SUPPLEMENTARY MATERIAL

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Abtract

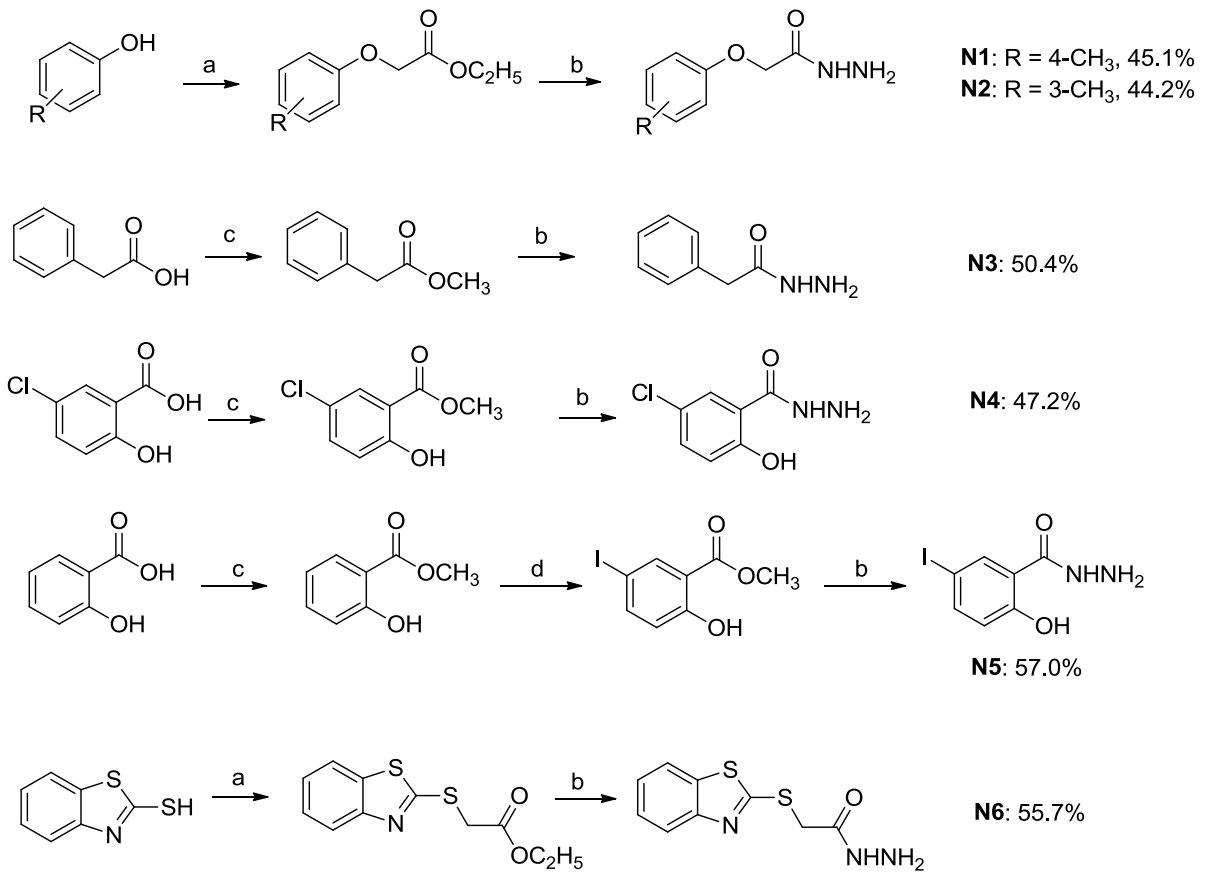
Twelve benzylidene derivatives, one Baeyer-Villiger oxidative, six imine derivatives were successfully designed and synthesized from phyllanthone. In the search for potential new anti-diabetic agents, phyllanthone along with its benzylidene and oxidation analogues were evaluated for enzyme inhibition against α-glucosidase. In the benzylidene series, most analogues displayed stronger activity than the mother compound. **1c** revealed the strongest activity, outperforming the acarbose positive control with an IC_{50} value of 19.59 µM. Phyllanthone and

its derivatives were then tested for cytotoxic activity against the K562 cell line. The imine analogues displayed the most powerful cytotoxic activity with **3c**, **3d** having IC_{50} values of 57.55 and 68.02 µM, respectively.

Keywords *Phyllanthus* (Phyllanthaceae); phyllanthone derivatives; *α*-glucosidase inhibition; cytotoxic activity

General procedure for the synthesis of hydrazine reagents N1-N6

Aryloxyaxetohydrazides (**N1**, m.p. 138-139^{o}C; **N2**, m.p. 105-106^{o}C) were prepared from appropriate phenols using the method in our previous work (Cong et al. 2007). Benzohydrazide (**N3**, m.p. 130-131^{o}C) was prepared from 2-phenylacetic acid by esterification and then hydrazination following the method of (Xu et al.2018). In the same manner with **N3**, 5-chloro-2-hydroxybenzohydrazide (**N4**, 174^{o}C) was prepared from 5-chloro-2-hydroxybenzoic acid following the method of (Xu et al. 2018). 2-Hydroxy-5-iodobenzohydrazide (**N5**, m.p. 178^{o}C) was prepared from salicylic acid according to the method in those published (Al-Omran and El-Khair, 2016).



Scheme S1. Pathway to preparation of hydrazides N1-N6. a: $ClCH_2CO_2C_2H_5/K_2CO_3$, acetone, refluxed, 24 h; b: N_2H_4 80%/Ethanol, refluxed, 6 h; c: CH_3OH/H_2SO_4, refluxed, 8 h; d: KI/ CH_3OH, NaClO, 12 h. Overall yield.

α-Glucosidase Inhibition Assay

α-Glucosidase inhibitory activity was determined using the method of Nguyen et al. (Nguyen et al. 2011) with slight modifications. The *α*-glucosidase (0.2 U/mL) and substrate (5.0 mM *p*-nitrophenyl-*α*-D-glucopyranoside) were dissolved in 100 mM pH 6.9 sodium phosphate buffer. The inhibitor (50 µL) was preincubated with *α*-glucosidase at 37°C for 20 min, and then the substrate (40 µL) was added to the reaction mixture. The enzymatic reaction was carried out at 37°C for 20 min and stopped by adding 0.2 M Na_2CO_3 (130 µL). Enzymatic activity was quantified by measuring absorbance at 405 nm. All samples were analyzed in triplicate at five different concentrations around the IC_{50} values, and the mean values were retained. The inhibition percentage (%) was calculated by the following equation: Inhibition (%) = [1 -

($A_{sample}/A_{control}$)] × 100. The IC_{50} values were calculated by log-linear regression using Microsoft Excel 2010.

Cytotoxic activity

All phyllanthol derivatives were applied to cytotoxic evaluation against K562 (chronic myelogenous leukemia) cell lines using doxorubixin as the positive control (Nguyen et al. 2019). All samples were experienced in triplicate at different concentrations to obtain the IC_{50} value of each compound.

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Table S1. α-Glucosidase inhibitory activity toward baker's yeast α-glucosidase of **1**, **1a-1l**, and **2**.

Compound	IC_{50} (μM)	Compound	IC_{50} (μM)
1a	146.45 ± 2.14	**1i**	154.81 ± 1.92
1b	>200	**1j**	>200
1c	19.59 ± 2.53	**1k**	>200
1d	>200	**1l**	>200
1e	>200	**2**	>200
1f	129.74 ± 4.17	**1**	>200
1g	>200	Acarbose	162.54 ± 0.19
1h	>200		

Table S2. Cytotoxic activity against K562 cell line of **1**, **1a-1l**, **2**, and **3a-3f**.

Compound	IC_{50} (μM)	Compound	IC_{50} (μM)
1a	>100	**2**	>100
1b	>100	**3a**	>100
1c	>100	**3b**	>100
1d	>100	**3c**	57.55 ± 2.52
1e	>100	**3d**	68.02 ± 3.71
1f	>100	**3e**	>100
1g	>100	**3f**	>100
1h	>100	**1**	98.82 ± 5.19
1i	>100	Doxorubixin	4.1 ± 0.1
1j	81.87 ± 3.41		
1k	>100		
1l	86.53 ± 5.90		

Phyllanthone (1)

^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.19 (*s*, 3H, CH_3-26), 1.07 (*s*, 3H, CH_3-23), 1.03 (*s*, 3H, CH_3-24), 0.97 (*s*, 3H, CH_3-25), 0.94 (*d*, 3H, J = 6.0 Hz, CH_3-29), 0.91 (*s*, 3H, CH_3-28), 0.88 (*d*, 3H, J = 6.0 Hz, CH_3-30), 0.63 (*d*, 1H, J = 5.5 Hz, CH_2-27a), 0.05 (*d*, 1H, J = 5.0 Hz, CH_2-27b); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 217.9 (C-3), 55.4 (C-5), 54.5 (C-9), 49.7 (C-18), 47.6 (C-4), 42.2 (C-22), 40.9 (C-19), 39.4 (C-1), 38.6 (C-20), 37.8 (C-6), 37.2 (C-10), 36.9 (C-8), 35.7 (C-12), 34.2 (C-2), 32.7 (C-14), 32.0 (C-17), 31.2 (C-21), 28.4 (C-28), 27.3 (C-16), 26.7 (C-23), 21.5 (C-15), 21.1 (C-30), 20.8 (C-24), 20.5 (C-13), 19.6 (C-11), 18.1 (C-7), 18.0 (C-29), 17.9 (C-26), 15.8 (C-25), 13.8 (C-27). Spectral data agreed with those published (Ndlebe et al. 2008).

(1S,2R,4aR,6aR,6bR,12aR,14aR,E)-11-Benzylidene-1,2,4a,6b,9,9,12a-heptamethyloctadecahydro-6a,14a-methanopicen-10(6bH)-one (1a)

Yield: 30.4 mg, 36.0% ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.54 (*m*, 1H, H-5′), 7.50 (*br*, 1H, H-1′), 7.41 (*m*, 2H, H-3′, H-7′), 7.33 (*m*, 1H, H-4′, H-6′), 2.94 (*d*, 1H, *J* = 16.5 Hz, H-1a), 2.18 (*d*, 1H, *J* = 16.0 Hz, H-1b), 1.21 (*s*, 3H, CH_3-26), 1.13 (*s*, 3H, CH_3-23), 1.03 (*s*, 3H, CH_3-24), 0.98 (*d*, 3H, *J* = 6.0 Hz, CH_3-29), 0.91 (*s*, 3H, CH_3-28), 0.89 (*br*, 3H, CH_3-30), 0.83 (*s*, 3H, CH_3-25), 0.70 (*d*, 1H, *J* = 5.5 Hz, CH_2-27a), 0.09 (*d*, 1H, *J* = 5.5 Hz, CH_2-27b); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 208.2 (C-3), 145.6 (C-2), 137.6 (C-1′), 134.3 (C-2′), 130.5 (C-4′; C-6′), 128.6 (C-3′; C-7′), 121.7 (C-5′), 54.4 (C-9), 53.3 (C-5), 48.5 (C-18), 47.1 (C-4), 44.3 (C-1), 42.2 (C-22), 40.9 (C-19), 38.6 (C-20), 37.3 (C-10), 36.8 (C-6), 36.7 (C-8), 35.6 (C-12), 32.7 (C-14), 32.5 (C-17), 31.2 (C-21), 29.6 (C-23), 28.4 (C-28), 27.3 (C-16), 26.3 (C-13), 22.4 (C-30), 21.4 (C-15), 20.9 (C-24), 20.3 (C-11), 18.2 (C-29), 18.1 (C-7), 17.5 (C-26), 15.5 (C-25), 13.6 (C-27). HRESIMS *m/z* calcd for $C_{37}H_{52}ONa$ $[M+Na]^+$ 535.3916, found 535.3917.

(1S,2R,4aR,6aR,6bR,12aR,14aR)-11-((E)-4-Fluorobenzylidene)-1,2,4a,6b,9,9,12a-heptamethyloctadecahydro-6a,14a-methanopicen-10(6bH)-one (1b)

Yield: 40.2 mg, 46.0%. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.46 (*br*, 1H, H-1′), 7.40 (*d*, 2H, *J* = 8.5 Hz, H-3′, H-7′), 7.09 (*t*, 2H, *J* = 8.5 Hz, H-4′, H-6′), 2.88 (*d*, 1H, *J* = 16.0 Hz, H-1a), 2.15 (*d*, 1H, *J* = 15.5 Hz, H-1b)**,** 1.18 (*s*, 3H, CH_3-26), 1.16 (*s*, 3H, CH_3-23), 1.12 (*s*, 3H, CH_3-24), 0.98 (*d*, 3H, *J* = 6.0 Hz, CH_3-29), 0.91 (*s*, 3H, CH_3-28), 0.89 (*br*, 3H, CH_3-30), 0.82 (*s*, 3H, CH_3-25), 0.69 (*d*, 1H, *J* = 5.5 Hz, CH_2-27a), 0.09 (*d*, 1H, *J* = 5.5 Hz, CH_2-27b); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 208.1 (C-3), 162.7 (C-5′, *J* = 248.8 Hz), 145.7 (C-2), 136.5 (C-1′), 133.9 (C-2′), 132.3 (C-3′; C-7′), 115.7 (C-4′; C-6′, *J* = 21.3 Hz), 54.4 (C-9), 53.2 (C-5), 48.5 (C-18), 45.4 (C-4), 44.3 (C-1), 42.1 (C-22), 40.9 (C-19), 38.5 (C-20), 37.2 (C-10), 36.8 (C-6), 36.7 (C-8), 35.5 (C-12), 32.5 (C-14), 32.1 (C-17), 31.2 (C-21), 29.6 (C-23), 28.4 (C-28), 27.3 (C-16), 26.6 (C-13), 22.4 (C-30), 21.4 (C-15), 20.9 (C-24), 20.3 (C-11), 18.2 (C-7), 18.1 (C-29), 17.5 (C-26), 15.5 (C-25), 13.6 (C-27). HRESIMS *m/z* calcd for $C_{37}H_{51}FOH$ $[M+H]^+$ 531.4002, found 531.4003.

(1S,2R,4aR,6aR,6bR,12aR,14aR,E)-11-(2-Fluorobenzylidene)-1,2,4a,6b,9,9,12a-heptamethyloctadecahydro-6a,14a-methanopicen-10(6bH)-one (1c)

Yield: 41.2 mg, 47.0%. ^{1}H-NMR (500 MHz, CDCl3) δ 7.58 (*br*, 1H, H-1′), 7.32 (*m*, 1H, H-7′), 7.26 (*br*, 1H, H-5′), 7.16 (*t*, 1H, *J* = 7.5 Hz, H-6′), 7.09 (*t*, 1H, *J* = 8.5 Hz, H-4′), 2.79 (*d*, 1H, *J* = 16.0 Hz, H-1a), 2.08 (*d*, 1H, *J* = 16.0 Hz, H-1b), 1.18 (*s*, 3H, CH_3-26), 1.16 (*s*, 3H, CH_3-23), 1.15 (*s*, 3H, CH_3-24), 0.96 (*br*, 3H, CH_3-29), 0.90 (*s*, 3H, CH_3-28), 0.88 (*br*, 3H, CH_3-30), 0.83 (*s*, 3H, CH_3-25), 0.67 (*br*, 1H, CH_2-27a), 0.07 (*br*, 1H, CH_2-27b). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 207.7 (C-3), 161.0 (C-3′, *J* = 248.8 Hz), 136.5 (C-2), 130.5 (C-1′), 130.3(C-5′), 130.2 (C-7′), 124.1 (C-2′), 123.9 (C-6′), 115.9 (C-4′, *J* = 22.5 Hz), 54.4 (C-5), 53.5 (C-9), 48.4 (C-18), 45.6 (C-4), 43.9 (C-1), 42.1 (C-22), 40.9 (C-19), 38.5 (C-20), 37.3 (C-10), 36.9 (C-6), 35.5

(C-8), 34.9 (C-12), 32.5 (C-14), 32.0 (C-17), 31.2 (C-21), 29.3 (C-23), 28.4 (C-28), 27.3 (C-16), 26.6 (C-13), 22.5 (C-30), 21.4 (C-15), 20.9 (C-24), 20.2 (C-11), 18.1 (C-29), 18.0 (C-7), 17.6 (C-26), 15.5 (C-25), 13.6 (C-27). HRESIMS *m/z* calcd for $C_{37}H_{51}FONa$ $[M+Na]^+$ 553.3822, found 553.3817.

(1S,2R,4aR,6aR,6bR,12aR,14aR)-11-((E)-4-Chlorobenzylidene)-1,2,4a,6b,9,9,12a-heptamethyloctadecahydro-6a,14a-methanopicen-10(6bH)-one (1d)

Yield: 45.4 mg, 50.3%. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.44 (*m*, 1H, H-1′), 7.37 (*d*, 2H, *J* = 8.5 Hz, H-3′, H-7′), 7.33 (*d*, 2H, *J* = 8.5 Hz, H-4′, H-6′), 2.87 (*d*, 1H, *J* = 16.5 Hz, H-1a), 2.14 (*d*, 1H, *J* = 16.0 Hz, H-1b), 1.18 (*s*, 3H, CH_3-26), 1.16 (*s*, 3H, CH_3-23), 1.13 (*s*, 3H, CH_3-24), 0.98 (*d*, 3H, *J* = 6.0 Hz, CH_3-29), 0.91 (*s*, 3H, CH_3-28), 0.89 (*d*, 3H, *J* = 5.5 Hz, CH_3-30), 0.82 (*s*, 3H, CH_3-25), 0.69 (*d*, 1H, *J* = 5.5 Hz, CH_2-27a), 0.09 (*d*, 1H, *J* = 5.5 Hz, CH_2-27b); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 208.4 (C-3), 140.1 (C-2), 136.3 (C-1′), 134.8 (C-5′), 134.6 (C-2′), 131.6 (C-3′; C-7′), 128.9 (C-4′; C-6′), 54.4 (C-9), 53.3 (C-5), 48.5 (C-18), 45.4 (C-4), 44.3 (C-1), 42.1 (C-22), 40.9 (C-19), 38.5 (C-20), 37.2 (C-10), 36.8 (C-6), 36.7 (C-8), 35.5 (C-12), 32.5 (C-14), 32.1 (C-17), 31.2 (C-21), 29.6 (C-23), 28.4 (C-28), 27.3 (C-16), 26.6 (C-13), 22.4 (C-30), 21.4 (C-15), 20.9 (C-24), 20.3 (C-11), 18.2 (C-7), 18.1 (C-29), 17.5 (C-26), 15.5 (C-25), 13.6 (C-27). HRESIMS *m/z* calcd for $C_{37}H_{51}ClONa$ $[M+Na]^+$ 569.3526, found 569.3529 (100.0 %), 571.3510 (37.9 %).

(1S,2R,4aR,6aR,6bR,12aR,14aR,E)-11-(3-Chlorobenzylidene)-1,2,4a,6b,9,9,12a-heptamethyloctadecahydro-6a,14a-methanopicen-10(6bH)-one (1e)

Yield: 37.9 mg, 42.0%. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.41 (*br*, 1H, H-1′), 7.37 (*br s*, 1H, H-3′), 7.32 (*d*, 1H, *J* = 7.5 Hz, H-7′), 7.30 (*br*, 1H, H-5′), 7.28 (*br*, 1H, H-6′), 2.88 (*d*, 1H, *J* = 16.5 Hz, H-1a), 2.14 (*d*, 1H, *J* = 16.5 Hz, H-1b), 1.18 (*s*, 3H, CH_3-26), 1.16 (*s*, 3H, CH_3-23), 1.13 (*s*, 3H, CH_3-24), 0.97 (*d*, 3H, *J* = 6.0 Hz, CH_3-29), 0.91 (*s*, 3H, CH_3-28), 0.88 (*d*, 3H, *J* = 5.5 Hz, CH_3-30), 0.83 (*s*, 3H, CH_3-25), 0.69 (*d*, 1H, *J* = 5.5 Hz, CH_2-27a), 0.08 (*d*, 1H, *J* = 5.5 Hz, CH_2-27b). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 208.0 (C-3), 137.9 (C-2), 136.0 (C-1′), 135.6 (C-2′), 134.5 (C-4′), 130.2 (C-6′), 129.8 (C-3′), 128.5 (C-5′), 128.1 (C-7′), 54.3 (C-5), 53.3 (C-9), 48.4 (C-18), 45.5 (C-4), 44.1 (C-1), 42.1 (C-22), 40.9 (C-19), 38.5 (C-20), 37.2 (C-10), 36.8 (C-6), 36.7 (C-8), 35.5 (C-12), 32.5 (C-14), 32.0 (C-17), 31.2 (C-21), 29.5 (C-23), 28.4 (C-28), 27.3 (C-16), 26.6 (C-13), 22.4 (C-30), 21.4 (C-15), 20.9 (C-24), 20.3 (C-11), 18.1 (C-29), 18.0 (C-7), 17.5 (C-26), 15.5 (C-25), 13.6 (C-27). HRESIMS *m/z* calcd for $C_{37}H_{51}ClONa$ $[M+Na]^+$ 569.3526 found 569.3529 (100.0 %), 571.3513(41.1 %).

(1S,2R,4aR,6aR,6bR,12aR,14aR)-11-((E)-2-Chlorobenzylidene)-1,2,4a,6b,9,9,12a-heptamethyloctadecahydro-6a,14a-methanopicen-10(6bH)-one (1f)

Yield: 57.3 mg, 63.5%. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.60 (*br*, 1H, H-1′), 7.41 (*m*, 1H, H-4′), 7.28 (*m*, 1H, H-5′), 7.27 (*m*, 1H, H-7′), 7.24 (*m*, 1H, H-6′), 2.74 (*d*, 1H, *J* = 15.5 Hz, H-1a), 1.99 (*d*, 1H, *J* = 16.0 Hz, H-1b), 1.17 (*s*, 3H, CH_3-26), 1.16 (*s*, 3H, CH_3-23), 1.15 (*s*, 3H, CH_3-24), 0.94 (*d*, 3H, *J* = 6.5 Hz, CH_3-29), 0.90 (*s*, 3H, CH_3-28), 0.87 (*d*, 3H, *J* = 5.5 Hz, CH_3-30), 0.85 (*s*, 3H, CH_3-25), 0.65 (*d*, 1H, *J* = 5.5 Hz, CH_2-27a), 0.05 (*d*, 1H, *J* = 5.5 Hz, CH_2-27b); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 207.9 (C-3), 136.2 (C-2), 134.9 (C-2′), 134.7 (C-3′), 134.6 (C-1′), 130.2 (C-7′), 129.8 (C-4′), 129.4 (C-5′), 126.5 (C-6′), 54.3 (C-5), 53.7 (C-9), 48.4 (C-18), 45.9 (C-4), 43.4 (C-1), 42.1 (C-22), 40.9 (C-19), 38.5 (C-20), 37.3 (C-10), 37.0 (C-6), 36.8 (C-8), 35.4 (C-12), 32.5 (C-14), 32.0 (C-17), 31.2 (C-21), 29.1 (C-23), 28.4 (C-28), 27.3 (C-16), 26.5 (C-13), 22.5 (C-30), 21.4 (C-15), 20.8 (C-24), 20.1 (C-11), 18.1 (C-29), 17.9 (C-7), 17.6 (C-26), 15.4 (C-25), 13.5 (C-27). HRESIMS *m/z* calcd for $C_{37}H_{52}ClO$ $[M+H]^+$ 547.3707, found 547.3700 (100.0 %), 549.3677 (35.1 %).

(1S,2R,4aR,6aR,6bR,12aR,14aR)-11-((E)-4-Bromobenzylidene)-1,2,4a,6b,9,9,12a-(heptamethyloctadecahydro-6a,14a-methanopicen-10(6bH)-one (1g)

Yield: 49.2 mg, 50.4%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.52 (*t*, 2H, *J* = 8.4 Hz, H-3′, H-7′), 7.41 (*br*, 1H, H-1′), 7.26 (*t*, 2H, *J* = 8.0 Hz, H-4′, H-6′), 2.86 (*d*, 1H, *J* = 16.0 Hz, H-1a), 2.13 (*d*, 1H, *J* = 16.0 Hz, H-1b), 1.18 (*s*, 3H, CH_3-26), 1.16 (*s*, 3H, CH_3-23), 1.13 (*s*, 3H, CH_3-24), 0.97 (*br*, 3H, CH_3-29), 0.91 (*s*, 3H, CH_3-28), 0.89 (*br*, 3H, CH_3-30), 0.82 (*s*, 3H, CH_3-25), 0.68 (*br*, 1H, CH_2-27a), 0.08 (*br*, 1H, CH_2-27b); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 208.1 (C-3), 139.9 (C-2), 136.3 (C-2′), 134.8 (C-1′), 131.8 (C-4′; C-6′), 131.7 (C-3′; C-7′), 122.8 (C-5′), 54.2 (C-9), 53.1 (C-5), 48.4 (C-18), 45.4 (C-4), 44.2 (C-1), 42.1 (C-22), 40.9 (C-19), 38.5 (C-20), 37.2 (C-10), 36.8 (C-6), 36.6 (C-8), 35.4 (C-12), 32.4 (C-14), 32.0 (C-17), 31.2 (C-21), 29.5 (C-23), 28.4 (C-28), 27.3 (C-16), 26.5 (C-13), 22.4 (C-30), 21.4 (C-15), 20.9 (C-24), 20.2 (C-11), 18.1 (C-7), 18.0 (C-29), 17.5 (C-26), 15.5 (C-25), 13.4 (C-27). HRESIMS *m/z* calcd for $C_{37}H_{51}BrONa$ $[M+Na]^+$ 613.3021, found 615.2998 (100.0 %), 613.3022 (94.3 %).

(1S,2R,4aR,6aR,6bR,12aR,14aR)-11-((E)-3-Bromobenzylidene)-1,2,4a,6b,9,9,12a-heptamethyloctadecahydro-6a,14a-methanopicen-10(6bH)-one (1h)

Yield: 51.8 mg, 53.1%. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.48 (*br*, 1H, H-1′), 7.39 (*br*, 1H, H-3′), 7.35 (*br*, 1H, H-5′), 7.28 (*br*, 1H, H-7′), 7.26 (*br*, 1H, H-6′), 2.83 (*d*, 1H, *J* = 16.0 Hz, H-1a), 2.19 (*d*, 1H, *J* = 16.5 Hz, H-1b), 1.15 (*s*, 3H, CH_3-26), 1.11 (*s*, 3H, CH_3-23), 1.08 (*s*, 3H, CH_3-24), 0.92 (*d*, 3H, *J* = 6.0 Hz, CH_3-29), 0.86 (*s*, 3H, CH_3-28), 0.79 (*br*, 3H, CH_3-30), 0.78 (*s*, 3H, CH_3-25), 0.64 (*d*, 1H, *J* = 5.5 Hz, CH_2-27a), 0.04 (*d*, 1H, *J* = 5.5 Hz, CH_2-27b); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 208.0 (C-3), 145.5 (C-2), 135.9 (C-1′), 135.8 (C-2′), 133.2 (C-3′), 131.3 (C-5′), 130.0 (C-6′), 128.4 (C-7′), 122.6 (C-4′), 54.4 (C-9), 53.3 (C-5), 48.4 (C-18), 47.0 (C-4),

44.1 (C-1), 42.1 (C-22), 40.9 (C-19), 38.6 (C-20), 37.2 (C-10), 36.9 (C-6), 36.5 (C-8), 35.5 (C-12), 32.7 (C-14), 32.2 (C-17), 31.3 (C-21), 29.5 (C-23), 28.4 (C-28), 27.3 (C-16), 26.3 (C-13), 22.9 (C-30), 21.4 (C-15), 20.9 (C-24), 20.2 (C-11), 18.2 (C-29), 18.1 (C-7), 17.5 (C-26), 15.5 (C-25), 13.6 (C-27). HRESIMS *m/z* calcd for $C_{37}H_{51}BrONa$ $[M+Na]^+$ 613.3021, found 615.3019 (100.0 %), 613.3021 (99.9 %).

(1S,2R,4aR,6aR,6bR,12aR,14aR,E)-11-(2-Bromobenzylidene)-1,2,4a,6b,9,9,12a-heptamethyloctadecahydro-6a,14a-methanopicen-10(6bH)-one (1i)

Yield: 73.4 mg, 75.2%.^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.59 (*t*, 1H, *J* = 1.6 Hz, H-1′), 7.35 (*m*, 1H, H-4′), 7.31 (*m*, 1H, H-6′), 7.20 (*m*, 1H, H-7′), 7.16 (*m*, 1H, H-5′), 2.71 (*d*, 1H, *J* = 16.0 Hz, H-1a), 2.08 (*d*, 1H, *J* = 16.0 Hz, H-1b), 1.19 (*s*, 3H, CH_3-26), 1.17 (*s*, 3H, CH_3-23), 1.14 (*s*, 3H, CH_3-24), 0.88 (*s*, 3H, CH_3-28), 0.85 (*d*, 3H, *J* = 6.0 Hz, CH_3-29), 0.82 (*s*, 3H, CH_3-25), 0.79 (*d*, 3H, *J* = 5.5 Hz, CH_3-30), 0.63 (*d*, 1H, *J* = 5.2 Hz, CH_2-27a), 0.04 (*d*, 1H, *J* = 5.6 Hz, CH_2-27b). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 208.1 (C-3), 145.5 (C-2), 136.9 (C-1′), 133.0 (C-2′), 130.3 (C-4′), 127.1 (C-7′), 125.0 (C-5′), 124.2 (C-6′), 121.5 (C-3′), 54.2 (C-5), 53.6 (C-9), 48.3 (C-18), 46.9 (C-4), 43.2 (C-1), 42.1 (C-22), 40.8 (C-19), 38.5 (C-20), 37.3 (C-10), 37.1 (C-6), 36.8 (C-8), 35.3 (C-12), 32.7 (C-14), 32.0 (C-17), 31.2 (C-21), 29.0 (C-23), 28.3 (C-28), 27.2 (C-16), 26.4 (C-13), 22.5 (C-30), 21.3 (C-15), 20.9 (C-24), 20.1 (C-11), 18.0 (C-29), 17.9 (C-7), 17.6 (C-26), 15.4 (C-25), 13.4 (C-27). HRESIMS *m/z* calcd for $C_{37}H_{51}BrONa$ $[M+Na]^+$ 613.3021, found 615.3001 (100.0 %), 613.3023 (97.0 %).

(1S,2R,4aR,6aR,6bR,12aR,14aR)-1,2,4a,6b,9,9,12a-Heptamethyl-11-((E)-4-nitrobenzylidene)octadecahydro-6a,14a-methanopicen-10(6bH)-one (1j)

Yield: 45.2 mg, 49.2%. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.25 (*d*, 2H, *J* = 8.5 Hz, H-4′, H-6′), 7.53 (*d*, 2H, *J* = 8.5 Hz, H-3′, H-7′), 7.49 (*br*, 1H, H-1′), 2.87 (*d*, 1H, *J* = 16.5 Hz, H-1a), 2.19 (*d*, 1H, *J* = 16.5 Hz, H-1b), 1.18 (*s*, 3H, CH_3-26), 1.17 (*s*, 3H, CH_3-23), 1.14 (*s*, 3H, CH_3-24), 0.97 (*d*, 3H, *J* = 6.0 Hz, CH_3-29), 0.91 (*s*, 3H, CH_3-28), 0.88 (*d*, 3H, *J* = 5.5 Hz, CH_3-30), 0.83 (*s*, 3H, CH_3-25), 0.68 (*d*, 1H, *J* = 5.5 Hz, CH_2-27a), 0.09 (*d*, 1H, *J* = 5.5 Hz, CH_2-27b); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 207.8 (C-3), 147.3 (C-5′), 142.7 (C-2), 137.9 (C-2′), 134.7 (C-1′), 130.8 (C-3′; C-7′), 123.8 (C-4′; C-6′), 54.3 (C-9), 53.3 (C-5), 48.4 (C-18), 45.6 (C-4), 44.3 (C-1), 42.1 (C-22), 40.9 (C-19), 38.5 (C-20), 37.2 (C-10), 36.8 (C-6), 36.7 (C-8), 35.4 (C-12), 32.5 (C-14), 32.0 (C-17), 31.2 (C-21), 29.5 (C-23), 28.4 (C-28), 27.3 (C-16), 26.6 (C-13), 22.5 (C-30), 21.4 (C-15), 20.9 (C-24), 20.2 (C-11), 18.2 (C-7), 18.1 (C-29), 17.5 (C-26), 15.6 (C-25), 13.6 (C-27). HRESIMS *m/z* calcd for $C_{37}H_{51}NO_3Na$ $[M+Na]^+$ 580.3767, found 580.3769.

(1S,2R,4aR,6aR,6bR,12aR,14aR)-1,2,4a,6b,9,9,12a-Heptamethyl-11-((E)-2-nitrobenzylidene)octadecahydro-6a,14a-methanopicen-10(6bH)-one (1k)

Yield: 32.3 mg, 35.1%. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.11 (*d*, 1H, *J* = 8.0 Hz, H-4′), 7.61 (*br*, 1H, H-1′), 7.50 (*t*, 1H, *J* = 7.8 Hz, H-5′), 7.47 (*t*, 1H, *J* = 7.8 Hz, H-6′), 7.28 (*dd*, 1H, *J* = 8.0, 3.0 Hz, H-7′), 2.55 (*d*, 1H, *J* = 16.0 Hz, H-1a), 1.98 (*d*, 1H, *J* = 16.5 Hz, H-1b), 1.19 (*s*, 3H, CH_3-26), 1.17 (*s*, 3H, CH_3-23), 1.14 (*s*, 3H, CH_3-24), 0.90 (*d*, 3H, *J* = 6.0 Hz, CH_3-29), 0.88 (*s*, 3H, CH_3-28), 0.85 (*br*, 3H, CH_3-30), 0.82 (*s*, 3H, CH_3-25), 0.60 (*d*, 1H, *J* = 5.5 Hz, CH_2-27a), 0.03 (*d*, 1H, *J* = 5.5 Hz, CH_2-27b); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 207.6 (C-3), 148.3 (C-3′), 145.6 (C-2), 136.3 (C-2′), 134.2 (C-1′), 133.3 (C-6′), 131.1 (C-5′), 128.9 (C-7′), 125.0 (C-4′), 54.3 (C-5), 53.9 (C-9), 48.3 (C-18), 47.0 (C-4), 43.0 (C-1), 42.1 (C-22), 40.9 (C-19), 38.5 (C-20), 37.3 (C-10), 37.2 (C-6), 36.8 (C-8), 35.4 (C-12), 32.7 (C-14), 32.0 (C-17), 31.2 (C-21), 28.7 (C-23), 28.3 (C-28), 27.3 (C-16), 26.2 (C-13), 22.5 (C-30), 21.4 (C-15), 20.8 (C-24), 20.0 (C-11), 18.0 (C-29), 17.9 (C-7), 17.6 (C-26), 15.4 (C-25), 13.5 (C-27). HRESIMS *m/z* calcd for $C_{37}H_{51}NO_3Na$ $[M+Na]^+$ 580.3767, found 580.3764.

(1S,2R,4aR,6aR,6bR,12aR,14aR)-11-((E)-4-Methoxybenzylidene)-1,2,4a,6b,9,9,12a-Heptamethyloctadecahydro-6a,14a-methanopicen-10(6bH)-one (1l)

Yield: 14.3 mg, 16%. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.48 (*br*, 1H, H-1′), 7.41 (*d*, 2H, *J* = 9.5 Hz, H-3', H-7′), 7.40 (*d*, 2H, *J* =8.5 Hz, H-4′, H-6′), 3.84 (*s*, 3H, 5′-OCH_3), 2.95 (*d*, 1H, *J* = 16.0 Hz, H-1a), 2.17 (*d*, 1H, *J* = 16.5 Hz, H-1b), 1.19 (*s*, 3H, CH_3-26), 1.16 (*s*, 3H, CH_3-23), 1.12 (*s*, 3H, CH_3-24), 0.99 (*d*, 3H, *J* = 6.0 Hz, CH_3-29), 0.92 (*s*, 3H, CH_3-28), 0.89 (*s*, 3H, CH_3-25), 0.82 (*br*, 3H, CH_3-30), 0.71 (*d*, 1H, *J* = 5.5 Hz, CH_2-27a), 0.09 (*d*, 1H, *J* = 5.5 Hz, CH_2-27b); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 208.1 (C-3), 160.0 (C-5′), 145.6 (C-2), 137.5 (C-1′), 132.3 (C-3′; C-7′), 128.9 (C-2′), 114.1 (C-4′; C-6′), 59.4 (5′-OCH_3), 55.5 (C-9), 53.1 (C-5), 48.5 (C-18), 45.2 (C-4), 44.5 (C-1), 42.2 (C-22), 40.9 (C-19), 38.6 (C-20), 37.3 (C-10), 36.8 (C-6), 36.6 (C-8), 35.6 (C-12), 32.5 (C-14), 32.1 (C-17), 31.2 (C-21), 29.8 (C-23), 28.4 (C-28), 27.3 (C-16), 26.6 (C-13), 22.4 (C-30), 21.4 (C-15), 20.9 (C-24), 20.3 (C-11), 18.2 (C-7), 18.1 (C-29), 17.5 (C-26), 15.5 (C-25), 13.6 (C-27). HRESIMS *m/z* calcd for $C_{38}H_{54}O_2Na$ $[M+Na]^+$ 565.4022, found 565.4027.

(7aR,7bR,9aR,12R,13S,13bR,15bR)-5,5,7a,9a,12,13,15b-Heptamethyloctadecahydro-7b,13b-methanochryseno[2,1-c]oxepin-3(2H)-one (2)

Yield: 15.6 mg, 42.2%. ^{1}H-NMR (500 MHz, Acetone-d_6) δ 1.39 (*s*, 3H, CH_3-23), 1.32 (*s*, 3H, CH_3-26), 1.20 (*s*, 3H, CH_3-24), 1.04 (*s*, 3H, CH_3-25), 0.92 (*d*, 3H, *J* = 5.0 Hz, CH_3-29), 0.90

(*s*, 3H, CH_3-28), 0.83 (*d*, 3H, *J* = 5.5 Hz, CH_3-30), 0.67 (*d*, 1H, *J* = 5.5 Hz, CH_2-27a), 0.06 (*d*, 1H, *J* = 5.5 Hz, CH_2-27b). ^{13}C-NMR (125 MHz, Acetone-d_6) δ 174.3 (C-3), 85.7 (C-4), 55.9 (C-5), 53.9 (C-9), 51.0 (C-18), 42.7 (C-22), 41.4 (C-19), 40.3 (C-8), 40.0 (C-1), 39.5 (C-10), 39.2 (C-20), 37.9 (C-6), 37.8 (C-12), 32.8 (C-2), 32.6 (C-14), 31.9 (C-17), 31.7 (C-21), 31.5 (C-23), 28.8 (C-28), 27.8 (C-16), 27.2 (C-13), 26.8 (C-26), 23.7 (C-11), 22.0 (C-15), 21.0 (C-30), 19.3 (C-7), 18.4 (C-29), 18.2 (C-25), 18.1 (C-24), 14.7 (C-27). HRESIMS *m/z* calcd for $C_{30}H_{48}O_2Na$ $[M+Na]^+$ 463.3552, found 463.3551.

