

Supplementary Information

Imidazole Fused Phenanthroline (PIP) Ligands for the Preparation of Multimodal Re(I) and ^{99m}Tc(I) Probes

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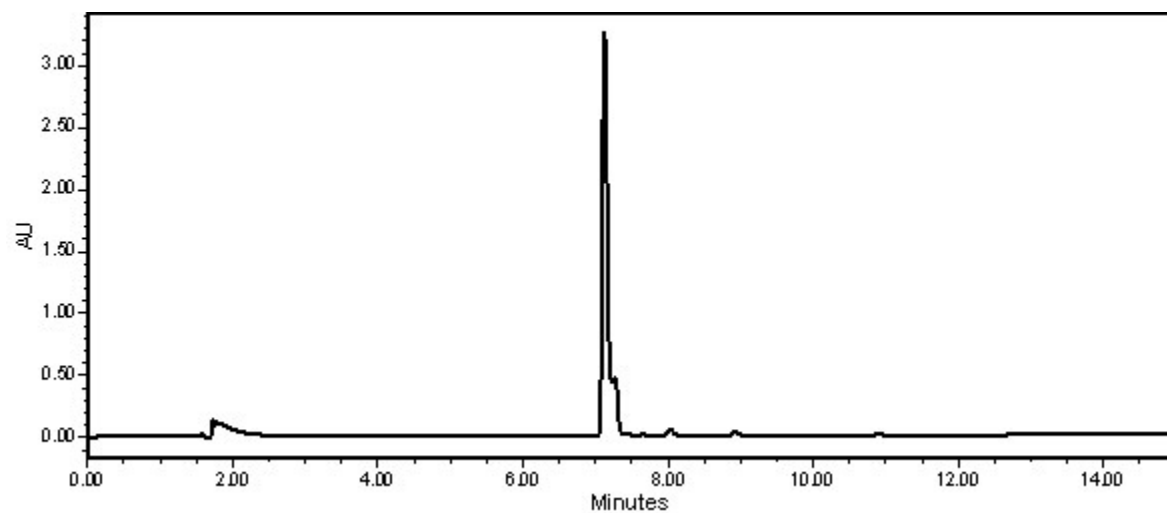


Figure S1. UV-HPLC trace of **3a** (Method B).

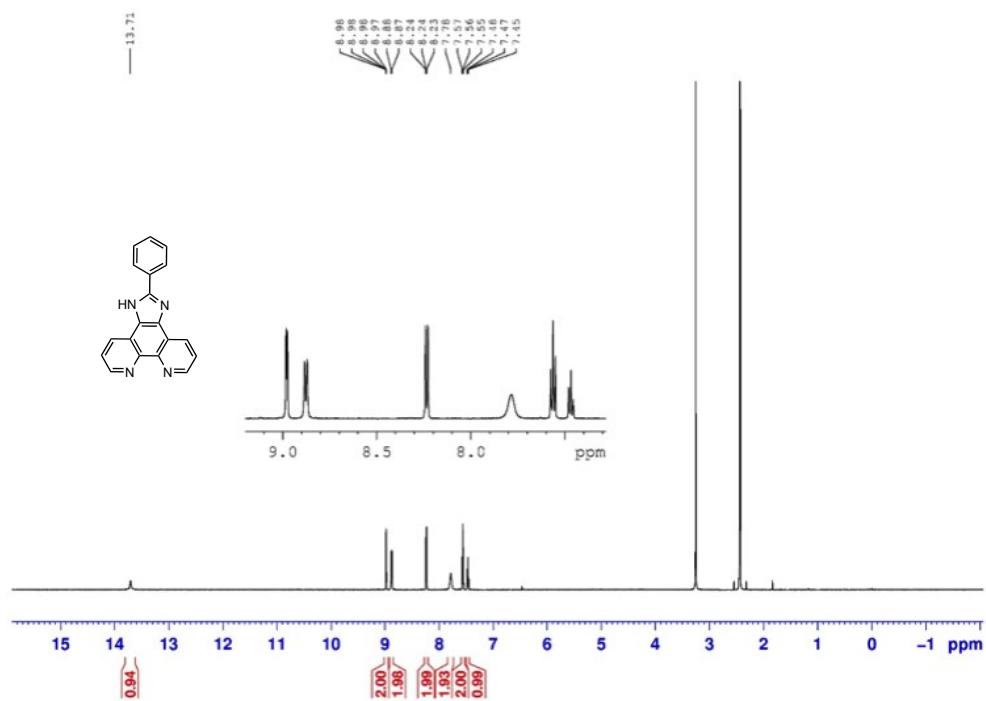


Figure S2. ^1H NMR spectrum ($(\text{CD}_3)_2\text{SO}$, 600 MHz) of **3a**.

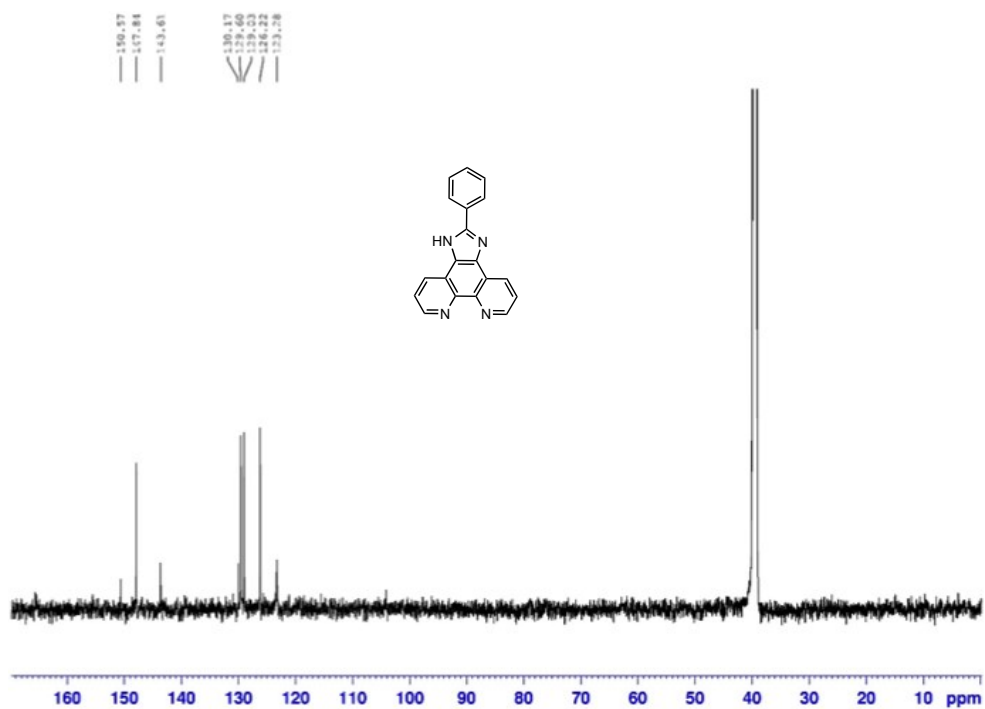


Figure S3. ^{13}C NMR spectrum ($(\text{CD}_3)_2\text{SO}$, 150 MHz) of the ligand **3a**.

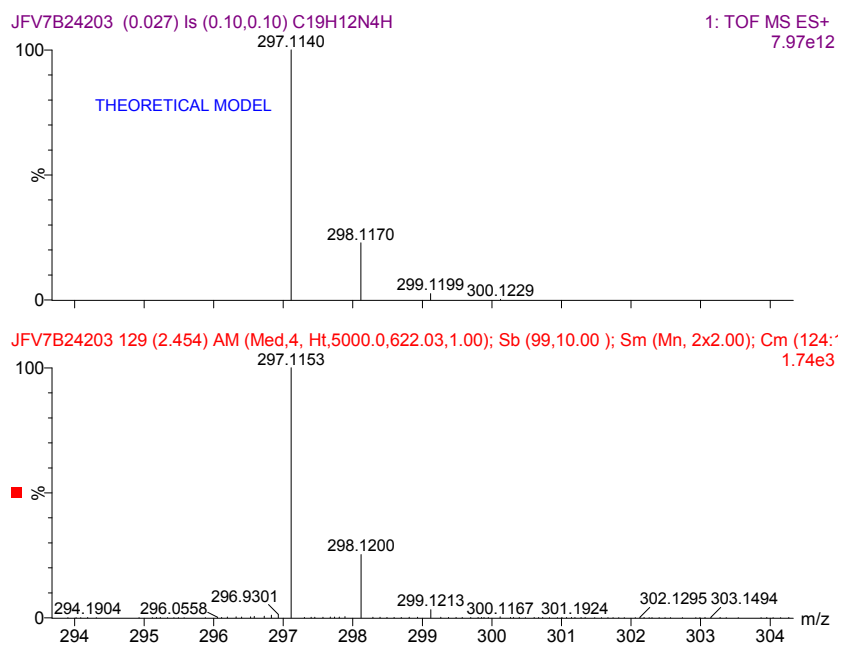


Figure S4. HRMS of **3a**.

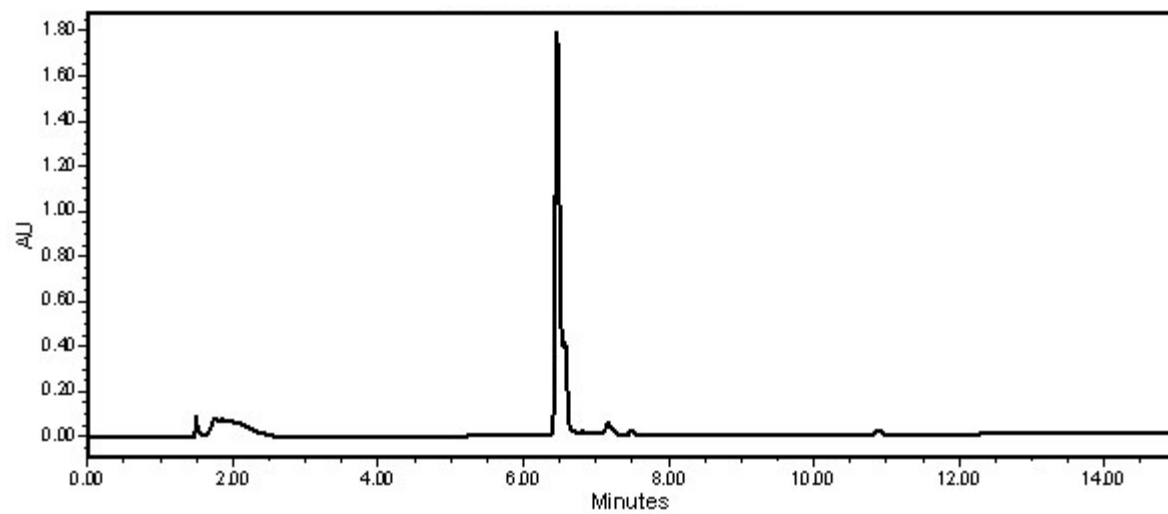


Figure S5. UV-HPLC trace of **3b** (Method B).

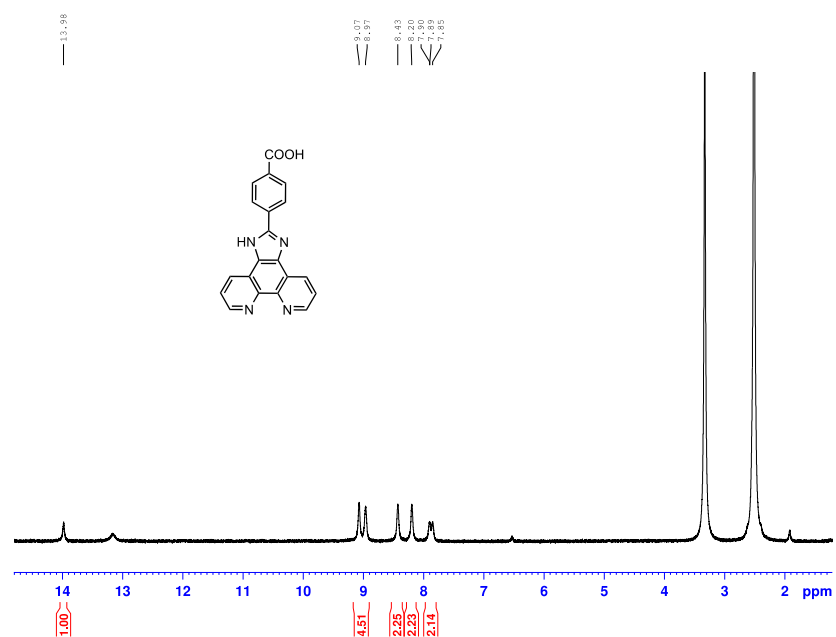


Figure S6. ^1H NMR spectrum ($(\text{CD}_3)_2\text{SO}$, 600 MHz) of **3b**.

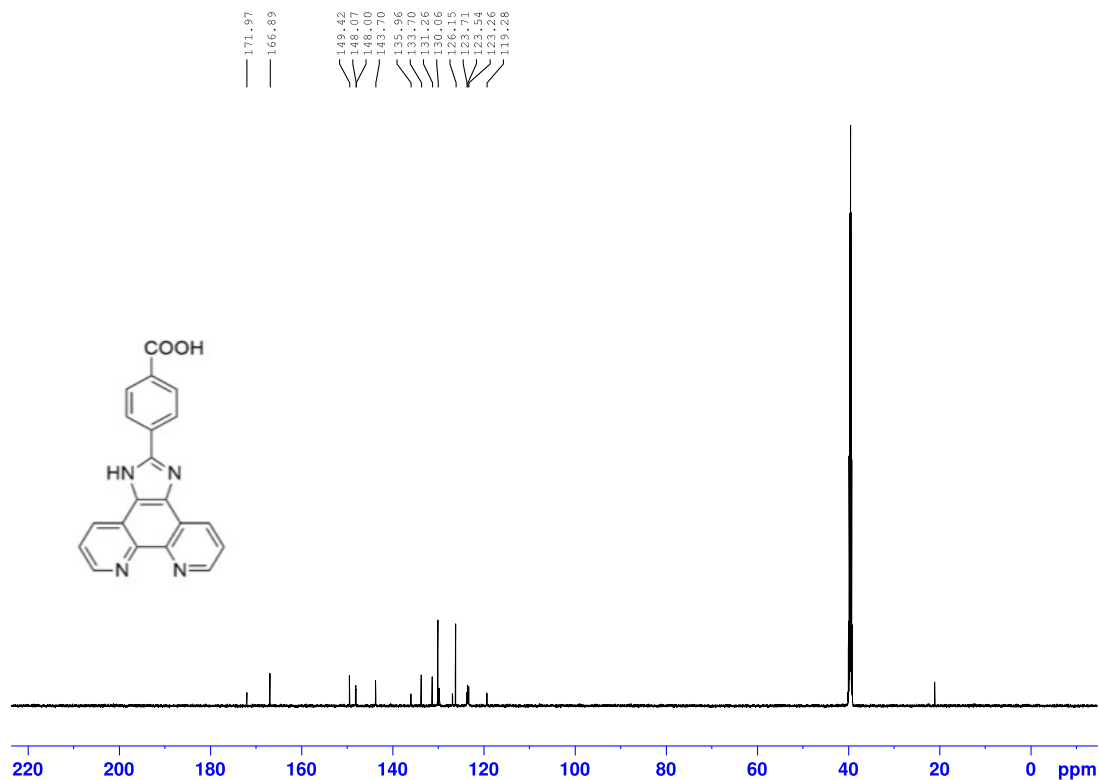


Figure S7. ¹³C NMR spectrum ((CD₃)₂SO, 150 MHz) of **3b**.

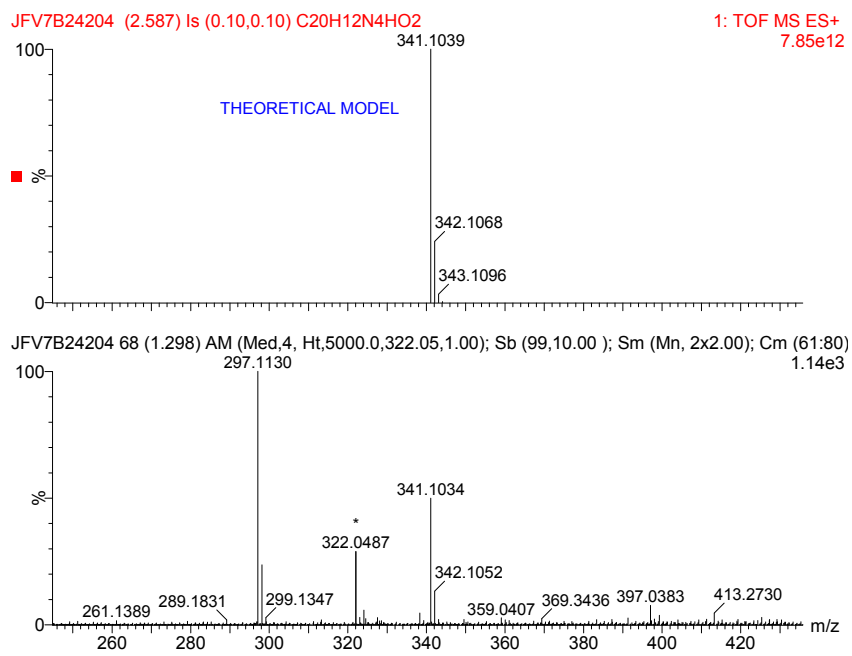


Figure S8. HRMS of **3b**.

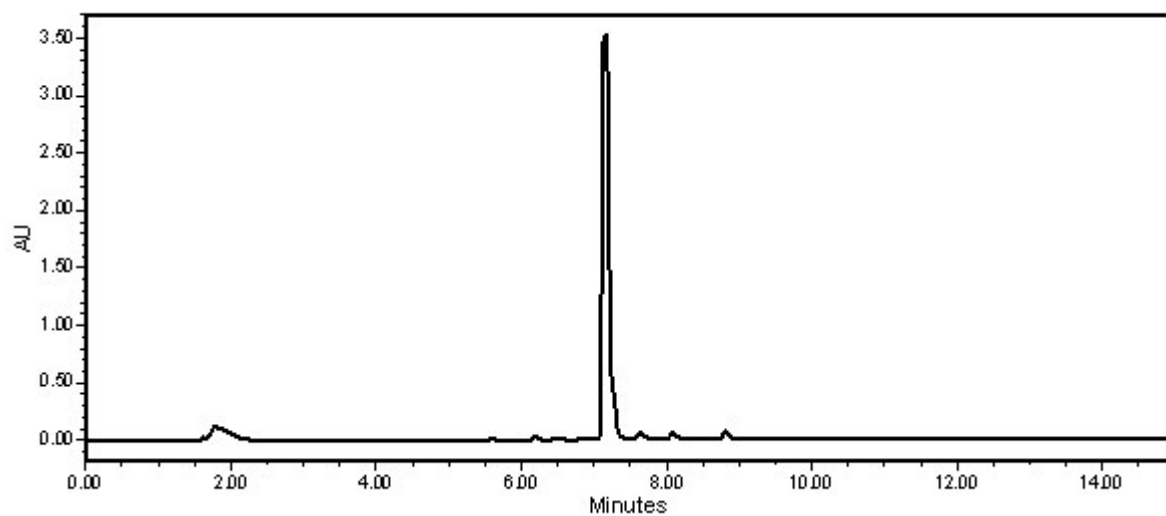


Figure S9. UV-HPLC trace of **3c** (Method B).

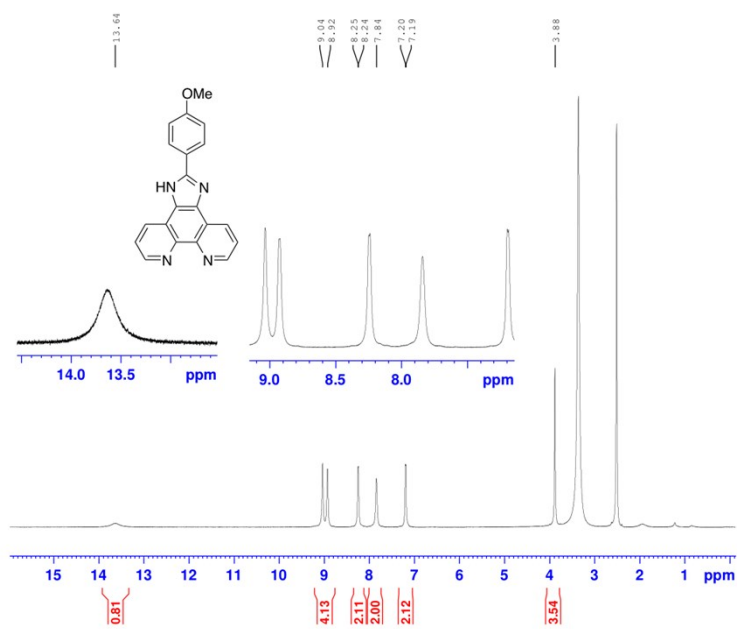


Figure S10. ¹H NMR spectrum (CD₃OD, 600 MHz) of **3c**.

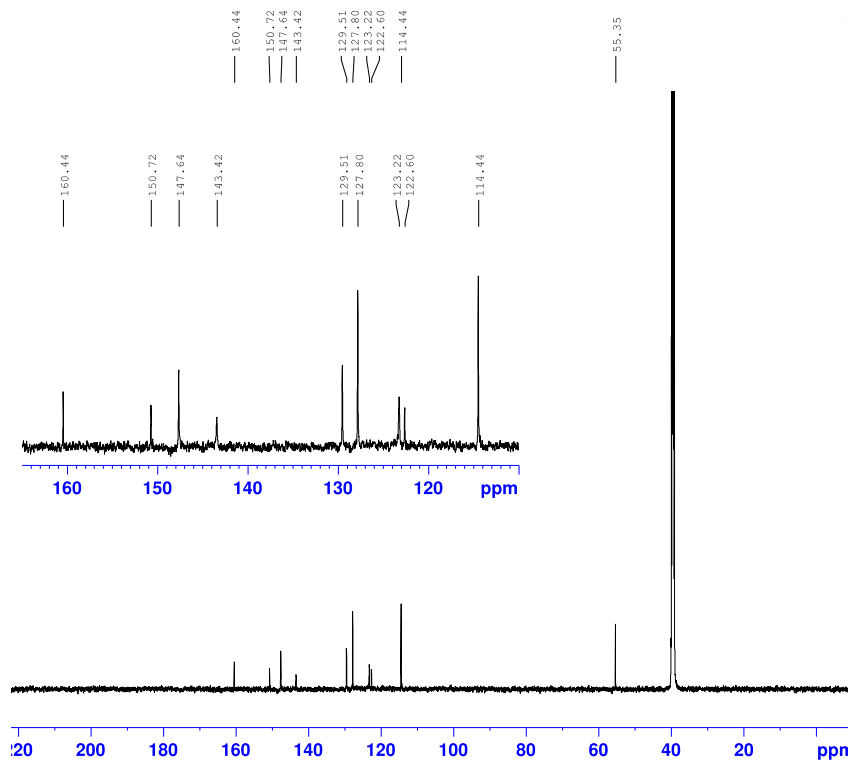


Figure S11. ^{13}C NMR spectrum (CD_3OD , 150 MHz) of **3c**.

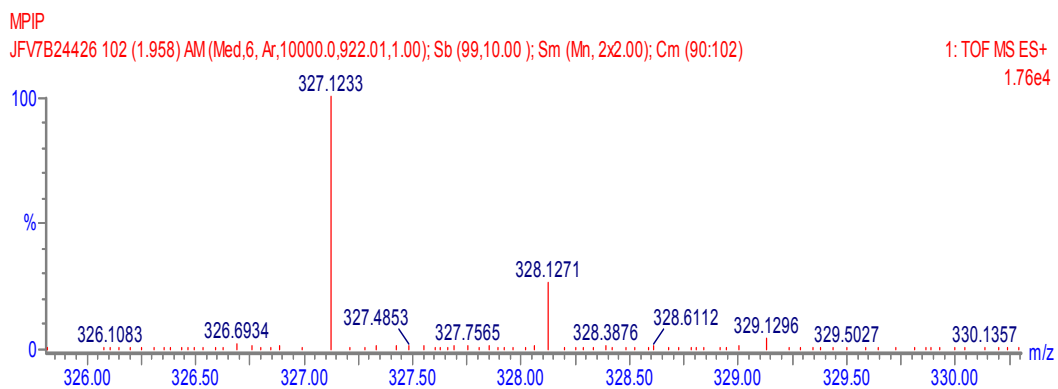


Figure S12. HRMS of **3c**.

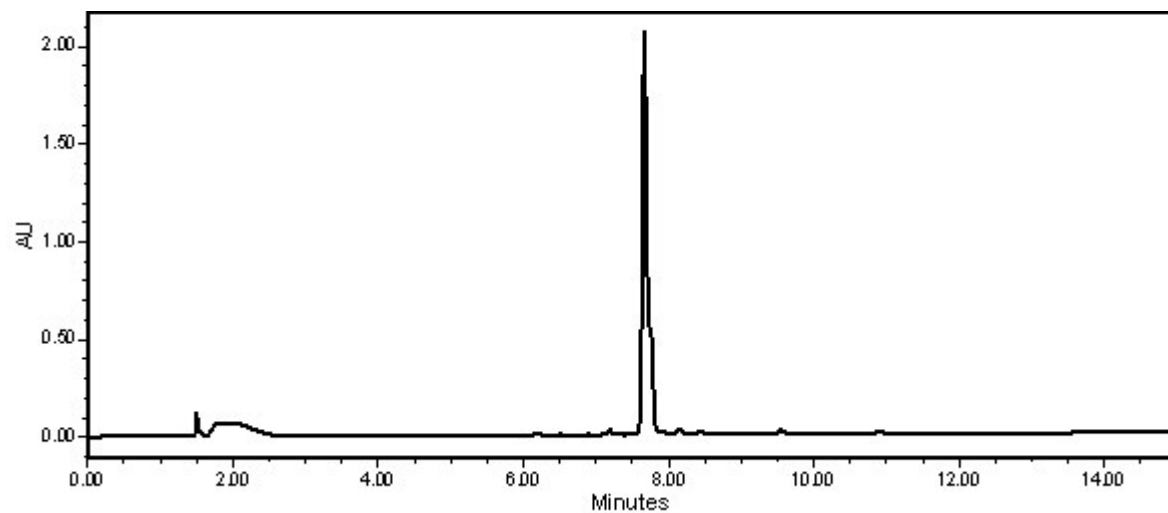


Figure S13. UV-HPLC trace of **3d** (Method B).

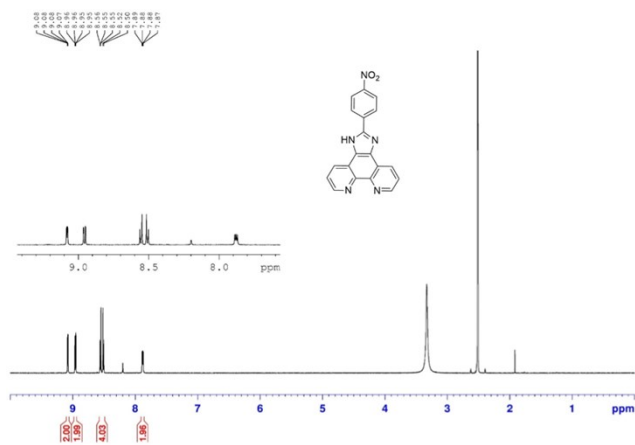


Figure S14. ^1H NMR spectrum ($(\text{CD}_3)_2\text{SO}$, 600 MHz) of **3d**.

