Fluorescent Cationic Fluorinated Oxazoliniums for Cysteine Bioconjugation *via* S_NAr Reaction†

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Supporting Information

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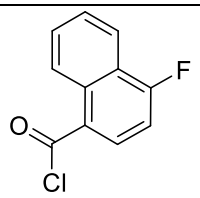
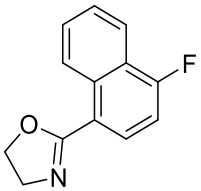
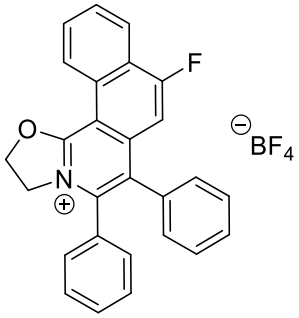
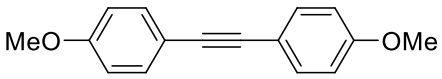
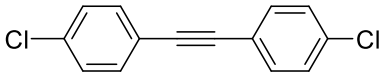
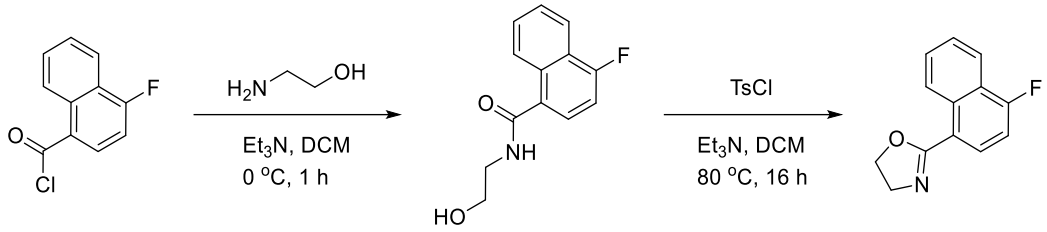
Literature References of Compounds

 4-Fluoro-1-naphthoyl chloride	(1) Z. Gao, J. Qian, H. Yang, X.-C. Hang, J. Zhang and G. Jiang, *Chem. Commun.* **2020**, *53*, 7265 – 7268. (2) Y. Hao and H. Huang, *Adv. Synth. Catal.* **2024**, *366*, 4066 – 4072.
 **S1a**	L.-Y. Tsang, A. Tantipanjaporn, K. K.-Y. Kung, H.-Y. Sit, W.-Y. O, A. K.-H. Chan, N. C.-H. Lai and M.-K. Wong, *Adv. Synth. Catal.* **2025**, *367*, e70023.
 **oxa-1**	L.-Y. Tsang, A. Tantipanjaporn, K. K.-Y. Kung, H.-Y. Sit, W.-Y. O, A. K.-H. Chan, N. C.-H. Lai and M.-K. Wong, *Adv. Synth. Catal.* **2025**, *367*, e70023.
 **S2b**	L. E. Sattler and G. Hilt, *Chem. Eur. J.* **2021**, *27*, 605 – 608.
 **S2c**	L. E. Sattler and G. Hilt, *Chem. Eur. J.* **2021**, *27*, 605 – 608.
$[Cp^*RhCl_2]_2$	J. W. Kang, K. Moseley and P. M. Maitlis, *J. Am. Chem. Soc.*, **1969**, *91*, 5970 – 5977.

General Procedures

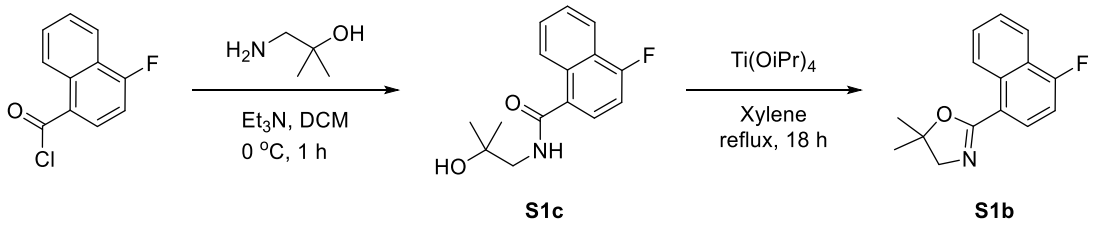
All reagents were commercially available and used without further purification. Milli-Q® water used as reaction solvent in peptide and protein modification and LC–MS was deionized using a Milli-Q® Gradient A10 system (Millipore, Billerica, USA). Flash column chromatography was performed using silica gel 60 (230-400 mesh ASTM) with *n*-hexane/ethyl acetate, dichloromethane/ethyl acetate or dichloromethane/acetone as eluent. All synthetic procedures requiring heating were performed in an oil bath, while heating of reaction mixtures for peptide and protein modifications were performed in Thermo Fisher Scientific Digital Block Heater and a water bath respectively. Circular dichroism measurements were conducted using JASCO J-1500 Circular Dichroism Spectrometer. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker Advance-III 400 MHz and 600 MHz FT-NMR. All chemical shifts are quoted on the scale in ppm using TMS or residual solvent as the internal standard. Coupling constants (*J*) are reported in Hertz (Hz) with the following splitting abbreviations: s = singlet, br s = broad singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublets of doublets, dt = doublet of triplets, t = triplet, td = triplet of doublets and m = multiplet. All the mass spectra were obtained on an ESI source of Agilent 6540 Ultra High Definition (UHD) Accurate-Mass Q-TOF LC/MS systems in positive and negative ion mode.

Synthesis of 2-Aryloxazolines S1a-b



S1a

This synthetic procedure follows our previously reported procedure.[1] 4-Fluoro-1-naphthoyl chloride (2.08 g, 10 mmol, 1 equiv.) in 10 mL of dry DCM was added dropwise into a 100 mL round bottom flask equipped with ethanolamine (0.67 mL, 11 mmol, 1.1 equiv.) in 40 mL of dry DCM and 10 mL of Et_3N at 0 °C. The reaction mixture was then stirred for 1 h at 0 °C. After warming the reaction mixture to ambient temperature, 4-toluenesulfonyl chloride (TsCl, 2.10 g, 11 mmol, 1.1 equiv.) and 5 mL of Et_3N were added, and the resulting mixture was heated at 80 °C for 16 h. The reaction was monitored by TLC analysis until all starting materials were consumed. After the reaction, the solvent was removed under pressure, and the residue was purified by flash column chromatography on silica gel using *n*-hexane/EtOAc as eluent to give **S1a**.

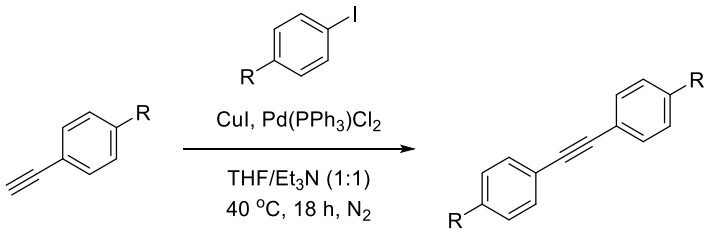


S1c **S1b**

4-Fluoro-1-naphthoyl chloride (1.10 g, 5.26 mmol, 1 equiv.) in 10 mL of dry DCM was added dropwise into a 100 mL round bottom flask equipped with 1-amino-2-methylpropan-2-ol (0.54 mL, 5.79 mmol, 1.1 equiv.) in 30 mL of dry DCM and 2.5 mL of Et_3N at 0 °C. After the reaction, the solvent was removed under pressure and the residue was purified by flash column chromatography on silica gel using *n*-hexane/

EtOAc as eluent to give hydroxy amide **S1c**. A Dean-Stark trap was set up with **S1c** (0.83 g, 3.17 mmol, 1 equiv.) and tetraisopropyl orthotinate (35% $Ti(OiPr)_4$ in tetraethyl orthotinate,11.9 uL, 0.317 mmol, 10 mol%) dissolved in 25 mL of xylene. The reaction mixture was stirred for 18 h under reflux. After the mixture was cooled down to room temperature, saturated $NaHCO_3$ solution was added, and solvent extraction was done using EtOAc. The residue was then purified by flash column chromatography on silica gel using *n*-hexane/EtOAc (25:1) as eluent to give **S1b**.

Synthesis of Diphenylacetylenes S2b-c



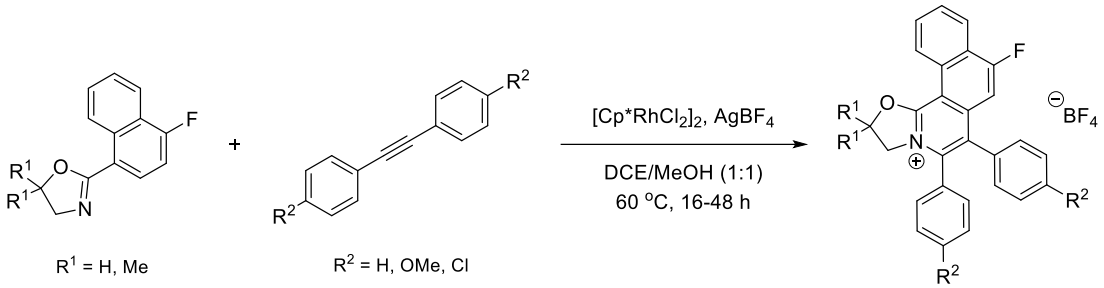
S2b: R = OMe
S2c: R = Cl

This synthetic procedure follows a previously reported procedure with slight modifications.[2] 4-Ethynylanisole (0.26 g, 2 mmol, 1.0 equiv.), 4-iodoanisole (0.52 g, 2.2 mmol, 1.1 equiv.), copper iodide (CuI, 34.3 mg, 0.18 mmol, 9 mol%) and bis(triphenylphosphine)palladium chloride ($Pd(PPh_3)_2Cl_2$, 42.1 mg, 0.06 mmol, 3 mol%) were added into a degassed Schlenk flask and filled with N_2 gas. A total of 10 mL of dry THF and Et_3N (1:1) was added into the flask. The reaction mixture was then stirred for 18 h at 40 °C. Solvent extraction was done using H_2O and DCM, and the combined organic layer was washed with brine, dried with anhydrous $MgSO_4$ and concentrated under vacuum. The residue was then purified by flash column chromatography on silica gel using *n*-hexane/EtOAc (20:1) as eluent to give **S2b**.

1-Ethynyl-4-chlorobenzene (1.37 g, 10 mmol, 1.0 equiv.) and 4-chloroiodobenzene

(2.62 g, 11 mmol, 1.1 equiv.) were used instead of 4-ethynylanisole and 4-iodoanisole to give **S2c**.

Synthesis of Oxazoliniums oxa-1-4



R^1 = H, Me
S1a-b

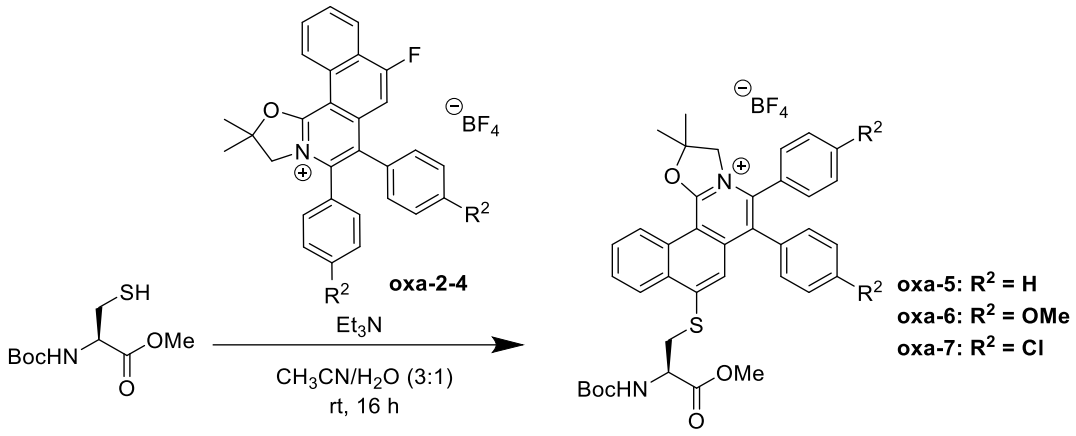
R^2 = H, OMe, Cl
S2a-c

oxa-1: R^1 = H R^2 = H
oxa-2: R^1 = Me R^2 = H
oxa-3: R^1 = Me R^2 = OMe
oxa-4: R^1 = Me R^2 = Cl

This synthetic procedure follows our previously reported procedure with minimal modifications.[1] A mixture of 2-aryloxazolines **S1a** or **S1b** (0.5 mmol, 1 equiv.), diphenylacetylenes **S2a-c** (0.75 mmol, 1.5 equiv.), (pentamethylcyclopentadienyl)rhodium(III) dichloride dimer ($[Cp^*RhCl_2]_2$, 15.5 mg, 0.025 mmol, 5 mol%), silver tetrafluoroborate ($AgBF_4$, 0.19 g, 1 mmol, 2 equiv.) in DCE/MeOH (10 mL, 1:1) was heated at 60 °C for 16-48 h. The reaction was monitored by TLC analysis until all starting materials were consumed. The reaction mixture was purified by column chromatography on silica gel using DCM/EtOAc (50:1) and preparative TLC using DCM/Acetone (20:1) as eluent to give the desired products **oxa-1-4**.

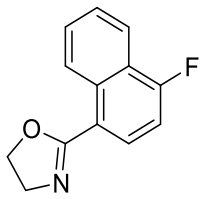
Note: Diphenylacetylene **S2a** (1,2-diphenylethyne, CAS: 501-65-5) was purchased from Leyan, China.

Synthesis of Model Compounds oxa-5-7



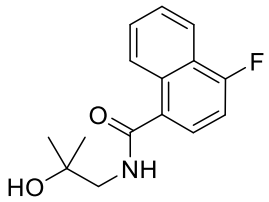
A mixture of *N*-Boc-L-cysteine methyl ester (35.3 mg, 0.15 mmol, 1.5 equiv.), **oxa-2-4** (0.1 mmol, 1 equiv.), Et_3N (27.9 μL, 0.2 mmol, 2 equiv.) in CH_3CN/H_2O (1 mL, 3:1) was stirred for 16 h at room temperature. The reaction was monitored by TLC analysis until all starting materials were consumed. The reaction mixture was purified by column chromatography on silica gel using DCM/Acetone (50:1) as eluent to give the desired products **oxa-5-7**.

Characterization Data of Compounds



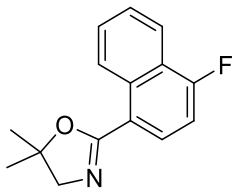
S1a

White solid, 0.839 g, 39% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.21 (d, *J* = 8.9 Hz, 1H), 8.21 – 8.11 (m, 1H), 8.07 (dd, *J* = 8.2, 5.7 Hz, 1H), 7.66 (ddd, *J* = 8.6, 6.8, 1.5 Hz, 1H), 7.59 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.15 (dd, *J* = 9.9, 8.2 Hz, 1H), 4.50 – 4.42 (m, 2H), 4.22 (t, *J* = 9.2 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.87, 160.78 (d, *J* = 257.5 Hz), 133.00 (d, *J* = 5.1 Hz), 129.66 (d, *J* = 9.4 Hz), 128.42 (2C), 126.63 (dd, *J* = 20.7, 2.3 Hz), 124.00 (d, *J* = 15.6 Hz), 120.90 (d, *J* = 6.1 Hz), 120.84, 108.66 (d, *J* = 20.8 Hz), 66.62, 55.87. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -116.87. **HRMS** (ESI) calcd. for $C_{13}H_{11}FNO^+$ $[M + H]^+$ 216.0825, found 216.0823.



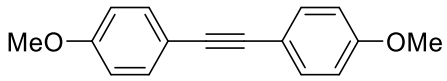
S1c

White solid, 1.17 g, 85% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (dt, *J* = 7.6, 2.0 Hz, 1H), 8.17 – 8.08 (m, 1H), 7.67 – 7.51 (m, 3H), 7.08 (dd, *J* = 10.0, 7.9 Hz, 1H), 6.50 (br s, 1H, NH), 3.53 (d, *J* = 6.1 Hz, 2H), 2.36 (br s, 1H, OH), 1.33 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.85, 159.95 (d, *J* = 256.0 Hz), 131.89 (d, *J* = 5.1 Hz), 130.45 (d, *J* = 4.5 Hz), 128.16, 126.82 (d, *J* = 1.9 Hz), 125.41 (d, *J* = 2.6 Hz), 125.26 (d, *J* = 9.2 Hz), 123.88 (d, *J* = 16.3 Hz), 120.79 (d, *J* = 5.8 Hz), 108.30 (d, *J* = 20.8 Hz), 71.06, 50.68, 27.44 (2C). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -118.24. **HRMS** (ESI) calcd. for $C_{15}H_{17}FNO_2^+$ $[M + H]^+$ 262.1243, found 262.1245.



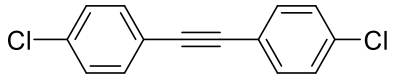
S1b

White solid, 0.756 g, 98% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.21 (d, *J* = 8.7 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.04 (dd, *J* = 8.2, 5.7 Hz, 1H), 7.65 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1H), 7.61 – 7.50 (m, 1H), 7.14 (dd, *J* = 9.9, 8.1 Hz, 1H), 3.91 (s, 2H), 1.54 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.61, 160.56 (d, *J* = 257.3 Hz), 132.89 (d, *J* = 5.0 Hz), 129.41 (d, *J* = 9.3 Hz), 128.23 (2C), 126.47 (dd, *J* = 11.3, 2.3 Hz), 123.86 (d, *J* = 15.8 Hz), 121.40 (d, *J* = 4.3 Hz), 120.76 (d, *J* = 6.3 Hz), 108.54 (d, *J* = 20.7 Hz), 82.96, 67.57, 27.40 (2C). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -117.15. **HRMS** (ESI) calcd. for $C_{15}H_{15}FNO^+$ $[M + H]^+$ 244.1138, found 244.1141.



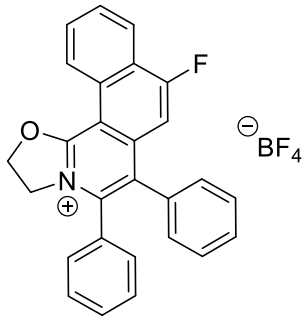
S2b

Pale yellow solid, 0.452 g, 95% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.8 Hz, 4H), 6.87 (d, *J* = 8.8 Hz, 4H), 3.83 (s, 6H).



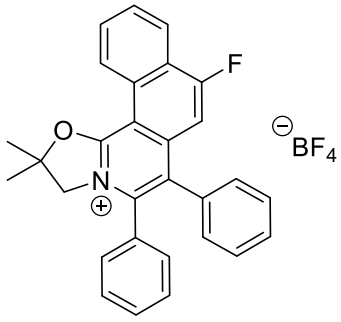
S2c

White solid, 0.734 g, 30% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 4H), 7.36 – 7.29 (m, 4H).



oxa-1

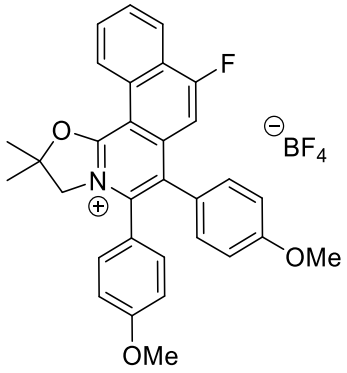
White solid, 98.2 mg, 41% yield. **^{1}H NMR** (600 MHz, DMSO-d_6) δ 9.32 (d, J = 8.5 Hz, 1H), 8.45 (d, J = 8.1 Hz, 1H), 8.21 (t, J = 7.8 Hz, 1H), 8.09 (t, J = 7.6 Hz, 1H), 7.45 (s, 5H), 7.40 (dd, J = 17.2, 7.2 Hz, 3H), 7.26 (d, J = 7.0 Hz, 2H), 7.12 (d, J = 11.4 Hz, 1H), 5.40 (t, J = 9.2 Hz, 2H), 4.65 (t, J = 9.1 Hz, 2H). **^{13}C NMR** (151 MHz, DMSO-d_6) δ 163.33 (d, J = 264.3 Hz), 159.63, 143.56 (d, J = 12.1 Hz), 141.66, 133.55, 132.52, 131.32, 131.16 (2C), 130.70, 130.54, 130.25 (d, J = 7.6 Hz), 129.88 (2C), 129.80 (d, J = 4.5 Hz), 129.28 (2C), 129.22, 129.17 (2C), 127.12, 123.80 (d, J = 18.1 Hz), 122.53 (d, J = 6.1 Hz), 108.95, 106.60 (d, J = 24.2 Hz), 73.09, 51.49. **^{19}F NMR** (565 MHz, DMSO-d_6) δ -105.70, -148.29. **HRMS** (ESI) calcd. for $C_{27}H_{19}FNO^+$ $[M - BF_4]^+$ 392.1445, found 392.1464; calcd. for BF_4^- $[M - C_{27}H_{19}FNO]^-$ 87.0035, found 87.0036.



oxa-2

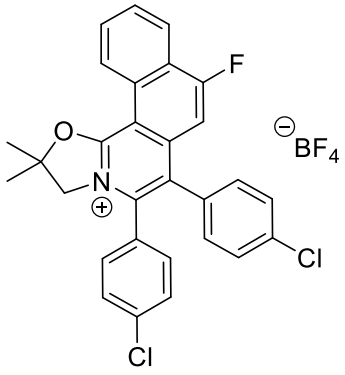
Brown solid, 0.122 g, 53% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.27 (d, J = 8.6 Hz, 1H), 8.32 (d, J = 8.2 Hz, 1H), 7.98 (t, J = 7.9 Hz, 1H), 7.89 (t, J = 7.7 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.37 – 7.26 (m, 8H), 7.15 (d, J = 11.3 Hz, 1H), 4.53 (s, 2H), 1.94 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.99 (d, *J* = 267.3 Hz), 158.09, 144.67, 141.08, 133.32, 131.30, 130.90 (2C), 130.75, 130.71, 130.21, 129.78 (2C), 129.33, 128.92 (2C), 128.69 (2C), 128.65, 127.26, 124.41 (d, *J* = 16.6 Hz), 122.07 (d, *J* = 7.6 Hz), 109.24, 106.94 (d, *J* = 24.2 Hz), 91.84, 60.57, 27.32 (2C). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -104.64, -153.48. **HRMS** (ESI) calcd. for $C_{29}H_{23}FNO^+$ $[M - BF_4]^+$ 420.1758, found 420.1760; calcd. for BF_4^- $[M - C_{29}H_{23}FNO]^-$ 87.0035, found 87.0036. **Melting point range**: 255.0-256.0 °C.



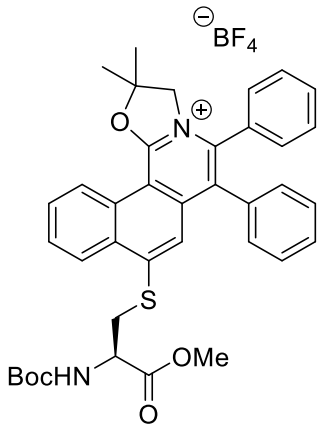
oxa-3

Orange solid, 93.6 mg, 33% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.26 (d, *J* = 8.6 Hz, 1H), 8.33 (d, *J* = 8.2 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.41 (dd, *J* = 8.7, 2.1 Hz, 2H), 7.18 (dd, *J* = 23.1, 9.8 Hz, 3H), 6.87 (dd, *J* = 11.7, 8.5 Hz, 4H), 4.57 (s, 2H), 3.80 (d, *J* = 8.9 Hz, 6H), 1.95 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.90 (d, *J* = 265.8 Hz), 160.61, 159.50, 157.90, 145.07 (d, *J* = 12.6 Hz), 141.45, 132.10, 131.30, 131.20 (2C), 131.30 (2C), 131.20, 130.87, 130.75 (d, *J* = 7.3 Hz), 129.24, 127.18, 125.50, 124.37 (d, *J* = 17.5 Hz), 122.86, 122.05 (d, *J* = 7.2 Hz), 114.38 (2C), 114.17 (2C), 108.98, 106.98 (d, *J* = 24.3 Hz), 91.59, 60.61, 55.33, 55.25, 27.32 (2C). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -104.95, -153.47. **HRMS** (ESI) calcd. for $C_{31}H_{27}FNO_3^+$ $[M - BF_4]^+$ 480.1969, found 480.2002; calcd. for BF_4^- $[M - C_{31}H_{27}FNO_3]^-$ 87.0035, found 87.0036. **Melting point range**: 238.0-243.0 °C.



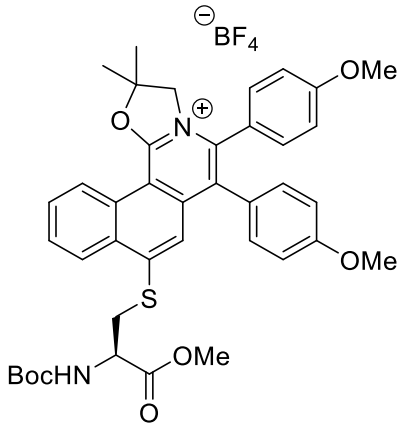
oxa-4

Orange solid, 91.0 mg, 31% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.24 (d, *J* = 8.6 Hz, 1H), 8.32 (d, *J* = 8.2 Hz, 1H), 7.98 (t, *J* = 7.9 Hz, 1H), 7.89 (t, *J* = 7.7 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.35 – 7.28 (m, 4H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.06 (d, *J* = 11.0 Hz, 1H), 4.45 (s, 2H), 1.90 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.13 (d, *J* = 267.0 Hz), 158.37, 144.46 (d, *J* = 12.8 Hz), 139.92, 136.78, 135.08, 132.21 (2C), 131.55 (d, *J* = 36.0 Hz), 131.29 (2C), 130.76 (d, *J* = 6.7 Hz), 129.82 (d, *J* = 4.1 Hz), 129.49, 129.41 (2C), 129.19 (2C), 128.93, 128.29, 127.21, 124.40 (d, *J* = 17.5 Hz), 122.14 (d, *J* = 6.7 Hz), 109.41, 106.64 (d, *J* = 24.2 Hz), 91.98, 60.43, 27.34 (2C). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -103.89, -153.17. **HRMS** (ESI) calcd. for $C_{29}H_{21}FCl_2NO^+$ $[M - BF_4)^+$ 488.0979, found 488.0981; calcd. for BF_4^- $[M - C_{29}H_{21}FCl_2NO]^-$ 87.0035, found 87.0036. **Melting point range**: 295.8-299.2 °C.



oxa-5

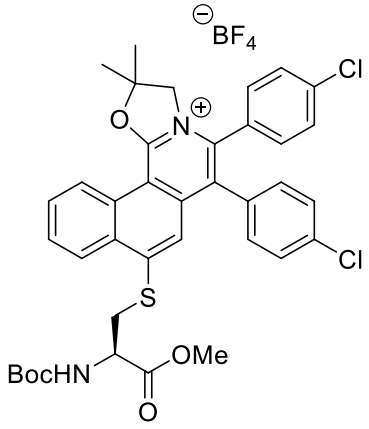
Yellow solid, 3.8 mg (purest fraction collected), 6% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.27 (d, *J* = 8.3 Hz, 1H), 8.44 (d, *J* = 8.1 Hz, 1H), 7.92 (t, *J* = 7.3 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 5.9 Hz, 1H), 7.44 – 7.27 (m, 10H), 5.25 (d, *J* = 7.4 Hz, 1H), 4.60 (d, *J* = 11.6 Hz, 1H), 4.52 (s, 1H), 4.44 (d, *J* = 12.0 Hz, 1H), 3.62 (s, 3H), 3.36 (dd, *J* = 13.0, 4.4 Hz, 1H), 3.16 (dd, *J* = 13.1, 6.2 Hz, 1H), 1.96 (d, *J* = 6.1 Hz, 3H), 1.93 (s, 3H), 1.41 (d, *J* = 15.1 Hz, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.40, 158.09, 154.98, 147.91, 141.77, 141.25, 133.47, 131.12, 130.93, 130.85, 130.67, 130.45, 130.11, 129.96 (2C), 129.67, 129.07, 128.97, 128.81, 128.67, 128.61, 128.54, 128.10, 127.54, 125.09, 119.61, 109.78, 91.59, 80.49, 60.46, 52.92, 52.09, 34.87, 28.22 (3C), 27.35, 27.11. **HRMS** (ESI) calcd. for $C_{38}H_{39}N_2O_5S^+$ $[M - BF_4]^+$ 635.2574, found 635.2580; calcd. for BF_4^- $[M - C_{38}H_{39}N_2O_5S]^-$ 87.0035, found 87.0036.



oxa-6

Orange solid, 5.8 mg (purest fraction collected, 7% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.25 (d, *J* = 8.3 Hz, 1H), 8.44 (d, *J* = 7.9 Hz, 1H), 7.90 (dd, *J* = 11.4, 4.2 Hz, 1H), 7.82 (t, *J* = 7.2 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.40 (s, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 9.0 Hz, 2H), 6.94 – 6.83 (m, 4H), 5.27 (d, *J* = 8.3 Hz, 1H), 4.61 (d, *J* = 11.9 Hz, 1H), 4.55 (d, *J* = 13.7 Hz, 1H), 4.46 (d, *J* = 12.2 Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 3.62 (s, 3H), 3.44 – 3.36 (m, 1H), 3.22 (d, *J* = 6.3 Hz, 1H), 1.94 (d, *J* = 6.7 Hz, 3H), 1.92 (s, 3H), 1.40 (d, *J* = 13.7 Hz, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.45, 160.57,

159.44, 157.92, 154.99, 147.66, 142.13, 141.65, 132.37, 132.13, 131.53, 131.15, 130.71, 130.36, 130.07, 129.00, 128.14, 127.49, 125.59, 125.14, 123.08, 119.93, 114.43, 114.35, 114.18, 114.09, 109.62, 91.27, 80.51, 60.57, 55.34, 55.21, 52.90, 52.08, 35.05, 28.21 (3C), 27.42, 27.16. **HRMS** (ESI) calcd. for $C_{40}H_{43}N_2O_7S^+$ $[M - BF_4]^+$ 695.2785, found 695.2788; calcd. for BF_4^- $[M - C_{40}H_{43}N_2O_7S]^-$ 87.0035, found 87.0036.



oxa-7

Orange solid, 8.8 mg (purest fraction collected, 11% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.24 (dd, *J* = 8.5, 1.2 Hz, 1H), 8.45 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.92 (ddd, *J* = 8.4, 7.2, 1.4 Hz, 1H), 7.83 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 7.57 (d, *J* = 8.6 Hz, 1H), 7.39 – 7.27 (m, 8H), 5.26 (d, *J* = 8.2 Hz, 1H), 4.54 (m, 2H), 4.44 – 4.30 (m, 1H), 3.64 (s, 3H), 3.39 (dd, *J* = 13.2, 4.8 Hz, 1H), 3.16 (dd, *J* = 13.2, 6.9 Hz, 1H), 1.94 (s, 3H), 1.90 (s, 3H), 1.38 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.54, 158.52, 155.12, 148.65, 141.65, 140.21, 136.86, 135.07, 132.69, 132.34, 131.92, 131.68, 131.19, 130.89, 130.72, 129.68, 129.45, 129.36 (2C), 129.24, 129.22, 129.14, 128.18, 127.65, 125.30, 119.31, 110.10, 91.71, 80.66, 60.54, 53.19, 52.06, 35.10, 28.34 (3C), 27.63, 27.31. **HRMS** (ESI) calcd. for $C_{38}H_{37}Cl_2N_2O_5S^+$ $[M - BF_4]^+$ 703.1795, found 703.1798; calcd. for BF_4^- $[M - C_{38}H_{37}Cl_2N_2O_5S]^-$ 87.0035, found 87.0036.

LC–MS and LC–MS/MS Analysis of Peptide Modification

LC-MS analyses for modification of peptides were performed by using an Agilent 6540 UHD Accurate-Mass Q-TOF LC/MS system equipped with an ion spray source and an Agilent 1290 Infinity LC, using an Agilent ZORBAX RRHD SB300-C18 (1.8 μm, 2.1 x 100 mm) column. 3 μL of sample was injected with a flow rate of 0.2 mL/min. Mobile phase A was made of Milli-Q® water containing 0.1% formic acid. Mobile phase B was made of HPLC grade acetonitrile containing 0.1% formic acid. Operating conditions optimized for the detection of reaction mixture were the following: Gas temperature: 300 °C, Drying gas: 8 L/min, Nebulizer: 35 psig, Sheath gas temperature: 380 °C, Sheath gas flow: 11 L/min, VCap: 3500 V, Nozzle voltage: 1000 V.

Table S1. The LC gradient for LC–MS analysis.

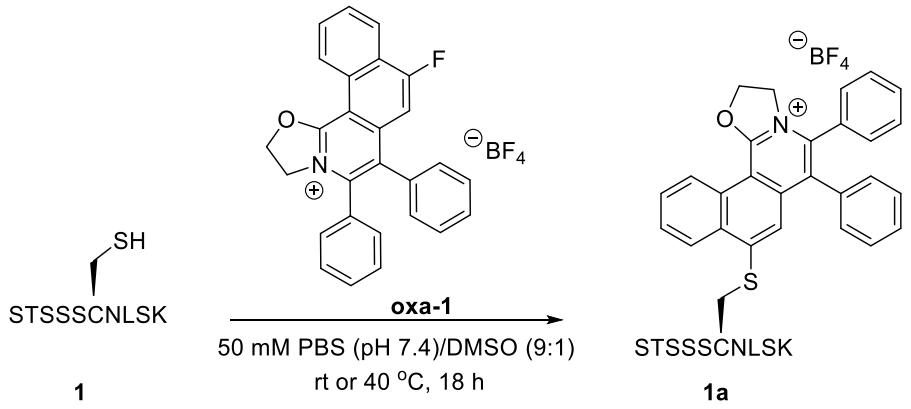
Time (min)	A (%)	B (%)	Flow rate (mL/min)
0	95	5	0.2
3	95	5	0.2
15	5	95	0.2
16	5	95	0.2
17	95	5	0.2
20	95	5	0.2

Calculation of Peptide Conversion

After data processing by MassHunter, peptide conversion at different time intervals was determined by measuring the relative peak intensities of starting and product in the mass spectrum as follows:

$$Peptide\ Conversion\ (\%) = \left(1 - \frac{Relative\ Peak\ Intensity\ of\ Starting}{Relative\ Peak\ Intensities\ of\ Starting\ and\ Product}\right) \times\ 100\%$$

General Procedure of Cysteine Arylation of Peptide 1 by oxa-1



Scheme S1. Arylation of cysteine-containing peptide **1** with **oxa-1**.

A mixture of STSSSCNLSK peptide **1** (10 μL of 1 mM in H_2O, 0.1 mM) and oxazolinium **oxa-1** (10 μL of 10mM in DMSO, 10 equiv., 1 mM) in 50 mM PBS (pH 7.4)/DMSO (9:1) (made up to 100 μL) was reacted at room temperature or 40 ℃ for 18 h. After the reaction, 3 μL of the crude mixture was taken out for LC-MS analysis.

General Procedure for Optimization of Conditions for Cysteine Arylation of Peptides by Fluorescent Oxazolinium Compounds

A mixture of STSSSCNLSK peptide **1** (10 μL of 1 mM in H_2O, 0.1 mM), oxazolinium **oxa-2** (stock solution of 5-10mM in DMSO) and tris(2-carboxyethyl)phosphine

hydrochloride (TCEP, stock solution of 10mM in H_2O) in 50 mM PBS (pH 7.4)/DMSO (9:1) (made up to 100 μL) was reacted at room temperature or 40 ℃ for 18 h. After the reaction, 3 μL of the crude mixture was taken out for LC-MS analysis.

General Procedure for Time-Course Study for Cysteine Arylation of Peptides by Fluorescent Oxazolinium Compounds

A mixture of peptide **1** (STSSSCNLSK) (40 μL of 1 mM in H_2O, 0.1 mM), oxazolinium **oxa-2** (40 μL of 5mM in DMSO, 5 equiv., 0.5 mM) and TCEP (4 μL of 10mM in H_2O, 1 equiv., 0.1 mM) in 50 mM PBS (pH 7.4)/DMSO (9:1) (made up to 400 μL) was reacted at 40 ℃ for 24 h. An aliquot amount of sample was taken out at 0.5 h, 1 h, 2 h, 4 h, 8 h, 16 h, 18 h and 24 h for LC-MS analysis.

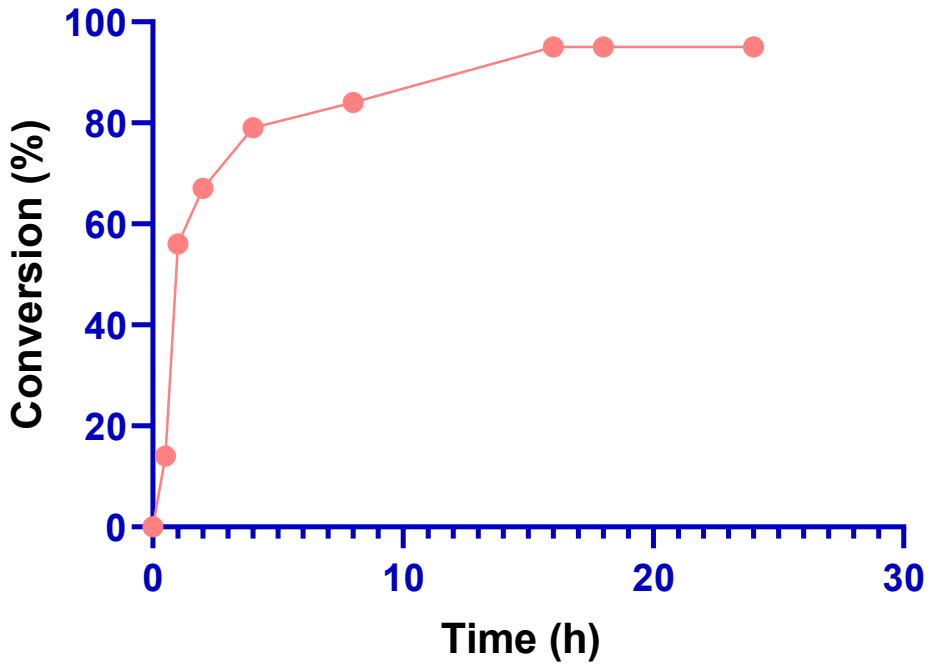


Figure S1. A time course study for cysteine arylation of peptide by **oxa-2**.

General Procedure for Absorption and Emission Spectra Measurement

The absorption and emission spectra were measured by Cary 60 UV-Vis single beam spectrophotometer and Cary eclipse fluorescence spectrophotometer, respectively. The excitation and emission slit for emission measurement were set at 5 nm with scan rate at 120 nm/min and medium PMT voltage.

Determination of the Fluorescence Quantum Yield

The calculated fluorescence quantum yields (Φ) for oxazolinium compounds **oxa-1-7** and oxazoline **S1b** were measured in DCM by using reference coumarin 153 (Φ = 0.54 in EtOH) as the standard reference.[3] The Φ were calculated according to following equation.

$$\Phi_{\text{sample}} = \Phi_{\text{standard}} \times \left(\frac{\text{Grad}_{\text{sample}}}{\text{Grad}_{\text{standard}}}\right) \times \left(\frac{\text{n}_{\text{sample}}}{\text{n}_{\text{standard}}}\right)^2$$

where Φ is the fluorescence quantum yield, Grad denotes the gradient from the plot of integrated fluorescence intensity vs absorbance, and η is the refractive index of the solvent.

Absorption and Fluorescence Spectra

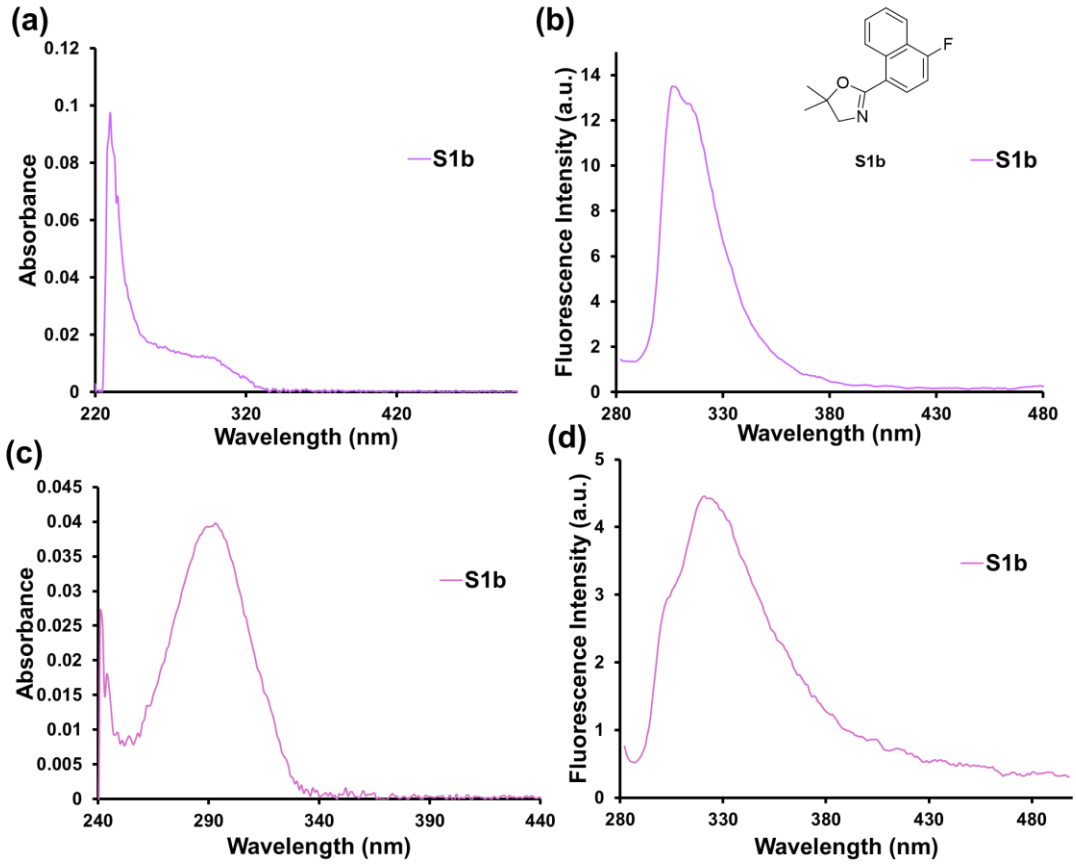


Figure S2. (a) Absorption and (b) fluorescence spectra of oxazoline **S1b**: λ_{ex} 270 nm, slit widths: 5/5 nm (1 μM in DCM); (c) absorption and (d) fluorescence spectra of oxazoline **S1b**: λ_{ex} 270 nm, slit widths: 5/5 nm (5 μM in 50 mM PBS (pH 7.4)/DMSO (9:1)).

