Supporting information for:

Total synthesis of phorbazole B

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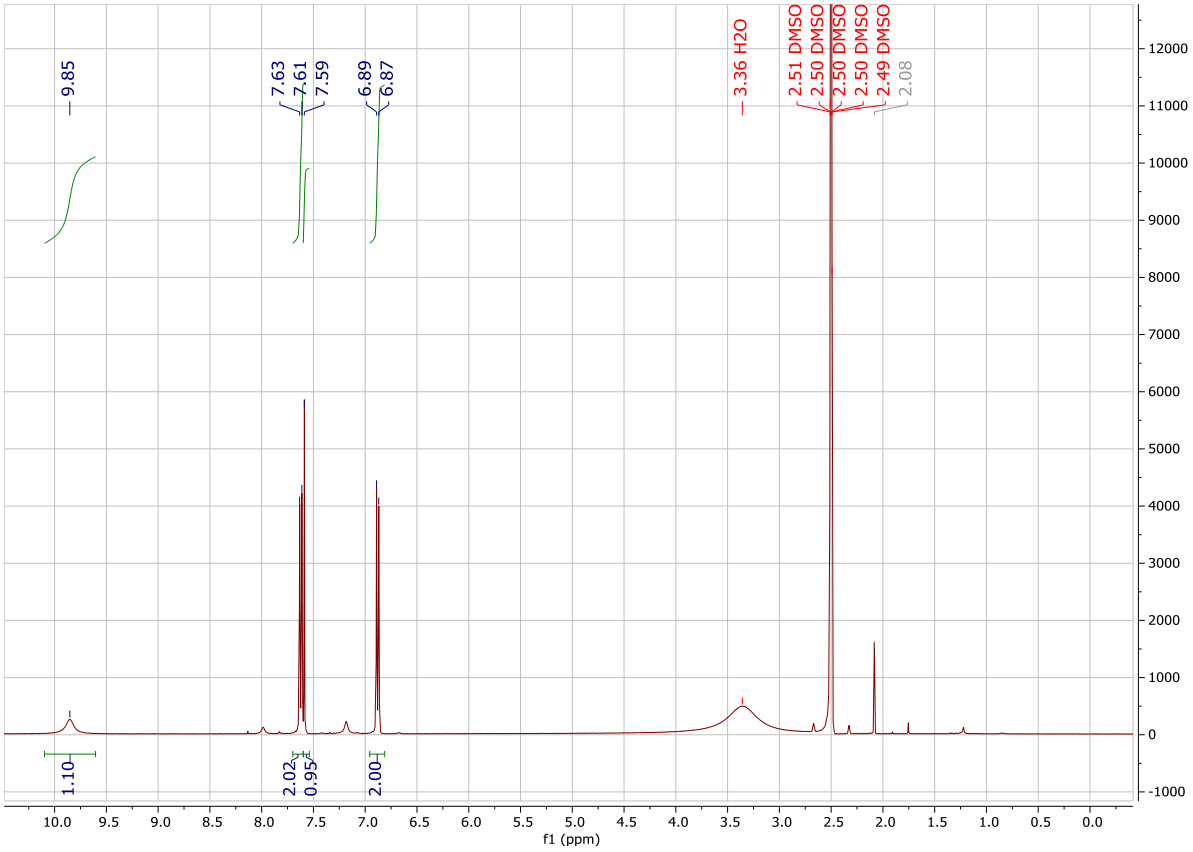


Figure S1. 1H-NMR spectrum (400 MHz) of phorbazole B (**2**)

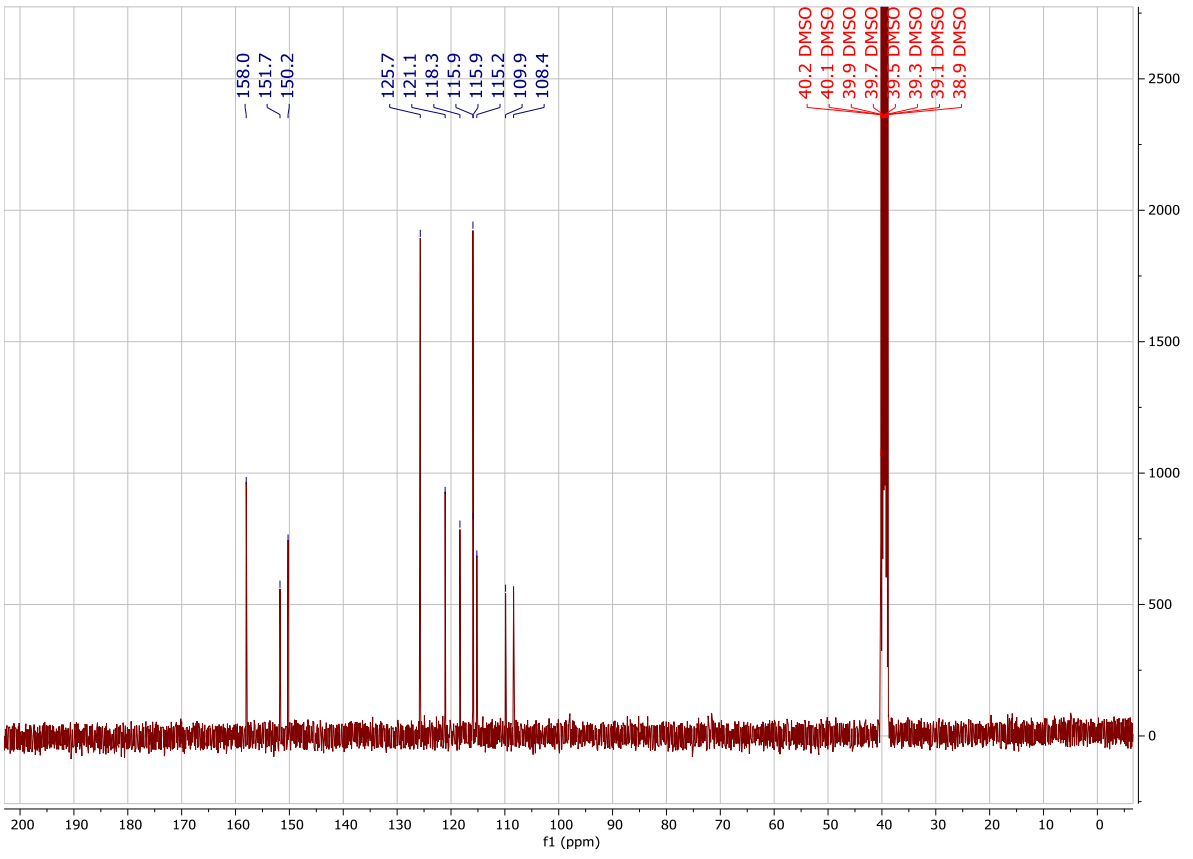


Figure S2. ^{13}C-NMR spectrum (101 MHz) of phorbazole B (**2**)

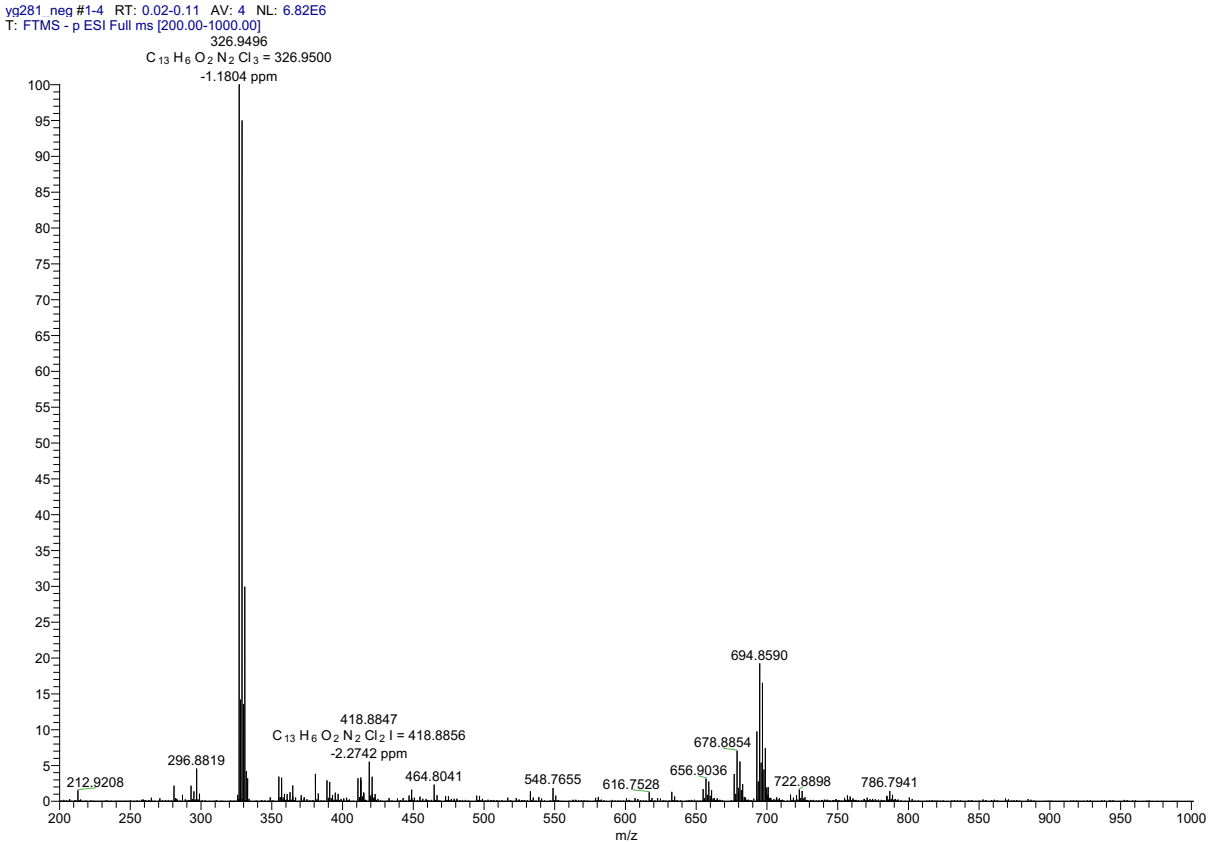
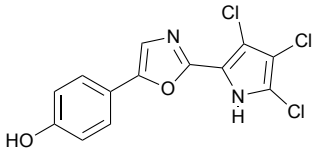


Figure S3. High resolution mass spectrum of phorbazole B (**2**)

Table S1. Comparison of the spectral data for synthetic and isolated phorbazole B (**2**)



Synthetic **2** ^{1}H-NMR, 400 MHz, $(CD_3)_2SO$	Isolated **2** ^{1}H-NMR, 500 MHz, $(CD_3)_2SO$
13.57 (s, 1H)	-
9.85 (s, 1H)	-
7.62 (d, *J* = 7.7 Hz, 2H)	7.63 (d, *J* = 8.0 Hz)
7.59 (s, 1H)	7.60 (s)
6.88 (d, *J* = 7.7 Hz, 2H)	6.88 (d, *J* = 8.0 Hz)
Synthetic **2** ^{13}C-NMR, 101 MHz, $(CD_3)_2SO$	Isolated **2** ^{13}C-NMR, 150 MHz, $(CD_3)_2SO$
158.0	158.0
151.7	151.6
150.2	150.3
125.7	125.7
121.1	121.1
118.3	118.3
115.9	115.9
115.8	115.8
115.2	115.0
109.9	109.9
108.4	108.6