(E)-N'-((1S,2R,4aR,6aR,6bR,12aR,14aR)-1,2,4a,6b,9,9,12a-Heptamethylhexadecahydro-6a,14a-methanopicen-10(6bH,11H,12bH)-ylidene)-2-(p-tolyloxy)acetohydrazide (3a)

Yield**:** 15.6 mg, 37**%**; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.77 (*s*, 1H, NH), 7.08 (*d*, 2H, *J* = 8.0 Hz, H-5′, H-7′), 6.87 (*d*, 2H, *J* = 8.5 Hz, H-4′, H-8′), 4.80 (*m*, 2H, H-2′), 2.30 (*s*, 3H, 6′-CH_3), 1.19 (*s*, 3H, CH_3-26), 1.16 (*s*, 3H, CH_3-23), 1.12 (*s*, 3H, CH_3-24), 1.06 (*s*, 3H, CH_3-25), 0.93 (*br s*, 3H, CH_3-29), 0.91 (*s*, 3H, CH_3-28), 0.87 (*d*, 3H, *J* = 5.0 Hz, CH_3-30), 0.62 (*t*, 1H, *J* = 5.0 Hz, CH_2-27a), 0.04 (*d*, 1H, *J* = 5.0 Hz, CH_2-27b); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 171.1 (C-1′), 167.3 (C-3), 155.2 (C-3′), 130.4 (C-5′-C-7′), 130.3 (C-6′), 114.8 (C-4′-C-8′), 67.3 (C-2′), 55.5 (C-5), 54.5 (C-9), 49.7 (C-18), 47.6 (C-4), 42.2 (C-22), 40.9 (C-19), 39.4 (C-1), 38.6 (C-20), 37.8 (C-6), 37.1 (C-10), 36.9 (C-8), 35.7 (C-12), 32.6 (C-14), 32.1 (C-17), 31.2 (C-21), 29.9 (C-13), 28.4 (C-28), 27.4 (C-16), 26.7 (C-23), 21.5 (6′-CH_3), 21.1 (C-30), 20.8 (C-15), 20.6 (C-24), 19.6 (C-11), 18.1 (C-29), 18.0 (C-2), 18.0 (C-7), 17.9 (C-26), 15.8 (C-25), 13.8 (C-27); HRESIMS *m/z* calcd for $C_{39}H_{59}N_2O_2$ $[M+H]^+$ 587.4577, found 587.4575.

(E)-N'-((1S,2R,4aR,6aR,6bR,12aR,14aR)-1,2,4a,6b,9,9,12a-Heptamethylhexadecahydro-6a,14a-methanopicen-10(6bH,11H,12bH)-ylidene)-2-(m-tolyloxy)acetohydrazide (3b)

Yield**:** 12.05 mg, 30**%**; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.19 (*m*, 1H, H-7′), 6.85 (*br*, 1H, H-6′), 6.80 (*m*, 1H, H-4′), 6.76 (*m*, 1H, H-8′), 4.82 (*m*, 1H, H-2′), 2.34 (*s*, 3H, 5′- CH_3), 1.19 (*s*, 3H, CH_3-26), 1.07 (*s*, 3H, CH_3-23), 1.03 (*s*, 3H, CH_3-24), 0.97 (*s*, 3H, CH_3-25), 0.93 (*br*, 3H, CH_3-29), 0.91 (*s*, 3H, CH_3-28), 0.87 (*d*, 3H, *J* = 5.5 Hz, CH_3-30), 0.63 (*d*, 1H, *J* = 5.5 Hz, H-27a), 0.05 (*d*, 1H, *J* = 5.5 Hz, H-27b); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 170.5 (C-1′), 162.0 (C-3), 157.2 (C-3′), 140.2 (C-5′), 129.7 (C-7′), 123.3 (C-6′), 115.5 (C-4′), 111.6 (C-8′), 67.1 (C-2′), 55.4 (C-5), 54.5 (C-9), 49.7 (C-18), 47.6 (C-4), 42.2 (C-22), 40.9 (C-19), 39.4 (C-1), 38.5 (C-20), 38.2 (C-10), 38.0 (C-6), 37.1 (C-8), 35.7 (C-12), 32.6 (C-14), 32.0 (C-17), 31.2 (C-21), 28.4 (C-28), 27.3 (C-16), 26.7 (C-13), 26.6 (C-23), 21.6 (C-15), 21.4 (C-24), 21.1 (C-30), 20.9 (5′-CH_3), 19.5 (C-11), 19.0 (C-2), 18.1 (C-29), 18.0 (C-26), 17.9 (C-7), 15.7 (C-25), 13.8 (C-27); HRESIMS *m/z* calcd for $C_{39}H_{59}N_2O_2$ $[M+H]^+$**:** 587.4577, found 587.4571.

(E)-N′-((1S,2R,4aR,6aR,6bR,12aR,14aR)-1,2,4a,6b,9,9,12a-Heptamethylhexadecahydro-6a,14a-methanopicen-10(6bH,11H,12bH)-ylidene)-2-phenylacetohydrazide (3c)

Yield**:** 13.7 mg, 35**%**; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.37 (*s*, 1H, NH), 7.34 (*d*, 2H, *J* = 7.0 Hz, H-5′-H-7′), 7.29 (*t*, 2H, *J* = 7.5 Hz, H-6′), 7.23 (*d*, 1H, *J* = 7.5 Hz, H-4′-H-8′), 4.00 (*m*, 2H, H-2′), 1.18 (*s*, 3H, CH_3-26), 1.06 (*s*, 3H, CH_3-23), 1.03 (*s*, 3H, CH_3-24), 0.97 (*s*, 3H, CH_3-25), 0.94 (*m*, 3H, CH_3-29), 0.91 (*s*, 3H, CH_3-28), 0.87 (*d*, 3H, *J* = 5.0 Hz, CH_3-30), 0.62 (*m*, 1H, CH_2-27a), 0.04 (*m*, 1H, CH_2-27b); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.7 (C-1′), 161.5 (C-3), 136.1 (C-3′), 129.7 (C-4′-C-8′), 128.7 (C-5′-C-7′), 127.0 (C-6′), 55.4 (C-5), 54.4 (C-9), 49.6 (C-18), 42.2 (C-22), 40-9 (C-19), 39.9 (C-4), 39.8 (C-2'), 39.4 (C-1), 38.5 (C-20), 38.1 (C-10), 38.0 (C-6), 37.8 (C-8), 35.6 (C-12), 32.6 (C-14), 32.0 (C-17), 31.2 (C-21), 28.4 (C-28), 27.3 (C-16), 26.9 (C-13), 26.6 (C-23), 21.4 (C-15), 21.1 (C-30), 20.9 (C-24), 19.5 (C-11), 18.1 (C-29), 18.0 (C-2), 18.0 (C-26), 117.9 (C-7), 15.8 (C-25), 13.7 (C-27); HRESIMS *m/z* calcd for $C_{38}H_{57}N_2O$ $[M+H]^+$**:** 557.4471, found 557.4462.

(E)-5-chloro-N′-((1S,2R,4aR,6aR,6bR,12aR,14aR)-1,2,4a,6b,9,9,12a-Heptamethylhexadecahydro-6a,14a-methanopicen-10(6bH,11H,12bH)-ylidene)-2-hydroxybenzohydrazide (3d)

Yield**:** 15.46 mg, 36.7**%**; ^{1}H-NMR (500 MHz, DMSO-d_6) δ 11.01 (*s*, 1H, 3′-OH), 7.88 (*d*, 1H, *J* = 2.5 Hz, H-7′), 7.42 (*t*, 1H, *J* = 8.0 Hz, H-5′), 6.99 (*d*, 1H, *J* = 8.5 Hz, H-4′), 1.17 (*s*, 3H, CH_3-26), 1.15 (*s*, 3H, CH_3-23), 1.06 (*s*, 3H, CH_3-24), 0.98 (*s*, 3H, CH_3-25), 0.90 (*br*, 3H, CH_3-29), 0.89 (*s*, 3H, CH_3-28), 0.85 (*br*, 3H, CH_3-30), 0.69 (*m*, 1H, CH_2-27a), 0.01 (*br*, 1H, CH_2-27b); ^{13}C-NMR (125 MHz, DMSO-d_6) δ 162.9 (C-1′), 158.9 (C-3), 156.5 (C-3′), 133.2 (C-5′), 128.1 (C-6′), 127.5 (C-7′), 123.6 (C-2′), 119.4 (C-4′), 55.2 (C-5), 54.2 (C-9), 49.4 (C-18), 47.0 (C-4), 42.2 (C-22), 40.6 (C-19), 38.8 (C-1), 38.3 (C-20), 37.9 (C-10), 37.7 (C-8), 36.8 (C-6), 35.5 (C-12), 32.4 (C-14), 32.0 (C-17), 31.0 (C-21), 28.4 (C-28), 27.1 (C-16), 26.6 (C-23), 26.4 (C-13), 21.4 (C-15), 21.1 (C-30), 21.0 (C-24), 19.3 (C-11), 18.3 (C-29), 18.0 (C-26), 17.8 (C-2), 17.7 (C-7), 15.7 (C-25), 13.4 (C-27); HRESIMS *m/z* calcd for $C_{37}H_{53}ClN_2O_2Na$ $[M+Na]^+$**:** 615.3693, found 615.3694.

(E)-N′-((1S,2R,4aR,6aR,6bR,12aR,14aR)-1,2,4a,6b,9,9,12a-Heptamethylhexadecahydro-6a,14a-methanopicen-10(6bH,11H,12bH)-ylidene)-2-hydroxy-5-iodobenzohydrazide (3e)

Yield**:** 19.3 mg, 57**%**; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.93 (*br s*, 1H, H-7′), 7.61 (*d*, 1H, *J* = 8.0 Hz, H-5′), 6.76 (*d*, 1H, *J* = 8.5 Hz, H-4′), 1.19 (*s*, 3H, CH_3-26), 1.07 (*s*, 3H, CH_3-23), 1.03 (*s*, 3H, CH_3-24), 0.98 (*s*, 3H, CH_3-25), 0.94 (*d*, 3H, *J* = 6.0 Hz, CH_3-29), 0.91 (*s*, 3H, CH_3-

28), 0.87 (*br*, 3H, CH_3-30), 0.65 (*t*, 1H, *J* = 5.5 Hz CH_2-27a), 0.05 (*br d*, 1H, *J* = 5.0 Hz, CH_2-27b); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 166.9 (C-3), 162.3 (C-1′), 155.6 (C-3′), 143.2 (C-5′), 134.7 (C-7′), 121.3 (C-4′), 110.2 (C-2′), 81.0 (C-6′), 55.5 (C-9), 53.4 (C-5), 49.8 (C-18), 45.2 (C-4), 42.1 (C-22), 40-9 (C-19), 38.6 (C-1), 38.5 (C-20), 37.0 (C-10), 36.3 (C-6), 36.2 (C-8), 35.4 (C-12), 32.5 (C-14), 32.0 (C-17), 31.2 (C-21), 28.4 (C-28), 27.3 (C-16), 26.6 (C-13), 26.4 (C-23), 22.8 (C-30), 21.4 (C-15), 20.9 (C-24), 19.4 (C-11), 19.1 (C-2), 18.1 (C-29), 18.0 (C-7), 17.7 (C-26), 15.7 (C-25), 13.6 (C-27); HRESIMS *m/z* calcd for $C_{37}H_{53}IN_2O_2Na$ $[M+Na]^+$**:** 707.3049, found 707.3087.

(E)-2-(benzo[d]thiazol-2-ylthio)-N'-((1S,2R,4aR,6aR,6bR,12aR,14aR)-1,2,4a,6b,9,9,12a-Heptamethylhexadecahydro-6a,14a-methanopicen-10(6bH,11H,12bH)-ylidene)acetohydrazide (3f)

Yield**:** 17.01 mg, 37**%**; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.90 (*d*, 1H, *J* = 8.0 Hz, H-8′), 7.77 (*d*, 1H, *J* = 7.5 Hz, H-5′), 7.45 (*m*, 1H, H-7′), 7.35 (*m*, 1H, H-6′), 4.26 (*m*, 1H, H-2′), 1.19 (*s*, 3H, CH_3-26), 1.07 (*s*, 3H, CH_3-23), 1.03 (*s*, 3H, CH_3-24), 0.97 (*s*, 3H, CH_3-25), 0.94 (*d*, 3H, *J* = 6.0 Hz, CH_3-29), 0.91 (*s*, 3H, CH_3-28), 0.87 (*d*, 3H, *J* = 5.5 Hz, CH_3-30), 0.63 (*d*, 1H, *J* = 5.5 Hz, H-27a), 0.05 (*d*, 1H, *J* = 5.5 Hz, H-27b); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 171.4 (C-1′), 165.3 (C-3′), 158.6 (C-3), 153.9 (C-9′), 135.3 (C-4′), 126.5 (C-7′), 125.0 (C-6′), 122.2 (C-8′), 121.3 (C-5′), 55.5 (C-5), 54.5 (C-9), 49.7 (C-18), 47.6 (C-4), 42.2 (C-22), 40.9 (C-19), 39.4 (C-1), 38.6 (C-20), 37.8 (C-6), 37.1 (C-10), 36.9 (C-8), 35.7 (C-12), 34.2 (C-2′), 32.6 (C-14), 32.1 (C-17), 31.2 (C-21), 28.4 (C-28), 27.5 (C-13), 27.3 (C-16), 26.7 (C-23), 21.5 (C-15), 21.1 (C-30), 20.8 (C-24), 19.8 (C-2), 19.6 (C-11), 18.1 (C-29), 18.0 (C-26), 17.9 (C-7), 15.8 (C-25), 13.8 (C-27); HRESIMS *m/z* calcd for $C_{39}H_{55}N_3OS_2Na$ $[M+Na]^+$ 668.3684, found 668.3675.

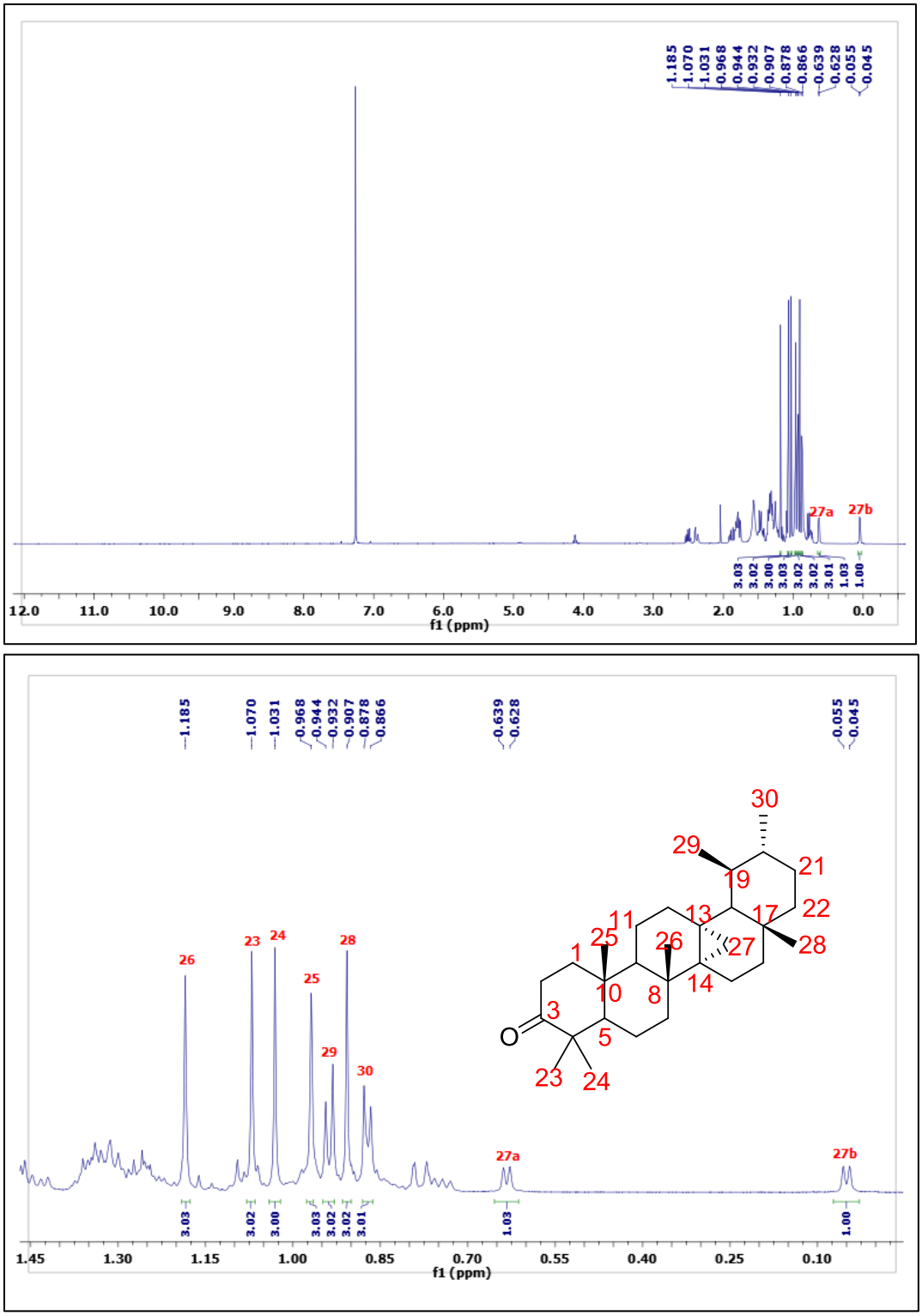


Figure S1. ^{1}H-NMR ($CDCl_3$, 500 MHz) spectrum of **1**.

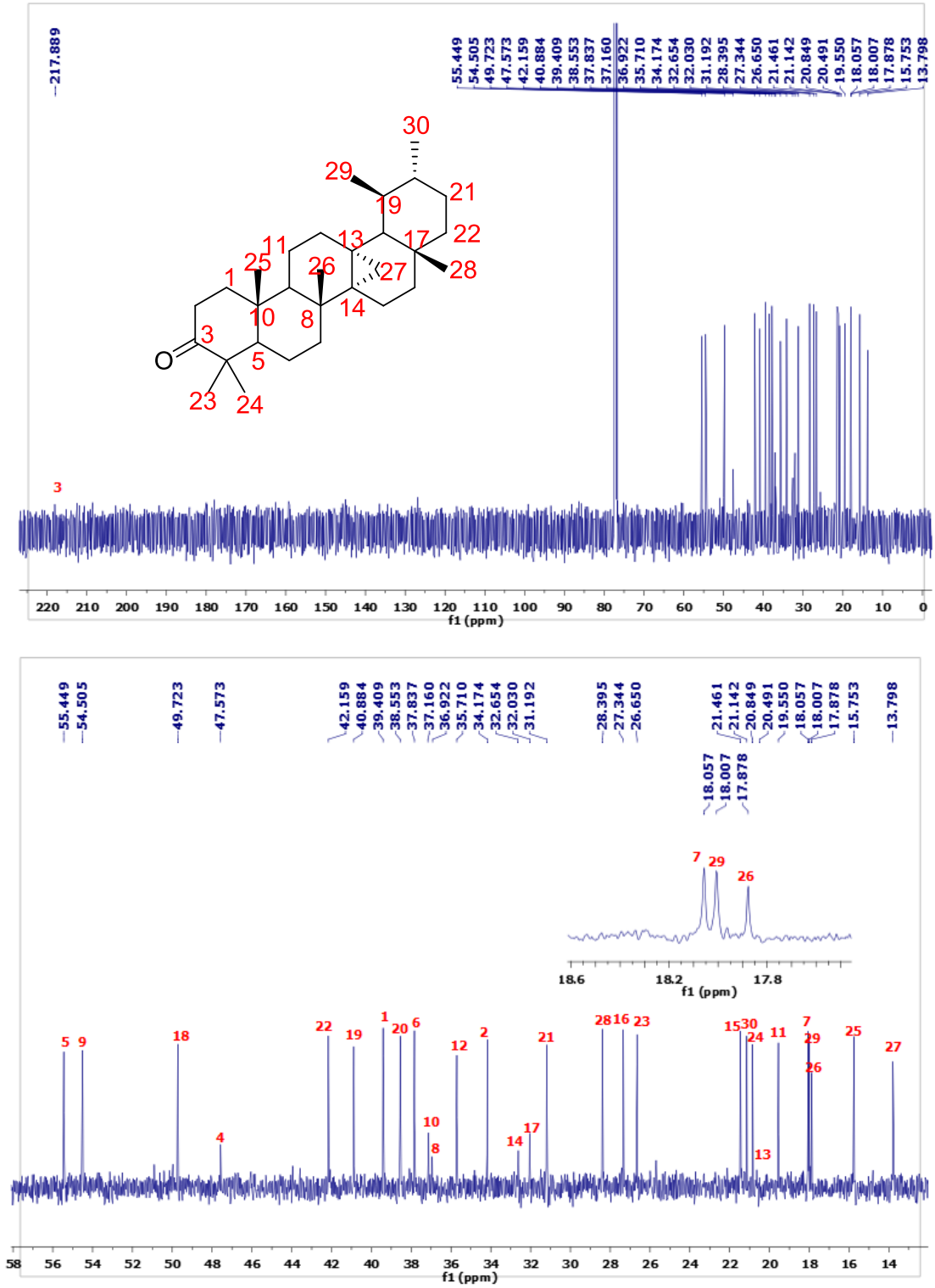
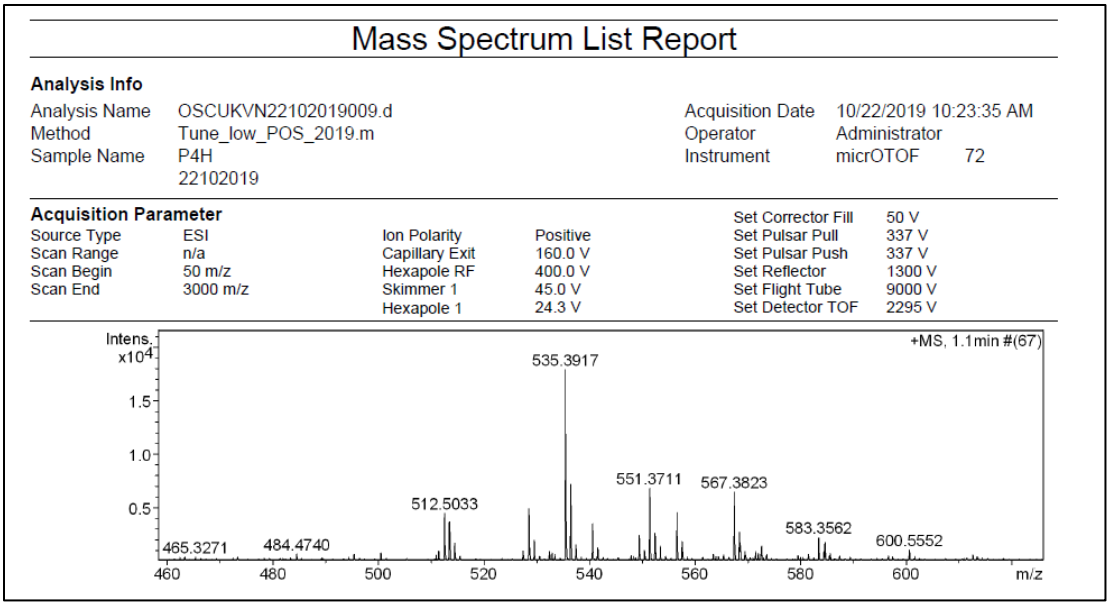
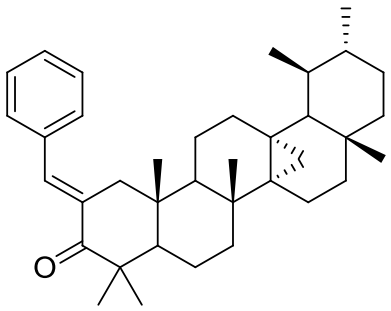


Figure S2. ^{13}C-NMR ($CDCl_3$, 125 MHz) spectrum of **1**.





Chemical Formula: $C_{37}H_{52}NaO$ $[M+Na]^+$
Exact Mass: 535.39159

Figure S3. HRESIMS spectrum of **1a**.

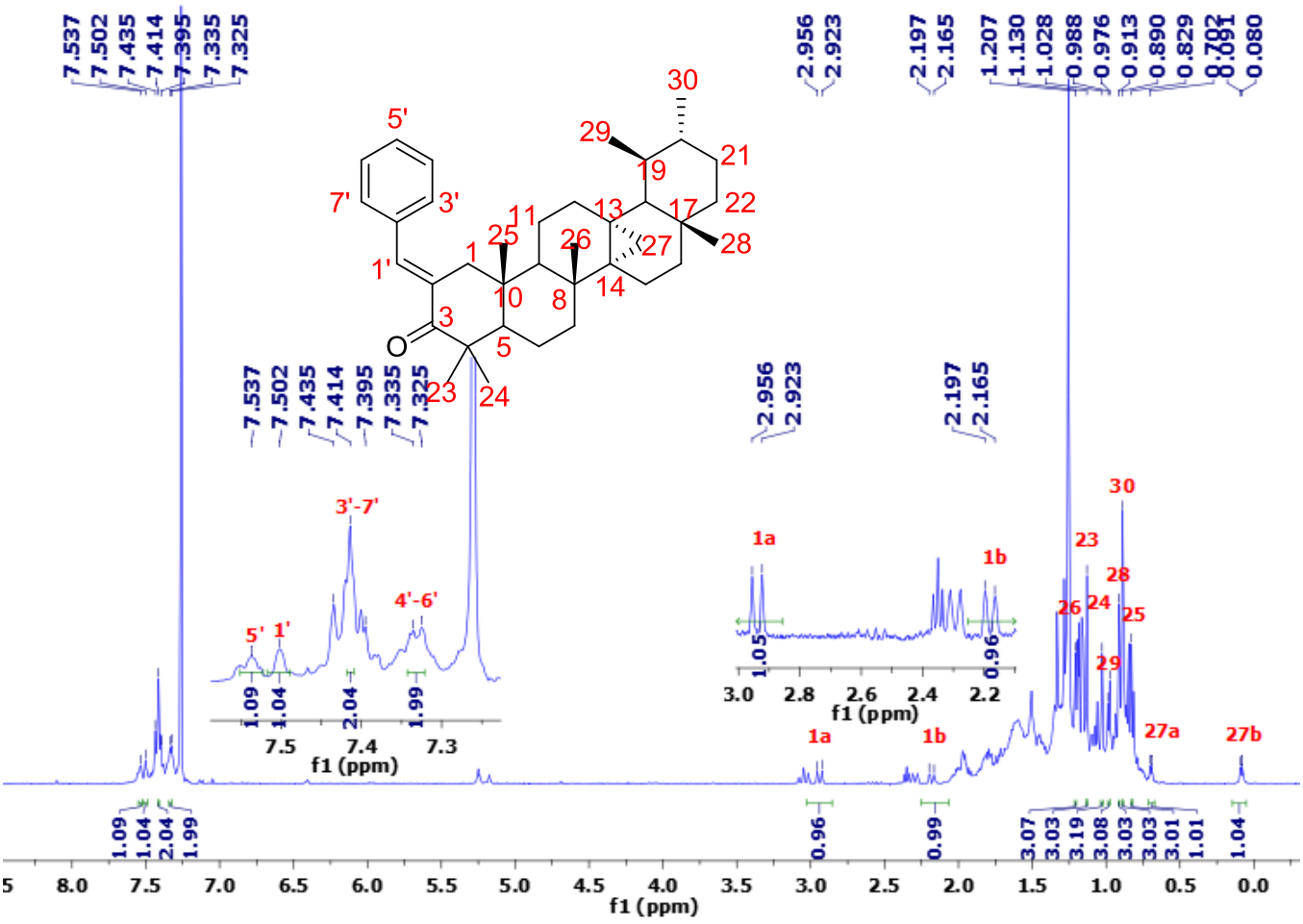


Figure S4. ^{1}H-NMR ($CDCl_3$, 500 MHz) spectrum of **1a**.

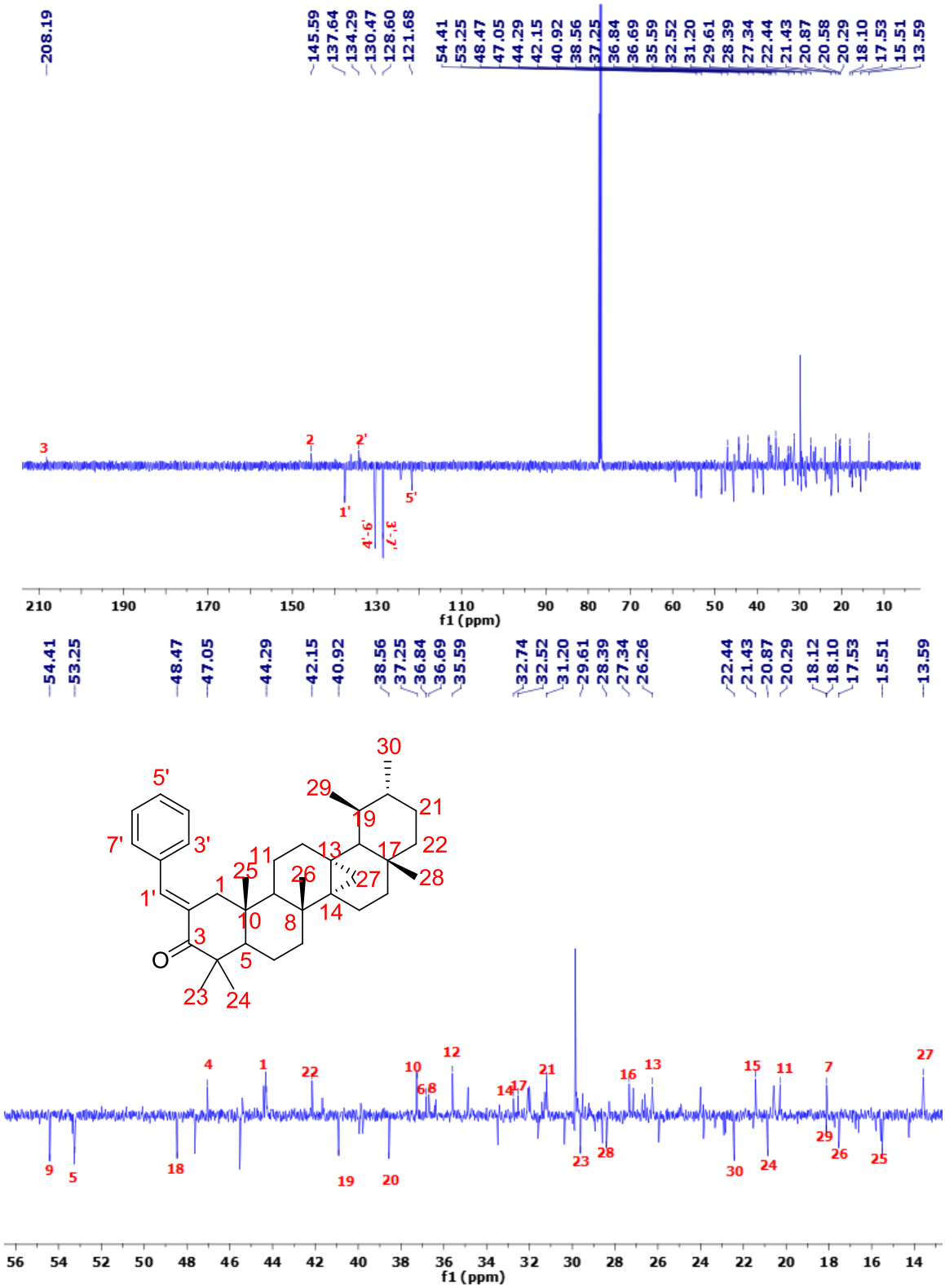


Figure S5. J-mod ($CDCl_3$, 125 MHz) spectrum of **1a**.

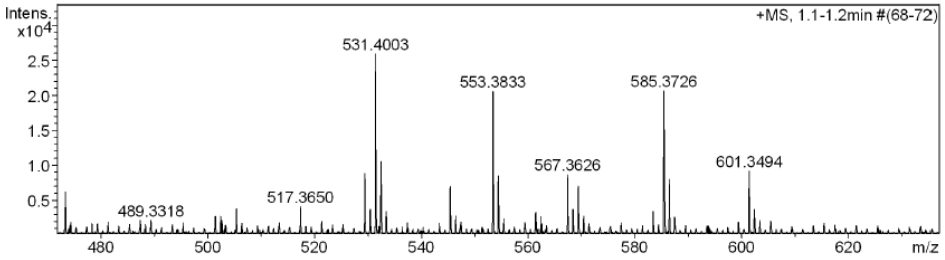
Mass Spectrum List Report

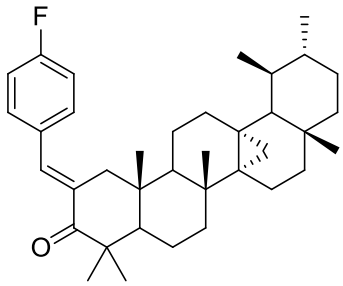
Analysis Info

Analysis Name	OSKVN04102019004.d	Acquisition Date	10/4/2019 11:46:27 AM
Method	Tune_low_POS_2019.m	Operator	Administrator
Sample Name	P4F	Instrument	micrOTOF 72
	P4F		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	50 V
Scan Range	n/a	Capillary Exit	250.0 V	Set Pulsar Pull	337 V
Scan Begin	50 m/z	Hexapole RF	400.0 V	Set Pulsar Push	337 V
Scan End	3000 m/z	Skimmer 1	60.0 V	Set Reflector	1300 V
		Hexapole 1	24.3 V	Set Flight Tube	9000 V
				Set Detector TOF	2295 V





Chemical Formula: $C_{37}H_{52}FO$ $[M+H]^+$
Exact Mass: 531.40022

Figure S6. HRESIMS spectrum of **1b**.

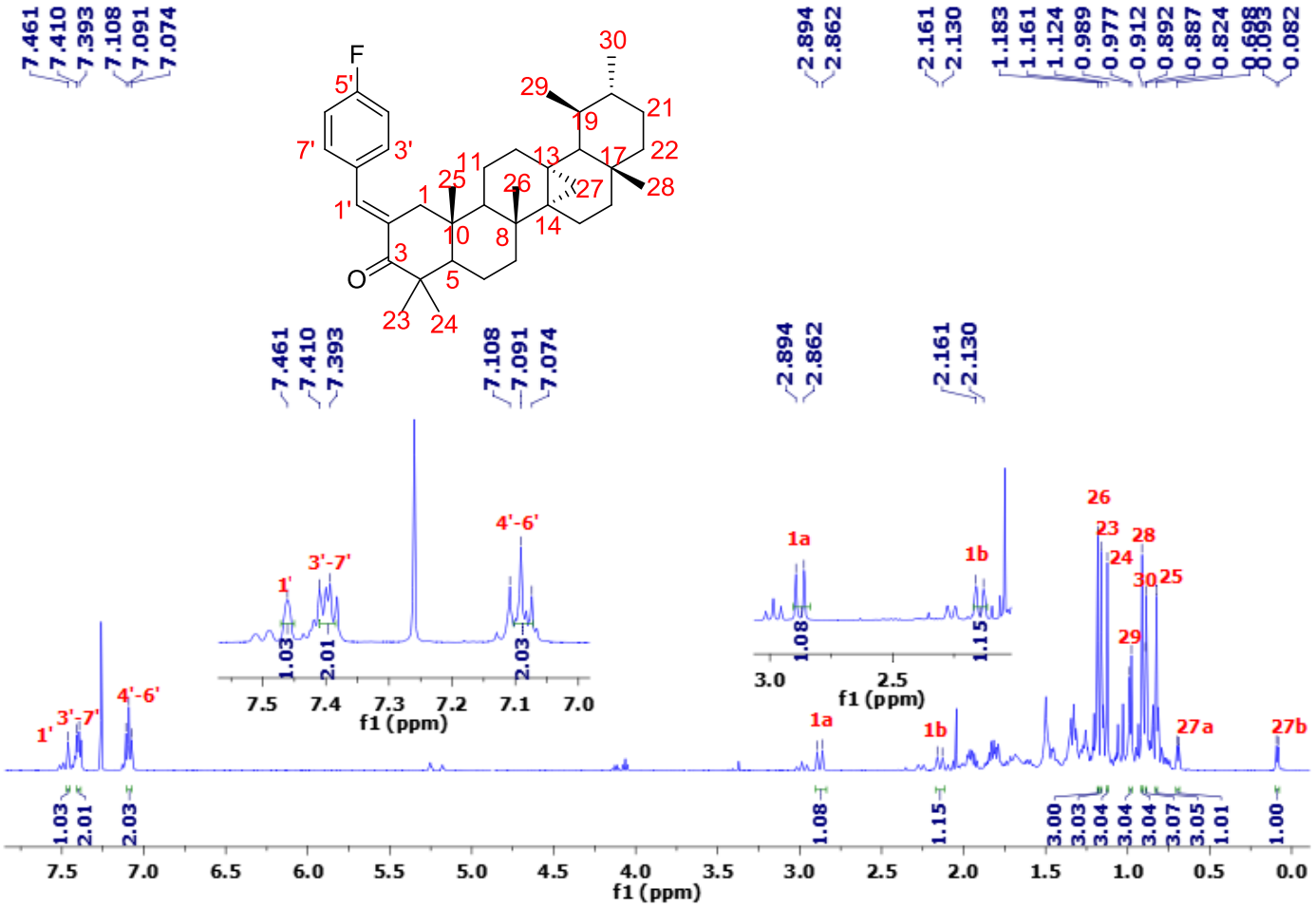


Figure S7. ^{1}H-NMR ($CDCl_3$, 500 MHz) spectrum of **1b**.

