

Supporting Information

For

Concise Synthesis and Biological Evaluation of C-Glycosyl Chalcone

Analogues Inspired by Natural Product Aspalathin

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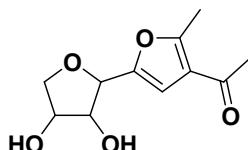
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Cytotoxicity assay

The MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium bromide) assay was performed. In vitro experiments were performed using HepG2 cell and MCF-7 cell. The cells were cultured in complete DMEM (high glucose) medium and RMPI-1640 medium in an atmosphere of 5% CO₂ at 37 °C respectively. Cells were seeded in a 96-well plate at a concentration of 1.0×10^4 cells/well and allowed to adhere overnight. Five replicates were prepared for each treatment and cultured for 48 or 72 h. After 20 µL of MTT (5 mg/mL) was added to each well, the cells were cultured for another 4 h. The supernatant was discarded. After 150 µL of DMSO was added to each well, the samples were incubated for 30 min and then swirled for 10 min. The absorbance (A) at 570 nm was measured using a microplate reader. Experiments were repeated three times and averaged.

Procedures and characterization data for compounds:

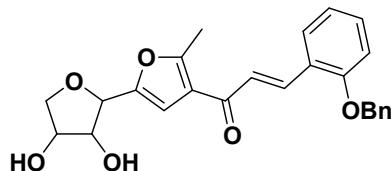
Compound 1



To a solution of glucose (1.8g, 10mmol) and acetylacetone (1.54ml 15mmol) in water (5mL) was added CoCl_2 (10% 0.13g) at room temperature. The reaction mixture was stirred and refluxed at 90°C overnight. After completion of the reaction as indicated by TLC (1:4 petroleum ether–ethyl acetate), the reaction mixture was extracted by ethyl acetate, and the organic layer was evaporated to dryness under reduced pressure. The residue was purified by recrystallization using petroleum ether and ethyl acetate and furnished pure compound **1** (1.97g, 75%).

^1H NMR (300 MHz, CDCl_3) δ 6.57 (s, 1H), 4.61 (d, J = 6.2 Hz, 1H), 4.32 (t, J = 4.6 Hz, 2H), 4.19 (dd, J = 10.0, 4.3 Hz, 1H), 3.85 (dd, J = 13.0, 3.7 Hz, 2H), 3.76 (s, 1H), 2.52 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 193.9, 158.2, 149.2, 121.1, 108.4, 75.9, 73.7, 72.1, 70.0, 28.1, 13.6. MS (ESI +C): $[\text{M} + \text{Na}]^+$, 250. Elemental Anal. Found: C (58.21%) H (6.38%) Calcd for $\text{C}_{22}\text{H}_{28}\text{O}_8$ = C (58.09%) H (6.45%).

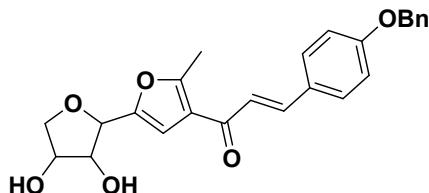
Compound 2a



To a solution of 3-Acetyl-5-C-(2,3-dihydroxy-1,4-anhydro-β-D-erythro-tetrofuranosyl)-2-methylfuran **1** (0.226g, 1.0mmol) and aromatic aldehydes (0.32g, 1.5mmol) in ethanol (4mL) was added NaOH (20%, 0.15mL) at room temperature. The reaction mixture was placed in a preheated oil bath and stirred at 60 °C for 6 h. After completion of the reaction as indicated by TLC (1:2 petroleum ether-ethyl acetate), the reaction mixture was evaporated to dryness under reduced pressure, then dissolved in dichloromethane, washed by brine. The organic phase was collected and dried over anhydrous Na_2SO_4 . The solvent was evaporated under reduced pressure and the residue was further purified by silica gel column chromatography using 2:1 petroleum ether-ethyl acetate to furnish pure products.

Obtained in 82% yield; orange powders; mp 120-121°C; ¹H NMR (500 MHz, CDCl₃) δ 7.95 (d, *J* = 15.8 Hz, 1H, =CH-Ar), 7.55 (dd, *J* = 7.6, 1.5 Hz, 1H, aromatic), 7.47 (m, *J* = 5.3, 3.1 Hz, 2H, aromatic), 7.44 – 7.32 (m, 3H, aromatic), 7.04 – 6.97 (m, 4H, aromatic, O=C-CH=), 6.98-7.01 (m, 2H, aromatic), 6.38 (s, 1H, H-furan), 5.14 (s, 2H, -CH₂Ph), 4.61 (d, *J* = 6.9 Hz, 1H, H-1), 4.40 (dd, *J* = 5.0, 1.9 Hz, 1H, H-3), 4.35 (d, *J* = 6.5 Hz, 1H, H-2), 4.25 (dd, *J* = 10.1, 4.9 Hz, 1H, H-4a), 3.90 (dd, *J* = 10.1, 3.0 Hz, 1H, H-4b), 3.24 (s, 1H, OH), 2.97 (s, 1H, OH), 2.53 (s, 3H, -CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 186.3, 159.9, 158.1, 149.3, 139.5, 131.5, 131.1, 128.8, 127.9, 125.1, 121.0, 112.3, 109.5, 74.5, 73.2, 71.0, 70.5, 14.5. LC-MS (ESI +H): 421.01. HRMS (ESI) m/z: calcd for C₂₅H₂₄O₆ [M + Na]⁺ 443.1573, found 443.1469.

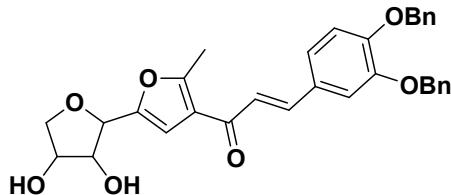
Compound 2b



To a solution of 3-Acetyl-5-C-(2,3-dihydroxy-1,4-anhydro-β-D-erythro-tetrofuranosyl)-2-methylfuran **1** (0.226g, 1.0mmol) and aromatic aldehydes (0.32g, 1.5mmol) in ethanol (4mL) was added NaOH (20%, 0.15mL) at room temperature. The reaction mixture was placed in a preheated oil bath and stirred at 60 °C for 6 h. After completion of the reaction as indicated by TLC (1:2 petroleum ether-ethyl acetate), the reaction mixture was evaporated to dryness under reduced pressure, then dissolved in dichloromethane, washed by brine. The organic phase was collected and dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure and the residue was further purified by silica gel column chromatography using 2:1 petroleum ether-ethyl acetate to furnish pure products.

Obtained in 85% yield; orange powders; mp 124.5-125.5°C; ¹H NMR (500 MHz, CDCl₃) δ 7.68 (d, *J* = 15.6 Hz, 1H, =CH-Ar), 7.54 (d, *J* = 8.7 Hz, 2H, aromatic), 7.46 – 7.37 (m, 5H, aromatic), 7.35 (d, *J* = 7.0 Hz, 1H, aromatic), 7.04 (d, *J* = 15.6 Hz, 1H, O=C-CH=), 6.98 (d, *J* = 8.8 Hz, 2H, aromatic), 6.71 (s, 1H, H-furan), 5.10 (s, 2H, -CH₂Ph), 4.69 (d, *J* = 6.4 Hz, 1H, H-1), 4.41 (m, 2H, H-2, H-3), 4.27 (dd, *J* = 10.1, 4.7 Hz, 1H, H-4a), 3.91 (dd, *J* = 10.1, 2.7 Hz, 1H, H-4b), 3.26 (s, 1H, OH), 2.96 (s, 1H, OH), 2.62 (s, 3H, -CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 185.9, 160.8, 159.7, 149.8, 143.3, 136.3, 130.2, 128.6, 127.4, 122.4, 121.4, 115.2, 109.2, 74.6, 73.2, 71.0, 70.0, 14.6. LC-MS (ESI +H): 421.08. HRMS (ESI) m/z: calcd for C₂₅H₂₄O₆ [M + Na]⁺ 443.1573, found 443.1466.

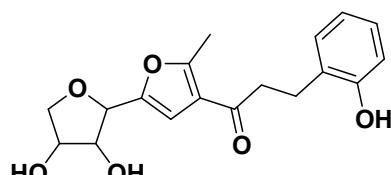
Compound 2c



To a solution of 3-Acetyl-5-C-(2,3-dihydroxy-1,4-anhydro- β -D-erythro-tetrofuranosyl)-2-methylfuran **1** (0.226g, 1.0mmol) and aromatic aldehydes (0.48g, 1.5mmol) in ethanol (4mL) was added NaOH (20%, 0.15mL) at room temperature. The reaction mixture was placed in a preheated oil bath and stirred at 60 °C for 6 h. After completion of the reaction as indicated by TLC (1:2 petroleum ether-ethyl acetate), the reaction mixture was evaporated to dryness under reduced pressure, then dissolved in dichloromethane, washed by brine. The organic phase was collected and dried over anhydrous Na_2SO_4 . The solvent was evaporated under reduced pressure and the residue was further purified by silica gel column chromatography using 2:1 petroleum ether-ethyl acetate to furnish pure products.

Obtained in 80% yield; orange powders; mp 123-123.5°C; ^1H NMR (500 MHz, CDCl_3) δ 7.58 (d, J = 15.6 Hz, 1H, =CH-Ar), 7.44 (dd, J = 14.3, 7.4 Hz, 4H, aromatic), 7.36 (t, J = 7.4 Hz, 4H, aromatic), 7.33 – 7.25 (m, 3H, aromatic), 7.16 (d, J = 1.8 Hz, 1H, aromatic), 7.11 (dd, J = 8.4, 1.8 Hz, 1H, aromatic), 6.91 (dd, J = 15.6, 12.0 Hz, 2H, aromatic, O=C-CH=), 6.68 (s, 1H, H-furan), 5.16 (d, J = 4.8 Hz, 4H, - CH_2Ph), 4.68 (d, J = 6.1 Hz, 1H, H-1), 4.40 – 4.33 (m, 2H, H-2, H-3), 4.23 (dd, J = 10.0, 4.6 Hz, 1H, H-4a), 3.89 (dd, J = 10.0, 2.1 Hz, 1H, H-4b), 2.56 (s, 3H, - CH_3). ^{13}C NMR (75 MHz, CDCl_3): δ 185.9, 159.7, 151.3, 150.0, 148.8, 143.6, 136.8, 136.5, 128.5, 127.9, 127.3, 127.1, 123.5, 122.4, 121.7, 114.1, 109.1, 74.6, 73.2, 71.4, 70.9, 14.6. LC-MS (ESI +H): 527.08. HRMS (ESI) m/z: calcd for $\text{C}_{32}\text{H}_{30}\text{O}_7$ [M + Na]⁺ 549.1992, found 549.1885.

