Supporting Information

Tandem Activated Caged Galactoside Prodrugs: Advancing Beyond Single Galactosidase Dependence

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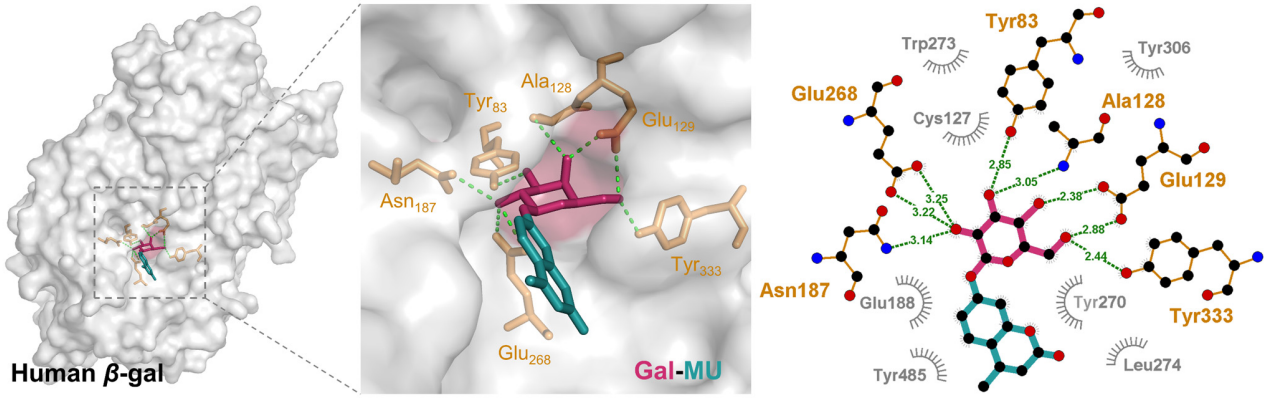


Figure S1. The docking of Gal-MU with human *β*-gal (PDB: 3THC). *β*-gal is shown as a grey surface, key amino acid residues interacting with the hydroxy groups are shown in yellow, and Gal-MU is shown as stick models with the galactose moiety in red and MU in green.

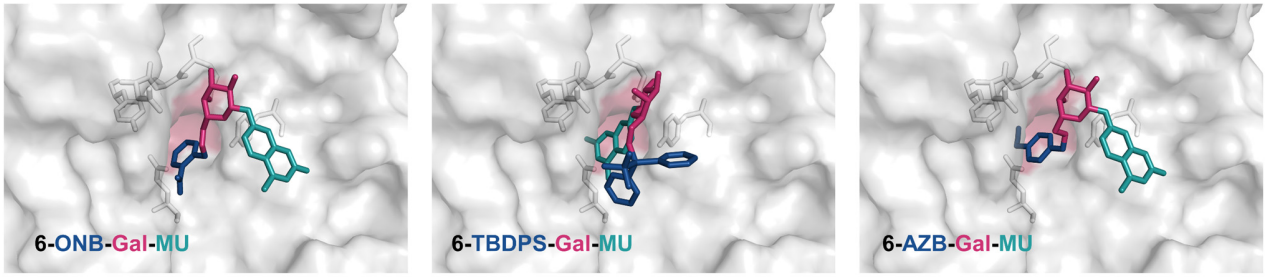


Figure S2. The docking of TACG model compounds with *A. oryzae β*-gal (PDB: 4IUG). *β*-gal is shown as a grey surface and TACG are shown as stick models with the galactose moiety in red, MU in green, and the masking group in blue.

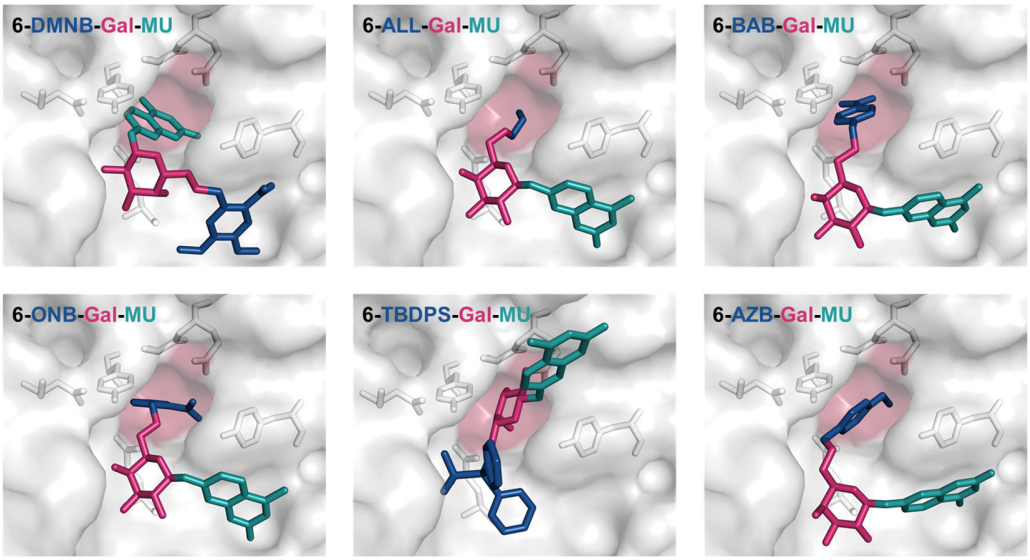
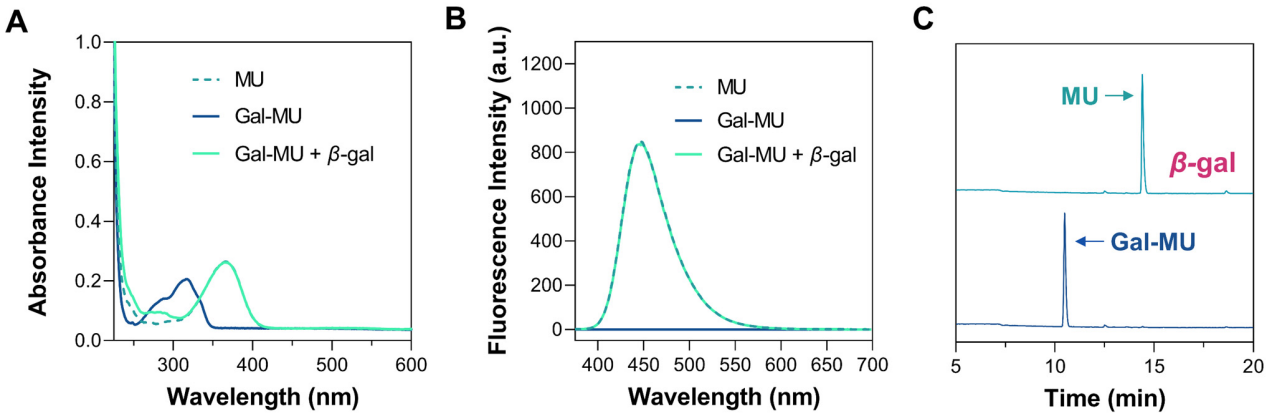


Figure S3. The docking of TACG model compounds with human *β*-gal (PDB: 3THC). *β*-gal is shown as a grey surface and TACG are shown as stick models with the galactose moiety in red, MU in green, and the masking group in blue.



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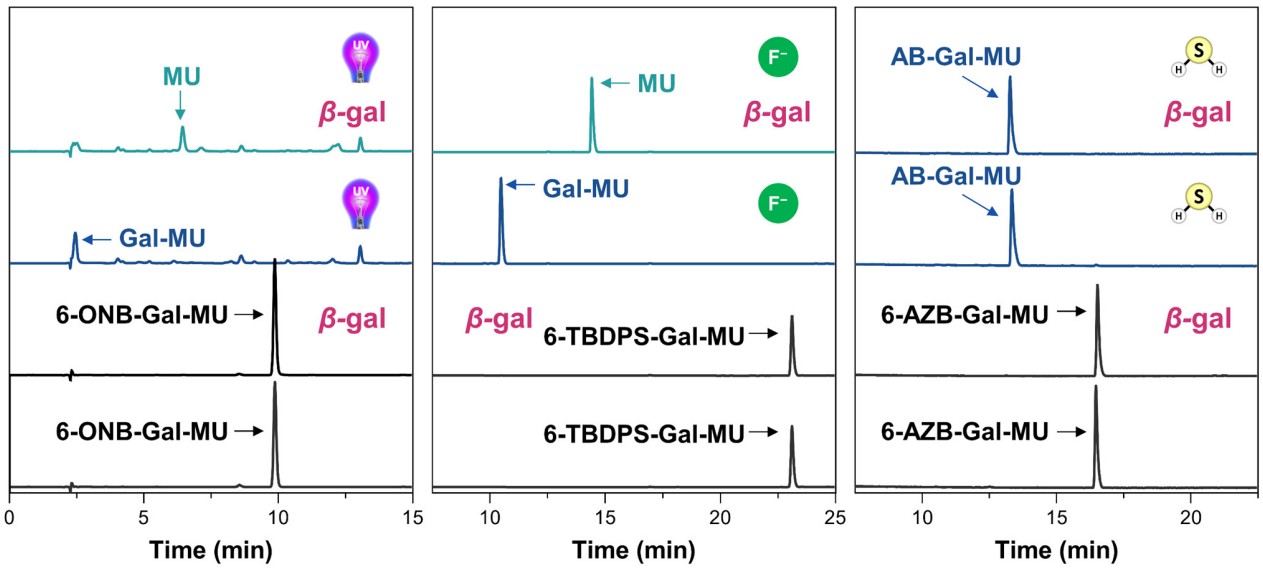
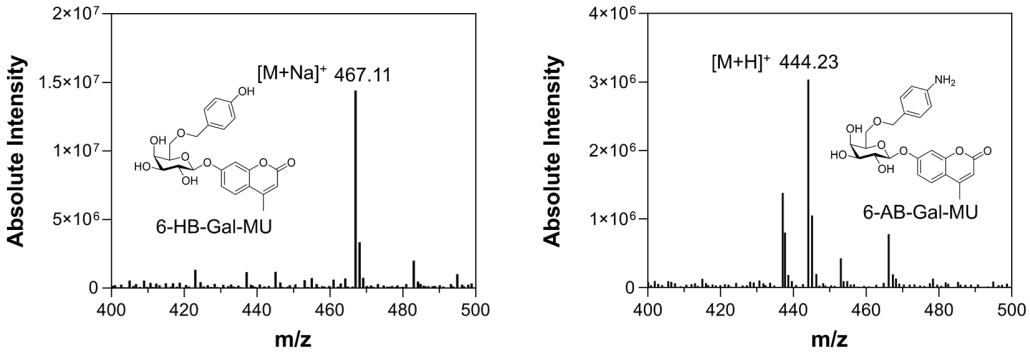


Figure S5. HPLC study of the dual-stimulus responsiveness TACG model compounds of 6-ONB-Gal-MU, 6-TBDPS-Gal-MU, and 6-AZB-Gal-MU.



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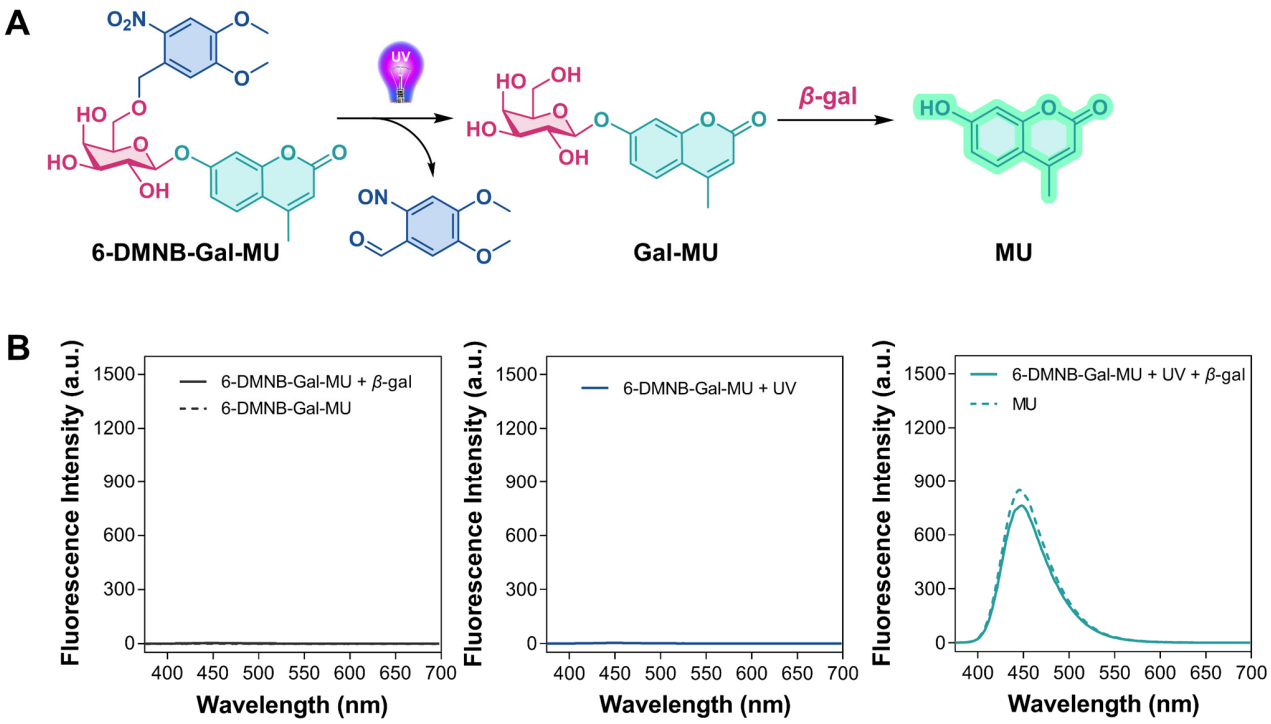

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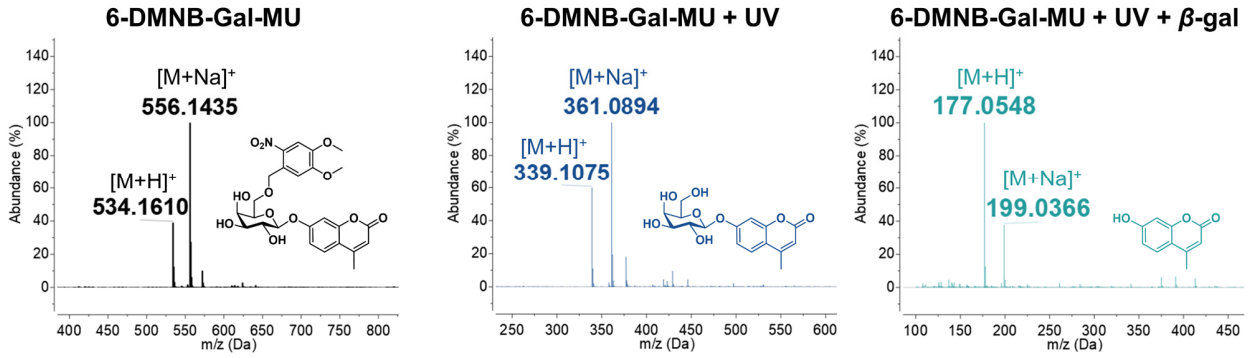

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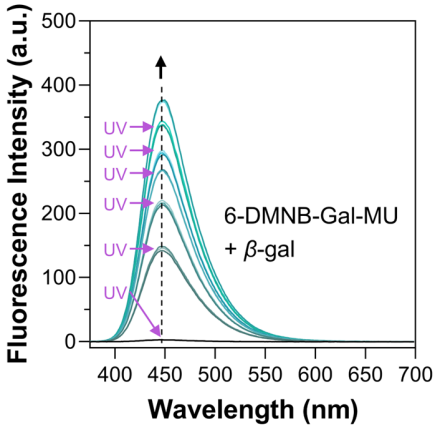
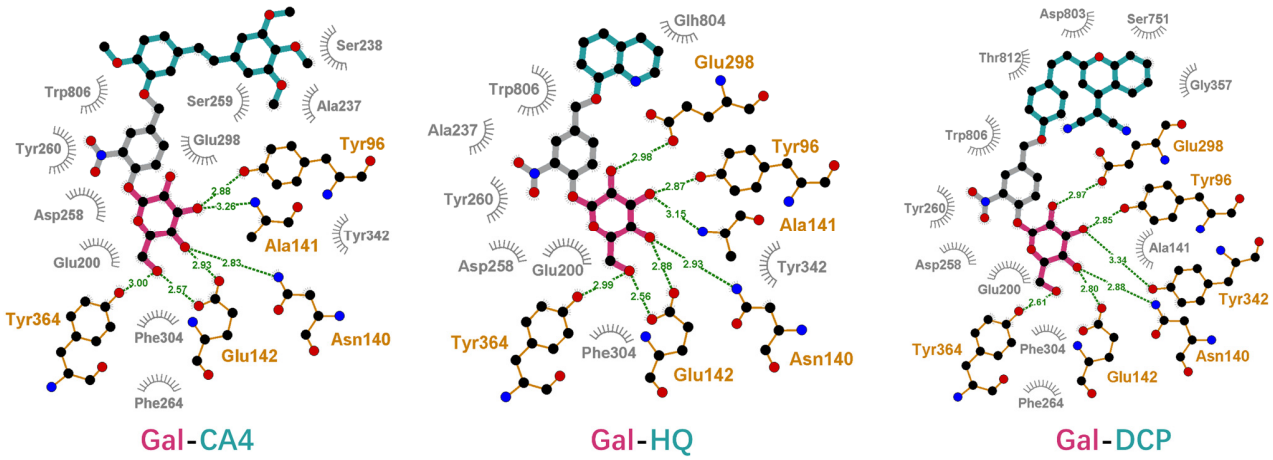


Figure S9. On-demand release of MU from 6-DMNB-Gal-MU solution containing β-gal under UV irradiation (5 seconds each) as recorded by fluorescence spectroscopy (λ_{ex} = 365 nm, λ_{em} = 448 nm).



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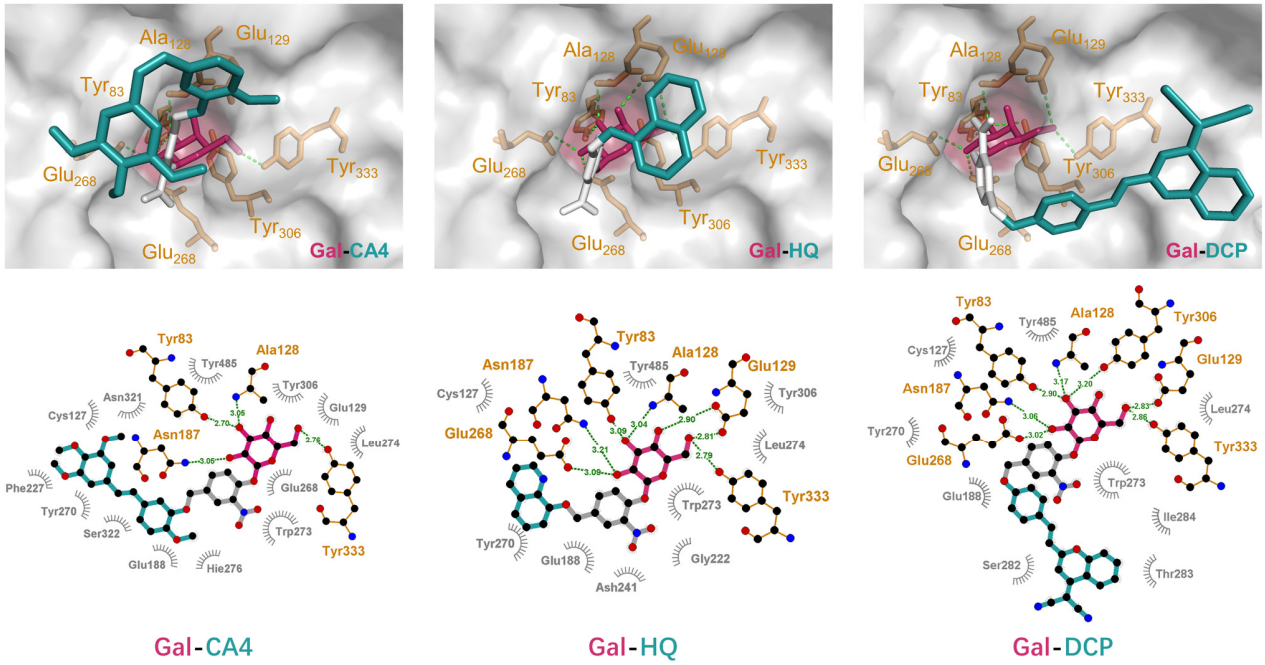
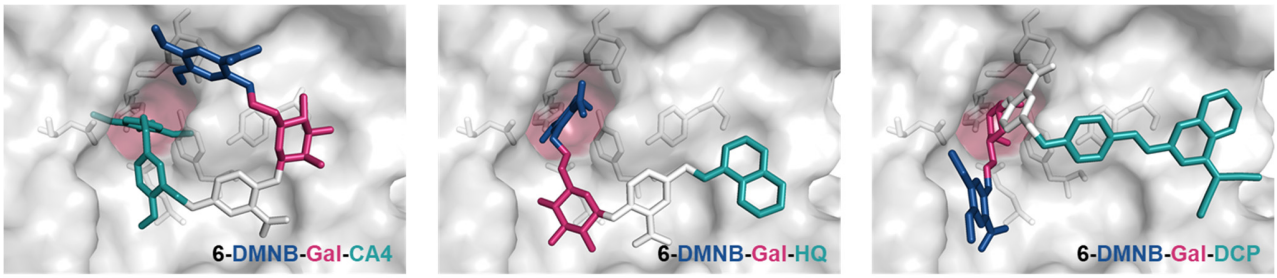


Figure S11. The docking of Gal-CA4, Gal-HQ, and Gal-DCP with human β-gal (PDB: 3THC). β-gal is shown as a grey surface, key amino acid residues interacting with the hydroxy groups are shown in yellow, and galactosides are shown as stick models with the galactose moiety in red, self-immolative spacer in light grey, and drug molecules in green.



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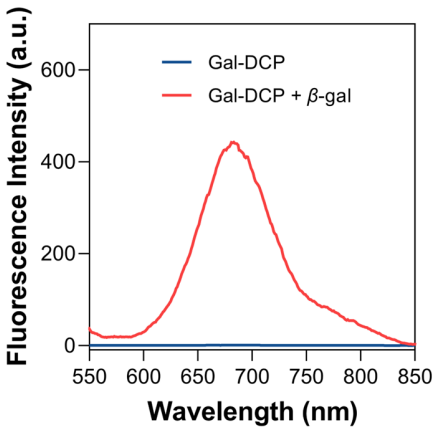

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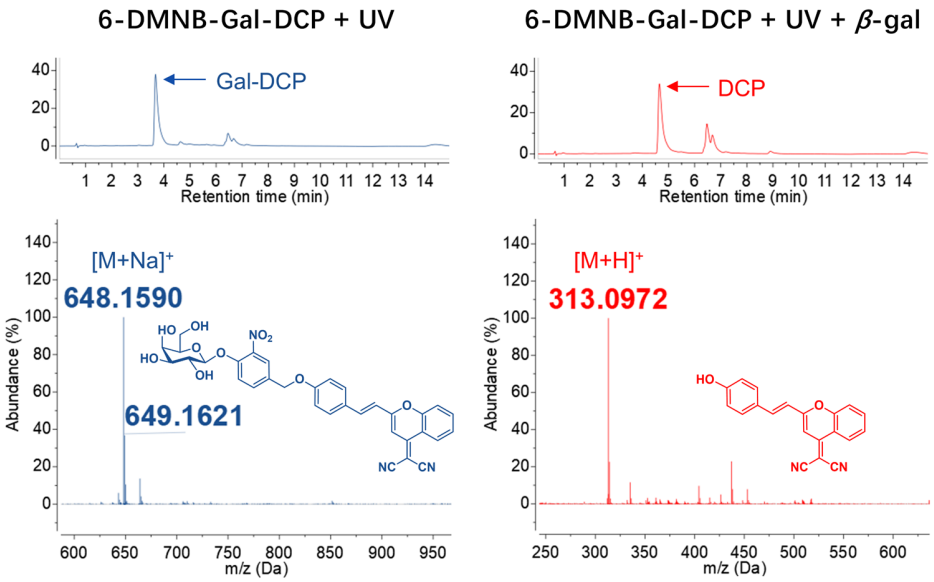

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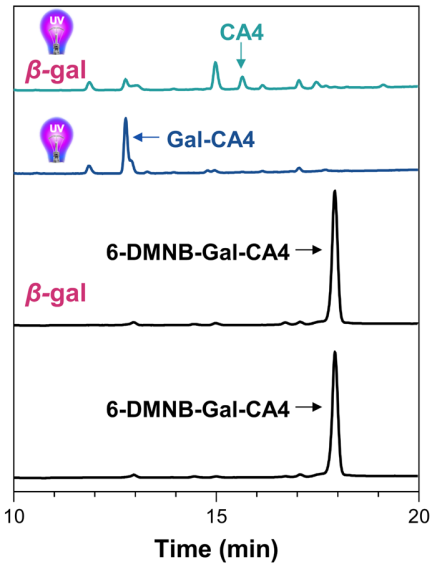

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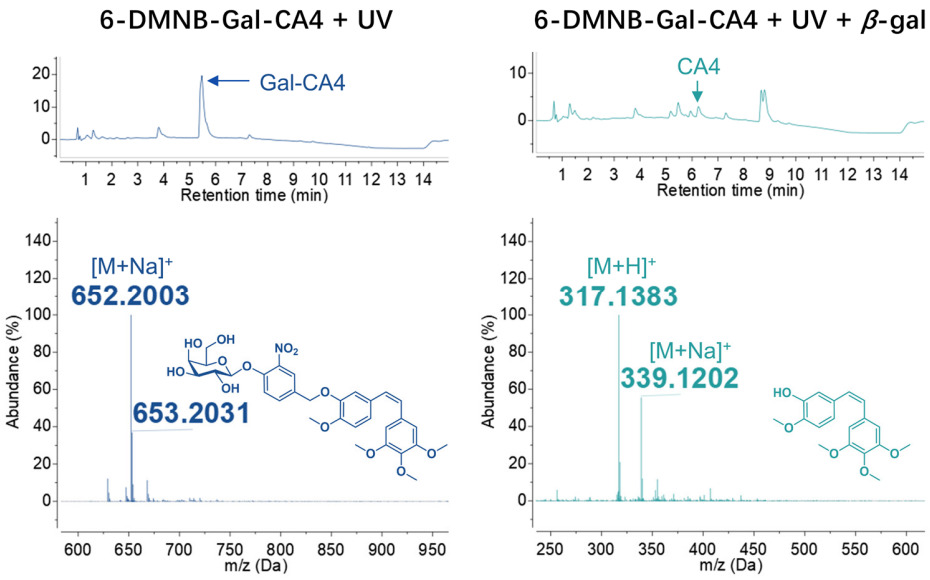

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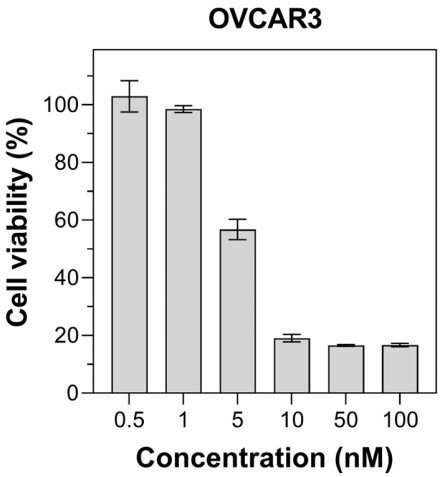

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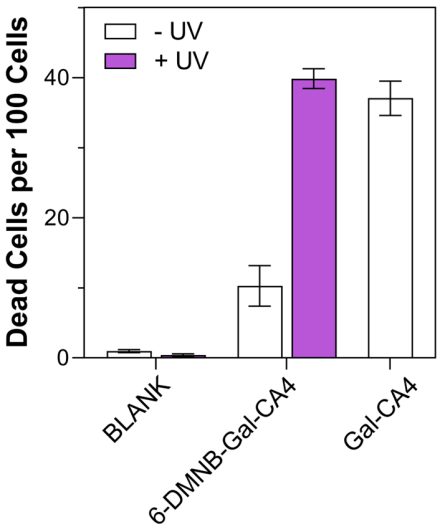

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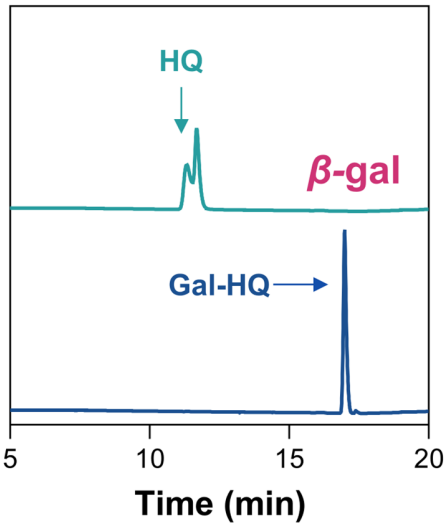

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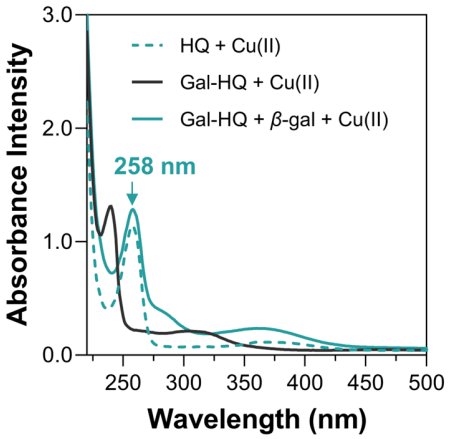

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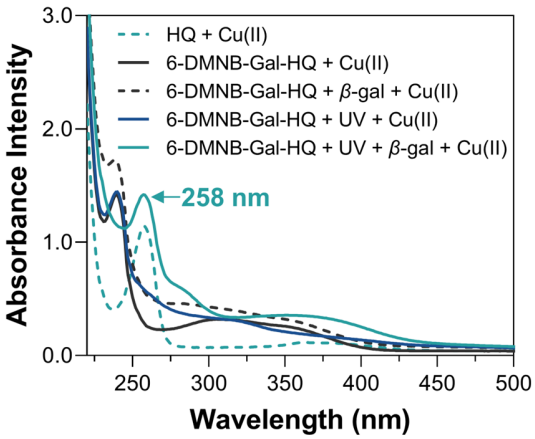

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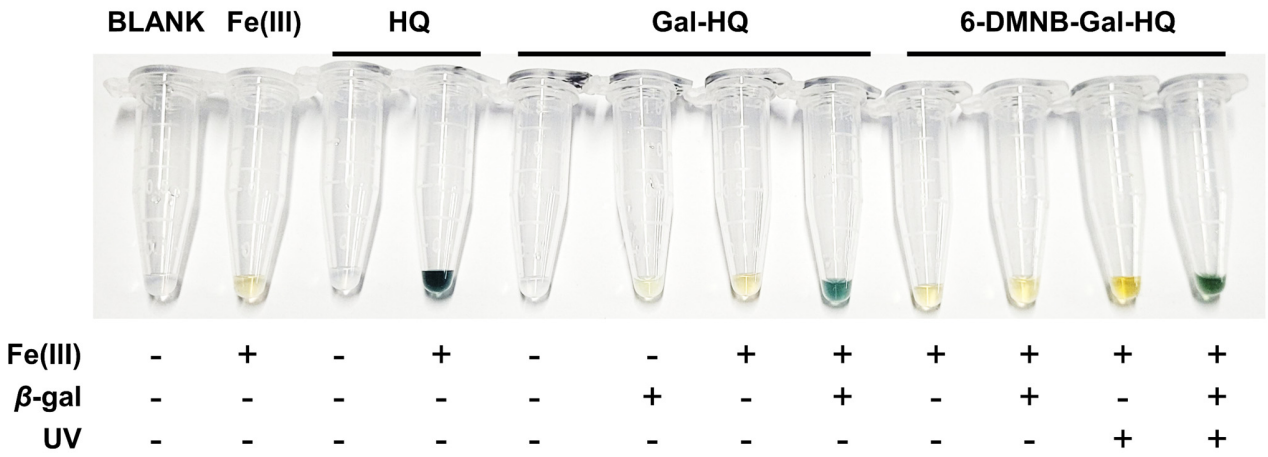

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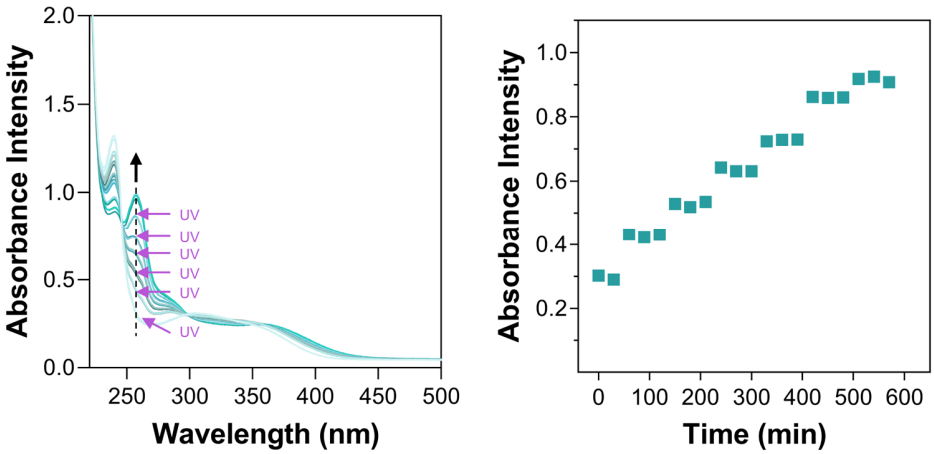

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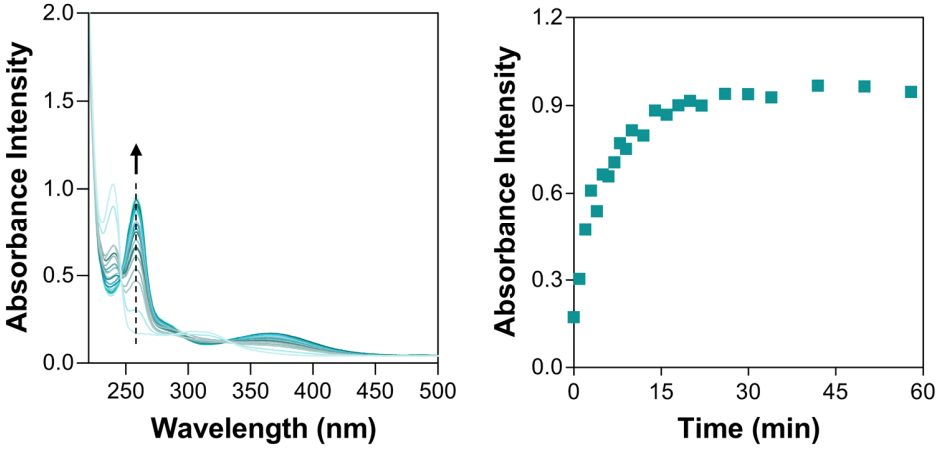

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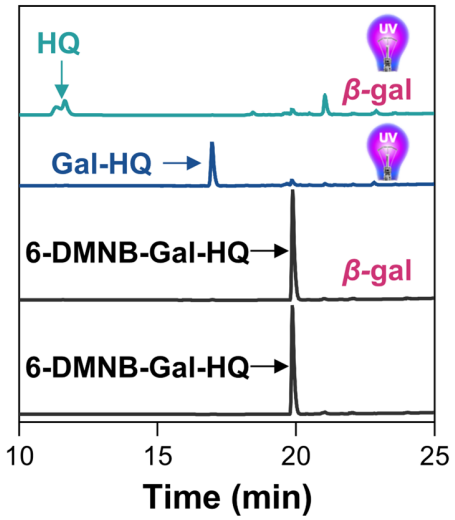

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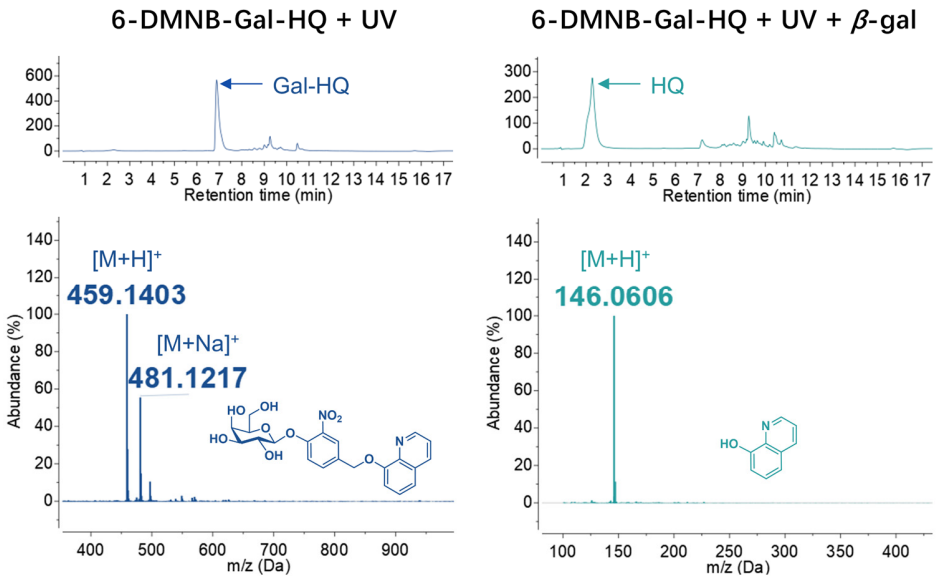

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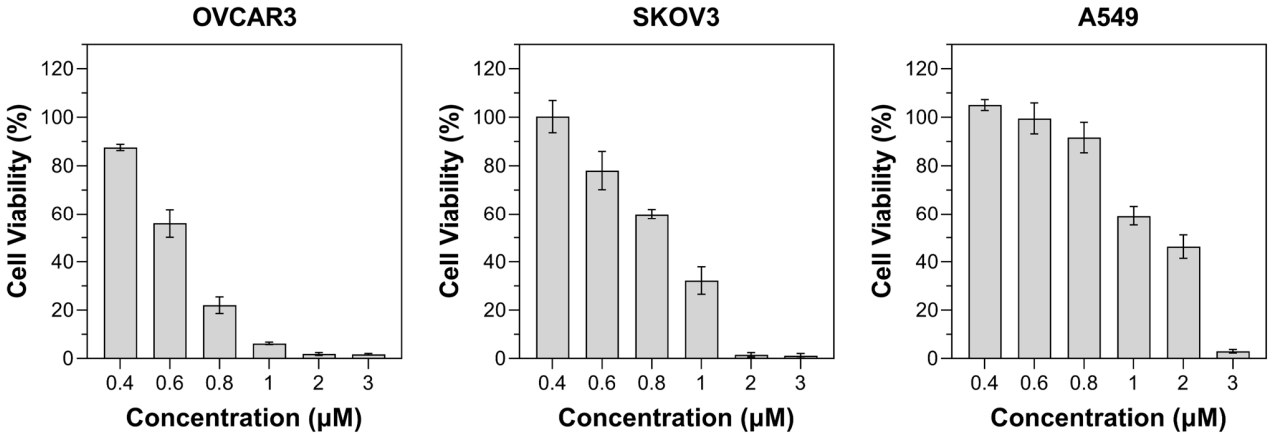

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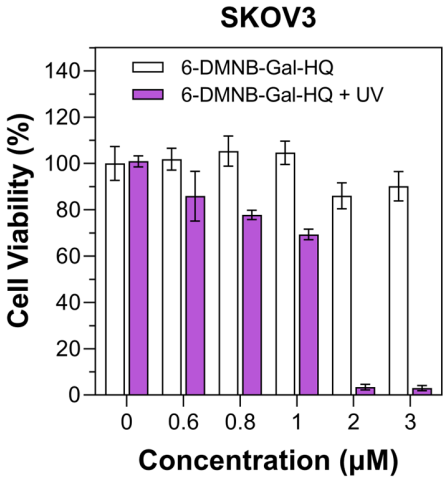

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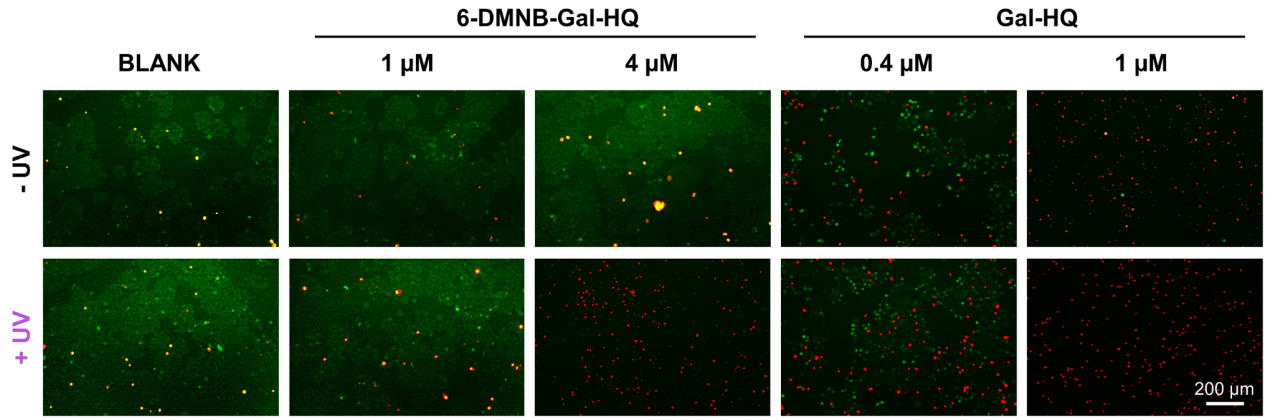

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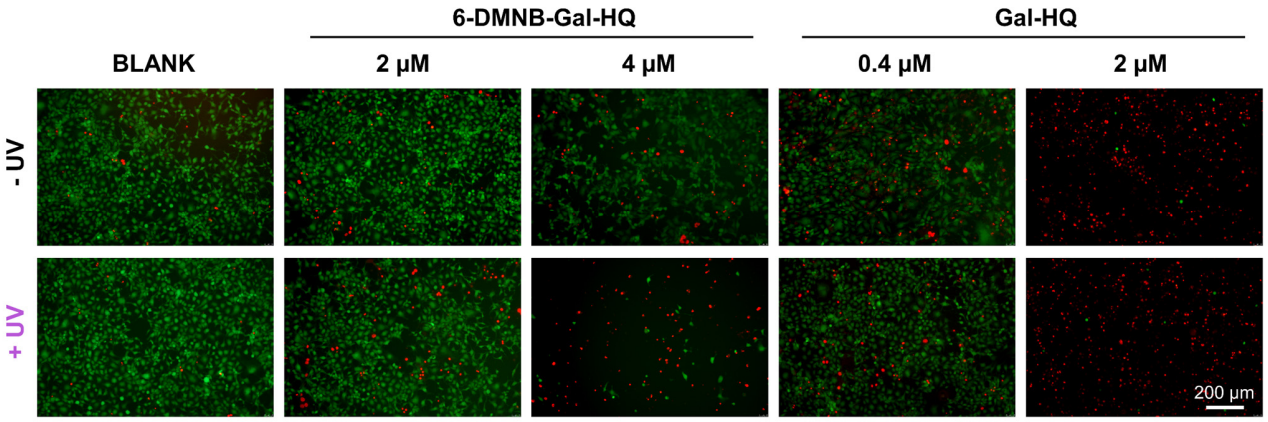

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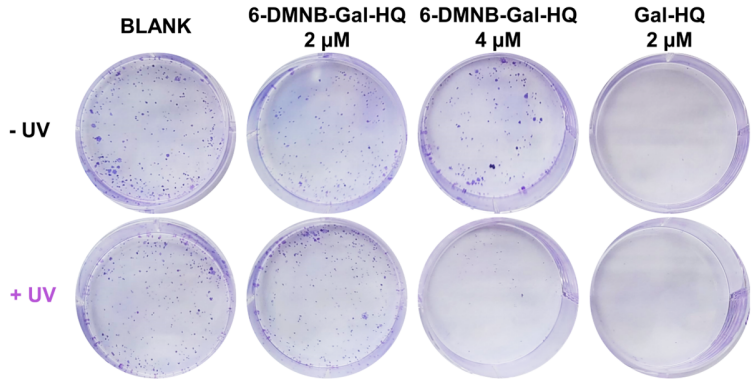

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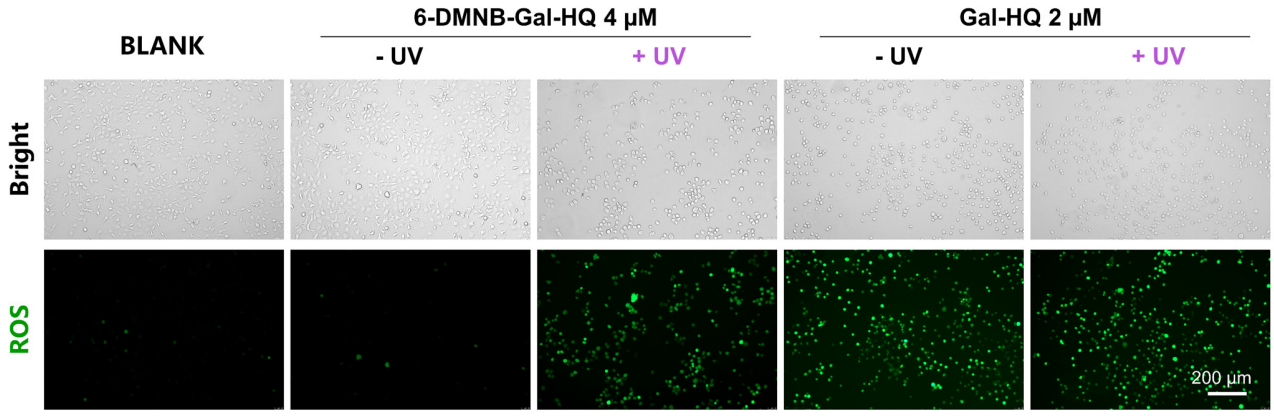

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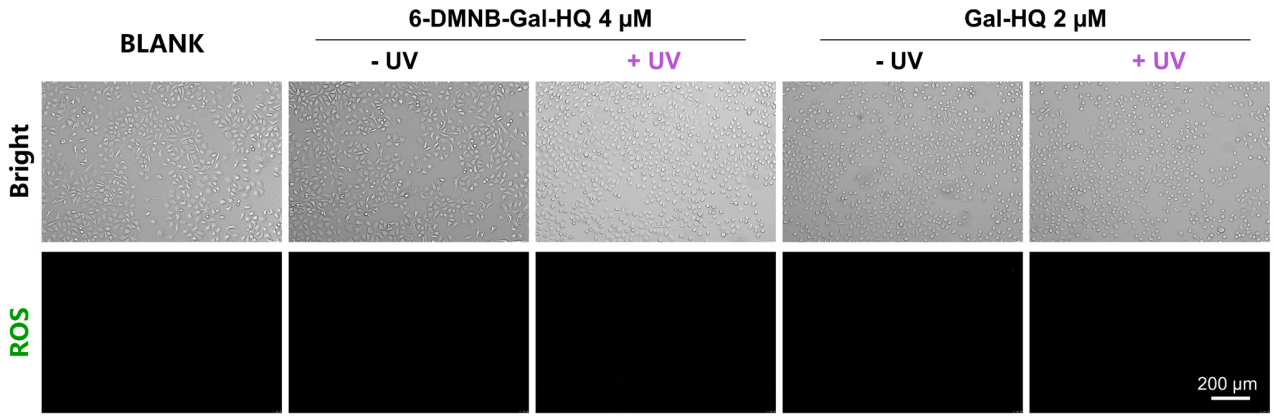

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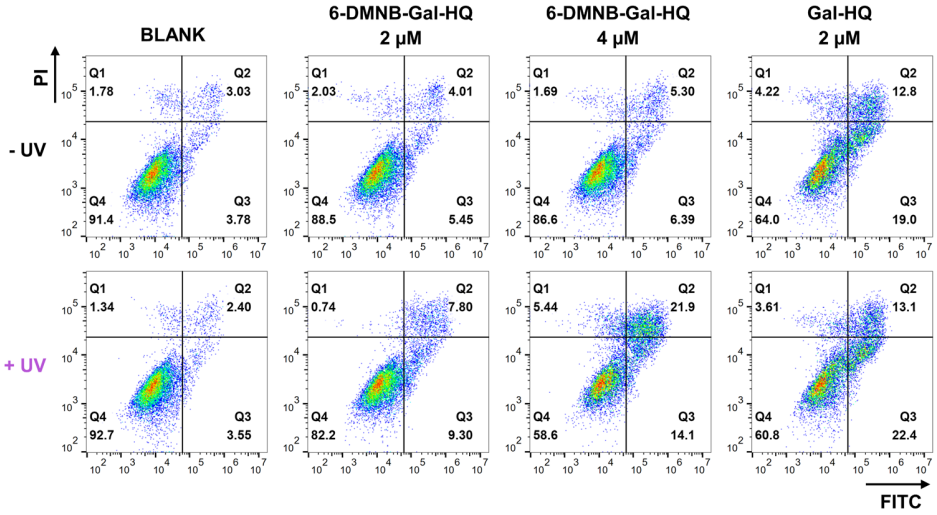
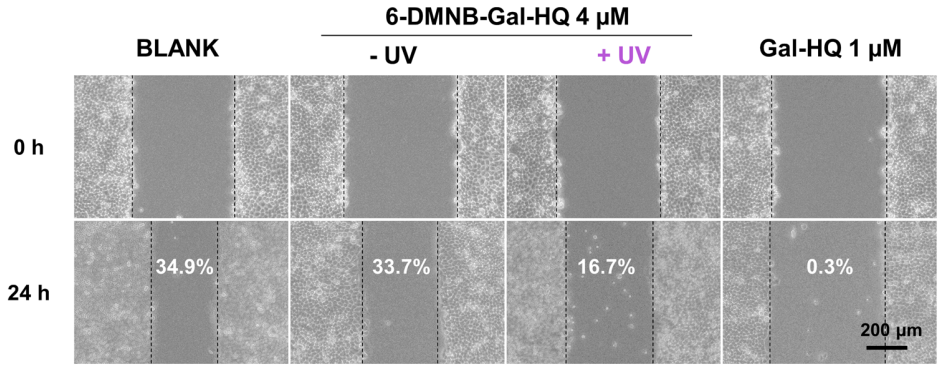


Figure S34. Annexin V-FITC/PI apoptosis assay evaluating the ability of 6-DMNB-Gal-HQ to induce apoptosis of SKOV3 cells with and without UV irradiation.



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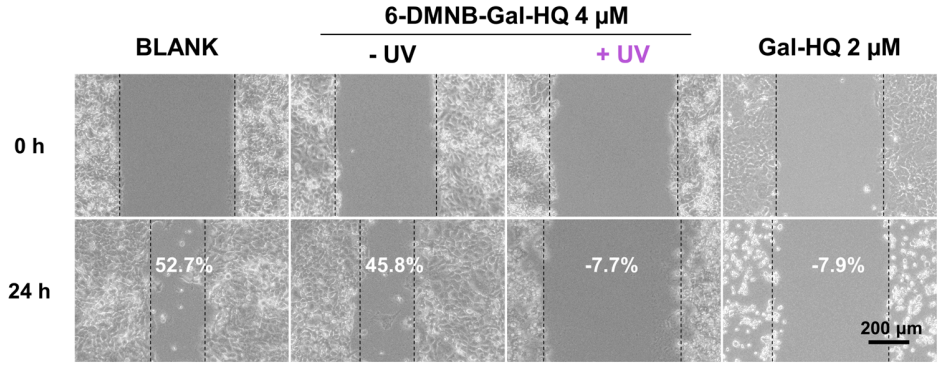
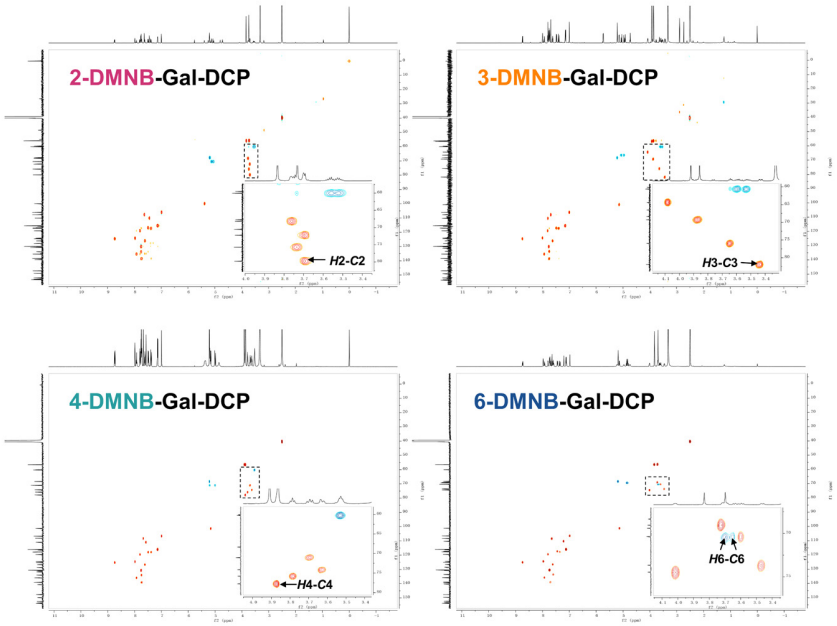


Figure S36. Wound healing assays indicating the cell migration inhibitory activity of 6-DMNB-Gal-HQ in SKOV3 cells. The number indicates the cell migration rate of each group.



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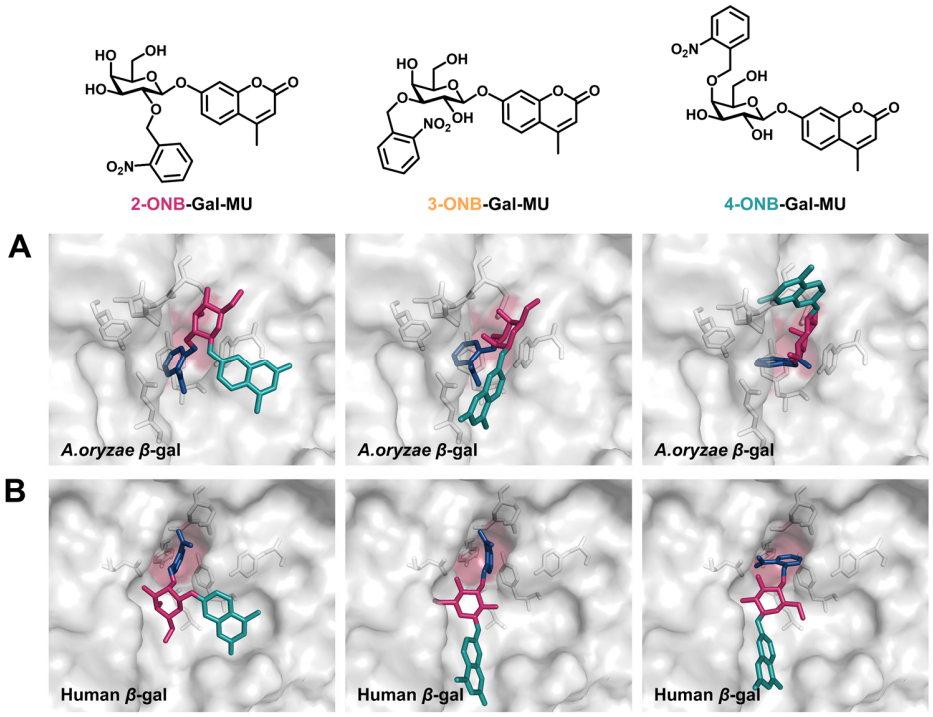


Figure S38. The docking of positional isomers of ONB-Gal-MU with (A) *A. oryzae* β-gal (PDB: 4IUG) and (B) human β-gal (PDB: 3THC). β-gal is shown as a grey surface, and ONB-Gal-MU are shown as stick models with the galactose moiety in red, MU in green, and the masking group in blue.

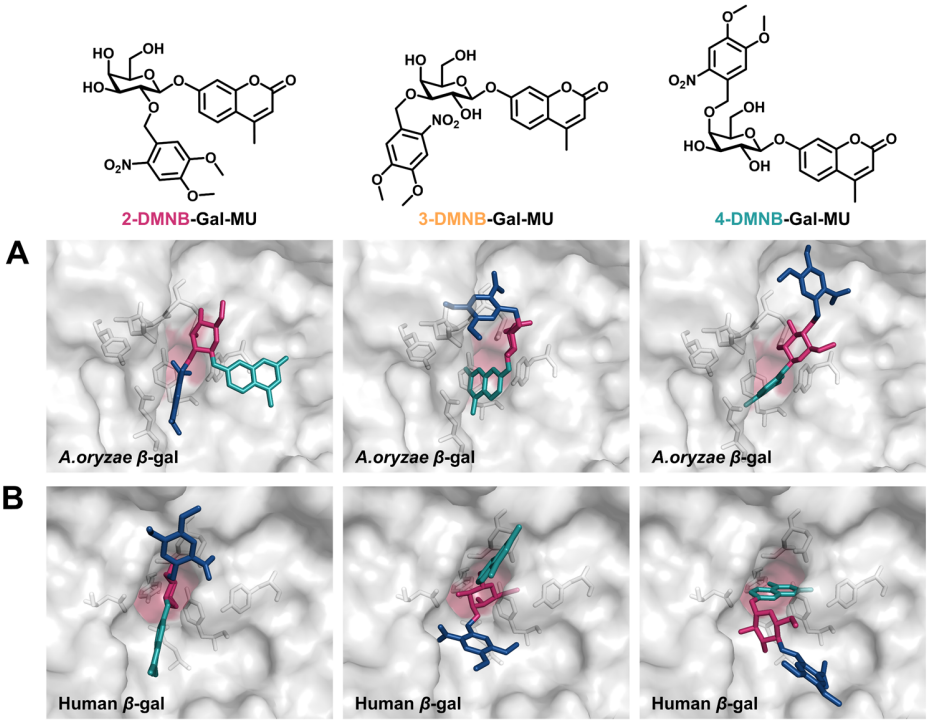


Figure S39. The docking of positional isomers of DMNB-Gal-MU with (A) *A. oryzae* *β*-gal (PDB: 4IUG) and (B) human *β*-gal (PDB: 3THC). *β*-gal is shown as a grey surface, and DMNB-Gal-MU are shown as stick models with the galactose moiety in red, MU in green, and the masking group in blue.

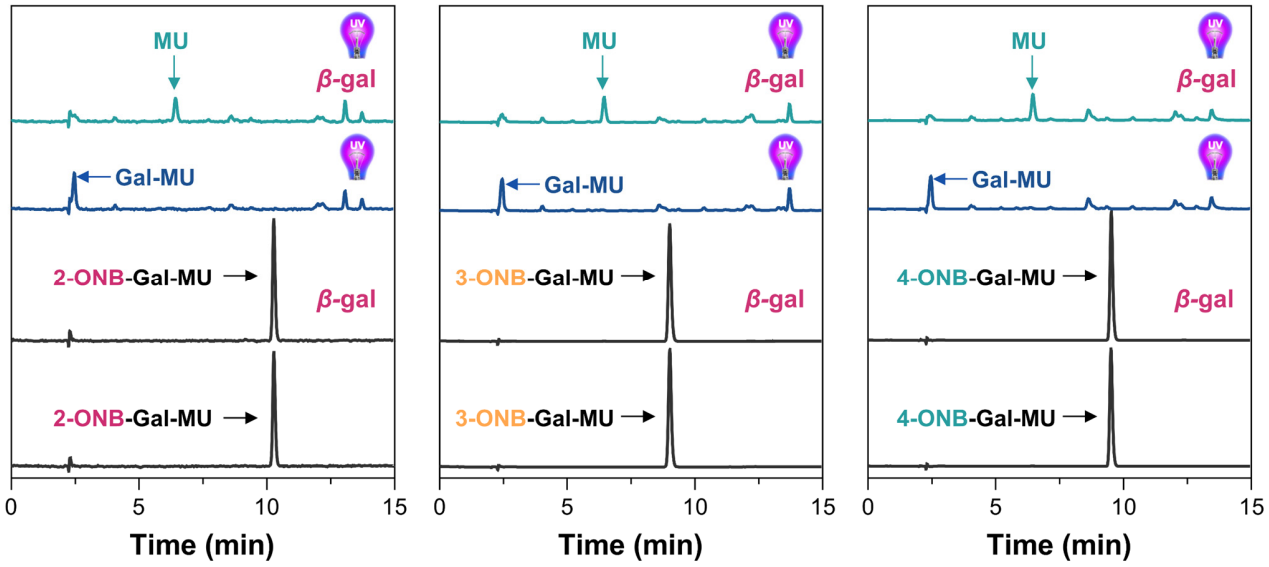


Figure S40. HPLC study of the dual-stimulus responsiveness of 2-ONB-Gal-MU, 3-ONB-Gal-MU, and 4-ONB-Gal-MU.

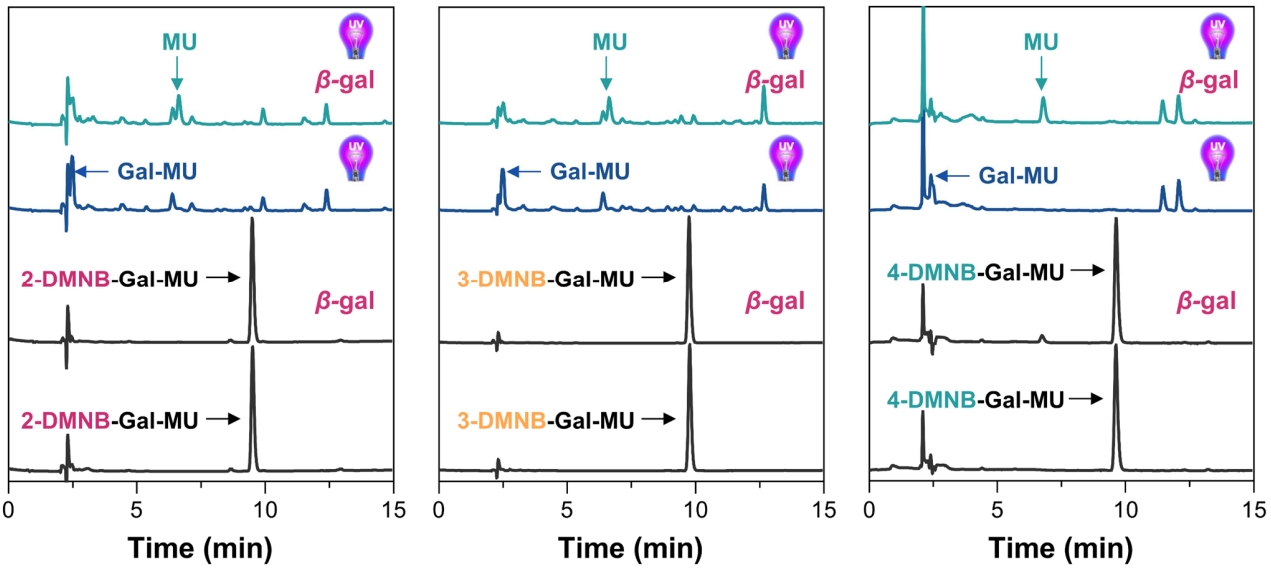


Figure S41. HPLC study of the dual-stimulus responsiveness of 2-DMNB-Gal-MU, 3-DMNB-Gal-MU, and 4-DMNB-Gal-MU.

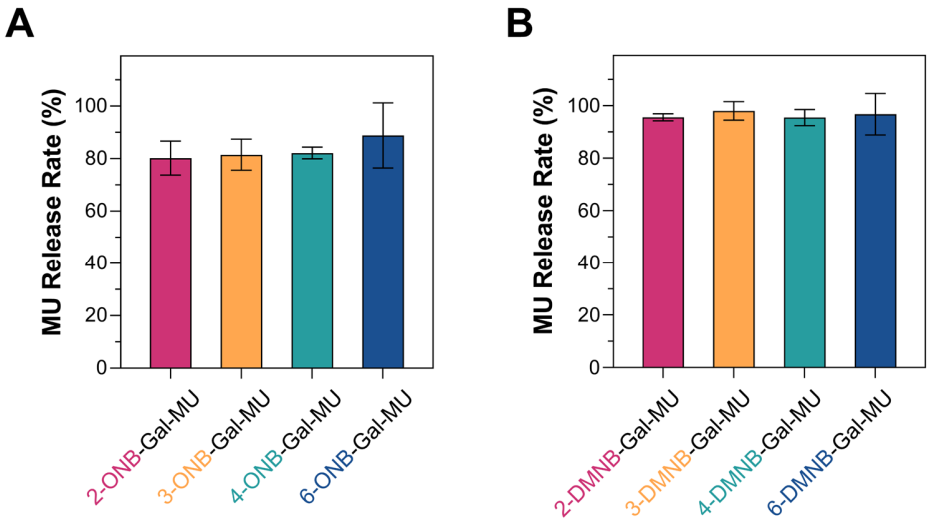


Figure S42. Quantitative analysis showing the MU release rate of positional isomers of ONB-Gal-MU and DMNB-Gal-MU, mean ± SD, n = 3.

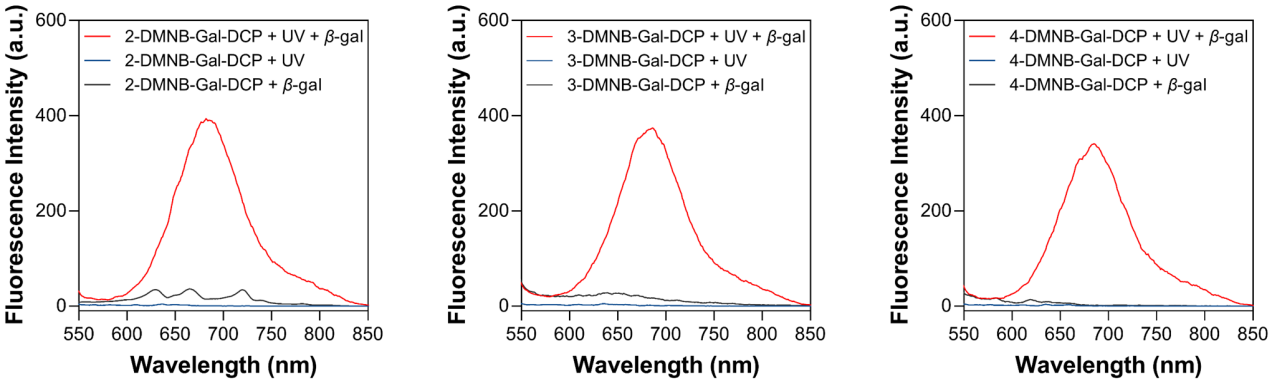


Figure S43. Fluorescence spectroscopy analysis of the dual-stimulus responsiveness of 2-DMNB-Gal-DCP, 3-DMNB-Gal-DCP, and 4-DMNB-Gal-DCP.

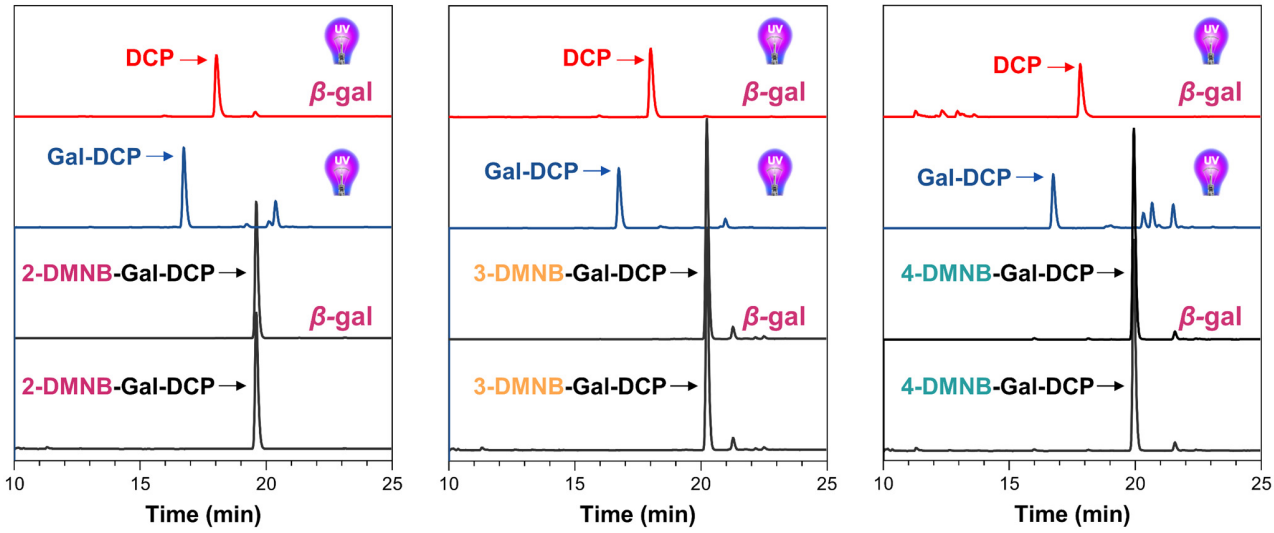


Figure S44. HPLC analysis of the dual-stimulus responsiveness of 2-DMNB-Gal-DCP, 3-DMNB-Gal-DCP, and 4-DMNB-Gal-DCP.

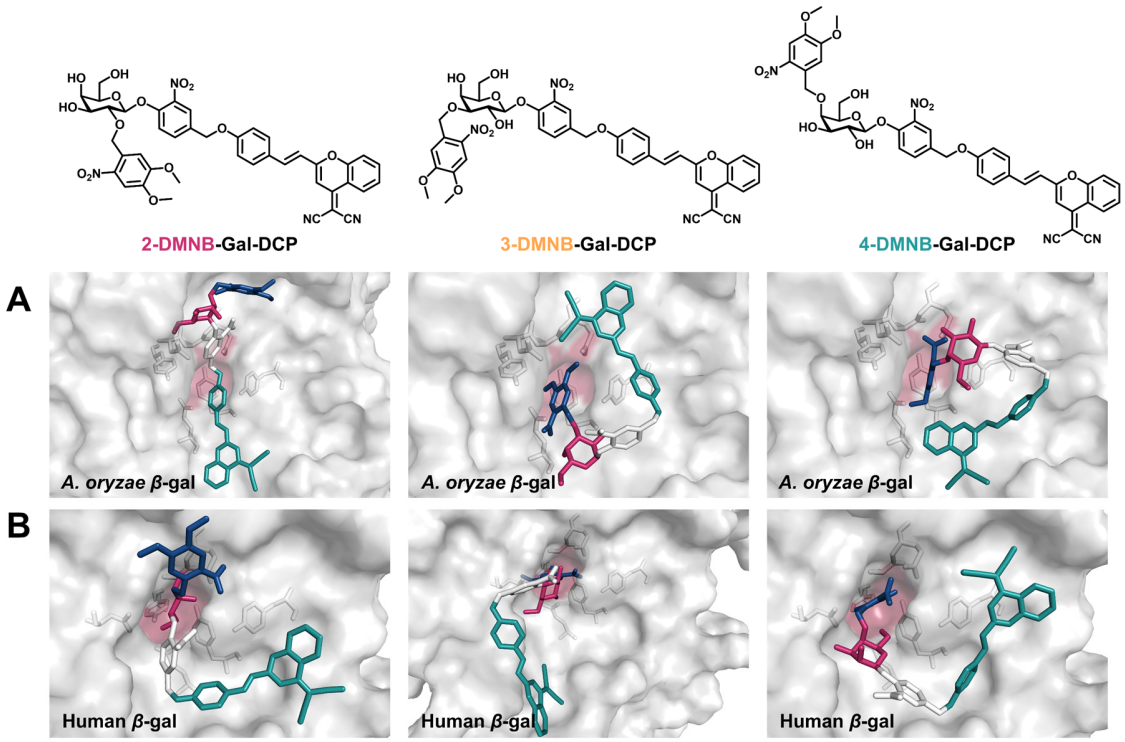


Figure S45. The docking of positional isomers of DMNB-Gal-DCP with (A) *A. oryzae* β-gal (PDB: 4IUG) and (B) human β-gal (PDB: 3THC). β-gal is shown as a grey surface, and DMNB-Gal-DCP are shown as stick models with the galactose moiety in red, DCP in green, self-immolative spacer in light grey, and the masking group in blue

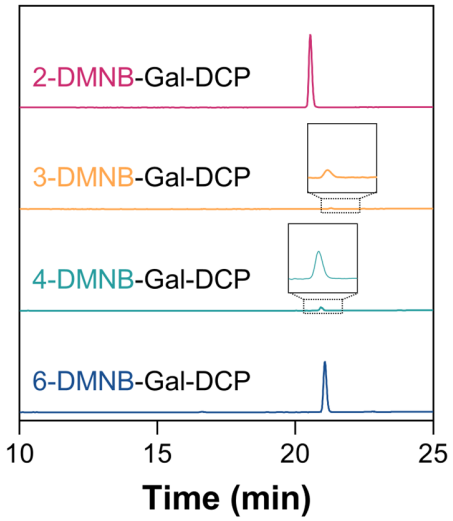


Figure S46. HPLC analysis comparing the uptake efficiency of DMNB-Gal-DCP isomers by OVCAR3 cells after a 3-hour incubation.

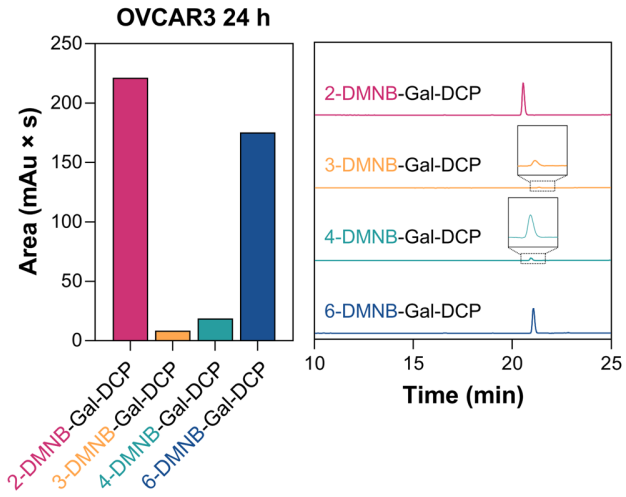


Figure S47. HPLC analysis comparing the uptake efficiency of DMNB-Gal-DCP isomers by OVCAR3 cells after a 24-hour incubation.

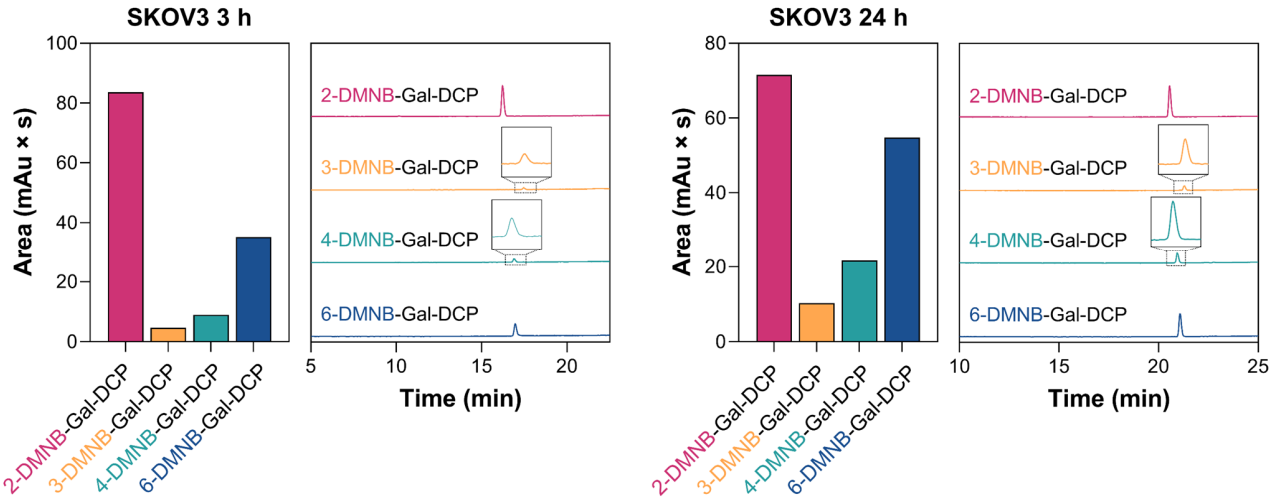


Figure S48. HPLC analysis comparing the uptake efficiency of DMNB-Gal-DCP isomers by SKOV3 cells.

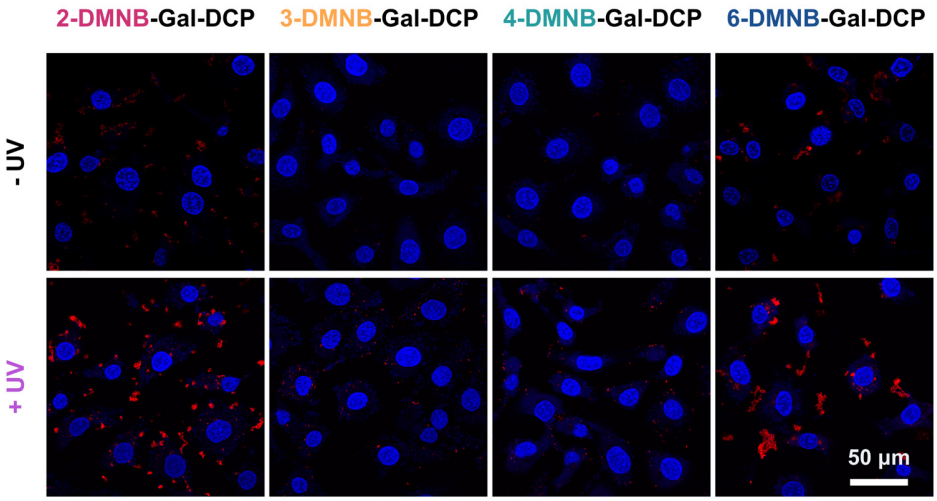


Figure S49. CLSM imaging comparing the ability of DMNB-Gal-DCP isomers to release DCP in SKOV3 cells.

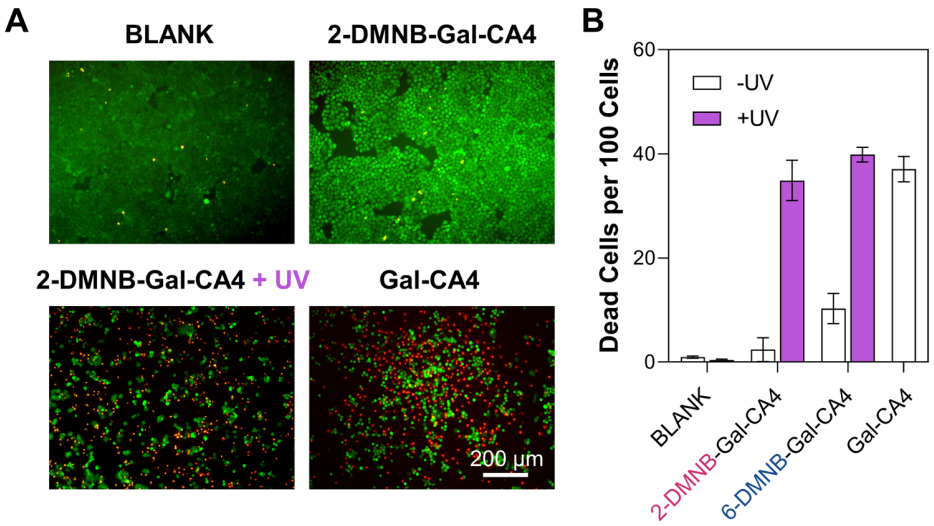


Figure S50. (A) Live/dead staining indicating the UV/*β*-gal-dependent cytotoxicity of 2-DMNB-Gal-CA4 on OVCAR3 cells. (B) Quantitative analysis of dead OVCAR3 cells after indicated treatments, mean ± SD, n = 3.

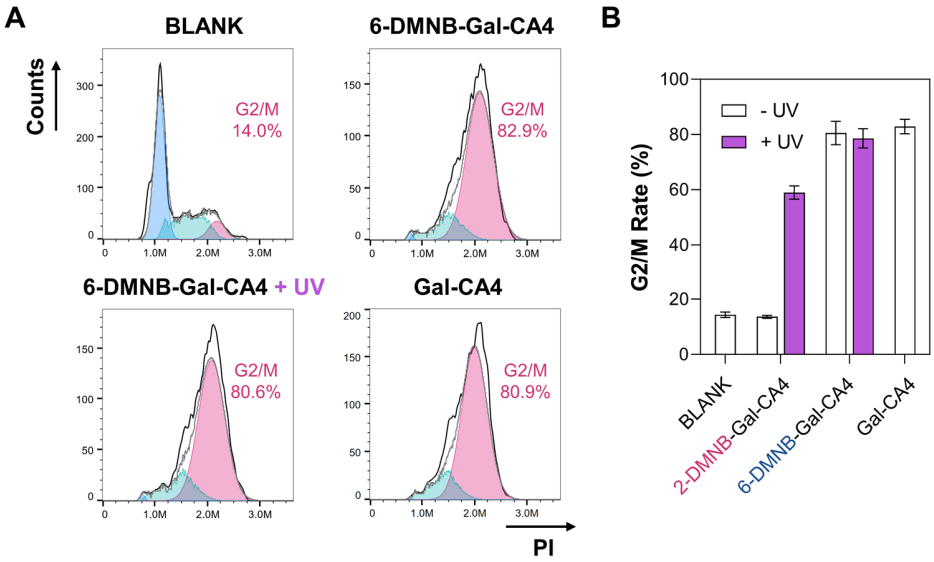


Figure S51. (A) The effects of 6-DMNB-Gal-CA4 on cell cycle of OVCAR3 cells with and without UV irradiation. (B) Quantitative analysis of the percentage of cells in G2/M phase after indicated treatments, mean ± SD, n = 3.

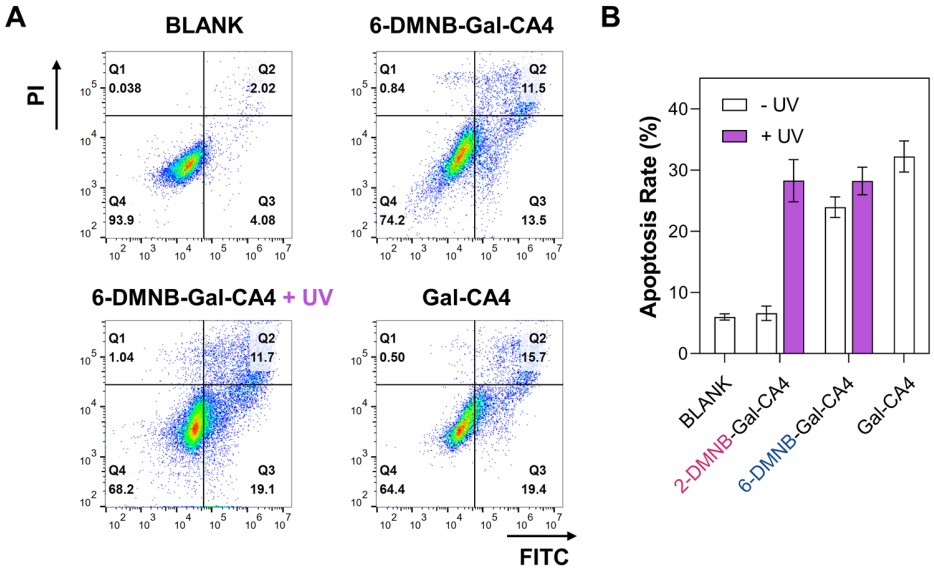


Figure S52. (A) Annexin V-FITC/PI apoptosis assay evaluating the ability of 6-DMNB-Gal-CA4 to induce apoptosis of OVCAR3 cells with and without UV irradiation. (B) Quantitative analysis of apoptotic cells after indicated treatments, mean ± SD, n = 3.

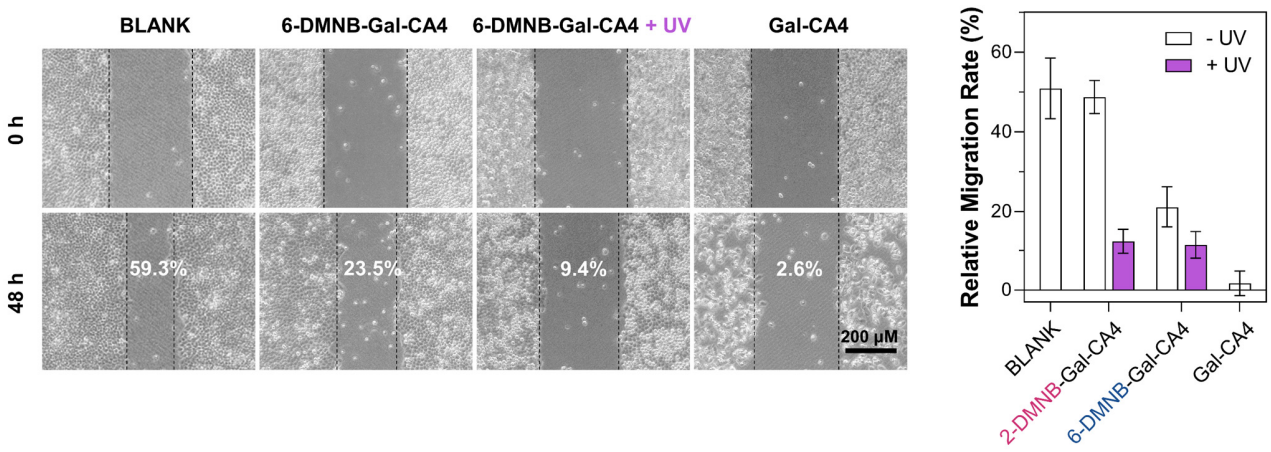


Figure S53. (A) Wound healing assays indicating the cell migration inhibitory activity of 6-DMNB-Gal-CA4 in OVCAR3 cells. (B) Quantitative analysis of cell migration rates after indicated treatments, mean ± SD, n = 3.

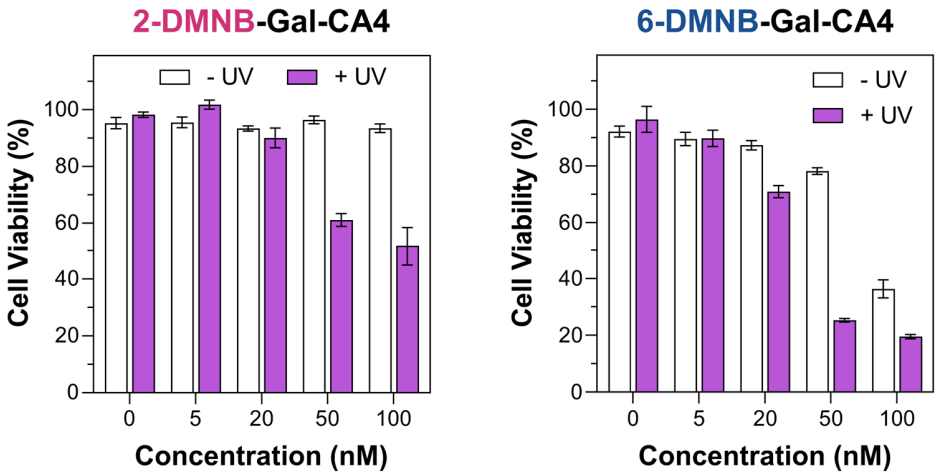


Figure S54. MTT assay measuring the toxicity of 2-DMNB-Gal-CA4 and 6-DMNB-Gal-CA4 on SKOV3 cells after a 48-hour incubation with and without UV irradiation, mean ± SD, n = 4.

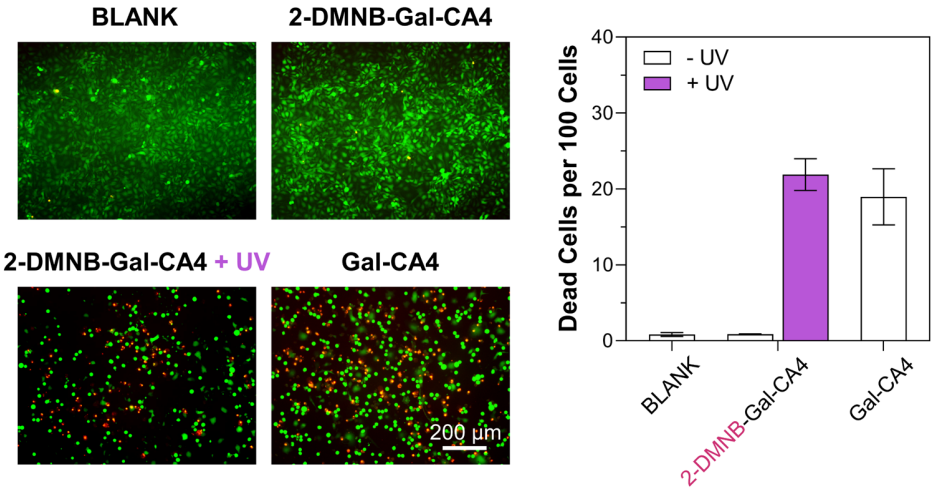


Figure S55. Live/dead staining indicating the UV/*β*-gal-dependent cytotoxicity of 2-DMNB-Gal-CA4 on SKOV3 cells with and without UV irradiation, mean ± SD, n = 3.

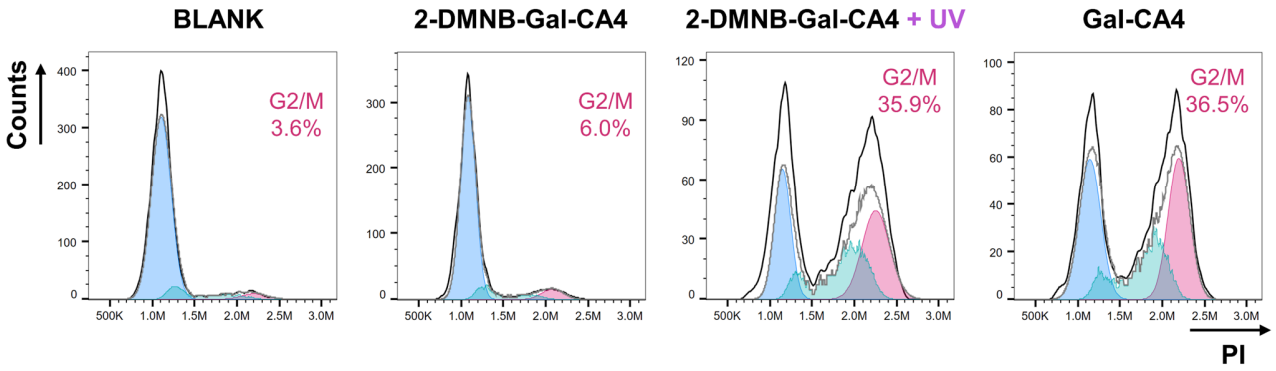


Figure S56. The effects of 2-DMNB-Gal-CA4 on cell cycle of SKOV3 cells.

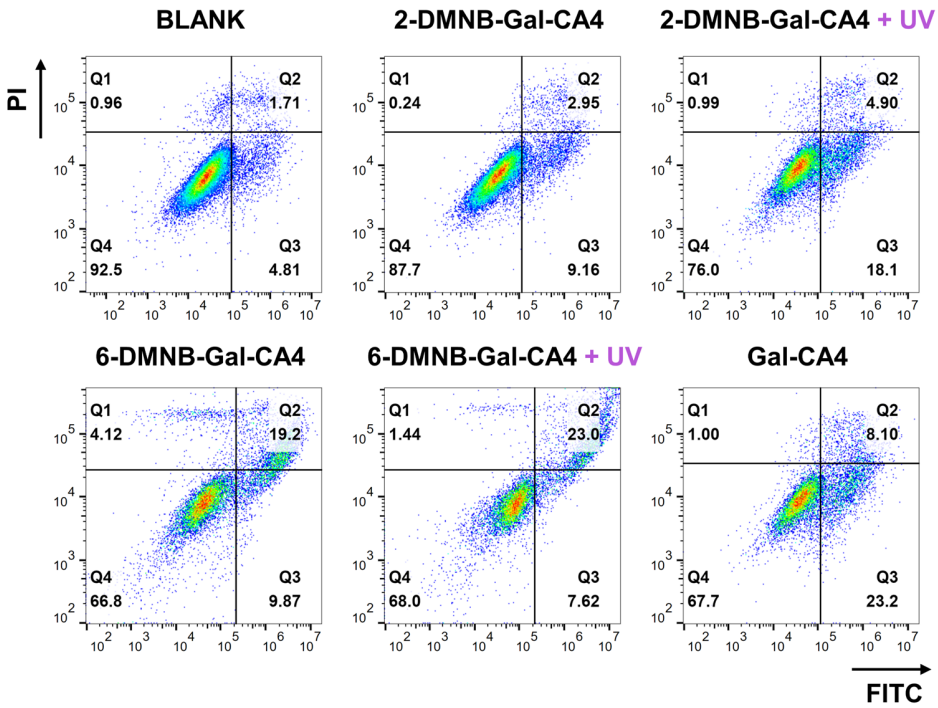


Figure S57. Annexin V-FITC/PI apoptosis assay comparing the ability of 2-DMNB-Gal-CA4 and 6-DMNB-Gal-CA4 to induce apoptosis of SKOV3 cells with and without UV irradiation.

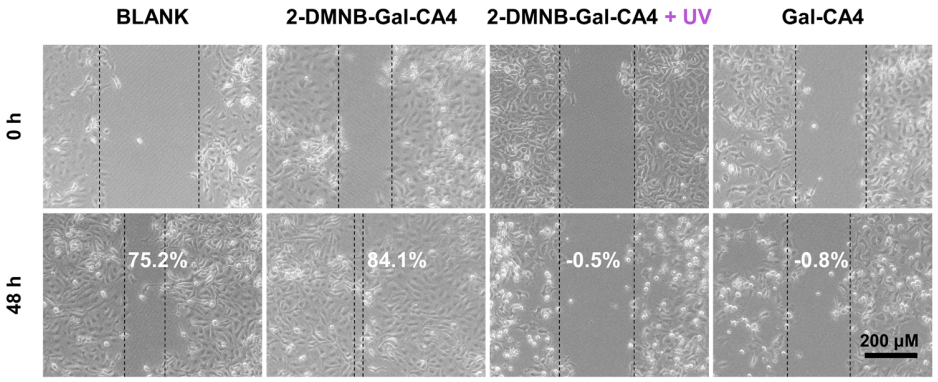


Figure S58. Wound healing assays indicating the cell migration inhibitory activity of 2-DMNB-Gal-CA4 in SKOV3 cells. The number indicates the cell migration rate of each group.

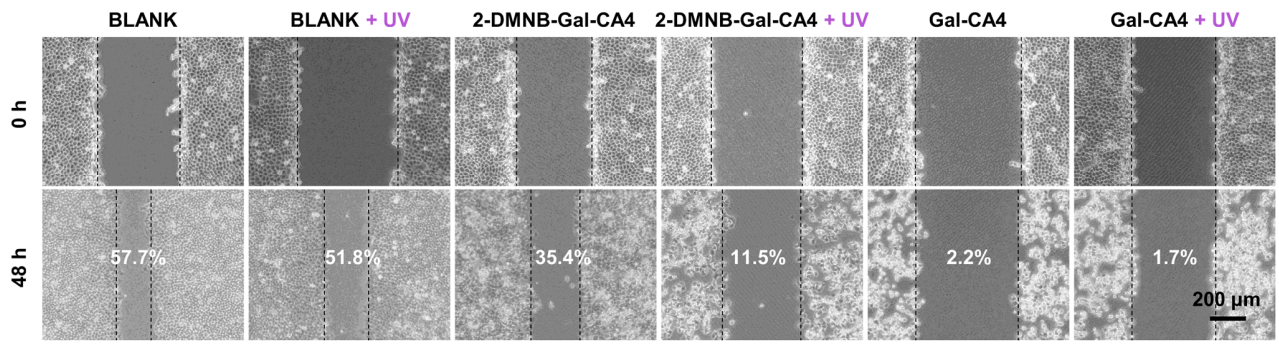


Figure S59. The one-well two-wound assay of OVCAR3 cells after indicated treatments. The number indicates the cell migration rate of each wound.

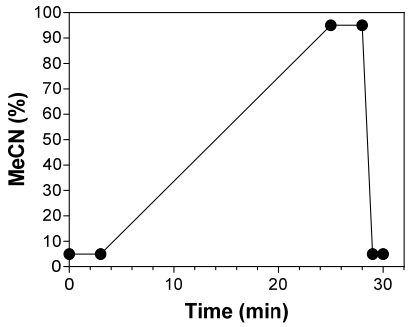
2. Analytical Studies

2.1 General information

A. oryzae β-gal (S27128-25ku, Shanghai Yuanye Bio-Technology, China) was commercially purchased. UV-vis spectroscopy was recorded using a Cary UV-vis Compact Peltier (Cary 3500, Agilent, USA). Fluorescence spectroscopy was recorded using a Cary Eclipse Fluorescence Spectrophotometer (G9800A, Agilent, USA). High resolution electrospray ionization mass spectroscopy (HRMS) was performed on a 6220 ESI-TOF mass spectrometer (Agilent, USA). Analytical HPLC was conducted using an Agilent 1260 Infinity system equipped with a reversed-phase column (250 mm × 4.6 mm, 5 μm, ZORBAX SB-C18) (Agilent, USA) and a diode array detector (1260 DAD VL, Agilent, USA). The column was eluted with a gradient system at a flow rate of 1 mL/min at 30 °C. The four gradient methods used are listed below:

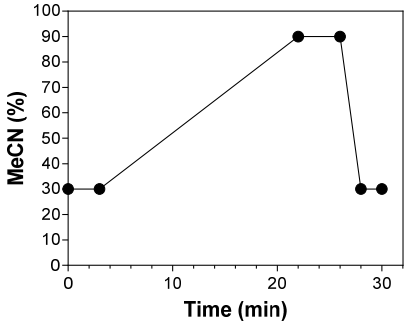
HPLC gradient method A

Time (min)	Phase A (%) H_2O	Phase B (%) MeCN
0	95	5
3	95	5
25	5	95
28	5	95
29	95	5
30	95	5



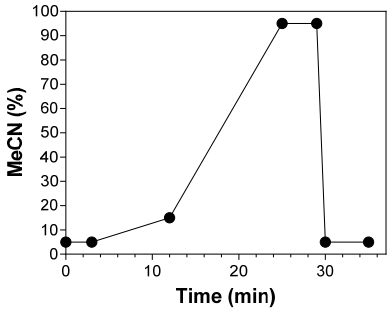
HPLC gradient method B

Time (min)	Phase A (%) H_2O	Phase B (%) MeCN
0	70	30
3	70	30
22	10	90
26	10	90
28	70	30
30	70	30



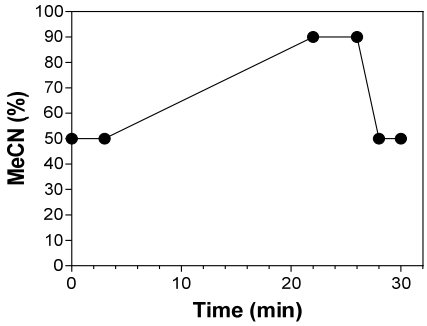
HPLC gradient method C

Time (min)	Phase A (%) H_2O	Phase B (%) MeCN
0	95	5
3	95	5
12	85	15
25	5	95
29	5	95
30	95	5
35	95	5



HPLC gradient method D

Time (min)	Phase A (%) H_2O	Phase B (%) MeCN
0	50	50
3	50	50
22	10	90
26	10	90
28	50	50
30	50	50



The detailed conditions for analytical studies involved in this work are summarized in Table S1:

Table S1. Conditions for analytical studies on the cargo-releasing behaviors of various galactosides.[a]

Galactosides	**Conc. (μM)**	**Solvent**	**β-Gal (U/mL)**	**Additional Trigger**	**Analytical Methods**
Gal-MU	10	MeCN/H_2O (1:1, v/v)	5	-	UV-vis spectroscopy; fluorescence spectroscopy (λ_{ex} = 365 nm)
Gal-MU	100	MeCN/H_2O (1:1, v/v)	25	-	HPLC (gradient A, 320 nm)
6-ONB-Gal-MU	100	MeCN/H_2O (1:1, v/v, 400 μL)	25	-	HPLC (gradient B, 254 nm)
6-ONB-Gal-MU	100	MeCN/H_2O (1:1, v/v, 400 μL)	-	UV[b]	HPLC (gradient B, 254 nm)
6-ONB-Gal-MU	100	MeCN/H_2O (1:1, v/v, 400 μL)	25	UV	HPLC (gradient B, 254 nm)
6-DMNB-Gal-MU	100	MeCN/H_2O (1:1, v/v, 400 μL)	25	-	HPLC (gradient A, 320 nm); HRMS
6-DMNB-Gal-MU	100	MeCN/H_2O (1:1, v/v, 400 μL)	-	UV	HPLC (gradient A, 320 nm); HRMS
6-DMNB-Gal-MU	100	MeCN/H_2O (1:1, v/v, 400 μL)	25	UV	HPLC (gradient A, 320 nm); HRMS
6-DMNB-Gal-MU	10	MeCN/H_2O (1:1, v/v)	5	-	fluorescence spectroscopy (λ_{ex} = 365 nm);
6-DMNB-Gal-MU	10	MeCN/H_2O (1:1, v/v)	-	UV	fluorescence spectroscopy (λ_{ex} = 365 nm);

Galactosides	**Conc. (μM)**	**Solvent**	**β-Gal (U/mL)**	**Additional Trigger**	**Analytical Methods**
6-DMNB-Gal-MU	10	MeCN/H_2O (1:1, v/v)	5	UV	fluorescence spectroscopy (λ_{ex} = 365 nm);
6-ALL-Gal-MU	100	MeCN/H_2O (1:1, v/v, 400 μL)	25	-	HPLC (gradient A, 320 nm)
6-ALL-Gal-MU	100	DMF/H_2O (1:1, v/v, 400 μL)	-	$Na_2Pd_2Cl_4$ (2 mM, 10 μL), TPPTS (6 mM, 10 μL), morpholine (30 mM, 10 μL)	HPLC (gradient A, 320 nm)
6-ALL-Gal-MU	100	DMF/H_2O (1:1, v/v, 400 μL)	-	$Na_2Pd_2Cl_4$ (2 mM, 10 μL), TPPTS (6 mM, 10 μL), morpholine (30 mM, 10 μL)	HPLC (gradient A, 320 nm)
6-TBDPS-Gal-MU	100	MeCN/H_2O (1:1, v/v, 400 μL)	25	-	HPLC (gradient A, 320 nm)
6-TBDPS-Gal-MU	100	MeCN/H_2O (1:1, v/v, 400 μL)	-	KF (2 mM, 10 μL) NaOH (100 μM, 10 μL)	HPLC (gradient A, 320 nm)
6-TBDPS-Gal-MU	100	MeCN/H_2O (1:1, v/v, 400 μL)	25	KF (2 mM, 10 μL) NaOH (100 μM, 10 μL)	HPLC (gradient A, 320 nm)
6-BAB-Gal-MU	100	MeCN/H_2O (1:1, v/v, 400 μL)	25	-	HPLC (gradient A, 320 nm);
6-BAB-Gal-MU	100	MeCN/H_2O (1:1, v/v, 400 μL)	-	H_2O_2 (2 mM, 10 μL)	HPLC (gradient A, 320 nm);

Galactosides	**Conc. (μM)**	**Solvent**	**β-Gal (U/mL)**	**Additional Trigger**	**Analytical Methods**
6-BAB-Gal-MU	100	MeCN/H_2O (1:1, v/v, 400 μL)	25	H_2O_2 (2 mM, 10 μL)	HPLC (gradient A, 320 nm); ESI-MS
6-AZB-Gal-MU	100	MeCN/H_2O (1:1, v/v, 400 μL)	25	-	HPLC (gradient A, 320 nm)
6-AZB-Gal-MU	100	MeCN/H_2O (1:1, v/v, 400 μL)	-	NaHS (2 mM, 10 μL)	HPLC (gradient A, 320 nm)
6-AZB-Gal-MU	100	MeCN/H_2O (1:1, v/v, 400 μL)	25	NaHS (2 mM, 10 μL)	HPLC (gradient A, 320 nm); ESI-MS
Gal-DCP	10	MeCN/H_2O (1:1, v/v)	5	-	fluorescence spectroscopy (λ_{ex} = 535 nm)
6-DMNB-Gal-DCP	10	MeCN/H_2O (1:1, v/v)	5		fluorescence spectroscopy (λ_{ex} = 535 nm)
6-DMNB-Gal-DCP	10	MeCN/H_2O (1:1, v/v)	-	UV	fluorescence spectroscopy (λ_{ex} = 535 nm)
6-DMNB-Gal-DCP	10	MeCN/H_2O (1:1, v/v)	5	UV	fluorescence spectroscopy (λ_{ex} = 535 nm)
6-DMNB-Gal-DCP	100	MeCN/H_2O (1:1, v/v, 400 μL)	25	-	HPLC (gradient B, 440 nm)
6-DMNB-Gal-DCP	100	MeCN/H_2O (1:1, v/v, 400 μL)	-	UV	HPLC (gradient B, 440 nm); LC-HRMS

Galactosides	**Conc. (μM)**	**Solvent**	**β-Gal (U/mL)**	**Additional Trigger**	**Analytical Methods**
6-DMNB-Gal-DCP	100	MeCN/H_2O (1:1, v/v, 400 μL)	25	UV	HPLC (gradient B, 440 nm); LC-HRMS
6-DMNB-Gal-CA4	100	MeCN/H_2O (1:1, v/v, 400 μL)	25	-	HPLC (gradient B, 254 nm)
6-DMNB-Gal-CA4	100	MeCN/H_2O (1:1, v/v, 400 μL)	-	UV	HPLC (gradient B, 254 nm); LC-HRMS
6-DMNB-Gal-CA4	100	MeCN/H_2O (1:1, v/v, 400 μL)	25	UV	HPLC (gradient B, 254 nm); LC-HRMS
Gal-HQ	10	MeCN/H_2O (1:1, v/v)	5	-	UV-vis spectroscopy (with 20 μM Cu(II))
Gal-HQ	100	MeCN/H_2O (1:1, v/v)	25	-	HPLC (gradient C, 254 nm)
6-DMNB-Gal-HQ	10	MeCN/H_2O (1:1, v/v, 400 μL)	5	-	UV-vis spectroscopy (with 20 μM Cu(II))
6-DMNB-Gal-HQ	10	MeCN/H_2O (1:1, v/v, 400 μL)	-	UV	UV-vis spectroscopy (with 20 μM Cu(II))
6-DMNB-Gal-HQ	10	MeCN/H_2O (1:1, v/v, 400 μL)	5	UV	UV-vis spectroscopy (with 20 μM Cu(II))
6-DMNB-Gal-HQ	100	MeCN/H_2O (1:1, v/v, 400 μL)	25	-	HPLC (gradient C, 254 nm)

Galactosides	**Conc. (μM)**	**Solvent**	**β-Gal (U/mL)**	**Additional Trigger**	**Analytical Methods**
6-DMNB-Gal-HQ	100	MeCN/H_2O (1:1, v/v, 400 μL)	-	UV	HPLC (gradient C, 254 nm); LC-HRMS
6-DMNB-Gal-HQ	100	MeCN/H_2O (1:1, v/v, 400 μL)	25	UV	HPLC (gradient C, 254 nm); LC-HRMS
2-, 3-, 4-ONB-Gal-MU	100	MeCN/H_2O (1:1, v/v)	25		HPLC (gradient B, 254 nm)
2-, 3-, 4-ONB-Gal-MU	100	MeCN/H_2O (1:1, v/v)	-	UV	HPLC (gradient B, 254 nm)
2-, 3-, 4-ONB-Gal-MU	100	MeCN/H_2O (1:1, v/v)	25	UV	HPLC (gradient B, 254 nm)
2-, 3-, 4-DMNB-Gal-MU	100	MeCN/H_2O (1:1, v/v)	25		HPLC (gradient B, 254 nm)
2-, 3-, 4-DMNB-Gal-MU	100	MeCN/H_2O (1:1, v/v)	-	UV	HPLC (gradient B, 254 nm)
2-, 3-, 4-DMNB-Gal-MU	100	MeCN/H_2O (1:1, v/v)	25	UV	HPLC (gradient B, 254 nm)
2-, 3-, 4-DMNB-Gal-DCP	10	MeCN/H_2O (1:1, v/v)	5		fluorescence spectroscopy (λ_{ex} = 535 nm)
2-, 3-, 4-DMNB-Gal-DCP	10	MeCN/H_2O (1:1, v/v)	-	UV	fluorescence spectroscopy (λ_{ex} = 535 nm)

Galactosides	**Conc. (μM)**	**Solvent**	***β*-Gal (U/mL)**	**Additional Trigger**	**Analytical Methods**
2-, 3-, 4-DMNB-Gal-DCP	10	MeCN/H_2O (1:1, v/v)	5	UV	fluorescence spectroscopy (λ_{ex} = 535 nm)
2-, 3-, 4-DMNB-Gal-DCP	100	MeCN/H_2O (1:1, v/v, 400 μL)	25	-	HPLC (gradient B, 440 nm)
2-, 3-, 4-DMNB-Gal-DCP	100	MeCN/H_2O (1:1, v/v, 400 μL)	-	UV	HPLC (gradient B, 440 nm);
2-, 3-, 4-DMNB-Gal-DCP	100	MeCN/H_2O (1:1, v/v, 400 μL)	25	UV	HPLC (gradient B, 440 nm);

[a]All solutions were incubated at 37 °C for 24 hours.

[b]365 nm, 3 min, 6 W, distance 9 cm

2.2 On demand release of MU from 6-DMNB-Gal-MU

A solution of 6-DMNB-Gal-MU (150 μM) in MeCN/H_2O (1:1, v/v) was incubated with *A. oryzae* β-gal (25 U/mL) at 37 °C. The solution was irradiated with UV light (365 nm, 5 seconds, 6 W, distance 9 cm) at 60, 150, 240, 330, 420, and 510 minutes. Every 30 minutes, an aliquot (200 μL) of the solution was diluted to 3 mL with MeCN/H_2O (1:1, v/v) and analyzed using fluorescence spectroscopy upon excitation at 365 nm to detect the amount of released MU.

2.3 β-Gal-dependent release of MU from 6-DMNB-Gal-MU

A solution of 6-DMNB-Gal-MU (150 μM) in MeCN/H_2O (1:1, v/v) was incubated with *A. oryzae* β-gal (0.5, 1.0, or 1.5 U/mL) at 37 °C. After irradiated with UV light (365 nm, 3 minutes, 6 W, distance 9 cm), an aliquot (200 μL) of the solution was taken at 2, 4, 6, 8, 10, and 15 minutes. The solution was diluted to 3 mL with MeCN/H_2O (1:1, v/v) and analyzed using fluorescence spectroscopy upon excitation at 365 nm to detect the amount of released MU.

2.4 On demand release of HQ from 6-DMNB-Gal-HQ

A solution of 6-DMNB-Gal-HQ (150 μM) in MeCN/H_2O (1:1, v/v) was incubated with *A. oryzae* β-gal (25 U/mL) at 37 °C. The solution was irradiated with UV light (365 nm, 5 seconds, 6 W, distance 9 cm) at 30, 120, 210, 300, 390, and 480 minutes. Every 30 minutes, an aliquot (200 μL) of the solution was diluted to 3 mL with MeCN/H_2O (1:1, v/v), and $CuCl_2$ was added to a final concentration of 20 μM. The solution was analyzed using UV-vis spectroscopy over the range of 210–500 nm.

3. Biological Studies

3.1 General information

Human ovarian cancer cell lines OVCAR3, SKOV3 and human lung cancer cell line A549 were obtained from the American Type Culture Collection (ATCC) (USA). The OVCAR3 and A549 cells were cultured in Dulbecco's Modified Eagle's Medium (DMEM) (Gibco, USA), and SKOV3 cells were cultured in McCoy's 5A modified medium (McCoy's 5A) (Servicebio, China). Mediums were supplemented with 1% penicillin and streptomycin (Gibco, USA) and 10% fetal bovine serum (FBS) (Gibco, USA). All cells were cultured at 37 °C with a standard gas atmosphere containing humidified 5% CO_2. When the cell density reached >70% of confluence, sub-culturing was performed. Unless otherwise noted, UV irradiation was conducted by a UV light (365 nm, 6 W) at a distance of 9 centimeters for 3 minutes.

3.2 Detection of intracellular *β*-gal activity

OVCAR3 cells (8×10^4 cells per well), SKOV3 cells (5×10^4 cells per well), and A549 cells (8×10^4 cells per well) were seeded in 12-well plates. After 24 hours, the cells were fixed for 15 minutes at room temperature using 4% paraformaldehyde (PFA). The activity of *β*-gal was detected using Lysosomal *β*-galactosidase Staining Kit (C0605, Beyotime, China) according to the manufacturer's instruction. The cells were imaged with an optical microscope (CKX53, Olympus, Japan).

3.3 Western blot analysis of intracellular *β*-gal level

OVCAR3 cells (2×10^6 cells per well), SKOV3 cells (1×10^6 cells per well), and A549 cells (2×10^6 cells per well) were seeded in 6-well plates and cultured for 24 hours at 37 °C with 5% CO_2. The cells were washed with PBS for three times, and protein was extracted using RIPA (strong) Lysis Buffer (P0013B, Beyotime, China) containing protease inhibitor (ST506, Beyotime, China). The concentration of protein was quantified by BCA Protein Assay Kit (P0010, Beyotime, China). After mixed with the SDS-PAGE protein loading buffer (P0015L, Beyotime, China), the solution was heated to 100 °C for 5 min. Samples with equal protein amount were added into the wells with 10% SDS-PAGE gel and were separated and transferred to polyvinylidene fluoride membranes (FFP32, Beyotime, China). The membranes were then blocked and incubated with anti-GLB1 *β*-gal (1/10000 dilution, ab128993, Abcam, UK) and anti-GAPDH (1/2000 dilution, 10494-1-AP, Proteintech, China) antibody at 4 °C overnight. The membranes were washed with TBST for three times and sequentially incubated with HRP-labeled goat anti-rabbit IgG(H+L) (A0208, Beyotime, China) for 2 h. The signals of protein were checked by the

chemiluminescence enhancement method using BeyoECL Plus Kit (P0018S, Beyotime, China) according to the manufacturer's instruction. The membranes were imaged using an imaging system (Tanon-5200, Tanon, China).

3.4 Intracellular DCP release

OVCAR3 cells (5×10^5 cells per well), SKOV3 cells (3×10^5 cells per well), and A549 cells (5×10^5 cells per well) were seeded in 6-well plates and cultured for 36 hours at 37 °C with 5% CO_2. The cells were incubated with DMNB-Gal-DCP (10 μM) for 18 hours. A subset of cells was exposed to UV light after 12 hours. The cells were digested by 0.25% trypsin-EDTA solution and washed with PBS twice by centrifugation (1000 × *g*, 5 minutes). After resuspended, the cells were analyzed using a flow cytometer (Accuri™ C6 Plus, BD Biosciences, USA).

OVCAR3 cells (2×10^5 cells per dish) and SKOV3 cells (1×10^5 cells per dish) were seeded in glass-bottomed cell culture dishes (801001, NEST Biotechnology, China) and incubated for 36 hours at 37 °C with 5% CO_2. The medium was subsequently removed, and the OVCAR3 and SKOV3 cells were incubated with DMEM and McCoy's 5A, respectively, with DMNB-Gal-DCP (10 μM) for 18 hours. After 12 hours of incubation, a subset of cells was exposed to UV for 3 minutes. The cells were washed with PBS for three times and fixed with 4% PFA for 15 minutes. After washing off PFA with PBS, Antifade Mounting Medium with DAPI (P0131-25ml, Beyotime, China) was added to the dishes and incubated with cells for 20 minutes at room temperature. The cells were imaged by confocal laser scanning microscopy (CLSM) (TCS SP8, Leica, Germany).

3.5 MTT assay

For the study of 6-DMNB-Gal-CA4, OVCAR3 cells (3×10^3 cells per well) were seeded in 96-well plates and incubated for 12 hours at 37 °C with 5% CO_2. The medium was subsequently removed, and the cells were incubated with DMEM under the same condition for 48 hours in the presence of (1) DMSO, (2) Gal-CA4, (3) 6-DMNB-Gal-CA4, and (4) 6-DMNB-Gal-CA4 with UV irradiation. For the group with UV irradiation, cells were exposed to UV for 3 minutes after 3 hours of incubation. After aspirating the drug containing medium, 100 μL of DMEM containing 10% MTT (Adamas-beta, China) (5 mg/mL in PBS, v/v) was added to each well, and the plates were incubated for another 3 hours at 37 °C. The absorbance value of each well was detected using a BioTek Synergy H4 multi-detection microplate plate reader (Agilent, USA) at the wavelength of 490 nm.

For the study of 2-DMNB-Gal-CA4, OVCAR3 cells (3×10^3 cells per well) or SKOV3 cells (2×10^3 cells per well) were seeded in 96-well plates and incubated for 12 hours at 37 °C with 5% CO_2. The medium was subsequently removed, and the cells were incubated with DMEM or McCoy's 5A under the same condition for 48 hours in the presence of (1) DMSO, (2) Gal-CA4, (3) 2-DMNB-Gal-CA4, and (4) 2-DMNB-Gal-CA4 with UV irradiation.

For the study of 6-DMNB-Gal-HQ, OVCAR3 cells (8×10^3 cells per well), SKOV3 cells (5×10^3 cells per well), and A549 cells (8×10^3 cells per well) were seeded in 96-well plates and incubated for 12 hours at 37 °C with 5% CO_2. The medium was subsequently removed, and the cells were incubated with DMEM or McCoy's 5A under the same condition for 24 hours in the presence of (1) DMSO, (2) Gal-HQ, (3) 6-DMNB-Gal-HQ, and (4) 6-DMNB-Gal-HQ with UV irradiation. All other conditions were maintained as described above.

3.6 Live/dead staining assay

For the study of DMNB-Gal-CA4, OVCAR3 cells (6×10^3 cells per well) or SKOV3 cells (3×10^3 cells per well) were seeded in 96-well plates and incubated for 12 hours at 37 °C with 5% CO_2. The medium was subsequently removed, and cells were incubated with DMEM and McCoy's 5A, respectively, under the same condition for 48 hours in the presence of: (1) DMSO, (2) DMSO with UV irradiation, (3) Gal-CA4 (50 nM), (4) DMNB-Gal-CA4 (100 nM), and (5) DMNB-Gal-CA4 (100 nM) with UV irradiation. For the groups with UV irradiation, cells were exposed to UV for 3 minutes after 3 hours of incubation. After washed with PBS, the cells were stained using Calcein/PI Cell Viability/Cytotoxicity Assay Kit (C2015M, Beyotime, China) according to the manufacturer's instruction, and imaged by a fluorescence microscope (DMi8, Leica, Germany).

For the study of 6-DMNB-Gal-HQ, OVCAR3 cells (8×10^3 cells per well) or SKOV3 cells (5×10^3 cells per well) were seeded in 96-well plates and cultured for 12 hours at 37 °C with 5% CO_2. The medium was subsequently removed, and the cells were incubated with DMEM or McCoy's 5A under the same condition with or without UV irradiation for 24 h in the presence of (1) DMSO, (2) Gal-HQ (0.4, 1 μM for OVCAR3, 0.4, 2 μM for SKOV3), and (3) 6-DMNB-Gal-HQ (1, 4 μM for OVCAR3, 2, 4 μM for SKOV3). All other conditions were maintained as described above.

3.7 Microtubule assembly inhibitory activity of DMNB-Gal-CA4

OVCAR3 cells (2×10^5 cells per dish) were seeded in glass-bottomed cell culture dishes (801001, NEST Biotechnology, China) and incubated for 24 hours at 37 °C with 5% CO_2. The medium was subsequently removed, and the cells were incubated with DMEM under the same condition for 9 hours in the presence of (1) DMSO, (2) Gal-CA4 (50 nM), (3) DMNB-Gal-CA4 (100 nM), and (4) DMNB-Gal-CA4 (100 nM) with UV irradiation. For the group with UV irradiation, cells were exposed to UV for 3 minutes after 3 hours of incubation.

For immunofluorescence study, the cells were first fixed with 4% PFA and then permeated with 0.1% Triton X-100. Next, the cells were blocked in PBST buffer containing 5% bovine serum albumin for 2 hours and incubated with the anti-α-tubulin antibody (1:2000) (ab7291, Abcam, UK) at 4 °C overnight. After the cells were washed with

PBST for three times (5 minutes each), goat anti-mouse IgG H&L (Alexa Fluor® 488) (1:1000) (ab150113, Abcam, UK) was added, followed by another 2-hour incubation at room temperature. The cell nuclei were stained with DAPI, and the cells were imaged using a CLSM (TCS SP8, Leica, Germany).

3.8 Colony formation assay

OVCAR3 cells (1×10^3 cells per well) or SKOV3 cells (1×10^3 cells per well) were seeded in 6-well plates and cultured for two weeks. When colony formed, the cells were incubated with or without UV for 24 hours in the presence of (1) DMSO, (2) Gal-HQ (1 μM for OVCAR3, 2 μM for SKOV3), and (3) 6-DMNB-Gal-HQ (1, 4 μM for OVCAR3, 2, 4 μM for SKOV3). For the groups with UV irradiation, cells were exposed to UV for 3 minutes after 3 hours of incubation. The cells were washed with PBS for three times and then fixed with 4% PFA for 15 minutes. Finally, the cells were stained with 0.1% crystal violet staining solution for 10 minutes.