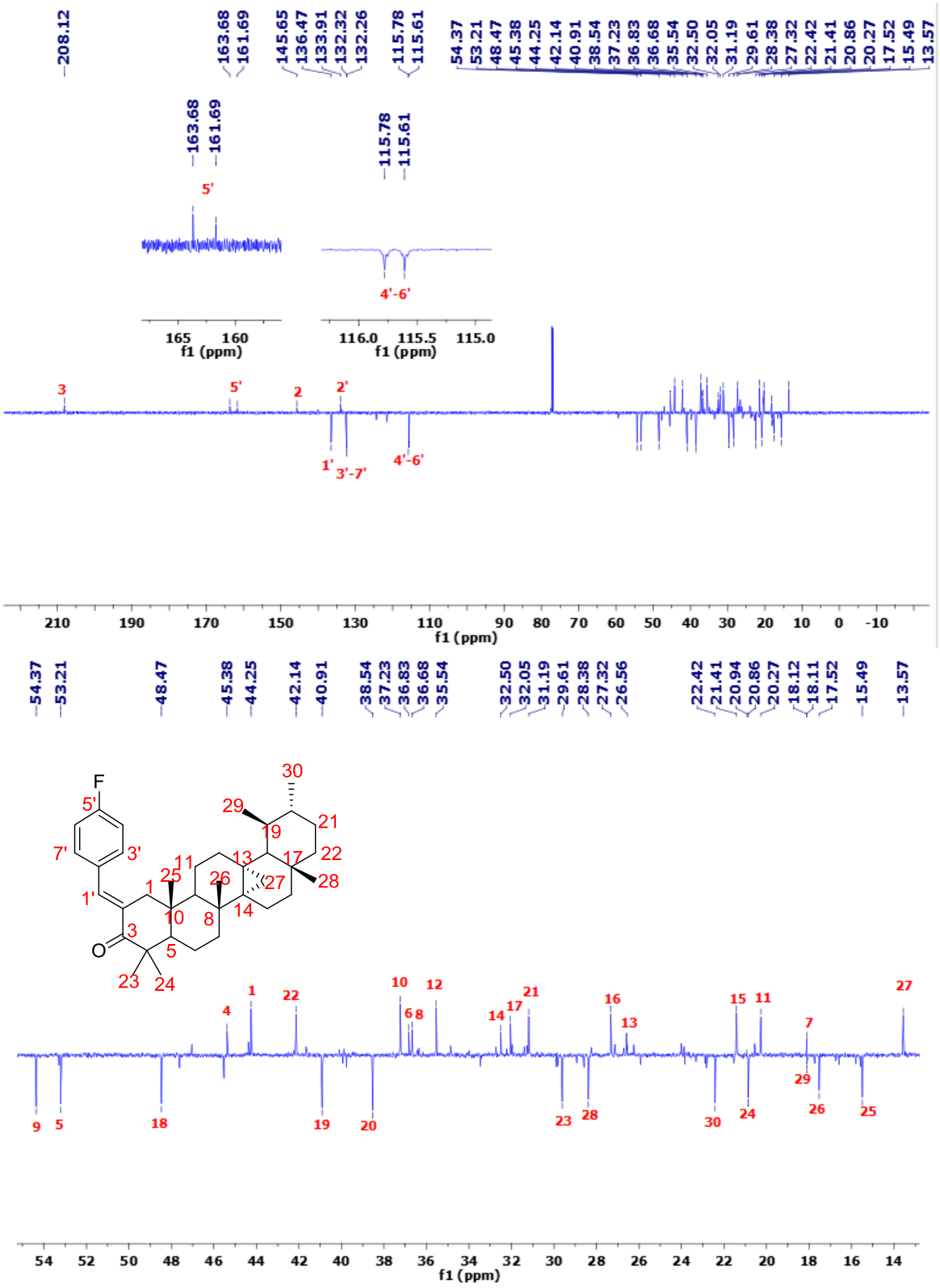


Figure S8. J-mod ($CDCl_3$, 125 MHz) spectrum of **1b**.

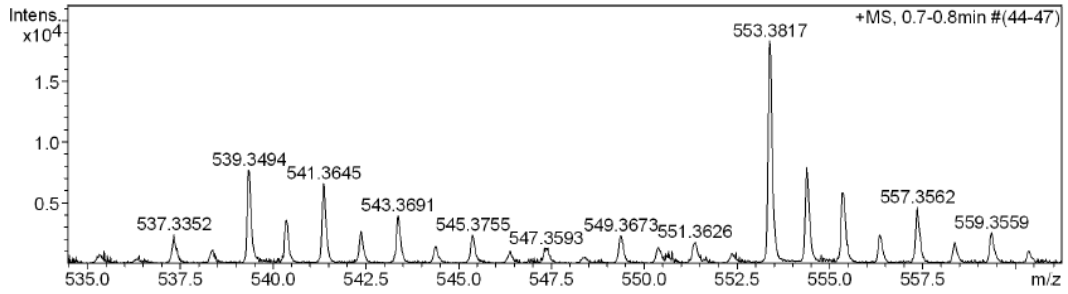
Mass Spectrum List Report

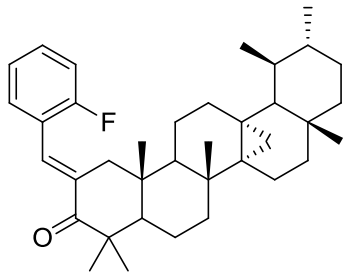
Analysis Info

Analysis Name	OSKVN04102019005.d	Acquisition Date	10/4/2019 11:49:01 AM
Method	Tune_low_POS_2019.m	Operator	Administrator
Sample Name	Tr1	Instrument	micrOTOF 72
	Tr1		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	50 V
Scan Range	n/a	Capillary Exit	180.0 V	Set Pulsar Pull	337 V
Scan Begin	50 m/z	Hexapole RF	400.0 V	Set Pulsar Push	337 V
Scan End	3000 m/z	Skimmer 1	60.0 V	Set Reflector	1300 V
		Hexapole 1	24.3 V	Set Flight Tube	9000 V
				Set Detector TOF	2295 V





Chemical Formula: $C_{37}H_{51}FNaO$ $[M+Na]^+$
Exact Mass: 553.38216

Figure S9. HRESIMS spectrum of **1c**.

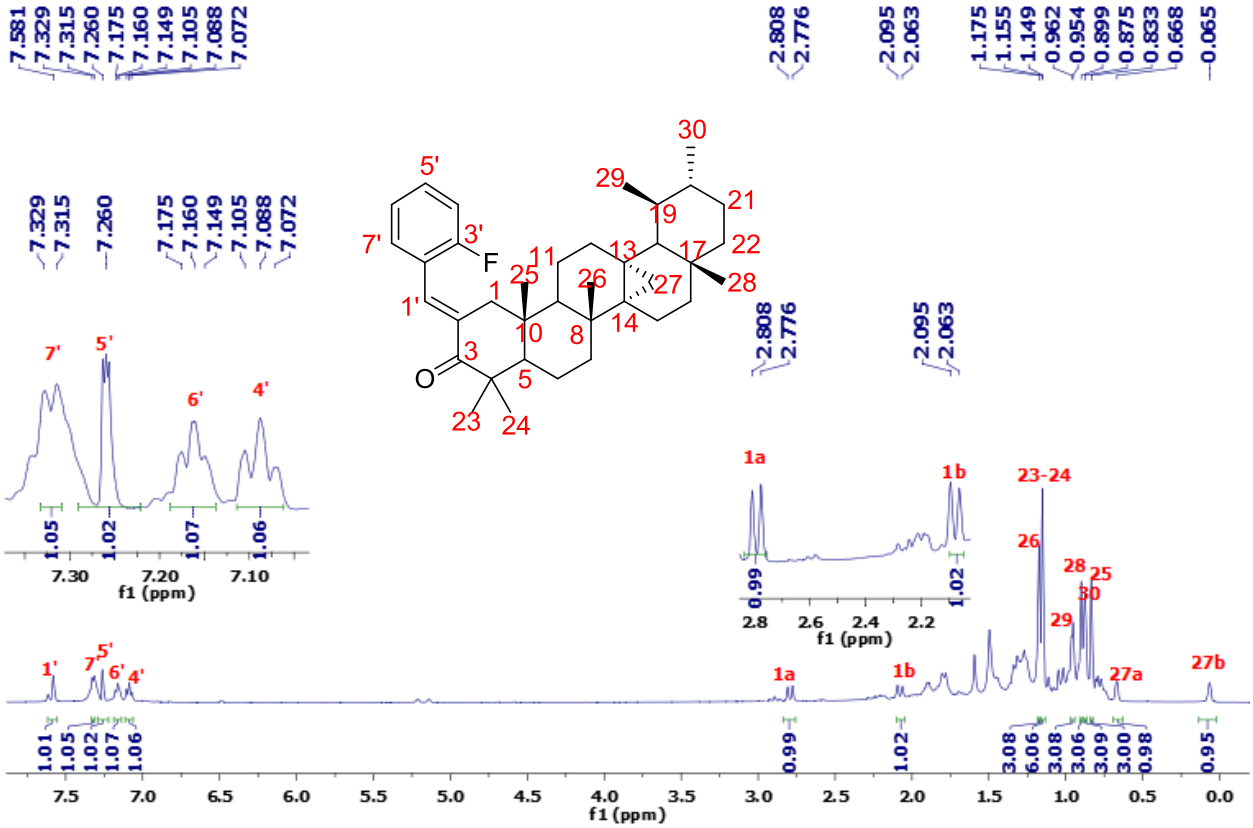


Figure S10. ^{1}H-NMR ($CDCl_3$, 500 MHz) spectrum of **1c**.

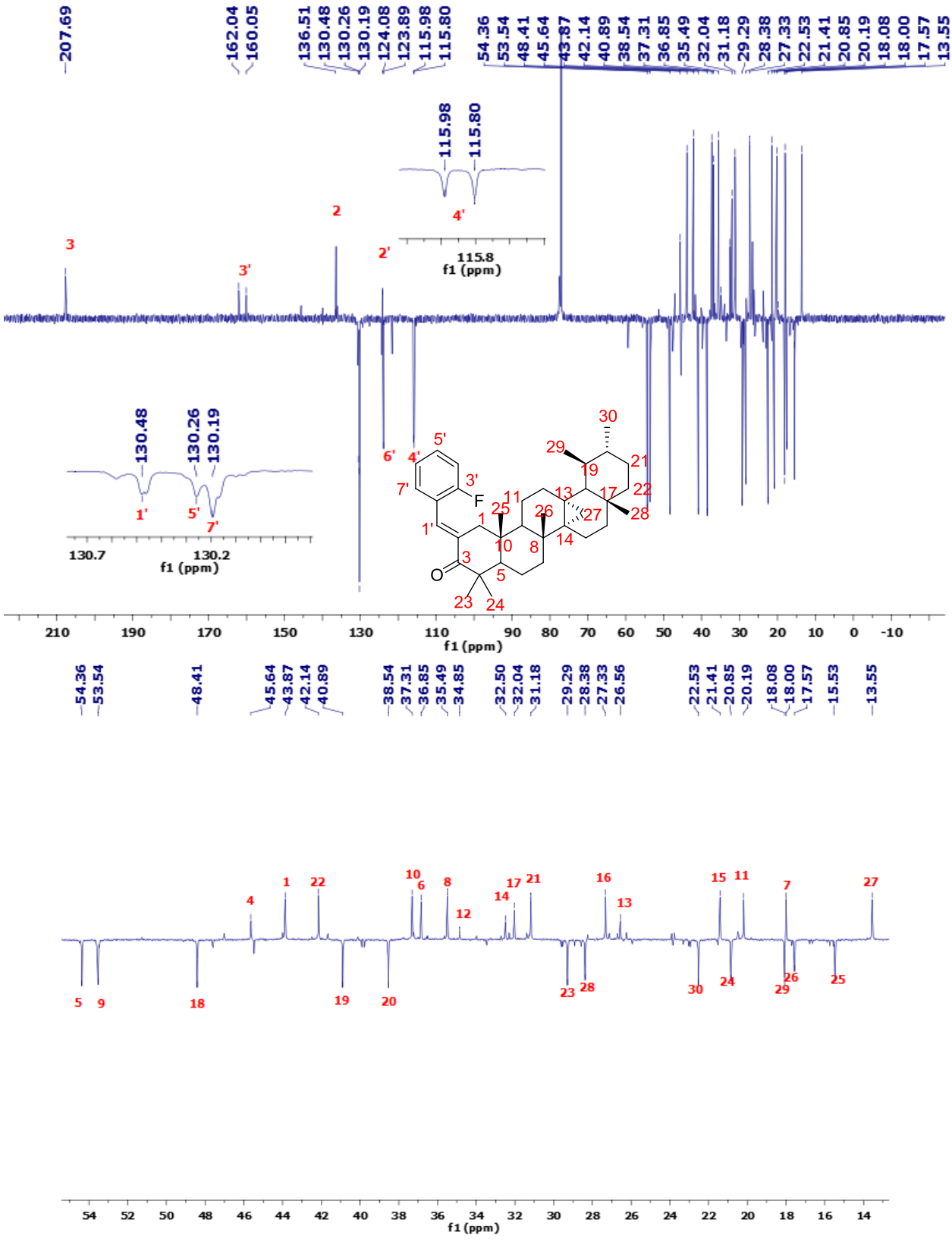


Figure S11. J-mod (CDCl3, 125 MHz) spectrum of **1c**.

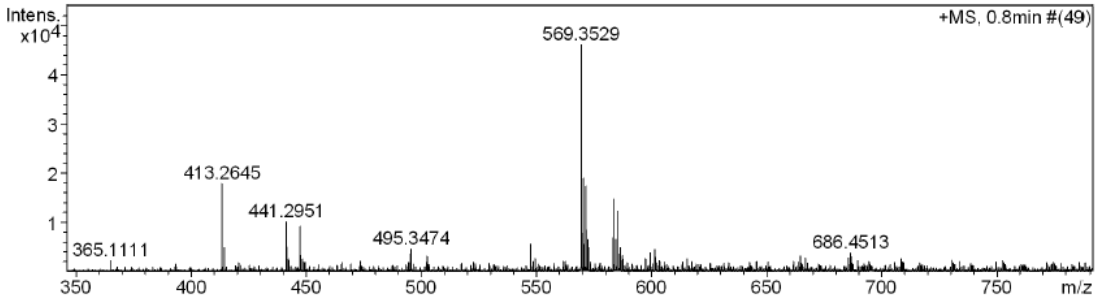
Mass Spectrum List Report

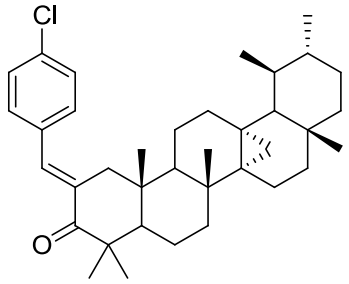
Analysis Info

Analysis Name	OSKVN04102019001_1.d	Acquisition Date	10/4/2019 11:40:50 AM
Method	Tune_low_POS_2019.m	Operator	Administrator
Sample Name	P4Cl	Instrument	micrOTOF 72
	P4Cl		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	50 V
Scan Range	n/a	Capillary Exit	250.0 V	Set Pulsar Pull	337 V
Scan Begin	50 m/z	Hexapole RF	400.0 V	Set Pulsar Push	337 V
Scan End	3000 m/z	Skimmer 1	60.0 V	Set Reflector	1300 V
		Hexapole 1	24.3 V	Set Flight Tube	9000 V
				Set Detector TOF	2295 V





Chemical Formula: $C_{37}H_{51}ClNaO$ $[M+Na]^+$
Exact Mass: 569.35261

Figure S12. HRESIMS spectrum of **1d**.

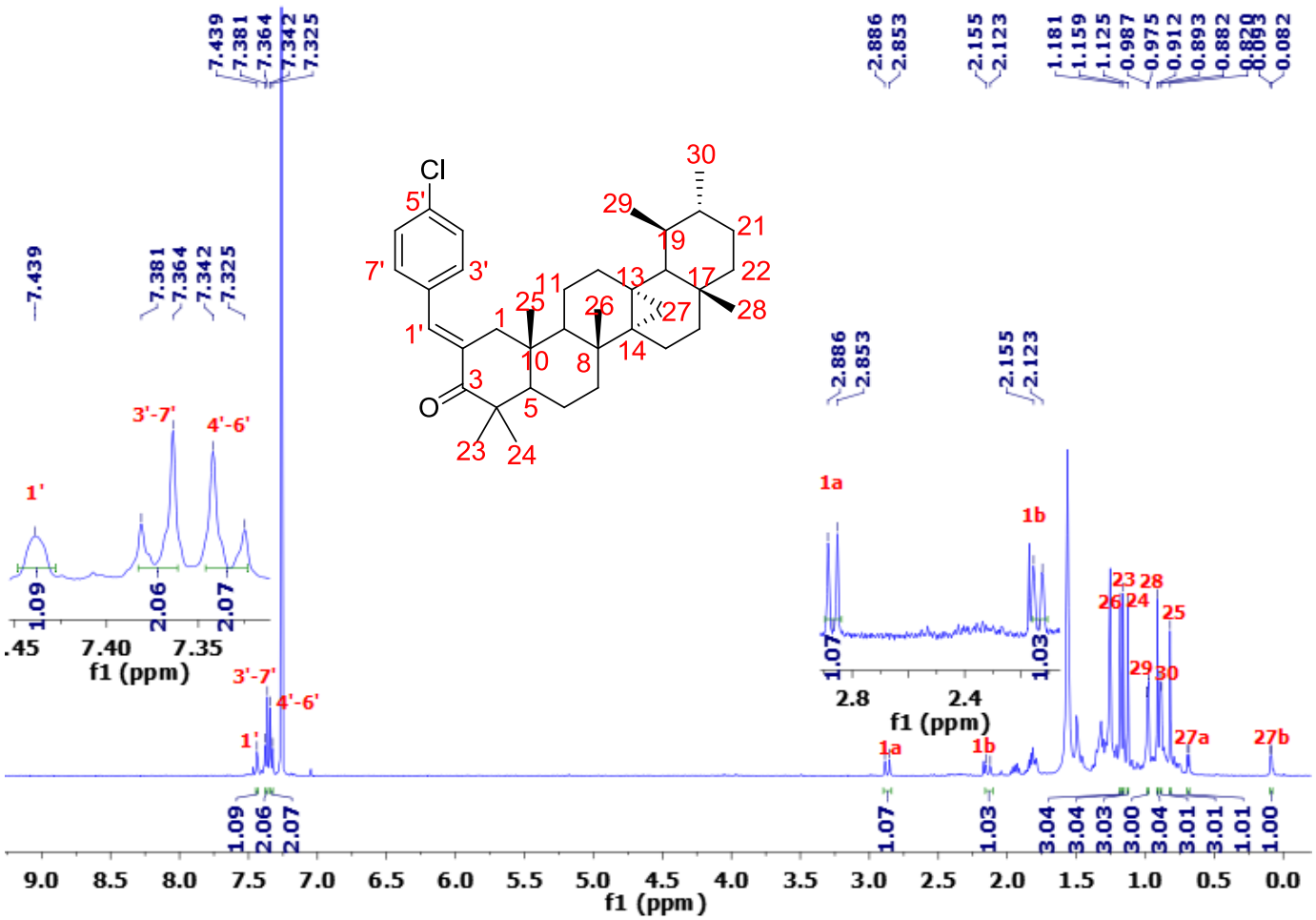


Figure S13. ^{1}H-NMR ($CDCl_3$, 500 MHz) spectrum of **1d**.

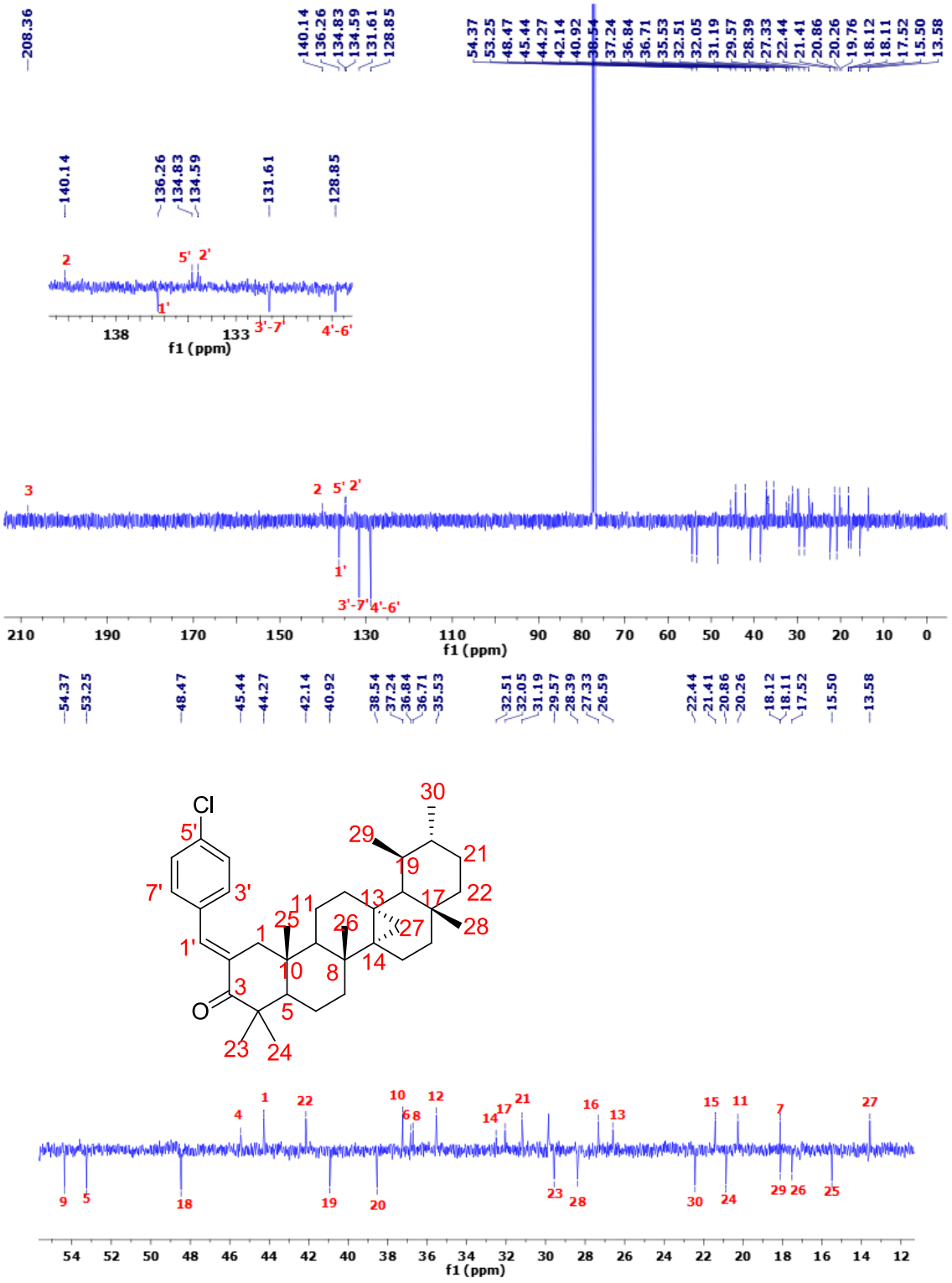


Figure S14. J-mod ($CDCl_3$, 125 MHz) spectrum of **1d**.

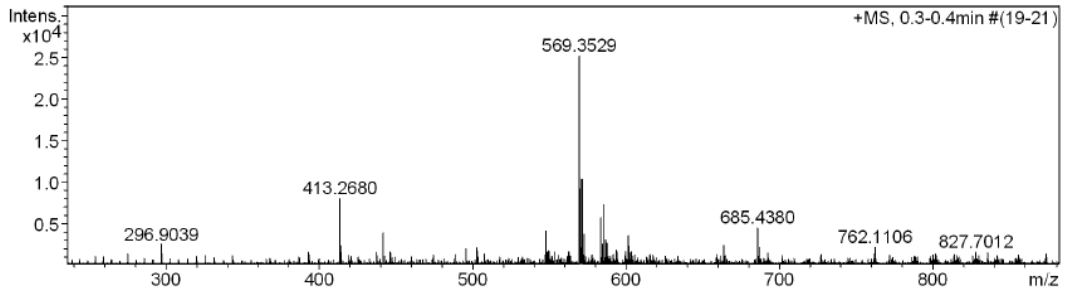
Mass Spectrum List Report

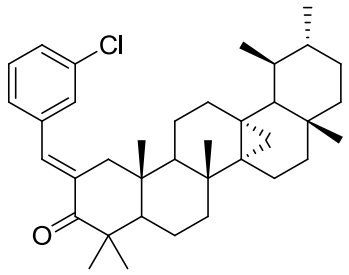
Analysis Info

Analysis Name	OSKVN04102019003.d	Acquisition Date	10/4/2019 11:44:49 AM
Method	Tune_low_POS_2019.m	Operator	Administrator
Sample Name	NG1	Instrument	micrOTOF 72
	NG1		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	50 V
Scan Range	n/a	Capillary Exit	250.0 V	Set Pulsar Pull	337 V
Scan Begin	50 m/z	Hexapole RF	400.0 V	Set Pulsar Push	337 V
Scan End	3000 m/z	Skimmer 1	60.0 V	Set Reflector	1300 V
		Hexapole 1	24.3 V	Set Flight Tube	9000 V
				Set Detector TOF	2295 V





Chemical Formula: $C_{37}H_{51}ClNaO$ $[M+Na]^+$
Exact Mass: 569.35261

Figure S15. HRESIMS spectrum of **1e**.

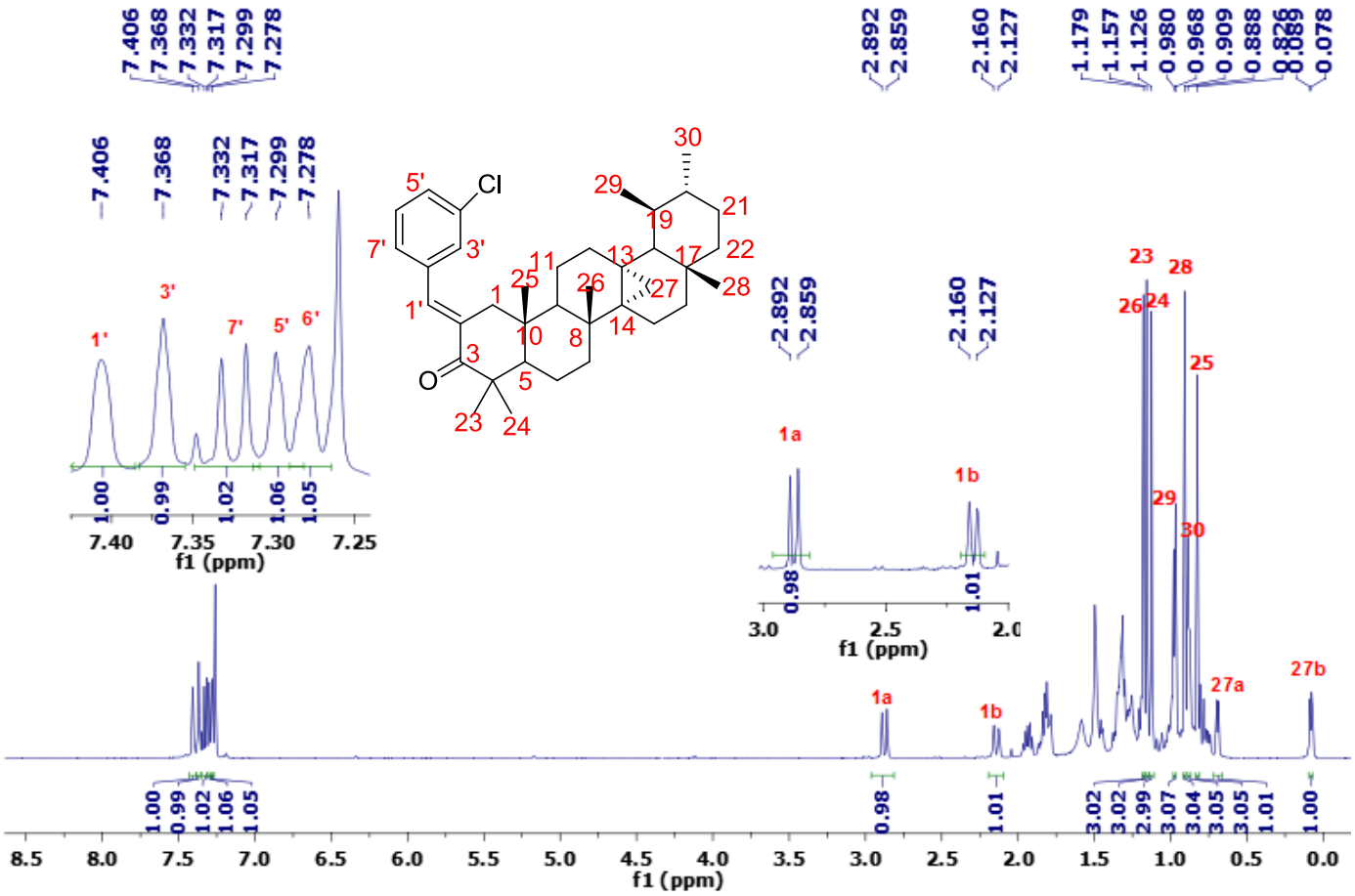


Figure S16. ^{1}H-NMR ($CDCl_3$, 500 MHz) spectrum of **1e**.

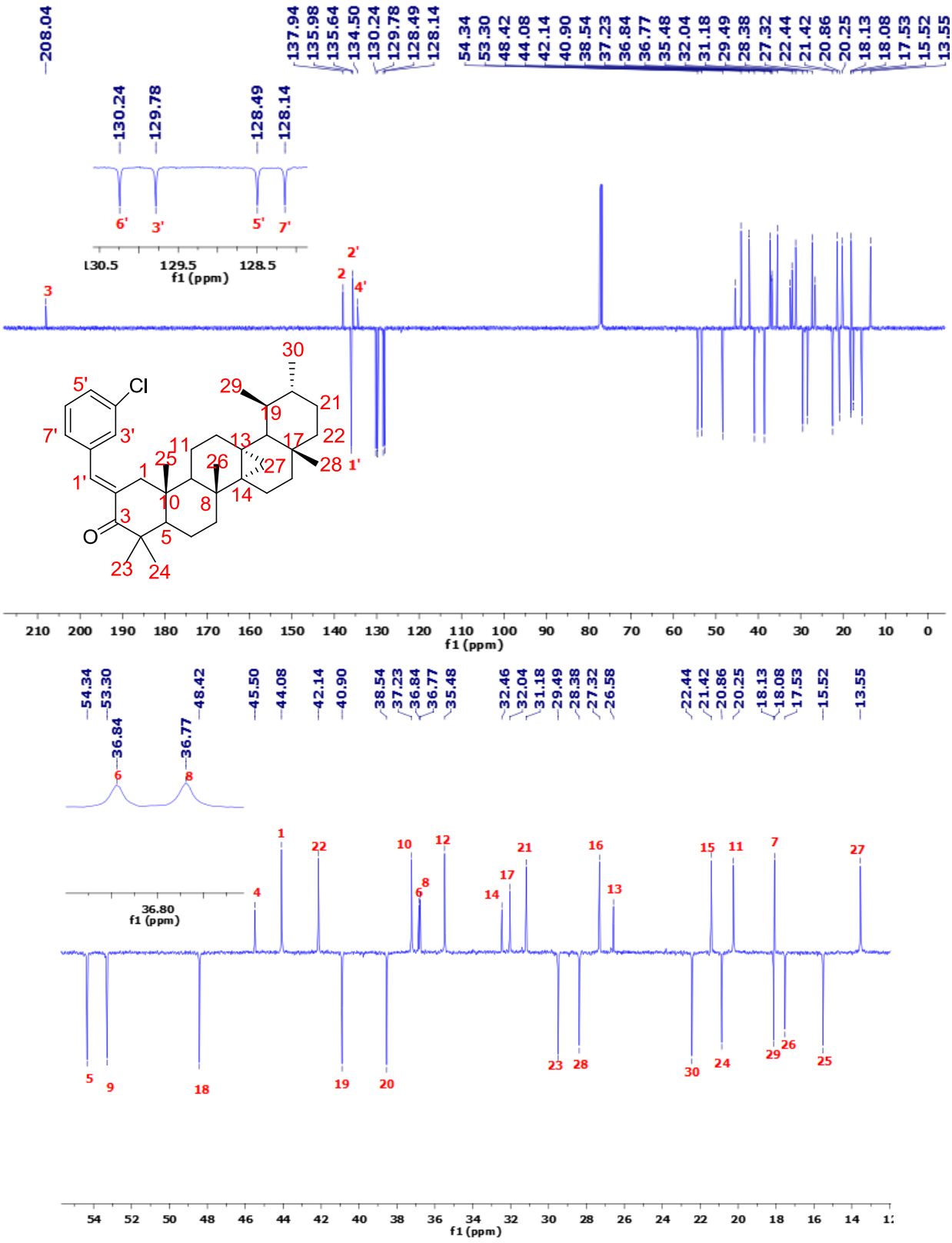
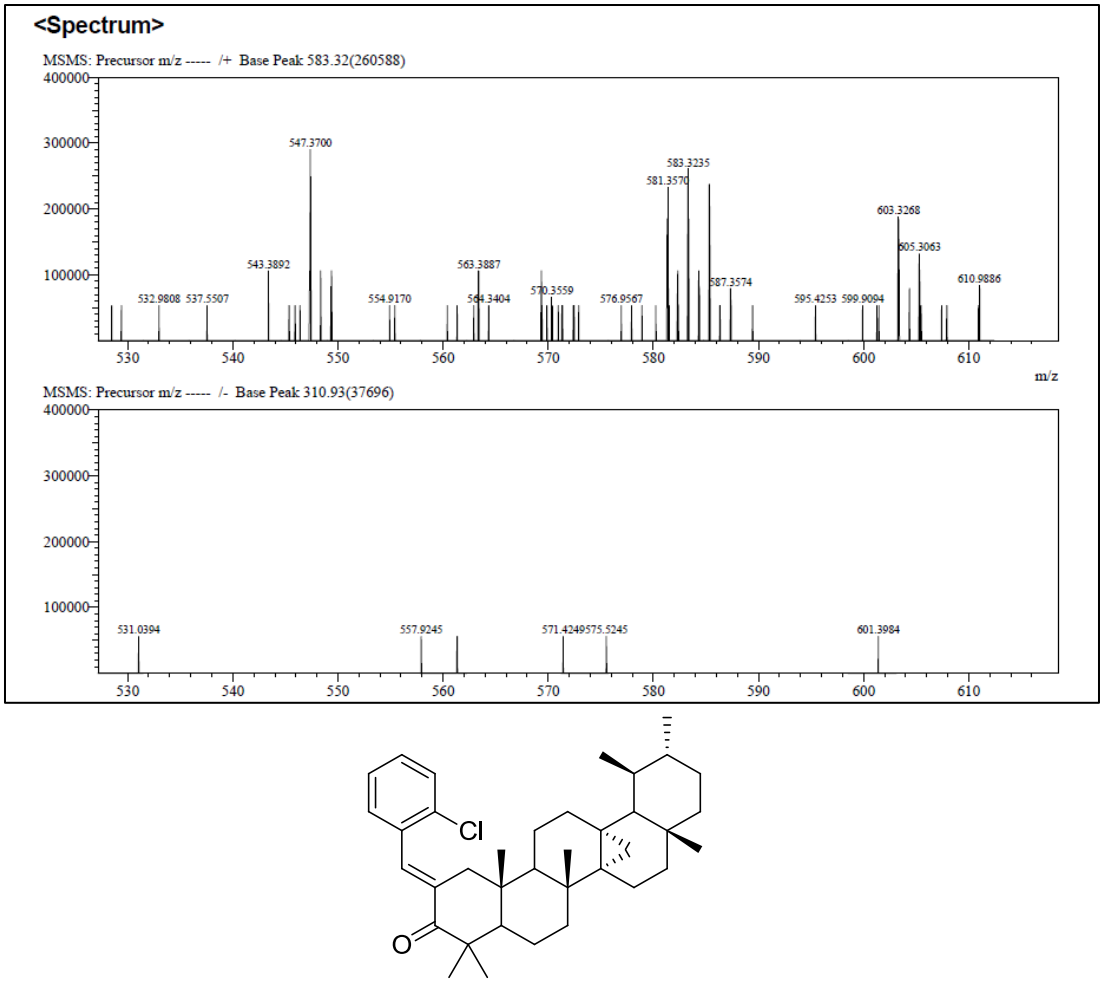


Figure S17. J-mod ($CDCl_3$, 125 MHz) spectrum of **1e.**



Chemical Formula: $C_{37}H_{52}ClO$ $[M+H]^+$
Exact Mass: 547.37067

Figure S18. HRESIMS spectrum of **1f**.

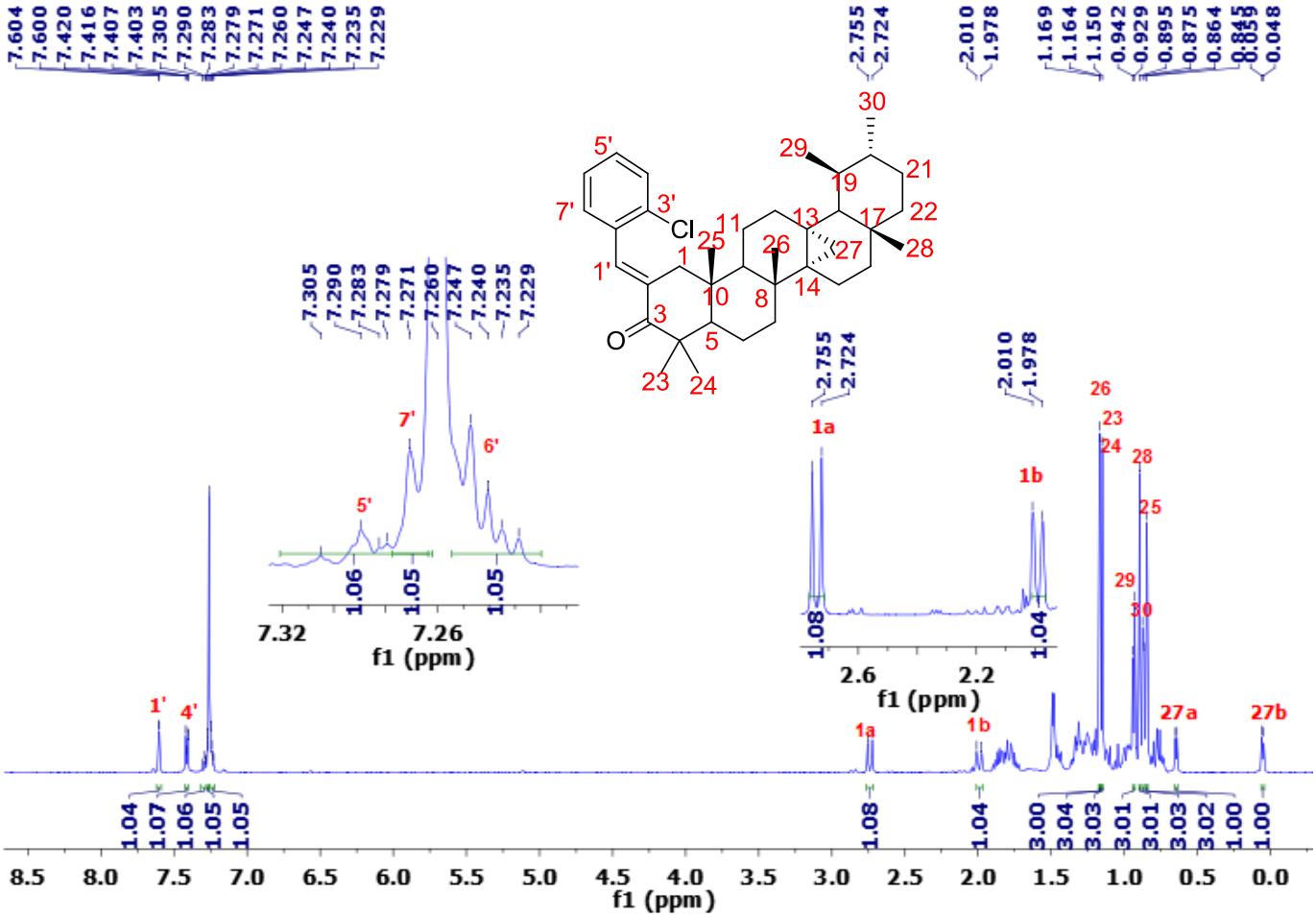


Figure S19. ^{1}H-NMR ($CDCl_3$, 500 MHz) spectrum of **1f**.