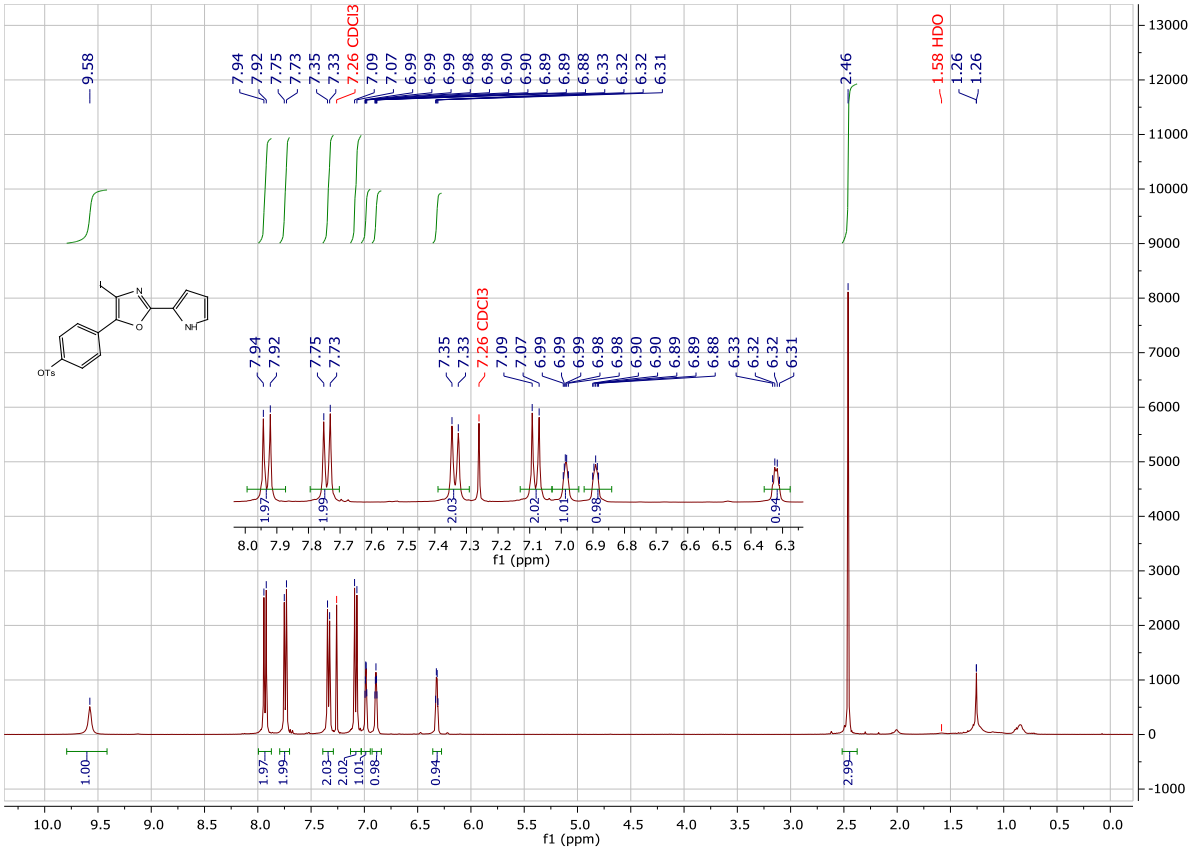


Figure S4. ^{1}H-NMR spectrum (400 MHz) of **13**

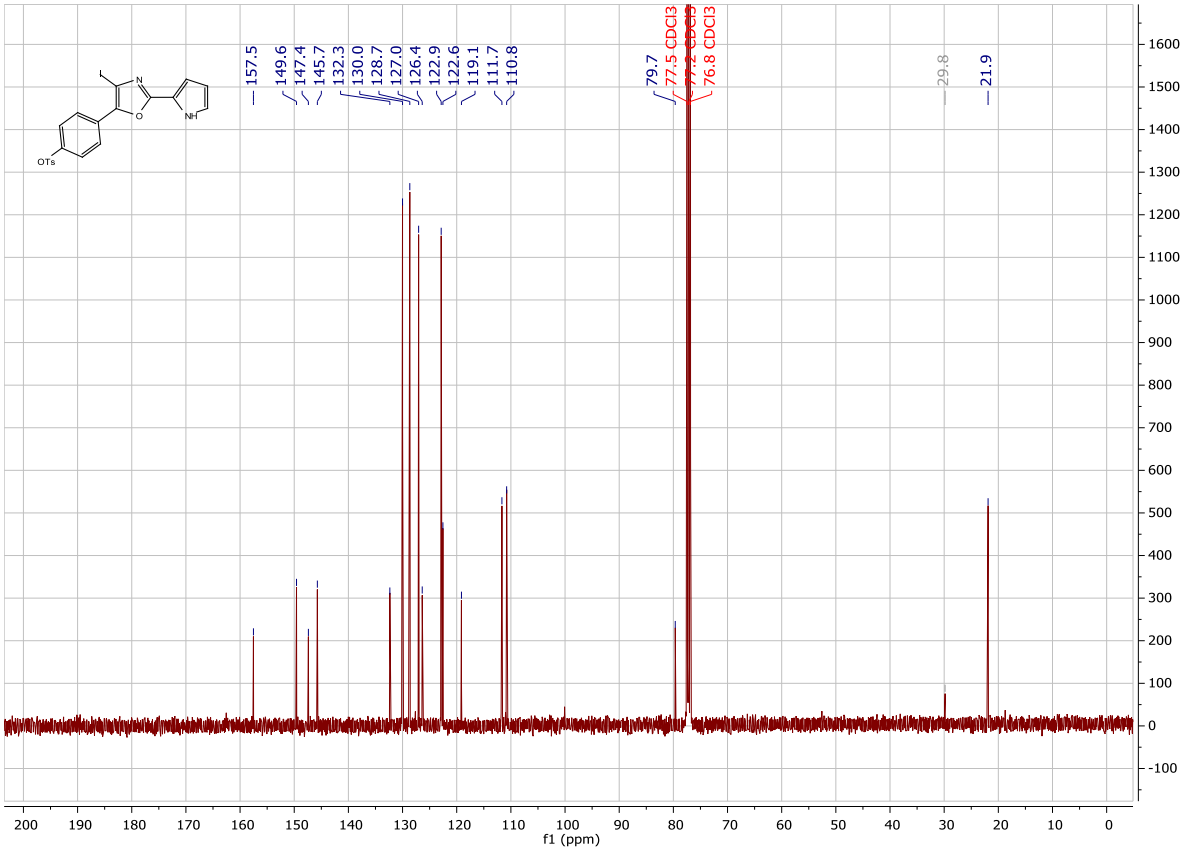


Figure S5. 13C-NMR spectrum (101 MHz) of **13**

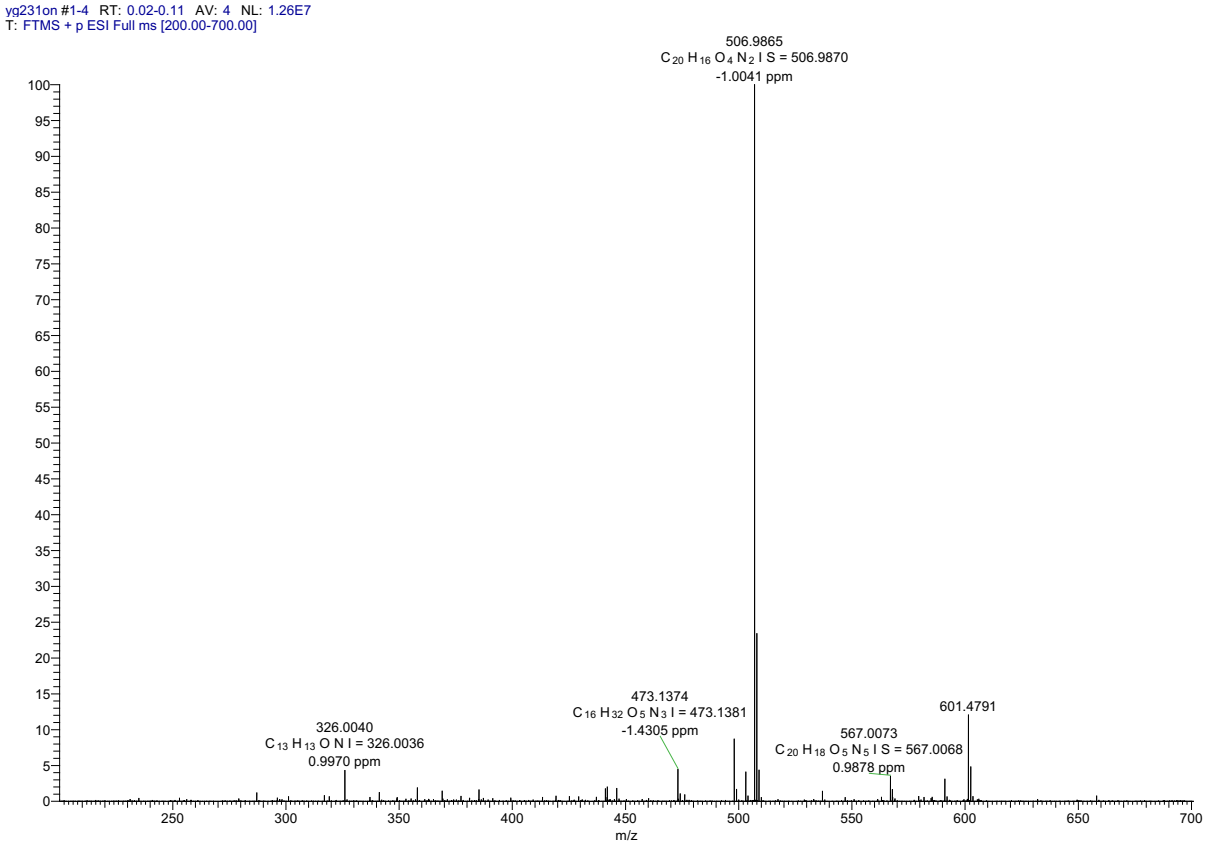


Figure S6. High resolution mass spectrum of **13**

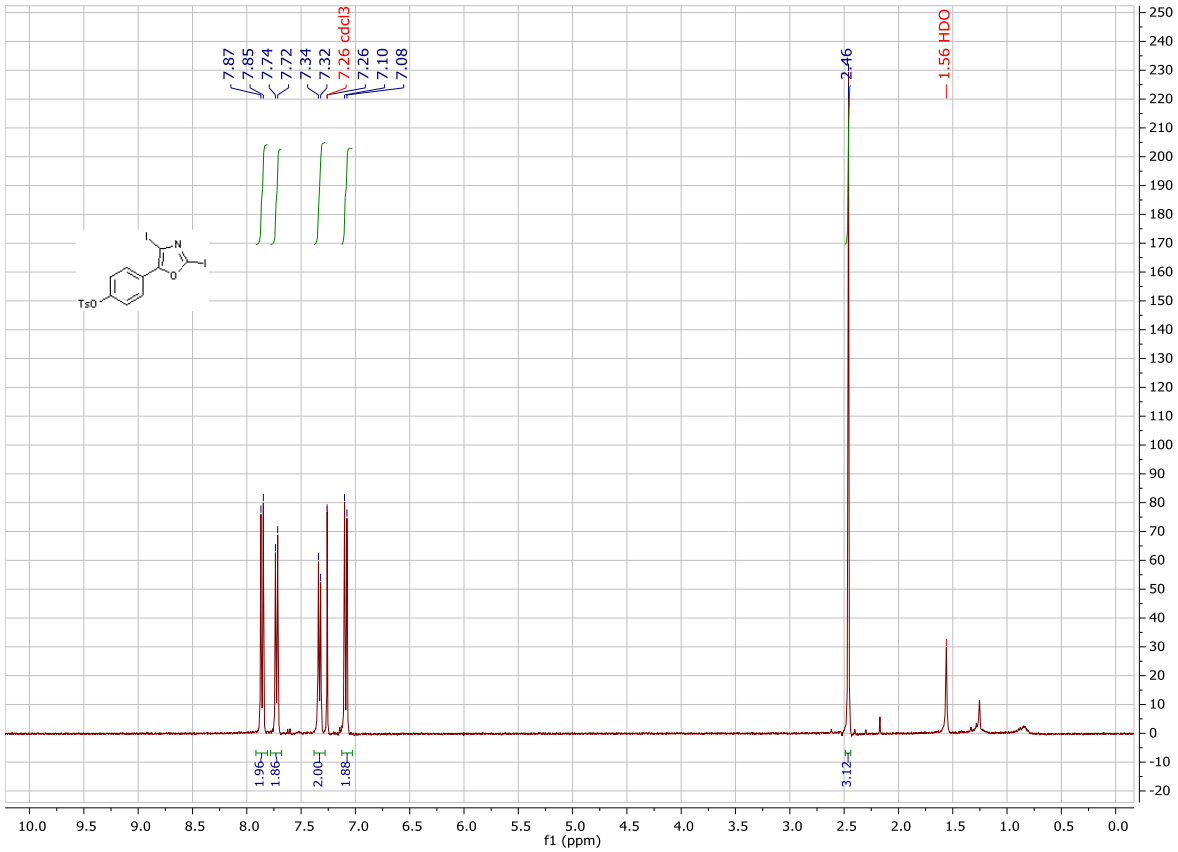


Figure S7. ^{1}H-NMR spectrum (400 MHz) of **14**

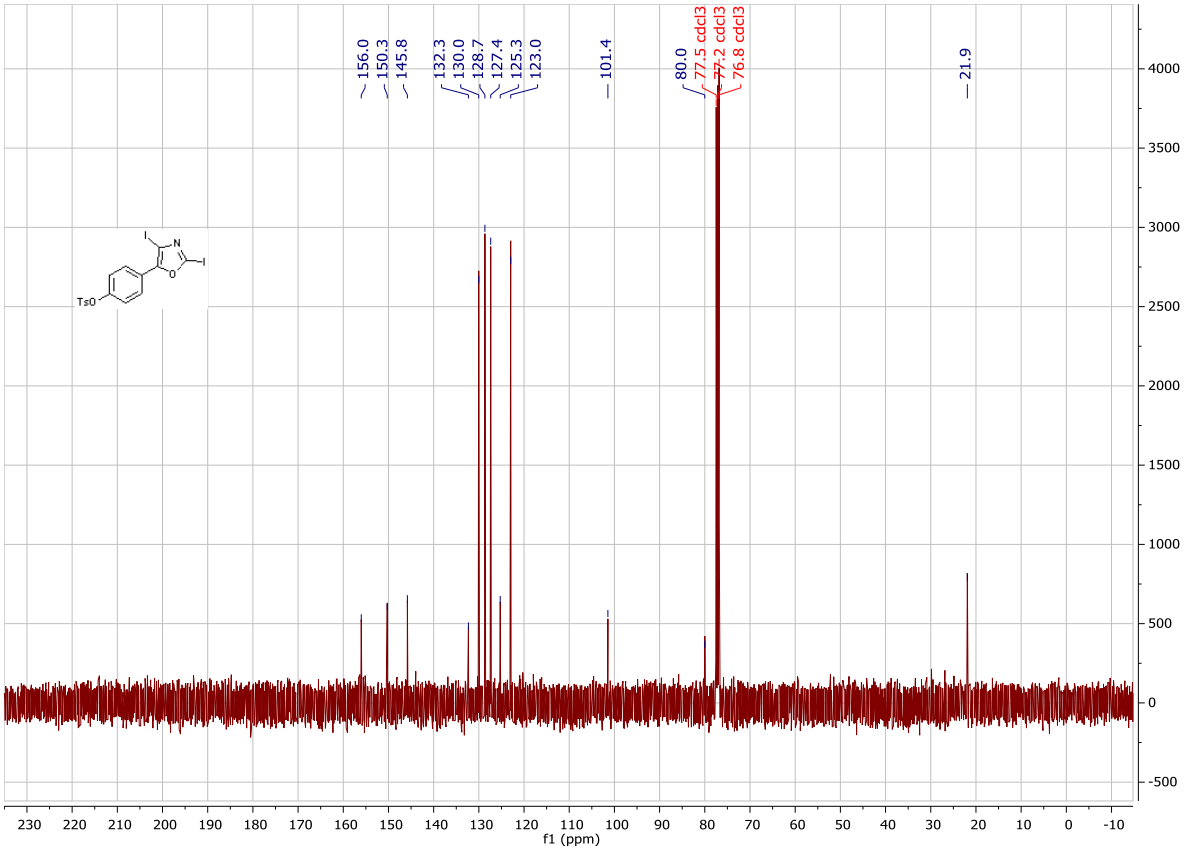


Figure S8. ^{13}C-NMR spectrum (101 MHz) of **14**

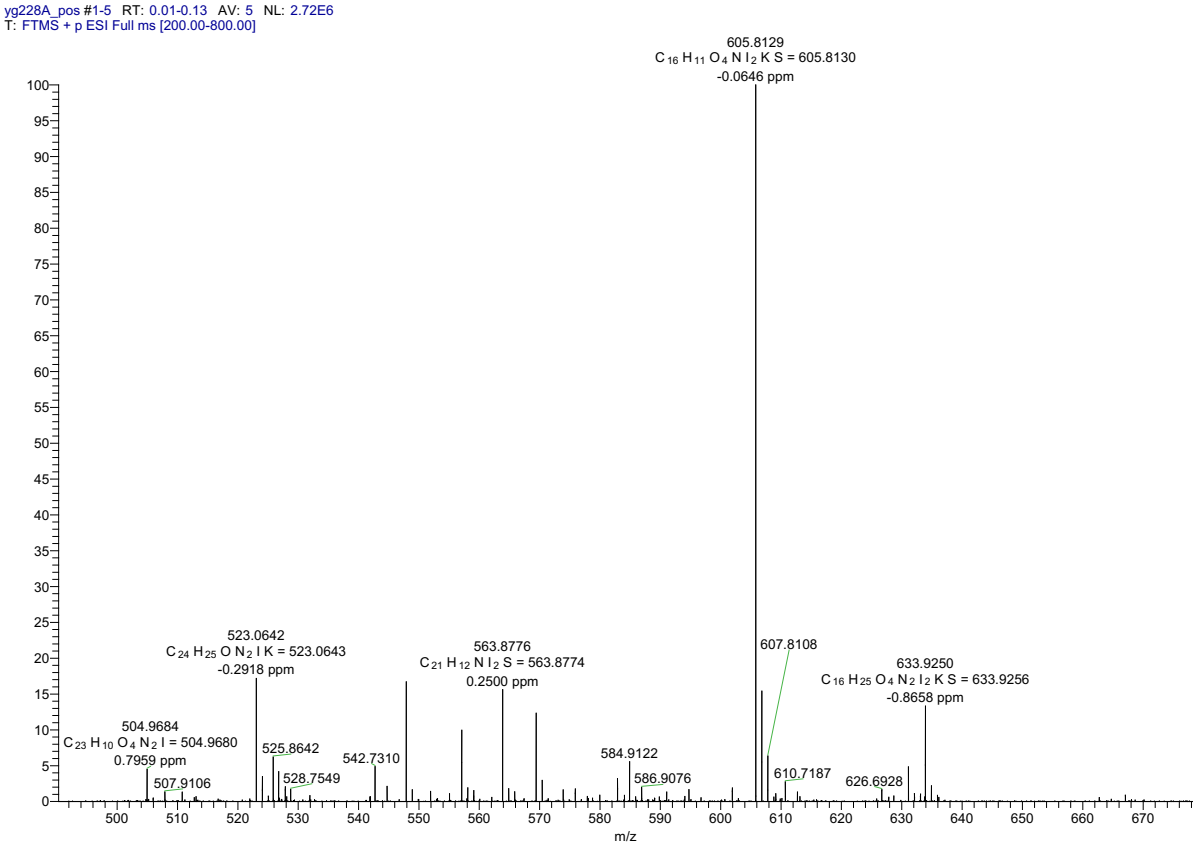


Figure S9. High resolution mass spectrum of **14**

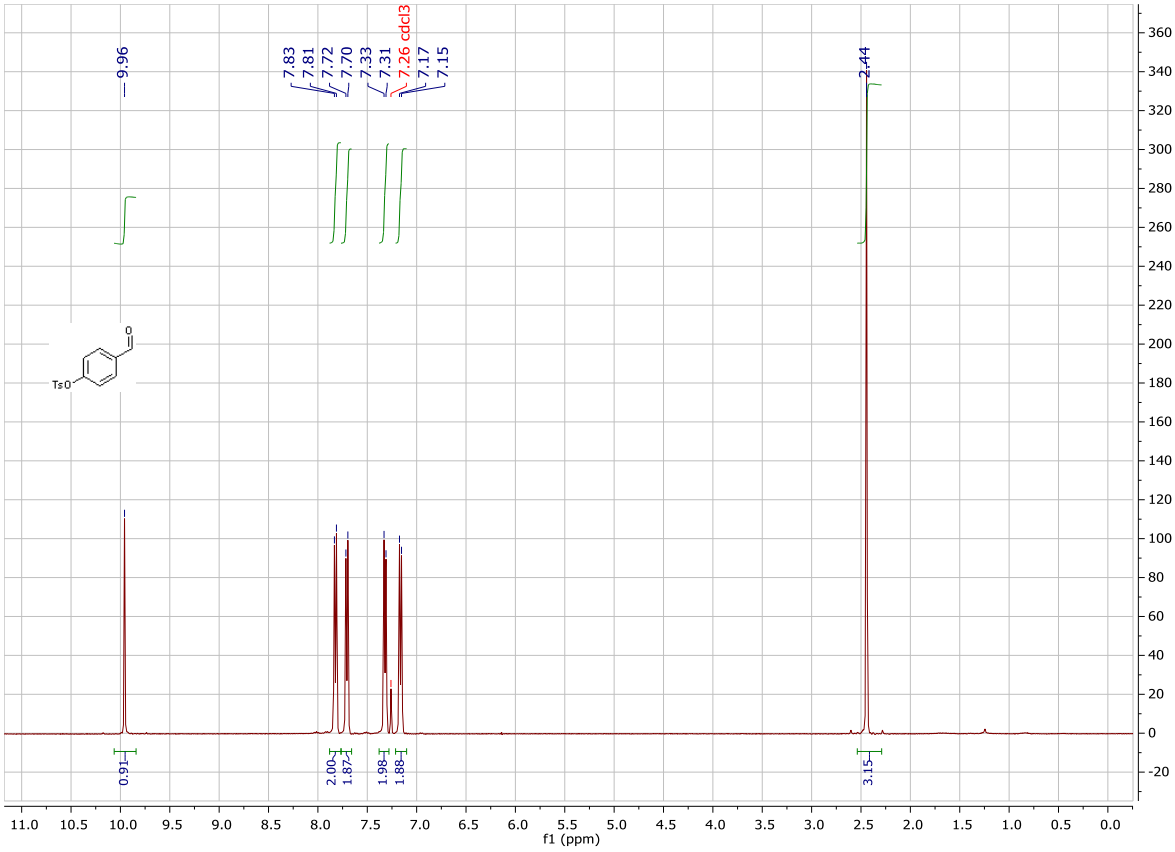