3.9 Detection of intracellular ROS

OVCAR3 cells (2×10^4 cells per well), SKOV3 cells (1×10^4 cells per well), and A549 cells (2×10^4 cells per well) were seeded in 48-well plates and cultured for 24 hours at 37 °C with 5% CO_2. The medium was subsequently removed, and the cells were incubated with DMEM or McCoy's 5A under the same condition for 6 hours in the presence of (1) DMSO, (2) Gal-HQ (1 μM for OVCAR3, 2 μM for SKOV3 and A549), (3) Gal-HQ (1 μM for OVCAR3, 2 μM for SKOV3 and A549) with UV irradiation, (4) 6-DMNB-Gal-HQ (4 μM), (5) 6-DMNB-Gal-HQ (4 μM) with UV irradiation. For the groups with UV irradiation, cells were exposed to UV for 3 minutes after 3 hours of incubation. The cells were washed with PBS and incubated with 2',7'-dichloro-dihydro-fluorescein diacetate (DCFH-DA) (10 μM) (S0033S, Beyotime, China) in FBS free medium for 20 minutes in the dark. The cells were imaged by a fluorescence microscope (DMi8, Leica, Germany).

3.10 Detection of activated caspase 3

OVCAR3 cells (2×10^4 cells per well) were seeded in 48-well plates and cultured for 24 hours at 37 °C with 5% CO_2. The medium was subsequently removed, and the cells were incubated with DMEM under the same condition with or without UV irradiation for 9 hours in the presence of (1) DMSO, (2) Gal-HQ (1 μM), (3) 6-DMNB-Gal-HQ (4 μM). For the groups with UV irradiation, cells were exposed to UV for 3 minutes after 3 hours of incubation. The cells were washed with PBS and stained using GreenNuc™ Caspase-3 Assay Kit for Live Cells

(C1168S, Beyotime, China) according to the manufacturer's instruction. The cells were imaged by a fluorescence microscope (DMi8, Leica, Germany).

3.11 Detection of apoptotic cells

For the study of 6-DMNB-Gal-HQ, OVCAR3 cells (5×10^5 cells per well) or SKOV3 cells (3×10^5 cells per well) were seeded in 6-well plates and cultured for 36 hours at 37 °C with 5% CO_2. The medium was subsequently removed, and the cells were incubated with DMEM or McCoy's 5A under the same condition with or without UV irradiation for 24 hours in the presence of (1) DMSO, (2) Gal-HQ (1 μM for OVCAR3, 2 μM for SKOV3), (3) 6-DMNB-Gal-HQ (4 μM for OVCAR3, 2, 4 μM for SKOV3). For the groups with UV irradiation, cells were exposed to UV for 3 minutes after 3 hours of incubation. The cells were digested by 0.25% trypsin-EDTA solution and washed with PBS for three times by centrifugation (1000 × *g*, 5 minutes). After stained using Annexin V-FITC Apoptosis Detection Kit (C1062L, Beyotime, China) according to the manufacturer's instruction, the apoptotic cells were analyzed by a flow cytometry (Accuri™ C6 Plus, BD Biosciences, USA).

For the study of 2-DMNB-Gal-CA4 and 6-DMNB-Gal-CA4, cells were divided into groups and treated with (1) DMSO, (2) Gal-CA4 (50 nM), (3) 2-DMNB-Gal-CA4 (100 nM), (4) 2-DMNB-Gal-CA4 (100 nM) with UV irradiation, (5) 6-DMNB-Gal-CA4 (100 nM), (6) 6-DMNB-Gal-CA4 (100 nM) with UV irradiation. All other conditions were maintained as described above.

3.12 Wound healing assay

For the study of 6-DMNB-Gal-HQ, OVCAR3 cells (5×10^6 cells per well) or SKOV3 cells (3×10^6 cells per well) were seeded in 6-well plates and cultured for 24 hours at 37 °C with 5% CO_2. A wound was scratched with a 200 μL sterile micropipette tip and washed gently with PBS. The medium was subsequently removed, and the cells were incubated with DMEM (2% FBS) or McCoy's 5A (2% FBS) under the same condition for 24 hours in the presence of (1) DMSO, (2) Gal-HQ (1 μM for OVCAR3, 2 μM for SKOV3), (3) 6-DMNB-Gal-HQ (4 μM), and (4) 6-DMNB-Gal-HQ (4 μM) with UV irradiation. For the groups with UV irradiation, cells were exposed to UV for 3 minutes after 3 hours of incubation. The cells were imaged with an optical microscope (CKX53, Olympus, Japan). The wound healing rates were quantified using ImageJ.

For the study of 2-DMNB-Gal-CA4 and 6-DMNB-Gal-CA4, cells were divided into groups and treated with (1) DMSO, (2) Gal-CA4 (50 nM), (3) DMNB-Gal-CA4 (100 nM), and (4) DMNB-Gal-CA4 (100 nM) with UV irradiation. All other conditions were maintained as described above.

3.13 Cellular uptake study

OVCAR3 cells (5×10^5 cells per well) or SKOV3 cells (3×10^5 cells per well) were seeded in 6-well plates and cultured for 36 hours. The cells were incubated with (1) 2-DMNB-Gal-DCP (10 μM), (2) 3-DMNB-Gal-DCP (10 μM), (3) 4-DMNB-Gal-DCP (10 μM), or (4) 6-DMNB-Gal-DCP (10 μM) for 3 or 24 hours. After digested by 0.25% trypsin-EDTA solution, the cells were washed with PBS twice by centrifugation (1000 × *g*, 5 minutes). After resuspended in ddH_2O (500 μL), the cells were lysed using three cycles of freeze-thaw (froze at -80 °C for 20 minutes, thawed at 37 °C for 20 minutes). To the resulting solution, MeCN (500 μL) was added and mixed. The mixture was incubated at 37 °C for 1 hour, and insoluble components were separated by centrifugation (12000 × *g*, 15 minutes). The final solution was analyzed using HPLC (Gradient method B or D) and detected at 440 nm.

3.14 Cell cycle analysis

OVCAR3 cells (5×10^5 cells per well) or SKOV3 cells (3×10^5 cells per well) were seeded in 6-well plates and were cultured for 36 hours. The medium was subsequently removed, and the cells were incubated with DMEM or McCoy's 5A under the same condition for 24 hours in the presence of (1) DMSO, (2) Gal-CA4 (50 nM), (3) DMNB-Gal-CA4 (100 nM), (4) DMNB-Gal-CA4 (100 nM) with UV irradiation. For the groups with UV irradiation, cells were exposed to UV for 3 minutes after 3 hours of incubation. The cells were digested by 0.25% trypsin-EDTA solution and washed with cold PBS for three times by centrifugation (1000 × *g*, 5 minutes). The collected cells were fixed with 75% ethanol at -20 °C overnight. The fixed cells were washed twice with PBS, and stained with staining solution containing RNase A and propidium iodide in the dark for 15 minutes using Cell Cycle and Apoptosis Analysis Kit (C1052, Beyotime, China). The cell cycle was analyzed by a flow cytometer (Accuri™ C6 Plus, BD Biosciences, USA).

3.15 One-well two-wound assay

OVCAR3 cells (5×10^6 cells per well) were seeded in 6-well plates and cultured for 36 hours with 5% CO_2 at 37 °C. Two wounds were scratched in one well with a 200 μL sterile micropipette tip and washed gently with PBS. The medium was subsequently removed, and the cells were incubated with DMEM under the same condition for 48 hours in the presence of (1) DMSO, (2) Gal-CA4 (50 nM), and (3) 2-DMNB-Gal-CA4 (100 nM). The wells were covered with aluminum foil, leaving only one wound exposed to UV irradiation after 3 hours of incubation. The migration of cells into wound area was observed and recorded using a microscope (CKX53, Olympus, Japan).

3.16 Anticancer activity in zebrafish

The zebrafish facility is accredited by the Association for Assessment and Accreditation of Laboratory Animal Care (AAALAC) and the Experimental Animal Ethics Committee of Hunter Biotechnology, Inc. (IACUC-2024-9245-01, Hangzhou, China). OVCAR3 cells labeled with CellTracker™ CM-DiI (Thermo Fisher, USA) were implanted into the yolk sac of AB/WT zebrafish at 2 days post-fertilization (dpf) at a density of 400 cells per fish. The Zebrafish were incubated at 34 °C for 24 hours. At 3 dpf, the zebrafish were randomly divided into four groups (n = 5) and injected with (1) saline, (2) 2-DMNB-Gal-CA4 (100 nM), (3) 2-DMNB-Gal-CA4 (100 nM) with UV irradiation, and (4) Gal-CA4 (100 nM) into the yolk sac. For the group with UV irradiation, the zebrafish were exposed to UV for 3 minutes at 3.5 dpf. All groups were then incubated at 34 °C. At 6 dpf, the fluorescence intensity of OVCAR3 cells was imaged using a fluorescence microscope (MVX10, Olympus, Japan).

3.17 Molecular docking study[1]

The molecular docking study of compounds with *β*-gal was performed using the crystal structures of human *β*-gal 3THC[2] and *A. oryzae β*-gal 4IUG[3] obtained from the Protein Data Bank at https://www.rcsb.org.

Water molecules and ions outside the binding pocket of *β*-gal were removed, and only the monomer of the enzymes was used for docking. Co-crystallized small molecules that located outside the binding pocket were removed. Hydrogens were added based on the protonation states of the protein and the ligand at a pH of 7.0 ± 2.0.

The galactose in the binding pocket was used for grid box generation. For Gal-MU, 6-MASK-Gal-MU, isomers of ONB-Gal-MU, and isomers of DMNB-Gal-MU, the grid size of 3THC was generated with an inner grid box of 10 Å × 10 Å × 10 Å and an outer box of 20 Å × 20 Å × 20 Å, and the grid size of 4IUG was generated with an inner grid box of 10 Å × 10 Å × 10 Å and an outer box of 30 Å × 30 Å × 30 Å. For Gal-CA4, Gal-HQ, Gal-DCP, and isomers of DMNB-Gal-DCP, the grid size was generated with an inner grid box of 10 Å × 10 Å × 10 Å and an outer box of 46 Å × 46 Å × 46 Å. The OPLS 2005 force field was applied for grid box generation.

Ligands were prepared using the Ligand Preparation module in Schrödinger Maestro, with pK_a values and protonation states determined at pH 7.0 using Epik. Glide SP was employed to generate binding conformations of the prepared ligands, utilizing a flexible ligand sampling method. The van der Waals radii were scaled by a factor of 0.80, and a partial charge cutoff of 0.25 was applied. Additionally, nitrogen inversion and ring conformation sampling options were utilized. Bias sampling of torsions was maintained for all predefined functional groups. Epik state penalties were incorporated into the docking score. Post-docking minimizations were conducted using the OPLS2005 force field. Conformations for compounds were obtained based on the rank by docking scores. The generated conformations were inspected and selected for generating binding maps in PyMOL and LigPlot+.

3.18 Statistical analysis

Data in this study were presented as the means with standard errors (means ± SD). Differences among groups were evaluated using one-way and two-way analysis of variance (ANOVA) with GraphPad Prism 7.0 software. The $P < 0.05$ was considered statistically significant.

4. Chemical Synthesis

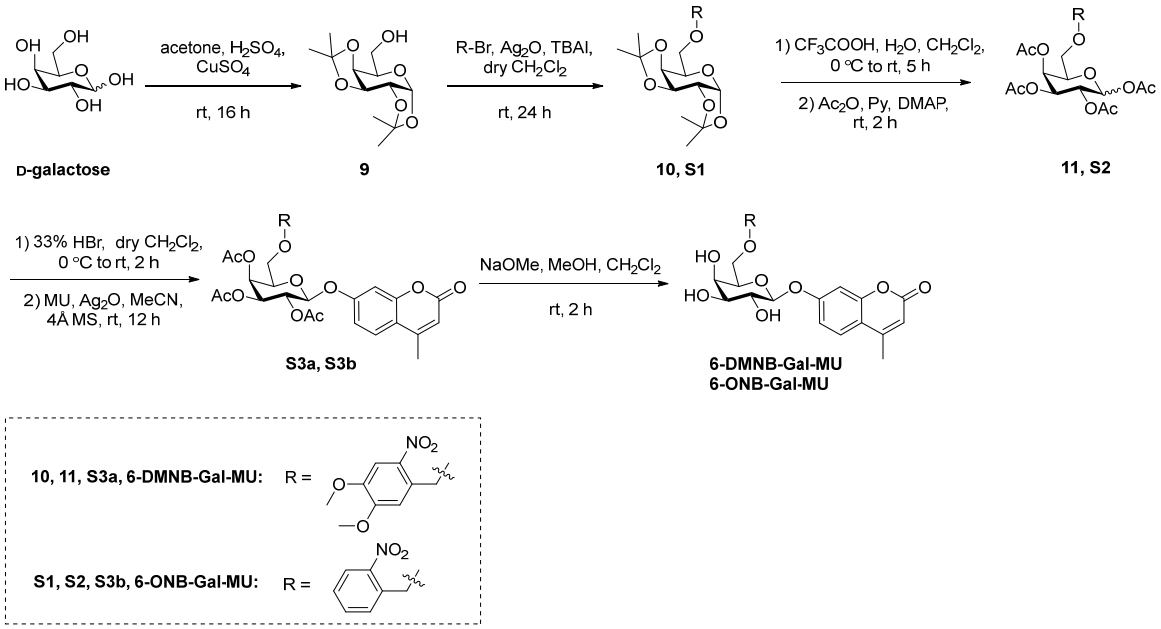
4.1 General information

Commercially available reagents were obtained from J&K scientific, Energy Chemical, Adamas-beta, and Bidepharm. All regents were used without further purification, and all reactions were carried out under argon atmosphere unless otherwise stated. The anhydrous solvents used in reactions were obtained from an MBraun MB-SPS 800 Dry Solvent System. Allyl 2,2,2-trichloroacetimidate, 4-(boronic acid pinacol ester)-benzyl 2,2,2-trichloroacetimidate, and 4-azidobenzyl 2,2,2-trichloroacetimidate were synthesized using a reported method.[4] Compound **S26** was prepared using a reported method.[5]

Analytical thin-layer chromatography (TLC) was carried out on pre-coated silica gel plate (0.2 mm thickness). Spots were visualized with a UV lamp (254 nm) or sugar stain (0.1% (v/v) 3-methoxyphenol, 2.5% (v/v) sulfuric acid in EtOH). Silica gel (200–300 mesh) were used for chromatography purification process.

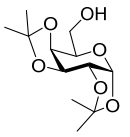
NMR spectra were recorded on a Brüker Avance III 400 MHz (Germany) or Brüker Avance NEO 600 MHz (Germany). All NMR chemical shifts (δ) were recorded in ppm and coupling constants (J) were reported in Hertz (Hz). For ^{1}H NMR spectra, the solvent signal (δ 0.00 (TMS), δ 7.26 ppm ($CDCl_3$), δ 2.50 ppm ($(CD_3)_2SO$), δ 1.56 ppm (H_2O in $CDCl_3$), or δ 3.33 ppm (H_2O in $(CD_3)_2SO$)) is used as an internal reference. For ^{13}C NMR spectra, the chemical shifts are reported relative to δ 77.06 ppm ($CDCl_3$) or δ 39.53 ppm ($(CD_3)_2SO$). The following abbreviations were used to explain the multiplicities: s = singlet, d =doublet, t = triplet, q = quartet, m = multiplet, and *etc*. Splitting patterns that could not be easily interpreted are designated as multiplet (m). Structural assignments were made with additional information from ^{1}H-^{1}H COSY and ^{1}H-^{13}C HSQC experiments. Electrospray ionization mass spectra (ESI-MS) were obtained on a TSQ quantum Ultra EMR mass spectrometer (Thermo Fisher, USA). High resolution electrospray ionization mass spectroscopy (HRMS) was performed on a 6220 ESI-TOF mass spectrometer (Agilent, USA).

4.2 Synthesis of *O*6-caged 4-methylumbelliferyl *β*-D-galactopyranoside



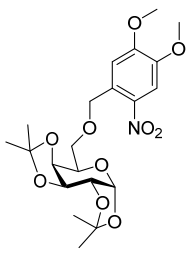
Scheme S1. The synthetic route to 6-DMNB-Gal-MU and 6-ONB-Gal-MU.

1,2:3,4-Di-*O*-isopropylidene-6-*O*-(4,5-dimethoxy-2-nitrobenzyl)-*α*-D-galactopyranoside, 10



9

To a solution of anhydrous $CuSO_4$ (2.83 g, 17.76 mmol, 1.6 eq.) in acetone (25 mL, dried over $MgSO_4$), concentrated H_2SO_4 (0.15 mL) and D-galactose (2.00 g, 11.10 mmol, 1.0 eq.) were added. After 16 hours, saturated $NaHCO_3$ (14 mL) was added, and the solution was extracted with ethyl acetate (EA). The organic phase was dried over Na_2SO_4 and concentrated. The residue was purified with silica gel chromatography using petroleum ether (PE) and EA (5:1, v/v) to afford **9** as colorless oil (2.51 g, 9.65 mmol, yield 87%).



10

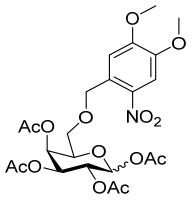
To a stirred mixture of **9** (1.03 g, 3.96 mmol, 1.0 eq.) and tetrabutylammonium iodide (TBAI) (731 mg, 1.98 mmol, 0.5 eq.) in CH_2Cl_2 (30 mL), Ag_2O (1.83 g, 7.91 mmol, 2.0 eq.) was added. The mixture was stirred for 10 min at room temperature. 4,5-Dimethoxy-2-nitrobenzyl bromide (DMNB-Br, 1.64 g, 5.94 mmol, 1.5 eq.) in dry CH_2Cl_2 (5 mL) was added, and the resulting solution was stirred for another 24 hours at room temperature. The reaction mixture was filtered through celite and then washed with water, saturated NH_4Cl, and brine. The organic layer was dried over Na_2SO_4. After concentration, the residue was then purified with silica gel chromatography using PE and EA (13:1, v/v) to afford **2a** as yellow oil (649 mg, 1.42 mmol, yield 36%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (s, 1H, Ar-H (DMNB)), 7.43 (s, 1H, Ar-H (DMNB)), 5.55 (d, J = 5.0 Hz, 1H, 1-H), 5.01 (d, J = 16.1, Hz, 1H, ArCH_2), 4.95 (d, J = 16.1, 1H, ArCH_2), 4.63 (dd, J = 7.9, 2.4 Hz, 1H, 3-H), 4.34 (dd, J = 5.0, 2.5 Hz, 1H, 2-H), 4.27 (dd, J = 7.9, 1.9 Hz, 1H, 4-H), 4.11 (ddd, J = 6.9, 4.5, 1.8 Hz, 1H, 5-H), 4.00 (s, 3H, $ArOCH_3$ (DMNB)), 3.94 (s, 3H, $ArOCH_3$ (DMNB)), 3.77 (qd, J = 10.4, 6.0 Hz, 2H, 6-H), 1.54 (s, 3H, CH_3 (isopropylidene)), 1.43 (s, 3H, CH_3 (isopropylidene)), 1.34 – 1.32 (m, 6H, CH_3 (isopropylidene)).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.0, 147.5, 139.1, 131.4, 109.7, 109.5, 108.7, 107.9, 96.5, 71.4, 70.8, 70.6, 70.2, 69.8, 67.1, 56.44, 56.38, 26.10, 26.05, 25.0, 24.5.

ESI-MS: found 478.2 $[M + Na]^+$.

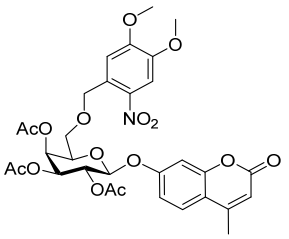
4-Methylumbelliferyl 2,3,4-tri-*O*-acetyl-6-*O*-(4,5-dimethoxy-2-nitrobenzyl)-*β*-D-galactopyranoside, S3a



11

A solution of **10** (620 mg, 1.36 mmol, 1.0 eq.) in CH_2Cl_2 (2 mL) was added to a stirred solution of CF_3COOH and H_2O (10 mL, 4:1, v/v) at 0 °C. After warmed to room temperature and stirred for 5 hours, the solution was concentrated under reduced pressure to get crude residue without further purification. After co-evaporated twice with toluene, pyridine (Py) (10 mL) and acetic anhydride (Ac_2O) (0.76 mL, 8.17 mmol, 6.0 eq.) were added, and the solution was stirred at room temperature for 2 hours. When TLC showed the completion of the reaction, the solution was diluted with CH_2Cl_2. The organic phase was washed sequentially with 1 M HCl, saturated $NaHCO_3$, and brine. After dried over Na_2SO_4 and concentrated, the residue was purified with silica gel chromatography using PE and EA (4:1, v/v) to afford **11** as yellow foam (658 mg, 1.21 mmol, yield 89%). The compound **11** was then used for the next step.

ESI-MS: found 566.2 $[M + Na]^+$.



S3a

Compound **11** (100 mg, 0.184 mmol, 1.0 eq.) was dissolved in CH_2Cl_2 (1 mL) and stirred at 0 °C for 10 min. Then 33% HBr in acetic acid (0.13 mL, 1.29 mmol, 7.0 eq.) was added. The mixture was warmed to room temperature and stirred for another 2 hours. When TLC showed the completion of the reaction, CH_2Cl_2 and saturated $NaHCO_3$ were added to the solution. The organic layer was separated and washed with saturated $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo to afford the brominated intermediate.

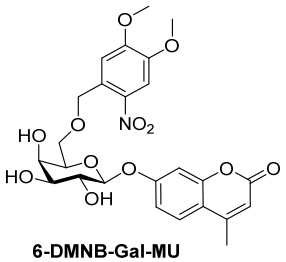
The brominated intermediate was dissolved in MeCN (0.5 mL) and added to a stirred mixture of 4-methylumbelliferone (39 mg, 0.221 mmol, 1.2 eq.), Ag_2O (85 mg, 0.369 mmol, 2.0 eq.), TBAI (34 mg, 0.092 mmol, 0.5 eq.), and 4Å MS in MeCN (0.5 mL). The solution was stirred at room temperature for 12 hours. When TLC showed the complete consumption of the brominated intermediate, the reaction mixture was filtered through celite. The organic layer was washed with Na_2CO_3, water, and brine. After dried over Na_2SO_4 and concentrated, the residue was purified with silica gel chromatography using PE and EA (1:1, v/v) to afford **S3a** as yellow foam (63 mg, 0.096 mmol, yield 52%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (s, 1H, Ar-H (DMNB)), 7.51 (d, J = 8.4 Hz, 1H, Ar-H (MU)), 7.19 (s, 1H, Ar-H (DMNB)), 6.99 – 6.94 (m, 2H, Ar-H (MU)), 6.19 (d, J = 1.5 Hz, 1H, Ar-H (MU)), 5.63 (d, J = 3.4 Hz, 1H, 4-H), 5.54 (dd, J = 10.5, 7.9 Hz, 1H, 2-H), 5.18 (d, J = 7.9 Hz, 1H, 1-H), 5.16 (dd, J = 10.5, 3.5 Hz, 1H, 3-H), 4.97 – 4.89 (m, 2H, $ArCH_2$), 4.18 (t, J = 6.5 Hz, 1H, 5-H), 3.94 (s, 3H, $ArOCH_3$ (DMNB)), 3.91 (s, 3H, $ArOCH_3$ (DMNB)), 3.81 (dd, J = 9.9, 6.5 Hz, 1H, 6-*H*), 3.72 (dd, J = 10.0, 6.4 Hz, 1H, 6-*H*), 2.40 (s, 3H, CH_3 (MU)), 2.17 (s, 3H, CH_3 (Ac)), 2.08 (s, 3H, CH_3 (Ac)), 2.02 (s, 3H, CH_3 (Ac)).

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.2, 170.1, 169.4, 160.7, 159.4, 154.9, 154.1, 152.1, 147.8, 139.0, 129.9, 125.9, 115.6, 113.7, 113.3, 109.6, 107.9, 104.2, 99.2, 72.6, 71.0, 70.3, 68.5, 68.3, 67.2, 56.5, 56.4, 20.8, 20.7, 20.6, 18.7.

ESI-MS: found 682.2 $[M + Na]^+$.

4-Methylumbelliferyl 6-*O*-(4,5-dimethoxy-2-nitrobenzyl)-*β*-D-galactopyranoside, 6-DMNB-Gal-MU



6-DMNB-Gal-MU

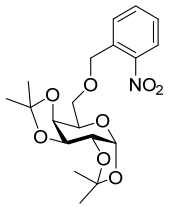
Compound **S3a** (60 mg, 0.091 mmol, 1.0 eq.) was dissolved in a mixture of CH_2Cl_2 and MeOH (1 mL, 1:1, v/v) containing NaOMe (5 M in MeOH, 18 μL, 1.0 eq.). After stirring at room temperature for 2 hours, H^+ resin was added to adjust the pH of solution to 7. The resin was filtered off, and the filtrate was concentrated. The crude product was purified with silica gel chromatography using MeOH and CH_2Cl_2 (1:25, v/v) to afford **6-DMNB-Gal-MU** as light-yellow solid (36 mg, 0.044 mmol, yield 48%).

^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 7.65 – 7.58 (m, 2H, Ar-H (DMNB), Ar-H (MU)), 7.23 (s, 1H, Ar-H (DMNB)), 7.02 (dd, J = 4.6, 2.4 Hz, 2H, Ar-H (MU)), 6.22 (d, J = 1.4 Hz, 1H, Ar-H (MU)), 5.30 (d, J = 5.1 Hz, 1H, OH), 5.08 (d, J = 7.7 Hz, 1H, 1-H), 4.98 (d, J = 5.1 Hz, 1H, OH), 4.85 (s, 2H, $ArCH_2$), 4.70 (d, J = 4.8 Hz, 1H, OH), 4.06 (dd, J = 7.9, 4.2 Hz, 1H, 5-H), 3.84 (s, 3H, $ArOCH_3$ (DMNB)), 3.74 – 3.70 (m, 5H, 4-H, 2-H, $ArOCH_3$ (DMNB)), 3.68 – 3.60 (m, 2H, 6-H), 3.50 – 3.46 (m, 1H, 3-H), 2.38 (d, J = 1.3 Hz, 3H, CH_3 (MU)).

^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 160.1, 160.0, 154.4, 153.4, 153.2, 147.2, 138.8, 130.1, 126.3, 114.0, 113.2, 111.7, 109.7, 108.0, 102.9, 100.2, 73.9, 73.0, 69.9, 68.9, 68.7, 56.0, 55.9, 18.0.

HRMS: m/z calculated $[M + Na]^+$ =556.1425, found 556.1428.

1,2:3,4-Di-*O*-isopropylidene-6-*O*-(2-nitrobenzyl)-*α*-D-galactopyranoside, S1



S1

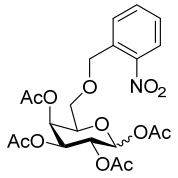
Compound **S1** was synthesized from **9** (250 mg, 0.960 mmol, 1.0 eq.) and 2-nitrobenzyl bromide (ONB-Br, 414 mg, 1.92 mmol, 2.0 eq.) using a procedure similar to that employed for the preparation of **10**. The crude product was purified with silica gel chromatography using PE and EA (13:1, v/v) to afford **S1** as yellow oil (121 mg, 0.307 mmol, yield 32% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, J = 8.2, 1.3 Hz, 1H, Ar-H (ONB)), 7.83 (dd, J = 7.8, 1.4 Hz, 1H, Ar-H (ONB)), 7.63 (td, J = 7.6, 1.3 Hz, 1H, Ar-H (ONB)), 7.42 (td, J = 7.8, 1.5 Hz, 1H, Ar-H (ONB)), 5.55 (d, J = 5.0 Hz, 1H, 1-H), 4.96 (s, 2H, $ArCH_2$), 4.62 (dd, J = 7.9, 2.4 Hz, 1H, 3-H), 4.33 (dd, J = 5.1, 2.4 Hz, 1H, 2-H), 4.28 (dd, J = 7.9, 1.9 Hz, 1H, 4-H), 4.07 (ddd, J = 7.2, 5.5, 1.9 Hz, 1H, 5-H), 3.81 – 3.68 (m, 2H, 6-H), 1.56 (s, 3H, CH_3 (isopropylidene)), 1.44 (s, 3H, CH_3 (isopropylidene)), 1.34 (s, 6H, CH_3 (isopropylidene)).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.3, 135.2, 133.6, 128.8, 127.9, 124.6, 109.4, 108.7, 96.4, 71.2, 70.7, 70.6, 70.0, 69.8, 66.7, 26.1, 26.0, 25.0, 24.5.

ESI-MS: found 418.2 $[M + Na]^+$.

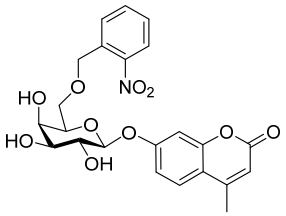
4-Methylumbelliferyl 6-*O*-(2-nitrobenzyl)-*β*-D-galactopyranoside, 6-ONB-Gal-MU



S2

Compound **S2** was synthesized from **S1** (100 mg, 0.253 mmol, 1.0 eq.) using a procedure similar to that employed for the preparation of **11**. The crude product was purified with silica gel chromatography using PE and EA (1:1, v/v) to afford **S2** as light yellow oil (90 mg, 0.187 mmol, yield 74%, α:β = 1:1).

ESI-MS: found 506.1 $[M + Na]^+$.



6-ONB-Gal-MU

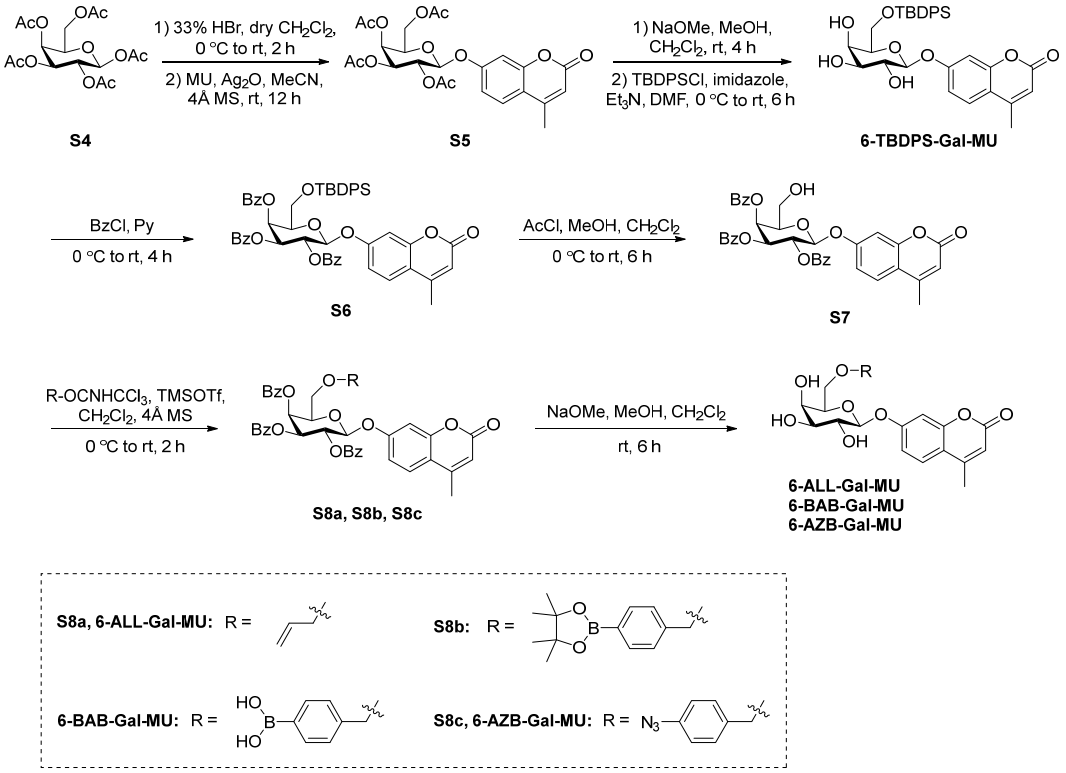
Compound **6-ONB-Gal-MU** was synthesized from **S2** (82 mg, 0.169 mmol, 1.0 eq.) and MU (30 mg, 0.170 mmol, 1.0 eq.) using a procedure similar to that employed for the preparation of **6-DMNB-Gal-MU**. The crude product was purified with silica gel chromatography using MeOH and CH_2Cl_2 (1:25, v/v) to afford **6-ONB-Gal-MU** as light-yellow solid (36 mg, 0.076 mmol, yield 45% over three steps).

^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.03 (dd, J = 8.2, 1.3 Hz, 1H, Ar-H (ONB)), 7.79 (d, J = 7.8 Hz, 1H, Ar-H (ONB)), 7.70 (td, J = 7.6, 1.3 Hz, 1H, Ar-H (ONB)), 7.66 (d, J = 8.7 Hz, 1H, Ar-H (MU)), 7.58 – 7.47 (m, 1H, Ar-H (ONB)), 7.07 (d, J = 2.4 Hz, 1H, Ar-H (MU)), 7.03 (dd, J = 8.8, 2.5 Hz, 1H, Ar-H (MU)), 6.24 (d, J = 1.5 Hz,

1H, Ar-H (MU)), 5.29 (d, J = 5.1 Hz, 1H, OH), 5.07 (d, J = 7.7 Hz, 1H, 1-H), 4.97 (d, J = 5.7 Hz, 1H, OH), 4.91 – 4.78 (m, 2H, $ArCH_2$), 4.71 (d, J = 4.8 Hz, 1H, OH), 4.03 (dd, J = 7.7, 4.1 Hz, 1H, 5-H), 3.77 – 3.68 (m, 2H, 4-H, 2-H), 3.69 – 3.58 (m, 2H, 6-H), 3.48 (ddd, J = 9.3, 5.7, 3.3 Hz, 1H, 3-H), 2.40 (d, J = 1.2 Hz, 3H, CH_3 (MU)).

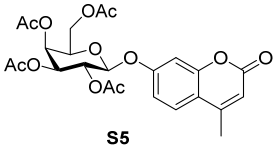
^{13}C NMR (101 MHz, $(CD_3)_2SO$)) δ 160.04, 160.03, 154.4, 153.2, 146.9, 134.5, 133.8, 128.4, 128.3, 126.3, 124.4, 114.0, 113.4, 111.6, 103.0, 100.2, 73.9, 73.0, 70.3, 69.9, 68.8, 68.6, 18.1.

HRMS: m/z calculated $[M + Na]^+$ = 496.1214, found 496.1217.



Scheme S2. The synthetic route to 6-TBDPS-Gal-MU[6], 6-ALL-Gal-MU, 6-AZB-Gal-MU, and 6-BAB-Gal-MU.

4-Methylumbelliferyl 2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranoside, S5



S5

Compound **S4** (1.30 g, 3.33 mmol, 1.0 eq.) was dissolved in CH_2Cl_2 (7 mL) and cooled to 0 °C for 10 min. Then 33% HBr in acetic acid (2.4 mL, 23.40 mmol, 7.0 eq.) was added. The solution was warmed to room

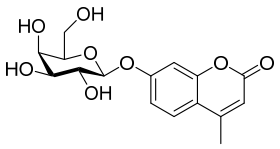
temperature and stirred for 2 hours. When TLC showed the completion of the reaction, CH_2Cl_2 and saturated $NaHCO_3$ were added. The organic layer was separated and washed with saturated $NaHCO_3$ and brine. After dried over Na_2SO_4 and filtered, the solvent was concentrated under reduced presser to afford a brominated intermediate.

To the brominated intermediate in MeCN (20 mL), 4Å molecular sieves, 4-methyl-umbelliferone (646 mg, 3.67 mmol, 1.1 eq.), Ag_2O (1.54 g, 6.67 mmol, 2.0 eq.), and TBAI (615 mg, 1.67 mmol, 0.5 eq.) were added sequentially. The reaction mixture was stirred at room temperature for 12 hours. When TLC showed complete consumption of the brominated intermediate, the reaction mixture was filtered through celite. The organic layer was washed with Na_2CO_3, water, and brine. After dried over Na_2SO_4 and concentrated, the residue was purified with silica gel chromatography using PE and EA (2:1, v/v) to afford **S5** as colorless oil (945 mg, 1.86 mmol, yield 56% over two steps).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, J = 8.7 Hz, 1H, Ar-H (MU)), 6.96 (d, J = 2.4 Hz, 1H, Ar-H (MU)), 6.93 (dd, J = 8.7, 2.5 Hz, 1H, Ar-H (MU)), 6.18 (q, J = 1.2 Hz, 1H, Ar-H (MU)), 5.50 (dd, J = 10.4, 7.9 Hz, 1H, 2-H), 5.47 (dd, J = 3.5, 1.1 Hz, 1H, 4-H), 5.15 – 5.12 (m, 2H, 3-H, 1-H), 4.23 – 4.15 (m, 2H, 6-H), 4.12 (ddd, J = 7.2, 5.6, 1.1 Hz, 1H, 5-H), 2.40 (d, J = 1.3 Hz, 3H, CH_3 (MU)), 2.18 (s, 3H, CH_3 (Ac)), 2.09 (s, 3H, CH_3 (Ac)), 2.06 (s, 3H, CH_3 (Ac)), 2.01 (s, 3H, CH_3 (Ac)).

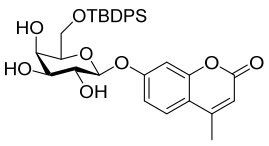
ESI-MS: found 539.5 $[M + Na]^+$.

4-Methylumbelliferyl 6-*O*-(*tert*-butyldiphenylsilyl)-*β*-D-galactopyranoside, 6-TBDPS-Gal-MU



Gal-MU

Compound **S5** (920 mg, 1.82 mmol, 1.0 eq.) was dissolved in a mixture of CH_2Cl_2 and MeOH (10 mL, 1:1, v/v) containing NaOMe (5 M in MeOH, 200 μL, 0.5 eq.). After stirring at room temperature for 4 hours, H^+ resin was added to adjust the pH of the solution to 7. The resin was filtered off and the filtrate was evaporated in vacuo to give the crude Gal-MU.



6-TBDPS-Gal-MU

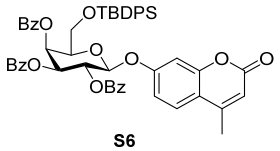
To a solution of Gal-MU (608 mg, 1.80 mmol, 1.0 eq.) in DMF (10 mL), imidazole (245 mg, 3.60 mmol, 2.0 eq.) was added, and the mixture was stirred at 0 °C for 10 min. Then *tert*-butylchlorodiphenylsilane (TBDPSCl) (0.70 mL, 2.70 mmol, 1.5 eq.) and Et_3N (250 μL, 1.80 mmol, 1.0 eq.) was added dropwise, and the mixture was warmed up to room temperature. The reaction mixture was stirred for another 6 hours. The solution was diluted with EA, and the organic layer was washed with water and brine. After dried over Na_2SO_4 and concentrated, the crude residue was purified with silica gel chromatography using PE and EA (1:1, v/v) to afford **6-TBDPS-Gal-MU** as colorless solid (882 mg, 1.53 mmol, yield 84% over two steps).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 – 7.58 (m, 4H, Ar-H), 7.44 – 7.27 (m, 7H, Ar-H × 6, Ar-H (MU)), 6.97 (dt, J = 8.7, 2.8 Hz, 1H, Ar-H (MU)), 6.88 (dq, J = 10.6, 2.7 Hz, 1H, Ar-H (MU)), 6.13 (dd, J = 8.5, 4.2 Hz, 1H, Ar-H (MU)), 4.93 (d, J = 7.8 Hz, 1H, 1-H), 4.13 (dd, J = 5.9, 3.0 Hz, 1H, 4-H), 4.02 (dd, J = 9.6, 7.8 Hz, 1H, 2-H), 3.98 – 3.87 (m, 2H, 6-H), 3.76 – 3.63 (m, 2H, 3-H, 5-H), 2.36 – 2.32 (m, 3H, CH_3 (MU)), 1.04 (s, 9H, $SiC(CH_3)_3$).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.1, 159.7, 154.7, 152.4, 135.63, 135.56, 132.8, 132.6, 130.0, 127.9, 127.8, 125.6, 115.0, 113.6, 112.8, 104.3, 100.5, 74.9, 73.6, 71.4, 68.9, 63.3, 26.8, 19.2, 18.7.

HRMS: m/z calculated $[M + Na]^+$ = 599.2072, found 599.2079.

4-Methylumbelliferyl 2,3,4-tri-*O*-benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)-*β*-D-galactopyranoside, S6



S6

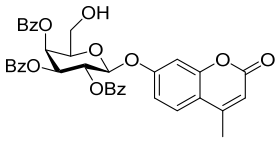
A solution of **6-TBDPS-Gal-MU** (650 mg, 1.13 mmol, 1.0 eq.) in Py (10 mL) was cooled to 0 °C for 10 min, benzoyl chloride (BzCl) (0.53 mL, 4.52 mmol, 4.0 eq.) was added dropwise. The reaction mixture was warmed up to room temperature and stirred for another 4 hours. When TLC showed the completion of the reaction, the solution was diluted with EA. The organic layer was washed sequentially with water, 1 M HCl, saturated $NaHCO_3$, and brine. After dried over Na_2SO_4 and concentrated, the residue was purified with silica gel chromatography using PE and EA (2:1, v/v) to afford **S6** as colorless oil (954 mg, 1.07 mmol, yield 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.99 (m, 2H, Ar-H), 7.97 – 7.88 (m, 2H, Ar-H), 7.86 – 7.78 (m, 2H, Ar-H), 7.67 – 7.61 (m, 3H, Ar-H), 7.52 – 7.35 (m, 12H, Ar-H × 11, Ar-H (MU)), 7.31 – 7.26 (m, 3H, Ar-H), 7.14 (t, J = 7.6 Hz, 2H, Ar-H), 7.03 – 6.91 (m, 2H, Ar-H (MU)), 6.16 (d, J = 1.4 Hz, 1H, Ar-H (MU)), 6.08 (dd, J = 3.3, 1.1 Hz, 1H, 4-H), 6.00 (dd, J = 10.4, 7.8 Hz, 1H, 2-H), 5.70 (dd, J = 10.4, 3.4 Hz, 1H, 3-H), 5.41 (d, J = 7.9 Hz, 1H, 1-H), 4.25 (t, J = 6.8 Hz, 1H, 5-H), 3.95 – 3.81 (m, 2H, 6-H), 2.35 (d, J = 1.2 Hz, 3H, CH_3 (MU)), 1.02 (s, 9H, $SiC(CH_3)_3$).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.6, 165.4, 165.2, 160.9, 159.5, 154.8, 152.1, 135.6, 135.5, 133.7, 133.50, 133.45, 133.3, 132.8, 132.4, 130.2, 130.0, 129.92, 129.90, 129.83, 129.76, 129.3, 129.2, 129.1, 128.9, 128.6, 128.53, 128.49, 128.3, 127.9, 127.7, 125.8, 115.6, 113.9, 113.2, 104.7, 99.6, 74.7, 71.8, 69.5, 67.7, 61.5, 26.7, 19.1, 18.7.

ESI-MS: found 911.2 $[M + Na]^+$.

4-Methylumbelliferyl 2,3,4-tri-*O*-benzoyl-*β*-D-galactopyranoside, S7



S7

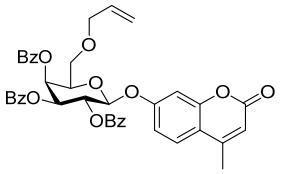
Compound **S6** (935 mg, 1.05 mmol, 1.0 eq.) was dissolved in a mixture of MeOH and CH_2Cl_2 (10 mL, 1:1, v/v). After the mixture was cooled to 0 °C and stirred for 10 min, AcCl (110 μL, 1.57 mmol, 1.5 eq.) was added dropwise. The reaction mixture was warmed up to room temperature and stirred for 6 hours. After concentrated, the crude product was purified with silica gel chromatography using PE and EA (1:1, v/v) to afford **S7** as white foam (615 mg, 0.945 mmol, yield 90%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 – 8.12 (m, 2H, Ar-H), 7.98 – 7.94 (m, 3H, Ar-H), 7.86 – 7.81 (m, 2H, Ar-H), 7.68 – 7.62 (m, 1H, Ar-H (MU)), 7.55 – 7.47 (m, 4H, Ar-H), 7.45 (tt, J = 7.3, 1.3 Hz, 1H, Ar-H), 7.38 (t, J = 7.9 Hz, 2H, Ar-H), 7.29 – 7.26 (m, 2H, Ar-H), 7.03 (d, J = 2.4 Hz, 1H, Ar-H (MU)), 6.97 (dd, J = 8.8, 2.4 Hz, 1H, Ar-H (MU)), 6.18 (d, J = 1.4 Hz, 1H, Ar-H (MU)), 6.13 (dd, J = 10.4, 7.9 Hz, 1H, 2-H), 5.94 (d, J = 3.4 Hz, 1H, 4-H), 5.71 (dd, J = 10.4, 3.4 Hz, 1H, 3-H), 5.50 (d, J = 7.9 Hz, 1H, 1-H), 4.27 – 4.22 (m, 1H, 5-H), 3.91 (dd, J = 12.0, 6.6 Hz, 1H, 6-*H*), 3.74 (dd, J = 12.0, 6.8 Hz, 1H, 6-*H*), 2.64 (s, 1H, OH), 2.38 (d, J = 1.3 Hz, 3H, CH_3 (MU)).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 165.5, 165.3, 160.9, 159.4, 154.8, 152.2, 134.0, 133.6, 133.5, 130.2, 129.84, 129.79, 129.0, 128.8, 128.7, 128.6, 128.5, 128.4, 125.8, 115.7, 113.8, 113.3, 104.7, 99.5, 74.7, 71.6, 69.5, 68.6, 60.5, 18.7.

ESI-MS: found 673.2 $[M + Na]^+$.

4-Methylumbelliferyl 6-*O*-allyl-2,3,4-tri-*O*-benzoyl-*β*-D-galactopyranoside, S8a



S8a

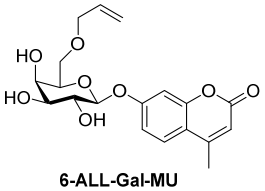
To a solution of **S7** (200 mg, 0.307 mmol, 1.0 eq.) in anhydrous CH_2Cl_2 (2 mL), allyl 2,2,2-trichloroacetimidate (124 mg, 0.614 mmol, 2.0 eq.) and 4Å MS were added. After the mixture was cooled to 0 °C and stirred for 20 min, trimethylsilyl trifluoromethanesulfonate (TMSOTf) (17 μL, 0.092 mmol, 0.3 eq.) was injected. The reaction was warmed up to room temperature and stirred for another 2 hours, and Et_3N was added to quench the reaction. The organic phase was diluted with CH_2Cl_2 and washed with saturated $NaHCO_3$ and brine. After dried over Na_2SO_4 and concentrated, the residue was purified with silica gel chromatography using PE and EA (3:1, v/v) to afford **S8a** as colorless oil (121 mg, 0.175 mmol, yield 57%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.10 (m, 2H, Ar-H), 8.01 – 7.94 (m, 2H, Ar-H), 7.87 – 7.80 (m, 2H, Ar-H), 7.69 – 7.62 (m, 1H, Ar-H (MU)), 7.59 – 7.43 (m, 5H, Ar-H), 7.39 (t, *J* = 7.8 Hz, 2H, Ar-H), 7.09 (d, *J* = 2.4 Hz, 1H, Ar-H (MU)), 7.01 (dd, *J* = 8.8, 2.5 Hz, 1H, Ar-H (MU)), 6.21 (d, *J* = 1.3 Hz, 1H, Ar-H (MU)), 6.07 (dd, *J* = 10.4, 7.9 Hz, 1H, 2-H), 6.02 (dd, *J* = 3.5, 1.1 Hz, 1H, 4-H), 5.93 – 5.78 (dddd, *J* = 17.2, 16.0, 10.6, 5.7 Hz, 1H, CH=C (ALL)), 5.69 (dd, *J* = 10.4, 3.4 Hz, 1H, 3-H), 5.45 (d, *J* = 7.9 Hz, 1H, 1-H), 5.25 (dq, *J* = 17.2, 1.6 Hz, 1H, C=CH_2 (ALL)), 5.15 (dq, *J* = 10.4, 1.4 Hz, 1H, C=CH_2 (ALL)), 4.33 (t, *J* = 6.3 Hz, 1H, 5-H), 4.04 (ddt, *J* = 12.7, 5.5, 1.4 Hz, 1H, OCH_2 (ALL)), 3.96 (ddt, *J* = 12.7, 5.8, 1.4 Hz, 1H, OCH_2 (ALL)), 3.79 – 3.68 (m, 2H, 6-H), 2.41 (d, *J* = 1.3 Hz, 3H, CH_3 (MU)).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.6, 165.5, 165.3, 160.9, 159.6, 154.9, 152.2, 134.0, 133.6, 133.5, 133.4, 130.0, 129.9, 129.8, 129.2, 129.1, 128.8, 128.7, 128.5, 128.4, 125.7, 117.8, 115.6, 114.1, 113.2, 104.8, 99.7, 73.7, 72.6, 71.7, 69.5, 68.2, 67.8, 18.7.

ESI-MS: found 713.1 $[M + Na]^+$.

4-Methylumbelliferyl 6-*O*-allyl-*β*-D-galactopyranoside, 6-ALL-Gal-MU



6-ALL-Gal-MU

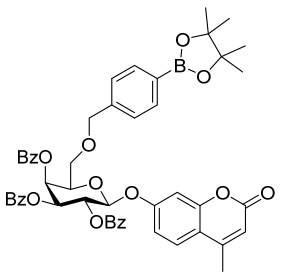
Compound **S8a** (100 mg, 0.145 mmol, 1.0 eq.) was dissolved in a mixture of CH_2Cl_2 and MeOH (1 mL, 1:4, v/v) containing NaOMe (5 M in MeOH, 20 μL, 1.0 eq.). After stirred at room temperature for 6 hours, H^+ resin was added to adjust the pH of the solution to 7. The resin was filtered off, and the filtrate was concentrated. The crude product was purified with silica gel chromatography using MeOH and CH_2Cl_2 (1:25, v/v) to afford **6-ALL-Gal-MU** as white solid (47 mg, 0.123 mmol, yield 85%).

^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 7.70 (d, J = 8.7 Hz, 1H, Ar-H (MU)), 7.08 – 7.00 (m, 2H, Ar-H (MU)), 6.25 (d, J = 1.4 Hz, 1H, Ar-H (MU)), 5.86 (ddt, J = 17.3, 10.4, 5.2 Hz, 1H, CH=C (ALL)), 5.28 (d, J = 5.1 Hz, 1H, OH), 5.24 (dq, J = 17.2, 1.9 Hz, 1H, CH_2 (ALL)), 5.11 (dq, J = 10.5, 1.7 Hz, 1H. CH_2 (ALL)), 5.03 (d, J = 7.7 Hz, 1H, 1-H), 4.95 (d, J = 5.7 Hz, 1H, OH), 4.67 (d, J = 4.7 Hz, 1H, OH), 3.96 (dt, J = 5.2, 1.6 Hz, 2H, CH_2 (ALL)), 3.91 (dd, J = 7.1, 4.8 Hz, 1H, 5-H), 3.68 (t, J = 4.2 Hz, 1H, 4-H), 3.65 – 3.55 (m, 2H, 2-H, 6-*H*), 3.53 – 3.43 (m, 2H, 3-H, 6-*H*), 2.41 (d, J = 1.3 Hz, 3H, CH_3 (MU)).

^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 160.14, 160.06, 154.4, 153.3, 135.2, 126.4, 116.2, 114.0, 113.4, 111.7, 103.1, 100.4, 73.8, 73.1, 71.2, 70.0, 69.3, 68.5, 18.1.

HRMS: m/z calculated $[M + H]^+$ = 379.1387, found 379.1389.

4-Methylumbelliferyl 2,3,4-tri-*O*-benzoyl-6-*O*-(4-(boronic acid pinacol ester)benzyl)-*β*-D-galactopyrano-side, S8b



S8b

Compound **S8b** was synthesized from **S7** (200 mg, 0.307 mmol, 1.0 eq.) and 4-(boronic acid pinacol ester)benzyl 2,2,2-trichloroacetimidate (BEB-OCNHCCl$_3$) (232 mg, 0.614 mmol, 2.0 eq.) using a procedure similar to that employed for the preparation of **S8a**. The crude product was purified with silica gel chromatography using PE and EA (7:4, v/v) to afford **S8b** as colorless oil (173 mg, 0.200 mmol, yield 65%).

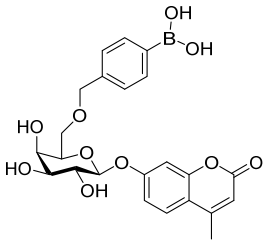
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.03 (m, 2H, Ar-H), 7.97 – 7.91 (m, 2H, Ar-H), 7.84 – 7.77 (m, 2H, Ar-H), 7.71 – 7.67 (m, 2H, Ar-H (BEB)), 7.65 – 7.59 (m, 1H, Ar-H (MU)), 7.54 – 7.41 (m, 5H, Ar-H), 7.36 (t, J = 7.8 Hz, 2H, Ar-H), 7.27 (ddd, J = 8.4, 6.9, 1.5 Hz, 4H, Ar-H (BEB) × 2, Ar-H × 2), 7.07 – 6.96 (m, 2H, Ar-H (MU)), 6.18 (d, J = 1.3 Hz, 1H, Ar-H (MU)), 6.08 – 5.98 (m, 2H, 2-H, 4-H), 5.67 (dd, J = 10.4, 3.4 Hz, 1H, 3-H), 5.43 (d,

J = 7.9 Hz, 1H, 1-H), 4.61 – 4.45 (m, 2H, $ArCH_2$), 4.38 – 4.29 (m, 1H, 5-H), 3.82 – 3.64 (m, 2H, 6-H), 2.38 (d, J = 1.3 Hz, 3H, CH_3 (MU)), 1.33 (s, 12H, CH_3 (BEB)).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 165.5, 165.3, 160.9, 159.5, 154.8, 152.2, 140.6, 134.9, 133.6, 133.5, 133.4, 130.0, 129.9, 129.8, 129.7, 129.12, 129.10, 128.8, 128.7, 128.5, 128.4, 127.0, 125.8, 115.6, 113.7, 113.2, 105.1, 99.6, 83.8, 75.1, 73.71, 73.67, 71.8, 69.5, 68.2, 68.0, 24.9, 18.7.

ESI-MS: found 889.2 $[M + Na]^+$.

4-Methylumbelliferyl 6-*O*-(4-(bornoic acid)benzyl)-*β*-D-galactopyranoside, 6-BAB-Gal-MU



6-BAB-Gal-MU

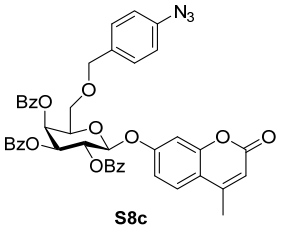
Compound **6-BAB-Gal-MU** was synthesized from **S8b** (150 mg, 0.173 mmol, 1.0 eq.) using the debenzoylation procedure similar to that employed for the preparation of **6-ALL-Gal-MU**. The crude product was purified using an Agilent 1260 Infinity system equipped with a reversed-phase semi-preparative column (250 mm × 4.6 mm, 5 μm, ZORBAX SB-C18) (Agilent, USA) and a diode array detector to afford **6-BAB-Gal-MU** as a colorless solid (15 mg, 0.032 mmol, yield 18%). The column was eluted with a gradient system of H_2O and MeCN at a flow rate of 2 mL/min at 30 °C. The gradient of MeCN (%) was: 5% (0–3 min), 5–30% (3–20 min), and 30–95% (20–25 min).

^1H NMR (600 MHz, $(CD_3)_2SO$) δ 7.99 (s, 2H, $B(OH)_2$), 7.72 (d, J = 7.6 Hz, 2H, Ar-H (BAB)), 7.65 (d, J = 8.6 Hz, 1H, Ar-H (MU)), 7.26 (d, J = 7.5 Hz, 2H, Ar-H (BAB)), 7.12 – 7.01 (m, 2H, Ar-H (MU)), 6.25 (s, 1H, Ar-H (MU)), 5.30 (d, J = 5.1 Hz, 1H, OH), 5.06 (d, J = 7.8 Hz, 1H, 1-H), 4.96 (d, J = 5.7 Hz, 1H, OH), 4.69 (d, J = 4.8 Hz, 1H, OH), 4.51 (d, J = 3.6 Hz, 2H, $ArCH_2$), 3.97 (t, J = 6.1 Hz, 1H, 5-H), 3.70 (d, J = 4.2 Hz, 1H, 4-H), 3.66 – 3.60 (m, 2H, 6-H), 3.55 (dd, J = 10.4, 7.4 Hz, 1H, 2-H), 3.50 – 3.45 (m, 1H, 3-H), 2.41 (s, 3H, CH_3 (MU)).

^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 160.2, 160.1, 154.4, 153.3, 140.3, 134.0, 126.4, 126.3, 114.1, 113.3, 111.7, 103.3, 100.4, 73.8, 73.1, 72.2, 70.0, 69.5, 68.6, 18.1.

HRMS: m/z calculated $[M + Na]^+$ = 495.1433, found 495.1437.

4-Methylumbelliferyl 2,3,4-tri-*O*-benzoyl-6-*O*-(4-azidobenzyl)-*β*-D-galactopyranoside, S8c



S8c

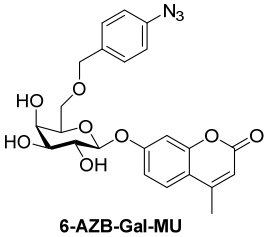
Compound **S8c** was synthesized from **S7** (200 mg, 0.307 mmol, 1.0 eq.) and 4-azidobenzyl 2,2,2-trichloroacetimidate (180 mg, 0.614 mmol, 2.0 eq.) using a procedure similar to that employed for the preparation of **S8a**. The crude product was purified with silica gel chromatography using PE and EA (3:2, v/v) to afford **S8c** as light-brown foam (108 mg, 0.138 mmol, yield 45%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.00 (m, 2H, Ar-H), 7.99 – 7.90 (m, 2H, Ar-H), 7.85 – 7.75 (m, 2H, Ar-H), 7.70 – 7.57 (m, 1H, Ar-H, (MU)), 7.55 – 7.41 (m, 5H, Ar-H), 7.36 (t, J = 7.7 Hz, 2H, Ar-H), 7.29 (d, J = 7.6 Hz, 2H, Ar-H), 7.24 – 7.19 (m, 2H, Ar-H (AZB)), 7.07 (d, J = 2.4 Hz, 1H, Ar-H (MU)), 6.95 (dd, J = 8.7, 2.5 Hz, 1H, Ar-H (MU)), 6.87 – 6.80 (m, 2H, Ar-H (AZB)), 6.20 (d, J = 1.4 Hz, 1H, Ar-H (MU)), 6.08 – 5.97 (m, 2H, 2-H, 4-H), 5.66 (dd, J = 10.4, 3.4 Hz, 1H, 3-H), 5.43 (d, J = 7.9 Hz, 1H, 1-H), 4.54 (d, J = 11.8 Hz, 1H, ArCH_2), 4.44 – 4.29 (m, 2H, ArCH_2, 5-H), 3.79 – 3.61 (m, 2H, 6-H), 2.39 (d, J = 1.2 Hz, 3H, CH_3 (MU)).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 165.6, 165.2, 154.0, 148.4, 147.7, 141.3, 139.0, 137.2, 137.1, 133.7, 133.4, 133.2, 131.9, 129.94, 129.91, 129.81, 129.76, 129.3, 128.9, 128.71, 128.66, 128.4, 128.3, 123.4, 119.51, 119.48, 109.8, 107.9, 100.8, 73.3, 71.7, 70.3, 69.1, 68.7, 68.0, 63.38, 63.36, 60.4, 56.6, 56.3, 21.0.

ESI-MS: found 804.2 $[M + Na]^+$.

4-Methylumbelliferyl 6-*O*-(4-azidobenzyl)-*β*-D-galactopyranoside, 6-AZB-Gal-MU



6-AZB-Gal-MU

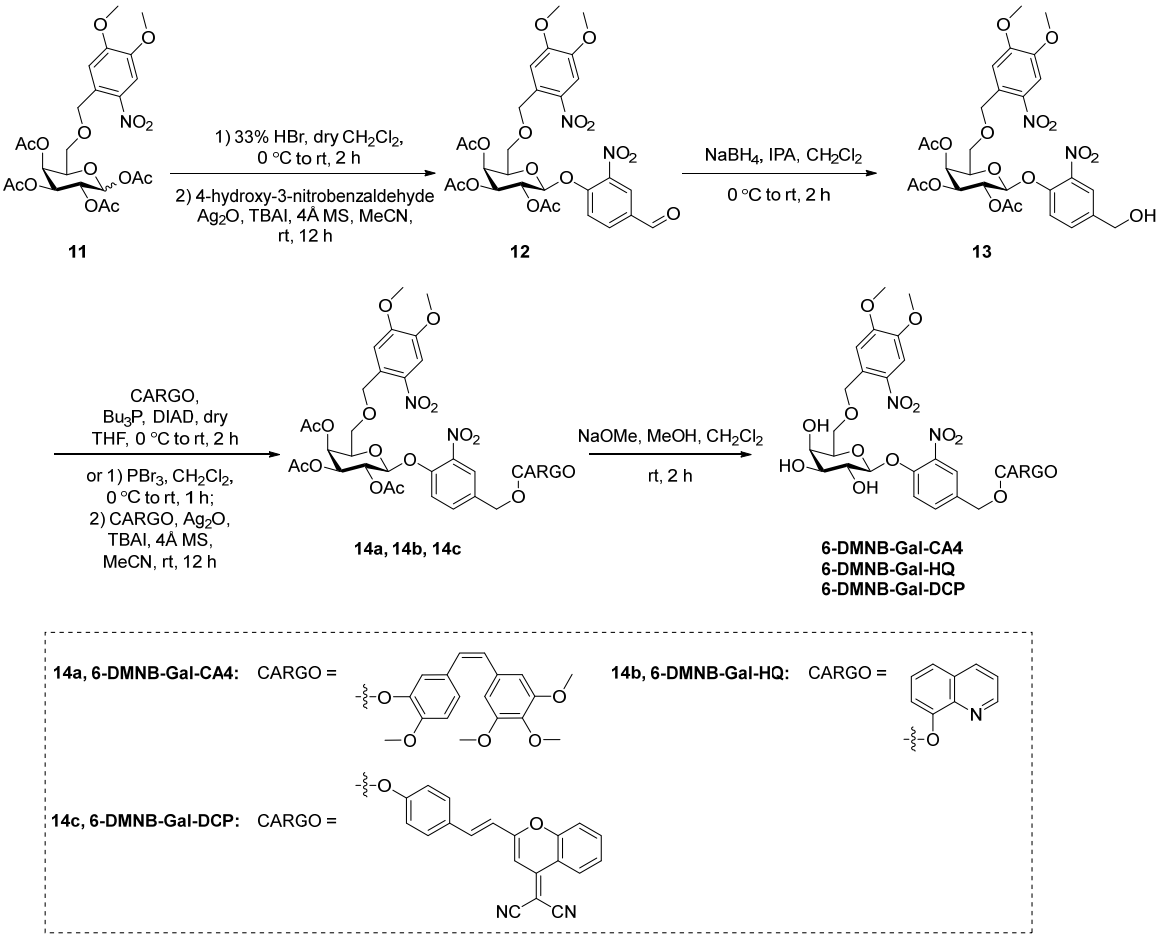
Compound **6-AZB-Gal-MU** was synthesized from **S8c** (80 mg, 0.102 mmol, 1.0 eq.) using the debenzoylation procedure similar to that employed for the preparation of **6-ALL-Gal-MU**. The crude product was purified with silica gel chromatography using MeOH and CH_2Cl_2 (1:25, v/v) to afford **6-AZB-Gal-MU** as white solid (35 mg, 0.075 mmol, yield 73%).

^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 7.68 (d, J = 8.8 Hz, 1H, Ar-H (MU)), 7.34 (d, J = 8.2 Hz, 2H, Ar-H (AZB)), 7.09 (d, J = 2.4 Hz, 1H, Ar-H (MU)), 7.07 – 7.00 (m, 3H, Ar-H (AZB) × 2, Ar-H (MU)), 6.26 (d, J = 1.6 Hz, 1H, Ar-H (MU)), 5.31 (d, J = 5.1 Hz, 1H, OH), 5.06 (d, J = 7.7 Hz, 1H, 1-H), 4.98 (d, J = 5.7 Hz, 1H, OH), 4.71 (d, J = 4.8 Hz, 1H, OH), 4.50 (d, J = 12.0 Hz, 1H, ArCH_2), 4.45 (d, J = 12.0 Hz, 1H, ArCH_2), 3.98 (dd, J = 7.8, 4.1 Hz, 1H, 5-H), 3.69 (t, J = 4.2 Hz, 1H, 4-H), 3.66 – 3.59 (m, 2H, 6-*H*, 2-H), 3.57 (dd, J = 10.5, 7.5 Hz, 1H, 6-*H*), 3.47 (ddd, J = 9.3, 5.6, 3.3 Hz, 1H, 3-H), 2.41 (d, J = 1.3 Hz, 3H, CH_3 (MU)).

^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 160.13, 160.10, 154.4, 153.3, 138.3, 135.6, 129.0, 126.4, 118.8, 114.0, 113.6, 111.7, 103.0, 100.2, 73.8, 73.0, 71.4, 70.0, 69.8, 68.7, 18.1.

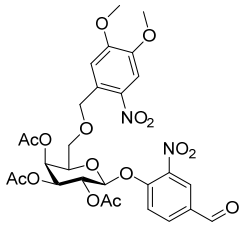
HRMS: m/z calculated $[M + Na]^+$ = 492.1377, found 492.1379.

4.3 Synthesis of *O*6-DMNB caged prodrugs



Scheme S3. The synthetic route to 6-DMNB-Gal-CA4, 6-DMNB-Gal-HQ, and 6-DMNB-Gal-DCP.

4-Formyl-2-nitrophenol 2,3,4-tri-*O*-acetyl-6-*O*-(4,5-dimethoxy-2-nitrobenzyl)-*β*-D-galactopyranoside, 12



12

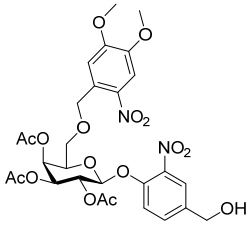
Compound **11** (1.03 g, 1.90 mmol, 1.0 eq.) was first brominated using the procedure described in Scheme S1. Then, to a solution of the brominated intermediate in MeCN, 4-hydroxy-3-nitrobenzaldehyde (380 mg, 2.27 mmol, 1.2 eq.), Ag_2O (746 mg, 3.22 mmol, 1.7 eq.), 4Å MS, and TBAI (280 mg, 0.758 mmol, 0.4 eq.) were added, and the mixture was stirred at room temperature for 12 hours. The organic layer was filtered through celite and washed with Na_2CO_3, water, and brine. After dried over Na_2SO_4 and concentrated, the residue was purified with silica gel chromatography using PE and EA (2:1, v/v) to afford **12** as light-yellow solid (641 mg, 0.985 mmol, yield 52%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H, ArCHO), 8.29 (d, J = 2.0 Hz, 1H, Ar-H), 8.01 (dd, J = 8.6, 2.0 Hz, 1H, Ar-H), 7.70 (s, 1H, Ar-H (DMNB)), 7.51 (d, J = 8.7 Hz, 1H, Ar-H), 7.15 (s, 1H, Ar-H (DMNB)), 5.66 – 5.57 (m, 2H, 4-H, 2-H), 5.26 (d, J = 7.9 Hz, 1H, 1-H), 5.15 (dd, J = 10.5, 3.4 Hz, 1H, 3-H), 4.99 – 4.87 (m, 2H, $ArCH_2$), 4.25 – 4.17 (m, 1H, 5-H), 3.96 (s, 3H, $ArOCH_3$), 3.94 (s, 3H, $ArOCH_3$), 3.82 (dd, J = 10.1, 6.7 Hz, 1H, 6-*H*), 3.75 (dd, J = 10.1, 6.1 Hz, 1H, 6-*H*), 2.17 (s, 3H, CH_3 (Ac)), 2.13 (s, 3H, CH_3 (Ac)), 2.02 (s, 3H, CH_3 (Ac)).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.6, 170.2, 170.1, 169.2, 154.0, 153.5, 148.0, 141.2, 139.3, 134.3, 131.4, 129.4, 126.7, 118.6, 109.8, 108.0, 100.2, 73.0, 70.7, 70.4, 68.4, 67.8, 67.0, 56.6, 56.4, 20.7, 20.62, 20.60.

ESI-MS: found 673.19 $[M + Na]^+$.

4-Hydroxymethyl-2-nitrophenol 2,3,4-tri-*O*-acetyl-6-*O*-(4,5-dimethoxy-2-nitrobenzyl)-*β*-D-galactopyranoside, 13



13

Compound **12** (620 mg, 0.953 mmol, 1.0 eq.) was dissolved in a mixture of CH_2Cl_2 and isopropyl alcohol (IPA) (10 mL, 4:1, v/v). After cooled to 0 °C and stirred for 10 min, $NaBH_4$ (54 mg, 1.429 mmol, 1.5 eq.) was added, and

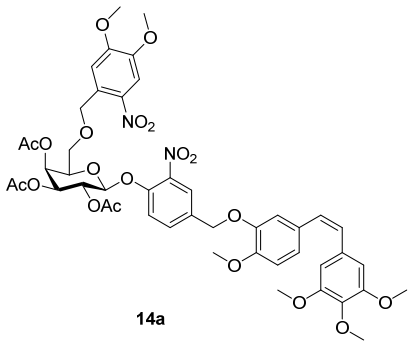
the mixture was warmed to room temperature. When TLC showed **12** was totally consumed after 2 hours, the solution was diluted with CH_2Cl_2. The organic phase was washed with water, saturated NH_4Cl, and brine. After dried over Na_2SO_4 and concentrated, the crude product was purified with silica gel chromatography using PE and EA (1:1, v/v) to afford **13** as light-yellow solid (572 mg, 0.877 mmol, yield 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 2.1 Hz, 1H, Ar-H), 7.69 (s, 1H, Ar-H (DMNB)), 7.45 (dd, J = 8.6, 2.1 Hz, 1H, Ar-H), 7.35 (d, J = 8.6 Hz, 1H, Ar-H), 7.17 (s, 1H, Ar-H (DMNB)), 5.63 – 5.57 (m, 1H, 4-H), 5.55 (dd, J = 10.5, 7.9 Hz, 1H, 2-H), 5.15 – 5.07 (m, 2H, 3-H, 1-H), 4.97 – 4.87 (m, 2H, $ArCH_2$ (DMNB)), 4.70 (s, 2H, $ArCH_2$), 4.13 (t, J = 6.5 Hz, 1H, 5-H), 3.94 (s, 3H, $ArOCH_3$), 3.91 (s, 3H, $ArOCH_3$), 3.77 (qd, J = 10.1, 6.4 Hz, 2H, 6-H), 2.16 (s, 3H, CH_3 (Ac)), 2.12 (s, 3H, CH_3 (Ac)), 2.00 (s, 3H, CH_3 (Ac)).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.24, 170.23, 169.5, 154.1, 148.5, 147.8, 141.3, 139.0, 137.1, 131.9, 129.9, 123.3, 119.6, 109.6, 107.9, 100.9, 72.7, 70.9, 70.3, 68.5, 68.0, 67.1, 63.5, 56.6, 56.4, 20.7, 20.6.

ESI-MS: found 675.15 $[M + Na]^+$.

(*Z*)-4-((2-Methoxy-5-(3,4,5-trimethoxystyryl)phenoxy)methyl)-2-nitrophenol 2,3,4-tri-*O*-acetyl-6-*O*-(4,5-dimethoxy-2-nitrobenzyl)-*β*-D-galactopyranoside, 14a



14a

Compound **13** (100 mg, 0.153 mmol, 1.0 eq.), CA4 (42 mg, 0.135 mmol, 1.1 eq.), and Bu_3P (38 μL, 0.153 mmol, 1.0 eq.) were dissolved in anhydrous THF (2 mL). The mixture was cooled to 0 °C, and diisopropyl azodicarboxylate (DIAD) (30 μL, 0.153 mmol, 1.0 eq.) was added. The reaction mixture was warmed to room temperature and stirred for another 2 hours. Upon completion, the reaction mixture was diluted with EA. The organic layer was washed with water, saturated NH_4Cl, and brine. After dried over Na_2SO_4 and concentrated, the residue was purified with silica gel chromatography using PE and EA (5:4, v/v) to afford **14a** as orange oil (121 mg, 0.127 mmol, yield 83%).

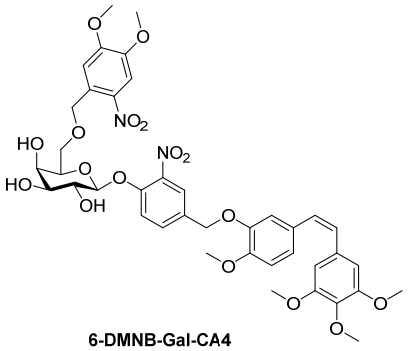
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, J = 2.1 Hz, 1H, Ar-H), 7.70 (s, 1H, Ar-H (DMNB)), 7.45 – 7.39 (m, 1H, Ar-H), 7.33 (d, J = 8.6 Hz, 1H, Ar-H), 7.19 (s, 1H, Ar-H (DMNB)), 6.91 (dt, J = 8.4, 1.7 Hz, 1H, Ar-H (CA4)), 6.84

– 6.78 (m, 2H, Ar-H (CA4)), 6.48 (s, 2H, Ar-H (CA4)), 6.48 – 6.41 (m, 2H, Ar-H (CA4)), 5.63 (d, J = 3.4 Hz, 1H, 4-H), 5.57 (dd, J = 10.3, 8.6 Hz, 1H, 2-H), 5.17 – 5.09 (m, 2H, 1-H, 3-H), 4.98 – 4.90 (m, 2H, $ArCH_2$ (DMNB)), 4.89 (s, 2H, $ArCH_2$ (DMNB)), 4.16 (t, J = 6.6 Hz, 1H, 5-H), 3.98 – 3.89 (m, 6H, $ArOCH_3$ (DMNB)), 3.86 (s, 3H, $ArOCH_3$ (CA4)), 3.84 – 3.77 (m, 3H, $ArOCH_3$ (CA4), 6-*H*), 3.73 (dd, J = 9.9, 6.5 Hz, 1H, 6-*H*), 3.68 (s, 6H, $ArOCH_3$ (CA4)), 2.16 (s, 3H, CH_3 (Ac)), 2.13 (s, 3H, CH_3 (Ac)), 2.01 (s, 3H, CH_3 (Ac)).

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.2, 169.4, 154.2, 153.1, 149.1, 148.9, 147.9, 147.2, 141.3, 139.1, 137.3, 133.2, 133.0, 132.4, 130.0, 129.9, 129.4, 129.1, 123.9, 123.4, 119.4, 115.0, 111.7, 109.6, 108.0, 106.1, 100.9, 72.5, 70.9, 70.3, 69.5, 68.3, 68.1, 67.1, 60.9, 56.6, 56.4, 56.02, 56.01, 20.7, 20.6.

ESI-MS: found 973.2 $[M + Na]^+$.

(*Z*)-4-((2-Methoxy-5-(3,4,5-trimethoxystyryl)phenoxy)methyl)-2-nitrophenol 6-*O*-(4,5-dimethoxy-2-nitrobenzyl)-*β*-D-galactopyranoside, 6-DMNB-Gal-CA4



6-DMNB-Gal-CA4

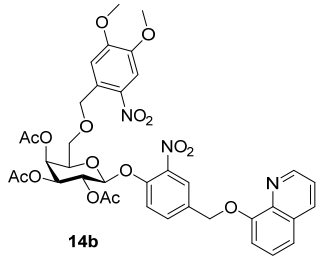
Compound **14a** (100 mg, 0.105 mmol, 1.0 eq.) was deacylated to give **6-DMNB-Gal-CA4** using a procedure similar to that employed for the preparation of **6-DMNB-Gal-MU**. The crude product was purified with silica gel chromatography using MeOH and CH_2Cl_2 (1:25, v/v) to afford **6-DMNB-Gal-CA4** as white solid (32 mg, 0.039 mmol, yield 37%).

^1H NMR (600 MHz, $(CD_3)_2SO$) δ 7.84 (d, J = 2.1 Hz, 1H, Ar-H), 7.66 (s, 1H, Ar-H (DMNB)), 7.48 (dd, J = 8.8, 2.1 Hz, 1H, Ar-H), 7.41 (d, J = 8.8 Hz, 1H, Ar-H), 7.22 (s, 1H, Ar-H (DMNB)), 6.95 – 6.89 (m, 2H, Ar-H (CA4)), 6.87 (dd, J = 8.4, 1.9 Hz, 1H, Ar-H (CA4)), 6.54 (s, 2H, Ar-H (CA4)), 6.50 – 6.41 (m, 2H, Ar-H (CA4)), 5.23 (d, J = 5.1 Hz, 1H, OH), 5.13 (d, J = 7.7 Hz, 1H, 1-H), 5.02 (d, J = 3.7 Hz, 1H, OH), 4.92 – 4.80 (m, 4H, $ArCH_2$, $ArCH_2$ (DMNB)), 4.77 (d, J = 4.5 Hz, 1H, OH), 4.01 (dd, J = 7.5, 4.4 Hz, 1H, 5-H), 3.83 (s, 3H, $ArOCH_3$ (DMNB)), 3.74 – 3.71 (m, 4H, 4-H, $ArOCH_3$ (DMNB)), 3.71 – 3.67 (m, 4H, 6-*H*, $ArOCH_3$ (CA4)), 3.65 – 3.61 (m, 4H, 6-*H*, $ArOCH_3$ (CA4)), 3.61 – 3.57 (m, 7H, 2-H, $ArOCH_3$ (CA4)), 3.47 (d, J = 9.6 Hz, 1H, 3-H).

^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 153.4, 152.6, 149.1, 148.6, 147.3, 147.0, 139.8, 139.0, 136.8, 132.9, 132.4, 130.7, 129.9, 129.3, 129.2, 128.7, 123.7, 122.2, 116.8, 114.7, 112.0, 109.8, 108.0, 106.0, 100.8, 73.9, 73.2, 69.9, 68.9, 68.6, 68.5, 60.0, 56.0, 55.8, 55.62, 55.59.

HRMS: m/z calculated $[M + Na]^+$ = 847.2532, found 847.2539.

2-Nitro-4-((quinolin-8-yloxy)methyl)phenol 2,3,4-tri-*O*-acetyl-6-*O*-(4,5-dimethoxy-2-nitrobenzyl)-*β*-D-galactopyranoside, 14b



14b

To a solution of **13** (100 mg, 0.153 mmol, 1.0 eq.) in anhydrous CH_2Cl_2 (1 mL), PBr_3 (7 μL, 0.077 mmol, 0.5 eq.) was injected under 0 °C. The mixture was warmed up to room temperature and stirred for another 1 hour. When TLC detected **13** was totally consumed, the solution was diluted with CH_2Cl_2. The organic layer was washed with saturated $NaHCO_3$ and brine. After dried over Na_2SO_4 and concentrated, the brominated intermediate was used directly for the next step.

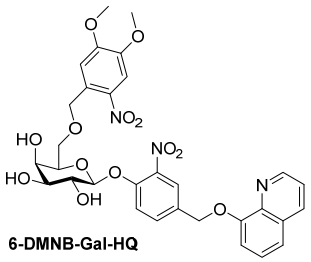
To a solution of the brominated intermediate and 4Å MS in anhydrous MeCN (1.5 mL), 8-hydroxyquinoline (27 mg, 0.184 mmol, 1.2 eq.), Ag_2O (71 mg, 0.306 mmol, 2.0 eq.) and TBAI (56 mg, 0.153 mmol, 1.0 eq.) was subsequentially added. When TLC showed the complete consumption of the bromide after 12 hours, Ag_2O was filtered out through celite. The organic layer was washed with Na_2CO_3, water, and brine. After dried over Na_2SO_4 and concentrated, the residue was purified with silica gel chromatography using PE and EA (1:1, v/v) to afford **14b** as colorless foam (43 mg, 0.055 mmol, yield 36%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (dd, J = 4.2, 1.7 Hz, 1H, Ar-H (HQ)), 8.15 (dd, J = 8.3, 1.7 Hz, 1H, Ar-H (HQ)), 7.97 (d, J = 2.1 Hz, 1H, Ar-H), 7.70 (d, J = 9.2 Hz, 2H, Ar-H (DMNB), Ar-H (HQ)), 7.50 – 7.37 (m, 4H, Ar-H (HQ) × 2, Ar-H × 2), 7.17 (s, 1H, Ar-H (DMNB)), 7.03 (dd, J = 7.1, 1.9 Hz, 1H, Ar-H (HQ)), 5.62 (dd, J = 3.4, 1.2 Hz, 1H, 4-H), 5.57 (dd, J = 10.5, 7.9 Hz, 1H, 2-H), 5.39 (s, 2H, $ArCH_2$), 5.15 – 5.08 (m, 2H, 1-H, 3-H), 4.92 (d, J = 3.9 Hz, 2H, $ArCH_2$ (DMNB)), 4.14 (td, J = 6.5, 1.2 Hz, 1H, 5-H), 3.93 (s, 3H, $ArOCH_3$ (DMNB)), 3.91 (s, 3H, $ArOCH_3$ (DMNB)), 3.80 (dd, J = 9.8, 6.5 Hz, 1H, 6-*H*), 3.73 (dd, J = 9.9, 6.5 Hz, 1H, 6-*H*), 2.16 (s, 3H, CH_3 (Ac)), 2.13 (s, 3H, CH_3 (Ac)), 2.01 (s, 3H, CH_3 (Ac)).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.17, 170.16, 169.4, 154.1, 153.8, 149.6, 149.0, 147.8, 141.3, 140.4, 139.0, 136.0, 133.1, 132.7, 129.8, 129.6, 126.5, 124.1, 121.8, 120.8, 119.7, 110.2, 109.5, 107.9, 100.9, 72.5, 70.9, 70.2, 69.3, 68.3, 68.0, 67.1, 56.5, 56.4, 20.7, 20.6.

ESI-MS: found 780.2 $[M + H]^+$.

2-Nitro-4-((quinolin-8-yloxy)methyl)phenol 6-*O*-(4,5-dimethoxy-2-nitrobenzyl)-*β*-D-galactopyranoside, 6-DMNB-Gal-HQ



6-DMNB-Gal-HQ

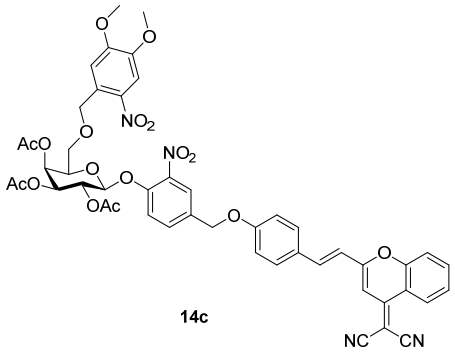
Compound **14b** (100 mg, 0.128 mmol, 1.0 eq.) was deacylated to give **6-DMNB-Gal-HQ** using a procedure similar to that employed for the preparation of **6-DMNB-Gal-MU**. The crude product was purified with silica gel chromatography using MeOH and CH_2Cl_2 (1:25, v/v) to afford **6-DMNB-Gal-HQ** as white solid (54 mg, 0.082 mmol, yield 64%).

^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 8.85 (dd, J = 4.1, 1.7 Hz, 1H, Ar-H (HQ)), 8.31 (dd, J = 8.3, 1.8 Hz, 1H, Ar-H (HQ)), 8.05 (d, J = 2.1 Hz, 1H, Ar-H), 7.70 (dd, J = 8.8, 2.2 Hz, 1H, Ar-H (HQ)), 7.66 (s, 1H, Ar-H (DMNB)), 7.58 – 7.44 (m, 4H, Ar-H (HQ) × 2, Ar-H × 2), 7.29 (dd, J = 7.4, 1.6 Hz, 1H, Ar-H (HQ)), 7.21 (s, 1H, Ar-H (DMNB)), 5.32 (s, 2H, $ArCH_2$), 5.25 (d, J = 5.1 Hz, 1H, OH), 5.14 (d, J = 7.7 Hz, 1H, 1-H), 4.99 (d, J = 5.6 Hz, 1H, OH), 4.91 – 4.80 (m, 2H, $ArCH_2$ (DMNB)), 4.77 (d, J = 4.4 Hz, 1H, OH), 4.02 (dd, J = 7.6, 4.5 Hz, 1H, 5-H), 3.83 (s, 3H, $ArOCH_3$), 3.77 – 3.67 (m, 5H, 4-H, 6-*H*, $ArOCH_3$), 3.67 – 3.57 (m, 2H, 6-*H*, 2-H), 3.47 (dd, J = 9.1, 4.5 Hz, 1H, 3-H).

^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 153.8, 153.4, 149.20, 149.17, 147.3, 139.9, 139.0, 135.9, 133.3, 130.9, 130.0, 129.1, 126.7, 124.1, 121.9, 120.3, 116.9, 110.5, 109.8, 108.0, 100.8, 73.9, 73.2, 69.9, 68.9, 68.6, 68.5, 56.0, 55.9.

HRMS: m/z calculated $[M + H]^+$ = 654.1930, found 654.1936.

(*E*)-4-((4-(2-(4-(Dicyanomethylene)-4*H*-chromen-2-yl)vinyl)phenoxy)methyl)-2-nitrophenol 2,3,4-tri-*O*-acetyl-6-*O*-(4,5-dimethoxy-2-nitrobenzyl)-*β*-D-galactopyranoside, 14c



14c

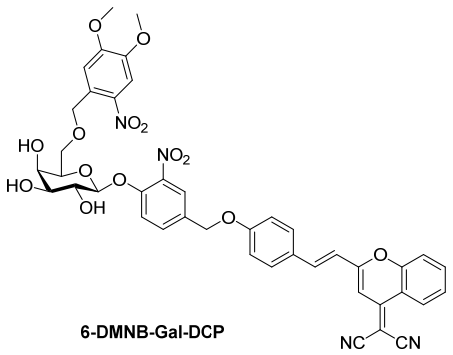
Compound **14c** was synthesized from **13** (80 mg, 0.123 mmol, 1.0 eq.) and DCP (42 mg, 0.135 mmol, 1.1 eq.) using a procedure similar to that employed for the preparation of **14a**. The crude product was purified with silica gel chromatography using PE and EA (2:1, v/v) to afford **14c** as orange solid (99 mg, 0.104 mmol, yield 85%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.93 (d, J = 8.4 Hz, 1H, Ar-H (DCP)), 7.89 (s, 1H, Ar-H), 7.74 (t, J = 7.9 Hz, 1H, Ar-H (DCP)), 7.70 (s, 1H, Ar-H (DMNB)), 7.63 – 7.50 (m, 5H, Ar-H (DCP) × 4, Ar-H), 7.48 – 7.41 (m, 2H, Ar-H (DCP), Ar-H), 7.18 (s, 1H, Ar-H (DMNB)), 7.02 (d, J = 8.2 Hz, 2H, Ar-H (DCP)), 6.86 (s, 1H, Ar-H (DCP)), 6.71 (d, J = 15.9 Hz, 1H, Ar-H (DCP)), 5.66 – 5.53 (m, 2H, 2-H, 4-H), 5.16 – 5.07 (m, 4H, 1-H, 3-H, $ArCH_2$), 4.97 – 4.90 (m, 2H, $ArCH_2$ (DMNB)), 4.14 (t, J = 6.6 Hz, 1H, 5-H), 3.96 – 3.91 (m, 6H, $ArOCH_3$), 3.80 (dd, J = 10.1, 7.4 Hz, 1H, 6-*H*), 3.75 (dd, J = 10.1, 6.4 Hz, 1H, 6-*H*), 2.18 – 2.12 (m, 6H, CH_3 (Ac)), 2.01 (s, 3H, CH_3 (Ac)).

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.2, 169.4, 160.1, 157.8, 156.8, 154.1, 152.9, 152.4, 151.1, 149.1, 148.0, 141.4, 139.2, 138.3, 134.6, 132.5, 129.8, 128.4, 126.00, 125.96, 124.1, 119.8, 118.6, 118.0, 117.1, 116.9, 115.8, 115.6, 109.7, 108.0, 106.5, 100.9, 72.8, 70.9, 70.4, 68.5, 68.4, 68.1, 67.2, 62.6, 56.6, 56.5, 20.7, 20.6.

ESI-MS: found 969.28 $[M + Na]^+$.

(*E*)-4-((4-(2-(4-(Dicyanomethylene)-4*H*-chromen-2-yl)vinyl)phenoxy)methyl)-2-nitrophenol 6-*O*-(4,5-dimethoxy-2-nitrobenzyl)-*β*-D-galactopyranoside, 6-DMNB-Gal-DCP



6-DMNB-Gal-DCP

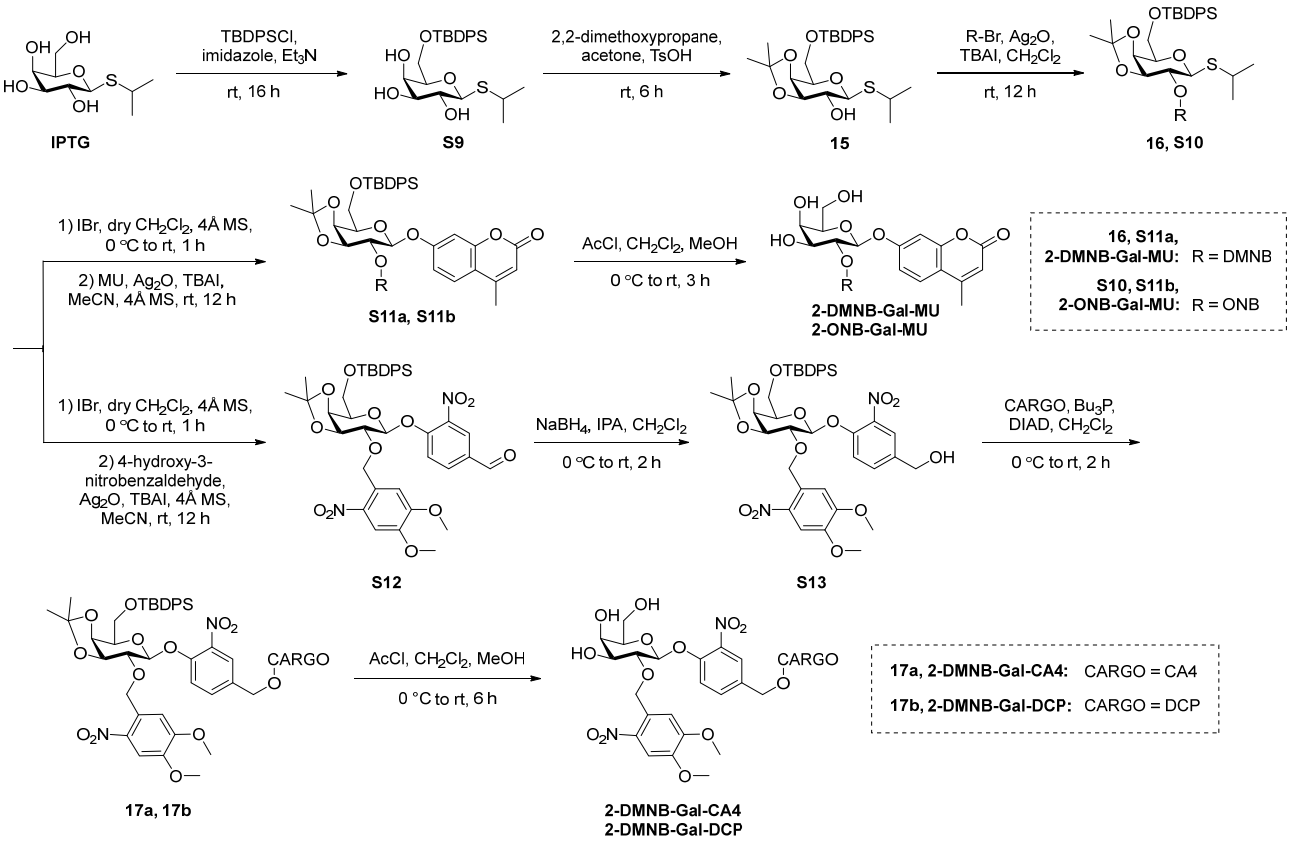
Compound **14c** (90 mg, 0.095 mmol, 1.0 eq.) was deacylated to give **6-DMNB-Gal-DCP** using a procedure similar to that employed for the preparation of **6-DMNB-Gal-MU**. The crude product was purified with silica gel chromatography using MeOH and CH_2Cl_2 (1:25, v/v) to afford **6-DMNB-Gal-DCP** as orange solid (53 mg, 0.064 mmol, yield 68%).

^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 8.74 (d, J = 8.3 Hz, 1H, Ar-H (DCP)), 7.97 (d, J = 2.1 Hz, 1H, Ar-H), 7.92 (t, J = 7.8 Hz, 1H, Ar-H (DCP)), 7.79 (d, J = 8.4 Hz, 1H, Ar-H (DCP)), 7.76 – 7.67 (m, 3H, Ar-H (DCP)), 7.64 (s, 1H, Ar-H (DMNB)), 7.64 – 7.57 (m, 2H, Ar-H (DCP), Ar-H), 7.44 (d, J = 8.8 Hz, 1H, Ar-H), 7.35 (d, J = 15.9 Hz, 1H, Ar-H (DCP)), 7.21 (s, 1H, Ar-H (DMNB)), 7.12 (d, J = 8.3 Hz, 2H, Ar-H (DCP)), 6.98 (s, 1H, Ar-H (DCP)), 5.22 (s, 1H, OH), 5.18 (s, 2H, $ArCH_2$), 5.14 (d, J = 7.7 Hz, 1H, 1-H), 4.97 (s, 1H, OH), 4.87 (d, J = 15.3 Hz, 1H, $ArCH_2$ (DMNB)), 4.82 (d, J = 15.3 Hz, 1H, $ArCH_2$ (DMNB)), 4.74 (s, 1H, OH), 4.02 (dd, J = 7.6, 4.3 Hz, 1H, 5-H), 3.83 (s, 3H, $ArOCH_3$ (DMNB)), 3.74 – 3.67 (m, 5H, 4-H, 6-*H*, $ArOCH_3$ (DMNB)), 3.65 – 3.58 (m, 2H, 6-*H*, 2-H), 3.49 – 3.43 (m, 1H, 3-H).

^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 159.9, 158.5, 153.4, 152.9, 152.0, 149.1, 147.3, 139.9, 139.0, 138.5, 135.3, 133.1, 130.4, 130.0, 129.9, 128.0, 126.1, 124.6, 124.0, 119.0, 117.3, 117.2, 117.1, 116.9, 115.9, 115.5, 109.8, 108.0, 106.1, 100.7, 73.9, 73.1, 69.9, 68.9, 68.5, 67.8, 59.6, 56.0, 55.8.

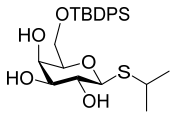
HRMS: m/z calculated $[M + Na]^+$ = 843.2120, found 843.2120.

4.4 Synthesis of *O*2-photocaged molecules



Scheme S4. The synthetic route to 2-DMNB-Gal-MU, 2-ONB-Gal-MU, 2-DMNB-Gal-CA4, and 2-DMNB-Gal-DCP.

Isopropyl 6-*O*-(*tert*-butyldiphenylsilyl)-*β*-D-thiogalatopyranoside, S9[7]



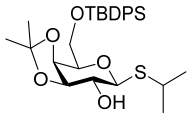
To a solution of **IPTG** (1.00 g, 4.20 mmol, 1.0 eq.) in DMF (20 mL), imidazole (571 mg, 8.39 mmol, 2.0 eq.) was added and stirred at 0 °C for 10 min. TBDPSCl (1.64 mL, 6.29 mmol, 1.5 eq.) and Et_3N (580 μL, 4.20 mmol, 1.0 eq.) was added dropwise, and the mixture was warmed to room temperature. After another 16 hours, the organic layer was diluted with EA and washed with water and brine. After dried over Na_2SO_4 and concentrated, the residue was purified by silica gel chromatography using PE and EA (2:3, v/v) to yield **S9** as colorless oil (1.16 g, 2.43 mmol, yield 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 4H, Ar-H), 7.47 – 7.34 (m, 6H, Ar-H), 4.36 (d, J = 9.5 Hz, 1H, 1-H), 4.08 (d, J = 3.1 Hz, 1H , 4-H), 3.88 (d, J = 5.7 Hz, 2H , 6-H), 3.67 (t, J = 9.3 Hz, 1H , 2-H), 3.58 (dd, J = 9.2, 3.0 Hz, 1H , 3-H), 3.53 (t, J = 5.7 Hz, 1H , 5-H), 3.20 (hept, J = 6.9 Hz, 1H, SCH), 3.09 (s, 3H, OH), 1.31 (d, J = 6.76 Hz, 6H, CH_3 (isopropylthio)), 1.05 (s, 9H, $C(CH_3)_3$ (TBDPS)).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 135.6, 133.1, 133.0, 129.9, 129.8, 127.8, 85.7, 78.5, 75.0, 70.7, 69.2, 63.3, 35.4, 26.8, 24.2, 24.0, 19.2.

ESI-MS: found 499.2 $[M + Na]^+$.

Isopropyl 3,4-*O*-isopropylidene-6-*O*-(*tert*-butyldiphenylsilyl)-*β*-D-thiogalatopyranoside, 15[7]



15

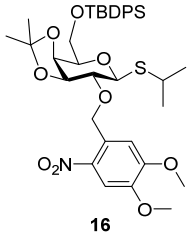
To a solution of **S9** (1.16 g, 2.43 mmol, 1.0 eq.) in acetone (20 mL), *p*-TsOH·H_2O (46 mg, 0.243 mmol, 0.1 eq.) and 2,2-dimethoxypropane (0.34 mL, 2.92 mmol, 1.2 eq.) were added. The mixture was stirred at room temperature for 6 hours. After quenched with Et_3N, the mixture was concentrated, and the residue was purified by silica gel chromatography using PE and EA (5:1, v/v) to yield **15** as a colorless foam (1.16 g, 2.24 mmol, yield 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 4H, Ar-H), 7.48 – 7.32 (m, 6H, Ar-H), 4.34 – 4.25 (m, 2H, 1-H, 4-H), 4.06 (dd, J = 7.0, 5.4 Hz, 1H, 3-H), 3.98 – 3.87 (m, 2H, 6-H), 3.85 (ddd, J = 7.5, 5.7, 2.1 Hz, 1H, 5-H), 3.52 (dd, J = 10.3, 7.0 Hz, 1H, 2-H), 3.19 (hept, J = 6.8 Hz, 1H, SCH), 2.41 (s, 1H, OH), 1.50 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.34 – 1.29 (m, 6H, CH_3 (isopropylthio)), 1.05 (s, 9H, $C(CH_3)_3$ (TBDPS)).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 135.6, 133.5, 133.4, 129.7, 127.8, 127.7, 110.1, 85.2, 79.0, 77.1, 73.4, 72.5, 62.9, 35.6, 28.2, 26.8, 26.3, 24.3, 24.0, 19.2.

ESI-MS: found 539.2 $[M + Na]^+$.

Isopropyl 2-*O*-(4,5-dimethoxy-2-nitrobenzyl)-3,4-*O*-isopropylidene-6-*O*-(*tert*-butyldiphenylsilyl)-*β*-D-thiogalatopyranoside, 16



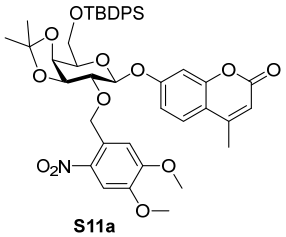
To a solution of **15** (1.12 g, 2.17 mmol, 1.0 eq.) in CH_2Cl_2 (20 mL), Ag_2O (1.00 g, 4.33mmol, 2.0 eq.), TBAI (402 mg, 1.09 mmol, 0.5 eq.), and 4Å MS were added and stirred for 10 min. Then DMNB-Br (898 mg, 3.25mmol, 1.5 eq.) in CH_2Cl_2 (5 mL) was added, and the resulting mixture was stirred for another 12 hours at room temperature. The reaction mixture was filtered through celite, and the organic layer was washed with water, saturated NH_4Cl, and brine. After dried over Na_2SO_4 and concentrated, the residue was purified with silica gel chromatography using PE and EA (20:1, v/v) to afford **16** as yellow oil (649 mg, 0.911 mmol, yield 42%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.67 (m, 4H, Ar-H), 7.65 (s, 1H, Ar-H (DMNB)), 7.50 (s, 1H, Ar-H (DMNB)), 7.47 – 7.34 (m, 6H, Ar-H), 5.29 – 5.14 (m, 2H, $ArCH_2$), 4.52 (d, J = 9.9 Hz, 1H, 1-H), 4.28 (dd, J = 5.5, 2.1 Hz, 1H, 4-H), 4.22 (dd, J = 6.8, 5.4 Hz, 1H, 3-H), 4.03 (s, 3H, $ArOCH_3$), 3.96 – 3.89 (m, 5H, 6-H, $ArOCH_3$), 3.84 (ddd, J = 7.1, 5.8, 2.1 Hz, 1H, 5-H), 3.47 (dd, J = 9.9, 6.7 Hz, 1H, 2-H), 3.27 (hept, J = 6.7 Hz, 1H, SCH), 1.39 (s, 3H, CH_3 (isopropylidene)), 1.34 – 1.27 (m, 9H, CH_3 (isopropylidene), CH_3 (isopropylthio) × 2), 1.05 (s, 9H, $C(CH_3)_3$ (TBDPS)).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.7, 147.6, 139.6, 135.7, 135.6, 133.5, 133.4, 130.7, 129.8, 127.8, 127.7, 110.5, 110.1, 107.7, 82.6, 80.1, 79.4, 73.7, 69.4, 63.0, 56.6, 56.4, 34.3, 28.0, 26.81, 26.79, 26.4, 23.9, 23.7, 19.2.

ESI-MS: found 734.20 $[M + Na]^+$.

4-Methylumbelliferyl 2-*O*-(4,5-dimethoxy-2-nitrobenzyl)-3,4-*O*-isopropylidene-6-*O*-(*tert*-butyldiphenylsilyl)-*β*-D-galatopyranoside, S11a



To a solution of **16** (100 mg, 0.140 mmol, 1.0 eq.) in dry CH_2Cl_2 (3 mL), 4Å MS and IBr (29 mg, 0.140 mmol, 1.0 eq.) were added at 0 °C. The reaction mixture was warmed up to room temperature and stirred for 1 hour. It

should be noticed that the position on TLC (PE:EA, 9:1, v/v) of the brominated intermediate was close to compound **16**. 4Å MS was filtered off, and the filtrate was washed sequentially with 10% $Na_2S_2O_3$ (w/w), saturated $NaHCO_3$, and brine. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to yield a crude brominated intermediate, which was used directly for the next step.

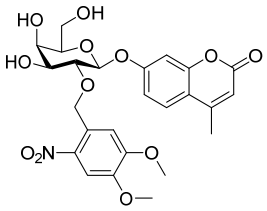
The crude brominated intermediate in MeCN (0.5 mL) was added to a stirred mixture of 4-methylumbelliferone (30 mg, 0.170 mmol, 1.2 eq.), Ag_2O (65 mg, 0.281 mmol, 2.0 eq.), TBAI (26 mg, 0.070 mmol, 0.5 eq.), and 4Å MS in MeCN (1 mL). After 12 hours, the reaction mixture was filtered through celite. The organic phase was washed with Na_2CO_3, water, and brine. After dried over Na_2SO_4 and concentrated, the residue was purified with silica gel chromatography using PE and EA (3:2, v/v) to afford **S11a** as yellow oil (59 mg, 0.073 mmol, yield 52%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.62 (m, 5H, Ar-H × 4, Ar-H (DMNB)), 7.47 – 7.31 (m, 8H, Ar-H × 6, Ar-H (MU) , Ar-H (DMNB)), 6.99 (dd, J = 8.7, 2.4 Hz, 1H, Ar-H (MU)), 6.92 (d, J = 2.4 Hz, 1H, Ar-H (MU)), 6.16 (d, J = 1.3 Hz, 1H, Ar-H (MU)), 5.39 – 5.24 (m, 2H, $ArCH_2$), 5.01 (d, J = 7.9 Hz, 1H, 1-H), 4.37 – 4.31 (m, 2H, 3-H, 4-H), 4.06 (td, J = 6.4, 5.9, 1.5 Hz, 1H, 5-H), 3.99 – 3.92 (m, 8H, $ArOCH_3$, 6-H), 3.73 – 3.65 (m, 1H, 2-H), 2.37 (d, J = 1.3 Hz, 3H, CH_3 (MU)), 1.42 (s, 3H, CH_3 (isopropylidene)), 1.35 (s, 3H, CH_3 (isopropylidene)), 1.06 (s, 9H, $C(CH_3)_3$ (TBDPS)).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 159.6, 154.9, 153.7, 152.2, 147.7, 139.6, 135.7, 135.6, 133.1, 130.6, 129.8, 127.8, 127.7, 125.8, 115.2, 113.8, 113.0, 110.4, 110.3, 107.9, 103.9, 100.2, 80.4, 78.6, 74.0, 73.2, 70.2, 62.7, 56.4, 28.0, 26.8, 26.4, 19.2, 18.7.

ESI-MS: found 834.33 $[M + Na]^+$.

4-Methylumbelliferyl 2-*O*-(4,5-dimethoxy-2-nitrobenzyl)-*β*-D-galatopyranoside, 2-DMNB-Gal-MU



2-DMNB-Gal-MU

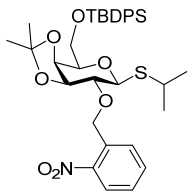
To a solution of **S11a** (50 mg, 0.0616 mmol, 1.0 eq.) in a mixture of MeOH and CH_2Cl_2 (1 mL, 4:1, v/v), AcCl (4.4 μL, 0.061 mmol, 1.0 eq.) was added. The solution was stirred at room temperature for 6 hours and concentrated. The crude product was purified by silica gel chromatography using MeOH and CH_2Cl_2 (1:20, v/v) to afford **2-DMNB-Gal-MU** (17.7 mg, 0.0320 mmol, yield 54%) as light-yellow solid.

^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 7.70 (d, J = 8.8 Hz, 1H, Ar-H (MU)), 7.64 (s, 1H, Ar-H (DMNB)), 7.53 (s, 1H, Ar-H (DMNB)), 7.05 – 6.90 (m, 2H, Ar-H (MU)), 6.35 – 6.19 (m, 1H, Ar-H (MU)), 5.44 – 5.05 (m, 4H, 1-H, OH, $ArCH_2$), 4.74 (s, 2H, OH), 3.84 (s, 3H, $ArOCH_3$), 3.79 (s, 3H, $ArOCH_3$), 3.78 – 3.65 (m, 4H, 4-H, 5-H, 3-H, 2-H), 3.55 (qd, J = 11.0, 6.1 Hz, 2H, 6-H), 2.40 (s, 3H, CH_3 (MU)).

^{13}C NMR (101 MHz, $(CD_3)_2SO$) δ 160.0, 159.6, 154.4, 153.4, 153.3, 147.2, 138.8, 130.8, 126.5, 114.3, 113.1, 111.8, 110.6, 107.7, 103.1, 100.3, 79.7, 75.7, 72.5, 70.1, 68.4, 60.3, 56.00, 55.98, 18.1.

HRMS: m/z calculated $[M + Na]^+$ = 556.1425, found 556.1425.

Isopropyl 2-*O*-(2-nitrobenzyl)-3,4-*O*-isopropylidene-6-*O*-(*tert*-butyldiphenylsilyl)-*β*-D-thiogalatopyranoside, S10



S10

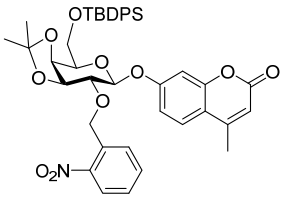
Compound **S10** was synthesized from **15** (400 mg, 0.774 mmol, 1.0 eq.) and 2-nitrobenzyl bromide (ONB-Br, 334 mg, 1.55 mmol, 2.0 eq.) using a procedure similar to that employed for the preparation of **16**. The residue was purified with silica gel chromatography using PE and EA (9:1, v/v) to afford **S10** as yellow oil (116 mg, 0.178 mmol, yield 23%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, J = 8.2, 1.3 Hz, 1H, Ar-H (ONB)), 7.91 (dd, J = 7.8, 1.3 Hz, 1H, Ar-H (ONB)), 7.73 – 7.67 (m, 4H, Ar-H), 7.64 (td, J = 7.6, 1.3 Hz, 1H, Ar-H (ONB)), 7.46 – 7.34 (m, 7H, Ar-H × 6, Ar-H (ONB)), 5.25 – 5.14 (m, 2H, $ArCH_2$), 4.48 (d, J = 9.8 Hz, 1H, 1-H), 4.27 (dd, J = 5.6, 2.0 Hz, 1H, 4-H), 4.20 (t, J = 6.1 Hz, 1H, 3-H), 3.97 – 3.88 (m, 2H, 6-H), 3.82 (td, J = 6.5, 2.0 Hz, 1H, 5-H), 3.46 (dd, J = 9.8, 6.7 Hz, 1H, 2-H), 3.25 (hept, J = 6.7 Hz, 1H, SCH), 1.38 (s, 3H, CH_3 (isopropylidene)), 1.33 – 1.28 (m, 9H, CH_3 (isopropylidene), CH_3 (isopropylthio) × 2), 1.05 (s, 9H, $C(CH_3)_3$ (TBDPS)).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 135.7, 135.6, 134.9, 133.5, 133.45, 133.43, 129.7, 129.5, 127.8, 127.73, 127.67, 124.5, 110.1, 82.6, 79.9, 79.3, 77.0, 73.6, 69.4, 63.0, 34.5, 27.9, 26.8, 26.3, 23.8, 23.6, 19.2.

ESI-MS: found 674.0 $[M + Na]^+$.

4-Methylumbelliferyl 2-*O*-(2-nitrobenzyl)-3,4-*O*-isopropylidene-6-*O*-(*tert*-butyldiphenylsilyl)-*β*-D-galatopyranoside, S11b



S11b

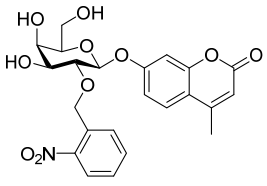
Compound **S11b** was synthesized from **S10** (100 mg, 0.153 mmol, 1.0 eq.) and 4-methylumbelliferone (27 mg, 0.153 mmol, 1.0 eq.) using a procedure similar to that employed for the preparation of **S11a**. The residue was purified with silica gel chromatography using PE and EA (3:1, v/v) to afford **S11b** as yellow oil (61 mg, 0.093 mmol, yield 53%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, J = 8.2, 1.3 Hz, 1H, Ar-H (ONB)), 7.86 (d, J = 7.7 Hz, 1H, Ar-H (ONB)), 7.73 – 7.58 (m, 5H, Ar-H × 4, Ar-H (ONB)), 7.46 – 7.30 (m, 8H, Ar-H × 6, Ar-H (ONB), Ar-H (MU)), 6.97 (dd, J = 8.7, 2.4 Hz, 1H, Ar-H (MU)), 6.91 (d, J = 2.4 Hz, 1H, Ar-H (MU)), 6.15 (d, J = 1.4 Hz, 1H, Ar-H (MU)), 5.28 (s, 2H, $ArCH_2$), 5.00 (d, J = 7.9 Hz, 1H, 1-H), 4.34 – 4.29 (m, 2H, 3-H, 4-H), 4.04 (dt, J = 6.5, 1.4 Hz, 1H, 5-H), 3.93 – 3.97 (m, J = 5.7 Hz, 2H, 6-H), 3.70 (dd, J = 7.8, 5.8 Hz, 1H, 2-H), 2.36 (d, J = 1.2 Hz, 3H, CH_3 (MU)), 1.45 (s, 3H, CH_3 (isopropylidene)), 1.35 (s, 3H, CH_3 (isopropylidene)), 1.06 (s, 9H, $C(CH_3)_3$ (TBDPS)).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 159.6, 154.9, 152.2, 147.6, 135.7, 135.6, 134.7, 133.4, 133.20, 133.19, 129.81, 129.79, 129.3, 128.1, 127.75, 127.72, 125.7, 124.7, 115.1, 113.6, 112.9, 110.4, 104.1, 99.9, 80.2, 78.7, 74.0, 73.1, 70.0, 62.7, 27.9, 26.8, 26.3, 19.2, 18.6.

ESI-MS: found 774.3 $[M + Na]^+$.

4-Methylumbelliferyl 2-*O*-(2-nitrobenzyl)-*β*-D-galatopyranoside, 2-ONB-Gal-MU



2-ONB-Gal-MU

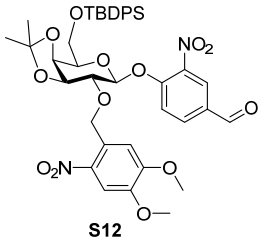
Compound **2-ONB-Gal-MU** was synthesized from **S11b** (55 mg, 0.084 mmol, 1.0 eq.) using a procedure similar to that employed for the preparation of **2-DMNB-Gal-MU**. The residue was purified with silica gel chromatography using MeOH and CH_2Cl_2 (1:24, v/v) to afford **2-ONB-Gal-MU** as light-yellow solid (23 mg, 0.051 mmol, yield 61%).

^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.04 (dd, J = 8.2, 1.3 Hz, 1H, Ar-H (ONB)), 7.91 (dd, J = 7.9, 1.4 Hz, 1H, Ar-H (ONB)), 7.77 – 7.66 (m, 2H, Ar-H (MU), Ar-H (ONB)), 7.54 (td, J = 7.8, 7.3, 1.5 Hz, 1H, Ar-H (ONB)), 7.01 (d, J = 2.4 Hz, 1H, Ar-H (MU)), 6.96 (dd, J = 8.8, 2.4 Hz, 1H, Ar-H (MU)), 6.26 (d, J = 1.4 Hz, 1H, Ar-H (MU)), 5.25 – 5.13 (m, 4H, 1-H, $ArCH_2$, OH), 4.77 (d, J = 4.9 Hz, 1H, OH), 4.74 (t, J = 5.5 Hz, 1H, OH), 3.77 – 3.72 (m, 2H, 4-H, 5-H), 3.71 – 3.64 (m, 2H, 3-H, 2-H), 3.60 – 3.47 (m, 2H, 6-H), 2.41 (d, J = 1.2 Hz, 3H, CH_3 (MU)).

^{13}C NMR (101 MHz, $(CD_3)_2SO$) δ 160.1, 159.7, 154.4, 153.3, 147.1, 134.8, 133.7, 129.2, 128.3, 126.5, 124.4, 114.2, 113.2, 111.8, 103.0, 99.7, 79.5, 75.6, 72.8, 70.1, 68.4, 60.3, 18.1.

HRMS: m/z calculated $[M + Na]^+$ = 496.1214, found 496.1219.

4-Formyl-2-nitrophenol 2-*O*-(4,5-dimethoxy-2-nitrobenzyl)-3,4-*O*-isopropylidene-6-*O*-(*tert*-butyldiphenylsilyl)-*β*-D-galatopyranoside, S12



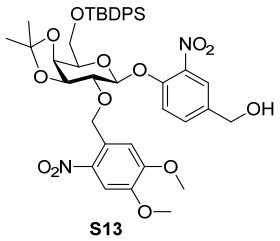
The crude bromide intermediate was synthesized from **16** (300 mg, 0.421 mmol, 1.0 eq.) using a procedure similar to that employed for the preparation of **S11a**. The crude brominated intermediate in MeCN (2 mL) was added dropwise to a mixture of 4-hydroxy-3-nitrobenzaldehyde (85 mg, 0.506 mmol, 1.2 eq.), Ag_2O (195 mg, 0.842 mmol, 2.0 eq.), TBAI (78 mg, 0.211 mmol, 0.5 eq.) and 4Å MS in MeCN (2 mL). When the brominated intermediate was totally consumed after 12 hours, the Ag_2O was filtered through celite. The organic layer was washed with Na_2CO_3, water, saturated $NaHCO_3$, and brine sequentially. After dried with Na_2SO_4 and concentrated, the residue was purified with silica gel chromatography using PE and EA (7:3, v/v) to afford **S12** as light-yellow oil (142 mg, 0.180 mmol, yield 42%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H, ArCHO), 8.31 (t, J = 1.6 Hz, 1H, Ar-H), 7.79 (dt, J = 8.7, 1.6 Hz, 1H, Ar-H), 7.71 – 7.60 (m, 5H, Ar-H × 4, Ar-H (DMNB)), 7.48 – 7.28 (m, 8H, Ar-H × 7, Ar-H (DMNB)), 5.24 (s, 2H, $ArCH_2$), 5.13 (d, J = 7.8 Hz, 1H, 1-H), 4.33 (t, J = 6.1 Hz, 1H, 3-H), 4.24 (dd, J = 5.6, 1.8 Hz, 1H, 4-H), 4.07 (t, J = 6.1 Hz, 1H, 5-H), 4.03 – 3.90 (m, 8H, 6-H, $ArOCH_3$ × 2), 3.77 (t, J = 7.2 Hz, 1H, 2-H), 1.40 (s, 3H, CH_3 (isopropylidene)), 1.31 (s, 3H, CH_3 (isopropylidene)), 1.07 (s, 9H, $C(CH_3)_3$ (TBDPS)).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.7, 154.1, 153.4, 147.9, 140.7, 140.2, 135.62, 135.56, 134.4, 133.2, 132.9, 130.6, 130.0, 129.9, 129.3, 127.84, 127.80, 126.9, 118.0, 111.3, 110.8, 108.1, 100.5, 79.7, 78.5, 75.0, 73.1, 70.6, 63.0, 56.5, 56.4, 27.8, 26.8, 26.3, 19.3.

ESI-MS: found 825.19 $[M + Na]^+$.

4-Hydroxymethyl-2-nitrophenol 2-*O*-(4,5-dimethoxy-2-nitrobenzyl)-3,4-*O*-isopropylidene-6-*O*-(*tert*-butyldiphenylsilyl)-*β*-D-galatopyranoside, S13



S13

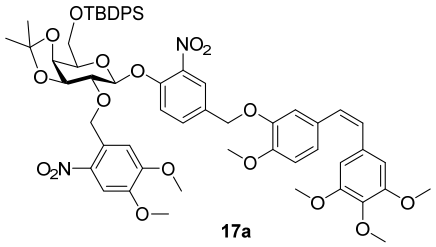
Compound **S12** (130 mg, 0.162 mmol, 1.0 eq.) was dissolved in a mixture of CH_2Cl_2 and IPA (2 mL, 4:1, v/v) and stirred at 0 ºC for 10 min. After $NaBH_4$ (12 mg, 0.324 mmol, 2.0 eq.) was added, the reaction was warmed to room temperature and monitored by TLC. When **S12** was totally consumed after 2 hours, the organic phase was washed with water, saturated NH_4Cl, saturated $NaHCO_3$, and brine. After dried with Na_2SO_4 and concentrated in vacuo, the residue was purified with silica gel chromatography using PE and EA (1:1, v/v) to afford **S13** as light-yellow oil (123 mg, 0.153 mmol, yield 94%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (s, J = 2.0 Hz, 1H, Ar-H), 7.72 – 7.61 (m, 5H, Ar-H × 4, Ar-H (DMNB)), 7.48 – 7.24 (m, 9H, Ar-H × 8, Ar-H (DMNB)), 5.25 (s, 2H, $ArCH_2$ (DMNB)), 5.01 (d, J = 7.9 Hz, 1H, 1-H), 4.68 – 4.61 (m, 2H, $ArCH_2$), 4.30 (dd, J = 6.7, 5.5 Hz, 1H, 3-H), 4.23 (dd, J = 5.6, 1.9 Hz, 1H, 4-H), 4.07 – 3.89 (m, 9H, 5-H, 6-H, $ArOCH_3$), 3.73 (dd, J = 7.9, 6.7 Hz, 1H, 2-H), 1.79 (t, J = 5.8 Hz, 1H, OH), 1.39 (s, 3H, CH_3 (isopropylidene)), 1.31 (s, 3H, CH_3 (isopropylidene)), 1.05 (s, 9H, $C(CH_3)_3$ (TBDPS)).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.5, 149.1, 147.8, 140.9, 140.1, 135.8, 135.7, 135.6, 133.3, 133.2, 132.1, 129.9, 129.83, 129.81, 127.8, 123.5, 118.9, 111.3, 110.6, 108.1, 101.0, 79.9, 78.8, 74.6, 73.3, 70.5, 63.7, 63.0, 56.5, 56.4, 27.8, 26.9, 26.3, 19.3.

ESI-MS: found 827.31 $[M + Na]^+$.

