10.1071/CH19364_AC

Australian Journal of Chemistry 2020, 73(9 & 10), 903-910

Supplementary Material

Developing tamoxifen-based chemical probes for use with a dual-modality fluorescence and optical coherence tomography imaging needle

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Fig S1:Bright field confocal image from the control MCF-7 culture. Note this is a different region to OCT imaging.

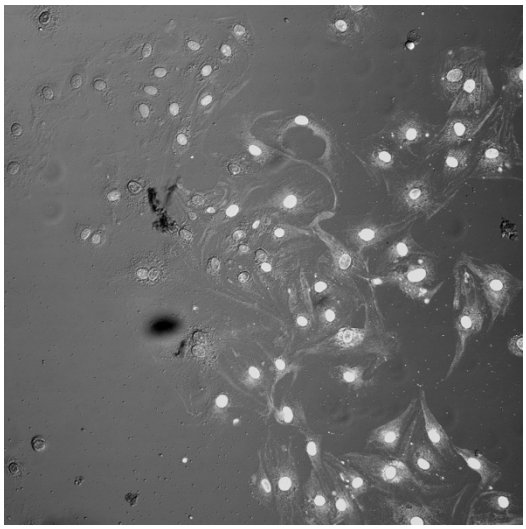


*Fig S2: Confocal images of ER-negative MDA-231 cell lines (left) control and (right) following incubation with conjugate for 1 hour of dosing with 10 μM **4**; Scale bar 0.5 mm.*

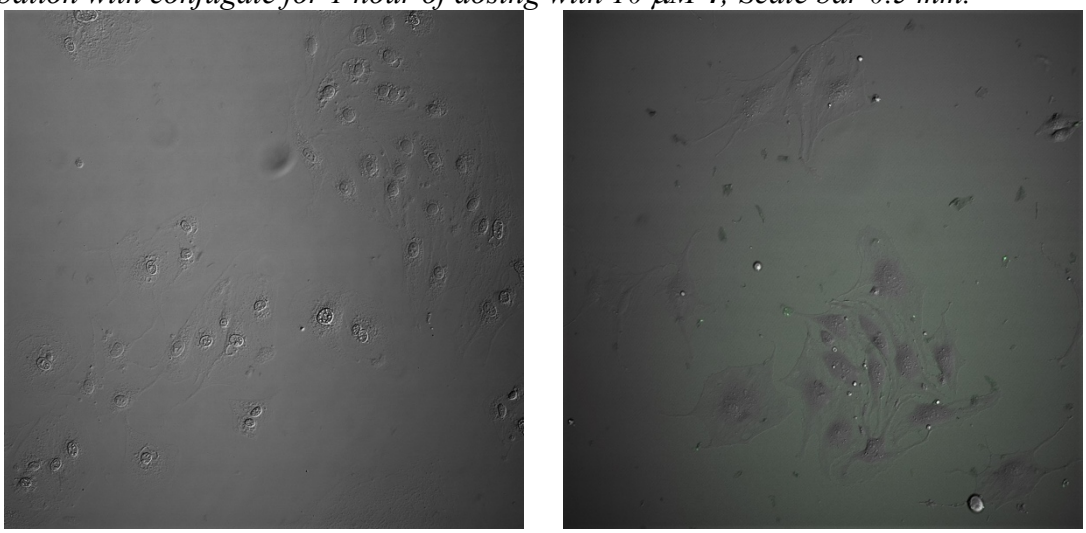


*Fig S3: Confocal images of ER-negative MDA-231 cell lines (left) control and (right) following incubation with conjugate for 1 hour of dosing with 10 μM **5**;*