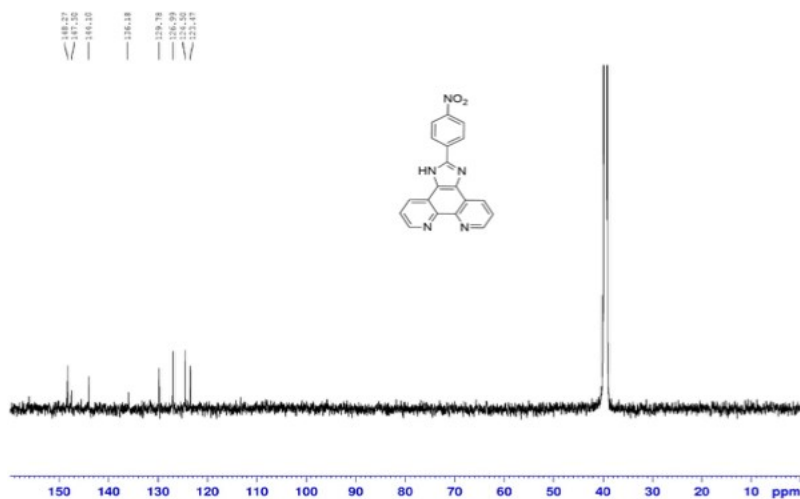


Figure S15. ¹³C NMR spectrum ((CD₃)₂SO, 150 MHz) of **3d**.

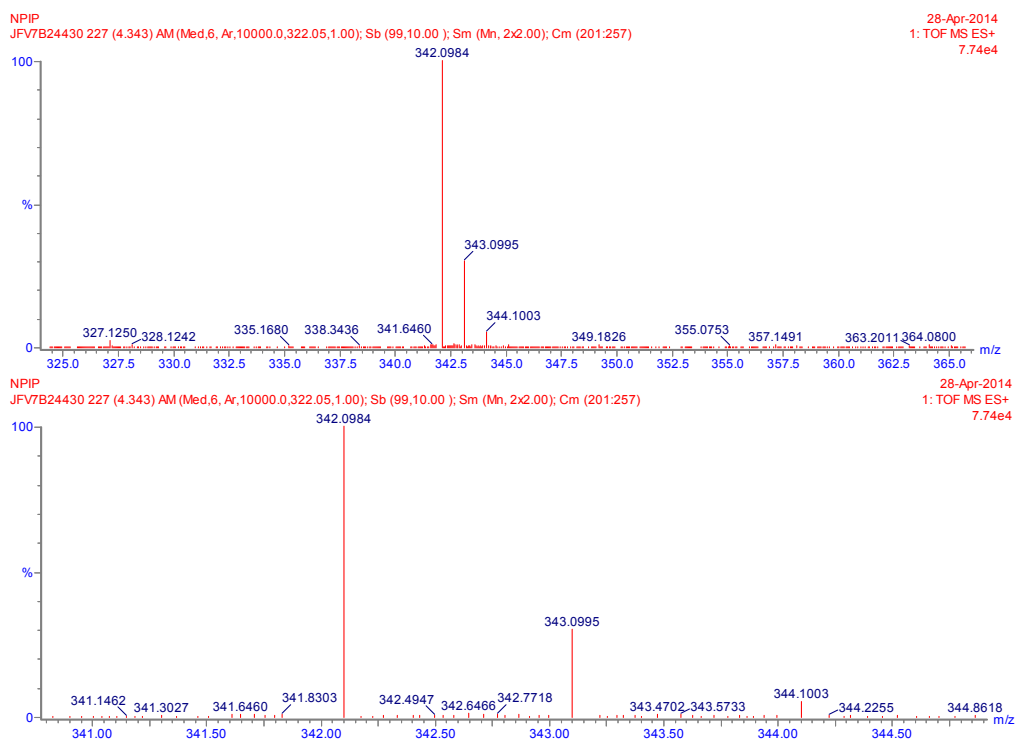


Figure S16. HRMS of **3d**.

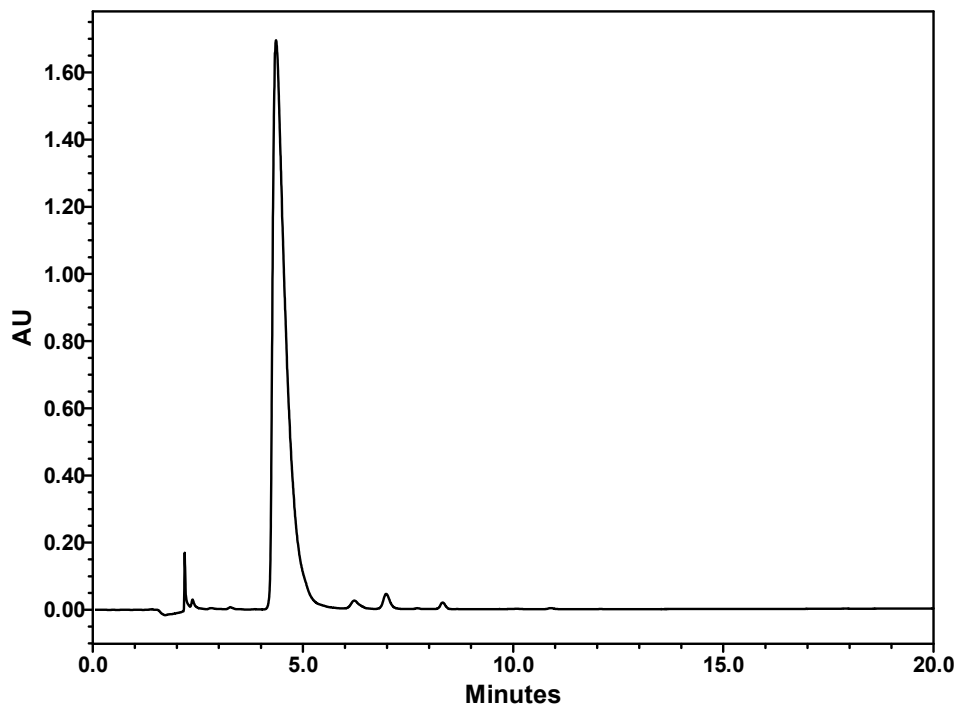


Figure S17. UV-HPLC trace of **3e** (Method C).

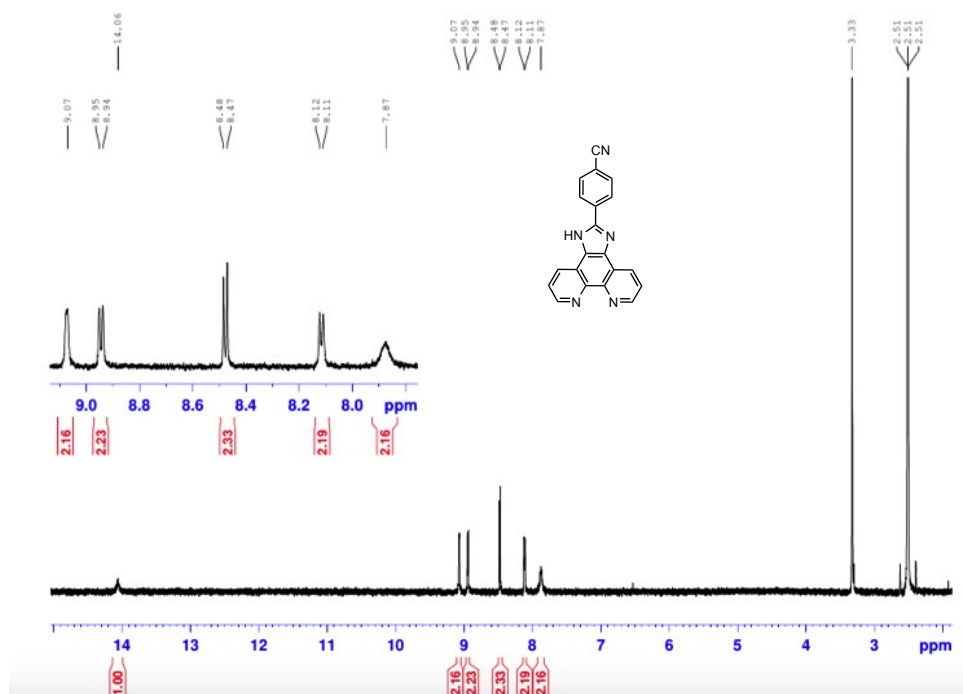


Figure S18. ^1H NMR spectrum ($(\text{CD}_3)_2\text{SO}$, 600 MHz) of **3e**.

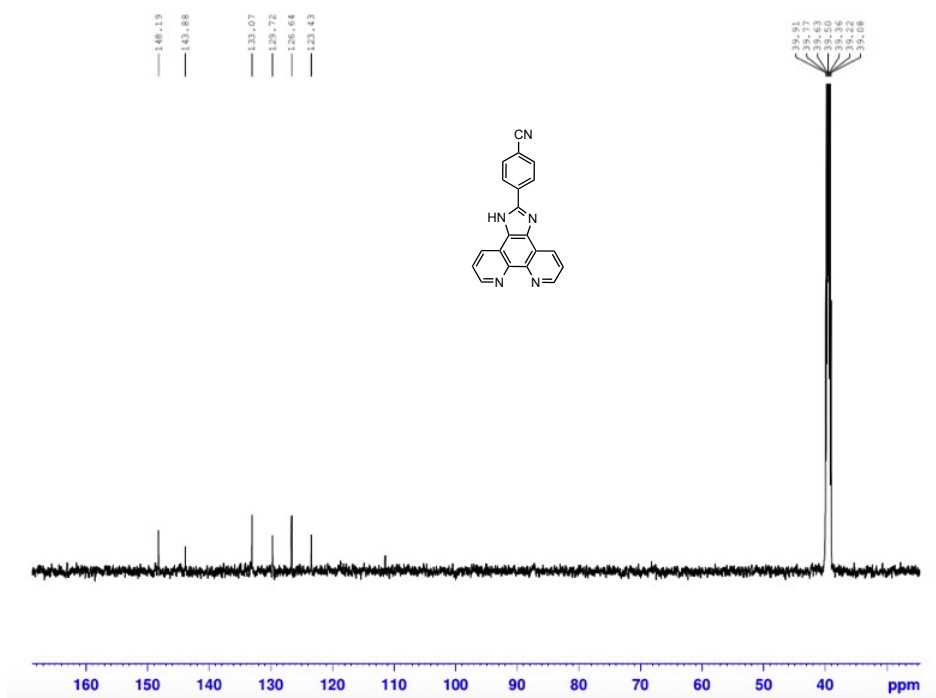


Figure S19. ¹³C NMR spectrum ((CD₃)₂SO, 150 MHz) of 3e.

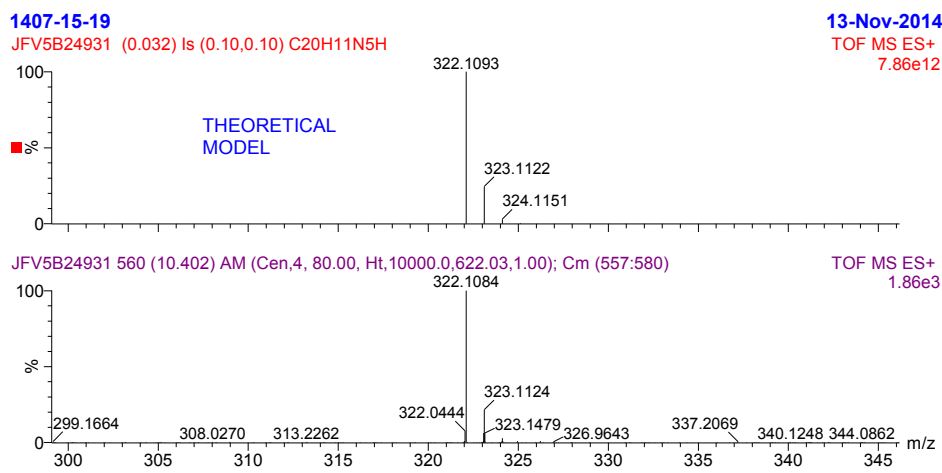


Figure S20. HRMS of 3e.

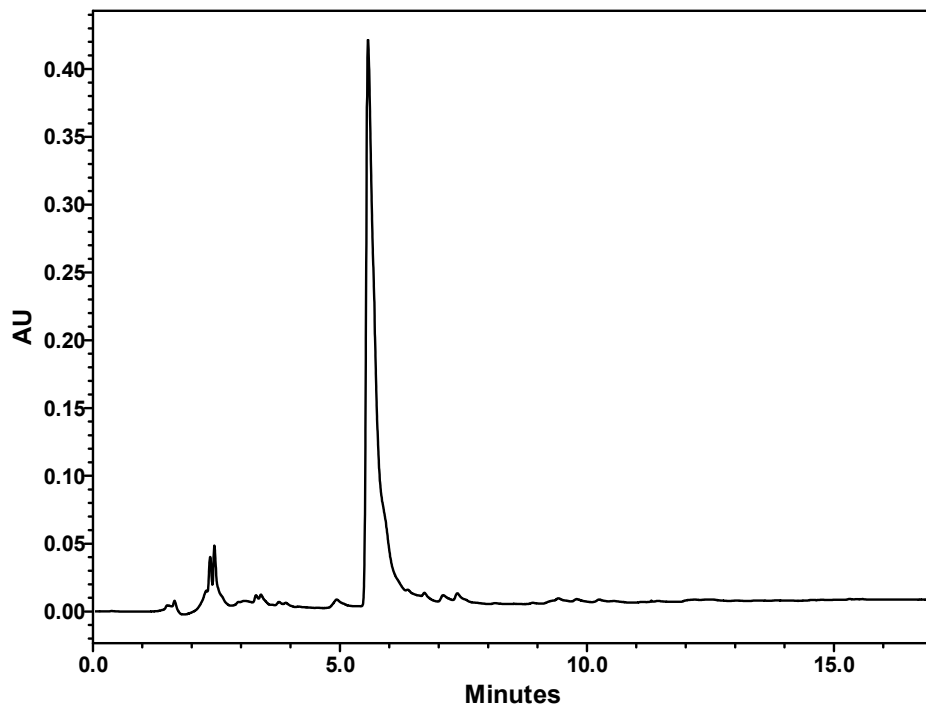


Figure S21. UV-HPLC trace of **3f** (Method C).

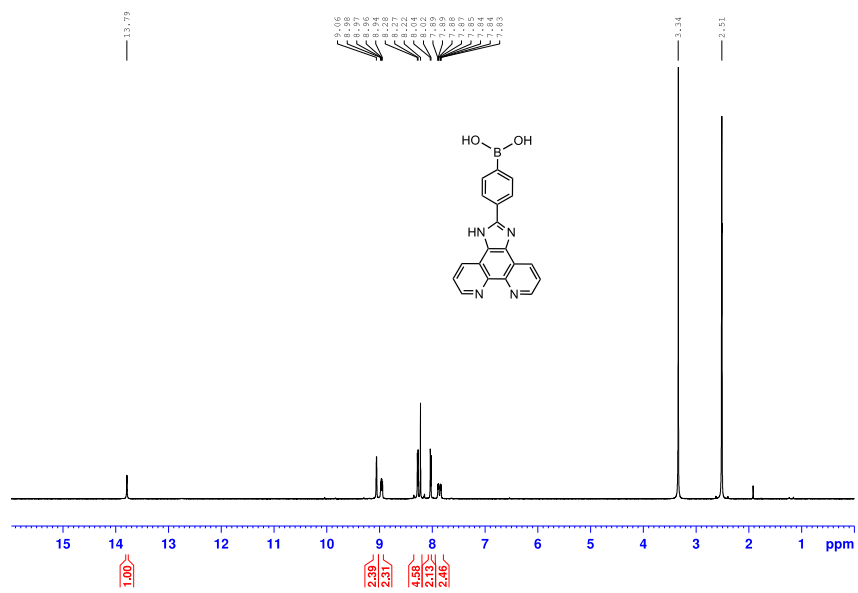


Figure S22. ^1H NMR ($(\text{CD}_3)_2\text{SO}$), 600 MHz) of **3f**.

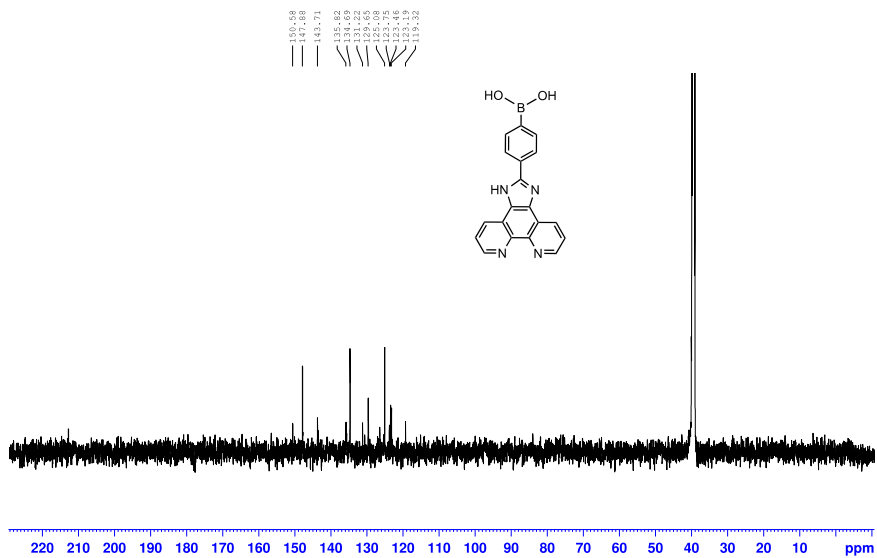


Figure S23. ¹³C NMR ((CD₃)₂SO), 150 MHz) of **3f**.

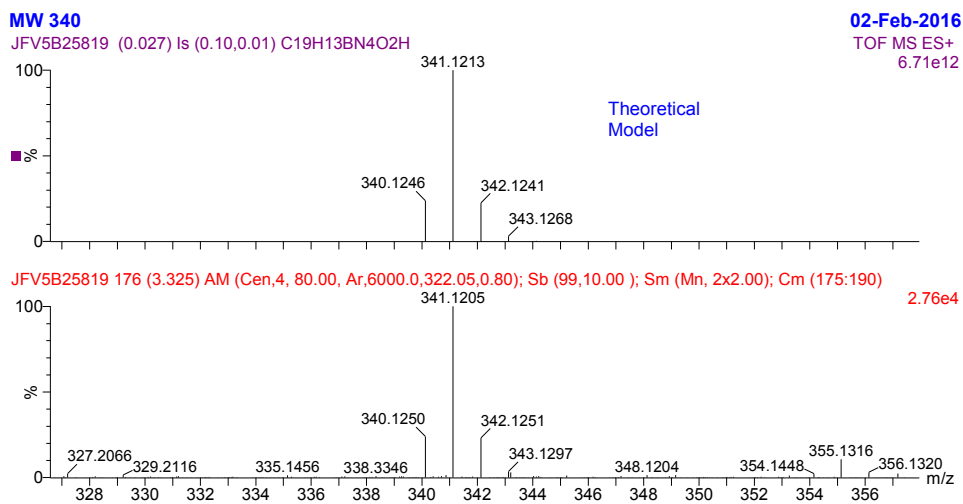


Figure S24. HRMS of **3f**.

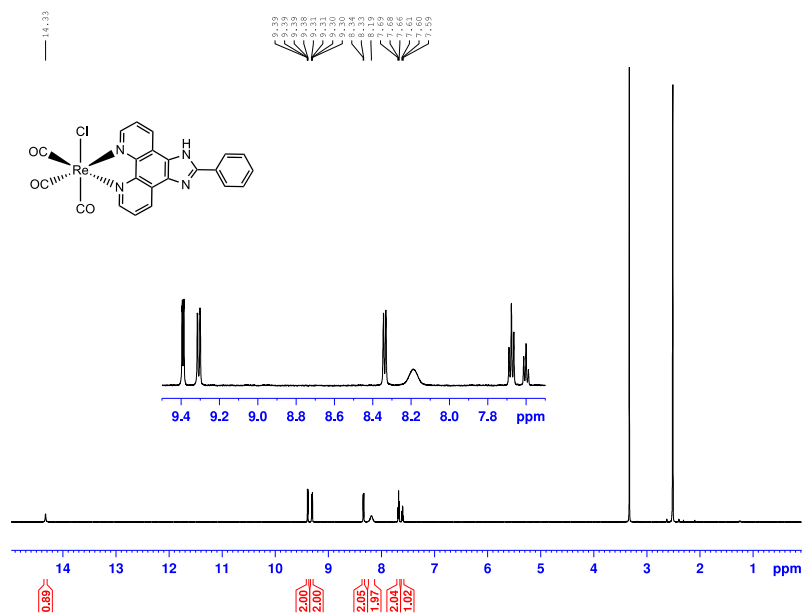


Figure S25. ¹H NMR spectrum ((CD₃)₂SO, 600 MHz) of **4a**.

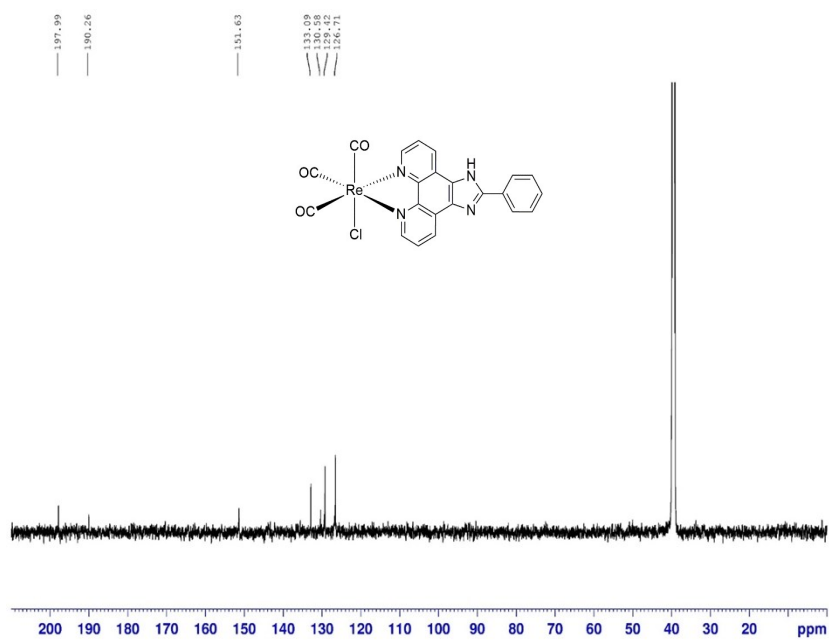


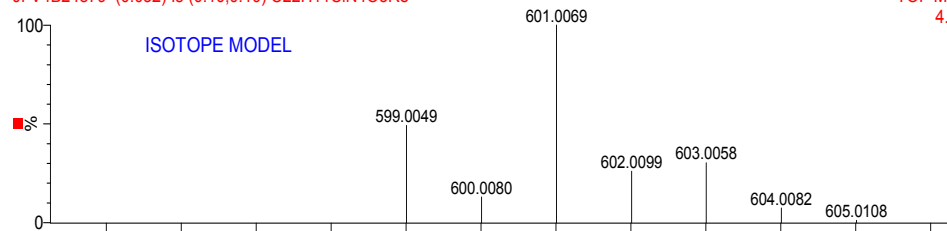
Figure S26. ¹³C NMR spectrum ((CD₃)₂SO, 150 MHz) of **4a**.

RePIPCI

JFV4B24879 (0.032) Is (0.10,0.10) C22H11ClN4O3Re

29-Oct-2014

TOF MS ES-
4.41e12



JFV4B24879 424 (8.100) AM (Cen,8, 80.00, Ht,10000.0,1033.99,1.00); Sb (99,10.00); Sm (Mn, 2x2.00); Cm (408:433)

TOF MS ES-
681

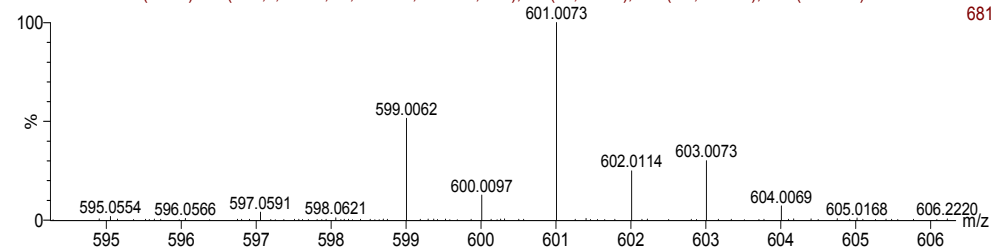


Figure S27. HRMS of **4a**.

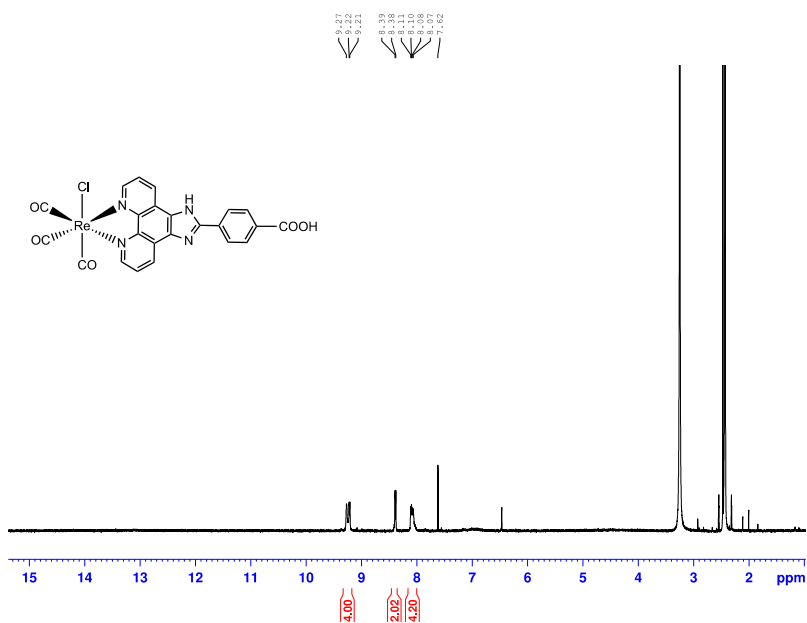


Figure S28. ¹H NMR spectrum ((CD₃)₂SO, 600 MHz) of **4b**.

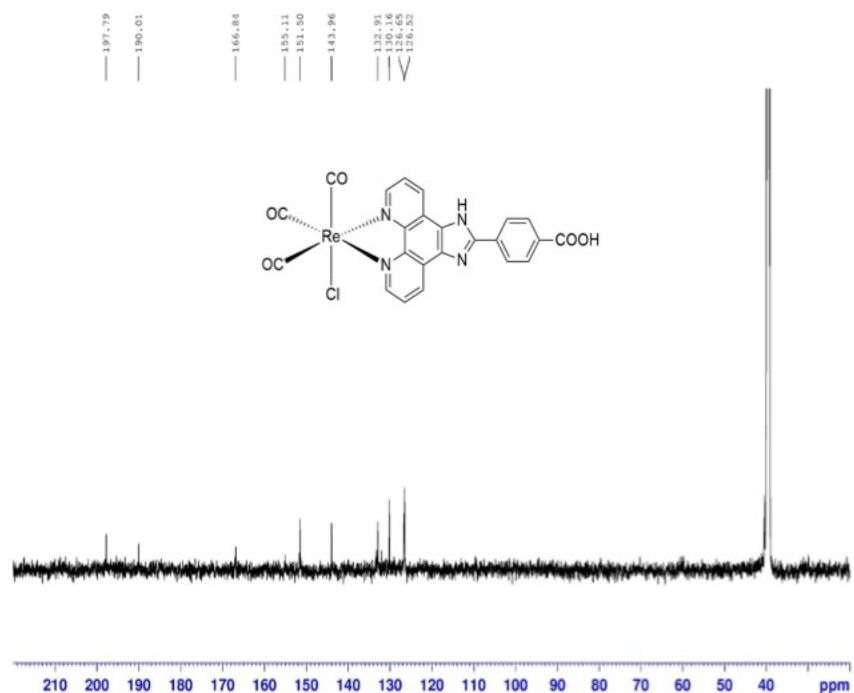


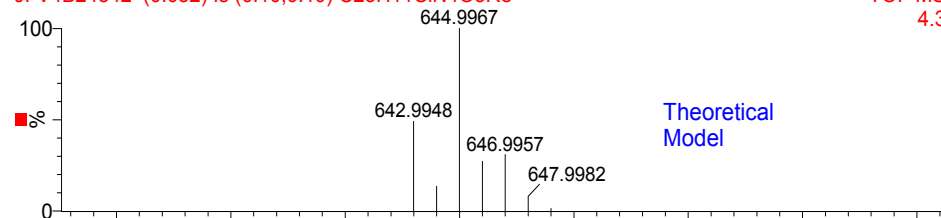
Figure S29. ^{13}C NMR spectrum ($(\text{CD}_3)_2\text{SO}$, 150 MHz) of **4b**.