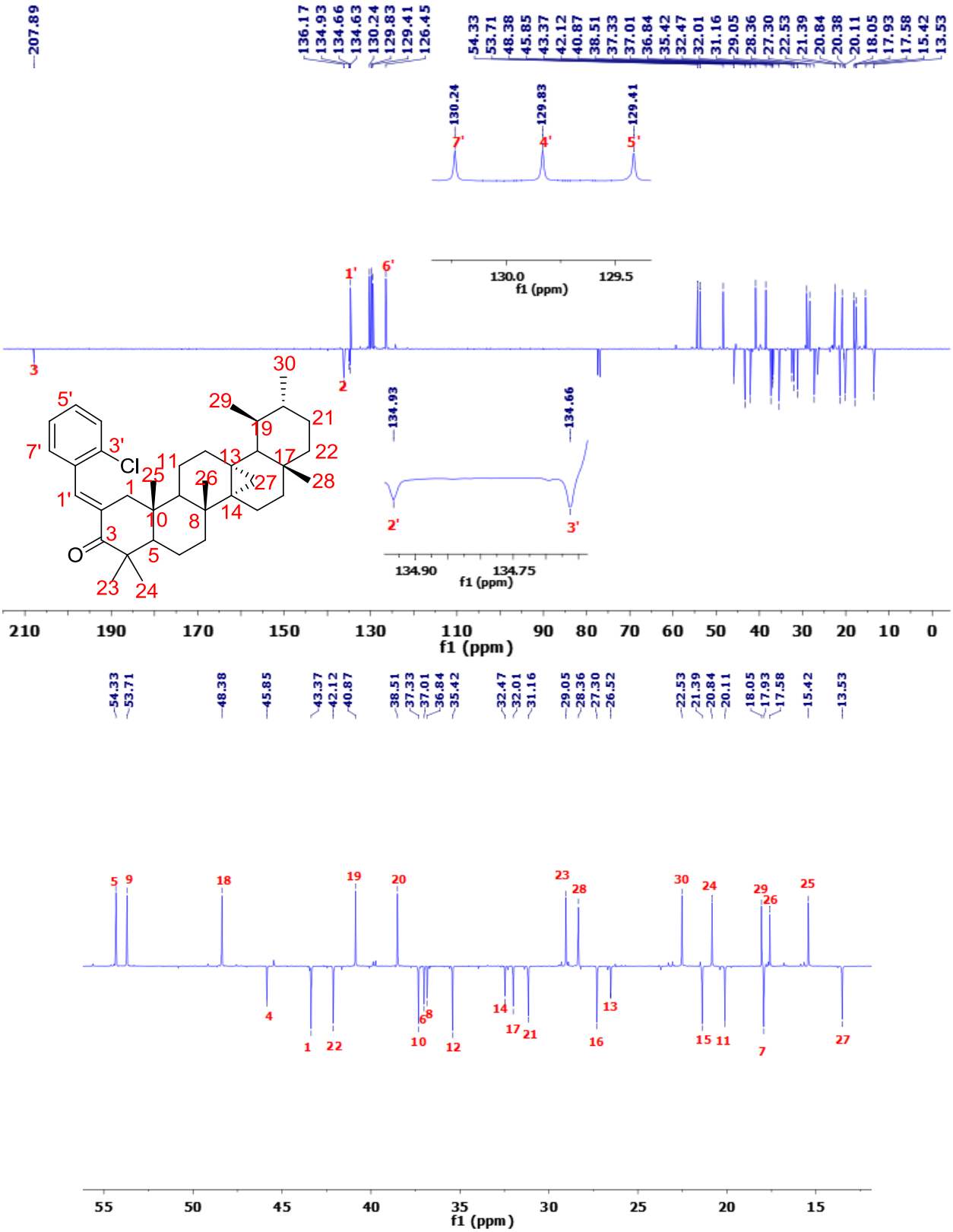


Figure S20. J-mod ($CDCl_3$, 125 MHz) spectrum of **1f**.

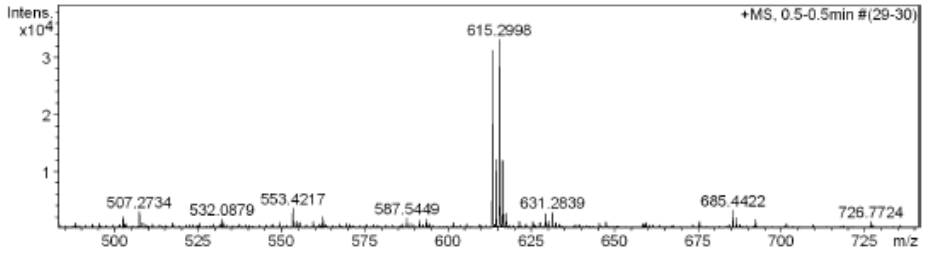
Mass Spectrum List Report

Analysis Info

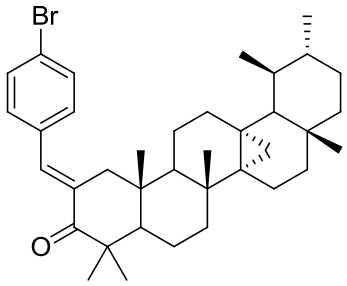
Analysis Name	OSKVN04102019008.d	Acquisition Date	10/4/2019 12:00:13 PM
Method	Tune_low_POS_2019.m	Operator	Administrator
Sample Name	Ph4Br	Instrument	micrOTOF 72
	Ph4Br		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	50 V
Scan Range	n/a	Capillary Exit	220.0 V	Set Pulsar Pull	337 V
Scan Begin	50 m/z	Hexapole RF	400.0 V	Set Pulsar Push	337 V
Scan End	3000 m/z	Skimmer 1	45.0 V	Set Reflector	1300 V
		Hexapole 1	24.3 V	Set Flight Tube	9000 V
				Set Detector TOF	2295 V



#	m/z	I	I %	S/N	Res.
1	144.9684	2233	6.7	14.8	7000
2	145.0077	2052	6.2	13.5	10240
3	161.0238	2060	6.2	13.7	18805
4	353.2632	10374	31.3	74.1	4658
5	354.2674	2346	7.1	16.3	4613
6	381.2940	12268	37.0	86.3	4909
7	382.2966	2919	8.8	20.0	5068
8	393.2916	5137	15.5	35.5	4705
9	413.2639	14500	43.8	100.3	4661
10	414.2669	3988	12.0	27.0	4684
11	425.2145	5286	16.0	35.8	4533
12	441.2952	6766	20.4	45.6	4689
13	447.3431	5305	16.0	35.5	4748
14	502.5515	2172	6.6	13.5	31319
15	507.2734	3075	9.3	19.4	4561
16	553.4217	3604	10.9	22.9	3557
17	562.4043	2190	6.6	13.6	31144
18	613.3022	31255	94.3	220.9	4940



Chemical Formula: $C_{37}H_{51}BrNaO$ $[M+Na]^+$
Exact Mass: 613.30210

Figure S21. HRESIMS spectrum of **1g**.

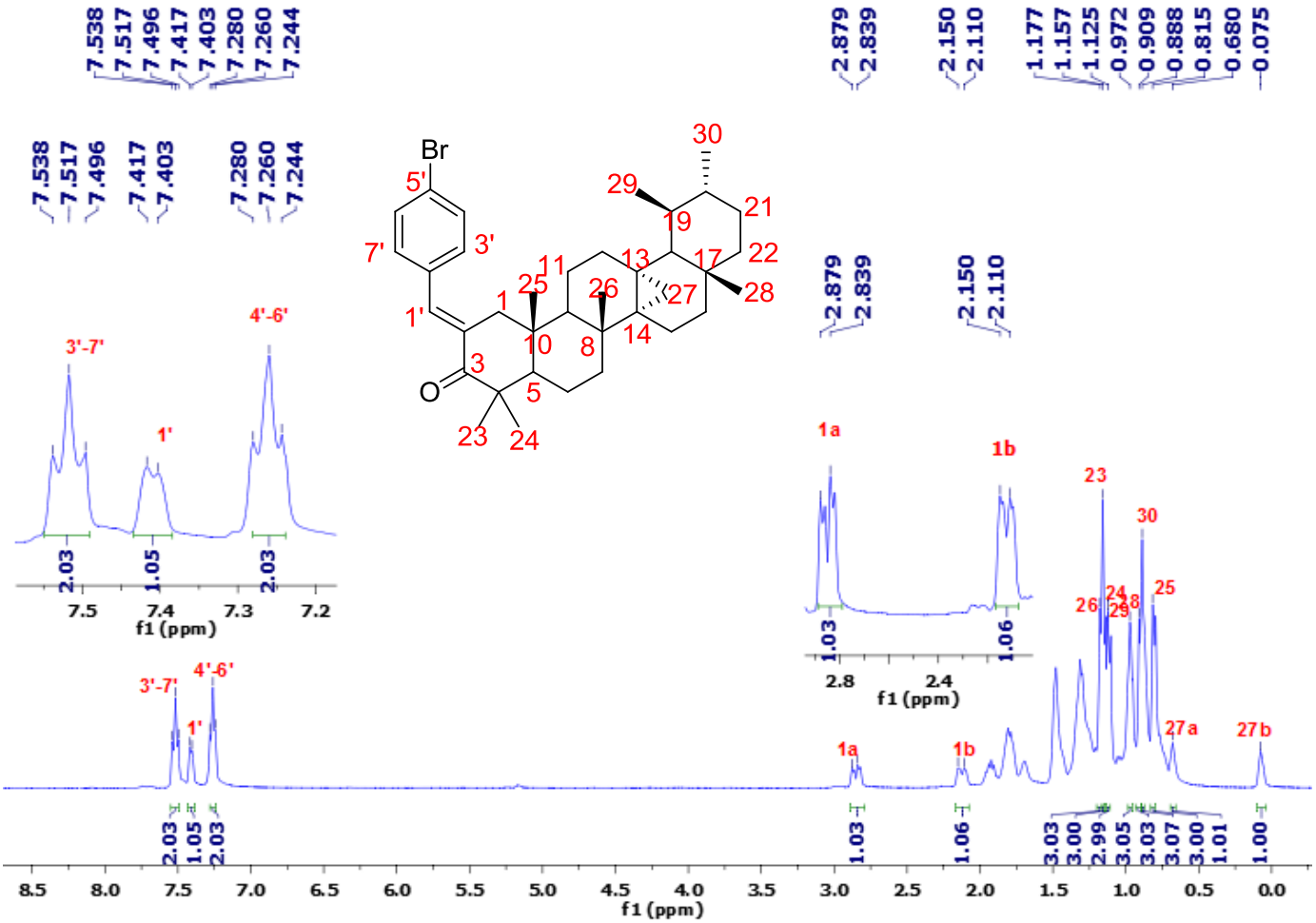


Figure S22. ^{1}H-NMR ($CDCl_3$, 400 MHz) spectrum of **1g**.

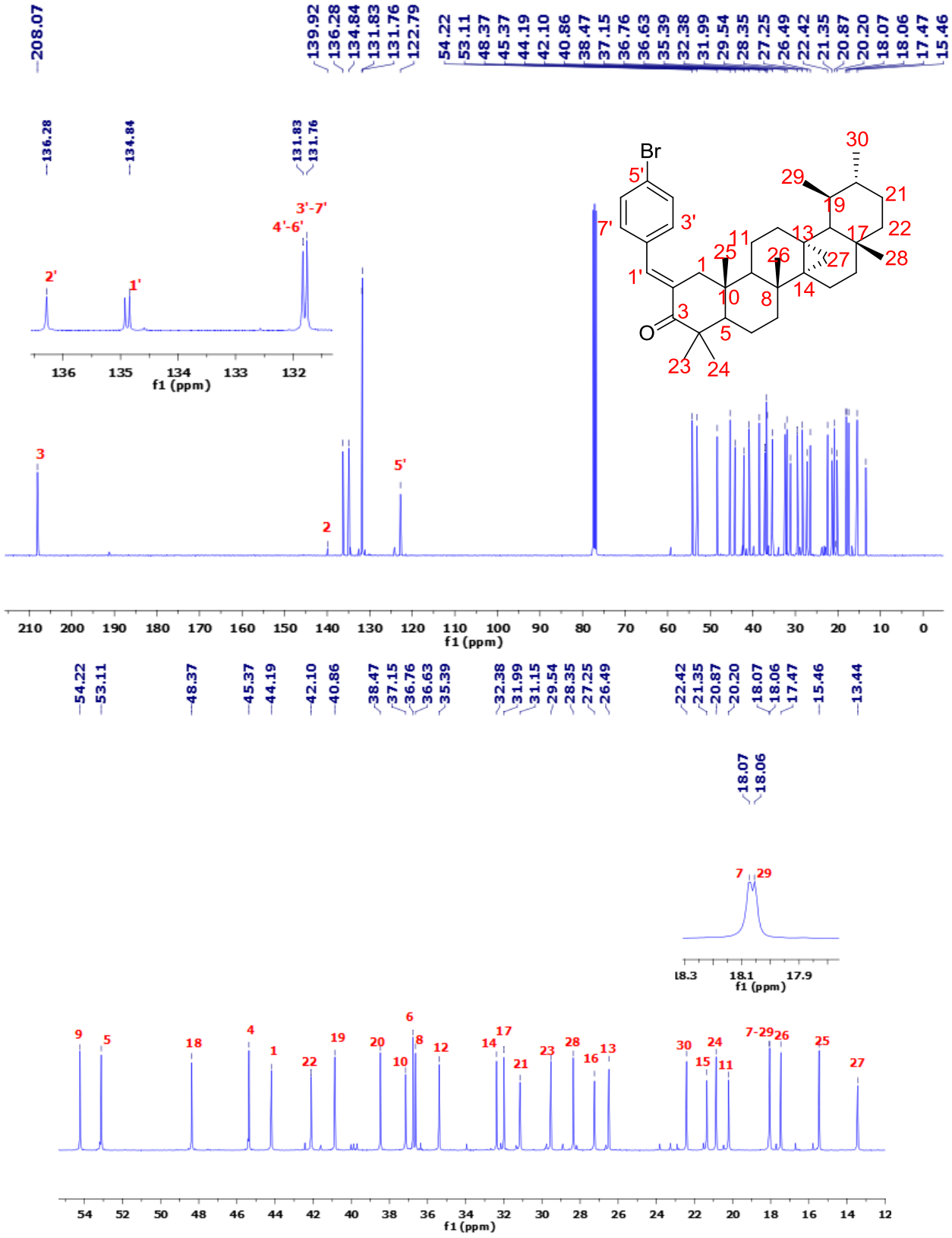


Figure S23. ^{13}C-NMR ($CDCl_3$, 100 MHz) spectrum of **1g**.

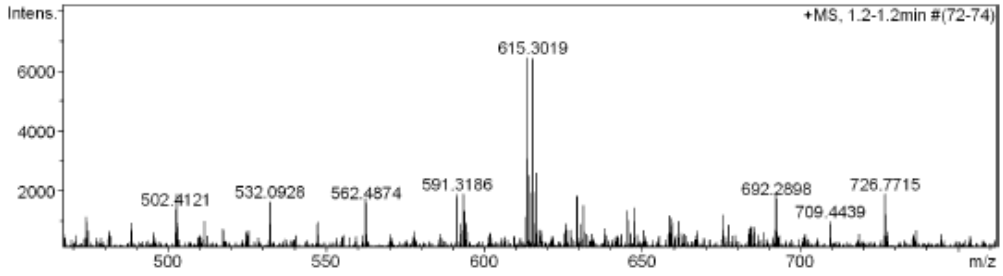
Mass Spectrum List Report

Analysis Info

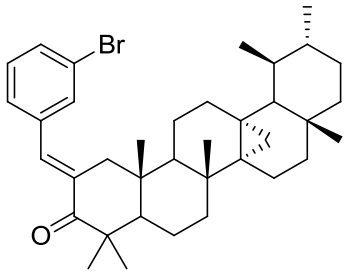
Analysis Name	OSKVN04102019007.d	Acquisition Date	10/4/2019 11:56:24 AM
Method	Tune_low_POS_2019.m	Operator	Administrator
Sample Name	Ph3Br Ph3Br	Instrument	micrOTOF 72

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	50 V
Scan Range	n/a	Capillary Exit	250.0 V	Set Pulsar Pull	337 V
Scan Begin	50 m/z	Hexapole RF	400.0 V	Set Pulsar Push	337 V
Scan End	3000 m/z	Skimmer 1	45.0 V	Set Reflector	1300 V
		Hexapole 1	24.3 V	Set Flight Tube	9000 V
				Set Detector TOF	2295 V



#	m/z	I	I %	S/N	Res.
1	89.2539	2433	37.8	16.3	13765
2	115.4493	2235	34.7	14.9	15033
3	129.7839	2552	39.6	17.1	14564
4	144.9783	2258	35.0	15.1	13888
5	296.8576	2356	36.6	17.4	20012
6	393.2902	1874	29.1	13.9	4247
7	414.2659	2596	40.3	19.2	5417
8	442.2988	4076	63.2	29.9	5118
9	447.3425	3744	58.1	27.4	4823
10	591.3186	1903	29.5	13.2	4964
11	593.3201	1897	29.4	13.2	5002
12	613.3021	6437	99.9	46.5	4780
13	614.3097	2529	39.2	17.9	4797
14	615.3019	6444	100.0	46.6	4743
15	616.3036	2619	40.6	18.5	5104
16	629.2839	1852	28.7	12.9	5142
17	726.7715	1907	29.6	13.6	41163



Chemical Formula: $C_{37}H_{51}BrNaO$ $[M+Na]^+$
Exact Mass: 613.30210

Figure S24. HRESIMS spectrum of **1h**.

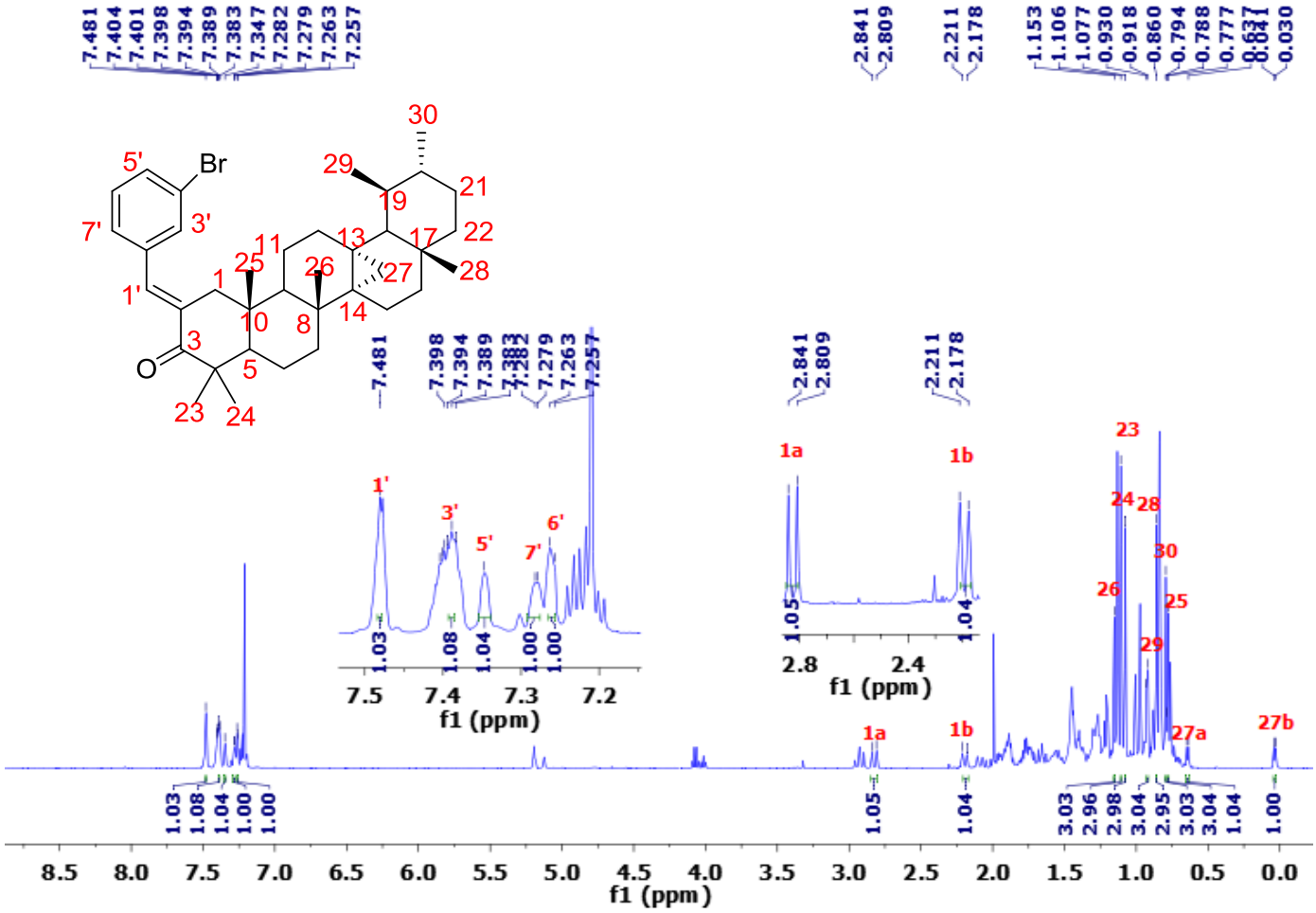


Figure S25. ^{1}H-NMR ($CDCl_3$, 500 MHz) spectrum of **1h**.

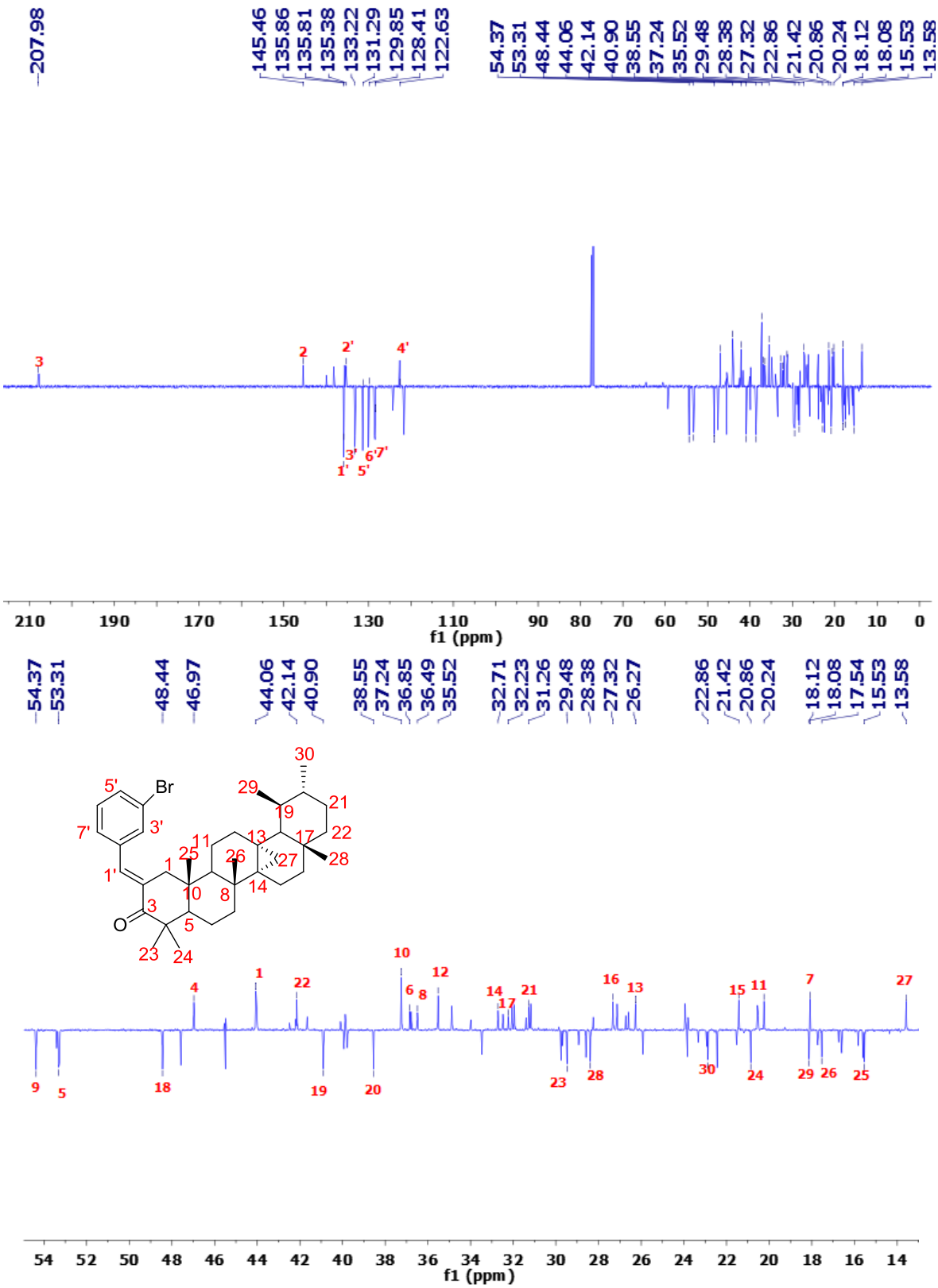


Figure S26. J-mod ($CDCl_3$, 125 MHz) spectrum of **1h**.

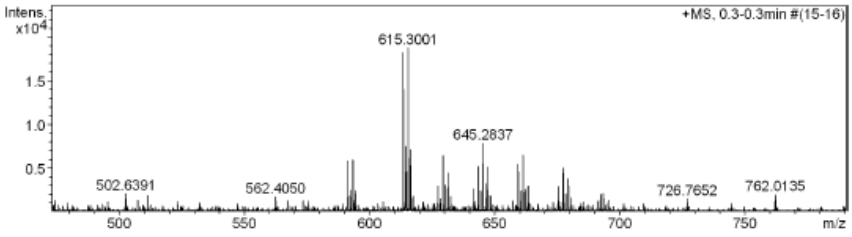
Mass Spectrum List Report

Analysis Info

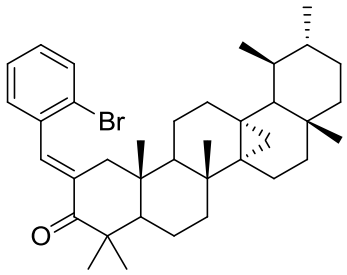
Analysis Name	OSKVN04102019006.d	Acquisition Date	10/4/2019 11:51:43 AM
Method	Tune_low_POS_2019.m	Operator	Administrator
Sample Name	Ph2Br	Instrument	micrOTOF 72
	Ph2Br		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	50 V
Scan Range	n/a	Capillary Exit	250.0 V	Set Pulsar Pull	337 V
Scan Begin	50 m/z	Hexapole RF	400.0 V	Set Pulsar Push	337 V
Scan End	3000 m/z	Skimmer 1	60.0 V	Set Reflector	1300 V
		Hexapole 1	24.3 V	Set Flight Tube	9000 V
				Set Detector TOF	2295 V



#	m/z	I	I %	S/N	Res.
1	296.8552	2637	14.1	18.6	20055
2	393.2946	2971	15.8	20.0	4370
3	413.2646	7987	42.6	53.2	4814
4	442.2994	13410	71.5	86.6	4891
5	447.3433	2995	16.0	18.8	4750
6	591.3175	5869	31.3	34.8	4849
7	592.3217	2513	13.4	14.5	4852
8	593.3194	5949	31.7	35.3	4896
9	613.3023	18192	97.0	110.6	4765
10	614.3046	7504	40.0	45.2	4836
11	615.3001	18753	100.0	114.1	4942
12	616.3050	7158	38.2	43.1	4911
13	627.2794	2982	15.9	17.7	4598
14	629.2851	6485	34.6	39.3	4806
15	630.2863	3121	16.6	18.6	5590
16	631.2895	4484	23.9	27.0	4717
17	641.2647	2651	14.1	15.8	4971



Chemical Formula: $C_{37}H_{51}BrNaO$ $[M+Na]^+$
Exact Mass: 613.30210

Figure S27. HRESIMS spectrum of **1i**.

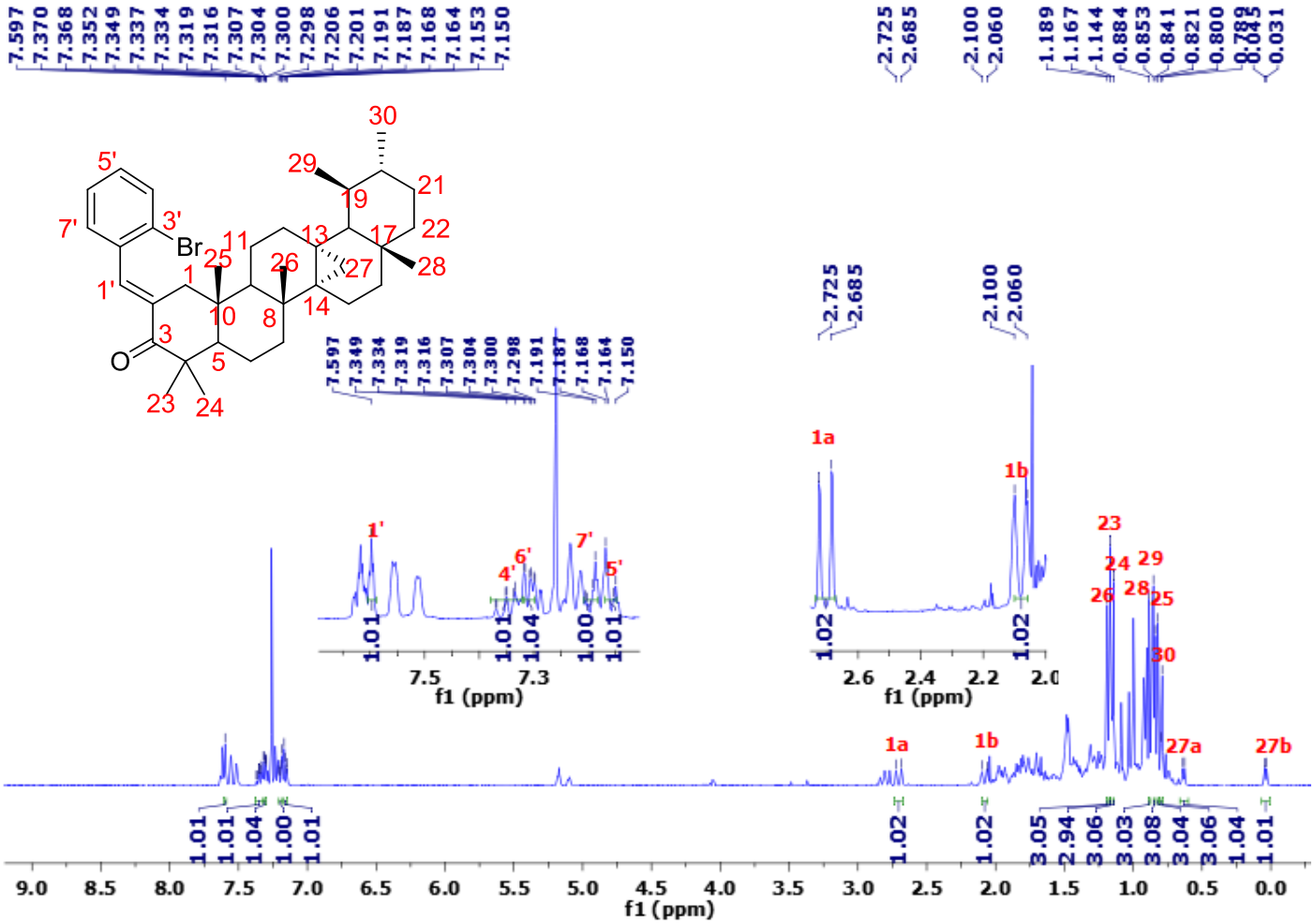


Figure S28. ^{1}H-NMR ($CDCl_3$, 400 MHz) spectrum of **1i**.

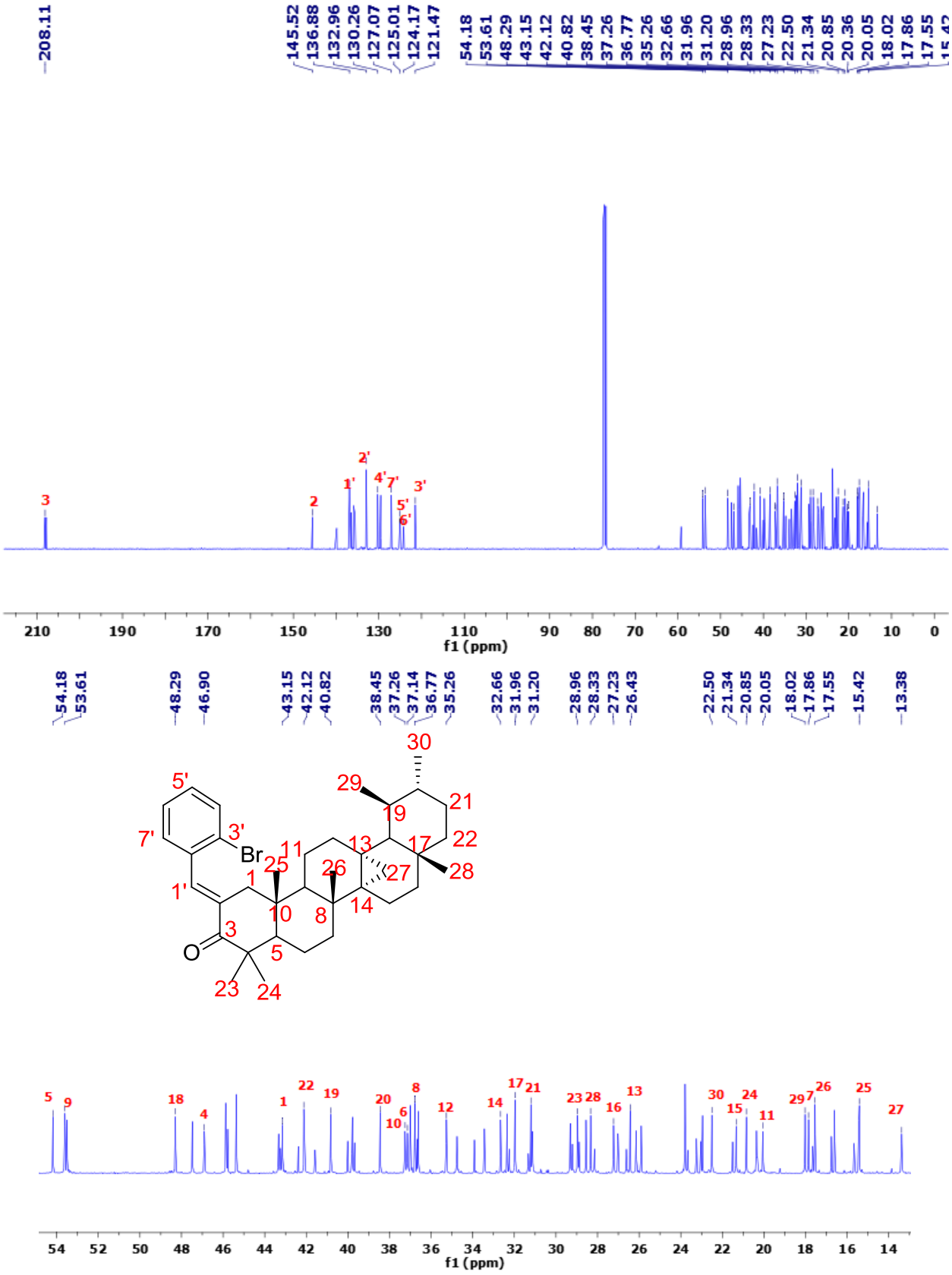


Figure S29. ^{13}C-NMR ($CDCl_3$, 100 MHz) spectrum of **1i**.

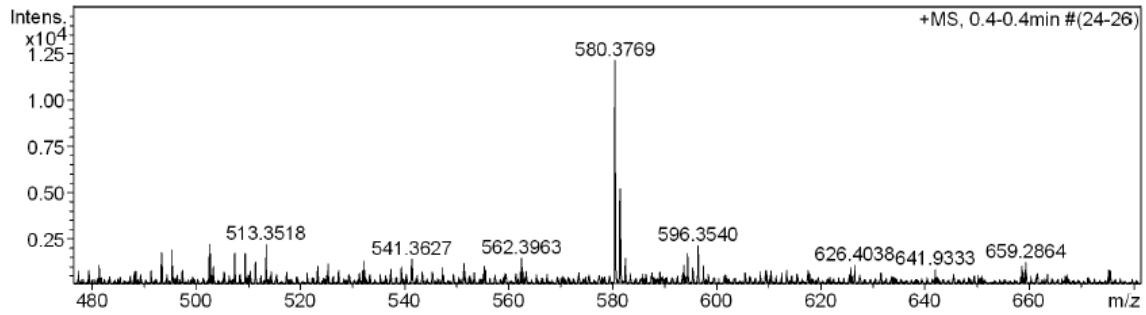
Mass Spectrum List Report

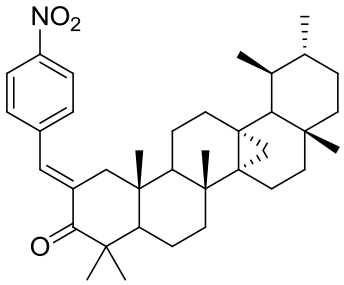
Analysis Info

Analysis Name	OSKVN04102019009_1.d	Acquisition Date	10/4/2019 12:04:42 PM
Method	Tune_low_POS_2019.m	Operator	Administrator
Sample Name	P4N	Instrument	micrOTOF 72
	P4N		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	50 V
Scan Range	n/a	Capillary Exit	280.0 V	Set Pulsar Pull	337 V
Scan Begin	50 m/z	Hexapole RF	400.0 V	Set Pulsar Push	337 V
Scan End	3000 m/z	Skimmer 1	45.0 V	Set Reflector	1300 V
		Hexapole 1	24.3 V	Set Flight Tube	9000 V
				Set Detector TOF	2295 V





Chemical Formula: $C_{37}H_{51}NNaO_3$ $[M+Na]^+$
Exact Mass: 580.37666

Figure S30. HRESIMS spectrum of **1j**.

