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^1H NMR and ^{13}C NMR Spectra.

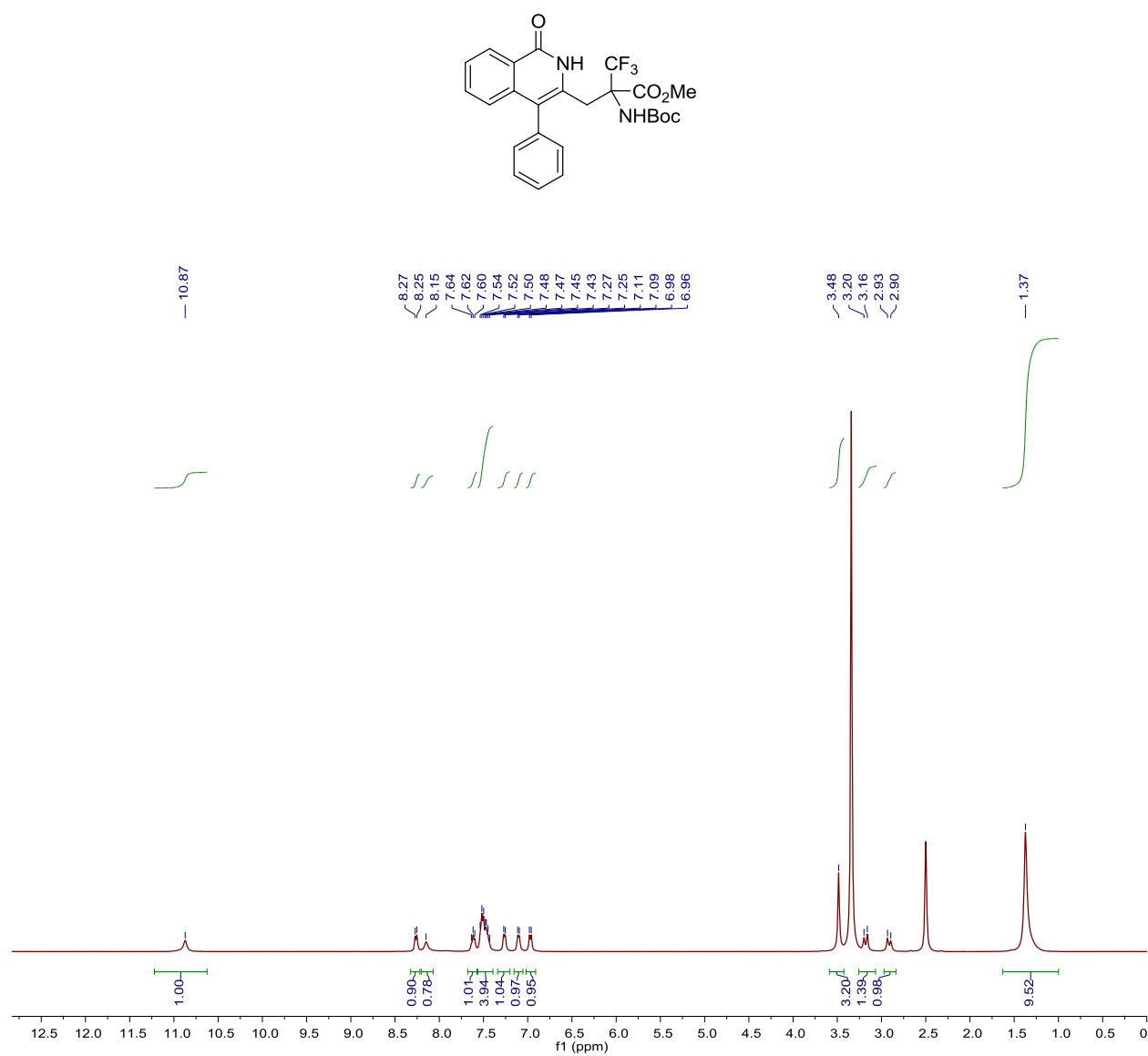


Figure S1. ^1H spectrum of **3a** in DMSO- d_6

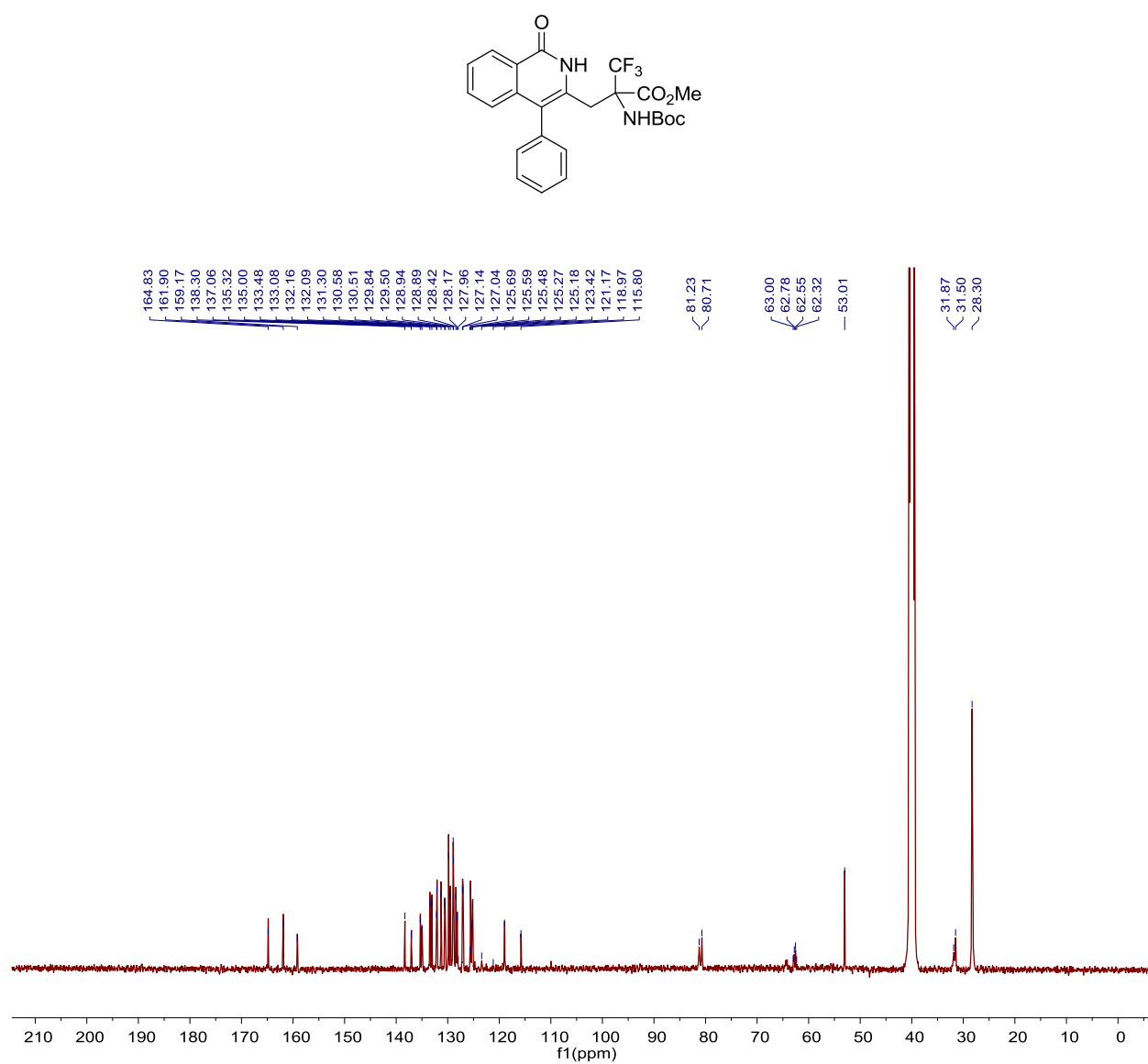


Figure S2. ^{13}C spectrum of **3a** in DMSO- d_6

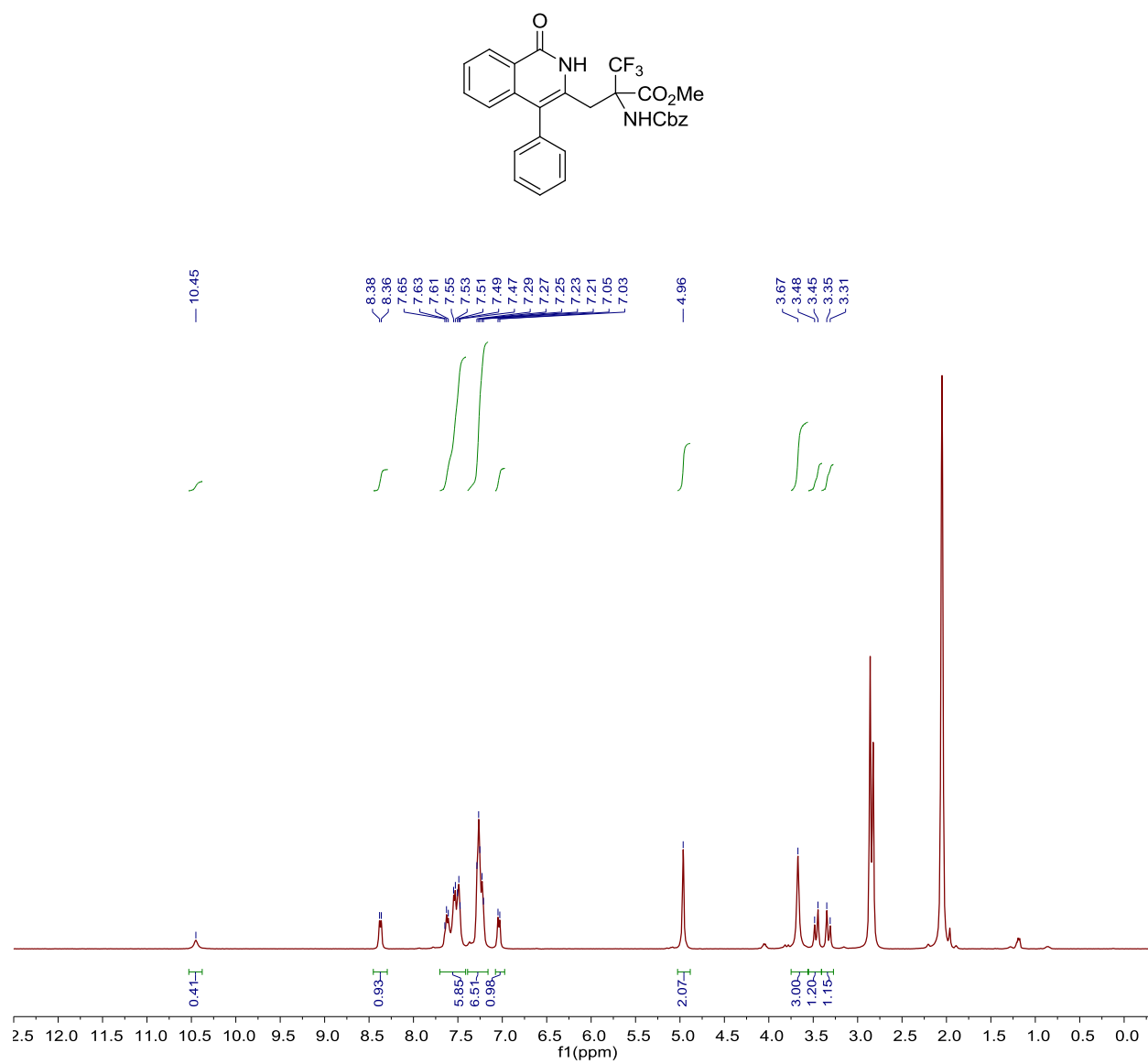


Figure S3. ¹H spectrum of **3b** in acetone-*d*₆

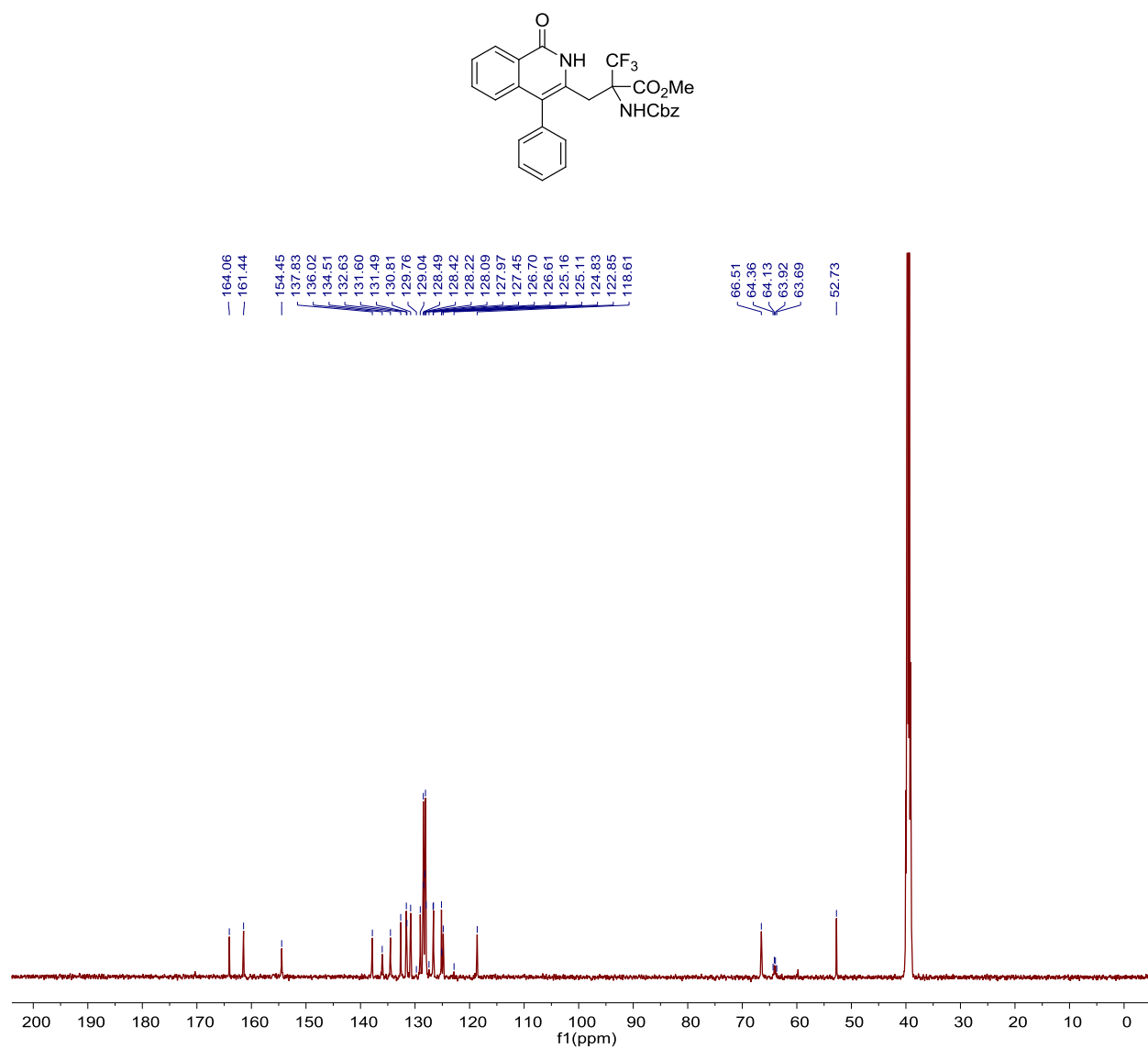


Figure S4. ^{13}C spectrum of **3b** in DMSO- d_6

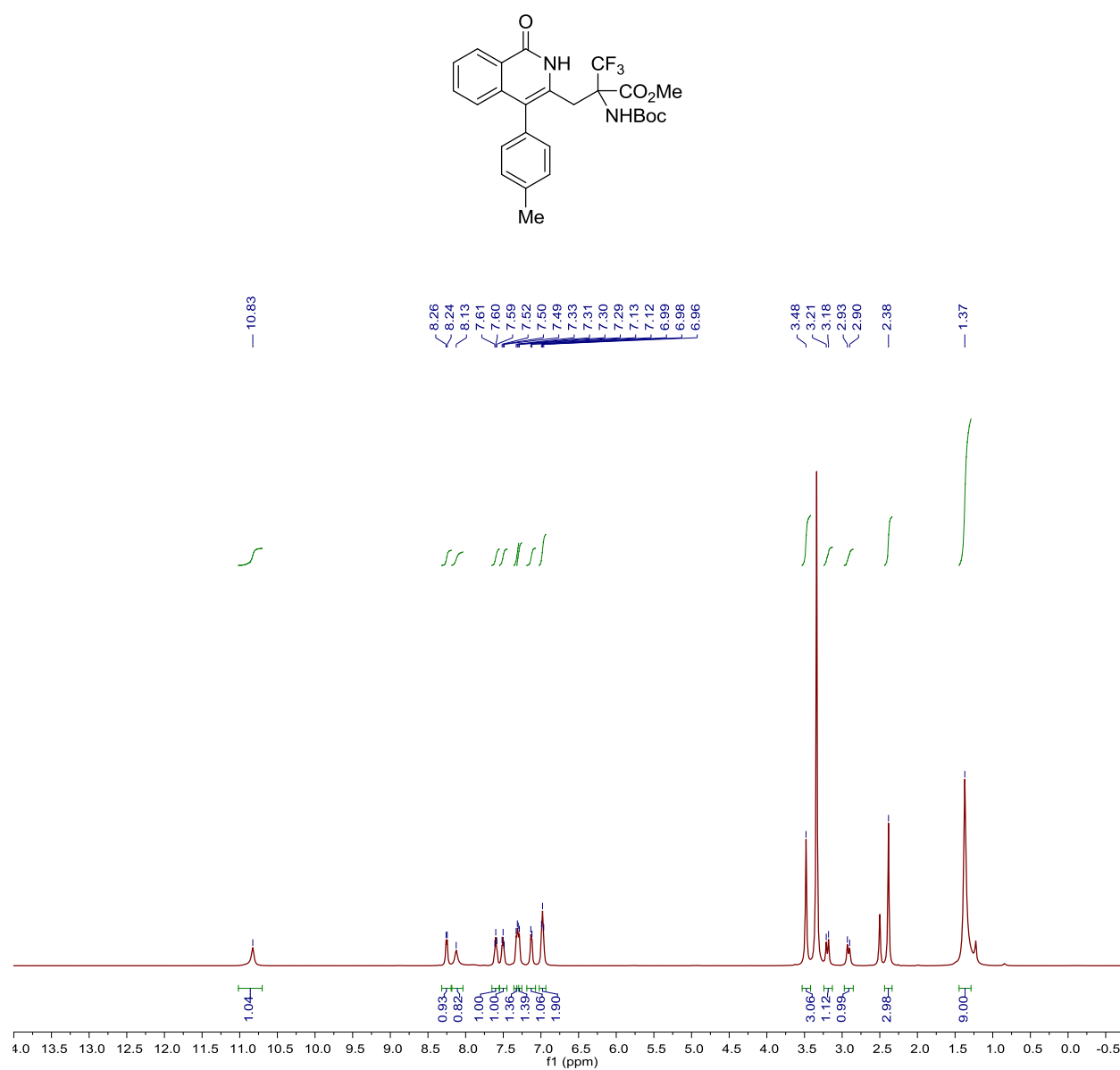


Figure S5. ^1H spectrum of **3c** in DMSO- d_6

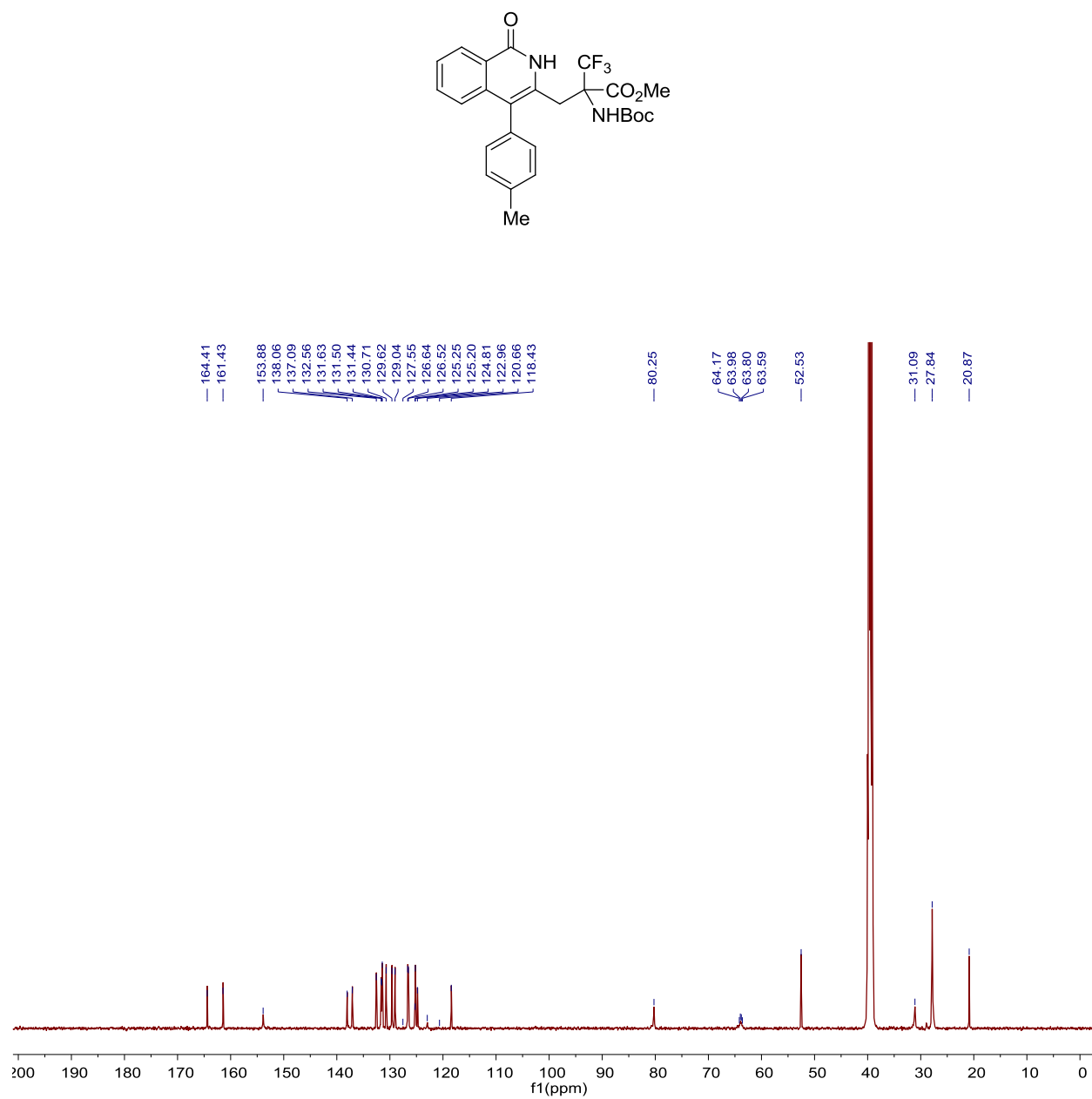


Figure S6. ^{13}C spectrum of **3c** in DMSO- d_6

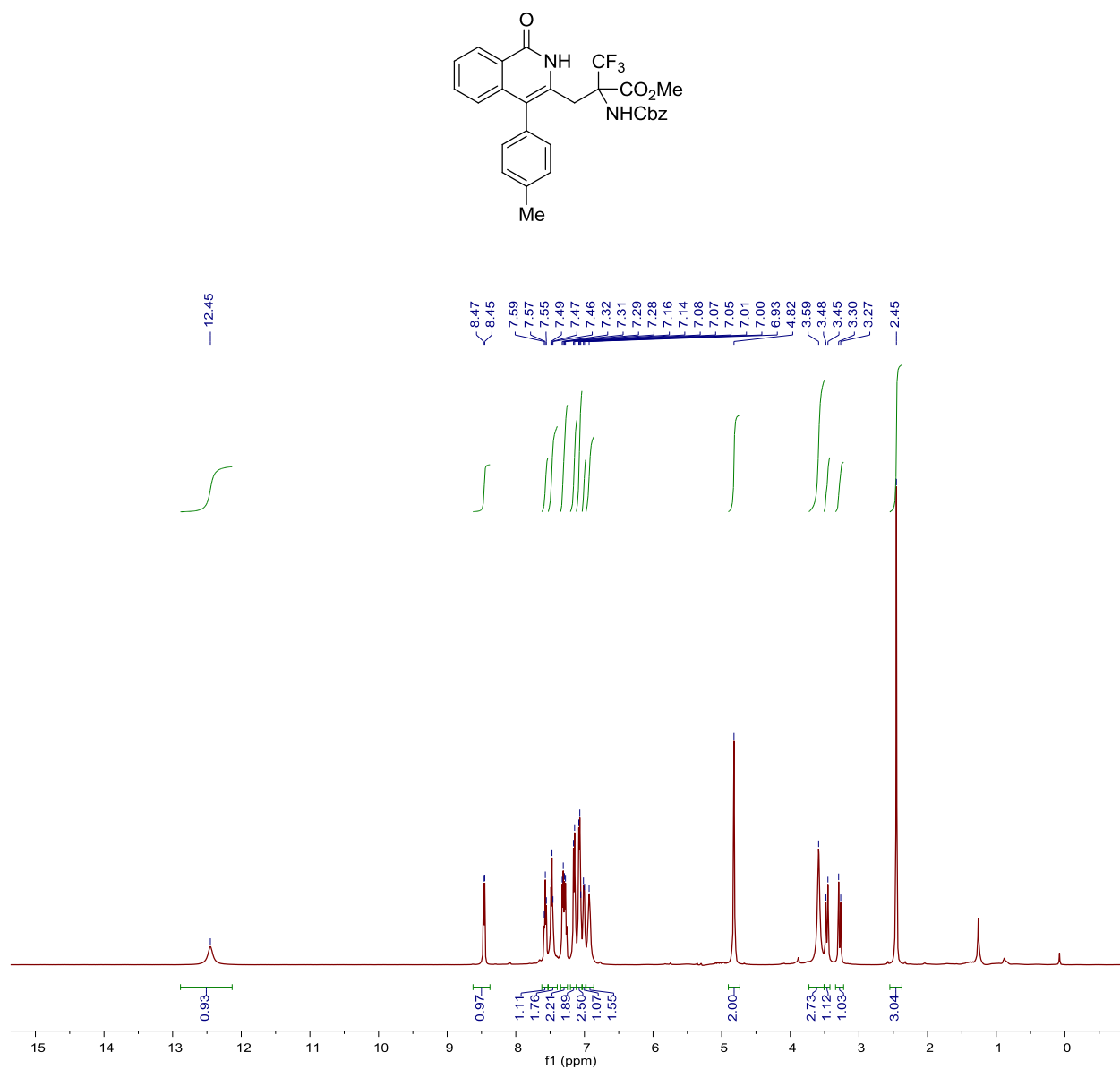


Figure S7. ^1H spectrum of **3d** in CDCl₃

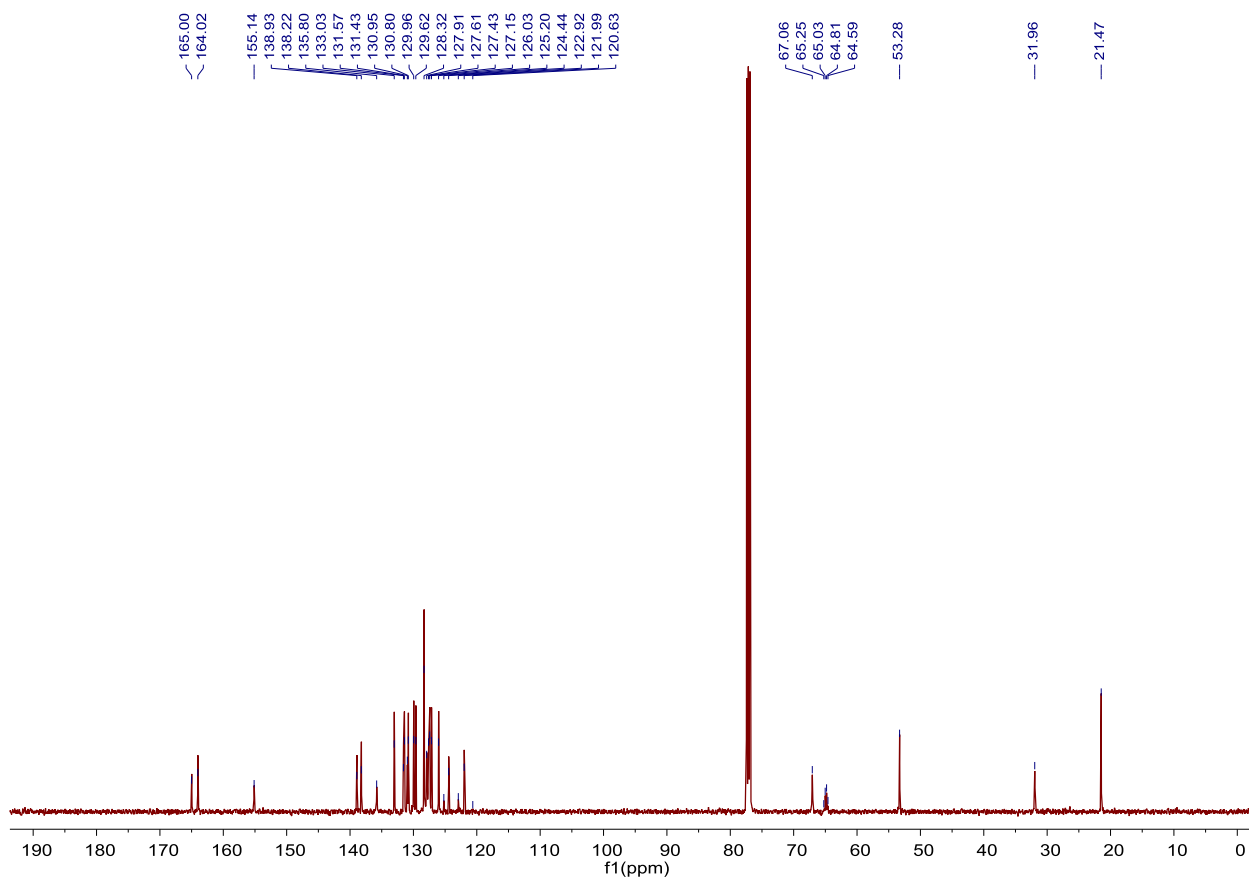
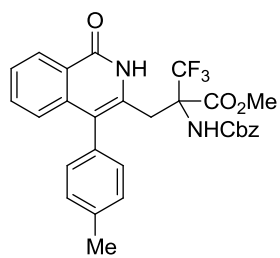