ReCPIPC

JFV4B24842 (0.032) Is (0.10,0.10) C₂₃H₁₁CIN₄O₅Re

17-Oct-2014

TOF MS ES-
4.36e12



JFV4B24842 438 (8.146) AM (Med,8, Ht,10000.0,734.01,1.00); Sb (10,10.00); Sm (Mn, 2x2.00); Cm (394:51 751

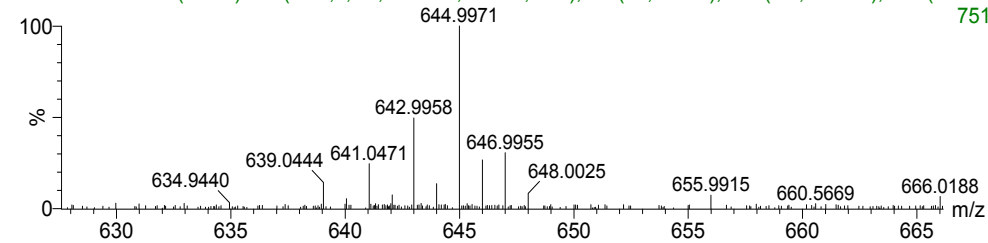


Figure S30. HRMS of **4b**.

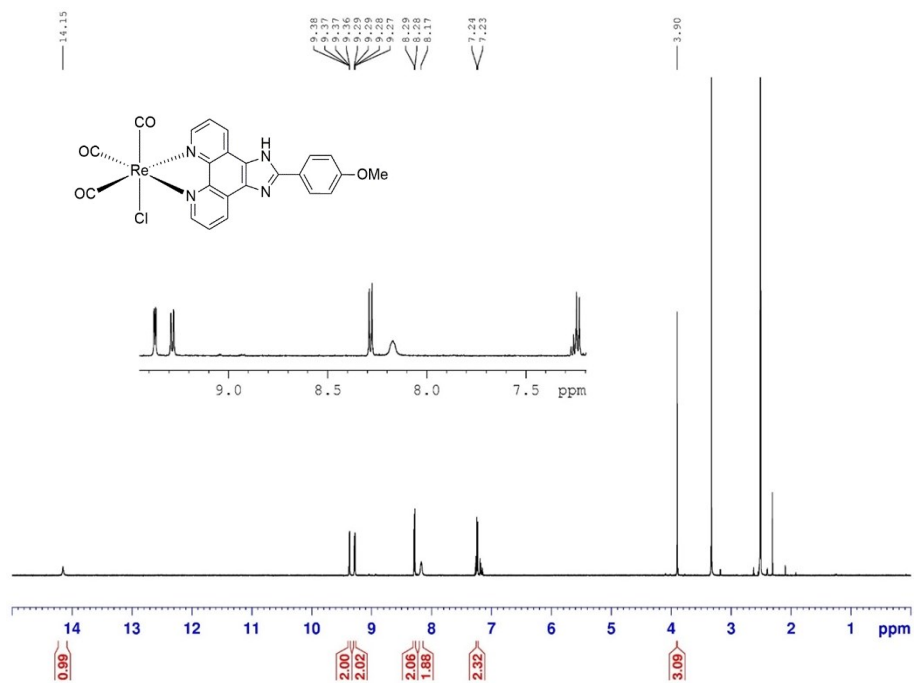


Figure S31. ¹H NMR spectrum ((CD₃)₂SO, 600 MHz) of **4c**.

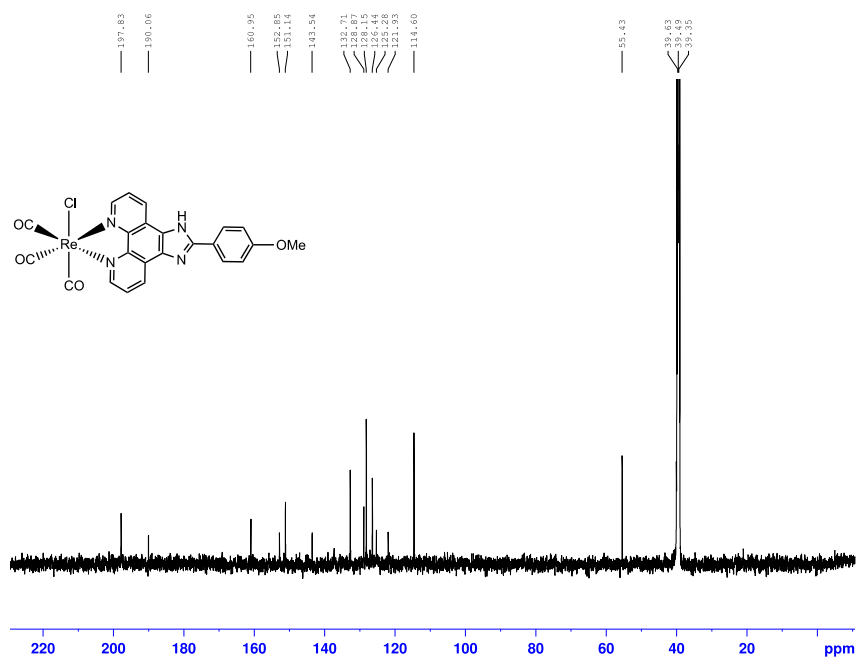
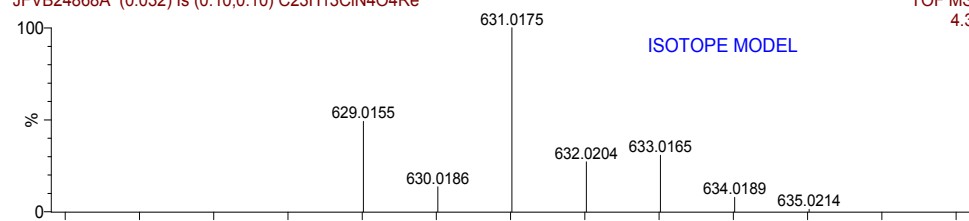


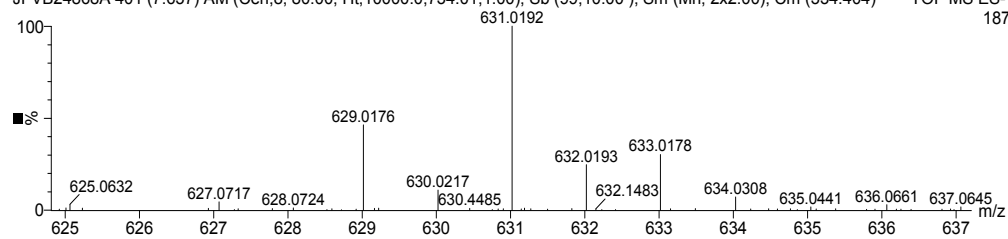
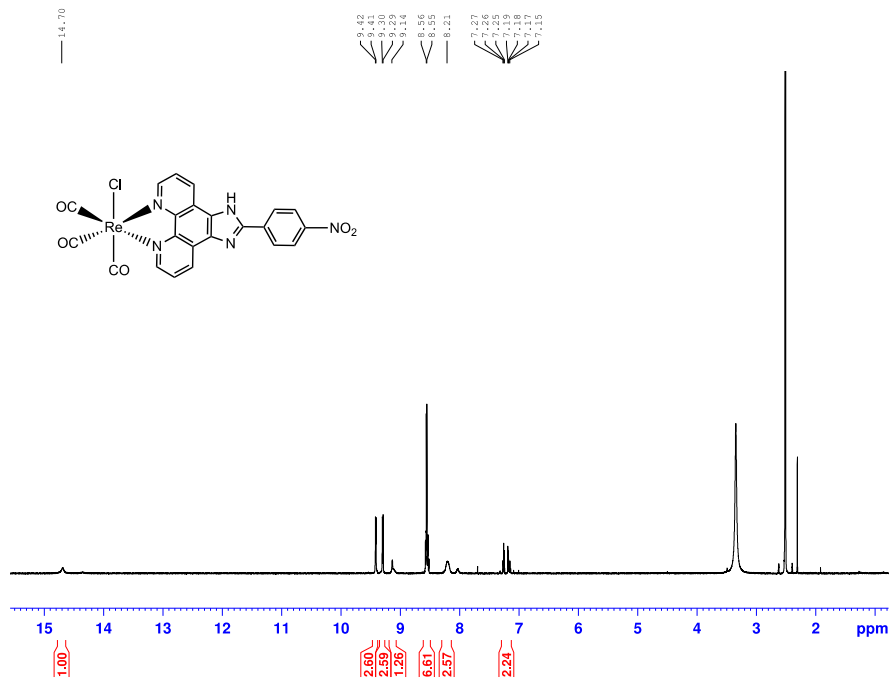
Figure S32. ¹³C NMR spectrum ((CD₃)₂SO, 150 MHz) of **4c**.

ReMPIPCIJFVB24868A (0.032) Is (0.10,0.10) C₂₃H₁₃CIN₄O₄Re

28-Oct-2014

TOF MS ES-
4.36e12

JFVB24868A 401 (7.637) AM (Cen,8, 80.00, Ht,10000.0,734.01,1.00); Sb (99,10.00); Sm (Mn, 2x2.00); Cm (334:404) TOF MS ES-187

Figure S33. HRMS of **4c**.Figure S34. ¹H NMR spectrum ((CD₃)₂SO, 600 MHz) of **4d**.

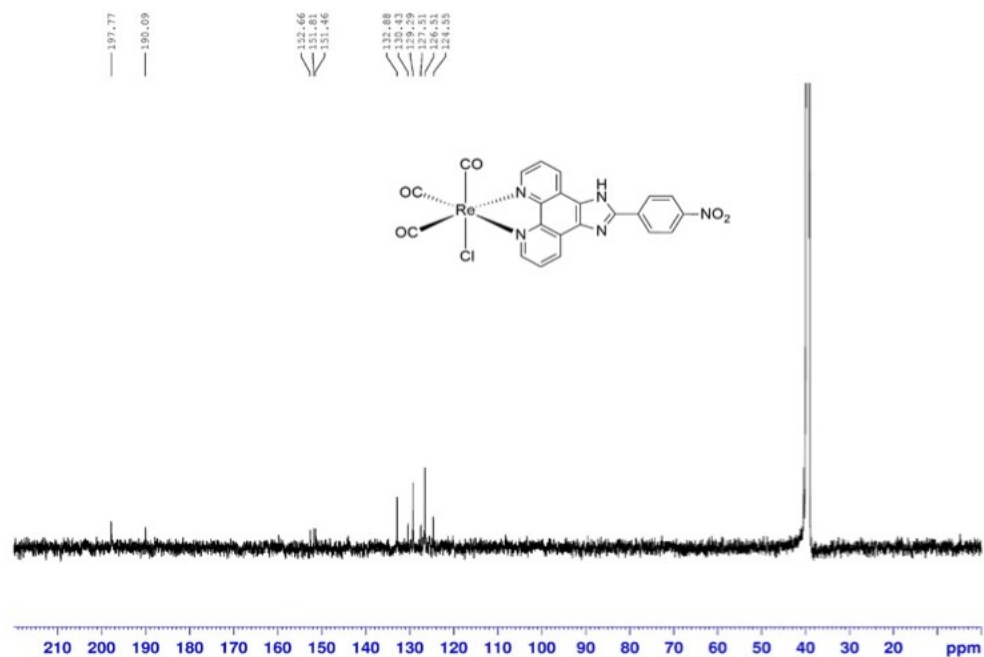


Figure S35. ^{13}C NMR spectrum ($(\text{CD}_3)_2\text{SO}$, 150 MHz) of **4d**.

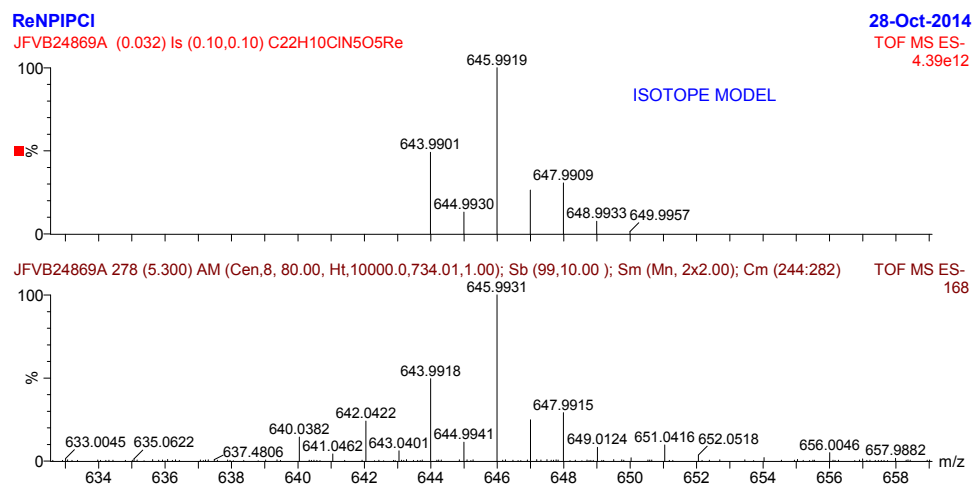


Figure S36. HRMS of **4d**.

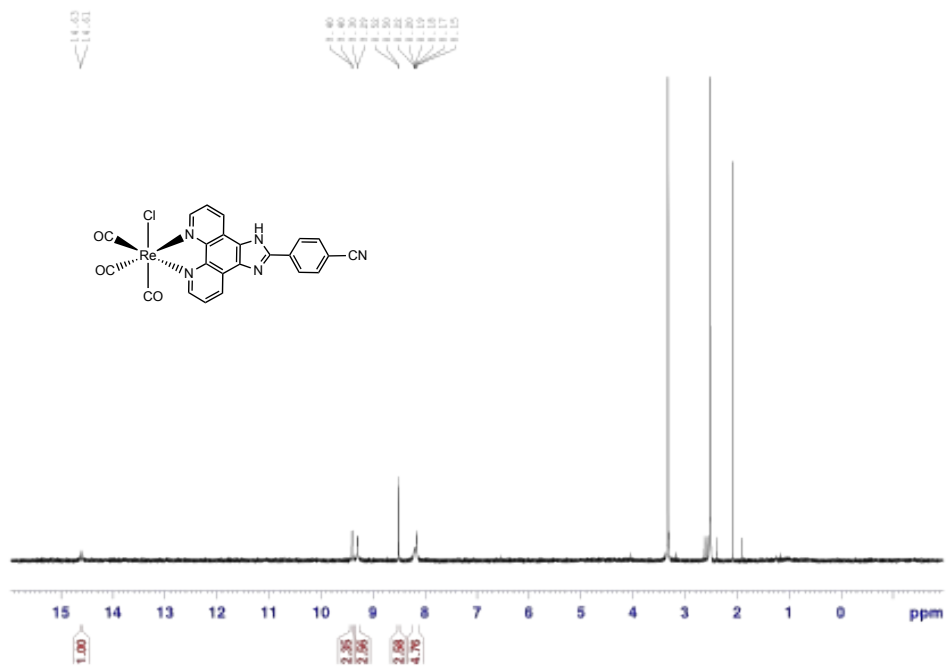


Figure S37. ¹H NMR spectrum ((CD₃)₂SO), 600 MHz) of 4e.

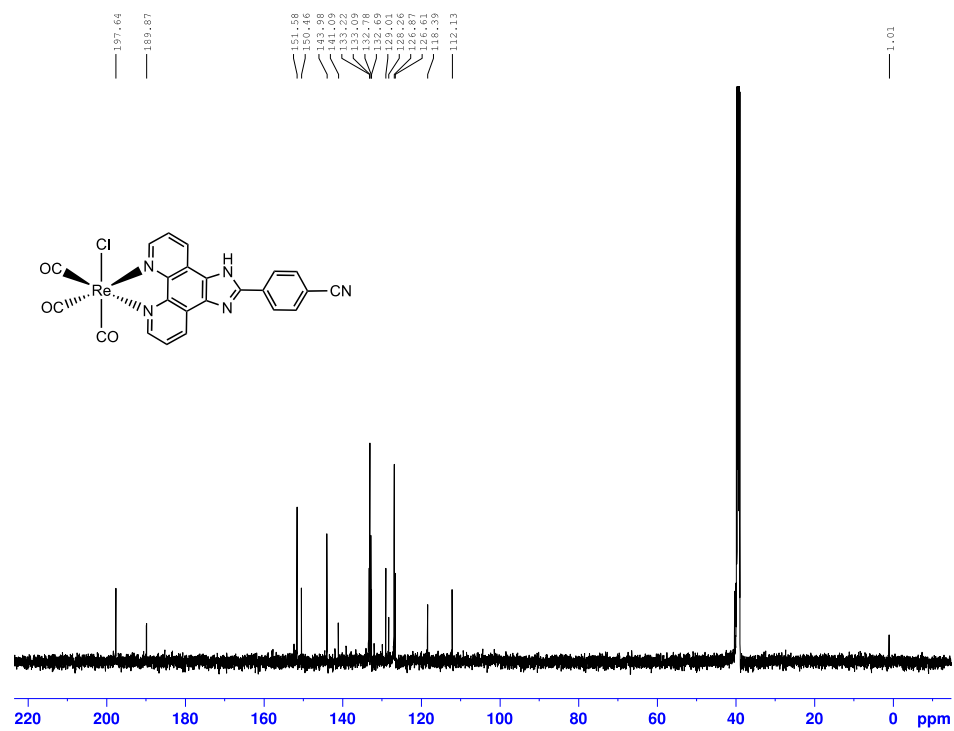


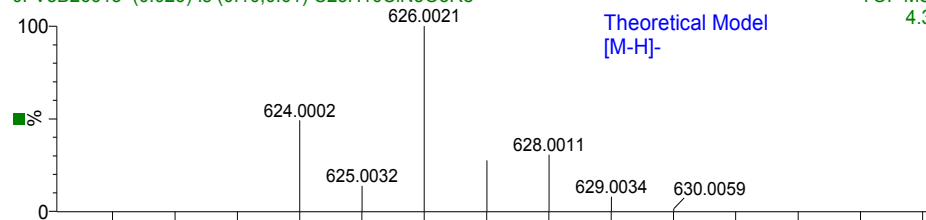
Figure S38. ¹³C NMR spectrum ((CD₃)₂SO), 600 MHz) of 4e.

MW 626

JFV5B26613 (0.026) Is (0.10,0.01) C₂₃H₁₀CIN₅O₃Re

06-Oct-2016

TOF MS ES-
4.36e12



JFV5B26613 302 (5.705) AM (Cen,4, 80.00, Ar,6500.0,735.01,0.80); Sb (99,10.00); Sm (Mn, 2x2.00); Cm (296:314 8.52e3

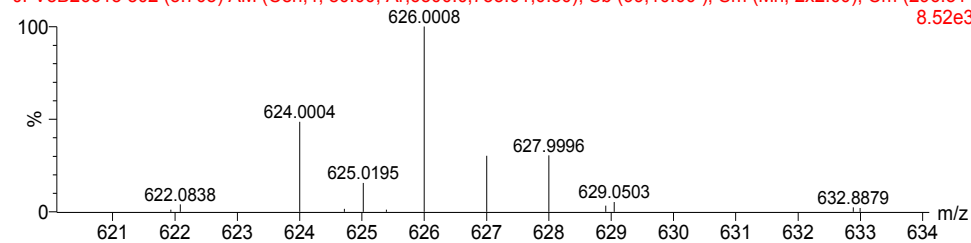


Figure S39. HRMS of 4e.

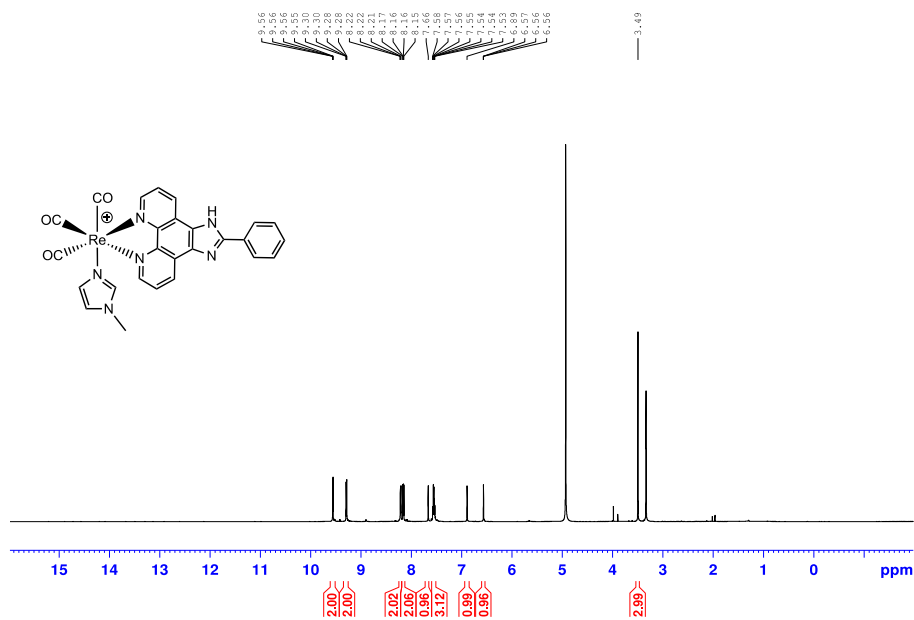


Figure S40. ¹H NMR spectrum (CD₃OD, 600 MHz) of 5a.

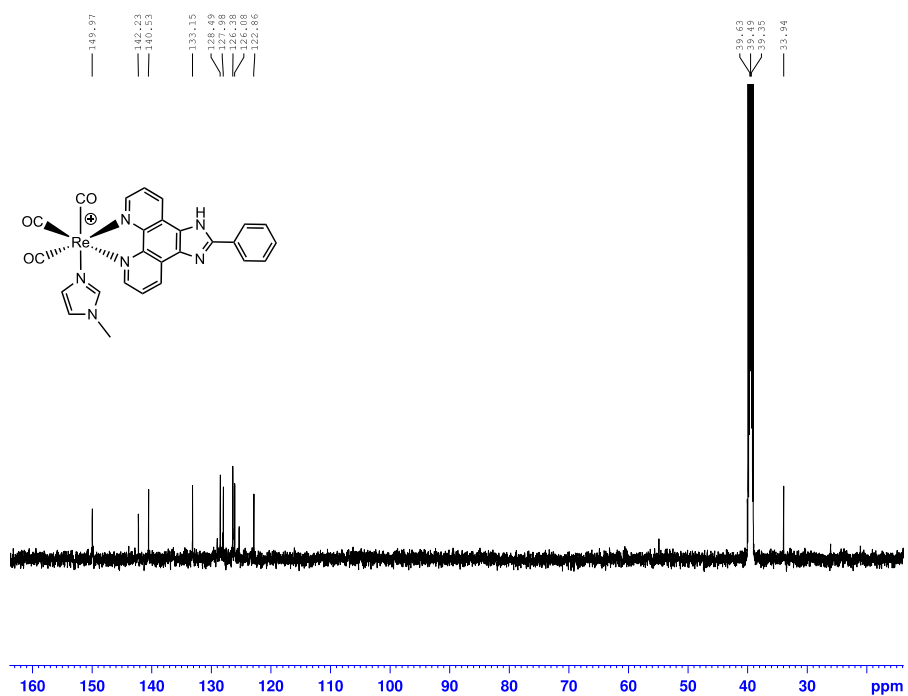


Figure S41. ¹³C NMR spectrum ((CD₃)₂SO, 150 MHz) of **5a**.

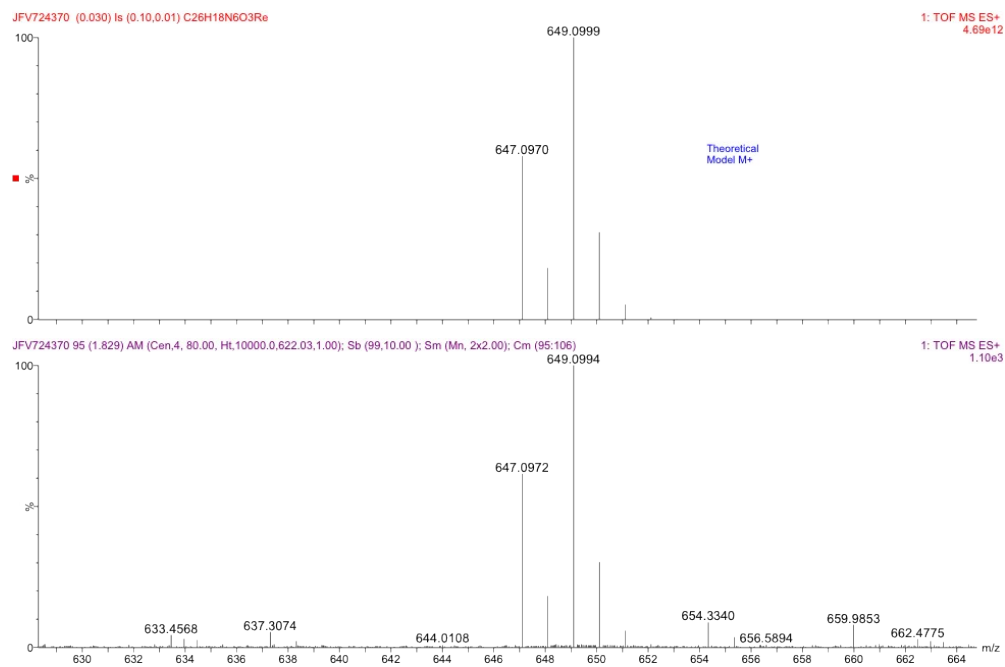


Figure S42. HRMS of **5a**.

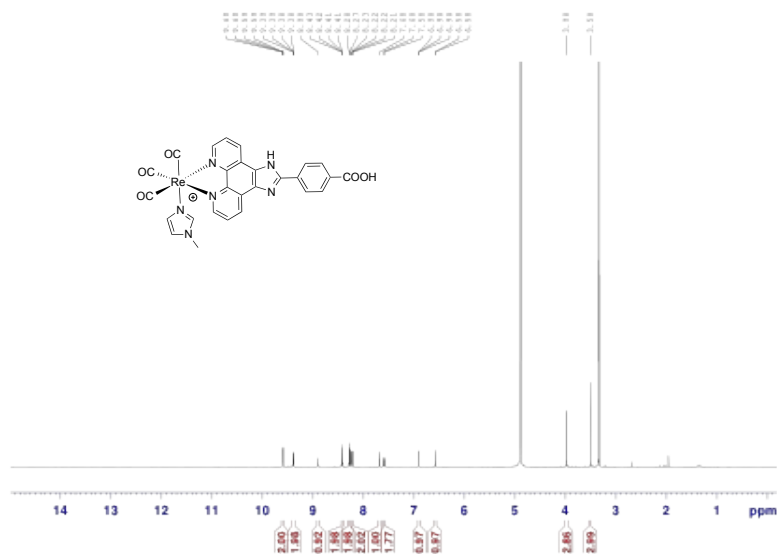


Figure S43. ¹H NMR spectrum (CD₃OD, 600 MHz) of **5b**.

