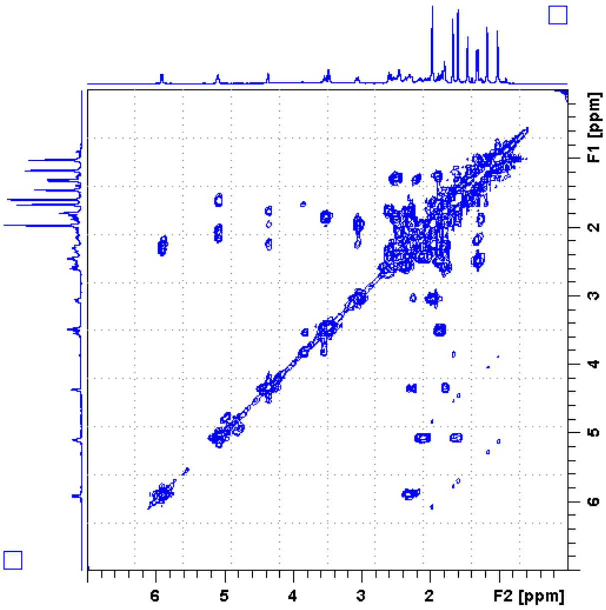
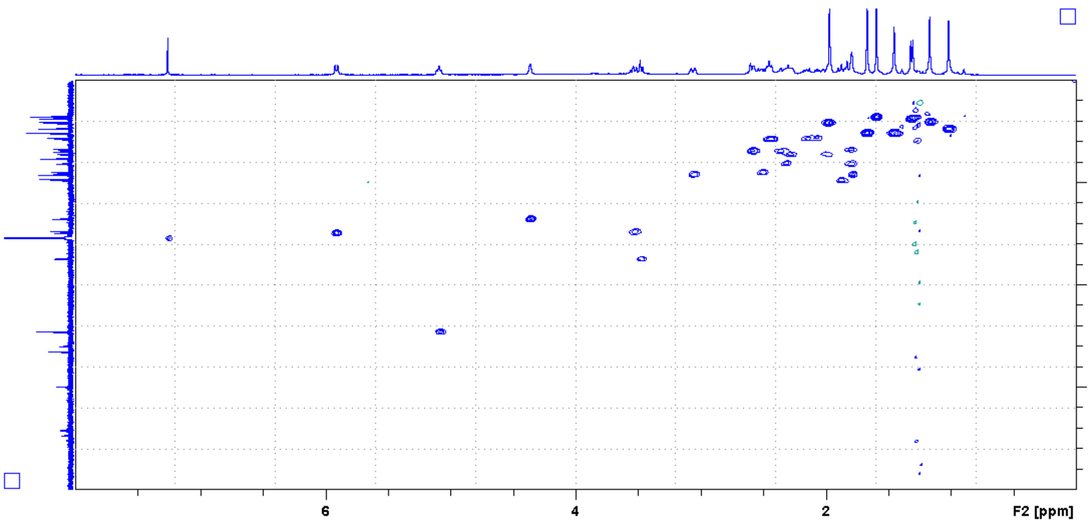
[ppm]

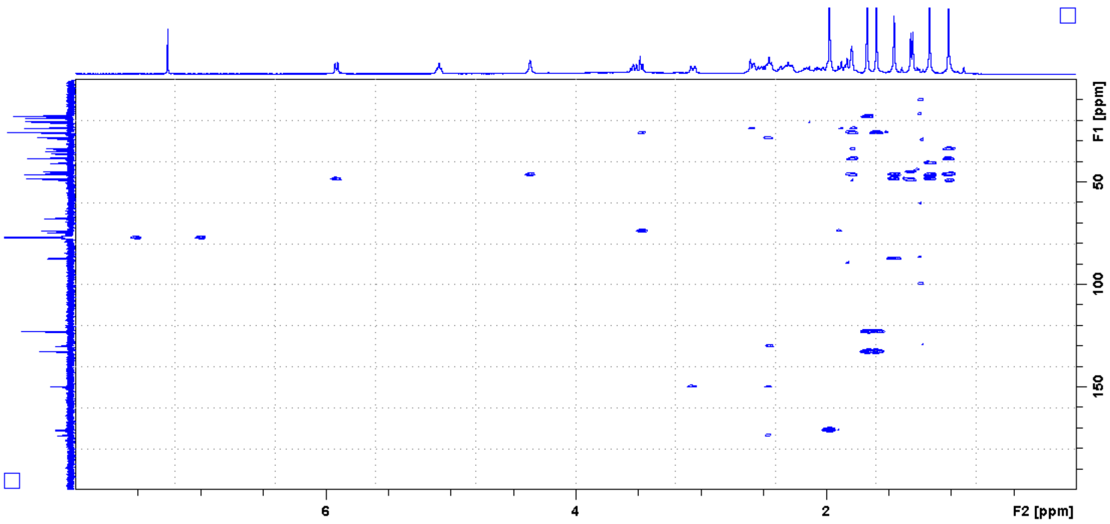
E


F1 [ppm]
2
3
4
5
6
6
5
4
3
2
F2 [ppm]

F


F1 [ppm]
50
100
150
6
4
2
F2 [ppm]

G



H

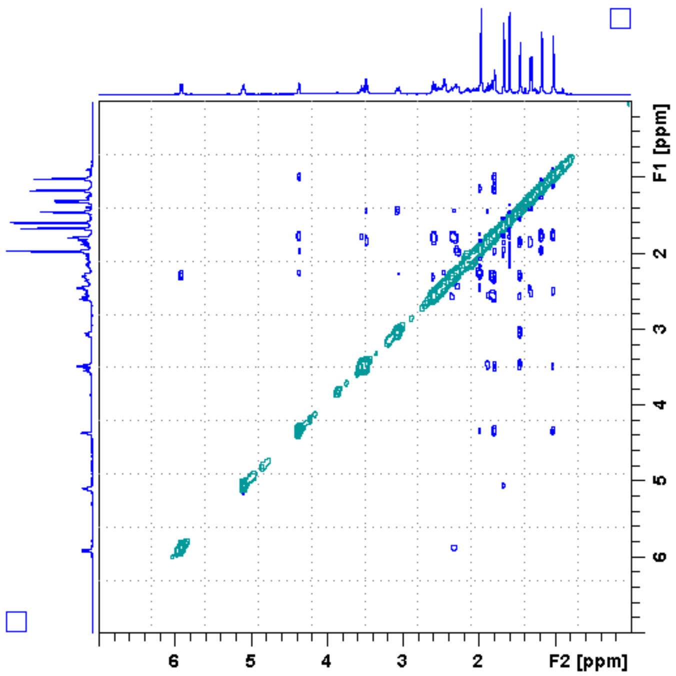
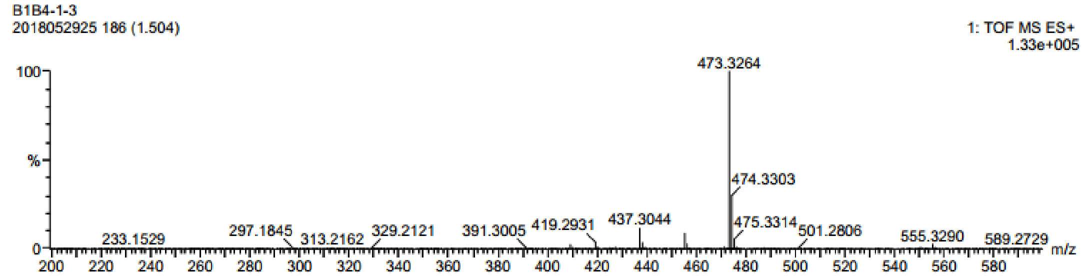


Figure S8 HRESIMS and NMR spectra of **12**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 400 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 100 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 100 MHz; (E) ^{1}H–^{1}H COSY spectrum in $CDCl_3$ at 400 MHz; (F) HSQC spectrum in $CDCl_3$ at 400 MHz; (G) HMBC spectrum in $CDCl_3$ at 400 MHz; (H) ROESY spectrum in $CDCl_3$ at 400 MHz.

A

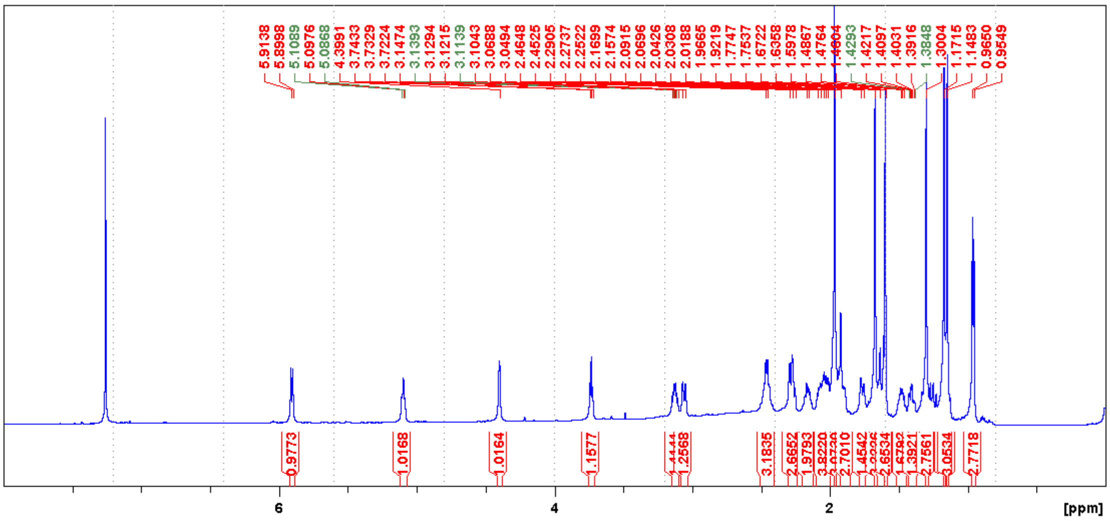
Monoisotopic Mass, Even Electron Ions
298 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1



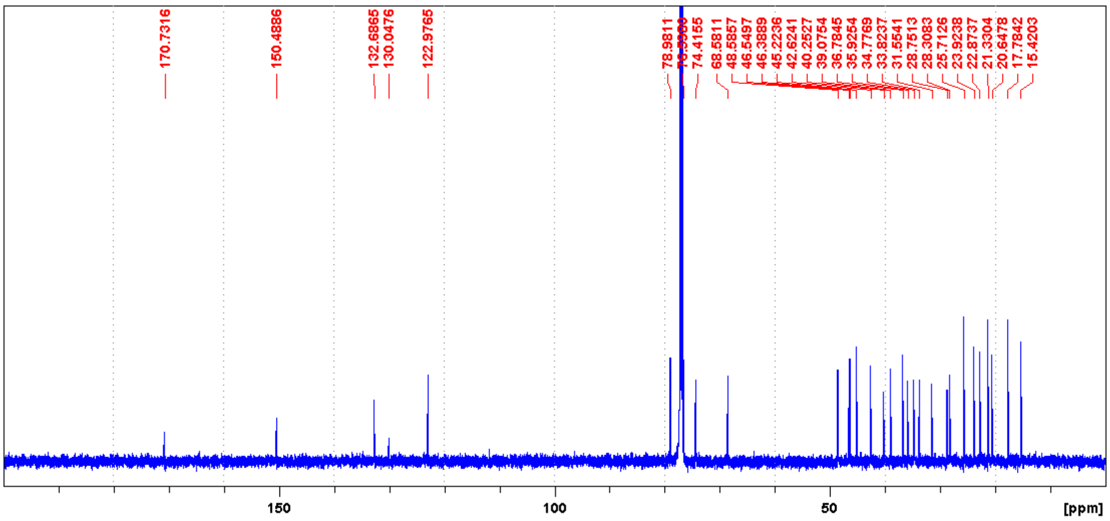
	Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
Minimum:					-1.5				
Maximum:			5.0	5.0	50.0				

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
555.3290	555.3298	-0.8	-1.4	7.5	76.5	0.030	97.08	C31 H48 O7 Na
	555.3263	2.7	4.9	19.5	80.0	3.534	2.92	C40 H43 O2

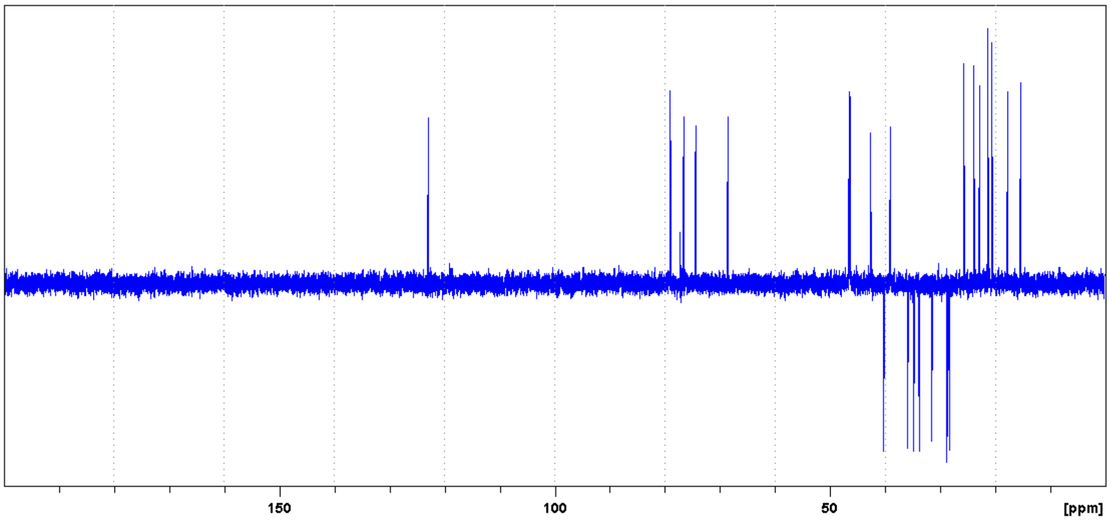
B



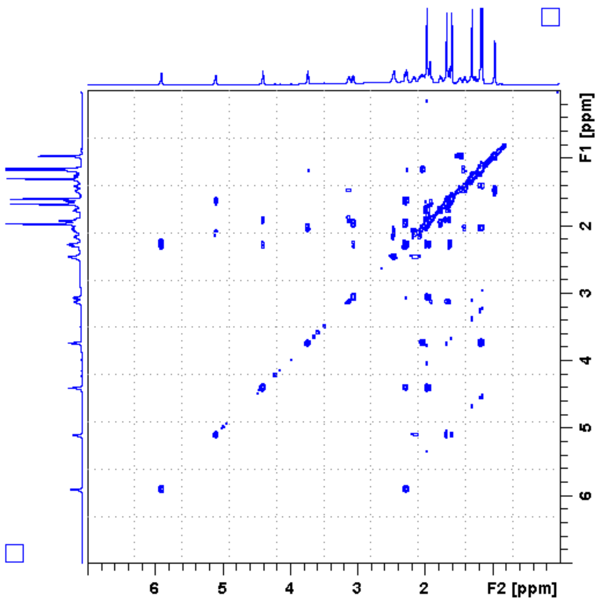
C



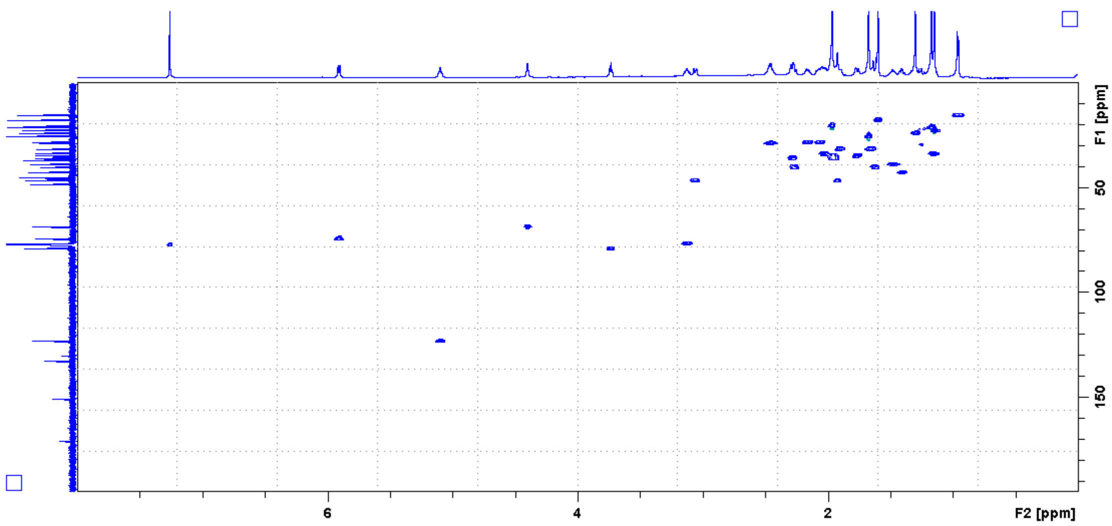
D


150
100
50
[ppm]

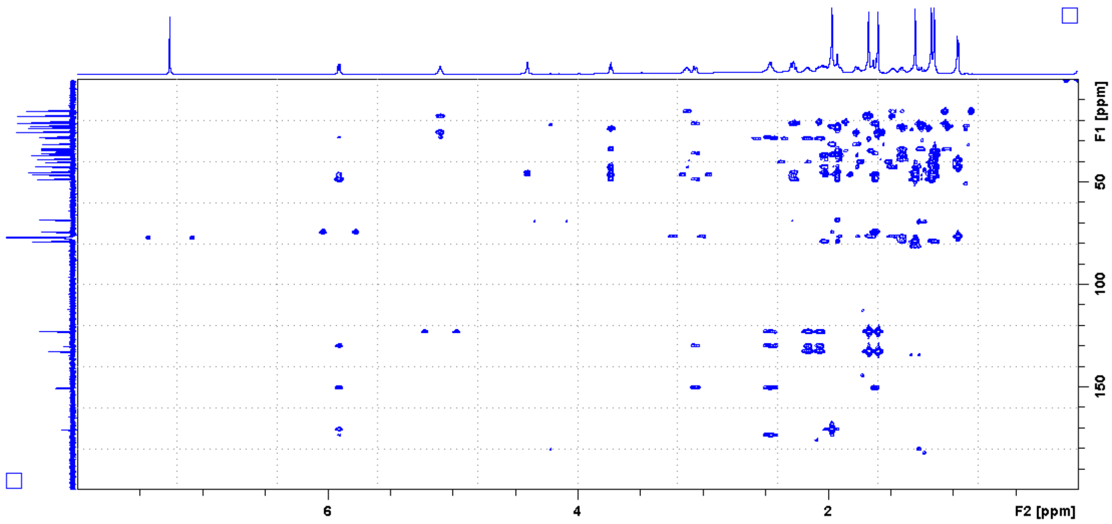
E


F1 [ppm]
2
3
4
5
6
5
4
3
2
F2 [ppm]

F


F1 [ppm]
50
100
150
6
4
2
F2 [ppm]

G



H

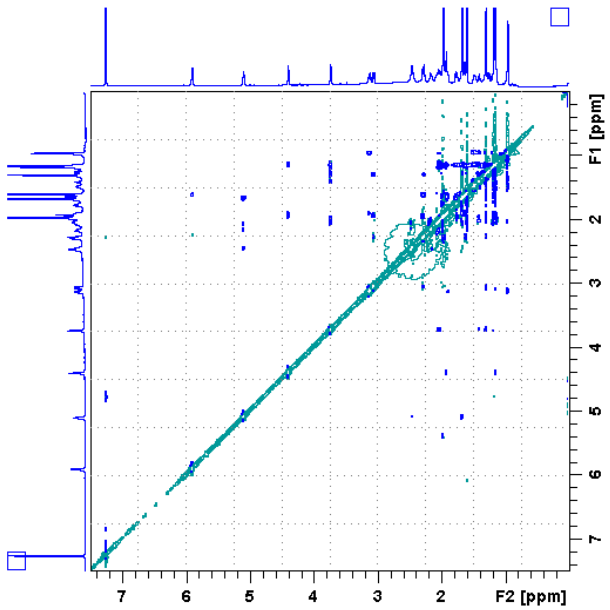
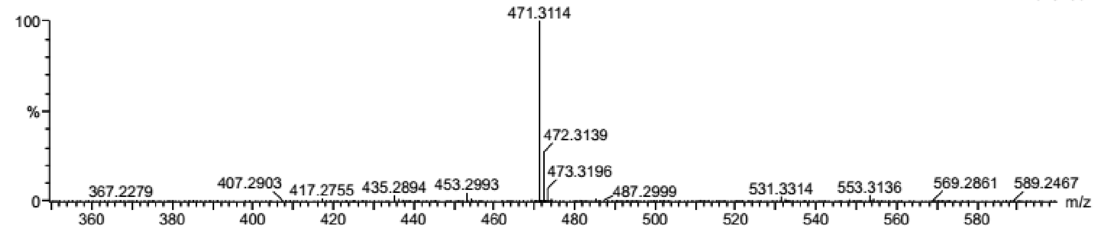


Figure S9 HRESIMS and NMR spectra of **13**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 600 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 150 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in $CDCl_3$ at 600 MHz; (F) HSQC spectrum in $CDCl_3$ at 600 MHz; (G) HMBC spectrum in $CDCl_3$ at 600 MHz; (H) NOESY spectrum in $CDCl_3$ at 600 MHz.

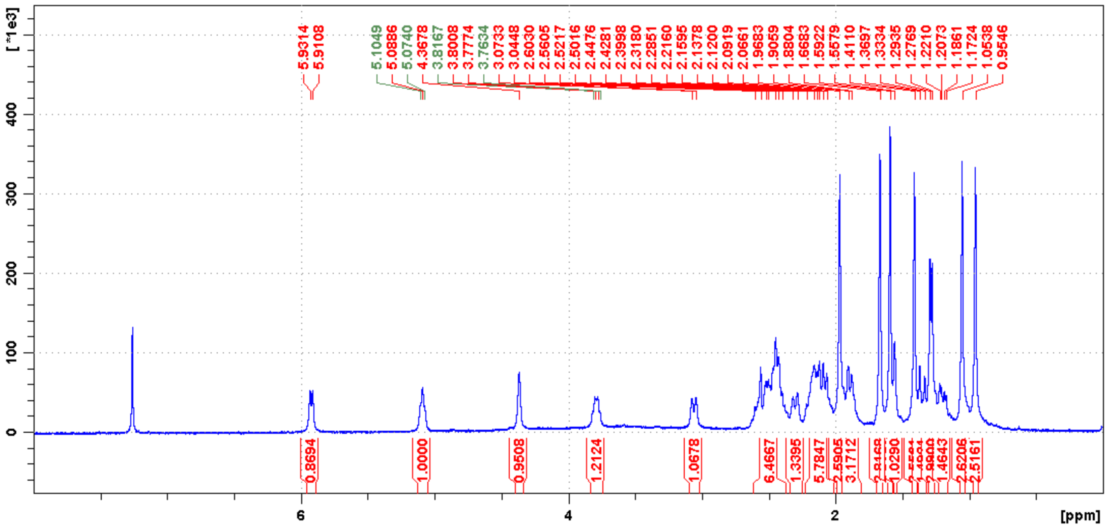
A

Monoisotopic Mass, Even Electron Ions
285 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
48
20190107_53 188 (1.518) 1: TOF MS ES+ 7.67e+004

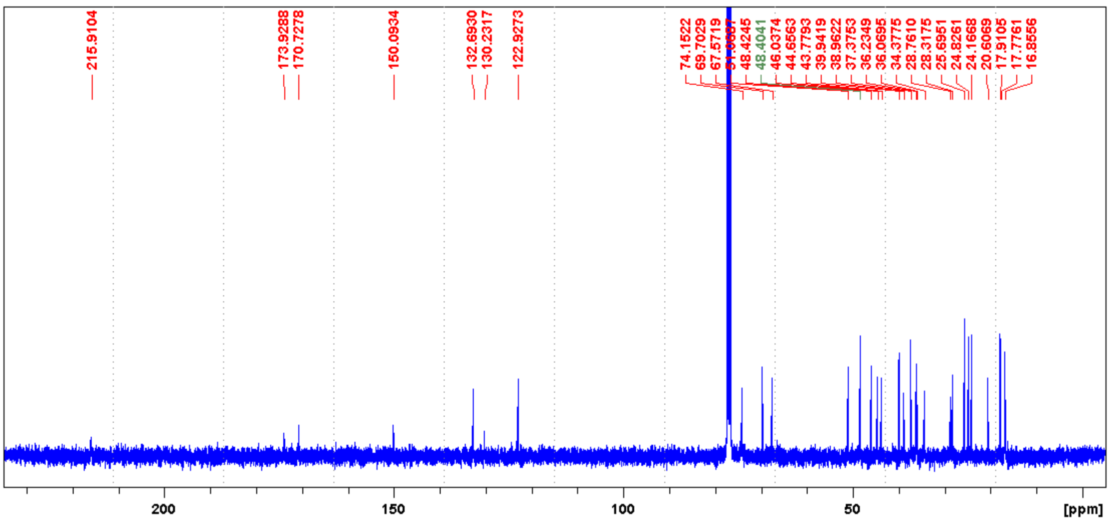


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
553.3136	553.3141	-0.5	-0.9	8.5	57.3	n/a	n/a	C31 H46 O7 Na

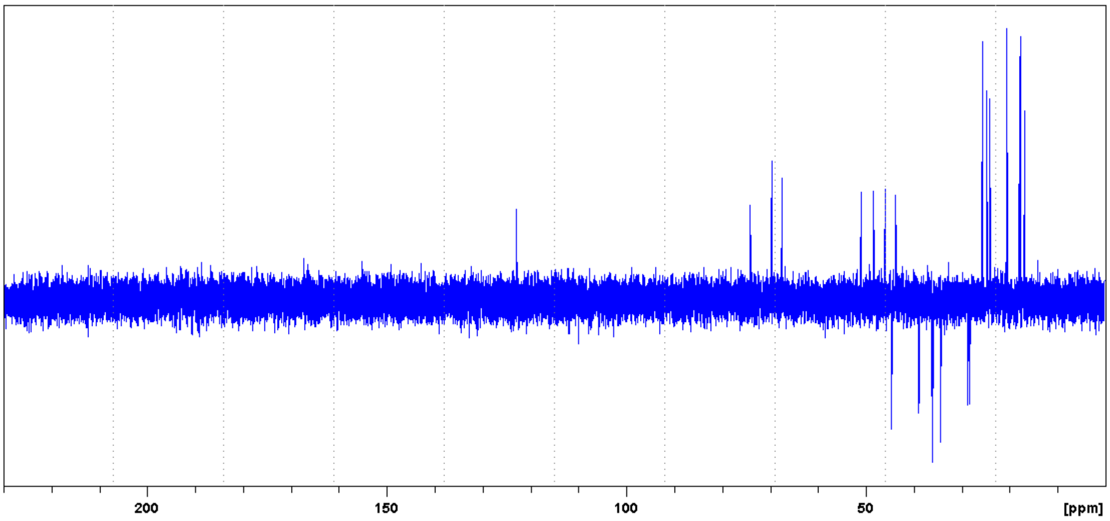
B



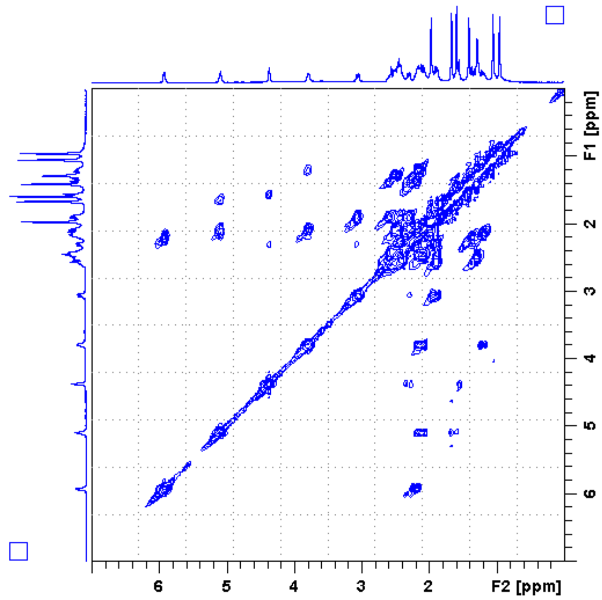
C



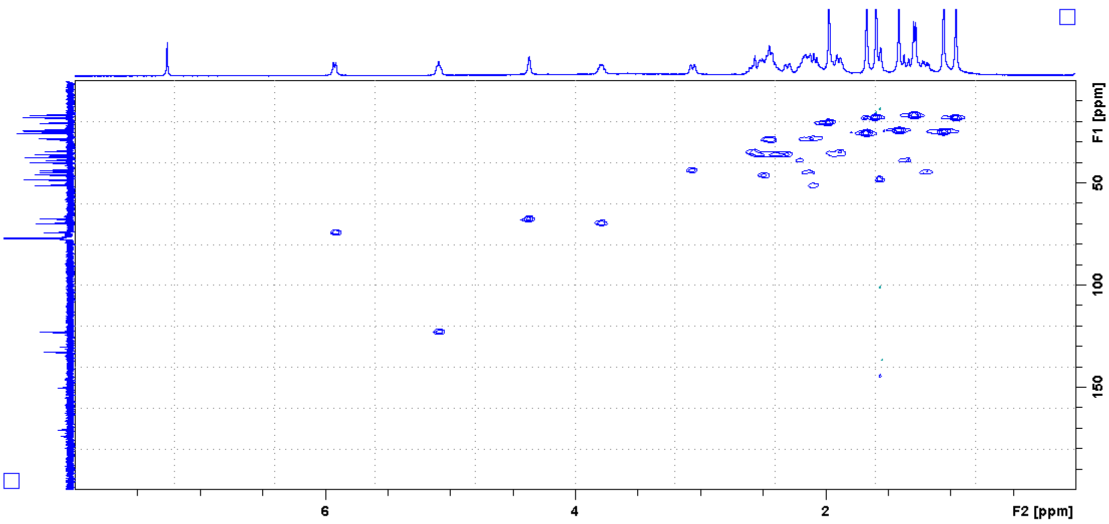
D


200
150
100
50
[ppm]

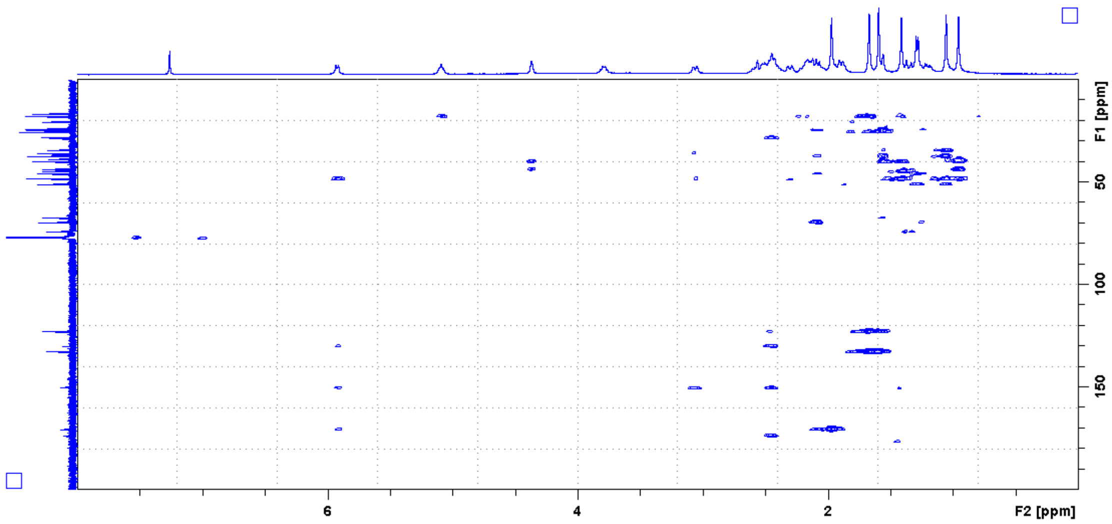
E


F1 [ppm]
2
3
4
5
6
5
4
3
2
F2 [ppm]

F


F1 [ppm]
50
100
150
6
4
2
F2 [ppm]

G



H

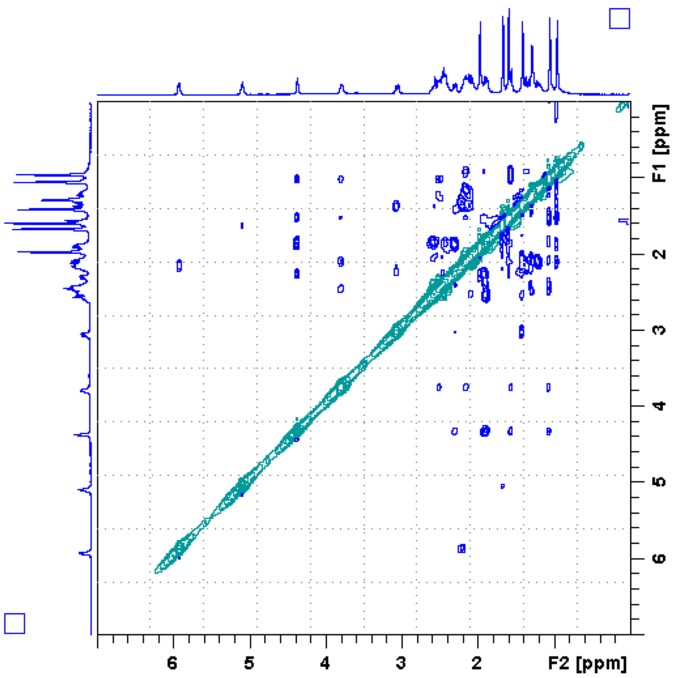
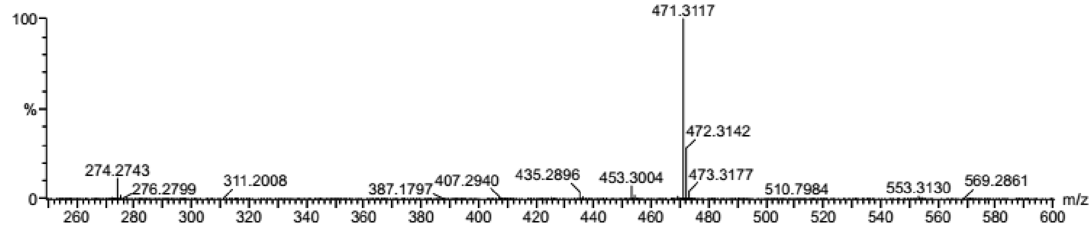


Figure S10 HRESIMS and NMR spectra of **14**.

(A) HRESIMS spectrum; (B) [1]H NMR spectrum in $CDCl_3$ at 400 MHz; (C) [13]C NMR spectrum in $CDCl_3$ at 100 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 100 MHz; (E) [1]H–[1]H COSY spectrum in $CDCl_3$ at 400 MHz; (F) HSQC spectrum in $CDCl_3$ at 400 MHz; (G) HMBC spectrum in $CDCl_3$ at 400 MHz; (H) ROESY spectrum in $CDCl_3$ at 400 MHz.

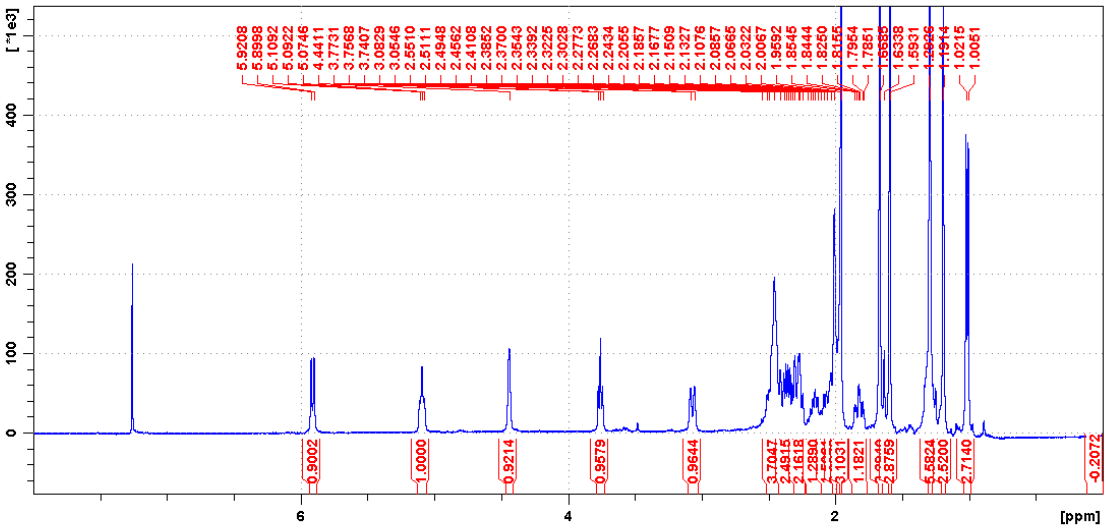
A

Monoisotopic Mass, Even Electron Ions
285 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500   H: 0-1000   O: 0-200   Na: 0-1
49
20190107_54 202 (1.635)   1: TOF MS ES+ 2.34e+005

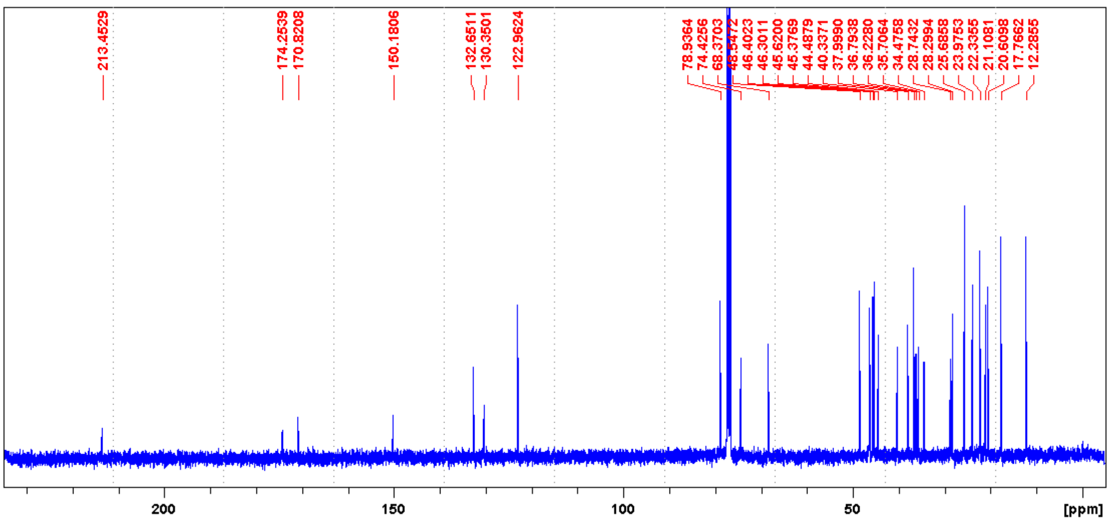


	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
553.3130	553.3141	-1.1	-2.0	8.5	79.8	0.135	87.41	C31 H46 O7 Na
	553.3107	2.3	4.2	20.5	81.8	2.072	12.59	C40 H41 O2

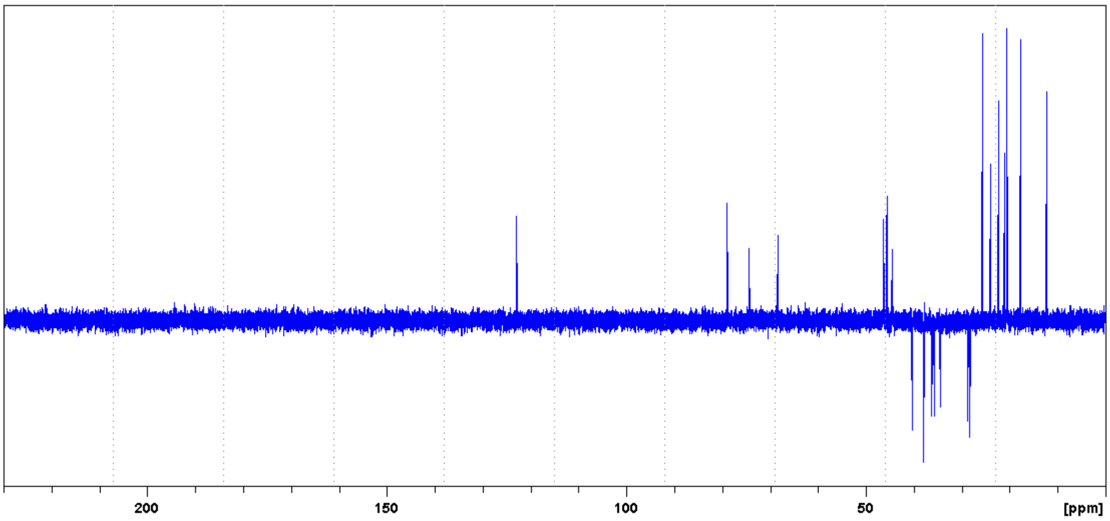
B



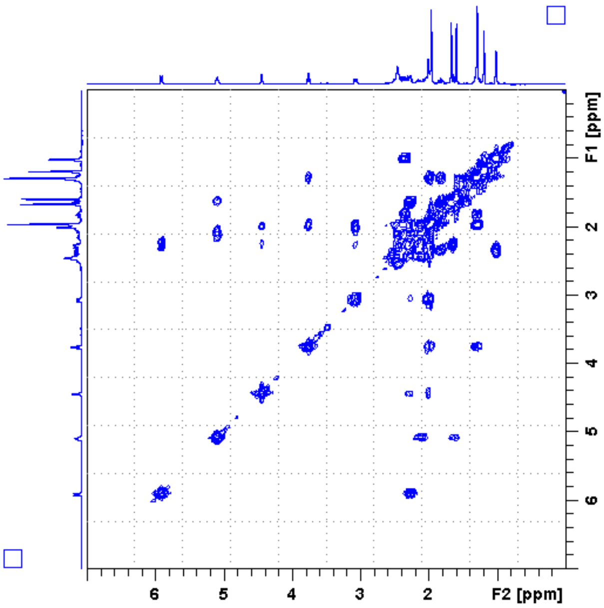
C



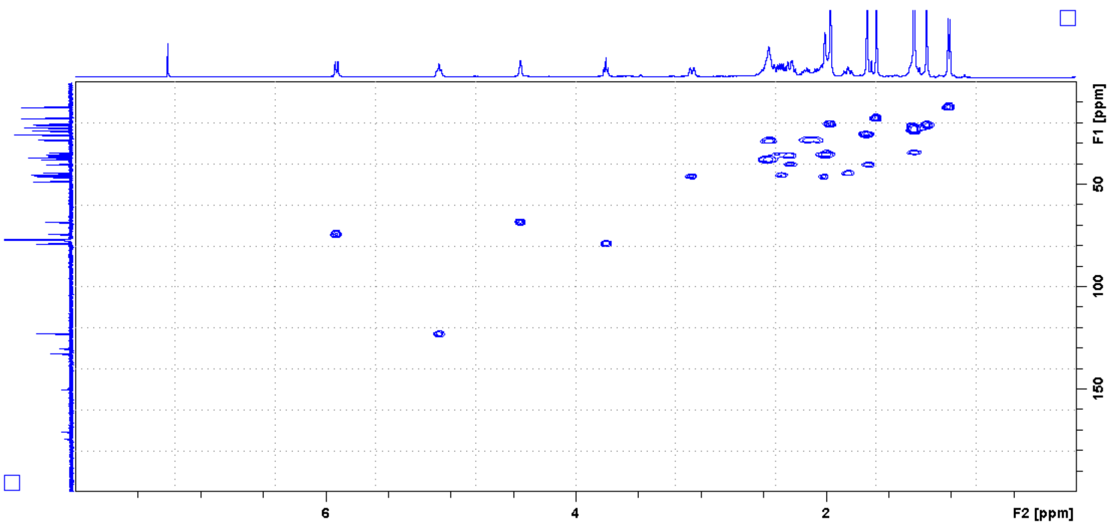
D


200
150
100
50
[ppm]

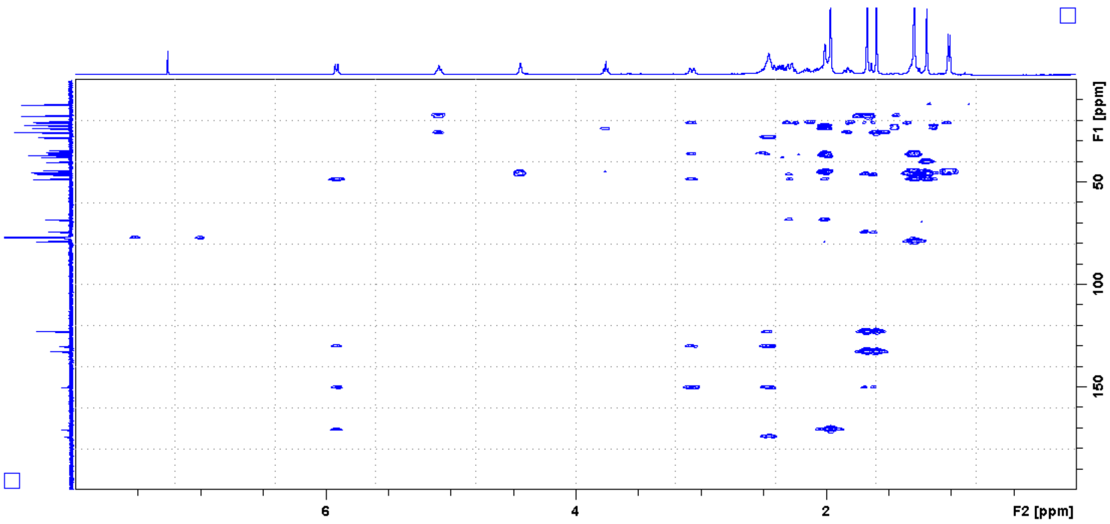
E


F1 [ppm]
2
3
4
5
6
6
5
4
3
2
F2 [ppm]

F


F1 [ppm]
50
100
150
6
4
2
F2 [ppm]

G



H

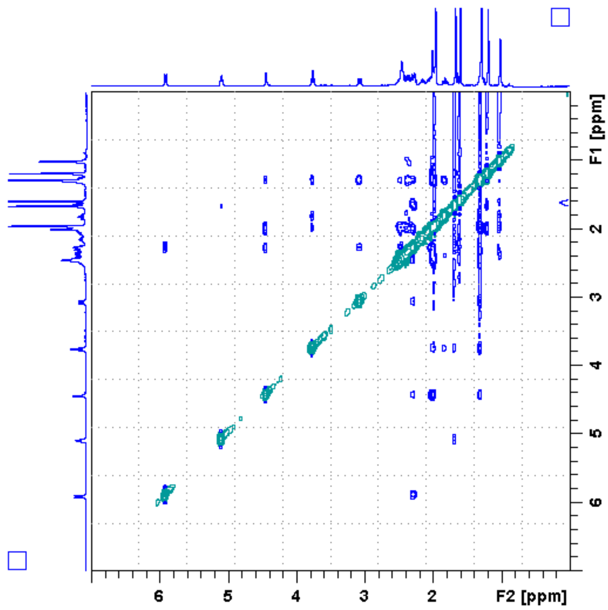
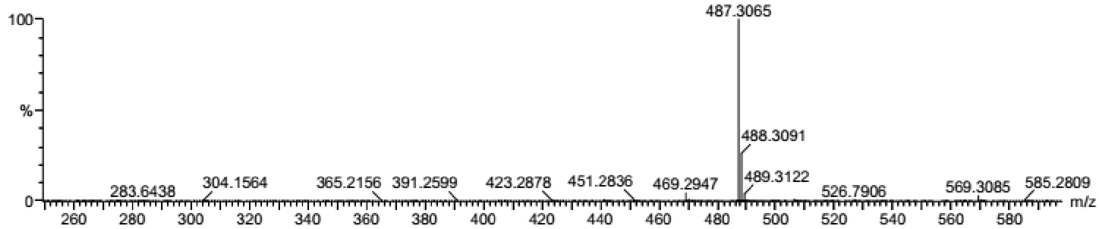


Figure S11 HRESIMS and NMR spectra of **15**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 400 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 100 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 100 MHz; (E) ^{1}H–^{1}H COSY spectrum in $CDCl_3$ at 400 MHz; (F) HSQC spectrum in $CDCl_3$ at 400 MHz; (G) HMBC spectrum in $CDCl_3$ at 400 MHz; (H) ROESY spectrum in $CDCl_3$ at 400 MHz.

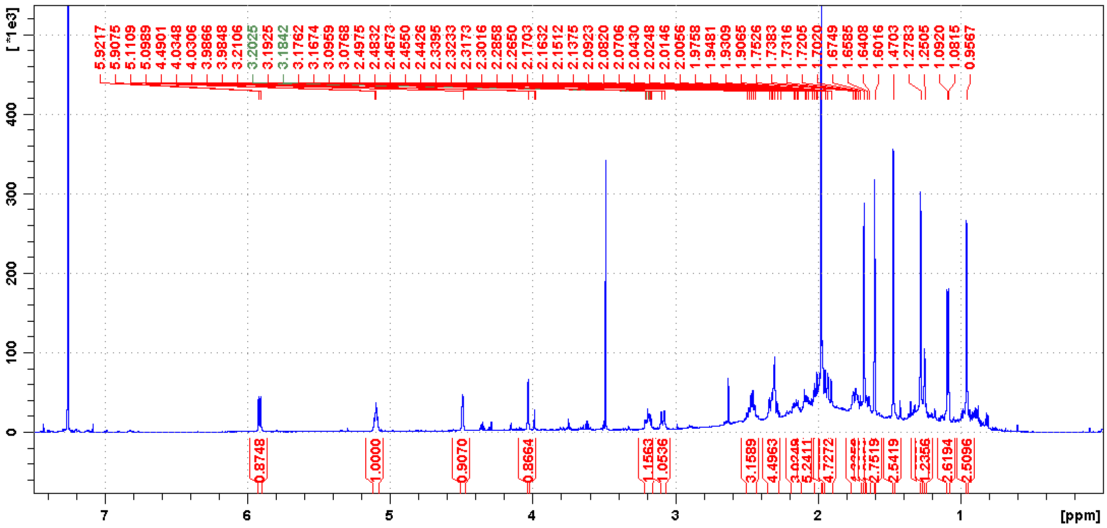
A

Monoisotopic Mass, Even Electron Ions
300 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
50
20190107_55 173 (1.406)

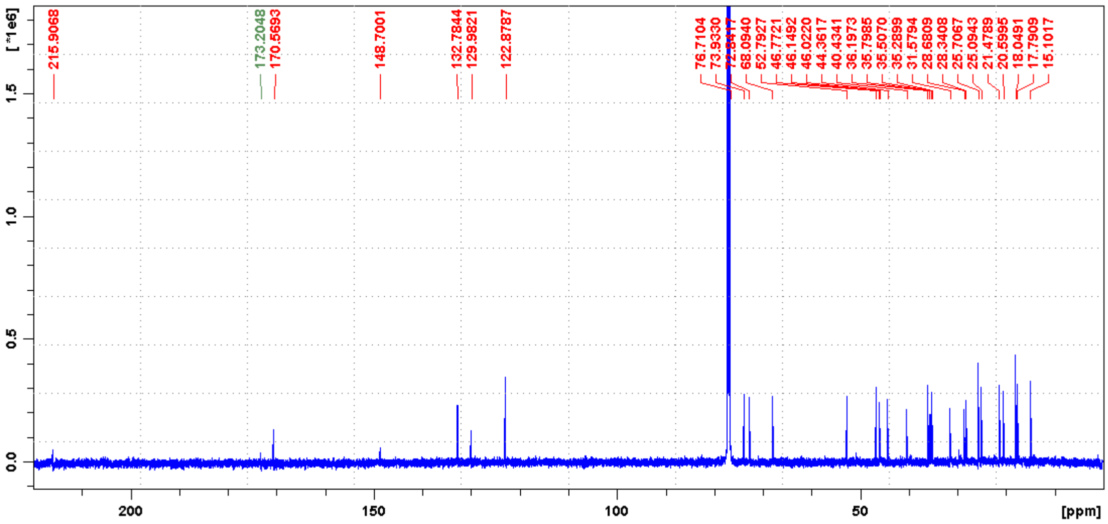


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
569.3085	569.3090	-0.5	-0.9	8.5	75.6	n/a	n/a	C31 H46 O8 Na

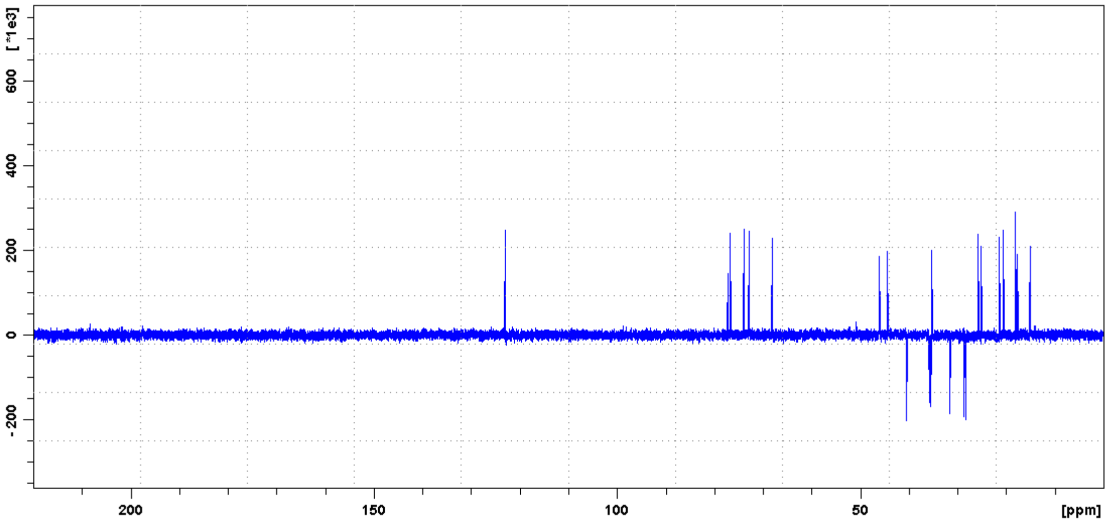
B



C



D


[*1e3]
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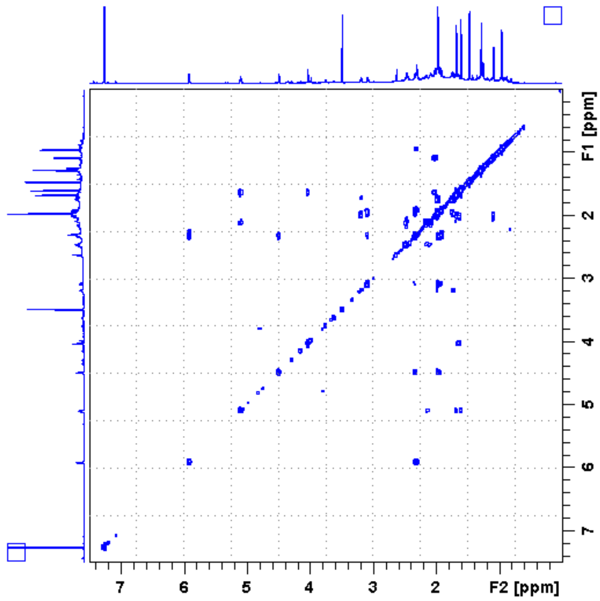
400
200
0
-200
200
150
100
50
[ppm]

E


F1 [ppm]
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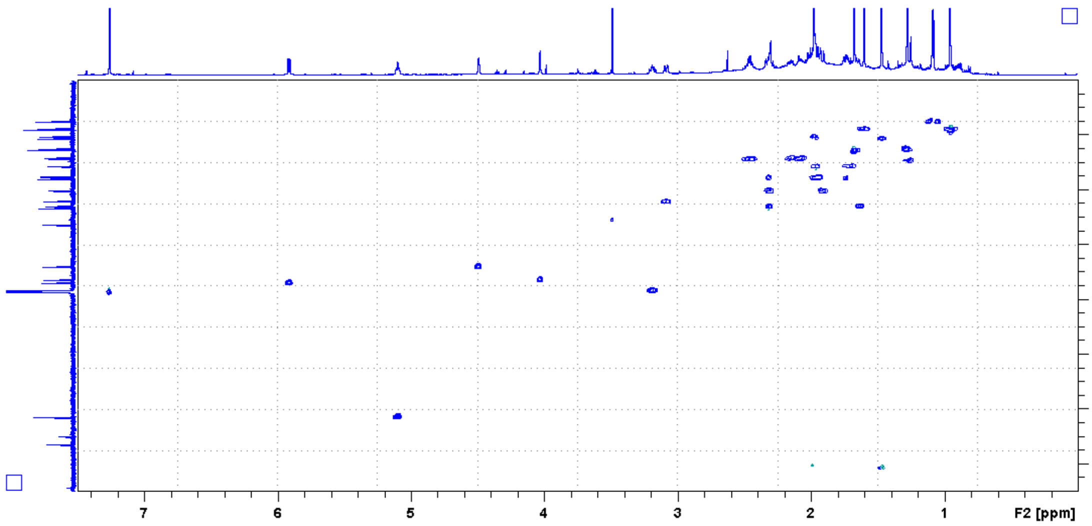
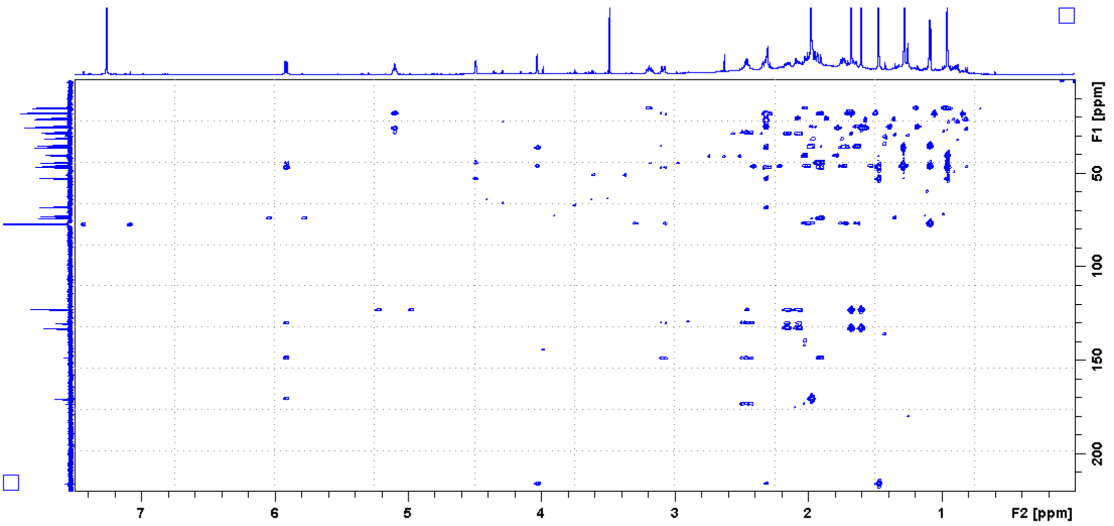
3
4
5
6
7
F2 [ppm]

F


F1 [ppm]
20
40
60
80
100
120
140
7
6
5
4
3
2
1
F2 [ppm]

G



H

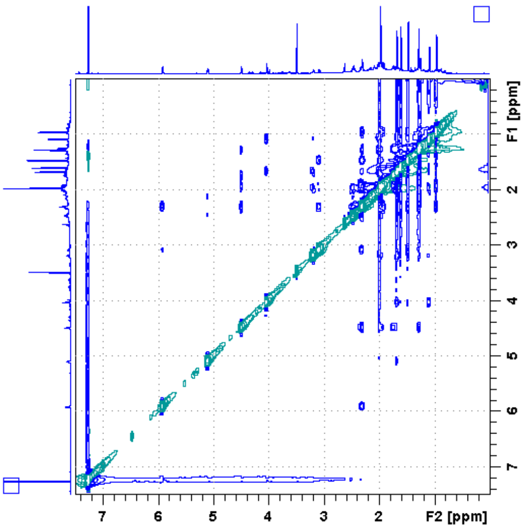
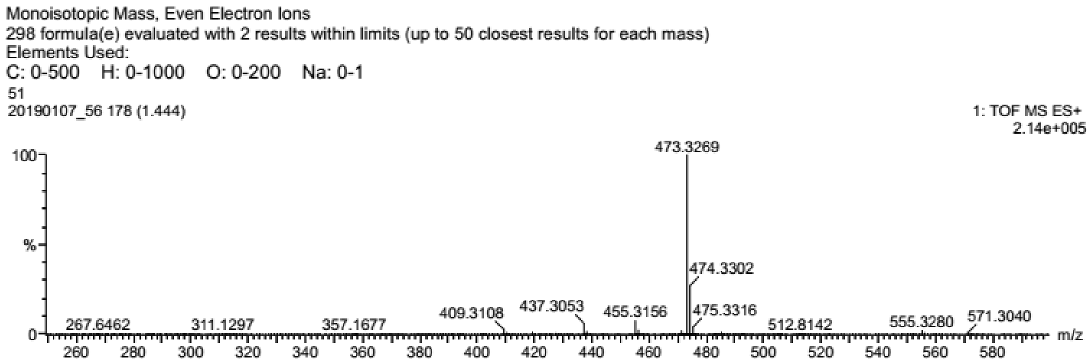


Figure S12 HRESIMS and NMR spectra of **17**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 600 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 150 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in $CDCl_3$ at 600 MHz; (F) HSQC spectrum in $CDCl_3$ at 600 MHz; (G) HMBC spectrum in $CDCl_3$ at 600 MHz; (H) ROESY spectrum in $CDCl_3$ at 400 MHz.

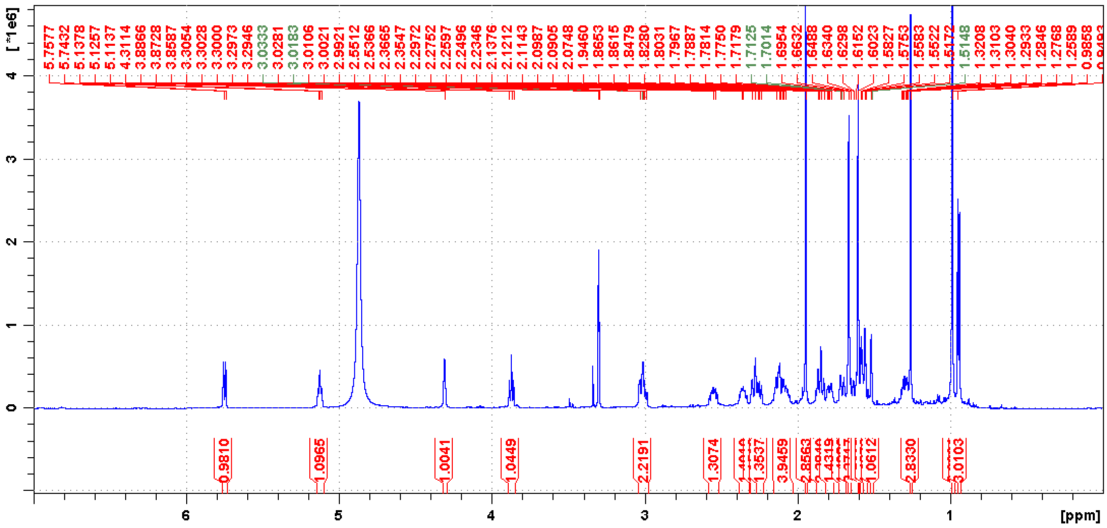
A



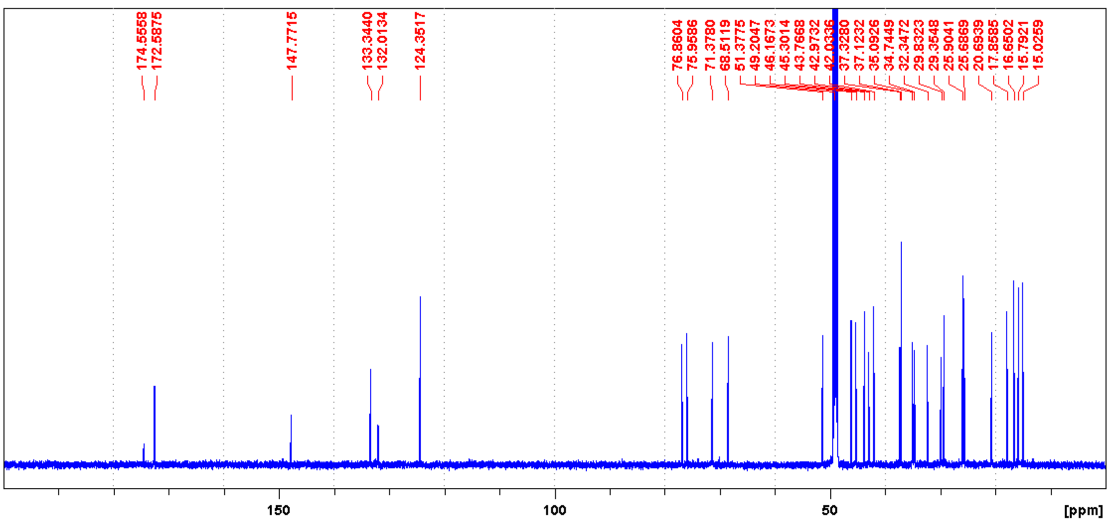
Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
555.3280	555.3298	-1.8	-3.2	7.5	59.8	0.006	99.36	C31 H48 O7 Na
	555.3263	1.7	3.1	19.5	64.9	5.049	0.64	C40 H43 O2

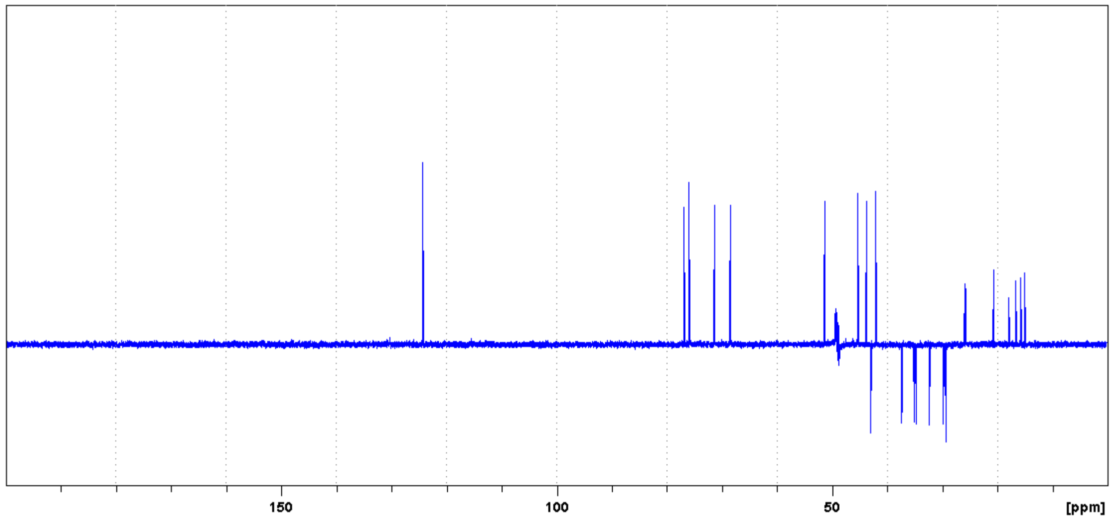
B



C



D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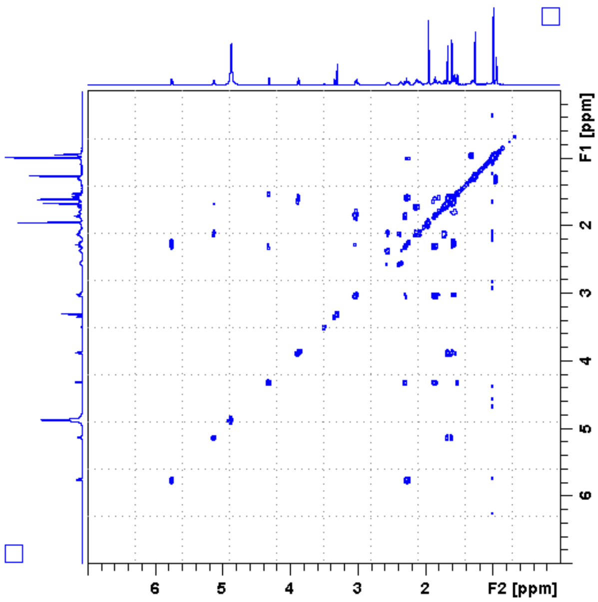
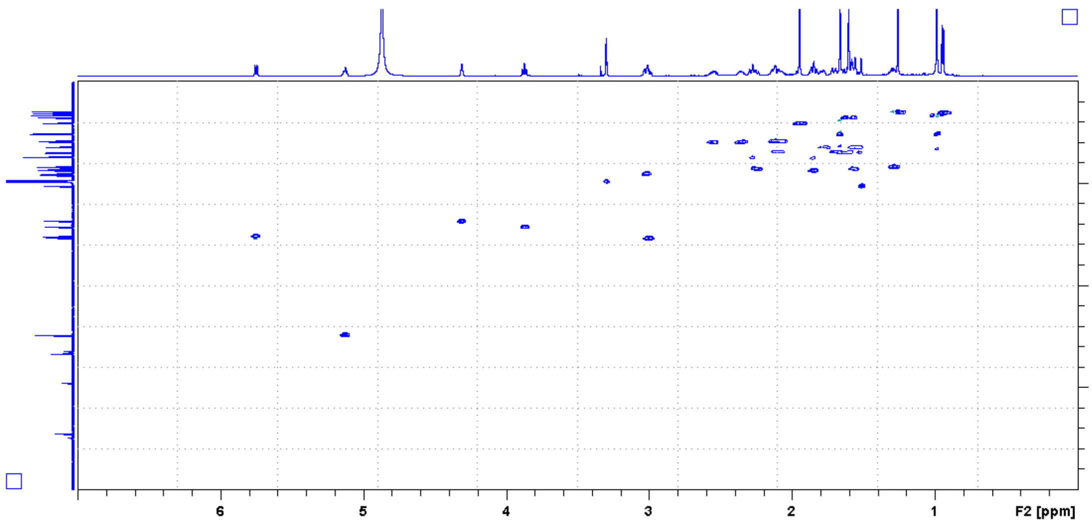
100
50
[ppm]

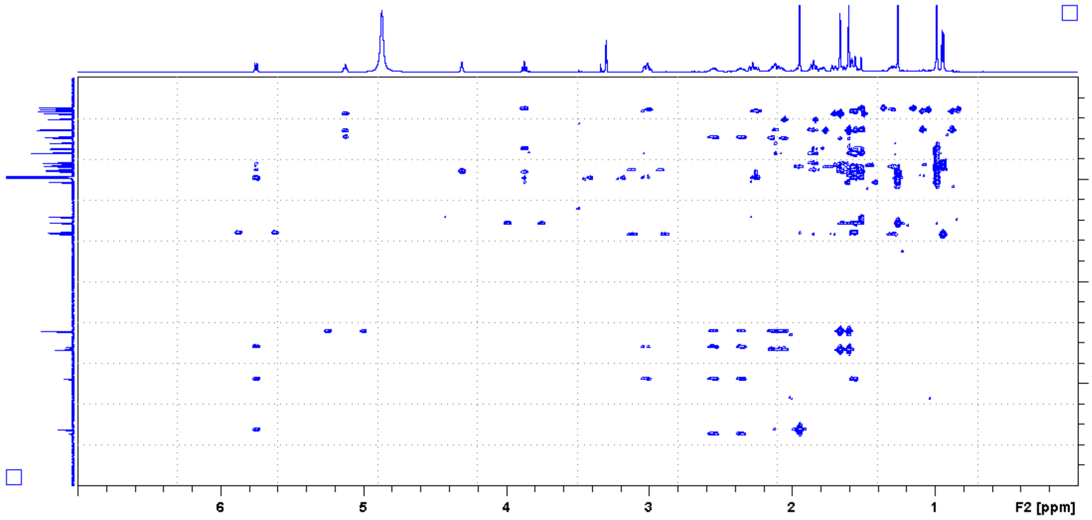
E


F1 [ppm]
2
3
4
5
6
6
5
4
3
2
F2 [ppm]

F


F1 [ppm]
50
100
150
6
5
4
3
2
1
F2 [ppm]

G



H

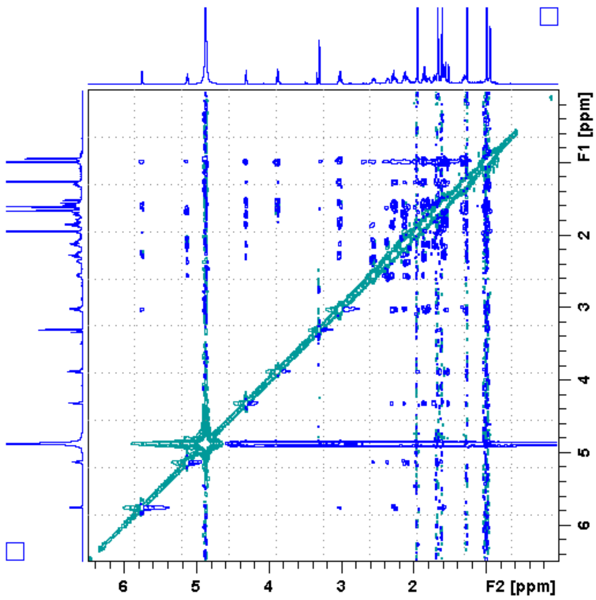
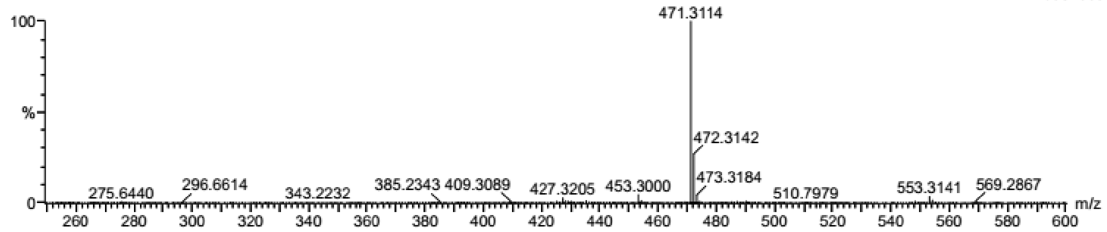


Figure S13 HRESIMS and NMR spectra of **18**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in CD_3OD at 600 MHz; (C) ^{13}C NMR spectrum in CD_3OD at 150 MHz; (D) DEPT 135 spectrum in CD_3OD at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in CD_3OD at 600 MHz; (F) HSQC spectrum in CD_3OD at 600 MHz; (G) HMBC spectrum in CD_3OD at 600 MHz; (H) NOESY spectrum in CD_3OD at 600 MHz.

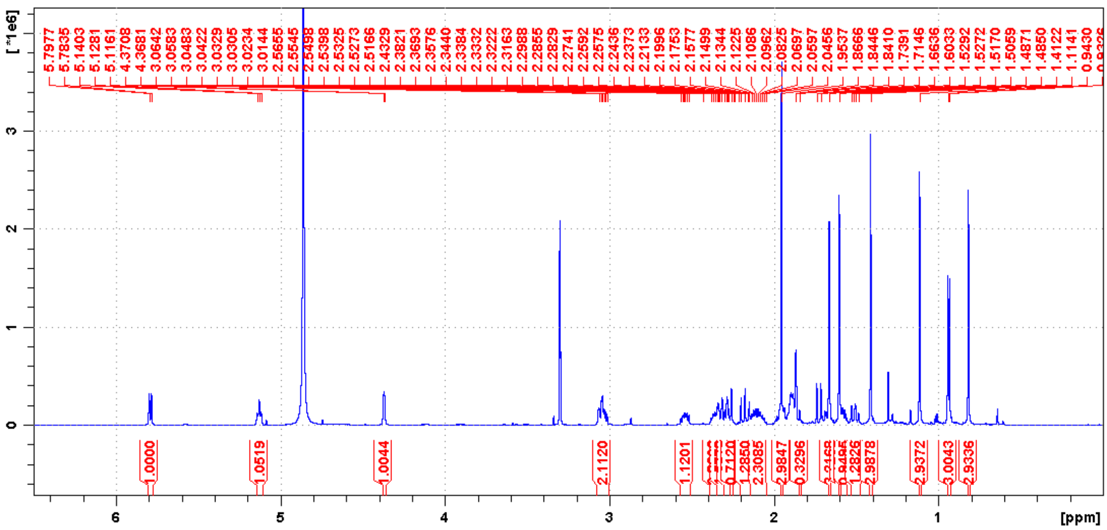
A

Monoisotopic Mass, Even Electron Ions
285 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500   H: 0-1000   O: 0-200   Na: 0-1
44
20190107_49 191 (1.541)   1: TOF MS ES+ 1.00e+005

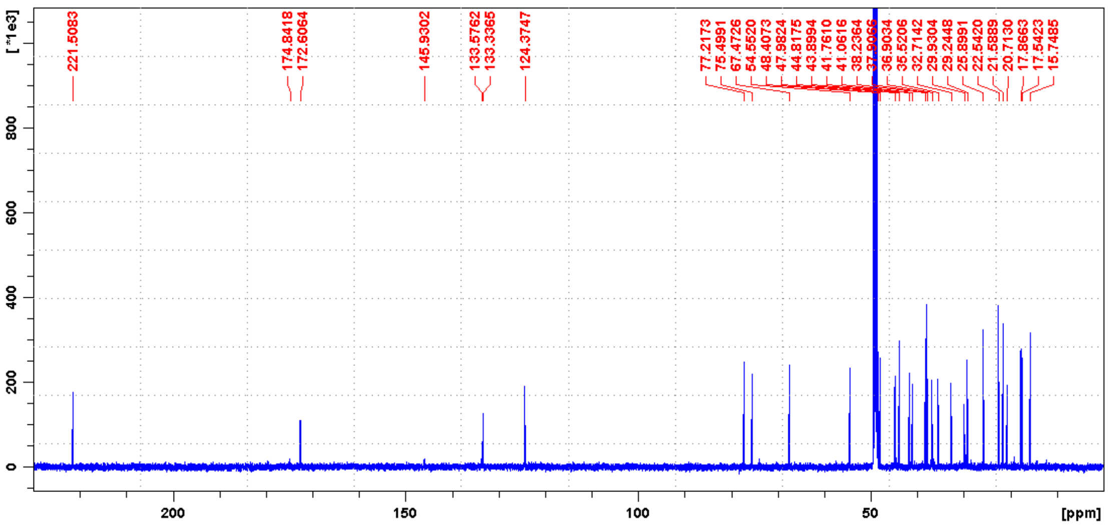


Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
553.3141	553.3141	0.0	0.0	8.5	36.3	1.883	15.21	C31 H46 O7 Na
	553.3165	-2.4	-4.3	11.5	34.6	0.165	84.79	C33 H45 O7

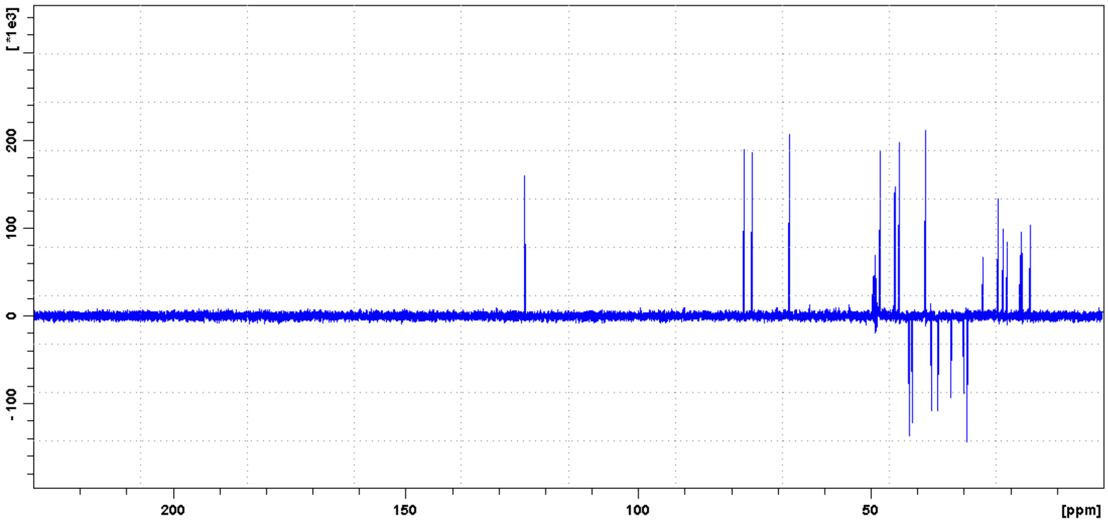
B



C



D



[*1e3]
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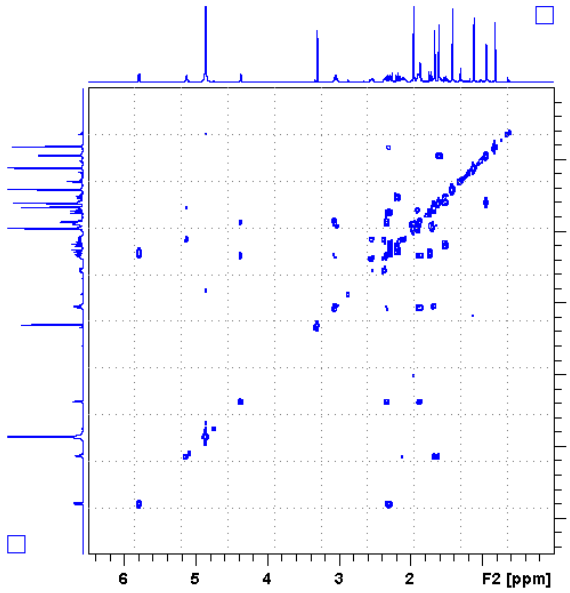
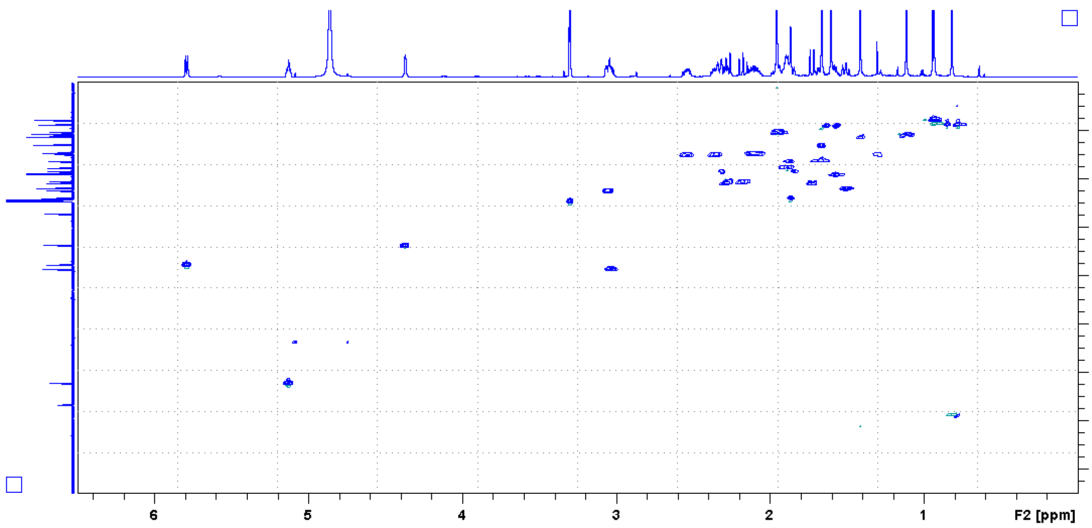
100
0
-100
200
150
100
50
[ppm]

E



F1 [ppm]
2
3
4
5
6
6
5
4
3
2
F2 [ppm]

F



F1 [ppm]
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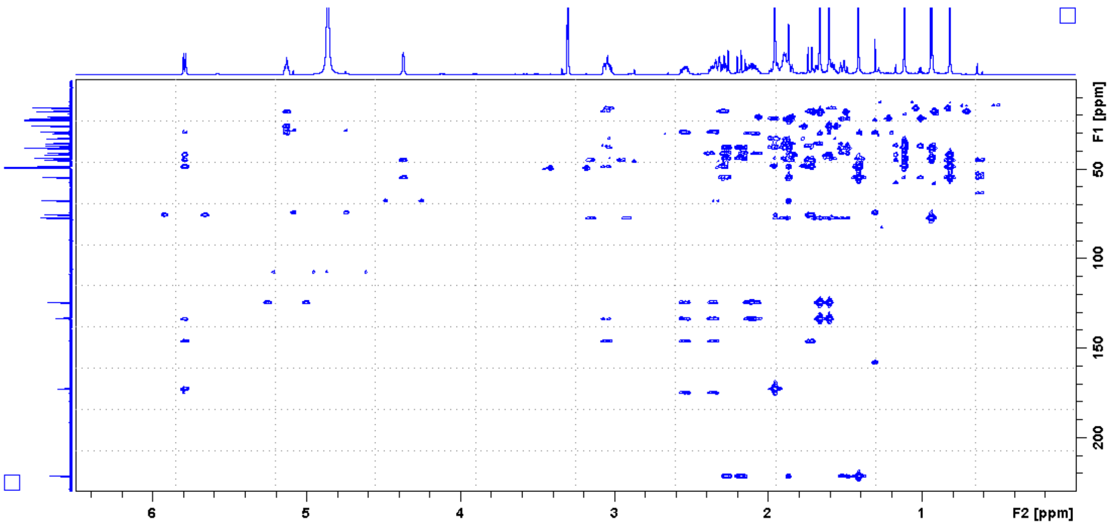
40
60
80
100
120
140
160
6
5
4
3
2
1
F2 [ppm]

G



H

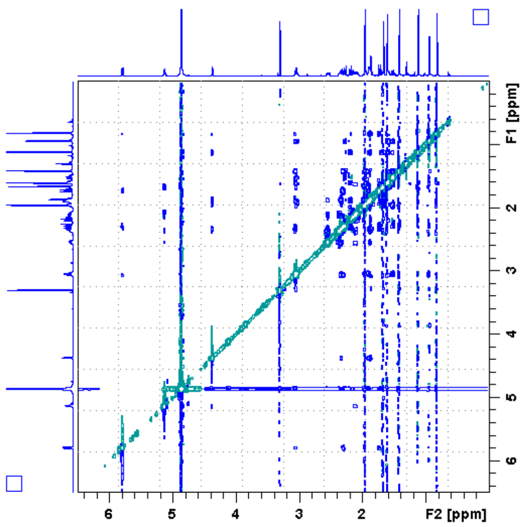


Figure S14 HRESIMS and NMR spectra of **19**.

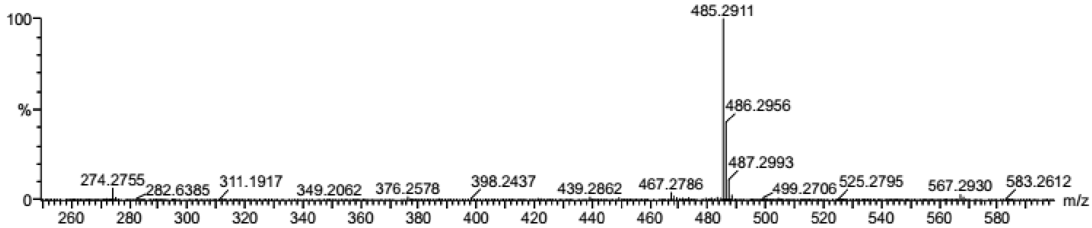
(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in CD_3OD at 600 MHz; (C) ^{13}C NMR spectrum in CD_3OD at 150 MHz; (D) DEPT 135 spectrum in CD_3OD at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in CD_3OD at 600 MHz; (F) HSQC spectrum in CD_3OD at 600 MHz; (G) HMBC spectrum in CD_3OD at 600 MHz; (H) NOESY spectrum in CD_3OD at 600 MHz.

A

Monoisotopic Mass, Even Electron Ions
310 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1

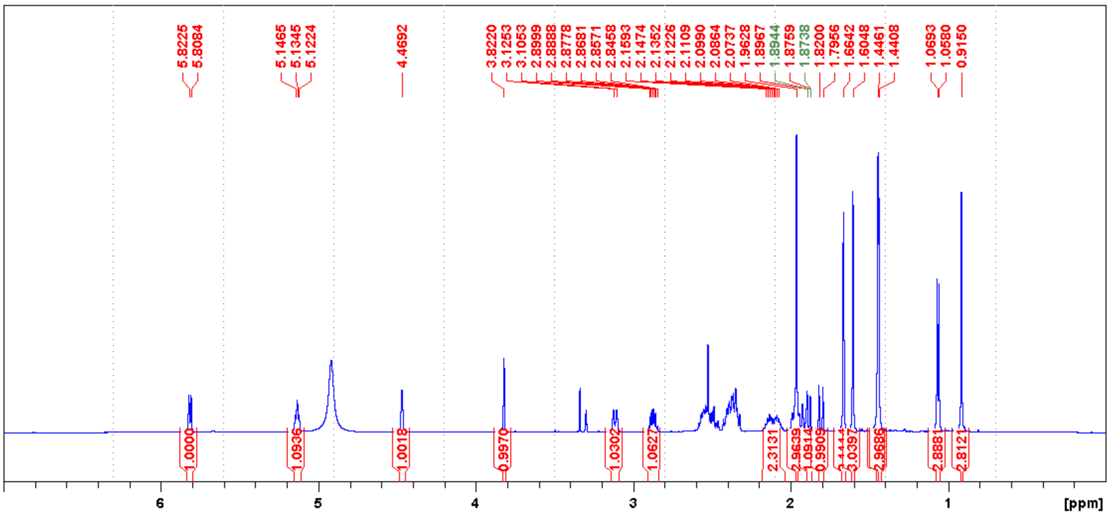
45
20190107_50 206 (1.664)

1: TOF MS ES+
6.99e+004

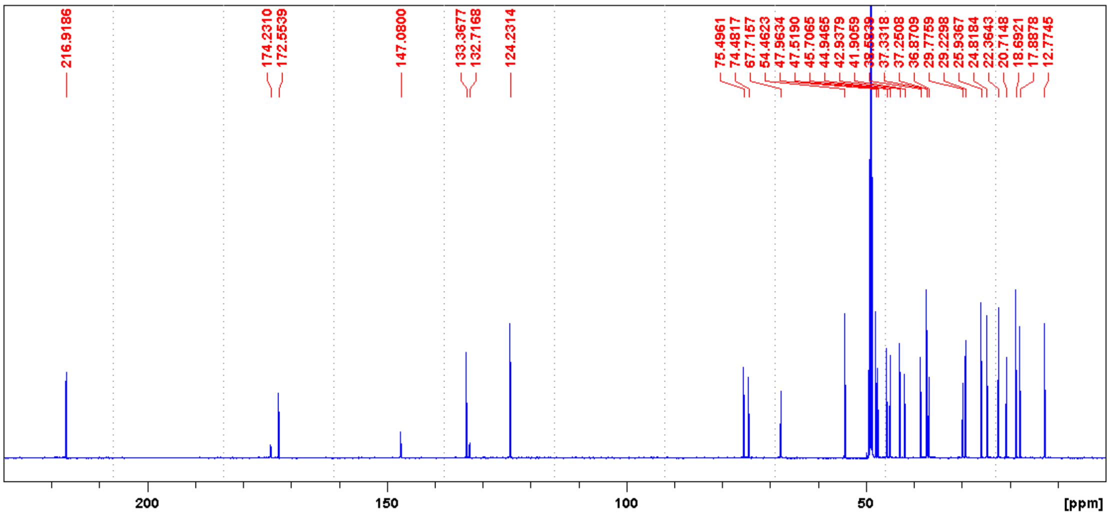


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
567.2930	567.2934	-0.4	-0.7	9.5	34.3	0.833	43.47	C31 H44 O8 Na
	567.2958	-2.8	-4.9	12.5	34.0	0.570	56.53	C33 H43 O8

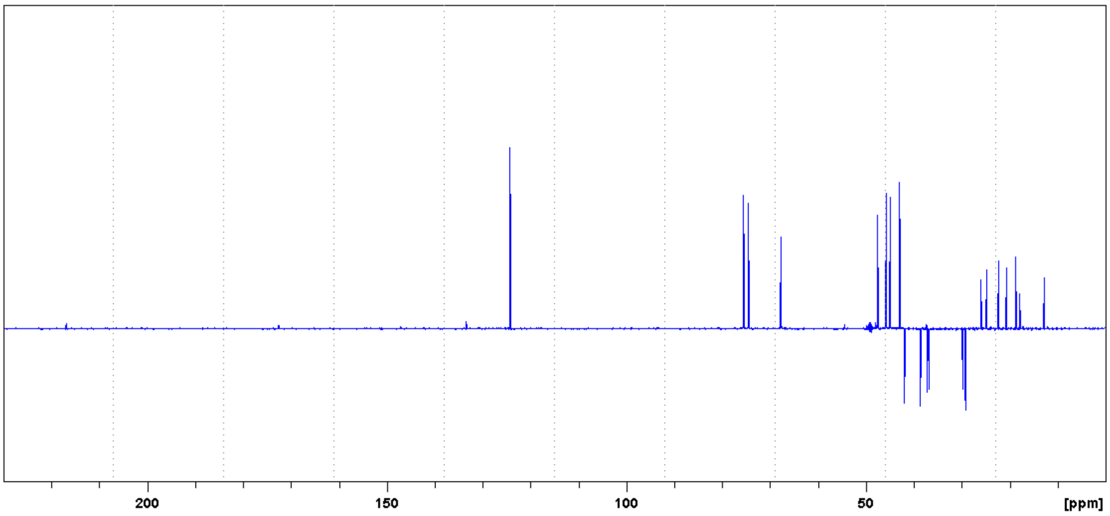
B



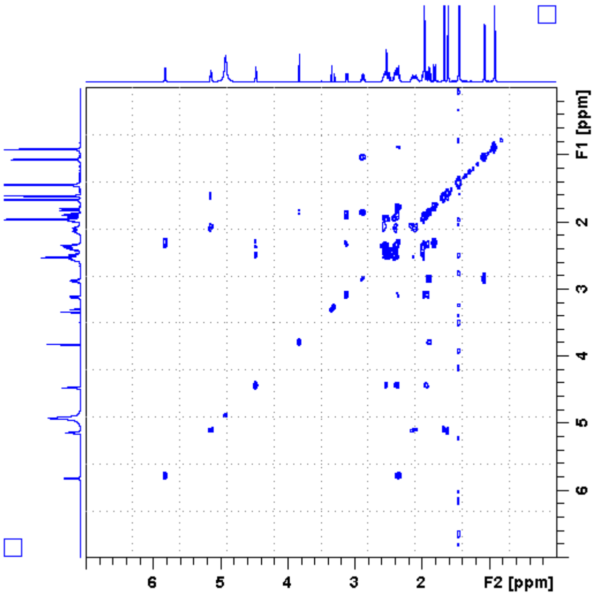
C



D


200
150
100
50
[ppm]

E


F1 [ppm]
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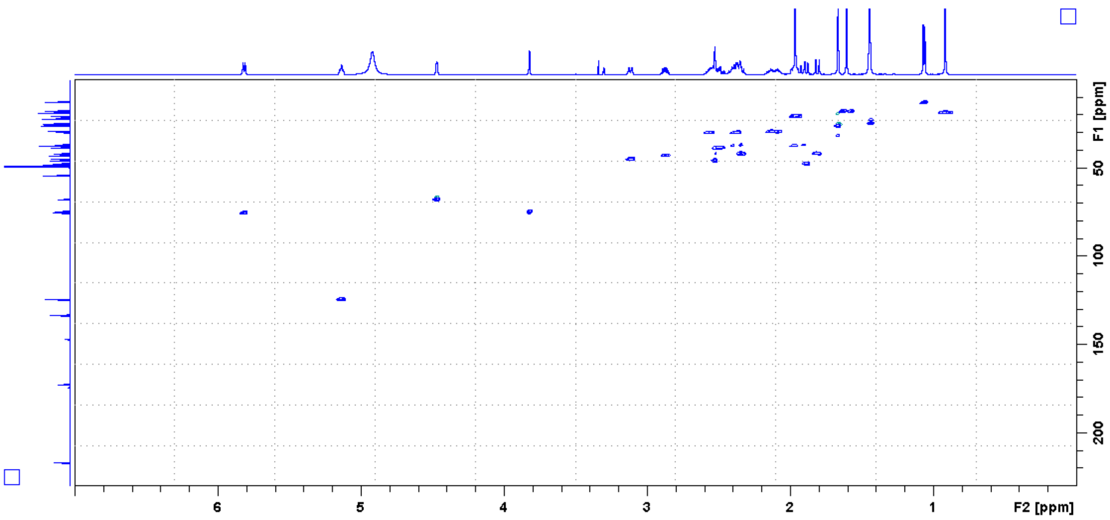
4
5
6
6
5
4
3
2
F2 [ppm]

F


F1 [ppm]
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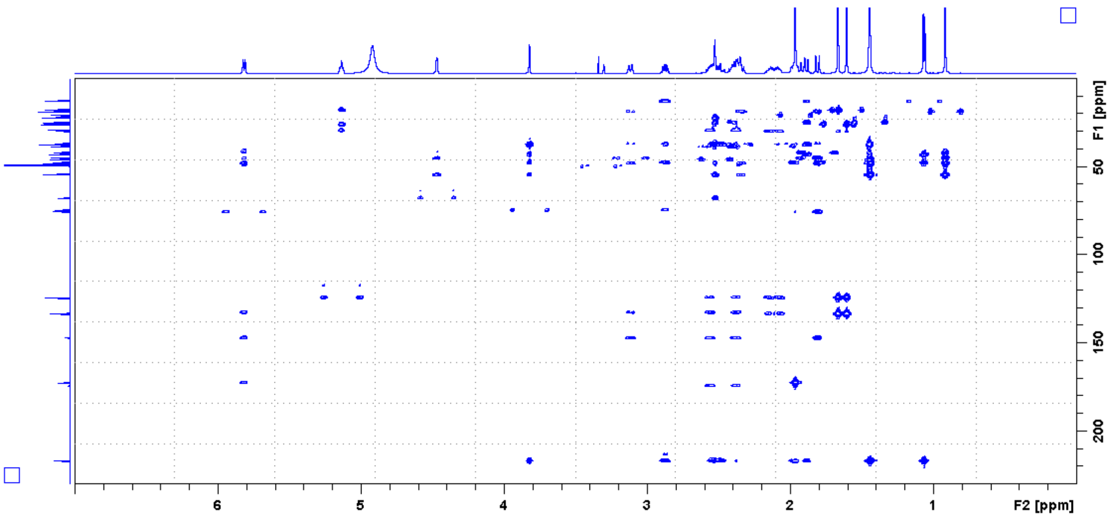
100
150
200
6
5
4
3
2
1
F2 [ppm]

G



H

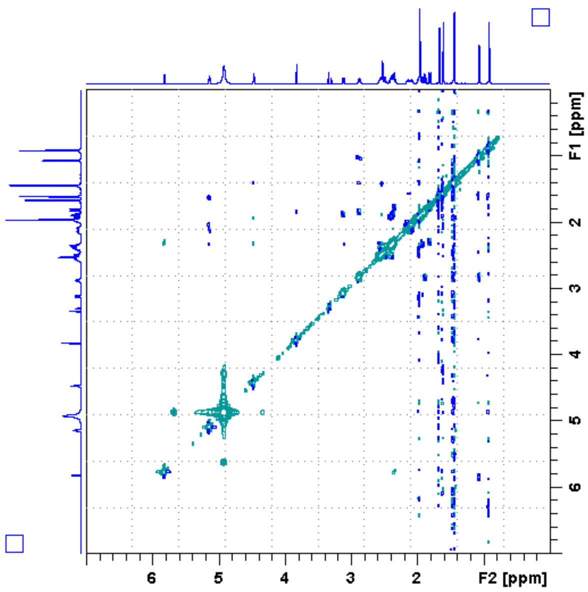
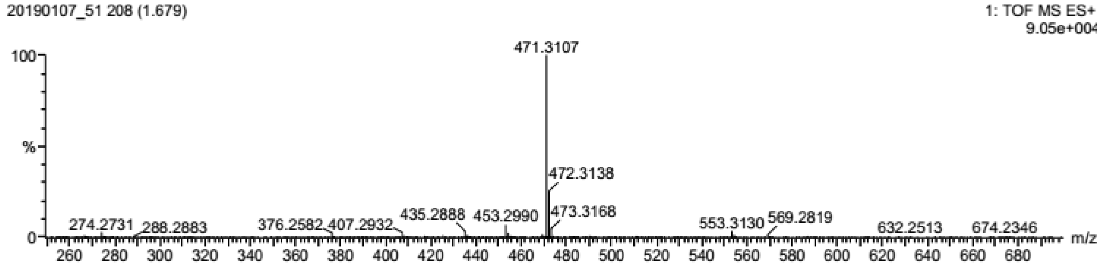


Figure S15 HRESIMS and NMR spectra of **20**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in CD_3OD at 600 MHz; (C) ^{13}C NMR spectrum in CD_3OD at 150 MHz; (D) DEPT 135 spectrum in CD_3OD at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in CD_3OD at 600 MHz; (F) HSQC spectrum in CD_3OD at 600 MHz; (G) HMBC spectrum in CD_3OD at 600 MHz; (H) NOESY spectrum in CD_3OD at 600 MHz.

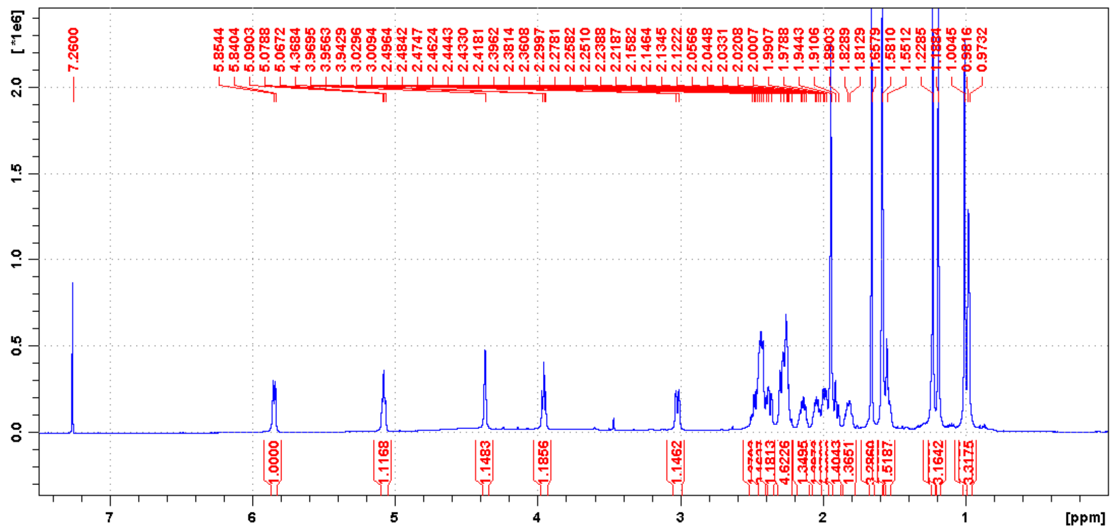
A

Monoisotopic Mass, Even Electron Ions
285 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
46
20190107_51 208 (1.679)

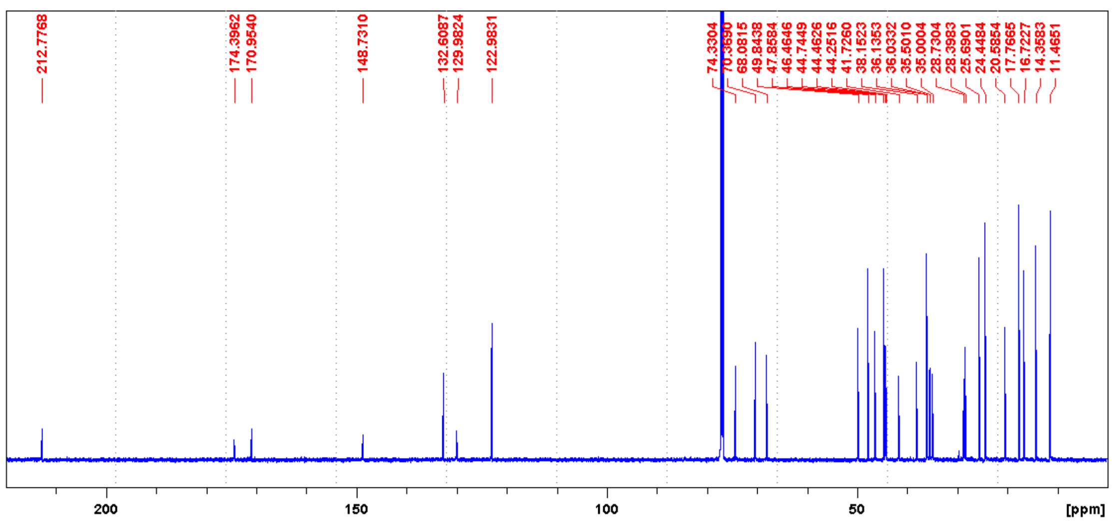


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
553.3130	553.3141	-1.1	-2.0	8.5	67.8	0.048	95.34	C31 H46 O7 Na
	553.3107	2.3	4.2	20.5	70.8	3.066	4.66	C40 H41 O2

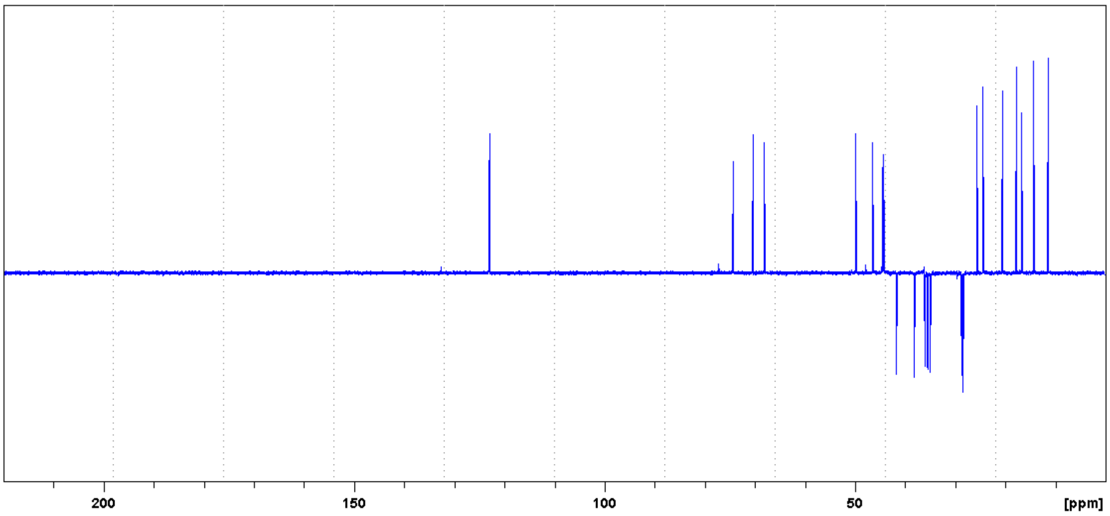
B



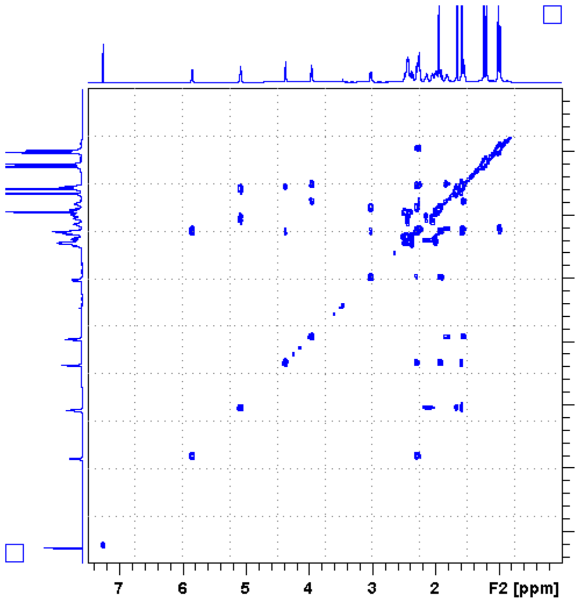
C



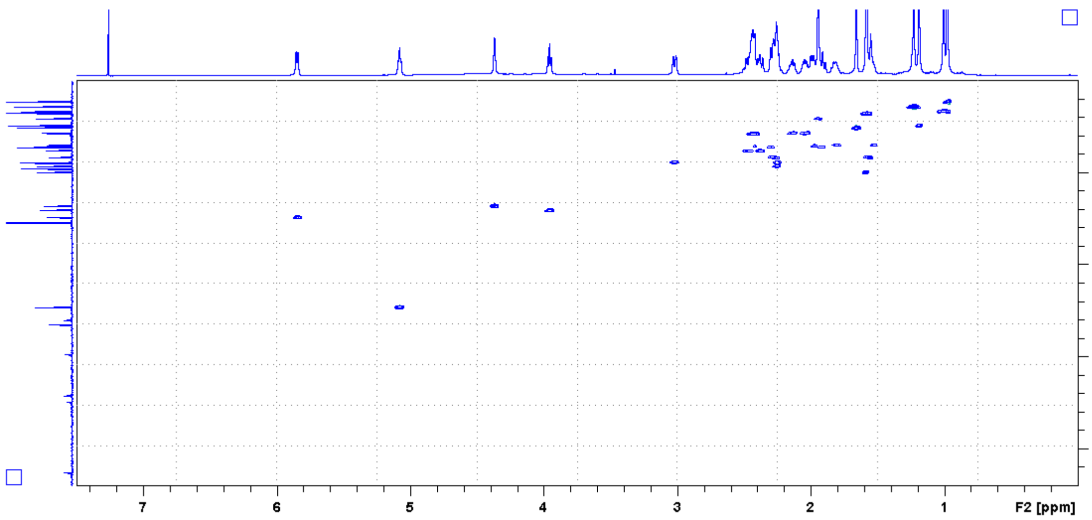
D



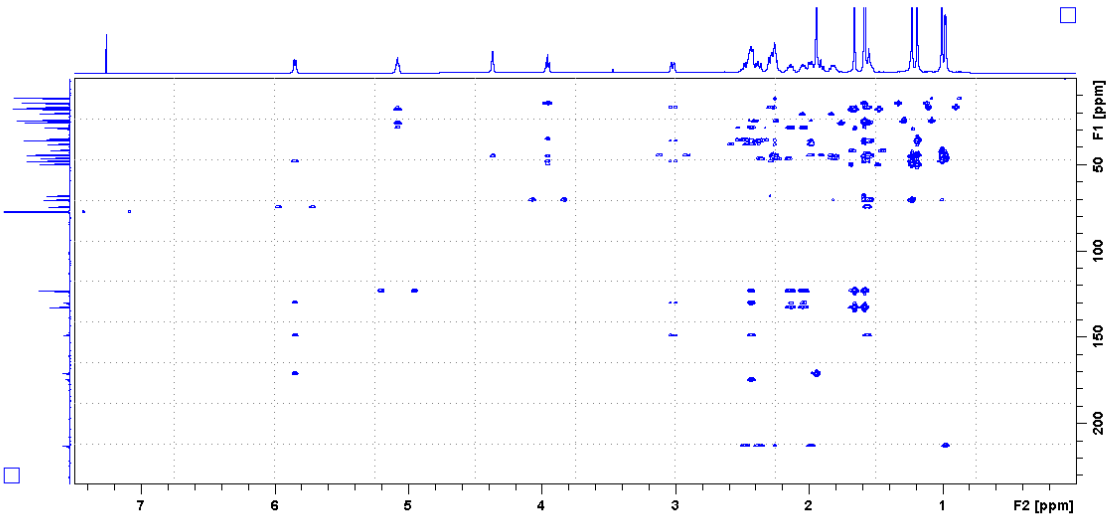
E



F



G



H

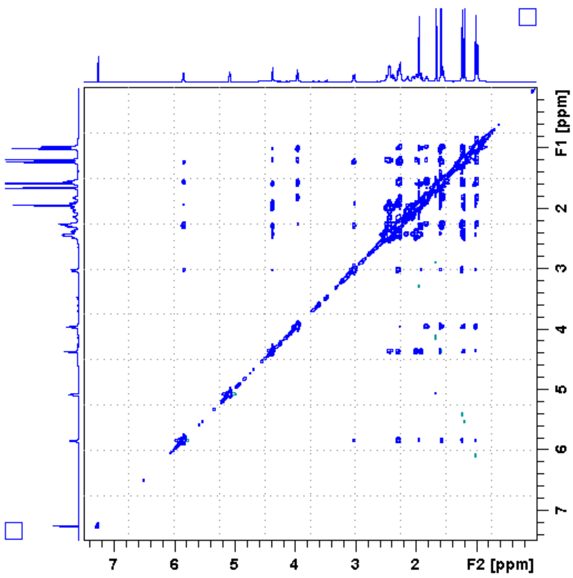
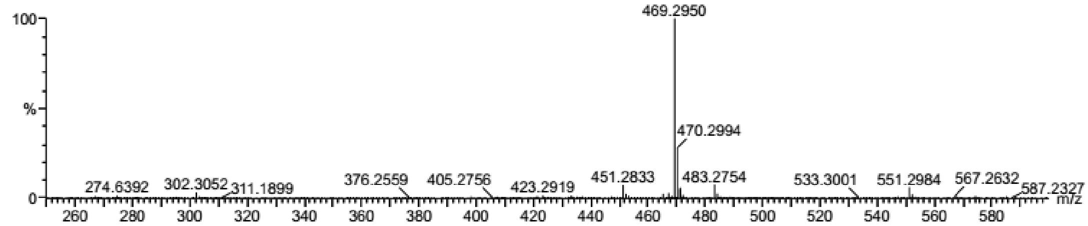


Figure S16 HRESIMS and NMR spectra of **21**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 600 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 150 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in $CDCl_3$ at 600 MHz; (F) HSQC spectrum in $CDCl_3$ at 600 MHz; (G) HMBC spectrum in $CDCl_3$ at 600 MHz; (H) NOESY spectrum in $CDCl_3$ at 600 MHz.

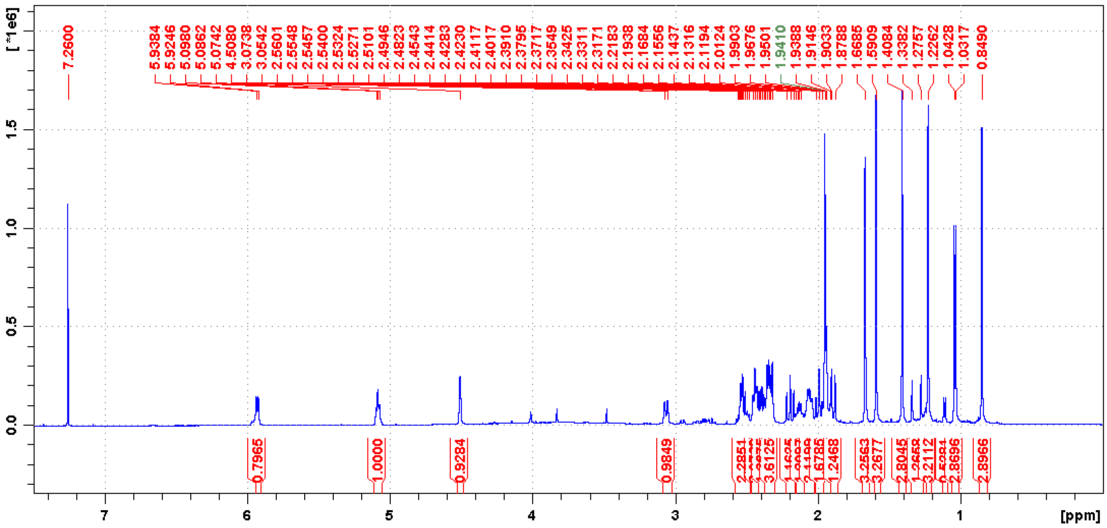
A

Monoisotopic Mass, Even Electron Ions
295 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
47
20190107_52 220 (1.780)

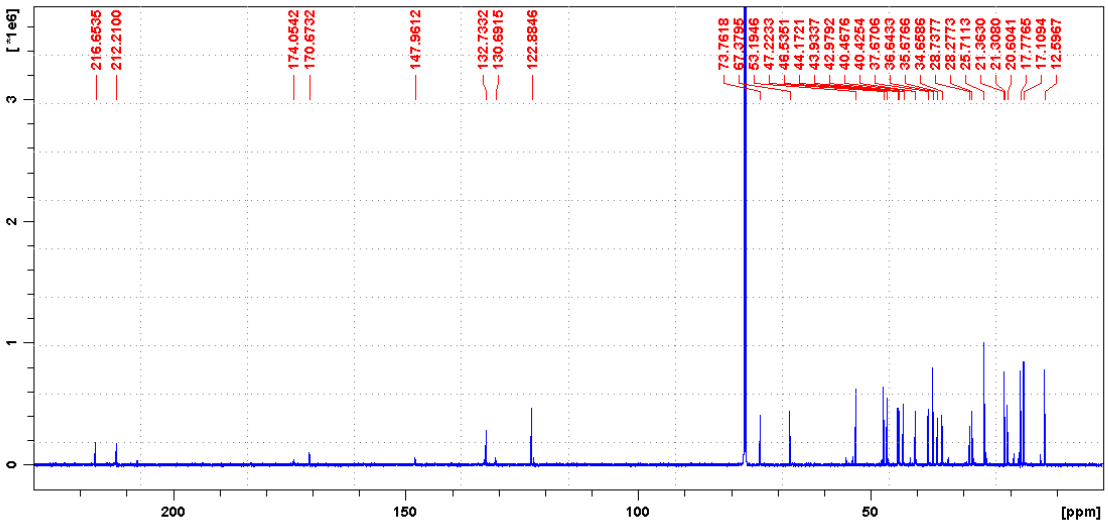


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
551.2984	551.2985	-0.1	-0.2	9.5	53.1	0.273	76.13	C31 H44 O7 Na
	551.3009	-2.5	-4.5	12.5	54.3	1.432	23.87	C33 H43 O7

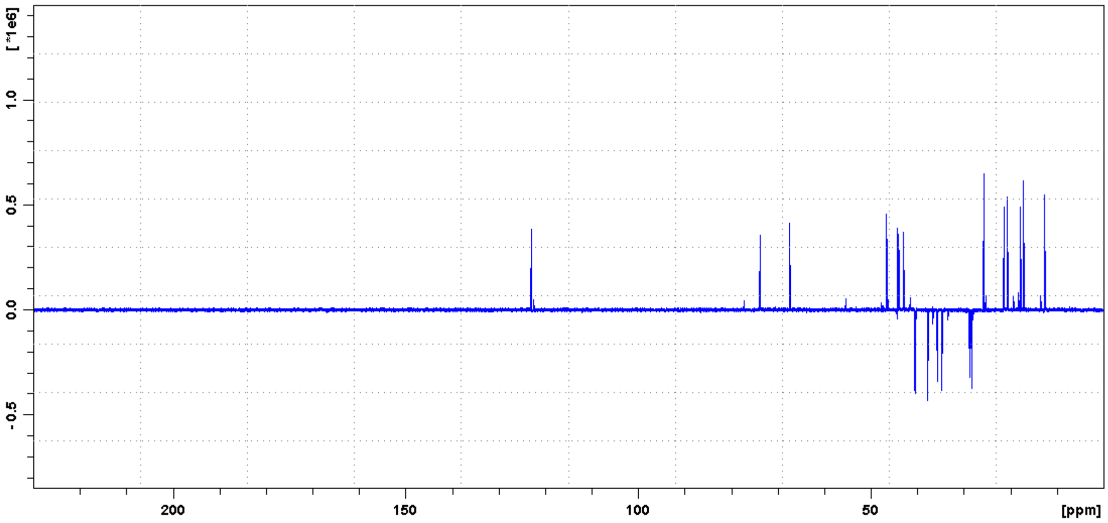
B



C



D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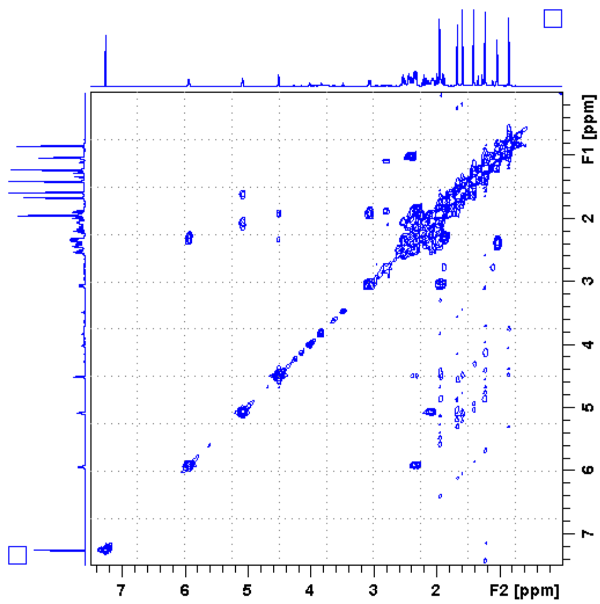
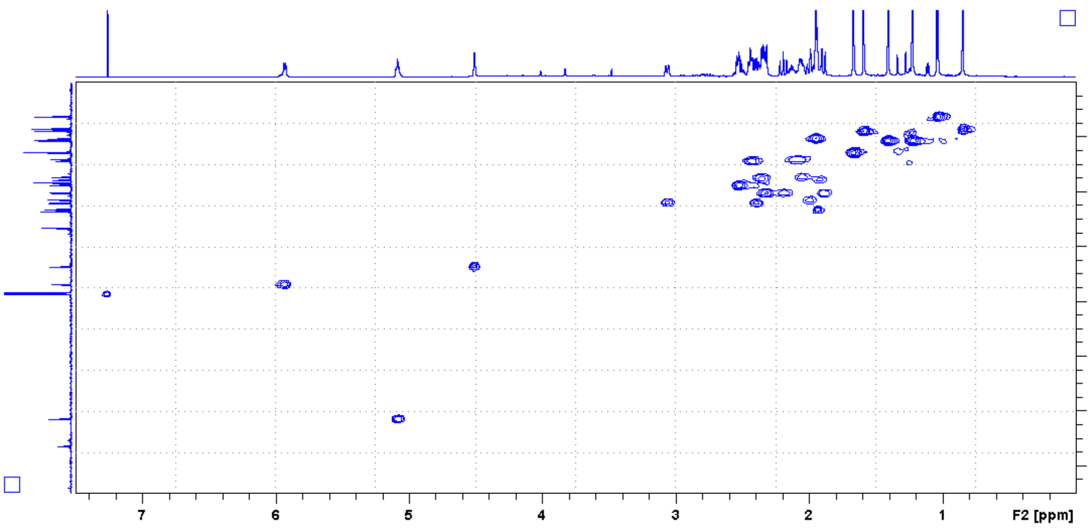
0.5
0.0
-0.5
200
150
100
50
[ppm]

E


F1 [ppm]
2
3
4
5
6
7
F2 [ppm]

F


F1 [ppm]
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140
7
6
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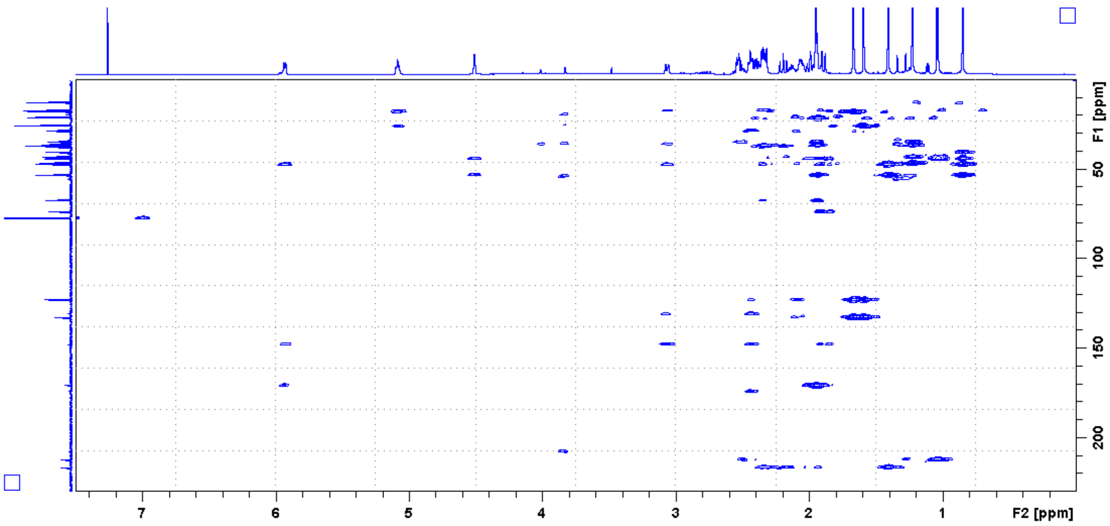
4
3
2
1
F2 [ppm]

G



H

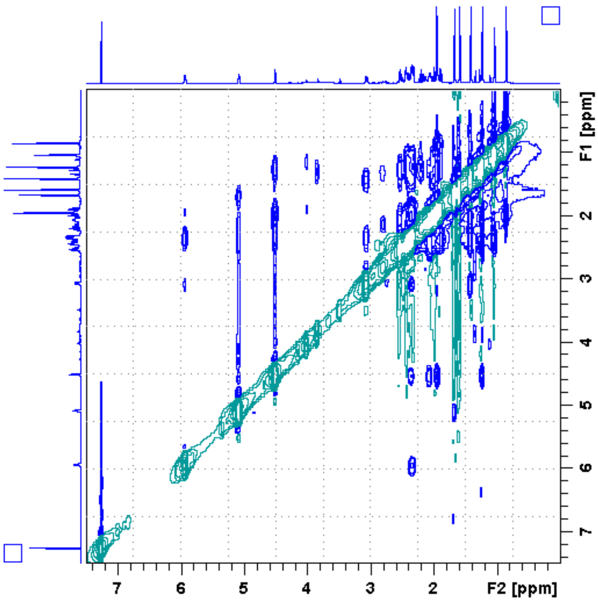
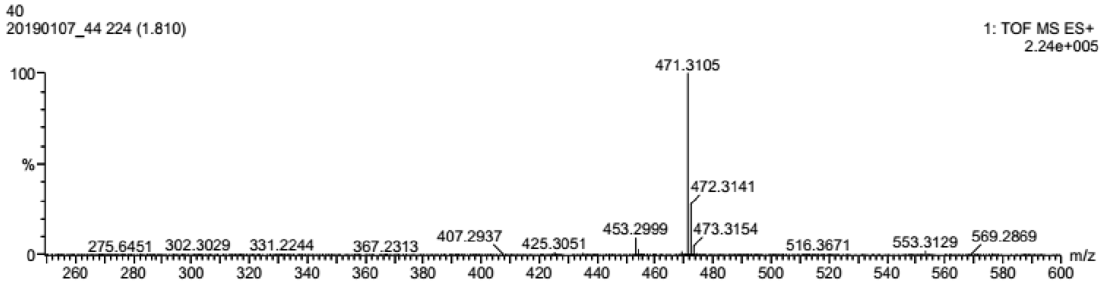


Figure S17 HRESIMS and NMR spectra of **22**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 600 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 150 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 150 MHz; (E) $^{1}H–^{1}H$ COSY spectrum in $CDCl_3$ at 400 MHz; (F) HSQC spectrum in $CDCl_3$ at 400 MHz; (G) HMBC spectrum in $CDCl_3$ at 400 MHz; (H) ROESY spectrum in $CDCl_3$ at 400 MHz.

