

Synthetic routes to novel fluorogenic pyronins and silicon analogs with far-red spectral properties and enhanced aqueous stability

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Abbreviations

The following abbreviations are used throughout the text of the Supplementary data: AcOH, acetic acid; anal., analysis; aq., aqueous; Ar, argon; ATR, attenuated total reflectance; CH₃CN, acetonitrile; DCM, dichloromethane; DMSO, dimethylsulfoxide; equiv., equivalent(s); ESI, electrospray ionization; EtOAc, ethyl acetate; FA, formic acid; HPLC, high-performance liquid chromatography; IC, ion chromatography; IR, infrared; LR, low resolution; NMR, nuclear magnetic resonance; PE, petroleum ether; RP, reversed-phase; tBu, *tert*-butyl; TFA, trifluoroacetic acid; TLC, thin-layer chromatography.

S1 Determination of TFA in samples of (Si-)pyronin dyes

TFA has been assayed by IC using the methodology described below. All solutions were prepared in ultrapure H₂O. A TFA standard solution (ca. 1.0 g/L) was prepared by weighing. The mother liquor was diluted to the standard solutions of 1, 2.5, 5 and 10 mg/L before injection. A precisely weighed amount of each (Si-)pyronin dye was solubilized in DMSO (1 mg/mL) and then diluted in ultrapure H₂O so that the concentration of TFA fits with the calibration curve. Two different dilutions were performed for each sample (system S1). The resulting concentrations of TFA allowed to calculate the mass percentage of TFA contained in each sample. System S1: IC (Thermo Scientific Dionex Ion Pac AS11-HC analytical column, 4 μm, 4 × 250 mm) with the mixture aq. 30 mM NaOH / ultrapure H₂O (9:1, v/v) as eluent (isocratic mode, 15 min), flow rate: 1.5 mL/min; column temperature: 30 °C; injection volume: 10 μL.

S2 Synthesized compounds

Please note: CH₃CN, DCM and toluene (HPLC-grade, Fisher Chemical or VWR) were dried over alumina cartridges immediately prior to use, by means of a solvent purification system PureSolv PS-MD-5 model from Innovative Technology.

3-Bromo-*N,N*-bisallylaniline (S1) [188745-07-5]¹

To a suspension of anhydrous K₂CO₃ (3.2 g, 23.2 mmol, 2 equiv.) in dry CH₃CN (20 mL) were added 3-bromoaniline (1.26 mL, 11.6 mmol, 1 equiv.) and allyl bromide (3.48 mL, 40.6 mmol, 3.5 equiv.), and the mixture was stirred at 80 °C overnight. After cooling down to room temperature, the mixture was filtered over a dicalite® 4158 pad which was rinsed with CH₃CN. The filtrate was evaporated to dryness and the resulting residue was purified by column chromatography over silica gel (VWR 63-200 μm, eluent: heptane/EtOAc 40:1, v/v) to give pure 3-bromo-*N,N*-bisallylaniline **S1** as an oil (2.70 g, 10.7 mmol, yield 92%). R_f

¹ Egawa T, Koide Y, Hanaoka K, Komatsu T, Terai T, Nagano T. Development of a fluorescein analogue, TokyoMagenta, as a novel scaffold for fluorescence probes in red region Chem. Commun. 2011; 47: 4162-4164. <https://doi.org/10.1039/c1cc00078k>

(heptane/EtOAc 40:1, v/v) = 0.48; IR (ATR): ν 3080, 3007, 2980, 2911, 2862, 1642, 1587, 1554, 1487, 1444, 1416, 1384, 1355, 1331, 1231, 1177, 1094, 981, 949, 917, 829, 794, 755, 679, 661, 553, 436; ^1H NMR (500 MHz, CDCl_3): δ 7.03 (t, $J = 8.2$ Hz, 1H), 6.83-6.77 (m, 2H), 6.60 (d, $J = 8.2$ Hz, 1H), 5.83 (m, 2H, $\text{H}_2\text{C}=\underline{\text{C}}\text{H}$ -allyl), 5.22-5.14 (m, 4H, $\underline{\text{H}}_2\text{C}=\text{CH}$ -allyl), 3.94-3.87 (d, 4H, $\underline{\text{C}}\text{H}_2$ -allyl); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$): δ 150.0, 133.4, 130.4, 123.5, 119.2, 116.4, 115.2, 111.0, 52.8.

6-Bromo-1-methylindoline (9) [86626-30-4]²

NaBH_3CN (1.6 g, 25.5 mmol, 5 equiv.) was added slowly to a solution of commercial 6-bromoindole (1.02 g, 5.1 mmol, 1 equiv.) and paraformaldehyde (1.53 g, 51 mmol, 10 equiv.) in glacial AcOH (50 mL). The resulting reaction mixture was stirred at room temperature for 2 h. The reaction was checked for completion by TLC (PE/EtOAc 5:1, v/v). Thereafter, the reaction was quenched with aq. sat. NaHCO_3 solution (150 mL). The resulting aq. phase was extracted with DCM (3×100 mL). The combined organic layers were dried over anhydrous Na_2SO_4 , filtered and finally evaporated to dryness. The resulting residue was purified by column chromatography over silica gel (VWR 63-200 μm , eluent: PE/EtOAc 10:1, v/v) to give pure 6-bromo-1-methylindoline **9** as a yellow oil (674 mg, 3.2 mmol, yield 62%). R_f (PE/EtOAc 10:1, v/v) = 0.48; IR (ATR): ν 2947, 2920, 2841 (broad), 1601, 1576, 1490, 1467, 1435, 1407, 1369, 1325, 1267, 1216, 1195, 1162, 1116, 1058, 989, 953, 870, 825, 801, 781, 711, 644, 579, 538, 467, 424; ^1H NMR (500 MHz, CDCl_3): δ 6.89 (d, $J = 7.7$ Hz, 1H), 6.75 (dd, $J = 7.7$ Hz, $J = 1.6$ Hz, 1H), 6.55 (d, $J = 1.6$ Hz, 1H), 3.33 (t, $J = 8.2$ Hz, 2H), 2.89 (t, $J = 8.2$ Hz, 2H), 2.74 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3): δ 154.9, 129.4, 125.4, 121.2, 120.2, 110.1, 56.3, 35.8, 28.4.

4-(Diallylamino)-2-bromobenzyl alcohol (11) [1398756-54-1]³

To a solution of 3-bromo-*N,N*-bisallylaniline **S1** (1.5 g, 5.97 mmol, 1 equiv.) in dry toluene were added dry DMF (600 μL , 7.76 mmol, 1.3 equiv.) and POCl_3 (675 μL , 7.20 mmol, 1.2 equiv.) under an Ar atmosphere. The resulting reaction mixture was stirred at 80 $^\circ\text{C}$ overnight. After cooling to room temperature, 50 mL of aq. 2.0 M NaOH was added to the mixture which was stirred for further 10 min. Thereafter, the aq. phase was extracted with DCM (3×90 mL) and the combined organic layers were dried over anhydrous Na_2SO_4 , filtered and finally evaporated to dryness. The residue was dissolved in absolute EtOH (15 mL) and NaBH_4 (225 mg, 5.97 mmol, 1 equiv.) was added. Then the resulting reaction mixture was stirred at room temperature for 50 min. Thereafter, solvent was evaporated under reduced pressure, then deionized H_2O was added to the residue and the aq. phase was extracted with DCM (3×20 mL). The combined organic layers were dried over anhydrous

² Koide Y, Urano Y, Hanaoka K, Piao W, Kusakabe M, Saito N, Terai T, Okabe T, Nagano T. Development of NIR Fluorescent Dyes Based on Si-rhodamine for in Vivo Imaging J. Am. Chem. Soc. 2012; 134: 5029-5031. <https://doi.org/10.1021/ja210375e>

³ Hanaoka K, Kagami Y, Piao W, Myochin T, Numasawa K, Kuriki Y, Ikeno T, Ueno T, Komatsu T, Terai T, Nagano T, Urano Y. Synthesis of unsymmetrical Si-rhodamine fluorophores and application to a far-red to near-infrared fluorescence probe for hypoxia Chem. Commun. 2018; 54: 6939-6942. <https://doi.org/10.1039/c8cc02451k>

Na₂SO₄, filtered and finally evaporated to dryness. The resulting residue was purified by flash-column chromatography over silica gel (VWR 63-200 μm, eluent: heptane/EtOAc 9:1, v/v) to give benzyl alcohol **11** as an oil (1.22 g, 4.3 mmol, yield 72%). R_f (heptane/EtOAc 9:1, v/v) = 0.25; ¹H NMR (500 MHz, CDCl₃): δ 7.21 (d, *J* = 8.5 Hz, 1H), 6.87 (d, *J* = 2.6 Hz, 2H), 6.61 (dd, *J* = 8.5 Hz, *J* = 2.6 Hz, 1H), 5.82 (m, H₂C=CH-allyl, 2H), 5.18 (m, H₂C=CH-allyl, 4H), 4.63 (d, *J* = 6.4 Hz, 2H), 3.90 (d, *J* = 4.7 Hz, CH₂-allyl, 4H), 1.78 (t, *J* = 6.4 Hz, OH, 1H); ¹³C NMR (126 MHz, CDCl₃): δ 149.6, 133.3, 130.6, 127.2, 124.6, 116.5, 116.2, 111.6, 65.2, 52.9.

Unsymmetrical bis(bromoaryl) derivative (**12**) [1617504-07-0]³

To a solution of benzyl alcohol **11** (309 mg, 1.10 mmol, 1 equiv.) and 6-bromo-1-methylindoline **9** (232 mg, 1.10 mmol, 1 equiv.) in dry DCM (20 mL) was added BF₃·Et₂O (276 μL, 2.20 mmol, 2 equiv.). The resulting reaction mixture was stirred at room temperature for 5 h. Thereafter, the reaction mixture was quenched with deionized H₂O (10 mL) and extracted with DCM (3 × 20 mL). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The resulting residue was purified by column chromatography over silica gel (VWR 63-200 μm, eluent: PE/DCM 7:3, v/v) to give **12** as a brown oil (452 mg, 0.95 mmol, yield 86%). R_f (PE/DCM 7:3, v/v) = 0.27; ¹H NMR (500 MHz, CDCl₃): δ 6.91 (d, *J* = 2.6 Hz, 1H), 6.80 (d, *J* = 8.6 Hz, 1H), 6.73 (s, 1H), 6.65 (s, 1H), 6.55 (dd, *J* = 8.6 Hz, *J* = 2.6 Hz, 1H), 5.87-5.78 (m, H₂C=CH-allyl, 2H), 5.17 (m, H₂C=CH-allyl, 4H), 3.97 (s, 2H), 3.87 (d, *J* = 4.9 Hz, CH₂-allyl, 4H), 3.29 (t, *J* = 8.1 Hz, 2H), 2.83 (t, *J* = 8.1 Hz, 2H), 2.73 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 153.1, 148.1, 133.5, 130.7, 130.2, 128.1, 127.0, 126.1, 125.5, 123.1, 116.3, 115.9, 111.6, 110.9, 56.3, 52.8, 40.2, 36.1, 28.4.

8-Bromojulolidine (**10**) [64230-25-7]⁴

3-Bromoaniline (632 μL, 5.8 mmol, 1 equiv.), Na₂CO₃ (2.44 g, 23.2 mmol, 4 equiv.) and 1-bromo-3-chloropropane (4.6 mL, 46.4 mmol, 8 equiv.) were stirred at 140 °C for 12 h. DMF (8 mL) was added and the reaction mixture was stirred at 160 °C for 6 h. After cooling to room temperature, excess of 1-bromo-3-chloropropane and DMF were removed under reduced pressure. Deionized H₂O (10 mL) was added and the resulting mixture was extracted with DCM (5 × 20 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The resulting residue was purified by column chromatography over silica gel (VWR 40-63 μm, eluent: heptane/EtOAc 9:1, v/v) to give **10** as a yellow oil (884 mg, 3.5 mmol, yield 60%). R_f (Heptane/EtOAc 9:1, v/v) = 0.56; ¹H NMR (500 MHz, CDCl₃): δ 6.76 (d, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 3.09-3.15 (m, 4H), 2.78 (t, *J* = 6.7 Hz, 2H), 2.70 (t, *J* = 6.7 Hz, 2H), 2.01-1.92 (m, 4H).

⁴ Lei Z, Li X, Luo X, He H, Zheng J, Qian X, Yang Y. Bright, Stable, and Biocompatible Organic Fluorophores Absorbing/Emitting in the Deep Near-Infrared Spectral Region *Angew. Chem., Int. Ed.* 2017; 56: 2979-2983. <https://doi.org/10.1002/anie.201612301>

Unsymmetrical bis(bromoaryl) derivative (**13**) [2219340-17-5]³

To a solution of benzyl alcohol **11** (537 mg, 2.14 mmol, 1 equiv.) and 8-bromojulolidine **10** (634 mg, 2.25 mmol, 1.05 equiv.) in dry DCM (20 mL) was added $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (836 μL , 6.42 mmol, 3 equiv.). The resulting reaction mixture was stirred at room temperature for 3 h. Thereafter, the reaction mixture was quenched with deionized H_2O (10 mL) and extracted with DCM (3×20 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by column chromatography over silica gel (VWR 40-63 μm , eluent: heptane/EtOAc 9:1, v/v) to give **13** as a colorless oil (874 mg, 1.7 mmol, yield 79%). ^1H NMR (500 MHz, CDCl_3): δ 6.90 (d, $J = 2.7$ Hz, 1H), 6.79 (d, $J = 8.6$ Hz, 1H), 6.54 (dd, $J = 8.6$ Hz, $J = 2.7$ Hz, 1H), 6.49 (s, 1H), 5.86-5.79 (m, 2H), 5.18 (dd, $J = 7.8$ Hz, $J = 1.6$ Hz, 2H), 5.15 (t, $J = 1.6$ Hz, 2H), 3.96 (s, 2H), 3.90-3.85 (m, 6H), 3.11-3.06 (m, 4H), 2.82 (t, $J = 6.7$ Hz, 2H), 2.64 (t, $J = 6.7$ Hz, 2H), 2.04-1.89 (m, 4H); ^{13}C NMR (126 MHz, CDCl_3): $\delta = 148.1, 143.0, 133.6, 130.6, 128.6, 127.2, 126.9, 125.6, 125.5, 121.3, 120.8, 116.3, 115.9, 111.7, 52.8, 50.1, 49.5, 40.8, 29.4, 27.5, 22.3, 22.0$

