# Supporting Information

*For*

# $^{19}$F-MRS/$^{1}$H-MRI Dual-Function Probe for Detection of β-Galactosidase Activity

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**CONTENTS:**

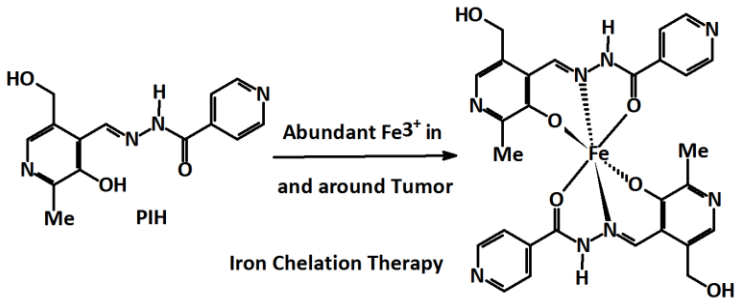


**Figure S1.** The illustration of iron chelation therapy.

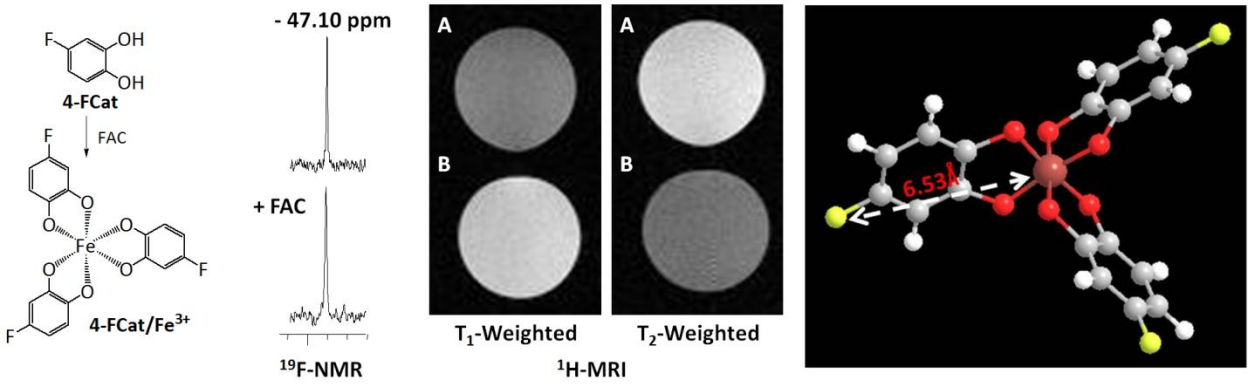


**Figure S2**. The $^{19}$F-MRS/$^{1}$H-MRI and molecular characterization of **4-FCAT** to **4-FCAT/Fe$^{3+}$**. **$^{19}$F-MRS**: (1) **4-FCAT** (1.2 mg, 9.0 μmol) in PBS (0.1 M, pH=7.4, 600 μL) at 25°C; (2) **4-FCAT** (1.2 mg, 9.0 μmol) in PBS (0.1 M, pH=7.4, 500 μL), FAC (796 μg, 3.0 μmol) in PBS (0.1 M, pH=7.4, 100 μL) at 25°C, $^{19}$F-NMR: Using the same parameters as in Figure 4. **$^{1}$H-MRI**: (**A**) Control, **4-FCAT** (12.0 mM) in PBS (0.1 M, pH=7.4) at 20-22°C; (**B**) Complex, **4-FCAT** (12.0 mM), FAC (4.0 mM) in PBS (0.1 M, pH=7.4) at 20-22°C; **Conditions**: (a) $T_1$-weighted $^{1}$H-MRI: Using the same parameters as in Figure 3; (b) $T_2$-weighted $^{1}$H-MRI: Using the same parameters as in Figure 6; **Molecular Modeling Calculation**: Using the same programs as in Figure 4, $r$=6.53 Å.