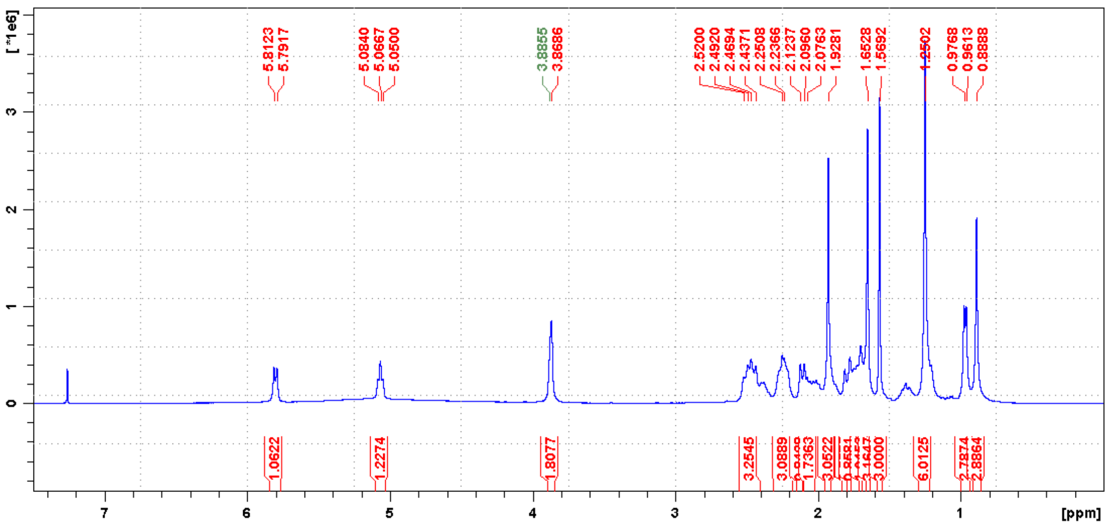
A

Monoisotopic Mass, Even Electron Ions
285 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1

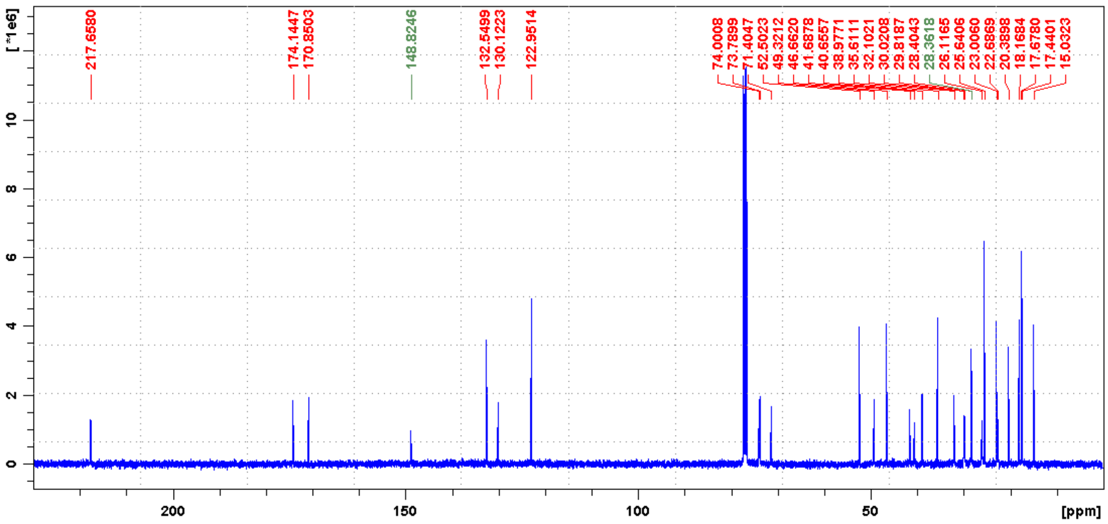


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
553.3129	553.3141	-1.2	-2.2	8.5	45.7	0.085	91.90	C31 H46 O7 Na
	553.3107	2.2	4.0	20.5	48.2	2.513	8.10	C40 H41 O2

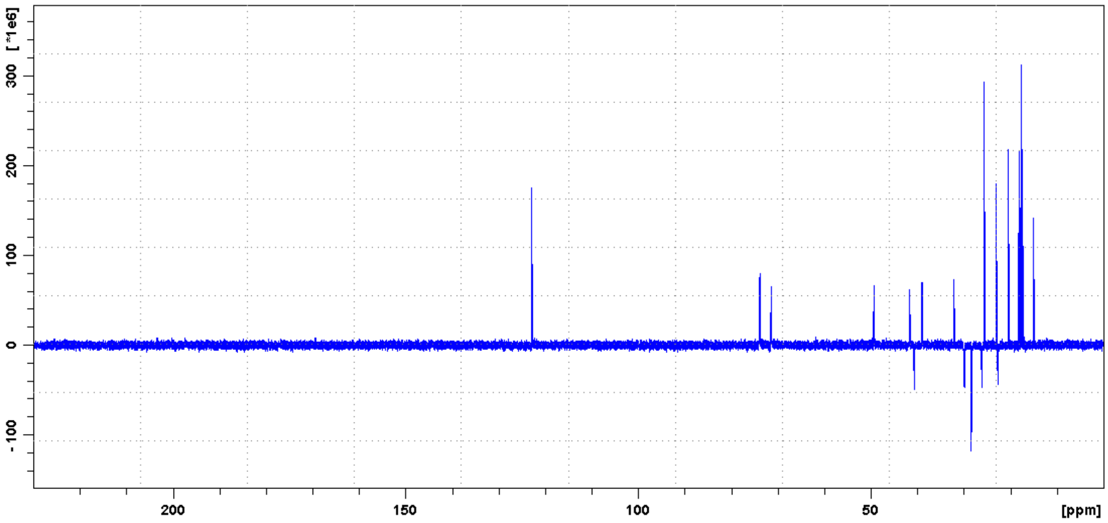
B



C



D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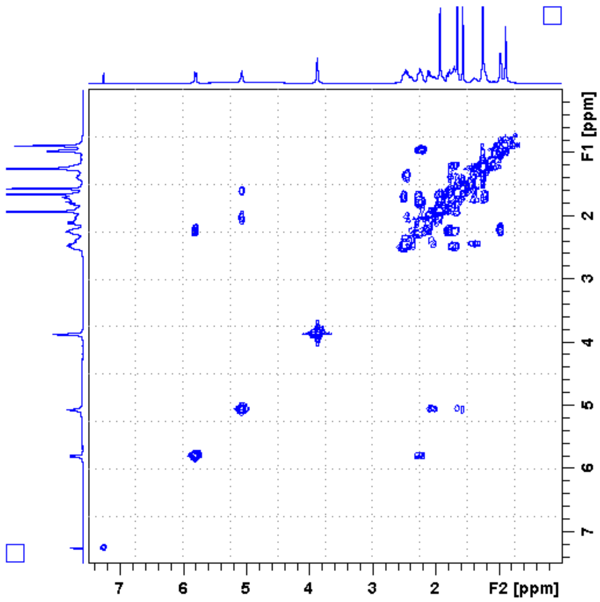
200
100
0
-100
200
150
100
50
[ppm]

E


F1 [ppm]
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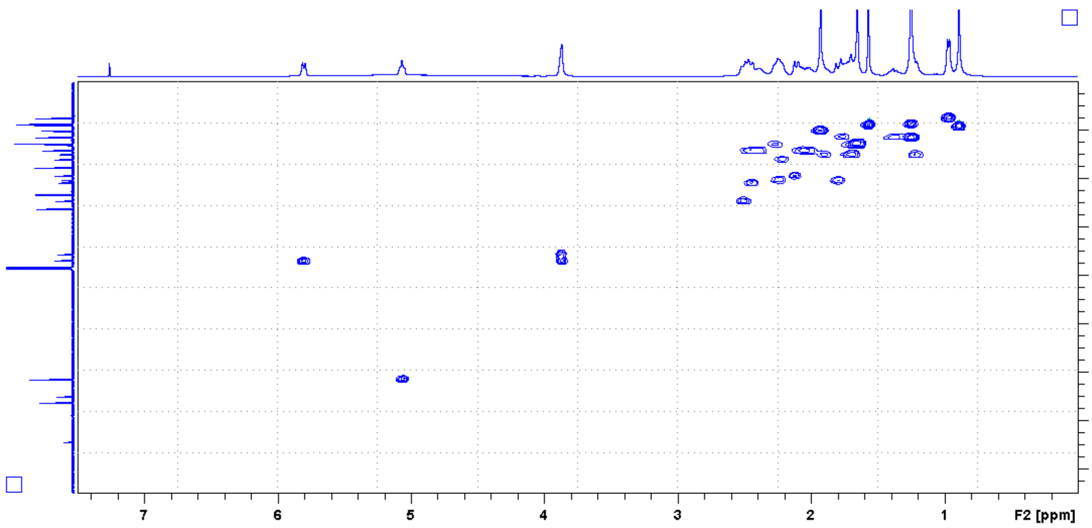
6
5
4
3
2
F2 [ppm]

F


F1 [ppm]
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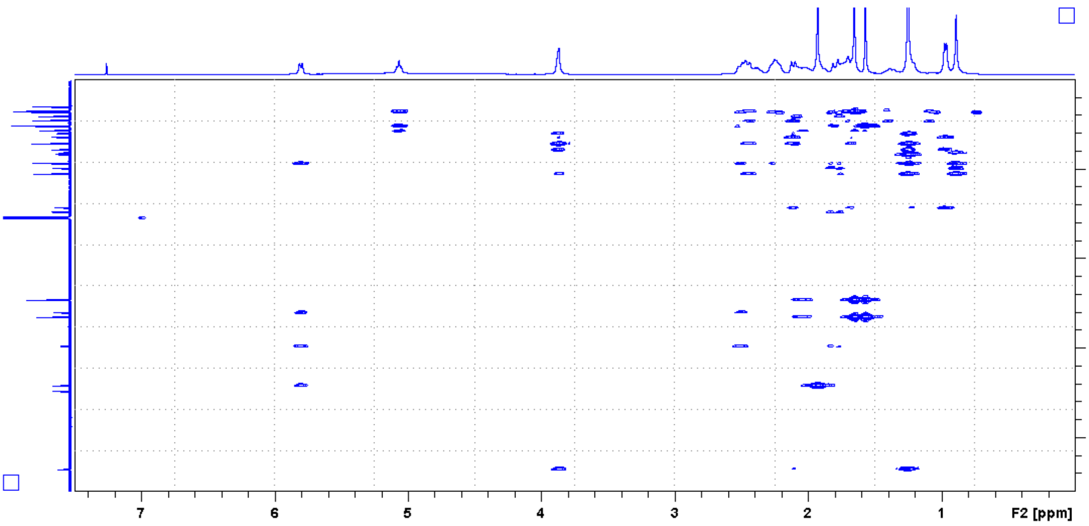
6
5
4
3
2
1
F2 [ppm]

G



H

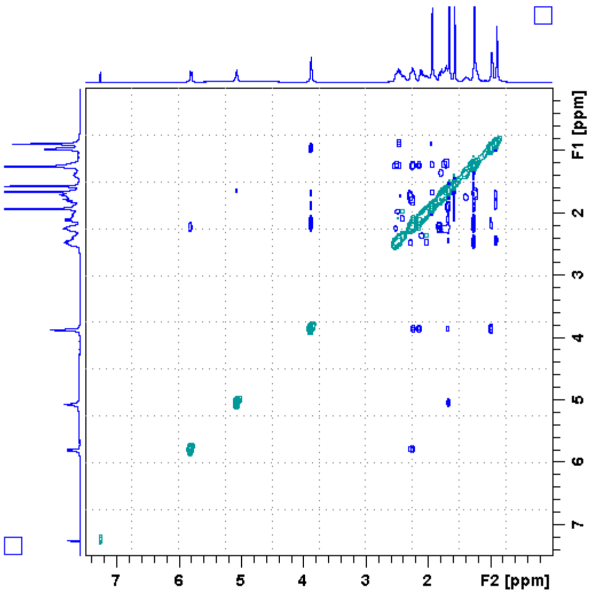
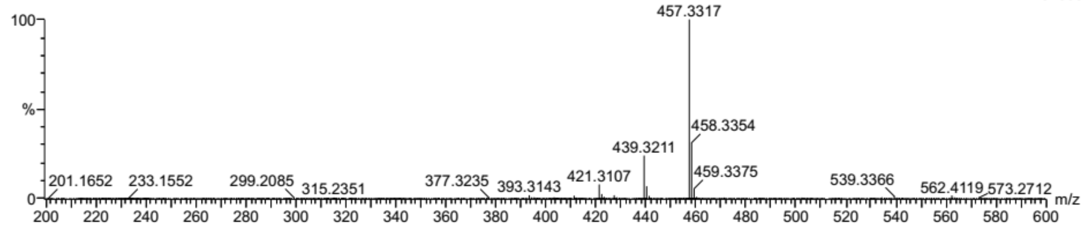


Figure S18 HRESIMS and NMR spectra of **23**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 400 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 100 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 100 MHz; (E) ^{1}H–^{1}H COSY spectrum in $CDCl_3$ at 400 MHz; (F) HSQC spectrum in $CDCl_3$ at 400 MHz; (G) HMBC spectrum in $CDCl_3$ at 400 MHz; (H) ROESY spectrum in $CDCl_3$ at 400 MHz.

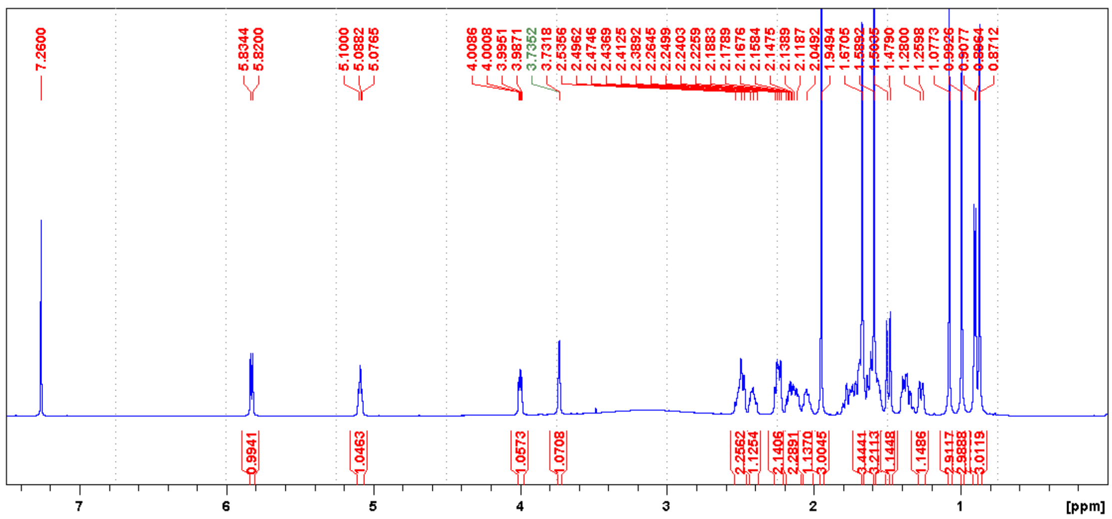
A

Monoisotopic Mass, Even Electron Ions
283 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
EC1B3-2-7
2018061120 242 (1.956)

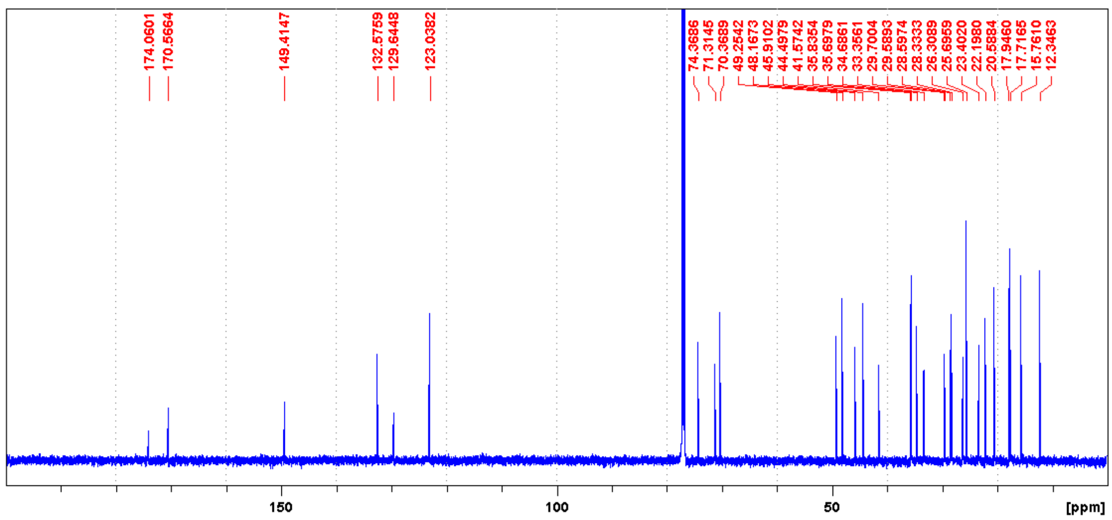


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
539.3366	539.3349	1.7	3.2	7.5	101.6	0.110	89.57	C31 H48 O6 Na
	539.3373	-0.7	-1.3	10.5	103.8	2.261	10.43	C33 H47 O6

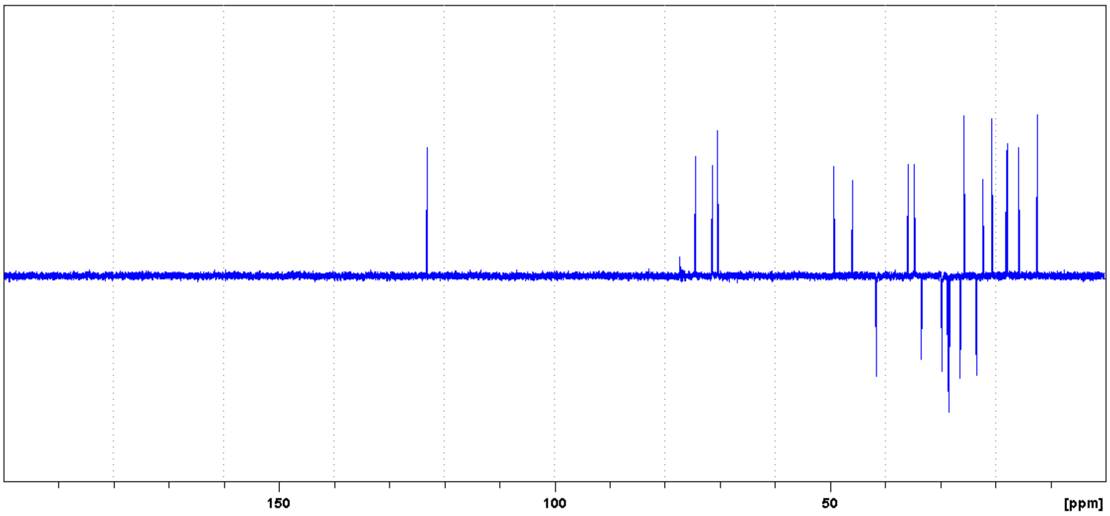
B



C



D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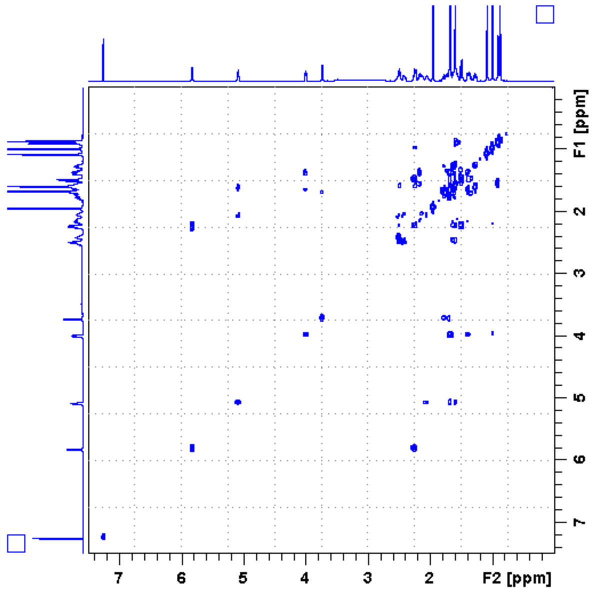
100
50
[ppm]

E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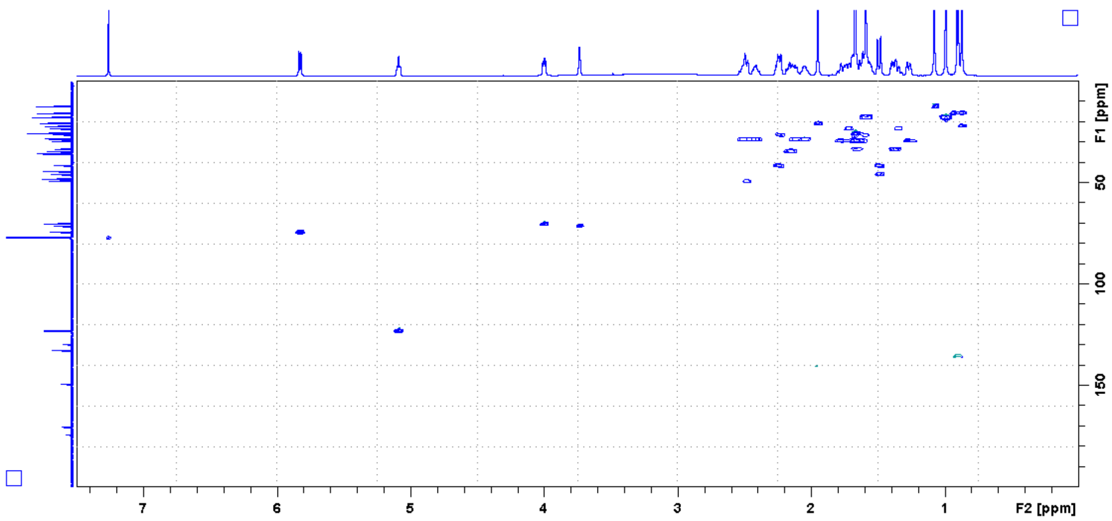
2
3
4
5
6
7
7
6
5
4
3
2
F2 [ppm]

F


F1 [ppm]
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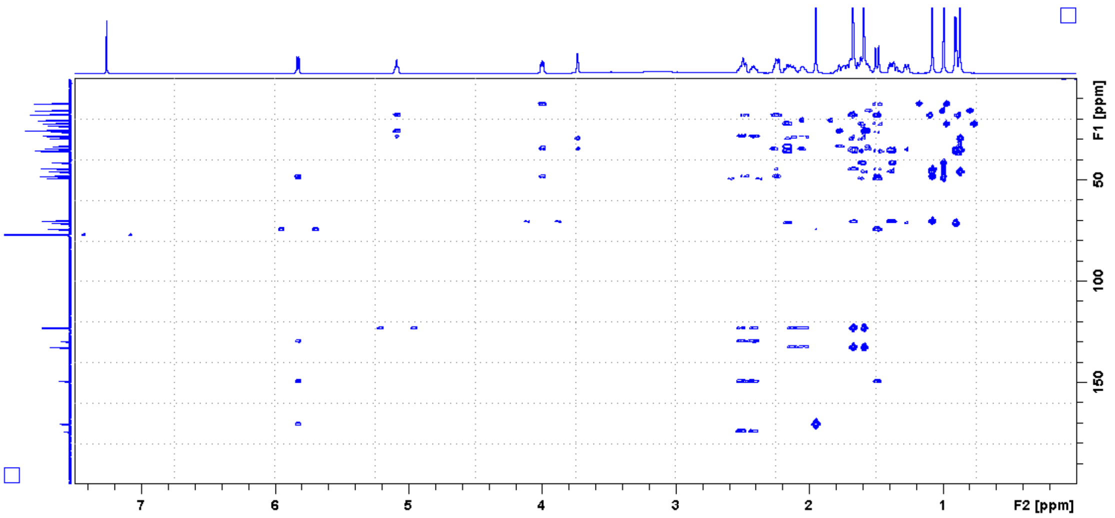
150
7
6
5
4
3
2
1
F2 [ppm]

G



H

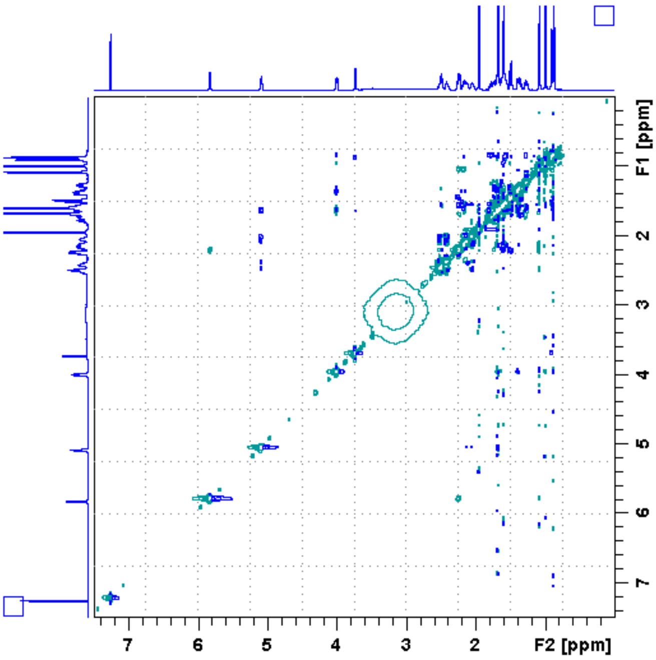
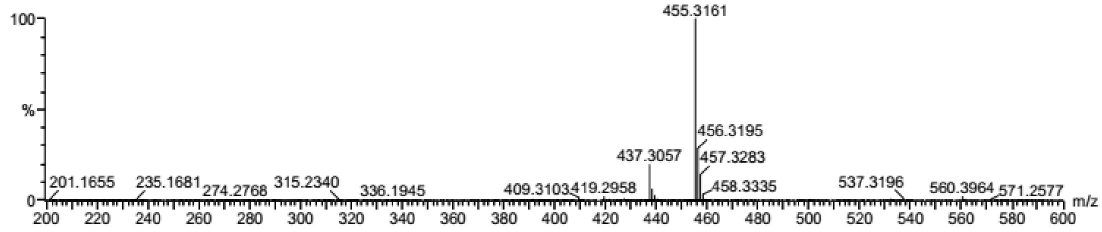


Figure S19 HRESIMS and NMR spectra of **24**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 600 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 150 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in $CDCl_3$ at 600 MHz; (F) HSQC spectrum in $CDCl_3$ at 600 MHz; (G) HMBC spectrum in $CDCl_3$ at 600 MHz; (H) ROESY spectrum in $CDCl_3$ at 600 MHz.

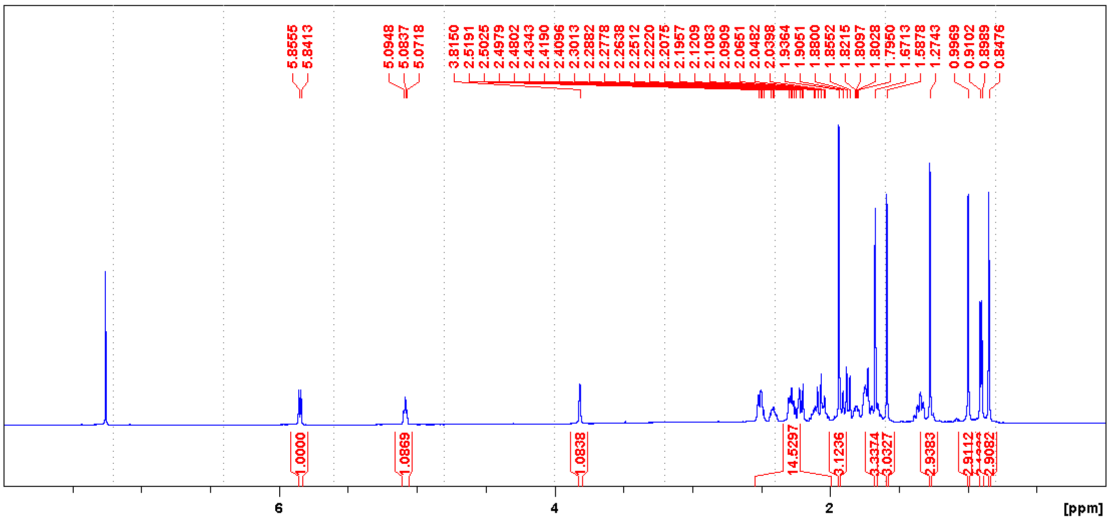
A

Monoisotopic Mass, Even Electron Ions
270 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
EC1B3-2-6
2018061119 249 (2.008)

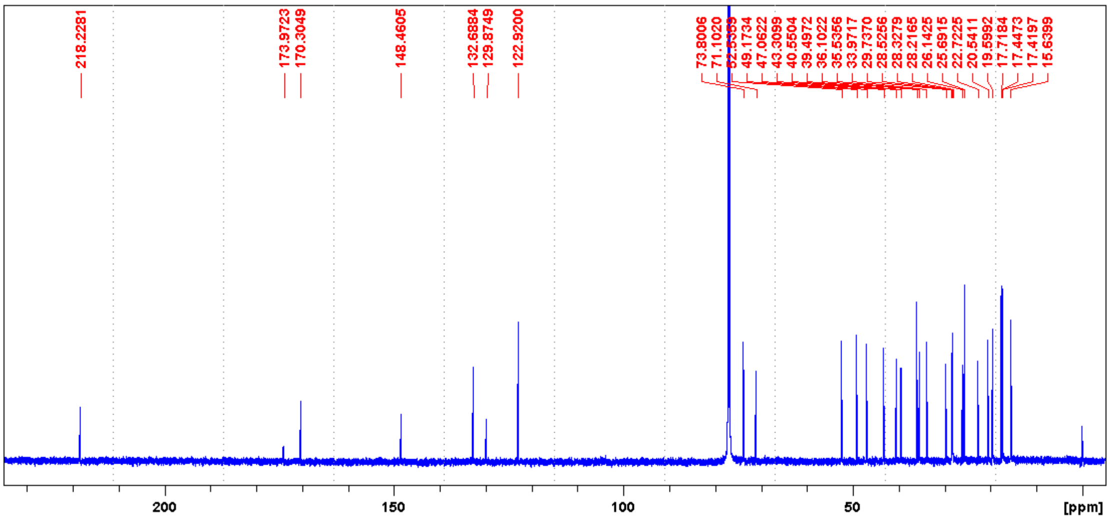


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
537.3196	537.3192	0.4	0.7	8.5	124.0	1.106	33.07	C31 H46 O6 Na
	537.3216	-2.0	-3.7	11.5	123.3	0.402	66.93	C33 H45 O6

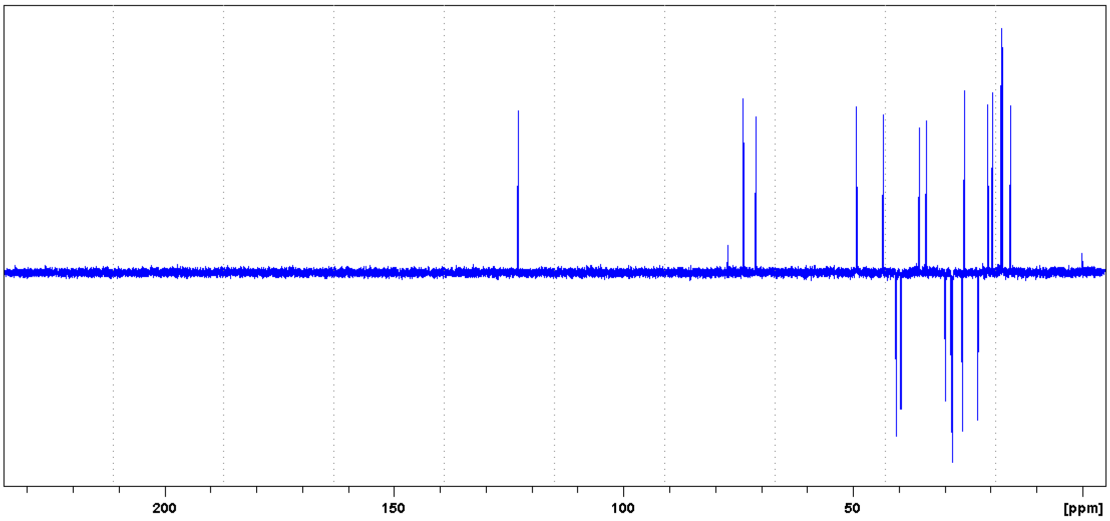
B



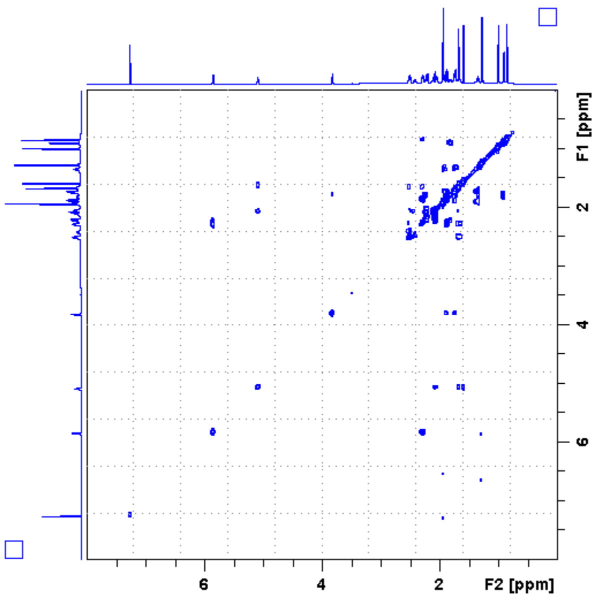
C



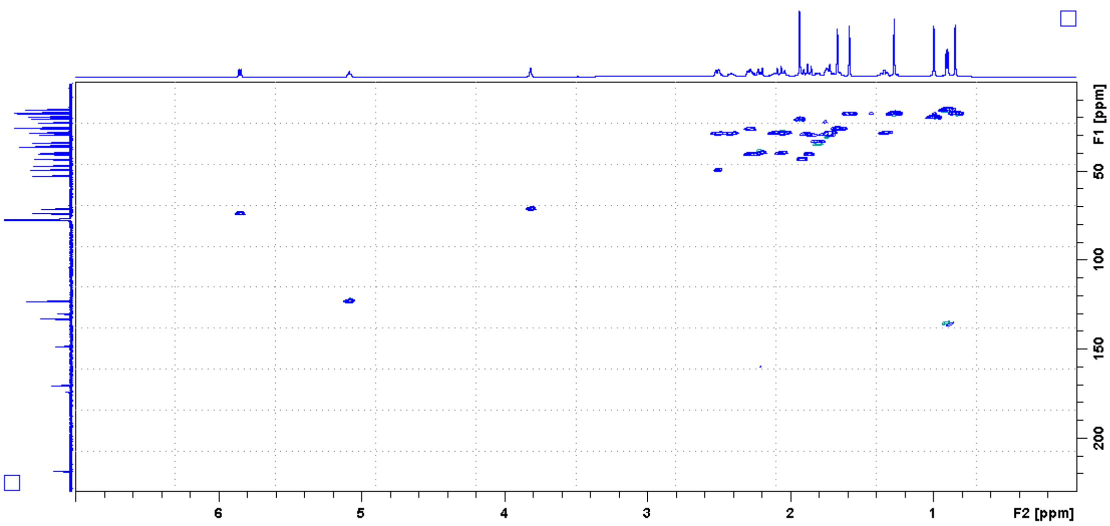
D


200
150
100
50
[ppm]

E


F1 [ppm]
2
4
6
6
4
2
F2 [ppm]

F


F1 [ppm]
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100
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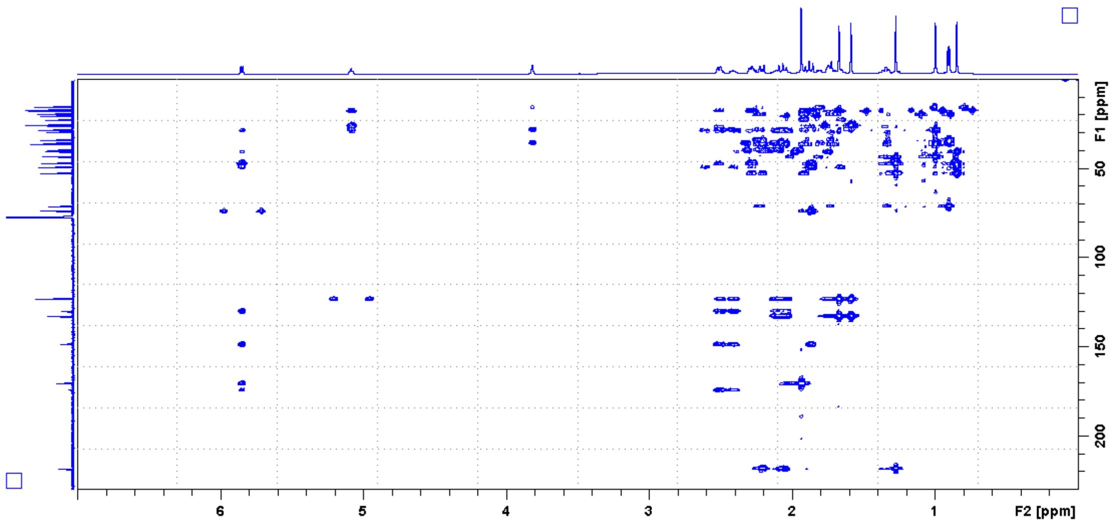
200
6
5
4
3
2
1
F2 [ppm]

G



H

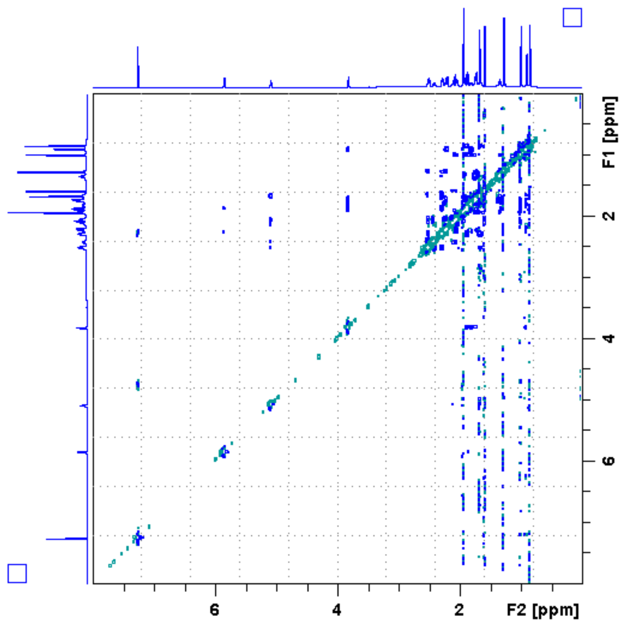


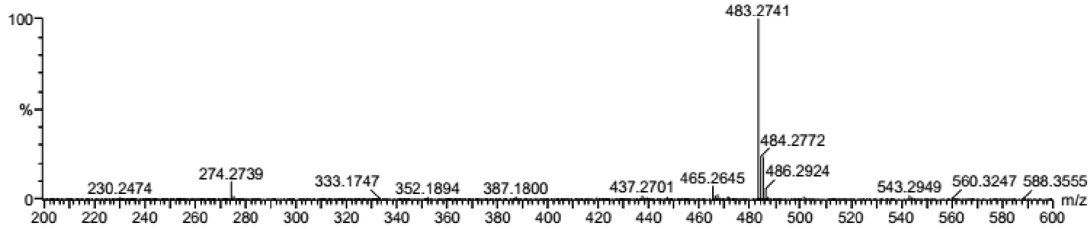
Figure S20 HRESIMS and NMR spectra of **25**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 600 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 150 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in $CDCl_3$ at 600 MHz; (F) HSQC spectrum in $CDCl_3$ at 600 MHz; (G) HMBC spectrum in $CDCl_3$ at 600 MHz; (H) NOESY spectrum in $CDCl_3$ at 600 MHz.

A

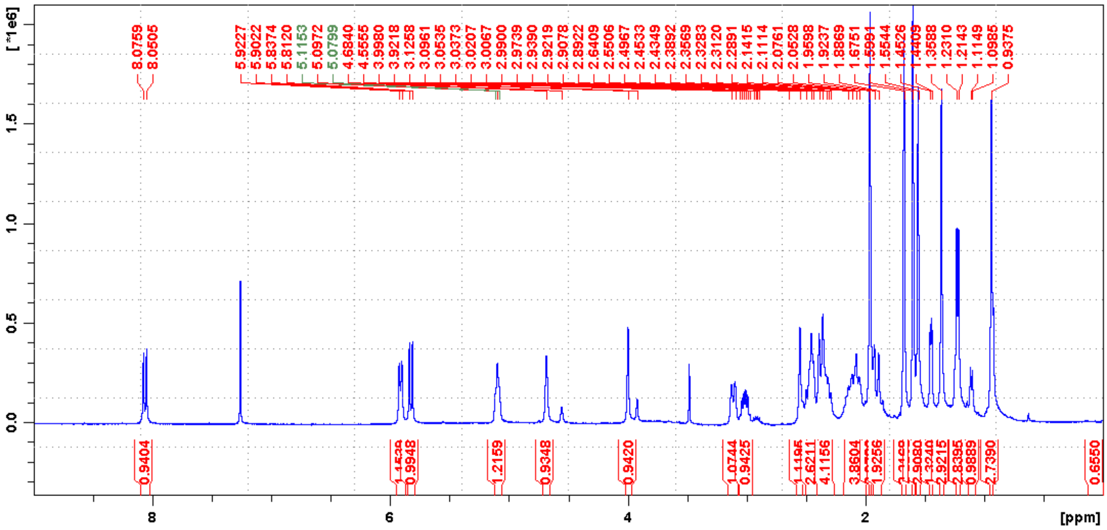
Monoisotopic Mass, Even Electron Ions
286 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
EB1-B3-2
20180423-39 195 (1.582)

1: TOF MS ES+
6.34e+004

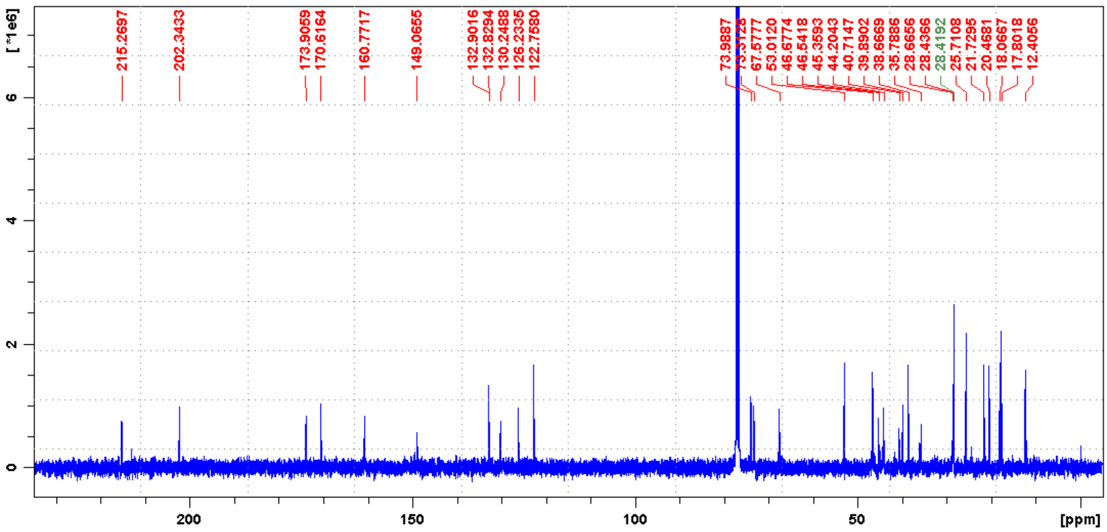


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
543.2949	543.2958	-0.9	-1.7	10.5	27.4	0.244	78.35	C31 H43 O8
	543.2934	1.5	2.8	7.5	28.7	1.530	21.65	C29 H44 O8 Na

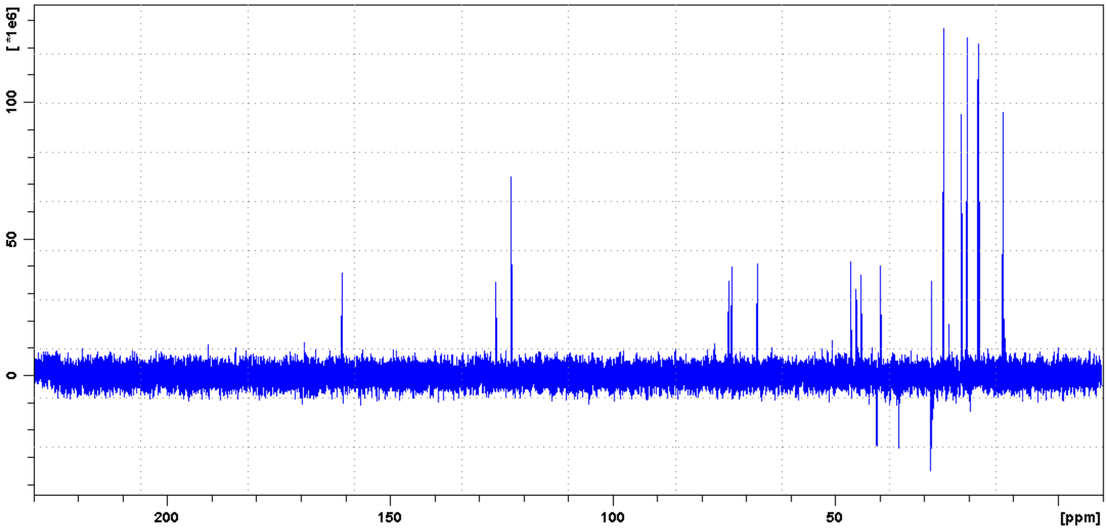
B



C



D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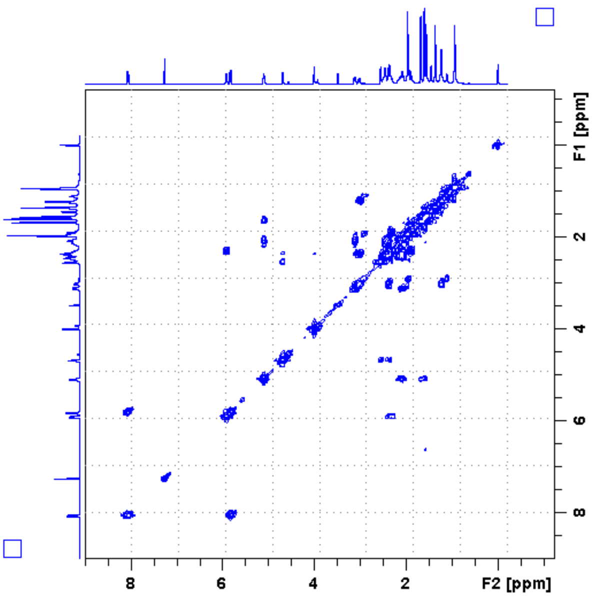
[ppm]

E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4
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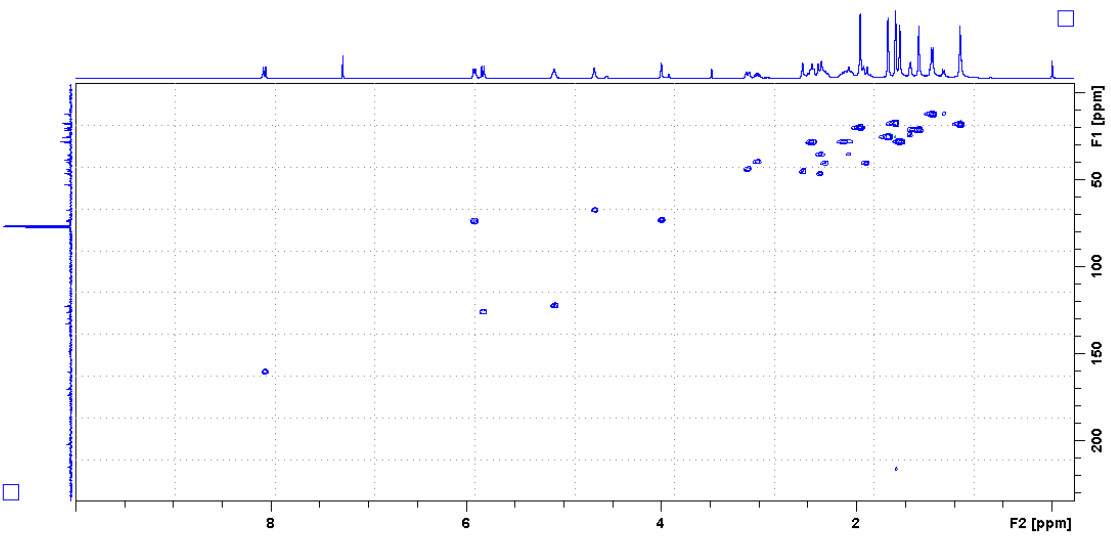
4
2
F2 [ppm]

F


F1 [ppm]
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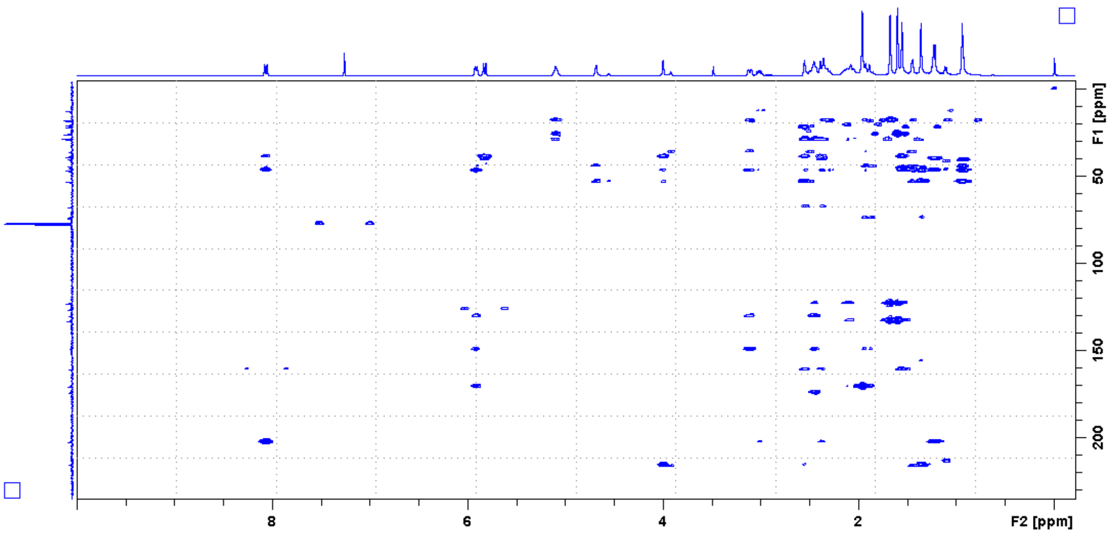
100
150
200
8
6
4
2
F2 [ppm]

G



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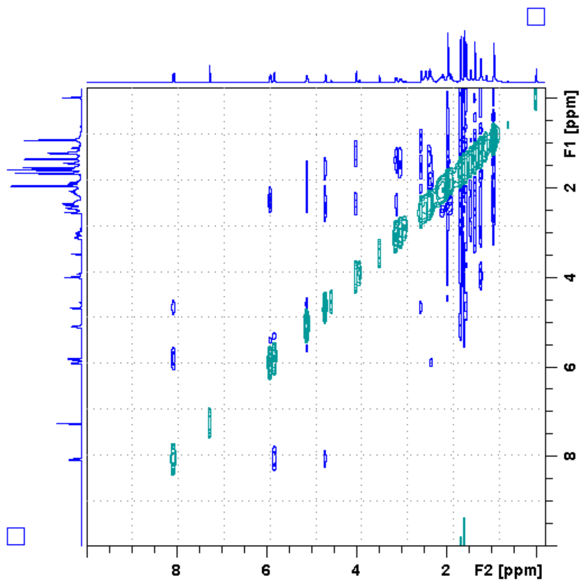
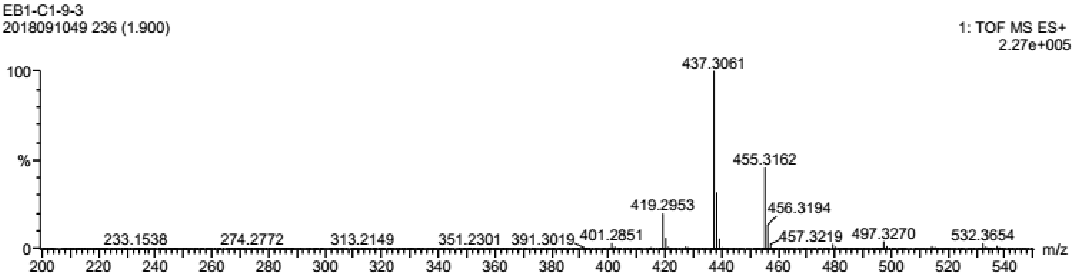


Figure S21 HRESIMS and NMR spectra of **26**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 400 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 100 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 100 MHz; (E) $^{1}H–^{1}H$ COSY spectrum in $CDCl_3$ at 400 MHz; (F) HSQC spectrum in $CDCl_3$ at 400 MHz; (G) **HMBC spectrum in $CDCl_3$ at 400 MHz; (H) ROESY spectrum in $CDCl_3$ at 400 MHz.**

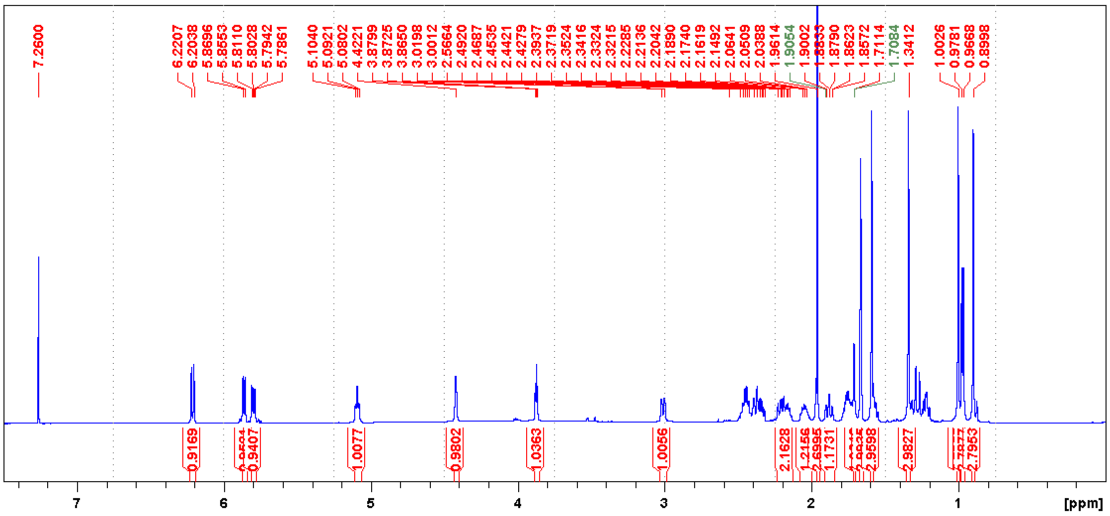
A

Monoisotopic Mass, Even Electron Ions
235 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1

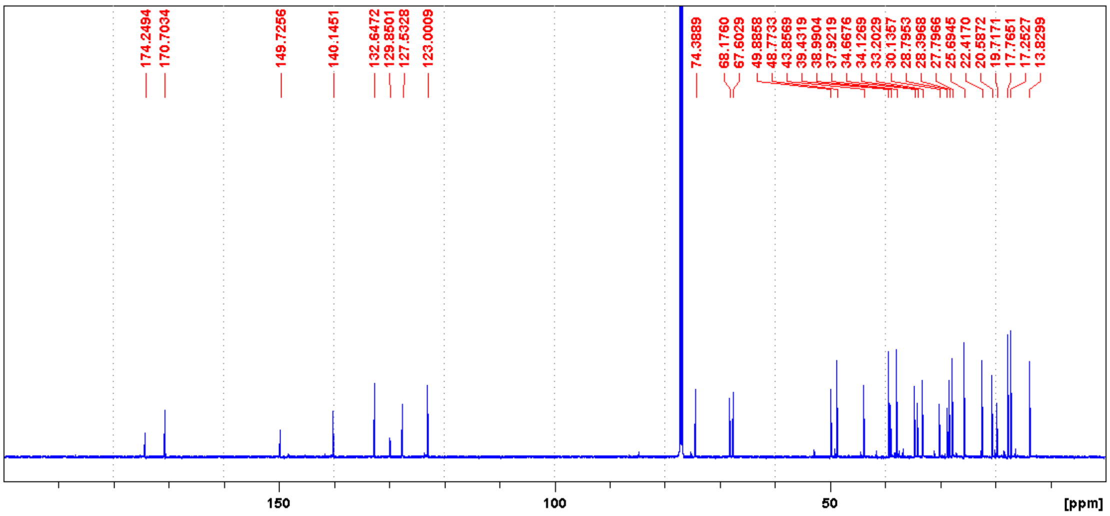


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
497.3270	497.3267	0.3	0.6	9.5	140.8	n/a	n/a	C31 H45 O5

B



C



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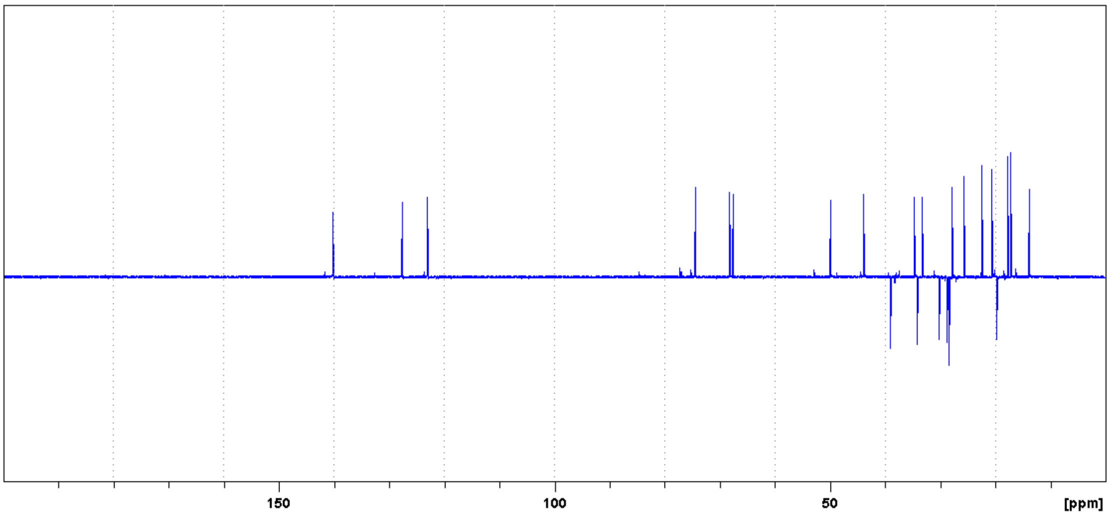
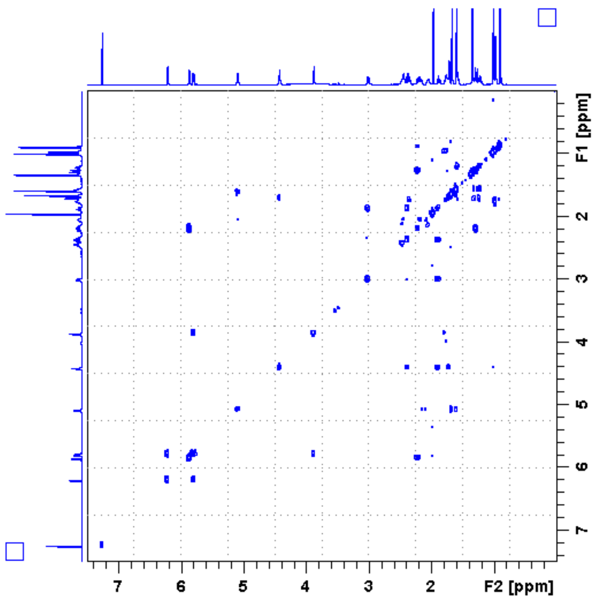
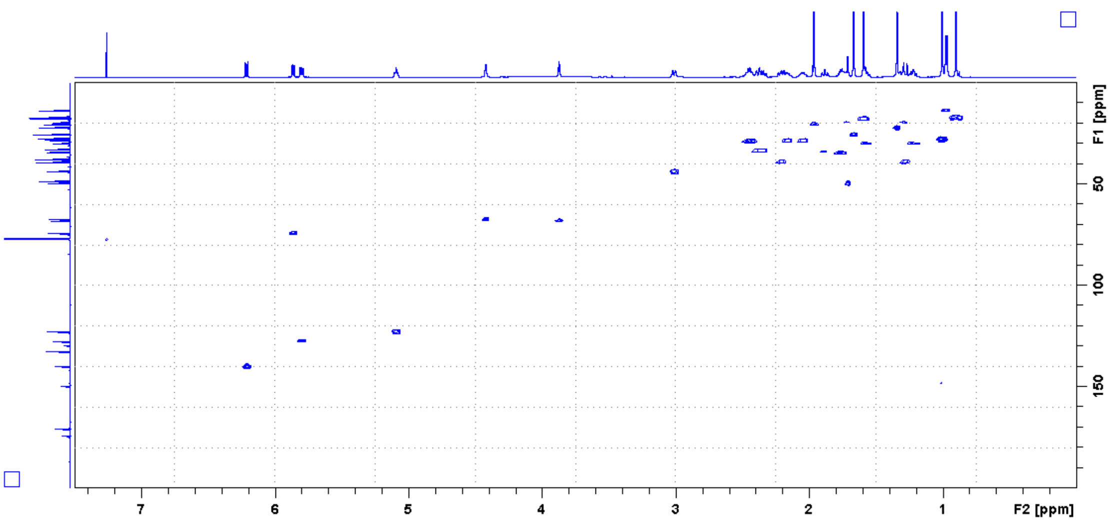


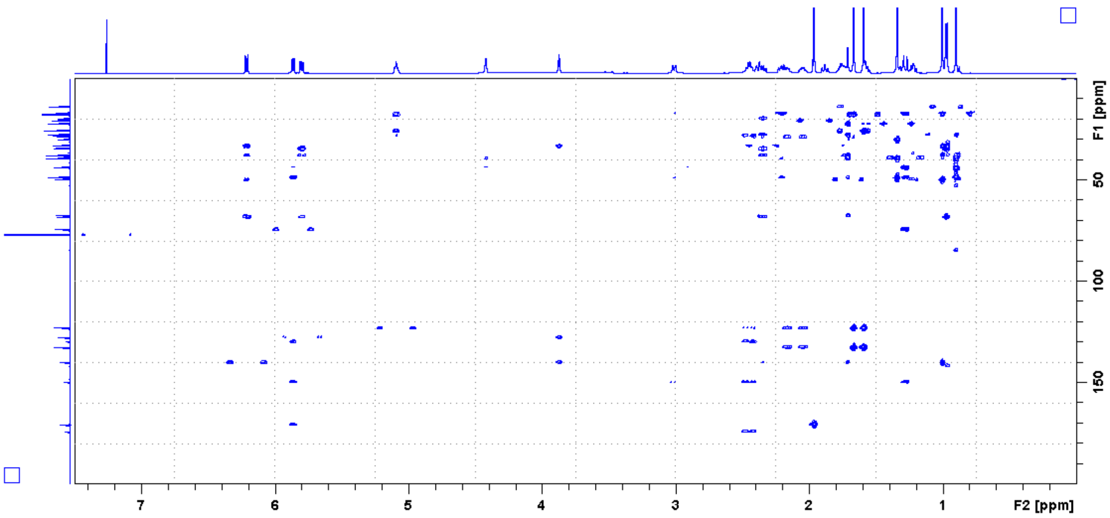
E



F



G



H

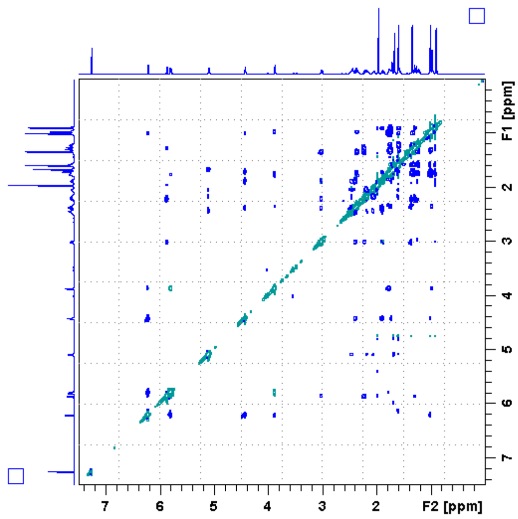
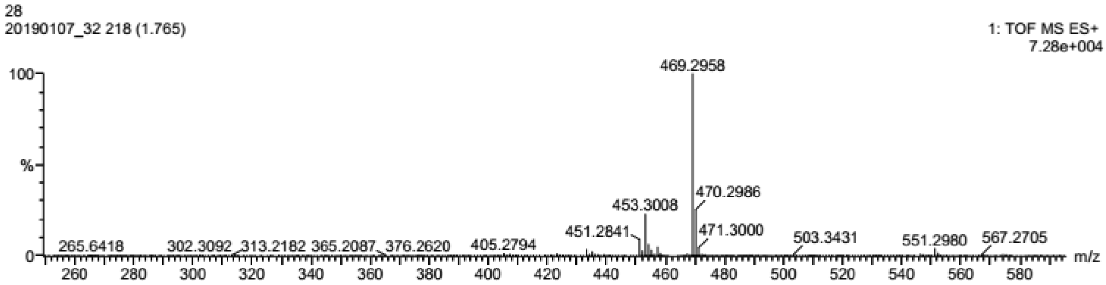


Figure S22 HRESIMS and NMR spectra of **29**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 600 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 150 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in $CDCl_3$ at 600 MHz; (F) HSQC spectrum in $CDCl_3$ at 600 MHz; (G) HMBC spectrum in $CDCl_3$ at 600 MHz; (H) ROESY spectrum in $CDCl_3$ at 600 MHz.

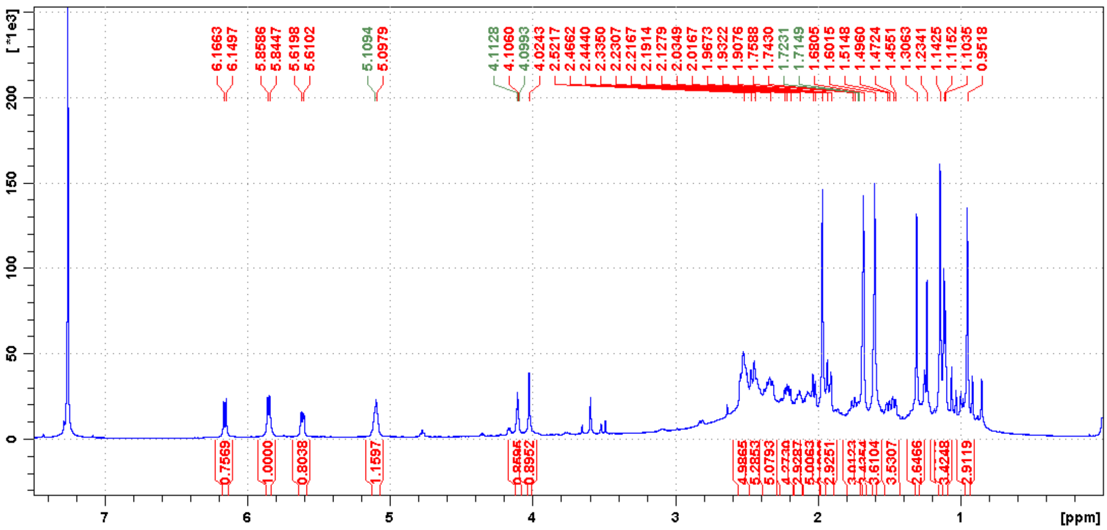
A

Monoisotopic Mass, Even Electron Ions
295 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1

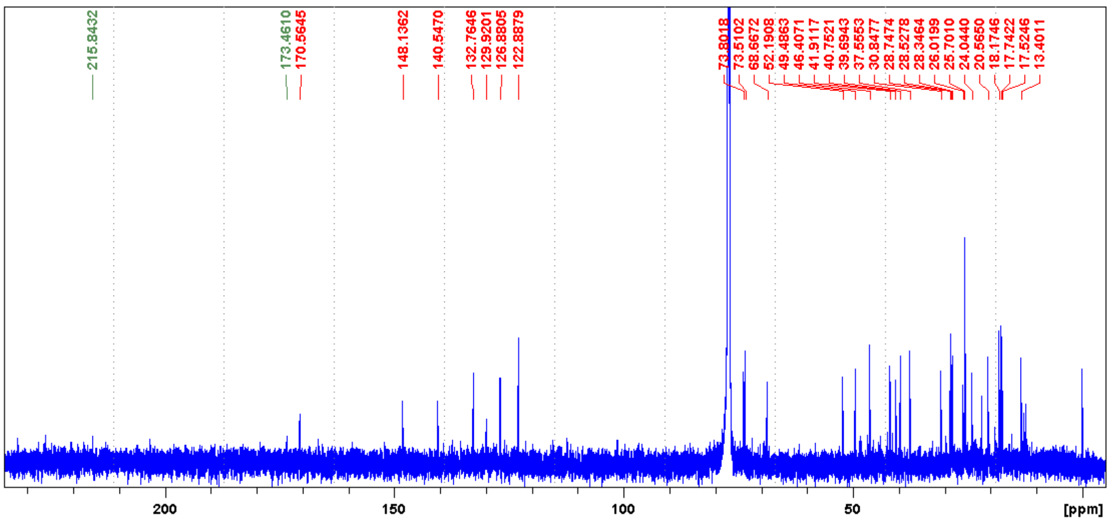


	Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
Minimum:					-1.5				
Maximum:			5.0	5.0	50.0				
	551.2980	551.2985	-0.5	-0.9	9.5	60.6	n/a	n/a	C31 H44 O7 Na

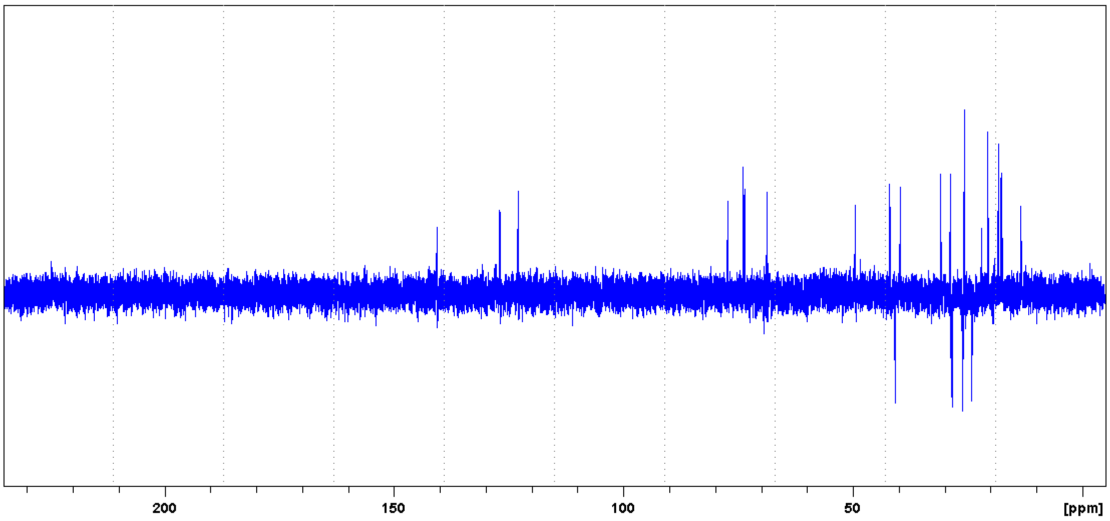
B



C



D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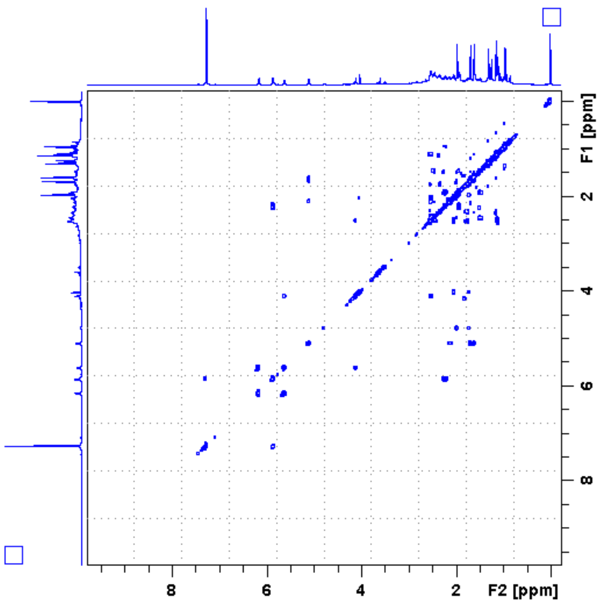
100
50
[ppm]

E


F1 [ppm]
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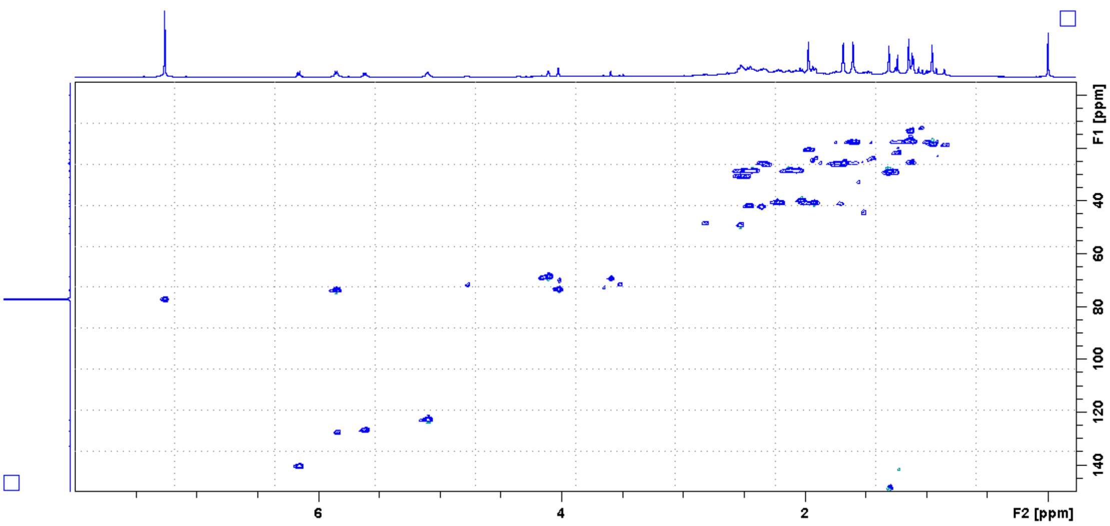
8
6
4
2
F2 [ppm]

F


F1 [ppm]
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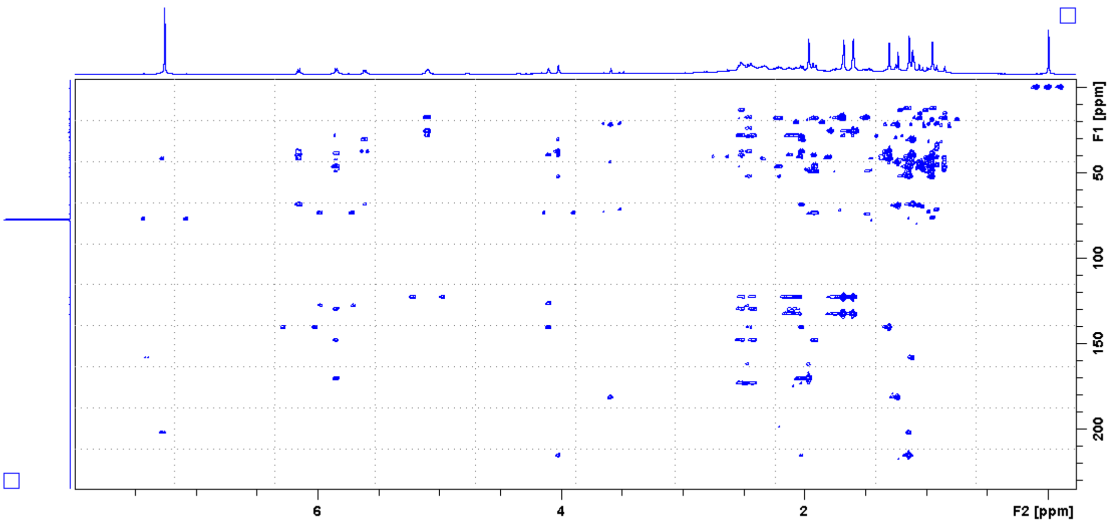
4
2
F2 [ppm]

G



H

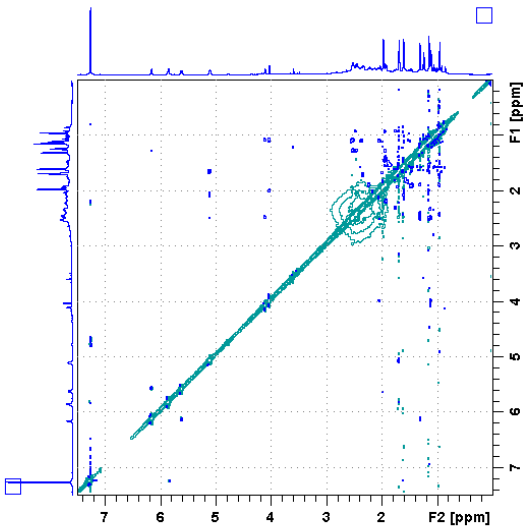
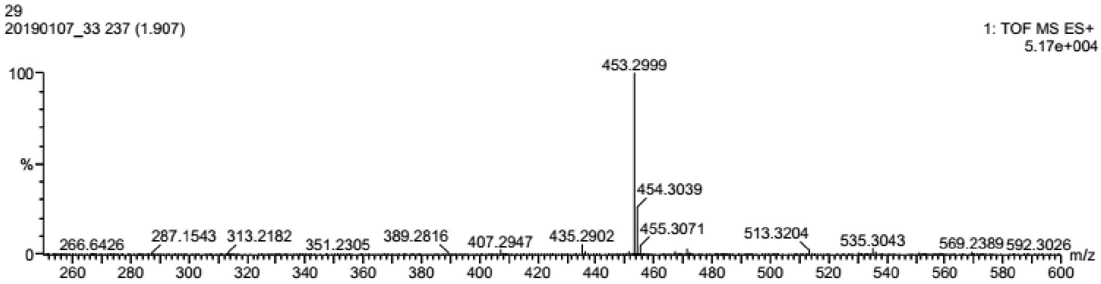


Figure S23 HRESIMS and NMR spectra of **30**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 600 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 150 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in $CDCl_3$ at 600 MHz; (F) HSQC spectrum in $CDCl_3$ at 600 MHz; (G) HMBC spectrum in $CDCl_3$ at 600 MHz; (H) NOESY spectrum in $CDCl_3$ at 600 MHz.

A

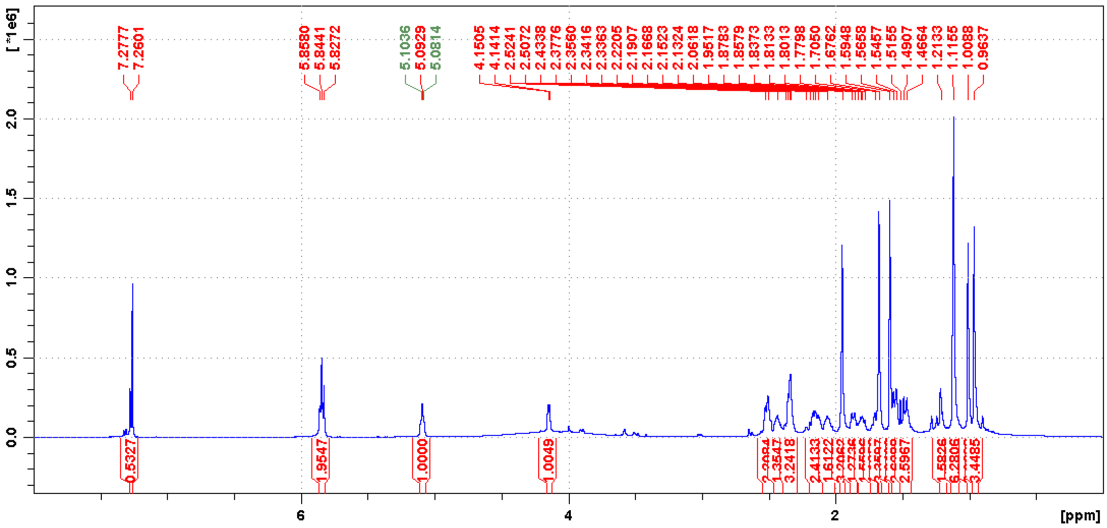
Monoisotopic Mass, Even Electron Ions
248 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500   H: 0-1000   O: 0-200   Na: 0-1



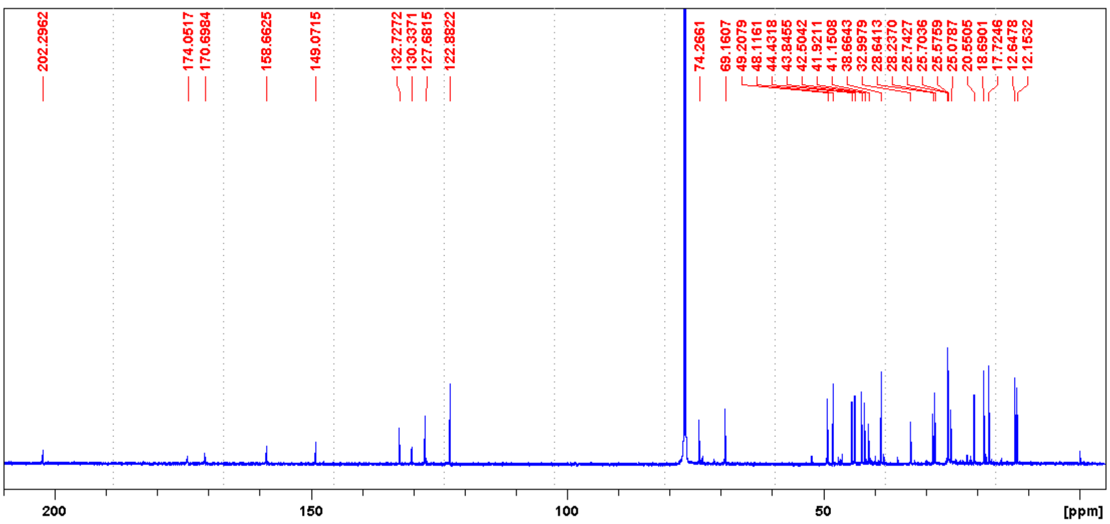
	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
513.3204	513.3216	-1.2	-2.3	9.5	32.5	0.749	47.26	C31 H45 O6
	513.3192	1.2	2.3	6.5	32.4	0.640	52.74	C29 H46 O6 Na

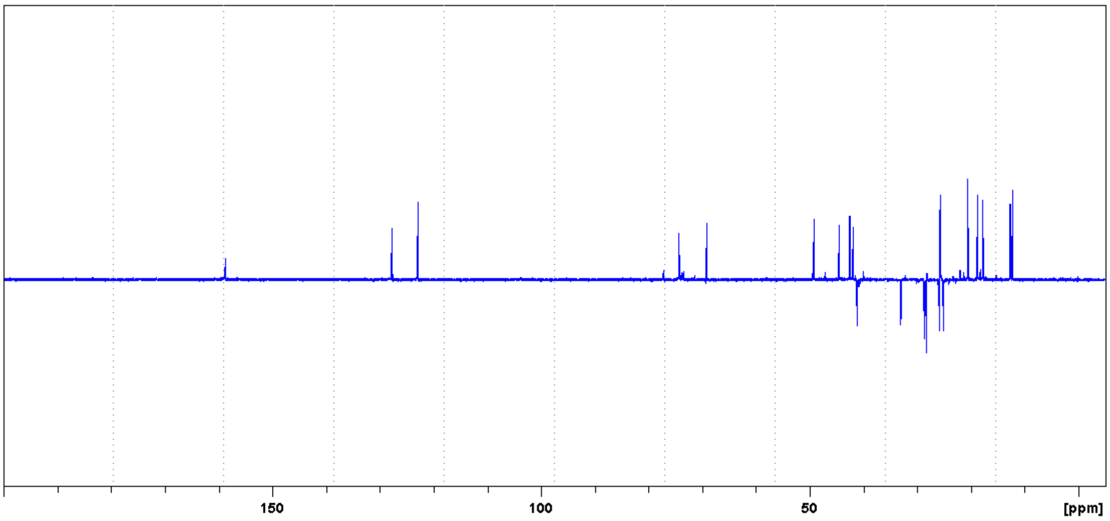
B



C



D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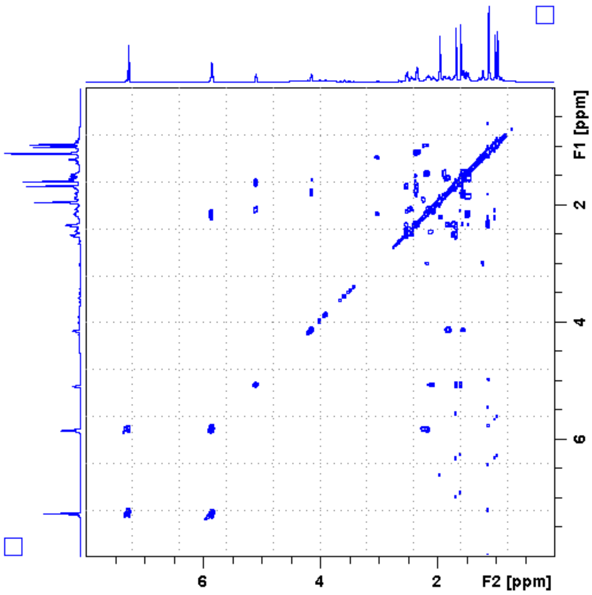
E


F1 [ppm]
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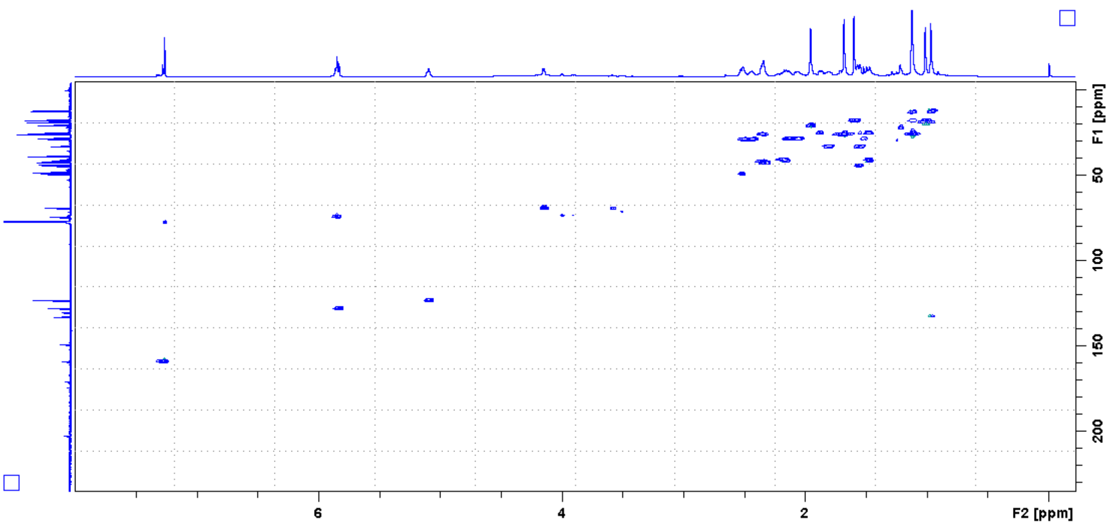
4
6
6
4
2
F2 [ppm]

F


F1 [ppm]
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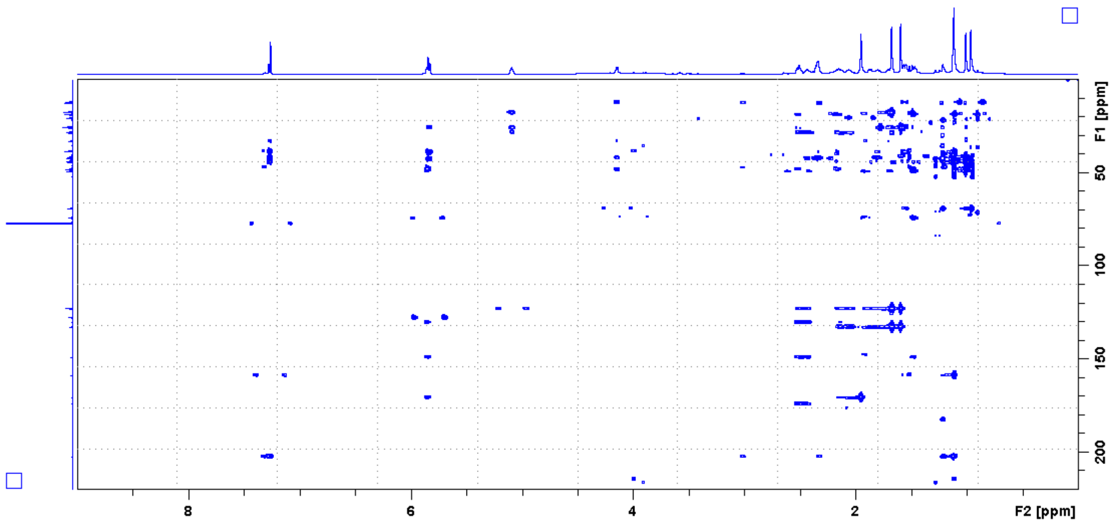
200
6
4
2
F2 [ppm]

G



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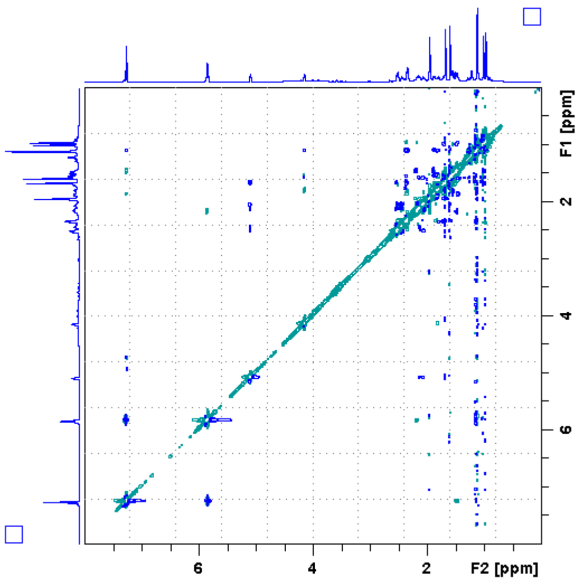
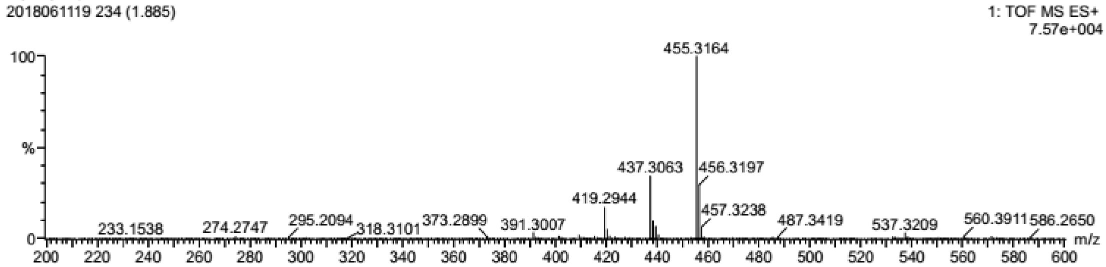


Figure S24 HRESIMS and NMR spectra of **31**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 600 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 150 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in $CDCl_3$ at 600 MHz; (F) HSQC spectrum in $CDCl_3$ at 600 MHz; (G) HMBC spectrum in $CDCl_3$ at 600 MHz; (H) NOESY spectrum in $CDCl_3$ at 600 MHz.

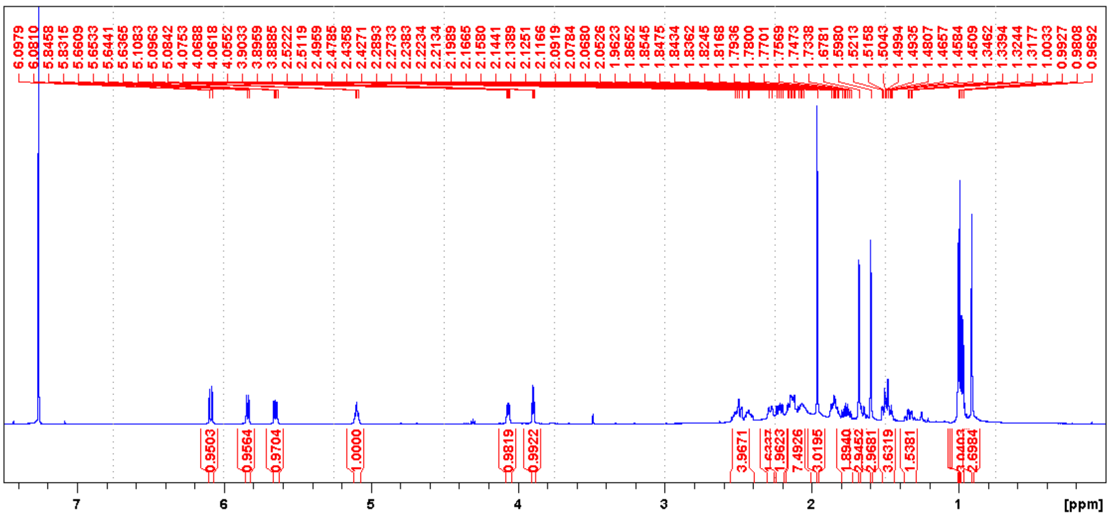
A

Monoisotopic Mass, Even Electron Ions
270 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
EC1B3-2-6
2018061119 234 (1.885)

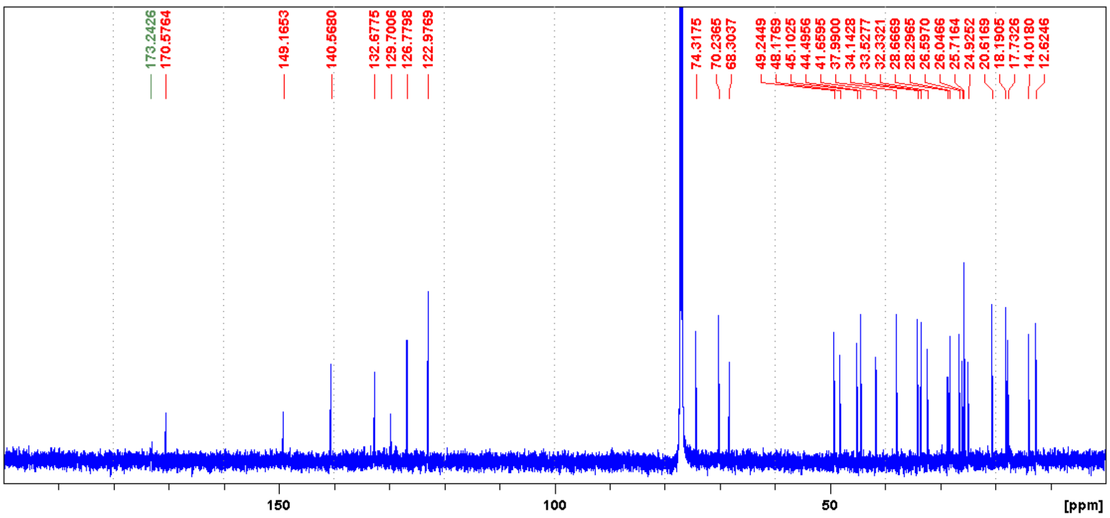


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
537.3209	537.3192	1.7	3.2	8.5	82.3	1.403	24.59	C31 H46 O6 Na
	537.3216	-0.7	-1.3	11.5	81.1	0.282	75.41	C33 H45 O6

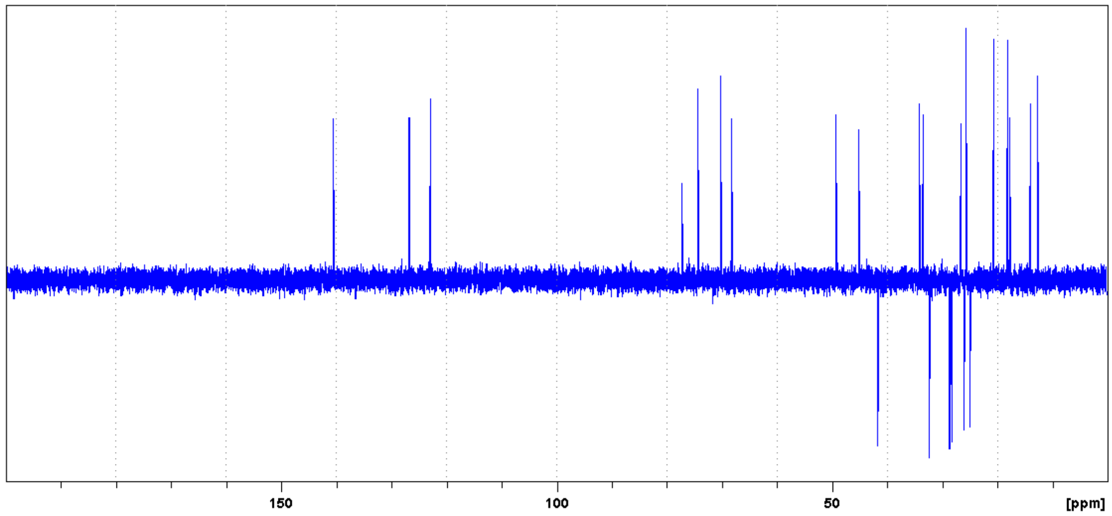
B



C



D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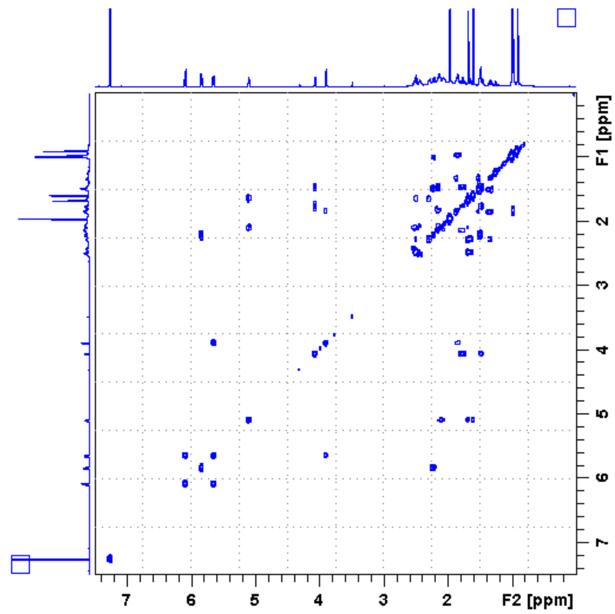
100
50
[ppm]

E


F1 [ppm]
F2 [ppm]
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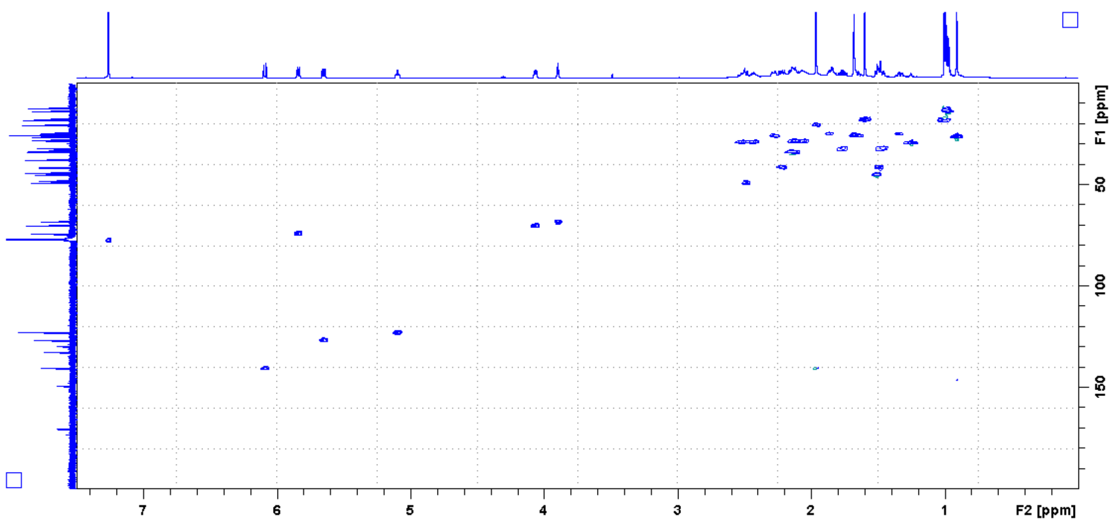
5
4
3
2

F


F1 [ppm]
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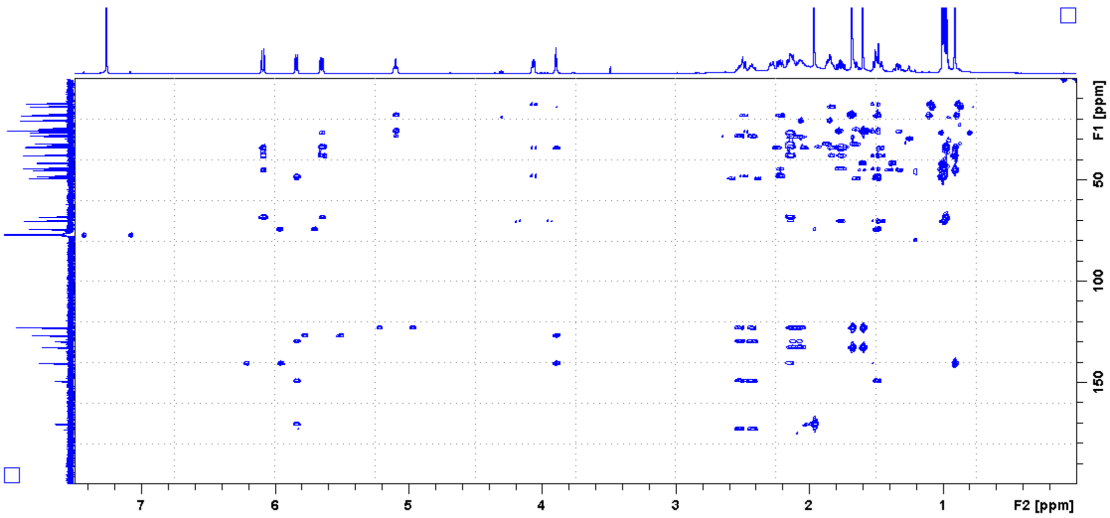
4
3
2
1

G



H

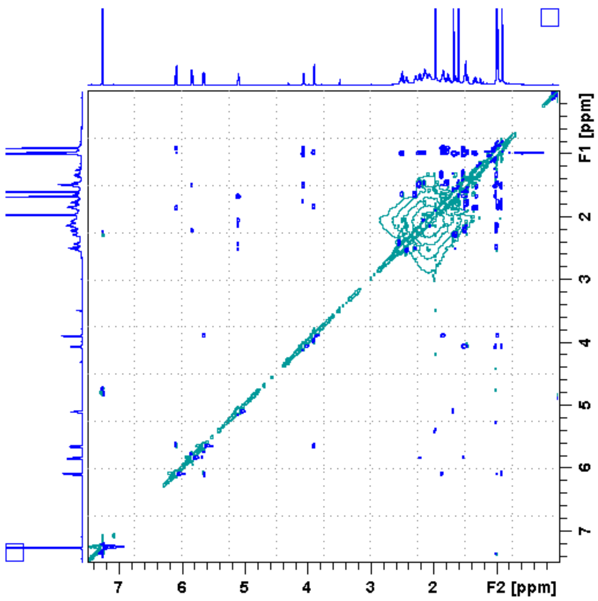
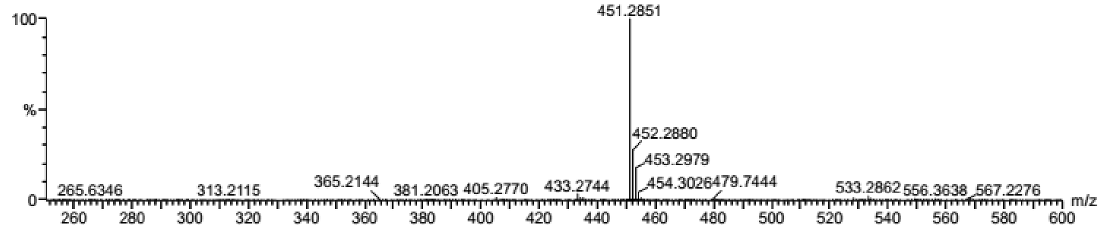


Figure S25 HRESIMS and NMR spectra of **32**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 600 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 150 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in $CDCl_3$ at 600 MHz; (F) HSQC spectrum in $CDCl_3$ at 600 MHz; (G) HMBC spectrum in $CDCl_3$ at 600 MHz; (H) NOESY spectrum in $CDCl_3$ at 600 MHz.

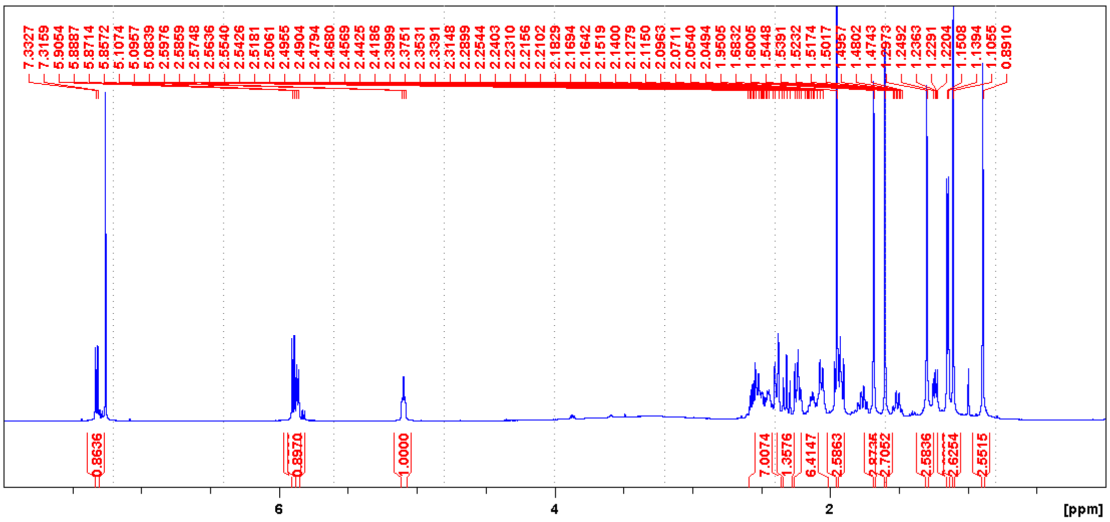
A

Monoisotopic Mass, Even Electron Ions
266 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
30
20190107_34 234 (1.885) 1: TOF MS ES+ 1.46e+005

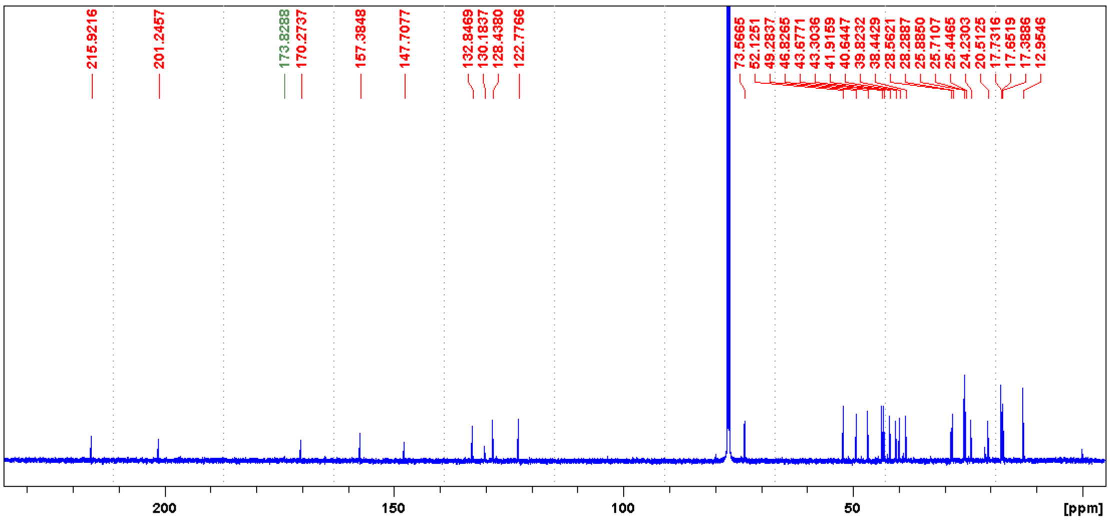


	Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
Minimum:					-1.5				
Maximum:			5.0	5.0	50.0				
	533.2862	533.2879	-1.7	-3.2	10.5	65.8	0.227	79.72	C31 H42 O6 Na
		533.2844	1.8	3.4	22.5	67.1	1.595	20.28	C40 H37 O

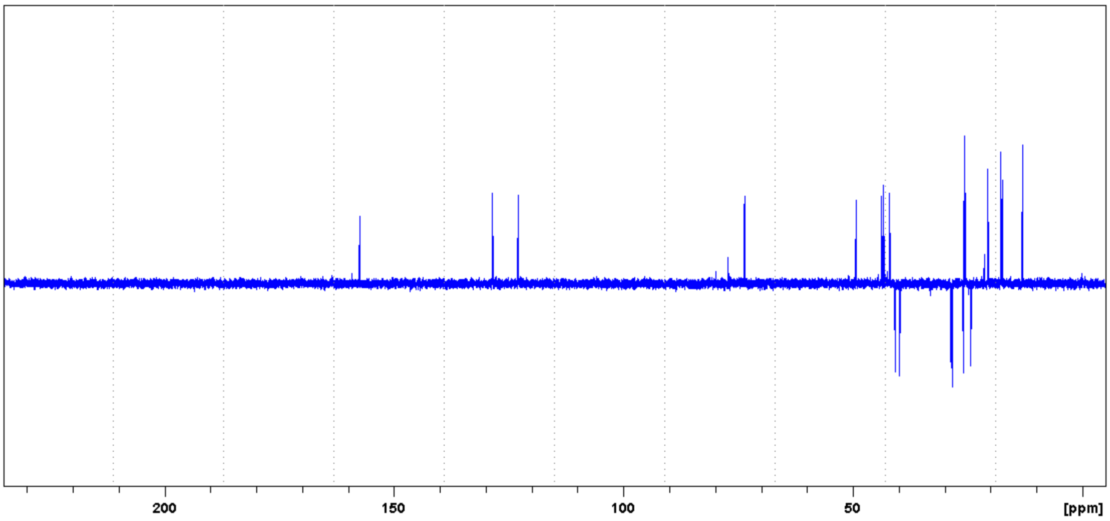
B



C



D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100
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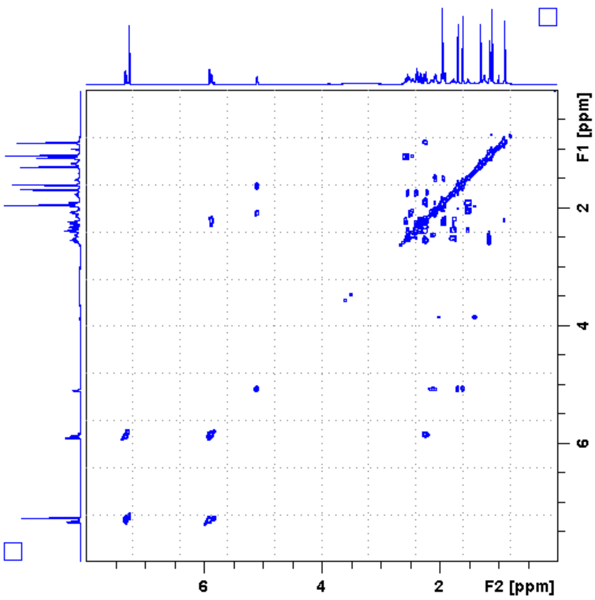
E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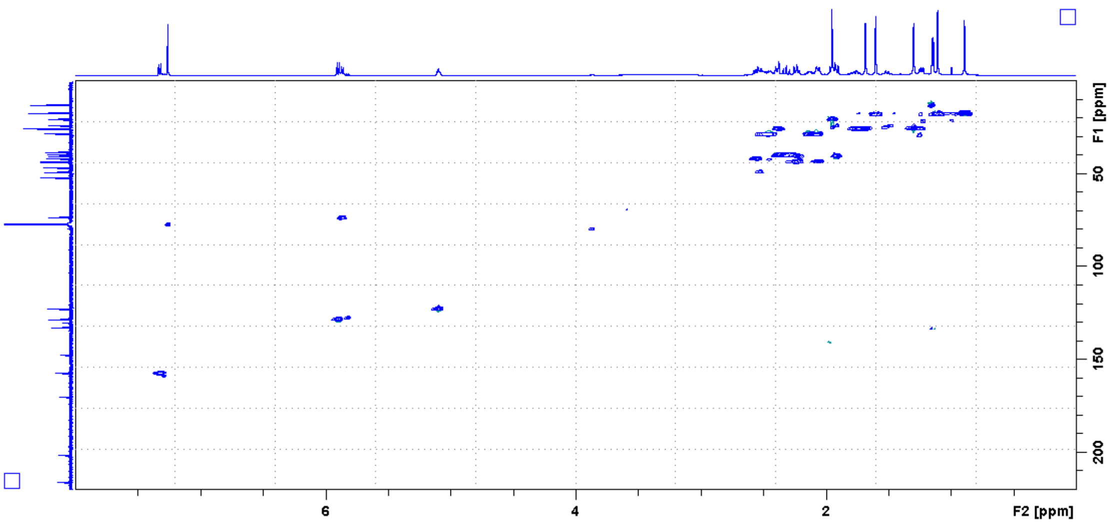
4
2
F2 [ppm]

F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4
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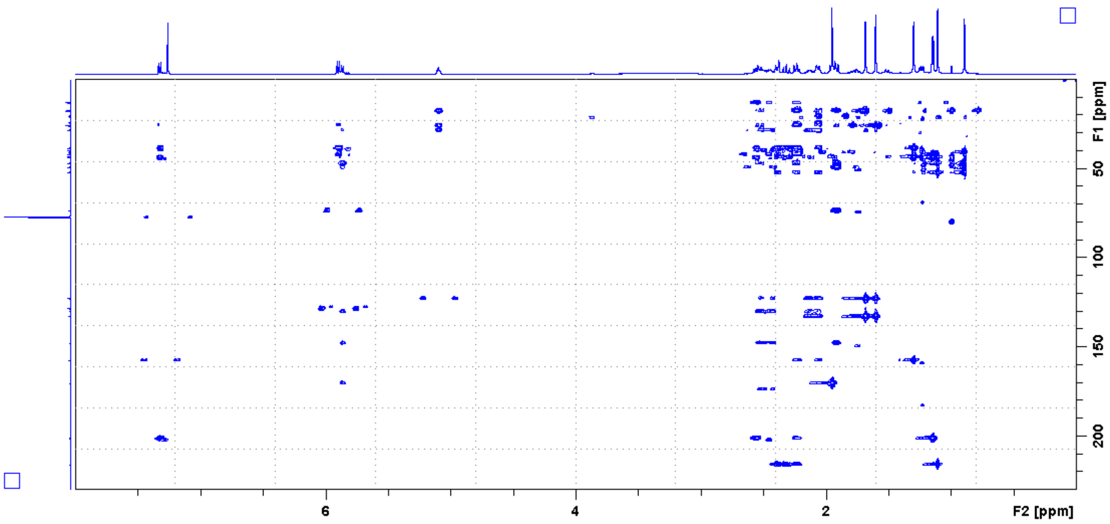
F2 [ppm]

G



H

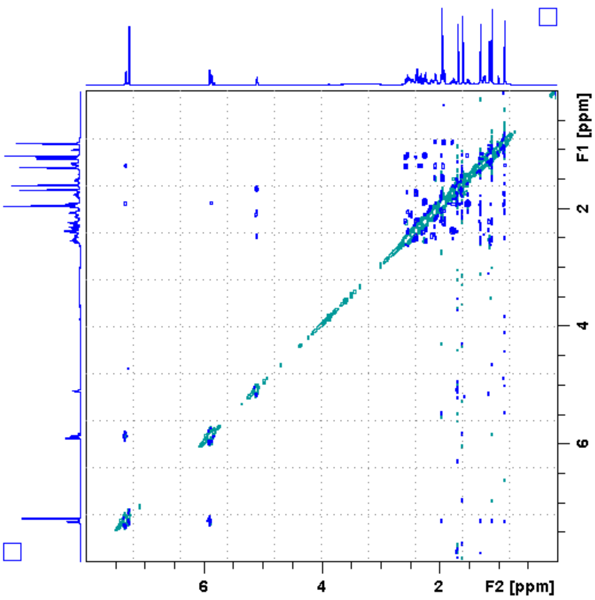
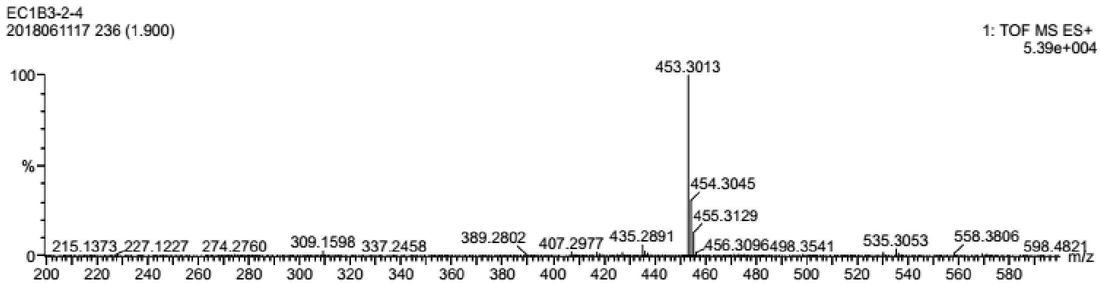


Figure S26 HRESIMS and NMR spectra of **33**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 600 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 150 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in $CDCl_3$ at 600 MHz; (F) HSQC spectrum in $CDCl_3$ at 600 MHz; (G) HMBC spectrum in $CDCl_3$ at 600 MHz; (H) NOESY spectrum in $CDCl_3$ at 600 MHz.