Compound 3a

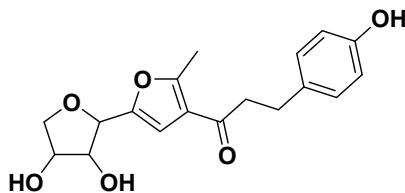


A suspension of compound **2a** (0.21 g, 0.5 mmol) and 10% Pd/C (50 mg) in dichloromethane (5 mL) –

MeOH (10 mL) was stirred under H₂ at atmospheric pressure for 4h. The reaction mixture was filtered, concentrated under a vacuum, and purified by silica gel column chromatography using 1:2 petroleum ether-ethyl acetate to furnish pure products.

Obtained in 63% yield; colourless oil; ¹H NMR (500 MHz, CDCl₃) δ 7.05 – 7.00 (m, 2H, aromatic), 6.80 (dd, *J* = 9.7, 3.6 Hz, 2H, aromatic), 6.56 (s, 1H, H-furan), 4.59 (d, *J* = 5.4 Hz, 1H, H-1), 4.34 – 4.24 (m, 2H, H-3, H-2), 4.17 (dd, *J* = 8.1, 1H, 3.8 Hz, H-4a), 3.83 (dd, *J* = 8.1, 2.3 Hz, 1H, H-4b), 3.04 (dd, *J* = 6.5, 3.5 Hz, 2H, O=C-CH₂-), 2.87 (dd, *J* = 7.5, 3.2 Hz, 2H, -CH₂-Ar), 2.50 (s, 3H, -CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 198.1, 160.2, 154.2, 150.0, 130.5, 127.9, 127.7, 120.9, 120.6, 117.2, 108.9, 74.6, 73.1, 70.9, 42.6, 23.3, 14.7. LC-MS (ESI +C): 333.08. HRMS (ESI) m/z: calcd for C₁₈H₂₀O₆ [M + Na]⁺ 355.1260, found 355.1154.

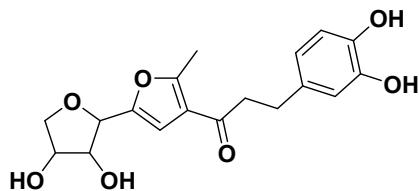
Compound 3b



A suspension of compound **2b** (0.21 g, 0.5 mmol) and 10% Pd/C (50 mg) in dichloromethane (5 mL) – MeOH (10 mL) was stirred under H₂ at atmospheric pressure for 4h. The reaction mixture was filtered, concentrated under a vacuum, and purified by silica gel column chromatography using 1:2 petroleum ether-ethyl acetate to furnish pure products.

Obtained in 67% yield; colourless oil; ¹H NMR (500 MHz, DMSO-d6) δ 9.13 (s, 1H, PhOH), 7.01 (d, *J* = 8.3 Hz, 2H, aromatic), 6.83 (s, 1H, H-furan), 6.64 (d, *J* = 8.2 Hz, 2H, aromatic), 5.09 (d, *J* = 6.1 Hz, 1H, OH), 4.99 (d, *J* = 3.2 Hz, 1H, OH), 4.46 (d, *J* = 6.6 Hz, 1H, H-1), 4.10 (t, *J* = 5.2 Hz, 2H, H-2, H-3), 4.00 (dd, *J* = 9.1, 3.9 Hz, 1H, H-4a), 3.69 – 3.50 (dd, *J* = 9.1, 3.9 Hz, 1H, H-4b), 2.99 (t, *J* = 7.5 Hz, 2H, O=C-CH₂-), 2.73 (t, *J* = 7.4 Hz, 2H, -CH₂-Ar), 2.50 (s, 5H, -CH₃). ¹³C NMR (75 MHz, DMSO-d6): δ 195.7, 157.7, 155.8, 151.6, 131.6, 129.6, 121.6, 115.4, 109.3, 76.2, 74.8, 73.1, 70.7, 42.8, 28.7, 14.5. LC-MS (ESI +C): 333.07. HRMS (ESI) m/z: calcd for C₁₈H₂₀O₆ [M + Na]⁺ 355.1260, found 355.1153.

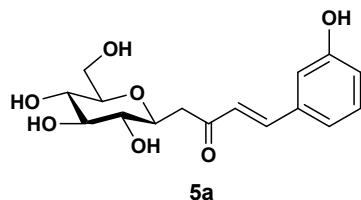
Compound 3c



A suspension of compound **2c** (0.26 g, 0.5 mmol) and 10% Pd/C (50 mg) in dichloromethane (5 mL) – MeOH (10 mL) was stirred under H₂ at atmospheric pressure for 4h. The reaction mixture was filtered, concentrated under a vacuum, and purified by silica gel column chromatography using 1:2 petroleum ether-ethyl acetate to furnish pure products.

Obtained in 70% yield; colourless oil; ¹H NMR (500 MHz, DMSO-d6) δ 8.70 (s, 1H, PhOH), 8.62 (s, 1H, PhOH), 6.83 (s, 1H, aromatic), 6.61 (m, 2H, aromatic, H-furan), 6.56 (dd, *J* = 8.1, 1.75 Hz, 1H, aromatic), 5.1 (d, 1H, OH), 5.0 (d, 1H, OH), 4.47 (d, *J* = 6.6 Hz, H-1), 4.12 (m, 2H, H-2, H-3), 4.02 (m, 1H, H-4a), 3.62 (dd, *J* = 9.1, 3.9 Hz, 1H, H-4b), 2.98 (t, *J* = 7.5 Hz, 2H, O=C-CH₂-), 2.70 (t, *J* = 7.4 Hz, 2H, -CH₂-Ar), 2.50 (s, 3H, -CH₃). ¹³C NMR (75 MHz, DMSO-d6): δ 195.7, 157.7, 151.5, 14.5, 143.6, 132.3, 121.6, 119.2, 116.1, 115.8, 109.3, 76.2, 74.8, 73.1, 70.7, 28.7, 14.5. LC-MS (ESI -H): 346.85. HRMS (ESI) m/z: calcd for C₁₈H₂₀O₇ [M + Na]⁺ 355.1260, found 371.1084.

Compound 5a

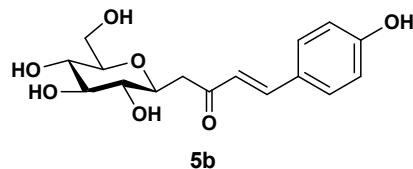


To a solution of 1-*C*-(β-D-glucopyranosyl)-propan-2-one (5.0 g, 23.0mmol) and 3-hydroxybenzaldehyde (3.42g 28.0mmol) in ethanol (4.5mL) was added TEA (0.11 mL, 0.77mmol) and proline (0.4g 3.45mmol) at room temperature. The reaction mixture was stirred at r.t. for 48 h. After completion of the reaction as indicated by TLC (1:2 petroleum ether-ethyl acetate), the product was precipitated in the solvent (ethanol). Then filtered the product and washed with cold water. The pure product was then obtained 5.07g, in 82.7% yield; light yellow powders; ¹H NMR (500 MHz, DMSO) δ 9.60 (s, 1H, PhOH), 7.50 (d, *J* = 16.2 Hz, 1H, H-9), 7.23 (t, *J* = 7.8 Hz, 1H, H-13), 7.14 (d, *J* = 7.6 Hz, 1H, H-11), 7.05 (s, 1H, H-10), 6.94 – 6.74 (m, 2H, H-8, H-12), 5.05 (bs, 1H, OH), 4.92 (d, *J* = 4.6 Hz, 1H, OH), 4.85 (d, *J* = 4.7 Hz, 1H, OH), 4.44 – 4.28 (m, 1H, OH), 3.61 (ddd, *J* = 15.3, 10.9, 3.6 Hz, 2H, H-1, H-6a), 3.51 – 3.38 (m, 1H, H-6b), 3.24 – 3.13 (m, 1H,

H-3), 3.12 – 3.01 (m, 2H, H-4, H-5), 3.01 – 2.88 (m, 2H, H-2, H-7a), 2.80 (dd, J = 16.1, 8.8 Hz, 1H, H-7b).

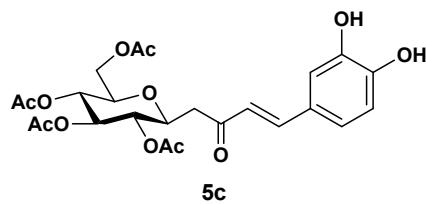
^{13}C NMR (126 MHz, DMSO): δ 197.5, 157.2, 141.7, 135.2, 129.4, 126.1, 118.9, 117.1, 114.2, 80.2, 77.6, 75.3, 73.0, 69.8, 60.6, 42.8. Elemental Anal. Found: C (59.18%) H (6.29%) Calcd for $\text{C}_{21}\text{H}_{28}\text{O}_7$ = C (59.25%) H (6.22%).

Compound 5b



To a solution of 1-*C*-(β -D-glucopyranosyl)-propan-2-one (5.0 g, 23.0mmol) and 4-hydroxybenzaldehyde (3.42g 28.0mmol) in ethanol (4.5mL) was added TEA (0.11 mL, 0.77mmol) and proline (0.4g 3.45mmol) at room temperature. The reaction mixture was stirred at r.t. for 48 h. After completion of the reaction as indicated by TLC (1:2 petroleum ether-ethyl acetate), the product was precipitated in the solvent (ethanol). Then filtered the product and washed with cold water. The pure product was then obtained 5.31g, in 85.6% yield; light yellow powders; ^1H NMR (500 MHz, DMSO) δ 7.53 (d, J = 8.5 Hz, 2H, H-10, H-12), 7.48 (d, J = 16.1 Hz, 1H, H-9), 6.79 (d, J = 8.4 Hz, 2H, H-11, H-13), 6.71 (d, J = 16.1 Hz, 1H, H-8), 3.65 – 3.52 (m, 2H, H-1, H-6a), 3.38 (dd, J = 11.7, 4.8 Hz, 1H, H-6b), 3.17 (t, J = 8.2 Hz, 1H, H-3), 3.11 – 2.99 (m, 1H, H-4, H-5), 2.94 (t, J = 9.1 Hz, 1H, H-2), 2.92 – 2.85 (m, 1H, H-7a), 2.74 (dd, J = 16.0, 8.8 Hz, 1H, H-7b). ^{13}C NMR (126 MHz, DMSO): δ 197.3, 159.1, 142.0, 129.9, 124.8, 122.9, 115.4, 80.1, 77.6, 75.4, 73.0, 69.8, 60.6, 42.7. Elemental Anal. Found: C (59.20%) H (6.32%) Calcd for $\text{C}_{21}\text{H}_{28}\text{O}_7$ = C (59.25%) H (6.22%).