S3 Analytical data

Fig. S1. IR (ATR) spectrum of compound 7

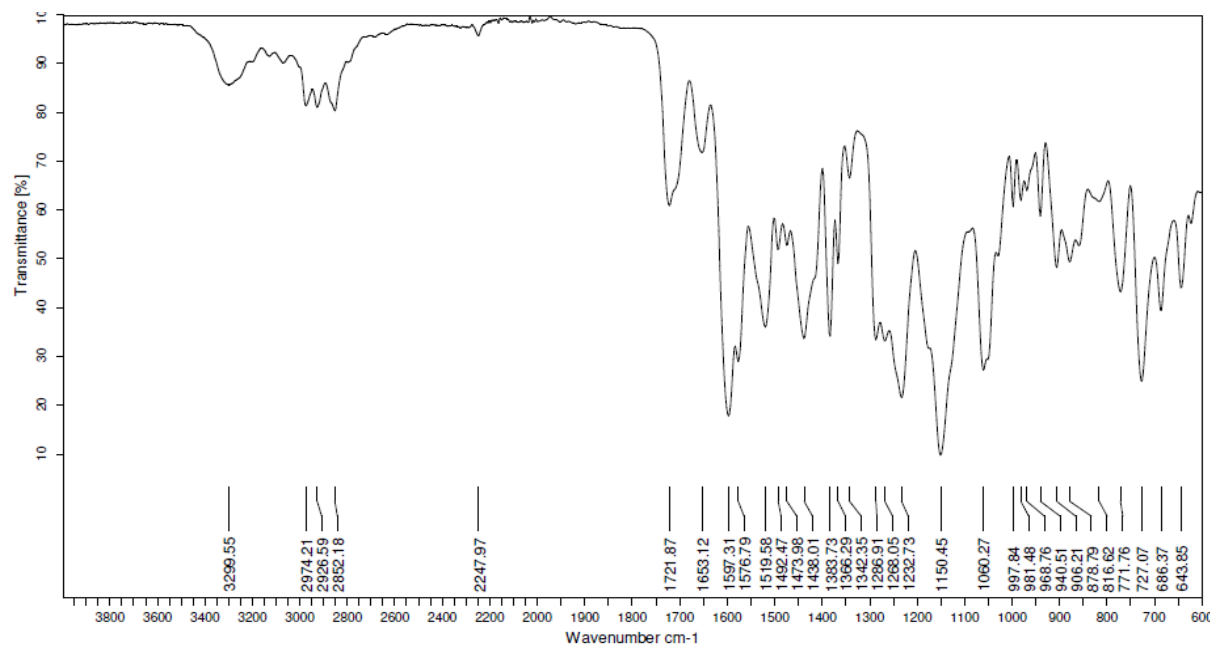


Fig. S2. ^1H NMR spectrum of compound 7 in CDCl_3 (500 MHz)

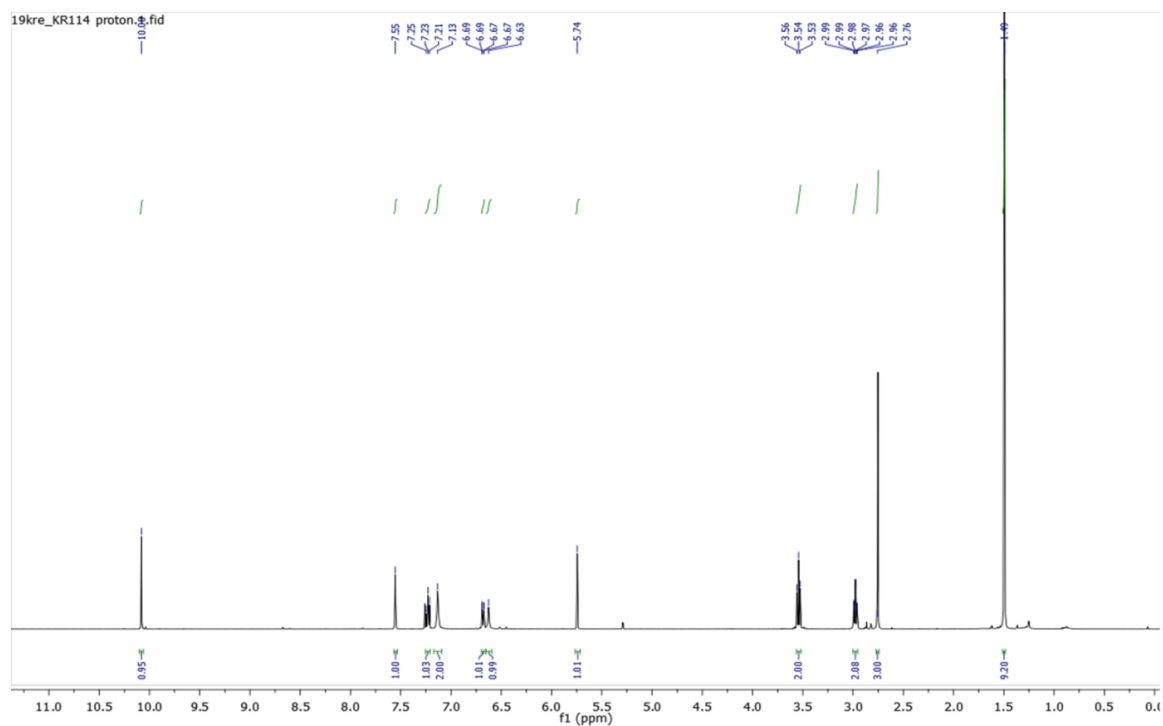


Fig. S3. ^{13}C NMR spectrum of compound 7 in CDCl_3 (126 MHz)

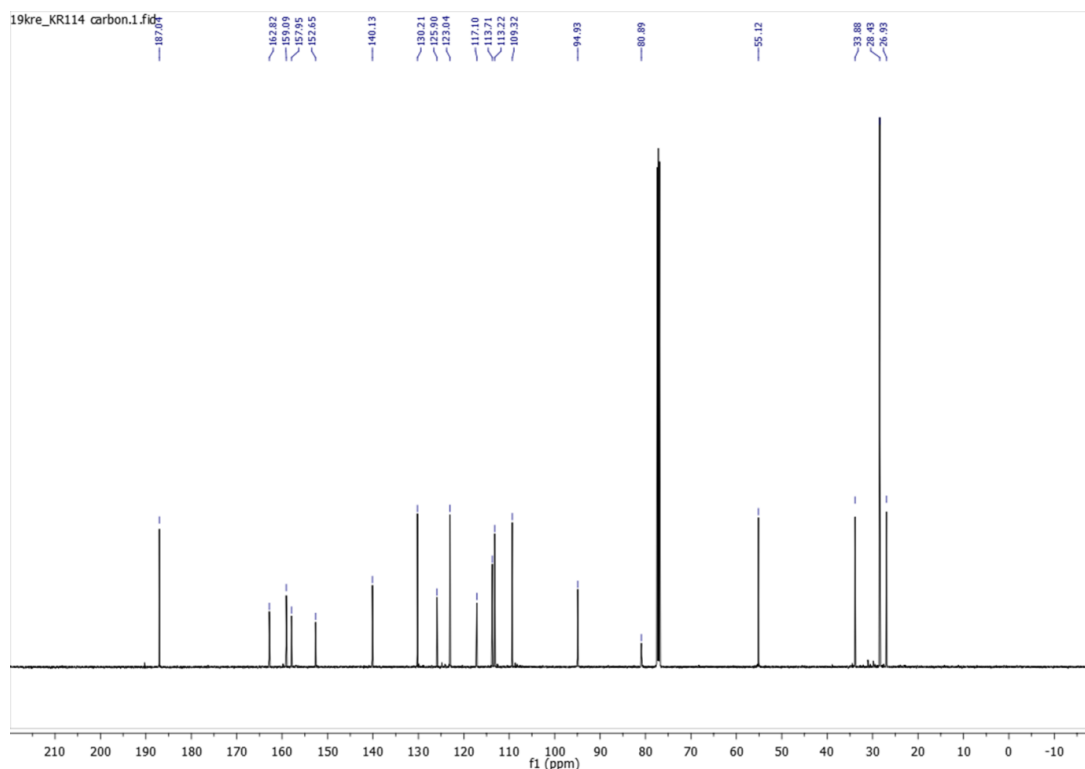


Fig. S4. LR mass spectrum (ESI, positive mode (left) and negative mode (right)) of compound 7

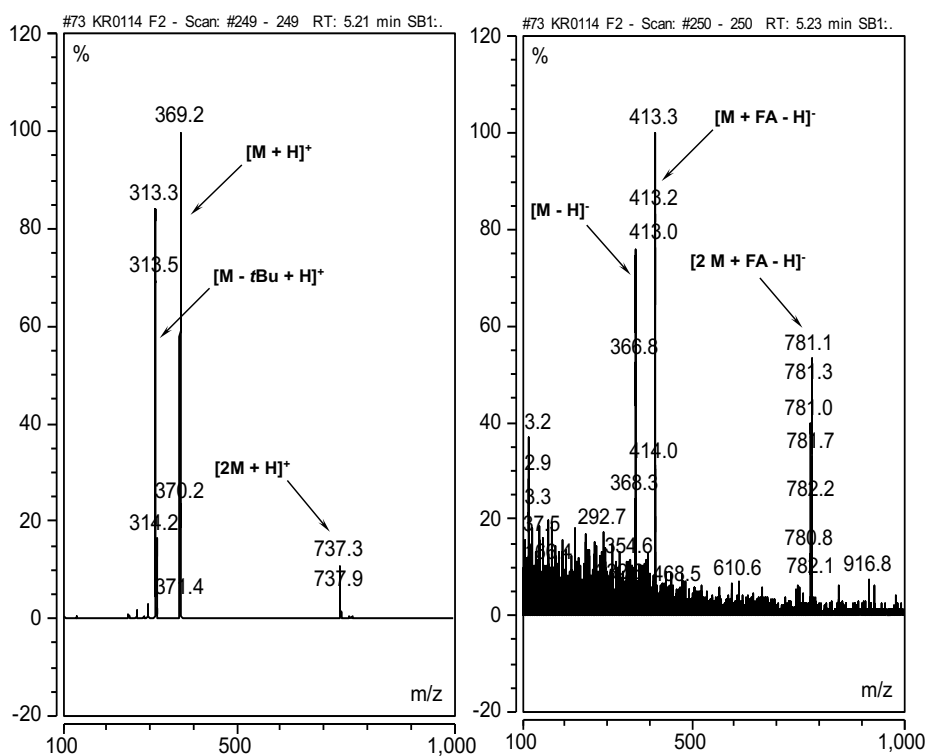


Fig. S5. RP-HPLC elution profile of compound 7 (system A, detection at 260 nm)

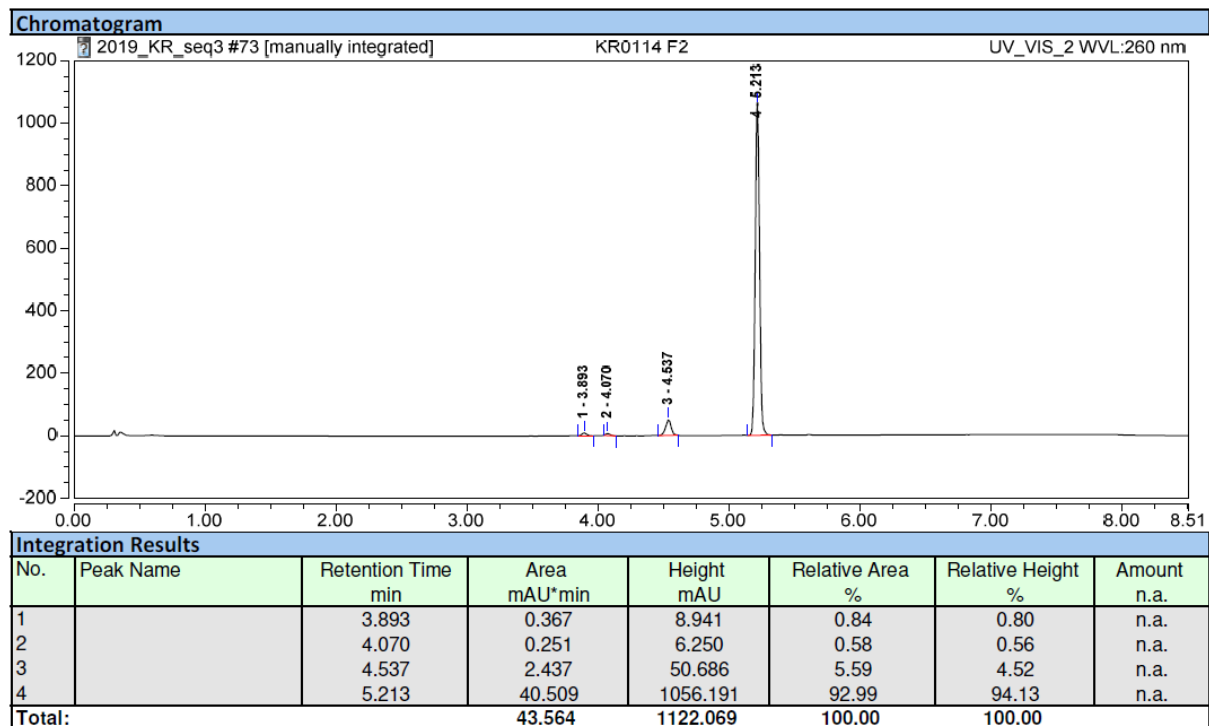


Fig. S6. IR (ATR) spectrum of pyronin 2

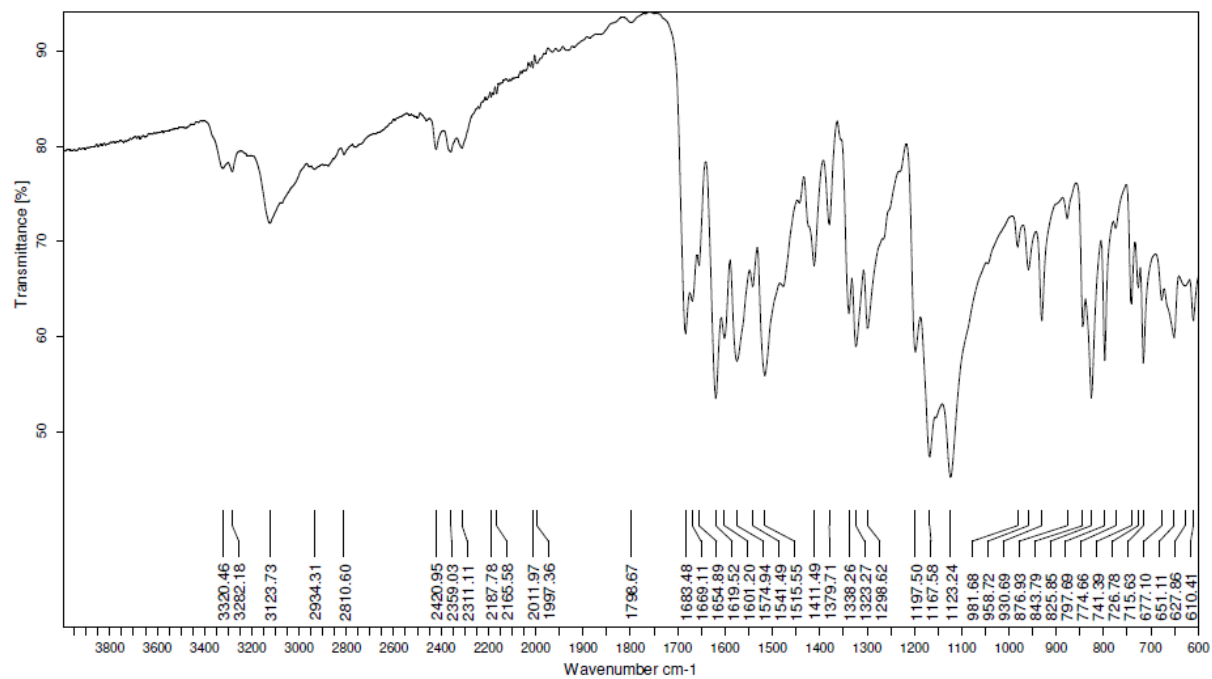


Fig. S7. ¹H NMR spectrum of pyronin 2 in CD₃OD (500 MHz)

