Supporting Information

Flavin based supramolecular gel displaying multi stimuli triggered sol-gel transition

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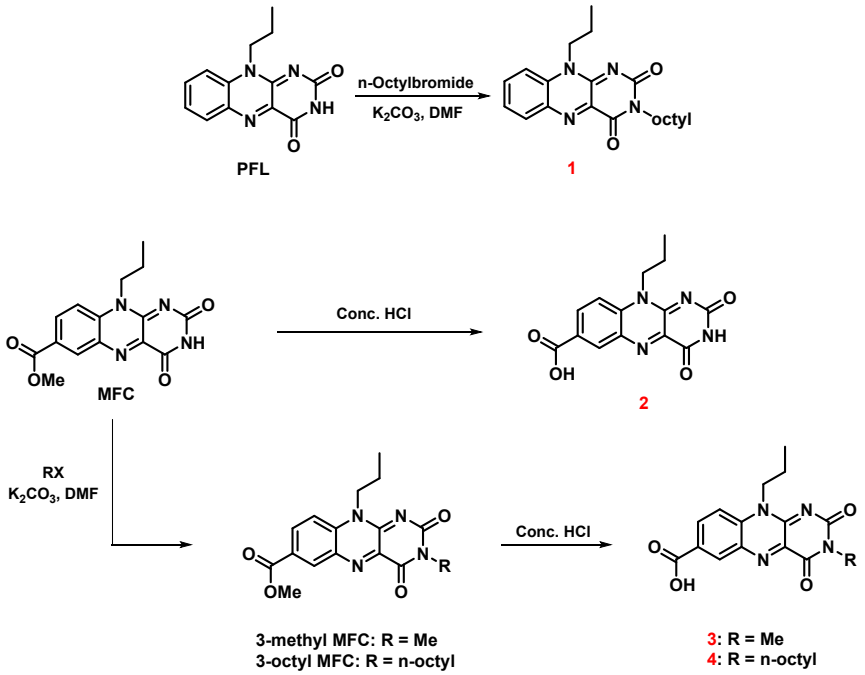
1. Synthetic Procedure



Scheme S1. Synthetic scheme for flavin derivatives **1-4**

Synthesis of 1.

To 10-propylisoalloxazine (PFL)[1] (0.2 g, 0.78 mmol) taken in 25 ml RB flask, added 4 mL DMF followed by addition of potassium carbonate (0.43 g, 3.12 mmol) and 1-bromooctane (0.67 mL, 3.9 mmol). Reaction was kept at 90 ^{o}C for 1.5 hours. After completion of reaction, monitored by TLC the contents were cooled and added water (10 mL). The precipitate obtained is suction filtrated and washed with 15 mL water and 10 mL diethyl ether. Yellow solid obtained is then dried to give **1** with an yield of 78%.

MP: 130-134 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (dd, J = 8.2, 1.2 Hz, 1H), 7.90 (ddd, J = 8.7, 7.2, 1.6 Hz, 1H), 7.64-7.6 (m, 2H), 4.67 (t, J = 7.9 Hz, 2H), 4.1 (t, J = 7.54 Hz, 2H), 1.98-1.88 (m, 2H), 1.76-1.68 (m, 2H), 1.41-1.26 (m, 10H), 1.14 (t, J = 7.4 Hz, 3H), 0.87 (t, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.45, 155.56, 148.78, 137.17, 135.90, 135.49, 133.41, 132.62, 126.26, 115.14, 46.13, 42.15, 31.79, 29.30, 29.16, 27.74, 26.95, 22.62, 20.47, 14.06, 11.22. HR-MS (ESI): m/z calcd. for $[C_{21}H_{29}N_4O_2]^+$ $([M+H])^+$: 369.2285; found: 369.2297.

Synthesis of 2.

To methylflavin carboxylate (MFC)[2] (0.5 g, 1.59 mmol) taken in 25 ml RB flask, added 5 ml conc. HCl. Kept the reaction for heating at 90 ^{o}C for 3 hours. Cooled the contents and added water and suction filtered to get flavin 2 as a yellow solid, yield 95%.

MP: 315-320 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.49 (s, 1H), 8.51 (d, J = 2.0 Hz, 1H), 8.34 (dd, J = 9.0, 2.0 Hz, 1H), 8.07 (d, J = 9.1 Hz, 1H), 4.53 (t, J = 7.8 Hz, 2H), 1.78-1.73 (m, 2H), 1.03 (t, J = 7.4 Hz, 3H). HR-MS (ESI): m/z calcd. for $[C_{14}H_{13}N_4O_4]^+$ $([M+H])^+$: 301.0931; found: 301.0923.

Synthesis of 3.

3-methyl MFC. MFC (0.5g, 1.6 mmol) was added to 25 ml RB flask, to it added 10 ml DMF followed by addition of potassium carbonate (0.44g, 3.18 mmol) and Methyl iodide (1.13 g, 7.96 mmol). Reaction was kept at 80 ^{o}C for 6 hours. After completion of reaction, it is then cooled and filtered the precipitate through suction filtration followed by washing with 20 ml water and 20 ml diethyl ether. 3-methyl MFC obtained is then dried to give yellow solid, yield 85%.

MP: 240-244 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, 1H, J = 1.9 Hz), 8.45 (dd, 1H, J = 9, 1.9 Hz), 7.65 (d, 1H, J = 9 Hz), 4.65 (t, 2H, J = 7.76 Hz), 3.98 (s, 3H), 3.49 (s, 3H), 1.92-1.87 (m, 2H), 1.11 (t, 3H, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.94, 159.26, 155.65, 149.04, 137.86, 135.52, 135.34, 135.06, 135.01, 128.05, 115.41, 52.85, 46.46, 28.84, 20.48, 11.2. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{16}H_{17}N_4O_4$: 351.1064 Found 351.1077.

Flavin 3. To 3-methyl MFC (0.5 g, 1.51 mmol) in 25 ml RB flask added 5 ml concentrated HCl. Kept the reaction for heating at 90 ^{o}C for 3 hours. Cooled the contents and added water and suction filtered to get **3** as yellow solid, yield 97%.

MP: 307-310 ^{o}C. ^{1}H NMR (400 MHz, Trifluoroacetic acid-d) δ 9.11 (d, 1H, J = 1.8 Hz), 8.88 (dd, 1H, J = 9.2, 1.9 Hz), 8.29 (d, 1H, J = 9.3 Hz), 4.79-4.83 (m, 2H), 3.56 (s, 3H), 2.03-1.97 (m, 2H), 1.18 (t, 3H, J = 7.3 Hz). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.5 (s, 1H), 8.5 (s, 1H), 8.35 (d, 1H, J = 8.8 Hz), 8.11 (d, 1H, J = 9 Hz), 4.58-4.55 (m, 2H), 3.3 (s, 3H), 1.8-1.74 (m, 2H), 1.04 (t, 3H, J

= 7.3 Hz). ^{13}C NMR (100 MHz, Trifluoroacetic acid-d) δ 168.18, 158.41, 149.71, 140.99, 139.72, 139.48, 136, 133.32, 133.28, 132.35, 117.72, 51.49, 28.5, 20.59, 8.41. HRMS (ESI) *m*/*z*: [M + Na]$^+$ calcd for $C_{15}H_{15}N_4O_4$: 337.0907 Found 337.0923.

Synthesis of 4.

3-octyl MFC. To Flavin **8** (0.1g, 0.318 mmol) in 25 ml RB flask, added 2 ml DMF followed by addition of potassium carbonate (0.175g, 1.27 mmol) and 1-bromooctane (0.27ml g, 1.59 mmol). Reaction was kept at 80 ^{o}C for 6 hours. After completion of reaction, monitored by TLC the contents were cooled and added water. The precipitate obtained is suction filtrated and washed with 10 ml water and 10 ml diethyl ether. 3-octyl MFC obtained is then dried to give yellow solid with a yield of 88%.