(*Z*)-4-((2-Methoxy-5-(3,4,5-trimethoxystyryl)phenoxy)methyl)-2-nitrophenol 2-*O*-(4,5-dimethoxy-2-nitrobenzyl)-3,4-*O*-isopropylidene-6-*O*-(*tert*-butyldiphenylsilyl)-*β*-D-galactopyranoside, 17a



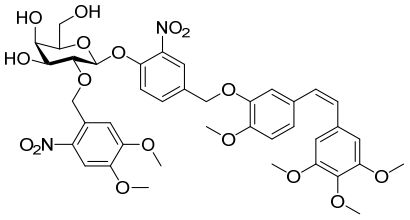
Compound **17a** was synthesized from **S13** (60 mg, 0.074 mmol, 1.0 eq.) and CA4 (23 mg, 0.074 mmol, 1.0 eq.) using a procedure similar to that employed for the preparation of **14a** (Scheme S3). The crude product was purified with silica gel chromatography using PE and EA (3:2, v/v) to afford **17a** as light-yellow oil (49 mg, 0.044 mmol, yield 60%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (s, 1H, Ar-H), 7.71 – 7.62 (m, 5H, Ar-H × 4, Ar-H (DMNB)), 7.45 – 7.29 (m, 8H, Ar-H × 7, Ar-H (DMNB)), 7.26 – 7.23 (m, 1H, Ar-H), 6.90 (d, J = 8.2 Hz, 1H, Ar-H (CA4)), 6.84 – 6.77 (m, 2H, Ar-H (CA4)), 6.48 (s, 2H, Ar-H (CA4)), 6.43 (s, 2H, Ar-H (CA4)), 5.25 (s, 2H, $ArCH_2$ (DMNB)), 5.02 (d, J = 7.8 Hz, 1H, 1-H), 4.85 (d, J = 3.5 Hz, 2H, $ArCH_2$), 4.30 (t, J = 6.2 Hz, 1H, 3-H), 4.24 (d, J = 5.8 Hz, 1H, 4-H), 4.01 (t, J = 6.61 Hz, 1H, 5-H), 3.97 (s, 3H, $ArOCH_3$ (DMNB)), 3.96 – 3.92 (m, 5H, $ArOCH_3$ (DMNB), 6-H), 3.84 (s, 3H, $ArOCH_3$ (CA4)), 3.81 (s, 3H, $ArOCH_3$ (CA4)), 3.72 (t, J = 7.4 Hz, 1H, 2-H), 3.67 (s, 6H, $ArOCH_3$ (CA4)), 1.40 (s, 3H, CH_3 (isopropylidene)), 1.31 (s, 3H, CH_3 (isopropylidene)), 1.04 (s, 9H, $C(CH_3)_3$ (TBDPS)).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 153.1, 149.4, 149.0, 147.7, 147.1, 140.8, 140.0, 135.7, 135.6, 133.2, 133.1, 132.9, 132.6, 132.0, 129.91, 129.89, 129.88, 129.8, 129.5, 129.1, 127.8, 124.0, 123.2, 118.6, 114.9, 111.6, 111.2, 110.5, 108.0, 106.0, 100.9, 79.8, 78.7, 74.4, 73.2, 70.5, 69.4, 62.9, 60.9, 56.5, 56.4, 55.99, 55.97, 27.9, 26.8, 26.3, 19.2.

ESI-MS: found 1125.5 $[M + Na]^+$.

(*Z*)-4-((2-Methoxy-5-(3,4,5-trimethoxystyryl)phenoxy)methyl)-2-nitrophenol 2-*O*-(4,5-dimethoxy-2-nitrobenzyl)-*β*-D-galatopyranoside, 2-DMNB-Gal-CA4



2-DMNB-Gal-CA4

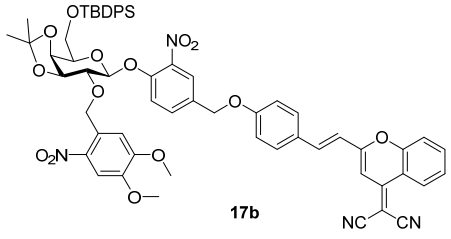
Compound **2-DMNB-Gal-CA4** was synthesized from **17a** (40 mg, 0.036 mmol, 1.0 eq.) using a procedure similar to that employed for the preparation of **2-DMNB-Gal-MU**. The crude product was purified with silica gel chromatography using MeOH and CH_2Cl_2 (1:24, v/v) to afford **2-DMNB-Gal-CA4** as white solid (16 mg, 0.019 mmol, yield 54%).

^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 7.85 (d, J = 2.1 Hz, 1H, Ar-H), 7.64 (s, 1H, Ar-H (DMNB)), 7.60 (dd, J = 8.8, 2.2 Hz, 1H , Ar-H), 7.46 (d, J = 9.5 Hz, 2H, Ar-H, Ar-H (DMNB)), 6.95 (d, J = 1.9 Hz, 1H, Ar-H (CA4)), 6.93 (d, J = 8.4 Hz, 1H, Ar-H (CA4)), 6.89 (dd, J = 8.3, 1.9 Hz, 1H, Ar-H (CA4)), 6.56 (s, 2H, Ar-H (CA4)), 6.51 (d, J = 12.2 Hz, 1H, Ar-H (CA4)), 6.47 (d, J = 12.2 Hz, 1H, Ar-H (CA4)), 5.38 (d, J = 7.6 Hz, 1H, 1-H), 5.14 (d, J = 15.7 Hz, 1H, ArCH_2 (DMNB)), 5.06 (d, J = 15.6 Hz, 1H, ArCH_2 (DMNB)), 4.90 (s, 2H, $ArCH_2$), 3.83 (s, 3H, $ArOCH_3$ (CA4)), 3.78 (s, 1H, 4-H), 3.76 – 3.72 (m, 7H, $ArOCH_3$ (DMNB), 5-H), 3.70 – 3.68 (m, 2H, 3-H, 2-H), 3.63 (s, 3H, $ArOCH_3$ (CA4)), 3.60 (s, 6H, $ArOCH_3$ (CA4)), 3.57 (dd, J = 11.0, 5.9 Hz, 1H, 6-*H*), 3.51 (dd, J = 10.9, 6.6 Hz, 1H, 6-*H*).

^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 153.3, 152.6, 148.9, 148.6, 147.1, 147.0, 139.3, 138.5, 136.8, 133.4, 132.4, 131.0, 130.7, 129.3, 129.2, 128.7, 123.9, 122.2, 116.9, 114.5, 112.0, 110.2, 107.8, 106.0, 100.1, 79.9, 75.8, 72.4, 70.5, 68.5, 68.1, 60.04, 60.02, 56.0, 55.8, 55.63, 55.61.

HRMS: m/z calculated $[M + Na]^+$ = 847.2532, found 847.2536.

(*E*)-4-((4-(2-(4-(Dicyanomethylene)-4*H*-chromen-2-yl)vinyl)phenoxy)methyl)-2-nitrophenol 2-*O*-(4,5-dimethoxy-2-nitrobenzyl)-3,4-*O*-isopropylidene-6-*O*-(*tert*-butyldiphenylsilyl)-*β*-D-galatopyranoside, 17b



17b

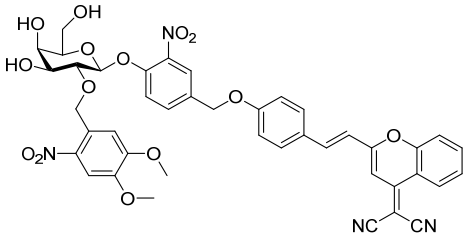
Compound **17b** was synthesized from **S13** (60 mg, 0.074 mmol, 1.0 eq.) and DCP (23 mg, 0.074 mmol, 1.0 eq.) using a procedure similar to that employed for the preparation of **17a**. The crude product was purified with silica gel chromatography using PE and EA (3:2, v/v) to afford **17b** as orange oil (51 mg, 0.047 mmol, yield 63%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.93 (dd, J = 8.4, 1.4 Hz, 1H, Ar-H (DCP)), 7.89 (d, J = 2.1 Hz, 1H, Ar-H), 7.74 (ddd, J = 8.5, 7.2, 1.5 Hz, 1H, Ar-H (DCP)), 7.69 – 7.62 (m, 5H, Ar-H, Ar-H (DMNB), Ar-H (DCP) × 3), 7.60 – 7.51 (m, 4H, Ar-H, Ar-H (DMNB), Ar-H (DCP) × 2), 7.48 – 7.40 (m, 3H, Ar-H), 7.39 – 7.32 (m, 7H, Ar-H), 6.99 – 6.95 (m, 2H, Ar-H (DCP)), 6.85 (s, 1H, Ar-H (DCP)), 6.69 (d, J = 15.9 Hz, 1H, Ar-H (DCP)), 5.26 (s, 2H, $ArCH_2$ (DMNB)), 5.07 – 5.02 (m, 3H, 1-H, $ArCH_2$), 4.31 (t, J = 6.1 Hz, 1H, 3-H), 4.23 (dd, J = 5.6, 2.0 Hz, 1H, 4-H), 4.03 (ddd, J = 7.0, 5.1, 2.0 Hz, 1H, 5-H), 4.01 – 3.91 (m, 8H, 6-H, $ArOCH_3$), 3.74 (dd, J = 7.8, 6.8 Hz, 1H, 2-H), 1.40 (s, 3H, CH_3 (isopropylidene)), 1.31 (s, 3H, CH_3 (isopropylidene)), 1.04 (s, 9H, $C(CH_3)_3$ (TBDPS)).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.1, 157.8, 153.4, 152.9, 152.4, 149.6, 147.8, 140.7, 140.0, 138.4, 135.65, 135.61, 134.6, 133.2, 133.1, 132.7, 131.2, 129.9, 129.83, 129.79, 129.7, 128.2, 127.82, 127.78, 126.0, 125.9, 124.2, 118.7, 118.6, 118.0, 116.9, 115.9, 115.5, 111.2, 110.6, 108.0, 106.5, 100.9, 79.9, 78.7, 74.7, 73.3, 70.5, 68.4, 63.0, 62.4, 56.5, 56.4, 27.9, 26.8, 26.3, 19.3.

ESI-MS: found 1121.4 $[M + Na]^+$.

(*E*)-4-((4-(2-(4-(Dicyanomethylene)-4*H*-chromen-2-yl)vinyl)phenoxy)methyl)-2-nitrophenol 2-*O*-(4,5-dimethoxy-2-nitrobenzyl)-*β*-D-galatopyranoside, 2-DMNB-Gal-DCP



2-DMNB-Gal-DCP

Compound **2-DMNB-Gal-DCP** was synthesized from **17b** (30 mg, 0.027 mmol, 1.0 eq.) using a procedure similar to that employed for the preparation of **2-DMNB-Gal-MU**. The crude product was purified with silica gel chromatography using MeOH and CH_2Cl_2 (1:20, v/v) to afford **2-DMNB-Gal-DCP** as orange solid (14 mg, 0.017 mmol, yield 62%).

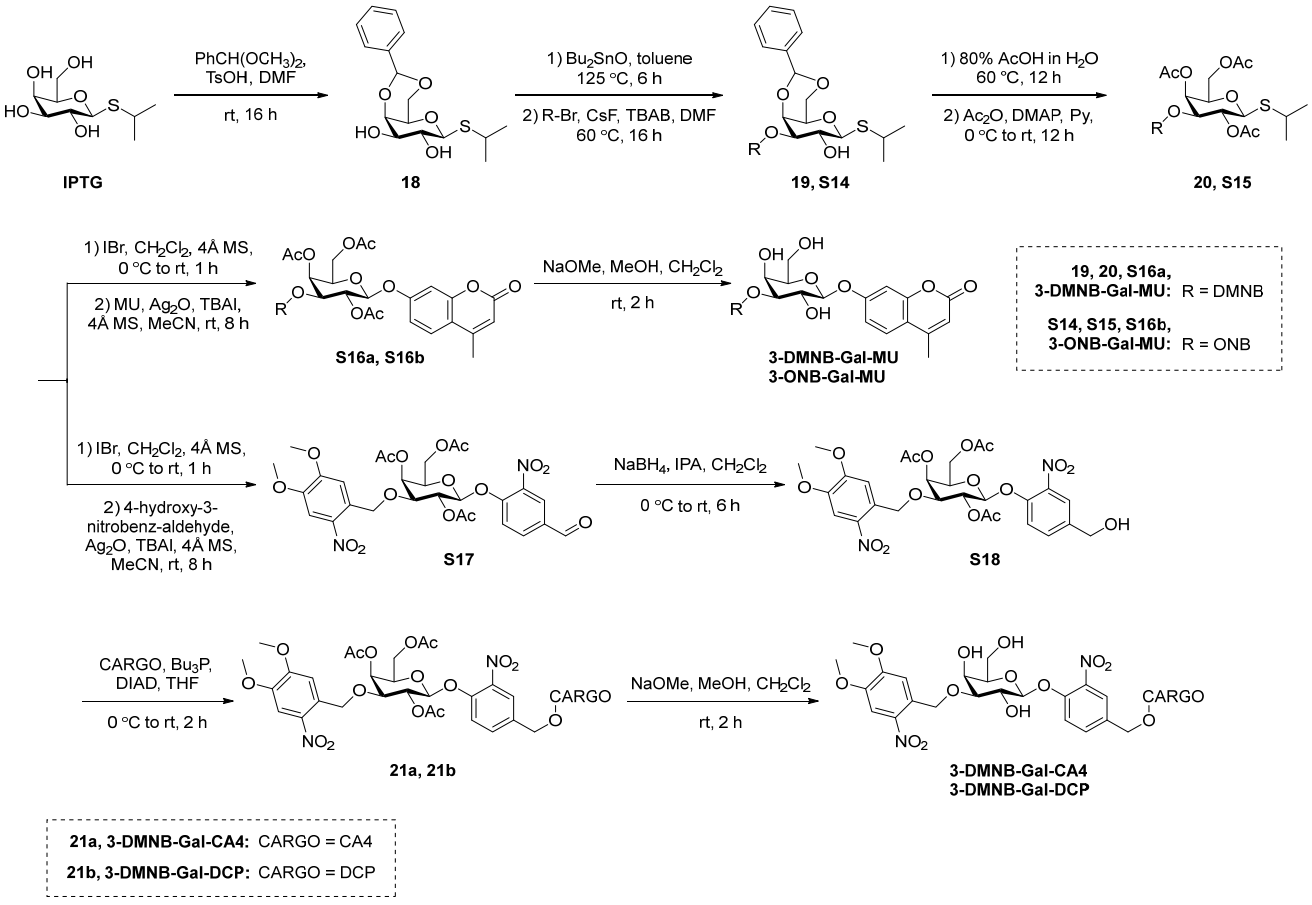
^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 8.74 (dd, J = 8.4, 1.4 Hz, 1H, Ar-H (DCP)), 7.98 (d, J = 2.1 Hz, 1H, Ar-H (DCP)), 7.93 (ddd, J = 8.5, 7.1, 1.5 Hz, 1H, Ar-H (DCP)), 7.82 – 7.71 (m, 5H, Ar-H (DCP) × 3, Ar-H, Ar-H (DMNB)), 7.64 – 7.60 (m, 2H, Ar-H, Ar-H (DCP)), 7.49 (d, J = 8.8 Hz, 1H, Ar-H), 7.45 (s, 1H, Ar-H (DMNB)), 7.39 (d, J = 16.0 Hz, 1H, Ar-H (DCP)), 7.14 (d, J = 8.5 Hz, 2H, Ar-H (DCP)), 7.00 (s, 1H, Ar-H (DCP)), 5.39 (d, J

= 7.2 Hz, 1H, 1-H), 5.25 (d, *J* = 5.7 Hz, 1H, OH), 5.20 (s, 2H, $ArCH_2$), 5.14 (d, *J* = 15.6 Hz, 1H, $ArCH_2$ (DMNB)), 5.06 (d, *J* = 15.5 Hz, 1H, $ArCH_2$ (DMNB)), 4.80 (d, *J* = 4.8 Hz, 1H, OH), 4.72 (t, *J* = 5.5 Hz, 1H, OH), 3.83 (s, 3H, $ArOCH_3$), 3.78 – 3.68 (m, 7H, $ArOCH_3$, 4-H, 5-H, 3-H, 2-H), 3.57 (dt, *J* = 11.1, 5.6 Hz, 1H, 6-*H*), 3.52 (dt, *J* = 11.2, 6.0 Hz, 1H, 6-*H*).

^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 159.9, 158.6, 153.3, 152.9, 152.0, 148.9, 147.1, 139.3, 138.54, 138.52, 135.4, 133.7, 130.8, 130.7, 130.1, 128.1, 126.1, 124.6, 124.3, 119.0, 117.4, 117.3, 117.1, 116.9, 115.9, 115.5, 110.2, 107.8, 106.1, 100.1, 79.9, 75.8, 72.3, 70.6, 68.3, 67.8, 60.1, 59.6, 56.0, 55.8.

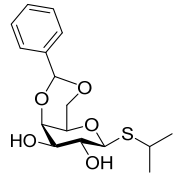
HRMS: m/z calculated $[M + Na]^+$ = 843.2120, found 843.2121.

4.5 Synthesis of *O*3-photocaged molecules



Scheme S5. The synthetic route to 3-DMNB-Gal-MU, 3-ONB-Gal-MU, 3-DMNB-Gal-CA4, and 3-DMNB-Gal-DCP.

Isopropyl 4,6-*O*-benzylidene-*β*-D-thiogalactopyranoside, 18[8]



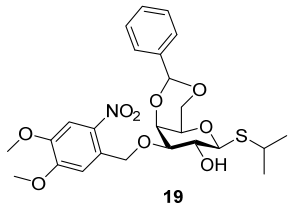
18

To a solution of **IPTG** (1.00 g, 4.23 mmol, 1.0 eq.) in anhydrous DMF (30 mL), benzaldehyde dimethyl acetal (0.76 mL, 5.04 mmol, 1.2 eq.) and *p*-TsOH·H_2O (160 mg, 0.84 mmol, 0.2 eq.) were added at room temperature. The reaction was stirred at 60 °C until TLC showed the completion of the reaction. The reaction was quenched with Et_3N and diluted with CH_2Cl_2 (90 mL). The organic phase was washed with water, saturated $NaHCO_3$, and brine. After dried over Na_2SO_4 and concentrated, the residue was purified with silica gel chromatography using PE and EA (1:1, v/v) to give **18** as white solid (1.01 g, 3.10 mmol, yield 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H, Ar-H), 7.37 (dt, J = 4.6, 2.9 Hz, 3H, Ar-H), 5.54 (s, 1H, PhCH), 4.41 (d, J = 9.5 Hz, 1H, 1-H), 4.33 (dd, J = 12.6, 1.5 Hz, 1H, 6-*H*), 4.25 (dd, J = 3.7, 1.2 Hz, 1H, 4-H), 4.03 (dd, J = 12.5, 1.9 Hz, 1H, 6-*H*), 3.77 (t, J = 9.3 Hz, 1H, 2-H), 3.68 (td, J = 8.7, 3.7 Hz, 1H, 3-H), 3.50 (q, J = 1.6 Hz, 1H, 5-H), 3.29 (p, J = 6.8 Hz, 1H, SCH), 2.68 (d, J = 8.7 Hz, 1H, OH), 2.62 (s, 1H, OH), 1.42 – 1.32 (m, 6H, CH_3 (isopropylthio)).

ESI-MS: found 349.1 $[M + Na]^+$.

Isopropyl 3-*O*-(4,5-dimethoxy-2-nitrobenzyl)-4,6-*O*-benzylidene-*β*-D-thiogalatopyranoside, 19



19

A mixture of **18** (600 mg, 1.84 mmol, 1.0 eq.) and Bu_2SnO (550 mg, 2.21 mmol, 1.2 eq.) in anhydrous toluene (20 mL) was heated to reflux for 6 hours. After the mixture was cooled to room temperature, the solvent was removed in vacuo. To the solution of crude tin ketal in DMF (15 mL), caesium fluoride (307 mg, 2.02 mmol, 1.1 eq.), TBAB (652 mg, 2.02 mmol, 1.1 eq.), and DMNB-Br (508 mg, 1.84 mmol, 1.0 eq.) were added. The resulting solution was stirred at 60 °C for 16 hours. After removing the DMF under reduced pressure, the residue was dissolved in CH_2Cl_2 and washed with water, saturated NH_4Cl and brine. The organic layer was dried over Na_2SO_4

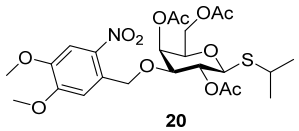
and filtered. After concentration, the residue was purified with silica gel chromatography using PE and EA (3:1, v/v) to give **19** as yellow solid (451 mg, 0.846 mmol, yield 46%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H, Ar-H (DMNB)), 7.54 (s, 1H, Ar-H (DMNB)), 7.52 – 7.45 (m, 2H, Ar-H), 7.37 – 7.30 (m, 3H, Ar-H), 5.52 (s, 1H, PhCH), 5.19 (d, J = 15.9 Hz, 1H, ArCH_2), 5.12 (d, J = 15.9 Hz, 1H, ArCH_2), 4.45 (d, J = 9.7 Hz, 1H, 1-H), 4.41 (dd, J = 3.6, 1.1 Hz, 1H, 4-H), 4.35 (dd, J = 12.5, 1.6 Hz, 1H, 6-*H*), 4.12 – 4.01 (m, 2H, 2-H, 6-*H*), 3.94 (s, 3H, $ArOCH_3$), 3.74 (s, 3H, $ArOCH_3$), 3.64 (dd, J = 9.2, 3.5 Hz, 1H, 3-H), 3.49 (q, J = 1.5 Hz, 1H, 5-H), 3.32 (hept, J = 6.7 Hz, 1H, SCH), 2.57 (s, 1H, OH), 1.45 – 1.33 (m, 6H, CH_3 (isopropylthio)).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.0, 147.6, 139.0, 137.9, 131.1, 129.1, 128.2, 126.5, 110.3, 107.8, 101.5, 86.1, 81.4, 73.2, 70.2, 69.5, 68.5, 67.9, 56.4, 56.3, 35.0, 24.6, 24.1.

ESI-MS: found 544.5 $[M + Na]^+$.

Isopropyl 3-*O*-(4,5-dimethoxy-2-nitrobenzyl)-2,4,6-tri-*O*-acetyl-*β*-D-thiogalatopyranoside, 20



20

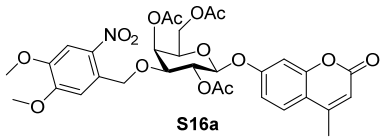
A solution of compound **19** (220 mg, 0.421 mmol, 1.0 eq.) in 80% AcOH in water (5 mL, v/v) was stirred at 60 °C for 12 hours. The solvent was removed under reduced pressure to give the debenzylidenated intermediate, which was directly used for the next step. To the crude intermediate, pyridine (5 mL), DMAP (26 mg, 0.211mmol, 0.5 eq.), and acetic anhydride (0.18 mL, 1.90 mmol, 4.5 eq.) was added at 0 °C. After warmed up to room temperature, the mixture was stirred for another 12 hours. EA was added to dilute the mixture, and the organic layer was washed with water, 1 M HCl, saturated $NaHCO_3$, and brine. After dried over anhydrous Na_2SO_4 and concentrated, the crude residue was purified by silica gel chromatography using PE and EA (2:1, v/v) to afford **20** as yellow foam (201 mg, 0.358 mmol, yield 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H, Ar-H (DMNB)), 7.18 (s, 1H, Ar-H (DMNB)), 5.63 (dd, J = 3.4, 1.1 Hz, 1H, 4-H), 5.25 (t, J = 9.8 Hz, 1H, 2-H), 5.10 (dd, J = 14.5, 0.9 Hz, 1H, ArCH_2), 4.91 (dd, J = 14.6, 0.8 Hz, 1H, ArCH_2), 4.58 (d, J = 10.1 Hz, 1H, 1-H), 4.17 (qd, J = 11.4, 6.7 Hz, 2H, 6-H), 3.99 (s, 3H, $ArOCH_3$), 3.94 (s, 3H, $ArOCH_3$), 3.90 (td, J = 6.6, 1.1 Hz, 1H, 5-H), 3.76 (dd, J = 9.4, 3.4 Hz, 1H, 3-H), 3.20 (hept, J = 6.8 Hz, 1H, SCH), 2.11 (s, 3H, CH_3 (Ac)), 2.07 (s, 3H, CH_3(Ac)), 2.06 (s, 3H, CH_3 (Ac)), 1.44 – 1.33 (m, 6H, CH_3 (isopropylthio)).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 170.2, 169.8, 154.1, 147.7, 138.8, 130.1, 109.6, 107.8, 83.7, 80.0, 74.5, 69.4, 66.7, 61.9, 56.7, 56.4, 35.6, 24.1, 23.8, 21.1, 20.81, 20.77.

ESI-MS: found 582.6 $[M + Na]^+$.

4-Methylumbelliferyl 3-*O*-(4,5-dimethoxy-2-nitrobenzyl)-2,4,6-tri-*O*-acetyl-*β*-D-thiogalatopyranoside, S16a



S16a

To a solution of **20** (150 mg, 0.268 mmol, 1.0 eq.) in dry CH_2Cl_2 (3 mL), IBr (61 mg, 0.295 mmol, 1.1 eq.) was added at 0 °C at the presence of 4Å MS. The reaction mixture was warmed up to room temperature and stirred for another 1 hour. 4Å MS was filtered off, and the filtrate was washed sequentially with 10% $Na_2S_2O_3$ (w/w), $NaHCO_3$, and brine. After dried over Na_2SO_4 and concentrated, the crude brominated intermediate was directly used for the next step.

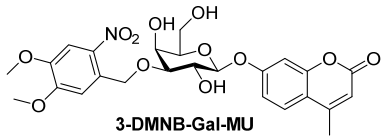
The crude brominated intermediate in MeCN (0.5 mL) was added to a stirred mixture of 4-methylumbelliferone (57 mg, 0.322 mmol, 1.2 eq.), Ag_2O (124 mg, 0.536 mmol, 2.0 eq.), 4Å MS, and TBAI (50 mg, 0.134 mmol, 0.5 eq.) in MeCN (1 mL). After 8 hours, when the brominated intermediate was used up, the reaction mixture was filtered through celite. The organic layer was washed with Na_2CO_3, water, and brine. After dried over Na_2SO_4 and concentrated, the residue was purified with silica gel chromatography using PE and EA (1:1, v/v) to afford **S16a** as yellow foam (94 mg, 0.142 mmol, yield 53%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (s, 1H, Ar-H (DMNB)), 7.52 (d, J = 8.7 Hz, 1H, Ar-H (MU)), 7.18 (s, 1H, Ar-H (DMNB)), 6.99 (d, J = 2.4 Hz, 1H, Ar-H (MU)), 6.95 (dd, J = 8.7, 2.4 Hz, 1H, Ar-H (MU)), 6.19 (d, J = 1.5 Hz, 1H, Ar-H (MU)), 5.67 (d, J = 3.3 Hz, 1H, 4-H), 5.54 (dd, J = 9.9, 8.0 Hz, 1H, 2-H), 5.16 – 5.09 (m, 2H, 1-H, ArCH_2), 4.94 (d, J = 14.2 Hz, 1H, ArCH_2), 4.23 (d, J = 6.5 Hz, 2H, 6-H), 4.10 (t, J = 6.5 Hz, 1H, 5-H), 4.00 (s, 3H, $ArOCH_3$), 3.95 (s, 3H, $ArOCH_3$), 3.87 (dd, J = 9.9, 3.4 Hz, 1H, 3-H), 2.41 (d, J = 1.3 Hz, 3H, CH_3 (MU)), 2.17 – 2.11 (m, 6H, CH_3 (Ac)), 2.07 (s, 3H, CH_3 (Ac)).

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.6, 170.1, 169.7, 160.8, 159.4, 154.9, 154.1, 152.2, 147.9, 138.9, 129.6, 125.7, 115.5, 114.1, 113.2, 109.8, 107.9, 104.1, 98.9, 78.7, 71.7, 70.2, 69.5, 66.2, 61.8, 56.7, 56.4, 21.0, 20.78, 20.75, 18.7.

ESI-MS: found 682.3 $[M + Na]^+$.

4-Methylumbelliferyl 3-*O*-(4,5-dimethoxy-2-nitrobenzyl)-*β*-D-thiogalatopyranoside, 3-DMNB-Gal-MU



3-DMNB-Gal-MU

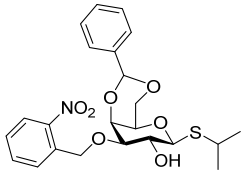
Compound **S16a** (60 mg, 0.091 mmol, 1.0 eq.) was deacylated to give **3-DMNB-Gal-MU** using a procedure similar to that employed for the preparation of **6-DMNB-Gal-MU** (Scheme S1). The crude product was purified with silica gel chromatography using MeOH and CH_2Cl_2 (1:25, v/v) to afford **3-DMNB-Gal-MU** as light-yellow solid (20 mg, 0.038 mmol, yield 42%).

^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 7.83 (s, 1H, Ar-H (DMNB)), 7.78 – 7.65 (m, 2H, Ar-H (MU), Ar-H (DMNB)), 7.15 – 6.98 (m, 2H, Ar-H (MU)), 6.25 (d, J = 1.4 Hz, 1H, Ar-H (MU)), 5.76 (d, J = 5.5 Hz, 1H, OH), 5.11 – 5.03 (m, 2H, 1-H, ArCH_2), 4.99 (d, J = 16.4 Hz, 1H, ArCH_2), 4.86 (d, J = 5.3 Hz, 1H, OH), 4.73 (t, J = 5.5 Hz, 1H, OH), 4.07 (t, J = 4.4 Hz, 1H, 4-H), 3.92 (s, 3H, $ArOCH_3$), 3.89 (ddd, J = 9.8, 7.9, 5.6 Hz, 1H, 2-H), 3.86 (s, 3H, $ArOCH_3$), 3.66 (t, J = 6.2 Hz, 1H, 5-H), 3.59 (dt, J = 11.2, 5.6 Hz, 1H, 6-*H*), 3.52 (dt, J = 10.7, 6.0 Hz, 1H, 6-*H*), 3.45 (dd, J = 9.6, 3.1 Hz, 1H, 3-H), 2.41 (d, J = 1.3 Hz, 3H, CH_3 (MU)).

^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 160.09, 160.06, 154.4, 153.7, 153.3, 147.1, 138.6, 131.5, 126.4, 114.1, 113.4, 111.7, 110.4, 107.8, 103.2, 100.4, 81.2, 75.4, 69.0, 66.2, 64.1, 60.2, 56.3, 56.0, 18.1.

HRMS: m/z calculated $[M + Na]^+$ = 556.1425, found 556.1430.

Isopropyl 3-*O*-(2-nitrobenzyl)-4,6-*O*-benzylidene-*β*-D-thiogalatopyranoside, S14



S14

Compound **S14** was synthesized from **18** (400 mg, 1.23 mmol, 1.0 eq.) and ONB-Br (398 mg, 1.85 mmol, 1.5 eq.) using a procedure similar to that employed for the preparation of **19**. The crude product was purified with silica gel chromatography using PE and EA (3:1, v/v) to afford **S14** as yellow solid (243 mg, 0.526 mmol, yield 43%).

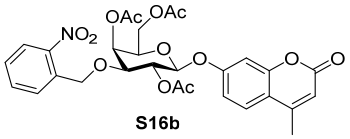
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, J = 8.2, 1.3 Hz, 1H, Ar-H (ONB)), 7.94 (dd, J = 7.8, 1.3 Hz, 1H, Ar-H (ONB)), 7.58 (td, J = 7.6, 1.3 Hz, 1H, Ar-H (ONB)), 7.53 – 7.45 (m, 2H, Ar-H), 7.41 (td, J = 7.8, 1.5 Hz, 1H, Ar-H (ONB)), 7.38 – 7.31 (m, 3H, Ar-H), 5.52 (s, 1H, PhCH), 5.16 (s, 2H, $ArCH_2$), 4.44 (d, J = 9.6 Hz, 1H, 1-H), 4.38 (dd, J = 3.5, 1.1 Hz, 1H, 4-H), 4.33 (dd, J = 12.4, 1.6 Hz, 1H, 6-*H*), 4.10 – 4.00 (m, 2H, 2-H, 6-*H*), 3.61 (dd, J =

9.2, 3.5 Hz, 1H, 3-H), 3.47 (q, J = 1.5 Hz, 1H, 5-H), 3.30 (hept, J = 6.7 Hz, 1H, SCH), 2.59 (d, J = 1.7 Hz, 1H, OH), 1.41 – 1.32 (m, 6H, CH_3 (isopropylthio)).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 137.8, 134.9, 133.7, 129.3, 129.0, 128.1, 128.1, 126.4, 124.5, 101.2, 85.9, 81.7, 73.4, 70.1, 69.5, 68.5, 68.4, 34.9, 24.5, 24.1.

ESI-MS: found 484.2 $[M + Na]^+$.

4-Methylumbelliferyl 3-*O*-(2-nitrobenzyl)-2,4,6-tri-*O*-acetyl-*β*-D-thiogalatopyranoside, S16b



S16b

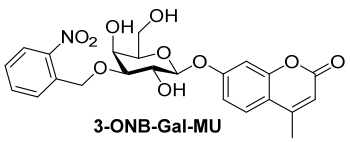
Compound **S16b** was synthesized from **S14** (200 mg, 0.433 mmol, 1.0 eq.) and 4-methylumbelliferone (91 mg, 0.520 mmol, 1.2 eq.) using a procedure similar to that employed for the preparation of **S16a**. The crude product was purified with silica gel chromatography using PE and EA (2:1, v/v) to afford **S16b** as light-yellow oil (156 mg, 0.260 mmol, yield 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, J = 8.0, 1.0 Hz, 1H, Ar-H), 7.68 – 7.61 (m, 2H, Ar-H), 7.52 (d, J = 8.7 Hz, 1H, Ar-H (MU)), 7.47 (ddd, J = 8.6, 5.5, 3.5 Hz, 1H, Ar-H), 6.98 (d, J = 2.4 Hz, 1H, Ar-H (MU)), 6.95 (dd, J = 8.7, 2.5 Hz, 1H, Ar-H (MU)), 6.20 (q, J = 1.2 Hz, 1H, Ar-H (MU)), 5.67 (dd, J = 3.4, 1.1 Hz, 1H, 4-H), 5.51 (dd, J = 10.0, 8.0 Hz, 1H, 2-H), 5.17 – 5.05 (m, 2H, 1-H, ArCH_2), 4.96 (d, J = 13.6 Hz, 1H, Ar-H-CH_2), 4.24 (d, J = 6.4 Hz, 2H, 6-H), 4.09 (td, J = 6.5, 1.1 Hz, 1H, 5-H), 3.85 (dd, J = 10.0, 3.4 Hz, 1H, 3-H), 2.42 (d, J = 1.2 Hz, 3H, CH_3 (MU)), 2.15 (s, 6H, CH_3 (Ac)), 2.09 (s, 3H, CH_3 (Ac)).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 170.2, 169.6, 160.8, 159.5, 154.9, 152.2, 147.2, 133.9, 133.6, 129.1, 128.5, 125.7, 124.9, 115.5, 114.1, 113.2, 104.0, 99.0, 78.5, 71.7, 69.8, 69.0, 65.7, 61.8, 20.9, 20.8, 20.7, 18.7.

ESI-MS: found 622.3 $[M + Na]^+$.

4-Methylumbelliferyl 3-*O*-(2-nitrobenzyl)-*β*-D-thiogalatopyranoside, 3-ONB-Gal-MU



3-ONB-Gal-MU

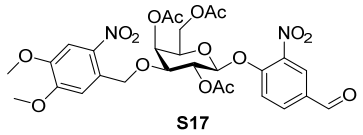
Compound **S16b** (100 mg, 0.167 mmol, 1.0 eq.) was deacylated to give **3-ONB-Gal-MU** using a procedure similar to that employed for the preparation of **6-DMNB-Gal-MU** (Scheme S1). The crude product was purified with silica gel chromatography using MeOH and CH_2Cl_2 (1:25, v/v) to afford **3-ONB-Gal-MU** as light-yellow solid (43 mg, 0.090 mmol, yield 54%).

^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.14 (dd, J = 7.9, 1.4 Hz, 1H, Ar-H), 8.09 (dd, J = 8.2, 1.3 Hz, 1H, Ar-H), 7.79 (td, J = 7.6, 1.3 Hz, 1H, Ar-H), 7.71 (d, J = 8.6 Hz, 1H, Ar-H (MU)), 7.60 – 7.52 (m, 1H, Ar-H), 7.10 – 7.00 (m, 2H, Ar-H (MU)), 6.25 (d, J = 1.4 Hz, 1H, Ar-H (MU)), 5.55 (d, J = 5.4 Hz, 1H, OH), 5.13 – 5.03 (m, 2H, 1-H, ArCH_2), 4.98 (d, J = 15.4 Hz, 1H, ArCH_2), 4.78 (d, J = 5.4 Hz, 1H, OH), 4.74 (t, J = 5.5 Hz, 1H, OH), 4.06 (dd, J = 5.8, 3.2 Hz, 1H, 4-H), 3.86 (ddd, J = 9.6, 7.7, 5.4 Hz, 1H, 2-H), 3.68 (t, J = 6.2 Hz, 1H, 5-H), 3.59 (dt, J = 11.2, 5.6 Hz, 1H, 6-*H*), 3.55 – 3.46 (m, 2H, 3-H, 6-*H*), 2.41 (d, J = 1.3 Hz, 3H, CH_3 (MU)).

^{13}C NMR (101 MHz, $(CD_3)_2SO$) δ 160.14, 160.08, 154.4, 153.3, 146.9, 135.4, 133.9, 129.0, 128.2, 126.4, 124.3, 114.1, 113.4, 111.7, 103.2, 100.4, 81.6, 75.4, 69.2, 66.7, 64.5, 60.2, 18.1.

HRMS: m/z calculated $[M + Na]^+$ = 496.1214, found 496.1216.

4-Formyl-2-nitrophenol 3-*O*-(4,5-dimethoxy-2-nitrobenzyl)-2,4,6-tri-*O*-acetyl-*β*-D-galatopyranoside, S17



S17

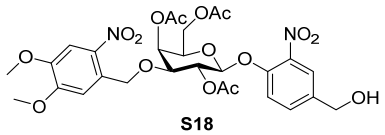
Compound **20** (150 mg, 0.268 mmol, 1.0 eq.) was brominated using a procedure similar to that employed during the preparation of **S16a**. The crude brominated intermediate in MeCN (1 mL) was added to a mixture of 4-hydroxy-3-nitrobenzaldehyde (54 mg, 0.322 mmol, 1.2 eq.), Ag_2O (130 mg, 0.563 mmol, 2.1 eq.), 4Å MS, and TBAI (50 mg, 0.134 mmol, 0.5 eq.) in MeCN (1.5 mL). After 8 hours, the mixture was filtered through celite and the organic layer was washed with Na_2CO_3, ddH_2O, and brine. After dried over solid Na_2SO_4 and concentrated, the residue was purified with silica gel chromatography using PE and EA (2:1, v/v) to afford **S17** as light-yellow solid (85 mg, 0.131 mmol, yield 49%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.98 (s, 1H, ArCHO), 8.30 (d, J = 1.9 Hz, 1H, Ar-H), 8.07 (dd, J = 8.6, 1.9 Hz, 1H, Ar-H), 7.71 (s, 1H, Ar-H (DMNB)), 7.50 (d, J = 8.6 Hz, 1H, Ar-H), 7.20 (s, 1H, Ar-H (DMNB)), 5.68 (d, J = 3.3 Hz, 1H, 4-H), 5.61 (dd, J = 9.9, 7.9 Hz, 1H, 2-H), 5.22 (d, J = 7.9 Hz, 1H, 1-H), 5.14 (d, J = 14.4 Hz, 1H, ArCH_2 (DMNB)), 4.92 (d, J = 14.3 Hz, 1H, ArCH_2 (DMNB)), 4.29 (dd, J = 11.6, 7.0 Hz, 1H, 6-*H*), 4.23 (dd, J = 11.6, 6.0 Hz, 1H, 6-*H*), 4.13 (t, J = 6.6 Hz, 1H, 5-H), 4.00 (s, 3H, $ArOCH_3$), 3.95 (s, 3H, $ArOCH_3$), 3.86 (dd, J = 10.2, 3.4 Hz, 1H, 3-H), 2.15 (s, 3H, CH_3 (Ac)), 2.11 (s, 6H, CH_3 (Ac)).

^{13}C NMR (151 MHz, $CDCl_3$) δ 188.6, 170.4, 170.0, 169.5, 154.2, 153.7, 147.9, 138.8, 133.9, 131.5, 129.7, 126.9, 118.8, 109.6, 108.0, 100.1, 78.5, 72.0, 69.5, 65.9, 61.7, 56.7, 56.4, 20.8, 20.73, 20.68.

ESI-MS: found 673.2 $[M + Na]^+$.

4-Hydroxymethyl-2-nitrophenol 3-*O*-(4,5-dimethoxy-2-nitrobenzyl)-2,4,6-tri-*O*-acetyl-*β*-D-galatopyranoside, S18



S18

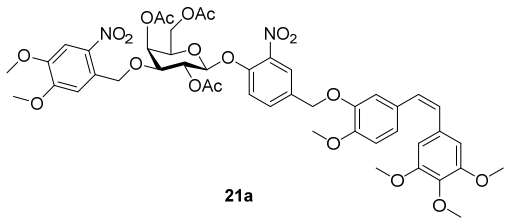
Compound **S18** was synthesized from **S17** (80 mg, 0.123 mmol, 1.0 eq.) using a procedure similar to that employed for the preparation of **S13** (Scheme S4). The crude product was purified with silica gel chromatography using PE and EA (1:1, v/v) to afford **S18** as light-yellow oil (74 mg, 0.114 mmol, yield 93%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, J = 2.1 Hz, 1H, Ar-H), 7.71 (s, 1H, Ar-H (DMNB)), 7.53 (dd, J = 8.7, 2.1 Hz, 1H, Ar-H), 7.37 (d, J = 8.6 Hz, 1H, Ar-H), 7.21 (s, 1H, Ar-H (DMNB)), 5.66 (d, J = 3.3 Hz, 1H, 4-H), 5.57 (dd, J = 9.9, 8.0 Hz, 1H, 2-H), 5.14 (d, J = 14.6 Hz, 1H, ArCH_2 (DMNB)), 5.07 (d, J = 8.0 Hz, 1H, 1-H), 4.91 (d, J = 14.5 Hz, 1H, ArCH_2 (DMNB)), 4.73 (s, 2H, $ArCH_2$), 4.29 (dd, J = 11.4, 6.9 Hz, 1H, 6-*H*), 4.21 (dd, J = 11.4, 6.2 Hz, 1H, 6-*H*), 4.05 (t, J = 6.6 Hz, 1H, 5-H), 4.00 (s, 3H, $ArOCH_3$), 3.95 (s, 3H, $ArOCH_3$), 3.83 (dd, J = 10.0, 3.3 Hz, 1H, 3-H), 2.18 – 2.09 (m, 9H, CH_3 (Ac)).

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.4, 170.1, 169.7, 154.2, 148.7, 147.8, 141.5, 138.8, 137.0, 131.7, 129.9, 123.3, 120.0, 109.6, 107.9, 100.9, 78.7, 71.6, 69.8, 69.4, 66.1, 63.6, 61.7, 56.7, 56.4, 20.9, 20.8, 20.7.

ESI-MS: found 675.5 $[M + Na]^+$.

(*Z*)-4-((2-Methoxy-5-(3,4,5-trimethoxystyryl)phenoxy)methyl)-2-nitrophenol 3-*O*-(4,5-dimethoxy-2-nitrobenzyl)-2,4,6-tri-*O*-acetyl-*β*-D-galactopyranoside, 21a



21a

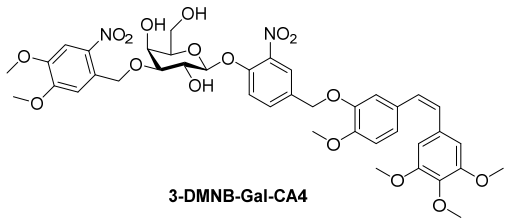
Compound **21a** was synthesized from **S18** (35 mg, 0.054 mmol, 1.0 eq.) and CA4 (17 mg, 0.054 mmol, 1.0 eq.) using a procedure similar to that employed for the preparation of **14a** (Scheme S3). The crude product was purified with silica gel chromatography using PE and EA (3:2, v/v) to afford **21a** as light-yellow oil (42 mg, 0.044 mmol, yield 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 2.3 Hz, 1H, Ar-H), 7.72 (s, 1H, Ar-H (DMNB)), 7.44 (dd, J = 8.6, 2.2 Hz, 1H, Ar-H), 7.32 (d, J = 8.6 Hz, 1H, Ar-H), 7.22 (s, 1H, Ar-H (DMNB)), 6.91 (dd, J = 8.3, 2.0 Hz, 1H, Ar-H (CA4)), 6.81 (m, J = 8.6 Hz, 2H, Ar-H (CA4)), 6.50 – 6.42 (m, 4H, Ar-H (CA4)), 5.66 (dd, J = 3.4, 1.1 Hz, 1H, 4-H), 5.57 (dd, J = 10.0, 8.0 Hz, 1H, 2-H), 5.15 (d, J = 15.1 Hz, 1H, ArCH_2 (DMNB)), 5.09 (d, J = 8.0 Hz, 1H, 1-H), 4.96 – 4.87 (m, 3H, ArCH_2 (DMNB), ArCH_2), 4.25 (qd, J = 11.3, 6.4 Hz, 2H, 6-H), 4.07 (t, J = 6.7 Hz, 1H, 5-H), 4.00 (s, 3H, $ArOCH_3$ (DMNB)), 3.95 (s, 3H, $ArOCH_3$ (DMNB)), 3.87 (s, 3H, $ArOCH_3$ (CA4)), 3.88 – 3.81 (m, 4H, 3-H, $ArOCH_3$ (CA4)), 3.69 (s, 6H, $ArOCH_3$ (CA4)), 2.15 – 2.10 (m, 9H, CH_3 (Ac)).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 170.1, 169.7, 154.2, 153.1, 149.02, 149.01, 147.7, 147.1, 141.3, 138.7, 133.1, 133.0, 132.5, 132.2, 130.0, 129.9, 129.5, 129.1, 125.1, 123.8, 119.7, 114.8, 111.6, 109.5, 107.8, 105.9, 100.7, 100.6, 78.7, 71.6, 69.7, 69.5, 66.1, 62.3, 61.0, 56.6, 56.3, 56.0, 55.9, 20.9, 20.8, 20.7.

ESI-MS: found 973.5 $[M + Na]^+$.

(*Z*)-4-((2-Methoxy-5-(3,4,5-trimethoxystyryl)phenoxy)methyl)-2-nitrophenol 3-*O*-(4,5-dimethoxy-2-nitrobenzyl)-*β*-D-galactopyranoside, 3-DMNB-Gal-CA4



3-DMNB-Gal-CA4

Compound **21a** (42 mg, 0.044 mmol, 1.0 eq.) was deacylated to give **3-DMNB-Gal-CA4** using a procedure similar to that employed for the preparation of **6-DMNB-Gal-CA4** (Scheme S3). The crude product was purified with silica gel chromatography using MeOH and CH_2Cl_2 (1:25, v/v) to afford **3-DMNB-Gal-CA4** as white solid (24 mg, 0.030 mmol, yield 68%).

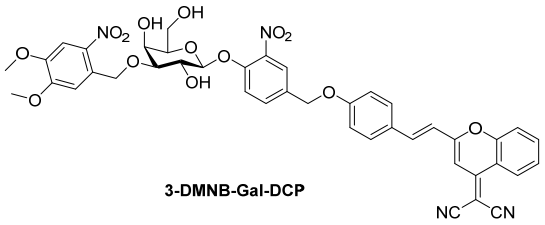
^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 7.86 (d, J = 2.2 Hz, 1H, Ar-H), 7.80 (s, 1H, Ar-H (DMNB)), 7.69 (s, 1H, Ar-H (DMNB)), 7.58 (dd, J = 8.8, 2.2 Hz, 1H, Ar-H), 7.43 (d, J = 8.8 Hz, 1H, Ar-H), 6.96 (d, J = 2.0 Hz, 1H, Ar-H (CA4)), 6.93 (d, J = 8.4 Hz, 1H, Ar-H (CA4)), 6.89 (dd, J = 8.4, 1.9 Hz, 1H, Ar-H (CA4)), 6.56 (s, 2H, Ar-H (CA4)), 6.53 – 6.44 (m, 2H, Ar-H (CA4)), 5.75 (d, J = 7.6 Hz, 1H, OH), 5.13 (d, J = 7.7 Hz, 1H, 1-H), 5.06 (d, J = 16.4 Hz, 1H, ArCH_2), 4.95 (d, J = 16.4 Hz, 1H, ArCH_2), 4.93 – 4.86 (m, 3H, $ArCH_2$ (DMNB), OH), 4.74 (t, J = 5.4 Hz, 1H,

OH), 4.12 – 4.03 (m, 1H, 4-H), 3.92 (s, 3H, $ArOCH_3$ (DMNB)), 3.89 – 3.82 (m, 4H, $ArOCH_3$ (DMNB), 2-H), 3.74 (s, 3H, $ArOCH_3$ (CA4)), 3.66 – 3.61 (m, 4H, $ArOCH_3$ (CA4), 5-H), 3.61 – 3.57 (m, 7H, $ArOCH_3$ (CA4) × 2, 6-*H*), 3.52 (dt, *J* = 11.1, 5.5 Hz, 1H, 6-*H*), 3.43 (dd, *J* = 9.6, 3.1 Hz, 1H, 3-H).

^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 153.8, 152.6, 149.2, 148.6, 147.1, 147.0, 139.8, 138.6, 136.7, 133.3, 132.4, 131.5, 130.7, 129.3, 128.8, 123.9, 122.2, 117.1, 114.4, 112.0, 110.4, 107.8, 105.9, 100.7, 81.4, 75.5, 68.8, 68.5, 66.0, 63.8, 60.09, 60.06, 56.3, 56.0, 55.64, 55.60.

HRMS: m/z calculated $[M + Na]^+$ = 847.2532, found 847.2536.

(*E*)-4-((4-(2-(4-(Dicyanomethylene)-4*H*-chromen-2-yl)vinyl)phenoxy)methyl)-2-nitrophenol 3-*O*-(4,5-dimethoxy-2-nitrobenzyl)-*β*-D-galatopyranoside, 3-DMNB-Gal-DCP



3-DMNB-Gal-DCP

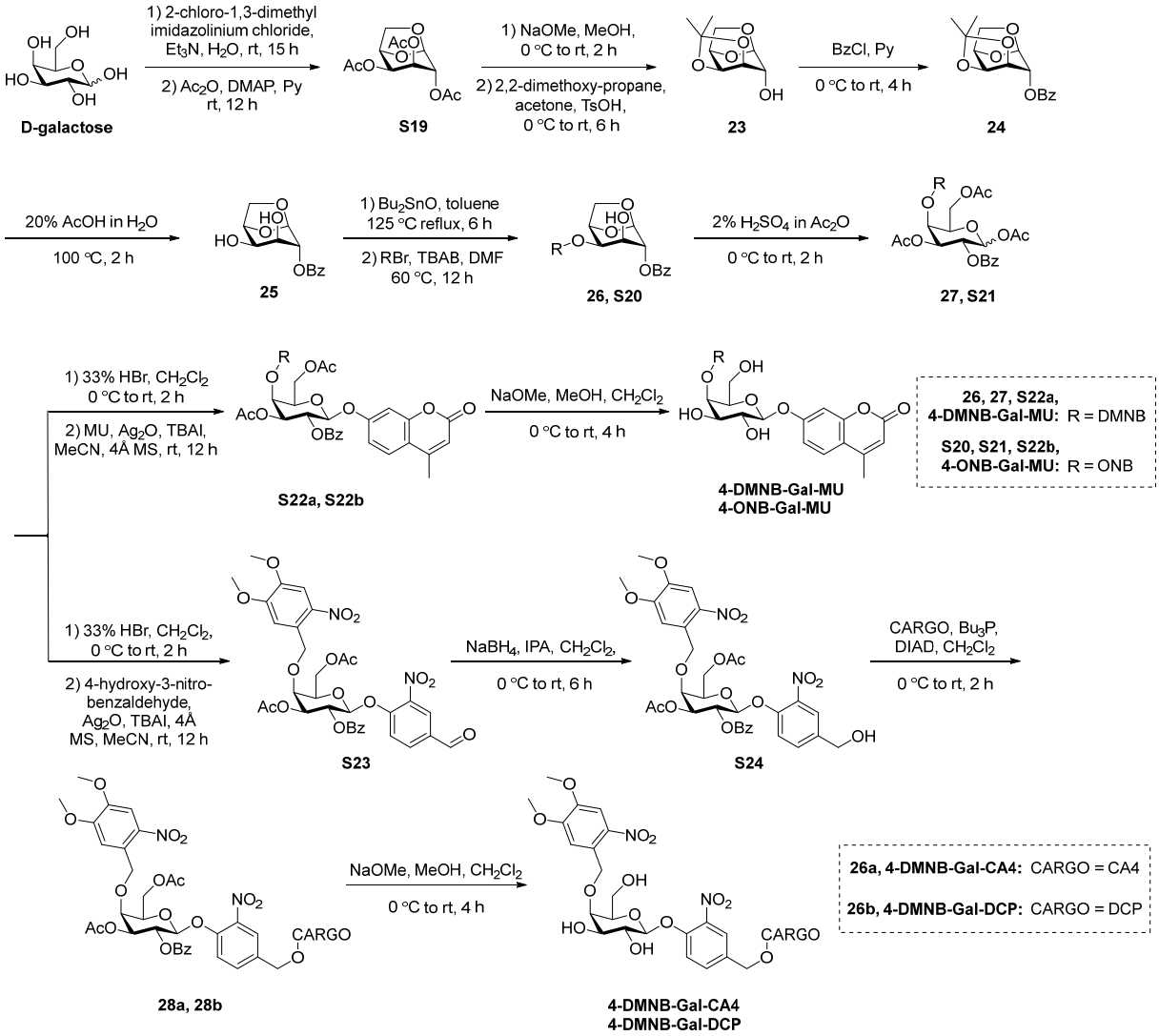
Compound **3-DMNB-Gal-DCP** was synthesized from **S18** (37 mg, 0.057 mmol, 1.0 eq.) using a procedure similar to that employed for the preparation of **6-DMNB-Gal-CA4** (Scheme S3). The residue was purified with silica gel chromatography using MeOH and CH_2Cl_2 (1:25, v/v) to afford **3-DMNB-Gal-DCP** as orange solid (21 mg, 0.026 mmol, yield 45% over two steps).

^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 8.74 (dd, *J* = 8.4, 1.4 Hz, 1H, Ar-H (DCP)), 8.00 (d, *J* = 2.1 Hz, 1H, Ar-H (DCP)), 7.93 (ddd, *J* = 8.5, 7.2, 1.5 Hz, 1H, Ar-H (DCP)), 7.80 (d, *J* = 8.3 Hz, 2H, Ar-H (DCP), Ar-H (DMNB)), 7.78 – 7.72 (m, 4H, Ar-H (DCP) × 3, Ar-H), 7.69 (s, 1H, Ar-H (DMNB)), 7.62 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H, Ar-H), 7.47 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.39 (d, *J* = 16.0 Hz, 1H, Ar-H (DCP)), 7.16 – 7.11 (m, 2H, Ar-H (DCP)), 7.00 (s, 1H, Ar-H (DCP)), 5.74 (d, *J* = 5.5 Hz, 1H, OH), 5.21 (s, 2H, $ArCH_2$), 5.14 (d, *J* = 7.7 Hz, 1H, 1-H), 5.06 (d, *J* = 16.4 Hz, 1H, ArCH_2 (DMNB)), 4.95 (d, *J* = 16.4 Hz, 1H, ArCH_2 (DMNB)), 4.91 (d, *J* = 5.1 Hz, 1H, OH), 4.73 (t, *J* = 5.4 Hz, 1H, OH), 4.08 (dd, *J* = 5.3, 3.2 Hz, 1H, 4-H), 3.92 (s, 3H, $ArOCH_3$), 3.89 – 3.83 (m, 4H, $ArOCH_3$, 2-H), 3.64 (t, *J* = 6.3 Hz, 1H, 5-H), 3.60 (dd, *J* = 10.8, 5.6 Hz, 1H, 6-*H*), 3.53 – 3.50 (m, 1H, 6-*H*), 3.43 (dd, *J* = 9.6, 3.1 Hz, 1H, 3-H).

^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 160.0, 158.6, 153.7, 153.0, 152.0, 149.2, 147.1, 139.9, 138.6, 138.5, 135.4, 133.5, 131.4, 130.5, 130.1, 128.1, 126.1, 124.6, 124.1, 119.0, 117.4, 117.18, 117.17, 117.1, 116.0, 115.5, 110.4, 107.8, 106.1, 100.7, 81.4, 75.5, 68.8, 67.9, 66.0, 63.9, 60.1, 59.6, 56.3, 56.0.

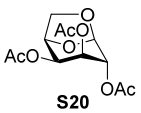
HRMS: m/z calculated $[M + Na]^+$ = 843.2120, found 843.2125.

4.6 Synthesis of *O*4-photocaged molecules



Scheme S6. The synthetic route to 4-DMNB-Gal-MU, 4-ONB-Gal-MU, 4-DMNB-Gal-CA4, and 4-DMNB-Gal-DCP.

1,6-Anhydro-2,3,4-tri-*O*-acetyl-D-galactopyranose, S19



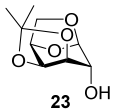
A mixture of D-galactose (1.00 g, 5.56 mmol, 1.0 eq.), 2-chloro-1,3-dimethyl imidazolinium chloride (5.00 g, 29.7 mmol, 5.3 eq.), and Et_3N (23 mL, 166.8 mmol, 30 eq.) in water (50 mL) was stirred for 30 min at 0 °C. The mixture was then warmed up to room temperature and stirred for another 15 hours. After concentrated under reduced pressure, the residue was co-evaporated with toluene twice to completely remove water. Pyridine (200 mL), DMAP (125 mg, 1.11 mmol, 0.2 eq.), and Ac_2O (2.6 mL, 27.8 mmol, 5.0 eq.) were added sequentially at 0 °C. After stirred for 15 min, the solution was warmed up to room temperature. After stirred for 12 hours, EA was added to dilute the reaction. The organic phase was washed with water, 1 M HCl, saturated $NaHCO_3$, and brine. After dried over Na_2SO_4 and concentrated, the crude product was purified by silica gel chromatography using PE and EA (2:1, v/v) to afford **S19** as colorless oil (1.12 g, 3.89 mmol, yield 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 (t, J = 1.4 Hz, 1H, 1-H), 5.30 – 5.20 (m, 2H, 3-H, 4-H), 4.76 (t, J = 1.5 Hz, 1H, 2-H), 4.51 – 4.42 (m, 1H, 5-H), 4.34 (d, J = 7.5 Hz, 1H, 6-*H*), 3.79 – 3.70 (m, 1H, 6-*H*), 2.13 (s, 6H, CH_3 (Ac)), 2.03 (s, 3H, CH_3 (Ac)).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 169.4, 169.3, 99.0, 72.2, 71.1, 67.5, 64.9, 64.6, 20.9, 20.8, 20.6.

ESI-MS: found 311.6 $[M + Na]^+$.

1,6-Anhydro-3,4-*O*-isopropylidene-D-galactopyranose, 23[9]



23

To a solution of **S19** (1.02 g, 3.54 mmol, 1.0 eq.) in MeOH (20 mL) was added NaOMe (95.6 mg, 1.77 mmol, 0.5 eq.) at room temperature. After stirred for 2 hours, H^+ resin was added to adjust the pH of the solution to 7. The resin was filtered off, and the filtrate was evaporated in vacuo to give the deacetylated product which was used directly for the next step.

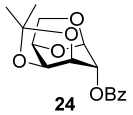
To the deacetylated intermediate, 2,2-dimethoxylpropane (0.87 mL, 7.08 mmol, 2.0 eq.), acetone (10 mL), and *p*-TsOH·H_2O (134 mg, 0.708 mmol, 0.2 eq.) was added sequentially at room temperature. After stirred at room temperature for another 6 hours, the reaction was quenched by Et_3N and concentrated. The residue was purified with silica gel chromatography using PE and EA (1:1, v/v) to furnish **23** as a white solid (615 mg, 3.04 mmol, yield 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39 (t, J = 1.4 Hz, 1H, 1-H), 4.50 (t, J = 5.6 Hz, 1H, 4-H), 4.47 – 4.41 (m, 1H, 5-H), 4.23 (dd, J = 6.9, 1.6 Hz, 1H, 3-H), 4.14 (dd, J = 7.6, 0.9 Hz, 1H, 6-*H*), 3.87 (s, 1H, 2-H), 3.62 (ddd, J = 7.8, 5.2, 1.0 Hz, 1H, 6-*H*), 2.05 (s, 1H, OH) 1.54 (s, 3H, CH_3 (isopropylidene)), 1.36 (s, 3H, CH_3 (isopropylidene)).

^{13}C NMR (101 MHz, $CDCl_3$) δ 108.9, 101.1, 76.3, 72.6, 70.3, 69.2, 63.6, 25.8, 24.4.

ESI-MS: found 225.4 $[M + Na]^+$.

1,6-Anhydro-2-*O*-benzoyl-3,4-*O*-isopropylidene-D-galactopyranose, 24[9]



24

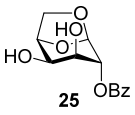
To a mixture of **23** (603 mg, 2.98 mmol, 1.0 eq.) and Py (12 mL), BzCl (0.42 mL, 3.58 mmol, 1.2 eq.) was added at 0 °C, and the reaction mixture was warmed to room temperature and stirred for another 4 hours. After removal of Py, EA was added to dilute the reaction, and the organic phase was washed sequentially with 1 M HCl, saturated $NaHCO_3$, and brine. After dried over Na_2SO_4 and concentrated, the residue was purified with silica gel chromatography using PE and EA (2:1, v/v) to afford **24** as a white oil (895 mg, 2.92 mmol, yield 98%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, J = 8.4, 1.4 Hz, 2H, Ar-H), 7.64 – 7.55 (m, 1H, Ar-H), 7.46 (dd, J = 8.5, 7.1 Hz, 2H, Ar-H), 5.51 (d, J = 1.2 Hz, 1H, 1-H), 5.14 (s, 1H, 2-H), 4.59 (t, J = 5.7 Hz, 1H, 4-H), 4.51 (dd, J = 7.4, 5.9 Hz, 1H, 5-H), 4.26 (dt, J = 7.2, 1.1 Hz, 1H, 3-H), 4.20 (dd, J = 7.6, 1.0 Hz, 1H, 6-*H*), 3.66 (dd, J = 7.6, 5.3 Hz, 1H, 6-*H*), 1.58 (s, 3H, CH_3 (isopropylidene)), 1.36 (s, 3H, CH_3 (isopropylidene)).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 133.5, 129.9, 129.4, 128.5, 109.0, 99.2, 74.1, 72.2, 71.9, 69.2, 63.4, 25.8, 24.3.

ESI-MS: found 329.24 $[M + Na]^+$.

1,6-Anhydro-2-*O*-benzoyl-D-galactopyranose, 25[9]



25

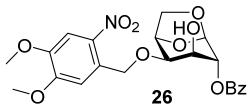
To compound **24** (860 mg, 2.81 mmol, 1.0 eq.), 20% AcOH (10 mL, v/v) was added, and the mixture was heated to 100 °C. After 2 hours, the solution was concentrated, and the resulting oil was co-evaporated with toluene twice. The crude product was purified with silica gel chromatography using PE and EA (1:2, v/v) to afford **25** as a white solid (650 mg, 2.44 mmol, yield 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.99 (m, 2H, Ar-H), 7.65 – 7.55 (m, 1H, Ar-H), 7.49 – 7.42 (m, 2H, Ar-H), 5.58 (t, J = 1.6 Hz, 1H, 1-H), 5.11 (t, J = 1.6 Hz, 1H, 2-H), 4.53 (td, J = 4.7, 1.5 Hz, 1H, 5-H), 4.32 (d, J = 7.8 Hz, 1H, 6-*H*), 4.15 – 4.04 (m, 2H, 3-H, 4-H), 3.75 – 3.69 (m, 1H, 6-*H*), 2.90 (s, 2H, OH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 133.7, 129.9, 129.1, 128.6, 99.4, 74.8, 72.7, 68.8, 64.7, 63.8.

ESI-MS: found 289.2 $[M + Na]^+$.

1,6-Anhydro-4-*O*-(4,5-dimethoxy-2-nitrobenzyl)-2-*O*-benzoyl-D-galactopyranose, 26



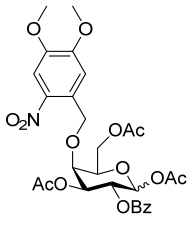
26

A mixture of **25** (200 mg, 0.751 mmol, 1.0 eq.) and Bu_2SnO (225 mg, 0.901 mmol, 1.2 eq.) in toluene (7 mL) was heated to reflux for 6 hours. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure to provide a crude tin ketal. TBAB (266 mg, 0.826 mmol, 1.1 eq.) and DMNB-Br (207 mg, 0.751 mmol, 1.0 eq.) were added to the crude tin ketal in DMF (7 mL), and the resulting solution was stirred at 60 °C for 12 hours. After removed DMF, the residue was dissolved in CH_2Cl_2 and washed with water, saturated NH_4Cl and brine. After dried over Na_2SO_4 and concentrated in vacuo, the crude product was purified with silica gel chromatography using PE and EA (7:3, v/v) to give **26** as yellow oil (194 mg, 0.421 mmol, yield 56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.98 (m, 2H, Ar-H), 7.69 (s, 1H, Ar-H (DMNB)), 7.63 – 7.53 (m, 1H, Ar-H), 7.45 (t, J = 7.8 Hz, 2H, Ar-H), 7.18 (s, 1H, Ar-H (DMNB)), 5.57 (t, J = 1.5 Hz, 1H, 1-H), 5.14 – 5.12 (m, 1H, 2-H), 5.09 – 5.07 (m, 2H, $ArCH_2$), 4.66 (td, J = 4.6, 1.3 Hz, 1H, 5-H), 4.45 (d, J = 7.4 Hz, 1H, 6-*H*), 4.32 – 4.26 (m, 1H, 3-H), 4.01 (t, J = 4.6 Hz, 1H, 4-H), 3.98 (s, 3H, $ArOCH_3$), 3.95 (s, 3H, $ArOCH_3$), 3.76 (ddd, J = 7.4, 5.2, 1.0 Hz, 1H, 6-*H*), 2.83 (s, 1H, OH).

ESI-MS: found 484.1 $[M + Na]^+$.

4-*O*-(4,5-Dimethoxy-2-nitrobenzyl)-2-*O*-benzoyl-1,3,6-tri-*O*-acetyl-D-galactopyranose, 27



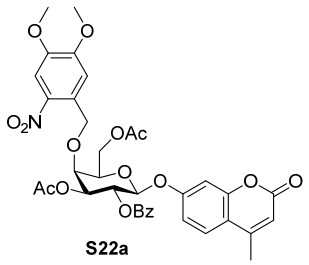
27

Compound **26** (150 mg, 0.325 mmol, 1.0 eq.) was dissolved in 2 mL of acetic anhydride containing 2% concentrated sulfuric acid. After 2 hours, the acetolysis mixture was poured on ice, and neutralized by solid $NaHCO_3$. The aqueous solution was extracted thoroughly with CH_2Cl_2. The organic layer was combined and washed with water, saturated $NaHCO_3$, and brine. After dried over Na_2SO_4 and concentrated in vacuo, the residue was purified

with silica gel chromatography using PE and EA (1:1, v/v) to afford **27** as a yellow foam (165 mg, 0.273 mmol, yield 84%, α:β = 5:1).

ESI-MS: found 628.2 $[M + Na]^+$.

4-Methylumbelliferyl 4-*O*-(4,5-dimethoxy-2-nitrobenzyl)-2-*O*-benzoyl-3,6-di-*O*-acetyl-*β*-D-galactopyranose, S22a



S22a

A solution of **27** (150 mg, 0.248 mmol, 1.0 eq.) in CH_2Cl_2 (2.5 mL) was cooled to 0 °C for 10 min, and then 33% HBr in acetic acid (0.28 mL, 1.73 mmol, 7.0 eq.) was added. The solution was warmed to room temperature. When TLC showed the completion of the reaction after 2 hours, CH_2Cl_2 and saturated $NaHCO_3$ was added to the solution. The organic layer was separated and washed with saturated $NaHCO_3$ and brine. After dried over Na_2SO_4 and concentrated, the crude brominated intermediate was used directly for the next step.

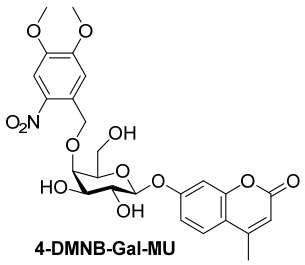
The crude brominated intermediate in MeCN (1 mL) was added to a stirred mixture of 4-methylumbelliferone (52 mg, 0.297 mmol, 1.2 eq.), Ag_2O (149 mg, 0.644 mmol, 2.6 eq.), 4Å MS, and TBAI (29 mg, 0.124 mmol, 0.5 eq.) in MeCN (1.5 mL). After 12 hours, the brominated intermediate was totally consumed, and the reaction mixture was filtered through celite. The organic layer was washed with Na_2CO_3, water, and brine. After dried over Na_2SO_4 and concentrated in vacuo, the residue was purified with silica gel chromatography using PE and EA (1:1, v/v) to afford **S22a** as yellow foam (93 mg, 0.129 mmol, yield 52%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dq, J = 8.1, 1.5, 1.1 Hz, 2H, Ar-H), 7.74 (s, 1H, Ar-H (DMNB)), 7.58 (ddt, J = 7.8, 6.9, 1.3 Hz, 1H, Ar-H), 7.51 (s, 1H, Ar-H (DMNB)), 7.49 – 7.40 (m, 3H, Ar-H × 2, Ar-H (MU)), 6.99 (d, J = 2.4 Hz, 1H, Ar-H (MU)), 6.89 (dd, J = 8.6, 2.4 Hz, 1H, Ar-H (MU)), 6.17 (q, J = 1.3 Hz, 1H, Ar-H (MU)), 5.96 (dd, J = 10.5, 7.8 Hz, 1H, 2-H), 5.37 (dd, J = 10.5, 2.9 Hz, 1H, 3-H), 5.32 – 5.24 (m, 2H, 1-H, ArCH_2), 5.10 (d, J = 15.3 Hz, 1H, ArCH_2), 4.50 (dd, J = 11.3, 7.3 Hz, 1H, 6-*H*), 4.30 (dd, J = 11.4, 5.2 Hz, 1H, 6-*H*), 4.23 (dd, J = 3.0, 1.2 Hz, 1H, 4-H), 4.19 – 4.13 (m, 1H, 5-H), 4.11 (s, 3H, $ArOCH_3$), 3.97 (s, 3H, $ArOCH_3$), 2.37 (d, J = 1.3 Hz, 3H, CH_3 (MU)), 2.15 (s, 3H, CH_3 (Ac)), 1.96 (s, 3H, CH_3 (Ac)).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 170.2, 165.2, 160.8, 159.4, 154.8, 154.2, 152.1, 147.8, 138.6, 133.6, 130.2, 129.8, 129.0, 128.6, 125.7, 115.5, 114.1, 113.2, 109.5, 107.8, 104.3, 99.3, 76.1, 73.2, 73.1, 72.3, 69.4, 62.4, 56.7, 56.4, 20.8, 20.7, 18.7.

ESI-MS: found 744.5 $[M + Na]^+$.

4-Methylumbelliferyl 4-*O*-(4,5-dimethoxy-2-nitrobenzyl)-*β*-D-galactopyranose, 4-DMNB-Gal-MU



4-DMNB-Gal-MU

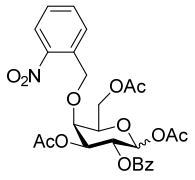
To a solution of **S22a** (70 mg, 0.097 mmol, 1.0 eq.) in a mixture of MeOH and CH_2Cl_2 (1 mL, 1:1, v/v), NaOMe (5 M in MeOH, 18 μL, 1.0 eq.) was added. After stirred at room temperature for 4 hours, H^+ resin was added to adjust the pH of the solution to 7. The resin was filtered off, and the filtrate was concentrated in vacuo. The crude product was purified with silica gel chromatography using MeOH and CH_2Cl_2 (1:25, v/v) to afford **4-DMNB-Gal-MU** as white solid (22 mg, 0.041 mmol, yield 42%).

^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 7.71 (d, J = 8.7 Hz, 1H, Ar-H (MU)), 7.66 (s, 1H, Ar-H (DMNB)), 7.57 (s, 1H, Ar-H (DMNB)), 7.06 (d, J = 2.4 Hz, 1H, Ar-H (MU)), 7.04 (dd, J = 8.7, 2.5 Hz, 1H, Ar-H (MU)), 6.25 (d, J = 1.4 Hz, 1H, Ar-H (MU)), 5.42 (d, J = 5.1 Hz, 1H, OH), 5.34 (d, J = 4.7 Hz, 1H, OH), 5.20 (d, J = 15.3 Hz, 1H, ArCH_2), 5.09 (d, J = 7.4 Hz, 1H, 1-H), 5.00 (d, J = 15.3 Hz, 1H, ArCH_2), 4.86 (t, J = 5.3 Hz, 1H, OH), 3.90 (s, 3H, $ArOCH_3$), 3.89 – 3.85 (m, 5H, $ArOCH_3$, 4-H), 3.83 (t, J = 6.6 Hz, 1H, 5-H), 3.71 (ddd, J = 9.2, 7.2, 4.0 Hz, 1H, 2-H), 3.66 (dt, J = 9.5, 3.5 Hz, 1H, 3-H), 3.57 – 3.52 (m, 2H, 6-H), 2.41 (d, J = 1.2 Hz, 3H, CH_3 (MU)).

^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 160.1, 160.0, 154.4, 153.28, 153.25, 147.2, 138.7, 131.0, 126.4, 114.1, 113.4, 111.7, 110.7, 107.7, 103.2, 100.4, 77.6, 75.3, 73.6, 70.62, 70.60, 59.9, 56.0, 18.1.

HRMS: m/z calculated $[M + Na]^+$ = 556.1425, found 556.1429.

4-*O*-(2-Nitrobenzyl)-2-*O*-benzoyl-1,3,6-tri-*O*-acetyl-D-galactopyranose, S21

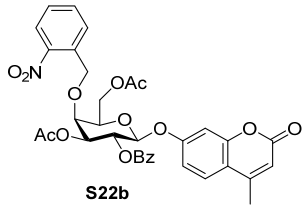


S21

Compound **S21** was synthesized from **25** (250 mg, 0.939 mmol, 1.0 eq.) and ONB-Br (215 mg, 1.410 mmol, 1.5 eq.) using a procedure similar to that employed for the preparation of **27**. The crude product was purified with silica gel chromatography using PE and EA (2:1, v/v) to afford **S21** as yellow oil (194 mg, 0.357 mmol, yield 38%, α:β = 6:1).

ESI-MS: found 568.1 $[M + Na]^+$.

4-Methylumbelliferyl 4-*O*-(2-nitrobenzyl)-2-*O*-benzoyl-3,6-di-*O*-acetyl-*β*-D-galactopyranose, S22b



S22b

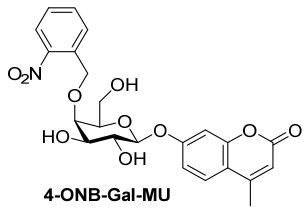
Compound **22b** was synthesized from **S21** (150 mg, 0.275 mmol, 1.0 eq.) and MU (48 mg, 0.275 mmol, 1.0 eq.) using a procedure similar to that employed for the preparation of **S22a**. The crude product was purified with silica gel chromatography using PE and EA (3:2, v/v) to afford **S22b** as yellow oil (80 mg, 0.121 mmol, yield 44%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, J = 8.2, 1.3 Hz, 1H, Ar-H (ONB)), 8.04 – 7.98 (m, 3H, Ar-H × 2, Ar-H (ONB)), 7.76 (td, J = 7.6, 1.3 Hz, 1H, Ar-H (ONB)), 7.61 – 7.55 (m, 1H, Ar-H (ONB)), 7.53 – 7.41 (m, 4H, Ar-H × 3, Ar-H (MU)), 7.00 (d, J = 2.4 Hz, 1H, Ar-H (MU)), 6.91 (dd, J = 8.8, 2.4 Hz, 1H, Ar-H (MU)), 6.17 (t, J = 1.3 Hz, 1H, Ar-H (MU)), 5.94 (dd, J = 10.5, 7.8 Hz, 1H, 2-H), 5.40 (dd, J = 10.5, 2.9 Hz, 1H, 3-H), 5.34 (d, J = 14.9 Hz, 1H, ArCH_2), 5.30 (d, J = 7.8 Hz, 1H, 1-H), 5.03 (d, J = 14.9 Hz, 1H, ArCH_2), 4.44 (dd, J = 11.4, 7.1 Hz, 1H, 6-*H*), 4.31 (dd, J = 11.4, 5.7 Hz, 1H, 6-*H*), 4.21 (dd, J = 3.0, 1.1 Hz, 1H, 4-H), 4.13 (ddd, J = 7.0, 5.7, 1.2 Hz, 1H, 5-H), 2.38 (d, J = 1.3 Hz, 3H, CH_3 (MU)), 2.14 (s, 3H, CH_3 (Ac)), 2.00 (s, 3H, CH_3 (Ac)).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 170.3, 165.2, 160.8, 159.4, 154.8, 152.2, 146.5, 134.4, 134.3, 133.6, 129.8, 129.1, 128.7, 128.6, 128.3, 125.6, 124.8, 115.5, 114.2, 113.2, 104.3, 99.4, 75.5, 73.2, 73.1, 71.7, 69.5, 62.3, 20.8, 20.7, 18.7.

ESI-MS: found 684.2 $[M + Na]^+$.

4-Methylumbelliferyl 4-*O*-(2-nitrobenzyl)-*β*-D-galactopyranose, 4-ONB-Gal-MU



4-ONB-Gal-MU

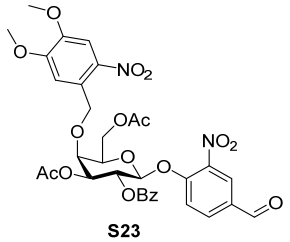
Compound **4-ONB-Gal-MU** was synthesized from **S22b** (52 mg, 0.078 mmol, 1.0 eq.) using a procedure similar to that employed for the preparation of **4-DMNB-Gal-MU**. The crude product was purified with silica gel chromatography using MeOH and CH_2Cl_2 (1:25, v/v) to afford **4-ONB-Gal-MU** as white solid (18 mg, 0.034 mmol, yield 43%).

^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.07 (dd, J = 8.2, 1.3 Hz, 1H, Ar-H (ONB)), 7.92 (dd, J = 7.9, 1.5 Hz, 1H, Ar-H (ONB)), 7.81 (td, J = 7.6, 1.3 Hz, 1H, Ar-H (ONB)), 7.71 (d, J = 8.6 Hz, 1H, Ar-H (MU)), 7.57 (td, J = 7.8, 1.5 Hz, 1H, Ar-H (ONB)), 7.10 – 7.01 (m, 2H, Ar-H (MU)), 6.25 (d, J = 1.4 Hz, 1H, Ar-H (MU)), 5.39 (d, J = 4.5 Hz, 1H, OH), 5.33 – 5.25 (m, 2H, OH, ArCH_2), 5.08 (d, J = 6.7 Hz, 1H, 1-H), 4.95 (d, J = 14.9 Hz, 1H, ArCH_2), 4.82 (t, J = 5.4 Hz, 1H, OH), 3.90 – 3.85 (m, 1H, 4-H), 3.87 – 3.79 (m, 1H, 5-H), 3.72 – 3.64 (m, 2H, 2-H, 3-H), 3.57 – 3.46 (m, 2H, 6-H), 2.41 (d, J = 1.3 Hz, 3H, CH_3 (MU)).

^{13}C NMR (101 MHz, $(CD_3)_2SO$) δ 160.13, 160.10, 154.4, 153.3, 146.7, 135.3, 133.9, 128.8, 128.2, 126.4, 124.3, 114.1, 113.4, 111.7, 103.2, 100.4, 77.1, 75.2, 73.7, 70.52, 70.48, 59.8, 18.1.

HRMS: m/z calculated $[M + Na]^+$ = 496.1214, found 496.1218.

4-Formyl-2-nitrophenol 4-*O*-(4,5-dimethoxy-2-nitrobenzyl)-2-*O*-benzoyl-3,6-di-*O*-acetyl-*β*-D-galatopyranoside, S23



S23

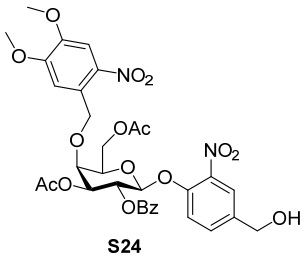
Compound **27** (200 mg, 0.330 mmol, 1.0 eq.) was brominated using a procedure similar to that employed during the preparation of **S22a**. The brominated intermediate in MeCN (1 mL) was added to a mixture of 4-hydroxy-3-nitrobenzaldehyde (66 mg, 0.396 mmol, 1.2 eq.), Ag_2O (162 mg, 0.759 mmol, 2.3 eq.), 4Å MS, and TBAI (61 mg, 0.165 mmol, 0.5 eq.) in MeCN (2 mL). When TLC showed the completion of the reaction after 12 hours, the reaction mixture was filtered through celite. The organic layer was washed with Na_2CO_3, water, and brine. After dried over solid Na_2SO_4 and concentrated, the residue was purified with silica gel chromatography using PE and EA (2:1, v/v) to afford **S23** as light-yellow oil (111 mg, 0.155 mmol, yield 47%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.94 (s, 1H, ArCHO), 8.24 (d, J = 2.0 Hz, 1H, Ar-H), 8.05 (dd, J = 8.7, 2.0 Hz, 1H, Ar-H), 8.03 – 7.98 (m, 2H, Ar-H), 7.73 (s, 1H, Ar-H (DMNB)), 7.60 – 7.55 (m, 1H, Ar-H), 7.52 – 7.41 (m, 4H, Ar-H (DMNB), Ar-H × 3), 6.02 (dd, J = 10.2, 7.5 Hz, 1H, 2-H), 5.43 (d, J = 7.5 Hz, 1H, 1-H), 5.39 (dd, J = 10.2, 2.9 Hz, 1H, 3-H), 5.23 (d, J = 14.9 Hz, 1H, ArCH_2), 5.13 (d, J = 15.1 Hz, 1H, ArCH_2), 4.52 (dd, J = 11.4, 7.1 Hz, 1H, 6-*H*), 4.28 (dd, J = 11.4, 5.9 Hz, 1H, 6-*H*), 4.24 (dd, J = 3.0, 1.4 Hz, 1H, 4-H), 4.19 (ddd, J = 7.2, 5.9, 1.4 Hz, 1H, 5-H), 4.12 (s, 3H, $ArOCH_3$), 3.97 (s, 3H, $ArOCH_3$), 2.10 (s, 3H, CH_3 (Ac)), 1.97 (s, 3H, CH_3 (Ac)).

^{13}C NMR (151 MHz, $CDCl_3$) δ 188.6, 170.4, 170.2, 164.9, 154.3, 153.5, 147.9, 141.2, 138.6, 133.9, 133.5, 131.3, 130.0, 129.9, 129.1, 128.5, 127.0, 118.4, 109.6, 107.9, 99.7, 75.5, 73.2, 72.5, 72.2, 68.8, 62.1, 56.8, 56.4, 20.8, 20.7.

ESI-MS: found 735.2 $[M + Na]^+$.

4-(Hydroxymethyl)-2-nitrophenol 4-*O*-(4,5-dimethoxy-2-nitrobenzyl)-2-*O*-benzoyl-3,6-di-*O*-acetyl-*β*-D-galatopyranoside, S24



S24

Compound **S24** was synthesized from **S23** (100 mg, 0.140 mmol, 1.0 eq.) using a procedure similar to that employed for the preparation of **S18** (Scheme S5). The crude product was purified with silica gel chromatography using PE and EA (3:2, v/v) to afford **S24** as light-yellow oil (89 mg, 0.125 mmol, yield 89%).

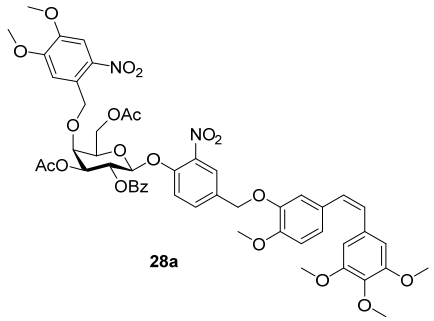
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (dd, J = 8.2, 1.4 Hz, 2H, Ar-H), 7.74 – 7.69 (m, 2H, Ar-H (DMNB), Ar-H), 7.59 – 7.54 (m, 1H, Ar-H), 7.54 (s, 1H, Ar-H (DMNB)), 7.50 (dd, J = 8.7, 2.2 Hz, 1H, Ar-H), 7.43 (t, J = 7.8 Hz, 2H, Ar-H), 7.31 (d, J = 8.6 Hz, 1H, Ar-H), 5.98 (dd, J = 10.4, 7.7 Hz, 1H, 2-H), 5.34 (dd, J = 10.4, 2.9 Hz, 1H, 3-

H), 5.27 (d, *J* = 7.7 Hz, 1H, 1-H), 5.22 (d, *J* = 15.2 Hz, 1H, ArC*H*$_2$), 5.11 (d, *J* = 15.3 Hz, 1H, ArC*H*$_2$), 4.68 (s, 2H, ArCH$_2$ (DMNB)), 4.50 (dd, *J* = 11.3, 6.9 Hz, 1H, 6-*H*), 4.25 (dd, *J* = 11.3, 6.3 Hz, 1H, 6-*H*), 4.20 (dd, *J* = 3.0, 1.2 Hz, 1H, 4-H), 4.13 (s, 3H, ArOCH$_3$), 4.09 (td, *J* = 7.9, 7.2, 1.9 Hz, 1H, 5-H), 3.97 (s, 3H, ArOCH$_3$), 2.09 (s, 3H, CH$_3$ (Ac)), 1.95 (s, 3H, CH$_3$ (Ac)).

^{13}C NMR (151 MHz, CDCl$_3$) δ 170.4, 170.3, 165.1, 154.4, 148.4, 147.8, 141.5, 138.4, 136.9, 133.4, 131.7, 130.3, 129.9, 129.3, 128.5, 123.4, 119.6, 109.6, 107.8, 100.6, 75.7, 72.9, 72.8, 72.2, 69.1, 63.5, 62.1, 56.9, 56.4, 20.8, 20.7.

ESI-MS: found 737.2 [M + Na]$^+$.

(*Z*)-4-((2-Methoxy-5-(3,4,5-trimethoxystyryl)phenoxy)methyl)-2-nitrophenol 4-*O*-(4,5-dimethoxy-2-nitrobenzyl)-2-*O*-benzoyl-3,6-di-*O*-acetyl--*β*-D-galactopyranoside, 28a



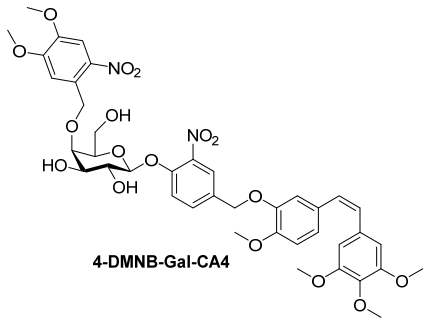
28a

Compound **28a** was synthesized from **S24** (35 mg, 0.049 mmol, 1.0 eq.) and CA4 (15 mg, 0.049 mmol, 1.0 eq.) using a procedure similar to that employed for the preparation of **14a** (Scheme S3). The crude product was purified with silica gel chromatography using PE and EA (3:2, v/v) to afford **28a** as colorless oil (35 mg, 0.034 mmol, yield 70%).

^{1}H NMR (600 MHz, CDCl$_3$) δ 8.06 – 8.00 (m, 2H, Ar-H), 7.75 – 7.71 (m, 2H, Ar-H (DMNB), Ar-H), 7.59 – 7.54 (m, 2H, Ar-H (DMNB), Ar-H), 7.47 – 7.38 (m, 3H, Ar-H), 7.29 – 7.26 (m, 1H, Ar-H), 6.89 (dd, *J* = 8.3, 2.0 Hz, 1H, Ar-H (CA4)), 6.82 – 6.76 (m, 2H, Ar-H (CA4)), 6.51 – 6.38 (m, 4H, Ar-H (CA4)), 5.99 (dd, *J* = 10.4, 7.7 Hz, 1H, 2-H), 5.37 (dd, *J* = 10.4, 3.0 Hz, 1H, 3-H), 5.33 (d, *J* = 7.7 Hz, 1H, 1-H), 5.23 (d, *J* = 15.3 Hz, 1H, ArC*H*$_2$ (DMNB)), 5.12 (d, *J* = 15.3 Hz, 1H, ArC*H*$_2$ (DMNB)), 4.87 (s, 2H, ArCH$_2$), 4.49 (dd, *J* = 11.2, 6.9 Hz, 1H, 6-*H*), 4.27 (dd, *J* = 11.3, 6.3 Hz, 1H, 6-*H*), 4.22 (dd, *J* = 3.0, 1.3 Hz, 1H, 4-H), 4.14 (s, 3H, ArOCH$_3$ (DMNB)), 3.97 (s, 3H, ArOCH$_3$ (DMNB)), 3.84 (s, 3H, ArOCH$_3$ (CA4)), 3.82 (s, 3H, ArOCH$_3$ (CA4)), 3.65 (s, 6H, ArOCH$_3$ (CA4)), 2.10 (d, *J* = 1.2 Hz, 3H, CH$_3$ (Ac)), 1.96 (d, *J* = 1.1 Hz, 3H, CH$_3$ (Ac)).

ESI-MS: found 1035.7 [M + Na]$^+$.

(*Z*)-4-((2-Methoxy-5-(3,4,5-trimethoxystyryl)phenoxy)methyl)-2-nitrophenol 4-*O*-(4,5-dimethoxy-2-nitrobenzyl)-*β*-D-galactopyranoside, 4-DMNB-Gal-CA4



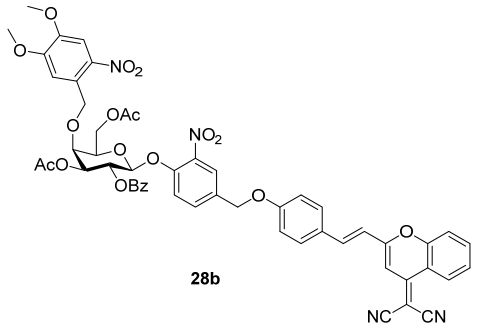
Compound **4-DMNB-Gal-CA4** was synthesized from **28a** (35 mg, 0.034 mmol, 1.0 eq.) using a procedure similar to that employed for the preparation of **4-DMNB-Gal-MU**. The crude product was purified with silica gel chromatography using MeOH and CH_2Cl_2 (1:25, v/v) to afford **4-DMNB-Gal-CA4** as white solid (23 mg, 0.028 mmol, yield 81%).

^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 7.85 (d, J = 2.1 Hz, 1H, Ar-H), 7.67 (s, 1H, Ar-H (DMNB)), 7.61 – 7.56 (m, 2H, Ar-H, Ar-H (DMNB)), 7.45 (d, J = 8.8 Hz, 1H, Ar-H), 6.96 (d, J = 1.9 Hz, 1H, Ar-H (CA4)), 6.93 (d, J = 8.3 Hz, 1H, Ar-H (CA4)), 6.89 (dd, J = 8.3, 1.9 Hz, 1H, Ar-H (CA4)), 6.56 (s, 2H, Ar-H (CA4)), 6.49 (q, J = 12.2 Hz, 2H, Ar-H (CA4)), 5.39 (d, J = 5.2 Hz, 1H, OH), 5.35 (d, J = 4.8 Hz, 1H, OH), 5.21 (d, J = 15.4 Hz, 1H, ArCH_2 (DMNB)), 5.15 (d, J = 7.5 Hz, 1H, 1-H), 5.00 (d, J = 15.5 Hz, 1H, ArCH_2 (DMNB)), 4.91 (s, 2H, $ArCH_2$), 4.86 (t, J = 5.4 Hz, 1H, OH), 3.91 (s, 3H, $ArOCH_3$ (DMNB)), 3.88 – 3.85 (m, 4H, $ArOCH_3$ (DMNB), 4-H), 3.78 (t, J = 6.7 Hz, 1H, 5-H), 3.74 (s, 3H, $ArOCH_3$), 3.69 (ddd, J = 9.7, 7.5, 5.2 Hz, 1H, 2-H), 3.64 – 3.59 (m, 10H, 3-H, $ArOCH_3$ × 3), 3.52 (ddd, J = 10.8, 7.1, 4.4 Hz, 2H, 6-H).

^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 153.4, 152.6, 149.1, 148.6, 147.1, 147.0, 140.1, 138.5, 136.7, 133.3, 132.4, 131.3, 130.9, 129.3, 128.8, 123.8, 122.2, 117.3, 114.4, 112.0, 110.4, 107.7, 105.9, 100.8, 77.3, 75.3, 73.7, 70.6, 68.6, 60.1, 59.7, 56.02, 55.98, 55.64, 55.60, 54.9.

HRMS: m/z calculated $[M + Na]^+$ = 847.2532, found 847.2540.

(*E*)-4-((4-(2-(4-(Dicyanomethylene)-4*H*-chromen-2-yl)vinyl)phenoxy)methyl)-2-nitrophenol 4-*O*-(4,5-dimethoxy-2-nitrobenzyl)-2-*O*-benzoyl-3,6-di-*O*-acetyl-*β*-D-galatopyranoside, 28b



28b

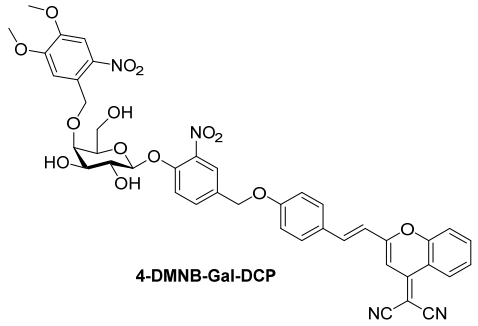
Compound **28b** was synthesized from **S24** (82 mg, 0.115 mmol, 1.0 eq.) and DCP (39 mg, 0.126mmol, 1.1 eq.) using a procedure similar to that employed for the preparation of **14a** (Scheme S3). The crude product was purified with silica gel chromatography using PE and EA (3:2, v/v) to afford **28b** as orange oil (88 mg, 0.087 mmol, yield 76%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.92 (d, J = 8.3 Hz, 1H, Ar-H (DCP)), 8.03 (d, J = 7.6 Hz, 2H, Ar-H), 7.83 (d, J = 2.2 Hz, 1H, Ar-H), 7.76 – 7.72 (m, 2H, Ar-H (DMNB), Ar-H (DCP)), 7.60 – 7.53 (m, 7H, Ar-H × 3, Ar-H (DCP) × 4), 7.45 (td, J = 7.7, 3.2 Hz, 3H, Ar-H, Ar-H (DMNB), Ar-H (DCP)), 7.38 (d, J = 8.6 Hz, 1H, Ar-H), 6.99 (d, J = 8.4 Hz, 2H, Ar-H (DCP)), 6.85 (s, 1H, Ar-H (DCP)), 6.70 (d, J = 15.8 Hz, 1H, Ar-H (DCP)), 6.00 (dd, J = 10.4, 7.6 Hz, 1H, 2-H), 5.36 (dd, J = 10.4, 2.9 Hz, 1H, 3-H), 5.31 (d, J = 7.6 Hz, 1H, 1-H), 5.23 (d, J = 15.2 Hz, 1H, ArCH_2 (DMNB)), 5.15 – 5.07 (m, 3H, ArCH_2 (DMNB), ArCH_2), 4.52 (dd, J = 11.3, 6.8 Hz, 1H, 6-*H*), 4.26 (dd, J = 11.3, 6.4 Hz, 1H, 6-*H*), 4.22 (d, J = 3.0 Hz, 1H, 4-H), 4.15 – 4.08 (m, 4H, 5-H, ArOCH_3), 3.97 (s, 3H, ArOCH_3), 2.09 (s, 3H, CH_3 (Ac)), 1.96 (s, 3H, CH_3 (Ac)).

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.4, 170.3, 165.1, 160.1, 157.8, 154.4, 152.9, 152.4, 149.0, 147.9, 141.5, 138.5, 138.3, 134.6, 133.4, 132.4, 132.3, 130.2, 129.9, 129.8, 129.3, 128.5, 128.3, 126.0, 125.9, 124.2, 119.6, 118.6, 117.9, 117.0, 116.9, 115.9, 115.5, 109.6, 107.8, 106.5, 100.4, 75.7, 72.9, 72.8, 72.2, 69.1, 68.4, 62.5, 62.0, 56.9, 56.4, 20.8, 20.7.

ESI-MS: found 1031.4 $[M + Na]^+$.

(*E*)-4-((4-(2-(4-(Dicyanomethylene)-4*H*-chromen-2-yl)vinyl)phenoxy)methyl)-2-nitrophenol 4-*O*-(4,5-dimethoxy-2-nitrobenzyl)-*β*-D-galatopyranoside, 4-DMNB-Gal-DCP



4-DMNB-Gal-DCP

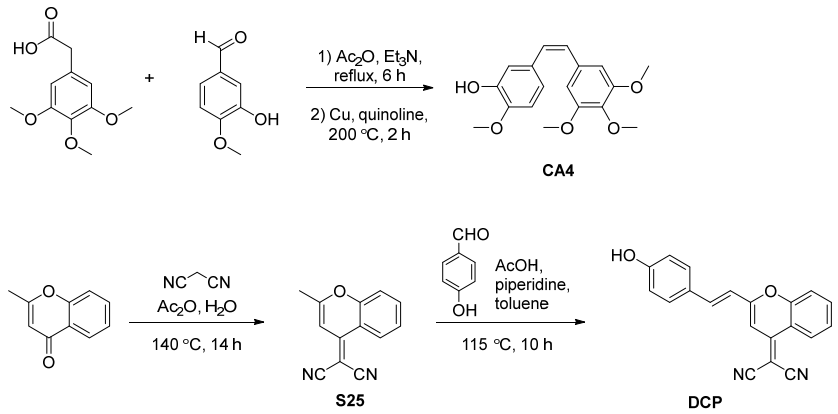
Compound **4-DMNB-Gal-DCP** was synthesized from **28b** (88 mg, 0.087 mmol, 1.0 eq.) using a procedure similar to that employed for the preparation of **4-DMNB-Gal-CA4**. The crude product was purified with silica gel chromatography using MeOH and CH_2Cl_2 (1:25, v/v) to afford **4-DMNB-Gal-DCP** as orange solid (41 mg, 0.050 mmol, yield 57%).

^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 8.74 (d, J = 8.3 Hz, 1H, Ar-H (DCP)), 7.99 (d, J = 2.1 Hz, 1H, Ar-H), 7.93 (t, J = 7.8 Hz, 1H, Ar-H (DCP)), 7.80 (d, J = 8.4 Hz, 1H, Ar-H (DCP)), 7.77 – 7.70 (m, 4H, Ar-H (DMNB), Ar-H (DCP) × 3), 7.67 (s, 1H, Ar-H (DMNB)), 7.62 (t, J = 7.8 Hz, 1H, Ar-H), 7.57 (s, 1H, Ar-H (DCP)), 7.49 (d, J = 8.8 Hz, 1H, Ar-H), 7.39 (d, J = 16.0 Hz, 1H, Ar-H (DCP)), 7.14 (d, J = 8.3 Hz, 2H, Ar-H (DCP)), 6.99 (s, 1H, Ar-H (DCP)), 5.47 –5.28 (m, 2H, OH), 5.24 – 5.18 (m, 3H, $ArCH_2$, ArCH_2 (DMNB)), 5.16 (d, J = 7.4 Hz, 1H, 1-H), 5.00 (d, J = 15.5 Hz, 1H, ArCH_2 (DMNB)), 4.85 (s, 1H, OH), 3.91 (s, 3H, $ArOCH_3$), 3.87 (d, J = 4.7 Hz, 4H, $ArOCH_3$, 4-H), 3.79 (t, J = 6.6 Hz, 1H, 5-H), 3.69 (t, J = 8.5 Hz, 1H, 2-H), 3.63 (dd, J = 9.9, 2.9 Hz, 1H, 3-H), 3.54 (q, J = 8.3, 5.9 Hz, 2H, 6-H).

^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 160.0, 158.6, 153.4, 153.0, 152.0, 149.2, 147.1, 140.1, 138.55, 138.51, 135.4, 133.5, 131.2, 130.6, 130.1, 128.1, 126.1, 124.6, 124.1, 119.0, 117.4, 117.1, 116.0, 115.5, 110.4, 107.7, 106.2, 100.8, 77.3, 75.3, 73.7, 70.6, 67.9, 59.8, 59.6, 56.02, 56.98.

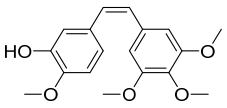
HRMS: m/z calculated $[M + Na]^+$ = 843.2120, found 843.2126.

4.7 Synthesis of CA4, DCP, Gal-CA4, Gal-HQ, and Gal-DCP



Scheme S7. The synthetic route to DCP and CA4.

Combretastatin A4, CA4[10]



CA4

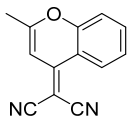
To a solution of 2-(3,4,5-trimethoxyphenyl) acetic acid (3.00 g, 13.26 mmol, 1.2 eq.) and 3-hydroxy-4-methoxy-benzaldehyde (1.68 g, 11.05 mmol, 1.0 eq.) in acetic anhydride (4 mL), triethylamine (2 mL) was added, and the mixture was heated to 110 °C under reflux. After 4 hours, the reaction mixture was cooled to room temperature and acidified with concentrated HCl. The cinnamic acid intermediate (2.12 g, 5.86 mmol, yield 53%) was separated by filtration.

To a solution of the cinnamic acid intermediate (2.00 g, 5.56 mmol, 1.0 eq.) in quinoline (20 mL), powdered copper (1.84 g, 28.8 mmol, 5.2 eq.) was added, and the resulting mixture was stirred at 200 °C for 2 hours. After cooled to room temperature, ether was added, and the copper was filtered off through celite. The organic layer was washed with 1 M HCl, saturated $NaHCO_3$, water, and brine. After dried over Na_2SO_4 and concentrated in vacuo, the residue was purified with silica column chromatography using PE and EA (7:1, v/v) to afforded **CA4** as a colorless oil (1.19 g, 3.76 mmol, yield 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (d, J = 2.1 Hz, 1H), 6.80 (dd, J = 8.3, 2.1 Hz, 1H), 6.73 (d, J = 8.3 Hz, 1H), 6.53 (s, 2H), 6.47 (d, J = 12.2 Hz, 1H), 6.41 (d, J = 12.2 Hz, 1H), 5.55 (s, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.70 (s, 6H).

HRMS: m/z calculated $[M + H]^+$ = 317.1384, found 317.1382.

2-(2-Methyl-4*H*-chromen-4-ylidene)-malononitrile, S25

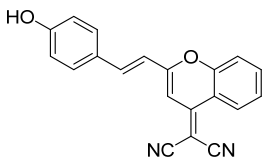


S25

A mixture of 2-methyl-4*H*-chromen-4-one (5.00 g, 31.2 mmol, 1.0 eq.) and malononitrile (2.36 mL, 37.5 mmol, 1.2 eq.) in acetic anhydride (25 mL) was refluxed at 140 °C. After 14 hours, H_2O (80 mL) was added to the residue, and the mixture was refluxed for another 0.5 hour, followed by extraction with CH_2Cl_2. The organic layers were dried over Na_2SO_4 and concentrated. The crude product was purified with silica column chromatography using PE and EA (6:1, v/v) to **S25** as a light orange solid (3.19 g, 10.2 mmol, yield 33%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 – 8.84 (m, 1H), 7.72 (ddd, J = 8.7, 7.2, 1.5 Hz, 1H), 7.50 – 7.40 (m, 2H), 6.71 (d, J = 0.8 Hz, 1H), 2.44 (d, J = 0.7 Hz, 3H).

2-(2-(4-Hydroxystyryl)-4*H*-chromen-4-ylidene) malononitrile, DCP[11]

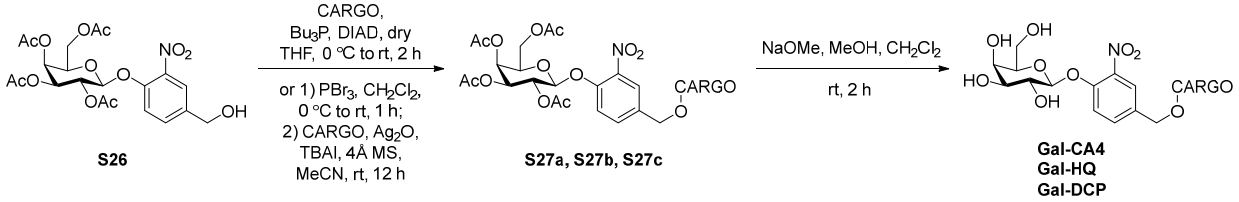


DCP

To a solution of **S25** (1.00 g, 4.80 mmol, 1.0 eq.) and 4-hydroxybenzaldehyde (703 mg, 5.76 mmol, 1.2 eq.) in toluene (30 mL), acetic acid (0.5 mL) and piperidine (1.0 mL) was added. The mixture was refluxed for 10 hours. Toluene was removed in vacuo, and the residue was purified with silica gel chromatography using PE and EA (3:2, v/v) to get the desired product DCP as a dark orange solid (674 mg, 2.16 mmol, yield 45%).

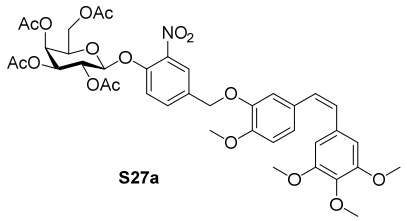
^{1}H NMR (600 MHz, $(CH_3)_2SO$) δ 8.82 – 8.44 (m, 1H), 7.85 (dt, J = 10.5, 5.3 Hz, 1H), 7.69 (t, J = 6.6 Hz, 1H), 7.62 – 7.48 (m, 4H), 7.15 (dd, J = 15.9, 5.2 Hz, 1H), 6.83 (t, J = 3.0 Hz, 3H).

HRMS: m/z calculated $[M + H]^+$ = 313.0972, found 313.0971.



Scheme S8. The synthetic route to Gal-CA4, Gal-HQ, and Gal-DCP.

(*Z*)-4-((2-Methoxy-5-(3,4,5-trimethoxystyryl)phenoxy)methyl)-2-nitrophenol 2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranoside, S27a



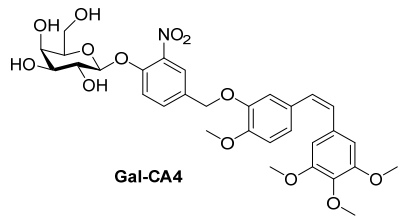
S27a

To a solution of **S26** (100 mg, 0.200 mmol, 1.0 eq.) in THF (2 mL), CA4 (70 mg, 0.221 mmol, 1.1 eq.) and Bu_3P (50 μL, 0.200 mmol, 1.0 eq.) dissolved in anhydrous THF (2 mL) were added. The mixture was then cooled to 0 °C. DIAD (40 μL, 0.203 mmol, 1.0 eq.) was added, and the reaction was allowed to rise to room temperature after 10 min and stirred for another 2 hours. Upon completion, the reaction mixture was diluted with EA (10 mL), washed with water, saturated NH_4Cl, and brine. After dried over Na_2SO_4 and concentrated, the residue was purified with silica gel chromatography using PE and EA (1:1, v/v) to afford **S27a** as colorless oil (108 mg, 0.135 mmol, yield 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 2.1 Hz, 1H, Ar-H), 7.42 (dd, J = 8.6, 2.1 Hz, 1H, Ar-H), 7.29 (d, J = 8.6 Hz, 1H, Ar-H), 6.90 (dd, J = 8.3, 1.9 Hz, 1H, Ar-H (CA4)), 6.84 – 6.77 (m, 2H, Ar-H (CA4)), 6.46 (d, J = 12.3 Hz, 4H, Ar-H (CA4)), 5.54 (dd, J = 10.5, 7.9 Hz, 1H, 2-H), 5.47 (d, J = 3.4 Hz, 1H, 4-H), 5.15 – 5.04 (m, 2H, 3-H, 1-H), 4.89 (s, 2H, $ArCH_2$), 4.28 – 4.13 (m, 2H, 6-H), 4.11 – 4.06 (m, 1H, 5-H), 3.86 (s, 3H, $ArOCH_3$ (CA4)), 3.82 (s, 3H, $ArOCH_3$ (CA4)), 3.68 (s, 6H, $ArOCH_3$ (CA4)), 2.18 (s, 3H, CH_3 (Ac)), 2.13 (s, 3H, CH_3 (Ac)), 2.07 (s, 3H, CH_3 (Ac)), 2.01 (s, 3H, CH_3 (Ac)).

ESI-MS: found 820.5 $[M + Na]^+$.

(*Z*)-4-((2-Methoxy-5-(3,4,5-trimethoxystyryl)phenoxy)methyl)-2-nitrophenol *β*-D-galactopyranoside, Gal-CA4



Gal-CA4

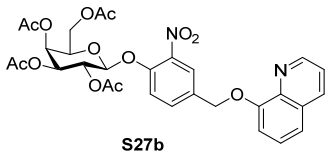
Compound **S27a** (98 mg, 0.123 mmol, 1.0 eq.) was deacylated with NaOMe (5 M in MeOH, 10 μL, 0.050 mmol, 0.4 eq.) in MeOH (1.5 mL). The residue was purified with silica gel chromatography using MeOH and CH_2Cl_2 (1:12, v/v) to afford **Gal-CA4** as white solid (48 mg, 0.076 mmol, yield 60%).

^{1}H NMR (600 MHz, $(CH_3)_2SO$) δ 7.85 (d, J = 2.1 Hz, 1H, Ar-H), 7.58 (dd, J = 8.8, 2.2 Hz, 1H, Ar-H), 7.42 (d, J = 8.8 Hz, 1H, Ar-H), 6.98 – 6.86 (m, 3H, Ar-H (CA4)), 6.56 (s, 2H, Ar-H (CA4)), 6.49 (q, J = 12.2 Hz, 2H, Ar-H (CA4)), 5.18 (d, J = 5.2 Hz, 1H, OH), 5.05 (d, J = 7.7 Hz, 1H, 1-H), 4.95 – 4.86 (m, 3H, OH, $ArCH_2$), 4.68 (t, J = 5.5 Hz, 1H, OH), 4.61 (d, J = 4.5 Hz, 1H, OH), 3.74 (s, 3H, $ArOCH_3$ (CA4)), 3.70 (t, J = 4.1 Hz, 1H, 4-H), 3.63 (s, 4H, $ArOCH_3$ (CA4), 5-H), 3.61 (s, 6H, $ArOCH_3$ (CA4)), 3.59 – 3.56 (m, 1H, 2-H), 3.54 (dd, J = 11.1, 5.5 Hz, 1H, 6-*H*), 3.52 – 3.47 (m, 1H, 6-*H*), 3.41 (ddd, J = 9.4, 5.9, 3.3 Hz, 1H, 3-H).

^{13}C NMR (151 MHz, $(CH_3)_2SO$) δ 152.6, 149.3, 148.6, 147.0, 139.8, 136.7, 133.3, 132.5, 130.6, 129.31, 129.29, 128.8, 123.8, 122.2, 117.1, 114.4, 112.0, 105.9, 101.0, 75.8, 73.3, 70.0, 68.6, 68.0, 60.2, 60.1, 55.65, 55.60.

HRMS: m/z calculated $[M+Na]^+$ = 652.2001, found 652.2005.

2-Nitro-4-((quinolin-8-yloxy)methyl)phenol 2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranoside, S27b



S27b

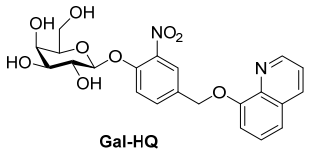
Compound **S27b** was synthesized from **S26** (110 mg, 0.220 mmol, 1.0 eq.) and HQ (32 mg, 0.220 mmol, 1.0 eq.) using a procedure similar to that employed for the preparation of **14b** (Scheme S3). The crude product was purified with silica gel chromatography using MeOH and CH_2Cl_2 (1:25, v/v) to afford **S27b** as orange solid (66 mg, 0.106 mmol, yield 48%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (dt, J = 4.3, 1.4 Hz, 1H, Ar-H (HQ)), 8.19 – 8.09 (m, 1H, Ar-H (HQ)), 7.96 (d, J = 2.1 Hz, 1H, Ar-H), 7.71 (dd, J = 8.6, 2.2 Hz, 1H, Ar-H (HQ)), 7.50 – 7.31 (m, 4H, Ar-H (HQ) × 2, Ar-H × 2), 7.02 (dd, J = 7.1, 1.8 Hz, 1H, Ar-H (HQ)), 5.53 (dd, J = 10.4, 7.9 Hz, 1H, 2-H), 5.45 (dd, J = 3.4, 1.1 Hz, 1H, 4-H), 5.40 (s, 2H, $ArCH_2$), 5.09 (dd, J = 10.5, 3.4 Hz, 1H, 3-H), 5.05 (d, J = 7.9 Hz, 1H, 1-H), 4.22 (dd, J = 11.4, 7.0 Hz, 1H, 6-*H*), 4.14 (dd, J = 11.4, 5.9 Hz, 1H, 6-*H*), 4.04 (ddd, J = 7.2, 6.0, 1.3 Hz, 1H, 5-H), 2.17 (s, 3H, CH_3(Ac)), 2.11 (s, 3H, CH_3(Ac)), 2.01 (s, 3H, CH_3(Ac)), 2.00 (s, 3H, CH_3(Ac)).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 170.2, 170.1, 169.4, 153.8, 149.6, 148.9, 141.4, 140.4, 136.0, 133.2, 132.5, 129.6, 126.5, 124.0, 121.8, 120.8, 120.2, 110.2, 100.8, 71.5, 70.6, 69.3, 67.9, 66.8, 61.4, 20.6, 20.6, 20.5.

ESI-MS: found 627.5 $[M + H]^+$.

2-Nitro-4-((quinolin-8-yloxy)methyl)phenol *β*-D-galactopyranoside, Gal-HQ



Gal-HQ

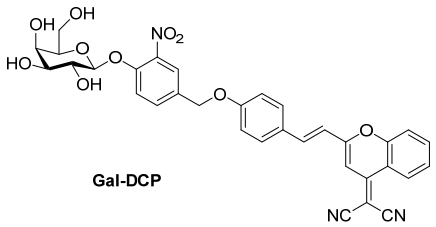
Compound **S27b** (66 mg, 0.106 mmol, 1.0 eq.) was deacylated with NaOMe in MeOH. The crude product was purified with silica gel chromatography using MeOH and CH_2Cl_2 (1:25, v/v) to afford **Gal-HQ** as white solid (39 mg, 0.087 mmol, yield 82%).

^{1}H NMR (400 MHz, $(CH_3)_2SO$) δ 8.88 (dd, J = 4.1, 1.8 Hz, 1H, Ar-H (HQ)), 8.33 (dd, J = 8.3, 1.8 Hz, 1H, Ar-H (HQ)), 8.06 (d, J = 2.2 Hz, 1H, Ar-H), 7.82 (dd, J = 8.8, 2.2 Hz, 1H, Ar-H (HQ)), 7.61 – 7.44 (m, 4H, Ar-H × 2, Ar-H (HQ) × 2), 7.32 (dd, J = 6.9, 2.1 Hz, 1H, Ar-H (HQ)), 5.34 (s, 2H, $ArCH_2$), 5.19 (d, J = 4.8 Hz, 1H, OH), 5.07 (d, J = 7.6 Hz, 1H, 1-H), 4.92 (d, J = 5.5 Hz, 1H, OH), 4.69 (t, J = 5.4 Hz, 1H, OH), 4.61 (d, J = 4.3 Hz, 1H, OH), 3.72 (t, J = 3.6 Hz, 1H, 4-H), 3.65 (t, J = 6.2 Hz, 1H, 5-H), 3.63 – 3.46 (m, 3H, 2-H, 6-H), 3.43 (dd, J = 9.1, 4.5 Hz, 1H, 3-H).

^{13}C NMR (101 MHz, $(CH_3)_2SO$) δ 153.8, 149.3, 149.2, 139.95, 139.85, 135.8, 133.5, 130.8, 129.1, 126.7, 124.0, 121.9, 120.2, 117.3, 110.4, 101.1, 75.8, 73.4, 70.0, 68.5, 68.0, 60.3.

HRMS: m/z calculated $[M+H]^+$ = 459.1398, found 459.1405.

(*E*)-4-((4-(2-(4-(Dicyanomethylene)-4*H*-chromen-2-yl)vinyl)phenoxy)methyl)-2-nitrophenol *β*-D-galatopyranoside, Gal-DCP



Gal-DCP

Compound **Gal-DCP** was synthesized from **S26** (160 mg, 0.320 mmol, 1.0 eq.) and DCP (110 mg, 0.352 mmol, 1.1 eq.) using a procedure similar to that employed for the preparation of **Gal-CA4**. The crude product was purified with silica gel chromatography using MeOH and CH_2Cl_2 (2:25, v/v) to afford **Gal-DCP** as orange solid (104 mg, 0.167 mmol, yield 52% over two steps).

^{1}H NMR (600 MHz, $(CH_3)_2SO$) δ 8.73 (d, J = 8.3 Hz, 1H, Ar-H (DCP)), 7.98 (d, J = 2.1 Hz, 1H, Ar-H), 7.92 (t, J = 7.7 Hz, 1H, Ar-H (DCP)), 7.79 (d, J = 8.4 Hz, Ar-H (DCP)), 7.77 – 7.70 (m, 4H, Ar-H (DCP)), 7.61 (t, J = 7.8 Hz, 1H, Ar-H), 7.46 (d, J = 8.7 Hz, 1H, Ar-H), 7.38 (d, J = 16.0 Hz, 1H, Ar-H (DCP)), 7.14 (d, J = 8.4 Hz, 2H,

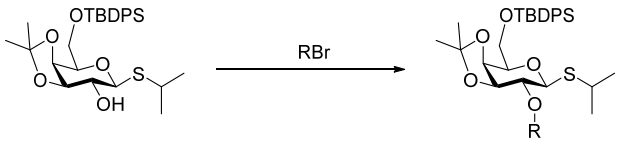
Ar-H (DCP)), 6.99 (s, 1H), 5.22 – 5.16 (m, 3H, OH, $ArCH_2$), 5.06 (d, *J* = 7.7 Hz, 1H, 1-H), 4.91 (d, *J* = 5.7 Hz, 1H, OH), 4.67 (t, *J* = 5.5 Hz, 1H, OH), 4.61 (d, *J* = 4.4 Hz, 1H, OH), 3.71 (t, *J* = 3.8 Hz, 1H, 4-H), 3.65 (t, *J* = 6.2 Hz, 1H, 5-H), 3.61 – 3.53 (m, 2H, 2-H, 6-*H*), 3.49 (dt, *J* = 11.0, 5.6 Hz, 1H, 6-H), 3.41 (dt, *J* = 9.0, 4.0 Hz, 1H, 3-H).

^{13}C NMR (151 MHz, $(CH_3)_2SO$) δ 160.0, 158.6, 152.9, 152.0, 149.3, 139.9, 138.6, 135.4, 133.5, 130.4, 130.1, 128.0, 126.1, 124.6, 124.0, 119.0, 117.4, 117.3, 117.2, 117.1, 116.0, 115.5, 106.1, 101.1, 75.8, 73.3, 70.0, 68.0, 67.9, 60.3, 59.6.

HRMS: m/z calculated $[M+Na]^+$ = 648.1589, found 648.1591.

4.8 Screen of reaction conditions

Table S2. Optimization of the conditions for *O*2 alkylation of **15**.

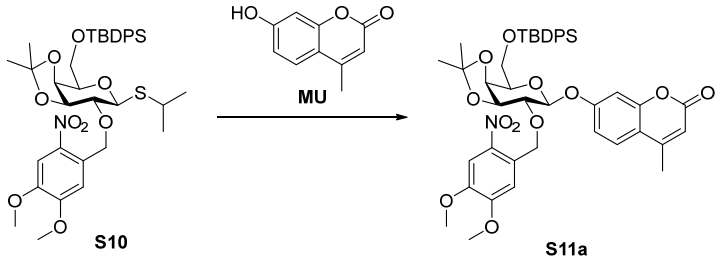


15

16: R = ONB
S10: R = DMNB

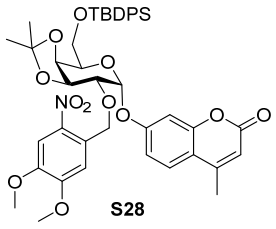
Entry	Base	Solvent	Catalyst	Temperature	Time (hours)	Yield
1	NaH (1.1 eq.)	DMF	-	0 °C	6	-
2	NaH (1.1 eq.)	DMF	-	rt	6	-
3	NaH (1.1 eq.)	DMF	-	70 °C	2	-
4	NaOH (1 M)	H_2O CH_2Cl_2	TBAB (1.0 eq.)	rt	4	46% (R = ONB) - (R = DMNB)
5	Ag_2O (2.0 eq.)	DMF	TBAI (0.2 eq.)	rt	16	16% (R = ONB) 24% (R = DMNB)
6	Ag_2O (2.0 eq.)	CH_2Cl_2	TBAI (0.5 eq.)	rt	16	23% (R = ONB) 42% (R = DMNB)

Table S3. Optimization of the conditions for glycosylation of the *O*2-DMNB intermediate.



Entry	Conditions	Yield
1	MU, NIS, TMSOTf, MeCN, 0 °C to rt, 1 hour	-
2	1) NBS, THF, H_2O, 0 °C to rt, 2 hours; 2) *N*-phenyl trifluoroacetimidoyl chloride, DBU, CH_2Cl_2, rt, 1 hour 3) MU, $BF_3{\cdot}Et_2O$, MeCN, 4Å MS, 0 °C, 1 hour	74% (α isomer **S28** as the dominant product)
3	1) IBr, CH_2Cl_2, 4Å MS, 0 °C to rt, 1 hour; 2) MU, CH_2Cl_2, H_2O, 1M NaOH, TBAB, rt, 6 hours	-
4	1) IBr, CH_2Cl_2, 4Å MS, 0 °C to rt, 1 hour; 2) MU, Ag_2O, MeCN, TBAI, rt, 8 hours	52%

4-Methylumbelliferyl 2-*O*-(4,5-dimethoxy-2-nitrobenzyl)-3,4-*O*-isopropylidene-6-*O*-(*tert*-butyldiphenylsilyl)-*α*-D-galatopyranoside, S28



To a solution of **S10** (100 mg, 0.140 mmol, 1.0 eq.) in a mixture of THF and water (1 mL, 1:1, v/v), *N*-bromosuccinimide (75 mg, 0.421 mmol, 3.0 eq.) was added at 0 °C and warmed to room temperature. After 2 hours, the solution was diluted with CH_2Cl_2 and washed with 10% $Na_2S_2O_3$ (w/w), saturated $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified with silica gel chromatography using PE and EA (2:1, v/v) to afford the hydrolyzed intermediate (86 mg, 0.132 mmol, 94%).