Figure S10. ^{1}H-NMR spectrum (400 MHz) of **15**

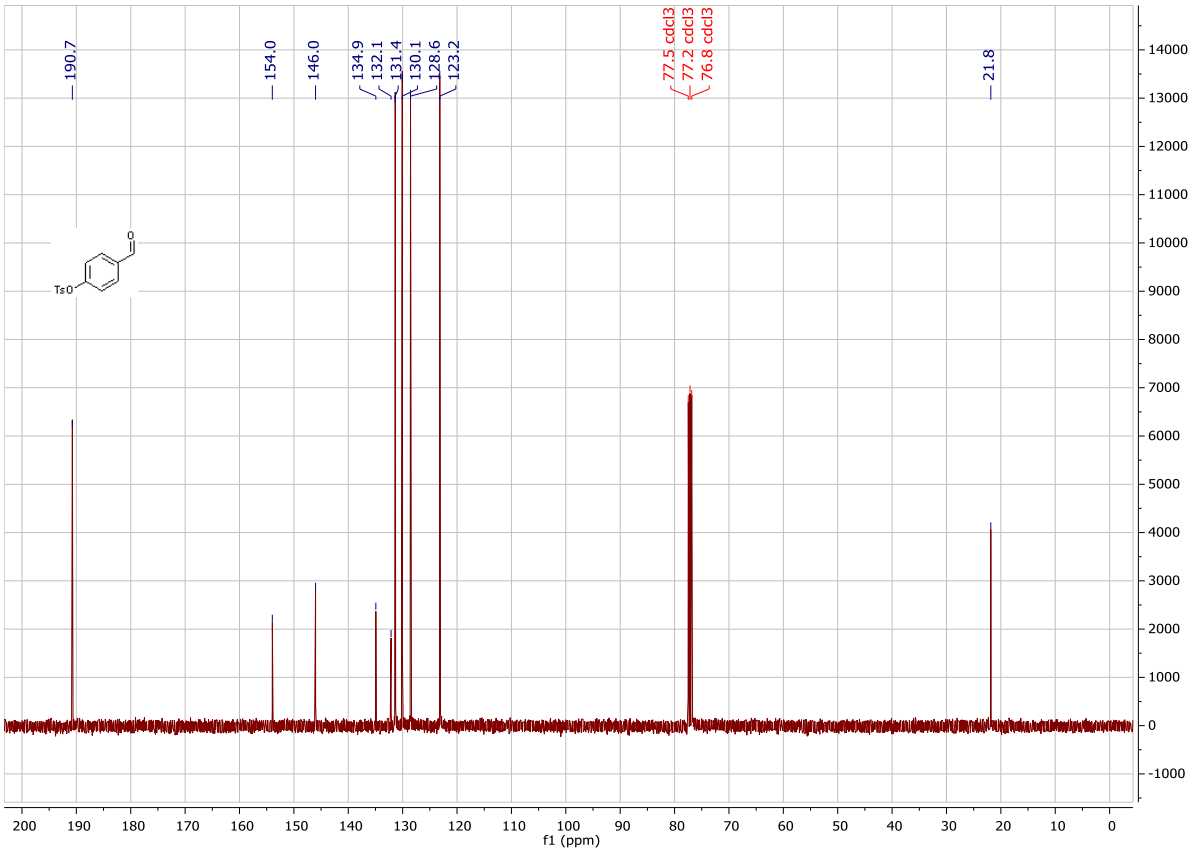


Figure S11. ^{13}C-NMR spectrum (101 MHz) of **15**

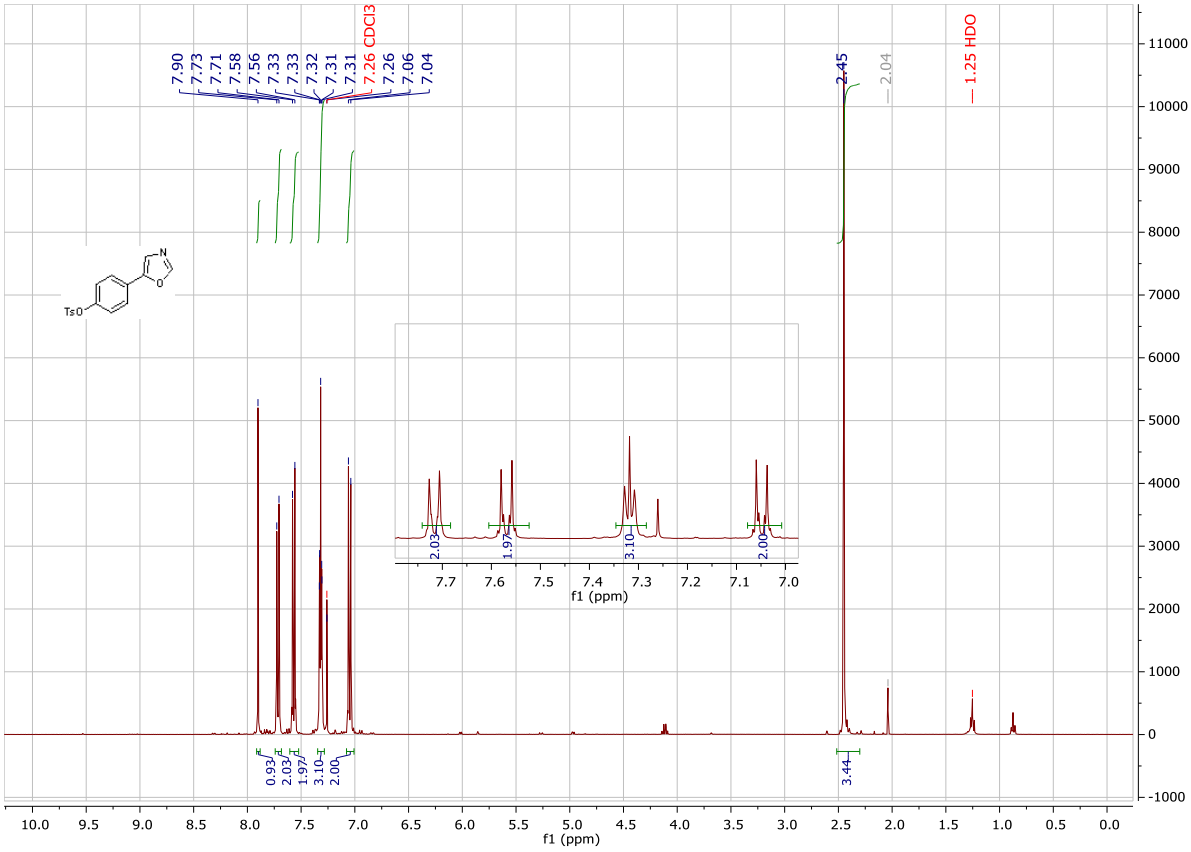


Figure S12. ^{1}H-NMR spectrum (400 MHz) of **16**

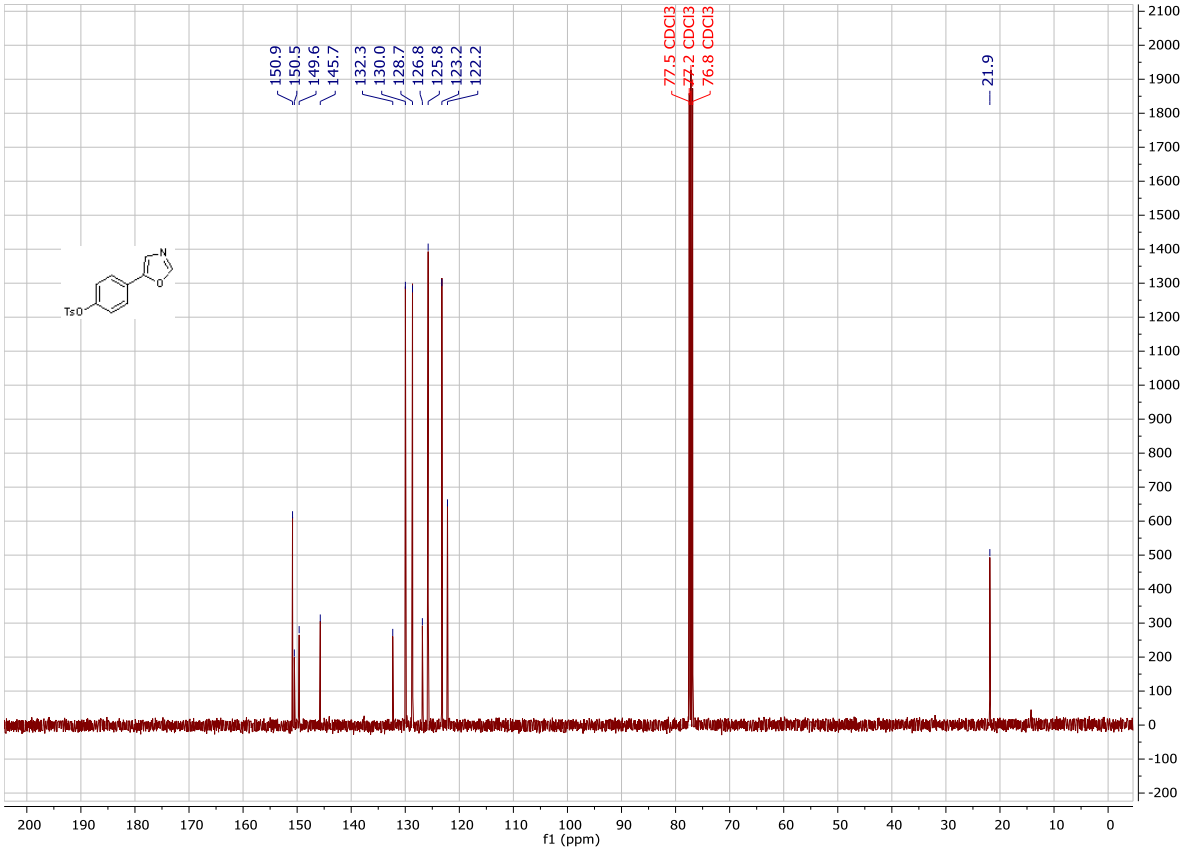


Figure S13. ^{13}C-NMR spectrum (101 MHz) of **16**

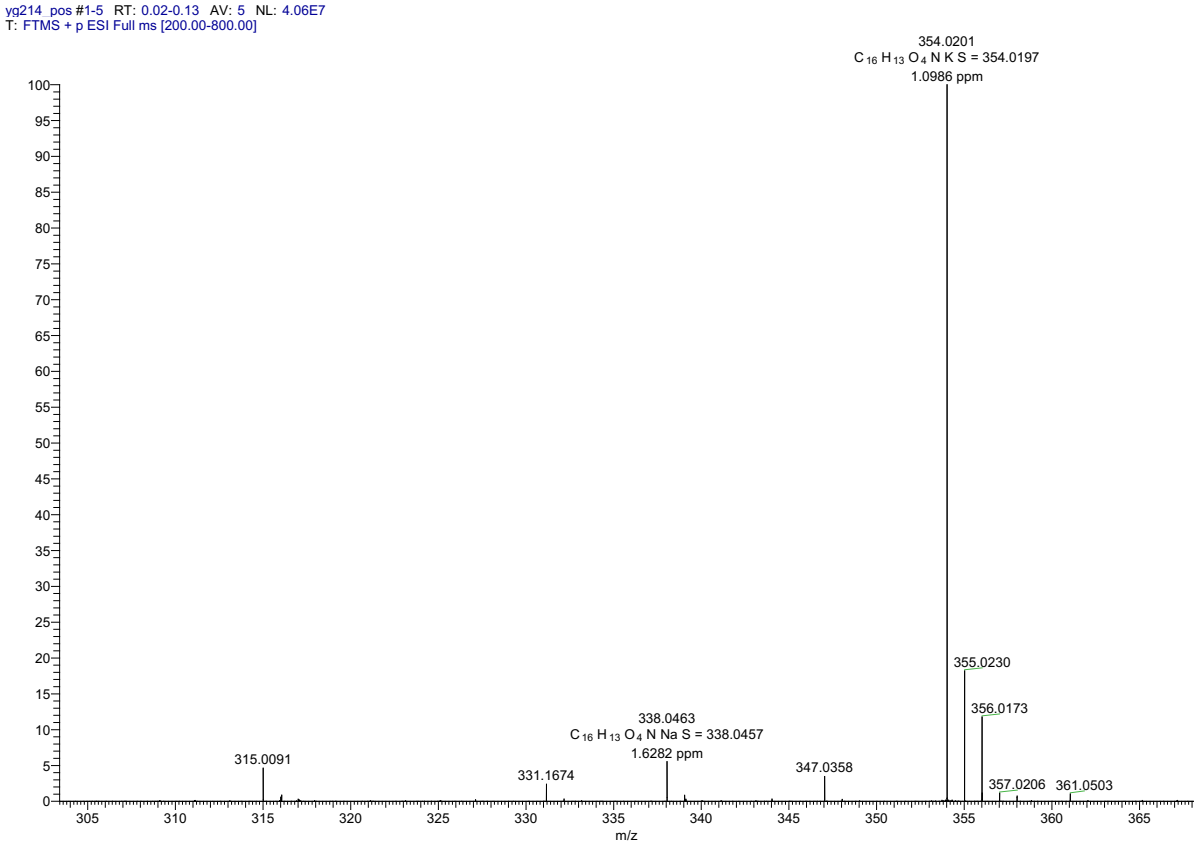


Figure S14.High resolution mass spectrum of **16.**

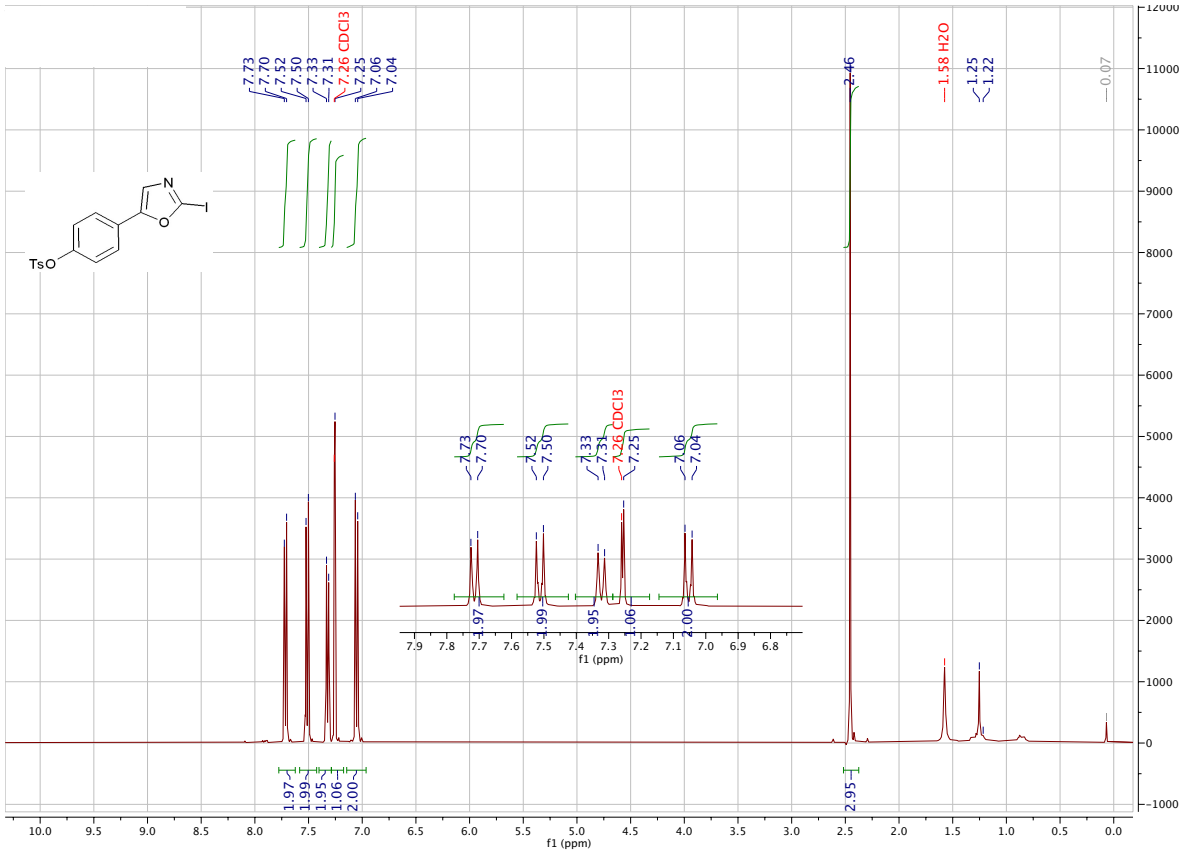


Figure S15. 1H-NMR spectrum (400 MHz) of **17**

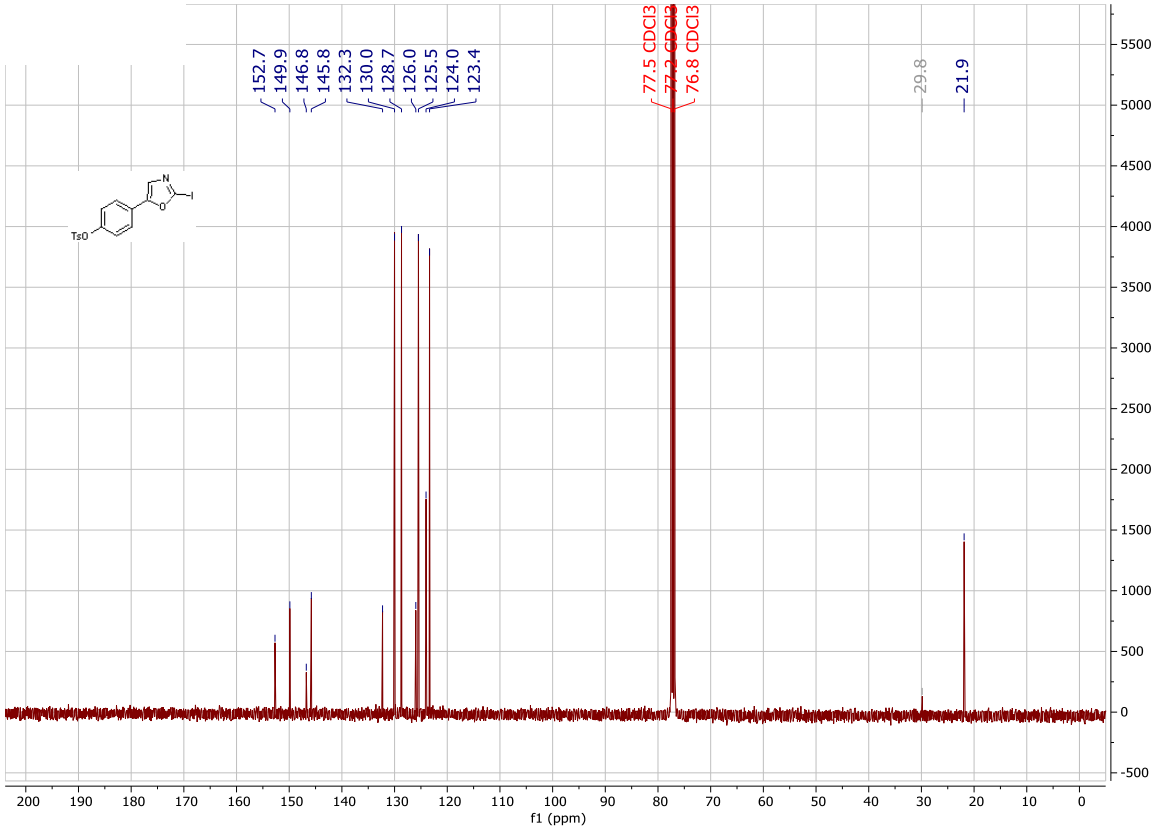