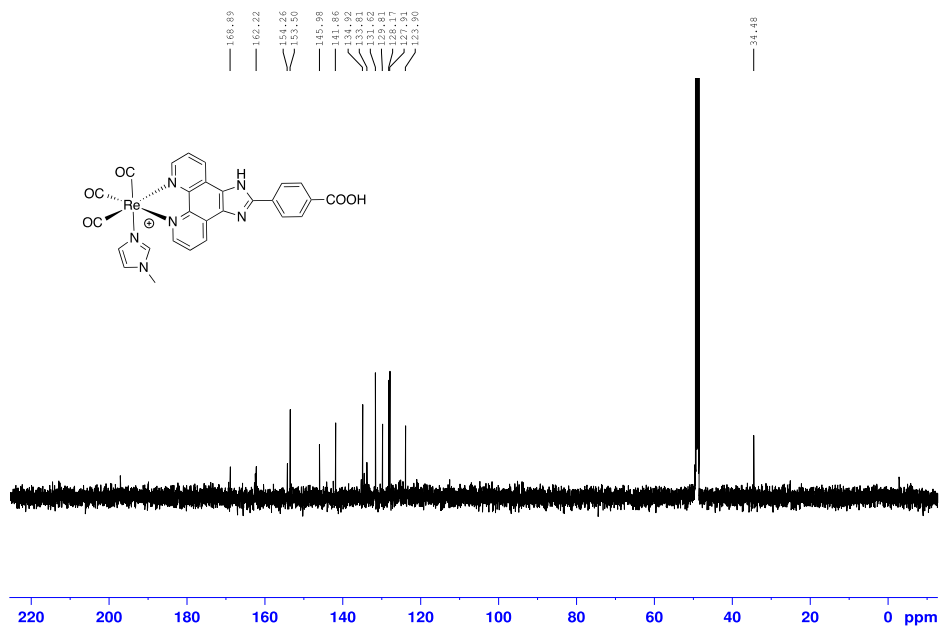


Figure S44. ¹³C NMR spectrum (CD₃OD, 150 MHz) of **5b**.

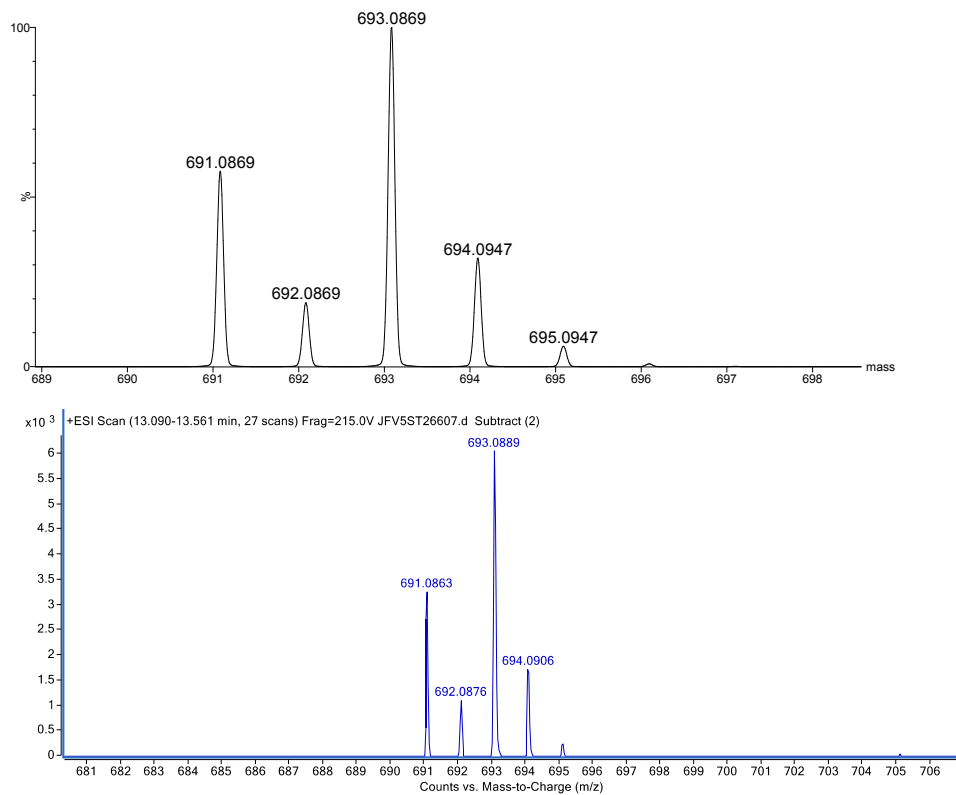


Figure S45. HRMS of **5b**.

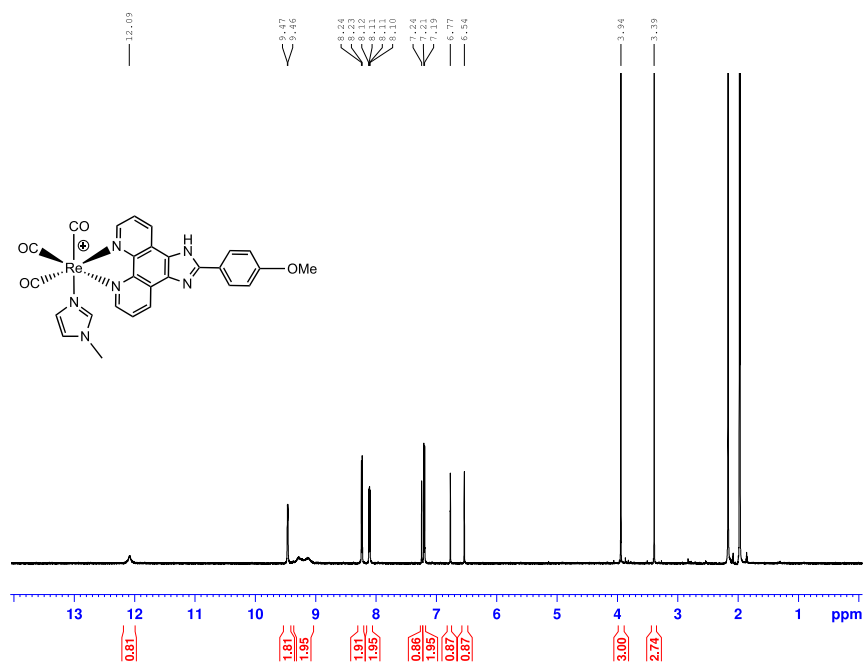


Figure S46. ^1H NMR spectrum (CD_3CN , 600 MHz) of **5c**.

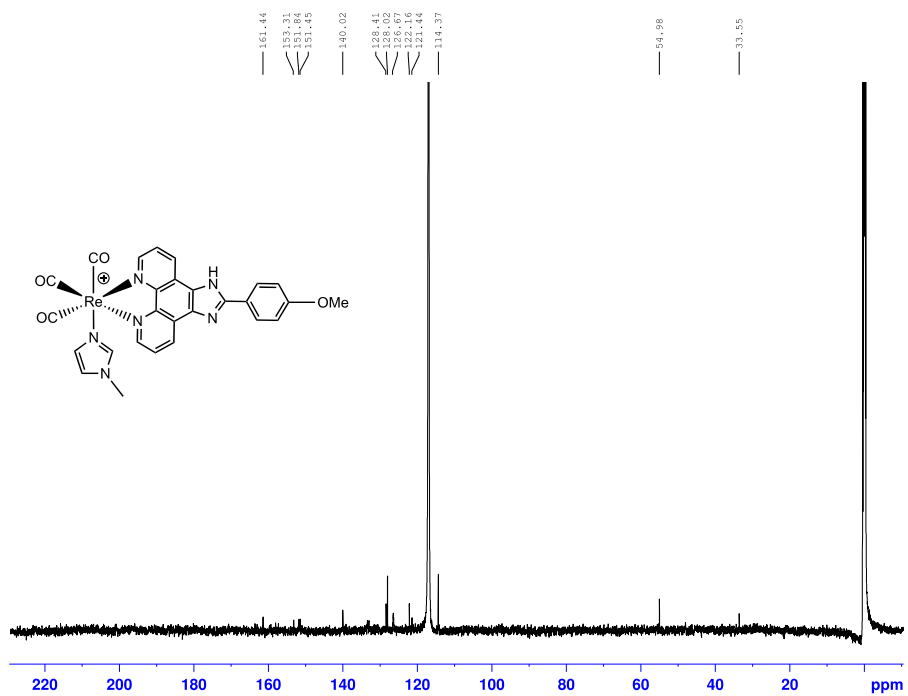


Figure S47. ^{13}C NMR spectrum (CD_3CN , 150 MHz) of **5c**.

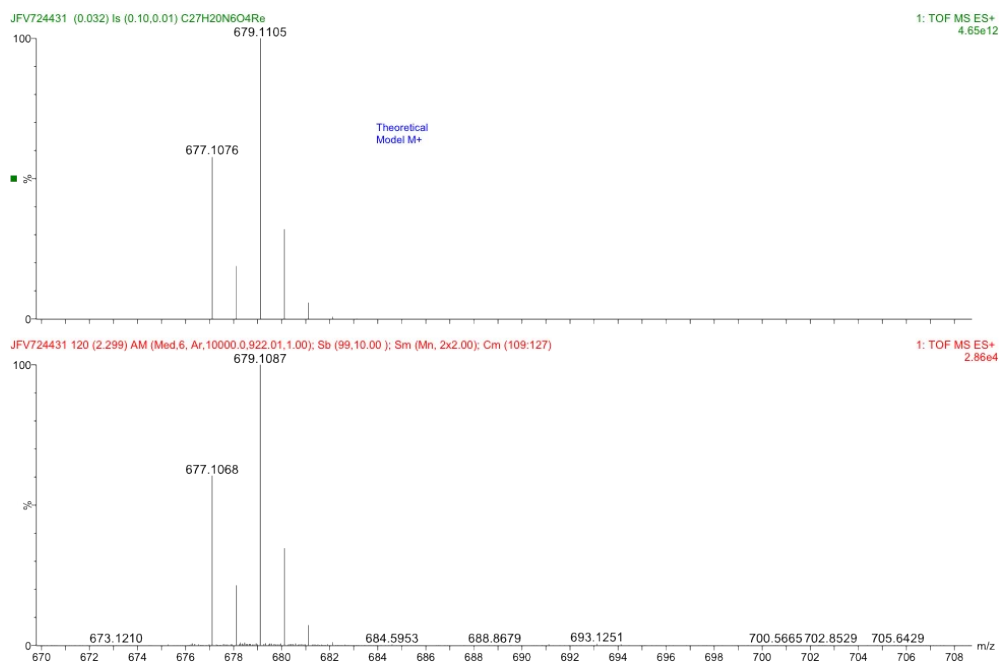


Figure S48. HRMS of **5c**.

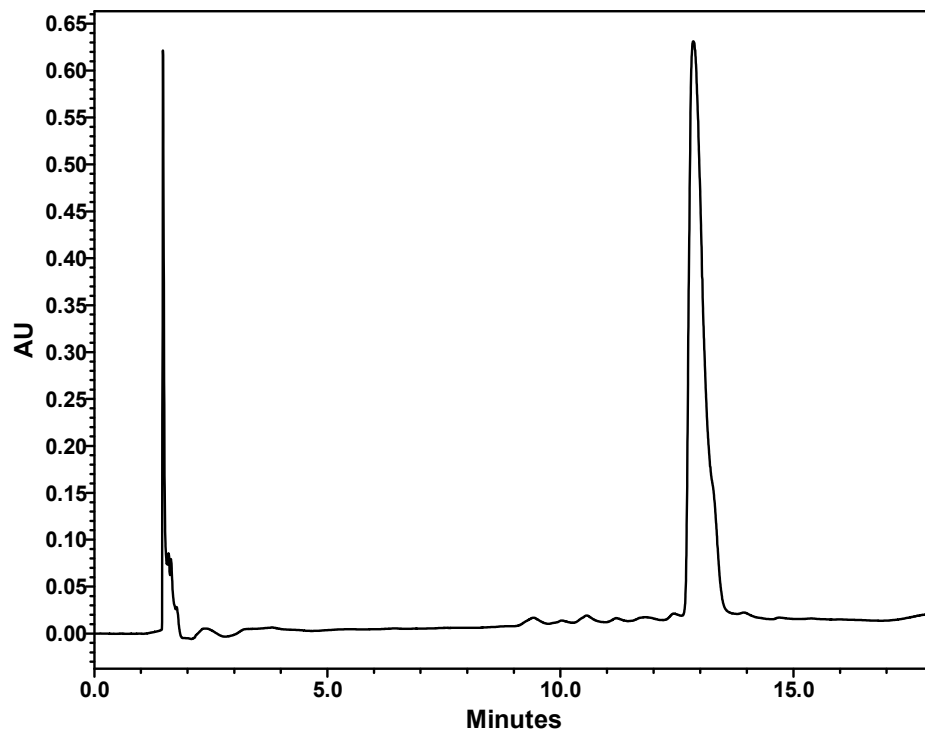


Figure S49. UV-HPLC trace of **5e** (Method D).

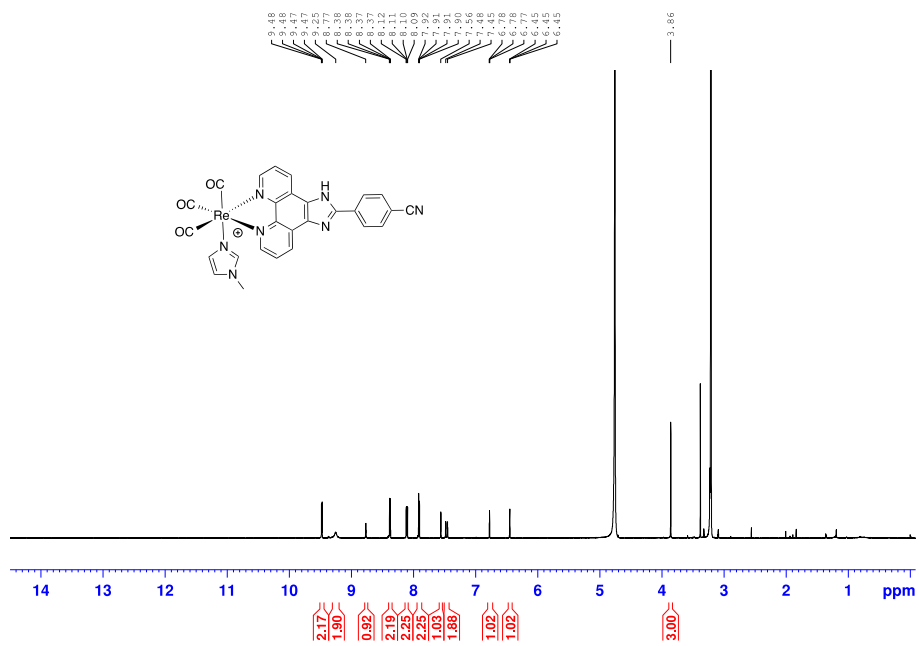


Figure S50. ^1H NMR spectrum (CD_3OD), 600 MHz) of **5e**.

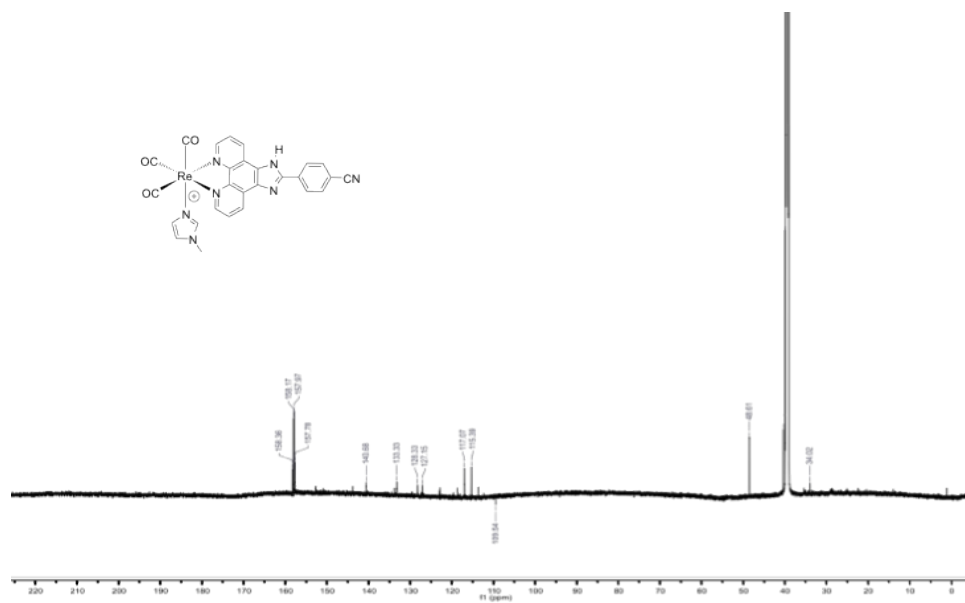


Figure S51. ^{13}C NMR Spectrum (CD_3OD), 150 MHz) of **5e**.

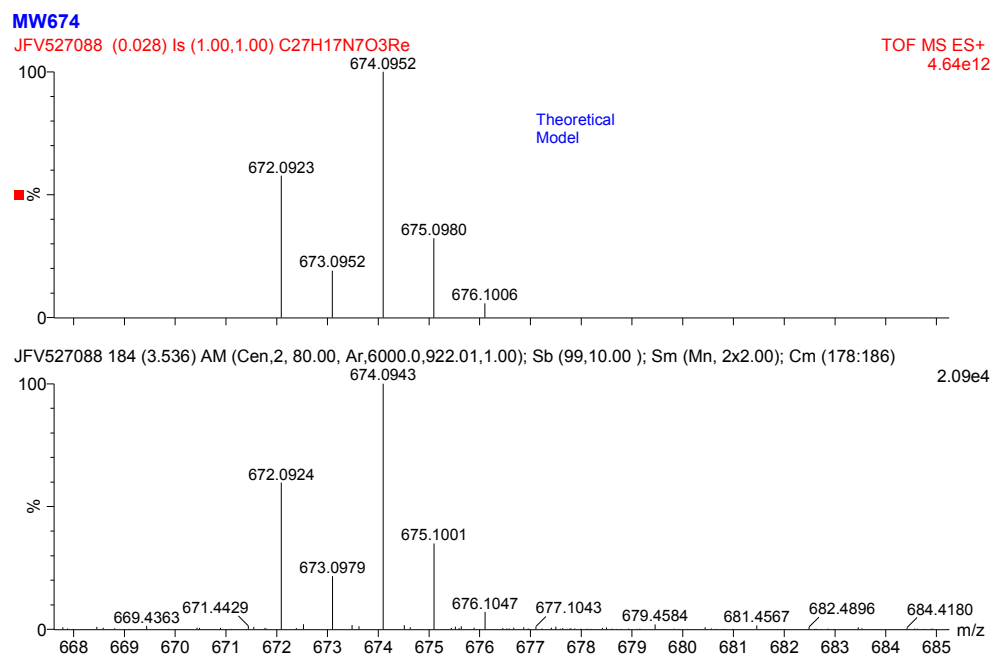


Figure S52. HRMS of **5e**.

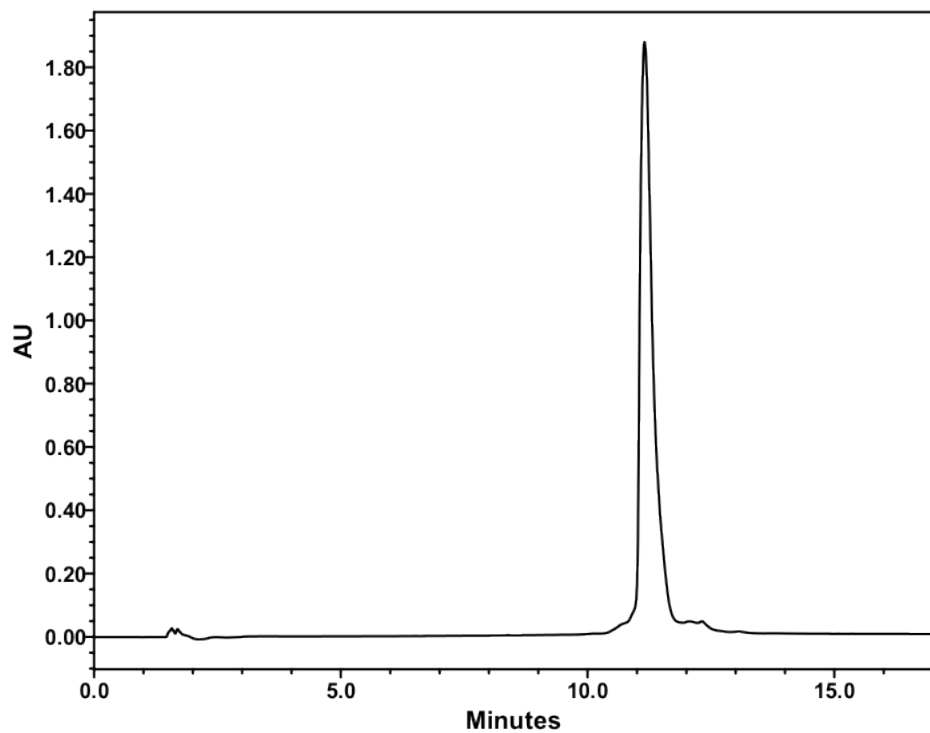


Figure S53. UV-HPLC trace of **5f** (Method D).

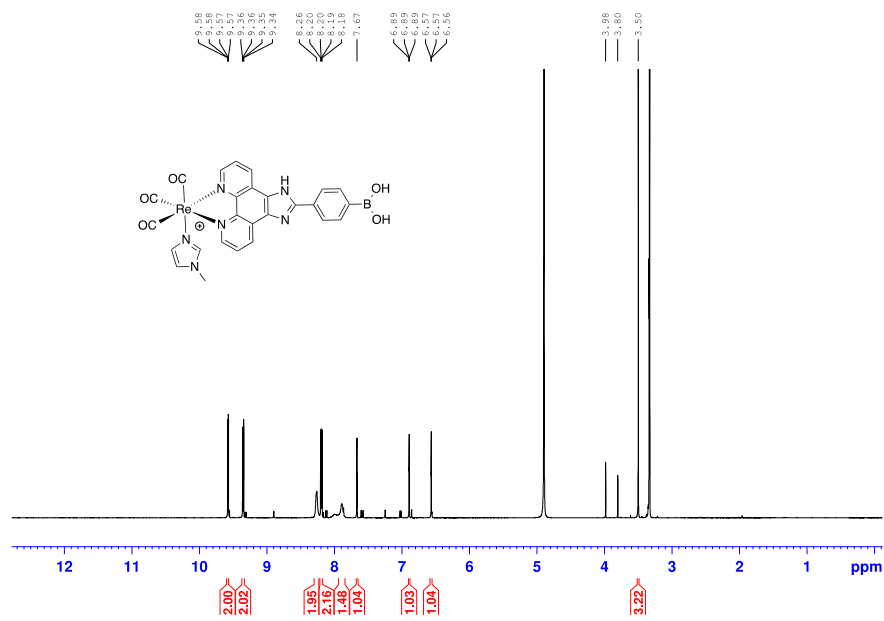


Figure S54. ¹H NMR spectrum (CD₃OD, 600 MHz) of **5f**.

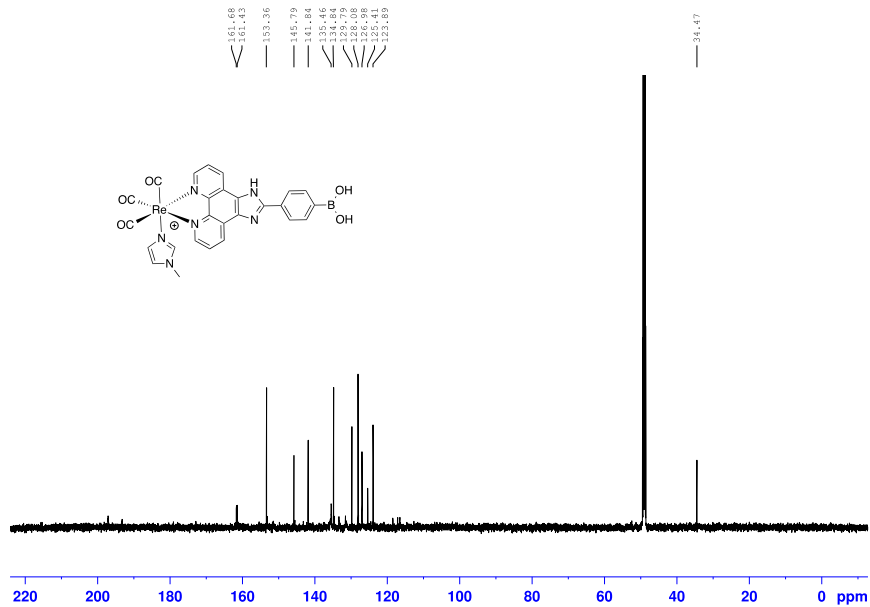


Figure S55. ^{13}C NMR spectrum (CD_3OD , 150 MHz) of **5f**.

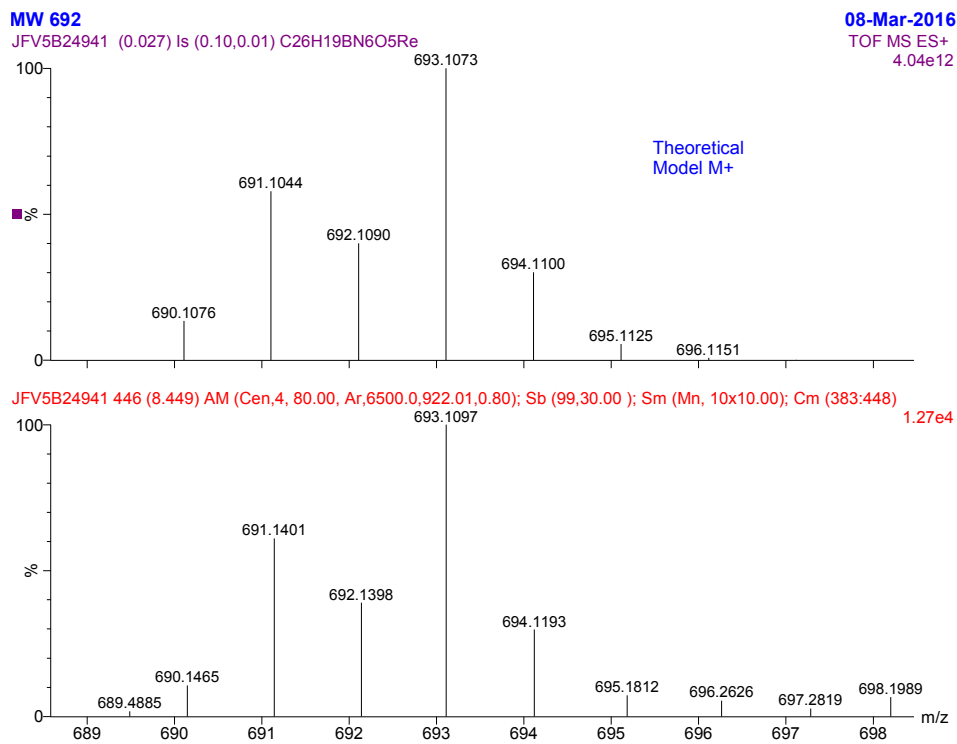


Figure S56. HRMS of **5f**.

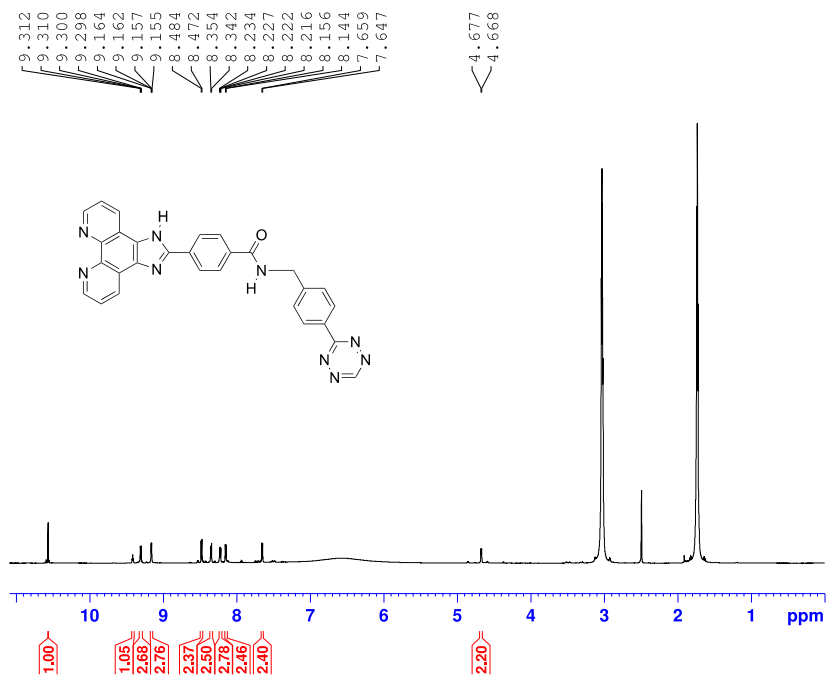


Figure S57. ¹H NMR spectrum ((CD₃)₂SO), 600 MHz) of **9**.