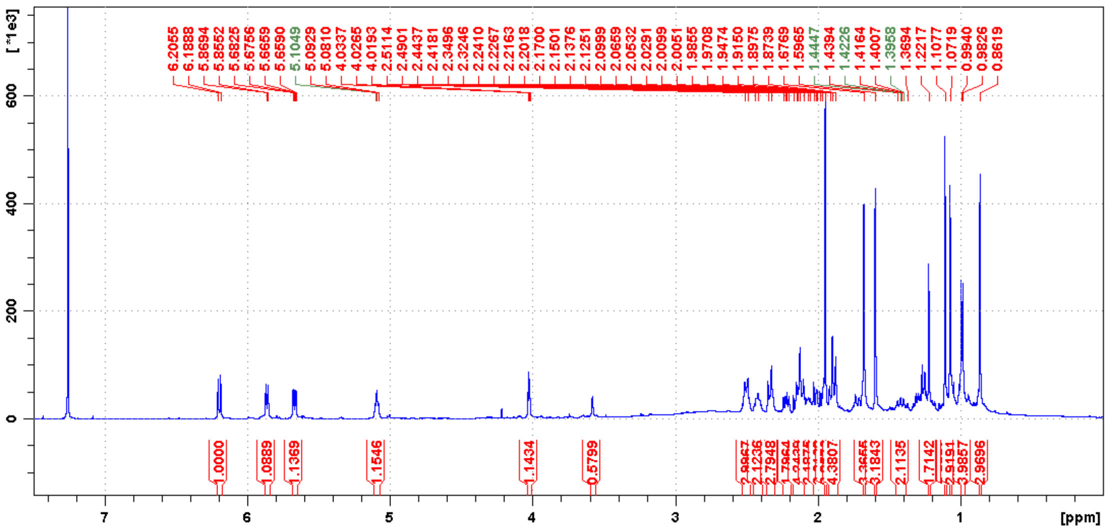
A

Monoisotopic Mass, Even Electron Ions
279 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1

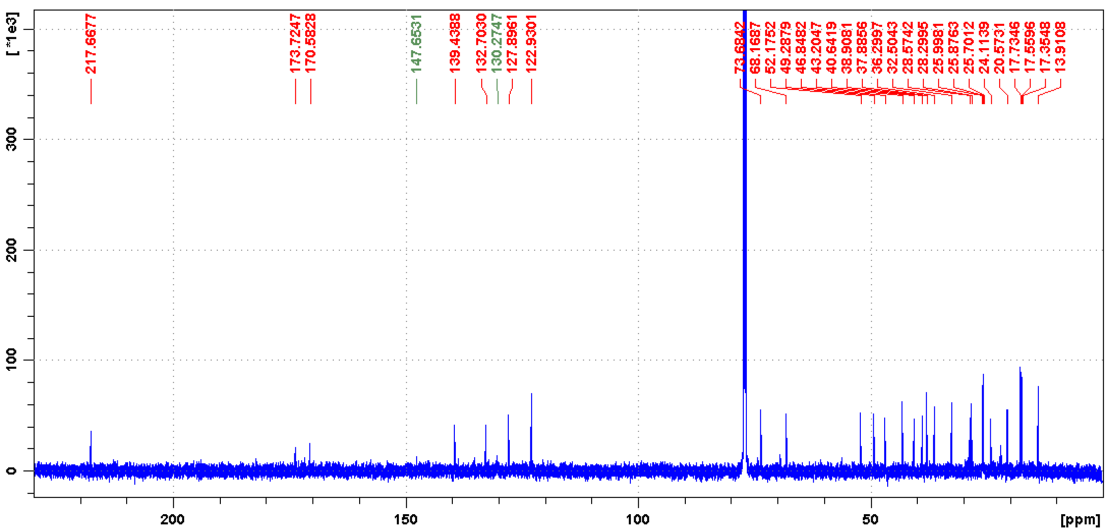


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
535.3053	535.3036	1.7	3.2	9.5	76.4	0.923	39.73	C31 H44 O6 Na
	535.3060	-0.7	-1.3	12.5	75.9	0.506	60.27	C33 H43 O6

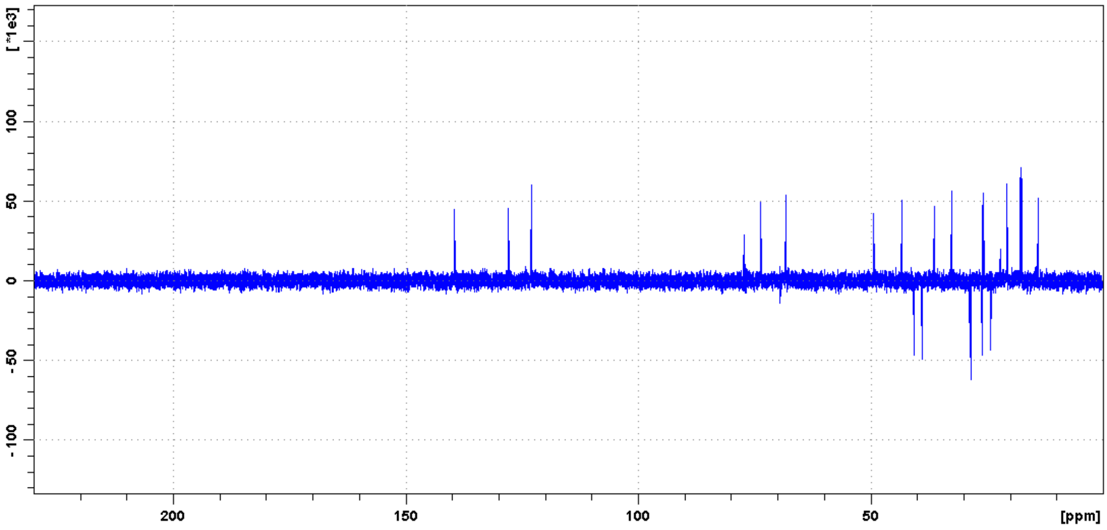
B



C



D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50
0
-50
-100
200
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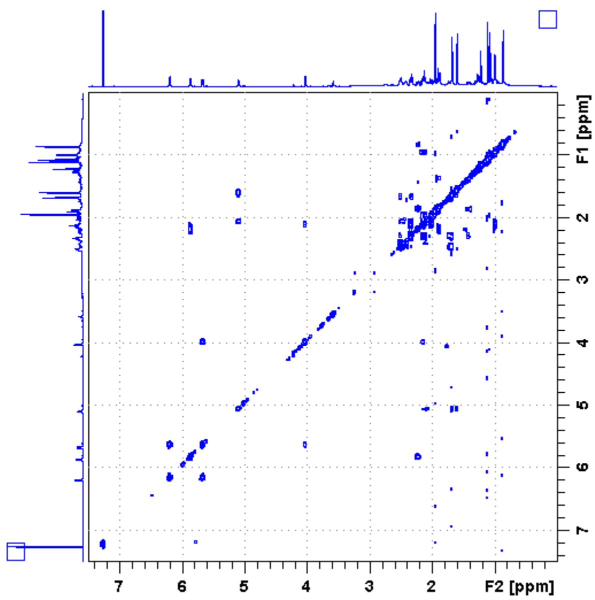
100
50
[ppm]

E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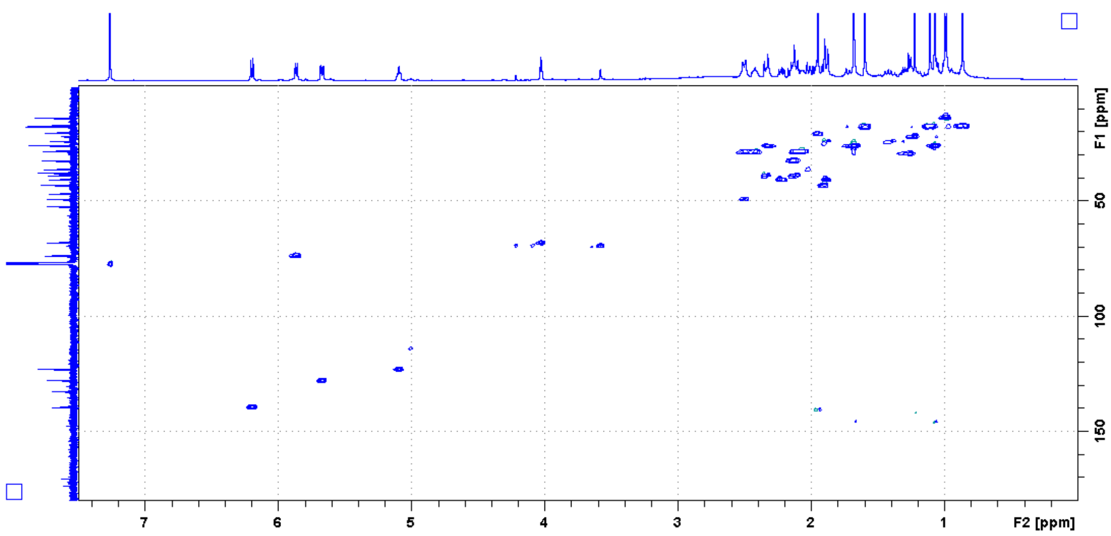
2
F2 [ppm]

F


F1 [ppm]
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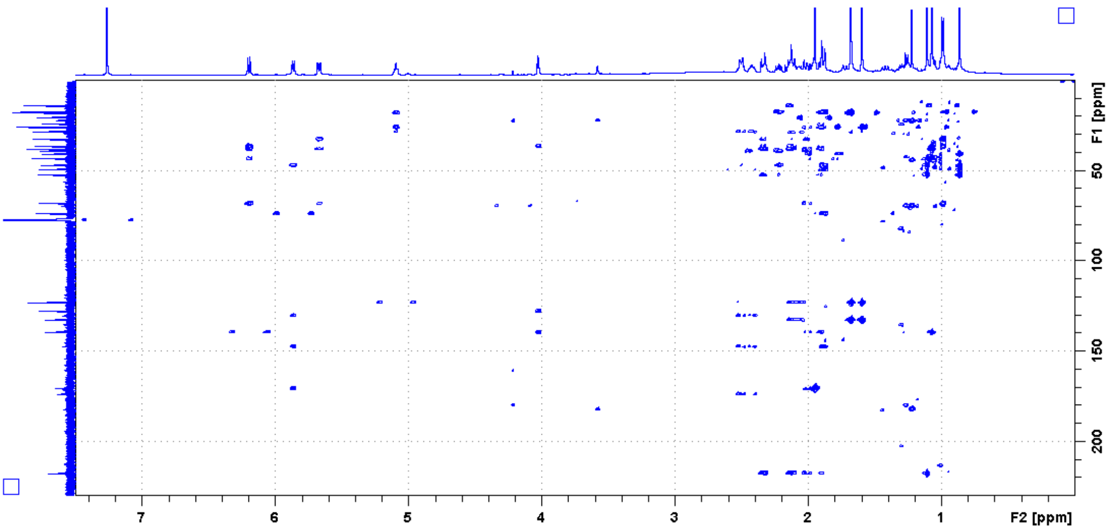
1
F2 [ppm]

G



H

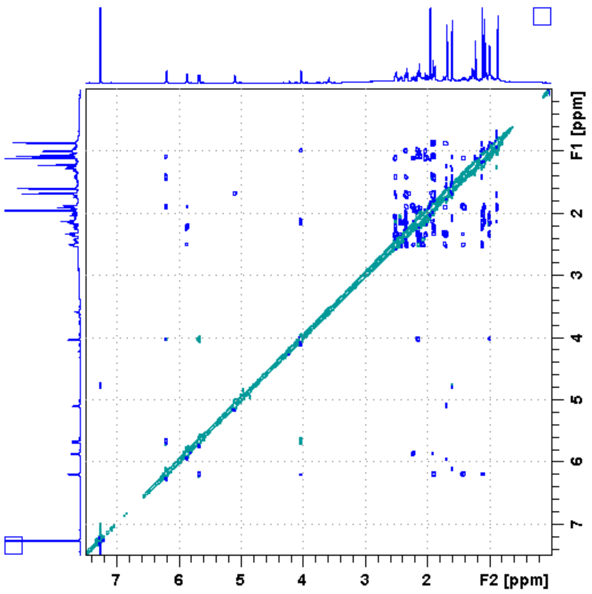
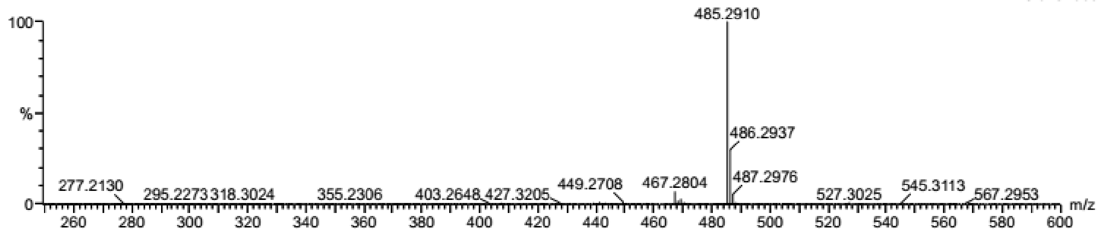


Figure S27 HRESIMS and NMR spectra of **34**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 600 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 150 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in $CDCl_3$ at 600 MHz; (F) HSQC spectrum in $CDCl_3$ at 600 MHz; (G) HMBC spectrum in $CDCl_3$ at 600 MHz; (H) ROESY spectrum in $CDCl_3$ at 600 MHz.

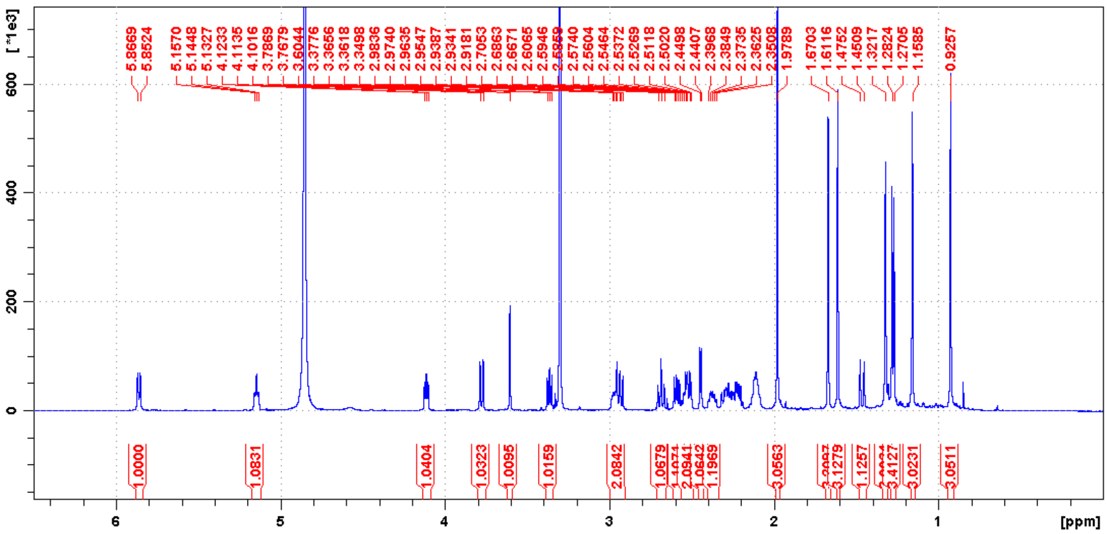
A

Monoisotopic Mass, Even Electron Ions
277 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
EB1-B4-70-1
20190527_12 193 (1.556)

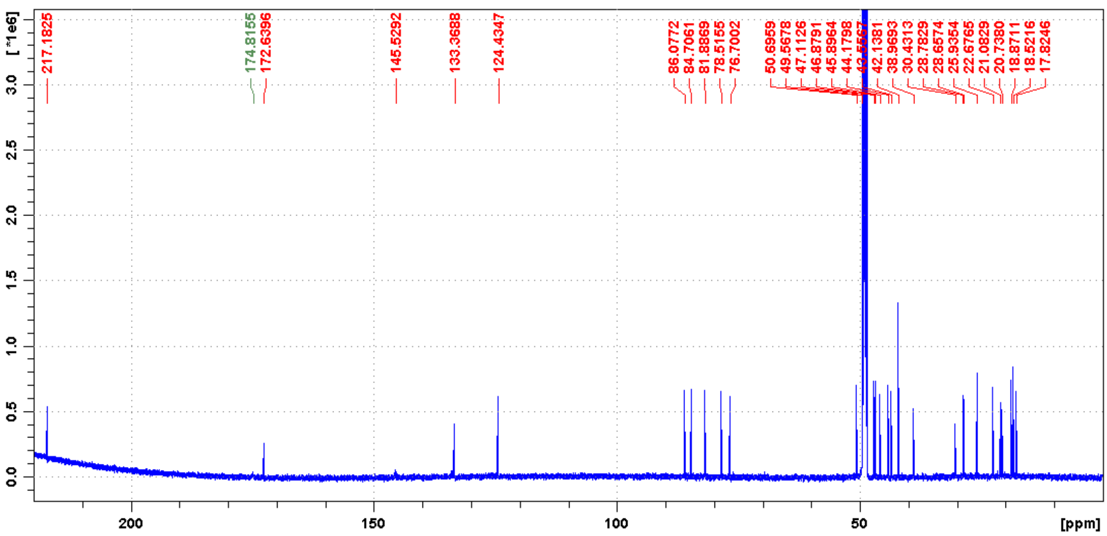


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
545.3113	545.3114	-0.1	-0.2	9.5	115.2	0.240	78.63	C31 H45 O8
	545.3090	2.3	4.2	6.5	116.5	1.543	21.37	C29 H46 O8 Na

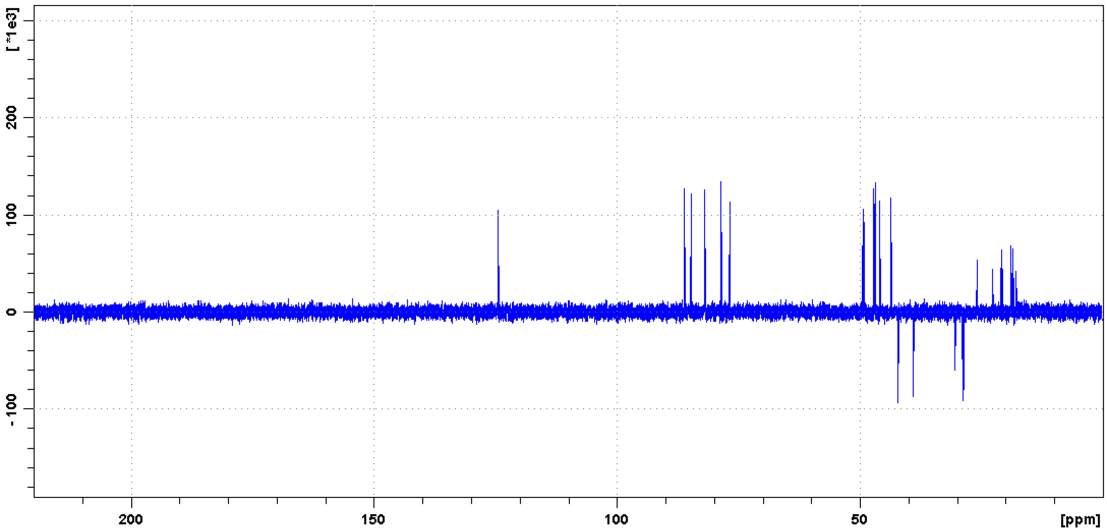
B



C



D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-100
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150
100
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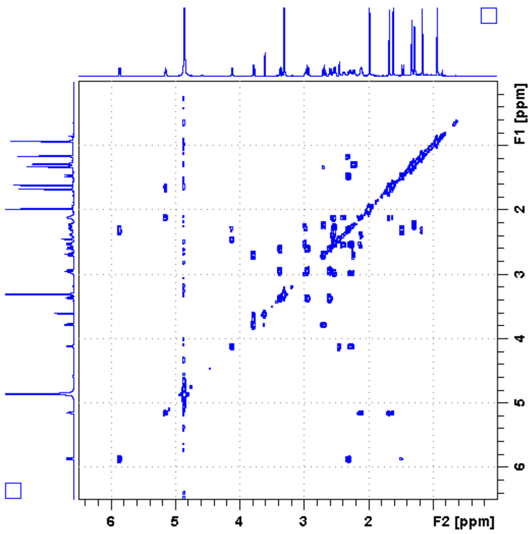
[ppm]

E


F1 [ppm]
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4
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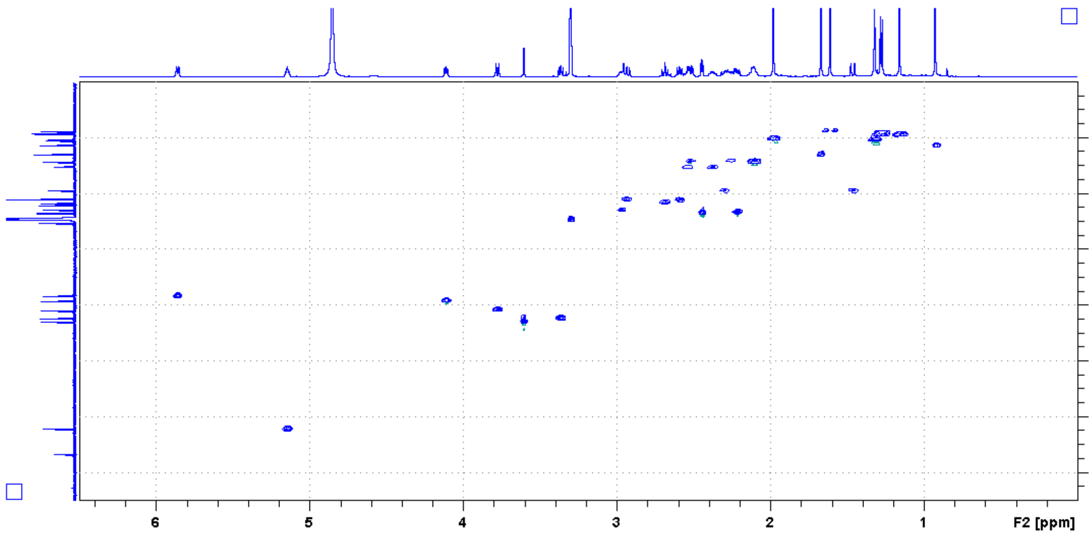
6
5
4
3
2
F2 [ppm]

F


F1 [ppm]
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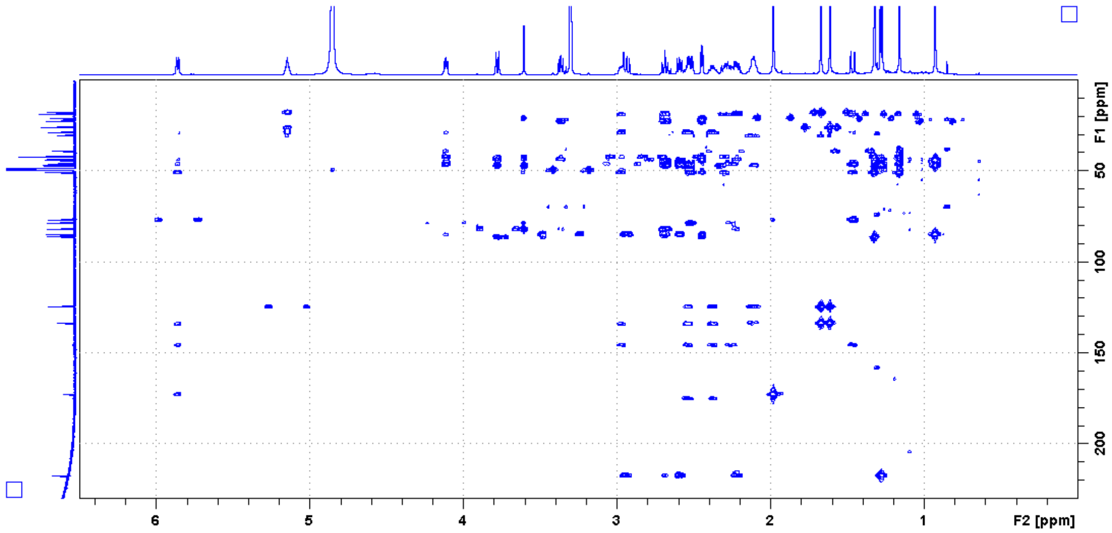
60
80
100
120
140
6
5
4
3
2
1
F2 [ppm]

G



H

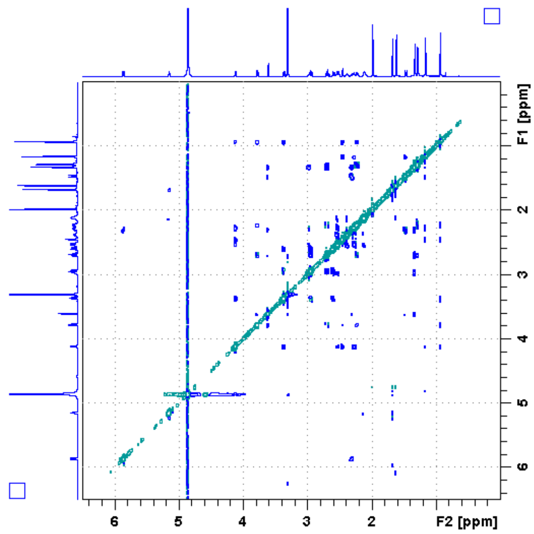
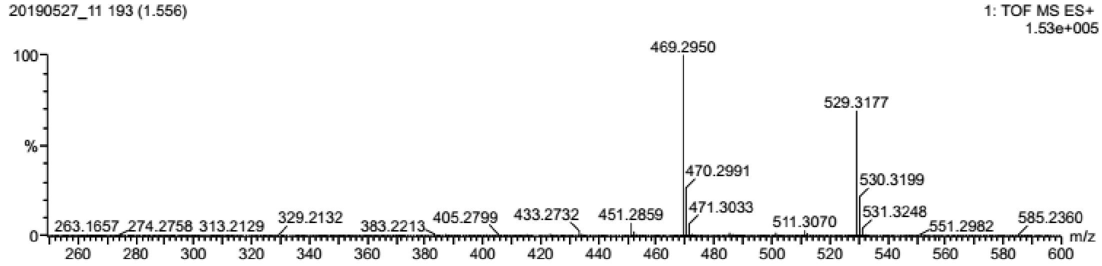


Figure S28 HRESIMS and NMR spectra of **35**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in CD_3OD at 600 MHz; (C) ^{13}C NMR spectrum in CD_3OD at 150 MHz; (D) DEPT 135 spectrum in CD_3OD at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in CD_3OD at 600 MHz; (F) HSQC spectrum in CD_3OD at 600 MHz; (G) HMBC spectrum in CD_3OD at 600 MHz; (H) ROESY spectrum in CD_3OD at 600 MHz.

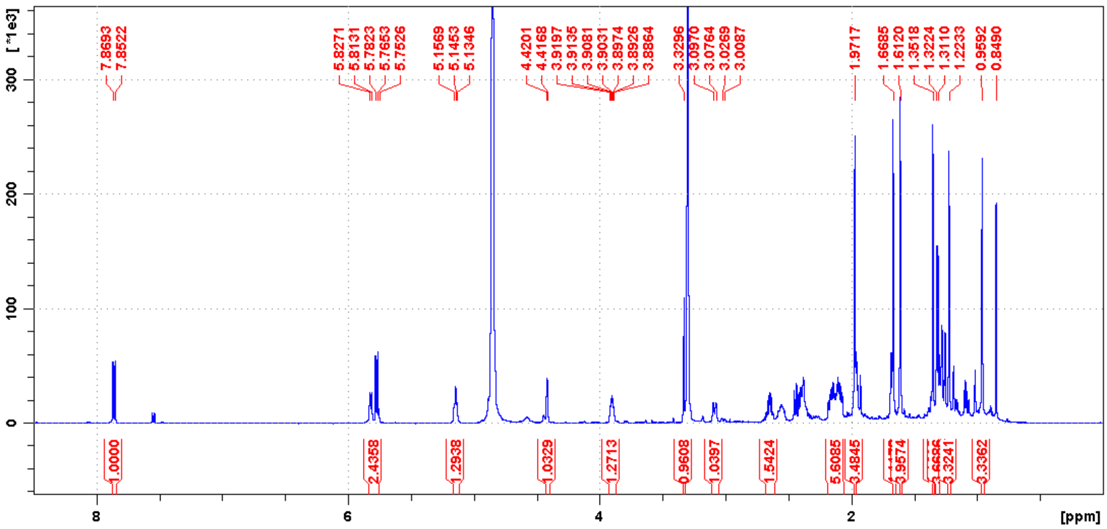
A

Monoisotopic Mass, Even Electron Ions
140 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200
EB1-B4-60-5
20190527_11 193 (1.556)

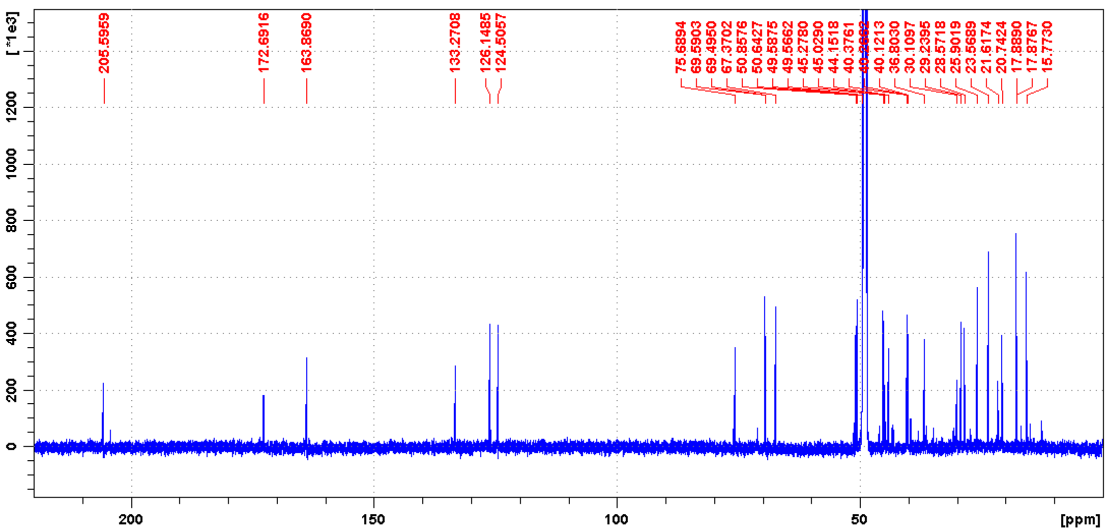


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
529.3177	529.3165	1.2	2.3	9.5	327.2	n/a	n/a	C31 H45 O7

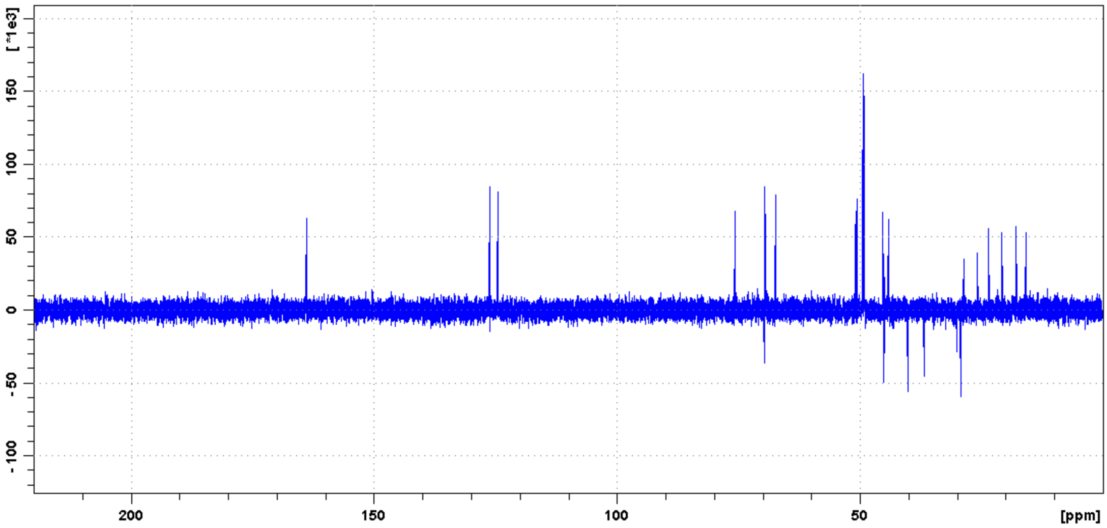
B



C



D



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-50
-100
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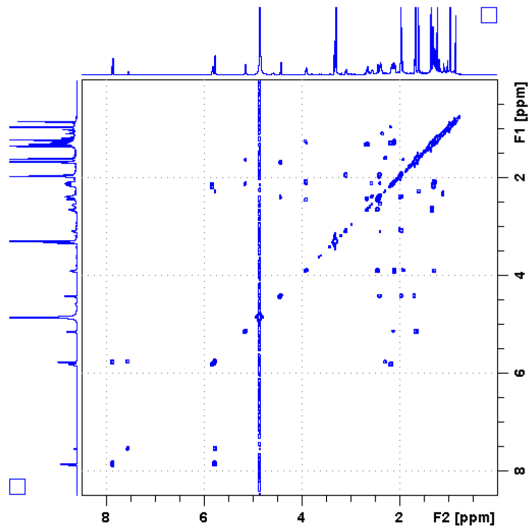
150
100
50
[ppm]

E



F1 [ppm]
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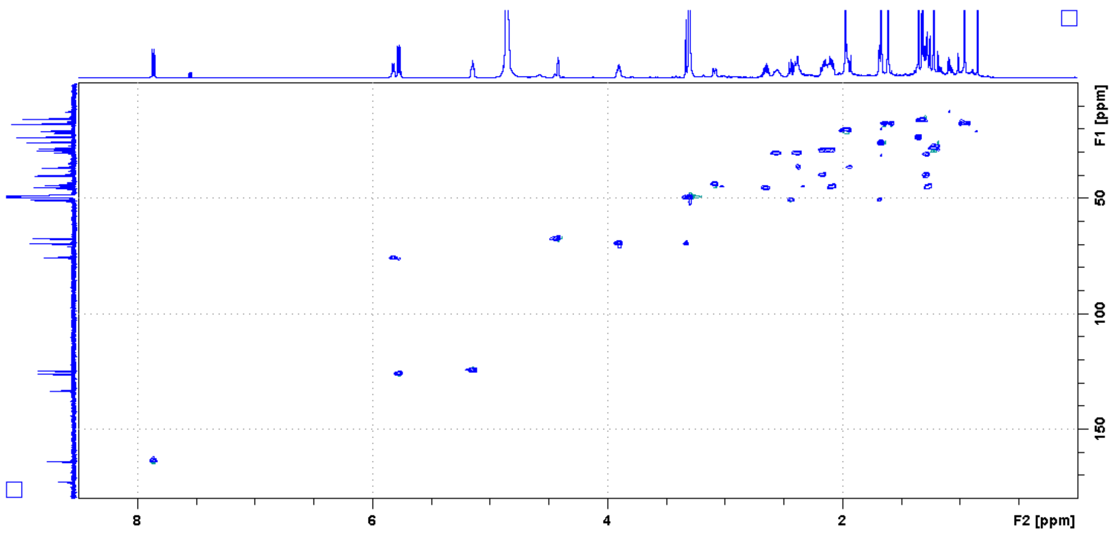
8
8
6
4
2
F2 [ppm]

F



F1 [ppm]
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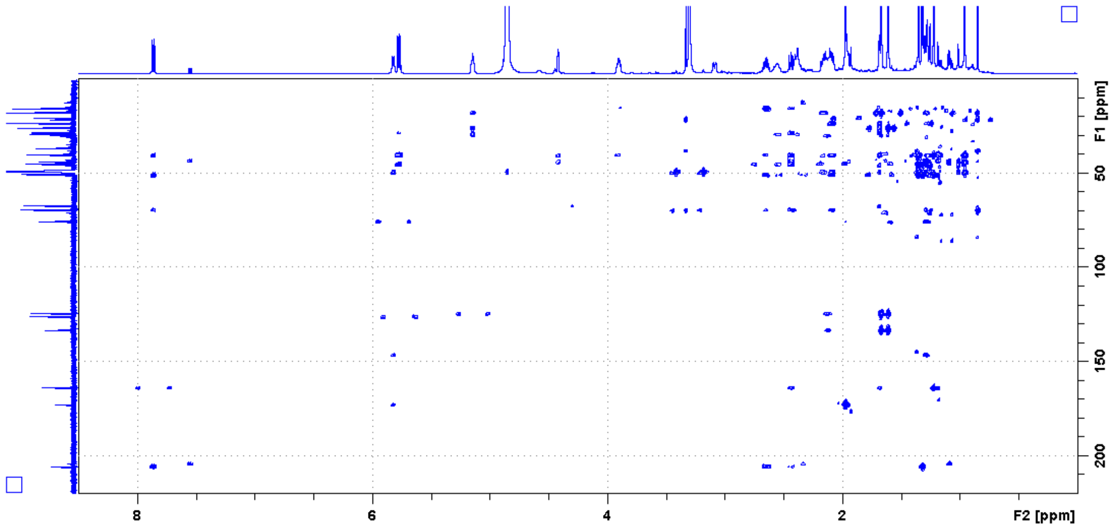
100
150
8
6
4
2
F2 [ppm]

G



H

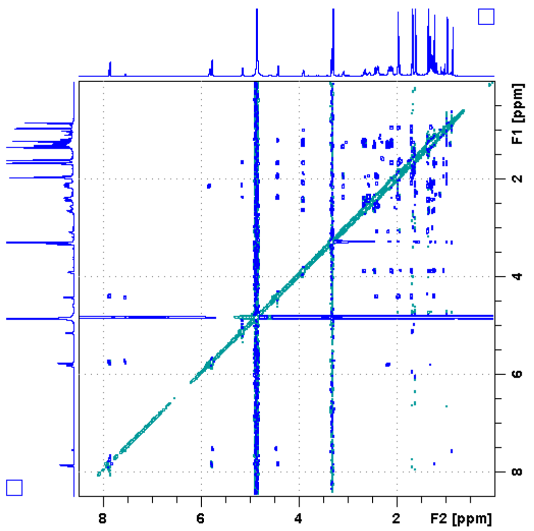
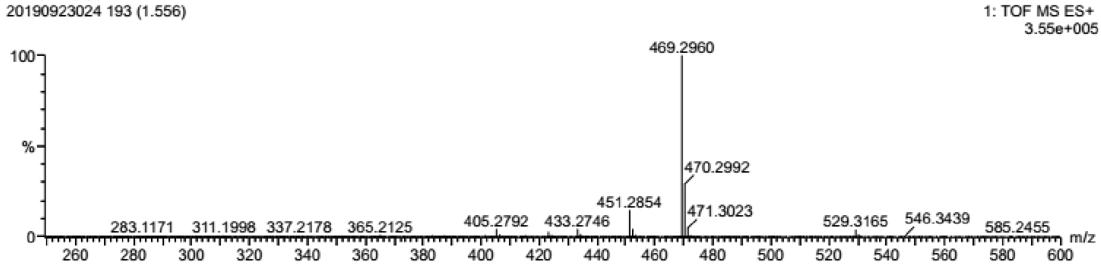


Figure S29 HRESIMS and NMR spectra of **36**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in CD_3OD at 600 MHz; (C) ^{13}C NMR spectrum in CD_3OD at 150 MHz; (D) DEPT 135 spectrum in CD_3OD at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in CD_3OD at 600 MHz; (F) HSQC spectrum in CD_3OD at 600 MHz; (G) HMBC spectrum in CD_3OD at 600 MHz; (H) ROESY spectrum in CD_3OD at 600 MHz.

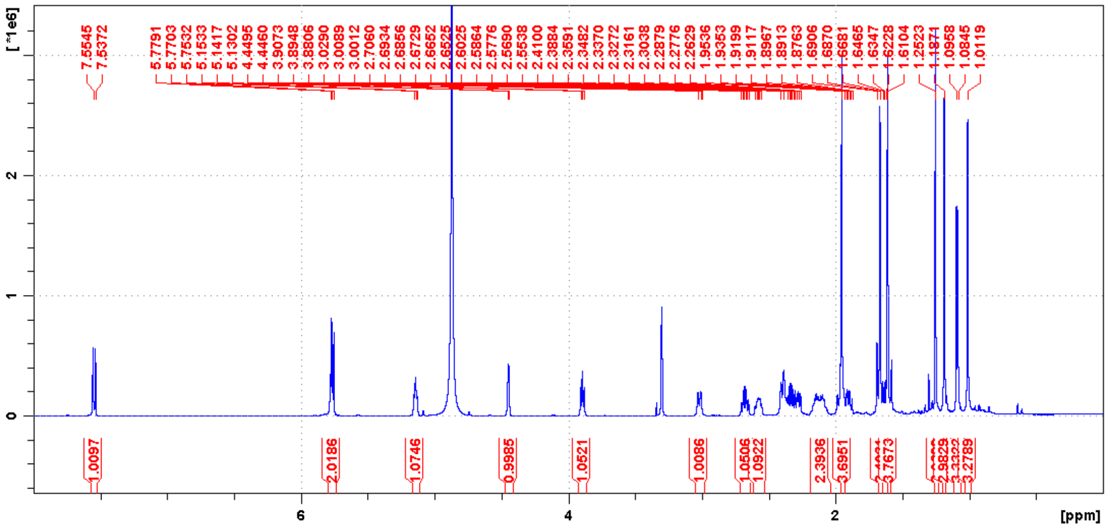
A

Monoisotopic Mass, Even Electron Ions
263 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
EB1C1-B3-80-4
20190923024 193 (1.556)

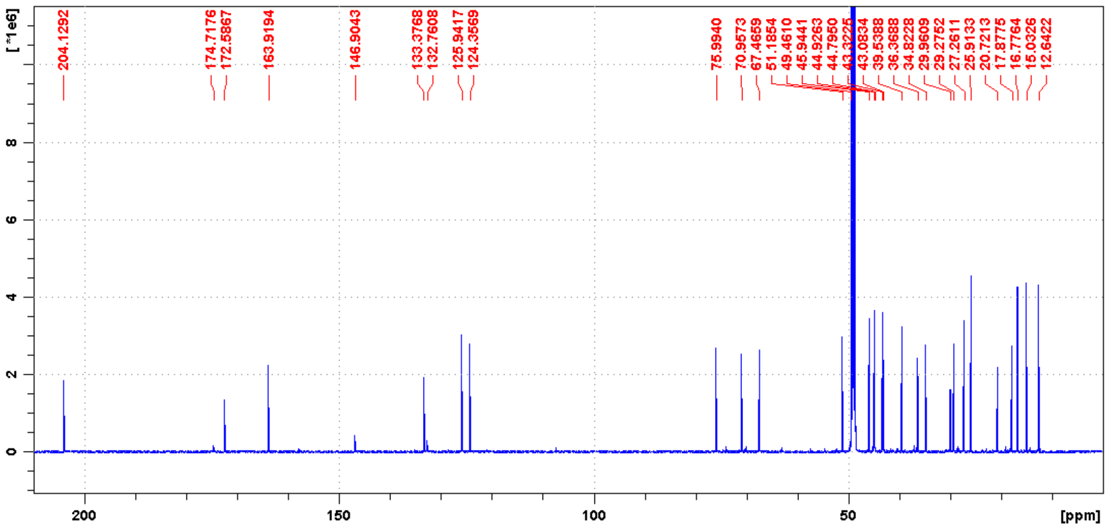


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
529.3165	529.3165	0.0	0.0	9.5	121.5	0.544	58.04	C31 H45 O7
	529.3141	2.4	4.5	6.5	121.8	0.868	41.96	C29 H46 O7 Na

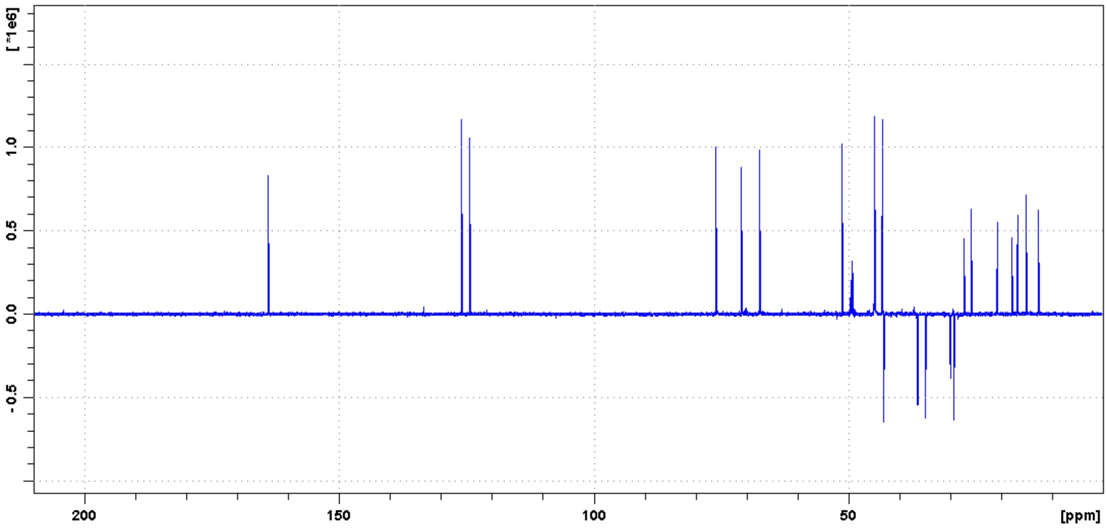
B



C



D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0.0
-0.5
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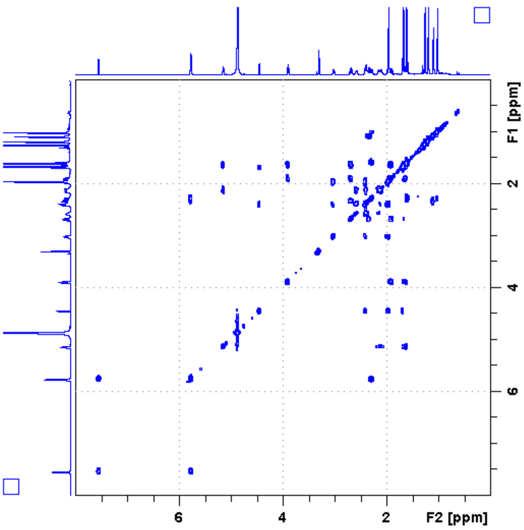
100
50
[ppm]

E


F1 [ppm]
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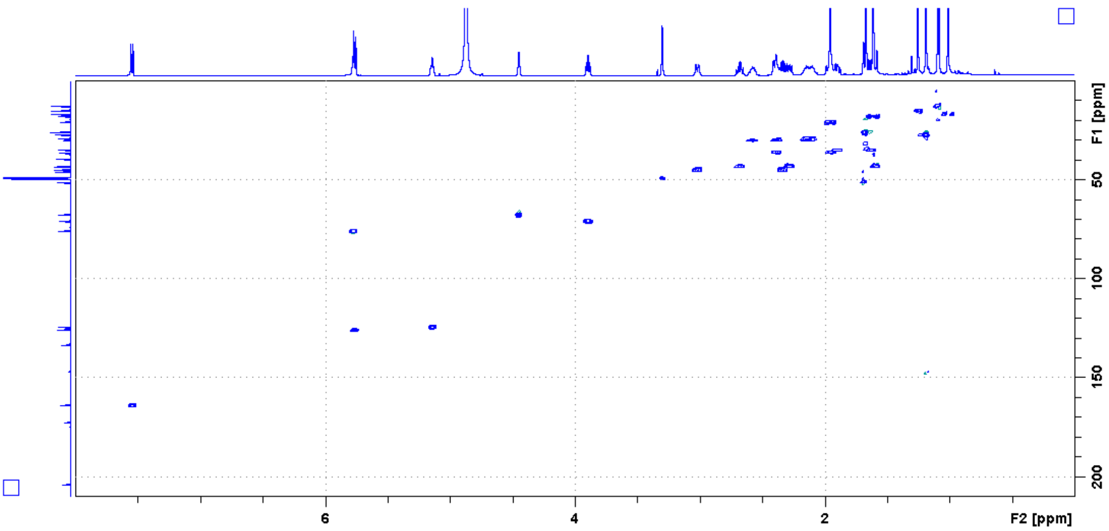
6
F2 [ppm]

F


F1 [ppm]
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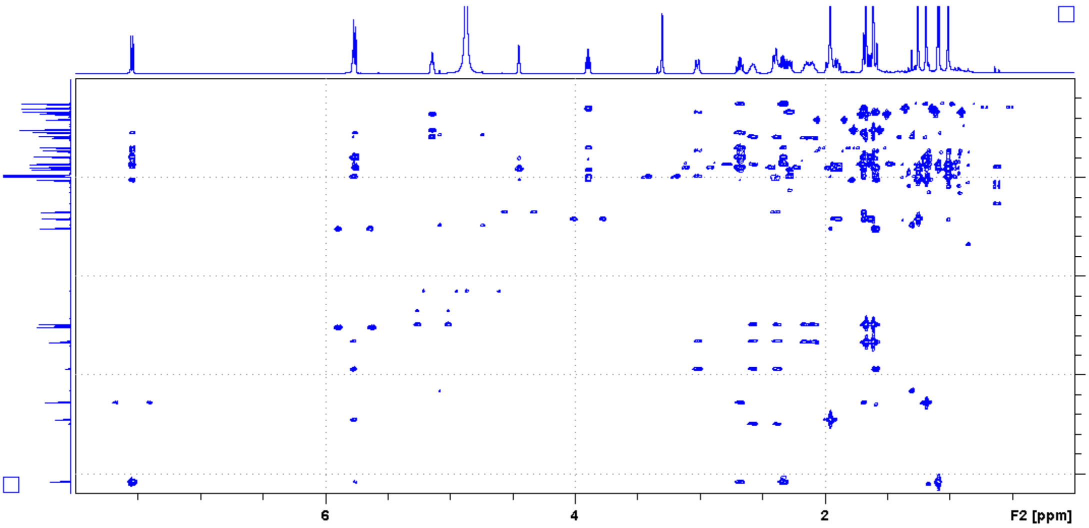
200
6
4
2
F2 [ppm]

G



H

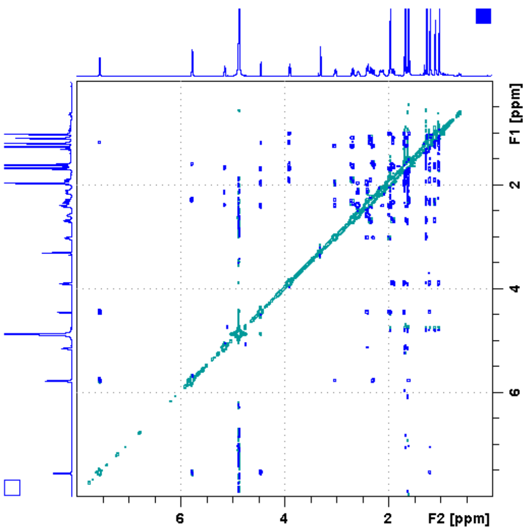
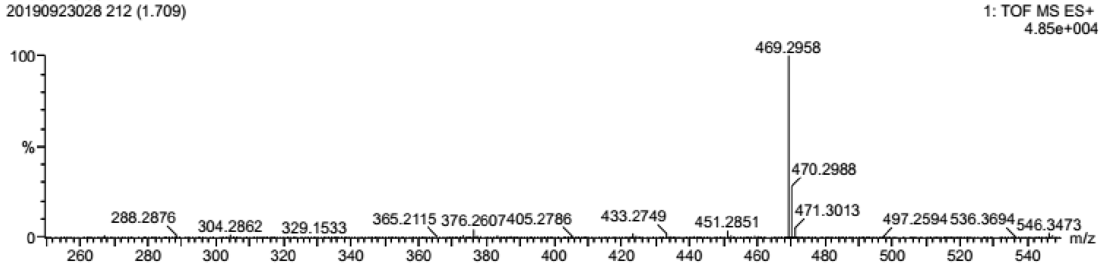


Figure S30 HRESIMS and NMR spectra of **37**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in CD_3OD at 600 MHz; (C) ^{13}C NMR spectrum in CD_3OD at 150 MHz; (D) DEPT 135 spectrum in CD_3OD at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in CD_3OD at 600 MHz; (F) HSQC spectrum in CD_3OD at 600 MHz; (G) HMBC spectrum in CD_3OD at 600 MHz; (H) ROESY spectrum in CD_3OD at 600 MHz.

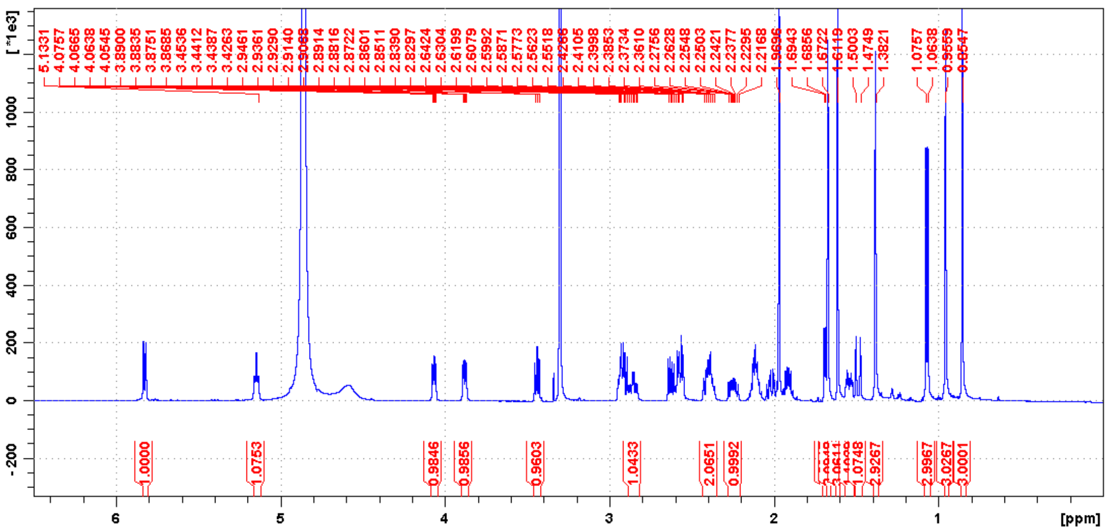
A

Monoisotopic Mass, Even Electron Ions
212 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
EB1C1-B3-80-7-2
20190923028 212 (1.709)

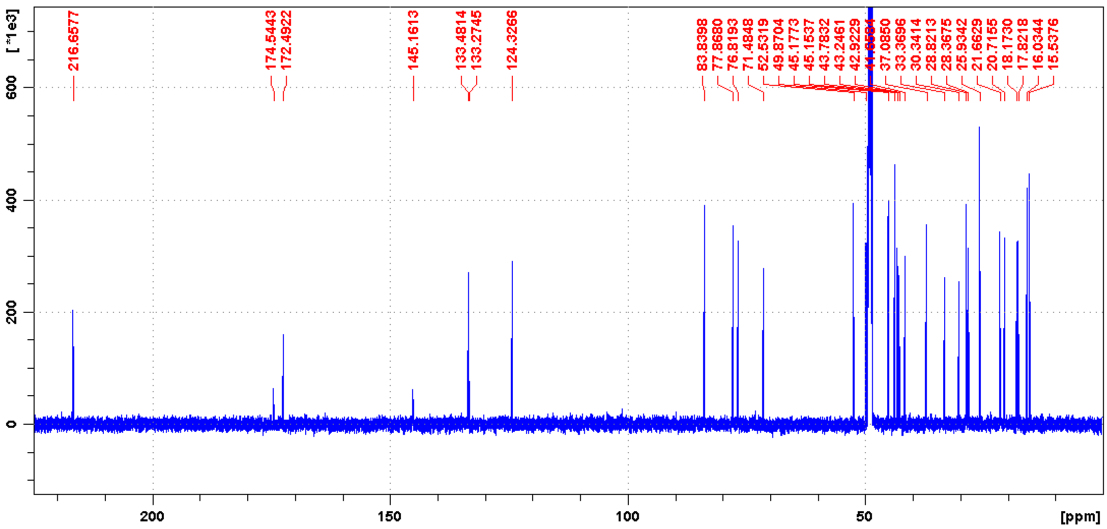


	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
469.2958	469.2954	0.4	0.9	9.5	254.3	n/a	n/a	C29 H41 O5

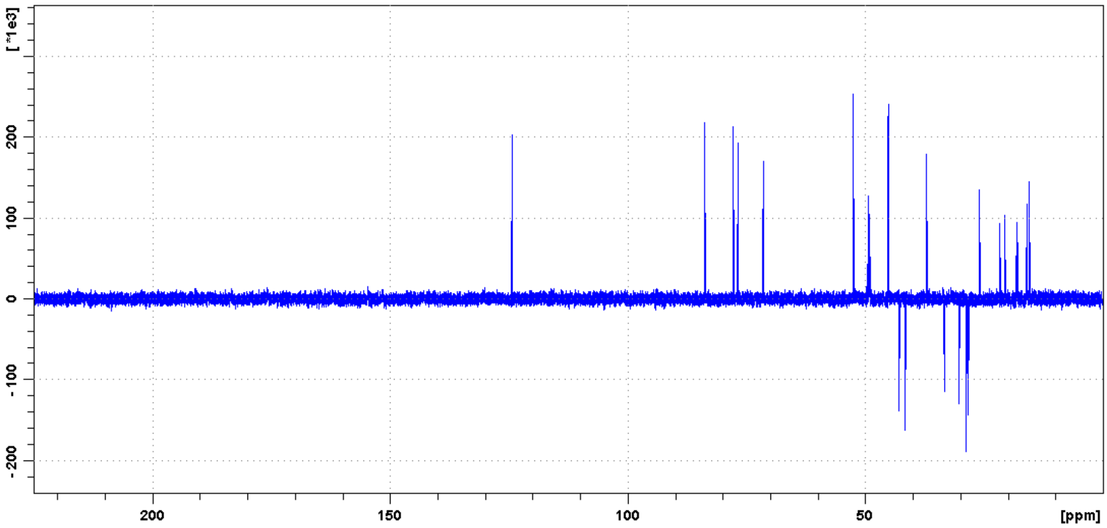
B



C



D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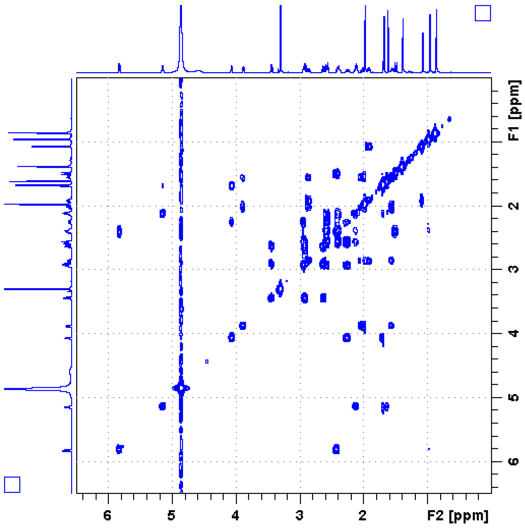
-200
200
150
100
50
[ppm]

E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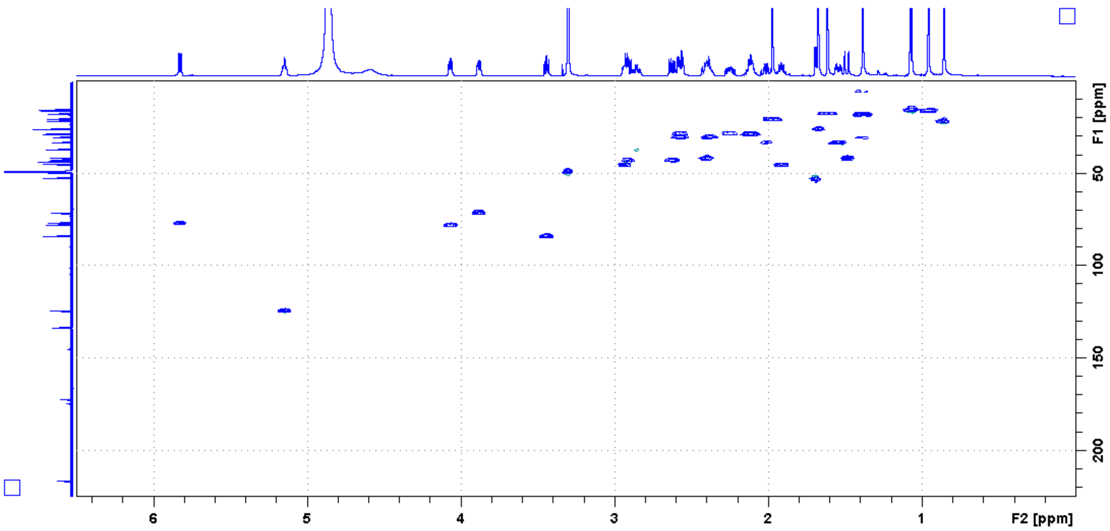
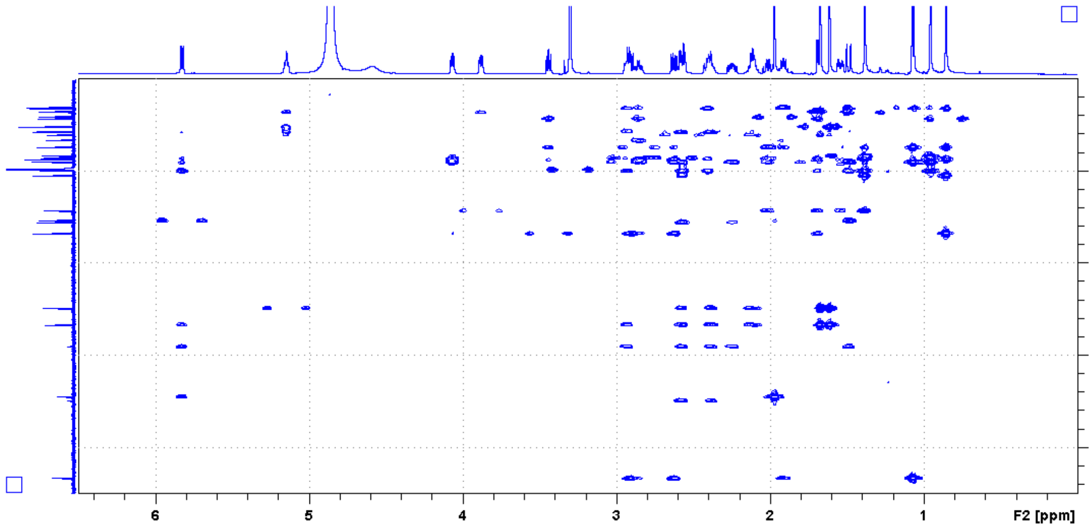

F1 [ppm]
F2 [ppm]

G



H

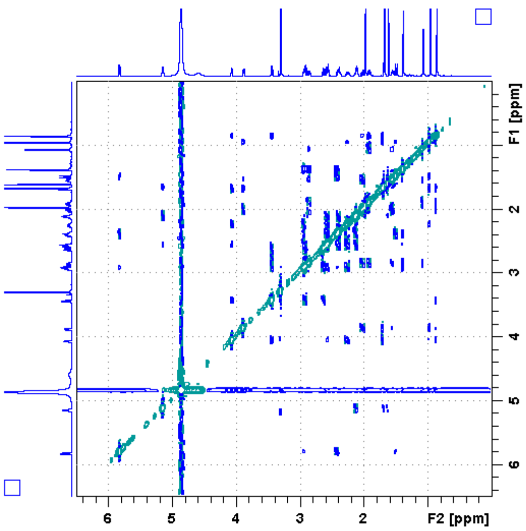
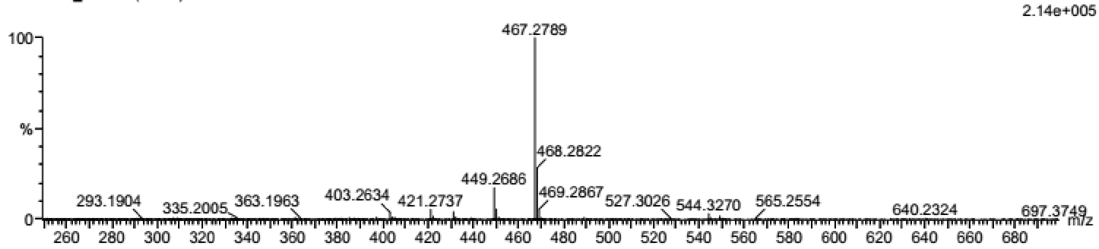


Figure S31 HRESIMS and NMR spectra of **38**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in CD_3OD at 400 MHz; (C) ^{13}C NMR spectrum in CD_3OD at 100 MHz; (D) DEPT 135 spectrum in CD_3OD at 100 MHz; (E) ^{1}H–^{1}H COSY spectrum in CD_3OD at 400 MHz; (F) HSQC spectrum in CD_3OD at 400 MHz; (G) HMBC spectrum in CD_3OD at 400 MHz; (H) ROESY spectrum in CD_3OD at 400 MHz.

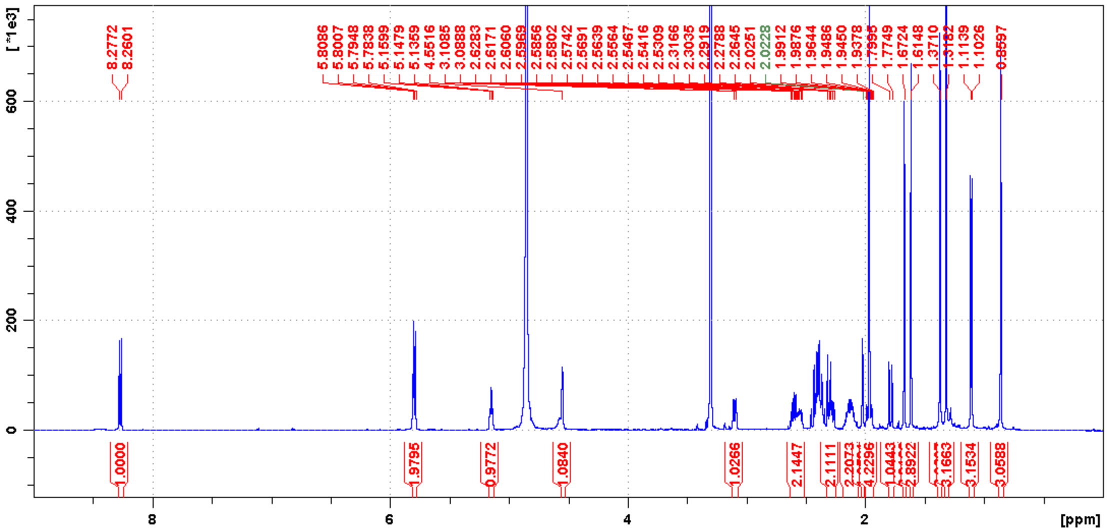
A

Monoisotopic Mass, Even Electron Ions
117 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200
EB1-B4-70-6-1
20190527_14 208 (1.683)

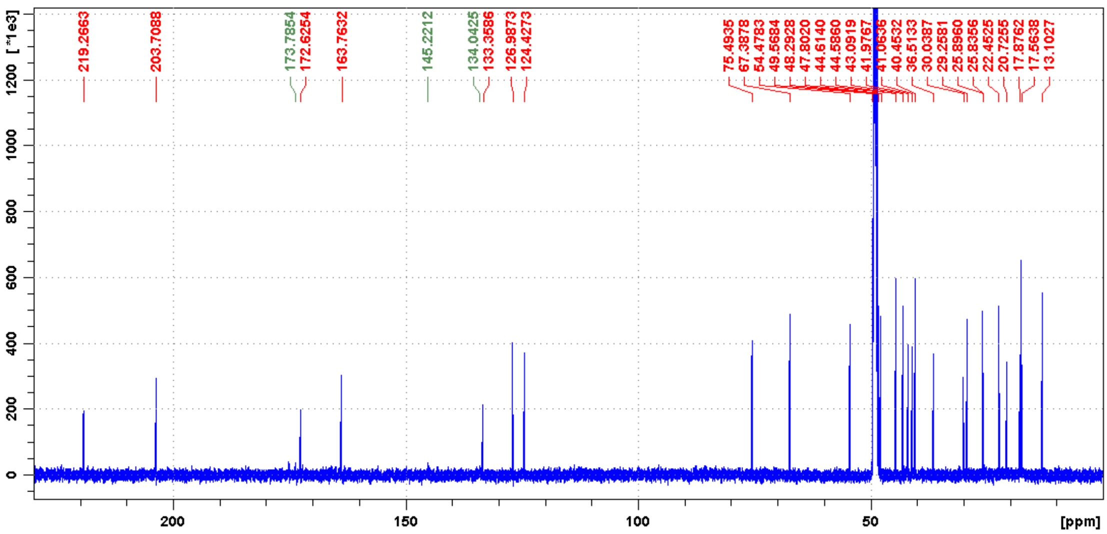


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
467.2789	467.2797	-0.8	-1.7	10.5	384.5	n/a	n/a	C29 H39 O5

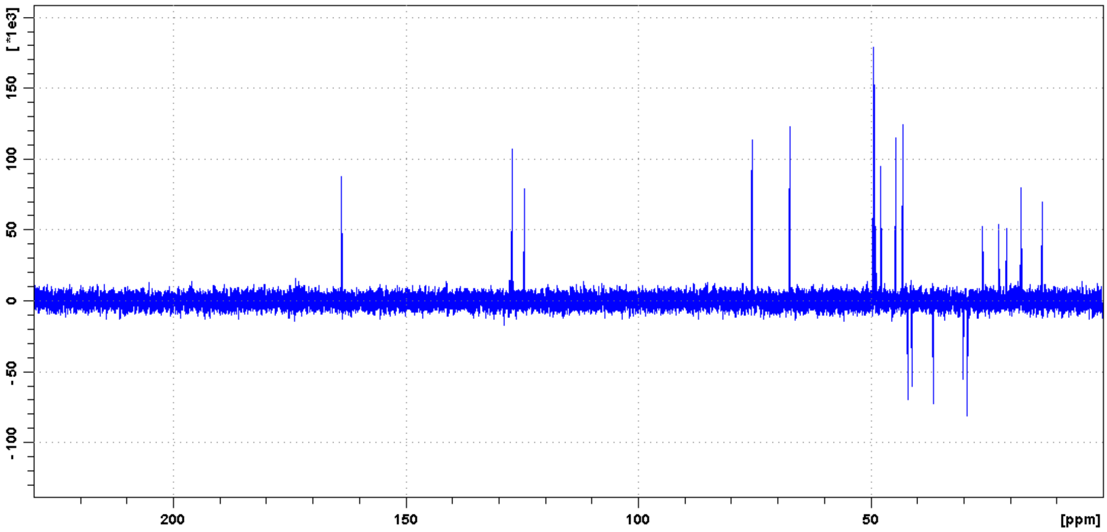
B



C



D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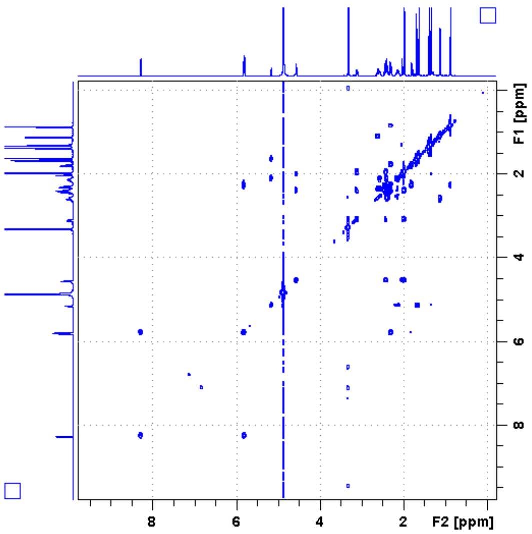
-50
-100
200
150
100
50
[ppm]

E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4
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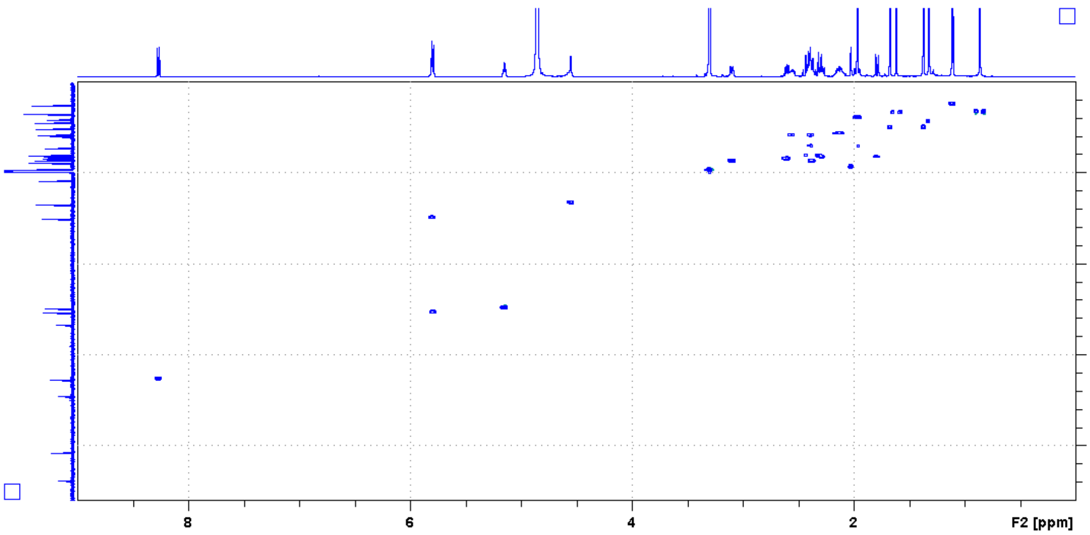
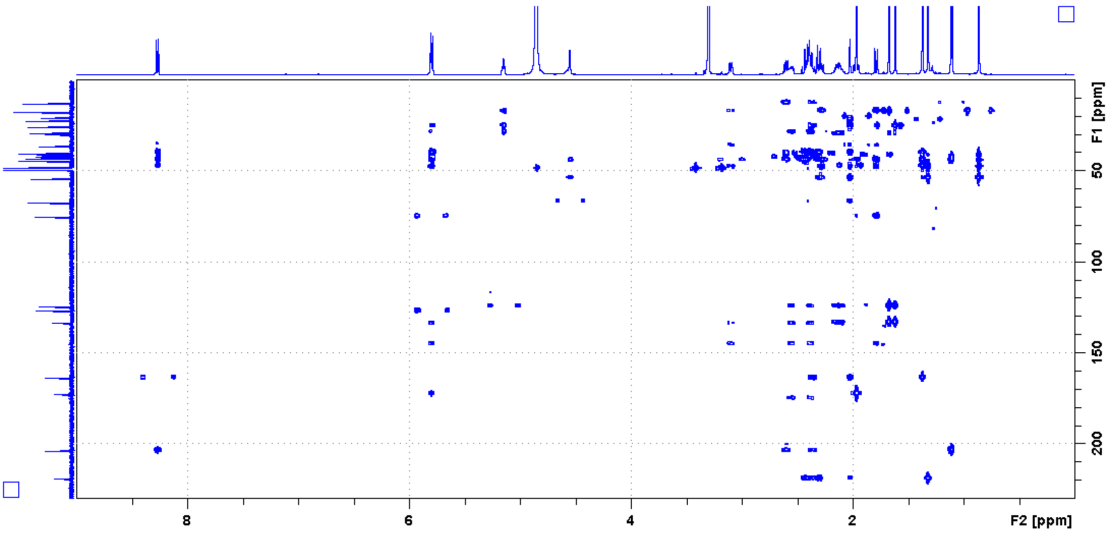
F2 [ppm]
F1 [ppm]

F


8
6
4
2
F2 [ppm]
F1 [ppm]
50
100
150
200

G



H

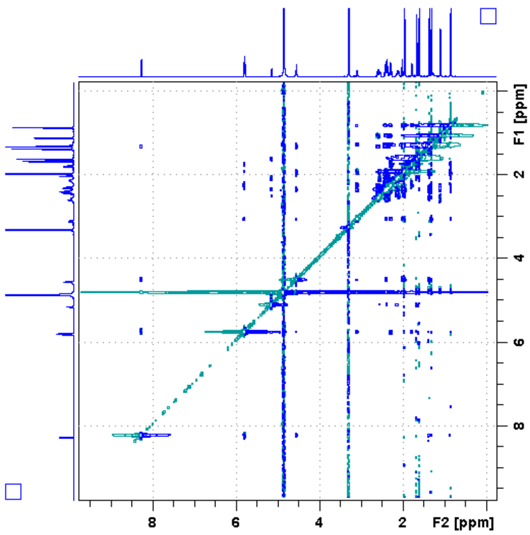
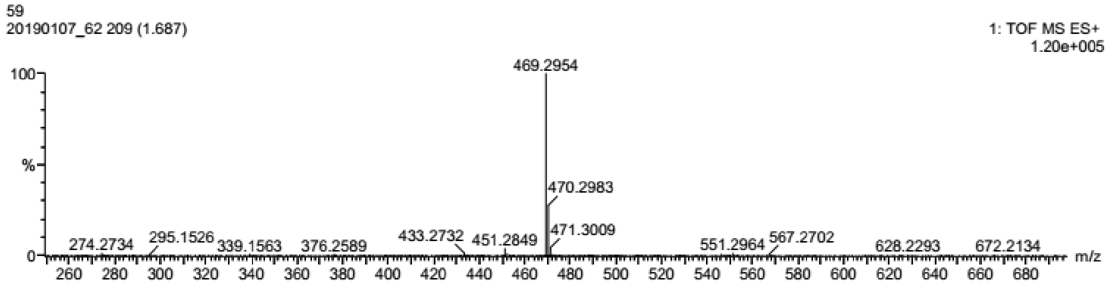


Figure S32 HRESIMS and NMR spectra of **39**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in CD_3OD at 600 MHz; (C) ^{13}C NMR spectrum in CD_3OD at 150 MHz; (D) DEPT 135 spectrum in CD_3OD at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in CD_3OD at 600 MHz; (F) HSQC spectrum in CD_3OD at 600 MHz; (G) HMBC spectrum in CD_3OD at 600 MHz; (H) ROESY spectrum in CD_3OD at 600 MHz.

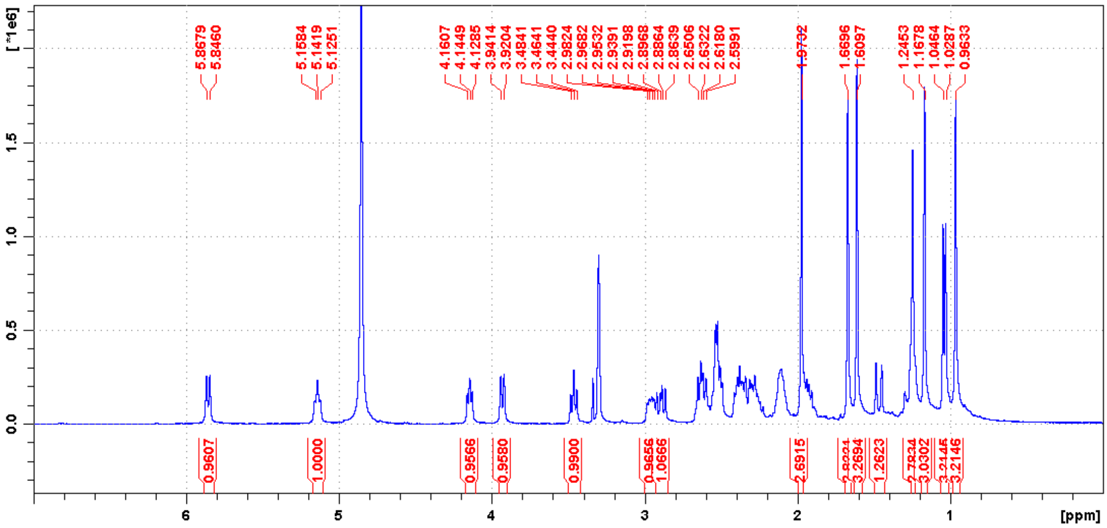
A

Monoisotopic Mass, Even Electron Ions
212 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500   H: 0-1000   O: 0-200   Na: 0-1

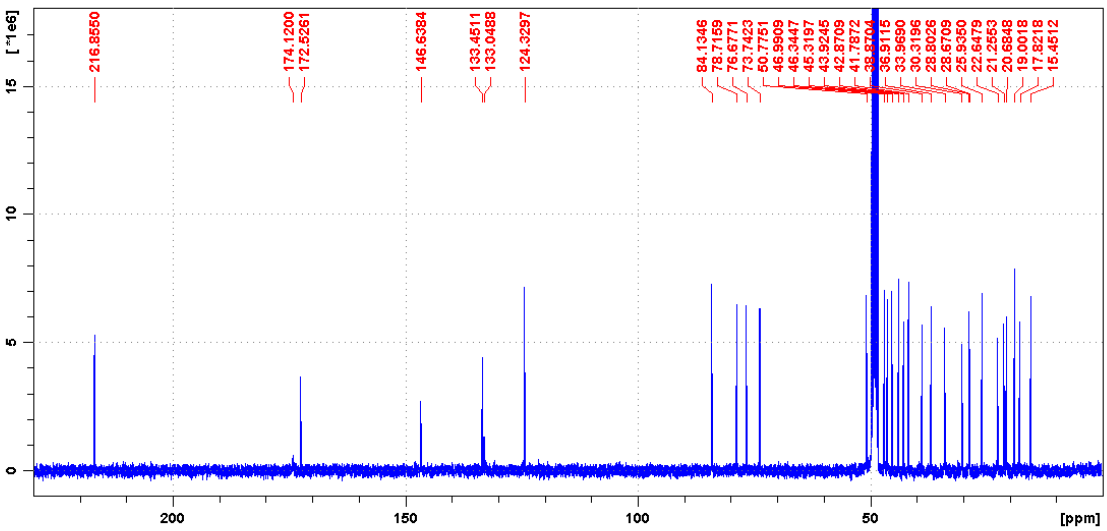


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
469.2954	469.2954	0.0	0.0	9.5	295.2	n/a	n/a	C29 H41 O5

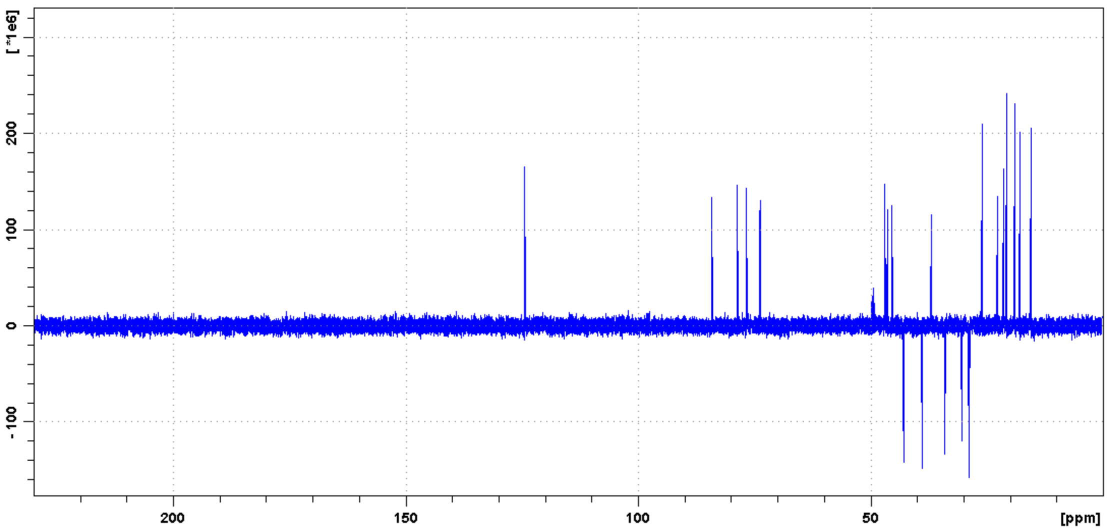
B



C



D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200
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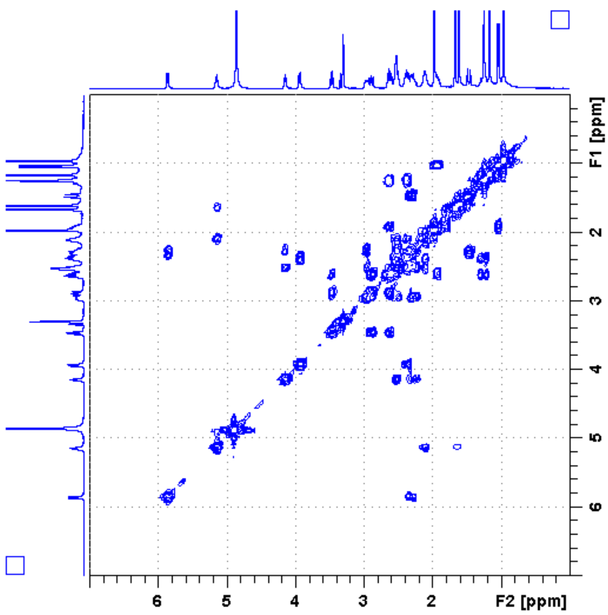
100
50
[ppm]

E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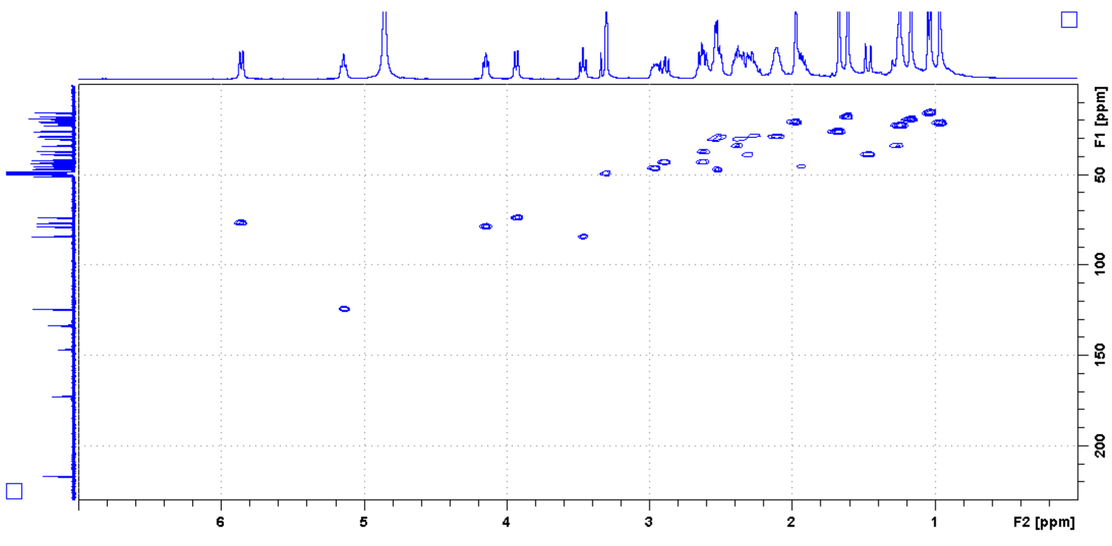
5
4
3
2
F2 [ppm]
F1 [ppm]

F


6
5
4
3
2
1
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F1 [ppm]
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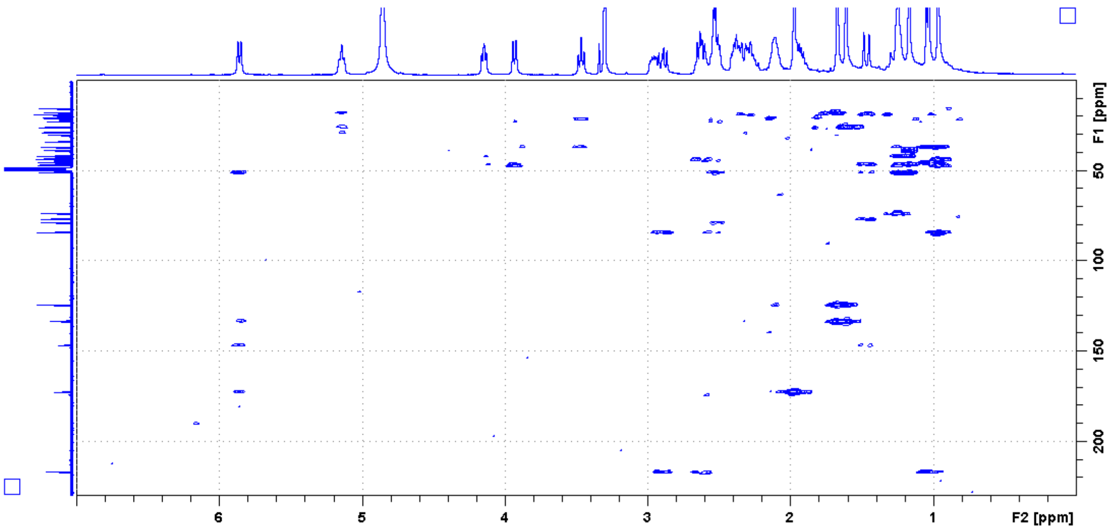
200

G



H

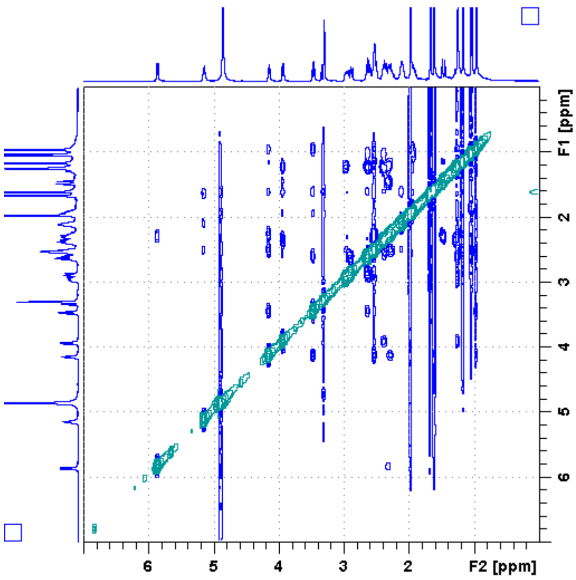
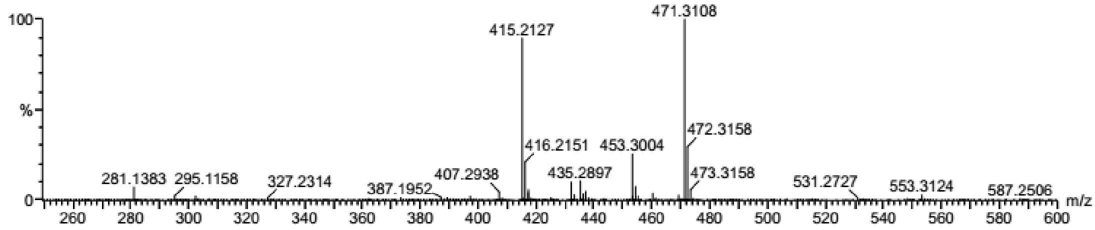


Figure S33 HRESIMS and NMR spectra of **40**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in CD_3OD at 400 MHz; (C) ^{13}C NMR spectrum in CD_3OD at 100 MHz; (D) DEPT 135 spectrum in CD_3OD at 100 MHz; (E) ^{1}H–^{1}H COSY spectrum in CD_3OD at 400 MHz; (F) HSQC spectrum in CD_3OD at 400 MHz; (G) HMBC spectrum in CD_3OD at 400 MHz; (H) ROESY spectrum in CD_3OD at 400 MHz.

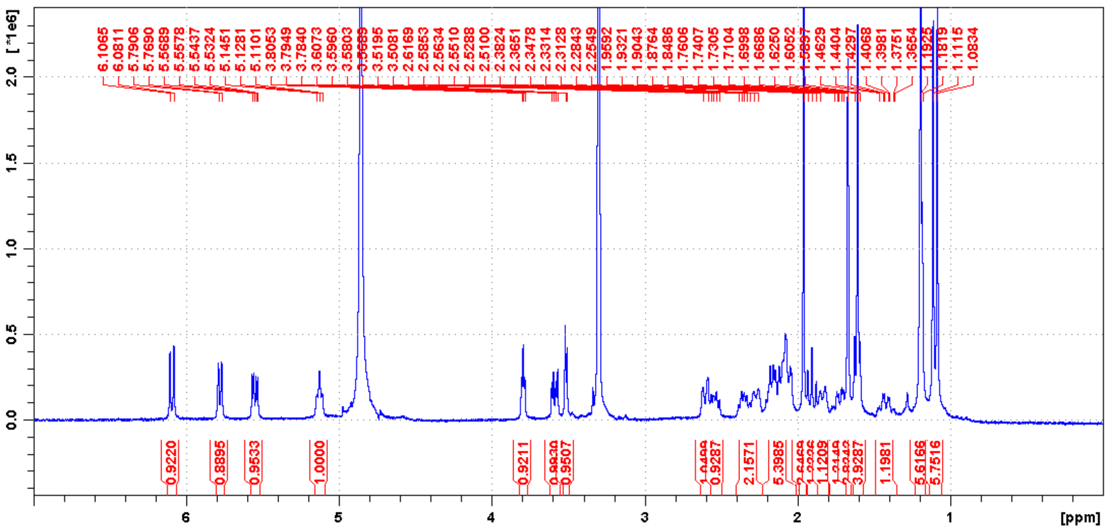
A

Monoisotopic Mass, Even Electron Ions
285 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
EB4C1-80-1-4
20190923048 219 (1.773)



Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
553.3124	553.3141	-1.7	-3.1	8.5	49.8	0.158	85.38	C31 H46 O7 Na
	553.3107	1.7	3.1	20.5	51.6	1.923	14.62	C40 H41 O2

B



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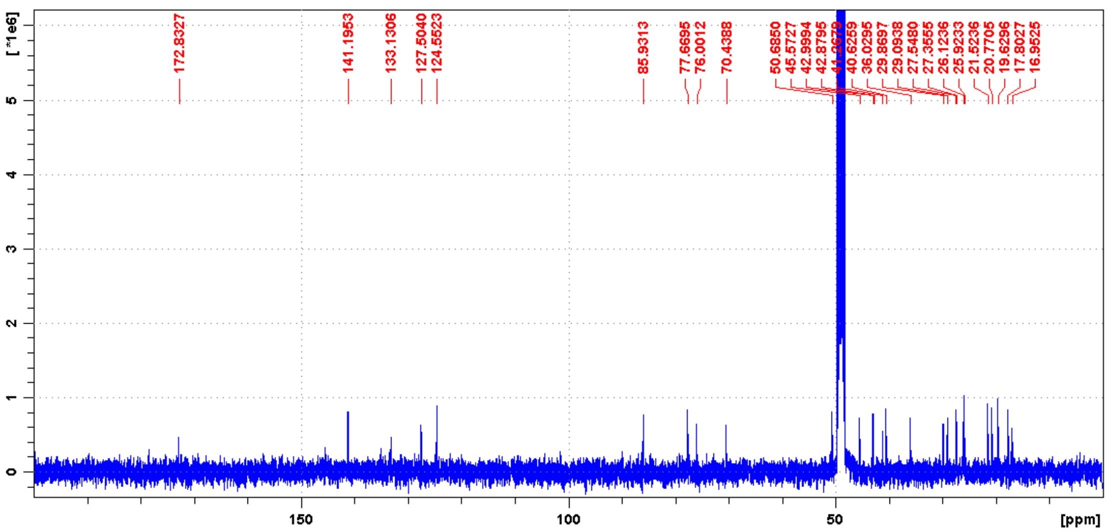

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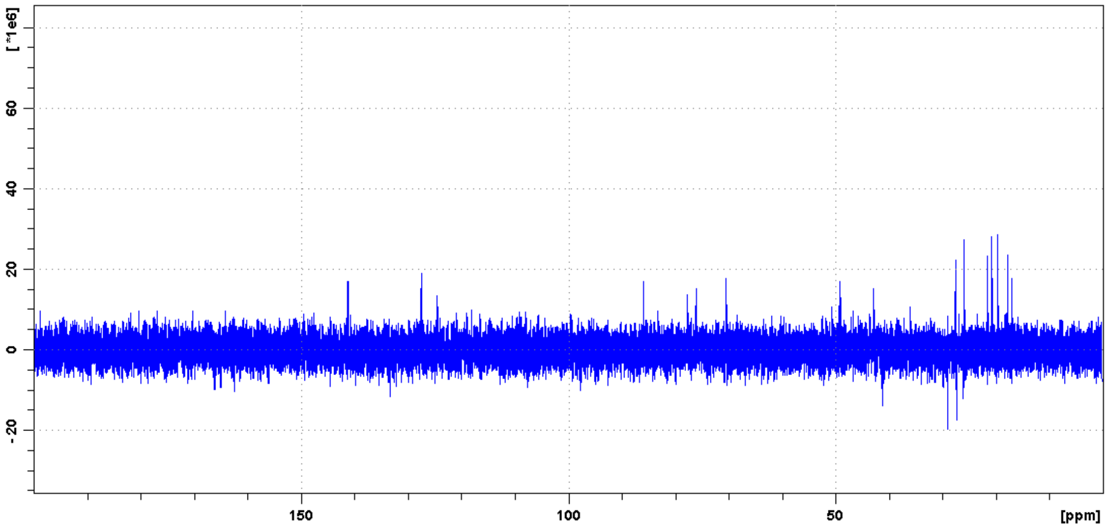

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[ppm]

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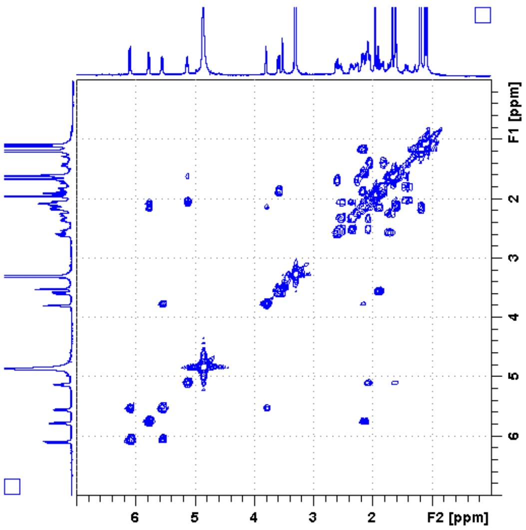

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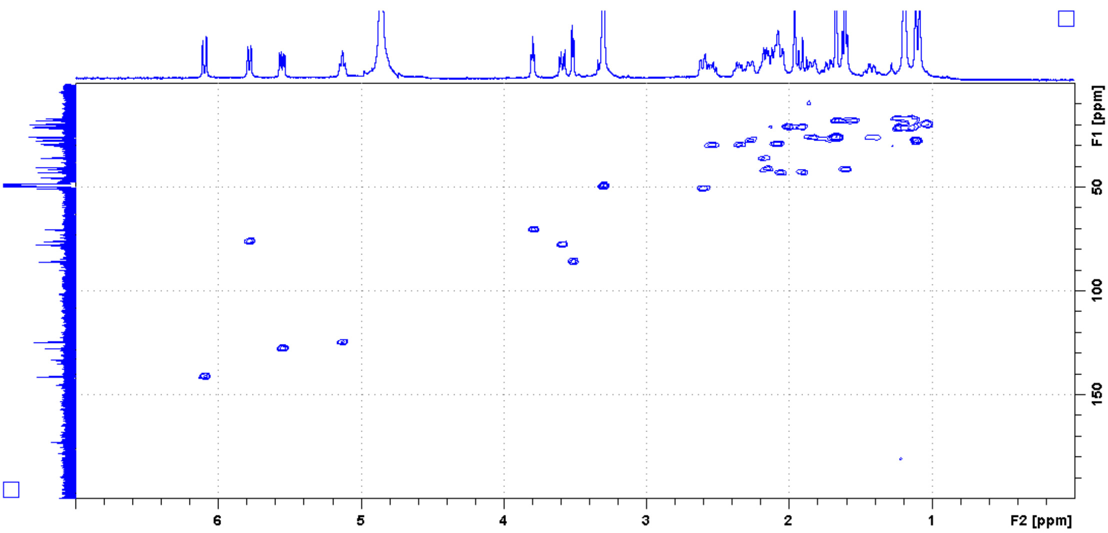
2
F2 [ppm]

F



F1 [ppm]
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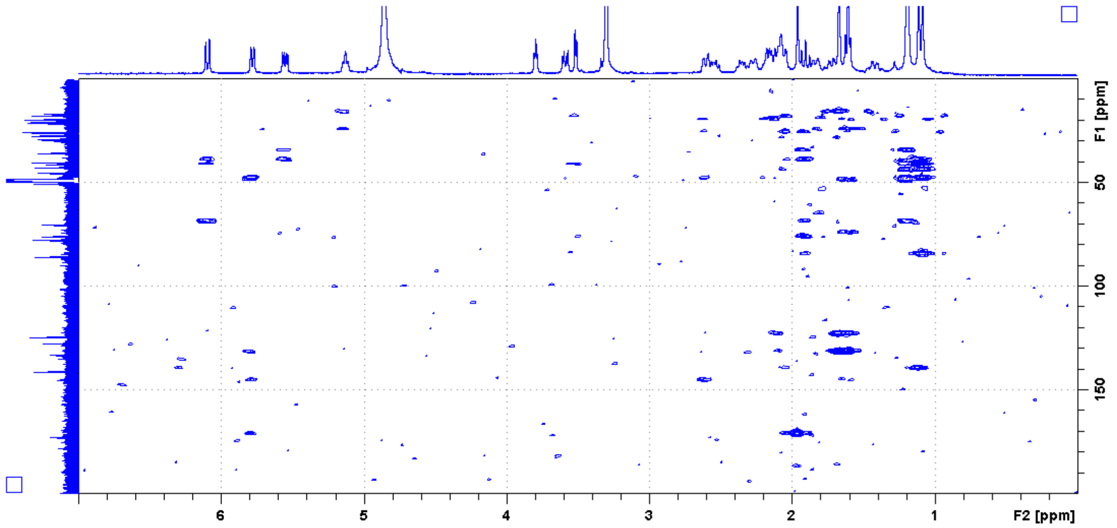
2
1
F2 [ppm]

G



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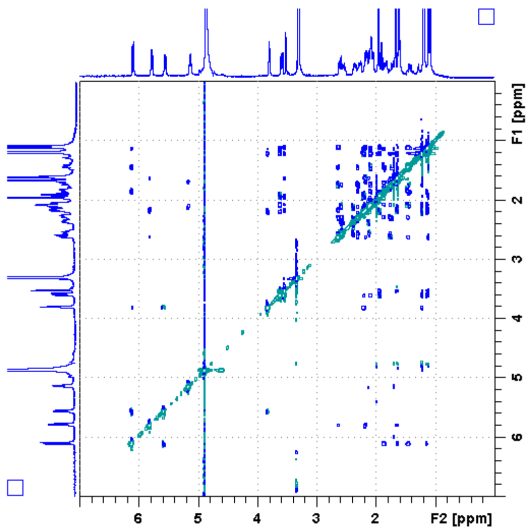
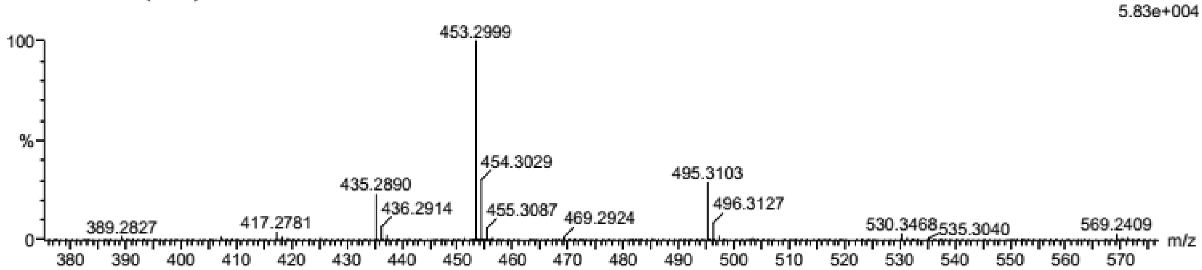


Figure S34 HRESIMS and NMR spectra of **41**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in CD_3OD at 400 MHz; (C) ^{13}C NMR spectrum in CD_3OD at 100 MHz; (D) DEPT 135 spectrum in CD_3OD at 100 MHz; (E) ^{1}H–^{1}H COSY spectrum in CD_3OD at 400 MHz; (F) HSQC spectrum in CD_3OD at 400 MHz; (G) HMBC spectrum in CD_3OD at 400 MHz; (H) ROESY spectrum in CD_3OD at 400 MHz.

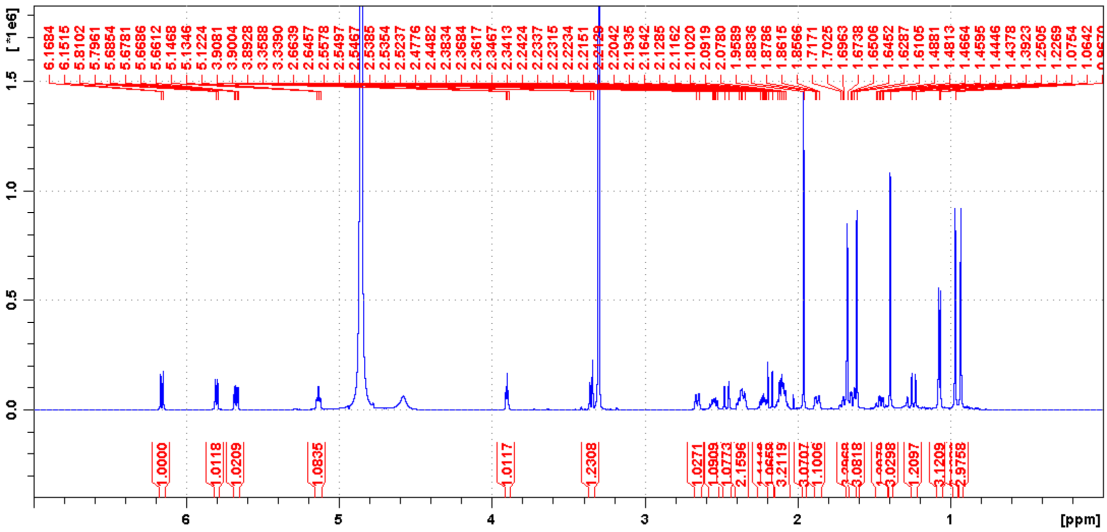
A

Monoisotopic Mass, Even Electron Ions
243 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-200 H: 0-1000 O: 0-200 Na: 0-1
EB4C1-80-3
20190923036 229 (1.848)
1: TOF MS ES+
5.83e+004

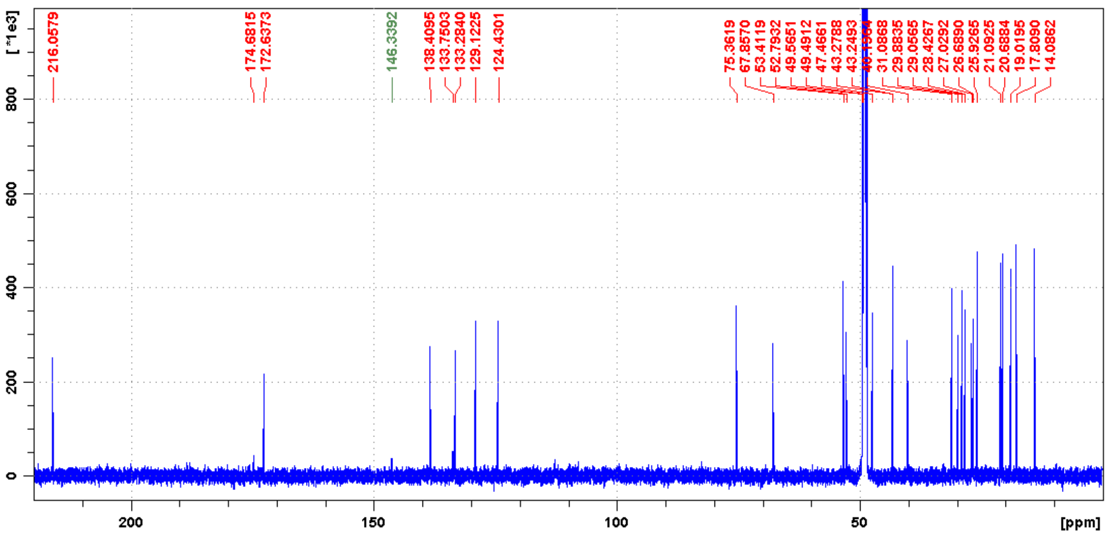


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
495.3103	495.3110	-0.7	-1.4	10.5	107.8	1.953	14.18	C31 H43 O5
	495.3086	1.7	3.4	7.5	106.0	0.153	85.82	C29 H44 O5 Na

B



C



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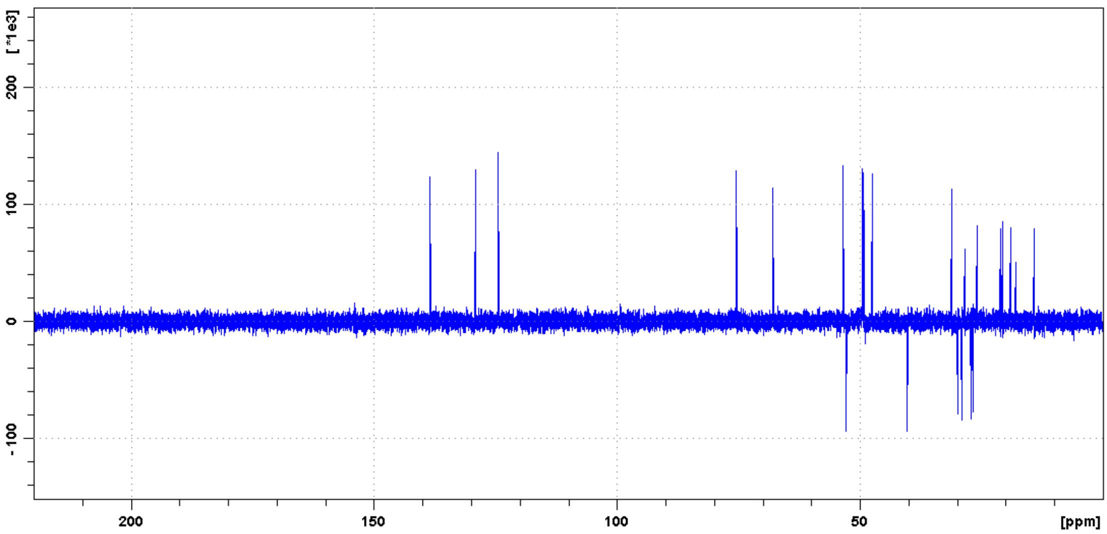
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[ppm]

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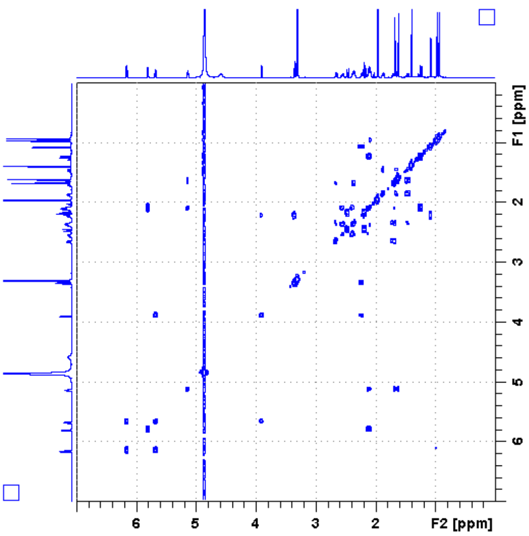
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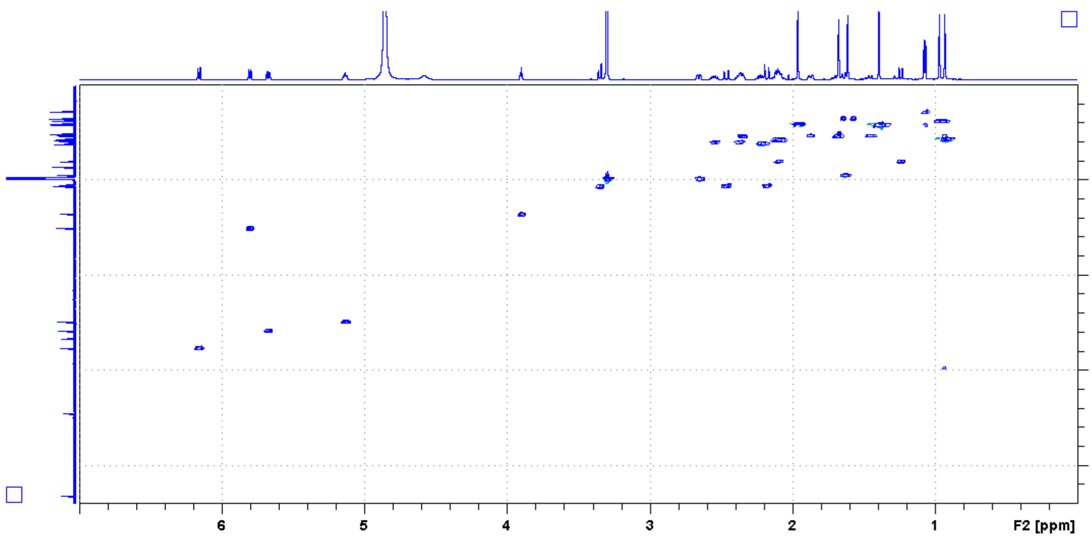
F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F2 [ppm]
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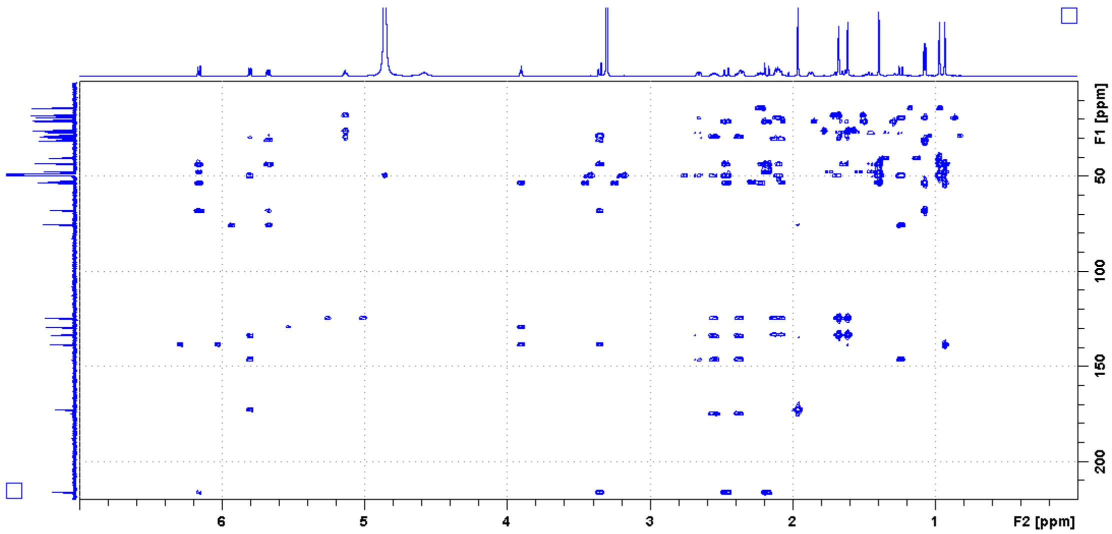
G



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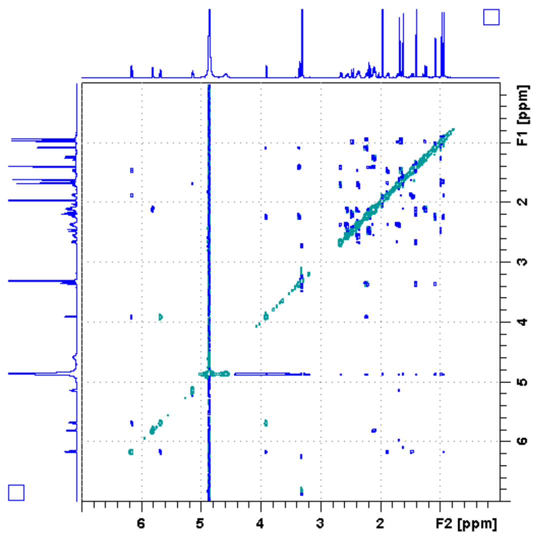


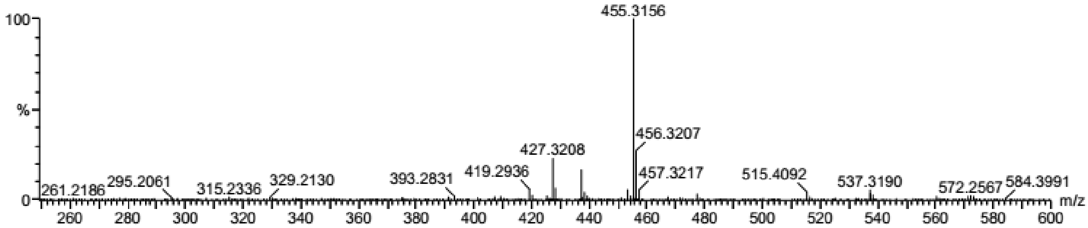
Figure S35 HRESIMS and NMR spectra of **42**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in CD_3OD at 600 MHz; (C) ^{13}C NMR spectrum in CD_3OD at 150 MHz; (D) DEPT 135 spectrum in CD_3OD at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in CD_3OD at 600 MHz; (F) HSQC spectrum in CD_3OD at 600 MHz; (G) HMBC spectrum in CD_3OD at 600 MHz; (H) ROESY spectrum in CD_3OD at 600 MHz.