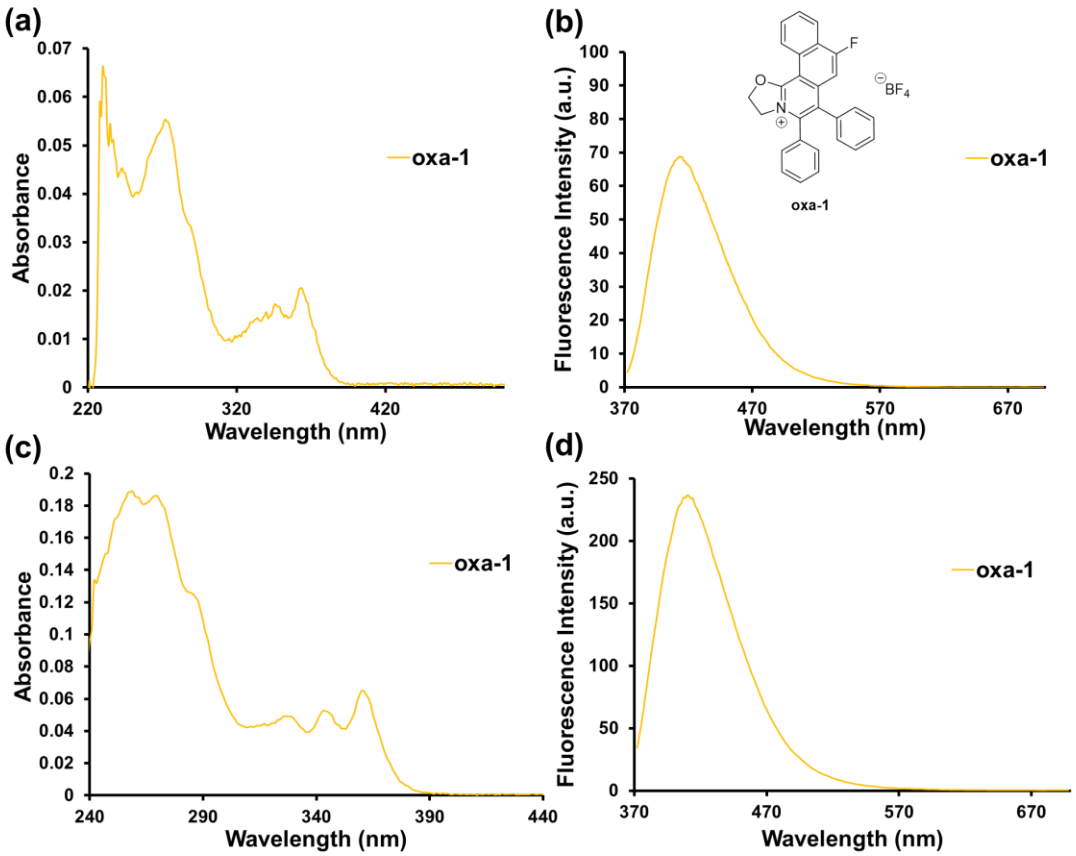


Figure S3. (a) Absorption and (b) fluorescence spectra of **oxa-1**: λ_{ex} 360 nm, slit widths: 5/5 nm (1 μM in DCM); (c) absorption and (d) fluorescence spectra of **oxa-1**: λ_{ex} 360 nm, slit widths: 5/5 nm (5 μM in 50 mM PBS (pH 7.4)/DMSO (9:1)).

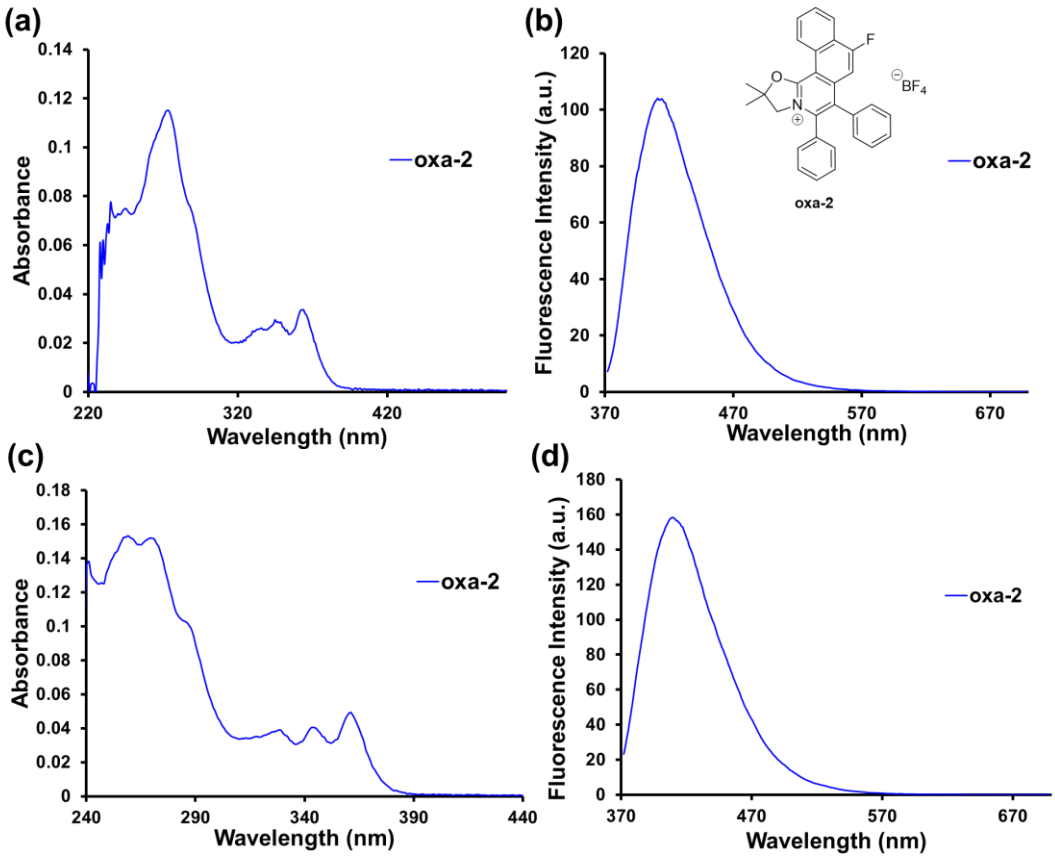


Figure S4. (a) Absorption and (b) fluorescence spectra of **oxa-2**: λ_{ex} 360 nm, slit widths: 5/5 nm (1 μM in DCM); (c) absorption and (d) fluorescence spectra of **oxa-2**: λ_{ex} 360 nm, slit widths: 5/5 nm (5 μM in 50 mM PBS (pH 7.4)/DMSO (9:1)).

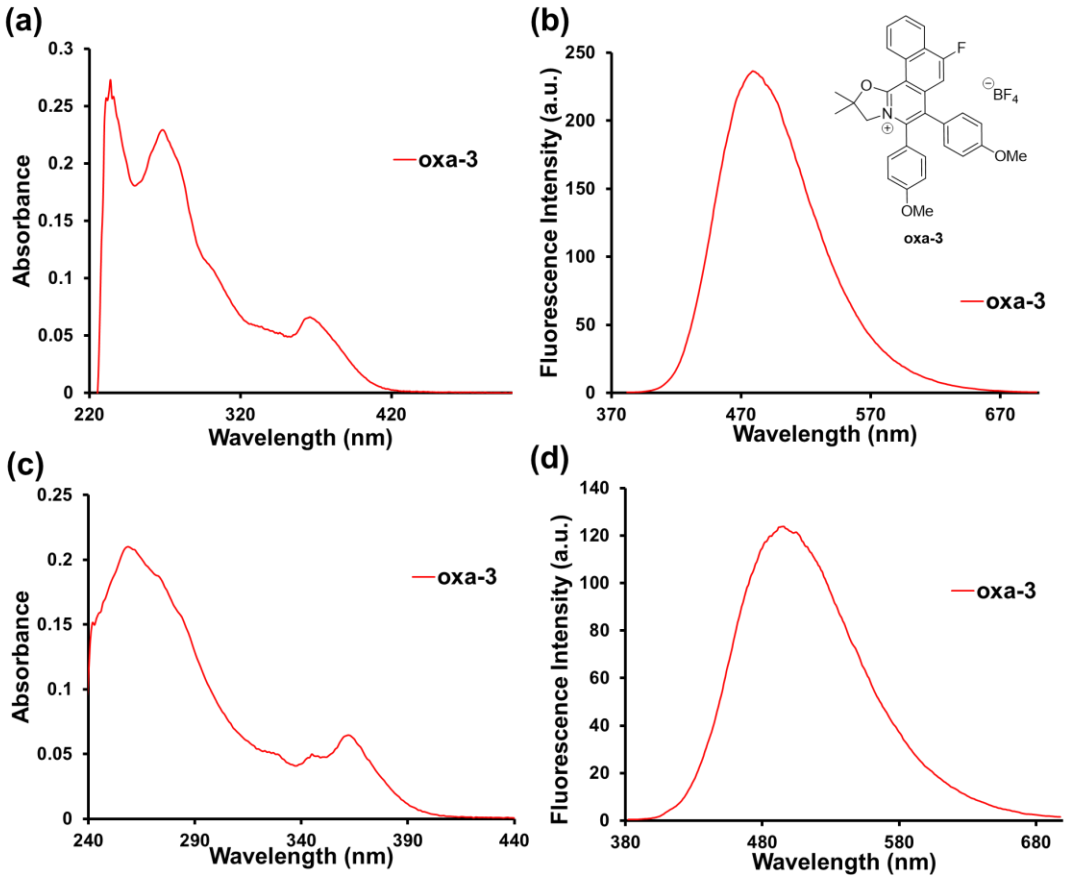


Figure S5. (a) Absorption and (b) fluorescence spectra of **oxa-3**: λ_{ex} 365 nm, slit widths: 5/5 nm (1 μM in DCM); (c) absorption and (d) fluorescence spectra of **oxa-3**: λ_{ex} 360 nm, slit widths: 5/5 nm (5 μM in 50 mM PBS (pH 7.4)/DMSO (9:1)).

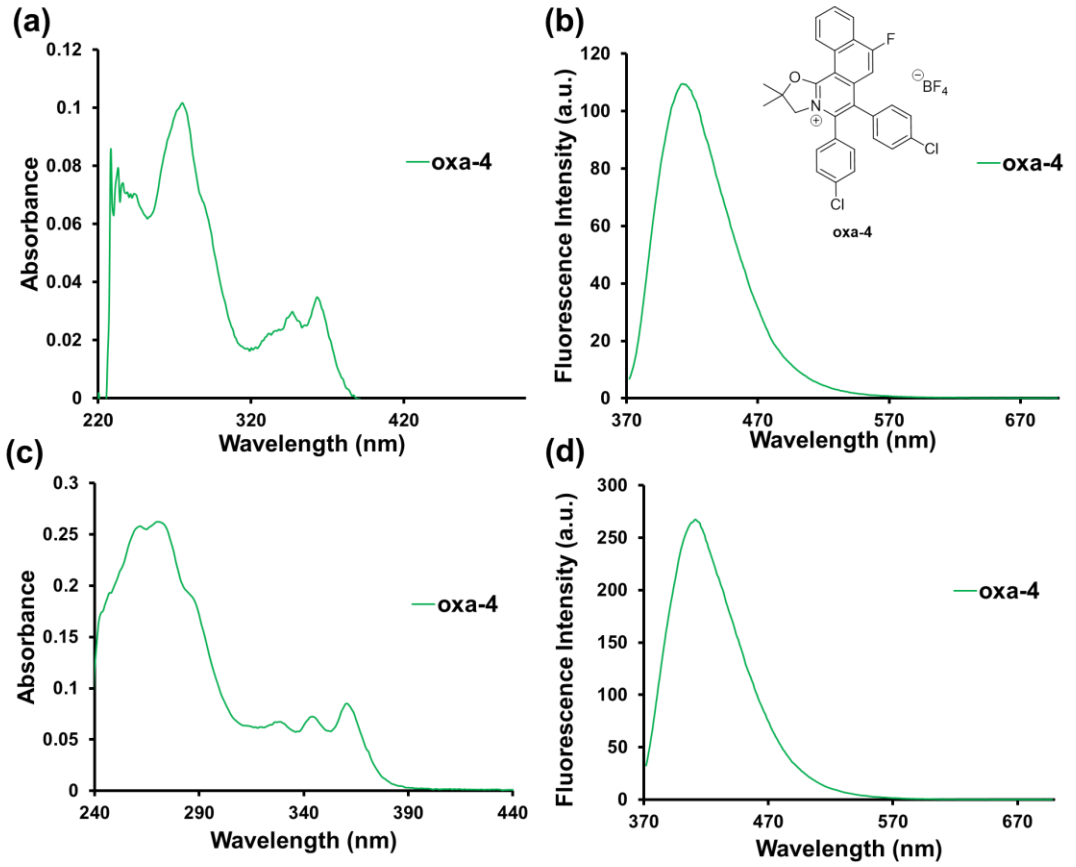


Figure S6. (a) Absorption and (b) fluorescence spectra of **oxa-4**: λ_{ex} 360 nm, slit widths: 5/5 nm (1 μM in DCM); (c) absorption and (d) fluorescence spectra of **oxa-4**: λ_{ex} 360 nm, slit widths: 5/5 nm (5 μM in 50 mM PBS (pH 7.4)/DMSO (9:1)).

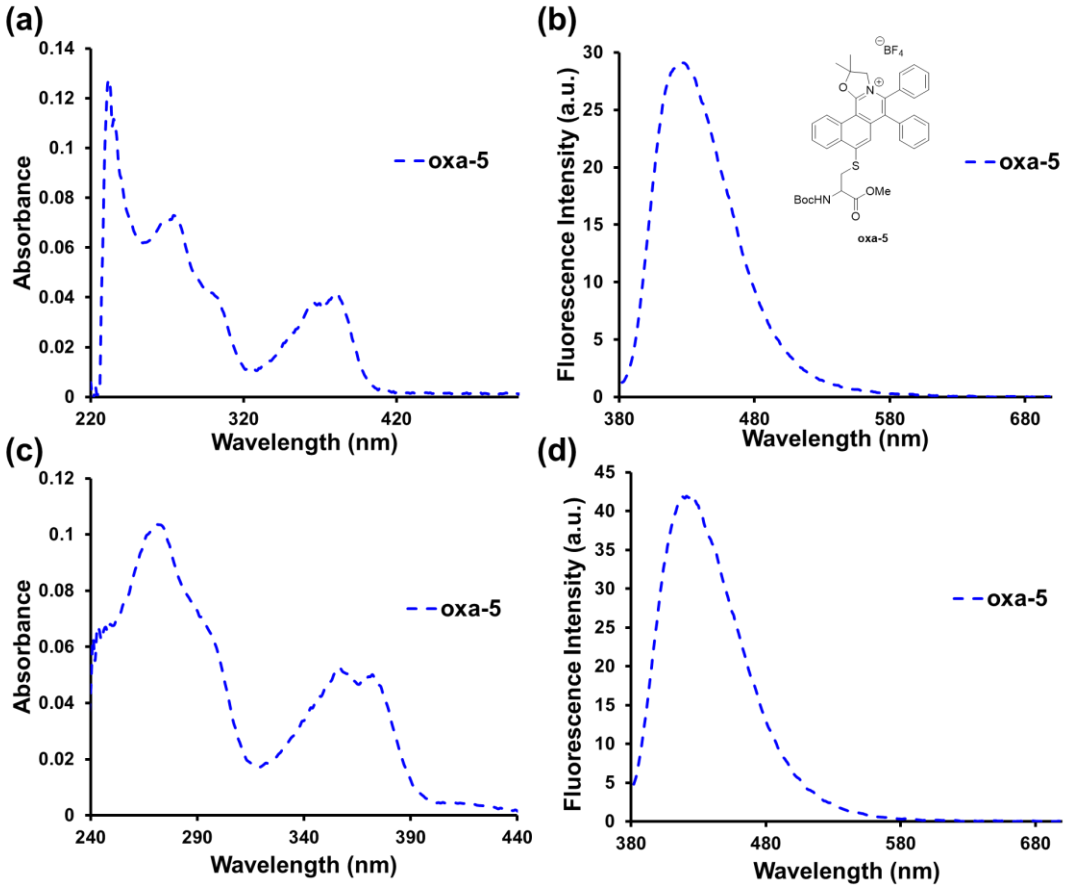


Figure S7. (a) Absorption and (b) fluorescence spectra of **oxa-5**: λ_{ex} 370 nm, slit widths: 5/5 nm (1 μM in DCM); (c) absorption and (d) fluorescence spectra of **oxa-5**: λ_{ex} 370 nm, slit widths: 5/5 nm (5 μM in 50 mM PBS (pH 7.4)/DMSO (9:1)).

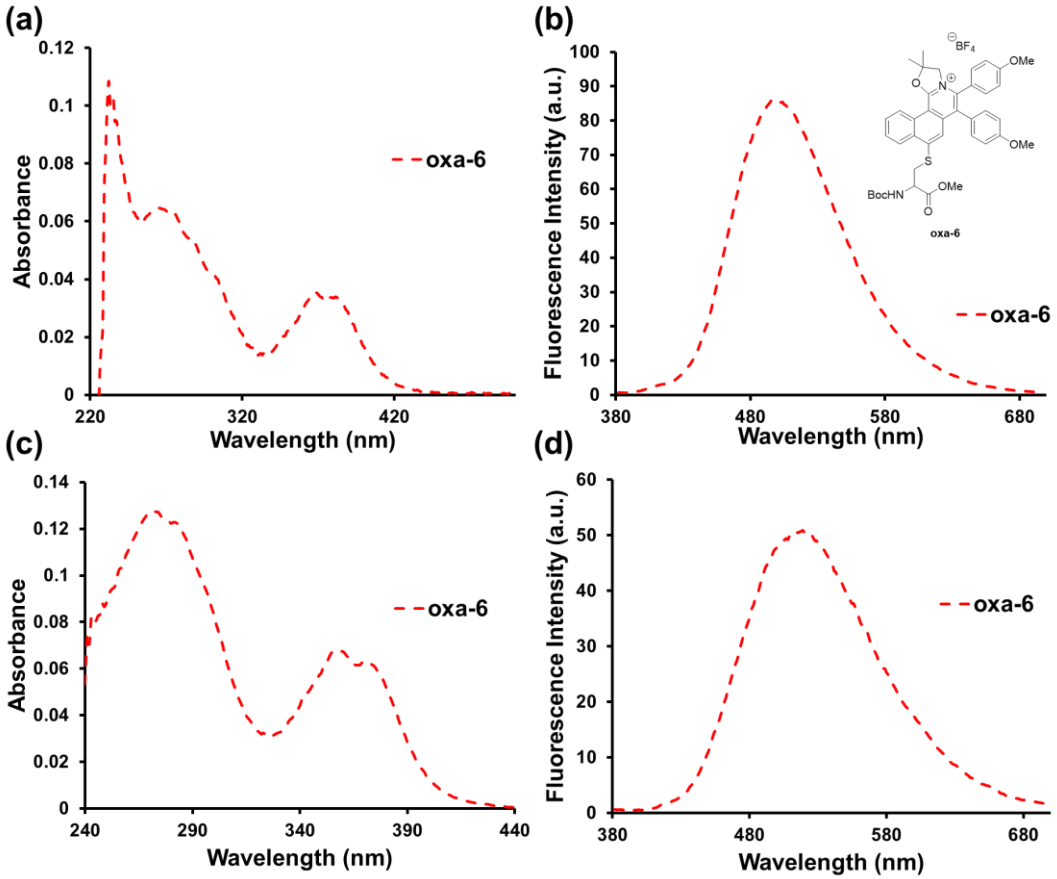


Figure S8. (a) Absorption and (b) fluorescence spectra of **oxa-6**: λ_{ex} 365 nm, slit widths: 5/5 nm (1 μM in DCM); (c) absorption and (d) fluorescence spectra of **oxa-6**: λ_{ex} 365 nm, slit widths: 5/5 nm (5 μM in 50 mM PBS (pH 7.4)/DMSO (9:1)).

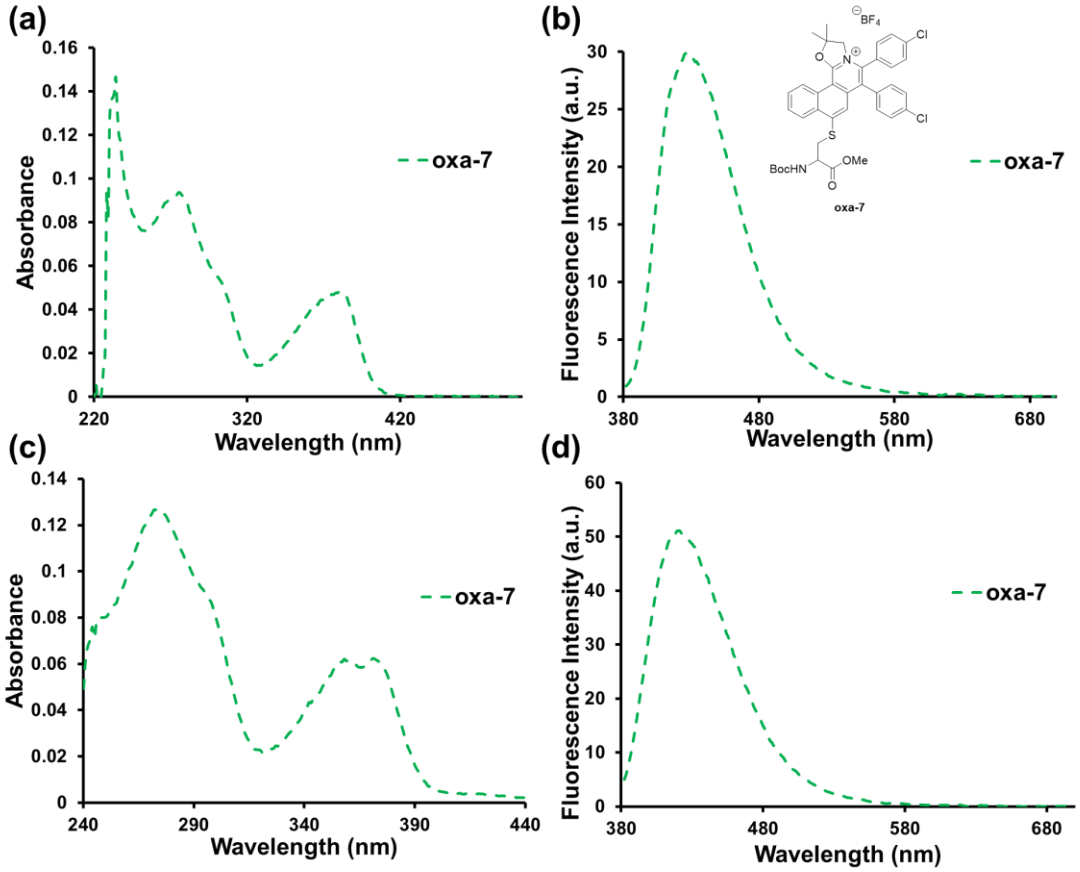


Figure S9. (a) Absorption and (b) fluorescence spectra of **oxa-7**: λ_{ex} 365 nm, slit widths: 5/5 nm (1 μM in DCM); (c) absorption and (d) fluorescence spectra of **oxa-7**: λ_{ex} 365 nm, slit widths: 5/5 nm (5 μM in 50 mM PBS (pH 7.4)/DMSO (9:1)).

Table S2. Photophysical properties of **S1b** and **oxa-1-7** in PBS (pH 7.4)/DMSO (9:1).

Entry	Compound	Max. Abs (nm)	Max. Em (nm)	Stokes Shift (nm)	ε (M^{-1} cm^{-1})	λ_{ex} (nm)	Φ_F[a]
1	**S1b**	293	320	27	7700	270	0.004
2	**oxa-1**	360	410	50	12600	360	0.36
3	**oxa-2**	360	410	50	9800	360	0.31
4	**oxa-3**	360	497	137	12800	360	0.28
5	**oxa-4**	360	410	50	16900	360	0.30
6	**oxa-5**	372	423	51	9600	370	0.09
7	**oxa-6**	372	518	146	12300	365	0.13
8	**oxa-7**	372	420	48	12600	365	0.08

[a] Quantum yields were measured using coumarin 153 (Φ_F = 0.54 in ethanol) as the standard reference.

Time-Dependent Density Functional Theory (TD-DFT) Calculation

All DFT calculations were performed using Gaussian 16/A.03 with B3LYP/6-31G* functional/basis set, and the PCM solvent model (solvent = DCM). The counter ion was omitted for all calculations. The ground state (S_0) geometry of **oxa-2** was first optimized with no imaginary vibrational frequency encountered, confirming the optimized stationary point to be local minimum. To simulate the electronic excitation of **oxa-2**, the optimized geometry was subjected to TD-DFT calculation (first 64 states). The first excited state (S_1) geometry was further optimized with no imaginary vibrational frequency encountered, then subjected to TD-DFT calculation to simulate the fluorescence ($S_1 \rightarrow S_0$) of **oxa-2**.

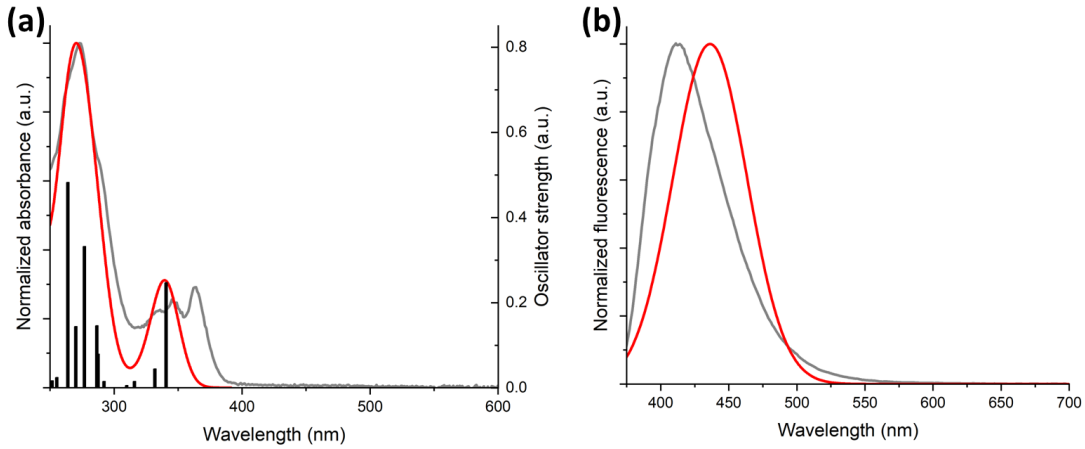


Figure S10. (a) Experimental (grey line) and Simulated (red line) absorption spectra of **oxa-2**, with the calculated wavelength vs. oscillator strength. The Simulated absorption spectrum assumes a Gaussian line-shape for each transition, with FWHM = 25 nm. (b) Experimental (grey line) and Simulated (red line) fluorescence spectra of **oxa-2**. The Simulated fluorescence spectrum assumes a Gaussian line-shape for the transition, with FWHM = 25 nm.

Table S3. TD-DFT calculated excitation energies and oscillator strengths of the **oxa-2**.

Excited state	Wavelength (nm)	Oscillator strength (*f*)	Excited state	Wavelength (nm)	Oscillator strength (*f*)
1	340.65	0.2471	33	206.62	0.001
2	331.94	0.0446	34	204.11	0.0214
3	315.95	0.0154	35	202.92	0.0169
4	309.81	0.0058	36	202.75	0.001
5	292.09	0.0153	37	201.17	0.0036
6	287.5	0.0791	38	200.87	0.0091
7	286.52	0.146	39	200.67	0.0132
8	276.91	0.332	40	197.85	0.0018
9	270.17	0.1443	41	197.45	0.0434
10	263.9	0.4825	42	197.09	0.0162
11	255.28	0.0244	43	196.6	0.0302
12	251.61	0.0167	44	195.46	0.0411
13	250.17	0.0036	45	194.76	0.0249
14	236.57	0.0406	46	191.56	0.0191
15	235.81	0.2109	47	191.42	0.021
16	233.27	0.0761	48	190.61	0.0171
17	232.07	0.0339	49	190.01	0.0037
18	228.18	0.0029	50	187.94	0.0062
19	226.67	0.0454	51	186.93	0.0011
20	223.02	0.0101	52	186.57	0.4744
21	219.54	0.006	53	185.02	0.1233
22	218.23	0.2739	54	183.6	0.0305
23	217.47	0.047	55	183.02	0.0364
24	216.16	0.0356	56	182.51	0.1847
25	215.58	0.0752	57	181.85	0.0165
26	214.1	0.0472	58	180.7	0.1217
27	213.41	0.002	59	180.21	0.0583
28	212.67	0.0204	60	179.71	0.0071
29	211.6	0.061	61	179.21	0.1128

30	209.19	0.0026	62	178.63	0.269
31	208.83	0.0307	63	178.56	0.0053
32	206.83	0.0149	64	178.06	0.0872

Table S4. Computed total energies and Cartesian coordinates of **oxa-2** at ground state.

Total electronic energy E = -1348.645681 Hartree

C	-5.839606941	-0.832140411	-0.018689598
C	-4.902287986	-1.844347340	0.027745058
C	-3.525125468	-1.533720861	0.018821829
C	-3.075548474	-0.178819747	-0.036608321
C	-4.067057910	0.831062794	-0.084315765
C	-5.413300638	0.507053245	-0.074958810
C	-2.543467375	-2.566875393	0.067444397
C	-1.641048792	0.069052563	-0.041057122
C	-0.708204675	-1.013204936	-0.004970050
C	-1.201177903	-2.346561362	0.057391051
C	0.712243779	-0.773537433	-0.010222137
C	1.186940331	0.518715130	-0.038390014
C	-1.069197255	1.357326843	-0.073851213
H	-6.899175054	-1.067737758	-0.012431476
H	-5.206341596	-2.883781629	0.070688661
H	-3.778643159	1.870214609	-0.129584625
H	-6.148964014	1.304886939	-0.112488203
H	-0.519619175	-3.185427833	0.097471169
C	0.575434230	2.985751053	-0.216042629
H	1.317579567	3.297036183	0.517383422
H	0.968201830	3.156444033	-1.221964853
O	-1.738249439	2.497218289	-0.132271280
C	-0.799281065	3.650931173	0.016589015
N	0.265661640	1.547687769	-0.060542539
C	-0.968945906	4.175699068	1.438213194
H	-0.310516233	5.036904031	1.591282047
H	-2.001334735	4.495024983	1.604342608
H	-0.713228636	3.410125129	2.177562930
C	-1.170614191	4.670693145	-1.047034222

H	-2.186316823	5.041186589	-0.882531595
H	-0.482731402	5.520466069	-0.992777059
H	-1.108041749	4.235269435	-2.048169154
C	2.627996339	0.897842703	-0.058475563
C	3.373838561	0.746858570	-1.235955802
C	3.244839488	1.412259622	1.092412997
C	4.720900656	1.109924821	-1.261201087
H	2.900409416	0.345863387	-2.126933775
C	4.592527791	1.770857135	1.061859922
H	2.676575620	1.517322685	2.012645131
C	5.331106447	1.622093239	-0.114454307
H	5.292092642	0.990692916	-2.177025815
H	5.065064844	2.161455594	1.958179245
H	6.380371055	1.901623342	-0.135833449
C	1.673858141	-1.919558318	0.035164369
C	1.930616768	-2.677978226	-1.116731797
C	2.320862007	-2.254805488	1.232894147
C	2.825877525	-3.747778870	-1.071837971
H	1.432775215	-2.426228976	-2.049184714
C	3.214704135	-3.325931600	1.275726690
H	2.122600665	-1.676978435	2.131047519
C	3.469923343	-4.073228493	0.123990362
H	3.020227771	-4.324569376	-1.971538124
H	3.710325673	-3.575611311	2.209516113
H	4.166629955	-4.905934440	0.158189740
F	-2.990267491	-3.830622510	0.128153614

Table S5. Computed total energies and Cartesian coordinates of **oxa-2** at excited state S1.

Total electronic energy E = -1348.529161 Hartree

C	-5.853406000	-0.841719000	-0.095653000
C	-4.920267000	-1.847452000	0.077214000
C	-3.537188000	-1.547973000	0.090051000
C	-3.084060000	-0.191012000	-0.067987000
C	-4.068905000	0.801562000	-0.242819000
C	-5.424438000	0.485710000	-0.257972000
C	-2.568408000	-2.567106000	0.259610000
C	-1.640277000	0.073790000	-0.025961000
C	-0.708107000	-1.040432000	0.067534000
C	-1.207634000	-2.336545000	0.254859000
C	0.719708000	-0.761890000	0.030813000
C	1.195775000	0.547913000	0.040997000
C	-1.085413000	1.339949000	-0.025131000
H	-6.913282000	-1.078705000	-0.107123000
H	-5.231090000	-2.878475000	0.202593000
H	-3.773698000	1.832092000	-0.372924000
H	-6.152880000	1.278686000	-0.398927000
H	-0.546378000	-3.179151000	0.410272000
C	0.531116000	2.984876000	-0.311876000
H	1.327767000	3.451746000	0.263721000
H	0.793993000	3.009676000	-1.377514000
O	-1.750485000	2.485880000	-0.184831000
C	-0.833223000	3.640461000	-0.038840000
N	0.281166000	1.598877000	0.122886000
C	-0.967306000	4.154862000	1.393411000
H	-0.332287000	5.035370000	1.534276000
H	-2.003580000	4.440364000	1.594953000
H	-0.667052000	3.390379000	2.117078000
C	-1.238901000	4.671132000	-1.080100000
H	-2.248655000	5.040141000	-0.877845000
H	-0.550792000	5.521733000	-1.044403000
H	-1.213375000	4.242491000	-2.085945000
C	2.620081000	0.894725000	-0.032860000

C	3.446756000	0.335014000	-1.041796000
C	3.194892000	1.797847000	0.892629000
C	4.797969000	0.657720000	-1.108699000
H	3.006380000	-0.313505000	-1.790769000
C	4.547048000	2.100339000	0.827489000
H	2.586273000	2.209439000	1.691446000
C	5.353187000	1.537218000	-0.176839000
H	5.414022000	0.233850000	-1.895281000
H	4.985196000	2.768446000	1.562270000
H	6.407327000	1.791425000	-0.228516000
C	1.687792000	-1.870130000	0.020384000
C	1.581733000	-2.915952000	-0.933368000
C	2.736253000	-1.934959000	0.984007000
C	2.497817000	-3.953543000	-0.941320000
H	0.799897000	-2.872457000	-1.683456000
C	3.631849000	-2.994547000	0.987199000
H	2.796274000	-1.170343000	1.749800000
C	3.522559000	-4.002885000	0.023779000
H	2.429051000	-4.730347000	-1.695880000
H	4.409774000	-3.043121000	1.741970000
H	4.225814000	-4.829661000	0.020260000
F	-3.008332000	-3.836788000	0.430650000

General Procedure for Scope Study for Cysteine Arylation of Cysteine-Containing Peptides by Fluorescent oxa-3

A mixture of peptide **1-7** (10 μL of 1 mM in H_2O, 1 equiv., 0.1 mM), **oxa-3** (10 μL of 5 mM in DMSO, 5 equiv., 0.5 mM) and TCEP (1 μL of 10 mM in H_2O, 1 equiv., 0.1 mM) in 50 mM PBS (pH 7.4)/DMSO (9:1) (made up to 100 μL) was reacted at 40 ℃ for 16 h. After the reaction, 3 μL of the crude mixture was taken out for LC-MS analysis. Results are shown in Table S5 and Figures S19-20, S23-42.

MS and MS/MS Spectra

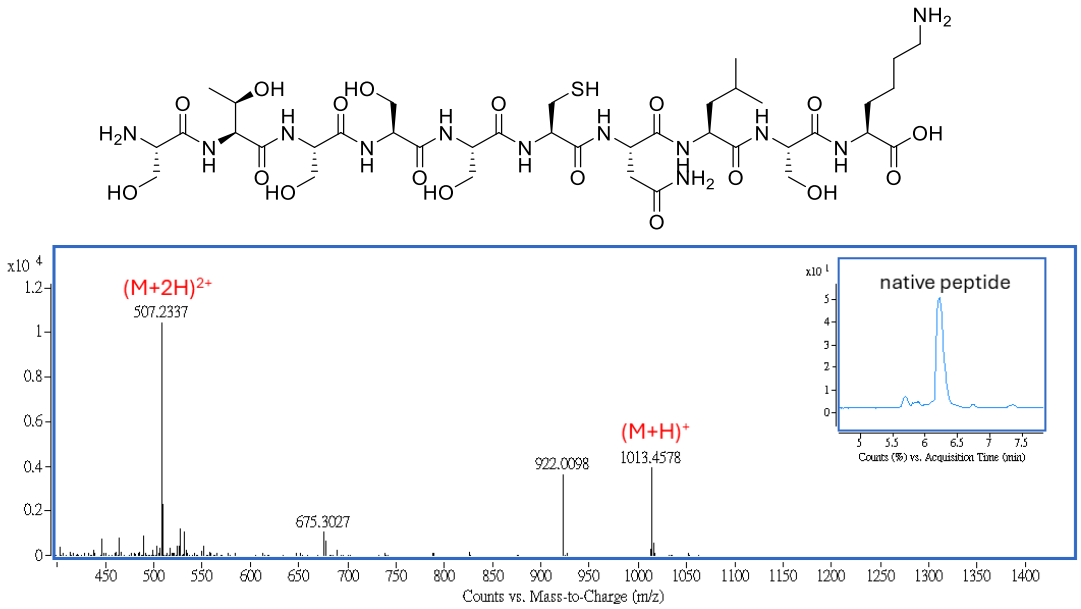


Figure S11. Mass spectrum and total ion chromatogram (inset) of native peptide **1** (STSSSCNLSK). **MS** (ESI) *m/z*: calcd. for $C_{38}H_{69}N_{12}O_{18}S^+$ $[M+H]^+$ 1013.45, found 1013.45.

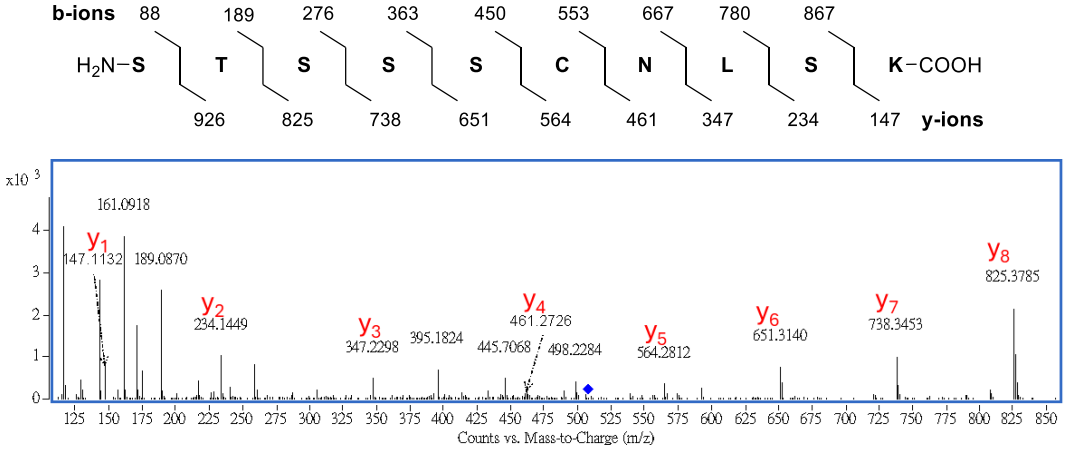


Figure S12. MS/MS spectrum of native peptide **1** (STSSSCNLSK) (ESI source, doubly charged ion of *m/z* = 507.2).