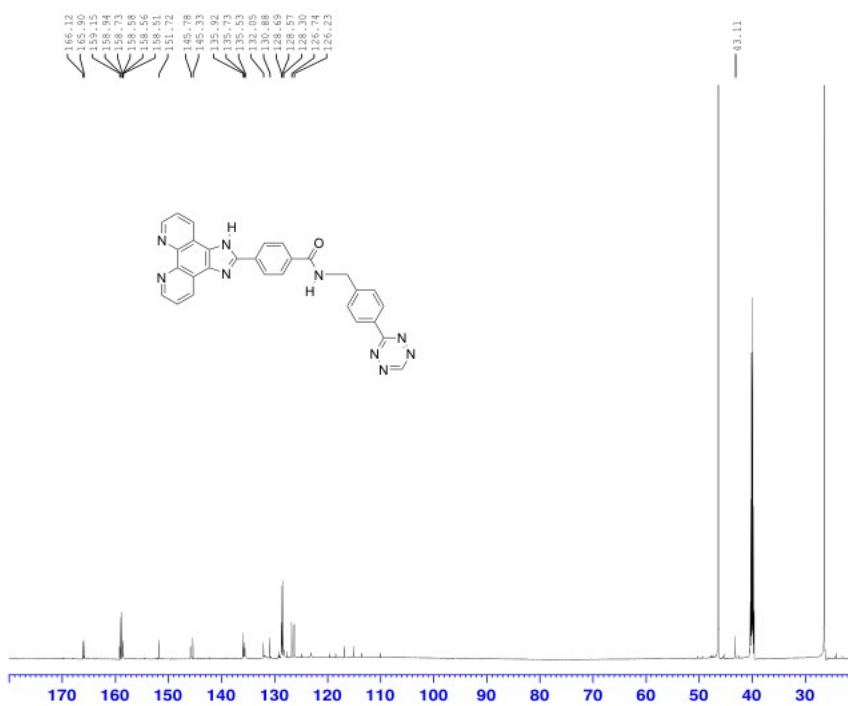


Figure S58. ¹³C NMR spectrum ((CD₃)₂SO), 150 MHz) of **9**.

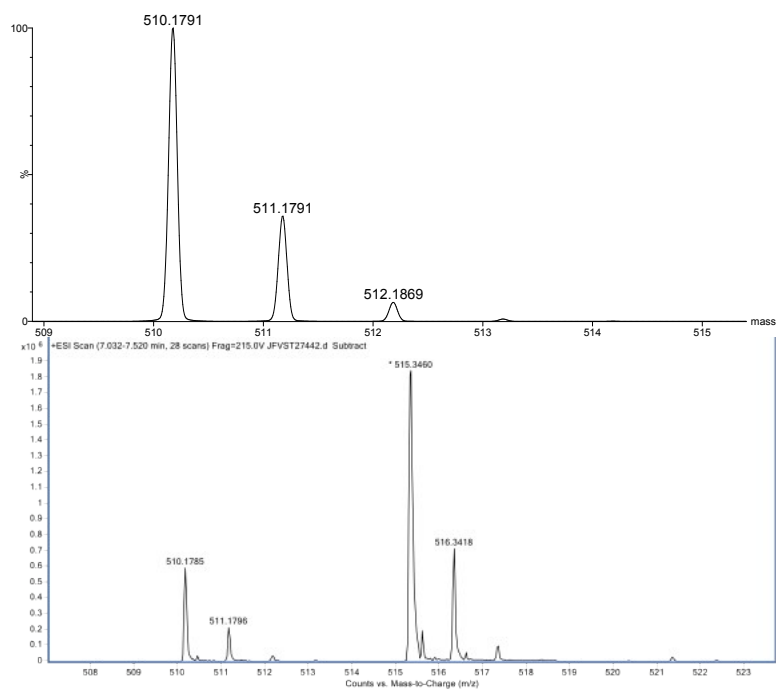


Figure S59. HRMS of **9**.

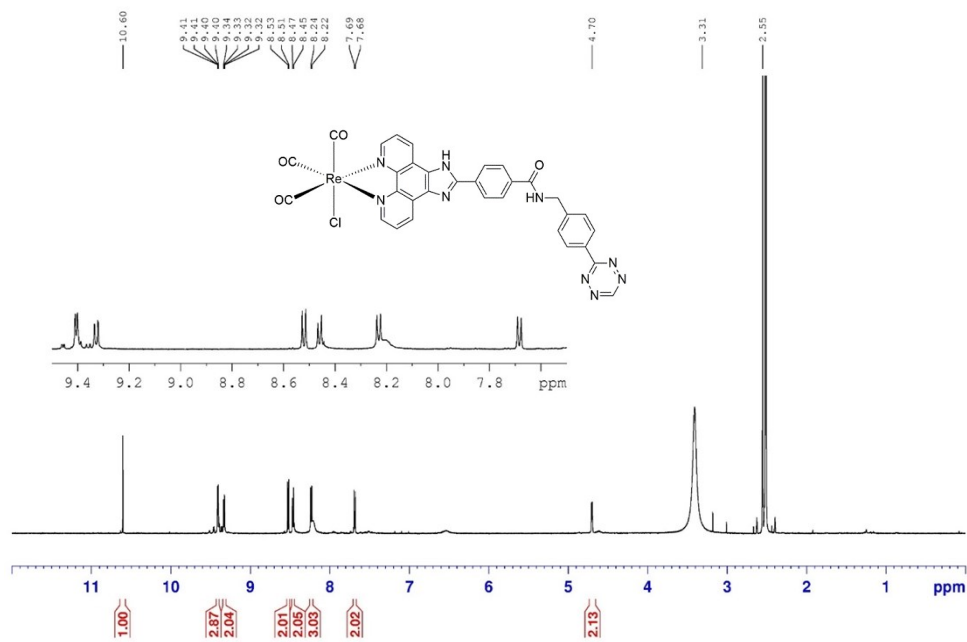


Figure S60. ^1H NMR spectrum ($(\text{CD}_3)_2\text{SO}$, 600 MHz) of **10**.

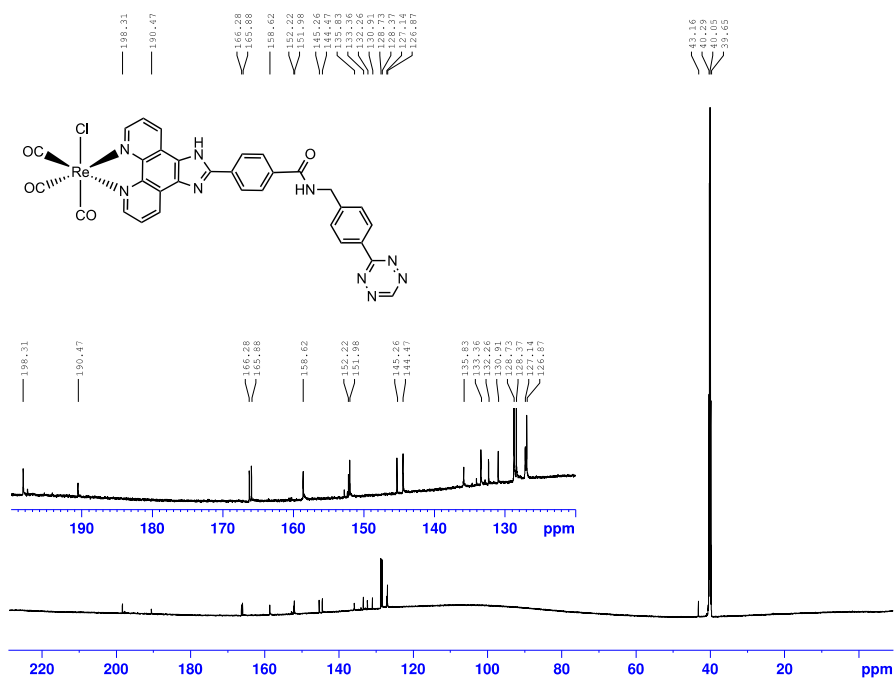


Figure S61. ^{13}C NMR spectrum ($(\text{CD}_3)_2\text{SO}$, 150 MHz) of **10**.

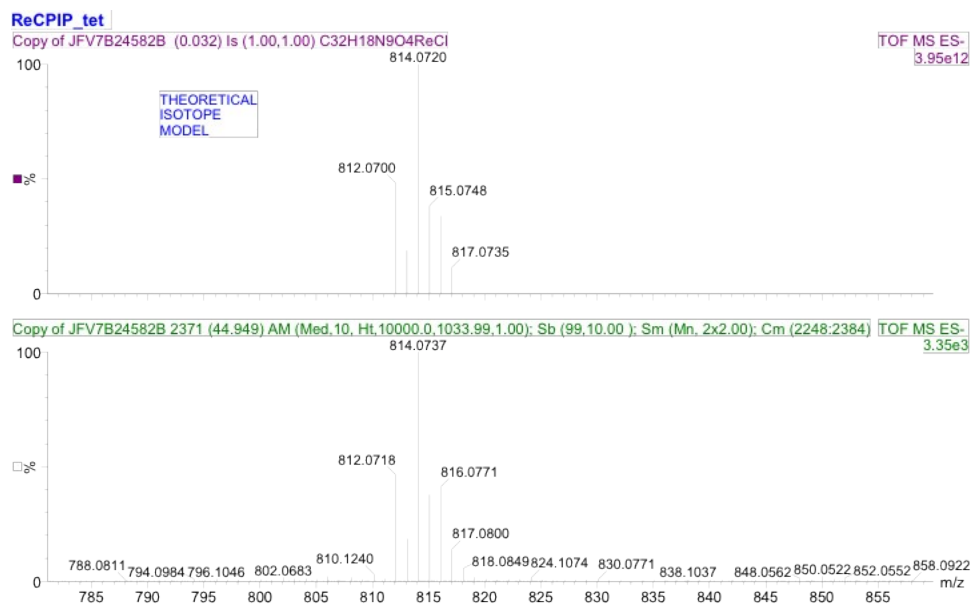


Figure S62. HRMS of **10**.

A saturated solution of sinapinic acid was prepared in TA30 solvent (30:70 [v/v] acetonitrile : 0.1% TFA in water). The samples were mixed in a 1:1 ratio with the matrix solution. 1 μ L was spotted on the plate and a protein solution of BSA was used as an external standard.

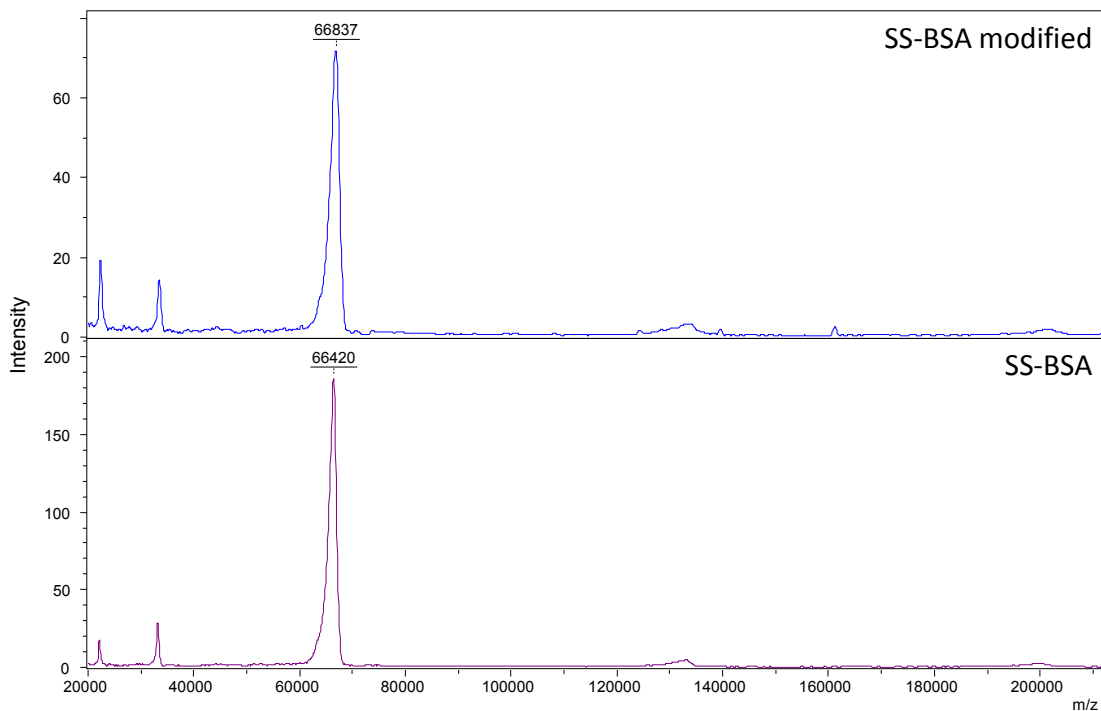


Figure S63. MALDI-TOF MS analysis of BSA samples top: **14** and bottom BSA.

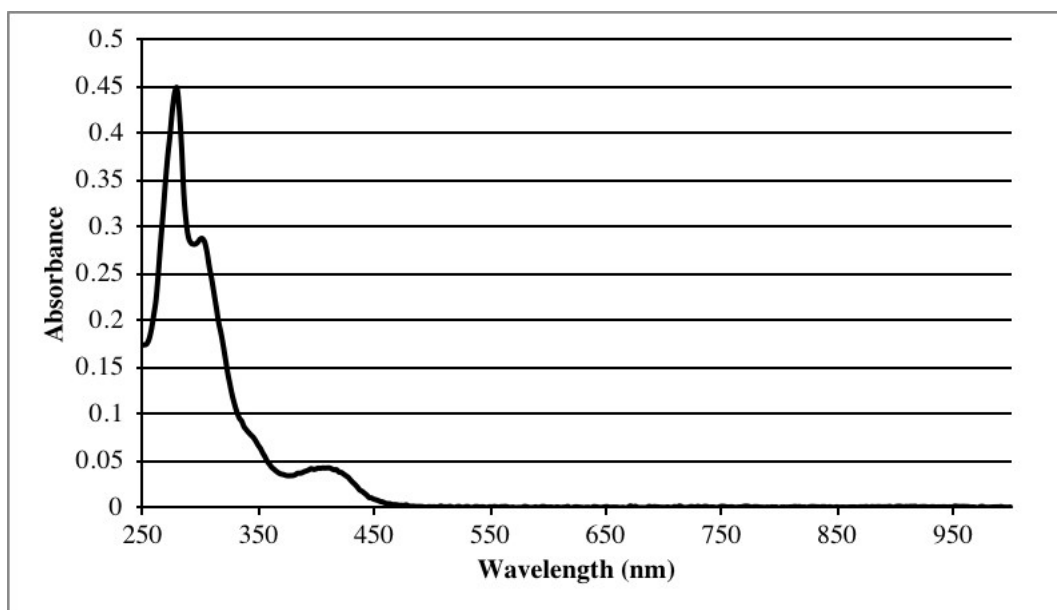


Figure S64. Absorbance spectrum of **4a** (278 nm, 0.44 a.u.; 304 nm, 0.28 a.u.; 406 nm, 0.39 a.u.)

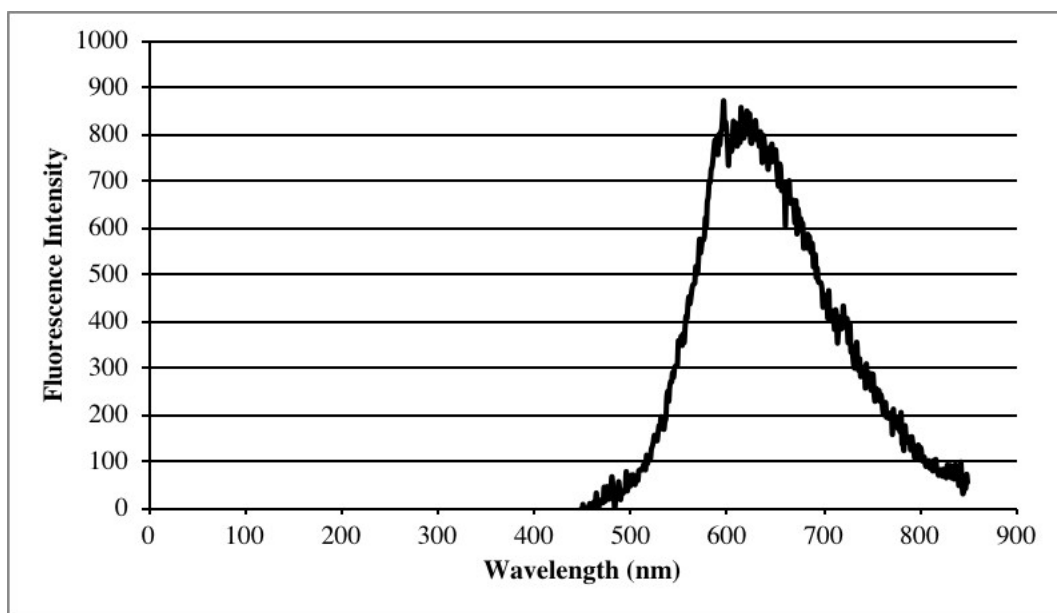


Figure S65. Emission spectrum of **4a** (λ_{ex} = 460 nm; 612 nm, 782 a.u.)

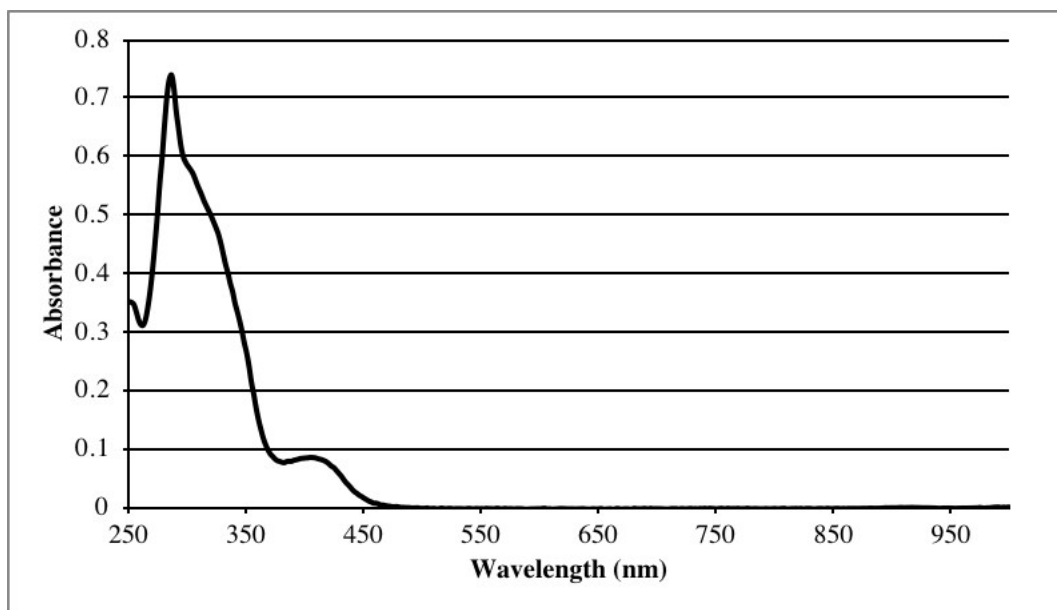


Figure S66. Absorbance spectrum of **4b** (284 nm, 0.73 a.u.; 302 nm, 0.58 a.u.; 404 nm, 0.087 a.u.)

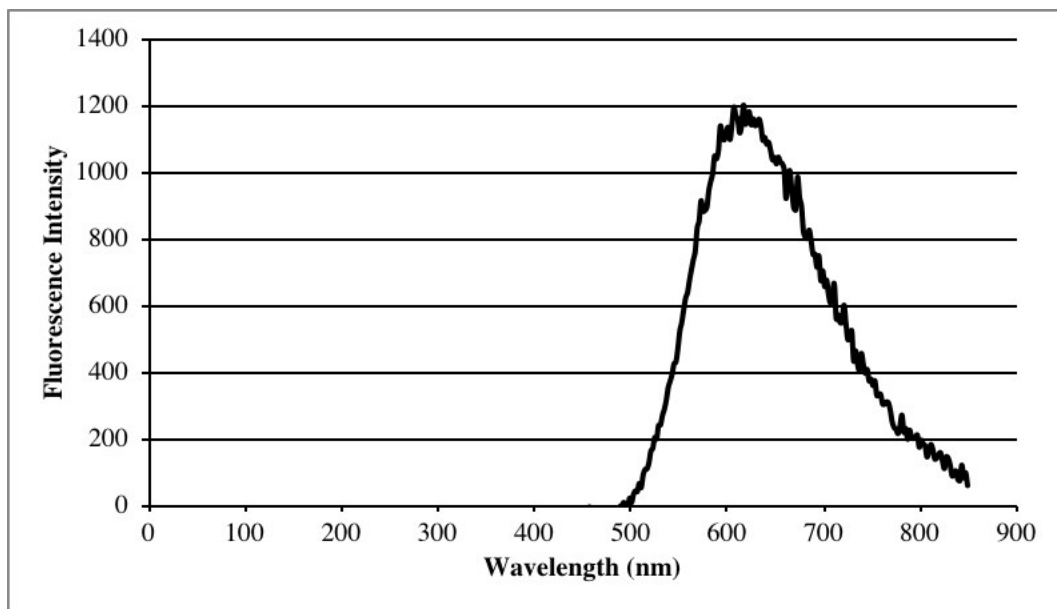


Figure S67. Emission spectrum of **4b** (λ_{ex} = 406 nm; 596 nm, 1166 a.u.)

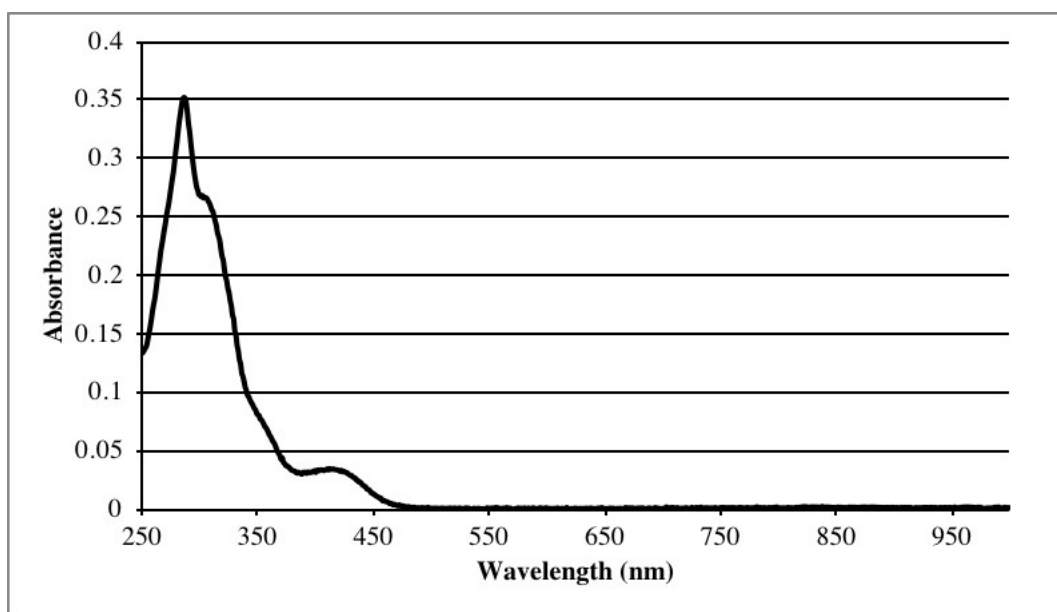


Figure S68. Absorbance spectrum of **4c** (283 nm, 0.34 a.u.; 303 nm, 0.27 a.u.; 412 nm, 0.034 a.u.).

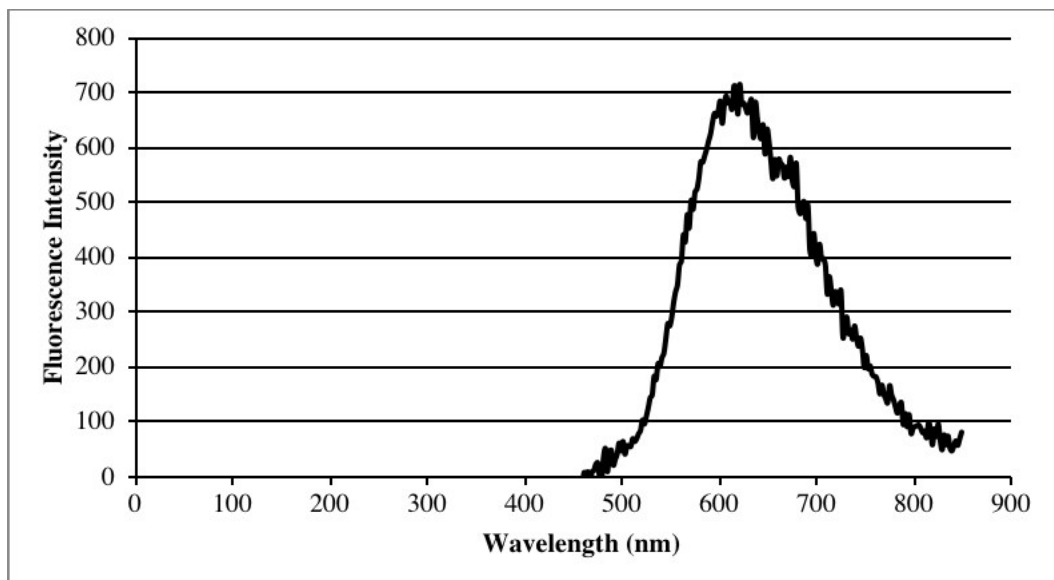


Figure S69. Emission spectrum of **4c** (λ_{ex} = 410 nm; 616 nm, 713 a.u.).

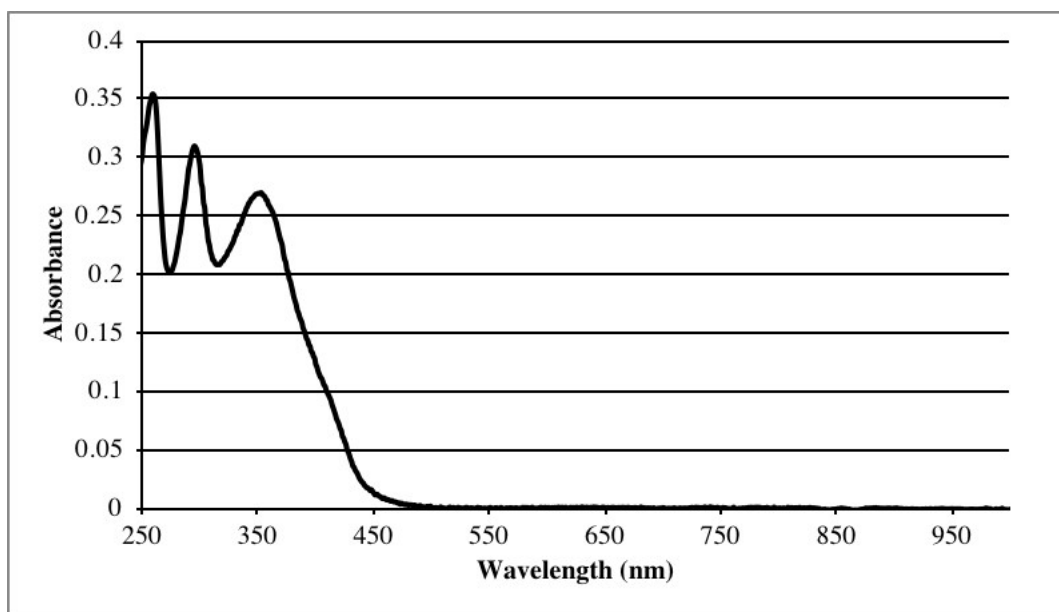


Figure S70. Absorbance spectrum of **4d** (259 nm, 0.35 a.u.; 293 nm, 0.304 a.u.; 344 nm, 0.26 a.u.; 351 nm, 0.094 a.u.).