A

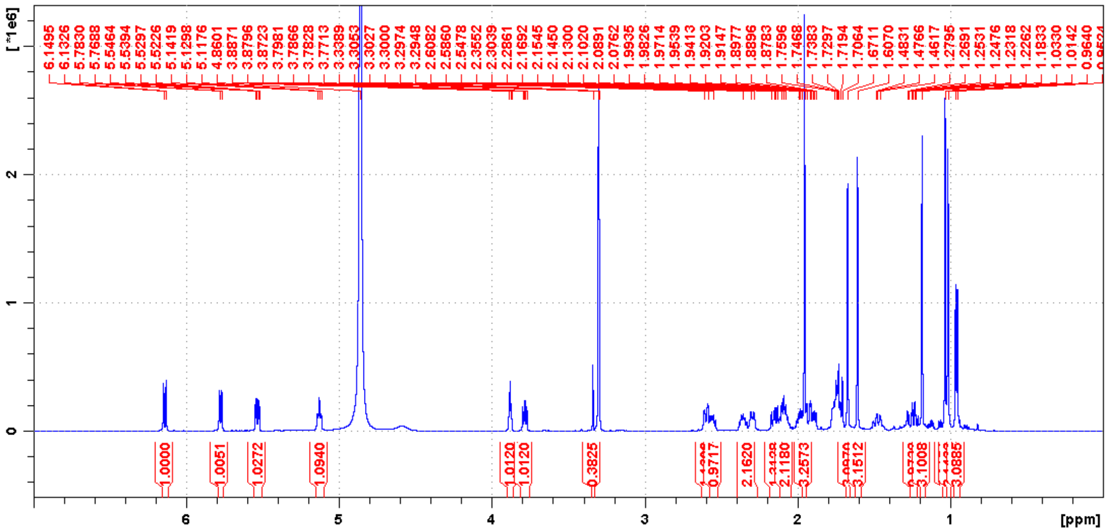
Monoisotopic Mass, Even Electron Ions
270 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
EB4C1-6-3-2
20190902-27 241 (1.948)

1: TOF MS ES+
1.52e+004

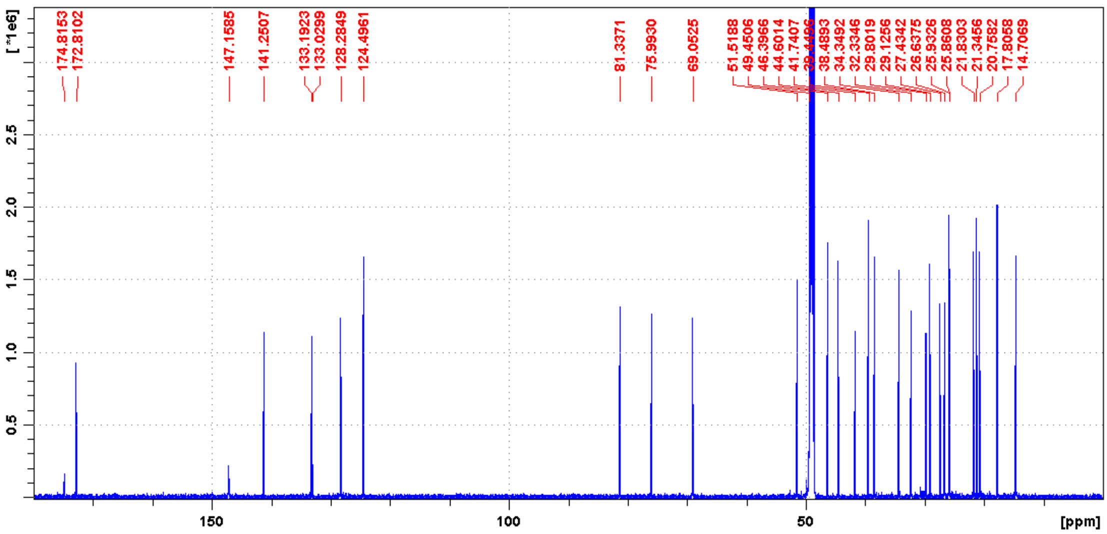


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
537.3190	537.3192	-0.2	-0.4	8.5	82.0	0.130	87.79	C31 H46 O6 Na
	537.3216	-2.6	-4.8	11.5	84.0	2.103	12.21	C33 H45 O6

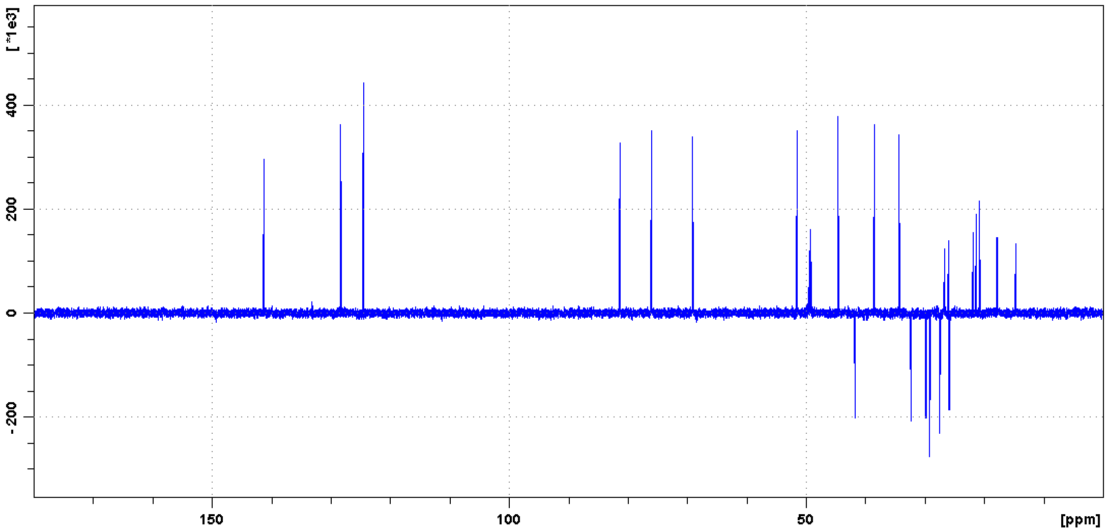
B



C



D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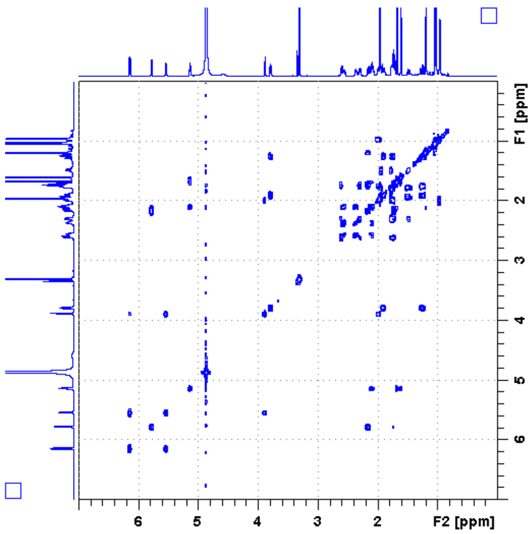
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F1 [ppm]

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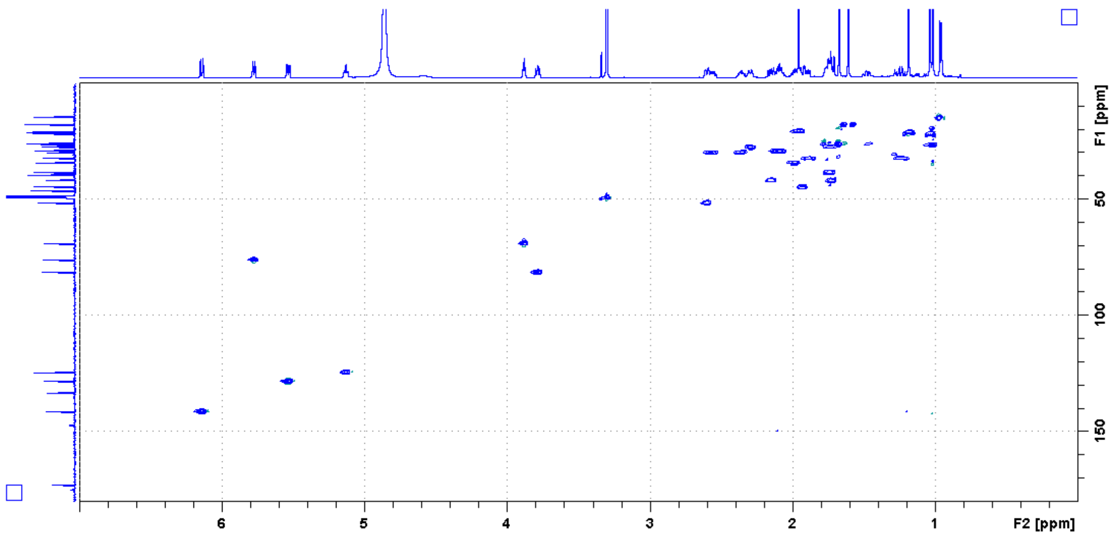
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F1 [ppm]
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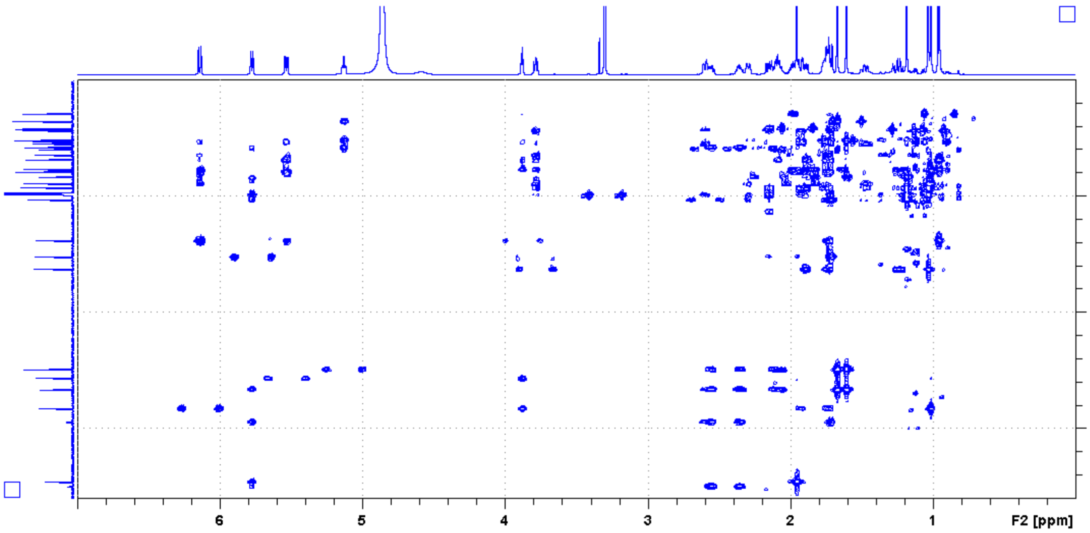
G



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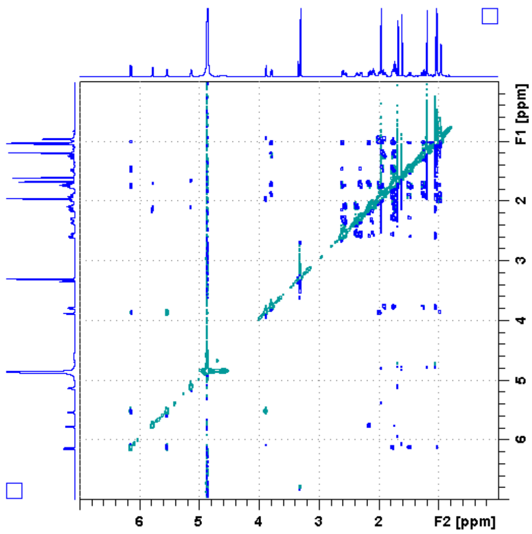
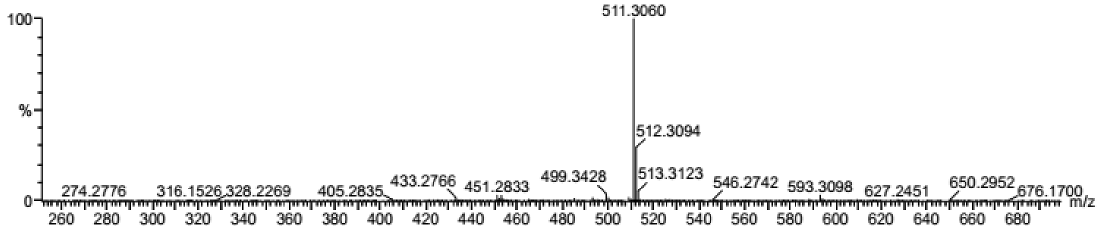


Figure S36 HRESIMS and NMR spectra of **43**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in CD_3OD at 600 MHz; (C) ^{13}C NMR spectrum in CD_3OD at 150 MHz; (D) DEPT 135 spectrum in CD_3OD at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in CD_3OD at 600 MHz; (F) HSQC spectrum in CD_3OD at 600 MHz; (G) HMBC spectrum in CD_3OD at 600 MHz; (H) ROESY spectrum in CD_3OD at 600 MHz.

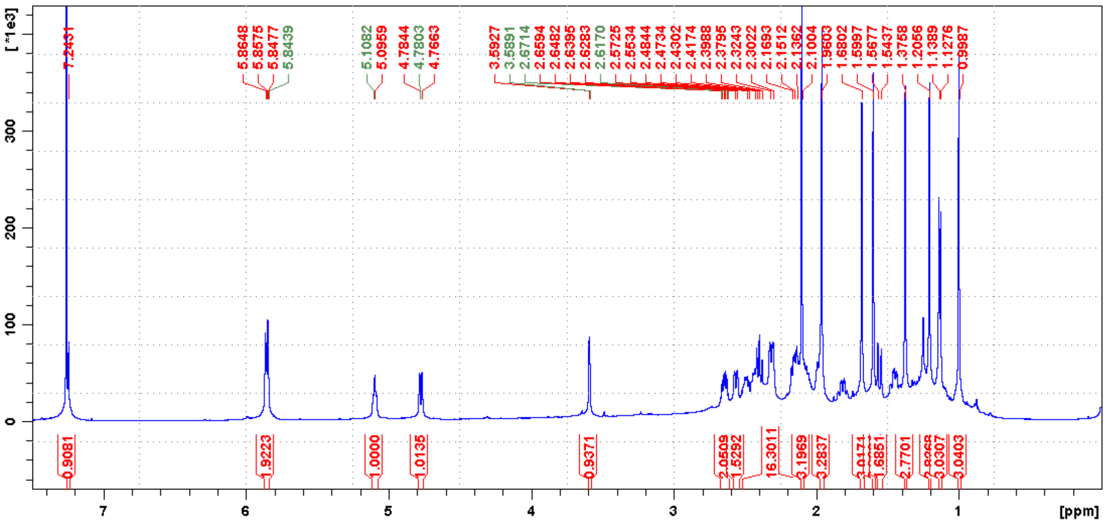
A

Monoisotopic Mass, Even Electron Ions
324 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
34
20190107_38 230 (1.855) 1: TOF MS ES+ 5.01e+004

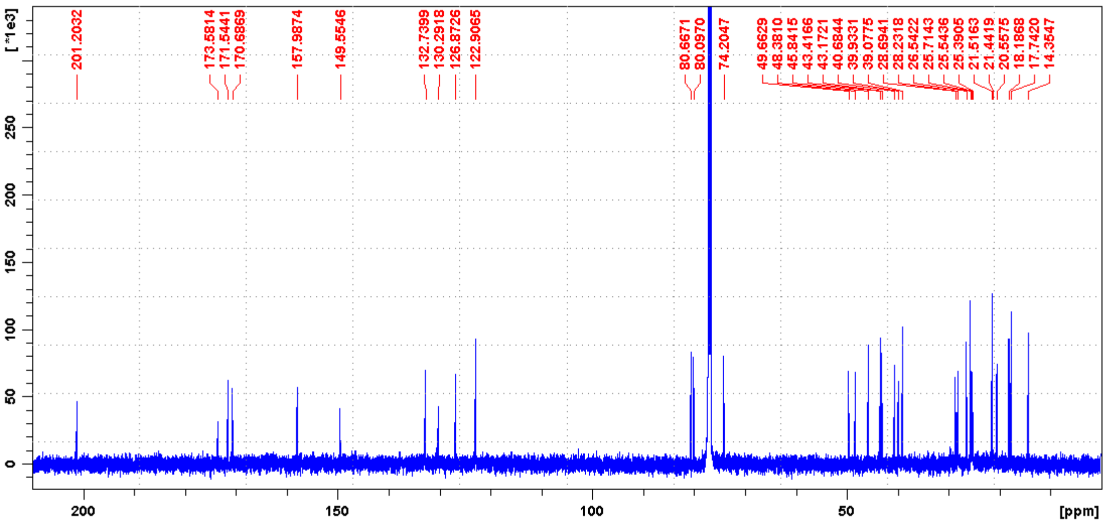


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
593.3098	593.3090	0.8	1.3	10.5	55.3	0.295	74.44	C33 H46 O8 Na
	593.3114	-1.6	-2.7	13.5	56.4	1.364	25.56	C35 H45 O8

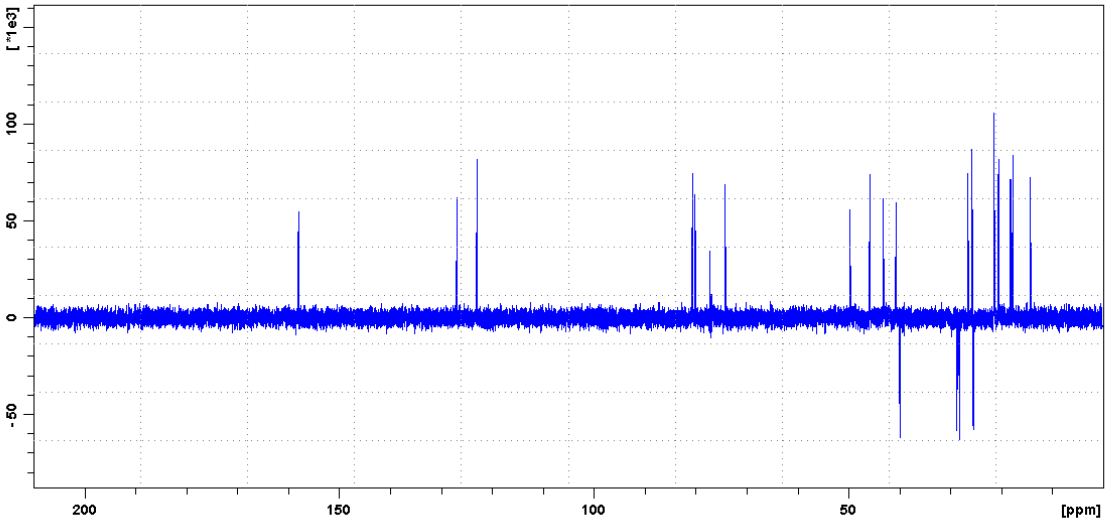
B



C



D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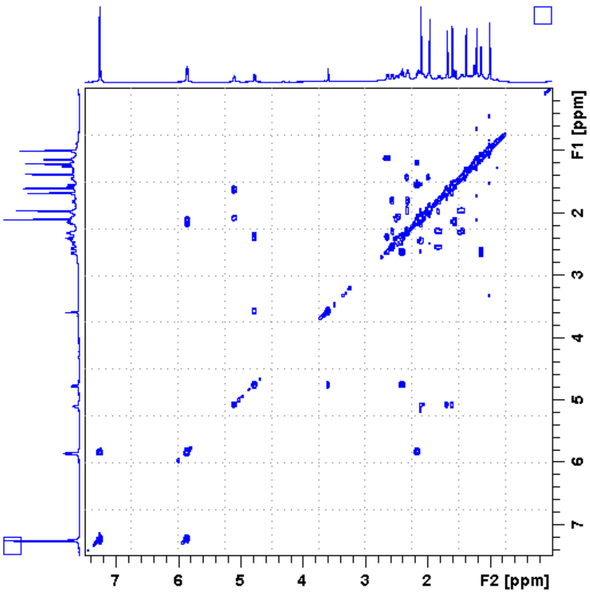
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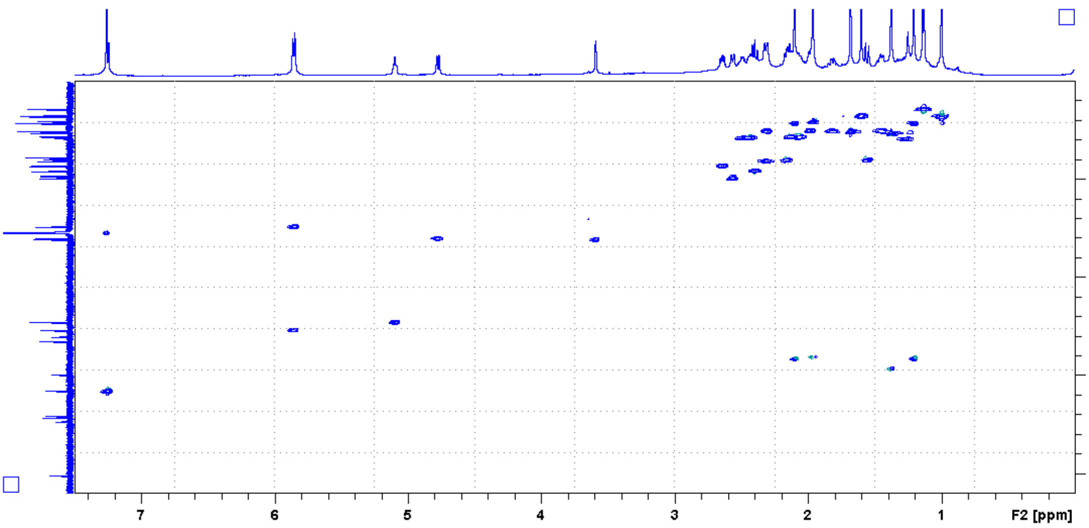
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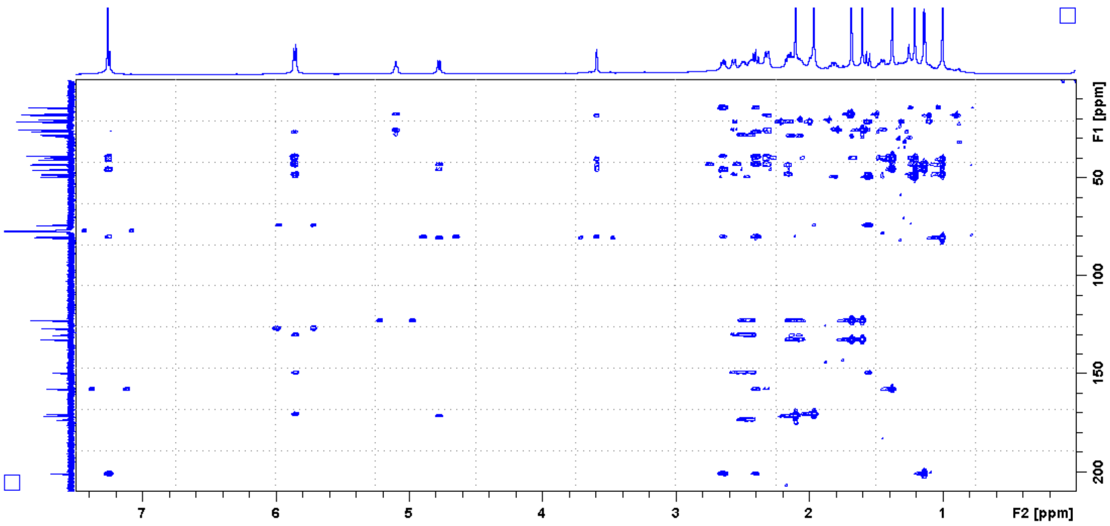
F2 [ppm]

G



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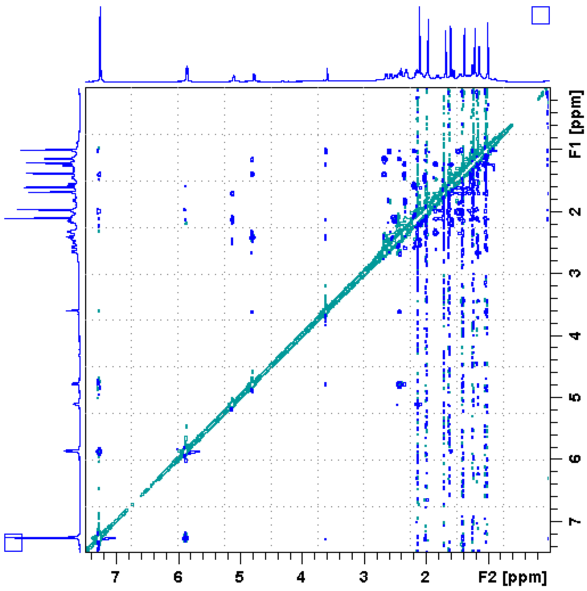
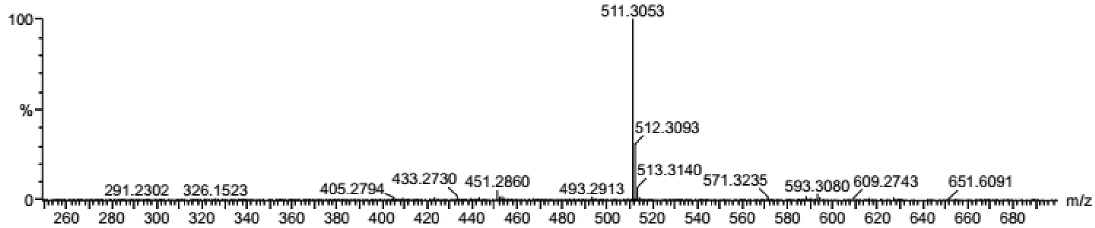


Figure S37 HRESIMS and NMR spectra of **44**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 600 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 150 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in $CDCl_3$ at 600 MHz; (F) HSQC spectrum in $CDCl_3$ at 600 MHz; (G) HMBC spectrum in $CDCl_3$ at 600 MHz; (H) NOESY spectrum in $CDCl_3$ at 600 MHz.

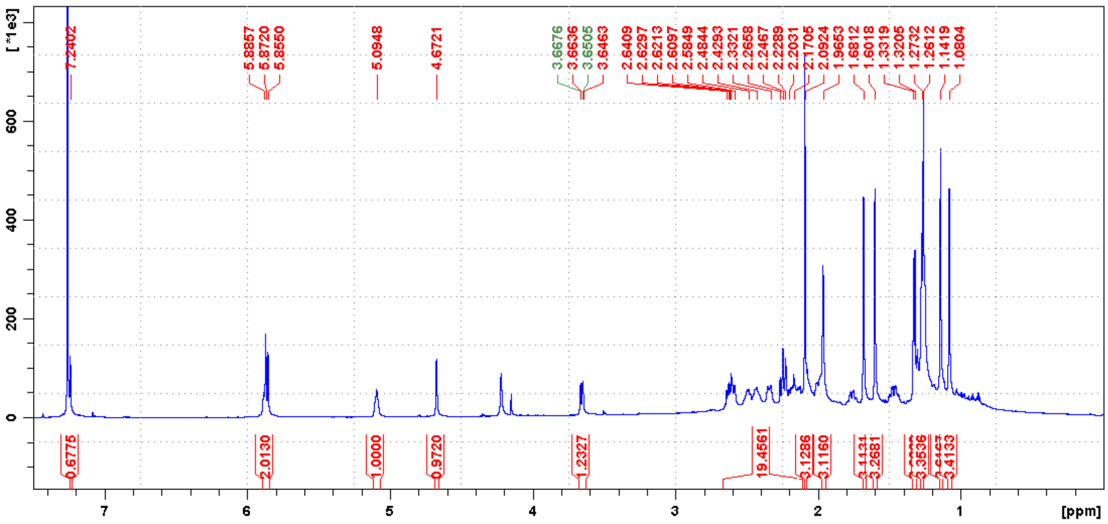
A

Monoisotopic Mass, Even Electron Ions
324 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
33
20190107_37 231 (1.862) 1: TOF MS ES+ 3.63e+004

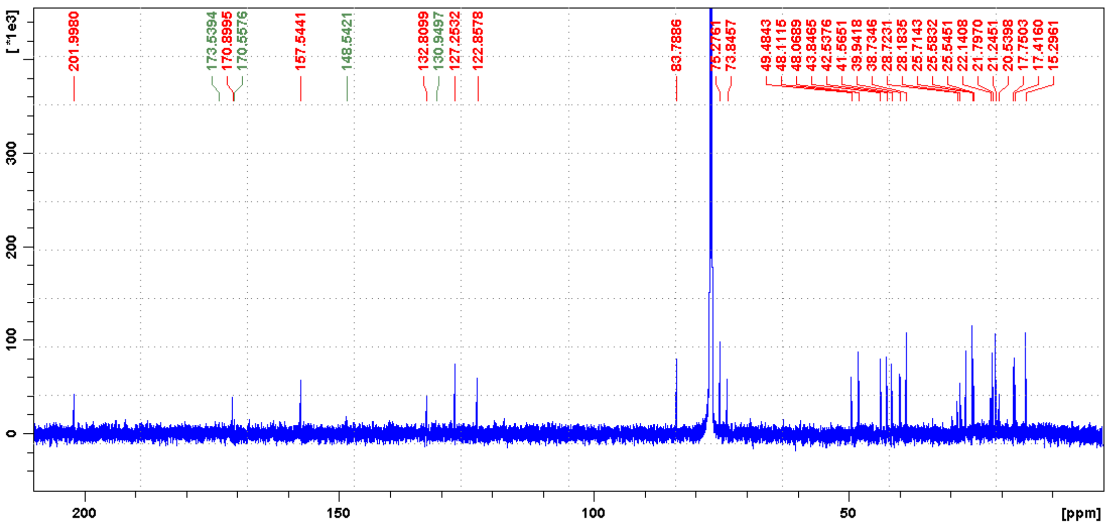


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
593.3080	593.3090	-1.0	-1.7	10.5	17.5	0.219	80.35	C33 H46 O8 Na
	593.3056	2.4	4.0	22.5	18.9	1.627	19.65	C42 H41 O3

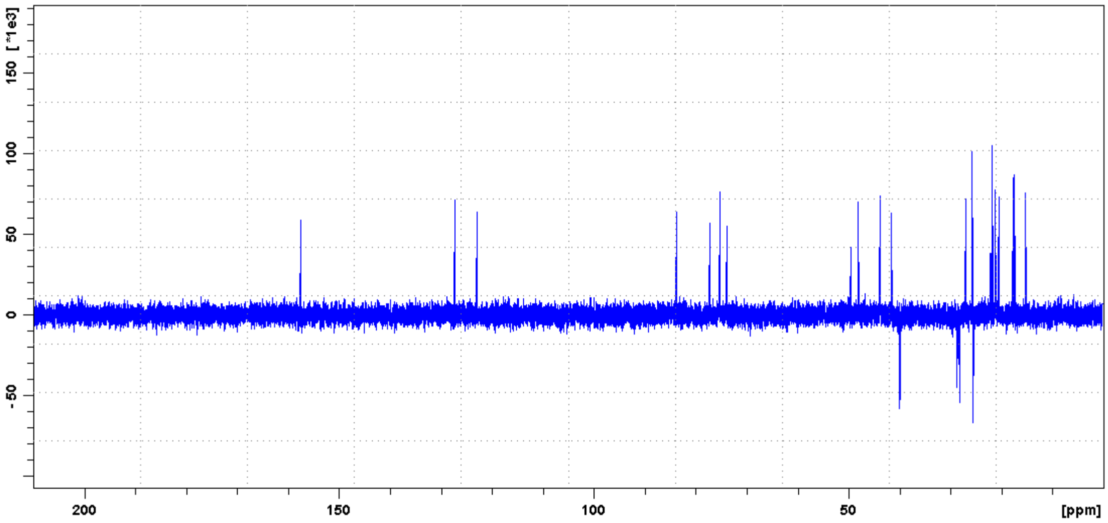
B



C



D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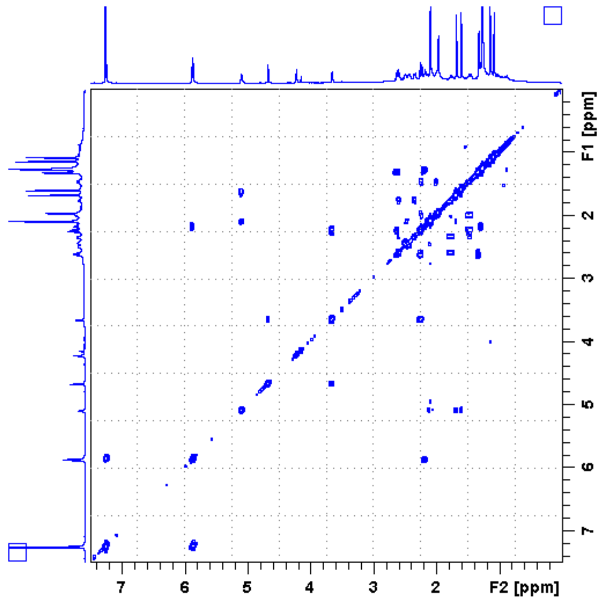
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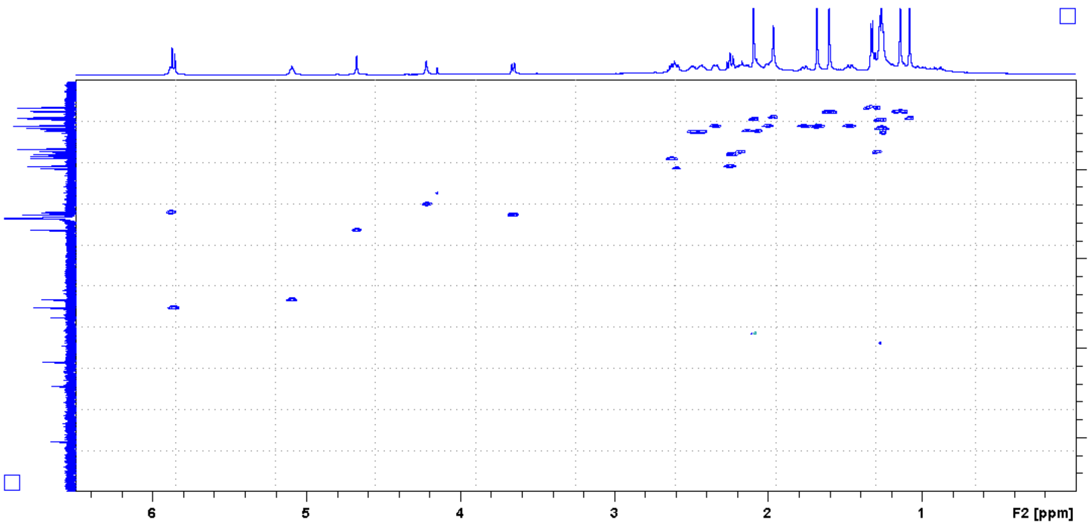
F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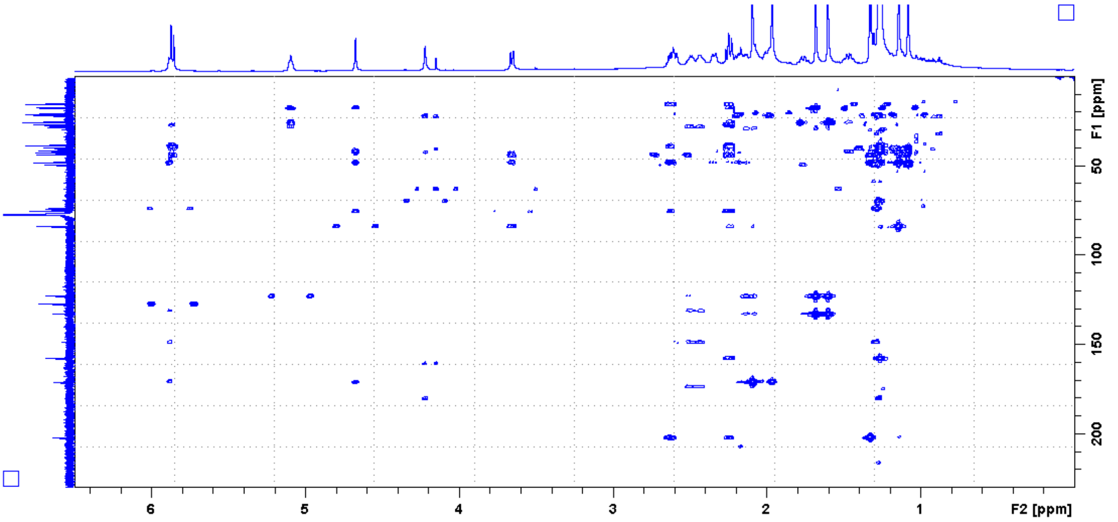
1
F2 [ppm]

G



H

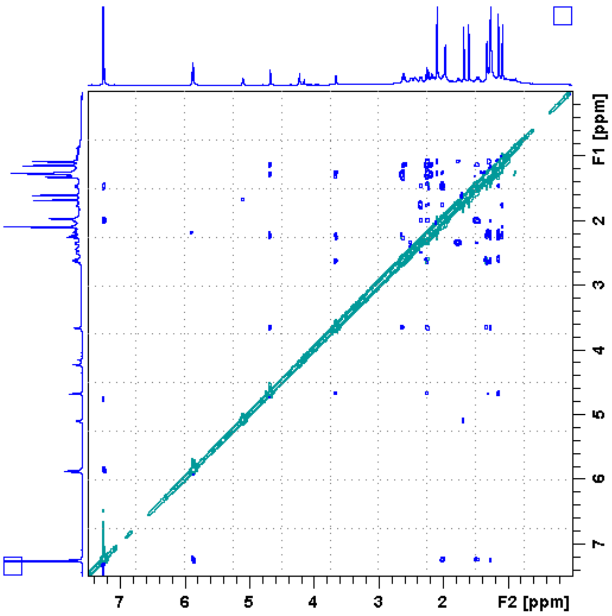


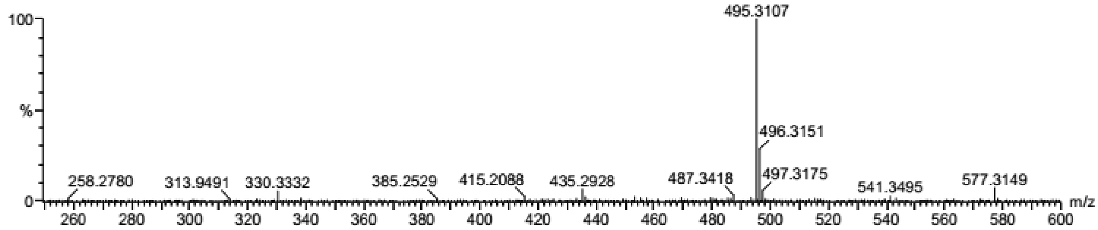
Figure S38 HRESIMS and NMR spectra of **45**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 600 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 150 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in $CDCl_3$ at 600 MHz; (F) HSQC spectrum in $CDCl_3$ at 600 MHz; (G) HMBC spectrum in $CDCl_3$ at 600 MHz; (H) ROESY spectrum in $CDCl_3$ at 600 MHz.

A

Monoisotopic Mass, Even Electron Ions
308 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
35
20190107_39 243 (1.964)

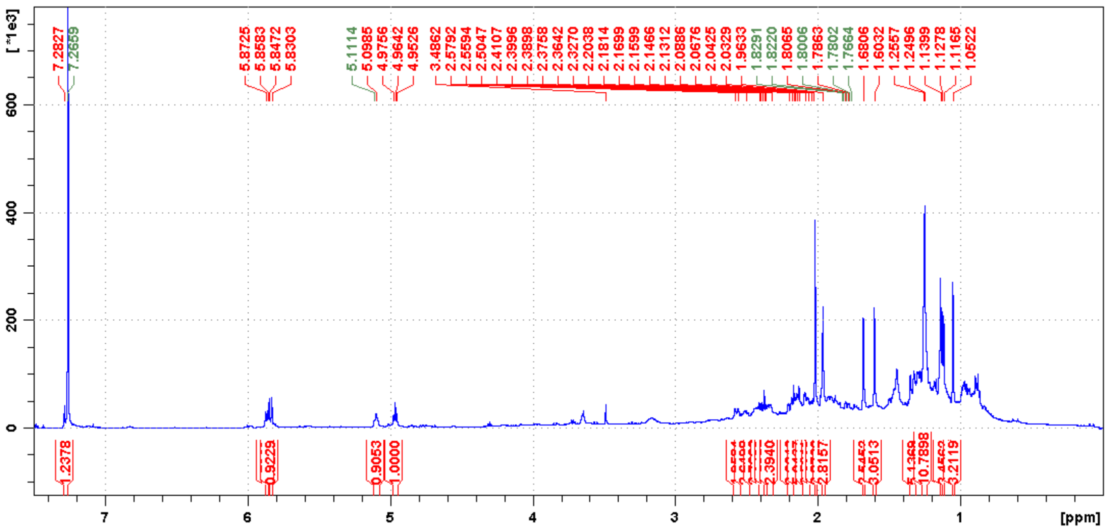
1: TOF MS ES+
6.09e+003



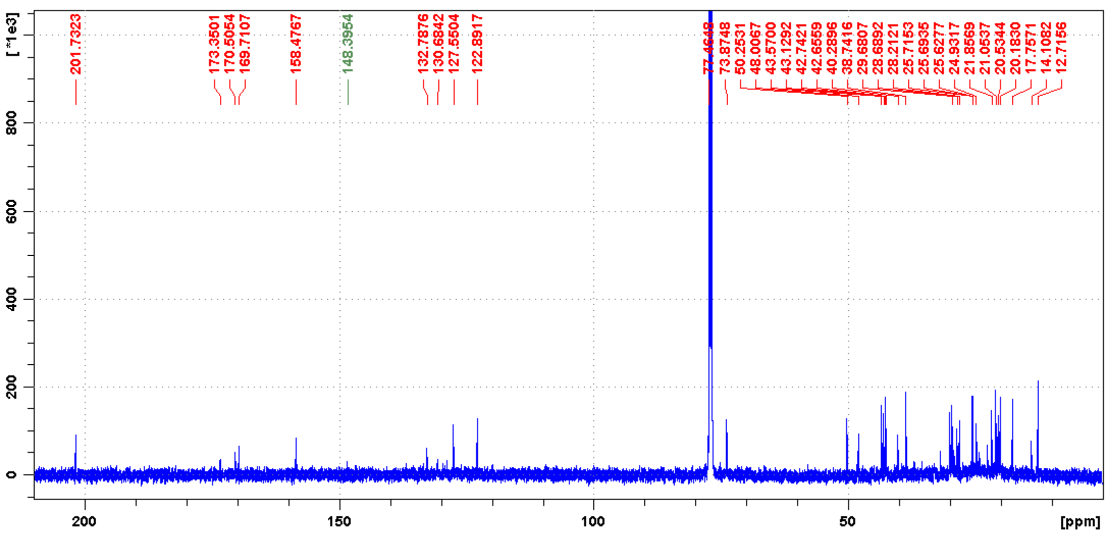
Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
577.3149	577.3141	0.8	1.4	10.5	41.6	0.236	78.98	C33 H46 O7 Na
	577.3165	-1.6	-2.8	13.5	42.9	1.560	21.02	C35 H45 O7

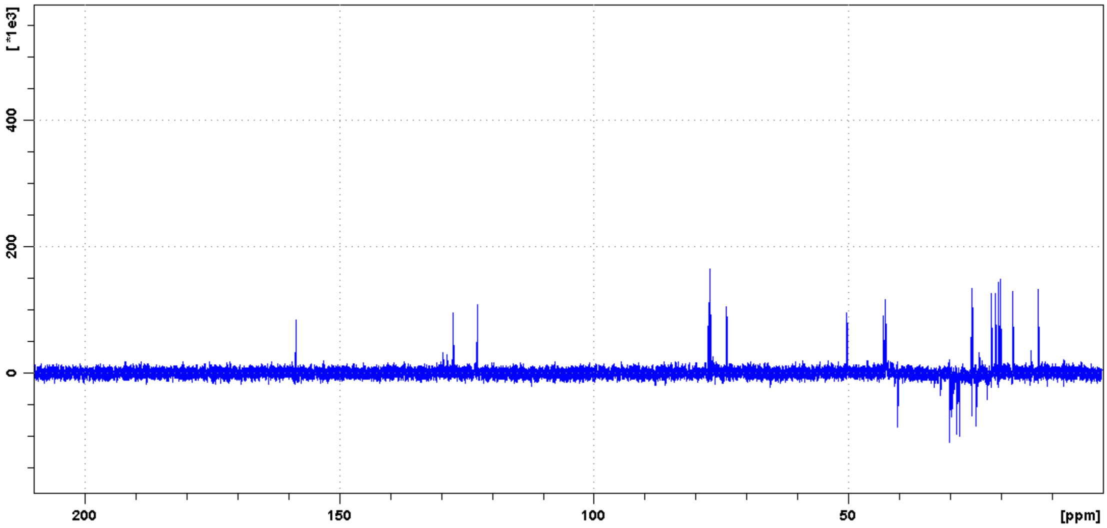
B



C



D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50
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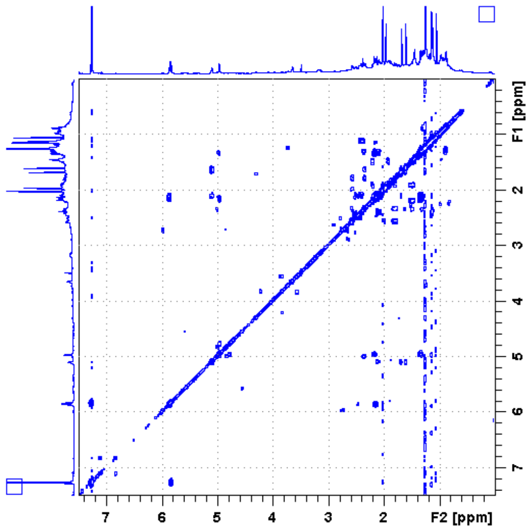
E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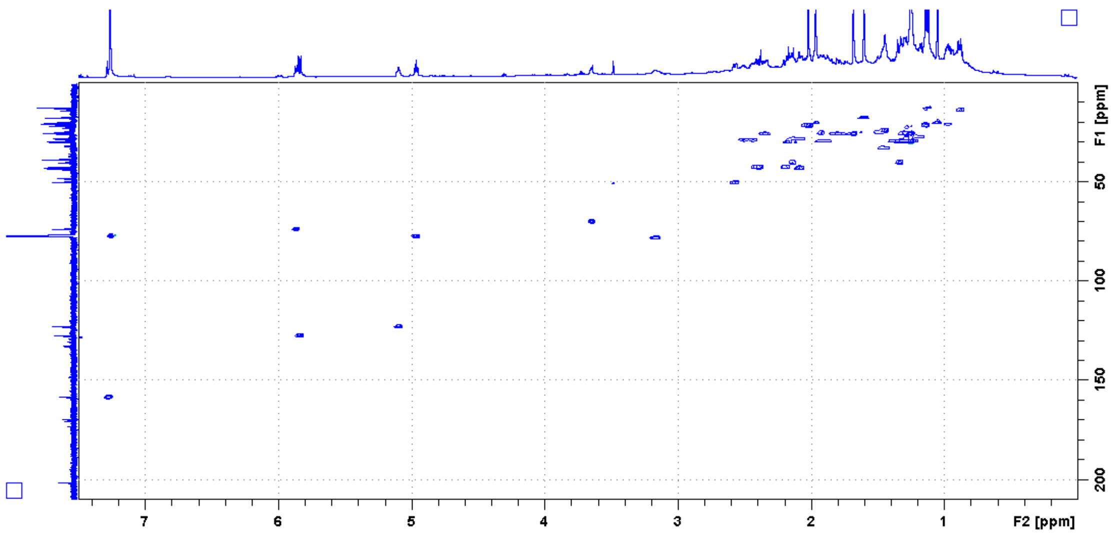
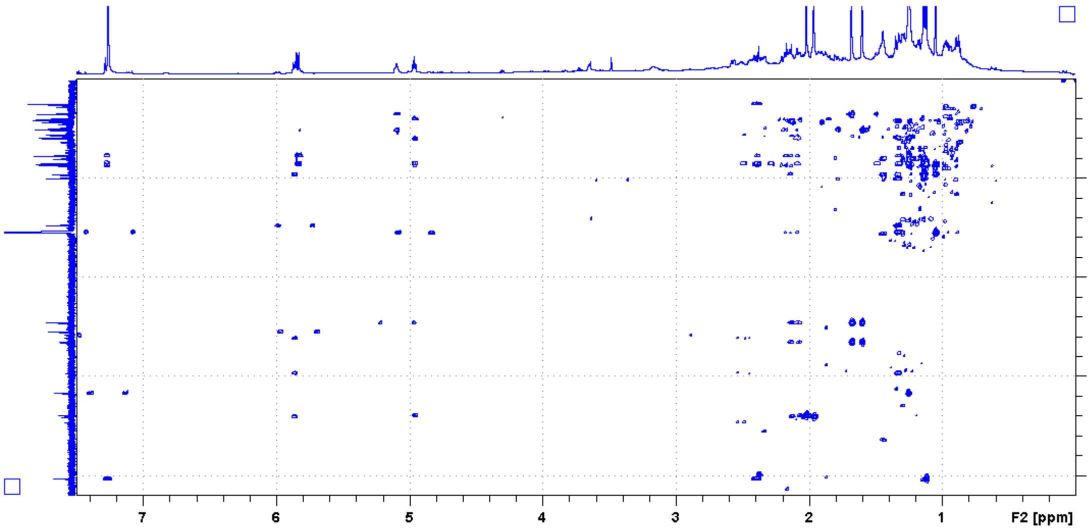
F


7
6
5
4
3
2
1
F2 [ppm]
50
100
150
200
F1 [ppm]

G



H

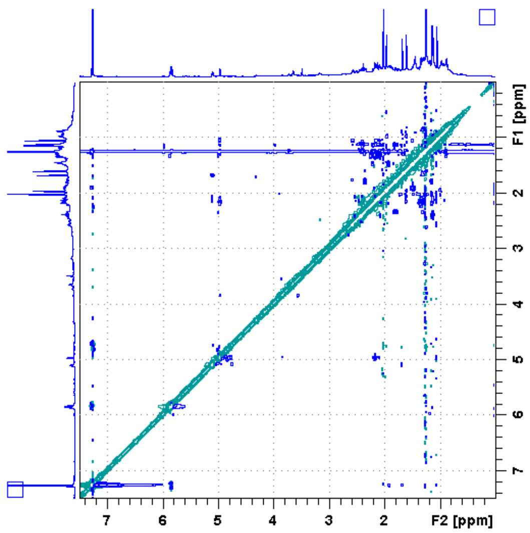
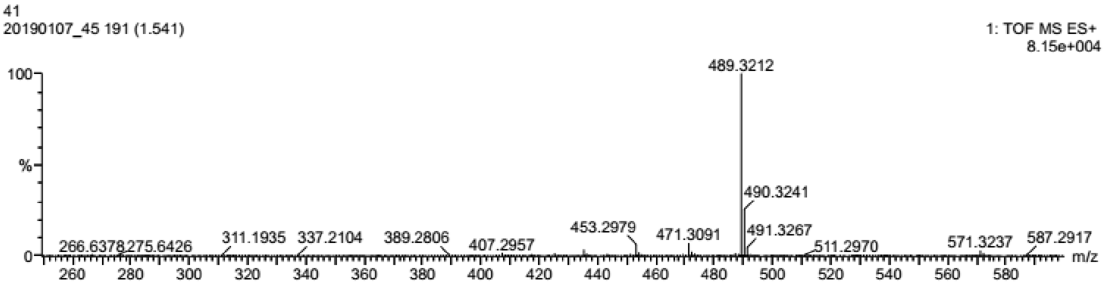


Figure S39 HRESIMS and NMR spectra of **46**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 600 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 150 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in $CDCl_3$ at 600 MHz; (F) HSQC spectrum in $CDCl_3$ at 600 MHz; (G) HMBC spectrum in $CDCl_3$ at 600 MHz; (H) NOESY spectrum in $CDCl_3$ at 600 MHz.

A

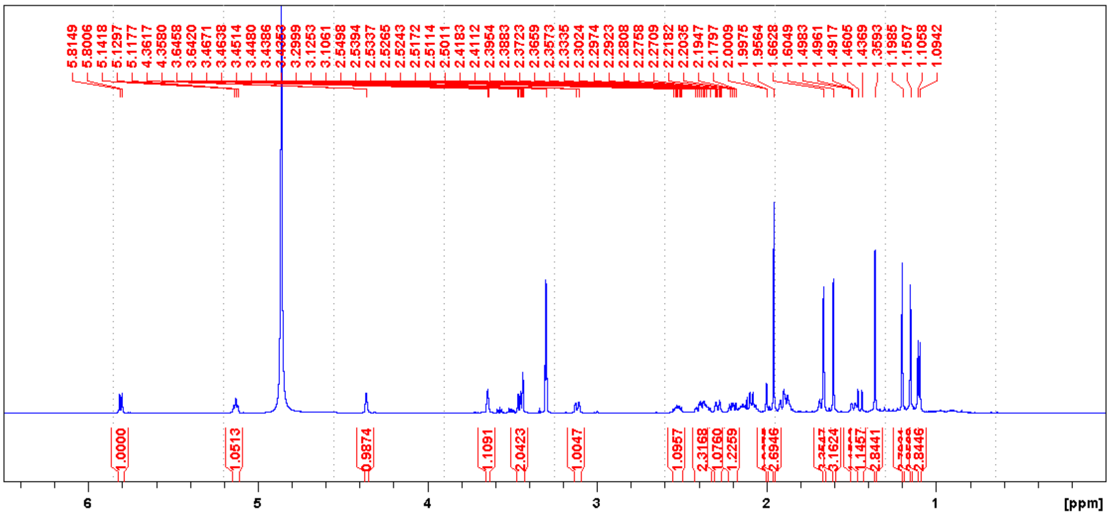
Monoisotopic Mass, Even Electron Ions
313 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1



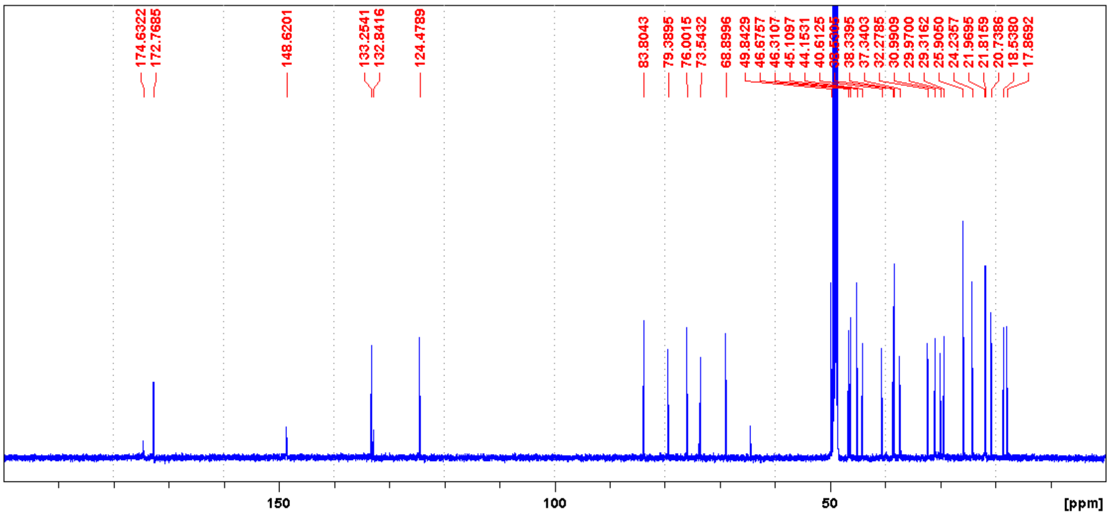
Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
571.3237	571.3247	-1.0	-1.8	7.5	62.0	0.164	84.87	C31 H48 O8 Na
	571.3212	2.5	4.4	19.5	63.8	1.888	15.13	C40 H43 O3

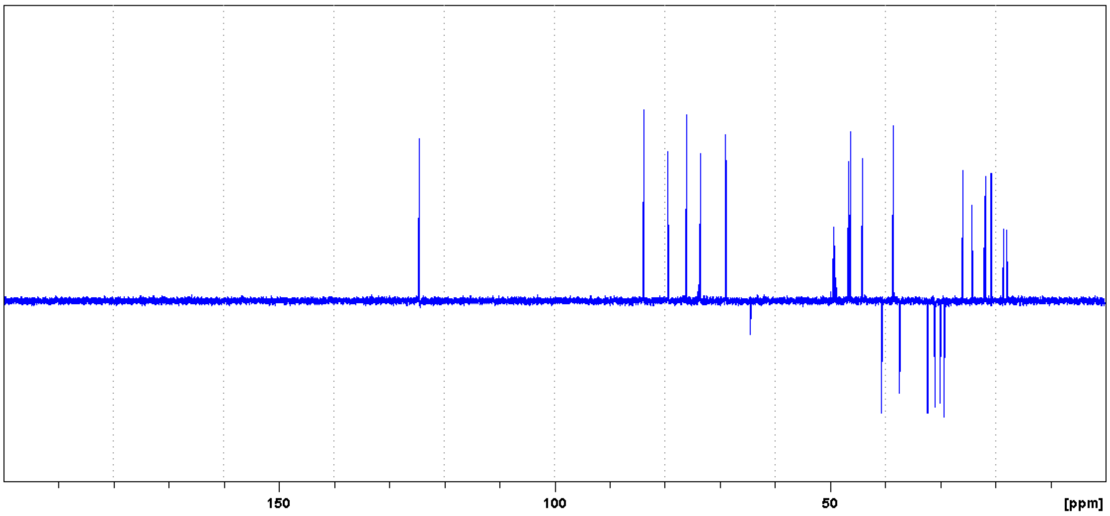
B



C



D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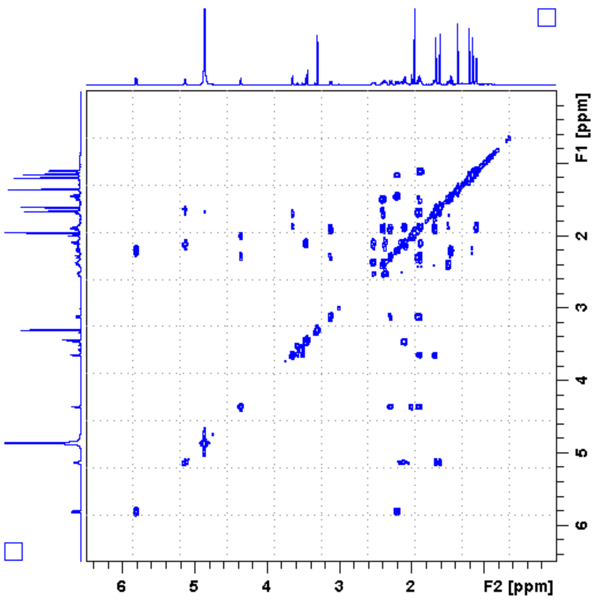
100
50
[ppm]

E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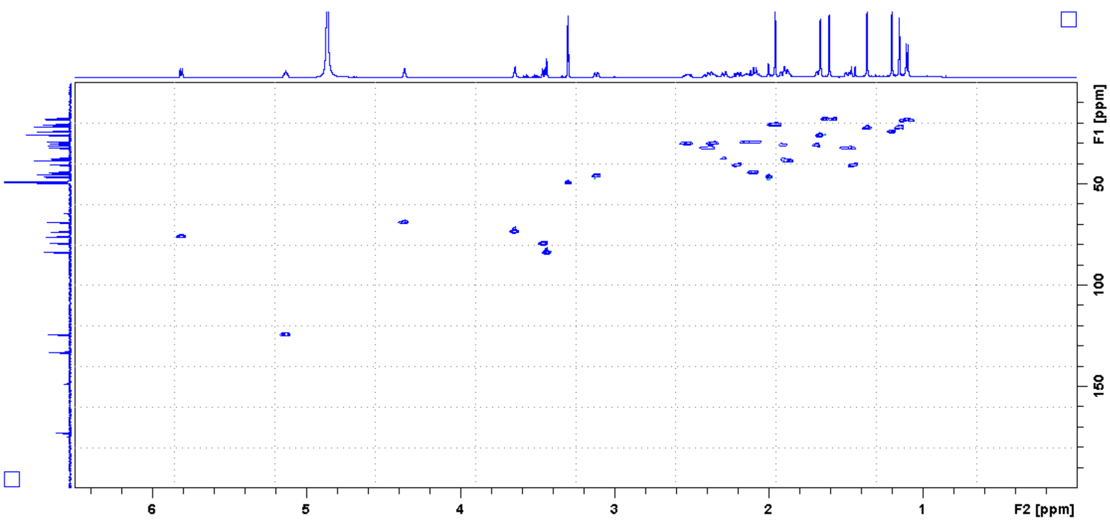
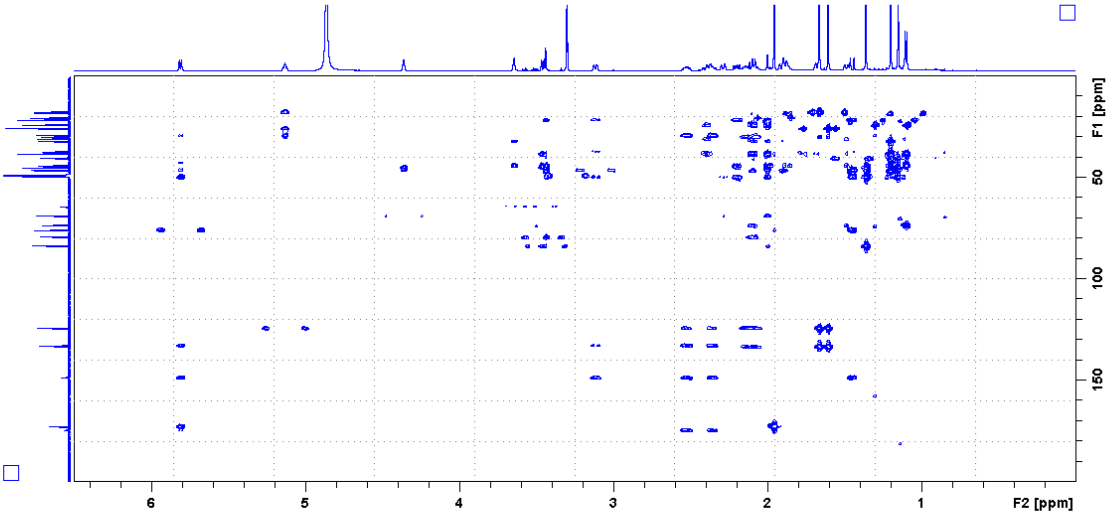
4
5
6
6
5
4
3
2
F2 [ppm]

F


F1 [ppm]
50
100
150
6
5
4
3
2
1
F2 [ppm]

G



H

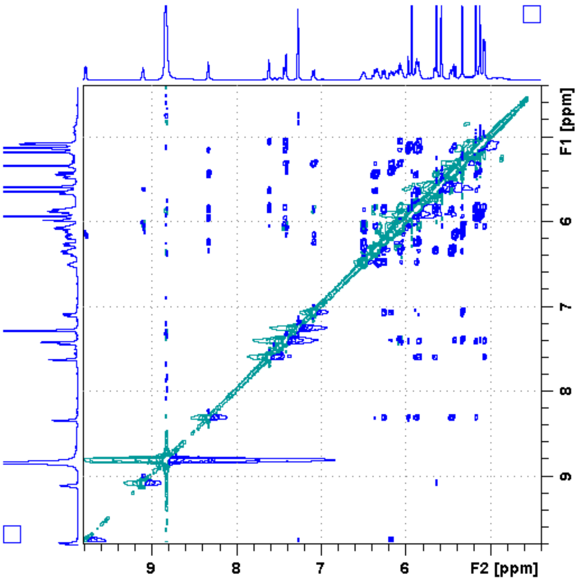
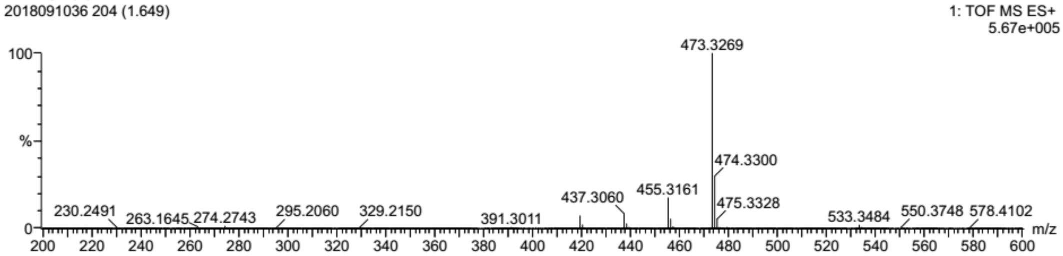


Figure S40 HRESIMS and NMR spectra of **47**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in CD_3OD at 600 MHz; (C) ^{13}C NMR spectrum in CD_3OD at 150 MHz; (D) DEPT 135 spectrum in CD_3OD at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in CD_3OD at 600 MHz; (F) HSQC spectrum in CD_3OD at 600 MHz; (G) HMBC spectrum in CD_3OD at 600 MHz; (H) ROESY spectrum in CD_3OD at 600 MHz.

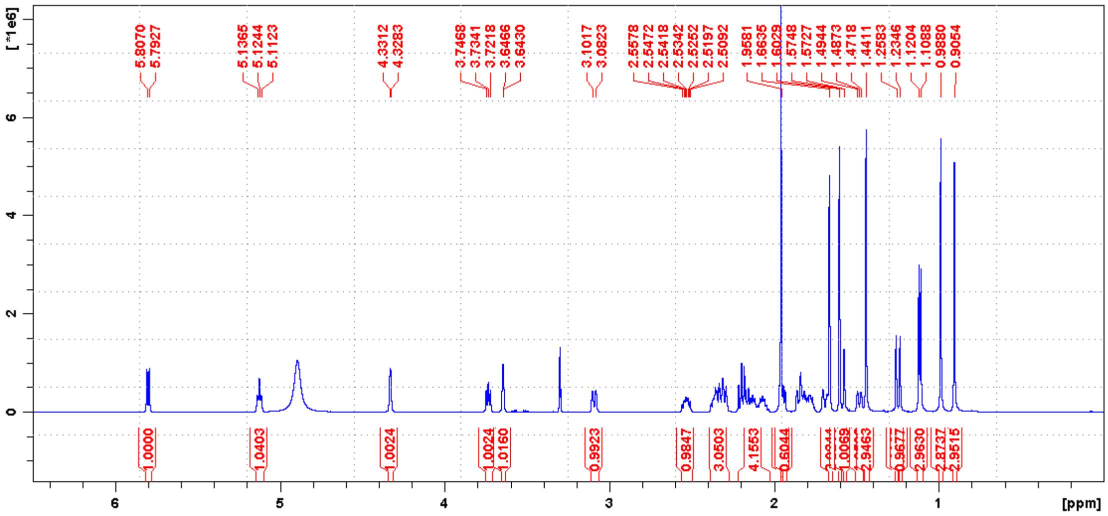
A

Monoisotopic Mass, Even Electron Ions
267 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
B1B4-C1-6-6
2018091036 204 (1.649)

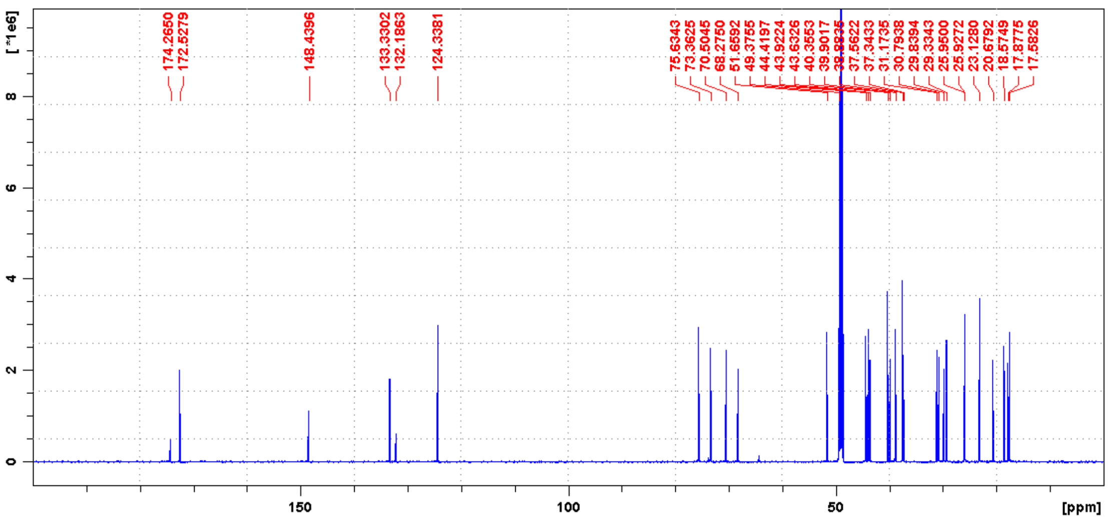


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
533.3484	533.3478	0.6	1.1	7.5	334.5	n/a	n/a	C31 H49 O7

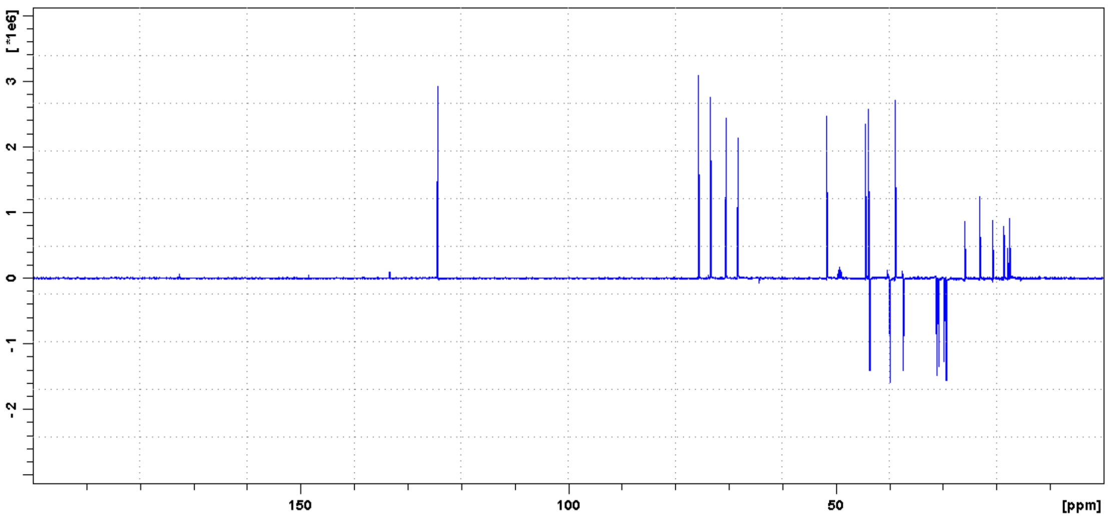
B



C



D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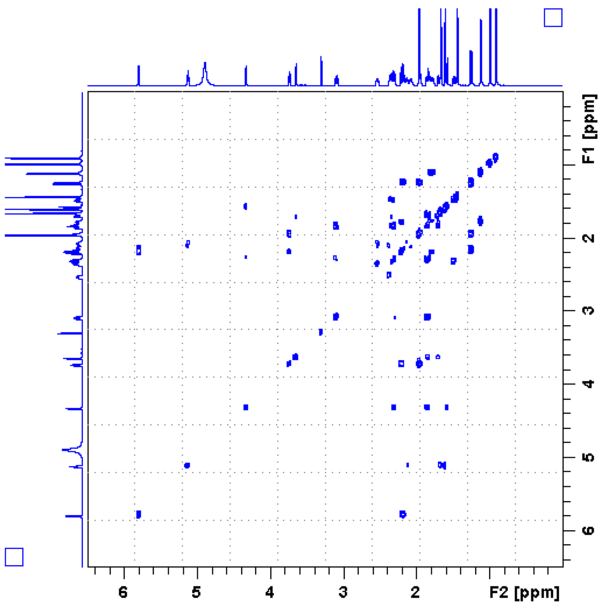
1
0
-1
-2
150
100
50
[ppm]

E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3
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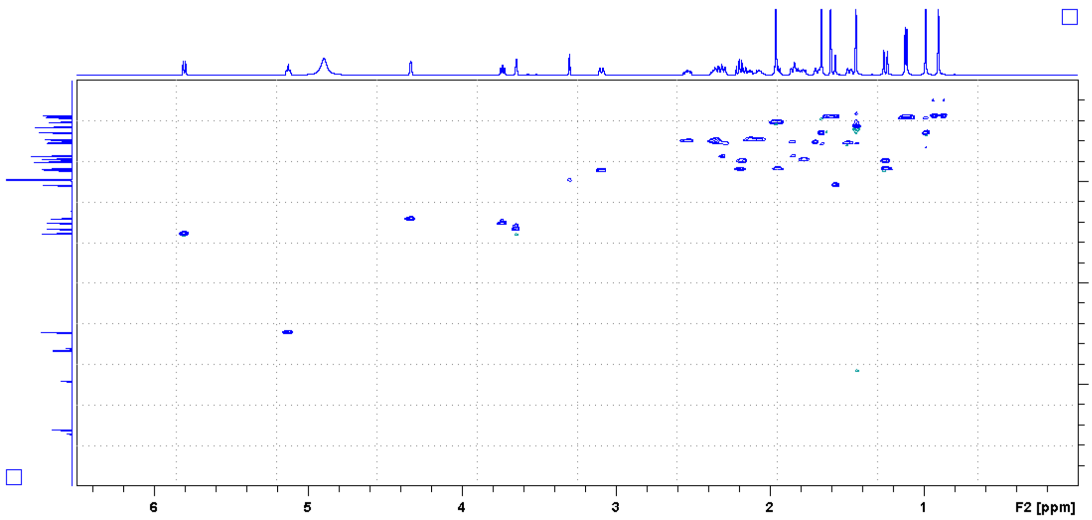
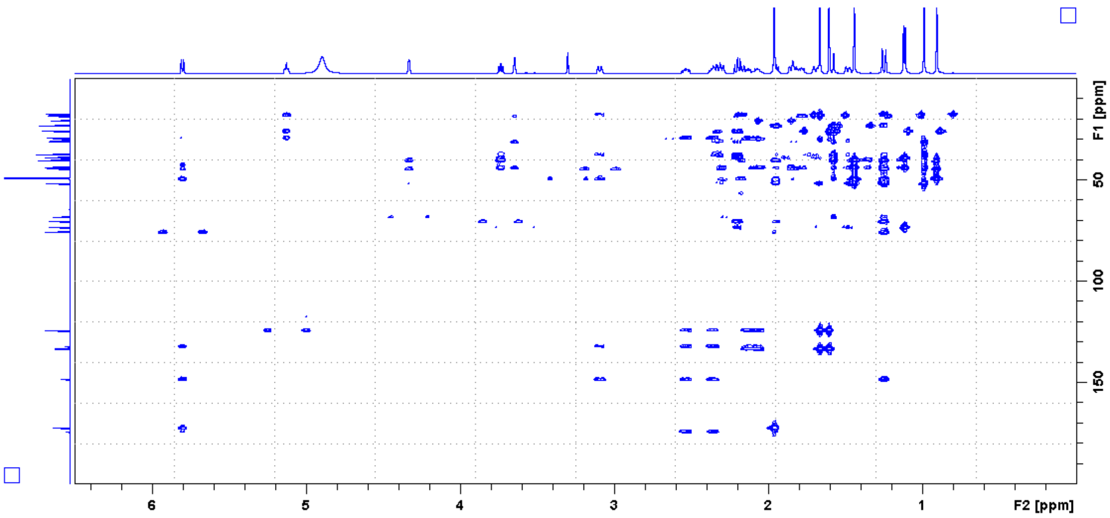
5
6
6
5
4
3
2
F2 [ppm]

F


F1 [ppm]
50
100
150
6
5
4
3
2
1
F2 [ppm]

G



H

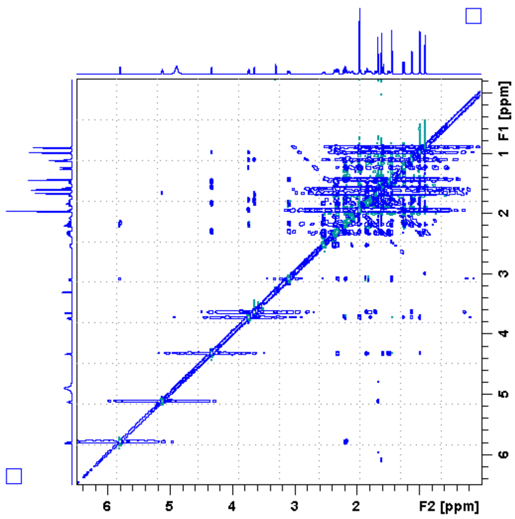
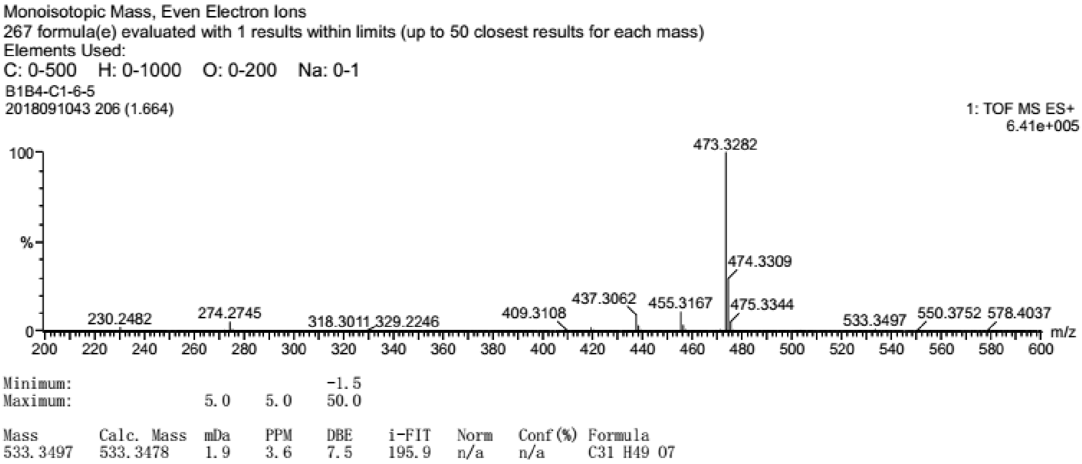


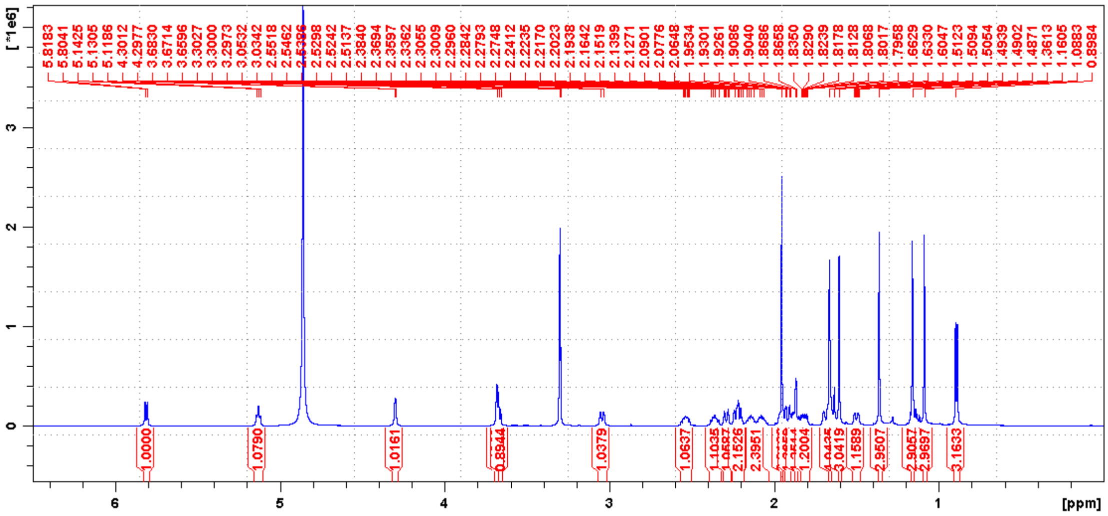
Figure S41 HRESIMS and NMR spectra of **48**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 600 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 150 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in $CDCl_3$ at 600 MHz; (F) HSQC spectrum in $CDCl_3$ at 600 MHz; (G) **HMBC spectrum in $CDCl_3$ at 600 MHz; (H) ROESY spectrum in $CDCl_3$ at 600 MHz.**

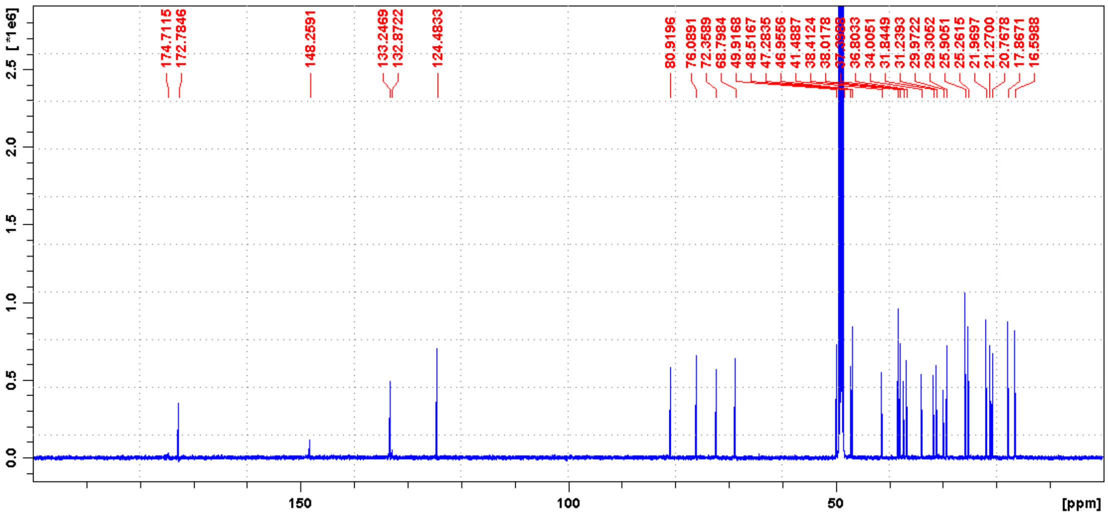
A


Monoisotopic Mass, Even Electron Ions
267 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
B1B4-C1-6-5
2018091043 206 (1.664)
1: TOF MS ES+
6.41e+005
473.3282
474.3309
475.3344
455.3167
437.3062
409.3108
318.3011
329.2246
274.2745
230.2482
533.3497
550.3752
578.4037
m/z
Minimum: -1.5
Maximum: 5.0 5.0 50.0
Mass Calc. Mass mDa PPM DBE i-FIT Norm Conf(%) Formula
533.3497 533.3478 1.9 3.6 7.5 195.9 n/a n/a C31 H49 O7

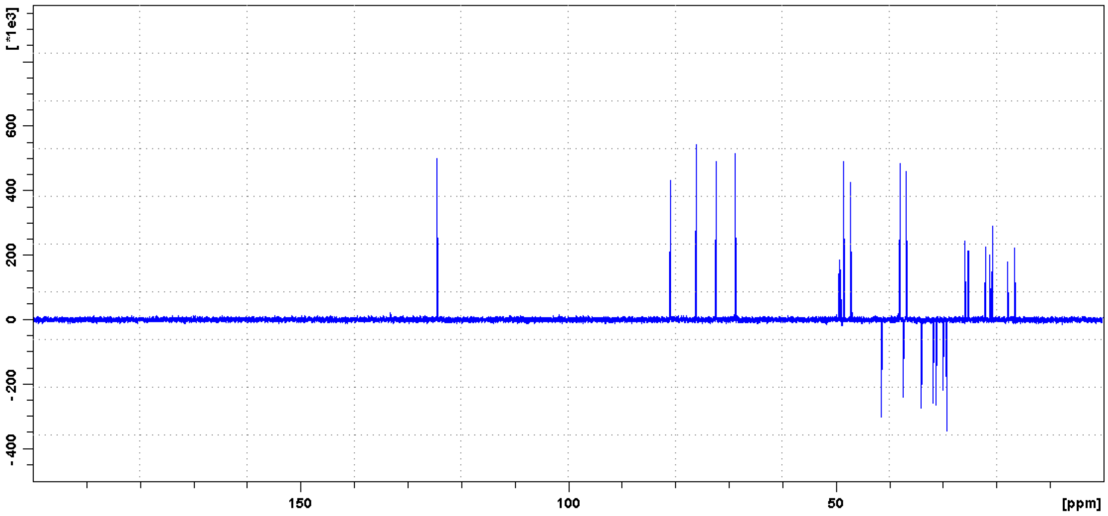
B


[*1e6]
[ppm]

C


174.7115
172.7846
148.2591
133.2469
132.8722
124.4833
80.9196
76.0891
72.3589
68.7984
49.9168
48.5167
47.2835
46.9556
41.4887
38.4124
38.0178
36.8033
34.0051
31.8449
31.2393
29.9722
29.3052
25.9051
25.2615
21.9697
21.2700
20.7678
17.8671
16.5988
[*1e6]
[ppm]

D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200
0
-200
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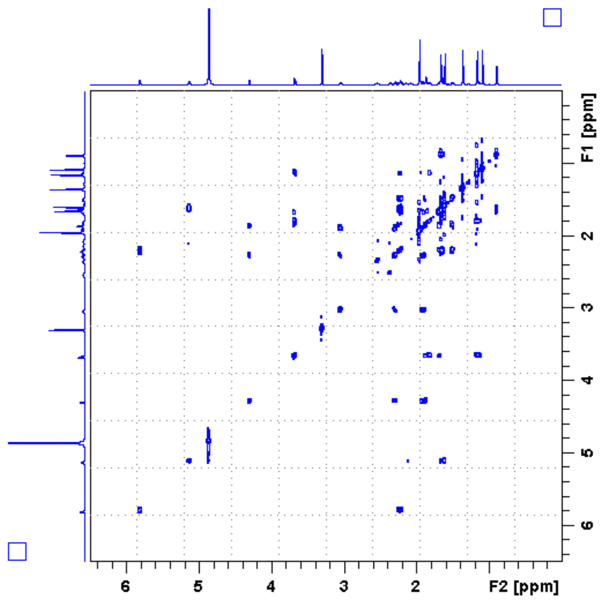
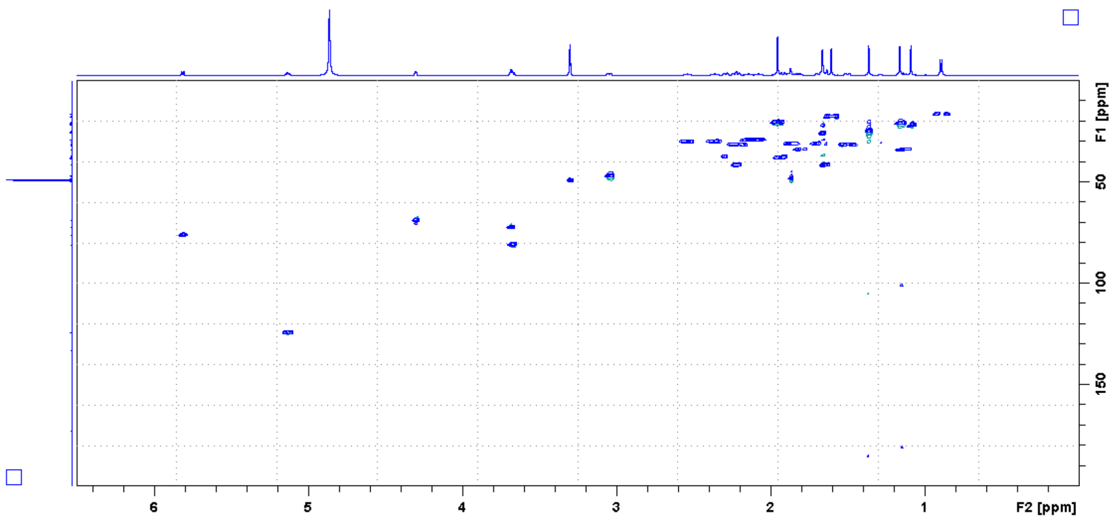
150
100
50
[ppm]

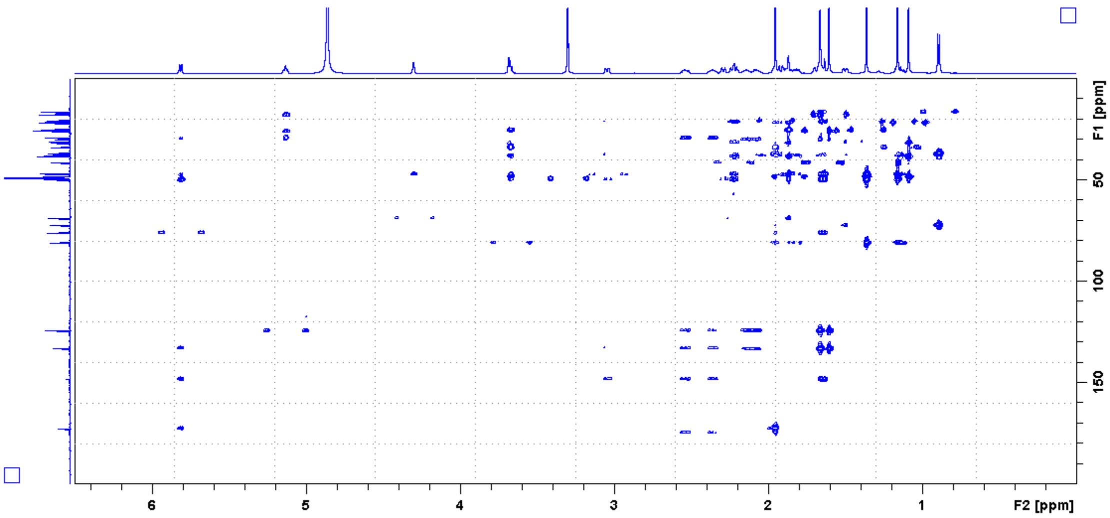
E


F1 [ppm]
2
3
4
5
6
6
5
4
3
2
F2 [ppm]

F


F1 [ppm]
50
100
150
6
5
4
3
2
1
F2 [ppm]

G



H

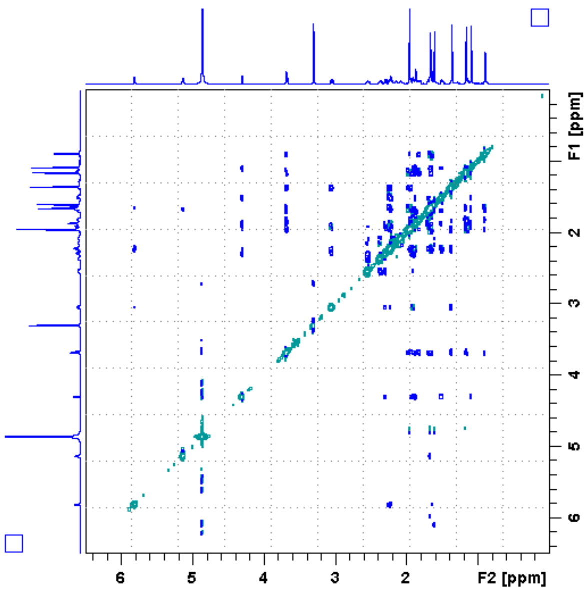
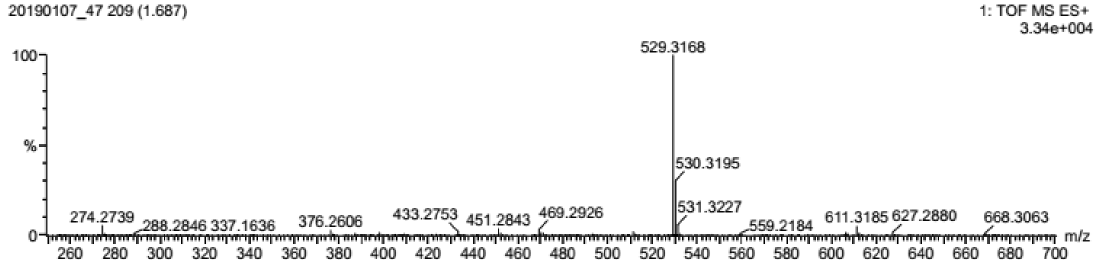


Figure S42 HRESIMS and NMR spectra of **49**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in CD_3OD at 600 MHz; (C) ^{13}C NMR spectrum in CD_3OD at 150 MHz; (D) DEPT 135 spectrum in CD_3OD at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in CD_3OD at 600 MHz; (F) HSQC spectrum in CD_3OD at 600 MHz; (G) HMBC spectrum in CD_3OD at 600 MHz; (H) ROESY spectrum in CD_3OD at 600 MHz.

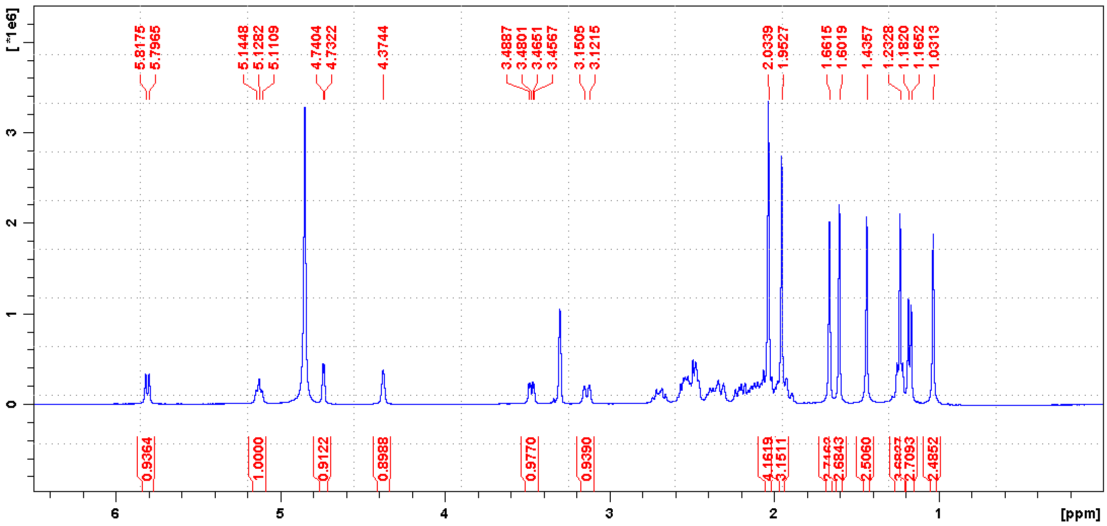
A

Monoisotopic Mass, Even Electron Ions
353 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
42
20190107_47 209 (1.687)

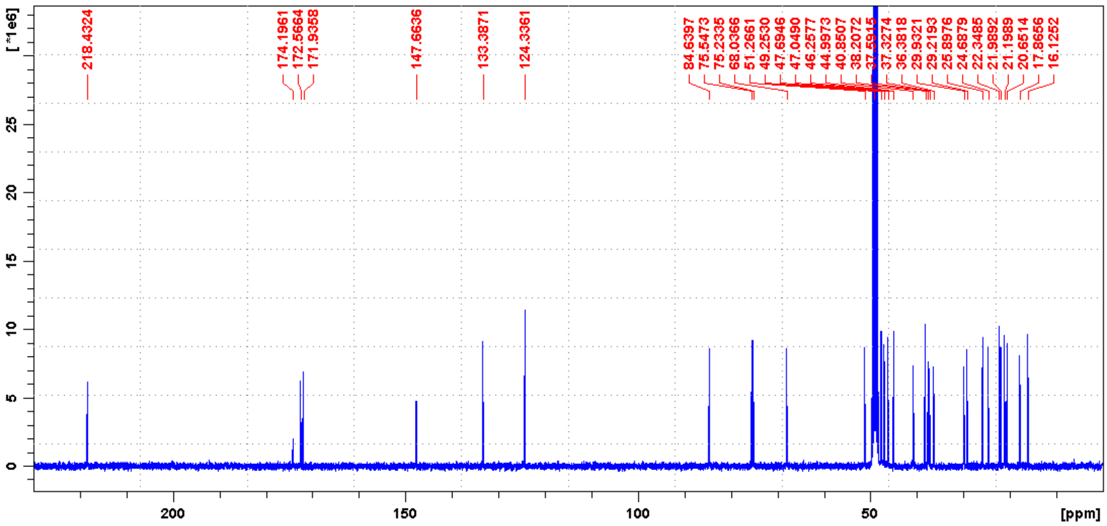


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
611.3185	611.3196	-1.1	-1.8	9.5	37.8	0.172	84.19	C33 H48 O9 Na
	611.3161	2.4	3.9	21.5	39.4	1.845	15.81	C42 H43 O4

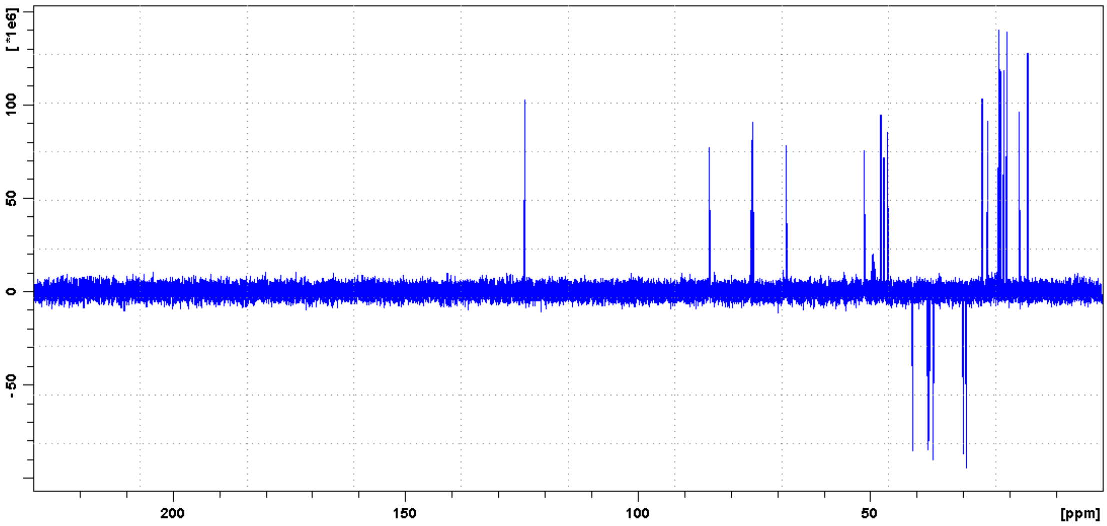
B



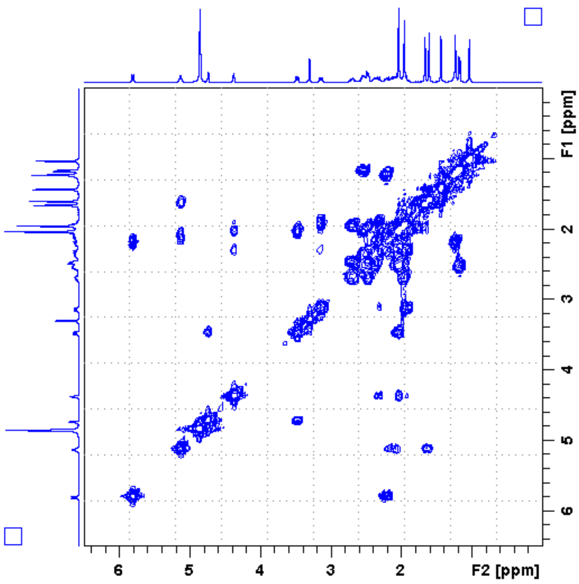
C



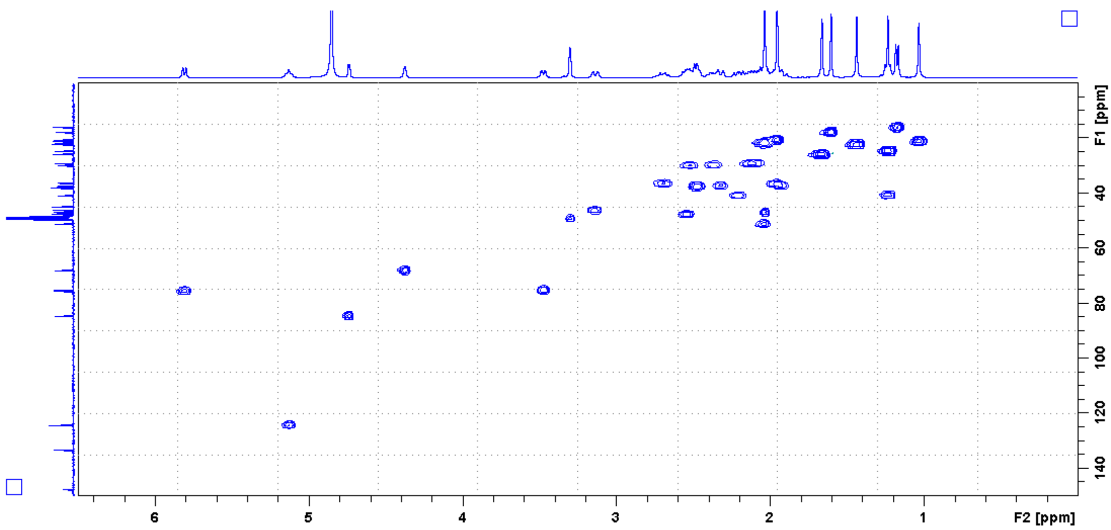
D



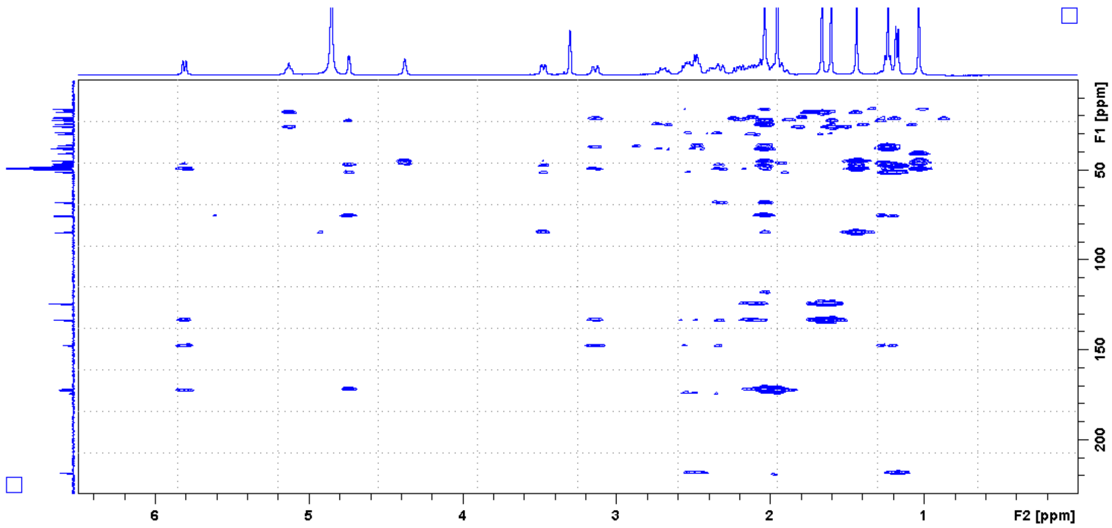
E



F



G



H

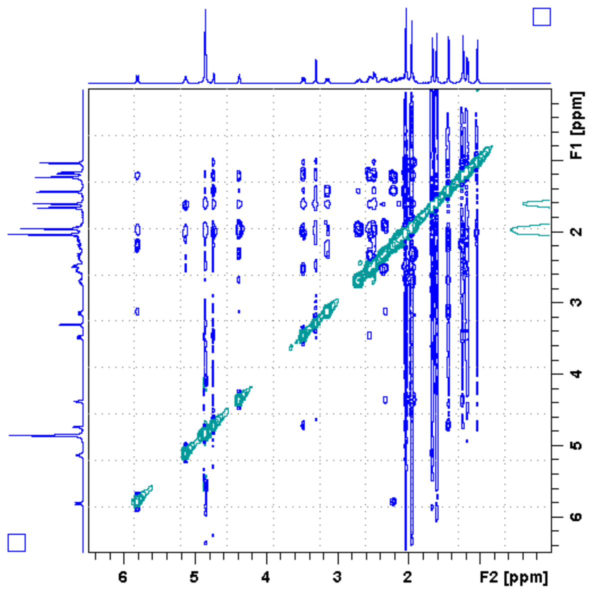
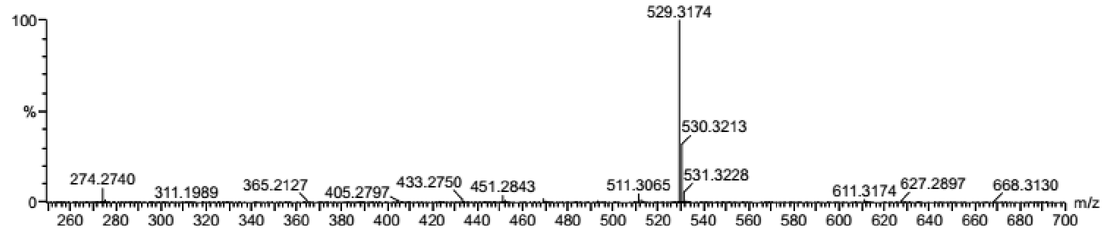


Figure S43 HRESIMS and NMR spectra of **50**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in CD_3OD at 400 MHz; (C) ^{13}C NMR spectrum in CD_3OD at 100 MHz; (D) DEPT 135 spectrum in CD_3OD at 100 MHz; (E) ^{1}H–^{1}H COSY spectrum in CD_3OD at 400 MHz; (F) HSQC spectrum in CD_3OD at 400 MHz; (G) HMBC spectrum in CD_3OD at 400 MHz; (H) ROESY spectrum in CD_3OD at 400 MHz.

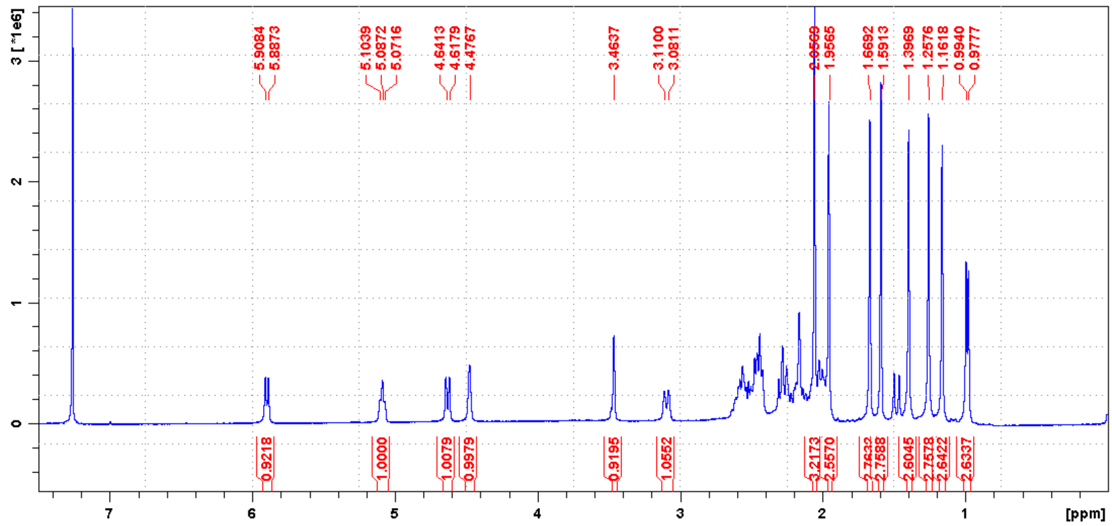
A

Monoisotopic Mass, Even Electron Ions
353 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
43
20190107_48 202 (1.634) 1: TOF MS ES+
2.02e+005

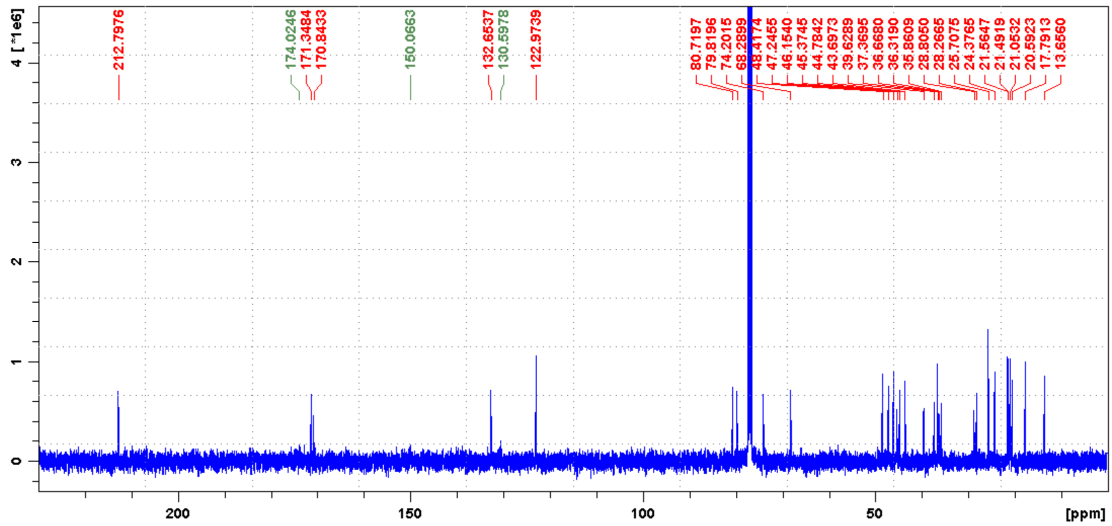


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
611.3174	611.3196	-2.2	-3.6	9.5	80.1	0.020	98.06	C33 H48 O9 Na
	611.3161	1.3	2.1	21.5	84.0	3.942	1.94	C42 H43 O4

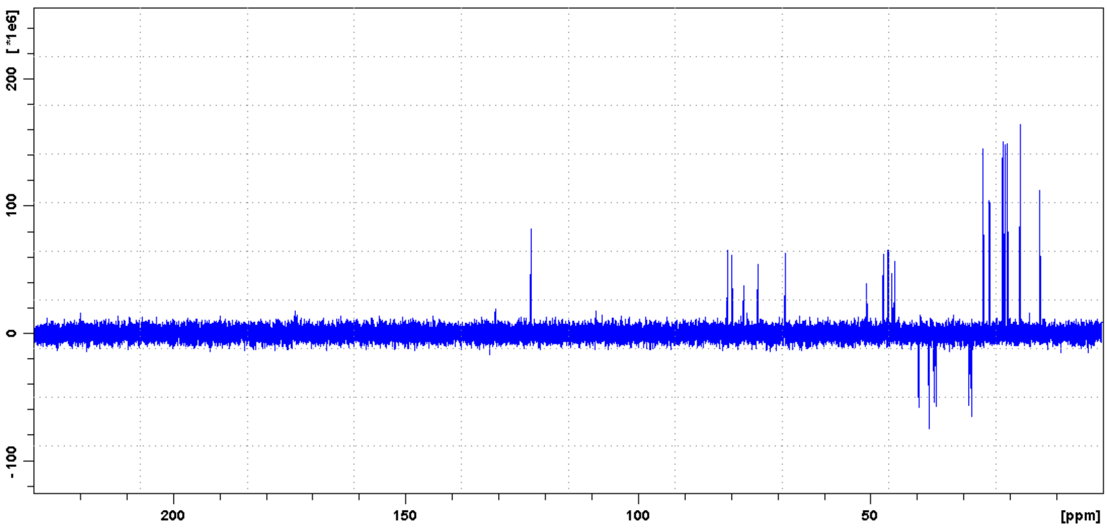
B



C



D


[*1e6]
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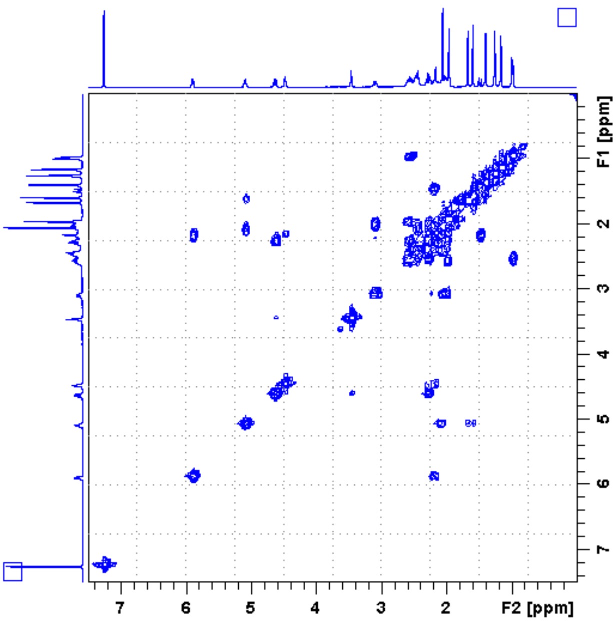
100
0
-100
200
150
100
50
[ppm]

E


F1 [ppm]
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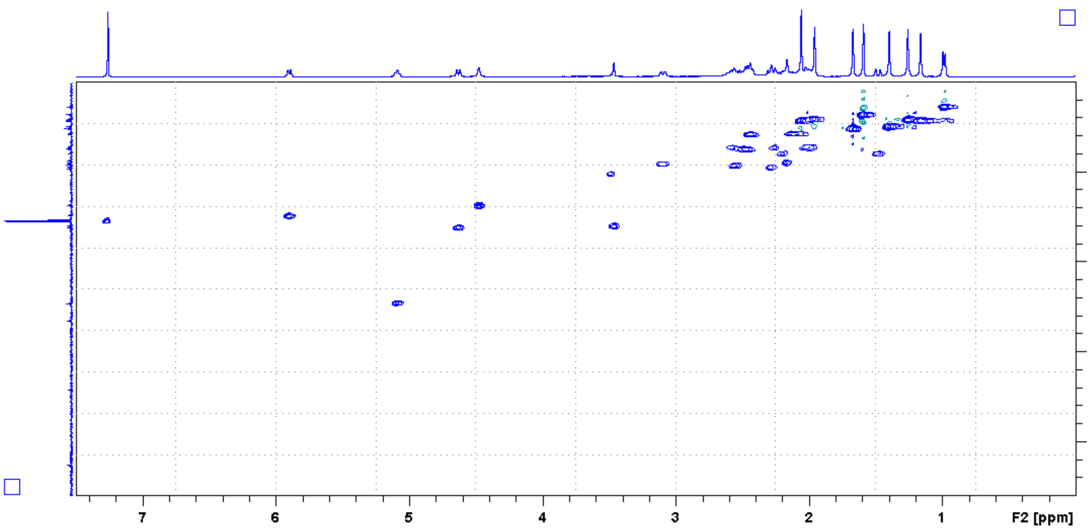
7
6
5
4
3
2
F2 [ppm]

F


F1 [ppm]
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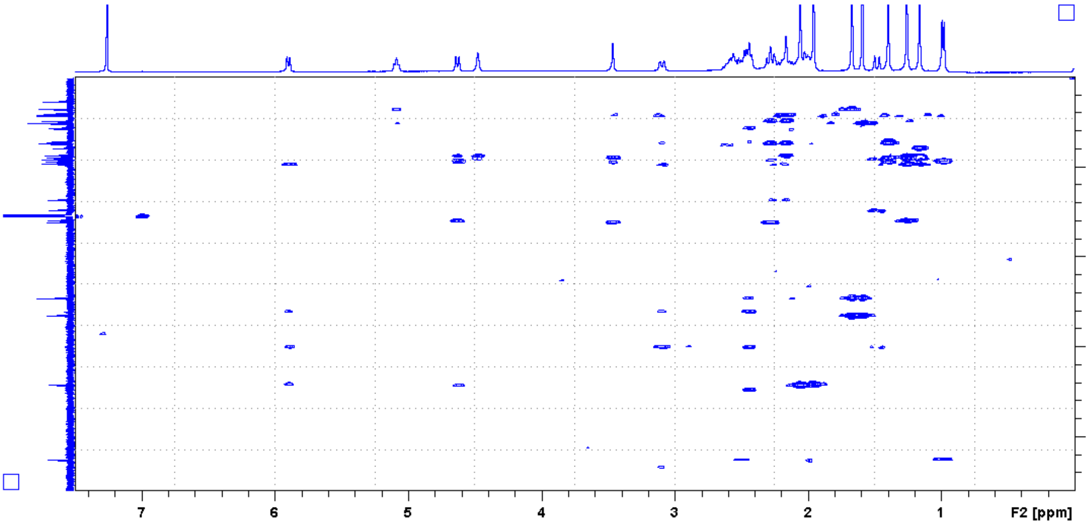
4
3
2
1
F2 [ppm]

G



H

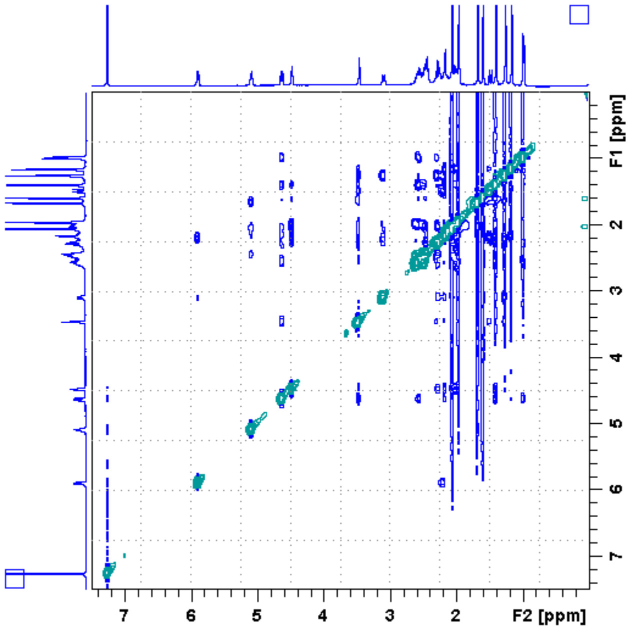
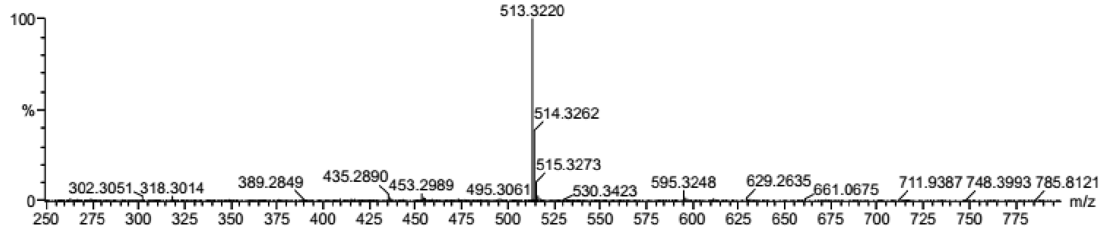


Figure S44 HRESIMS and NMR spectra of **51**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 400 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 100 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 100 MHz; (E) ^{1}H–^{1}H COSY spectrum in $CDCl_3$ at 400 MHz; (F) HSQC spectrum in $CDCl_3$ at 400 MHz; (G) HMBC spectrum in $CDCl_3$ at 400 MHz; (H) ROESY spectrum in $CDCl_3$ at 400 MHz.