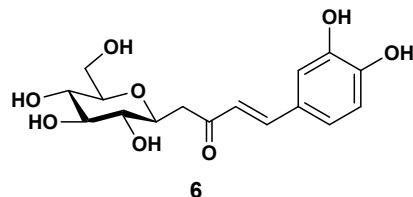
Compound 5c



To a solution of compound 4c (5.0 g, 23.0mmol) and 3,4-dihydroxybenzaldehyde (3.87g 28.0mmol) in ethanol (4.5mL) was added TEA (0.11 mL, 0.77mmol) and proline (0.4g 3.45mmol) at room temperature. The reaction mixture was stirred at r.t. for 48 h. After completion of the reaction as indicated by TLC (1:2 petroleum ether-ethyl acetate), the product was purified by silica gel column chromatography using 1:1

petroleum ether-ethyl acetate to furnish pure products 6.15g, in 92.3% yield; light yellow powders; ¹H NMR (500 MHz, CDCl₃) δ 7.45 (d, *J* = 16.1 Hz, 1H, H-9), 7.13 (s, 1H, H-10), 6.98 (d, *J* = 8.3 Hz, 1H, H-12), 6.88 (d, *J* = 8.3 Hz, 1H, H-11), 6.56 (d, *J* = 16.1 Hz, 1H, H-8), 5.22 (t, *J* = 9.4 Hz,), 5.08 (t, *J* = 9.5 Hz), 4.97 (t, *J* = 9.5 Hz), 4.24 (dd, *J* = 12.4, 4.9 Hz, 1H, H-6a), 4.09 – 3.98 (m, 2H, H-5, H-6b), 3.71 (ddd, *J* = 10.0, 3.8, 1.8 Hz, 1H, H-1), 2.97 (dd, *J* = 16.2, 6.9 Hz, 1H, H-7a), 2.65 (dd, *J* = 16.2, 2.4 Hz, 1H, H-7b), 2.01 (m, 12H, Ac). ¹³C NMR (126 MHz, CDCl₃): δ 196.1, 190.7, 170.3, 169.4, 169.2, 168.8, 146.5, 143.7, 143.3, 126.0, 122.8, 122.4, 114.6, 113.3, 74.7, 73.3, 73.2, 70.7, 67.7, 61.3, 41.4, 19.7. Elemental Anal. Found: C (56.63%) H (5.59%) Calcd for C₂₁H₂₈O₇ = C (56.69%) H (5.55%).

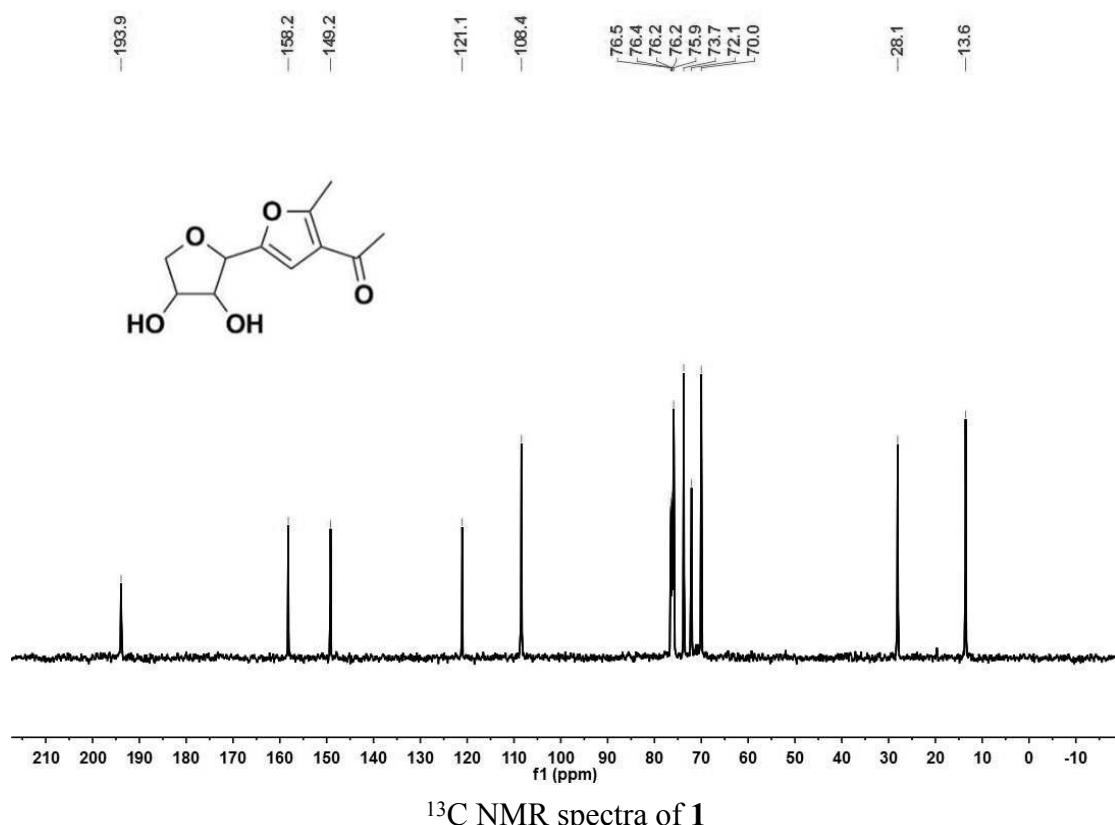
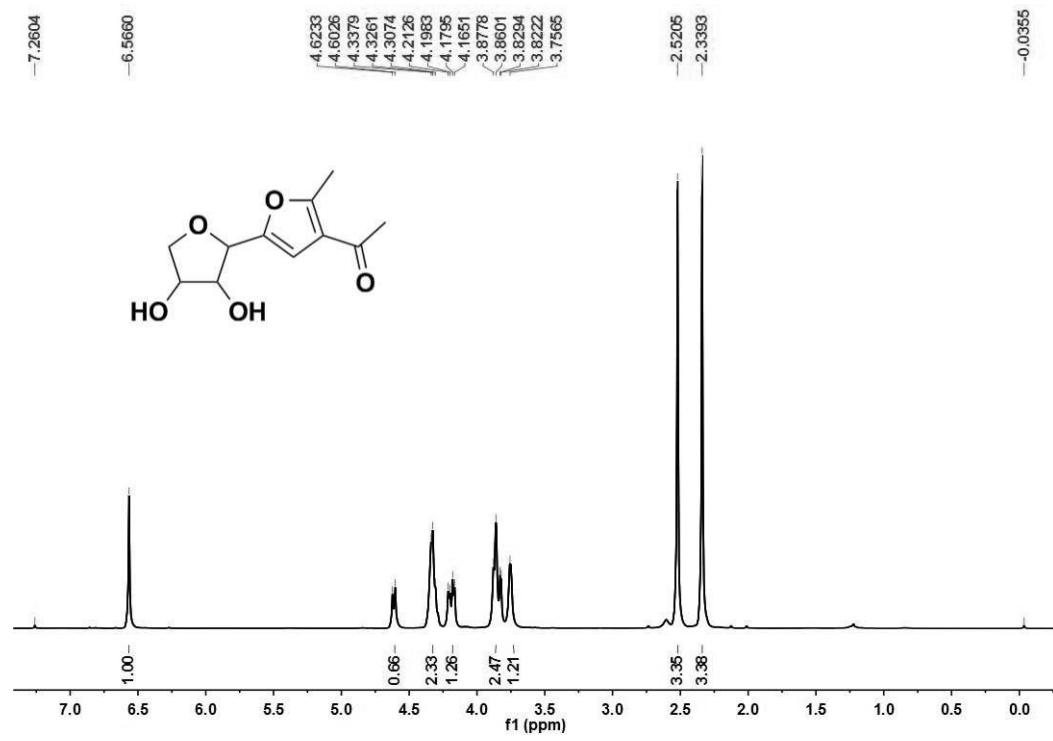
Compound 6

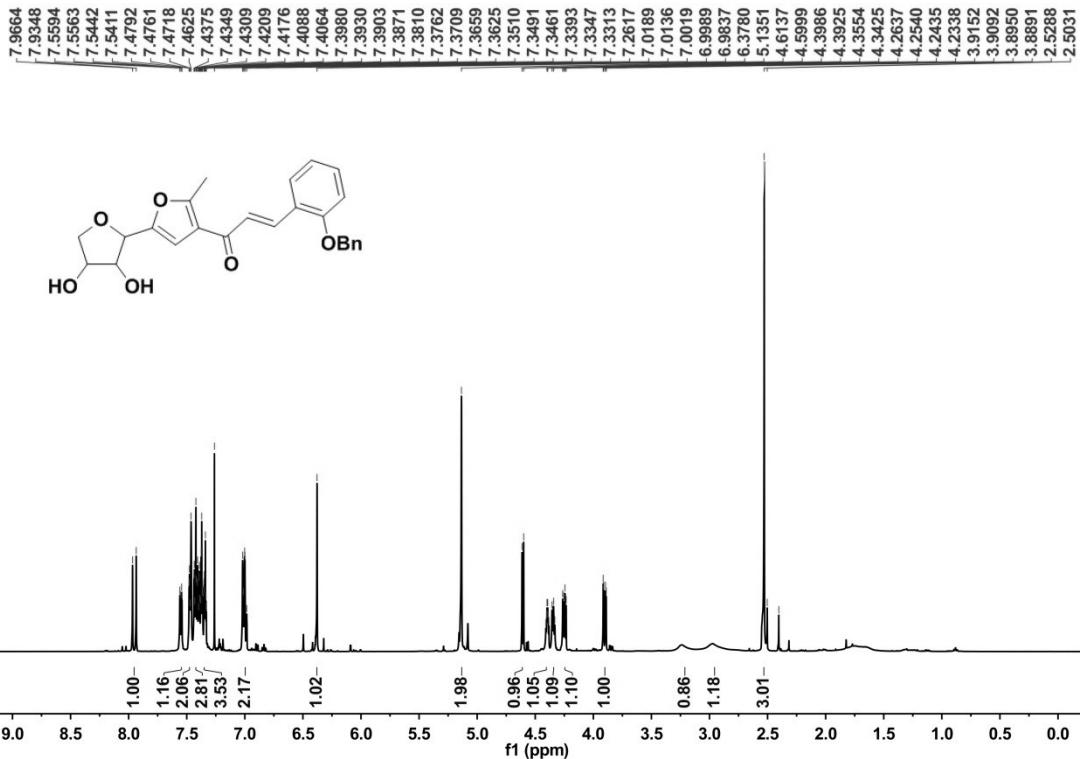


To a solution of compound **5c** (0.5 g, 0.98 mmol) and MeONa (0.1 g 1.56 mmol) in methanol (10 mL) was stirred at room temperature for 2h. After completion of the reaction, the mixture was treated with cation exchange resin (sodium form) to reach pH 5. The resin was filtered and methanol was evaporated. The final product was obtained 0.25g, in 75.1% yield; yellow oil, ¹H NMR (500 MHz, DMSO) δ 7.50 (d, *J* = 16.1 Hz, 1H, H-9), 7.12 (s, 1H, H-10), 6.99 (d, *J* = 8.3 Hz, 1H, H-12), 6.80 (d, *J* = 8.3 Hz, 1H, H-11), 6.54 (d, *J* = 16.1 Hz, H-8), 5.05 (bs, 1H, OH), 4.92 (bs, 1H, OH), 4.85 (bs, 1H, OH), 4.43 – 4.22 (m, 1H, H-4), 3.61 (ddd, *J* = 12.2, 9.3, 3.6 Hz, 2H, H-1, H-6a), 3.42 (dd, *J* = 12.4, 4.9 Hz, H-6b), 3.24 – 3.12 (m, 1H, H-3), 3.12 – 3.01 (m, 2H, H-4, H-5), 3.00 – 2.89 (m, 2H, H-2, H-7a), 2.80 (dd, *J* = 16.2, 8.6 Hz, 1H, H-7b).