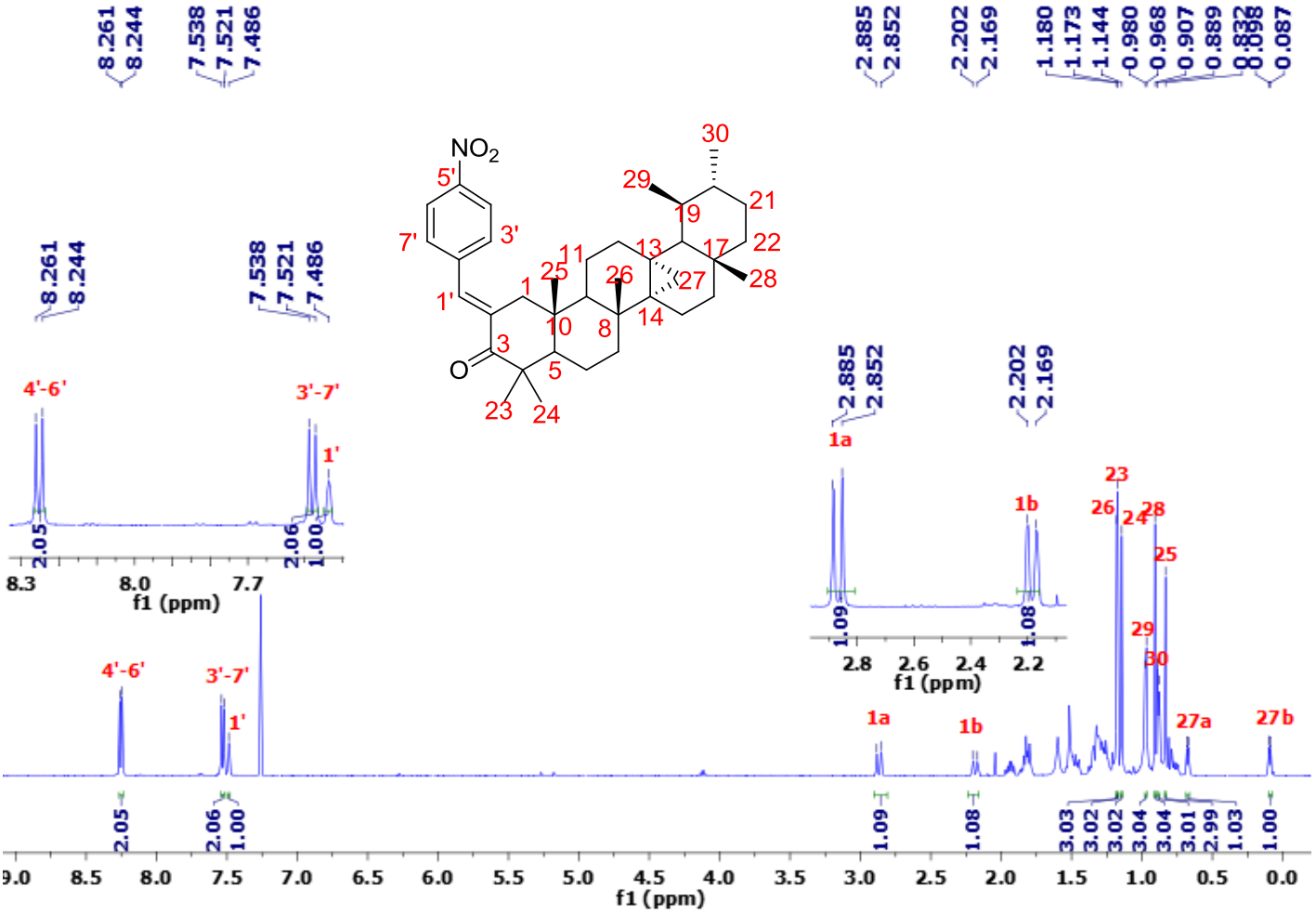


Figure S31. ^{1}H-NMR ($CDCl_3$, 500 MHz) spectrum of **1j**.

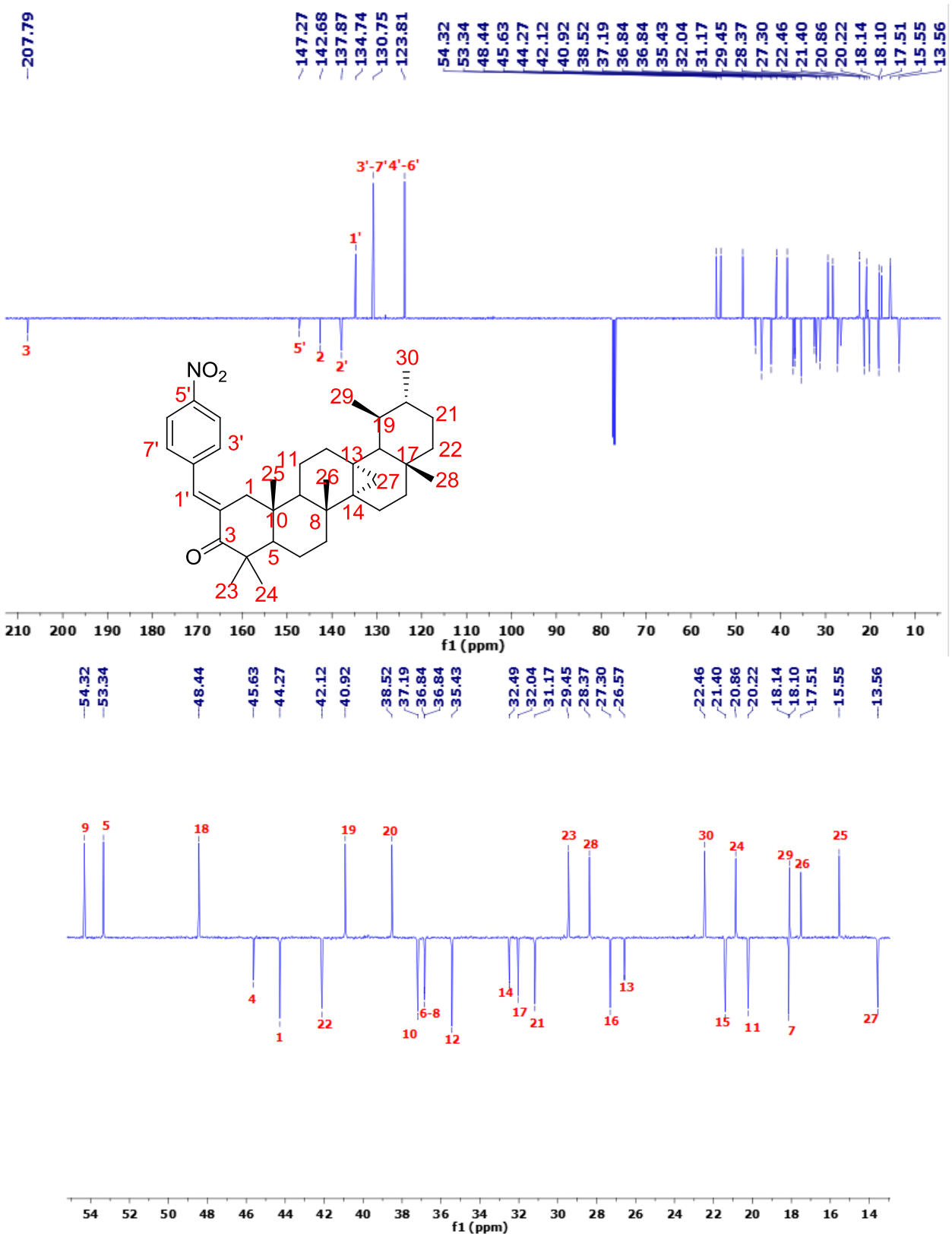


Figure S32. J-mod ($CDCl_3$, 125 MHz) spectrum of **1j**.

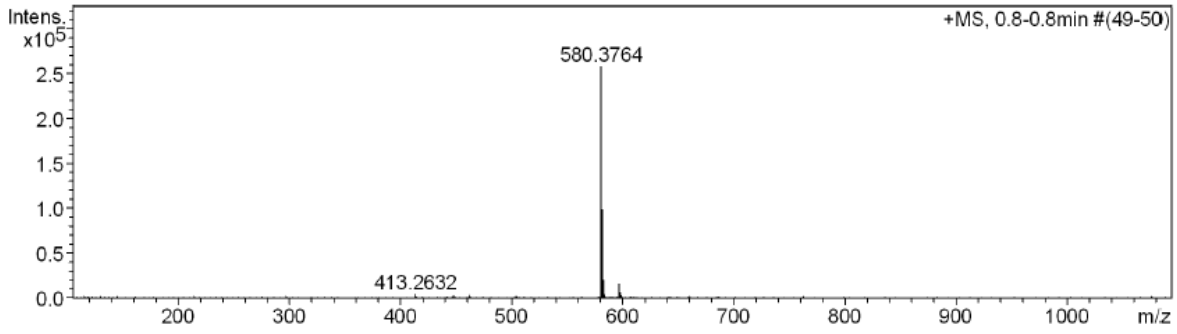
Mass Spectrum List Report

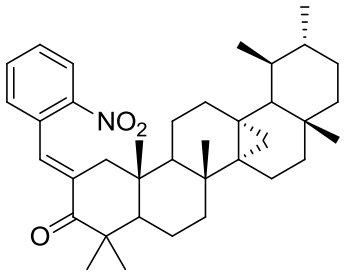
Analysis Info

Analysis Name	OSKVN04102019010.d	Acquisition Date	10/4/2019 12:07:46 PM
Method	Tune_low_POS_2019.m	Operator	Administrator
Sample Name	P2N	Instrument	micrOTOF 72
	P2N		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	50 V
Scan Range	n/a	Capillary Exit	280.0 V	Set Pulsar Pull	337 V
Scan Begin	50 m/z	Hexapole RF	400.0 V	Set Pulsar Push	337 V
Scan End	3000 m/z	Skimmer 1	45.0 V	Set Reflector	1300 V
		Hexapole 1	24.3 V	Set Flight Tube	9000 V
				Set Detector TOF	2295 V





Chemical Formula: $C_{37}H_{51}NNaO_3$ $[M+Na]^+$
Exact Mass: 580.37666

Figure S33. HRESIMS spectrum of **1k**.

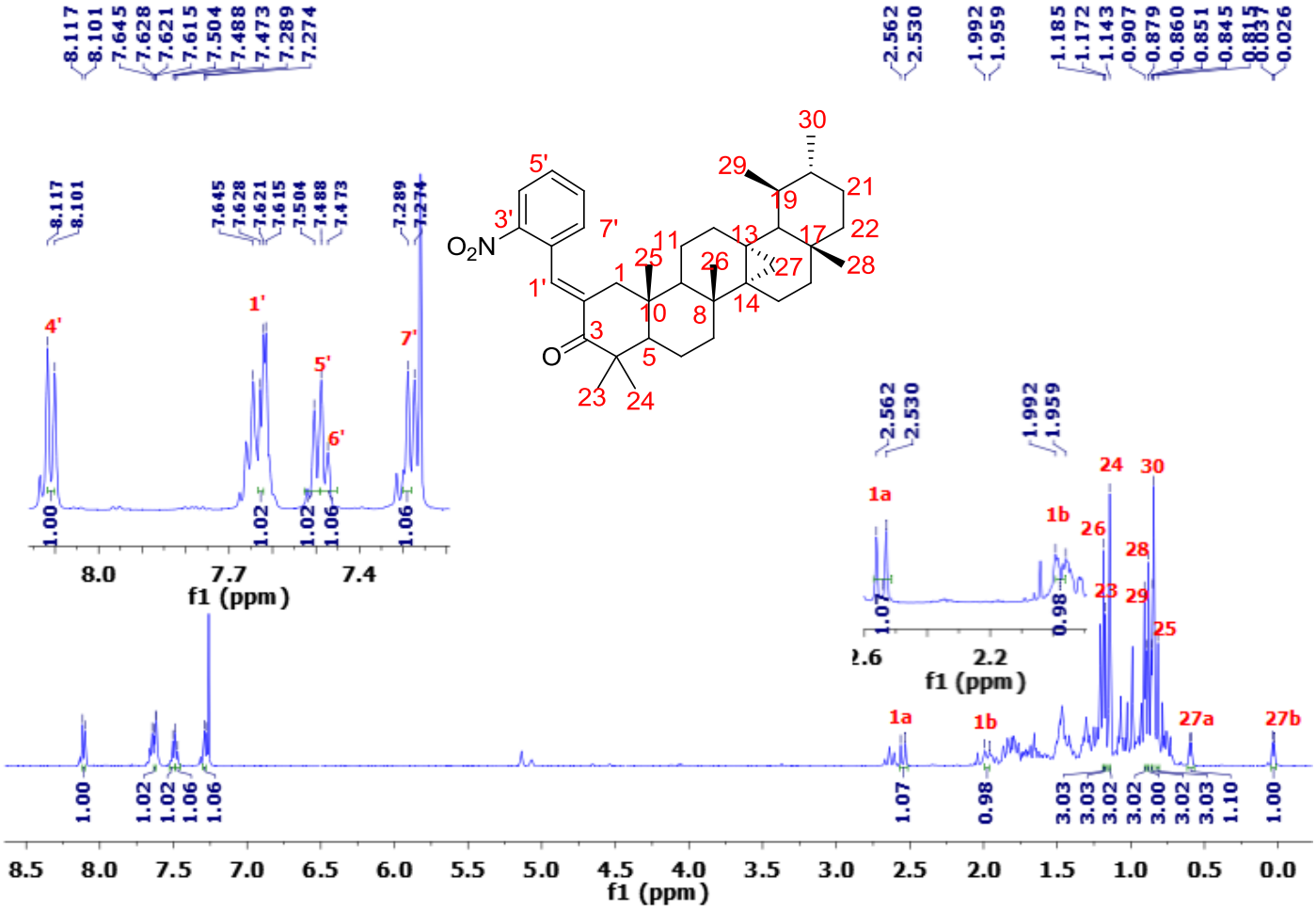


Figure S34. ^{1}H-NMR ($CDCl_3$, 500 MHz) spectrum of **1k**.

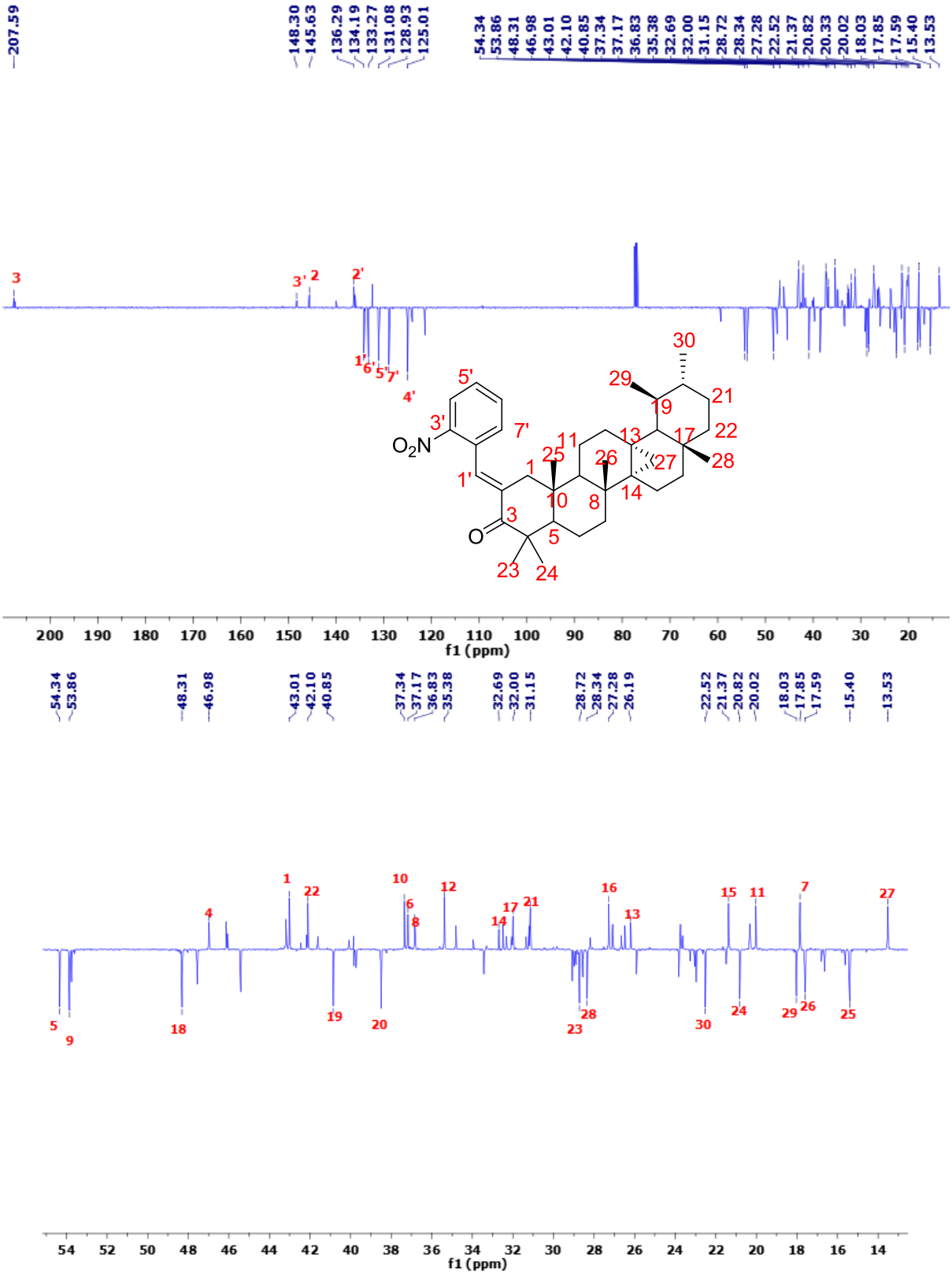


Figure S35. J-mod ($CDCl_3$, 125 MHz) spectrum of **1k**.

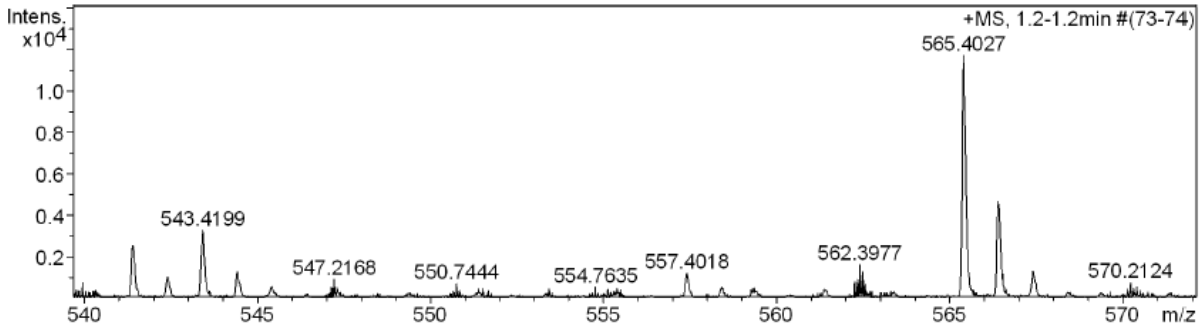
Mass Spectrum List Report

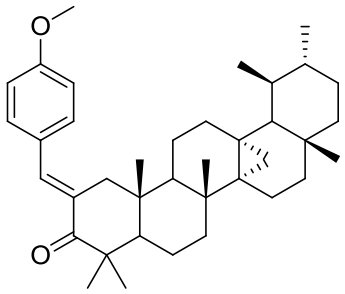
Analysis Info

Analysis Name	OSKVN04102019011.d	Acquisition Date	10/4/2019 12:11:49 PM
Method	Tune_low_POS_2019.m	Operator	Administrator
Sample Name	P4OMe	Instrument	micrOTOF 72
	P4OMe		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	50 V
Scan Range	n/a	Capillary Exit	180.0 V	Set Pulsar Pull	337 V
Scan Begin	50 m/z	Hexapole RF	400.0 V	Set Pulsar Push	337 V
Scan End	3000 m/z	Skimmer 1	45.0 V	Set Reflector	1300 V
		Hexapole 1	24.3 V	Set Flight Tube	9000 V
				Set Detector TOF	2295 V





Chemical Formula: $C_{38}H_{54}NaO_2$ $[M+Na]^+$
Exact Mass: 565.40215

Figure S36. HRESIMS spectrum of **1l**.

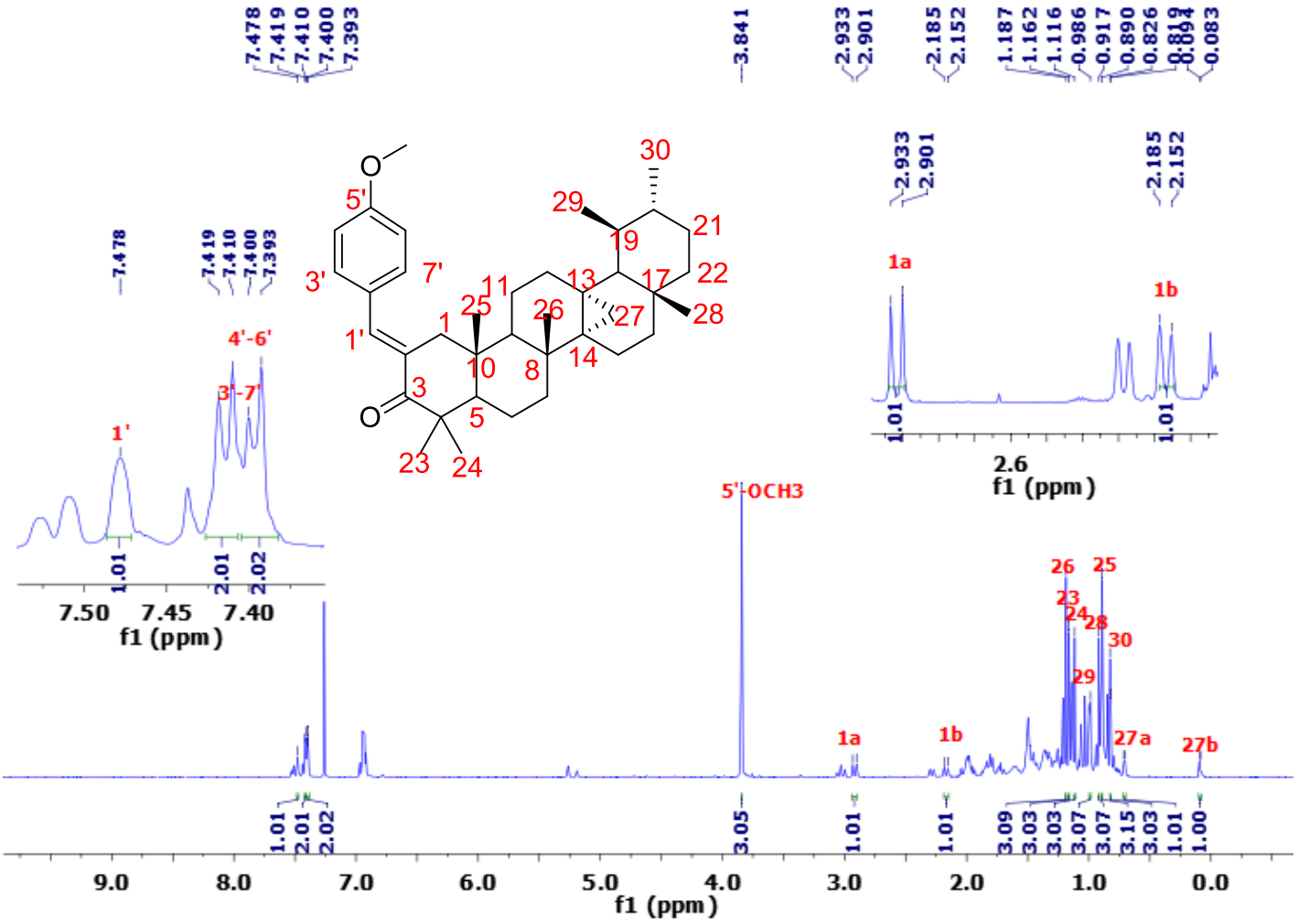


Figure S37. ^{1}H-NMR ($CDCl_3$, 500 MHz) spectrum of **1l**.

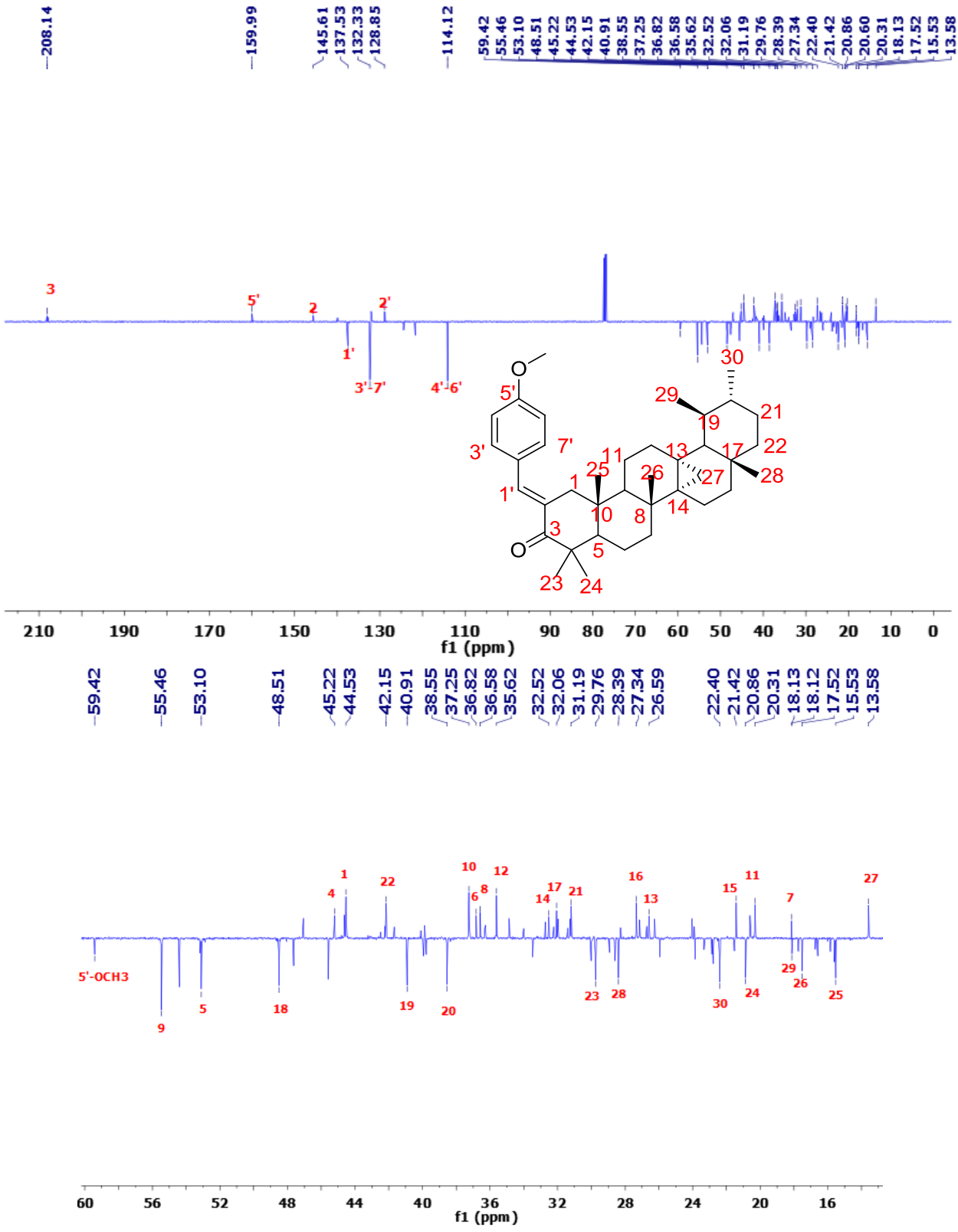


Figure S38. J-mod ($CDCl_3$, 125 MHz) spectrum of **1l**.

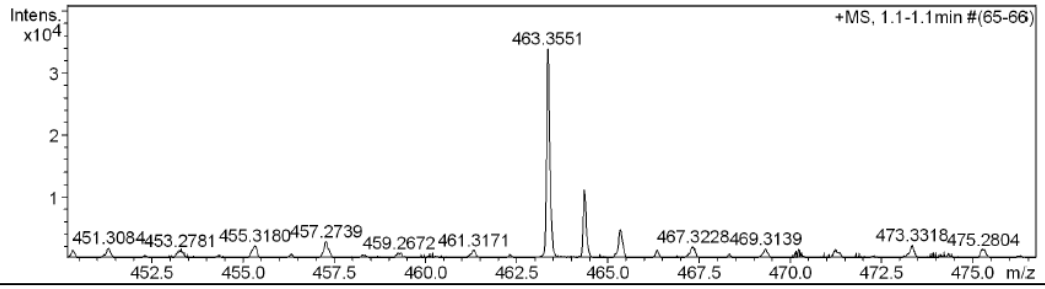
Mass Spectrum List Report

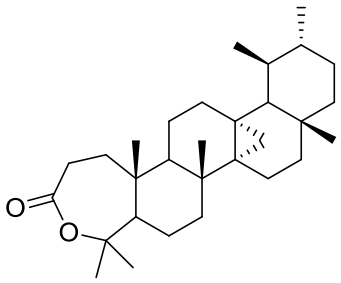
Analysis Info

Analysis Name	OSKVN04102019016.d	Acquisition Date	10/4/2019 12:27:29 PM
Method	Tune_low_POS_2019.m	Operator	Administrator
Sample Name	Trang Truong (TT) LU8	Instrument	micrOTOF 72

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	50 V
Scan Range	n/a	Capillary Exit	250.0 V	Set Pulsar Pull	337 V
Scan Begin	50 m/z	Hexapole RF	400.0 V	Set Pulsar Push	337 V
Scan End	3000 m/z	Skimmer 1	45.0 V	Set Reflector	1300 V
		Hexapole 1	24.3 V	Set Flight Tube	9000 V
				Set Detector TOF	2295 V





Chemical Formula: $C_{30}H_{48}NaO_2$ $[M+Na]^+$
Exact Mass: 463.35520

Figure S39. HRESIMS spectrum of **2**.

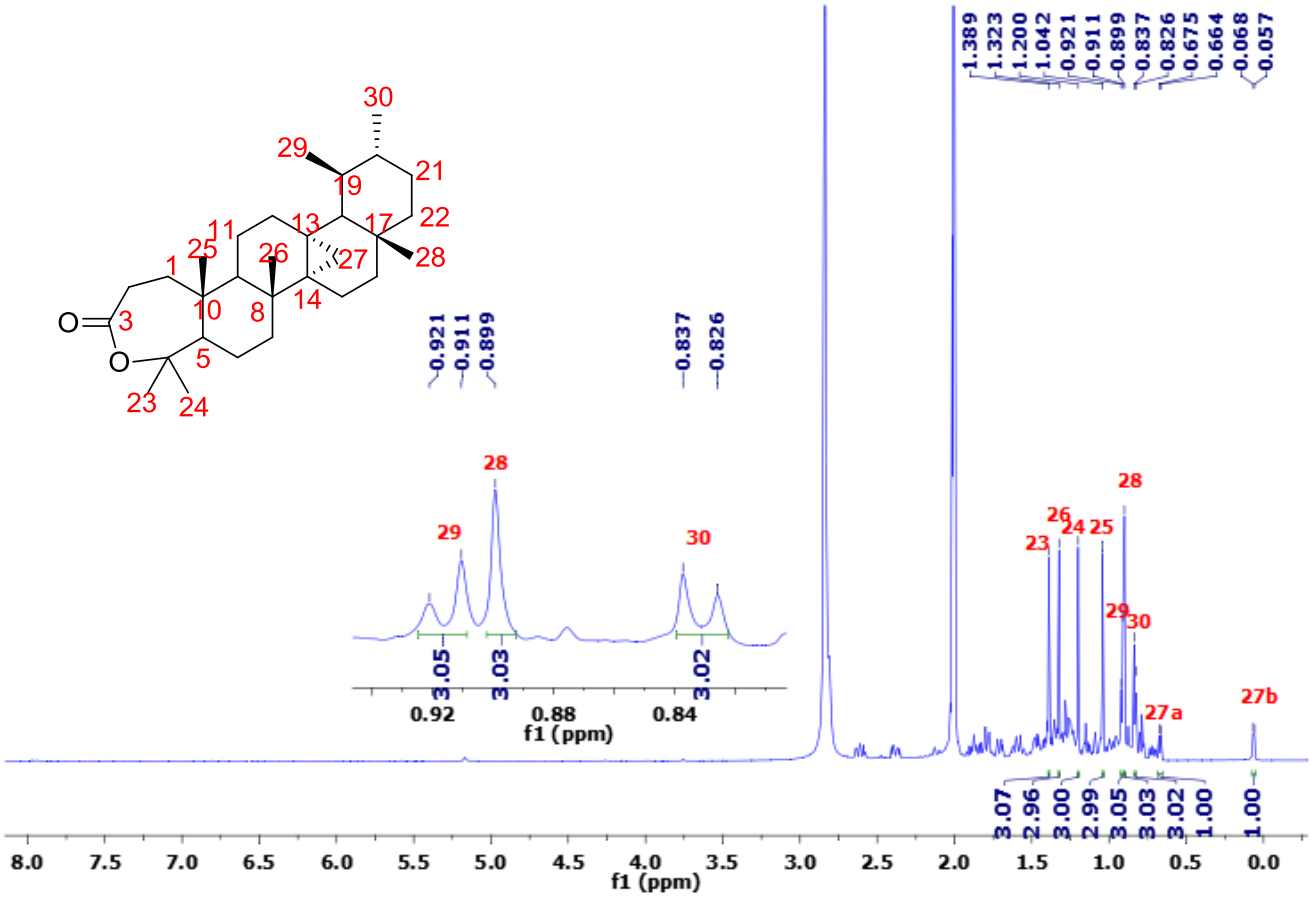


Figure S40. ^{1}H-NMR (Acetone-d_6, 500 MHz) spectrum of **2**.

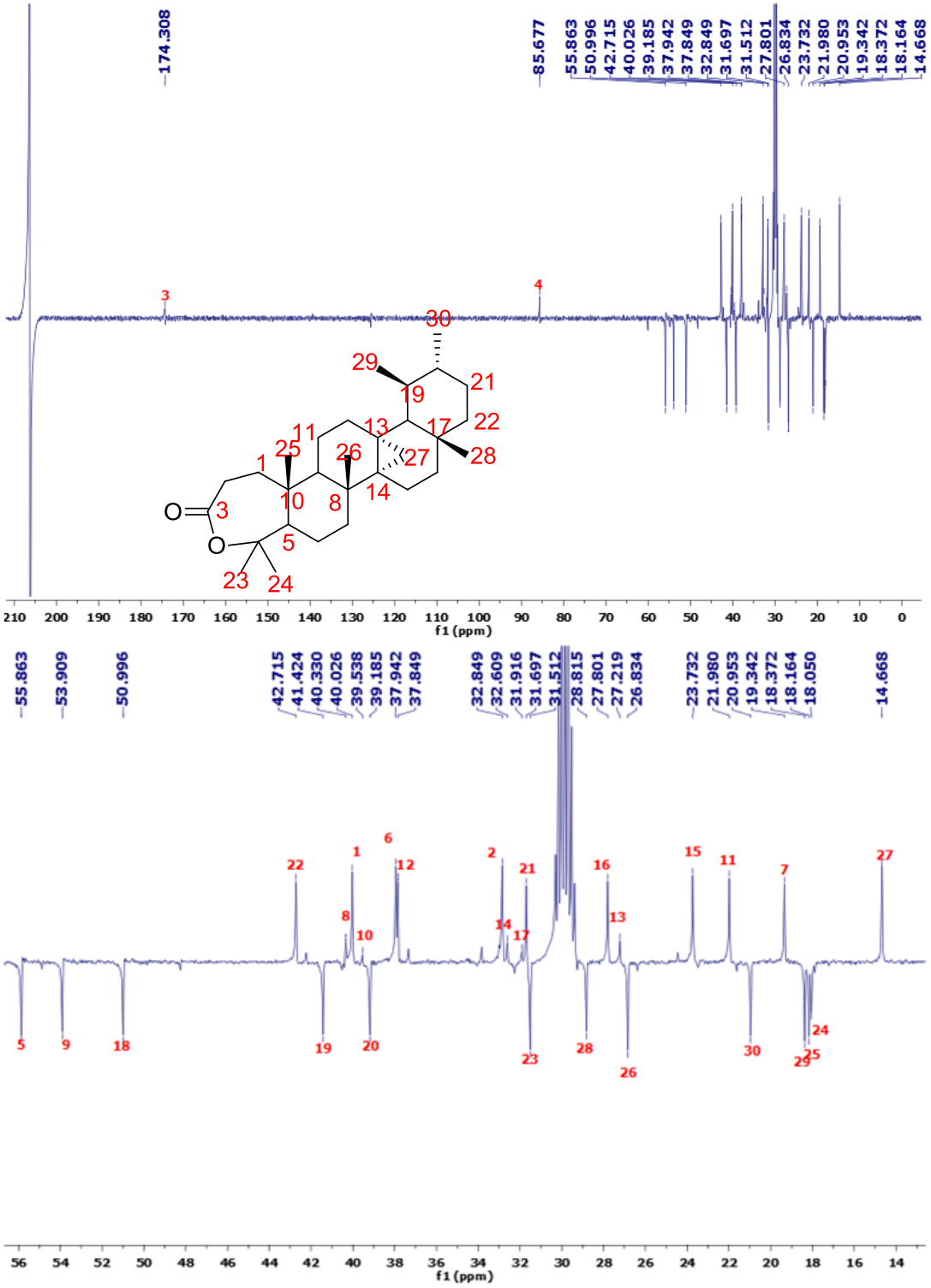
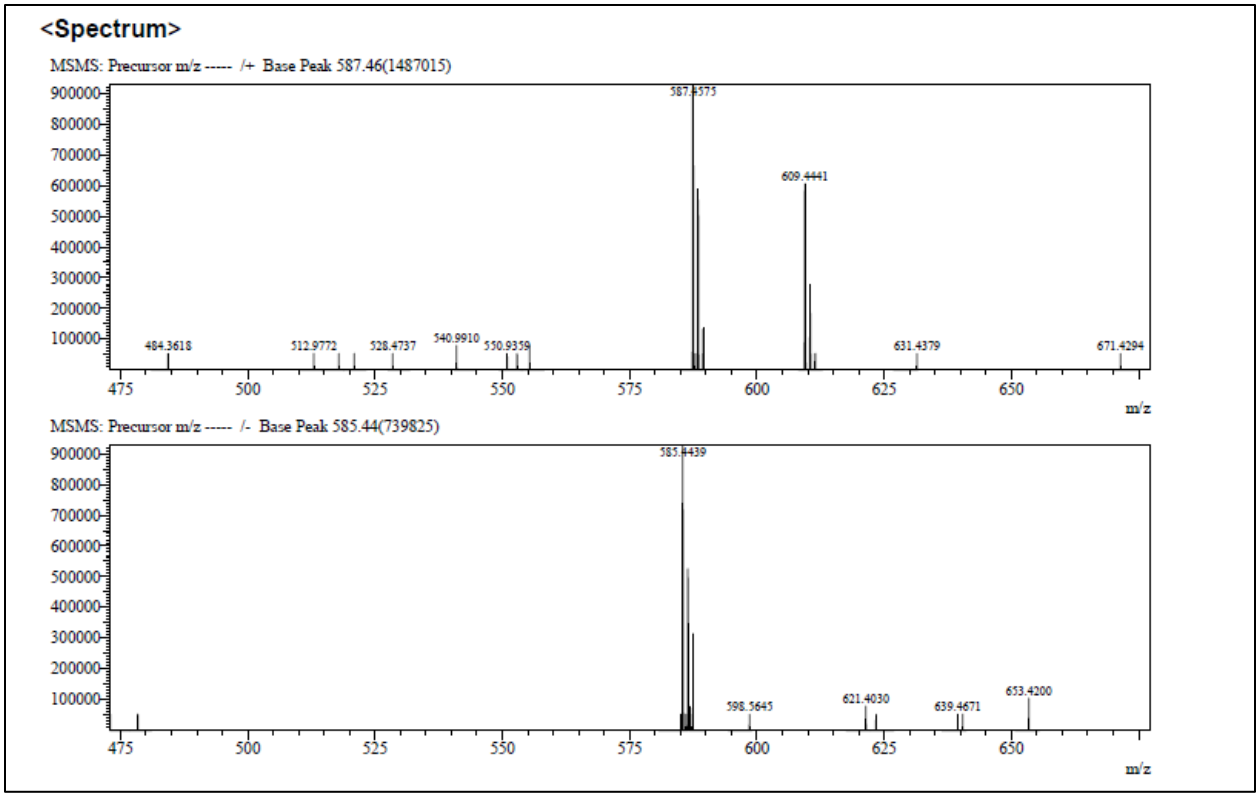
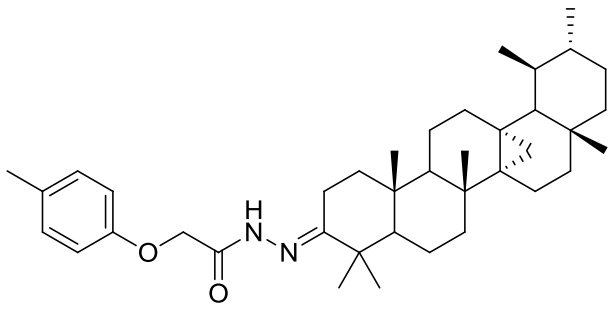


Figure S41. J-mod (Acetone-d_6, 125 MHz) spectrum of **2**.