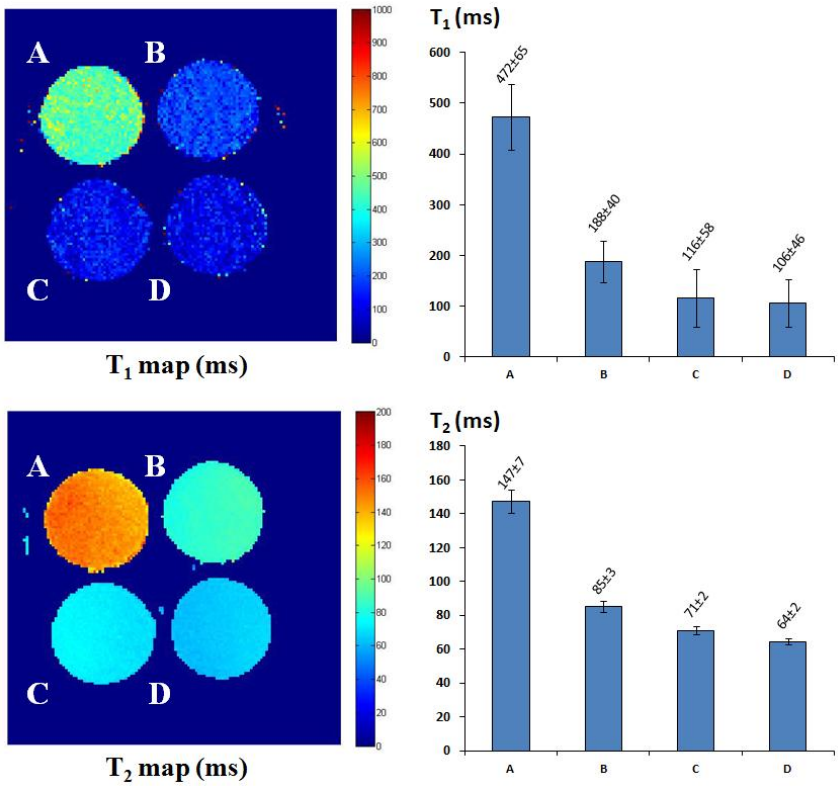


**Figure S3.** $^{1}$H-MRI detection of β-gal activity. **Conditions:** $^{1}$H-MRI, 200 MHz, 1 mm slice, 128x128, 40mmx40mm, $T_1$-weighted imaging: TR=500 ms, TE=15 ms; $T_2$-weighted imaging: TR=2000 ms, TE=60 ms. **(A)** control, **MGD-3-FCAT** (3.5 mg, 12.1 μmol), FAC (4.0 μmol), TFA (2.0 μmol), PBS (1.0 mL); **(B) MGD-3-FCAT** (1.2 mg, 4.1 μmol), FAC (4.0 μmol), β-gal (E801A, 10 units), TFA (2.0 μmol), PBS (1.0 mL); **(C) MGD-3-FCAT** (2.4 mg, 8.3 μmol), FAC (4.0 μmol), β-gal (E801A, 10 units), TFA (2.0 μmol), PBS (1.0 mL); **(D) MGD-3-FCAT** (3.5 mg, 12.1 μmol), FAC (4.0 μmol), β-gal (E801A, 10 units), TFA (2.0 μmol), PBS (1.0 mL) at 37°C in 30 mins.