A

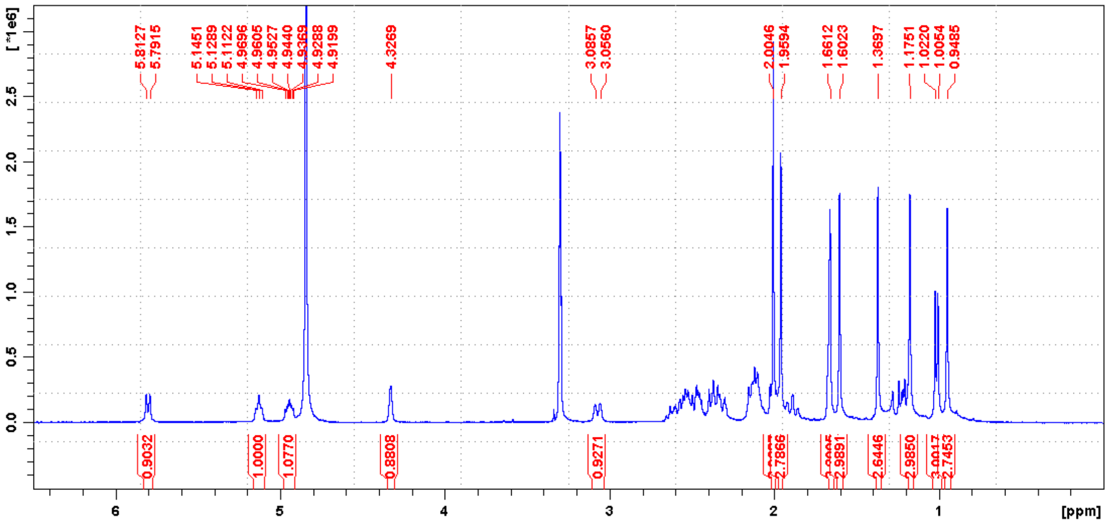
Monoisotopic Mass, Even Electron Ions
336 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
36
20190107_40 223 (1.803) 1: TOF MS ES+ 2.09e+004



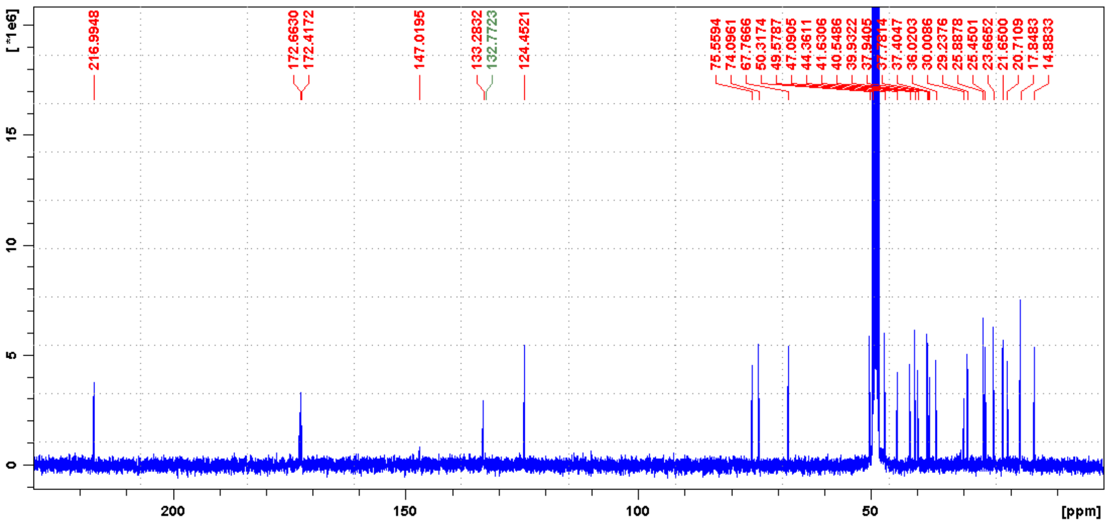
	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
595.3248	595.3247	0.1	0.2	9.5	25.7	0.218	80.44	C33 H48 O8 Na
	595.3271	-2.3	-3.9	12.5	27.1	1.632	19.56	C35 H47 O8

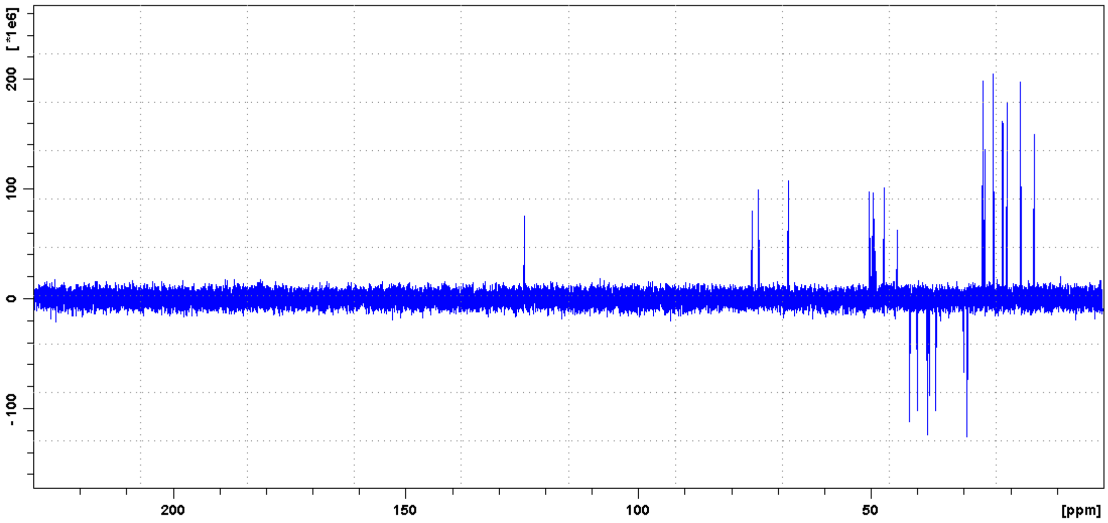
B



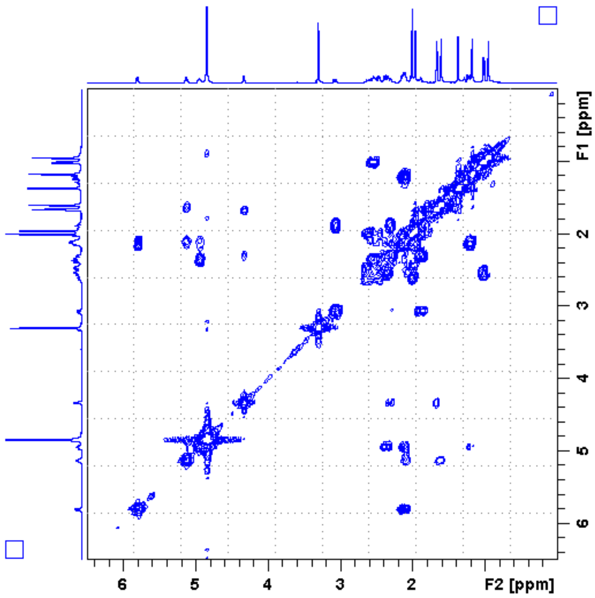
C



D


[*1e6]
200
100
0
-100
200
150
100
50
[ppm]

E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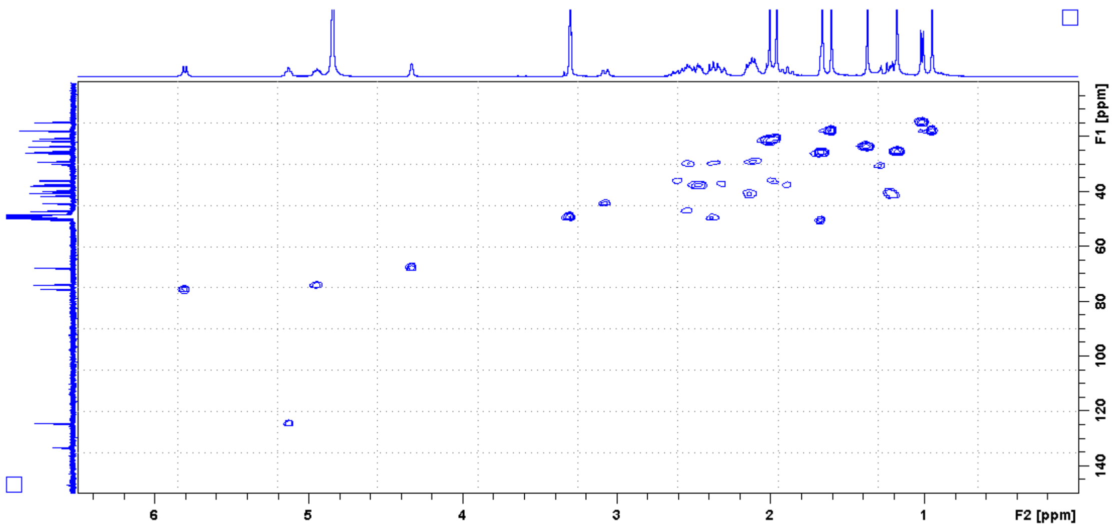
2
F2 [ppm]

F


F1 [ppm]
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60
80
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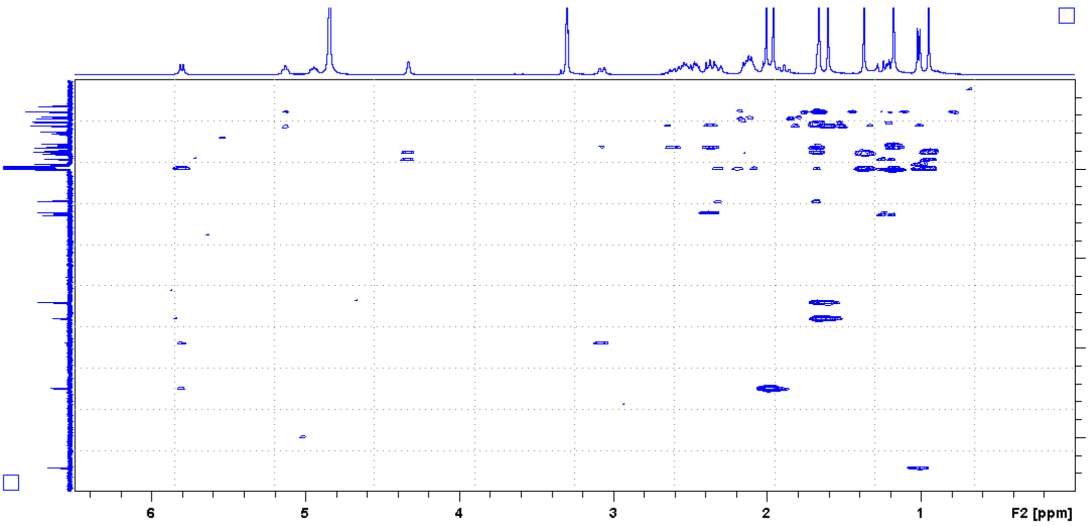
140
6
5
4
3
2
1
F2 [ppm]

G



H

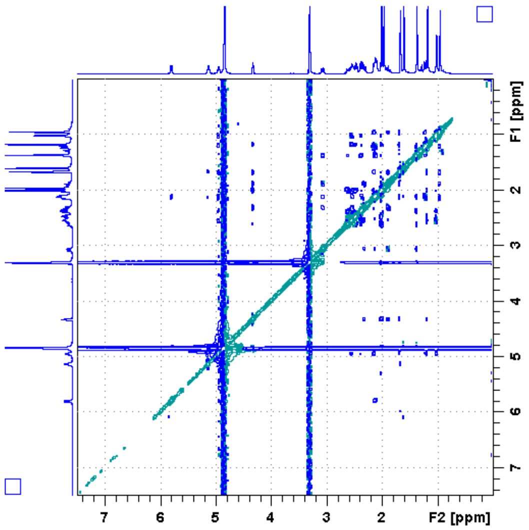
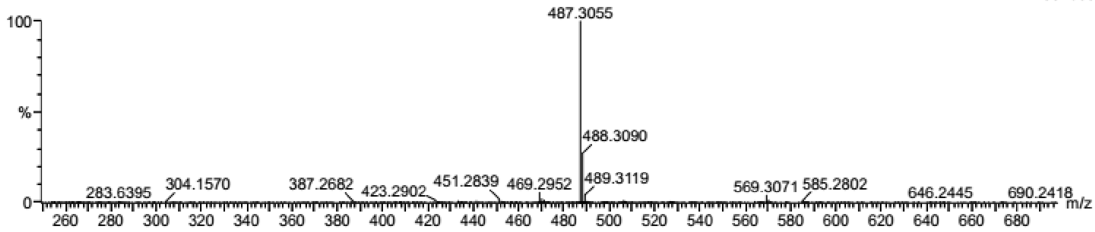


Figure S45 HRESIMS and NMR spectra of **52**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in CD_3OD at 400 MHz; (C) ^{13}C NMR spectrum in CD_3OD at 100 MHz; (D) DEPT 135 spectrum in CD_3OD at 100 MHz; (E) ^{1}H–^{1}H COSY spectrum in CD_3OD at 400 MHz; (F) HSQC spectrum in CD_3OD at 400 MHz; (G) HMBC spectrum in CD_3OD at 400 MHz; (H) ROESY spectrum in CD_3OD at 600 MHz.

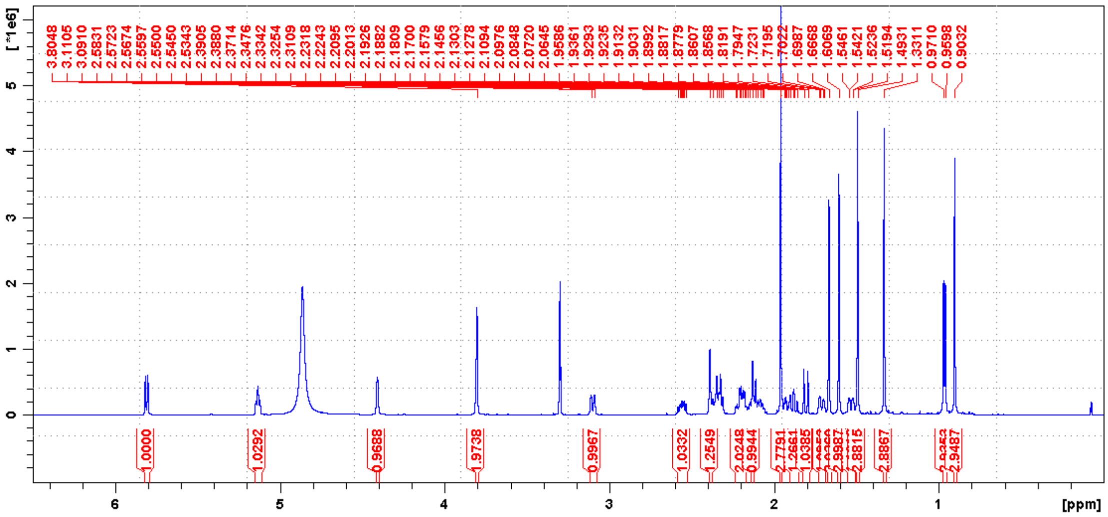
A

Monoisotopic Mass, Even Electron Ions
300 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
37
20190107_41 188 (1.518)

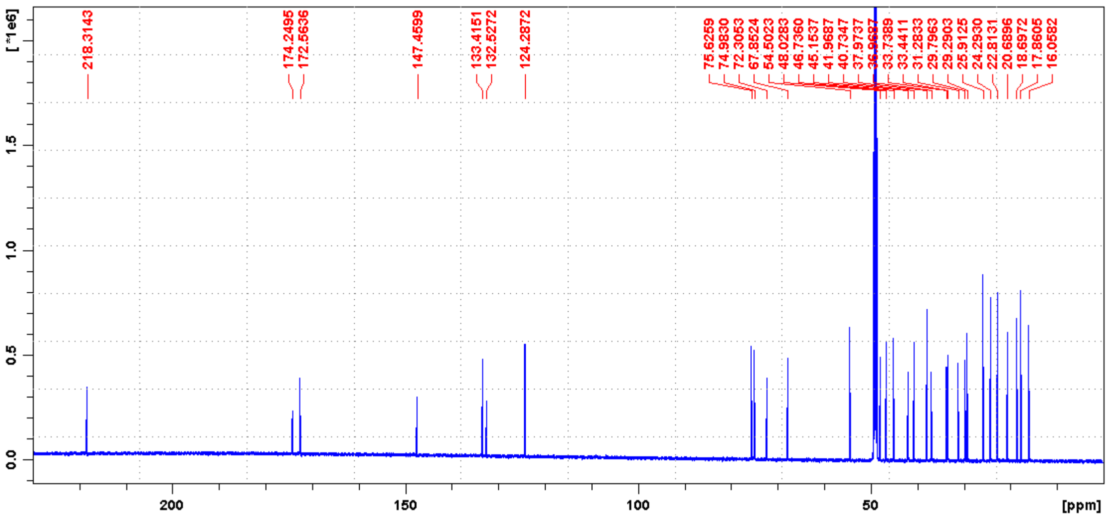


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
569.3071	569.3056	1.5	2.6	20.5	76.8	3.337	3.55	C40 H41 O3
	569.3090	-1.9	-3.3	8.5	73.5	0.036	96.45	C31 H46 O8 Na

B



C



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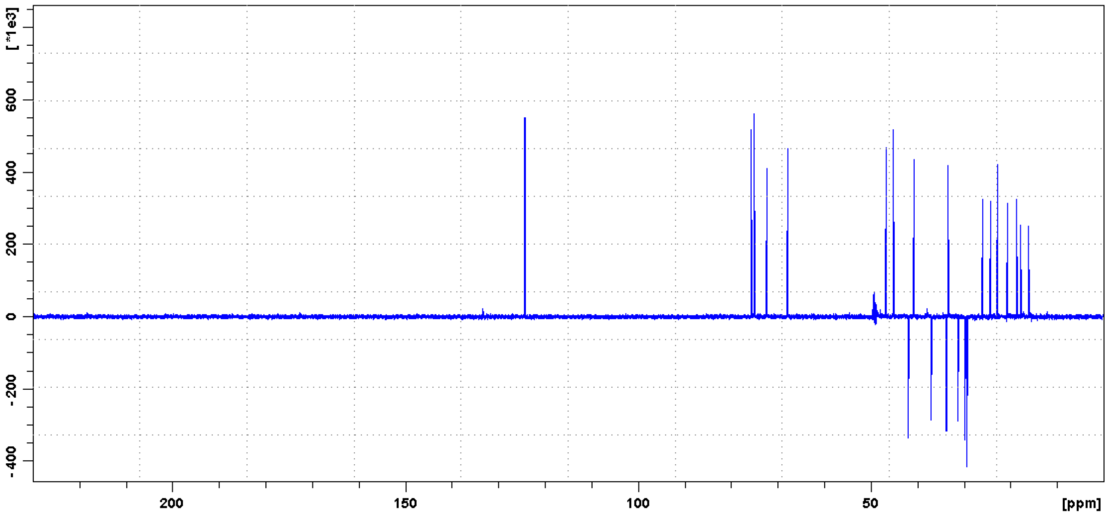

[*1e3]
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-400
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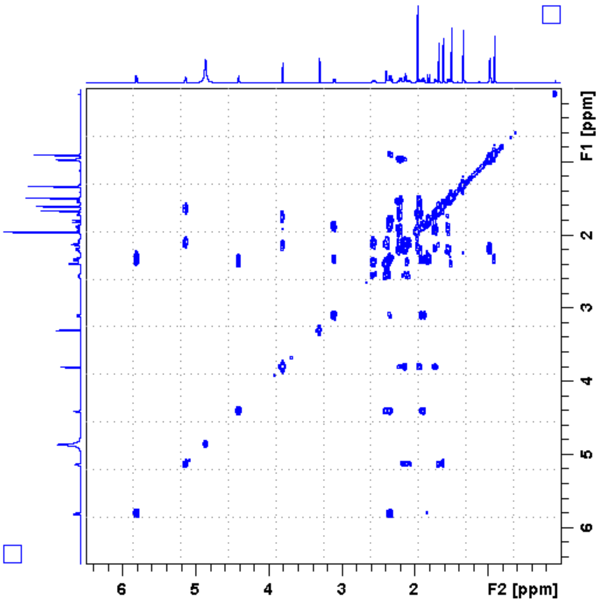
[ppm]

E



F1 [ppm]
2
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4
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6
6
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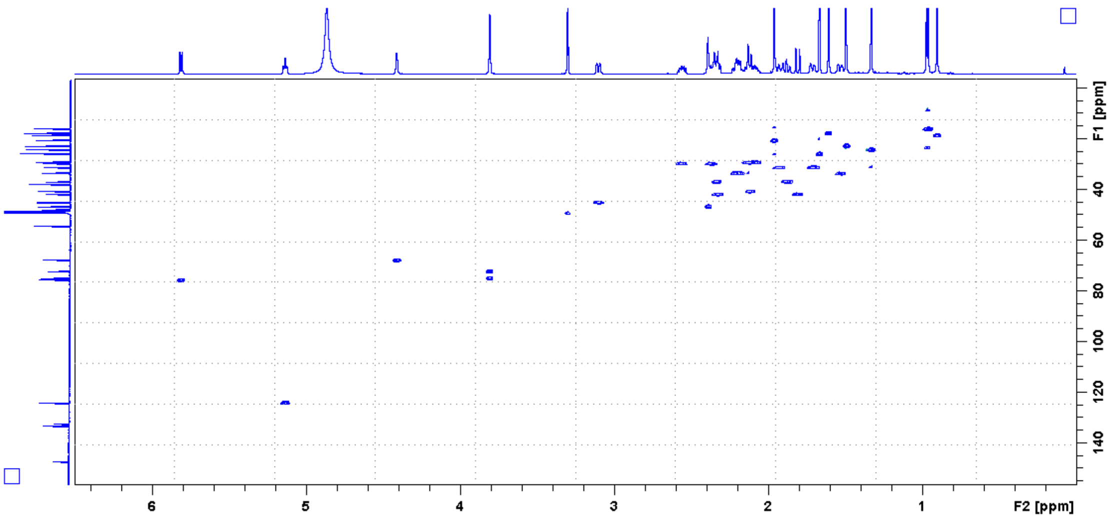
4
3
2
F2 [ppm]

F



F1 [ppm]
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80
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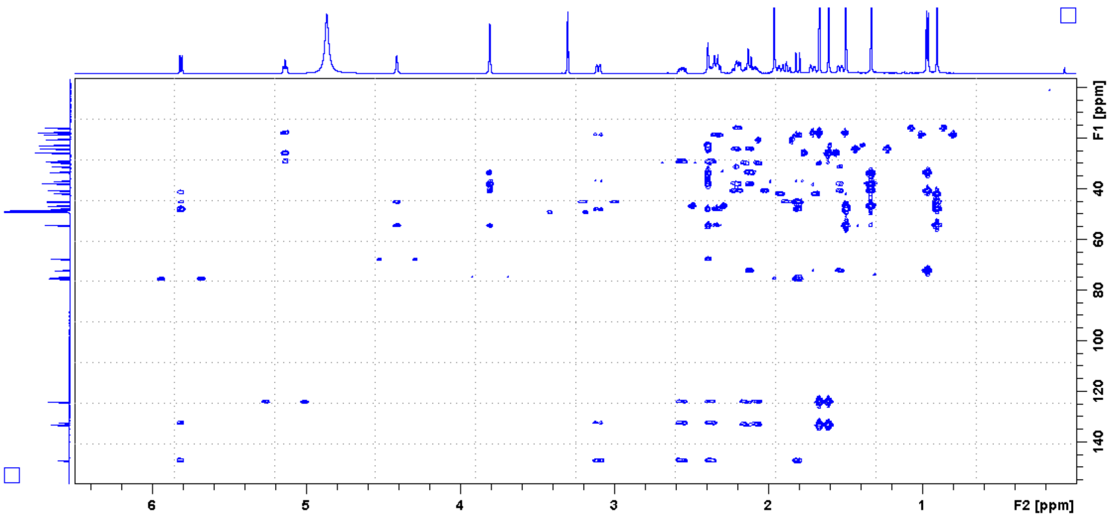
6
5
4
3
2
1
F2 [ppm]

G



H

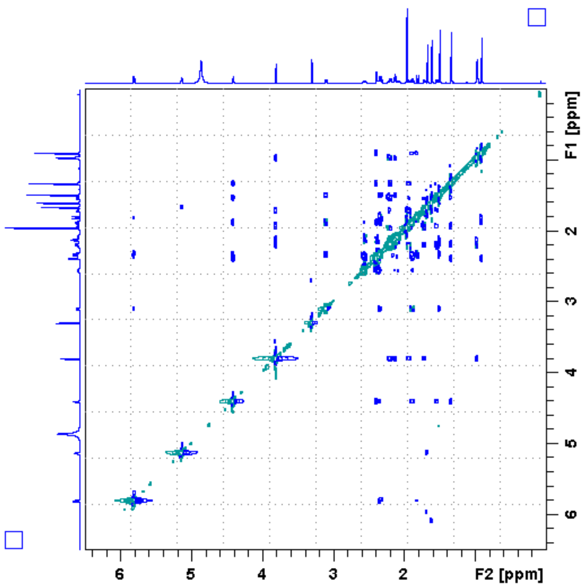
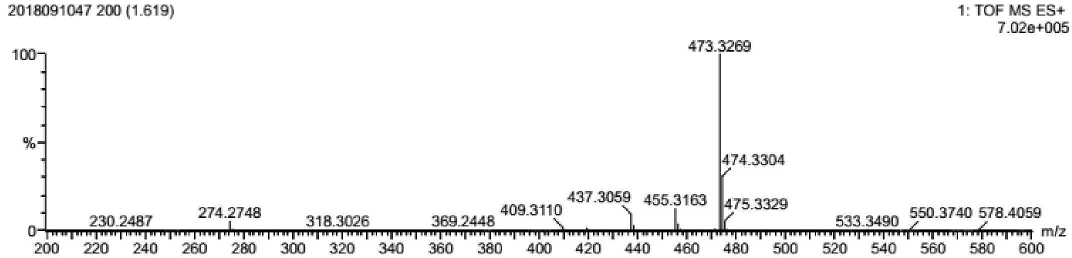


Figure S46 HRESIMS and NMR spectra of **55**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in CD_3OD at 600 MHz; (C) ^{13}C NMR spectrum in CD_3OD at 150 MHz; (D) DEPT 135 spectrum in CD_3OD at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in CD_3OD at 600 MHz; (F) HSQC spectrum in CD_3OD at 600 MHz; (G) HMBC spectrum in CD_3OD at 600 MHz; (H) ROESY spectrum in CD_3OD at 600 MHz.

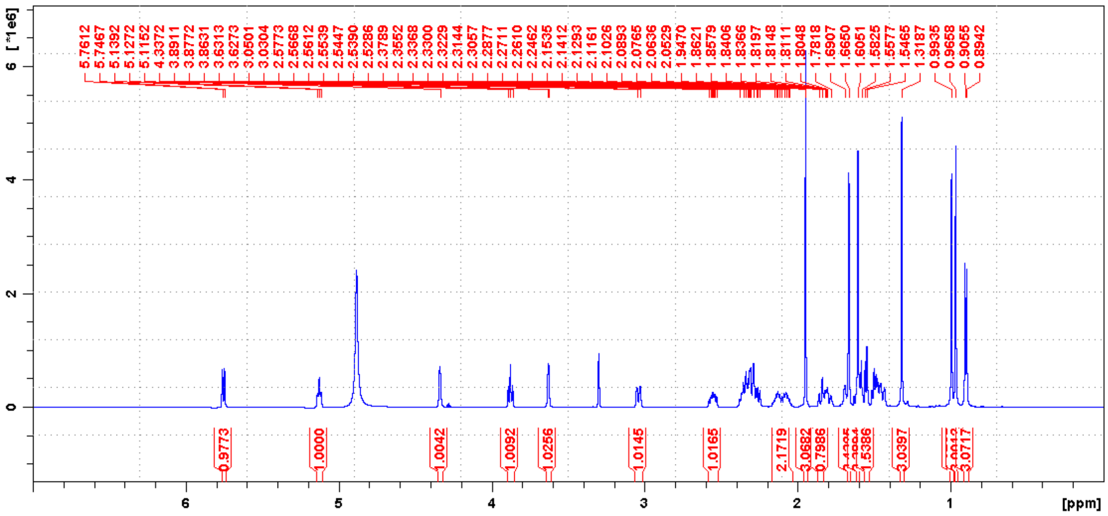
A

Monoisotopic Mass, Even Electron Ions
267 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
B3B1-C1-2-4
2018091047 200 (1.619)

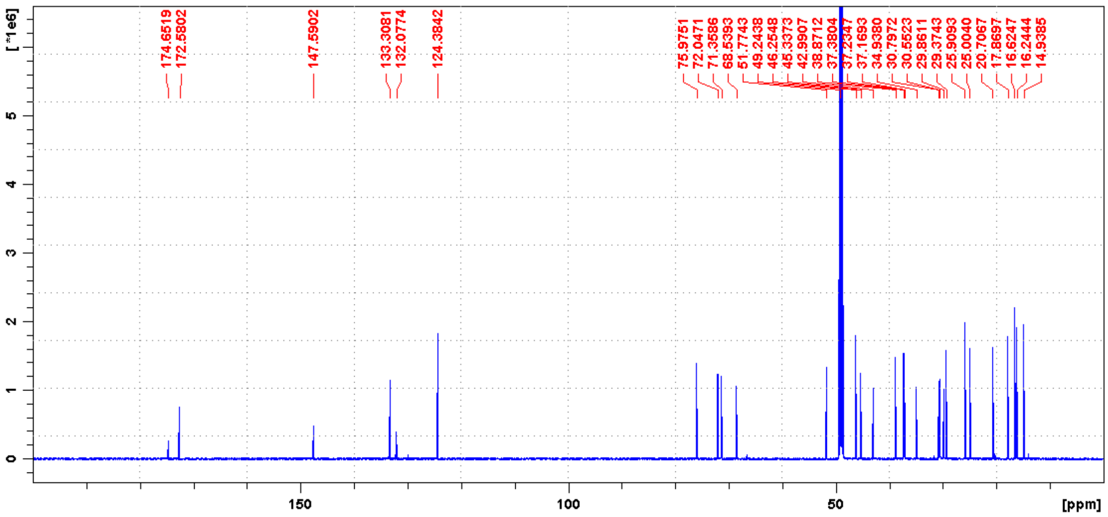


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
533.3490	533.3478	1.2	2.2	7.5	312.1	n/a	n/a	C31 H49 O7

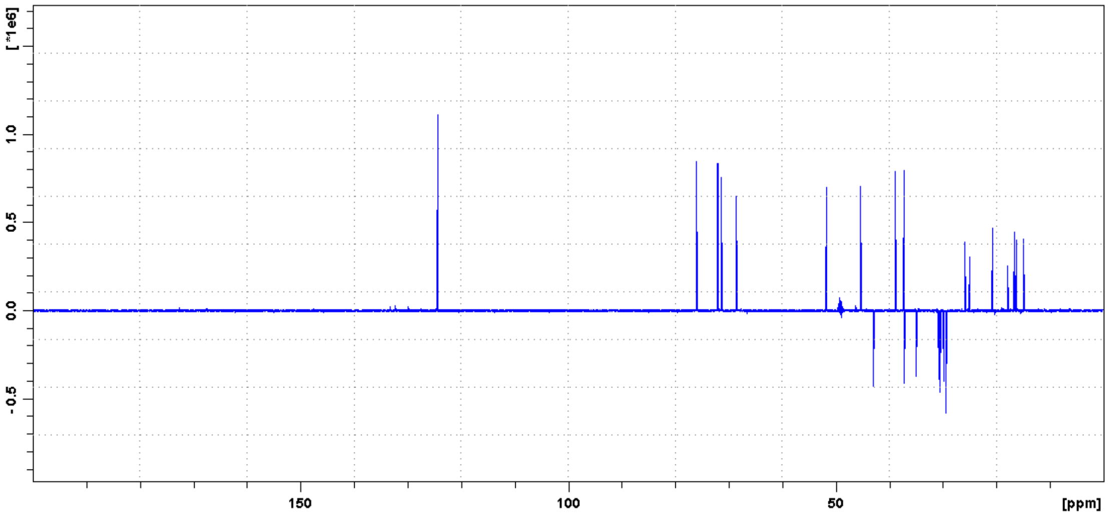
B



C



D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0.0
-0.5
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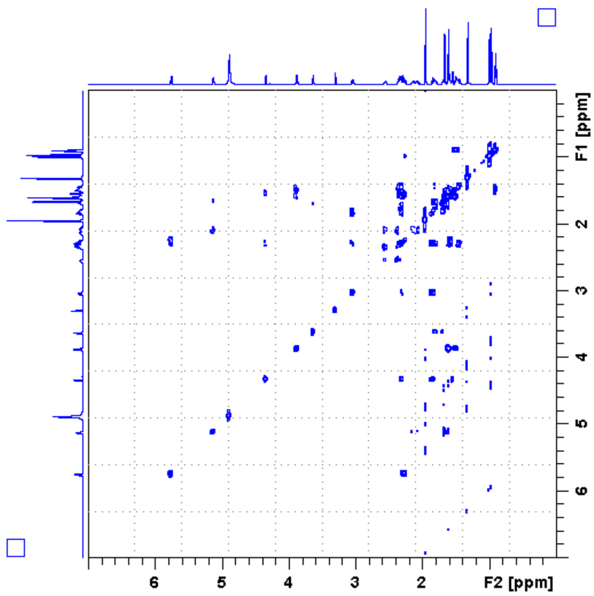
100
50
[ppm]

E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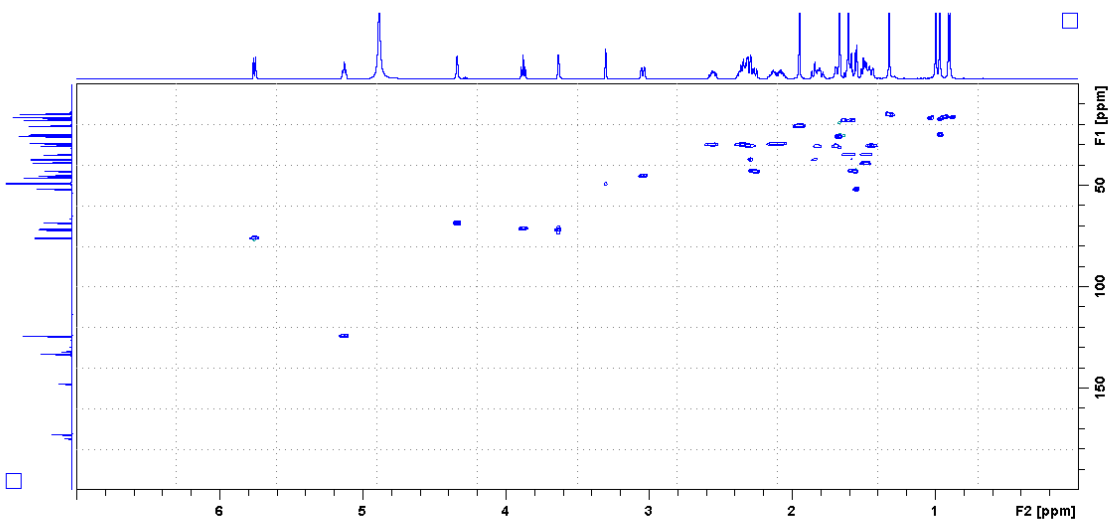
5
6
F2 [ppm]

F


F1 [ppm]
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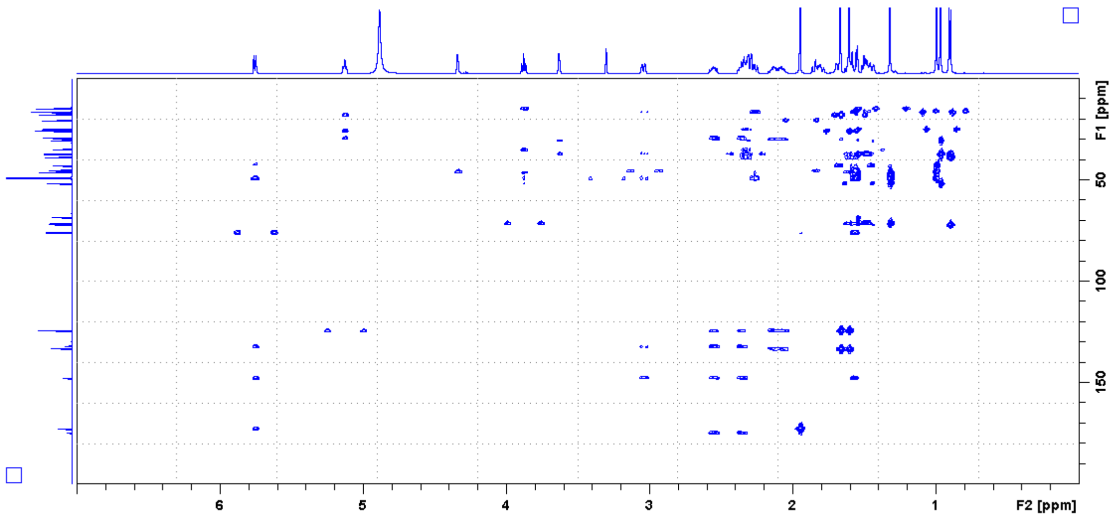
4
3
2
1
F2 [ppm]

G



H

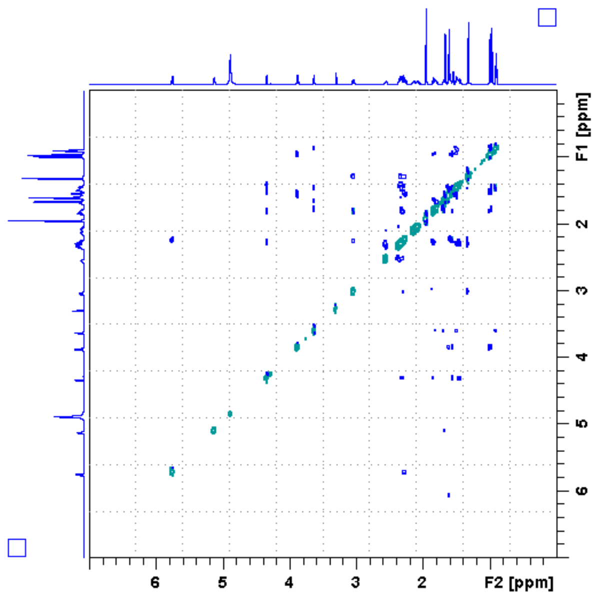
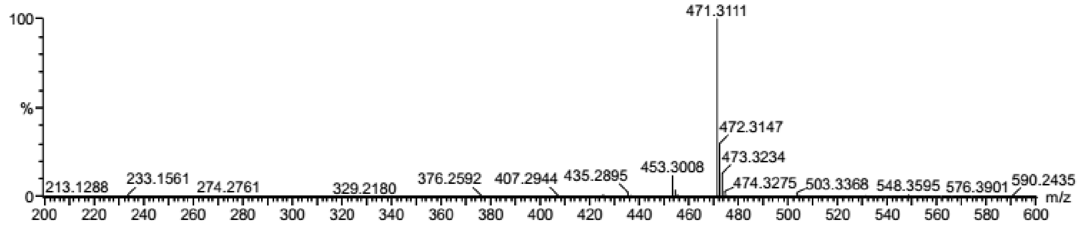


Figure S47 HRESIMS and NMR spectra of **56**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in CD_3OD at 600 MHz; (C) ^{13}C NMR spectrum in CD_3OD at 150 MHz; (D) DEPT 135 spectrum in CD_3OD at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in CD_3OD at 600 MHz; (F) HSQC spectrum in CD_3OD at 600 MHz; (G) HMBC spectrum in CD_3OD at 600 MHz; (H) ROESY spectrum in CD_3OD at 600 MHz.

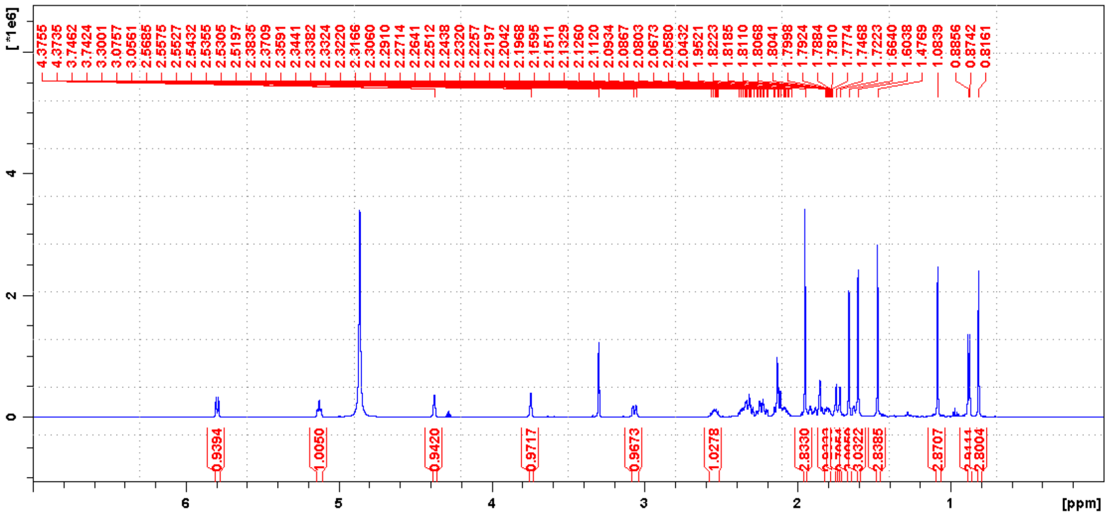
A

Monoisotopic Mass, Even Electron Ions
275 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
B3B1-C1-2-8
2018091040 215 (1.732)

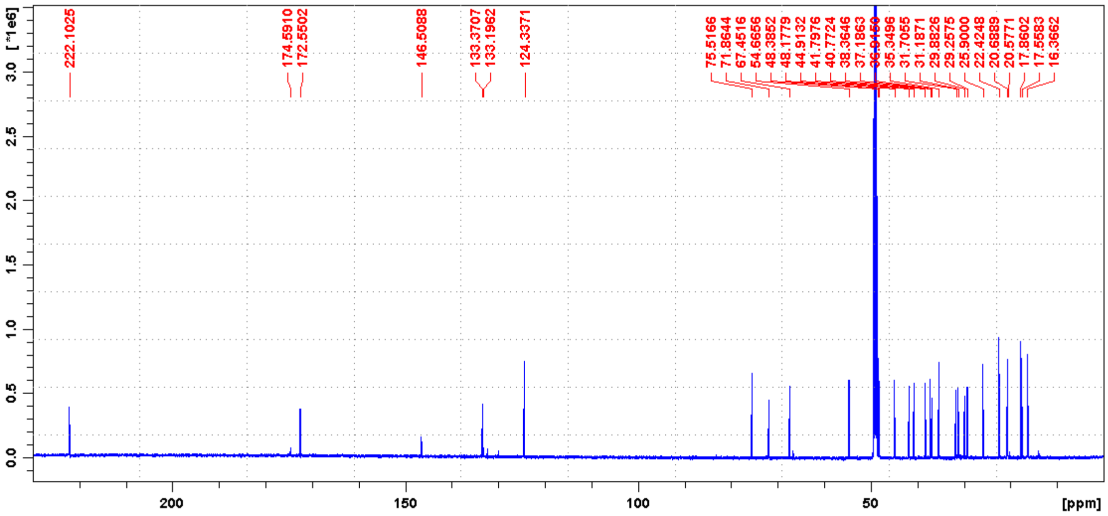


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
531.3325	531.3322	0.3	0.6	8.5	225.5	n/a	n/a	C31 H47 O7

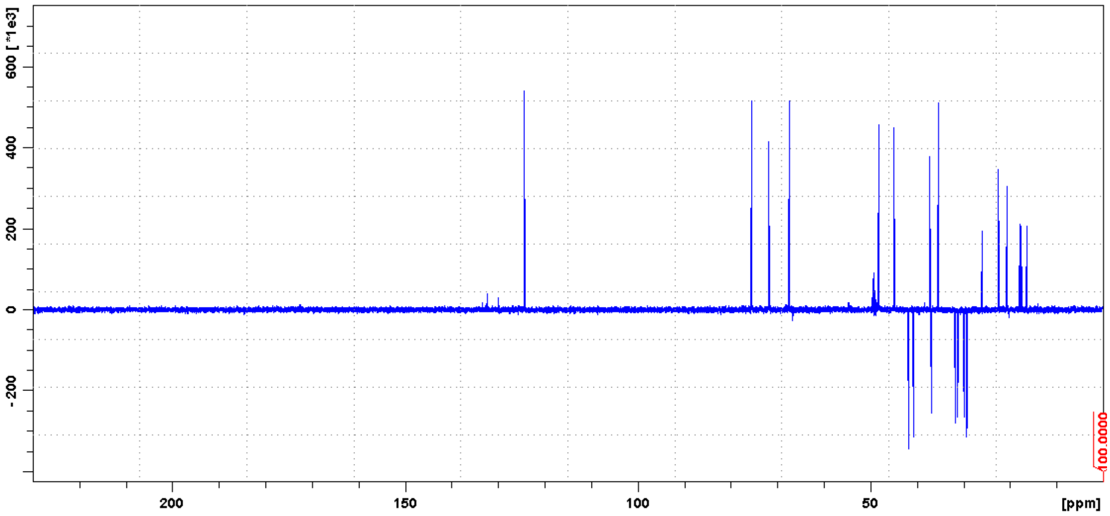
B



C



D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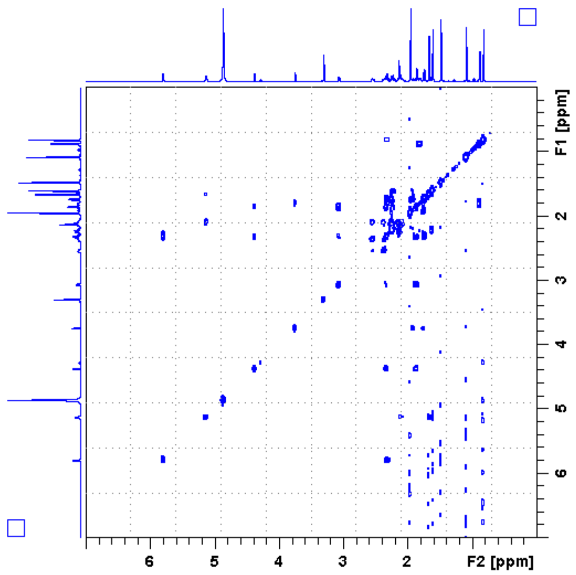
200
0
-200
200
150
100
50
[ppm]
100.0000

E


F1 [ppm]
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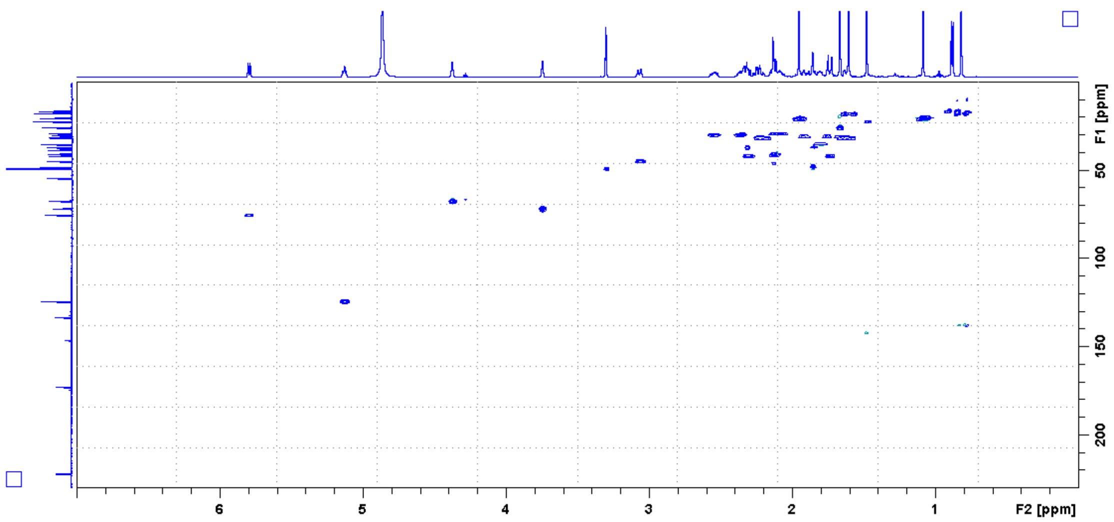
4
3
2
F2 [ppm]

F


F1 [ppm]
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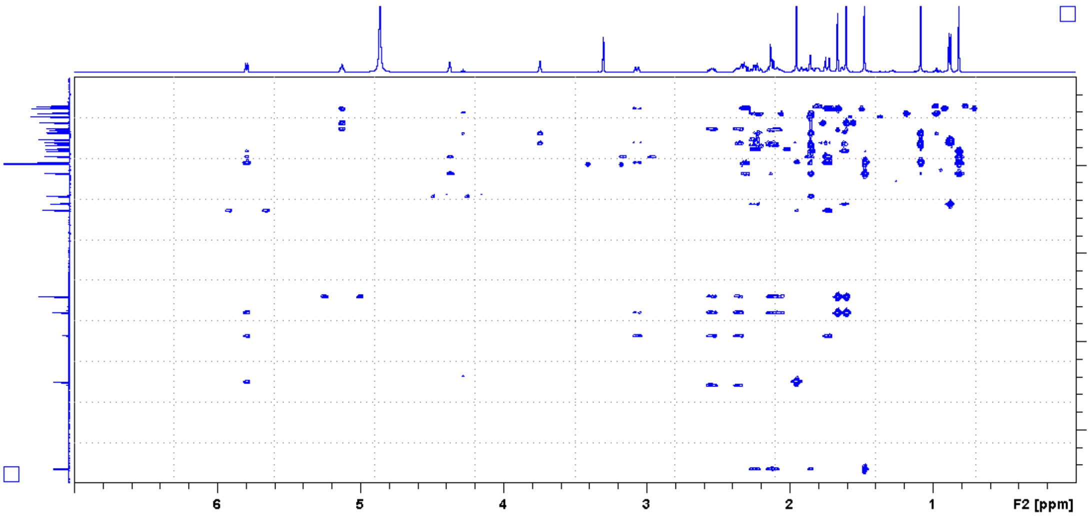
1
F2 [ppm]

G



H

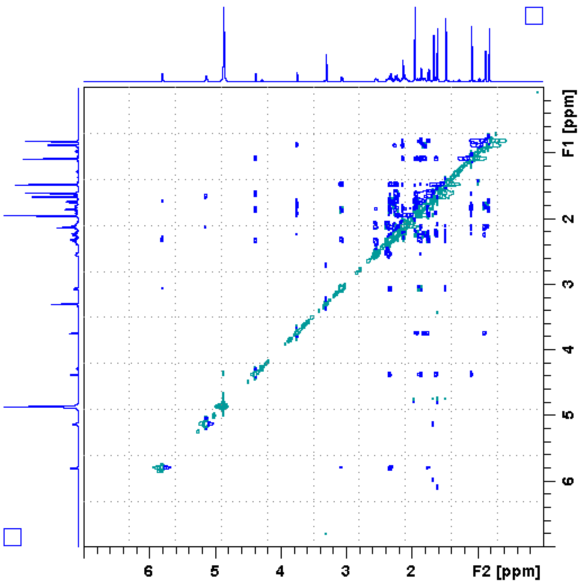
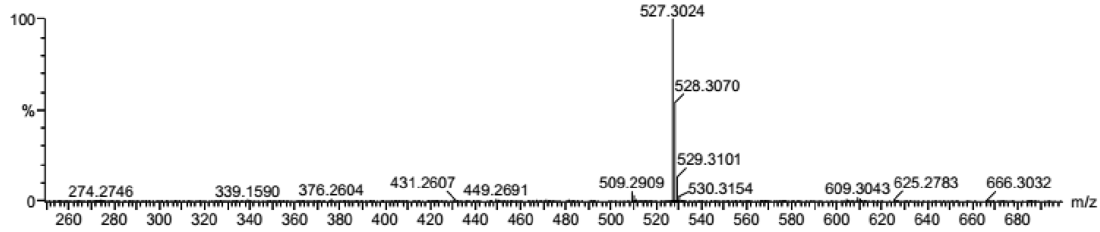


Figure S48 HRESIMS and NMR spectra of **57**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in CD_3OD at 600 MHz; (C) ^{13}C NMR spectrum in CD_3OD at 150 MHz; (D) DEPT 135 spectrum in CD_3OD at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in CD_3OD at 600 MHz; (F) HSQC spectrum in CD_3OD at 600 MHz; (G) HMBC spectrum in CD_3OD at 600 MHz; (H) ROESY spectrum in CD_3OD at 600 MHz.

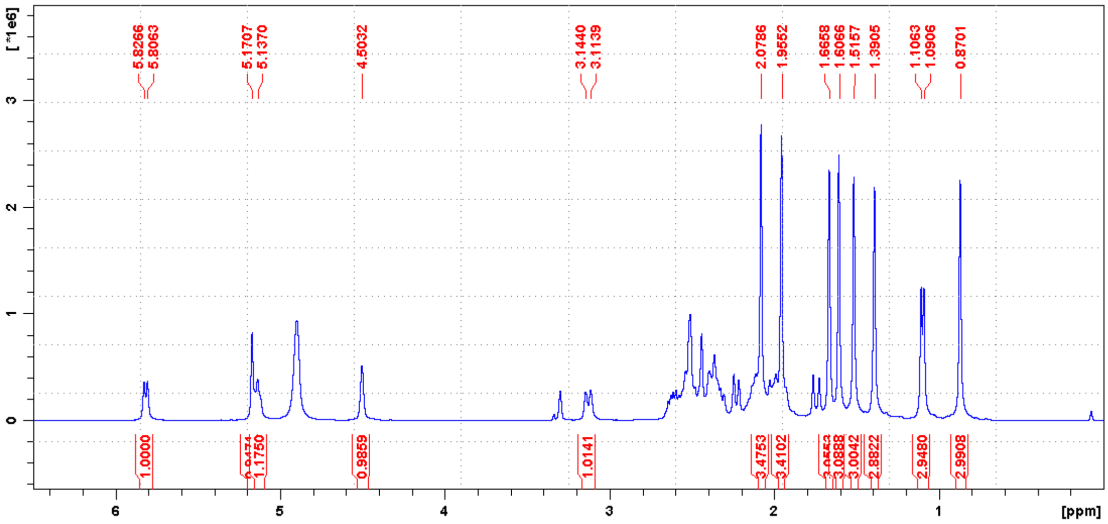
A

Monoisotopic Mass, Even Electron Ions
339 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
38
20190107_42 210 (1.694)

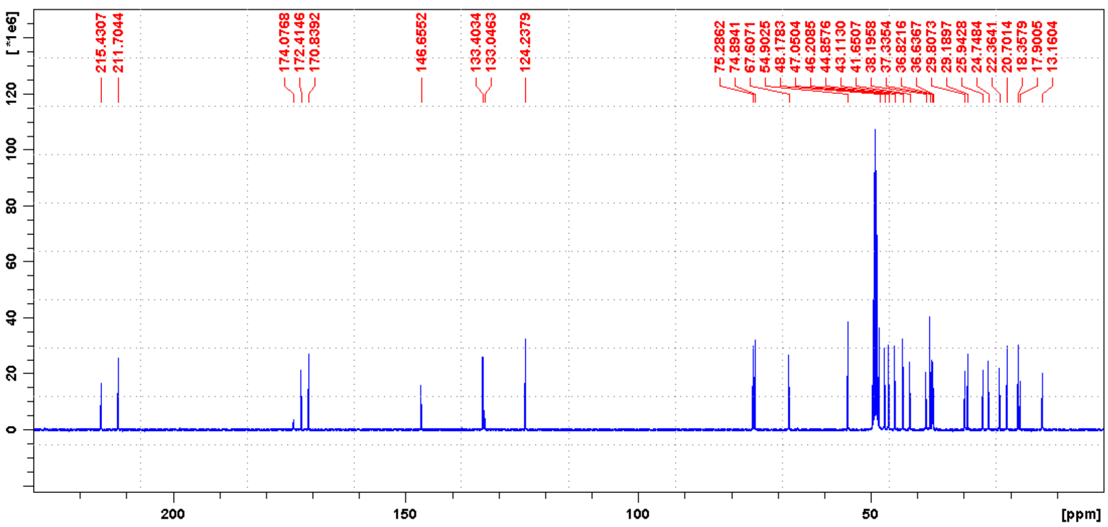


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
609.3043	609.3040	0.3	0.5	10.5	52.0	0.629	53.33	C33 H46 O9 Na
	609.3064	-2.1	-3.4	13.5	52.1	0.762	46.67	C35 H45 O9

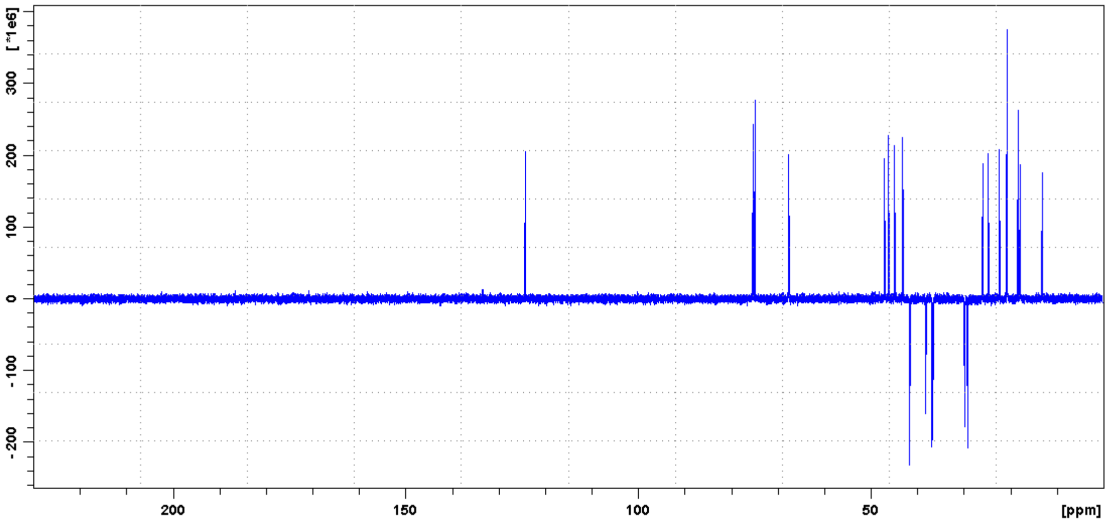
B



C



D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-100
-200
200
150
100
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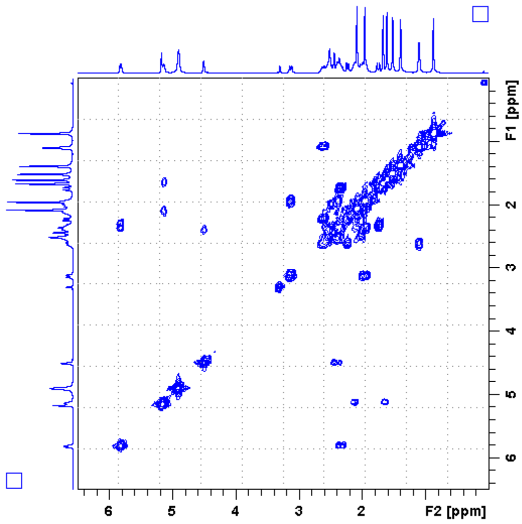
[ppm]

E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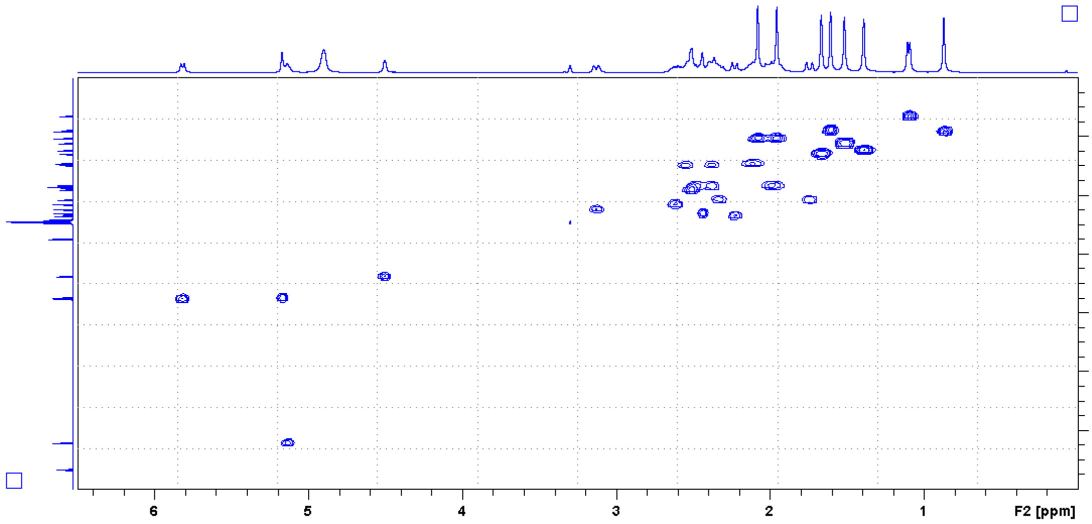
2
F2 [ppm]

F


F1 [ppm]
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5
4
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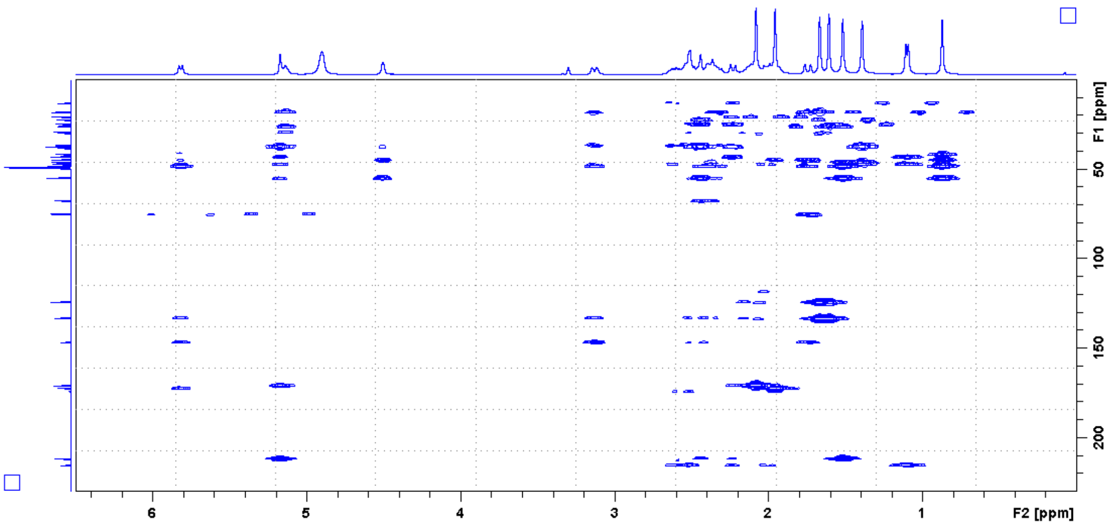
2
1
F2 [ppm]

G



H

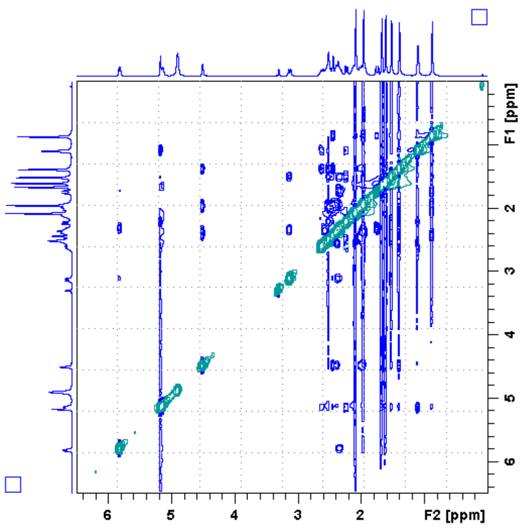
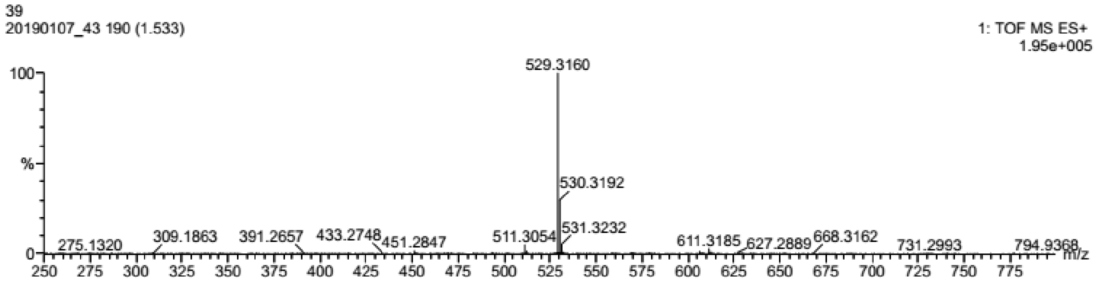


Figure S49 HRESIMS and NMR spectra of **58**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in CD_3OD at 400 MHz; (C) ^{13}C NMR spectrum in CD_3OD at 100 MHz; (D) DEPT 135 spectrum in CD_3OD at 100 MHz; (E) ^{1}H–^{1}H COSY spectrum in CD_3OD at 400 MHz; (F) HSQC spectrum in CD_3OD at 400 MHz; (G) HMBC spectrum in CD_3OD at 400 MHz; (H) ROESY spectrum in CD_3OD at 400 MHz.

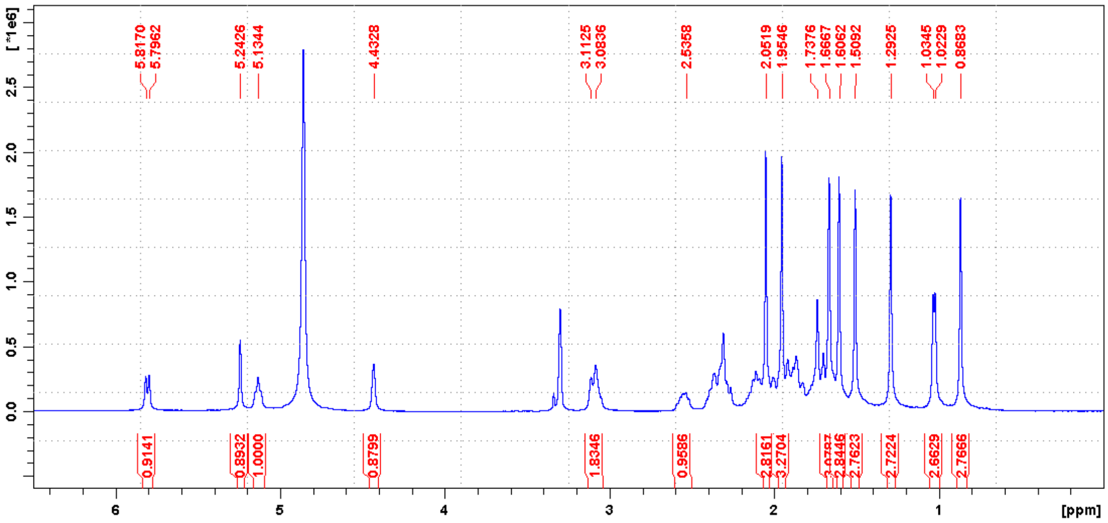
A

Monoisotopic Mass, Even Electron Ions
353 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1

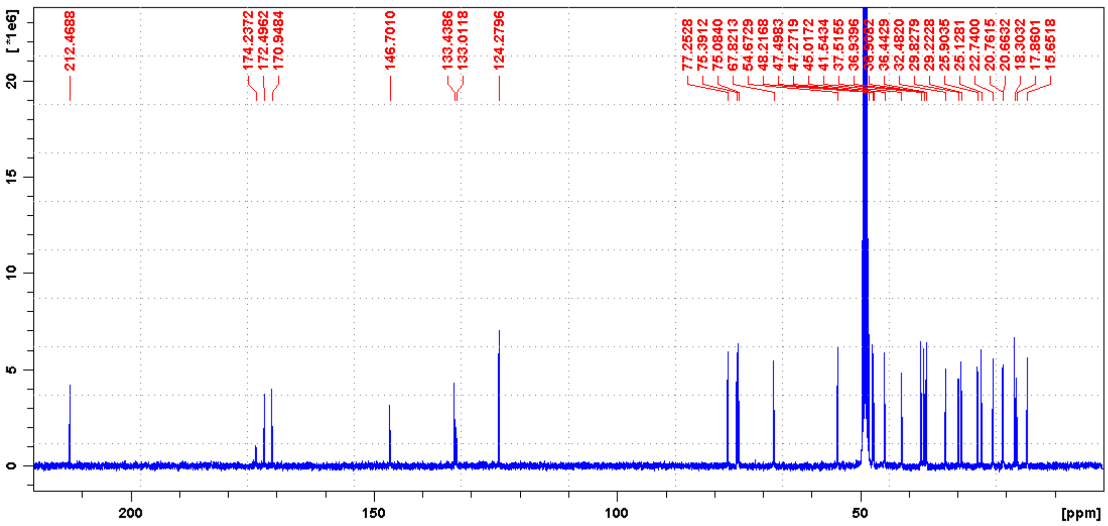


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
611.3185	611.3196	-1.1	-1.8	9.5	79.2	0.001	99.91	C33 H48 O9 Na
	611.3161	2.4	3.9	21.5	86.3	7.067	0.09	C42 H43 O4

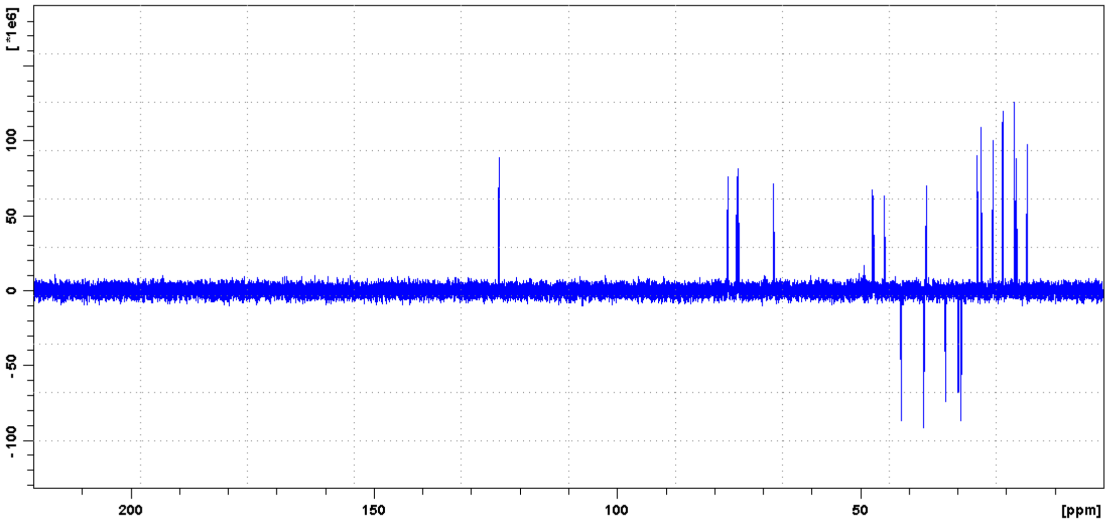
B



C



D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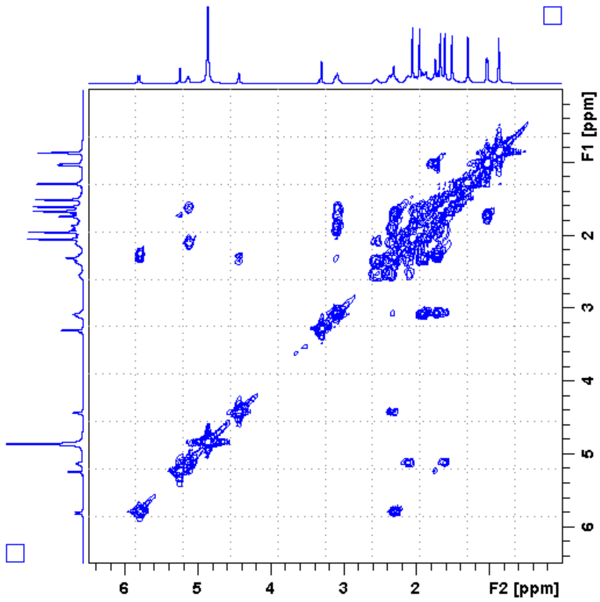
0
-50
-100
200
150
100
50
[ppm]

E


F1 [ppm]
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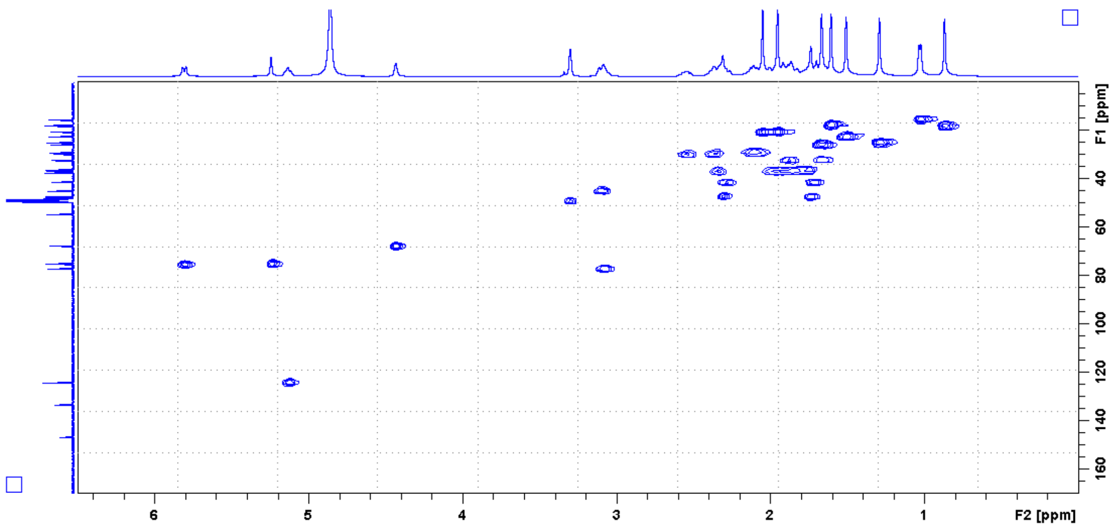
5
4
3
2
F2 [ppm]

F


F1 [ppm]
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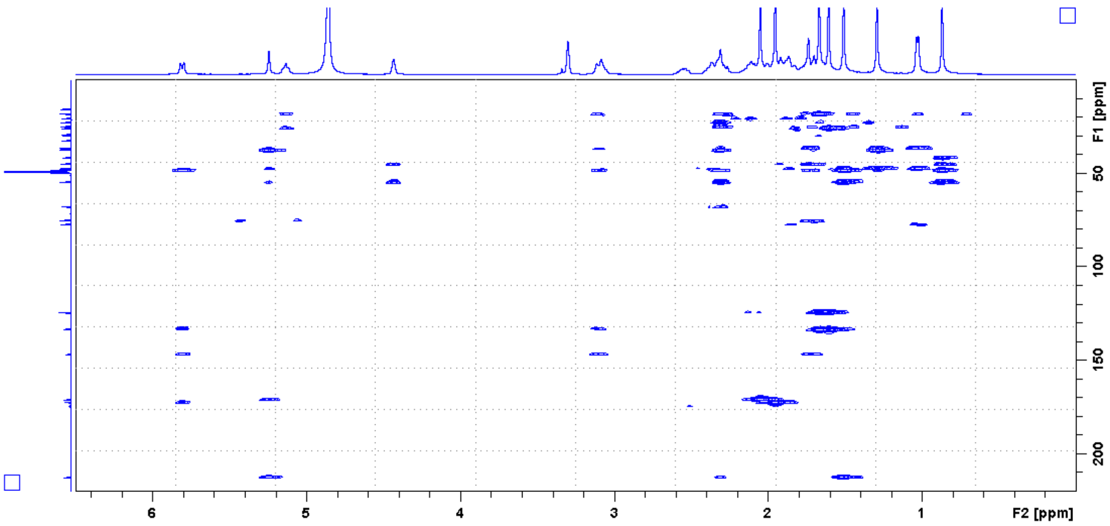
6
5
4
3
2
1
F2 [ppm]

G



H

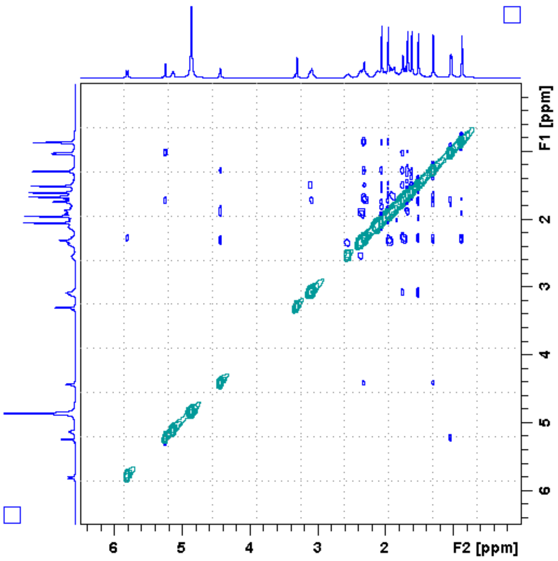
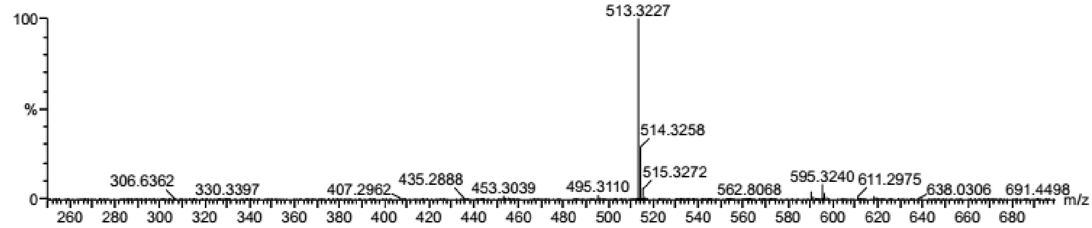


Figure S50 HRESIMS and NMR spectra of **59**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in CD_3OD at 400 MHz; (C) ^{13}C NMR spectrum in CD_3OD at 100 MHz; (D) DEPT 135 spectrum in CD_3OD at 100 MHz; (E) ^{1}H–^{1}H COSY spectrum in CD_3OD at 400 MHz; (F) HSQC spectrum in CD_3OD at 400 MHz; (G) HMBC spectrum in CD_3OD at 400 MHz; (H) ROESY spectrum in CD_3OD at 400 MHz.

A

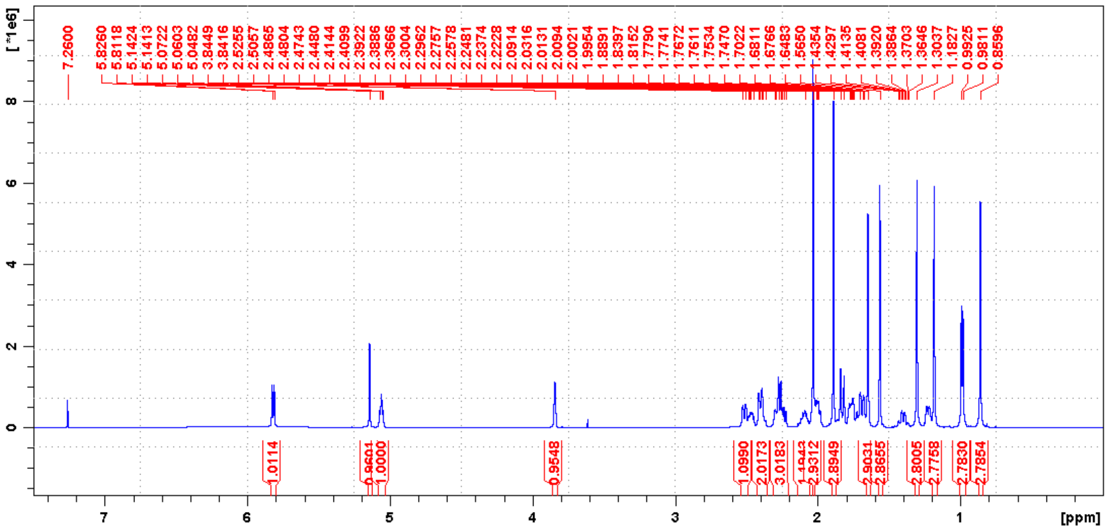
Monoisotopic Mass, Even Electron Ions
336 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
32
20190107_36 243 (1.964)



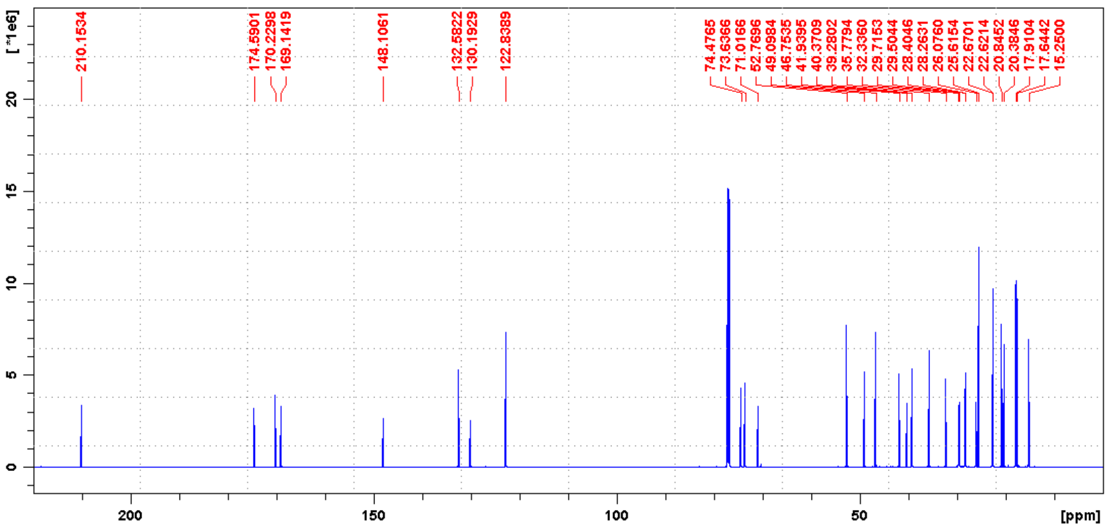
Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
595.3240	595.3247	-0.7	-1.2	9.5	82.4	0.050	95.17	C33 H48 O8 Na
	595.3212	2.8	4.7	21.5	85.4	3.030	4.83	C42 H43 O3

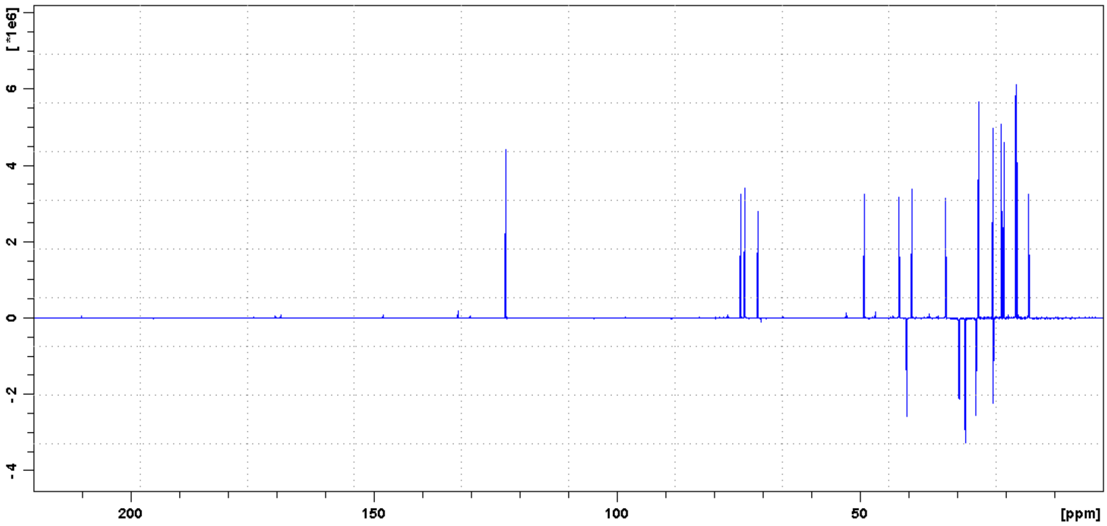
B



C



D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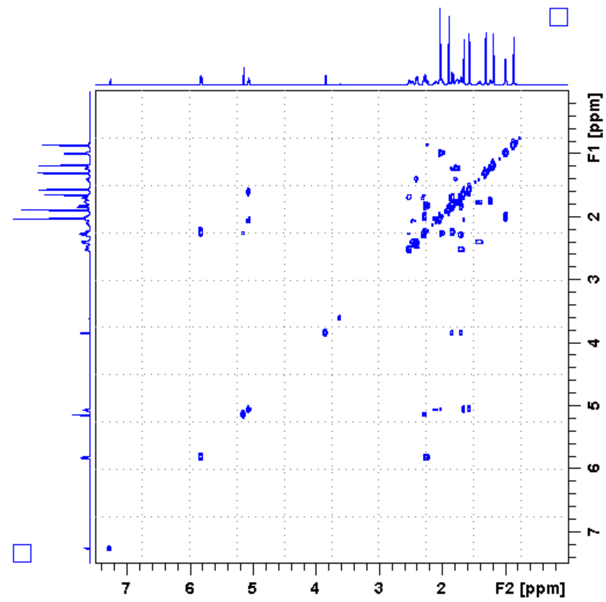
4
2
0
-2
-4
200
150
100
50
[ppm]

E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7
7
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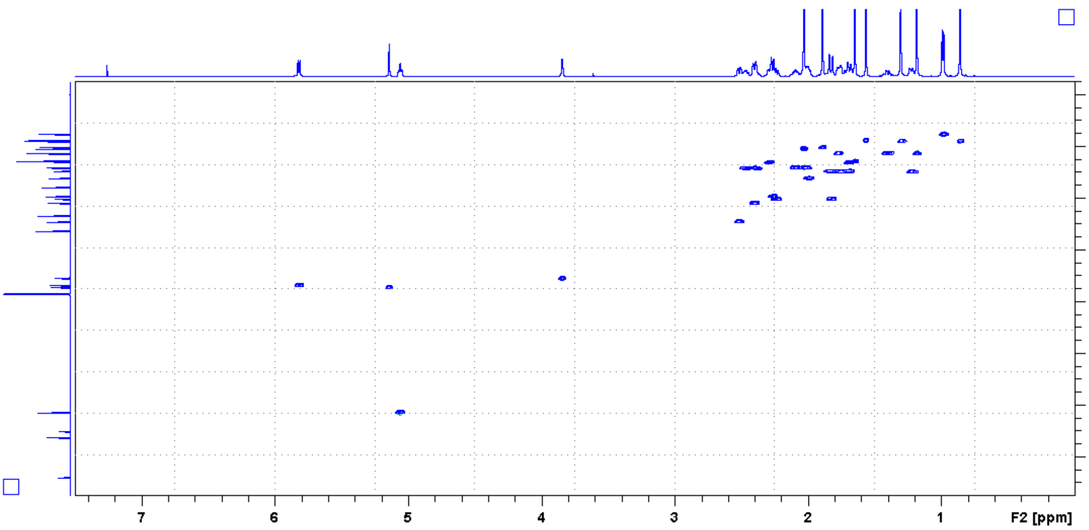
5
4
3
2
F2 [ppm]

F


F1 [ppm]
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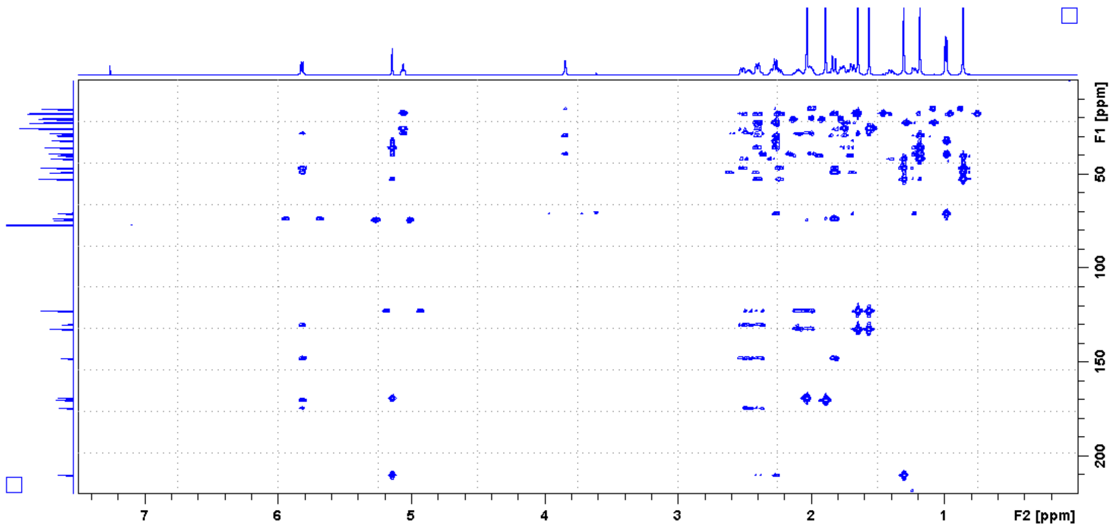
1
F2 [ppm]

G



H

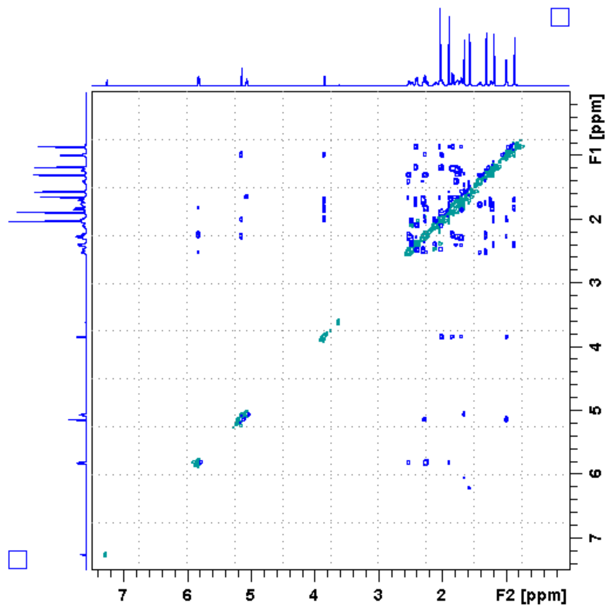
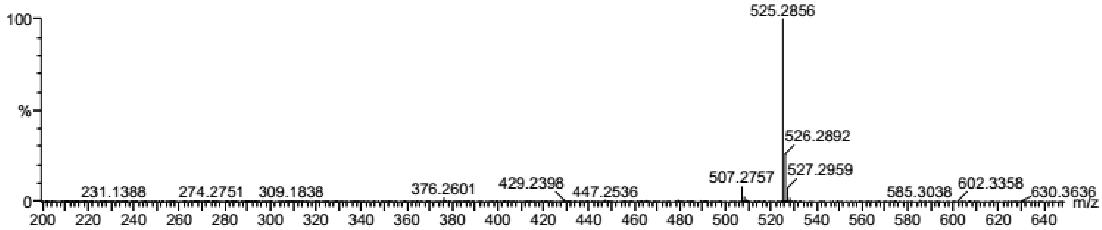


Figure S51 HRESIMS and NMR spectra of **60**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 600 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 150 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in $CDCl_3$ at 600 MHz; (F) HSQC spectrum in $CDCl_3$ at 600 MHz; (G) HMBC spectrum in $CDCl_3$ at 600 MHz; (H) ROESY spectrum in $CDCl_3$ at 600 MHz.

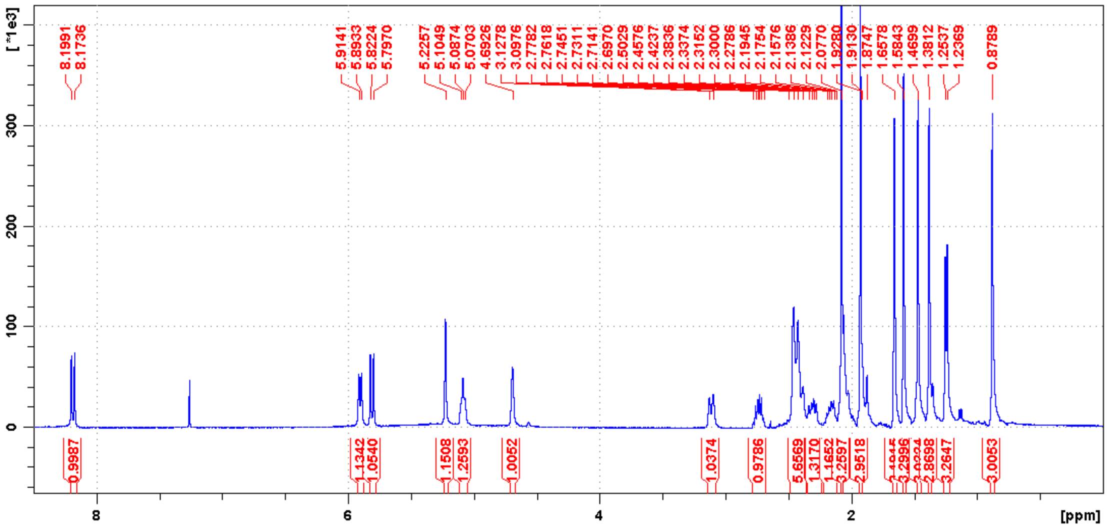
A

Monoisotopic Mass, Even Electron Ions
315 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
EB1-B3D1-5
20180423-45 207 (1.672)

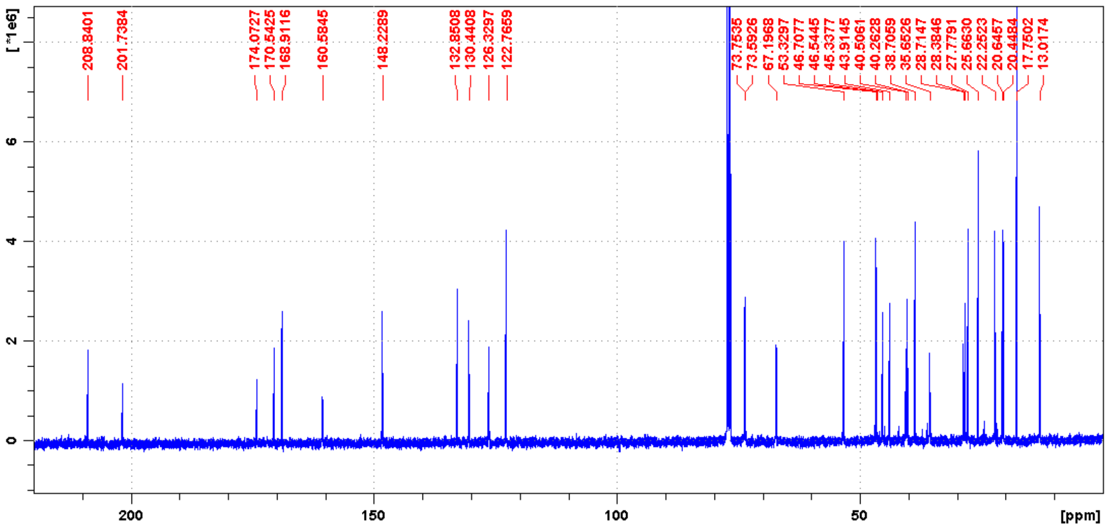


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
585.3038	585.3064	-2.6	-4.4	11.5	24.7	0.903	40.54	C33 H45 O9
	585.3040	-0.2	-0.3	8.5	24.4	0.520	59.46	C31 H46 O9 Na

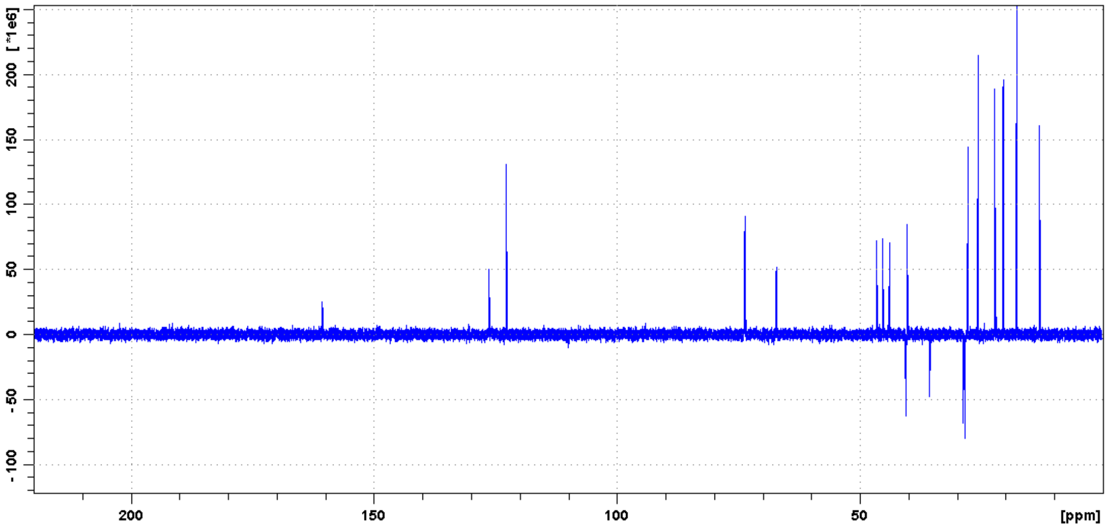
B



C



D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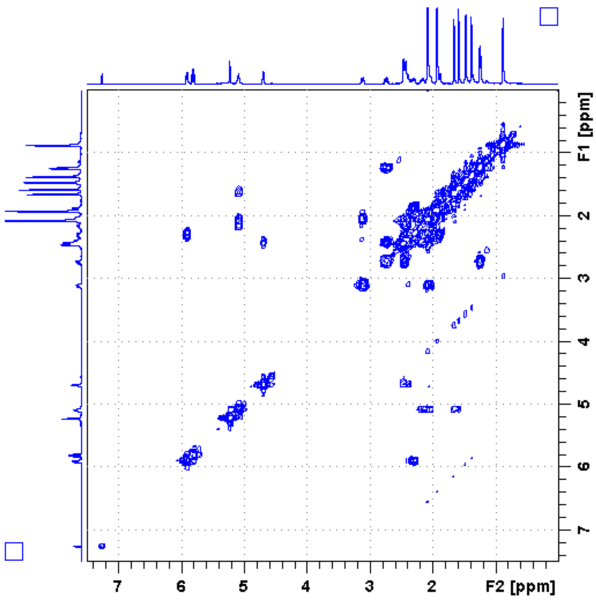
0
-50
-100
200
150
100
50
[ppm]

E


F1 [ppm]
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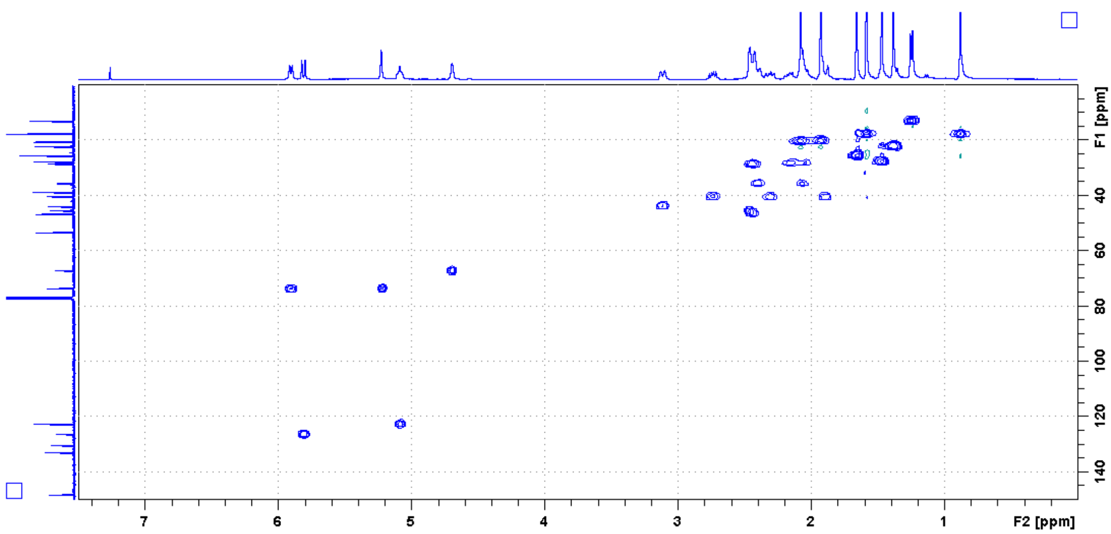
7
7
6
5
4
3
2
F2 [ppm]

F


F1 [ppm]
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80
100
120
140
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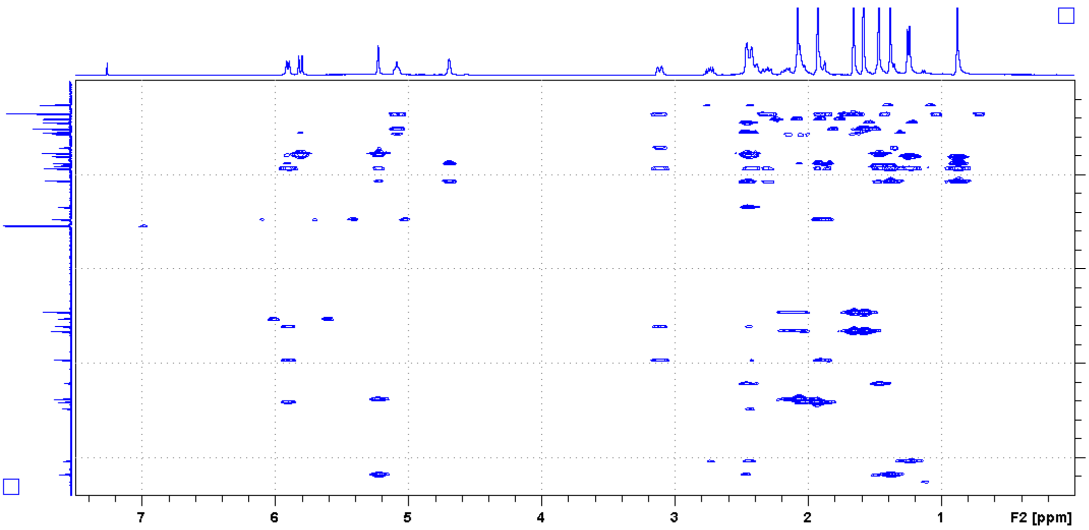
6
5
4
3
2
1
F2 [ppm]

G



H

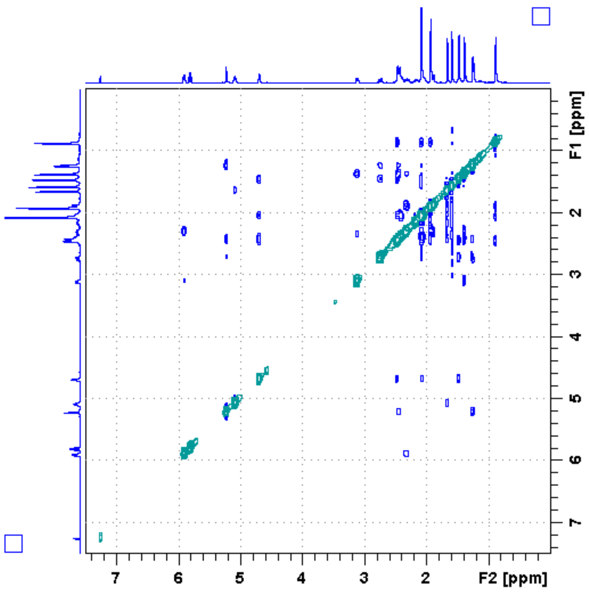
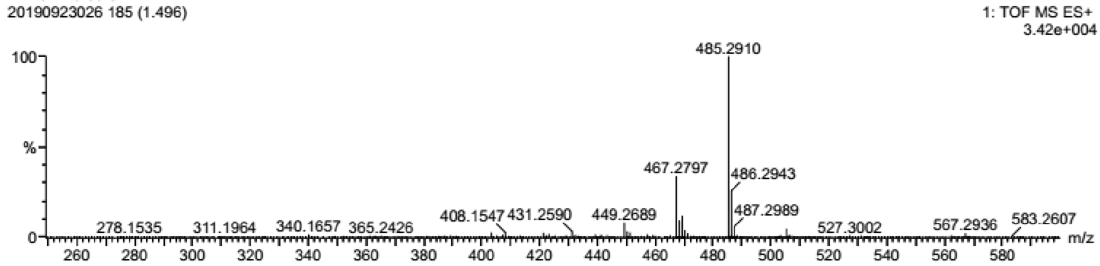


Figure S52 HRESIMS and NMR spectra of **61**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 400 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 100 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 100 MHz; (E) ^{1}H–^{1}H COSY spectrum in $CDCl_3$ at 400 MHz; (F) HSQC spectrum in $CDCl_3$ at 400 MHz; (G) HMBC spectrum in $CDCl_3$ at 400 MHz; (H) ROESY spectrum in $CDCl_3$ at 400 MHz.

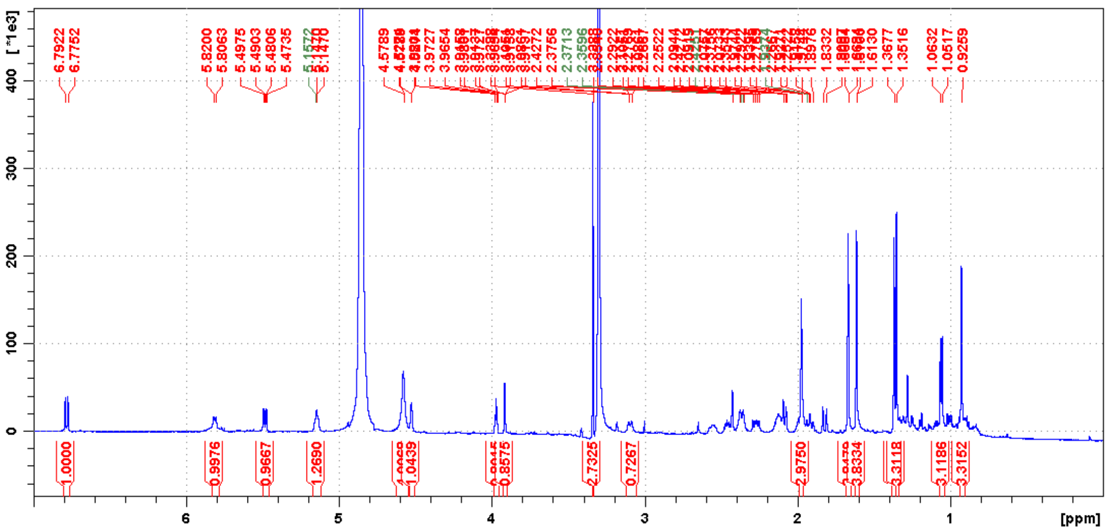
A

Monoisotopic Mass, Even Electron Ions
310 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
EB1C1-B3-80-3
20190923026 185 (1.496)

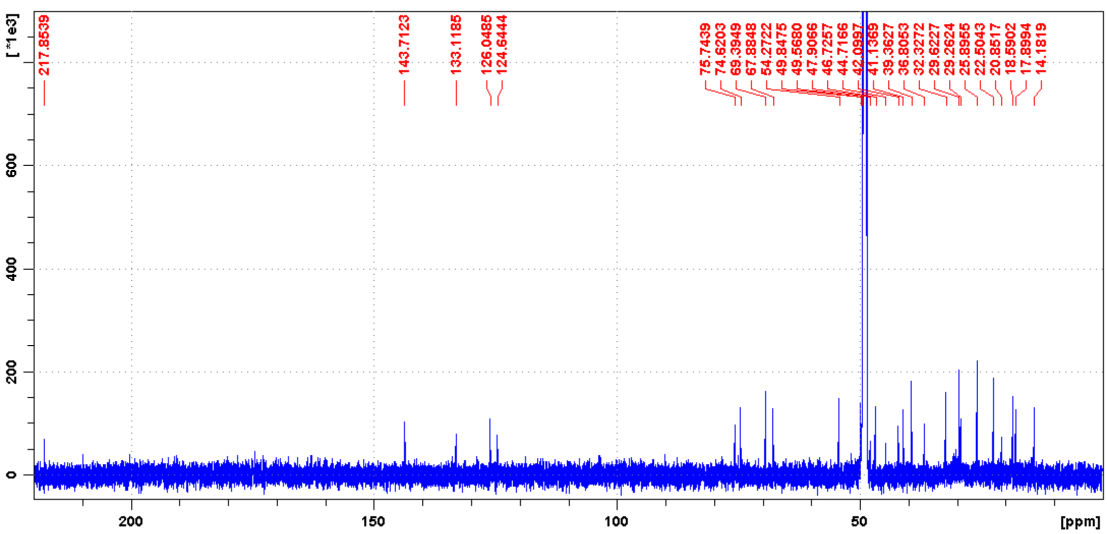


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
567.2936	567.2934	0.2	0.4	9.5	84.2	0.173	84.08	C31 H44 O8 Na
	567.2958	-2.2	-3.9	12.5	85.9	1.838	15.92	C33 H43 O8

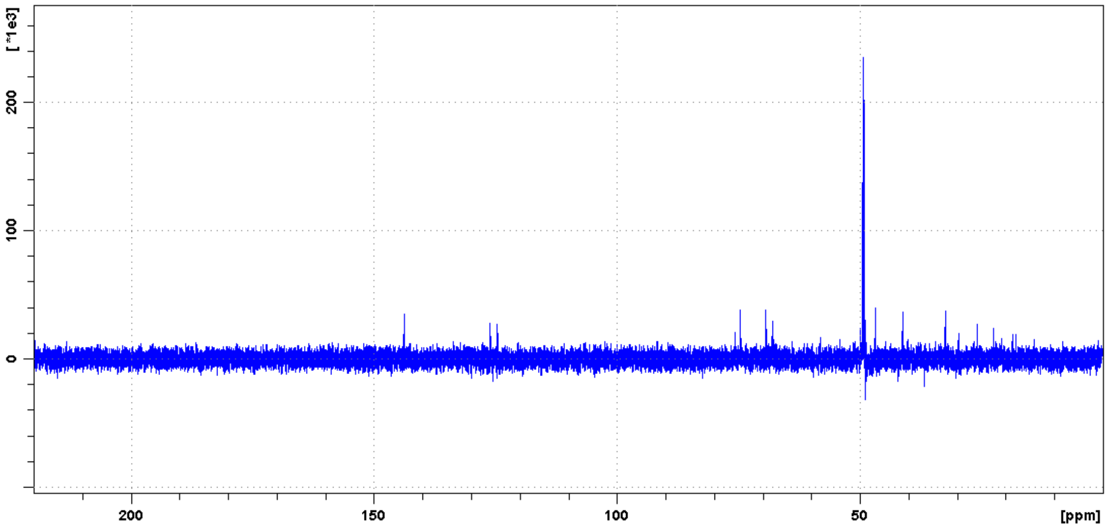
B



C



D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200
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100
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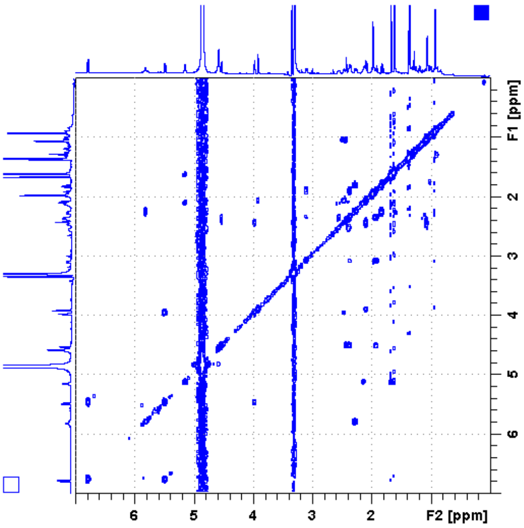
[ppm]

E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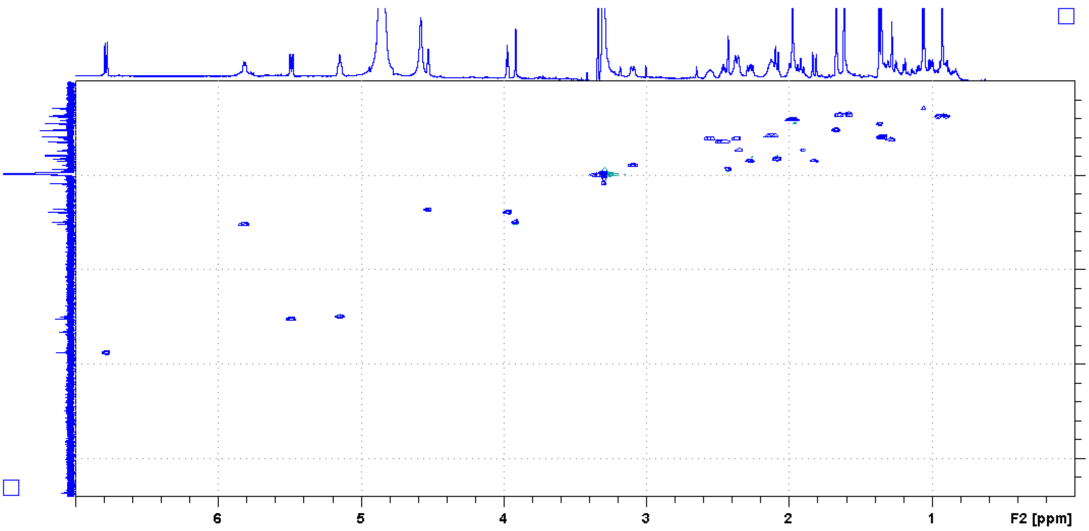
2
F2 [ppm]

F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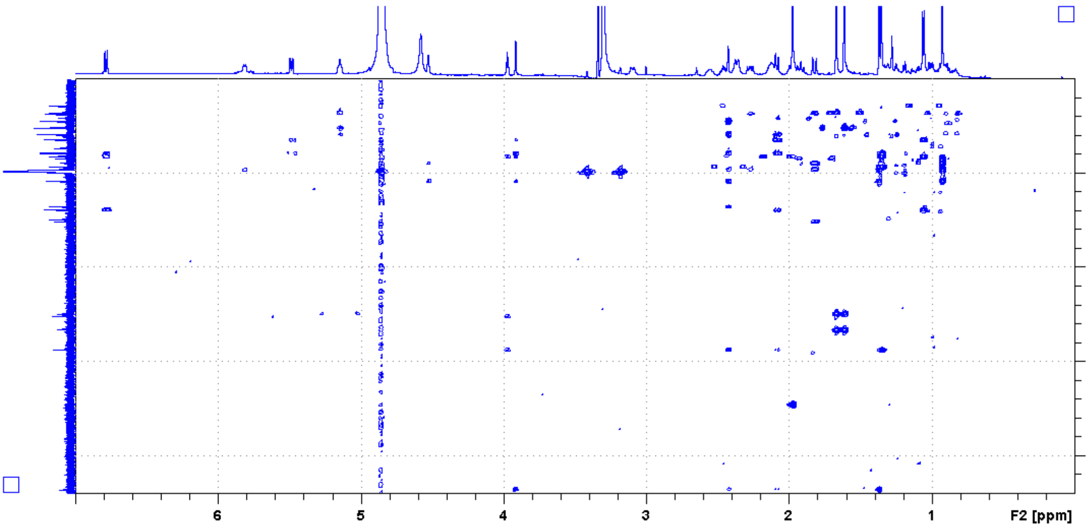
150
200
6
5
4
3
2
1
F2 [ppm]

G



H

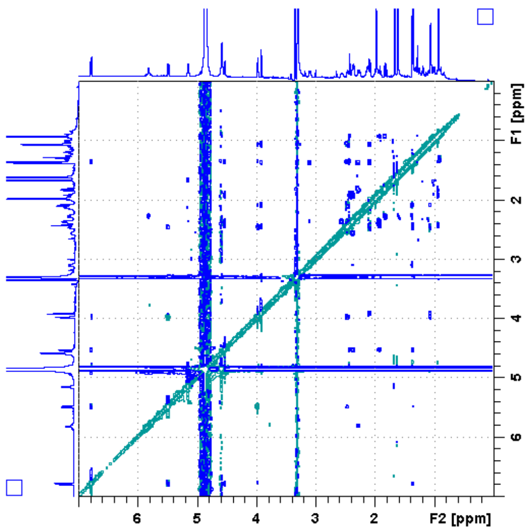
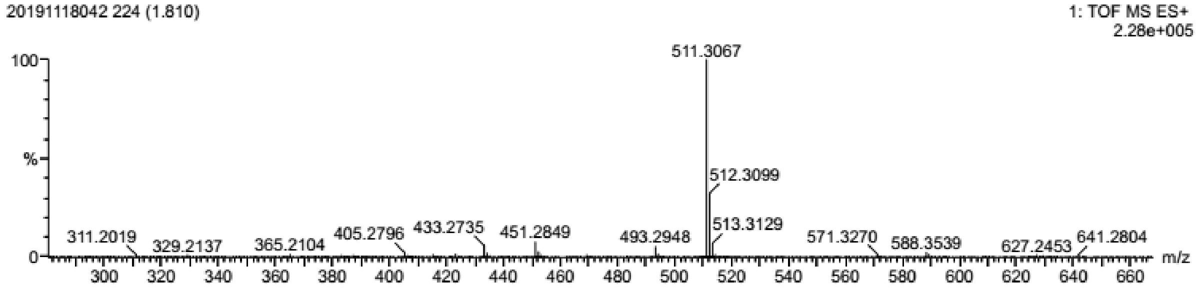


Figure S53 HRESIMS and NMR spectra of **62**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in CD_3OD at 600 MHz; (C) ^{13}C NMR spectrum in CD_3OD at 150 MHz; (D) DEPT 135 spectrum in CD_3OD at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in CD_3OD at 600 MHz; (F) HSQC spectrum in CD_3OD at 600 MHz; (G) HMBC spectrum in CD_3OD at 600 MHz; (H) ROESY spectrum in CD_3OD at 600 MHz.