To a solution of the hydrolyzed intermediate (86 mg, 0.132 mmol, 1.0 eq.) in anhydrous CH_2Cl_2 (1 mL), *N*-phenyl trifluoroacetimidoyl chloride (43 μL, 0.264 mmol, 2.0 eq.) and DBU (10 μL, 0.066 mmol, 0.5 eq.) were

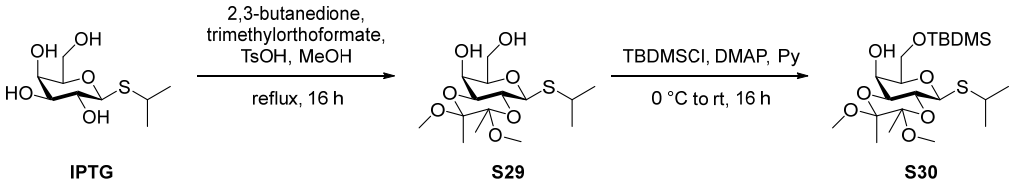
added. When TLC showed complete conversion after 1 hour, the solvent was then evaporated, and the residue was purified with silica gel chromatography using PE and EA (2:1, v/v) to afford the to give a trifluoro-acetimidate donor (99 mg, 0.120 mmol, 91%).

To a solution of trifluoroacetimidate donor (99 mg, 0.120 mmol, 1.0 eq.) in anhydrous MeCN (6 mL), MU (32 mg, 0.180 mmol, 1.5 eq.) and 4Å MS were added. The mixture was stirred at 0 °C for 10 min, and $BF_3{\cdot}Et_2O$ (1.5 μL, 0.012 mmol, 0.1 eq.) was added. After stirred for 1 hour at room temperature, 4Å MS were filtered off, and the mixture was washed with saturated $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by silica gel chromatography using PE and EA (2:1, v/v) to afford **S28** as light yellow oil (72 mg, 0.089 mmol, 74%, α:β = 5:1).

^{1}H NMR (600 MHz, $CDCl_3$, α) δ 7.67 (s, 1H, Ar-H (DMNB)), 7.61 – 7.58 (m, 3H, Ar-H), 7.47 (d, J = 8.7 Hz, 1H, Ar-H (Mu)), 7.43 (s, 1H, Ar-H (DMNB)), 7.40 – 7.35 (m, 3H, Ar-H), 7.31 (td, J = 7.4, 3.9 Hz, 4H, Ar-H), 7.09 – 7.04 (m, 2H, Ar-H (Mu)), 6.19 (d, J = 1.4 Hz, 1H, Ar-H (Mu)), 5.69 (d, J = 3.3 Hz, 1H, 1-H), 5.21 – 5.10 (m, 2H, $ArCH_2$ (DMNB)), 4.57 (dd, J = 7.6, 5.5 Hz, 1H, 3-H), 4.33 (dd, J = 5.5, 2.5 Hz, 1H, 4-H), 3.97 – 3.95 (m, 1H, 5-H), 3.95 (s, 4H, $ArOCH_3$), 3.94 (s, 3H, $ArOCH_3$), 3.93 – 3.90 (m, 1H, 6-H), 3.86 (dd, J = 10.4, 6.8 Hz, 1H, 6-H), 3.76 (dd, J = 7.7, 3.3 Hz, 1H, 2-H), 2.40 (d, J = 1.2 Hz, 3H, CH_3 (MU)), 1.45 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 0.97 (s, 9H, $SiC(CH_3)_3$).

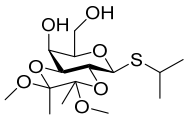
ESI-MS: found 834.6 $[M + Na]^+$.

Attempted synthesis of *O*4-photocaged intermediate from IPTG



IPTG S29 S30

Isopropyl 2,3-*O*-(2',3'-dimethoxybutane-2',3'-diyl)-*β*-D-galactopyranoside, S29[7]



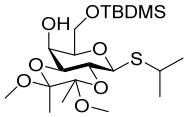
S29

To a solution of IPTG (1.00 g, 4.20 mmol, 1.0 eq.) in methanol (15 mL), 2,3-butanedione (0.45 mL, 5.1 mmol, 1.2 eq.), trimethylorthoformate (1.5 mL, 15.1 mmol, 3.6 eq.), and *p*-$TsOH{\cdot}H_2O$ (100 mg, 0.576 mmol, 0.14 eq.) were added. The solution was stirred under reflux for 16 hours and quenched with Et_3N (50 μL). After concentrated,

the residue was purified with silica gel chromatography using PE and EA (7:3, v/v) to yield **S29** (770 mg, 2.18 mmol, 52%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.64 (d, J = 9.9 Hz, 1H, 1-H), 3.99 (dd, J = 3.2, 1.2 Hz, 1H, 4-H), 3.99 – 3.87 (m, 2H, 2-H, 6-*H*), 3.80 (dd, J = 11.8, 4.6 Hz, 1H, 6-*H*), 3.76 (dd, J = 9.9, 3.1 Hz, 1H, 3-H), 3.60 (ddd, J = 6.4, 4.7, 1.3 Hz, 1H, 5-H), 3.27 (s, 3H, OCH_3), 3.29 – 3.18 (m, 4H, OCH_3, SCH), 1.40 – 1.19 (m, 12H, CH_3 × 2, CH_3 (isopropylthio) × 2).

Isopropyl 6-*O*-(*tert*-butyldimethylsilyl)-2,3-*O*-(2',3'-dimethoxybutane-2',3'-diyl)-*β*-D-galactopyranoside, S30[7]

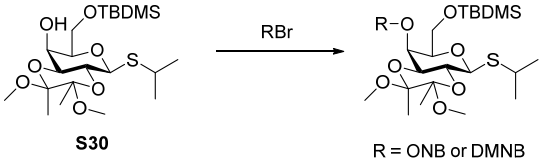


S30

To a solution of **S29** (700 mg, 1.99 mmol, 1.0 eq.) in pyridine (10 mL), DMAP (72 mg, 3.78 mmol, 0.3 eq.) and TBDMSCl (301 mg, 28.8 mmol, 3.0 eq.) were added at 0 °C. The reaction was warmed to room temperature and stirred for 11 hours. After quenched with ice-cold water (50 mL), the mixture was extracted with EA. The organic layer was separated and washed with water, saturated $NaHCO_3$ and brine. After dried over Na_2SO_4 and concentrated, the residue was purified with silica gel chromatography using PE and EA (9:1, v/v) **S30** as colorless oil (780 mg, 1.67 mmol, 84%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.62 (d, J = 9.8 Hz, 1H, 1-H), 4.01 (d, J = 2.7 Hz, 1H, 4-H), 3.97 – 3.85 (m, 2H, 6-H), 3.80 (dd, J = 10.3, 5.5 Hz, 1H, 6-H), 3.74 (dd, J = 9.8, 3.0 Hz, 1H, 2-H), 3.59 – 3.51 (m, 1H, 5-H), 3.28 (s, 3H, OCH_3), 3.27 (s, 3H, OCH_3), 1.34 – 1.29 (m, 12H, CH_3 × 2, CH_3 (isopropylthio) × 2), 0.89 (s, 9H, $SiC(CH_3)_3$ (TBDMS)), 0.09 – 0.07 (m, 6H, $SiCH_3$ (TBDMS)).

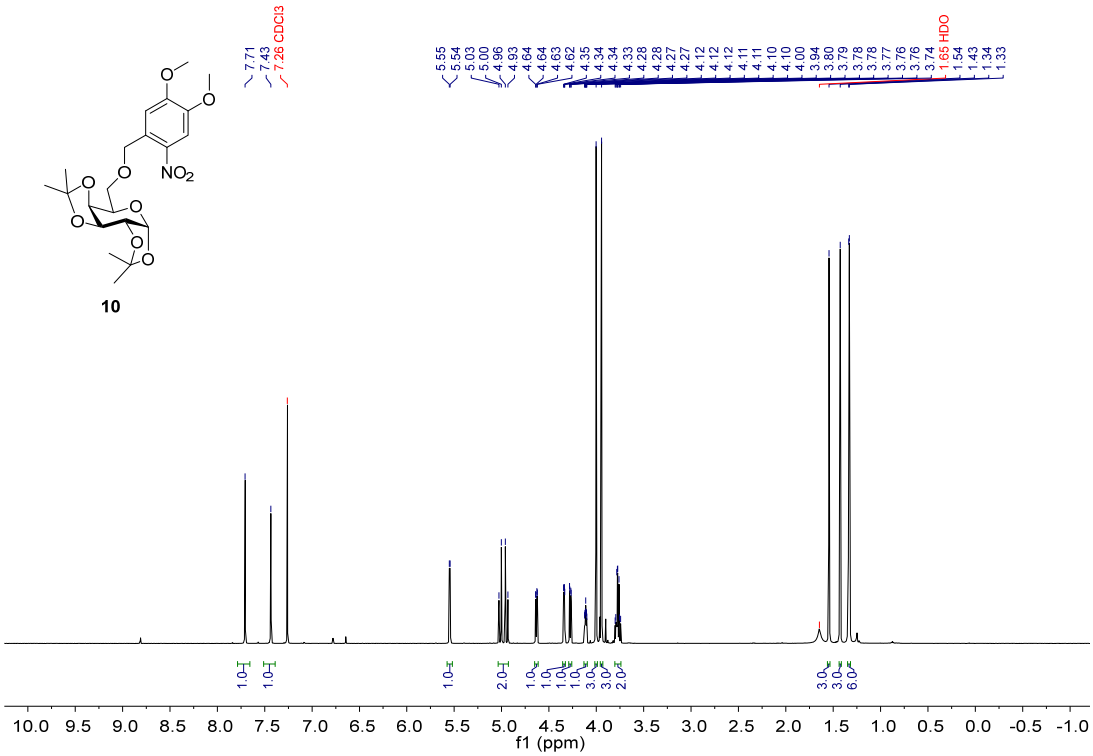
Table S4 Attempted conditions for *O*4 alkylation of **S30**.



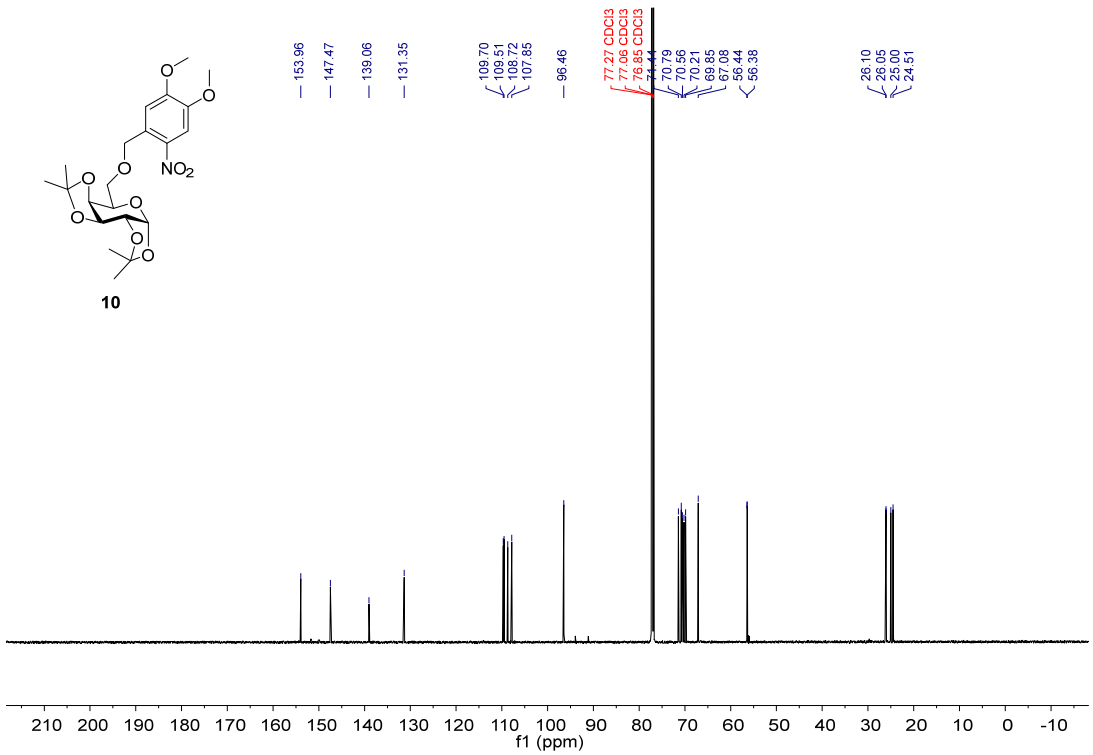
Entry	Base	Solvent	Catalyst	Temperature	Time (hours)	Yield
1	NaH (1.1 eq.)	THF	-	0–70 °C	12	-
2	NaH (2.0 eq.)	DMF	-	0–70 °C	12	-
3	K_2CO_3 (3.0 eq.)	Acetone	TBAB (0.1 eq.)	reflux	12	-
4	NaOH (1 M)	H_2O CH_2Cl_2	TBAB (1.0 eq.)	rt	4	-
5	Ag_2O (2.0 eq.)	DMF	TBAI (0.2 eq.)	rt–100 °C	32	-
6	Ag_2O (2.0 eq.)	CH_2Cl_2	TBAI (0.5 eq.)	rt	16	-

5. NMR Spectra

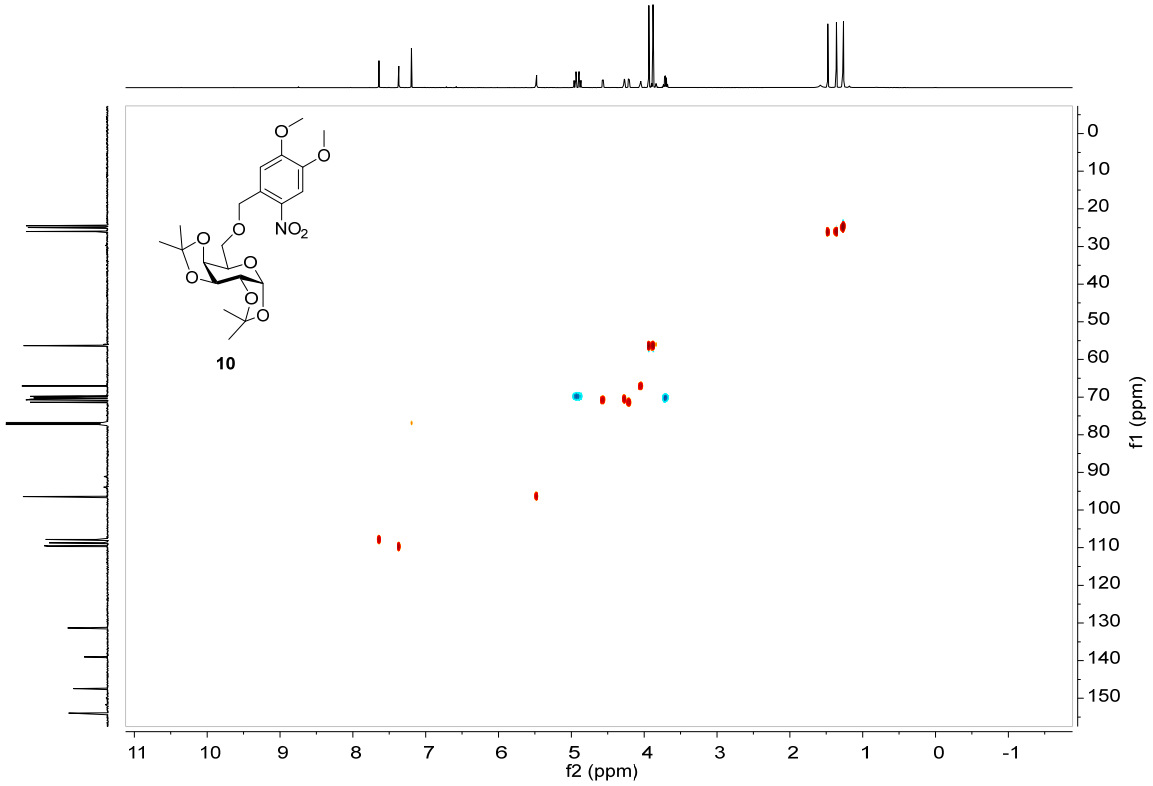
^{1}H NMR ($CDCl_3$, 600 MHz) of compound 10



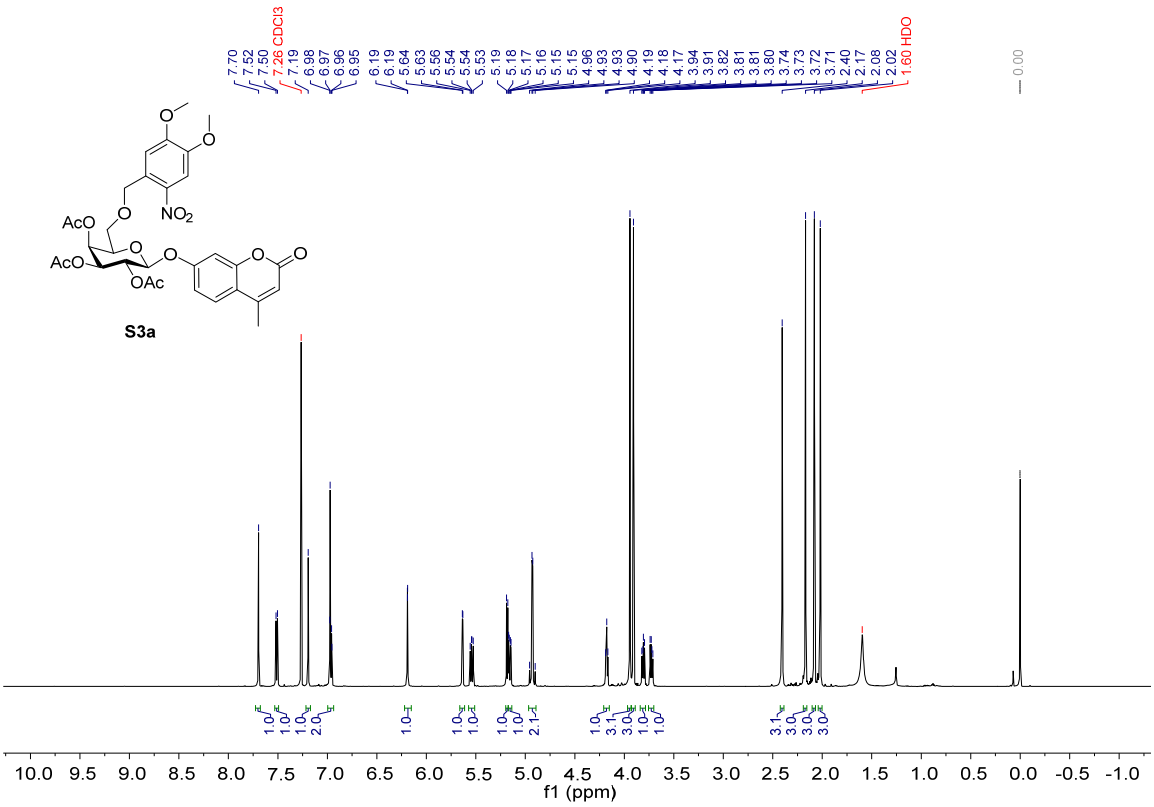
^{13}C NMR ($CDCl_3$, 151 MHz) of compound 10



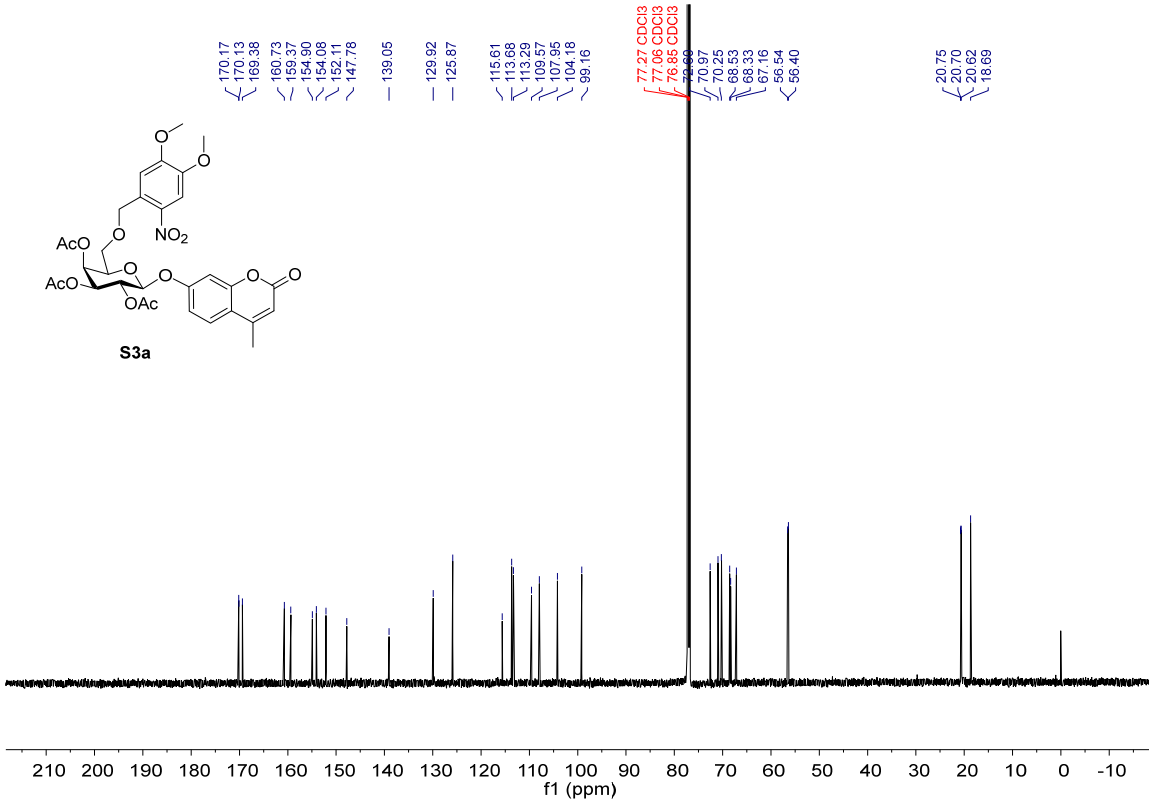
^{1}H-^{13}C HSQC NMR ($CDCl_3$, 600 MHz) of compound 10



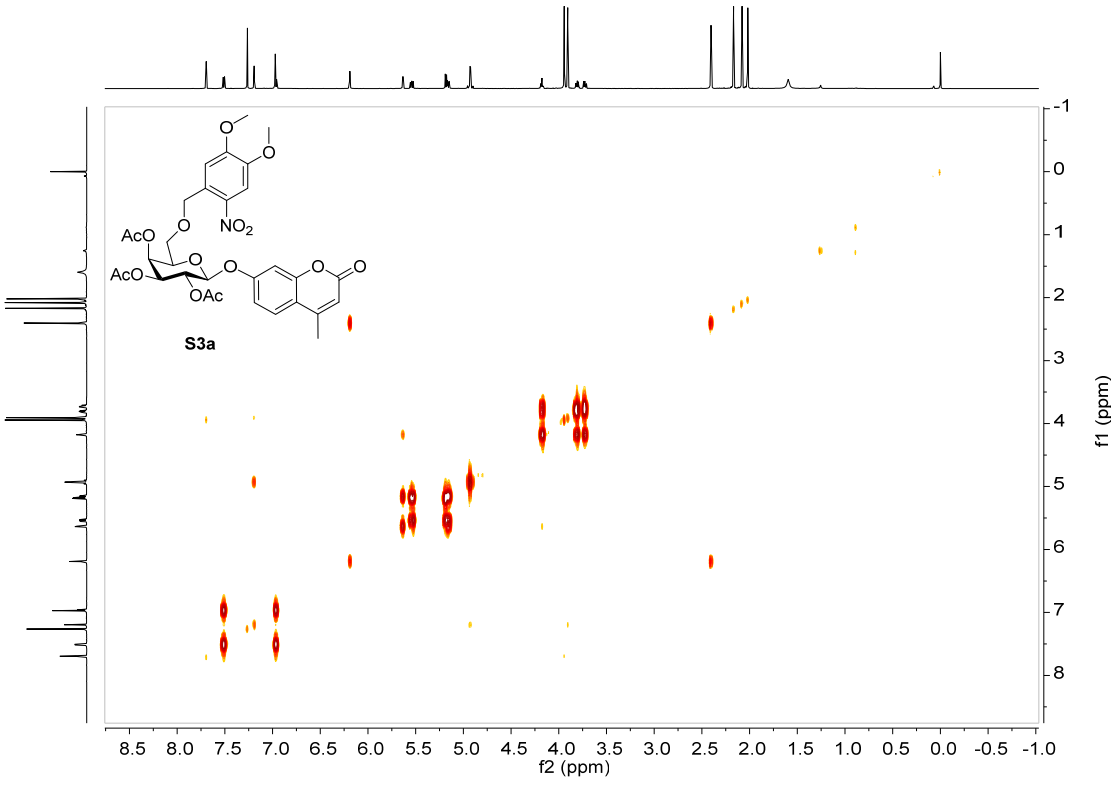
^{1}H NMR ($CDCl_3$, 600 MHz) of compound S3a



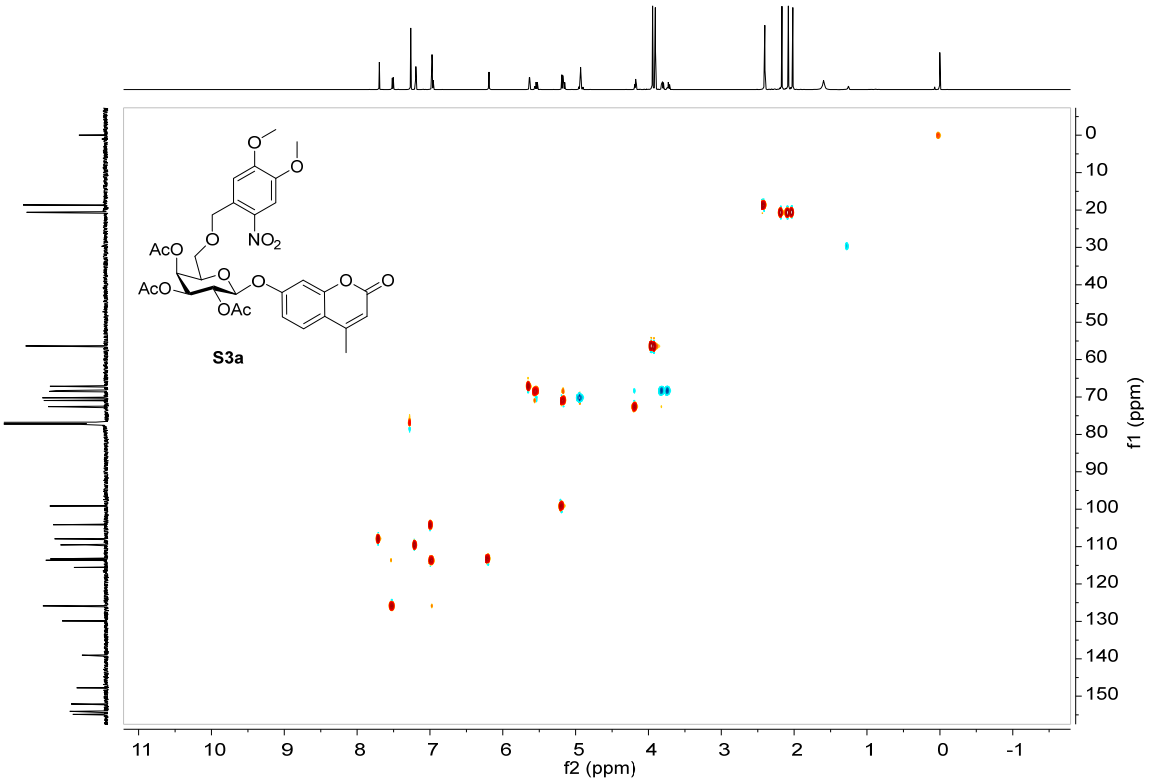
^{13}C NMR ($CDCl_3$, 151 MHz) of compound S3a



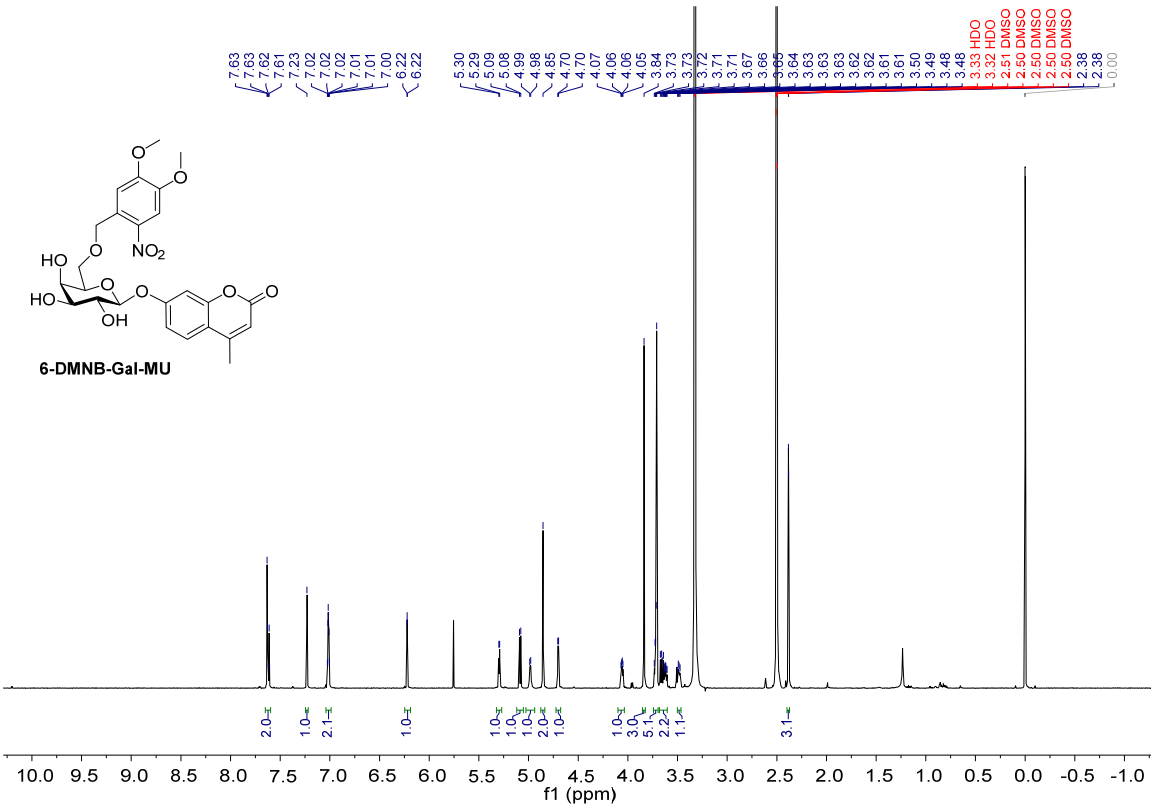
^{1}H-^{1}H COSY NMR ($CDCl_3$, 600 MHz) of compound S3a



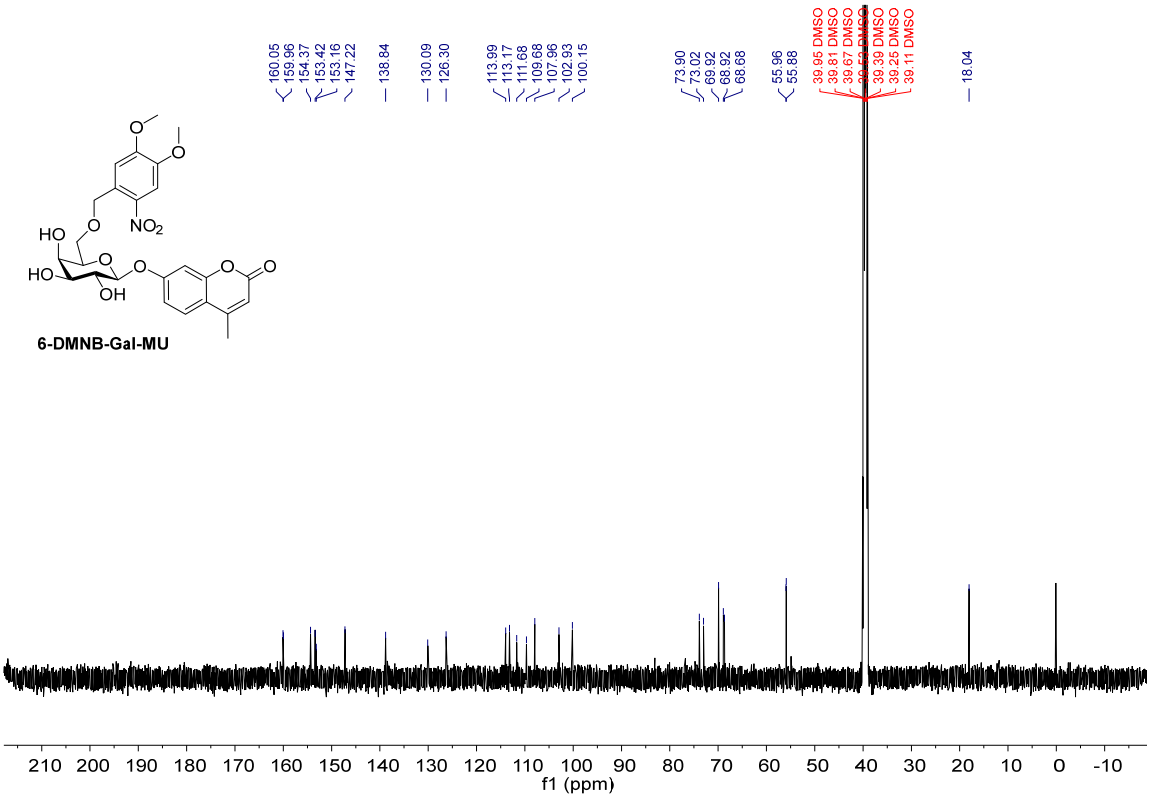
^{1}H-^{13}C HSQC NMR ($CDCl_3$, 600 MHz) of compound S3a



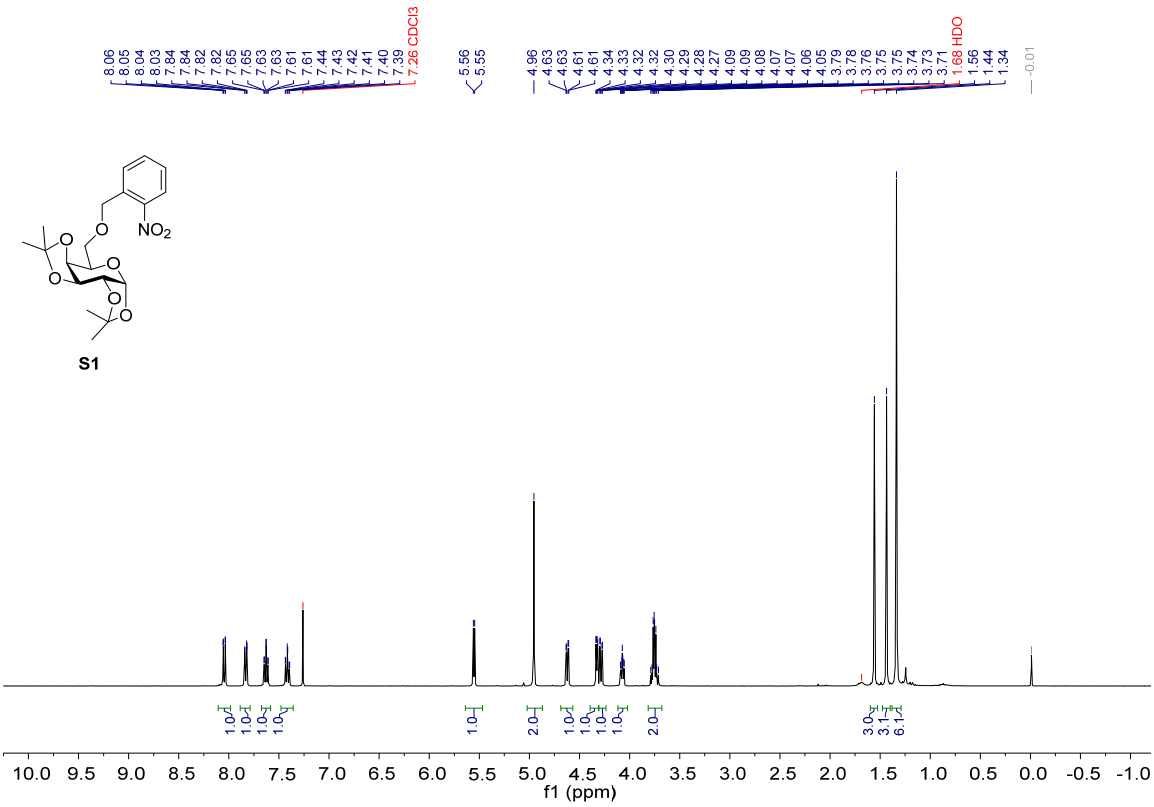
^{1}H NMR ($(CD_3)_2SO$, 600 MHz) of compound 6-DMNB-Gal-MU



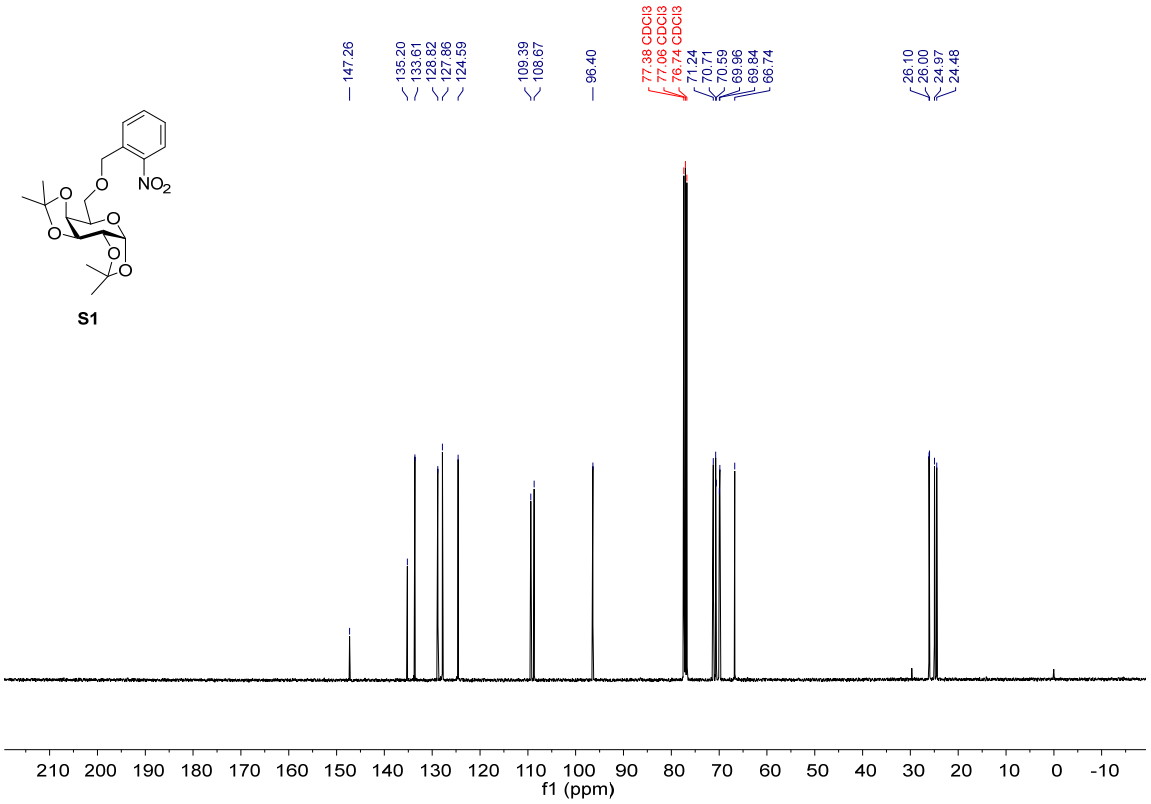
^{13}C NMR ($(CD_3)_2SO$, 151 MHz) of compound 6-DMNB-Gal-MU



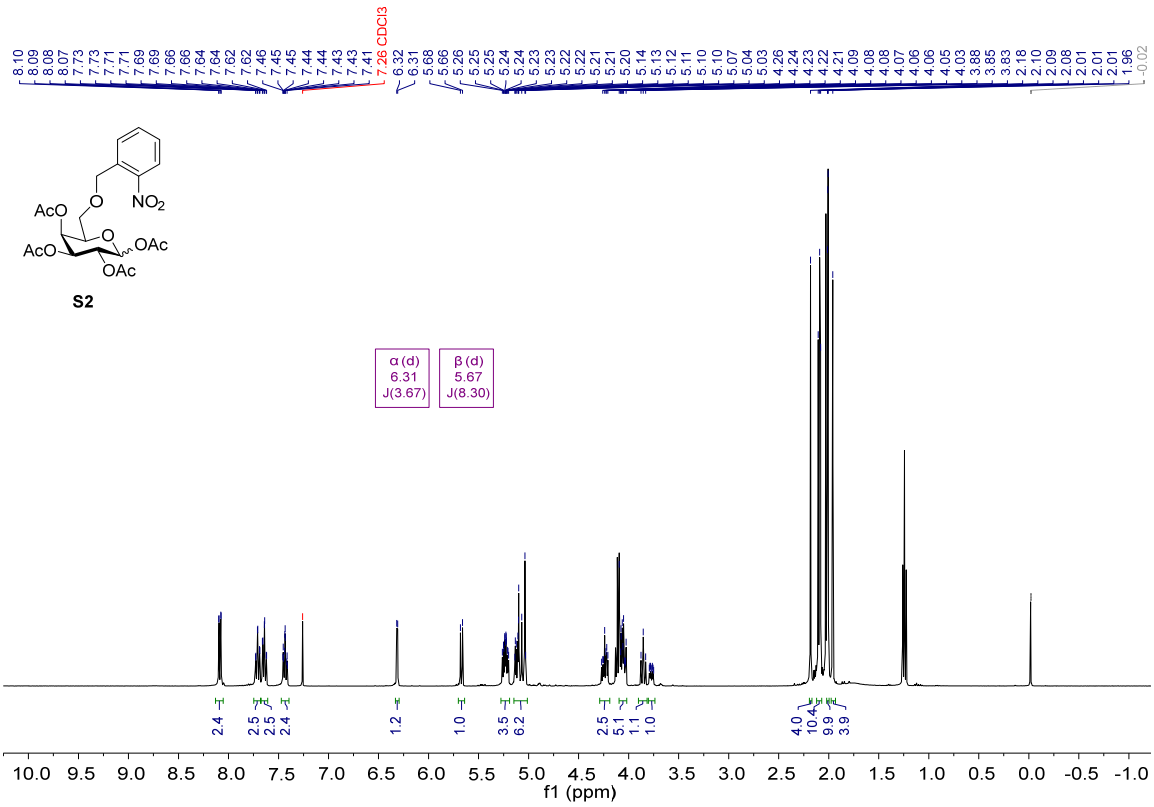
^{1}H NMR ($CDCl_3$, 400 MHz) of compound S1



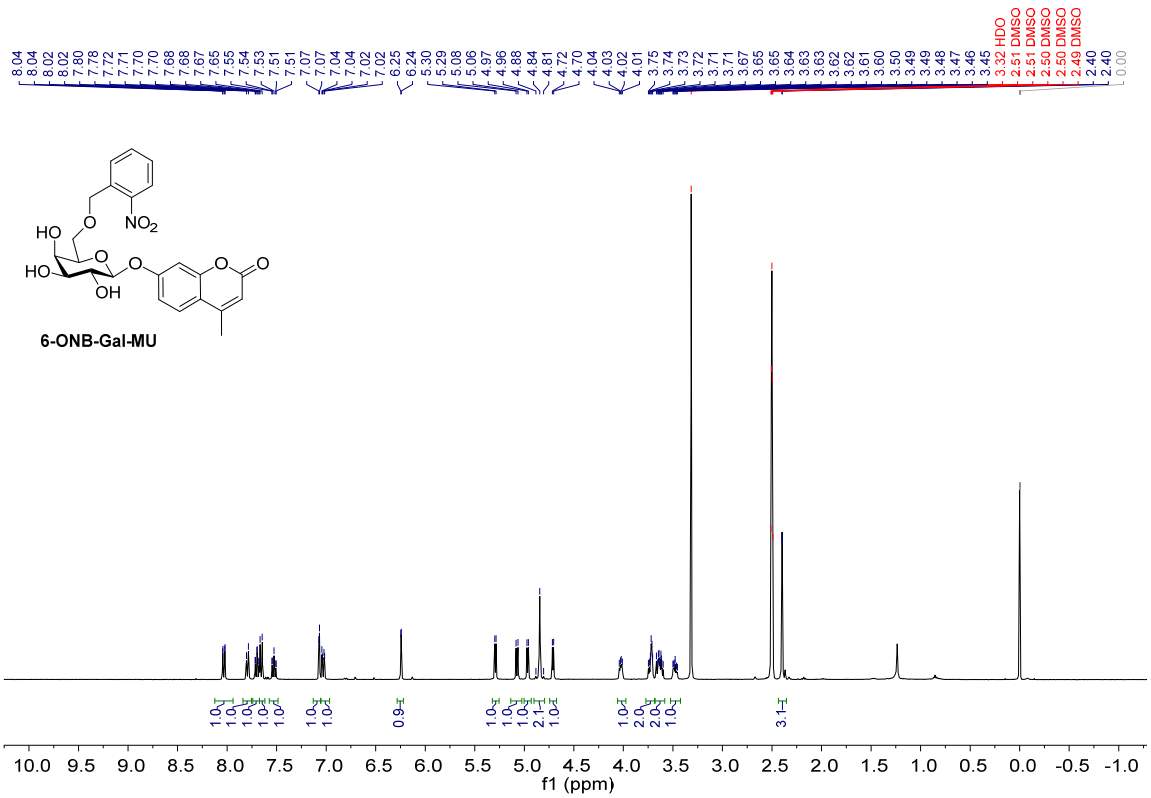
^{13}C NMR ($CDCl_3$, 101 MHz) of compound S1



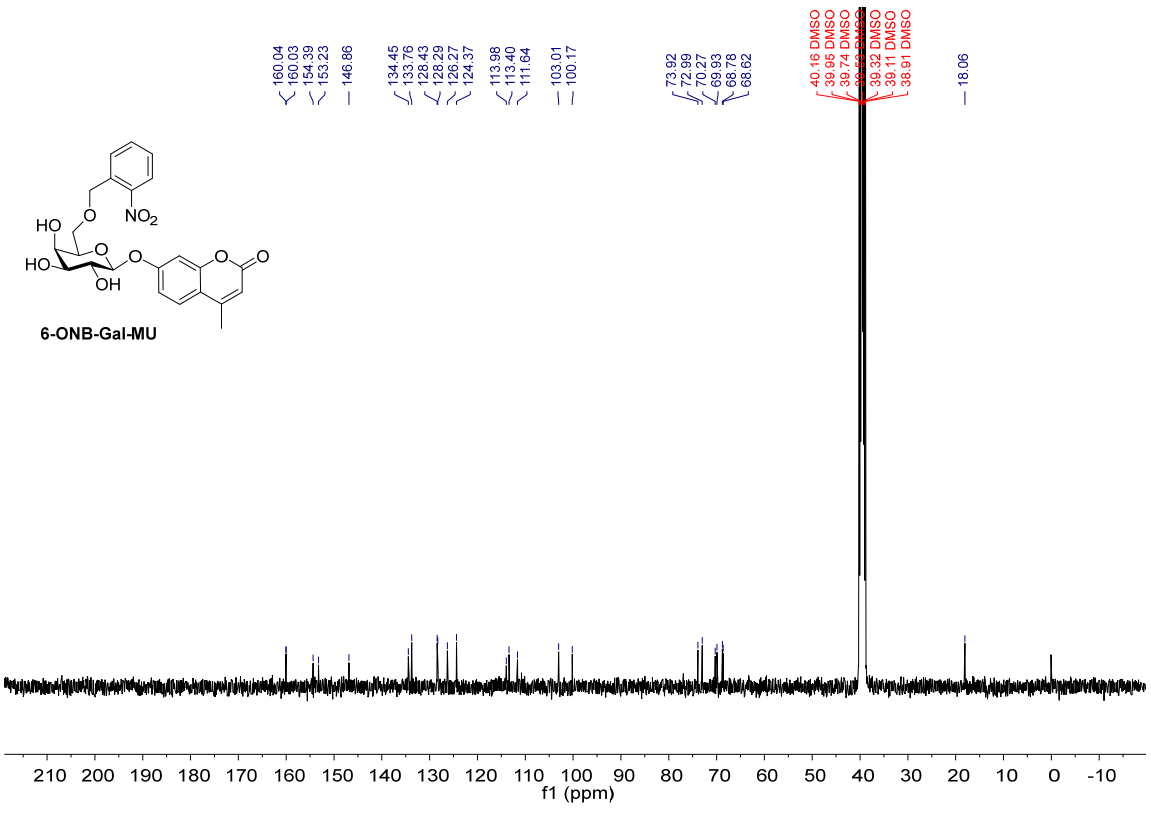
^{1}H NMR ($CDCl_3$, 400 MHz) of compound S2



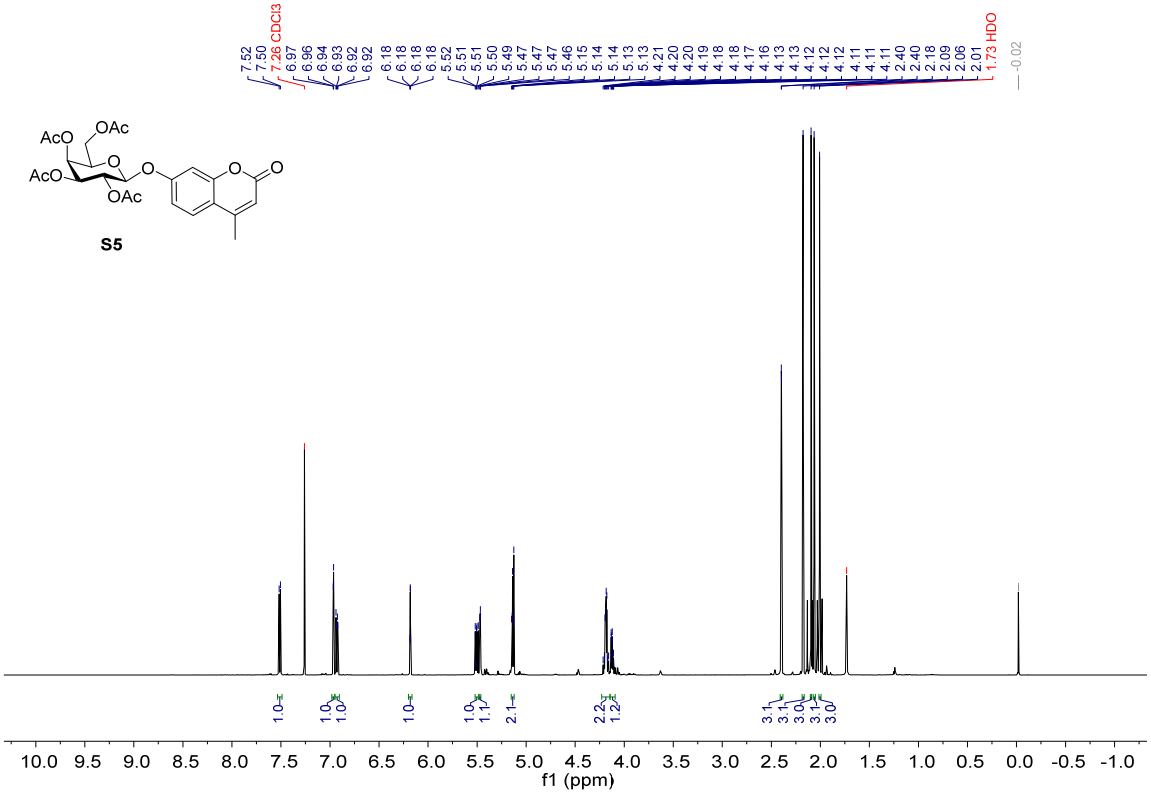
^{1}H NMR ($(CD_3)_2SO$, 400 MHz) of compound 6-ONB-Gal-MU



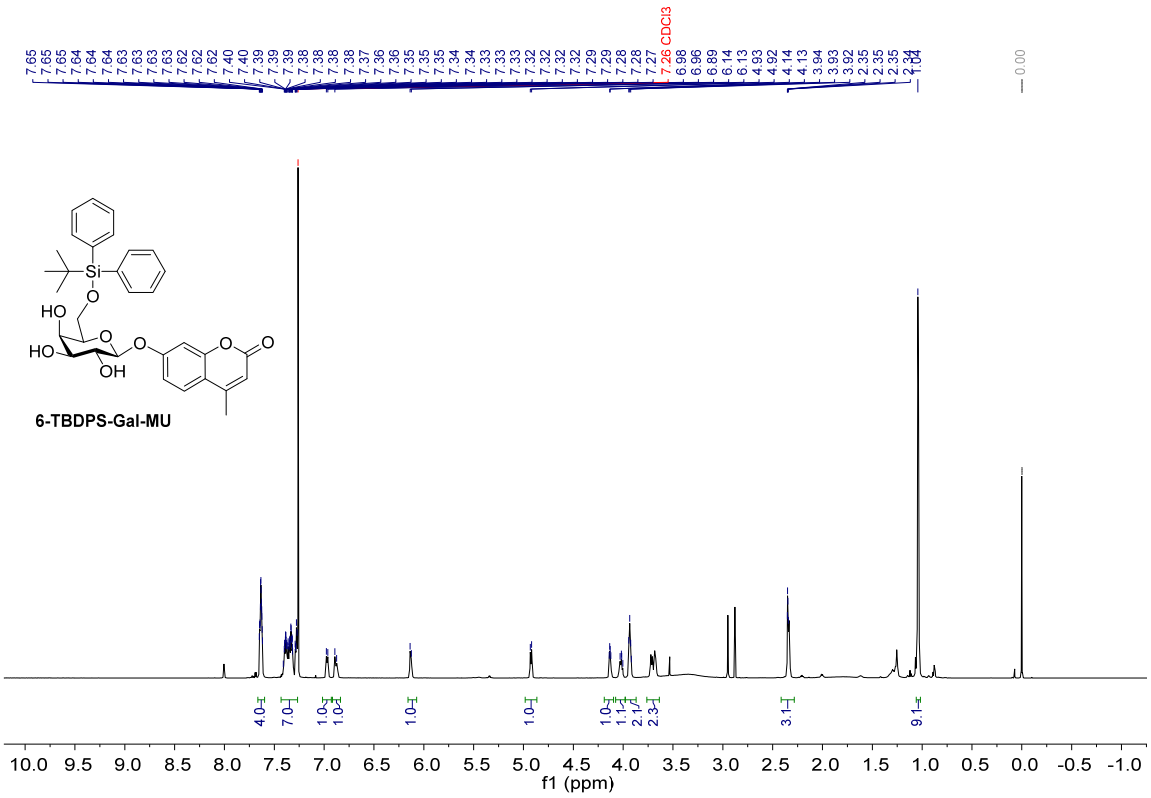
^{13}C NMR ($(CD_3)_2SO$, 101 MHz) of compound 6-ONB-Gal-MU



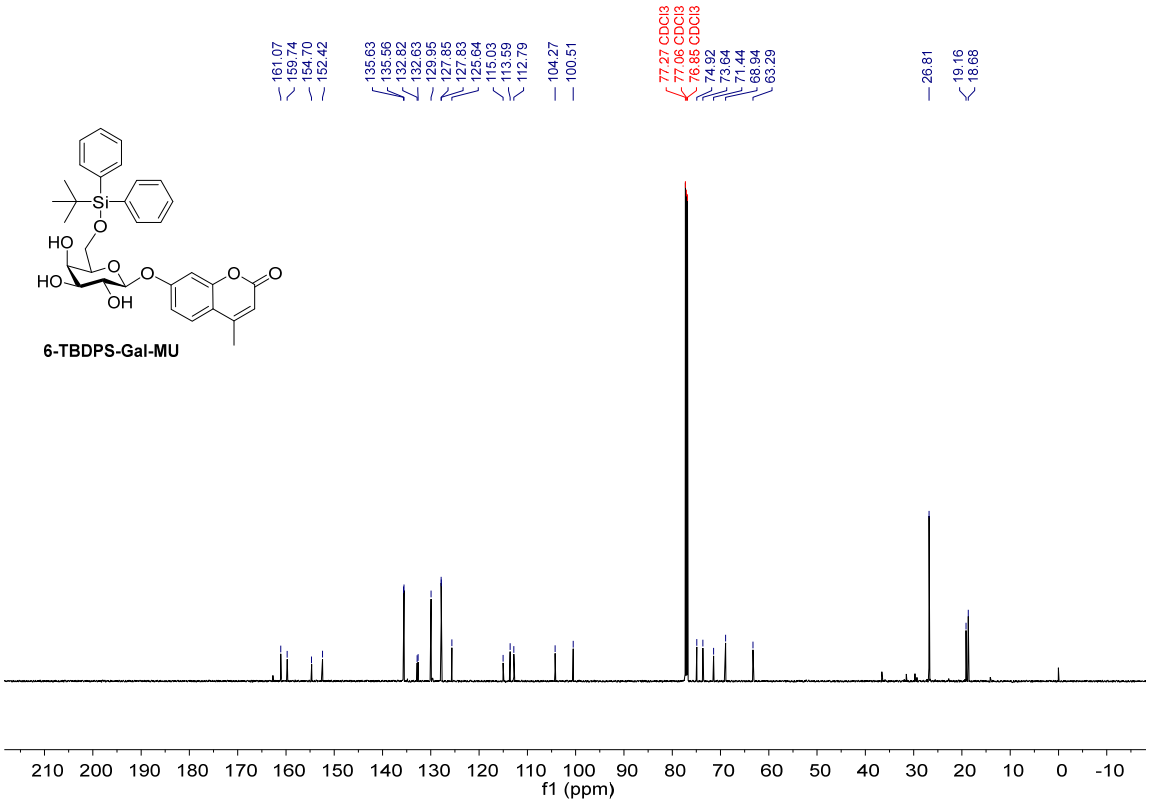
^{1}H NMR ($CDCl_3$, 600 MHz) of compound S5



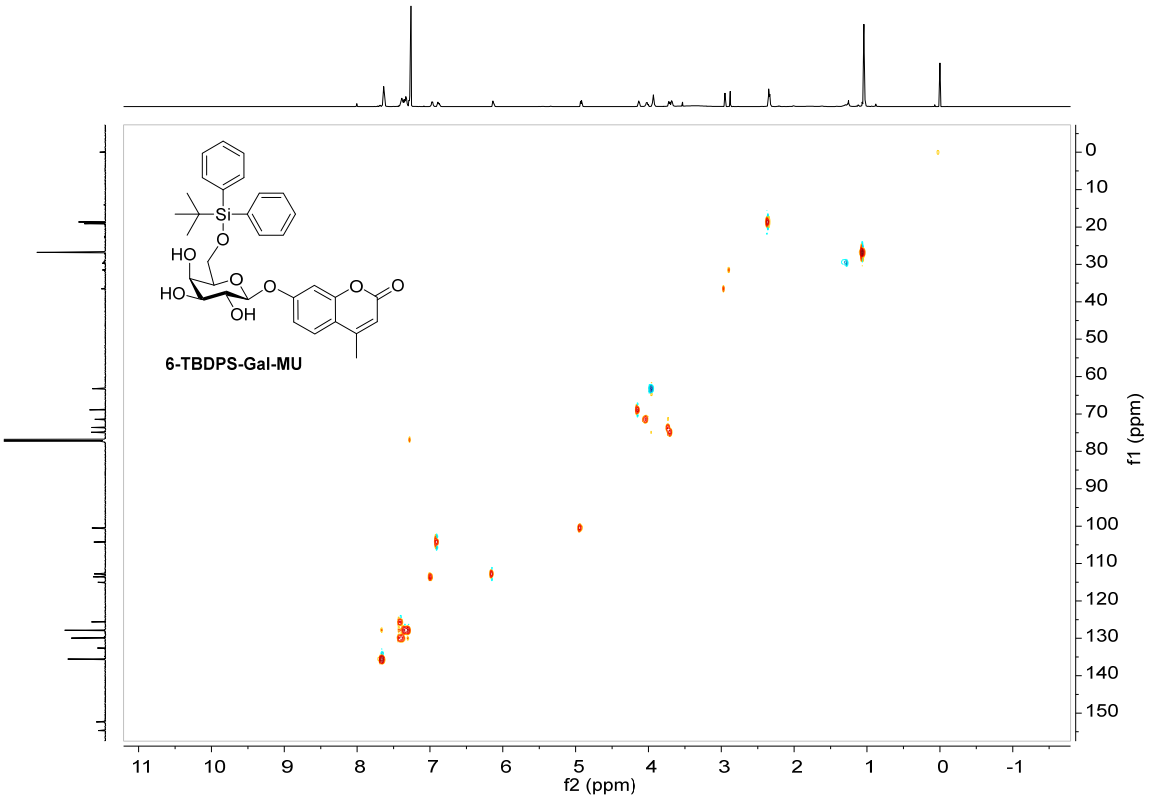
^{1}H NMR ($CDCl_3$, 600 MHz) of compound 6-TBDPS-Gal-MU



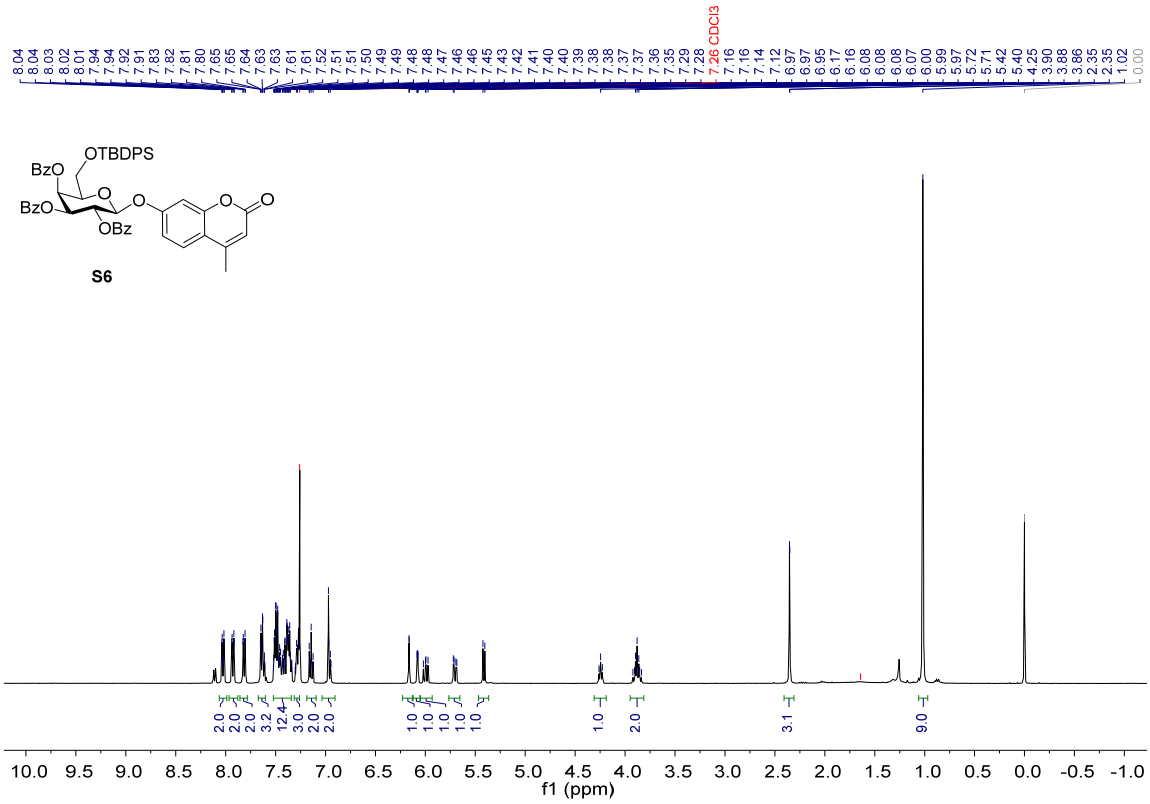
^{13}C NMR ($CDCl_3$, 151 MHz) of compound 6-TBDPS-Gal-MU



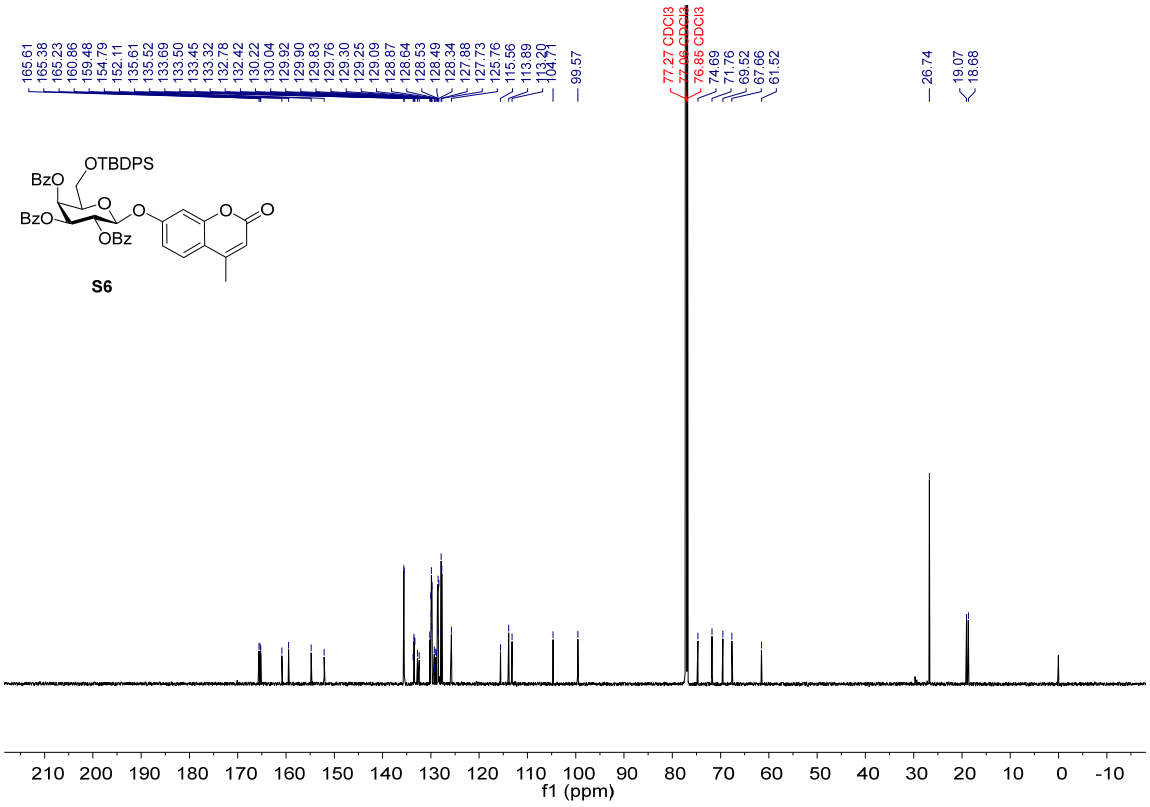
^{1}H-^{13}C HSQC NMR ($CDCl_3$, 600 MHz) of compound 6-TBDPS-Gal-MU



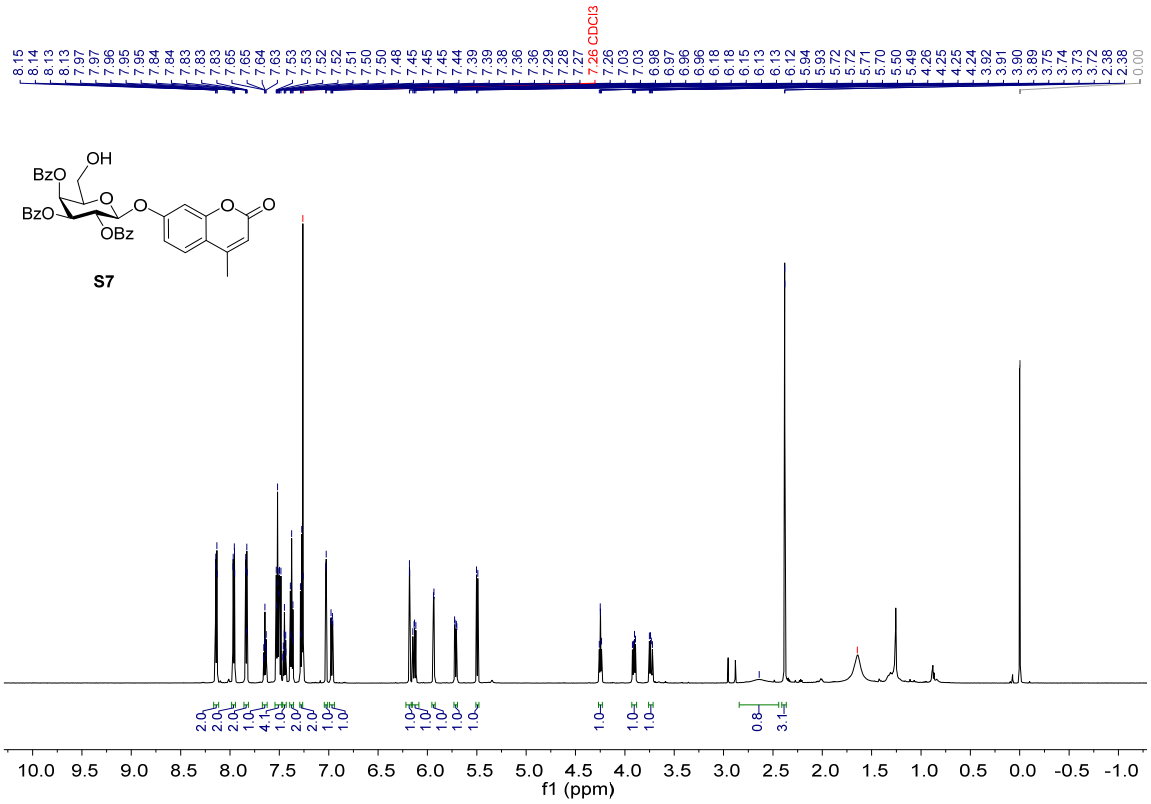
^{1}H NMR ($CDCl_3$, 400 MHz) of compound S6



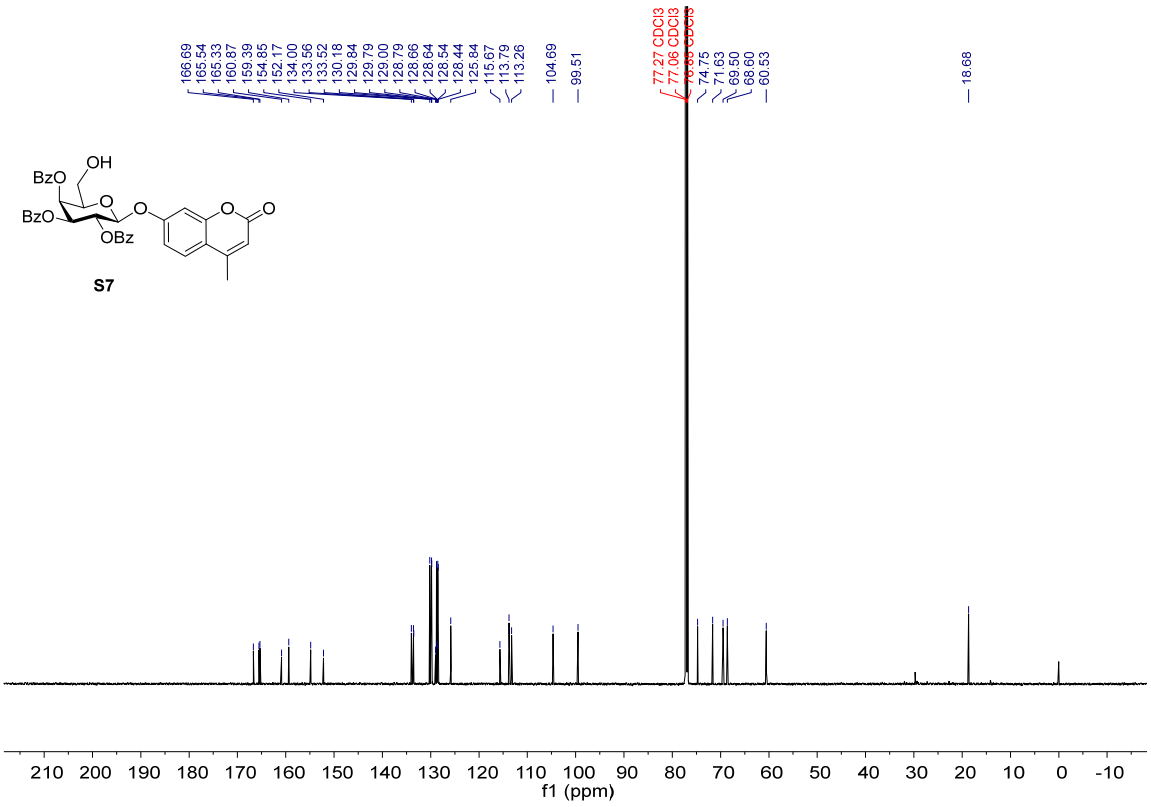
^{13}C NMR ($CDCl_3$, 151 MHz) of compound S6



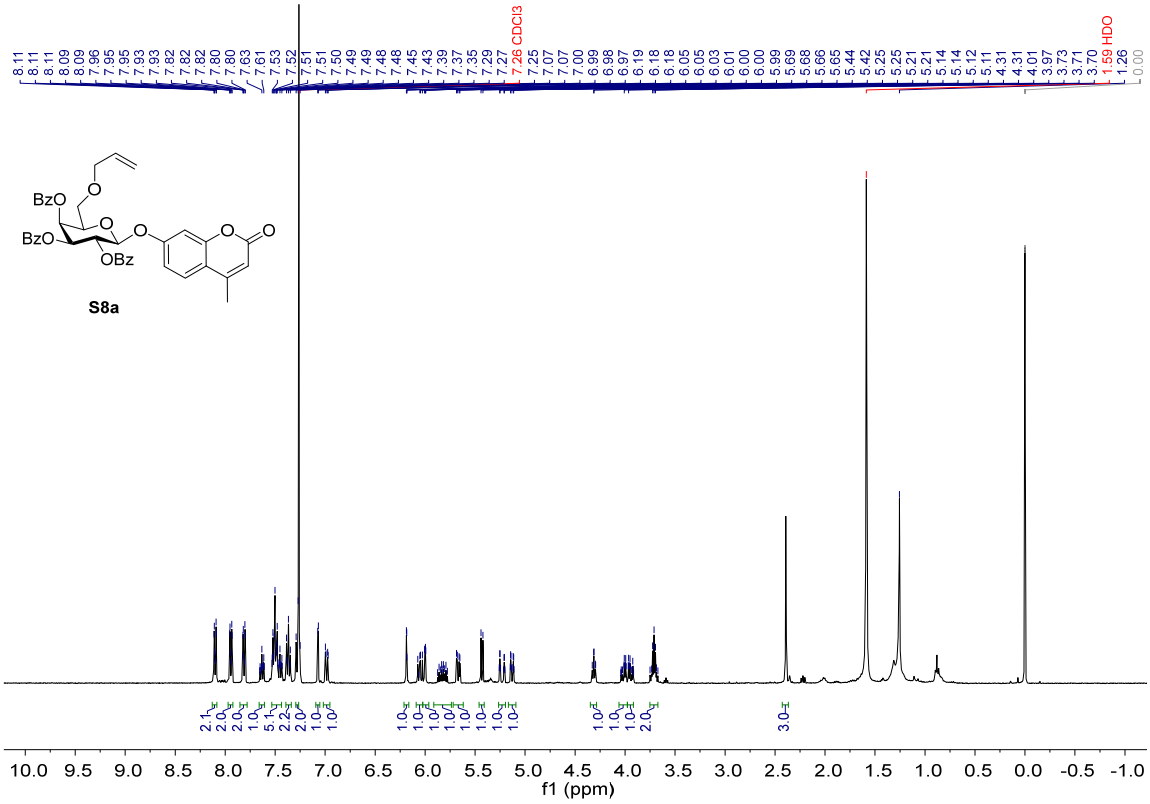
^{1}H NMR ($CDCl_3$, 600 MHz) of compound S7



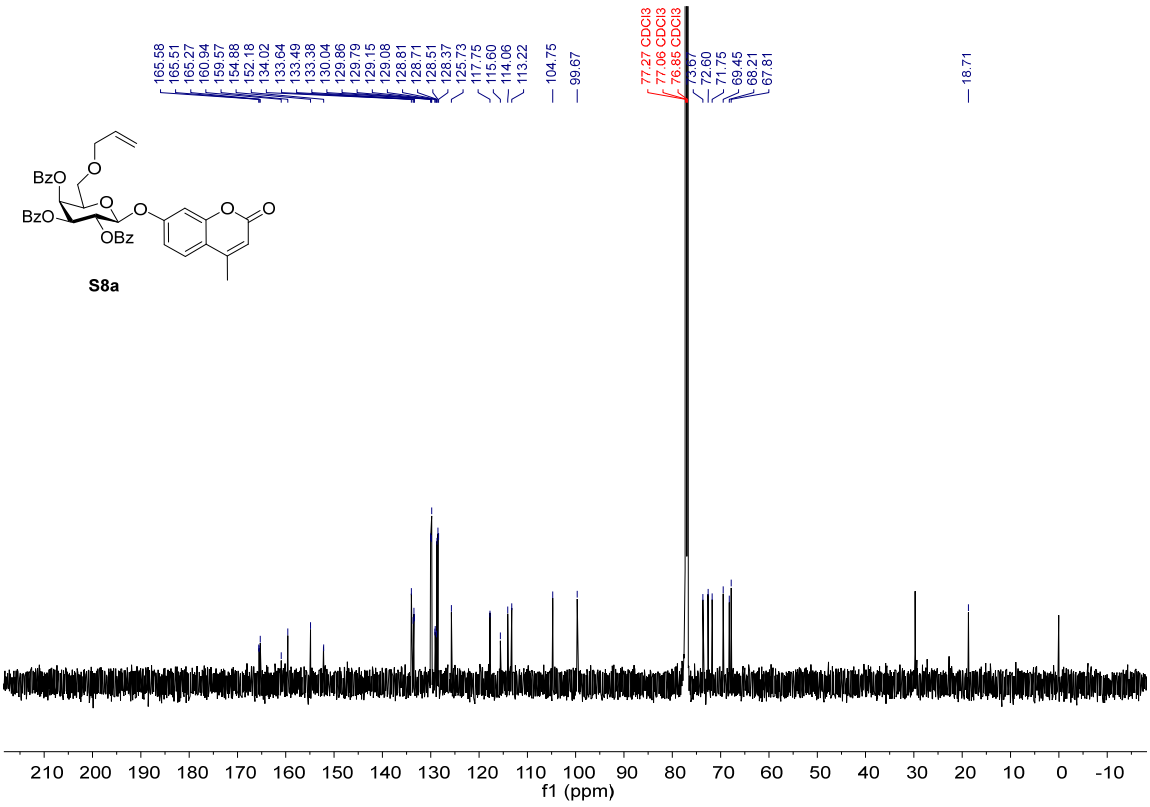
^{13}C NMR ($CDCl_3$, 151 MHz) of compound S7



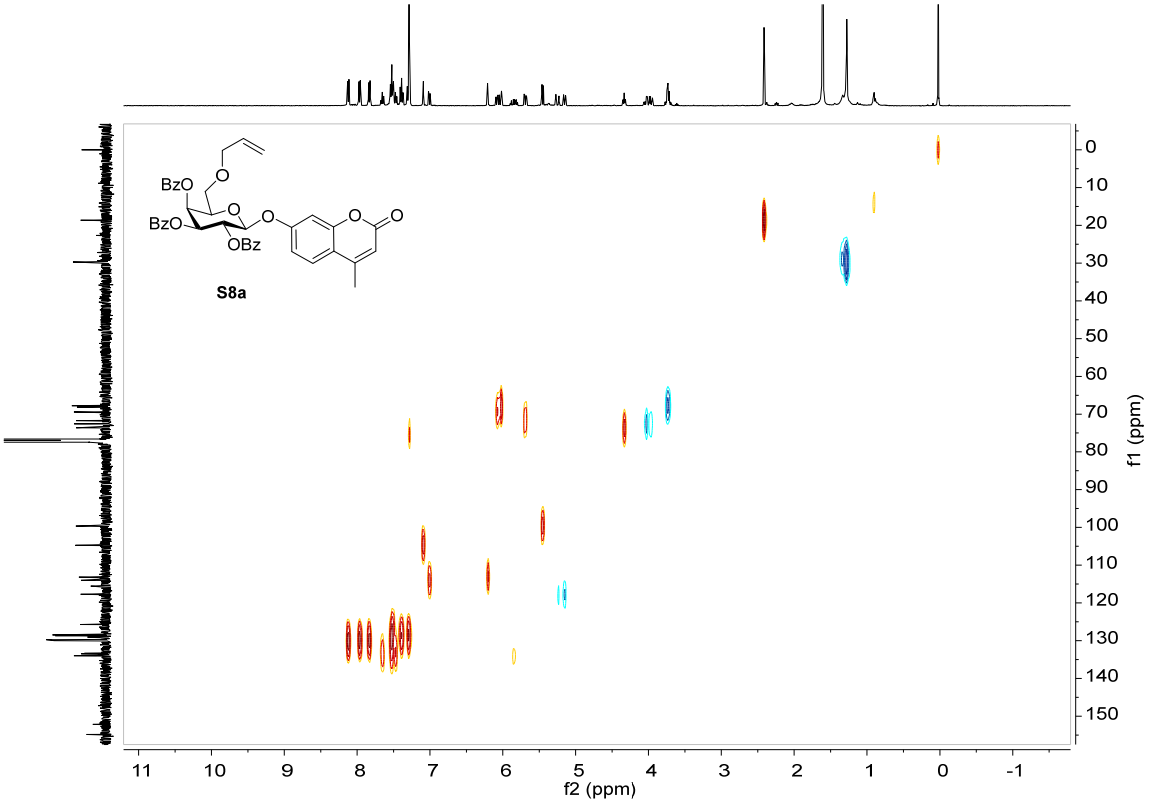
^{1}H NMR ($CDCl_3$, 400 MHz) of compound S8a



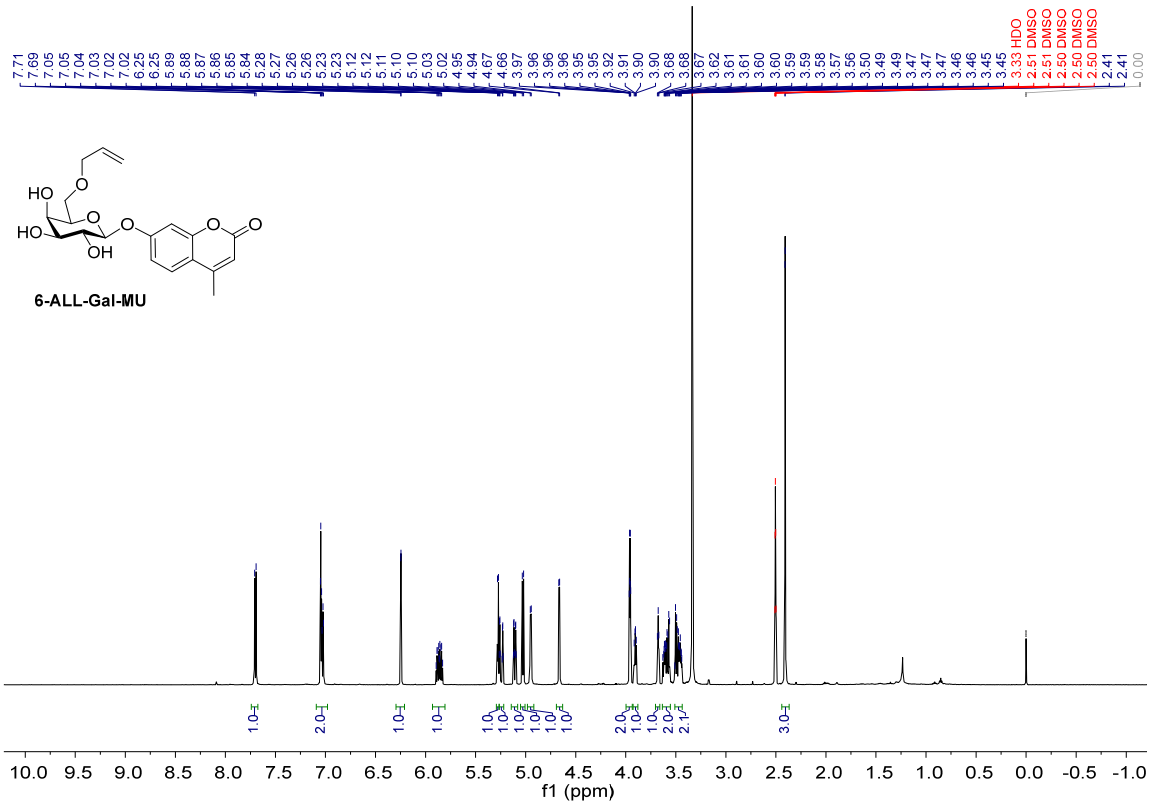
^{13}C NMR ($CDCl_3$, 151 MHz) of compound S8a



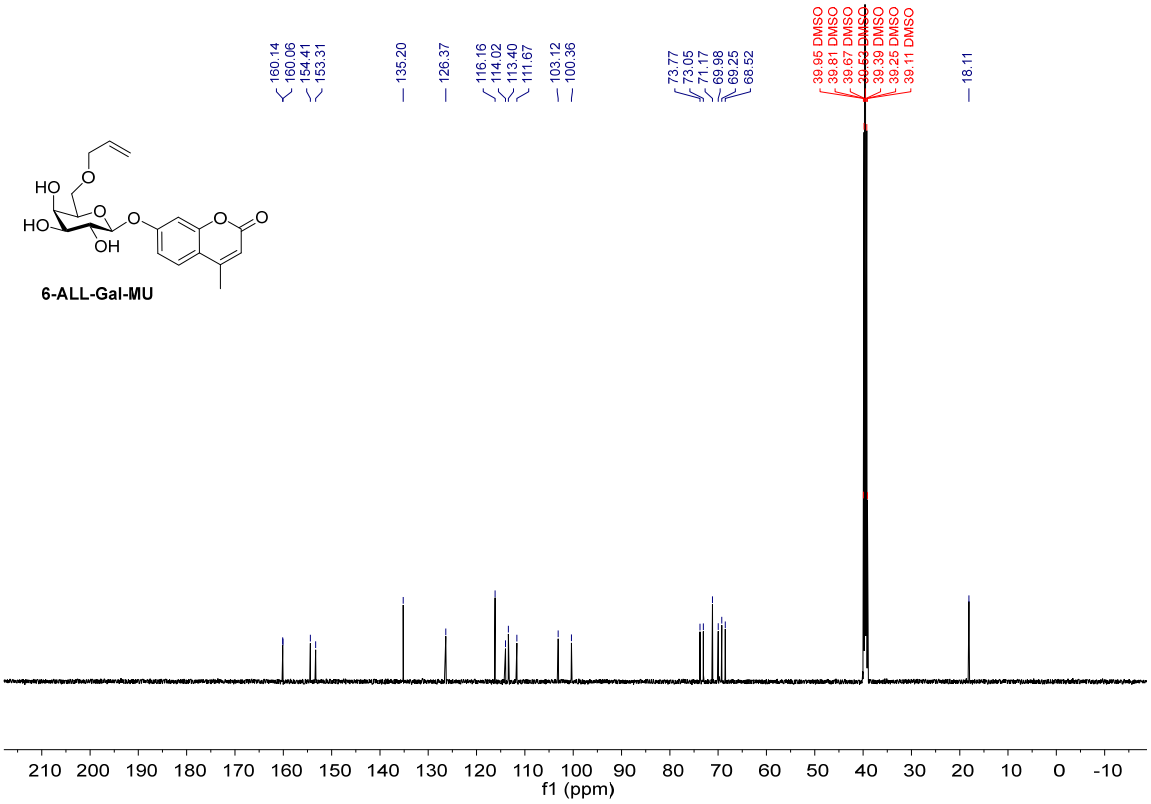
^{1}H-^{13}C HSQC NMR ($CDCl_3$, 600 MHz) of compound S8a



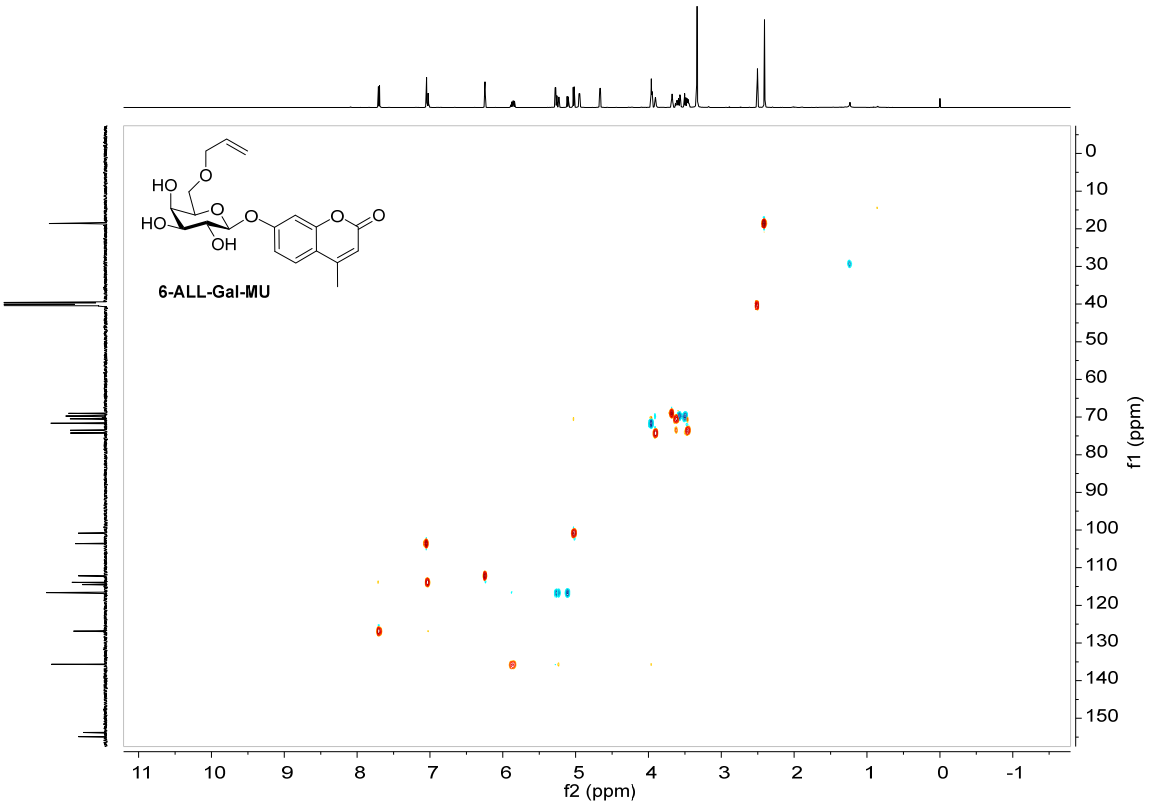
^{1}H NMR ($(CD_3)_2SO$, 600 MHz) of compound 6-ALL-Gal-MU



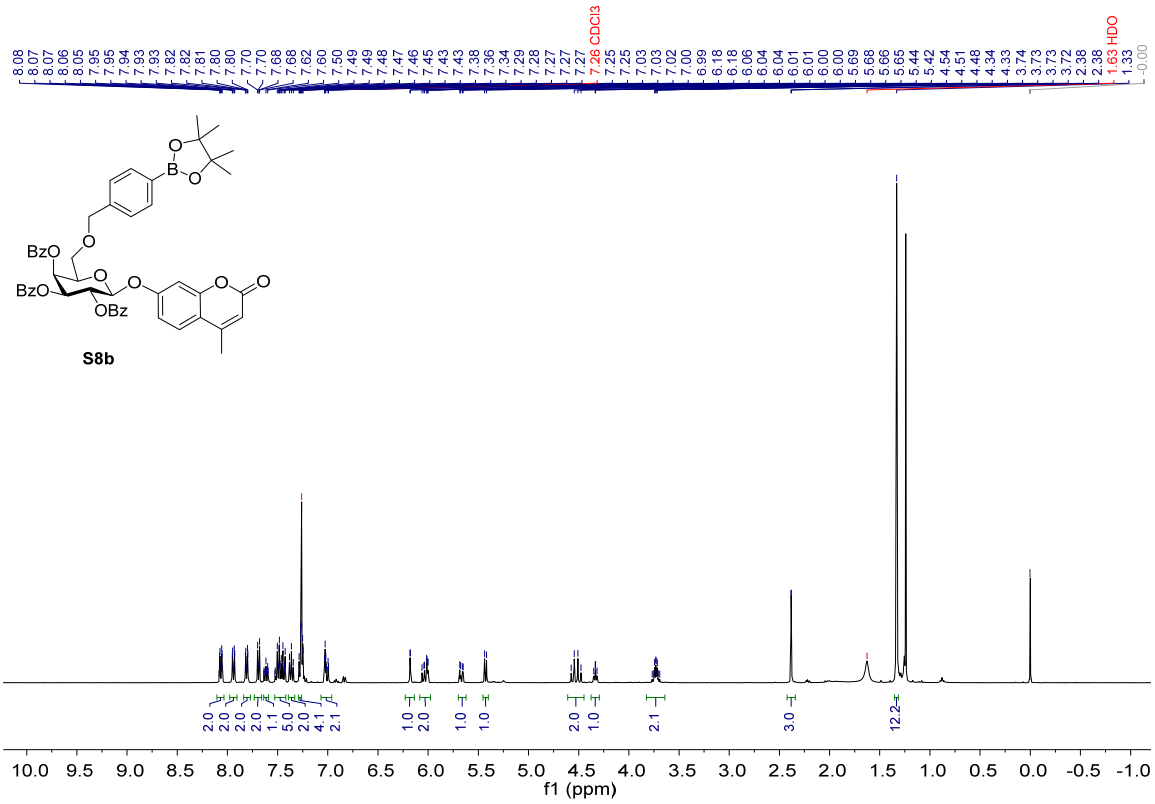
^{13}C NMR ((CD$_3$)$_2$SO, 151 MHz) of compound 6-ALL-Gal-MU



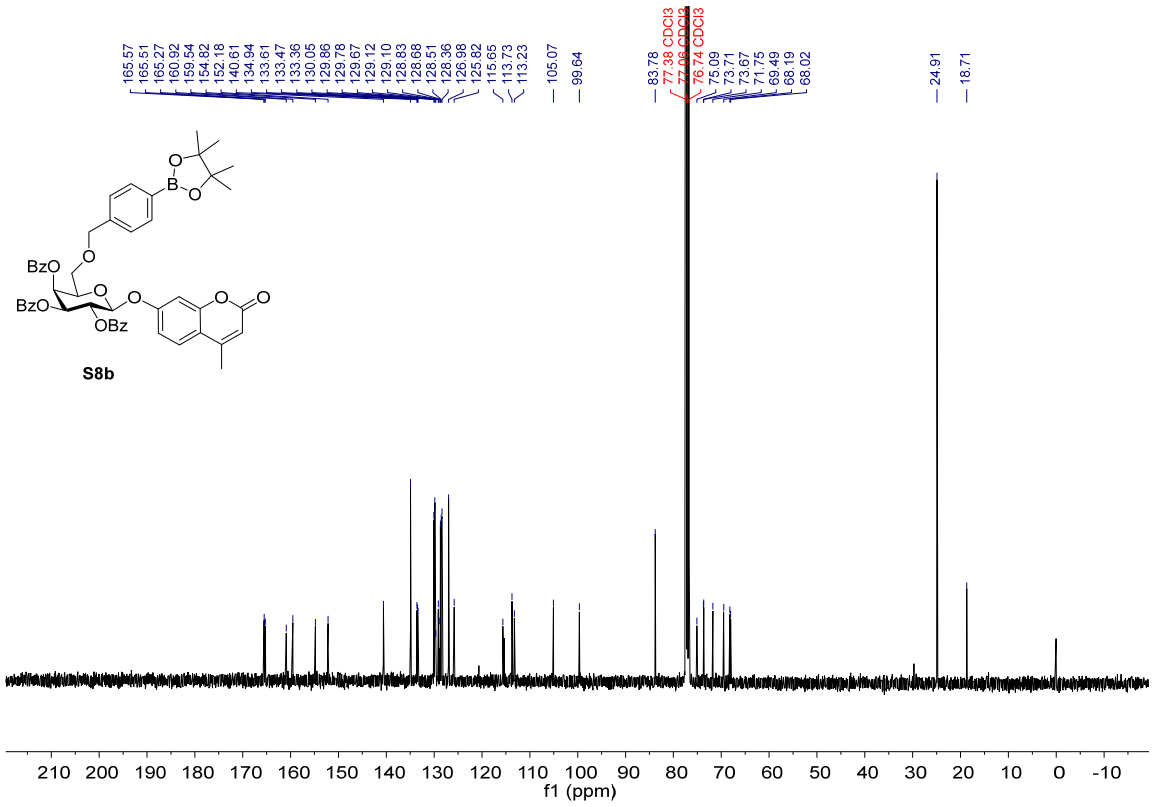
^{1}H-^{13}C HSQC NMR ((CD$_3$)$_2$SO, 600 MHz) of compound 6-ALL-Gal-MU



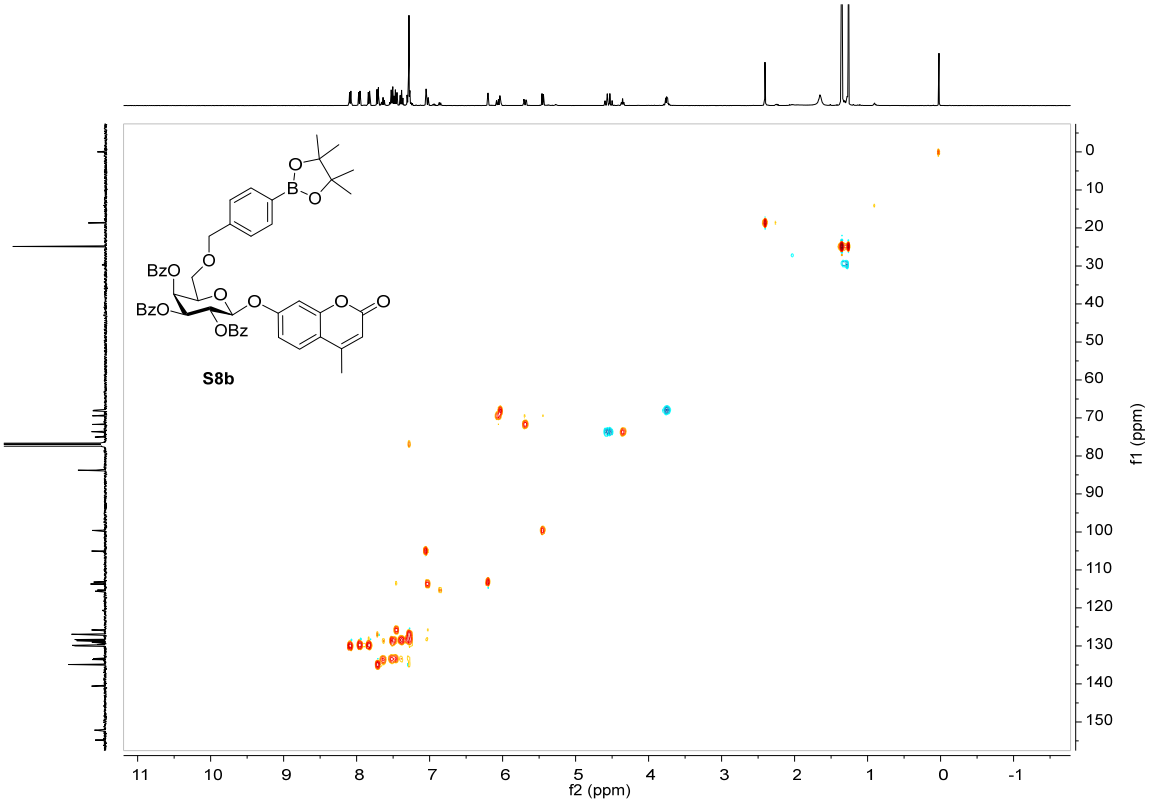
^{1}H NMR ($CDCl_3$, 400 MHz) of compound S8b



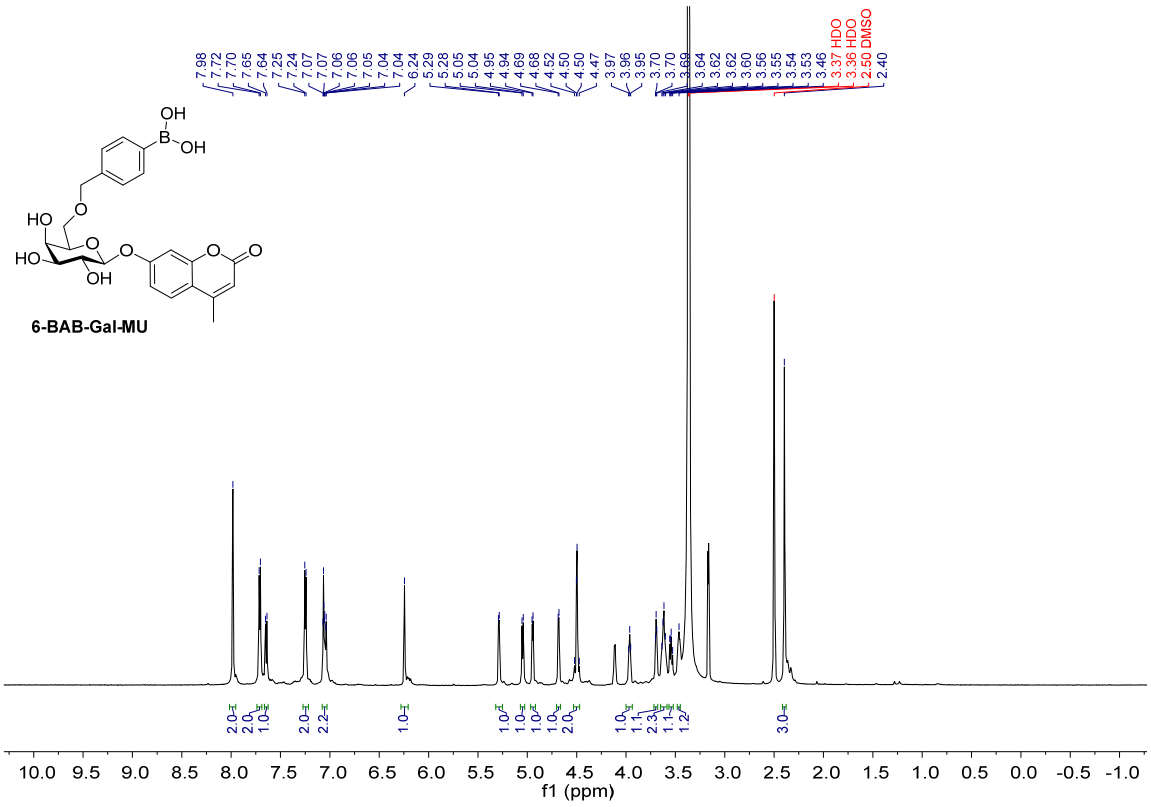
^{13}C NMR ($CDCl_3$, 101 MHz) of compound S8b



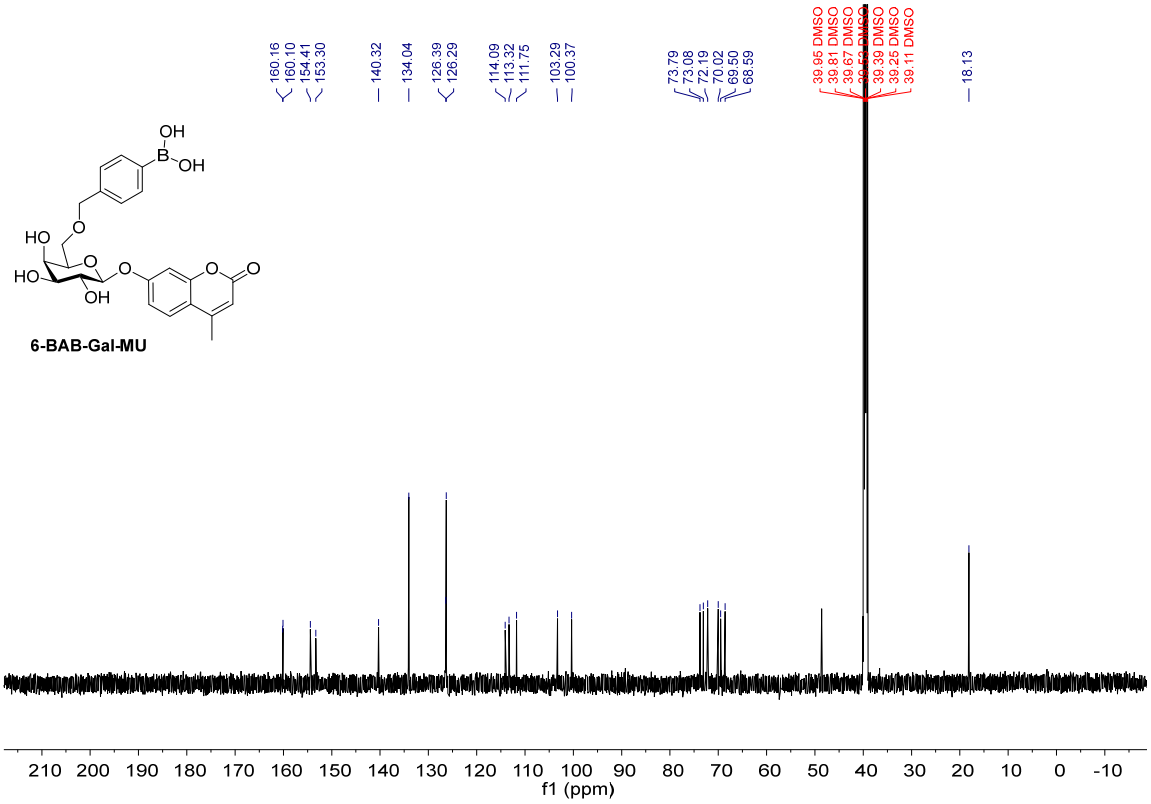
^{1}H-^{13}C HSQC NMR ($CDCl_3$, 400 MHz) of compound S8b



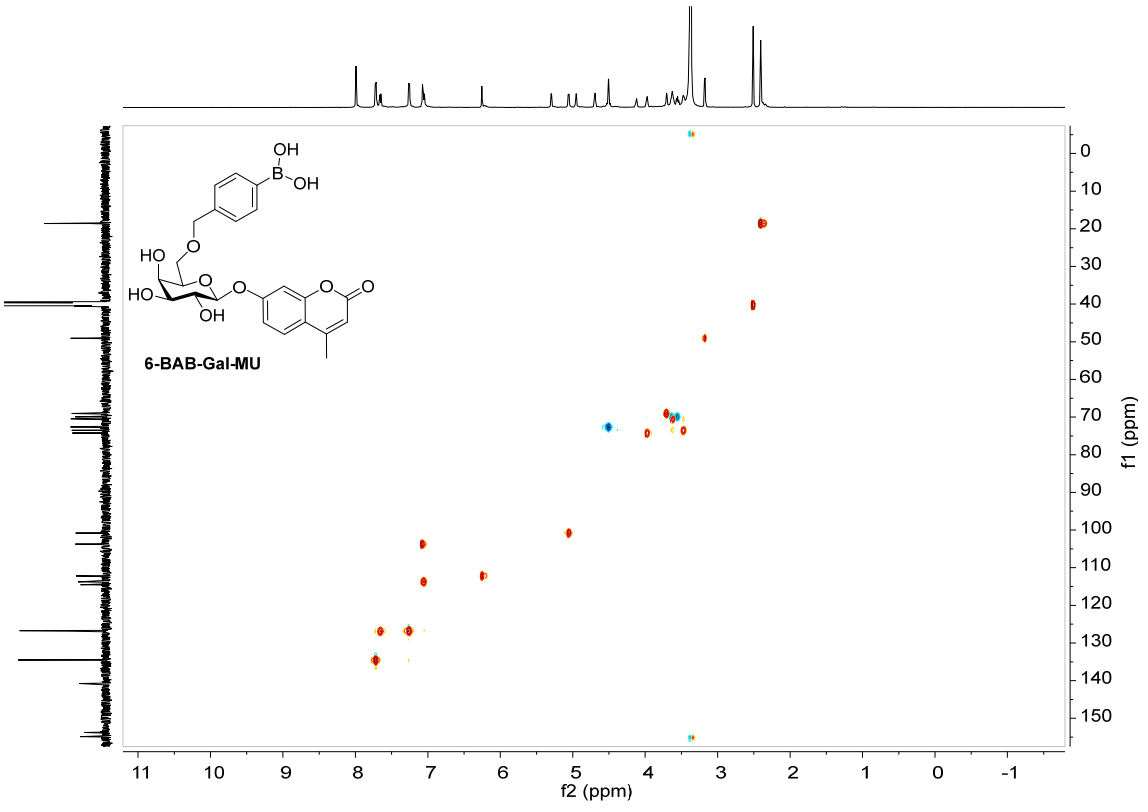
^{1}H NMR ($(CD_3)_2SO$, 600 MHz) of compound 6-BAB-Gal-MU



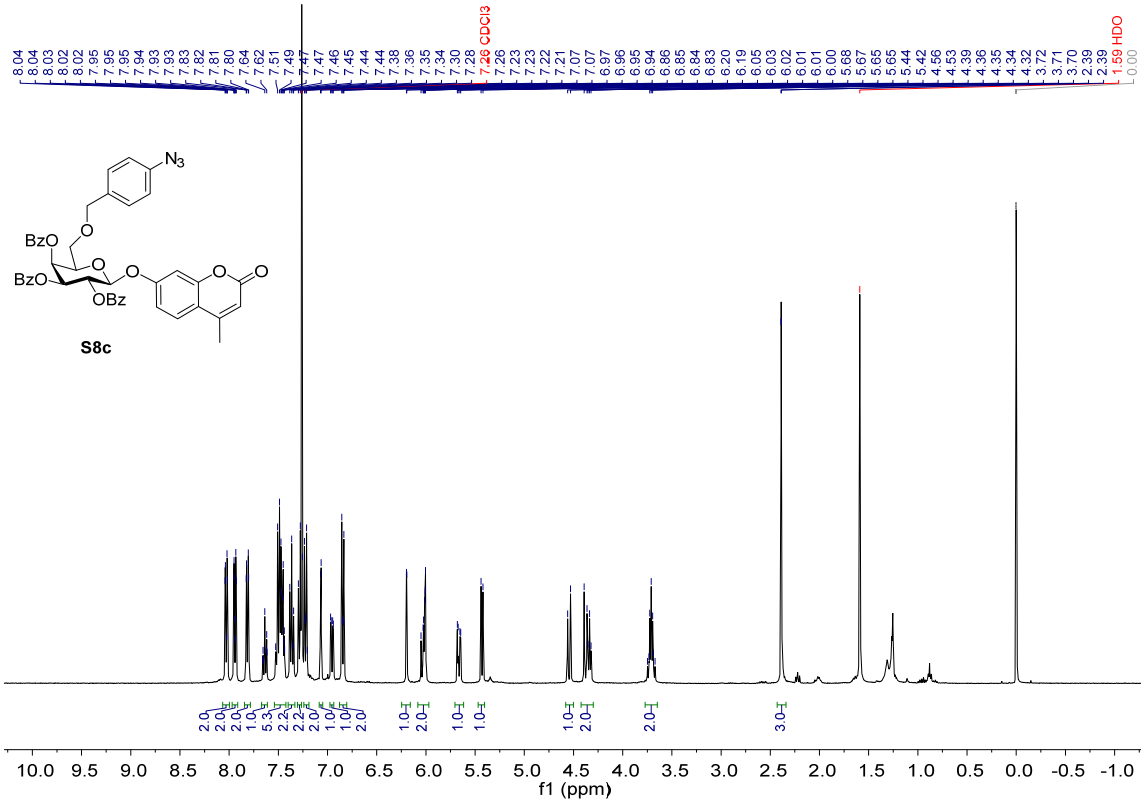
^{13}C NMR ((CD$_3$)$_2$SO, 151 MHz) of compound 6-BAB-Gal-MU



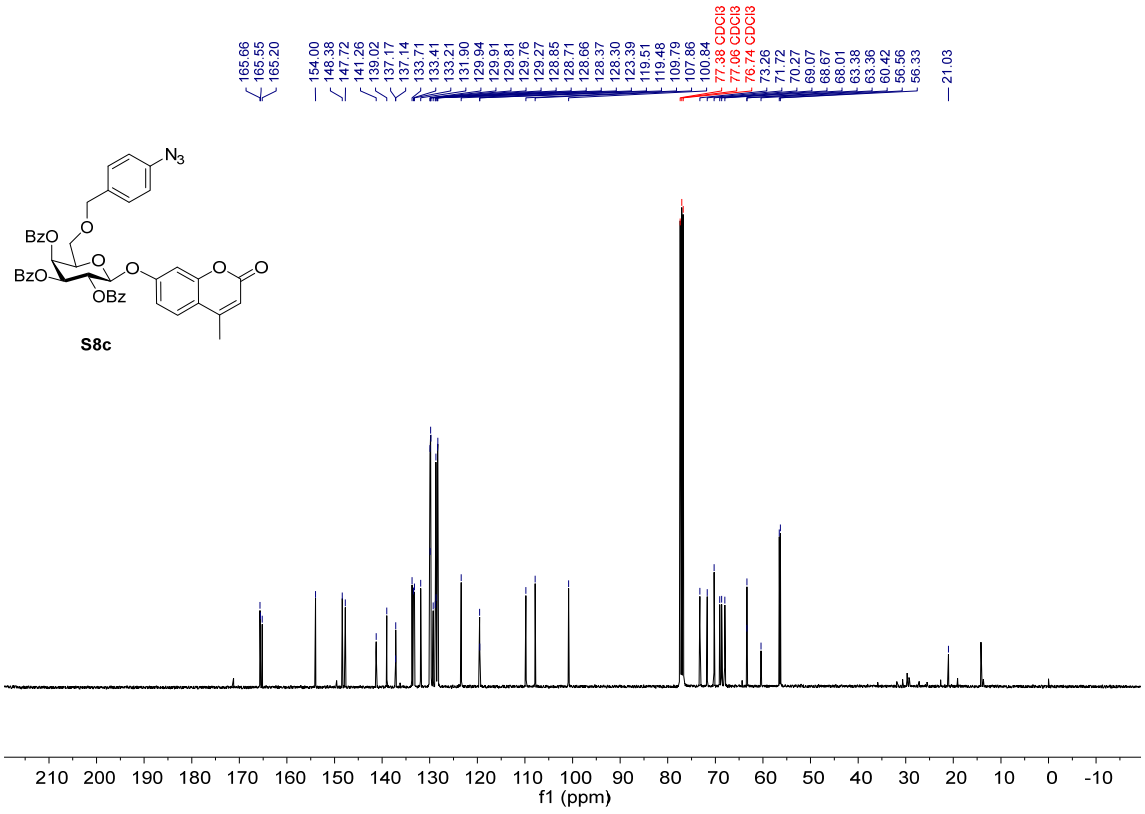
^{1}H-^{13}C HSQC NMR ((CD$_3$)$_2$SO, 600 MHz) of compound 6-BAB-Gal-MU



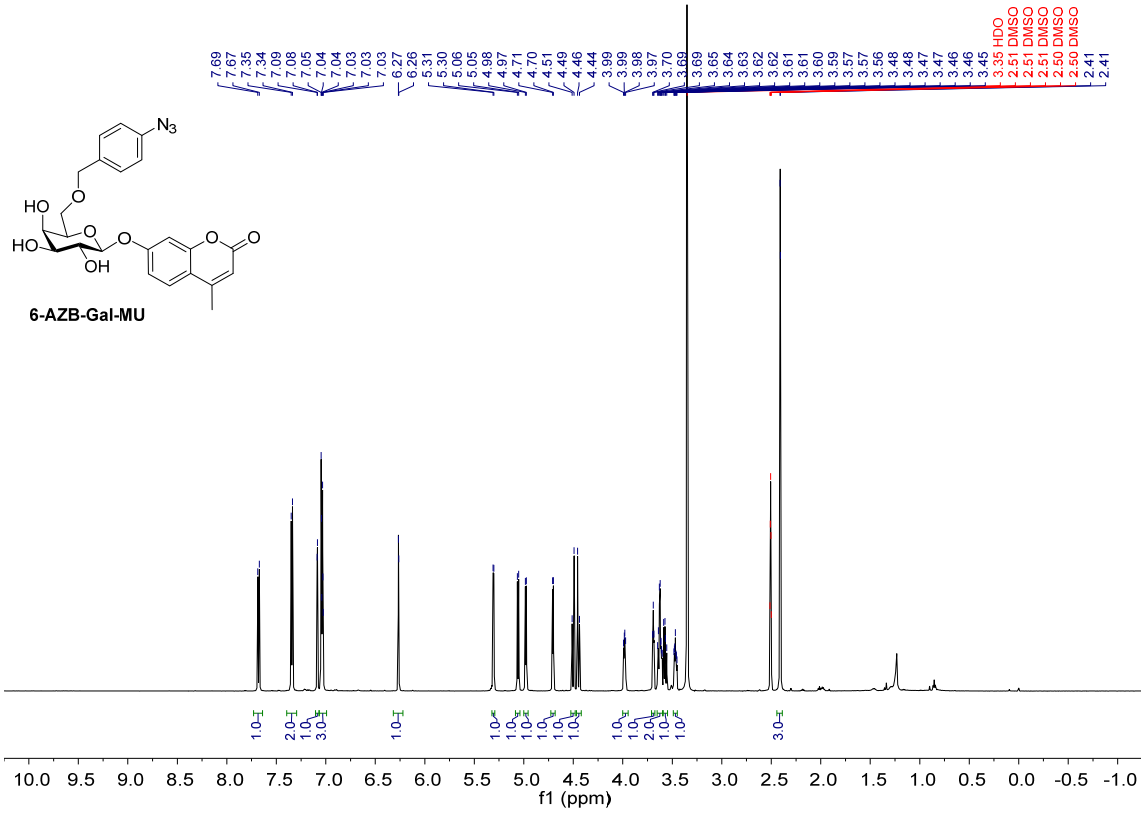
^{1}H NMR ($CDCl_3$, 400 MHz) of compound S8c



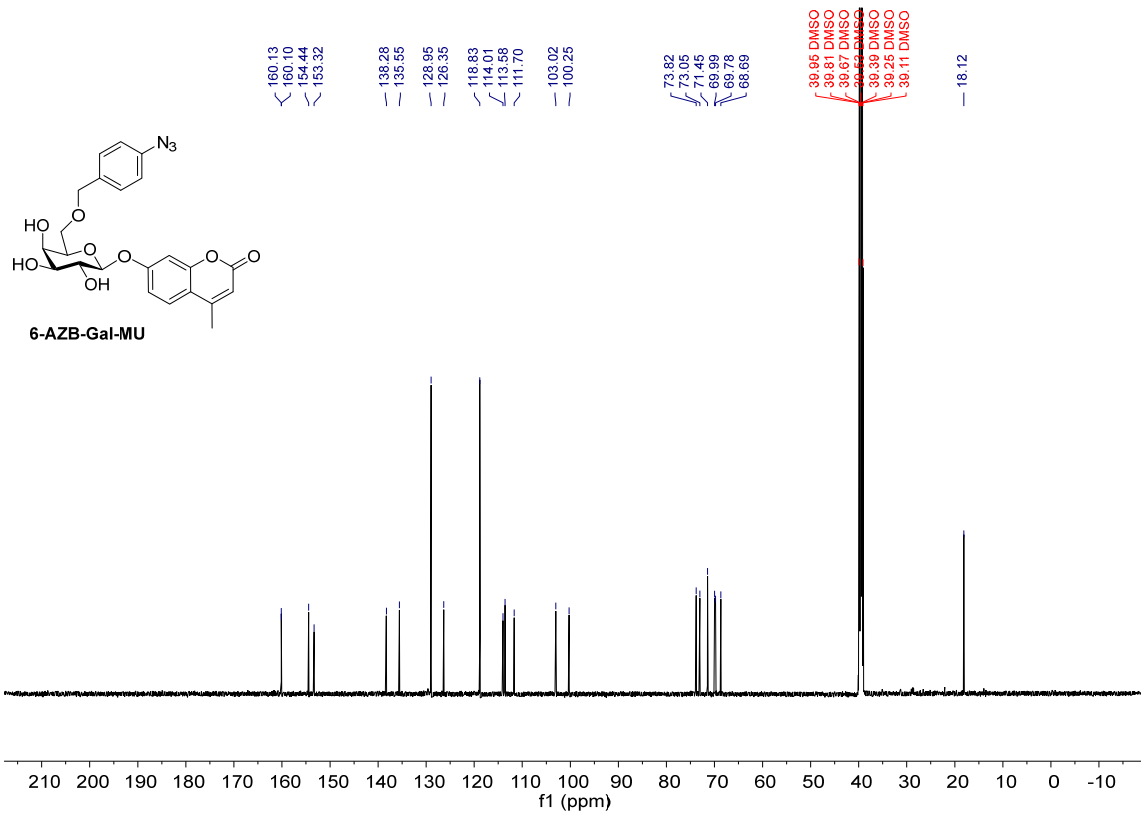
^{13}C NMR ($CDCl_3$, 101 MHz) of compound S8c