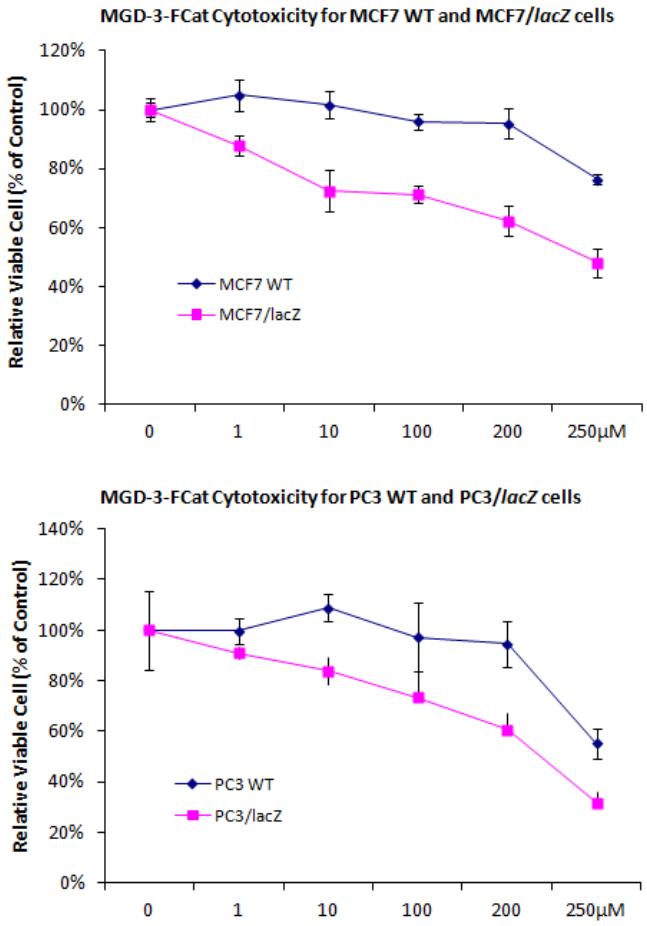


**Figure S4.** The cytotoxicity of **MGD-3-FCAT** to wild-type and *lacZ* expressing MCF7 and PC3 cells.

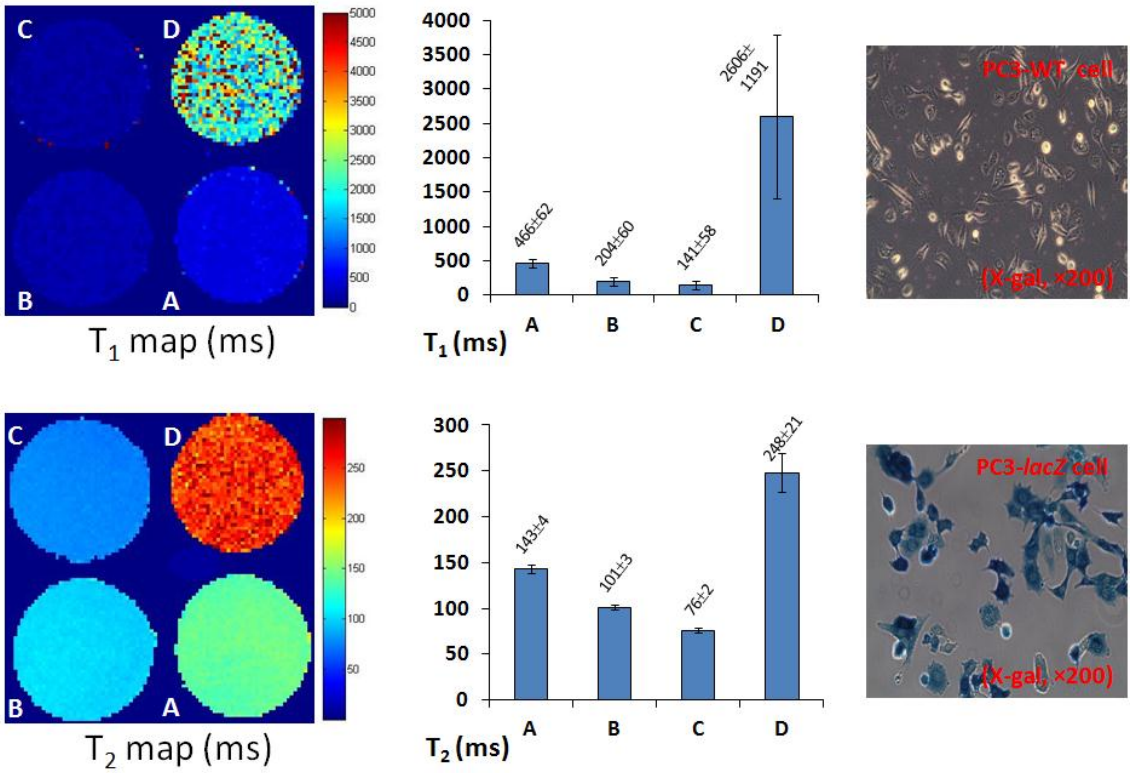


**Figure S5.** *In vitro* $^{1}$H-MRI detection of *lacZ* gene expression in PC3-*lacZ* cells after 25-hour incubation at 37°C. **$^{1}$H-MRI Conditions:** Using the same parameters as in Figure S3. **(A)** control, **MGD-3-FCAT** (3.5 mg, 12.1 µmol), FAC (4.0 µmol), TFA (2.0 µmol), PC3-WT cells ($5\times10^{6}$) in PBS (0.1M, pH=7.4, 800 µL); **(B) MGD-3-FCAT** (3.5 mg, 12.1 µmol), FAC (4.0 µmol), TFA (2.0 µmol), PC3-*lacZ* cells ($5\times10^{6}$) in PBS (0.1M, pH=7.4, 800 µL); **(C) MGD-3-FCAT** (7.0 mg, 24.1 µmol), FAC (8.0 µmol), TFA (2.0 µmol), MCF7-*lacZ* cells ($1\times10^{7}$) in PBS (0.1M, pH=7.4, 800 µL); **(D) MGD-3-FCAT** (3.5 mg, 12.1 µmol), without FAC, TFA (2.0 µmol), PC3-*lacZ* cells ($5\times10^{6}$) in PBS (0.1M, pH=7.4, 800 µL). **Histology:** β-gal activity validation in PC3-*lacZ* cells with deep blue (bottom) and no activity in PC3-WT cells (top), X-gal staining (×200).

**Synthesis of Ligands.** *General procedure* - A solution of aldehyde (2.50 mmol) in anhydrous EtOH (15 mL) containing AcOH (20 μL) was stirred vigorously with aroylhydrazide (2.50 mmol) at 80°C under $N_2$ until TLC showed the reaction was completed, then coevaporated with toluene to dryness *in vacuo*., and crystallized from EtOH-$H_2O$.

Pyridoxal isonicotinoylhydrazone (**PIH**), 644 mg, white crystals, $\delta_H$: 12.39, 11.47 (2 H, 2br, 2-OH & NH), 9.10 (1 H, s, CH=N), 8.83 (2 H, d, $J_{2',3'} = J_{5',6'}$ = 4.0 Hz, H-3',5'), 7.97 (1H, s, H-6), 7.88 (2 H, d, H-2',6'), 5.43 (1 H, t, $J_{H\text{-}5,HO\text{-}5}$ = 4.0 Hz, $\alpha^5$-OH), 4.62 (2 H, d, $CH_2$-5), 3.34 (3H, s, $CH_3$-2) ppm; $\delta_C$: 161.55 (s, PyCO), 150.70 ~ 120.03 (m, CH=N, Ar-C), 58.92 (s, $CH_2$-5), 18.86 (s, $CH_3$-2) ppm.

Anal. Calcd. for $C_{14}H_{14}N_4O_3$ (%): C, 58.74, H, 4.93, N, 19.57; Found: C, 58.70, H, 4.91, N, 19.56.

Salicylaldehyde benzoylhydrazone (**SBH**), 570 mg, white needles, $\delta_H$: 12.14, 11.34 (2 H, 2br, OH & NH), 8.67 (1 H, s, CH=N), 7.97 ~ 6.92 (9H, m, Ar-H) ppm; $\delta_C$: 162.83 (PhCO), 157.48 ~ 116.42 (CH=N, Ar-C) ppm.

Anal. Calcd. for $C_{14}H_{12}N_2O_2$ (%): C, 69.99, H, 5.03, N, 11.66; Found: C, 69.97, H, 5.01, N, 11.63.

Salicylaldehyde isonicotinoylhydrazone (**SIH**), 567 mg, white crystals, $\delta_H$: 12.32, 11.13 (2 H, 2br, OH & NH), 8.83 (1 H, s, CH=N), 8.71 ~ 6.93 (8H, m, Ar-H) ppm; $\delta_C$: 161.33 (PyCO), 157.48 ~ 116.44 (CH=N, Ar-C) ppm.

Anal. Calcd. for $C_{13}H_{11}N_3O_2$ (%): C, 64.72, H, 4.60, N, 17.42; Found: C, 64.70, H, 4.57, N, 17.40.