MP: 192-194 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.95 (s, 1H), 8.47 (d, *J* = 8.9 Hz, 1H), 7.66 (d, *J* = 9.0 Hz, 1H), 4.65 (t, *J* = 7.62 Hz, 2H), 4.09 (t, *J* = 7.4 Hz, 2H), 4 (s, 3H), 1.97-1.87 (m, 2H), 1.75-1.68 (s, 2H), 1.39-1.26 (m, 10H), 1.15 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 6.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.01, 159.00, 155.34, 149.04, 138.08, 135.44, 135.38, 135.05, 135.00, 127.95, 115.33, 52.85, 46.39, 42.27, 31.80, 29.29, 29.17, 27.70, 26.95, 22.64, 20.45, 14.09, 11.23. HR-MS (ESI): m/z calcd. for $[C_{23}H_{31}N_4O_4]^+$ ([M+H])$^+$: 427.234; found: 427.2328.

Flavin 4. To 3-octyl MFC (0.2 g, 0.469 mmol) in 25 ml RB flask added 5 ml concentrated HCl. Kept the reaction for heating at 90 ^{o}C for 3 hours. Cooled the contents and added water and suction filtered, washed with water to give **4** as yellow solid, yield 97%.

MP: 245-250 ^{o}C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 13.51 (s, 1H), 8.52 (d, *J* = 1.9 Hz, 1H), 8.34 (dd, *J* = 9, 1.9 Hz, 1H), 8.09 (d, *J* = 9.1 Hz, 1H), 4.55 (t, *J* = 7.68 Hz, 2H), 3.87 (t, *J* = 7.32 Hz, 2H), 1.81-1.72 (m, 2H), 1.59-1.56 (m, 2H), 1.29-1.26 (m, 10H), 1.04 (t, *J* = 7.4 Hz, 3H), (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 165.85, 158.93, 154.80, 149.40, 138.95, 135.20, 134.31, 134.21, 132.65, 127.84, 116.92, 45.61, 40.94, 31.22, 28.74, 28.58, 27.24, 26.38, 22.07, 19.80, 13.92, 10.94. HR-MS (ESI): m/z calcd. for $[C_{22}H_{29}N_4O_4]^+$ ([M+H])$^+$: 413.2183; found: 413.2191.