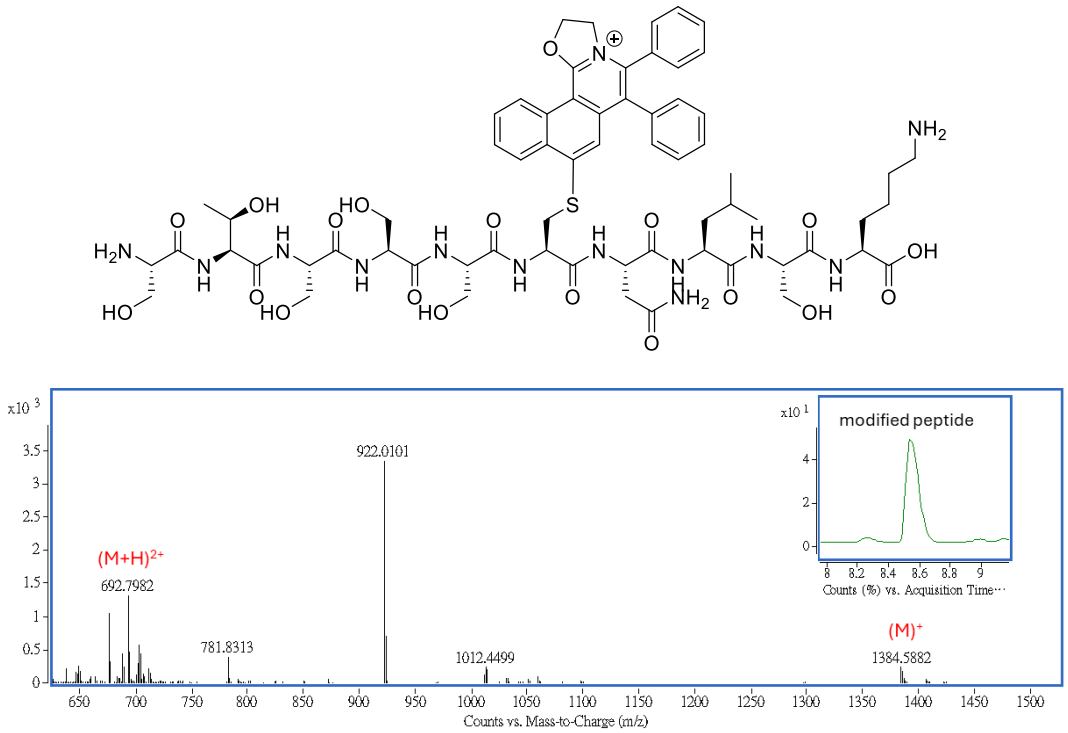


Figure S13. Mass spectrum and total ion chromatogram (inset) of modified peptide **1a**. **MS** (ESI) *m/z*: calcd. for $C_{65}H_{86}N_{13}O_{19}S^+$ $[M]^+$ 1384.58, found 1384.58.

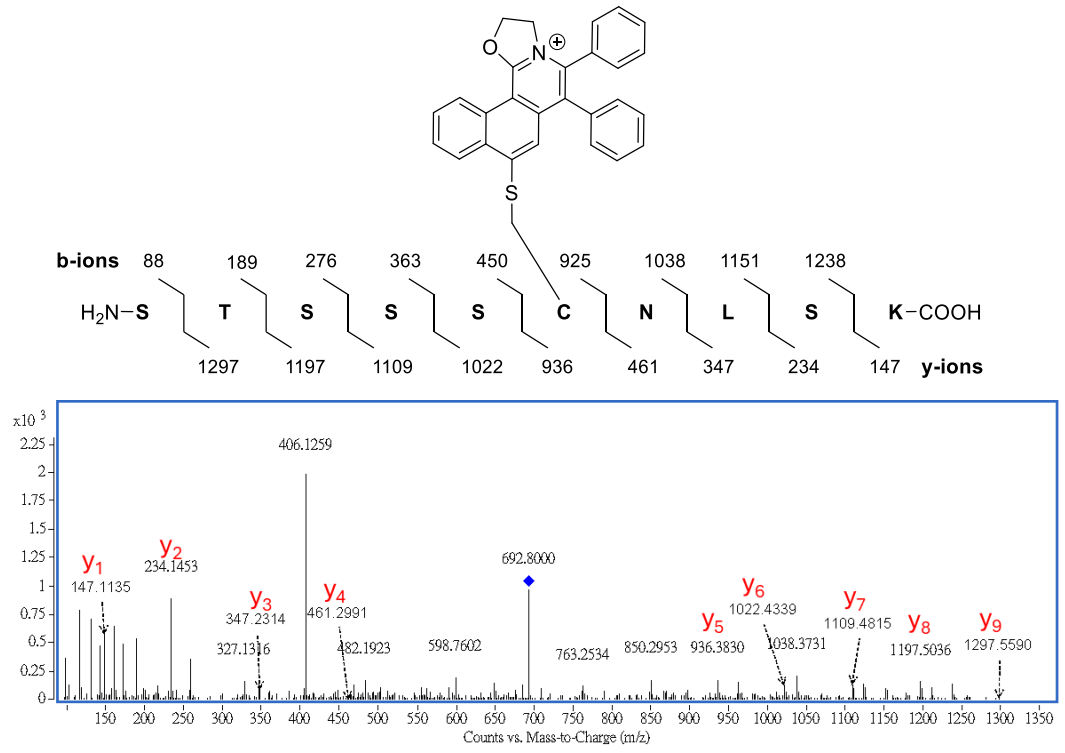


Figure S14. MS/MS spectrum of modified peptide **1a** (ESI source, doubly charged ion of *m/z* = 692.8).

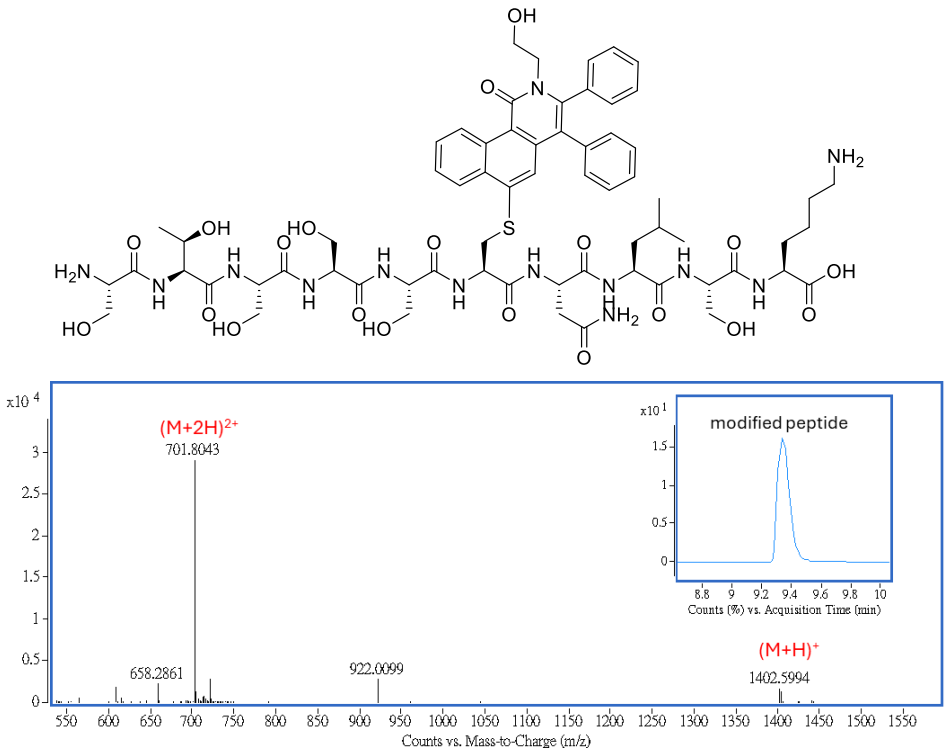


Figure S15. Mass spectrum and total ion chromatogram (inset) of modified peptide **1a'**. **MS** (ESI) *m/z*: calcd. for $C_{65}H_{88}N_{13}O_{20}S^+$ $[M+H]^+$ 1402.59, found 1402.59.

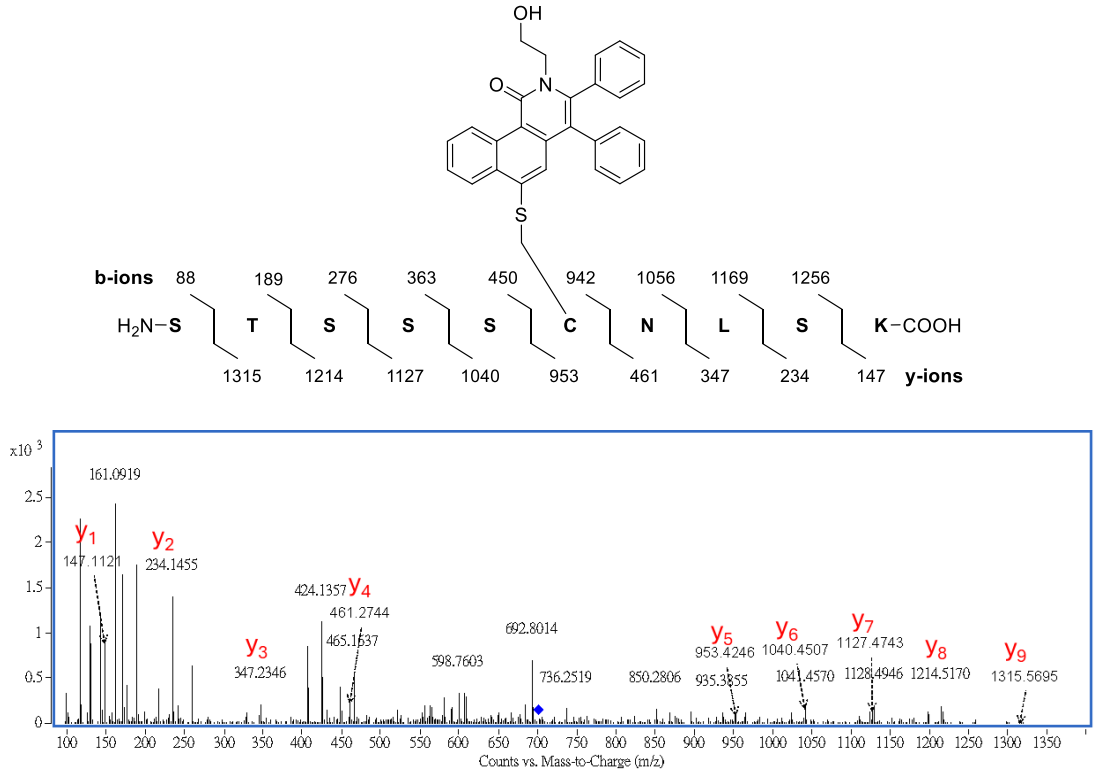


Figure S16. MS/MS spectrum of modified peptide **1a'** (ESI source, doubly charged ion of *m/z* = 701.8).

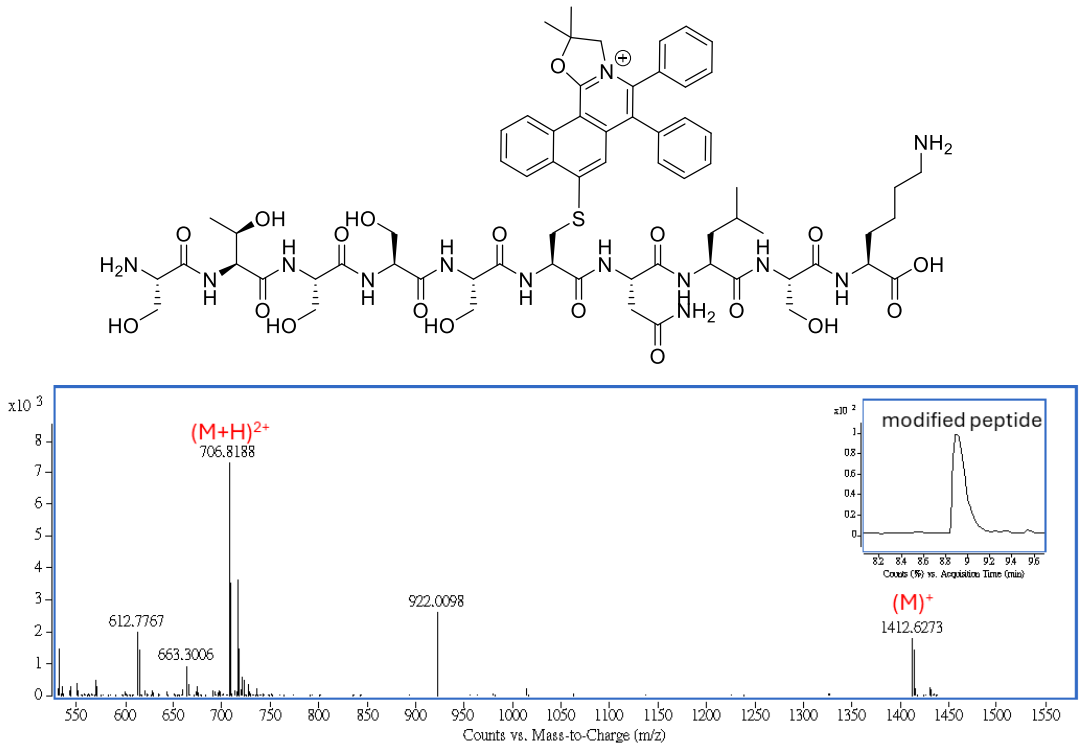


Figure S17. Mass spectrum and total ion chromatogram (inset) of modified peptide **1b**. **MS** (ESI) *m/z*: calcd. for $C_{67}H_{90}N_{13}O_{19}S^+$ $[M]^+$ 1412.61, found 1412.62.

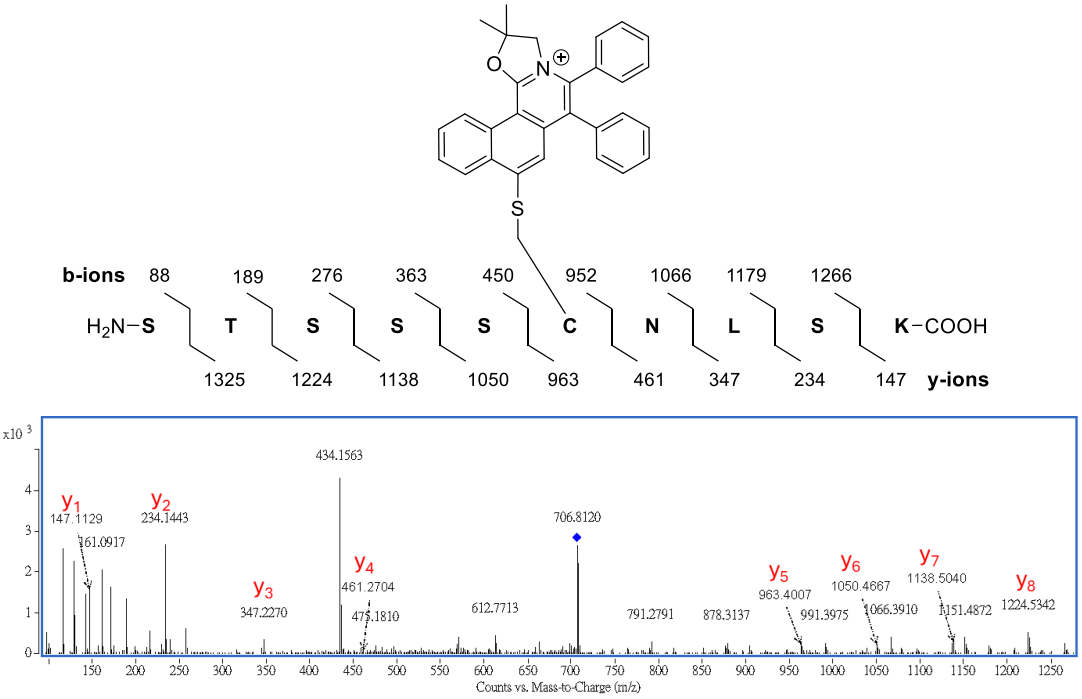


Figure S18. MS/MS spectrum of modified peptide **1b** (ESI source, doubly charged ion of *m/z* = 706.8).

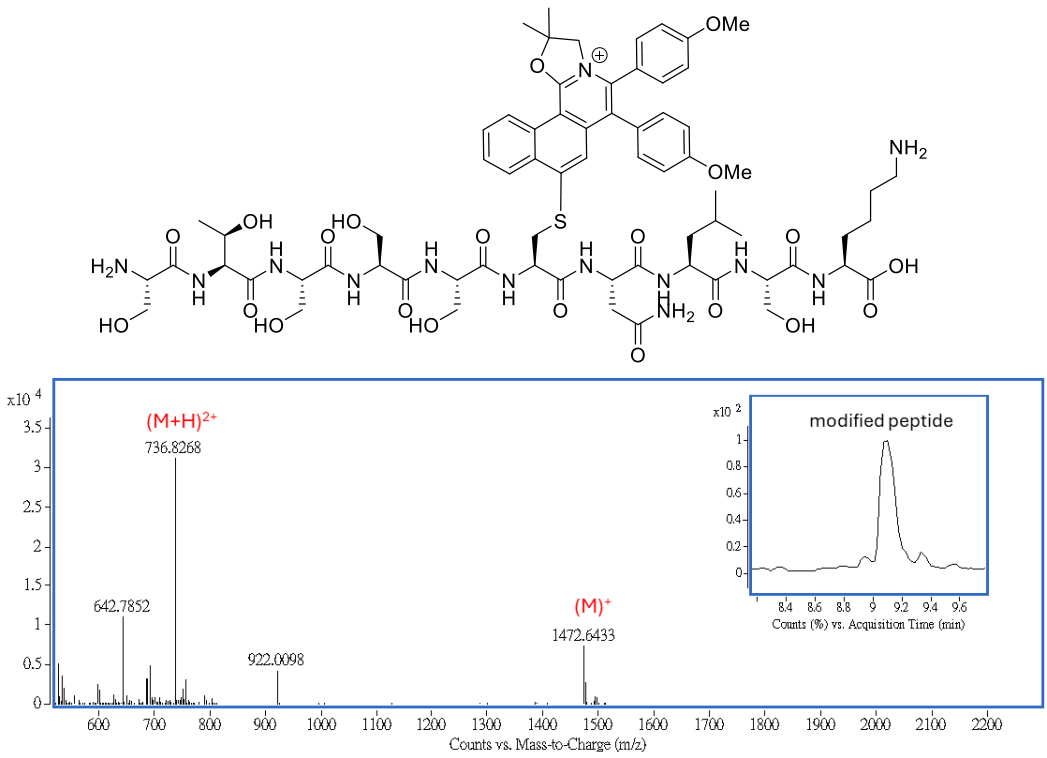


Figure S19. Mass spectrum and total ion chromatogram (inset) of modified peptide **1c**. **MS** (ESI) *m/z*: calcd. for $C_{69}H_{94}N_{13}O_{21}S^+$ $[M]^+$ 1472.64, found 1472.64.

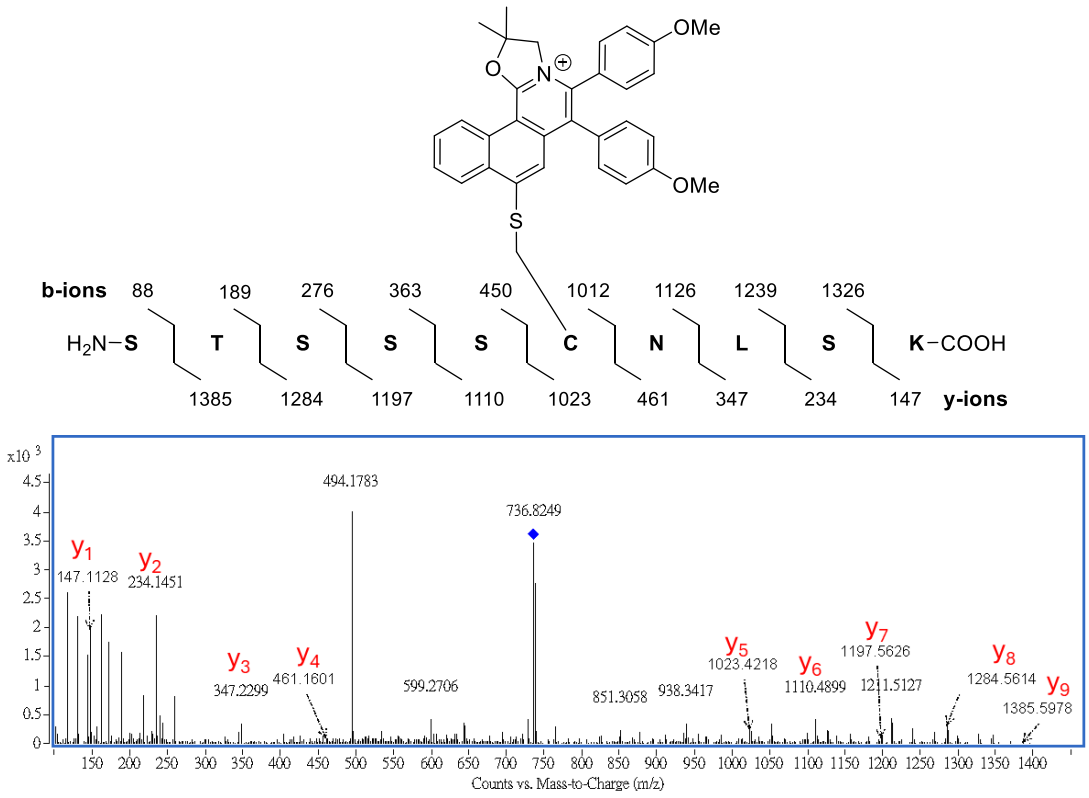


Figure S20. MS/MS spectrum of modified peptide **1c** (ESI source, doubly charged ion of *m/z* = 736.8).

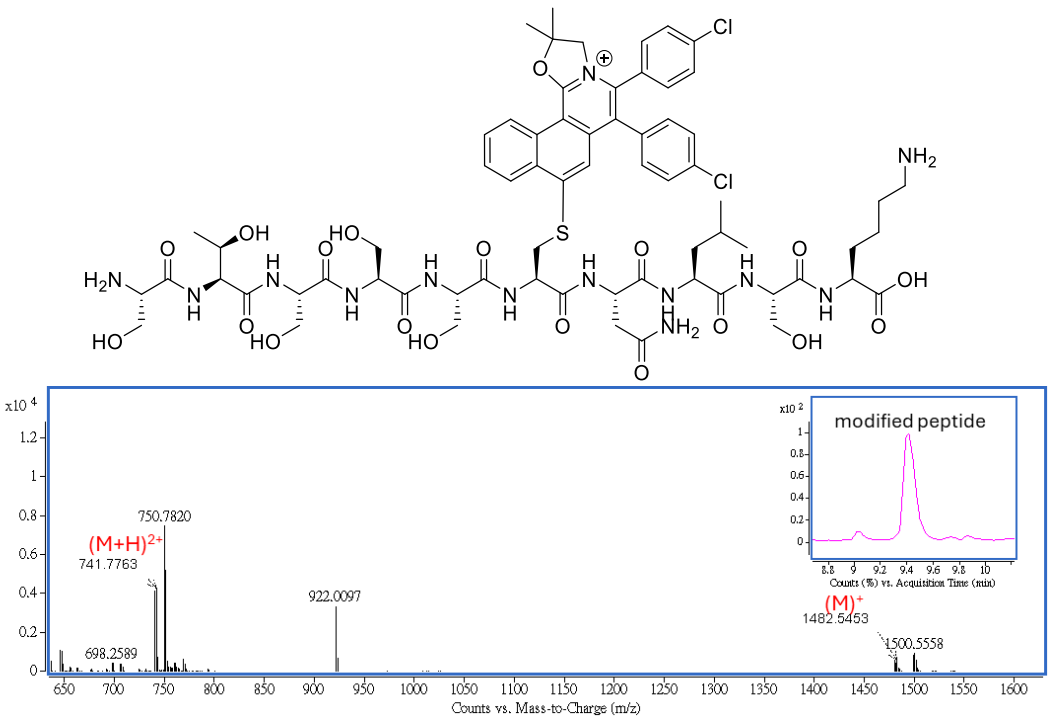


Figure S21. Mass spectrum and total ion chromatogram (inset) of modified peptide **1d**. **MS** (ESI) *m/z*: calcd. for $C_{67}H_{88}Cl_2N_{13}O_{19}S^+$ $[M]^+$ 1482.54, found 1482.54.

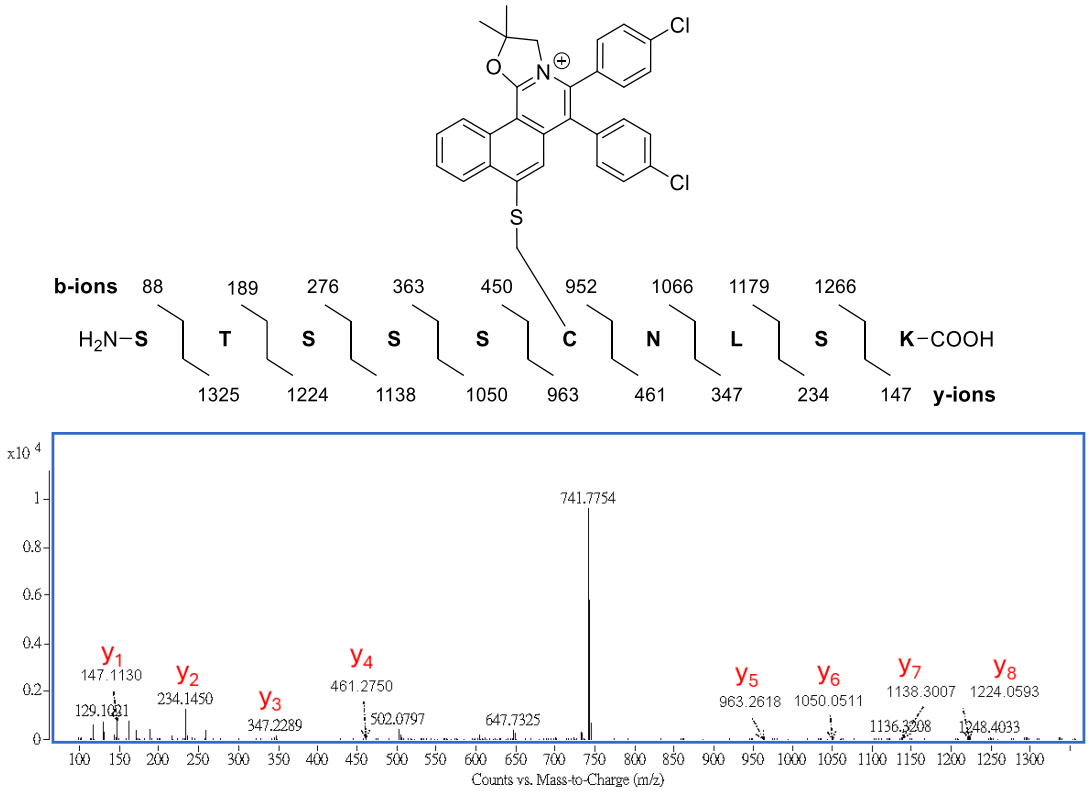


Figure S22. MS/MS spectrum of modified peptide **1d** (ESI source, doubly charged ion of *m/z* = 741.7).

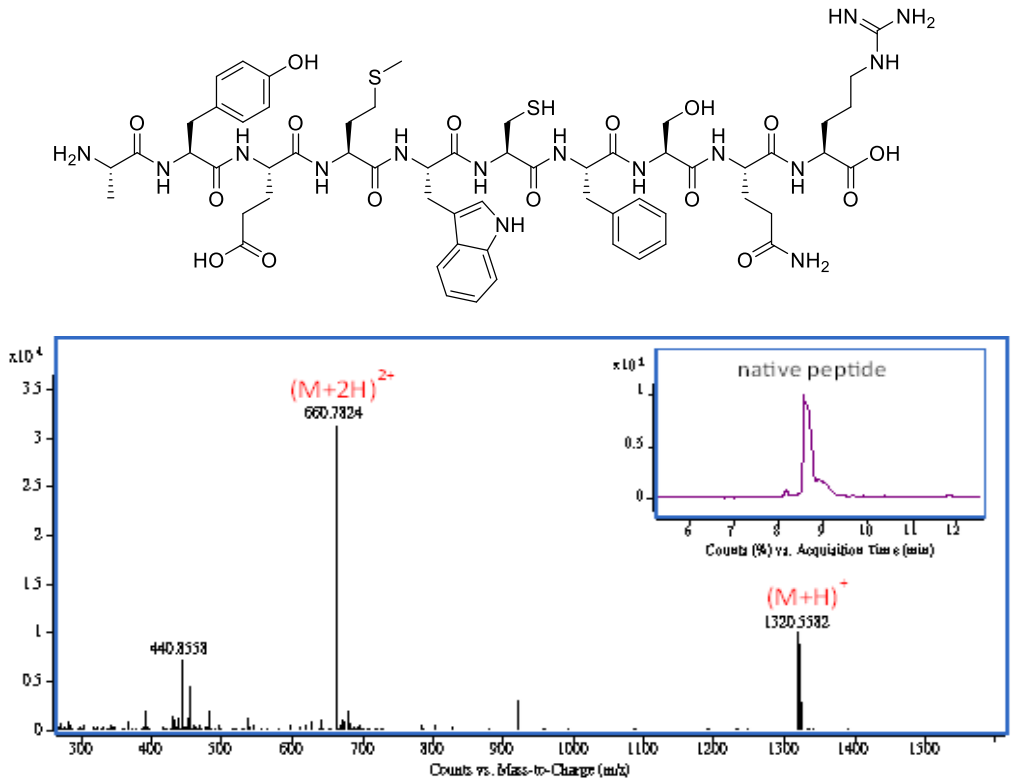


Figure S23. Mass spectrum and total ion chromatogram (inset) of native peptide **2** (AYEMWCFSQR). **MS** (ESI) *m/z*: calcd. for $C_{59}H_{82}N_{15}O_{16}S_2^+$ $[M+H]^+$ 1320.55, found 1320.55.

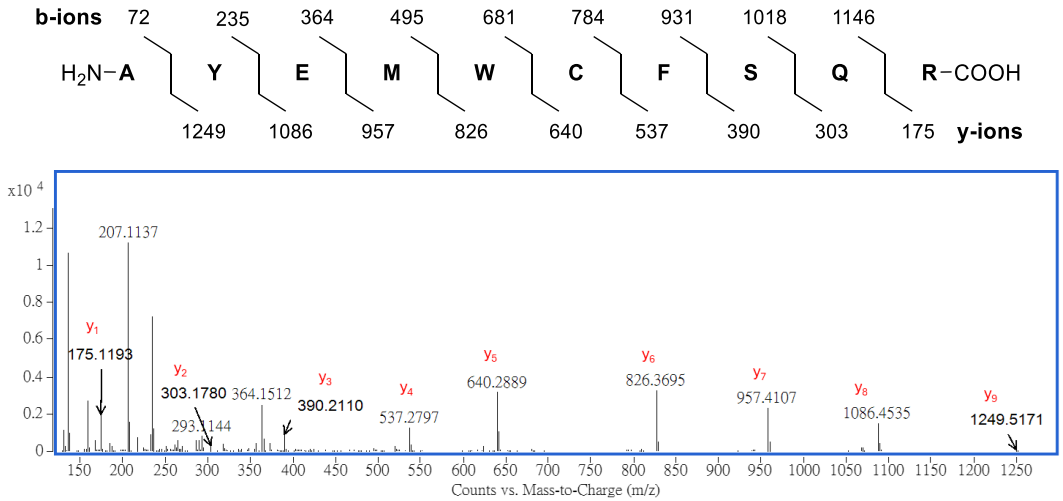


Figure S24. MS/MS spectrum of native peptide **2** (AYEMWCFSQR) (ESI source, doubly charged ion of *m/z* = 660.7).

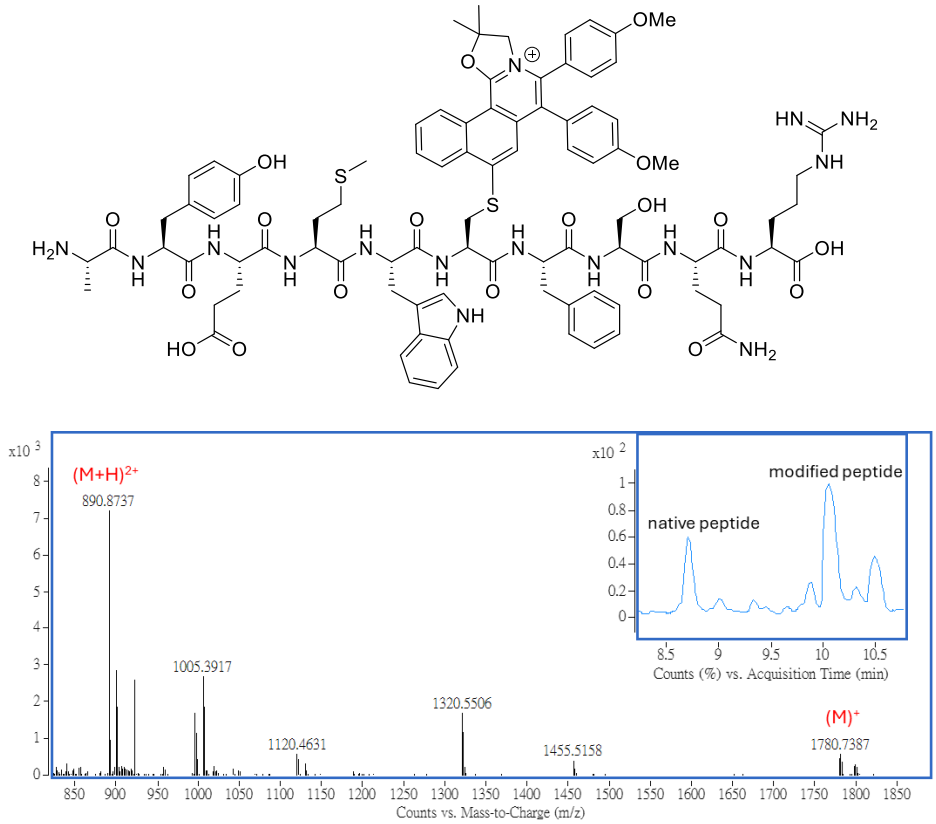


Figure S25. Mass spectrum and total ion chromatogram (inset) of modified peptide **2a**. **MS** (ESI) *m/z*: calcd. for $C_{90}H_{107}N_{16}O_{19}S_2^+$ $[M]^+$ 1780.73, found 1780.73.

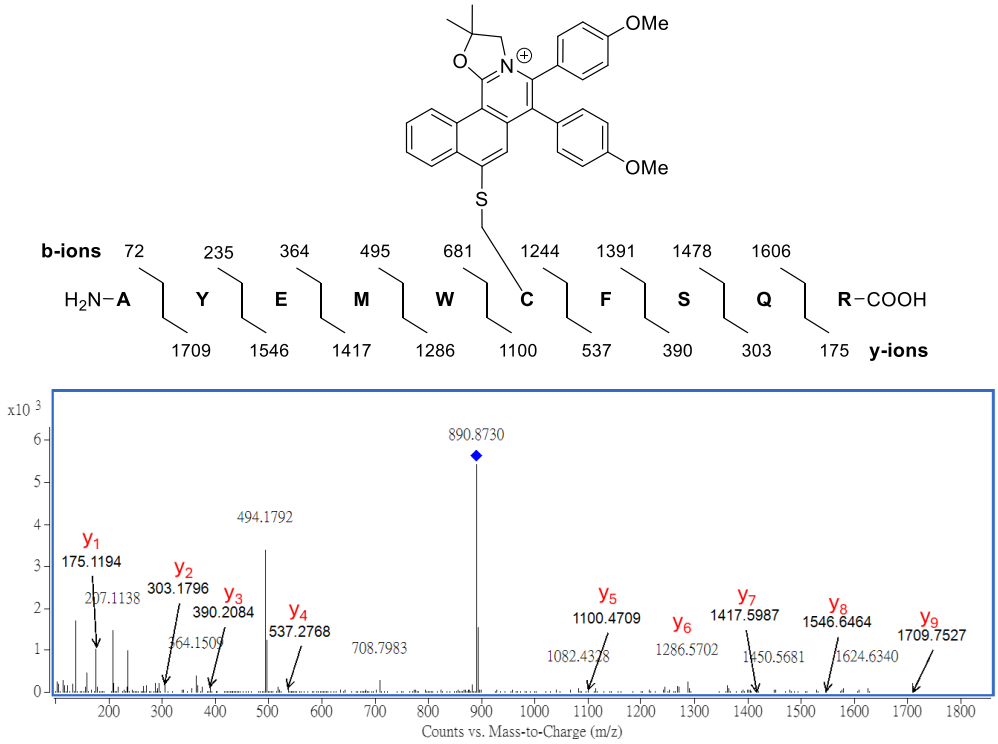


Figure S26. MS/MS spectrum of modified peptide **2a** (ESI source, doubly charged ion of *m/z* = 890.8).

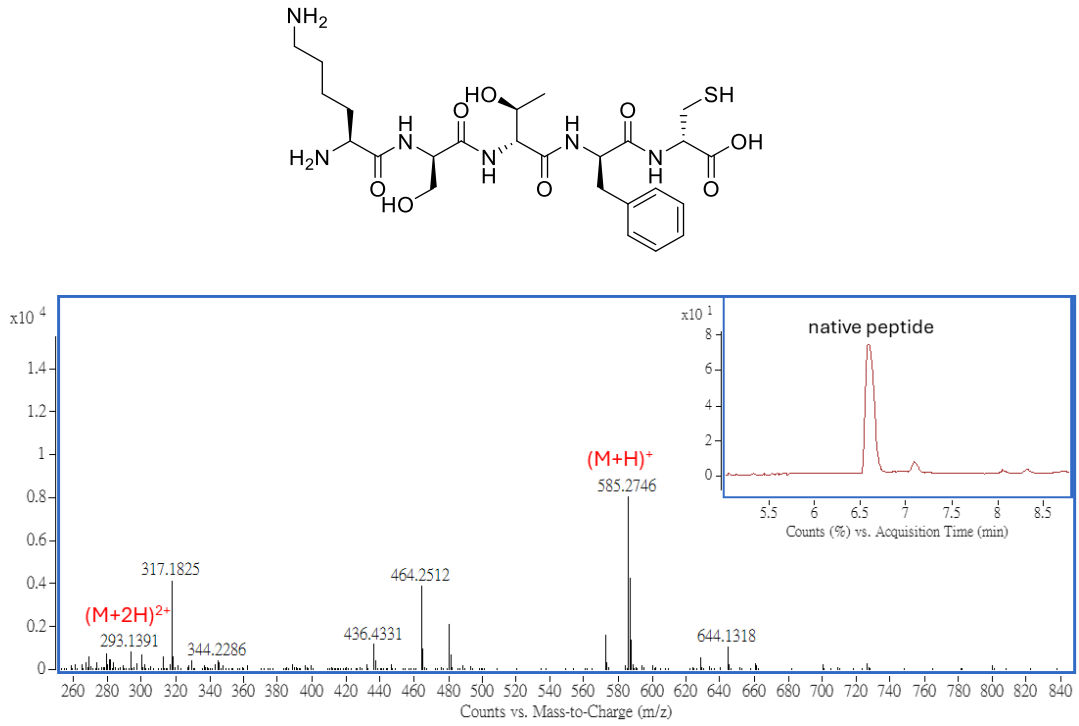


Figure S27. Mass spectrum and total ion chromatogram (inset) of native peptide **3** (KSTFC). **MS** (ESI) *m/z*: calcd. for $C_{25}H_{41}N_6O_8S^+$ $[M+H]^+$ 585.27, found 585.27.

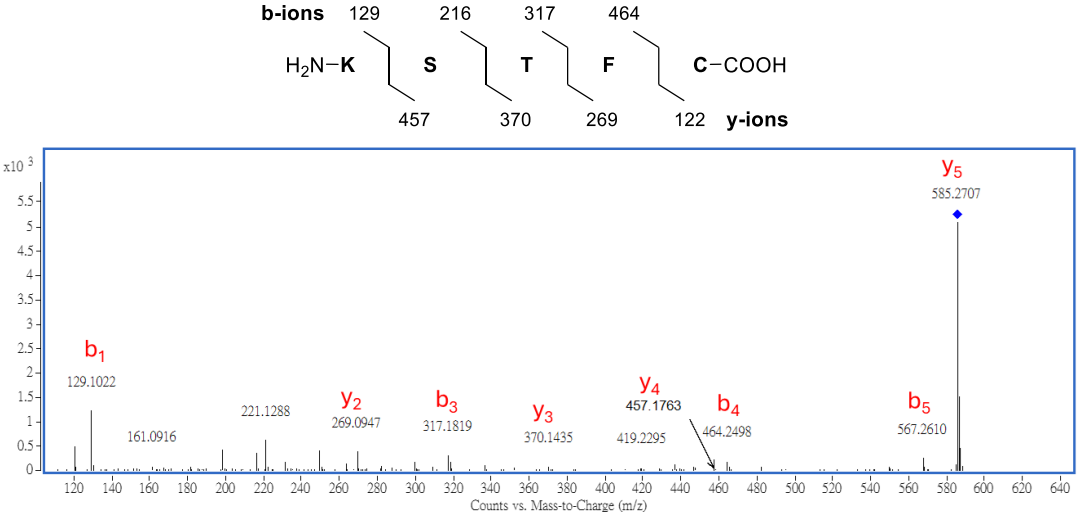


Figure S28. MS/MS spectrum of native peptide **3** (KSTFC) (ESI source, singly charged ion of *m/z* = 585.2).