Salicylaldehyde nicotinoylhydrazone (**SNH**), 579 mg, light yellow crystals, $\delta_H$: 12.28, 11.19 (2 H, 2br, OH & NH), 9.13 (1 H, s, CH=N), 8.80 ~ 6.92 (8H, m, Ar-H) ppm; $\delta_C$: 161.43 (PyCO), 157.46 ~ 116.43 (CH=N, Ar-C) ppm.

Anal. Calcd. for $C_{13}H_{11}N_3O_2$ (%):C, 64.72, H, 4.60, N, 17.42; Found: C, 64.69, H, 4.58, N, 17.39.

2-Hydroxyl-5-fluorobenzaldehyde benzoylhydrazone (***p*-FSBH**), 581 mg, white crystals, $\delta_H$: 12.17, 11.07 (2 H, 2br, 2-OH & NH), 8.65 (1 H, s, CH=N), 7.97 ~ 6.93 (8H, m, Ar-H) ppm; $\delta_C$: 162.97 (s, PhCO), 156.51 ~ 113.82 (m, CH=N, Ar-C) ppm.

Anal. Calcd. for $C_{14}H_{11}N_2O_2F$ (%): C, 65.11, H, 4.29, N, 10.85; Found: C, 65.08, H, 4.27, N, 10.83.

2-Hydroxyl-benzaldehyde 4-fluorobenzoylhydrazone (**SBHF-*p***), 601 mg, white needles, $\delta_H$: 12.14, 11.29 (2 H, 2s, 2-OH & NH), 8.65 (1 H, s, CH=N), 8.06 ~ 6.90 (8H, m, Ar-H) ppm; $\delta_C$: 165.54 (s, PhCO), 163.05 ~ 115.45 (m, CH=N, Ar-C) ppm.

Anal. Calcd. for $C_{14}H_{11}N_2O_2F$ (%): C, 65.11, H, 4.29, N, 10.85; Found: C, 65.09, H, 4.26, N, 10.82.

**Fe-Complex Preparation.** *General procedure* - To a solution of ligand (2.0 mmol for **PIH**, **SBH**, **SIH**, **SNH**, ***p*-FSBH** and **SBHF-*p***; 3.0 mmol for **3-FCAT** and **4-FCAT**) and $Et_3N$ (323 mg, 3.2 mmol) in anhydrous MeOH (100 mL) was added dropwise a solution of $Fe(ClO_4)_3{\cdot}6H_2O$ (460 mg, 1.0 mmol) in anhydrous MeOH (50 mL) with stirring at gently refluxing under $N_2$ for 30 min. Upon cooling, a fine black precipitate was obtained, which was filtered off, washed with EtOH then $Et_2O$, and dried in the vacuum.

**PIH/Fe$^{3+}$** Complex, $[Fe(PIH\text{-}H)_2](ClO_4){\cdot}3H_2O$ (576 mg) as black powders. Anal. Calcd. for $C_{28}H_{32}ClFeN_8O_{13}$ (%): C, 43.12, H, 4.14, N, 14.37; Found: C, 43.08, H, 4.09, N, 14.32.

**SBH/Fe$^{3+}$** Complex, $[Fe(SBH\text{-}H)_2](ClO_4){\cdot}3H_2O$ (770 mg) as black powders. Anal. Calcd. for $C_{28}H_{28}ClFeN_4O_{11}$ (%): C, 48.89, H, 4.10, N, 8.15; Found: C, 48.81, H, 4.03, N, 8.07.

**SIH/Fe$^{3+}$** Complex, $[Fe(SIH\text{-}H)_2](ClO_4){\cdot}3H_2O$ (635 mg) as black powders. Anal. Calcd. for $C_{26}H_{26}ClFeN_6O_{11}$ (%): C, 45.27, H, 3.80, N, 12.18; Found: C, 45.18, H, 3.73, N, 12.11.

**SNH/Fe$^{3+}$** Complex, $[Fe(SNH\text{-}H)_2](ClO_4){\cdot}3H_2O$ (717 mg) as black powders. Anal. Calcd. for $C_{26}H_{26}ClFeN_6O_{11}$ (%): C, 45.27, H, 3.80, N, 12.18; Found: C, 45.21, H, 3.71, N, 12.13.

***p*-FSBH/Fe$^{3+}$** Complex, $[Fe(p\text{-}FSBH\text{-}H)_2](ClO_4){\cdot}3H_2O$ (594 mg) as black powders. Anal. Calcd. for $C_{28}H_{26}ClFeN_4O_{11}F_2$ (%): C, 46.46, H, 3.62, N, 7.74; Found: C, 46.39, H, 3.54, N, 7.63.

**SBHF-*p*/Fe$^{3+}$** Complex, [Fe(SBHF-*p*-H)$_2$](ClO$_4$)·3H$_2$O (695 mg) as black powders. Anal. Calcd. for $C_{28}H_{26}ClFeN_4O_{11}F_2$ (%): C, 46.46, H, 3.62, N, 7.74; Found: C, 46.41, H, 3.52, N, 7.65.

**3-FCAT/Fe$^{3+}$** Complex, $(Et_3NH)_3[Fe(3\text{-}FCAT\text{-}2H)_3]\cdot H_2O$ (392 mg) as black powders. Anal. Calcd. for $C_{36}H_{69}FeN_3O_7F_3$ (%): C, 56.24, H, 9.05, N, 5.47; Found: C, 56.16, H, 8.95, N, 5.41.