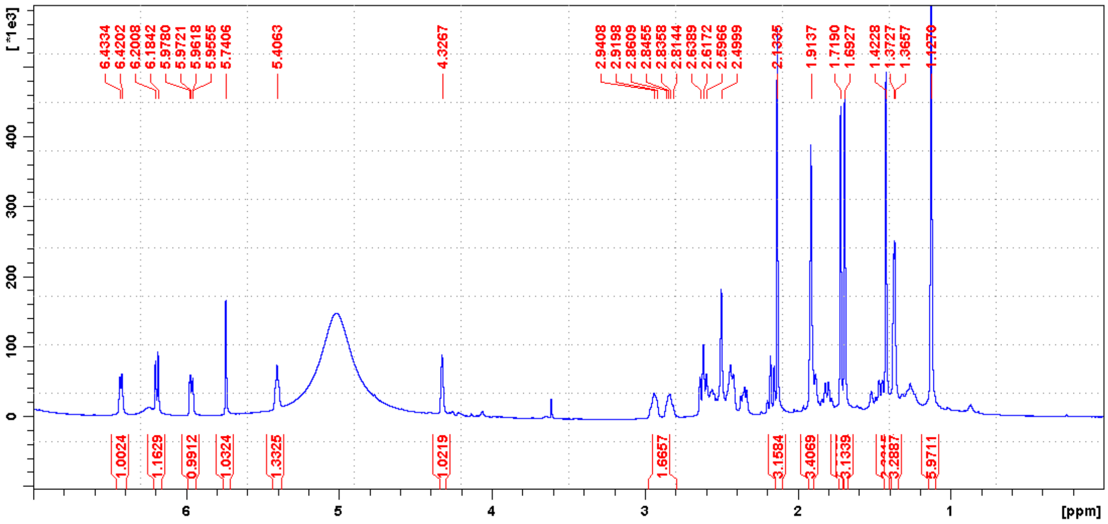
A

Monoisotopic Mass, Even Electron Ions
313 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-200 H: 0-1000 O: 0-200 Na: 0-1
EB4C1D2-80-1
20191118042 224 (1.810)

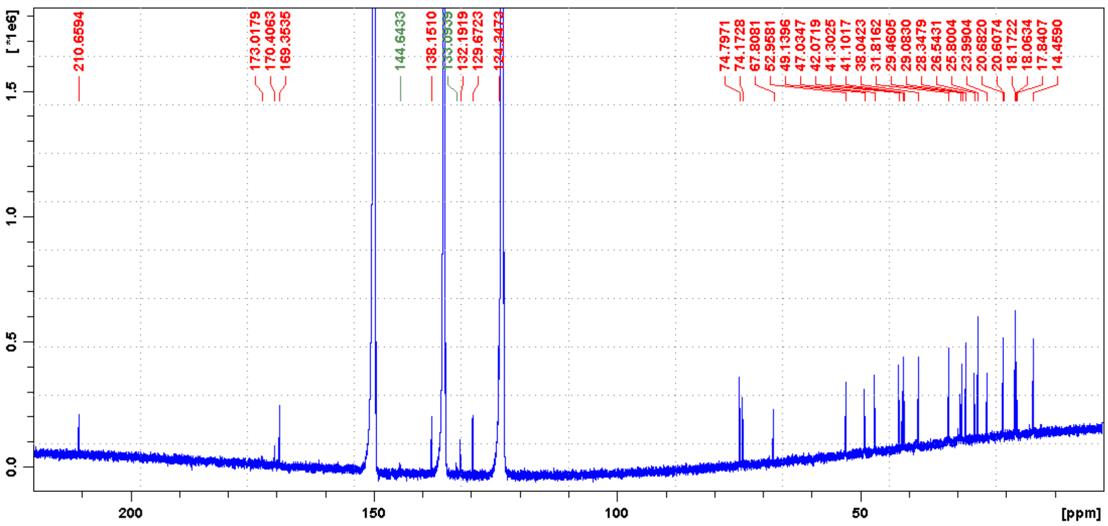


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
571.3270	571.3271	-0.1	-0.2	10.5	73.4	1.369	25.45	C33 H47 O8
	571.3247	2.3	4.0	7.5	72.3	0.294	74.55	C31 H48 O8 Na

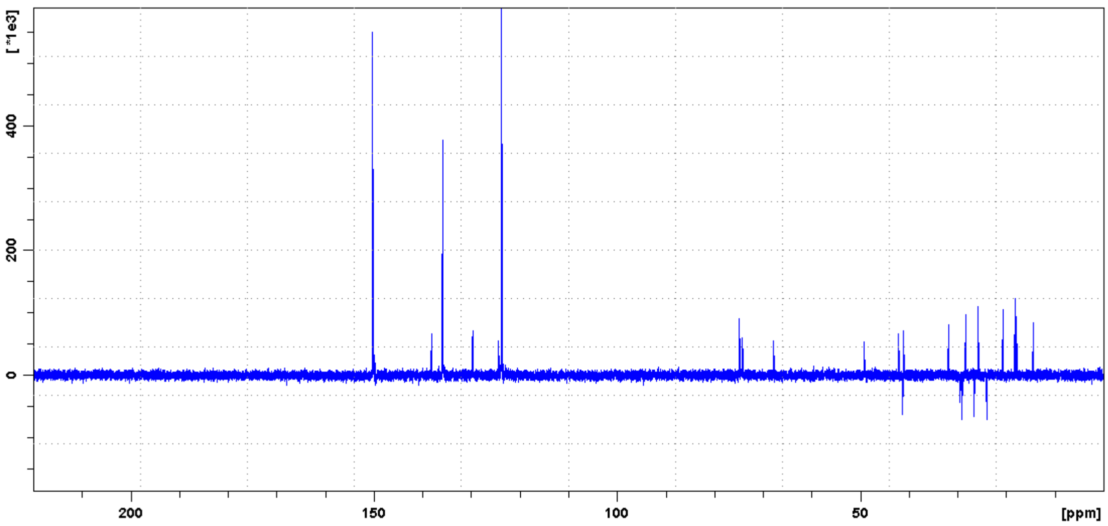
B



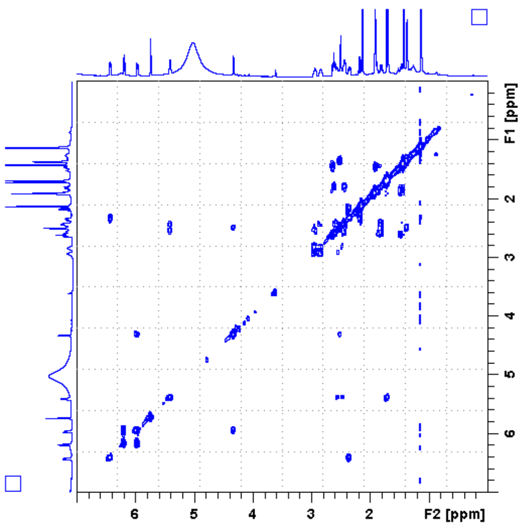
C



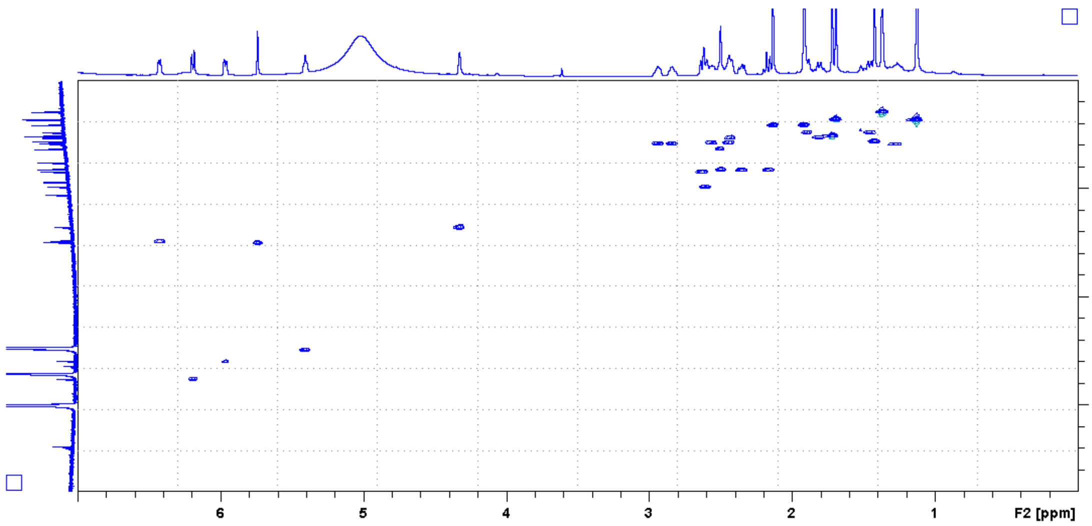
D



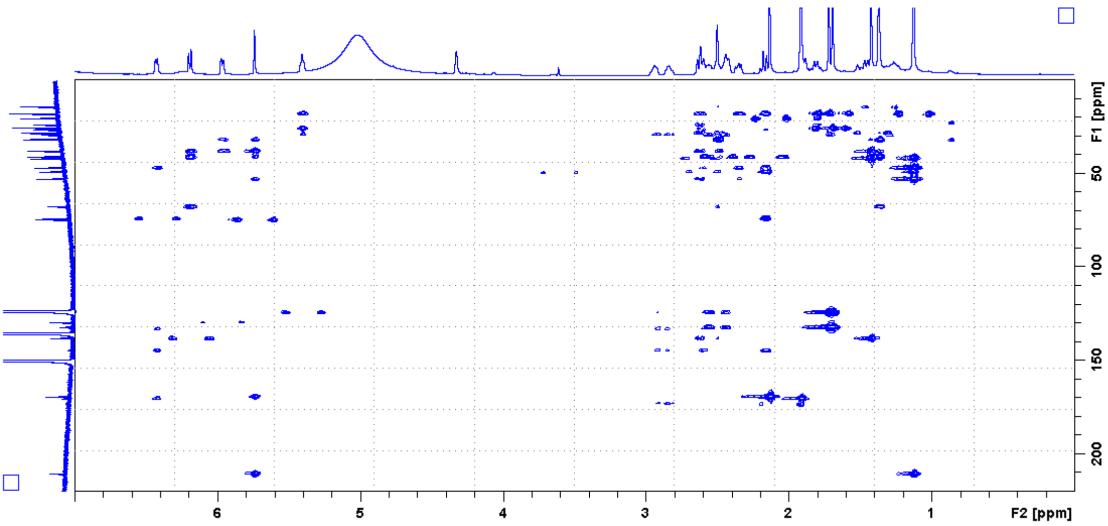
E



F



G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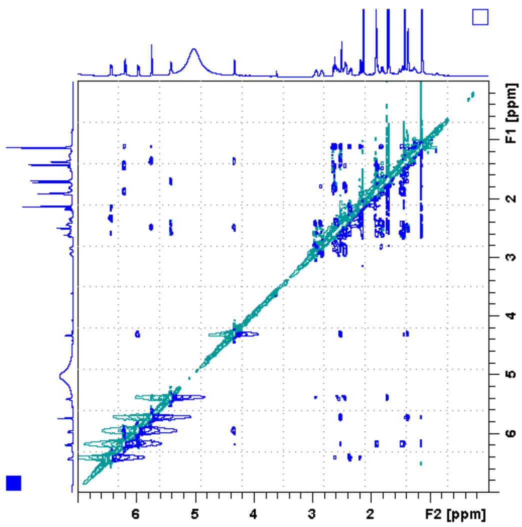
F2 [ppm]

H


F1 [ppm]
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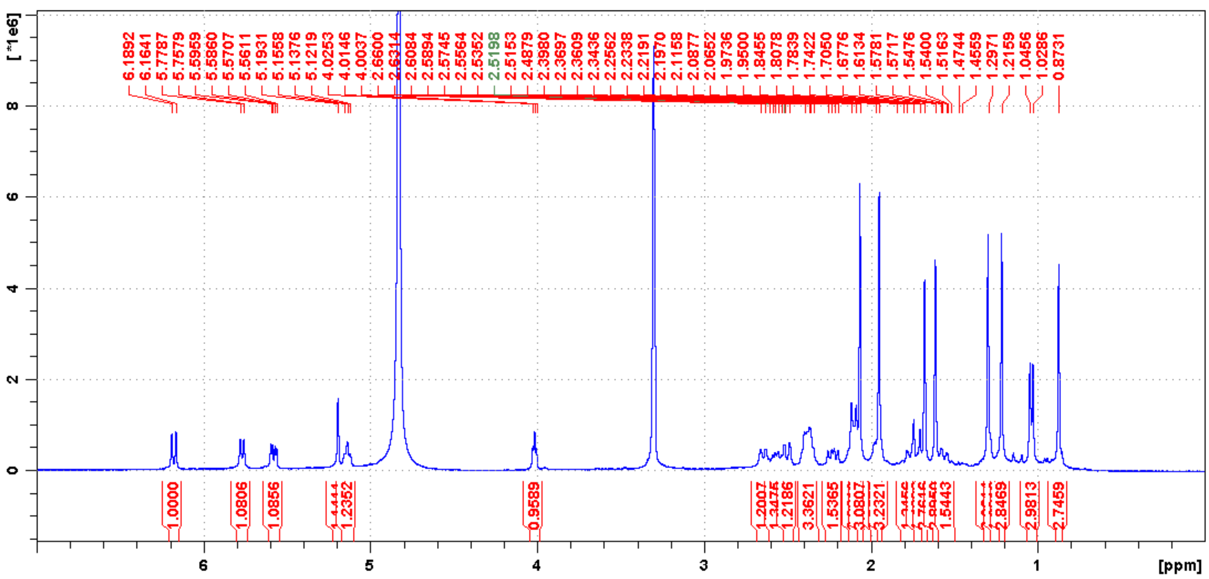
6
5
4
3
2
F2 [ppm]

I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5.1931
5.1558
5.1376
5.1219
4.0253
4.0146
4.0037
2.6600
2.6314
2.6084
2.5894
2.5745
2.5564
2.5352
2.5198
2.5153
2.4879
2.3980
2.3697
2.3609
2.3436
2.2562
2.2338
2.2191
2.1970
2.1158
2.0877
2.0652
1.9736
1.9500
1.8455
1.8078
1.7839
1.7422
1.7050
1.6776
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1.5717
1.5476
1.5400
1.5163
1.4744
1.4559
1.2971
1.2159
1.0456
1.0286
0.8731
1.0000
1.0806
1.0856
1.2352
0.9589
1.2007
1.2186
3.3621
1.5365
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1.5443
2.8469
2.9813
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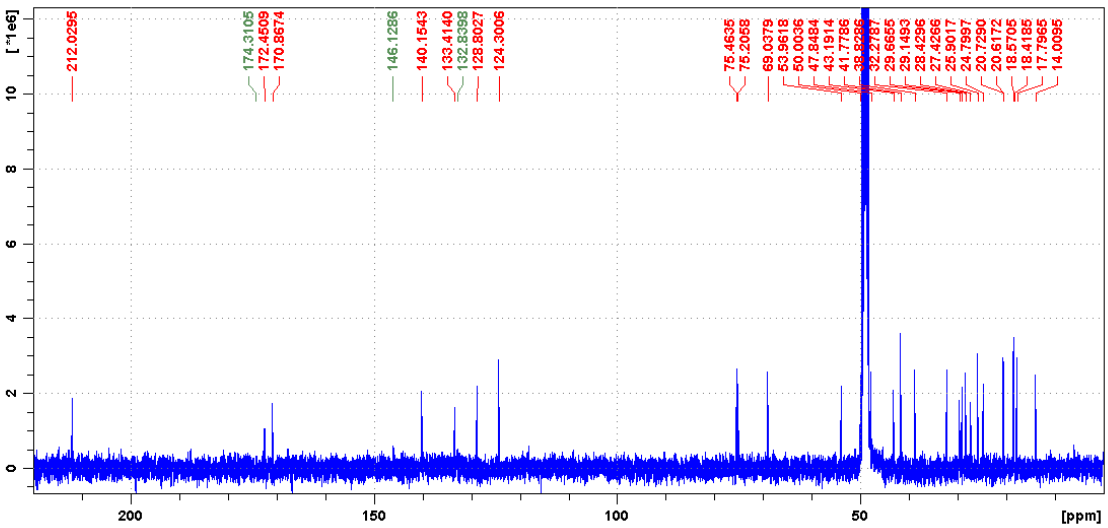
[ppm]

J



K

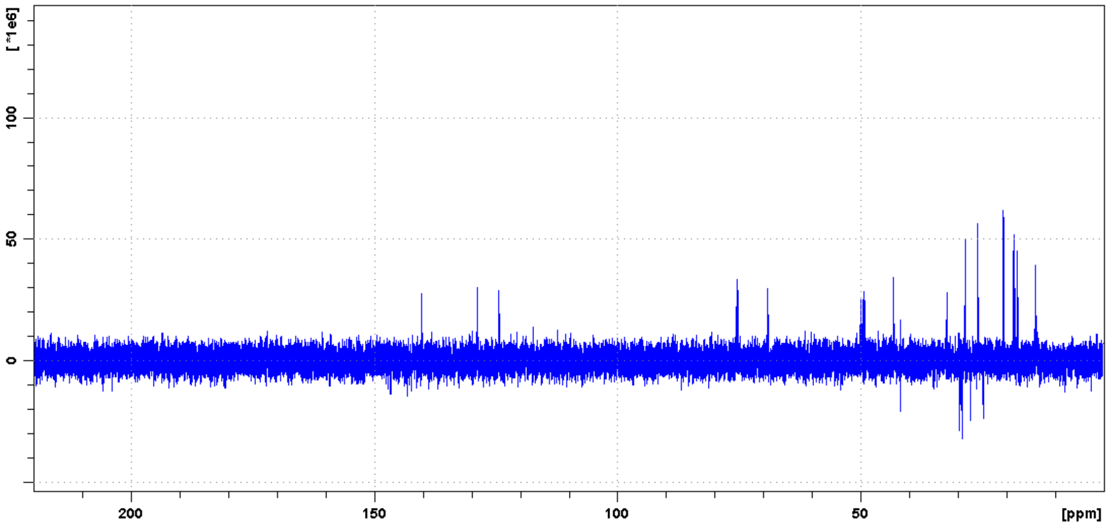
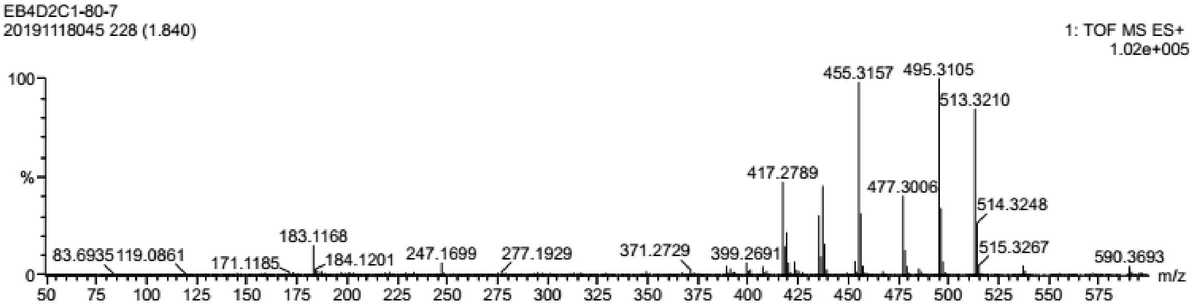


Figure S54 HRESIMS and NMR spectra of **63**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in pyridine-d_5 at 600 MHz; (C) ^{13}C NMR spectrum in pyridine-d_5 at 150 MHz; (D) DEPT 135 spectrum in pyridine-d_5 at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in pyridine-d_5 at 600 MHz; (F) HSQC spectrum in pyridine-d_5 at 600 MHz; (G) HMBC spectrum in pyridine-d_5 at 600 MHz; (H) ROESY spectrum in pyridine-d_5 at 600 MHz; (I) ^{1}H NMR spectrum in CD_3OD at 400 MHz; (J) ^{13}C NMR spectrum in CD_3OD at 100 MHz; (K) DEPT 135 spectrum in CD_3OD at 100 MHz.

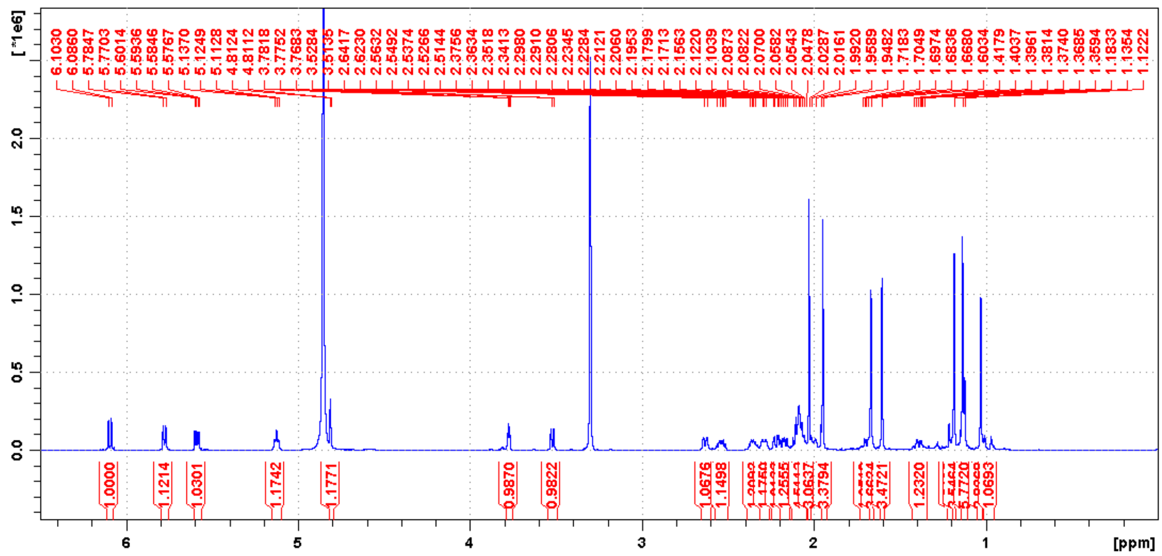
A

Monoisotopic Mass, Even Electron Ions
248 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
EB4D2C1-80-7
20191118045 228 (1.840)

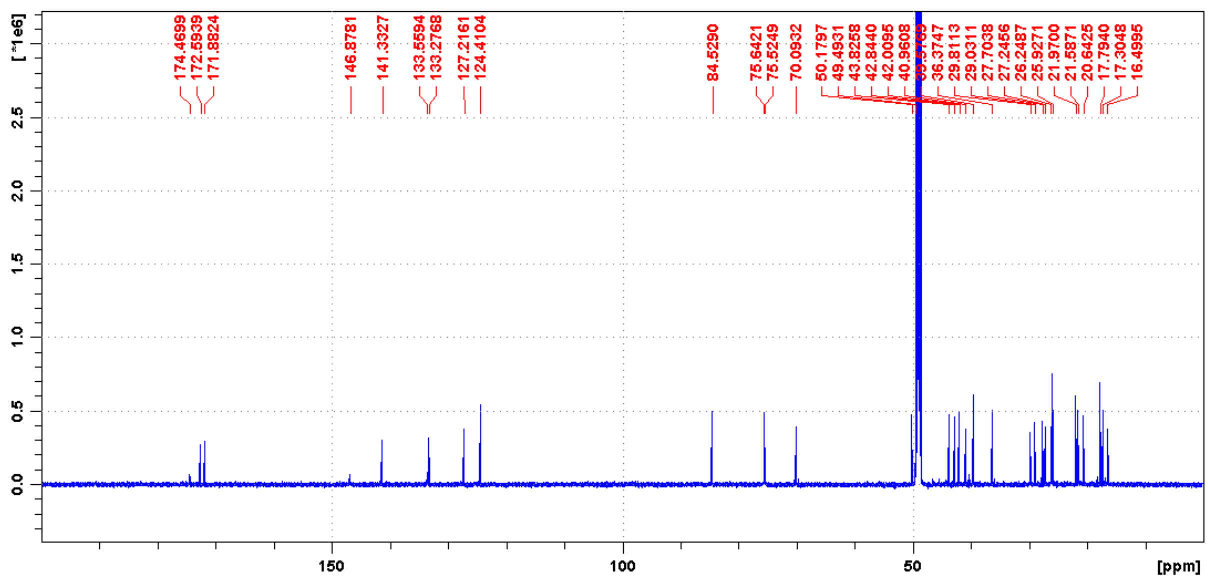


Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
513.3210	513.3216	-0.6	-1.2	9.5	264.4	2.362	9.42	C31 H45 O6
	513.3192	1.8	3.5	6.5	262.2	0.099	90.58	C29 H46 O6 Na

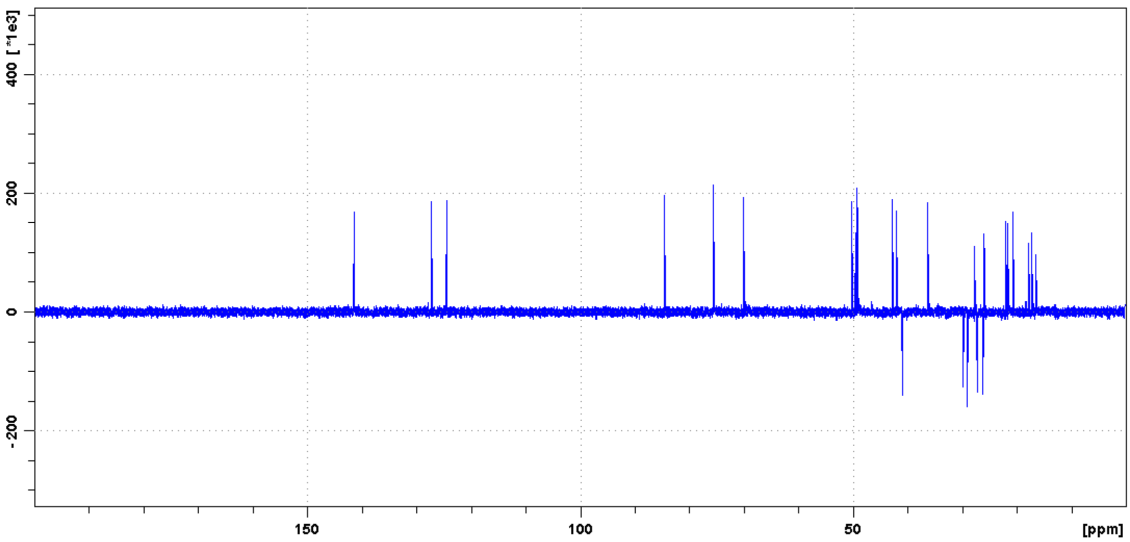
B



C



D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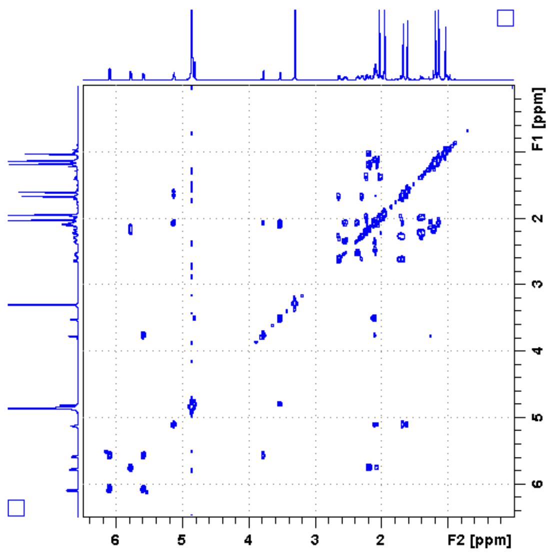
[ppm]

E


F1 [ppm]
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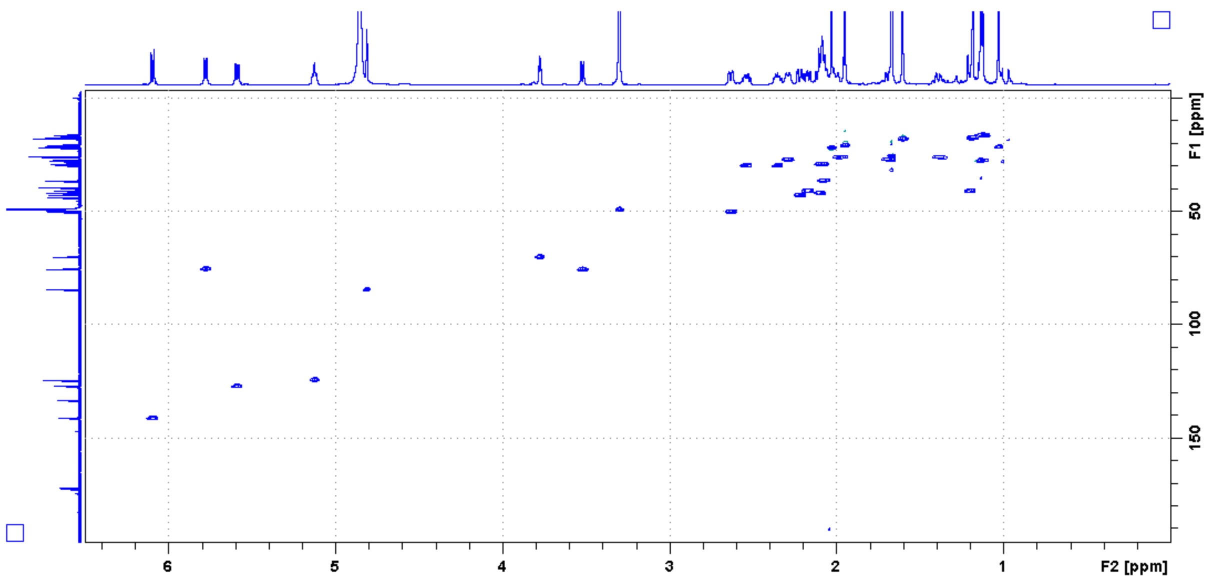
6
F2 [ppm]

F


F1 [ppm]
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150
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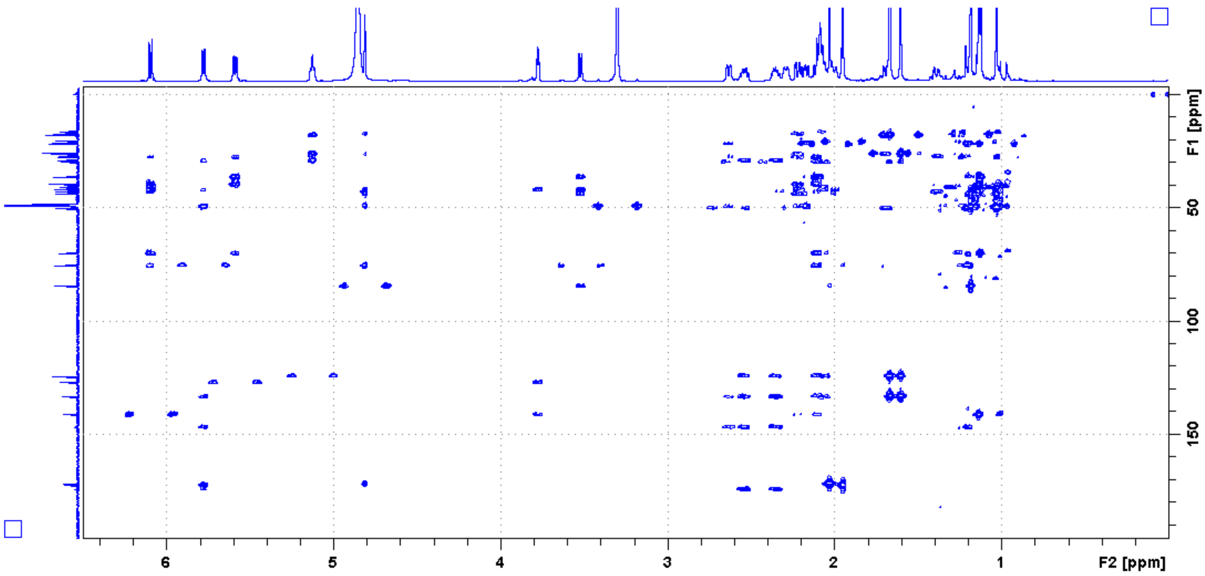
5
4
3
2
1
F2 [ppm]

G



H

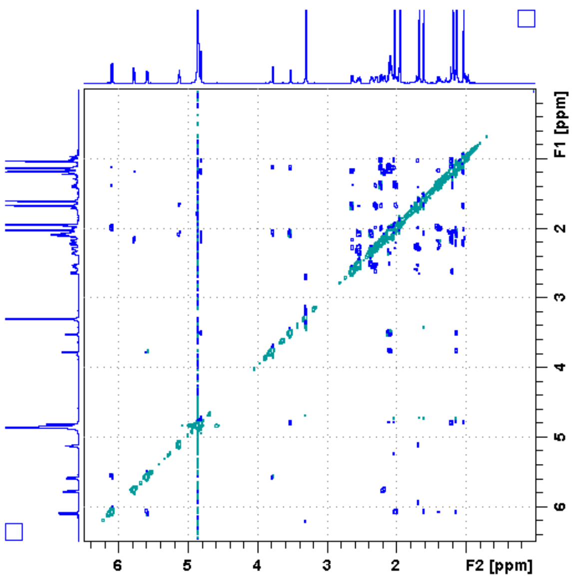
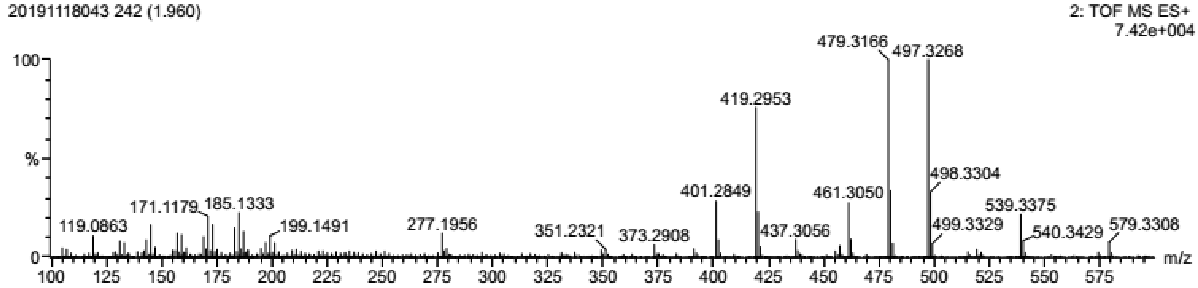


Figure S55 HRESIMS and NMR spectra of **64**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in CD_3OD at 600 MHz; (C) ^{13}C NMR spectrum in CD_3OD at 150 MHz; (D) DEPT 135 spectrum in CD_3OD at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in CD_3OD at 600 MHz; (F) HSQC spectrum in CD_3OD at 600 MHz; (G) HMBC spectrum in CD_3OD at 600 MHz; (H) ROESY spectrum in CD_3OD at 600 MHz.

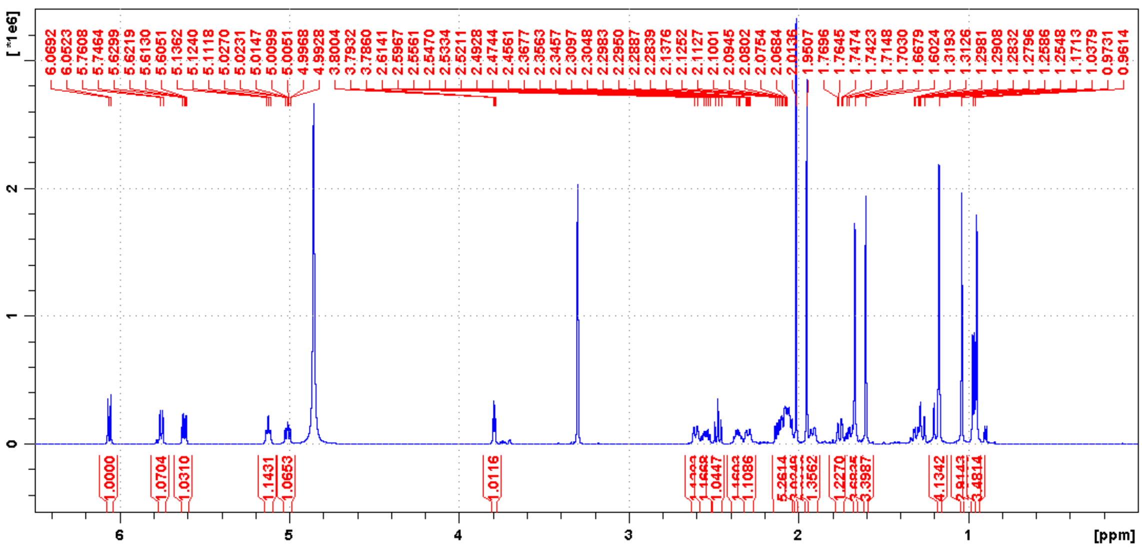
A

Monoisotopic Mass, Even Electron Ions
321 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
EB4C1D2-80-8
20191118043 242 (1.960)

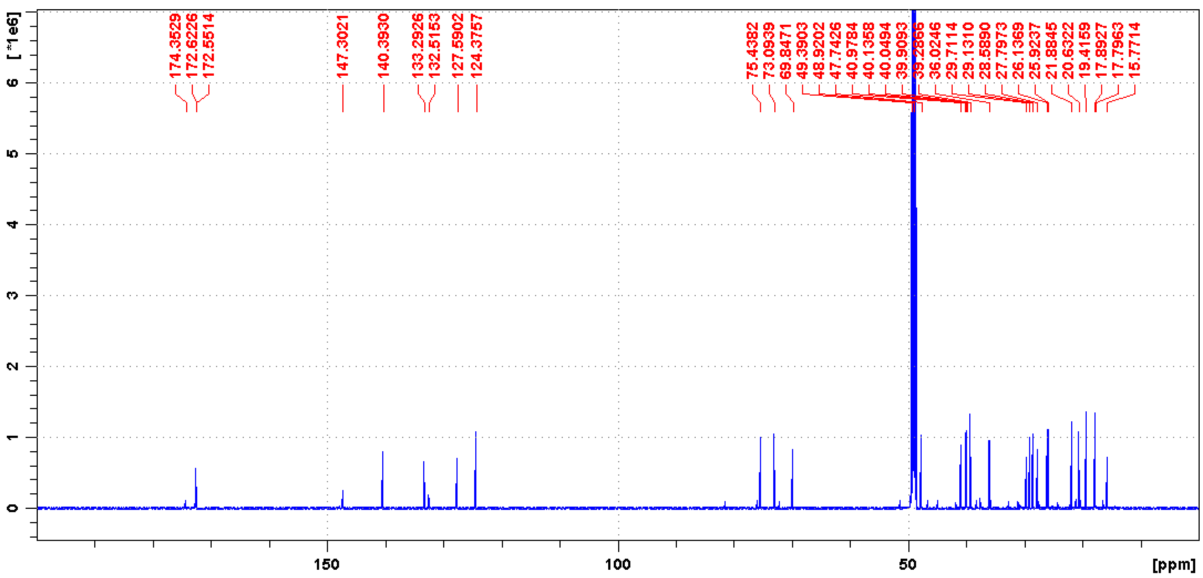


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
579.3308	579.3298	1.0	1.7	9.5	78.9	0.592	55.33	C33 H48 O7 Na
	579.3322	-1.4	-2.4	12.5	79.1	0.806	44.67	C35 H47 O7

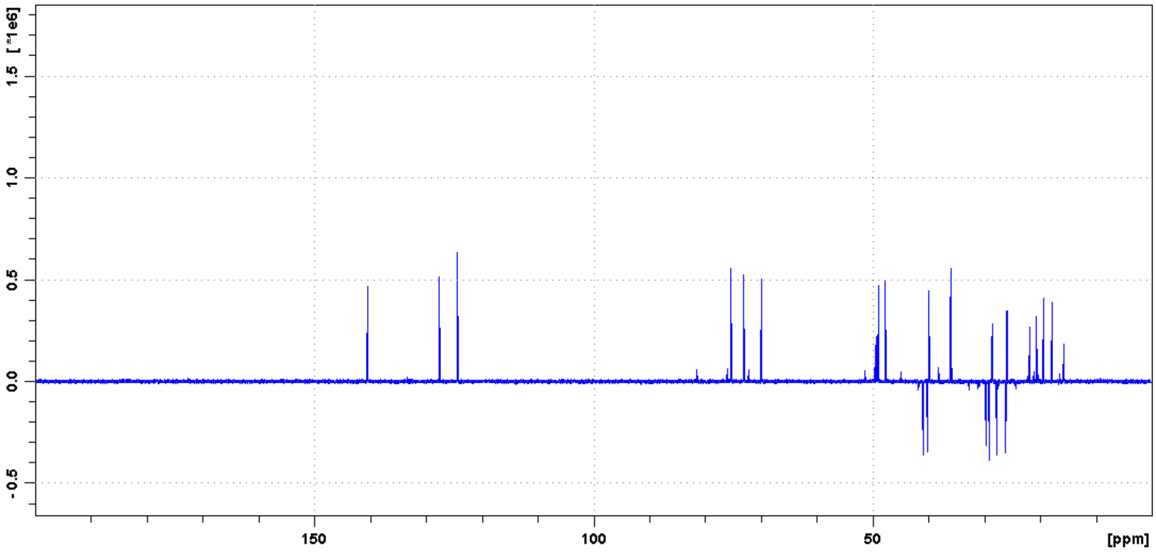
B



C



D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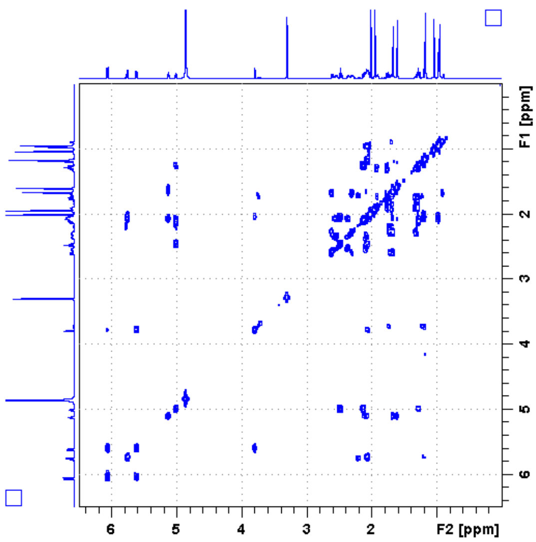
[ppm]

E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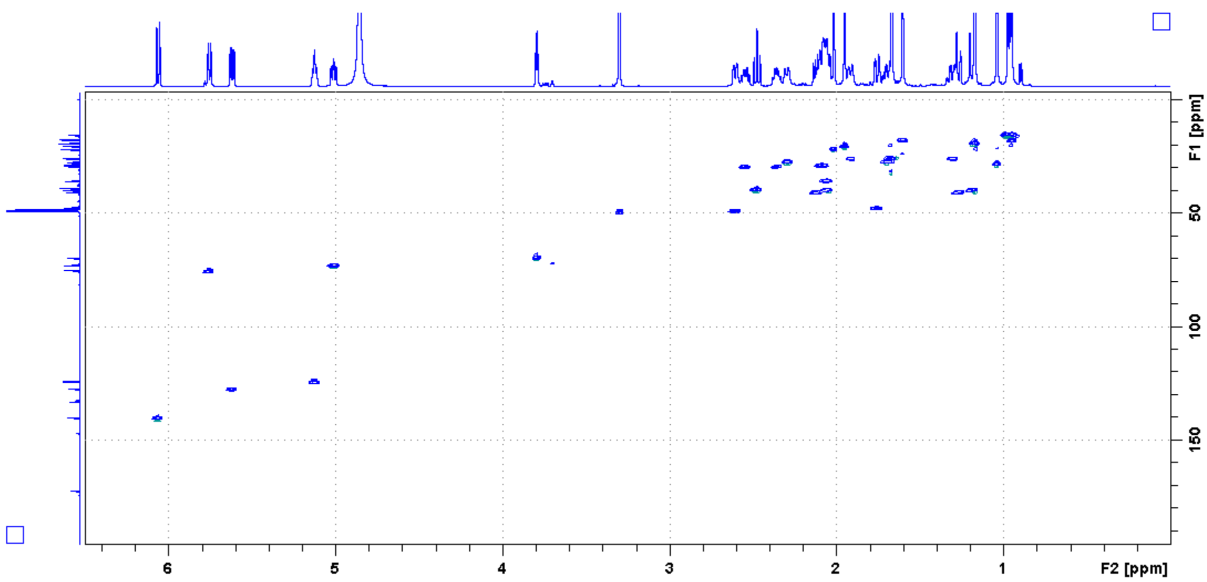
3
2
F2 [ppm]

F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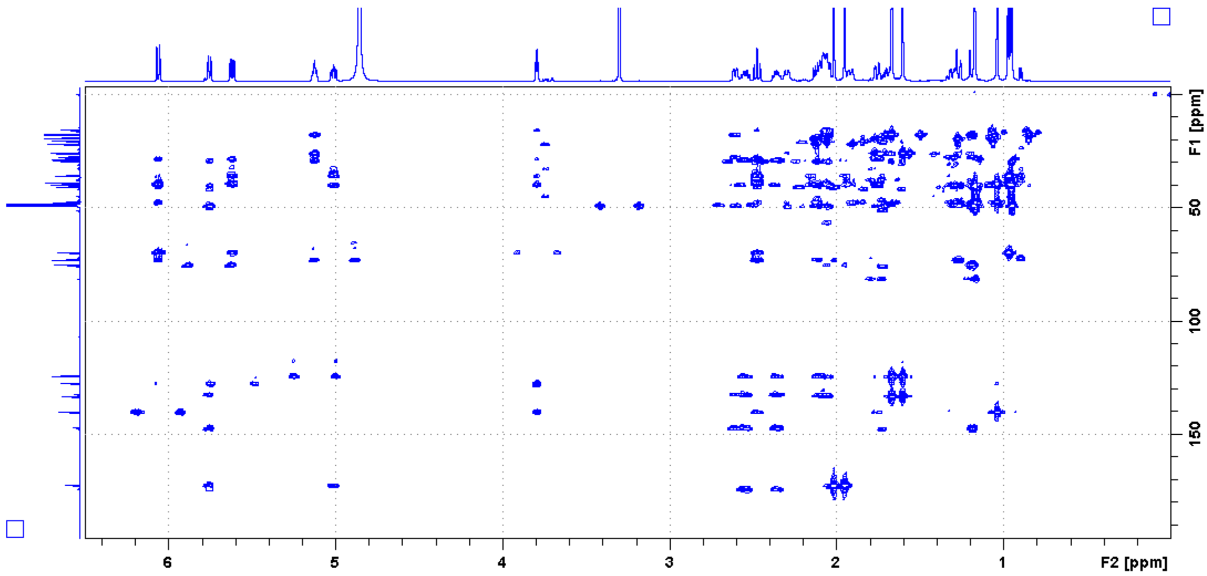
F2 [ppm]

G



H

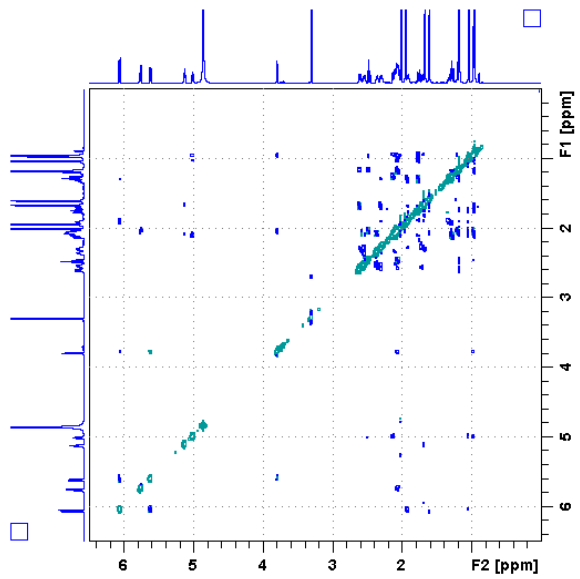
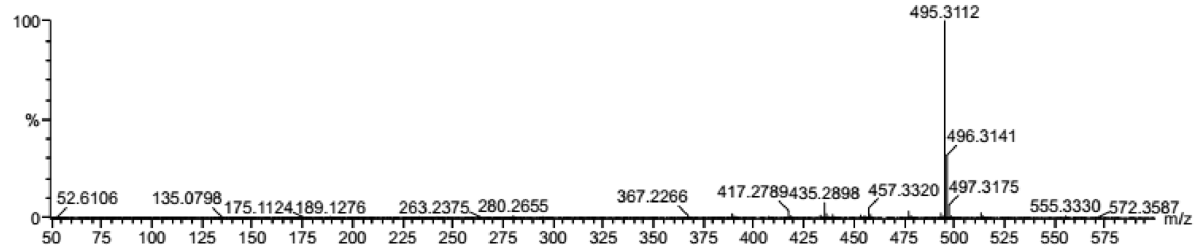


Figure S56 HRESIMS and NMR spectra of **65**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in CD_3OD at 600 MHz; (C) ^{13}C NMR spectrum in CD_3OD at 150 MHz; (D) DEPT 135 spectrum in CD_3OD at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in CD_3OD at 600 MHz; (F) HSQC spectrum in CD_3OD at 600 MHz; (G) HMBC spectrum in CD_3OD at 600 MHz; (H) ROESY spectrum in CD_3OD at 600 MHz.

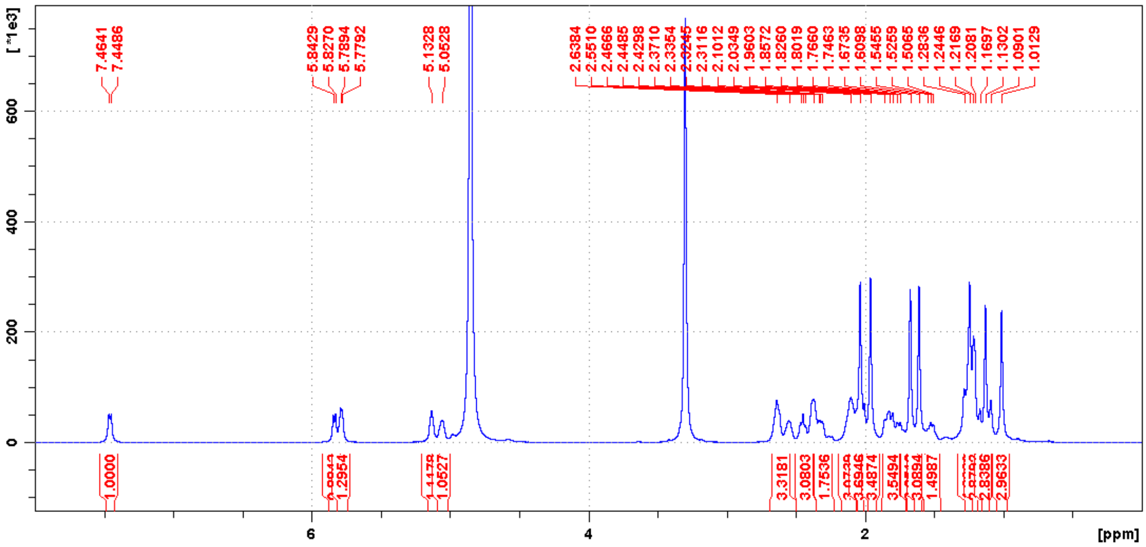
A

Monoisotopic Mass, Even Electron Ions
298 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-200 H: 0-1000 O: 0-200 Na: 0-1
EB4C1D2-80-6
20191118044 248 (2.001)

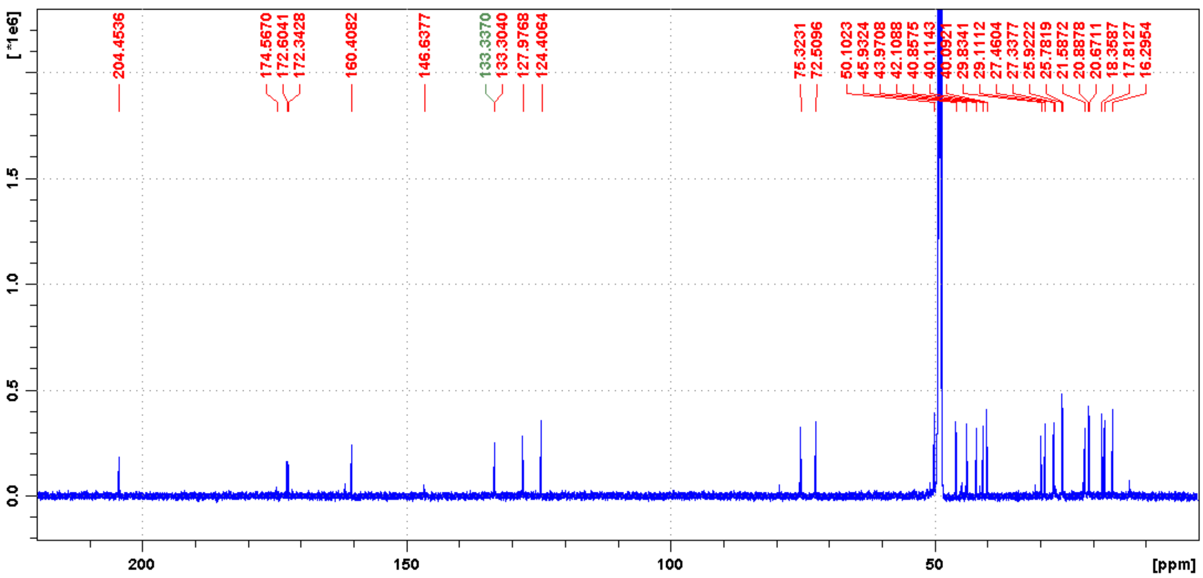


Minimum:				-1.5					
Maximum:		5.0	5.0	50.0					
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula	
555.3330	555.3322	0.8	1.4	10.5	88.0	0.161	85.09	C33 H47 O7	
	555.3356	-2.6	-4.7	-1.5	89.8	1.903	14.91	C24 H52 O12 Na	

B



C



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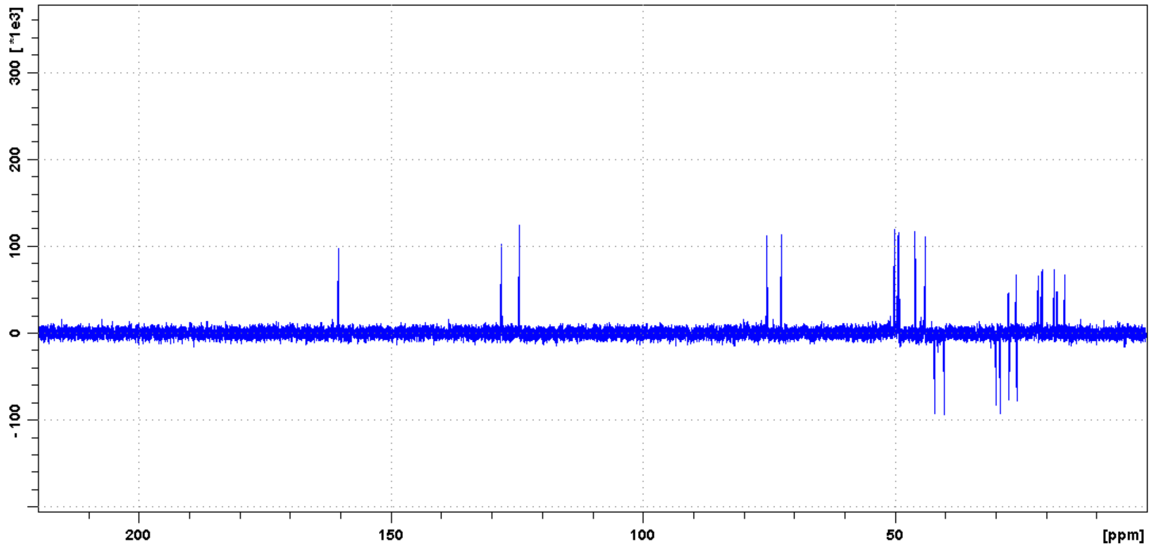
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0
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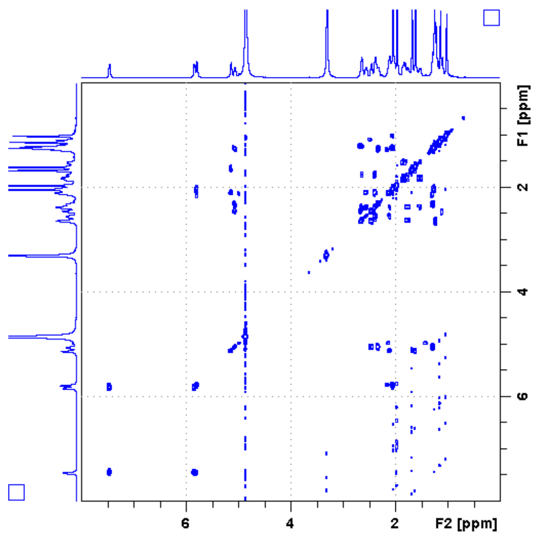
200
150
100
50
[ppm]

E


F1 [ppm]
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6
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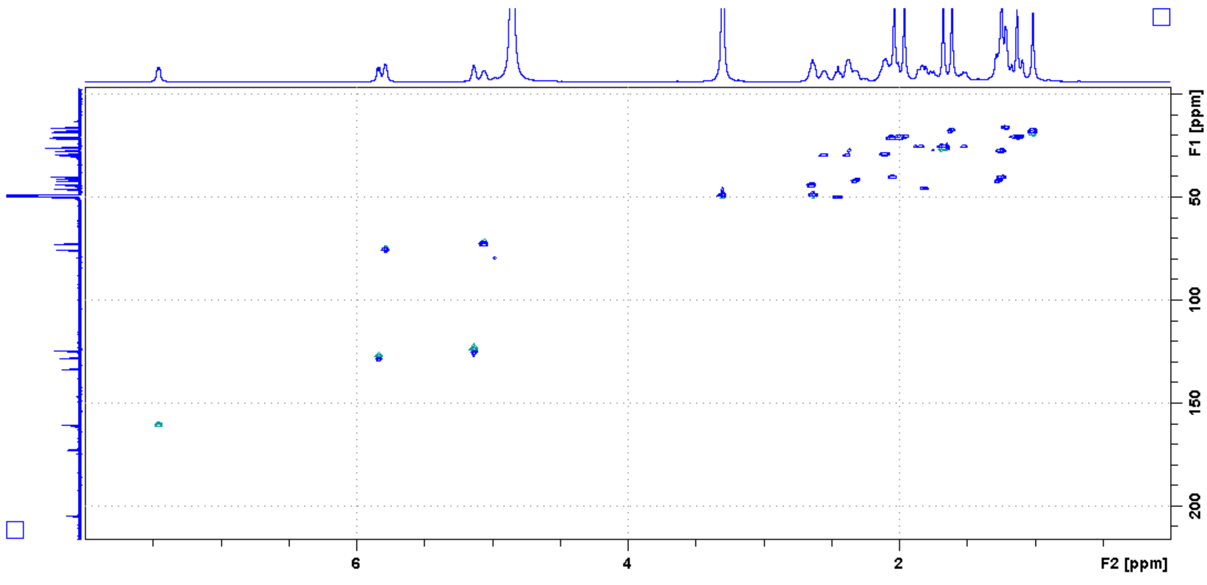
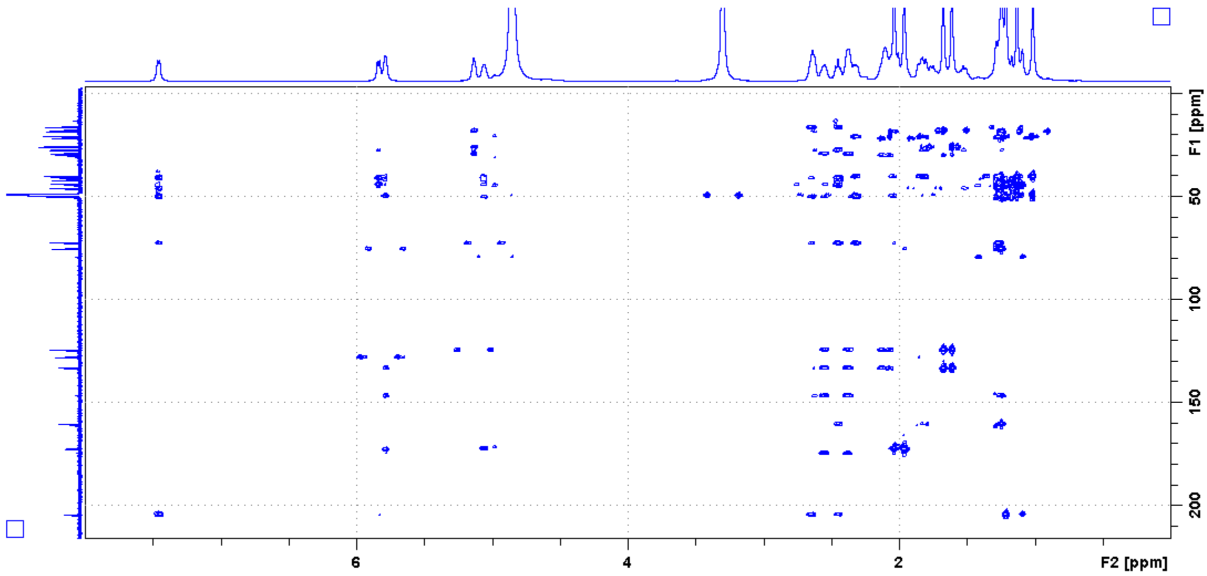
4
2
F2 [ppm]

F


F1 [ppm]
50
100
150
200
6
4
2
F2 [ppm]

G



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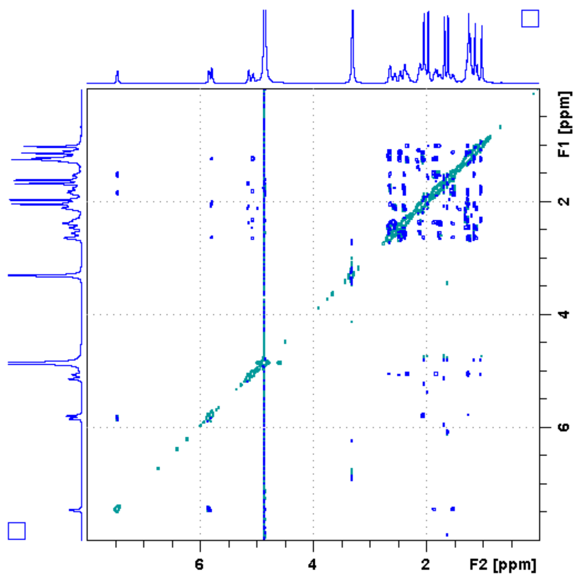
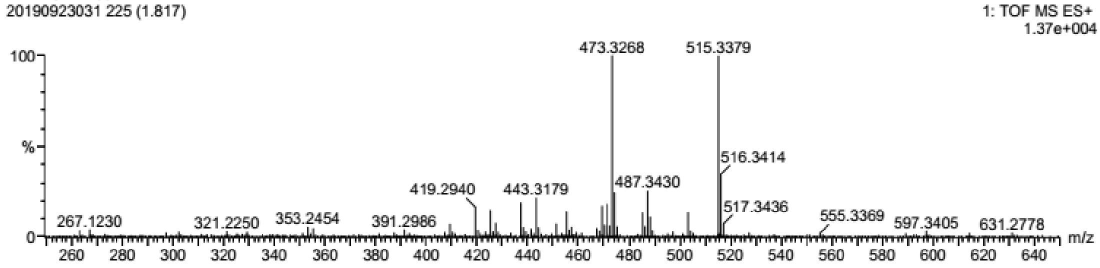


Figure S57 HRESIMS and NMR spectra of **66**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in CD_3OD at 600 MHz; (C) ^{13}C NMR spectrum in CD_3OD at 150 MHz; (D) DEPT 135 spectrum in CD_3OD at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in CD_3OD at 600 MHz; (F) HSQC spectrum in CD_3OD at 600 MHz; (G) HMBC spectrum in CD_3OD at 600 MHz; (H) ROESY spectrum in CD_3OD at 600 MHz.

A

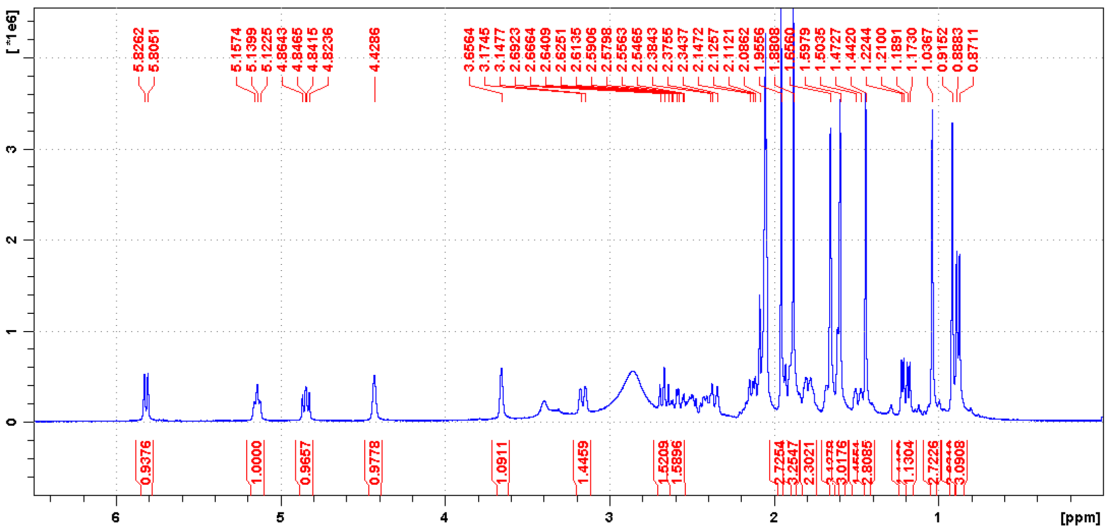
Monoisotopic Mass, Even Electron Ions
328 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
B1B4-C1D2-80-2
20190923031 225 (1.817)



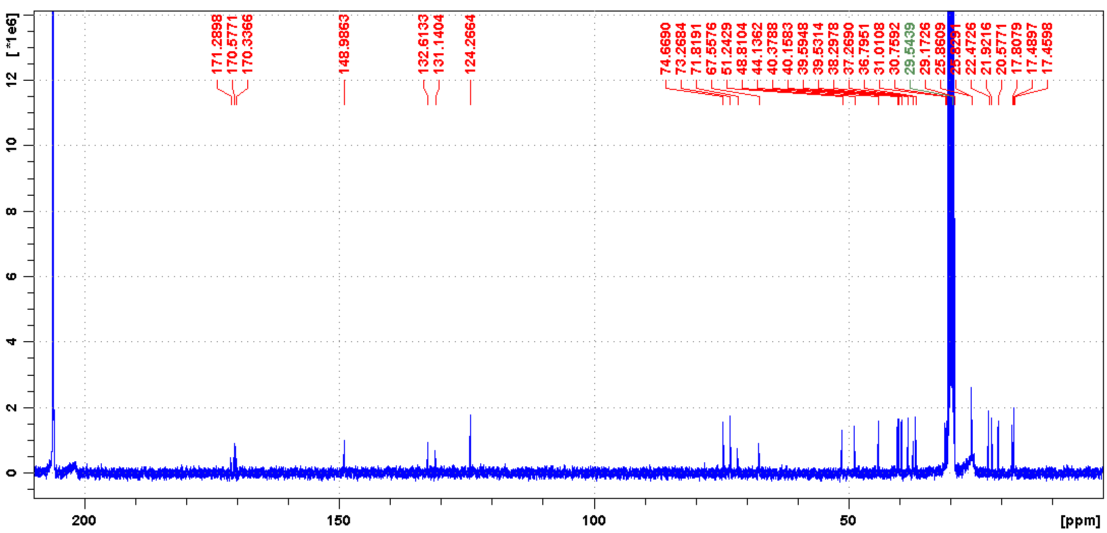
	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
597.3405	597.3403	0.2	0.3	8.5	52.6	0.737	47.84	C33 H50 O8 Na
	597.3427	-2.2	-3.7	11.5	52.5	0.651	52.16	C35 H49 O8

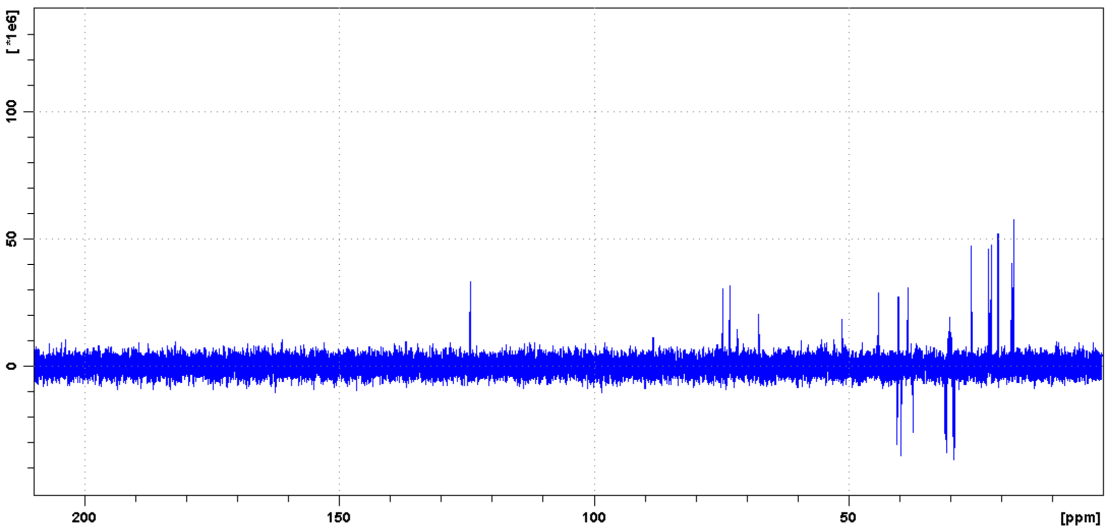
B



C



D



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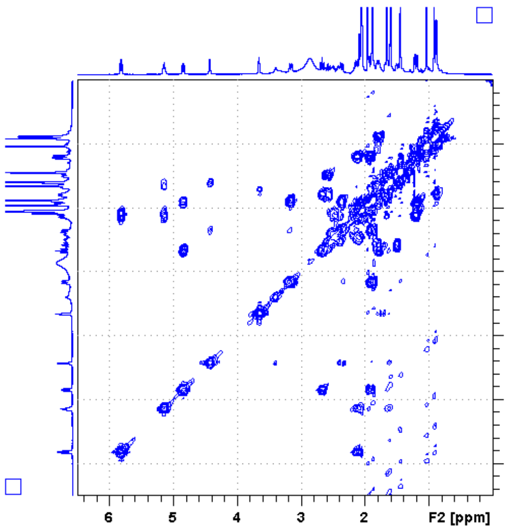
0
200
150
100
50
[ppm]

E



F1 [ppm]
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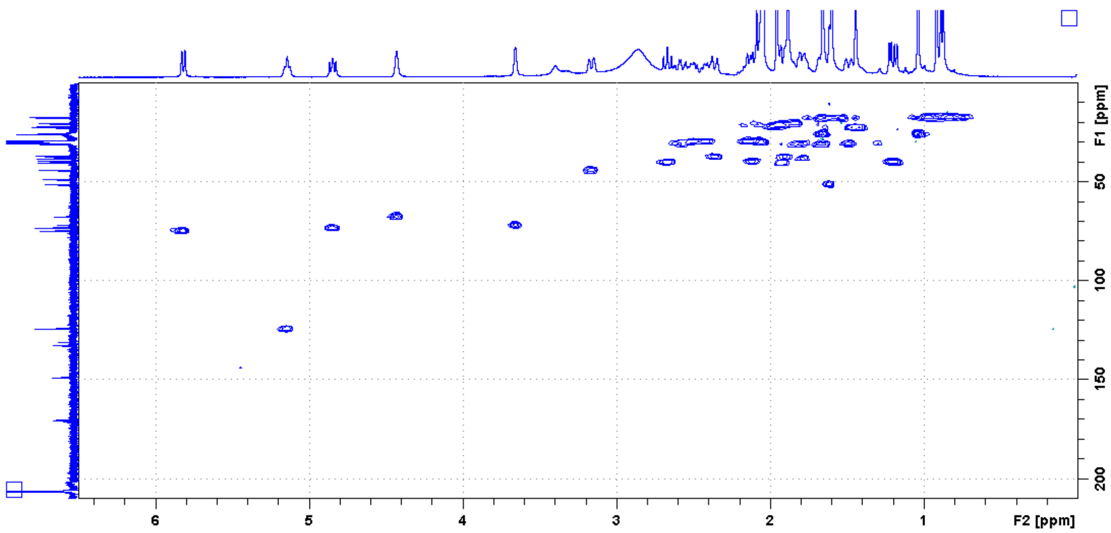
6
5
4
3
2
F2 [ppm]

F



F1 [ppm]
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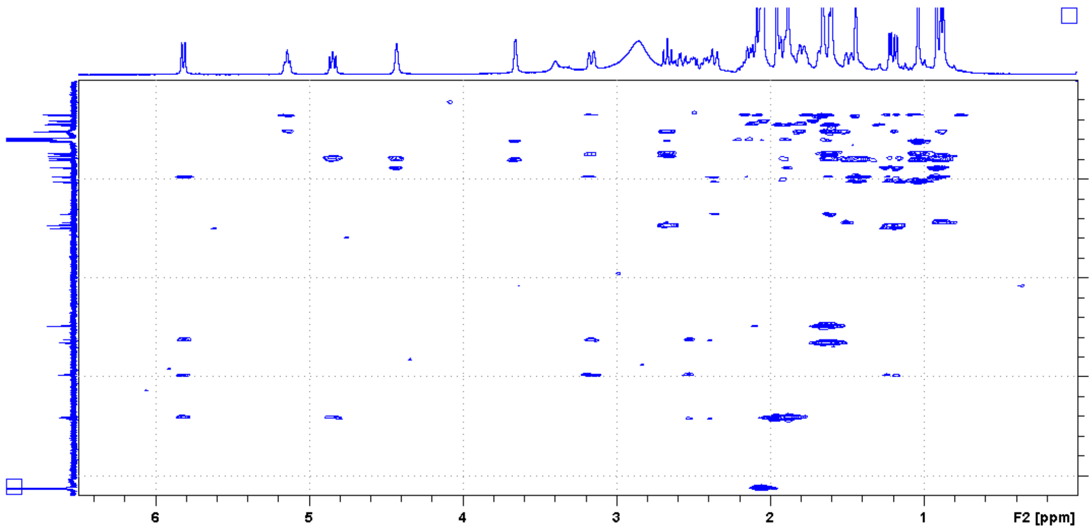
200
6
5
4
3
2
1
F2 [ppm]

G



H

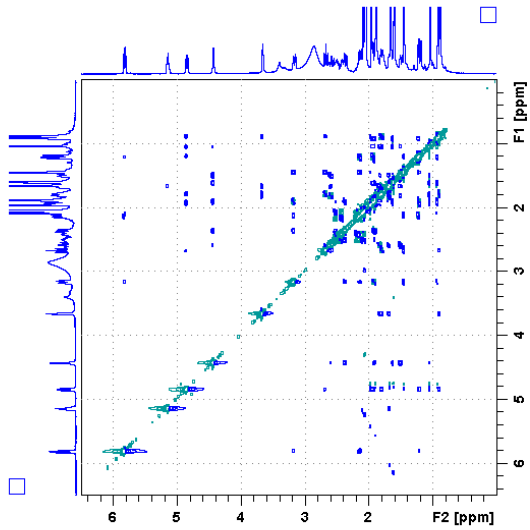
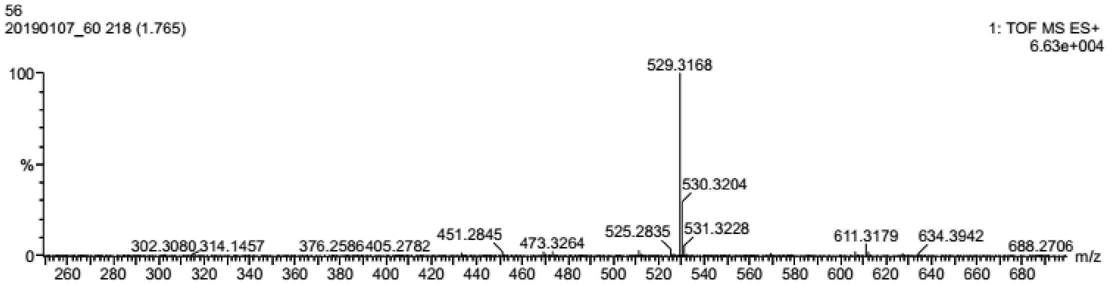


Figure S58 HRESIMS and NMR spectra of **67**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in acetone-d_6 at 400 MHz; (C) ^{13}C NMR spectrum in acetone-d_6 at 100 MHz; (D) DEPT 135 spectrum in acetone-d_6 at 100 MHz; (E) ^{1}H–^{1}H COSY spectrum in acetone-d_6 at 400 MHz; (F) HSQC spectrum in acetone-d_6 at 400 MHz; (G) HMBC spectrum in acetone-d_6 at 400 MHz; (H) ROESY spectrum in acetone-d_6 at 400 MHz.

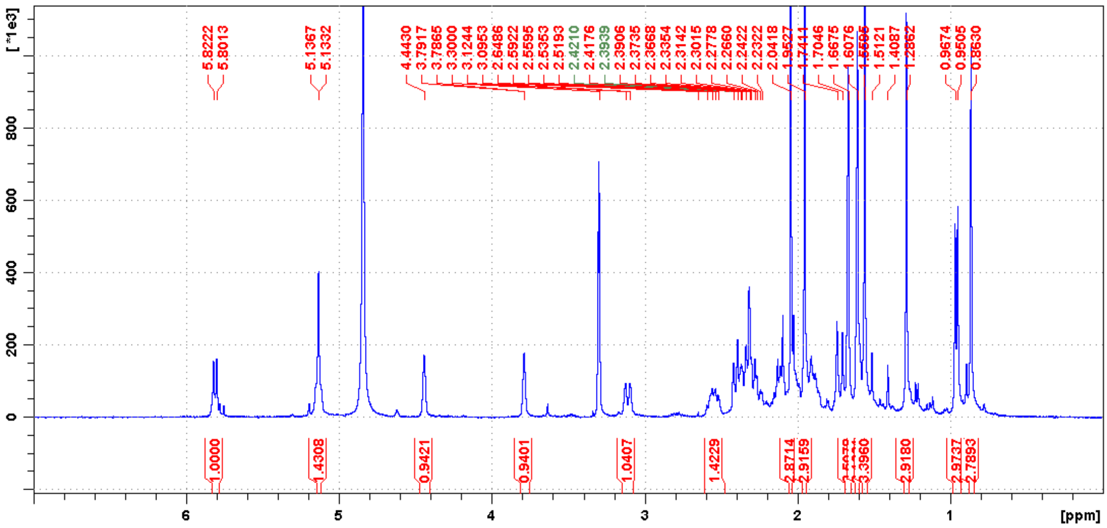
A

Monoisotopic Mass, Even Electron Ions
353 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1

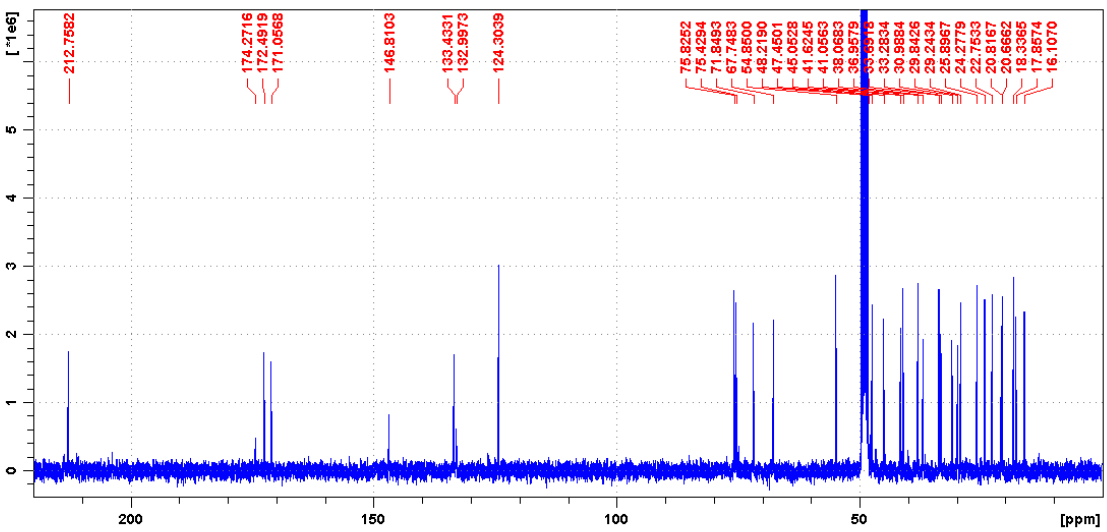


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
611.3179	611.3196	-1.7	-2.8	9.5	50.9	0.023	97.77	C33 H48 O9 Na
	611.3161	1.8	2.9	21.5	54.6	3.804	2.23	C42 H43 O4

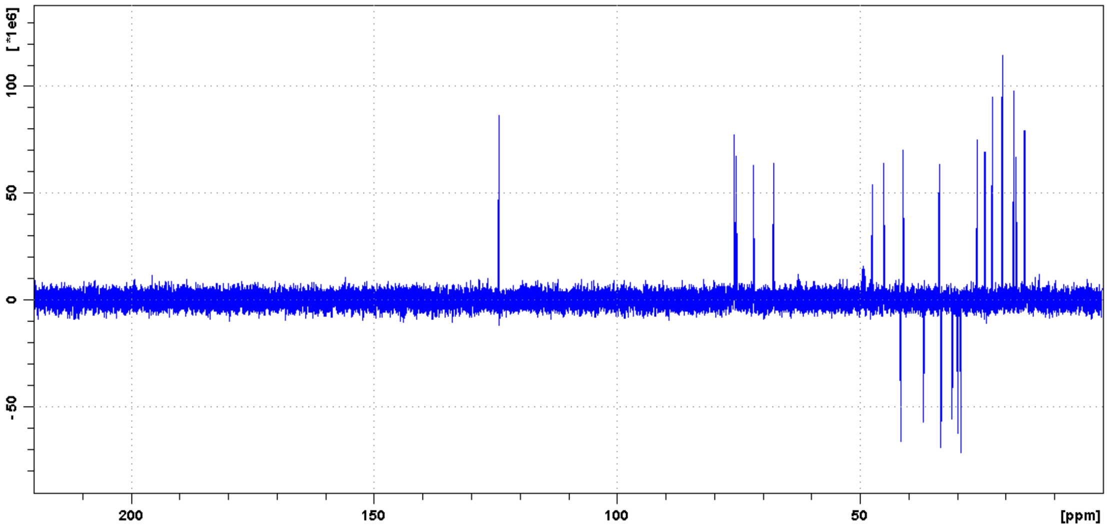
B



C



D



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-50
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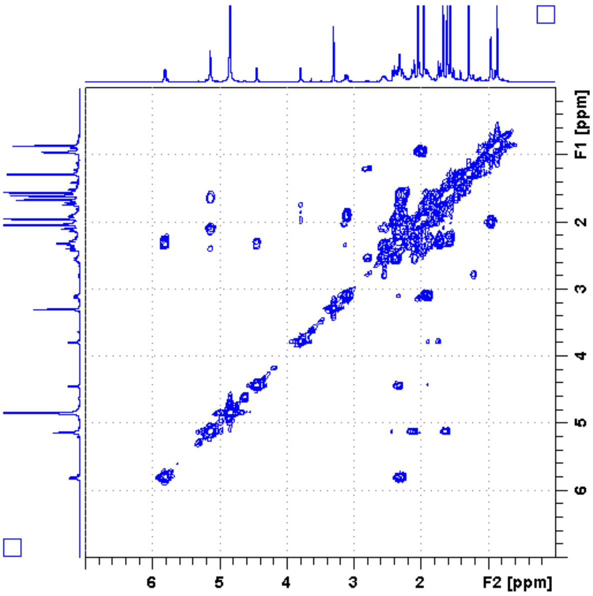
150
100
50
[ppm]

E



F1 [ppm]
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5
6
6
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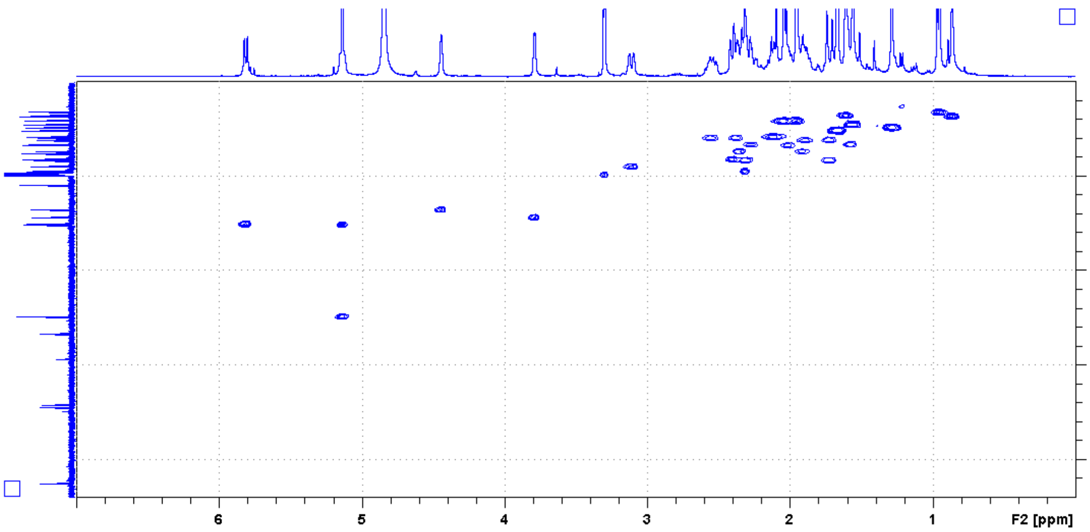
4
3
2
F2 [ppm]

F



F1 [ppm]
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150
200
6
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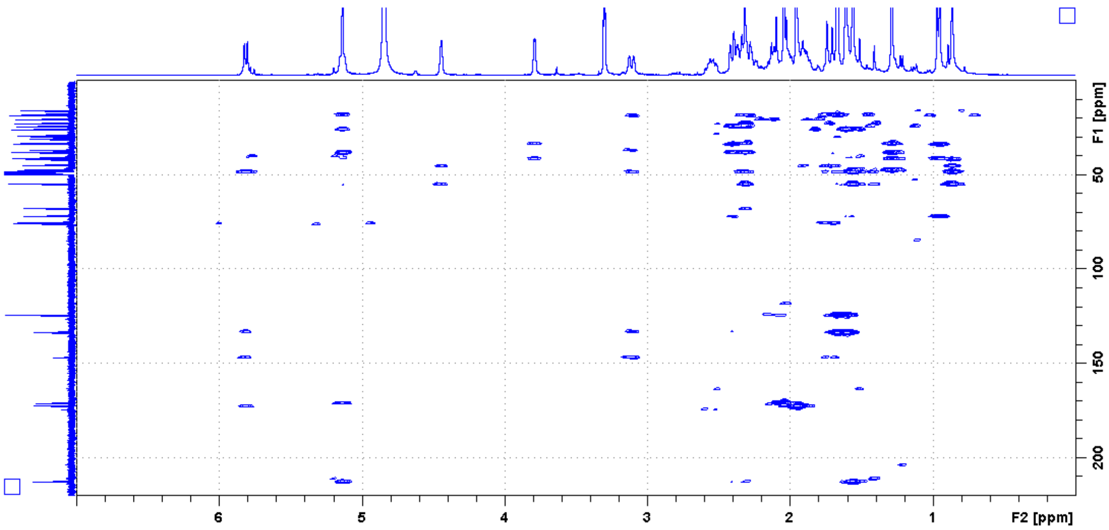
4
3
2
1
F2 [ppm]

G



H

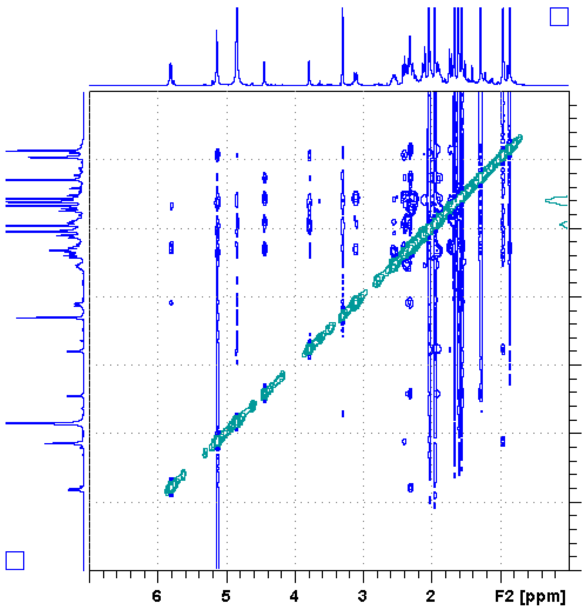
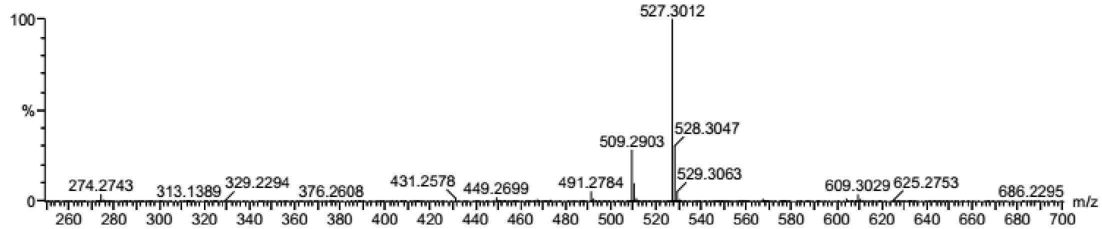


Figure S59 HRESIMS and NMR spectra of **68**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in CD_3OD at 400 MHz; (C) ^{13}C NMR spectrum in CD_3OD at 100 MHz; (D) DEPT 135 spectrum in CD_3OD at 100 MHz; (E) ^{1}H–^{1}H COSY spectrum in CD_3OD at 400 MHz; (F) HSQC spectrum in CD_3OD at 400 MHz; (G) HMBC spectrum in CD_3OD at 400 MHz; (H) ROESY spectrum in CD_3OD at 400 MHz.

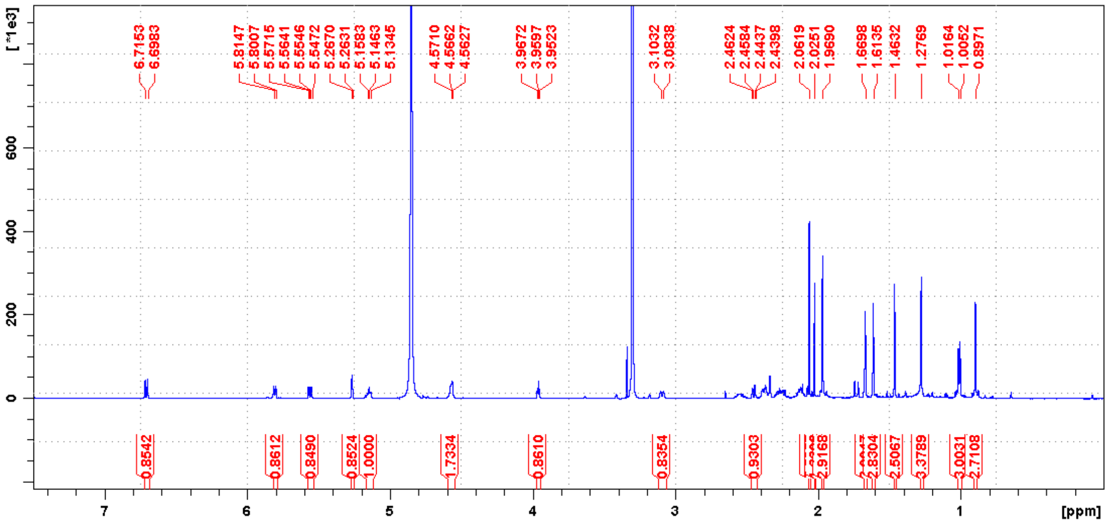
A

Monoisotopic Mass, Even Electron Ions
339 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 Na: 0-1
57
20190107_61 205 (1.657) 1: TOF MS ES+ 1.22e+005

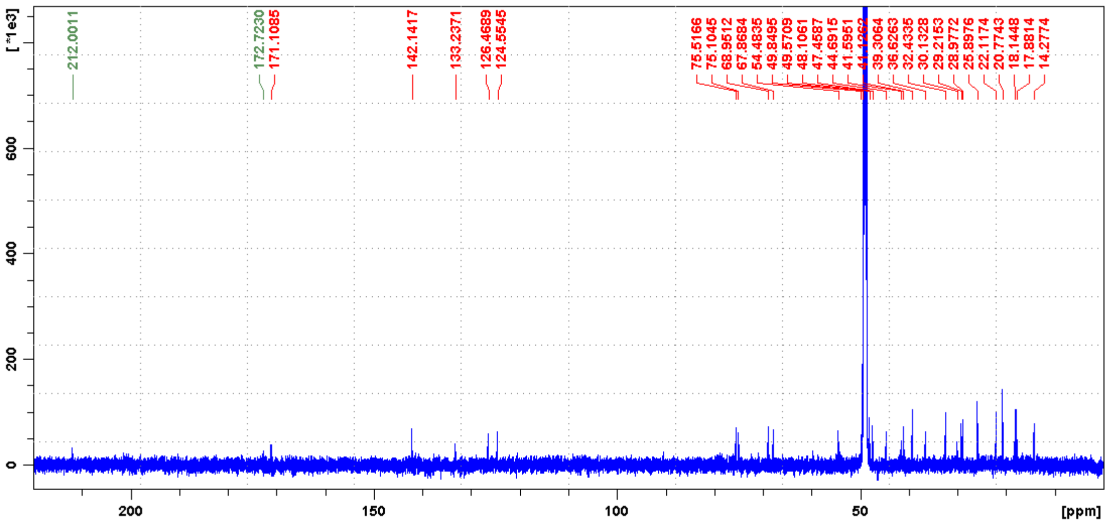


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
609.3029	609.3040	-1.1	-1.8	10.5	58.5	0.018	98.25	C33 H46 O9 Na
	609.3005	2.4	3.9	22.5	62.5	4.046	1.75	C42 H41 O4

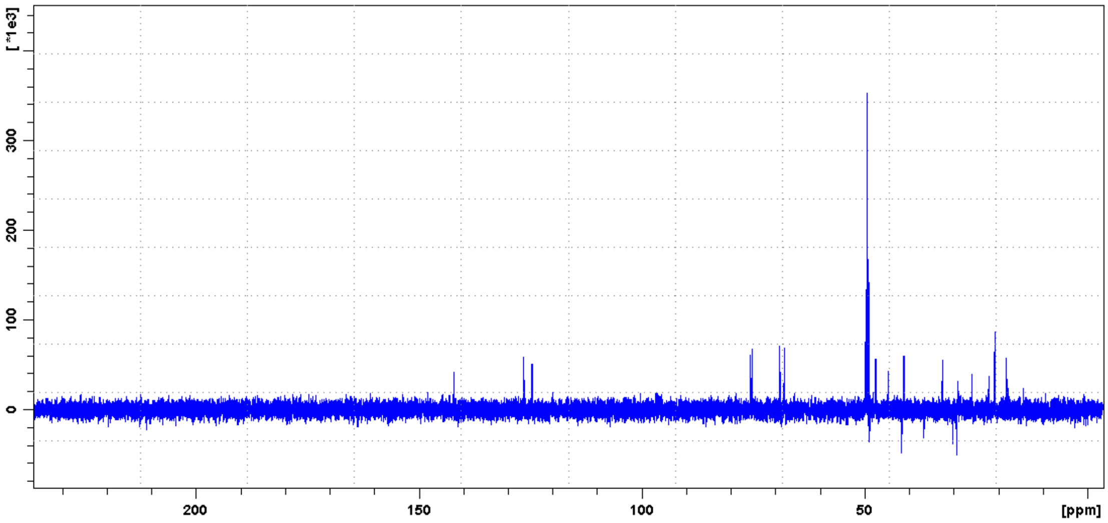
B



C



D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[ppm]

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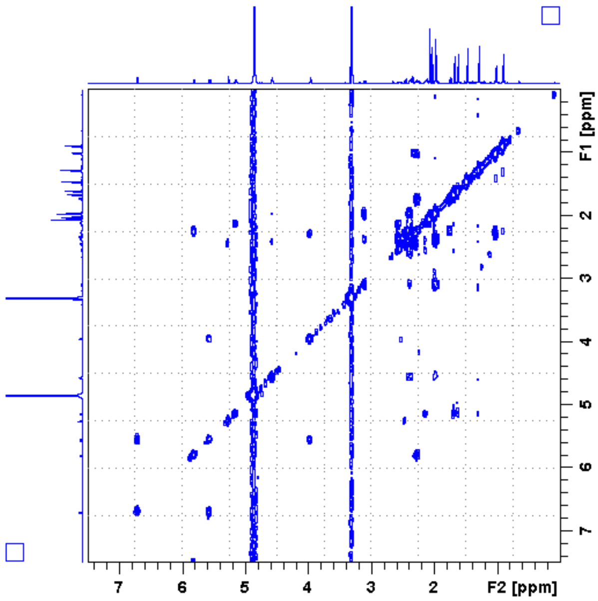
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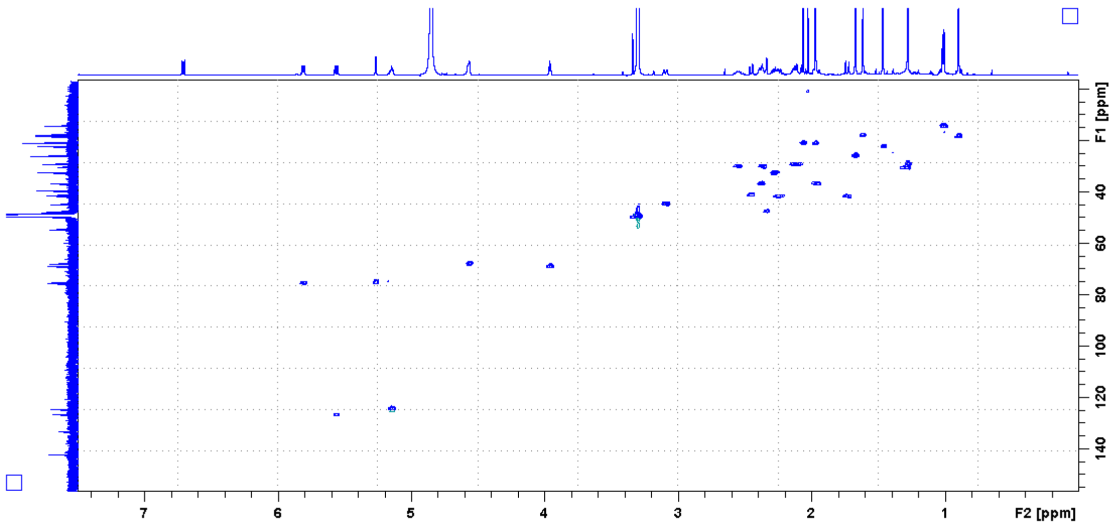
2
F2 [ppm]

F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140
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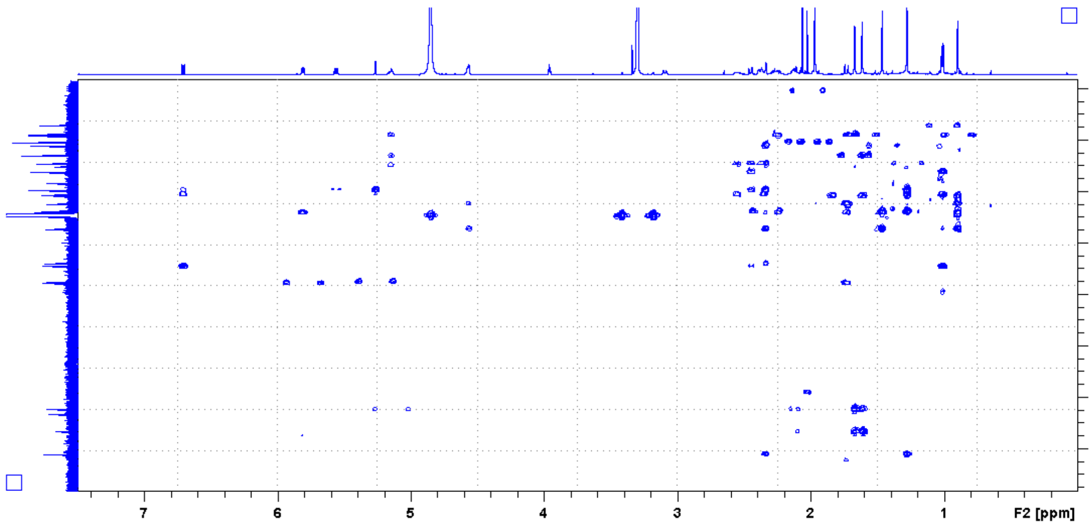
6
5
4
3
2
1
F2 [ppm]

G



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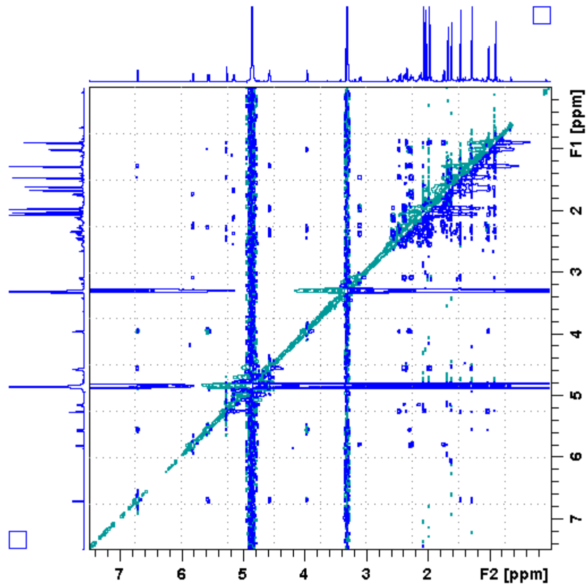
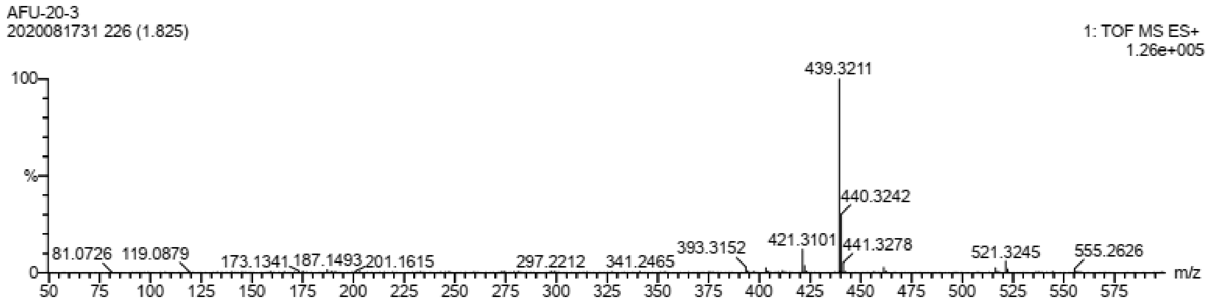


Figure S60 HRESIMS and NMR spectra of **69**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in CD_3OD at 600 MHz; (C) ^{13}C NMR spectrum in CD_3OD at 150 MHz; (D) DEPT 135 spectrum in CD_3OD at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in CD_3OD at 600 MHz; (F) HSQC spectrum in CD_3OD at 600 MHz; (G) HMBC spectrum in CD_3OD at 600 MHz; (H) ROESY spectrum in CD_3OD at 600 MHz.

A

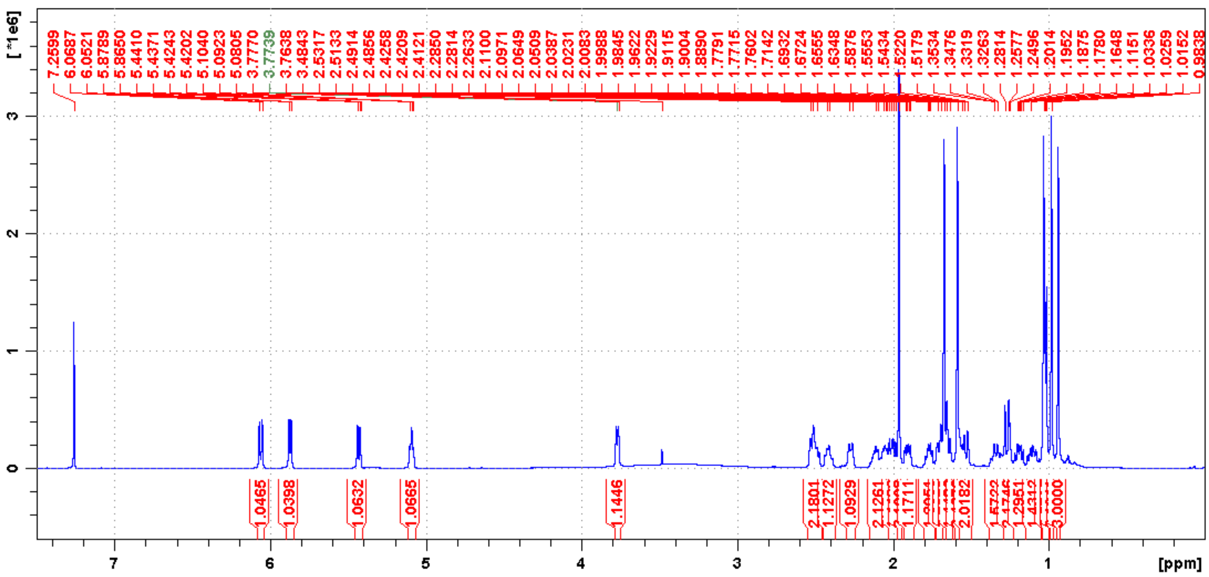
Monoisotopic Mass, Even Electron Ions
256 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-200 H: 0-1000 O: 0-200 Na: 0-1



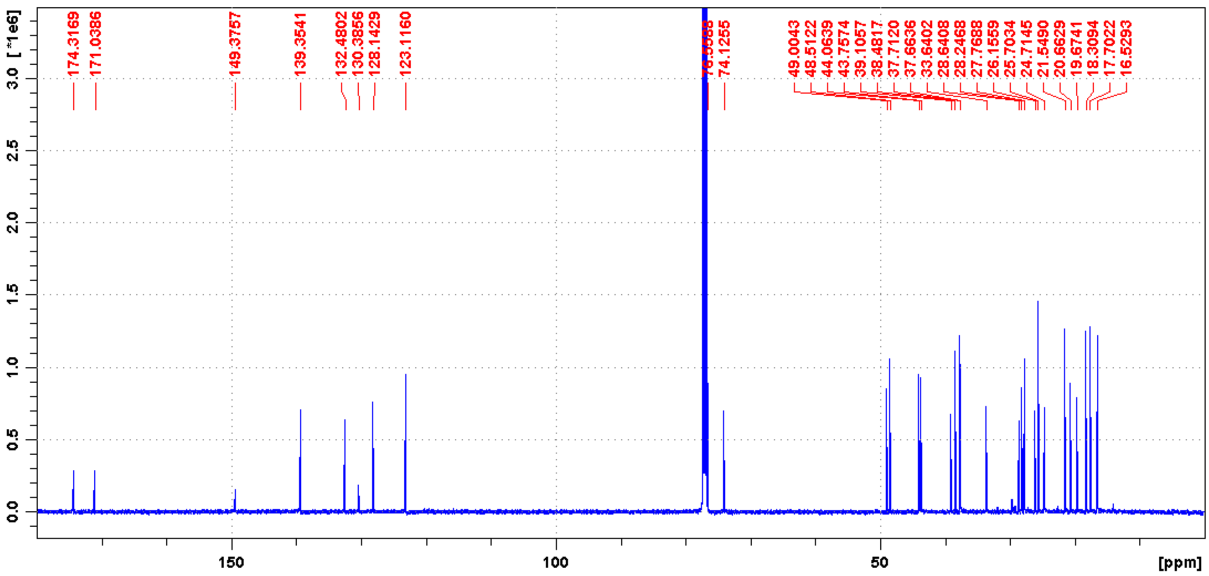
Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
521.3245	521.3243	0.2	0.4	8.5	89.0	0.075	92.82	C31 H46 O5 Na
	521.3267	-2.2	-4.2	11.5	91.6	2.634	7.18	C33 H45 O5

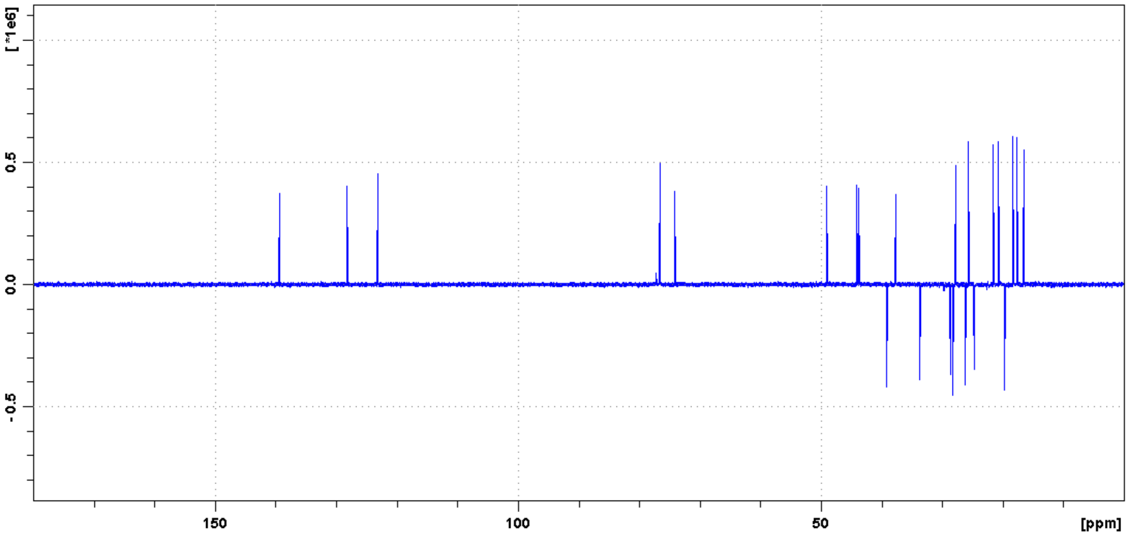
B



C



D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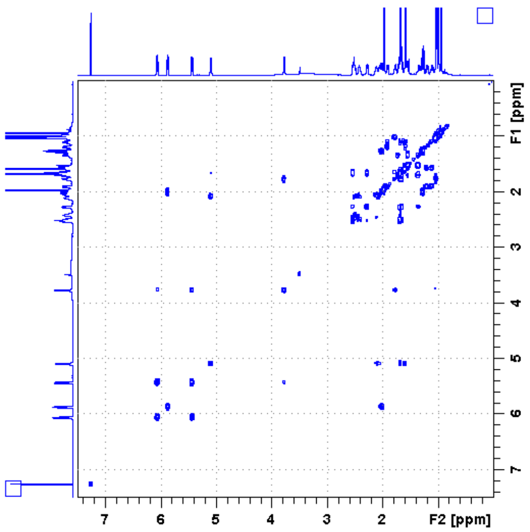
100
50
[ppm]

E


F1 [ppm]
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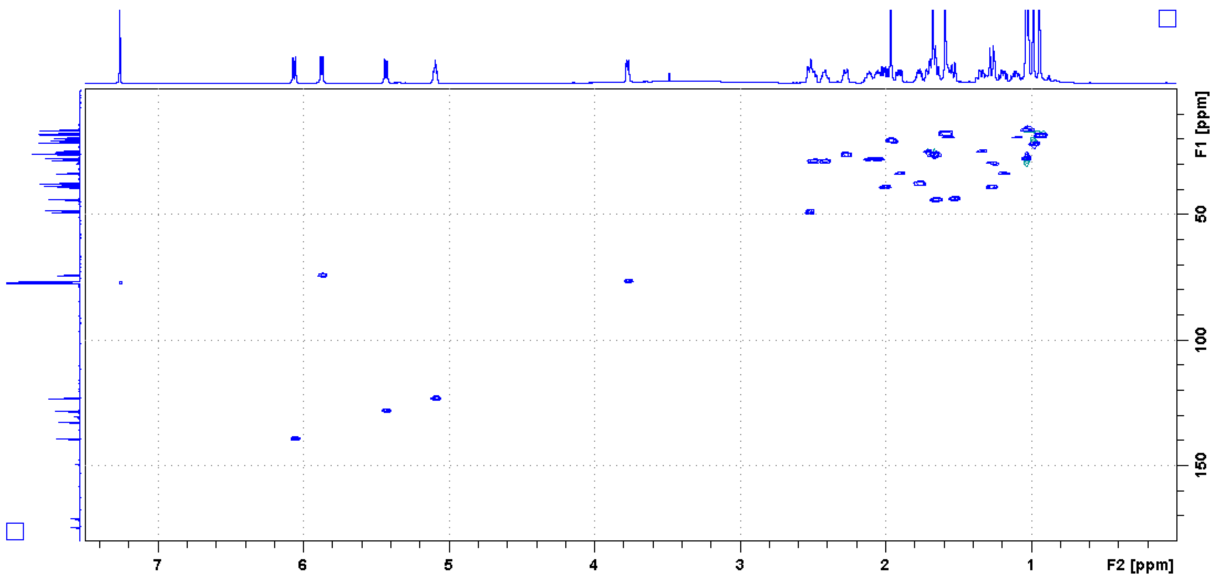
6
7
F2 [ppm]

F


F1 [ppm]
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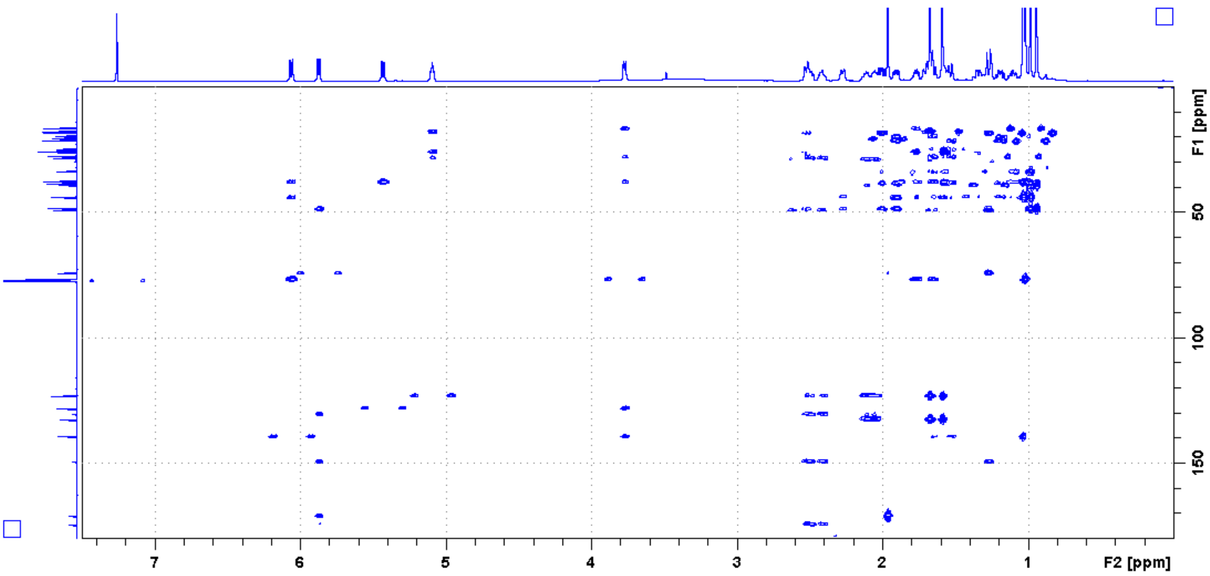
3
2
1
F2 [ppm]

G



H

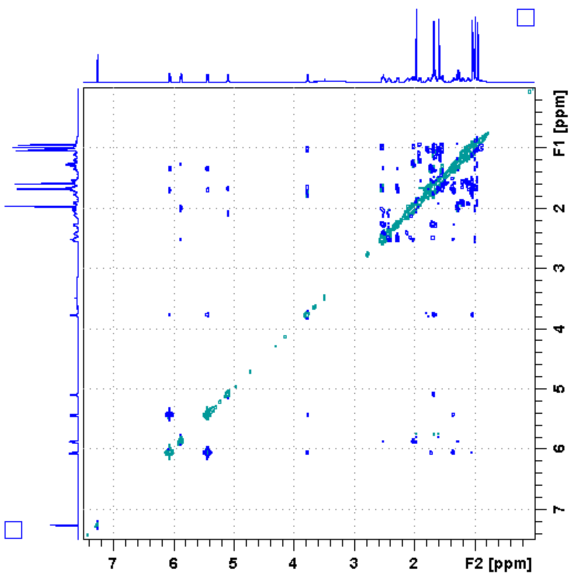


Figure S61 HRESIMS and NMR spectra of **81**.

(A) HRESIMS spectrum; (B) ^{1}H NMR spectrum in $CDCl_3$ at 600 MHz; (C) ^{13}C NMR spectrum in $CDCl_3$ at 150 MHz; (D) DEPT 135 spectrum in $CDCl_3$ at 150 MHz; (E) ^{1}H–^{1}H COSY spectrum in $CDCl_3$ at 600 MHz; (F) HSQC spectrum in $CDCl_3$ at 600 MHz; (G) HMBC spectrum in $CDCl_3$ at 600 MHz; (H) ROESY spectrum in $CDCl_3$ at 600 MHz.

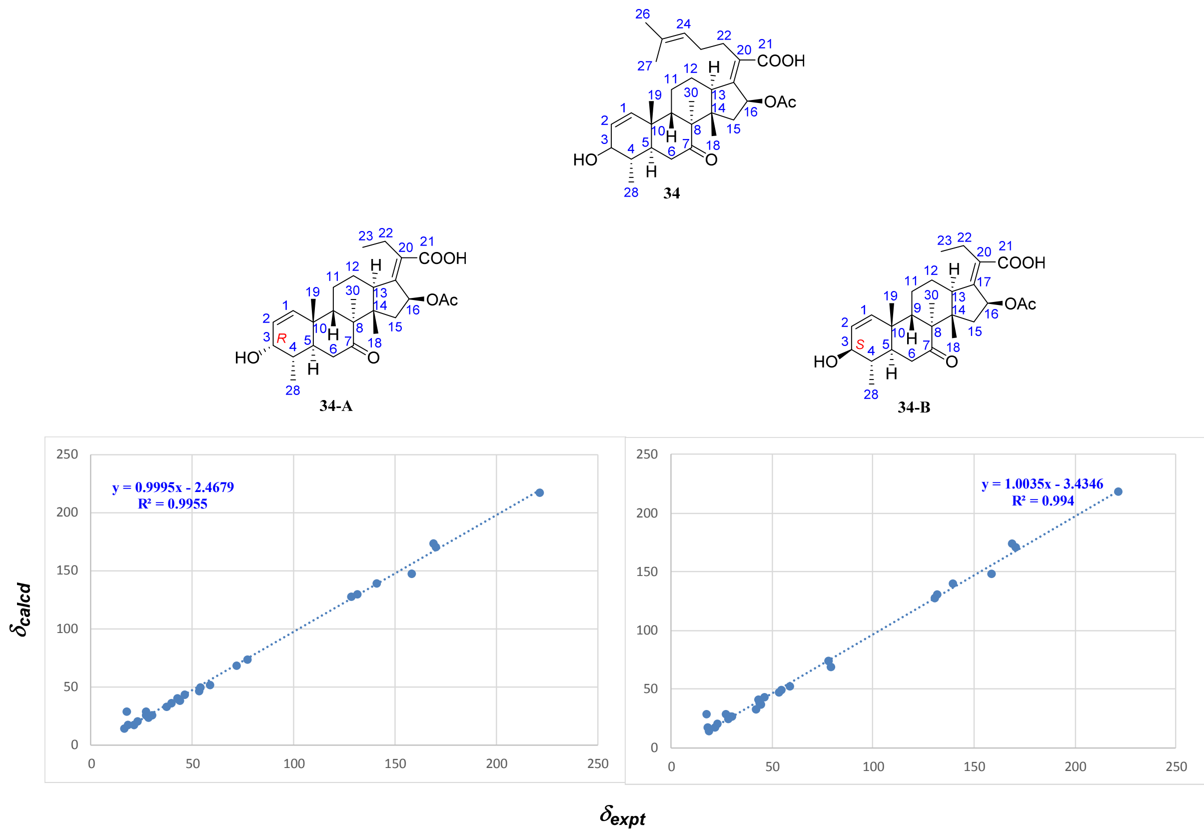


Figure S62 Linear correlation between calculated [13]C NMR chemical shift values of **34-A/34-B** and experimental values of **34**.

Based on the R^2 values, the relative configuration of **34** is assigned as 3*R**,4*S**,5*S**,8*S**, *S**,10*S**,13*R**,14*S**,16*S**.

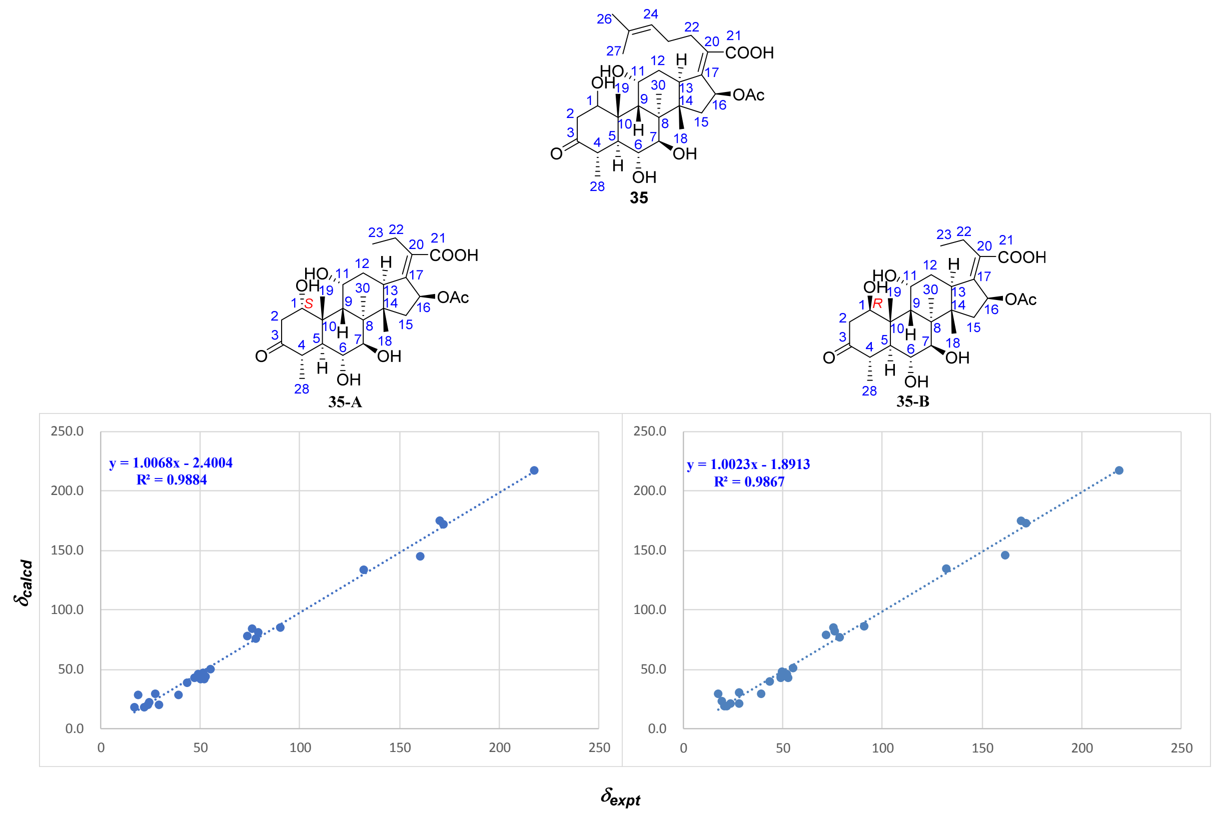
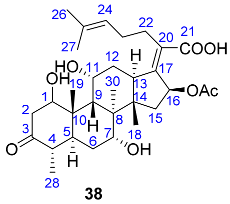
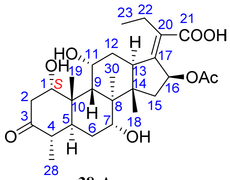


Figure S63 Linear correlation between calculated ^{13}C NMR chemical shift values of **35-A/35-B** and experimental values of **35**.

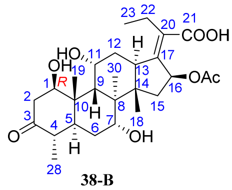
Based on the R^2 values, the relative configuration of **35** is assigned as 1*S**,4*S**,5*S**,6*R**,7*R**,8*S**,9*S**,10*S**,11*R**,13*R**,14*S**,16*S**.



38



38-A



38-B

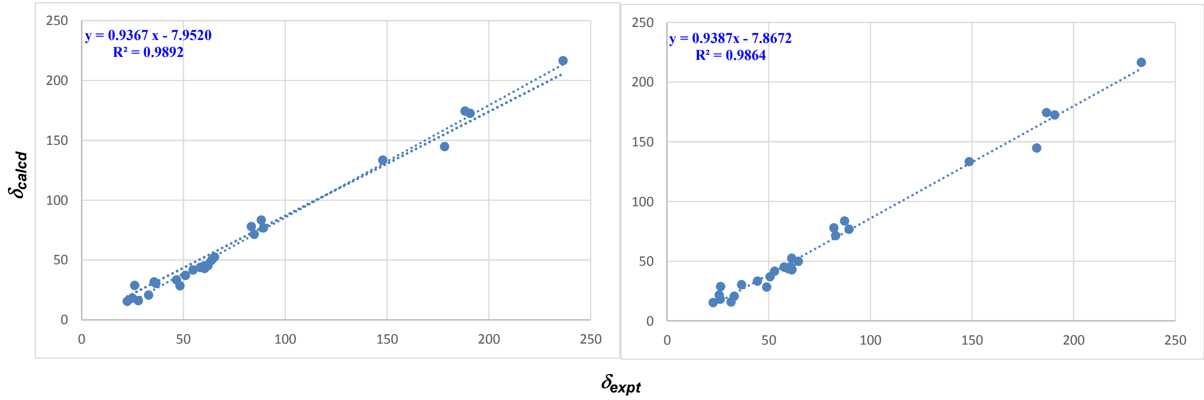
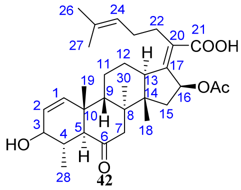
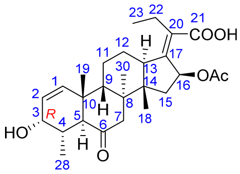


Figure S64 Linear correlation between calculated ^{13}C NMR chemical shift values of **38-A/38-B** and experimental values of **38**.

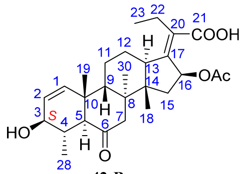
Based on the R^2 values, the relative configuration of **38** is assigned as 1*S**,4*S**,5*S**,7*R**,8*S**,9*S**,10*S**,11*R**,13*R**,14*S**,16*S**.



42



42-A



42-B

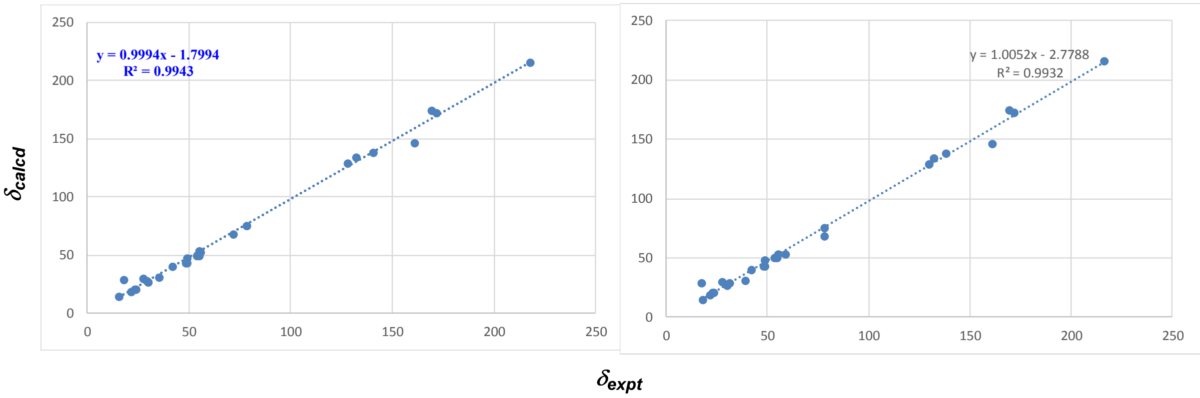


Figure S65 Linear correlation between calculated ^{13}C NMR chemical shift values of **42-A/42-B** and experimental values of **42**.

Based on the R^2 values, the relative configuration of **42** is assigned as 3*R**,4*S**,5*S**,8*S**,9*S**,10*R**,13*R**,14*S**,16*S**.

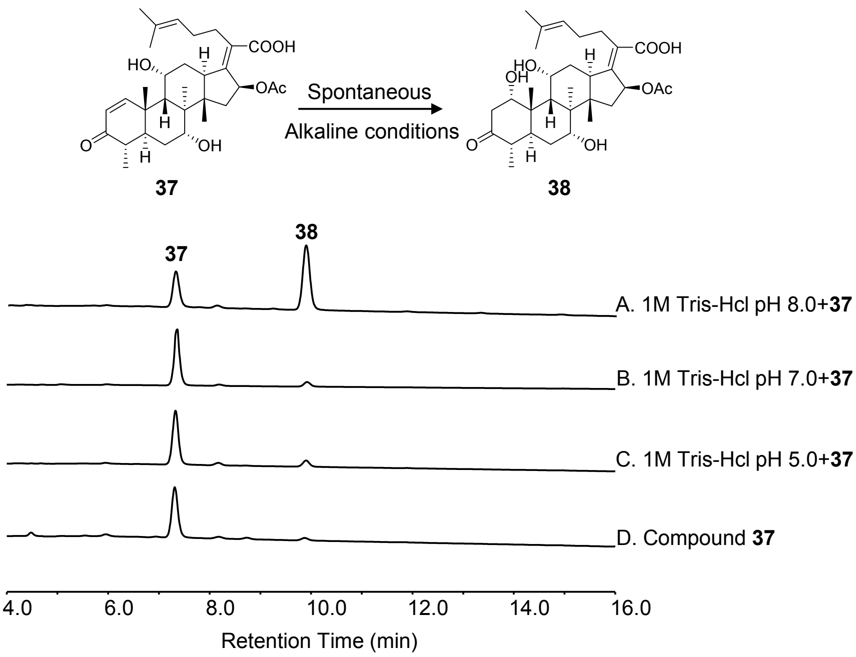
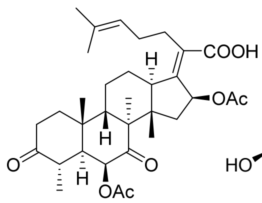
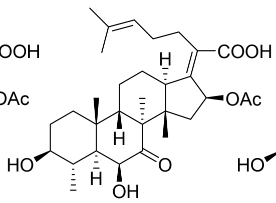


Figure S66 HPLC analysis for spontaneous 1,4-addition of **37** in Tri-HCl buffer.