Figure S8. ^{13}C spectrum of **3d** in CDCl_3

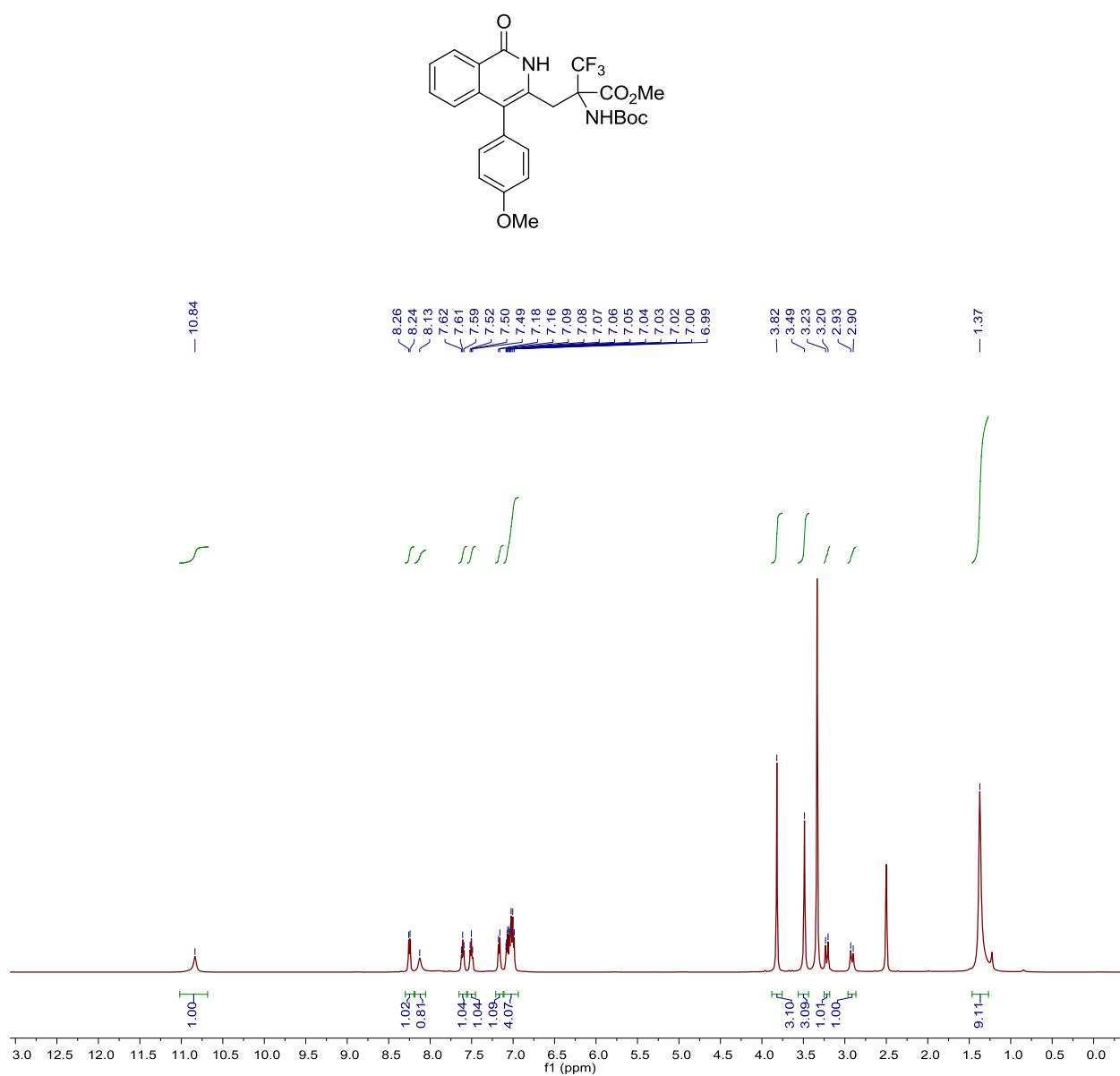


Figure S9. ¹H spectrum of **3e** in DMSO-*d*₆

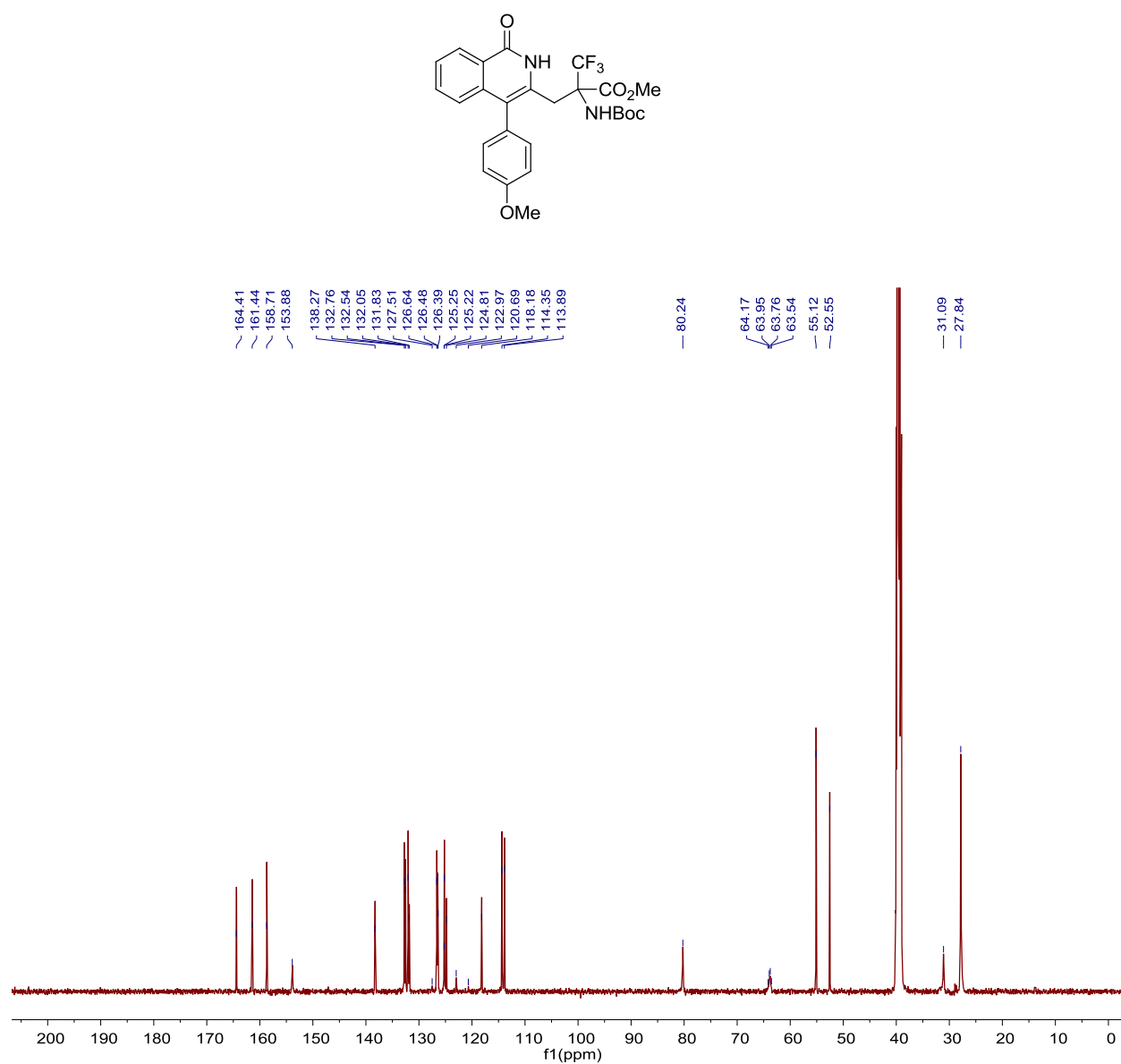


Figure S10. ^{13}C spectrum of **3e** in DMSO- d_6

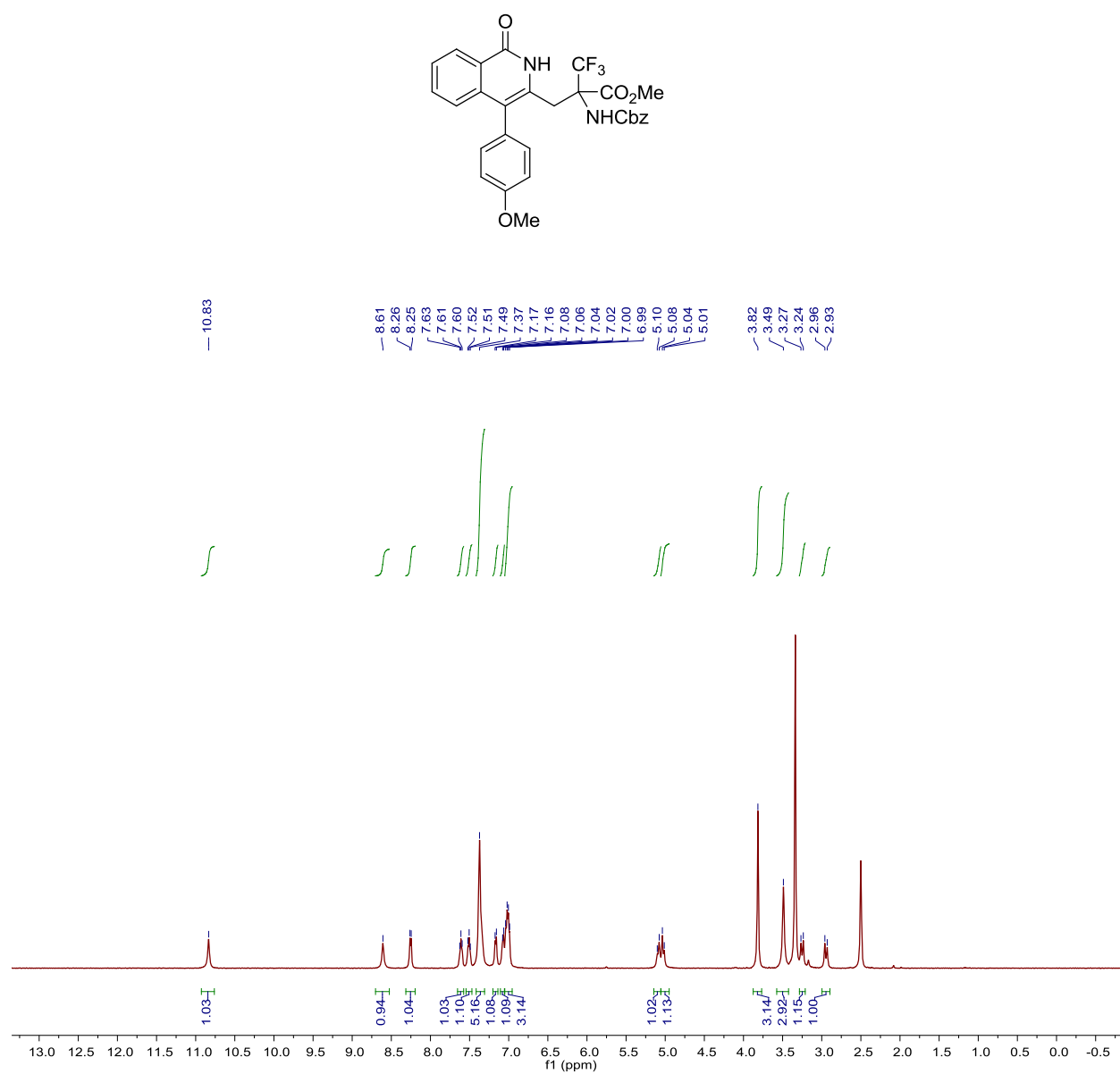


Figure S11. ^1H spectrum of **3f** in DMSO- d_6

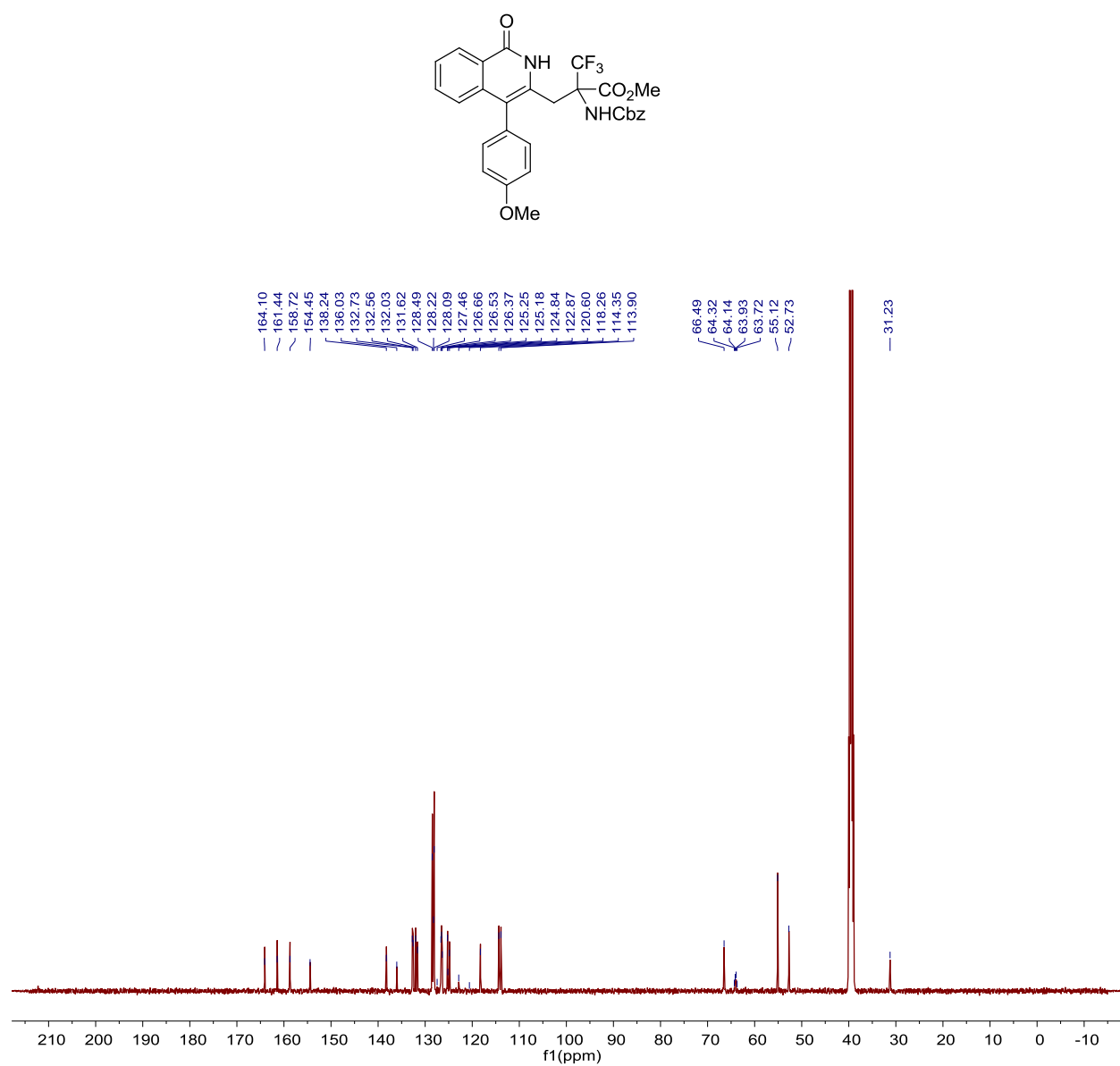


Figure S12. ^{13}C spectrum of **3f** in $\text{DMSO}-d_6$

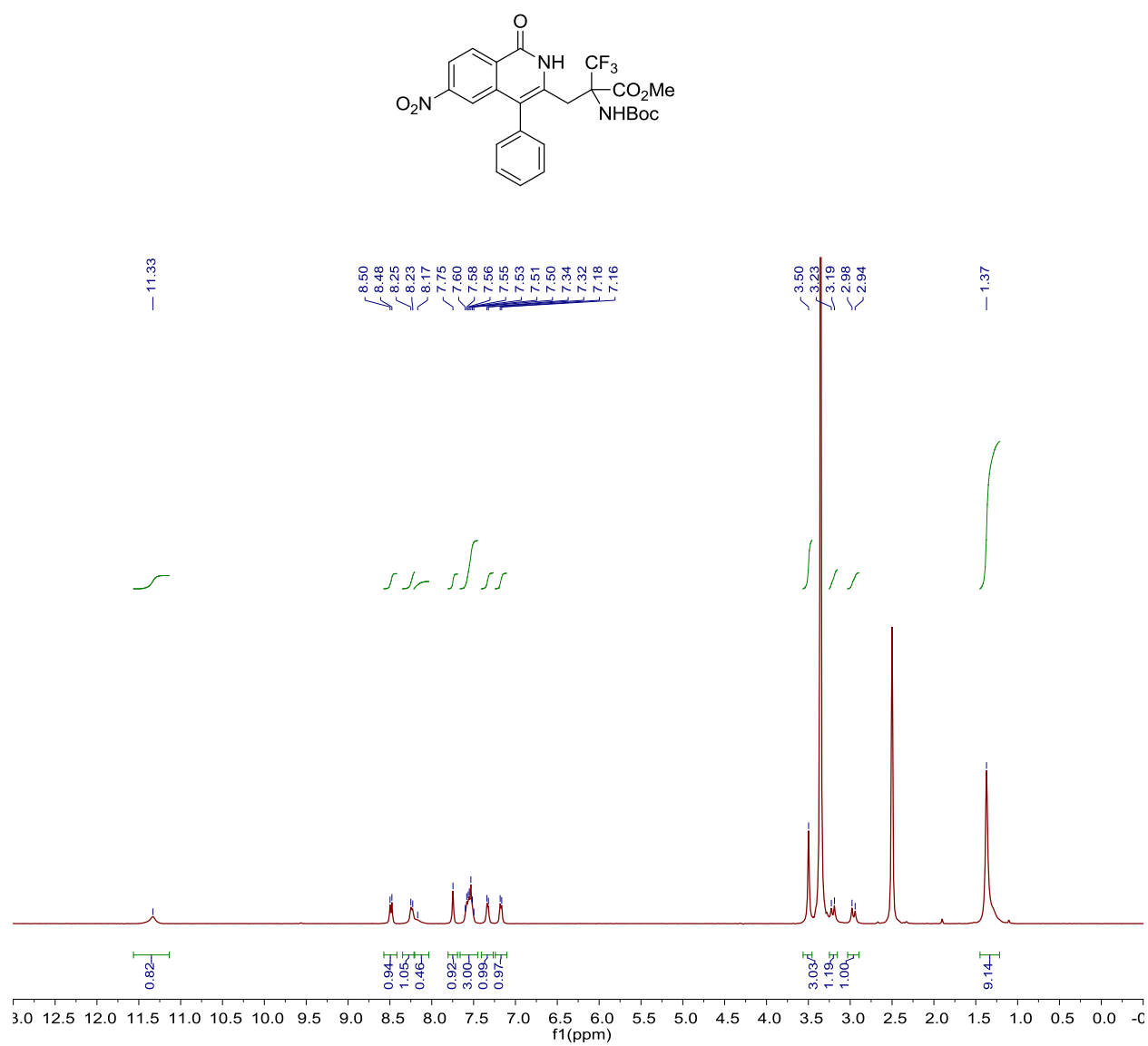


Figure S13. ^1H spectrum of **3g** in DMSO- d_6

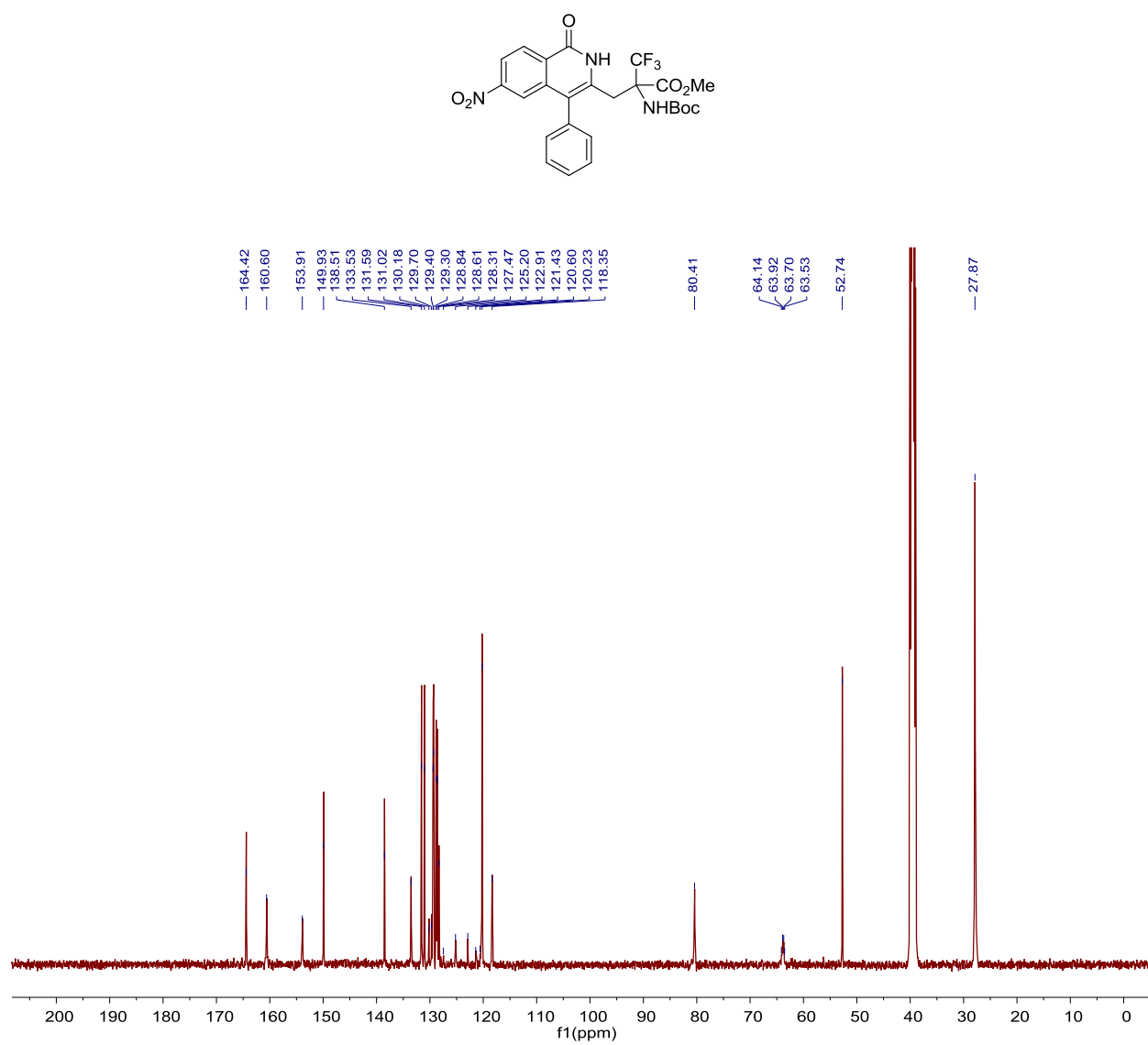


Figure S14. ^{13}C spectrum of **3g** in DMSO- d_6

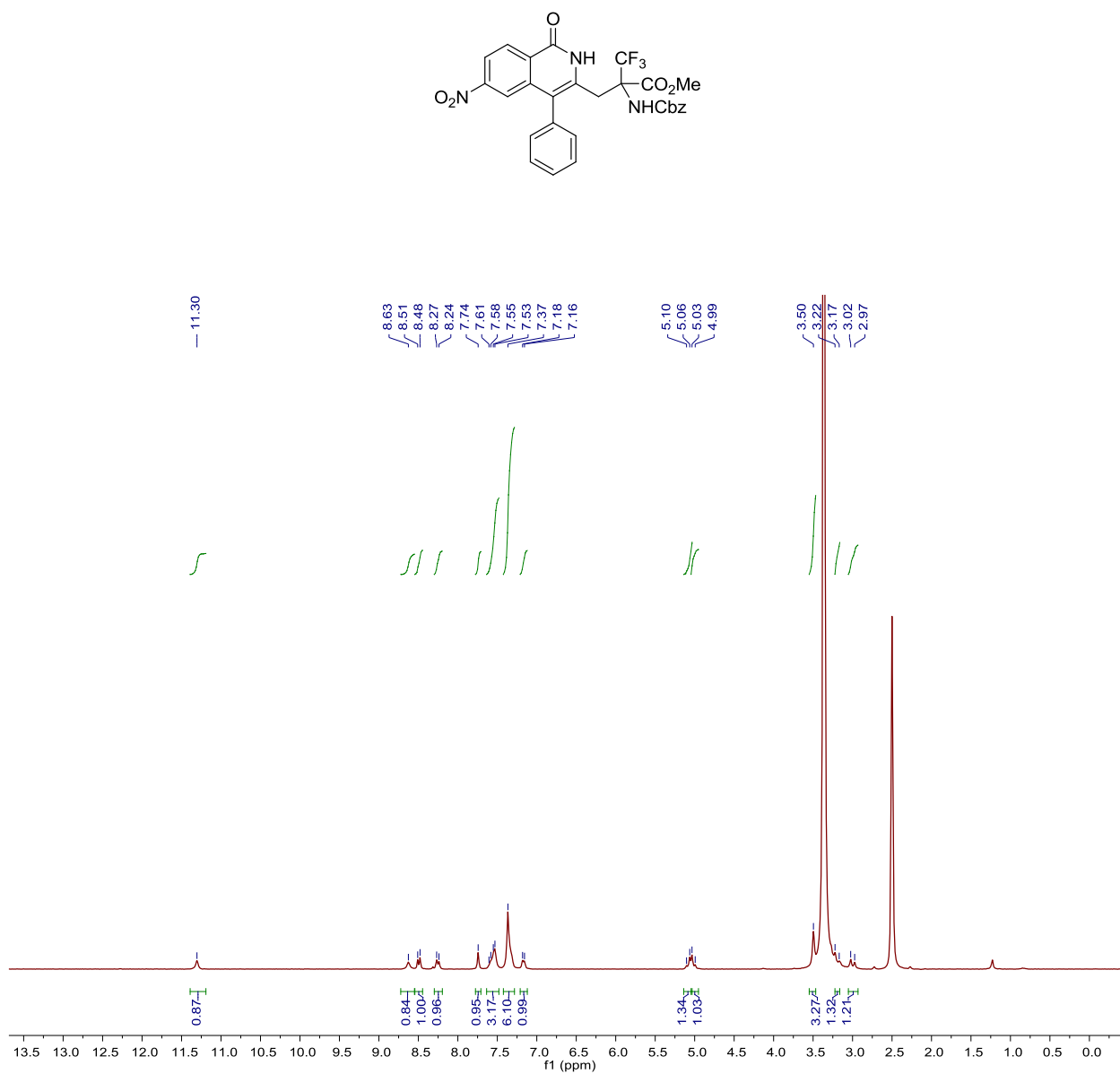


Figure S15. ^1H spectrum of **3h** in DMSO- d_6

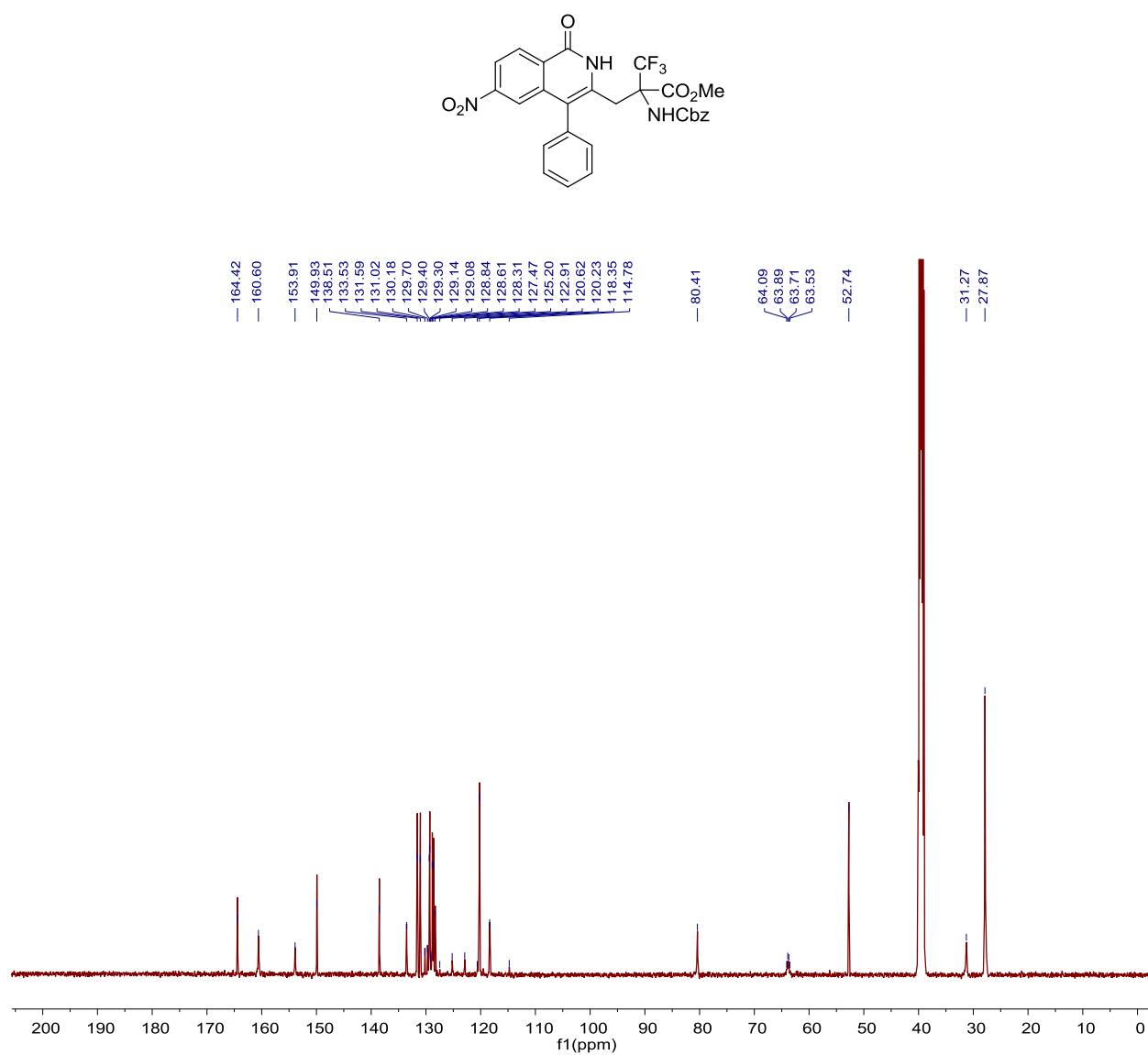


Figure S16. ^{13}C spectrum of **3h** in $\text{DMSO}-d_6$

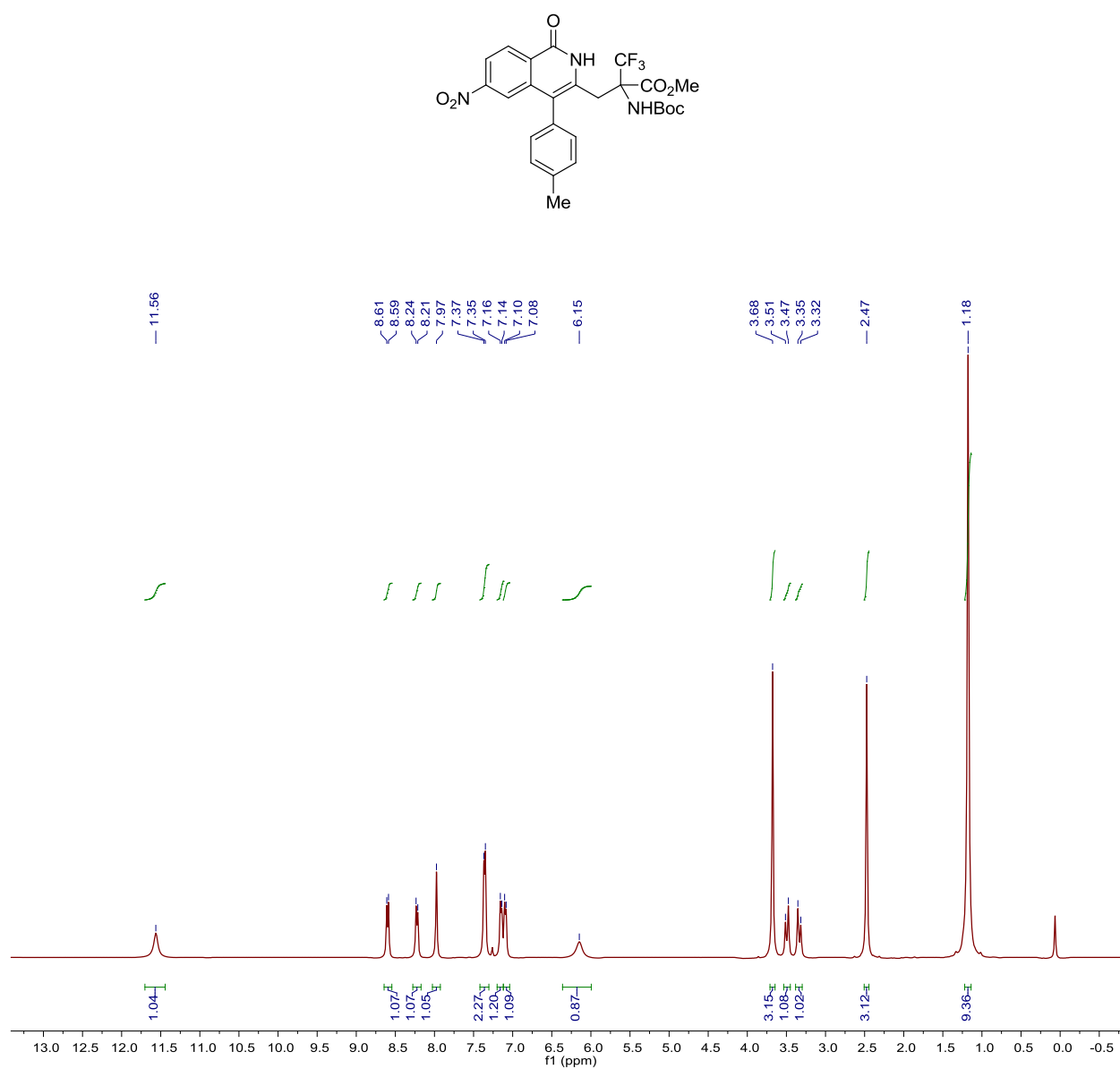


Figure S17. ^1H spectrum of **3i** in CDCl₃

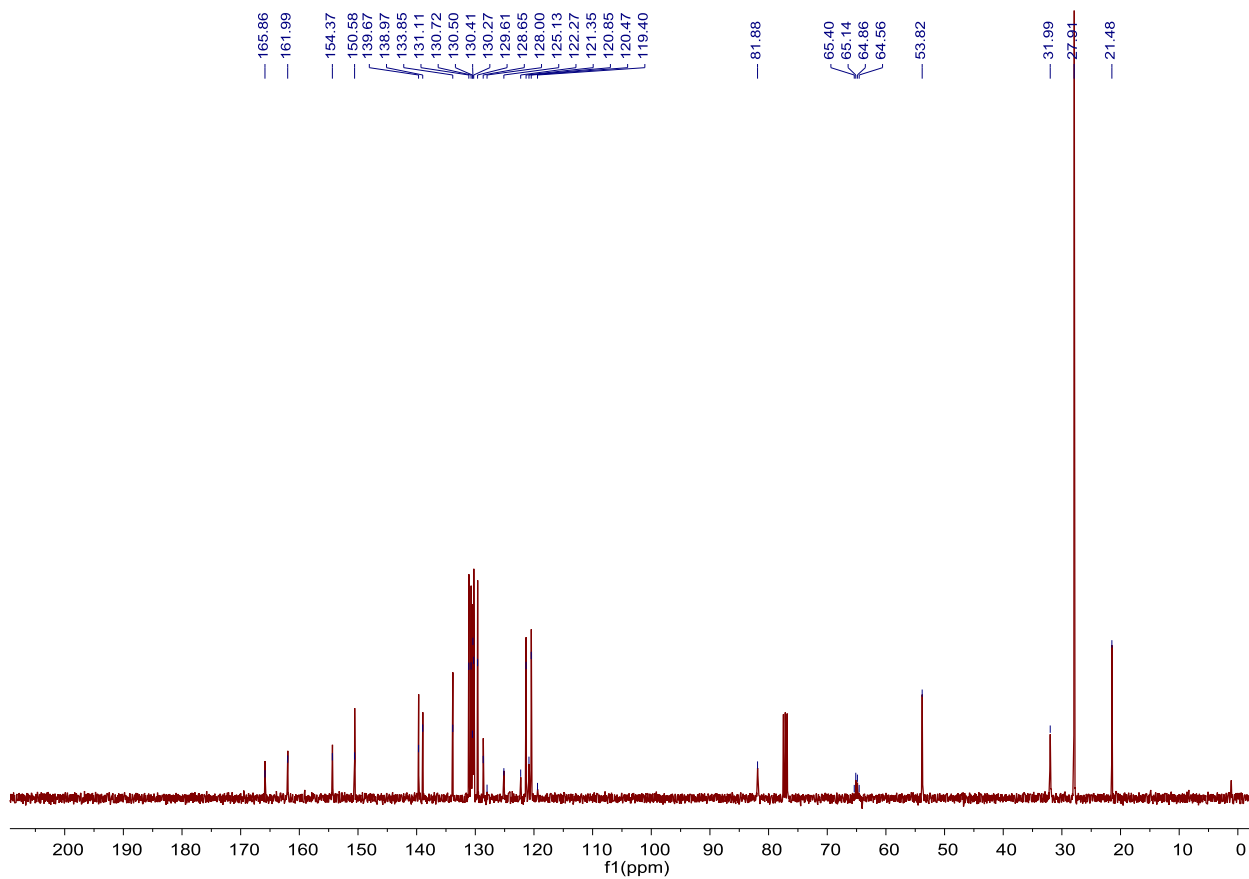
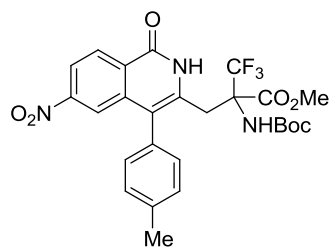


Figure S18. ^{13}C spectrum of **3i** in CDCl_3

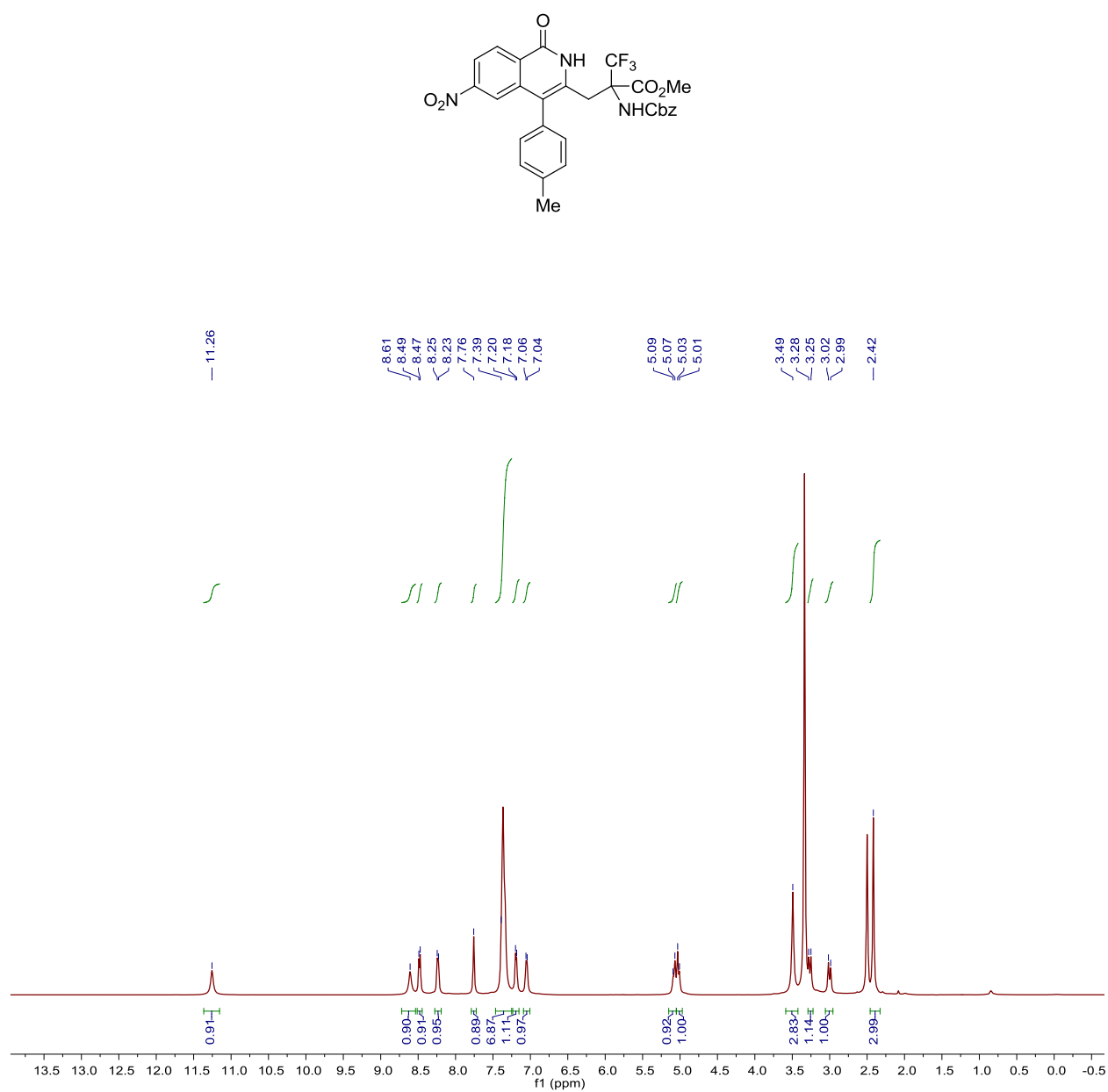


Figure S19. ^1H spectrum of **3j** in DMSO- d_6

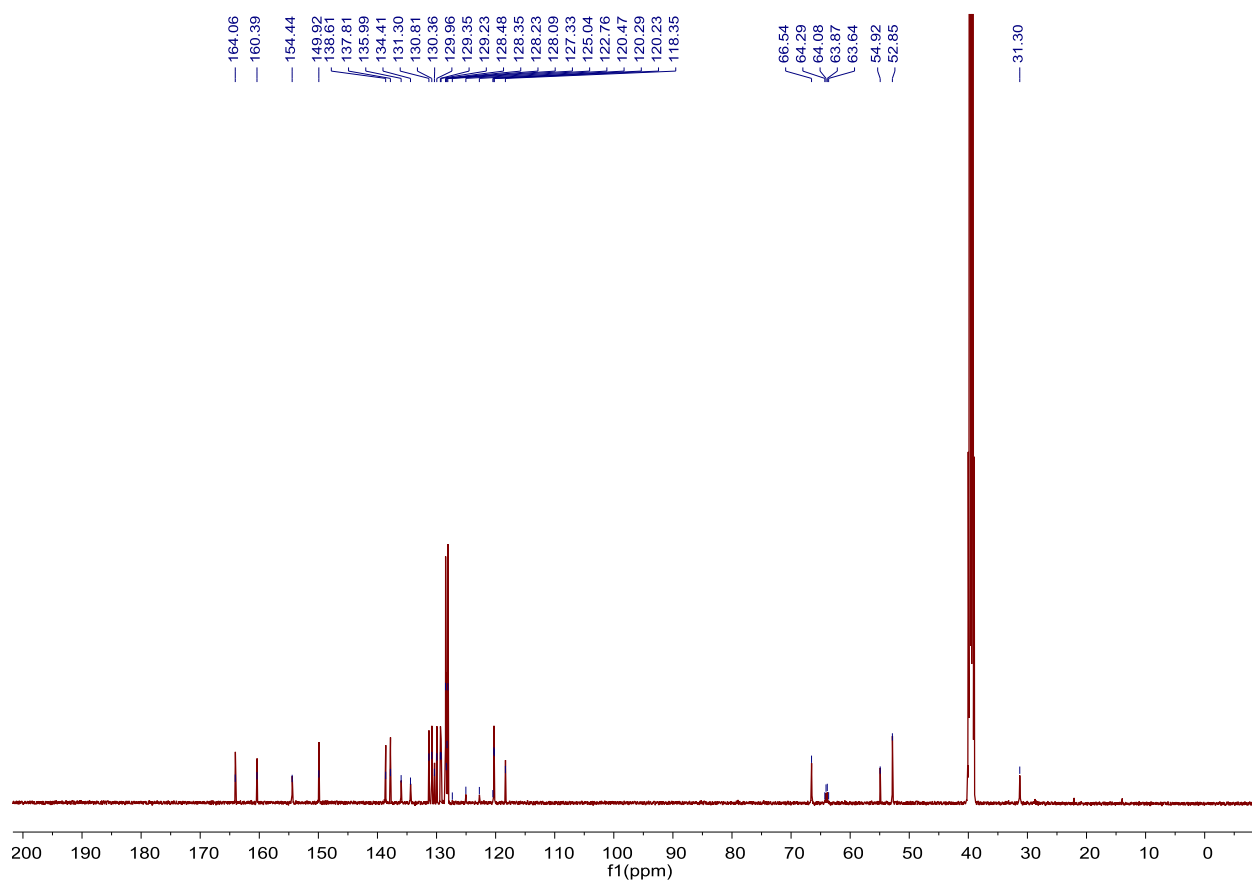
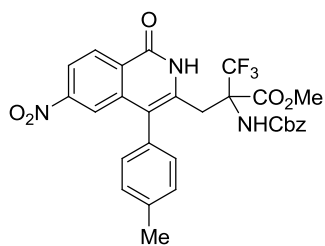


Figure S20. ^{13}C spectrum of **3j** in $\text{DMSO-}d_6$

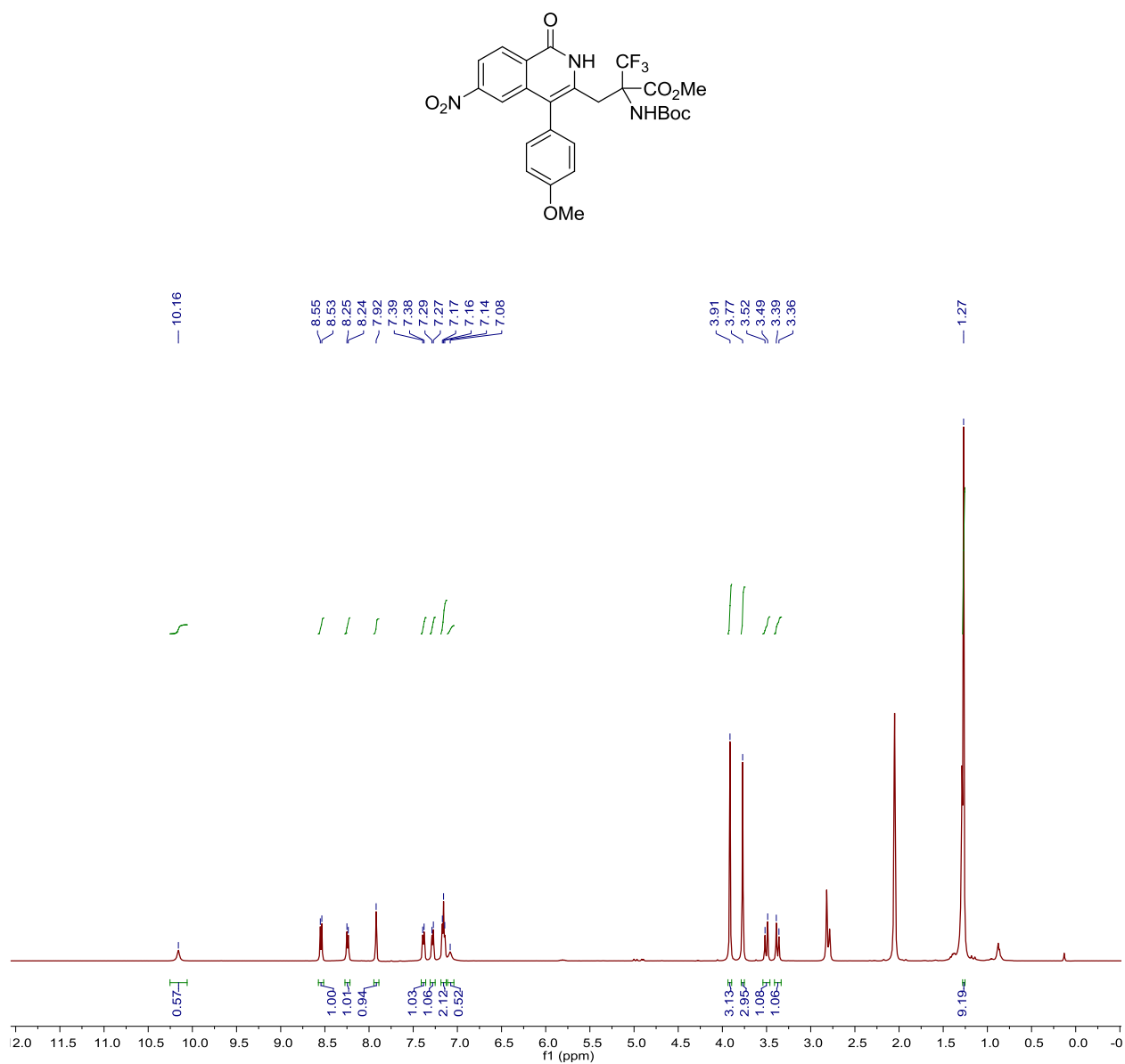


Figure S21. ^1H spectrum of **3k** in $\text{acetone-}d_6$

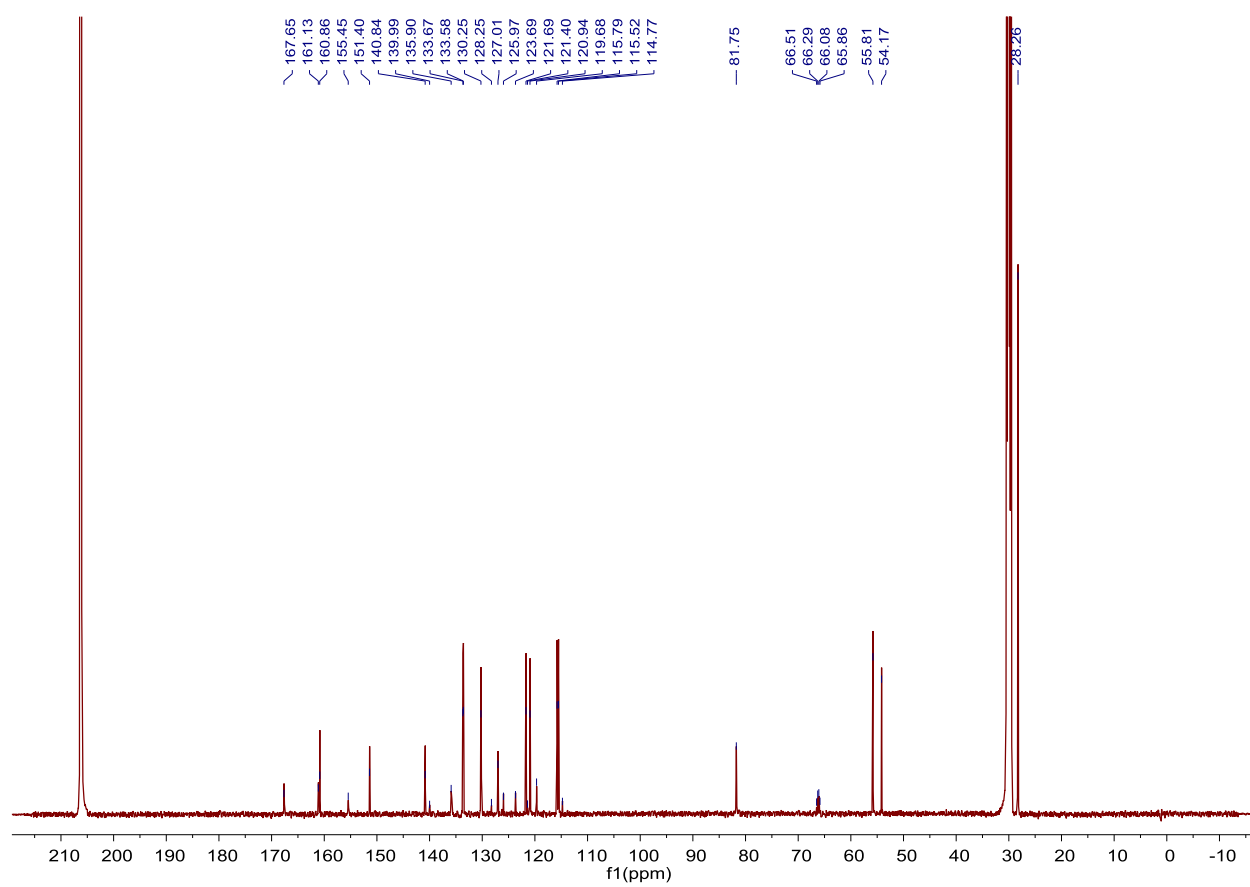
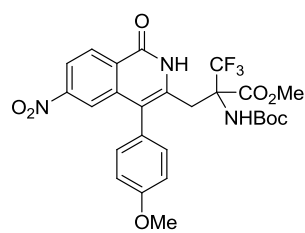