2. List of NMR

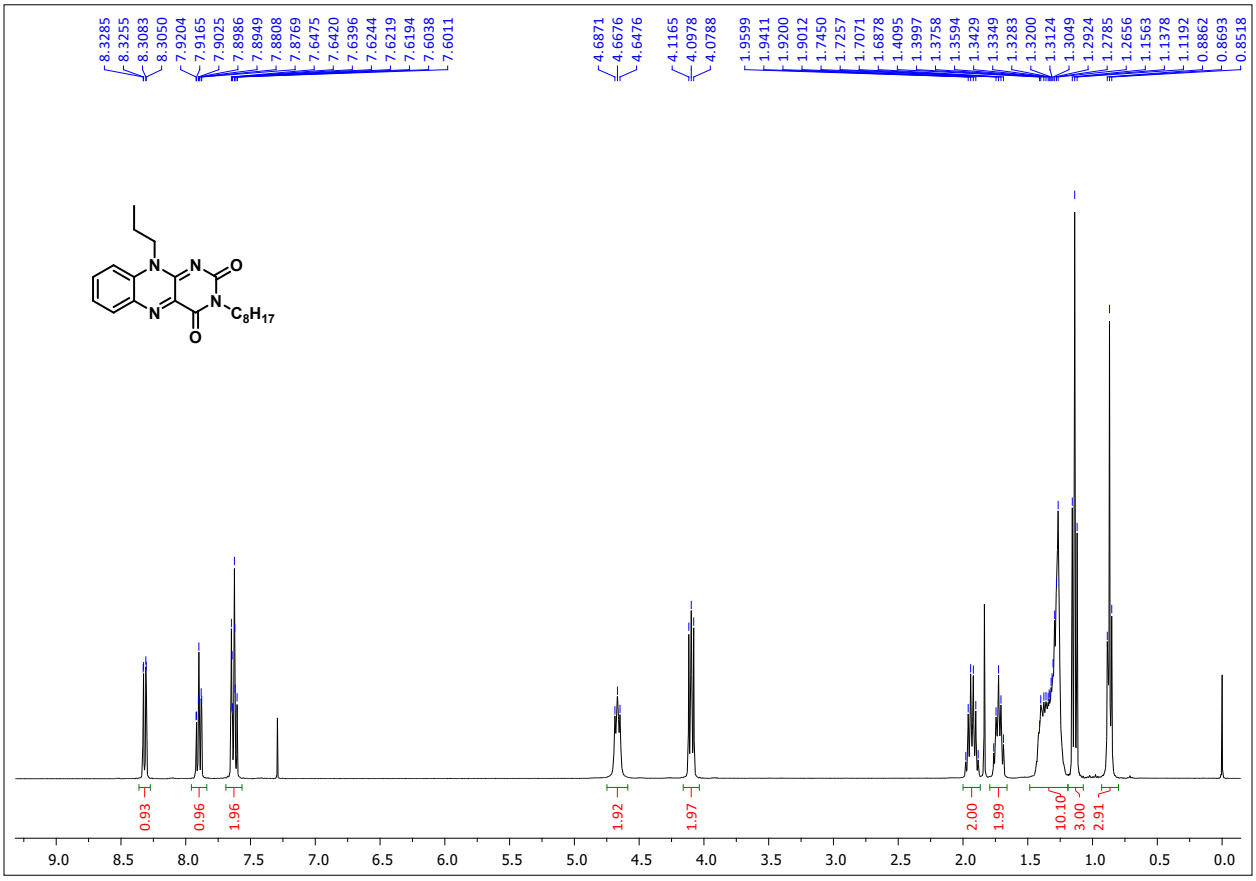


Figure S1. ^{1}H NMR of **1** in $CDCl_3$

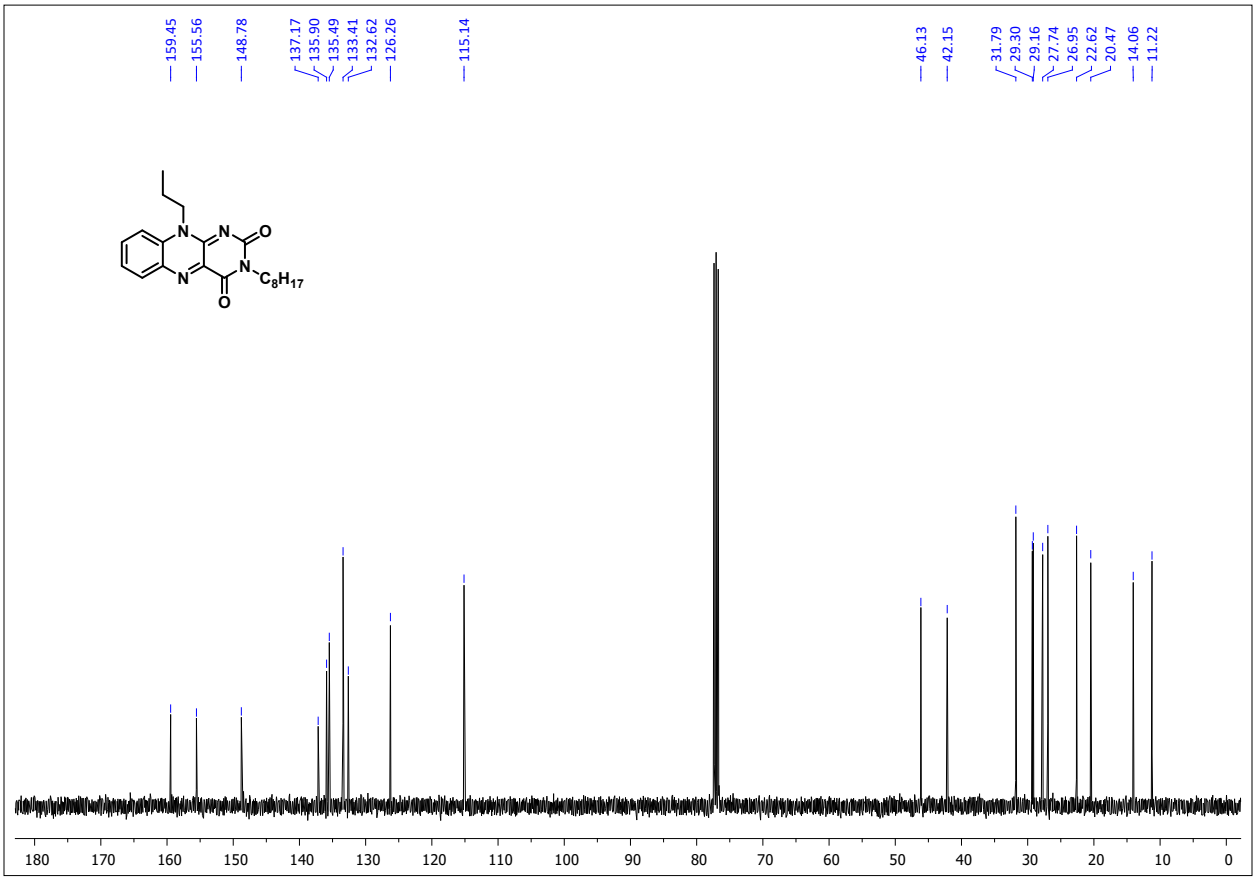


Figure S2. ^{13}C NMR of **1** in $CDCl_3$

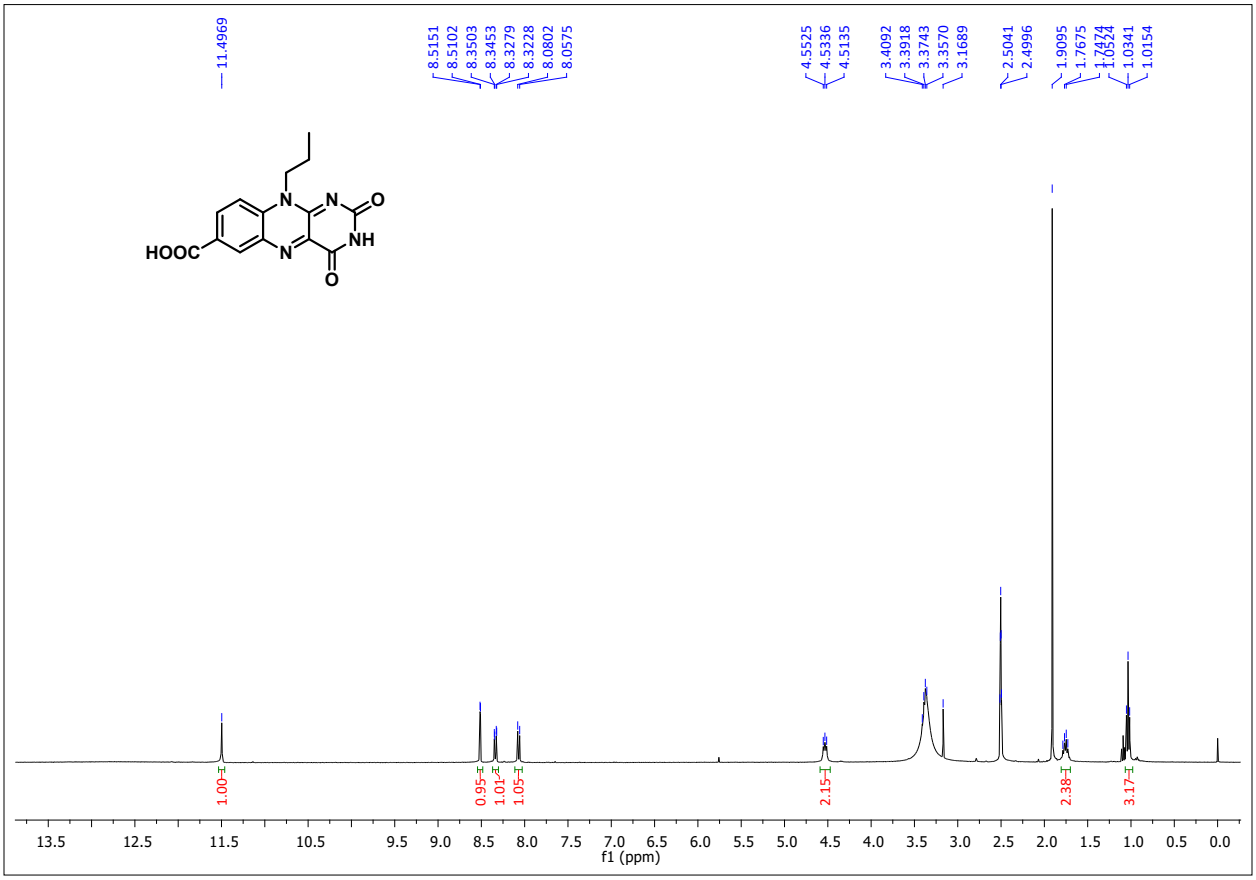


Figure S3. ^{1}H NMR of **2** in DMSO-d_6

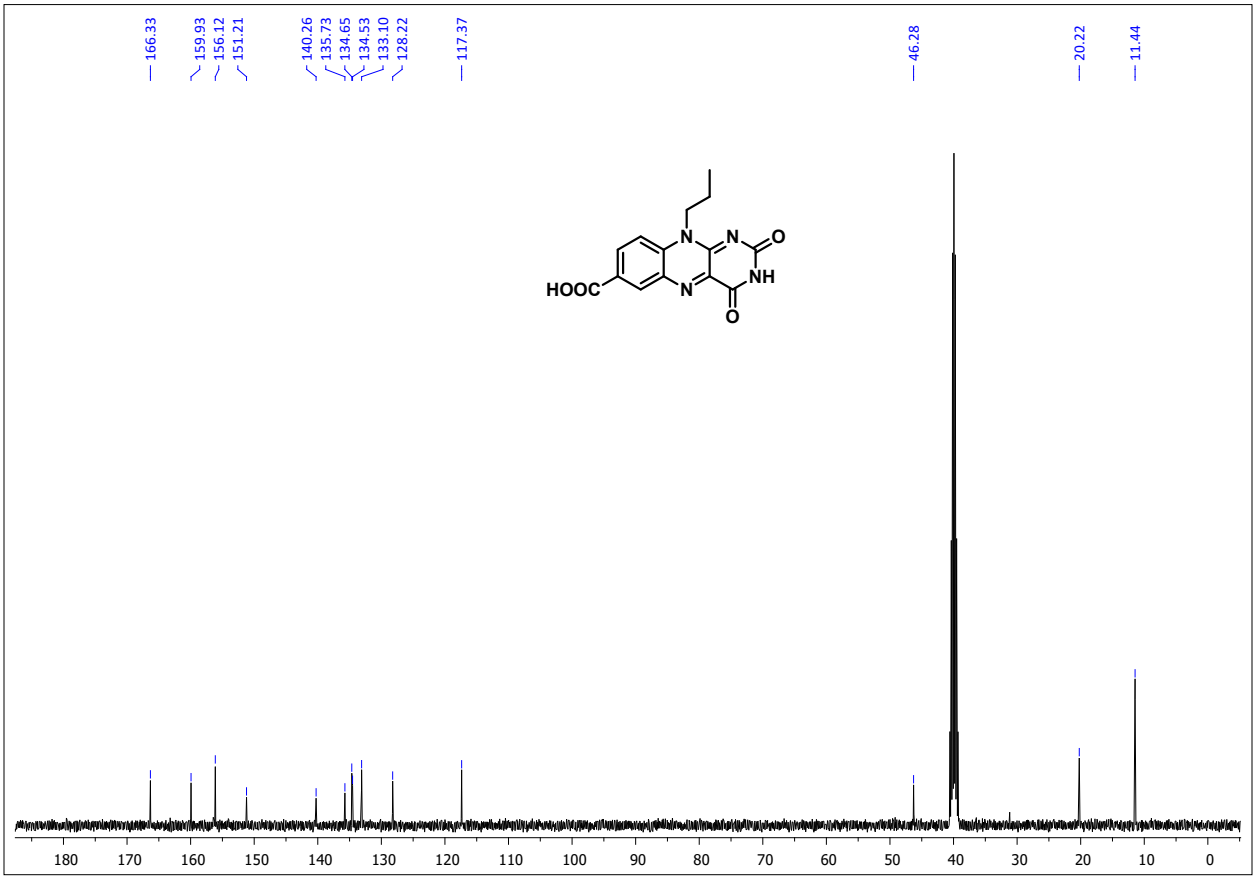