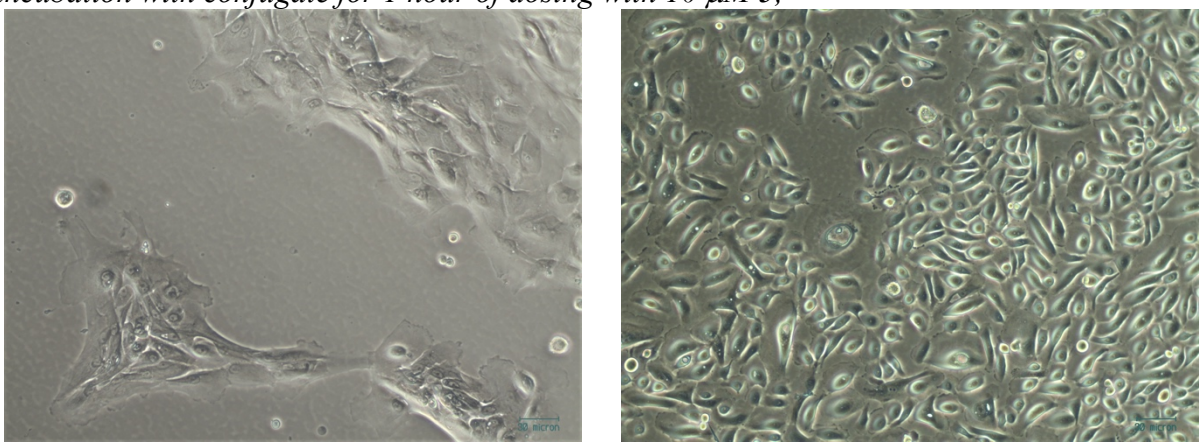
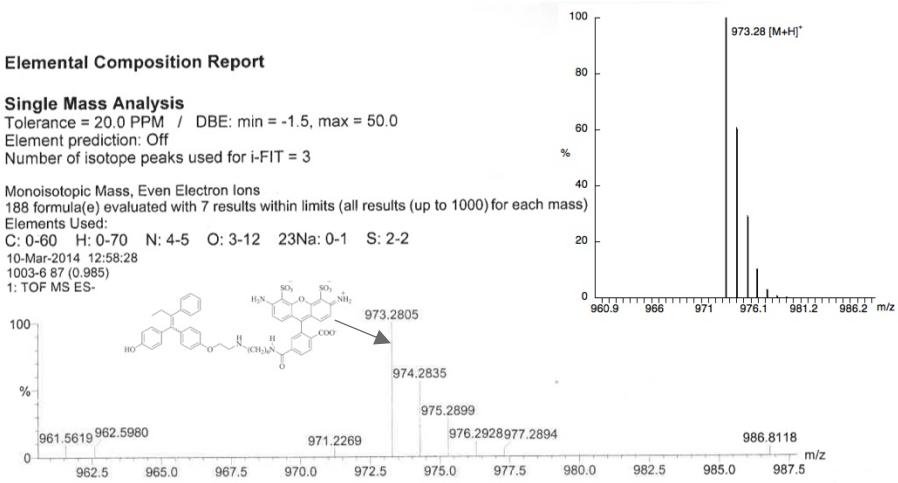


Fig. S4: HRMS of compound 4 with the exact mass of $C_{51}H_{49}N_4O_{12}S_2$ $[M + H]^+$ 973.2788 having good agreement with the observed mass 973.2805; Inset to HRMS contains the simulated fragmentation pattern.



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
Minimum:		5.0	20.0	-1.5			
Maximum:				50.0			
973.2805	973.2788	1.7	1.7	29.5	16.2	1.0	C51 H49 N4 O12 S2
	973.2764	4.1	4.2	26.5	16.2	0.9	C49 H50 N4 O12 23Na S2
	973.2858	-5.3	-5.4	39.5	18.6	3.4	C60 H46 N4 O4 23Na S2
	973.2730	7.5	7.7	38.5	18.6	3.4	C58 H45 N4 O7 S2
	973.2706	9.9	10.2	35.5	18.4	3.2	C56 H46 N4 O7 23Na S2
	973.2917	-11.2	-11.5	30.5	17.5	2.3	C53 H50 N4 O9 23Na S2
	973.2941	-13.6	-14.0	33.5	18.5	3.3	C55 H49 N4 O9 S2

*Fig. S5: HPLC chromatogram of **4** prior to purification; Peak with a retention time 27.57 min corresponds to compound isolated for HRMS in Fig. S1.*