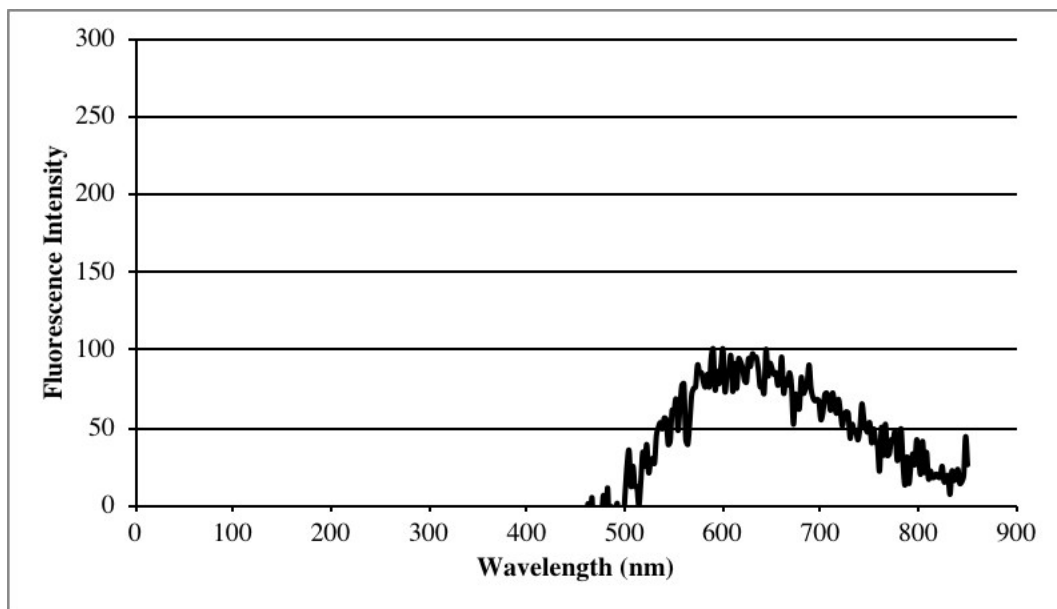


Figure S71. Emission spectrum of **4d** (λ_{ex} = 351 nm; 649 nm, 69 a.u.).

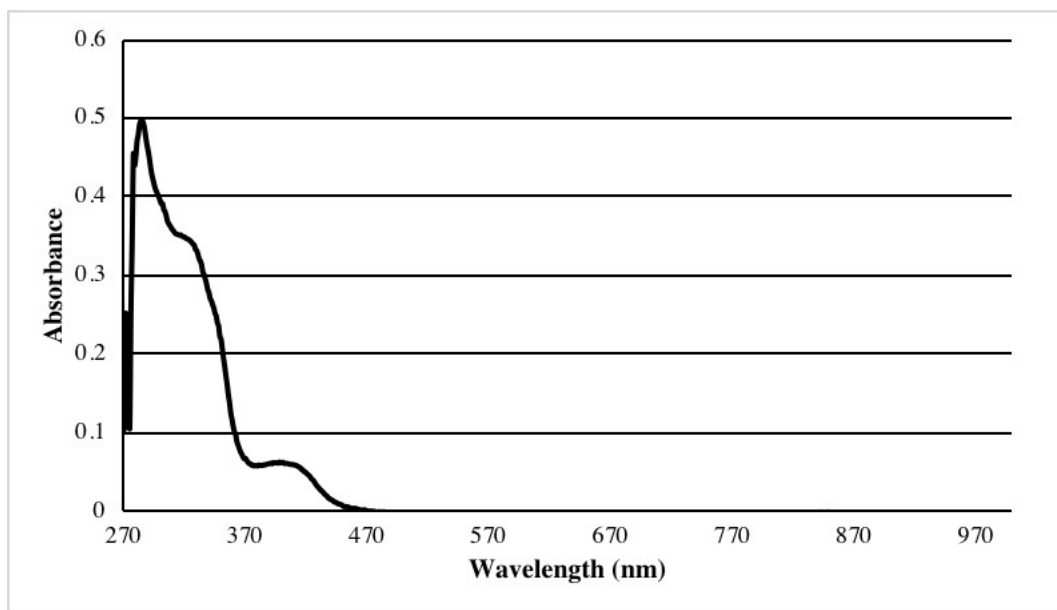


Figure S72. Absorbance spectrum of **4e** (286 nm, 0.497 a.u.; 324 nm, 0.35 a.u.; 399 nm, 0.061 a.u.).

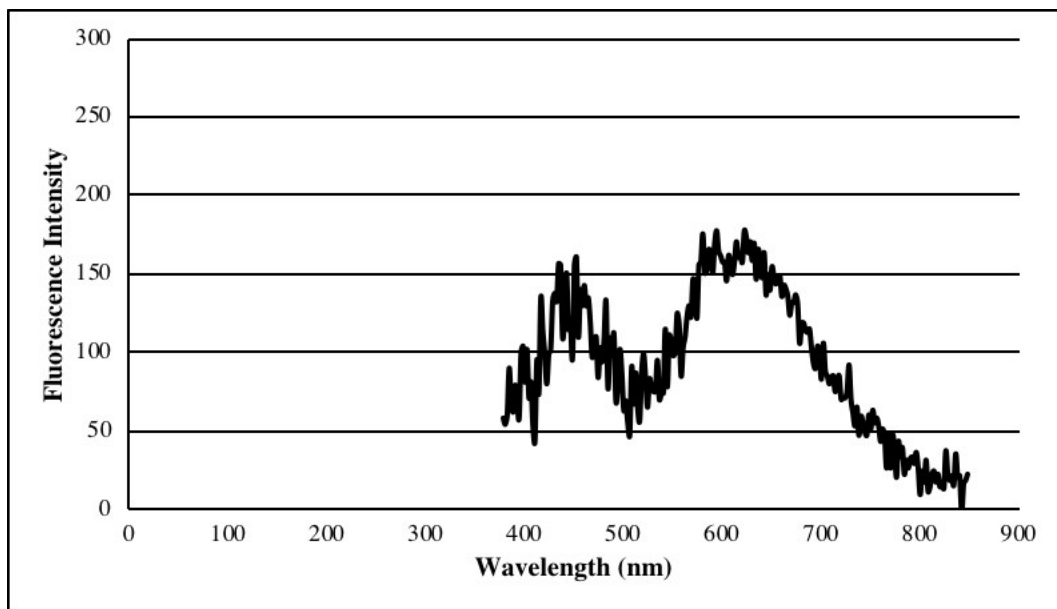


Figure S73. Emission spectrum of **4e** (λ_{ex} = 365 nm; 451 nm, 156 a.u.; 611 nm, 150 a.u.).

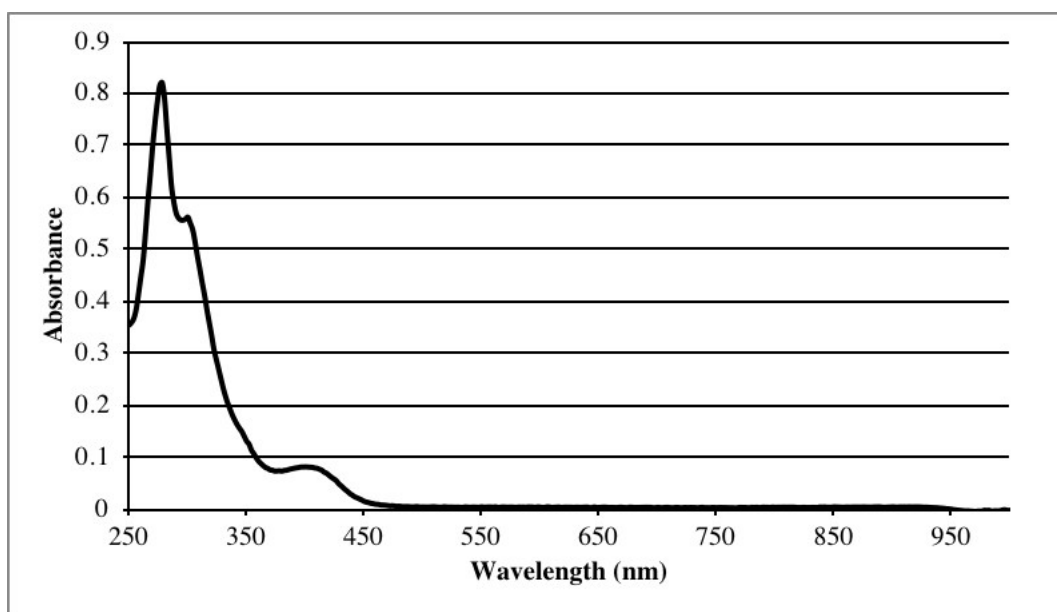


Figure S74. Absorbance spectrum of **5a** (276 nm, 0.81 a.u.; 302 nm, 0.55 a.u.; 400 nm, 0.08 a.u.).

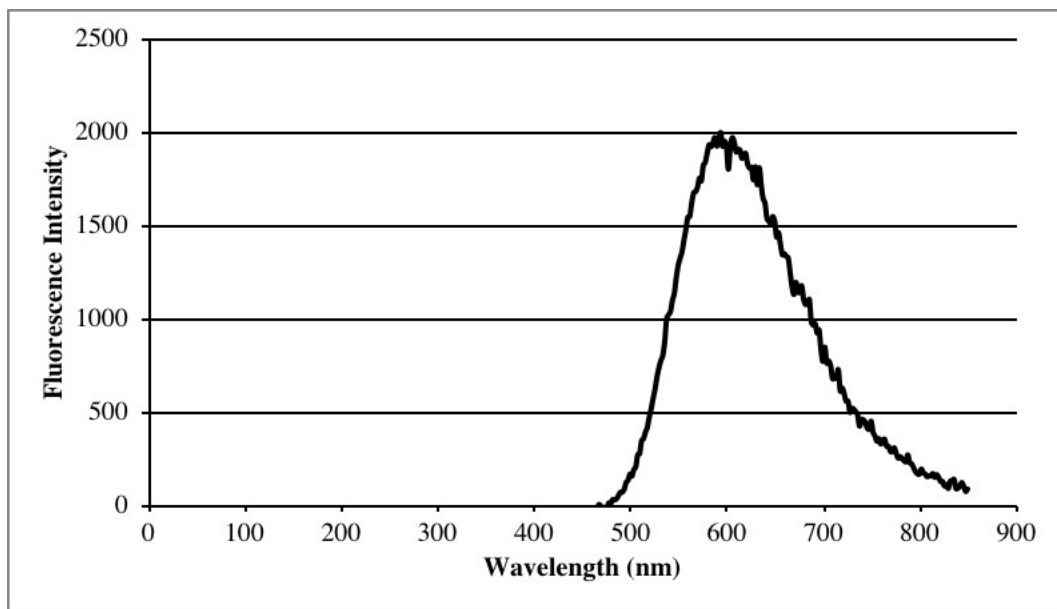


Figure S75. Emission spectrum of **5a** ($\lambda_{\text{ex}} = 400 \text{ nm}$; 594 nm, 1916 a.u.).

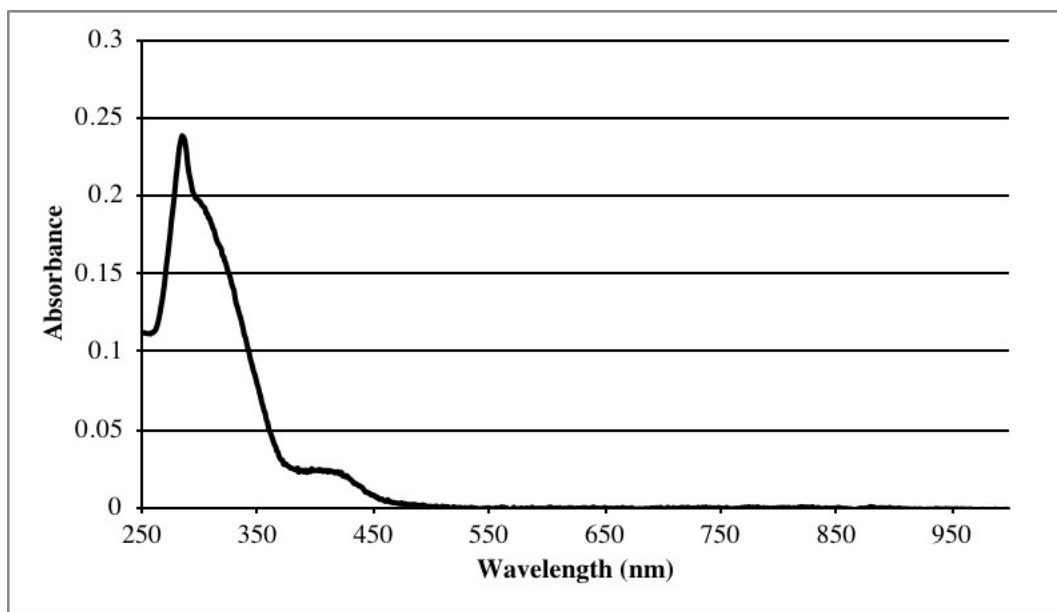


Figure S76. Absorbance spectrum of **5b** (282 nm, 0.23 a.u.; 302 nm, 0.19 a.u.; 407 nm, 0.024 a.u.).

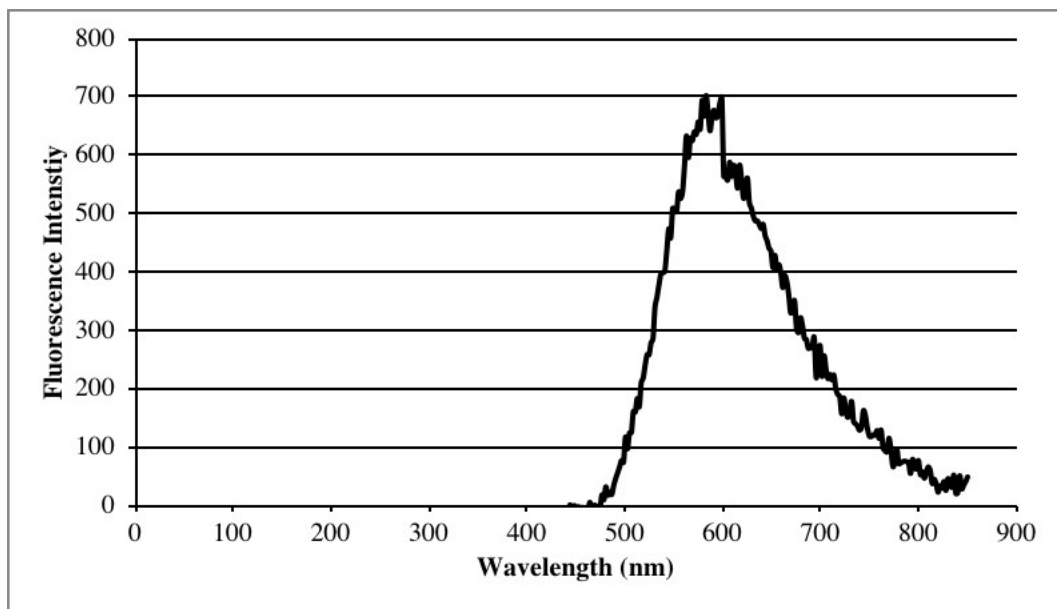


Figure S77. Emission spectrum of **5b** (λ_{ex} = 407 nm; 595 nm, 667 a.u.).

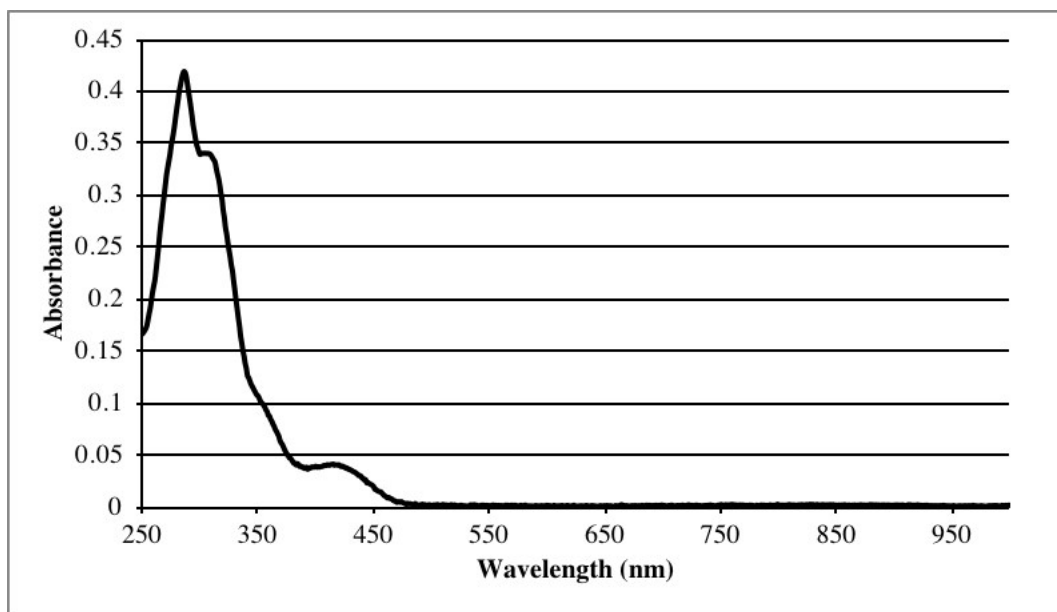


Figure S78. Absorbance spectrum of **5c** (283 nm, 0.40 a.u.; 299 nm, 0.34 a.u.; 414 nm, 0.039 a.u.).

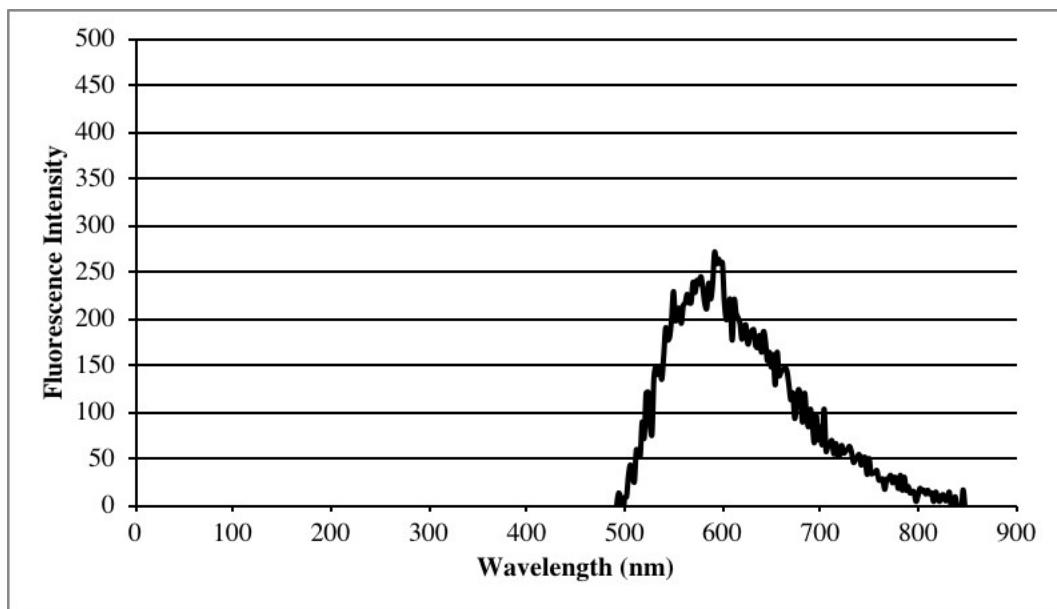


Figure S79. Emission spectrum of **5c** ($\lambda_{\text{ex}} = 422 \text{ nm}$; 574 nm, 213 a.u.).

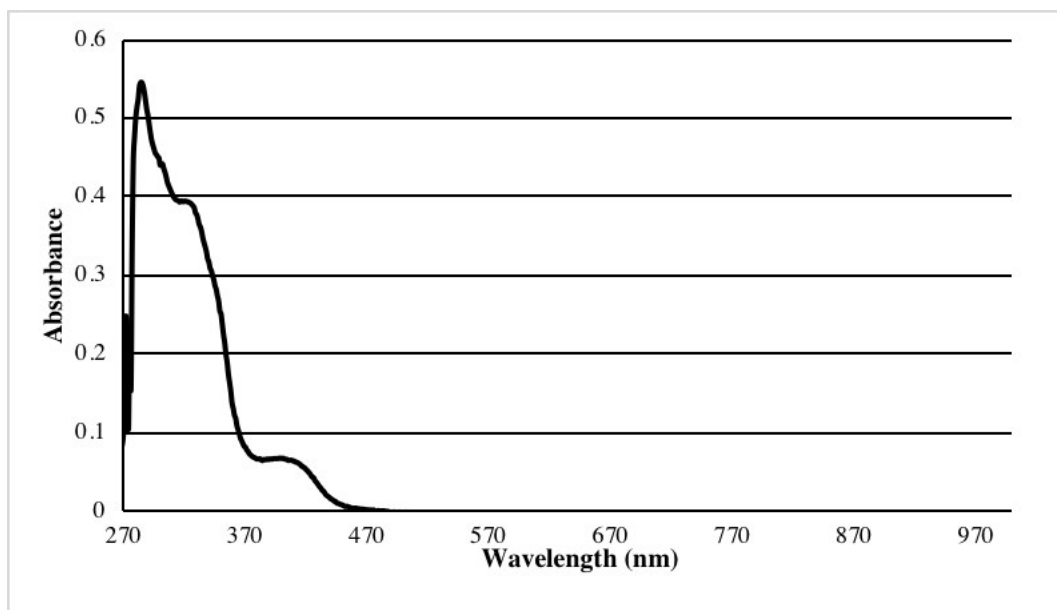


Figure S80. Absorbance spectrum of **5e** (284 nm, 0.54 a.u.; 314 nm, 0.40 a.u.; 399 nm, 0.068 a.u.).

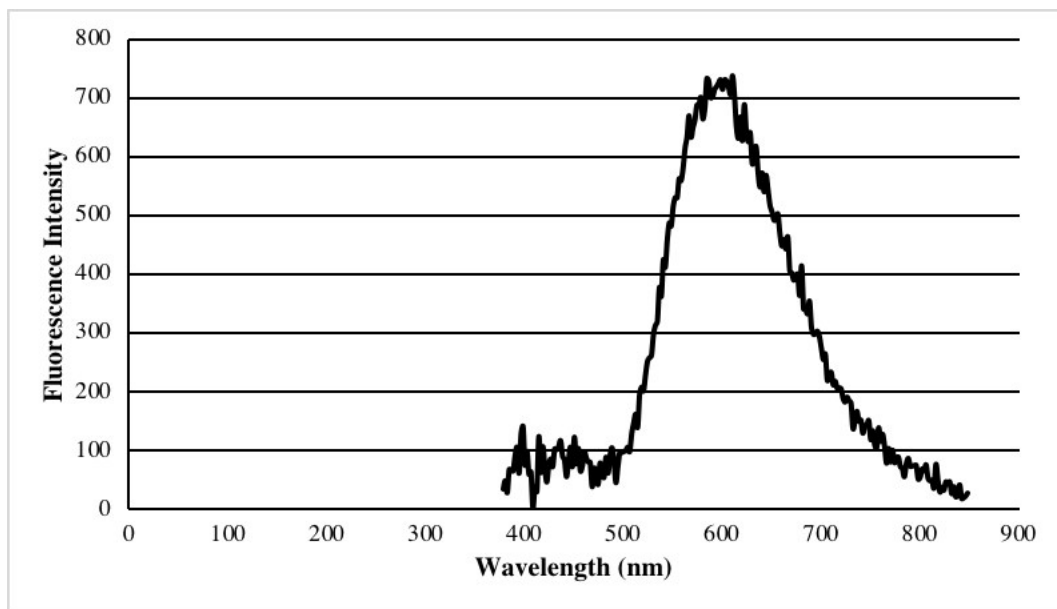


Figure S81. Emission spectrum of **5e** ($\lambda_{\text{ex}} = 365 \text{ nm}; 611 \text{ nm}, 735 \text{ a.u.}$).

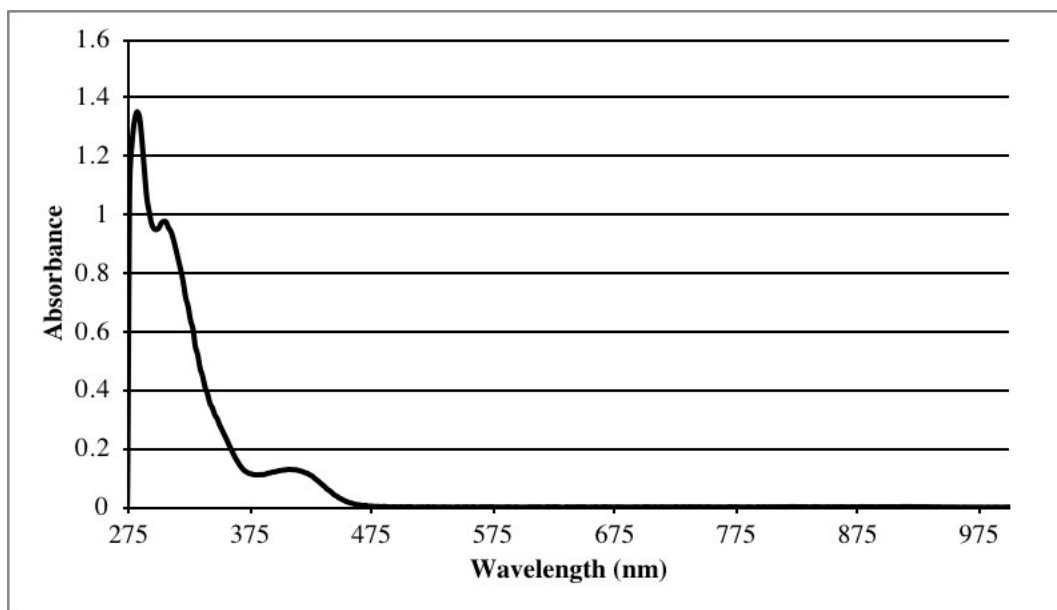


Figure S82. Absorbance spectrum of **5f** (282 nm, 1.35 a.u.; 306 nm, 0.97 a.u.; 406 nm, 0.128 a.u.).

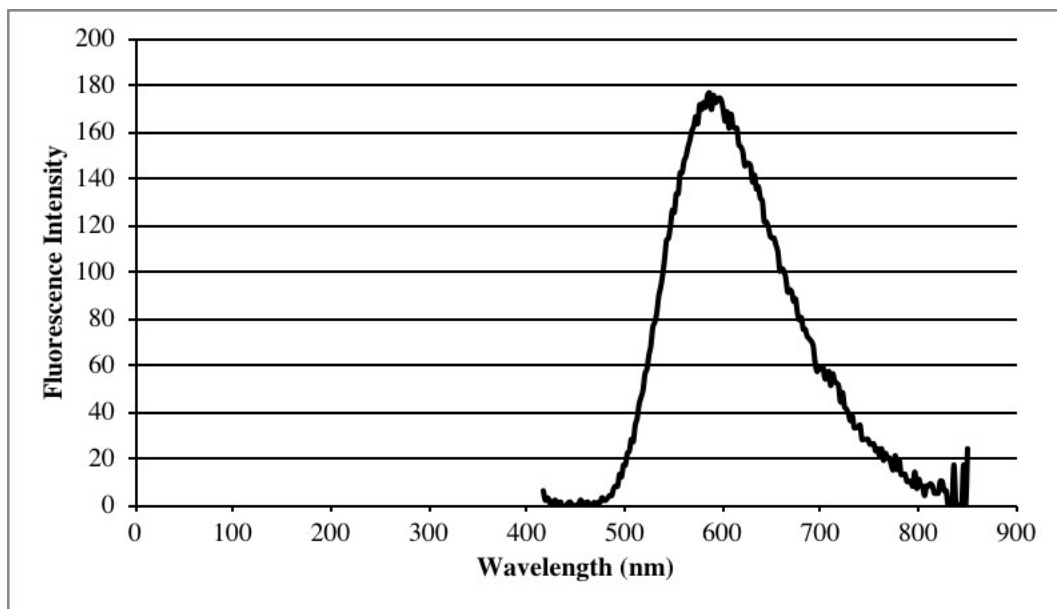


Figure S83. Emission spectrum of **5f** ($\lambda_{\text{ex}} = 406 \text{ nm}$; 586 nm, 176 a.u.).