Figure S22. ^{13}C spectrum of **3k** in acetone- d_6

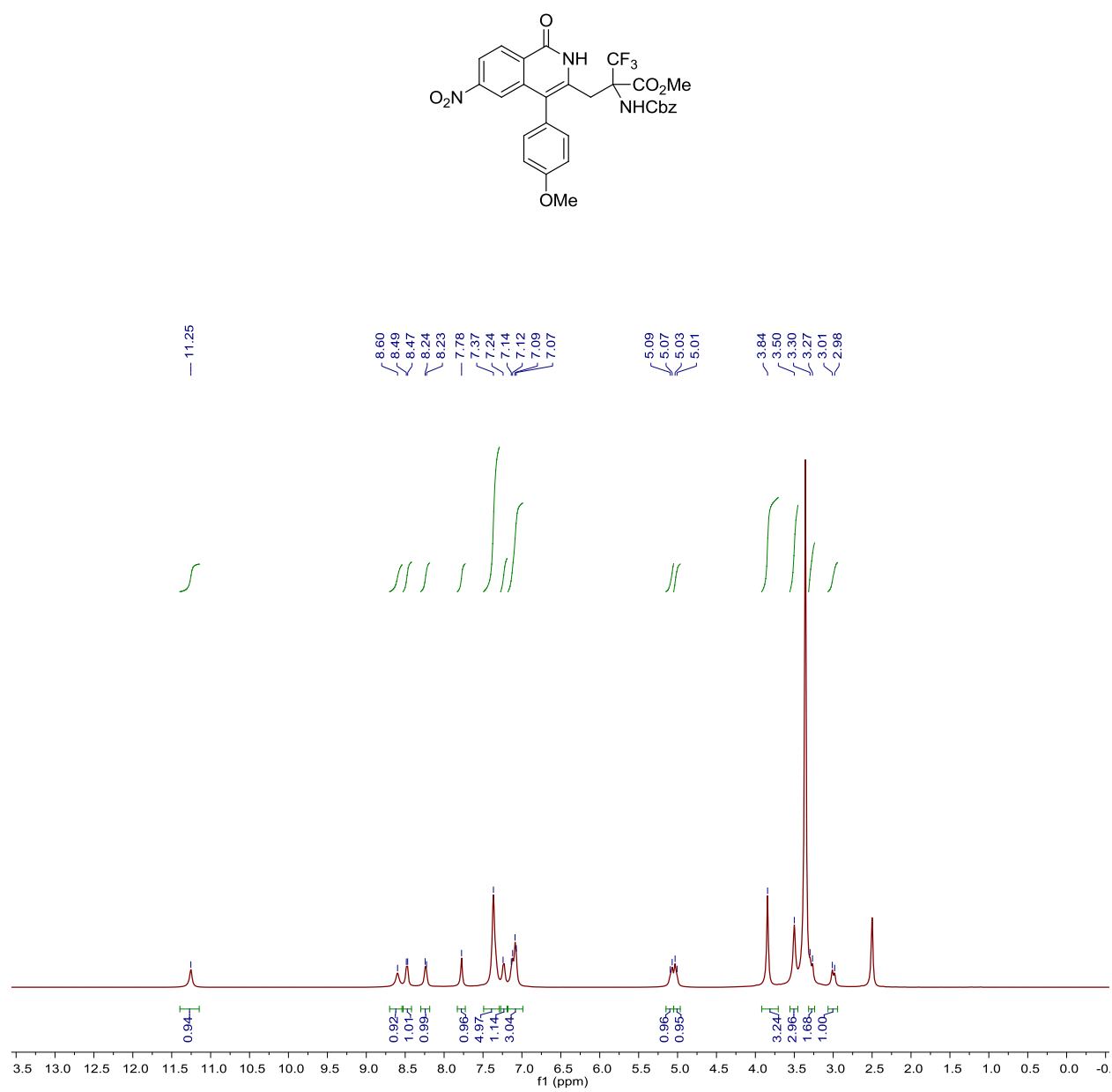


Figure S23. ^1H spectrum of **31** in DMSO- d_6

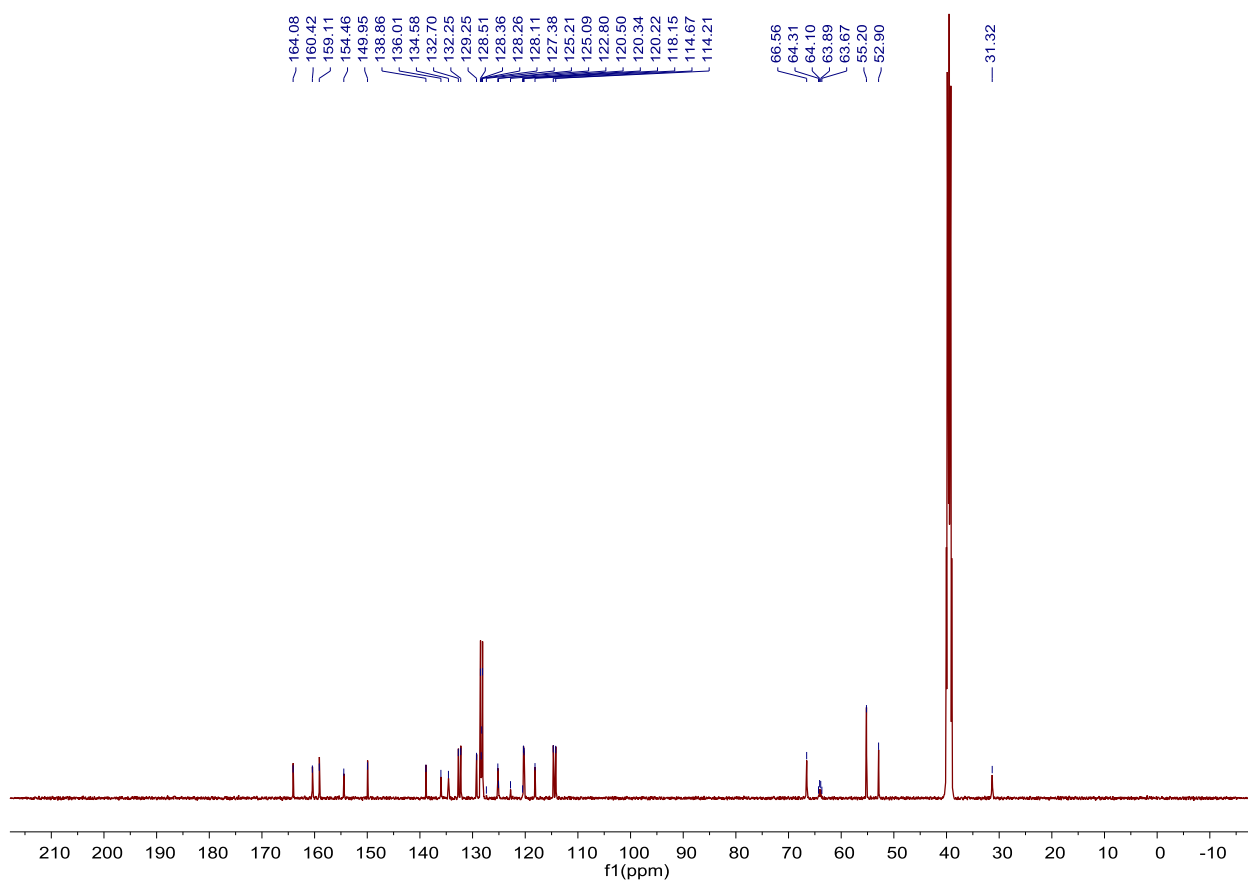
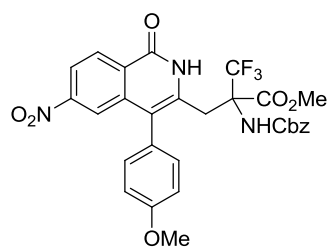


Figure S24. ^{13}C spectrum of **31** in $\text{DMSO-}d_6$

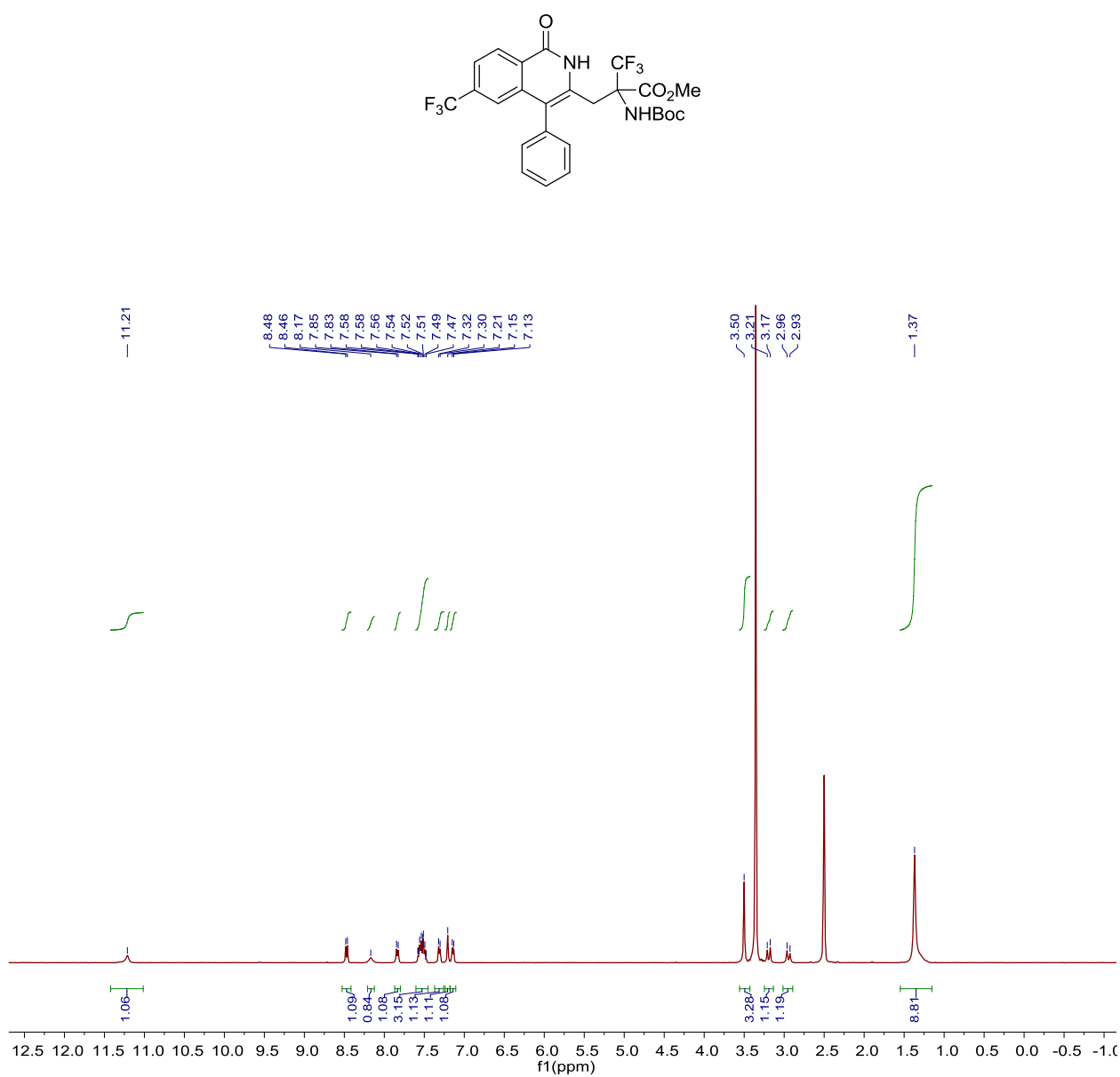


Figure S25. ^1H spectrum of **3m** in DMSO- d_6

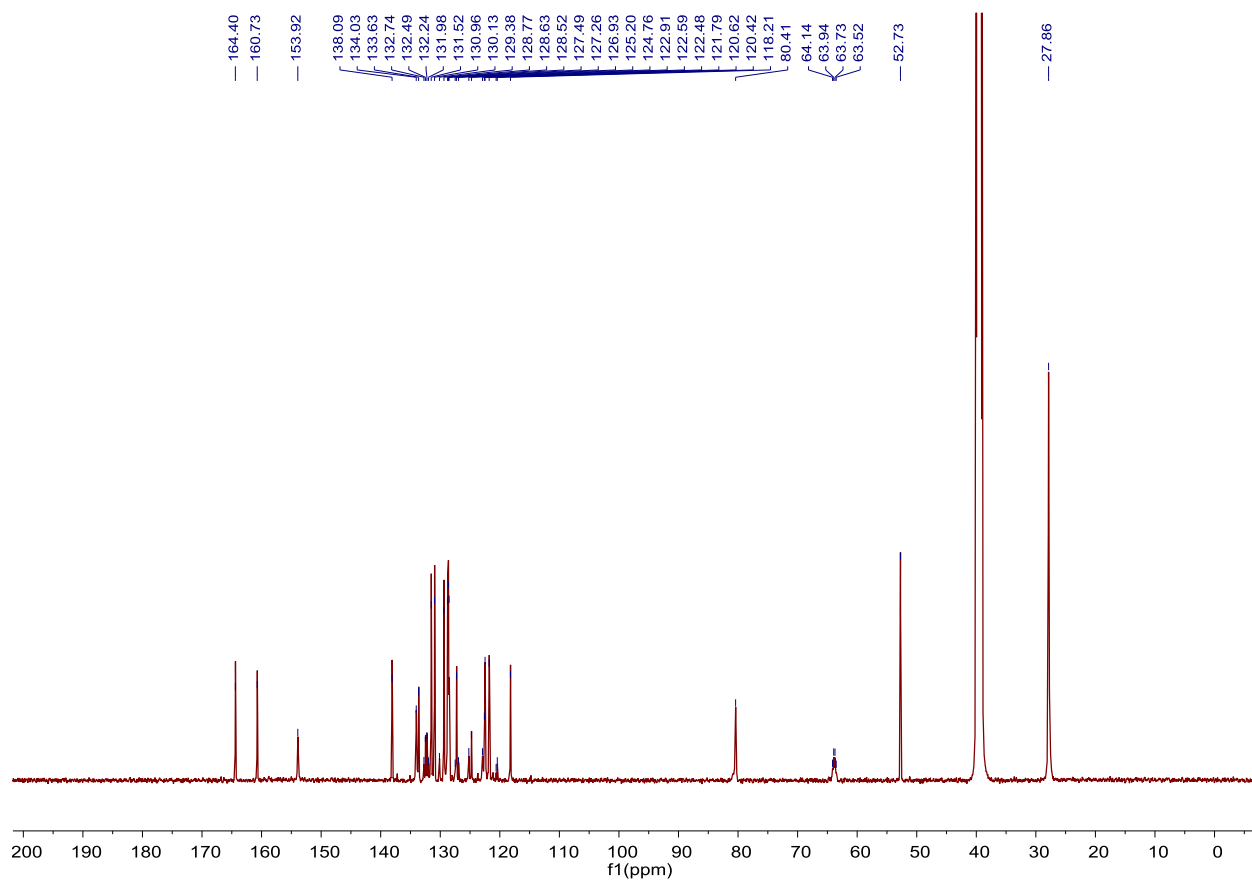
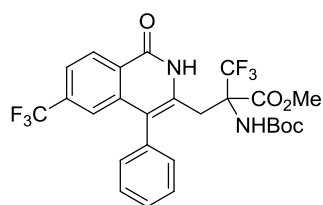


Figure S26. ^{13}C spectrum of **3m** in $\text{DMSO-}d_6$

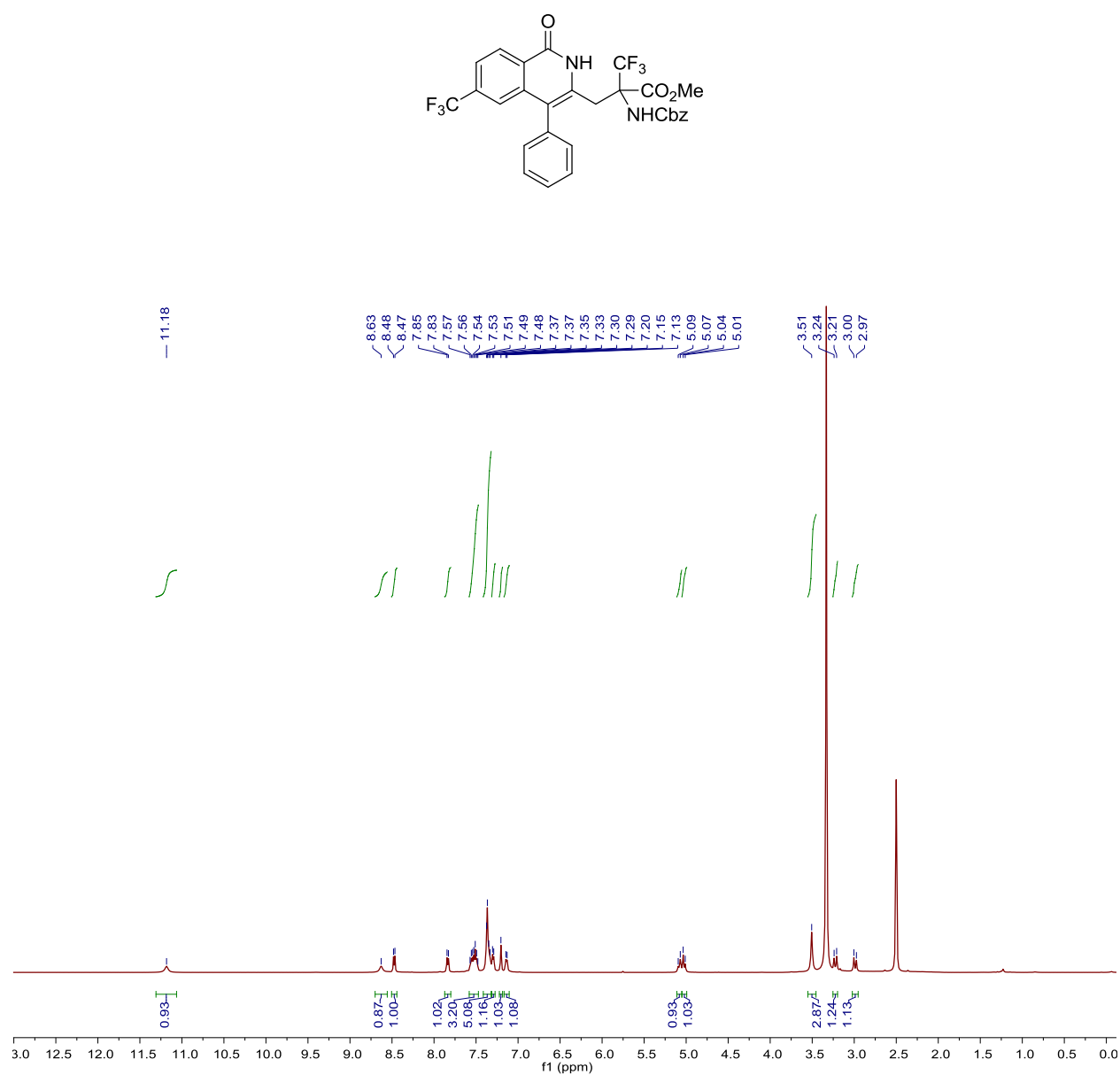


Figure S27. ¹H spectrum of **3n** in DMSO-*d*₆

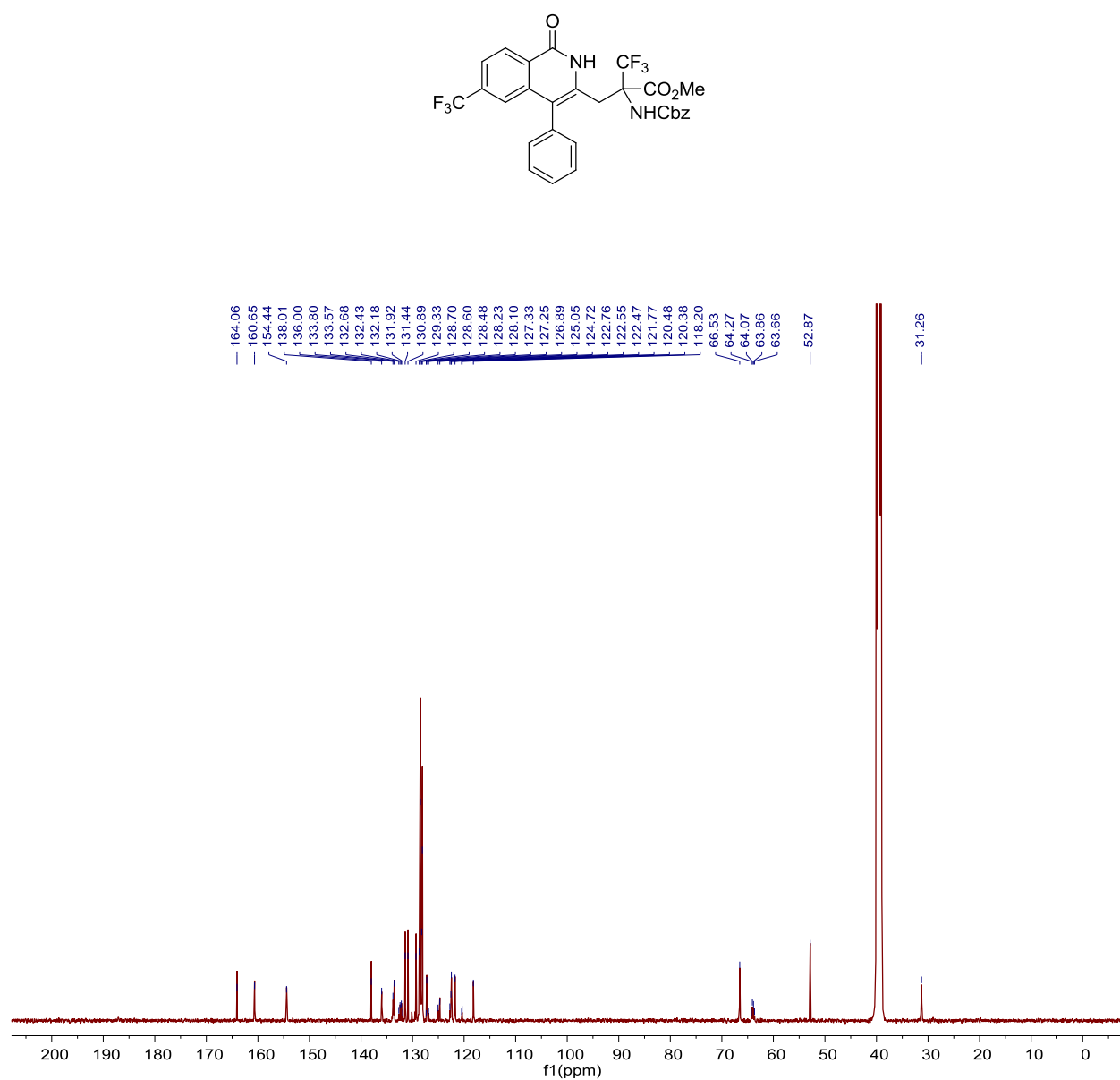


Figure S28. ^{13}C spectrum of **3n** in $\text{DMSO}-d_6$

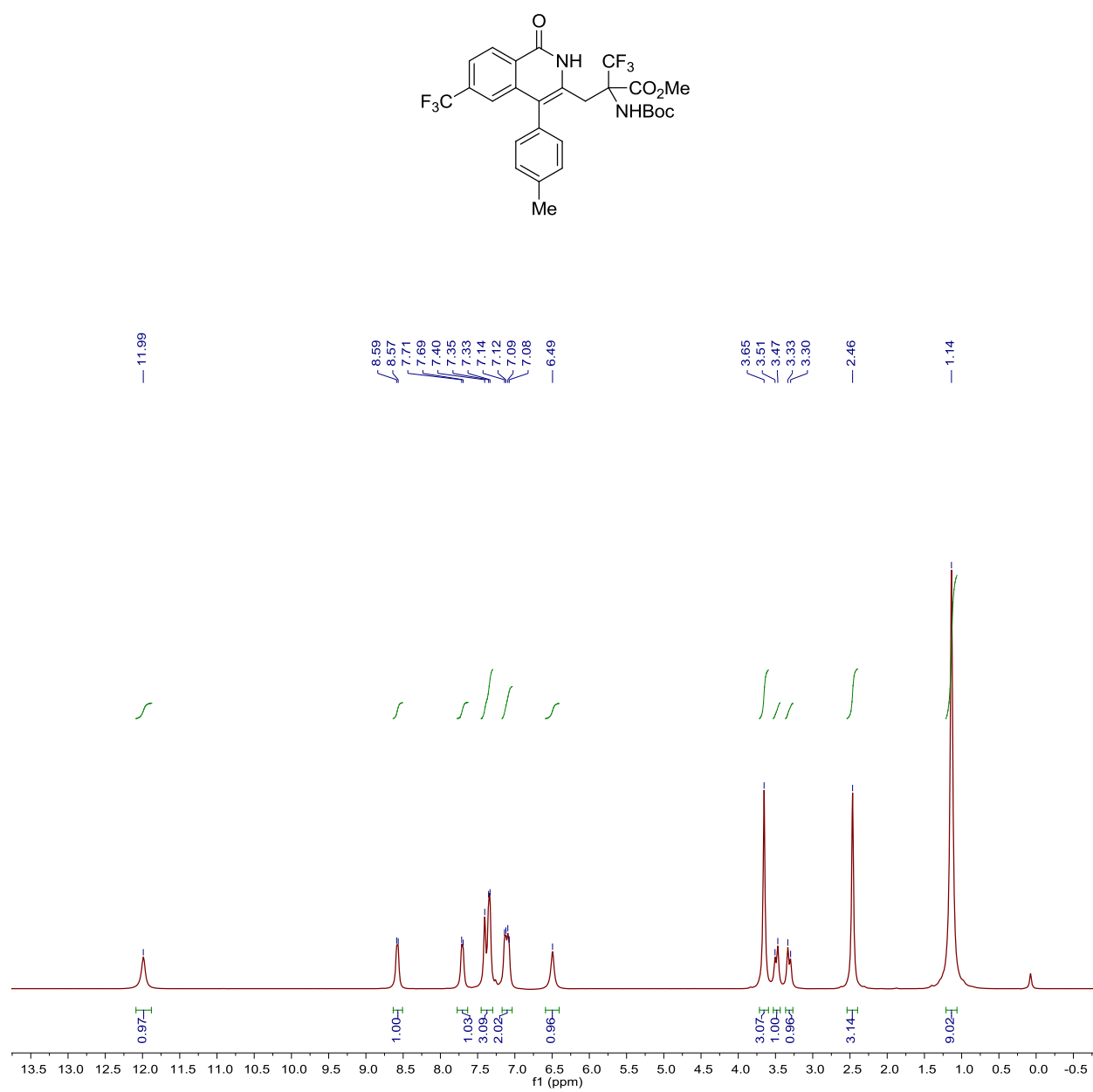


Figure S29. ^1H spectrum of **3o** in CDCl_3

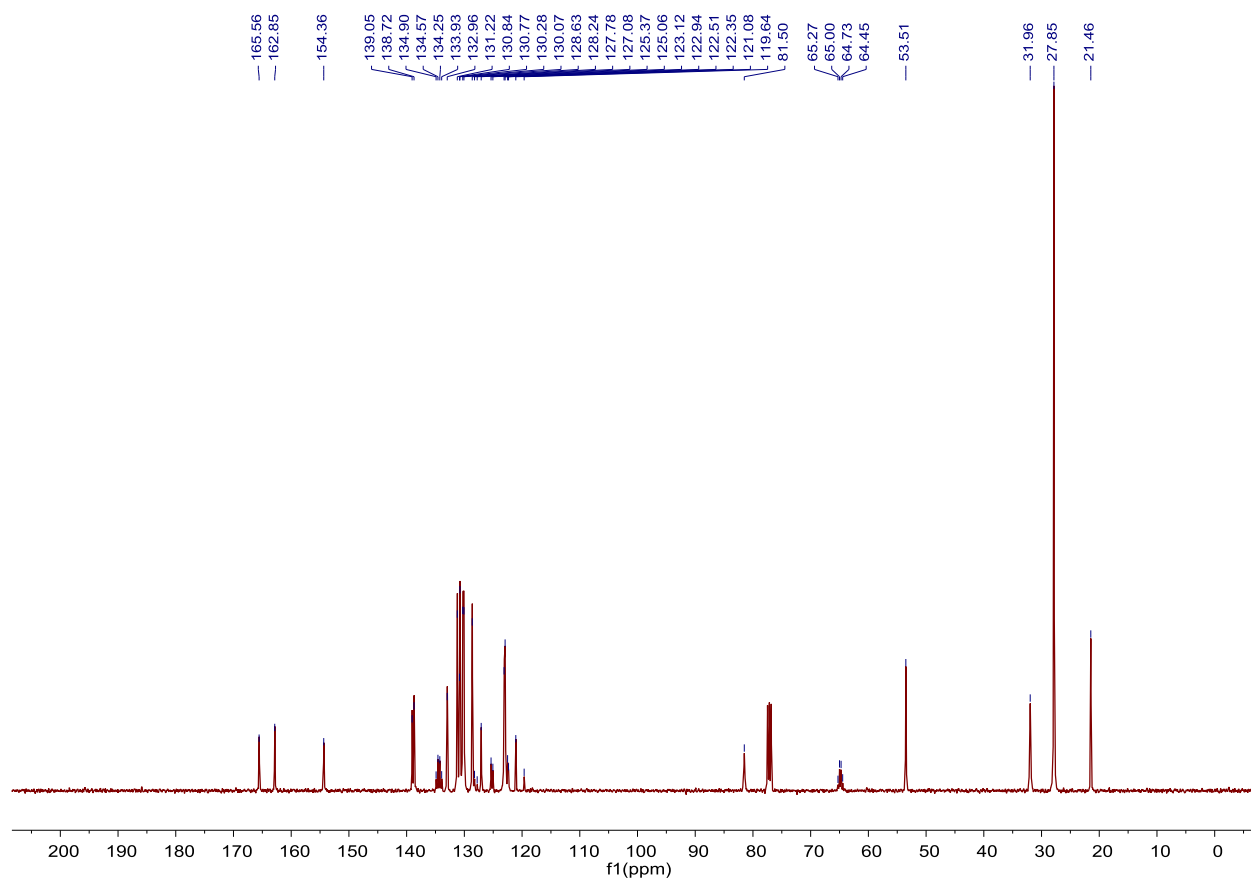
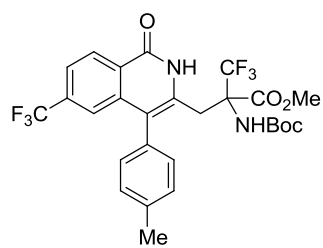


Figure S30. ^{13}C spectrum of **3o** in CDCl_3

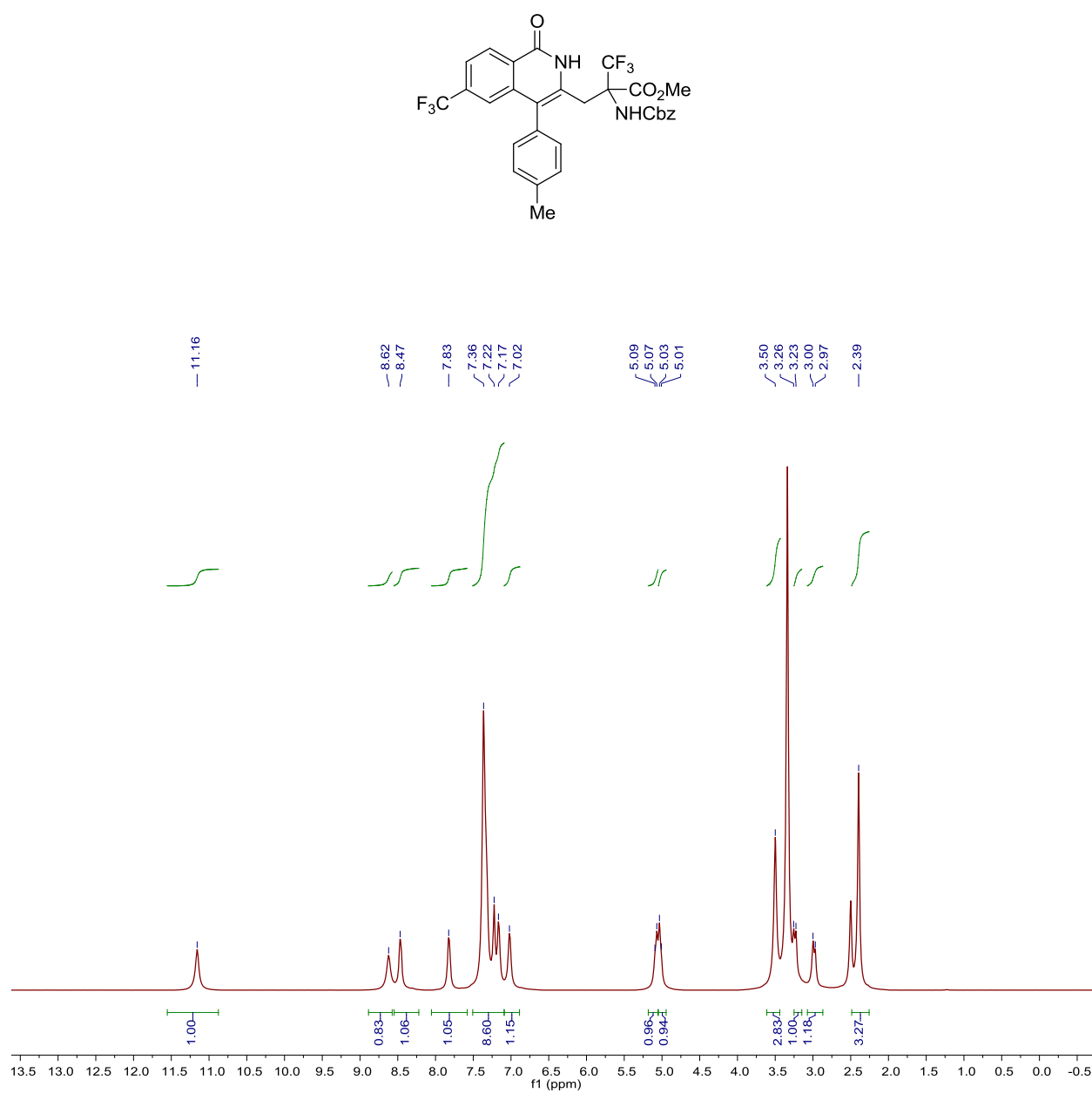


Figure S31. ¹H spectrum of **3p** in DMSO-*d*₆

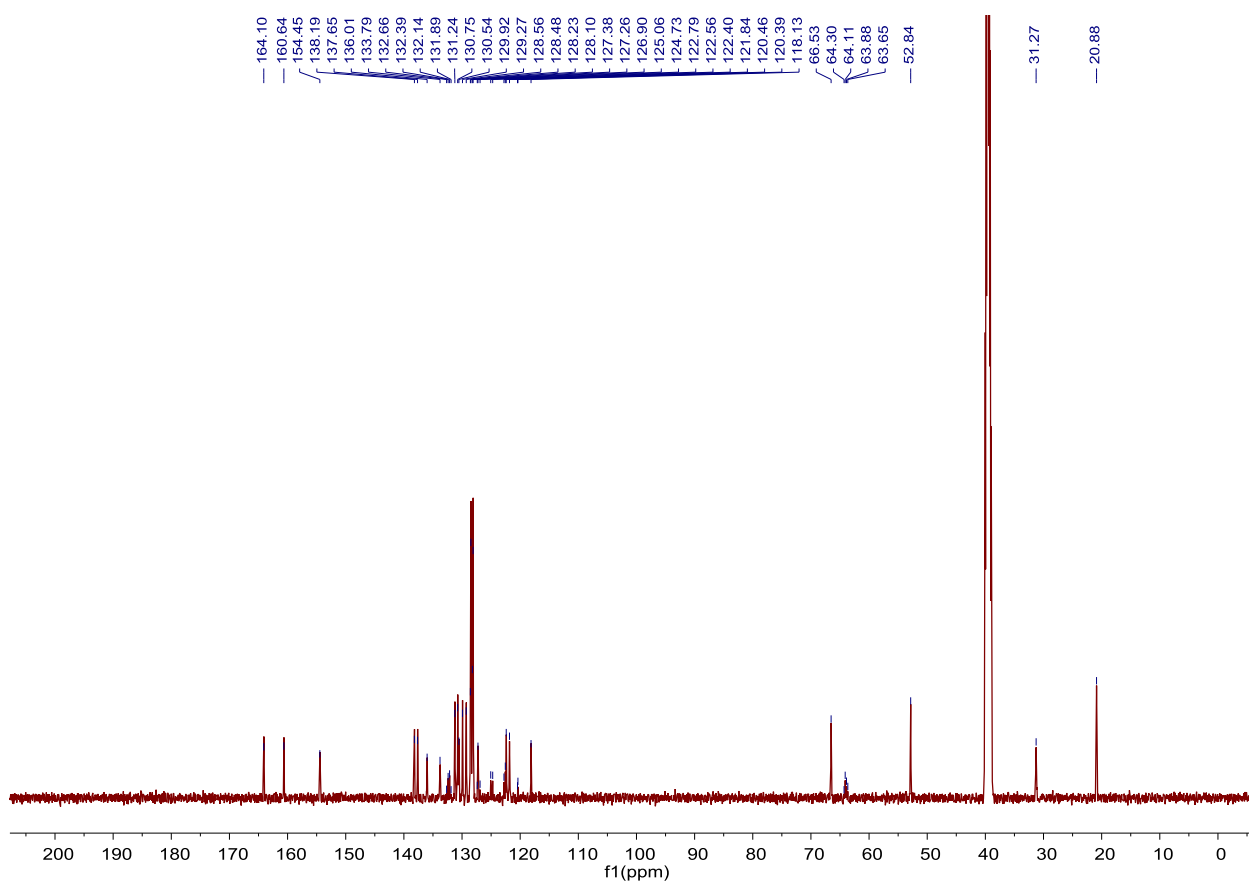
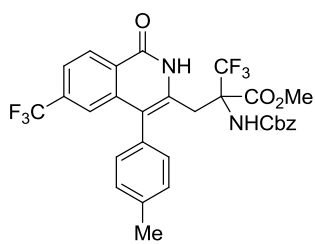


Figure S32. ^{13}C spectrum of **3p** in $\text{DMSO-}d_6$

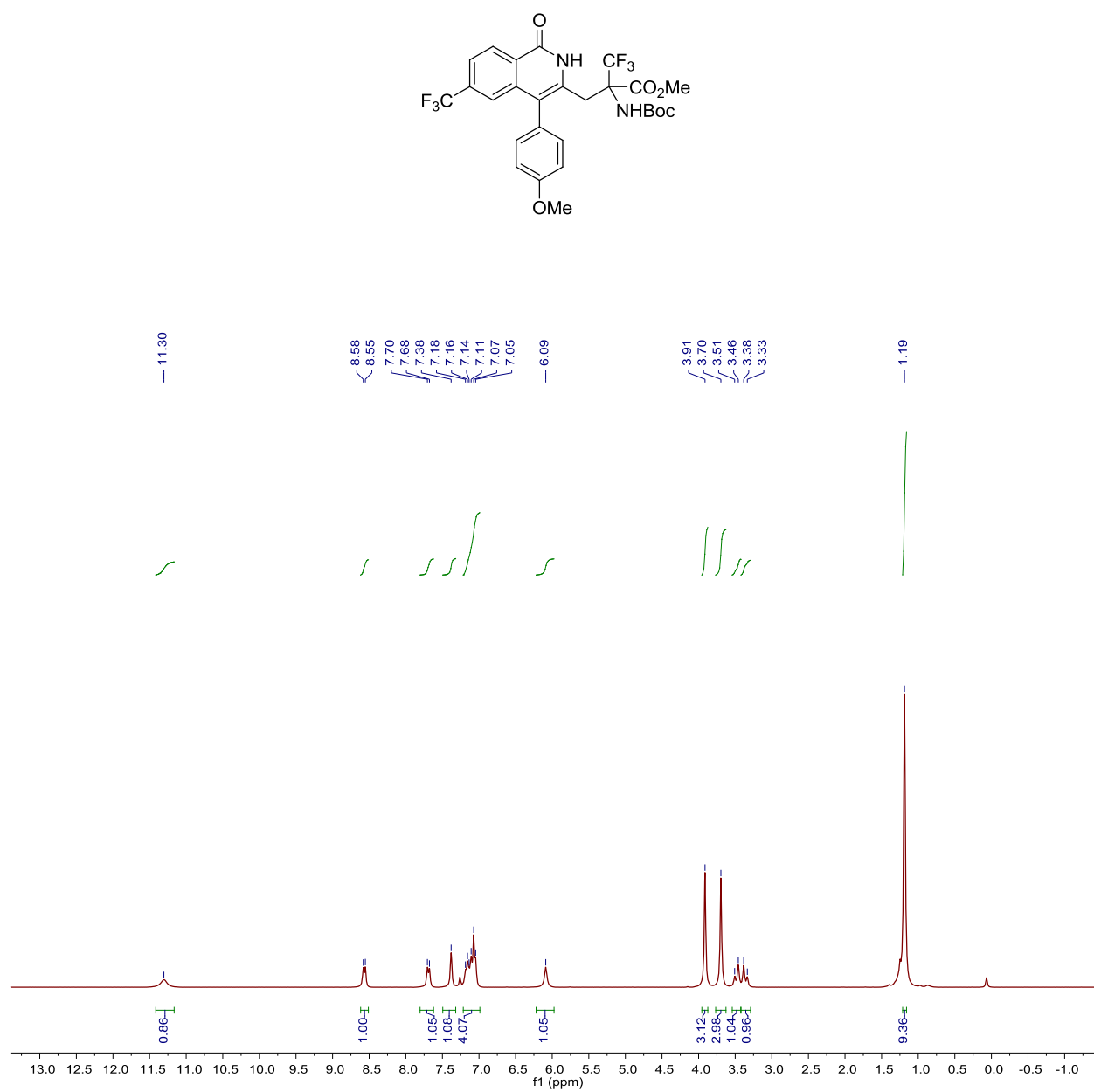


Figure S33. ^1H spectrum of **3q** in CDCl_3

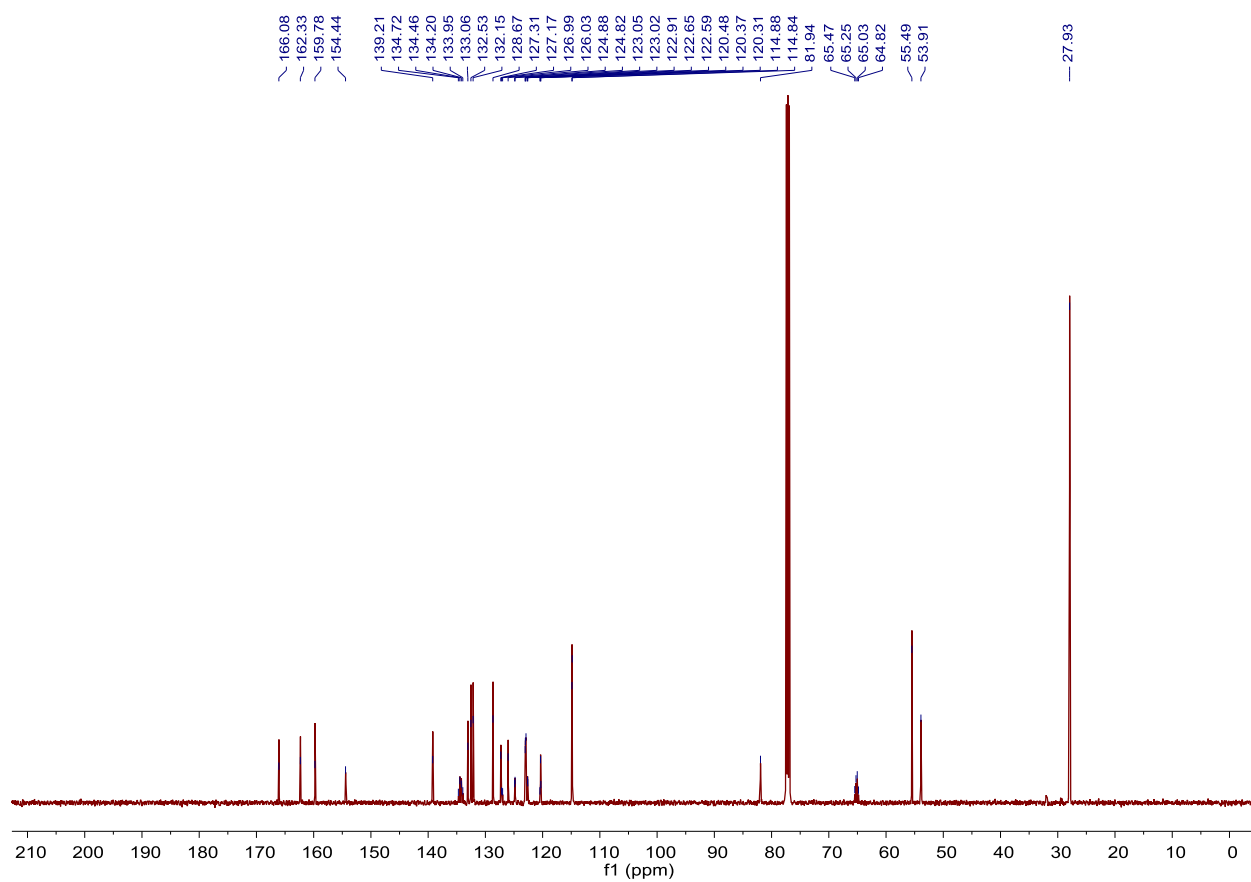
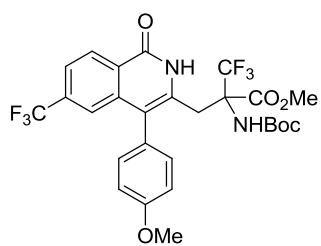