**4-FCAT/Fe$^{3+}$** Complex, $(Et_3NH)_3[Fe(4\text{-}FCAT\text{-}2H)_3]\cdot H_2O$ (484 mg) as black powders. Anal. Calcd. for $C_{36}H_{69}FeN_3O_7F_3$ (%):C, 56.24, H, 9.05, N, 5.47; Found: C, 56.18, H, 8.99, N, 5.42.

**Molecular Characterization of 3- and 4-FCAT β-*D*-Galactopyranosides.**

1-*O*-(2', 3', 4', 6'-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-3-fluorocatechol **MG-3-FCAT** (1.09 g, 95%), $R_f$ 0.45 (3**:**2 cyclohexane-EtOAc), $\delta_H$ ($CDCl_3$, 400MHz): 6.54 (1 H, t, $^3J_{F3,H4}$ = $J_{4,5}$ = 12.0 Hz, H-4), 6.91 (1 H, dd, $J_{5,6}$ = 8.0 Hz, $J_{4,5}$ = 12 Hz, H-5), 6.65 (1 H, d, $J_{5,6}$ = 8.0 Hz, H-6), 6.79 (1 H, s, HO-2, exchangeable with $D_2O$), 4.74 (1 H, d, $J_{1',2'}$ = 8.0 Hz, H-1'), 5.40 (1 H, dd, $J_{2',3'}$ = 10.2 Hz, H-2'), 5.03 (1 H, dd, $J_{3',4'}$ = 4.0 Hz, H-3'), 5.35 (1 H, d, $J_{4',5'}$ = 3.6 Hz, H-4'), 3.99 (1 H, m, H-5'), 4.14 (1 H, dd, $J_{5',6a'}$ = 7.8 Hz, $J_{6a',6b'}$ = 12.0 Hz, H-6a'), 4.08 (1 H, dd, $J_{5',6b'}$ = 3.7 Hz, H-6b'), 2.12, 2.06, 1.96, 1.92 (12 H, 4s, 4 × $CH_3CO$) ppm; $\delta_C$ ($CDCl_3$, 100MHz): 170.43, 170.15, 169.97, 169.76 (4 × $CH_3$**C**O), 125.95 (d, $^3J_{F\text{-}C}$ = 9.0 Hz, C-1), 107.50 (d, $^2J_{F\text{-}C}$ = 19.0 Hz, C-2), 155.37 (d, $^1J_{F\text{-}C}$ = 245.0 Hz, C-3), 132.80 (d, $^2J_{F\text{-}C}$ = 13.0 Hz, C-4), 150.96 (C-5), 112.38 (d, $^3J_{F\text{-}C}$ = 3.0 Hz, C-6), 104.16 (C-1'), 68.34 (C-2'),

70.37 (C-3'), 66.77 (C-4'), 71.66 (C-5'), 61.11 (C-6'), 20.67, 20.51, 20.41, 20.26 (4 × **C**$H_3$CO) ppm.

Anal. Calcd. for $C_{20}H_{23}O_{11}F$ (%): C, 52.40, H, 5.06; Found: C, 52.38, H, 5.04.

2-*O*-(2', 3', 4', 6'-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-4-fluorocatechol **MG-4-FCAT** (1.01 g, 88%), $R_f$ 0.56 (1**:**1 cyclohexane-EtOAc), $\delta_H$ ($CDCl_3$, 400MHz): 6.77 (1 H, dd, $^3J_{F4,H3}$ = 12.0, $J_{3,5}$ = 3.8 Hz, H-3), 6.71 (1 H, dd, $J_{5,6}$ = 4.0 Hz, $^3J_{F4,H5}$ = 12.0, H-5), 6.87 (1 H, dd, $^4J_{F4,H6}$ = 8.0 Hz, H-6), 5.77 (1 H, s, HO-1, exchangeable with $D_2O$), 4.94 (1 H, d, $J_{1',2'}$ = 8.0 Hz, H-1'), 5.46 (1 H, dd, $J_{2',3'}$ = 10.4 Hz, H-2'), 5.14 (1 H, dd, $J_{3',4'}$ = 3.2 Hz, H-3'), 5.45 (1 H, d, $J_{4',5'}$ = 2.8 Hz, H-4'), 4.11 (1 H, m, H-5'), 4.14 (1 H, dd, $J_{5',6a'}$ = 7.6 Hz, $J_{6a',6b'}$ = 11.2 Hz, H-6a'), 4.08 (1 H, dd, $J_{5',6b'}$ = 5.6 Hz, H-6b'), 2.20, 2.16, 2.10, 2.06 (12 H, 4s, 4 × $CH_3$CO) ppm; $\delta_C$ ($CDCl_3$, 100MHz): 170.57, 170.27, 170.10, 169.86 (4 × $CH_3$**C**O), 143.31 (C-1), 116.21 (d, $^3J_{F-C}$ = 9.0 Hz, C-2), 104.83 (d, $^2J_{F-C}$ = 26.8 Hz, C-3), 156.12 (d, $^1J_{F-C}$ = 248.0 Hz, C-4), 110.95 (d, $^2J_{F-C}$ = 22.4 Hz, C-5), 144.06 (d, $^3J_{F-C}$ = 10.4 Hz, C-6), 101.61 (C-1'), 69.10 (C-2'), 70.47 (C-3'), 66.87 (C-4'), 71.67 (C-5'), 61.54 (C-6'), 21.00, 20.74, 20.70, 20.67 (4 × **C**$H_3$CO) ppm.

Anal. Calcd. for $C_{20}H_{23}O_{11}F$ (%): C, 52.40, H, 5.06; Found: C, 52.37, H, 5.03.