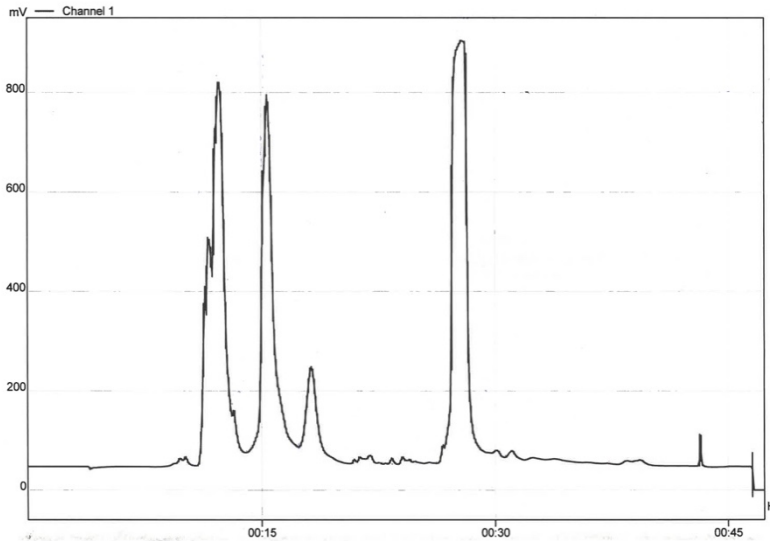
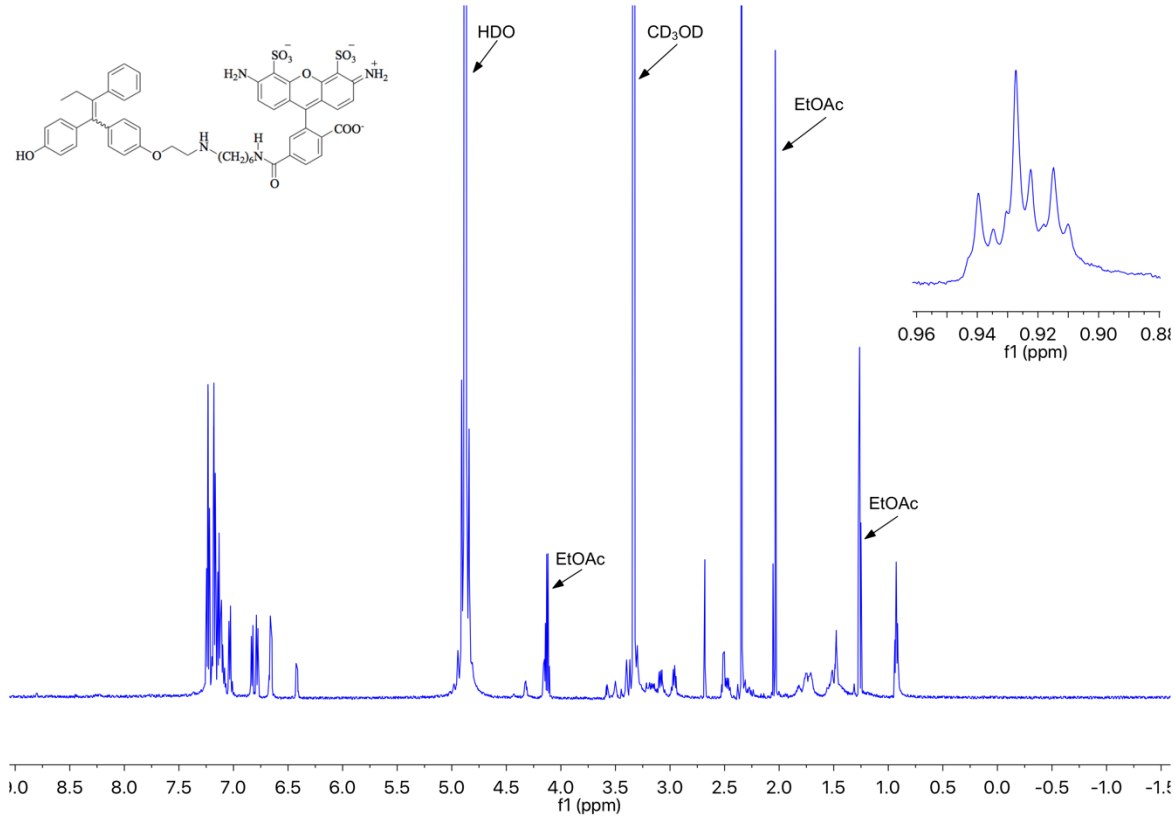


*Fig. S6: [1]H NMR spectrum of **4**. The inset shows the signal from the methyl group of the but-1-ene is an overlay of two triplets associated with the E and Z isomers.*