Figure S34. ^{13}C spectrum of **3q** in CDCl_3

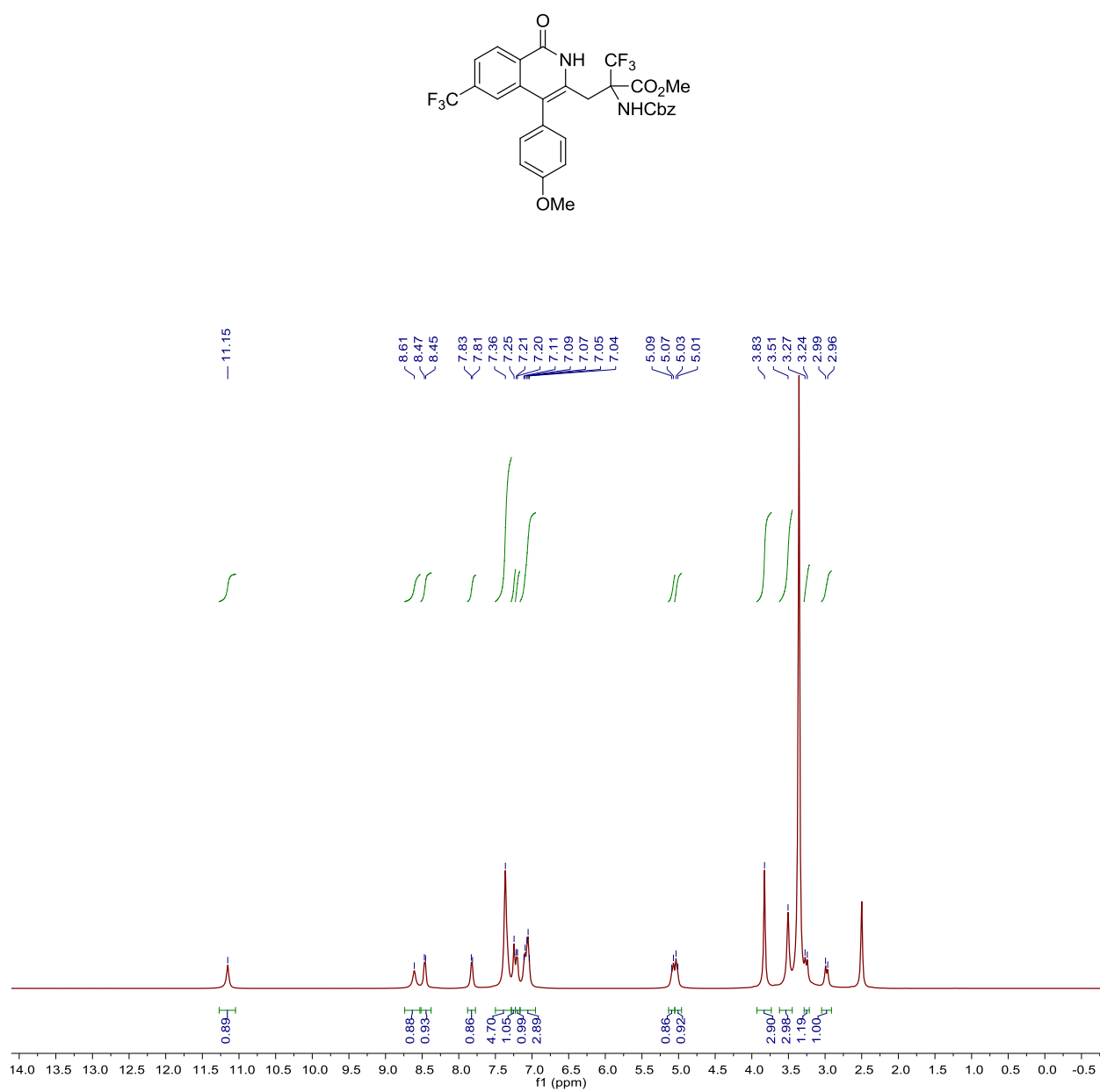


Figure S35. ¹H spectrum of **3r** in DMSO-*d*₆

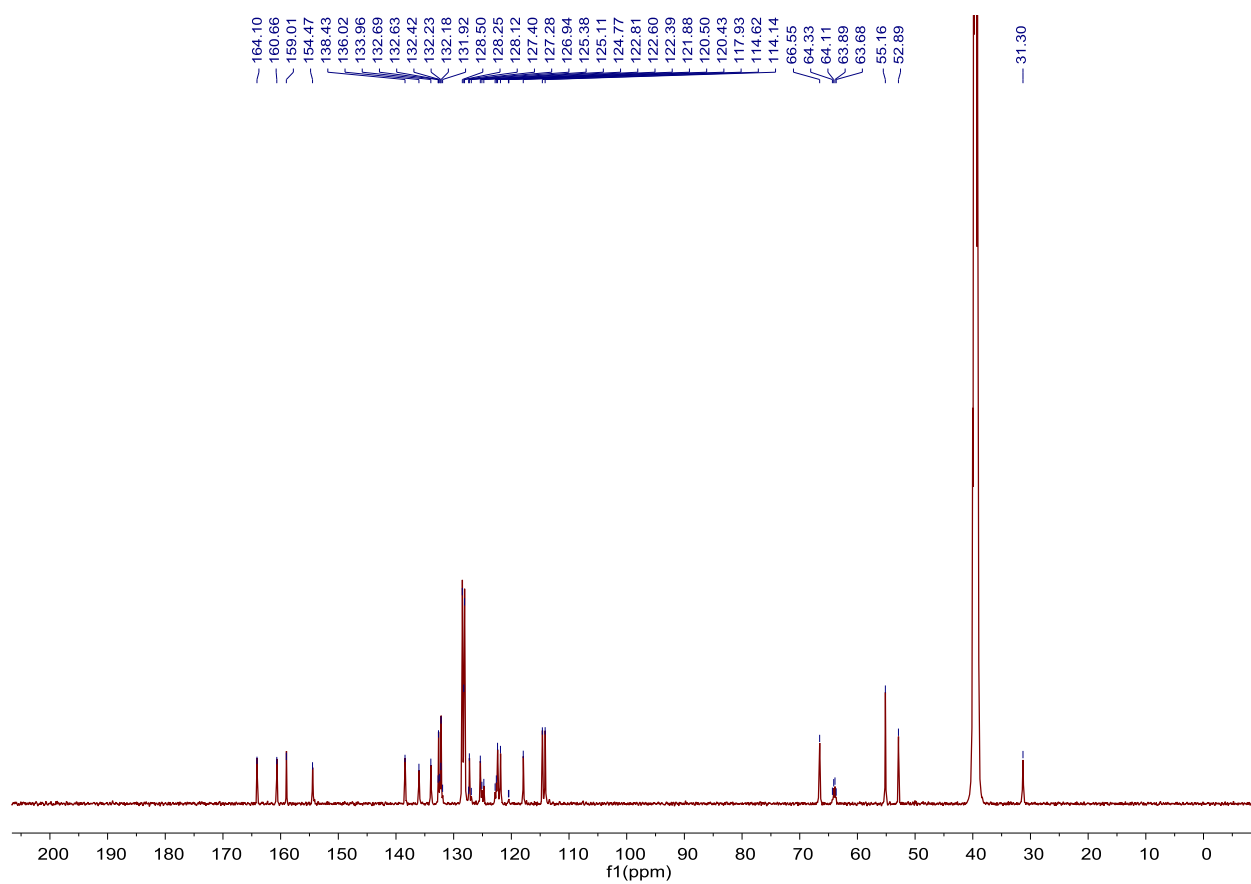
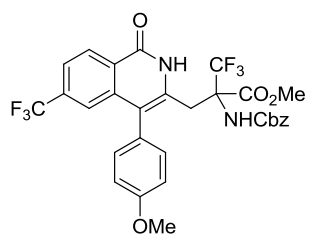


Figure S36. ^{13}C spectrum of **3r** in $\text{DMSO-}d_6$

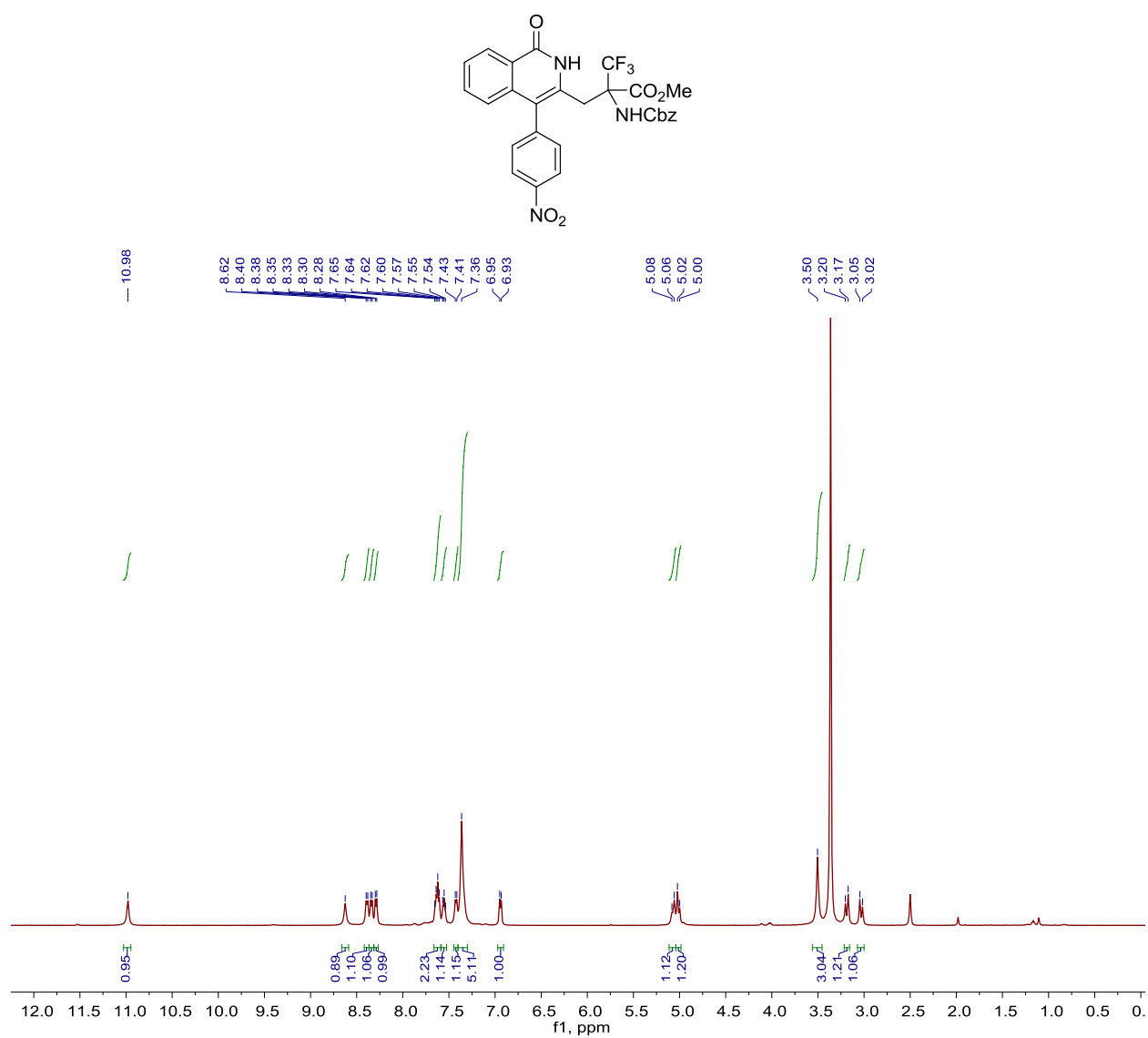


Figure S37. ¹H spectrum of **3s** in DMSO-*d*₆

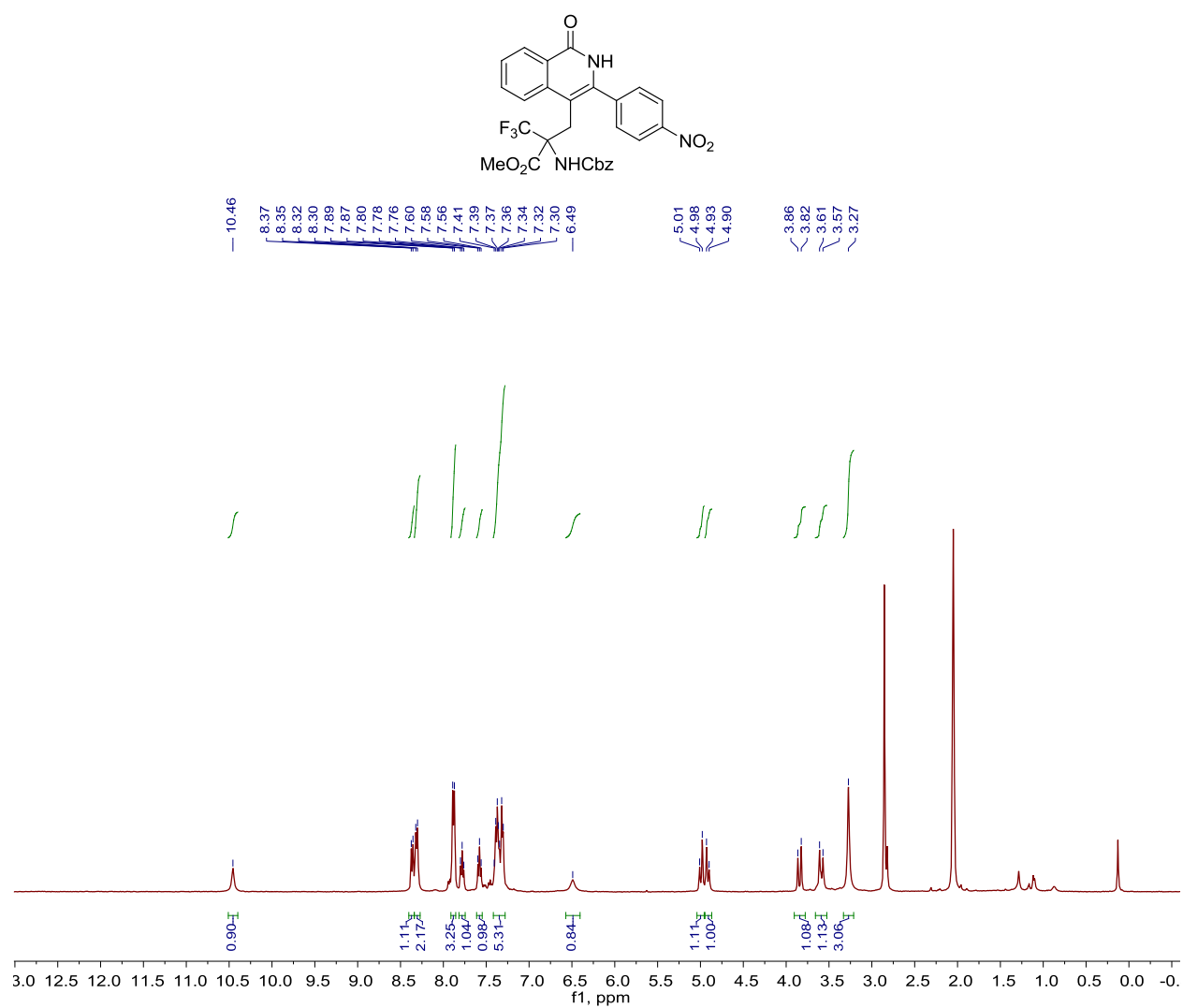


Figure S39. ^1H spectrum of **3t** in acetone- d_6

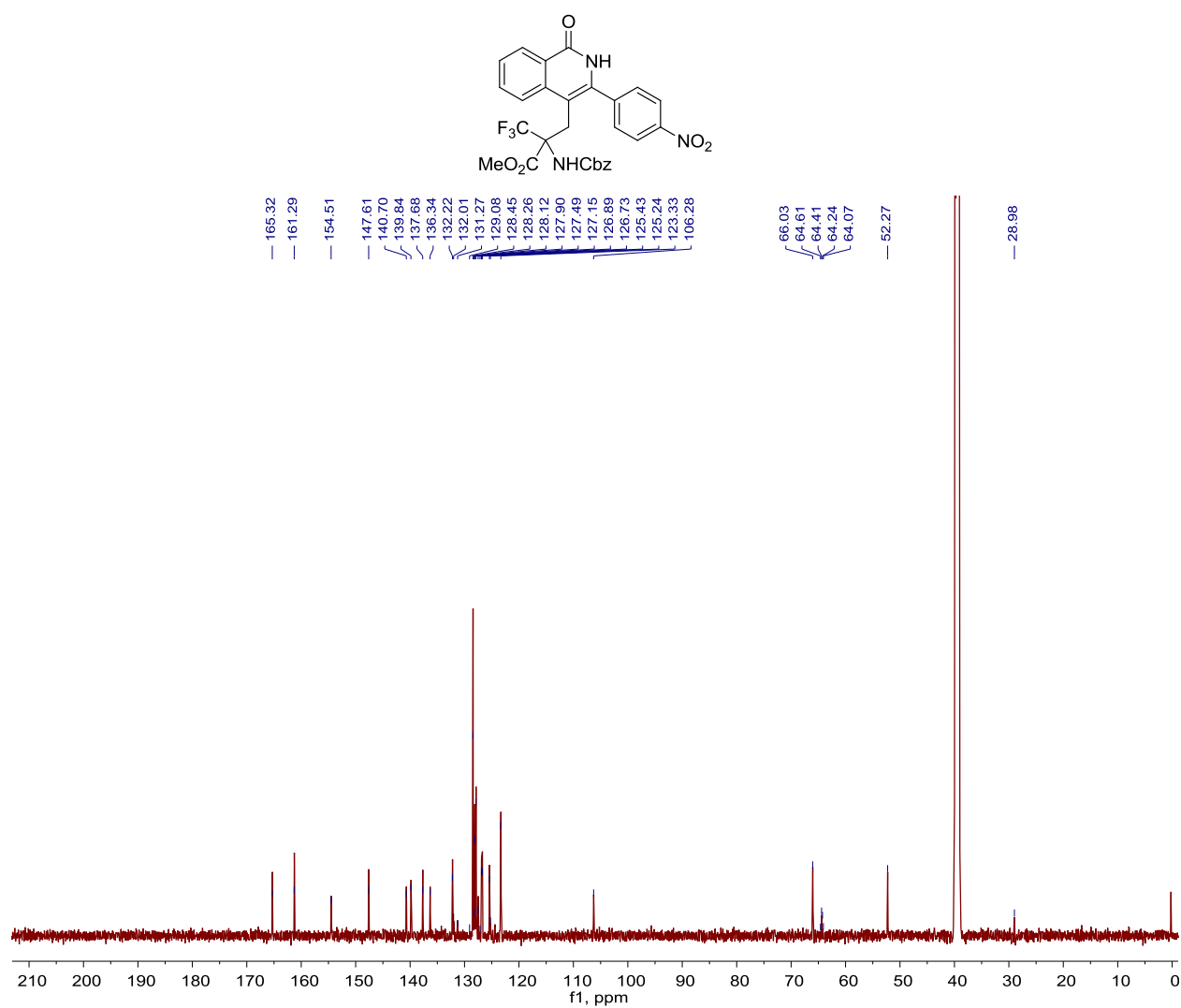


Figure S40. ^{13}C spectrum of **3t** in $\text{DMSO-}d_6$

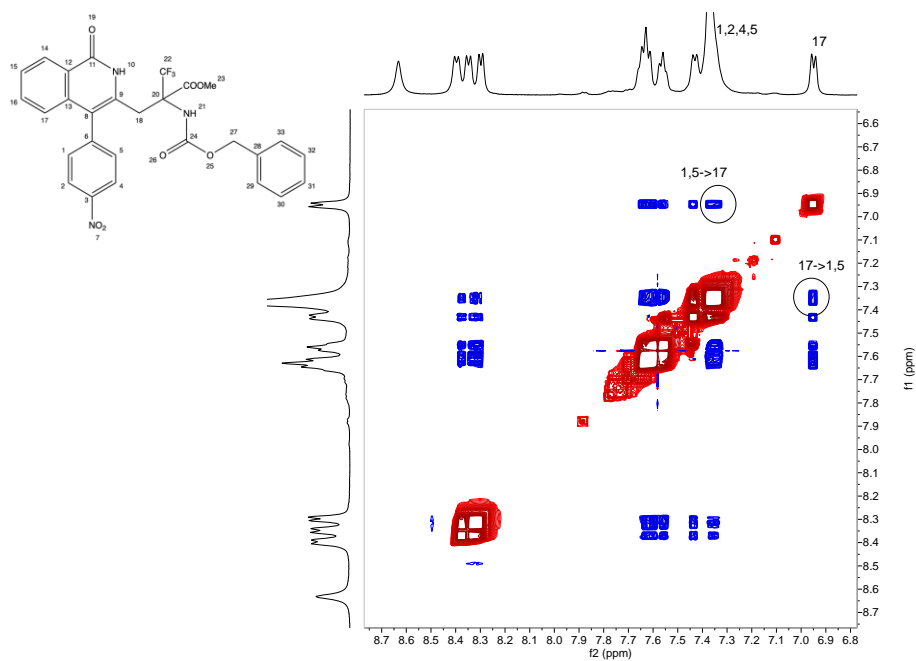


Figure S41. ROESY NMR of **3s** in DMSO-*d*₆

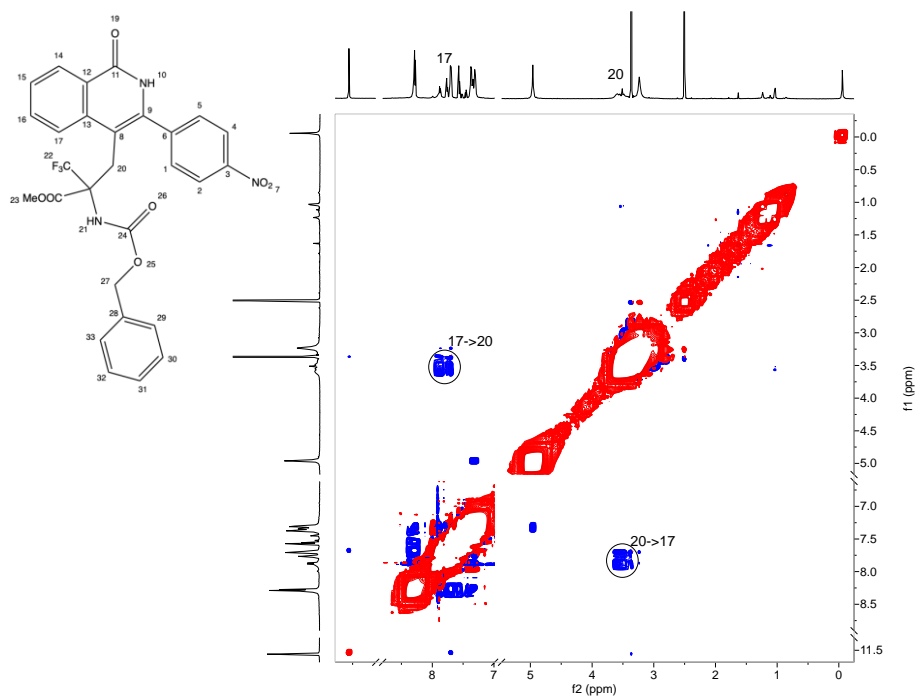


Figure S42. ROESY NMR of **3t** in DMSO-*d*₆

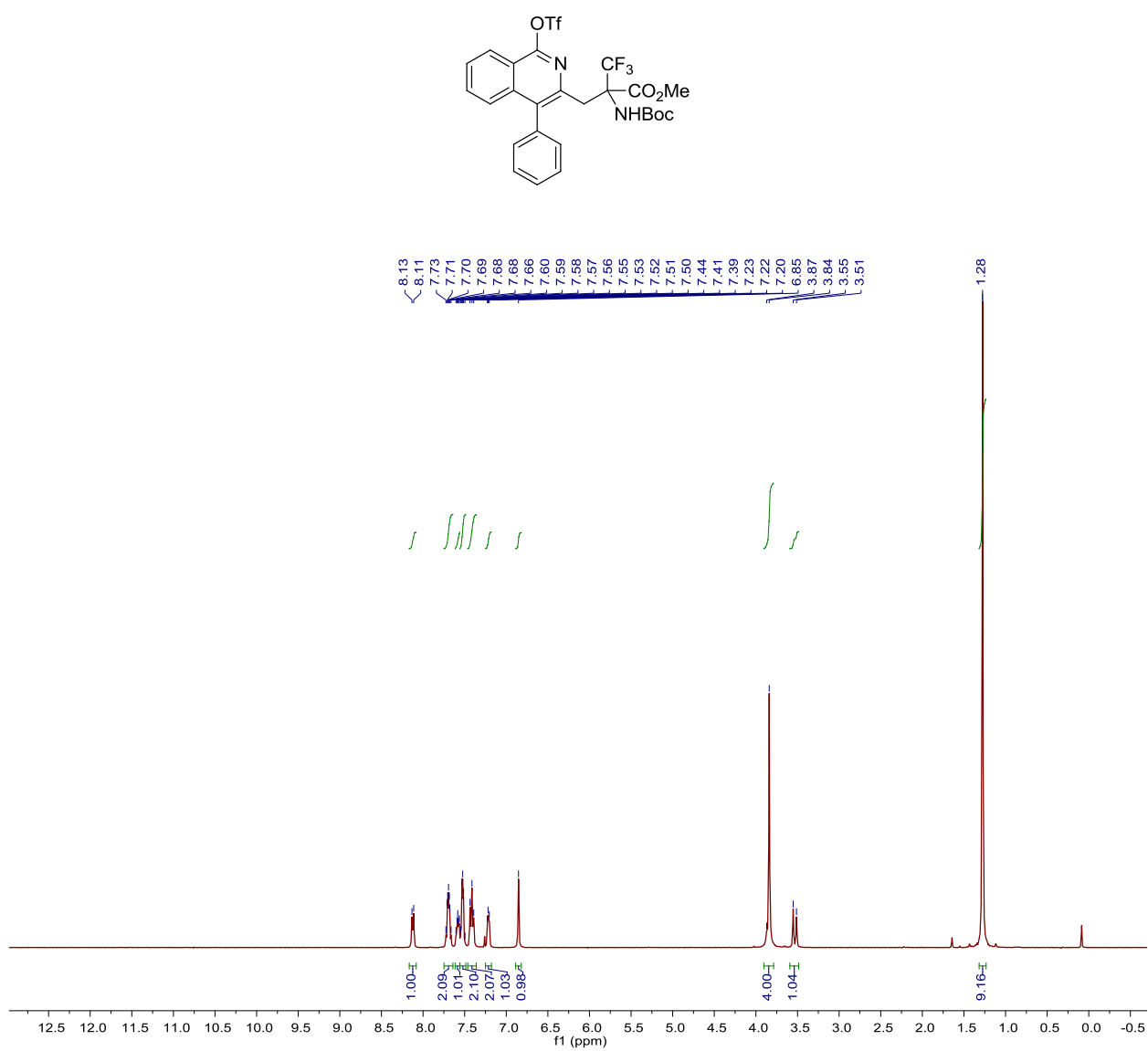


Figure S43. ^1H spectrum of **4a** in CDCl_3

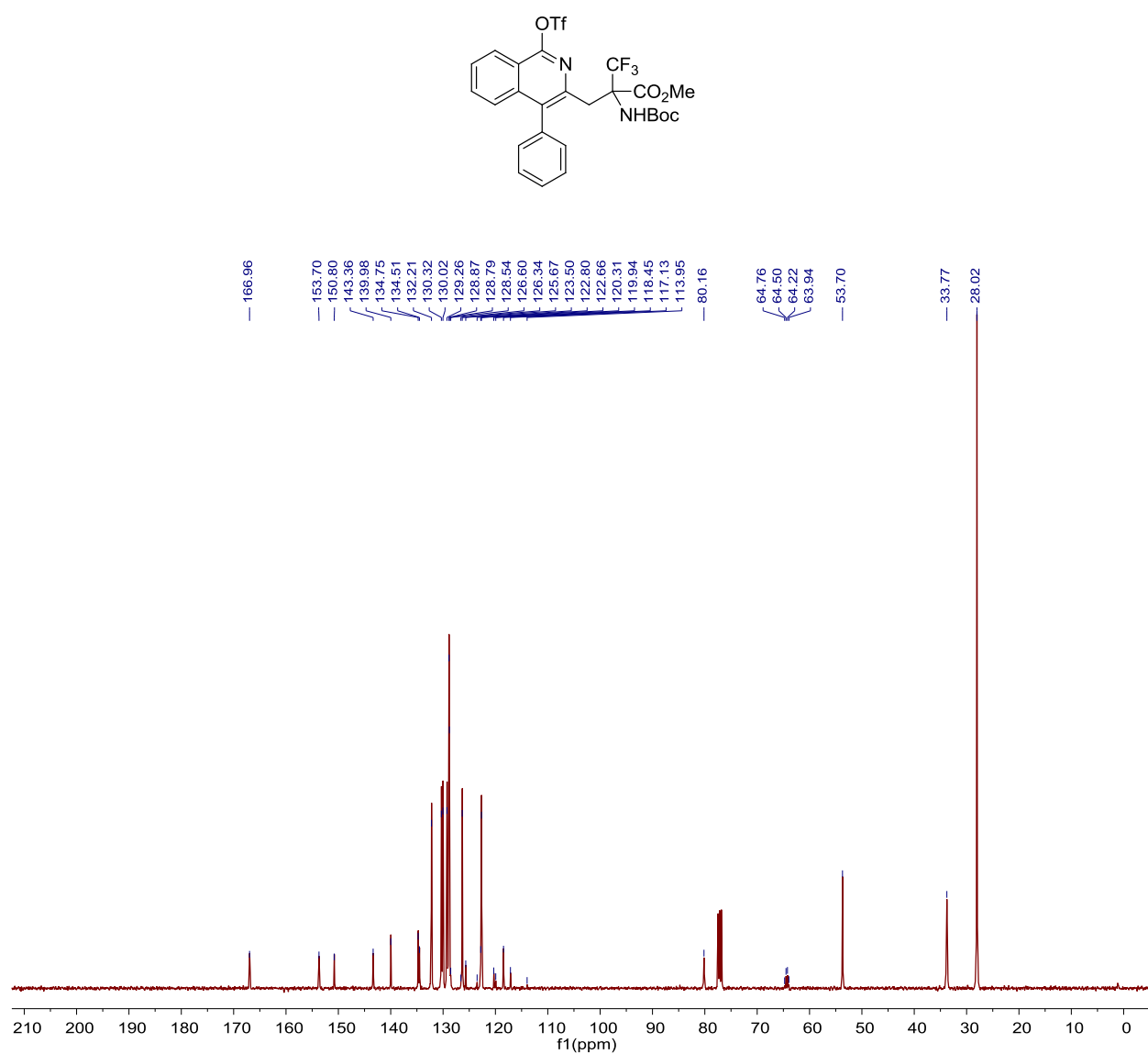


Figure S44. ^{13}C spectrum of **4a** in CDCl₃

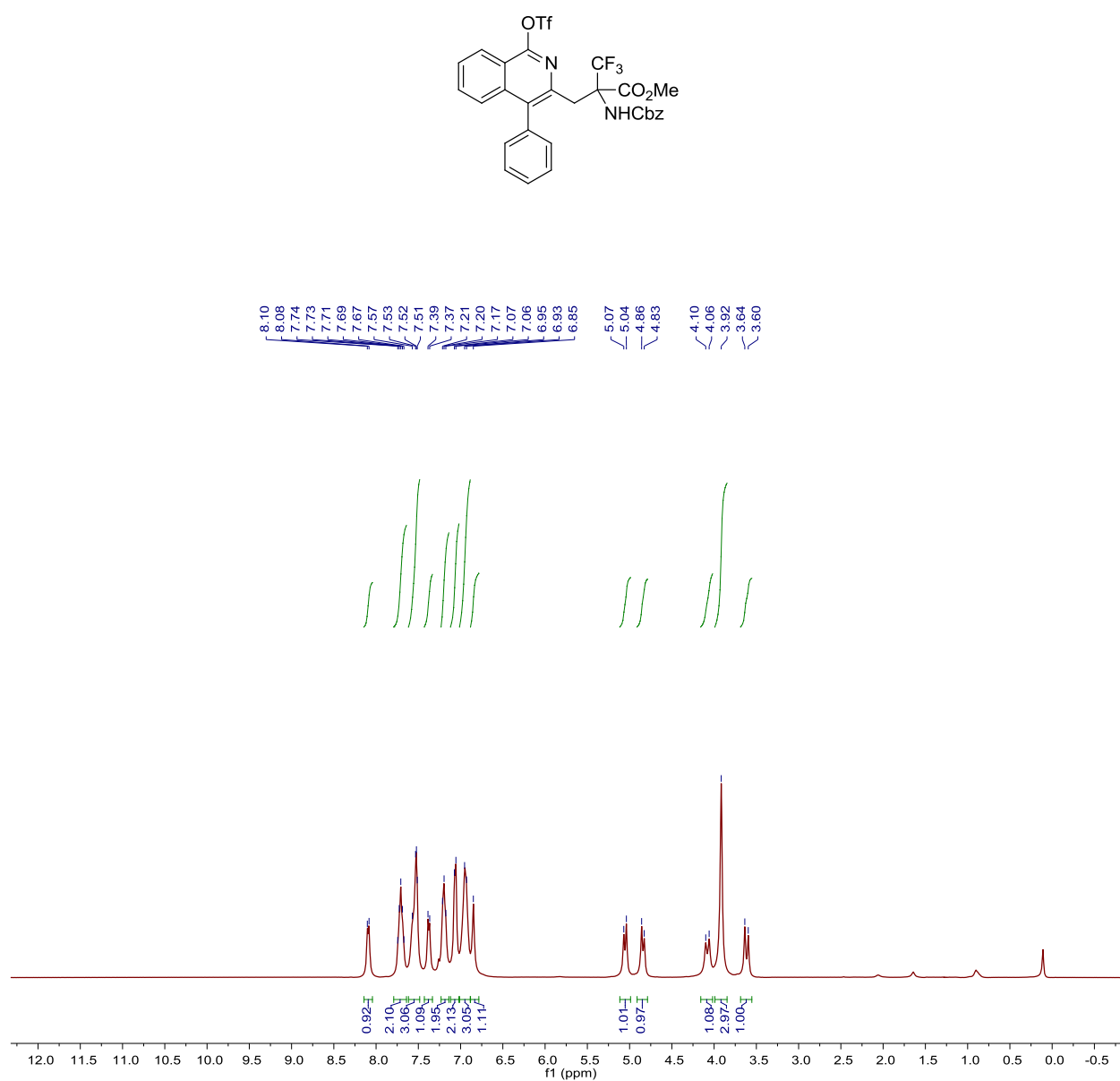


Figure S45. ^1H spectrum of **4b** in CDCl₃

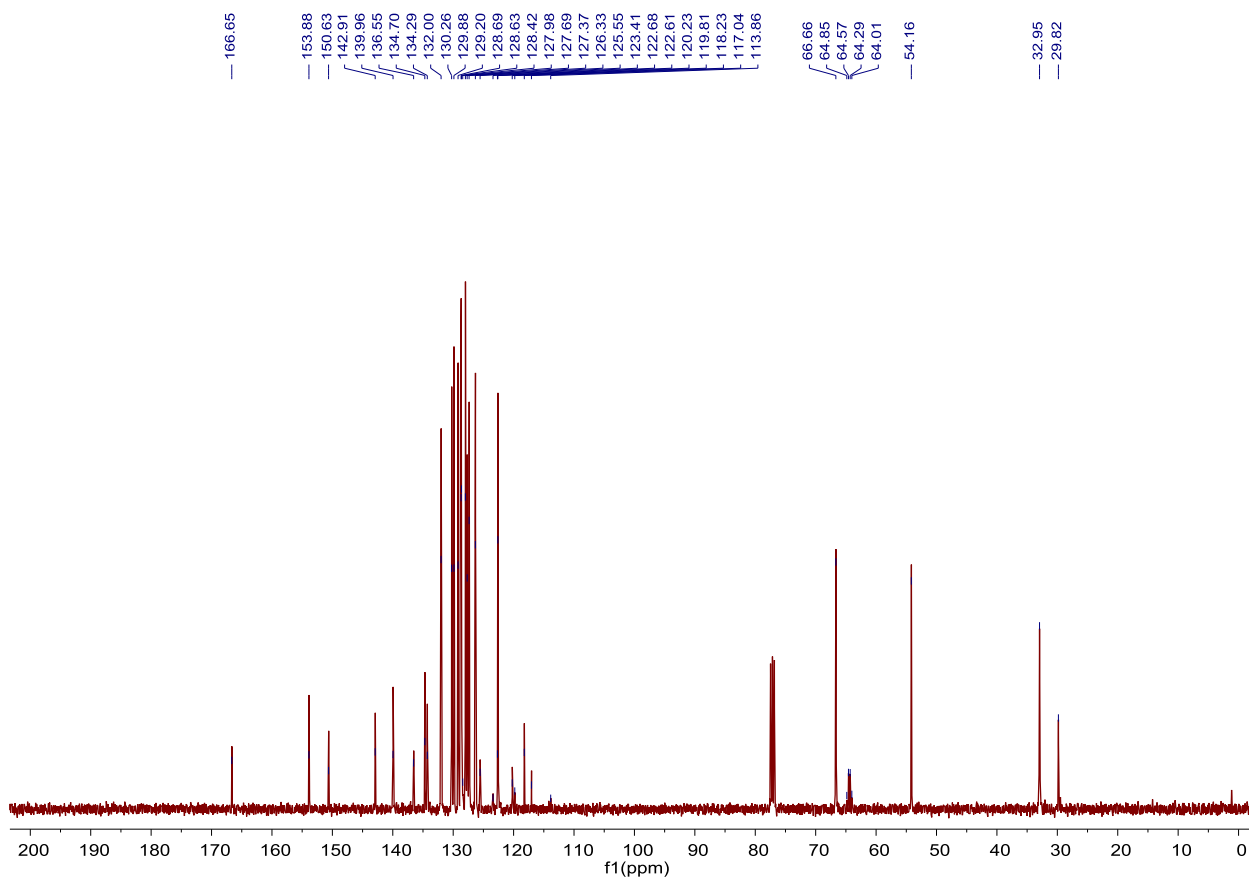
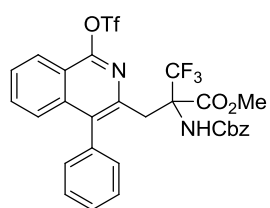