Figure S16. ^{13}C-NMR spectrum (101 MHz) of **17**

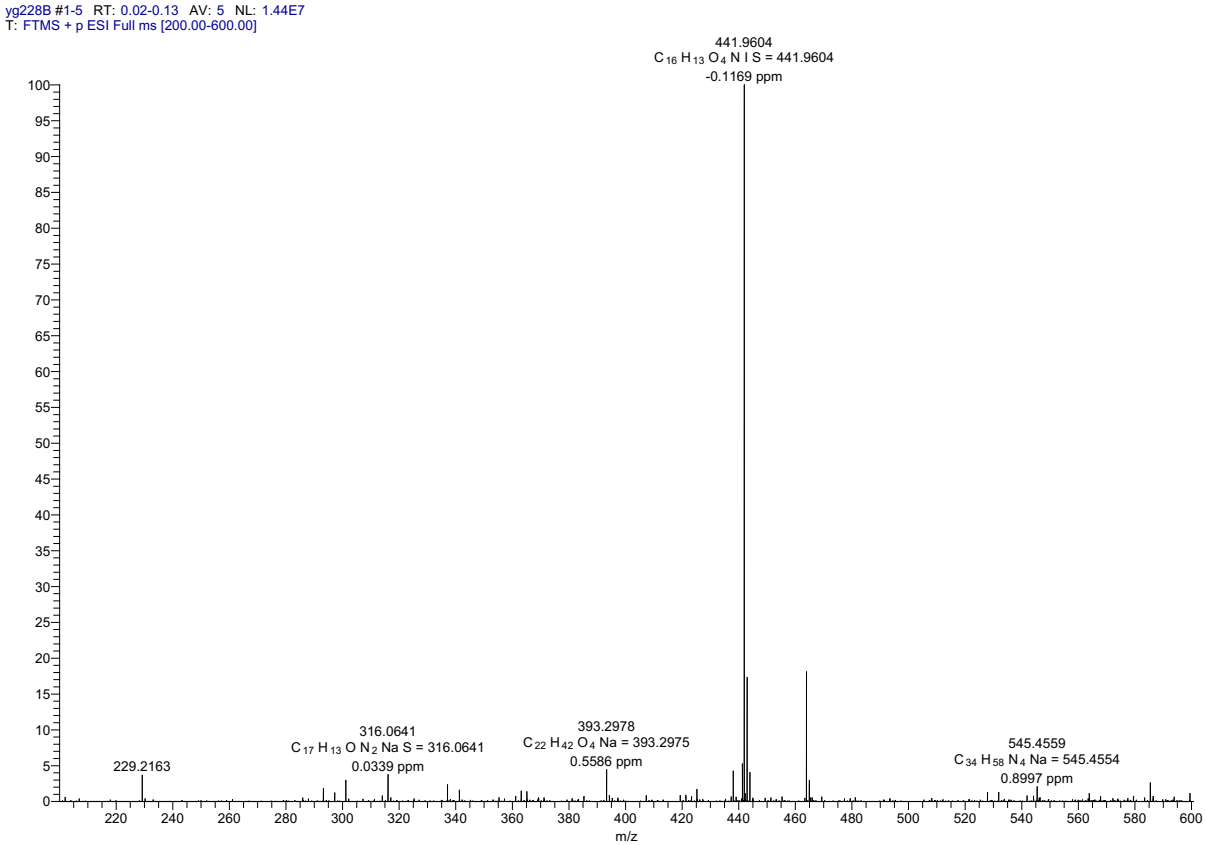


Figure S17.High resolution mass spectrum of **17.**

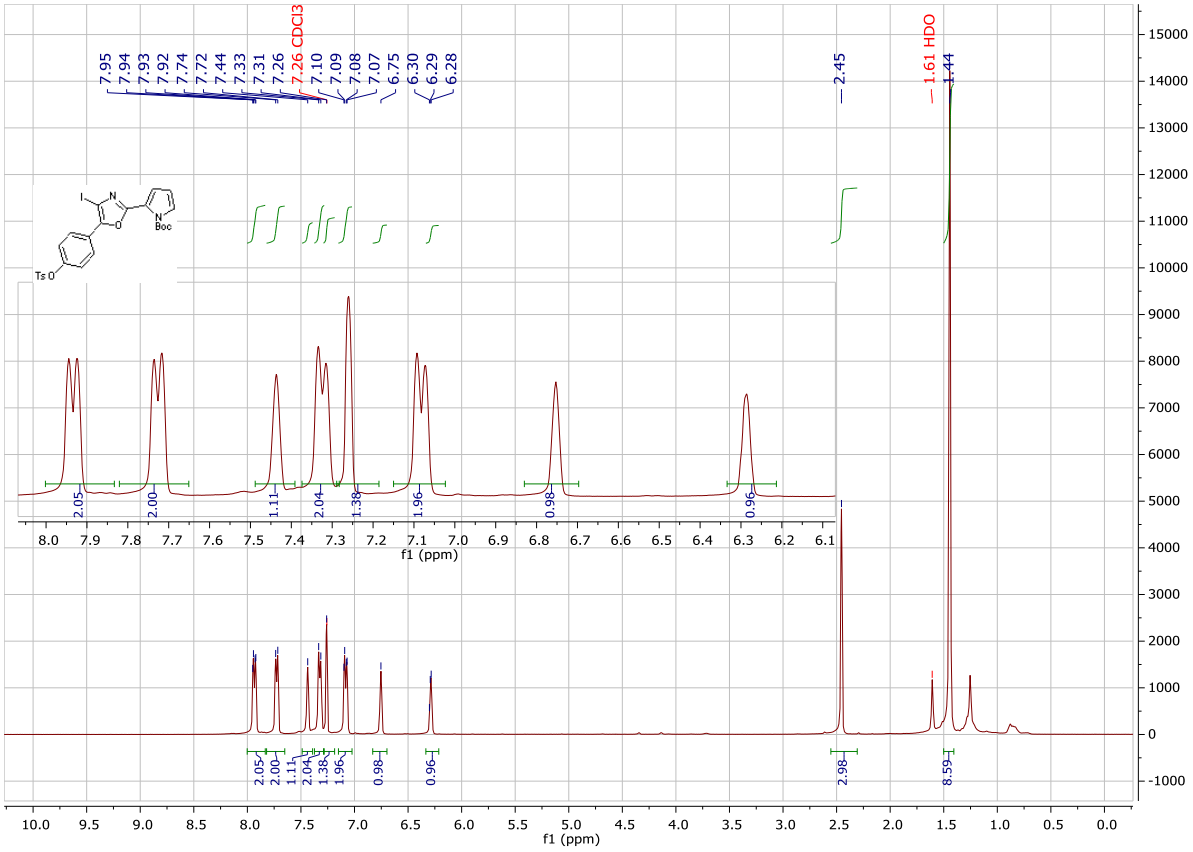


Figure S18. ^{1}H-NMR spectrum (400 MHz) of **18**

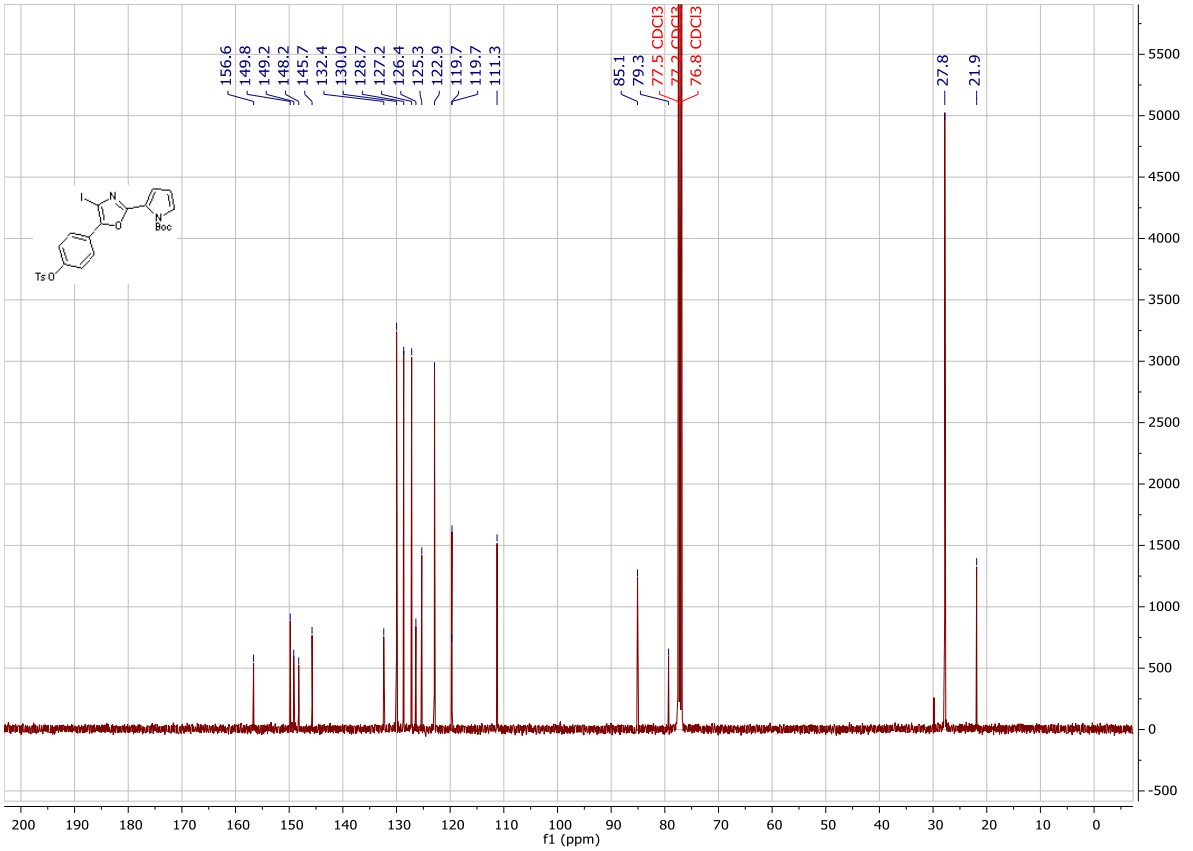


Figure S19. ^{13}C-NMR spectrum (101 MHz) of **18**

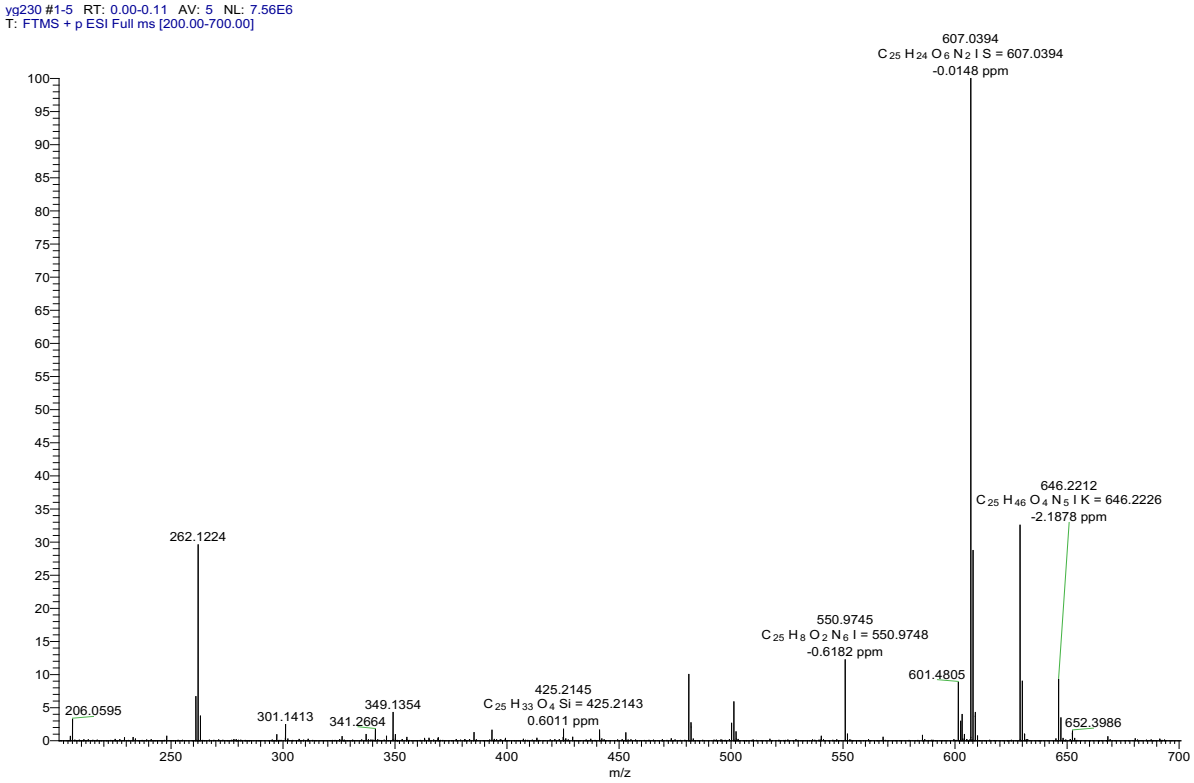


Figure S20.High resolution mass spectrum of **18.**

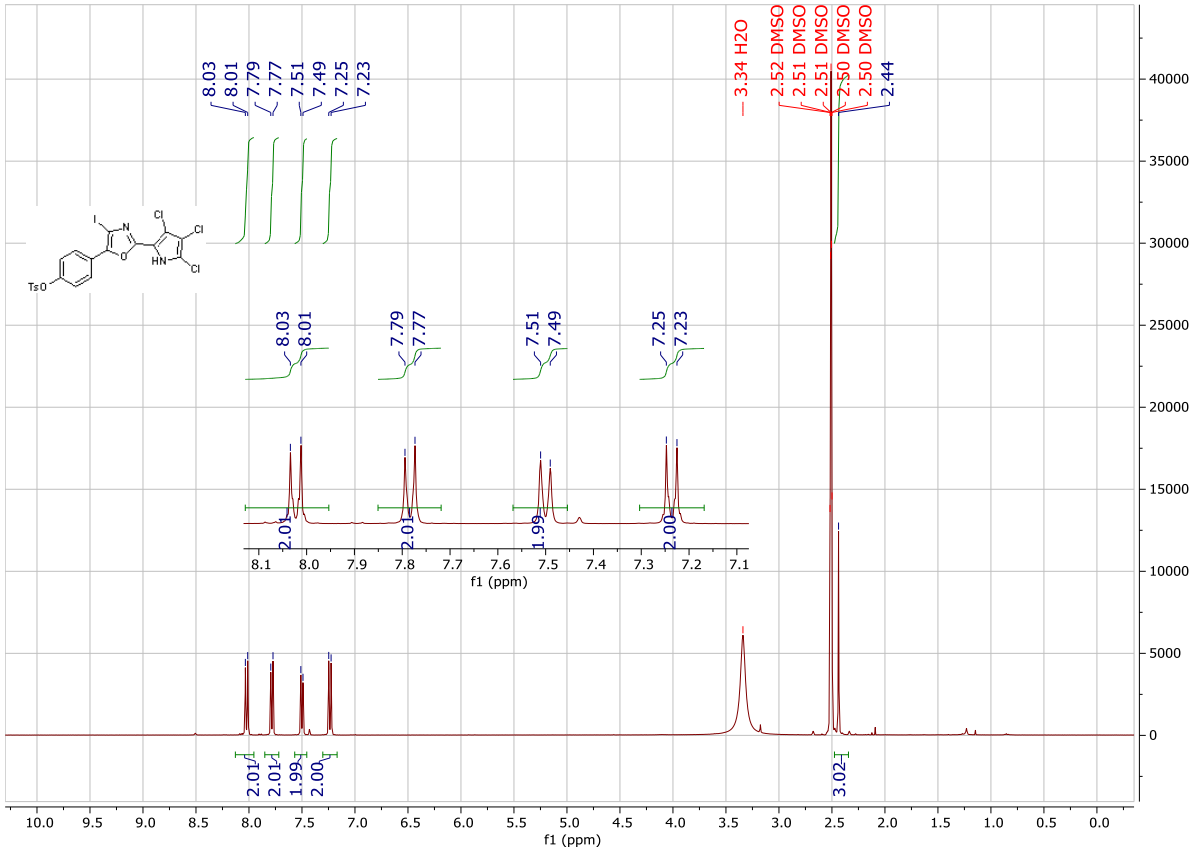


Figure S21. 1H-NMR spectrum (400 MHz) of **19**.

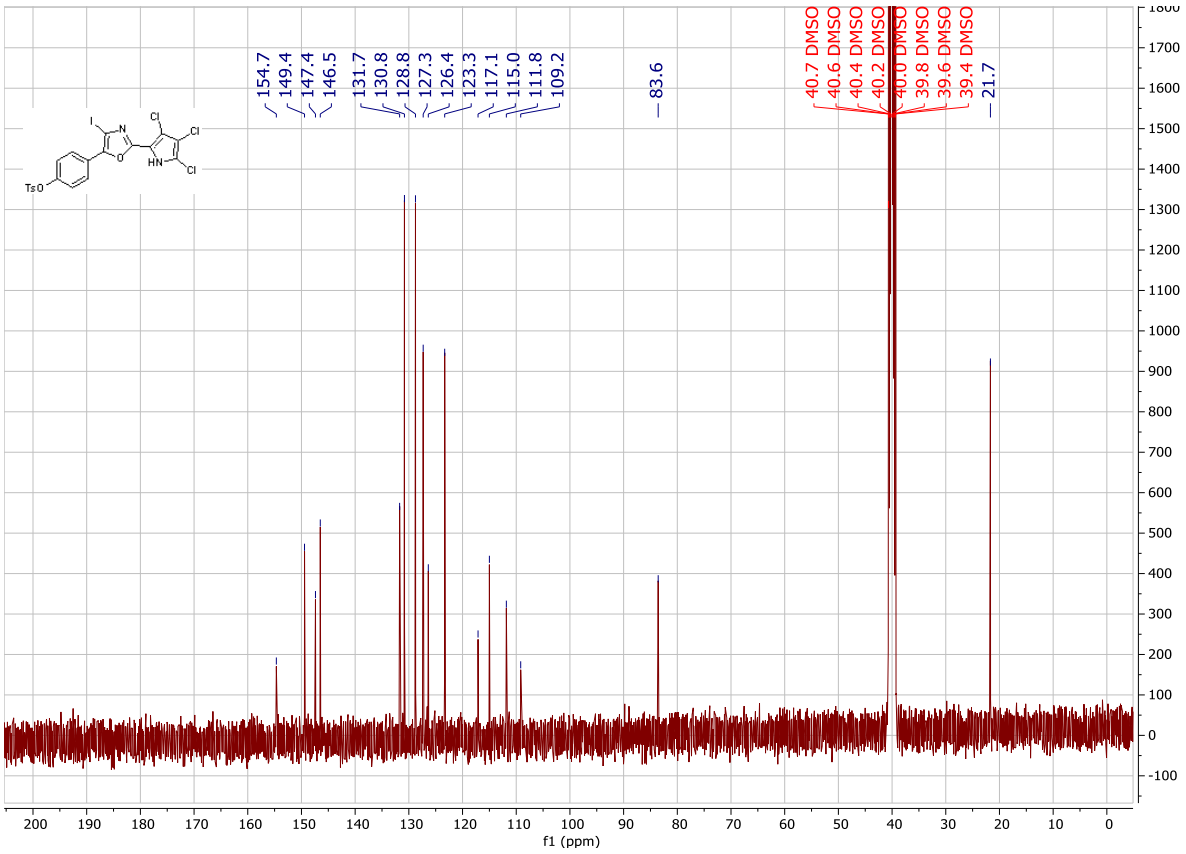


Figure S22. 13C-NMR spectrum (101 MHz) of **19**.