[1]H NMR (600.13 MHz, CD_3OD): δ= 7.25-7.01 (17H, m), 6.83 (1H, dd, J=7.9, 2.1 Hz), 6.78 (1H, dd, J=7.8, 1.9 Hz), 6.67-6.64 (1H, m), 3.40 (1H, t, br), 3.09 (1H, t J=7.6 Hz), 2.96 (1H, t, J=7.6 Hz), 2.53-2.43 (1H, m), 2.34 (5H, s), 1.85-1.68 (3H, m), 1.56-1.35(4H, m) 0.93 (3H, t, J=8.9 Hz). The low mass of the final product resulted in insufficient sample being available for a fully resolved [1]H NMR. Insufficient sample for NMR has also seen in the literature for another Alexa Fluor™ conjugate of **3** involving Alexa Fluor-546.[1] The high cost of these fluorophores compared to others such as fluorescein and BODIPY FL warrant the majority of the product (~0.2 mg) being used in cell lines, with only a small amount left for characterisation by mass spectrometry. We have attempted to provide some characterisation through NMR, with 38 of the 41 protons being assigned with appropriate integration. However, the protons of the CH_2 in the aminoethoxy region (3.4-4.3 ppm) were complicated by the occurrence of E/Z isomers. The spectrum has a similar pattern to other reported conjugates of **3**.[1]

[1] E. L. Ricket et al., *Bioconjugate Chem.* **2010**, 21, 903-910.

Fig. S7: [1]H NMR spectrum (600 MHz, CD_3OD) *of* ***5***

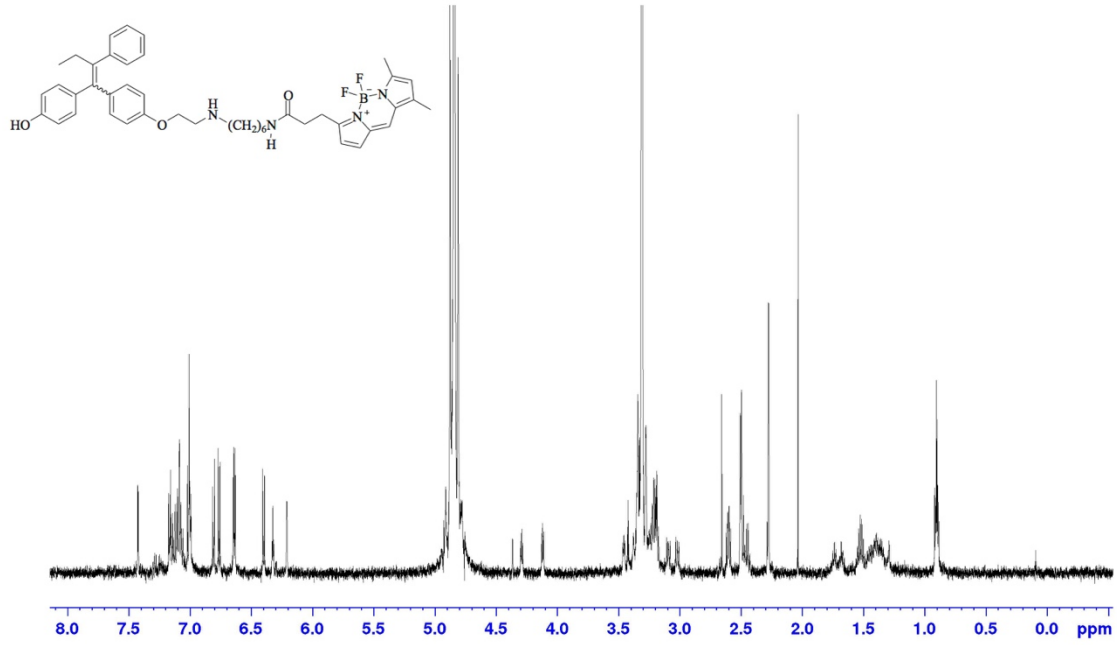


Fig. S8: HRMS (ESI-TOF) of compound ***5*** *calc. for* $C_{44}H_{52}BF_2N_4O_3$ *[M + H]*$^+$ *733.4095, found 733.4080;* $C_{44}H_{51}BF_2N_4O_3Na$ *[M + Na]*$^+$ *755.3920 found 755.3928. Inset to HRMS contains the simulated fragmentation pattern for [M + H]*$^+$.