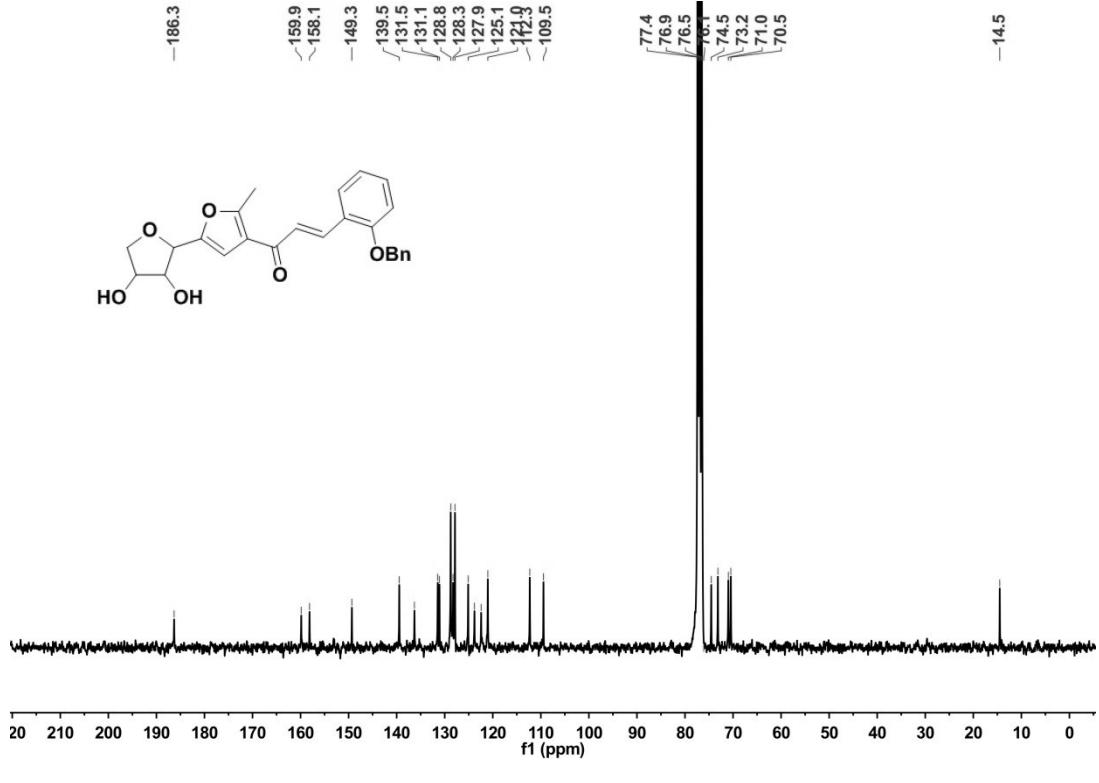
¹³C NMR (126 MHz, DMSO): δ 197.3, 147.4, 144.1, 143.5, 126.1, 122.9, 122.6, 114.8, 113.6, 80.1, 77.6, 75.4, 73.1, 69.8, 60.6, 42.7. Elemental Anal. Found: C (56.39%) H (5.98%) Calcd for C₂₁H₂₈O₇ = C (56.47%) H (5.92%).

NMR Spectra for compounds

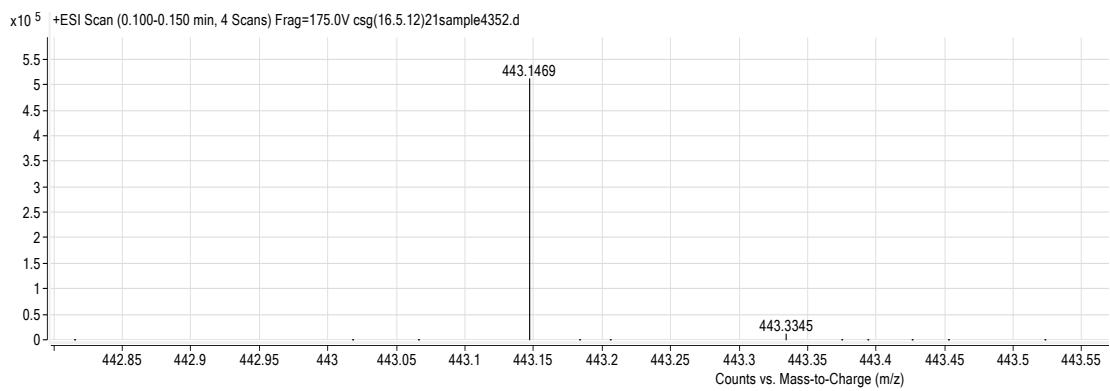




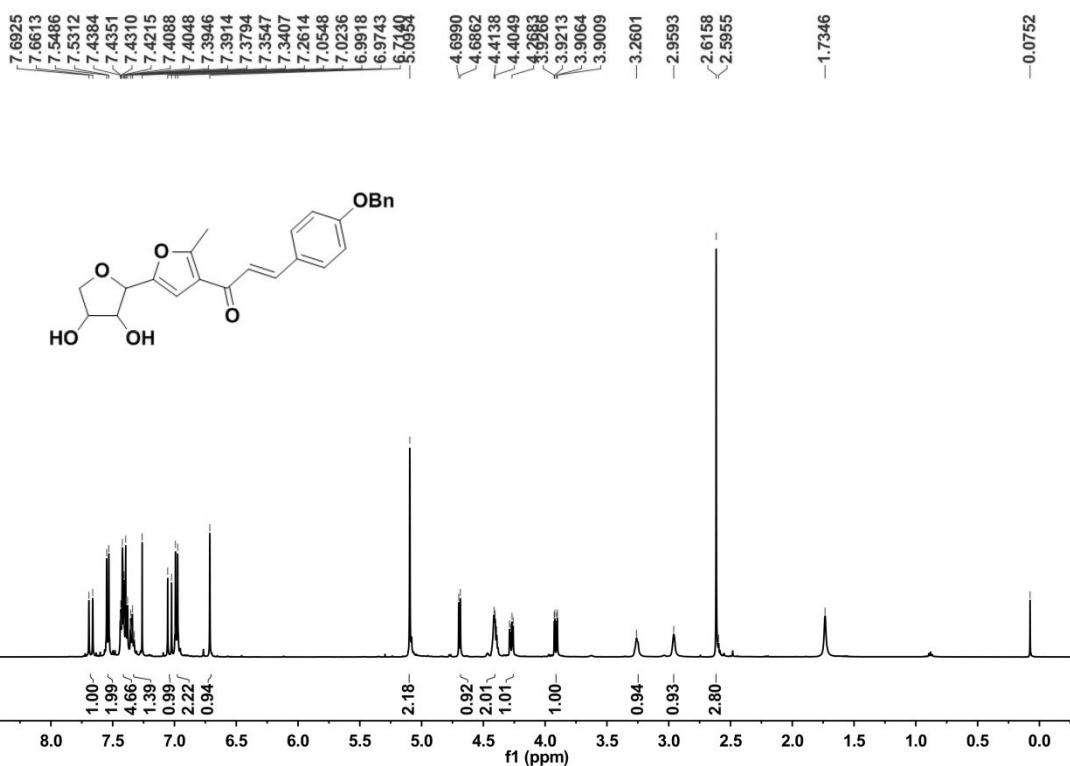
¹H NMR spectra of **2a**



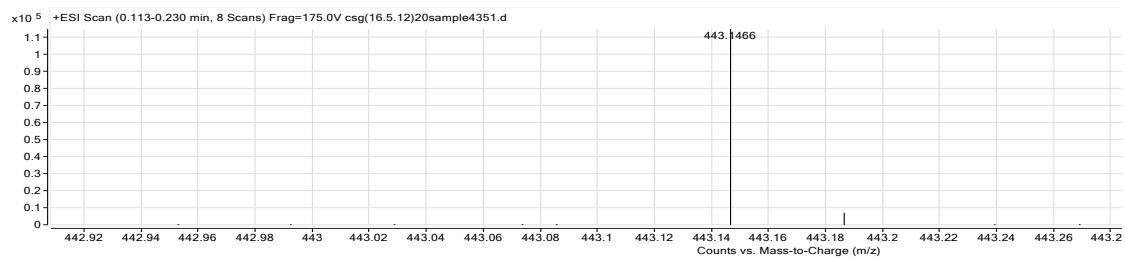
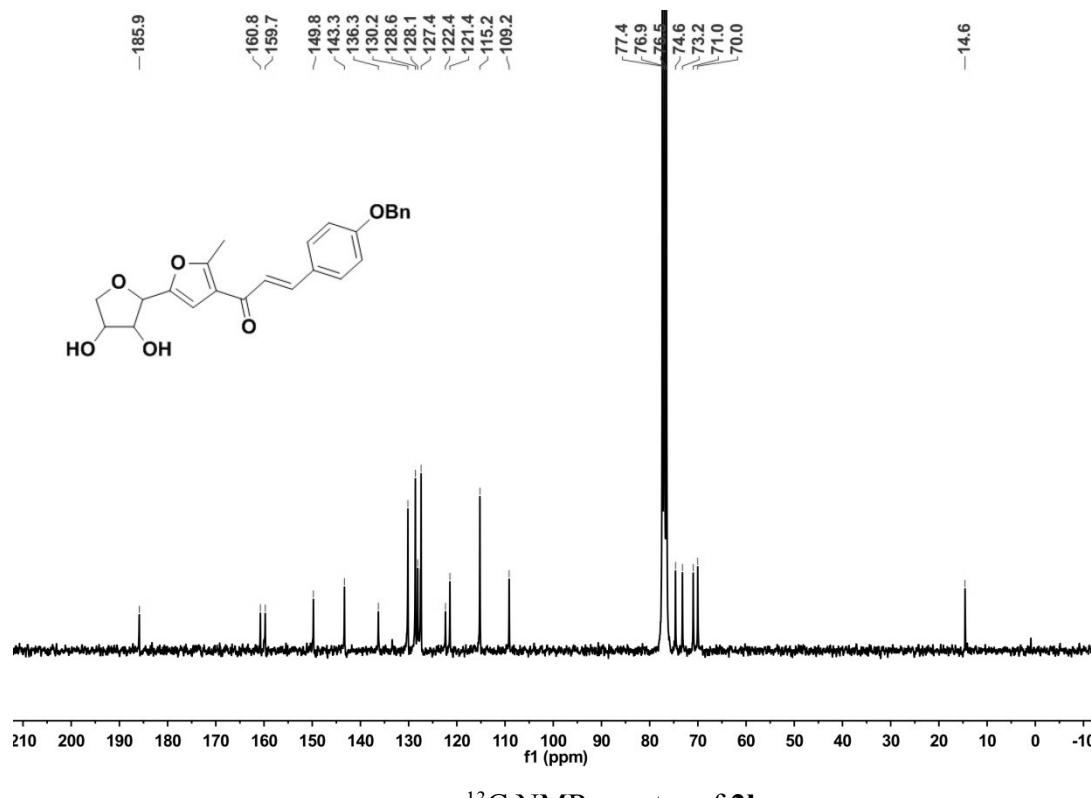
¹³C NMR spectra of **2a**