Figure S46. ^{13}C spectrum of **4b** in CDCl_3

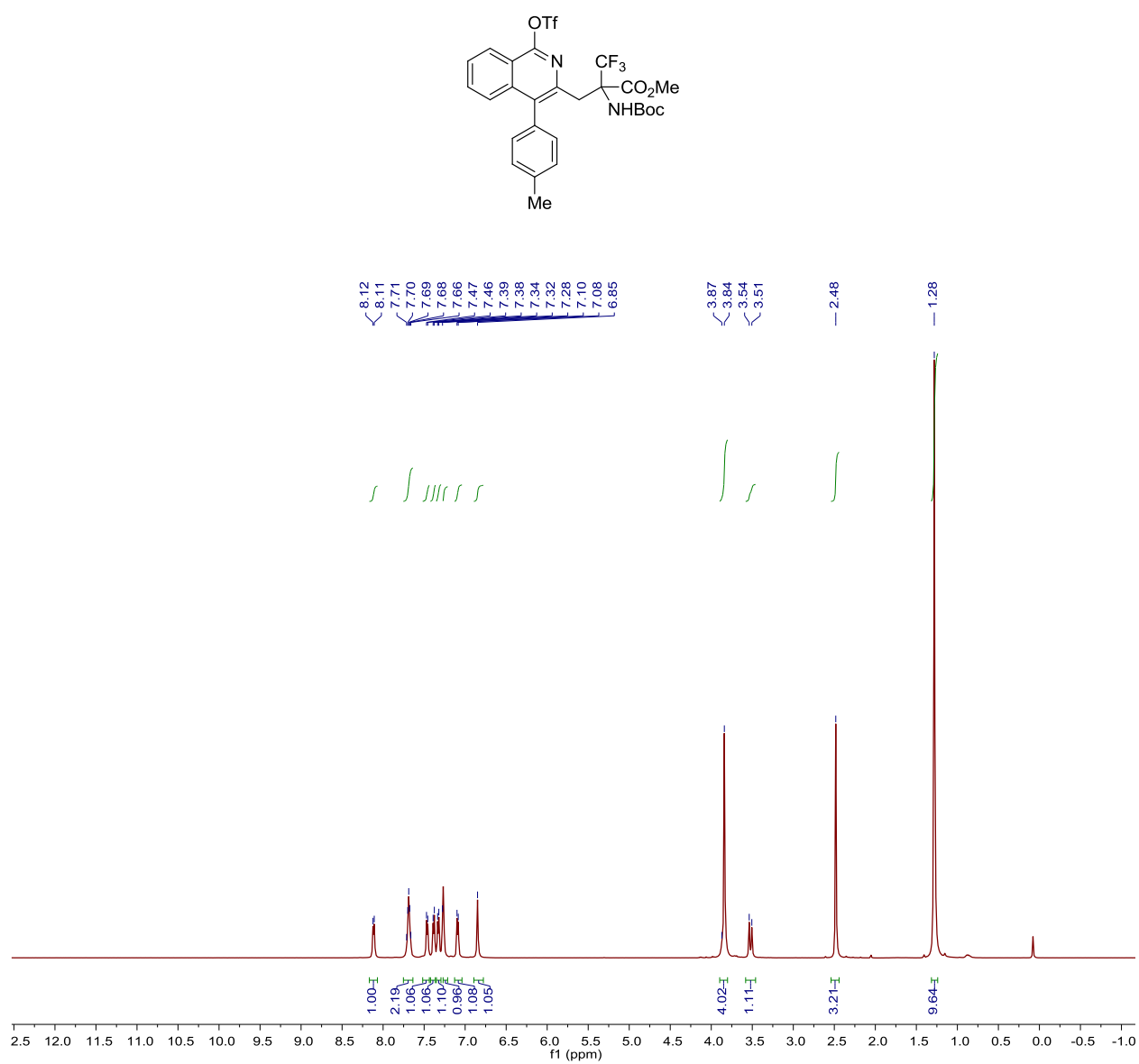


Figure S47. ^1H spectrum of **4c** in CDCl₃

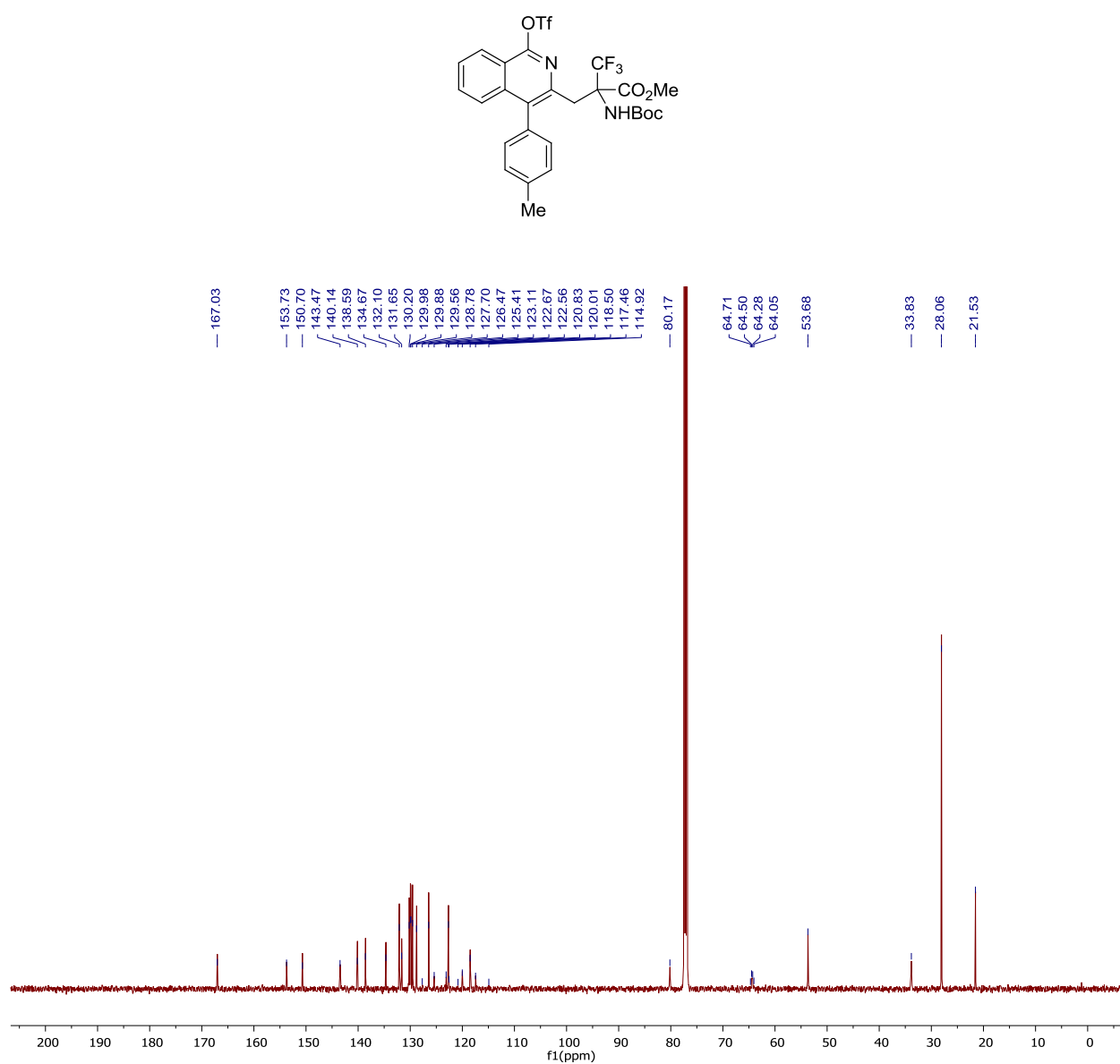


Figure S48. ^{13}C spectrum of **4c** in CDCl_3

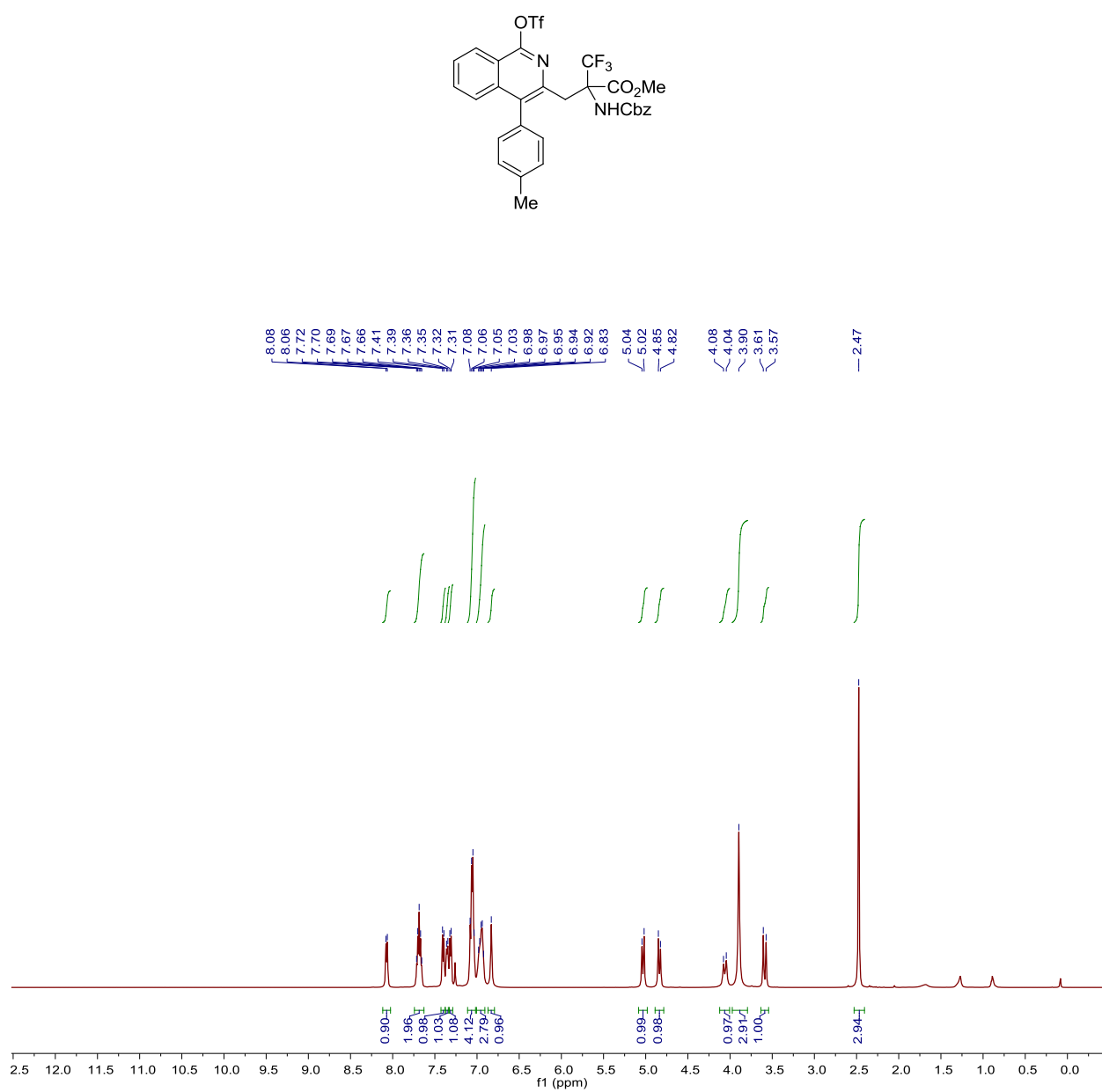


Figure S49. ^1H spectrum of **4d** in CDCl₃

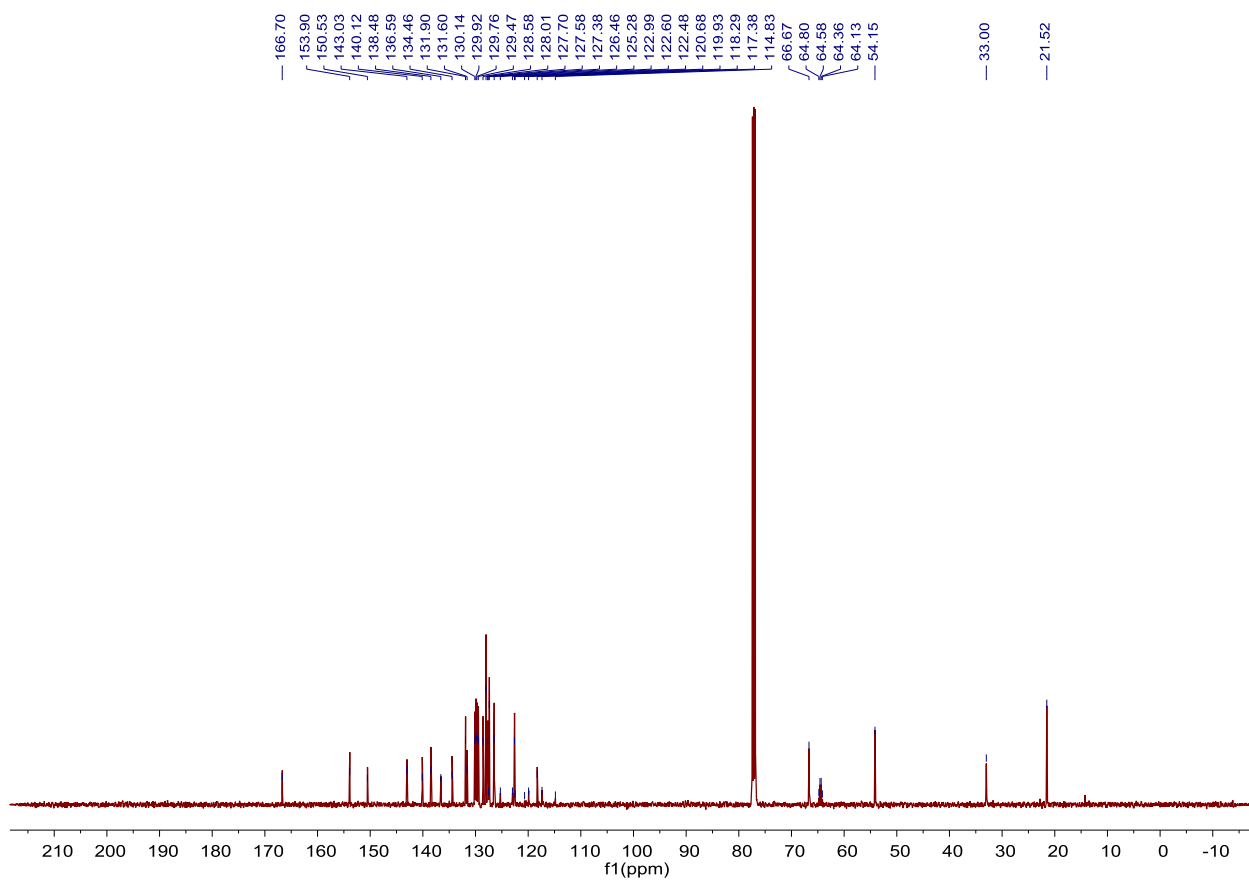
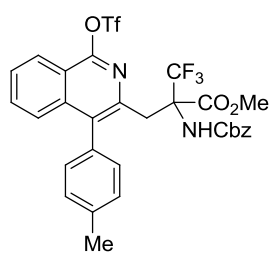


Figure S50. ^{13}C spectrum of **4d** in CDCl_3

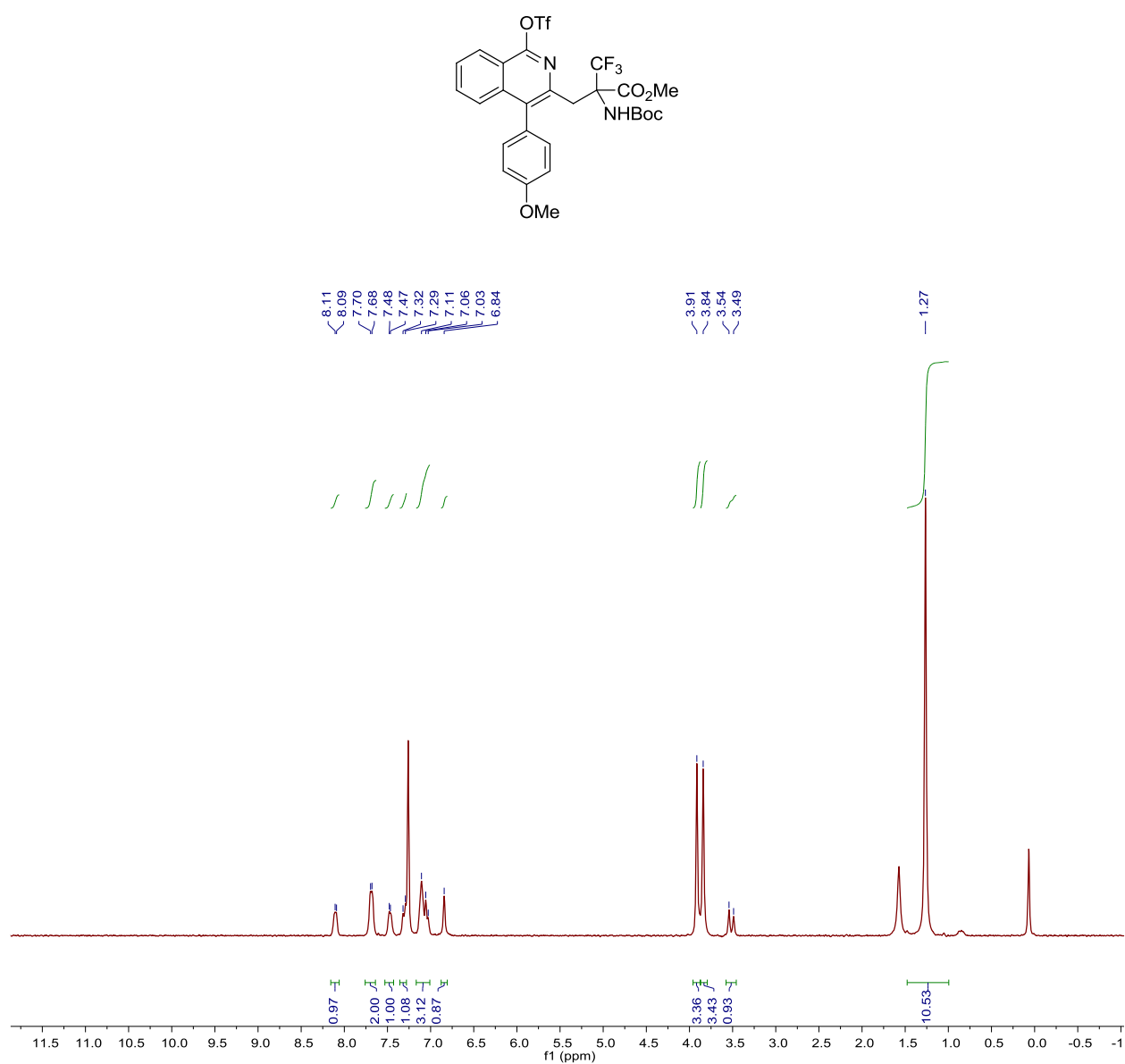


Figure S51. ^1H spectrum of **4e** in CDCl₃

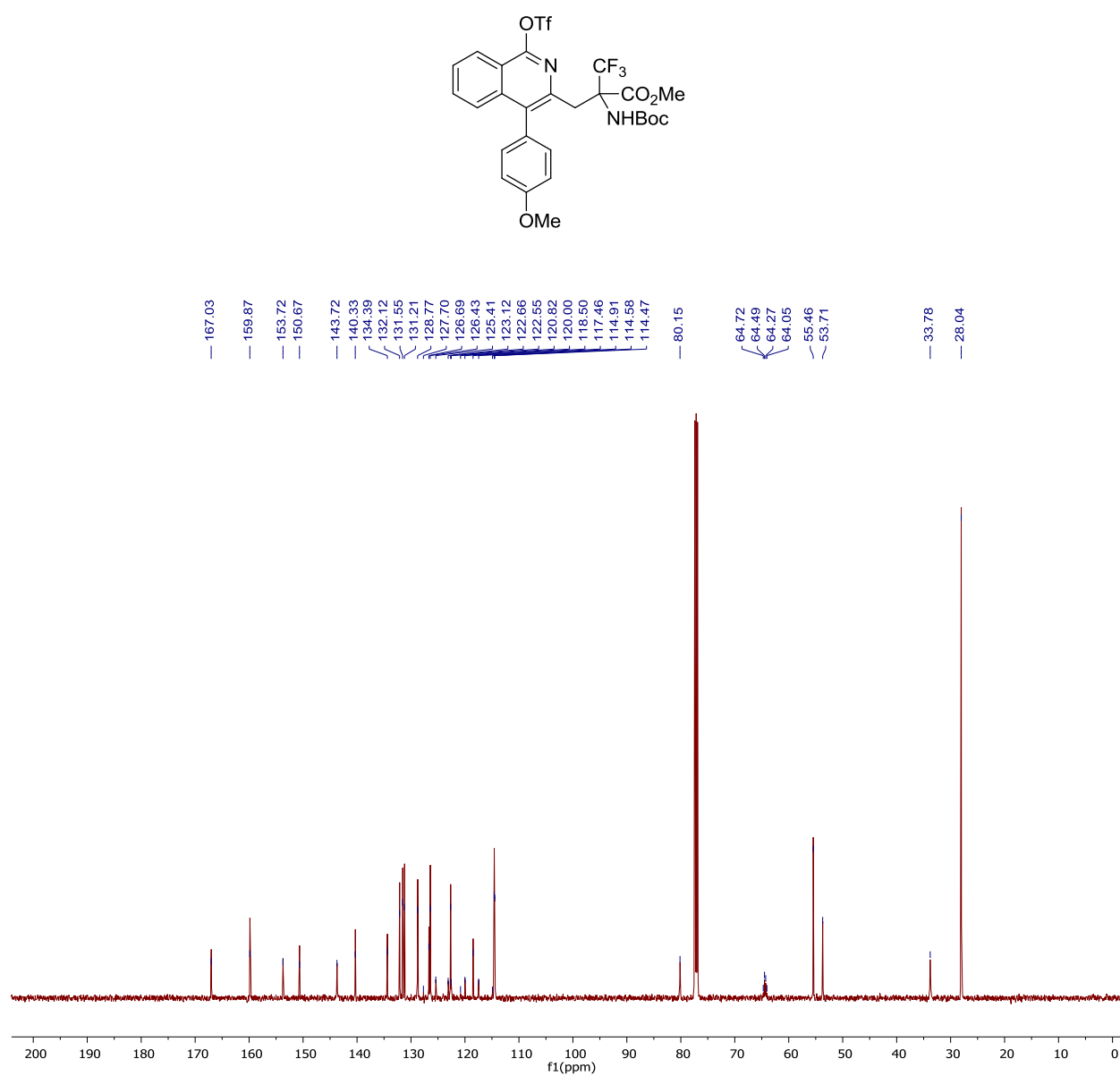


Figure S52. ^{13}C spectrum of **4e** in CDCl₃

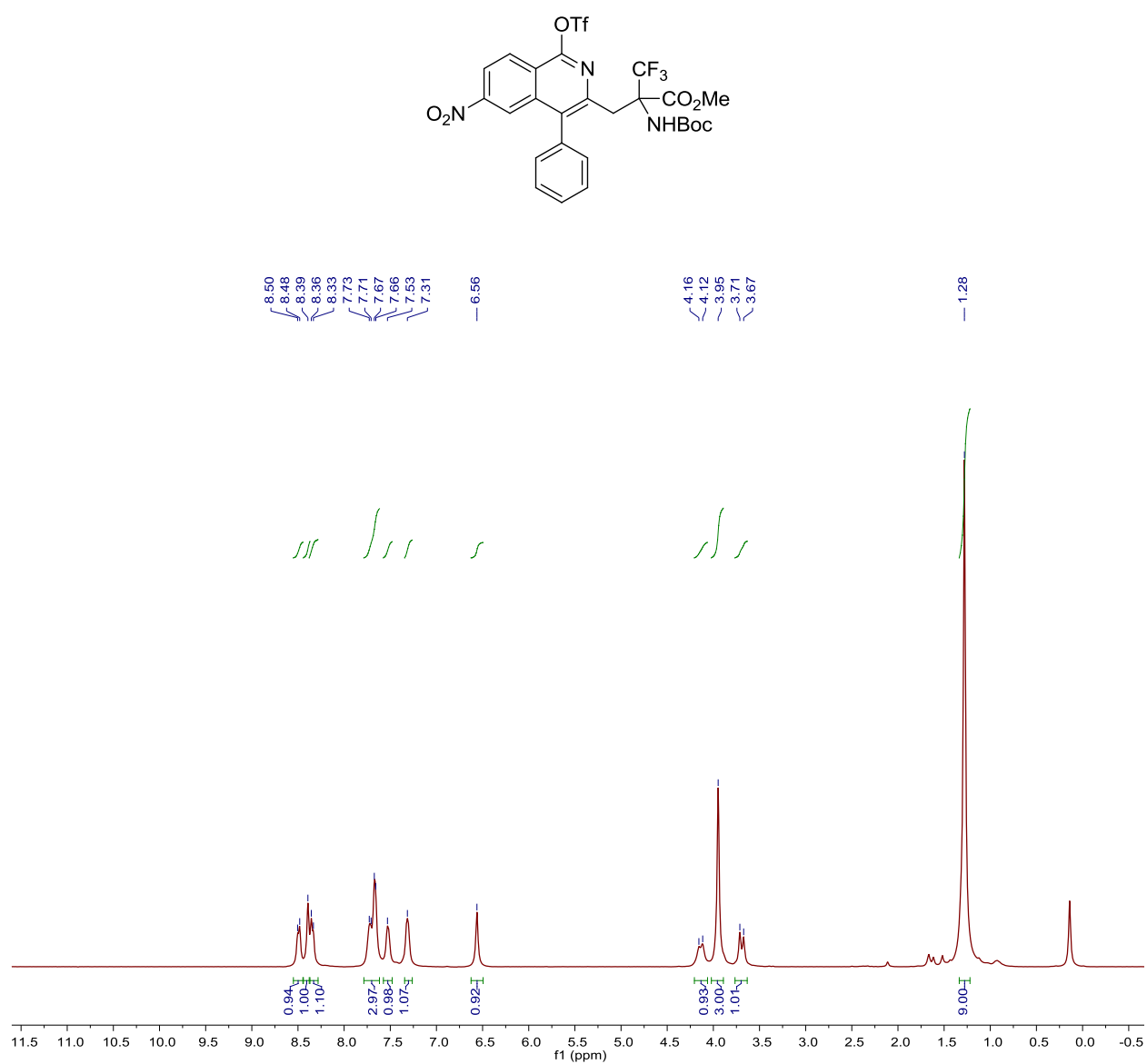


Figure S53. ^1H spectrum of **4f** in CDCl_3

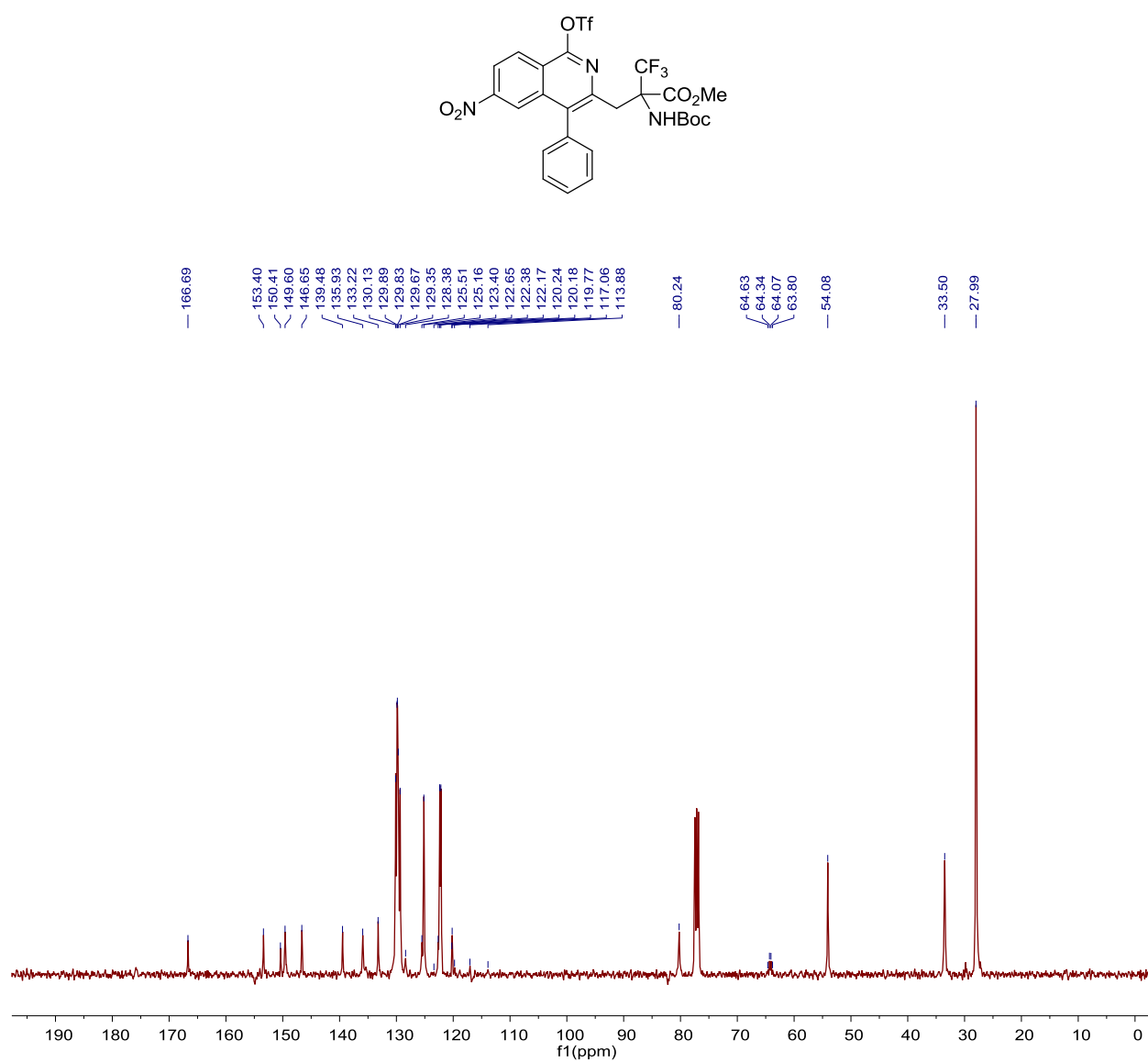


Figure S54. ^{13}C spectrum of **4f** in CDCl₃

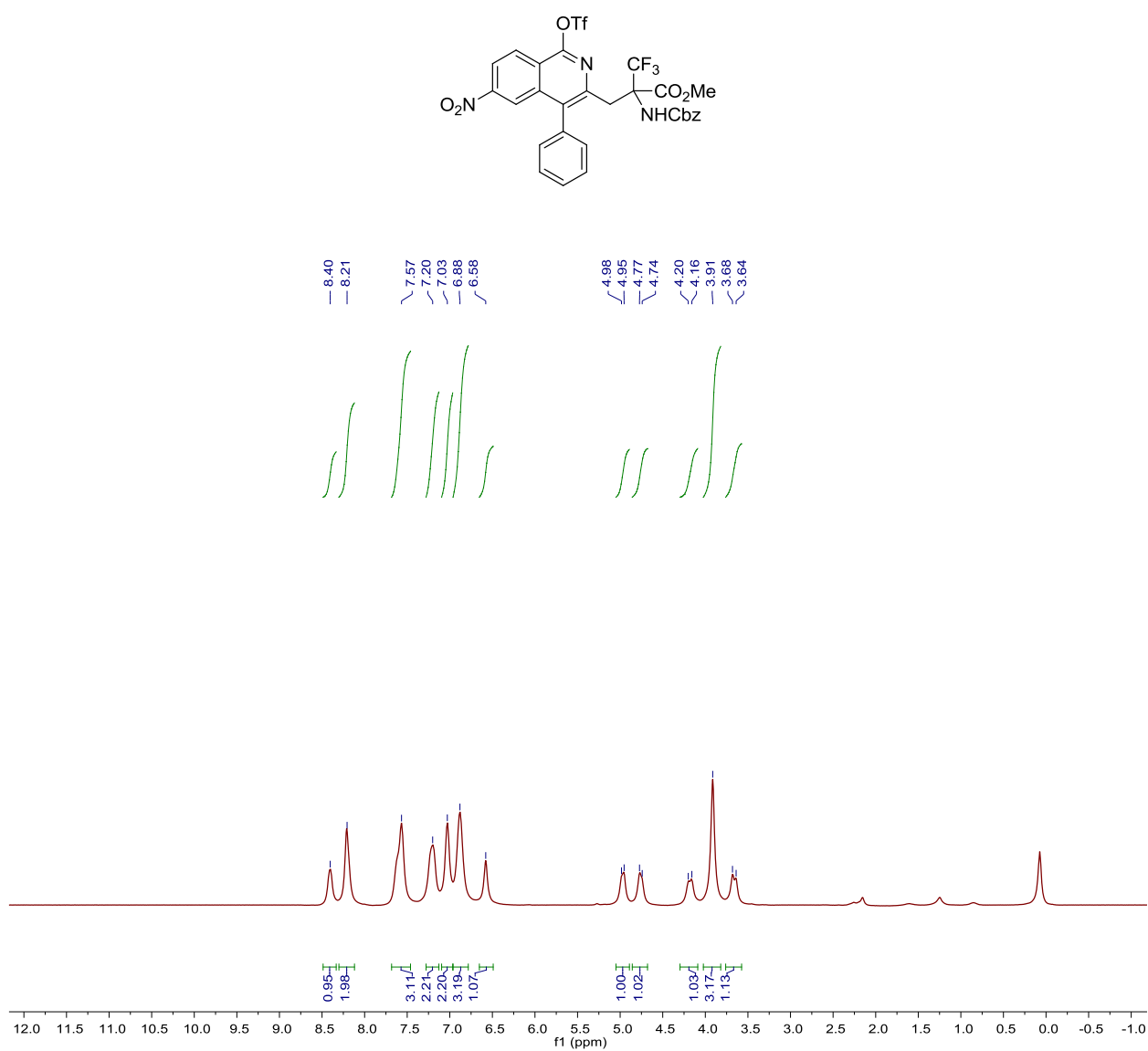


Figure S55. ^1H spectrum of **4g** in CDCl₃

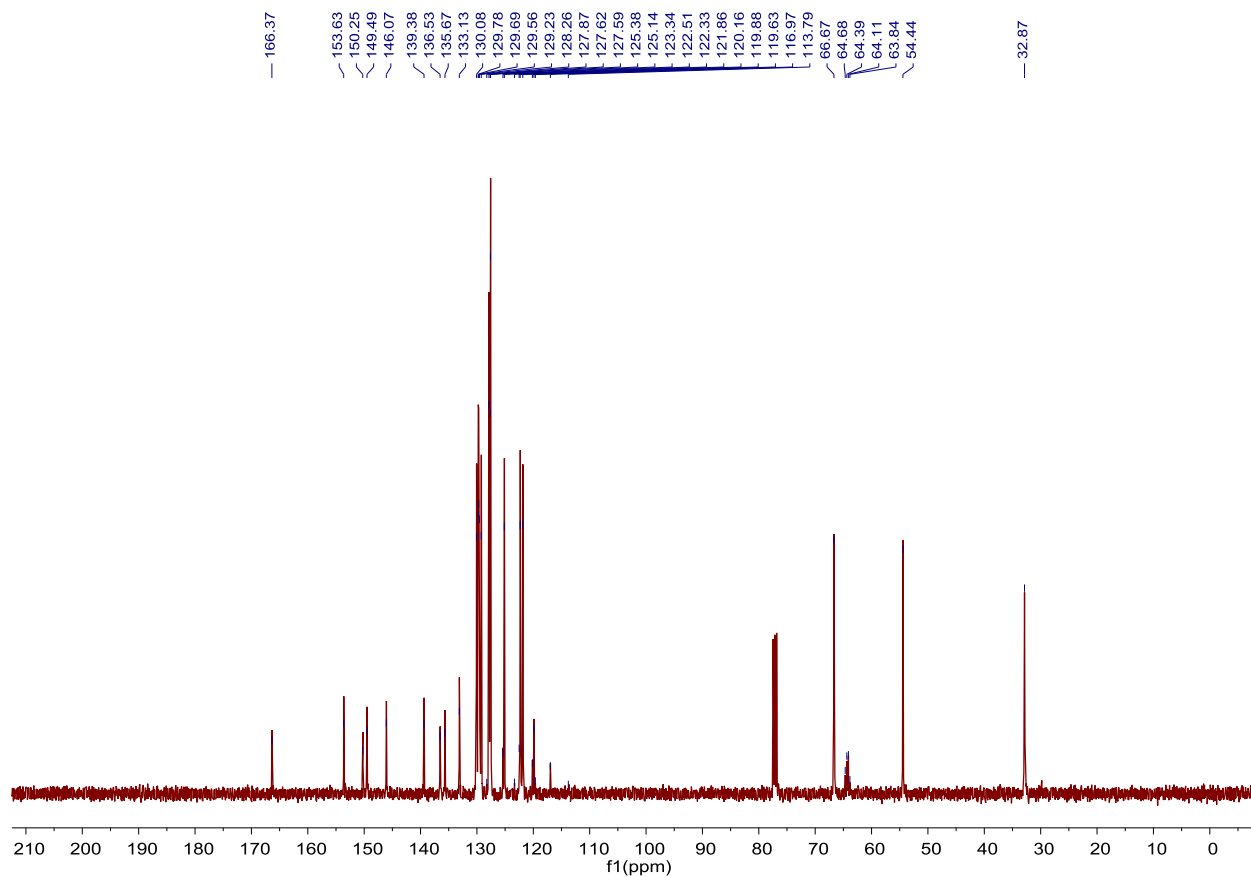
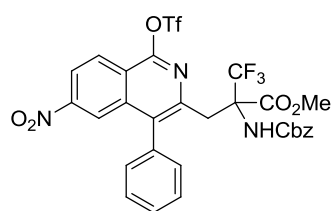


Figure S56. ^{13}C spectrum of **4g** in CDCl_3

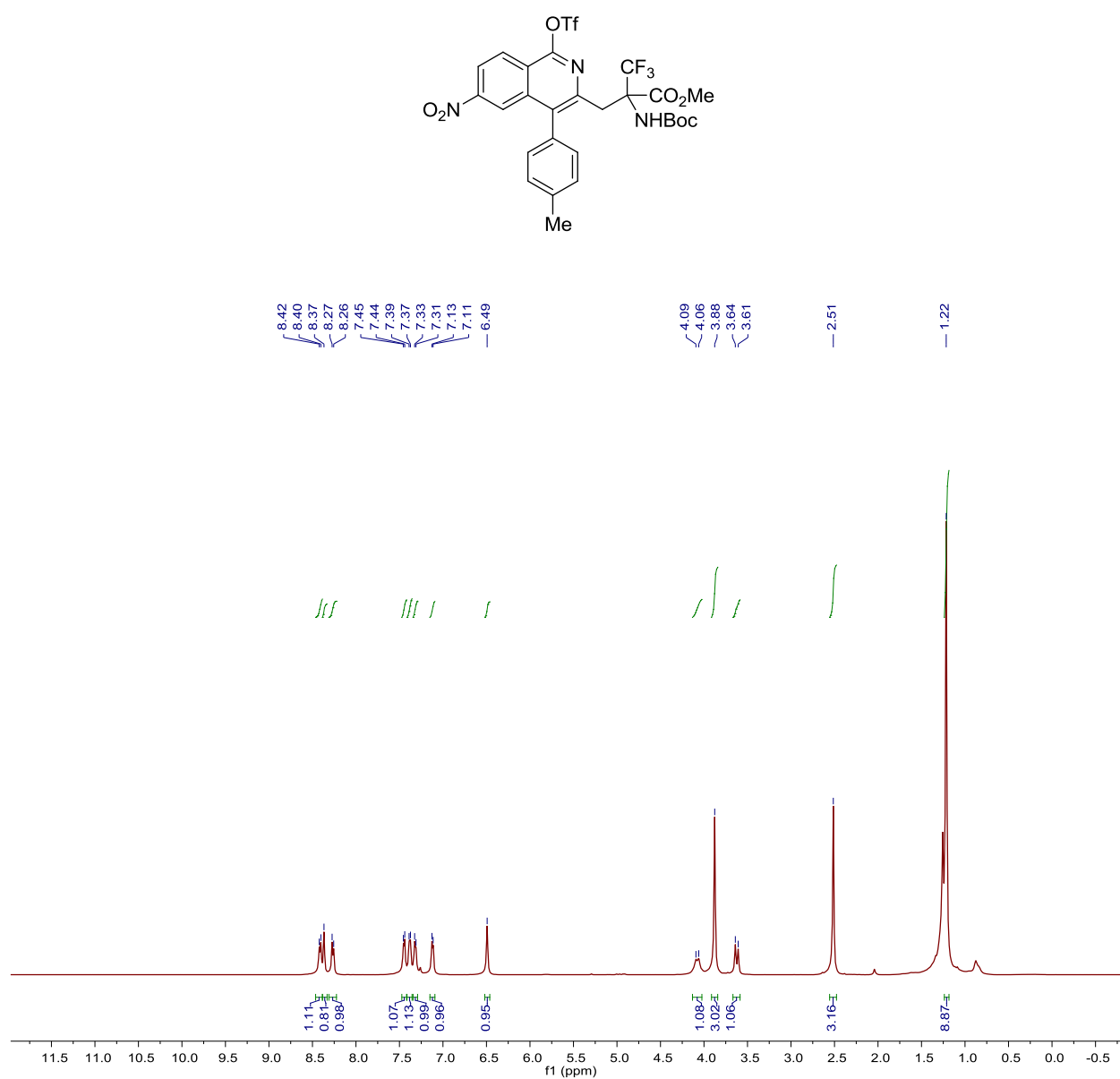


Figure S57. ^1H spectrum of **4h** in CDCl₃

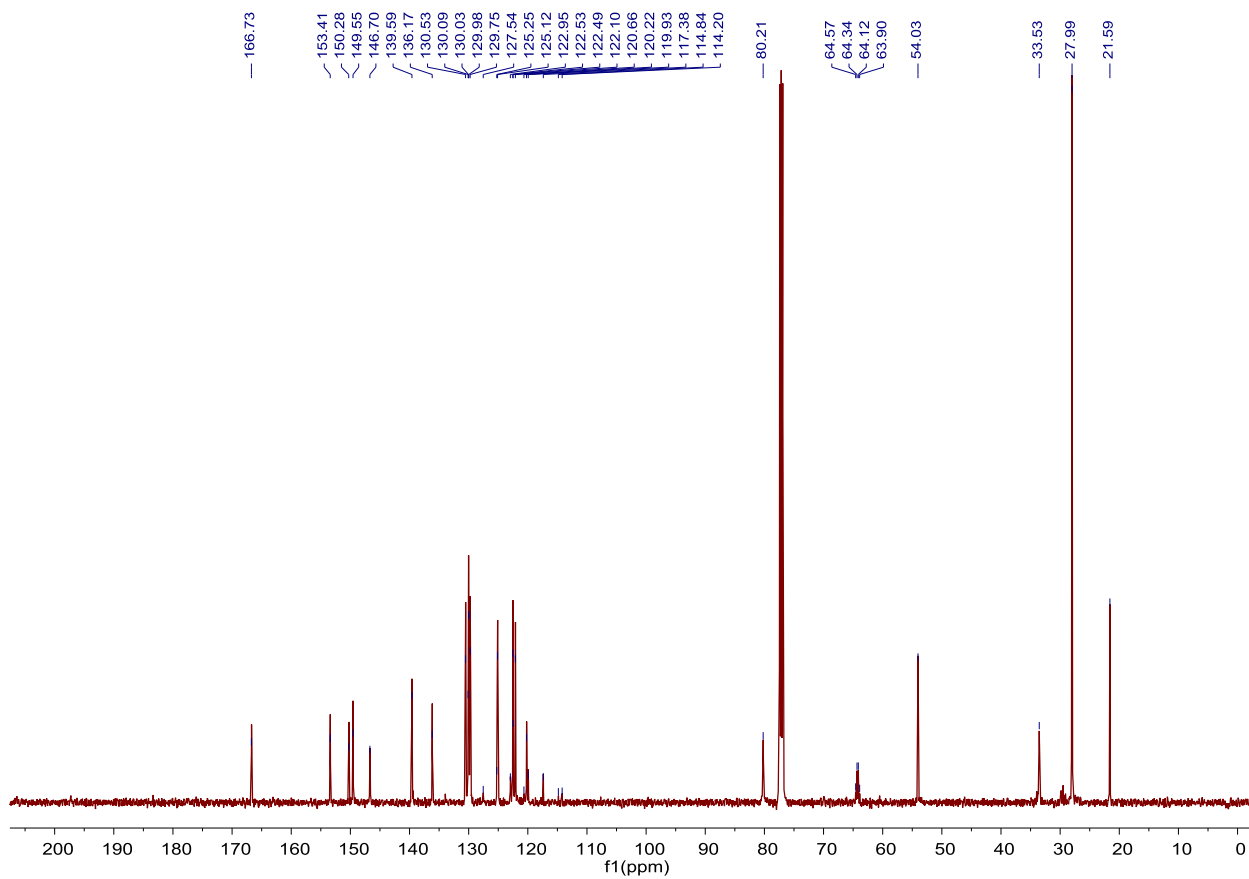
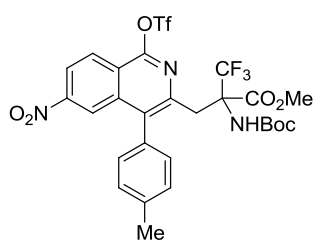


Figure S58. ^{13}C spectrum of **4h** in CDCl_3

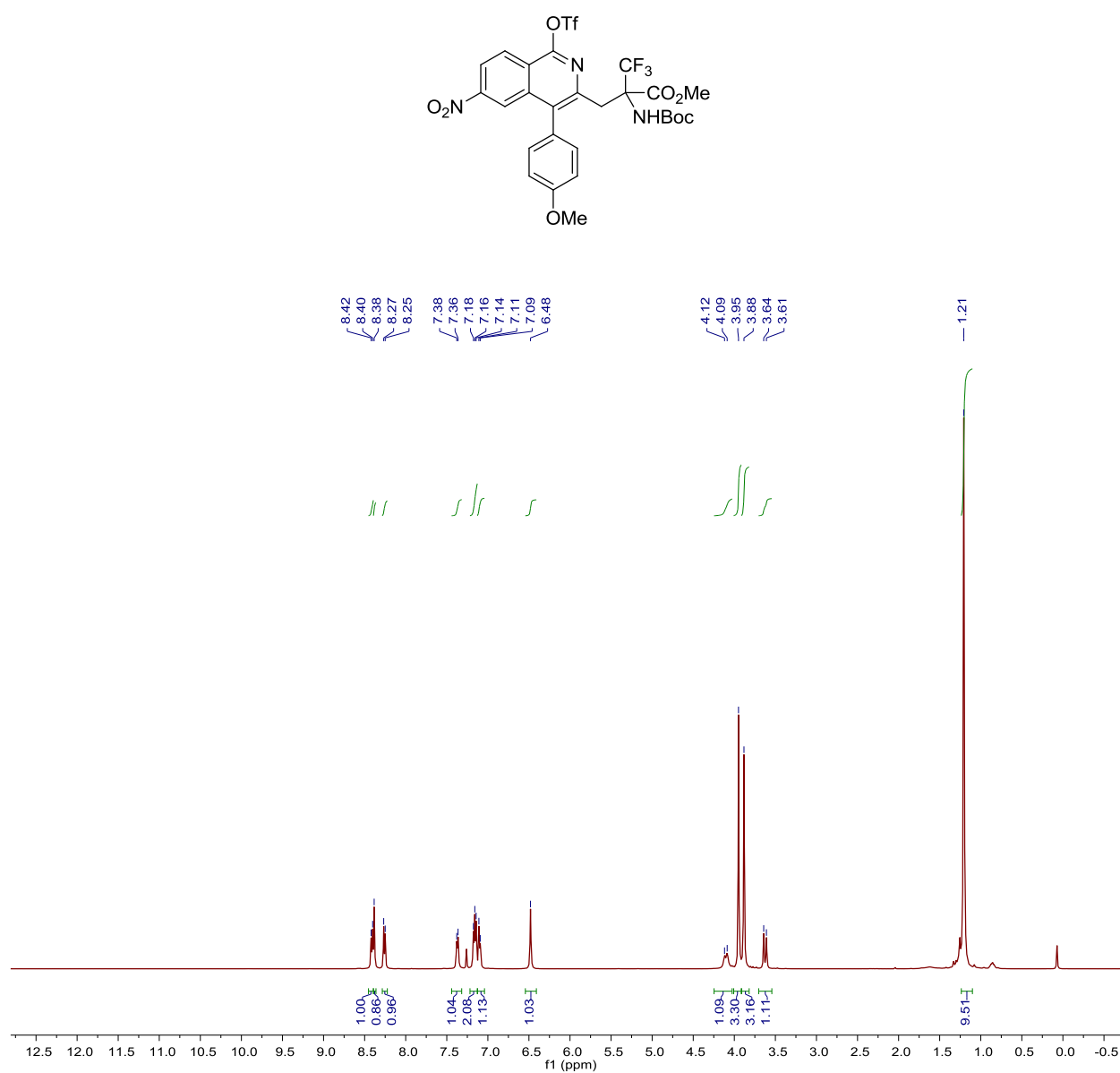


Figure S59. ^1H spectrum of **4i** in CDCl₃

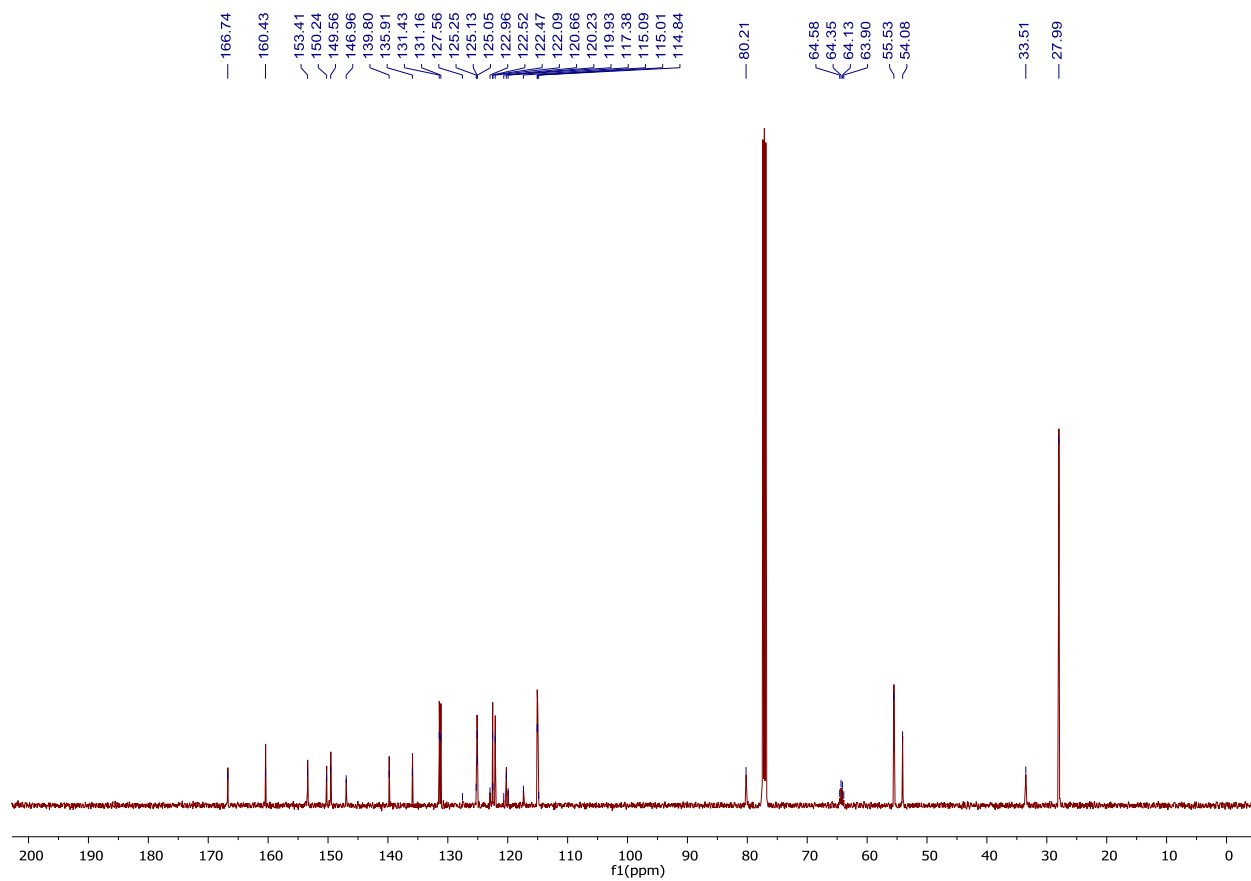
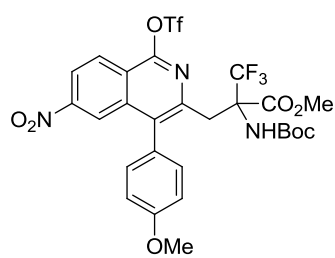