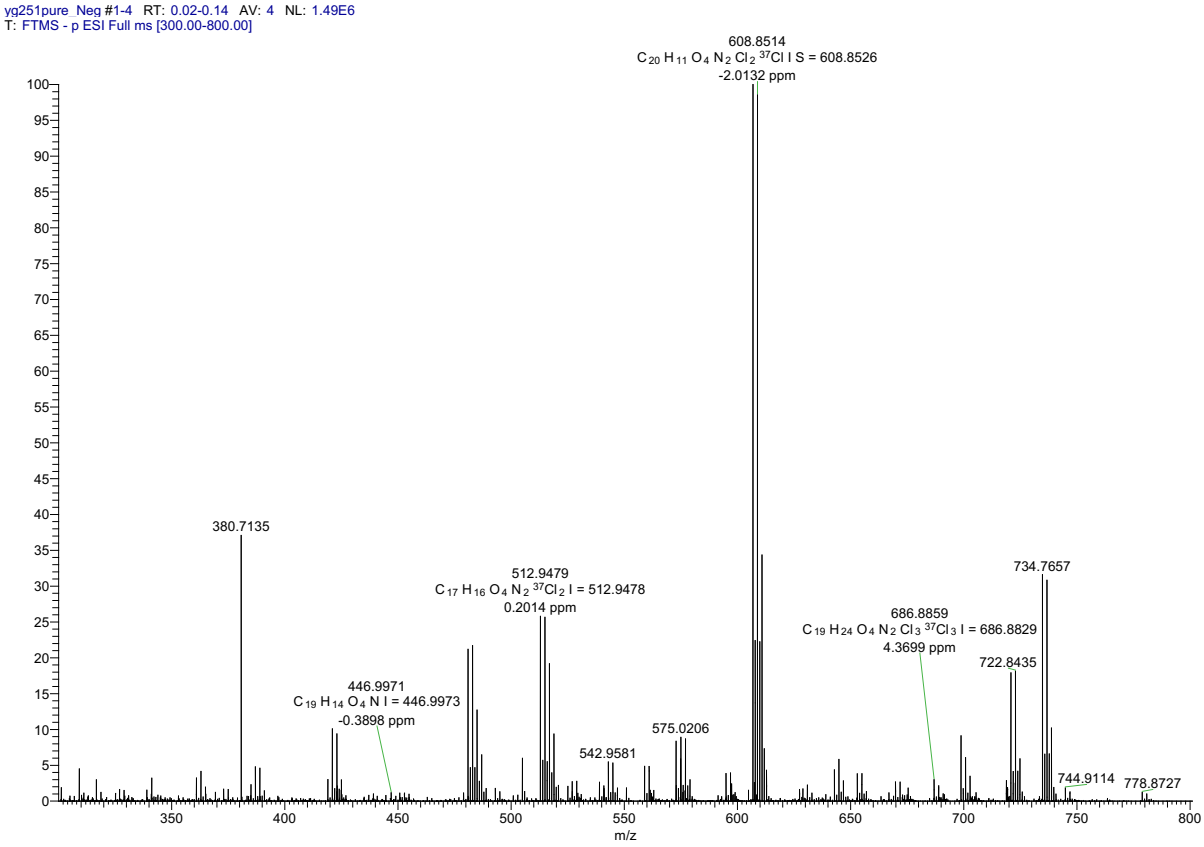


Figure S23.High resolution mass spectrum of **19.**

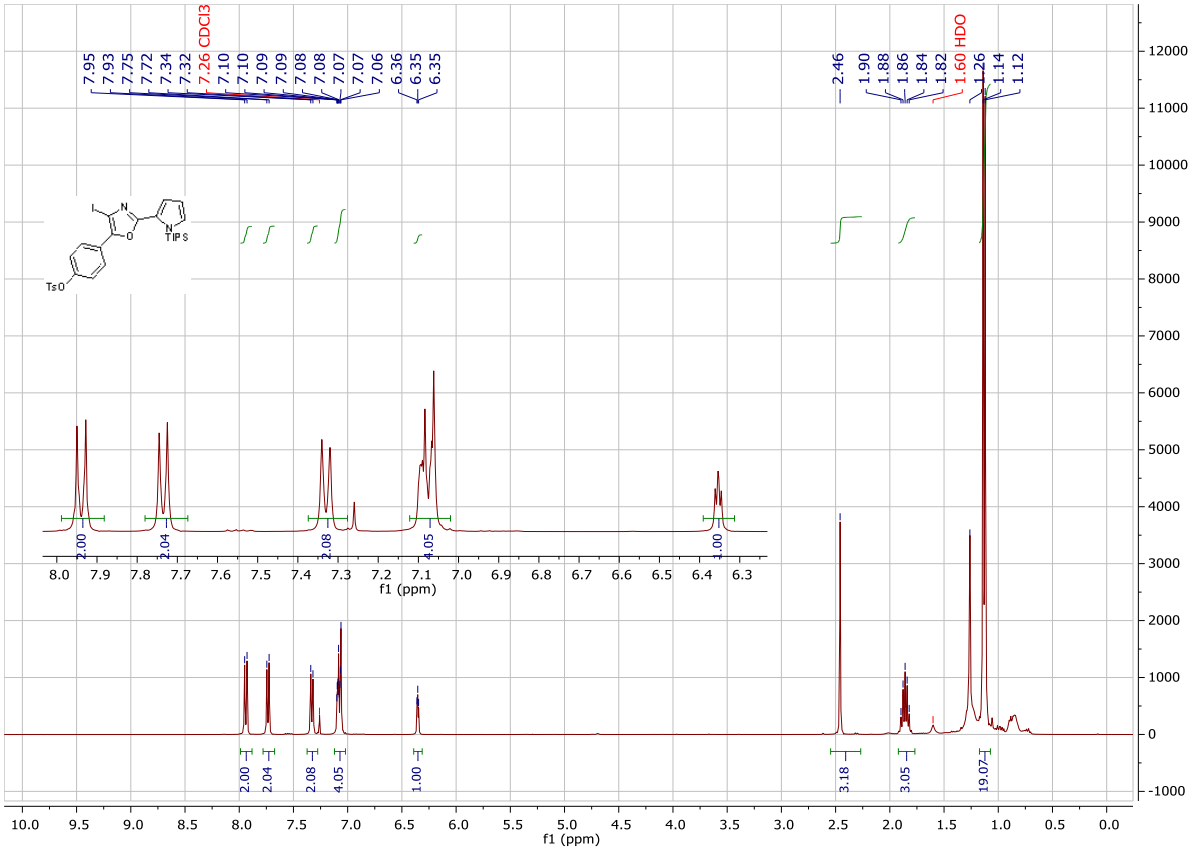


Figure S24. ^{1}H-NMR spectrum (400 MHz) of **20b**

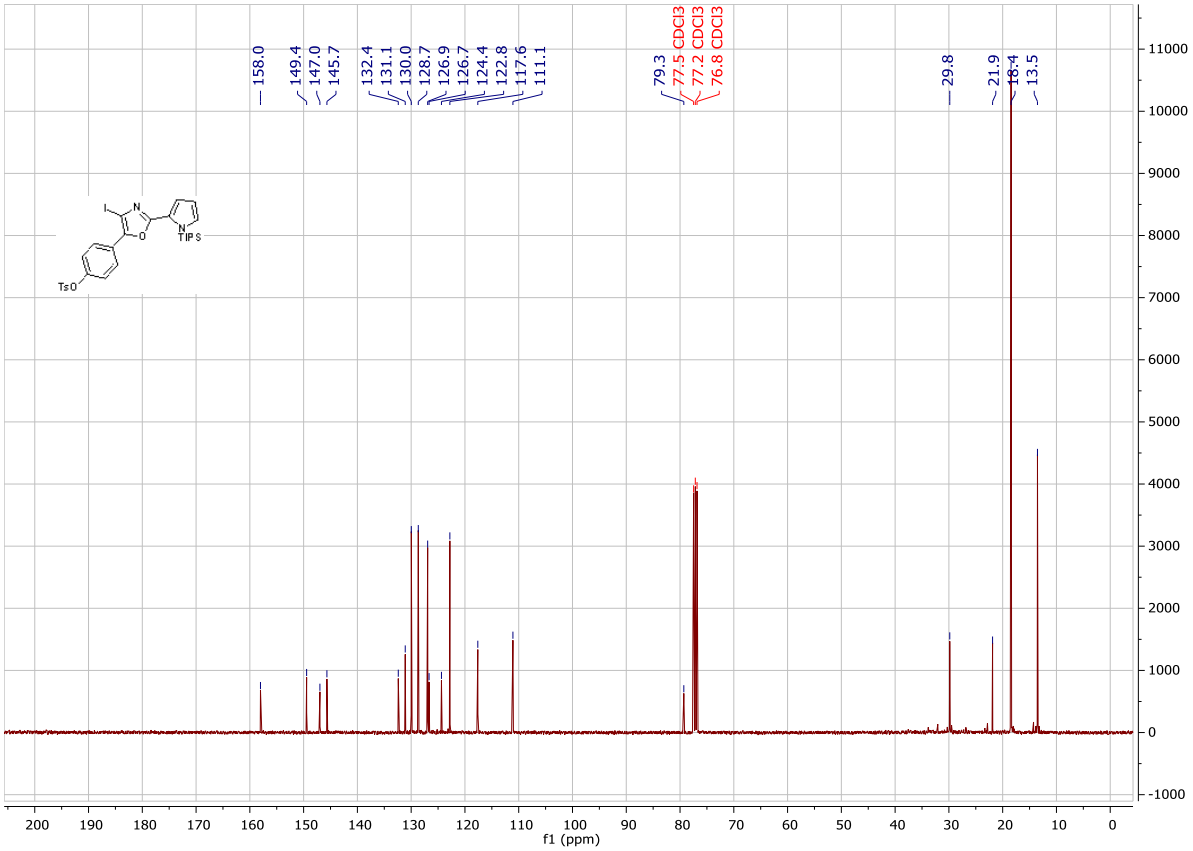


Figure S25. ^{13}C-NMR spectrum (101 MHz) of **20b**.

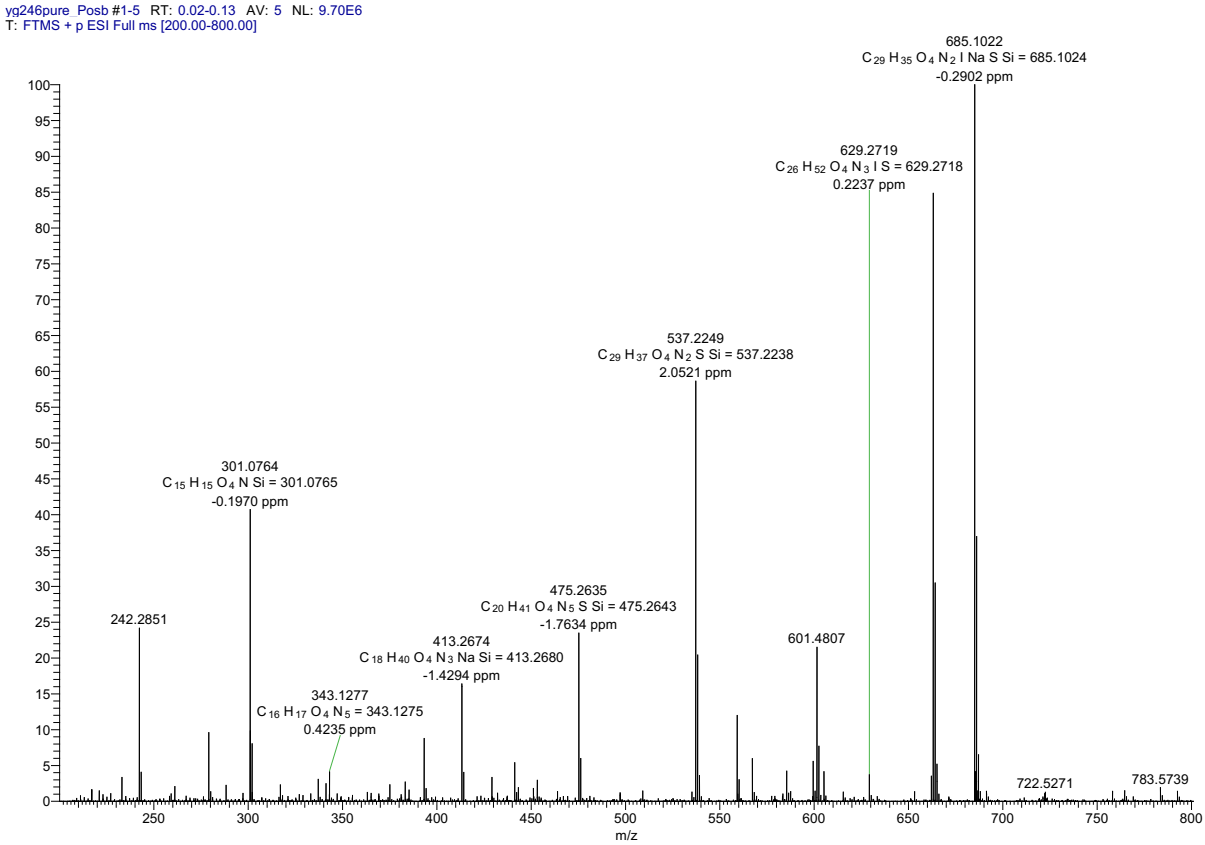


Figure S26. High resolution mass spectrum of **20b**

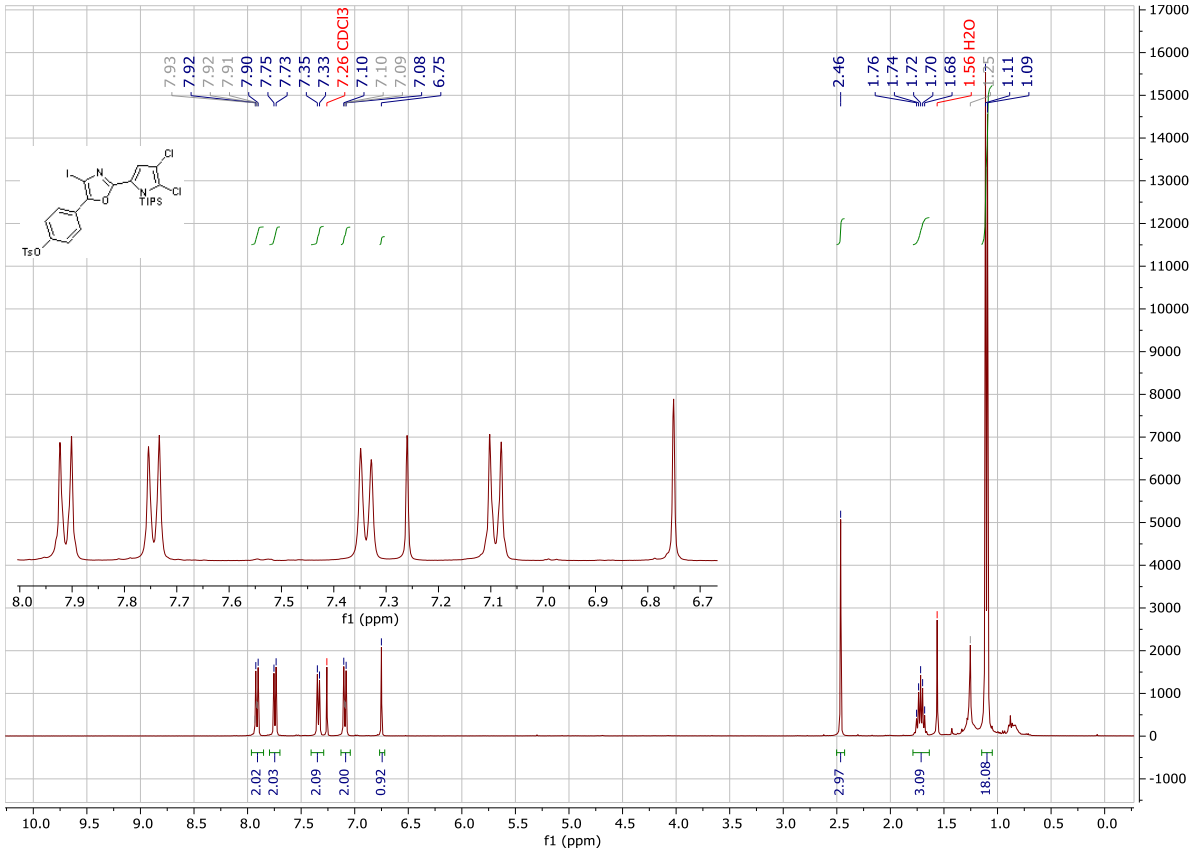


Figure S27. ^{1}H-NMR (400 MHz) spectrum of **21**.