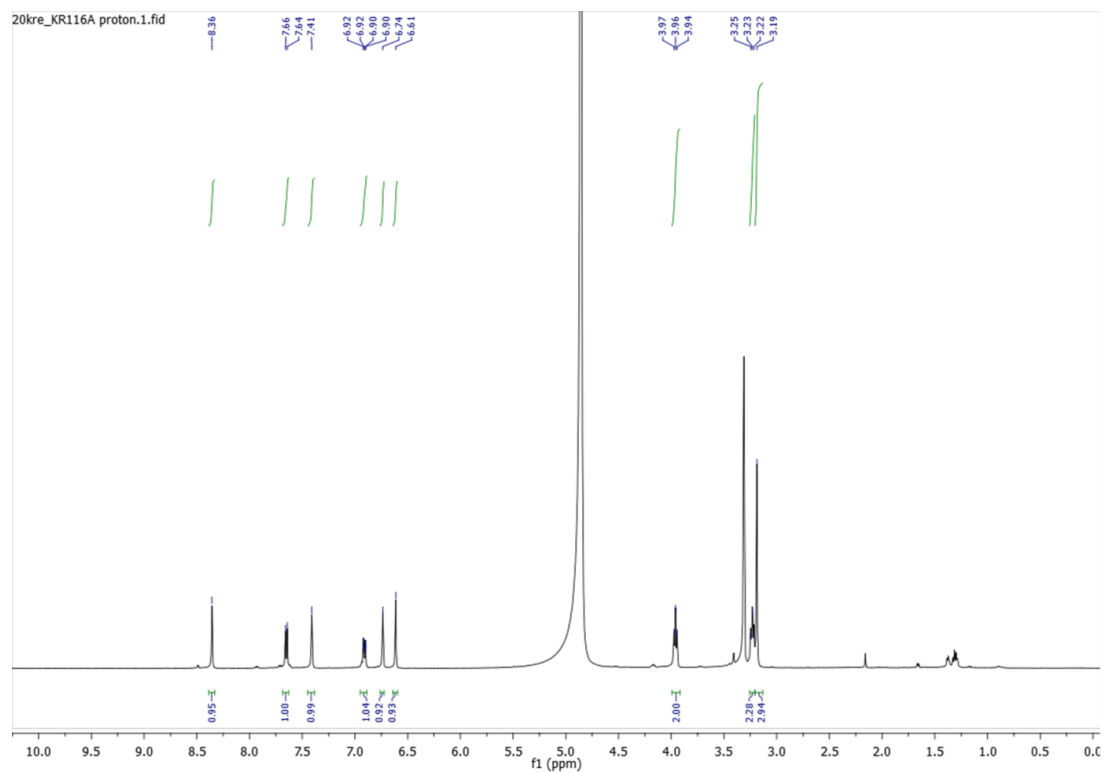


Fig. S8. ¹³C NMR spectrum of pyronin 2 in CD₃OD (126 MHz)

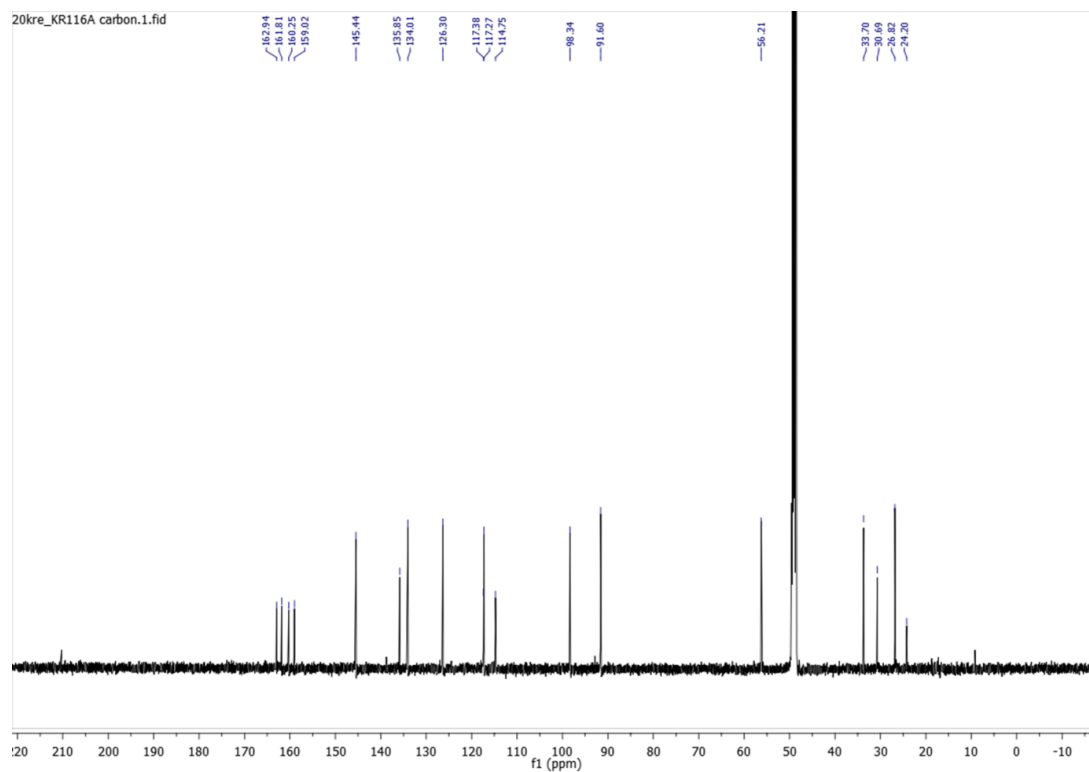


Fig. S9. ^{19}F NMR spectrum of pyronin 2 in CD_3OD (470 MHz)

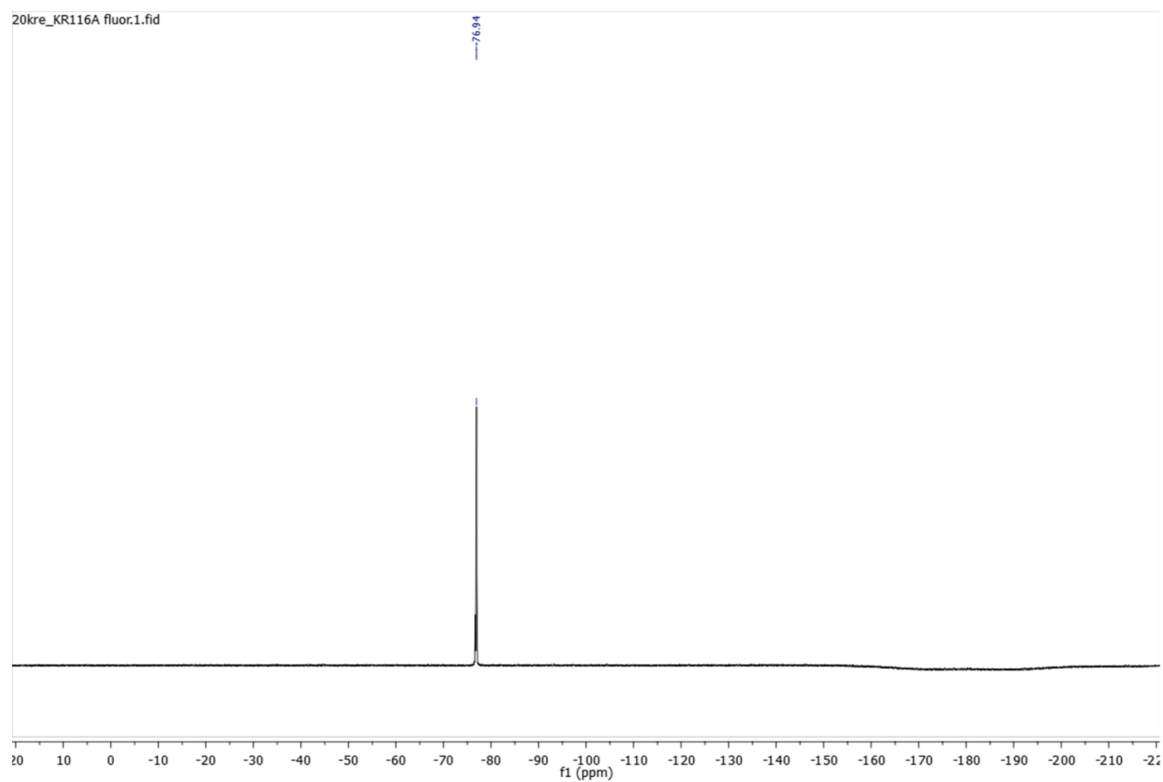


Fig. S10. LR mass spectrum (ESI, positive mode) of pyronin 2

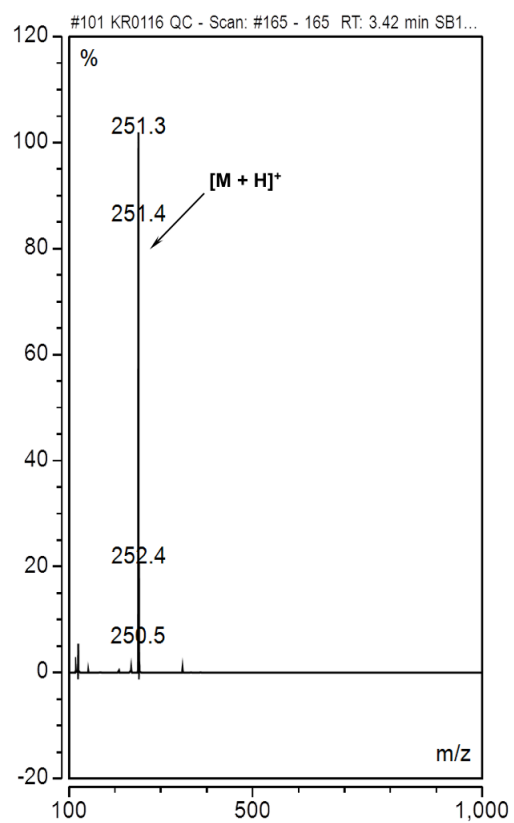


Fig. S11. RP-HPLC elution profile of pyronin 2 (system A, detection at 260 nm)

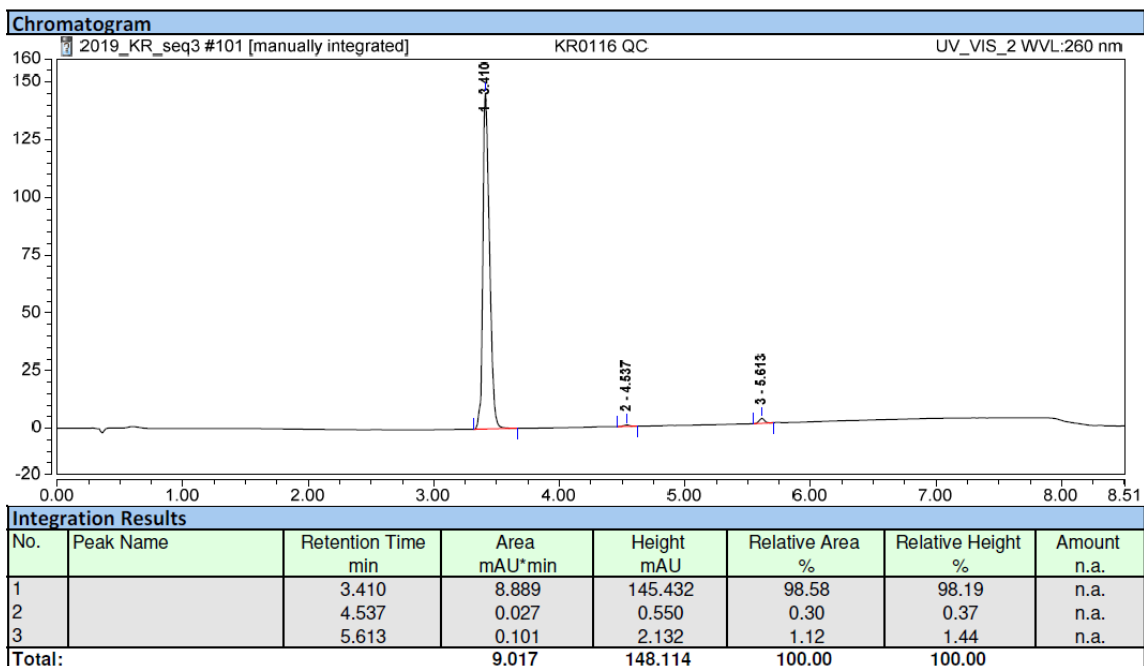


Fig. S12. RP-HPLC elution profile of pyronin 2 (system A, detection at 450 nm)