1-*O*-(β-*D*-galactopyranosyl)-3-fluorocatechol **MGD-3-FCAT** (577.46 mg, 96%), $R_f$ 0.40 (1**:**2 EtOAc-MeOH), $\delta_H$ (DMSO-$d_6$, 400MHz): 6.69 (1 H, dd, $^3J_{F3,H4}$ = 10.0 Hz, $J_{4,5}$ = 3.6 Hz, H-4), 6.95 (1 H, ddd, $^4J_{F3,H5}$ = 10.0 Hz, $J_{5,6}$ = 6.8 Hz, H-5), 6.65 (1 H, d, H-6), 7.32 (1 H, s, HO-2, exchangeable with $D_2O$), 4.62 (1 H, d, $J_{1',2'}$ = 8.0 Hz, H-1'), 4.58 - 3.64 (4H, br, HO-2', 3', 4', 6', exchangeable with $D_2O$), 3.63 (1 H, dd, $J_{2',3'}$ = 9.8 Hz, H-2'), 3.67 (1 H, dd, $J_{3',4'}$

= 2.8 Hz, H-3'), 3.38 (1 H, d, $J_{4',5'}$ = 3.2 Hz, H-4'), 3.57 (1 H, m, H-5'), 3.45 (1 H, dd, $J_{5',6a'}$ = 6.8 Hz, $J_{6a',6b'}$ = 11.2 Hz, H-6a'), 3.41 (1 H, dd, $J_{5',6b'}$ = 2.8 Hz, H-6b') ppm; $\delta_C$ (DMSO-$d_6$, 100MHz): 124.80 (d, $^3J_{F\text{-}C}$ = 8.9 Hz, C-1), 106.76 (d, $^2J_{F\text{-}C}$ = 19.3 Hz, C-2), 155.70 (d, $^1J_{F\text{-}C}$ = 244.1 Hz, C-3), 132.99 (d, $^2J_{F\text{-}C}$ = 13.4 Hz, C-4), 151.82 (d, $^3J_{F\text{-}C}$ = 3.8 Hz, C-5), 112.61 (C-6), 105.75 (C-1'), 71.32 (C-2'), 73.06 (C-3'), 68.01 (C-4'), 75.75 (C-5'), 60.11 (C-6') ppm.

Anal. Calcd. for $C_{12}H_{15}O_7F$ (%): C, 49.66, H, 5.21; Found: C, 49.62, H, 5.18.

2-*O*-(β-*D*-galactopyranosyl)-4-fluorocatechol **MGD-4-FCAT** (565.43 mg, 94%), $R_f$ 0.43 (1**:**2 EtOAc-MeOH), $\delta_H$ (DMSO-$d_6$, 400MHz): 6.77 (1 H, dd, $^3J_{F4,H3}$ = 8.8 Hz, $J_{3,5}$ = 6.0 Hz, H-3), 6.66 (1 H, ddd, $^3J_{F4,H5}$ = 30.0 Hz, $J_{5,6}$ = 8.4 Hz, H-5), 6.95 (1 H, dd, $^4J_{F4,H6}$ = 2.8 Hz, H-6), 7.30 (1 H, s, HO-1, exchangeable with $D_2O$), 4.67 (1 H, d, $J_{1',2'}$ = 8.0 Hz, H-1'), 4.88 - 3.65 (4H, br, HO-2', 3', 4', 6', exchangeable with $D_2O$), 3.58 (1 H, dd, $J_{2',3'}$ = 10.2 Hz, H-2'), 3.41 (1 H, dd, $J_{3',4'}$ = 3.2 Hz, H-3'), 3.68 (1 H, d, $J_{4',5'}$ = 3.2 Hz, H-4'), 3.53 - 3.48 (3 H, m, H-5', H-6') ppm; $\delta_C$ (DMSO-$d_6$, 100MHz): 143.27 (d, $^4J_{F\text{-}C}$ = 2.2 Hz, C-1), 115.90 (d, $^3J_{F\text{-}C}$ = 9.7 Hz, C-2), 104.23 (d, $^2J_{F\text{-}C}$ = 23.0 Hz, C-3), 155.19 (d, $^1J_{F\text{-}C}$ = 232.9 Hz, C-4), 108.25 (d, $^2J_{F\text{-}C}$ = 21.6 Hz, C-5), 145.73 (d, $^3J_{F\text{-}C}$ = 11.2 Hz, C-6), 102.68 (C-1'), 70.40 (C-2'), 72.65 (C-3'), 68.27 (C-4'), 75.90 (C-5'), 60.62 (C-6') ppm.

Anal. Calcd. for $C_{12}H_{15}O_7F$ (%): C, 49.66, H, 5.21; Found: C, 49.64, H, 5.19.

1,2-di-*O*-(2', 3', 4', 6'-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-**3**-fluorocatechol **FG-3-FCAT** (1.83 g, 93%), $R_f$ 0.35 (1**:**1 cyclohexane-EtOAc), $\delta_H$ ($CDCl_3$, 400MHz): 6.63 (1 H, ddd, $^3J_{F3,H4}$ = 12.0 Hz, $J_{4,5}$ = 8.0 Hz, $J_{4,6}$ = 4.0 Hz, H-4), 6.98 (1 H, dd, $J_{5,6}$ = 12.0 Hz, H-5), 6.74 (1 H, d, H-6), 4.80 (2 H, d, $J_{1',2'}$ = $J_{1'',2''}$ = 8.0 Hz, H-1', 1''), 5.50 (2 H, dd, $J_{2',3'}$ = $J_{2'',3''}$ = 10.2