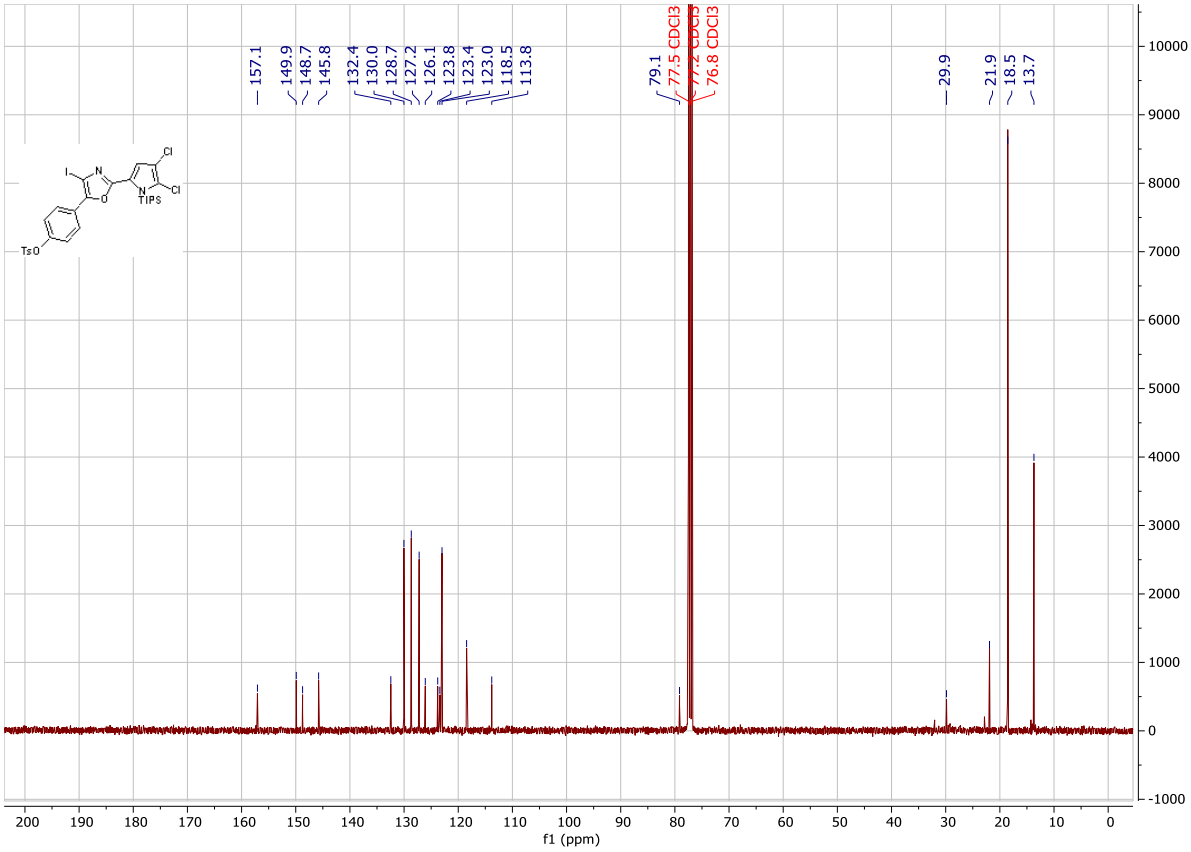


Figure S28. ^{13}C-NMR (101 MHz) spectrum of **21**.

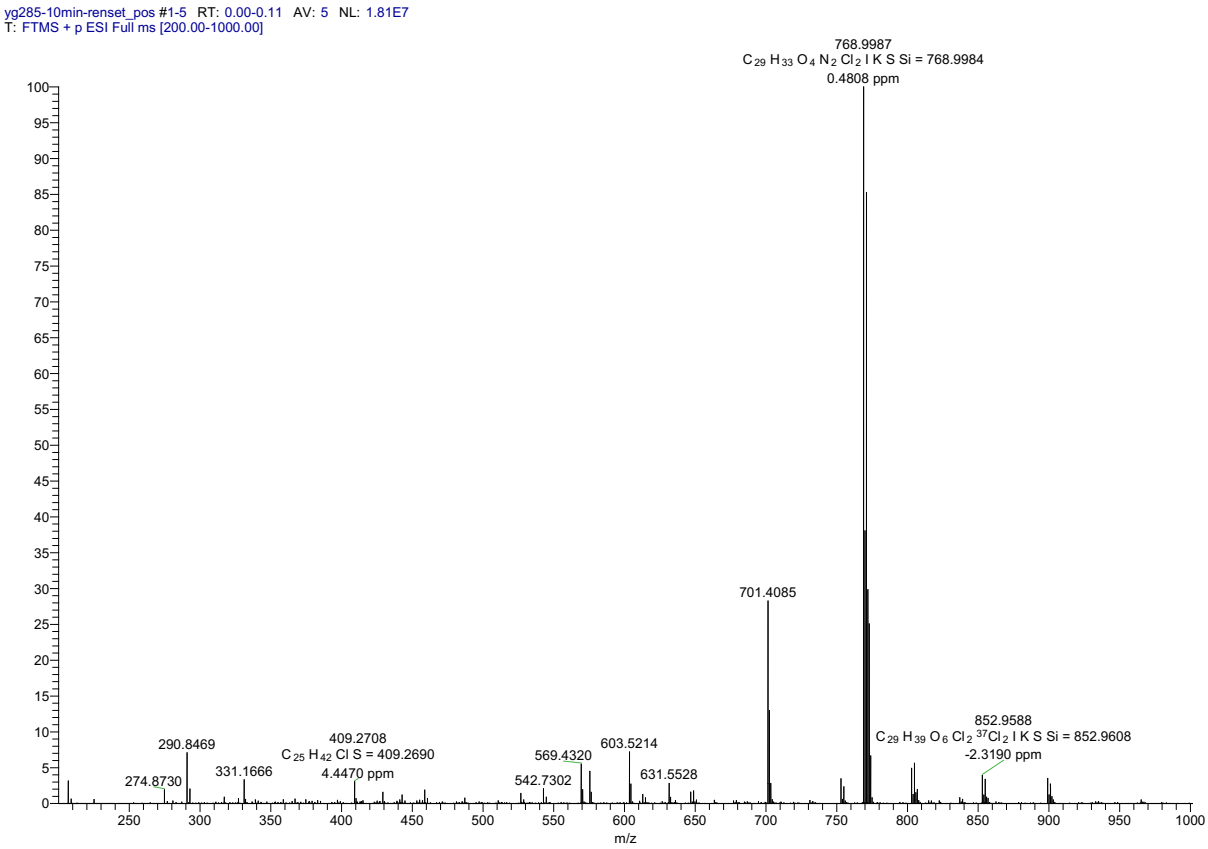


Figure S29. High resolution mass spectrum of **21**.

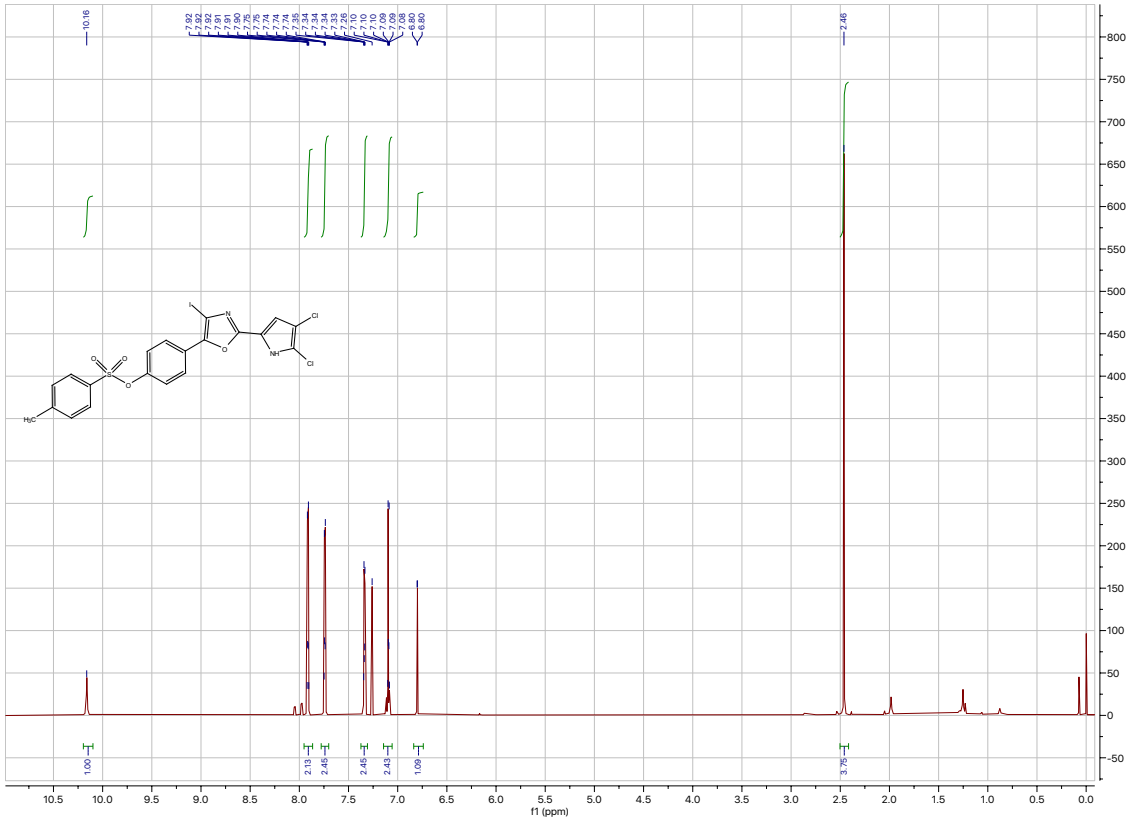


Figure S30. ^{1}H-NMR (850 MHz) spectrum of **22**.

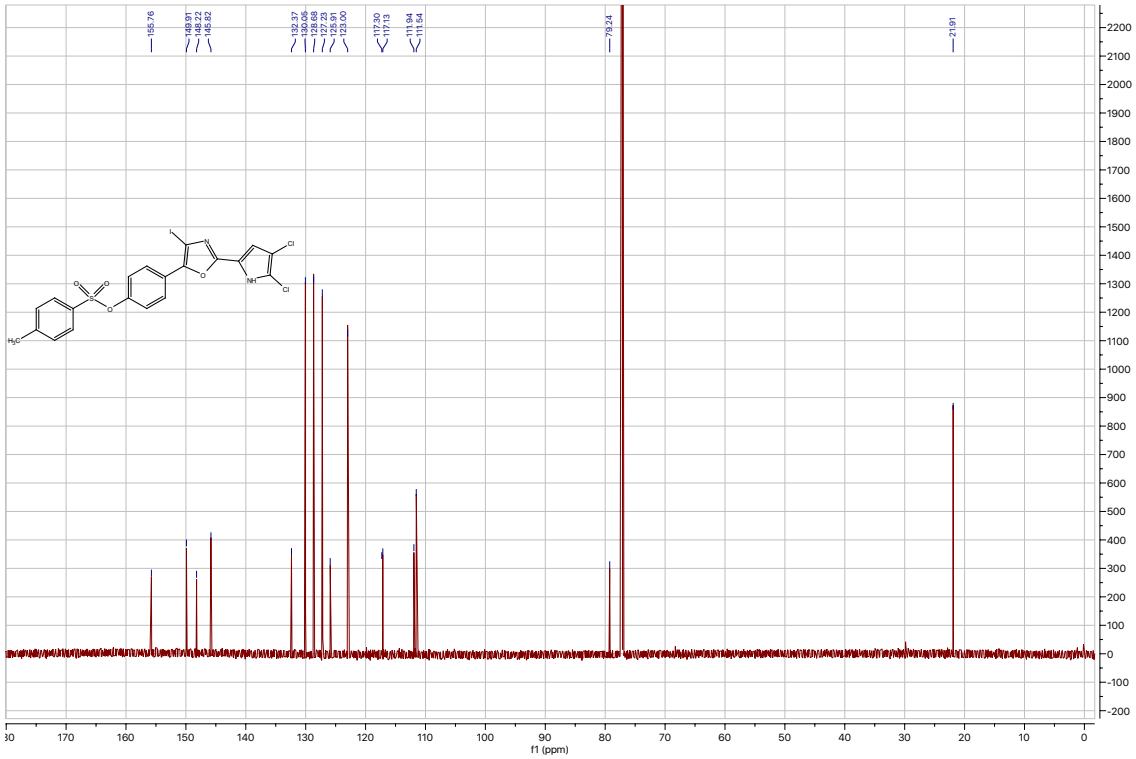


Figure S31. ^{13}C-NMR (126 MHz) spectrum of **22**.

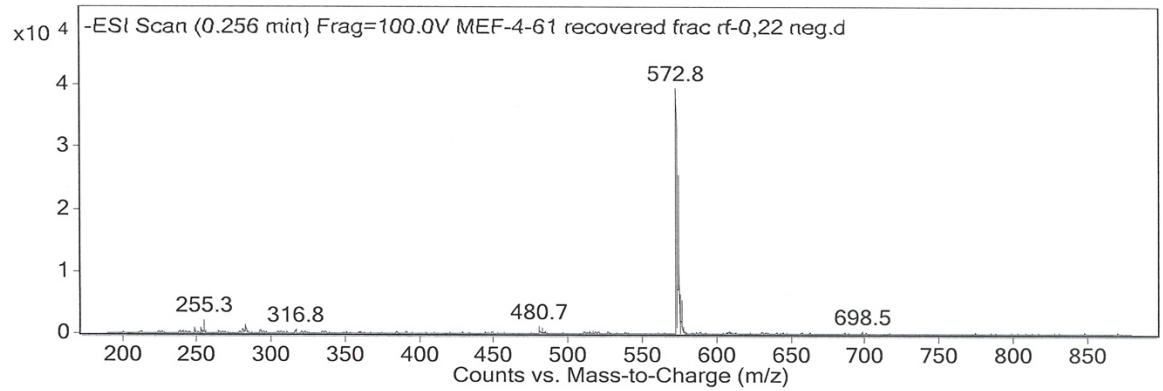


Figure S32. Low resolution MS of **22**.

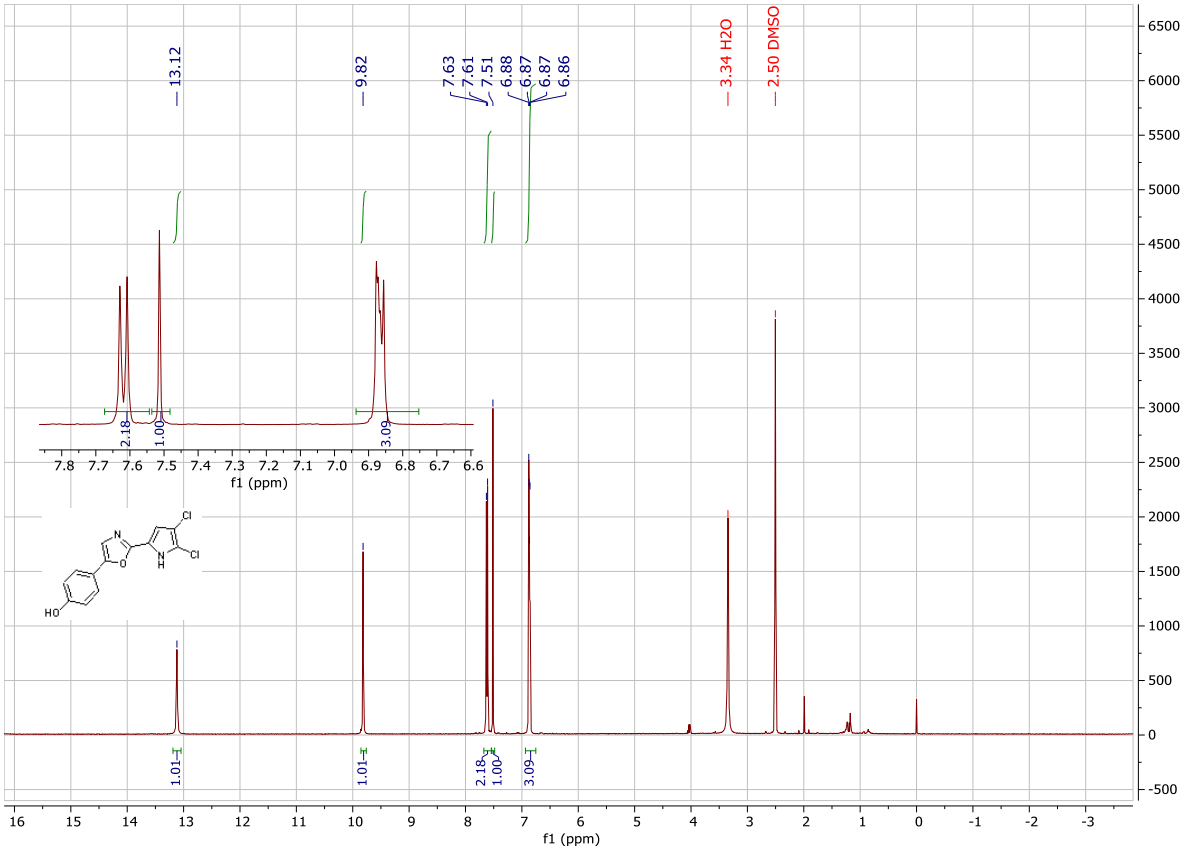


Figure S33. ^{1}H-NMR (400 MHz) spectrum of **23**.