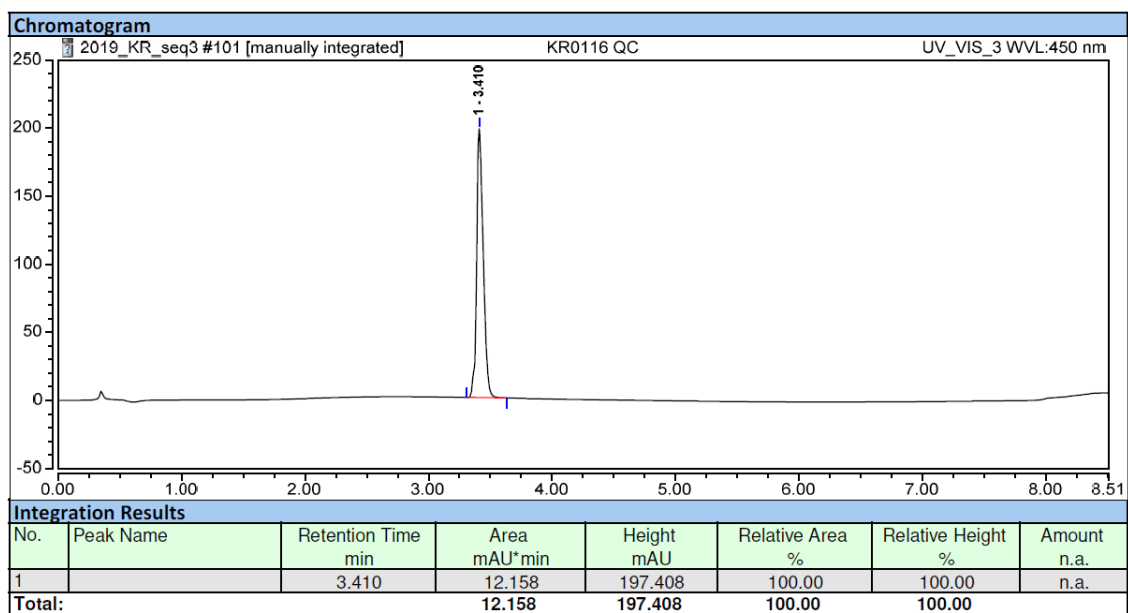


Fig. S13. RP-HPLC elution profile of pyronin 2 (system A, detection at 500 nm)

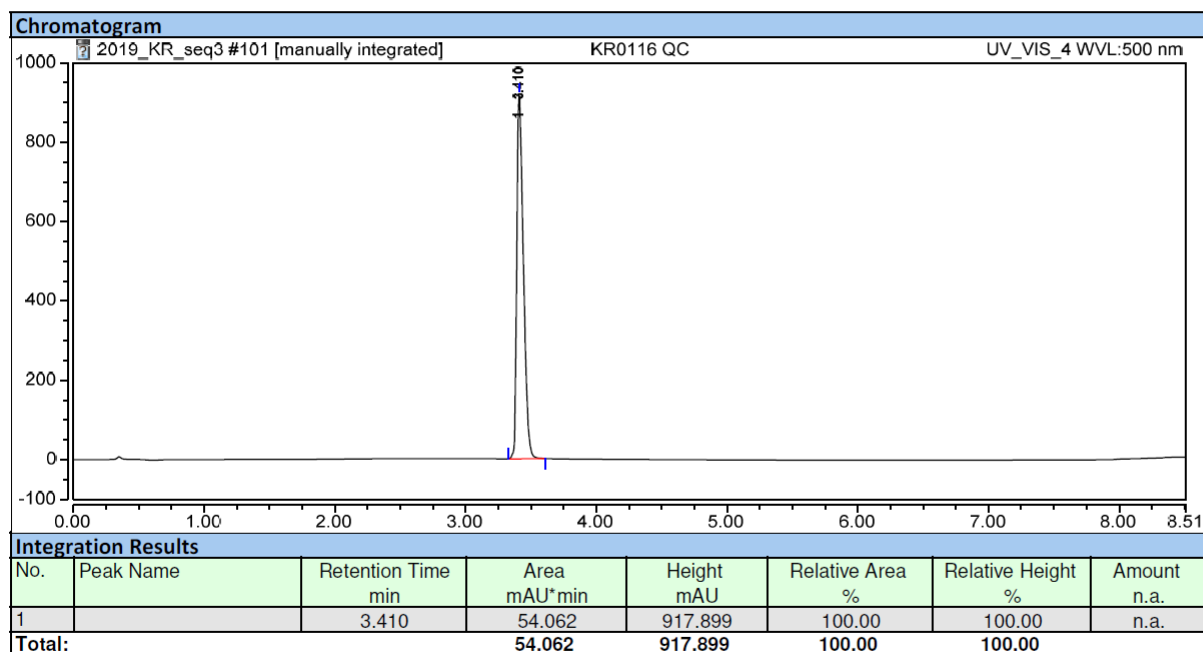


Fig. S14. TFA determination by IC - results for sample of pyronin 2

Concentration	1.0 mg/mL in DMSO	
Sample dilution factor	100	50
Raw data ppm	3.421	6.918
Content in wt %	34.21	34.59
Average content in wt %	34.40	

Fig. S15. IR (ATR) spectrum of compound 8

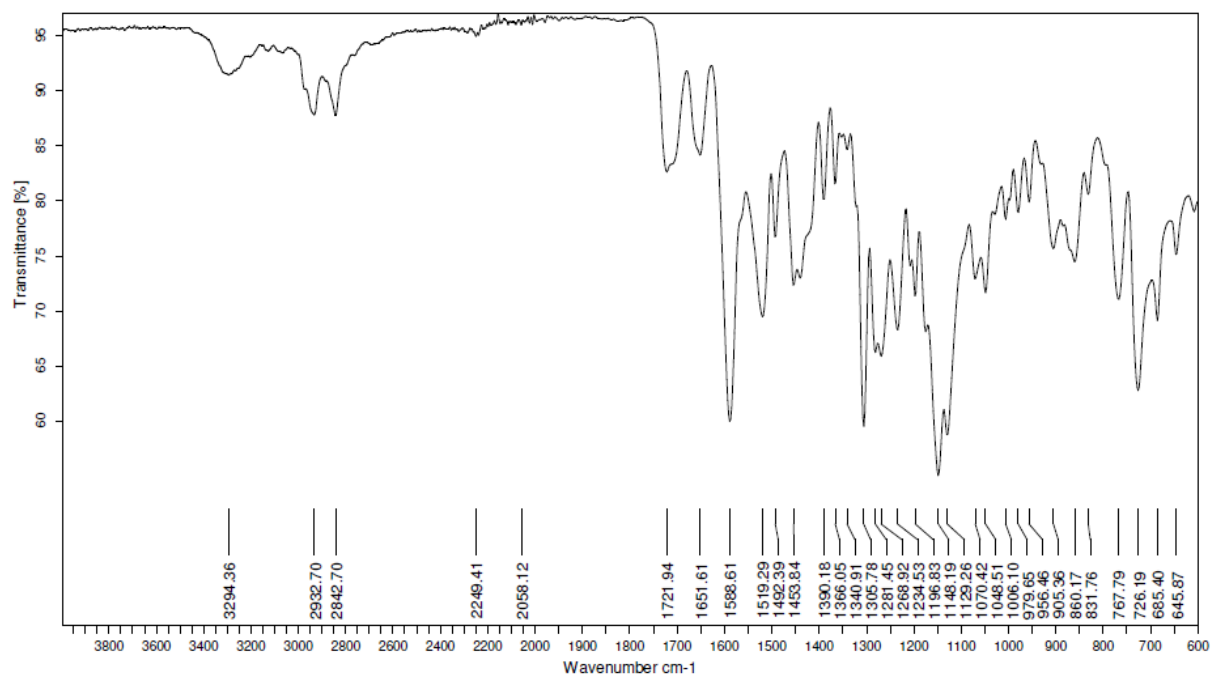


Fig. S16. ¹H NMR spectrum of compound 8 in CDCl₃ (500 MHz)

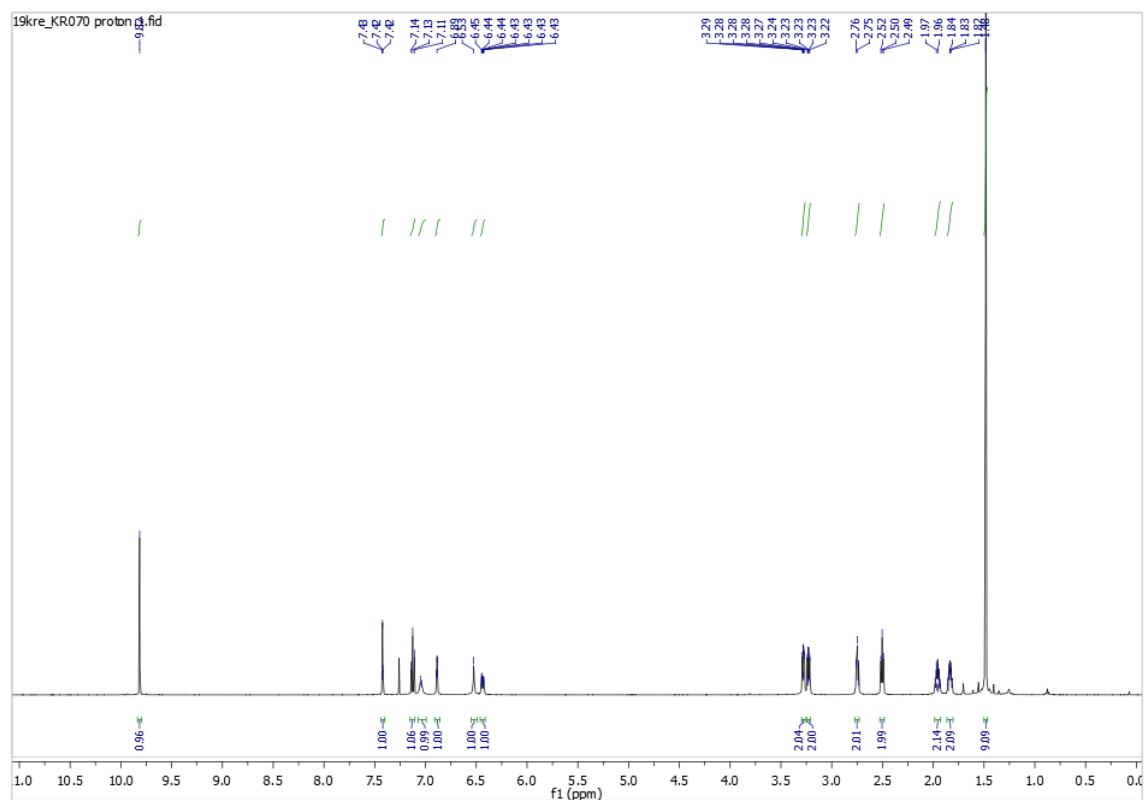


Fig. S17. ^{13}C NMR spectrum of compound 8 in CDCl_3 (126 MHz)

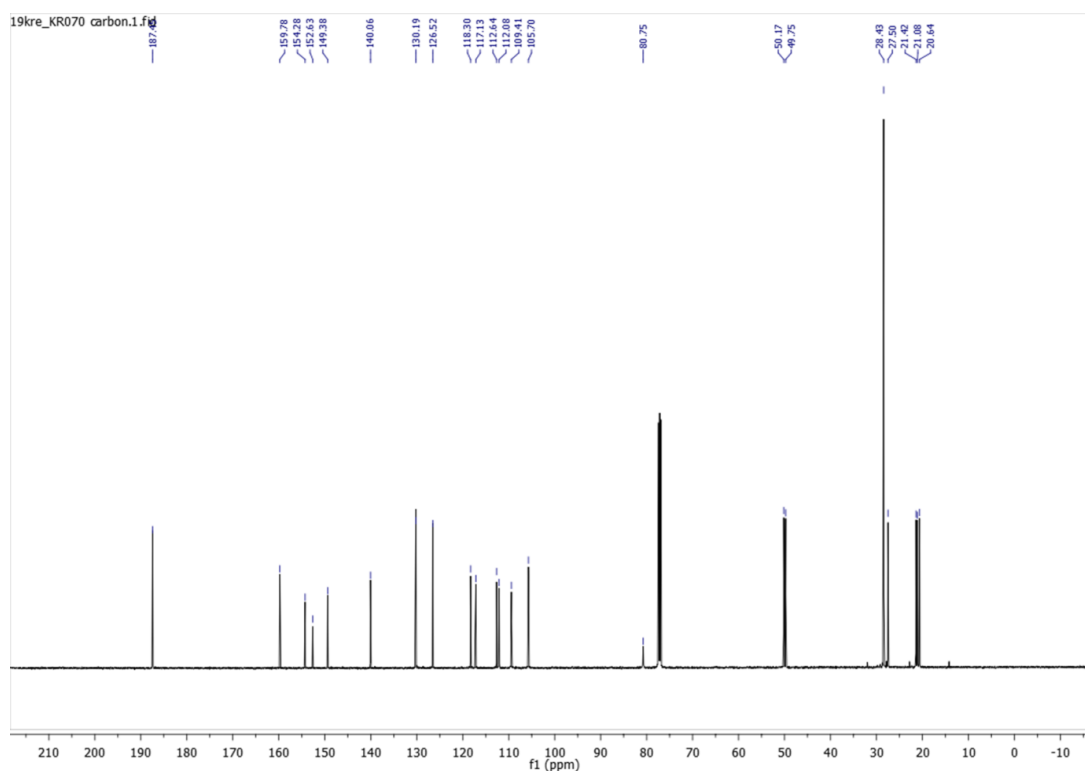


Fig. S18. LR mass spectrum (ESI, positive mode (left) and negative mode (right) of compound 8