Figure S4. ^{13}C NMR of **2** in DMSO-d_6

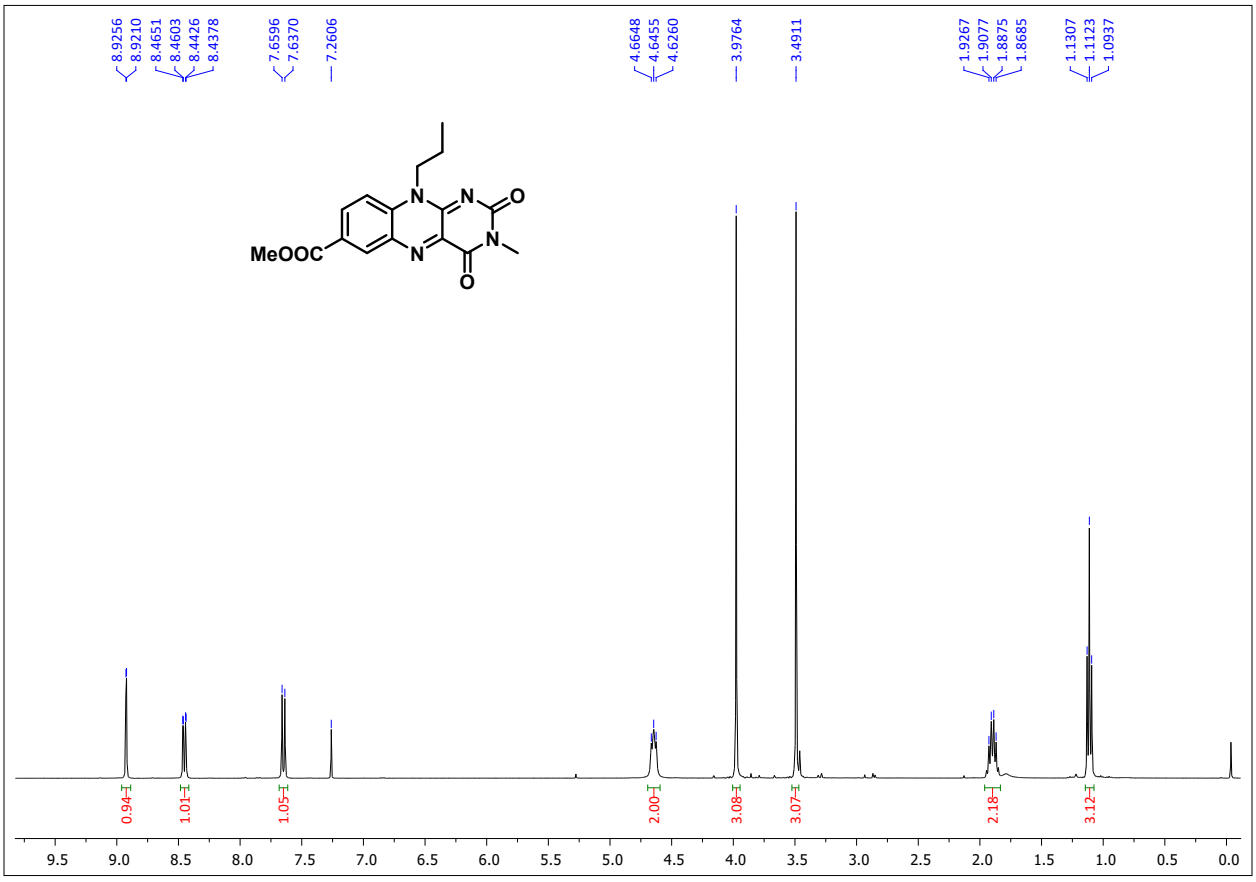


Figure S5. ^{1}H NMR of **3-methyl MFC** in $CDCl_3$

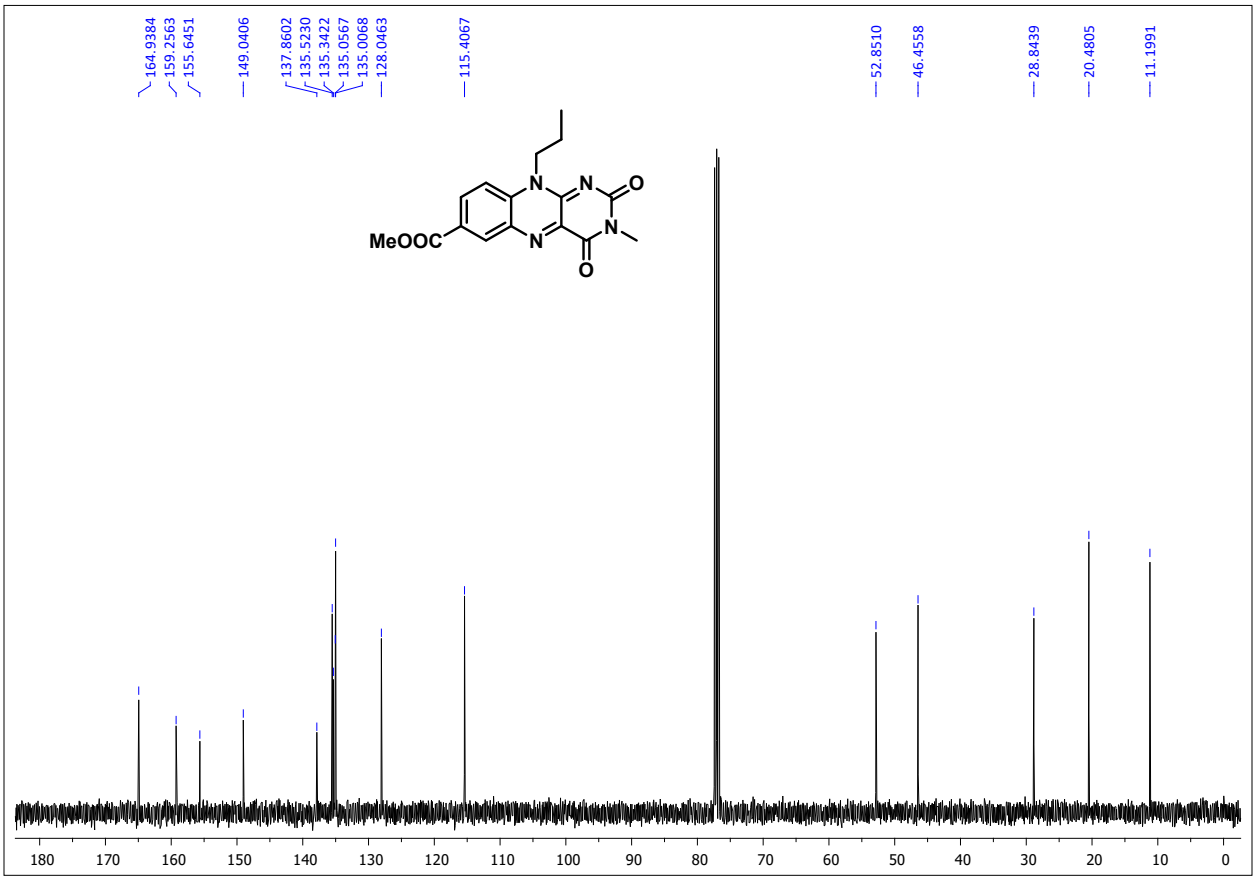


Figure S6. ^{13}C NMR of **3-methyl MFC** in $CDCl_3$

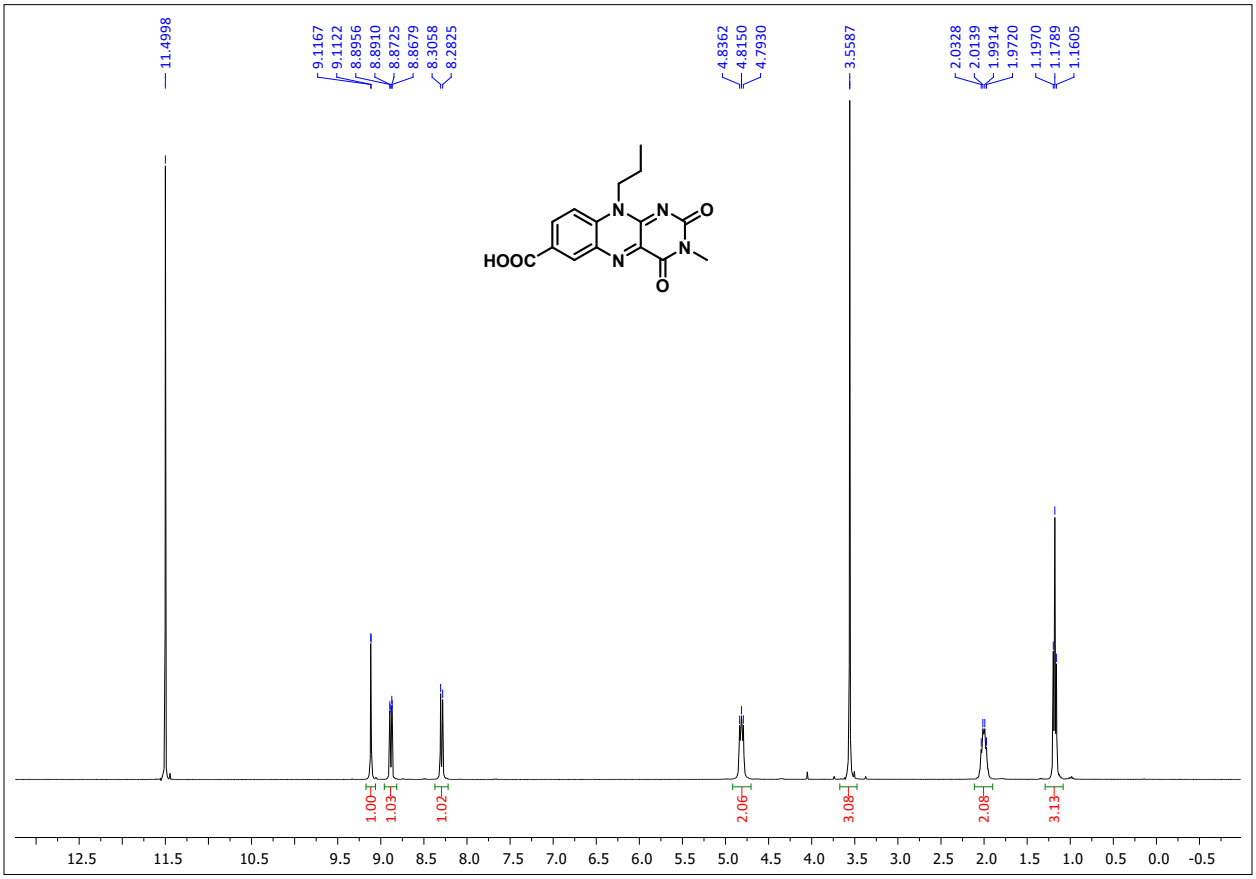