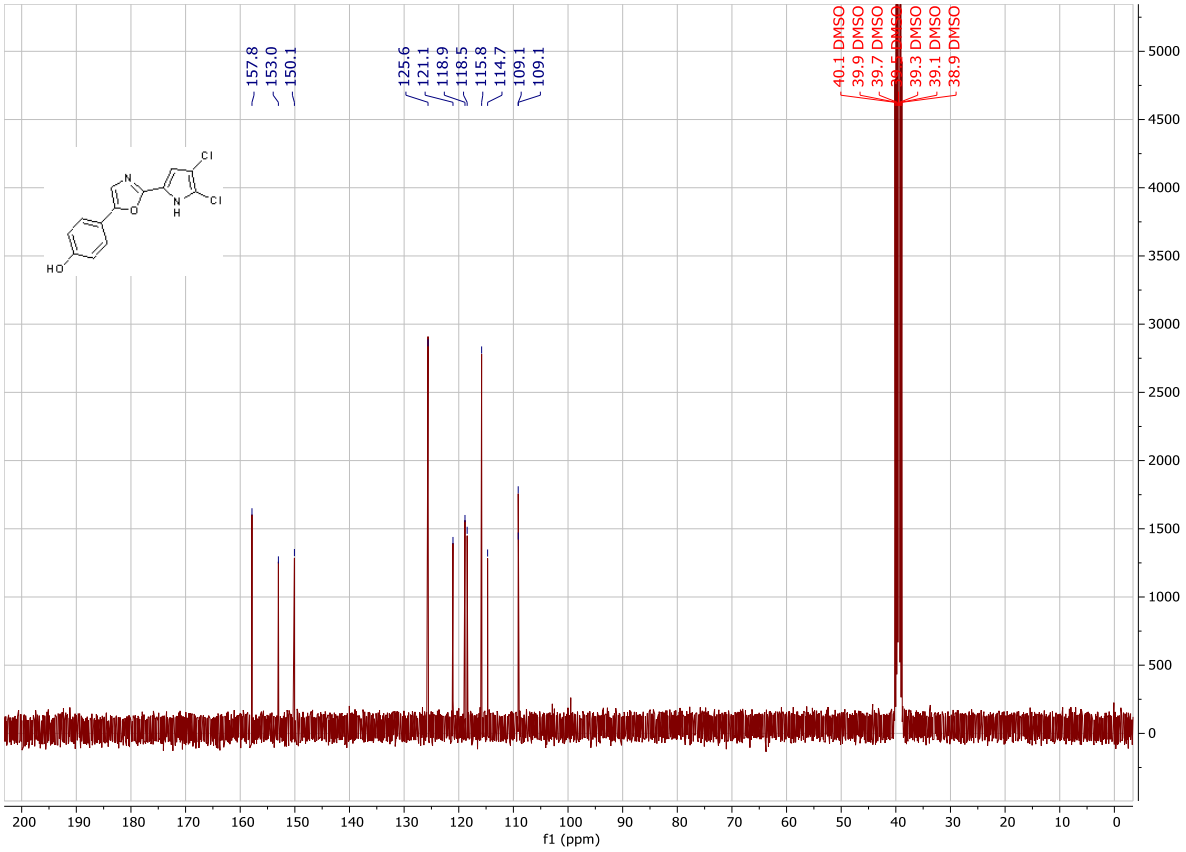


Figure S34. ^{13}C-NMR (101 MHz) spectrum of **23**.

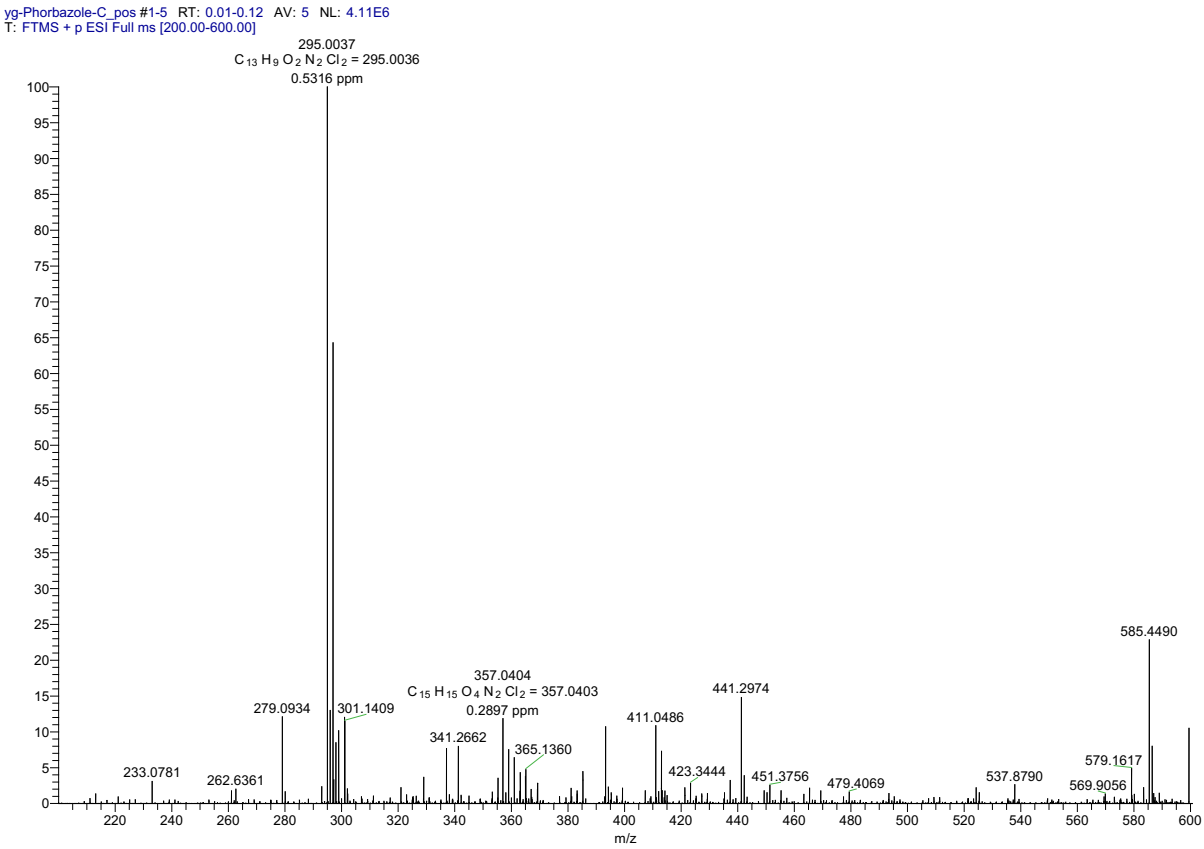
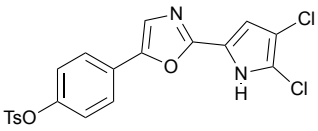


Figure S35.High resolution mass spectrum of **23**.

Synthesis of 4-(2-(4,5-Dichloro-1H-pyrrol-2-yl)oxazol-5-yl)phenyl 4-methylbenzenesulfonate (**24**)



Dichlorinated pyrrole **21** (20 mg, 27 µmol) was dissolved in ethanol (0.5 mL) and concentrated HCl (50 µL) was added. A precipitate formed immediately, but dissolved again within one minute. After 5 minutes, zinc (18 mg, 0.27 mmol) was added and the reaction mixture was heated at reflux for 2 h. The reaction mixture was cooled to rt and then adsorbed onto a Biotage snaplet precolumn, evaporated and purified by flash chromatography using a Biotage SNAP Ultra column using 0-100 % ethyl acetate in heptane to give the title compound.
Colourless solid; yield 5 mg (41 %); mp.: 188-192°C (dec); ^{1}H-NMR (400 MHz, $SO(CD_3)_2$) δ = 11.95 (s, 1H), 7.79 (m, 4H), 7.63 (s, 1H), 7.50 (d, *J* = 7.9, 2H), 7.14 (d, *J* = 8.6, 2H), 6.93 (s, 1H), 2.49 (s, 3H); ^{13}C-NMR (101 MHz, $CO(CD_3)_2$) δ = 149.3, 149.1, 146.0, 132.3, 130.1, 128.5, 126.9, 125.3, 124.1, 123.1, 110.4, 109.9, 20.7 (three more peaks visible in HMBC); HRMS (ESI) *m/z* calcd. for $C_{20}H_{13}O_4N_2Cl_2S$ [M-H]$^-$: 446.9973; found: 466.9969.

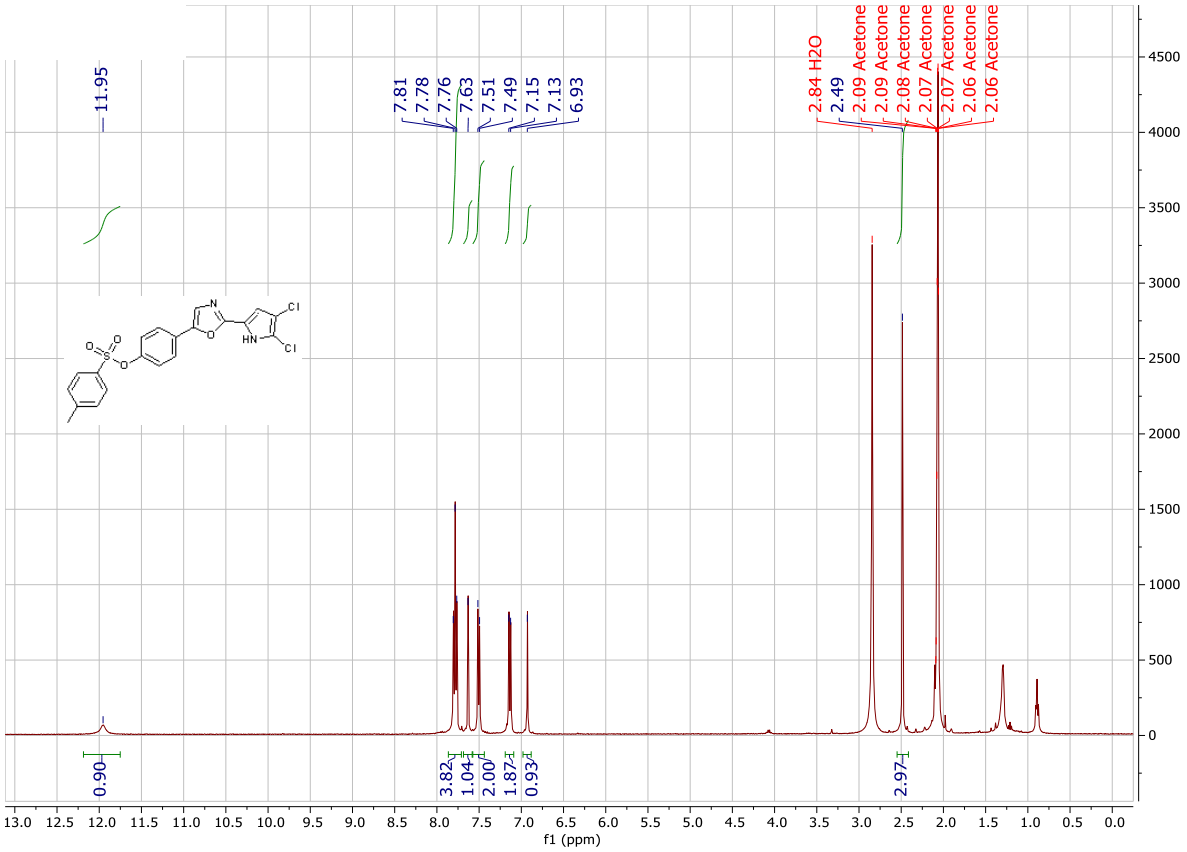


Figure S36. ^{1}H-NMR (400 MHz) spectrum of **24**.

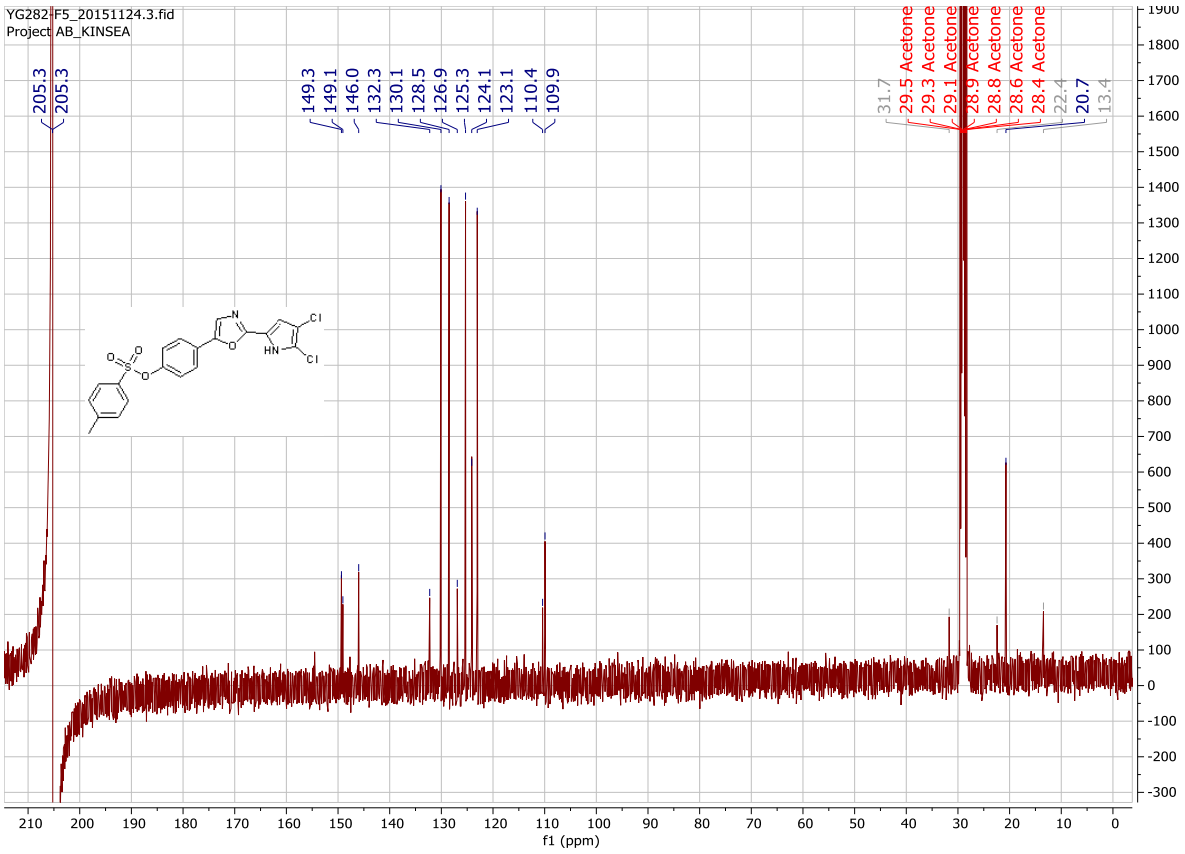


Figure S37. ^{13}C-NMR (101 MHz) spectrum of **24**.

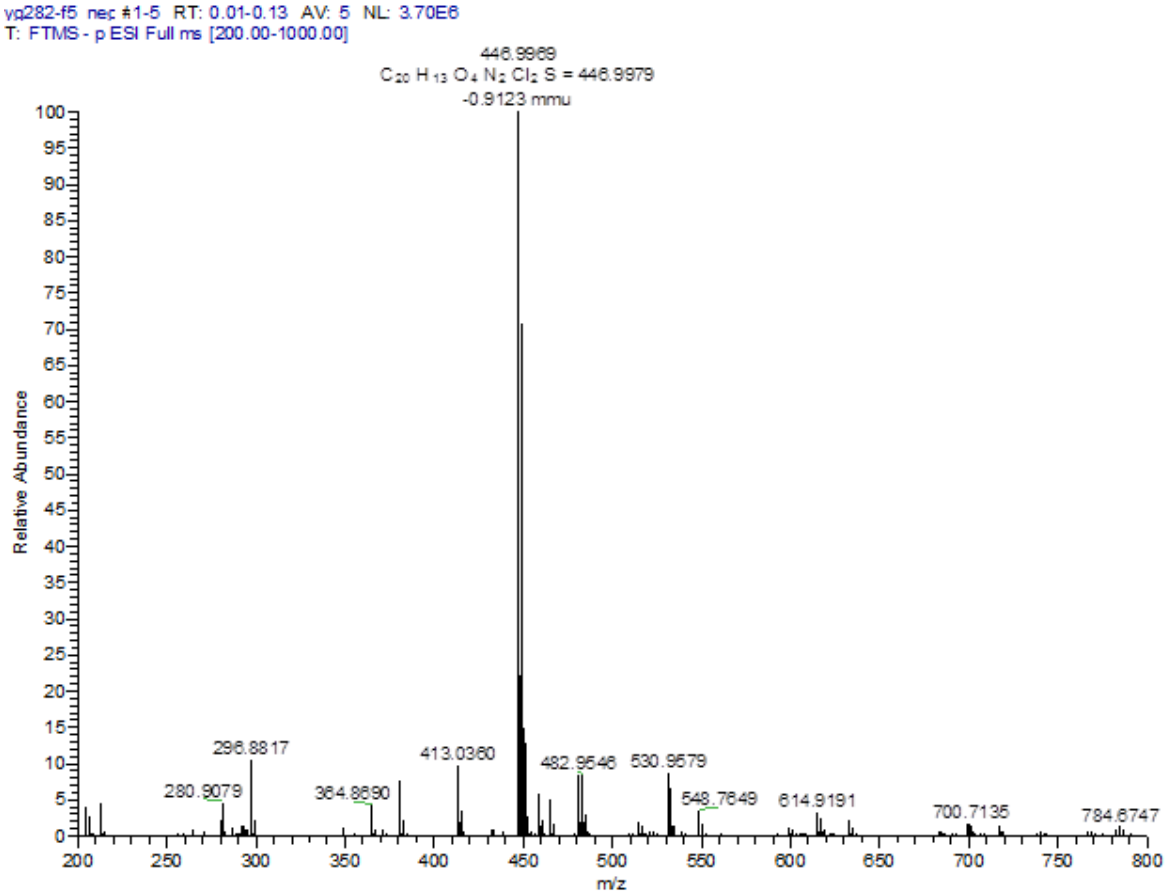


Figure S35.High resolution mass spectrum of **24**.