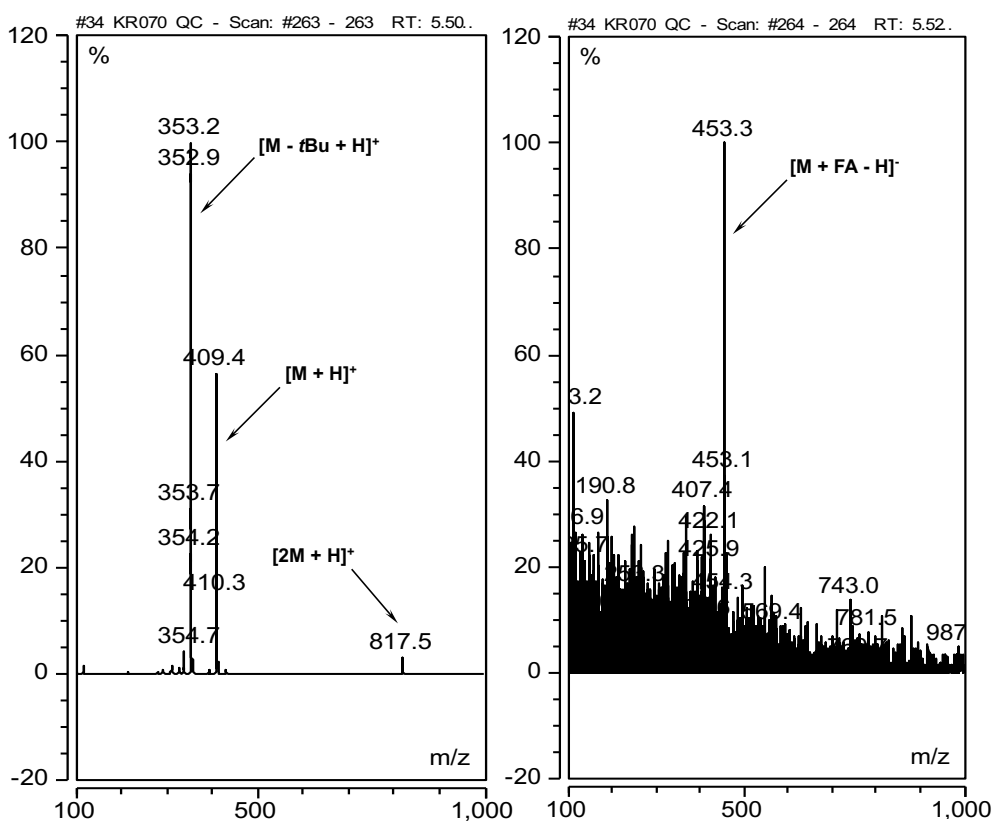


Fig. S19. RP-HPLC elution profile of compound 8 (system A, detection at 260 nm)

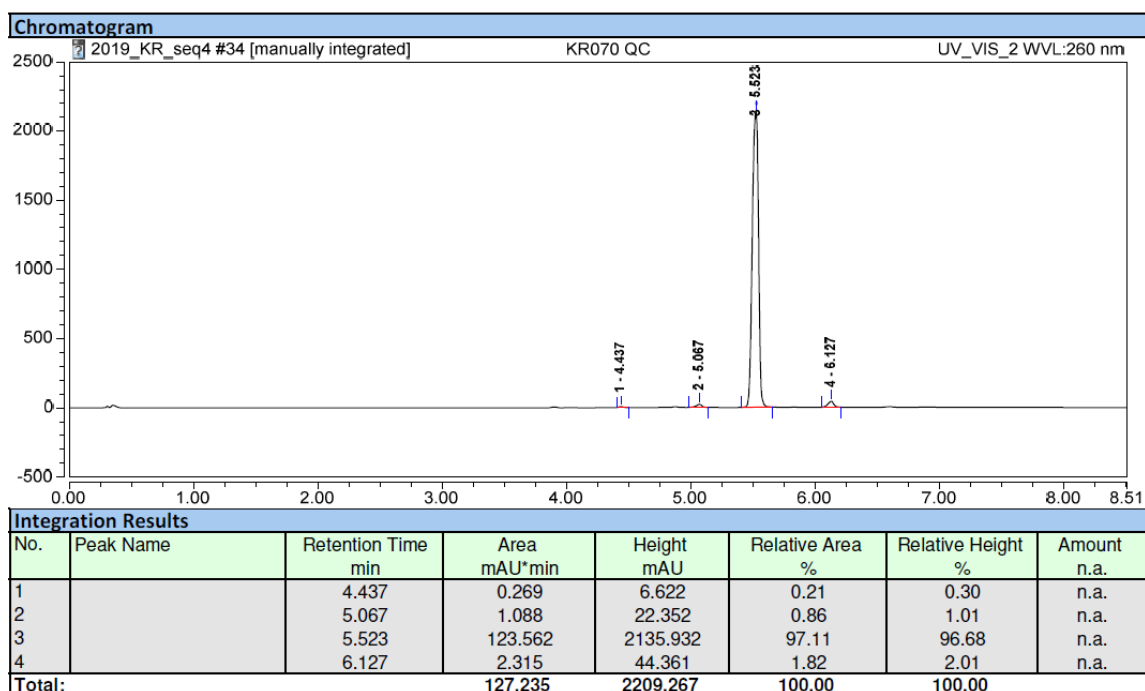


Fig. S20. IR (ATR) spectrum of pyronin 3

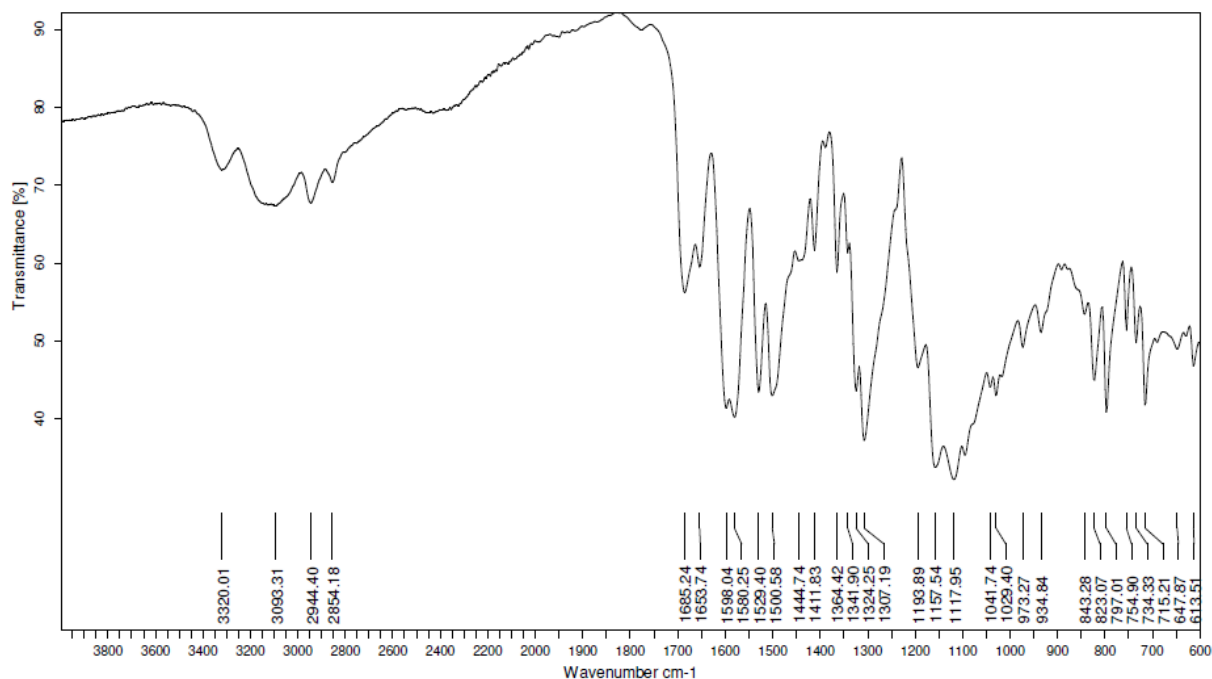


Fig. S21. ^1H NMR spectrum of pyronin 3 in CD_3OD (500 MHz)

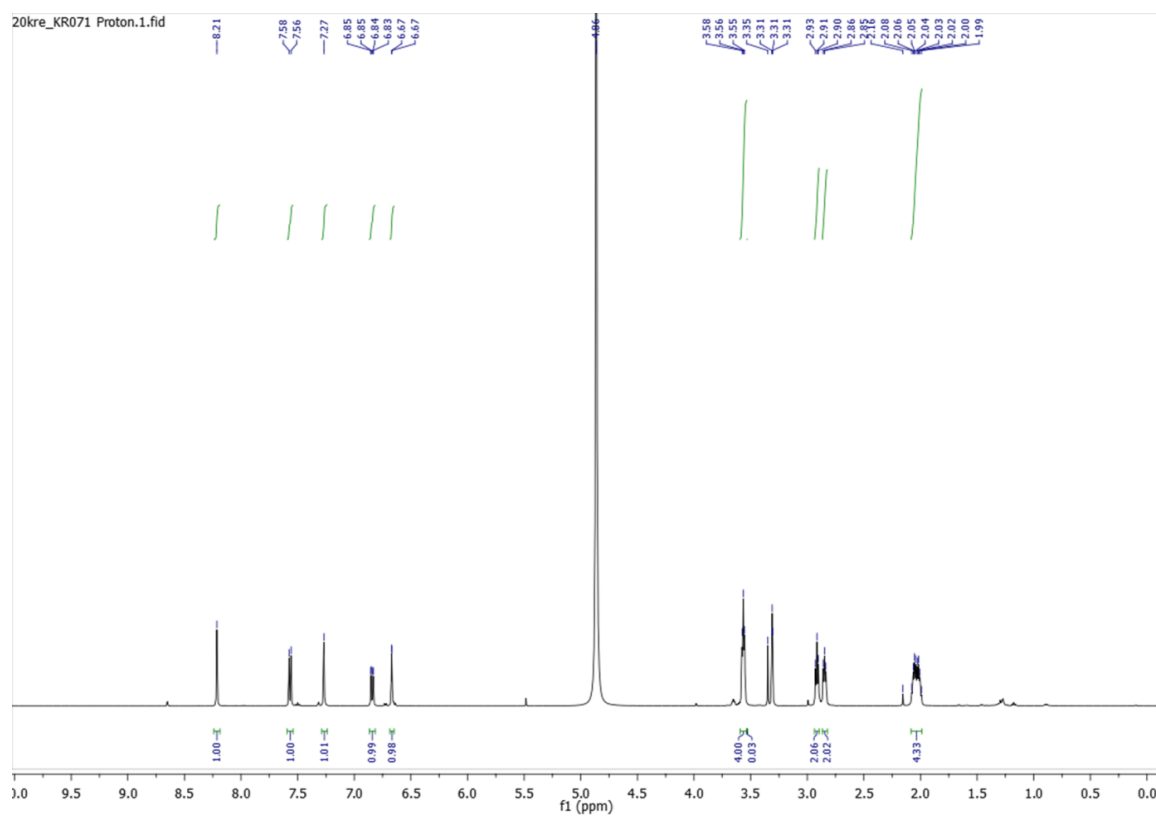


Fig. S22. ^{13}C NMR spectrum of pyronin 3 in CD_3OD (126 MHz)

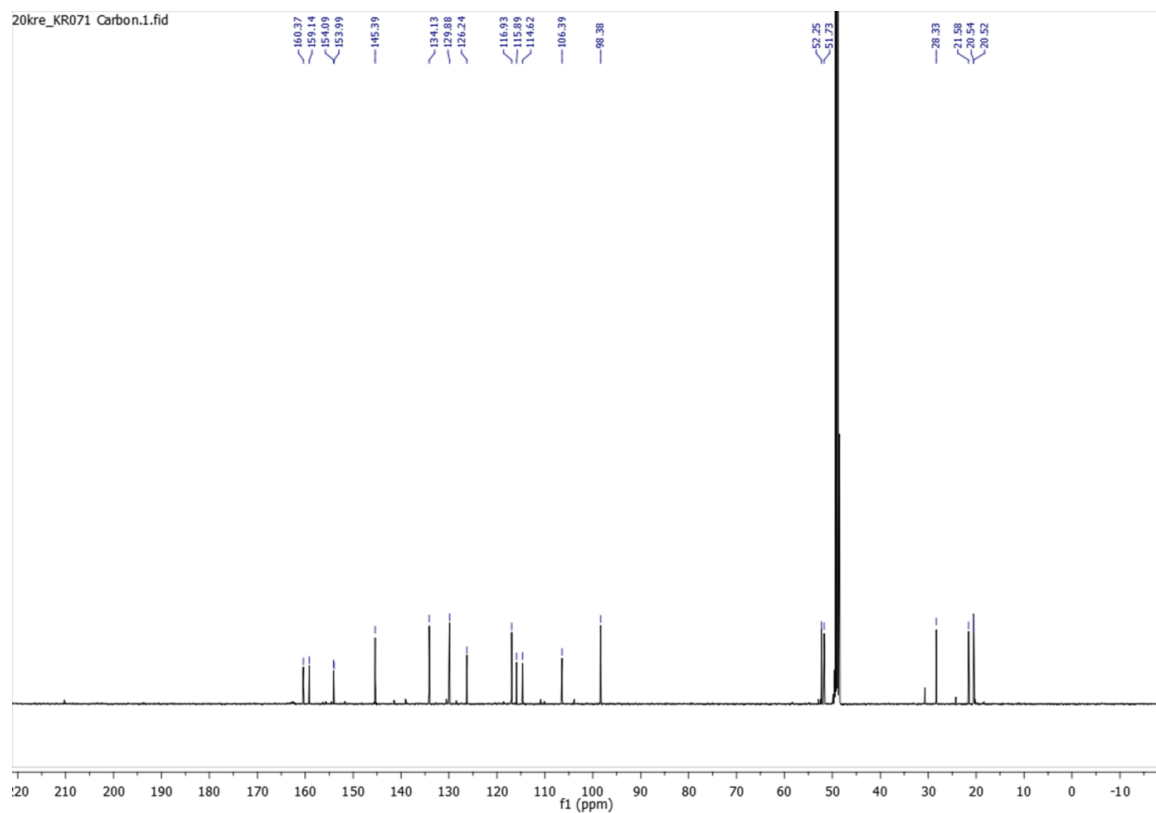


Fig. S23. ^{19}F NMR spectrum of pyronin 3 in CD_3OD (470 MHz)