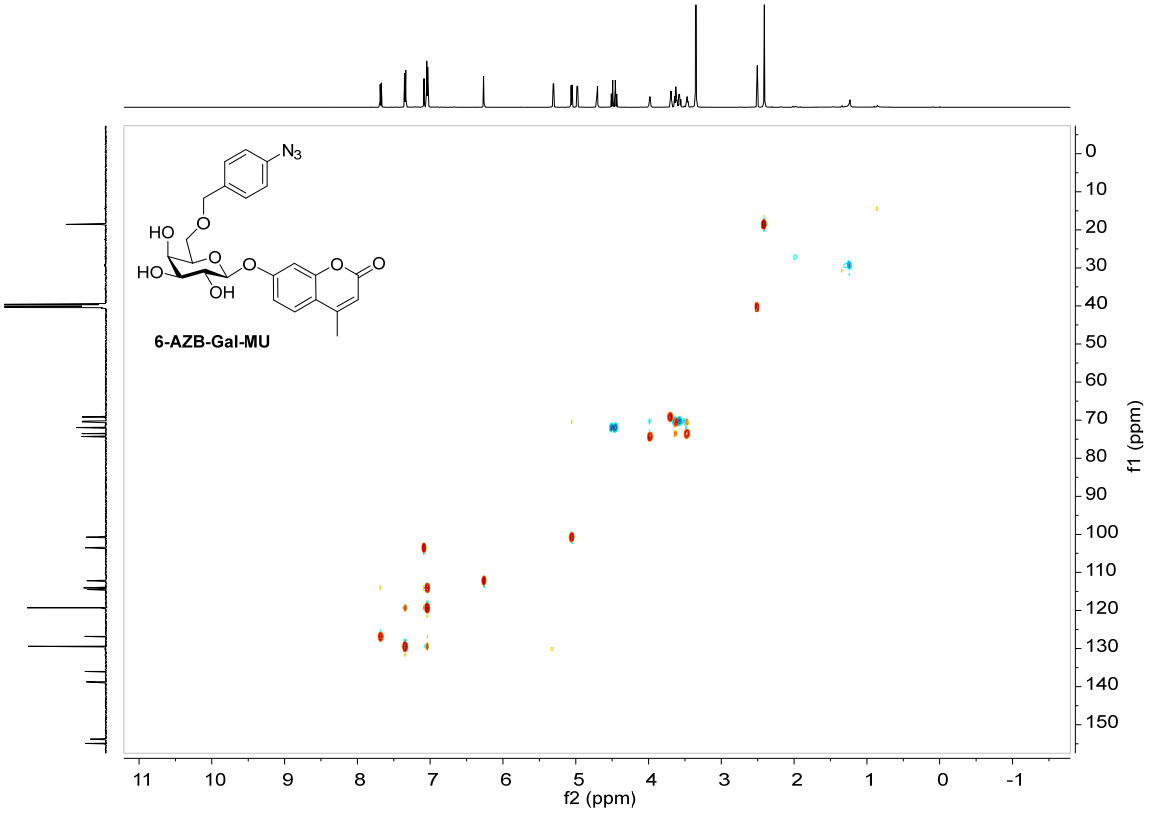
^{1}H NMR ($(CD_3)_2SO$, 600 MHz) of compound 6-AZB-Gal-MU



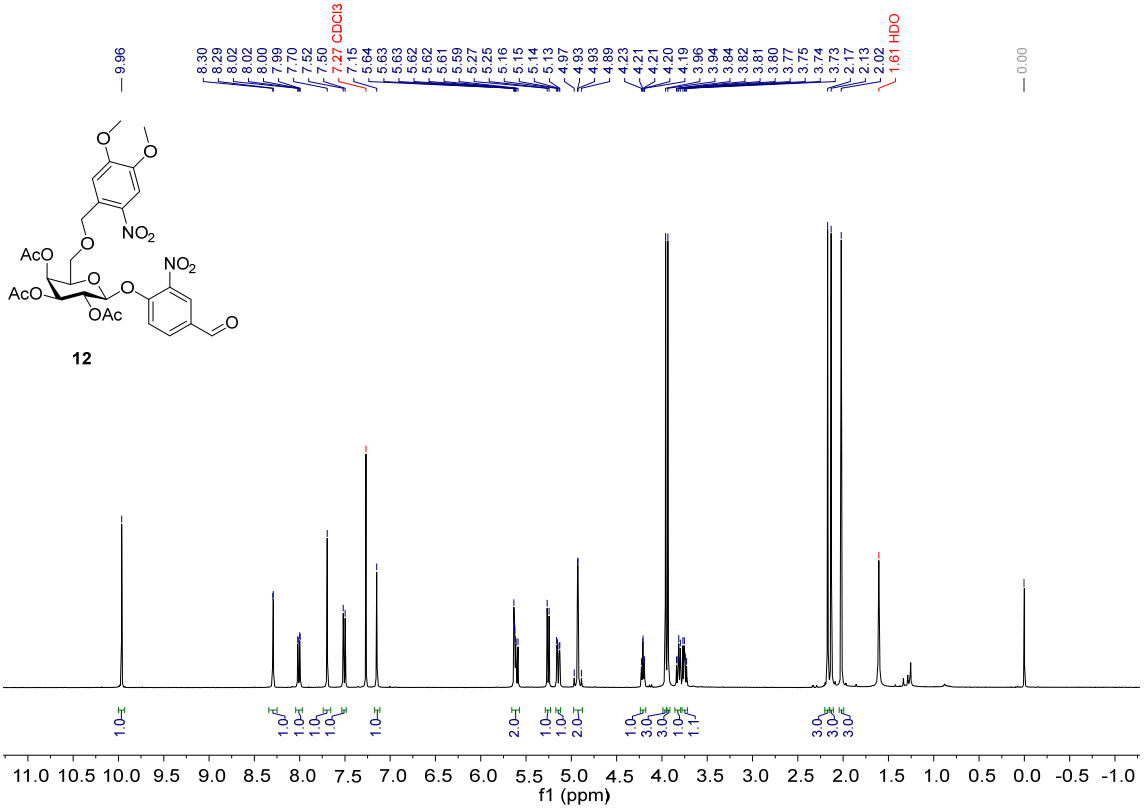
^{13}C NMR ($(CD_3)_2SO$, 151 MHz) of compound 6-AZB-Gal-MU



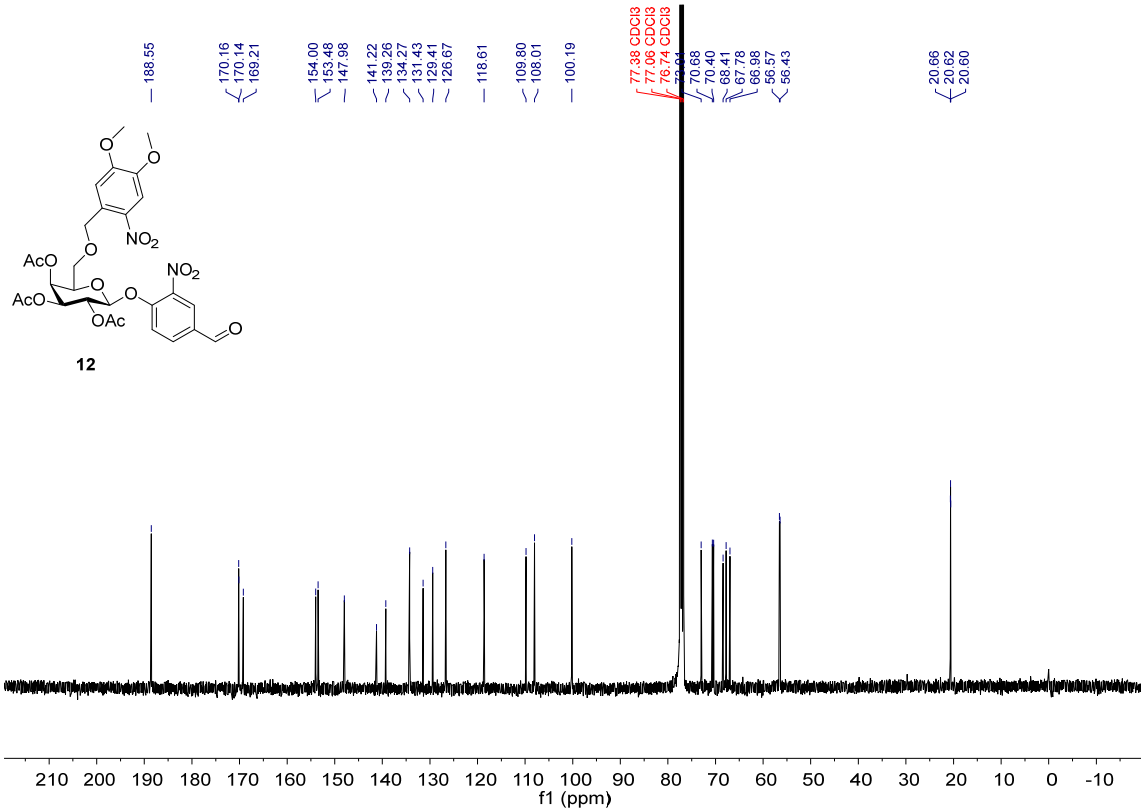
^{1}H-^{13}C HSQC NMR ($(CD_3)_2SO$, 600 MHz) of compound 6-AZB-Gal-MU



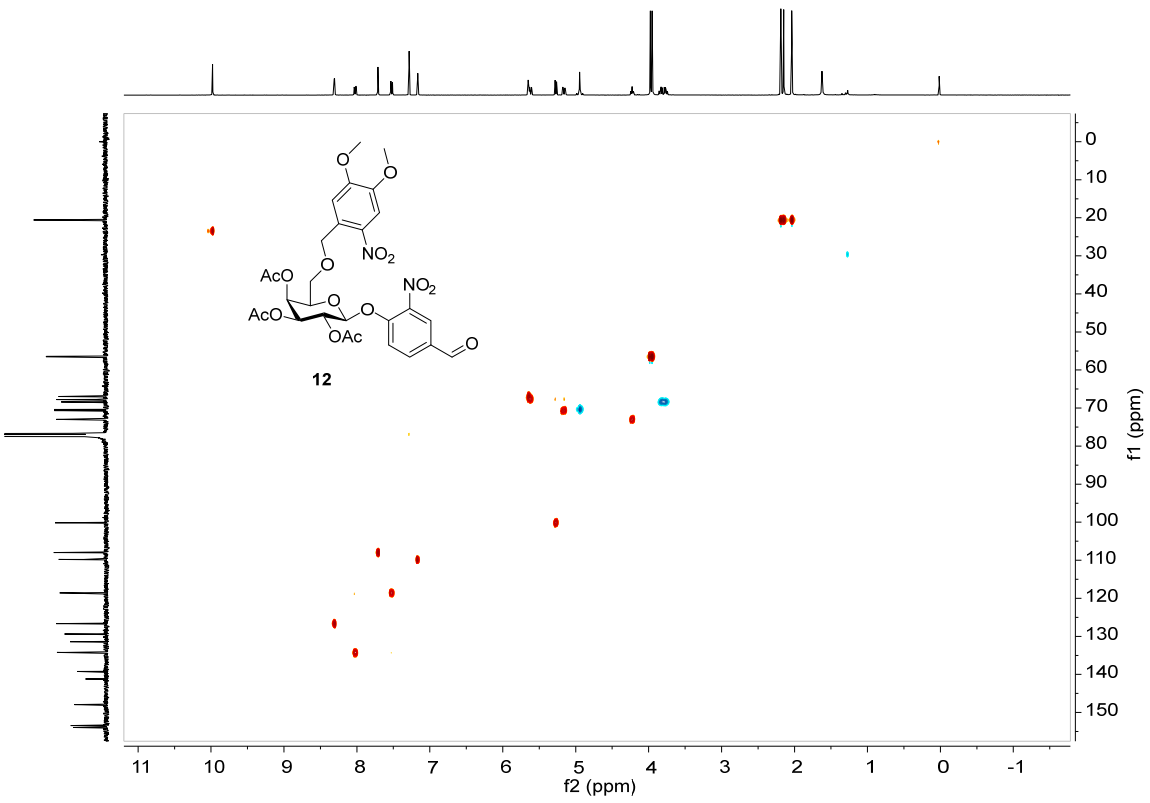
^{1}H NMR ($CDCl_3$, 400 MHz) of compound 12



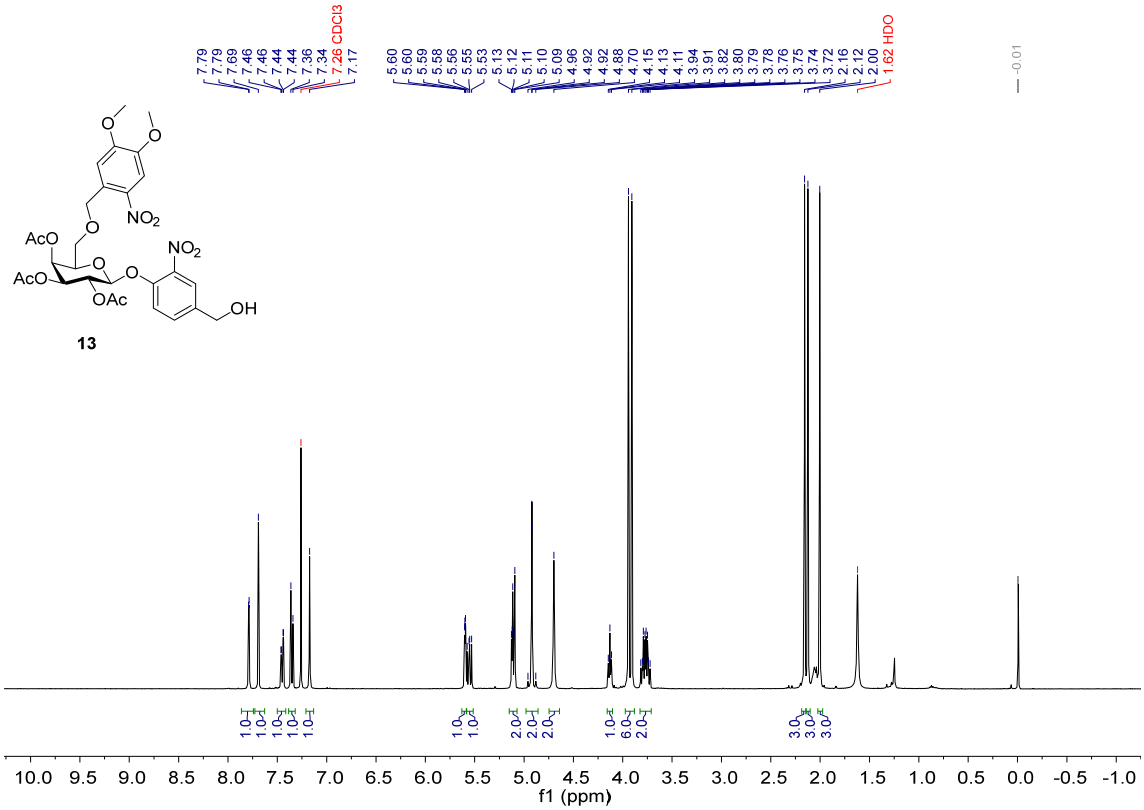
^{13}C NMR ($CDCl_3$, 101 MHz) of compound 12



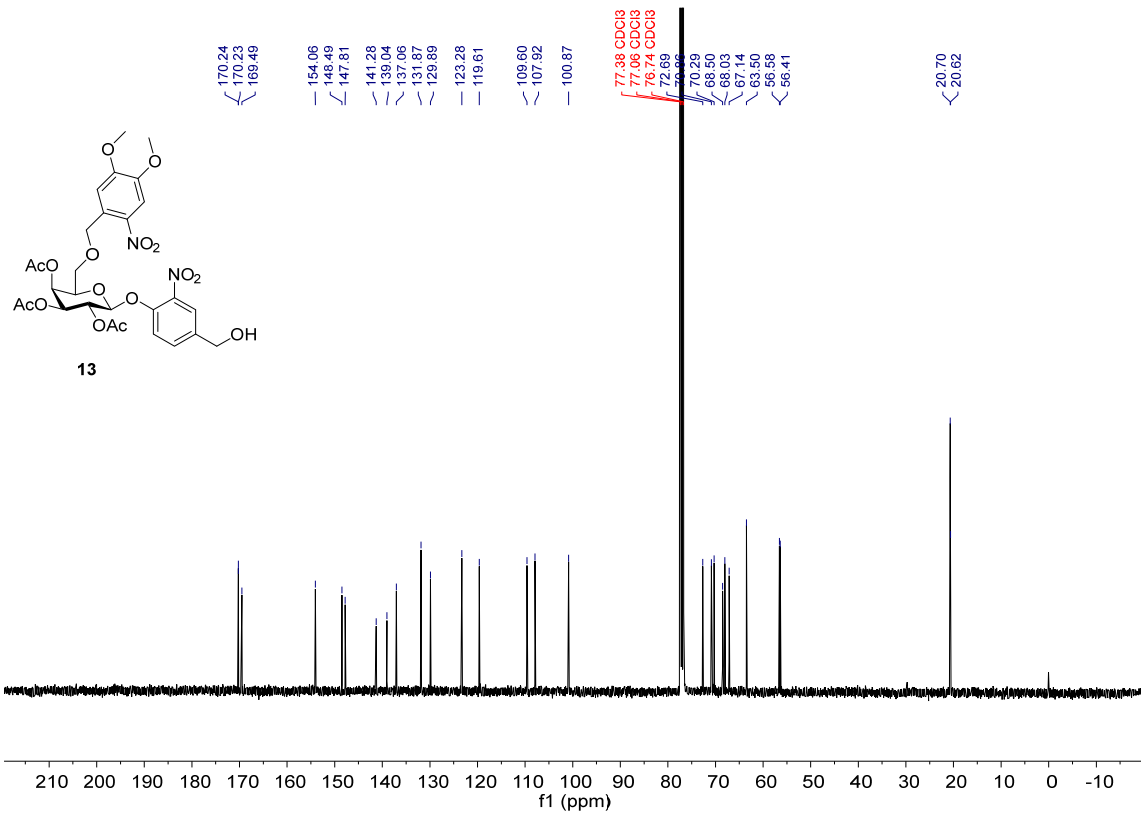
^{1}H-^{13}C HSQC NMR ($CDCl_3$, 400 MHz) of compound 12



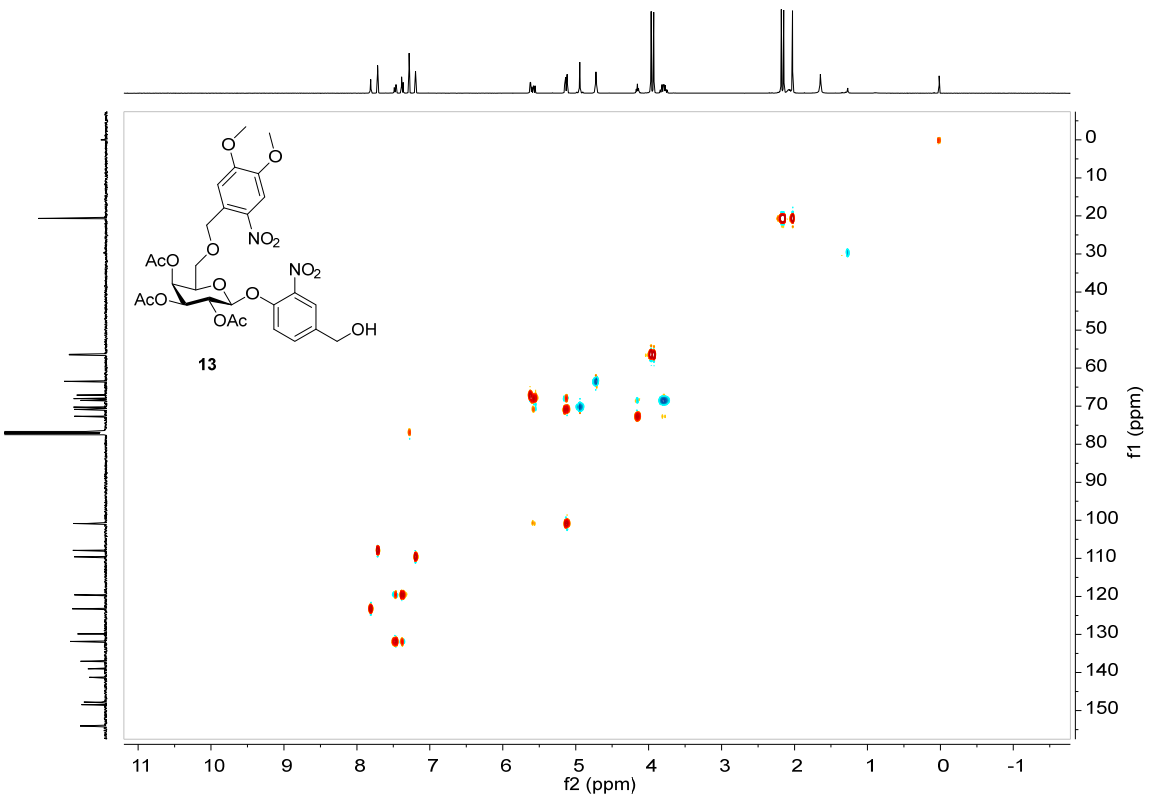
^{1}H NMR ($CDCl_3$, 400 MHz) of compound 13



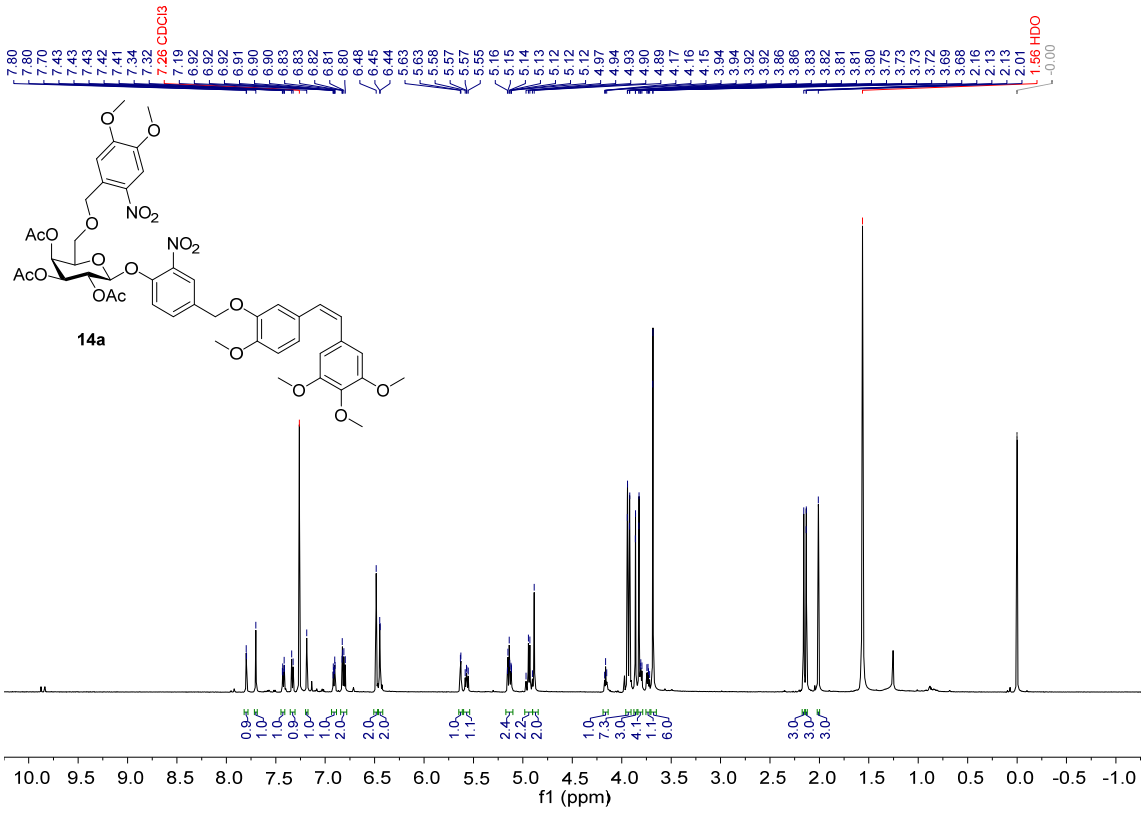
^{13}C NMR ($CDCl_3$, 101 MHz) of compound 13



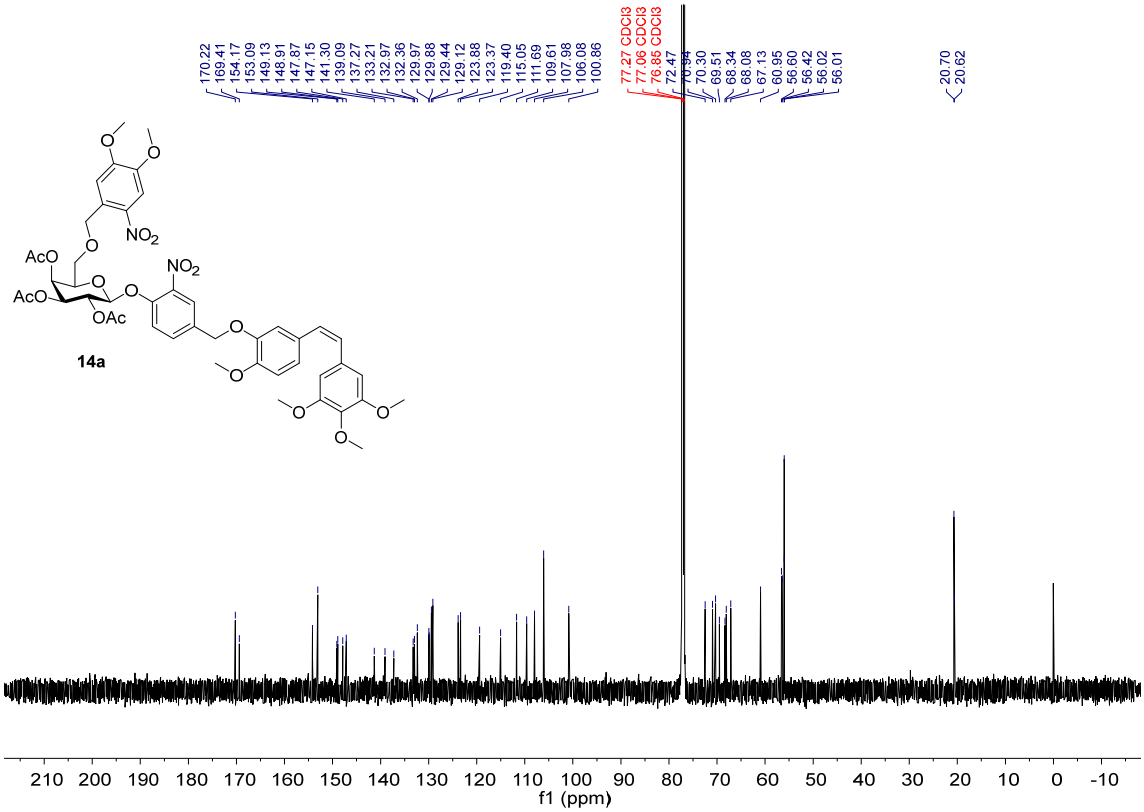
^{1}H-^{13}C HSQC NMR ($CDCl_3$, 400 MHz) of compound 13



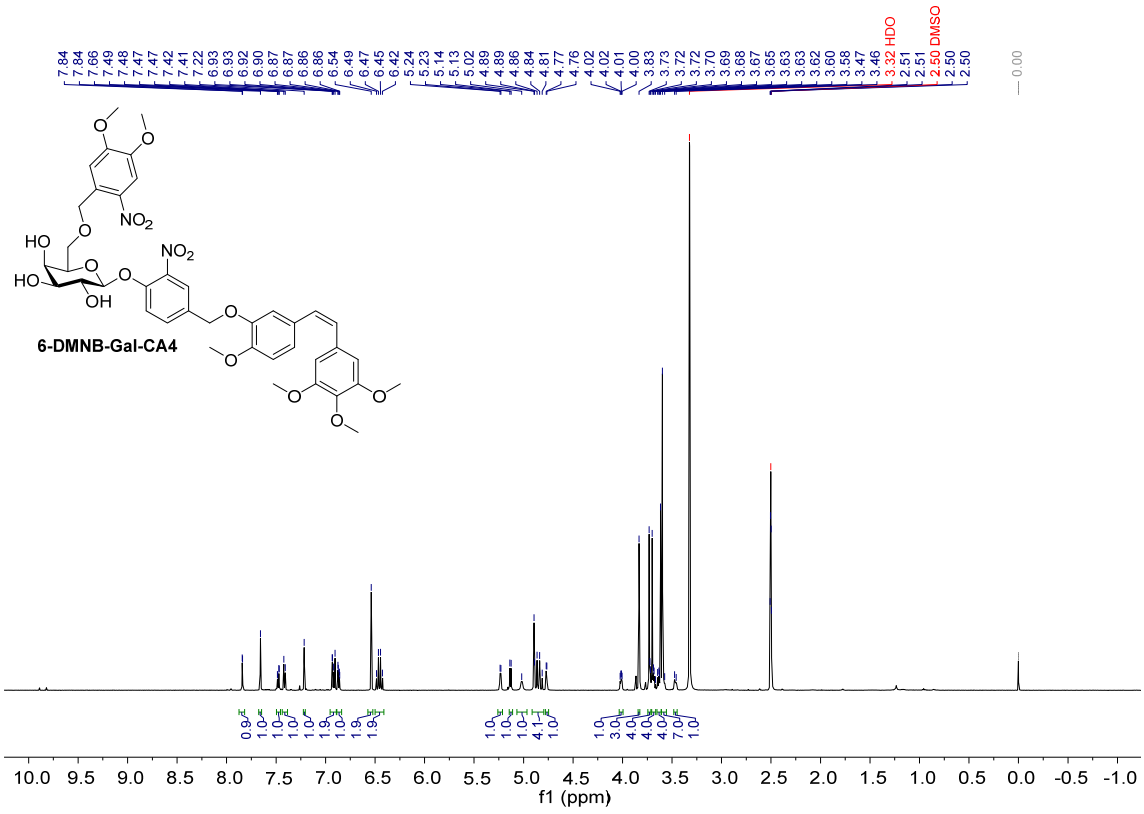
^{1}H NMR ($CDCl_3$, 600 MHz) of compound 14a



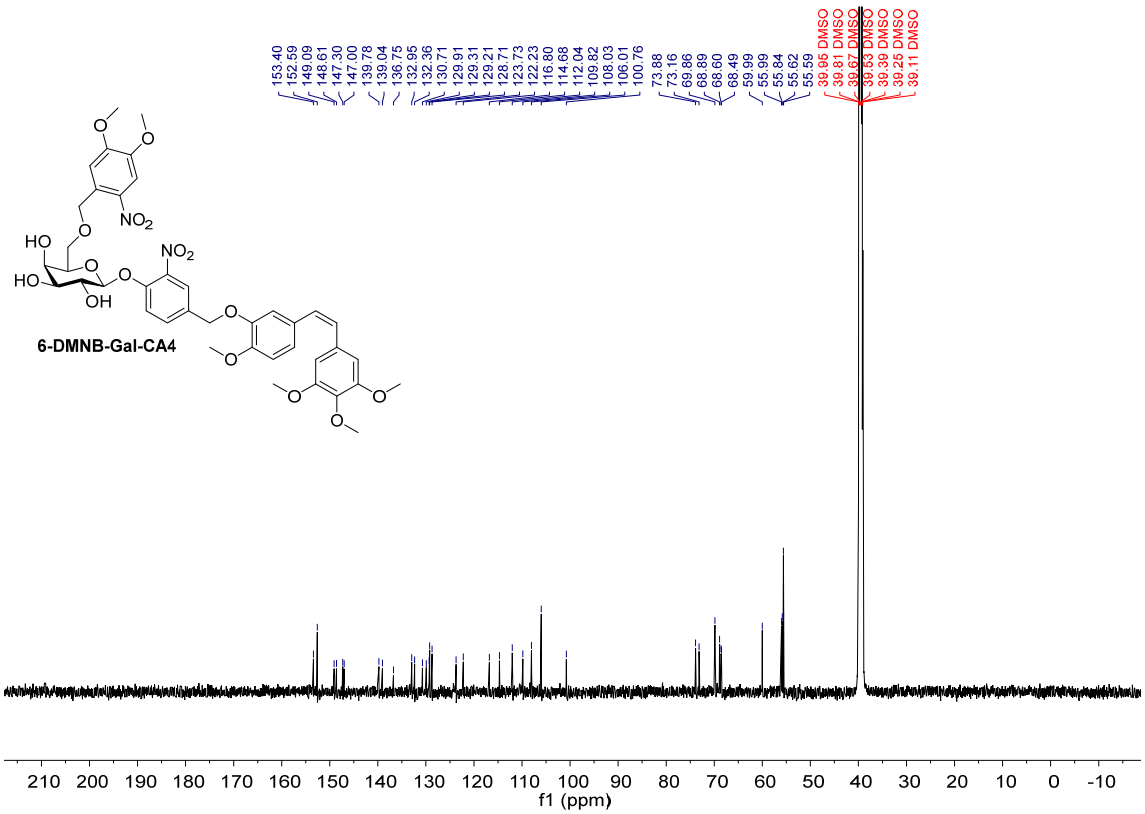
^{13}C NMR ($CDCl_3$, 151 MHz) of compound 14a



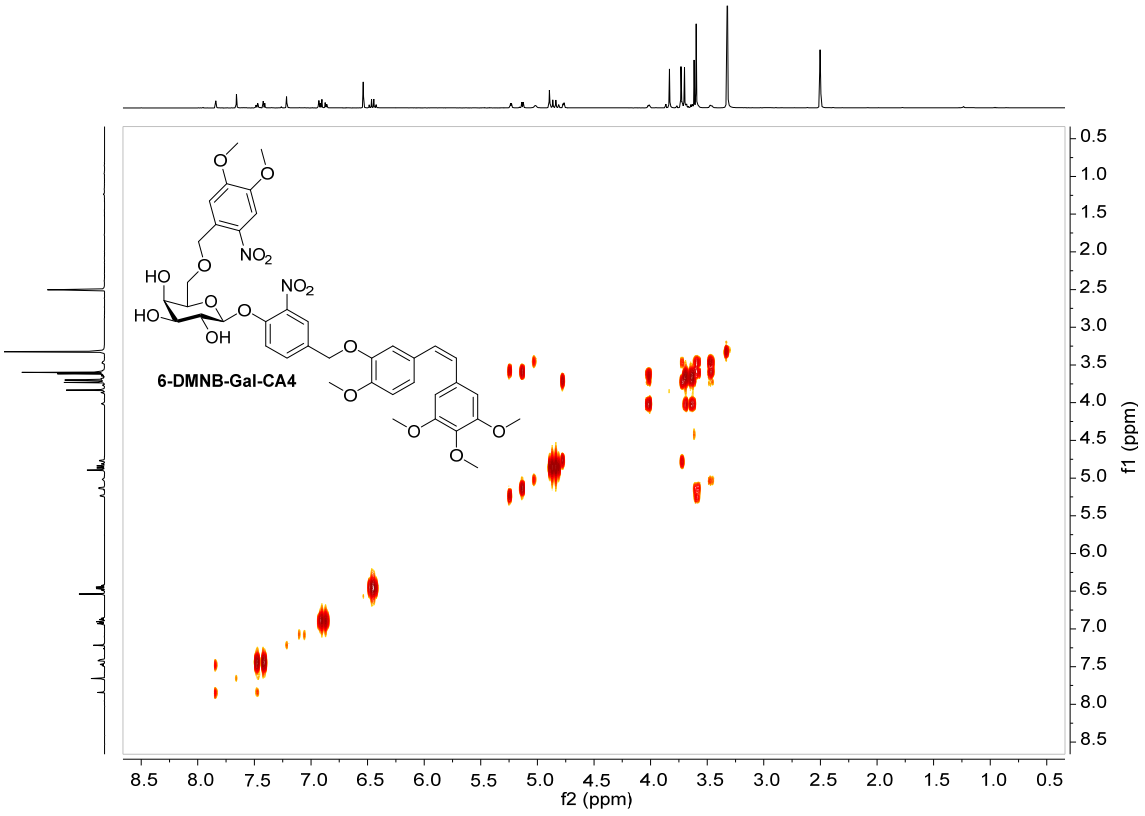
^{1}H NMR ($(CD_3)_2SO$, 600 MHz) of compound 6-DMNB-Gal-CA4



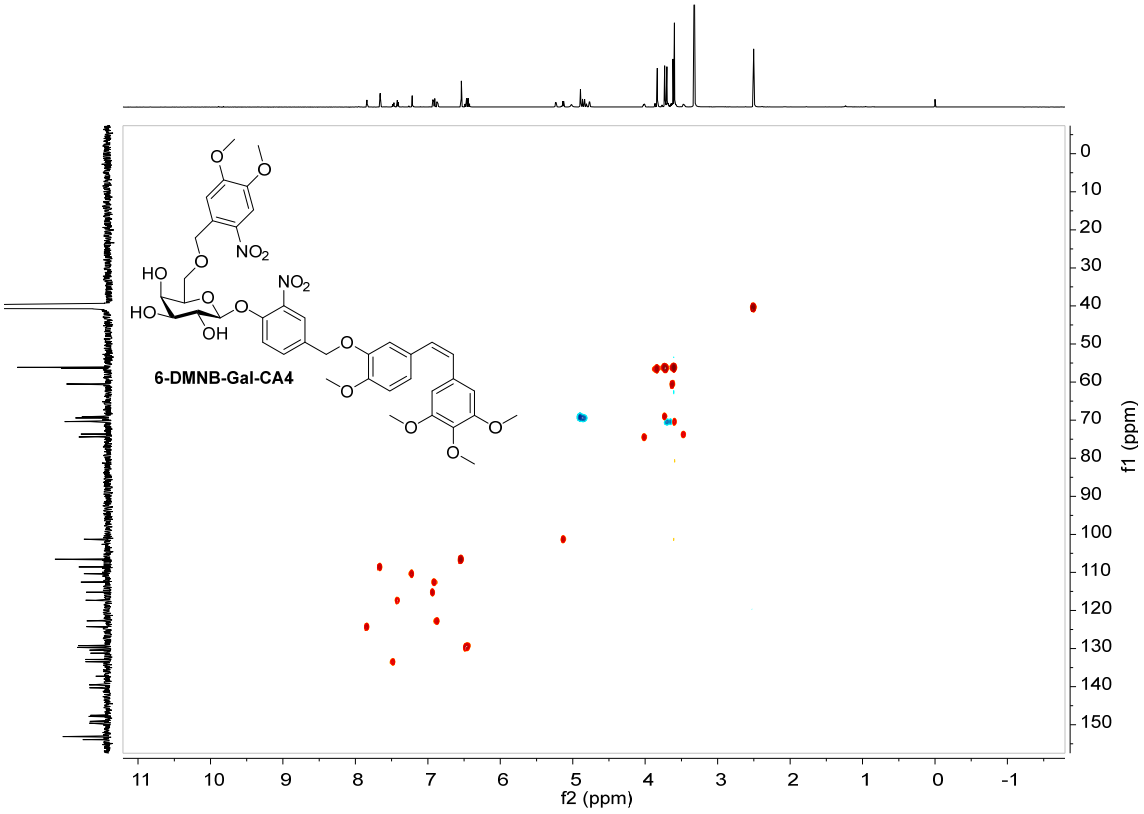
^{13}C NMR ($(CD_3)_2SO$, 151 MHz) of compound 6-DMNB-Gal-CA4



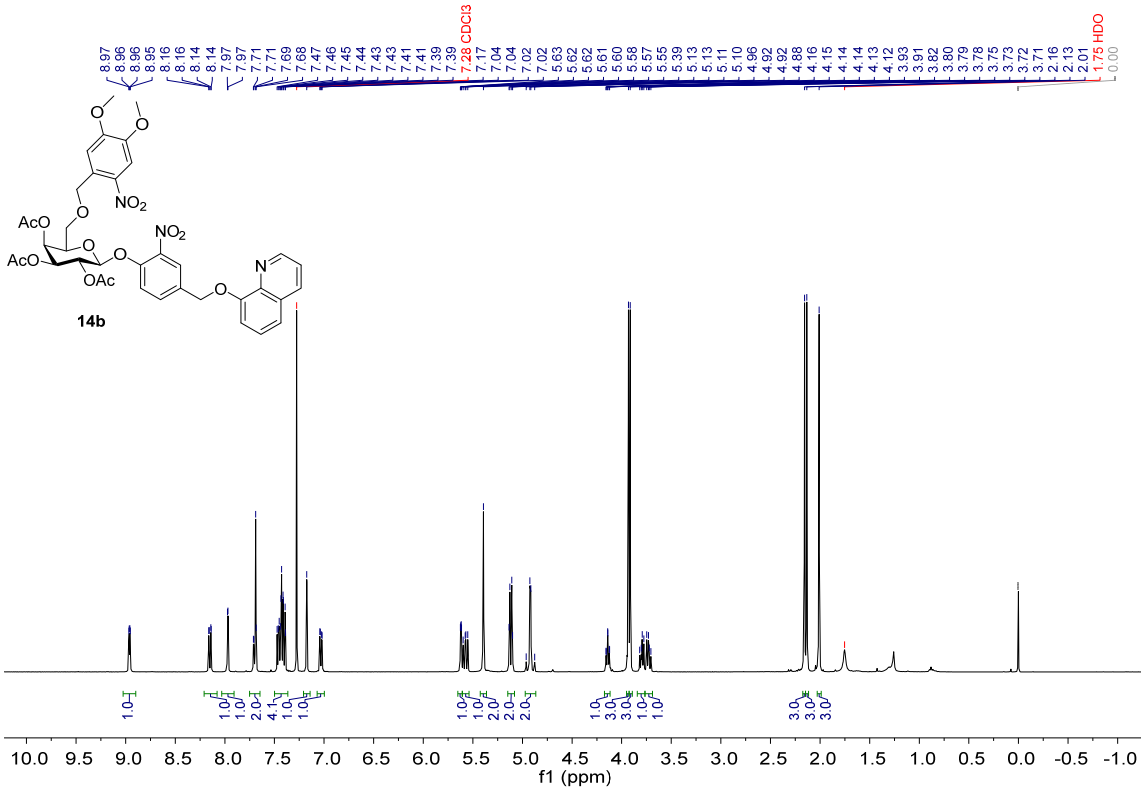
^{1}H-^{1}H COSY NMR ($(CD_3)_2SO$, 600 MHz) of compound 6-DMNB-Gal-CA4



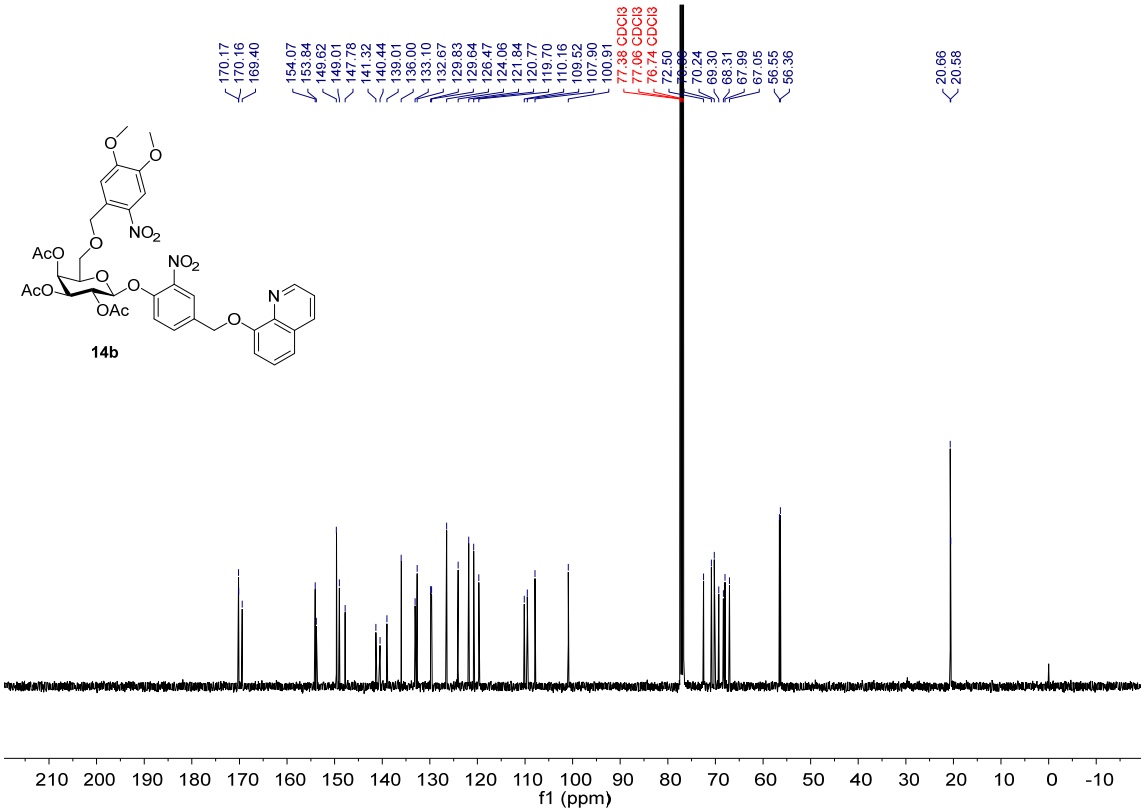
^{1}H-^{13}C HSQC NMR ($(CD_3)_2SO$, 600 MHz) of compound 6-DMNB-Gal-CA4



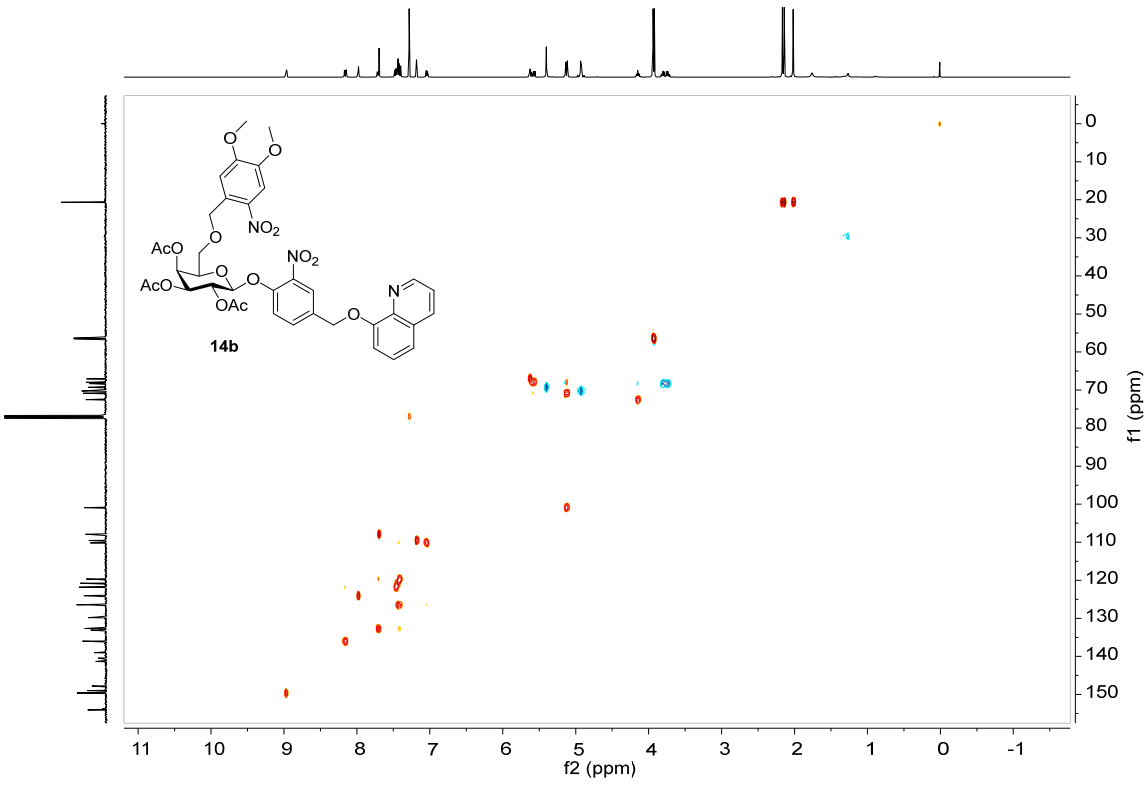
^{1}H NMR ($CDCl_3$, 400 MHz) of compound 14b



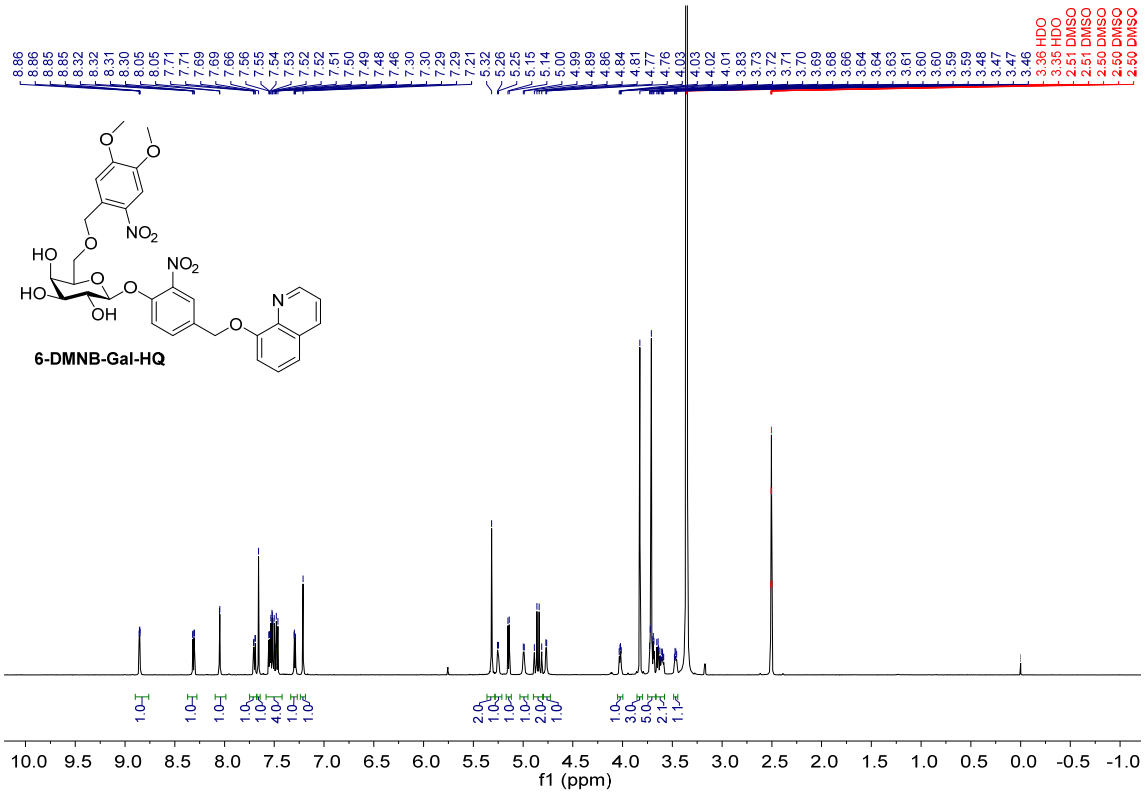
^{13}C NMR ($CDCl_3$, 101 MHz) of compound 14b



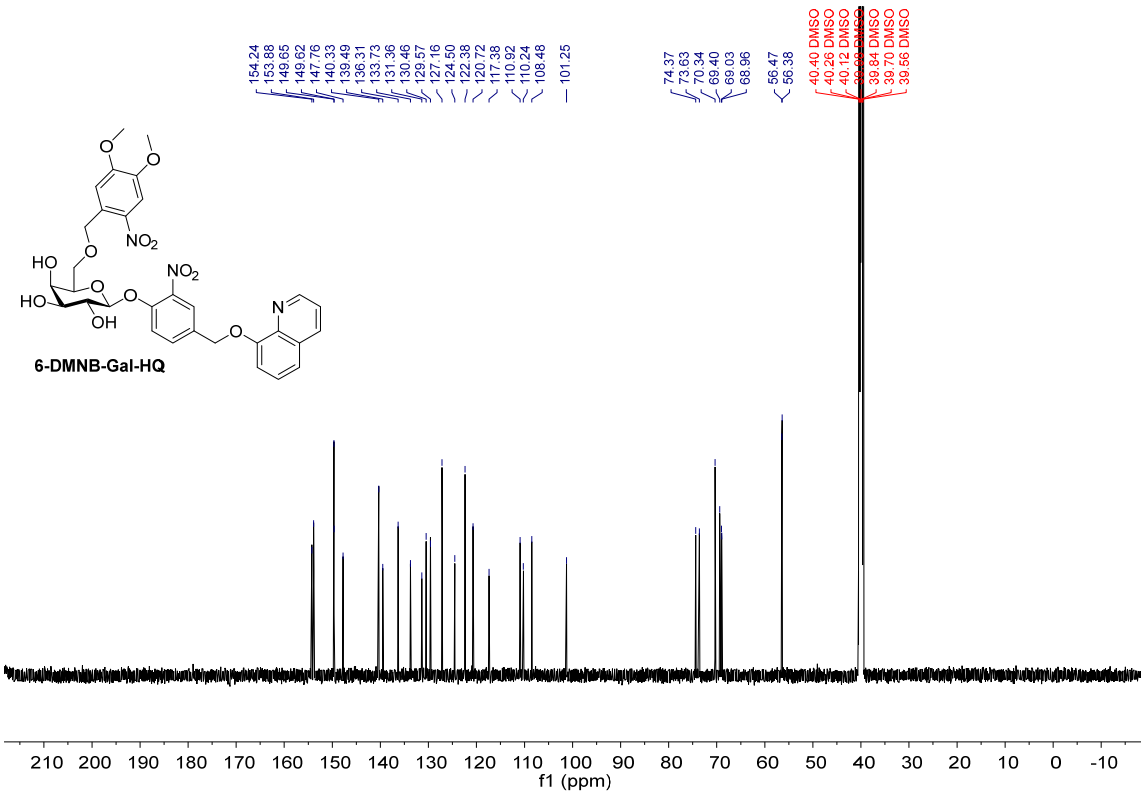
^{1}H-^{13}C HSQC NMR ($CDCl_3$, 400 MHz) of compound 14b



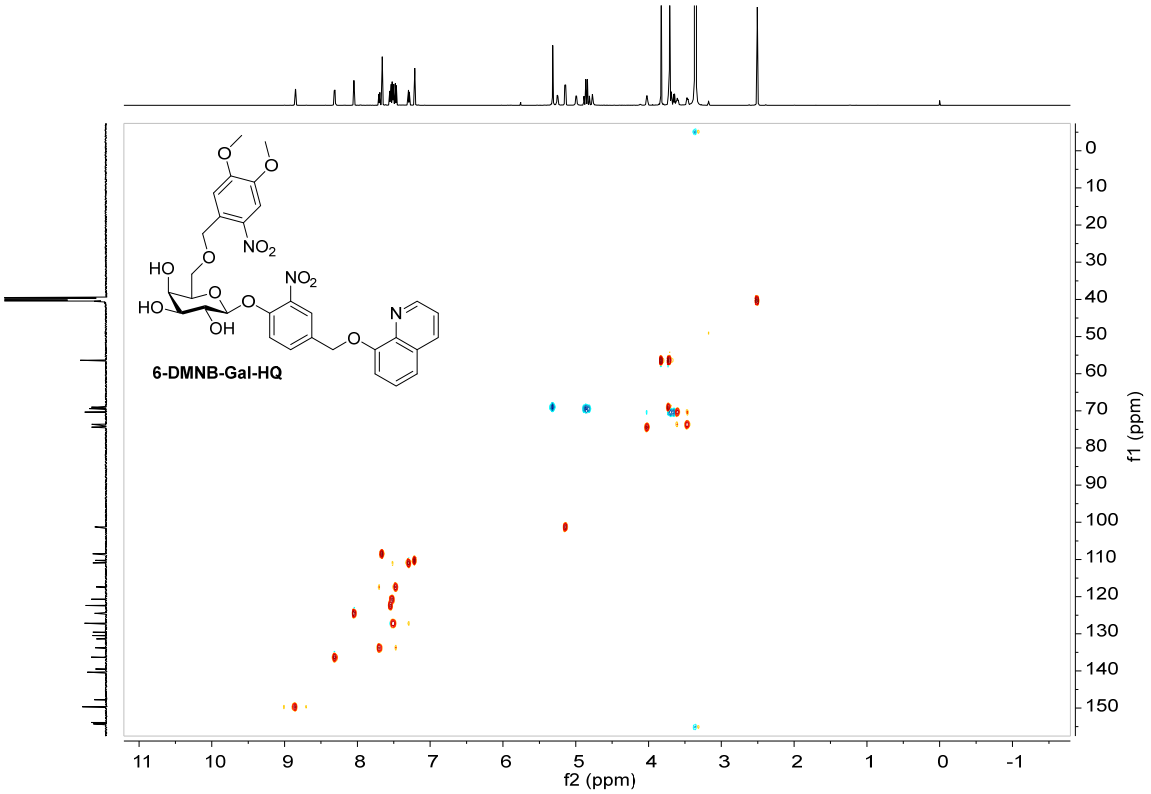
^{1}H NMR ($(CD_3)_2SO$, 600 MHz) of compound 6-DMNB-Gal-HQ



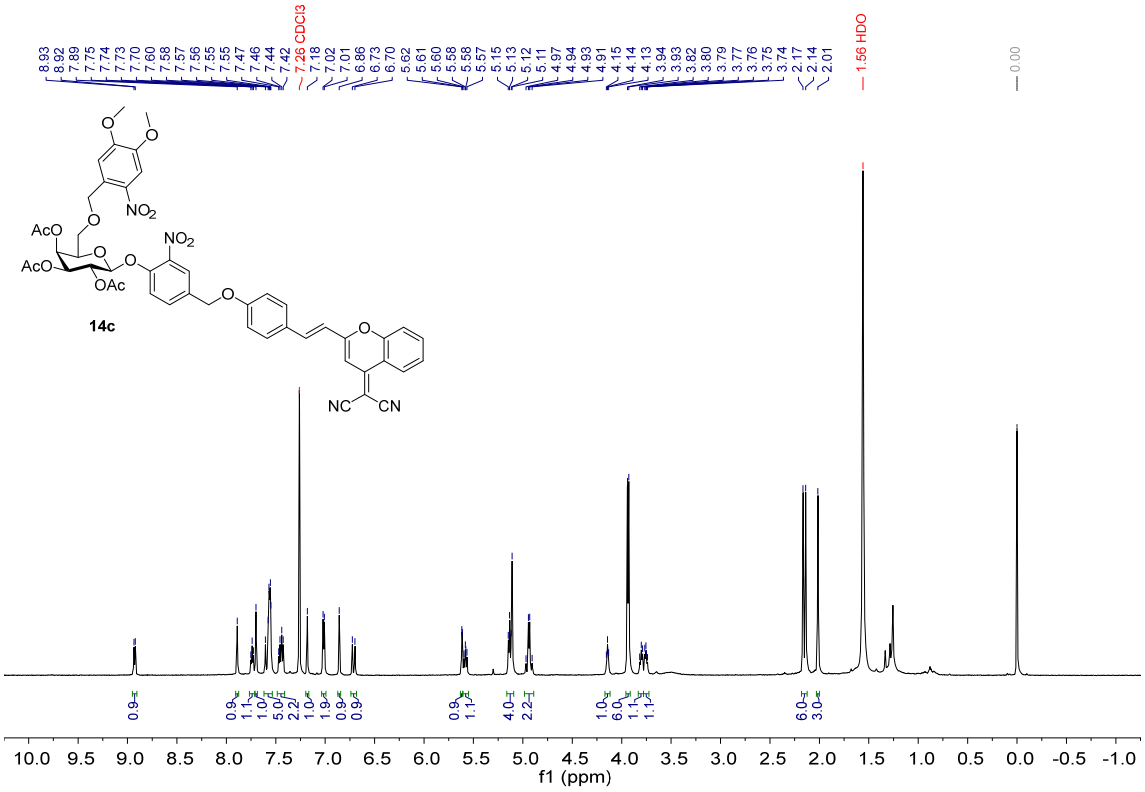
^{13}C NMR ($(CD_3)_2SO$, 151 MHz) of compound 6-DMNB-Gal-HQ



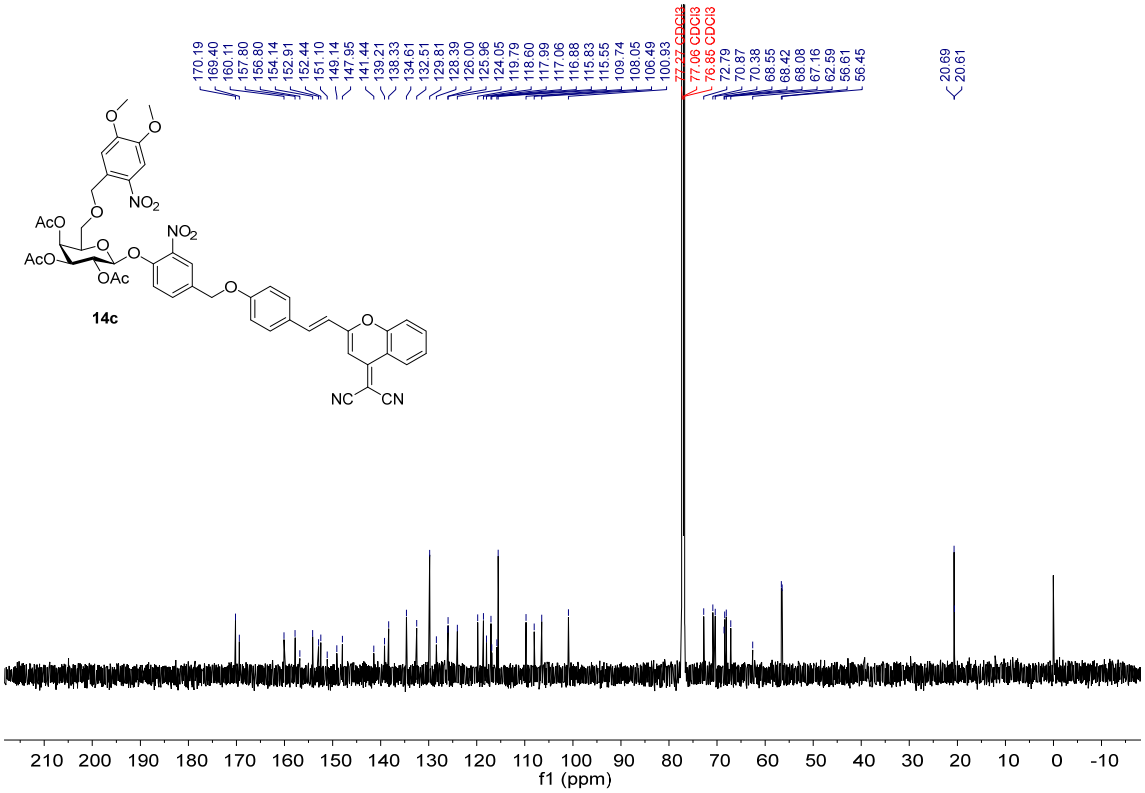
^{1}H-^{13}C HSQC NMR ($(CD_3)_2SO$, 600 MHz) of compound 6-DMNB-Gal-HQ



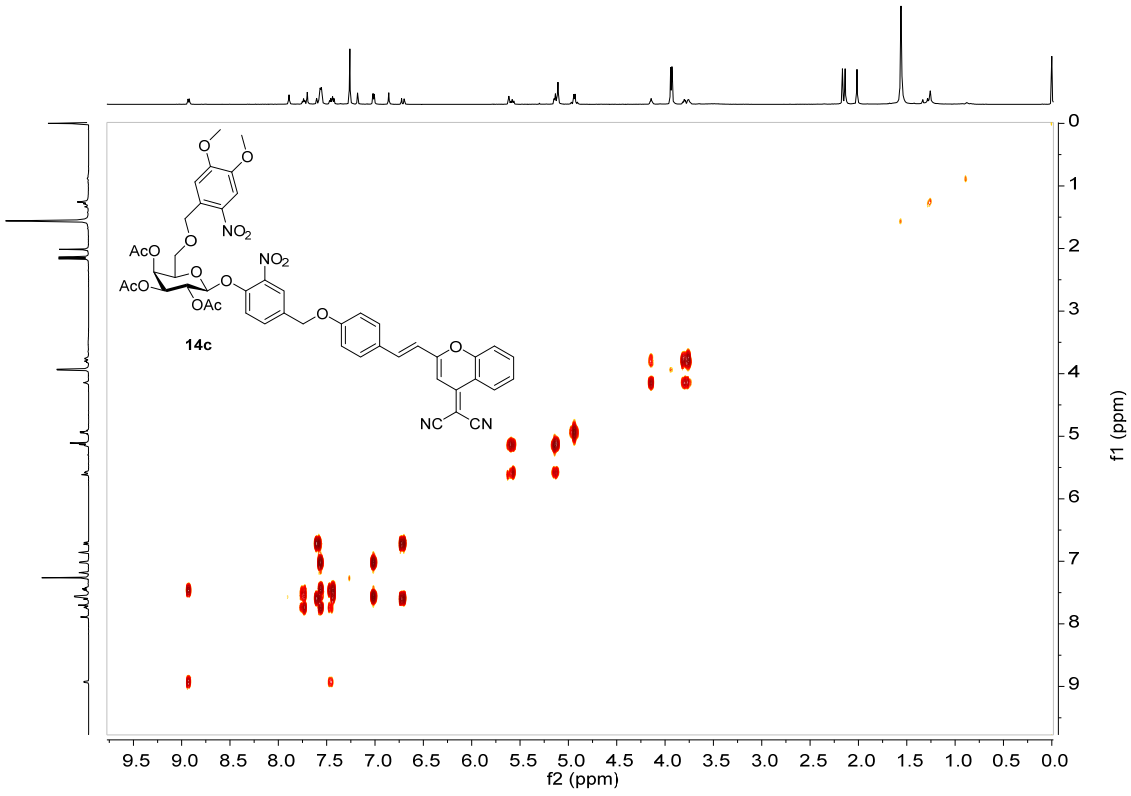
^{1}H NMR ($CDCl_3$, 600 MHz) of compound 14c



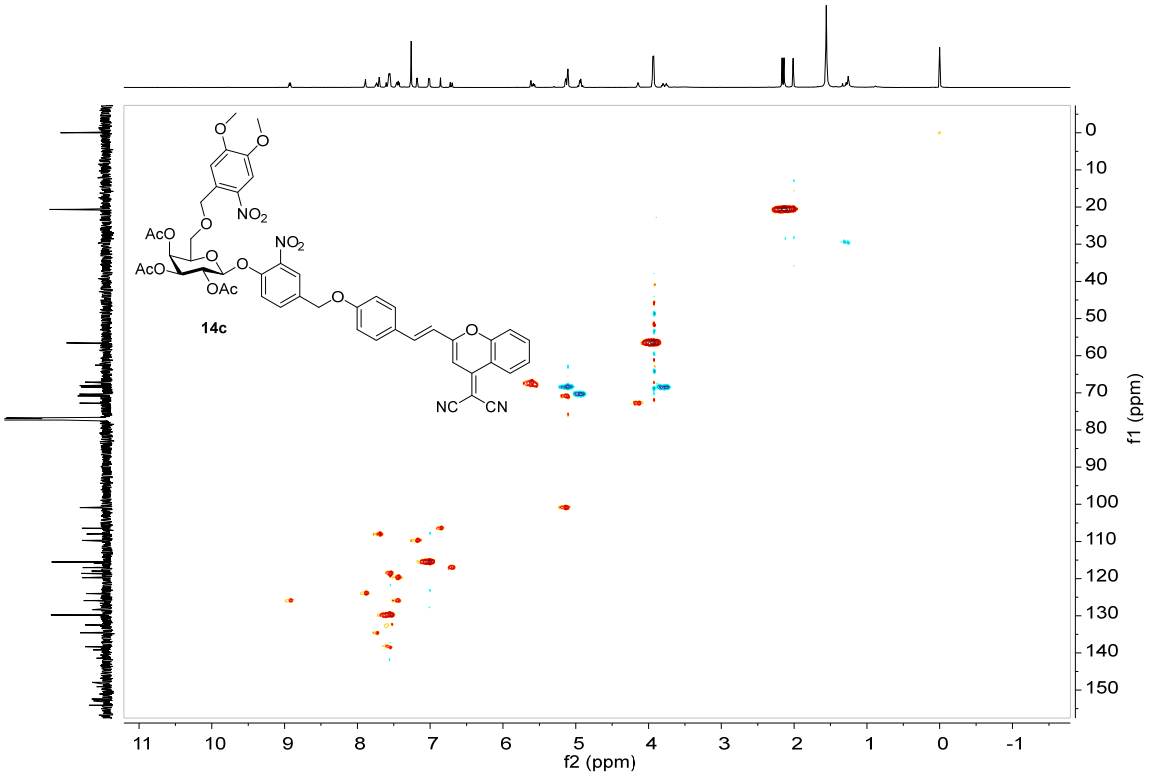
^{13}C NMR ($CDCl_3$, 151 MHz) of compound 14c



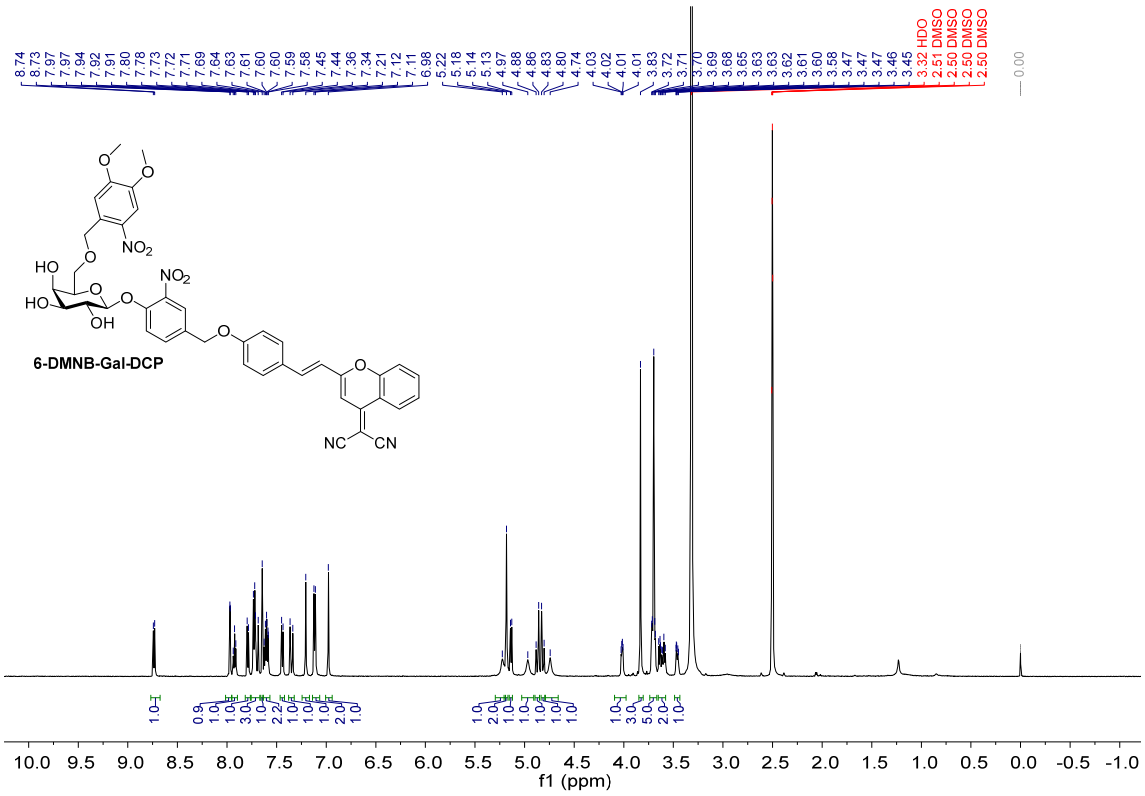
^{1}H-^{1}H COSY NMR ($CDCl_3$, 600 MHz) of compound 14c



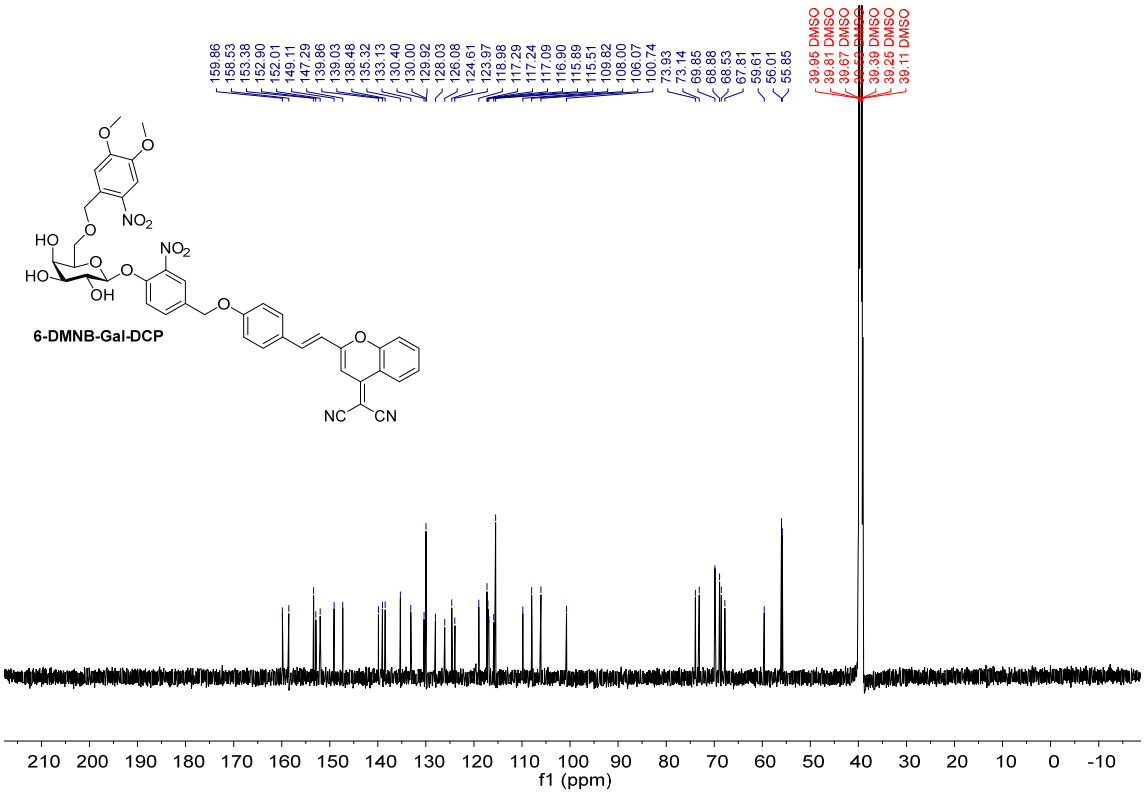
^{1}H-^{13}C HSQC NMR ($CDCl_3$, 600 MHz) of compound 14c



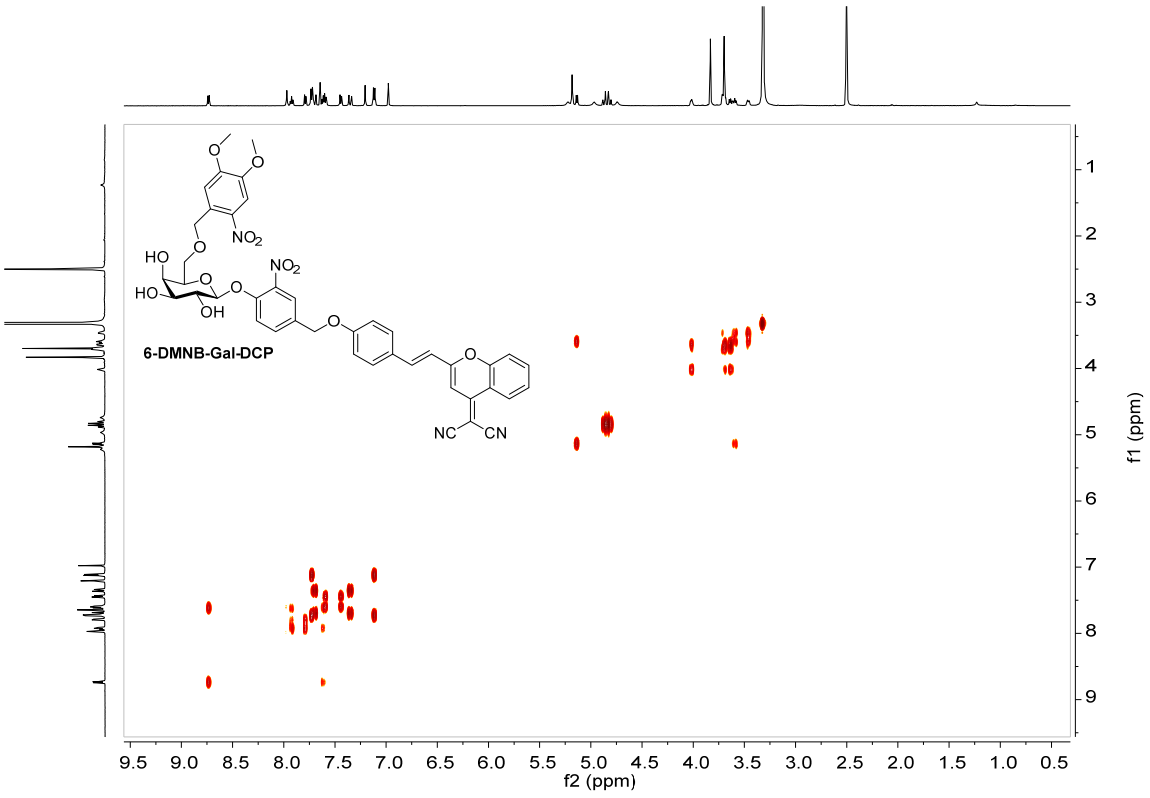
^{1}H NMR ($(CD_3)_2SO$, 600 MHz) of compound 6-DMNB-Gal-DCP



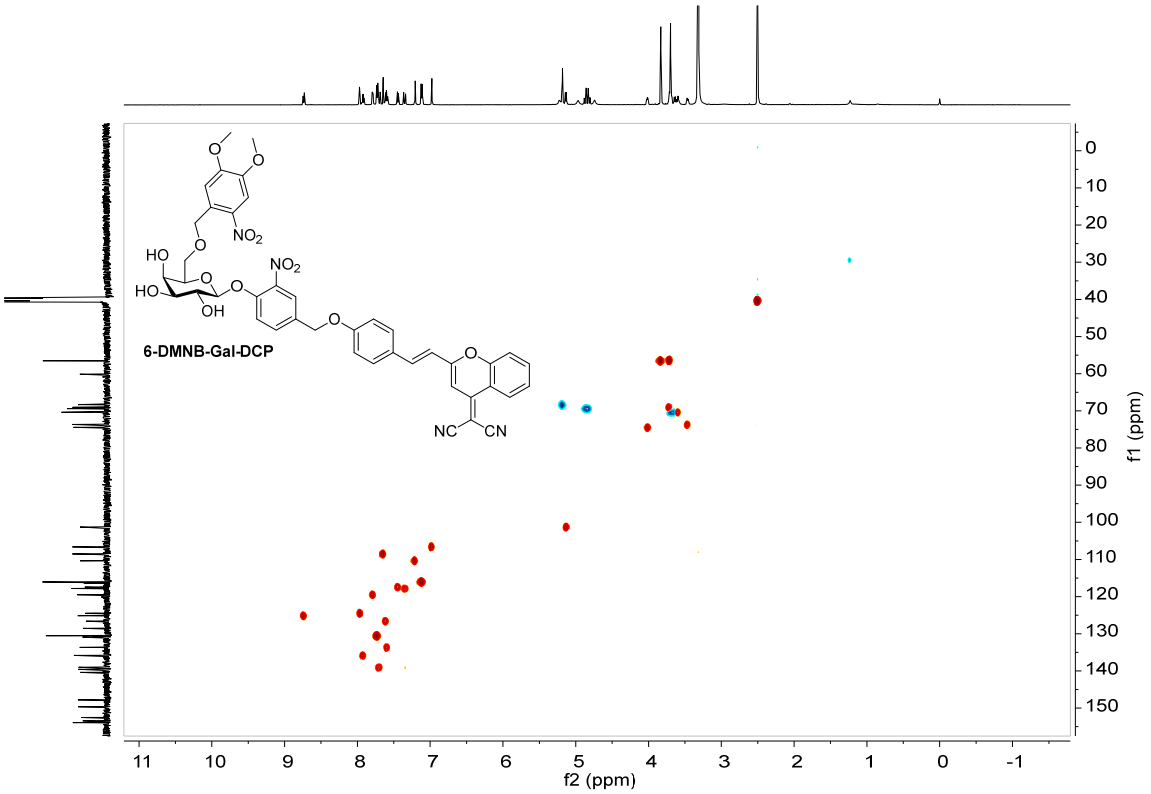
^{13}C NMR ((CD$_3$)$_2$SO, 151 MHz) of compound 6-DMNB-Gal-DCP



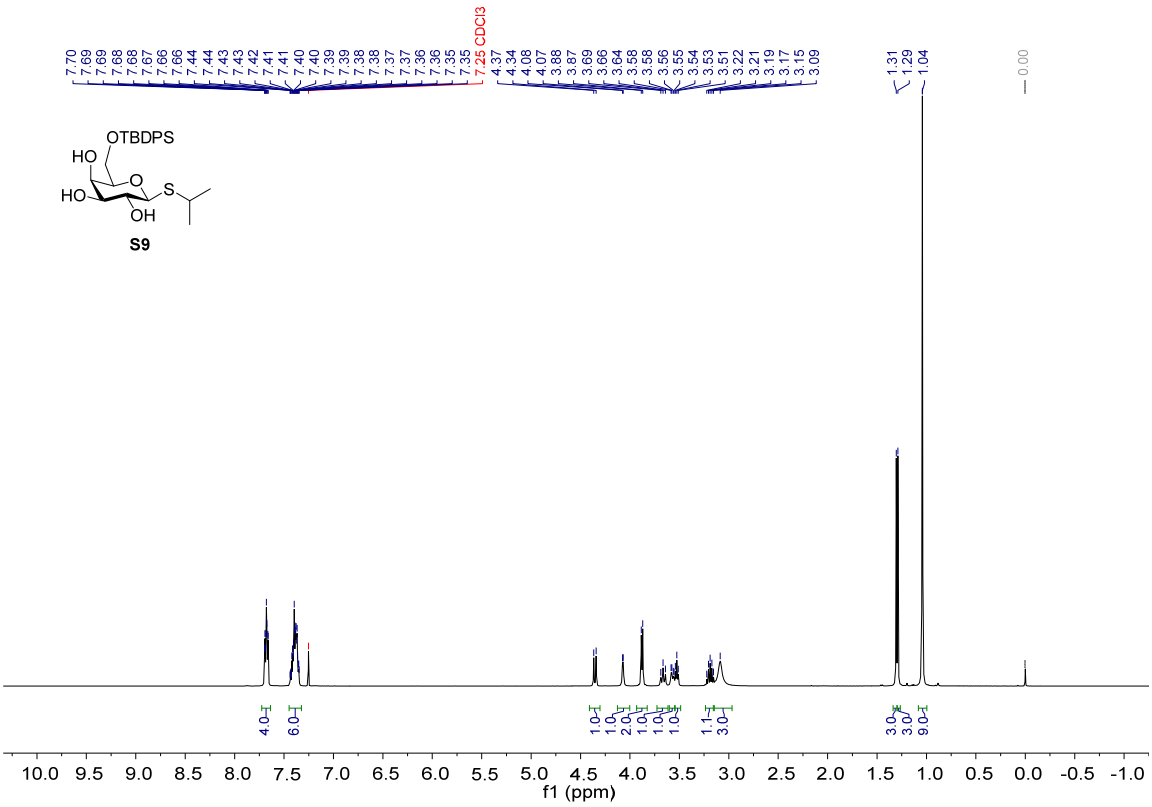
^{1}H-^{1}H COSY NMR ((CD$_3$)$_2$SO, 600 MHz) of compound 6-DMNB-Gal-DCP



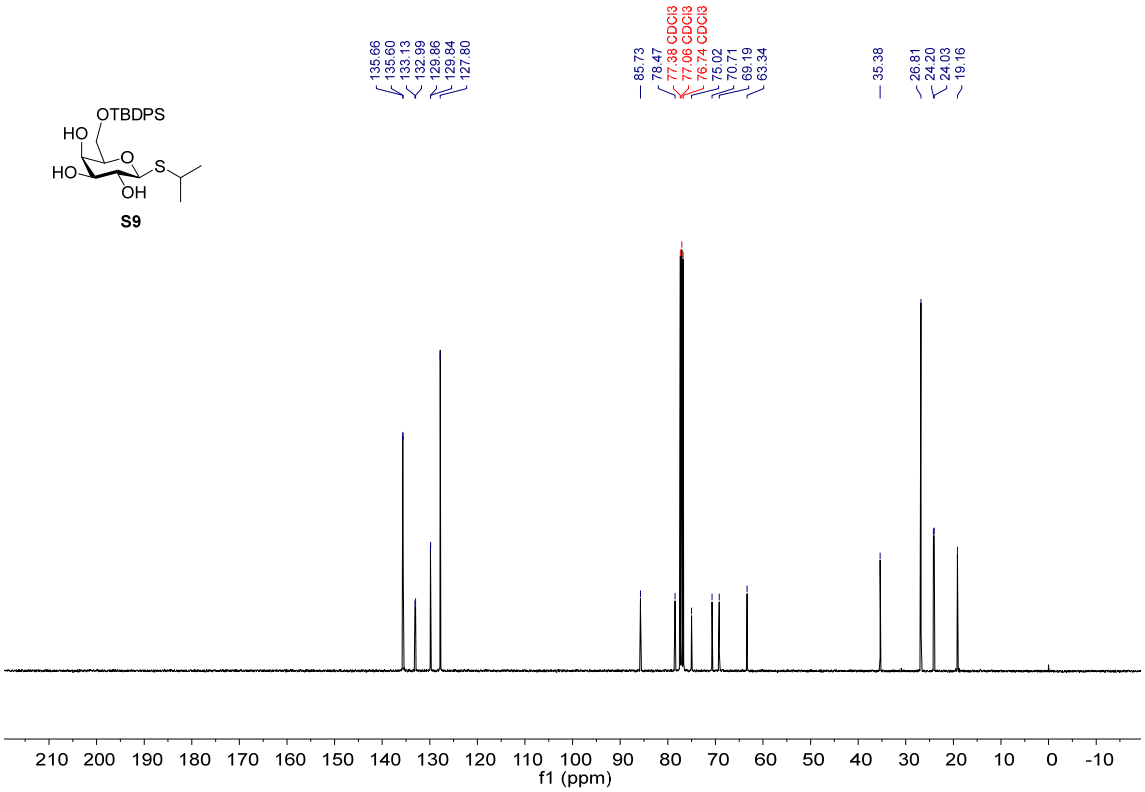
^{1}H-^{13}C HSQC NMR ($(CD_3)_2SO$, 600 MHz) of compound 6-DMNB-Gal-DCP



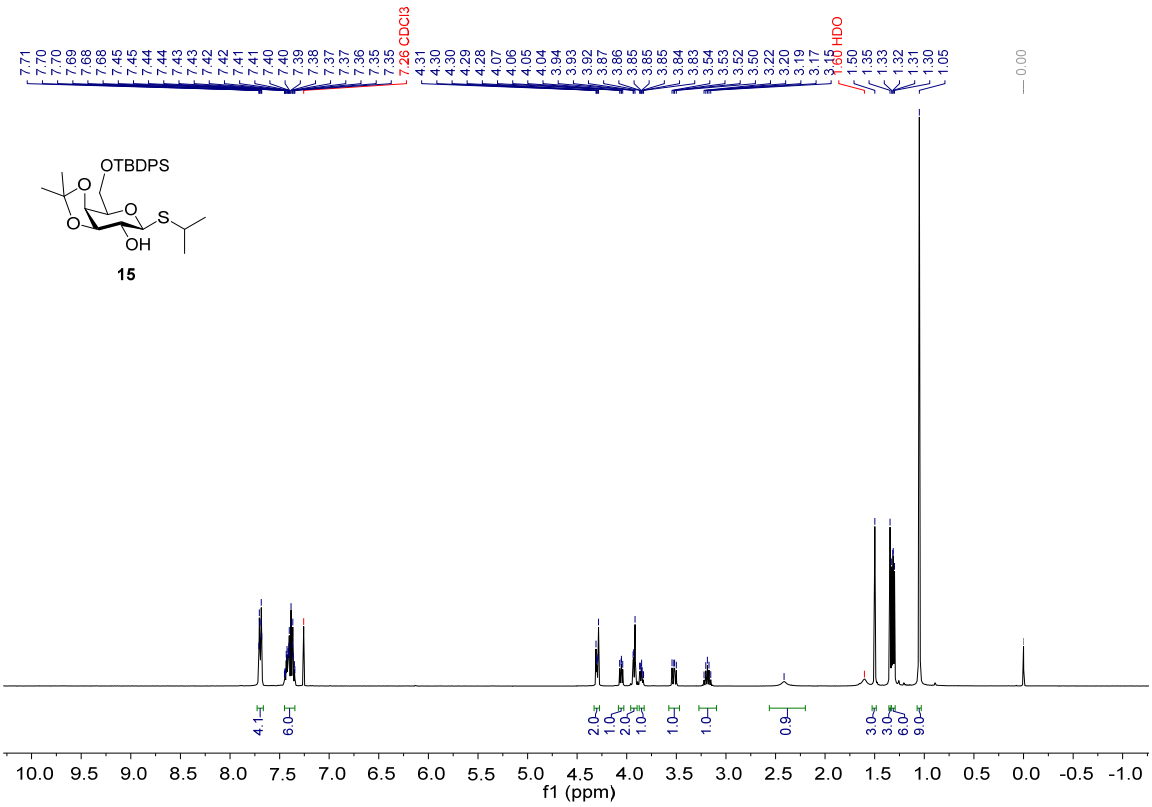
^{1}H NMR ($CDCl_3$, 400 MHz) of compound S9



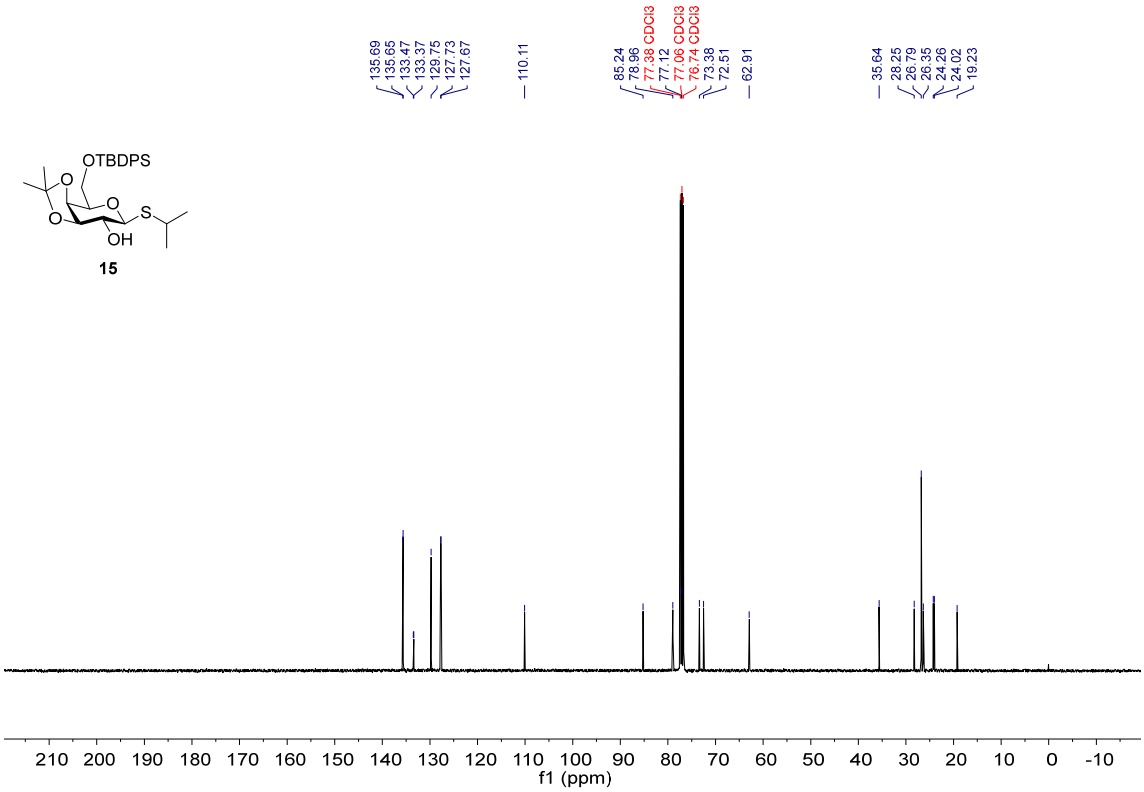
^{13}C NMR ($CDCl_3$, 101 MHz) of compound S9



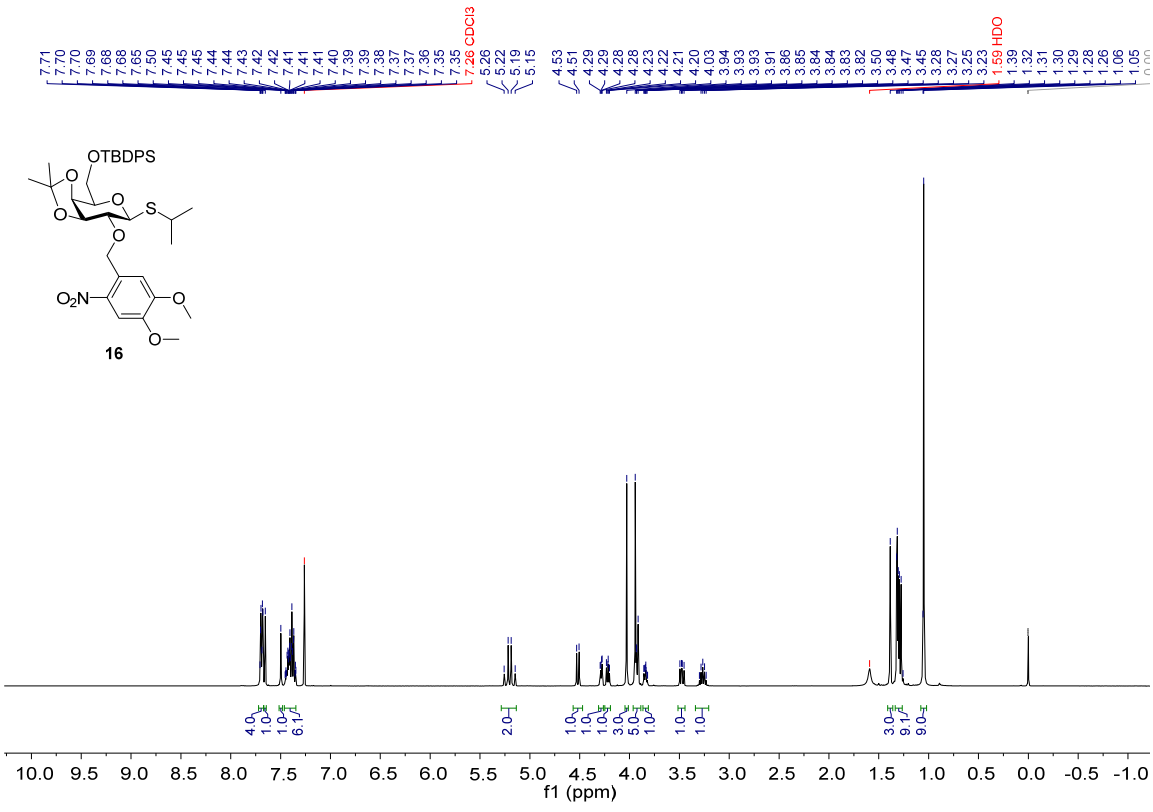
^{1}H NMR ($CDCl_3$, 400 MHz) of compound 15



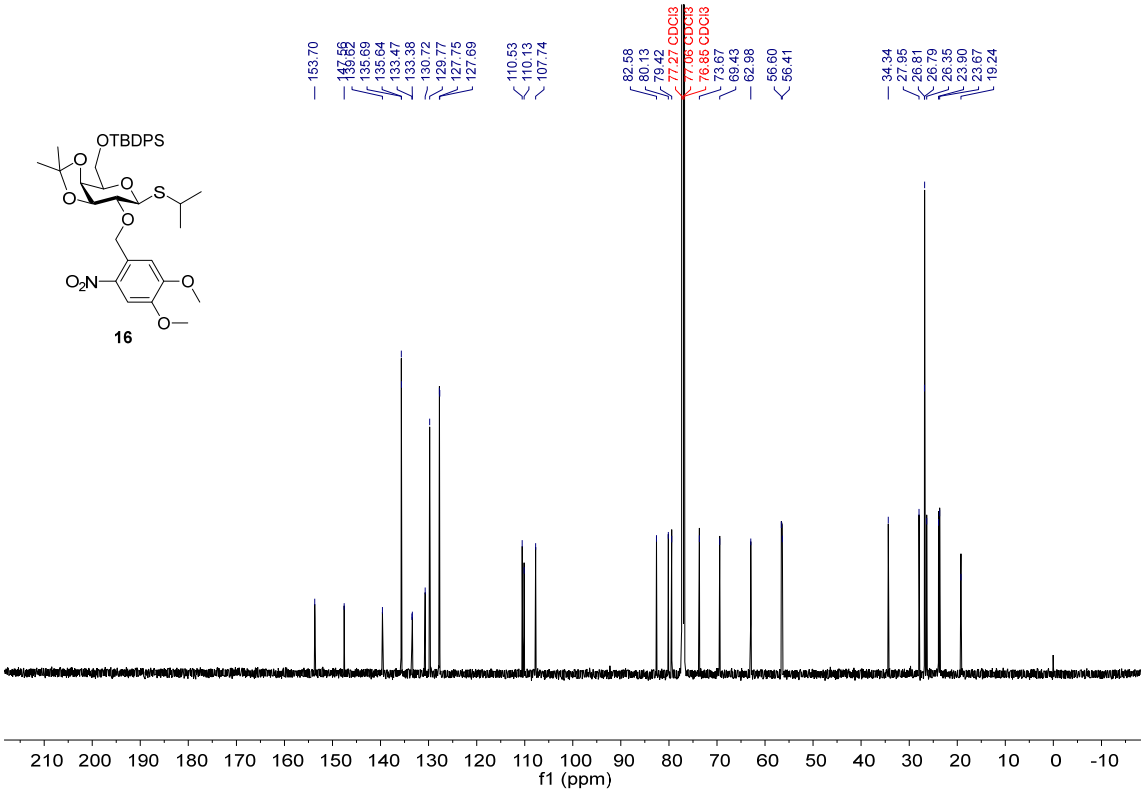
^{13}C NMR ($CDCl_3$, 101 MHz) of compound 15



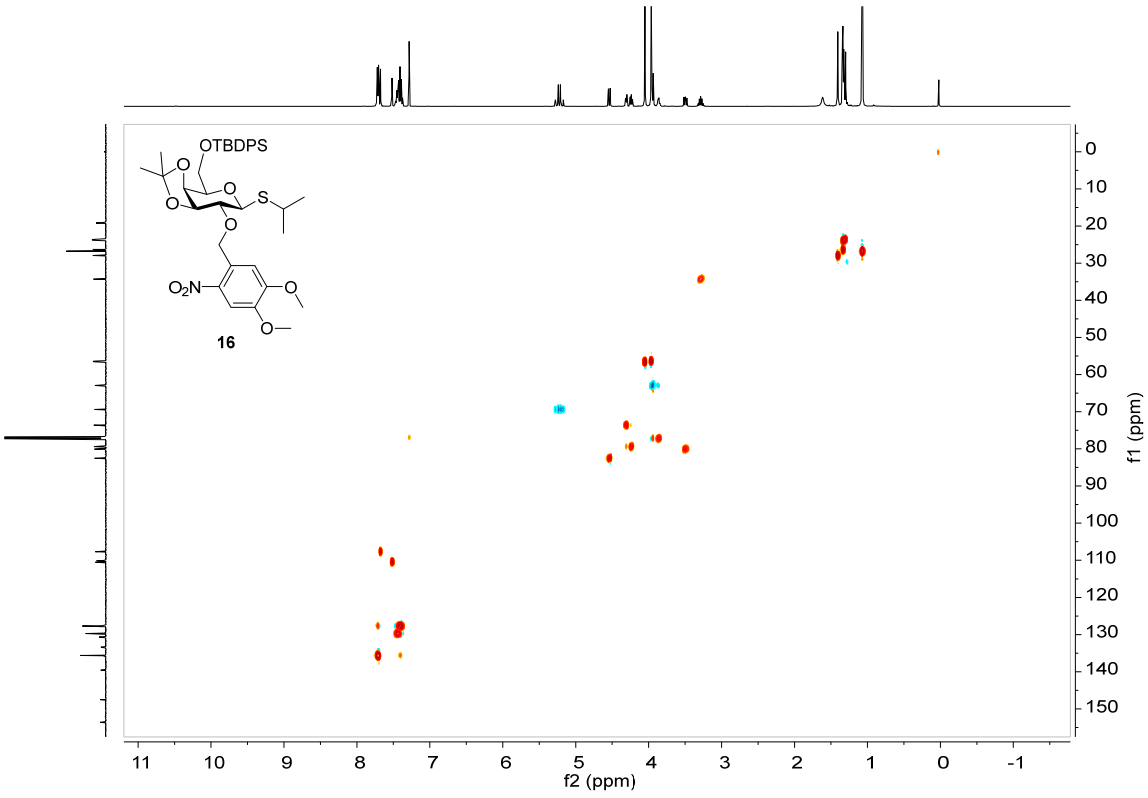
^{1}H NMR ($CDCl_3$, 400 MHz) of compound 16



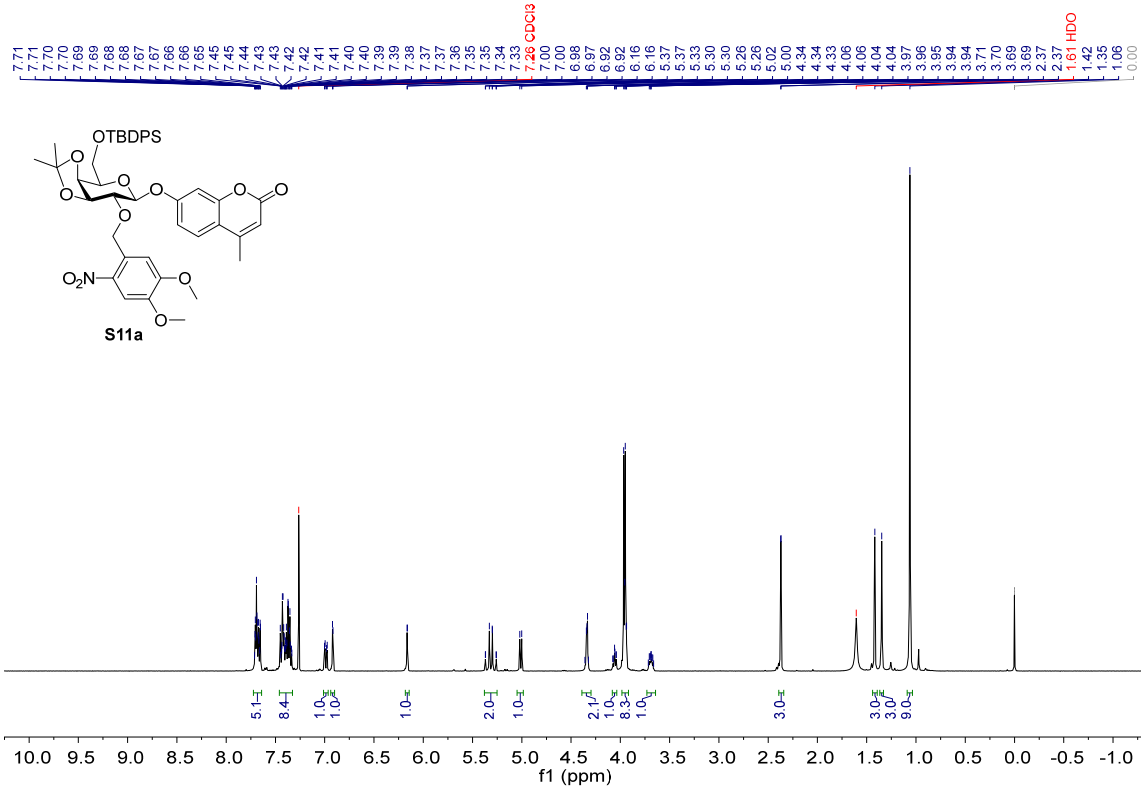
^{13}C NMR ($CDCl_3$, 101 MHz) of compound 16



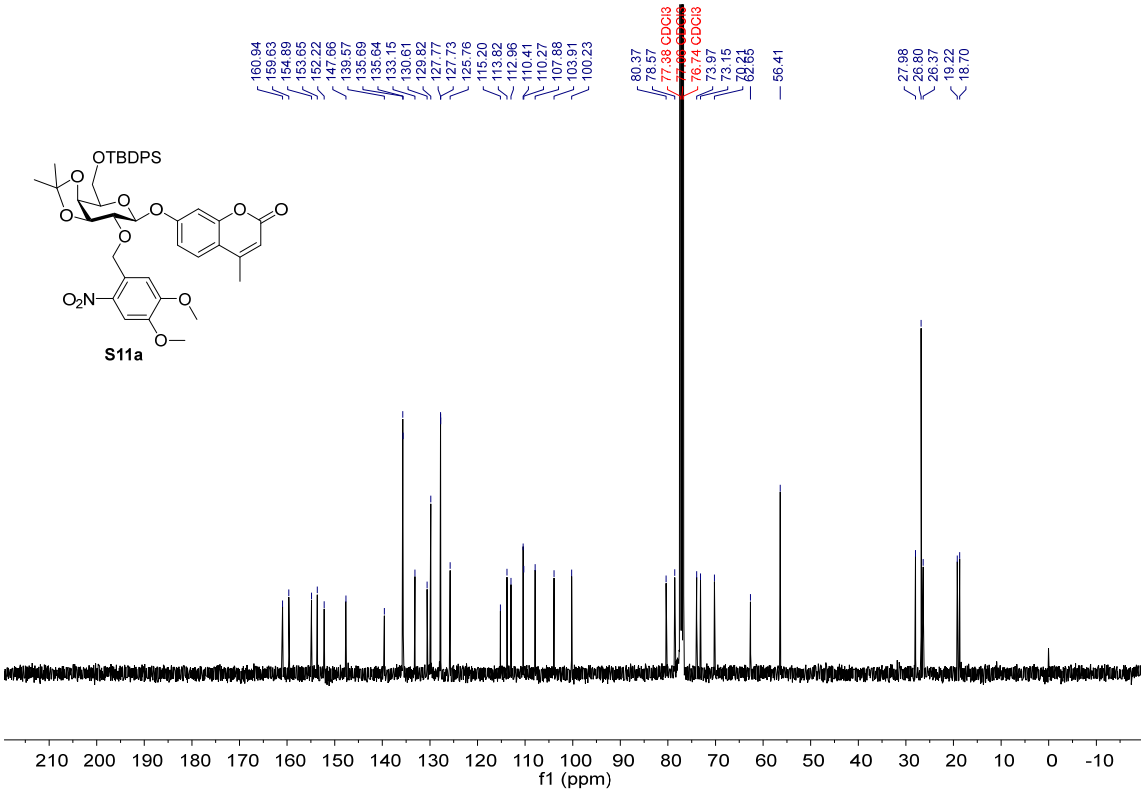
^{1}H-^{13}C HSQC NMR ($CDCl_3$, 400 MHz) of compound 16



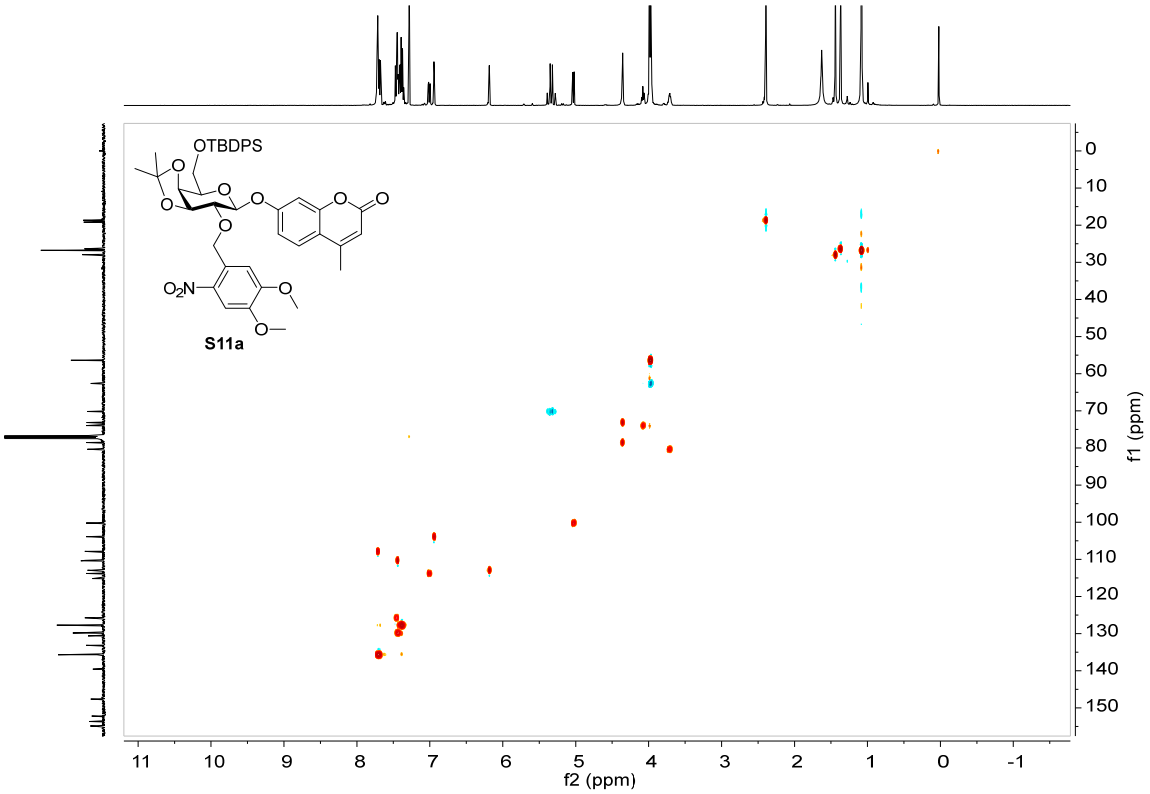
^{1}H NMR ($CDCl_3$, 400 MHz) of compound S11a



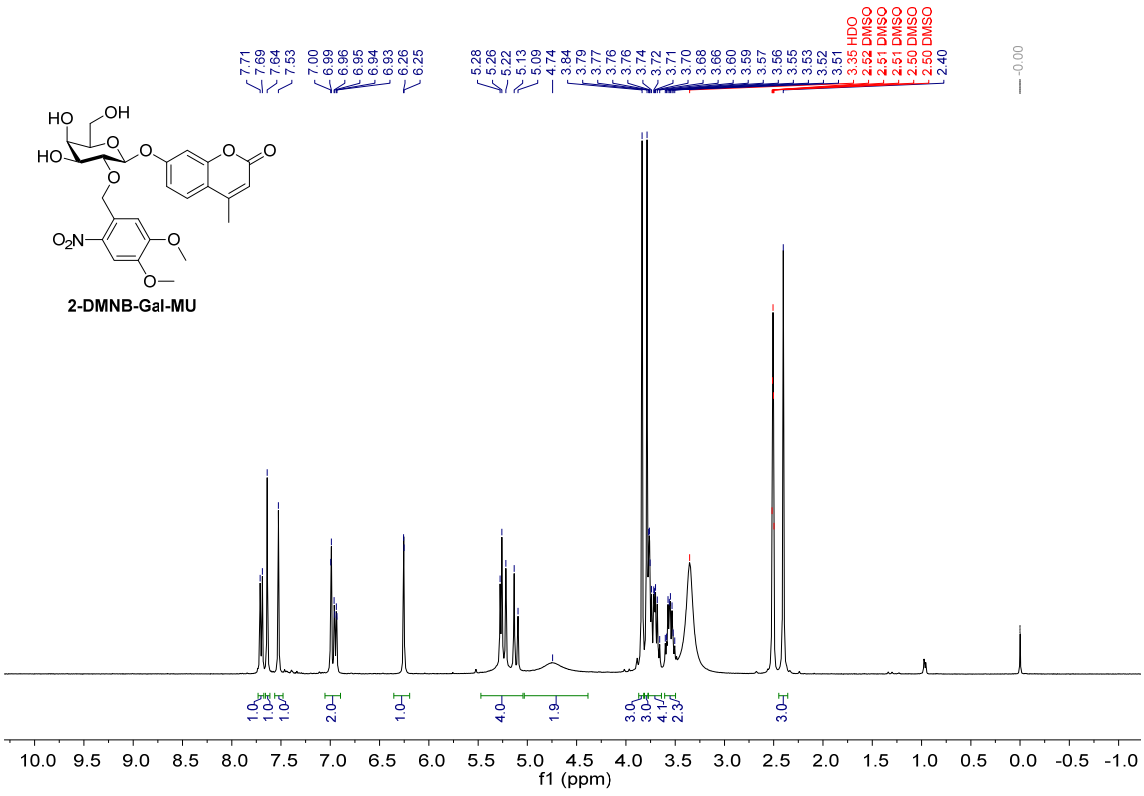
^{13}C NMR ($CDCl_3$, 101 MHz) of compound S11a



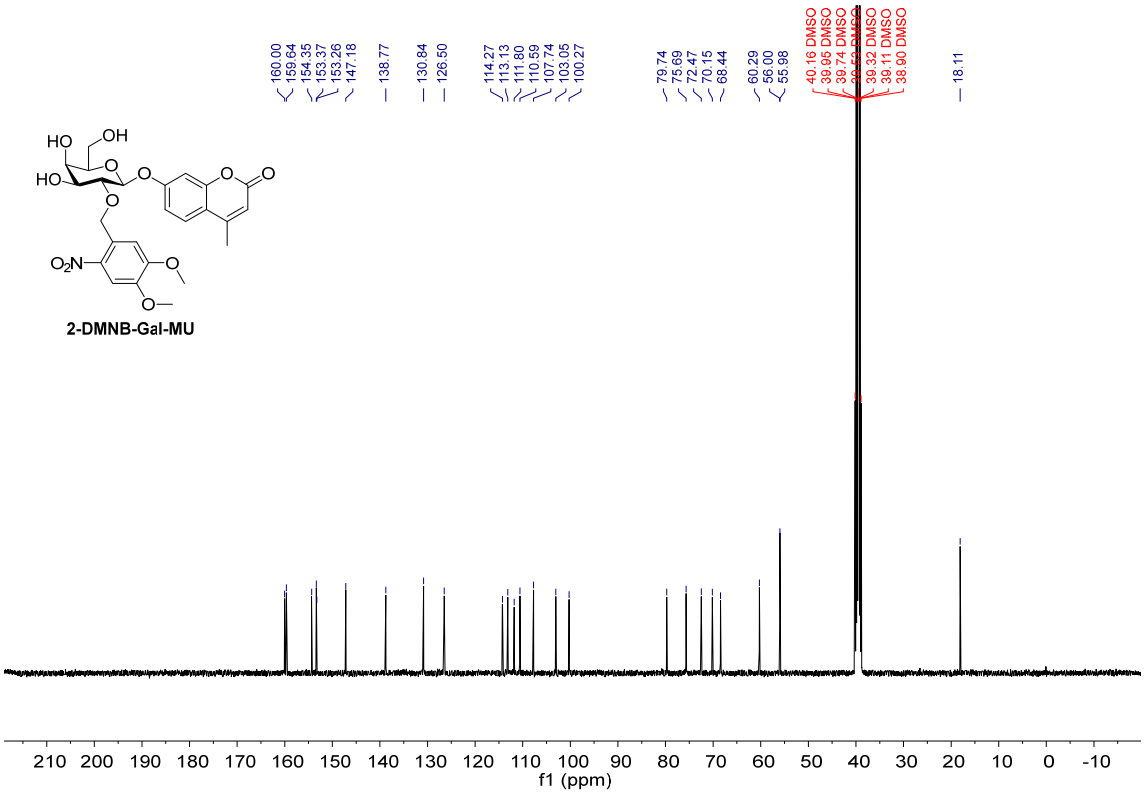
^{1}H-^{13}C HSQC NMR ($CDCl_3$, 400 MHz) of compound S11a



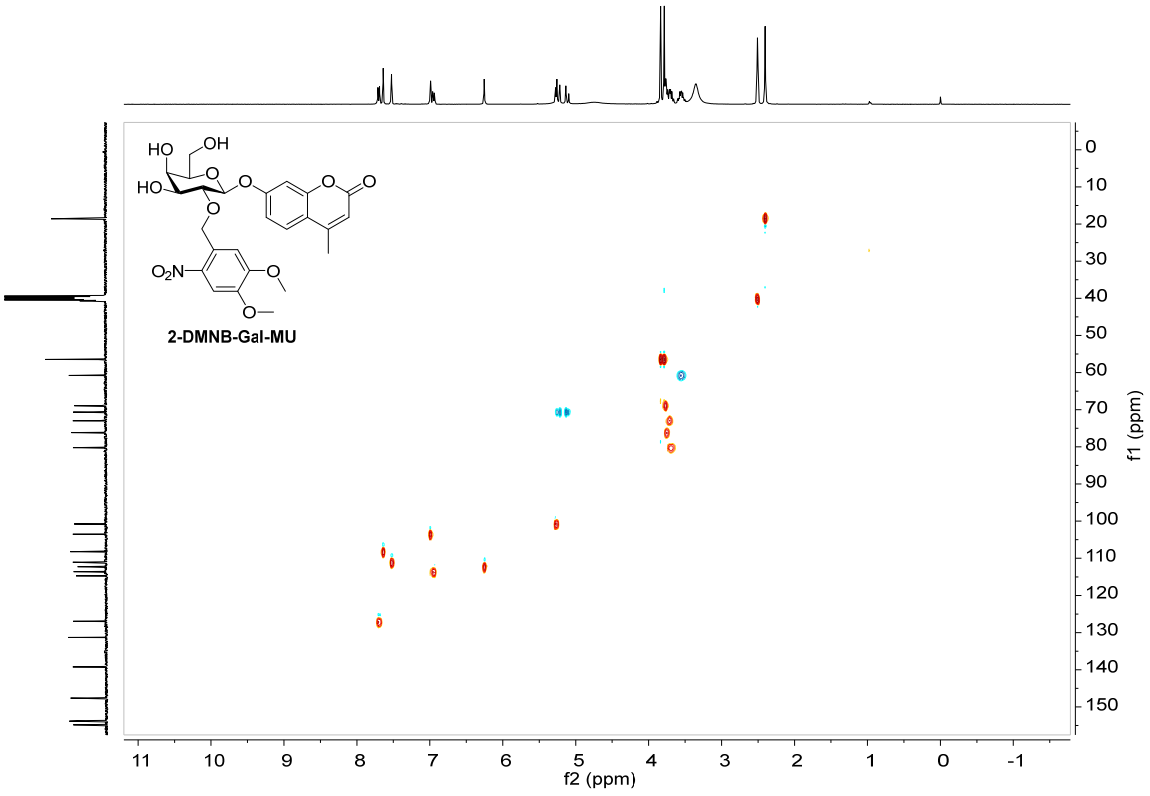
^{1}H NMR ($(CD_3)_2SO$, 400 MHz) of compound 2-DMNB-Gal-MU