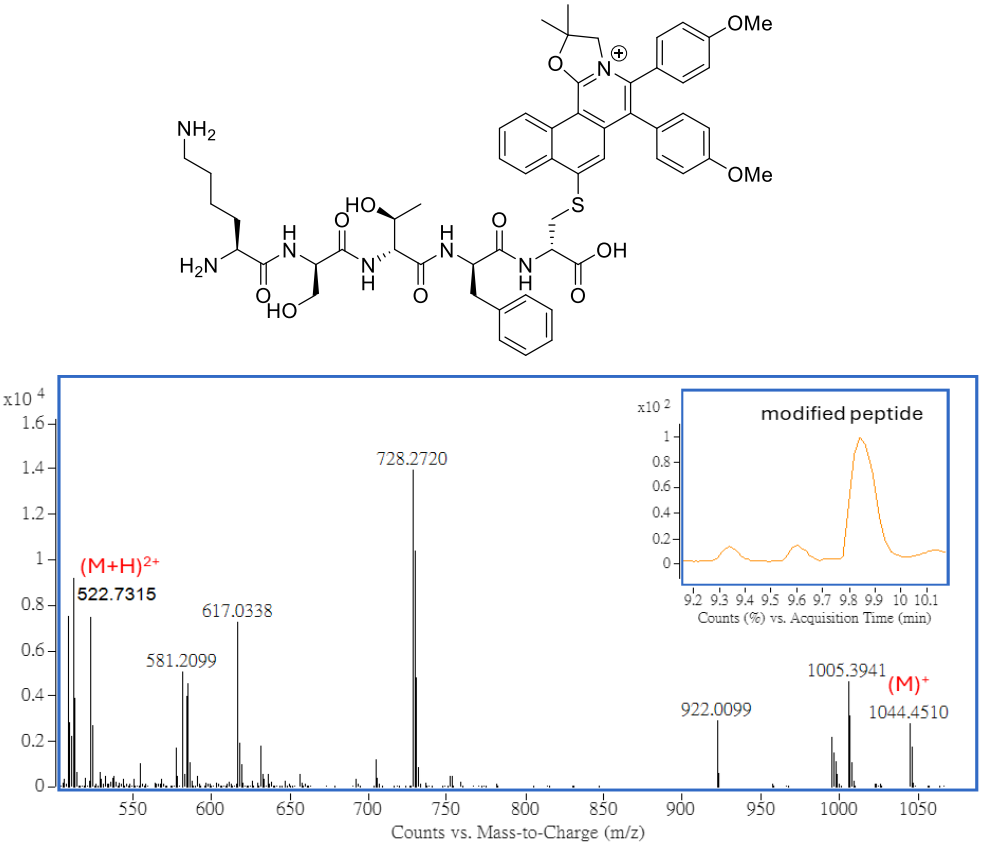


Figure S29. Mass spectrum and total ion chromatogram (inset) of modified peptide **3a**. **MS** (ESI) *m/z*: calcd. for $C_{56}H_{66}N_7O_{11}S^+$ $[M]^+$ 1044.45 found 1044.45.

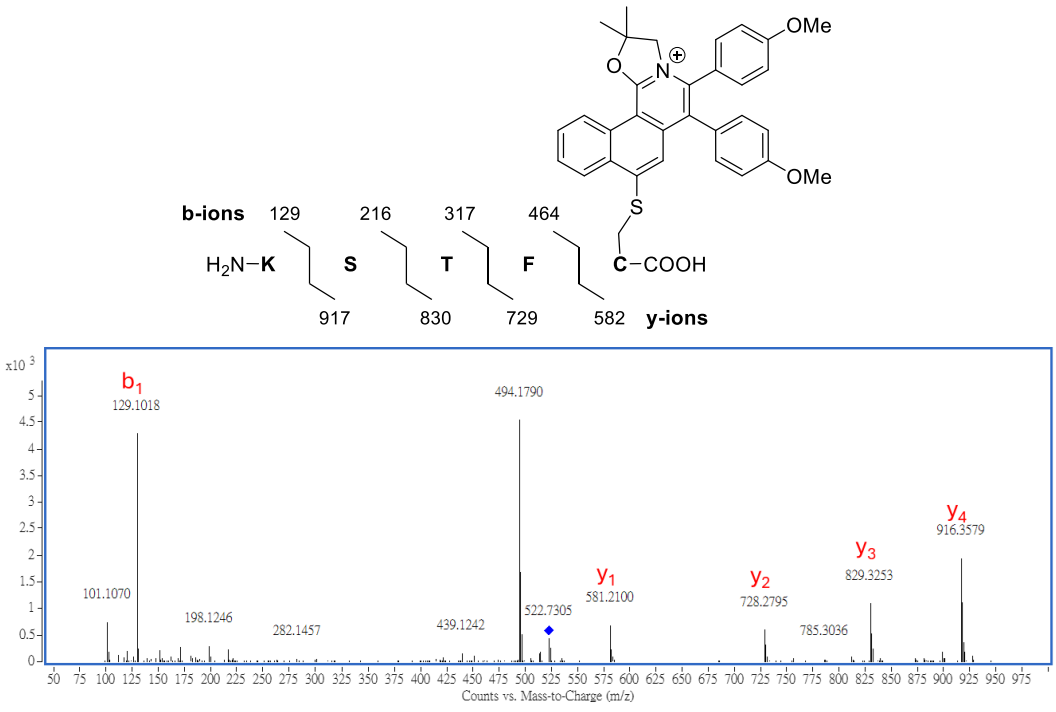


Figure S30. MS/MS spectrum of modified peptide **3a** (ESI source, doubly charged ion of *m/z* = 522.7).

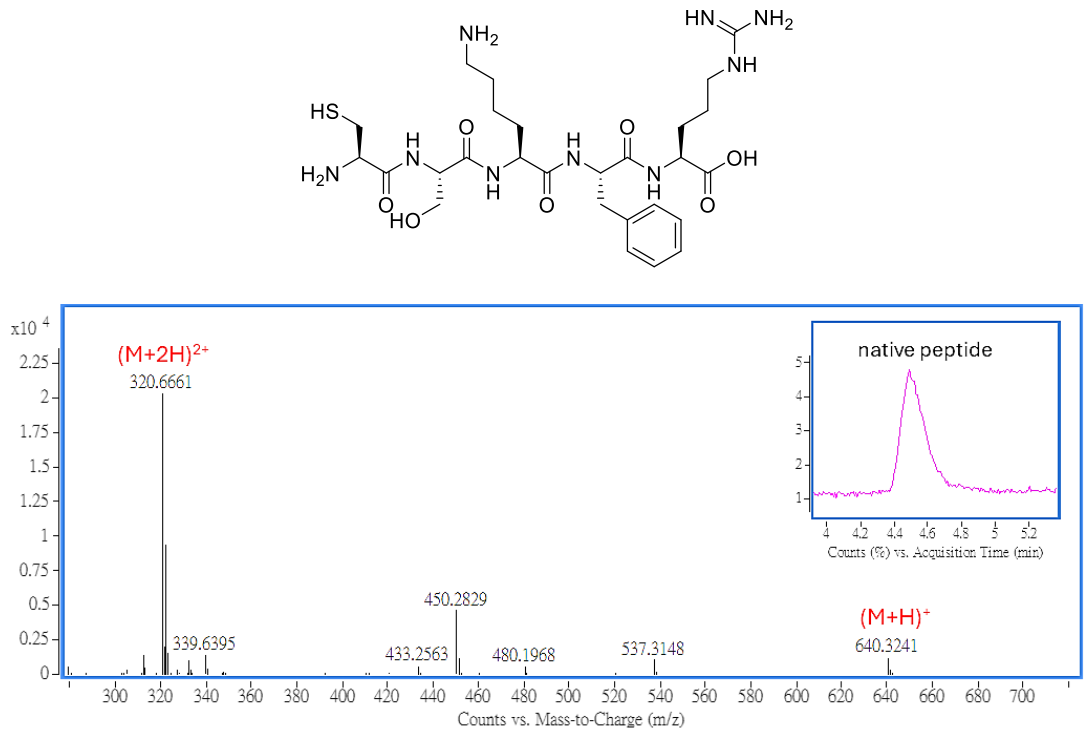
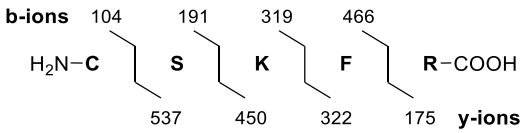


Figure S31. Mass spectrum and total ion chromatogram (inset) of native peptide **4** (CSKFR). **MS** (ESI) *m/z*: calcd. for $C_{27}H_{46}N_9O_7S^+$ $[M+H]^+$ 640.32, found 640.32.



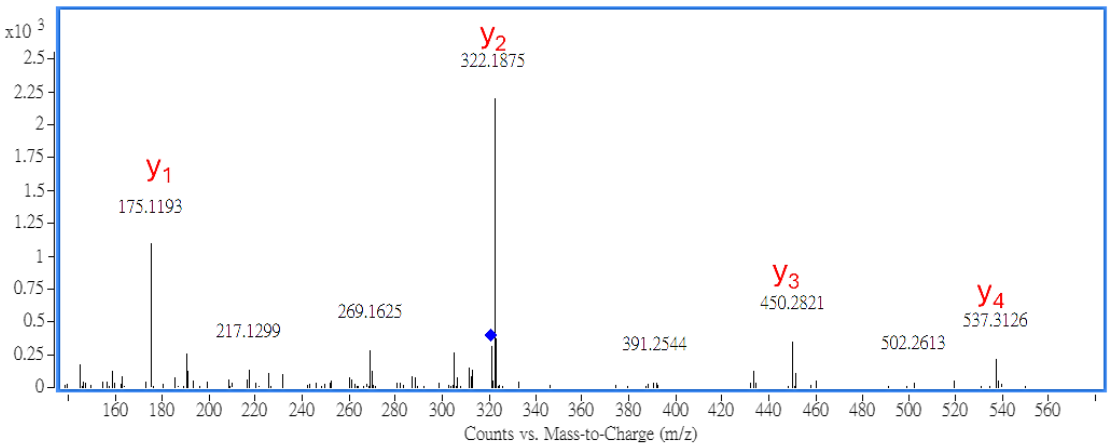


Figure S32. MS/MS spectrum of native peptide **4** (CSKFR) (ESI source, doubly charged ion of *m/z* = 320.6).

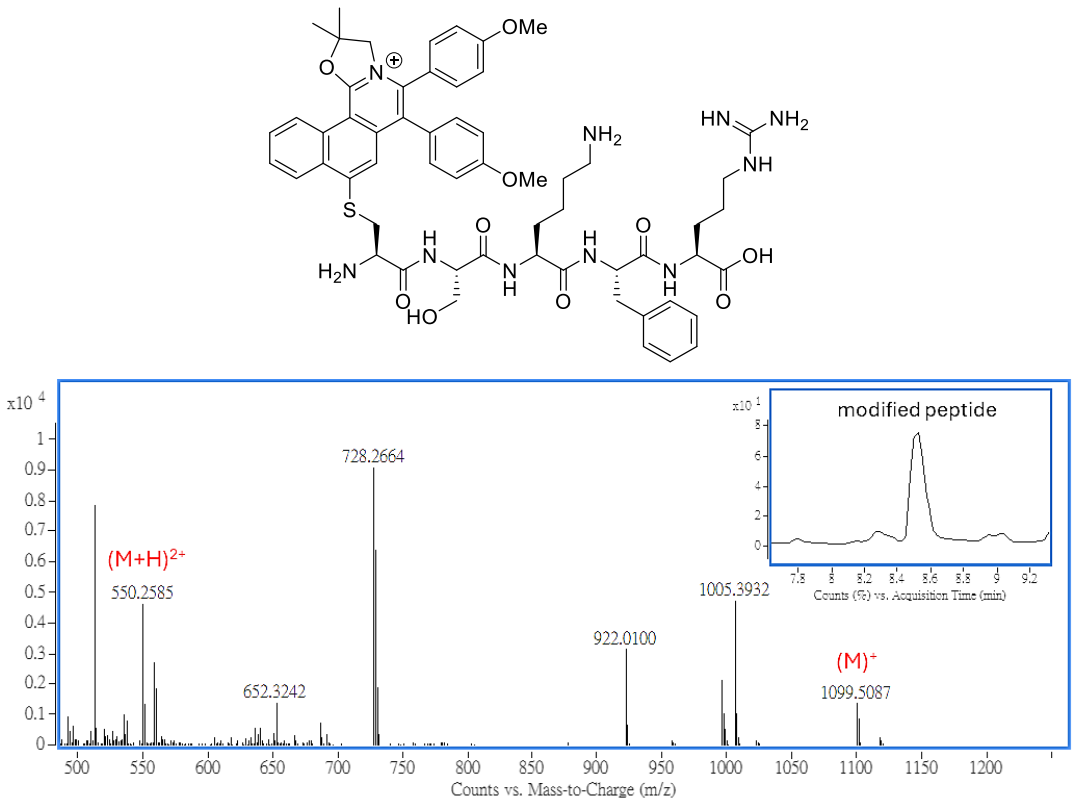


Figure S33. Mass spectrum and total ion chromatogram (inset) of modified peptide **4a**. **MS** (ESI) *m/z*: calcd. for $C_{58}H_{71}N_{10}O_{10}S^+$ $[M]^+$ 1099.50, found 1099.50.

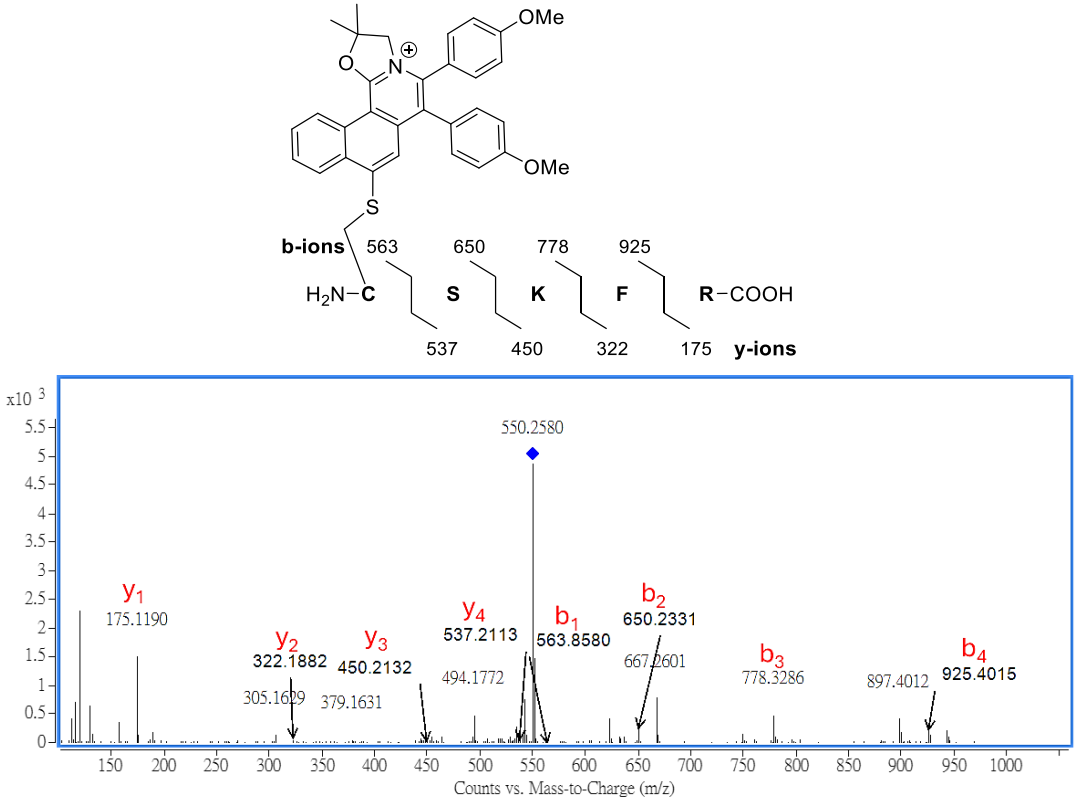


Figure S34. MS/MS spectrum of modified peptide **4a** (ESI source, doubly charged ion of *m/z* = 550.2).

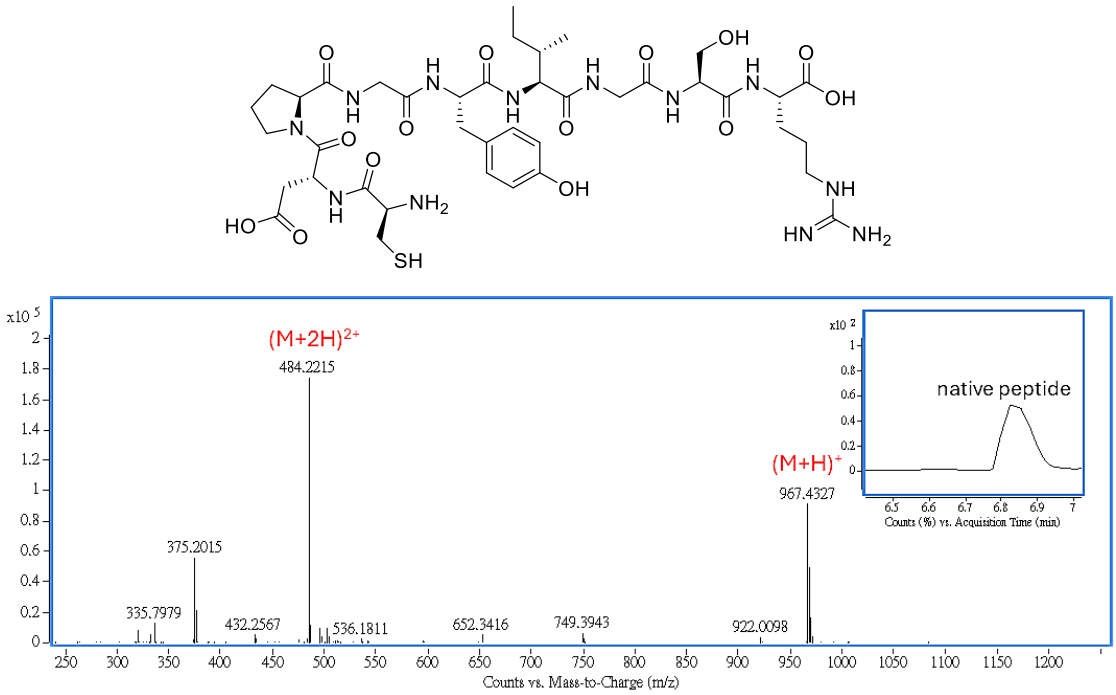


Figure S35. Mass spectrum and total ion chromatogram (inset) of native peptide **5** (CDPGYIGSR). **MS** (ESI) *m/z*: calcd. for $C_{40}H_{63}N_{12}O_{14}S^+$ $[M+H]^+$ 967.43, found 967.43.

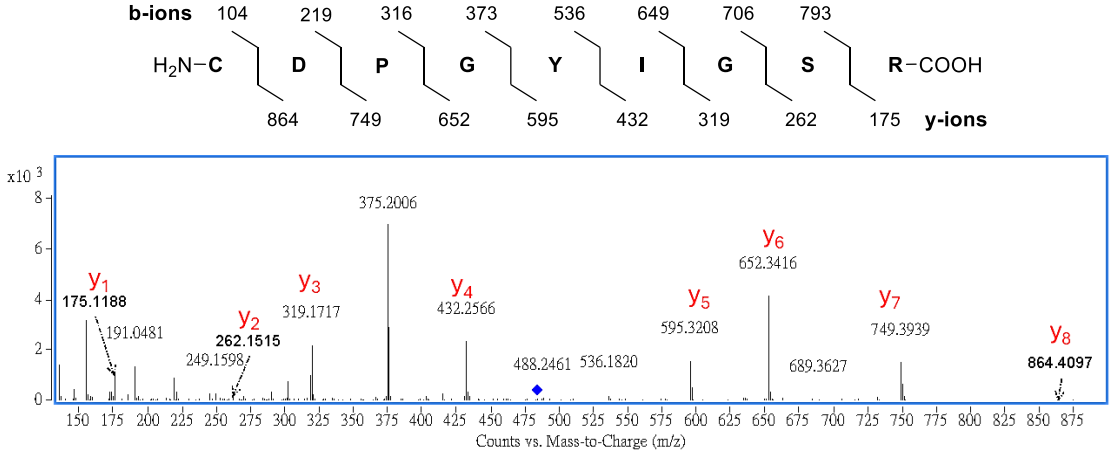


Figure S36. MS/MS spectrum of native peptide **5** (CDPGYIGSR) (ESI source, doubly charged ion of *m/z* = 484.2).

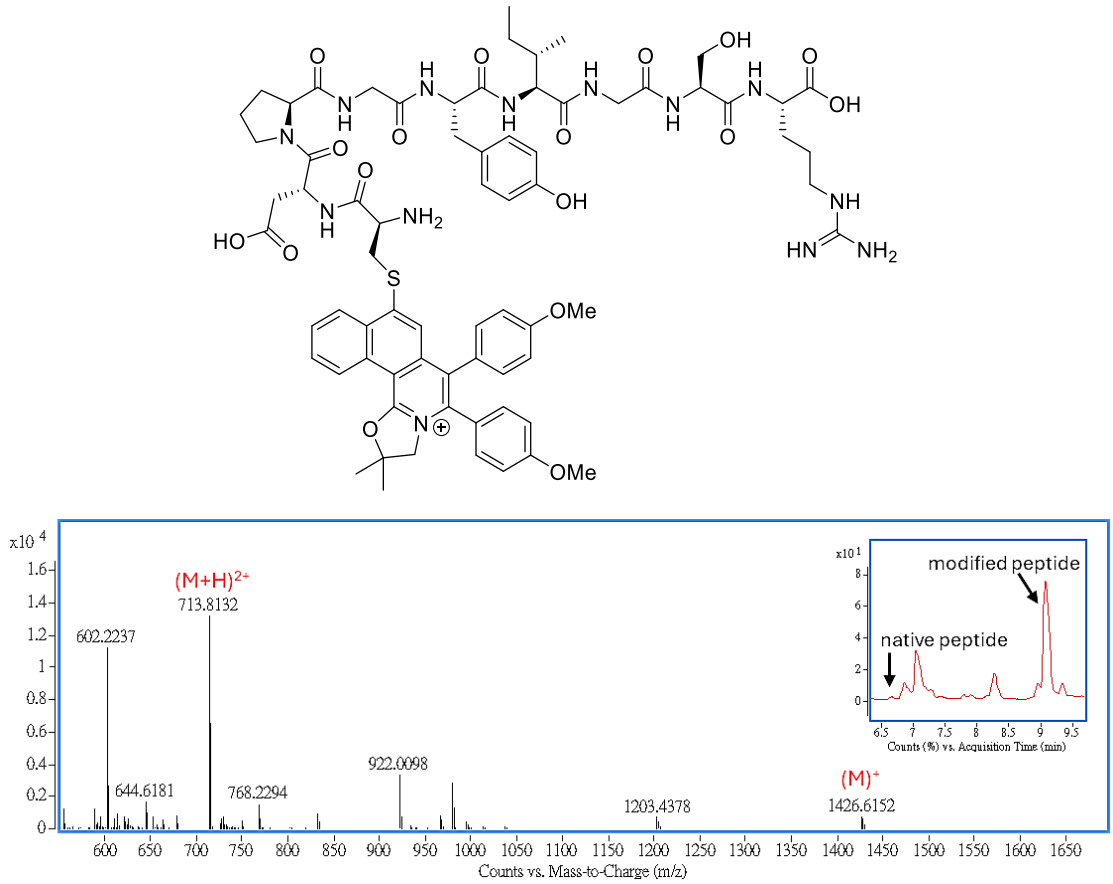


Figure S37. Mass spectrum and total ion chromatogram (inset) of modified peptide **5a**. **MS** (ESI) calcd. for $C_{71}H_{88}N_{13}O_{17}S^+$ $[M]^+$ 1426.61, found 1426.61.

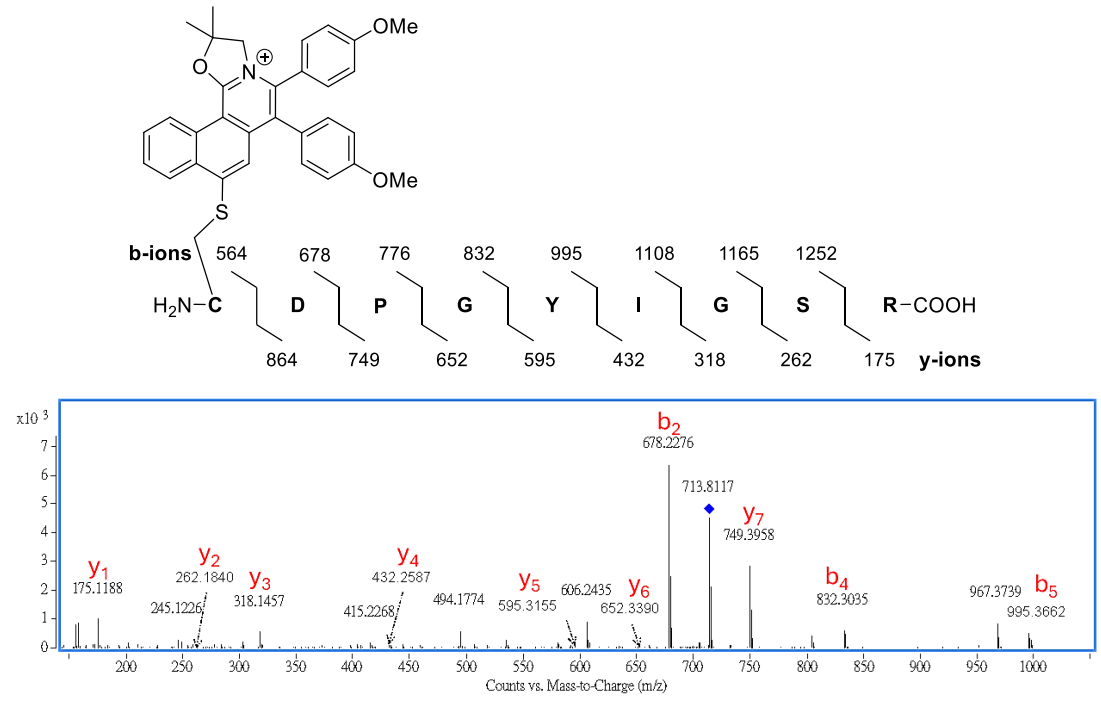


Figure S38. MS/MS spectrum of modified peptide **5a** (ESI source, doubly charged ion of *m/z* = 713.8).

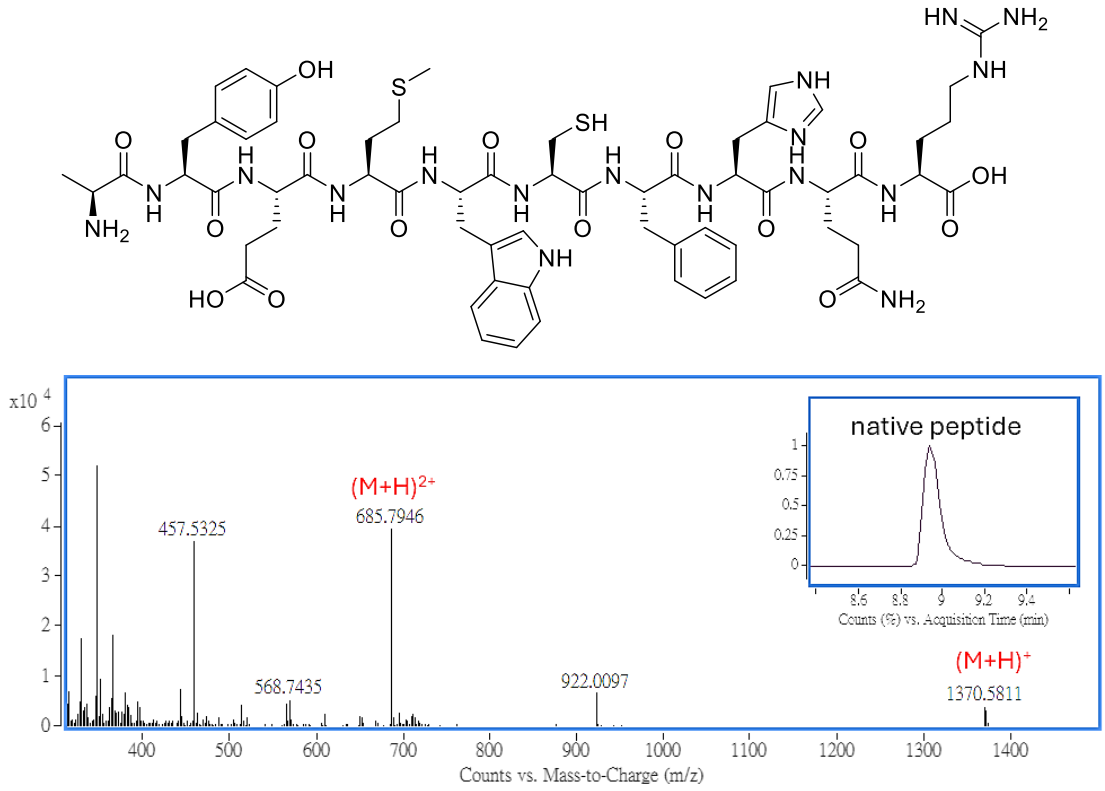


Figure S39. Mass spectrum and total ion chromatogram (inset) of native peptide **6** (AYEMWCFHQR). **MS** (ESI) *m/z*: calcd. for $C_{62}H_{84}N_{17}O_{15}S_2^+$ $[M+H]^+$ 1370.57, found 1370.58.

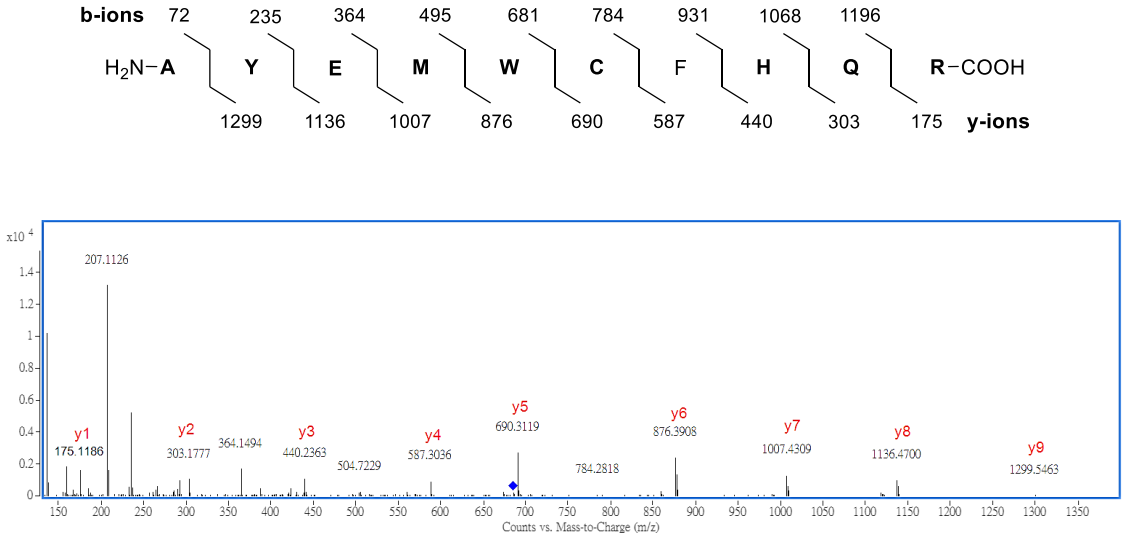


Figure S40. MS/MS spectrum of native peptide **6** (AYEMWCFHQR) (ESI source, doubly charged ion of *m/z* = 685.7).

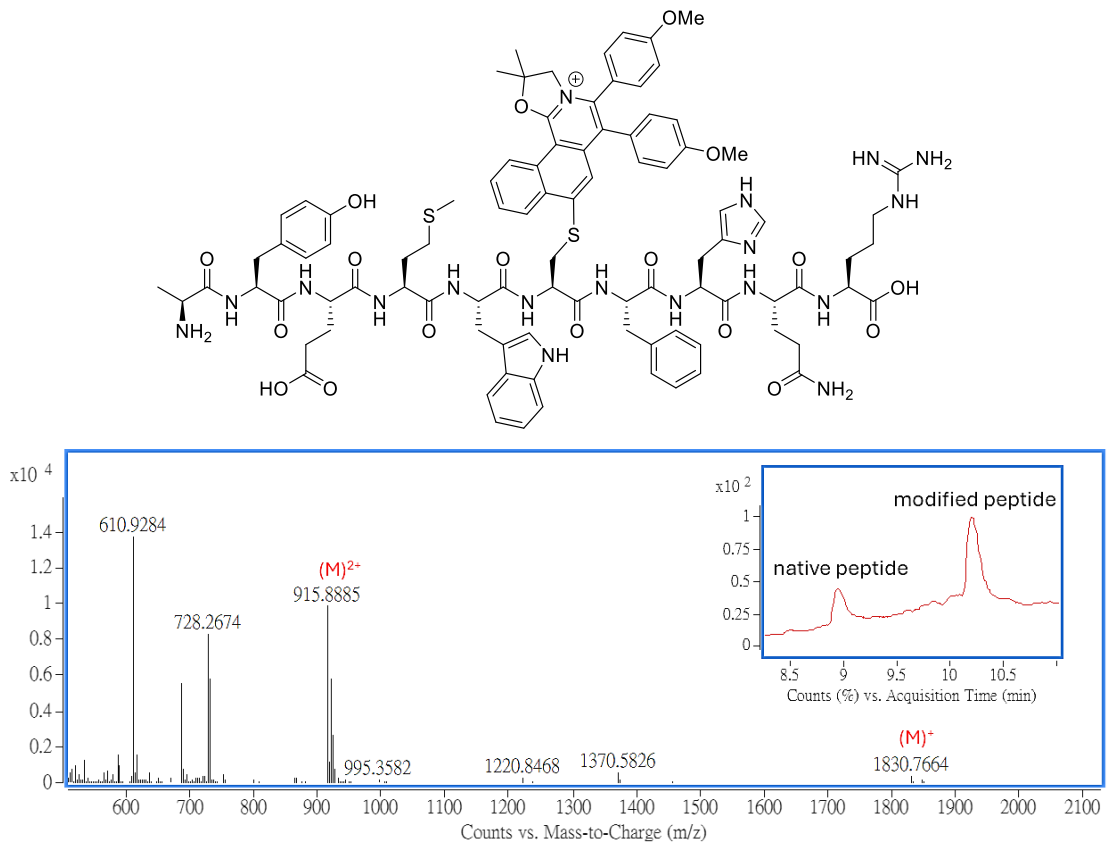


Figure S41. Mass spectrum and total ion chromatogram (inset) of modified peptide **6a**. **MS** (ESI) calcd. for $C_{93}H_{109}N_{18}O_{18}S_2^+$ $[M]^+$ 1830.76, found 1830.76.

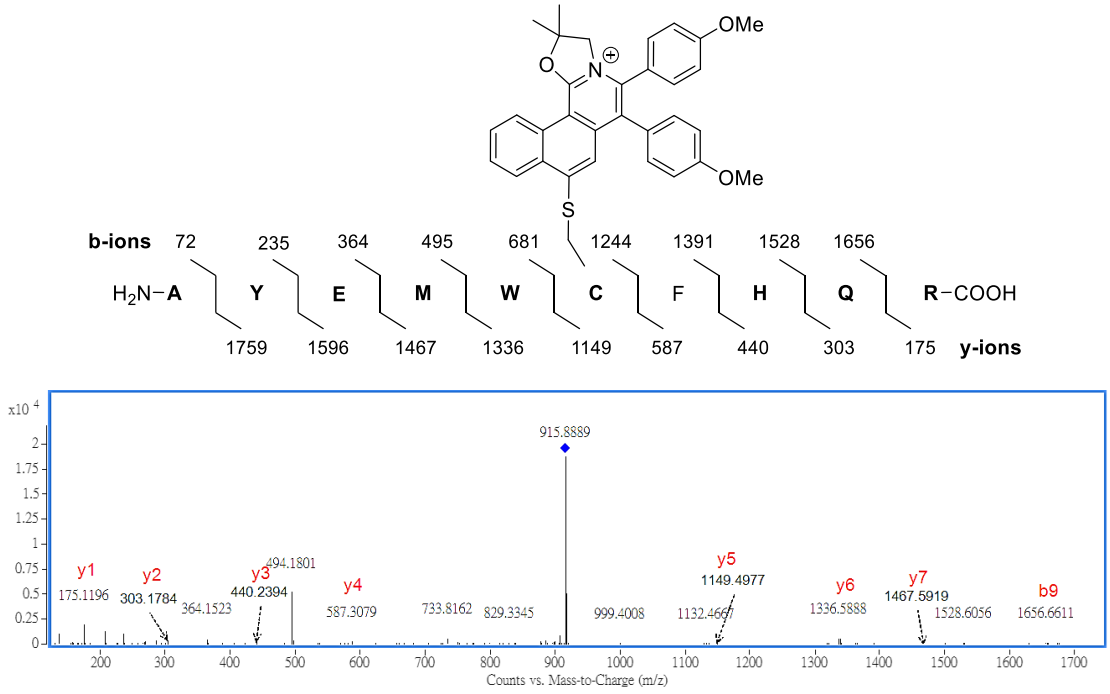


Figure S42. MS/MS spectrum of modified peptide **6a** (ESI source, doubly charged ion of m/z = 915.8).

General Procedure for UPLC-PDA for Modification of Peptides by oxazoliniums

Crude reaction mixtures of peptide modification by oxazoliniums **oxa-2-4** were subjected to UPLC-PDA analysis. UPLC-PDA analysis was performed by using Waters ACQUITY H-Class UPLC with PDA Detector, and an Agilent ZORBAX RRHD SB300-C18 (1.8 μm, 2.1 x 100 mm) column. 10 μL of sample was injected with a flow rate of 0.2 mL/min. Mobile phase A was made of Milli-Q® water containing 0.1% formic acid. Mobile phase B was made of HPLC grade acetonitrile containing 0.1% formic acid. PDA analysis was conducted at $\lambda = 254$ nm.

Table S6. The LC gradient for UPLC-PDA analysis.

Time (min)	A (%)	B (%)	Flow rate (mL/min)
0	95	5	0.2
3	95	5	0.2
15	5	95	0.2
16	5	95	0.2
17	95	5	0.2
20	95	5	0.2

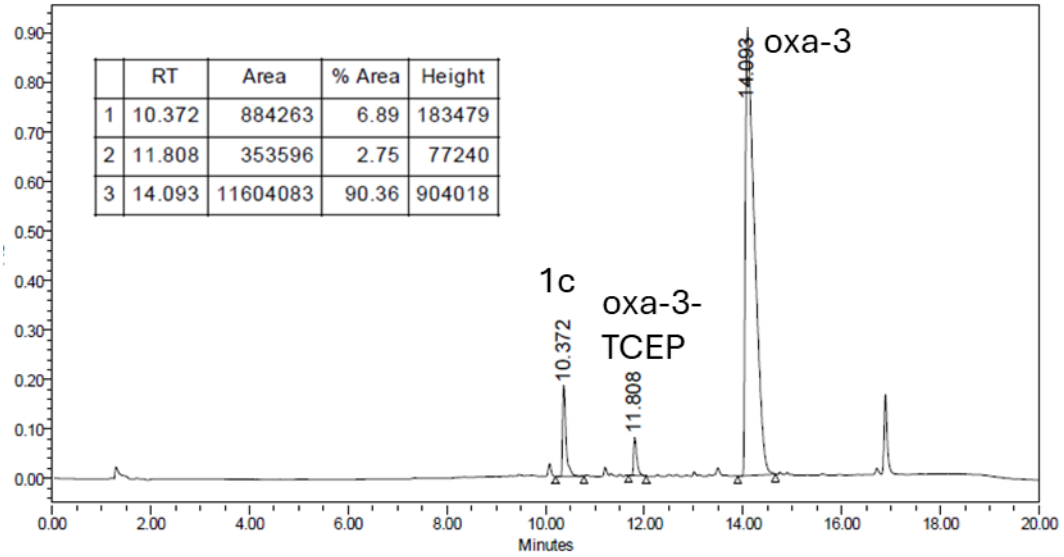


Figure S43. LC chromatogram of crude mixture of modified peptide **1c** at λ = 360 nm.