Hz, H-2', 2''), 5.09 (2 H, dd, $J_{3',4'} = J_{3'',4''}$ = 4.0 Hz, H-3', 3''), 5.43 (2 H, d, $J_{4',5'} = J_{4'',5''}$ = 4.0 Hz, H-4',''), 4.04 (2 H, t, $J_{5',6a'} = J_{5'',6a''}$ = 8.0 Hz, H-5', 5''), 4.22 (2 H, dd, $J_{6a',6b'} = J_{6a'',6b''}$ = 12.0 Hz, H-6a', 6a''), 4.16 (2 H, dd, $J_{5',6b'} = J_{5'',6b''}$ = 4.0 Hz, H-6b', 6b''), 2.20, 2.15, 2.05, 2.03 (24 H, 4s, 8 × $CH_3CO$) ppm; $\delta_C$ ($CDCl_3$, 100MHz): 170.43, 170.25, 170.15, 170.03, 169.98, 169.77, 169.49, 169.42 (8 × $CH_3$**C**O), 125.97 (d, $^3J_{F\text{-}C}$ = 10.0 Hz, C-1), 107.53 (d, $^2J_{F\text{-}C}$ = 19.0 Hz, C-2), 155.37 (d, $^1J_{F\text{-}C}$ = 245.0 Hz, C-3), 132.80 (d, $^2J_{F\text{-}C}$ = 14.0 Hz, C-4), 150.95 (C-5), 112.37 (d, $^3J_{F\text{-}C}$ = 3.0 Hz, C-6), 101.42 (C-1'), 100.40 (C-1''), 68.33 (C-2', 2''), 70.37 (C-3', 3''), 67.02 (C-4'), 66.76 (C-4''), 71.66 (C-5', 5''), 61.26 (C-6'), 61.11 (C-6''), 20.92, 20.83, 20.70, 20.64, 20.53, 20.51, 20.45, 20.44 (8 × **C**$H_3$CO) ppm; ESIMS: *m/z* 789 [$M^+$] (17%), 790 [M+1] (9%).

Anal. Calcd. for $C_{34}H_{41}O_{20}F$ (%): C, 51.78, H, 5.24; Found: C, 51.74, H, 5.21.

1,2-di-*O*-(2', 3', 4', 6'-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-4-fluorocatechol **FG-4-FCAT** (1.69 g, 86%), $R_f$ 0.42 (1**:**1 cyclohexane-EtOAc), $\delta_H$ ($CDCl_3$, 400MHz): 6.76 (1 H, dd, $^3J_{F4,H3}$ = 12.0 Hz, $J_{3,5}$ = 4.0 Hz, H-3), 6.73 (1 H, ddd, $^3J_{F4,H5}$ = 30.0 Hz, $J_{5,6}$ = 8.0 Hz, H-5), 6.88 (1 H, dd, $^4J_{F4,H6}$ = 9.0 Hz, H-6), 4.85 (1 H, d, $J_{1',2'}$ = 8.0 Hz, H-1'), 4.94 (1 H, d, $J_{1'',2''}$ = 8.0 Hz, H-1''), 5.48 (2 H, dd, $J_{2',3'} = J_{2'',3''}$ = 10.0 Hz, H-2', 2''), 5.12 (1 H, dd, $J_{3',4'}$ = 4.0 Hz, H-3'), 5.15 (1 H, dd, $J_{3'',4''}$ = 4.0 Hz, H-3''), 5.45 (2 H, d, $J_{4',5'} = J_{4'',5''}$ = 4.0 Hz, H-4', 4''), 4.06 (2 H, t, $J_{5',6a'} = J_{5'',6a''}$ = 7.6 Hz, H-5', 5''), 4.24 (2 H, dd, $J_{6a',6b'} = J_{6a'',6b''}$ = 11.8 Hz, H-6a', 6a''), 4.19 (2 H, dd, $J_{5',6b'} = J_{5'',6b''}$ = 3.8 Hz, H-6b', 6b''), 2.20, 2.14, 2.13, 2.09, 2.07, 2.05, 2.03, 2.02 (24 H, 8s, 8 × $CH_3CO$) ppm; $\delta_C$ ($CDCl_3$, 100MHz): 170.64, 170.62, 170.60, 170.34, 170.18, 169.79, 169.59, 169.52 (8 × $CH_3$**C**O), 143.34 (d, $^4J_{F\text{-}C}$ = 2.9 Hz, C-1), 116.26 (d, $^3J_{F\text{-}C}$ = 9.0 Hz, C-2), 104.86 (d, $^2J_{F\text{-}C}$ = 26.0 Hz, C-3), 156.19 (d, $^1J_{F\text{-}C}$ = 238.0 Hz, C-4), 110.98 (d, $^2J_{F\text{-}C}$

= 22.3 Hz, C-5), 144.09 (d, $^{3}J_{F\text{-}C}$ = 10.4 Hz, C-6), 101.62 (C-1'), 102.85 (C-1''), 69.13 (C-2', 2''), 70.50 (C-3'), 70.61 (C-3''), 66.88 (C-4'), 66.90 (C-4''), 71.61 (C-5'), 71.70 (C-5''), 61.37 (C-6'), 61.58 (C-6''), 21.02, 20.77, 20.73, 20.70 (8 × **C**$H_3$CO) ppm; ESIMS: *m/z* 789 [$M^+$] (25%), 790 [M+1] (11%).

Anal. Calcd. for $C_{34}H_{41}O_{20}F$ (%): C, 51.78, H, 5.24; Found: C, 51.75, H, 5.20.