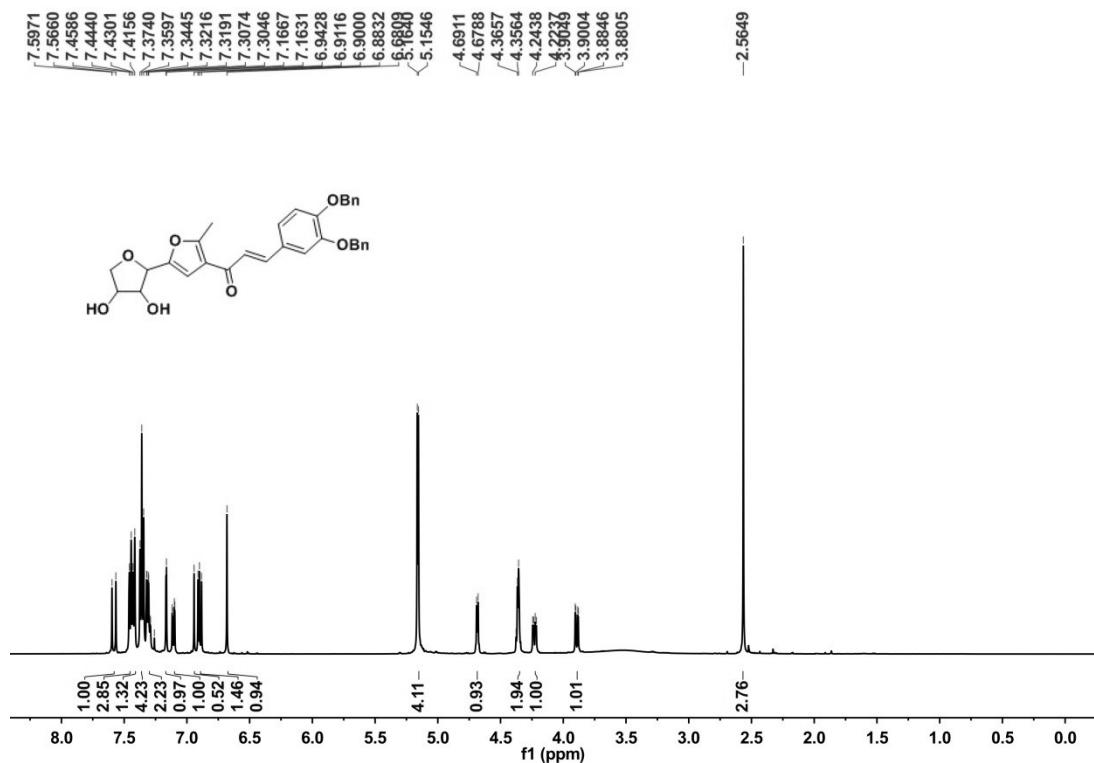
HRMS spectra of **2a**



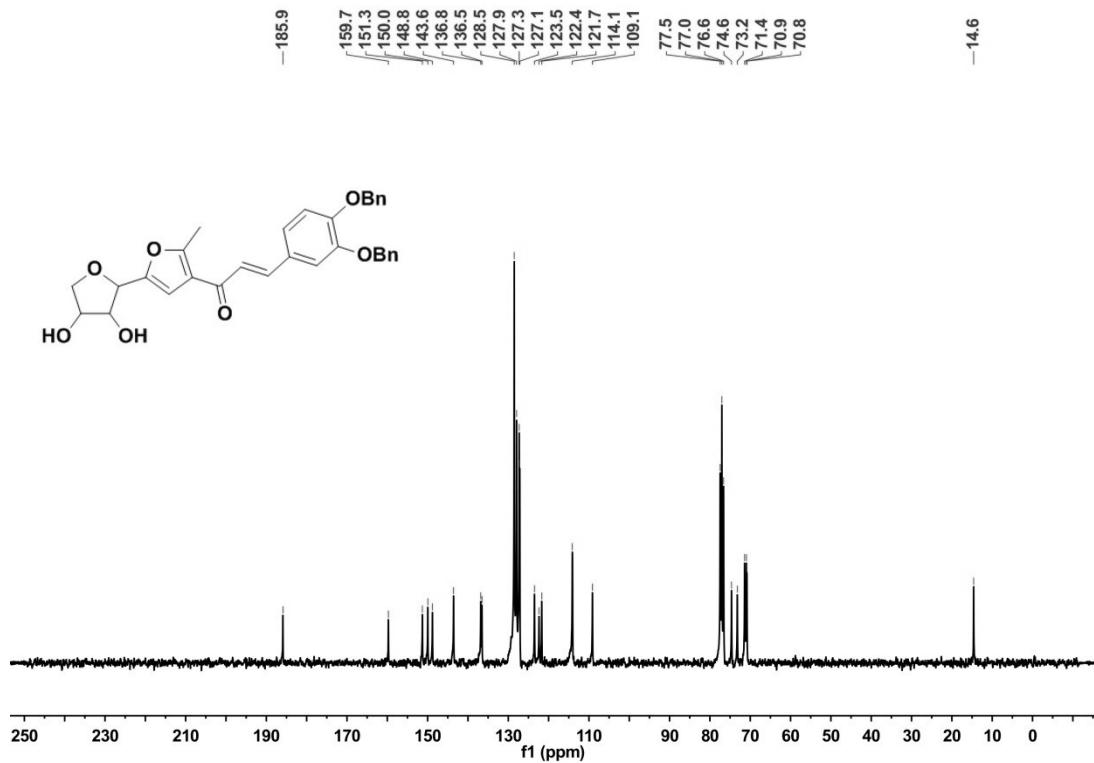
¹H NMR spectra of **2b**



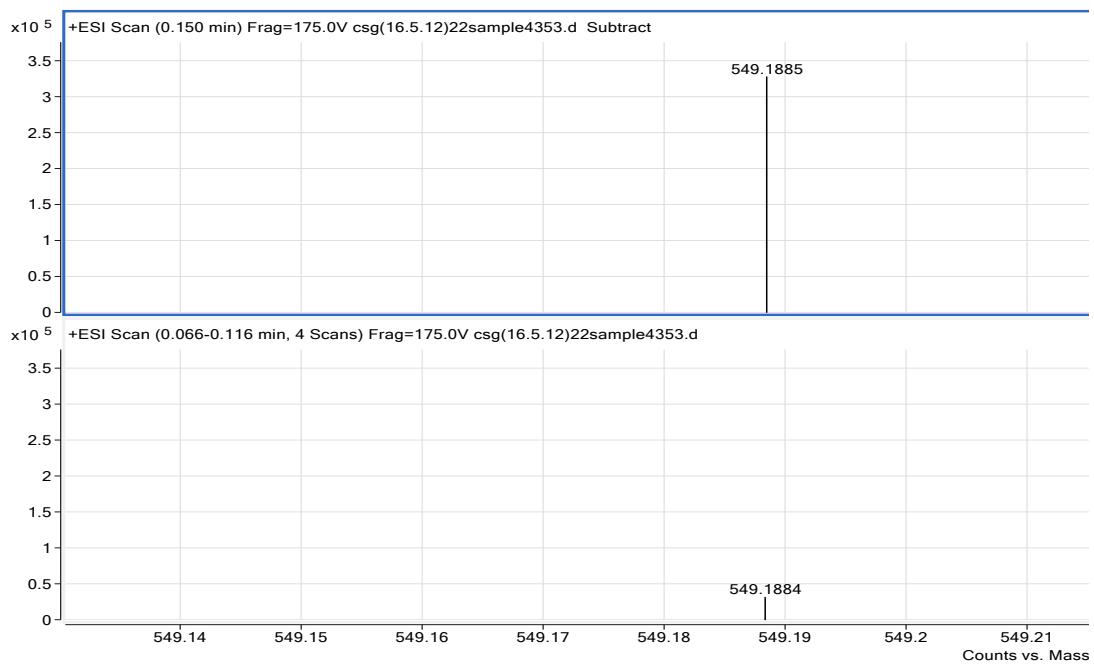
HRMS spectra of **2b**



¹H NMR spectra of **2c**

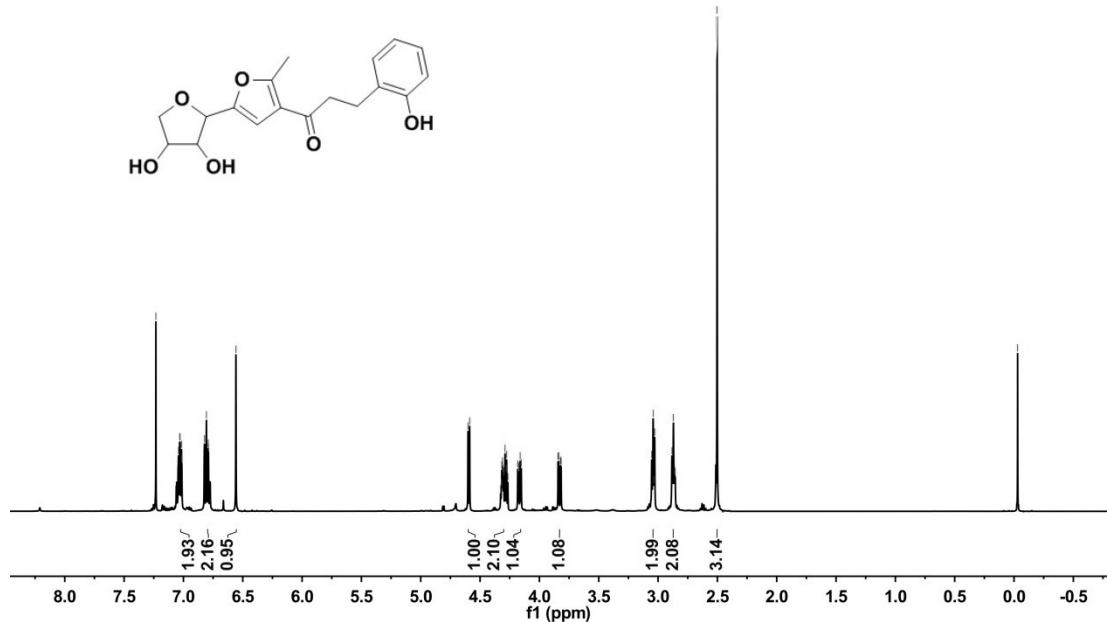


¹³C NMR spectra of **2c**

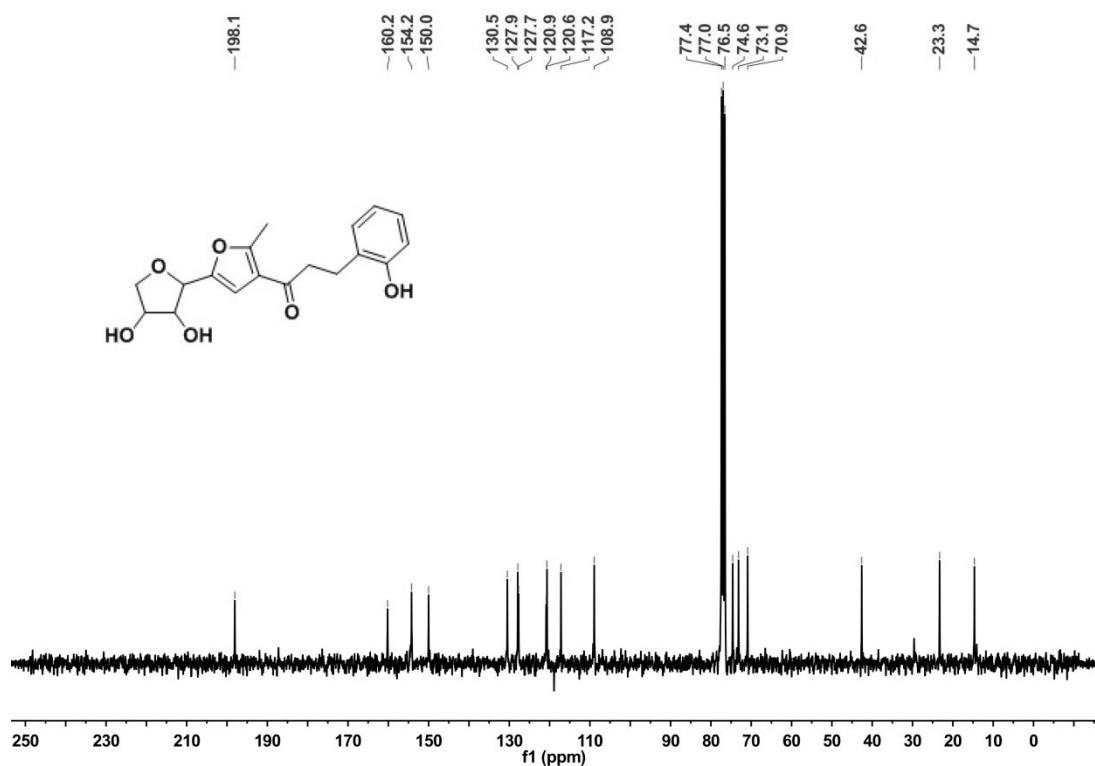