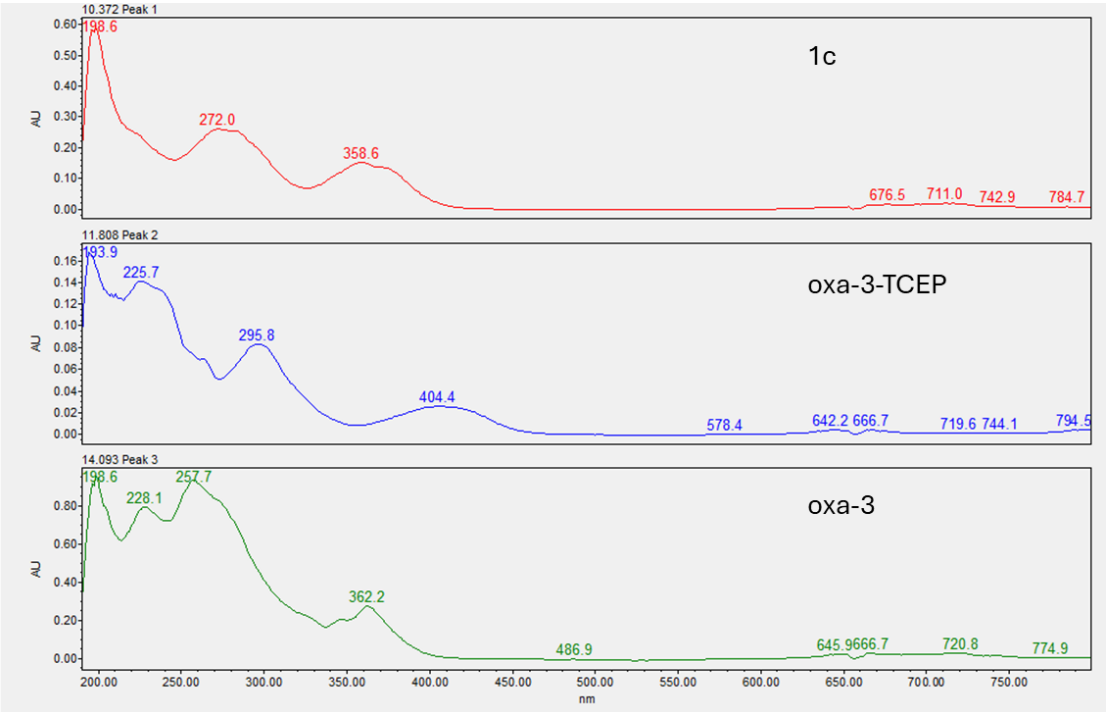


Figure S44. UV spectra at λ = 254 nm of crude mixture of modified peptide **1c**

Note: **Oxa-3-TCEP** was observed by MS in the control crude mixture of **oxa-3** and TCEP in PBS. The fraction from UPLC-PDA analysis at 11.808 minute was collected and subjected to LC/MS analysis with the same conditions as stated in page S16. Under

the conditions for LC/MS analysis, the peak was eluted at 10.5 minute and was found to have the same m/z found in both crude reaction mixture and crude control mixture.

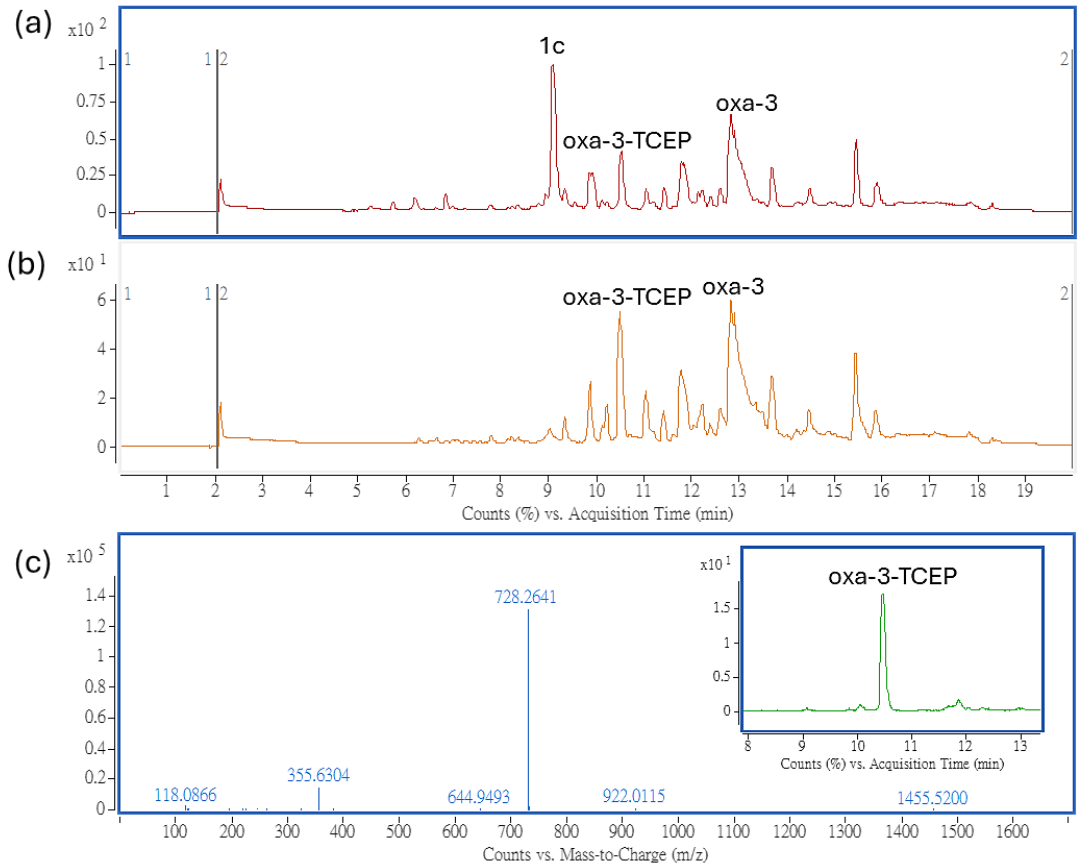


Figure S45. (a) Total ion chromatogram for the crude mixture of peptide model **1c**. (b) TIC for the control crude mixture without peptide **1**. (c) Mass spectrum and total ion chromatogram (inset) for **oxa-3-TCEP** fraction. **MS** (ESI) *m/z*: calcd. for $C_{40}H_{40}FNO_9P$ $[M]^+$ 728.24, found 728.26.

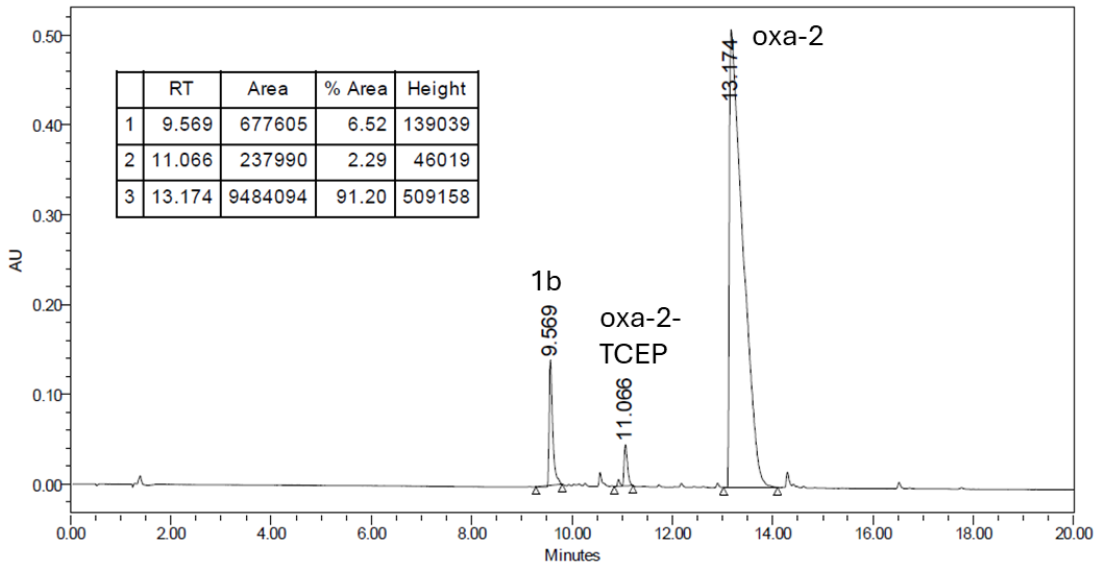


Figure S46. LC chromatogram of crude mixture of modified peptide **1b** at λ = 360 nm.

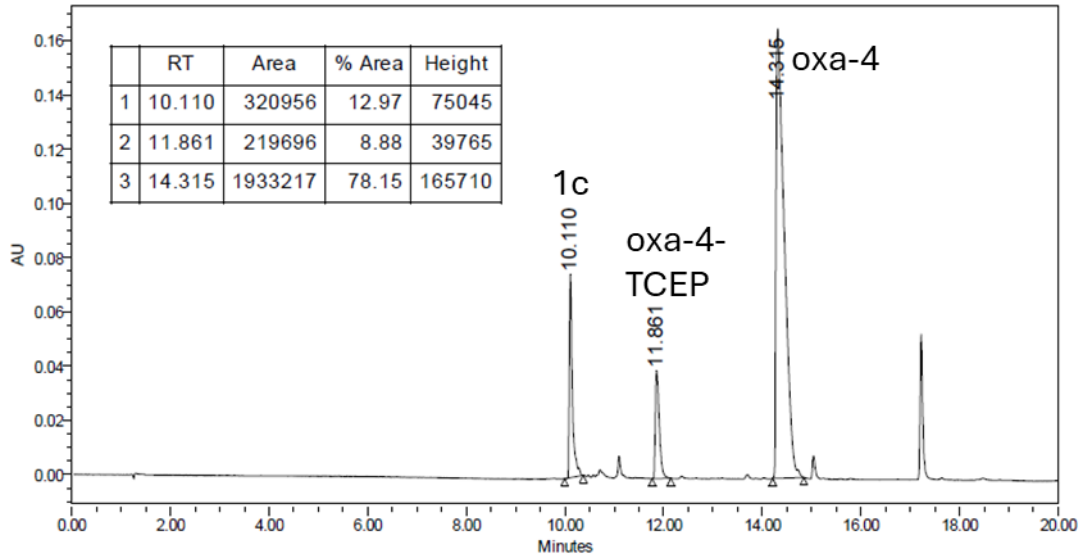


Figure S47. LC chromatogram of crude mixture of modified peptide **1c** at λ = 360 nm.

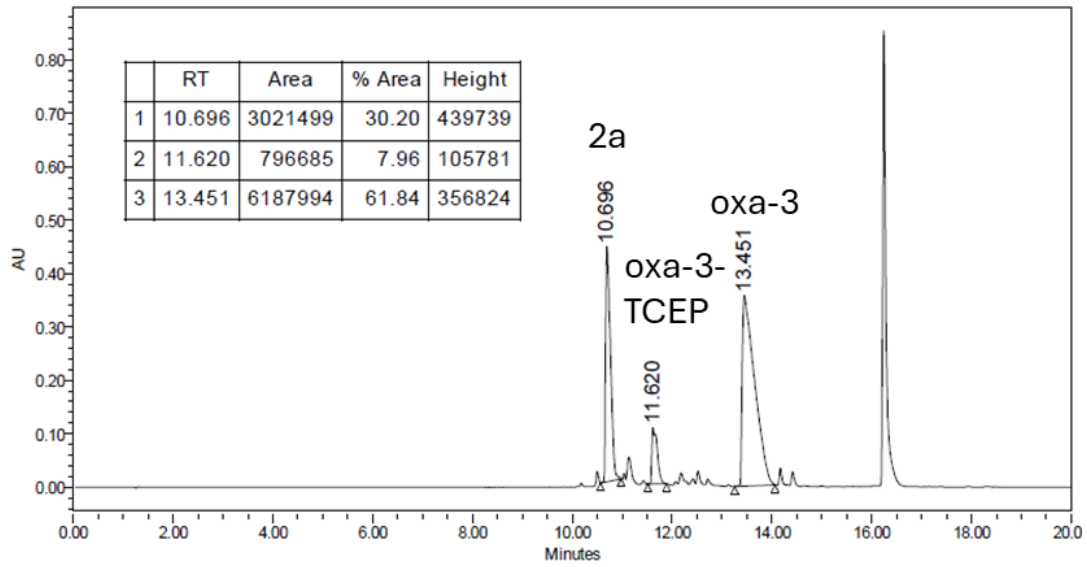


Figure S48. LC chromatogram of crude mixture of modified peptide **2a** at λ = 360 nm.

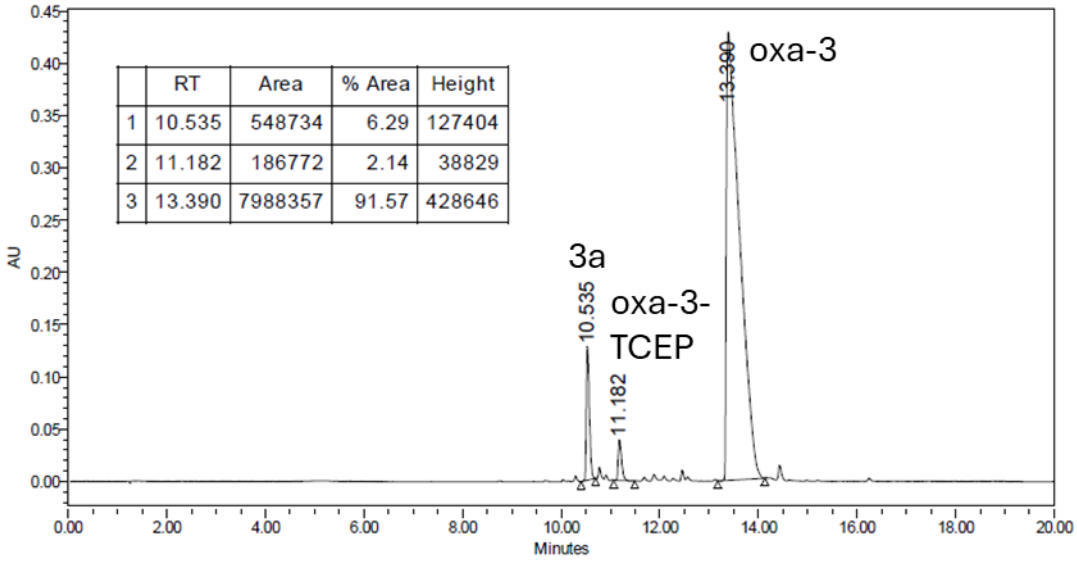


Figure S49. LC chromatogram of crude mixture of modified peptide **3a** at λ = 360 nm.

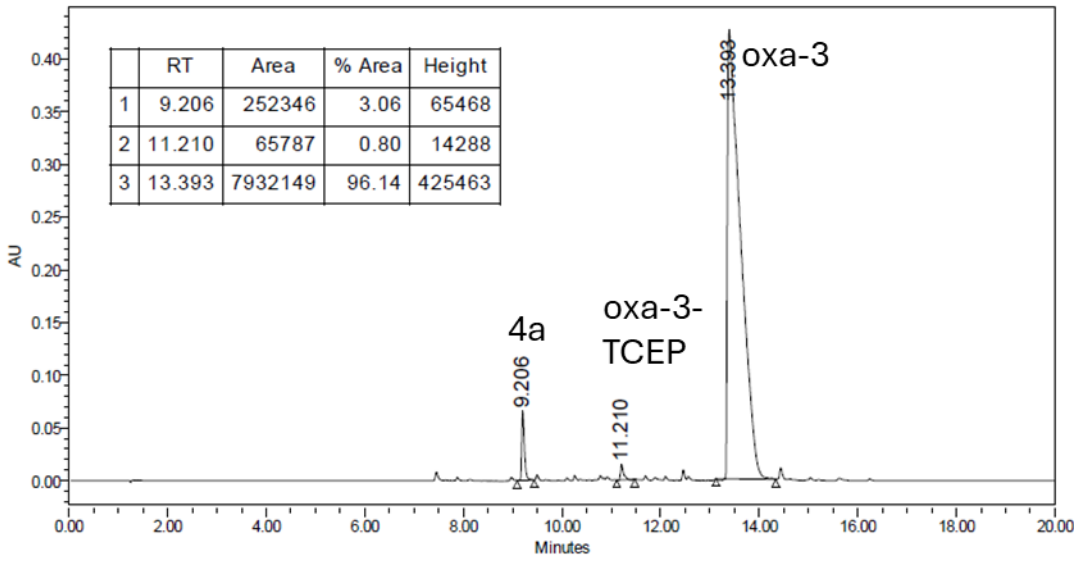


Figure S50. LC chromatogram of crude mixture of modified peptide **4a** at λ = 360 nm.

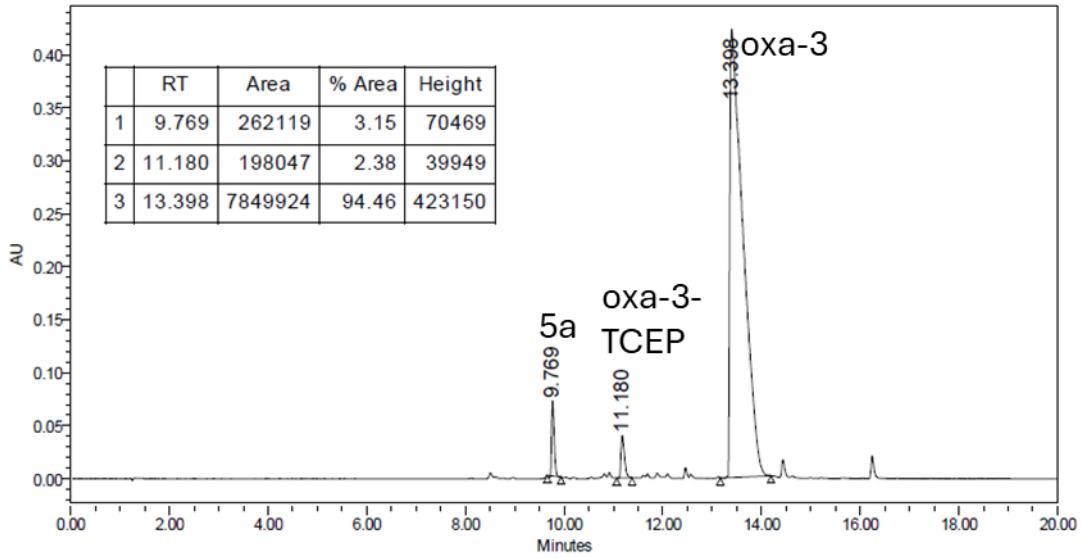


Figure S51. LC chromatogram of crude mixture of modified peptide **5a** at λ = 360 nm.

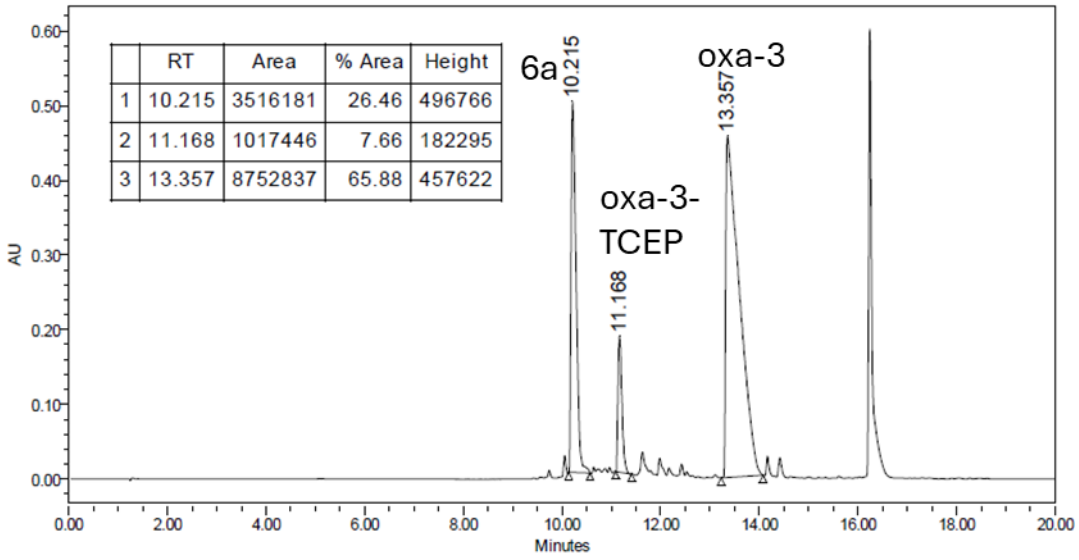


Figure S52. LC chromatogram of crude mixture of modified peptide **6a** at λ = 360 nm.

LC–MS Analysis of Protein Modification

The crude reaction mixture from the protein labelling for SDS-PAGE experiment were subjected to LC-MS analysis. LC-MS analyses were performed by using an Agilent 6540 UHD Accurate-Mass Q-TOF LC/MS system equipped with an ion spray source and an Agilent 1290 Infinity LC, using an Agilent ZORBAX RRHD SB300-C3 (1.8 μm, 2.1 x 100 mm) column. 3 μL of sample was injected with a flow rate of 0.3 mL/min. Mobile phase A was made of Milli-Q® water containing 0.1% formic acid. Mobile phase B was made of HPLC grade acetonitrile containing 0.1% formic acid. Operating conditions optimized for the detection of reaction mixture were the following: Gas temperature: 300 °C, Drying gas: 8 L/min, Nebulizer: 35 psig, Sheath gas temperature: 380 °C, Sheath gas flow: 11 L/min, VCap: 3500 V, Nozzle voltage: 1000 V.

Table S7. The LC gradient for LC–MS analysis.

Time (min)	A (%)	B (%)	Flow rate (mL/min)
0	95	5	0.3
2	95	5	0.3
12	5	95	0.3
13	5	95	0.3
13.1	95	5	0.3
15	95	5	0.3

Calculation of Protein Conversion

After data processing by MassHunter, protein conversion at different time intervals was determined by measuring the relative peak intensities of starting and product in the mass spectrum as follows:

$$Protein\ Conversion\ (\%) = \left(1 - \frac{Relative\ Peak\ Intensity\ of\ Starting}{Relative\ Peak\ Intensities\ of\ Starting\ and\ Product}\right) \times\ 100\%$$

General Procedure for Cysteine Arylation of Cysteine-Containing Protein by Fluorescent oxa-3

A mixture of BSA or HSA (10 μL of 1 mM in H_2O, 1 equiv., 0.1 mM) and **oxa-3** (10 μL of 5 mM in DMSO, 5 equiv., 0.5 mM) in 50 mM PBS (pH 7.4)/DMSO (9:1) (80 μL) was reacted at 40 ℃ for 16 h. After the reaction, 5 μL of the crude mixture was drawn and marked up to 100 μL using Milli-Q water. 3 μL of the diluted mixture was taken out for LC-MS analysis. Results are shown in Figures S53-64.

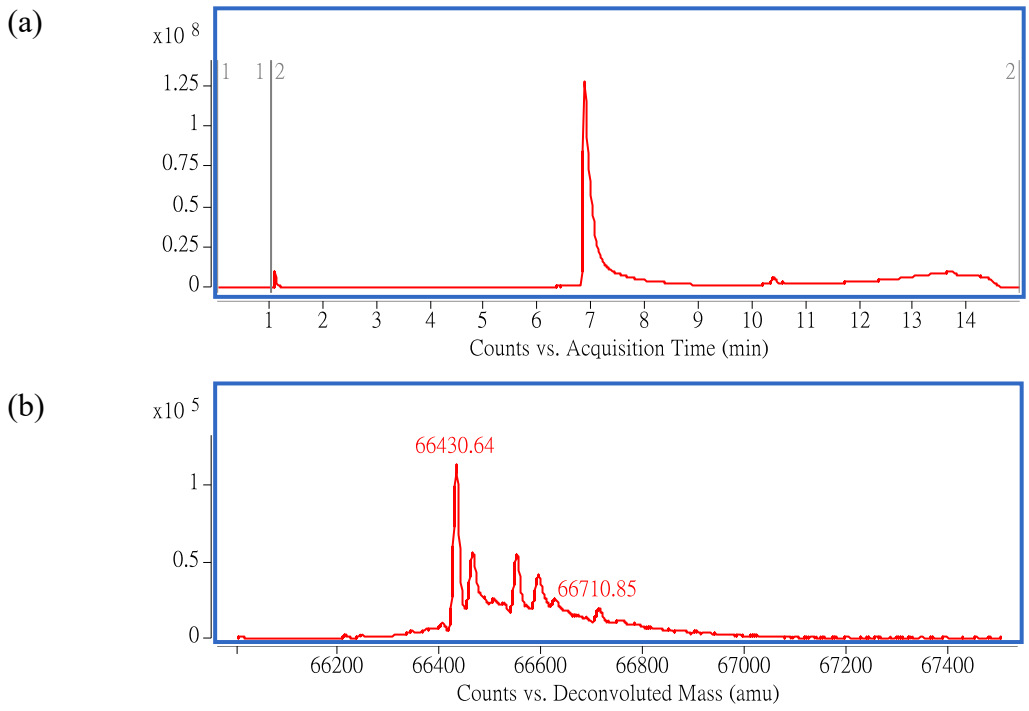


Figure S53. (a) Total ion chromatogram and (b) deconvoluted mass spectrum of non-modified BSA.

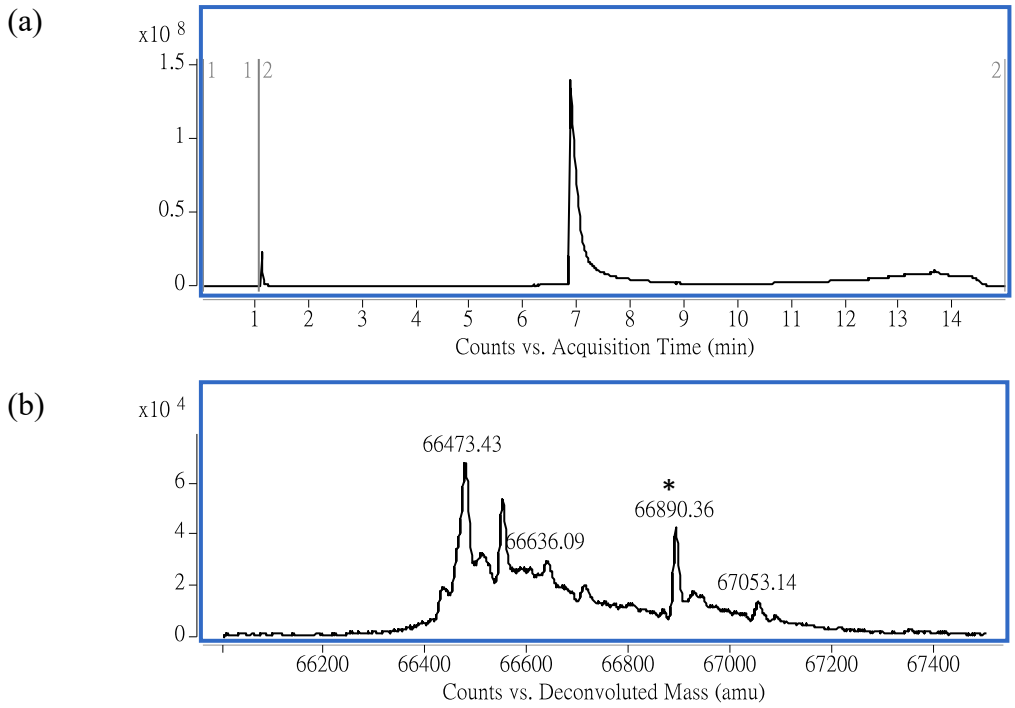


Figure S54. (a) Total ion chromatogram and (b) deconvoluted mass spectrum of the reaction mixture of BSA with 5 equiv. of compound **oxa-3** (* = **oxa-3**-modified BSA).

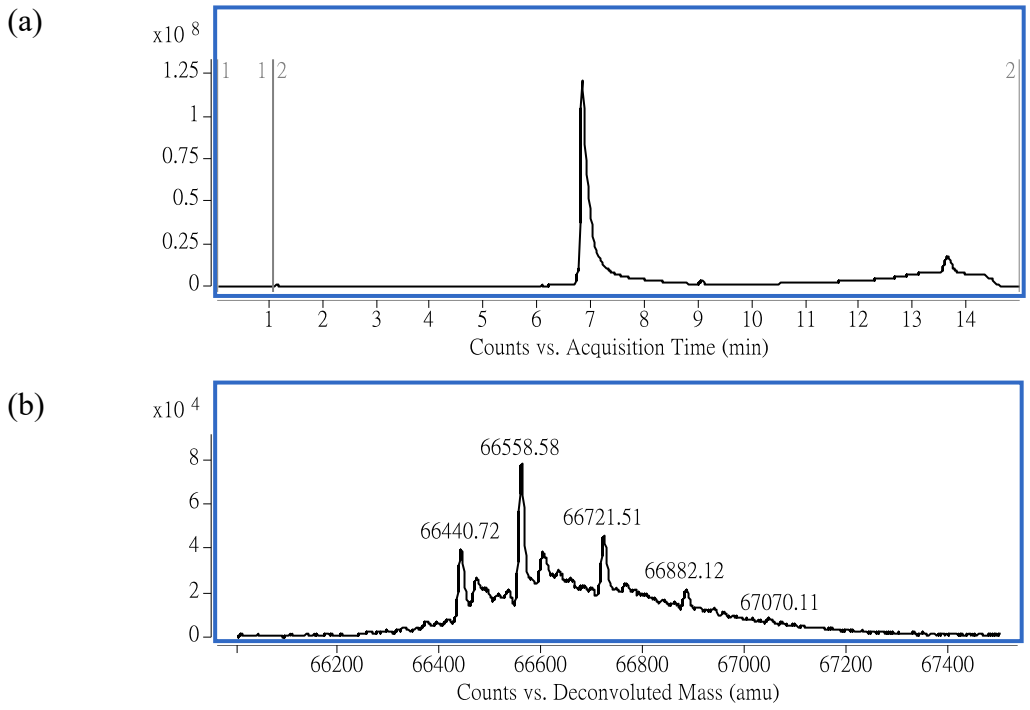


Figure S55. (a) Total ion chromatogram and (b) deconvoluted mass spectrum of non-modified HSA.

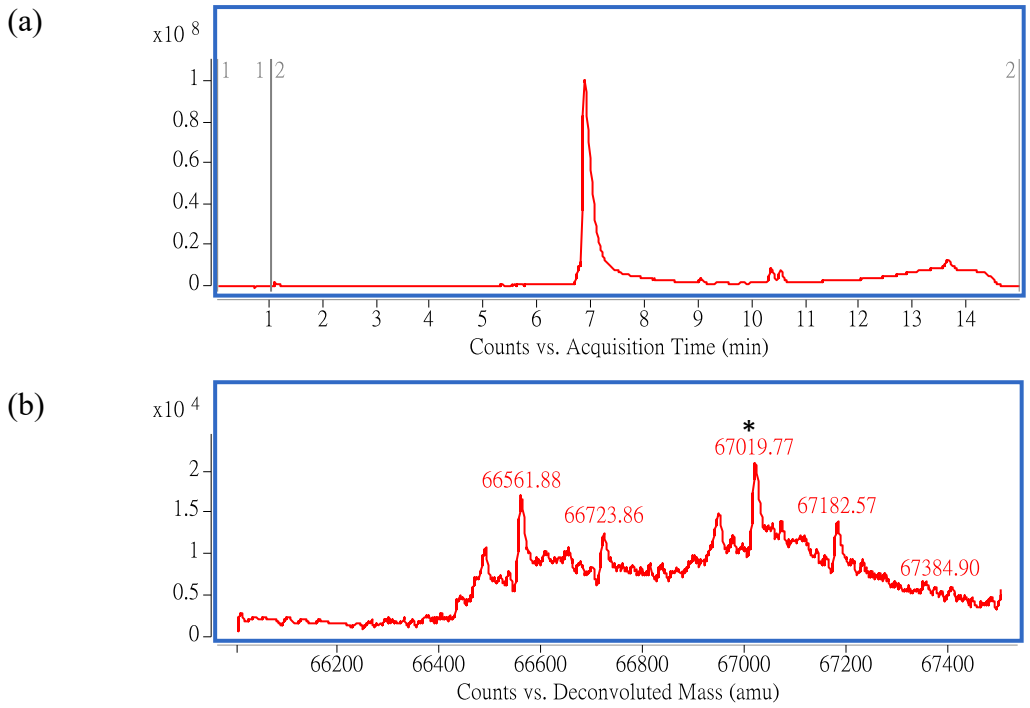


Figure S56. (a) Total ion chromatogram and (b) deconvoluted mass spectrum of the reaction mixture of HSA with 5 equiv. of compound **oxa-3** (* = **oxa-3**-modified HSA).

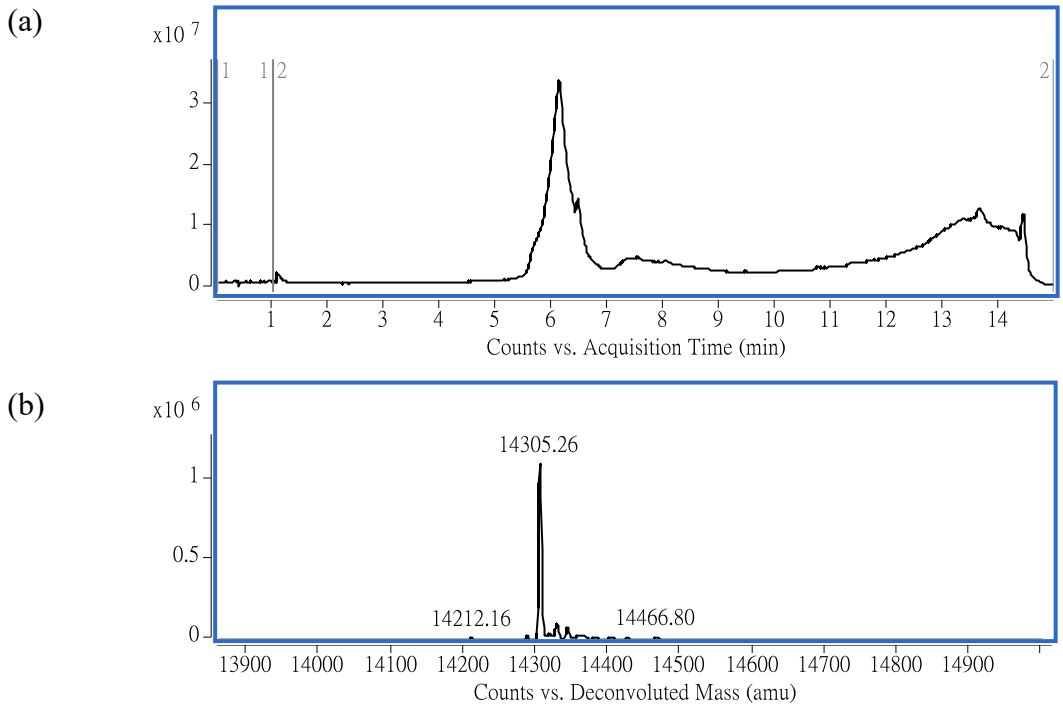


Figure S57. (a) Total ion chromatogram and (b) deconvoluted mass spectrum of non-modified lysozyme.

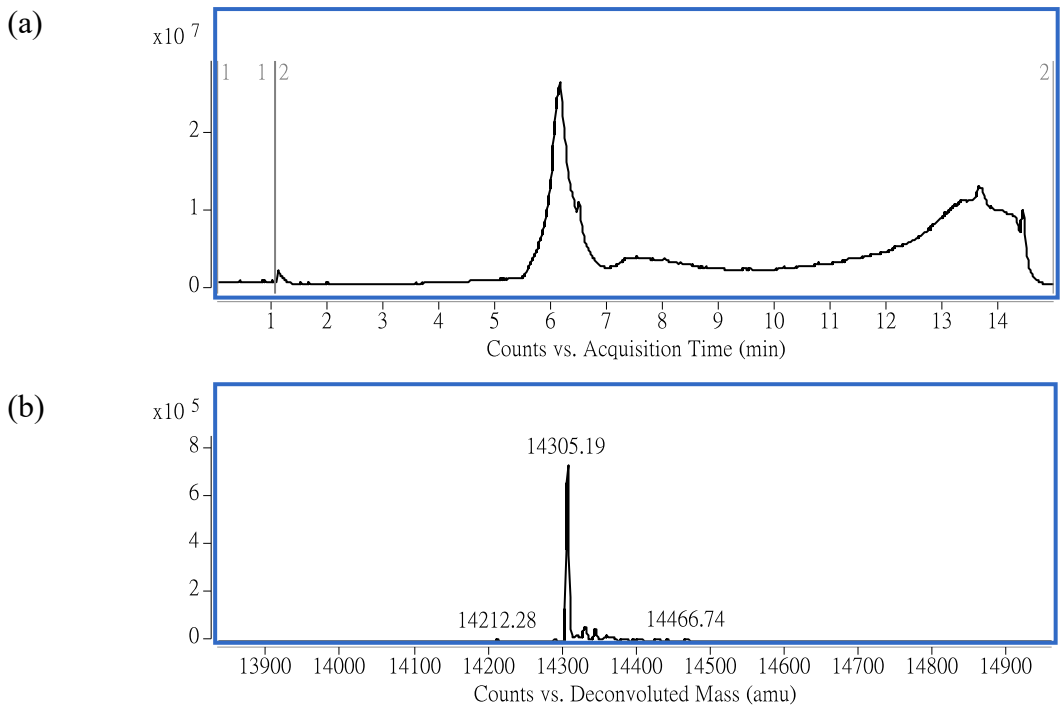


Figure S58. (a) Total ion chromatogram and (b) deconvoluted mass spectrum of the reaction mixture of lysozyme with 5 equiv. of compound **oxa-3**.

Protease Digestion for LC-MS/MS analysis

Using BSA as an example, a ratio of 1:50 to 1:100 of trypsin (V5280, Promega)/BSA and a ratio of 1:10:25 to 1:20:50 of trypsin (V5280, Promega)/chymotrypsin (V1061, Promega)/BSA were used for the protease digestion. The reaction mixture was incubated at 37 °C for 24 h and the protease-digested mixture was quenched by adding TFA to a final concentration of 1% for LC-MS/MS analysis. The above digestion procedures were repeated by using other native proteins and protein conjugates.

LC-MS analyses of the digested protein and protein conjugates were then performed by using an Agilent 6540 UHD Accurate-Mass Q-TOF LC/MS system equipped with an ion spray source and an Agilent 1290 Infinity LC, using an Agilent ZORBAX RRHD SB300-C18 (1.8 μm, 2.1 x 100 mm) column. 10 μL of sample was injected with a flow rate of 0.3 mL/min. Mobile phase A was made of Milli-Q® water containing 0.1% formic acid. Mobile phase B was made of HPLC grade acetonitrile containing 0.1% formic acid. Operating conditions optimized for the detection of reaction mixture were the following: Gas temperature: 300 °C, Drying gas: 8 L/min, Nebulizer: 35 psig, Sheath gas temperature: 380 °C, Sheath gas flow: 11 L/min, VCap: 3500 V, Nozzle voltage: 1000 V.

Table S8. The LC gradient for LC–MS/MS analysis.