1,2-di-*O*-(β-*D*-galactopyranosyl)-3-fluorocatechol **FGD-3-FCAT** (774.36 mg, 90%), $R_f$ 0.37 (1:4 EtOAc-MeOH), $\delta_H$ (DMSO-$d_6$, 400MHz): 6.92 (1 H, dd, $^{3}J_{F3,H4}$ = 9.1 Hz, $J_{4,5}$ = 3.8 Hz, H-4), 7.06 (1 H, ddd, $^{4}J_{F3,H5}$ = 4.0 Hz, $J_{5,6}$ = 8.2 Hz, H-5), 6.88 (1 H, d, H-6), 5.34 (2 H, d, $J$ = 4.0 Hz, HO-2', 2'', exchangeable with $D_2O$), 4.34 (2 H, br, HO-3', 3'', exchangeable with $D_2O$), 4.90 (2 H, br, HO-4', 4'', exchangeable with $D_2O$), 4.55 (2 H, br, HO-6', 6'', exchangeable with $D_2O$), 4.83 (1 H, d, $J_{1',2'}$ = 8.0 Hz, H-1'), 4.69 (1 H, d, $J_{1'',2''}$ = 8.0 Hz, H-1''), 3.69 (1 H, dd, $J_{2',3'}$ = 10.2 Hz, H-2'), 3.71 (1 H, dd, $J_{2'',3''}$ = 10.0 Hz, H-2''), 3.38 (1 H, dd, $J_{3',4'}$ = 3.2 Hz, H-3'), 3.42 (1 H, dd, $J_{3'',4''}$ = 3.6 Hz, H-3''), 3.58 (2 H, m, H-4', 4''), 3.33 (2 H, m, H-5', 5''), 3.54 (4 H, m, H-6', 6'') ppm; $\delta_C$ (DMSO-$d_6$, 100MHz): 124.94 (d, $^{3}J_{F\text{-}C}$ = 9.0 Hz, C-1), 110.86 (d, $^{2}J_{F\text{-}C}$ = 20.0 Hz, C-2), 156.99 (d, $^{1}J_{F\text{-}C}$ = 245.0 Hz, C-3), 135.34 (d, $^{2}J_{F\text{-}C}$ = 13.0 Hz, C-4), 152.37 (d, $^{3}J_{F\text{-}C}$ = 4.0 Hz, C-5), 113.80 (C-6), 104.95 (C-1'), 103.57 (C-1''), 72.33 (C-2'), 71.59 (C-2''), 74.19 (C-3'), 73.64 (C-3''), 69.37 (C-4'), 69.30 (C-4''), 76.42 (C-5'), 76.13 (C-5''), 61.67 (C-6'), 61.17 (C-6'') ppm.

Anal. Calcd. for $C_{18}H_{25}O_{12}F$ (%): C, 47.79, H, 5.57; Found: C, 47.74, H, 5.53.

1,2-di-*O*-(β-*D*-galactopyranosyl)-4-fluorocatechol **FGD-4-FCAT** (731.34 mg, 85%), $R_f$ 0.42 (1:4 EtOAc-MeOH), $\delta_H$ (DMSO-$d_6$, 400MHz): 6.77 (1 H, dd, $^{3}J_{F4,H3}$ = 8.8 Hz, $J_{3,5}$ = 5.6

Hz, H-3), 6.67 (1 H, ddd, $^{3}J_{F4,H5}$ = 26.4 Hz, $J_{5,6}$ = 8.4 Hz, H-5), 6.95 (1 H, dd, $^{4}J_{F4,H6}$ = 3.2 Hz, H-6), 5.90 - 5.10 (8H, br, HO-2', 2'', 3', 3'', 4', 4'', 6', 6'', exchangeable with $D_2O$), 4.53 (1 H, d, $J_{1',2'}$ = 7.6 Hz, H-1'), 4.67 (1 H, d, $J_{1'',2''}$ = 7.6 Hz, H-1''), 3.62 (2 H, dd, $J_{2',3'} = J_{2'',3''}$ = 10.0 Hz, H-2', 2''), 3.42 (2 H, dd, $J_{3',4'} = J_{3'',4''}$ = 4.0 Hz, H-3', 3''), 3.69 (1 H, d, $J_{4',5'} = J_{4'',5''}$ = 3.2 Hz, H-4', 4''), 3.57 - 3.51 (6 H, m, H-5', 5'', 6', 6'') ppm; $\delta_C$ (DMSO-$d_6$, 100MHz): 143.42 (d, $^{4}J_{F-C}$ = 2.3 Hz, C-1), 115.86 (d, $^{3}J_{F-C}$ = 9.7 Hz, C-2), 104.22 (d, $^{2}J_{F-C}$ = 26.8 Hz, C-3), 155.05 (d, $^{1}J_{F-C}$ = 232.9 Hz, C-4), 108.18 (d, $^{2}J_{F-C}$ = 22.3 Hz, C-5), 145.77 (d, $^{3}J_{F-C}$ = 10.4 Hz, C-6), 102.82 (C-1'), 104.35 (C-1''), 70.34 (C-2'), 70.53 (C-2''), 72.62 (C-3'), 72.70 (C-3''), 68.13 (C-4'), 68.19 (C-4''), 75.78 (C-5'), 75.87 (C-5'), 60.48 (C-6'), 60.55 (C-6') ppm.

Anal. Calcd. for $C_{18}H_{25}O_{12}F$ (%): C, 47.79, H, 5.57; Found: C, 47.75, H, 5.54.