Figure S7. ^{1}H NMR of **3** in Trifluoroaceticacid-d

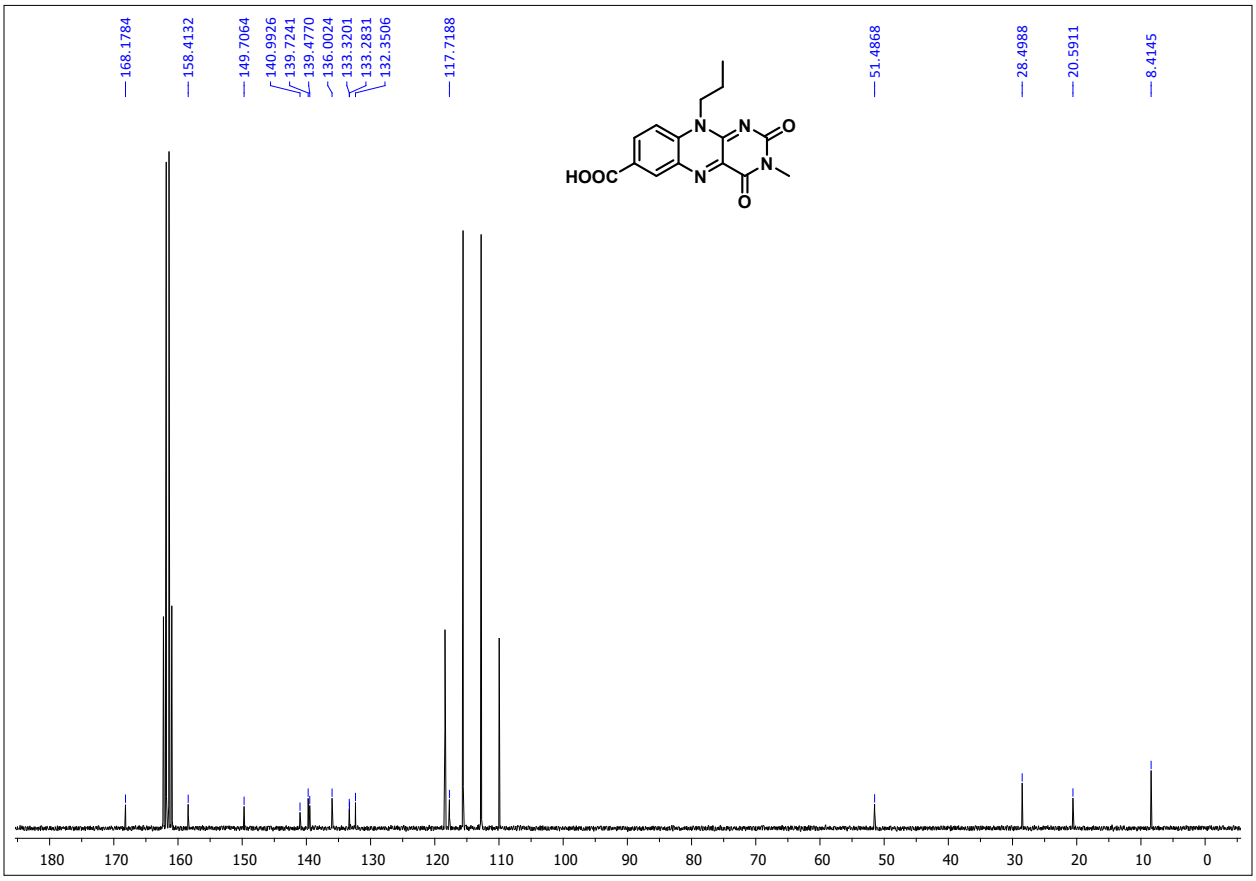


Figure S8. ^{13}C NMR of **3** in Trifluoroaceticacid-d

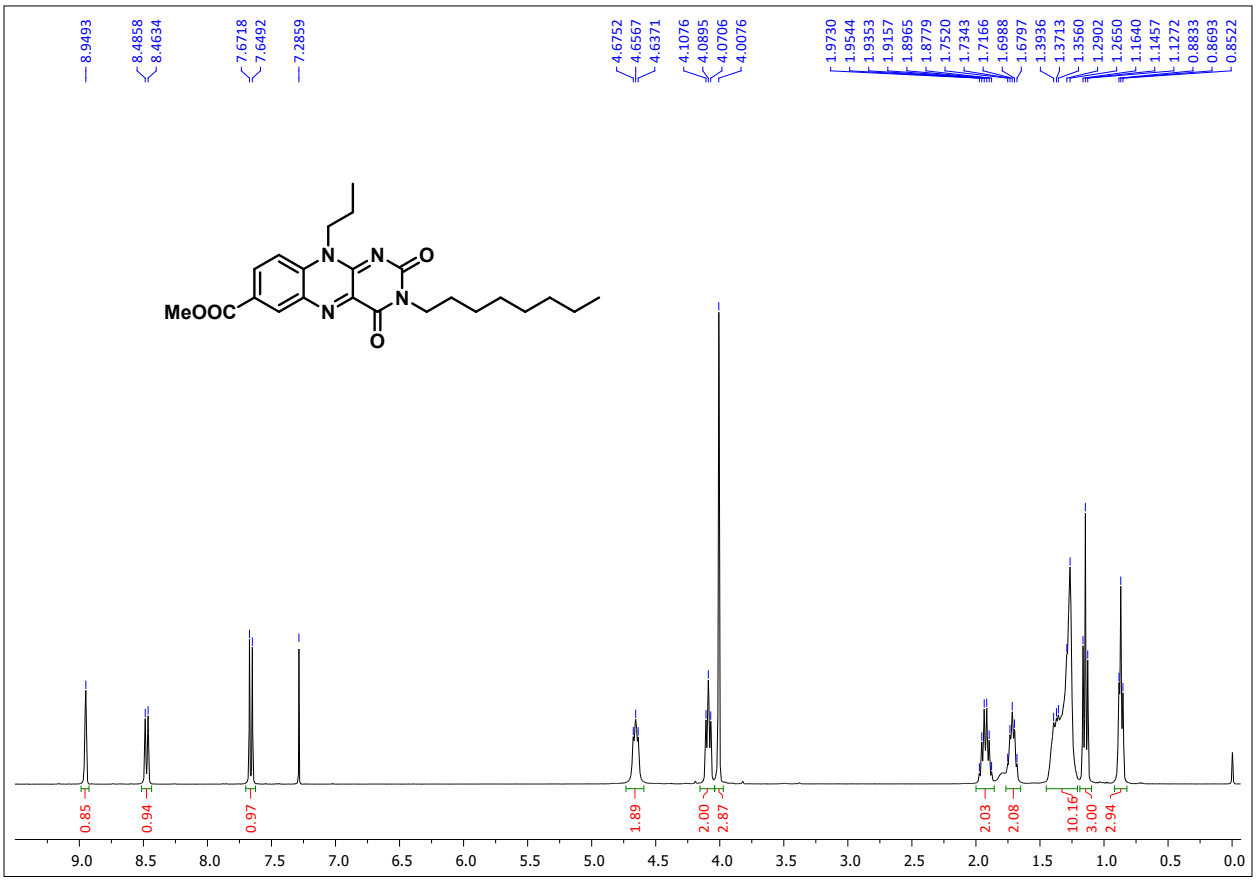


Figure S9. ^{1}H NMR of **3-octyl MFC** in $CDCl_3$

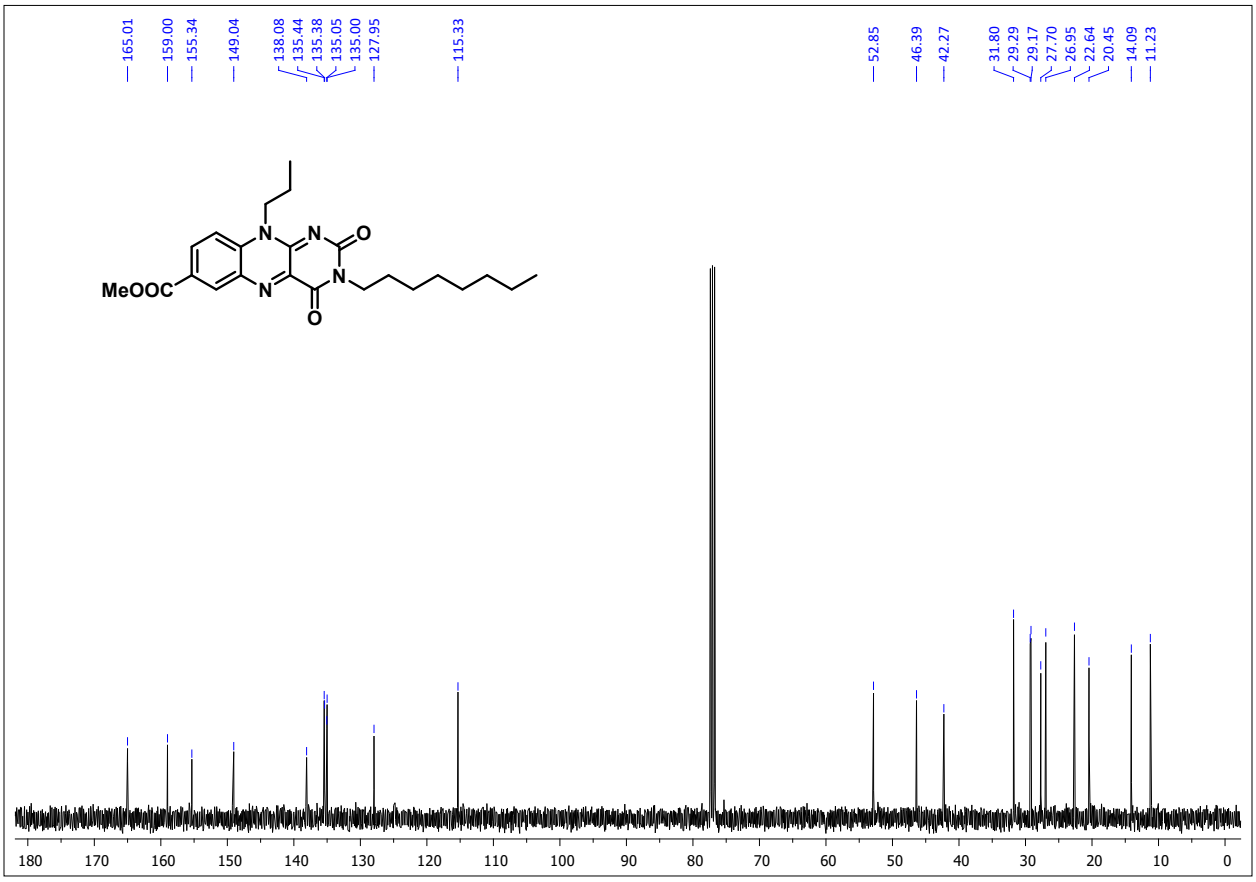


Fig S10. ^{13}C NMR of **3-octyl MFC** in $CDCl_3$