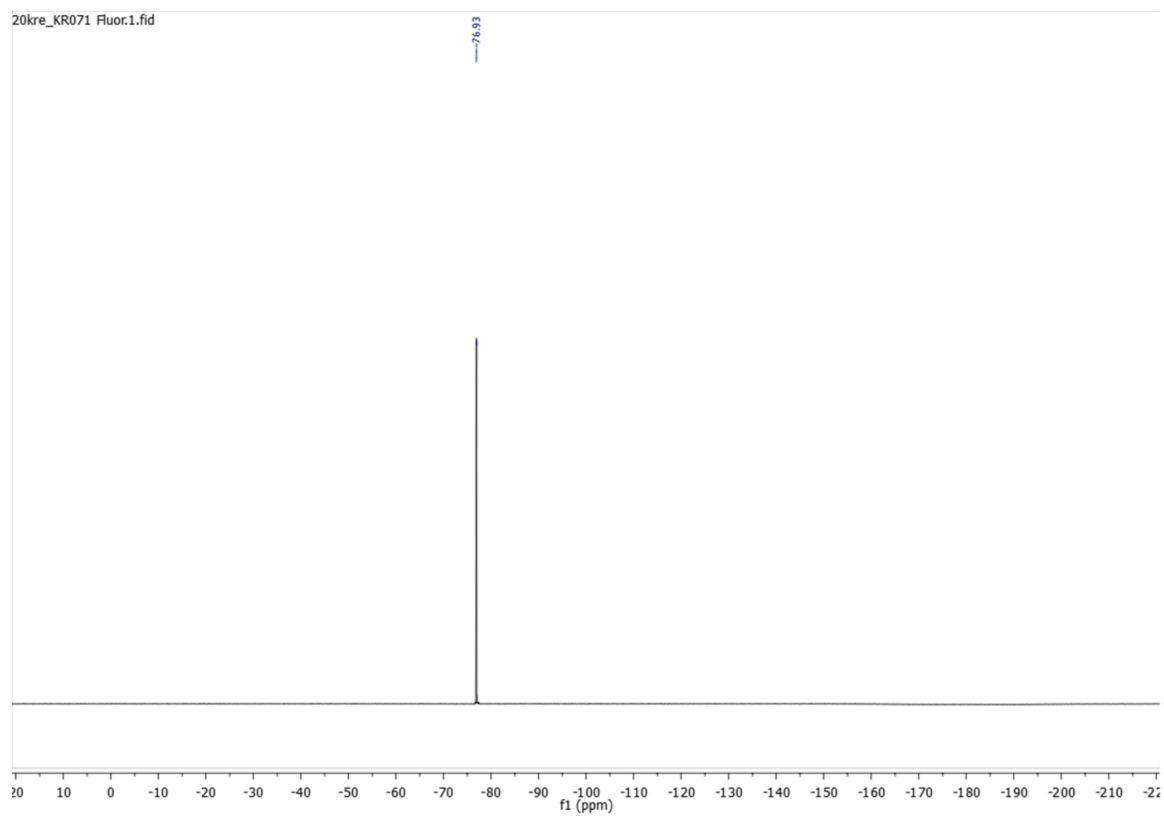


Fig. S24. LR mass spectrum (ESI, positive mode) of pyronin 3

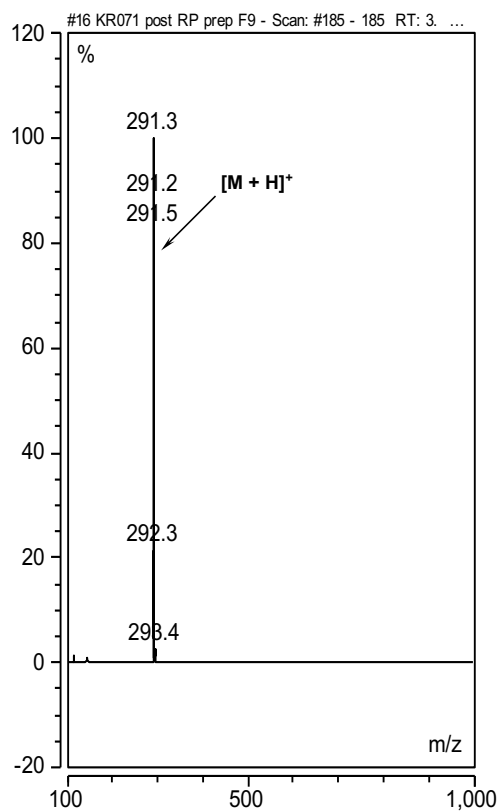


Fig. S25. RP-HPLC elution profile of pyronin 3 (system A, detection at 260 nm)

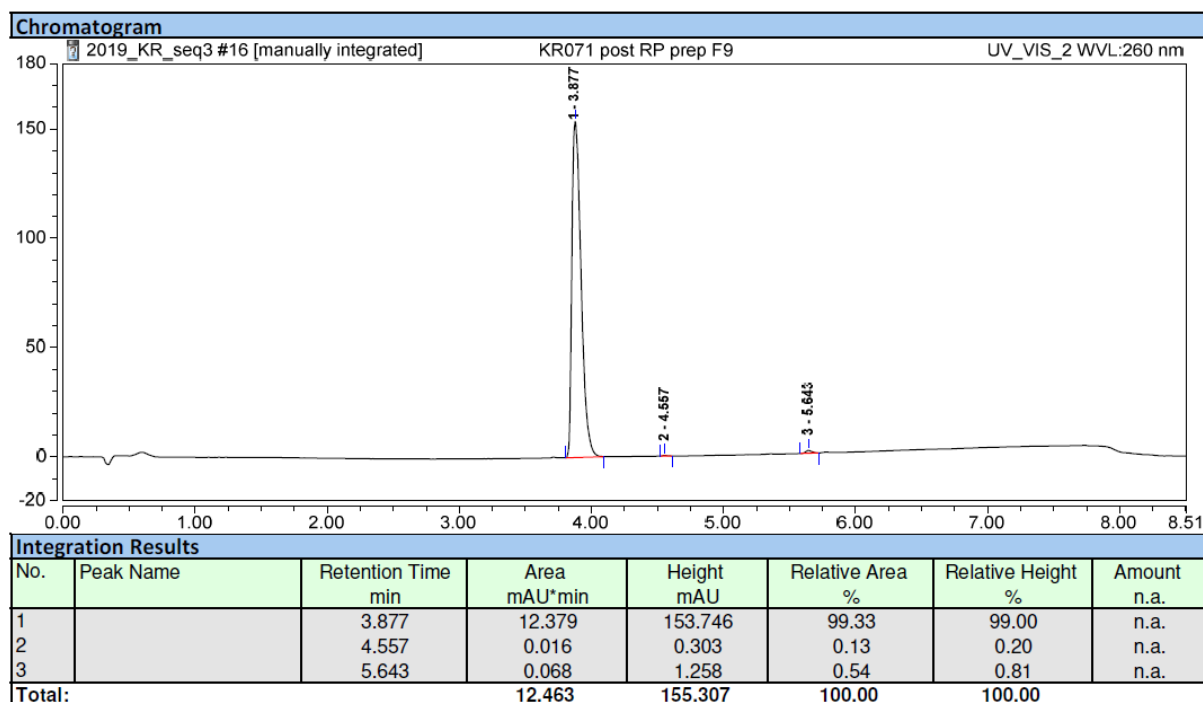


Fig. S26. RP-HPLC elution profile of pyronin 3 (system A, detection at 450 nm)

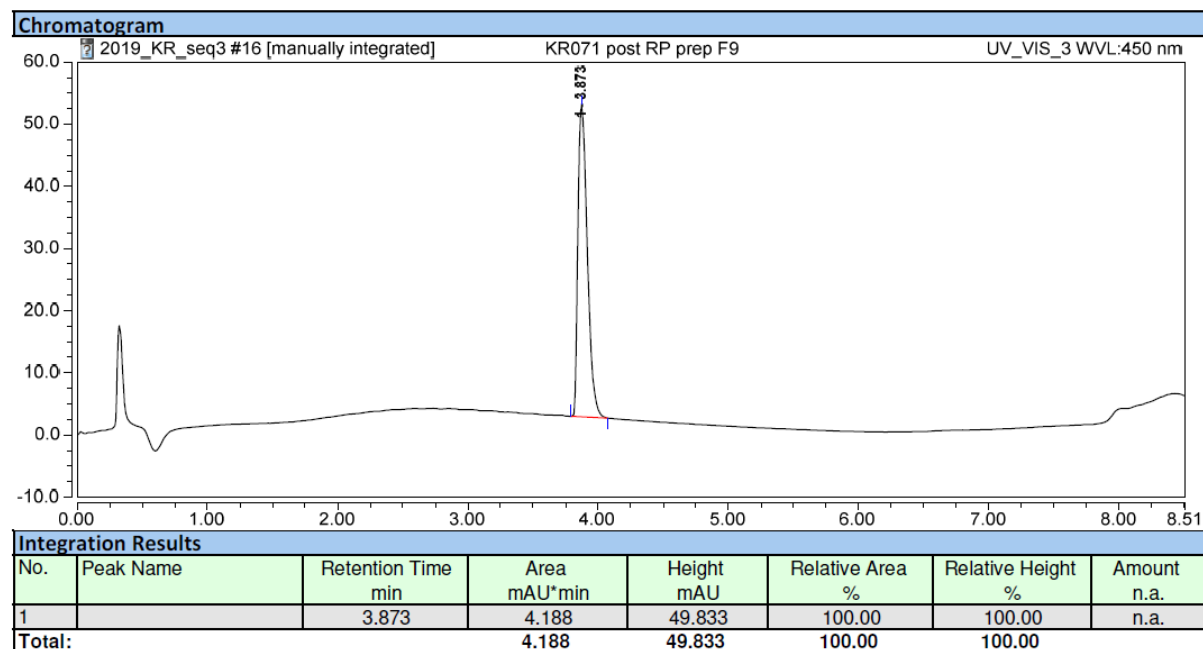


Fig. S27. RP-HPLC elution profile of pyronin 3 (system A, detection at 500 nm)

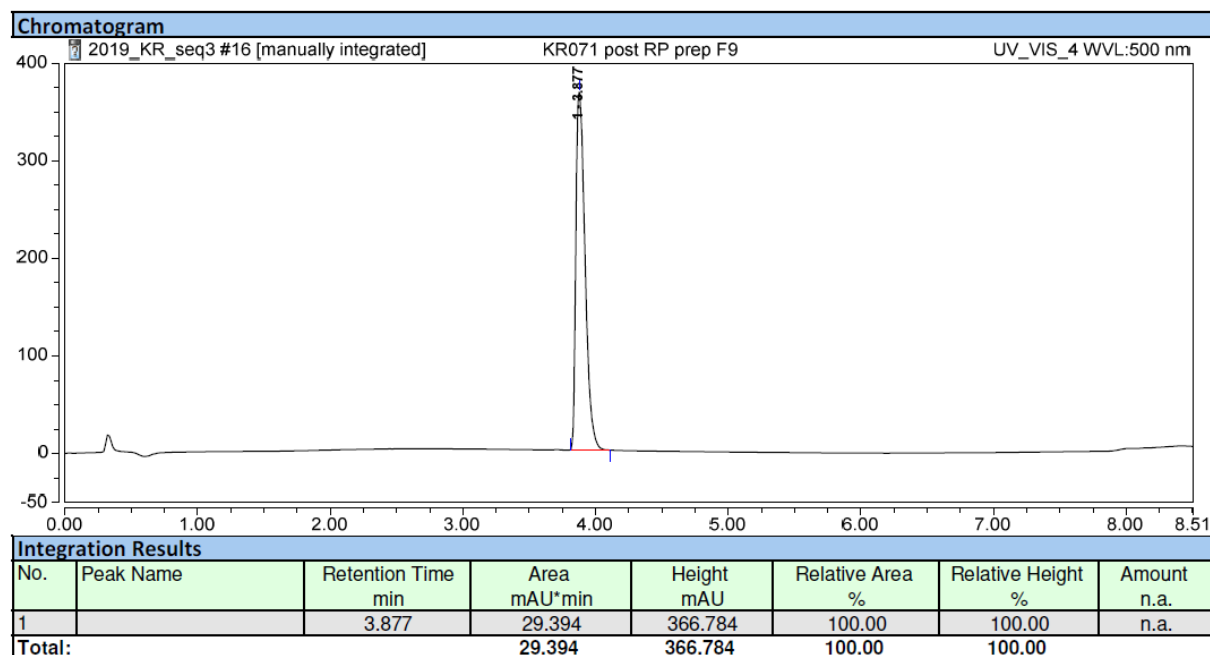
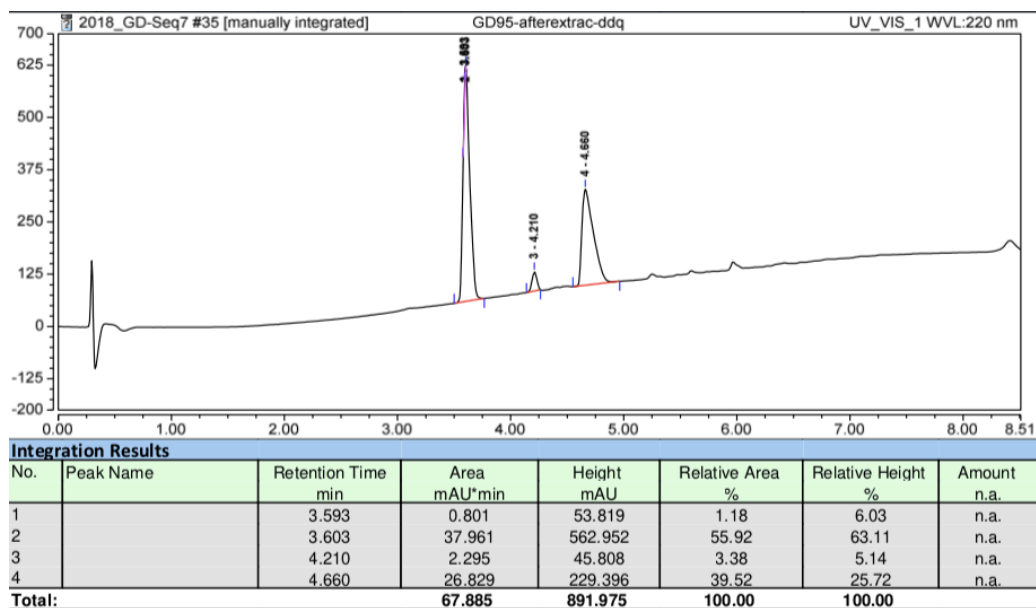


Fig. S28. TFA determination by IC - results for sample of pyronin 3

Concentration	1.0 mg/mL in DMSO	
	100	50
Sample dilution factor	100	50
Raw data ppm	3.352	6.906
Content in wt %	33.52	34.53
Average content in wt %	34.03	

Fig. S29. RP-HPLC elution profiles of impure *N,N*-diallyl Si-pyrone 14 (system A, detection at 220 nm)^a



^apeak at $t_R = 3.6$ min assigned to residual DDQ, peak at $t_R = 4.2$ min assigned to Si-xanthone and peak at $t_R = 4.6$ min assigned to Si-pyrone 14.