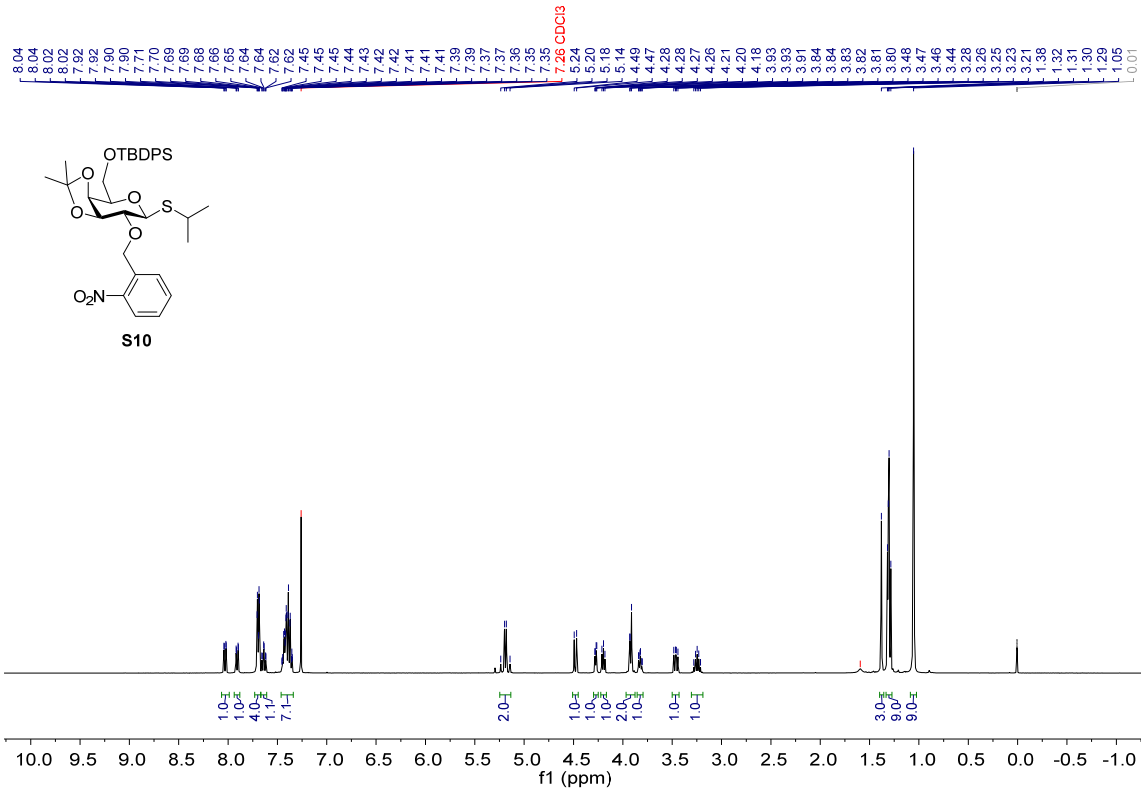
^{13}C NMR ($(CD_3)_2SO$, 101 MHz) of compound 2-DMNB-Gal-MU



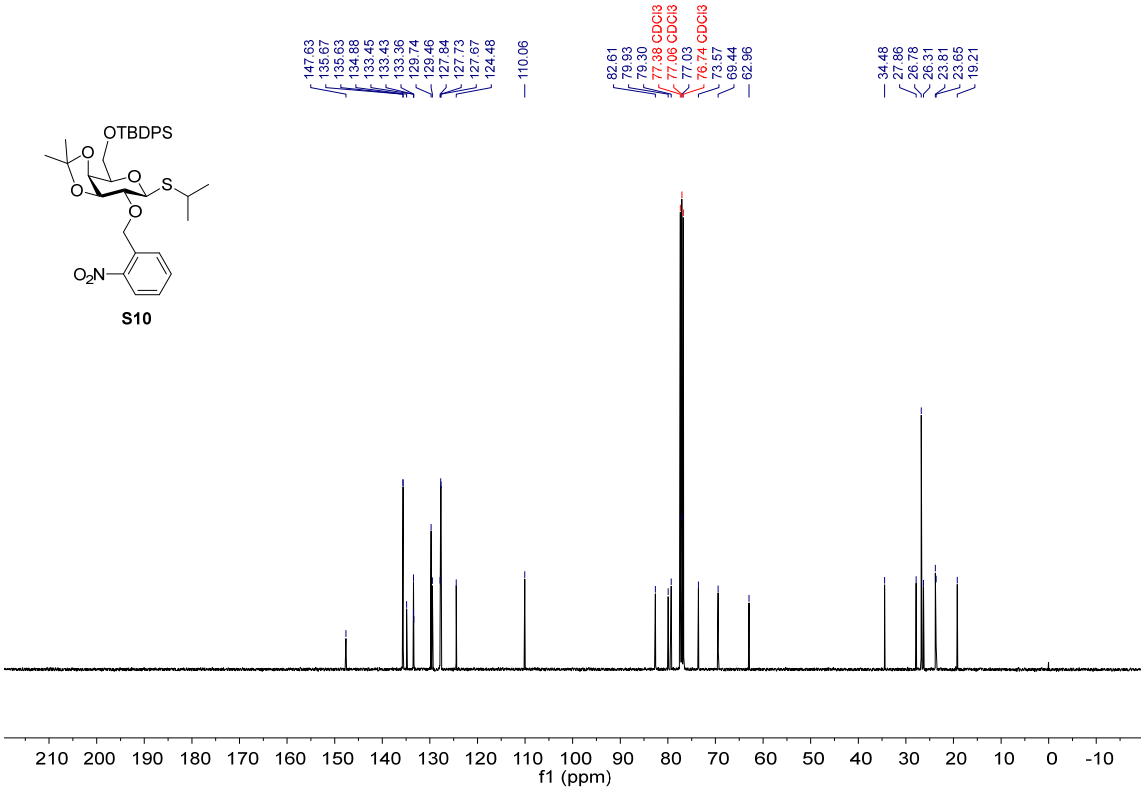
^{1}H-^{13}C HSQC NMR ($(CD_3)_2SO$, 400 MHz) of compound 2-DMNB-Gal-MU



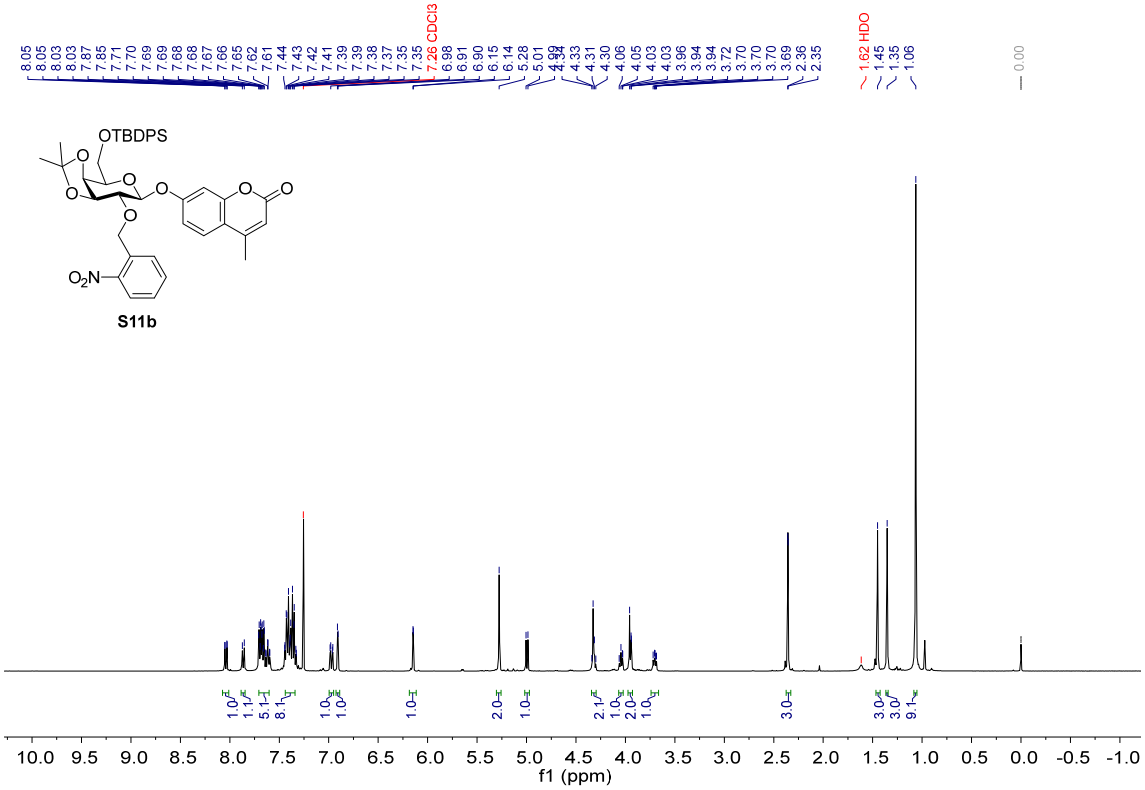
^{1}H NMR ($CDCl_3$, 400 MHz) of compound S10



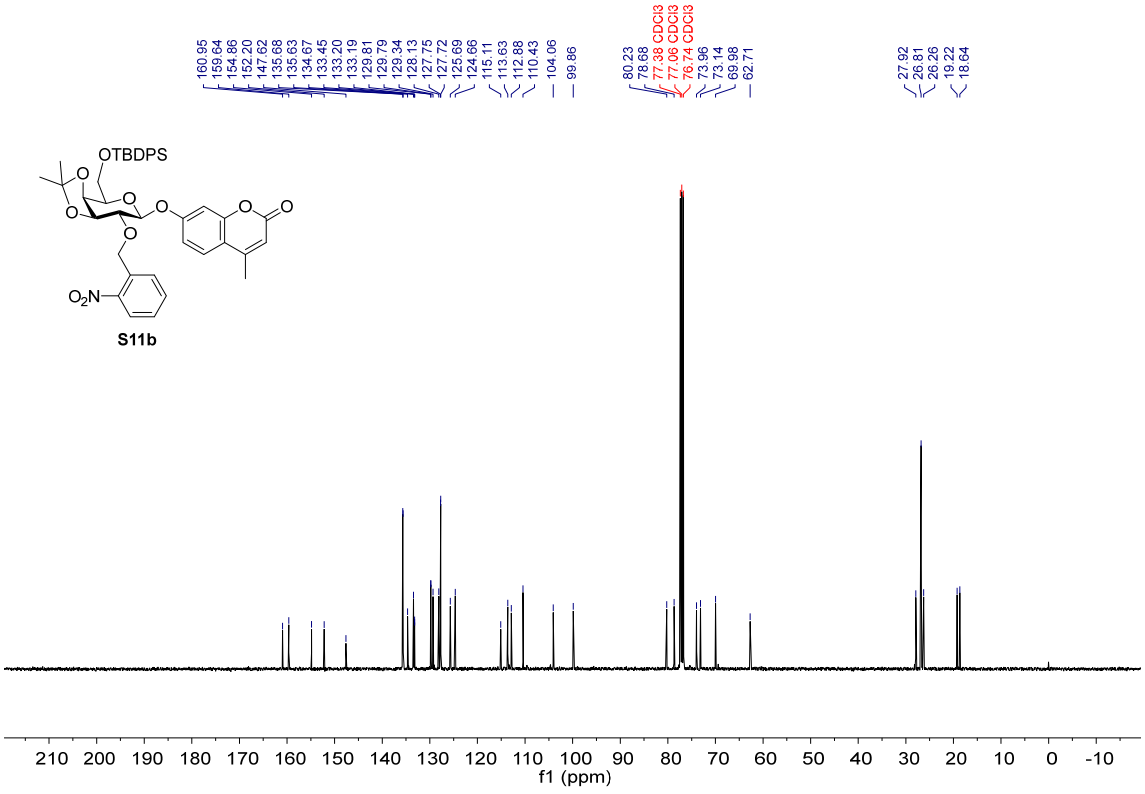
^{13}C NMR ($CDCl_3$, 101 MHz) of compound S10



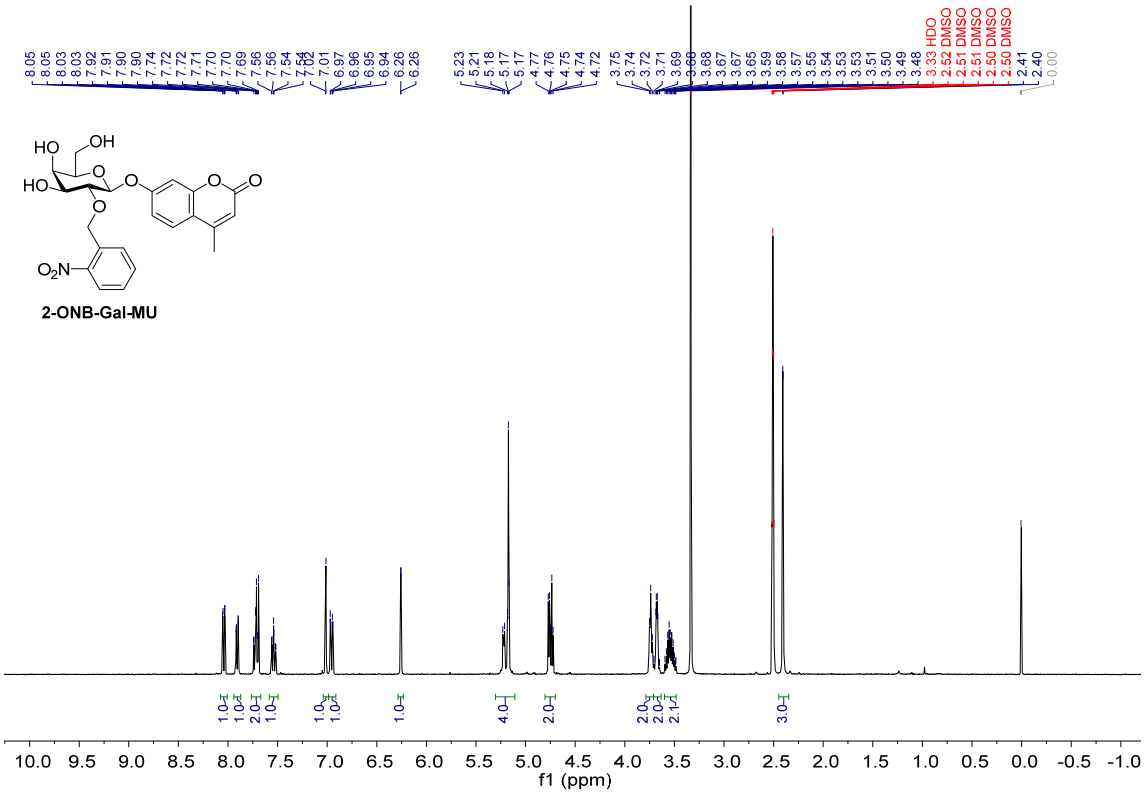
^{1}H NMR ($CDCl_3$, 400 MHz) of compound S11b



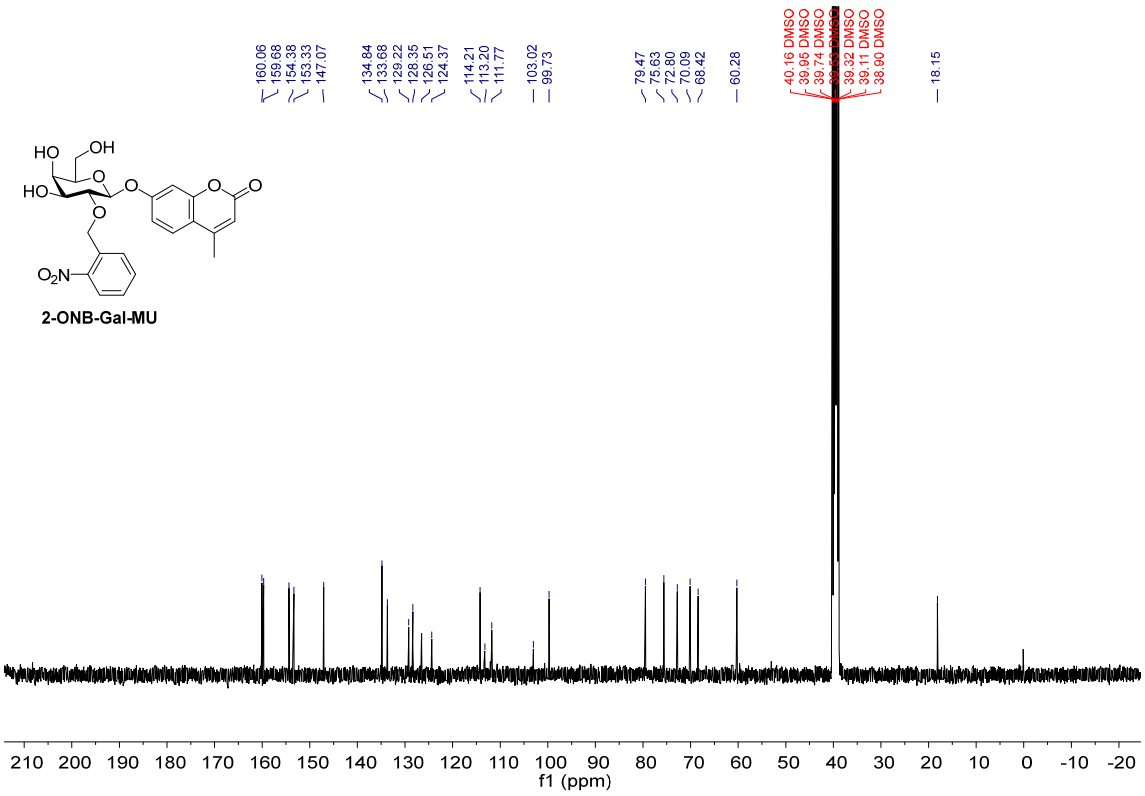
^{13}C NMR ($CDCl_3$, 101 MHz) of compound S11b



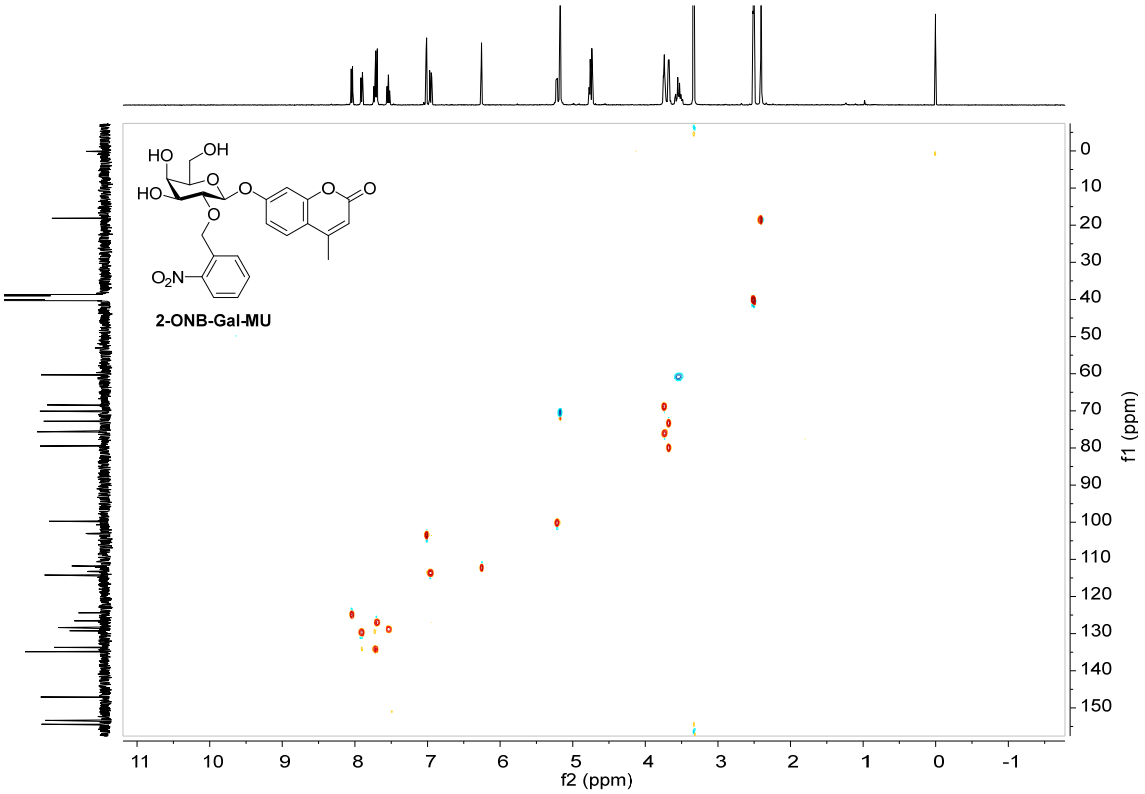
^{1}H NMR ($(CD_3)_2SO$, 400 MHz) of compound 2-ONB-Gal-MU



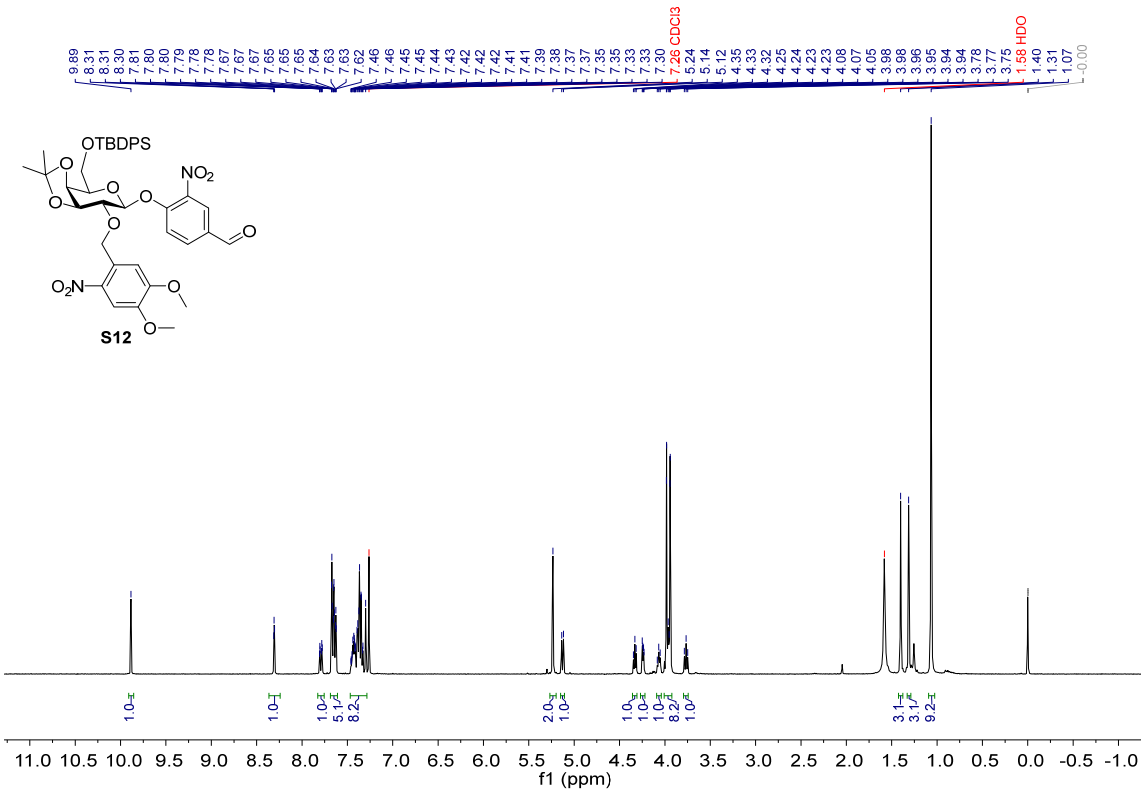
^{13}C NMR ($(CD_3)_2SO$, 101 MHz) of compound 2-ONB-Gal-MU



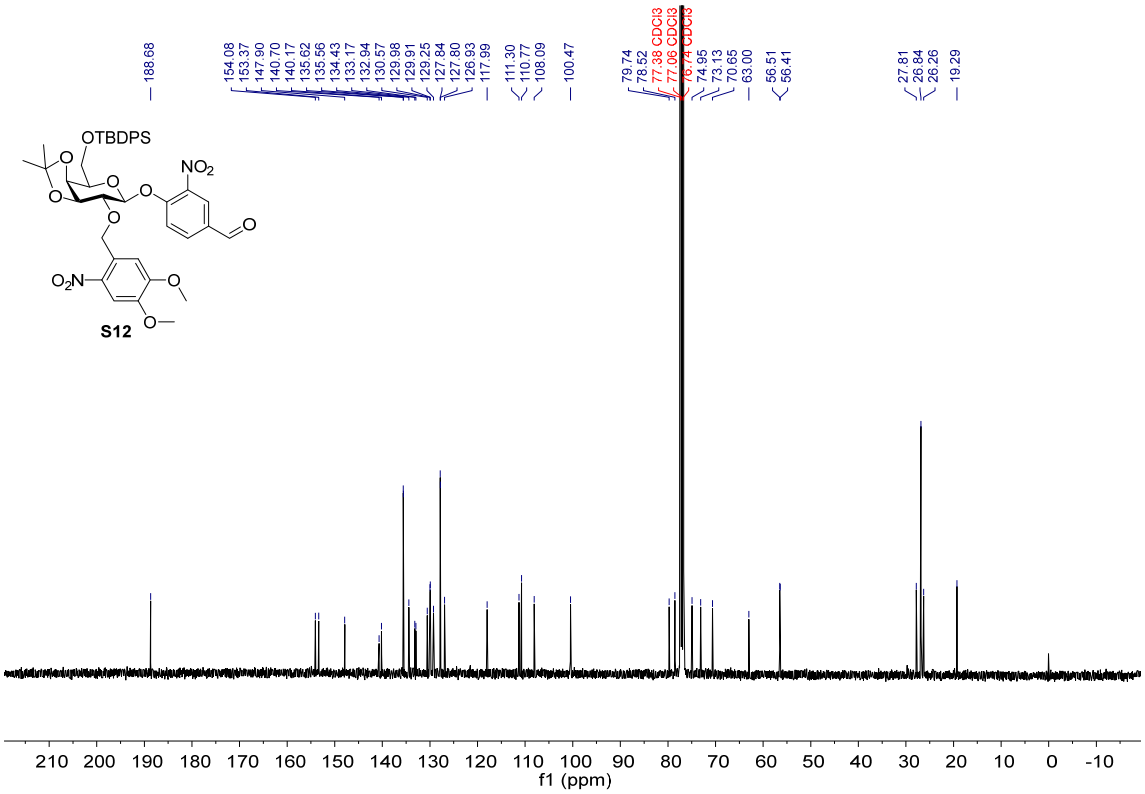
^{1}H-^{13}C HSQC NMR ($(CD_3)_2SO$, 400 MHz) of compound 2-ONB-Gal-MU



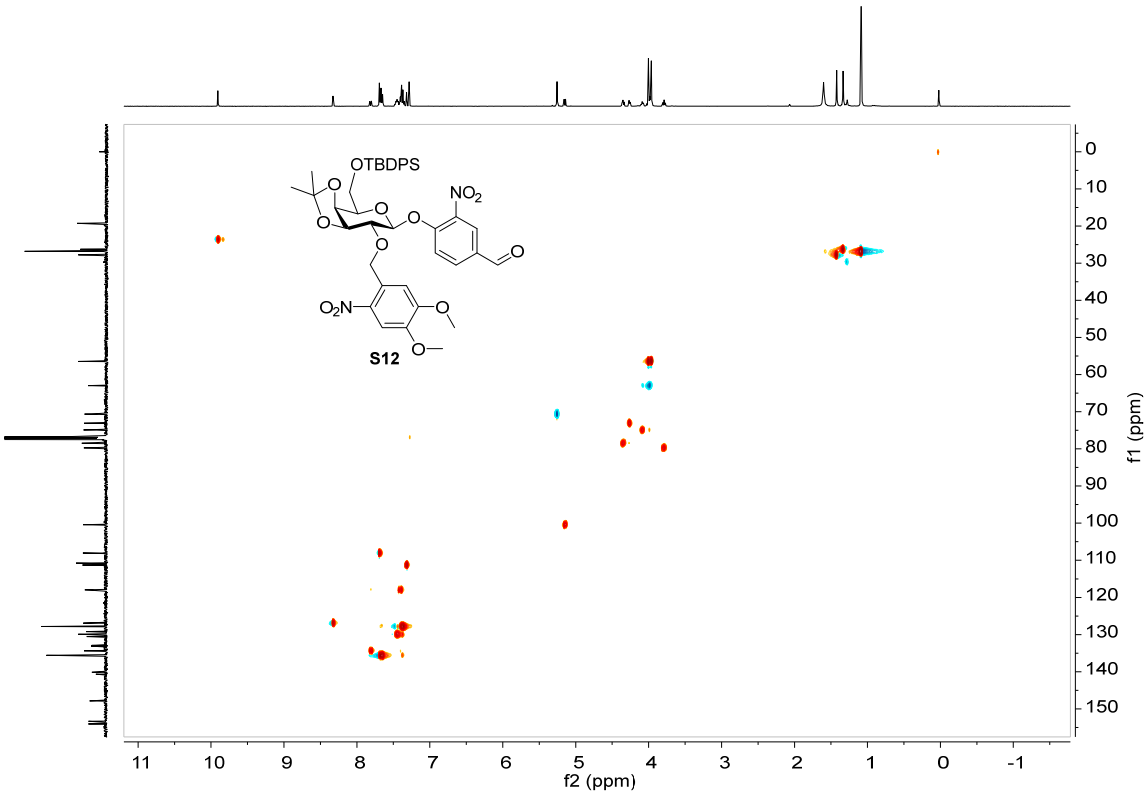
^{1}H NMR ($CDCl_3$, 400 MHz) of compound S12



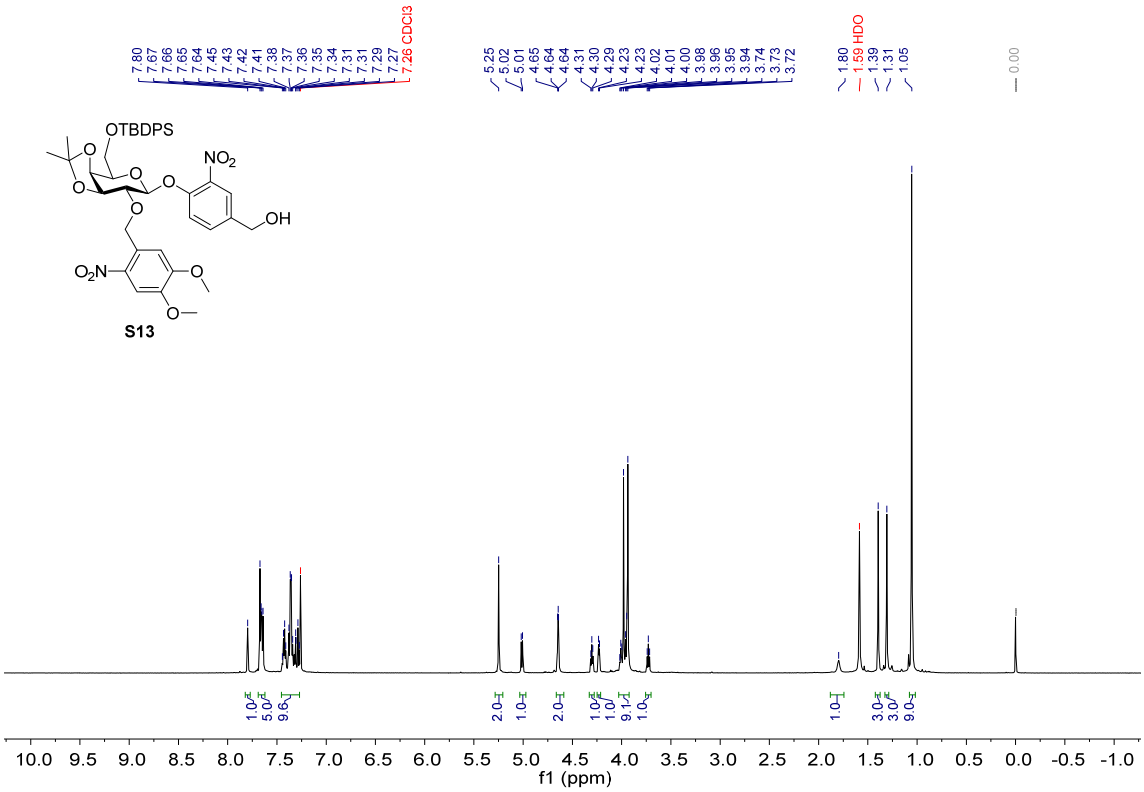
^{13}C NMR ($CDCl_3$, 101 MHz) of compound S12



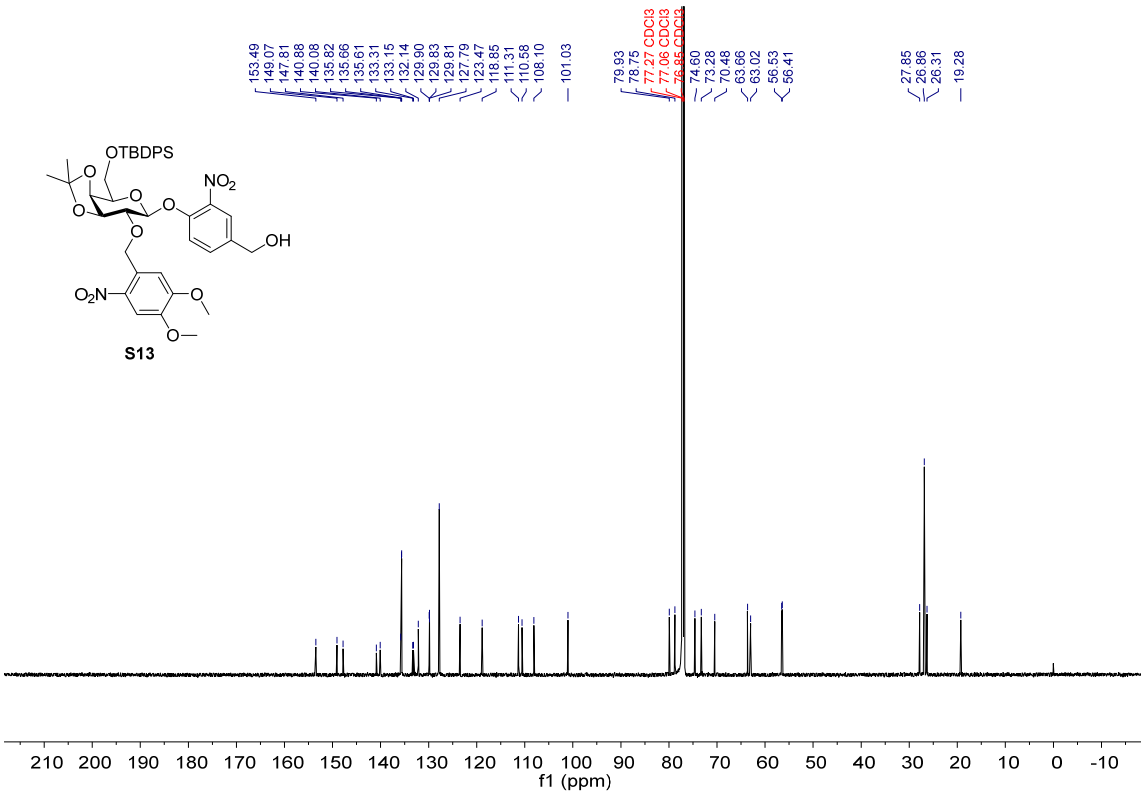
^{1}H-^{13}C HSQC NMR ($CDCl_3$, 400 MHz) of compound S12



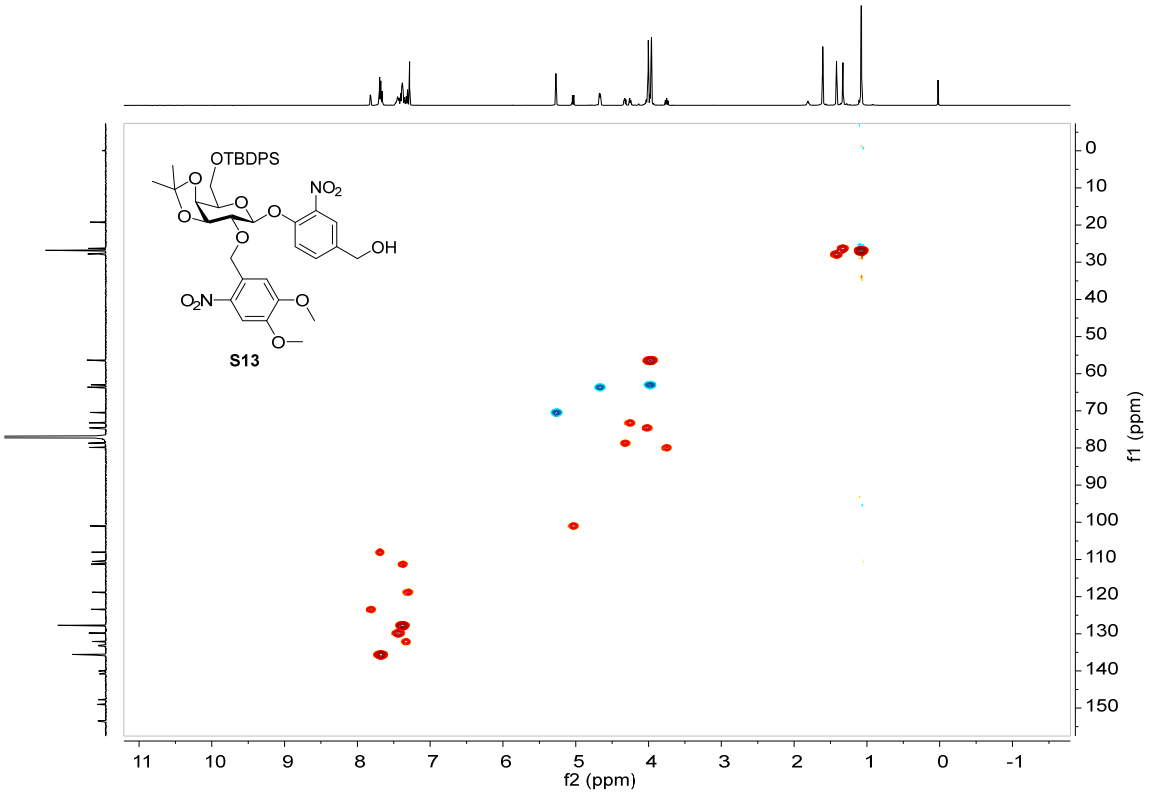
^{1}H NMR ($CDCl_3$, 600 MHz) of compound S13



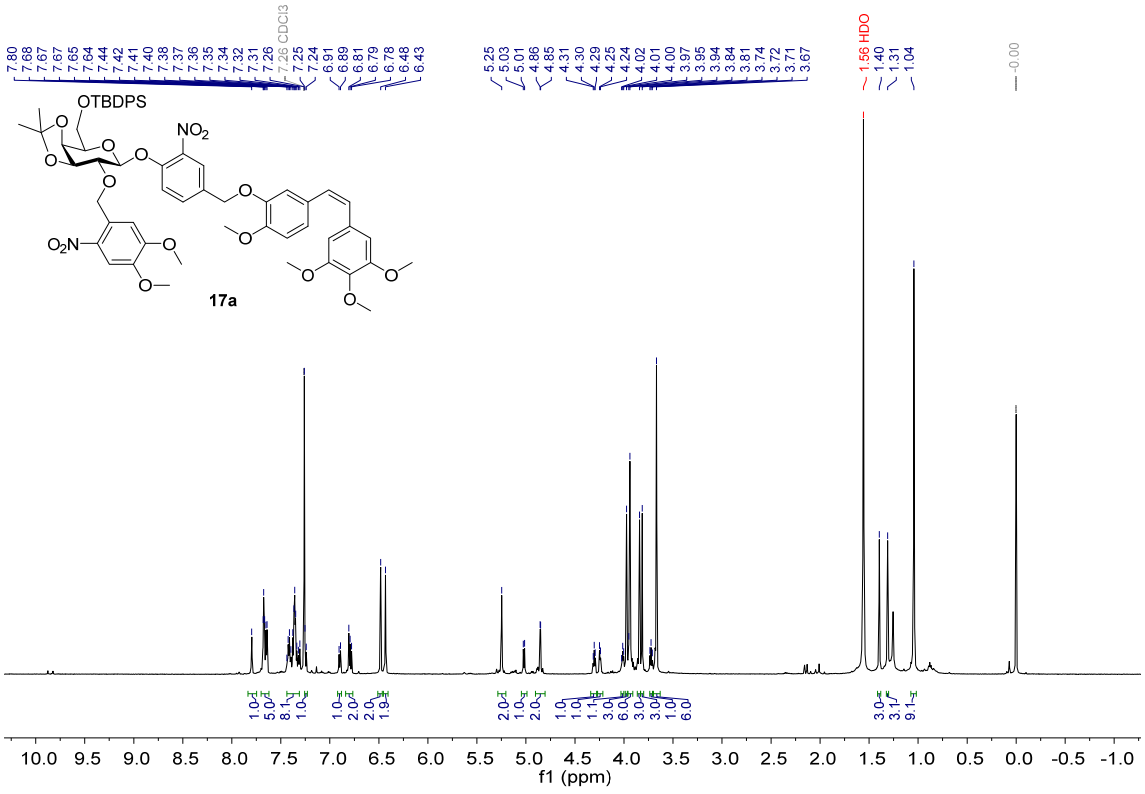
^{13}C NMR ($CDCl_3$, 151 MHz) of compound S13



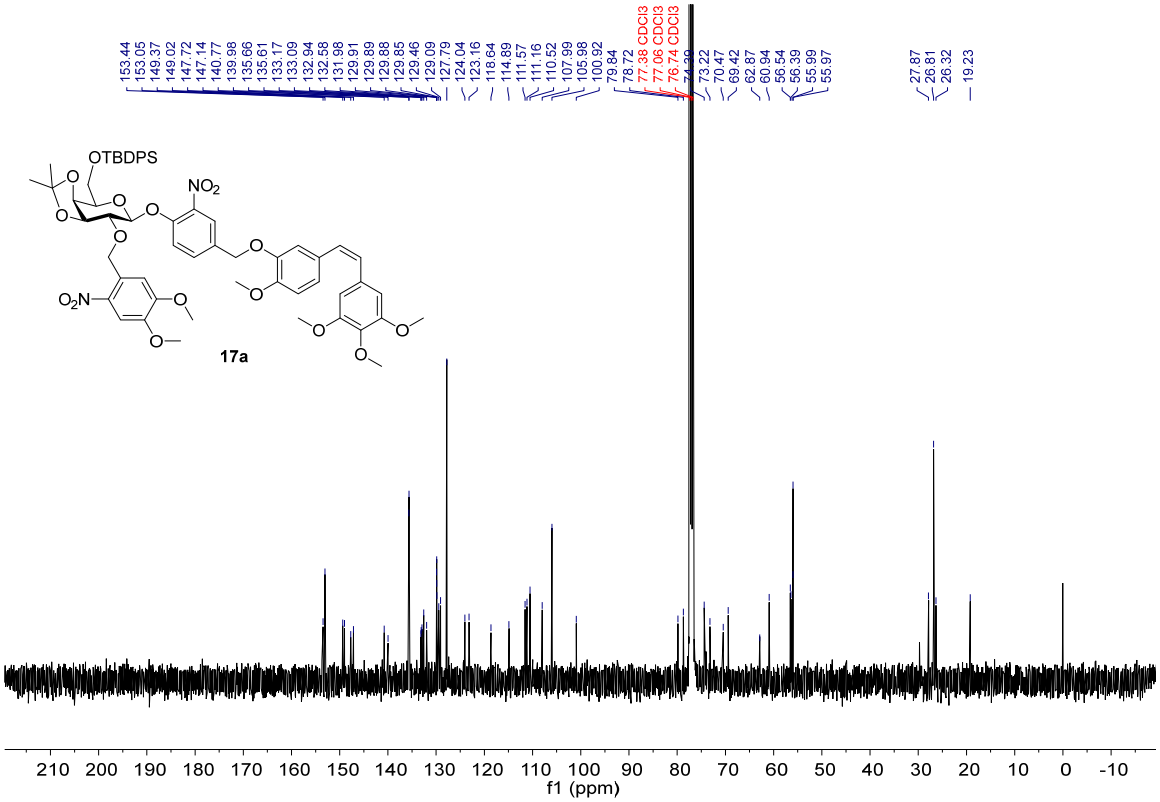
^{1}H-^{13}C HSQC NMR ($CDCl_3$, 600 MHz) of compound S13



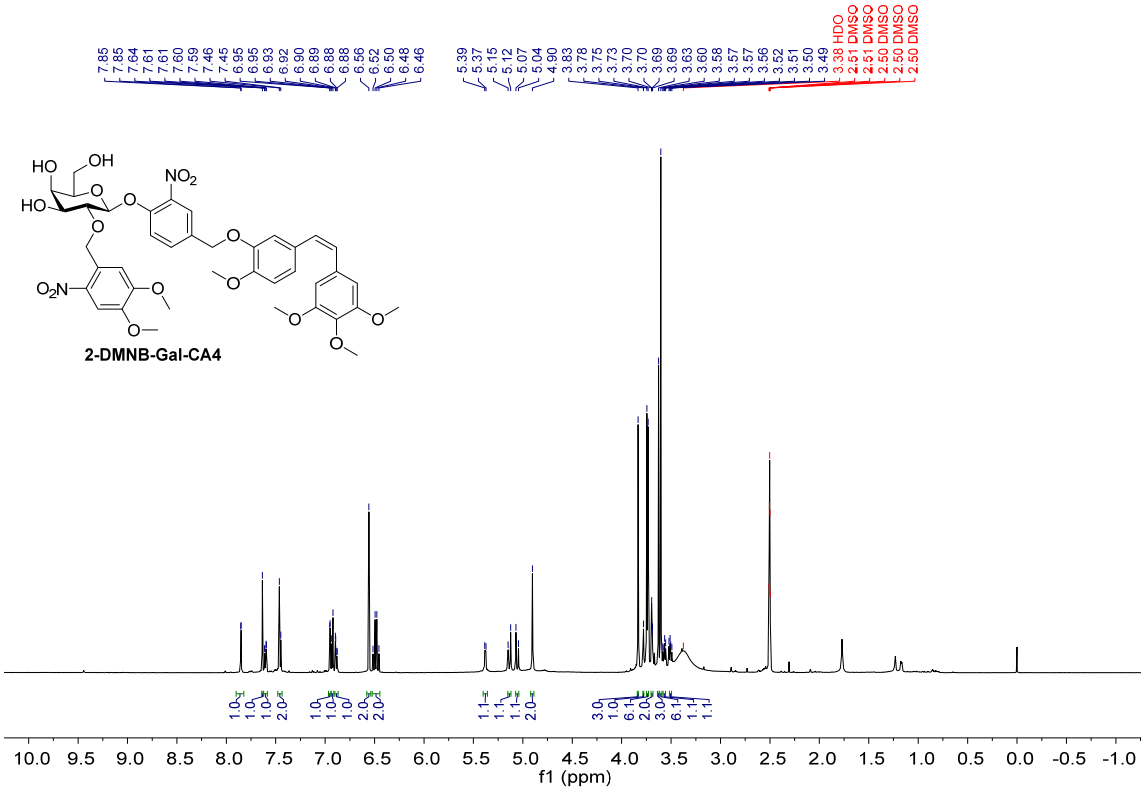
^{1}H NMR ($CDCl_3$, 600 MHz) of compound 17a



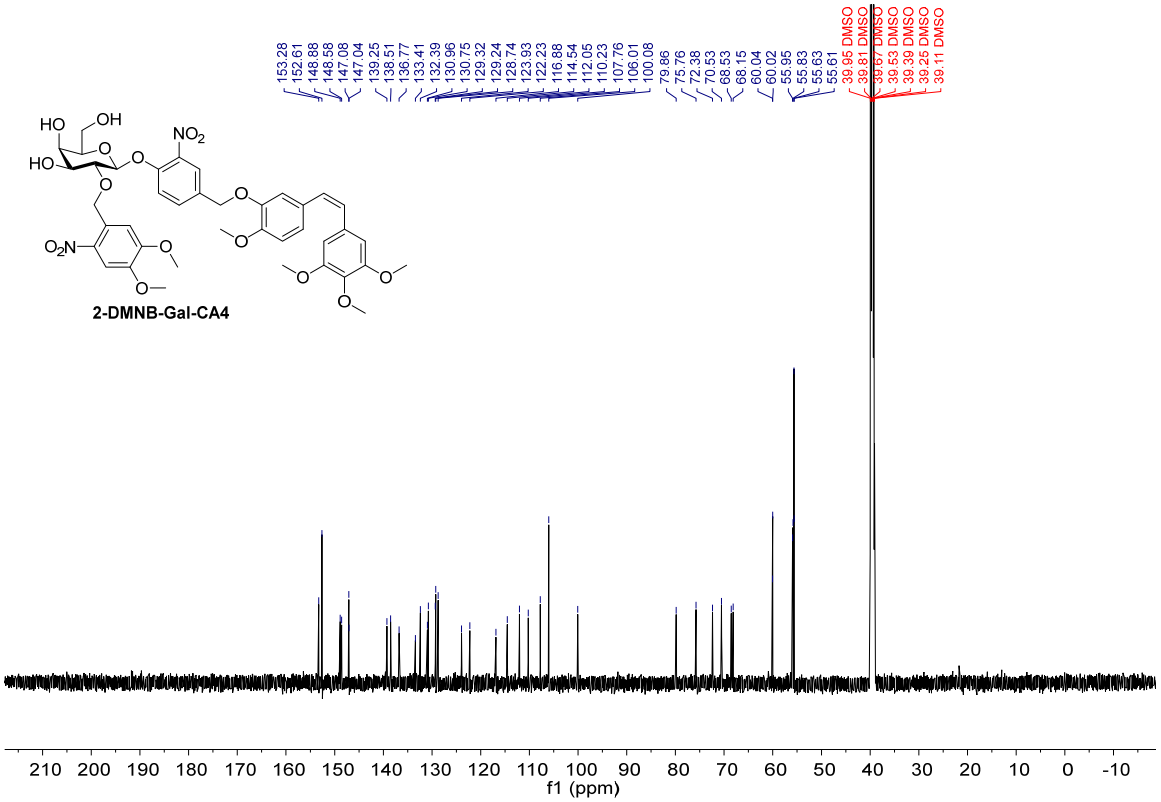
^{13}C NMR ($CDCl_3$, 101 MHz) of compound 17a



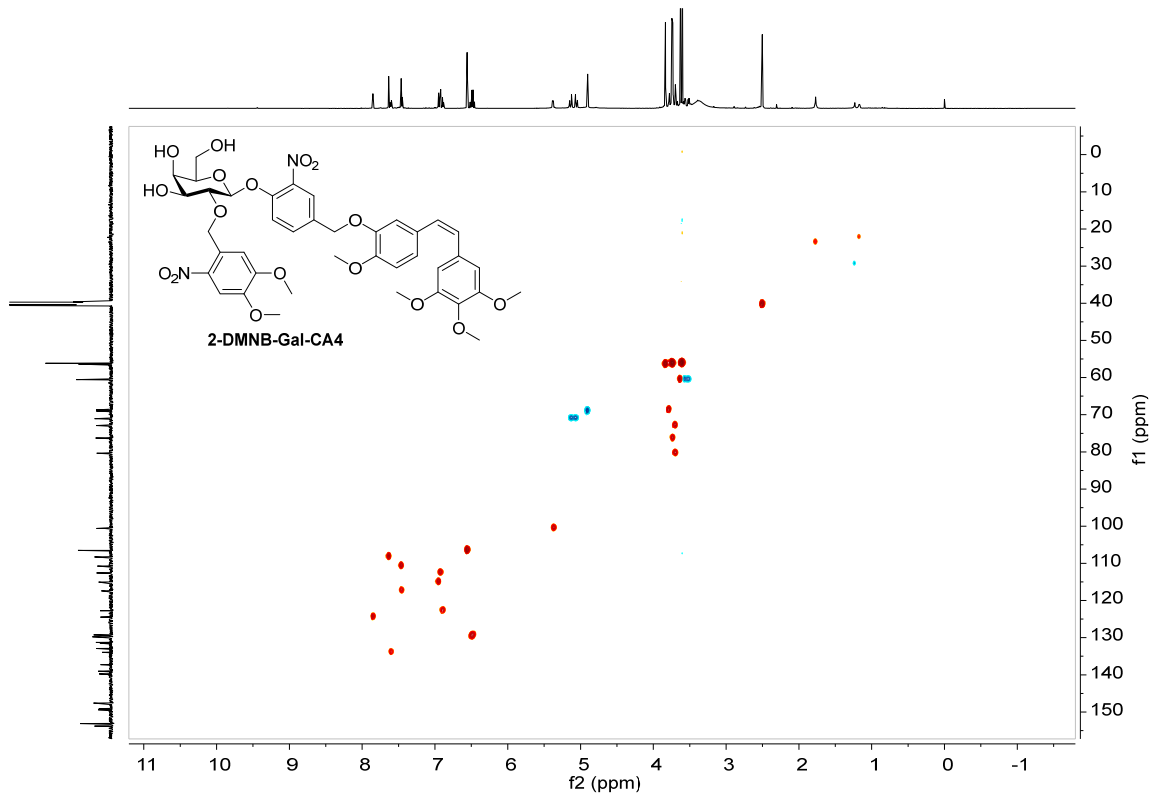
^{1}H NMR ($(CD_3)_2SO$, 600 MHz) of compound 2-DMNB-Gal-CA4



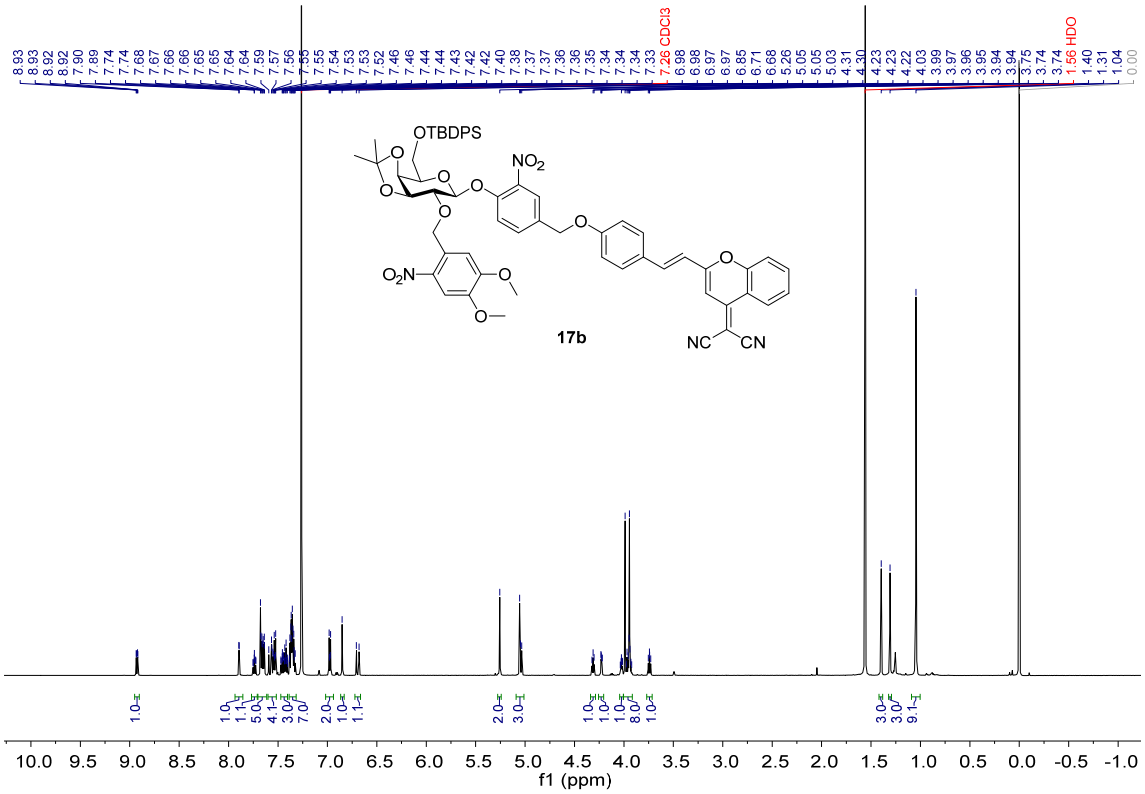
^{13}C NMR ((CD$_3$)$_2$SO, 151 MHz) of compound 2-DMNB-Gal-CA4



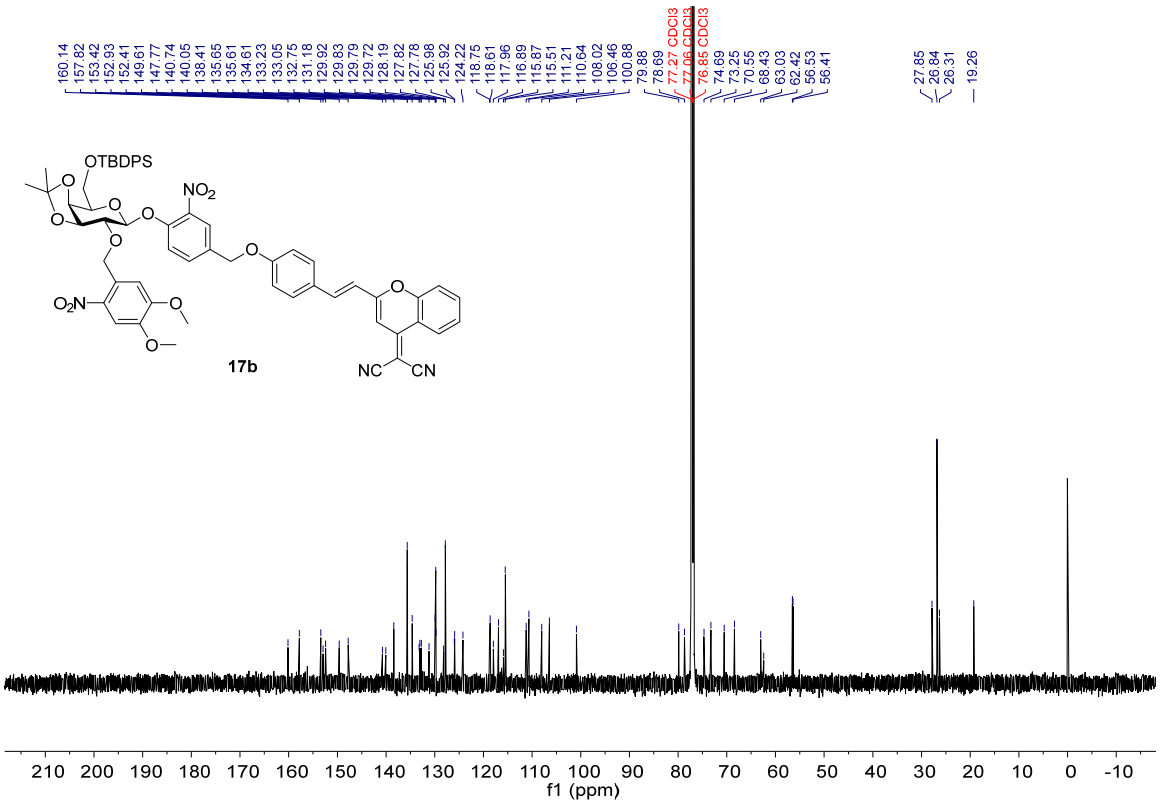
^{1}H-^{13}C HSQC NMR ((CD$_3$)$_2$SO, 600 MHz) of compound 2-DMNB-Gal-CA4



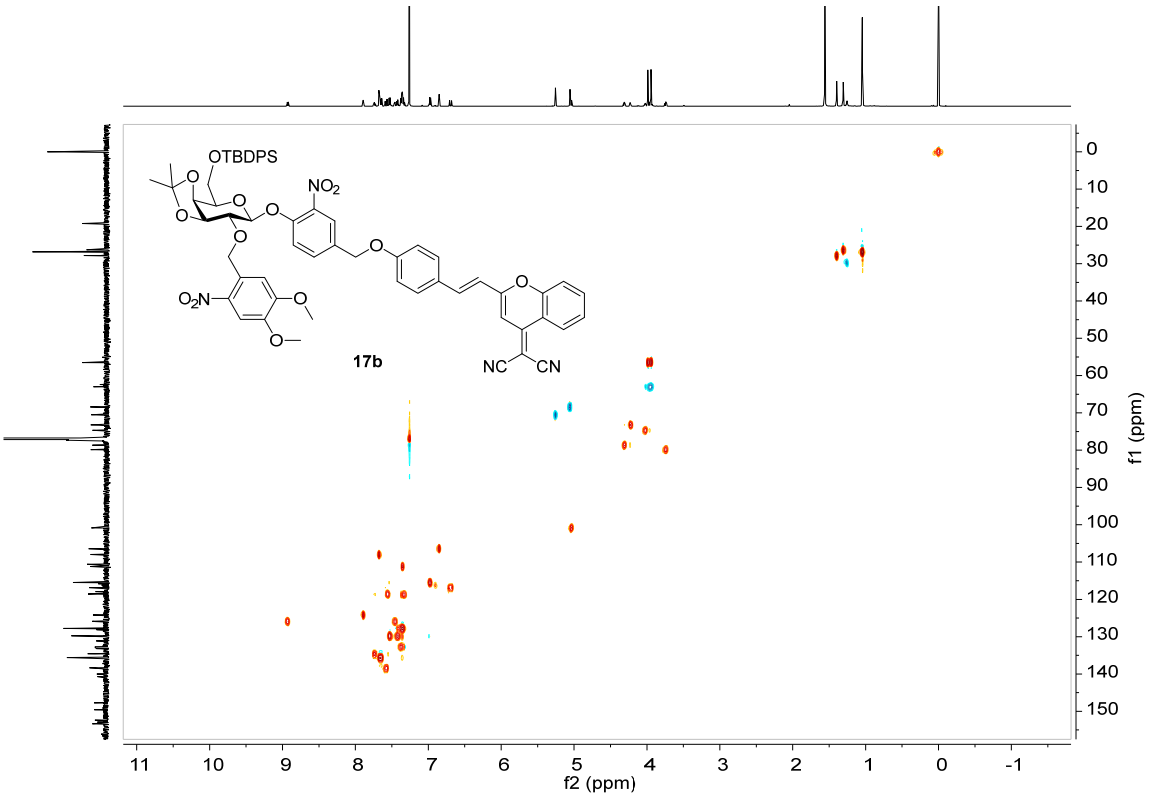
^{1}H NMR ($CDCl_3$, 600 MHz) of compound 17b



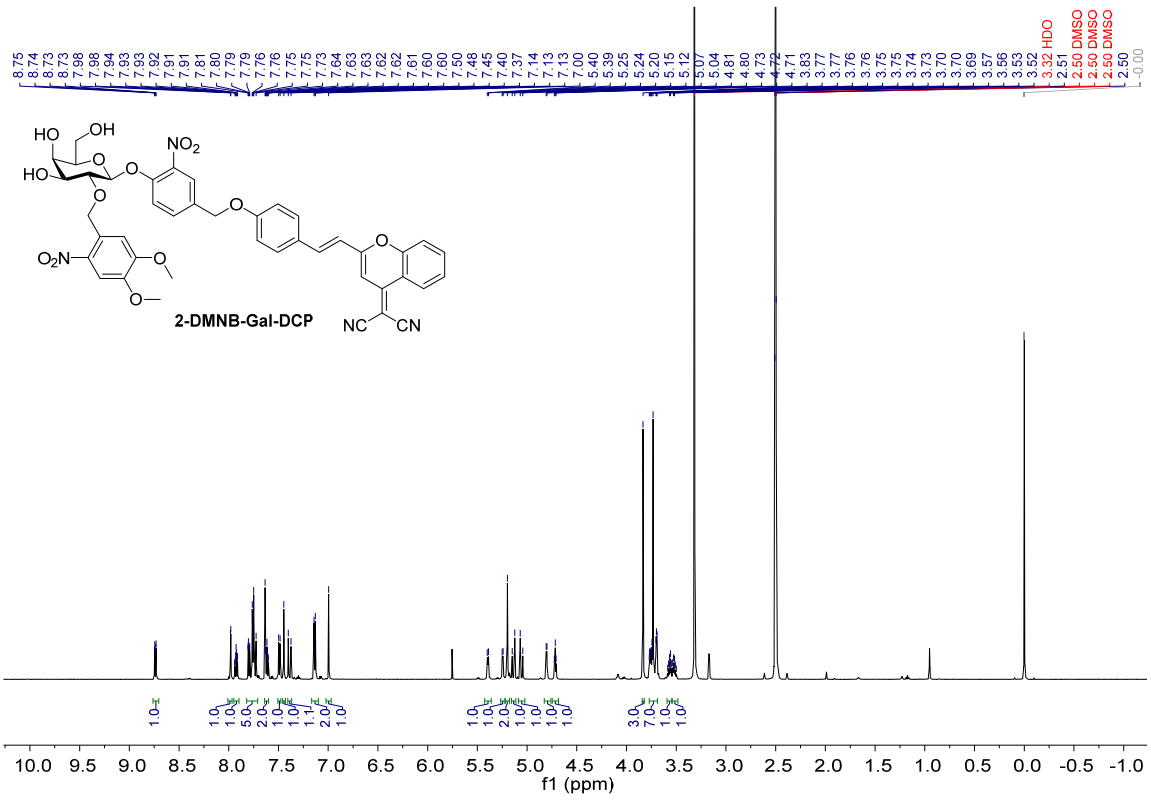
^{13}C NMR ($CDCl_3$, 151 MHz) of compound 17b



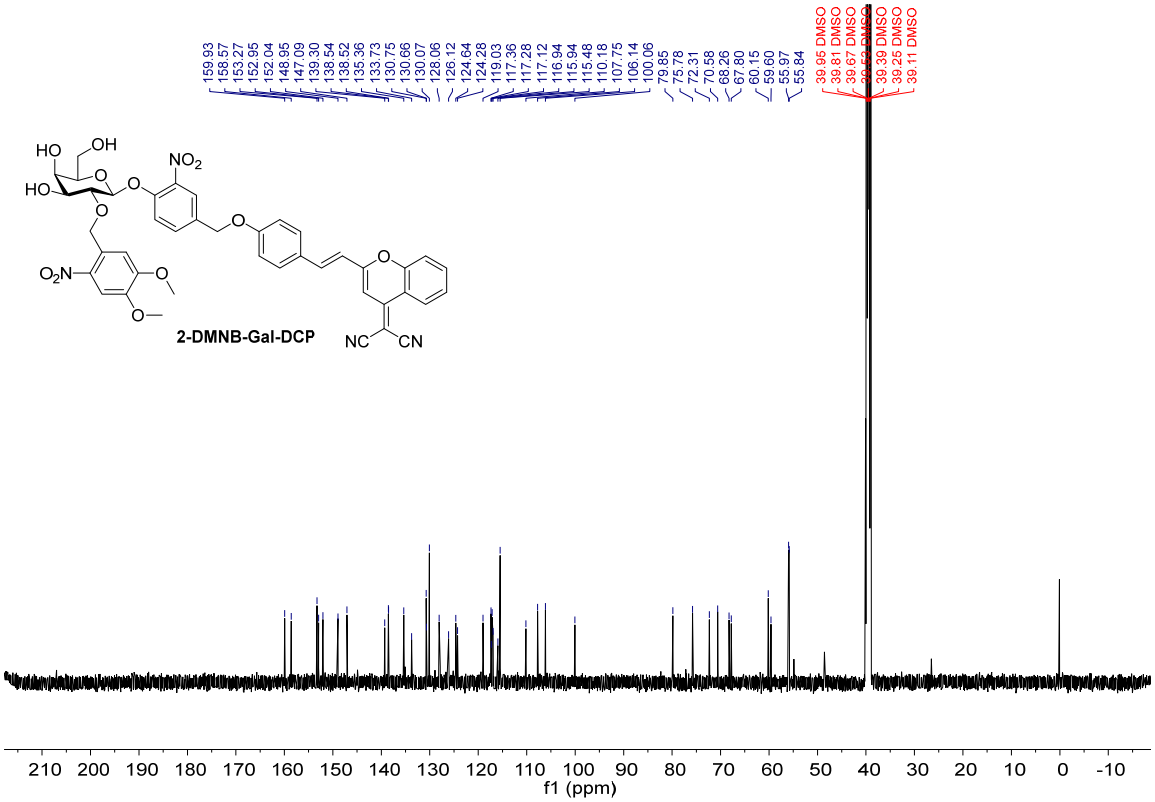
^{1}H-^{13}C HSQC NMR ($CDCl_3$, 600 MHz) of compound 17b



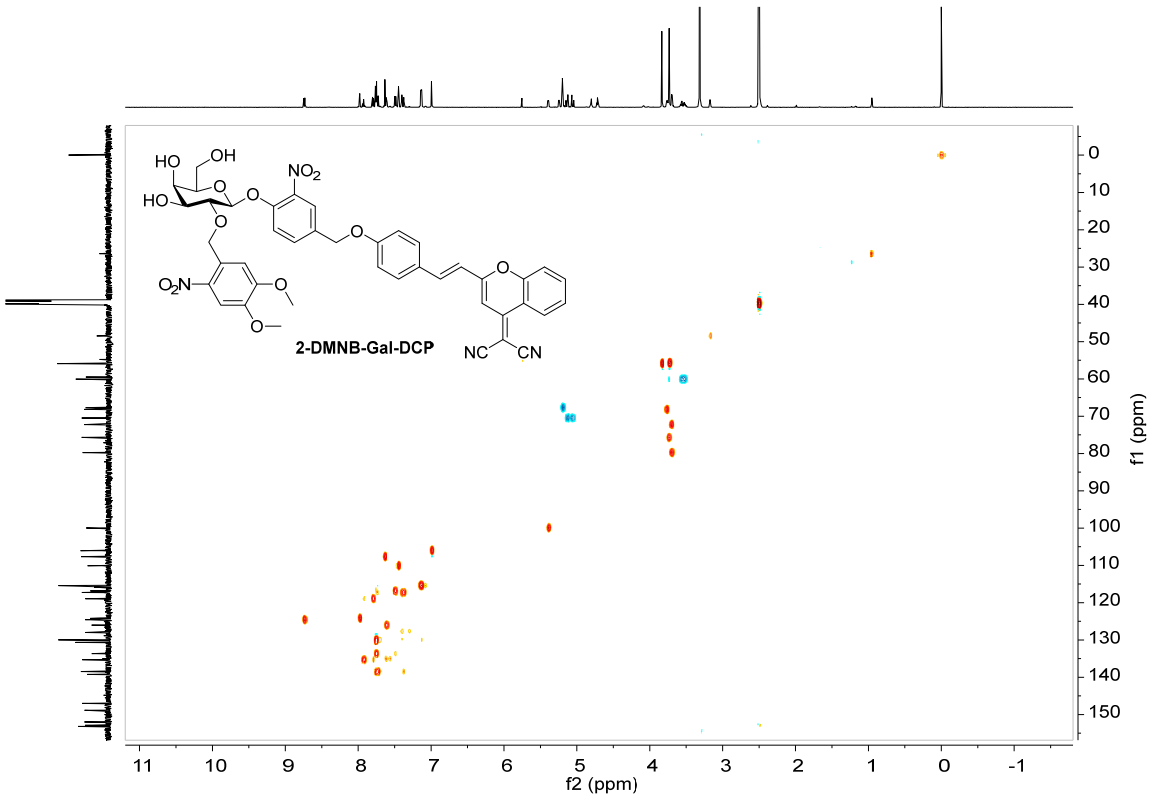
^{1}H NMR ($(CD_3)_2SO$, 600 MHz) of compound 2-DMNB-Gal-DCP



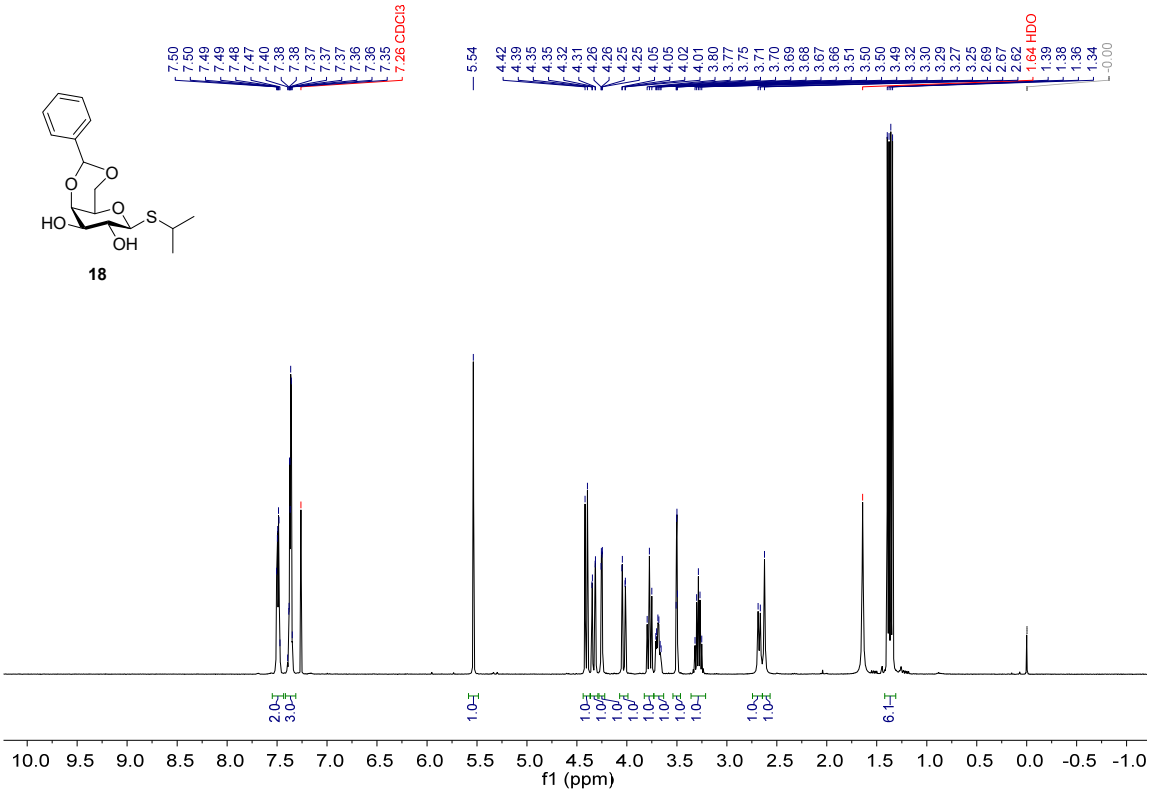
^{13}C NMR ((CD$_3$)$_2$SO, 151 MHz) of compound 2-DMNB-Gal-DCP



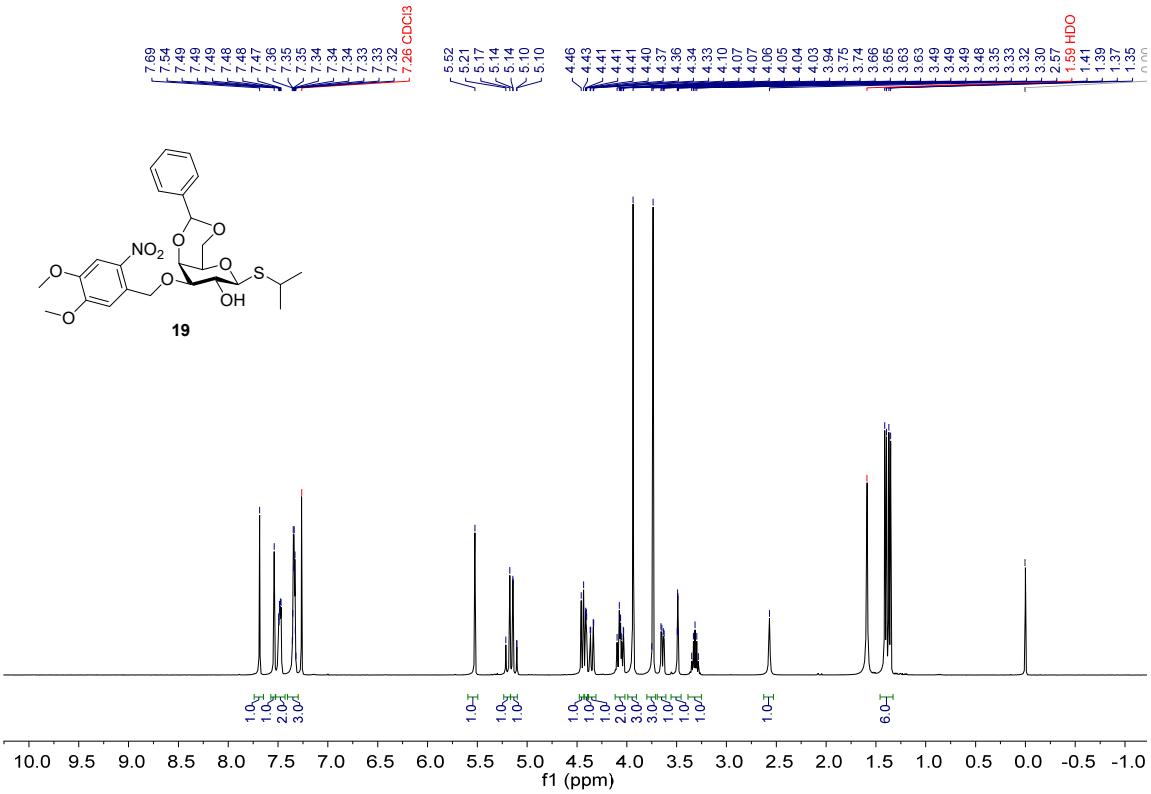
^{1}H-^{13}C HSQC NMR ((CD$_3$)$_2$SO, 600 MHz) of compound 2-DMNB-Gal-DCP



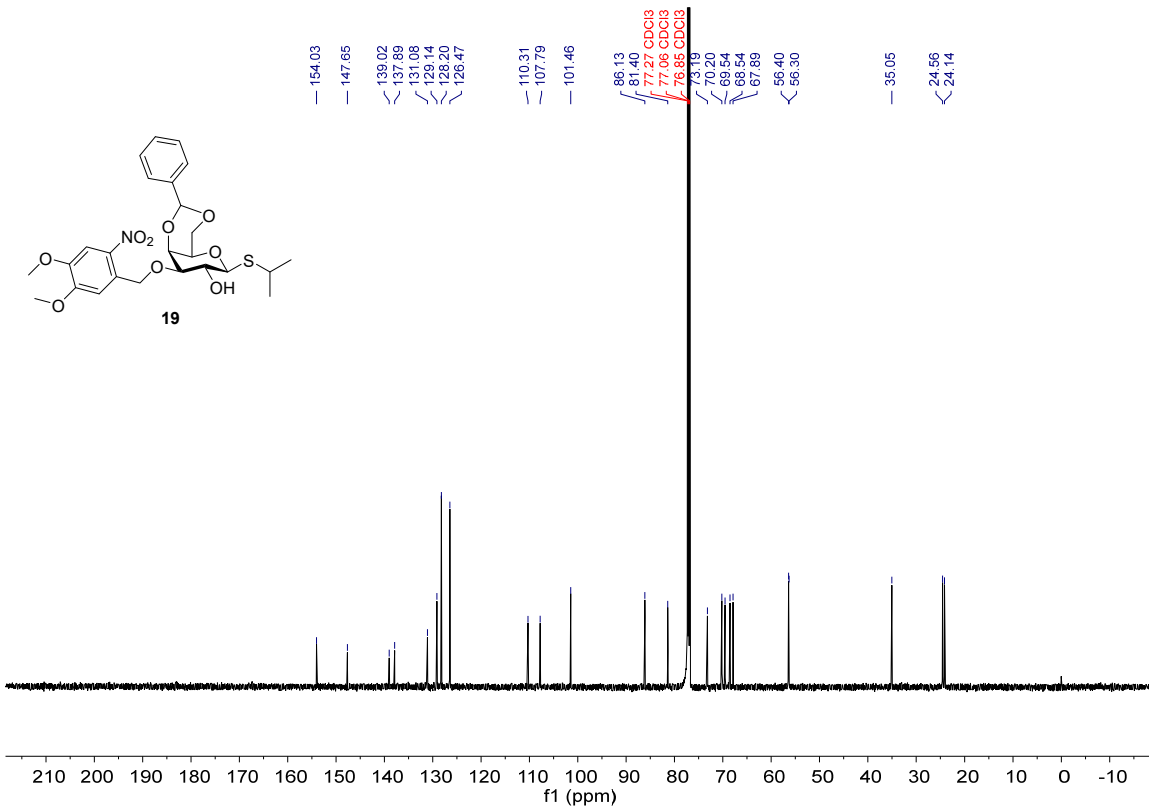
^{1}H NMR ($CDCl_3$, 400 MHz) of compound 18



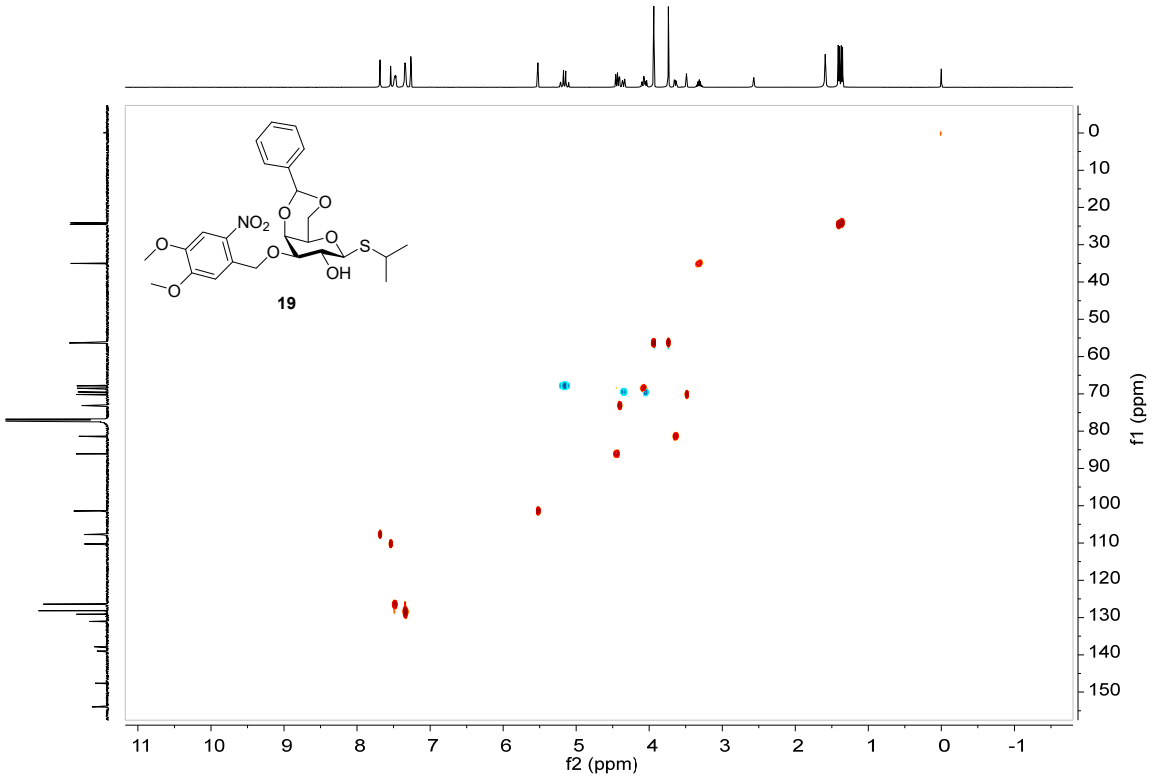
^{1}H NMR ($CDCl_3$, 400 MHz) of compound 19



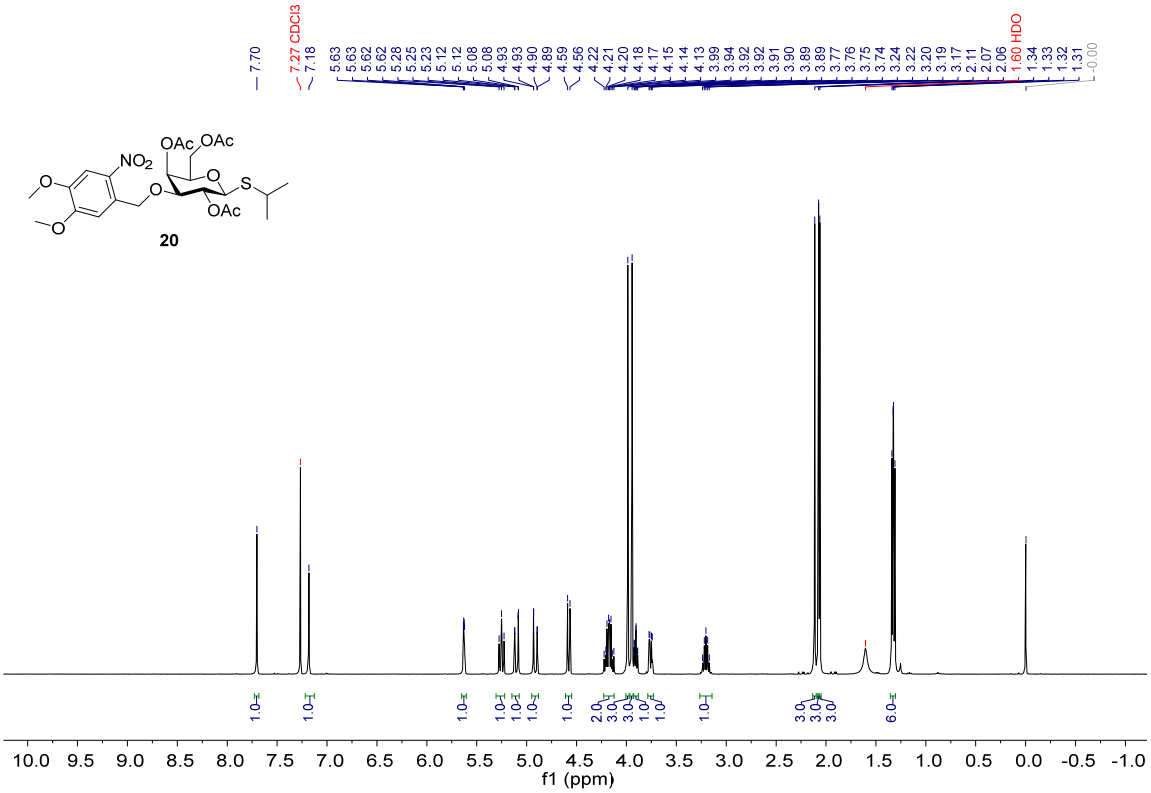
^{13}C NMR ($CDCl_3$, 151 MHz) of compound 19



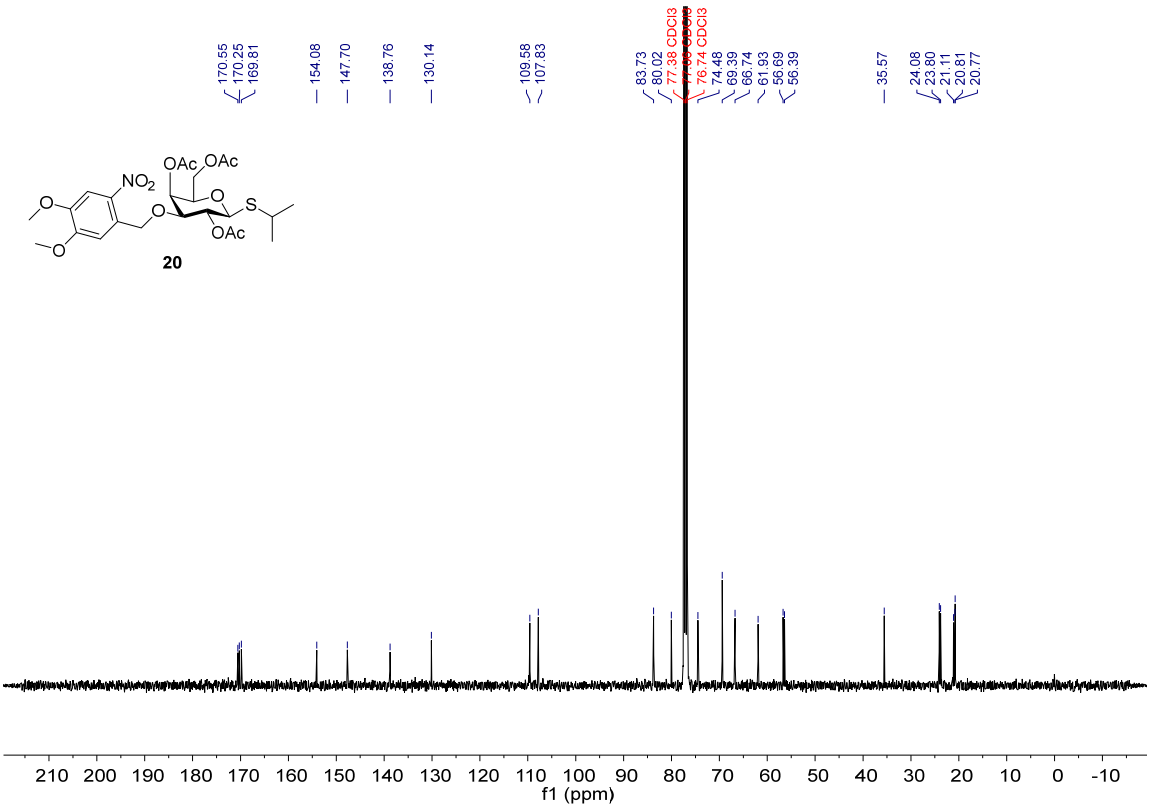
^{1}H-^{13}C HSQC NMR ($CDCl_3$, 400 MHz) of compound 19



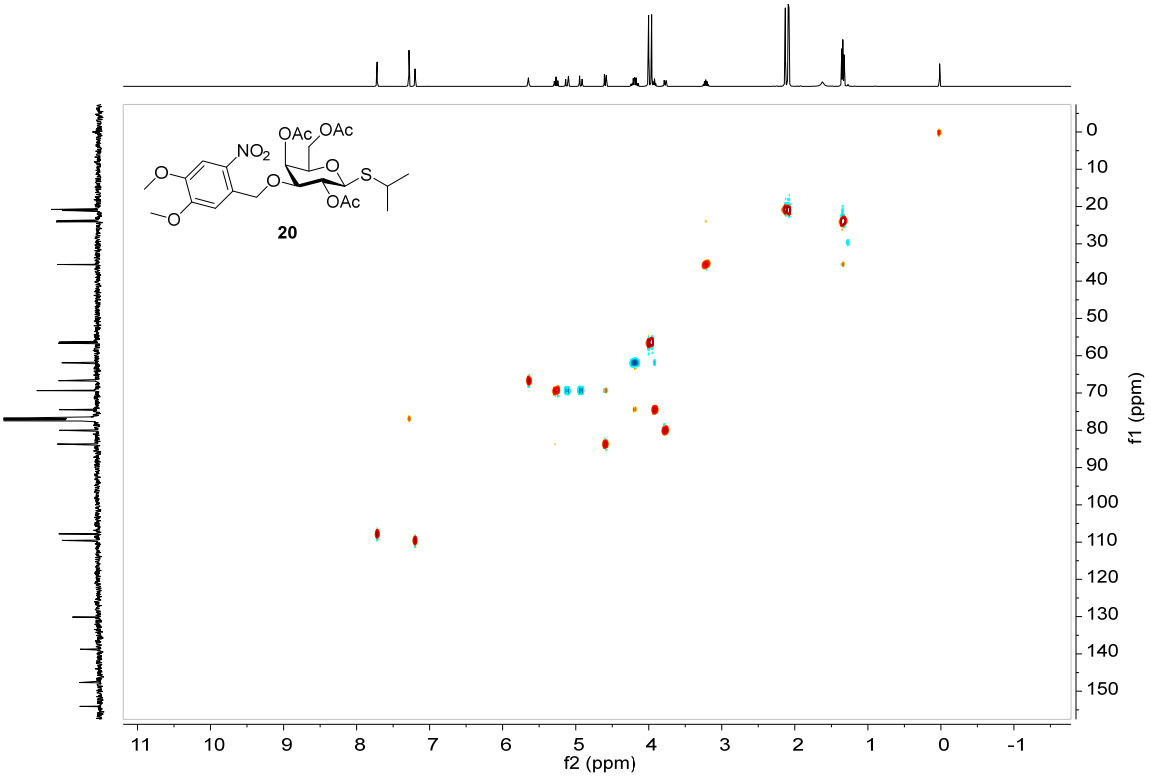
^{1}H NMR ($CDCl_3$, 400 MHz) of compound 20



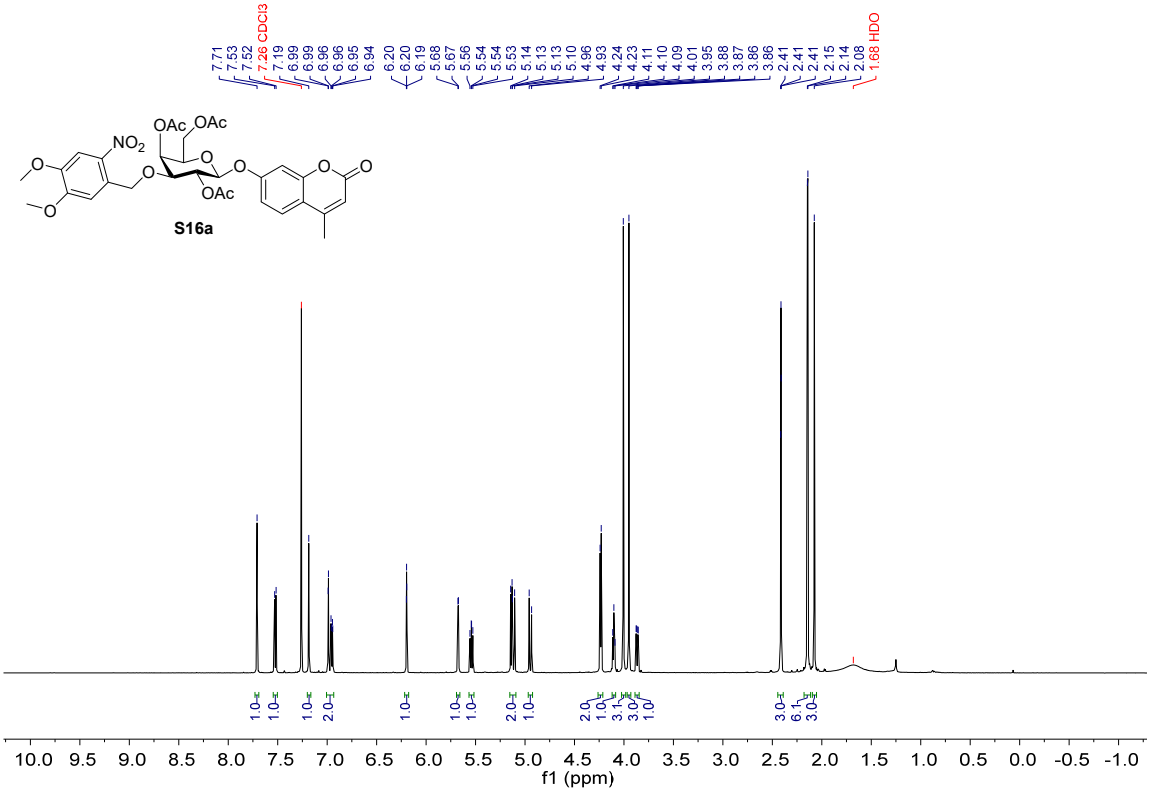
^{13}C NMR ($CDCl_3$, 101 MHz) of compound 20



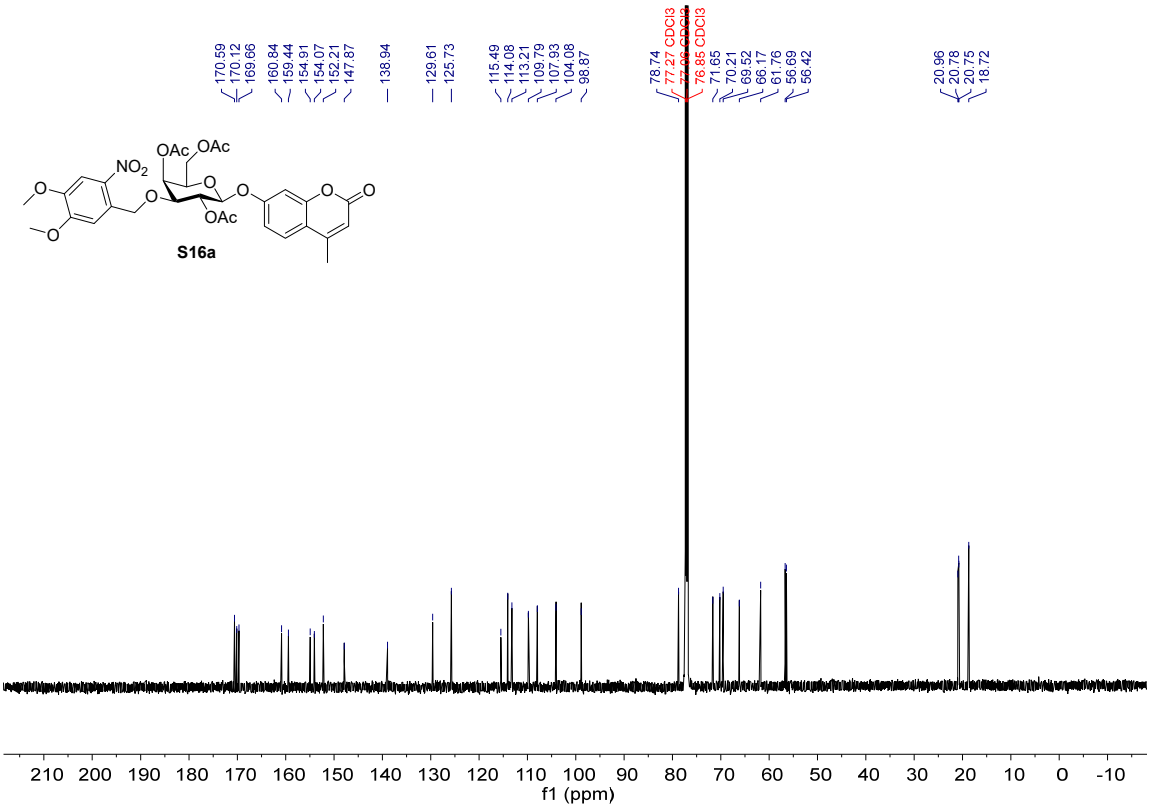
^{1}H-^{13}C HSQC NMR ($CDCl_3$, 400 MHz) of compound 20



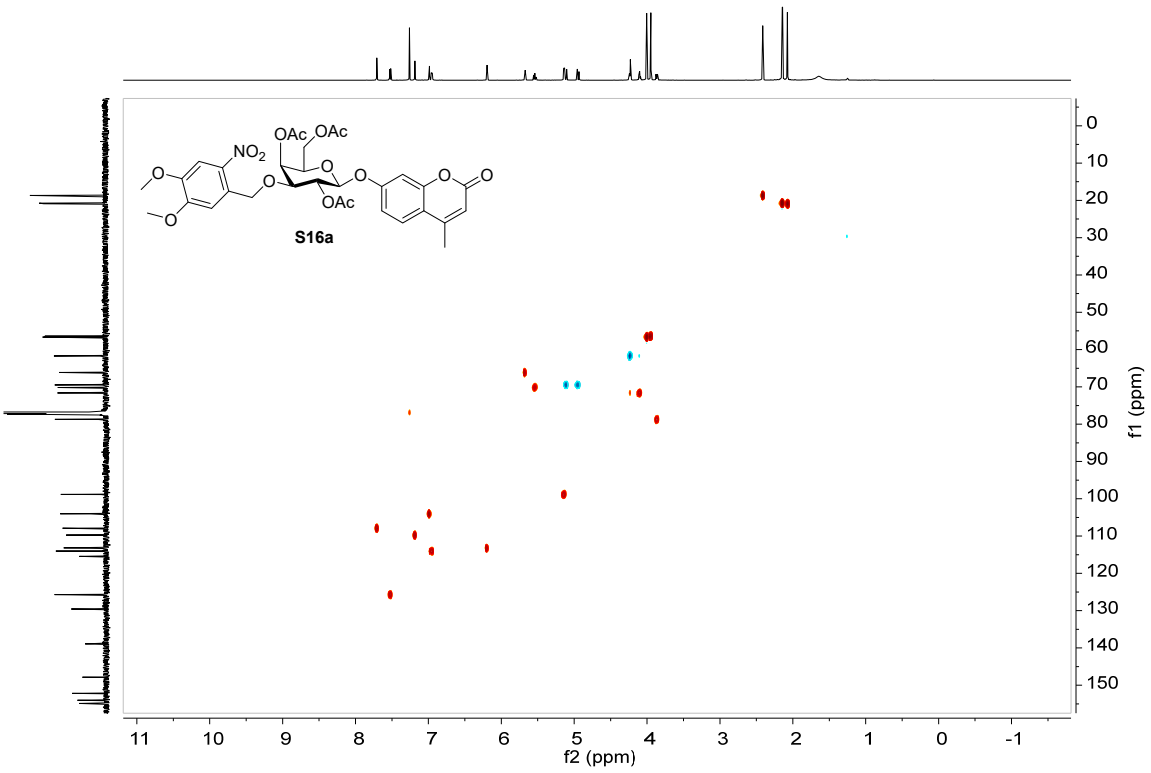
^{1}H NMR ($CDCl_3$, 600 MHz) of compound S16a



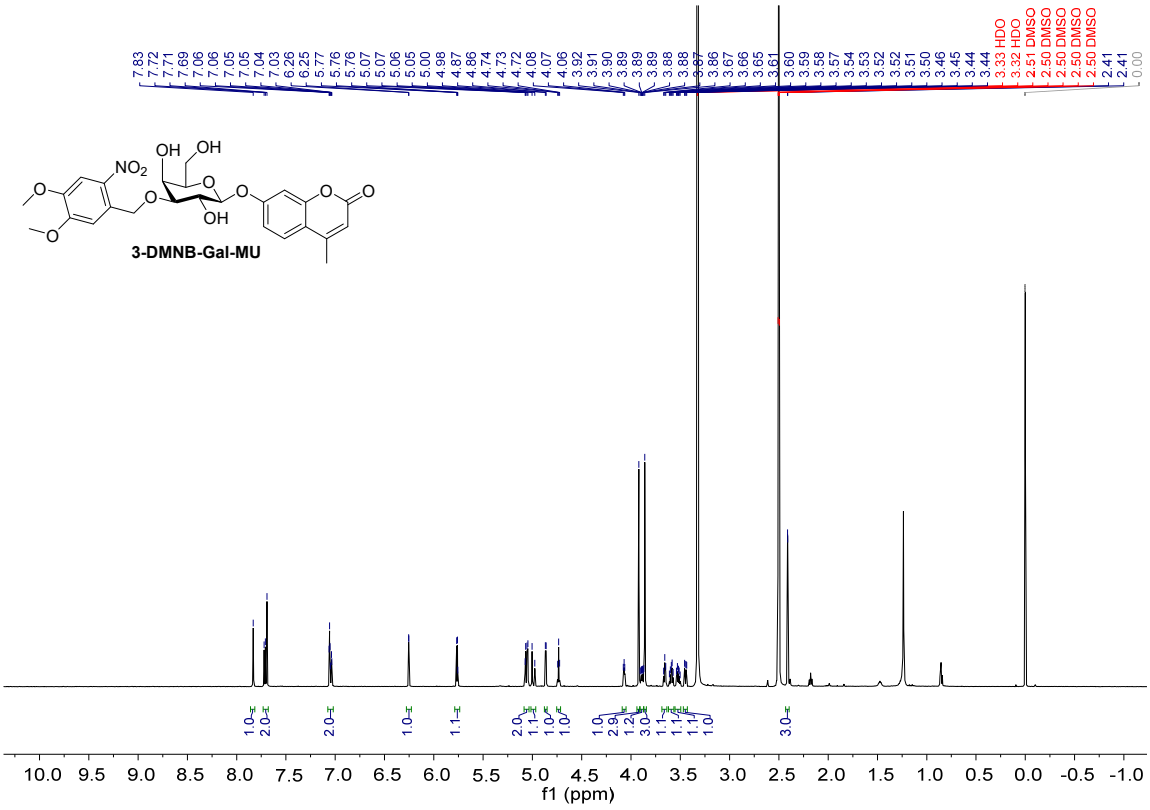
^{13}C NMR ($CDCl_3$, 151 MHz) of compound S16a



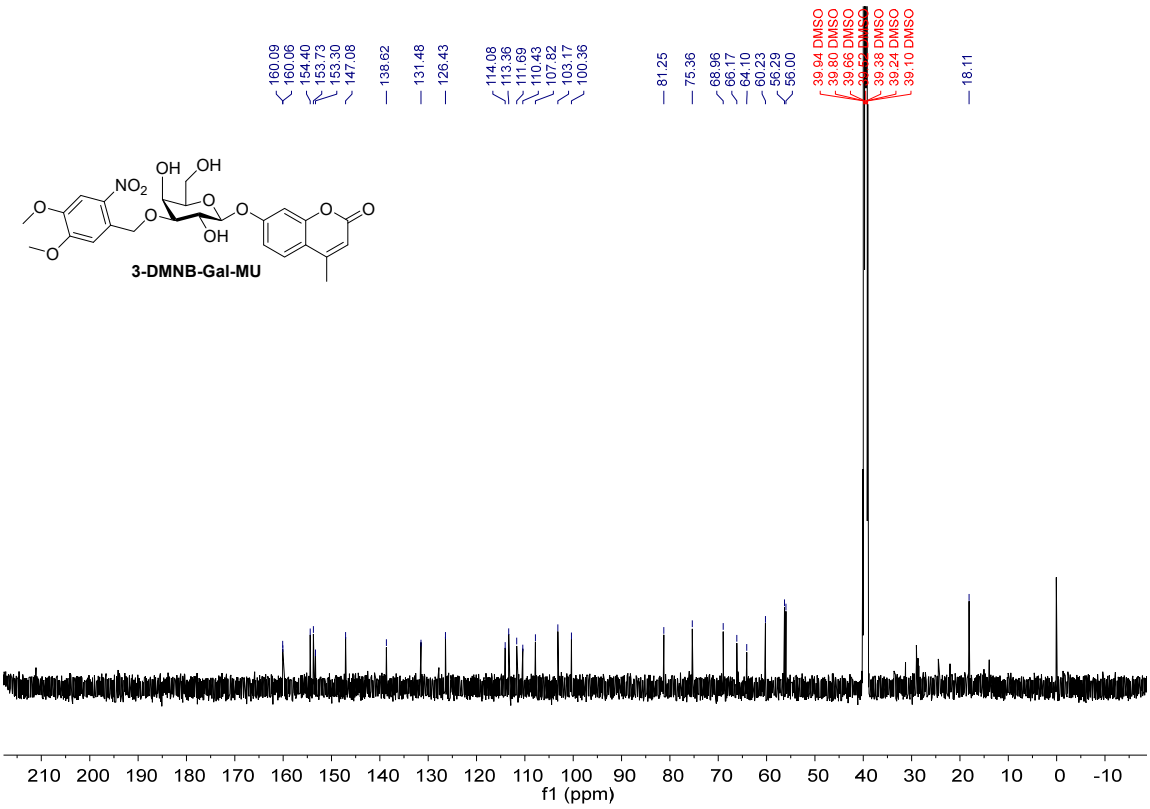
^{1}H-^{13}C HSQC NMR ($CDCl_3$, 600 MHz) of compound S16a



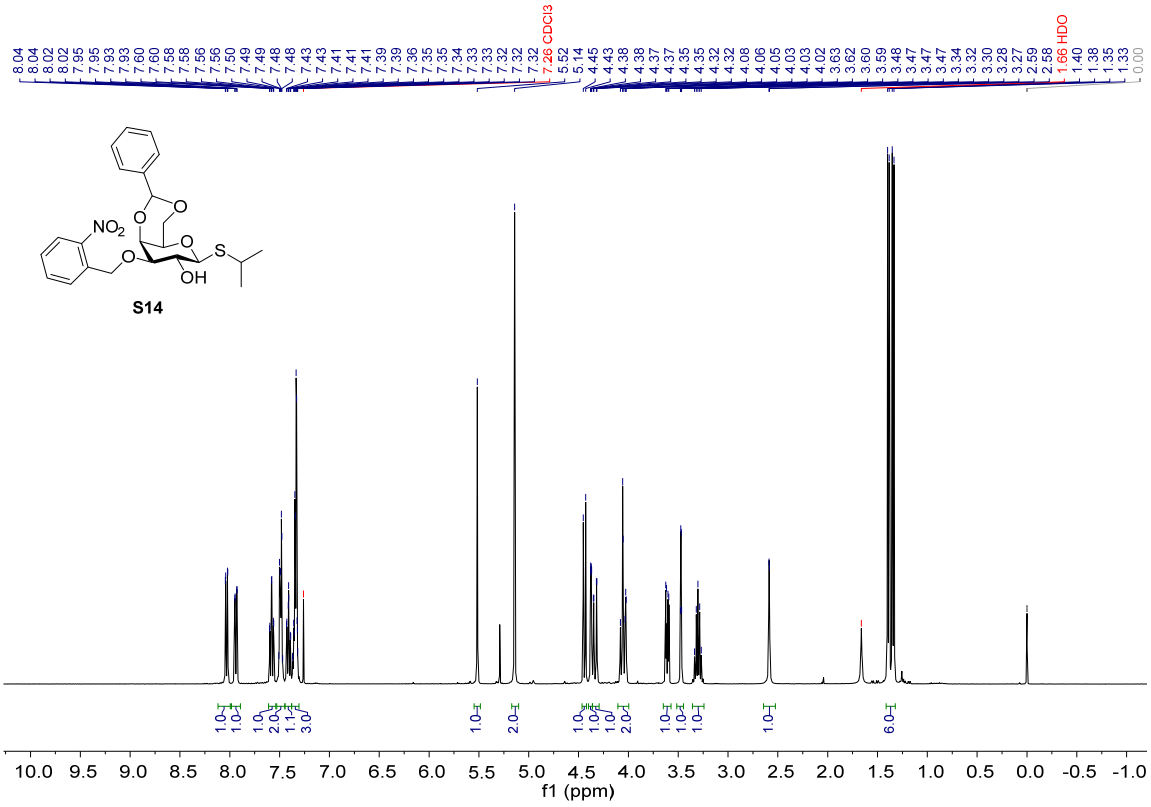
^{1}H NMR ((CD$_3$)$_2$SO, 600 MHz) of compound 3-DMNB-Gal-MU



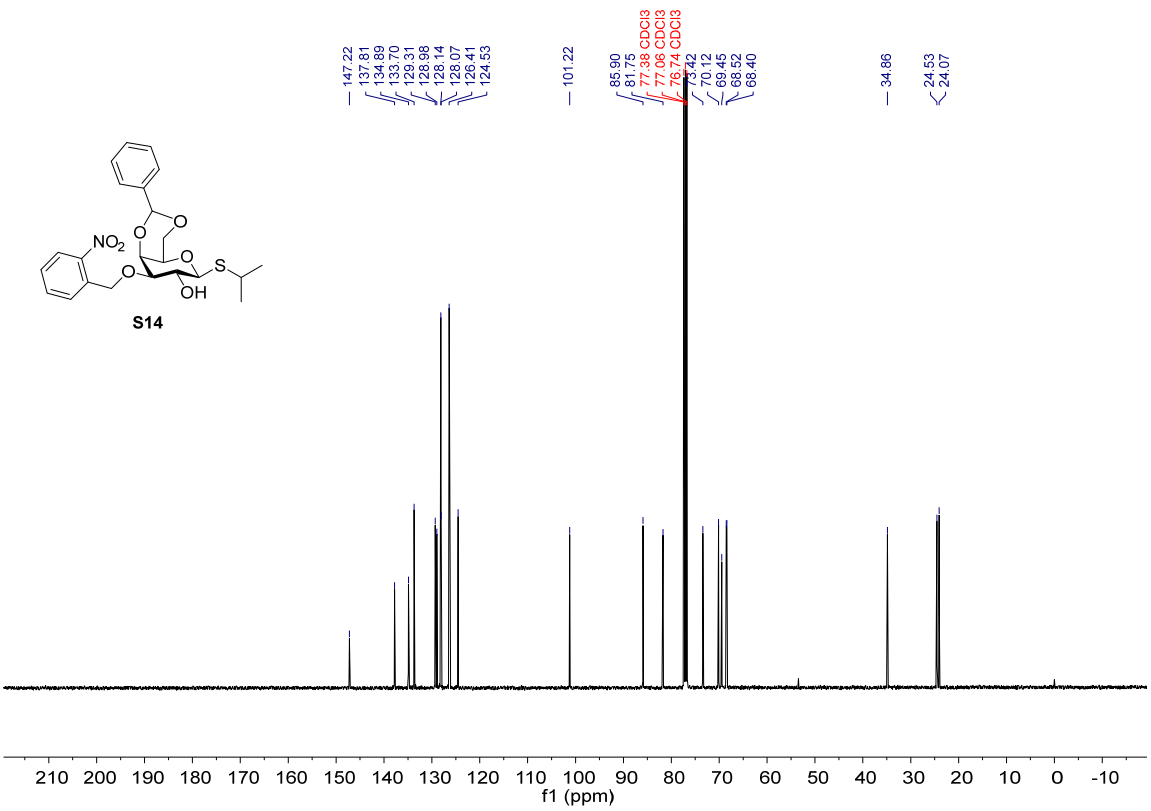
^{13}C NMR ((CD$_3$)$_2$SO, 151 MHz) of compound 3-DMNB-Gal-MU



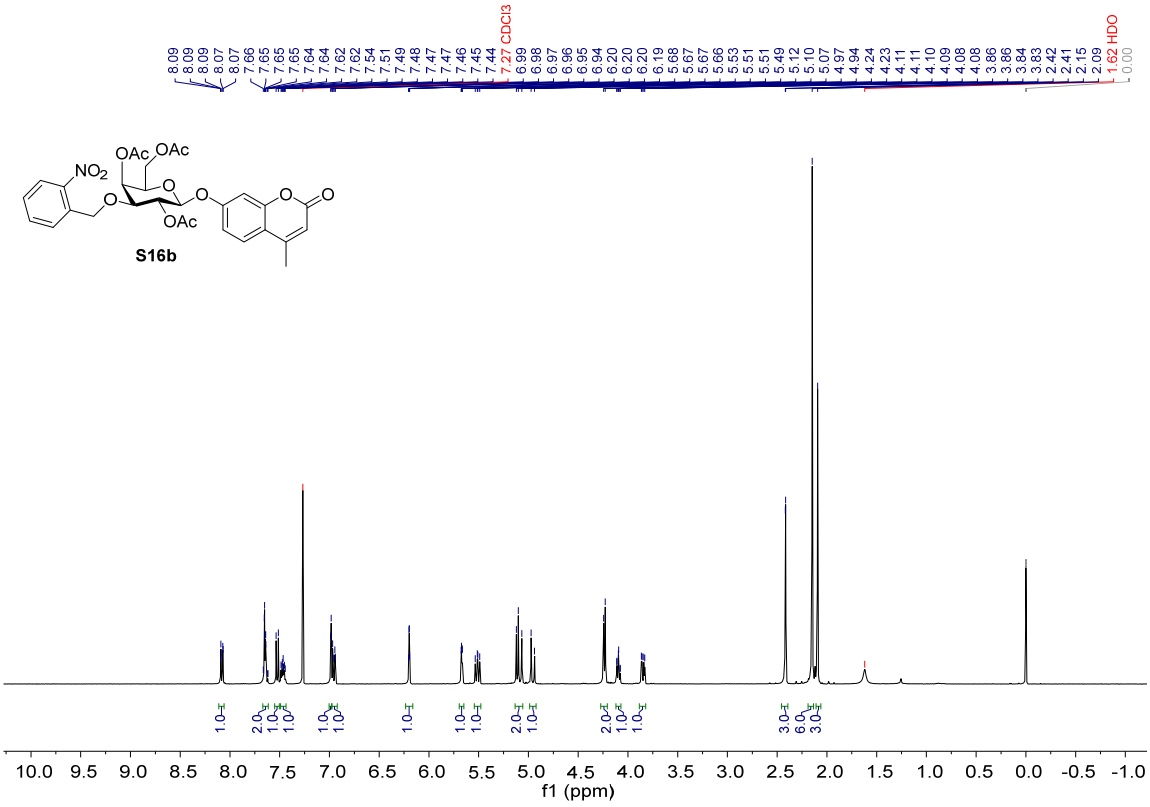
^{1}H NMR ($CDCl_3$, 400 MHz) of compound S14



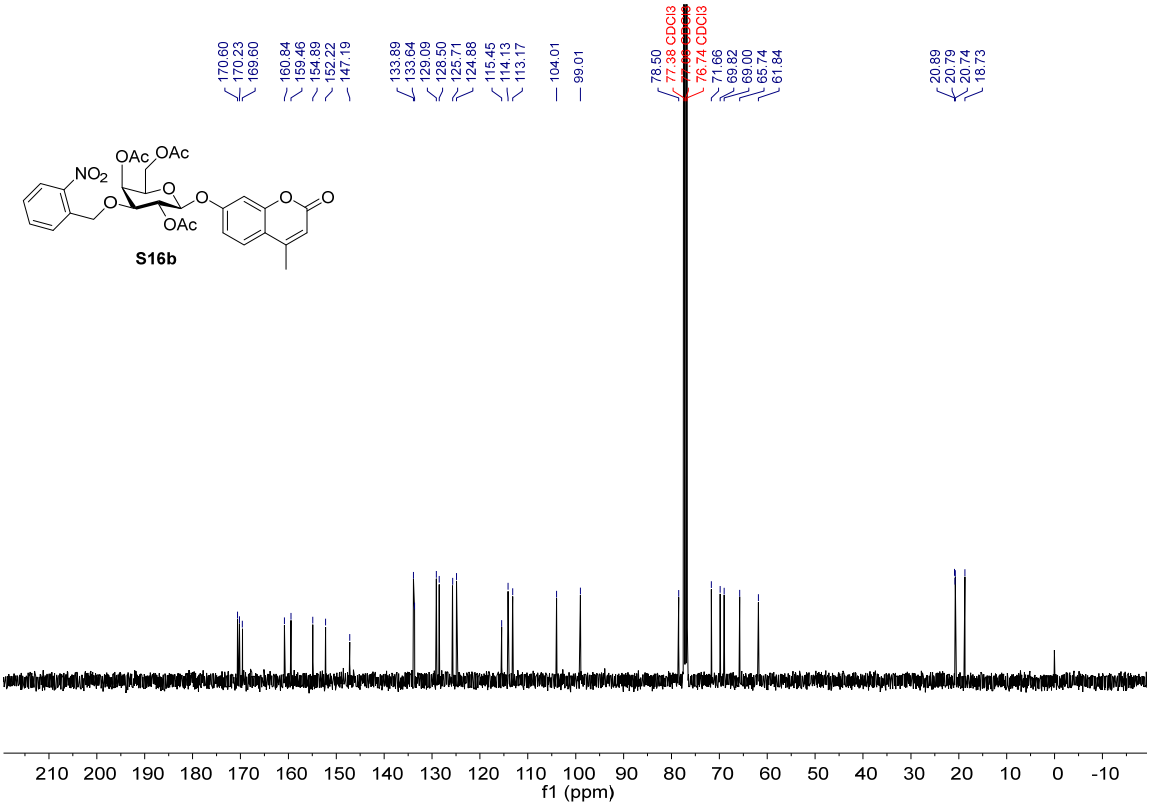
^{13}C NMR ($CDCl_3$, 101 MHz) of compound S14



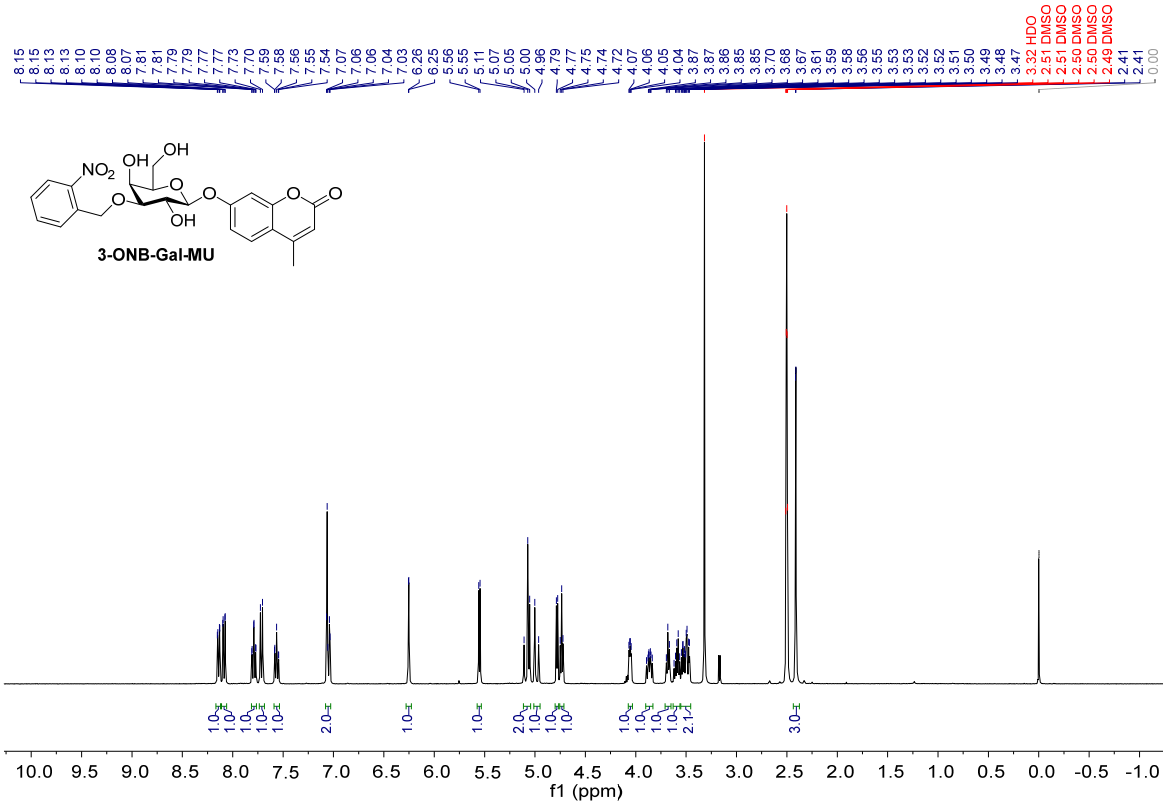
^{1}H NMR ($CDCl_3$, 400 MHz) of compound S16b