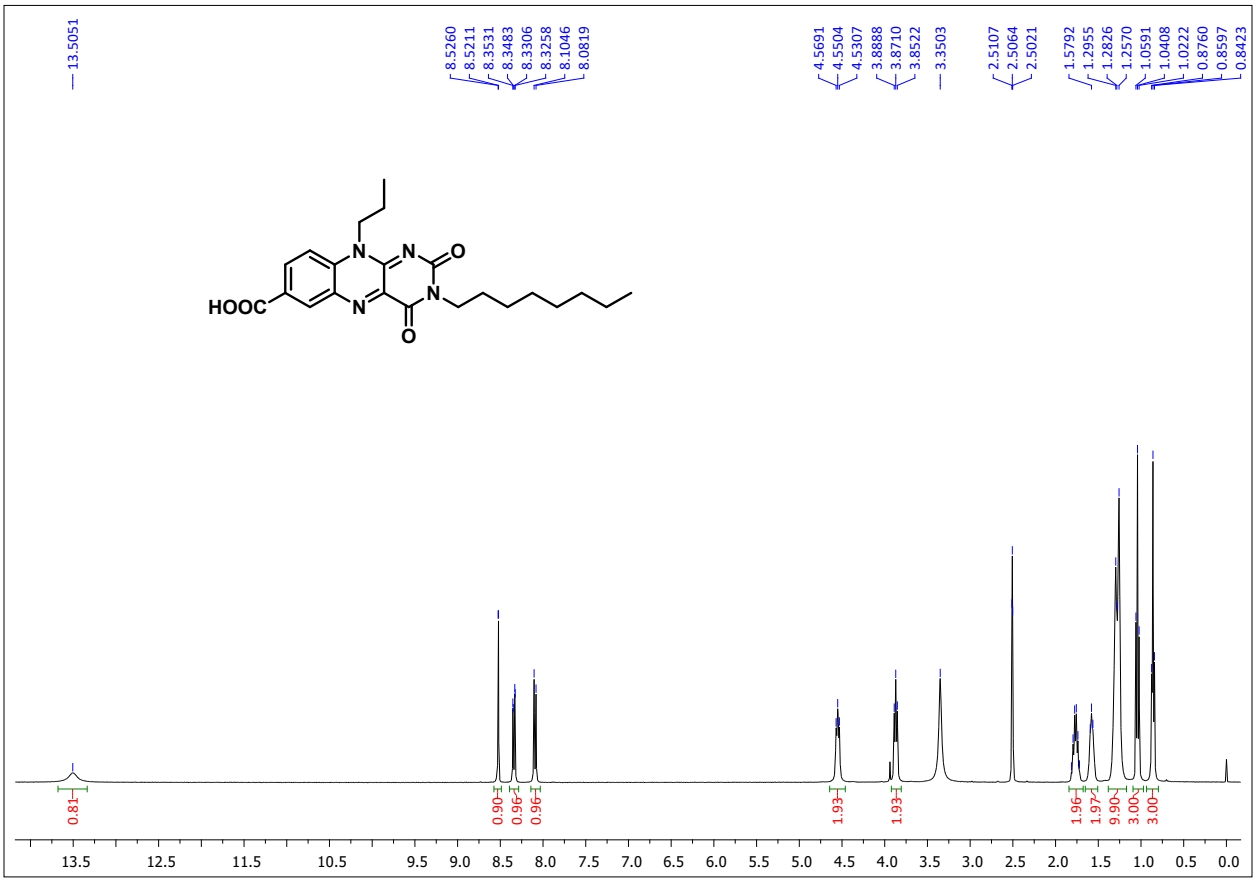


Figure S11. ^{1}H NMR of **4** in DMSO-d_6

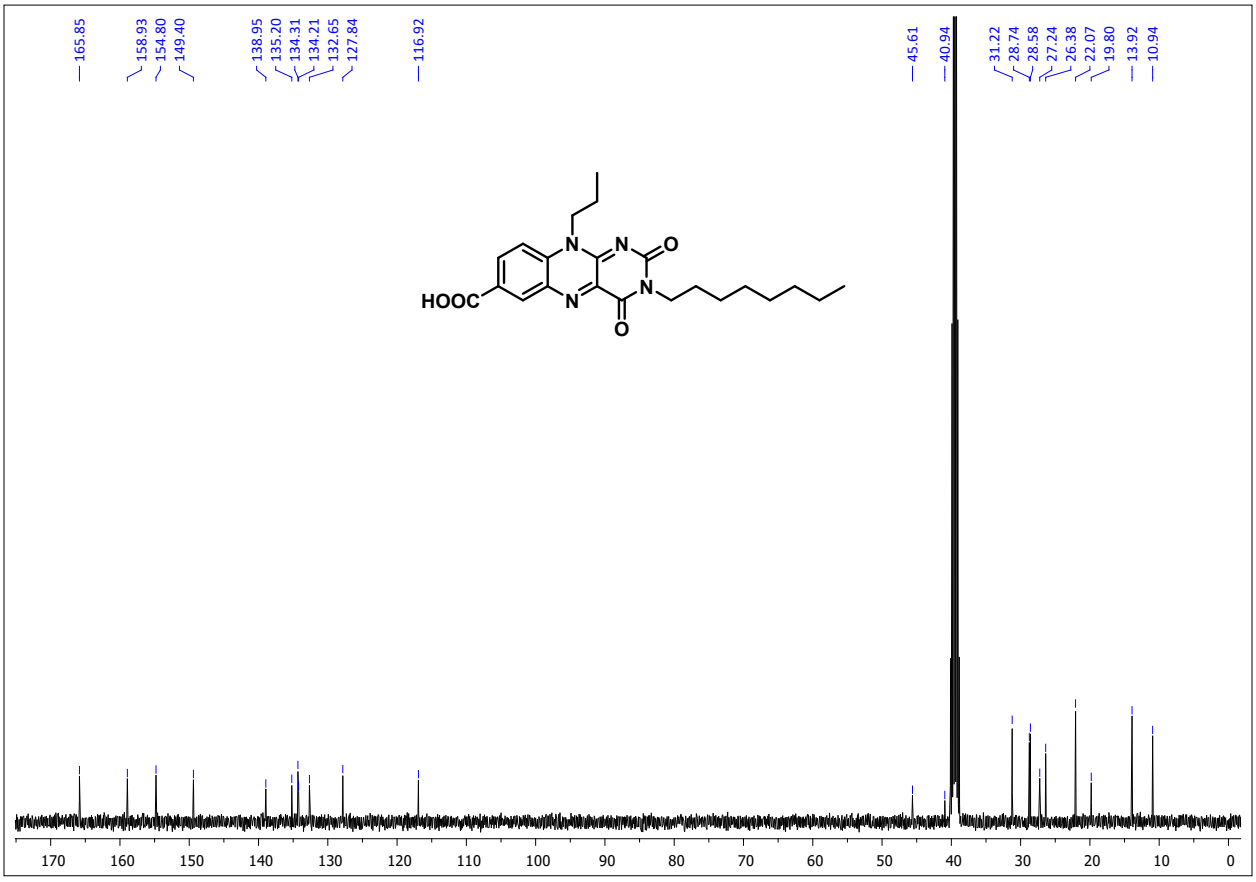


Figure S12. ^{13}C NMR of **4** in DMSO-d_6

3. List of HRMS

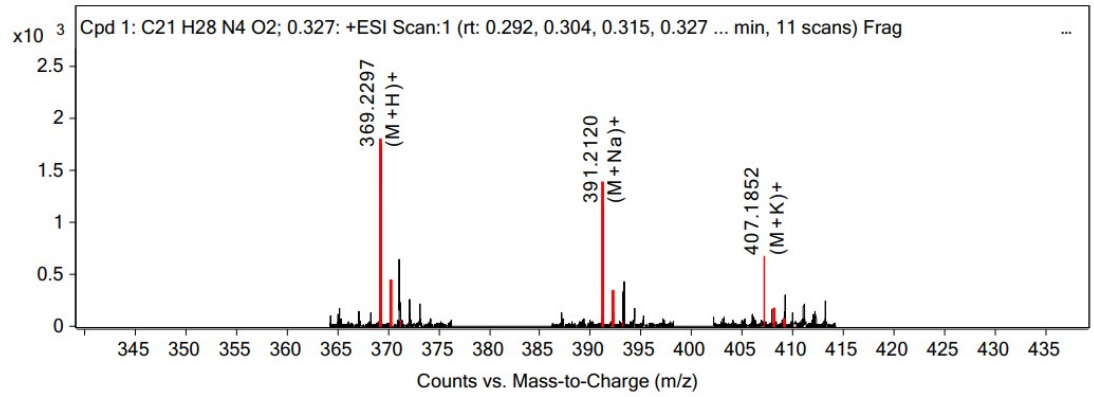


Figure S13. HRMS spectra of **1**