HRMS spectra of **2c**

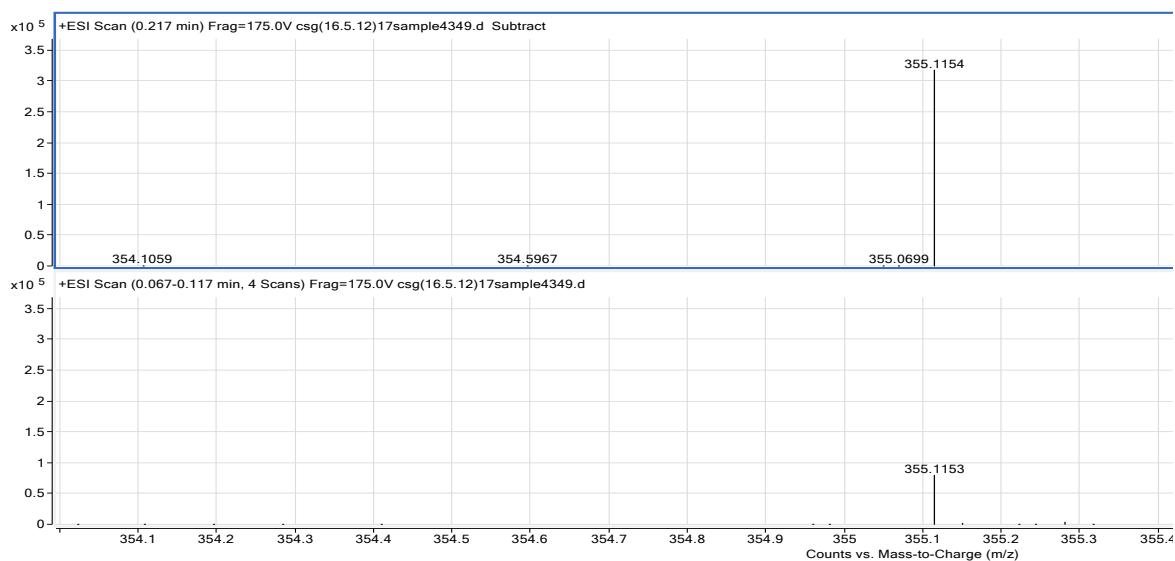
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4.6015
4.5880
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4.2762
4.1825
4.1730
4.1623
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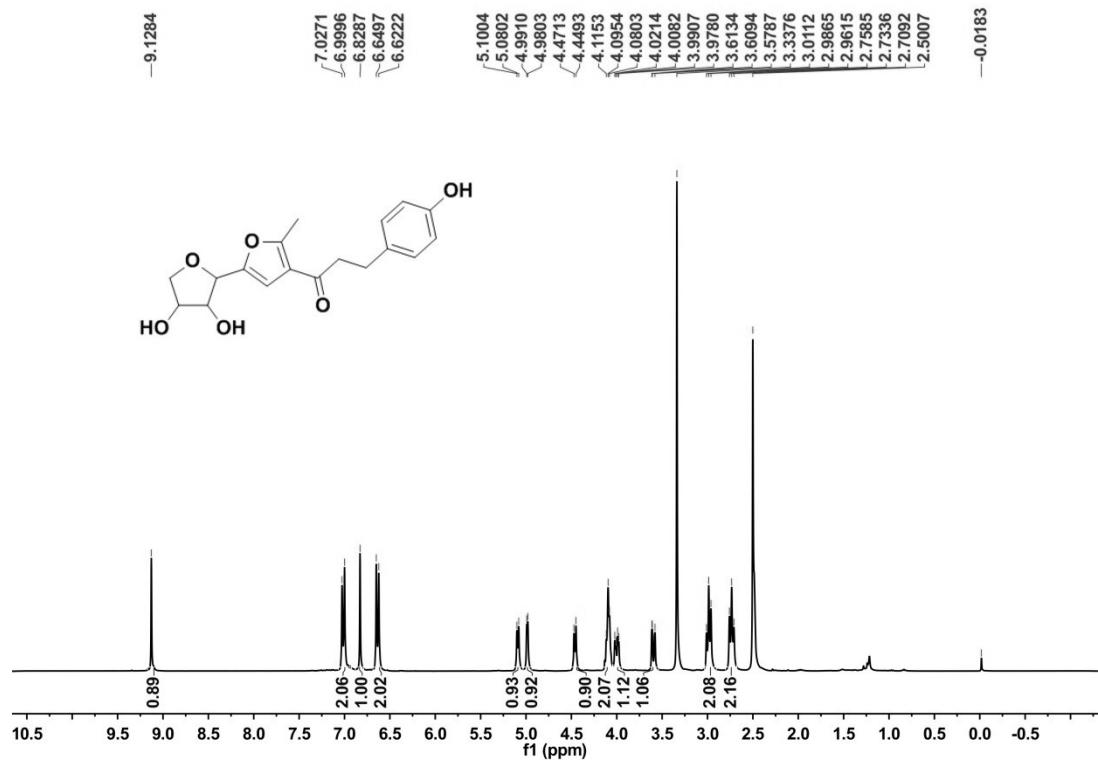