Time (min)	A (%)	B (%)	Flow rate (mL/min)
0	95	5	0.3
2	95	5	0.3
32	10	90	0.3
35	5	95	0.3
36	95	5	0.3
40	95	5	0.3

LC-MS/MS Results of oxa-3-modified BSA

Sequence of Bovine Serum Albumin (BSA), PDB ID: 4F5S (MW: 66433)

DTHKSEIAHRFKDLGEEHFKGLVLIAFSQYLQQ**C*(34)**PFDEHVKLVNELTEFA
KTCVADESHAGCEKSLHTLFGDELCKVASLRETYGDMADCCEKQEPERNECF
LSHKDDSPDLPKLKPDPNTLCDEFKADEKKFWGKYLYEIARRHPYFYAPELLY
YANKYNGVFQECCQAEDKGACLLPKIETMREKVLTSSARQRLRCASIQKFGE
RALKAWSVARLSQK*(221)FPKAEFVEVTKLVTDLTKVHKECCHGDLLECADD
RADLAKYICDNQDTISSKLKECCDKPLLEKSHCIAEVEKDAIPENLPPLTADFA
EDKDVCKNYQEAKDAFLGSFLYEYSRRHPEYAVSVLLRLAKEYEATLEECCA
KDDPHACYSTVFDKLKHLVDEPQNLIKQNCDQFEKLGEYGFQNALIVRYTRK
VPQVSTPTLVEVSRSLGKVGTRCCTKPESERMPCTEDYLSLILNRLCVLHEKTP
VSEKVTKCCTESLVNRRPCFSALTPDETYVPKAFDEKLFTFHADICTLPDTEKQ
IKK*(524)QTALVELLKHKPKATEEQLKTVMENFVAFVDKCCAADDKEACFAV
EGPKLVVSTQTALA

C*(amino acid position) = Observed **oxa-3**-modified cysteine

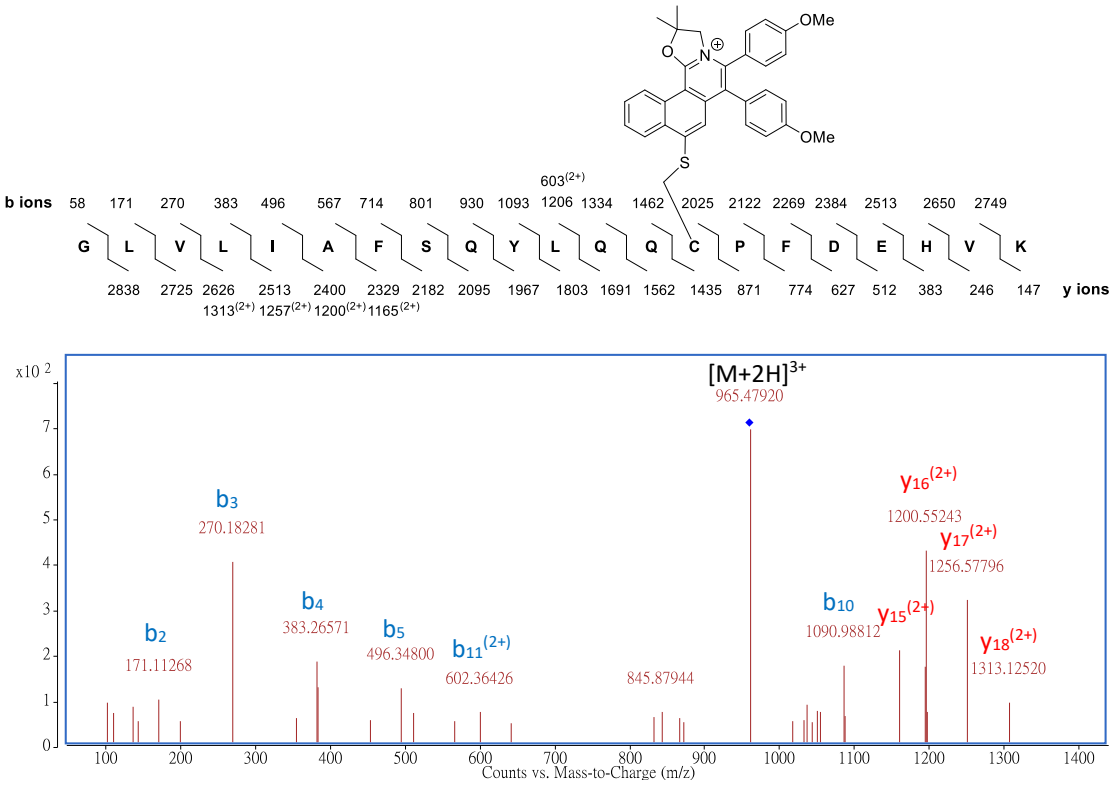


Figure S59. MS/MS spectrum of tryptic peptide GLVLIAFSQYLQQ**C*(34)**PFDEHVK derived from **oxa-3**-modified BSA. (ESI source, triply charged ion of *m/z* = 965.4827).

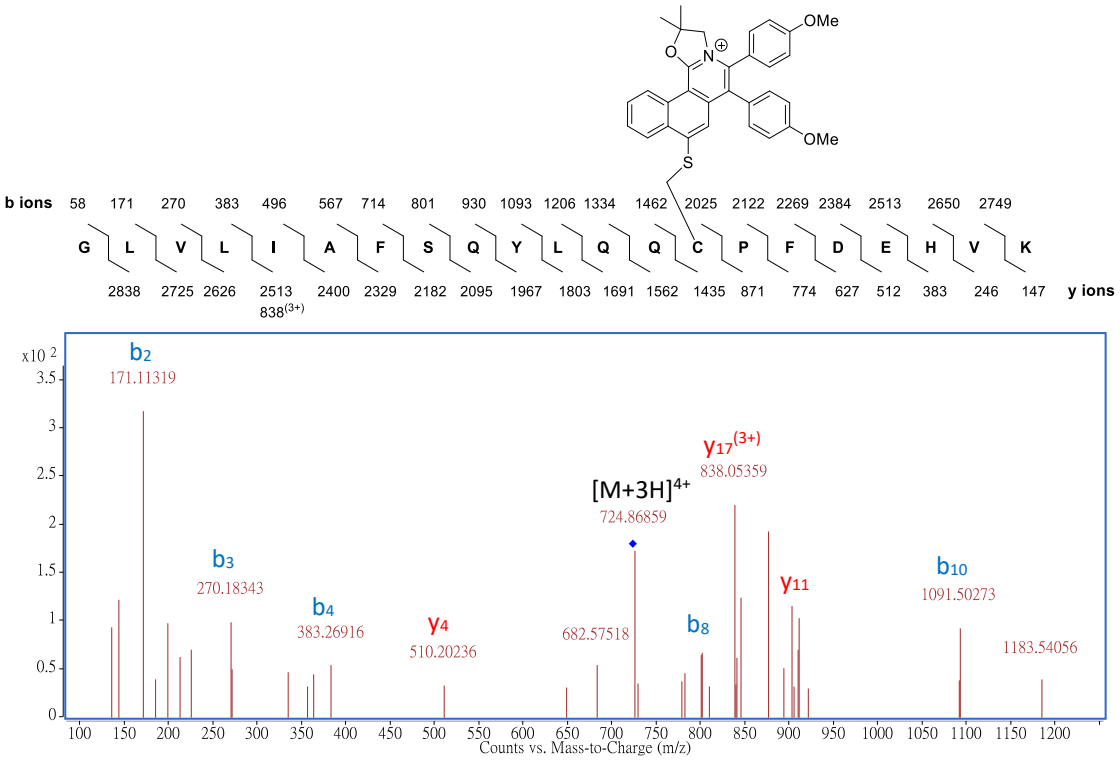


Figure S60. MS/MS spectrum of tryptic peptide GLVLIAFSQYLQQ**C*(34)**PFDEHVK derived from **oxa-3**-modified BSA. (ESI source, quarterly charged ion of *m/z* = 724.3640).

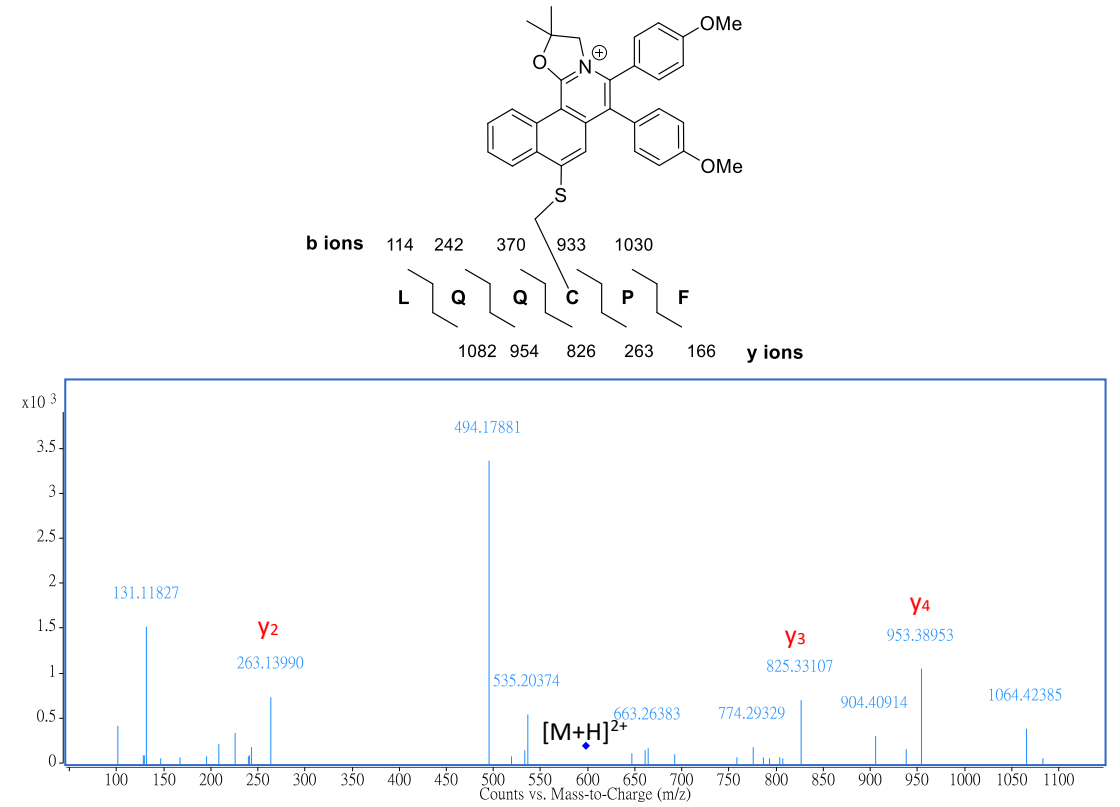


Figure S61. MS/MS spectrum of tryptic and chymotryptic peptide LQQ**C*(34)**PF derived from **oxa-3**-modified BSA. (ESI source, doubly charged ion of *m/z* = 597.7720).

LC-MS/MS Results of oxa-3-modified HSA
Sequence of Human Serum Albumin (HSA), PDB ID: 1AO6 (MW: 66558)

DAHKSEVAHRFKDLGEENFKALVLIAFAQYLQQ**C*(34)**PFEDHVKLVNEVTEF
AKTCVADESAENCDKSLHTLFGDKLCTVATLRETYGEMADCCAKQEPERNEC
FLQHKDDNPNLPRLVRPEVDVMCTAFHDNEETFLKKYLYEIARRHPYFYAPEL
LFFAKRYKAAFTECCQAADKAACLLPKLDELRDEGKASSAKQRLKCASLQKF
GERAFKAWAVARLSQRFPKAEFAEVSKLVTDLTKVHTECCHGDLLECADDRA
DLAKYICENQDSISSKLKECCEKPLLEKSHCIAEVENDEMPADLPSLAADFVES
KDVCKNYAEAKDVFLGMFLYEYARRHPDYSVVLLLRLAKTYETTLEKCCAA
ADPHECYAKVFDEFKPLVEEPQNLIKQNCELFEQLGEYKFQNALLVRYTKKVP
QVSTPTLVEVSRNLGKVGSKCCKHPEAKRMPCAEDYLSVVLNQLCVLHEKTP
VSDRVTKCCTESLVNRRPCFSALEVDETYVPKEFNAETFTFHADICTLSEKERQ
IKKQTALVELVKHKPKATKEQLKAVMDDFAAFVEKCCKADDKETCFAEEGKK
LVAASQAALGL

C*(amino acid position) = Observed **oxa-3**-modified cysteine

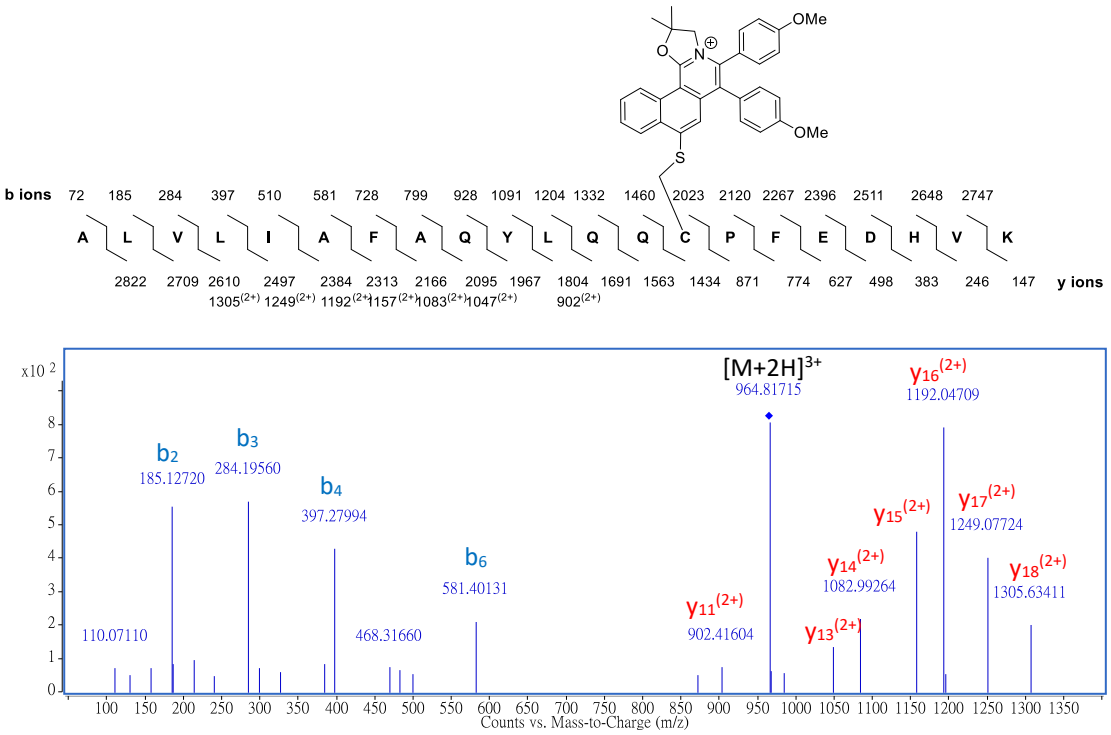


Figure S62. MS/MS spectrum of tryptic peptide ALVLIAFAQYLQQC***(34)**PFEDHVK derived from **oxa-3**-modified HA. (ESI source, triply charged ion of *m/z* = 964.8231).

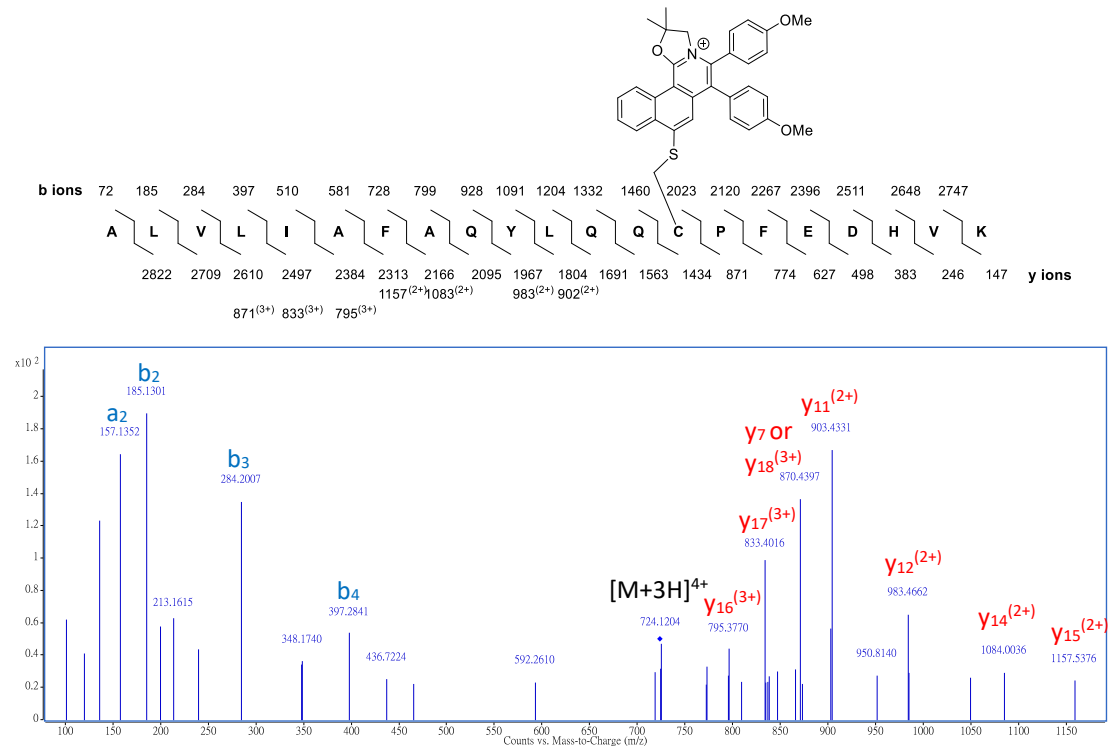


Figure S63. MS/MS spectrum of tryptic peptide ALVLIAFAQYLQQC***(34)**PFEDHVK derived from **oxa-3**-modified HSA. (ESI source, quarterly charged ion of *m/z* = 724.1204).

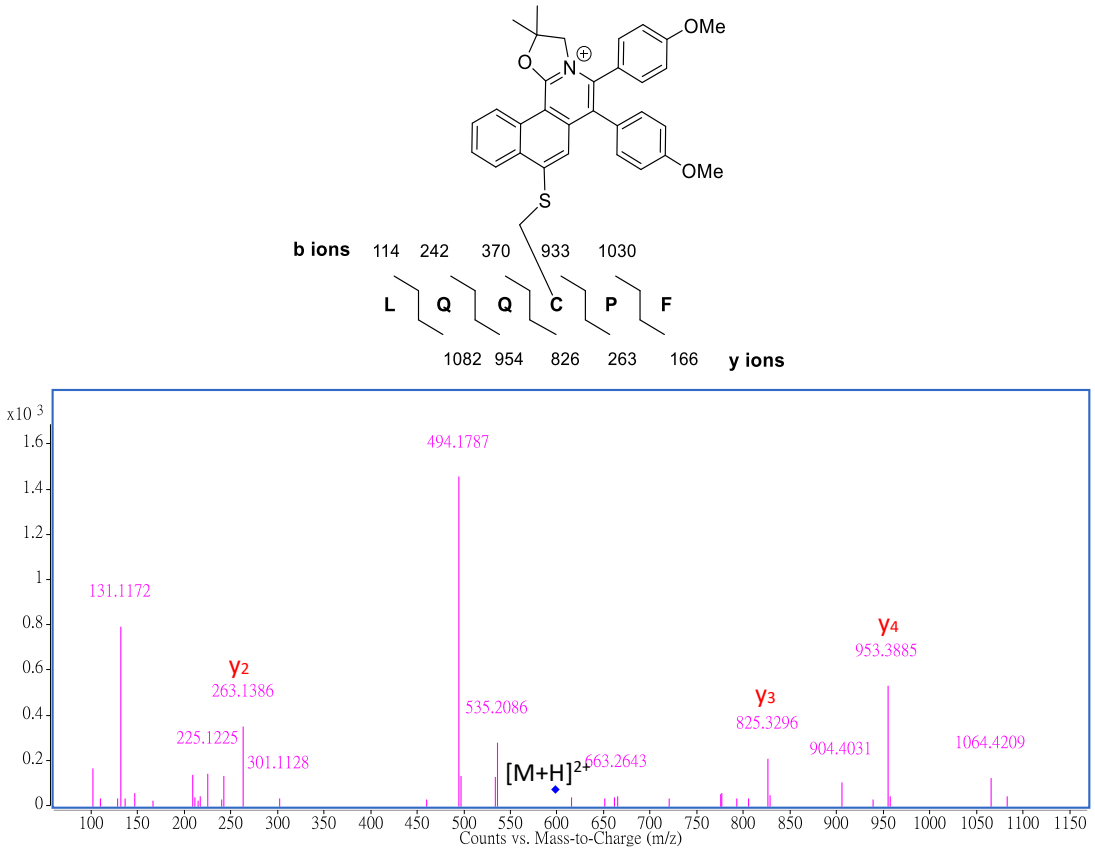


Figure S64. MS/MS spectrum of tryptic and chymotryptic peptide LQQ**C*(34)**PF derived from **oxa-3**-modified HSA. (ESI source, doubly charged ion of *m/z* = 597.7711).

General Procedure for SDS-PAGE Analysis

Native proteins and protein conjugates were subjected to SDS-PAGE analysis under reducing conditions. Using BSA as an example, 3 μL of native BSA or **oxa-3**-modified BSA (0.1 mM) was mixed with 7 μL of Milli-Q water in a 1.5 mL Eppendorf tube to give a protein solution with a concentration of 20 μg/μl. Then, 10 μL 2X reducing sample loading buffer was added into the protein solution and then boiled under a hot water bath for 10 minutes. The above reaction was repeated by using HSA and lysozyme instead of BSA. Samples were analyzed by SDS-PAGE by loading all boiled samples in each lane on a 15% SDS-PAGE and running in a Mini-PROTEAN® Tetra Cell (Bio-Rad, USA) at 150 V at room temperature for 45 min. After SDS-PAGE separation, the protein and protein conjugates were visualized at UV 360 nm with a MaestroGen UltraBright® UV Transilluminator MLB-21 and finally stained with Coomassie blue. Results are shown in Figure S65.

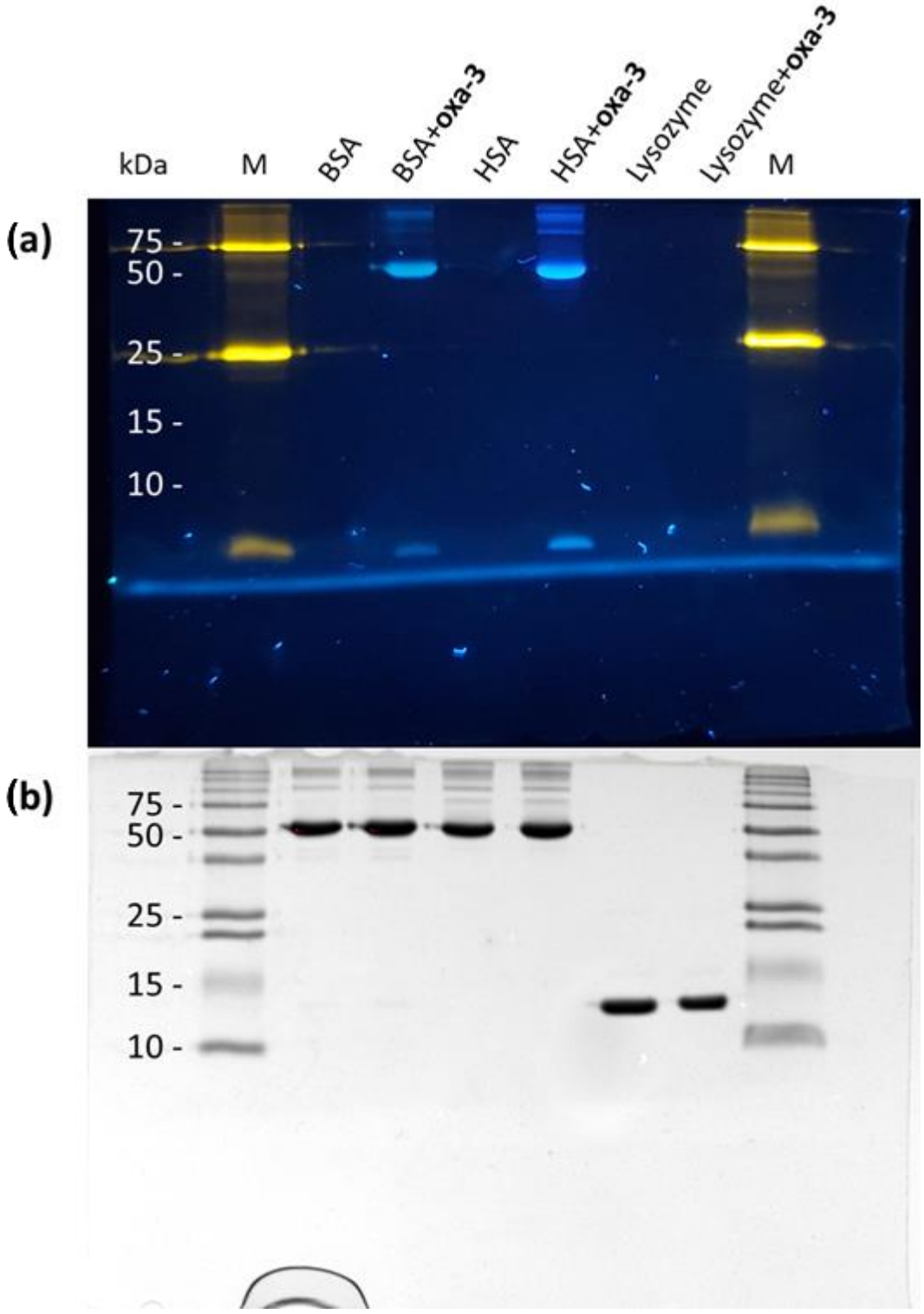


Figure S65. SDS-PAGE analysis of native proteins and **oxa-3**-modified proteins visualized (a) at UV 365 nm and (b) after Coomassie Blue staining.

General Procedure for Cytotoxicity Test by using MTS Assay

HeLa cells were cultured in Dulbecco's Modified Eagle's Medium (DMEM) (Gibco) supplemented, 10% v/v Fetal Bovine Serum (Gibco), and 100 U/ml penicillin (Gibco), 100 μg/ml streptomycin (Gibco) at 37 °C with 5% CO_2.

MTS assay was performed by using 96-well plate. $5x10^3$ HeLa cells were seeded in each well and allowed to attach for 24 h at 37 °C with 5% CO_2. The cells were subsequently incubated with different concentrations of oxazolinium for 24 h at 37 °C with 5% CO_2. A 50 mM oxazolinium stock solution was prepared in DMSO and diluted to different concentrations ranging from 0.2 μM to 200 μM. After 24 h, 20 μL of MTS reagent (CellTiter 96® AQueous one solution cell proliferation assay, Promega Corporation Cat. # G4000) was added into each well and incubated at 37 °C with 5% CO_2 for 1 h. Absorbance at 490 nm was measured on Ledetect 96 Microplate Reader. GraphPad Prism was used to calculate the IC_{50} values. The cell viability percentage was calculated according to the following Equation:

$$\text{Cell viability\%} = (A_{sample} - A_{blank})/A_{control} - A_{blank}) \times 100$$

Where A_{sample} means the absorbance of the experiment where the cells incubated with the different concentration of the oxazolinium, $A_{control}$ represents the average control experiments (the cells without the oxazolinium), and A_{blank} is the absorbance of different concentration of the oxazolinium (without cells).

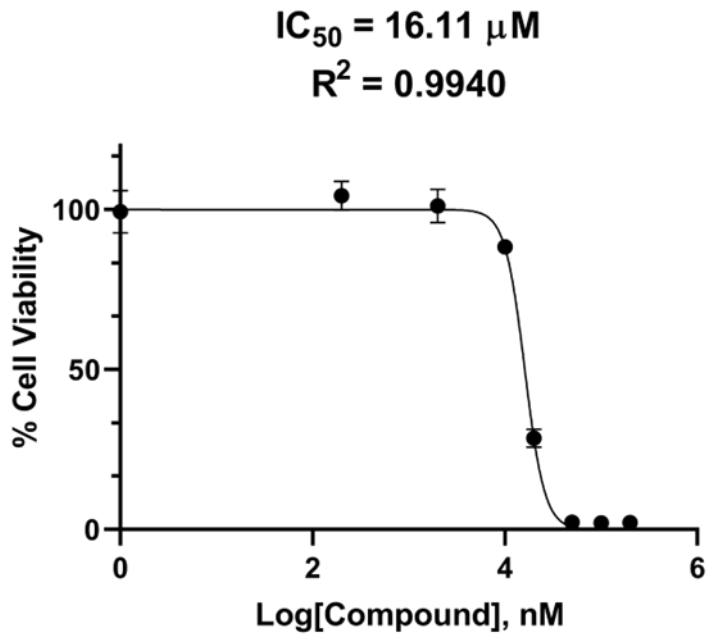


Figure S66. IC_{50} graph of HeLa cells incubated with **oxa-3**.

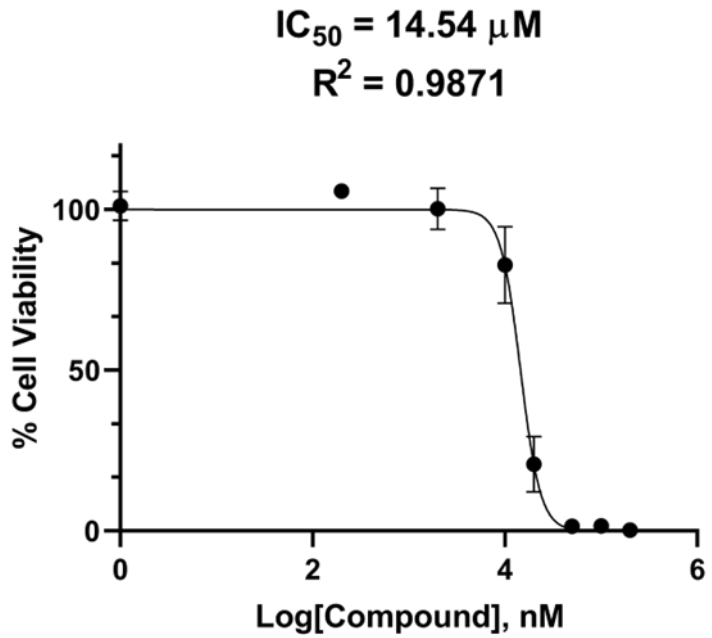


Figure S67. IC_{50} graph of HeLa cells incubated with **oxa-6**.

General Procedure for Live Cell Imaging to Study Subcellular Localization

HeLa cells ($1.5x10^5$ cells) were seeded into the 35 mm glass bottom dishes and cultured at 37 ºC with 5% CO_2 for 24 h. A 50 mM oxazolinium stock solution was prepared in DMSO. The cells were then added oxazolinium (5 uM) mixed with MitoTracker™ Red FM (MTR, 500 nM) and incubated at 37 °C with 5% CO_2 for 15 min. Afterward, the cells were washed with DPBS to get rid of the extra oxazolinium and imaged by a Leica TCS SPE confocal microscope with a 40 oil-immersion objective lens. Pearson's correlation coefficients were determined with ImageJ. Results are shown in Figure S68.

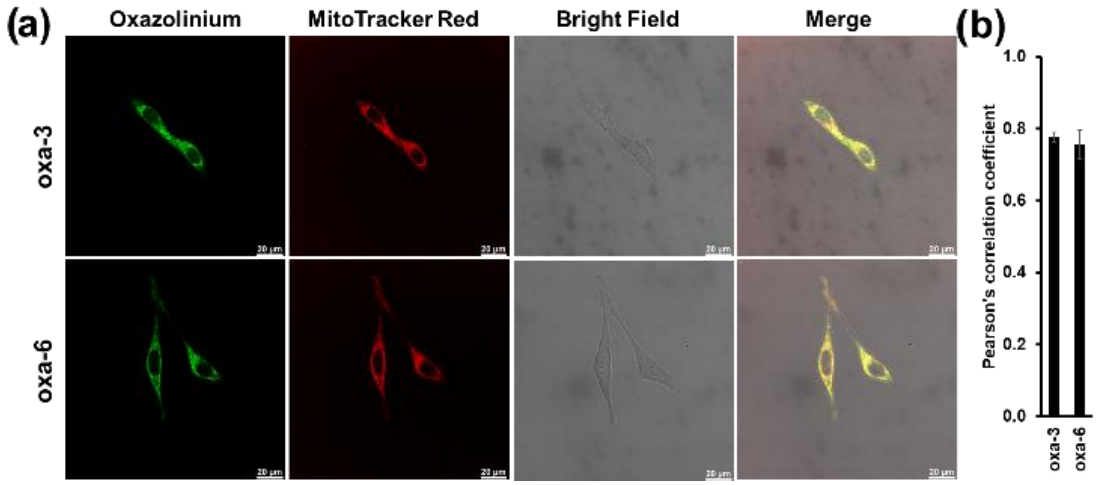


Figure S68. (a) Live cell images of HeLa cells incubated with 5 μM **oxa-3** and **oxa-6** and 500 nM MTR for 15 min at 37 ºC. First column indicated the green channel of oxazoliniums (λ_{ex} = 405 nm, λ_{em}= 460-530 nm). Second column indicated the red channel for MTR (λ_{ex} = 561 nm, λ_{em} = 620-660 nm). Third column indicated bright-field images. Last column indicated merged images from the three channels. Scale bar = 20 μm. (b) Pearson's correlation coefficient of colocalization between oxazoliniums and MTR. Data were presented as mean +/- S.D.

General Procedure for Modification of GSH by oxa-3

A mixture of glutathione (10 μL of 10 mM in H_2O, 1 equiv., 1 mM), **oxa-3** (10 μL of 10 mM in DMSO, 1 equiv., 1 mM) and TCEP (10 μL of 10 mM in H_2O, 1 equiv., 1 mM) in 50 mM PBS (pH 7.4)/DMSO (9:1) (made up to 100 μL) was incubated at 40 ℃ for 15 min. After the reaction, 3 μL of the crude mixture was taken out for LC-MS analysis. Results are shown in Figures S69-71.

LC-MS analysis for modification of GSH was performed by using an Agilent 6540 UHD Accurate-Mass Q-TOF LC/MS system equipped with an ion spray source and an Agilent 1290 Infinity LC, using an Agilent ZORBAX RRHD SB300-C18 (1.8 μm, 2.1 x 100 mm) column. 3 μL of sample was injected with a flow rate of 0.3 mL/min. Mobile phase A was made of Milli-Q® water containing 0.1% formic acid. Mobile phase B was made of HPLC grade acetonitrile containing 0.1% formic acid. Operating conditions optimized for the detection of reaction mixture were the following: Gas temperature: 320 °C, Drying gas: 8 L/min, Nebulizer: 35 psig, Sheath gas temperature: 380 °C, Sheath gas flow: 11 L/min, VCap: 3500 V, Nozzle voltage: 1000 V.

Table S9. The LC gradient for LC–MS analysis.

Time (min)	A (%)	B (%)	Flow rate (mL/min)
0	95	5	0.3
1	95	5	0.3
7	1	99	0.3
7.10	95	5	0.3
10	95	5	0.3

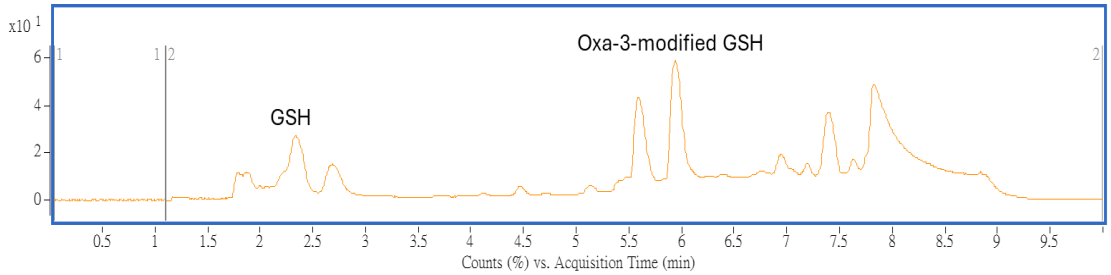


Figure S69. Total ion chromatograph of crude mixture of GSH (1 mM) and **oxa-3** (1 equiv.) in presence of TCEP (1 equiv.) in PBS (pH 7.4)/DMSO (9:1).

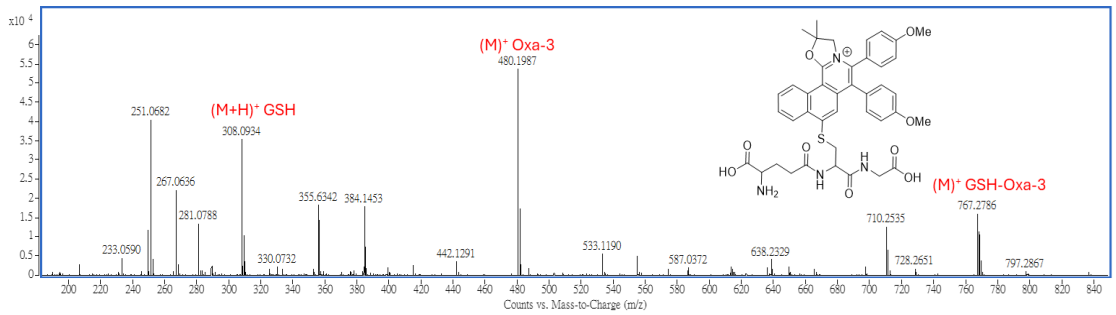


Figure S70. MS spectra of crude mixture of GSH and **oxa-3**.

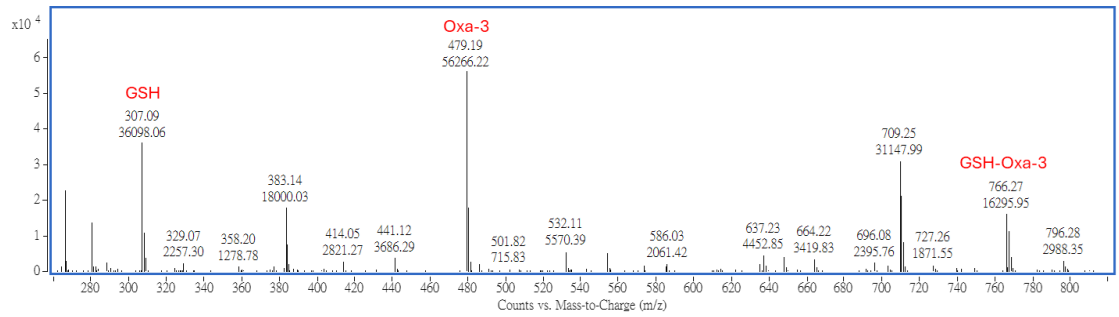


Figure S71. Deconvoluted MS spectra of crude mixture of GSH and **oxa-3**.

CD Spectra

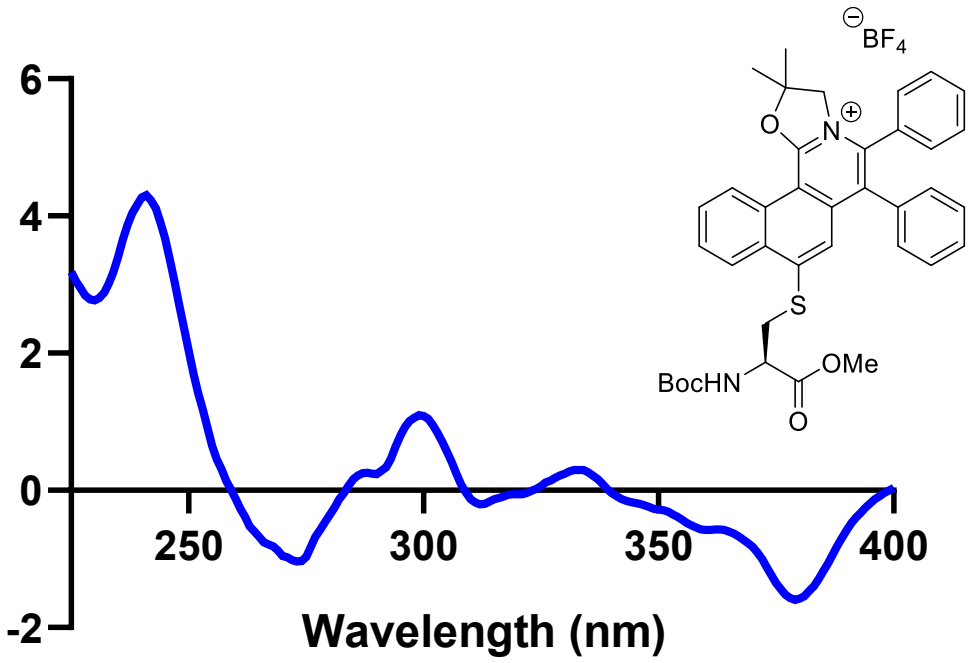


Figure S72. CD spectra of compound **oxa-5** in DCM (0.5 mM).

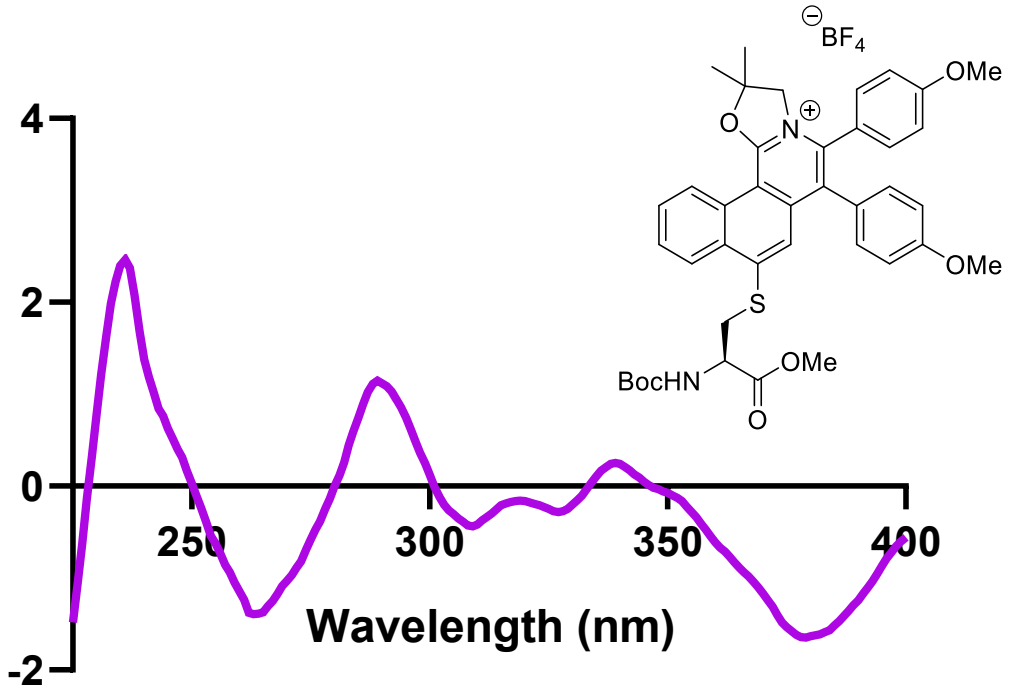


Figure S73. CD spectra of compound **oxa-6** in DCM (0.5 mM).