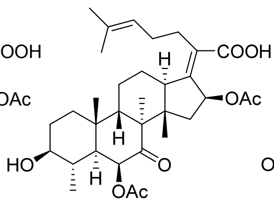
(A) **37** incubated in 1 mol/L Tris-HCl buffer (pH 8.0); (B) **37** incubated in 1 mol/L Tris-HCl buffer (pH 7.0); (C) **37** incubated in 1 mol/L Tris-HCl buffer (pH 5.0); (D) Compound **37**.



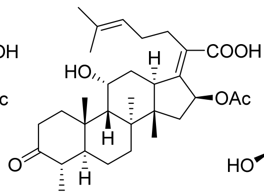
70



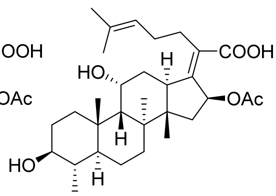
71



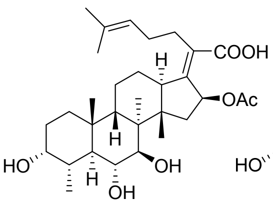
72



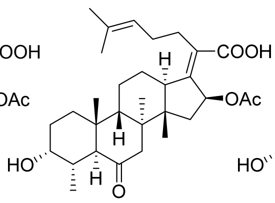
73



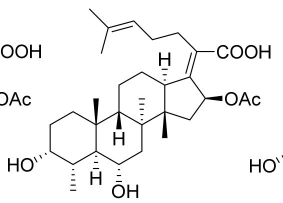
74



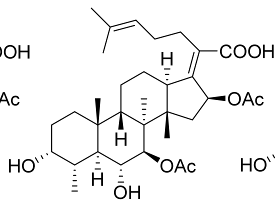
75



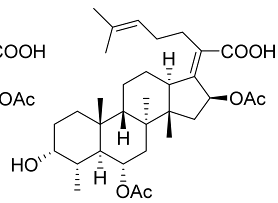
76



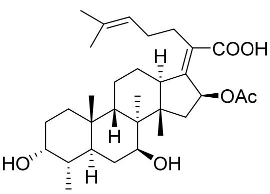
77



78

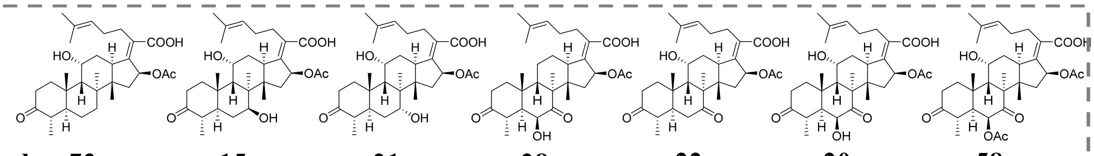


79

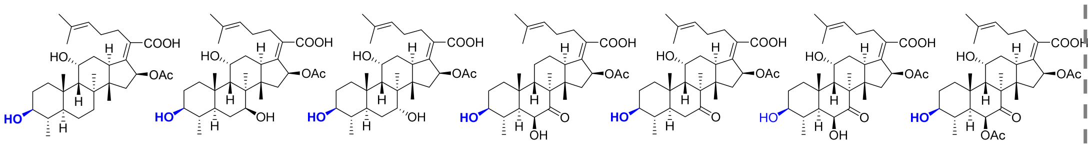


80

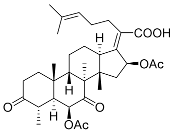
Figure S67 Previously isolated fusidane-type antibiotics during the biosynthetic study of helvolic acid, fusidic acid and cephalosporin P_1.



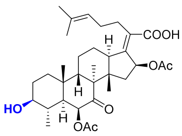
Compound	73	15	21	28	22	20	58
MIC	1	32	8	8	128	32	128



Compound	74	13	18	71	19	17	59
MIC	16	>128	128	>128	>128	>128	>128



Compound	70
MIC	32



Compound	72
MIC	>128

Figure S68 Comparison of anti-*S. aureus* 209P activity of fusidane-type antibiotics featured with 3-keto and 3*β*-OH.

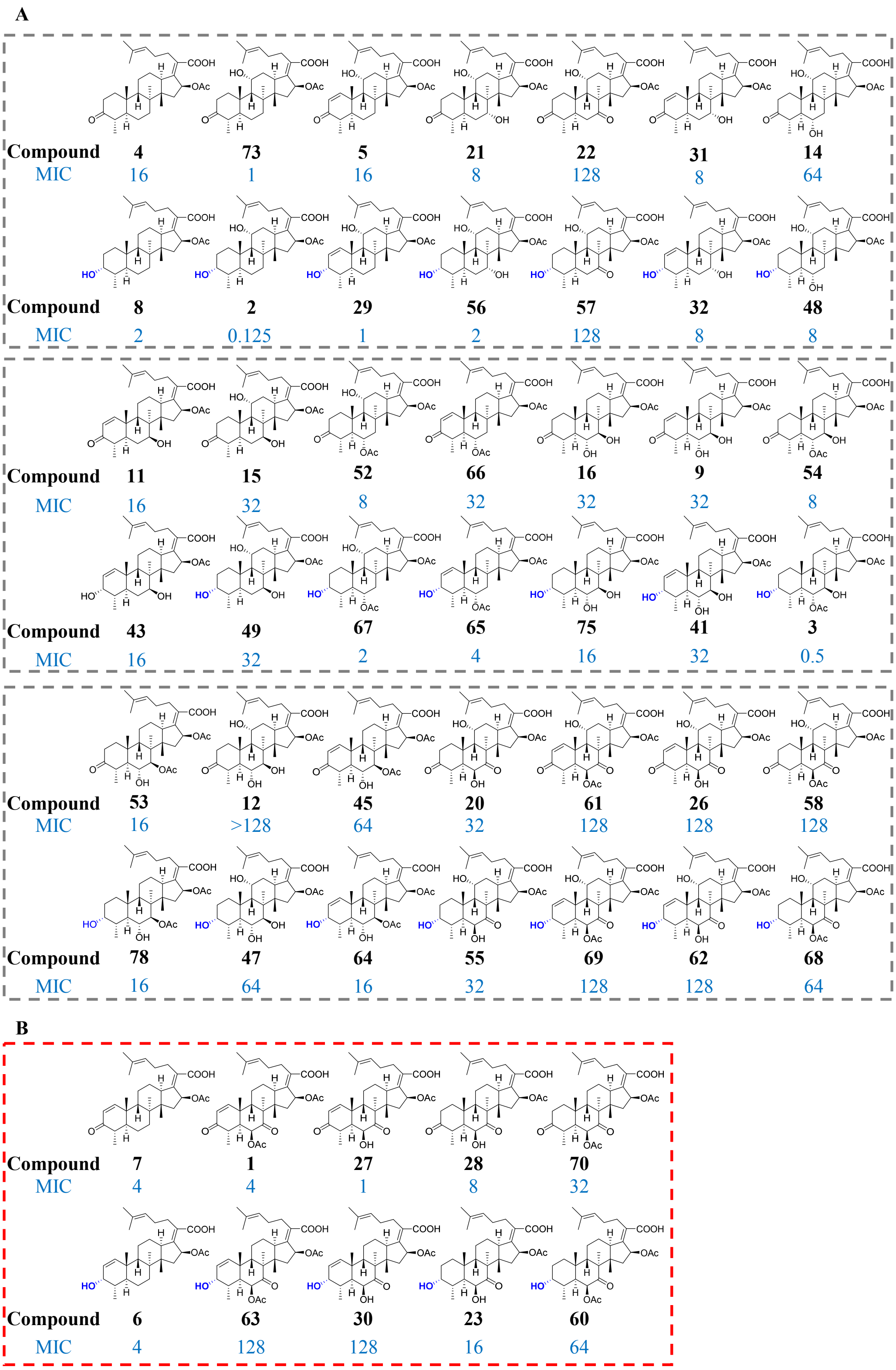


Figure S69 Comparison of anti-*S. aureus* 209P activity of fusidane-type antibiotics featured with 3-keto and 3*α*-OH.

(A) For most fusidane-type antibiotics, 3*α*-OH has the positive effect on the activity; (B) For a few fusidane-type antibiotics, 3*α*-OH has the negative effect on the activity.

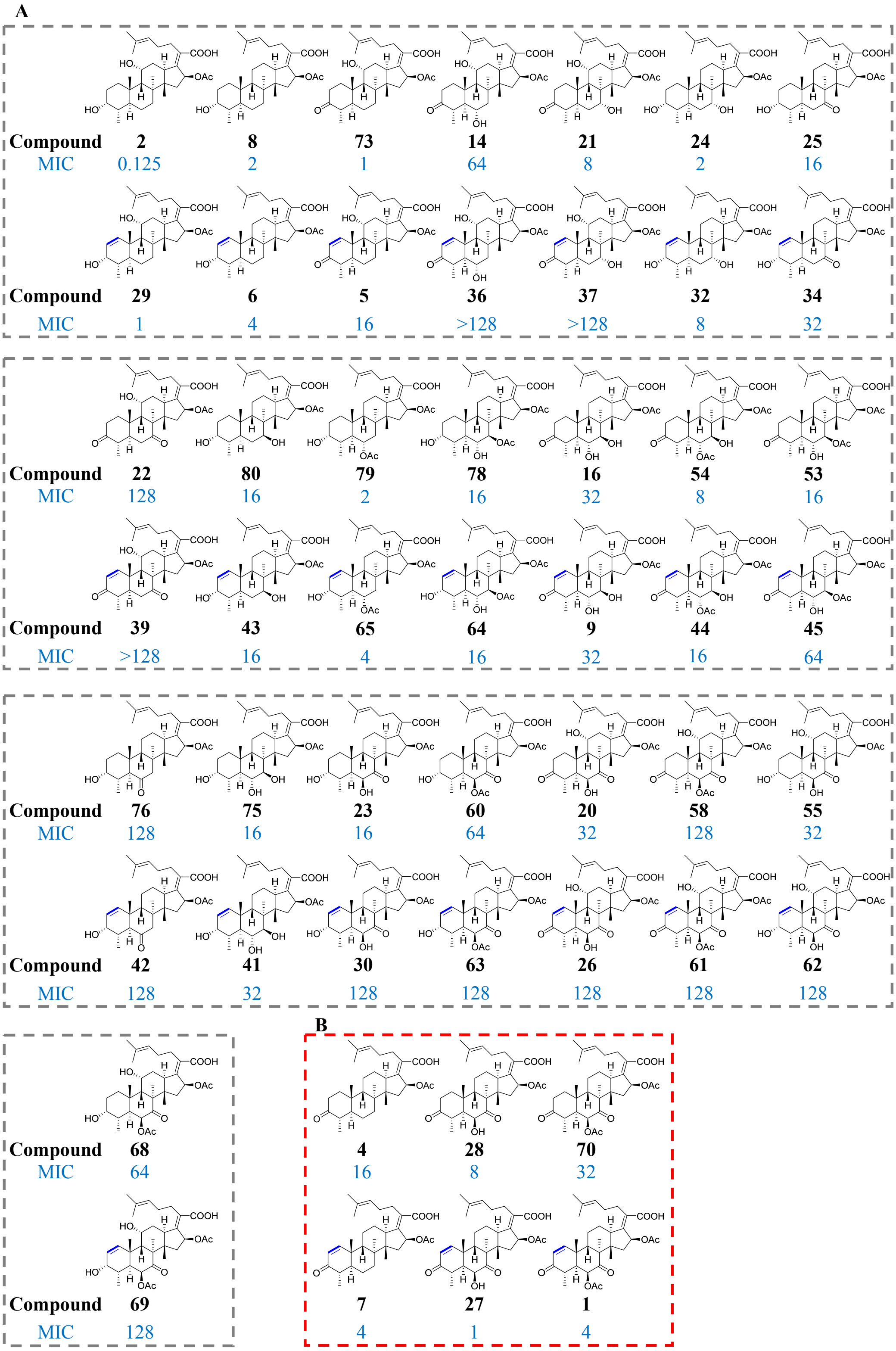
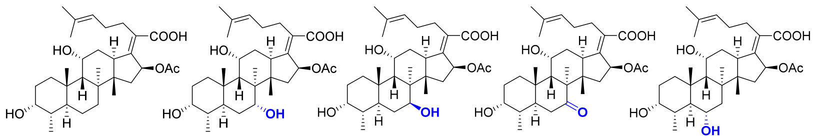
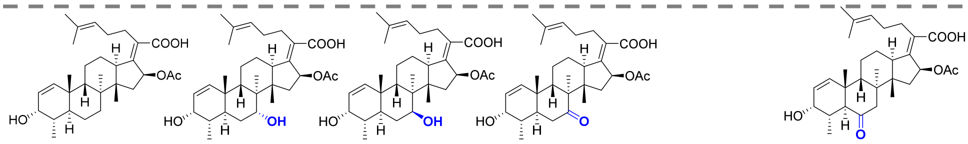


Figure S70 The effect of the C1/C2 double bond on anti-*S. aureus* 209P activity.

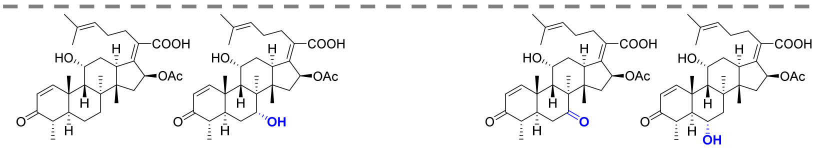
(A) For most fusidane-type antibiotics, the C1/C2 double bond has the negative effect; (B) For a few fusidane-type antibiotics, the C1/C2 double bond has the positive effect.



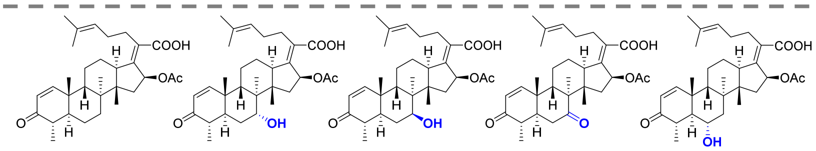
Compound	2	56	49	57	48
MIC	0.125	2	32	128	8



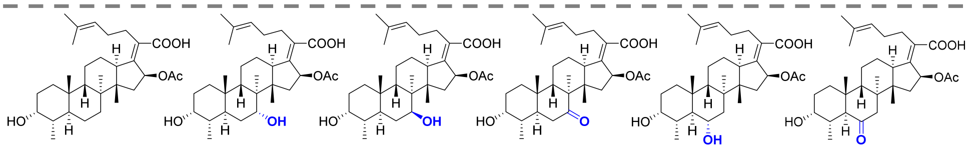
Compound	6	32	43	34	42
MIC	4	8	16	32	128



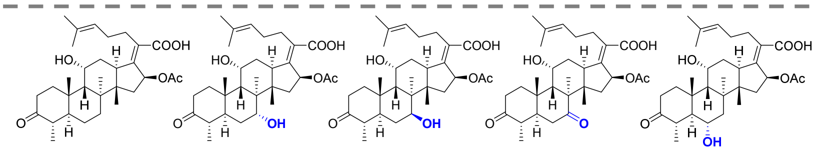
Compound	5	37	39	36
MIC	16	>128	>128	>128



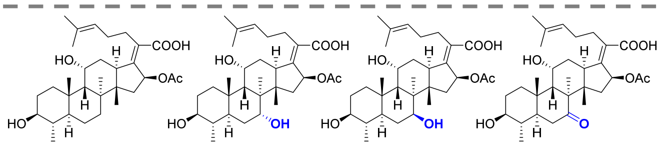
Compound	7	31	11	33	10
MIC	4	8	16	32	128



Compound	8	24	80	25	77	76
MIC	2	2	16	16	4	128



Compound	73	21	15	22	14
MIC	1	8	32	128	64



Compound	74	18	13	19
MIC	16	128	>128	>128

Figure S71 The detrimental effect of mono-oxidation at C6 or C7 on anti-*S. aureus* 209P activity.

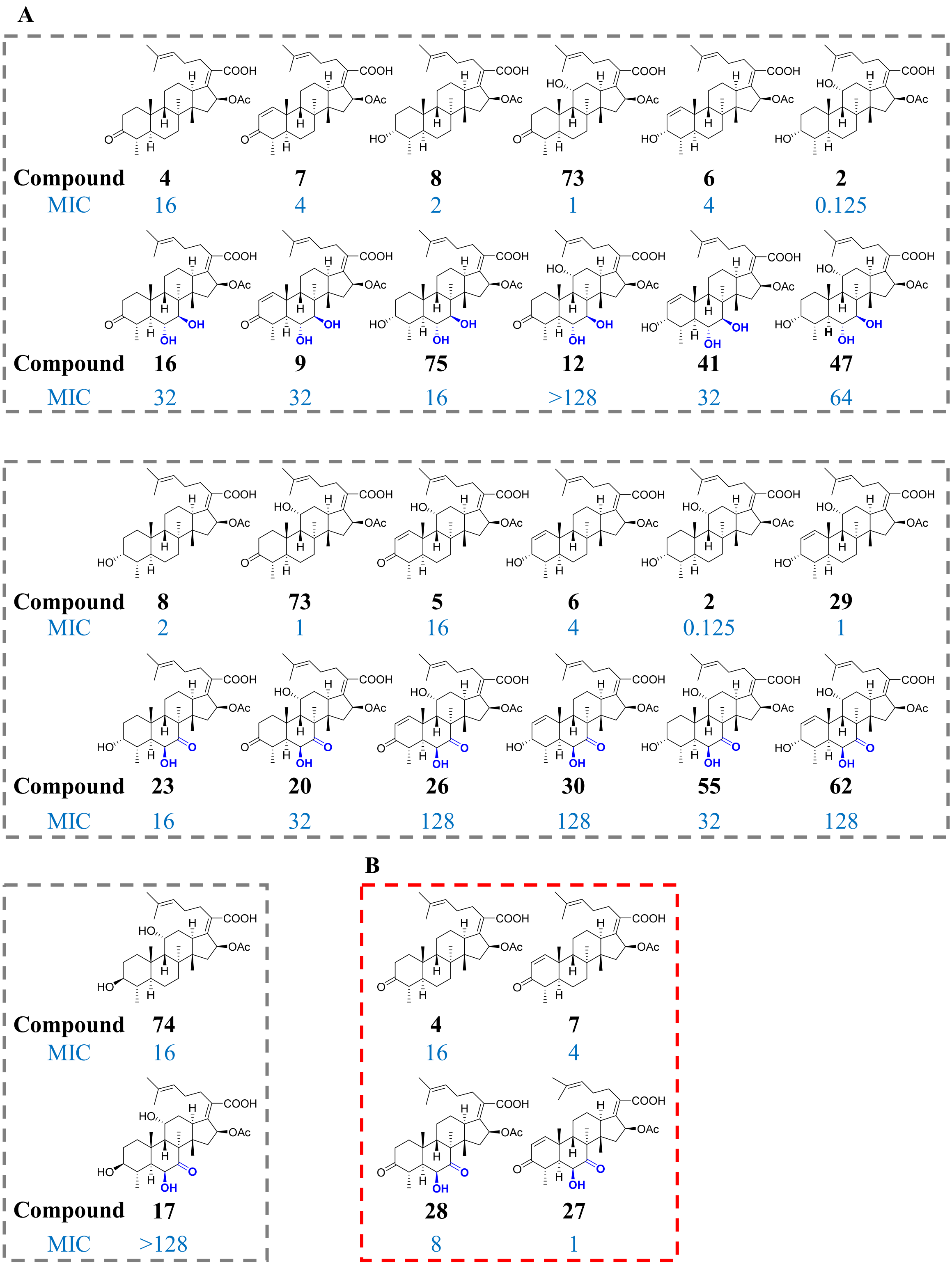
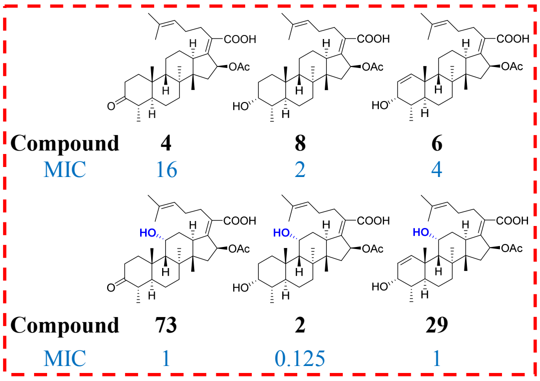


Figure S72 The effect of dual-oxidation at C6 and C7 on anti-*S. aureus* 209P activity.

(A) For most fusidane-type antibiotics, the dual-oxidation at C6 and C7 has the negative effect; (B) For a few fusidane-type antibiotics, the dual-oxidation at C6 and C7 has the positive effect.

A



B

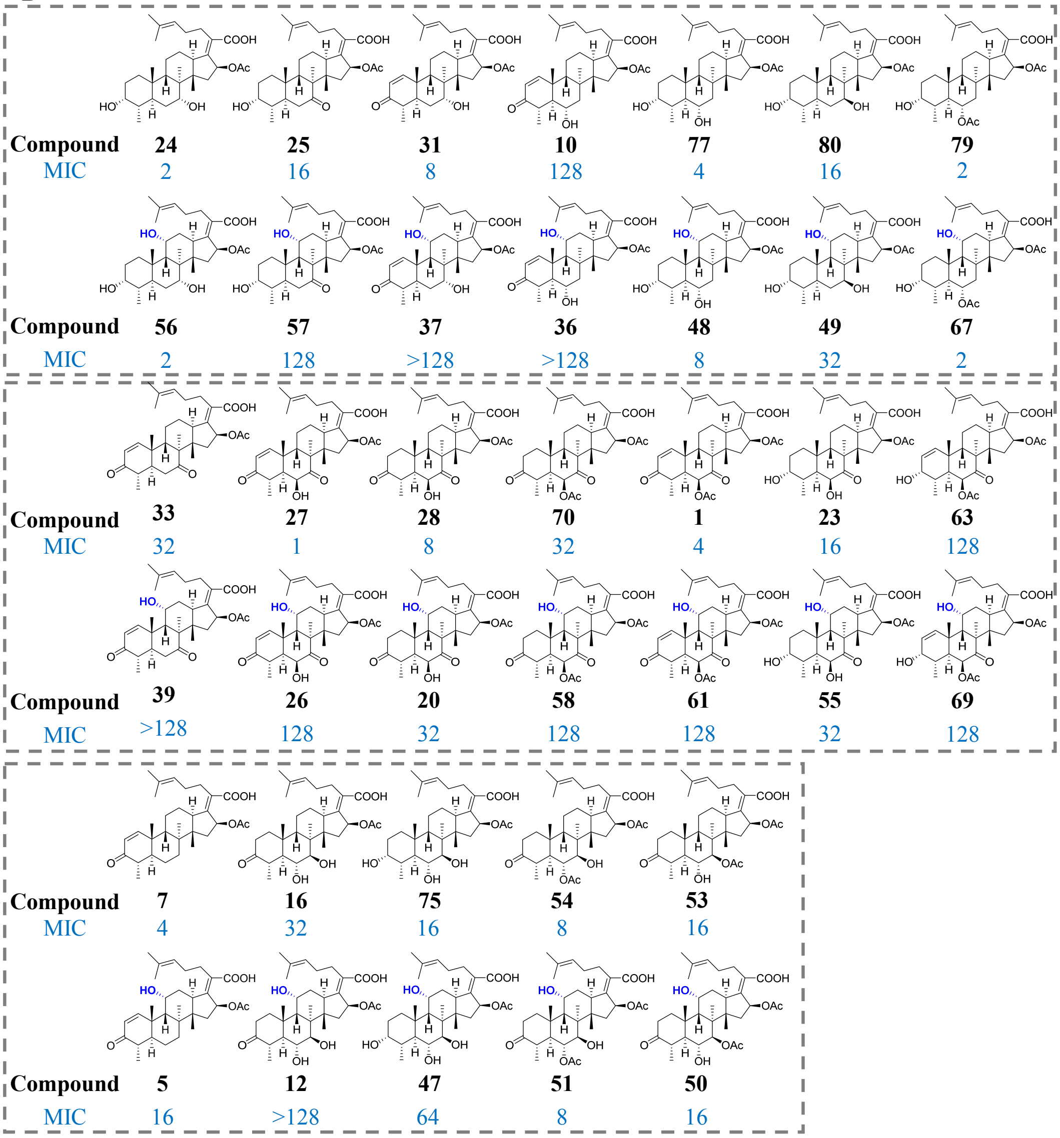
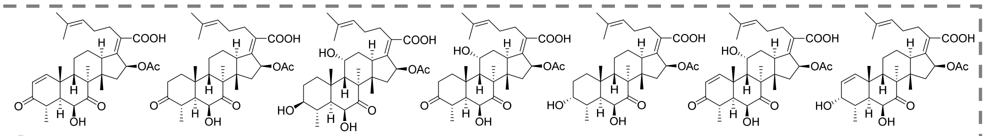


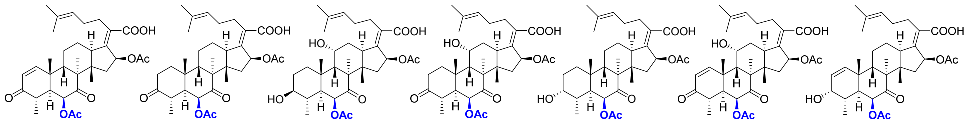
Figure S73 The effect of C11α-hydroxylation on anti-*S. aureus* 209P activity.

(A) For a few fusidane-type antibiotics, C11α-hydroxylation has the positive effect; (B) For most fusidane-type antibiotics, C11α-hydroxylation has the negative effect.

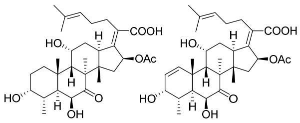
A



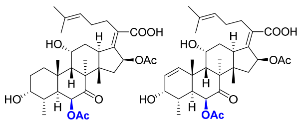
Compound	27	28	17	20	23	26	30
MIC	1	8	>128	32	16	128	128



Compound	1	70	59	58	60	61	63
MIC	4	32	>128	128	64	128	128

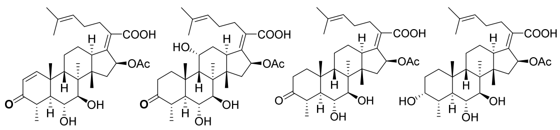


Compound	55	62
MIC	32	128

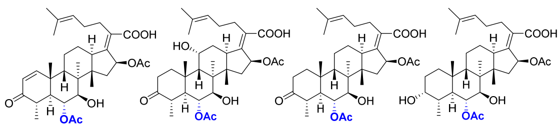


Compound	68	69
MIC	64	128

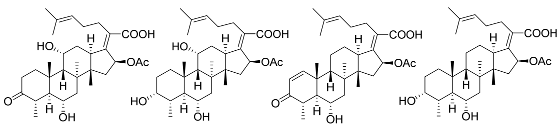
B



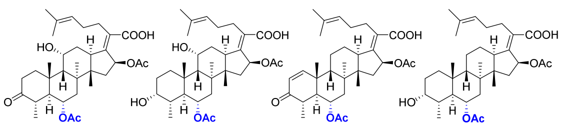
Compound	9	12	16	75
MIC	32	>128	32	16



Compound	44	51	54	3
MIC	16	8	8	0.5



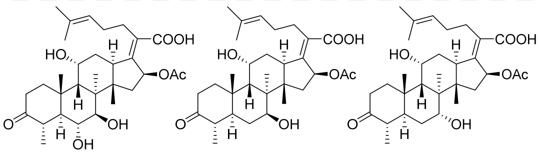
Compound	14	48	10	77
MIC	64	8	128	4



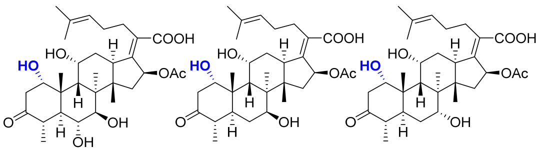
Compound	52	67	66	79
MIC	8	2	32	2

Figure S74 The effect of acetylation of 6-OH on anti-*S. aureus* 209P activity.

(A) Acetylation of 6*β*-OH has the negative effect; (B) Acetylation of 6*α*-OH has the positive effect.



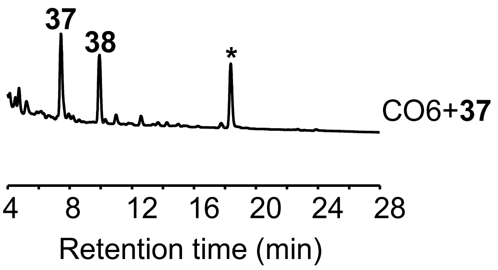
Compound	12	15	21
MIC	>128	32	8



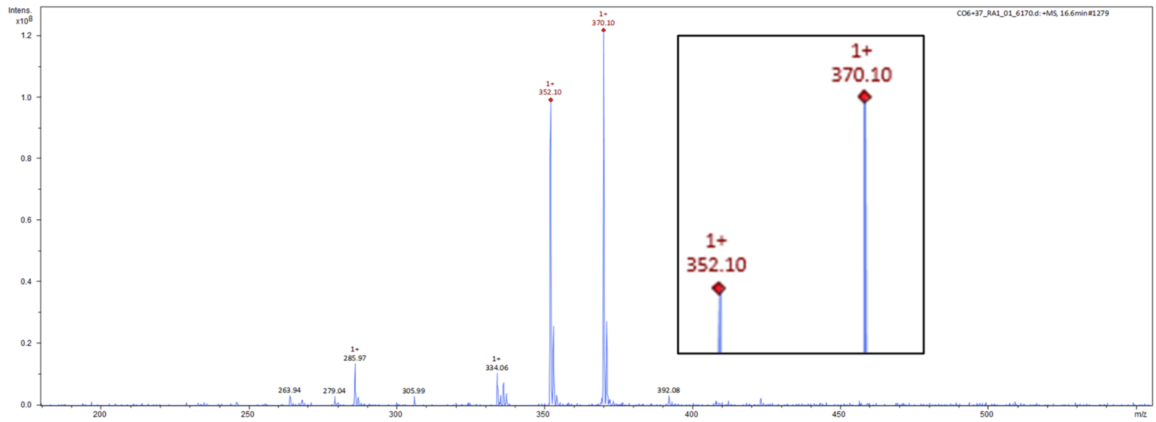
Compound	35	40	38
MIC	>128	>128	>128

Figure S75 C1*α*-hydroxylation has the negative effect on anti-*S. aureus* 209P activity.

A



B



C

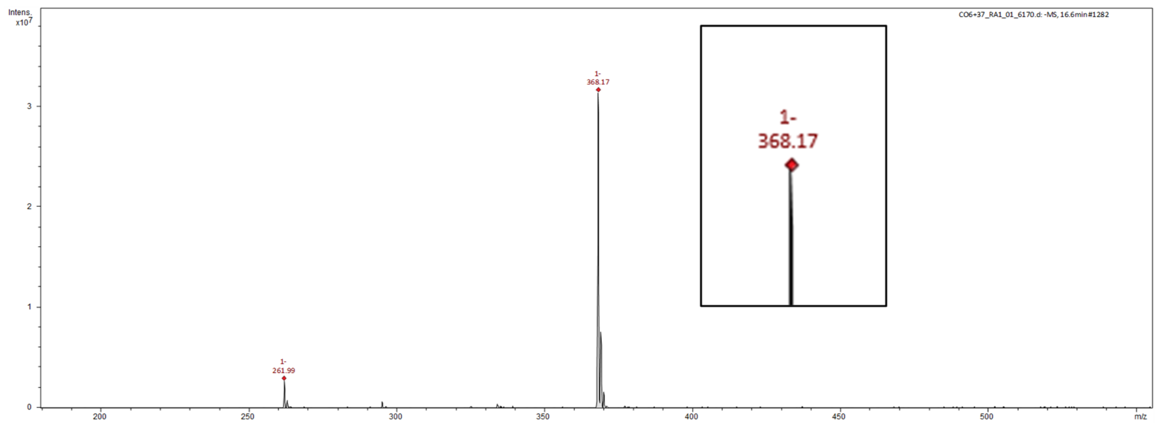


Figure S76 Analysis of the impurity peak in the feeding experiment using CO6 as the host. (A) The HPLC profile of CO6 incubated with **37**; (B) The positive mass spectrum of the impurity peak labelled with asterisk; (C) The negative mass spectrum of the impurity peak labelled with asterisk.

Supporting Tables

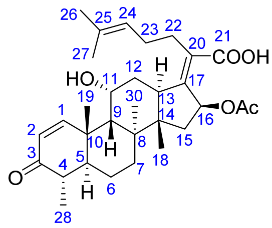
Table S1 Eight post-tailoring genes from *hel*, *fus* and *cep* clusters.

Tailoring gene	Annotated enzyme function
helE	3-Ketosteroid-Δ^1-dehydrogenase
helB3	Cytochrome P450 monooxygenase
helD1	Acetyl transferase
fusB1	Cytochrome P450 monooxygenase
fusC1	Short chain dehydrogenase/reductase
cepB4	Cytochrome P450 monooxygenase
cepC2	Short chain dehydrogenase/reductase
cepD2	Acetyl transferase

Table S2 All gene combinations and the obtained products.

Gene combination	Transformant	Product
Two-gene combination		
helE + fusB1	AOS1	**5**
helE + fusC1	AOS2	**6**, **7**, **8**
helE + cepB4	AOS3	**7**, **9**, **10**, **11**
fusB1 + cepB4	AOS4	**12**, **13**, **14**, **15**, **16**
fusB1 + helB3	AOS5	**17**, **18**, **19**, **20**, **21**, **22**
fusC1 + helB3	AOS6	**23**, **24**, **25**
Three-gene combination		
helE + fusB1 + helB3	AOS7	**26**, **27**, **28**
helE + fusB1 + fusC1	AOS8	**2**, **5**, **29**
helE + fusC1 + helB3	AOS9	**24**, **25**, **27**, **30**, **31**, **32**, **33**, **34**
helE + fusB1 + cepB4	AOS10	**9**, **11**, **35**, **36**, **37**, **38**, **39**, **40**
helE + fusC1 + cepB4	AOS11	**9**, **11**, **41**, **42**, **43**
helE + cepB4 + cepD2	AOS12	**7**, **11**, **44**, **45**, **46**
fusB1 + cepB4 + fusC1	AOS13	**15**, **47**, **48**, **49**
fusB1 + cepB4 + cepD2	AOS14	**50**, **51**, **52**, **53**, **54**
fusB1 + helB3 + fusC1	AOS15	**17**, **23**, **55**, **56**, **57**
fusB1 + helB3 + helD1	AOS16	**18**, **19**, **21**, **58**, **59**
fusC1 + helB3 + helD1	AOS17	**23**, **25**, **60**
Four-gene combination		
helE + fusB1 + helB3 + helD1	AOS18	**1**, **26**, **27**, **61**
helE + fusB1 + helB3 + fusC1	AOS19	**5**, **26**, **27**, **37**, **38**, **62**
helE + fusC1 + helB3 + helD1	AOS20	**24**, **25**, **27**, **30**, **31**, **33**, **63**
helE + cepC1 + fusB1 + cepB4	AOS21	**16**, **75**
helE + fusB1 + cepB4 + cepD2	AOS22	**5**, **44**, **53**
helE + fusC1 + cepB4 + cepD2	AOS23	**64**, **65**, **66**
fusB1 + fusC1 + cepB4 + cepD2	AOS24	**3**, **15**, **46**, **67**
fusB1 + fusC1 + helB3 + helD1	AOS25	**56**, **68**
Five-gene combination		
helE+ fusB1 + fusC1 + helB3 + helD1	AOS26	**23**, **60**, **68**, **69**
helE+ fusB1 + fusC1 + cepB4 + cepD2	AOS27	**5**, **9**, **29**

Table S3 NMR data for **5** (^{1}H for 400 MHz and ^{13}C for 100 MHz in $CDCl_3$).

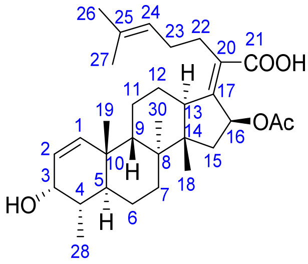


5

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	160.4, CH	7.66, d (10.3)	2	3, 5, 9, 10	11
2	126.6, CH	5.85, d (10.3)	1	4, 10	
3	202.2, C				
4	43.4, CH	2.35	5, 28		19
5	42.8, CH	2.41	4, 6a, 6b	4	28, 30
6	21.0, CH_2	a: 1.76	5, 6b, 7a, 7b		
		b: 1.33	5, 6a, 7a, 7b		
7	31.8, CH_2	a: 1.77	6a, 6b, 7b		
		b: 1.24	6a, 6b, 7a		
8	38.8, C				
9	49.2, CH	1.70, br s	11	1, 10, 11, 19, 30	18, 19
10	39.1, C				
11	67.5, CH	4.50, br s	9, 12a, 12b	9, 10, 13	1, 19
12	35.5, CH_2	a: 2.37	11, 12b, 13	11, 14	
		b: 2.00	11, 12a, 13	13	
13	44.0, CH	3.04, br d (11.5)	12a, 12b	12, 14, 17, 18, 20	15a, 16, 30
14	48.7, C				
15	39.1, CH_2	a: 2.17	15b, 16	14, 18	13
		b: 1.33	15a, 16	13, 14, 16, 17	
16	74.3, CH	5.89, br d (8.5)	15a, 15b	14, 17, 20, 16-<u>C</u>OCH3	13
17	150.3, C				
18	17.8, CH_3	0.94, s		8, 13, 14, 15	9
19	26.7, CH_3	1.21, s		1, 5, 9, 10	4, 9, 11
20	130.0, C				
21	174.5, C				
22	28.8, CH_2	2.45	23a, 23b	17, 20, 21, 23, 24	24
23	28.3, CH_2	a: 2.17	22, 23b, 24	24, 25	
		b: 2.08	22, 23a, 24	24, 25	
24	122.8, CH	5.09, br t (7.0)	23a, 23b, 26, 27	22, 23, 26, 27	22, 26
25	132.8, C				
26	25.7, CH_3	1.67, br s	24	24, 25, 27	24
27	17.8, CH_3	1.59, br s	24	24, 25, 26	
28	12.5, CH_3	1.12, d (6.6)	4	3, 4, 5	5
30	23.5, CH_3	1.28, s		7, 8, 9, 14	5, 13
16-<u>C</u>OCH3	170.5, C				
16-CO<u>C</u>H3	20.5, CH_3	1.96, s		16-<u>C</u>OCH3	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S4 NMR data for **6** (^{1}H for 600 MHz and ^{13}C for 150 MHz in $CDCl_3$).



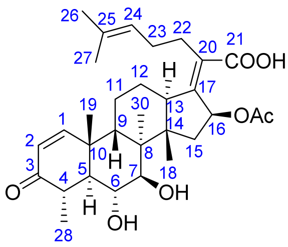
6

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	NOESY	δ_H (J in Hz)[b]
1	141.1, CH	6.15, d (9.8)	2	3, 5, 9, 10	11a, 19	6.15, d (10.0)
2	126.9, CH	5.61, br d (9.8)	1, 3	3, 4, 10		5.62, dd (10.0, 4.3)
3	68.8, CH	3.94, br s	2, 4	1, 2, 5	28	3.94, t (4.4)
4	33.1, CH	1.95	3, 5, 28	5, 10, 28	19	1.97
5	38.3, CH	1.83, br t (11.9)	4, 6a, 6b	1, 3, 4, 10, 19	28, 30	1.83, td (11.6, 1.9)
6	19.1, CH_2	a: 1.60	5, 6b, 7a, 7b	5, 10	28	a: 1.61
		b: 1.11	5, 6a, 7a, 7b	4, 5, 7, 10		b: 1.12
7	33.5, CH_2	a: 1.91	6a, 6b, 7b	5, 6, 14, 30		a: 1.92
		b: 1.24	6a, 6b, 7a	6, 8, 9, 30		b: 1.25
8	38.6, C					
9	44.2, CH	1.55, br d (13.3)	11a, 11b	1, 10, 11, 19, 30	18, 19	1.56, dd (12.9, 3.1)
10	38.3, C					
11	24.8, CH_2	a: 1.72	9, 11b, 12a, 12b	10	1, 19	a: 1.73
		b: 1.35	9, 11a, 12a, 12b	9	30	b: 1.36
12	26.2, CH_2	a: 2.28, br d (11.1)	11a, 11b, 12b, 13	9, 14		a: 2.29
		b: 1.68	11a, 11b, 12a, 13	11, 13		b: 1.69
13	49.0, CH	2.54	12a, 12b	12, 14, 17, 18	30	2.55
14	48.5, C					
15	39.2, CH_2	a: 2.04	15b, 16	8, 14, 18		a: 2.05
		b: 1.30	15a, 16	13, 14, 16, 17, 18		b: 1.30
16	74.2, CH	5.84, br d (7.6)	15a, 15b	14, 17, 20, 16-CO<u>C</u>H3		5.84, br d (8.3)
17	150.4, C					
18	18.3, CH_3	0.94, s		8, 13, 14, 15	9	0.95, s
19	26.2, CH_3	0.94, s		1, 5, 9, 10	1, 4, 9, 11a	0.95, s
20	129.6, C					
21	173.8, C					
22	28.6, CH_2	a: 2.51	22b, 23a, 23b	17, 20, 21, 23, 24	24	a: 2.53
		b: 2.43	22a, 23a, 23b	17, 20, 21, 23, 24	24	b: 2.44
23	28.3, CH_2	a: 2.12	22a, 22b, 23b, 24	20, 22, 24, 25		a: 2.13
		b: 2.06	22a, 22b, 23a, 24	20, 22, 24, 25		b: 2.07
24	123.0, CH	5.09, br s	23a, 23b, 26, 27	23, 26, 27	22a, 22b, 26	5.11, t (7.1)
25	132.6, C					
26	25.7, CH_3	1.68, br s	24	24, 25, 27	24	1.68, br s
27	17.7, CH_3	1.59, br s	24	24, 25, 26		1.61, br s
28	14.2, CH_3	0.98, d (6.0)	4	3, 4, 5	3, 5, 6a	0.98, d (6.8)
30	21.7, CH_3	1.01, s		7, 8, 9, 14	5, 13, 11b	1.02, s
16-<u>C</u>OCH3	170.6, C					
16-CO<u>C</u>H3	20.6, CH_3	1.96, s		16-<u>C</u>OCH3		1.98, s

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

The ^{1}H NMR data of **6** obtained *via* chemical derivatization were measured at low concentrations of the compound in $CDCl_3$.

Table S5 NMR data for **9** (^{1}H for 600 MHz and ^{13}C for 150 MHz in $CDCl_3$).

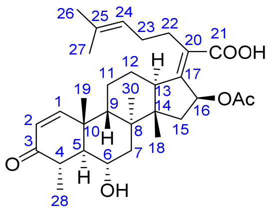


9

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H—^{1}H COSY	HMBC	NOESY
1	157.4, CH	7.28, d (10.1)	2	3, 5, 9, 10, 19	11a, 11b
2	127.9, CH	5.85, d (10.1)	1	4, 10	
3	203.2, C				
4	42.5, CH	2.73, dq (12.0, 6.7)	5, 28	3, 5, 6, 10, 28	6, 19
5	49.2, CH	1.96	4, 6	1, 4, 6, 7, 10, 19, 28	7, 28, 30
6	74.2, CH	3.71, dd (11.1, 8.2)	5, 7	5, 7, 10	4, 19
7	87.1, CH	3.51, d (8.2)	6	5, 6, 8, 9, 30	5
8	45.1, C				
9	42.7, CH	1.95	11a, 11b	8, 10, 11, 30	18
10	40.3, C				
11	24.5, CH_2	a: 1.71	9, 11b, 12a, 12b		1
		b: 1.54 qd (13.3, 4.1)	9, 11a, 12a, 12b		1, 13
12	25.8, CH_2	a: 2.34	11a, 11b, 12b, 13	11	
		b: 1.80	11a, 11b, 12a, 13	13, 14, 17	
13	50.7, CH	2.60, br d (10.9)	12a, 12b	14, 17, 18, 20	11b, 16, 30
14	47.7, C				
15	40.9, CH_2	a: 2.20, dd (14.2, 8.5)	15b, 16	8, 14, 18	30
		b: 1.81	15a, 16	13, 14, 16, 17, 18	
16	74.2, CH	5.89, br d (8.5)	15a, 15b	14, 17, 20, 16-<u>C</u>OCH$_3$	13, 30
17	148.8, C				
18	20.8, CH_3	1.22, s		8, 13, 14, 15	9
19	27.5, CH_3	1.23, s		1, 5, 9, 10	4, 6
20	130.4, C				
21	173.8, C				
22	28.6, CH_2	a: 2.51	22b, 23a, 23b	17, 20, 21, 23, 24	24
		b: 2.44	22a, 23a, 23b	17, 20, 21, 23, 24	24
23	28.3, CH_2	a: 2.13	22a, 22b, 23b, 24	20, 22, 24, 25	
		b: 2.07	22a, 22b, 23a, 24	20, 22, 24, 25	
24	122.9, CH	5.10, br t (7.4)	23a, 23b, 26, 27	23, 26, 27	22a, 22b, 26
25	132.7, C				
26	25.7, CH_3	1.68, br s	24	24, 25, 27	24
27	17.7, CH_3	1.60, br s	24	24, 25, 26	
28	17.3, CH_3	1.42, d (6.9)	4	3, 4, 5	5
30	21.4, CH_3	1.10, s		7, 8, 9, 14	5, 13, 15a, 16
16-<u>C</u>OCH$_3$	171.0, C				
16-CO<u>C</u>H$_3$	20.7, CH_3	1.98, s		16-<u>C</u>OCH$_3$	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S6 NMR data for **10** (^{1}H for 600 MHz and ^{13}C for 150 MHz in $CDCl_3$).

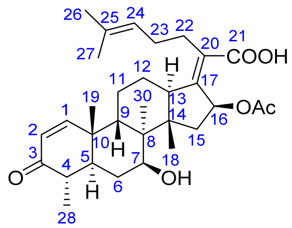


10

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	NOESY
1	157.6, CH	7.27, d (10.3)	2	3, 5, 9, 10	
2	127.7, CH	5.86, d (10.3)	1	4, 10	
3	203.1, C				
4	43.0, CH	2.70, dq (11.9, 6.9)	5, 28	3, 5, 6, 10, 28	19
5	51.7, CH	2.16, t (11.6)	4, 6	1, 3, 4, 6, 7, 10, 19, 28	30
6	69.1, CH	3.91, ddd (10.7, 8.2, 6.7)	5, 7a, 7b	5, 7, 10	9, 19
7	45.6, CH_2	a: 2.32, dd (13.8, 6.7)	6, 7b	5, 6, 8, 9, 14, 30	18
		b: 1.17	6, 7a	6, 30	
8	39.2, C				
9	44.0, CH	1.65, dd (12.7, 2.8)	11a, 11b	1, 8, 10, 11, 19, 30	6, 18
10	39.8, C				
11	24.6, CH_2	a: 1.74	9, 11b, 12a, 12b	8, 9	
		b: 1.46	9, 11a, 12a, 12b	8, 9, 12, 13	
12	26.0, CH_2	a: 2.36	11a, 11b, 12b, 13		
		b: 1.72	11a, 11b, 12a, 13	11, 13	18
13	48.7, CH	2.57, br d (11.6)	12a, 12b	12, 14, 17, 18, 20	16, 30
14	48.2, C				
15	39.1, CH_2	a: 2.06	15b, 16	8, 14, 18	30
		b: 1.35, br d (14.2)	15a, 16	13, 16, 17, 18	18
16	73.9, CH	5.87, br d (8.2)	15a, 15b	14, 17, 20, 16-<u>C</u>OCH_3	13
17	149.7, C				
18	18.3, CH_3	1.01, s		8, 13, 14, 15	7a, 9, 12b, 15b
19	27.3, CH_3	1.18, s		1, 5, 9, 10	4, 6
20	129.9, C				
21	172.9, C				
22	28.6, CH_2	a: 2.51	22b, 23a, 23b	17, 20, 21, 23, 24	24
		b: 2.45	22a, 23a, 23b	17, 20, 21, 23, 24	24
23	28.3, CH_2	a: 2.14	22a, 22b, 23b, 24	20, 22, 24, 25	
		b: 2.08	22a, 22b, 23a, 24	20, 22, 24, 25	
24	122.8, CH	5.10, br t (6.9)	23a, 23b, 26, 27	23, 26, 27	22a, 22b, 26
25	132.8, C				
26	25.7, CH_3	1.68, br s	24	24, 25, 27	24
27	17.7, CH_3	1.60, br s	24	24, 25, 26	
28	17.0, CH_3	1.43, d (6.9)	4	3, 4, 5	
30	21.0, CH_3	1.10, s		7, 8, 9, 14	5, 13, 15a
16-<u>C</u>OCH_3	170.5, C				
16-CO<u>C</u>H_3	20.6, CH_3	1.98, s		16-<u>C</u>OCH_3	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S7 NMR data for **11** (^{1}H for 400 MHz and ^{13}C for 100 MHz in $CDCl_3$).

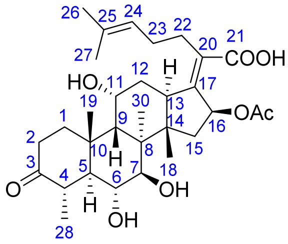


11

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	159.2, CH	7.29, d (10.2)	2	3, 5, 10	11a, 11b
2	127.6, CH	5.81, d (10.2)	1	4, 10	
3	202.4, C				
4	42.4, CH	2.44	5, 28		19
5	44.5, CH	1.93	4, 6a, 6b	1, 4, 6, 7, 10, 19	28, 30
6	32.9, CH_2	a: 1.98	5, 6b, 7		
		b: 1.39	5, 6a, 7	7	
7	79.7, CH	3.86, dd (8.7, 6.9)	6a, 6b	6, 9, 30	30
8	45.0, C				
9	43.0, CH	2.03	11a, 11b	8, 10, 19, 30	18, 19
10	39.0, C				
11	24.8, CH_2	a: 1.82	9, 11b, 12a, 12b	8, 13	1
		b: 1.51, qd (14.4, 4.0)	9, 11a, 12a, 12b		1
12	25.8, CH_2	a: 2.33	11a, 11b, 12b, 13	14	
		b: 1.80	11a, 11b, 12a, 13	13	
13	50.8, CH	2.58, br d (10.4)	12a, 12b	12, 14, 17, 18, 20	16, 30
14	48.0, C				
15	40.7, CH_2	a: 2.18, dd (14.4, 8.8)	15b, 16	14, 18	30
		b: 1.73, br d (14.4)	15a, 16	13, 14, 16, 17, 18	
16	74.3, CH	5.86, br d (8.4)	15a, 15b	14, 17, 20, 16-<u>C</u>OCH₃	13
17	149.1, C				
18	21.2, CH_3	1.21, s		8, 13, 14, 15	9
19	25.7, CH_3	1.22, s		1, 5, 9, 10	4, 9
20	130.4, C				
21	174.5, C				
22	28.6, CH_2	2.46	23	17, 20, 21, 23, 24	24
23	28.2, CH_2	2.09	22, 24	22, 24, 25	
24	122.9, CH	5.09, br t (7.1)	23, 26, 27	23, 26, 27	22, 26
25	132.6, C				
26	25.7, CH_3	1.67, br s	24	24, 25, 27	24
27	17.7, CH_3	1.59, br s	24	24, 25, 26	
28	12.9, CH_3	1.13, d (6.7)	4	3, 4, 5	5
30	21.2, CH_3	0.98, s		7, 8, 9, 14	5, 7, 13, 15a
16-<u>C</u>OCH₃	170.8, C				
16-CO<u>C</u>H₃	20.6, CH_3	1.95, s		16-<u>C</u>OCH₃	

[a]The indiscernible signals due to overlap or the complex multiplicity are reported without designating multiplicity.

Table S8 NMR data for **12** (^{1}H for 400 MHz and ^{13}C for 100 MHz in $CDCl_3$).

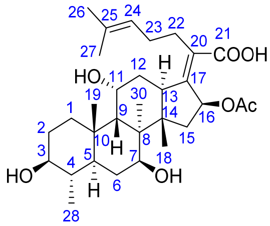


12

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	33.8, CH_2	a: 2.58	1b, 2a, 2b	19	30
		b: 1.80	1a, 2a, 2b	5, 10, 19	
2	34.9, CH_2	a: 2.58	1a, 1b, 2b		
		b: 2.36	1a, 1b, 2a	3	
3	217.8, C				
4	45.1, CH	2.50	5, 28		6, 19
5	48.9, CH	1.87, t (10.6)	4, 6	6, 7, 19	7, 28, 30
6	73.9, CH	3.53, dd (10.4, 8.3)	5, 7	7	4, 9, 19
7	87.3, CH	3.48, d (8.2)	6	6, 30	5, 30
8	46.4, C				
9	46.2, CH	1.78	11	1, 5, 8, 10, 19, 30	6, 18, 19
10	38.5, C				
11	67.8, CH	4.36, br s	9, 12a, 12b	8, 9, 13	19
12	36.3, CH_2	a: 2.28	11, 12b, 13	14	22
		b: 1.99	11, 12a, 13		18
13	46.3, CH	3.06, br d (12.7)	12a, 12b	12, 14, 17, 20	16, 30
14	48.3, C				
15	40.8, CH_2	a: 2.31	15b, 16	14	30
		b: 1.79	15a, 16	8	18
16	74.5, CH	5.91, br d (8.3)	15a, 15b	14, 17, 20, 16-<u>C</u>OCH$_3$	13
17	149.9, C				
18	20.4, CH_3	1.17, s		8, 13, 14, 15	9, 12b, 15b
19	23.8, CH_3	1.02, s		1, 5, 9, 10	4, 6, 9, 11
20	130.2, C				
21	173.8, C				
22	28.8, CH_2	2.45	23a, 23b	17, 20, 21, 23, 24,	12a, 24
23	28.3, CH_2	a: 2.14	22, 23b, 24		
		b: 2.08	22, 23a, 24		
24	122.9, CH	5.09, br t (6.9)	23a, 23b, 26, 27	26, 27	22, 26
25	132.7, C				
26	25.7, CH_3	1.67, br s	24	24, 25, 27	24
27	17.8, CH_3	1.59, br s	24	24, 25, 26	
28	18.8, CH_3	1.31, d (6.9)	4	3, 4, 5	5
30	25.8, CH_3	1.45, s		7, 8, 9, 14	1a, 5, 7, 13, 15a
16-<u>C</u>OCH$_3$	171.1, C				
16-CO<u>C</u>H$_3$	20.7, CH_3	1.97, s		16-<u>C</u>OCH$_3$	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S9 NMR data for **13** ([1]H for 600 MHz and [13]C for 150 MHz in $CDCl_3$).

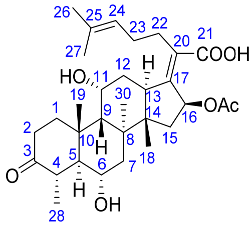


13

Position	δC, type	δH (*J* in Hz)[a]	[1]H–[1]H COSY	HMBC	NOESY
1	34.8, CH_2	a: 1.97	1b, 2a, 2b	2, 10, 19	
		b: 1.77	1a, 2a, 2b	2, 3, 5, 10	
2	31.6, CH_2	a: 1.91	1a, 1b, 2b, 3	3	
		b: 1.66	1a, 1b, 2a, 3	1, 3	
3	76.6, CH	3.13, td (10.8, 4.9)	2a, 2b, 4	2, 4, 5, 28	28
4	39.1, CH	1.48	3, 5, 28	3, 5	19
5	42.6, CH	1.41, td (11.8, 4.0)	4, 6a, 6b	3, 4, 6, 7, 10, 19	7, 28, 30
6	33.8, CH_2	a: 2.03	5, 6b, 7	5, 7, 8, 10	19
		b: 1.16	5, 6a, 7	7	
7	79.0, CH	3.73, t (6.2)	6a, 6b	5, 6, 8, 9, 14, 30	5, 30
8	45.2, C				
9	46.5, CH	1.92, br s	11	1, 7, 8, 10, 11, 14, 19, 30	18, 19
10	36.8, C				
11	68.6, CH	4.40, br s	9, 12a, 12b	8, 13	19
12	35.9, CH_2	a: 2.29	11, 12b, 13	11	
		b: 1.96	11, 12a, 13		
13	46.4, CH	3.06, br d (11.6)	12a, 12b	12, 14, 17, 18, 20	16, 30
14	48.6, C				
15	40.3, CH_2	a: 2.26	15b, 16	8, 14, 18	30
		b: 1.62, br d (14.4)	15a, 16	13, 14, 16, 17, 18	18
16	74.4, CH	5.91, br d (8.4)	15a, 15b	13, 14, 17, 20, 16-<u>C</u>OCH3	13
17	150.5, C				
18	21.3, CH_3	1.17, s		8, 13, 14, 15	9, 15b
19	22.9, CH_3	1.15, s		1, 5, 9, 10	4, 6a, 9, 11
20	130.0, C				
21	173.8, C				
22	28.8, CH_2	2.46	23a, 23b	17, 20, 21, 23, 24	24
23	28.3, CH_2	a: 2.16	22, 23b, 24	20, 22, 24, 25	
		b: 2.06	22, 23a, 24	20, 22, 24, 25	
24	123.0, CH	5.10, br t (6.6)	23a, 23b, 26, 27	23, 26, 27	22, 26
25	132.7, C				
26	25.7, CH_3	1.67, br s	24	24, 25, 27	24
27	17.8, CH_3	1.60, br s	24	24, 25, 26	
28	15.4, CH_3	0.96, d (6.1)	4	3, 4, 5	3, 5
30	23.9, CH_3	1.30, s		7, 8, 9, 14	5, 7, 13, 15a
16-<u>C</u>OCH3	170.7, C				
16-CO<u>C</u>H3	20.6, CH_3	1.97, s		16-<u>C</u>OCH3	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S10 NMR data for **14** (^{1}H for 400 MHz and ^{13}C for 100 MHz in $CDCl_3$).

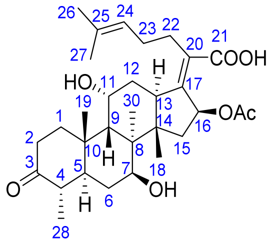


14

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	34.4, CH_2	a: 2.58	1b, 2a, 2b		5, 30
		b: 1.89	1a, 2a, 2b	3, 5	19
2	36.1, CH_2	a: 2.53	1a, 1b, 2b	1, 3	
		b: 2.41	1a, 1b, 2a	1, 3	19
3	215.9, C				
4	46.0, CH	2.49	5, 28		6, 19
5	51.1, CH	2.10	4, 6	4, 6, 10, 19	1a, 30
6	69.7, CH	3.79	5, 7a, 7b		4, 9, 19, 28
7	44.7, CH_2	a: 2.15	6, 7b	9, 14	9, 18
		b: 1.20, dd (14.0, 5.5)	6, 7a		
8	39.9, C				
9	48.4, CH	1.56, br s	11	1, 8, 10, 11, 19, 30	6, 7a, 12b, 18, 19
10	37.4, C				
11	67.6, CH	4.37, br s	9, 12a, 12b	8, 13	19
12	36.2, CH_2	a: 2.30, br d (13.2)	11, 12b, 13	14	
		b: 1.90	11, 12a, 13		9, 18
13	43.8, CH	3.06, br d (11.4)	12a, 12b	12, 14, 17, 18, 20	15a, 16, 30
14	48.4, C				
15	39.0, CH_2	a: 2.20	15b, 16	18	13
		b: 1.36, br d (14.5)	15a, 16	16	18
16	74.2, CH	5.93, br d (8.2)	15a, 15b	14, 17, 20, 16-<u>C</u>OCH3	13
17	150.1, C				
18	17.9, CH_3	0.95, s		8, 13, 14, 15	7a, 9, 12b, 15b
19	24.8, CH_3	1.05, s		1, 5, 9, 10	1b, 2b, 4, 6, 9, 11
20	130.2, C				
21	173.9, C				
22	28.8, CH_2	2.45	23	17, 20, 21, 23, 24	24
23	28.3, CH_2	2.11	22, 24	24	
24	122.9, CH	5.09, br t (6.5)	23, 26, 27	26, 27	22, 26
25	132.7, C				
26	25.7, CH_3	1.67, br s	24	24, 25, 27	24
27	17.8, CH_3	1.59, br s	24	24, 25, 26	
28	16.9, CH_3	1.29, d (6.6)	4	3, 4, 5	6
30	24.2, CH_3	1.41, s		7, 8, 9, 14	1a, 5, 13
16-<u>C</u>OCH3	170.7, C				
16-CO<u>C</u>H3	20.6, CH_3	1.97, s		16-<u>C</u>OCH3	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S11 NMR data for **15** (^{1}H for 400 MHz and ^{13}C for 100 MHz in $CDCl_3$).

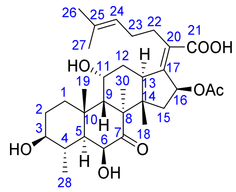


15

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	35.7, CH_2	a: 2.39	1b, 2		
		b: 1.99	1a, 2		
2	38.0, CH_2	2.46	1a, 1b	3	19
3	213.5, C				
4	45.6, CH	2.35	5, 28	2	19
5	44.5, CH	1.82, td (11.8, 4.0)	4, 6a, 6b		7, 28, 30
6	34.5, CH_2	a: 1.99	5, 6b, 7		
		b: 1.29	5, 6a, 7		
7	78.9, CH	3.76, t (6.5)	6a, 6b	5, 8, 30	5, 30
8	45.4, C				
9	46.4, CH	2.01, br s	11	1, 7, 8, 10, 11, 12, 14, 19, 30	18, 19
10	36.8, C				
11	68.4, CH	4.44, br s	9, 12a, 12b	8, 13	19
12	36.2, CH_2	a: 2.29	11, 12b, 13	9, 11, 13, 14	
		b: 1.99	11, 12a, 13		
13	46.3, CH	3.07, br d (11.3)	12a, 12b	12, 14, 17, 18, 20	16, 30
14	48.5, C				
15	40.3, CH_2	a: 2.28	15b, 16	13, 14, 18	
		b: 1.65	15a, 16	13, 14, 16, 17, 18	
16	74.4, CH	5.91, br d (8.4)	15a, 15b	14, 17, 20, 16-<u>C</u>OCH3	13
17	150.2, C				
18	21.1, CH_3	1.19, s		8, 13, 14, 15	9
19	22.3, CH_3	1.29, s		1, 5, 9, 10	2, 4, 9, 11
20	130.4, C				
21	174.3, C				
22	28.7, CH_2	2.45	23	17, 20, 21, 23, 24	24
23	28.3, CH_2	2.11	22, 24	24, 25	
24	123.0, CH	5.09, br t (7.0)	23, 26, 27	26, 27	22, 26
25	132.7, C				
26	25.7, CH_3	1.67, br s	24	24, 25, 27	24
27	17.8, CH_3	1.59, br s	24	24, 25, 26	
28	12.3, CH_3	1.01, d (6.6)	4	3, 4, 5	5
30	24.0, CH_3	1.29, s		7, 8, 9, 14	5, 7, 13
16-<u>C</u>OCH3	170.8, C				
16-CO<u>C</u>H3	20.6, CH_3	1.96, s		16-<u>C</u>OCH3	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S12 NMR data for **17** (^{1}H for 600 MHz and ^{13}C for 150 MHz in $CDCl_3$).



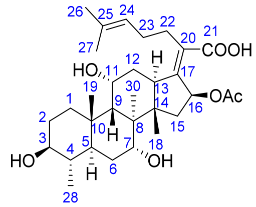
17

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H—^{1}H COSY	HMBC	ROESY[b]
1	35.5, CH_2	a: 1.97	1b, 2a, 2b	2, 3, 19	3
		b: 1.74	1a, 2a, 2b	2, 3, 5	11
2	31.6, CH_2	a: 1.95	1a, 1b, 2b, 3	1	
		b: 1.72	1a, 1b, 2a, 3	1, 3, 4	
3	76.7, CH	3.19, td (10.9, 5.3)	2a, 2b, 4	2, 4, 28	1a, 5, 28
4	35.3, CH	2.01	3, 5, 28	3, 5, 28	19
5	46.0, CH	1.65, br d (10.6)	4, 6	1, 3, 4, 19	3
6	72.8, CH	4.03, d (2.5)	5	5, 7, 8, 10	28
7	215.9, C				
8	52.8, C				
9	46.1, CH	2.30, br s	11	7, 8, 10, 11, 19, 30	18, 19
10	36.2, C				
11	68.1, CH	4.49, br s	9, 12a, 12b	8, 13	1b, 19
12	35.8, CH_2	a: 2.32	11, 12b, 13	11	
		b: 1.96	11, 12a, 13		
13	44.4, CH	3.09, br d (11.5)	12a, 12b	12, 14, 17, 18, 20	16, 30
14	46.8, C				
15	40.4, CH_2	a: 2.31	15b, 16	18	
		b: 1.91	15a, 16	13, 14, 16, 17, 18	
16	73.9, CH	5.91, br d (8.5)	15a, 15b	13, 14, 17, 20, 16-<u>C</u>OCH3	13
17	148.7, C				
18	18.0, CH_3	0.96, s		8, 13, 14, 15	9
19	25.1, CH_3	1.28, s		1, 5, 9, 10	4, 9, 11
20	130.0, C				
21	173.2, C				
22	28.7, CH_2	2.46	23a, 23b	17, 20, 21, 23, 24	24
23	28.3, CH_2	a: 2.14	22, 23b, 24	20, 22, 24, 25	
		b: 2.07	22, 23a, 24	20, 22, 24, 25	
24	122.9, CH	5.10, br t (7.2)	23a, 23b, 26, 27	23, 26, 27	22, 26
25	132.8, C				
26	25.7, CH_3	1.67, br s	24	24, 25, 27	24
27	17.8, CH_3	1.60, br s	24	24, 25, 26	
28	15.1, CH_3	1.08, d (6.3)	4	3, 4, 5	3, 6
30	21.5, CH_3	1.47, s		7, 8, 9, 14	13
16-<u>C</u>OCH3	170.6, C				
16-CO<u>C</u>H3	20.6, CH_3	1.98, s		16-<u>C</u>OCH3	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

[b]The data is recorded at 400 MHz.

Table S13 NMR data for **18** (^{1}H for 600 MHz and ^{13}C for 150 MHz in CD_3OD).

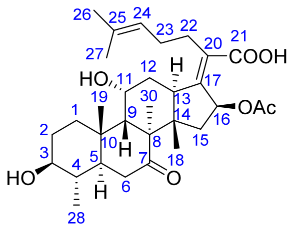


18

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H—^{1}H COSY	HMBC	NOESY
1	34.7, CH_2	a: 2.11	1b, 2a, 2b	2, 3, 10, 19	3, 11
		b: 1.71, dt (13.5, 3.6)	1a, 2a, 2b	3	11, 19
2	32.3, CH_2	a: 1.77	1a, 1b, 2b, 3	1	
		b: 1.55	1a, 1b, 2a, 3	10	
3	76.9, CH	3.00	2a, 2b, 4	2, 4, 28	1a, 5, 28
4	42.0, CH	1.29	3, 5, 28	3, 5	19
5	43.8, CH	1.85	4, 6a, 6b	3, 4, 6, 10, 19	3, 28, 30
6	35.1, CH_2	a: 1.67	5, 6b, 7	7, 8	
		b: 1.59	5, 6a, 7		
7	71.4, CH	3.87, t (8.3)	6a, 6b	6, 8, 9, 14, 30	9, 18
8	46.2, C				
9	51.4, CH	1.51, d (1.4)	11	7, 8, 10, 11, 14, 19, 30	7, 18, 19
10	37.1, C				
11	68.5, CH	4.31, br s	9, 12a, 12b	8, 13	1a, 1b, 19
12	37.3, CH_2	a: 2.29	11, 12b, 13	11, 14	
		b: 1.84	11, 12a, 13	13	18
13	45.3, CH	3.02	12a, 12b	11, 12, 14, 17, 18, 20	16, 30
14	49.2, C				
15	43.0, CH_2	a: 2.25	15b, 16	8, 14, 18	30
		b: 1.57	15a, 16	13, 14, 16, 17, 18	
16	76.0, CH	5.75, br d (8.7)	15a, 15b	13, 14, 15, 17, 20, 16-<u>C</u>OCH$_3$	13
17	147.8, C				
18	16.7, CH_3	0.99, s		8, 13, 14, 15	7, 9, 12b
19	25.7, CH_3	0.99, s		1, 5, 9, 10	1b, 4, 9, 11
20	132.0, C				
21	174.6, C				
22	29.8, CH_2	a: 2.55	22b, 23	17, 20, 21, 23, 24	24
		b: 2.35	22a, 23	17, 20, 21, 23, 24	24
23	29.4, CH_2	2.09	22a, 22b, 24	20, 22, 24, 25	
24	124.4, CH	5.13, br t (7.3)	23, 26, 27	23, 26, 27	22a, 22b, 26
25	133.3, C				
26	25.9, CH_3	1.66, br s	24	24, 25, 27	24
27	17.9, CH_3	1.60, br s	24	24, 25, 26	
28	15.8, CH_3	0.95, d (6.3)	4	3, 4, 5	3, 5
30	15.0, CH_3	1.26, s		7, 8, 9, 14	5, 13, 15a
16-<u>C</u>OCH$_3$	172.6, C				
16-CO<u>C</u>H$_3$	20.7, CH_3	1.95, s		16-<u>C</u>OCH$_3$	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S14 NMR data for **19** (^{1}H for 600 MHz and ^{13}C for 150 MHz in CD_3OD).

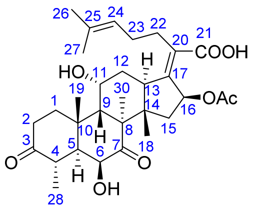


19

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	NOESY
1	35.5, CH_2	1.90	2a, 2b	2, 3, 5, 10, 19	
2	32.7, CH_2	a: 1.87	1, 2b, 3	1, 3	
		b: 1.67	1, 2a, 3	3	19
3	77.2, CH	3.03	2a, 2b, 4	2, 4, 5, 28	5, 28
4	38.2, CH	1.57	3, 5, 28	3, 5, 28	19
5	43.9, CH	1.50	4, 6a, 6b	1, 3, 4, 6, 7, 10, 19	3, 28, 30
6	41.1, CH_2	a: 2.26	5, 6b	5, 7, 8, 10	28
		b: 2.18, t (14.6)	5, 6a	5, 7, 10	19
7	221.5, C				
8	54.6, C				
9	48.0, CH	1.86, br s	11	1, 7, 8, 10, 11, 14, 19, 30	18, 19
10	37.9, C				
11	67.5, CH	4.37, br d (1.6)	9, 12a, 12b	8, 10, 13	19
12	36.9, CH_2	a: 2.32	11, 12b, 13		
		b: 1.84	11, 12a, 13	13	
13	44.8, CH	3.05	12a, 12b	12, 14, 17, 18, 20	16, 30
14	48.4, C				
15	41.8, CH_2	a: 2.29	15b, 16	8, 14, 18	30
		b: 1.72, br d (14.7)	15a, 16	13, 14, 16, 17, 18	18
16	75.5, CH	5.79, br d (8.5)	15a, 15b	13, 14, 15, 17, 20, 16-<u>C</u>OCH$_3$	13
17	145.9, C				
18	17.5, CH_3	0.82, s		8, 13, 14, 15	9, 15b
19	21.6, CH_3	1.11, s		1, 5, 9, 10	2b, 4, 6b, 9, 11
20	133.6, C				
21	174.8, C				
22	29.9, CH_2	a: 2.54	22b, 23	17, 20, 21, 23, 24	24
		b: 2.35	22a, 23	17, 20, 21, 23, 24	24
23	29.2, CH_2	2.10	22a, 22b, 24	22, 24, 25	
24	124.4, CH	5.13, br t (7.3)	23, 26, 27	23, 26, 27	22a, 22b, 26
25	133.3, C				
26	25.9, CH_3	1.66, br s	24	24, 25, 27	24
27	17.9, CH_3	1.60, br s	24	24, 25, 26	
28	15.7, CH_3	0.93, d (6.2)	4	3, 4, 5	3, 5, 6a
30	22.5, CH_3	1.41, s		7, 8, 9, 14	5, 13, 15a
16-<u>C</u>OCH$_3$	172.6, C				
16-CO<u>C</u>H$_3$	20.7, CH_3	1.95, s		16-<u>C</u>OCH$_3$	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S15 NMR data for **20** (^{1}H for 600 MHz and ^{13}C for 150 MHz in CD_3OD).

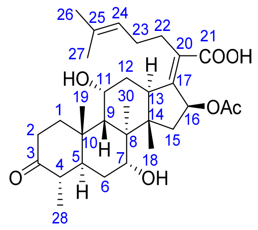


20

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	NOESY
1	37.3, CH_2	a: 2.40	1b, 2	2, 3, 10, 19	
		b: 1.98	1a, 2	2, 5, 10	
2	38.6, CH_2	2.50	1a, 1b	1, 3, 10	
3	216.9, C				
4	42.9, CH	2.87, dq (13.3, 6.7)	5, 28	3, 5, 6, 10, 28	19
5	47.5, CH	1.88, dd (12.5, 1.8)	4, 6	1, 3, 4, 7, 10, 19, 28	
6	74.5, CH	3.82, br s	5	4, 5, 7, 8, 10	30
7	216.9, C				
8	54.5, C				
9	45.7, CH	2.53, br s	11	1, 5, 7, 8, 10, 11, 14, 19, 30	19
10	37.3, C				
11	67.7, CH	4.47, br s	9, 12a, 12b	8, 13	19
12	36.9, CH_2	a: 2.35	11, 12b, 13	11, 14	
		b: 1.92	11, 12a, 13	13	
13	44.9, CH	3.12, br d (12.0)	12a, 12b	12, 14, 17. 18. 20	30
14	48.0, C				
15	41.9, CH_2	a: 2.34	15b, 16	8, 14, 18	
		b: 1.81, br d (14.6)	15a, 16	13, 14, 16, 17, 18	
16	75.5, CH	5.81, br d (8.5)	15a, 15b	13, 14, 15, 17, 20, 16-<u>C</u>OCH$_3$	
17	147.1, C				
18	18.7, CH_3	0.92, s		8, 13, 14, 15	
19	24.8, CH_3	1.45, s		1, 5, 9, 10	4, 9, 11
20	132.7, C				
21	174.2, C				
22	29.8, CH_2	a: 2.55	22b, 23a, 23b	17, 20, 21, 23, 24	24
		b: 2.37	22a, 23a, 23b	17, 20, 21, 23, 24	24
23	29.2, CH_2	a: 2.14	22a, 22b, 23b, 24	22, 24, 25	27
		b: 2.08	22a, 22b, 23a, 24	22, 24, 25	27
24	124.2, CH	5.13, br t (7.2)	23a, 23b, 26, 27	23, 26, 27	22a, 22b, 26
25	133.4, C				
26	25.9, CH_3	1.66, br s	24	24, 25, 27	24
27	17.9, CH_3	1.60, br s	24	24, 25, 26	23a, 23b
28	12.8, CH_3	1.06, d (6.8)	4	3, 4, 5	
30	22.4, CH_3	1.44, s		7, 8, 9, 14	6, 13
16-<u>C</u>OCH$_3$	172.6, C				
16-CO<u>C</u>H$_3$	20.7, CH_3	1.96, s		16-<u>C</u>OCH$_3$	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S16 NMR data for **21** ([1]H for 600 MHz and [13]C for 150 MHz in $CDCl_3$).

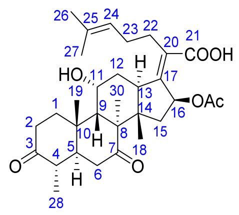


21

Position	δ_C, type	δ_H (J in Hz)[a]	[1]H–[1]H COSY	HMBC	NOESY
1	35.5, CH_2	a: 2.42	1b, 2a, 2b	2, 10, 19	11
		b: 1.97	1a, 2a, 2b	2, 3, 5, 10, 19	11
2	38.2, CH_2	a: 2.48	1a, 1b, 2b	1, 3	
		b: 2.37, br d (12.4)	1a, 1b, 2a	3, 10	
3	212.8, C				
4	46.5, CH	2.26	5, 28	2, 3, 5, 10, 28	19
5	44.5, CH	2.25	4, 6a, 6b	3, 4, 10, 19, 28	28, 30
6	35.0, CH_2	a: 1.82	5, 6b, 7	4, 5, 7	
		b: 1.53	5, 6a, 7	5, 7, 10	
7	70.4, CH	3.96, t (7.9)	6a, 6b	5, 6, 8, 9, 14, 30	9, 18, 19
8	44.7, C				
9	49.8, CH	1.59	11	7, 8, 10, 11, 12, 14, 19, 30	7, 12b, 18, 19
10	36.1, C				
11	68.1, CH	4.37, br s	9, 12a, 12b	8, 9, 10, 12, 13	1a, 1b, 19
12	36.0, CH_2	a: 2.30	11, 12b, 13	9, 11, 14	
		b: 1.92	11, 12a, 13	13	9, 18
13	44.3, CH	3.02, br d (12.1)	12a, 12b	11, 12, 14, 17, 18, 20	16, 30
14	47.9, C				
15	41.7, CH_2	a: 2.27	15b, 16	14, 18	
		b: 1.56	15a, 16	8, 14, 16, 17, 18	
16	74.3, CH	5.85, br d (8.4)	15a, 15b	13, 14, 17, 20, 16-<u>C</u>OCH3	13, 30
17	148.7, C				
18	16.7, CH_3	1.00, s		8, 13, 14, 15	7, 9, 12b
19	24.4, CH_3	1.19, s		1, 5, 9, 10	4, 7, 9, 11
20	130.0, C				
21	174.4, C				
22	28.7, CH_2	2.43	23a, 23b	17, 20, 21, 23, 24	24
23	28.4, CH_2	a: 2.13	22, 23b, 24	20, 22, 24, 25	
		b: 2.04	22, 23a, 24	20, 22, 24, 25	
24	123.0, CH	5.08, br t (6.8)	23a, 23b, 26, 27	23, 26, 27	22, 26
25	132.6, C				
26	25.7, CH_3	1.66, br s	24	24, 25, 27	24
27	17.8, CH_3	1.58, br s	24	24, 25, 26	
28	11.5, CH_3	0.98, d (5.0)	4	3, 4, 5	5
30	14.4, CH_3	1.23, s		7, 8, 9, 14	5, 13, 16
16-<u>C</u>OCH3	171.0, C				
16-CO<u>C</u>H3	20.6, CH_3	1.94, s		16-<u>C</u>OCH3	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S17 NMR data for **22** (^{1}H for 600 MHz and ^{13}C for 150 MHz in $CDCl_3$).



22

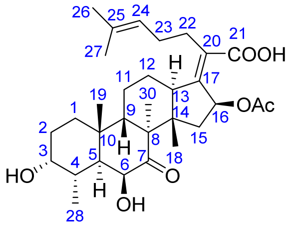
Position	δ_C, type	δ_H (J in Hz)[a]	^1H–^1H COSY[b]	HMBC[b]	ROESY[b]
1	34.7, CH_2	a: 2.36	1b, 2	9, 10, 19	
		b: 2.05	1a, 2	3, 19	
2	37.7, CH_2	2.52	1a, 1b	1, 3	19
3	212.2, C				
4	44.2, CH	2.40	5, 28	3, 5, 10	19
5	43.0, CH	1.99	4, 6a, 6b	4	30
6	40.4[c], CH_2	a: 2.32	5, 6b	7, 10	
		b: 2.19, t (14.7)	5, 6a	5, 7, 10	
7	216.7, C				
8	53.2, C				
9	46.5, CH	1.94, d (1.3)	11	1, 7, 8, 10, 11, 19, 30	18, 19
10	36.6, C				
11	67.4, CH	4.51, br s	9, 12a, 12b	8, 13	19
12	35.7, CH_2	a: 2.34	11, 12b, 13	11, 14	
		b: 1.91	11, 12a, 13		
13	43.9, CH	3.06, br d (11.8)	12a, 12b	12, 14, 17, 18, 20	16, 30
14	47.2, C				
15	40.5[c], CH_2	a: 2.32	15b, 16	18	
		b: 1.89, br d (14.7)	15a, 16	13, 14, 16, 17	
16	73.8, CH	5.93, br d (8.3)	15a, 15b	14, 17, 16-<u>C</u>OCH3	13
17	148.0, C				
18	17.1, CH_3	0.85, s		8, 13, 14, 15	9
19	21.3[d], CH_3	1.23, s		1, 5, 9, 10	2, 4, 9, 11
20	130.7, C				
21	174.1, C				
22	28.7, CH_2	2.42	23	17, 20, 21, 23, 24	24
23	28.3, CH_2	2.09	22, 24	22, 24, 25	
24	122.9, CH	5.09, br t (7.1)	23, 26, 27	26, 27	22, 26
25	132.7, C				
26	25.7, CH_3	1.67, br s	24	24, 25, 27	24
27	17.8, CH_3	1.59, br s	24	24, 25, 26	
28	12.6, CH_3	1.03, d (6.7)	4	3, 4, 5	
30	21.4[d], CH_3	1.41, s		7, 8, 9, 14	5, 13
16-<u>C</u>OCH3	170.7, C				
16-CO<u>C</u>H3	20.6, CH_3	1.95, s		16-<u>C</u>OCH3	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

[b]The data were recorded at 400 MHz.

[c,d]Assignment might be interchanged.

Table S18 NMR data for **23** (^{1}H for 400 MHz and ^{13}C for 100 MHz in $CDCl_3$).

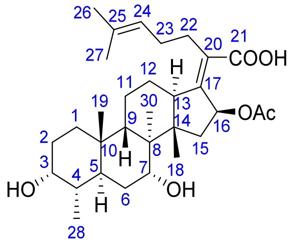


23

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	30.0, CH_2	a: 1.71	1b, 2a, 2b	19	
		b: 1.23	1a, 2a, 2b		
2	29.8, CH_2	a: 1.90	1a, 1b, 2b, 3		
		b: 1.70	1a, 1b, 2a, 3	3, 4, 10	
3	71.4, CH	3.89, br s	2a, 2b, 4	1, 2, 5, 28	
4	32.1, CH	2.23	3, 5, 28	5, 28	19
5	39.0, CH	2.12	4, 6,	1, 3, 4, 7, 10, 19	28, 30
6	73.8, CH	3.87, br s	5	4, 5, 7, 8, 10	28
7	217.7, C				
8	52.5, C				
9	41.7, CH	2.45	11a, 11b	1, 8, 10, 14, 19, 30	18, 19
10	35.6, C				
11	22.7, CH_2	a: 1.76	9, 11b, 12a, 12b	8	
		b: 1.38	9, 11a, 12a, 12b		13
12	26.1, CH_2	a: 2.27	11a, 11b, 12b, 13	9, 14	
		b: 1.71	11a, 11b, 12a, 13		
13	49.3, CH	2.51	12a, 12b	12, 14, 17, 18, 20	11b, 15a, 16, 30
14	46.7, C				
15	40.7, CH_2	a: 2.25	15b, 16	8, 14, 18	13
		b: 1.80	15a, 16	13, 14, 16, 17, 18	18
16	74.0, CH	5.80, br d (8.2)	15a, 15b	14, 17, 20, 16-<u>C</u>OCH3	13
17	148.8, C				
18	18.2, CH_3	0.89, s		8, 13, 14, 15	9, 15b
19	23.0, CH_3	1.25, s		1, 5, 9, 10	4, 9
20	130.1, C				
21	174.1, C				
22	28.4, CH_2	2.43	23	17, 20, 21, 23, 24	24
23	28.4, CH_2	2.06	22, 24	20, 22, 24, 25	
24	123.0, CH	5.07, br t (6.7)	23, 26, 27	23, 26, 27	22, 26
25	132.5, C				
26	25.6, CH_3	1.65, br s	24	24, 25, 27	24
27	17.7, CH_3	1.57, br s	24	24, 25, 26	
28	15.0, CH_3	0.97, d (6.2)	4	3, 4, 5	5, 6
30	17.4, CH_3	1.25, s		7, 8, 9, 14	5, 13
16-<u>C</u>OCH3	170.9, C				
16-CO<u>C</u>H3	20.4, CH_3	1.93, s		16-<u>C</u>OCH3	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S19 NMR data for **24** (^{1}H for 600 MHz and ^{13}C for 150 MHz in $CDCl_3$).

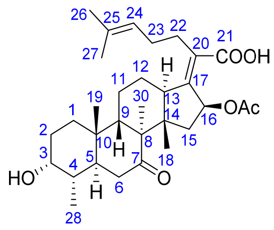


24

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	29.6, CH_2	a: 1.60	1b, 2a, 2b	2, 9, 10, 19	
		b: 1.27, br d (12.1)	1a, 2a, 2b	2, 3, 5	
2	29.7, CH_2	a: 1.77	1a, 1b, 2b, 3	1	
		b: 1.69	1a, 1b, 2a, 3	1	
3	71.3, CH	3.73, br s	2a, 2b, 4	1, 2, 5, 28	28
4	35.8, CH	1.55	3, 5, 28	5, 6, 28	19
5	34.7, CH	2.15	4, 6a, 6b	1, 3, 4, 6, 10, 19, 28	28, 30
6	33.4, CH_2	a: 1.66	5, 6b, 7	4, 5, 7, 8, 10	
		b: 1.37	5, 6a, 7	4, 5, 7, 8, 10	
7	70.4, CH	4.00, dd (8.1, 4.7)	6a, 6b	5, 6, 8, 14, 30	9, 18, 19
8	44.5, C				
9	45.9, CH	1.48	11a, 11b	8, 10, 12, 19, 30	7, 18, 19
10	35.7, C				
11	23.4, CH_2	a: 1.71	9, 11b, 12a, 12b		
		b: 1.35	9, 11a, 12a, 12b	8, 9, 10	
12	26.3, CH_2	a: 2.23	11a, 11b, 12b, 13	11, 14	
		b: 1.60	11a, 11b, 12a, 13	9, 11, 13	
13	49.3, CH	2.48	12a, 12b	12, 14, 17, 18, 20	16, 30
14	48.2, C				
15	41.6, CH_2	a: 2.24	15b, 16	8, 14, 18	30
		b: 1.49	15a, 16	13, 14, 16, 17, 18	18
16	74.4, CH	5.83, br d (8.6)	15a, 15b	14, 17, 20, 16-$\underline{C}OCH_3$	13
17	149.4, C				
18	17.9, CH_3	0.99, s		8, 13, 14, 15	7, 9, 15b
19	22.2, CH_3	0.87, s		1, 5, 9, 10	4, 7, 9
20	129.6, C				
21	174.1, C				
22	28.6, CH_2	a: 2.50	22b, 23a, 23b	17, 20, 21, 23, 24	24
		b: 2.40	22a, 23a, 23b	17, 20, 21, 23, 24	24
23	28.3, CH_2	a: 2.11	22a, 22b, 23b, 24	20, 22, 24, 25	
		b: 2.05	22a, 22b, 23a, 24	20, 22, 24, 25	
24	123.0, CH	5.09, br t (7.1)	23a, 23b, 26, 27	23, 26, 27	22a, 22b, 26
25	132.6, C				
26	25.7, CH_3	1.67, br s	24	24, 25, 27	24
27	17.7, CH_3	1.59, br s	24	24, 25, 26	
28	15.8, CH_3	0.90, d (6.8)	4	3, 4, 5	3, 5
30	12.3, CH_3	1.08, s		7, 8, 9, 14	5, 13, 15a
16-$\underline{C}OCH_3$	170.6, C				
16-$CO\underline{C}H_3$	20.6, CH_3	1.95, s		16-$\underline{C}OCH_3$	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S20 NMR data for **25** (^{1}H for 600 MHz and ^{13}C for 150 MHz in $CDCl_3$).

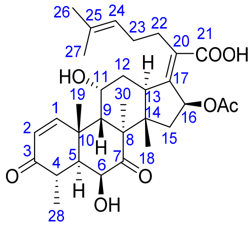


25

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	NOESY
1	28.2, CH_2	a: 1.72	1b, 2a, 2b	2, 10, 19	
		b: 1.33	1a, 2a, 2b	2, 3, 5, 10	
2	29.7, CH_2	a: 1.89	1a, 1b, 2b, 3		
		b: 1.75	1a, 1b, 2a, 3	3, 4, 10	
3	71.1, CH	3.82, br s	2a, 2b, 4	1, 5, 28	28
4	34.0, CH	1.81	3, 5, 28	5, 28	19
5	35.5, CH	2.21	4, 6a, 6b	1, 3, 4, 6, 7, 10, 19	28, 30
6	39.5, CH_2	a: 2.20	5, 6b	4, 7, 8, 10	
		b: 2.07	5, 6a	5, 7, 10	19
7	218.2, C				
8	52.5, C				
9	43.3, CH	1.91	11a, 11b	1, 8, 10, 11, 19, 30	18, 19
10	36.1, C				
11	22.7, CH_2	a: 1.74	9, 11b, 12a, 12b		
		b: 1.34	9, 11a, 12a, 12b	9	
12	26.1, CH_2	a: 2.28	11a, 11b, 12b, 13		
		b: 1.65	11a, 11b, 12a, 13	11, 13	18
13	49.2, CH	2.51	12a, 12b	12, 14, 17, 18, 20	16, 30
14	47.1, C				
15	40.6, CH_2	a: 2.28	15b, 16	8, 14, 18	
		b: 1.87	15a, 16	13, 14, 16, 17, 18	18
16	73.8, CH	5.85, br d (8.5)	15a, 15b	13, 14, 15, 17, 20, 16-<u>C</u>OCH$_3$	13
17	148.5, C				
18	17.4, CH_3	0.85, s		8, 13, 14, 15	9, 12b, 15b
19	19.6, CH_3	1.00, s		1, 5, 9, 10	4, 6b, 9
20	129.9, C				
21	174.0, C				
22	28.5, CH_2	a: 2.50	22b, 23a, 23b	17, 20, 21, 23, 24	24
		b: 2.41	22a, 23a, 23b	17, 20, 21, 23, 24	24
23	28.3, CH_2	a: 2.10	22a, 22b, 23b, 24	20, 22, 24, 25	27
		b: 2.04	22a, 22b, 23a, 24	20, 22, 24, 25	27
24	122.9, CH	5.08, br t (6.7)	23a, 23b, 26, 27	23, 26, 27	22a, 22b, 26
25	132.7, C				
26	25.7, CH_3	1.67, br s	24	24, 25, 27	24
27	17.7, CH_3	1.59, br s	24	24, 25, 26	23a, 23b
28	15.6, CH_3	0.90, d (6.8)	4	3, 4, 5	3, 5
30	17.4, CH_3	1.27, s		7, 8, 9, 14	5, 13
16-<u>C</u>OCH$_3$	170.3, C				
16-CO<u>C</u>H$_3$	20.5, CH_3	1.94, s		16-<u>C</u>OCH$_3$	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S21 NMR data for **26** (^{1}H for 400 MHz and ^{13}C for 100 MHz in $CDCl_3$).

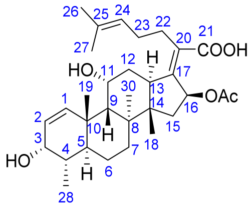


26

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	160.8, CH	8.06, d (10.2)	2	3, 5, 10	11
2	126.2, CH	5.83, d (10.2)	1	4, 10	
3	202.3, C				
4	39.9, CH	3.02, dq (13.1, 6.5)	5, 28	3, 5, 28	19
5	46.5, CH	2.38	4, 6	1, 3, 4, 10, 19	30
6	73.3, CH	4.0, br s	5	5, 7, 8, 10	28
7	215.3, C				
8	53.0, C				
9	45.4, CH	2.55, br s	11	1, 7, 8, 10, 11, 14, 19, 30	18, 19
10	38.7, C				
11	67.6, CH	4.68, br s	9, 12a, 12b	8, 13	1, 19
12	35.8, CH_2	a: 2.37	11, 12b, 13	11, 14	
		b: 2.08	11,12a, 13		
13	44.2, CH	3.11, br d (11.9)	12a, 12b	12, 14, 17, 18, 20	16, 30
14	46.7, C				
15	40.7, CH_2	a: 2.32	15b, 16	18	
		b: 1.91, br d (14.7)	15a, 16	13, 16, 17, 18	
16	74.0, CH	5.92, br d (8.2)	15a, 15b	14, 17, 20, 16-COC<u>H</u>$_3$	13
17	149.1, C				
18	18.1, CH_3	0.94, s		8, 13, 14, 15	9
19	28.4, CH_3	1.55, s		1, 5, 9, 10	4, 9, 11
20	130.2, C				
21	173.9, C				
22	28.7, CH_2	2.45	23	17, 20, 21, 23, 24	
23	28.4, CH_2	2.13	22, 24	22, 24, 25	
24	122.8, CH	5.09, br t (6.6)	23, 26, 27	23, 26, 27	26
25	132.9, C				
26	25.7, CH_3	1.68, br s	24	24, 25 ,27	24
27	17.8, CH_3	1.60, br s	24	24, 25, 26	
28	12.4, CH_3	1.22, d (6.7)	4	3, 4, 5	6
30	21.7, CH_3	1.36, s		7, 8, 9, 14	5, 13
16-<u>C</u>OCH$_3$	170.6, C				
16-CO<u>C</u>H$_3$	20.5, CH_3	1.96, s		16-<u>C</u>OCH$_3$	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S22 NMR data for **29** (^{1}H for 600 MHz and ^{13}C for 150 MHz in $CDCl_3$).

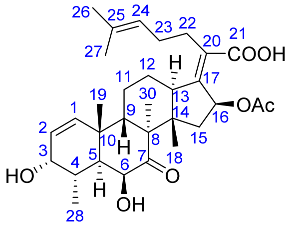


29

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	140.1, CH	6.21, d (10.1)	2	3, 5, 9, 10, 19	3, 11, 19
2	127.5, CH	5.80, dd (10.1, 4.9)	1, 3	3, 4, 10	
3	68.2, CH	3.87, t (4.9)	2, 4	1, 2, 5, 28	1, 28
4	34.7, CH	1.76	3, 5, 28	5, 10, 28	19
5	33.2, CH	2.35	4, 6a, 6b	1, 3, 4, 6, 10, 19	28, 30
6	19.7, CH_2	a: 1.72	5, 6b, 7a, 7b	10	
		b: 1.29	5, 6a, 7a, 7b		
7	30.1, CH_2	a: 1.58	6a, 6b, 7b	8, 30	18, 19
		b: 1.22	6a, 6b, 7a	9	
8	39.4, C				
9	49.9, CH	1.71, d (1.8)	11	1, 7, 8, 10, 11, 14, 19, 30	12b, 18, 19
10	37.9, C				
11	67.6, CH	4.42, br s	9, 12a, 12b	8, 13	1, 19
12	34.1, CH_2	a: 2.38	11, 12b, 13	14	
		b: 1.88, td (12.7, 3.1)	11, 12a, 13	13	9, 18
13	43.9, CH	3.01, br d (12.4)	12a, 12b	12, 14, 17, 18, 20	15a, 16, 30
14	48.8, C				
15	39.0, CH_2	a: 2.21, dd (14.6, 9.0)	15b, 16	8, 14, 16, 18	13, 30
		b: 1.28, br d (14.4)	15a, 16	13, 14, 16, 17, 18	18
16	74.4, CH	5.86, br d (8.6)	15a, 15b	13, 14, 17, 20, 16-<u>C</u>OCH₃	13
17	149.7, C				
18	17.3, CH_3	0.90, s		8, 13, 14, 15	7a, 9, 12b, 15b
19	27.8, CH_3	1.00, s		1, 5, 9, 10	1, 4, 7a, 9, 11
20	129.9, C				
21	174.2, C				
22	28.8, CH_2	2.45	23a, 23b	17, 20, 21, 23, 24	24
23	28.4, CH_2	a: 2.16	22, 23b, 24	20, 22, 24, 25	
		b: 2.04	22, 23a, 24	20, 22, 24, 25	
24	123.0, CH	5.09, br t (7.1)	23a, 23b, 26, 27	23, 26, 27	22, 26
25	132.6, C				
26	25.7, CH_3	1.67, br s	24	24, 25, 27	24
27	17.8, CH_3	1.59, br s	24	24, 25, 26	
28	13.8, CH_3	0.97, d (6.8)	4	3, 4, 5	3, 5
30	22.4, CH_3	1.34, s		7, 8, 9, 14	5, 13, 15a
16-<u>C</u>OCH₃	170.7, C				
16-CO<u>C</u>H₃	20.6, CH_3	1.96, s		16-<u>C</u>OCH₃	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S23 NMR data for **30** (^{1}H for 600 MHz and ^{13}C for 150 MHz in $CDCl_3$).

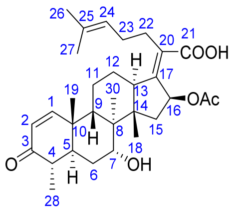


30

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	NOESY
1	140.5, CH	6.16, d (10.0)	2	3, 5, 9, 10	11a, 19, 30
2	126.9, CH	5.62, dd (10.0, 4.1)	1, 3	4, 10	
3	68.7, CH	4.11, t (4.1)	2, 4	1, 2, 5	28
4	30.8, CH	2.51	3, 5, 28	5, 10, 28	19
5	39.7, CH	2.03, br d (10.9)	4, 6	1, 3, 4, 7, 10, 19	30
6	73.5, CH	4.02, br s	5	4, 5, 7, 8, 10	28
7	215.8, C				
8	52.2, C				
9	41.9, CH	2.46	11a, 11b	1, 8, 10, 11, 19, 30	18, 19
10	37.6, C				
11	24.0, CH_2	a: 1.92	9, 11b, 12a, 12b	12, 13	1, 19
		b: 1.45	9, 11a, 12a, 12b	9	
12	26.0, CH_2	a: 2.33	11a, 11b, 12b, 13	9	
		b: 1.75	11a, 11b, 12a, 13		18
13	49.5, CH	2.53	12a, 12b	12, 14, 17, 18, 20	16, 30
14	46.4, C				
15	40.8, CH_2	a: 2.21, dd (15.2, 8.4)	15b, 16	8, 14, 18	30
		b: 1.92	15a, 16	13, 14, 16, 17, 18	18
16	73.8, CH	5.85, br d (8.3)	15a, 15b	14, 17, 20, 16-<u>C</u>OCH$_3$	13
17	148.1, C				
18	18.2, CH_3	0.95, s		8, 13, 14, 15	9, 12b, 15b
19	28.7, CH_3	1.31, s		1, 5, 9, 10	1, 4, 9, 11a
20	129.9, C				
21	173.5, C				
22	28.5, CH_2	a: 2.51	22b, 23a, 23b	17, 20, 21, 23, 24	24
		b: 2.43	22a, 23a, 23b	17, 20, 21, 23, 24	24
23	28.3, CH_2	a: 2.12	22a, 22b, 23b, 24	20, 22, 24, 25	
		b: 2.06	22a, 22b, 23a, 24	20, 22, 24, 25	
24	122.9, CH	5.10, br t (7.0)	23a, 23b, 26, 27	23, 26, 27	22a, 22b, 26
25	132.8, C				
26	25.7, CH_3	1.68, br s	24	24, 25, 27	24
27	17.7, CH_3	1.60, br s	24	24, 25, 26	
28	13.4, CH_3	1.11, d (7.0)	4	3, 4, 5	3, 6
30	17.5, CH_3	1.14, s		7, 8, 9, 14	1, 5, 13, 15a
16-<u>C</u>OCH$_3$	170.6, C				
16-CO<u>C</u>H$_3$	20.6, CH_3	1.97, s		16-<u>C</u>OCH$_3$	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity

Table S24 NMR data for **31** (^{1}H for 600 MHz and ^{13}C for 150 MHz in $CDCl_3$).

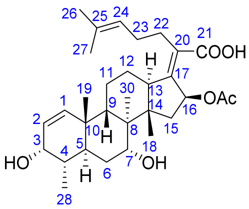


31

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	NOESY
1	158.7, CH	7.27, d (10.1)	2	3, 5, 9, 10	11a, 11b, 19
2	127.7, CH	5.83, d (10.1)	1	3, 4, 10	
3	202.3, C				
4	42.5, CH	2.35	5, 28	3, 5, 28	19
5	41.9, CH	2.35	4, 6a, 6b	3, 4, 6, 10, 19	28, 30
6	33.0, CH_2	a: 1.81	5, 6b, 7	5, 7, 8, 10	
		b: 1.55	5, 6a, 7	7, 10	
7	69.2, CH	4.15, br d (7.4)	6a, 6b	5, 6, 8, 14, 30	
8	43.8, C				
9	44.4, CH	1.56	11a, 11b	7, 8, 10, 30	18
10	38.7, C				
11	25.1, CH_2	a: 1.88	9, 11b, 12a, 12b	9	1
		b: 1.48	9, 11a, 12a, 12b	9, 12, 13	1
12	25.7, CH_2	a: 2.35	11a, 11b, 12b, 13		
		b: 1.70	11a, 11b, 12a, 13	13	
13	49.2, CH	2.52	12a, 12b	12, 14, 17, 18, 20	16
14	48.1, C				
15	41.2, CH_2	a: 2.19	15b, 16	8, 14, 18	30
		b: 1.49	15a, 16	13, 14, 18	
16	74.3, CH	5.85, br d (8.3)	15a, 15b	13, 14, 17, 20, 16-<u>C</u>OCH$_3$	13
17	149.1, C				
18	18.7, CH_3	1.01, s		8, 13, 14, 15	9
19	25.6, CH_3	1.12, s		1, 5, 9, 10	1, 4
20	130.3, C				
21	174.1, C				
22	28.6, CH_2	a: 2.50	22b, 23a, 23b	17, 20, 21, 23, 24	24
		b: 2.43	22a, 23a, 23b	17, 20, 21, 23, 24	24
23	28.2, CH_2	a: 2.13	22a, 22b, 23b, 24	20, 22, 24, 25	
		b: 2.06	22a, 22b, 23a, 24	20, 22, 24, 25	
24	122.9, CH	5.09, br t (6.9)	23a, 23b, 26, 27	23, 26, 27	22a, 22b, 26
25	132.7, C				
26	25.7, CH_3	1.68, br s	24	24, 25, 27	24
27	17.7, CH_3	1.59, br s	24	24, 25, 26	
28	12.6, CH_3	1.12, d (6.0)	4	3, 4, 5	5
30	12.2, CH_3	0.96, s		7, 8, 9, 14	5, 15a
16-<u>C</u>OCH$_3$	170.7, C				
16-CO<u>C</u>H$_3$	20.6, CH_3	1.95, s		16-<u>C</u>OCH$_3$	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S25 NMR data for **32** (^{1}H for 600 MHz and ^{13}C for 150 MHz in $CDCl_3$).

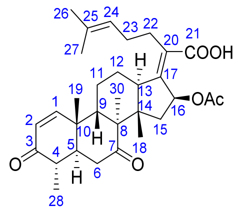


32

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	NOESY
1	140.6, CH	6.09, d (10.1)	2	3, 5, 9, 10	11a, 19
2	126.8, CH	5.65, dd (10.1, 4.6)	1, 3	3, 4, 10	
3	68.3, CH	3.90, t (4.4)	2, 4	1, 2, 5	28
4	33.5, CH	1.83	3, 5, 28	5, 10, 28	19
5	34.1, CH	2.14	4, 6a, 6b	1, 3, 4, 6, 7, 10, 19	28, 30
6	32.3, CH_2	a: 1.76, td (14.1, 8.2)	5, 6b, 7	4, 5, 7, 8, 10	19, 28
		b: 1.46	5, 6a, 7	5, 7, 10	28
7	70.2, CH	4.07, dd (8.1, 3.9)	6a, 6b	5, 14, 30	9, 18, 19
8	44.5, C				
9	45.1, CH	1.51	11a, 11b	7, 8, 10, 11, 12, 19, 30	7, 18, 19
10	38.0, C				
11	24.9, CH_2	a: 1.86	9, 11b, 12a, 12b		1
		b: 1.33, qd (13.1, 4.1)	9, 11a, 12a, 12b	9, 12	30
12	26.0, CH_2	a: 2.29	11a, 11b, 12b, 13		
		b: 1.65	11a, 11b, 12a, 13	11, 13	18
13	49.2, CH	2.49	12a, 12b	12, 14, 17, 18, 20	16, 30
14	48.2, C				
15	41.7, CH_2	a: 2.22, dd (14.9, 8.4)	15b, 16	8, 14, 18	30
		b: 1.49	15a, 16	13, 14, 16, 17, 18	
16	74.3, CH	5.84, br d (8.6)	15a, 15b	13, 14, 17, 20, 16-<u>C</u>OCH$_3$	13
17	149.2, C				
18	18.2, CH_3	1.00, s		8, 13, 14, 15	7, 9, 12b
19	26.6, CH_3	0.91, s		1, 5, 9, 10	1, 4, 6a, 7, 9
20	129.7, C				
21	173.2, C				
22	28.7, CH_2	a: 2.51	22b, 23a, 23b	17, 20, 21, 23, 24	24
		b: 2.42	22a, 23a, 23b	17, 20, 21, 23, 24	24
23	28.3, CH_2	a: 2.13	22a, 22b, 23b, 24	20, 22, 24, 25	
		b: 2.06	22a, 22b, 23a, 24	20, 22, 24, 25	
24	123.0, CH	5.10, br t (7.3)	23a, 23b, 26, 27	23, 26, 27	22a, 22b, 26
25	132.7, C				
26	25.7, CH_3	1.68, br s	24	24, 25, 27	24
27	17.7, CH_3	1.60, br s	24	24, 25, 26	
28	14.0, CH_3	0.98, d (7.0)	4	3, 4, 5	3, 5, 6a, 6b
30	12.6, CH_3	0.99, s		7, 8, 9, 14	5, 11b, 13, 15a
16-<u>C</u>OCH$_3$	170.6, C				
16-CO<u>C</u>H$_3$	20.6, CH_3	1.96, s		16-<u>C</u>OCH$_3$	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S26 NMR data for **33** (^{1}H for 600 MHz and ^{13}C for 150 MHz in $CDCl_3$).

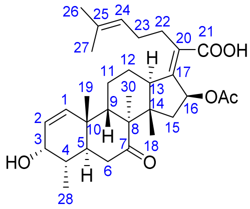


33

Position	δ_C, type	δ_H (*J* in Hz)[a]	^{1}H–^{1}H COSY	HMBC	NOESY
1	157.4, CH	7.32, d (10.1)	2	3, 5, 10, 19	11a, 19, 30
2	128.4, CH	5.89, d (10.0)	1	3, 4, 10	
3	201.2, C				
4	41.9, CH	2.56	5, 28	3, 5, 6, 10, 28	19
5	43.7, CH	2.23	4, 6a, 6b	1, 3, 4, 6, 7, 10, 19, 28	30
6	39.8, CH_2	a: 2.38	5, 6b	4, 5, 7, 8, 10	
		b: 2.31, t (14.6)	5, 6a	5, 7, 10	19
7	215.9, C				
8	52.1, C				
9	43.3, CH	2.06	11a, 11b	1, 8, 10, 11, 30	12b, 18, 19
10	38.4, C				
11	24.2, CH_2	a: 1.93	9, 11b, 12a, 12b	12	1, 19
		b: 1.51, qd (13.0, 3.4)	9, 11a, 12a, 12b	8, 9	30
12	25.9, CH_2	a: 2.39	11a, 11b, 12b, 13		
		b: 1.76, qd (13.0, 3.8)	11a, 11b, 12a, 13	13	9, 18
13	49.3, CH	2.53	12a, 12b	12, 14, 17, 18, 20	16, 30
14	46.8, C				
15	40.6, CH_2	a: 2.24	15b, 16	8, 14, 18	
		b: 1.91	15a, 16	13, 14, 16, 17, 18	18
16	73.6, CH	5.86, br d (8.5)	15a, 15b	13, 14, 17, 20, 16-$\underline{C}OCH_3$	13
17	147.7, C				
18	17.4, CH_3	0.89, s		8, 13, 14, 15	9, 12b, 15b
19	25.4, CH_3	1.30, s		1, 5, 9, 10	1, 4, 6b, 9, 11a
20	130.2, C				
21	173.8, C				
22	28.6, CH_2	a: 2.50	22b, 23a, 23b	17, 20, 21, 23, 24	24
		b: 2.43	22a, 23a, 23b	17, 20, 21, 23, 24	24
23	28.3, CH_2	a: 2.13	22a, 22b, 23b, 24	20, 22, 24, 25	
		b: 2.07	22a, 22b, 23a, 24	20, 22, 24, 25	
24	122.8, CH	5.10, br t (7.0)	23a, 23b, 26, 27	23, 26, 27	22a, 22b, 26
25	132.8, C				
26	25.7, CH_3	1.68, br s	24	24, 25, 27	24
27	17.7, CH_3	1.60, br s	24	24, 25, 26	
28	13.0, CH_3	1.14, d (6.8)	4	3, 4, 5	
30	17.7, CH_3	1.11, s		7, 8, 9, 14	1, 5, 11b, 13
16-$\underline{C}OCH_3$	170.3, C				
16-$CO\underline{C}H_3$	20.5, CH_3	1.95, s		16-$\underline{C}OCH_3$	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S27 NMR data for **34** (^{1}H for 600 MHz and ^{13}C for 150 MHz in $CDCl_3$).

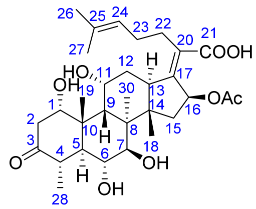


34

Position	δ_C, type	δ_H (*J* in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	139.4, CH	6.20, d (10.0)	2	3, 5, 9, 10	11a, 11b, 19
2	127.9, CH	5.67, dd (10.1, 4.1)	1, 3	3, 4, 10	
3	68.2, CH	4.03, t (4.3)	2, 4	1, 2, 5	28
4	32.5, CH	2.14	3, 5, 28	28	19
5	36.3, CH	2.01	4, 6a, 6b	1, 3, 4, 6, 7, 9, 10, 19	28, 30
6	38.9, CH_2	a: 2.34	5, 6b	4, 5, 7, 8, 10	28
		b: 2.12	5, 6a	4, 5, 7, 10	19, 28
7	217.7, C				
8	52.2, C				
9	43.2, CH	1.91	11a, 11b	1, 5, 7, 8, 10, 11, 12, 19	18, 19
10	37.9, C				
11	24.1, CH_2	a: 1.89	9, 11b, 12a, 12b	12	1, 19
		b: 1.41	9, 11a, 12a, 12b	9	1, 13, 30
12	26.0, CH_2	a: 2.32	11a, 11b, 12b, 13		
		b: 1.71	11a, 11b, 12a, 13		18
13	49.3, CH	2.51	12a, 12b	12, 14, 17, 18, 20	11b, 15a, 16, 30
14	46.8, C				
15	40.6, CH_2	a: 2.22, dd (14.8, 8.6)	15b, 16	8, 14, 18	13, 30
		b: 1.89	15a, 16	13, 14, 16, 17, 18	18
16	73.7, CH	5.86, br d (8.5)	15a, 15b	13, 14, 17, 20, 16-<u>C</u>OCH$_3$	13
17	147.7, C				
18	17.4, CH_3	0.86, s		8, 13, 14, 15	9, 12b, 15b
19	25.9, CH_3	1.07, s		1, 5, 9, 10	1, 4, 6b, 9, 11a
20	130.3, C				
21	173.7, C				
22	28.6, CH_2	a: 2.49	22b, 23a, 23b	17, 20, 21, 23, 24	24
		b: 2.42	22a, 23a, 23b	17, 20, 21, 23, 24	24
23	28.3, CH_2	a: 2.12	22a, 22b, 23b, 24	20, 22, 24, 25	
		b: 2.06	22a, 22b, 23a, 24	20, 22, 24, 25	
24	122.9, CH	5.09, br t (7.1)	23a, 23b, 26, 27	23, 26, 27	22a, 22b, 26
25	132.7, C				
26	25.7, CH_3	1.68, br s	24	24, 25, 27	24
27	17.7, CH_3	1.60, br s	24	24, 25, 26	
28	13.9, CH_3	0.99, d (6.8)	4	3, 4, 5	3, 5, 6a, 6b
30	17.6, CH_3	1.11, s		7, 8, 9, 14	5, 11b, 13, 15a
16-<u>C</u>OCH$_3$	170.6, C				
16-CO<u>C</u>H$_3$	20.6, CH_3	1.95, s		16-<u>C</u>OCH$_3$	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S28 NMR data for **35** (^{1}H for 600 MHz and ^{13}C for 150 MHz in CD_3OD).

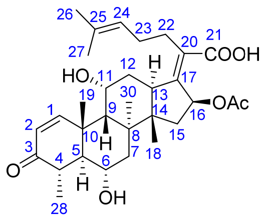


35

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	84.7, CH	3.36, dd (9.5, 7.2)	2a, 2b	5, 19	11, 19
2	42.1, CH_2	a: 2.94, dd (12.4, 9.5)	1, 2b	1, 3	5
		b: 2.59, dd (12.4, 7.2)	1, 2a	1, 3, 4, 10	
3	217.2, C				
4	46.9, CH	2.22	5, 28	3, 5, 6, 28	6, 19
5	43.6, CH	2.69, t (11.4)	4, 6	1, 3, 4, 6, 10, 19, 28	2a, 7, 28, 30
6	81.9, CH	3.78, br d (11.4)	5, 7	4, 5, 7, 8	4, 9, 19
7	86.1, CH	3.60, br s	6	5, 6, 8, 9, 14, 30	5, 15a, 15b, 30
8	42.1, C				
9	47.1, CH	2.45, d (5.5)	11	1, 7, 8, 10, 14, 19, 30	6, 18, 19
10	44.2, C				
11	78.5, CH	4.11, br dd (7.7, 5.7)	9, 12a, 12b	8, 13	1, 19
12	28.7, CH_2	a: 2.52	11, 12b, 13	9, 11, 13, 14	
		b: 2.26	11, 12a, 13	11, 13, 17	18
13	45.9, CH	2.97, dd (12.1, 5.8)	12a, 12b	8, 12, 14, 17, 18, 20	16, 30
14	50.7, C				
15	39.0, CH_2	a: 2.30	15b, 16	8, 14, 18	7, 30
		b: 1.46, br d (14.6)	15a, 16	13, 14, 16, 17, 18	7, 18
16	76.7, CH	5.86, br d (8.7)	15a, 15b	13, 14, 17, 20, 16-<u>C</u>OCH$_3$	13
17	145.5, C				
18	18.9, CH_3	1.16, s		8, 13, 14, 15	9, 12b, 15b
19	22.7, CH_3	0.93, s		1, 5, 9, 10	1, 4, 6, 9, 11
20	134.0, C				
21	174.9, C				
22	30.4, CH_2	a: 2.54	22b, 23	17, 20, 21, 23, 24	24
		b: 2.37	22a, 23	17, 20, 21, 23, 24	24
23	28.8, CH_2	2.11	22a, 22b, 24	22, 24, 25	
24	124.4, CH	5.14, br t (7.3)	23, 26, 27	23, 26, 27	22a, 22b, 26
25	133.4, C				
26	25.9, CH_3	1.67, br s	24	24, 25, 27	24
27	17.8, CH_3	1.61, br s	24	24, 25, 26	
28	18.5, CH_3	1.28, d (7.1)	4	3, 4, 5	5
30	21.1, CH_3	1.32, s		7, 8, 9, 14	5, 7, 13, 15a
16-<u>C</u>OCH$_3$	172.6, C				
16-CO<u>C</u>H$_3$	20.7, CH_3	1.98, s		16-<u>C</u>OCH$_3$	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S29 NMR data for **36** (^{1}H for 600 MHz and ^{13}C for 150 MHz in CD_3OD).

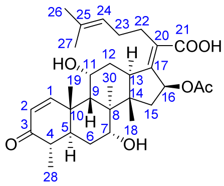


36

Position	δ_C, type	δ_H (J in Hz)[a]	^1H–^1H COSY	HMBC	ROESY
1	163.9, CH	7.86, d (10.2)	2	3, 5, 9, 10	11, 19
2	126.1, CH	5.77, d (10.2)	1	4, 10	
3	205.6, C				
4	45.3, CH	2.65	5, 28	3, 5, 6, 10, 28	6, 19
5	50.9, CH	2.44, dd (11.8, 9.8)	4, 6	1, 3, 6, 7, 10, 19, 28	28, 30
6	69.5, CH	3.90	5, 7a, 7b	8, 10	4, 9, 19, 28
7	45.0, CH_2	a: 2.09	6, 7b	5, 6, 8, 14, 30	9, 18
		b: 1.28	6, 7a	6	
8	40.3, C				
9	50.6, CH	1.68, br s	11	1, 8, 10, 11, 14, 19, 30	6, 7a, 12b, 18, 19
10	40.4, C				
11	67.4, CH	4.42, br s	9, 12a, 12b	8, 13	1, 19
12	36.8, CH_2	a: 2.39	11, 12b, 13		
		b: 1.94	11, 12a, 13	13	9, 18
13	44.2, CH	3.08, br d (12.4)	12a, 12b	14, 17	15a, 16, 30
14	49.6, C				
15	40.1, CH_2	a: 2.17	15b, 16	8, 14, 18	13
		b: 1.29	15a, 16	13, 14, 16, 17, 18	18
16	75.7, CH	5.82, br d (8.4)	15a, 15b	14, 17, 20, 16-<u>C</u>OCH3	13
17	146.6, C				
18	17.9, CH_3	0.96, s		8, 13, 14, 15	7a, 9, 12b, 15b
19	28.6, CH_3	1.22, s		1, 5, 9, 10	1, 4, 6, 9, 11
20	134.1, C				
21	175.1, C				
22	30.1, CH_2	a: 2.57	22b, 23	17, 20, 21, 23, 24	24
		b: 2.38	22a, 23	17, 20, 21, 23, 24	24
23	29.2, CH_2	2.12	22a, 22b, 24	22, 24, 25	
24	124.5, CH	5.15, br t (7.0)	23, 26, 27	23, 26, 27	22a, 22b, 26
25	133.3, C				
26	25.9, CH_3	1.67, br s	24	24, 25, 27	24
27	17.9, CH_3	1.61, br s	24	24, 25, 26	
28	15.8, CH_3	1.32, d (6.8)	4	3, 4, 5	5, 6
30	23.6, CH_3	1.35, s		7, 8, 9, 14	5, 13
16-<u>C</u>OCH3	172.7, C				
16-CO<u>C</u>H3	20.7, CH_3	1.97, s		16-<u>C</u>OCH3	

[a]The indiscernible signals due to overlap or the complex multiplicity are reported without designating multiplicity.

Table S30 NMR data for **37** (^{1}H for 600 MHz and ^{13}C for 150 MHz in CD_3OD).

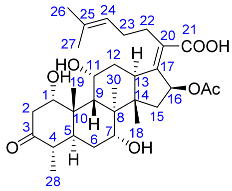


37

Position	δ_C, type	δ_H (*J* in Hz)[a]	^1H–^1H COSY	HMBC	ROESY
1	163.9, CH	7.55, d (10.4)	2	2, 3, 5, 9, 10, 19	11, 19
2	125.9, CH	5.76. d (10.3)	1	10	
3	204.1, C				
4	44.8, CH	2.33	5, 28	3, 5, 6, 10, 28	19
5	43.3, CH	2.68, td (12.3, 7.6)	4, 6a, 6b	1, 3, 4, 6, 9, 10, 19, 28	28, 30
6	34.8, CH_2	a: 1.91	5, 6b, 7	4, 5, 7, 8	
		b: 1.64	5, 6a, 7	5, 7, 10	28
7	71.0, CH	3.90, t (7.6)	6a, 6b	6, 8, 9, 14, 30	9, 18, 19
8	46.0, C				
9	51.2, CH	1.69, d (2.1)	11	1, 5, 7, 8, 10, 11, 14, 19, 30	7, 12b, 18, 19
10	39.5, C				
11	67.5, CH	4.45, br s	9, 12a, 12b	8, 9, 10, 13	1, 19
12	36.4, CH_2	a: 2.39	11, 12b, 13	9, 11, 14	
		b: 1.96	11, 12a, 13	13	9, 18, 22a
13	44.9, CH	3.02, br d (12.4)	12a, 12b	12, 14, 17, 18, 20	15a, 16, 30
14	49.5, C				
15	43.1, CH_2	a: 2.28, dd (15.1, 8.8)	15b, 16	8, 14, 18	13, 30
		b: 1.60	15a, 16	13, 14, 16, 17, 18	18
16	76.0, CH	5.77, br d (8.3)	15a, 15b	13, 14, 17, 20, 16-<u>C</u>OCH3	13
17	146.9, C				
18	16.8, CH_3	1.01, s		8, 13, 14, 15	7, 9, 12b, 15b
19	27.3, CH_3	1.19, s		1, 5, 9, 10	1, 4, 7, 9, 11
20	132.8, C				
21	174.7, C				
22	30.0, CH_2	a: 2.59	22b, 23	17, 20, 21, 23, 24	12b, 24
		b: 2.38	22a, 23	17, 20, 21, 23, 24	24
23	29.3, CH_2	2.12	22a, 22b, 24	22, 24, 25	
24	124.4, CH	5.14, br t (7.0)	23, 26, 27	23, 26, 27	22a, 22b, 26
25	133.4, C				
26	25.9, CH_3	1.67, br s	24	24, 25, 27	24
27	17.9, CH_3	1.61, br s	24	24, 25, 26	
28	12.6, CH_3	1.09, d (6.7)	4	3, 4, 5	5, 6b
30	15.0, CH_3	1.25, s		7, 8, 9, 14	5, 13, 15a
16-<u>C</u>OCH3	172.6, C				
16-CO<u>C</u>H3	20.7, CH_3	1.95, s		16-<u>C</u>OCH3	

[a]The indiscernible signals due to overlap or the complex multiplicity are reported without designating multiplicity

Table S31 NMR data for **38** (^{1}H for 400 MHz and ^{13}C for 100 MHz in CD_3OD).