Fig. S30. LR mass spectrum (ESI, positive mode) of Si-xanthone (left) and *N,N*-diallyl Si-pyrone 14 (right)

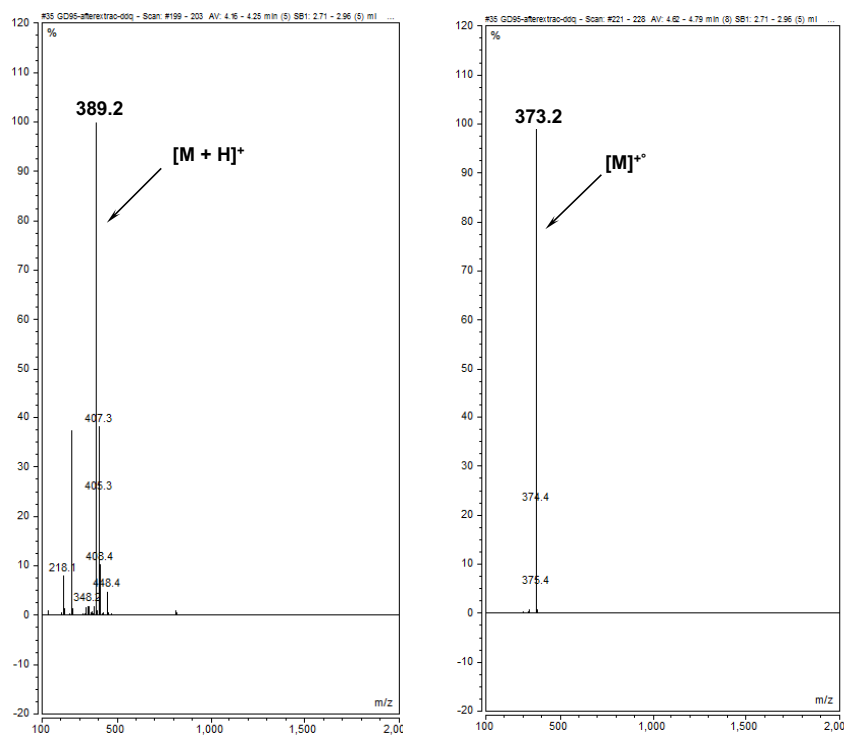


Fig. S31. IR (ATR) spectrum of Si-pyronin 4

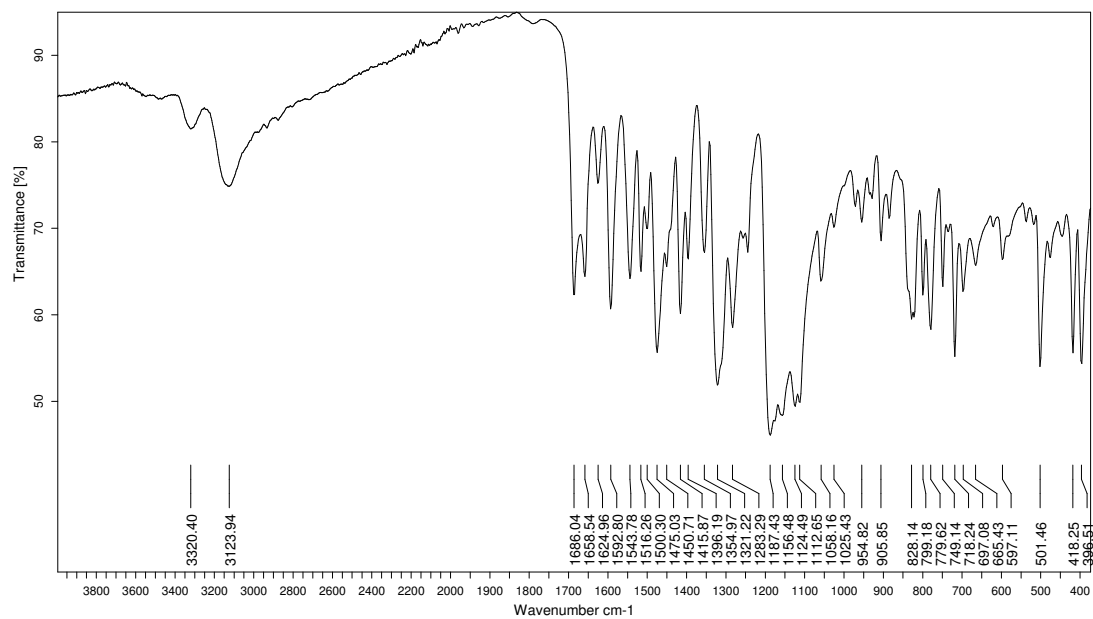


Fig. S32. ¹H NMR spectrum of Si-pyronin 4 in CD₃CN (500 MHz)

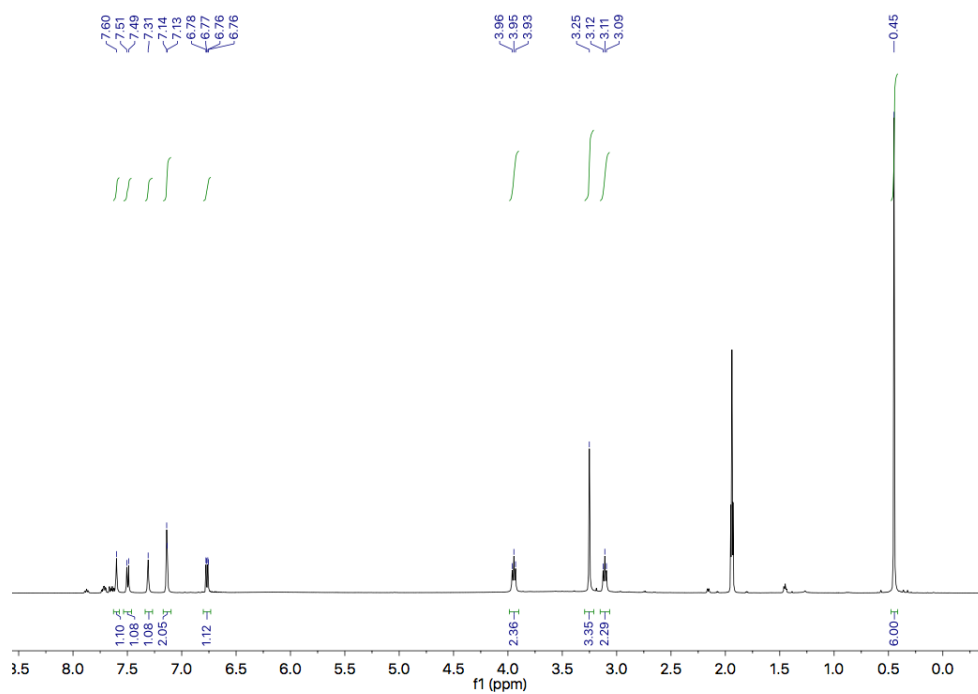


Fig. S33. ^{13}C NMR spectrum of Si-pyronin 4 in CD_3CN (126 MHz)

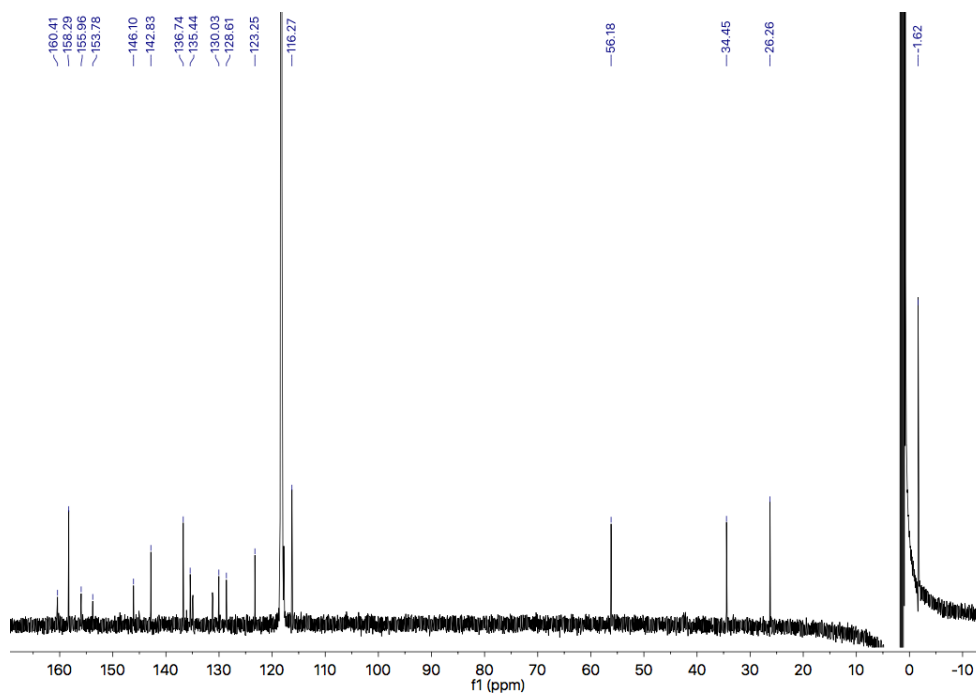


Fig. S34. ^{19}F NMR spectrum of Si-pyronin 4 in CD_3CN (470 MHz)

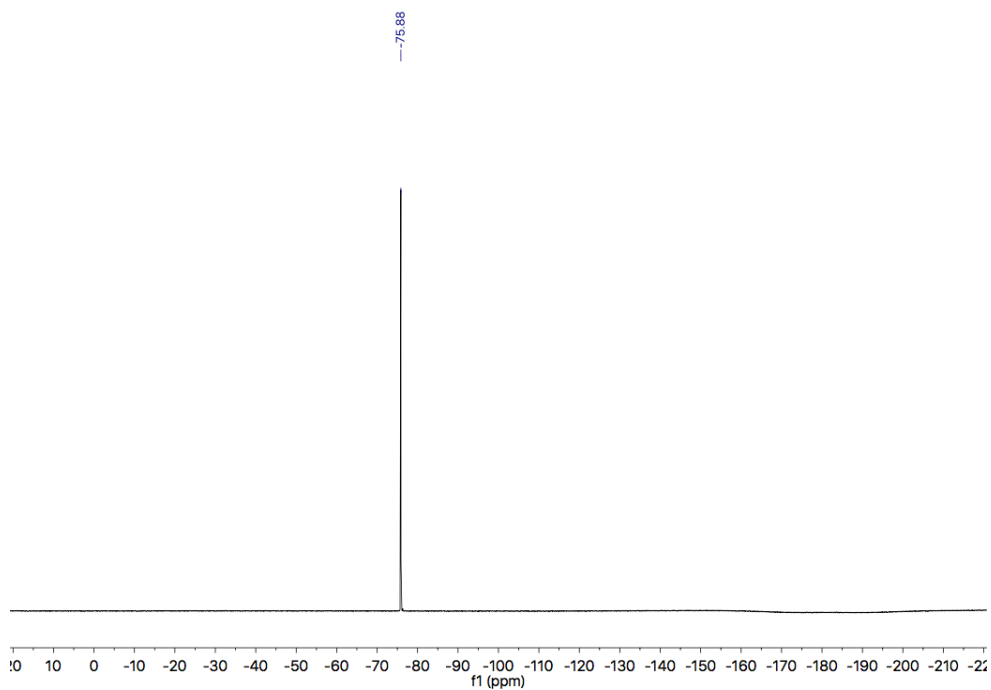
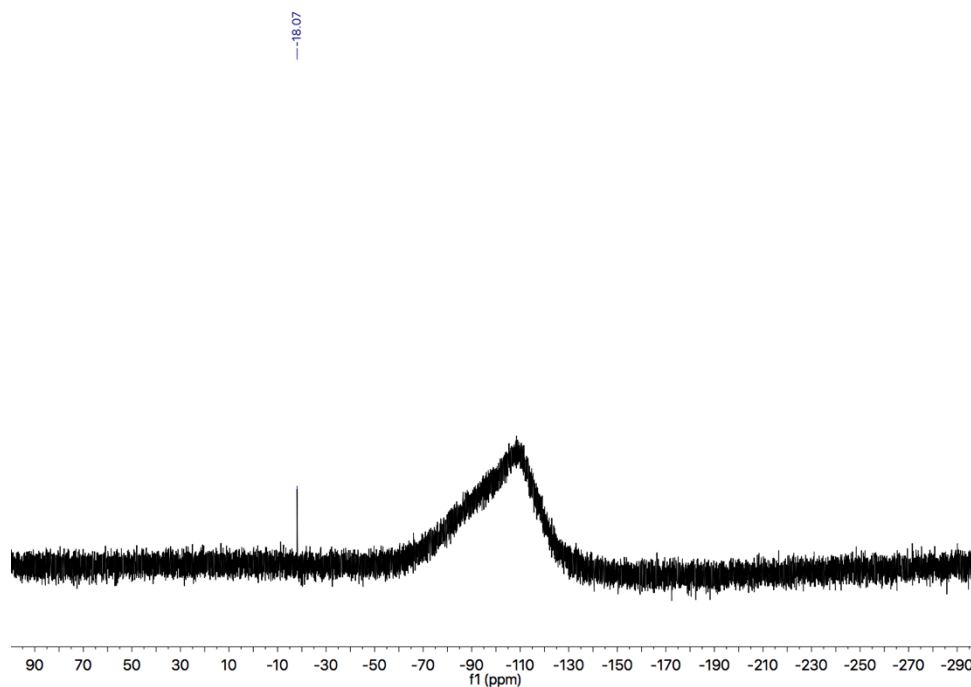


Fig. S35. ^{29}Si NMR spectrum of Si-pyronin 4 in CD_3CN (99 MHz)



Please note: broad background peak at -109 ppm from the NMR glass tube (silicates).