Figure S60. ^{13}C spectrum of **4i** in CDCl_3

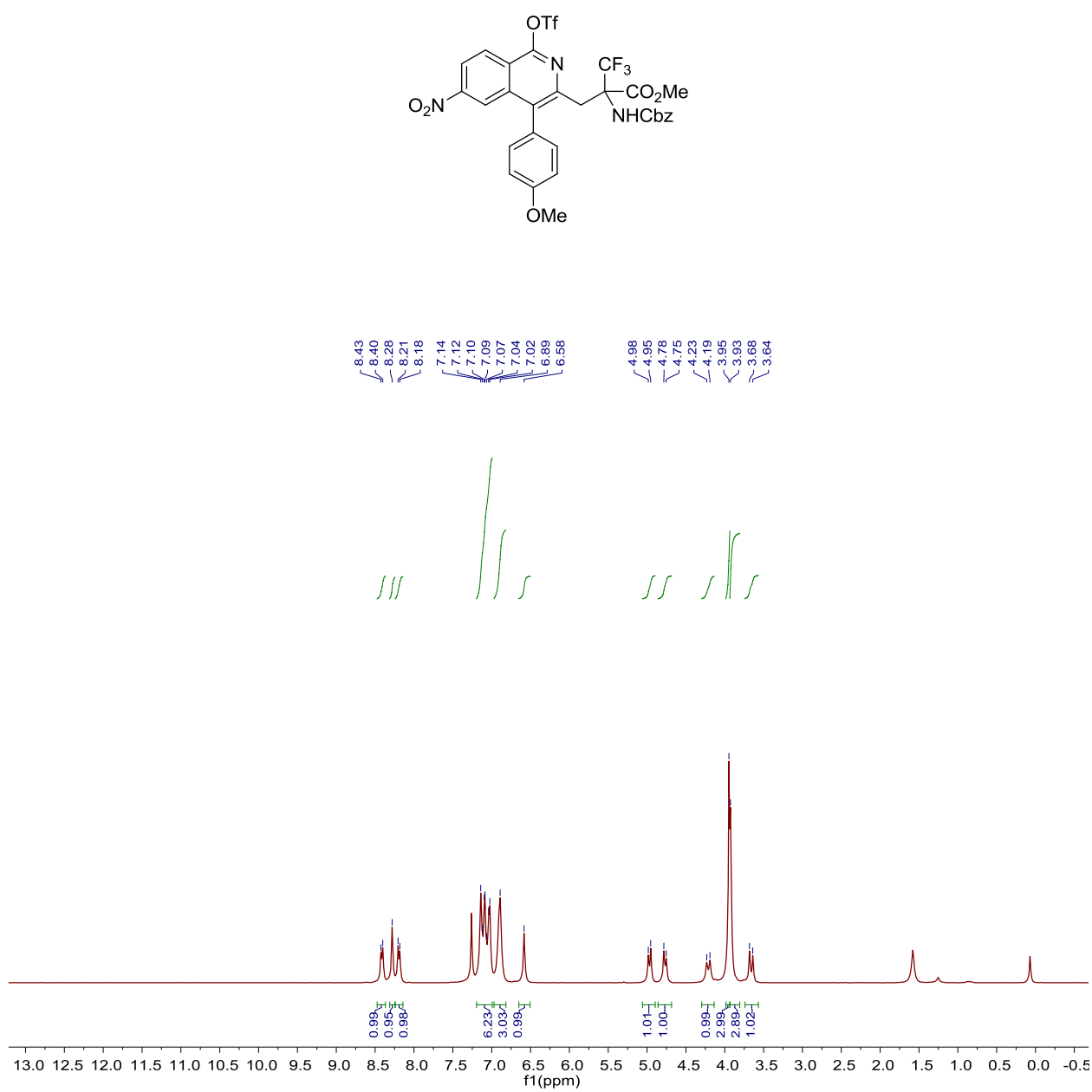


Figure S61. ^1H spectrum of **4j** in CDCl₃

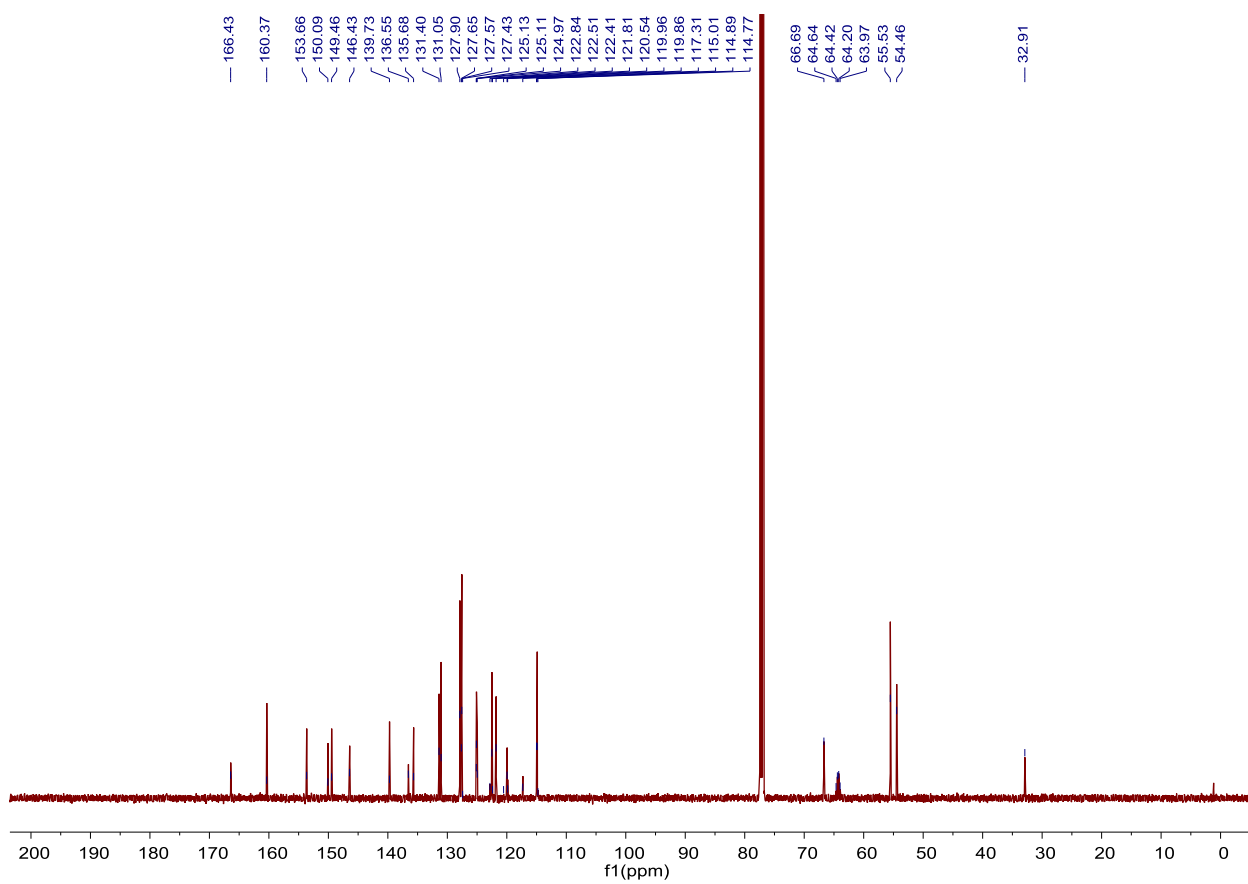
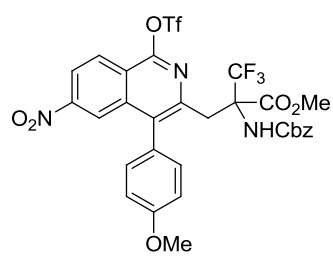


Figure S62. ^{13}C spectrum of **4j** in CDCl_3

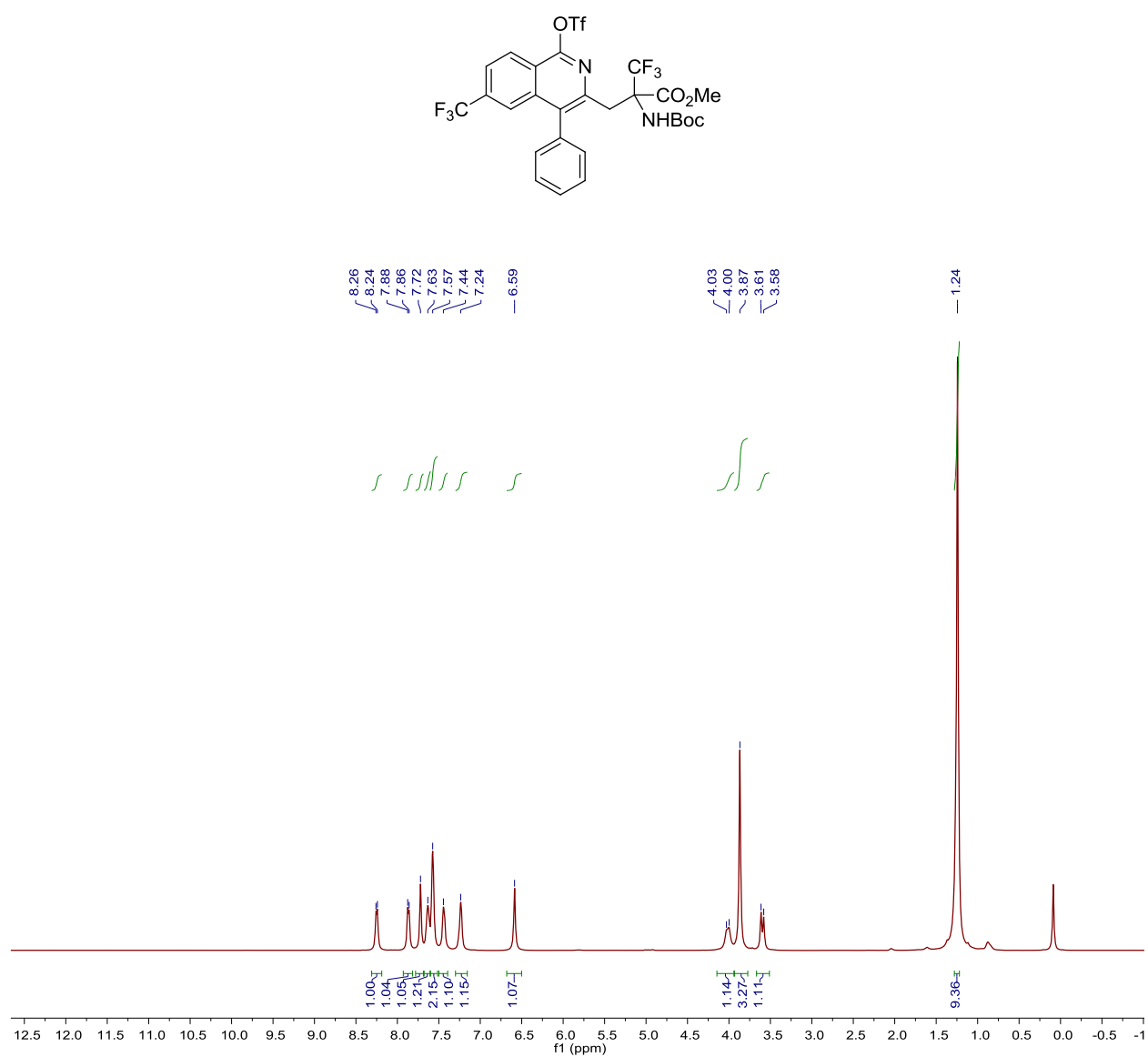


Figure S63. ^1H spectrum of **4k** in CDCl_3

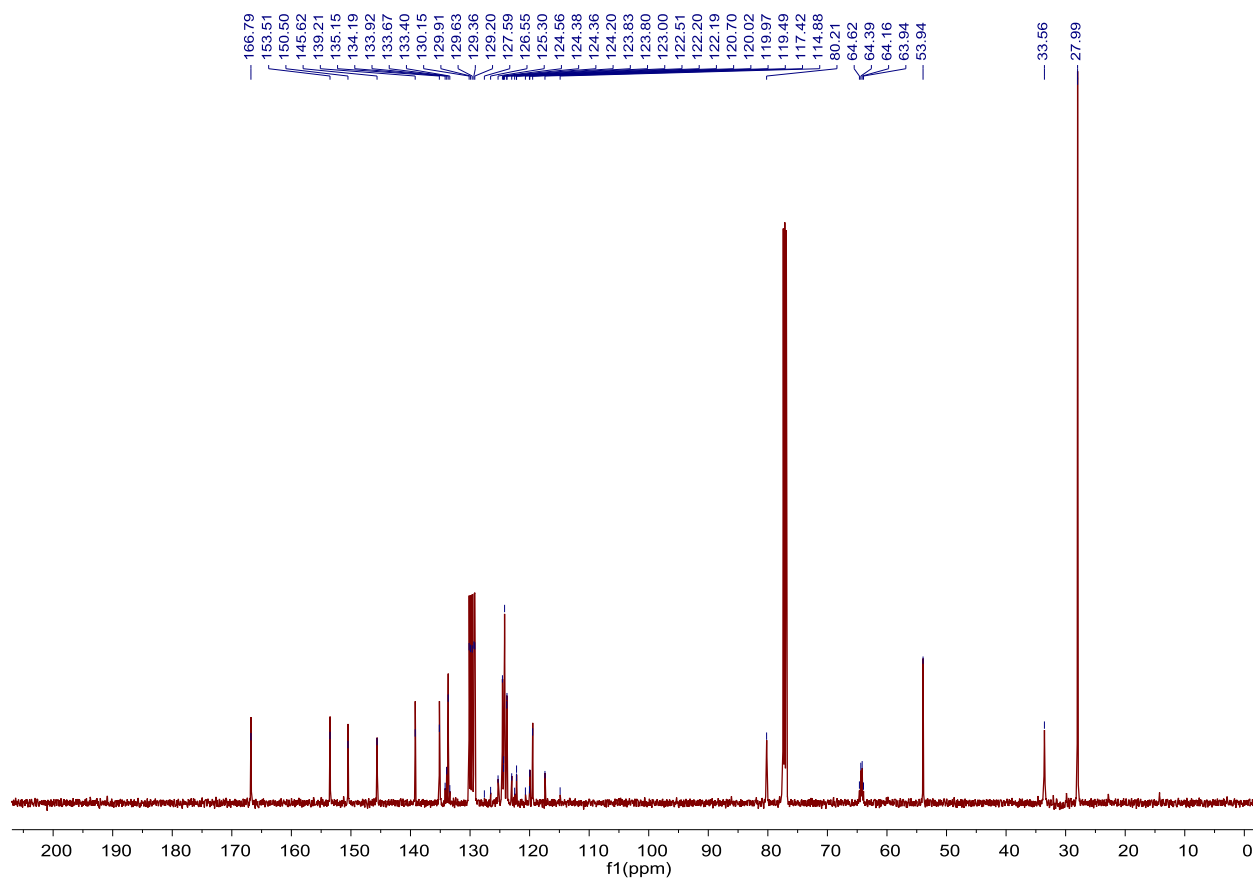
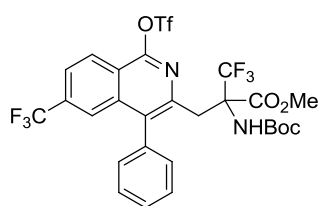


Figure S64. ^{13}C spectrum of **4k** in CDCl_3

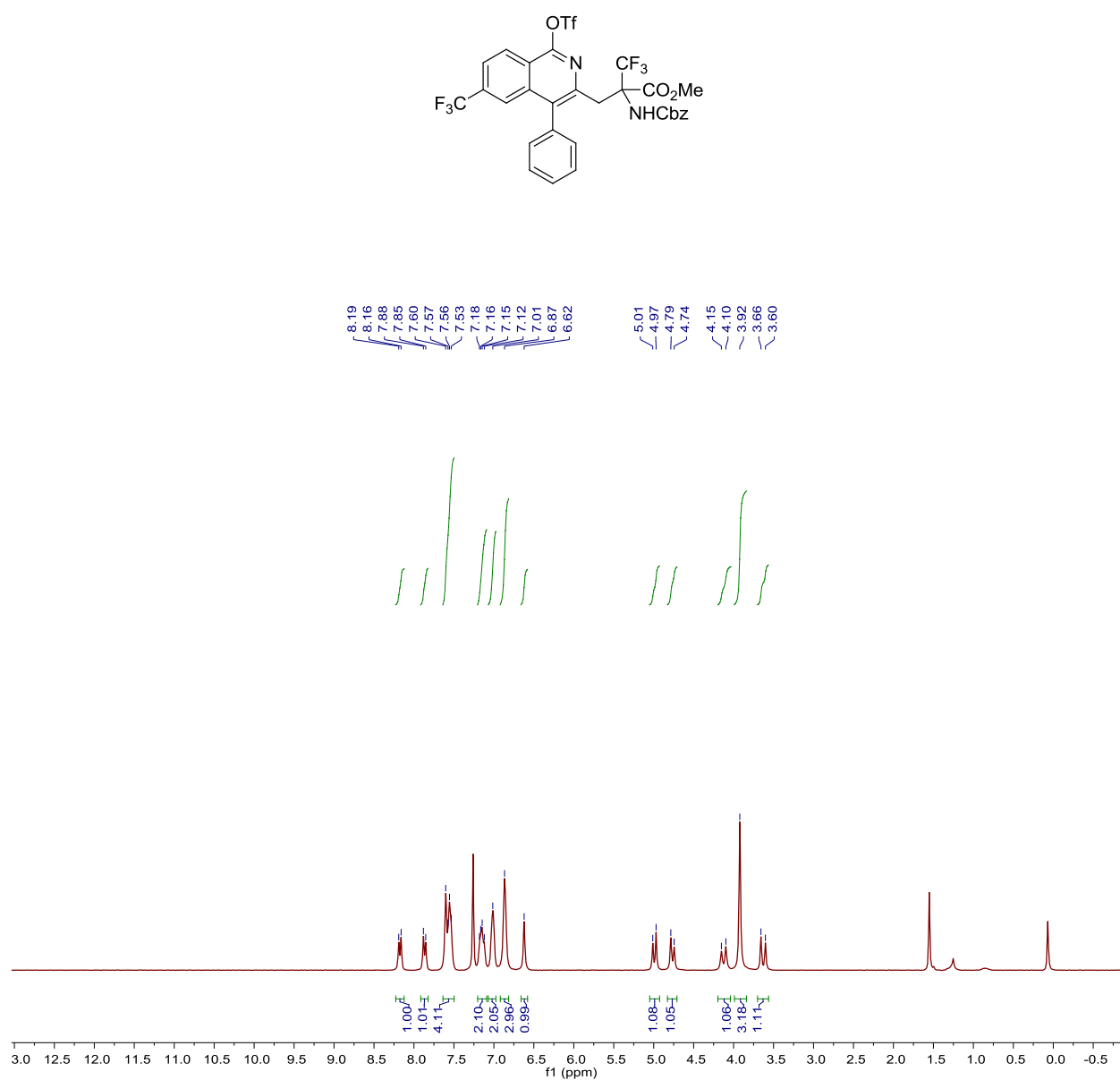


Figure S65. ^1H spectrum of **4l** in CDCl₃

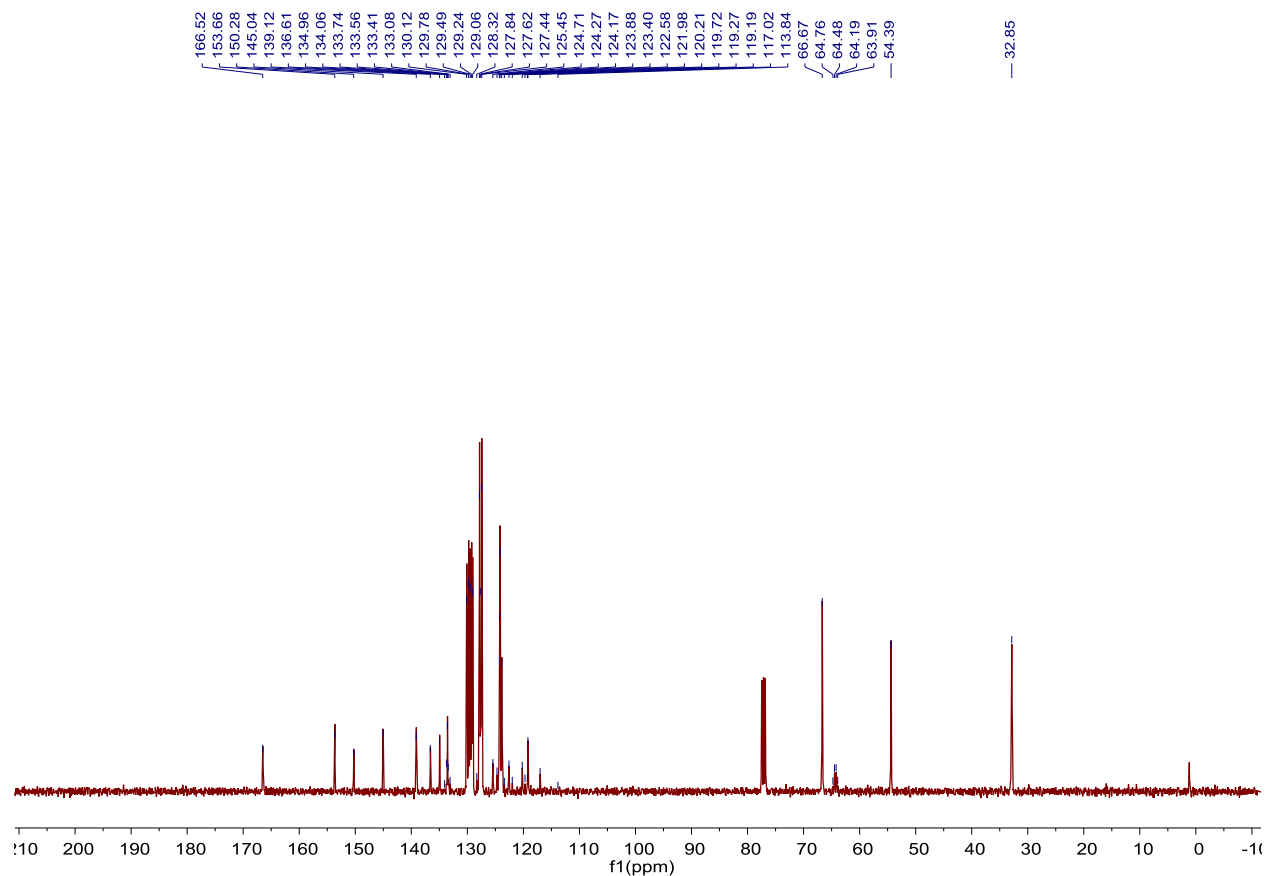
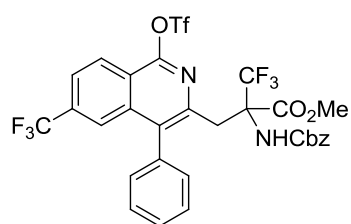


Figure S66. ^{13}C spectrum of **4l** in CDCl_3

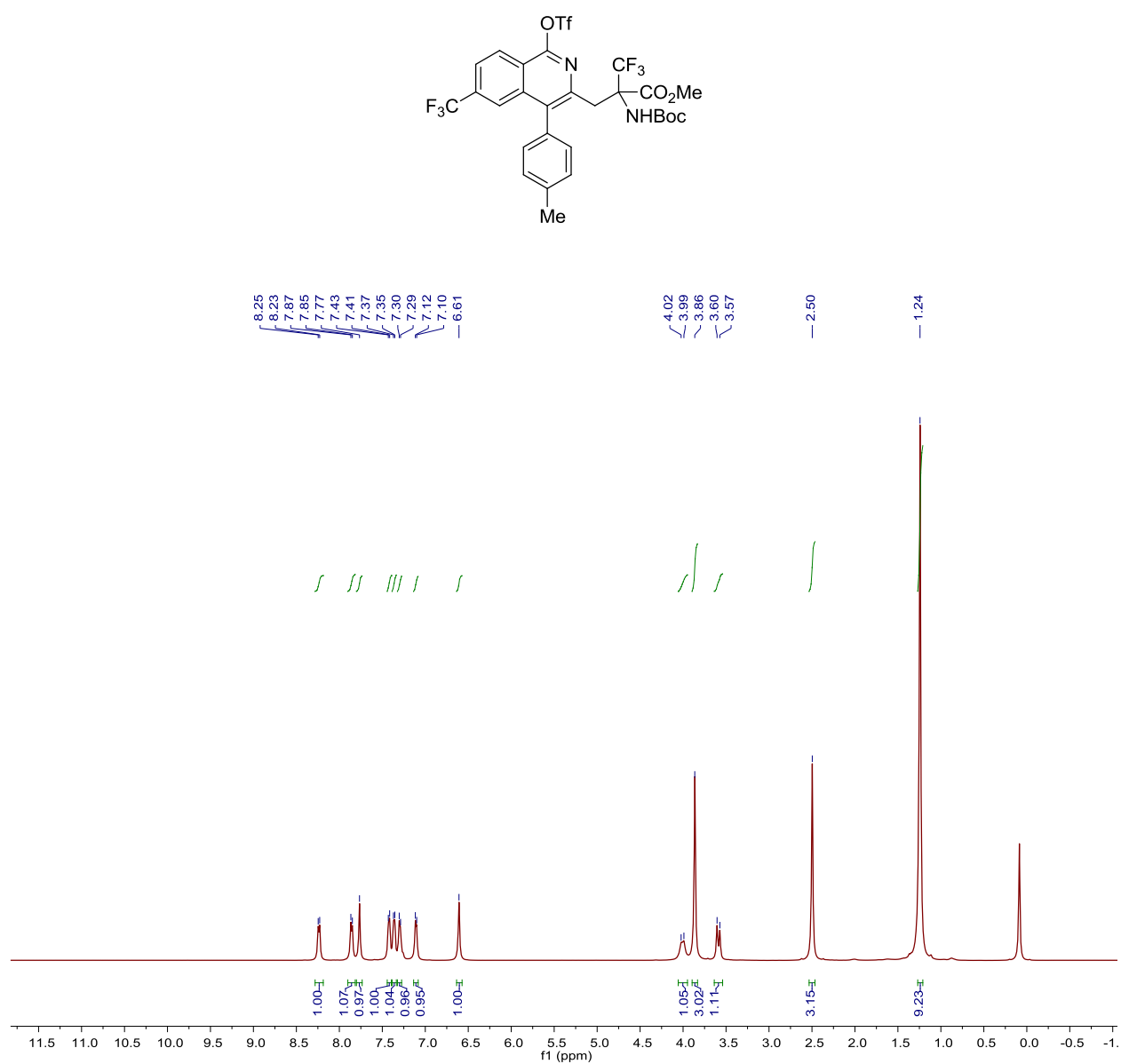


Figure S67. ^1H spectrum of **4m** in CDCl_3

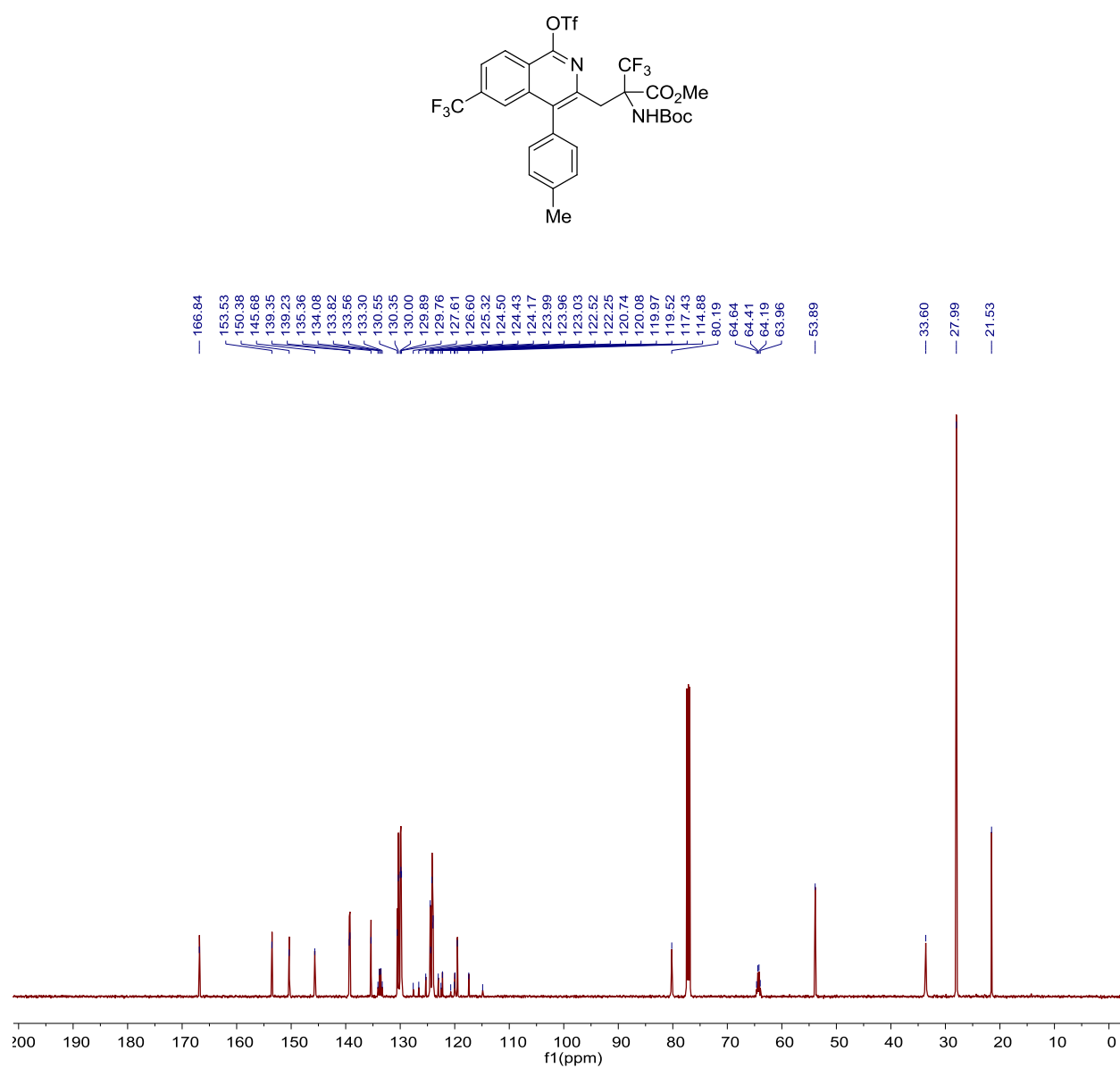


Figure S68. ^{13}C spectrum of **4m** in CDCl₃

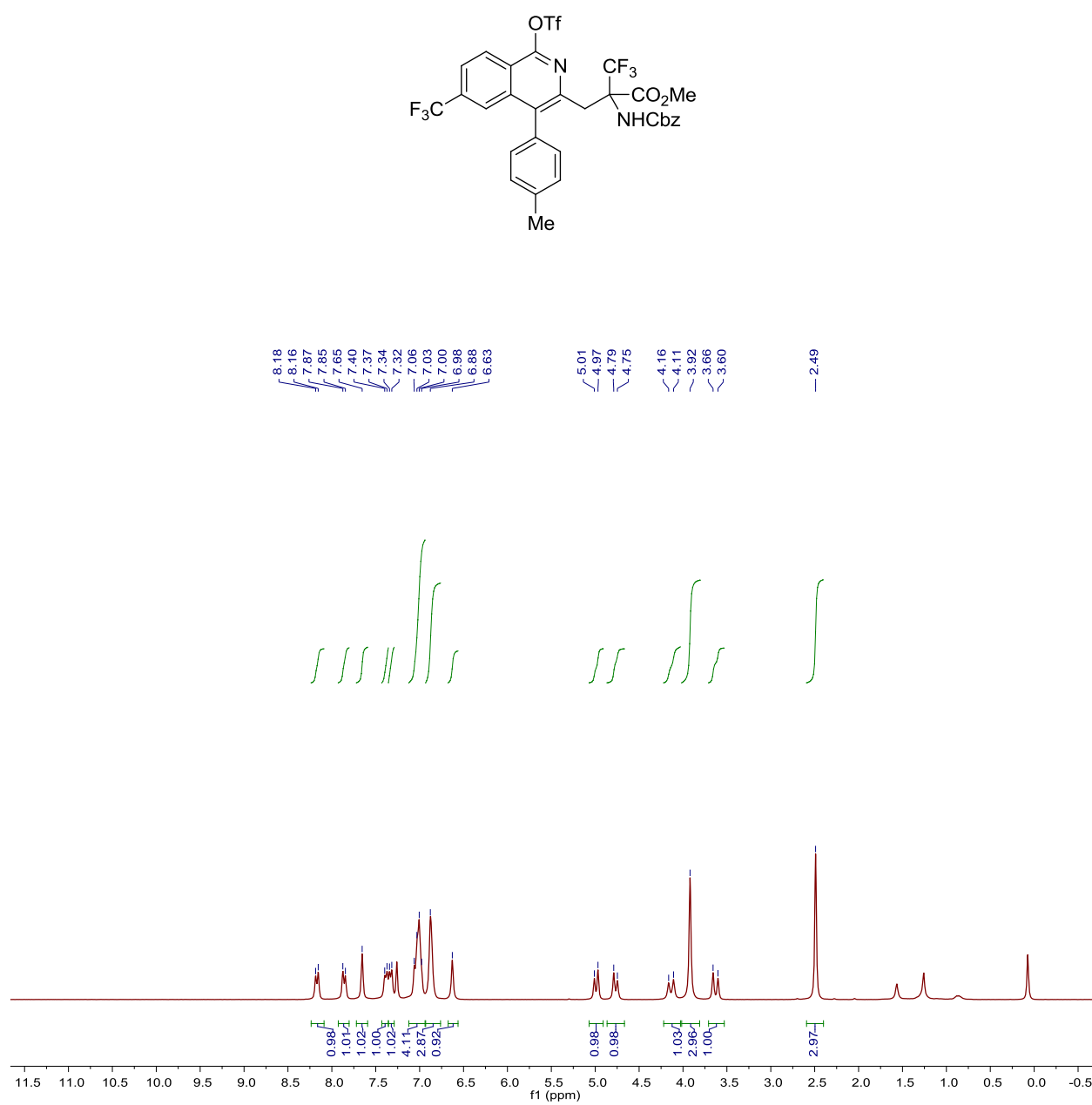


Figure S69. ^1H spectrum of **4n** in CDCl₃

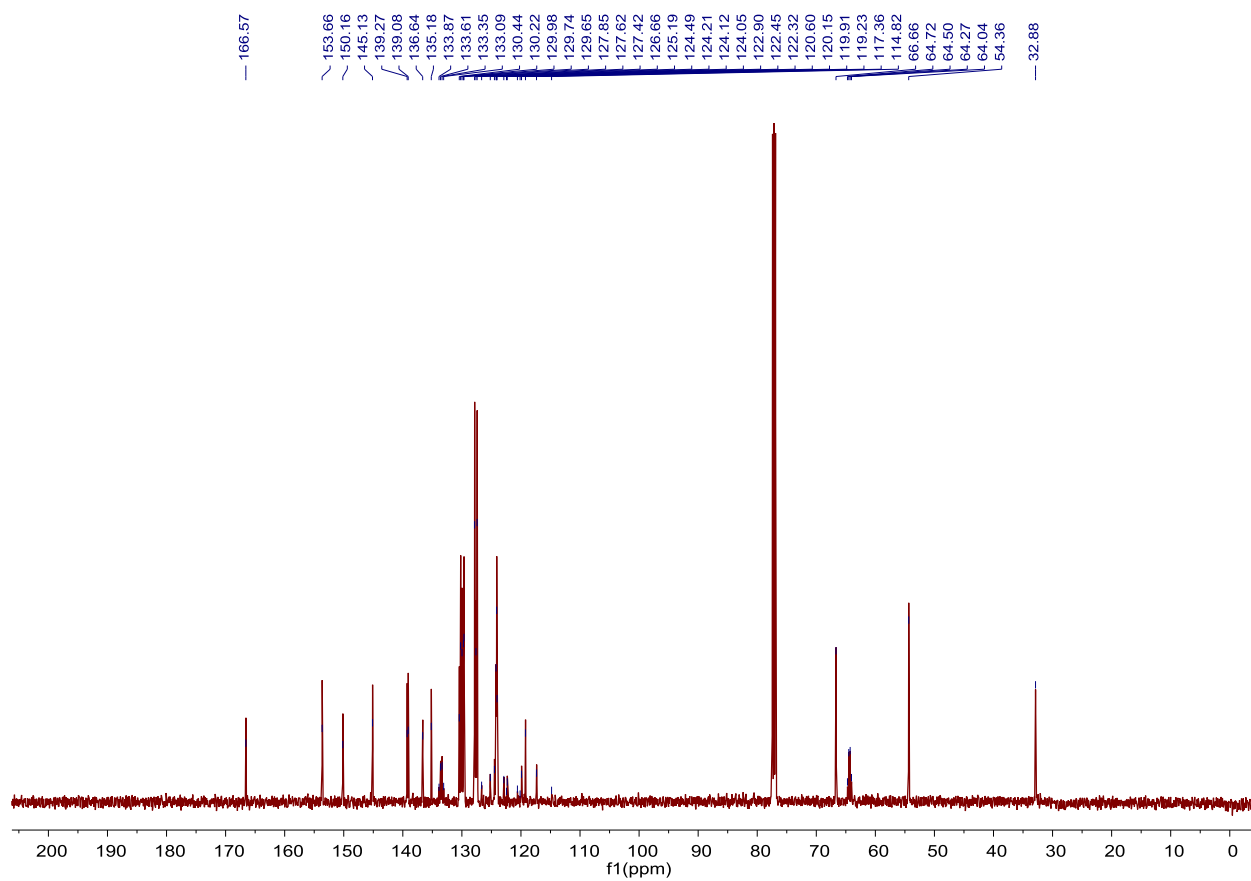
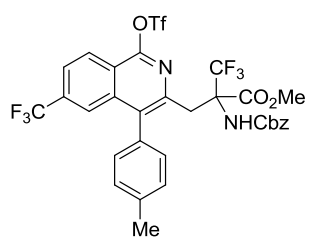


Figure S70. ^{13}C spectrum of **4n** in CDCl_3

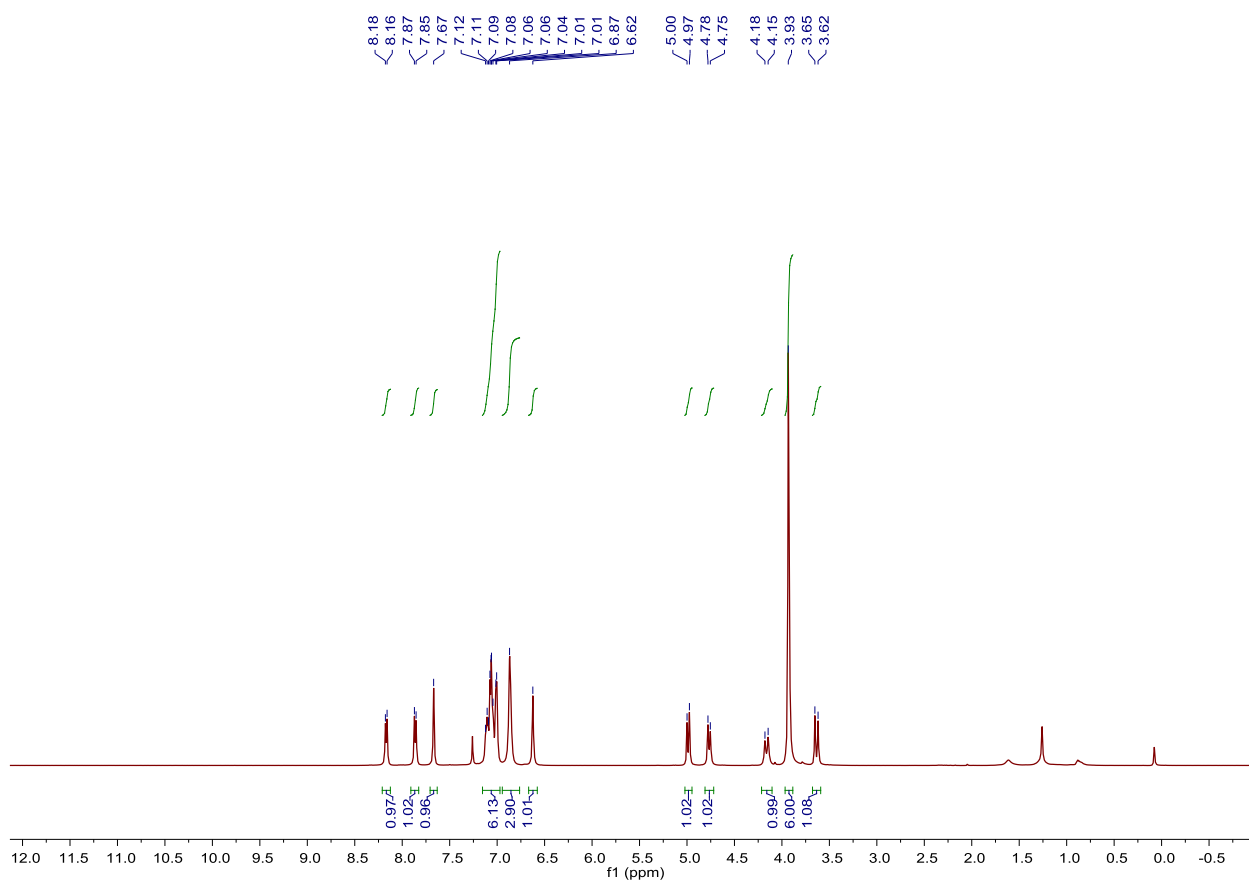
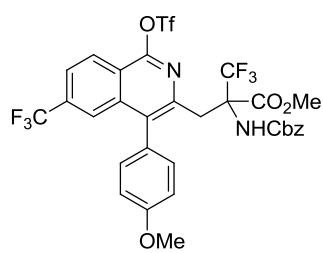