Chemical Formula: $C_{39}H_{59}N_2O_2$ $[M+H]^+$
Exact Mass: 587.45765

Figure S42. HRESIMS spectrum of **3a**.

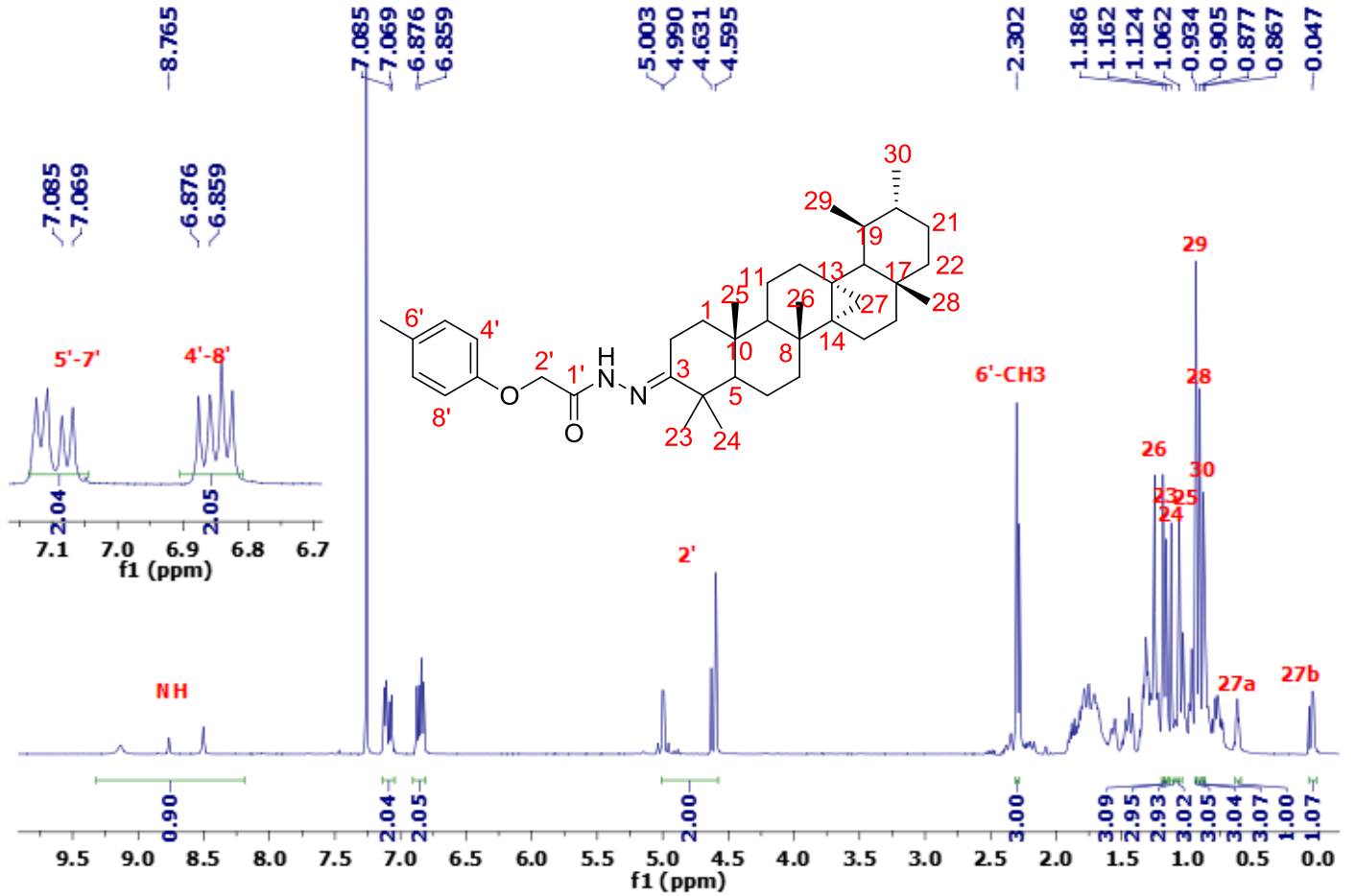


Figure S43. ^{1}H-NMR ($CDCl_3$, 500 MHz) spectrum of **3a**.

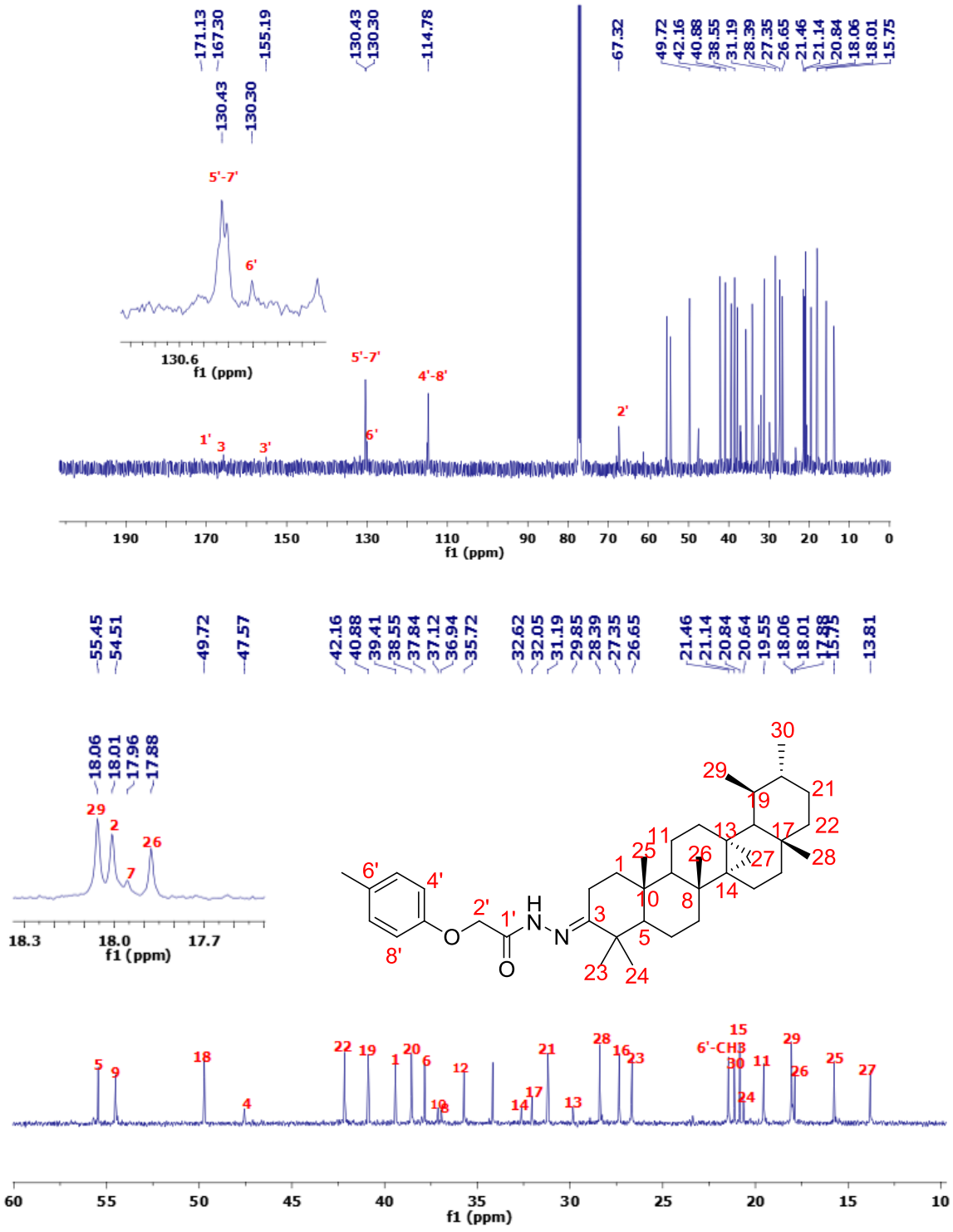


Figure S44. ^{13}C-NMR ($CDCl_3$, 125 MHz) spectrum of **3a**.

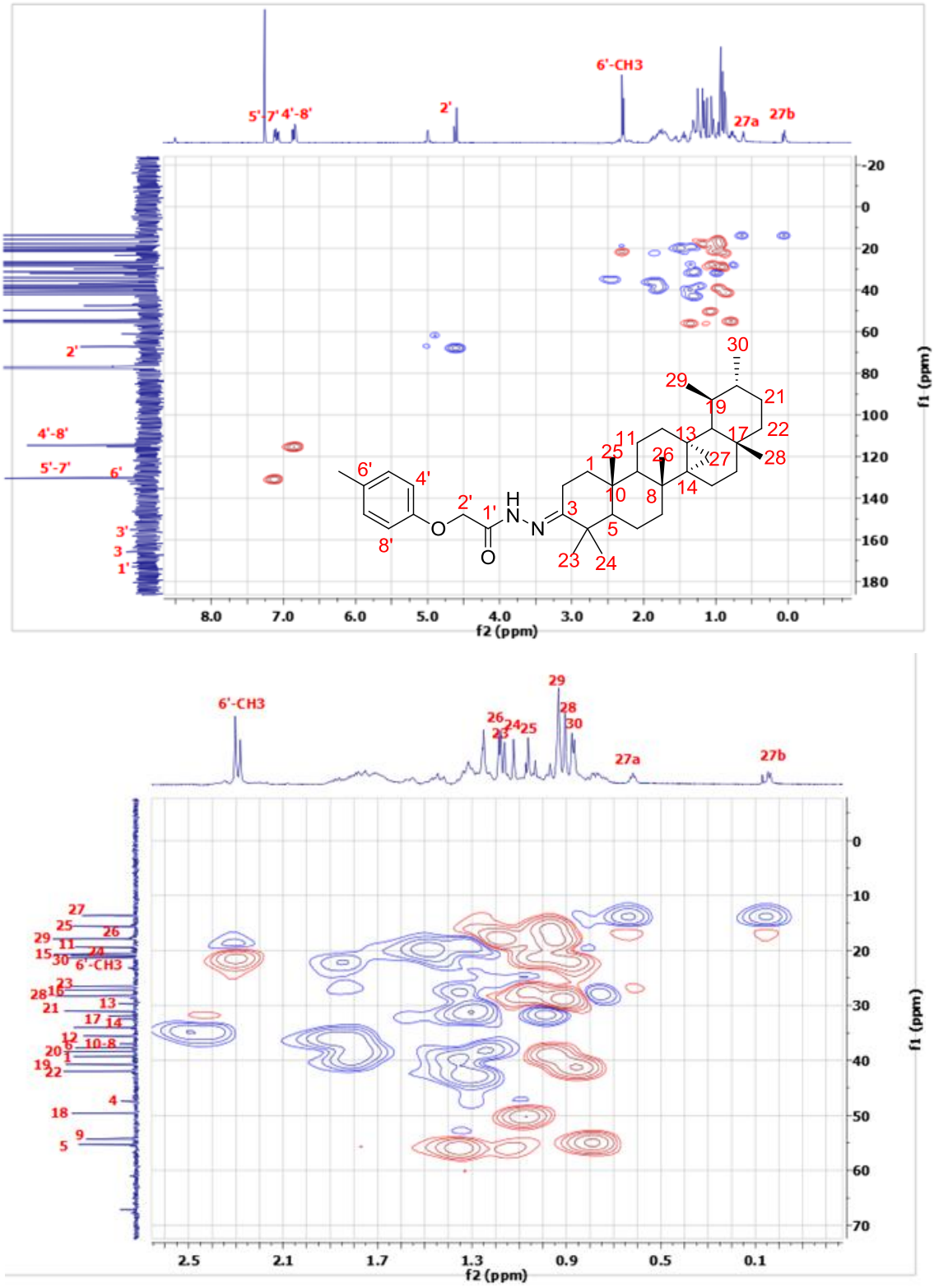


Figure S45. HSQC ($CDCl_3$) spectrum of **3a**.

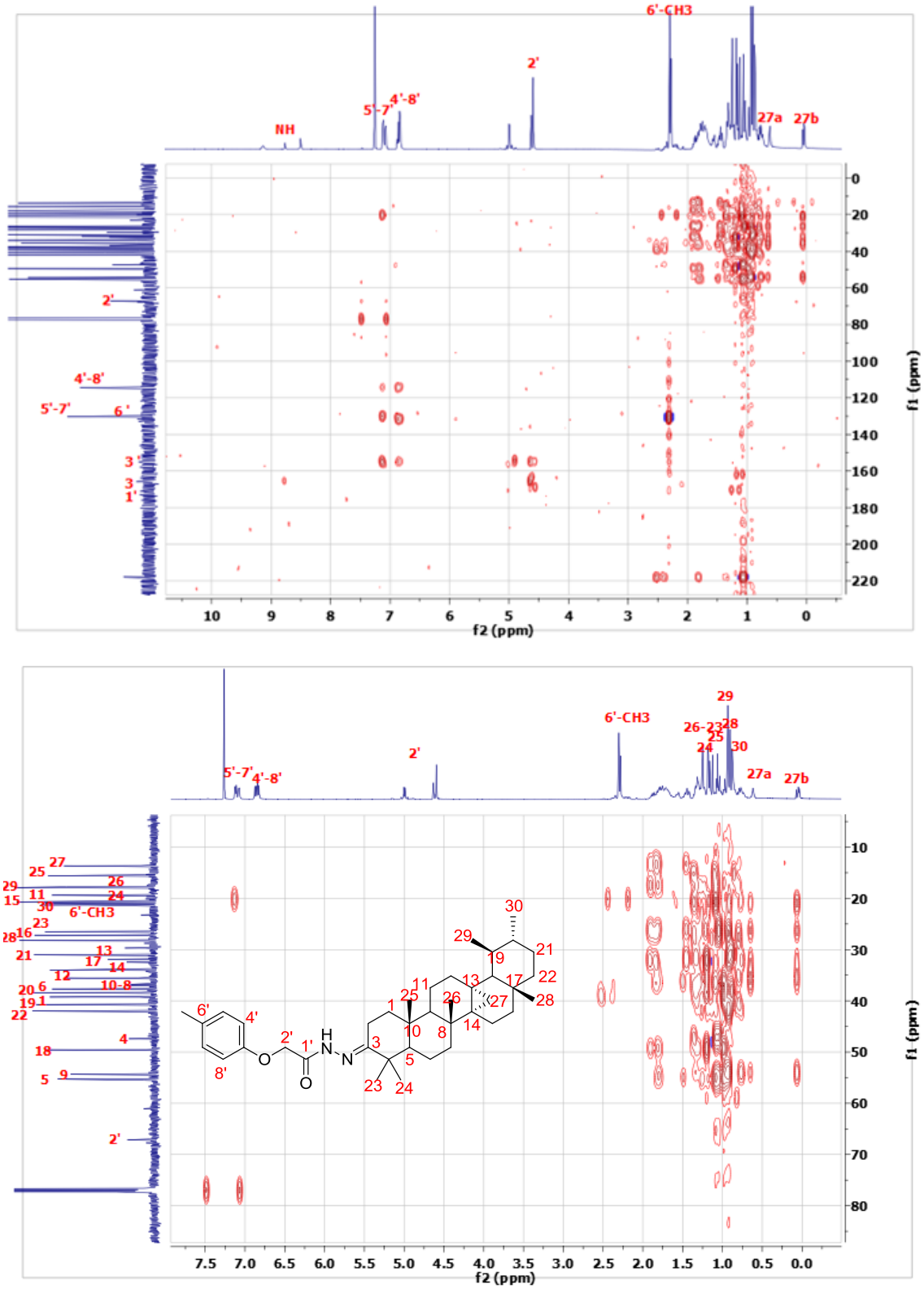
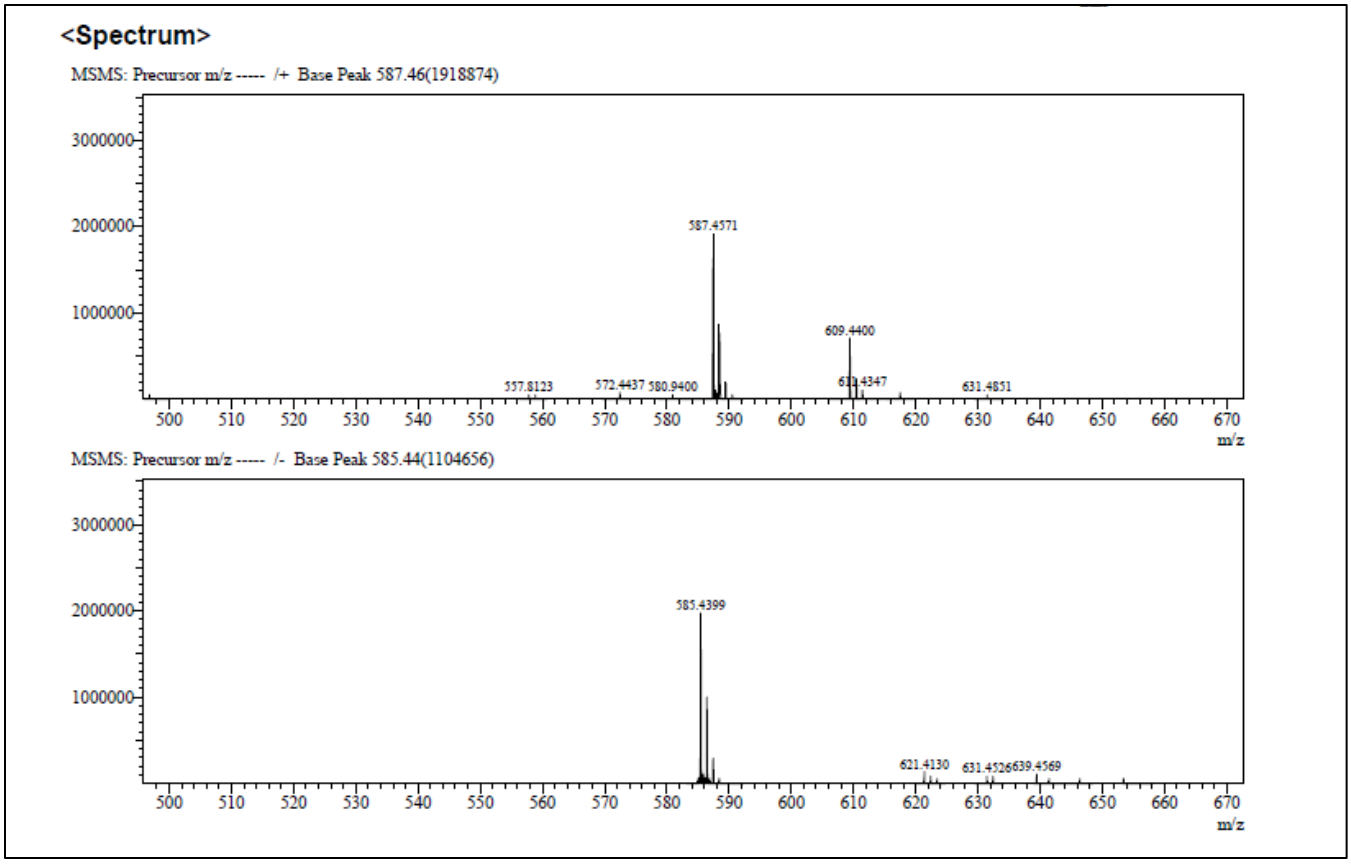
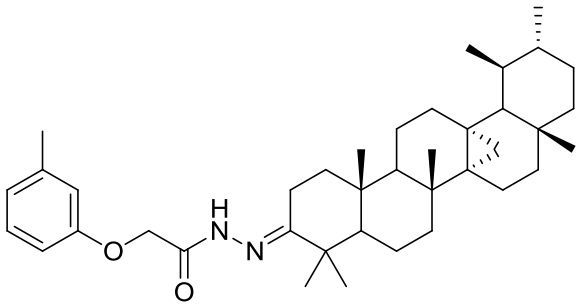


Figure S46. HMBC ($CDCl_3$) spectrum of **3a**.





Chemical Formula: $C_{39}H_{59}N_2O_2$ $[M+H]^+$
Exact Mass: 587.45765

Figure S47. HRESIMS spectrum of **3b**.

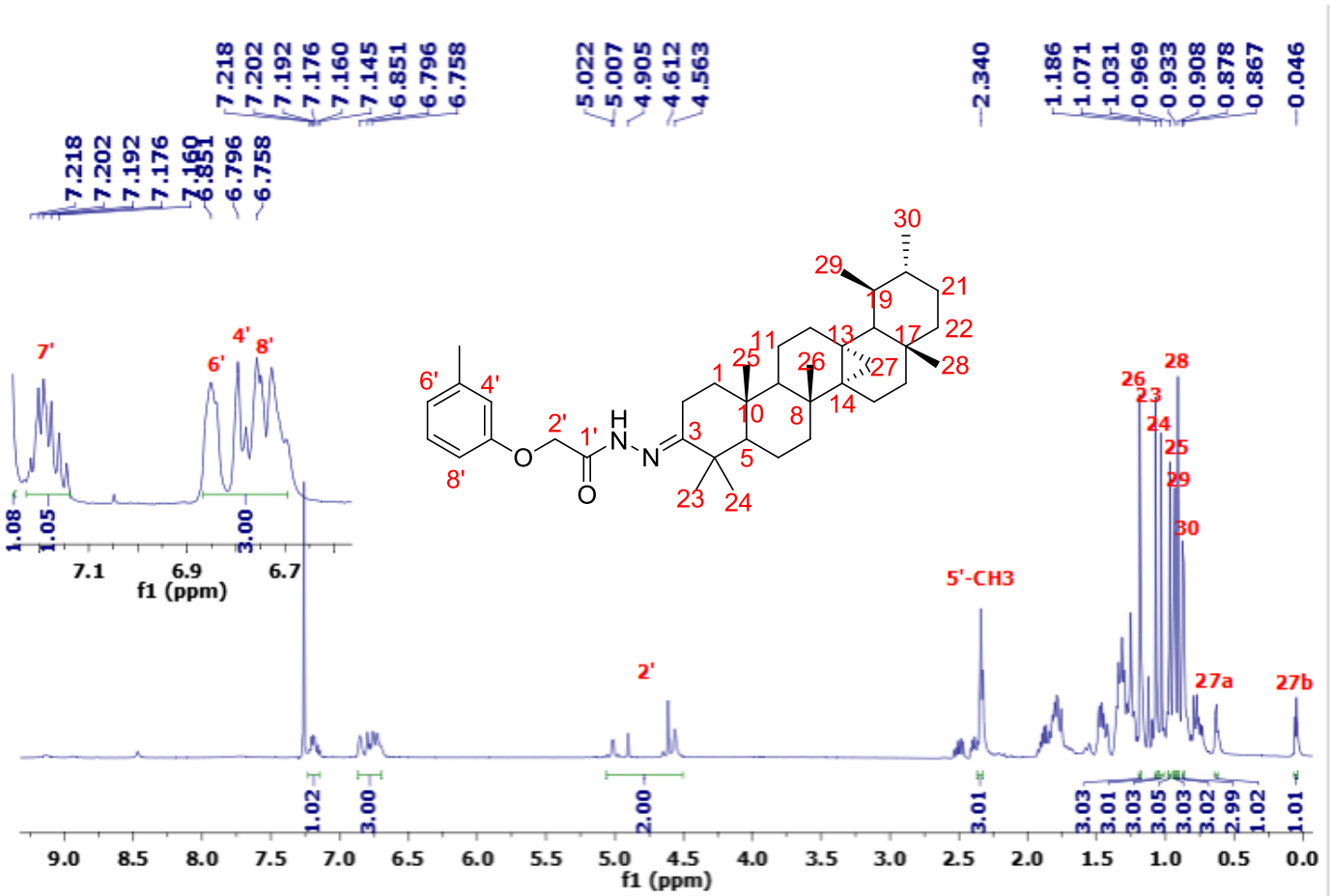


Figure S48. ^{1}H-NMR ($CDCl_3$, 500 MHz) spectrum of **3b**.

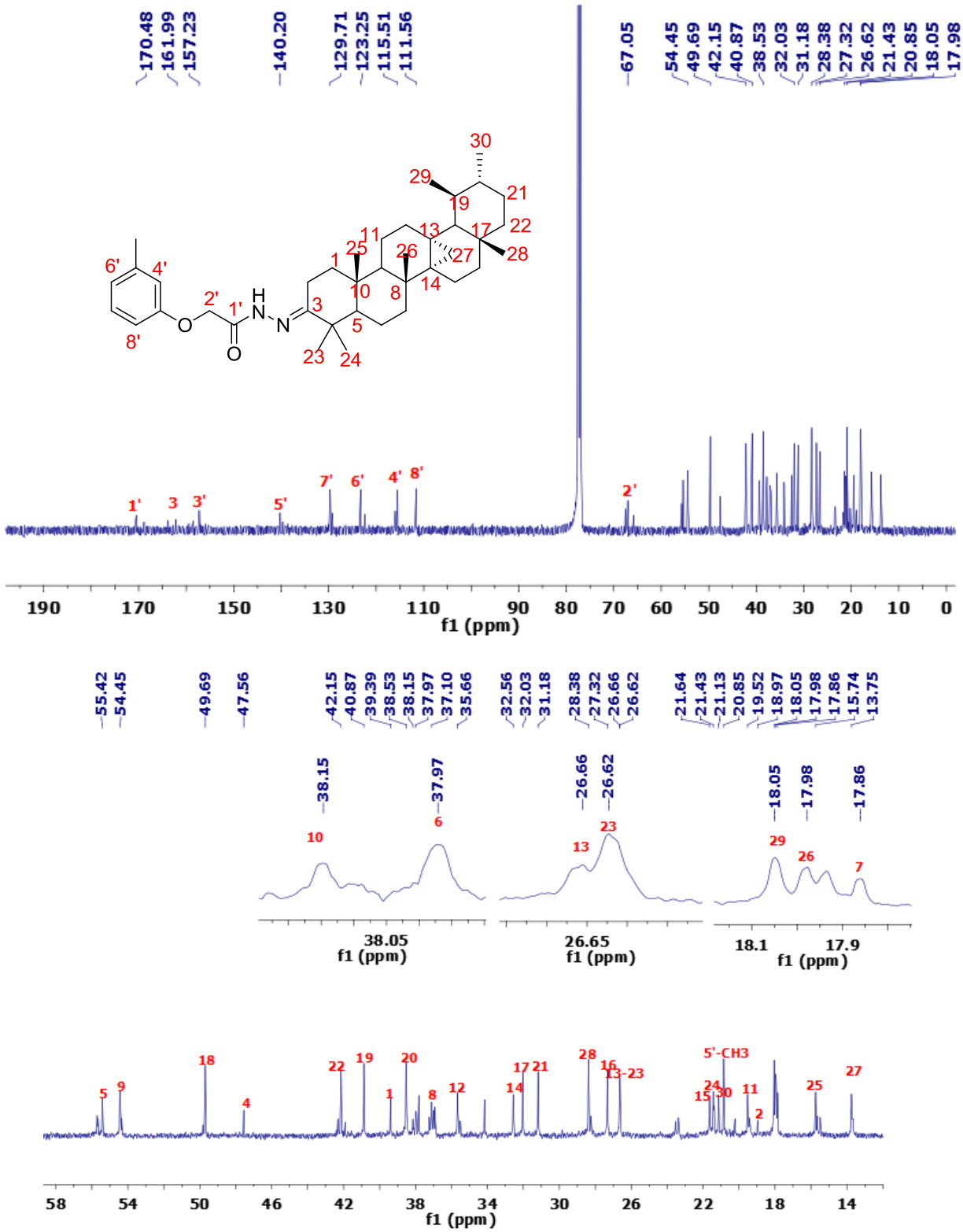


Figure S49. ^{13}C-NMR ($CDCl_3$, 125 MHz) spectrum of **3b**.

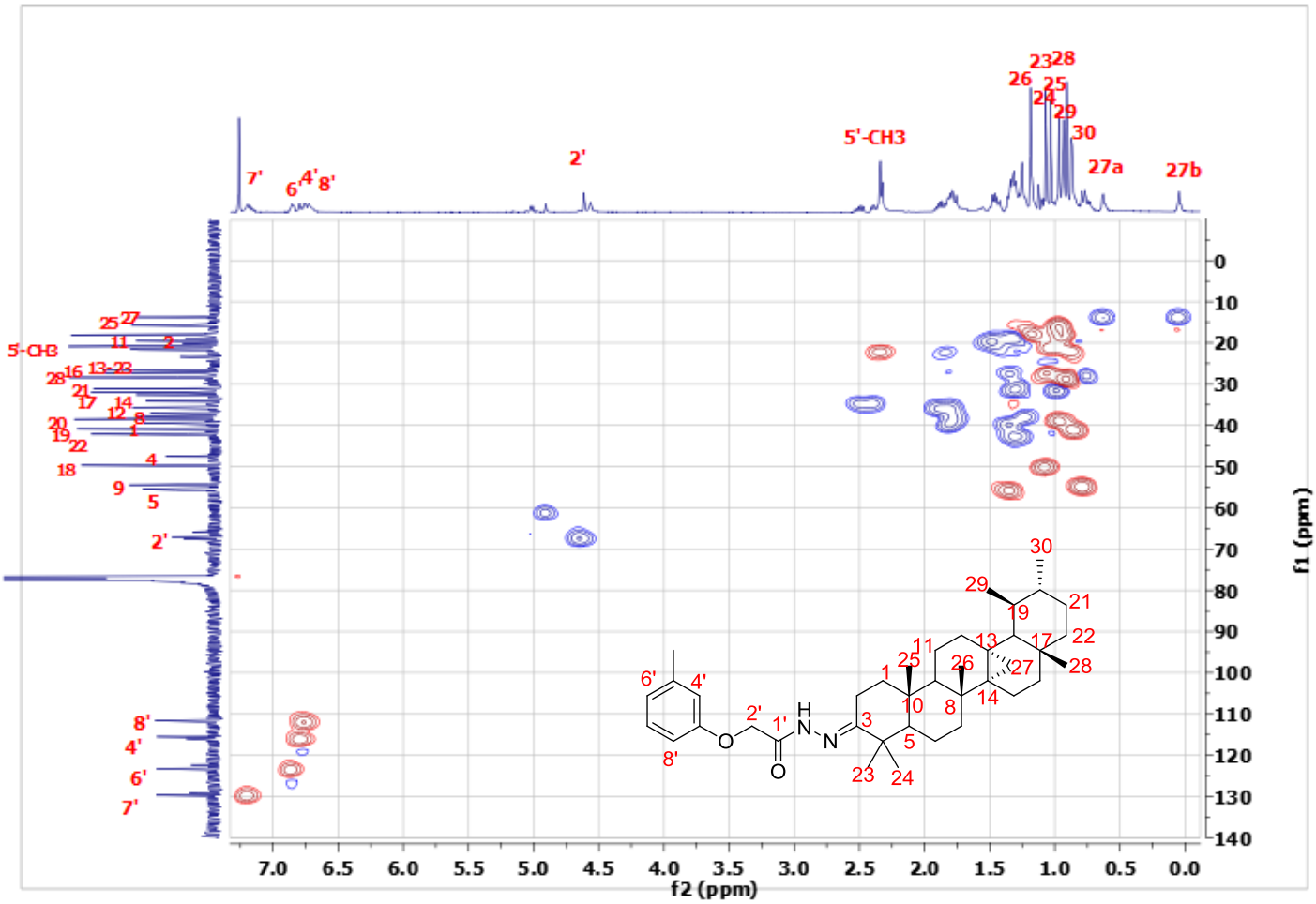


Figure S50. HSQC ($CDCl_3$) spectrum of **3b**.