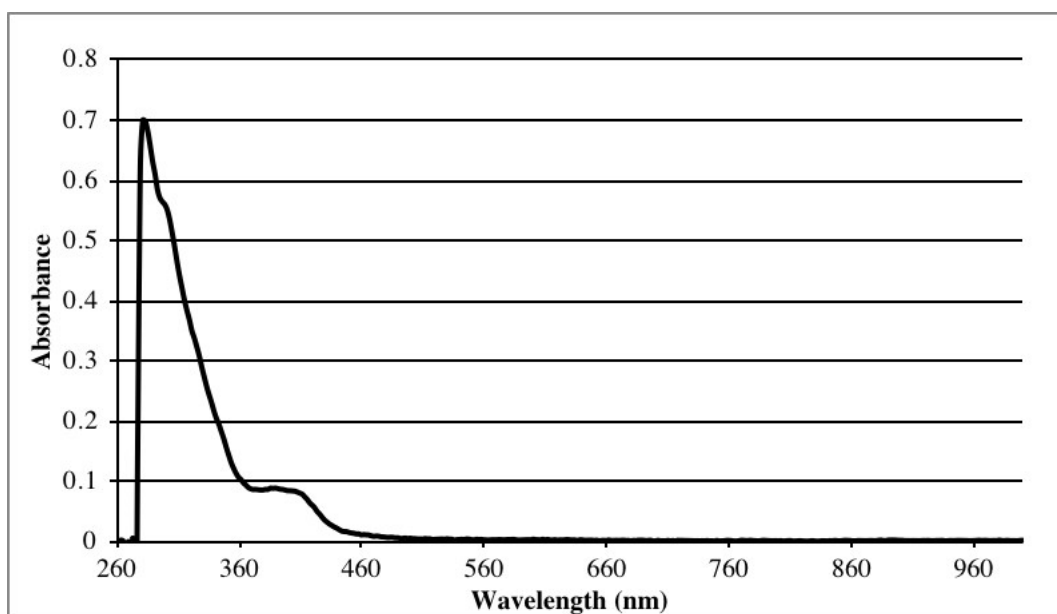


Figure S84. Absorbance spectrum of **9a** (282 nm, 0.70 a.u.; 300 nm, 0.56 a.u.; 402 nm, 0.084 a.u.).

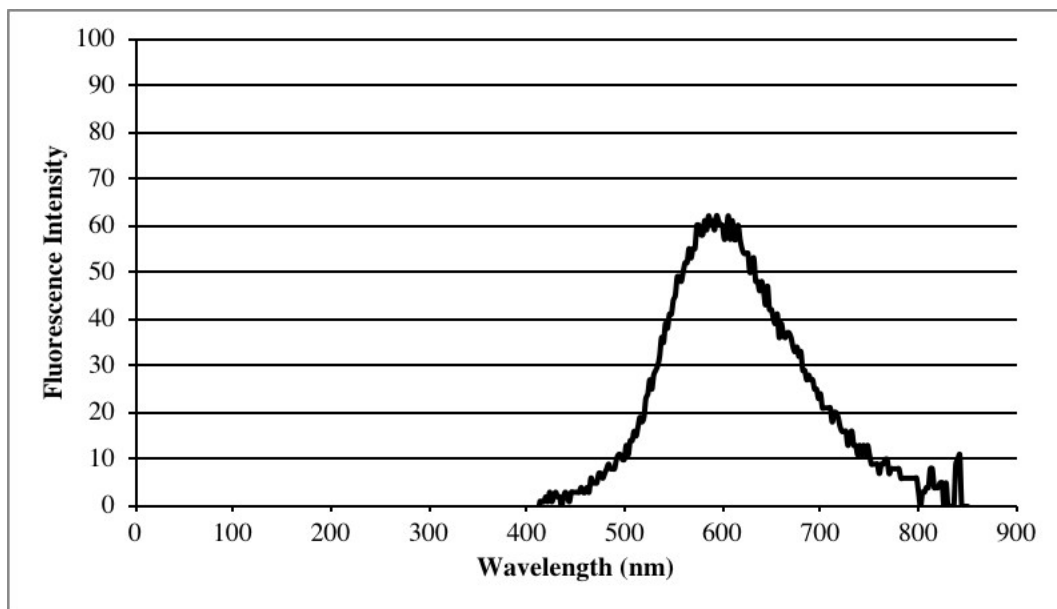


Figure S85. Emission spectrum of **9a** ($\lambda_{\text{ex}} = 402 \text{ nm}$; 594 nm, 62 a.u.).

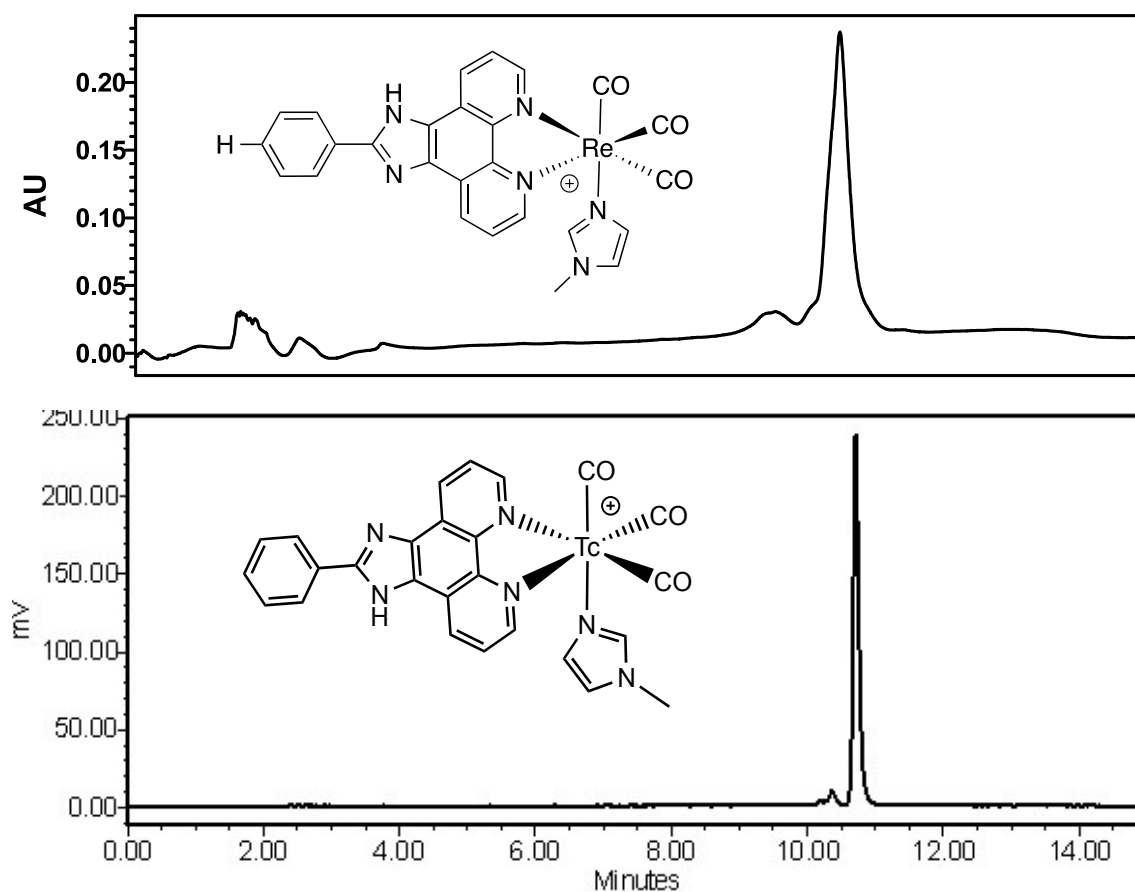


Figure S86. UV-HPLC trace of **5a** (top) and γ -HPLC trace of **7a** (bottom) (Method B).

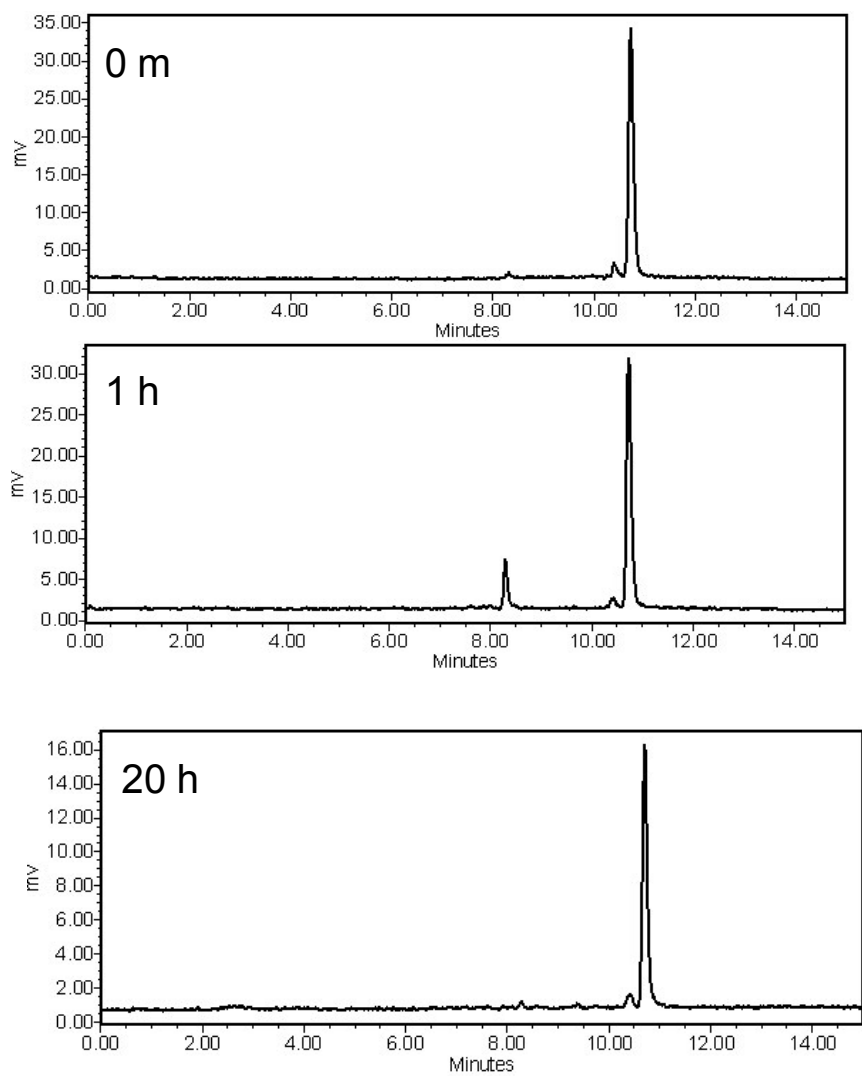


Figure S87. γ -HPLC trace of 7a after 1 and 20 h in saline (Method B).

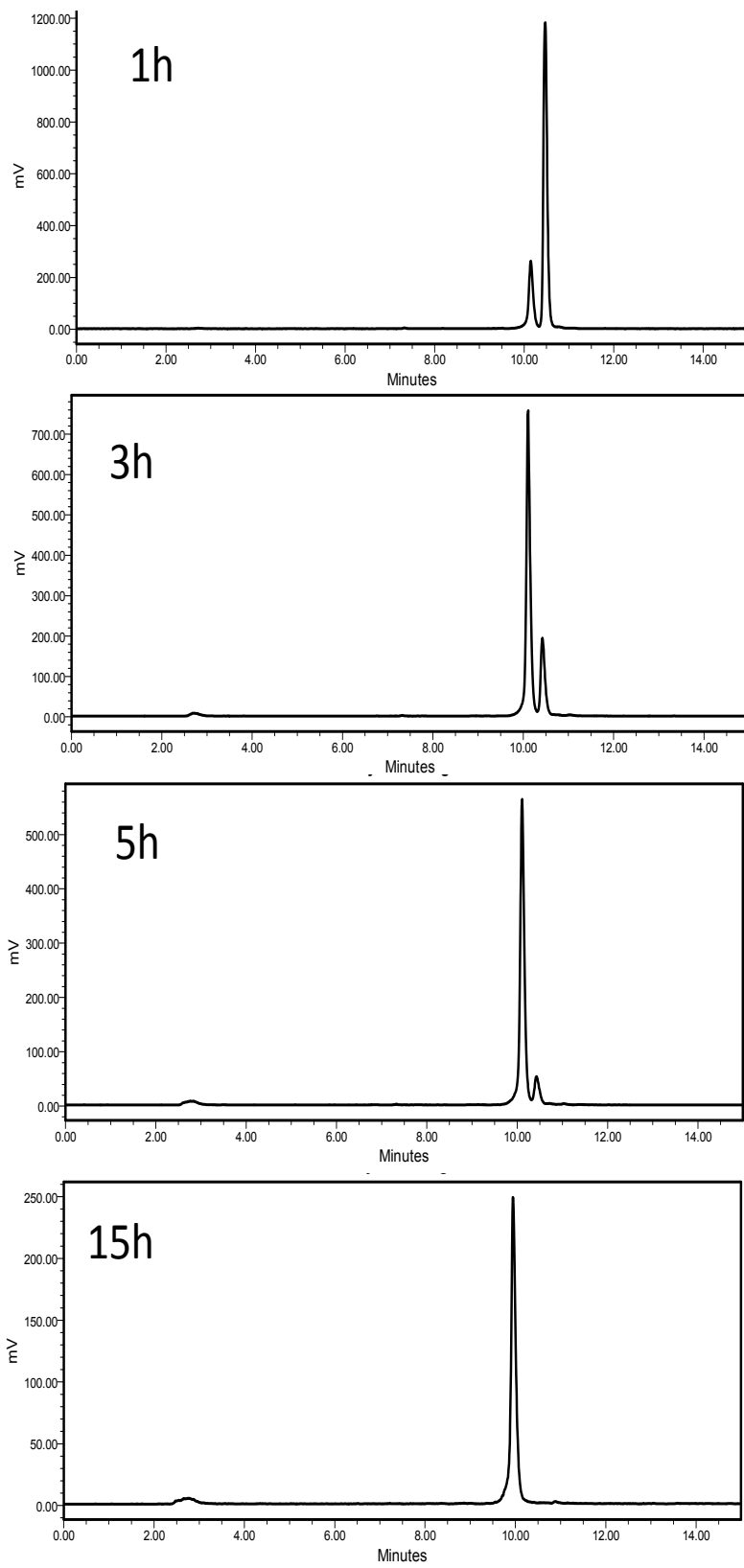


Figure S88. γ -HPLC trace of 7a with histidine challenge (Method B).

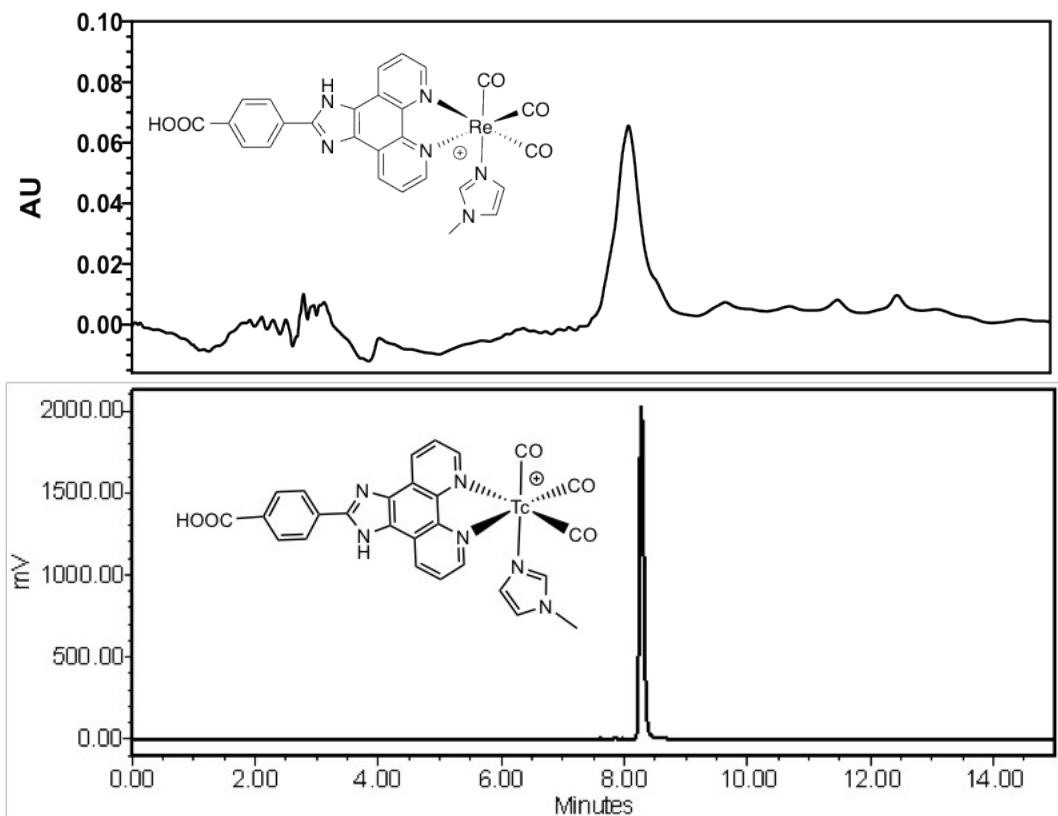


Figure S89. UV-HPLC trace of **5b** (top) and γ -HPLC trace of **7b** (bottom) (Method B).

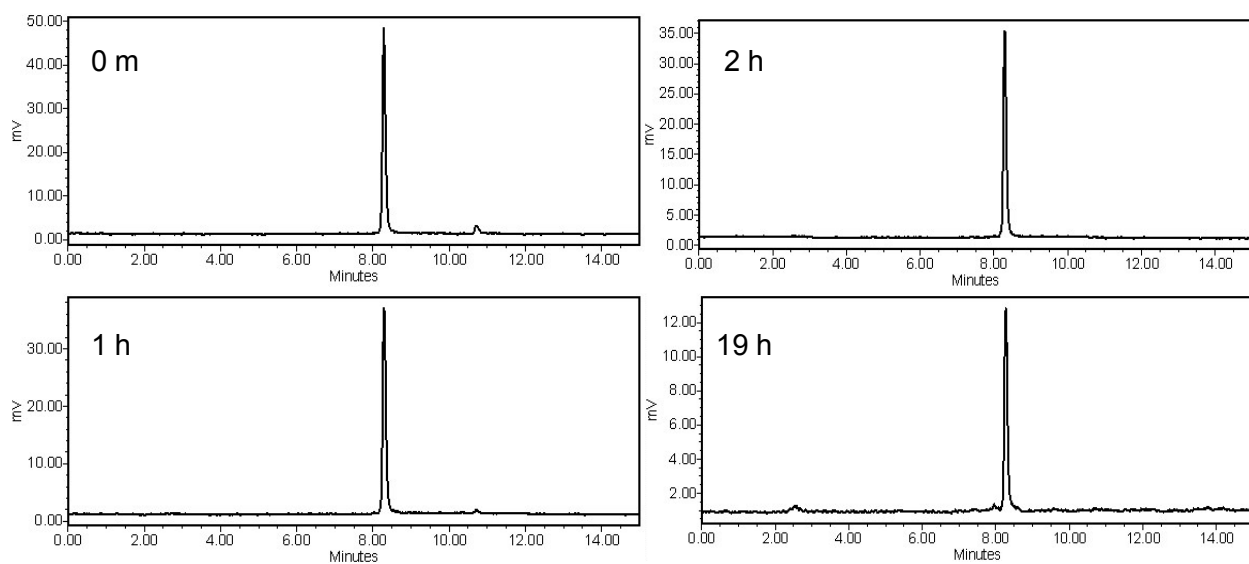


Figure S90. γ -HPLC trace of **7b** after 1, 2 and 19 h in saline (Method B).

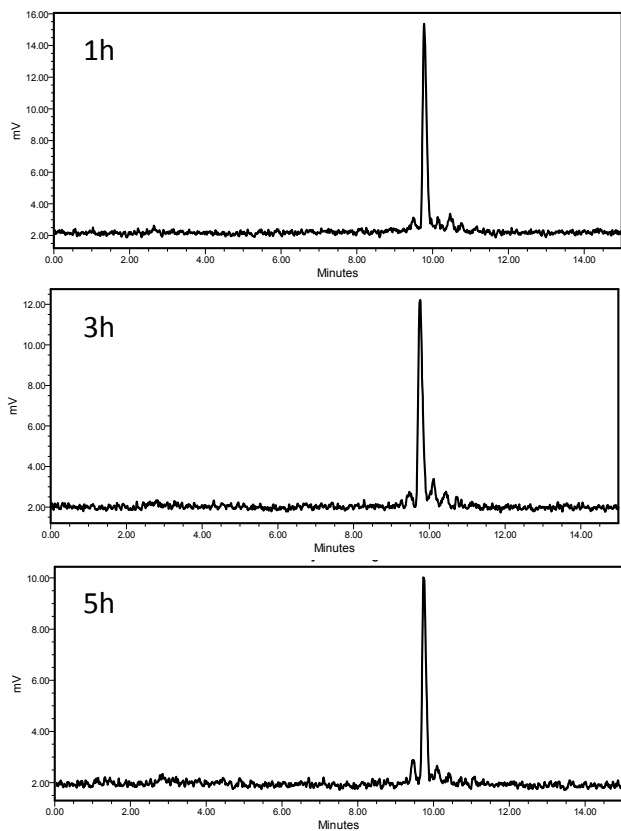


Figure S91. γ -HPLC trace of **7b** after 1, 3 and 5 h in histidine (Method B).

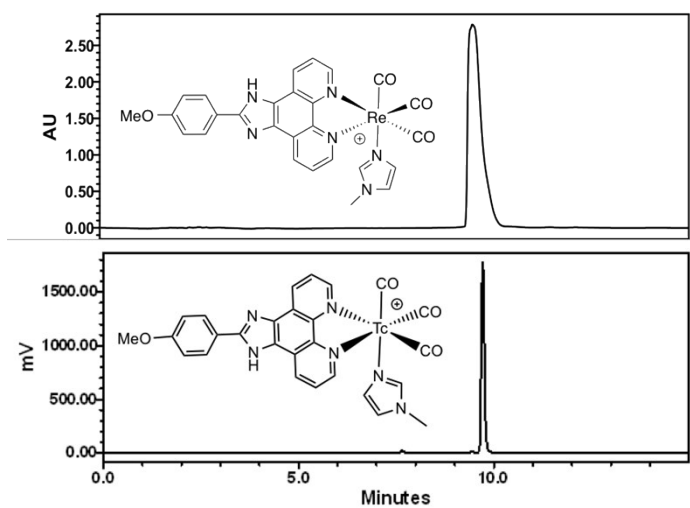


Figure S92. UV-HPLC trace of **5c** (top) and γ -HPLC trace of **7c** (bottom) (Method B).

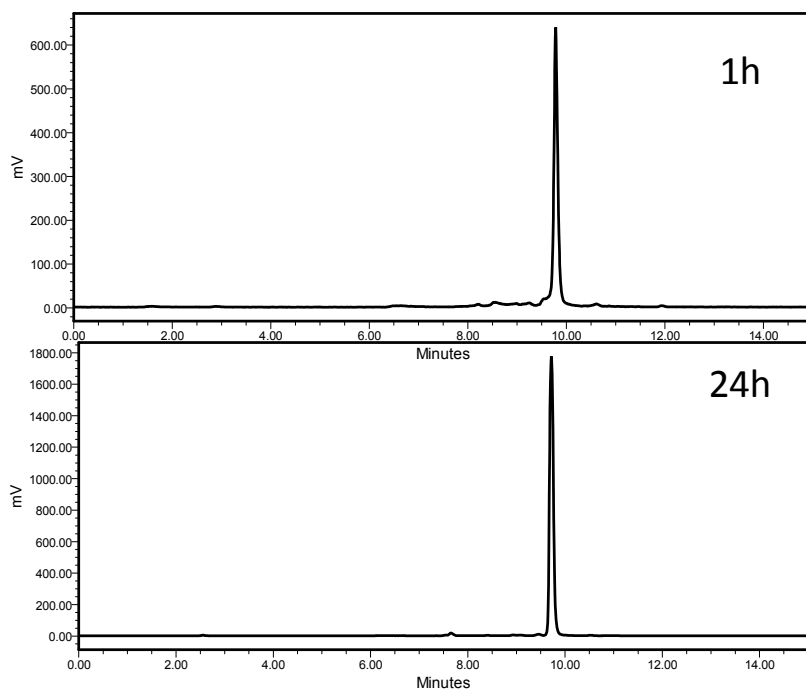


Figure S93. γ -HPLC trace of 7c after 1 and 24 h in saline (Method B).

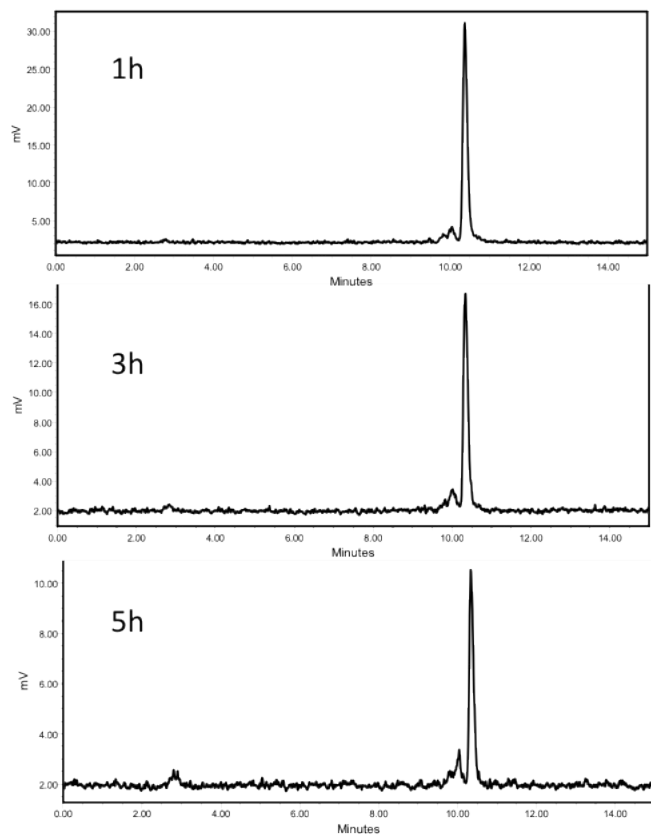


Figure S94. γ -HPLC trace of 7c after 1, 3 and 5 h in histidine (Method B).