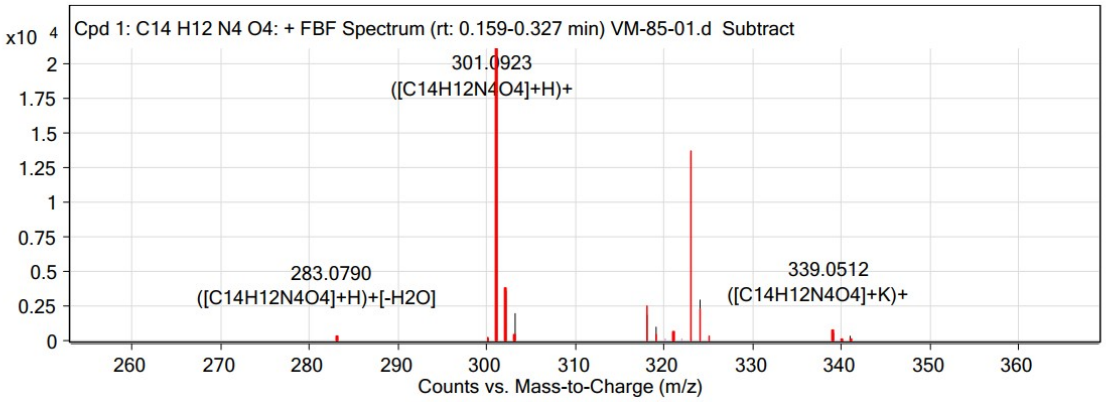


Figure S14. HRMS of **2** in DMSO-d_6

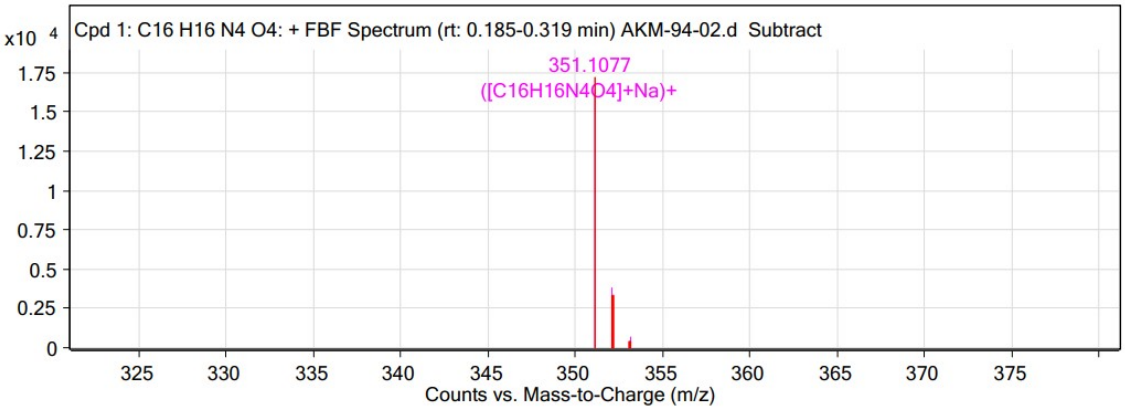


Figure S15. HRMS of **3-methyl MFC**

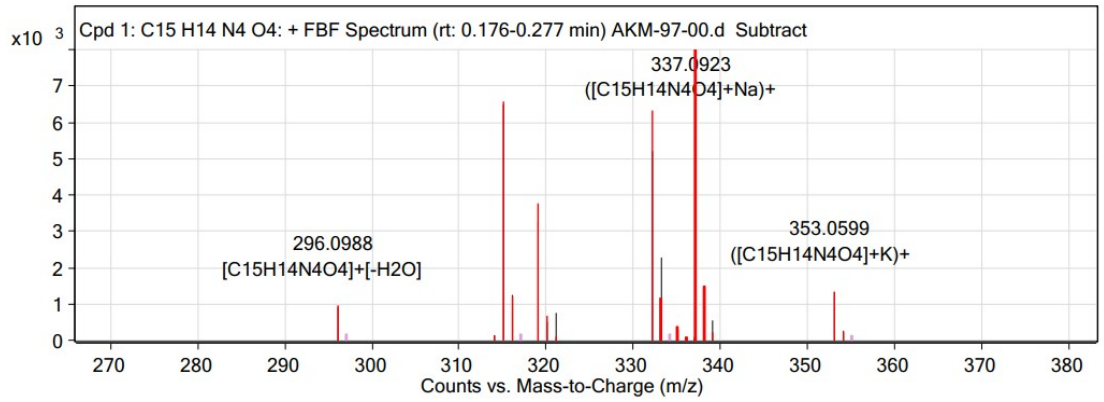


Figure S16. HRMS of **3**

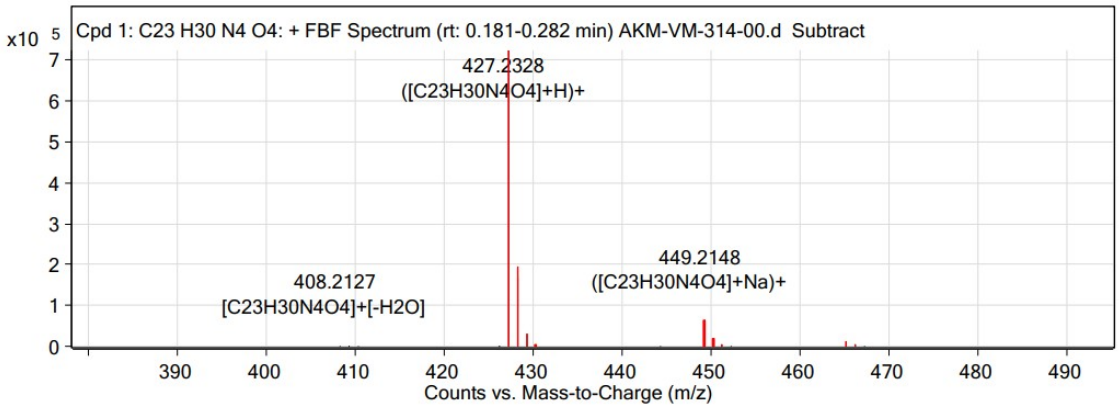


Figure S17. HRMS of **3-octyl MFC**