Figure S71. ^1H spectrum of **4o** in CDCl_3

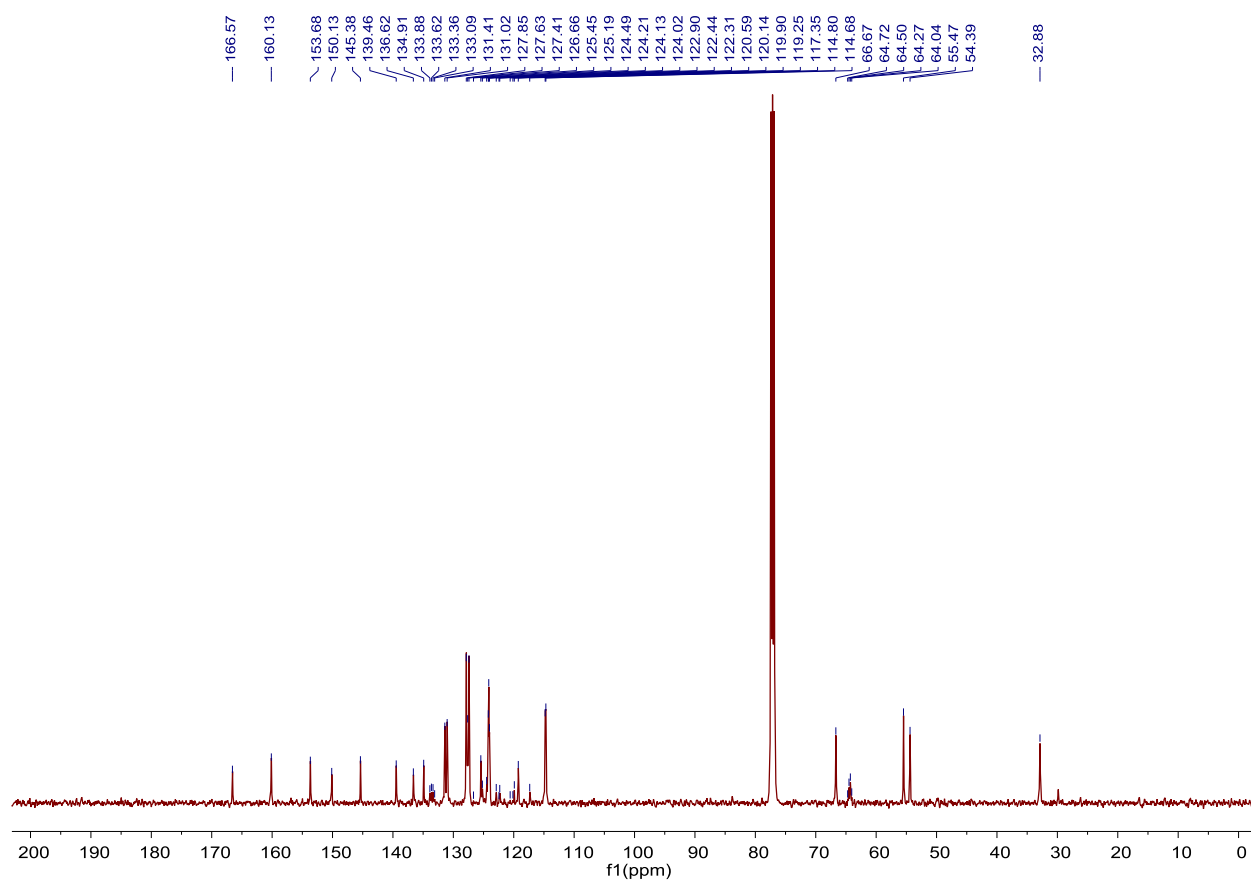
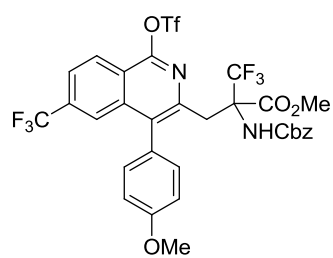


Figure S72. ^{13}C spectrum of **40** in CDCl_3

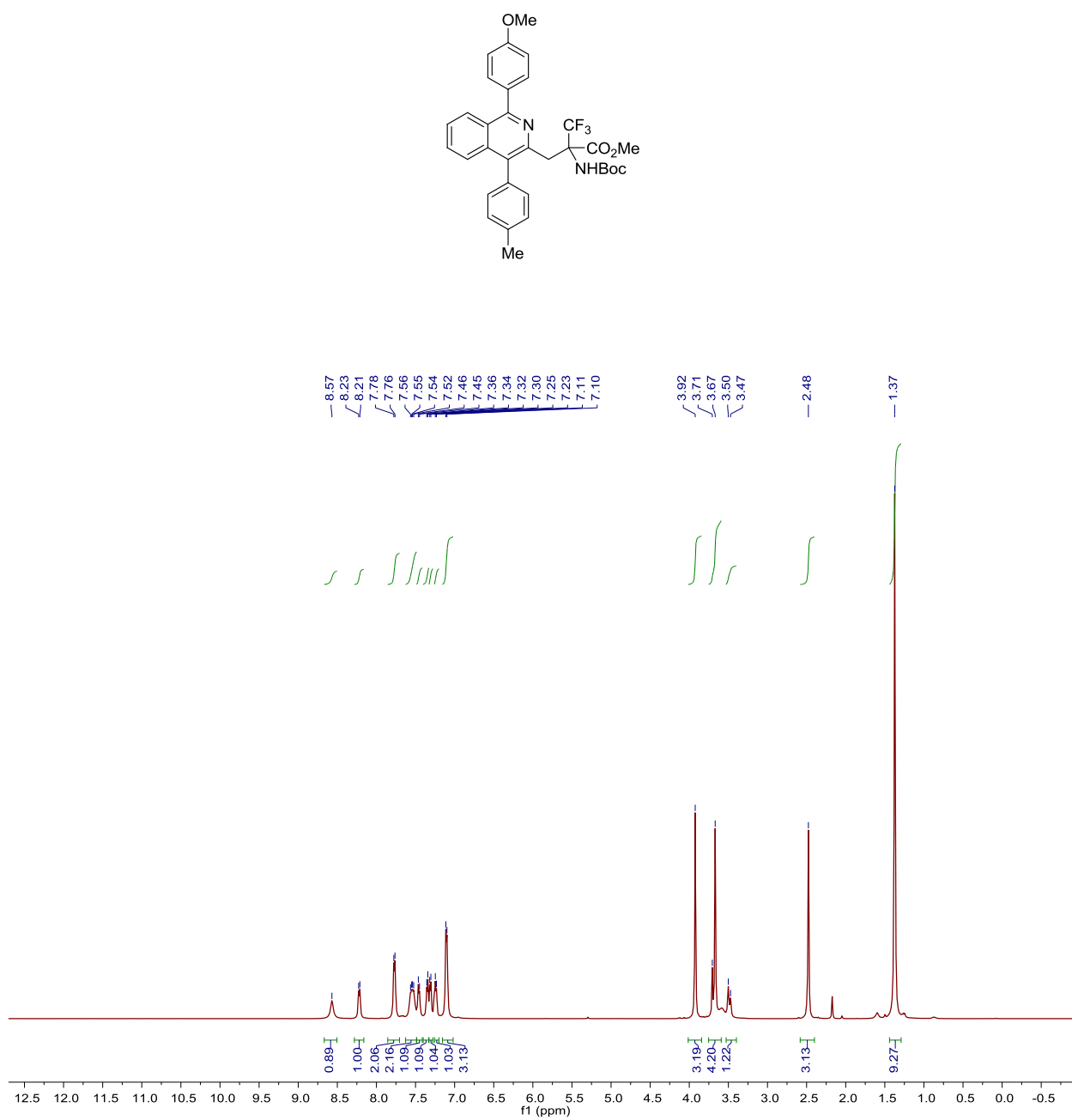


Figure S73. ^1H spectrum of **5a** in CDCl₃

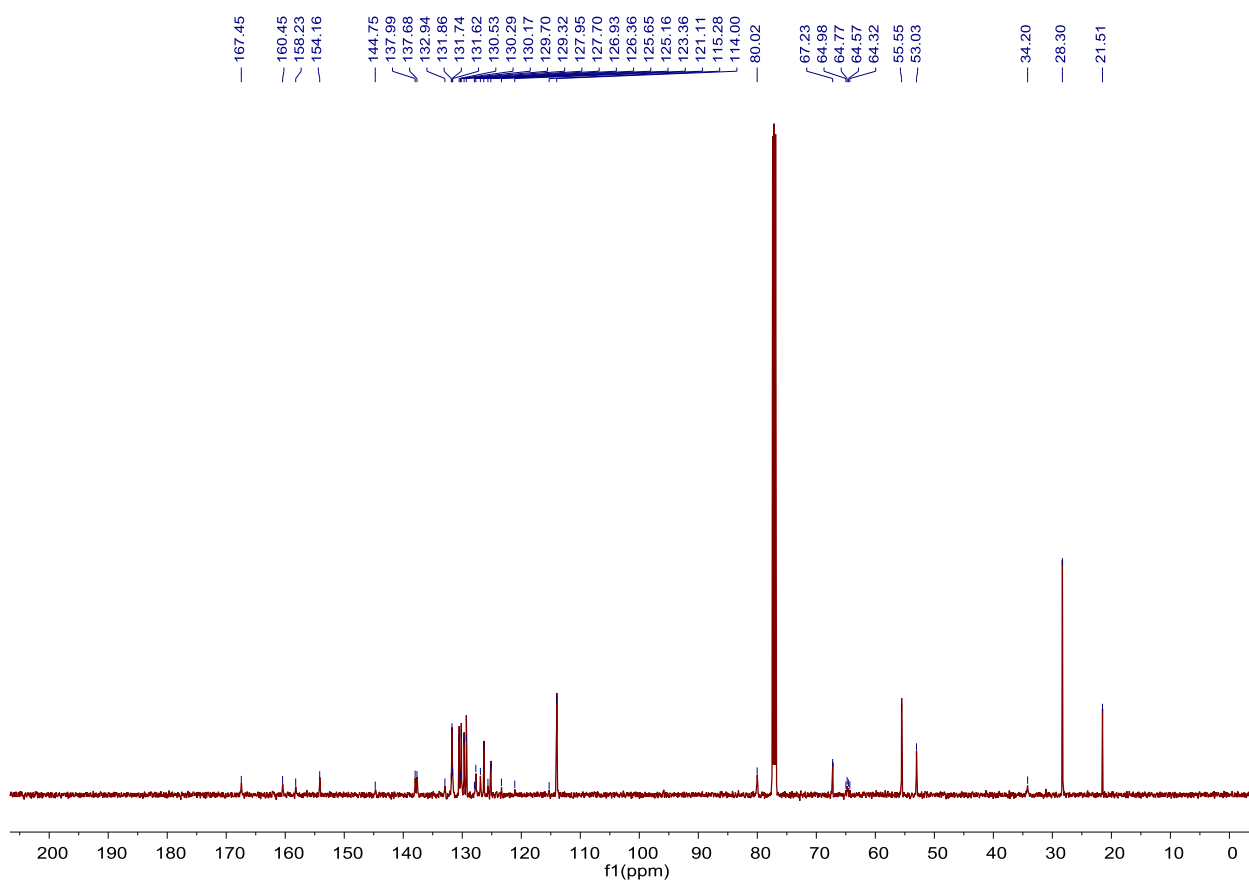
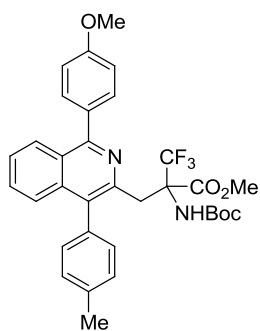


Figure S74. ^{13}C spectrum of **5a** in CDCl_3

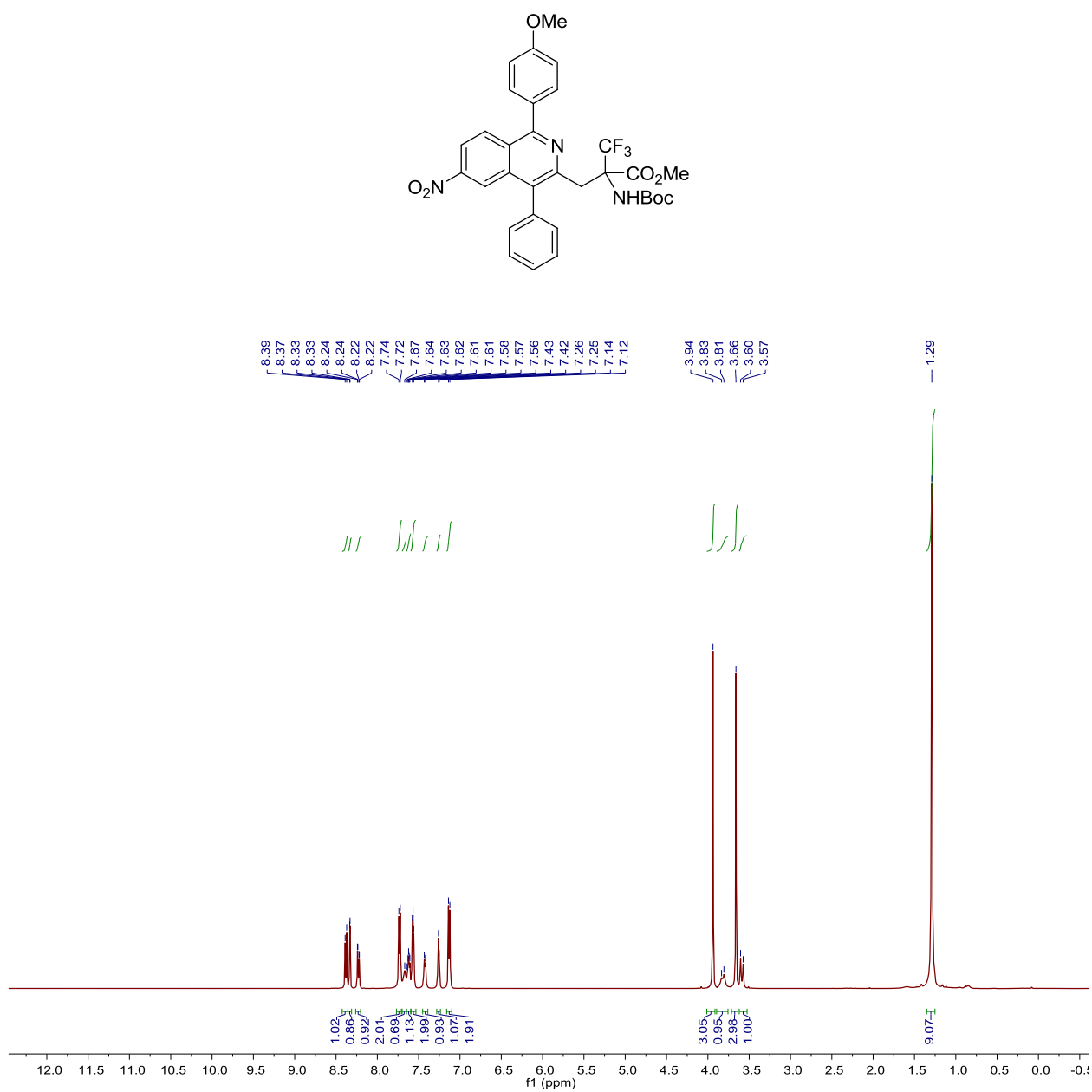


Figure S75. ¹H spectrum of **5b** in CDCl₃

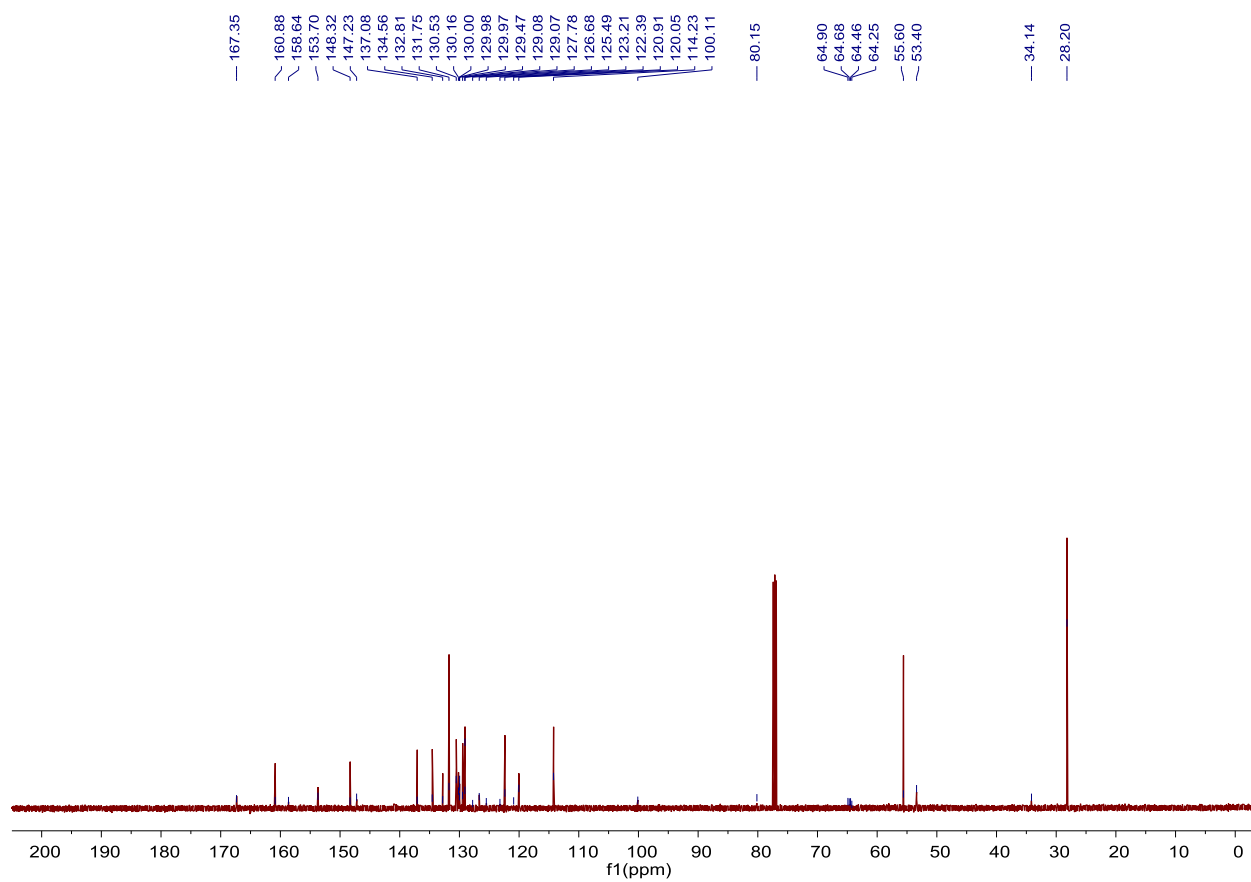
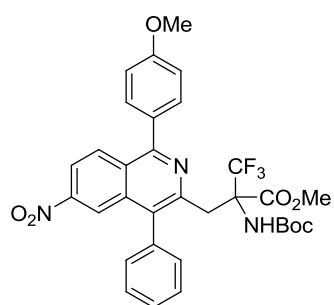


Figure S76. ^{13}C spectrum of **5b** in CDCl_3

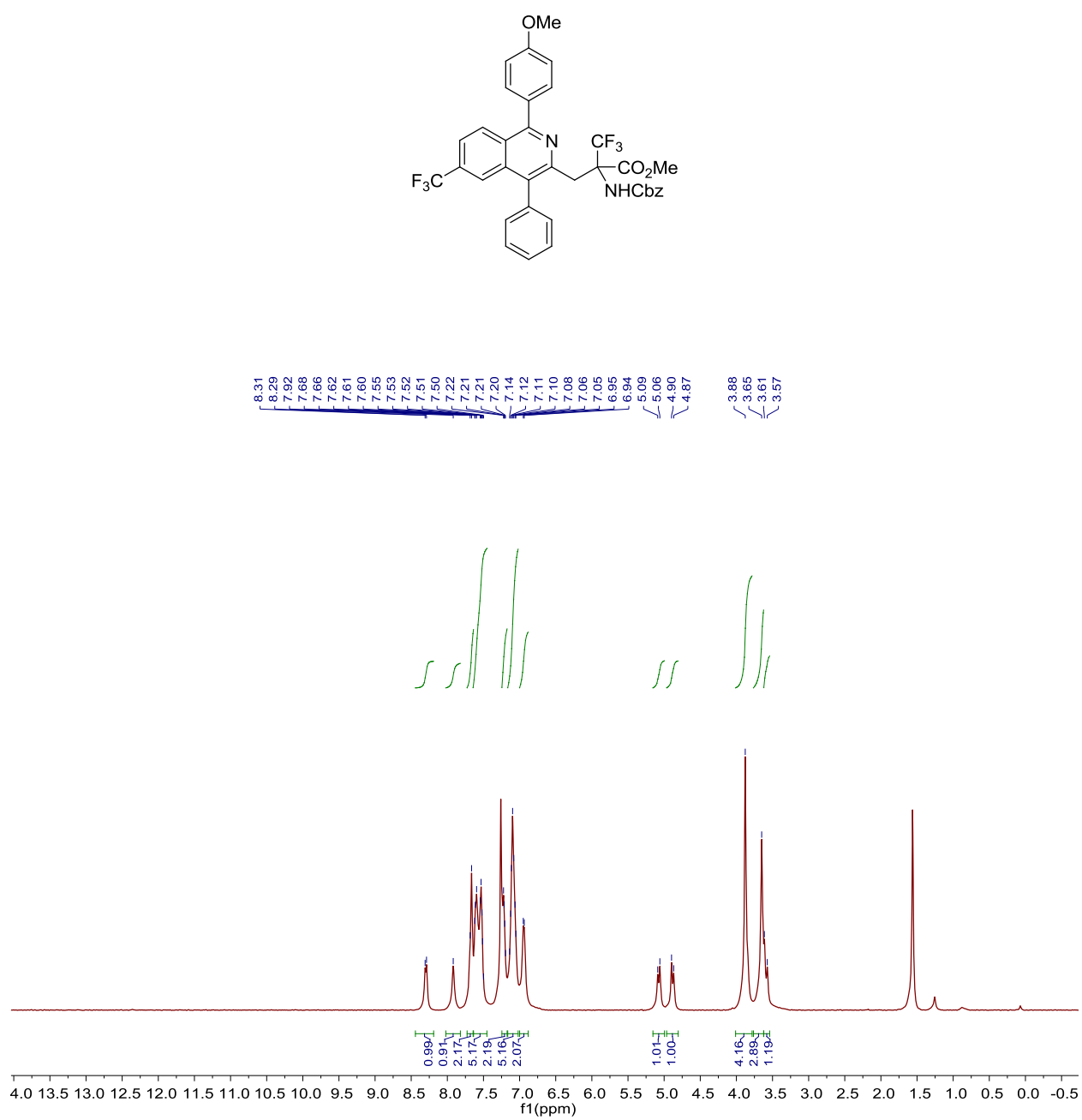


Figure S77. ¹H spectrum of **5c** in CDCl₃

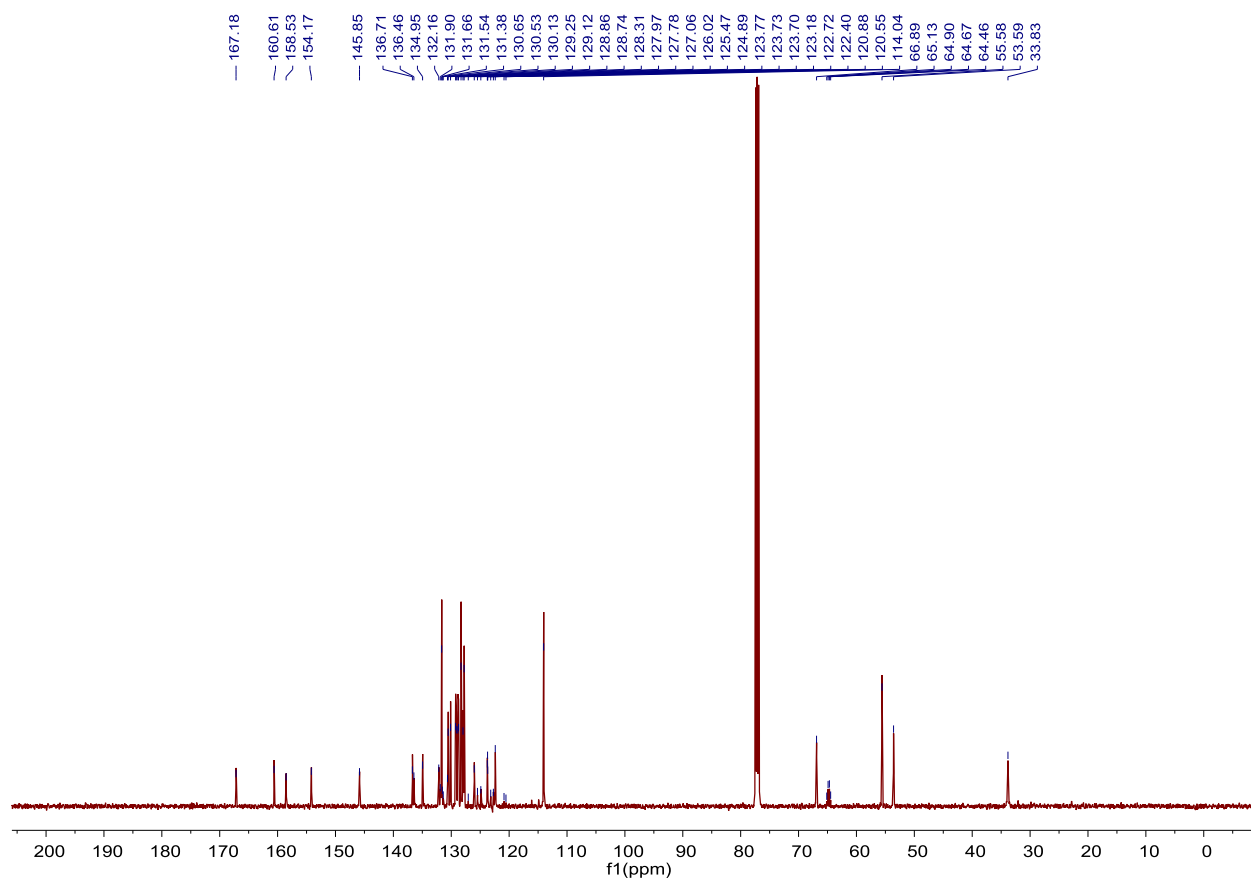
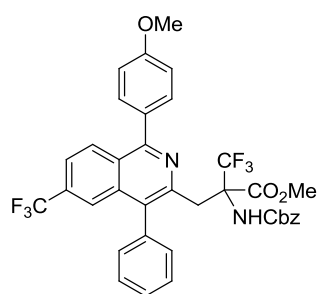


Figure S78. ^{13}C spectrum of **5c** in CDCl_3

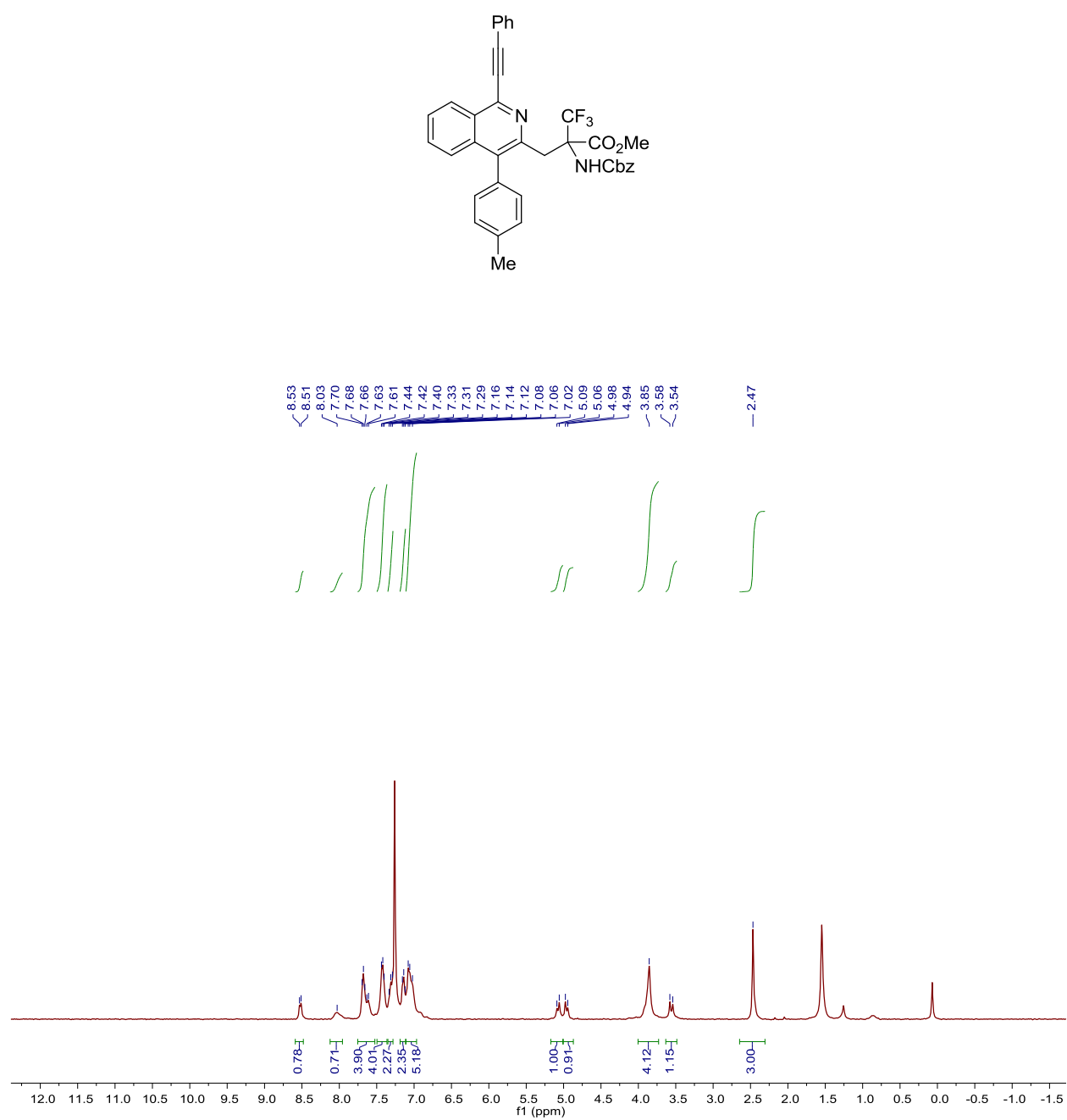


Figure S79. ^1H spectrum of **6a** in CDCl₃

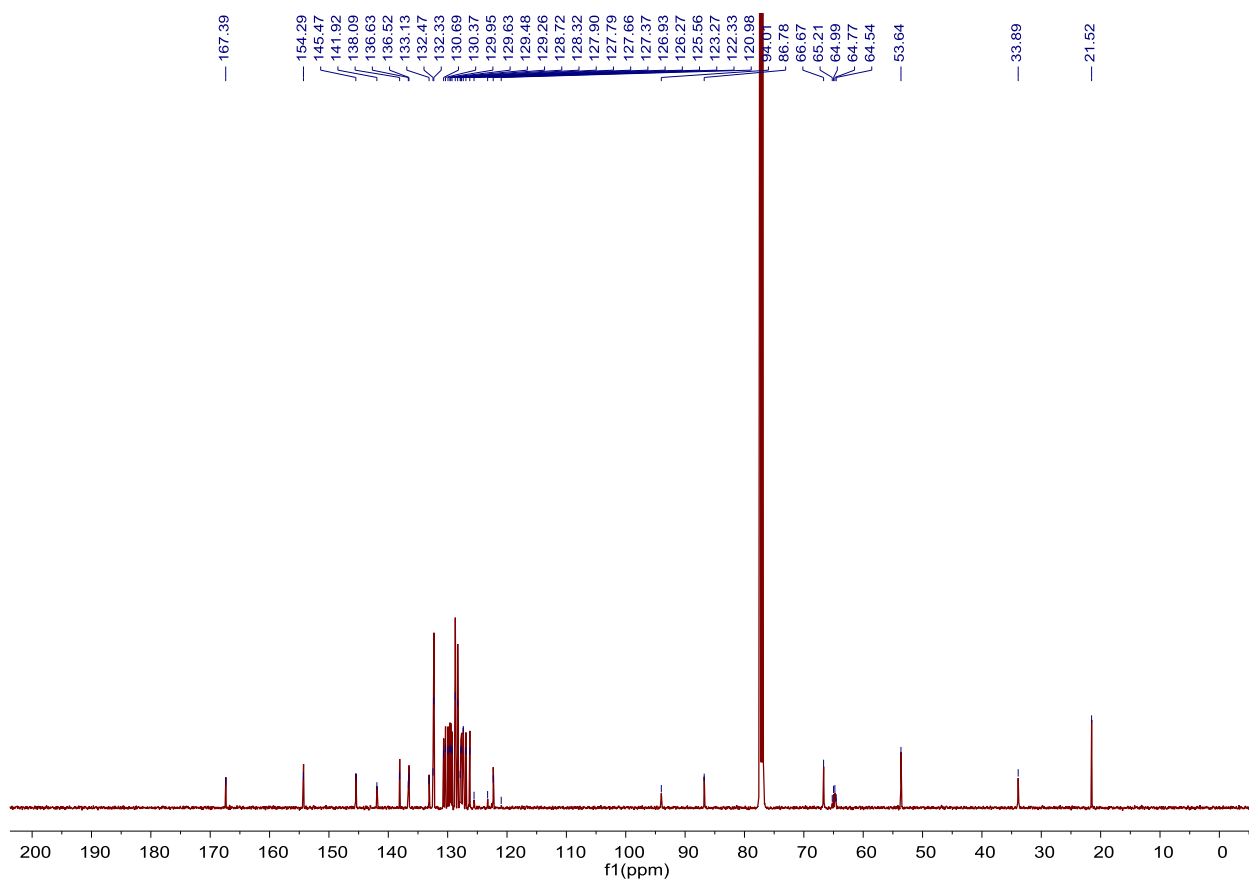
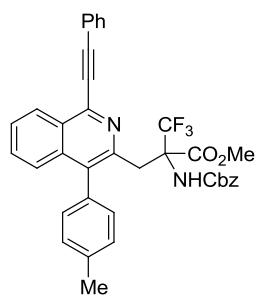


Figure S80. ^{13}C spectrum of **6a** in CDCl_3

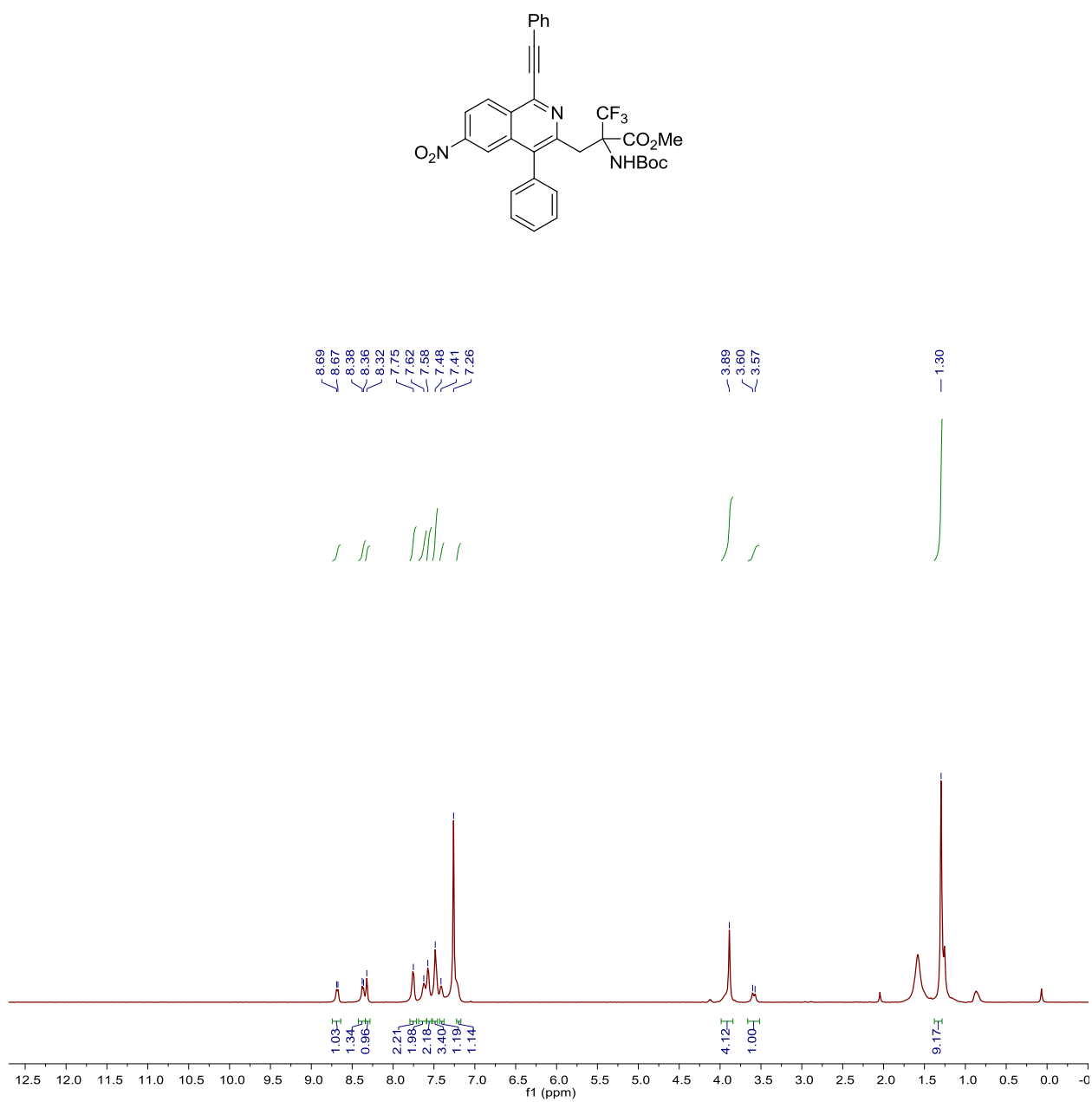


Figure S81. ^1H spectrum of **6b** in CDCl_3

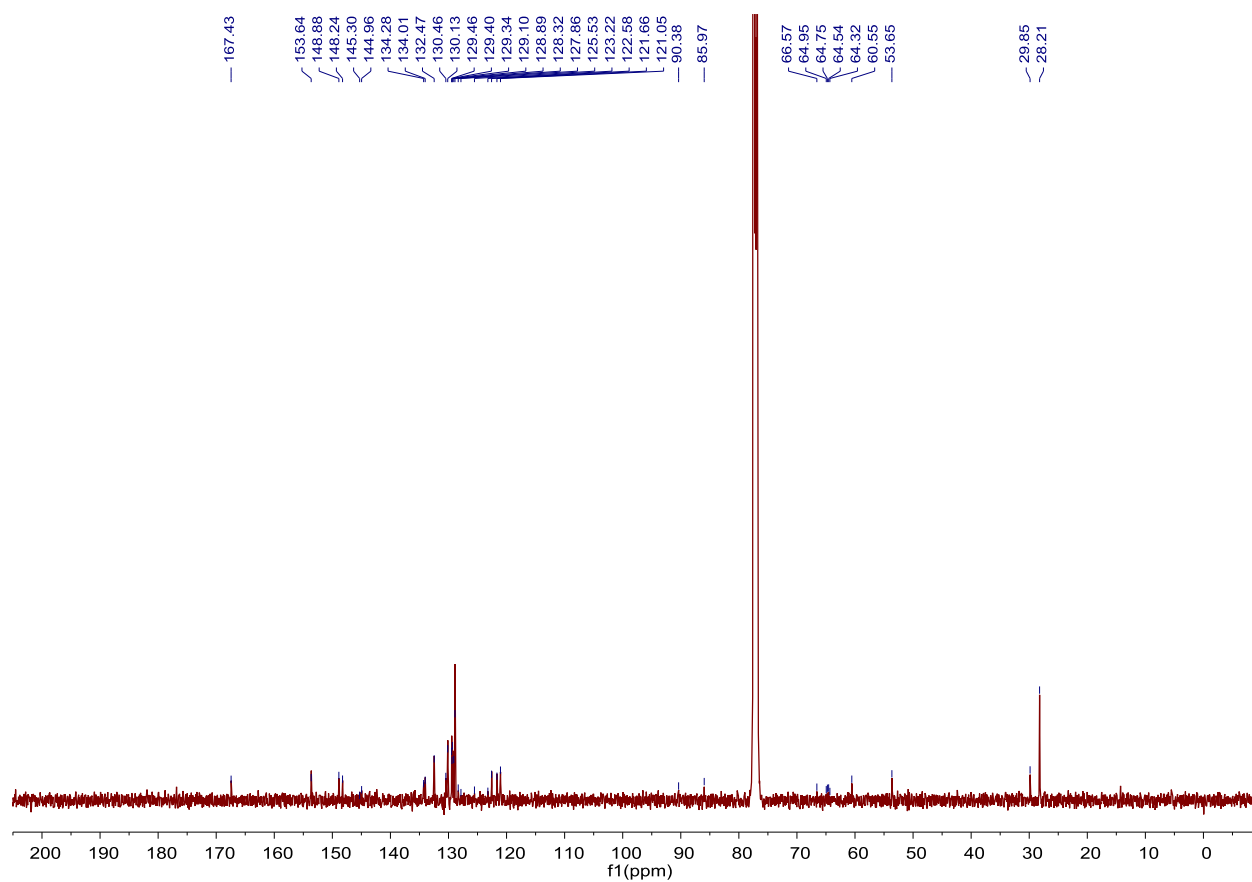
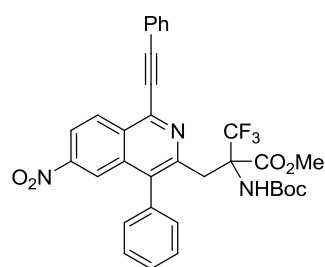