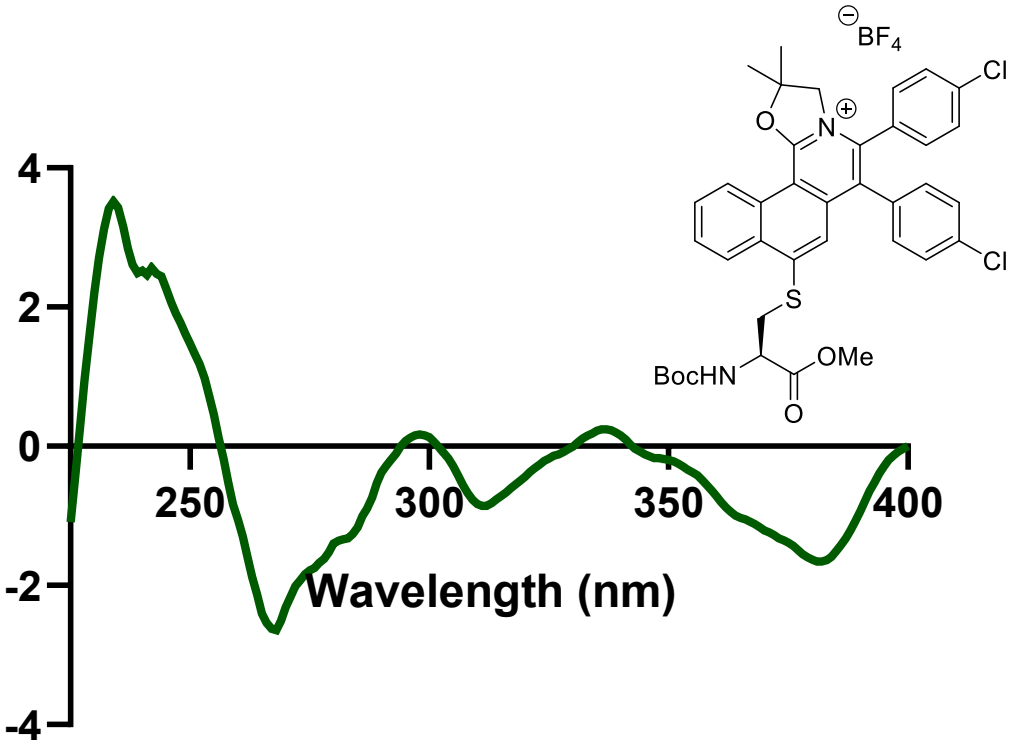
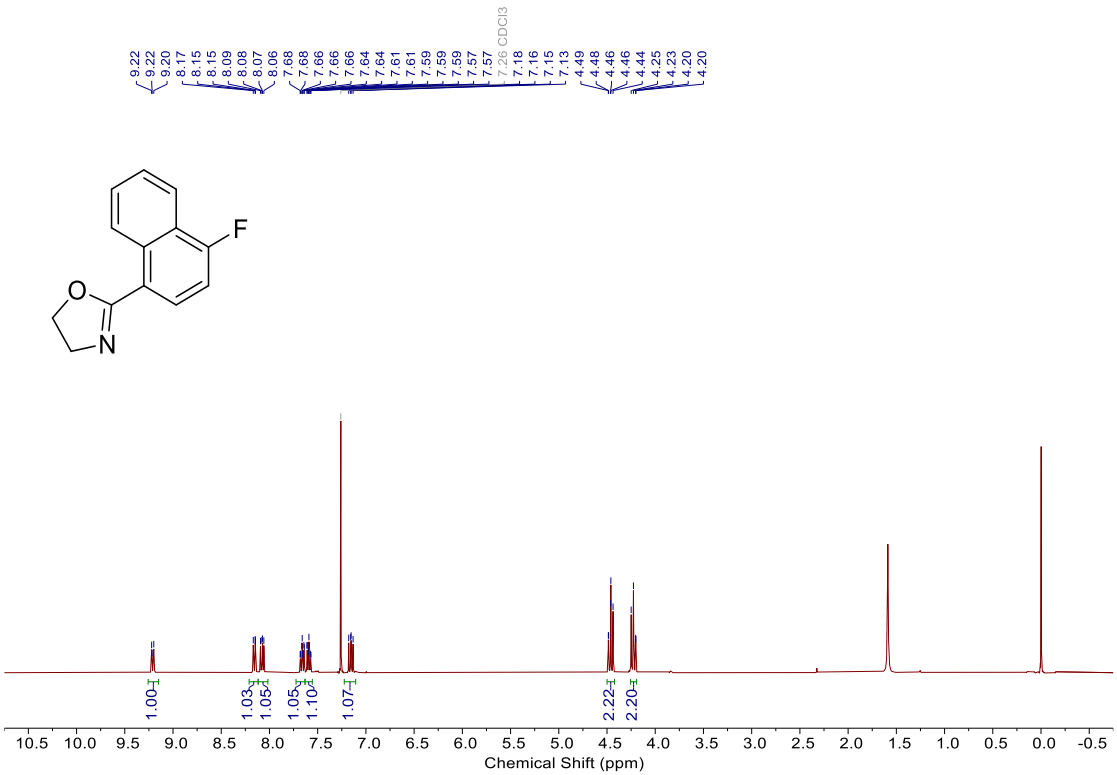


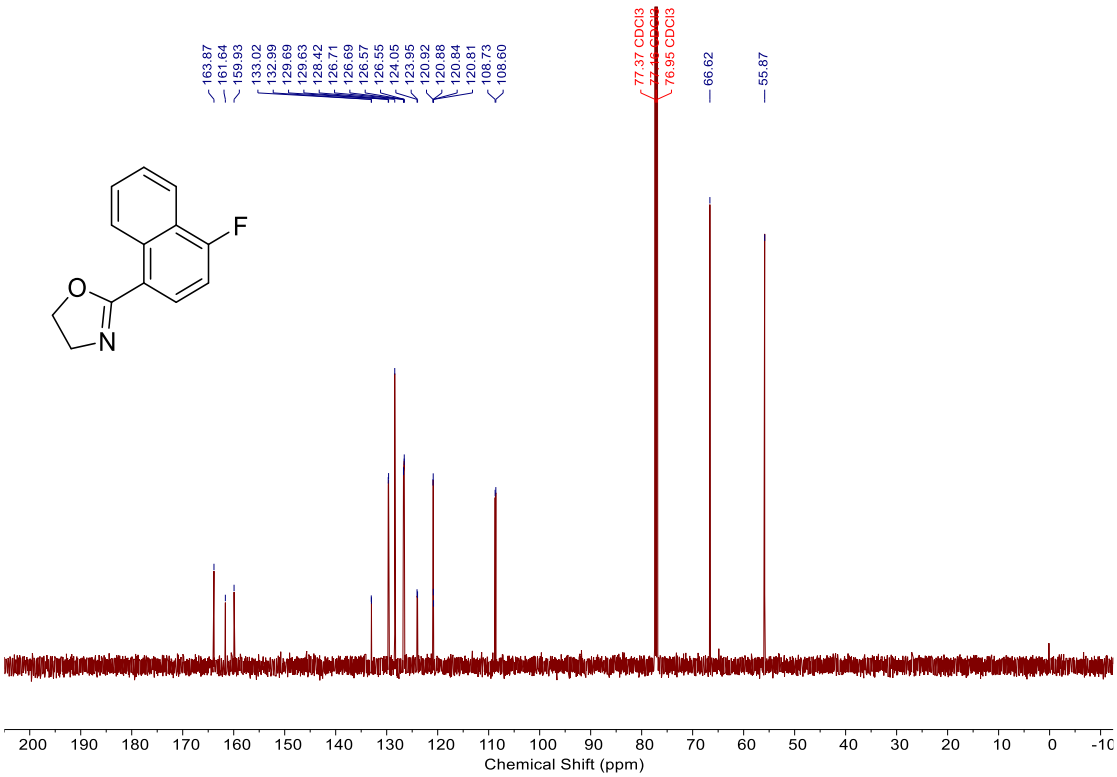
Figure S74. CD spectra of compound **oxa-7** in DCM (0.5 mM).

NMR Spectra

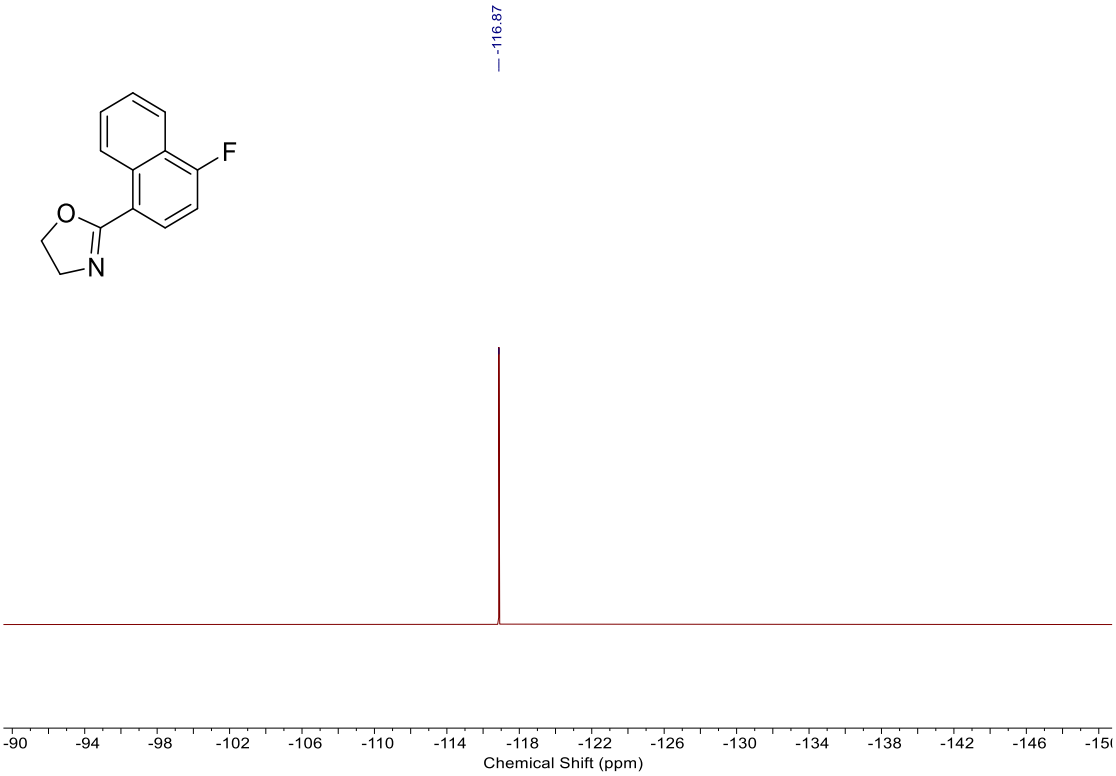
^{1}H NMR (400 MHz) of Compound S1a



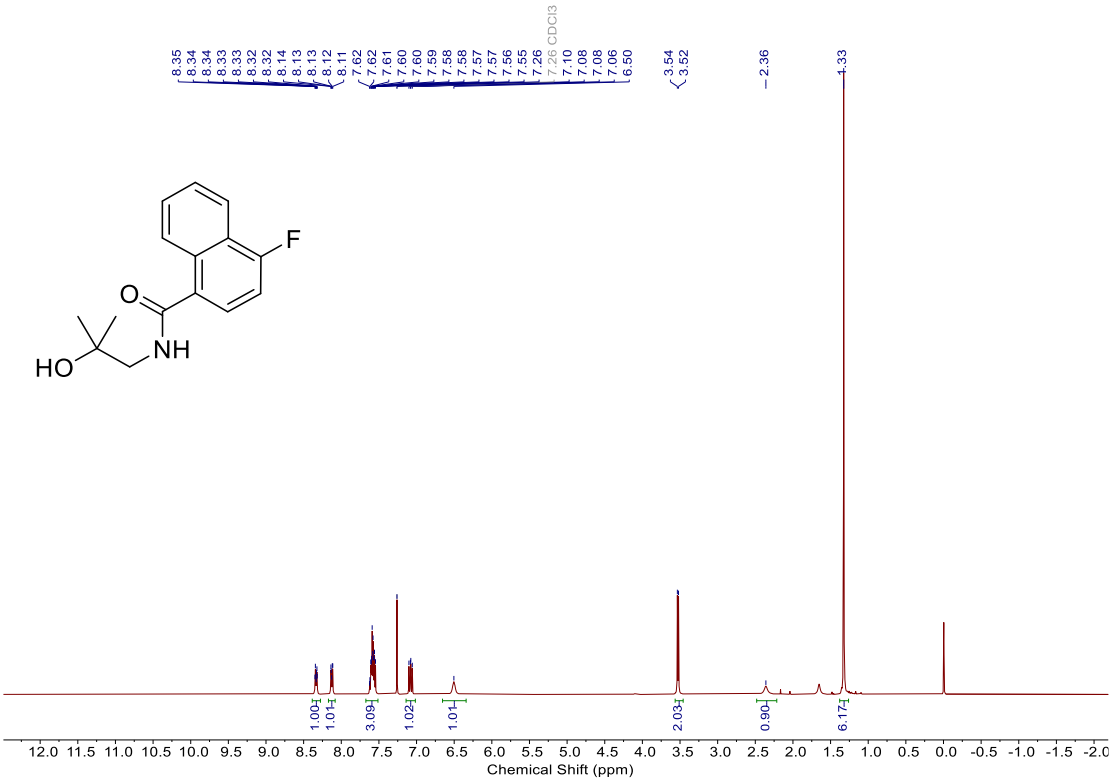
^{13}C NMR (151 MHz) of Compound S1a



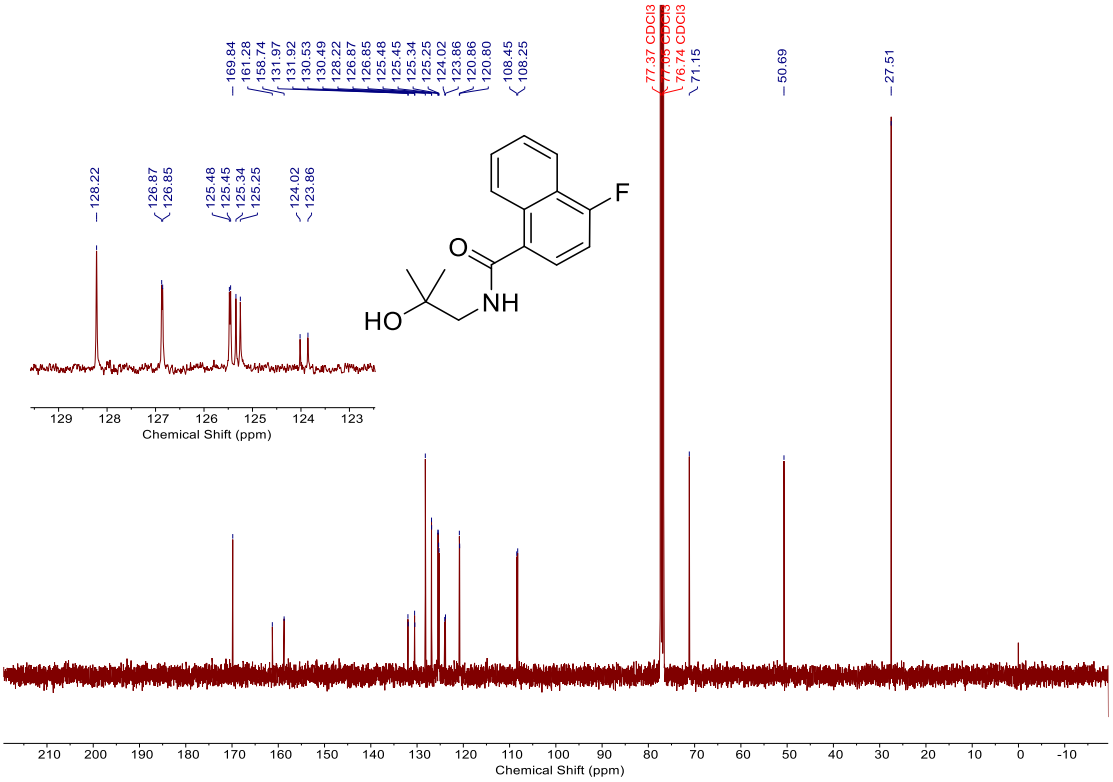
^{19}F NMR (565 MHz) of Compound S1a



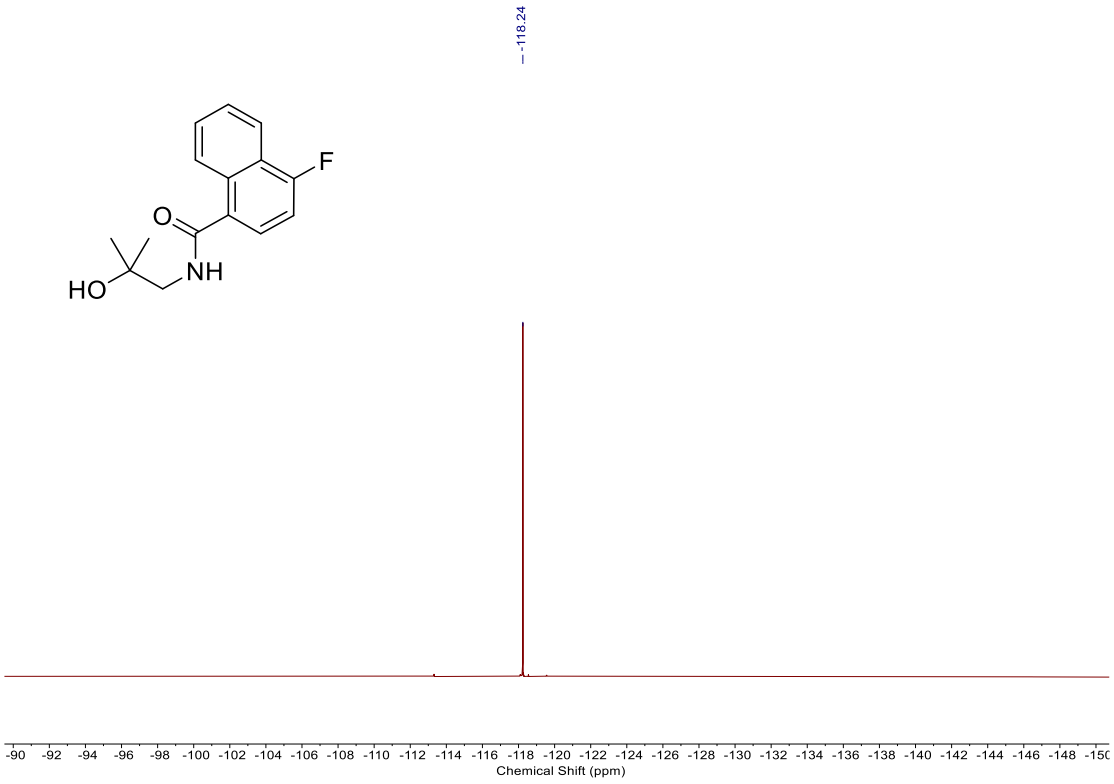
^{1}H NMR (400 MHz) of Compound S1c



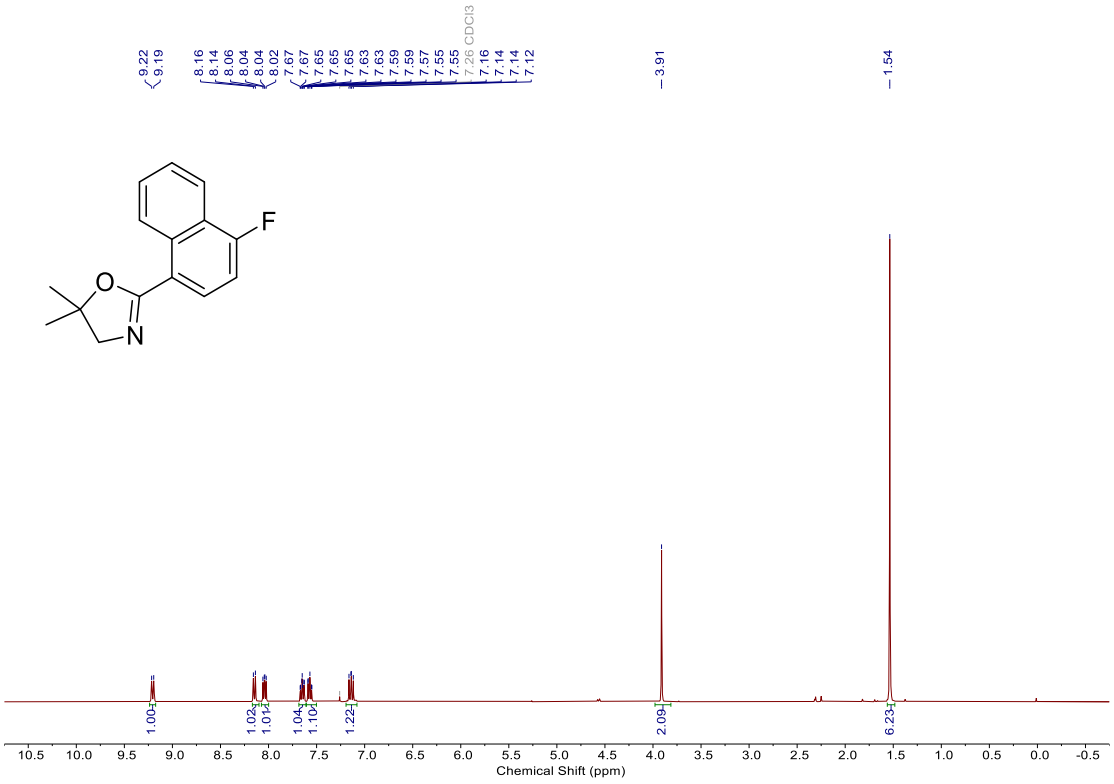
^{13}C NMR (101 MHz) of Compound S1c



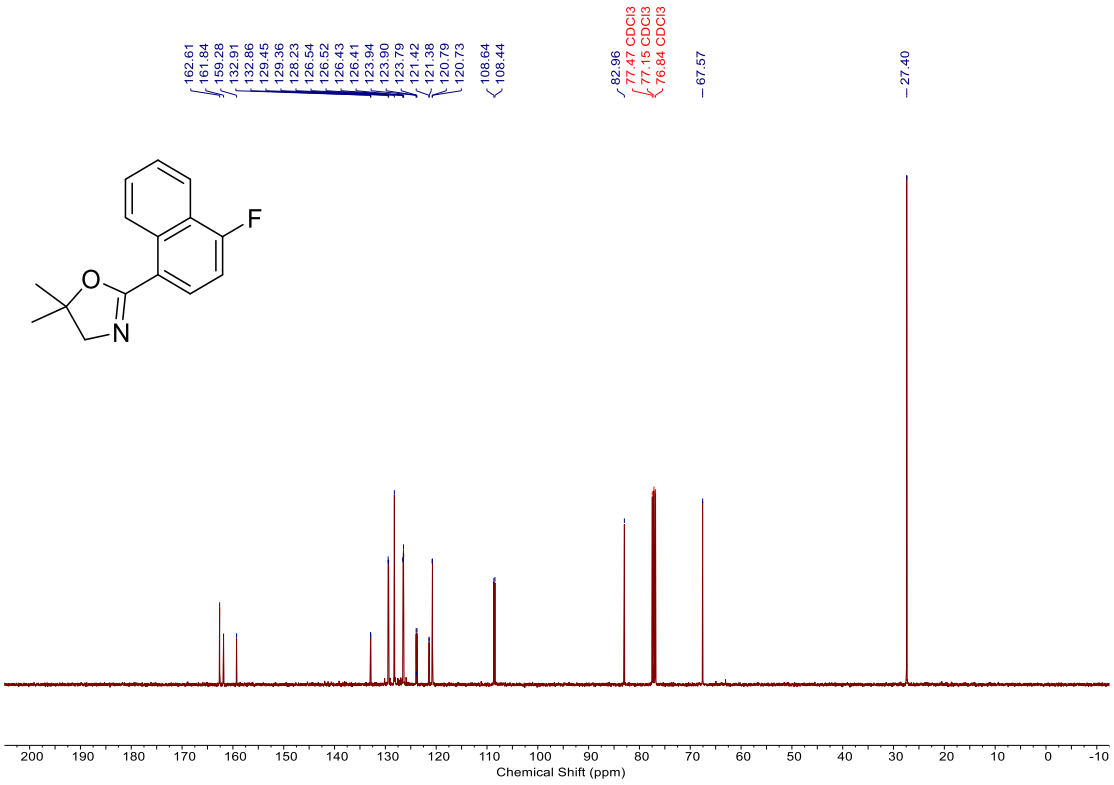
^{19}F NMR (565 MHz) of Compound S1c



^{1}H NMR (400 MHz) of Compound S1b



^{13}C NMR (101 MHz) of Compound S1b



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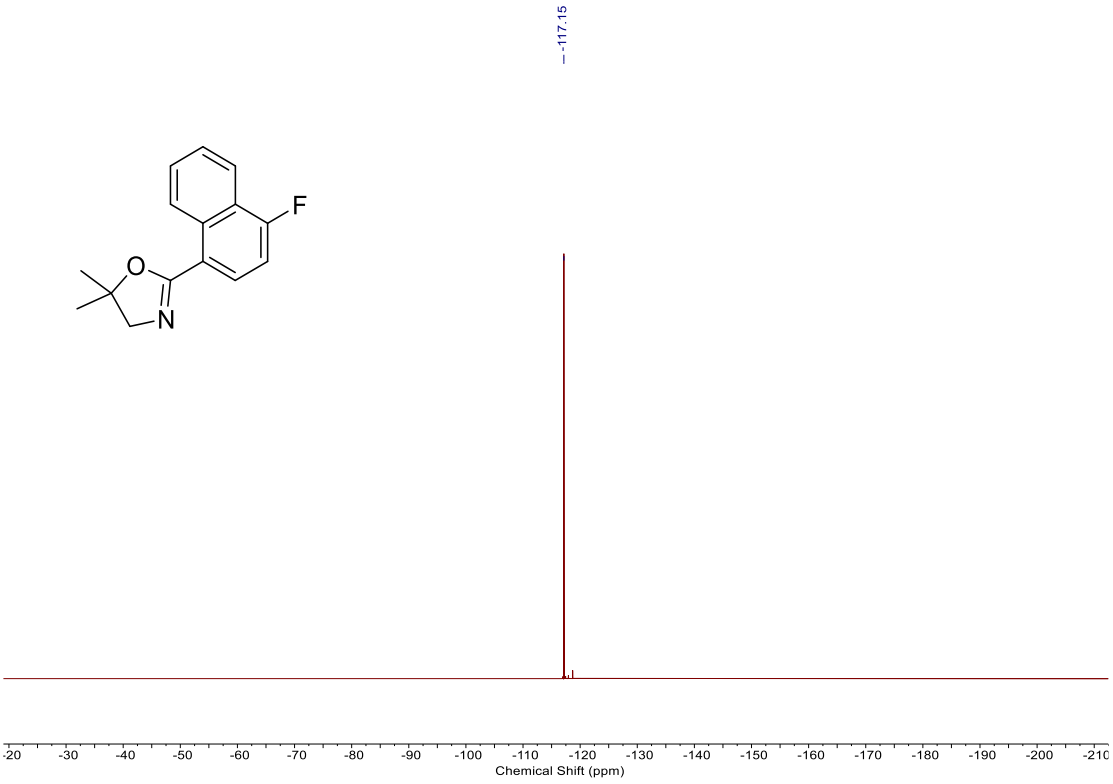
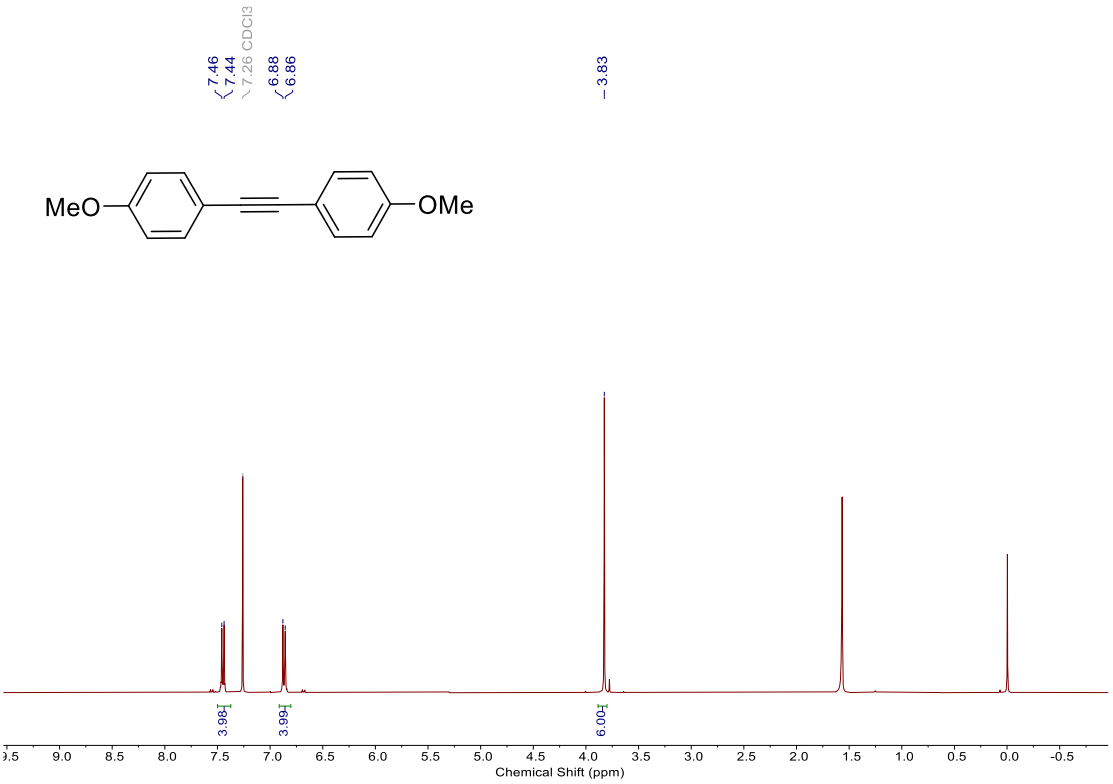
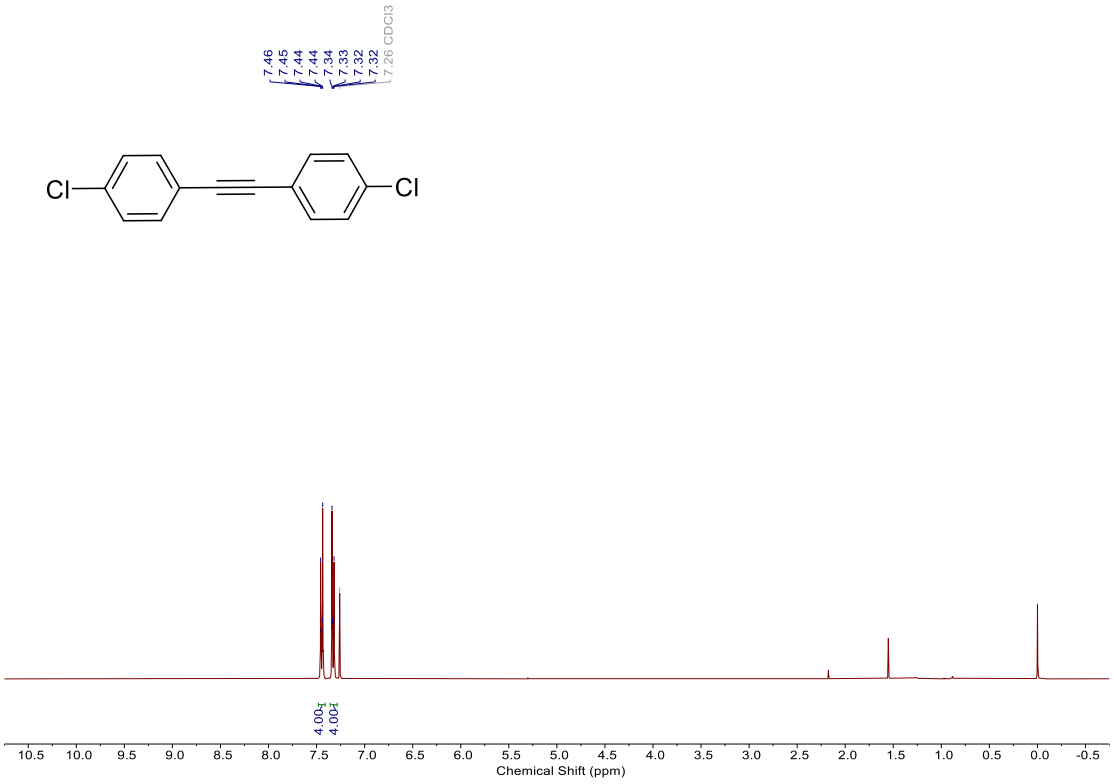


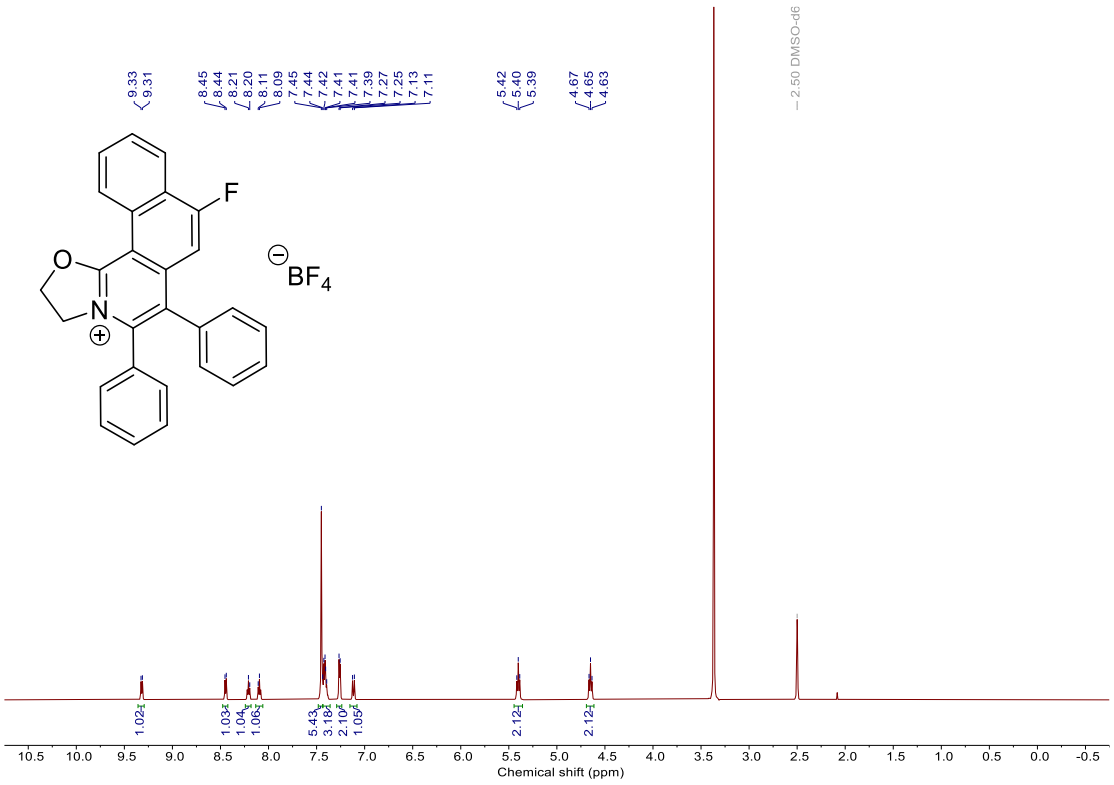
^{1}H NMR (400 MHz) of Compound S2b



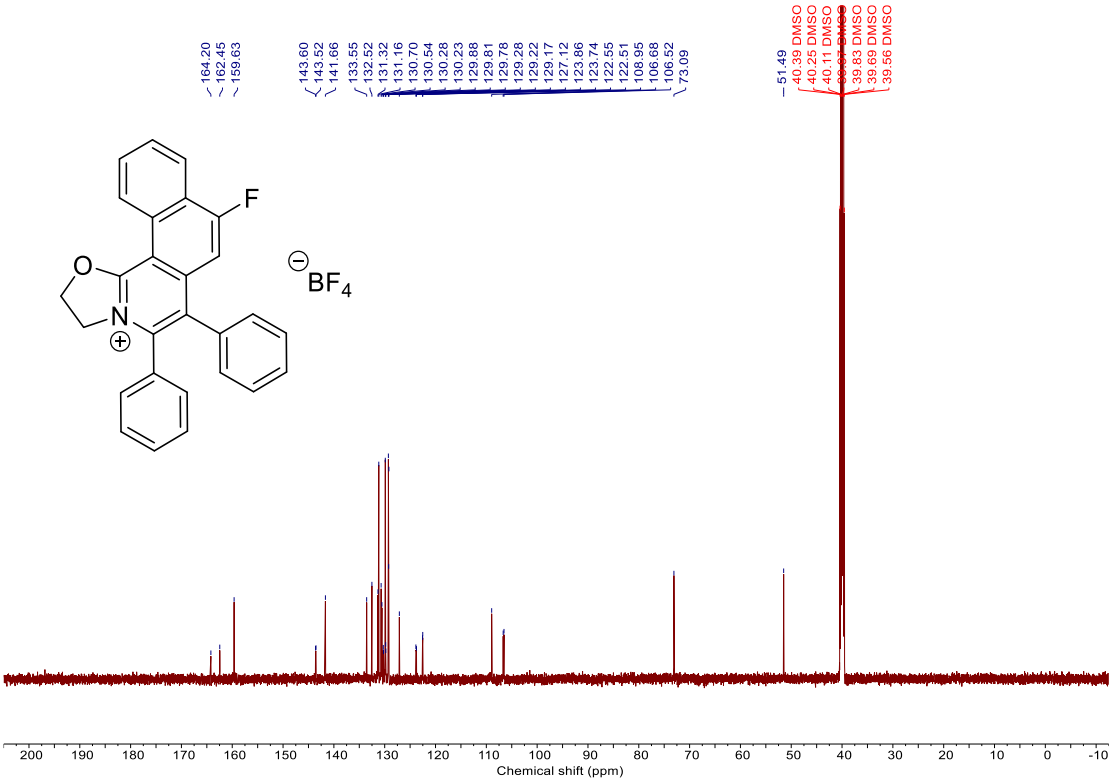
^{1}H NMR (400 MHz) of Compound S2c



^{1}H NMR (600 MHz) of Compound oxa-1



^{13}C NMR (151 MHz) of Compound oxa-1



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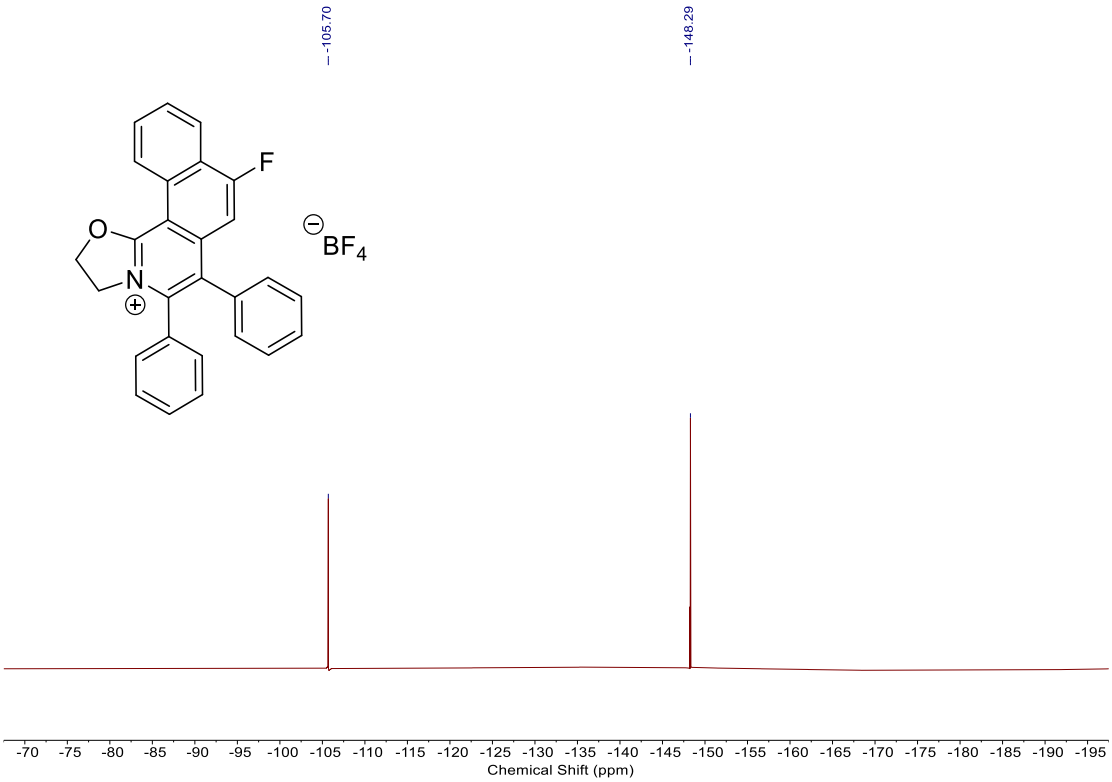
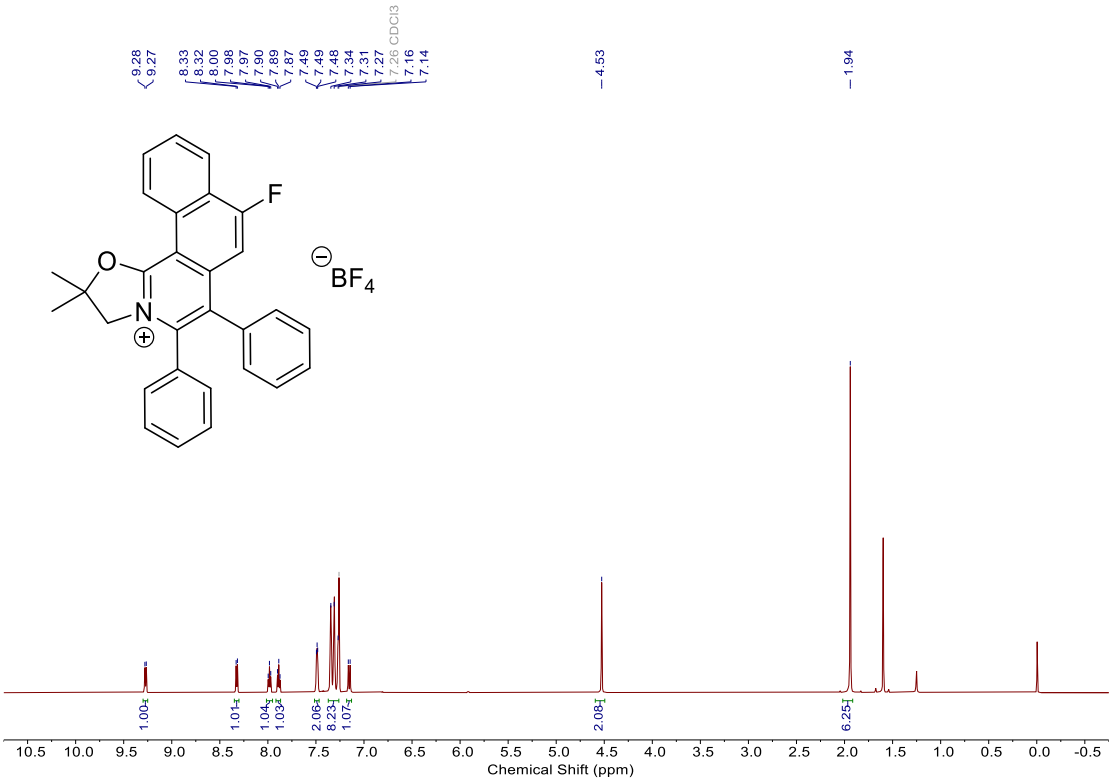