¹H NMR spectra of **3a**

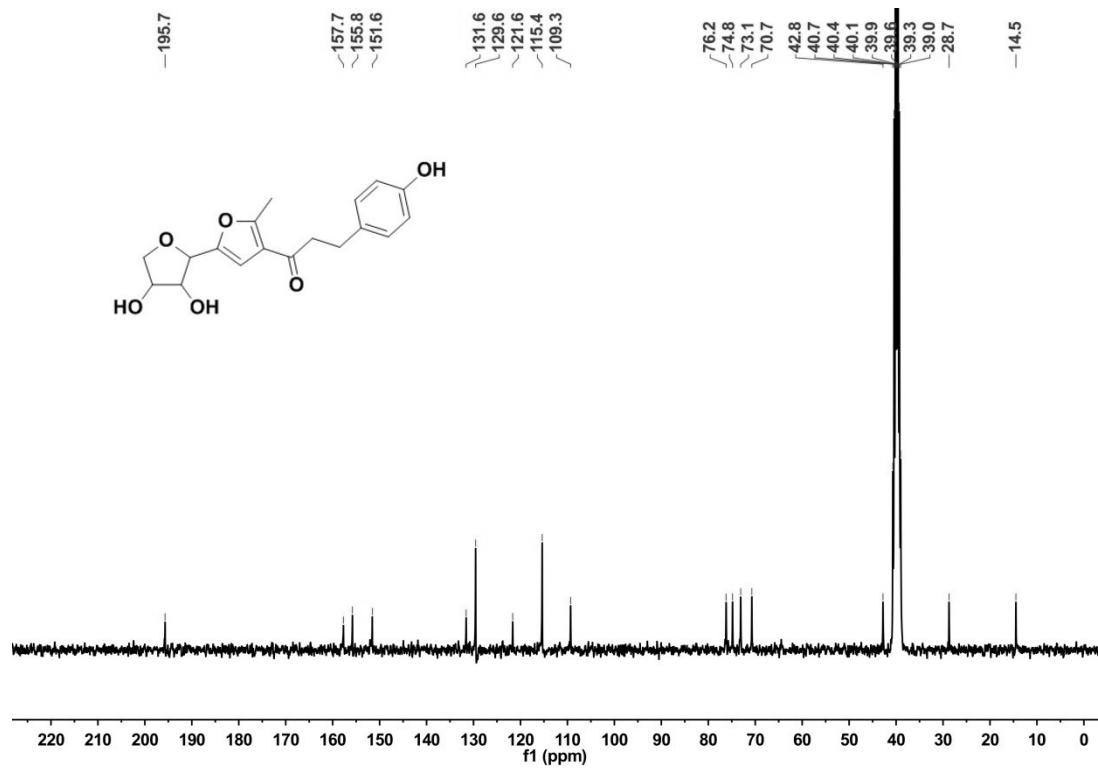


^{13}C NMR spectra of **3a**

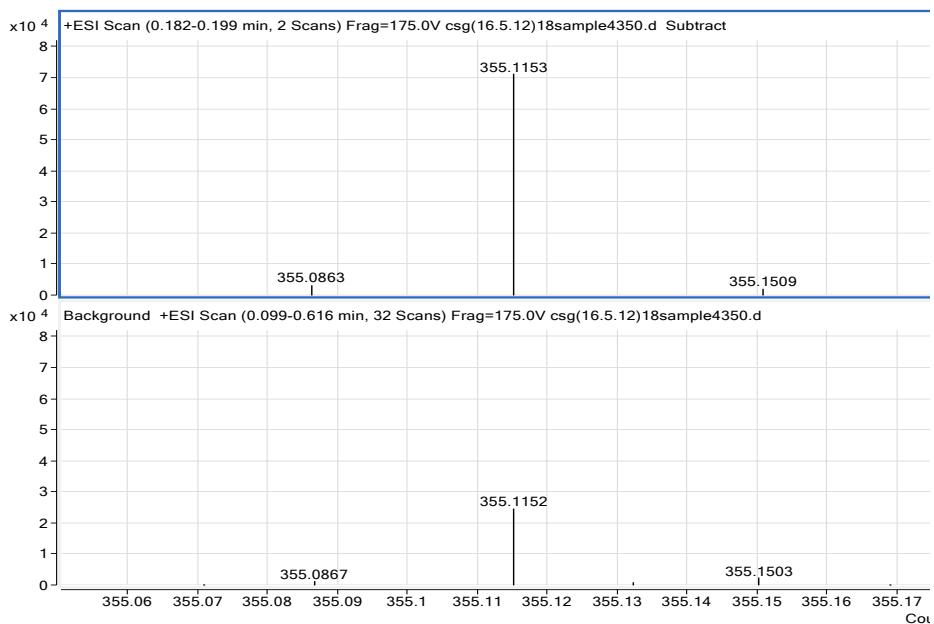




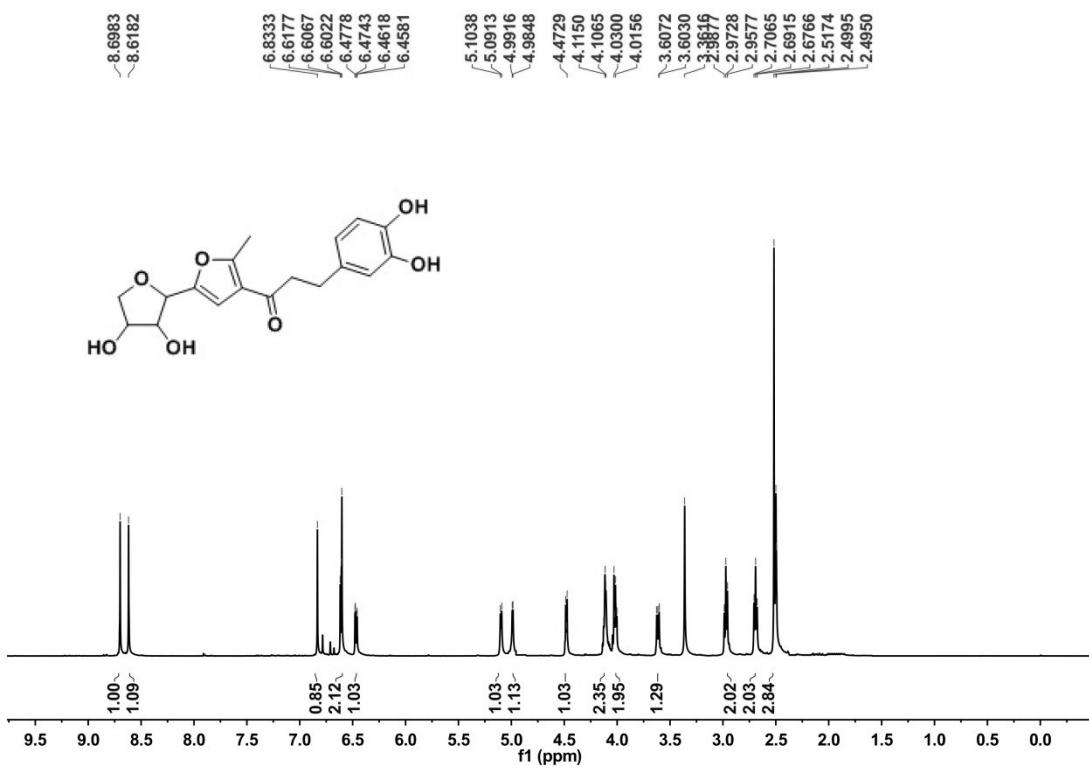
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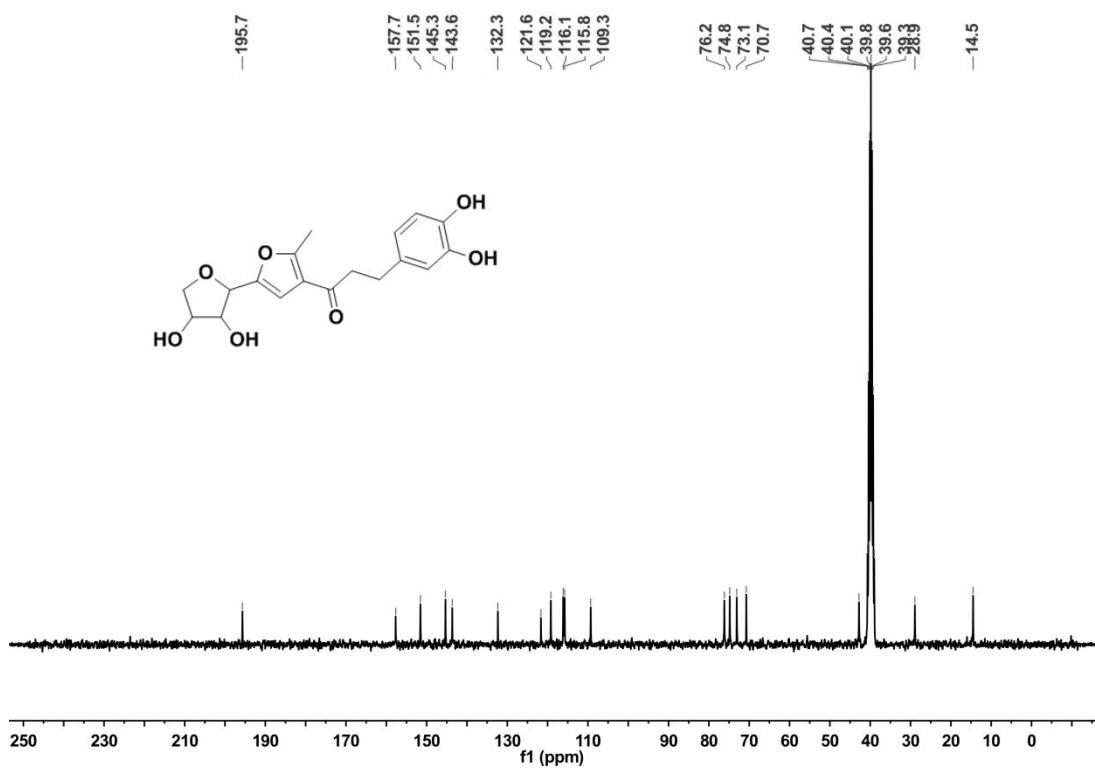
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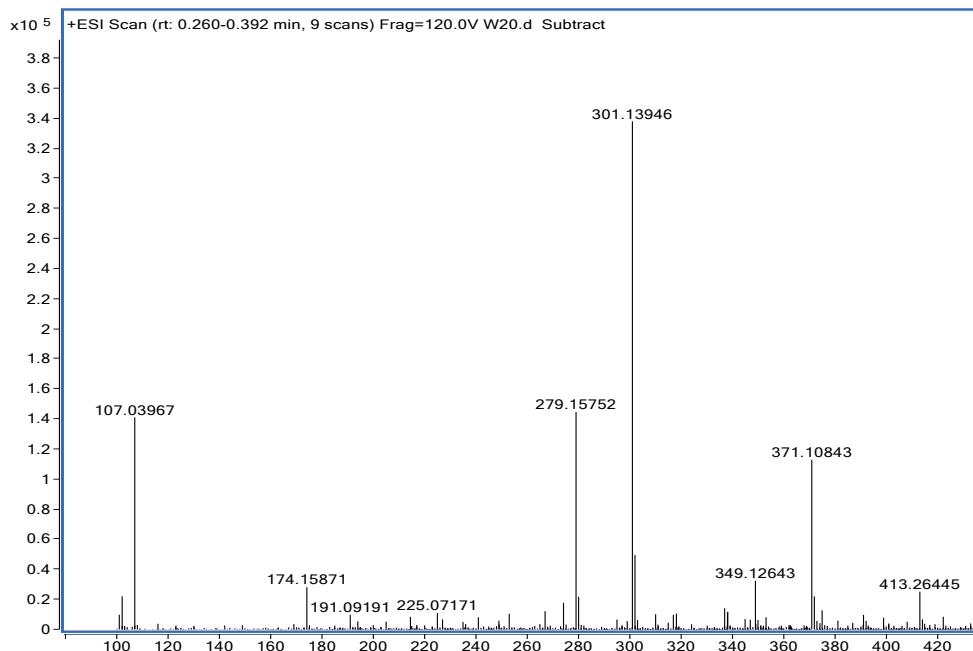
HRMS spectra of **3b**