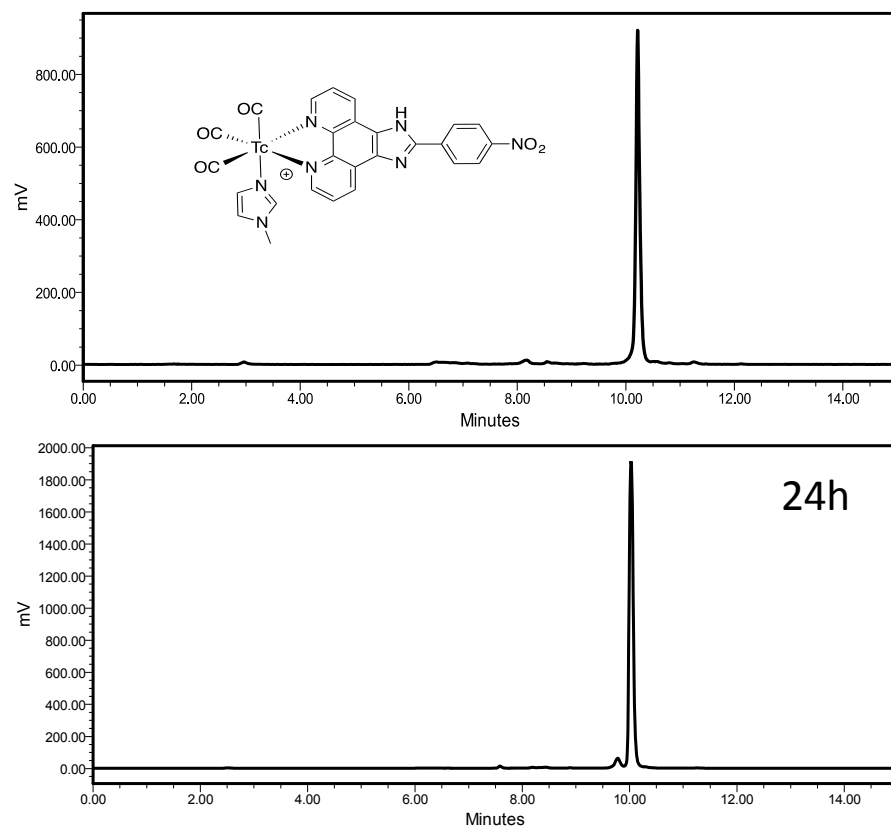


Figure S95. γ -HPLC trace of **7d** before (top) and after 24 h (bottom) in saline (Method B).

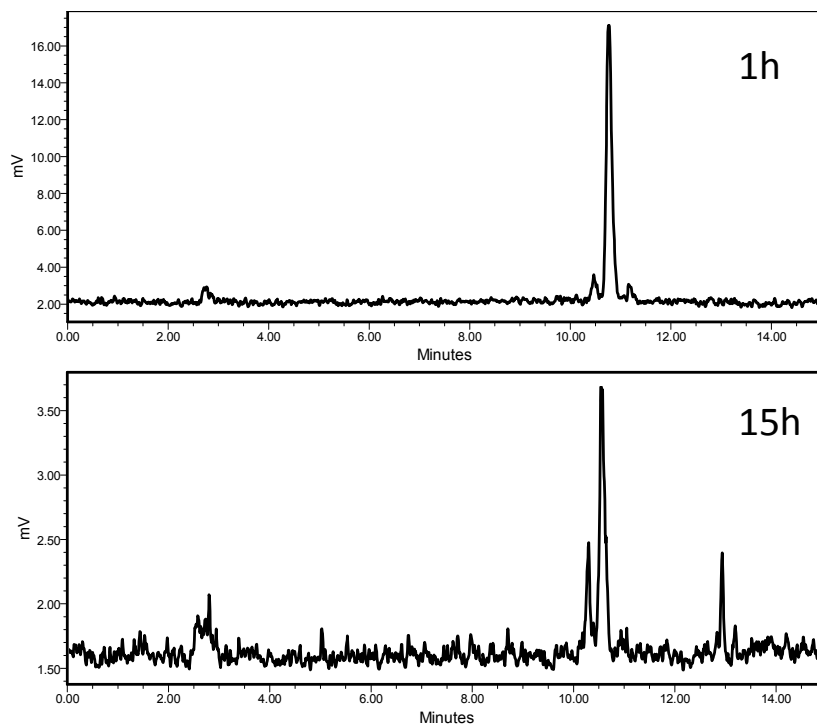


Figure S96. γ -HPLC trace of **7d** after 1 and 15 h in histidine (Method B).

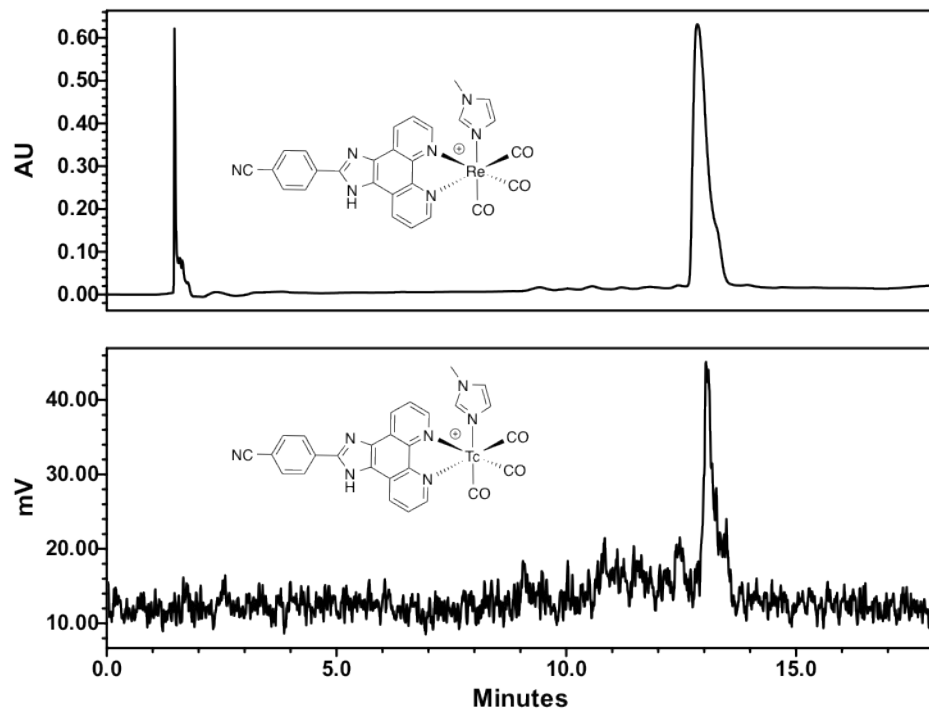


Figure S97. UV-HPLC trace of **5e** (top) and γ -HPLC trace of **7e** (bottom) (Method D).

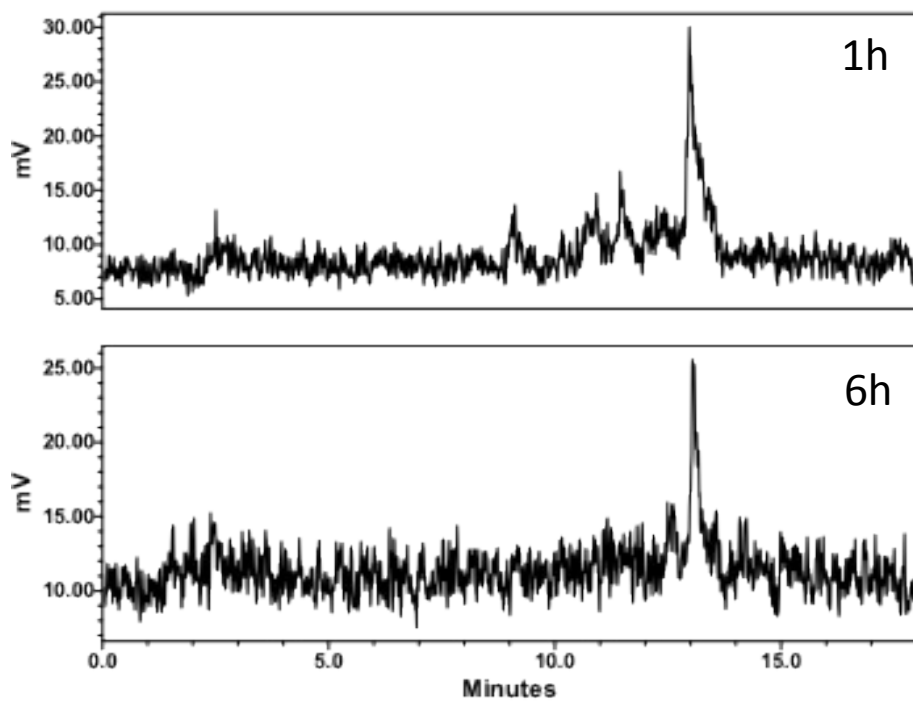


Figure S98. γ -HPLC trace of **7e** after 1 and 6 h in saline (Method D).

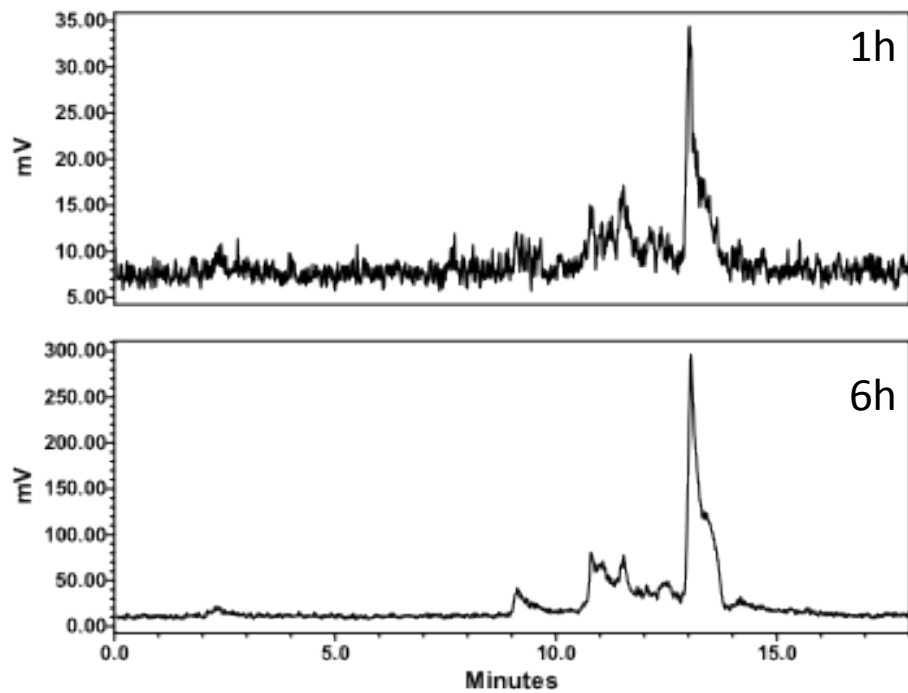


Figure S99. γ -HPLC trace of **7e** after 1 and 6 h in cysteine (Method D).

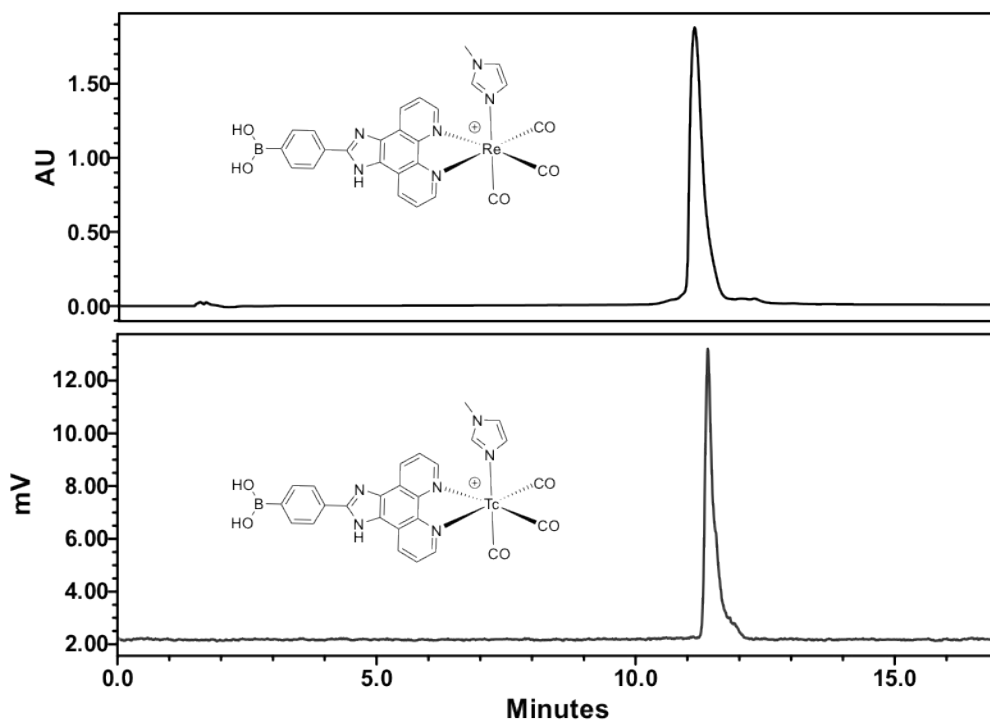


Figure S100. UV-HPLC trace of **5f** (top) and γ -HPLC trace of **7f** (bottom) (Method D).

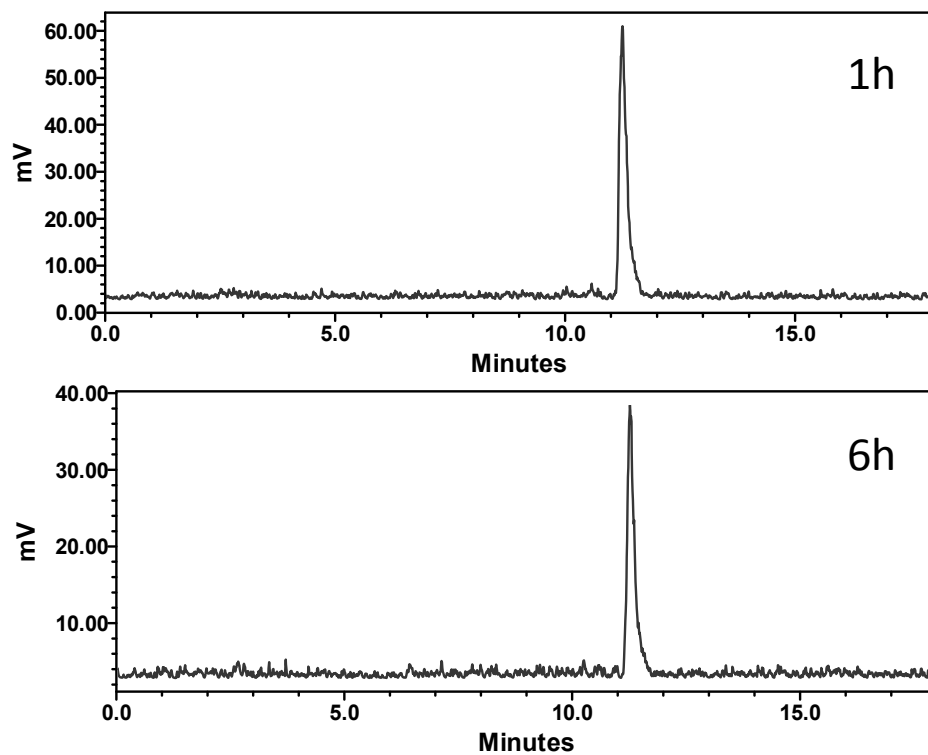


Figure S101. γ -HPLC trace of **7f** after 1 and 6 h in saline (Method D).

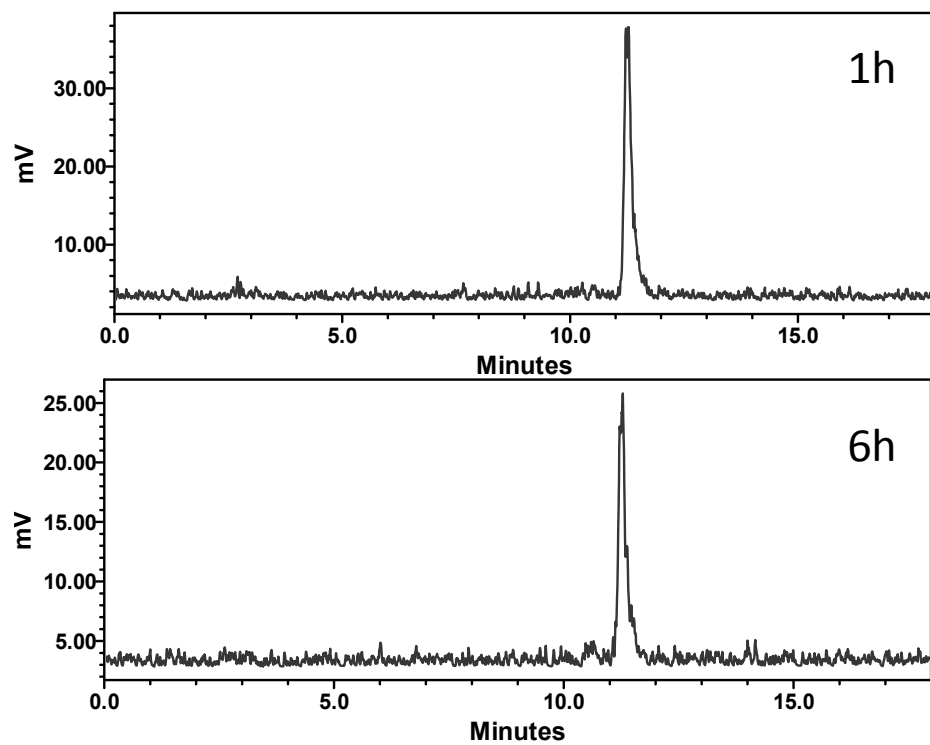


Figure S102. γ -HPLC trace of **7f** after 1 and 6 h in cysteine (Method D).

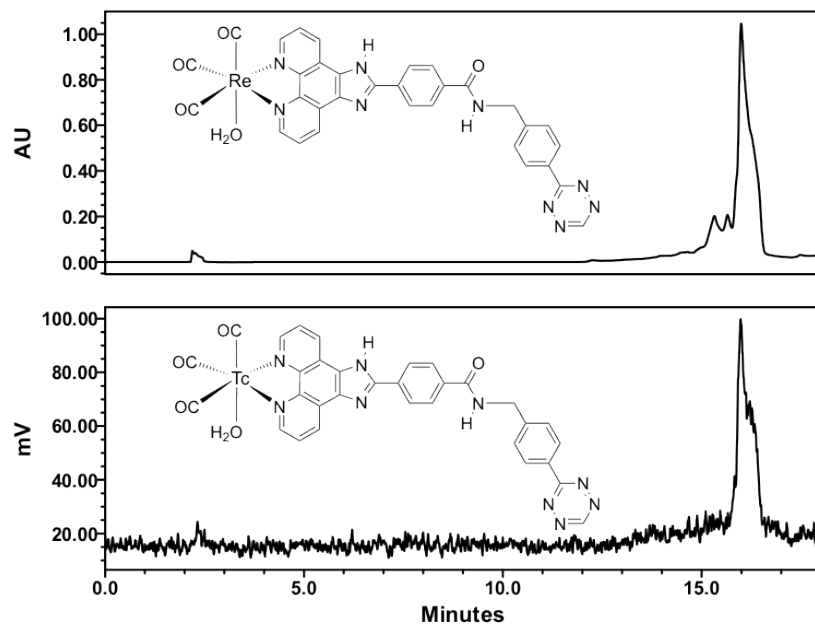


Figure S103. UV-HPLC trace of **10** (top) and γ -HPLC trace of **12** (bottom) (Method C).

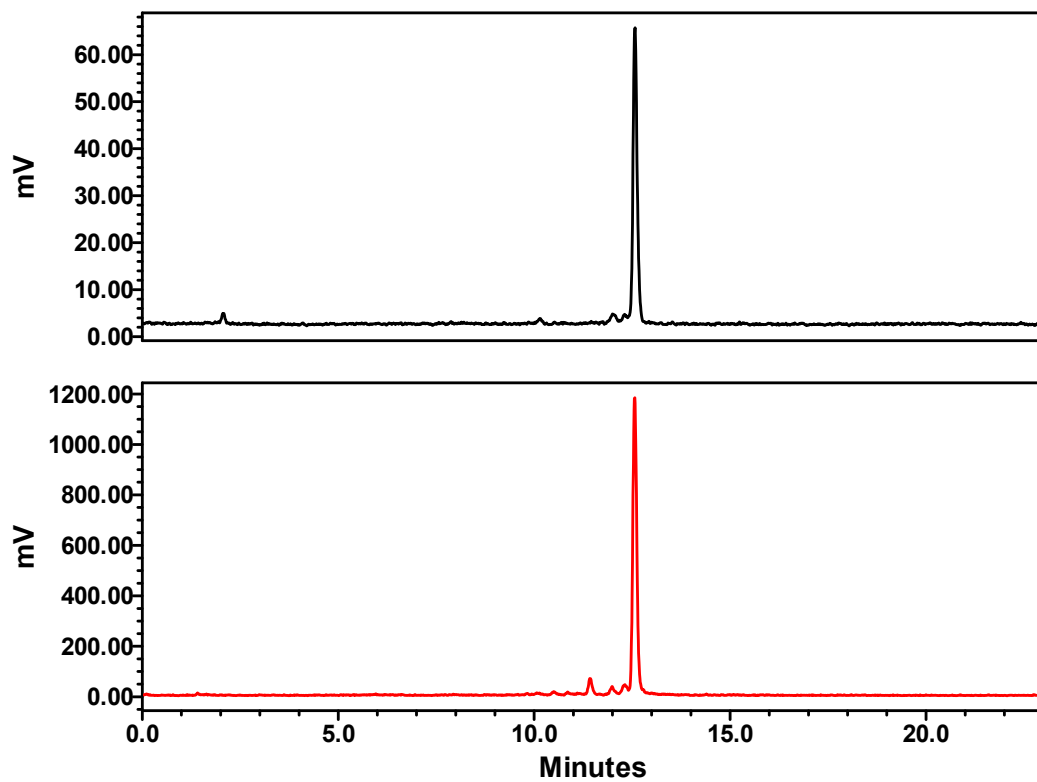


Figure S104. γ -HPLC trace of **12** after 0 and 6 h in saline (Method C).

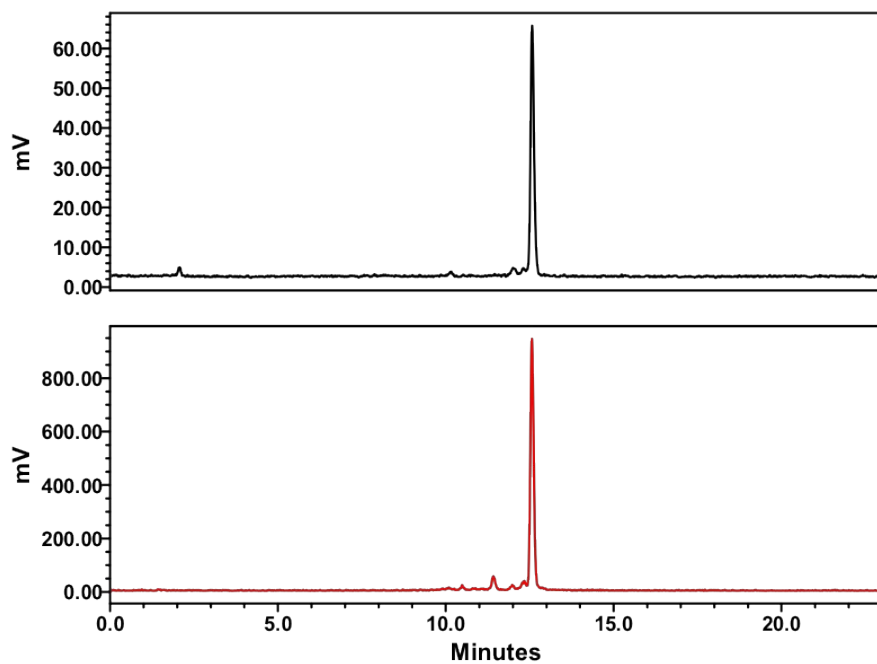


Figure S105. γ -HPLC trace of **12** after 0 and 6 h in cysteine (Method C).

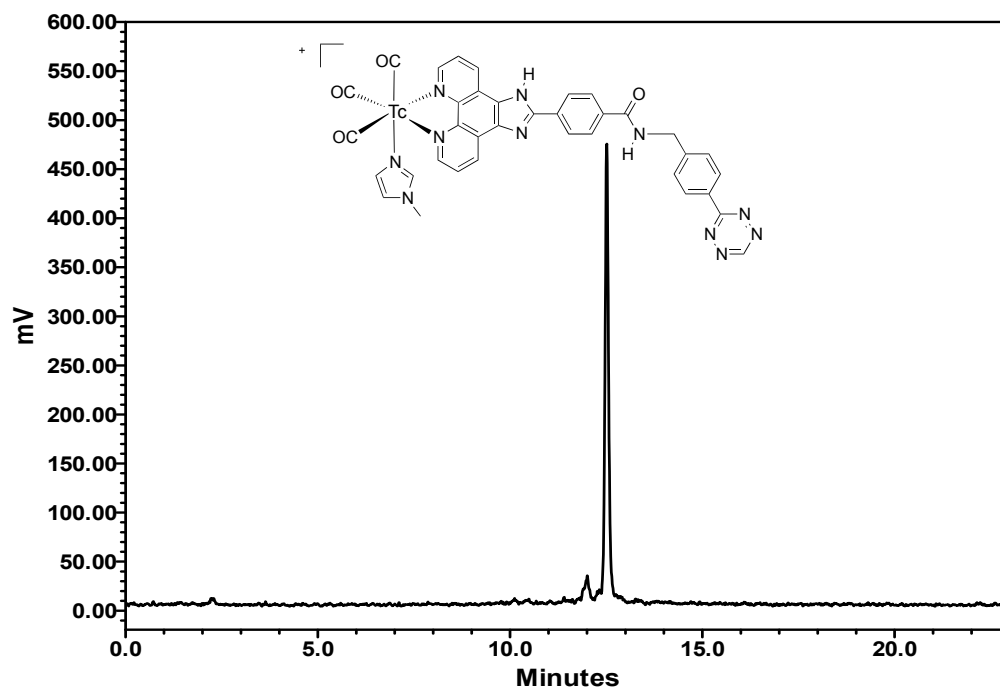


Figure S106. γ -HPLC trace of **13** (Method E).

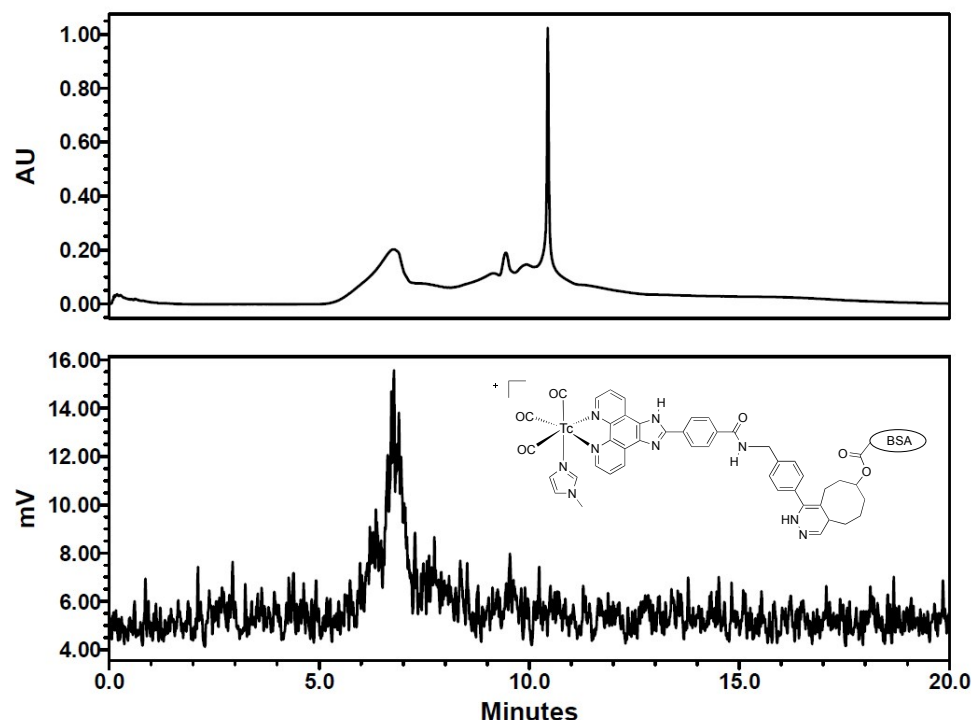


Figure S107. UV-HPLC trace of **15** (top) and γ -HPLC trace of **15** (bottom) (Method F).