Fig. S36. LR mass spectrum (ESI, positive mode) of Si-pyronin 4

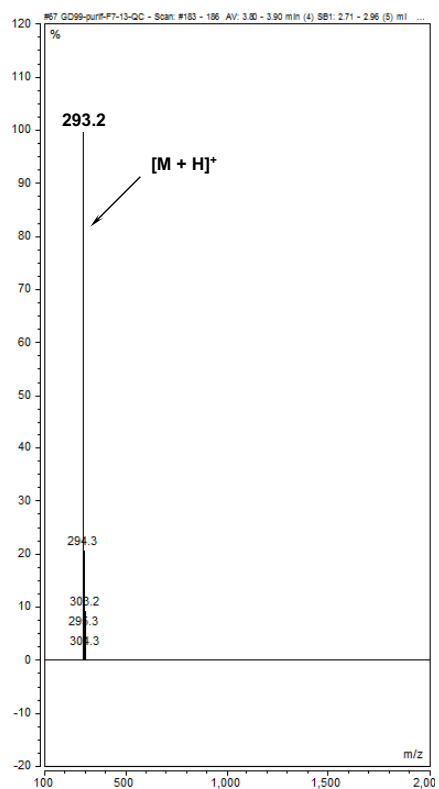


Fig. S37. RP-HPLC elution profile of Si-pyronin 4 (system A, detection at 300 nm)

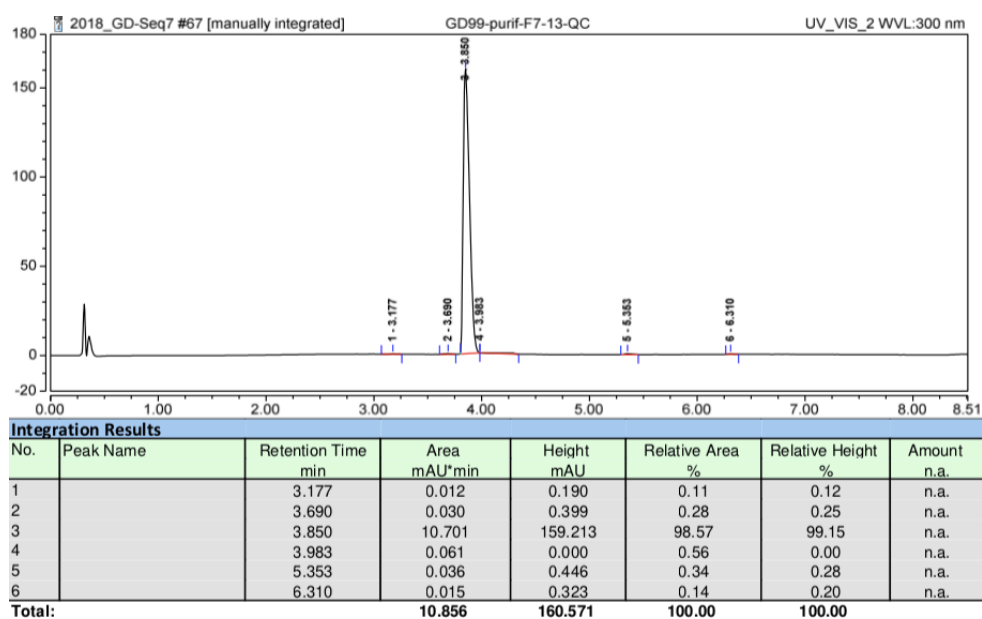
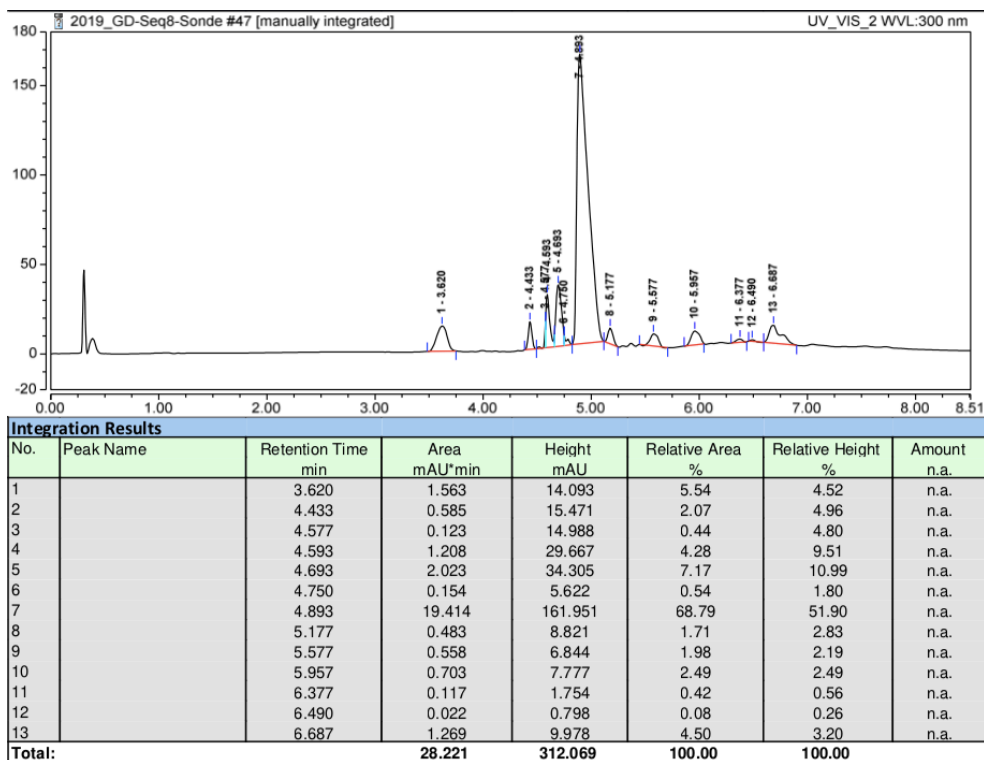


Fig. S38. TFA determination by IC - results for sample of Si-pyronin 4

Concentration	1.0 mg/mL in DMSO	
Sample dilution factor	100	50
Raw data ppm	3.641	7.577
Content in wt %	30.60	31.84
Average content in wt %	31.22	

Fig. S39. RP-HPLC elution profiles of impure *N,N*-diallyl Si-pyronin 15 (system A, detection at 300 nm)^a



^apeak at $t_R = 3.6$ min assigned to residual DDQ, peak at $t_R = 4.8$ min assigned to pyronin 15.

Fig. S40. LR mass spectrum (ESI, positive mode) of *N,N*-diallylamino Si-pyronin 15

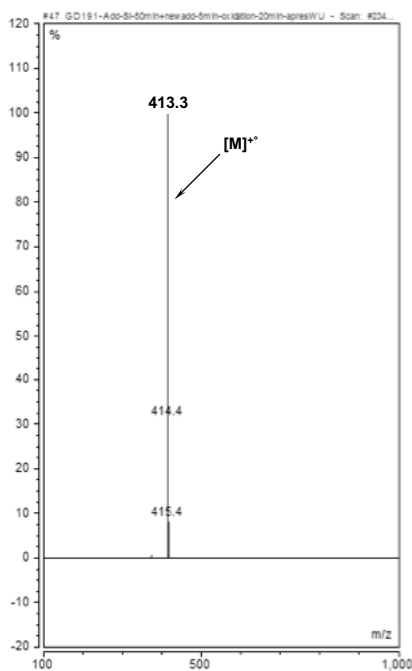


Fig. S41. RP-HPLC elution profiles of Si-pyronin 5 (system A, detection at 300 nm)

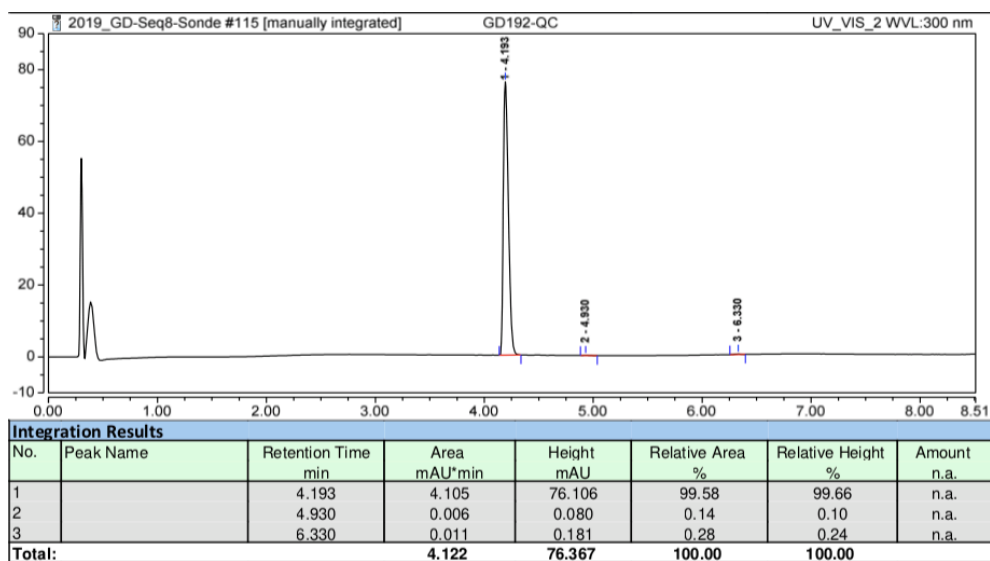


Fig. S42. LR mass spectrum (ESI, positive mode) of Si-pyronin 5

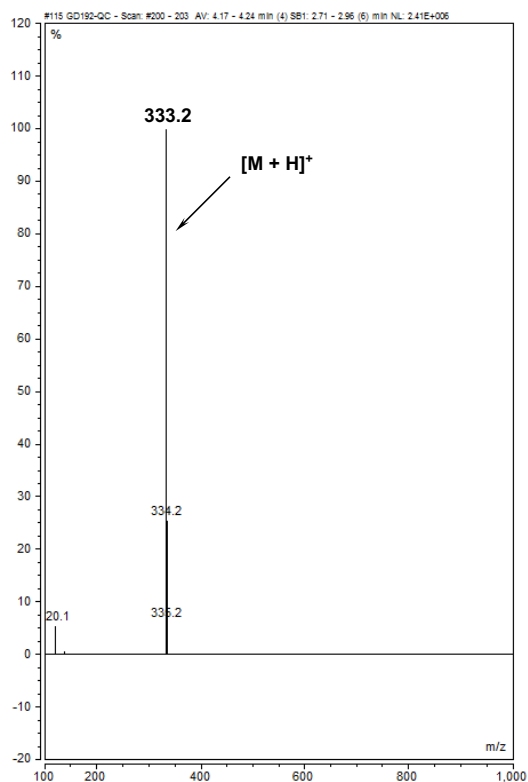


Fig. S43. TFA determination by IC - results for sample of Si-pyronin 5

Concentration	1.0 mg/mL in DMSO	
Sample dilution factor	100	50
Raw data ppm	3.418	6.957
Content in wt %	34.18	34.79
Average content in wt %	34.48	

Fig. S44. pH-Dependant maximum absorbance (626 nm or 620 nm) curve for Si-pyronins 4 (top) and 5 (bottom) (concentration: 5.0 μ M or 3.5 μ M in the corresponding buffer, 15 min of incubation before absorbance measurement) - fitted curves

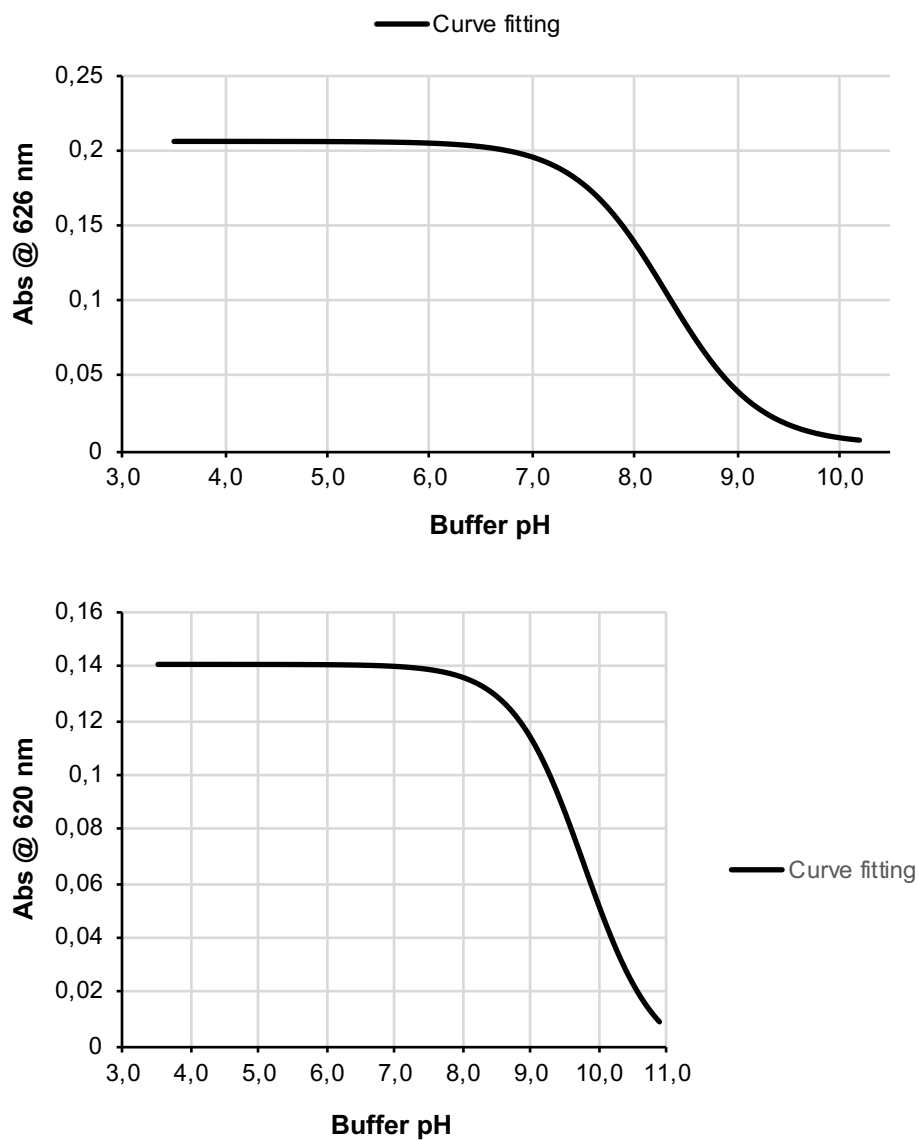
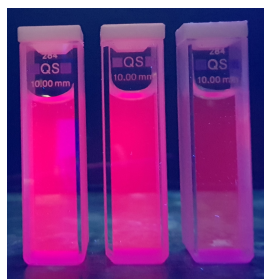


Fig. S45 Picture of solutions (concentration: 3.5 μM) of Si-pyronin dye 5 in various buffer (top), under illumination at 365 nm (bottom)



Left: NaOAc buffer (100 mM, pH 3.2)
Middle: PBS (100 mM, pH 7.4)
Right: NaHCO_3 - Na_2CO_3 buffer (66 mM, pH 10.2)