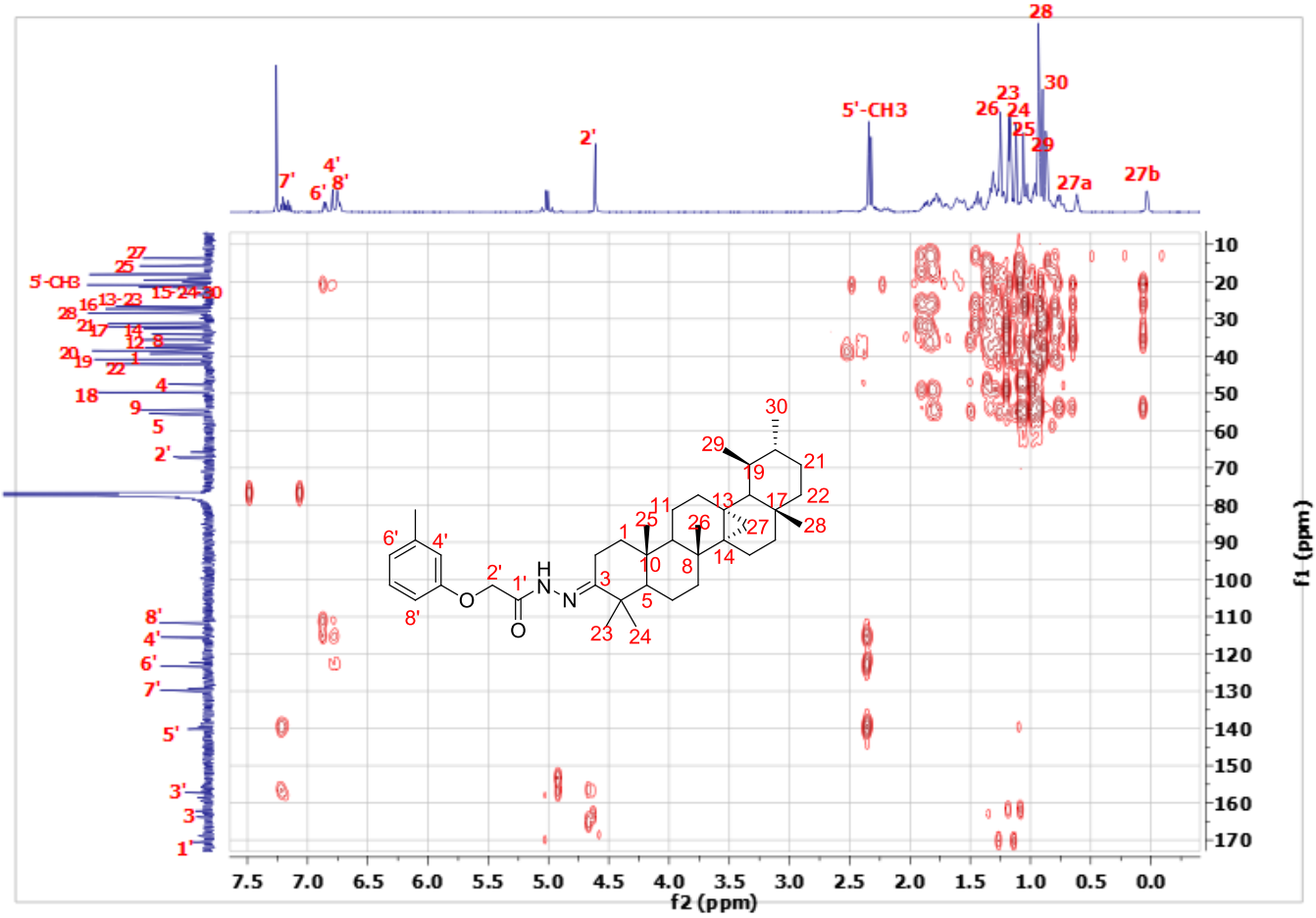
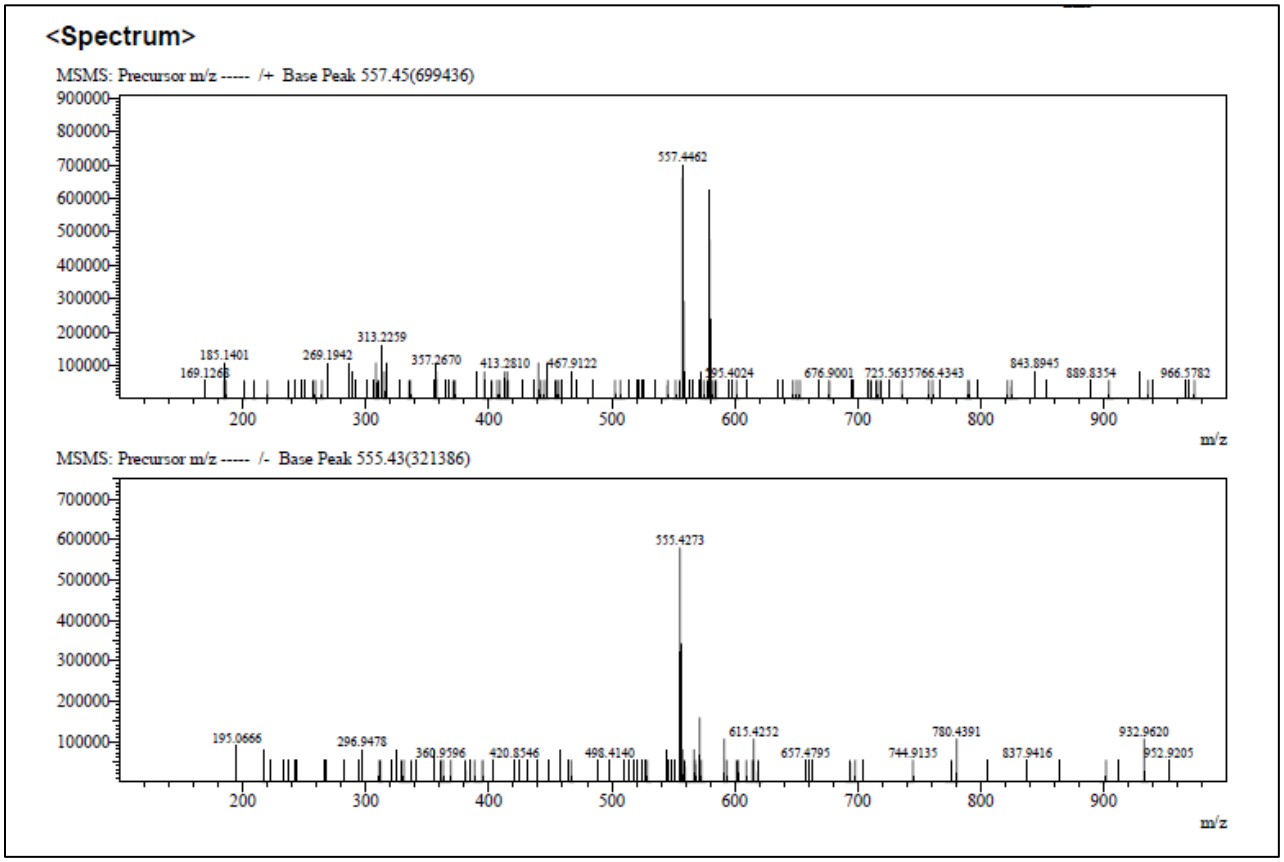
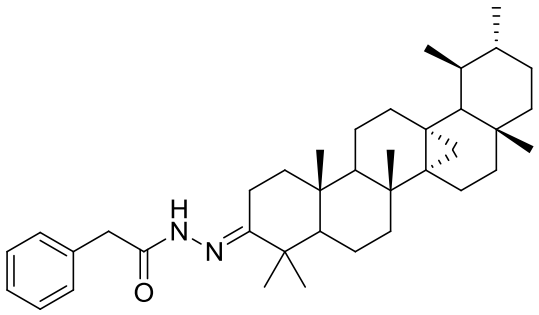


Figure S51. HMBC ($CDCl_3$) spectrum of **3b**.





Chemical Formula: $C_{38}H_{57}N_2O$ $[M+H]^+$
Exact Mass: 557.44709

Figure S52. HRESIMS spectrum of **3c**.

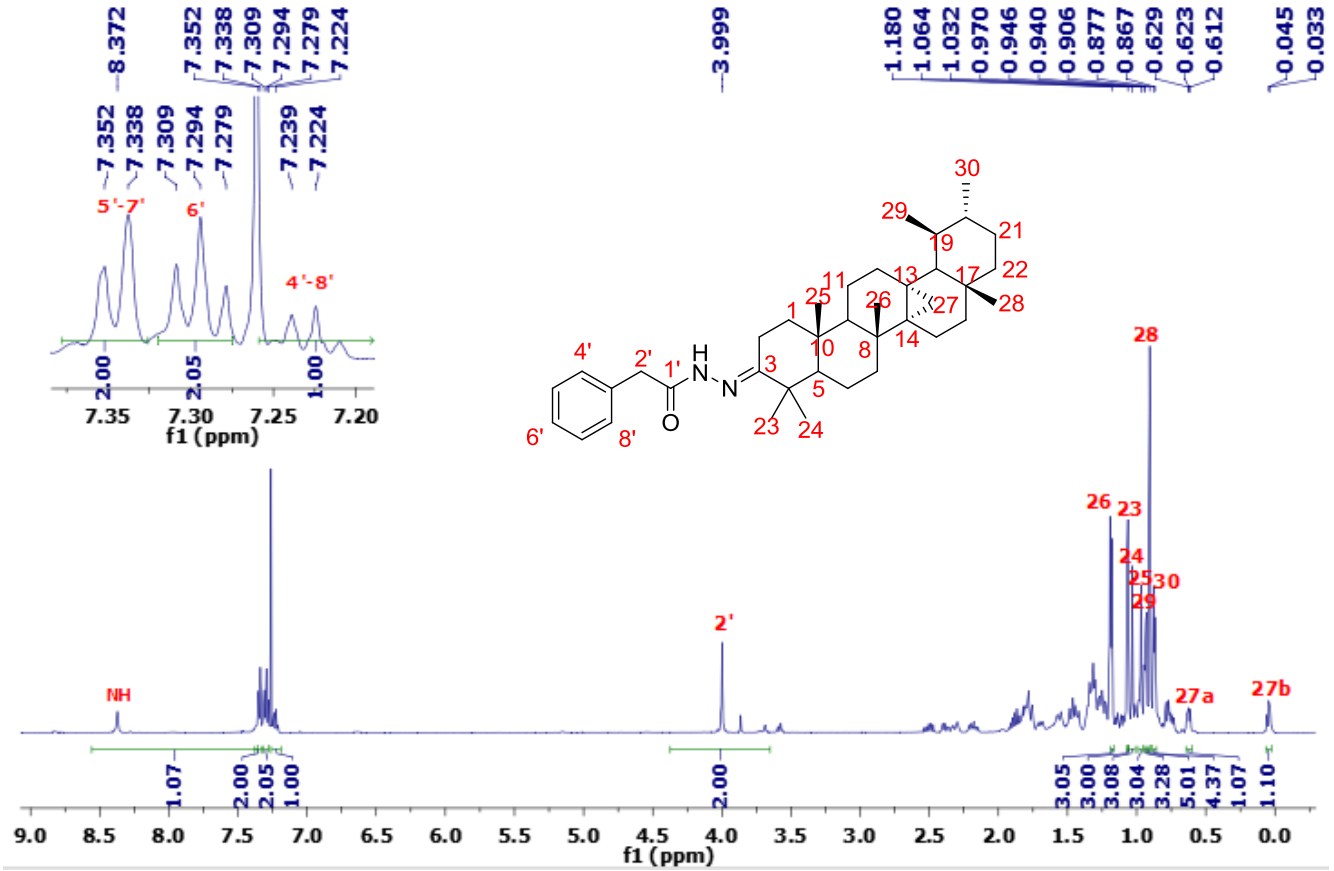


Figure S53. ^{1}H-NMR ($CDCl_3$, 500 MHz) spectrum of **3c**.

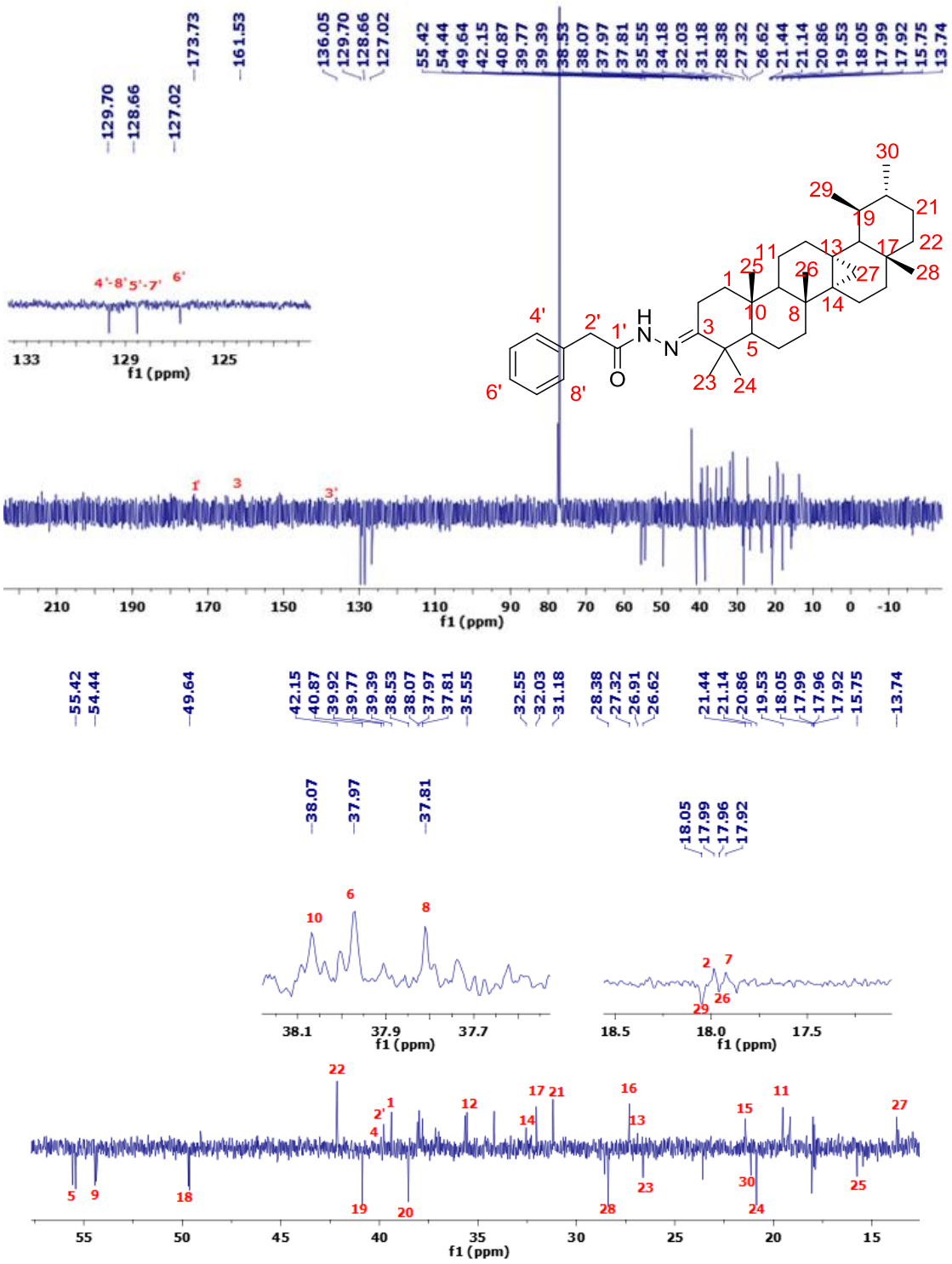


Figure S54. J-mod ($CDCl_3$, 125 MHz) spectrum of **3c**.

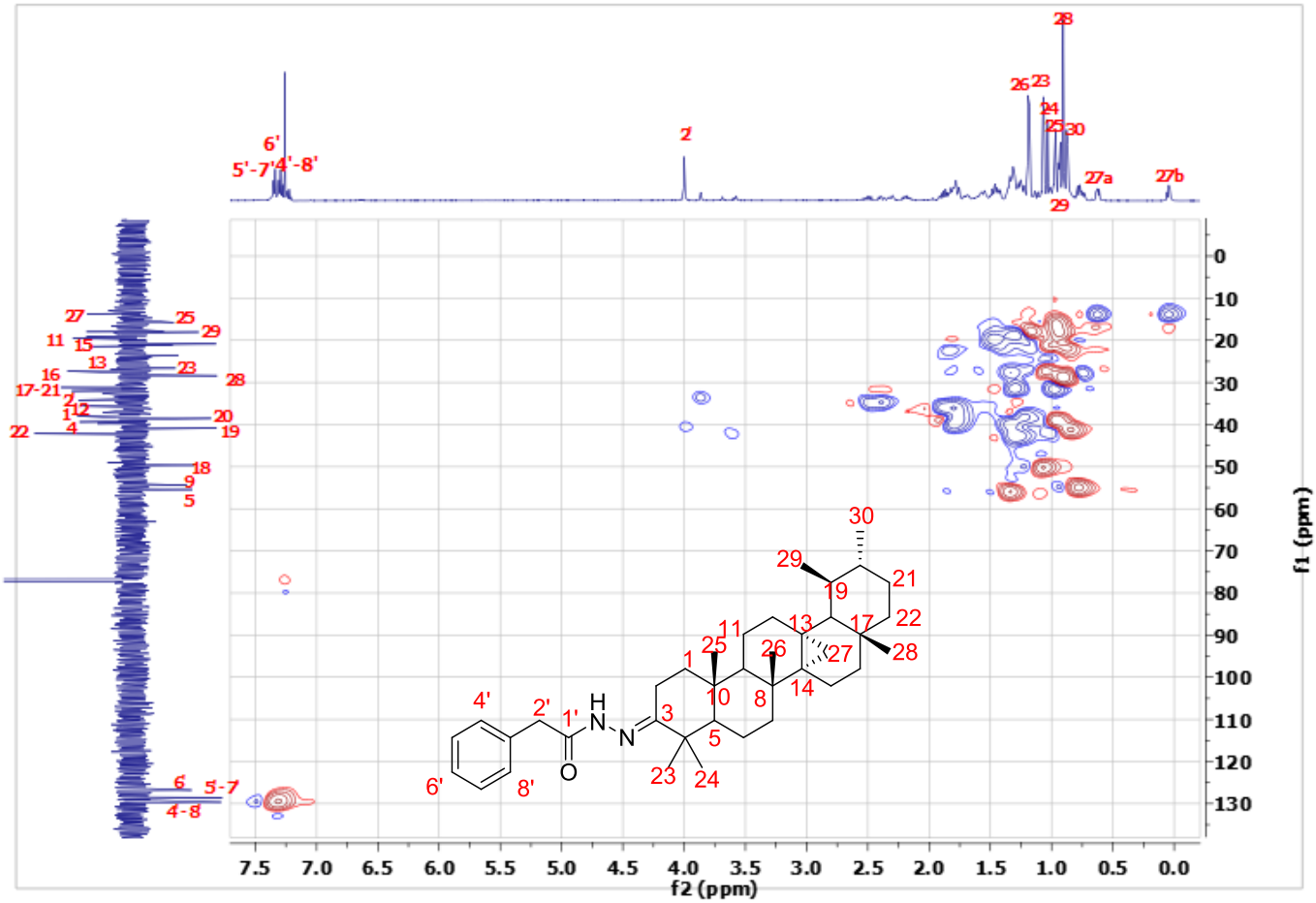


Figure S55. HSQC ($CDCl_3$) spectrum of **3c**.

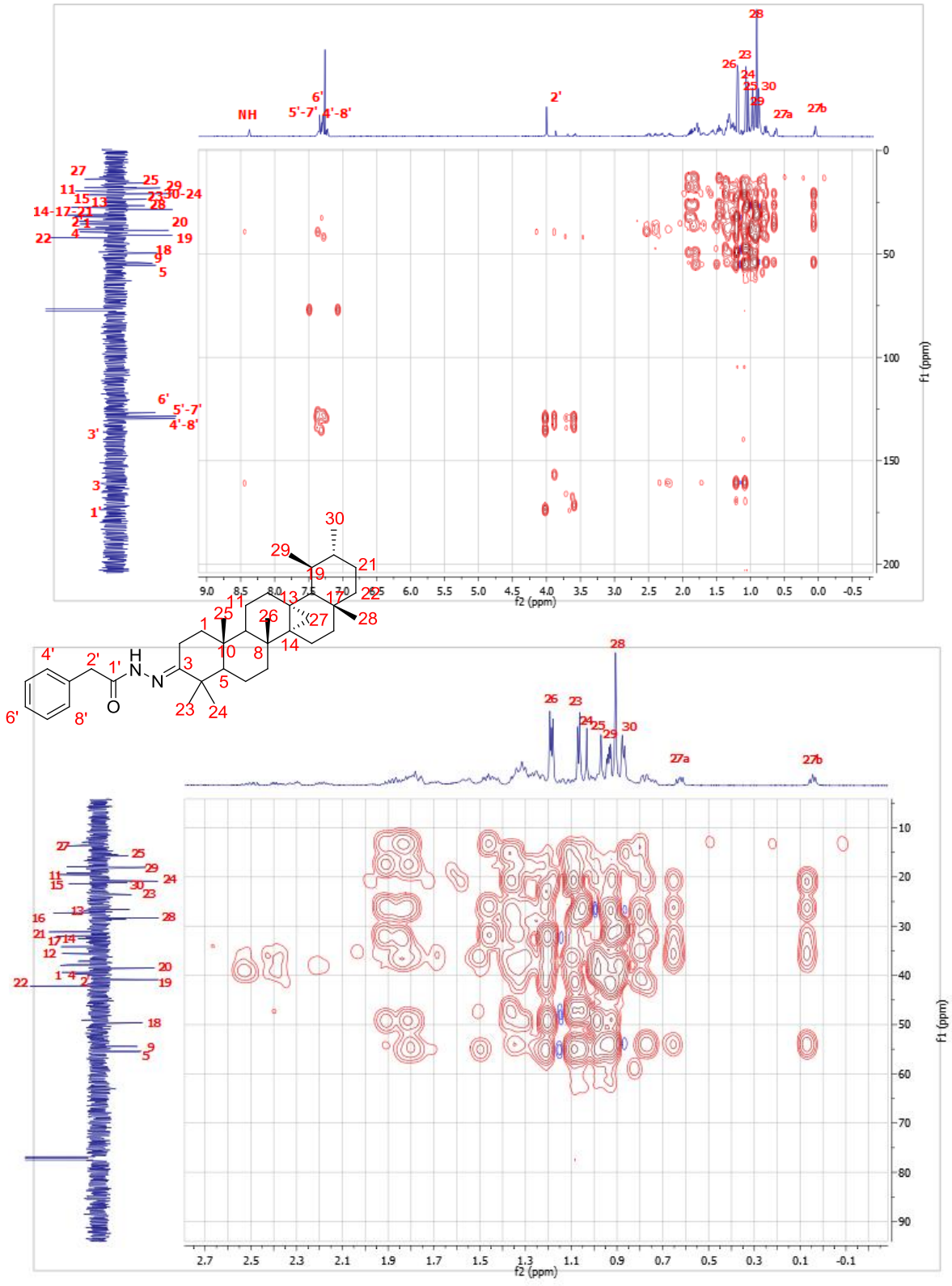
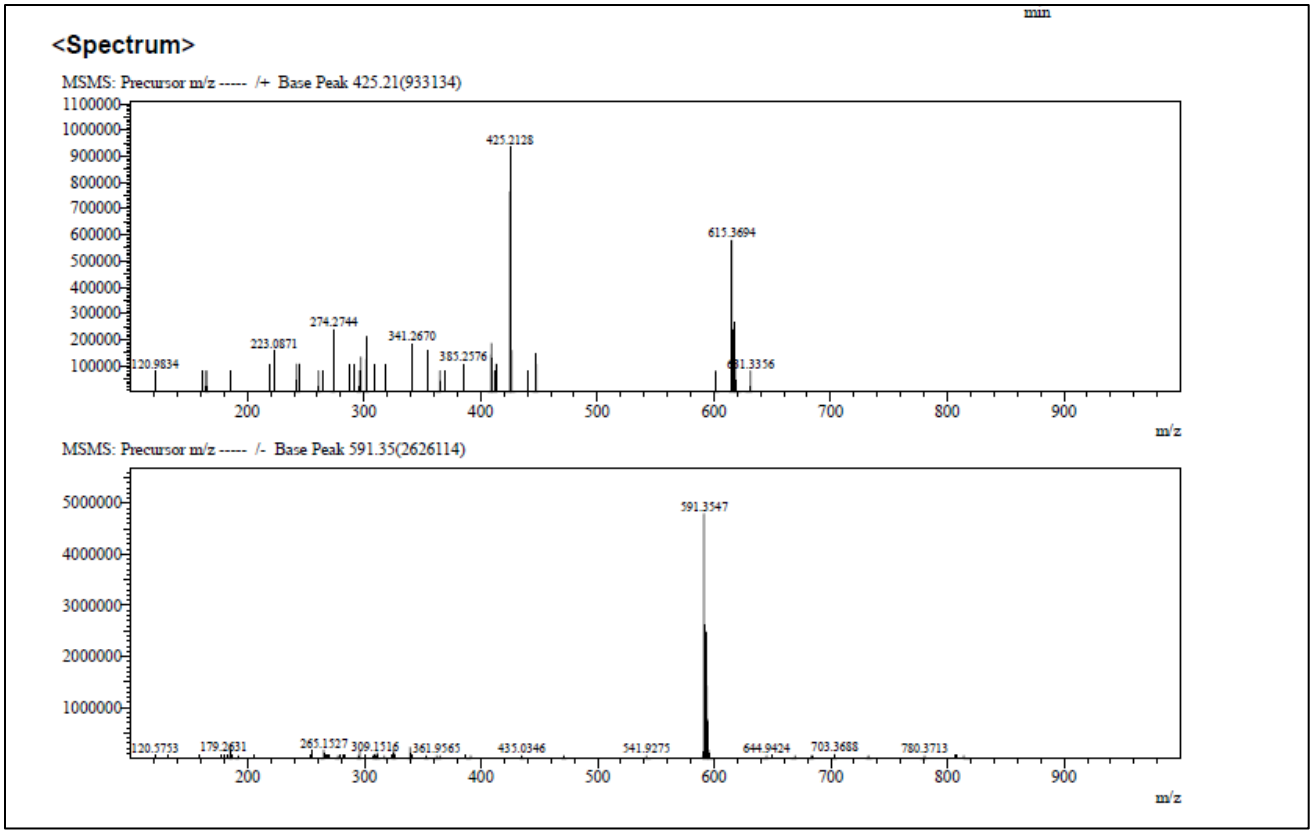
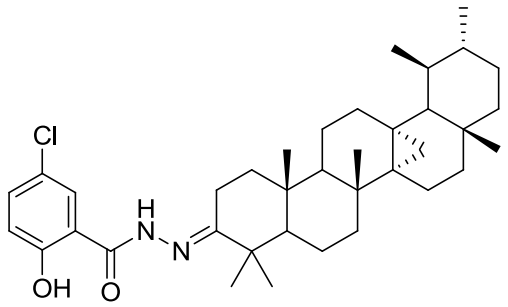


Figure S56. HMBC ($CDCl_3$) spectrum of **3c**.





Chemical Formula: $C_{37}H_{53}ClN_2NaO_2$ $[M+Na]^+$
Exact Mass: 615.36933

Figure S57. HRESIMS spectrum of **3d**.

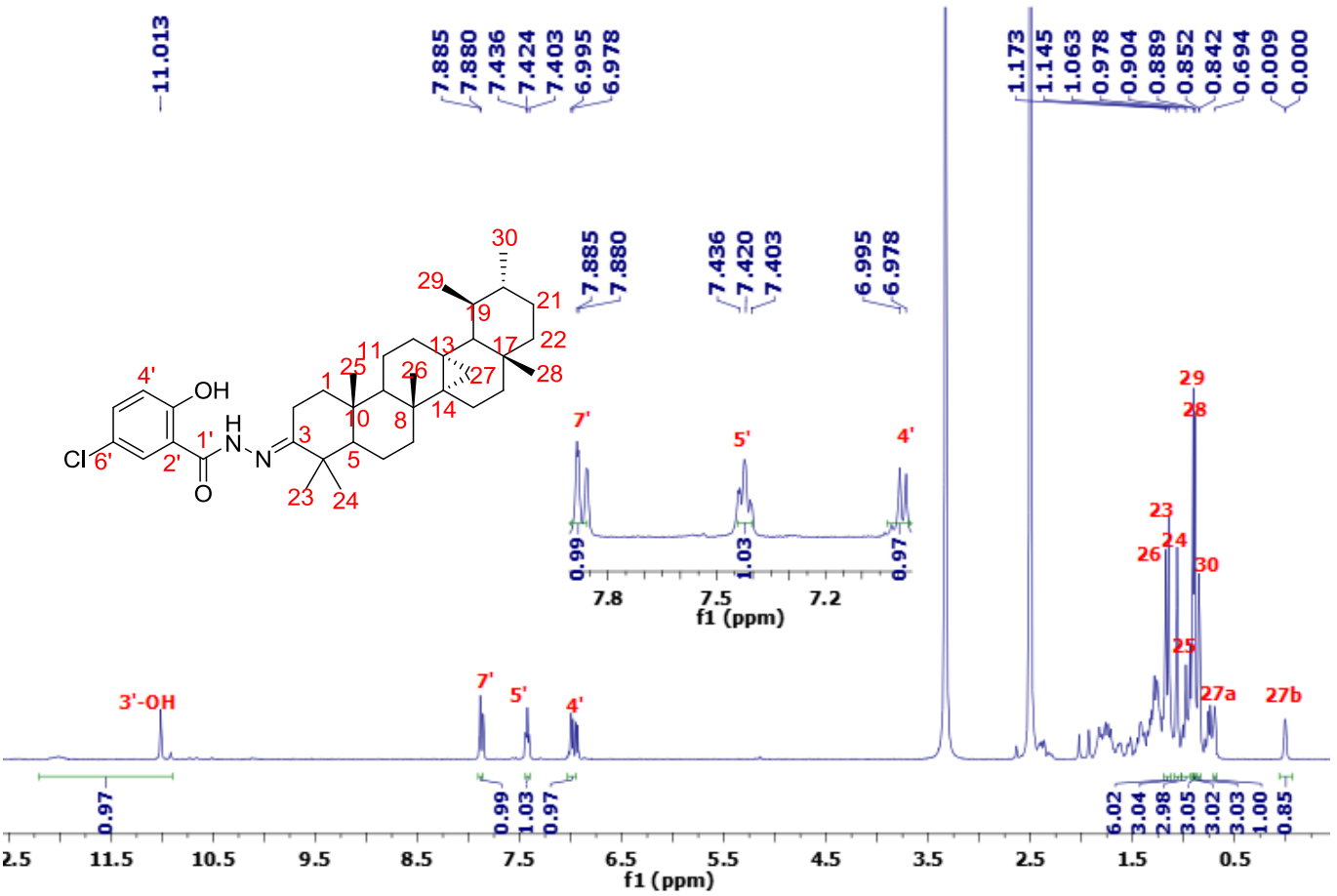


Figure S58. ^{1}H-NMR (DMSO-d_6, 500 MHz) spectrum of **3d**.

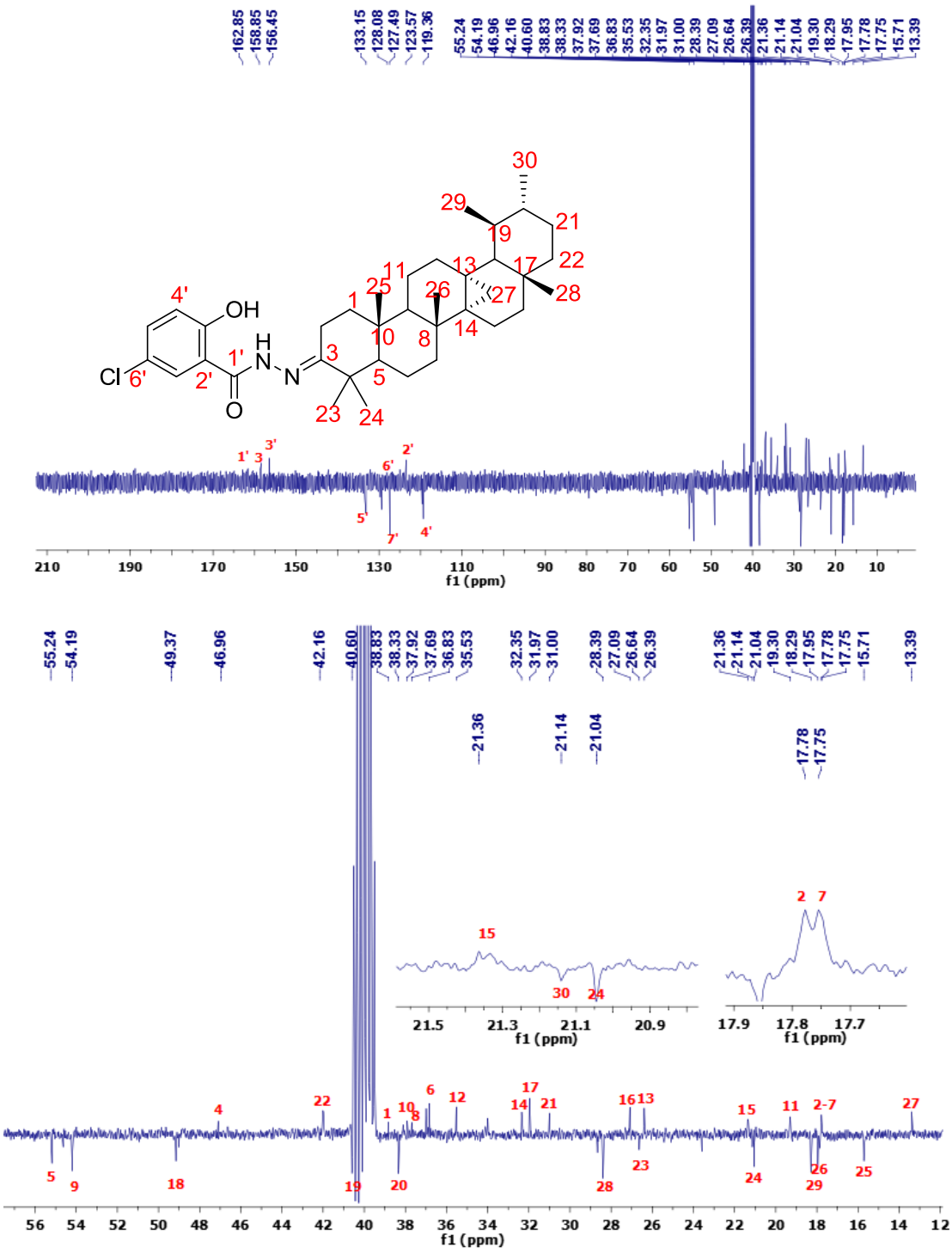


Figure S59. J-mod (DMSO-d_6, 125 MHz) spectrum of **3d**.

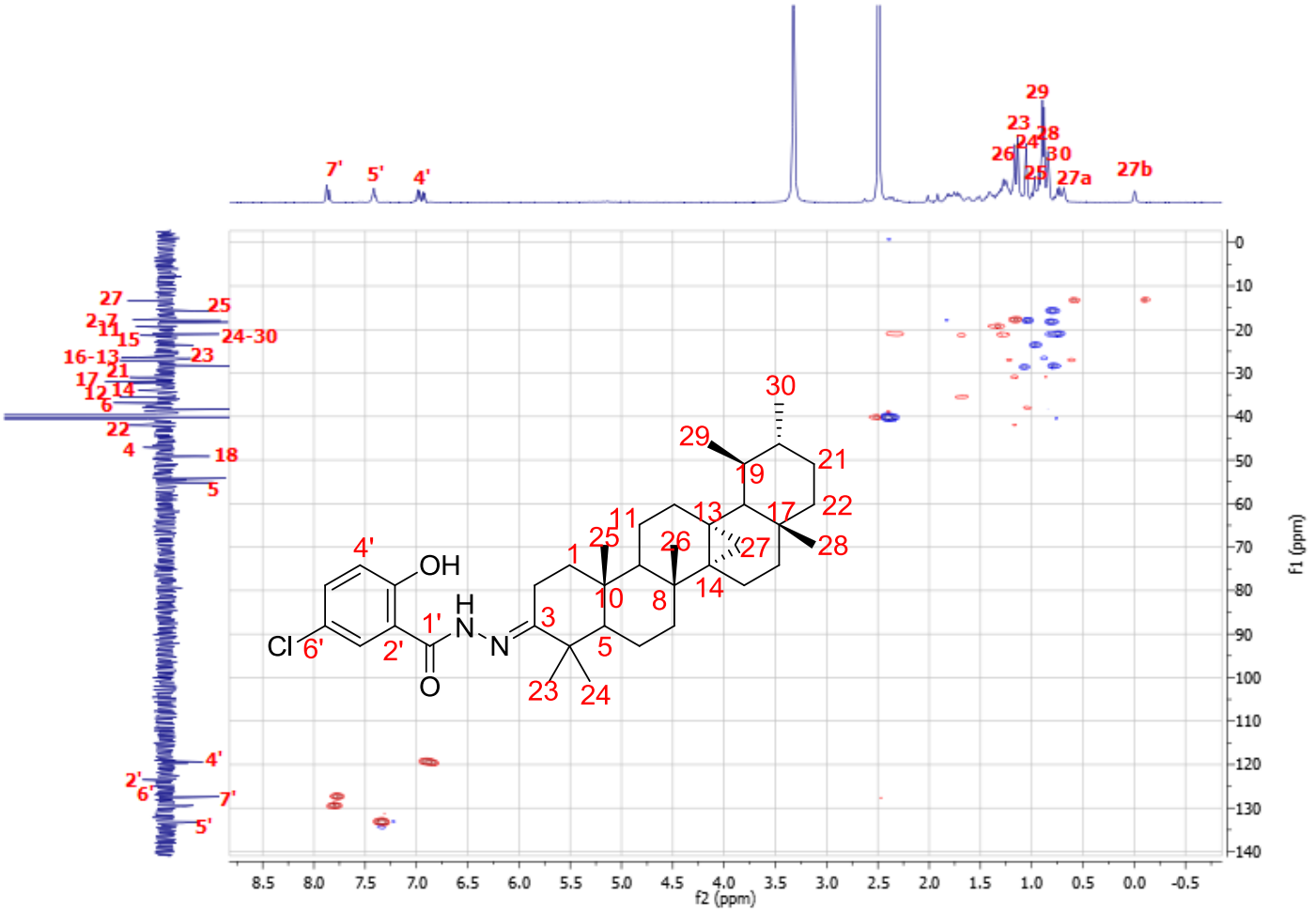


Figure S60. HSQC (DMSO-d_6) spectrum of **3d**.