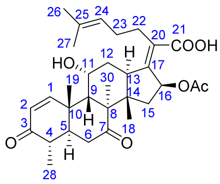
38

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	83.8, CH	3.44, dd (8.8, 7.5)	2a, 2b	5, 10, 19	11, 19
2	42.9, CH_2	a: 2.91	1, 2b	1, 3	
		b: 2.62	1, 2a	1, 3, 10	
3	216.6, C				
4	45.2[b], CH	1.91	5, 28	3, 5, 28	19
5	37.1, CH	2.86	4, 6a, 6b		28, 30
6	33.4, CH_2	a: 2.00	5, 6b, 7	5, 8	
		b: 1.54	5, 6a, 7		
7	71.5, CH	3.88, dd (9.0, 3.9)	6a, 6b	8, 30	9, 18
8	43.2, C				
9	52.5, CH	1.69	11	7, 19	7, 18, 19
10	43.8, C				
11	77.9, CH	4.06, br dd (7.0, 5.6)	9, 12a, 12b	8, 10, 13	1, 19
12	28.4, CH_2	a: 2.56	11, 12b, 13	9, 11, 13, 14	
		b: 2.24, ddd (15.0, 12.4, 7.6)	11, 12a, 13	13	18
13	45.1[b], CH	2.93	12a, 12b	17	16, 30
14	49.9, C				
15	41.7, CH_2	a: 2.40	15b, 16	14, 18	30
		b: 1.49, br d (15.5)	15a, 16	13, 14, 16, 17, 18	
16	76.8, CH	5.83, br d (8.6)	15a, 15b	14, 17, 20, 16-<u>C</u>OCH3	13
17	144.8, C				
18	16.0, CH_3	0.96, s		8, 13, 14, 15	7, 9, 12b
19	21.7, CH_3	0.85, s		1, 5, 9, 10	1, 4, 9, 11
20	133.4, C				
21	174.5				
22	30.4, CH_2	a: 2.57	22b, 23	17, 23	
		b: 2.38	22a, 23	17, 23	
23	28.8, CH_2	2.11	22a, 22b, 24	22, 24, 25	
24	124.4, CH	5.15, br t (6.8)	23, 26, 27	23, 26, 27	26
25	133.4, C				
26	25.9, CH_3	1.67, br s	24	24, 25, 27	24
27	17.8, CH_3	1.61, br s	24	24, 25, 26	
28	15.5, CH_3	1.07, d (7.1)	4	3, 4, 5	5
30	18.2, CH_3	1.38, s		7, 8, 9, 14	5, 13, 15a
16-<u>C</u>OCH3	172.5, C				
16-CO<u>C</u>H3	20.7, CH_3	1.97, s		16-<u>C</u>OCH3	

[a]The indiscernible signals due to overlap or the complex multiplicity are reported without designating multiplicity.

[b]The data are interchangeable.

Table S32 NMR data for **39** (^{1}H for 600 MHz and ^{13}C for 150 MHz in CD_3OD).

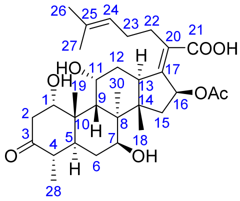


39

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	163.8, CH	8.27, d (10.3)	2	3, 5, 9, 10	11
2	127.0, CH	5.79, d (10.3)	1	4, 10	
3	203.7, C				
4	43.1, CH	2.60	5, 28	3, 5, 6, 10, 28	19
5	44.6, CH	2.37	4, 6a, 6b	1, 4, 6, 7, 10, 19	28, 30
6	41.1, CH_2	a: 2.43	5, 6b	5, 10, 7	19
		b: 2.31	5, 6a	4, 5, 8, 10	28
7	219.3, C				
8	54.5, C				
9	47.8, CH	2.02, br s	11	1, 7, 8, 10, 11, 14, 19, 30	18, 19
10	40.5, C				
11	67.4, CH	4.55, br s	9, 12a, 12b	8, 13	1, 19
12	36.5, CH_2	a: 2.40	11, 12b, 13	11	
		b: 1.96	11, 12a, 13	13	18, 22a
13	44.6, CH	3.10, br d (11.8)	12a, 12b	12, 14, 17, 18, 20	15a, 16, 30
14	48.3, C				
15	42.0, CH_2	a: 2.29	15b, 16	14, 18	13, 30
		b: 1.79, br d (14.8)	15a, 16	13, 14, 16, 17, 18	18
16	75.5, CH	5.80, br d (8.3)	15a, 15b	14, 17, 20, 16-<u>C</u>OCH3	13
17	145.2, C				
18	17.6, CH_3	0.86, s		8, 13, 14, 15	9, 12b, 15b
19	25.8, CH_3	1.37, s		1, 5, 9, 10	4, 6a, 9, 11
20	134.1, C				
21	175.1, C				
22	30.0, CH_2	a: 2.56	22b, 23	17, 20, 21, 23, 24	12b, 24
		b: 2.38	22a, 23	17, 20, 21, 23, 24	24
23	29.3, CH_2	2.13	22a, 22b, 24	22, 24, 25	
24	124.4, CH	5.15, br t (7.2)	23, 26, 27	23, 26, 27	22a, 22b, 26
25	133.4, C				
26	25.9, CH_3	1.67, br s	24	24, 25, 27	24
27	17.9, CH_3	1.61, br s	24	24, 25, 26	
28	13.1, CH_3	1.11, d (6.8)	4	3, 4, 5	5, 6b
30	22.5, CH_3	1.32, s		7, 8, 9, 14	5, 13, 15a
16-<u>C</u>OCH3	172.6, C				
16-CO<u>C</u>H3	20.7, CH_3	1.96, s		16-<u>C</u>OCH3	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S33 NMR data for **40** (^{1}H for 400 MHz and ^{13}C for 100 MHz in CD_3OD).

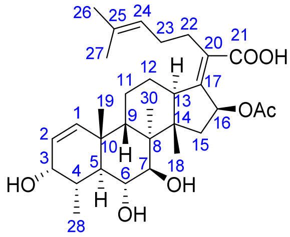


40

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	84.1, CH	3.46, t (8.0)	2a, 2b	5, 19	11, 19
2	42.9, CH_2	a: 2.89, dd (13.4, 9.2)	1, 2b	1, 3	
		b: 2.63	1, 2a	3, 10	
3	216.9, C				
4	45.3, CH	1.93	5, 28		19
5	36.9, CH	2.62	4, 6a, 6b	3, 10	28, 30
6	34.0, CH_2	a: 2.38	5, 6b, 7		
		b: 1.26	5, 6a, 7		
7	73.7, CH	3.93, br d (8.4)	6a, 6b	5, 9, 30	
8	41.8, C				
9	47.0, CH	2.52	11	1, 8, 10, 11, 12, 14, 30	12b, 18, 19
10	43.9, C				
11	78.7, CH	4.14, br t (6.6)	9, 12a, 12b	8, 13	1, 19
12	28.7, CH_2	a: 2.50	11, 12b, 13		
		b: 2.26	11, 12a, 13		9
13	46.3, CH	2.96, dd (11.7, 5.7)	12a, 12b		30
14	50.8, C				
15	38.9, CH_2	a: 2.31	15b, 16	18	
		b: 1.47, br d (14.6)	15a, 16	13, 14, 16, 17, 18	
16	76.7, CH	5.86, br d (8.8)	15a, 15b	14, 17, 20, 16-<u>C</u>OCH3	
17	146.6, C				
18	19.0, CH_3	1.17, s		8, 13, 14, 15	9
19	21.3, CH_3	0.96, s		1, 5, 9, 10	1, 4, 9, 11
20	133.0, C				
21	174.1, C				
22	30.3, CH_2	a: 2.54	22b, 23	21	
		b: 2.37	22a, 23		
23	28.8, CH_2	2.11	22a, 22b, 24	24	
24	124.3, CH	5.14, br t (6.7)	23, 26, 27	23, 26, 27	26
25	133.5, C				
26	25.9, CH_3	1.67, br s	24	24, 25, 27	24
27	17.8, CH_3	1.61, br s	24	24, 25, 26	
28	15.5, CH_3	1.04, d (7.1)	4	3, 4, 5	5
30	22.6, CH_3	1.25, s		7, 8, 9, 14	5, 13
16-<u>C</u>OCH3	172.5, C				
16-CO<u>C</u>H3	20.7, CH_3	1.97, s		16-<u>C</u>OCH3	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S34 NMR data for **41** (^{1}H for 400 MHz and ^{13}C for 100 MHz in CD_3OD).

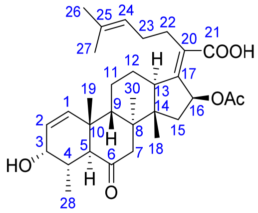


41

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	141.2, CH	6.09, d (10.2)	2	3, 5, 10	11a, 11b, 19
2	127.5, CH	5.55, dd (10.1, 4.4)	1, 3	4, 10	
3	70.4, CH	3.79, t (4.4)	2, 4		28
4	36.0, CH	2.16	3, 5, 28		19
5	43.0, CH	1.90, t (11.2)	4, 6	3, 4, 6, 7, 10, 19	7, 28, 30
6	77.7, CH	3.59, dd (10.8, 4.5)	5, 7		9, 19, 28
7	85.9, CH	3.51, d (4.6)	6	5, 9	5, 30
8	45.6, C				
9	42.9, CH	2.05	11a, 11b	1, 8, 10, 19, 30	6, 18, 19
10	40.6, C				
11	26.1, CH_2	a: 1.83	9, 11b, 12a, 12b		1, 19
		b: 1.42, qd (13.3, 4.3)	9, 11a, 12a, 12b		1, 30
12	27.4, CH_2	a: 2.27	11a, 11b, 12b, 13		
		b: 1.72	11a, 11b, 12a, 13		18
13	50.7, CH	2.61	12a, 12b	14, 17, 18	16, 30
14	49.6, C				
15	41.3, CH_2	a: 2.15	15b, 16	18	30
		b: 1.61	15a, 16	13, 16, 17	18
16	76.0, CH	5.78, br d (8.6)	15a, 15b	14, 17, 20, 16-<u>C</u>OCH3	13
17	146.8, C				
18	21.5, CH_3	1.19, s		8, 13, 14, 15	9, 12b, 15b
19	27.5, CH_3	1.11, s		1, 5, 9, 10	1, 4, 6, 9, 11a
20	133.5, C				
21	175.3, C				
22	29.9, CH_2	a: 2.54	22b, 23		24
		b: 2.35	22a, 23		24
23	29.1, CH_2	2.09	22a, 22b, 24	24, 25	
24	124.6, CH	5.13, br t (7.2)	23, 26, 27	26, 27	22a, 22b, 26
25	133.1, C				
26	25.9, CH_3	1.67, br s	24	24, 25, 27	24
27	17.8, CH_3	1.61, br s	24	24, 25, 26	
28	17.0, CH_3	1.19, d (6.4)	4	3, 4, 5	3, 5, 6
30	19.6, CH_3	1.08, s		7, 8, 9, 14	5, 7, 11b, 13, 15a
16-<u>C</u>OCH3	172.8, C				
16-CO<u>C</u>H3	20.8, CH_3	1.96, s		16-<u>C</u>OCH3	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S35 NMR data for **42** (^{1}H for 600 MHz and ^{13}C for 150 MHz in CD_3OD).

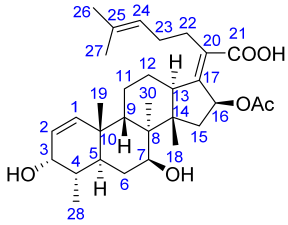


42

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	138.4, CH	6.16, d (10.1)	2	3, 5, 9, 10	11a, 11b, 19
2	129.1, CH	5.67, dd (10.1, 4.4)	1, 3	3, 4, 10	
3	67.9, CH	3.90, t (4.6)	2, 4	1, 2, 5	28
4	31.1, CH	2.22	3, 5, 28	5, 10, 28	19
5	53.4, CH	3.35, d (11.9)	4	1, 3, 4, 6, 10, 19	28, 30
6	216.1, C				
7	52.8, CH_2	a: 2.46, d (17.6)	7b	5, 6, 8, 14, 30	9, 18
		b: 2.18, d (17.6)	7a	6, 8, 9, 30	30
8	43.2, C				
9	47.5, CH	1.64, dd (13.1, 3.2)	11a, 11b	8, 10, 19, 30	7a, 18, 19
10	43.3, C				
11	26.7, CH_2	a: 1.87, dq (13.3, 3.0)	9, 11b, 12a, 12b		1, 19
		b: 1.45, qd (13.0, 4.1)	9, 11a, 12a, 12b	9, 10, 12	1, 13
12	27.0, CH_2	a: 2.36	11a, 11b, 12b, 13		
		b: 1.69	11a, 11b, 12a, 13	11, 13, 14	18, 22a
13	49.6, CH	2.66, br d (10.9)	12a, 12b	12, 14, 17, 18, 20	11b, 15a, 16, 30
14	49.5, C				
15	40.2, CH_2	a: 2.11	15b, 16	8, 13, 14, 18	13, 30
		b: 1.24, br d (14.2)	15a, 16	14, 16, 17, 18	18
16	75.4, CH	5.80, br d (8.5)	15a, 15b	13, 14, 17, 20, 16-<u>C</u>OCH3	13
17	146.3, C				
18	19.0, CH_3	0.97, s		8, 13, 14, 15	7a, 9, 12b, 15b
19	28.4, CH_3	0.93, s		1, 5, 9, 10	1, 4, 9, 11a
20	133.8, C				
21	174.7, C				
22	29.9, CH_2	a: 2.55	22b, 23	17, 20, 21, 23, 24	12b, 24
		b: 2.36	22a, 23	17, 20, 21, 23, 24	24
23	29.1, CH_2	2.10	22a, 22b, 24	22, 24, 25	
24	124.4, CH	5.13, br t (7.3)	23, 26, 27	23, 26, 27	22a, 22b, 26
25	133.3, C				
26	25.9, CH_3	1.67, br s	24	24, 25, 27	24
27	17.8, CH_3	1.61, br s	24	24, 25, 26	
28	14.1, CH_3	1.07, d (6.7)	4	3, 4, 5	3, 5
30	21.1, CH_3	1.39, s		7, 8, 9, 14	5, 7b, 13, 15a
16-<u>C</u>OCH3	172.6, C				
16-CO<u>C</u>H3	20.7, CH_3	1.96, s		16-<u>C</u>OCH3	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S36 NMR data for **43** (^{1}H for 600 MHz and ^{13}C for 150 MHz in CD_3OD).

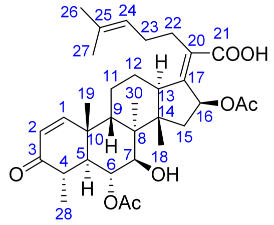


43

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	141.3, CH	6.14, d (10.1)	2	3, 5, 9, 10, 19	11a, 11b, 19
2	128.3, CH	5.53, dd (10.0, 4.2)	1, 3	3, 4, 10	
3	69.1, CH	3.88, t (4.5)	2, 4	1, 2, 4, 5	28
4	34.3, CH	1.99	3, 5, 28	5, 10, 28	19
5	38.5, CH	1.74	4. 6a, 6b	1, 3, 4, 6, 7, 10, 19	7, 30
6	32.3, CH_2	a: 1.89	5, 6b, 7	4, 7, 8, 10	
		b: 1.24, td (12.6, 9.6)	5, 6a, 7	5, 7, 10	
7	81.3, CH	3.78, dd (9.2, 6.9)	6a, 6b	5, 6, 8, 9, 30	5, 30
8	46.4, C				
9	44.6, CH	1.93	11a, 11b	1, 8, 10, 11, 19, 30	18, 19
10	39.4, C				
11	25.9, CH_2	a: 1.77	9, 11b, 12a, 12b		1
		b: 1.47	9, 11a, 12a, 12b	9, 12	1, 13
12	27.4, CH_2	a: 2.30	11a, 11b, 12b, 13	9, 11, 13, 14	
		b: 1.74	11a, 11b, 12a, 13		
13	51.5, CH	2.60, br d (11.5)	12a, 12b	12, 14, 17, 18, 20	11b, 15a, 16, 30
14	49.5, C				
15	41.7, CH_2	a: 2.15, dd (14.5, 8.8)	15b, 16	8, 14, 16, 18	13, 30
		b: 1.72	15a, 16	13, 14, 16, 17, 18	18
16	76.0, CH	5.78, br d (8.5)	15a, 15b	13, 14, 17, 20, 16-<u>C</u>OCH3	13
17	147.2, C				
18	21.3, CH_3	1.18, s		8, 13, 14, 15	9, 15b
19	26.6, CH_3	1.01, s		1, 5, 9, 10	1, 4, 9
20	133.0, C				
21	174.8, C				
22	29.8, CH_2	a: 2.56	22b, 23	17, 20, 21, 23, 24	24
		b: 2.35	22a, 23	17, 20, 21, 23, 24	24
23	29.1, CH_2	2.10	22a, 22b, 24	22, 24, 25	
24	124.5, CH	5.13, br t (7.3)	23, 26, 27	23, 26, 27	22a, 22b, 26
25	133.2, C				
26	25.9, CH_3	1.67, br s	24	24, 25, 27	24
27	17.8, CH_3	1.61, br s	24	24, 25, 26	
28	14.7, CH_3	0.96, d (7.0)	4	3, 4, 5	3
30	21.8, CH_3	1.03, s		7, 8, 9, 14	5, 7, 13, 15a
16-<u>C</u>OCH3	172.8, C				
16-CO<u>C</u>H3	20.8, CH_3	1.95, s		16-<u>C</u>OCH3	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S37 NMR data for **44** (^{1}H for 600 MHz and ^{13}C for 150 MHz in $CDCl_3$).

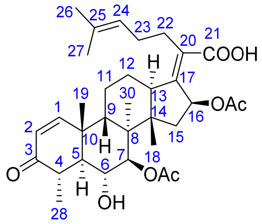


44

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	NOESY
1	158.0, CH	7.25, d (10.3)	2	3, 5, 9, 10	11a, 19
2	126.9, CH	5.86, d (10.3)	1	4, 10	
3	201.2, C				
4	43.2, CH	2.64, dq (12.6, 6.7)	5, 28	3, 5, 6, 10, 28	19
5	45.8, CH	2.40, t (11.7)	4, 6	1, 3, 4, 6, 10, 19, 28	7, 28, 30
6	80.1, CH	4.78, dd (10.8, 2.5)	5, 7	4, 5, 7, 6-COCH3	19, 28
7	80.7, CH	3.59, d (2.0)	6	5, 6, 8, 9, 14, 30	5, 30
8	43.4, C				
9	40.7, CH	2.32	11a, 11b	1, 7, 8, 10, 11, 12, 14, 19, 30	18, 19
10	39.1, C				
11	25.4, CH_2	a: 1.99	9, 11b, 12a, 12b		1
		b: 1.45, qd (13.0, 3.8)	9, 11a, 12a, 12b	12, 13	30
12	25.5, CH_2	a: 2.31	11a, 11b, 12b, 13		
		b: 1.81, qd (12.5, 3.8)	11a, 11b, 12a, 13	11, 13	18
13	49.7, CH	2.57, br d (11.2)	12a, 12b	11, 14, 17, 18, 20	30
14	48.4, C				
15	39.9, CH_2	a: 2.16	15b, 16	8, 14, 16, 18	30
		b: 1.56, br d (14.4)	15a, 16	13, 14, 16, 17, 18	18
16	74.2, CH	5.85, br d (8.2)	15a, 15b	14, 17, 20, 16-COCH3	
17	149.6, C				
18	21.4, CH_3	1.21, s		8, 13, 14, 15	9, 12b, 15b
19	26.5, CH_3	1.38, s		1, 5, 9, 10	1, 4, 6, 9
20	130.3, C				
21	173.6, C				
22	28.7, CH_2	a: 2.49	22b, 23a, 23b	17, 20, 21, 23, 24	24
		b: 2.43	22a, 23a, 23b	17, 20, 21, 23, 24	24
23	28.2, CH_2	a: 2.13	22a, 22b, 23b, 24	20, 22, 24, 25	
		b: 2.06	22a, 22b, 23a, 24	20, 22, 24, 25	
24	122.9, CH	5.10, br t (6.8)	23a, 23b, 26, 27	26, 27	22a, 22b, 26
25	132.7, C				
26	25.7, CH_3	1.68, br s	24	24, 25, 27	24
27	17.7, CH_3	1.60, br s	24	24, 25, 26	
28	14.4, CH_3	1.13, d (6.8)	4	3, 4, 5	5, 6
30	18.2, CH_3	1.00, s		7, 8, 9, 14	5, 7, 11b, 13, 15a
6-COCH3	171.5, C				
6-COCH3	21.5, CH_3	2.10, s		6-COCH3	
16-COCH3	170.7, C				
16-COCH3	20.6, CH_3	1.96, s		16-COCH3	

[a] The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S38 NMR data for **45** (^{1}H for 600 MHz and ^{13}C for 150 MHz in $CDCl_3$).

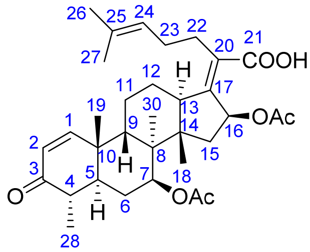


45

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	157.5, CH	7.25, d (10.2)	2	3, 5, 9, 10	11a, 11b, 19
2	127.3, CH	5.86, d (10.2)	1	4, 10	
3	202.0, C				
4	43.8, CH	2.63	5, 28	3, 5, 6, 10, 28	6, 19
5	48.1, CH	2.25, t (11.2)	4, 6	1, 3, 4, 6, 7, 10, 28	7, 28, 30
6	75.3, CH	3.66, dd (10.4, 2.4)	5, 7	4, 5, 7, 8	4, 19, 28
7	83.8, CH	4.67, d (2.2)	6	5, 6, 8, 9, 14, 30, 7-<u>C</u>OCH$_3$	5, 15a, 15b, 30
8	42.5, C				
9	41.6, CH	2.23	11a, 11b	1, 8, 10, 11, 12, 14, 30	12b, 18, 19
10	38.7, C				
11	25.5, CH$_2$	a: 1.99	9, 11b, 12a, 12b		1, 19
		b: 1.47, qd (13.4, 4.5)	9, 11a, 12a, 12b	9, 12	1, 13, 30
12	25.6, CH$_2$	a: 2.35, br d (11.5)	11a, 11b, 12b, 13	9, 14	
		b: 1.76, qd (12.5, 3.9)	11a, 11b, 12a, 13	13	9, 18
13	49.5, CH	2.59	12a, 12b	12, 17, 18, 20	11b, 16, 30
14	48.1, C				
15	39.9, CH$_2$	a: 2.18	15b, 16	8, 14, 18	7, 30
		b: 1.29	15a, 16	13, 16, 17, 18	7
16	73.8, CH	5.88, br d (8.3)	15a, 15b	14, 17, 20, 16-<u>C</u>OCH$_3$	13
17	148.5, C				
18	21.2, CH$_3$	1.08, s		8, 13, 14, 15	9, 12b
19	22.1, CH$_3$	1.26, s		1, 5, 9, 10	1, 4, 6, 9, 11a
20	130.9, C				
21	173.5, C				
22	28.7, CH$_2$	a: 2.49	22b, 23a, 23b	17, 20, 21, 23, 24	24
		b: 2.43	22a, 23a, 23b	17, 20, 21, 23, 24	24
23	28.2, CH$_2$	a: 2.14	22a, 22b, 23b, 24	22, 24, 25	
		b: 2.07	22a, 22b, 23a, 24	22, 24, 25	
24	122.9, CH	5.10, br t (6.8)	23a, 23b, 26, 27	23, 26, 27	22a, 22b, 26
25	132.8, C				
26	25.7, CH$_3$	1.68, br s	24	24, 25, 27	24
27	17.8, CH$_3$	1.60, br s	24	24, 25, 26	
28	15.3, CH$_3$	1.33, d (6.8)	4	3, 4, 5	5, 6
30	17.4, CH$_3$	1.14, s		7, 8, 9, 14	5, 7, 11b, 13, 15a
7-<u>C</u>OCH$_3$	170.9, C				
7-CO<u>C</u>H$_3$	21.8, CH$_3$	2.09, s		7-<u>C</u>OCH$_3$	
16-<u>C</u>OCH$_3$	170.6, C				
16-CO<u>C</u>H$_3$	20.5, CH$_3$	1.97, s		16-<u>C</u>OCH$_3$	

[a] The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S39 NMR data for **46** (^{1}H for 600 MHz and ^{13}C for 150 MHz in $CDCl_3$).

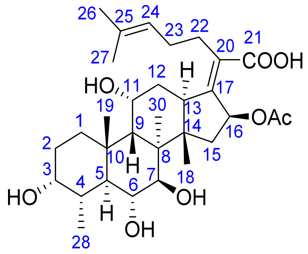


46

Position	δ_C, type	δ_H (J in Hz) [a]	^{1}H–^{1}H COSY	HMBC	NOESY
1	158.5, CH	7.27, d (10.1)	2	3, 5, 10	19
2	127.6, CH	5.84, d (10.1)	1	4, 10	
3	201.7, C				
4	42.7, CH	2.39	5, 28	3, 5, 10, 28	19
5	43.1, CH	2.09	4, 6a, 6b	4, 6, 7, 9, 10, 19	28, 30
6	29.7, CH_2	a: 2.15	5, 6b, 7	5, 7, 10	
		b: 1.33	5, 6a, 7	4, 7, 10	
7	77.5, CH	4.96, t (6.8)	6a, 6b	6, 9, 14, 30, 7-<u>C</u>OCH$_3$	30
8	43.6, C				
9	42.7, CH	2.19	11a, 11b	7, 8, 10, 11, 12, 19, 30	18
10	38.7, C				
11	24.9, CH_2	a: 1.92	9, 11b, 12a, 12b		19
		b: 1.48	9, 11a, 12a, 12b	9, 12	30
12	25.7, CH_2	a: 2.35	11a, 11b, 12b, 13		
		b: 1.79	11a, 11a, 12b, 13	13	18
13	50.3, CH	2.57, br d (11.9)	12a, 12b	11, 14, 17, 18, 20	30
14	48.0, C				
15	40.3, CH_2	a: 2.14	15b, 16	8, 14, 18	
		b: 1.33	15a, 16	13, 14, 16, 17, 18	
16	73.9, CH	5.87, br d (8.5)	15a, 15b	14, 17, 20, 16-<u>C</u>OCH$_3$	
17	148.4, C				
18	21.1, CH_3	1.14, s		8, 13, 14, 15	9, 12b
19	25.6, CH_3	1.25, s		1, 5. 9, 10	1, 4, 11a
20	130.7, C				
21	173.4, C				
22	28.7, CH_2	a: 2.50	22b, 23a, 23b	17, 20, 21, 24	
		b: 2.43	22a, 23a, 23b	17, 20, 21, 24	
23	28.2, CH_2	a: 2.14	22a, 22b, 23b, 24	20, 24, 25	
		b: 2.07	22a, 22b, 23a, 24	20, 24, 25	
24	122.9, CH	5.10, br t (6.7)	23a, 23b, 26, 27	26, 27	26
25	132.8, C				
26	25.7, CH_3	1.68, br s	24	24, 25, 27	24
27	17.8, CH_3	1.60, br s	24	24, 25, 26	
28	12.7, CH_3	1.12, d (6.8)	4	3, 4, 5	5
30	20.2, CH_3	1.05, s		7. 8, 9, 14	5, 7, 11b, 13
7-<u>C</u>OCH$_3$	169.7, C				
7-CO<u>C</u>H$_3$	21.9, CH_3	2.02, s		7-CO<u>C</u>H$_3$	
16-<u>C</u>OCH$_3$	170.5, C				
16-CO<u>C</u>H$_3$	20.5, CH_3	1.96, s		16-<u>C</u>OCH$_3$	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S40 NMR data for **47** ([1]H for 600 MHz and [13]C for 150 MHz in CD_3OD).

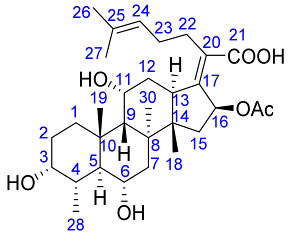


47

Position	δ_C, type	δ_H (J in Hz)[a]	[1]H–[1]H COSY	HMBC	ROESY
1	32.3, CH_2	a: 2.39	1b, 2a, 2b	2, 10, 19	11
		b: 1.49	1a, 2a, 2b	2, 3, 5, 10	11
2	31.0, CH_2	a: 1.91	1a, 1b, 2b, 3	1, 4	
		b: 1.68	1a, 1b, 2a, 3	4	
3	73.5, CH	3.64	2a, 2b, 4	1, 5, 28	
4	38.5, CH	1.87	3, 5, 28	5, 28	6, 19
5	44.2, CH	2.10	4, 6	1, 3, 4, 6, 7, 9, 10, 19, 28	28, 30
6	79.4, CH	3.46, dd (9.4, 2.0)	5, 7	4, 5, 7, 8	4, 19, 28
7	83.8, CH	3.44, d (2.0)	6	5, 6, 8, 9, 14, 30	15a, 15b, 30
8	45.1, C				
9	46.7, CH	2.00, d (2.0)	11	1, 7, 8, 10, 11, 14, 19, 30	18, 19
10	38.3, C				
11	68.9, CH	4.36	9, 12a, 12b	8, 13	1a, 1b, 19
12	37.3, CH_2	a: 2.29, dt (13.0, 3.0)	11, 12b, 13	11, 13, 14	
		b: 1.90	11, 12a, 13	9, 13	
13	46.3, CH	3.11, br d (11.5)	12a, 12b	12, 14, 17, 18, 20	15a, 30
14	49.8, C				
15	40.6, CH_2	a: 2.20, dd (14.1, 8.6)	15b, 16	8, 14, 16, 18	7, 13, 30
		b: 1.45, br d (14.2)	15a, 16	13, 14, 16, 17, 18	7, 18
16	76.0, CH	5.81, br d (8.6)	15a, 15b	13, 14, 15, 17, 20, 16-<u>C</u>OCH3	
17	148.6, C				
18	21.8, CH_3	1.15, s		8, 13, 14, 15	9, 15b
19	24.2, CH_3	1.20, s		1, 5, 9, 10	4, 6, 9, 11
20	132.8, C				
21	174.6, C				
22	30.0, CH_2	a: 2.53	22b, 23	17, 20, 21, 23, 24	
		b: 2.35	22a, 23	17, 20, 21, 23, 24	
23	29.3, CH_2	2.10	22a, 22b, 24	22, 24, 25	
24	124.5, CH	5.13, br t (7.3)	23, 26, 27	23, 26, 27	26
25	133.3, C				
26	25.9, CH_3	1.66, br s	24	24, 25, 27	24
27	17.9, CH_3	1.60, br s	24	24, 25, 26	
28	18.5, CH_3	1.10, br d (7.0)	4	3, 4, 5	5, 6
30	22.0, CH_3	1.36, s		7, 8, 9, 14	5, 7, 13, 15a
16-<u>C</u>OCH3	172.8, C				
16-CO<u>C</u>H3	20.7, CH_3	1.96, s		16-<u>C</u>OCH3	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S41 NMR data for **48** (^{1}H for 600 MHz and ^{13}C for 150 MHz in CD_3OD).

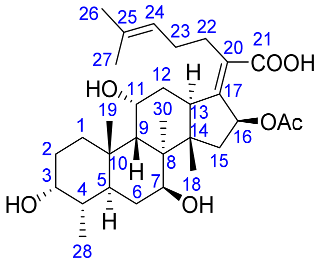


48

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	31.2, CH_2	a: 2.32	1b, 2a, 2b	2, 10, 19	
		b: 1.48	1a, 2a, 2b	2, 3, 9, 10	11
2	30.8, CH_2	a: 1.84	1a, 1b, 2b, 3	1	
		b: 1.69	1a, 1b, 2a, 3	3, 4, 10	
3	73.4, CH	3.64	2a, 2b, 4	1, 5, 28	28
4	38.9, CH	1.78	3, 5, 28	5, 28	6
5	43.9, CH	2.20, dd (11.9, 9.5)	4, 6	1, 3, 4, 6, 10, 19	28, 30
6	70.5, CH	3.73, br dd (9.4, 6.7)	5, 7a, 7b	4, 5, 7, 8, 10	4, 19, 28
7	43.6, CH_2	a: 1.95	6, 7b	5, 6, 8, 9, 14, 30	
		b: 1.25	6, 7a	6, 8, 9, 14, 30	
8	40.4, C				
9	51.7, CH	1.57, d (1.3)	11	1, 8, 10, 11, 12, 14, 19, 30	18, 19
10	37.6, C				
11	68.3, CH	4.33	9, 12a, 12b	8, 9, 13	1b, 19
12	37.3, CH_2	a: 2.30	11, 12b, 13	11, 13, 14	
		b: 1.85	11, 12a, 13	13, 14	
13	44.4, CH	3.09, br d (11.6)	12a, 12b	12, 14, 17, 18, 20	15a, 16, 30
14	49.4, C				
15	39.9, CH_2	a: 2.18	15b, 16	8, 14, 18	13, 30
		b: 1.25	15a, 16	8, 13, 14, 16, 17, 18	18
16	75.6, CH	5.80, br d (8.6)	15a, 15b	13, 14, 17, 20, 16-<u>C</u>OCH3	13
17	148.4, C				
18	17.6, CH_3	0.91, s		8, 13, 14, 15	9, 15b
19	25.9, CH_3	0.99, s		1, 5, 9, 10	6, 9, 11
20	132.2, C				
21	174.3, C				
22	29.8, CH_2	a: 2.53	22b, 23a, 23b	17, 20, 21, 23, 24	24
		b: 2.35	22a, 23a, 23b	17, 20, 21, 23, 24	24
23	29.3, CH_2	a: 2.12	22a, 22b, 23b, 24	20, 22, 24, 25	
		b: 2.06	22a, 22b, 23a, 24	20, 22, 24, 25	
24	124.3, CH	5.12, br t (7.3)	23, 26, 27	23, 26, 27	22a, 22b, 26
25	133.3, C				
26	26.0, CH_3	1.66, br s	24	24, 25, 27	24
27	17.9, CH_3	1.60, br s	24	24, 25, 26	
28	18.6, CH_3	1.12, d (7.0)	4	3, 4, 5	3, 5, 6
30	23.1, CH_3	1.44, s		7, 8, 9, 14	5, 13, 15a
16-<u>C</u>OCH3	172.5, C				
16-CO<u>C</u>H3	20.7, CH_3	1.96, s		16-<u>C</u>OCH3	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S42 NMR data for **49** (^{1}H for 600 MHz and ^{13}C for 150 MHz in CD_3OD).

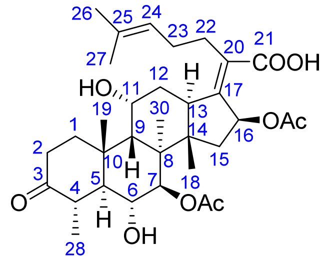


49

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	31.8, CH_2	a: 2.21	1b, 2a, 2b	2, 3, 9, 10, 19	
		b: 1.50	1a, 2a, 2b	2, 3, 5	11
2	31.2, CH_2	a: 1.88	1a, 1b, 2b, 3		
		b: 1.68	1a, 1b, 2a, 3	3	
3	72.4, CH	3.68	2a, 2b, 4	1, 5	28
4	36.8, CH	1.65	3, 5, 28	5, 28	19
5	38.0, CH	1.94	4, 6a, 6b	1, 3, 4, 6, 7, 10, 19	7, 28, 30
6	34.0, CH_2	a: 1.82, ddd (13.4, 6.7, 3.6)	5, 6b, 7	5, 7	28
		b: 1.14, td (12.4, 7.6)	5, 6a, 7	5, 7, 8	
7	80.9, CH	3.67	6a, 6b	5, 6, 9, 30	5, 30
8	47.0, C				
9	48.5, CH	1.87, d (1.9)	11	1, 8, 10, 11, 14, 19, 30	18, 19
10	38.4, C				
11	68.8, CH	4.30	9, 12a, 12b	8, 13	1b, 19
12	37.4, CH_2	a: 2.30, dt (12.9, 2.8)	11, 12b, 13	11, 13, 14	
		b: 1.90	11, 12a, 13	13	22a
13	47.3, CH	3.04, br d (11.4)	12a, 12b	12, 14, 17, 18, 20	15a, 16, 30
14	49.9, C				
15	41.5, CH_2	a: 2.22	15b, 16	8, 14, 16, 18	13, 30
		b: 1.65	15a, 16	13, 14, 16, 17, 18	18
16	76.1, CH	5.81, br d (8.5)	15a, 15b	13, 14, 17, 20, 16-<u>C</u>OCH$_3$	13
17	148.3, C				
18	21.3, CH_3	1.16, s		8, 13, 14, 15	9, 15b
19	22.0, CH_3	1.09, s		1, 5, 9, 10	4, 9, 11
20	132.9, C				
21	174.7, C				
22	30.0, CH_2	a: 2.54	22b, 23	17, 20, 21, 23, 24	12b, 24
		b: 2.35	22a, 23	17, 20, 21, 23, 24	24
23	29.3, CH_2	2.10	22a, 22b, 24	22, 24, 25	
24	124.5, CH	5.13, br t (7.1)	23, 26, 27	23, 26, 27	22a, 22b, 26
25	133.2, C				
26	25.9, CH_3	1.66, br s	24	24, 25, 27	24
27	17.9, CH_3	1.60, br s	24	24, 25, 26	
28	16.6, CH_3	0.89, d (6.8)	4	3, 4, 5	3, 5, 6a
30	25.3, CH_3	1.36, s		7, 8, 9, 14	5, 7, 13, 15a
16-<u>C</u>OCH$_3$	172.8, C				
16-CO<u>C</u>H$_3$	20.8, CH_3	1.96, s		16-<u>C</u>OCH$_3$	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S43 NMR data for **50** (^{1}H for 400 MHz and ^{13}C for 100 MHz in CD_3OD).

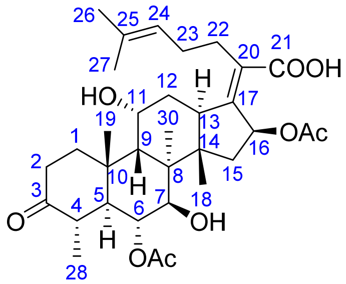


50

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	36.4, CH_2	a: 2.70	1b, 2	3, 10, 19	
		b: 1.95	1a, 2		
2	37.6, CH_2	2.48	1a, 1b	1, 3, 10	
3	218.4, C				
4	47.7, CH	2.54	5, 28	5, 28	6, 19
5	51.3, CH	2.04	4, 6	1, 4, 6, 7, 10, 19, 28	7, 30
6	75.2, CH	3.47, dd (9.4, 3.4)	5, 7	4, 5, 7, 8	4, 19, 28
7	84.6, CH	4.74, d (3.4)	6	5, 6, 9, 30, 7-$\underline{C}OCH_3$	5, 15b, 30
8	45.0, C				
9	47.0, CH	2.03	11	1, 7, 8, 10, 11, 14, 19, 30	18, 19
10	38.2, C				
11	68.0, CH	4.37, br s	9, 12a, 12b	8, 10, 13	19
12	37.3, CH_2	a: 2.32	11, 12b, 13	9, 11, 14	
		b: 1.92	11, 12a, 13	13	
13	46.3, CH	3.14, br d (11.6)	12a, 12b	12, 14, 17, 18, 20	15a, 16, 30
14	49.3, C				
15	40.9, CH_2	a: 2.21, dd (14.6, 8.9)	15b, 16	14, 18	13, 30
		b: 1.23	15a, 16	16, 17	7
16	75.5, CH	5.81, br d (8.4)	15a, 15b	13, 14, 17, 20, 16-$\underline{C}OCH_3$	13
17	147.7, C				
18	21.2, CH_3	1.03, s		8, 13, 14, 15	9
19	24.7, CH_3	1.23, s		1, 5, 9, 10	4, 6, 9, 11
20	133.4, C				
21	174.2, C				
22	29.9, CH_2	a: 2.53	22b, 23	17, 20, 21, 23, 24	24
		b: 2.37	22a, 23	17, 20, 21, 23, 24	24
23	29.2, CH_2	2.12	22a, 22b, 24	22, 24, 25	
24	124.3, CH	5.13, br t (6.6)	23, 26, 27	23, 26, 27	22a, 22b, 26
25	133.4, C				
26	25.9, CH_3	1.66, br s	24	24, 25, 27	24
27	17.9, CH_3	1.60, br s	24	24, 25, 26	
28	16.1, CH_3	1.17, d (6.7)	4	3, 4, 5	6
30	22.3, CH_3	1.44, s		7, 8, 9, 14	5, 7, 13, 15a
7-$\underline{C}OCH_3$	171.9, C				
7-$CO\underline{C}H_3$	22.0, CH_3	2.03, s		7-$\underline{C}OCH_3$	
16-$\underline{C}OCH_3$	172.6, C				
16-$CO\underline{C}H_3$	20.7, CH_3	1.95, s		16-$\underline{C}OCH_3$	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S44 NMR data for **51** (^{1}H for 400 MHz and ^{13}C for 100 MHz in $CDCl_3$).

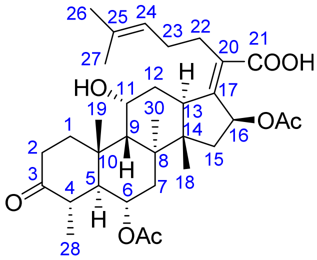


51

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	35.9, CH_2	a: 2.59	1b, 2	2	
		b: 2.00	1a, 2	3, 10	
2	37.4, CH_2	2.47	1a, 1b	1, 3	
3	212.8, C				
4	46.2, CH	2.54	5, 28	3	6, 19
5	47.2, CH	2.28, t (10.5)	4, 6	4, 6, 10, 19	7, 28, 30
6	80.7, CH	4.63, br d (9.4)	5, 7	4, 5, 7, 8, 6-<u>C</u>OCH$_3$	4, 19, 28
7	79.8, CH	3.46, br s	6	5, 6, 9, 30	5, 15b, 30
8	43.7, C				
9	44.8, CH	2.16, br s	11	8, 10, 11, 14, 19, 30	18, 19
10	36.7, C				
11	68.3, CH	4.48, br s	9, 12a, 12b	8, 13	19
12	36.3, CH_2	a: 2.25	11, 12b, 13	11, 14	
		b: 2.00	11, 12a, 13		
13	45.4, CH	3.09, br d (11.6)	12a, 12b	12, 14, 17, 18, 20	16, 30
14	48.4, C				
15	39.6, CH_2	a: 2.21	15b, 16	18	
		b: 1.48, br d (14.2)	15a, 16	13, 14, 16, 17	7
16	74.2, CH	5.90, br d (8.4)	15a, 15b	14, 17, 20, 16-<u>C</u>OCH$_3$	13
17	150.1, C				
18	21.5, CH_3	1.16, s		8, 13, 14, 15	9
19	24.4, CH_3	1.40, s		1, 5, 9, 10	4, 6, 9, 11
20	130.6, C				
21	174.0, C				
22	28.8, CH_2	2.43	23	17, 20, 21, 23, 24	24
23	28.3, CH_2	2.09	22, 24	22, 24	
24	123.0, CH	5.09, br t (6.7)	23, 26, 27	26, 27	22, 26
25	132.7, C				
26	25.7, CH_3	1.67, br s	24	24, 25, 27	24
27	17.8, CH_3	1.59, br s	24	24, 25, 26	
28	13.7, CH_3	0.99, d (6.5)	4	3, 4, 5	5, 6
30	21.1, CH_3	1.26, s		7, 8, 9, 14	5, 7, 13
6-<u>C</u>OCH$_3$	171.3, C				
6-CO<u>C</u>H$_3$	21.6, CH_3	2.06, s		6-<u>C</u>OCH$_3$	
16-<u>C</u>OCH$_3$	170.8, C				
16-CO<u>C</u>H$_3$	20.6, CH_3	1.96, s		16-<u>C</u>OCH$_3$	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S45 NMR data for **52** (^{1}H for 400 MHz and ^{13}C for 100 MHz in CD_3OD).



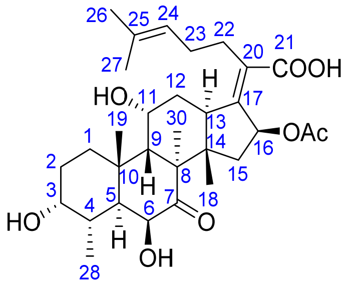
52

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY[b]
1	36.0, CH_2	a: 2.61	1b, 2	2	5
		b: 1.98	1a, 2		11
2	37.8, CH_2	2.46	1a, 1b		
3	217.0, C				
4	47.1, CH	2.54	5, 28		6, 19
5	49.6, CH	2.37, dd (12.4, 9.8)	4, 6	6, 10, 19	1a, 28, 30
6	74.1, CH	4.95, ddd (10.2, 6.9, 3.6)	5, 7a, 7b		4, 19, 28
7	41.6, CH_2	a: 2.14	6, 7b		9, 18
		b: 1.20	6, 7a	30	
8	40.5, C				
9	50.3, CH	1.67	11	8, 10, 11, 14, 19, 30	7a, 12b, 18, 19
10	37.9, C				
11	67.8, CH	4.33, br s	9, 12a, 12b	8, 13	1b, 19
12	37.4, CH_2	a: 2.32	11, 12b, 13	11, 14	
		b: 1.89, td (13.0, 2.0)	11, 12a, 13		9, 18
13	44.4, CH	3.07, br d (11.9)	12a, 12b	12, 17	15a, 16, 30
14	49.4, C				
15	39.8, CH_2	a: 2.13	15b, 16	14	13, 30
		b: 1.23	15a, 16	13	18
16	75.6, CH	5.80, br d (8.5)	15a, 15b	14, 17, 16-$\underline{C}OCH_3$	13
17	147.0, C				
18	17.8, CH_3	0.95, s		8, 13, 14, 15	7a, 9, 12b, 15b
19	25.5, CH_3	1.18, s		1, 5, 9, 10	4, 6, 9, 11
20	132.8, C				
21	#				
22	30.0, CH_2	a: 2.53	22b, 23		24
		b: 2.37	22a, 23		24
23	29.2, CH_2	2.11	22a, 22b, 24		
24	124.5, CH	5.13, br t (6.5)	23, 26, 27	26, 27	22a, 22b, 26
25	133.3, C				
26	25.9, CH_3	1.66, br s	24	24, 25, 27	24
27	17.8, CH_3	1.60, br s	24	24, 25, 26	
28	14.9, CH_3	1.01, d (6.6)	4	3, 4, 5	5, 6
30	23.7, CH_3	1.37, s		7, 8, 9, 14	5, 13, 15a
6-$\underline{C}OCH_3$	172.4, C				
6-$CO\underline{C}H_3$	21.7, CH_3	2.00, s		6-$\underline{C}OCH_3$	
16-$\underline{C}OCH_3$	172.7, C				
16-$CO\underline{C}H_3$	20.7, CH_3	1.96, s		16-$\underline{C}OCH_3$	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

[b]The data were measured in CD_3OD at 600 MHz; [#] The data is not observed.

Table S46 NMR data for **55** (^{1}H for 600 MHz and ^{13}C for 150 MHz in CD_3OD).

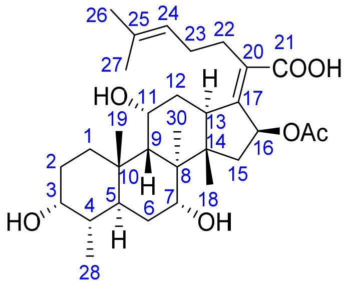


55

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	33.7, CH_2	a: 2.20	1b, 2a, 2b	2, 5, 10, 19	
		b: 1.53	1a, 2a, 2b	2, 3, 5, 10	11
2	31.3, CH_2	a: 1.94	1a, 1b, 2b, 3		19
		b: 1.71	1a, 1b, 2a, 3	3, 4, 10	
3	72.3, CH	3.81, br s	2a, 2b, 4	1, 4, 5	28
4	33.4, CH	2.19	3, 5, 28	5, 10, 28	19
5	40.7, CH	2.12	4, 6	1, 3, 4, 7, 10, 19	28, 30
6	75.0, CH	3.80, br s	5	4, 5, 7, 8, 10	28
7	218.3, C				
8	54.5, C				
9	46.7, CH	2.39, d (1.5)	11	1, 7, 8, 10, 11, 14, 19, 30	12b, 18, 19
10	38.0, C				
11	67.9, CH	4.41, br s	9, 12a, 12b	8, 10, 13	1b, 19
12	37.0, CH_2	a: 2.34	11, 12b, 13		
		b: 1.88, td (12.6, 2.3)	11, 12a, 13	13	9, 18
13	45.2, CH	3.10, br d (11.7)	12a, 12b	12, 14, 17, 18, 20	16, 30
14	48.0, C				
15	42.0, CH_2	a: 2.33	15b, 16	8, 14, 18	30
		b: 1.81, br d (14.6)	15a, 16	13, 14, 16, 17, 18	18
16	75.6, CH	5.81, br d (8.5)	15a, 15b	13, 14, 15, 17, 20, 16-<u>C</u>OCH$_3$	13
17	147.5, C				
18	18.7, CH_3	0.90, s		8, 13, 14, 15	9, 12b, 15b
19	24.3, CH_3	1.33, s		1, 5, 9, 10	2a, 4, 9, 11
20	132.5, C				
21	174.2, C				
22	29.8, CH_2	a: 2.56	22b, 23	17, 20, 21, 23, 24	24
		b: 2.37	22a, 23	17, 20, 21, 23, 24	24
23	29.3, CH_2	2.11	22a, 22b, 24	22, 24, 25	
24	124.3, CH	5.13, br t (7.3)	23, 26, 27	23, 26, 27	22a, 22b, 26
25	133.4, C				
26	25.9, CH_3	1.67, br s	24	24, 25, 27	24
27	17.9, CH_3	1.61, br s	24	24, 25, 26	
28	16.1, CH_3	0.97, d (6.7)	4	3, 4, 5	3, 5, 6
30	22.8, CH_3	1.49, s		7, 8, 9, 14	5, 13, 15a
16-<u>C</u>OCH$_3$	172.6, C				
16-CO<u>C</u>H$_3$	20.7, CH_3	1.96, s		16-<u>C</u>OCH$_3$	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S47 NMR data for **56** (^{1}H for 600 MHz and ^{13}C for 150 MHz in CD_3OD).

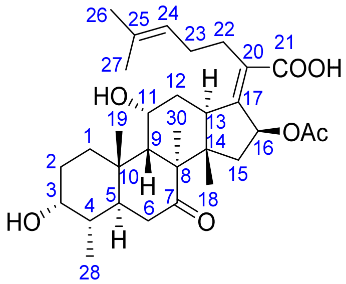


56

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	30.6, CH_2	a: 2.31	1b, 2a, 2b	5, 10, 19	
		b: 1.44	1a, 2a, 2b		11
2	30.8, CH_2	a: 1.81	1a, 1b, 2b, 3		19
		b: 1.68	1a, 1b, 2a, 3		
3	72.0, CH	3.63, br s	2a, 2b, 4	1, 2, 5	28
4	38.9, CH	1.49	3, 5, 28	10, 28	19
5	37.2, CH	2.33	4, 6a, 6b	4, 6	28, 30
6	34.9, CH_2	a: 1.60	5, 6b, 7	4, 5, 7, 8	
		b: 1.48	5, 6a, 7	7, 10	
7	71.4, CH	3.88, t (8.3)	6a, 6b	6, 8, 9, 14, 30	9, 18, 19
8	46.3, C				
9	51.8, CH	1.55, br s	11	7, 8, 10, 11, 19, 30	7, 18, 19
10	37.4, C				
11	68.5, CH	4.34, br s	9, 12a, 12b	8, 13	1b, 19
12	37.2, CH_2	a: 2.30	11, 12b, 13		
		b: 1.84	11, 12a, 13	13	18, 22a
13	45.3, CH	3.04, br d (11.8)	12a, 12b	12, 14, 17, 18, 20	16, 30
14	49.2, C				
15	43.0, CH_2	a: 2.27, dd (14.9, 8.9)	15b, 16	8, 14, 18	30
		b: 1.57, br d (14.9)	15a, 16	13, 14, 16, 17, 18	
16	76.0, CH	5.76, br d (8.7)	15a, 15b	13, 14, 15, 17, 20, 16-<u>C</u>OCH3	13
17	147.6, C				
18	16.6, CH_3	0.99, s		8, 13, 14, 15	7, 9, 12b
19	25.0, CH_3	0.97, s		1, 5, 9, 10	2a, 4, 7, 9, 11
20	132.1, C				
21	174.7, C				
22	29.9, CH_2	a: 2.55	22b, 23a, 23b	17, 20, 21, 23, 24	12b, 24
		b: 2.35	22a, 23a, 23b	17, 20, 21, 23, 24	24
23	29.4, CH_2	a: 2.13	22a, 22b, 23b, 24	20, 22, 24, 25	
		b: 2.08	22a, 22b, 23a, 24	20, 22, 24, 25	
24	124.4, CH	5.13, br t (7.3)	23a, 23b, 26, 27	23, 26, 27	22a, 22b, 26
25	133.3, C				
26	25.9, CH_3	1.67, br s	24	24, 25, 27	24
27	17.9, CH_3	1.61, br s	24	24, 25, 26	
28	16.2, CH_3	0.90, d (6.8)	4	3, 4, 5	3, 5
30	14.9, CH_3	1.32, s		7, 8, 9, 14	5, 13, 15a
16-<u>C</u>OCH3	172.6, C				
16-CO<u>C</u>H3	20.7, CH_3	1.95, s		16-<u>C</u>OCH3	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S48 NMR data for **57** (^{1}H for 600 MHz and ^{13}C for 150 MHz in CD_3OD).



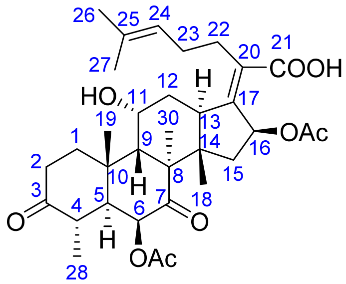
57

Position	δ_C, type	δ_H (J in Hz)[a]	^1H–^1H COSY	HMBC	ROESY
1	31.7, CH_2	a: 2.21	1b, 2a, 2b	2, 10, 19	
		b: 1.62	1a, 2a, 2b	2, 3, 5, 10	11, 19
2	31.2, CH_2	a: 1.92	1a, 1b, 2b, 3		19
		b: 1.75	1a, 1b, 2a, 3		
3	71.9, CH	3.74, br s	2a, 2b, 4	1, 5	28
4	35.3, CH	1.81	3, 5, 28	5, 28	19
5	37.2, CH	2.23[b]	4, 6	3, 4, 6, 7, 10, 19	30
6	40.8, CH_2	2.13	5	5, 7, 8, 10	
7	222.1, C				
8	54.7, C				
9	48.2, CH	1.85	11	1, 7, 8, 10, 11, 14, 19, 30	18, 19
10	38.4, C				
11	67.5, CH	4.37, br s	9, 12a, 12b	8, 13	1b, 19
12	36.9, CH_2	a: 2.32	11, 12b, 13	11, 14	
		b: 1.85	11, 12a, 13	11, 13, 14	
13	44.9, CH	3.07, br d (11.8)	12a, 12b	12, 14, 17, 18, 20	16, 30
14	48.4, C				
15	41.8, CH_2	a: 2.31	15b, 16	8, 14, 18	30
		b: 1.73, br d (14.8)	15a, 16	13, 14, 16, 17, 18	18
16	75.5, CH	5.79, br d (8.5)	15a, 15b	13, 14, 15, 17, 20, 16-<u>C</u>OCH$_3$	13
17	146.5, C				
18	17.6, CH_3	0.82, s		8, 13, 14, 15	9, 15b
19	20.6, CH_3	1.08, s		1, 5, 9, 10	1b, 2a, 4, 9, 11
20	133.2, C				
21	174.6, C				
22	29.9, CH_2	a: 2.54	22b, 23	17, 20, 21, 23, 24	24
		b: 2.35	22a, 23	17, 20, 21, 23, 24	24
23	29.3, CH_2	2.09	22a, 22b, 24	22, 24, 25	
24	124.3, CH	5.13, br t (7.3)	23, 26, 27	23, 26, 27	22a, 22b, 26
25	133.4, C				
26	25.9, CH_3	1.66, br s	24	24, 25, 27	24
27	17.9, CH_3	1.60, br s	24	24, 25, 26	
28	16.4, CH_3	0.88, br d (6.8)	4	3, 4, 5	3
30	22.4, CH_3	1.48, s		7, 8, 9, 14	5, 13, 15a
16-<u>C</u>OCH$_3$	172.6, C				
16-CO<u>C</u>H$_3$	20.7, CH_3	1.95, s		16-<u>C</u>OCH$_3$	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

[b]The chemical shift was confirmed by ^1H-^1H COSY, HMBC and ROESY.

Table S49 NMR data for **58** (^{1}H for 400 MHz and ^{13}C for 100 MHz in CD_3OD).

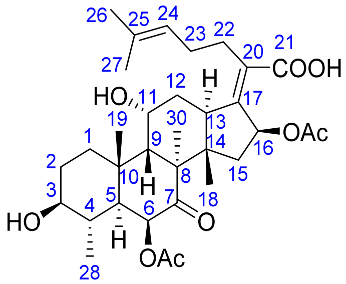


58

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	36.6, CH_2	a: 2.49	1b, 2	19	
		b: 2.01	1a, 2	3, 5	
2	38.2, CH_2	2.51	1a, 1b	3, 10	
3	215.4, C				
4	43.1, CH	2.61	5, 28	3, 5, 28	6, 19
5	47.1, CH	2.23, br d (12.1)	4, 6	3, 4, 7, 10, 19, 28	28, 30
6	74.9, CH	5.17, br s	5	4, 5, 7, 8, 10, 6-<u>C</u>OCH3	4, 28
7	211.7, C				
8	54.9, C				
9	46.2, CH	2.44, br s	11	7, 8, 10, 11, 12, 19, 30	12b, 18, 19
10	37.3, C				
11	67.6, CH	4.50, br s	9, 12a, 12b	8, 10, 13	19
12	36.8, CH_2	a: 2.37	11, 12b, 13	9, 11, 14	
		b: 1.99	11, 12a, 13	13	9
13	44.9, CH	3.13, br d (12.0)	12a, 12b	11, 12, 14, 17, 18, 20	16, 30
14	48.2, C				
15	41.7, CH_2	a: 2.34	15b, 16	8, 14, 18	30
		b: 1.74, br d (14.5)	15a, 16	13, 14, 16, 17, 18	18
16	75.3, CH	5.81, br d (8.1)	15a, 15b	13, 14, 17, 20, 16-<u>C</u>OCH3	13
17	146.7, C				
18	18.4, CH_3	0.87, s		8, 13, 14, 15	9, 15b
19	24.7, CH_3	1.39, s		1, 5, 9, 10	4, 9, 11
20	133.0, C				
21	174.1, C				
22	29.8, CH_2	a: 2.55	22b, 23	17, 20, 21, 23, 24	
		b: 2.38	22a, 23	17, 20, 21, 23, 24	
23	29.2, CH_2	2.12	22a, 22b, 24	22, 24, 25	
24	124.2, CH	5.14, br t (6.9)	23, 26, 27	23, 26, 27	26
25	133.4, C				
26	25.9, CH_3	1.67, br s	24	24, 25, 27	24
27	17.9, CH_3	1.61, br s	24	24, 25, 26	
28	13.2, CH_3	1.10, d (6.3)	4	3, 4, 5	5, 6
30	22.4, CH_3	1.52, s		7, 8, 9, 14	5, 13, 15a
6-<u>C</u>OCH3	170.8, C				
6-CO<u>C</u>H3	20.7, CH_3	2.08, s		6-<u>C</u>OCH3	
16-<u>C</u>OCH3	172.4, C				
16-CO<u>C</u>H3	20.7, CH_3	1.96, s		16-<u>C</u>OCH3	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S50 NMR data for **59** (^{1}H for 400 MHz and ^{13}C for 100 MHz in CD_3OD).

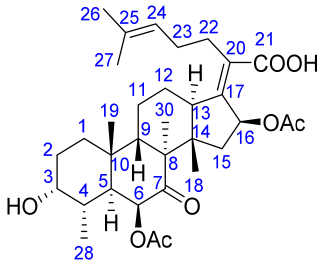


59

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	36.9, CH_2	a: 1.99	1b, 2a, 2b		
		b: 1.84	1a, 2a, 2b	2, 3, 10	
2	32.5, CH_2	a: 1.88	1a, 1b, 2b, 3	3, 4	
		b: 1.66	1a, 1b, 2a, 3		
3	77.3, CH	3.07	2a, 2b, 4	1	28
4	47.5, CH	1.75	3, 5, 28	5, 6	19
5	36.4, CH	1.73	4, 6	6	28, 30
6	75.1, CH	5.24, br s	5	4, 7, 8, 10, 6-<u>C</u>OCH3	28
7	212.5, C				
8	54.7, C				
9	47.3, CH	2.31, br s	11	7, 8, 10, 11, 14, 19, 30	18, 19
10	37.5, C				
11	67.8, CH	4.43, br s	9, 12a, 12b	8, 9, 10, 13	19
12	36.9, CH_2	a: 2.34	11, 12b, 13	14	
		b: 1.92	11, 12a, 13	13	
13	45.0, CH	3.09	12a, 12b	12, 14, 17, 18, 20	16, 30
14	48.2, C				
15	41.5, CH_2	a: 2.28	15b, 16	8, 14, 18	
		b: 1.71	15a, 16	13, 14, 16, 17	
16	75.4, CH	5.81, br d (8.3)	15a, 15b	14, 15, 17, 20, 16-<u>C</u>OCH3	13
17	146.7, C				
18	18.3, CH_3	0.87, s		8, 13, 14, 15	9
19	25.1, CH_3	1.29, s		1, 5, 9, 10	4, 9, 11
20	133.0, C				
21	174.2, C				
22	29.8, CH_2	a: 2.55	22b, 23	17, 20, 21, 23	
		b: 2.36	22a, 23	17, 20, 21, 23	
23	29.2, CH_2	2.10	22a, 22b, 24	22, 24, 25	
24	124.3, CH	5.13, br t (7.2)	23, 26, 27	23, 26, 27	26
25	133.4, C				
26	25.9, CH_3	1.67, br s	24	24, 25, 27	24
27	17.9, CH_3	1.61, br s	24	24, 25, 26	
28	15.7, CH_3	1.03, d (4.6)	4	3, 4, 5	3, 5, 6
30	22.7, CH_3	1.51, s		7, 8, 9, 14	5, 13
6-<u>C</u>OCH3	170.9, C				
6-CO<u>C</u>H3	20.8, CH_3	2.05, s		6-<u>C</u>OCH3	
16-<u>C</u>OCH3	172.5, C				
16-CO<u>C</u>H3	20.7, CH_3	1.95, s		16-<u>C</u>OCH3	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S51 NMR data for **60** (^1H for 600 MHz and ^{13}C for 150 MHz in $CDCl_3$).

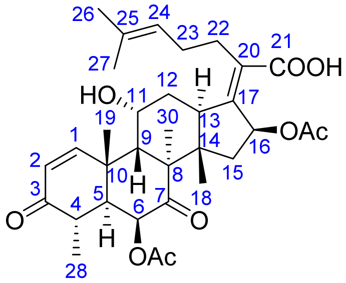


60

Position	δ_C, type	δ_H (J in Hz)[a]	^1H–^1H COSY	HMBC	ROESY
1	29.7, CH_2	a: 1.75	1b, 2a, 2b	2, 10, 19	
		b: 1.23	1a, 2a, 2b	3, 5, 10	
2	29.5, CH_2	a: 1.83	1a, 1b, 2b, 3	1	
		b: 1.69	1a, 1b, 2a, 3	3, 4, 10	
3	71.0, CH	3.84, br s	2a, 2b, 4	1, 2, 5, 28	28
4	32.3, CH	1.99	3, 5, 28	5, 28	19
5	39.3, CH	2.26	4, 6	1, 3, 4, 7, 10, 19	28, 30
6	74.5, CH	5.14, br s	5	4, 5, 7, 8, 10, 6-<u>C</u>OCH3	28
7	210.2, C				
8	52.8, C				
9	41.9, CH	2.40	11a, 11b	1, 7, 8, 10, 11, 12, 19, 30	12b, 18, 19
10	35.8, C				
11	22.6, CH_2	a: 1.77	9, 11b, 12a, 12b		
		b: 1.40, qd (13.1, 3.4)	9, 11a, 12a, 12b	9	13
12	26.1, CH_2	a: 2.29	11a, 11b, 12b, 13		
		b: 1.69	11a, 11b, 12a, 13	13	9
13	49.1, CH	2.52, br d (11.9)	12a, 12b	12, 14, 17, 18, 20	11b, 16, 30
14	46.8, C				
15	40.4, CH_2	a: 2.24	15b, 16	8, 14, 18	30
		b: 1.83, br d (14.5)	15a, 16	13, 14, 16, 17, 18	18
16	73.6, CH	5.81, br d (8.5)	15a, 15b	13, 14, 17, 20, 16-<u>C</u>OCH3	13
17	148.1, C				
18	17.9, CH_3	0.86, s		8, 13, 14, 15	9, 15b
19	22.7, CH_3	1.18, s		1, 5, 9, 10	4, 9
20	130.2, C				
21	174.6, C				
22	28.4, CH_2	a: 2.47	22b, 23a, 23b	17, 20, 21, 23, 24	24
		b: 2.40	22a, 23a, 23b	17, 20, 21, 23, 24	24
23	28.3, CH_2	a: 2.09	22a, 22b, 23b, 24	22, 24, 25	
		b: 2.01	22a, 22b, 23a, 24	22, 24, 25	
24	122.8, CH	5.06, br t (7.1)	23a, 23b, 26, 27	23, 26, 27	22a, 22b, 26
25	132.6, C				
26	25.6, CH_3	1.65, br s	24	24, 25, 27	24
27	17.6, CH_3	1.57, br s	24	24, 25, 26	
28	15.3, CH_3	0.99, d (6.8)	4	3, 4, 5	3, 5, 6
30	17.9, CH_3	1.30, s		7, 8, 9, 14	5, 13, 15a
6-<u>C</u>OCH3	169.1, C				
6-CO<u>C</u>H3	20.8, CH_3	2.03, s		6-<u>C</u>OCH3	
16-<u>C</u>OCH3	170.2, C				
16-CO<u>C</u>H3	20.4, CH_3	1.89, s		16-<u>C</u>OCH3	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S52 NMR data for **61** (^{1}H for 400 MHz and ^{13}C for 100 MHz in $CDCl_3$).

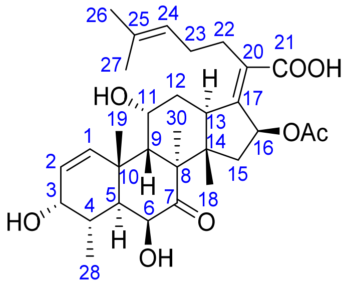


61

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	160.6, CH	8.19, d (10.2)	2	3, 5, 9, 10	11
2	126.3, CH	5.81, d (10.2)	1	4, 10	
3	201.7, C				
4	40.3, CH	2.74, dq (13.2, 6.6)	5, 28	3, 5, 28	6, 19
5	46.5, CH	2.42	4, 6	1, 3, 4, 10, 19, 28	28, 30
6	73.6, CH	5.23, br s	5	4, 5, 7, 8, 10, 6-$\underline{C}OCH_3$	4, 28
7	208.8, C				
8	53.3, C				
9	45.3, CH	2.46	11	1, 7, 8, 10, 11, 14, 19, 30	12b, 18, 19
10	38.7, C				
11	67.2, CH	4.69, br s	9, 12a, 12b	8, 10, 13	1, 19
12	35.7, CH_2	a: 2.39	11, 12b, 13	9, 11	
		b: 2.06	11, 12a, 13	13	9, 18
13	43.9, CH	3.12, br d (12.1)	12a, 12b	11, 12, 14, 17, 18, 20	16, 30
14	46.7, C				
15	40.5, CH_2	a: 2.31, dd (15.0, 8.9)	15b, 16	8, 14, 18	30
		b: 1.91, br d (15.3)	15a, 16	13, 14, 16, 17, 18	18
16	73.8, CH	5.91, br d (8.3)	15a, 15b	13, 14, 17, 20, 16-$\underline{C}OCH_3$	13
17	148.2, C				
18	17.8, CH_3	0.88, s		8, 13, 14, 15	9, 12b, 15b
19	27.8, CH_3	1.47, s		1, 5, 9, 10	4, 9, 11
20	130.4, C				
21	174.1, C				
22	28.7, CH_2	2.44	23a, 23b	17, 20, 21, 24	24
23	28.4, CH_2	a: 2.15	22, 23b, 24	20, 22, 24, 25	
		b: 2.04	22, 23a, 24	20, 22, 24, 25	
24	122.8, CH	5.09, br t (7.0)	23a, 23b, 26, 27	23, 26, 27	22, 26
25	132.9, C				
26	25.7, CH_3	1.66, br s	24	24, 25, 27	24
27	17.8, CH_3	1.58, br s	24	24, 25, 26	
28	13.0, CH_3	1.24, d (6.7)	4	3, 4, 5	5, 6
30	22.3, CH_3	1.38, s		7, 8, 9, 14,	5, 13, 15a
6-$\underline{C}OCH_3$	168.9, C				
6-$CO\underline{C}H_3$	20.6, CH_3	2.08, s		6-$\underline{C}OCH_3$	
16-$\underline{C}OCH_3$	170.5, C				
16-$CO\underline{C}H_3$	20.4, CH_3	1.93, s		16-$\underline{C}OCH_3$	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S53 NMR data for **62** ([1]H for 600 MHz and [13]C for 150 MHz in CD_3OD).



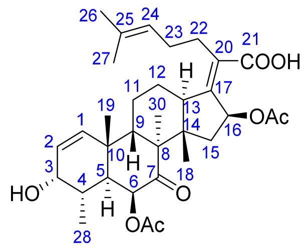
62

Position	δC, type	δH (J in Hz)[a]	[1]H–[1]H COSY	HMBC	ROESY
1	143.7, CH	6.79, d (10.2)	2	3, 5, 10	11, 19
2	126.0, CH	5.49, dd (10.2, 4.3)	1, 3	4, 10	
3	69.4, CH	3.97, t (4.4)	2, 4	1, 2, 5	28
4	32.3, CH	2.46	3, 5, 28	28	19
5	41.1, CH	2.08, dd (11.2, 1.5)	4, 6	1, 3, 4, 10, 19	28, 30
6	74.6, CH	3.91, d (1.5)	5	4, 5, 7, 8, 10	28
7	217.9, C				
8	54.3, C				
9	46.7, CH	2.43, br s	11	1, 7, 8, 10, 11, 14, 19, 30	12b, 18, 19
10	39.4, C				
11	67.9, CH	4.53, br s	9, 12a, 12b	8, 13	1, 19
12	36.8, CH_2	a: 2.37	11, 12b, 13		
		b: 1.91, br t (13.0)	11, 12a, 13	13	9, 18
13	44.7, CH	3.10, br d (11.4)	12a, 12b		15a, 30
14	47.9, C				
15	42.1, CH_2	a: 2.27, dd (15.3, 8.7)	15b, 16	14, 18	13, 30
		b: 1.82, br d (14.7)	15a, 16	13, 14, 16, 18	18
16	75.7, CH	5.81, br d (8.2)	15a, 15b	14	
17	#				
18	18.6, CH_3	0.93, s		8, 13, 14, 15	9, 12b, 15b
19	29.6, CH_3	1.35, s		1, 5, 9, 10	1, 4, 9, 11
20	#				
21	#				
22	30.2, CH_2	a: 2.56	22b, 23		
		b: 2.37	22a, 23		
23	29.3, CH_2	2.13	22a, 22b, 24		
24	124.6, CH	5.15, br t (6.1)	23, 26, 27	23, 26, 27	26
25	133.1, C				
26	25.9, CH_3	1.67, br s	24	24, 25, 27	24
27	17.9, CH_3	1.61, br s	24	24, 25, 26	
28	14.2, CH_3	1.06, d (6.9)	4	3, 4, 5	3, 5, 6
30	22.5, CH_3	1.37, s		7, 8, 9, 14	5, 13, 15a
16-<u>C</u>OCH3	172.8, C				
16-CO<u>C</u>H3	20.9, CH_3	1.97, s		16-<u>C</u>OCH3	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

[#]Data are not observed in NMR spectra.

Table S54 NMR data for **63** (^{1}H for 600 MHz and ^{13}C for 150 MHz in pyridine-d_5).



63

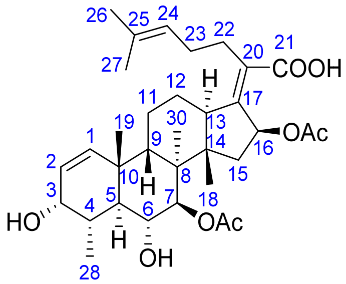
Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY	δ_C, type[b]	δ_H (J in Hz)[a,b]
1	138.2, CH	6.19, d (10.0)	2	3, 5, 10	11a, 11b, 19	140.2, CH	6.18, d (10.0)
2	129.7, CH	5.97, dd (9.7, 3.5)	1, 3	4, 10		128.8, CH	5.58, dd (10.1, 4.0)
3	67.8, CH	4.33, br s	2, 4	1, 2, 5	28	69.0, CH	4.01, t (4.3)
4	31.8, CH	2.50	3, 5, 28	3, 5, 10, 28	19	32.3, CH	2.36
5	41.1, CH	2.51	4, 6	1, 3, 4, 7, 9, 10, 19	30	41.8, CH	2.10
6	74.8, CH	5.74, br s	5	4, 5, 7, 8, 10, 6-<u>C</u>OCH3	28	75.5, CH	5.19, br s
7	210.7, C					212.0, C	
8	53.0, C					54.0, C	
9	42.1, CH	2.62	11a, 11b	1, 7, 8, 10, 11, 19, 30	18, 19	43.2, CH	2.50
10	38.0, C					38.8, C	
11	24.0, CH2	a: 1.90	9, 11b, 12a, 12b	8, 13	1	24.8, CH2	a: 1.96
		b: 1.46	9, 11a, 12a, 12b		1, 30		b: 1.56
12	26.5, CH2	a: 2.43	11a, 11b, 12b, 13	14		27.4, CH2	a: 2.38
		b: 1.81, br q (13.6)	11a, 11b, 12a, 13	11, 13	18		b: 1.77
13	49.1, CH	2.60	12a, 12b	12, 14, 17, 18	16, 30	50.0, CH	2.65, br d (11.4)
14	47.0, C					47.8, C	
15	41.3, CH2	a: 2.35, dd (14.2, 8.8)	15b, 16	8, 14, 18	30	41.8, CH2	a: 2.23, dd (14.8, 9.0)
		b: 2.17	15a, 16	13, 14, 16, 17, 18	18		b: 1.73
16	74.2, CH	6.43, br d (8.4)	15a, 15b	13, 14, 17, 20, 16-<u>C</u>OCH3	13	75.2, CH	5.77, br d (8.3)
17	144.6, C					146.1, C	
18	18.1, CH3	1.13, s		8, 13, 14, 15	9, 12b, 15b	18.4, CH3	0.87, s
19	28.3, CH3	1.42, s		1, 5, 9, 10	1, 4, 9	28.4, CH3	1.30, s
20	133.1, C					132.8, C	
21	173.0, C					#	
22	29.5, CH2	a: 2.94	22b, 23a, 23b	17, 20, 21, 23, 24	24	29.7, CH2	a: 2.57
		b: 2.84	22a, 23a, 23b	17, 20, 21, 23, 24	24		b: 2.38
23	29.1, CH2	a: 2.57	22a, 22b, 23b, 24	22, 24, 25		29.1, CH2	2.11
		b: 2.44	22a, 22b, 23a, 24	22, 24, 25			
24	124.3, CH	5.41, br t (6.4)	23a, 23b, 26, 27	23, 26, 27	22a, 22b, 26	124.3, CH	5.14, br t (7.3)
25	132.2, C					133.4, C	
26	25.8, CH3	1.72, br s	24	24, 25, 27	24	25.9, CH3	1.68, br s
27	17.8, CH3	1.69, br s	24	24, 25, 26		17.8, CH3	1.61, br s
28	14.5, CH3	1.37, d (4.2)	4	3, 4, 5	3, 6	14.0, CH3	1.04, d (6.8)
30	18.2, CH3	1.13, s		7, 8, 9, 14	5, 11b, 13, 15a	18.6, CH3	1.22, s
6-<u>C</u>OCH3	169.4, C					170.9, C	
6-CO<u>C</u>H3	20.7, CH3	2.13, s		6-<u>C</u>OCH3		20.7, CH3	2.07, s
16-<u>C</u>OCH3	170.4, C					172.5, C	
16-CO<u>C</u>H3	20.6, CH3	1.91, s		16-<u>C</u>OCH3		20.6, C	1.95, s

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

[b]The data were measured in CD_3OD (^{1}H NMR for 400 MHz and ^{13}C NMR for 100 MHz).

[#]The data is not observed in NMR spectra.

Table S55 NMR data for **64** (^{1}H for 600 MHz and ^{13}C for 150 MHz in CD_3OD).

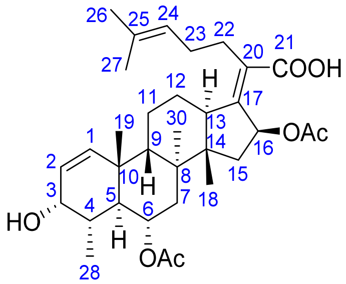


64

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	141.3, CH	6.09, d (10.2)	2	3, 5, 10, 19	11a, 11b, 19
2	127.2, CH	5.59, dd (10.2, 4.7)	1, 3	3, 4, 10	
3	70.1, CH	3.78, t (4.0)	2, 4	1, 2, 5	28
4	36.4, CH	2.07	3, 5, 28	5	19
5	42.0, CH	2.09	4, 6	1, 3, 4, 6, 10, 19	28, 30
6	75.6, CH	3.52, br d (9.8)	5, 7	4, 5, 7, 8	19
7	84.5, CH	4.81, br s	6	6, 8, 9, 14, 30, 7-<u>C</u>OCH$_3$	30
8	43.8, C				
9	42.8, CH	2.22, dd (13.4, 3.7)	11a, 11b	1, 5, 8, 10, 11, 14, 19, 30	12b, 18, 19
10	39.6, C				
11	26.2, CH$_2$	a: 2.00	9, 11b, 12a, 12b		1
		b: 1.39, qd (13.0, 4.4)	9, 11ba 12a, 12b	9, 12	1, 13, 30
12	27.2, CH$_2$	a: 2.29	11a, 11b, 12b, 13		
		b: 1.69	11a, 11b, 12a, 13	11, 13	9, 18
13	50.2, CH	2.63, br d (11.2)	12a, 12b	12, 14, 17, 18, 20	11b, 15a, 16, 30
14	49.5, C				
15	41.0, CH$_2$	a: 2.18, dd (14.4, 9.2)	15b, 16	8, 14, 18,	13
		b: 1.20, br d (14.4)	15a, 16	13, 16, 17, 18	18
16	75.5, CH	5.78, br d (8.6)	15a, 15b	14, 17, 20, 16-<u>C</u>OCH$_3$	13
17	146.9, C				
18	21.6, CH$_3$	1.03, s		8, 13, 14, 15	9, 12b, 15b, 7-COC<u>H</u>$_3$
19	27.7, CH$_3$	1.14, s		1, 5, 9, 10	1, 4, 6, 9
20	133.6, C				
21	174..5, C				
22	29.8, CH$_2$	a: 2.54, dt (13.2, 7.6)	22b, 23	17, 20, 21, 23, 24	24
		b: 2.35	22a, 23	17, 20, 21, 23, 24	24
23	29.0, CH$_2$	2.08	22a, 22b, 24	22, 24, 25	
24	124.4, CH	5.12, br t (7.2)	23, 26, 27	23, 26, 27	22a, 22b, 26
25	133.3, C				
26	25.9, CH$_3$	1.67, br s	24	24, 25, 27	24
27	17.8, CH$_3$	1.60, br s	24	24, 25, 26	
28	16.5, CH$_3$	1.13, d (5.8)	4	3, 4, 5	3, 5
30	17.3, CH$_3$	1.18, s		7, 8, 9, 14	5, 7, 11b, 13
7-<u>C</u>OCH$_3$	171.9, C				
7-CO<u>C</u>H$_3$	22.0, CH$_3$	2.03, s		7-<u>C</u>OCH$_3$	18
16-<u>C</u>OCH$_3$	172.6, C				
16-CO<u>C</u>H$_3$	20.6, CH$_3$	1.95, s		16-<u>C</u>OCH$_3$	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity

Table S56 NMR data for **65** (^{1}H for 600 MHz and ^{13}C for 150 MHz in CD_3OD).

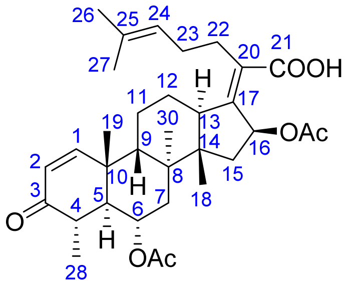


65

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	140.4, CH	6.06, d (10.1)	2	3, 5, 9, 10, 19	11a, 11b, 19
2	127.6, CH	5.62, dd (10.1, 4.8)	1, 3	3, 4, 10	
3	69.8, CH	3.79, t (4.3)	2, 4	1, 2, 4, 5, 28	28
4	36.0, CH	2.06	3, 5, 28	5, 28	6, 19
5	39.9, CH	2.47, t (11.0)	4, 6	1, 3, 4, 6, 7, 9, 10, 19	28, 30
6	73.1, CH	5.01, ddd (10.8, 7.3, 2.4)	5, 7a, 7b	4, 5, 8, 6-<u>C</u>OCH$_3$	4, 19, 28
7	41.0, CH$_2$	a: 2.12, dd (14.9, 7.4)	6, 7b	5, 6, 8, 9, 14, 30	18
		b: 1.27, dd (14.9, 2.3)	6, 7a	6, 8, 9, 14, 30	
8	40.0, C				
9	47.7, CH	1.76, dd (13.3, 3.1)	11a, 11b	1, 5, 10, 11, 19, 30	18, 19
10	39.3, C				
11	26.1, CH$_2$	a: 1.92	9, 11b, 12a, 12b	9	1
		b: 1.30, qd (13.0, 4.0)	9, 11ba 12a, 12b	8, 9, 12	1, 13, 30
12	27.8, CH$_2$	a: 2.30	11a, 11b, 12b, 13		
		b: 1.69	11a, 11b, 12a, 13	11, 13	18
13	48.9, CH	2.61, br d (11.5)	12a, 12b	12, 14, 17, 18, 20	11b, 15a, 16, 30
14	49.4, C				
15	40.1, CH$_2$	a: 2.06	15b, 16	14, 16, 18	13
		b: 1.19, br d (14.6)	15a, 16	13, 16, 17, 18	18
16	75.4, CH	5.75, br d (8.6)	15a, 15b	14, 15, 17, 20, 16-<u>C</u>OCH$_3$	13
17	147.3, C				
18	17.9, CH$_3$	0.95, s		8, 13, 14, 15	7a, 9, 12b, 15b
19	28.6, CH$_3$	1.04, s		1, 5, 9, 10	1, 4, 6, 9
20	132.5, C				
21	174.4, C				
22	29.7, CH$_2$	a: 2.55, dt (13.1, 7.6)	22b, 23	17, 20, 21, 23, 24	24
		b: 2.36	22a, 23	17, 20, 21, 23, 24	24
23	29.1, CH$_2$	2.09	22a, 22b, 24	22, 24, 25	
24	124.4, CH	5.12, br t (7.3)	23, 26, 27	23, 26, 27	22a, 22b, 26
25	133.3, C				
26	25.9, CH$_3$	1.67, br s	24	24, 25, 27	24
27	17.8, CH$_3$	1.60, br s	24	24, 25, 26	
28	15.8, CH$_3$	0.97, d (7.0)	4	3, 4, 5	3, 5, 6
30	19.4, CH$_3$	1.17, s		7, 8, 9, 14	5, 11b, 13
6-<u>C</u>OCH$_3$	172.6, C				
6-CO<u>C</u>H$_3$	21.9, CH$_3$	2.01, s		6-CO<u>C</u>H$_3$	
16-<u>C</u>OCH$_3$	172.6, C				
16-CO<u>C</u>H$_3$	20.6, CH$_3$	1.95, s		16-<u>C</u>OCH$_3$	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S57 NMR data for **66** (^{1}H for 600 MHz and ^{13}C for 150 MHz in CD_3OD).

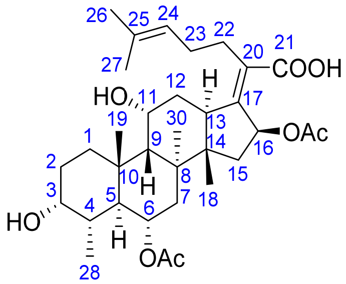


66

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	160.4, CH	7.46, d (9.3)	2	3, 5, 9, 10	11a, 11b
2	128.0, CH	5.84, d (9.5)	1	3, 4, 10	
3	204.5, C				
4	44.0, CH	2.65	5, 28	3, 5, 6, 10, 28	6, 19
5	50.1, CH	2.45, t (10.9)	4, 6	1, 3, 4, 6, 7, 10, 19, 28	28, 30
6	72.5, CH	5.05	5, 7a, 7b	4, 5, 7, 10, 6-<u>C</u>OCH$_3$	4, 9, 19
7	42.1, CH$_2$	a: 2.32	6, 7b	6, 8, 14, 30	18
		b: 1.27	6, 7a	6, 8, 30	
8	40.1, C				
9	45.9, CH	1.81	11a, 11b	1, 8, 11, 19, 30	6, 18, 19
10	40.9, C				
11	25.8, CH$_2$	a: 1.85	9, 11b, 12a, 12b	8	1
		b: 1.53	9, 11a, 12a, 12b	9, 12	1, 30
12	27.3, CH$_2$	a: 2.37	11a, 11b, 12b, 13		
		b: 1.76	11a, 11b, 12a, 13		
13	48.9, CH	2.63	12a, 12b	12, 14, 17, 18, 20	16, 30
14	49.3, C				
15	40.1, CH$_2$	a: 2.04	15b, 16	8, 14, 18	30
		b: 1.24	15a, 16	8, 14, 16, 17, 18	18
16	75.3, CH	5.78, br d (7.1)	15a, 15b	14, 17, 20, 16-<u>C</u>OCH$_3$	13
17	146.6, C				
18	18.4, CH$_3$	1.01, s		8, 13, 14, 15	7a, 9, 15b
19	27.5, CH$_3$	1.24, s		1, 5, 9, 10	4, 6, 9
20	133.3, C				
21	174.6, C				
22	29.8, CH$_2$	a: 2.55	22b, 23	17, 20, 21, 23, 24	24
		b: 2.38	22a, 23	17, 20, 21, 23, 24	24
23	29.1, CH$_2$	2.10	22a, 22b, 24	20, 22, 24, 25	
24	124.4, CH	5.13	23, 26, 27	23, 26, 27	22a, 22b, 26
25	133.3, C				
26	25.9, CH$_3$	1.67, br s	24	24, 25, 27	24
27	17.8, CH$_3$	1.61, br s	24	24, 25, 26	
28	16.3, CH$_3$	1.21, d (5.3)	4	3, 4, 5	5
30	20.9, CH$_3$	1.13, s		7. 8, 9, 14	5, 11b, 13, 15a
6-<u>C</u>OCH$_3$	172.3, C				
6-CO<u>C</u>H$_3$	21.6, CH$_3$	2.03, s		6-<u>C</u>OCH$_3$	
16-<u>C</u>OCH$_3$	172.6, C				
16-CO<u>C</u>H$_3$	20.7, CH$_3$	1.96, s		16-<u>C</u>OCH$_3$	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity

Table S58 NMR data for **67** (^{1}H for 400 MHz and ^{13}C for 100 MHz in acetone-d_6).

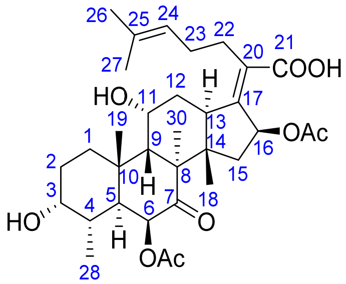


67

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	30.8, CH_2	a: 2.59	1b, 2a, 2b		
		b: 1.49, br d (13.8)	1a, 2a, 2b	3, 5	11, 19
2	31.0, CH_2	a: 1.79	1a, 1b, 2b, 3		
		b: 1.67	1a, 1b, 2a, 3		
3	71.8, CH	3.66, br s	2a, 2b, 4	1, 5	28
4	38.3, CH	1.79	3, 5, 28		6, 19
5	40.2, CH	2.67, t (10.4)	4, 6	1, 3, 4, 6, 10, 19	28, 30
6	73.3, CH	4.84, br dd (9.6, 7.1)	5, 7a, 7b	8, 6-<u>C</u>OCH3	4, 19, 28
7	40.4, CH_2	a: 1.92	6, 7b	8, 30	
		b: 1.19	6, 7a	6, 8, 9	
8	39.5, C				
9	51.2, CH	1.61	11	8, 10, 11, 14, 19, 30	12b, 18, 19
10	36.8, C				
11	67.6, CH	4.43, br s	9, 12a, 12b	8, 13	1b, 19
12	37.3, CH_2	a: 2.36	11, 12b, 13	9, 11, 14	
		b: 1.90	11, 12a, 13	13	9, 18
13	44.1, CH	3.16. br d (11.8)	12a, 12b	12, 14, 17, 18, 20	15a, 16, 30
14	48.8, C				
15	39.6, CH_2	a: 2.12	15b, 16	14, 18	13, 30
		b: 1.21	15a, 16	13, 14, 16, 17, 18	18
16	74.7, CH	5.82, br d (8.4)	15a, 15b	14, 17, 20, 16-<u>C</u>OCH3	13
17	149.0, C				
18	17.5, CH_3	0.92, s		8, 13, 14, 15	9, 12b, 15b
19	25.9, CH_3	1.04, s		1, 5, 9, 10	1b, 4, 6, 9, 11
20	131.1, C				
21	171.3, C				
22	29.5, CH_2	a: 2.52	22b, 23	17, 20, 21	24
		b: 2.41	22a, 23	17, 20, 21	24
23	29.2, CH_2	2.10	22a, 22b, 24	24	
24	124.3, CH	5.14, br t (7.0)	23, 26, 27	26, 27	22a, 22b, 26
25	132.6, C				
26	25.8, CH_3	1.66, br s	24	24, 25, 27	24
27	17.8, CH_3	1.60, br s	24	24, 25, 26	
28	17.5, CH_3	0.88, d (6.9)	4	3, 4, 5	3, 5, 6
30	22.5, CH_3	1.44, s		7, 8, 9, 14	5, 13, 15a
6-<u>C</u>OCH3	170.6, C				
6-CO<u>C</u>H3	21.9, CH_3	1.96, s		6-<u>C</u>OCH3	
16-<u>C</u>OCH3	170.3, C				
16-CO<u>C</u>H3	20.6, CH_3	1.88, s		16-<u>C</u>OCH3	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S59 NMR data for **68** ([1]H for 400 MHz and [13]C for 100 MHz in CD_3OD).

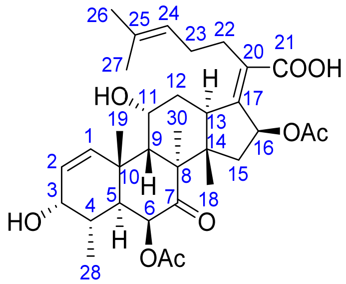


68

Position	δC, type	δH (J in Hz)[a]	[1]H–[1]H COSY	HMBC	ROESY
1	33.3, CH_2	a: 2.28	1b, 2a, 2b		
		b: 1.58	1a, 2a, 2b	3, 5	11
2	31.0, CH_2	a: 1.90	1a, 1b, 2b, 3		
		b: 1.74	1a, 1b, 2a, 3		
3	71.8, CH	3.79, br s	2a, 2b, 4	1, 5	28
4	33.7, CH	2.02	3, 5, 28		19
5	41.1, CH	2.41, dd (10.8, 1.4)	4, 6	3, 4, 7, 10, 19	28, 30
6	75.8, CH	5.14, d (1.4)	5	4, 5, 7, 8, 10, 6-<u>C</u>OCH3	28
7	212.8, C				
8	54.9, C				
9	47.5, CH	2.31, br s	11	1, 7, 8, 10, 11, 14, 19, 30	18, 19
10	38.1, C				
11	67.7, CH	4.44, br s	9, 12a, 12b	8, 13	1b, 19
12	37.0, CH_2	a: 2.35	11, 12b, 13		
		b: 1.92	11, 12a, 13	13	
13	45.1, CH	3.11, br d (11.6)	12a, 12b	12, 14, 17, 18, 20	16, 30
14	48.2, C				
15	41.6, CH_2	a: 2.31	15b, 16	8, 14, 18	30
		b: 1.72, br d (14.6)	15a, 16	13, 14, 16, 17	
16	75.4, CH	5.81, br d (8.4)	15a, 15b	14, 17, 20, 16-<u>C</u>OCH3	13
17	146.8, C				
18	18.3, CH_3	0.86, s		8, 13, 14, 15	9
19	24.3, CH_3	1.29, s		1, 5, 9, 10	4, 9, 11
20	133.0, C				
21	174.3, C				
22	29.8, CH_2	a: 2.55	22b, 23	17, 20, 21, 23	
		b: 2.38	22a, 23	17, 20, 21, 23	
23	29.2, CH_2	2.12	22a, 22b, 24	22, 24, 25	
24	124.3, CH	5.13	23, 26, 27	23, 26, 27	26
25	133.4, C				
26	25.9, CH_3	1.67, br s	24	24, 25, 27	24
27	17.9, CH_3	1.61, br s	24	24, 25, 26	
28	16.1, CH_3	0.96, d (6.8)	4	3, 4, 5	3, 5, 6
30	22.8, CH_3	1.56, s		7, 8, 9, 14	5, 13, 15a
6-<u>C</u>OCH3	171.1, C				
6-CO<u>C</u>H3	20.8, CH_3	2.04, s		6-<u>C</u>OCH3	
16-<u>C</u>OCH3	172.5, C				
16-CO<u>C</u>H3	20.7, CH_3	1.95, s		16-<u>C</u>OCH3	

[a]The indiscernible signals due to overlap or the complex multiplicity are reported without designating multiplicity.

Table S60 NMR data for **69** (^{1}H for 600 MHz and ^{13}C for 150 MHz in CD_3OD).



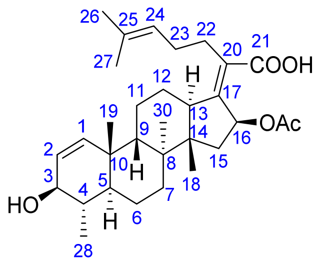
69

Position	δ_C, type	δ_H (J in Hz)[a]	^1H–^1H COSY	HMBC	ROESY
1	142.1, CH	6.71, d (10.2)	2	3, 5, 10	11
2	126.5, CH	5.56, dd (10.1, 4.4)	1, 3	10	
3	69.0, CH	3.96, t (4.5)	2, 4		28
4	32.4, CH	2.28	3, 5, 28		19
5	41.1, CH	2.45, dd (11.2, 2.4)	4, 6	3, 4, 9, 10, 19	28, 30
6	75.1, CH	5.27, d (2.3)	5	4, 5, 7, 10, 6-<u>C</u>OCH3	28
7	212.0, C				
8	54.5, C				
9	47.5, CH	2.34, d (1.6)	11	1, 5, 7, 8, 10, 11, 14, 19, 30	12b, 18, 19
10	39.3, C				
11	67.9, CH	4.56	9, 12a, 12b	8, 13	1, 19
12	36.6, CH2	a: 2.39	11, 12b, 13		
		b: 1.96	11, 12a, 13	13	9, 18
13	44.7, CH	3.09, br d (11.6)	12a, 12b		15a, 16, 30
14	48.1, C				
15	41.6, CH2	a: 2.25	15b, 16	8, 14, 18	13, 30
		b: 1.73, br d (14.6)	15a, 16	13, 14, 16, 17, 18	18
16	75.5, CH	5.81, br d (8.4)	15a, 15b	13, 14, 16-<u>C</u>OCH3	13
17	144.4, C[b]				
18	18.1, CH3	0.90, s		8, 13, 14, 15	9, 12b, 15b
19	29.0, CH3	1.28, s		1, 5, 9, 10	4, 9, 11
20	#				
21	#				
22	30.1, CH2	a: 2.55	22b, 23	23, 24	
		b: 2.37	22a, 23	23, 24	
23	29.2, CH2	2.12	22a, 22b, 24	22, 24, 25	
24	124.6, CH	5.15, br t (7.2)	23, 26, 27	23, 26, 27	26
25	133.2, C				
26	25.9, CH3	1.67, br s	24	24, 25, 27	24
27	17.9, CH3	1.61, br s	24	24, 25, 26	
28	14.3, CH3	1.01, d (6.7)	4	3, 4, 5	3, 5, 6
30	22.1, CH3	1.46, s		7, 8, 9, 14	5, 13, 15a
6-<u>C</u>OCH3	171.1, C				
6-CO<u>C</u>H3	20.8, CH3	2.06, s		6-<u>C</u>OCH3	
16-<u>C</u>OCH3	172.7, C				
16-CO<u>C</u>H3	20.8, CH3	1.97, s		16-<u>C</u>OCH3	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

[b]The data is observed in the HMBC spectrum.[#]The data are not observed in NMR spectra.

Table S61 NMR data for **81** (^{1}H for 600 MHz and ^{13}C for 150 MHz in $CDCl_3$).



81

Position	δ_C, type	δ_H (J in Hz)[a]	^{1}H–^{1}H COSY	HMBC	ROESY
1	139.4, CH	6.06, br d (10.4)	2, 3	3, 5, 10	11a, 11b, 19
2	128.1, CH	5.44, dd (10.0, 2.3)	1, 3	4, 10	11a, 11b, 19
3	76.6, CH	3.77, br d (7.9)	1, 2, 4	1, 2, 4, 28	5, 28
4	37.7, CH	1.77	3, 5, 28	3, 5, 10, 28	19
5	44.1, CH	1.65	4, 6a, 6b	1, 3, 4, 6, 7, 9, 10, 19	3, 30
6	19.7, CH_2	a: 1.57	5, 6b, 7a, 7b	4, 5, 7, 8, 10	
		b: 1.10	5, 6a, 7a, 7b	4, 5, 7, 10	
7	33.6, CH_2	a: 1.91, br dd (14.3, 7.1)	6a, 6b, 7b	5, 6, 8, 14, 30	18
		b: 1.19	6a, 6b, 7a	6, 8, 9, 30	
8	38.5, C				
9	43.8, CH	1.53, dd (12.8, 2.5)	11a, 11b	1, 5, 8, 10, 11, 19, 30	18, 19
10	37.7, C				
11	24.7, CH_2	a: 1.70	9, 11b, 12a, 12b		1, 2
		b: 1.34, qd (12.9, 3.5)	9, 11a, 12a, 12b	9, 12	1, 2, 13
12	26.2, CH_2	a: 2.27	11a, 11b, 12b, 13	9, 14	
		b: 1.65	11a, 11b, 12a, 13	11, 13	
13	49.0, CH	2.52	12a, 12b	12, 14, 17, 18, 20	11b, 15a, 16, 30
14	48.5, C				
15	39.1, CH_2	a: 2.00, dd (14.6, 8.9)	15b, 16	8, 13, 14, 18,	13, 30
		b: 1.27, br d (14.2)	15a, 16	14, 16, 17, 18	18
16	74.1, CH	5.85, br d (8.3)	15a, 15b	14, 17, 20, 16-<u>C</u>OCH3	13
17	149.4, C				
18	18.3, CH_3	0.94, s		8, 13, 14, 15	7a, 9, 15b
19	27.8, CH_3	1.03, s		1, 5, 9, 10	1, 2, 4, 9
20	130.4, C				
21	174.3, C				
22	28.6, CH_2	a: 2.50	22b, 23a, 23b	17, 20, 21, 23, 24	24
		b: 2.42	22a, 23a, 23b	17, 20, 21, 23, 24	24
23	28.2, CH_2	a: 2.11	22a, 22b, 23b, 24	20, 22, 24, 25	
		b: 2.05	22a, 22b, 23a, 24	20, 22, 24, 25	
24	123.1, CH	5.09, br t (7.0)	23a, 23b, 26, 27	23, 26, 27	22a, 22b, 26
25	132.5, C				
26	25.7, CH_3	1.67, br s	24	24, 25, 27	24
27	17.7, CH_3	1.59, br s	24	24, 25, 26	
28	16.5, CH_3	1.02, d (6.4)	4	3, 4, 5	3
30	21.5, CH_3	0.98, s		7, 8, 9, 14	5, 13, 15a
16-<u>C</u>OCH3	171.0, C				
16-CO<u>C</u>H3	20.7, CH_3	1.96, s		16-<u>C</u>OCH3	

[a]The indiscernible signals from overlap or the complex multiplicity are reported without designating multiplicity.

Table S62 The Boltzmann distribution for two possible structures (**34-A** and **34-B**) of **34**.

34-A		**34-B**	
Conformer	Contribution (%)	Conformer	Contribution (%)
1	26.06	1	35.62
2	6.25	2	8.36
3	4.73	3	3.78
4	13.84	4	28.83
5	20.92	5	5.26
6	6.75	6	9.30
7	3.37	7	3.12
8	3.72	8	4.34
9	10.83	9	1.40
10	3.53		

Table S63 The Boltzmann distribution for two possible structures (**35-A** and **35-B**) of **35**.

35-A		**35-B**			
Conformer	Contribution (%)	Conformer	Contribution (%)	Conformer	Contribution (%)
1	12.68	1	3.46	20	4.99
2	2.45	2	1.22	21	5.47
3	3.92	3	3.29	22	3.67
4	8.85	4	3.43	23	4.2
5	2.77	5	1.59	24	3.7
6	2.37	6	2.6	25	3.89
7	7.07	7	2.53	26	1.97
8	11.51	8	4.53	27	1.89
9	4.60	9	1.25	28	1.16
10	3.52	10	4.23	29	1.59
11	7.83	11	1.52	30	1.57
12	5.75	12	1.52	31	3.22
13	3.38	13	2.62	32	1.08
14	2.42	14	1.48	33	1.08
15	5.83	15	5.81	34	1.92
16	4.98	16	2.03	35	1.51
17	3.00	17	1.96	36	1.86
18	5.11	18	1.25	37	3.51
19	1.95	19	1.59	38	3.64

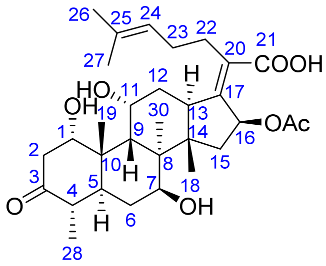
Table S64 The Boltzmann distribution for two possible structures (**38-A** and **38-B**) of **38**.

38-A		**38-B**			
Conformer	Contribution (%)	Conformer	Contribution (%)	Conformer	Contribution (%)
1	3.47	1	1.39	18	2.10
2	1.95	2	4.95	19	2.51
3	4.52	3	3.57	20	1.59
4	2.73	4	2.25	21	1.52
5	10.94	5	1.61	22	11.29
6	14.42	6	2.65	23	7.94
7	6.07	7	1.69	24	3.79
8	8.12	8	1.64	25	2.50
9	2.72	9	5.98	26	1.88
10	1.86	10	3.98	27	2.95
11	1.25	11	7.19	28	1.85
12	5.06	12	8.06		
13	1.44	13	5.54		
14	12.36	14	3.25		
15	15.71	15	1.30		
16	4.66	16	3.08		
17	2.71	17	1.97		

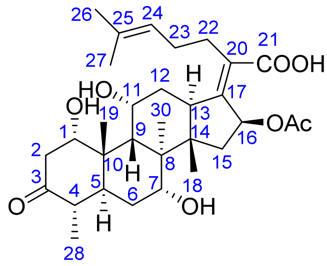
Table S65 The Boltzmann distribution for two possible structures (**42-A** and **42-B**) of **42**.

42-A		**42-B**	
Conformer	Contribution (%)	Conformer	Contribution (%)
1	4.02	1	25.98
2	12.98	2	8.08
3	14.16	3	28.67
4	1.28	4	16.30
5	4.30	5	3.24
6	4.74	6	3.61
7	4.37	7	2.06
8	14.27	8	3.93
9	2.54	9	1.25
10	8.11	10	4.38
11	15.68	11	2.51
12	9.19		
13	4.37		

Table S66 Comparison of the chemical shifts of compounds **38** and **40**.



40



38

	40	**38**
Position	δ_C, type	δ_C, type
1	84.1, CH	83.8, CH
2	42.9, CH_2	42.9, CH_2
3	216.9, C	216.6, C
4	45.3, CH	45.2, CH
5	36.9, CH	37.1, CH
10	43.9, C	43.8, C
19	21.3, CH_3	21.7, CH_3

The relative configuration of **40** is assigned as 1*S**,4*S**,5*S**,7*S**,8*S**,9*S**,10*S**,11*R**,13*R**,14*S**,16*S**.

Table S67 R square (R^2) of the linear correlations, mean absolute error (MAE) values and DP4+ probabilities of **34-A/34-B** and **42-A/42-B** of **34** and **42**, respectively.

No.	**34**	**34-A**		**34-B**		**42**	**42-A**		**42-B**	
	δ_{exptl}	$\delta_{corr.}$	AE	$\delta_{corr.}$	AE	δ_{exptl}	$\delta_{corr.}$	AE	$\delta_{corr.}$	AE
1	139.4	138.32	1.08	136.27	3.13	138.4	138.33	0.07	136.31	2.09
2	127.9	126.08	1.82	127.11	0.79	129.1	126.17	2.93	127.85	1.25
3	68.2	69.61	1.41	75.69	7.49	67.9	69.72	1.82	75.83	7.93
4	32.5	35.03	2.53	38.45	5.95	31.1	33.18	2.08	36.22	5.12
5	36.3	37.37	1.07	41.05	4.75	53.4	52.94	0.46	56.49	3.09
6	38.9	40.52	1.62	40.19	1.29	216.1	215.36	0.74	214.25	1.85
7	217.7	218.77	1.07	218.63	0.93	52.8	53.90	1.10	52.87	0.07
8	52.2	56.16	3.96	55.59	3.39	43.2	46.83	3.63	45.76	2.56
9	43.2	43.50	0.30	42.65	0.55	47.5	47.33	0.17	46.30	1.20
10	37.9	41.64	3.74	40.32	2.42	43.3	47.39	4.09	46.05	2.75
11	24.1	25.61	1.51	24.66	0.56	26.7	28.08	1.38	27.20	0.50
12	26.0	27.44	1.44	26.58	0.58	27	28.28	1.28	27.50	0.50
13	49.3	51.63	2.33	50.88	1.58	49.6	53.06	3.46	52.39	2.79
14	46.8	50.68	3.88	49.86	3.06	49.5	51.87	2.37	51.14	1.64
15	40.6	40.46	0.14	39.64	0.96	40.2	40.17	0.03	39.40	0.80
16	73.7	74.92	1.22	74.26	0.56	75.4	76.17	0.77	75.69	0.29
17	147.7	155.59	7.89	155.39	7.69	146.3	158.72	12.42	158.67	12.37
18	17.4	15.85	1.55	14.61	2.79	19	19.53	0.53	18.73	0.27
19	25.9	24.64	1.26	25.73	0.17	28.4	27.46	0.94	28.48	0.08
20	130.3	128.78	1.52	128.31	1.99	133.8	130.01	3.79	129.82	3.98
21	173.7	166.36	7.34	165.96	7.74	174.7	167.50	7.20	167.44	7.26
22	28.6	24.68	3.92	23.76	4.84	29.9	25.82	4.08	24.99	4.91
23	28.3	14.91	13.39	13.96	14.34	29.1	15.94	13.16	15.03	14.07
28	13.9	14.02	0.12	14.96	1.06	14.1	13.83	0.27	15.15	1.05
30	17.6	18.86	1.26	18.10	0.50	21.1	22.09	0.99	21.01	0.09
16-<u>C</u>OCH3	170.6	167.67	2.93	167.39	3.21	172.6	169.84	2.76	169.85	2.75
16-CO<u>C</u>H3	20.6	20.25	0.35	19.35	1.25	20.7	21.29	0.59	20.44	0.26
MAE		2.20		2.66			2.71		3.02	
R^2		0.9955		0.9940			0.9943		0.9932	
DP4+		100.0%		0.00%			100.00%		0.00%	

AE: absolute error; MAE: mean absolute error.

Based on the values of MAE, R^2 and DP4+, the relative configuration of **34** is assigned as 3*R**,4*S**,5*S**,8*S**,9*S**,10*S**,13*R**,14*S**,16*S**, and the relative configuration of **42** is assigned as 3*R**,4*S**,5*S**,8*S**,9*S**,10*R**,13*R**,14*S**,16*S**.

Table S68 R square (R^2) of the linear correlations, mean absolute error (MAE) values and DP4+ probabilities of **35-A/35-B** and **38-A/38-B** of **35** and **38**, respectively.

No.	**35**	**35-A**		**35-B**		**38**	**38-A**		**38-B**	
	δ_{exptl}	$\delta_{corr.}$	AE	$\delta_{corr.}$	AE	δ_{exptl}	$\delta_{corr.}$	AE	$\delta_{corr.}$	AE
1	84.7	74.02	10.68	73.57	11.13	83.4	74.73	8.67	74.04	9.76
2	42.1	47.98	5.88	47.19	5.09	42.9	48.53	5.63	49.67	6.77
3	217.2	216.63	0.57	216.95	0.25	216.6	213.53	3.07	211.17	**5.43**
4	46.9	46.92	0.02	47.73	0.83	45.2	50.17	4.97	46.18	0.98
5	43.6	44.81	1.21	46.89	3.29	37.1	39.85	2.75	39.71	2.61
6	81.9	77.25	4.65	73.91	7.99	33.4	35.77	2.37	33.84	0.44
7	86.1	88.19	2.09	88.85	2.75	71.5	71.50	0.00	69.91	1.59
8	42.1	49.59	7.49	50.55	8.45	43.2	48.76	5.56	49.75	6.55
9	47.1	49.03	1.93	47.58	0.48	52.5	53.16	0.66	49.66	2.84
10	44.2	50.25	6.05	49.45	5.25	43.8	46.66	2.86	48.01	4.21
11	78.5	71.09	7.41	69.82	8.68	77.9	70.11	7.79	69.16	8.74
12	28.7	36.87	8.17	37.21	8.51	28.4	37.35	8.95	38.07	9.67
13	45.9	48.64	2.74	49.80	3.90	45.1	48.46	3.36	49.33	4.23
14	50.7	52.91	2.21	53.22	2.52	49.9	51.86	1.96	52.69	2.79
15	39.0	41.01	2.01	41.15	2.15	41.7	43.33	1.63	41.74	0.04
16	76.7	75.60	1.10	76.76	0.06	76.8	75.65	1.15	76.13	0.67
17	145.5	159.03	13.53	159.77	14.27	144.8	159.01	14.21	162.87	18.07
18	18.9	19.60	0.70	18.54	0.36	16	18.21	2.21	21.59	5.59
19	22.7	21.73	0.97	17.64	5.06	31.7	25.44	6.26	16.14	5.56
20	134.0	130.04	3.96	130.29	3.71	133.4	130.64	2.76	131.64	1.76
21	174.9	168.51	6.39	167.77	7.13	174.5	168.42	6.08	167.40	7.10
22	30.4	25.13	5.27	25.96	4.44	30.4	26.24	4.16	26.50	3.90
23	28.8	16.20	12.60	15.79	13.01	28.8	16.48	12.32	16.74	12.06
28	18.5	14.41	4.09	19.64	1.14	15.5	13.06	2.44	13.37	2.13
30	21.1	26.53	5.43	26.01	4.91	18.2	15.43	2.77	16.69	1.51
16-<u>C</u>OCH3	172.6	170.55	2.05	170.29	2.31	172.5	170.74	1.76	171.13	1.37
16-CO<u>C</u>H3	20.7	20.97	0.27	21.39	0.69	20.7	22.90	2.20	23.08	2.38
MAE		4.42		4.75			4.39		4.77	
R^2		0.9884		0.9867			0.9892		0.9864	
DP4+		99.98%		0.02%			100.00%		0.00%	

AE: absolute error; MAE: mean absolute error.

Based on the values of MAE, R^2 and DP4+, the relative configuration of **35** is assigned as 1*S**,4*S**,5*S**,6*R**,7*R**,8*S**,9*S**,10*S**,11*R**,13*R**,14*S**,16*S**, and the relative configuration of **38** is assigned as 1*S**,4*S**,5*S**,7*R**,8*S**,9*S**,10*S**,11*R**,13*R**,14*S**,16*S**.

Table S69 Comparison of the coupling constants of compounds containing C1–C2 double bond and C3-hydroxyl group.

Compound	**6**	**81**	**29**	**30**	**32**	**34**
$^3J_{(H-3, H-4)}$ in Hz	4.4	7.9	4.9	4.1	4.4	4.3
Compound	**41**	**42**	**43**	**63**	**64**	**65**
$^3J_{(H-3, H-4)}$ in Hz	4.4	4.6	4.5	4.3	4.0	4.3
Compound	**69**					
$^3J_{(H-3, H-4)}$ in Hz	4.5					

Based on the coupling constants between H-3 and H-4, 3-OH in **29**, **30**, **32**, **34**, **41**–**43**, **63**–**65**, and **69** were determined to be α-oriented.

Table S70 Primers used for constructing recombinant plasmids.

Primer name	Sequence (5′ to 3′)	Usage
Inf-pBarI-HindIII-F	TGATTACGCCAAGCTCGACTCCAATCTTCAAGAGC	Construction of recombinant pBarI and pPTRI plasmids containing one or two genes using the ClonExpress®II One Step Cloning Kit or ClonExpress®MultiS One Step Cloning Kit
Inf-pTA-Tamy-R1	AACGCGCTCGCGAGCAAGTACCATACAGTACCGCG	
Inf-pTA-Parm-F1	GCTCGCGAGCGCGTTCCACTGCATCATCAGTCTAG	
Inf-pBarI-HindIII-R	GCAGGCATGCAAGCTGTAAGATACATGAGCTTCGG	
Inf-pPTRI-HindIII-F	TGATTACGCCAAGCTCGACTCCAATCTTCAAGAGC	
Inf-pPTRI-HindIII-R	GCAGGCATGCAAGCTGTAAGATACATGAGCTTCGG	

Table S71 Plasmids used in the study.

Plasmid	Characteristic	Source
pTAex3	Plasmid containing *argB* maker gene cassette for gene expression in *A. oryzae* NSAR1, (*Amp*^{R})	Fujii, et al.[3]
pBarI	Plasmid containing *bar* maker gene cassette for gene expression in *A. oryzae* NSAR1, (*Amp*^{R})	Matsuda, et al.[4]
pPTRI	Plasmid containing *ptrA* maker gene cassette for gene expression in *A. oryzae* NSAR1, (*Amp*^{R})	TaKaRa
pTAex3-*helB3*	pTAex3 containing *helB3* whose expression is regulated by *amyB* promoter, (*Amp*^{R})	Lv, et al.[5]
pTAex3-*helD1*	pTAex3 containing *helD1* whose expression is regulated by *amyB* promoter, (*Amp*^{R})	
pTAex3-*helE*	pTAex3 containing *helE* whose expression is regulated by *amyB* promoter, (*Amp*^{R})	
pTAex3-*fusC1*	pTAex3 containing *fusC1* whose expression is regulated by *amyB* promoter, (*Amp*^{R})	Cao, et al.[6]
pTAex3-*fusB1*	pTAex3 containing *fusB1* whose expression is regulated by *amyB* promoter, (*Amp*^{R})	
pPTRI-*fusC1*	pPTRI containing *fusC1* whose expressions is regulated by *amyB* promoter, (*Amp*^{R})	
pTAex3-*cepB4*	pTAex3 containing *cepB4* whose expression is regulated by *amyB* promoter, (*Amp*^{R})	Cao, et al.[7]
pTAex3-*cepD2*	pTAex3 containing *cepD2* whose expression is regulated by *amyB* promoter, (*Amp*^{R})	
pPTRI-*cepB4*	pPTRI containing *cepB4* whose expressions is regulated by *amyB* promoter, (*Amp*^{R})	
pPTRI-*cepD2*	pPTRI containing *cepD2* whose expressions is regulated by *amyB* promoter, (*Amp*^{R})	
pPTRI-*helD1*	pPTRI containing *helD1* whose expressions is regulated by *amyB* promoter, (*Amp*^{R})	This work
pPTRI-*helB3*	pPTRI containing *helB3* whose expressions is regulated by *amyB* promoter, (*Amp*^{R})	This work
pPTRI-*helB3-fusC1*	pPTRI containing *helB3* and *fusC1* whose expressions are independently regulated by *amyB* promoter, (*Amp*^{R})	This work
pPTRI-*helB3-helD1*	pPTRI containing *helB3* and *helD1* whose expressions are independently regulated by *amyB* promoter, (*Amp*^{R})	This work
pPTRI-*fusB1-helD1*	pPTRI containing *fusB1* and *helD1* whose expressions are independently regulated by *amyB* promoter, (*Amp*^{R})	This work
pPTRI-*cepB4-cepD2*	pPTRI containing *cepB4* and *cepD2* whose expressions are independently regulated by *amyB* promoter, (*Amp*^{R})	Cao, et al.[7]
pPTRI-*cepB4-cepC2*	pPTRI containing *cepB4* and *cepC2* whose expressions are independently regulated by *amyB* promoter, (*Amp*^{R})	
pBarI-*helE-cepB4*	pBarI containing *helE and cepB4* whose expressions are independently regulated by *amyB* promoter, (*Amp*^{R})	This work
pBarI-*helE-fusB1*	pBarI containing *helE and fusB1* whose expressions are independently regulated by *amyB* promoter, (*Amp*^{R})	This work
pBarI-*helE-fusC1*	pBarI containing *helE and fusC1* whose expressions are independently regulated by *amyB* promoter, (*Amp*^{R})	This work
pBarI-*helB3-fusB1*	pBarI containing *helB3 and fusB1* whose expressions are independently regulated by *amyB* promoter, (*Amp*^{R})	This work
pBarI-*helB3-fusC1*	pBarI containing *helB3 and fusC1* whose expressions are independently regulated by *amyB* promoter, (*Amp*^{R})	This work
pBarI-*fusB1-cepB4*	pBarI containing *fusB1 and cepB4* whose expressions are independently regulated by *amyB* promoter, (*Amp*^{R})	This work
pBarI-*fusC1-cepD2*	pBarI containing *fusC1 and cepD2* whose expressions are independently regulated by *amyB* promoter, (*Amp*^{R})	This work

Table S72 Strains used in the study.

Strain	Characteristic	Source
E. coli DH5*α*	Host for general plasmid cloning	TaKaRa
A. oryzae NSAR1	Host for gene expression, a quadruple auxotrophic mutant strain (*niaD*⁻, *sC*⁻, *ΔargB*, *adeA*⁻)	Jin, et al.[8]
AOS0	*A. oryzae* NSAR1 transformant harboring *helA*, *helB1*, *helC*, *helB2*, *helD2* and *helB4*	Lv, et al.[5]
AOS1	Transformant with addition of *helE and fusB1* into AOS0	This work
AOS2	Transformant with addition of *helE and fusC1* into AOS0	This work
AOS3	Transformant with addition of *helE and cepB4* into AOS0	This work
AOS4	Transformant with addition of *fusB1 and cepB4* into AOS0	This work
AOS5	Transformant with addition of *helB3 and fusB1* into AOS0	This work
AOS6	Transformant with addition of *helB3 and fusC1* into AOS0	This work
AOS7	Transformant with addition of *helE, fusB1 and helB3* into AOS0	This work
AOS8	Transformant with addition of *helE, fusB1 and fusC1* into AOS0	This work
AOS9	Transformant with addition of *helE, fusC1 and helB3* into AOS0	This work
AOS10	Transformant with addition of *helE, cepB4 and fusB1* into AOS0	This work
AOS11	Transformant with addition of *helE, cepB4 and fusC1* into AOS0	This work
AOS12	Transformant with addition of *helE, cepB4 and cepD2* into AOS0	This work
AOS13	Transformant with addition of *fusB1, cepB4 and fusC1* into AOS0	This work
AOS14	Transformant with addition of *fusB1, cepB4 and cepD2* into AOS0	This work
AOS15	Transformant with addition of *fusB1, helB3 and fusC1* into AOS0	This work
AOS16	Transformant with addition of *fusB1, helB3 and helD1* into AOS0	This work
AOS17	Transformant with addition of *helB3, fusC1 and helD1* into AOS0	This work
AOS18	Transformant with addition of *helE, fusB1, helB3 and helD1* into AOS0	This work
AOS19	Transformant with addition of *helE, fusB1, helB3 and fusC1* into AOS0	This work
AOS20	Transformant with addition of *helE, fusC1, helB3 and helD1* into AOS0	This work
AOS21	Transformant with addition of *helE, fusB1, cepB4 and cepC2* into AOS0	This work
AOS22	Transformant with addition of *helE, fusB1, cepB4 and cepD2* into AOS0	This work
AOS23	Transformant with addition of *helE, fusC1, cepB4 and cepD2* into AOS0	This work
AOS24	Transformant with addition of *fusB1, cepB4, fusC1 and cepD2* into AOS0	This work
AOS25	Transformant with addition of *fusB1, fusC1, helB3 and helD1* into AOS0	This work
AOS26	Transformant with addition of *helE, fusB1, fusC1, helB3 and helD1* into AOS0	This work
AOS27	Transformant with addition of *helE, fusB1, fusC1, cepB4 and cepD2* into AOS0	This work
AOS28	*A. oryzae* NSAR1 transformant harboring *helB3*	This work
COS6	*A. oryzae* NSAR1 transformant harboring *cepB4*	Cao, et al.[7]
COS7	*A. oryzae* NSAR1 transformant harboring *cepD2*	

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