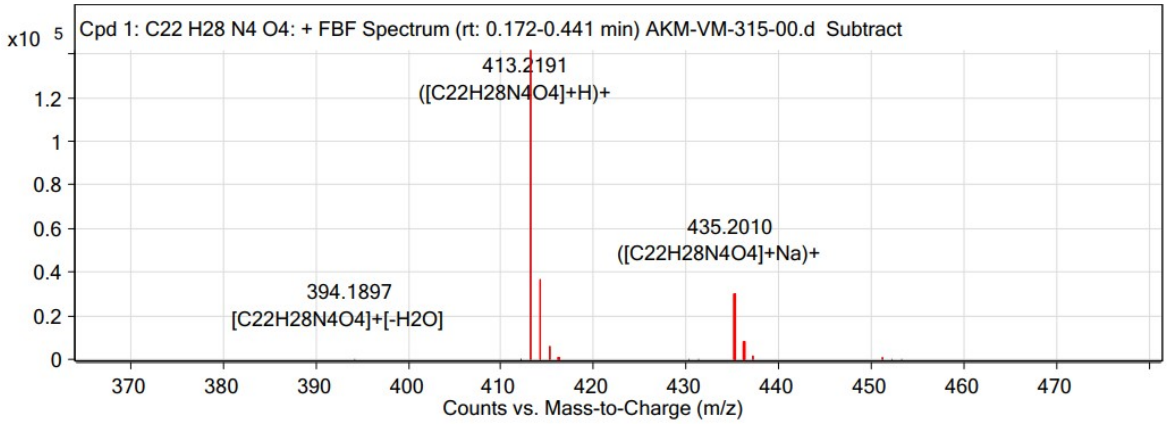


Figure S18. HRMS of **4**

4. References

(1) M. S. S. V. Mouli and A. K. Mishra, *CrystEngComm* 2022, **24**, 2221-2225.

(2) (a) M. S. S. V. Mouli and A. K. Mishra, *J. Chem. Sci.*, 2022, **134**, 59. (b) M. S. S. V. Mouli and A. K. Mishra, *RSC Adv.*, 2022, **12**, 3990-3995.