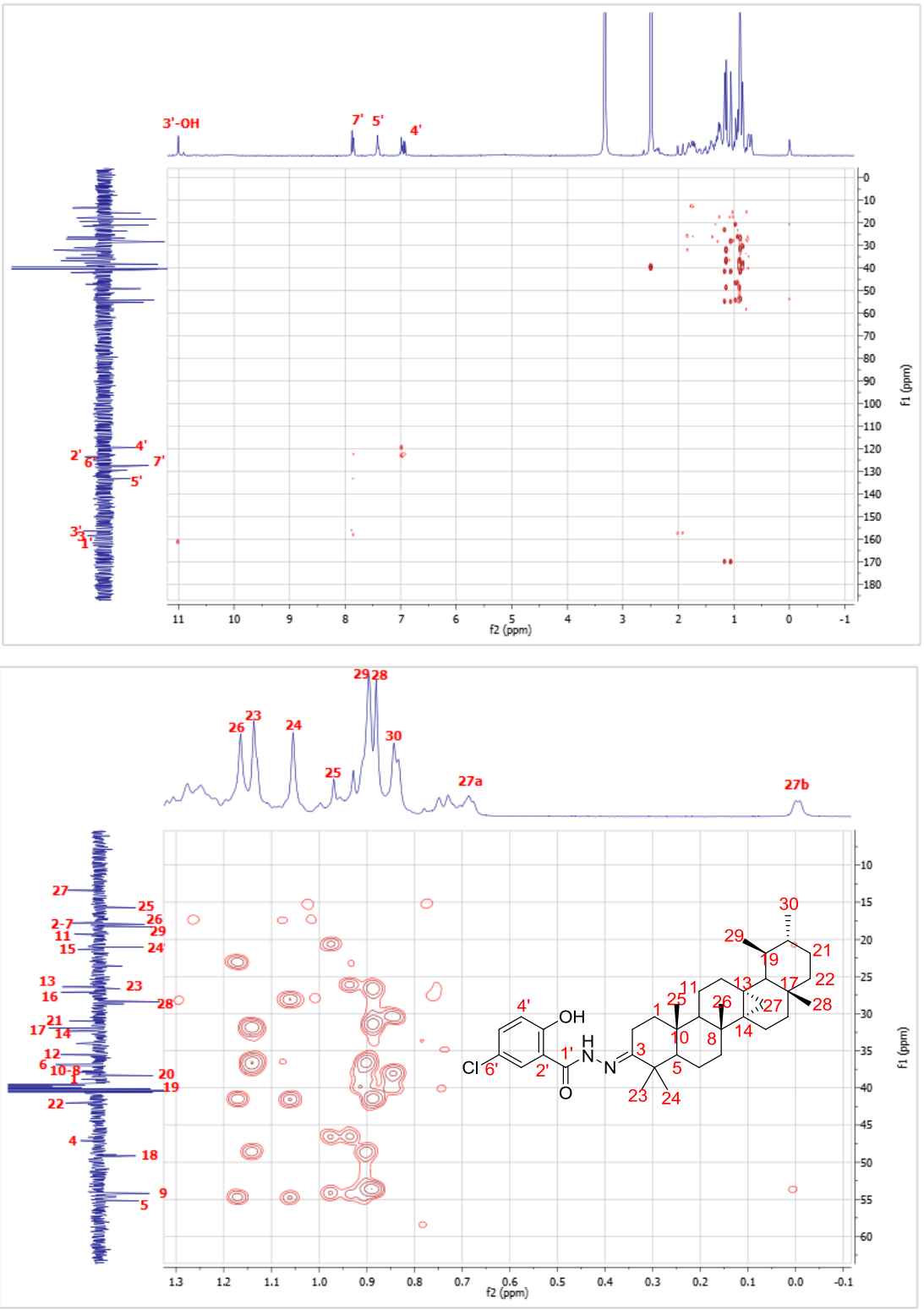
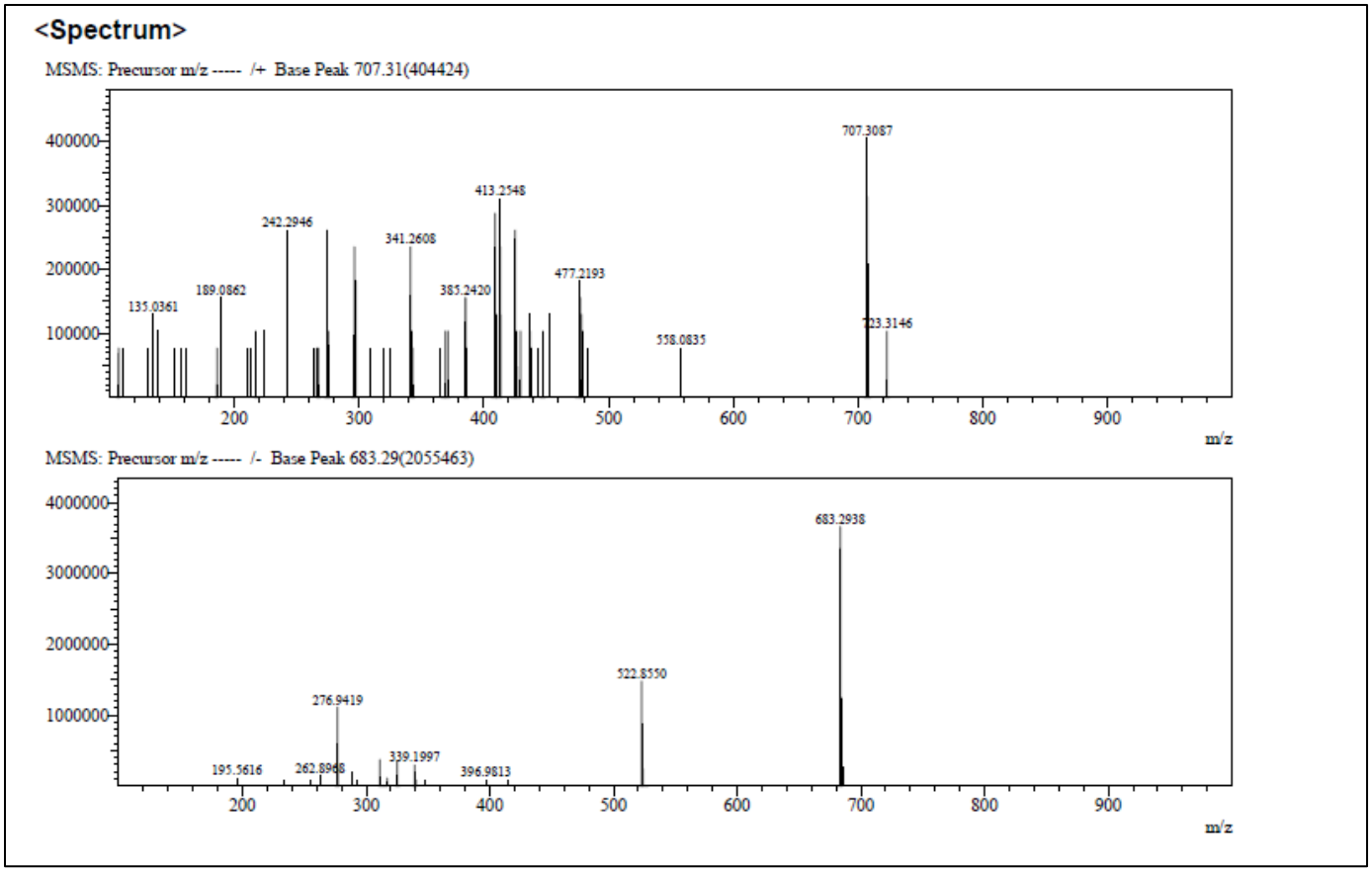
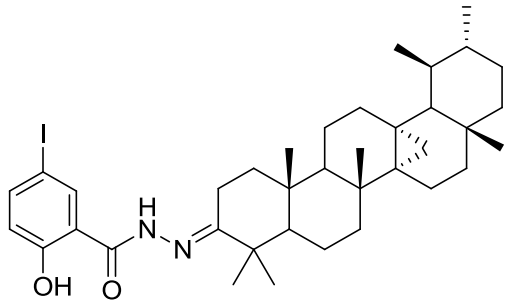


Figure S61. HMBC (DMSO-d_6) spectrum of **3d**.





Chemical Formula: $C_{37}H_{53}IN_2NaO_2$ $[M+Na]^+$
Exact Mass: 707.30494

Figure S62. HRESIMS spectrum of **3e**.

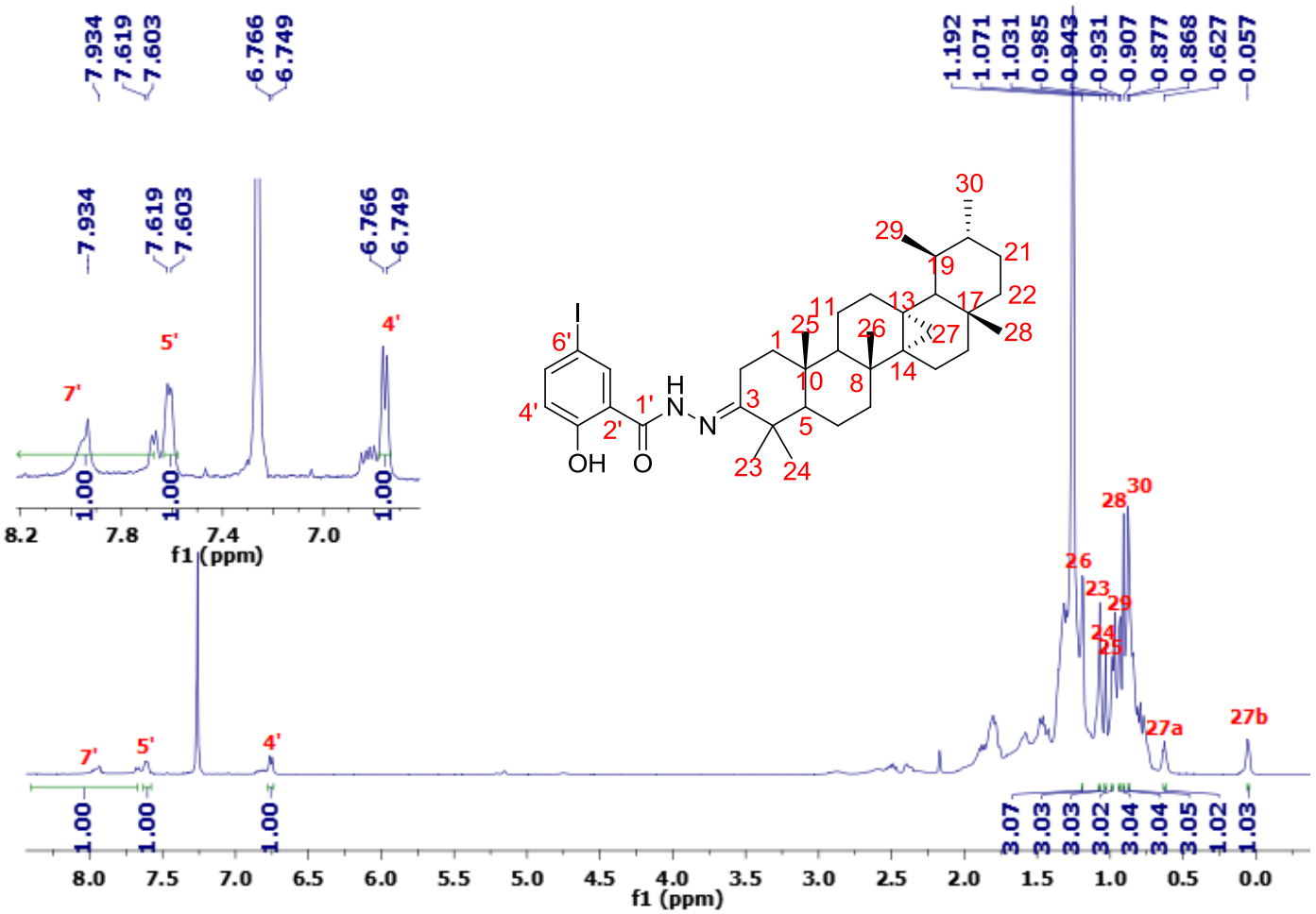


Figure S63. ^{1}H-NMR ($CDCl_3$, 500 MHz) spectrum of **3e**.

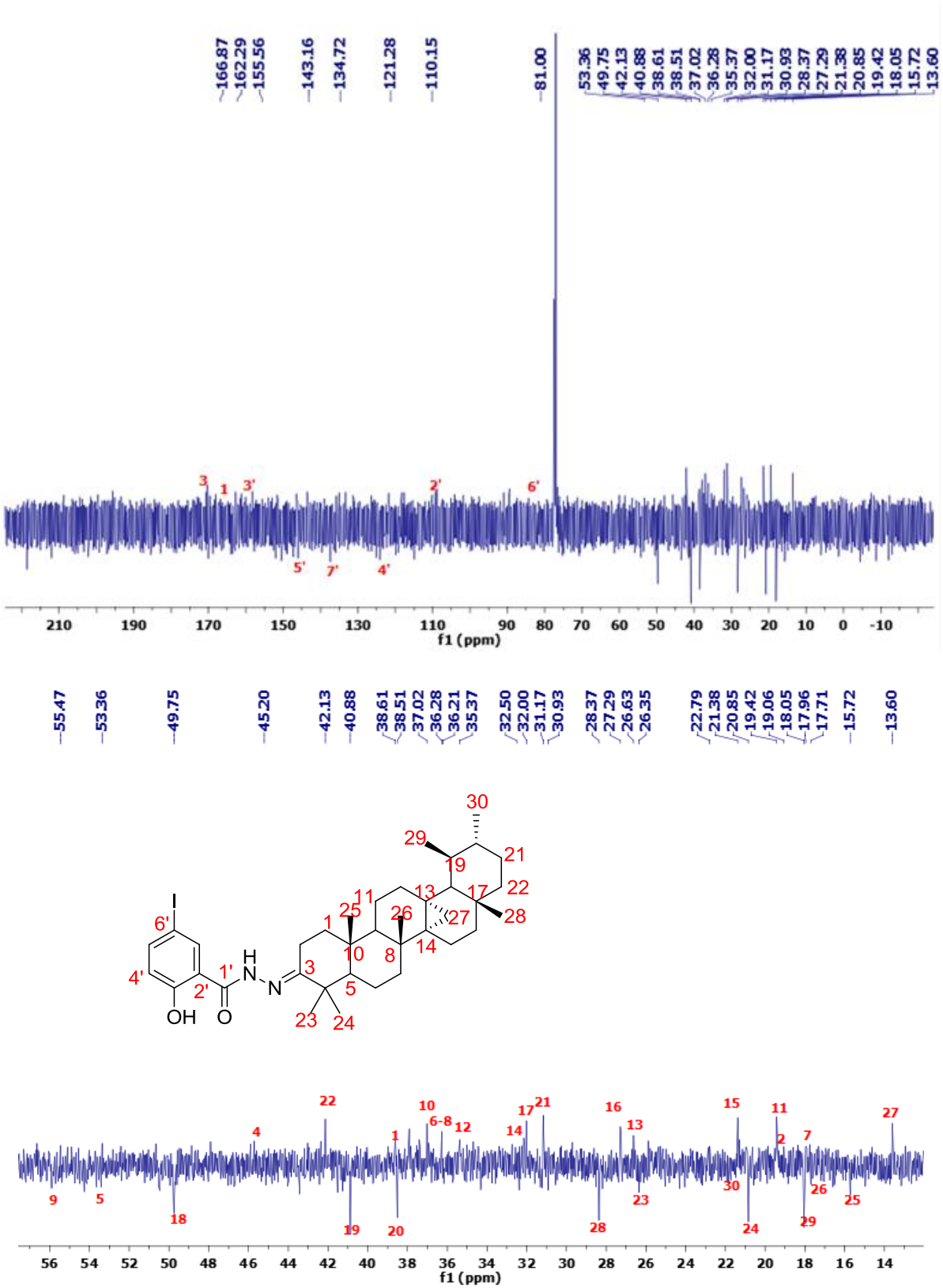


Figure S64. J-mod ($CDCl_3$, 125 MHz) spectrum of **3e**.

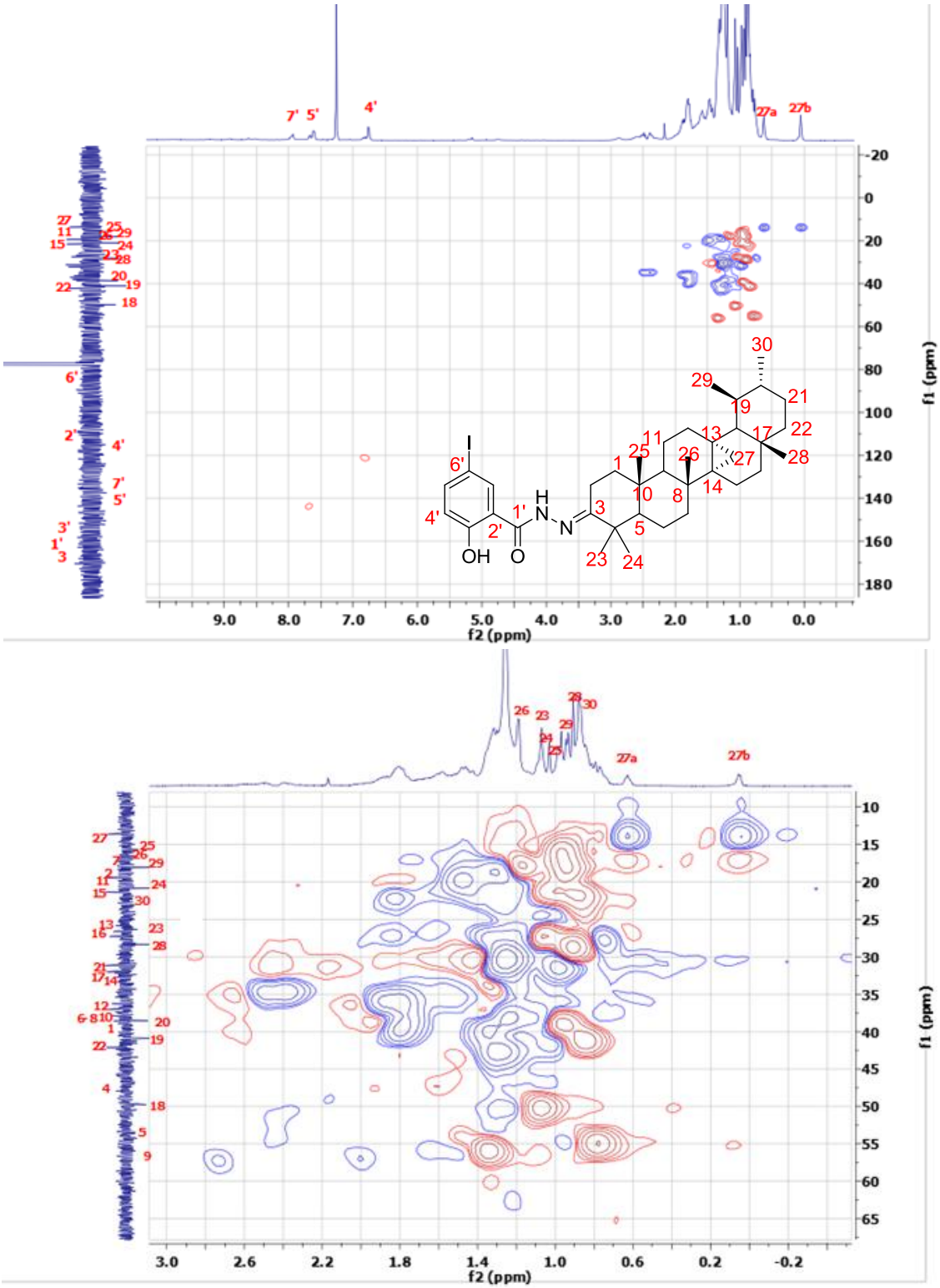


Figure S65. HSQC ($CDCl_3$) spectrum of **3e**.

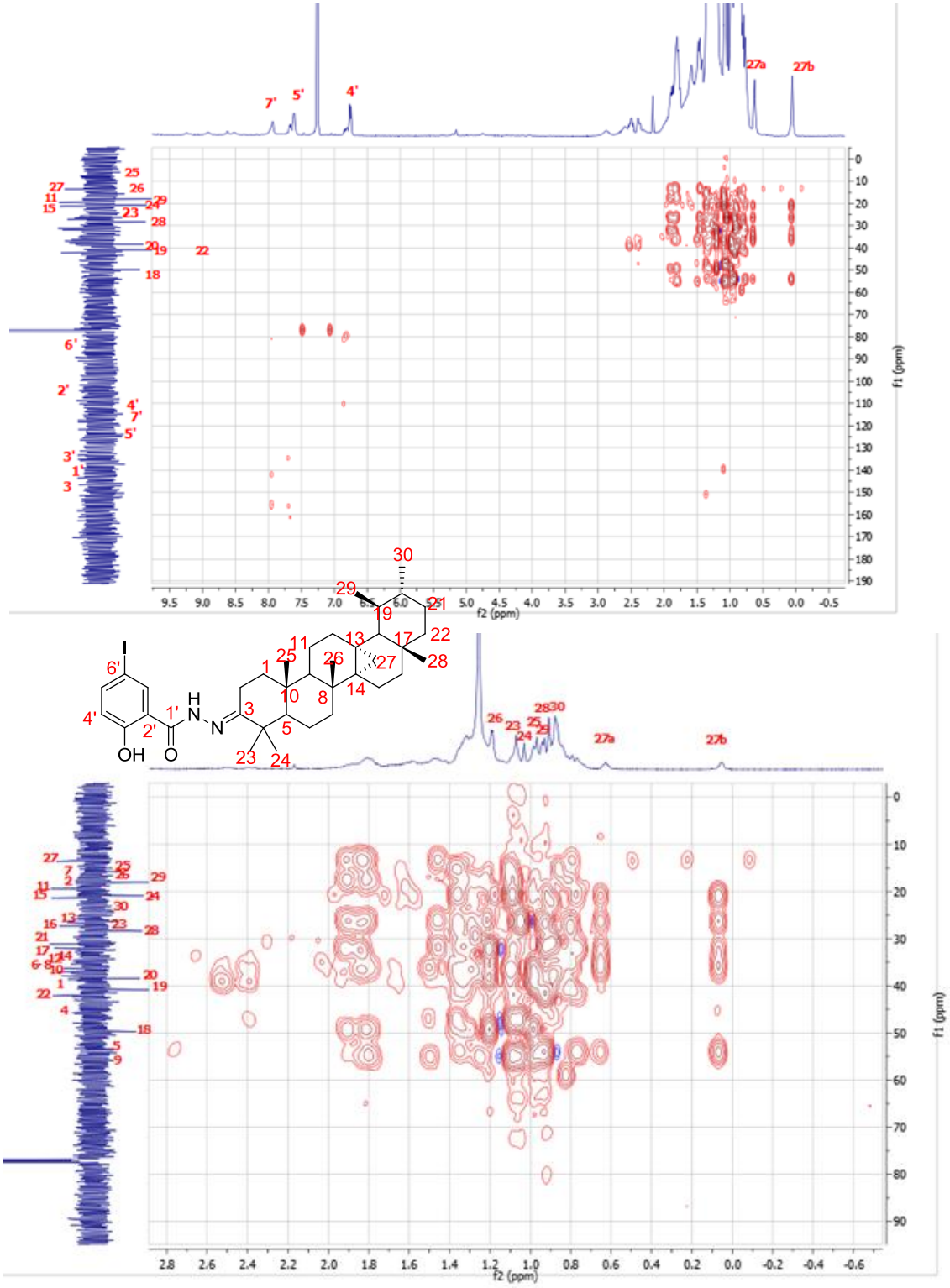
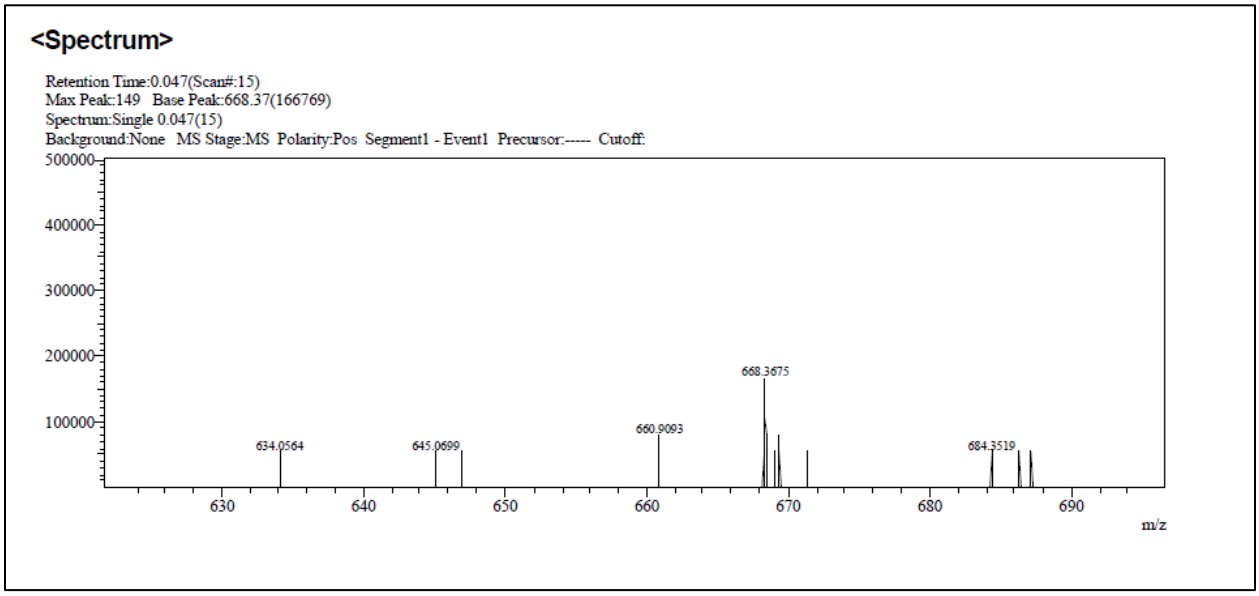
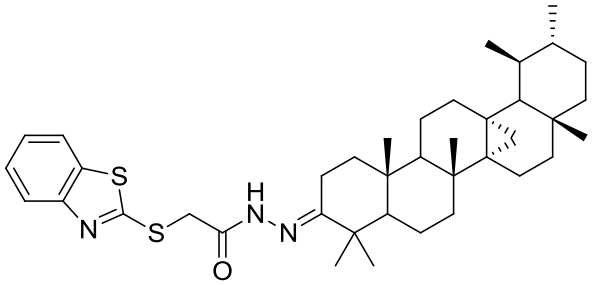


Figure S66. HMBC ($CDCl_3$) spectrum of **3e**.





Chemical Formula: $C_{39}H_{55}N_3NaOS_2$ $[M+Na]^+$
Exact Mass: 668.36842

Figure S67. HRESIMS spectrum of **3f**.

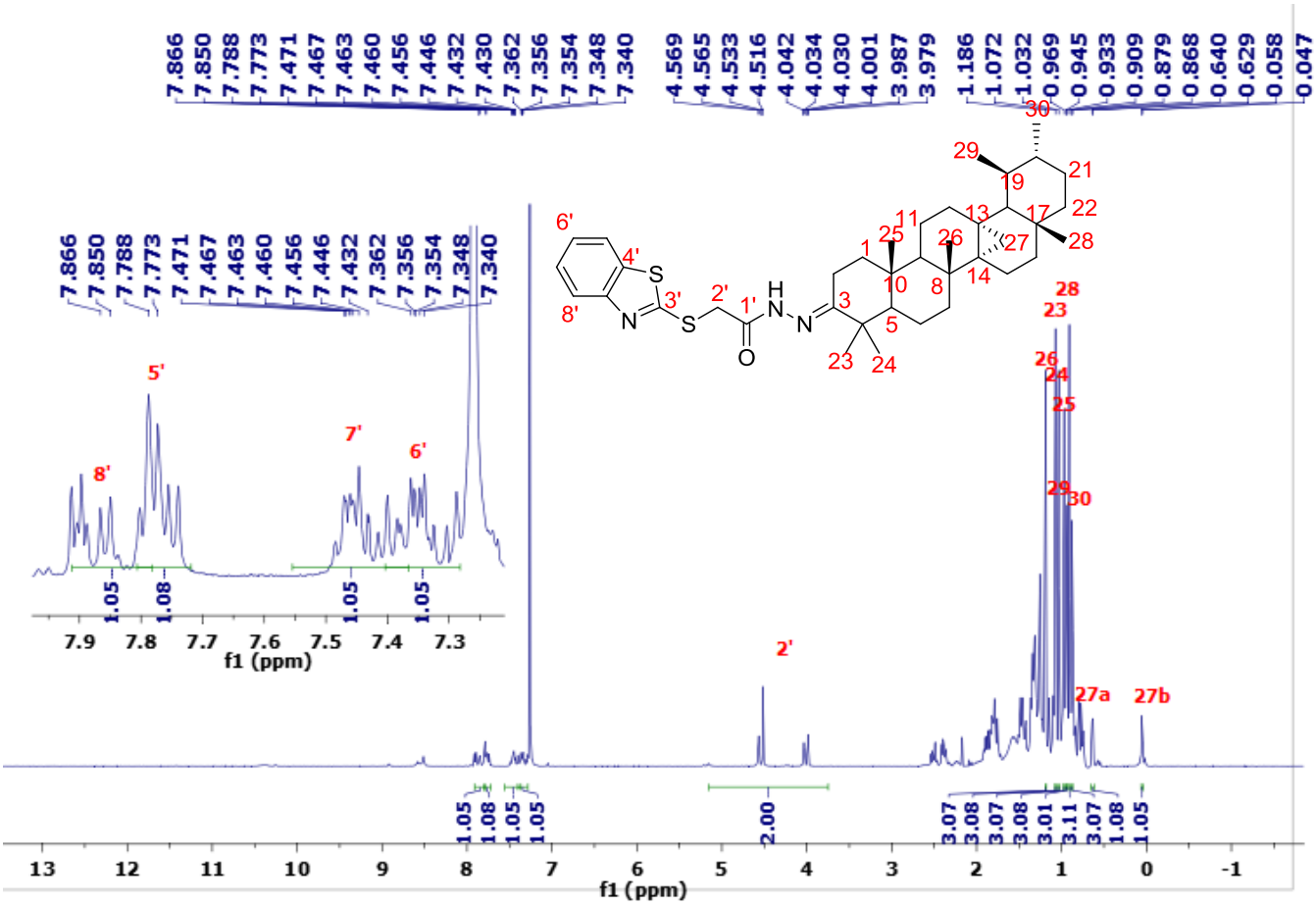


Figure S68. ^{1}H-NMR ($CDCl_3$, 500 MHz) spectrum of **3f**.

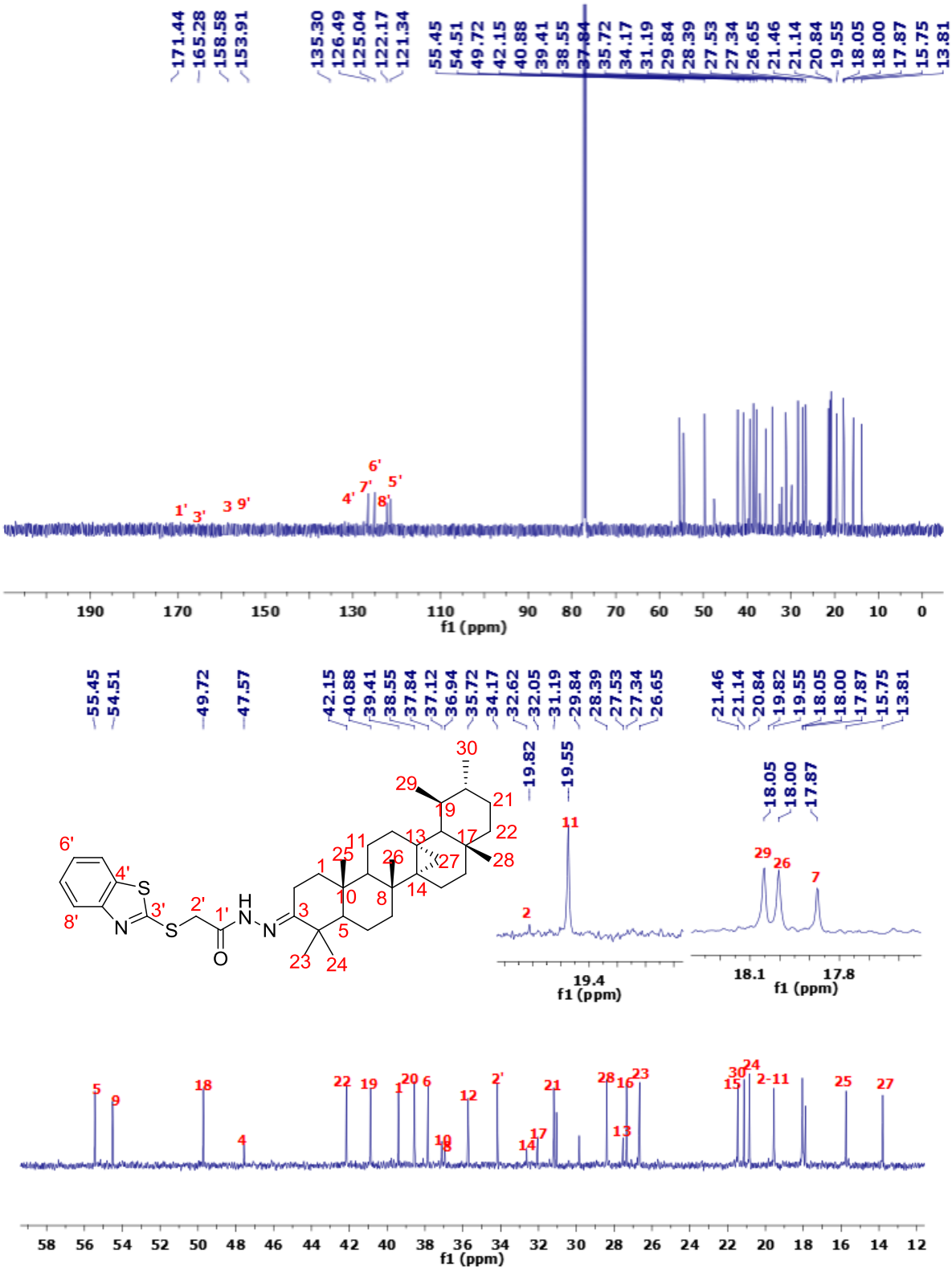


Figure S69. ^{13}C-NMR ($CDCl_3$, 125 MHz) spectrum of **3f**.

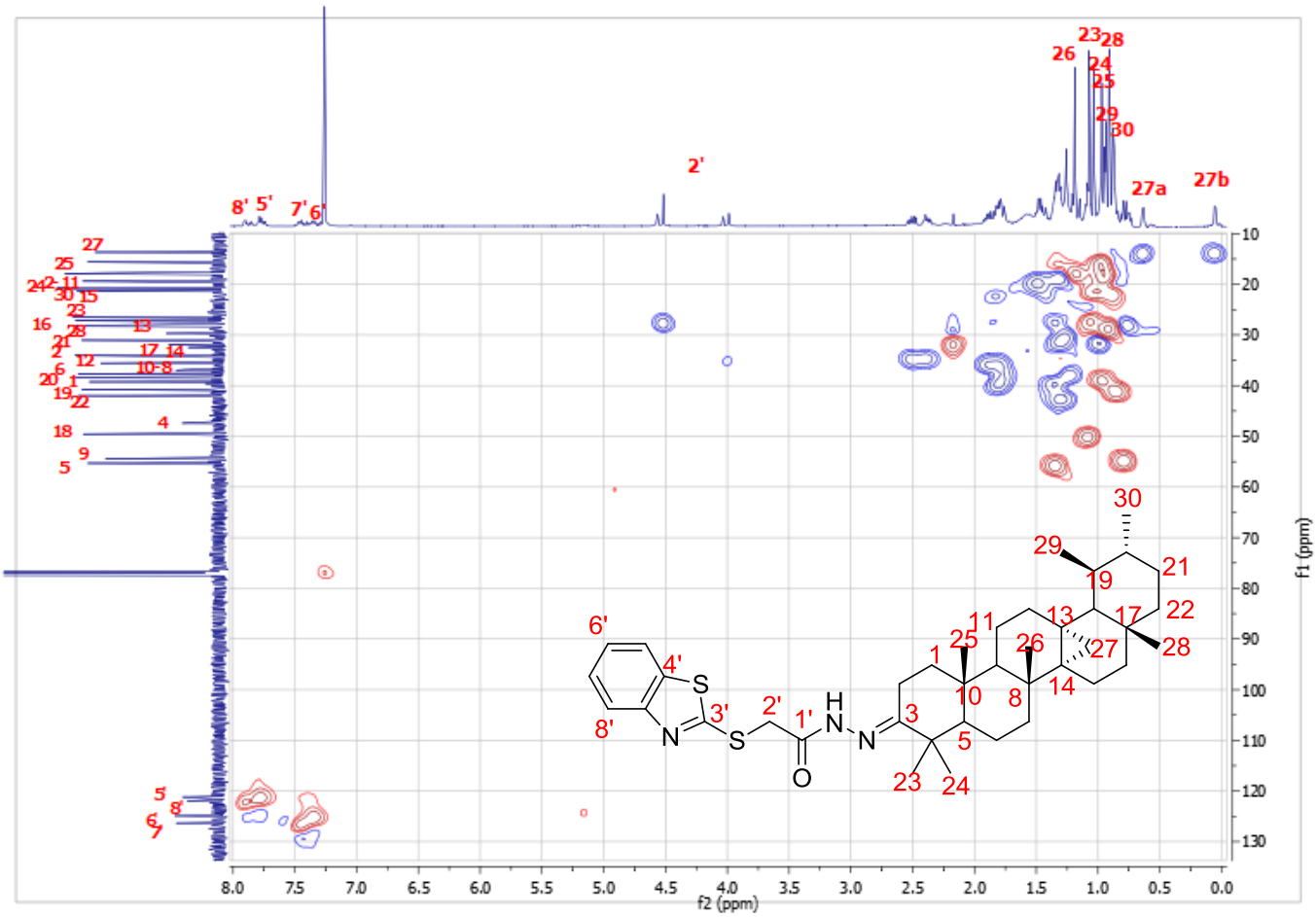


Figure S70. HSQC ($CDCl_3$) spectrum of **3f**.

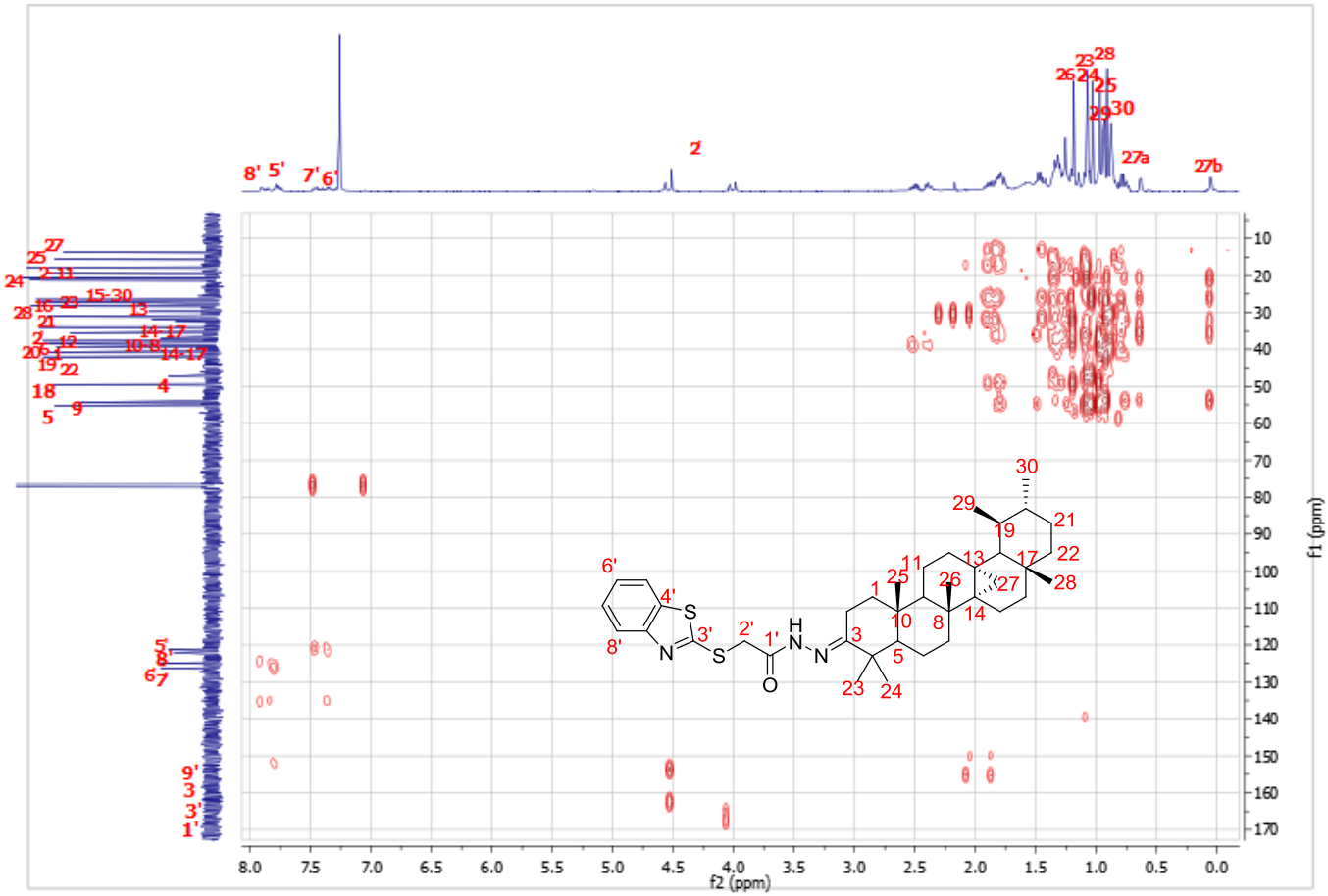


Figure S71. HMBC ($CDCl_3$) spectrum of **3f**.