Figure S82. ^{13}C spectrum of **6b** in CDCl_3

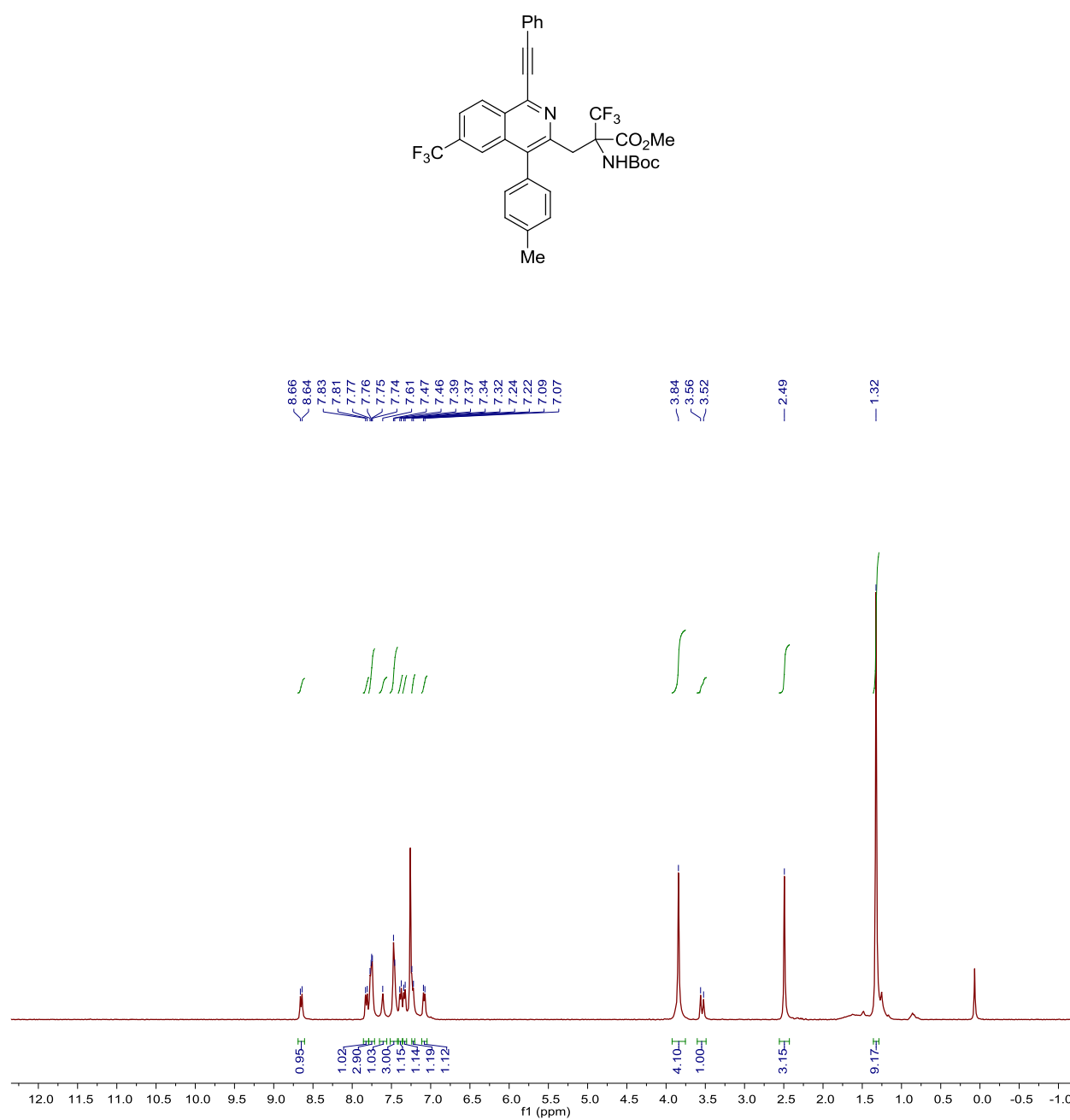


Figure S83. ^1H spectrum of **6c** in CDCl_3

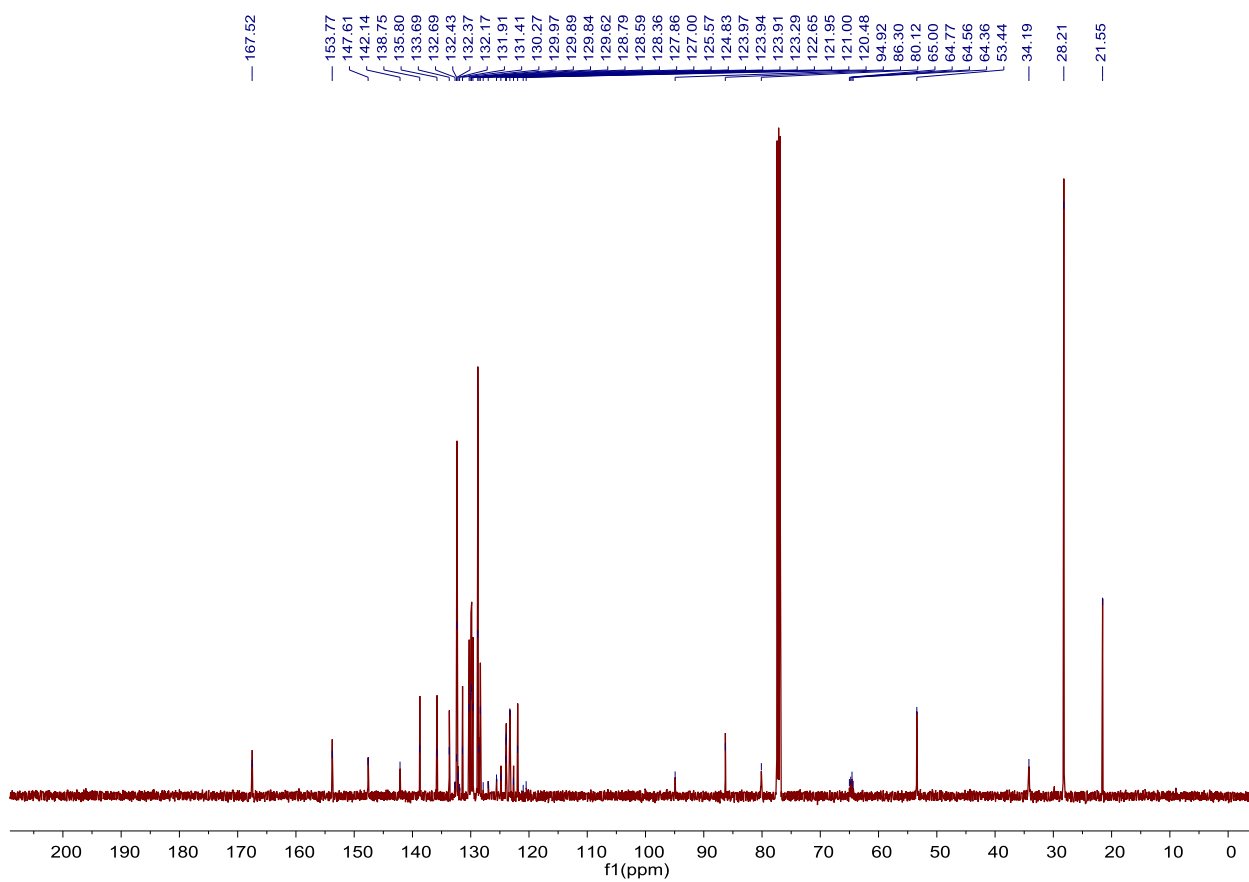
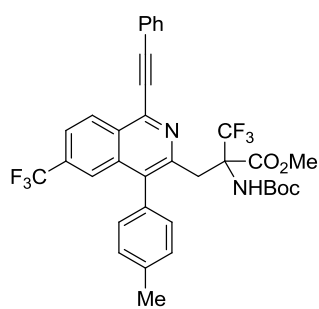


Figure S84. ^{13}C spectrum of **6c** in CDCl_3

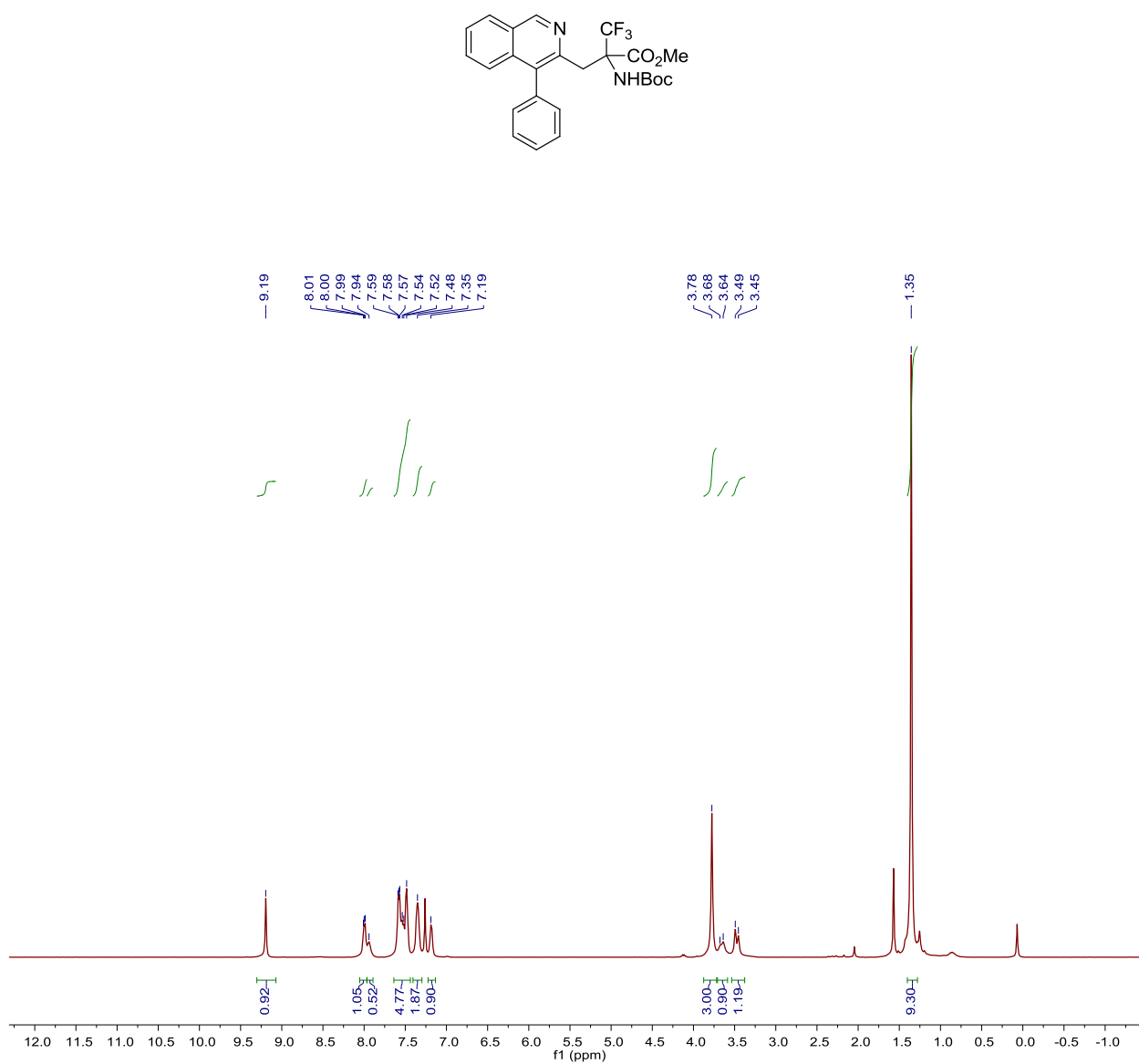


Figure S85. ^1H spectrum of **7a** in CDCl₃

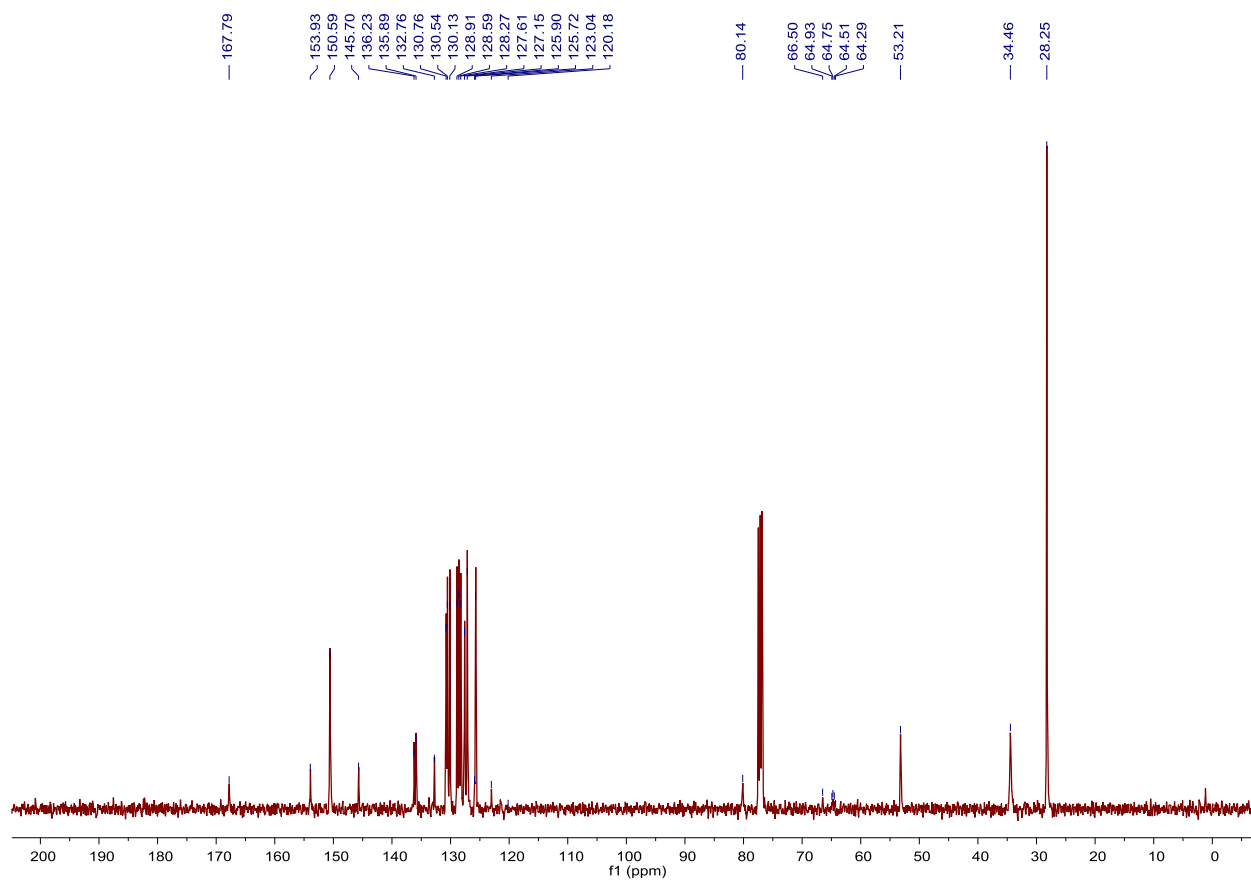
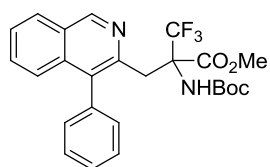


Figure S86. ^{13}C spectrum of **7a** in CDCl_3

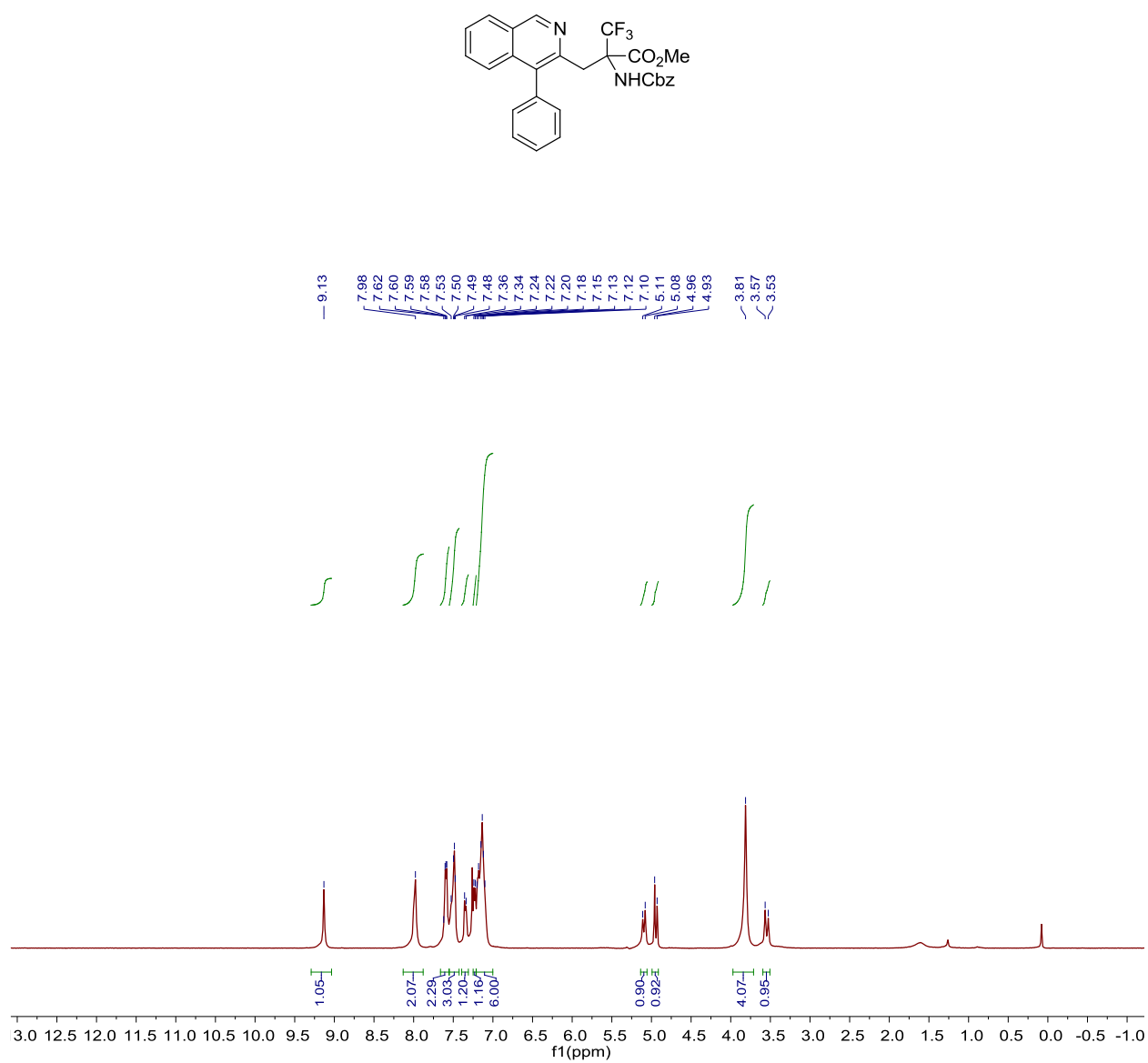


Figure S87. ^1H spectrum of **7b** in CDCl₃

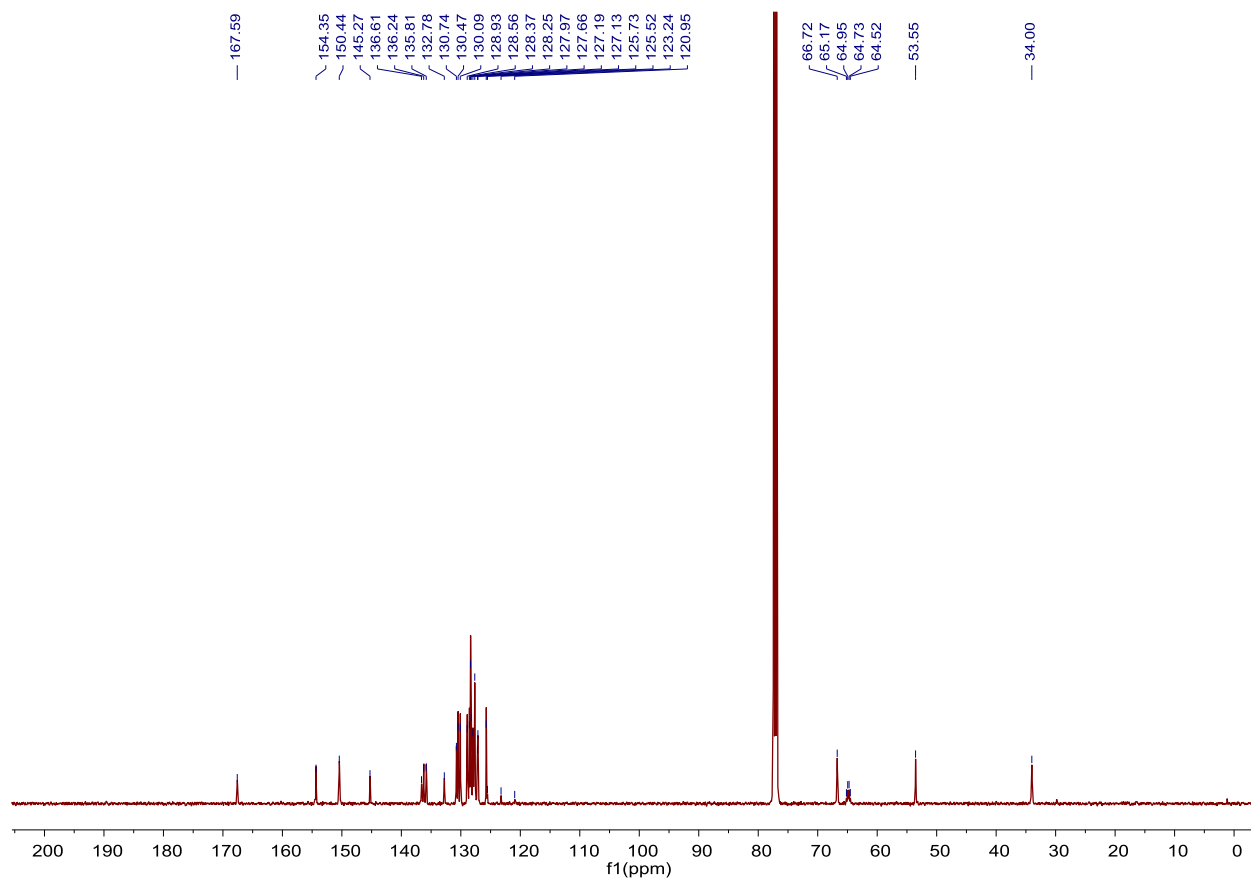
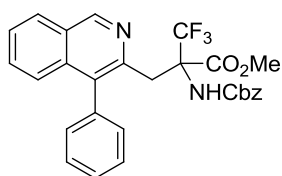


Figure S88. ^{13}C spectrum of **7b** in CDCl_3

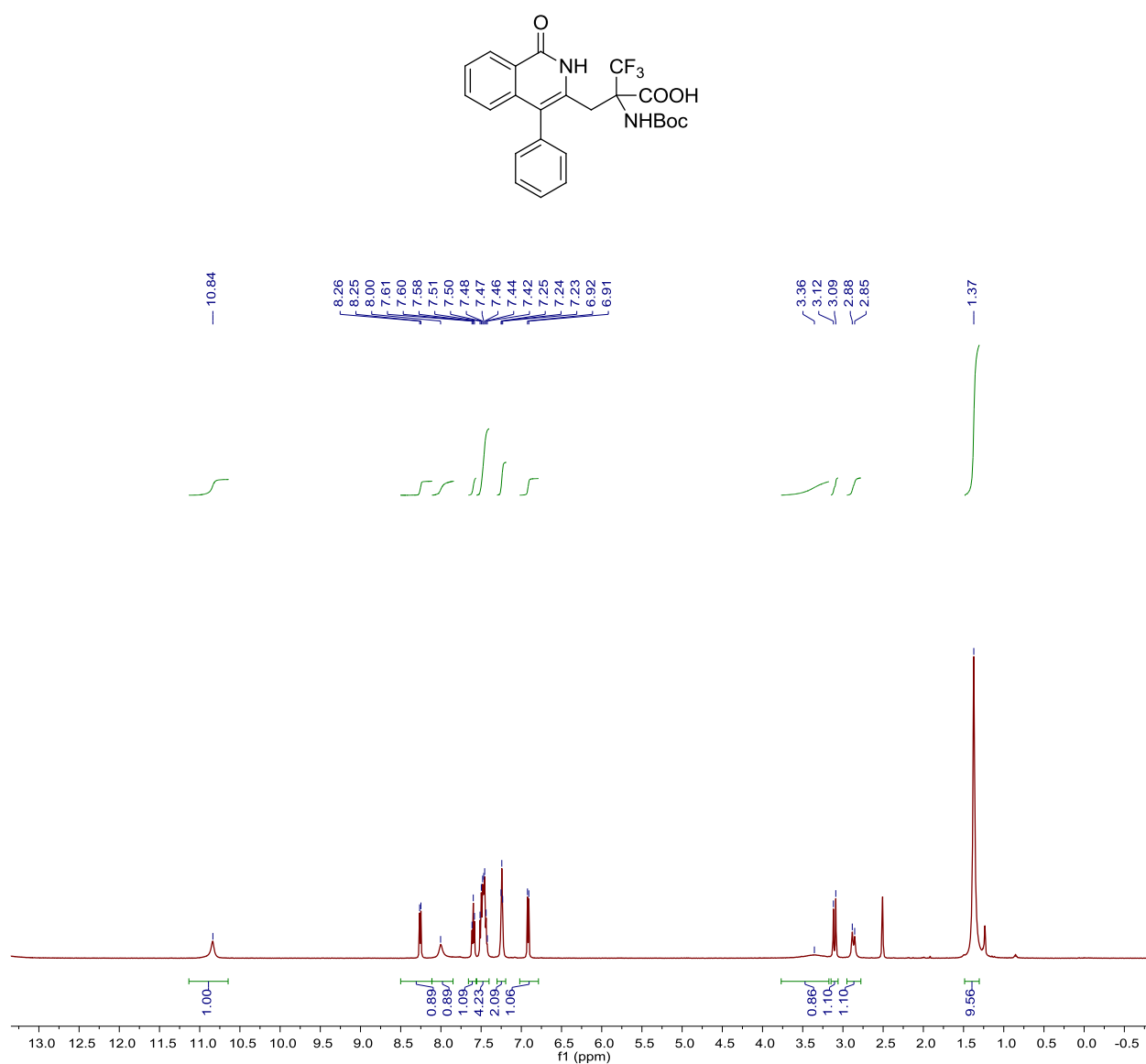


Figure S89. ^1H spectrum of **8** in DMSO- d_6

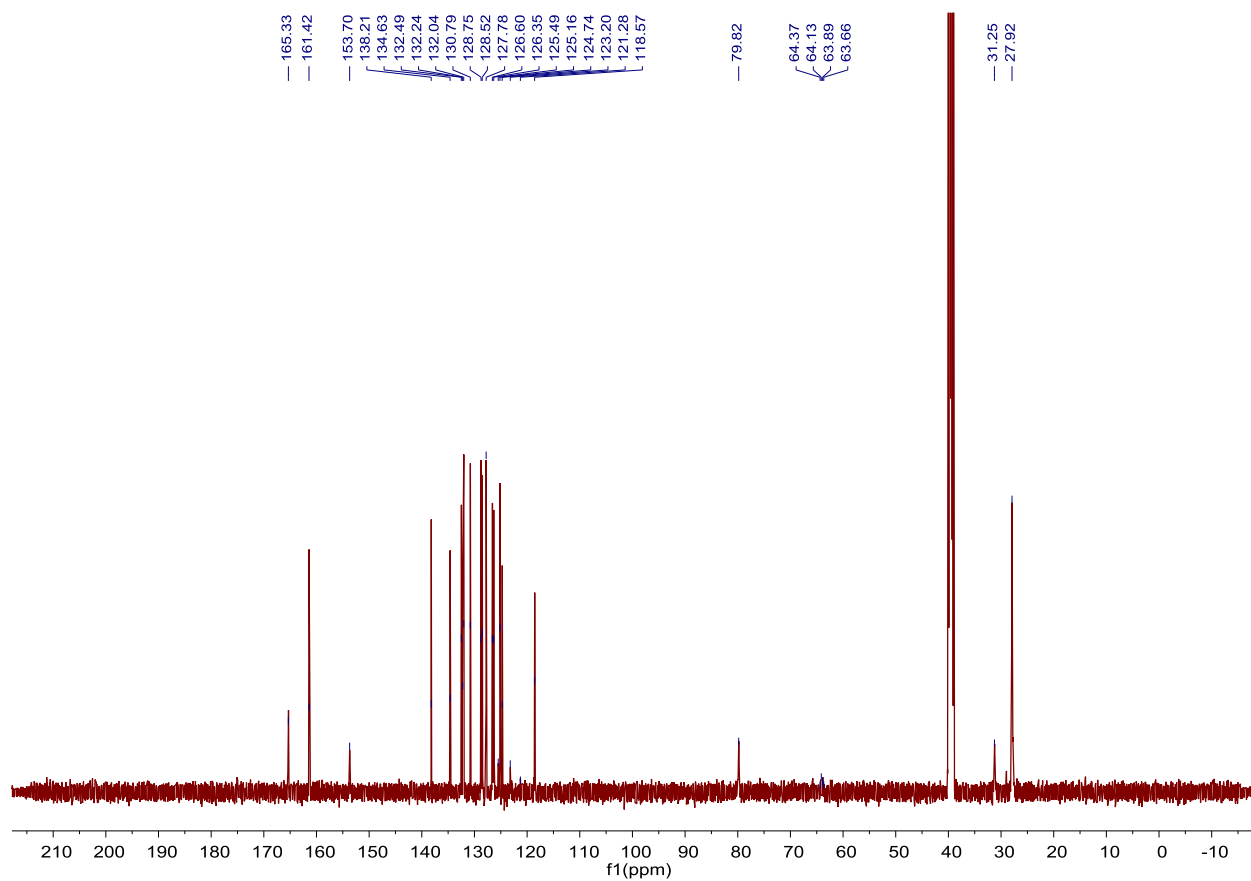
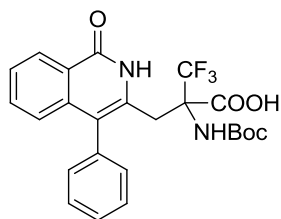


Figure S90. ^{13}C spectrum of **8** in $\text{DMSO-}d_6$

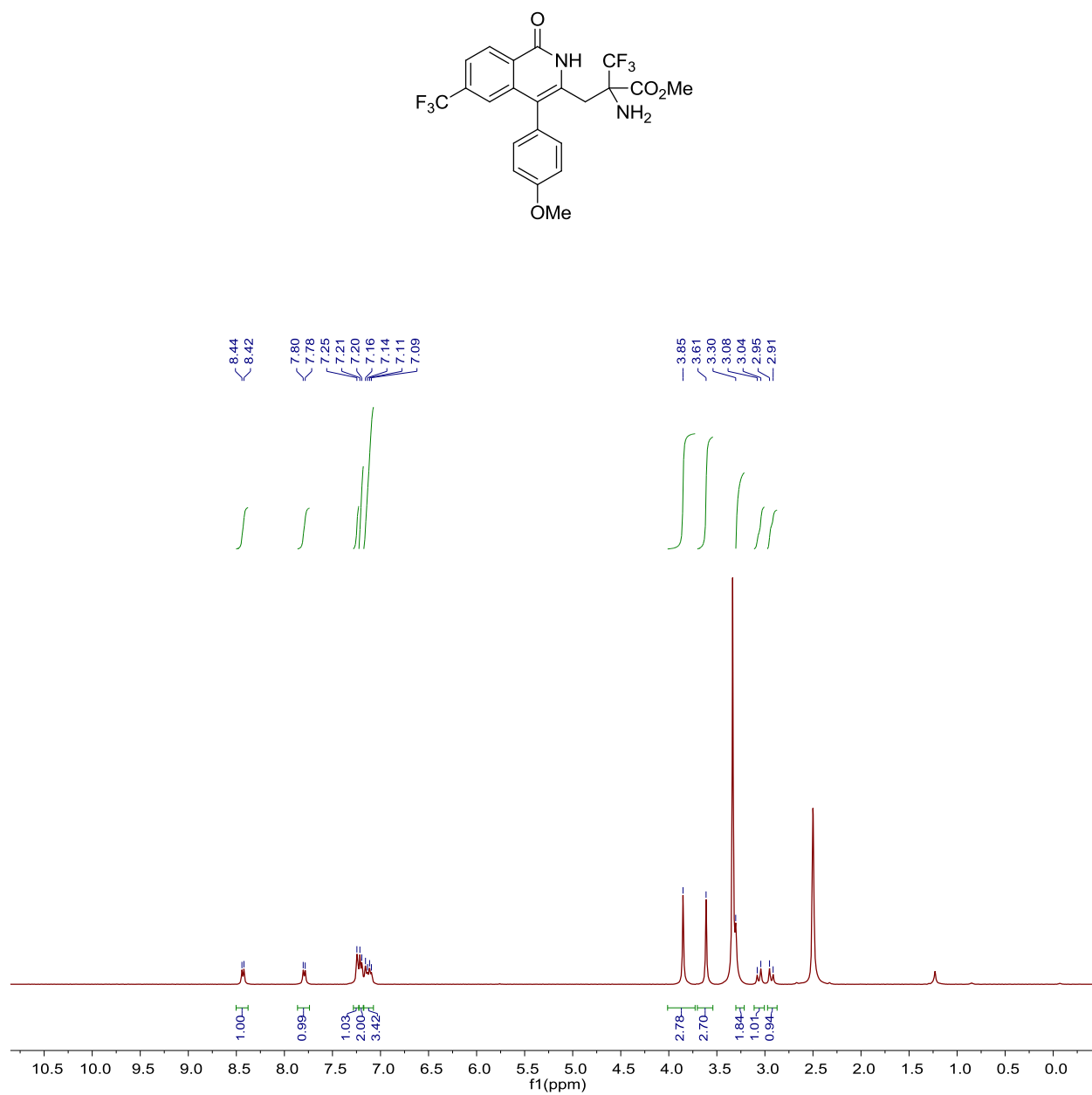


Figure S91. ^1H spectrum of **9** in DMSO- d_6

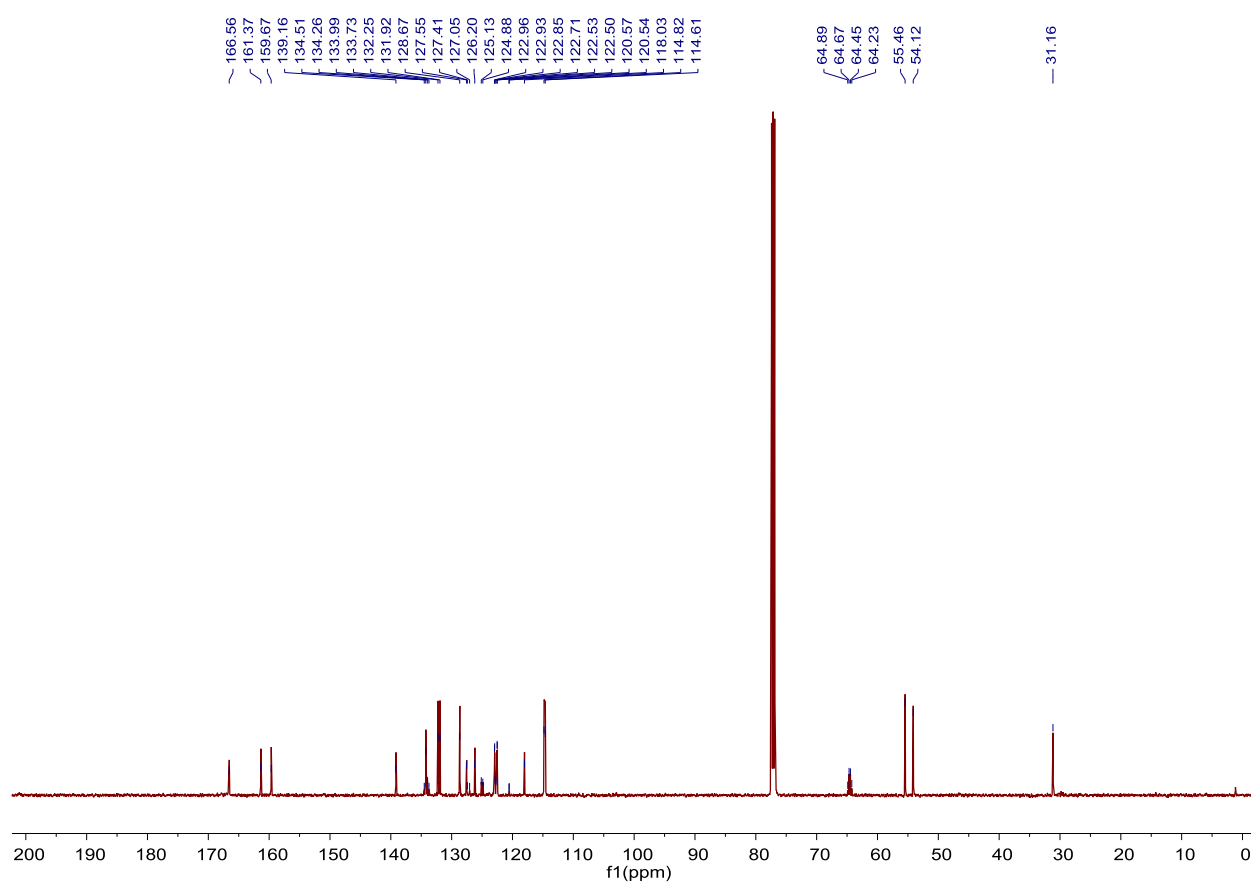
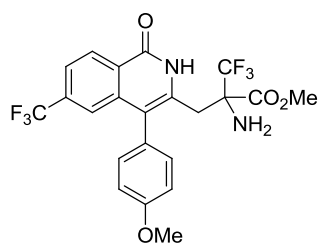
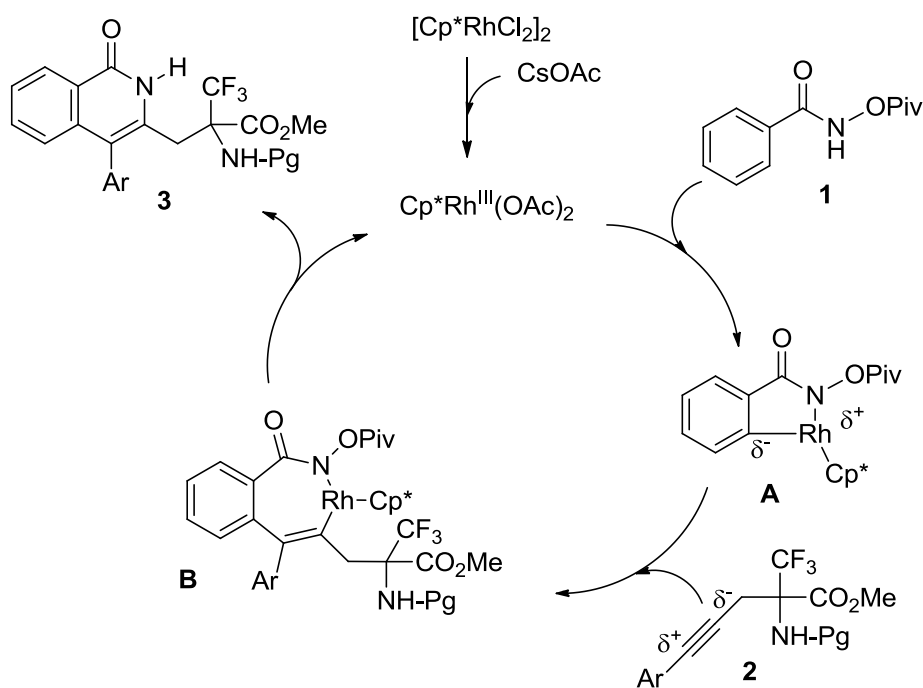


Figure S92. ^{13}C spectrum of **9** in CDCl_3

2. Proposed mechanism of [4+2]-annulation

A plausible reaction mechanism of regioselective [4+2]-annulation of aryl hydroxamate with internal acetylene-containing α -CF₃- α -amino esters **2** is depicted in Scheme 1S. After dissociation of the rhodium dimer, ligand exchange of the monomer with the present cesium salts provides a rhodium(III)-carboxylate species. Precomplexation to the directing N-pivaloyloxy amide moiety is followed by C-H activation to form rhodacycle **A**. The regioselective insertion of the alkyne triple bond into the C-Rh bond provides a seven-membered rhodacycle intermediate **B**. The observed selectivity can be probably explained by the coordination of Rh with the donor atom of alkyne according to its inherent polarity. Next, a concerted or stepwise C-N bond forming/N-O bond cleaving event occurs, affording the annulation product **3**, and releasing the Rh(III) catalyst.



Scheme 1S. Proposed mechanism.

3. X-ray Diffraction Study

Table S1. Crystal data, data collection and structure refinement parameters for **3a**

CCDC	2217085
Formula	C ₂₅ H ₂₅ F ₃ N ₂ O ₅
molecular wt	490.47
crystal size (mm)	0.20×0.12×0.02
crystal syst	monoclinic
space group	C2/c
Temperature (K)	150(2)
<i>a</i> (Å)	26.096(5)
<i>b</i> (Å)	13.702(4)
<i>c</i> (Å)	13.291(4)
β (deg)	95.018(9)
<i>V</i> (Å ³)	4734(2)
<i>Z</i>	8
<i>d</i> _{calc} (g·cm ⁻³)	1.376
linear absorption μ (cm ⁻¹)	1.11
<i>T</i> _{min} / <i>T</i> _{max}	0.769/0.862
2 θ _{max} (deg)	50
no. of unique reflns (<i>R</i> _{int})	4143 (0.1334)
no. of obs reflns (<i>I</i> > 2 σ (<i>I</i>))	1782
no. of params	329
<i>R</i> ₁ (on <i>F</i> for obsd reflns) ^a	0.0693
<i>wR</i> ₂ (on <i>F</i> ² for all reflns) ^b	0.1704
<i>GOOF</i>	0.975
Largest diff. peak/hole (e Å ⁻³)	0.263/-0.246

$$^a R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$^b wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma w(F_o^2)^2 \}^{1/2}$$

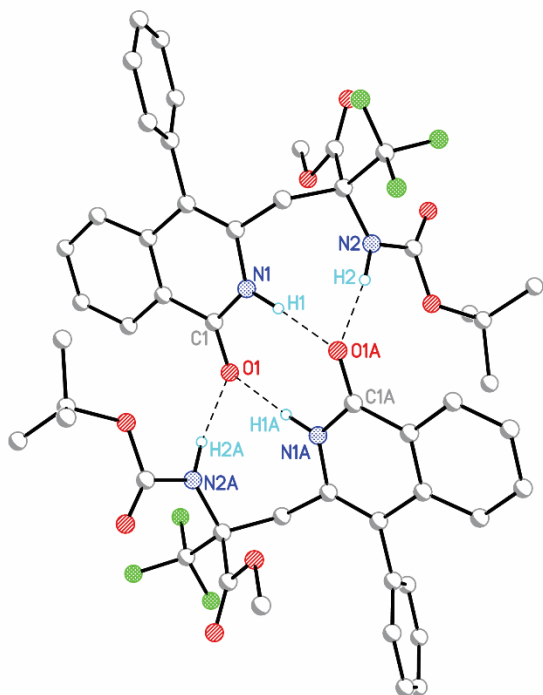


Figure S93. H-bonded dimer in the crystal of **3a**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(1)#1	0.96(6)	1.91(5)	2.873(5)	175(3)
N(2)-H(2)...O(1)#1	1.00(4)	1.88(4)	2.862(5)	170(4)

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1/2, -y+1/2, -z+1$