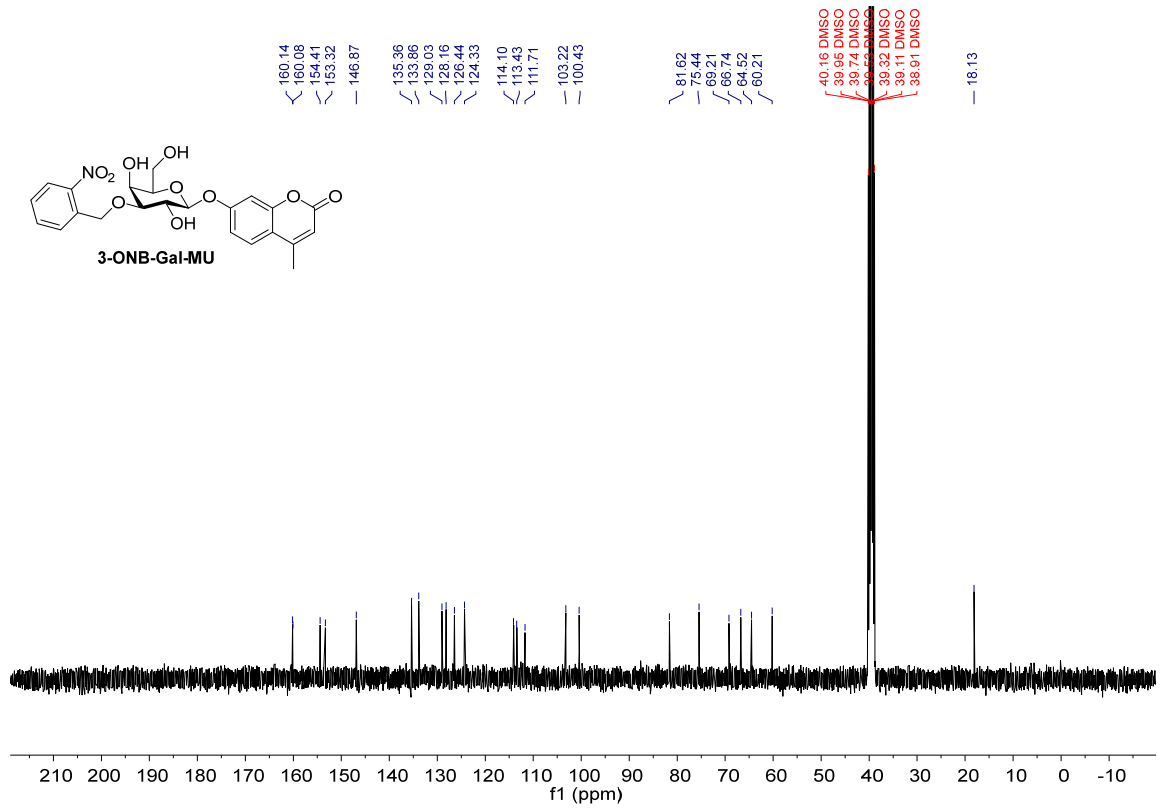
^{13}C NMR ($CDCl_3$, 101 MHz) of compound S16b



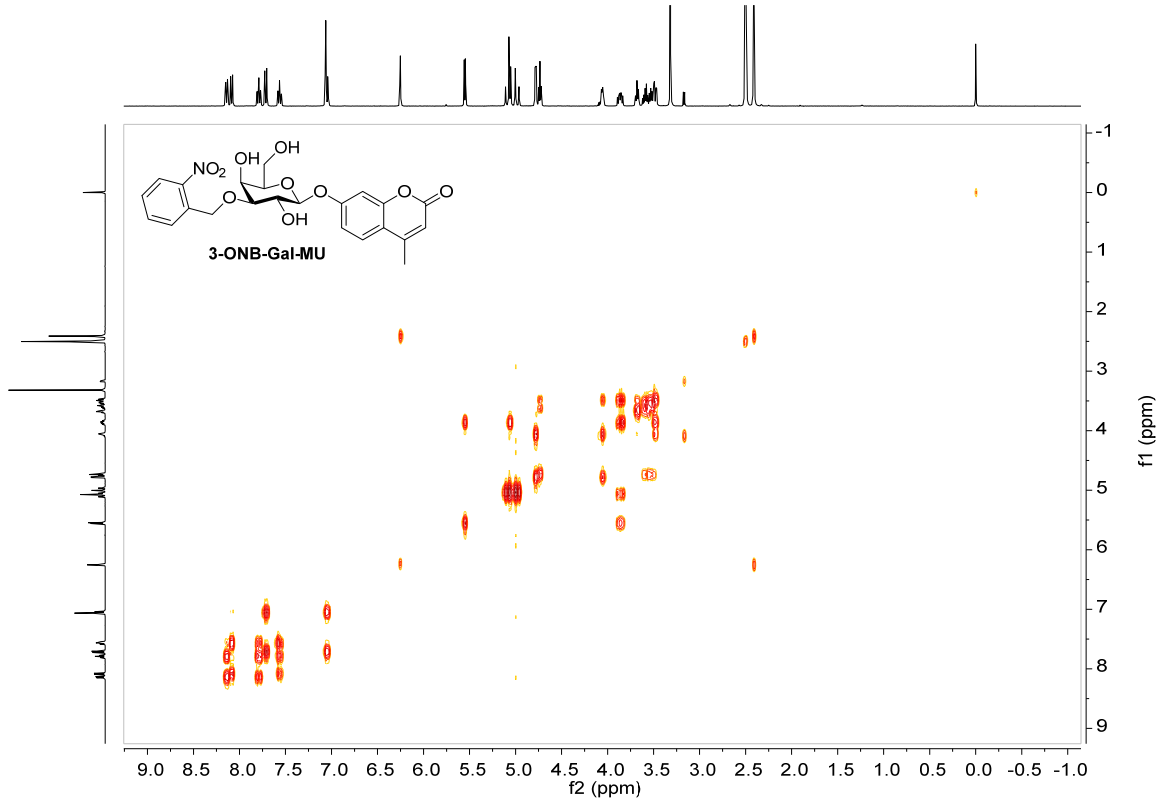
^{1}H NMR ($(CD_3)_2SO$, 400 MHz) of compound 3-ONB-Gal-MU



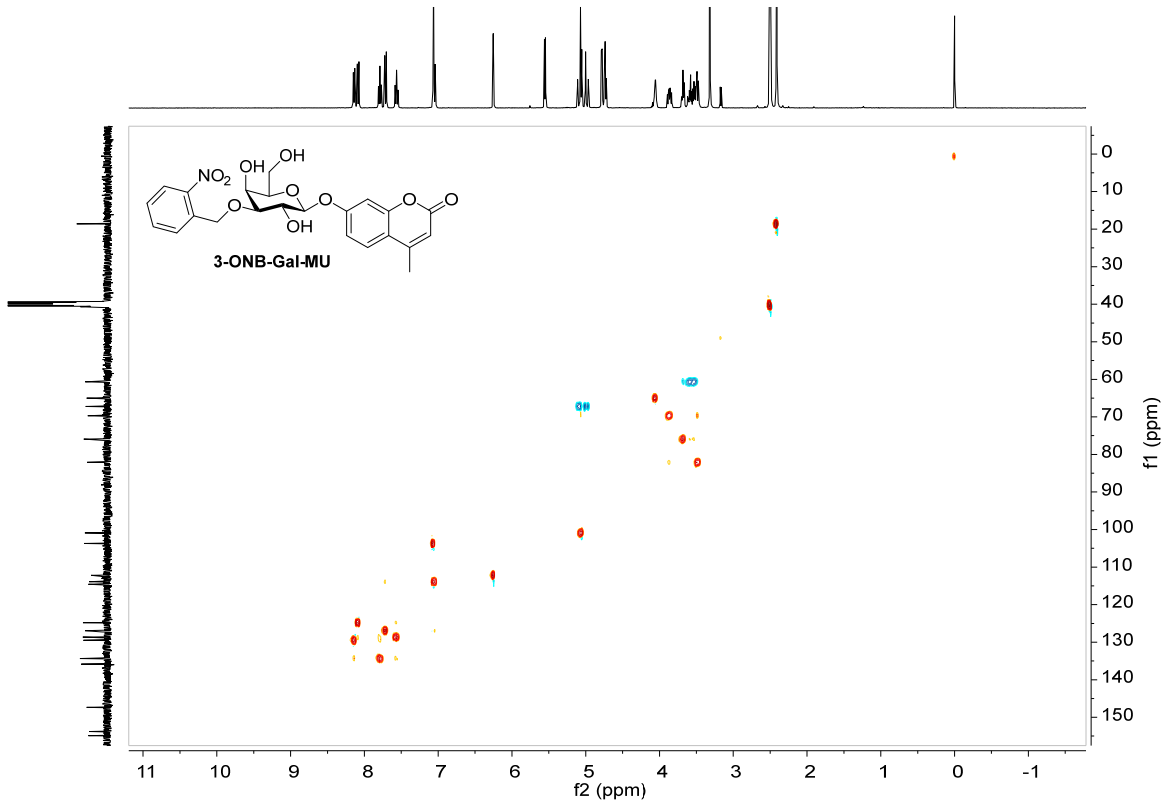
^{13}C NMR ($(CD_3)_2SO$, 101 MHz) of compound 3-ONB-Gal-MU



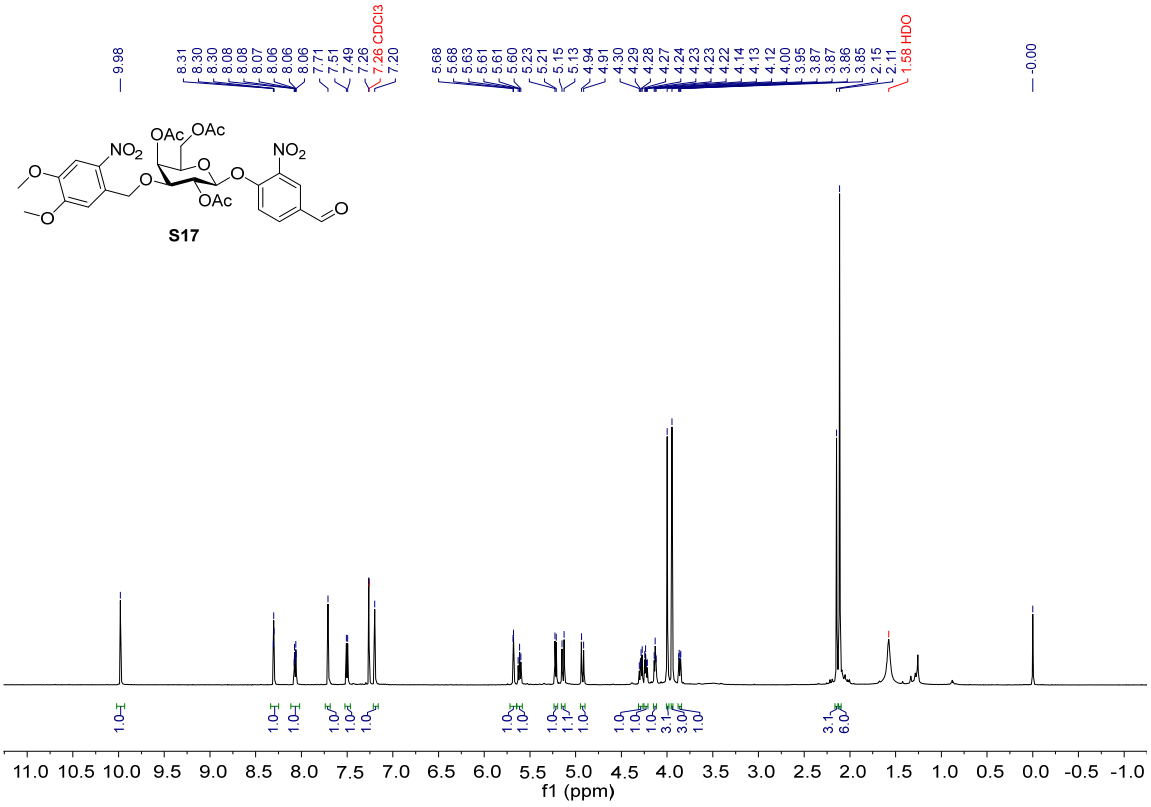
^{1}H-^{1}H COSY NMR ((CD$_3$)$_2$SO, 400 MHz) of compound 3-ONB-Gal-MU



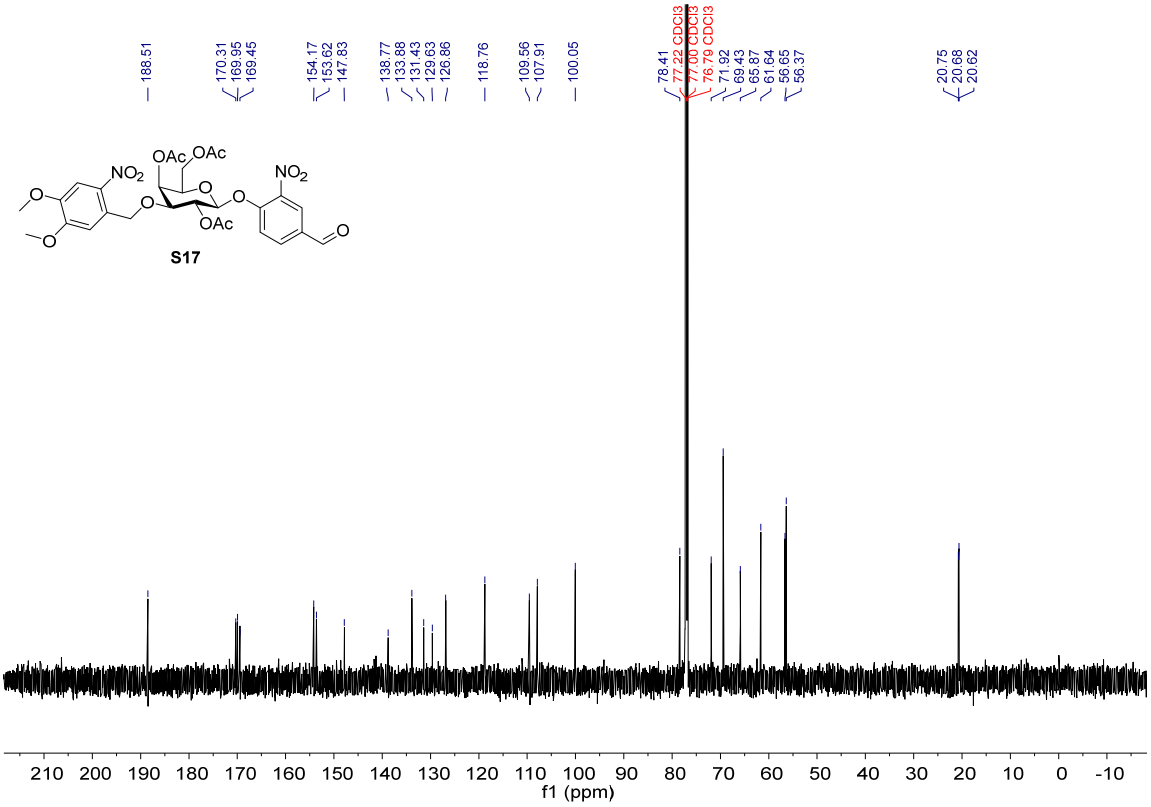
^{1}H-^{13}C HSQC NMR ((CD$_3$)$_2$SO, 400 MHz) of compound 3-ONB-Gal-MU



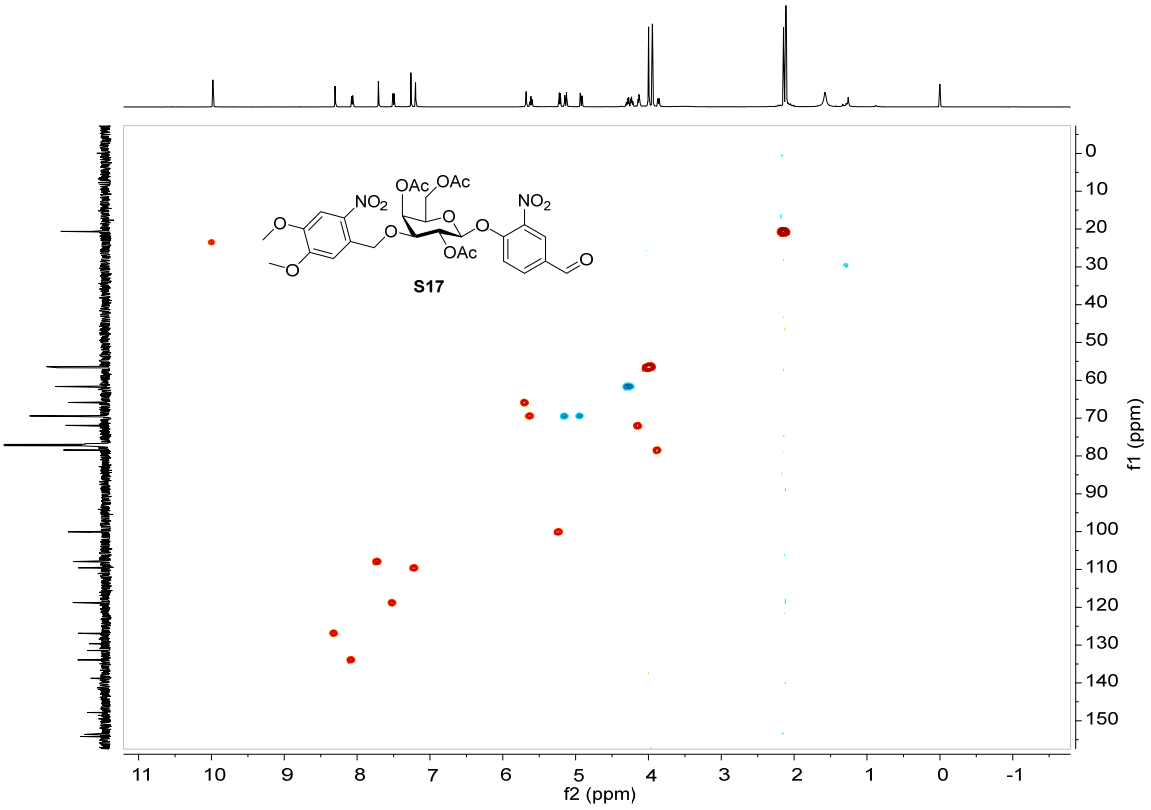
^{1}H NMR ($CDCl_3$, 600 MHz) of compound S17



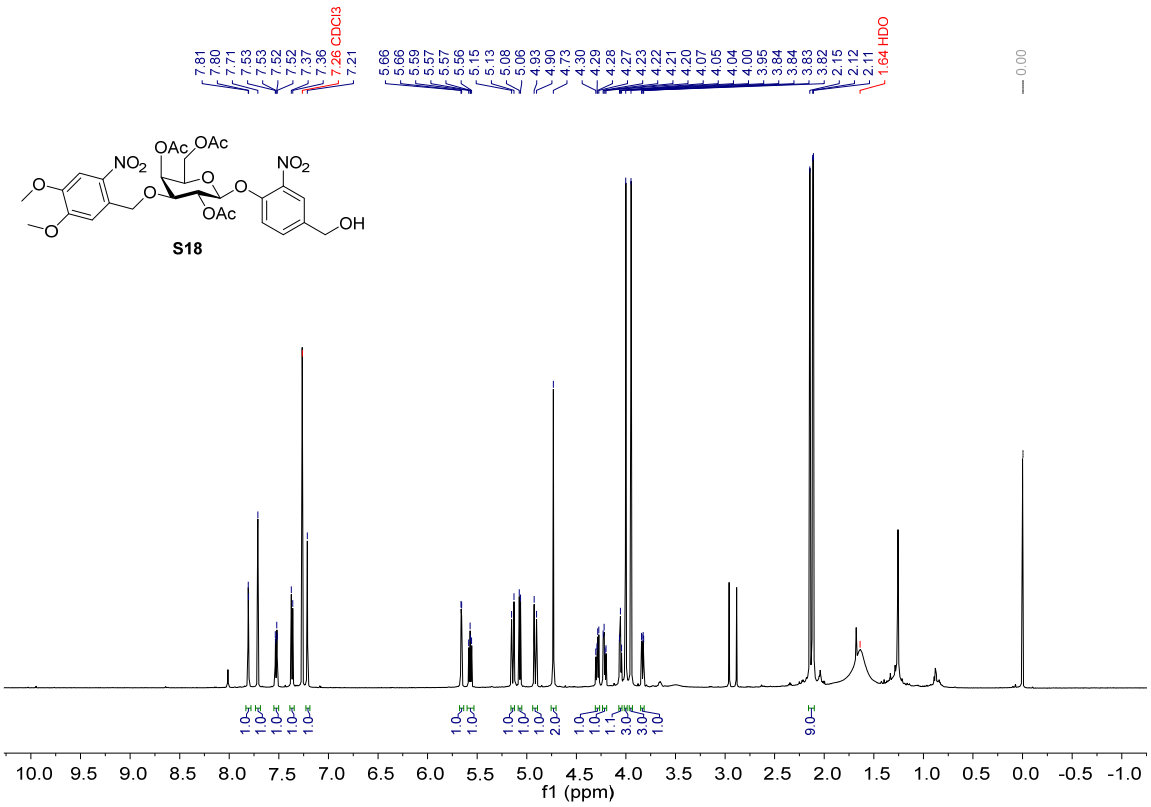
^{13}C NMR ($CDCl_3$, 151 MHz) of compound S17



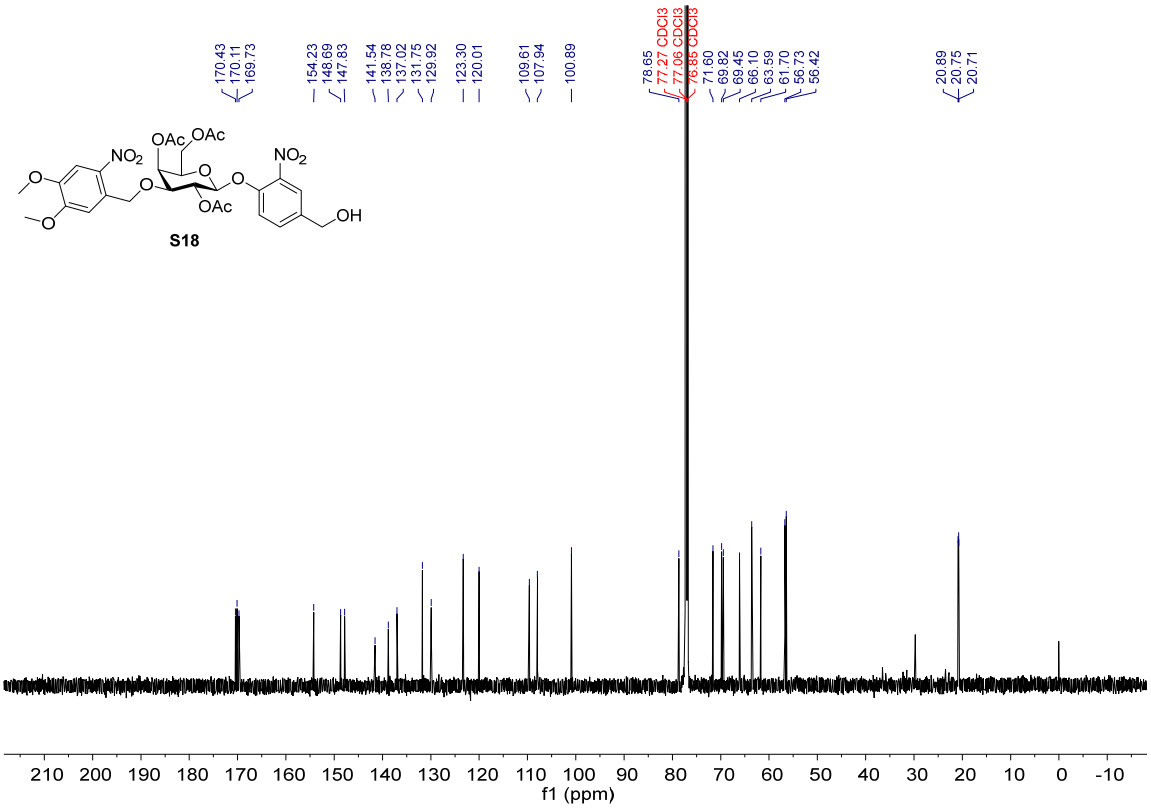
^{1}H-^{13}C HSQC NMR ($CDCl_3$, 400 MHz) of compound S17



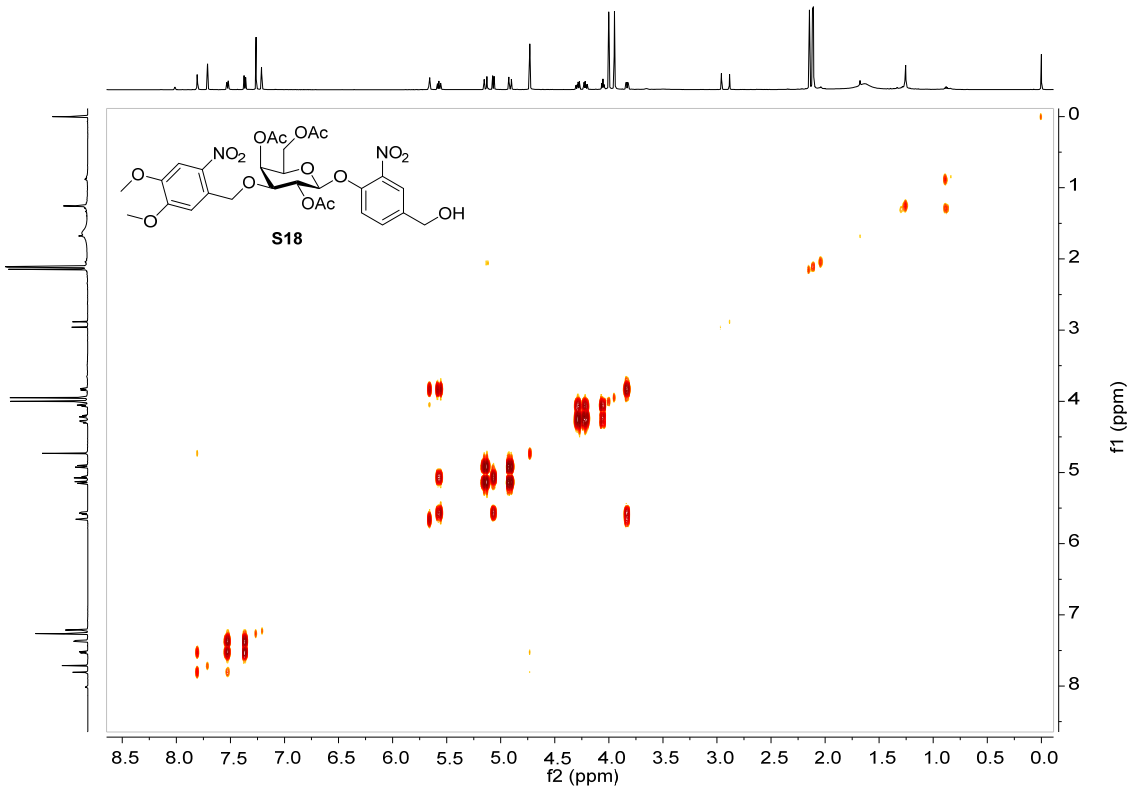
^{1}H NMR ($CDCl_3$, 600 MHz) of compound S18



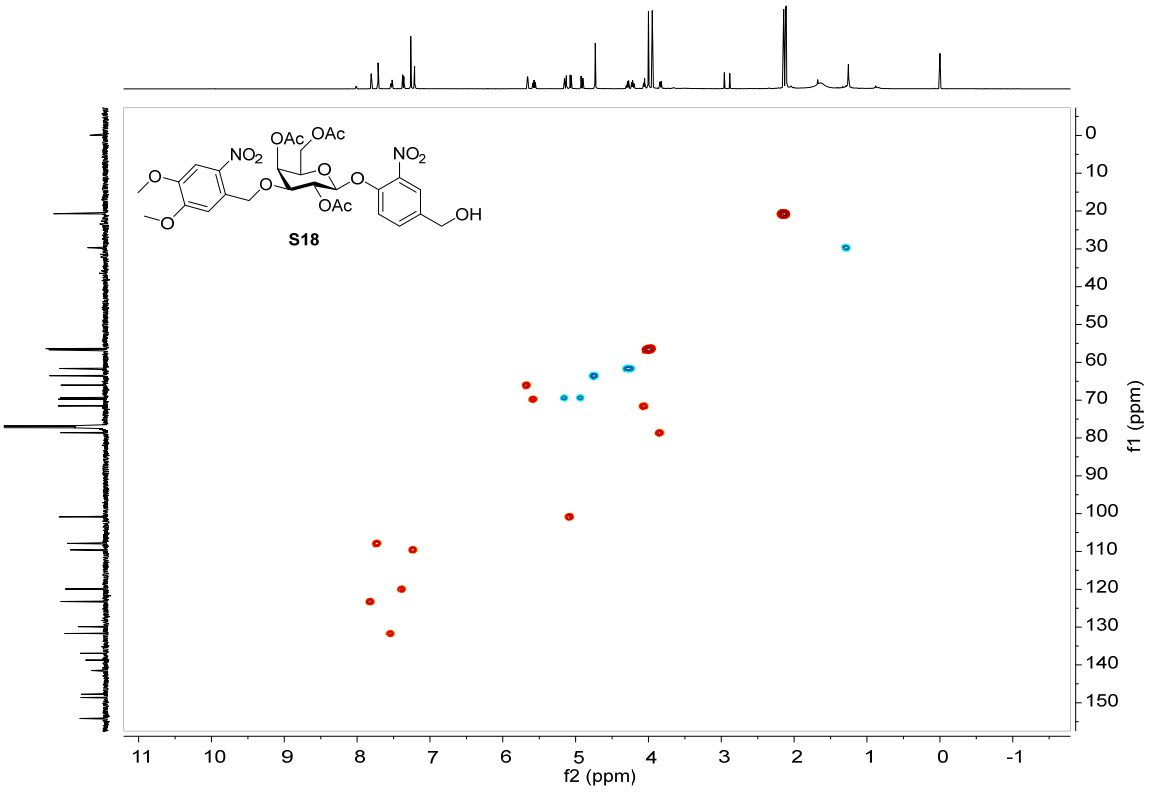
^{13}C NMR ($CDCl_3$, 151 MHz) of compound S18



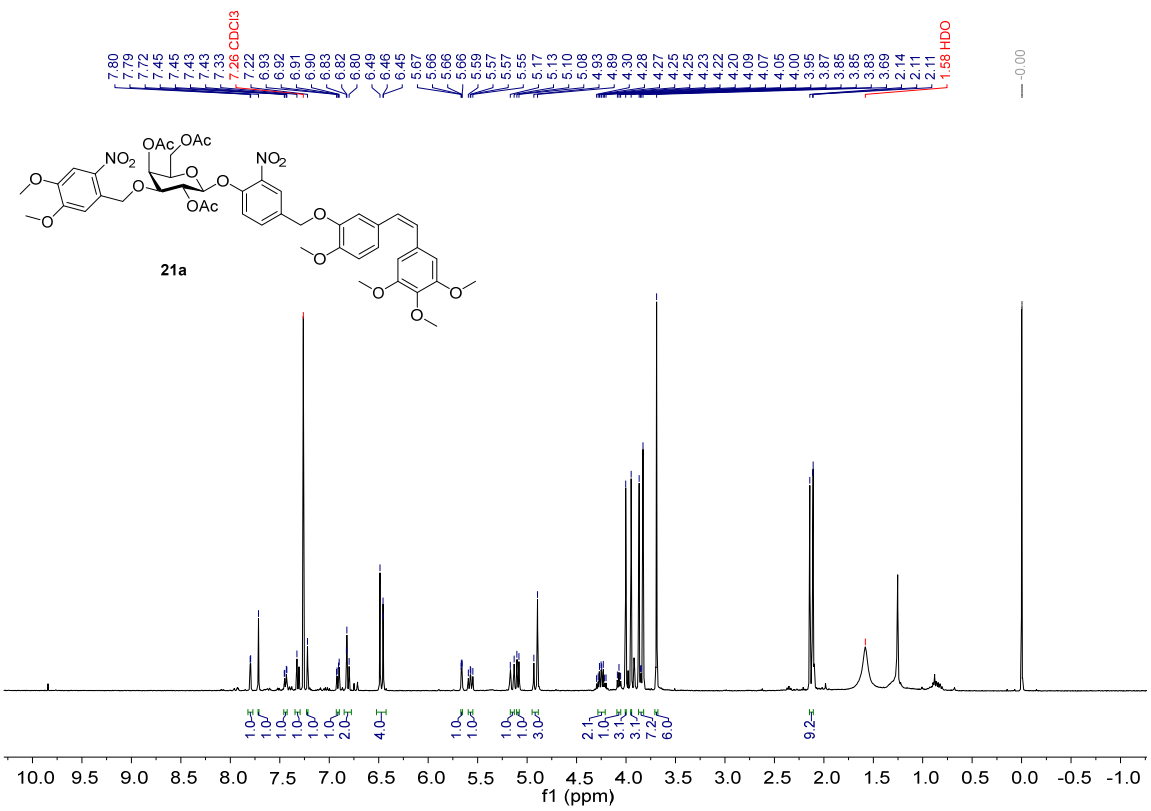
^{1}H-^{1}H COSY NMR ($CDCl_3$, 600 MHz) of compound S18



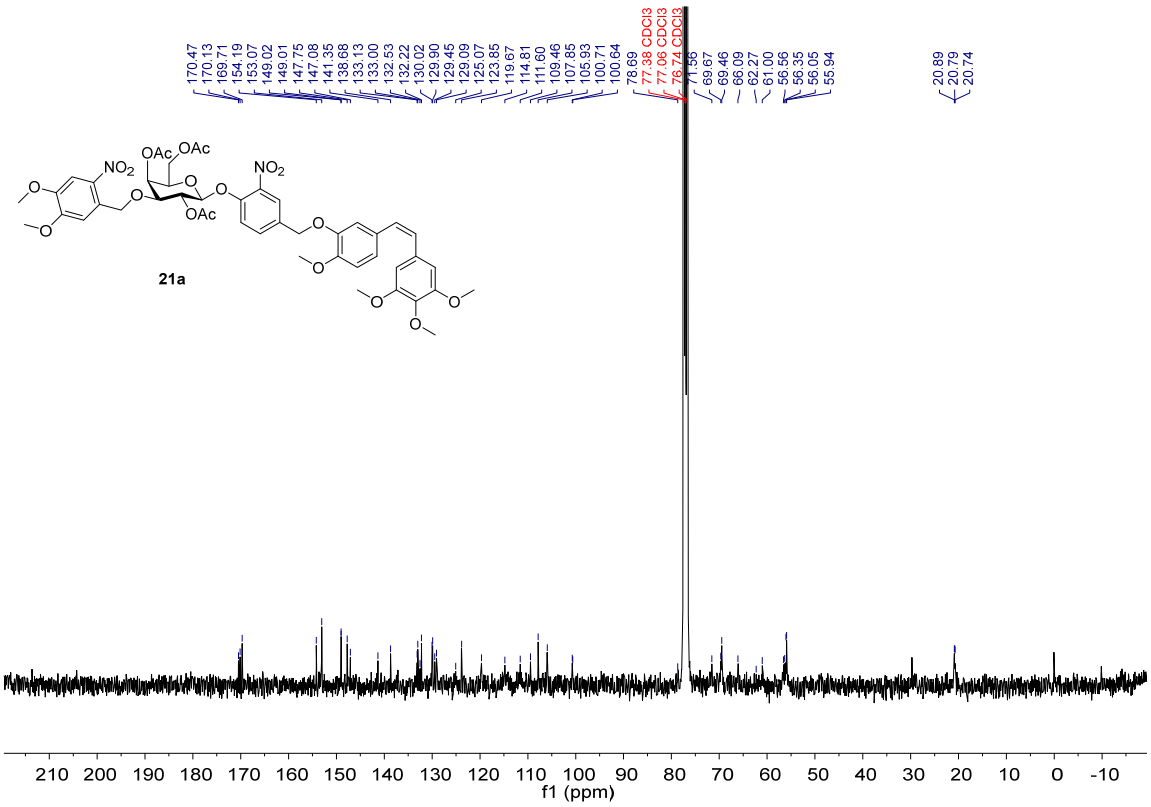
^{1}H-^{13}C HSQC NMR ($CDCl_3$, 600 MHz) of compound S18



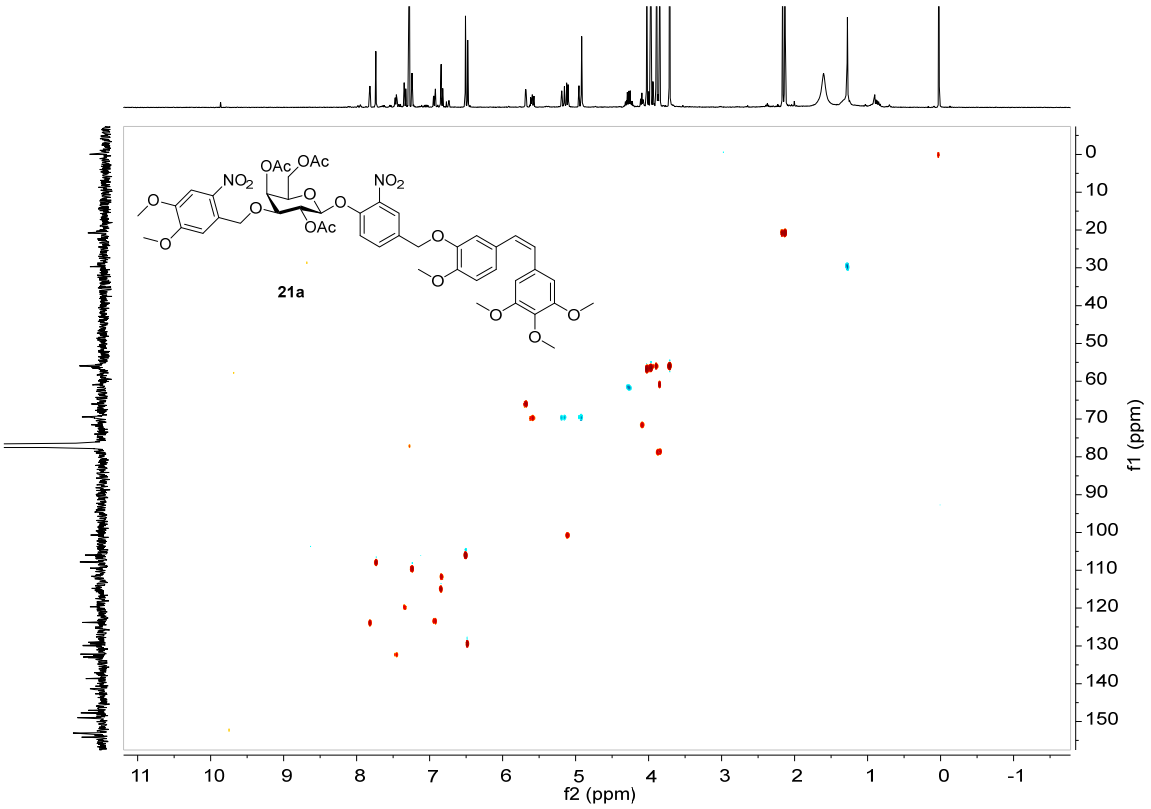
^{1}H NMR ($CDCl_3$, 400 MHz) of compound 21a



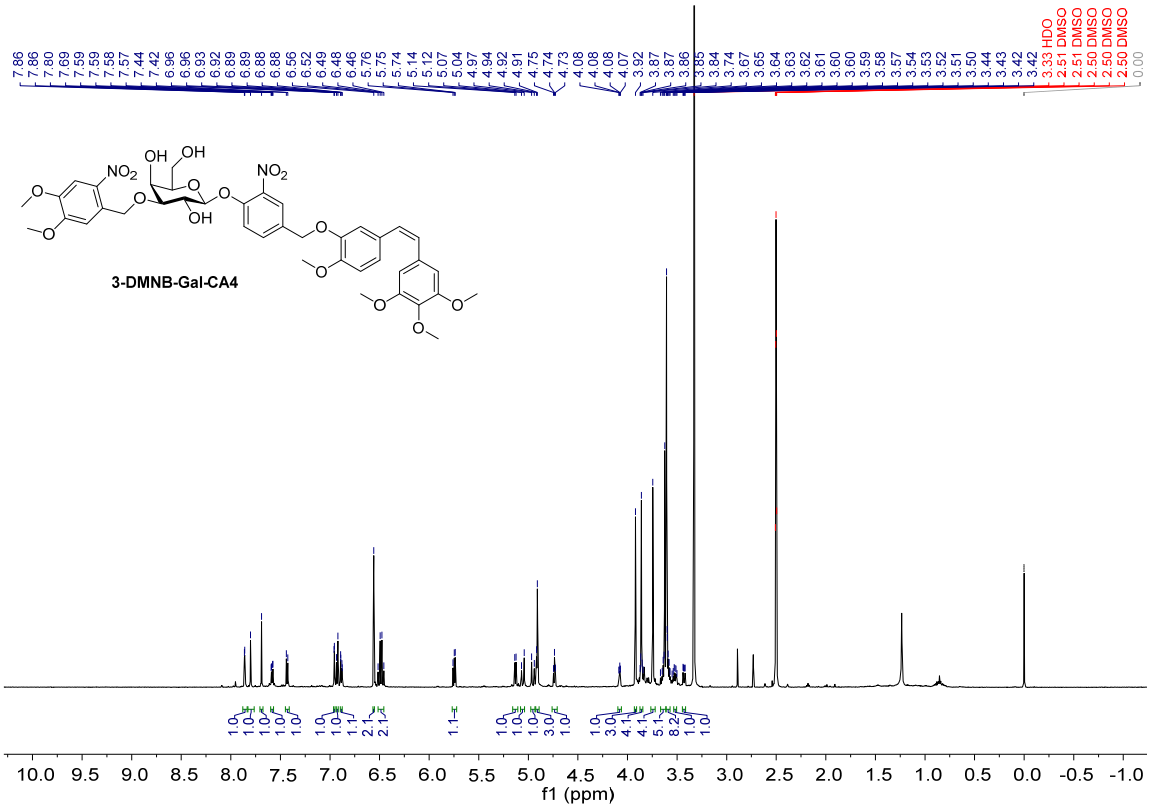
^{13}C NMR ($CDCl_3$, 101 MHz) of compound 21a



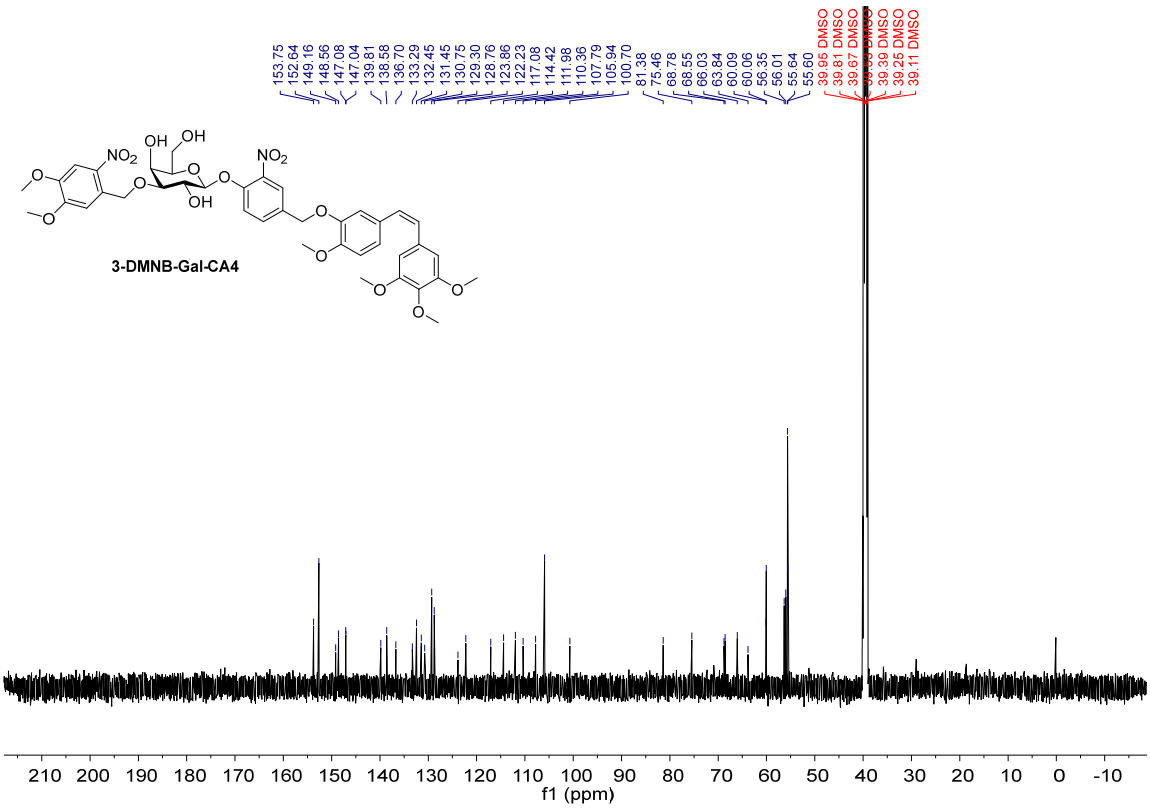
^{1}H-^{13}C HSQC NMR ($CDCl_3$, 400 MHz) of compound 21a



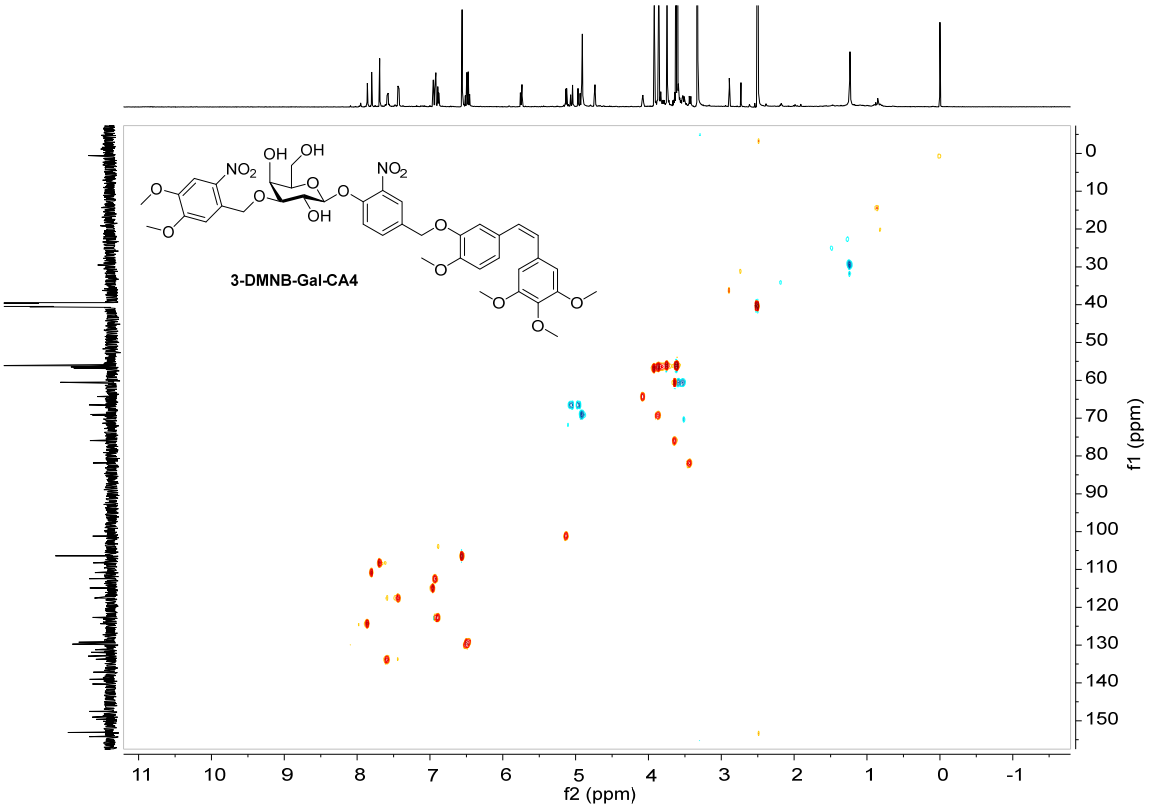
^{1}H NMR ($(CD_3)_2SO$, 600 MHz) of compound 3-DMNB-Gal-CA4



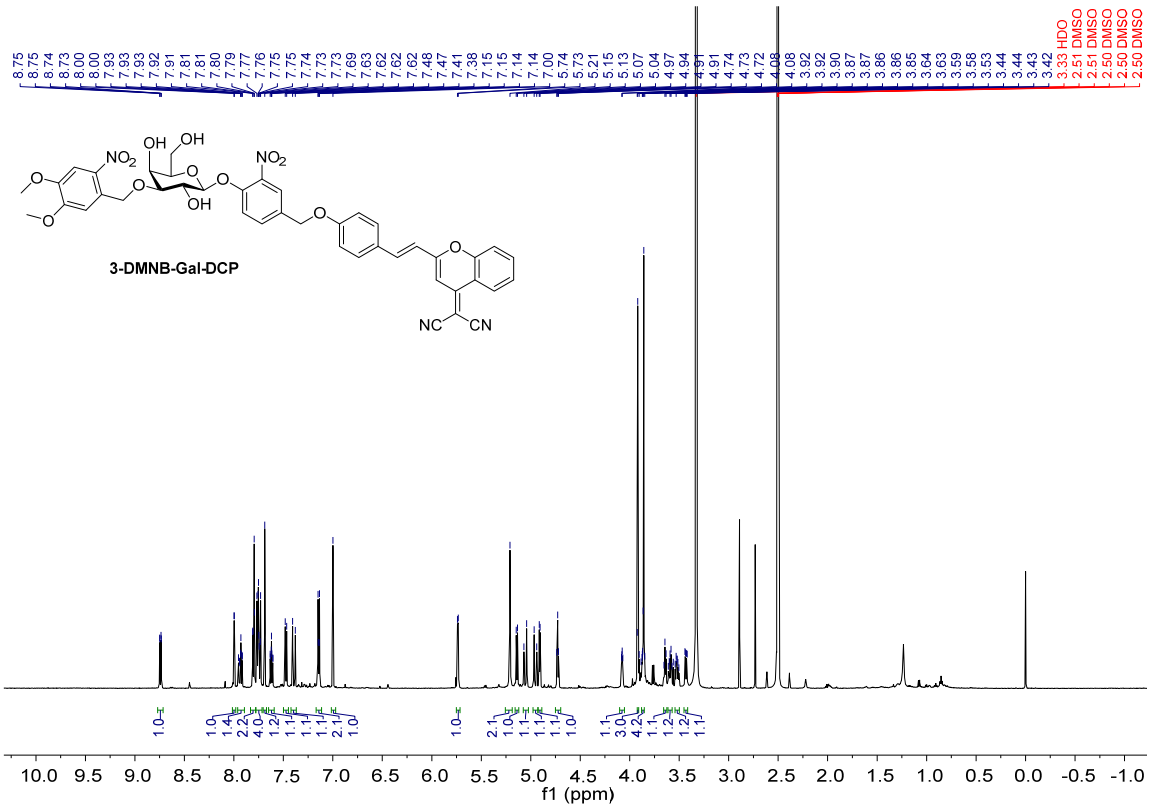
^{13}C NMR ($(CD_3)_2SO$, 151 MHz) of compound 3-DMNB-Gal-CA4



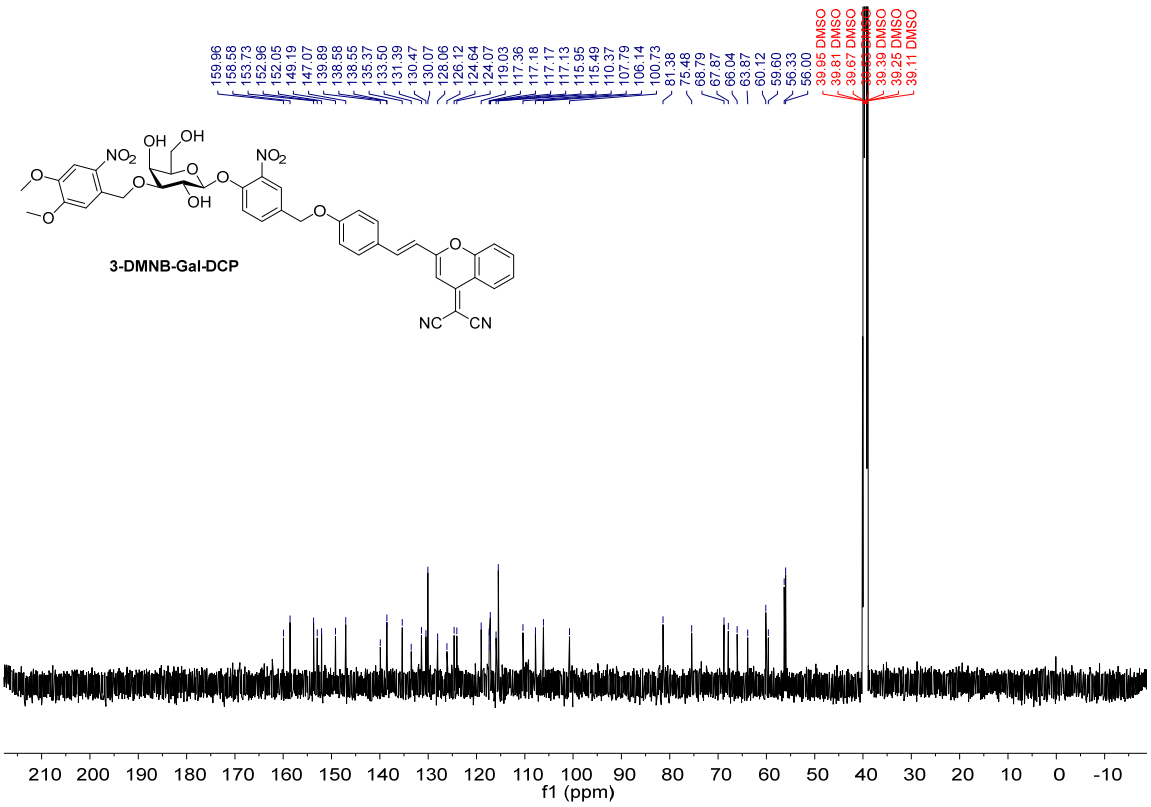
^{1}H-^{13}C HSQC NMR ((CD$_3$)$_2$SO, 600 MHz) of compound 3-DMNB-Gal-CA4



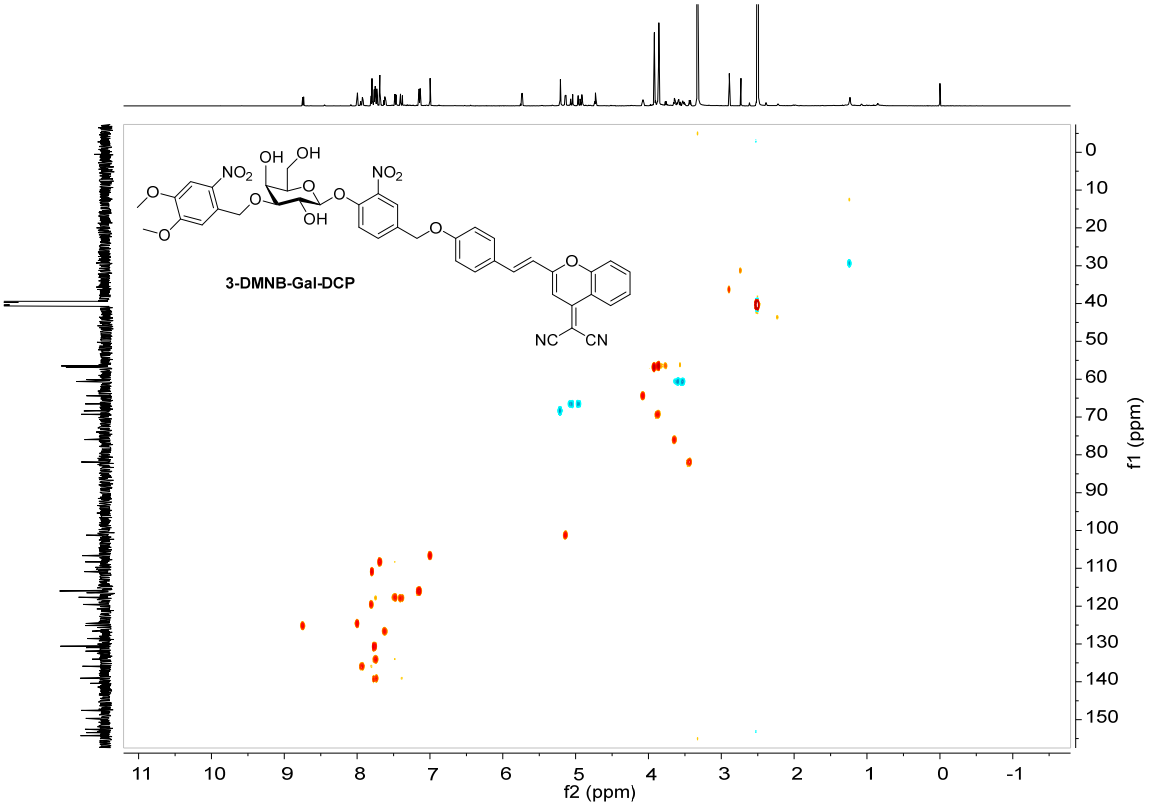
^{1}H NMR ((CD$_3$)$_2$SO, 600 MHz) of compound 3-DMNB-Gal-DCP



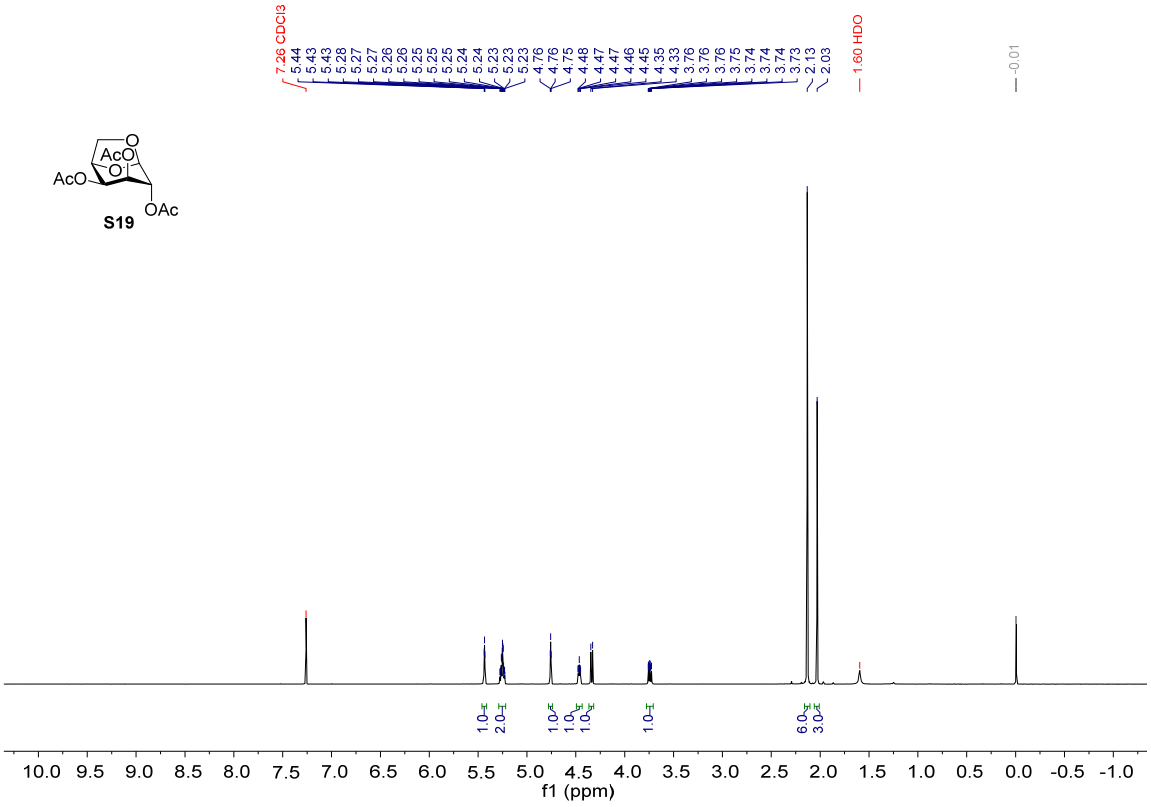
^{13}C NMR ((CD$_3$)$_2$SO, 151 MHz) of compound 3-DMNB-Gal-DCP



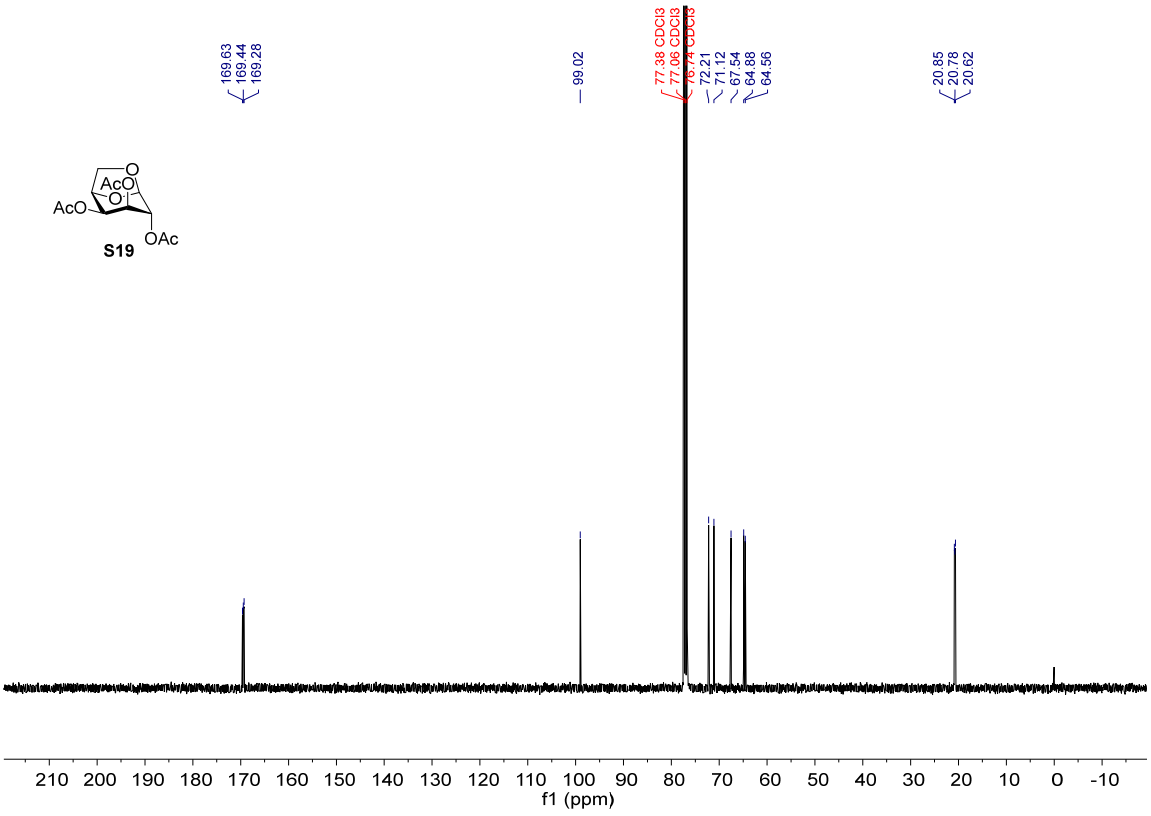
^{1}H-^{13}C HSQC NMR ((CD$_3$)$_2$SO, 600 MHz) of compound 3-DMNB-Gal-DCP



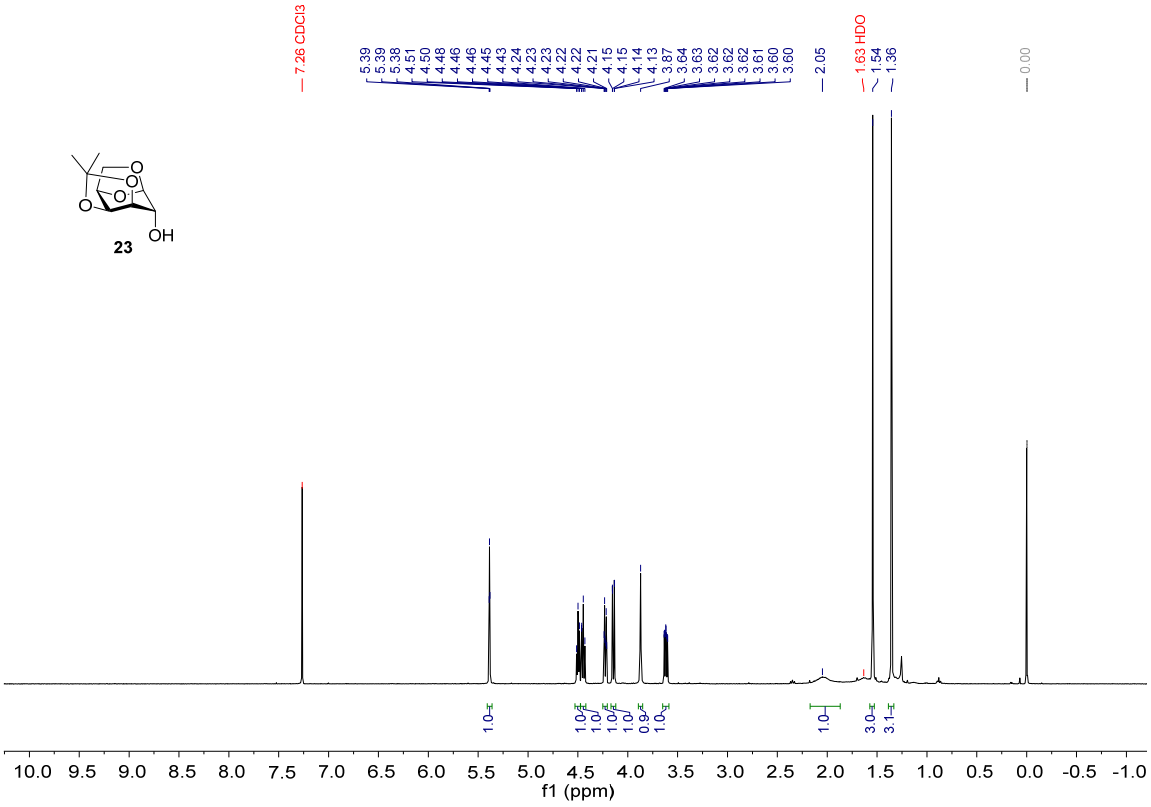
^{1}H NMR ($CDCl_3$, 400 MHz) of compound S19



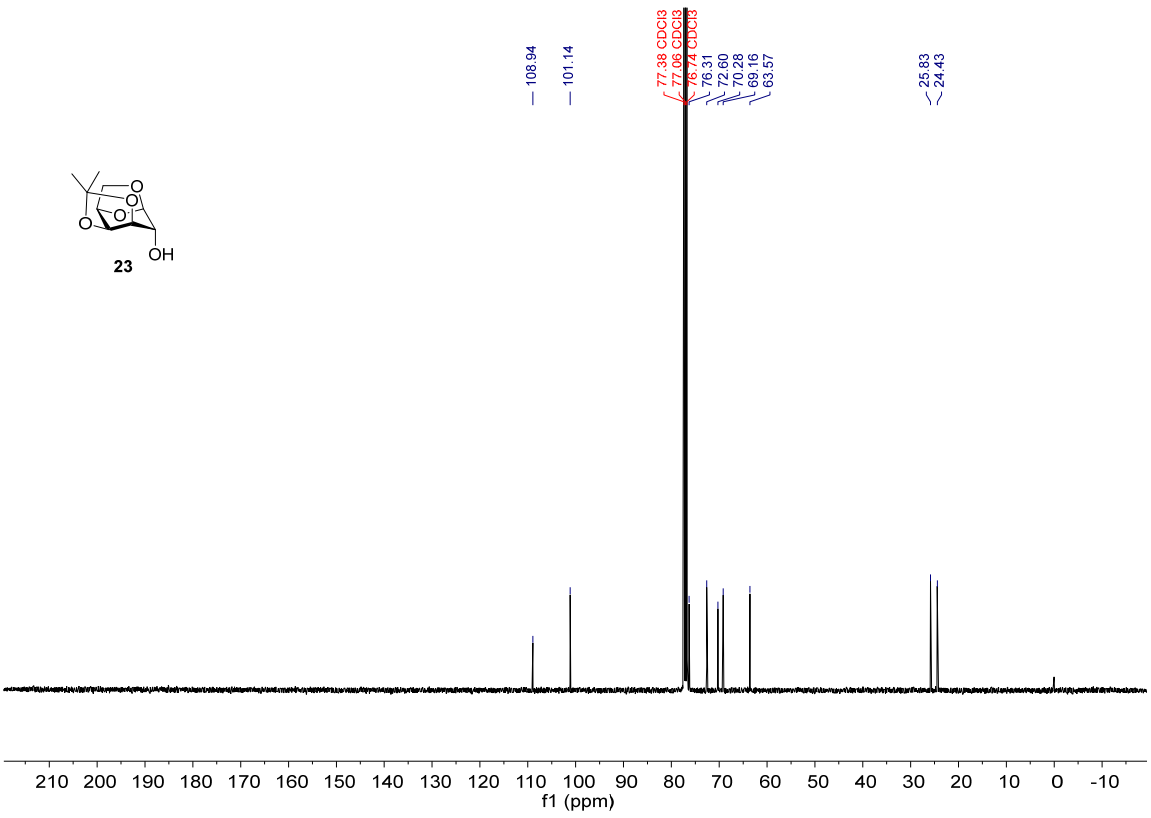
^{13}C NMR ($CDCl_3$, 101 MHz) of compound S19



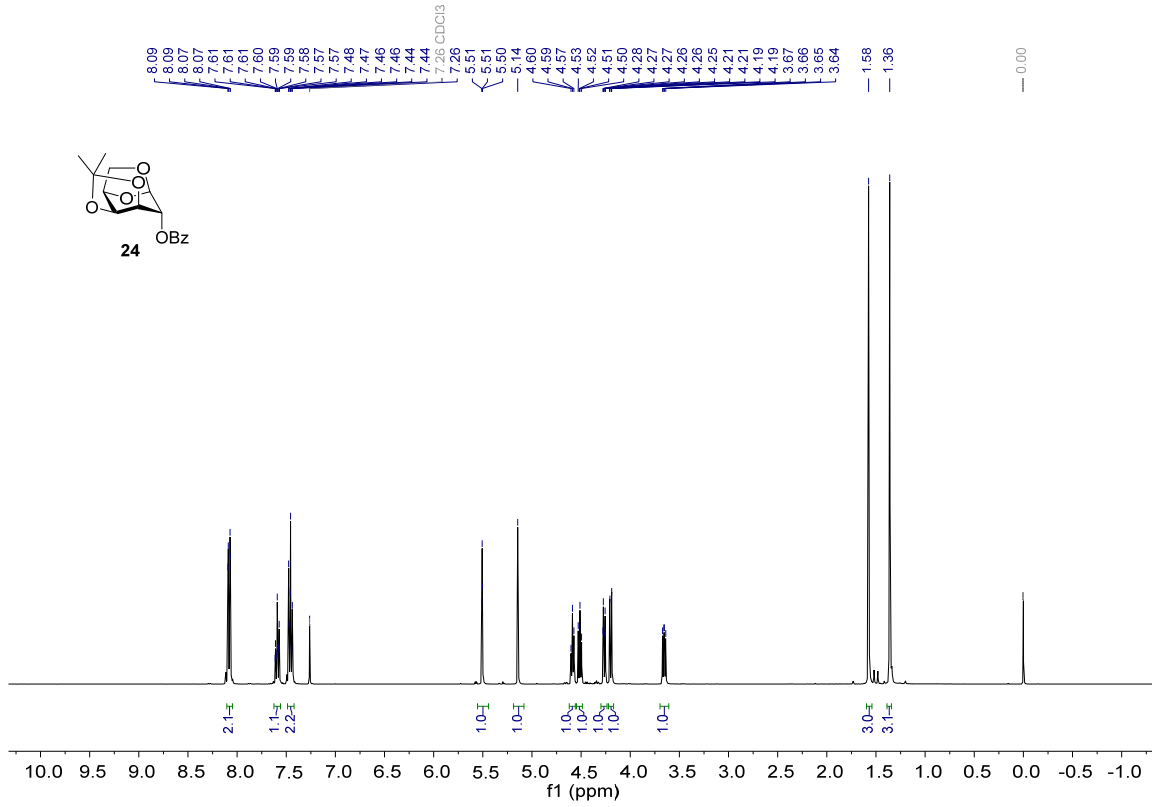
^{1}H NMR ($CDCl_3$, 400 MHz) of compound 23



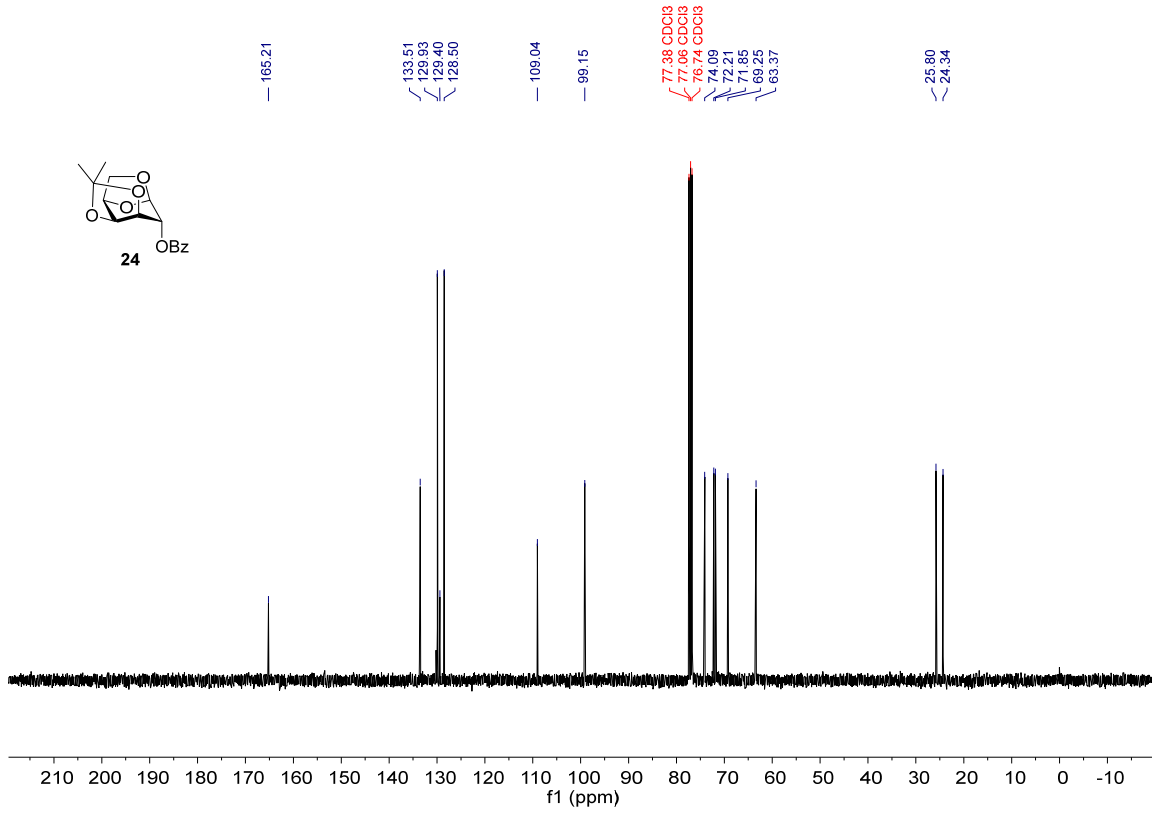
^{13}C NMR ($CDCl_3$, 101 MHz) of compound 23



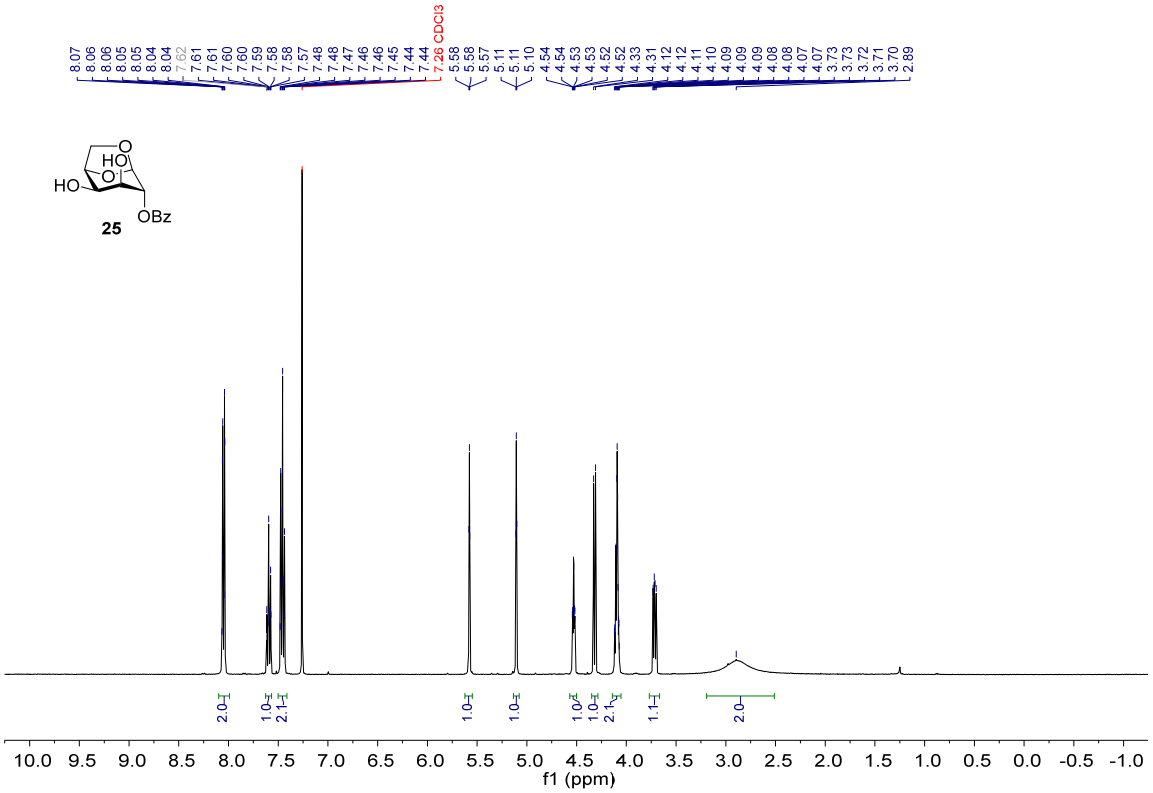
^{1}H NMR ($CDCl_3$, 400 MHz) of compound 24



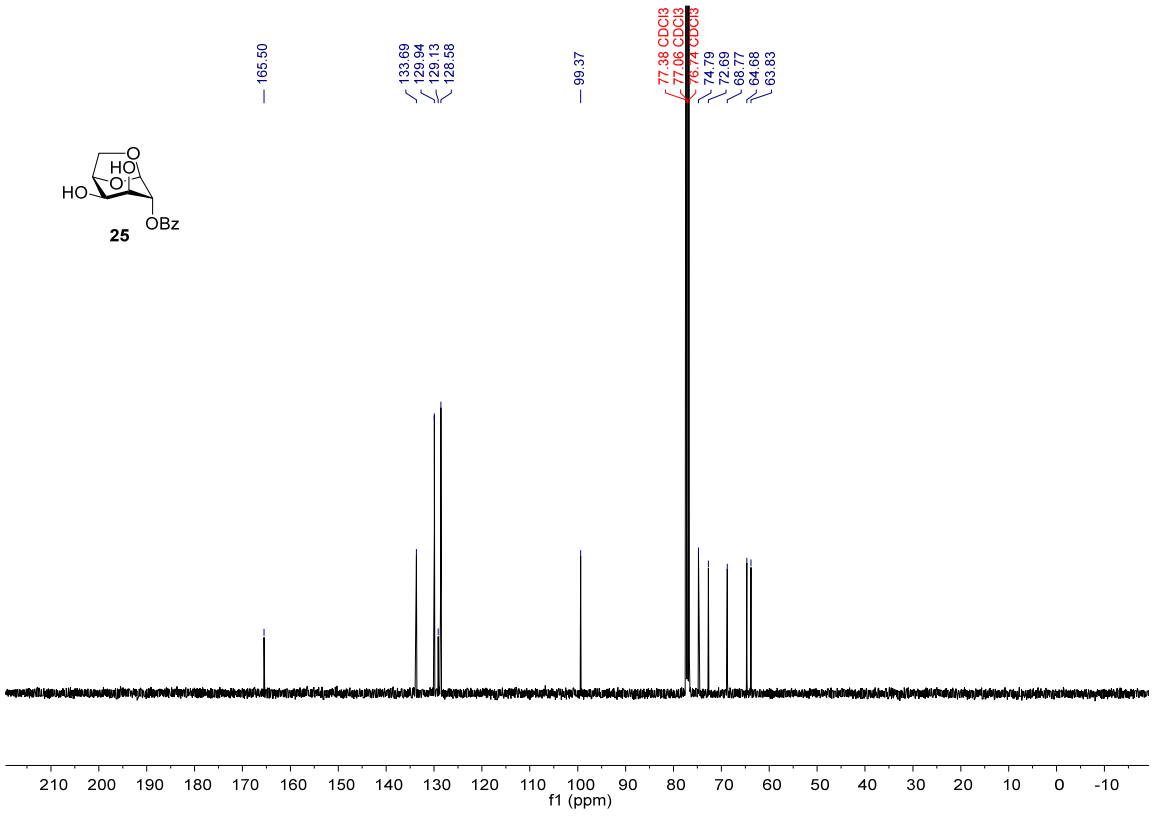
^{13}C NMR ($CDCl_3$, 101 MHz) of compound 24



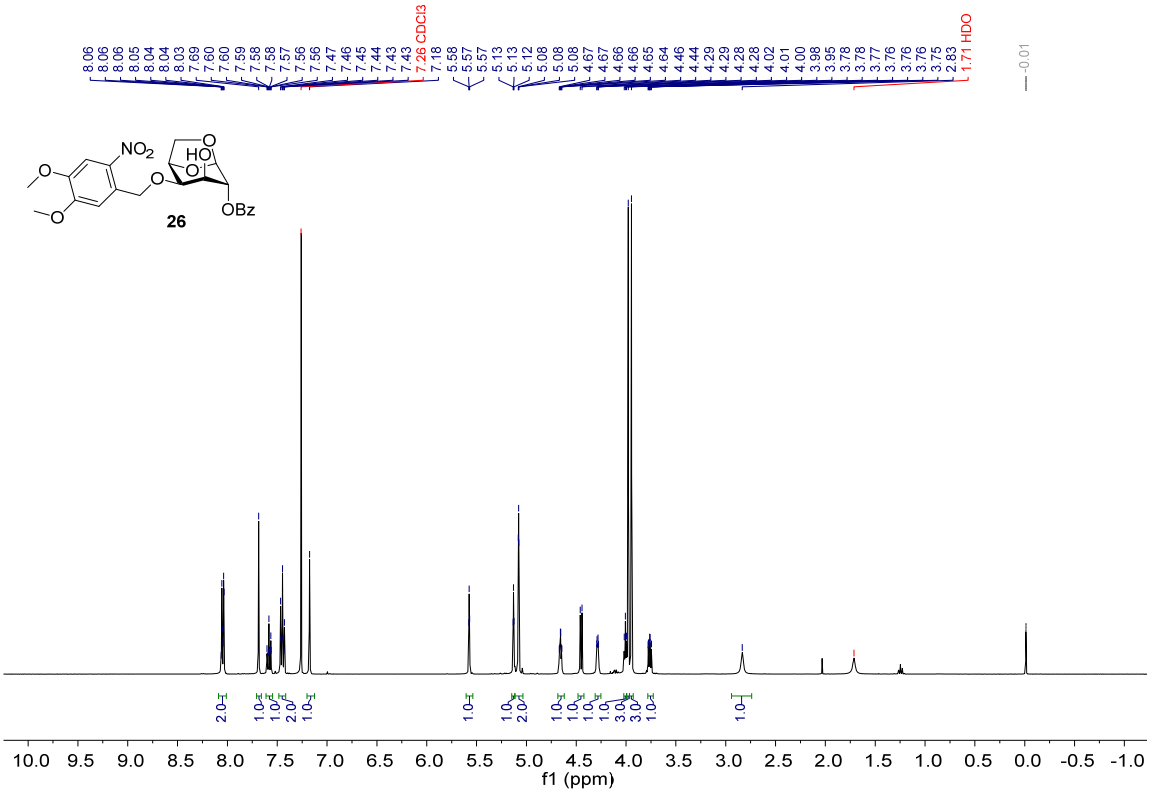
^{1}H NMR ($CDCl_3$, 400 MHz) of compound 25



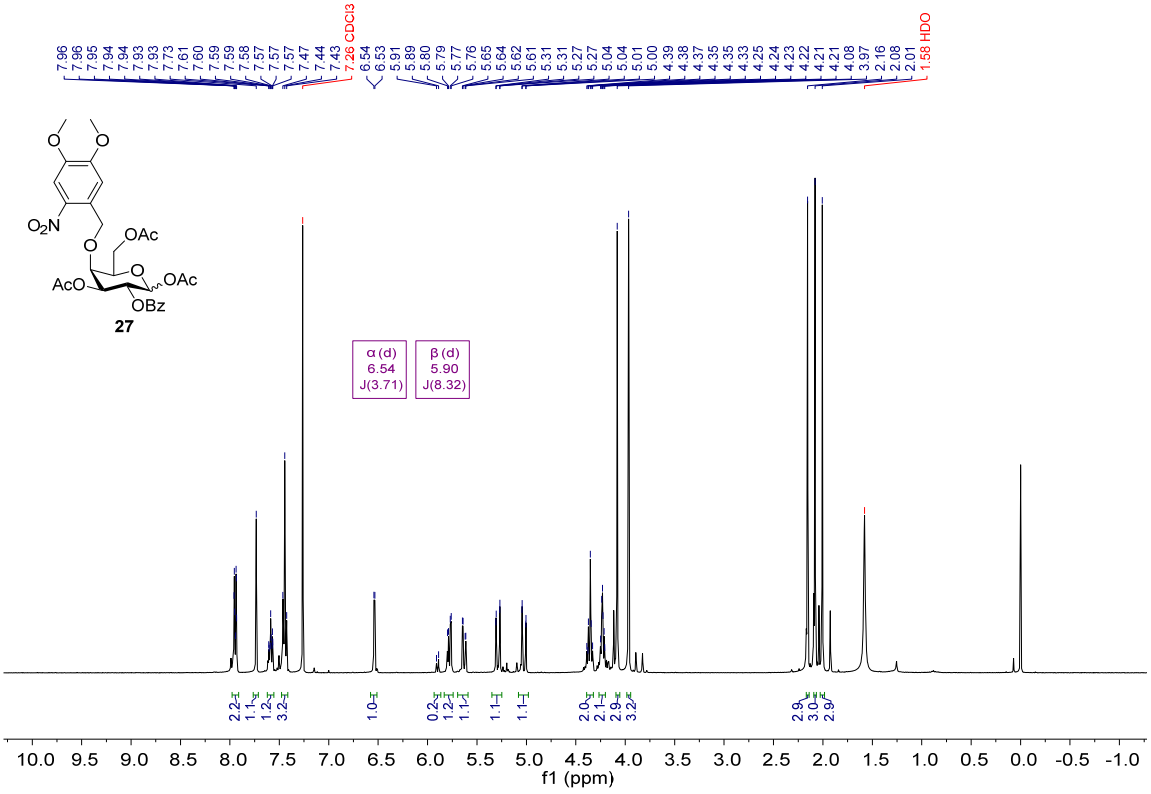
^{13}C NMR ($CDCl_3$, 101 MHz) of compound 25



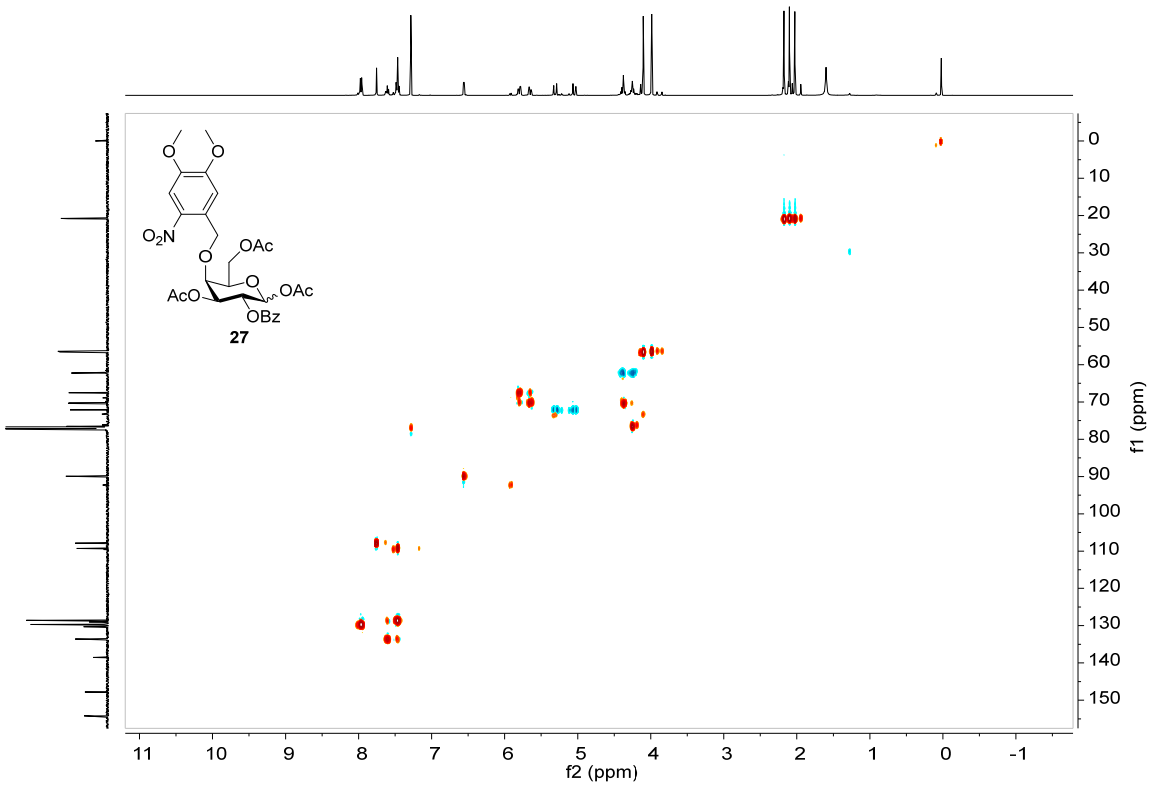
^{1}H NMR ($CDCl_3$, 400 MHz) of compound 26



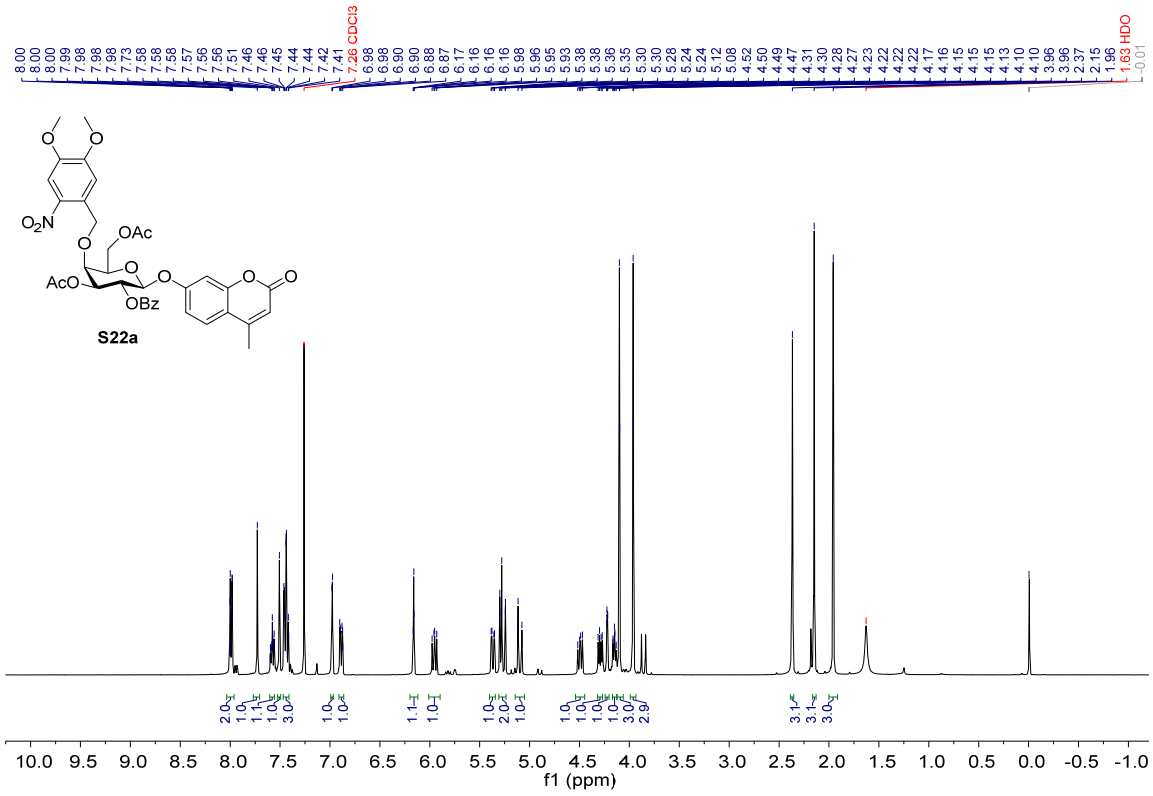
^{1}H NMR ($CDCl_3$, 400 MHz) of compound 27



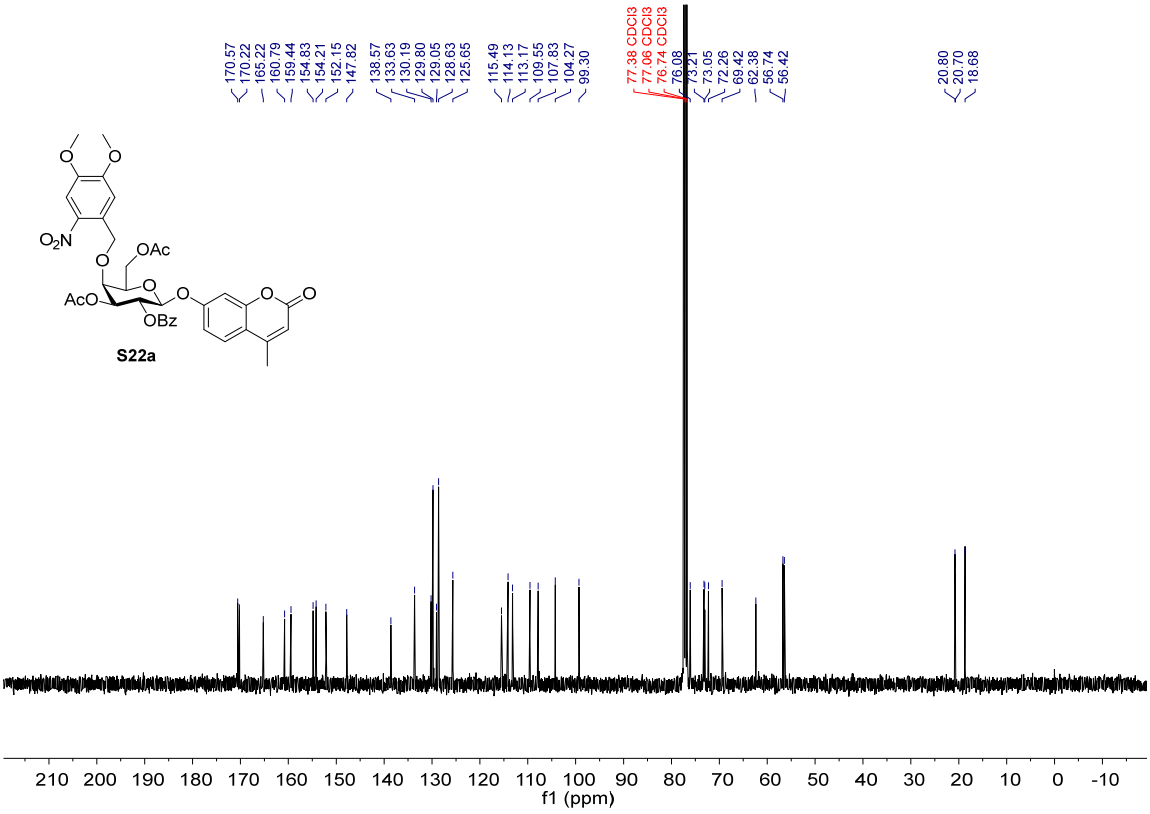
^{1}H-^{13}C HSQC NMR ($CDCl_3$, 400 MHz) of compound 27



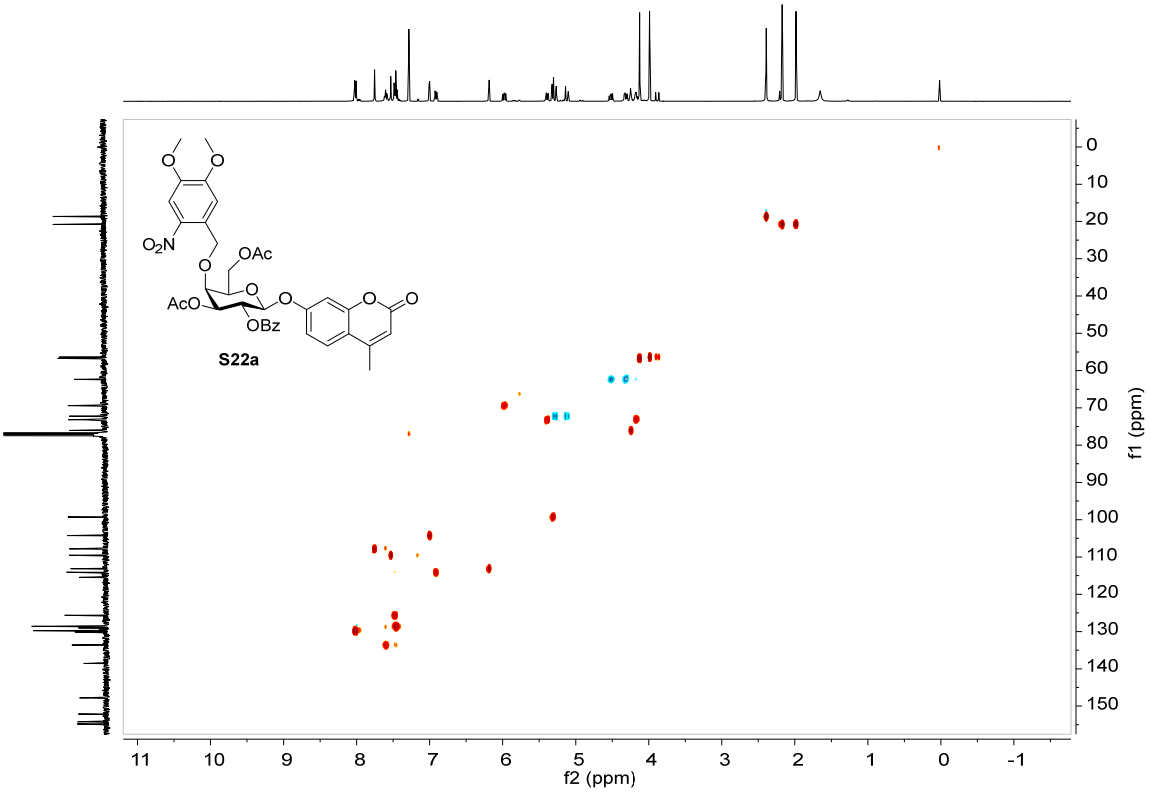
^{1}H NMR ($CDCl_3$, 400 MHz) of compound S22a



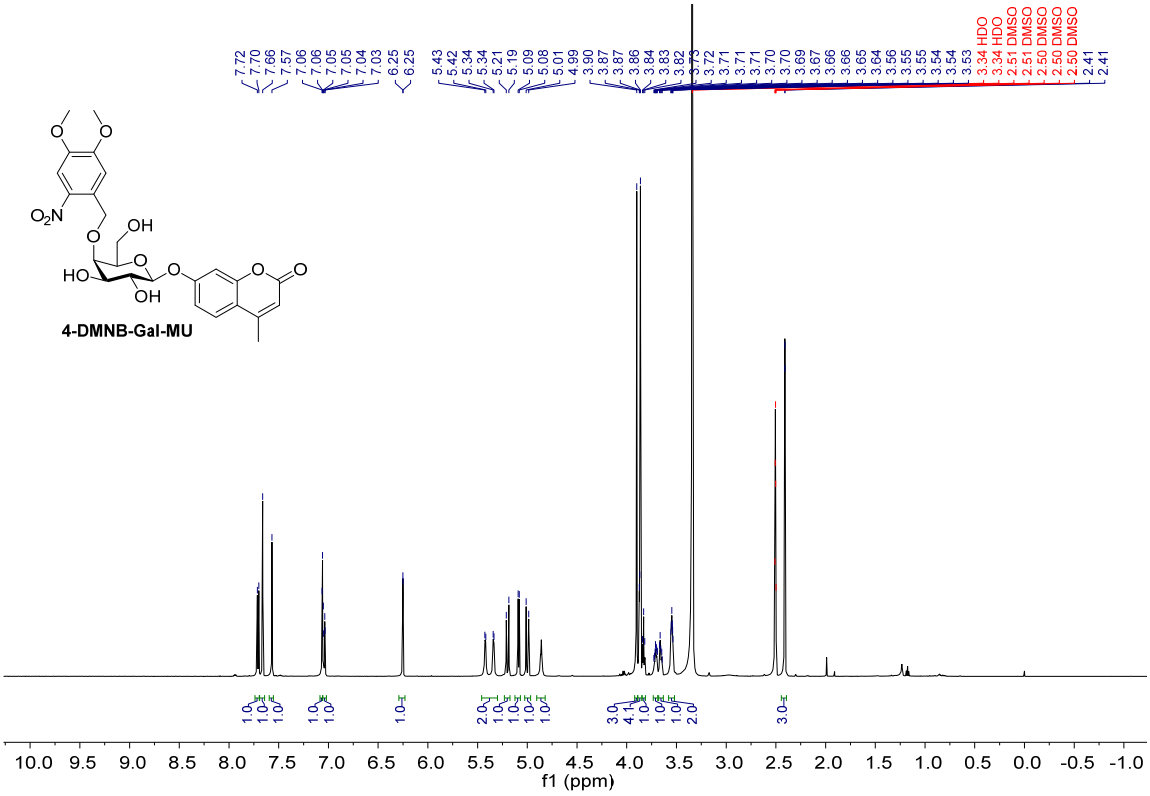
^{13}C NMR ($CDCl_3$, 101 MHz) of compound S22a



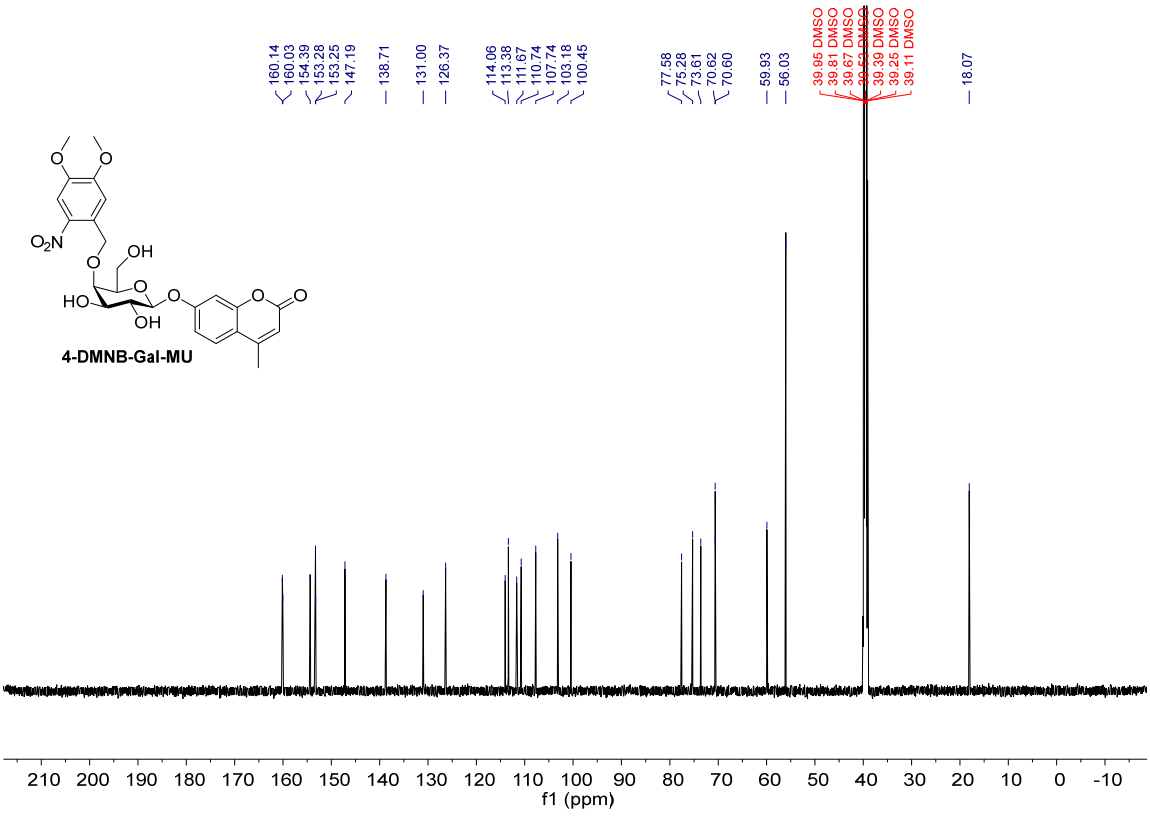
^{1}H-^{13}C HSQC NMR ($CDCl_3$, 400 MHz) of compound S22a



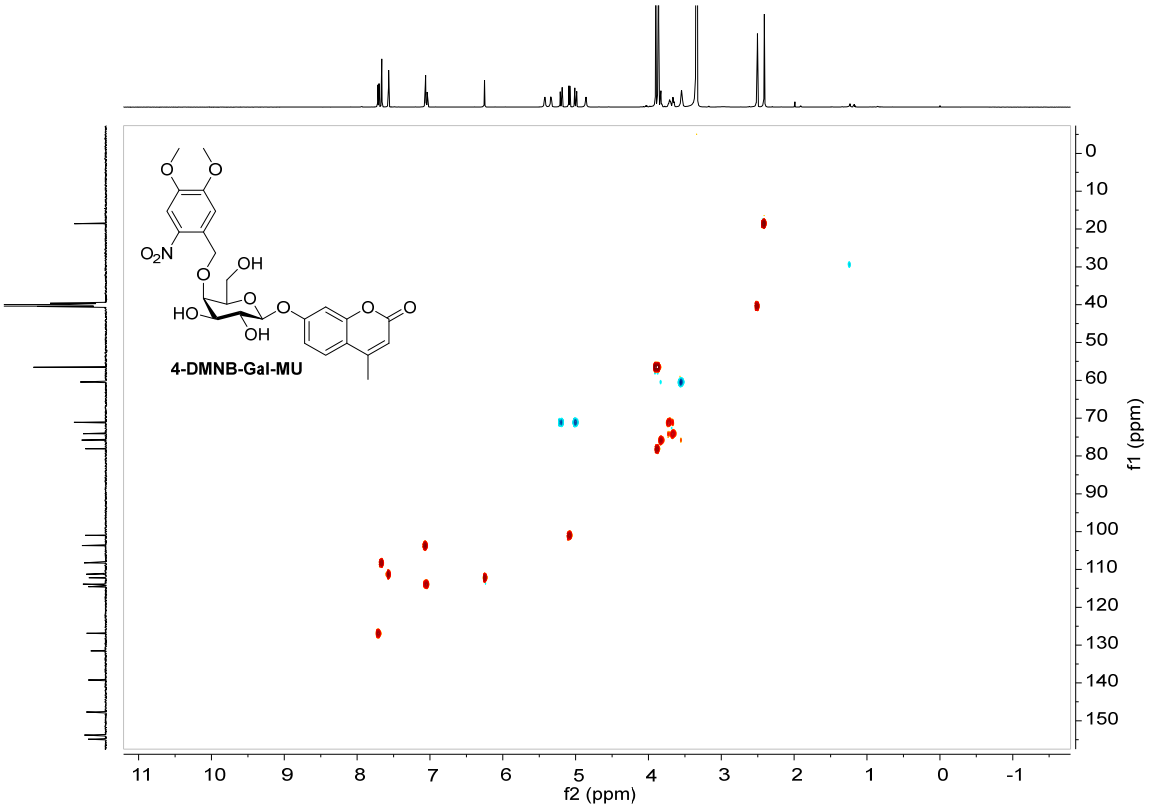
^{1}H NMR ((CD$_3$)$_2$SO, 600 MHz) of compound 4-DMNB-Gal-MU



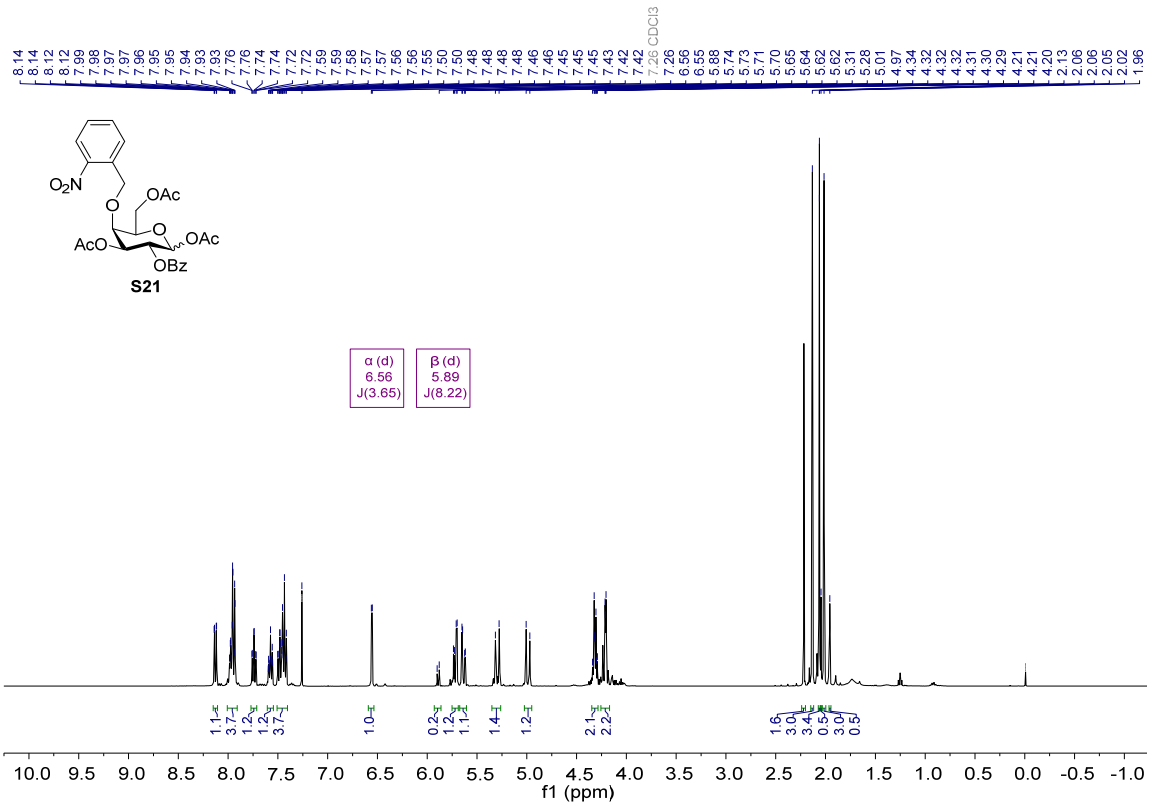
^{13}C NMR ((CD$_3$)$_2$SO, 151 MHz) of compound 4-DMNB-Gal-MU



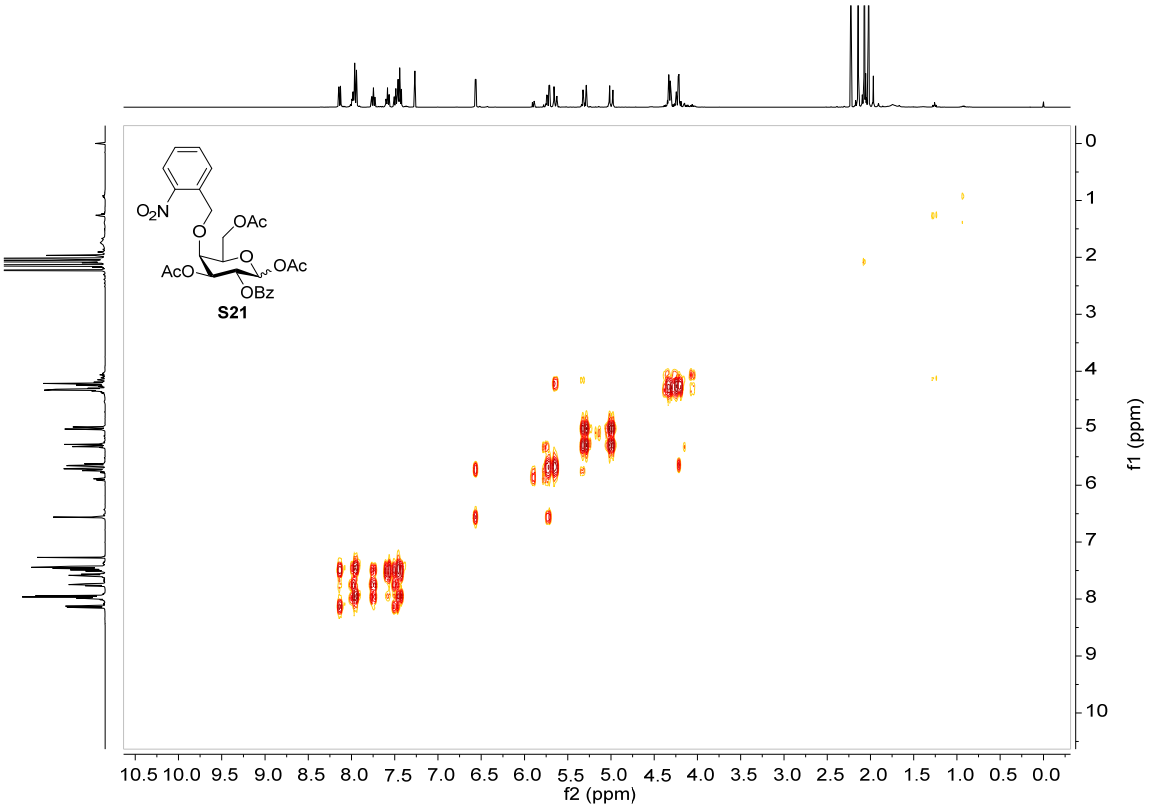
^{1}H-^{13}C HSQC NMR ($(CD_3)_2SO$, 600 MHz) of compound 4-DMNB-Gal-MU



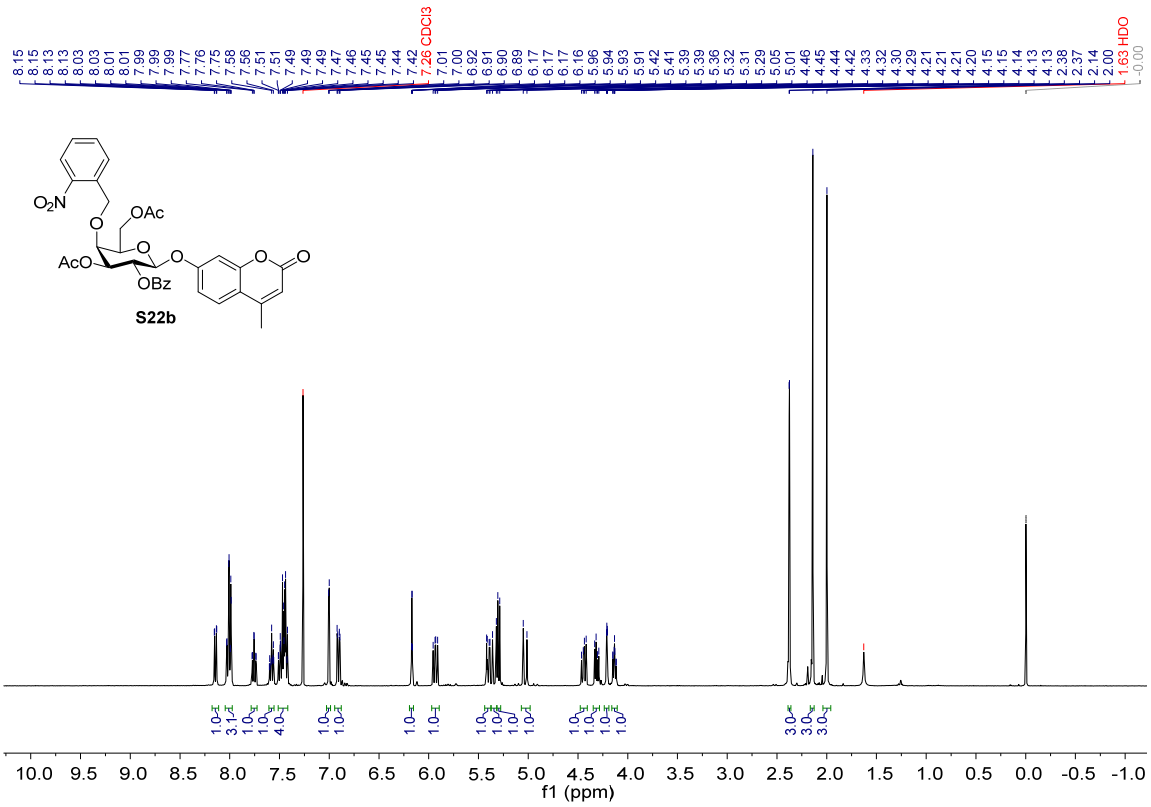
^{1}H NMR ($CDCl_3$, 400 MHz) of compound S21



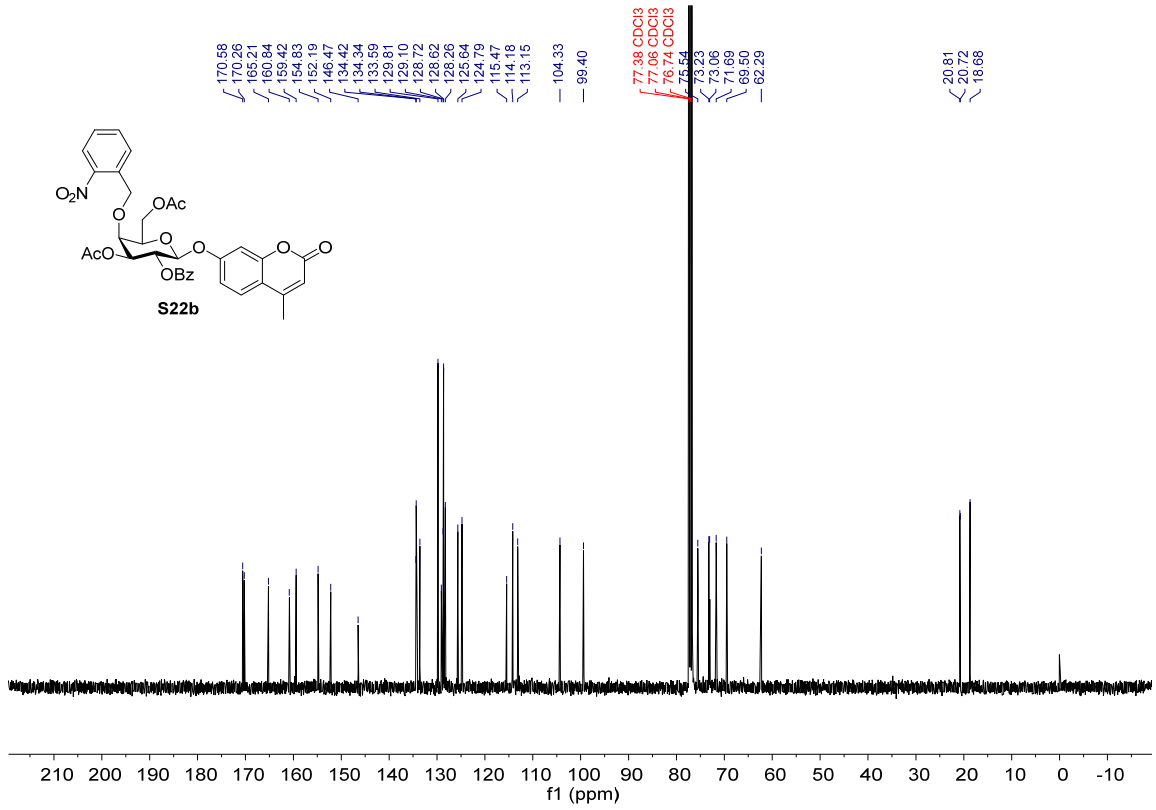
^{1}H-^{1}H COSY NMR ($CDCl_3$, 101 MHz) of compound S21