^{1}H NMR (600 MHz) of Compound oxa-2



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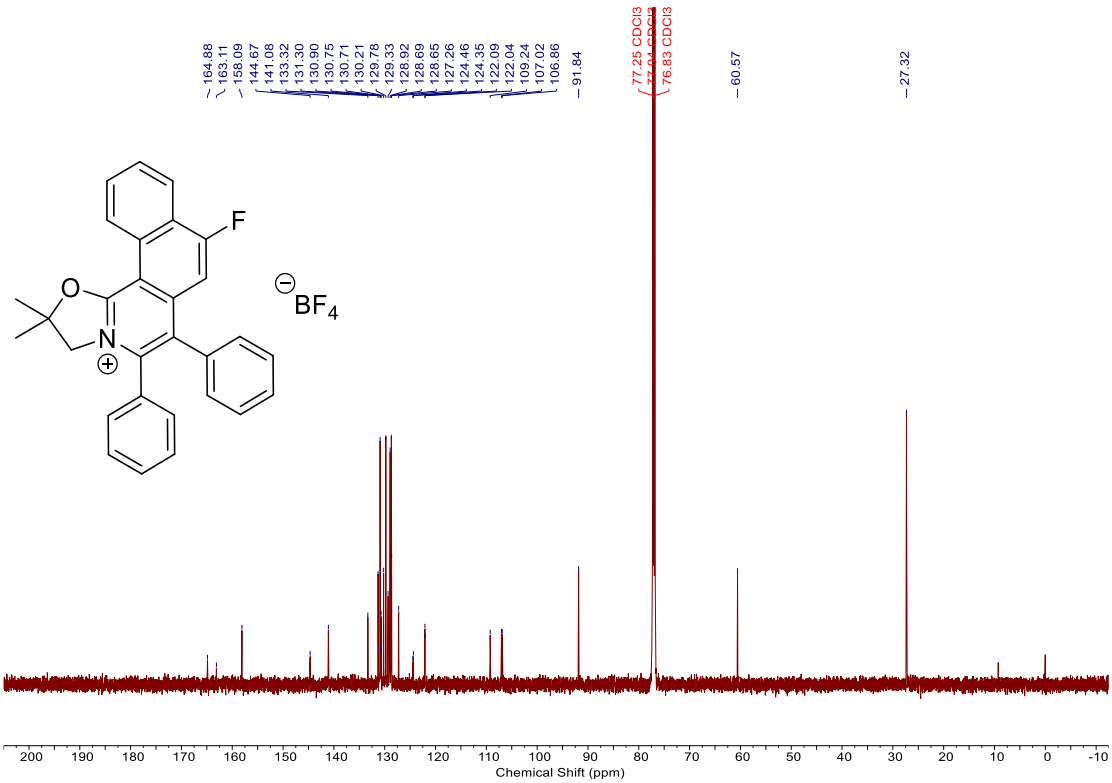

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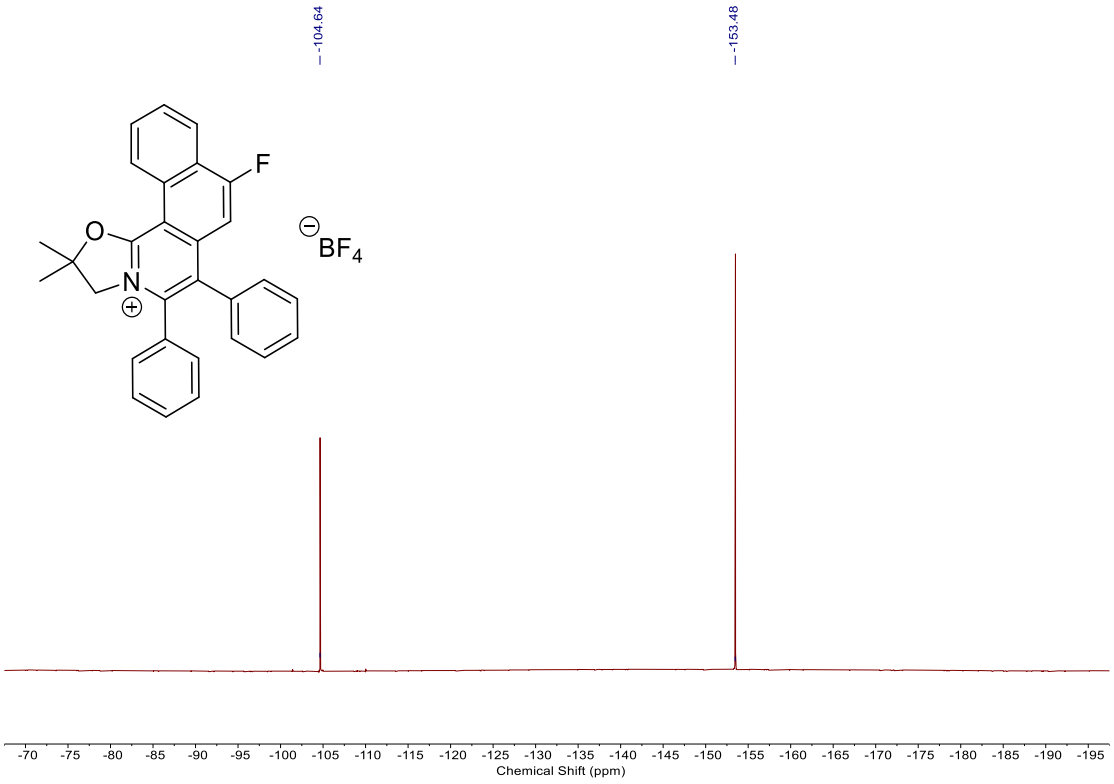
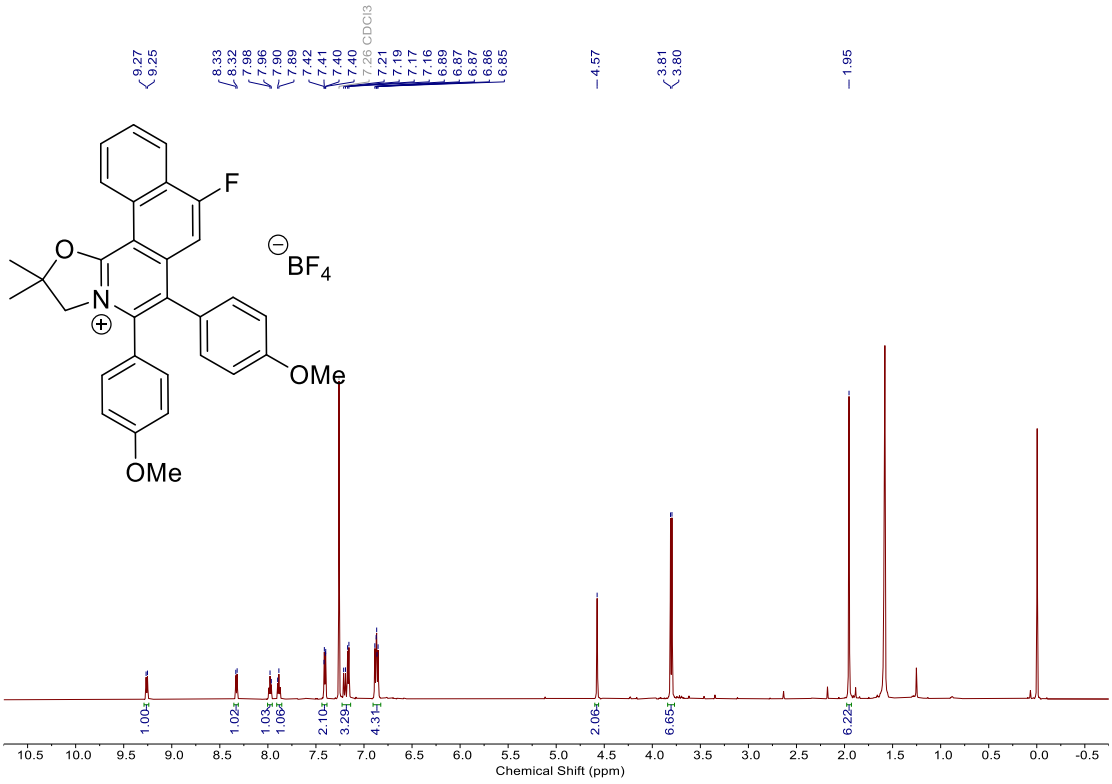
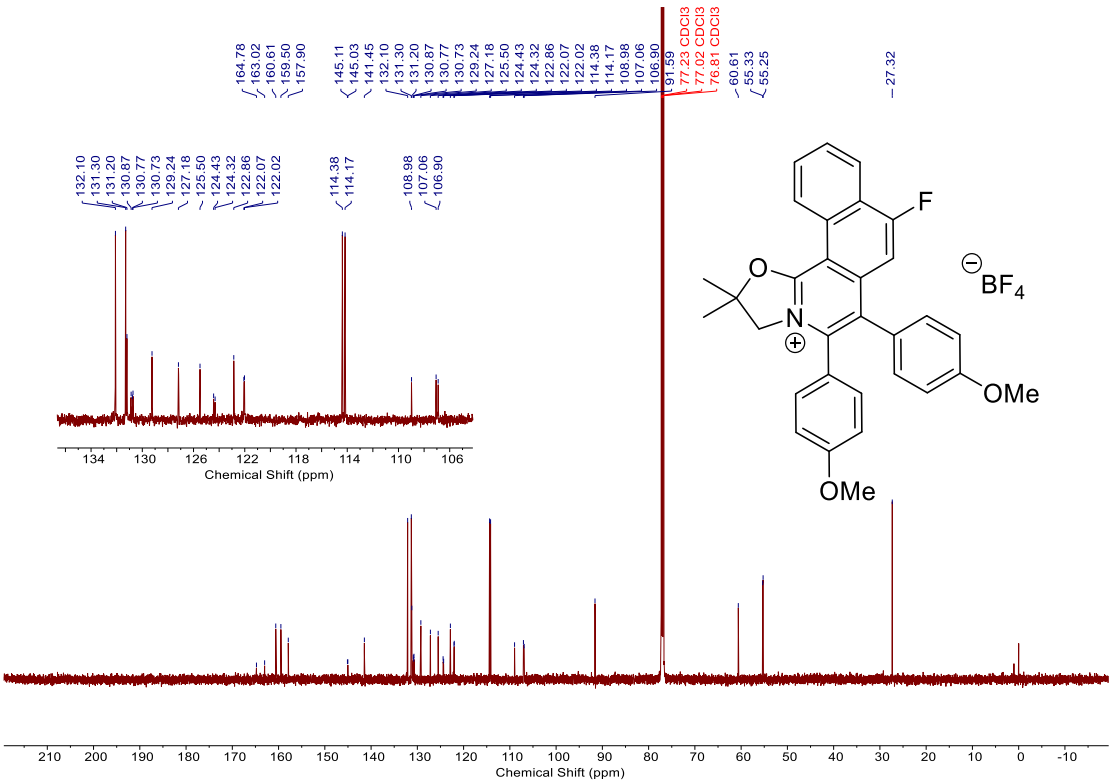


^{1}H NMR (600 MHz) of Compound oxa-3



^{13}C NMR (151 MHz) of Compound oxa-3



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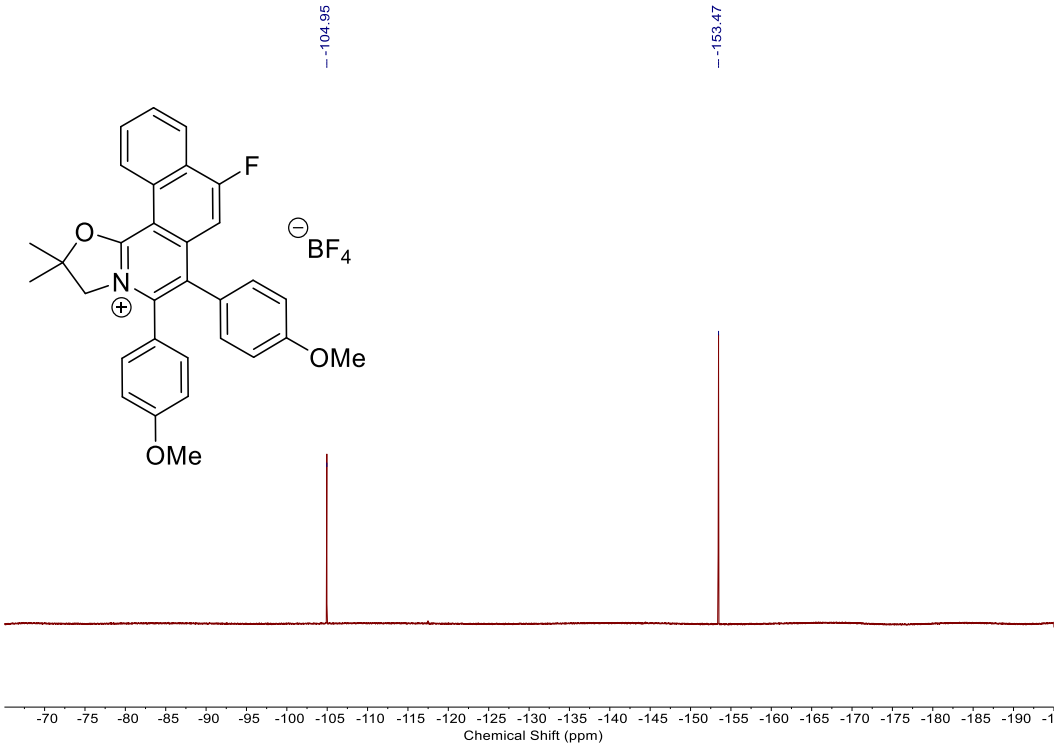
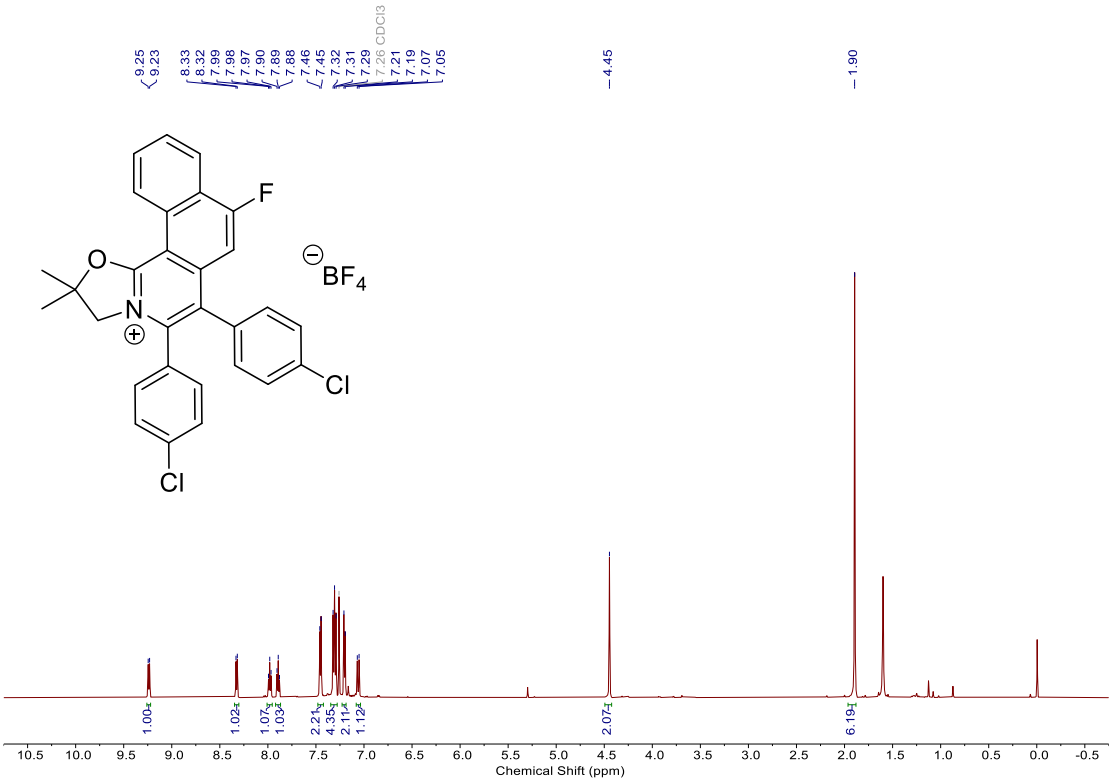


^{1}H NMR (600 MHz) of Compound oxa-4



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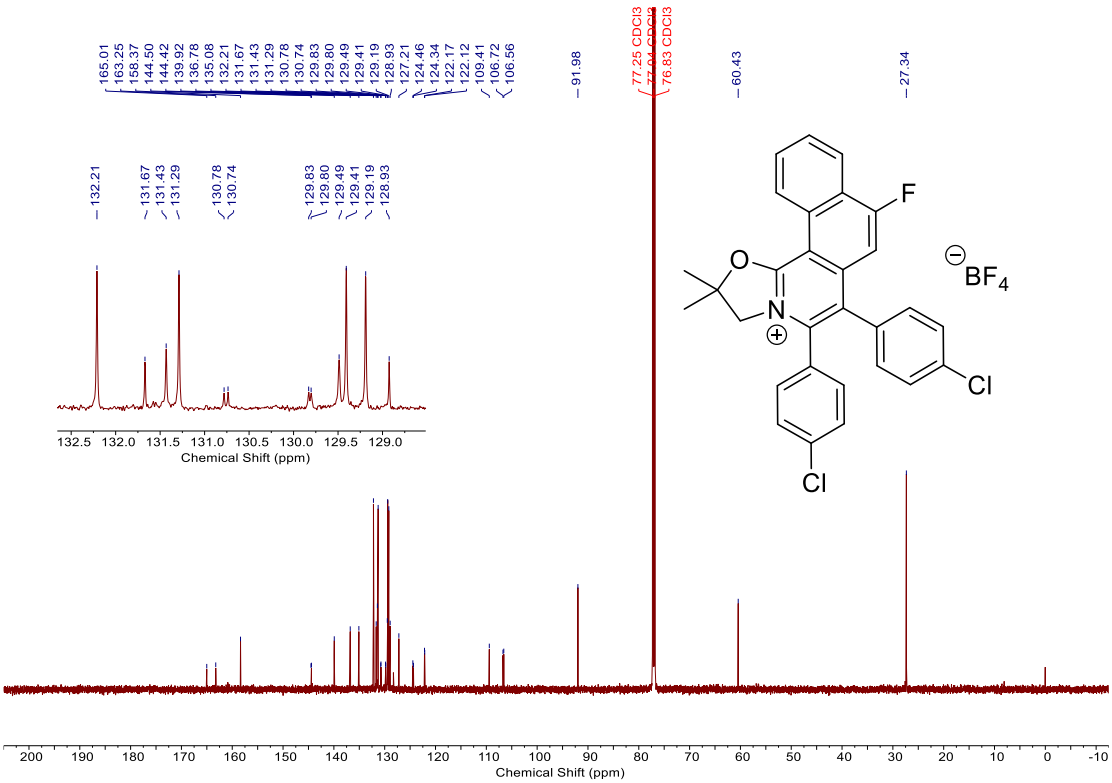
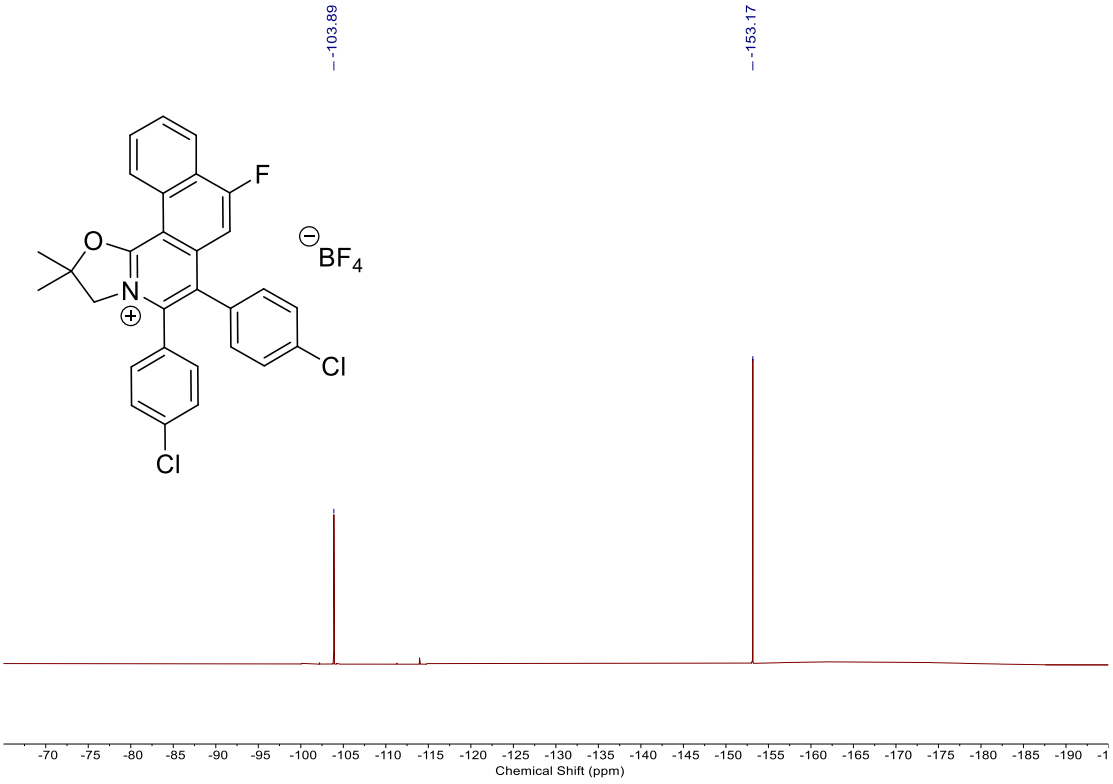
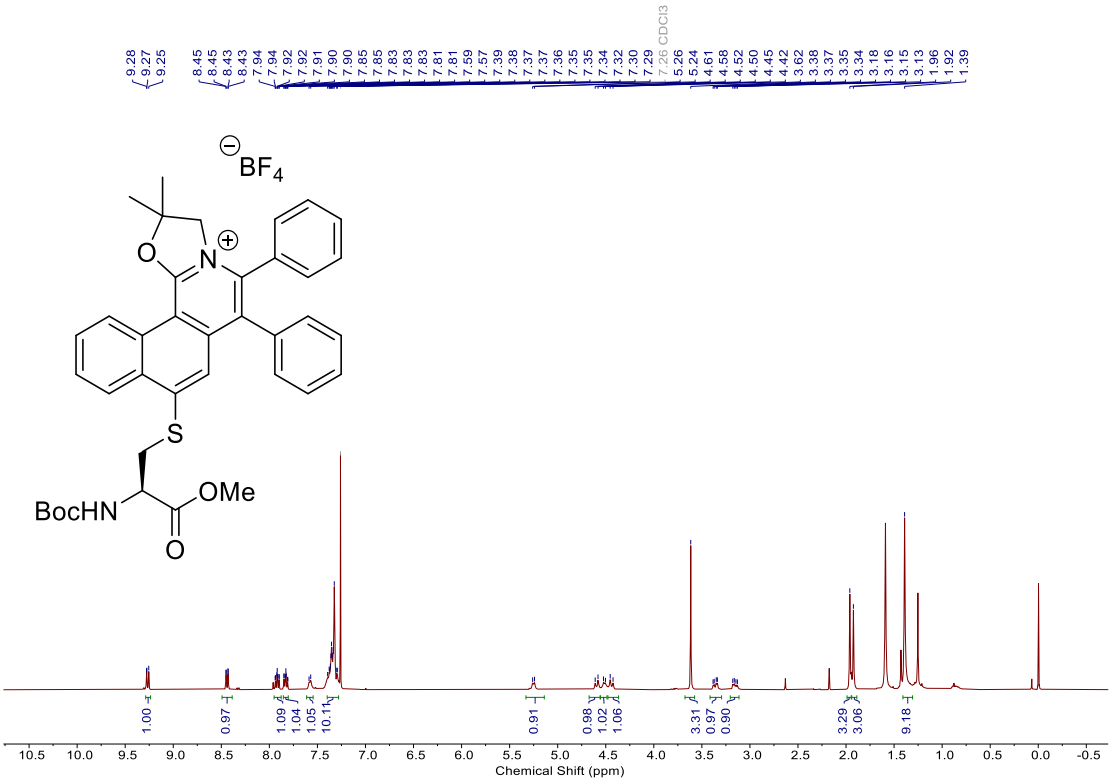


^{19}F NMR (565 MHz) of Compound oxa-4



^{1}H NMR (400 MHz) of Compound oxa-5



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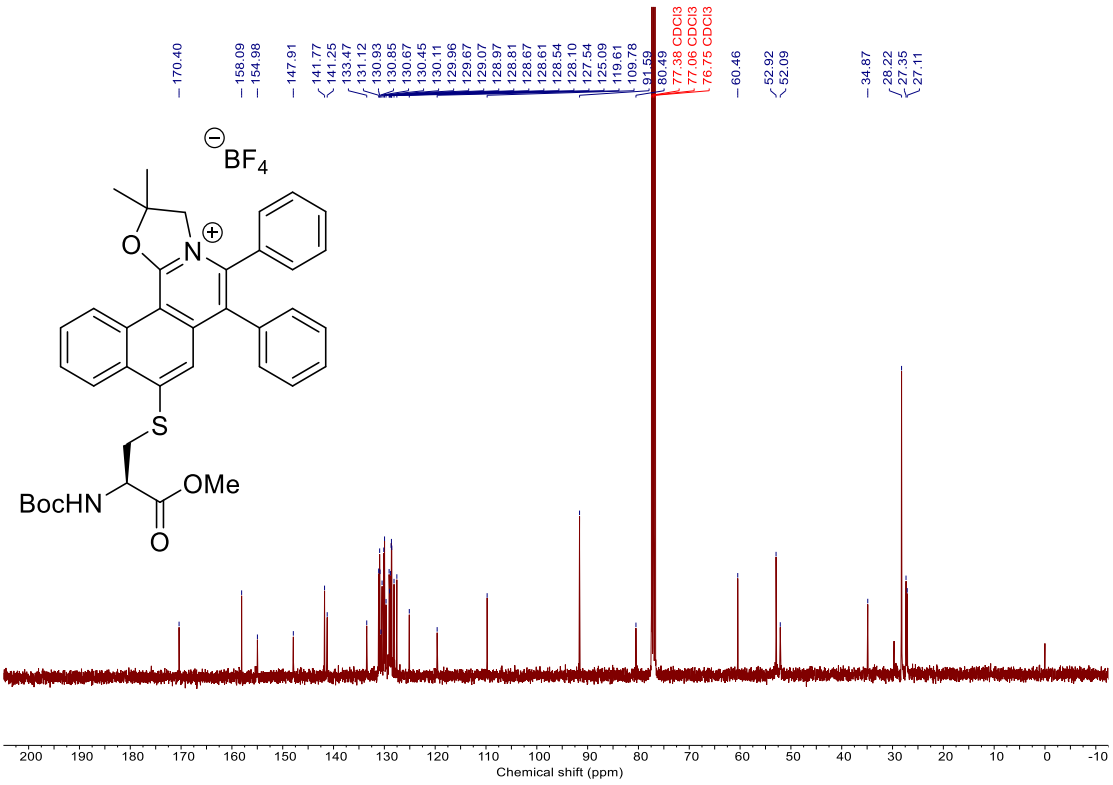

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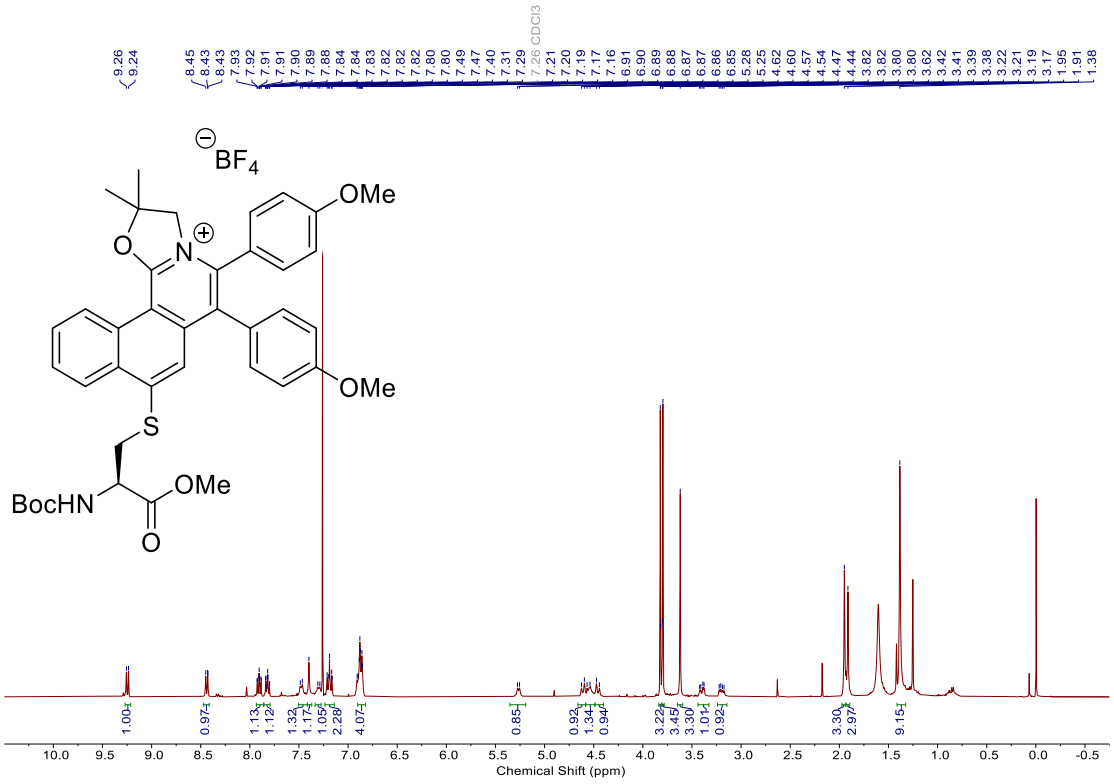
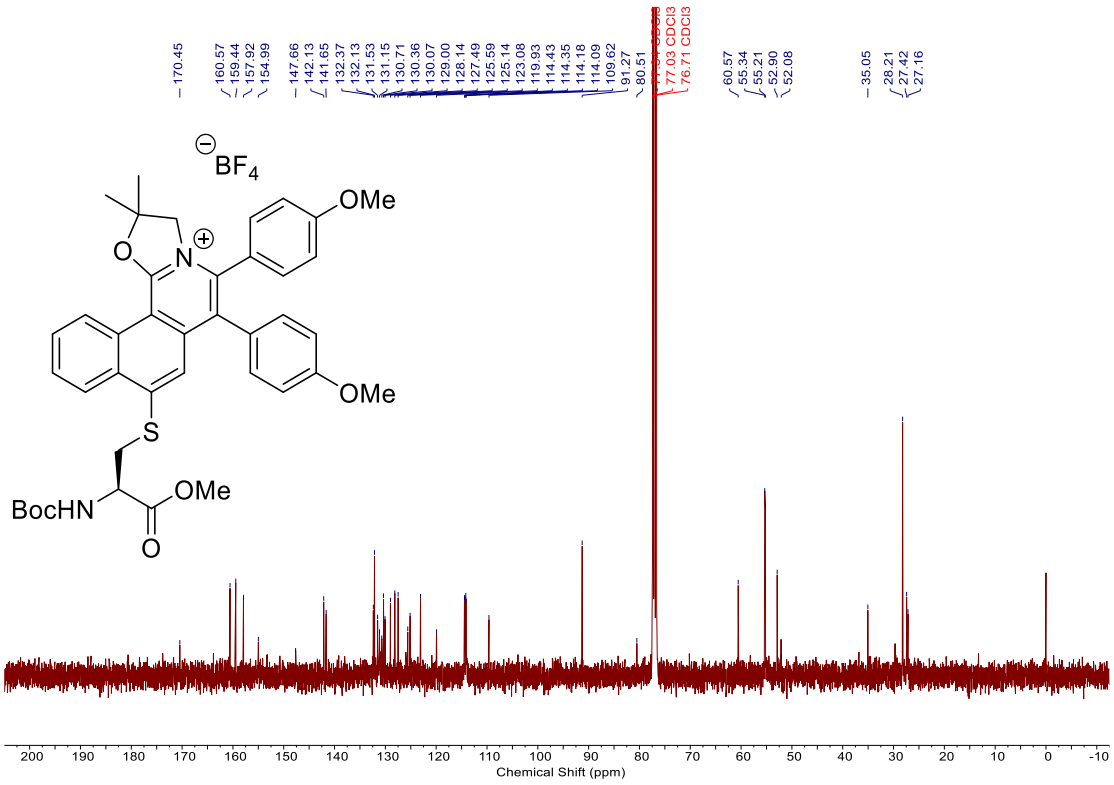


^{13}C NMR of (101 MHz) Compound oxa-6



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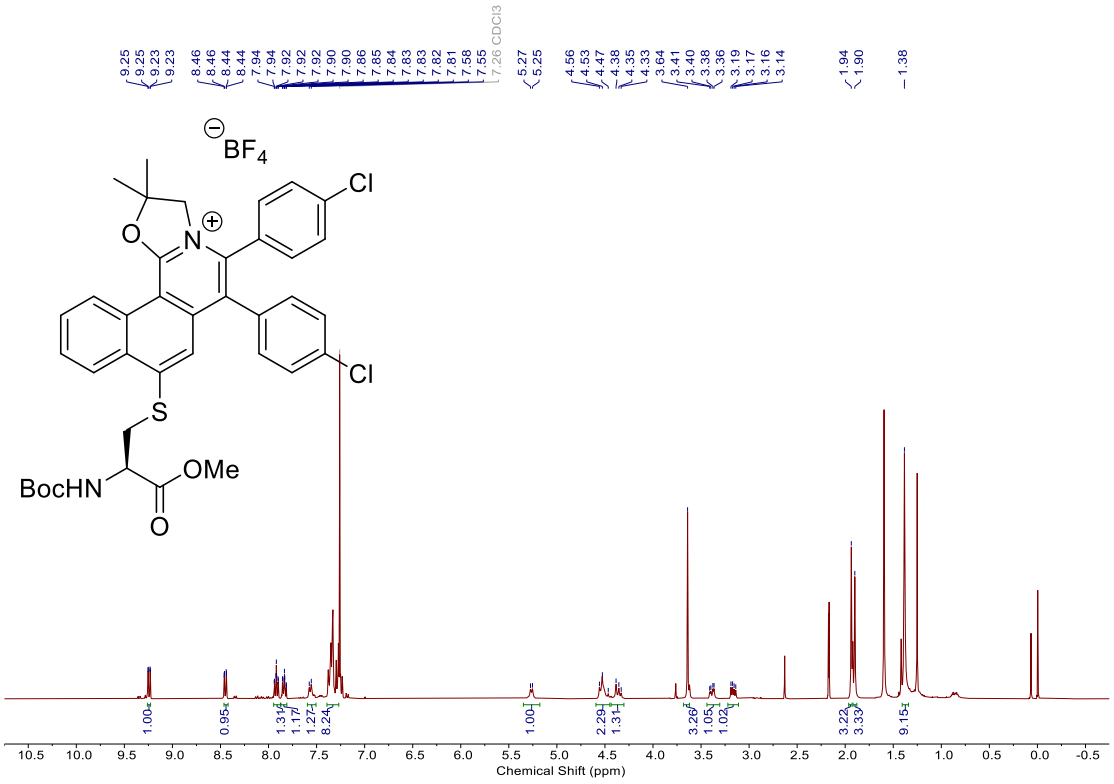

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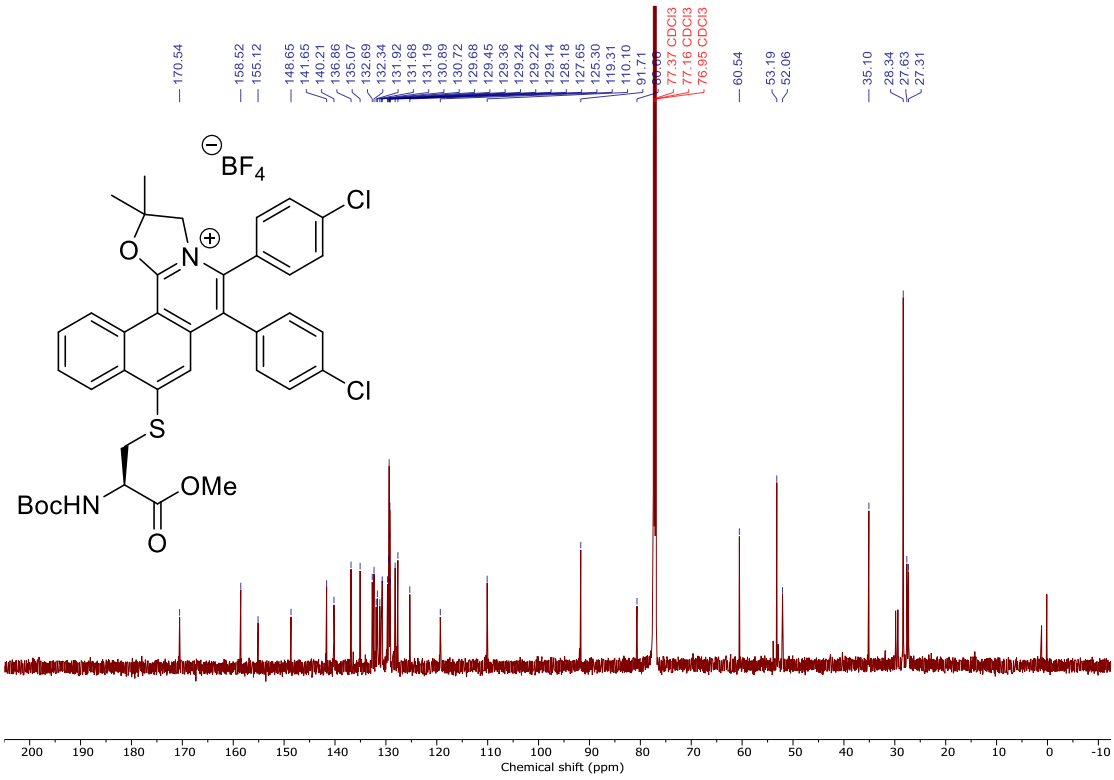

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