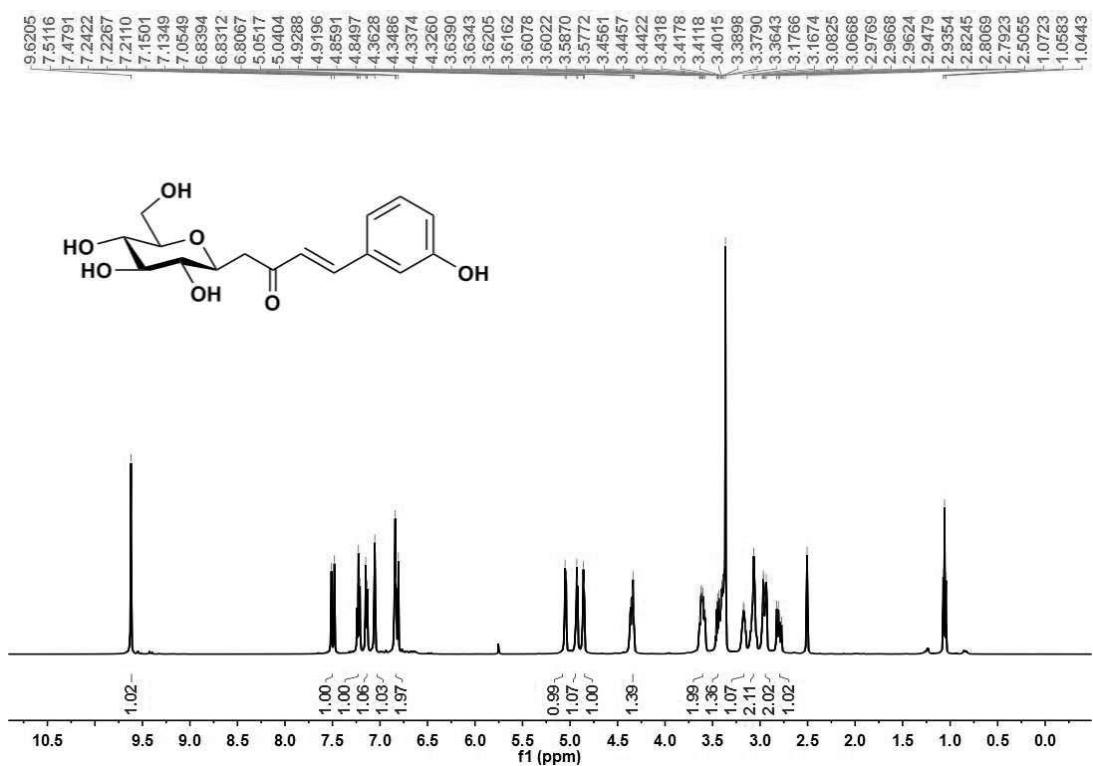
¹H NMR spectra of **3c**



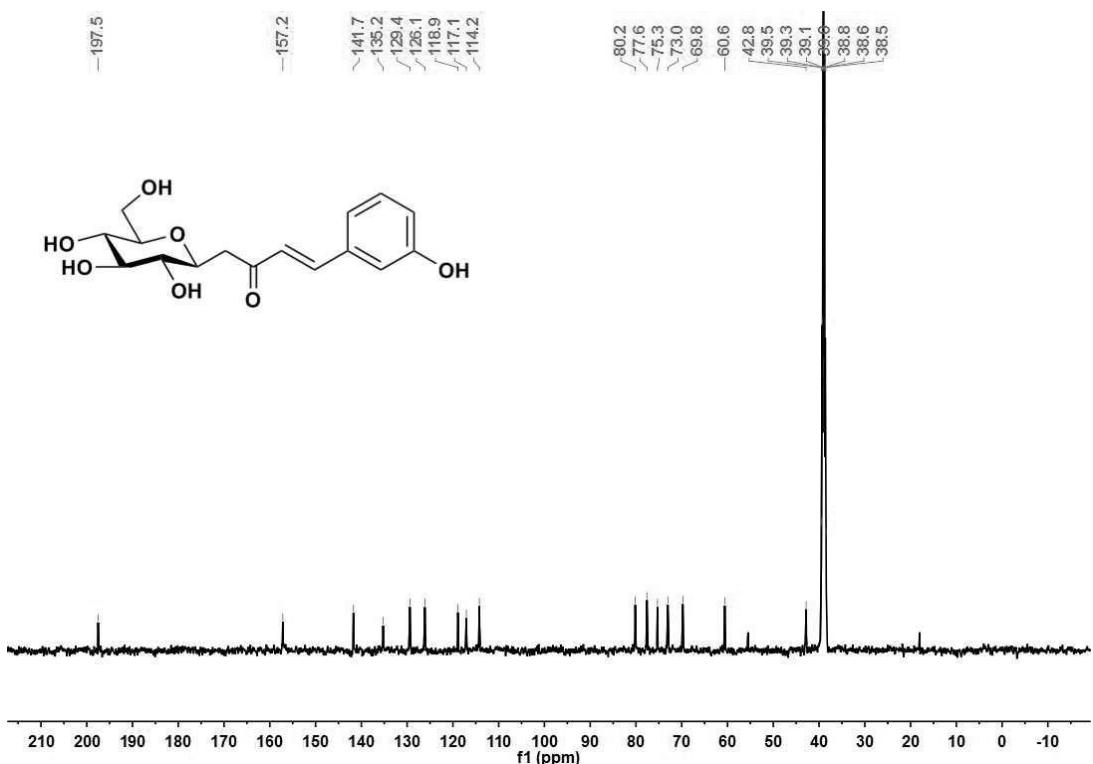
^{13}C NMR spectra of **3c**



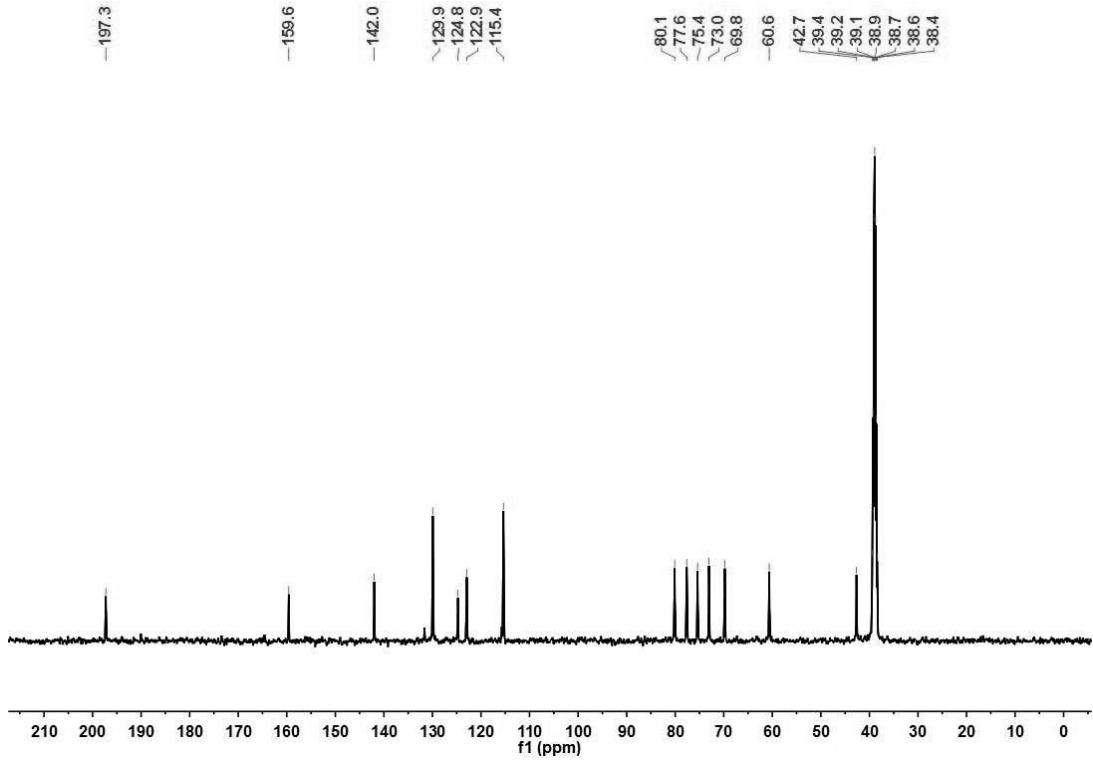
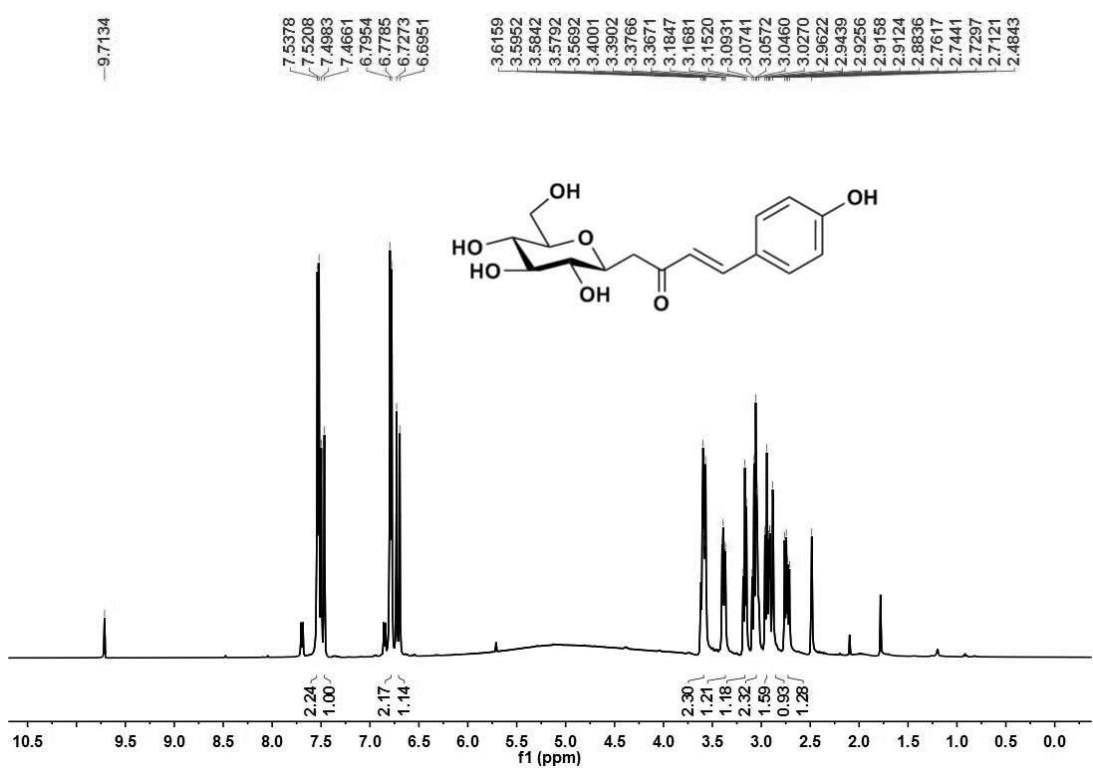
HRMS spectra of **3c**



¹H NMR spectra of **5a**



¹³C NMR spectra of **5a**



¹³C NMR spectra of **5b**