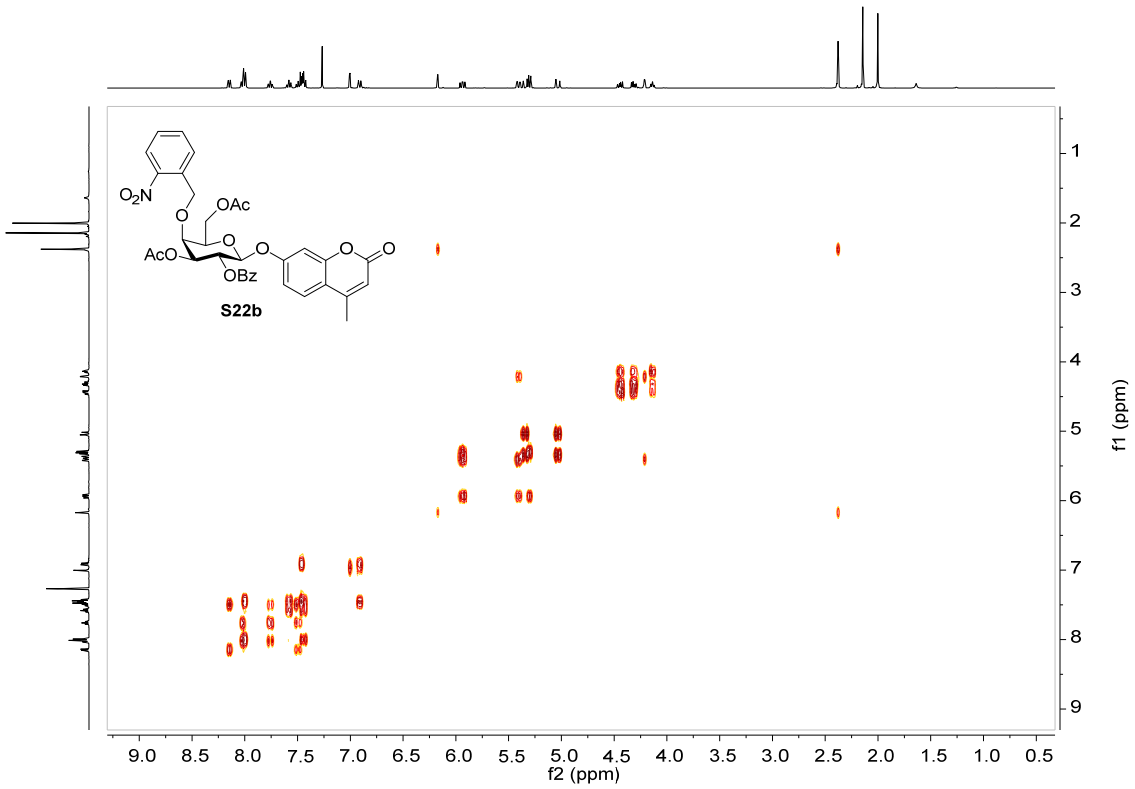
^{1}H NMR ($CDCl_3$, 400 MHz) of compound S22b



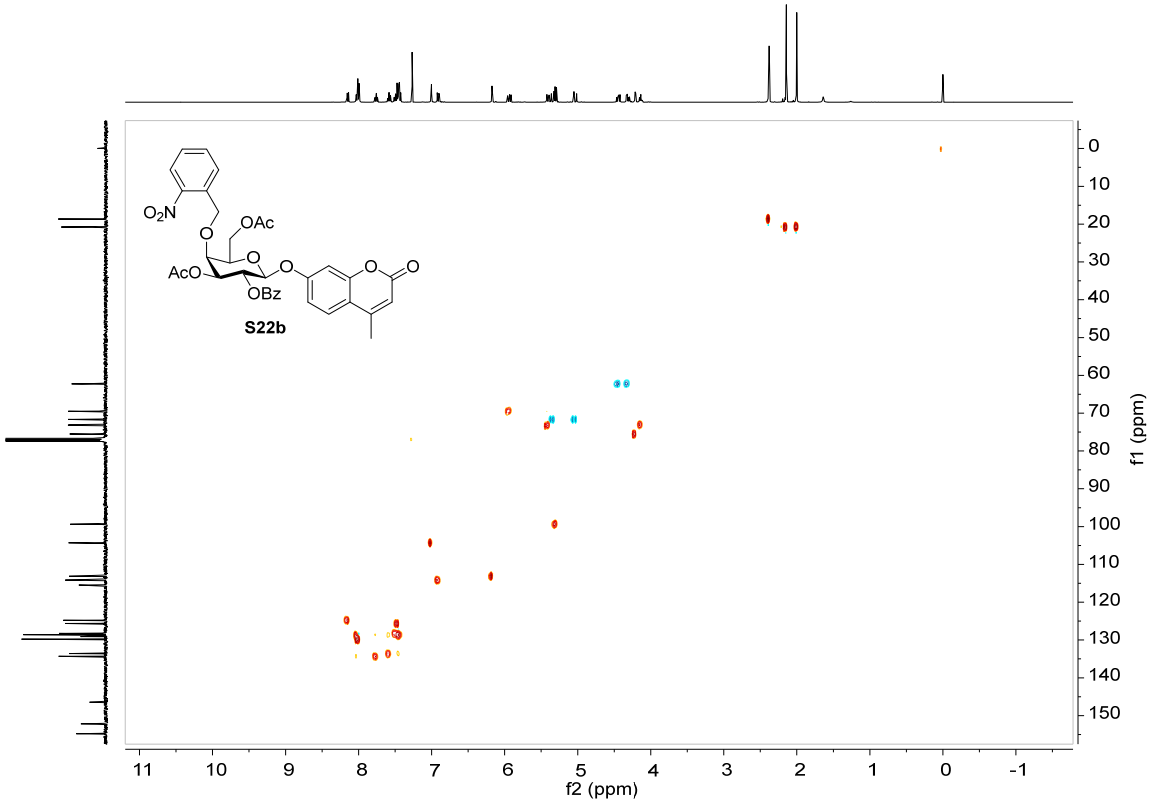
^{13}C NMR ($CDCl_3$, 101 MHz) of compound S22b



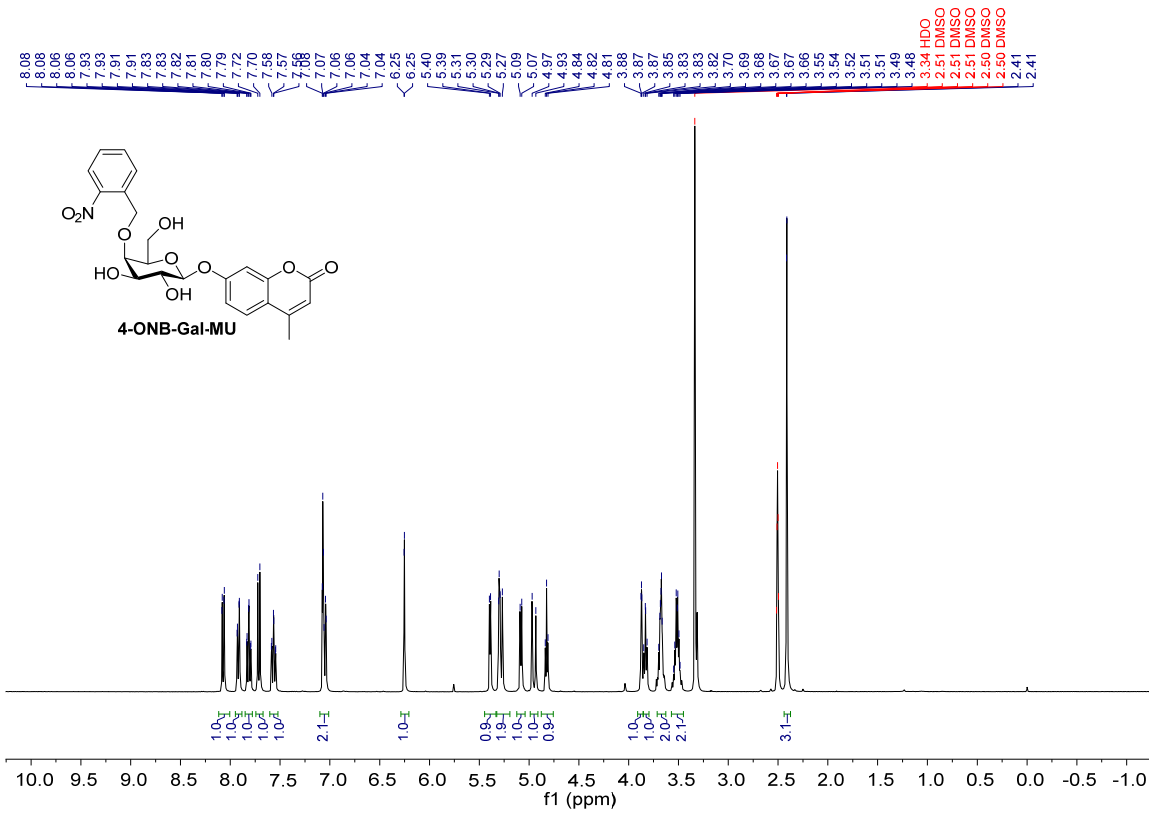
^{1}H-^{1}H COSY NMR ($CDCl_3$, 400 MHz) of compound S22b



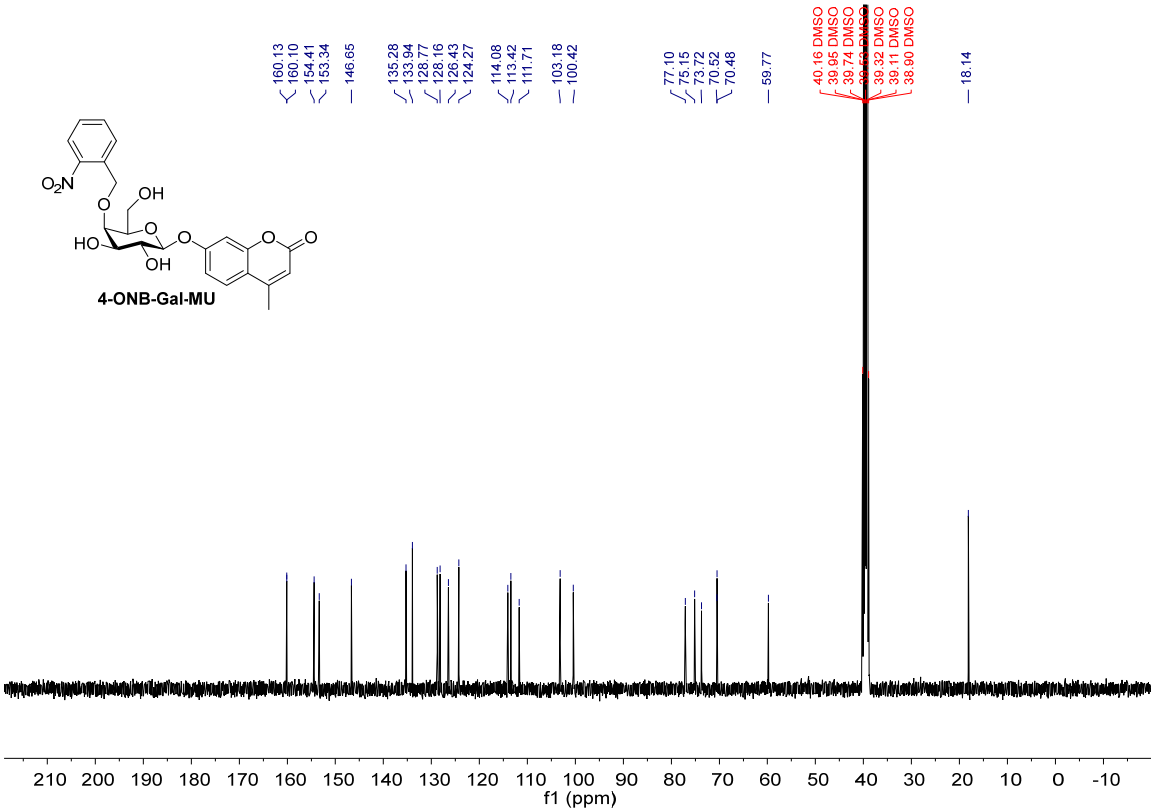
^{1}H-^{13}C HSQC NMR ($CDCl_3$, 400 MHz) of compound S22b



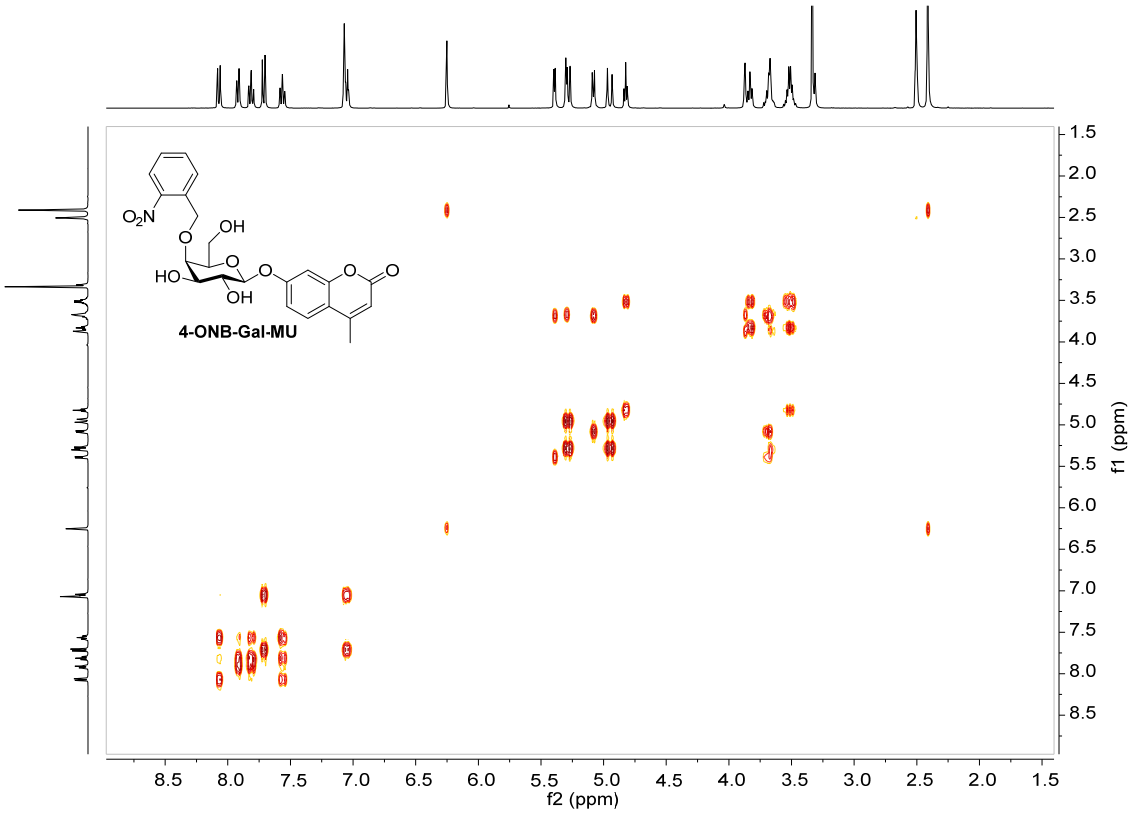
^{1}H NMR ($(CD_3)_2SO$, 400 MHz) of compound 4-ONB-Gal-MU



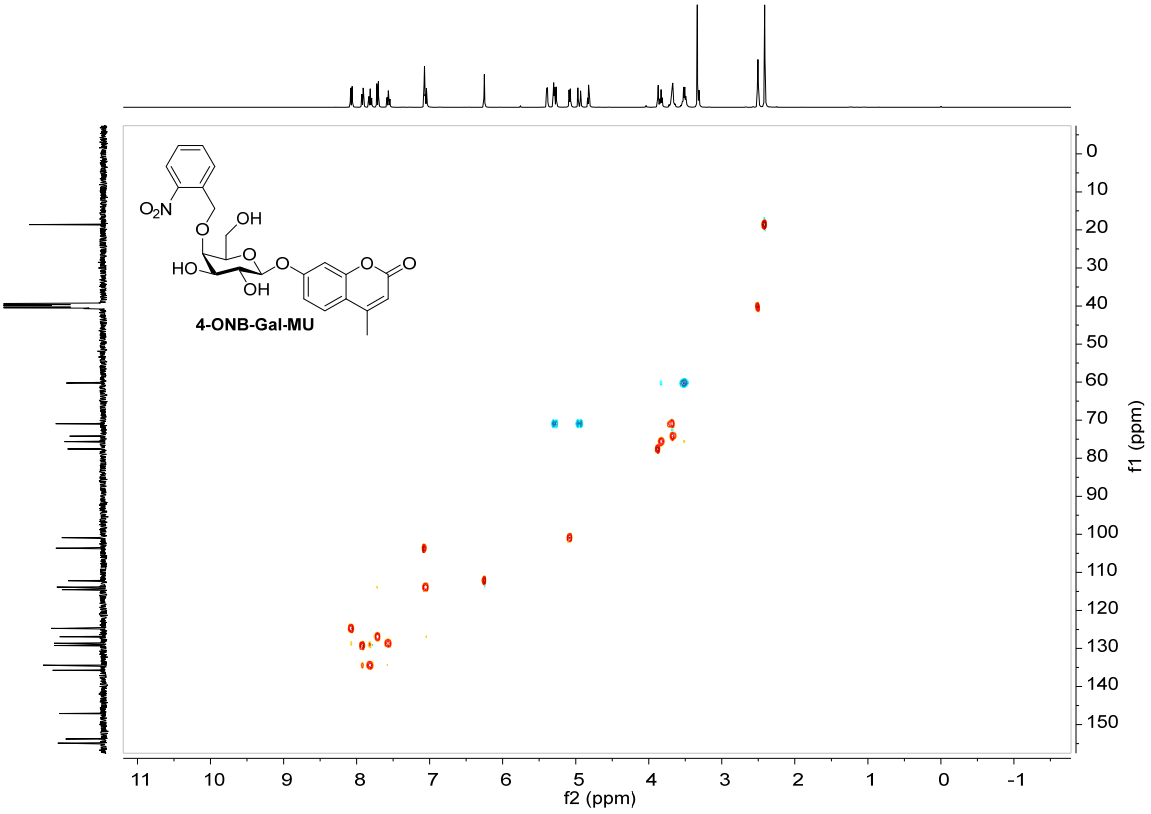
^{13}C NMR ((CD$_3$)$_2$SO, 101 MHz) of compound 4-ONB-Gal-MU



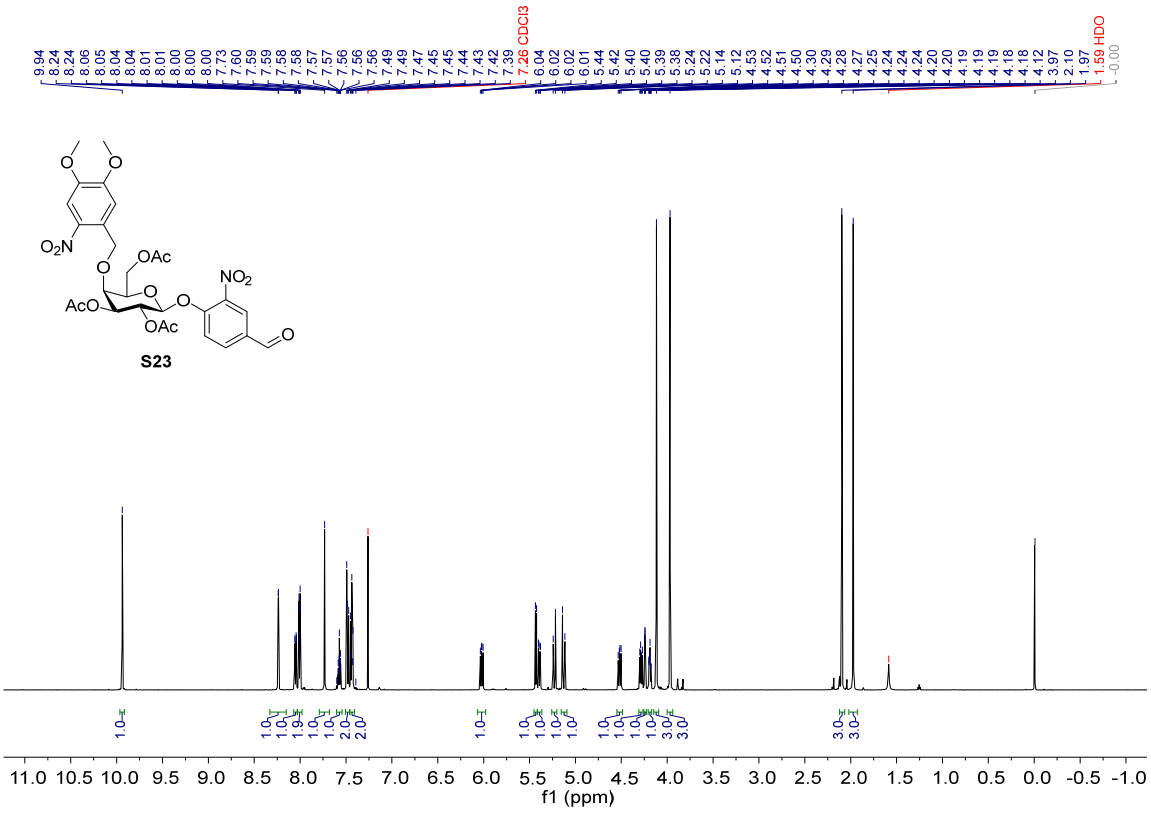
^{1}H-^{1}H COSY NMR ((CD$_3$)$_2$SO, 400 MHz) of compound 4-ONB-Gal-MU



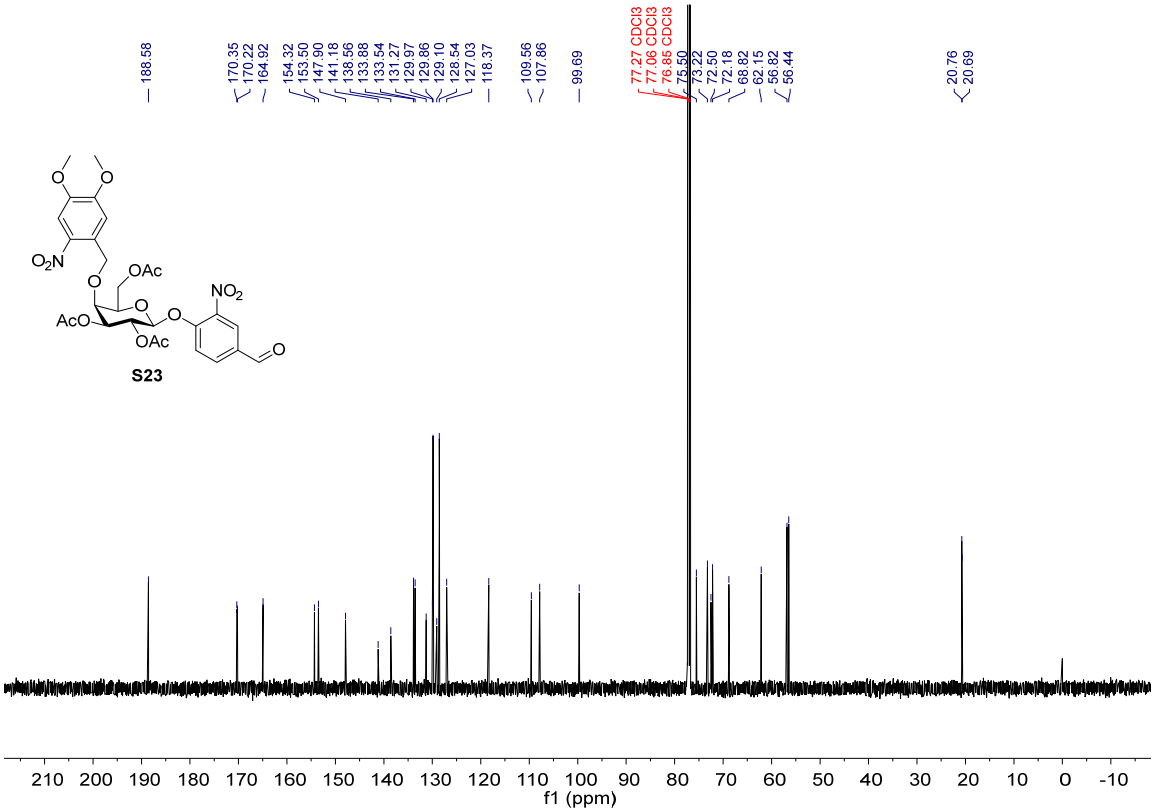
^{1}H-^{13}C HSQC NMR ($(CD_3)_2SO$, 400 MHz) of compound 4-ONB-Gal-MU



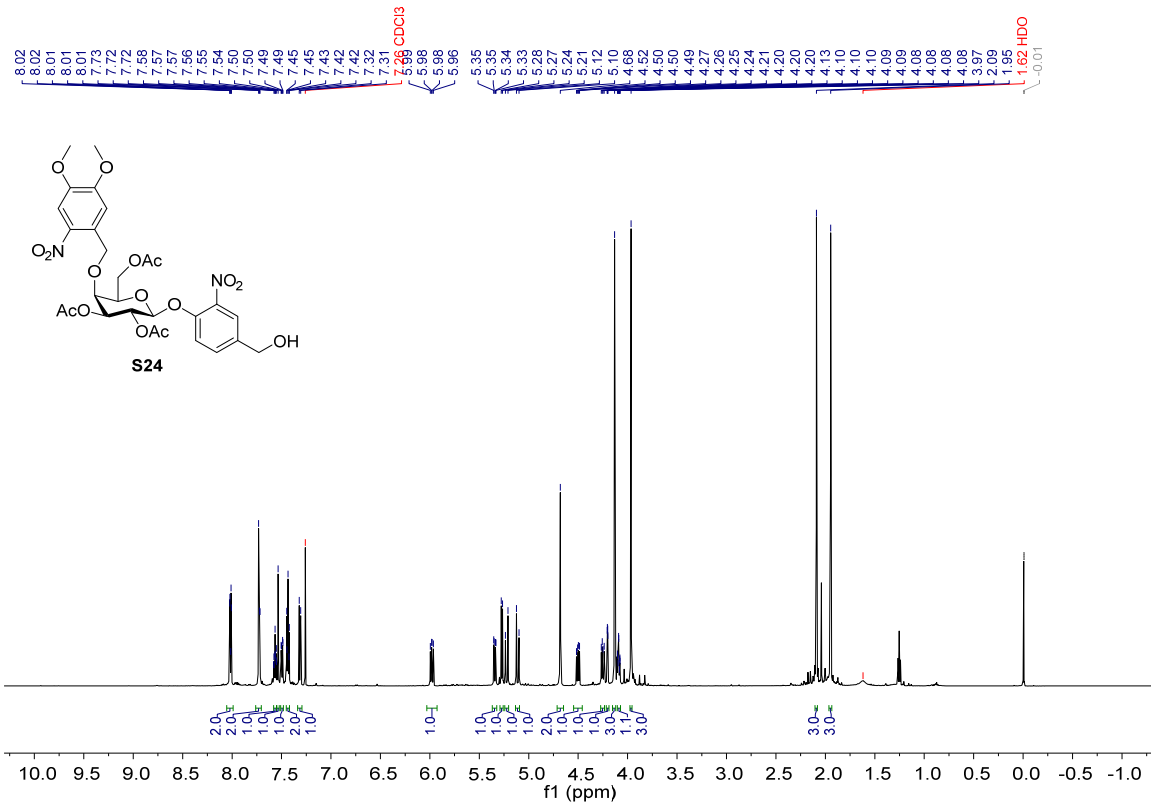
^{1}H NMR ($CDCl_3$, 600 MHz) of compound S23



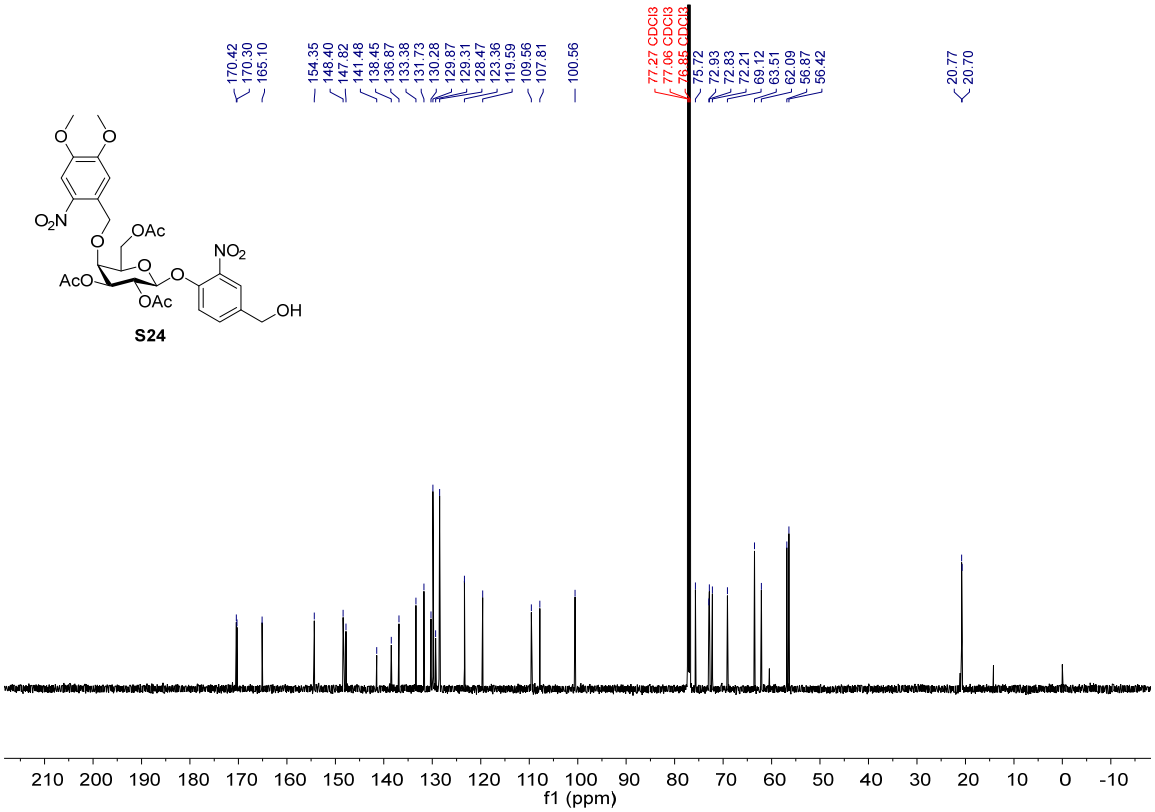
^{13}C NMR ($CDCl_3$, 151 MHz) of compound S23



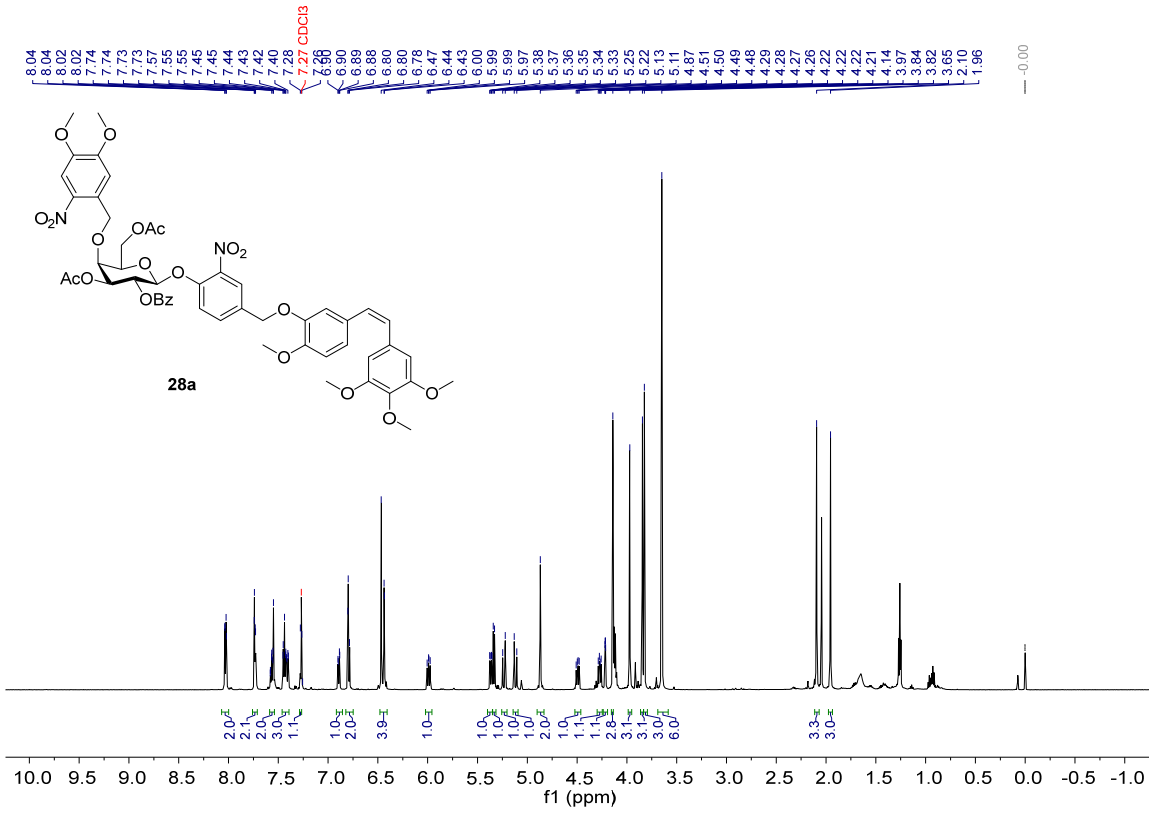
^{1}H NMR ($CDCl_3$, 600 MHz) of compound S24



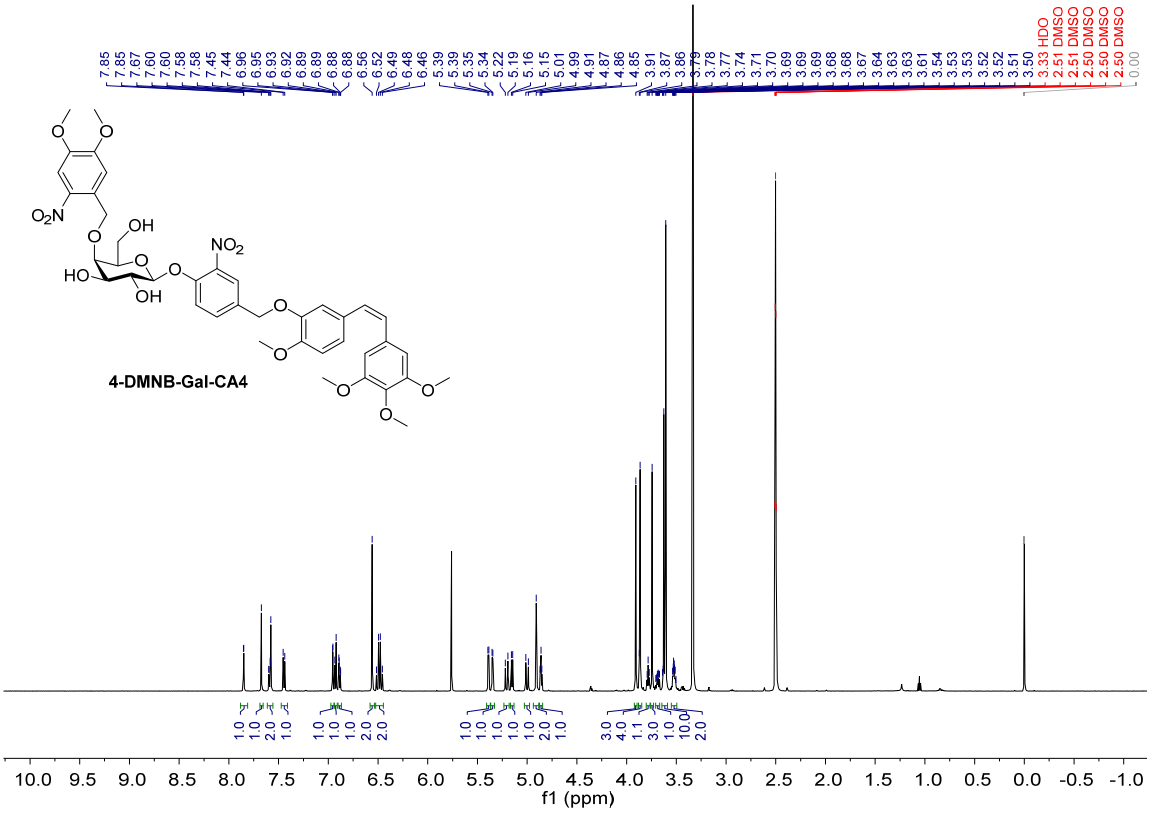
^{13}C NMR ($CDCl_3$, 151 MHz) of compound S24



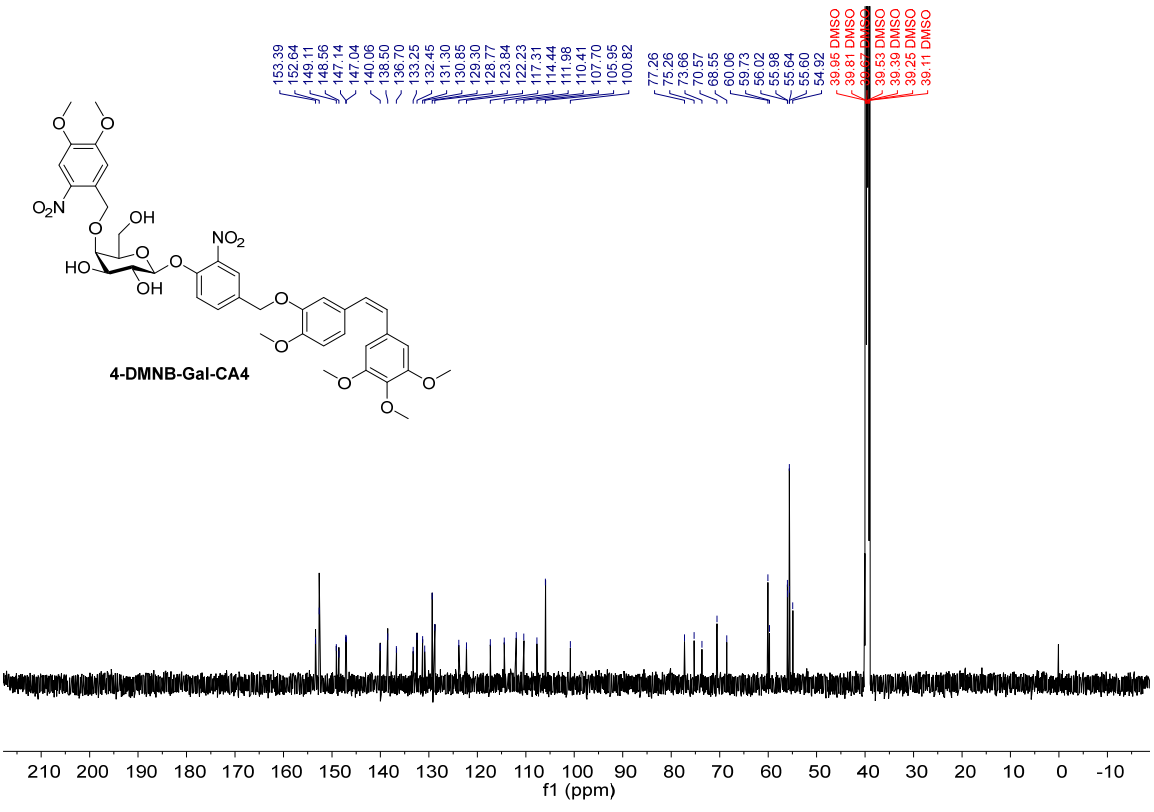
^{1}H NMR ($CDCl_3$, 600 MHz) of compound 28a



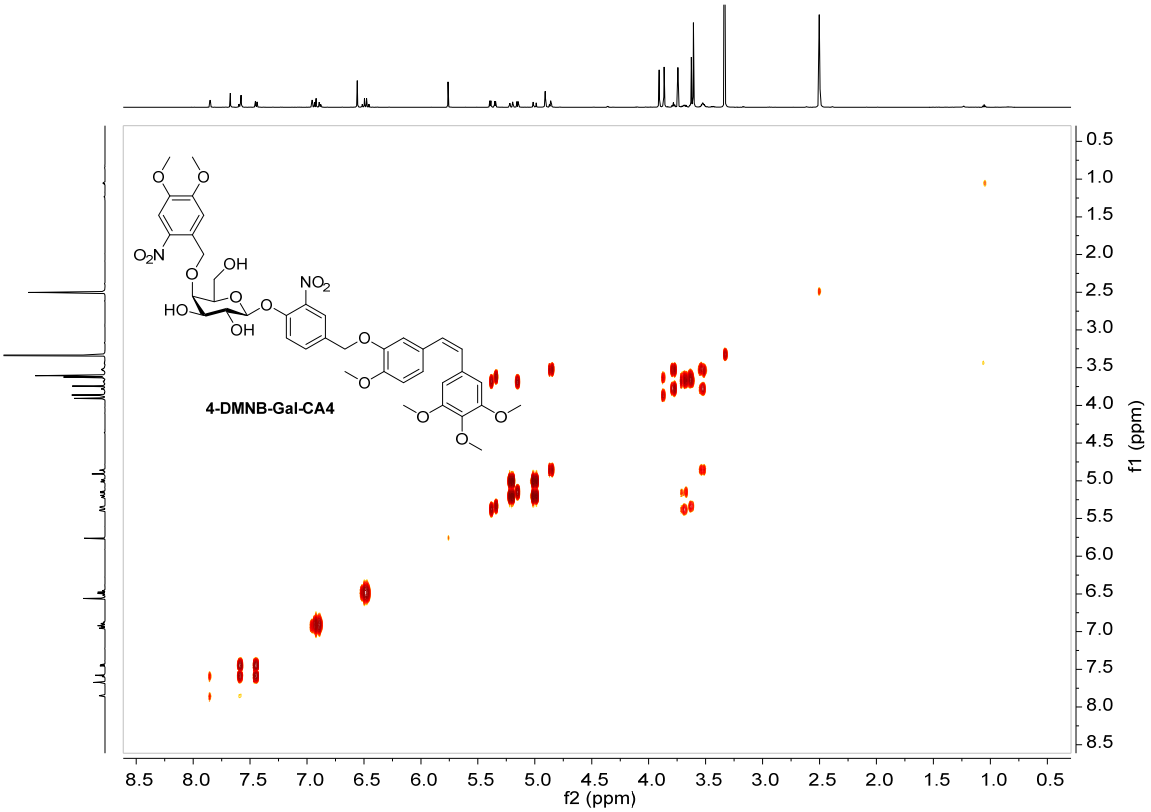
^{1}H NMR ((CD$_3$)$_2$SO, 600 MHz) of compound 4-DMNB-Gal-CA4



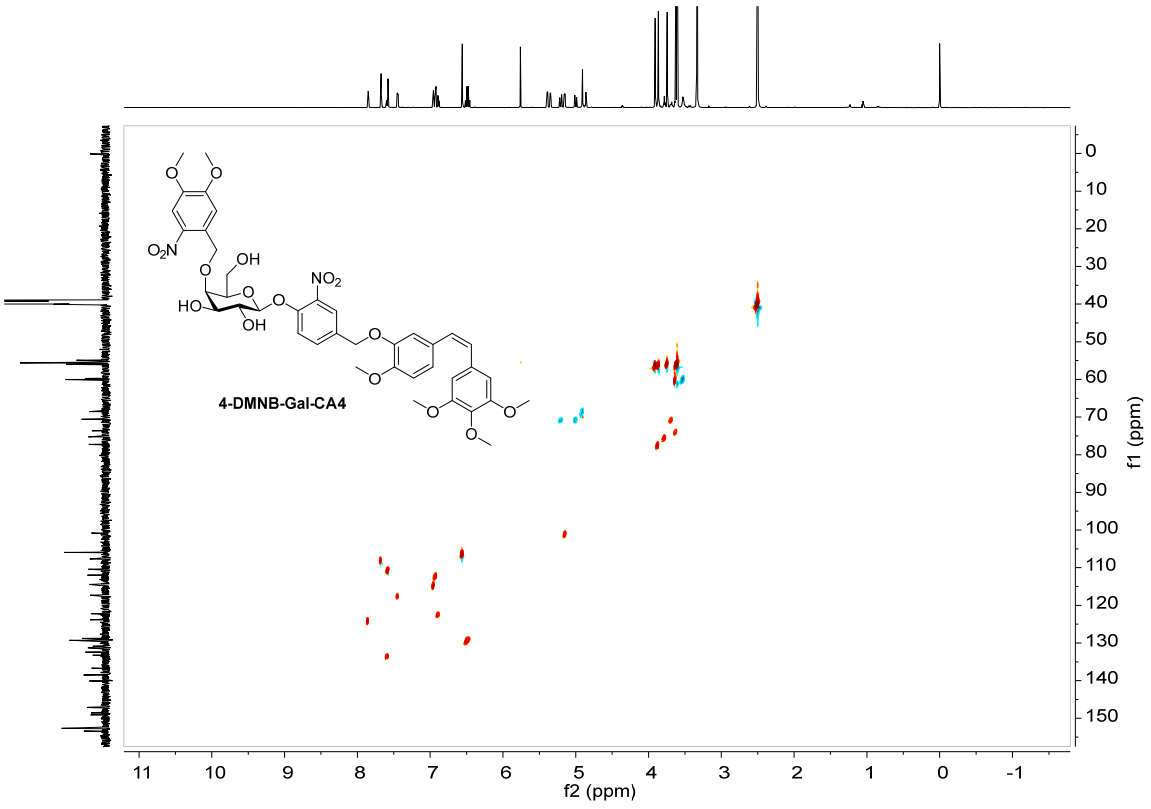
^{13}C NMR ((CD$_3$)$_2$SO, 151 MHz) of compound 4-DMNB-Gal-CA4



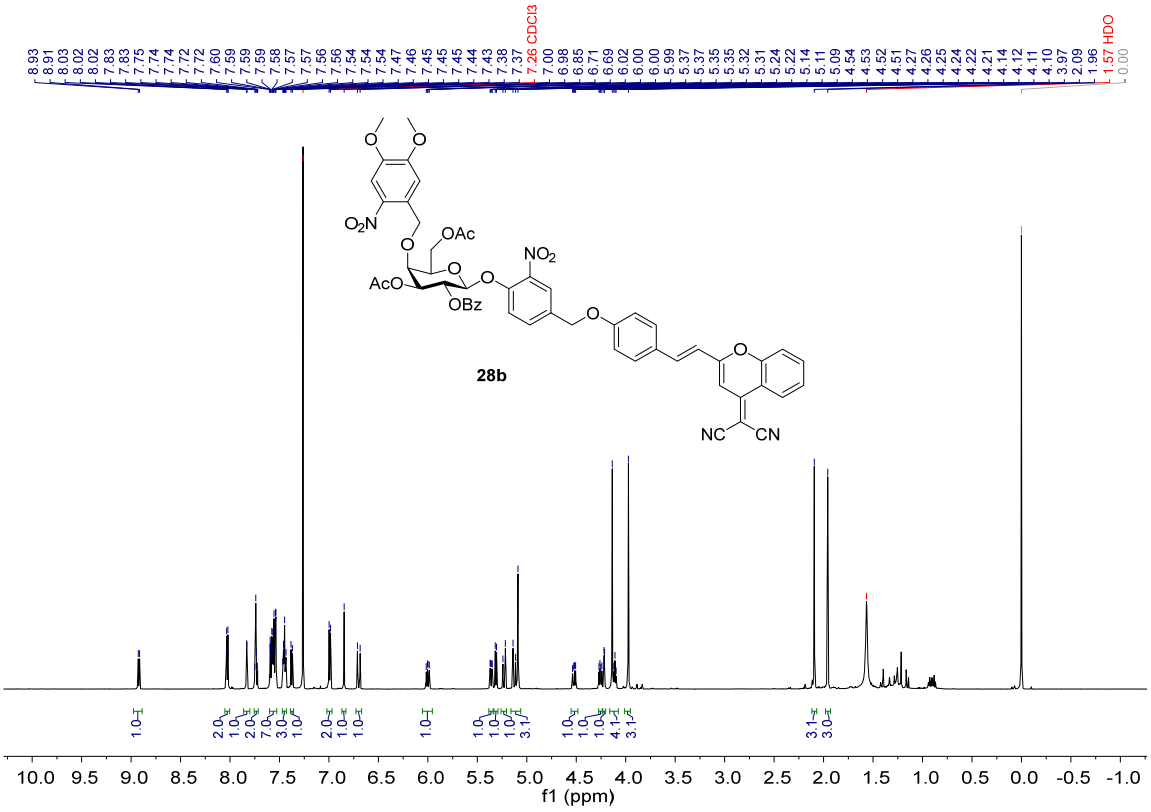
^{1}H-^{1}H COSY NMR ((CD$_3$)$_2$SO, 600 MHz) of compound 4-DMNB-Gal-CA4



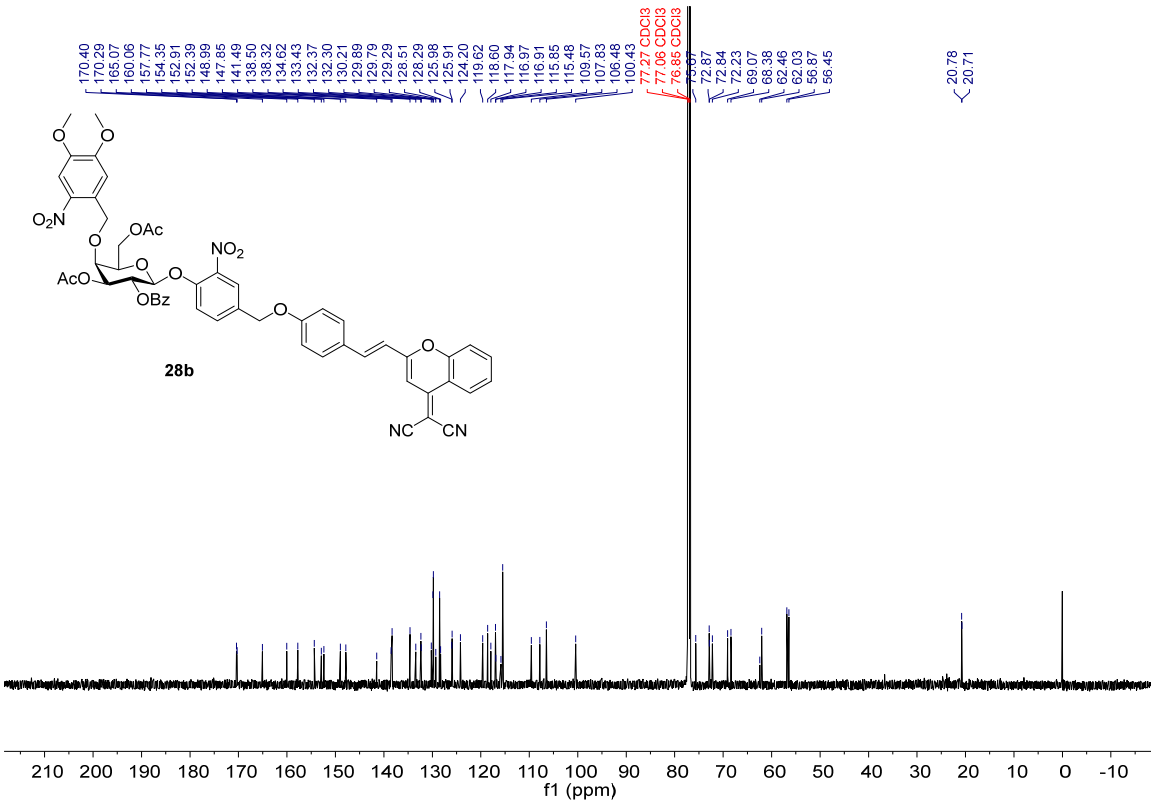
^{1}H-^{13}C HSQC NMR ((CD$_3$)$_2$SO, 600 MHz) of compound 4-DMNB-Gal-CA4



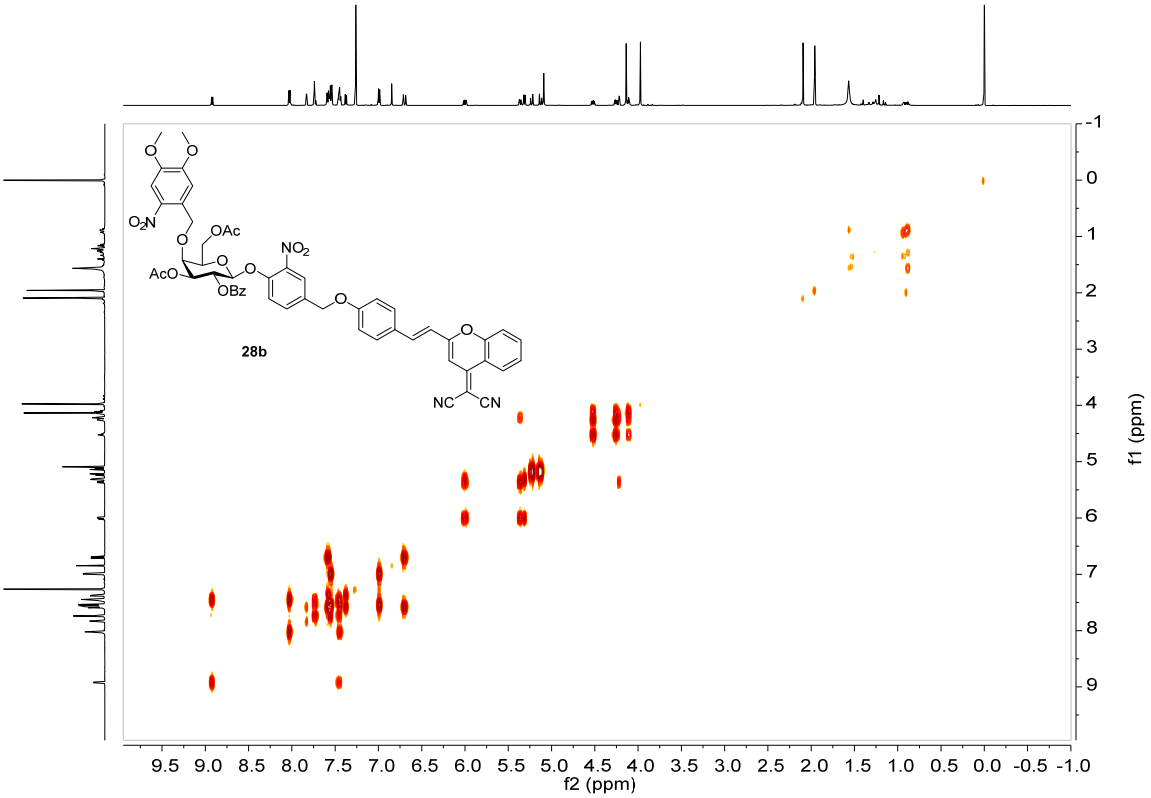
^{1}H NMR ($CDCl_3$, 600 MHz) of compound 28b



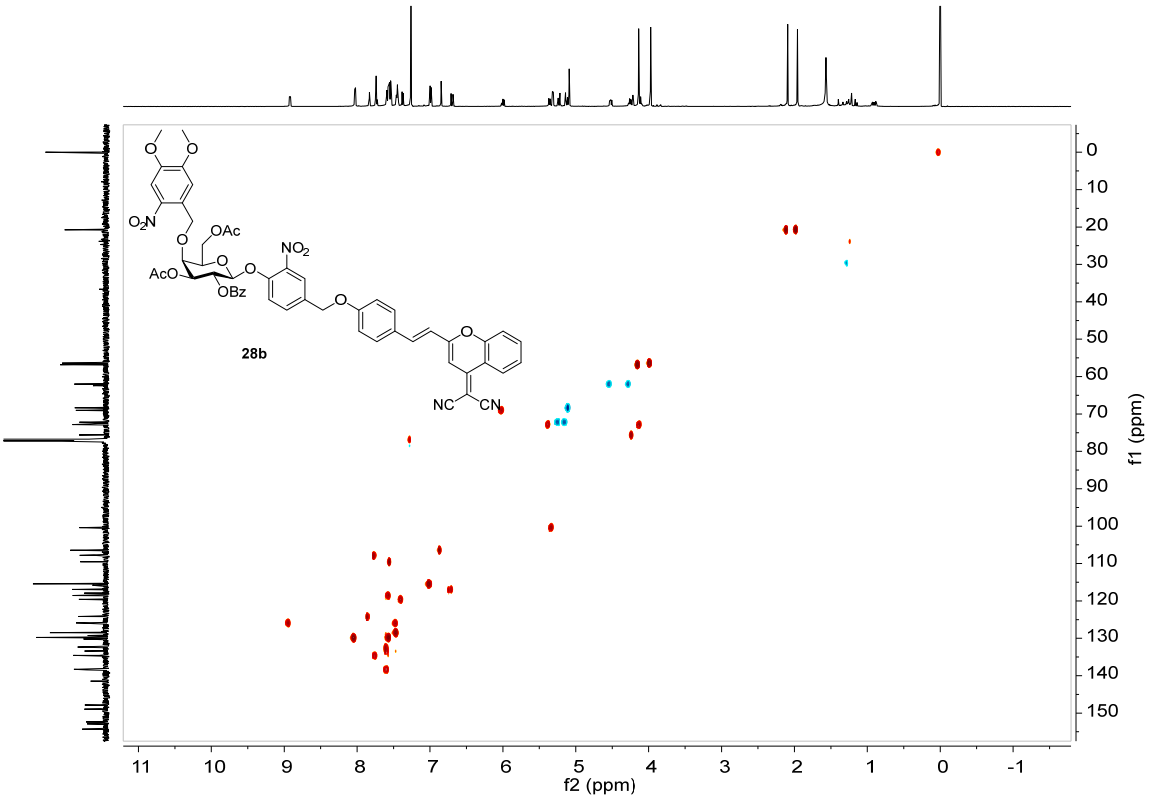
^{13}C NMR ($CDCl_3$, 151 MHz) of compound 28b



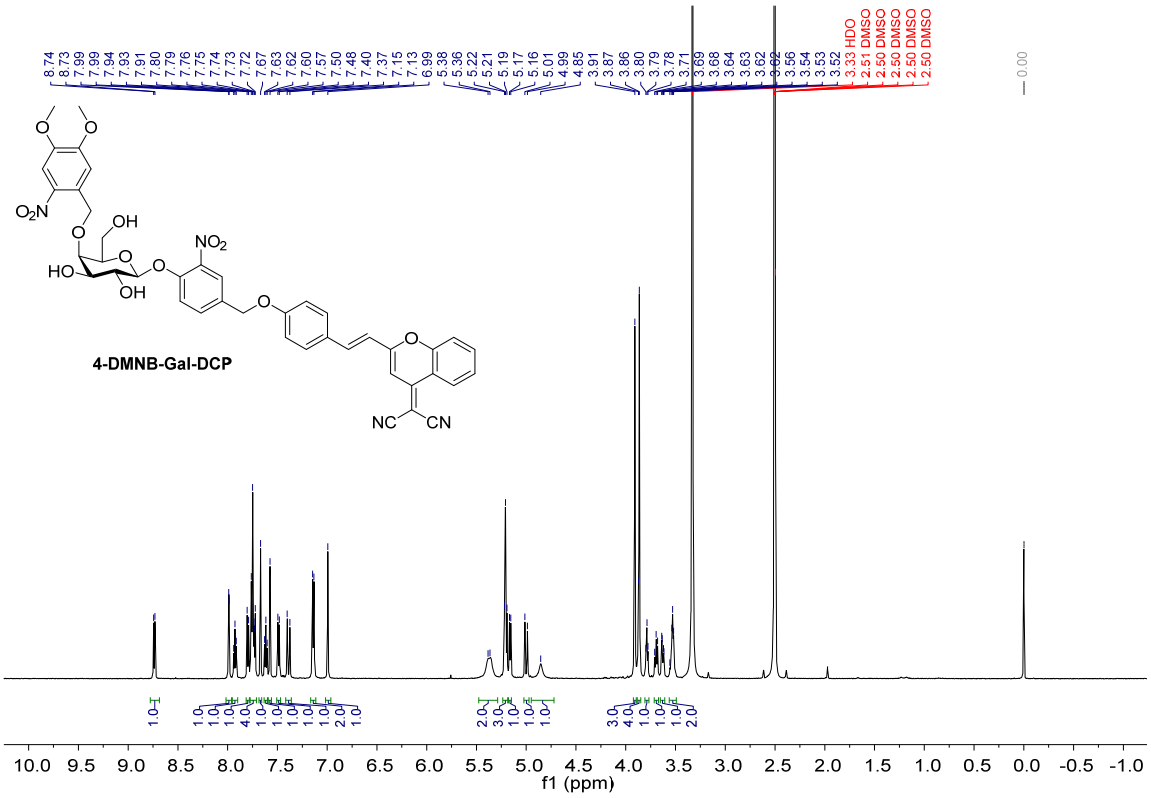
^{1}H-^{1}H COSY NMR ($CDCl_3$, 600 MHz) of compound 28b



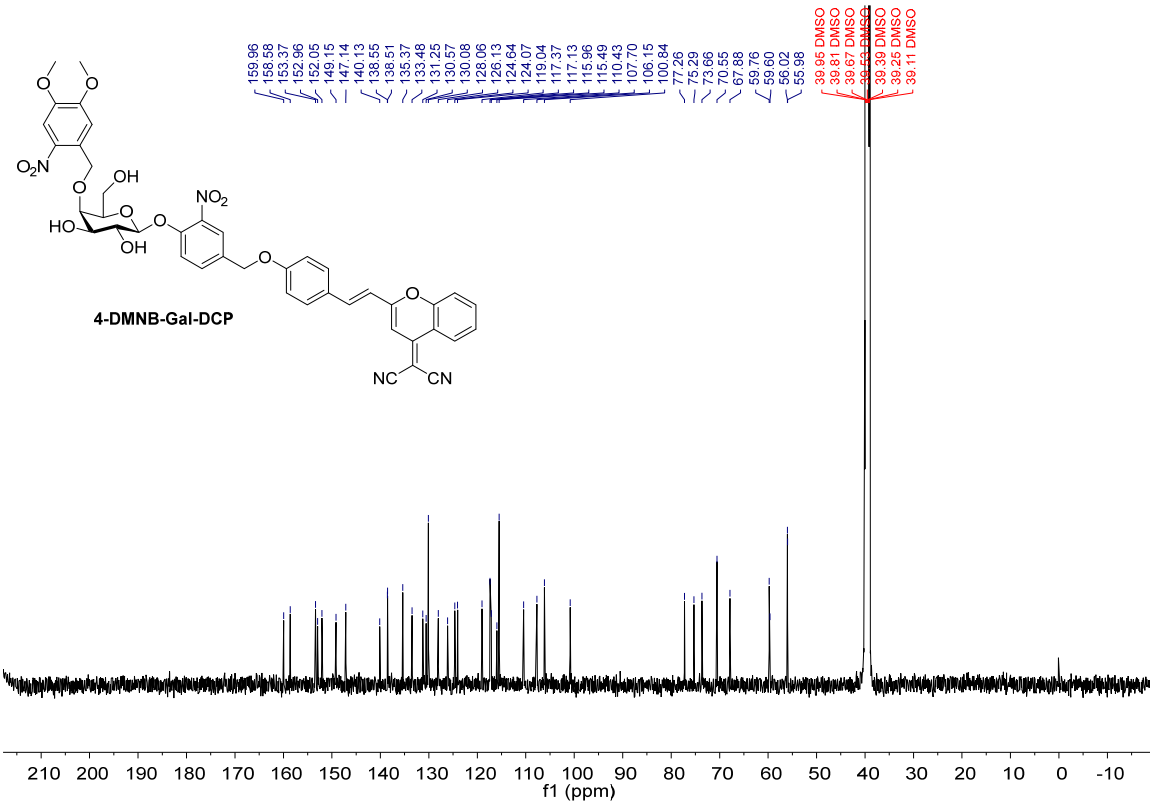
^{1}H-^{13}C HSQC NMR ($CDCl_3$, 600 MHz) of compound 28b



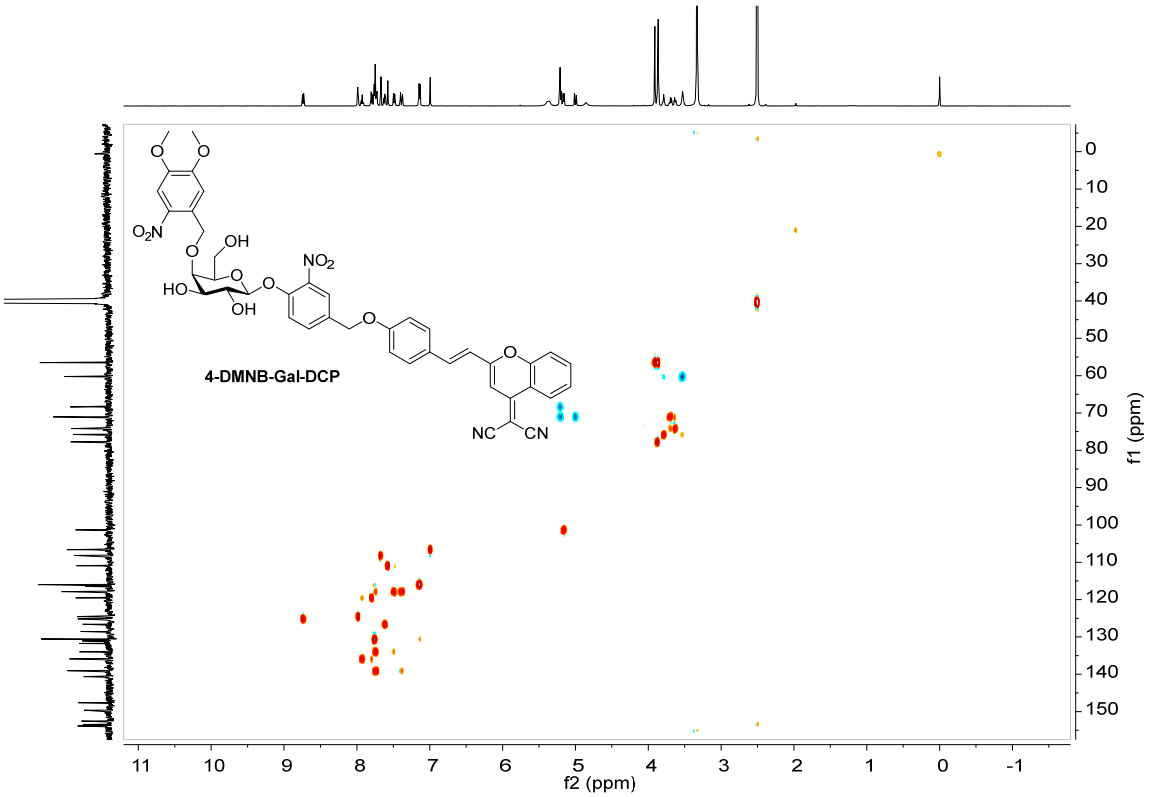
^{1}H NMR ($(CD_3)_2SO$, 600 MHz) of compound 4-DMNB-Gal-DCP



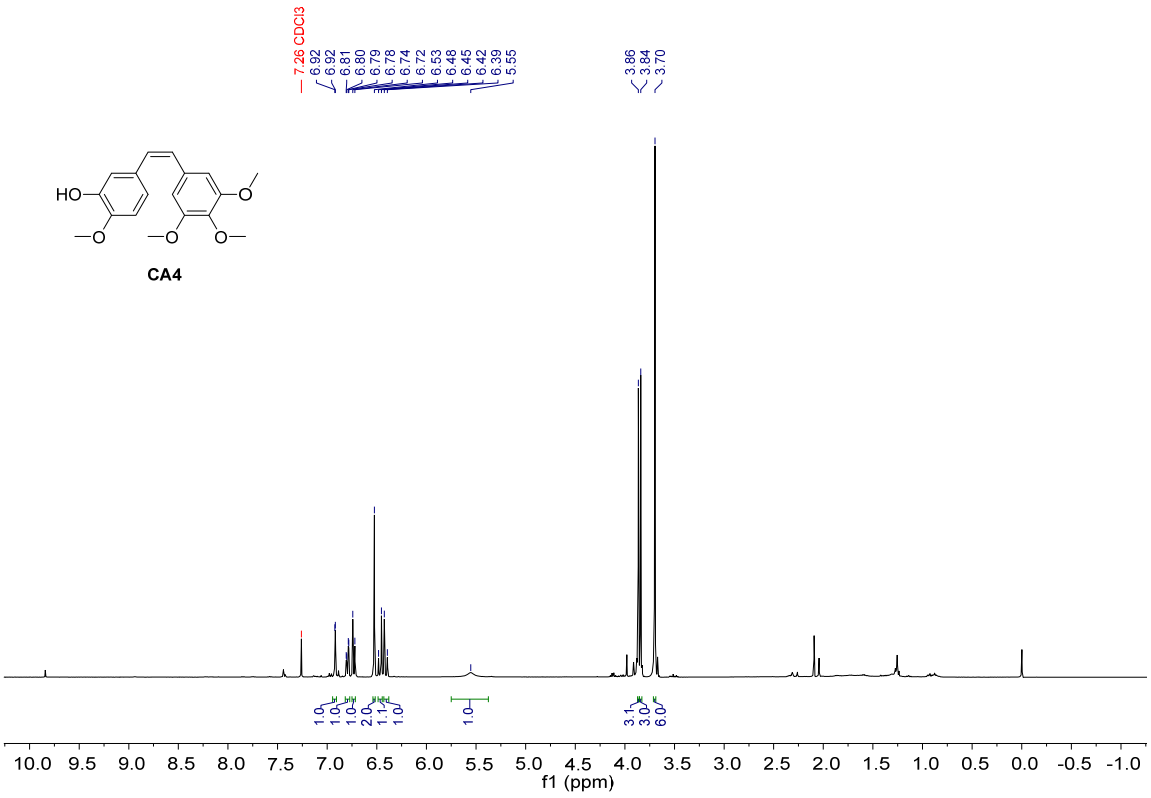
^{13}C NMR ($(CD_3)_2SO$, 151 MHz) of compound 4-DMNB-Gal-DCP



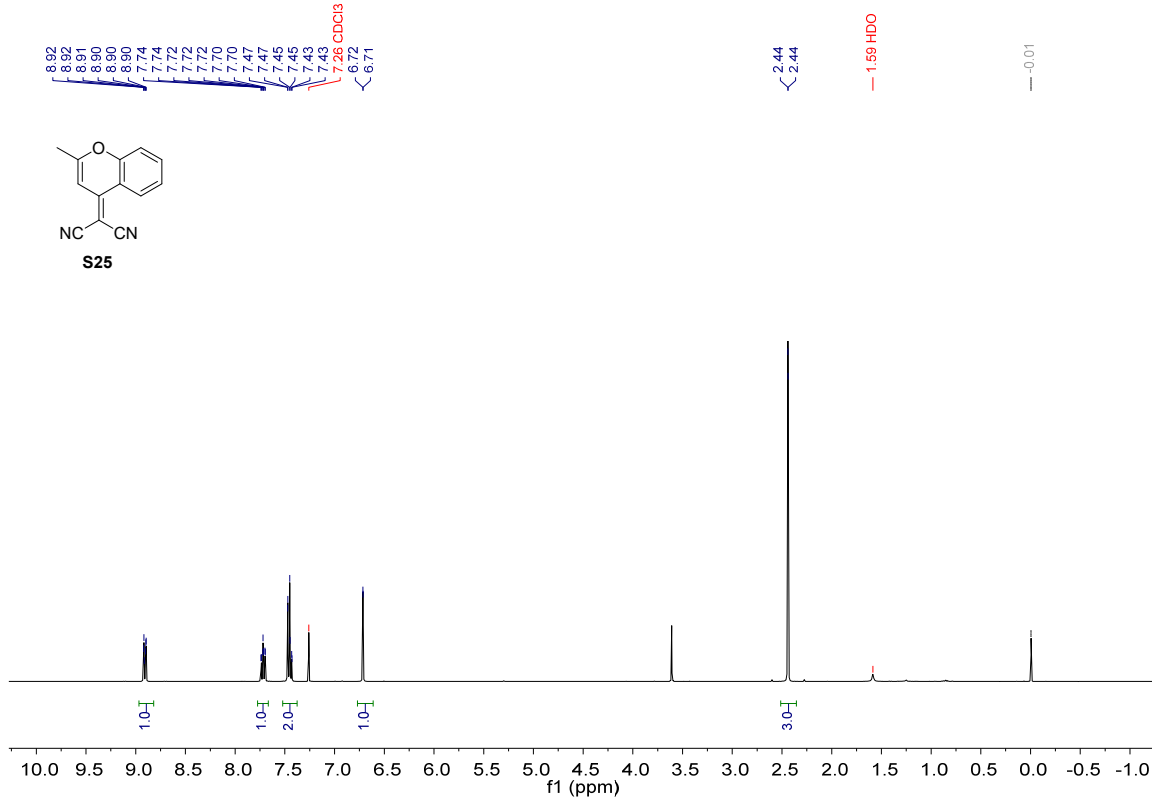
^{1}H-^{13}C HSQC NMR ($(CD_3)_2SO$, 600 MHz) of compound 4-DMNB-Gal-DCP



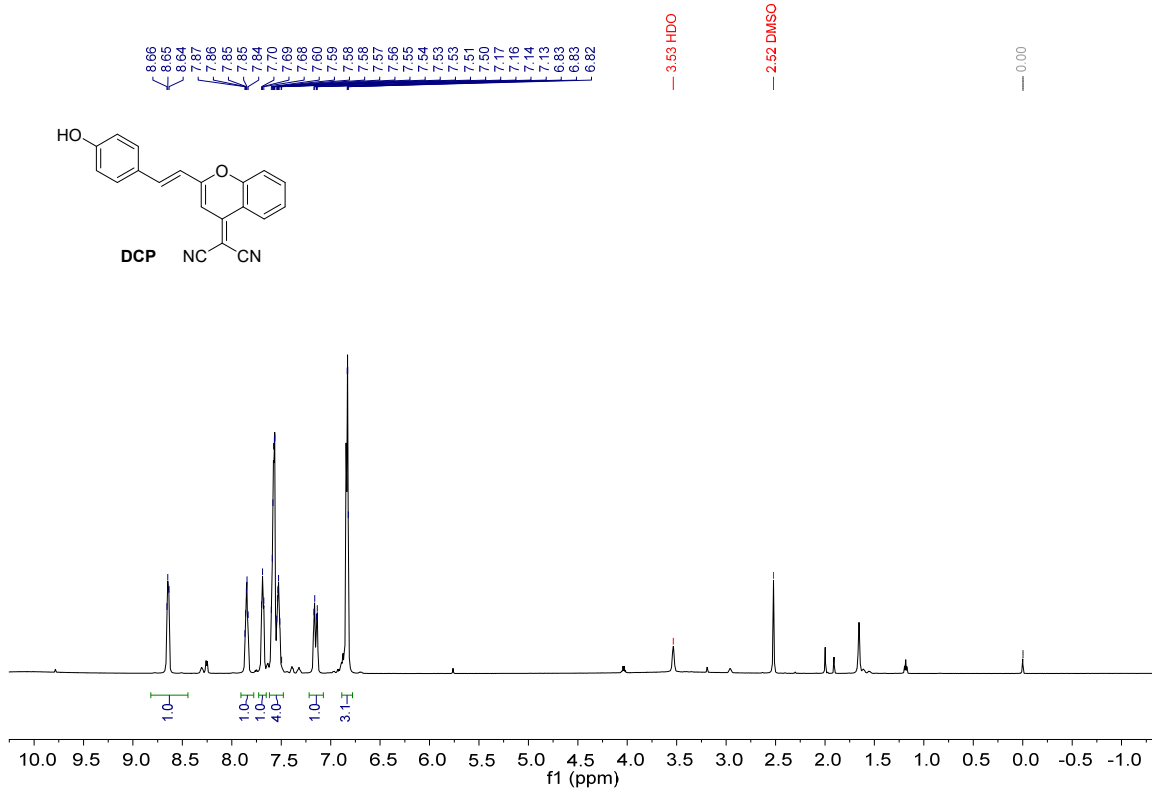
^{1}H NMR ($CDCl_3$, 400 MHz) of compound CA4



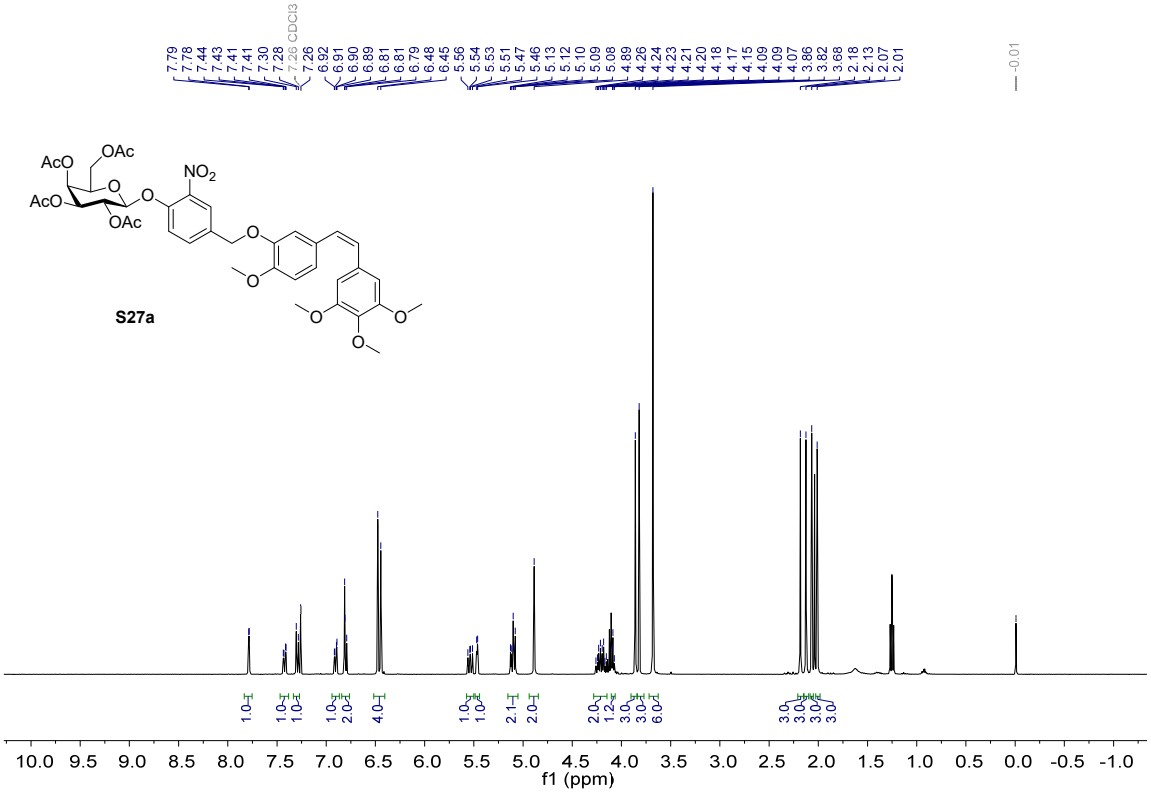
^{1}H NMR ($CDCl_3$, 400 MHz) of compound S25



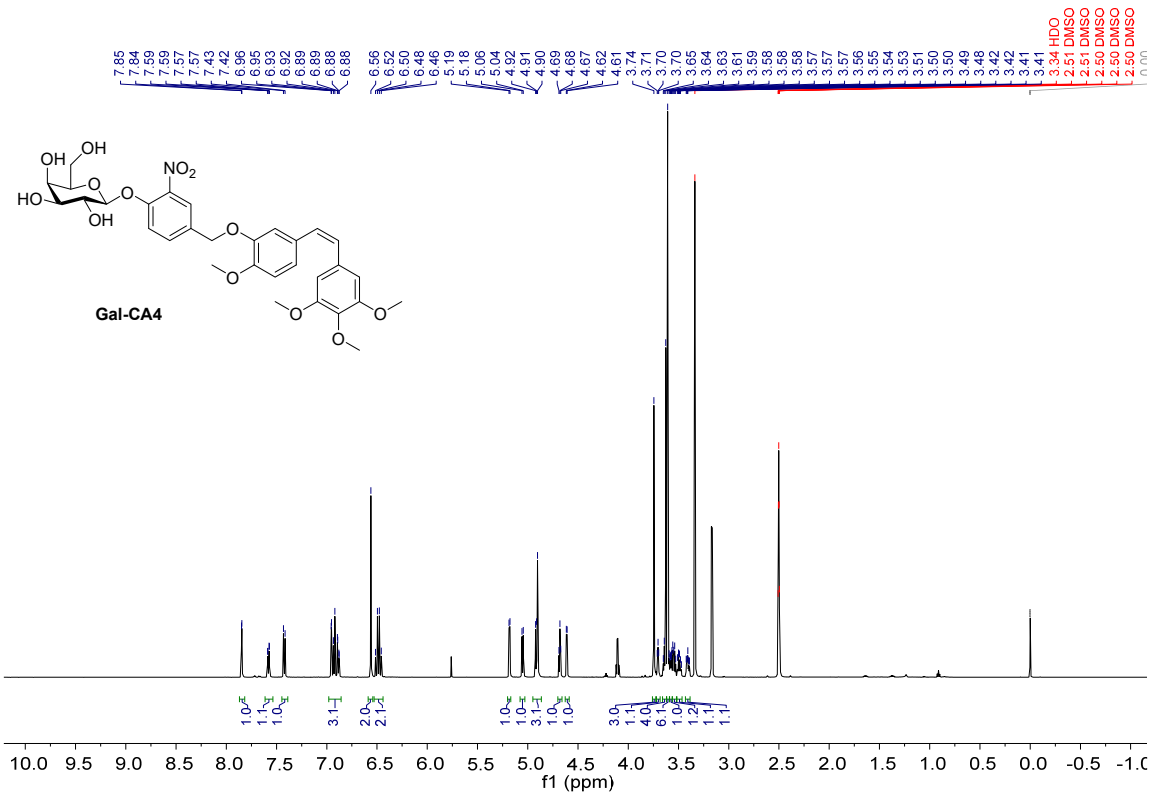
^{1}H NMR ($(CD_3)_2SO$, 400 MHz) of compound DCP



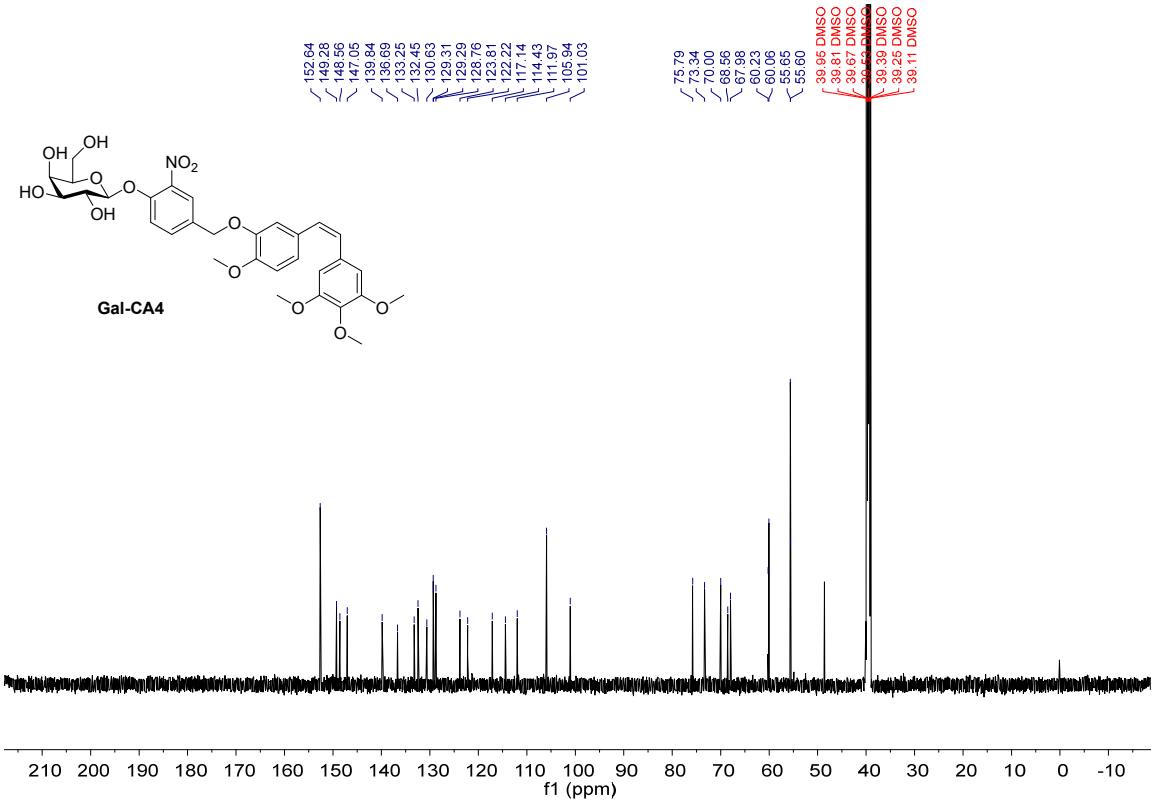
^{1}H NMR ($CDCl_3$, 400 MHz) of compound S27a



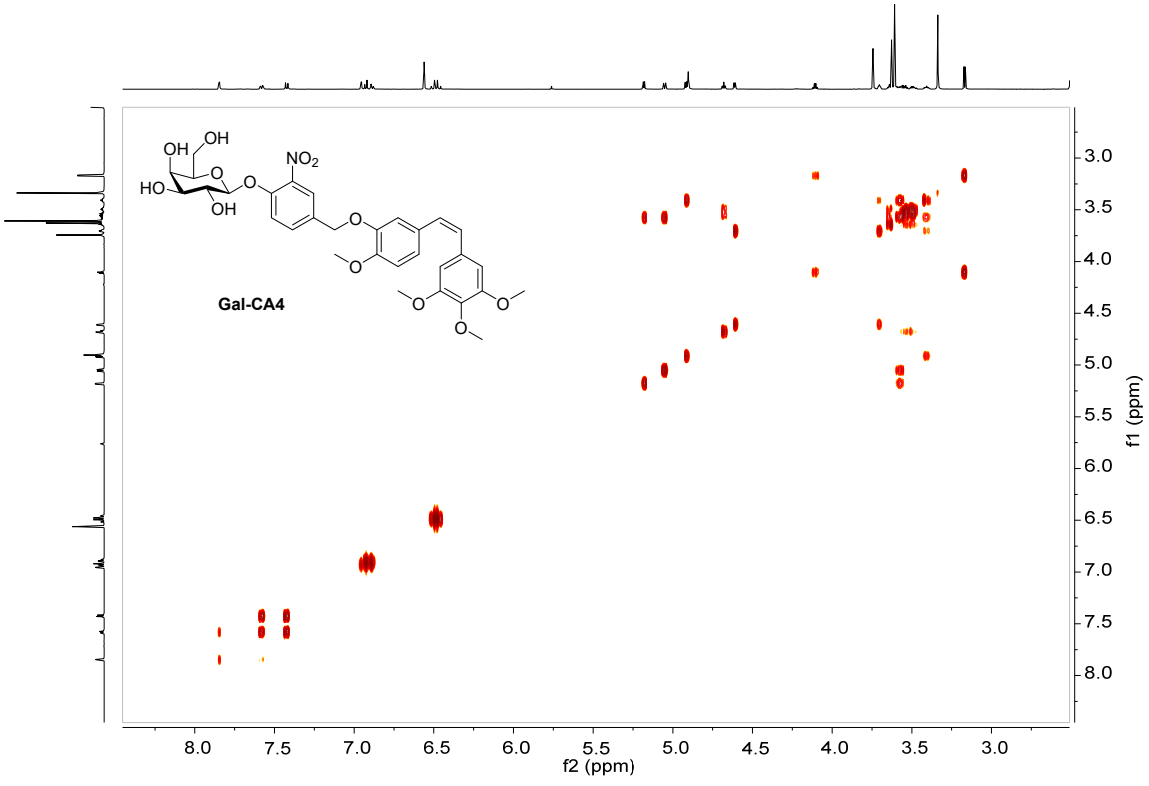
^{1}H NMR ($(CD_3)_2SO$, 600 MHz) of compound Gal-CA4



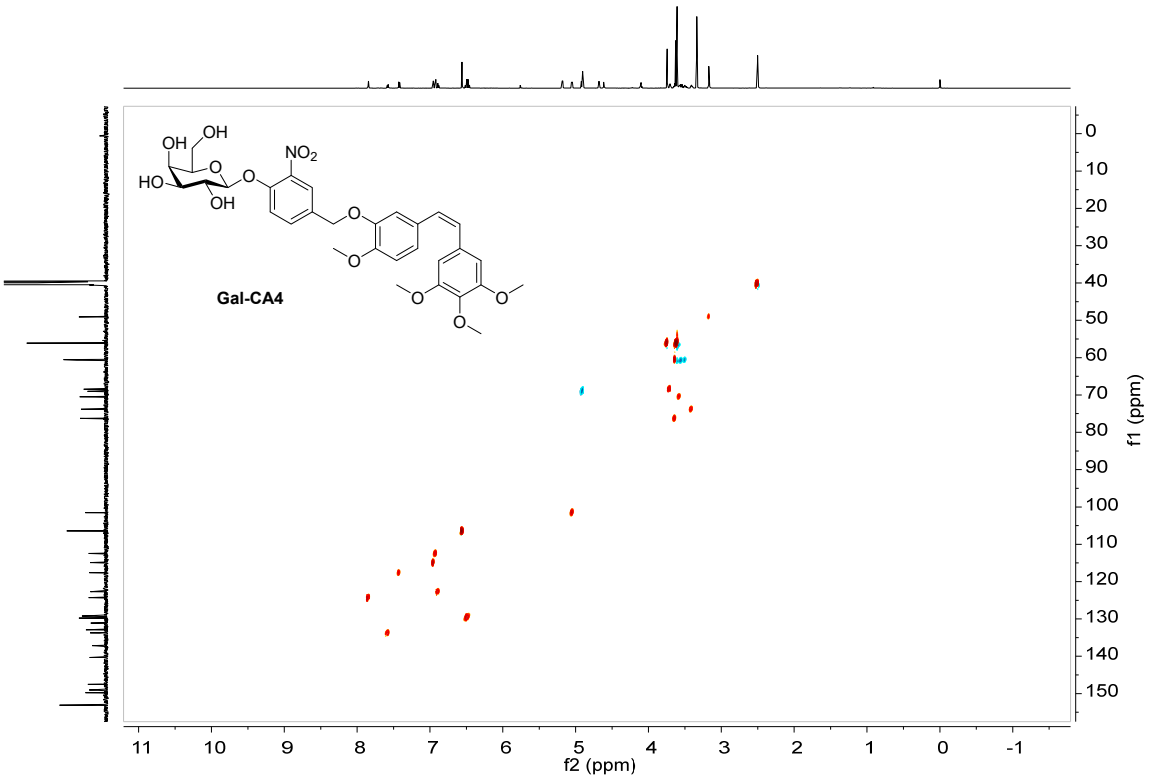
^{13}C NMR ($(CD_3)_2SO$, 151 MHz) of compound Gal-CA4



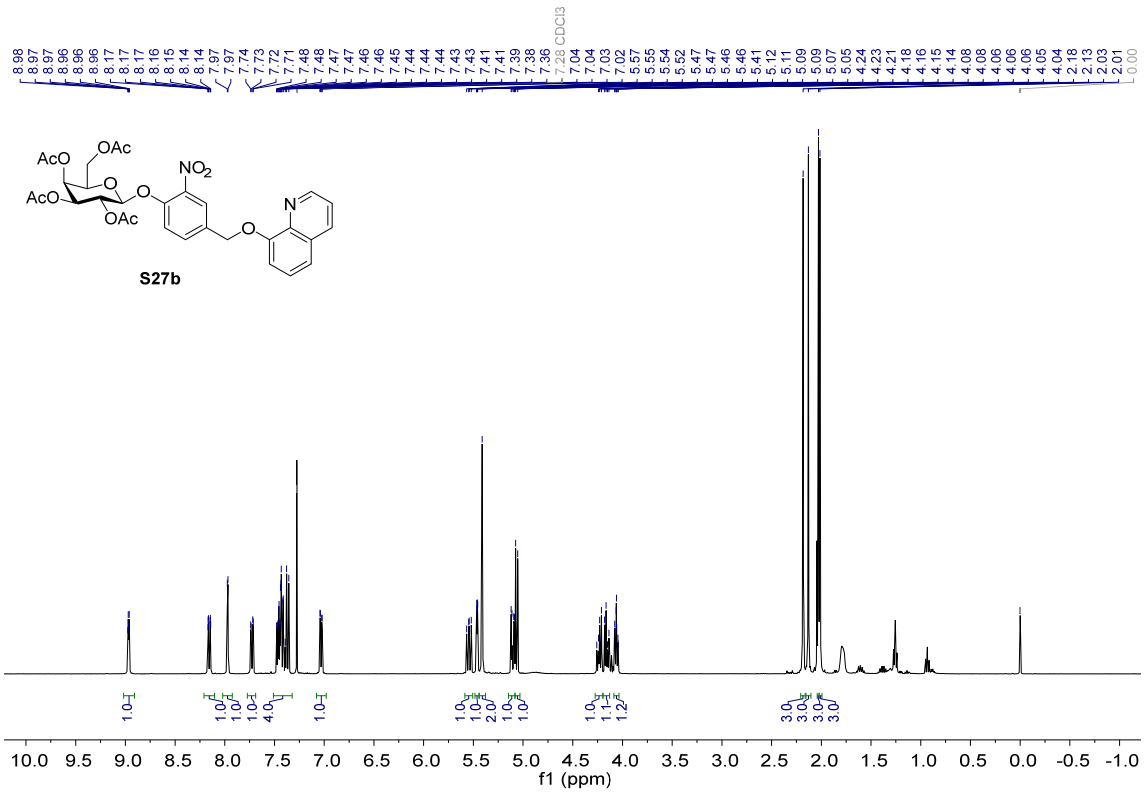
^{1}H-^{1}H COSY NMR ($(CD_3)_2SO$, 600 MHz) of compound Gal-CA4



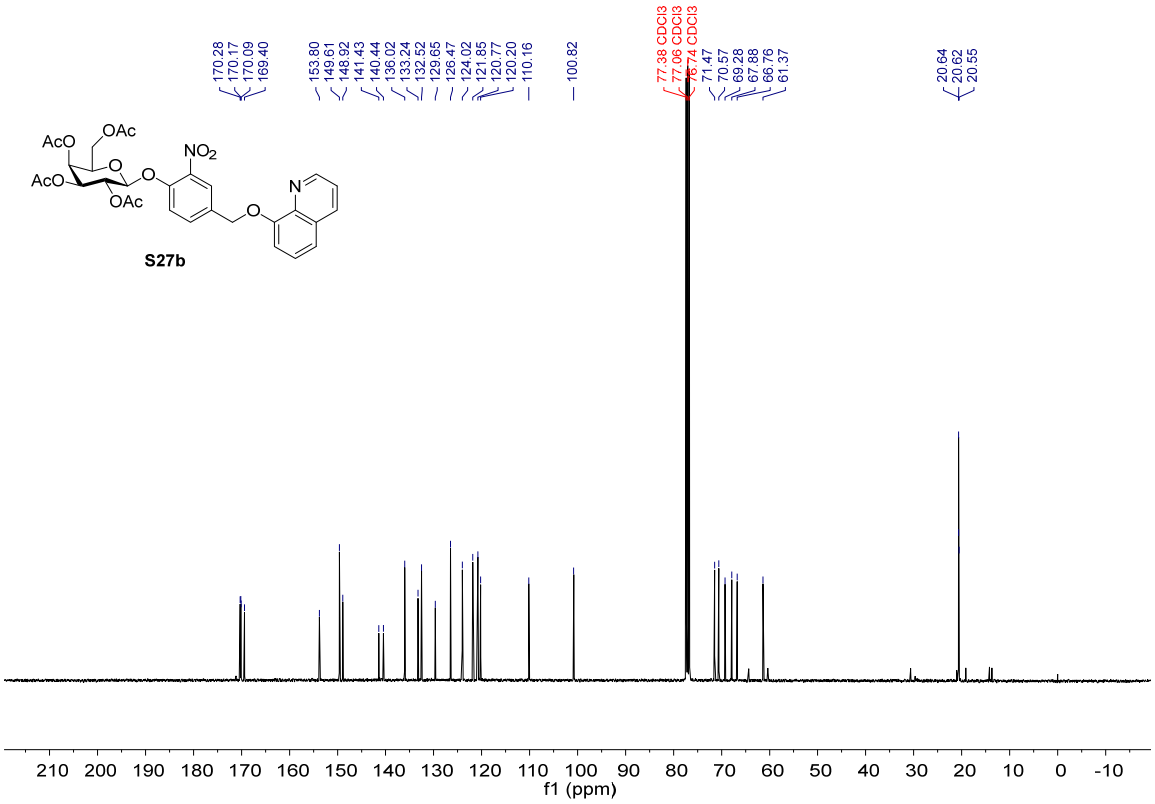
^{1}H-^{13}C HSQC NMR ($(CD_3)_2SO$, 600 MHz) of compound Gal-CA4



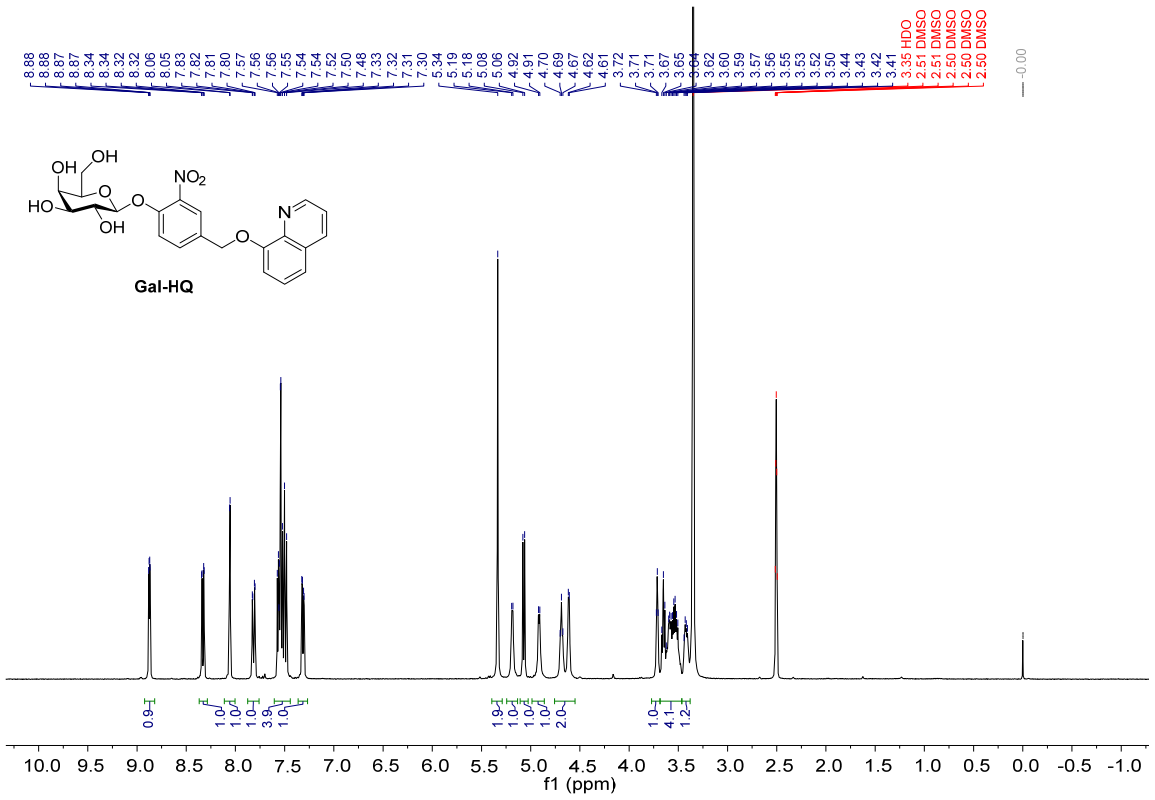
^{1}H NMR ($CDCl_3$, 400 MHz) of compound S27b



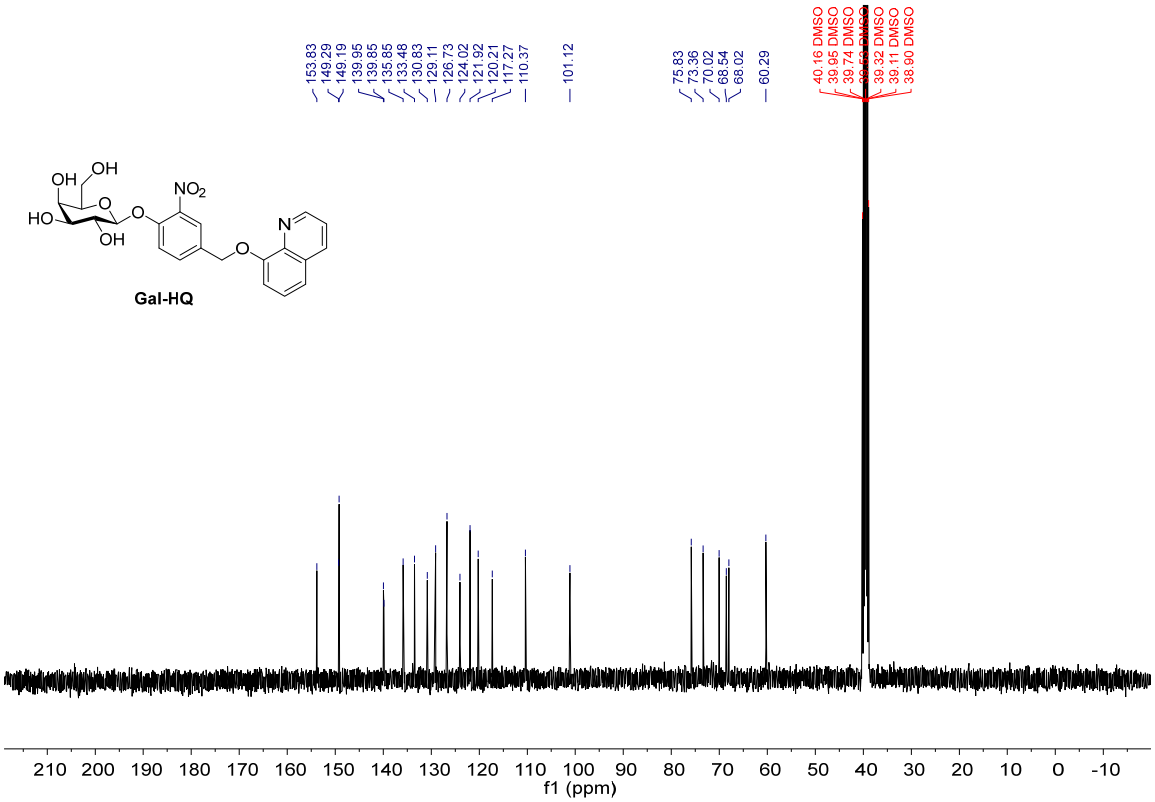
^{13}C NMR ($CDCl_3$, 101 MHz) of compound S27b



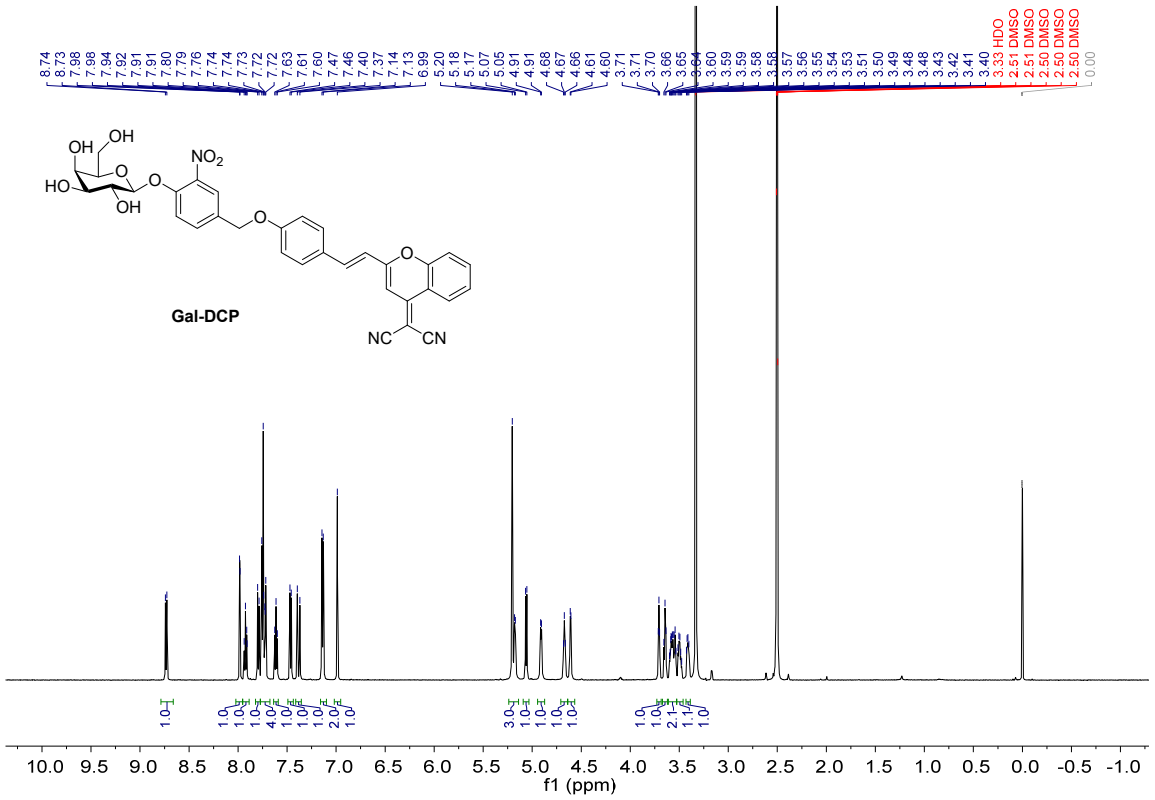
^{1}H NMR ($(CD_3)_2SO$, 400 MHz) of compound Gal-HQ



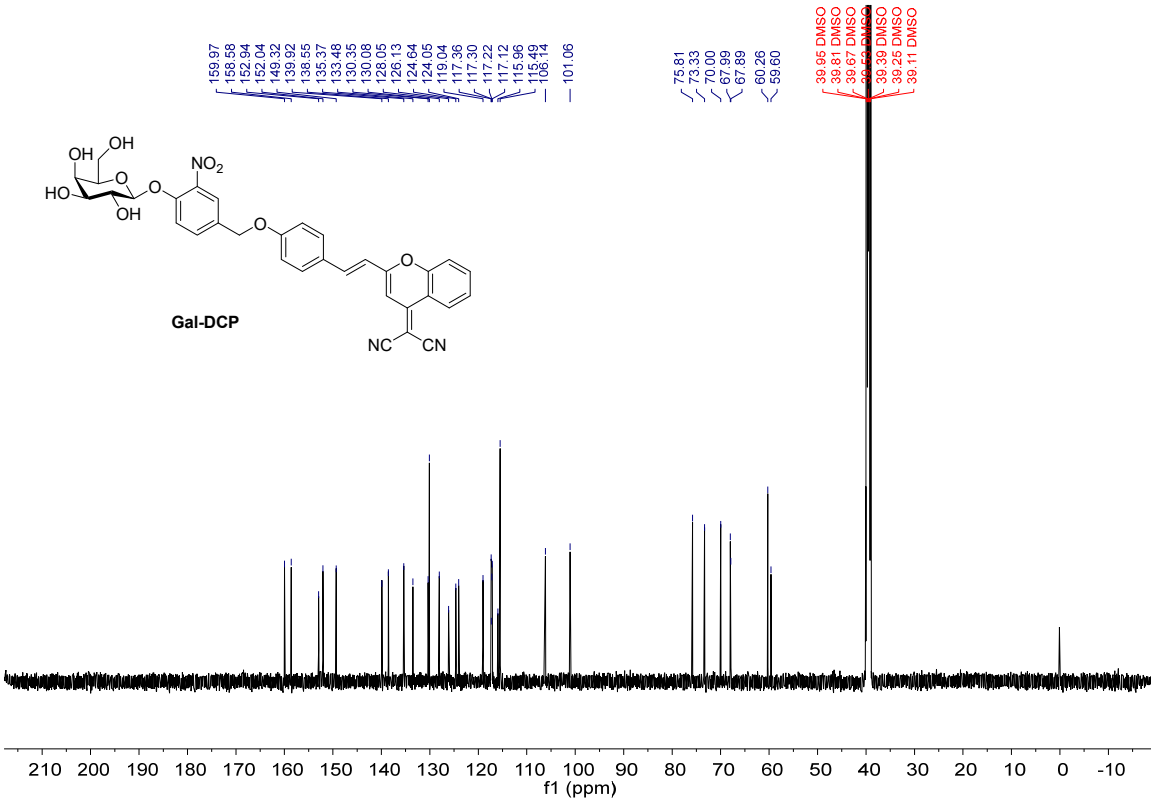
^{13}C NMR ((CD$_3$)$_2$SO, 101 MHz) of compound Gal-HQ



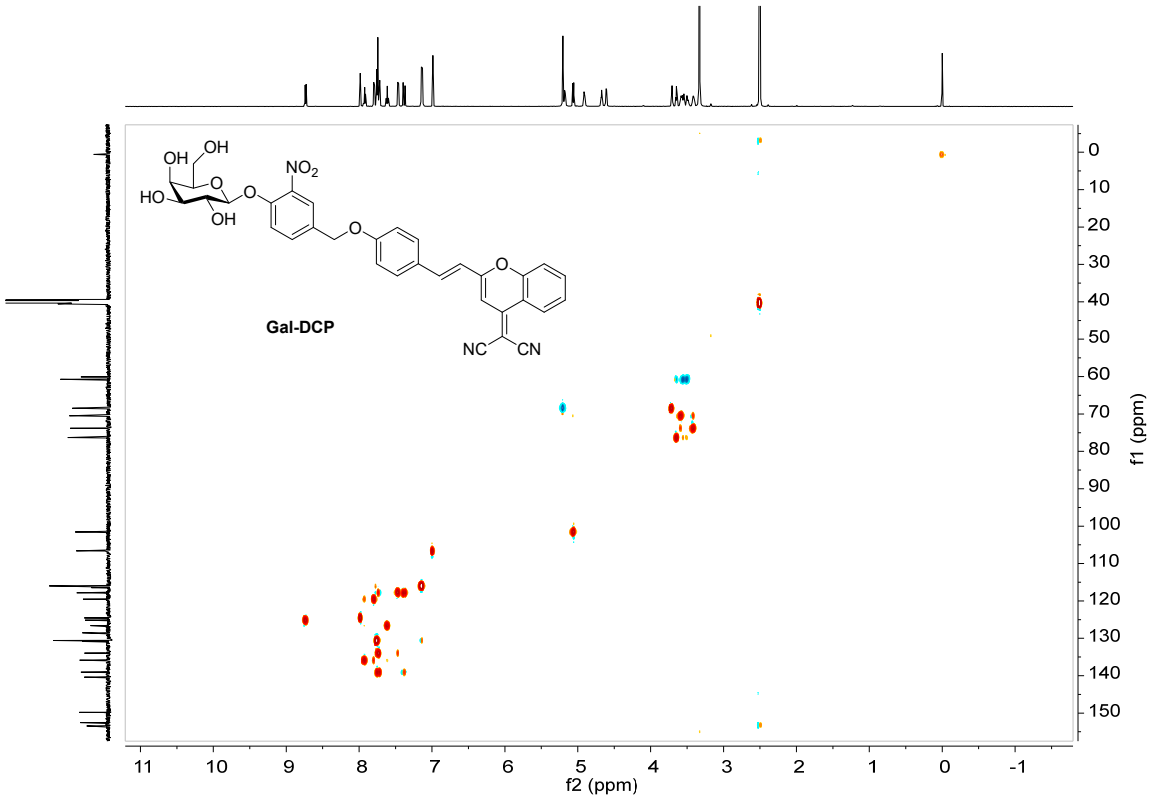
^{1}H NMR ((CD$_3$)$_2$SO, 600 MHz) of compound Gal-DCP



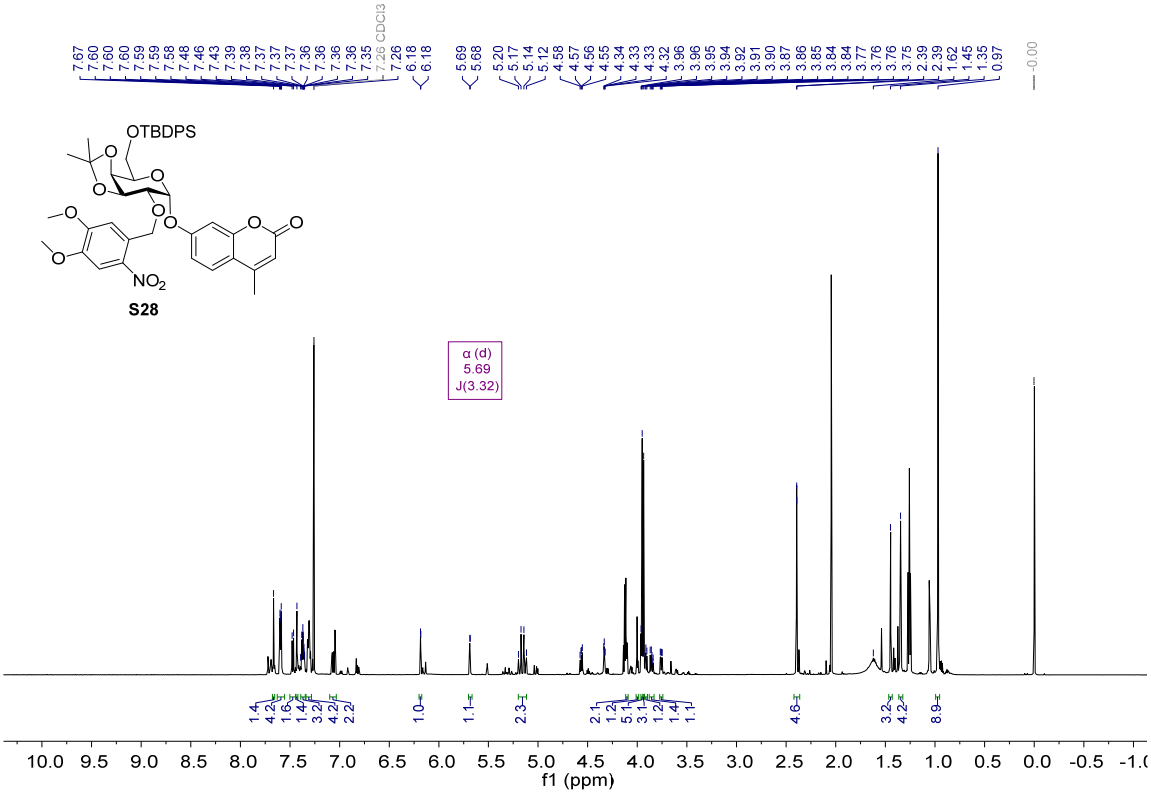
^{13}C NMR ($(CD_3)_2SO$, 151 MHz) of compound Gal-DCP



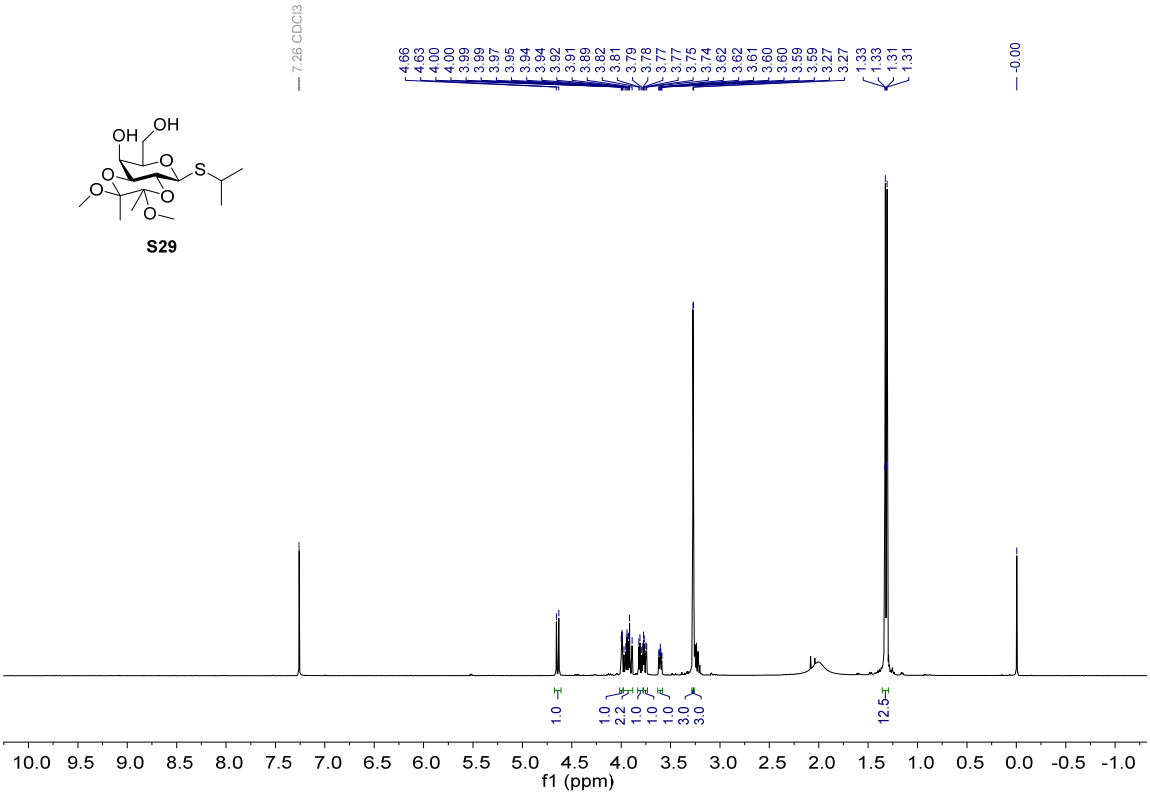
^{1}H-^{13}C HSQC NMR ($(CD_3)_2SO$, 600 MHz) of compound Gal-DCP



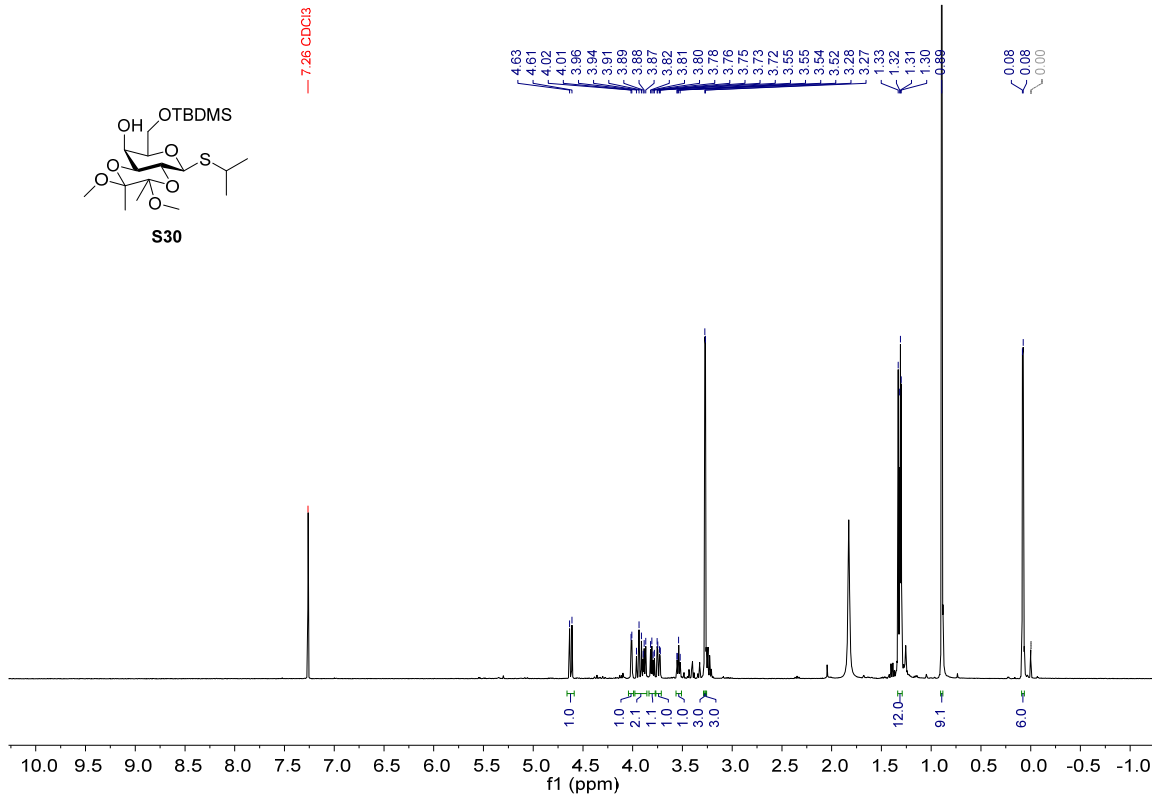
^{1}H NMR ($CDCl_3$, 600 MHz) of compound S28



^{1}H NMR ($CDCl_3$, 400 MHz) of compound S29



^{1}H NMR ($CDCl_3$, 400 MHz) of compound S30



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