Structural assignment for **21** and **24**

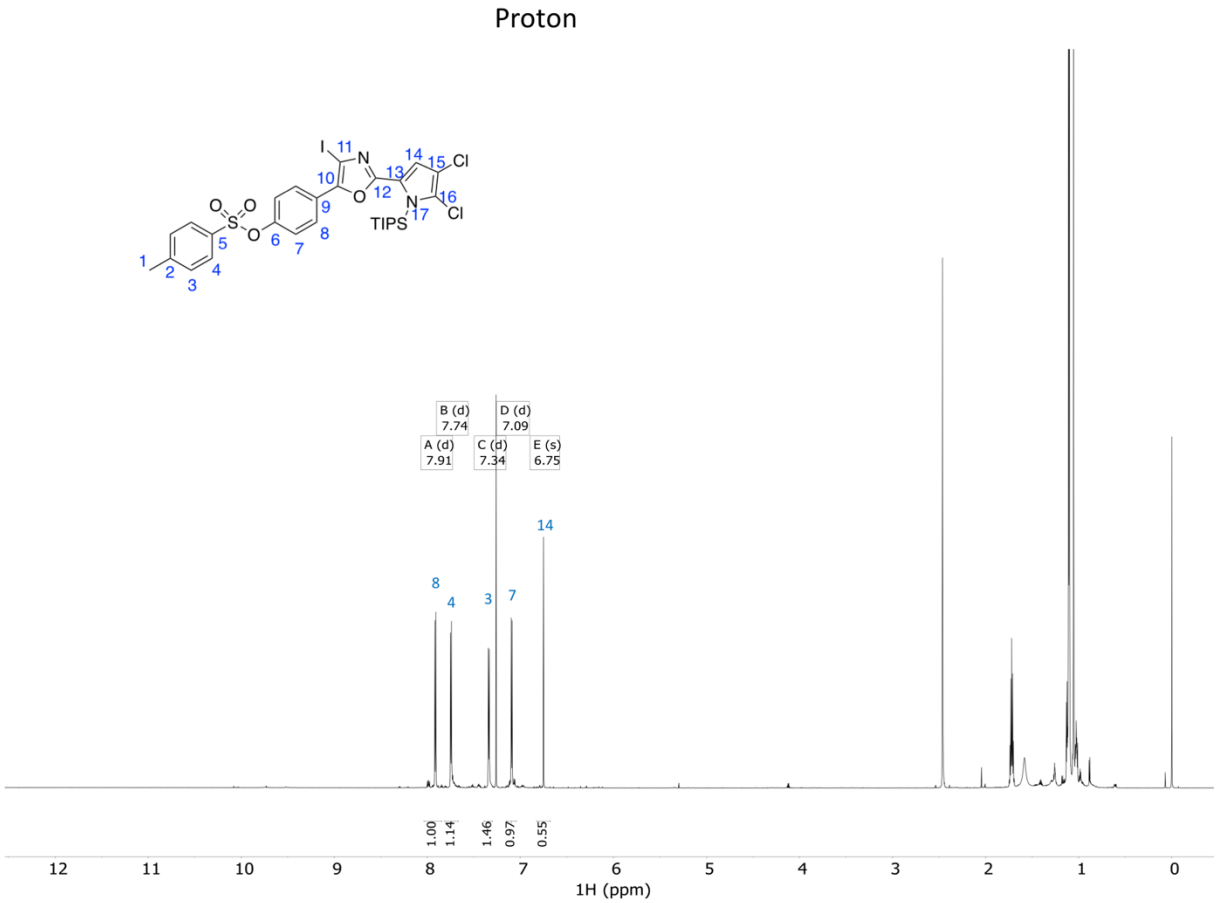


Figure S36. ^{1}H-NMR (850 MHz) spectrum of **21**.

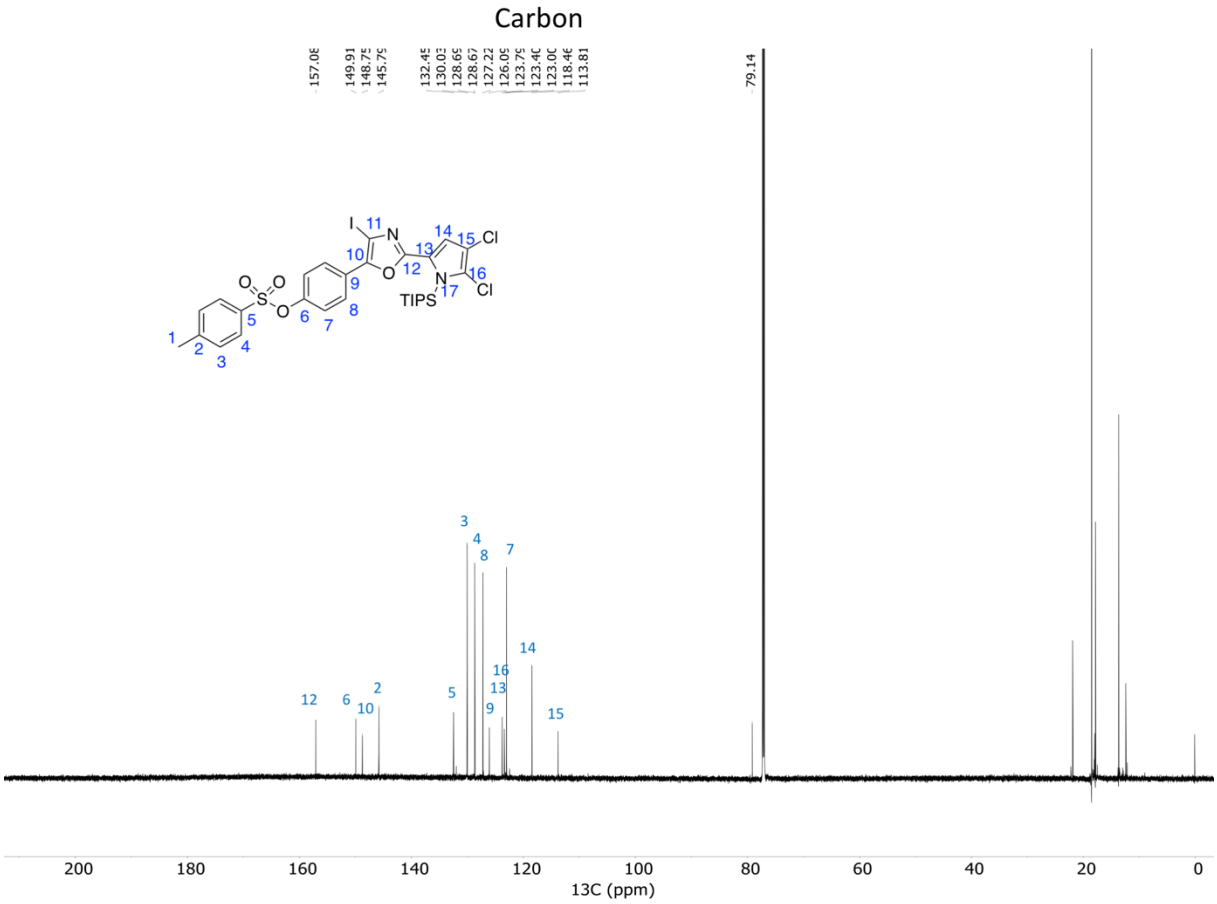


Figure S37. ^{13}C-NMR (214 MHz) spectrum of **21.**

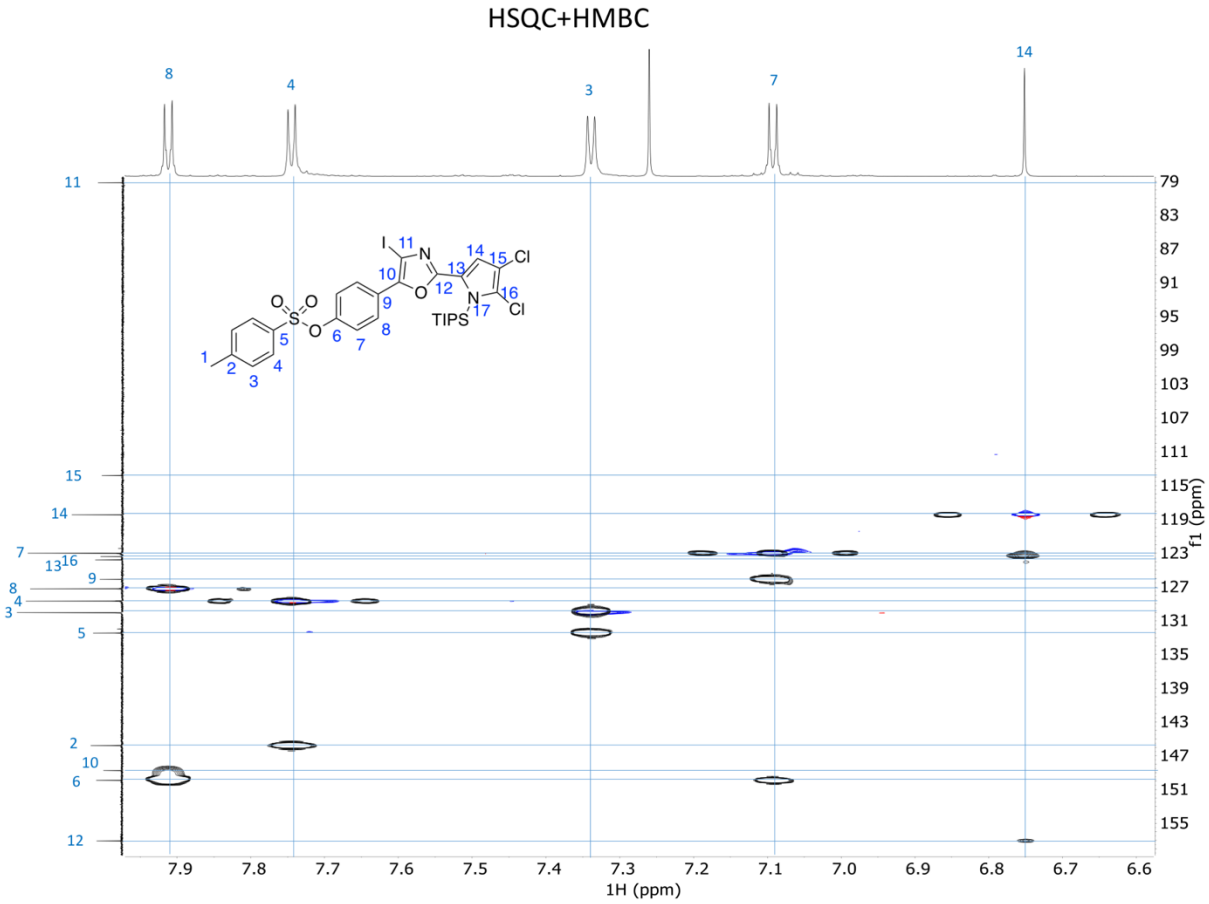


Figure S38. Superimposed HSQC and HMBC of **21**.

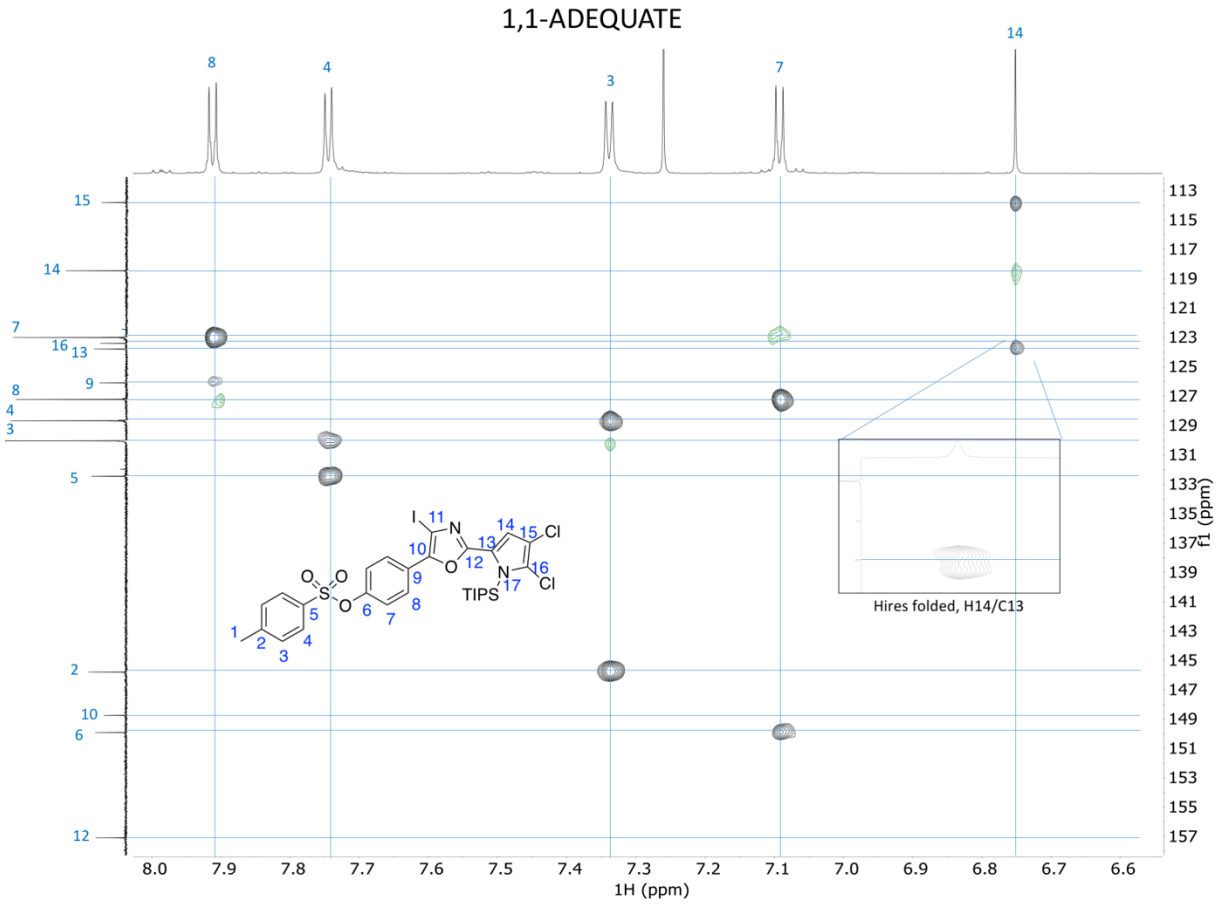


Figure S39. 1,1-ADEQUATE of **21**.

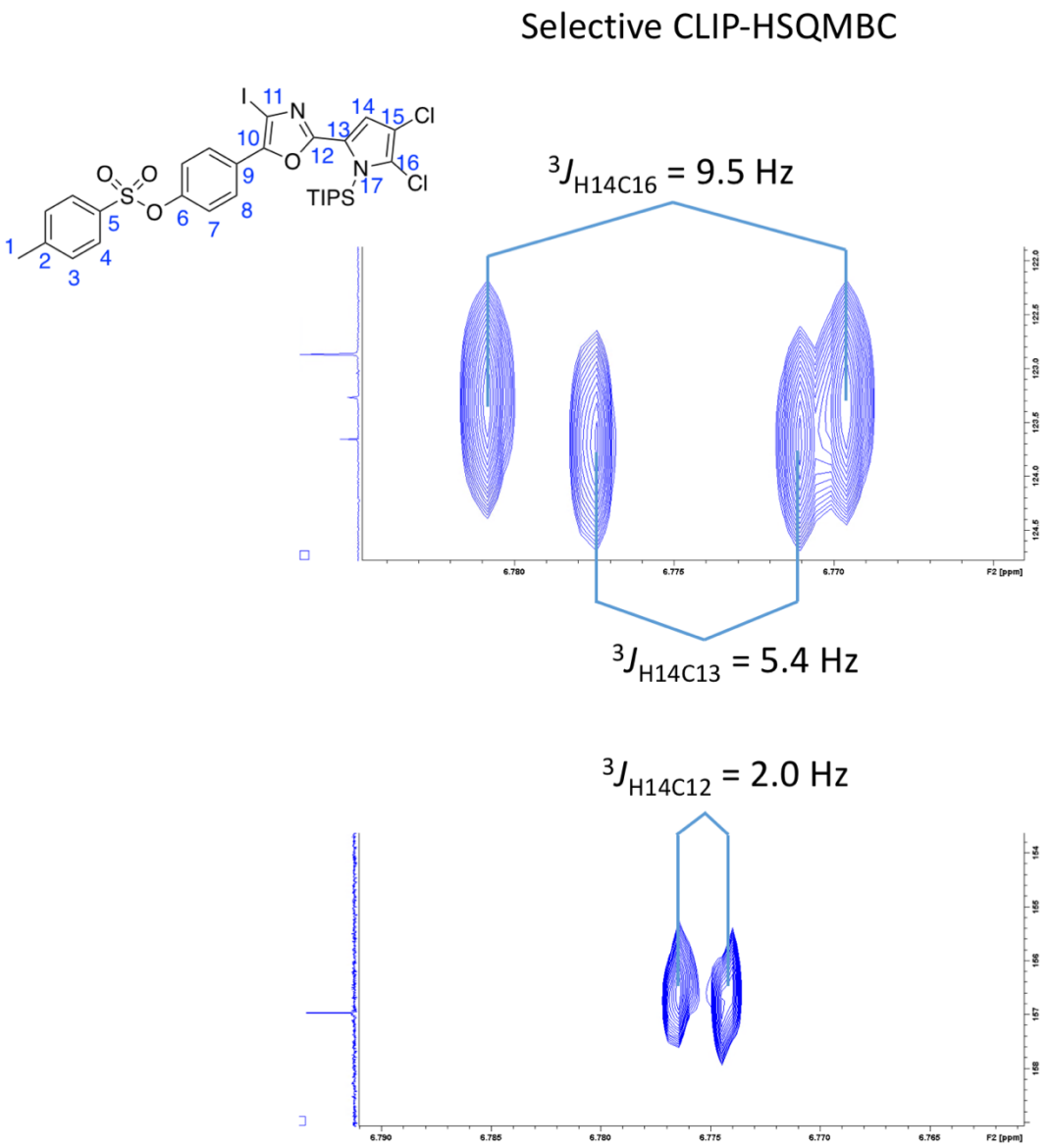


Figure S40. Selective CLIP-HSQMBC spectra of **21**.

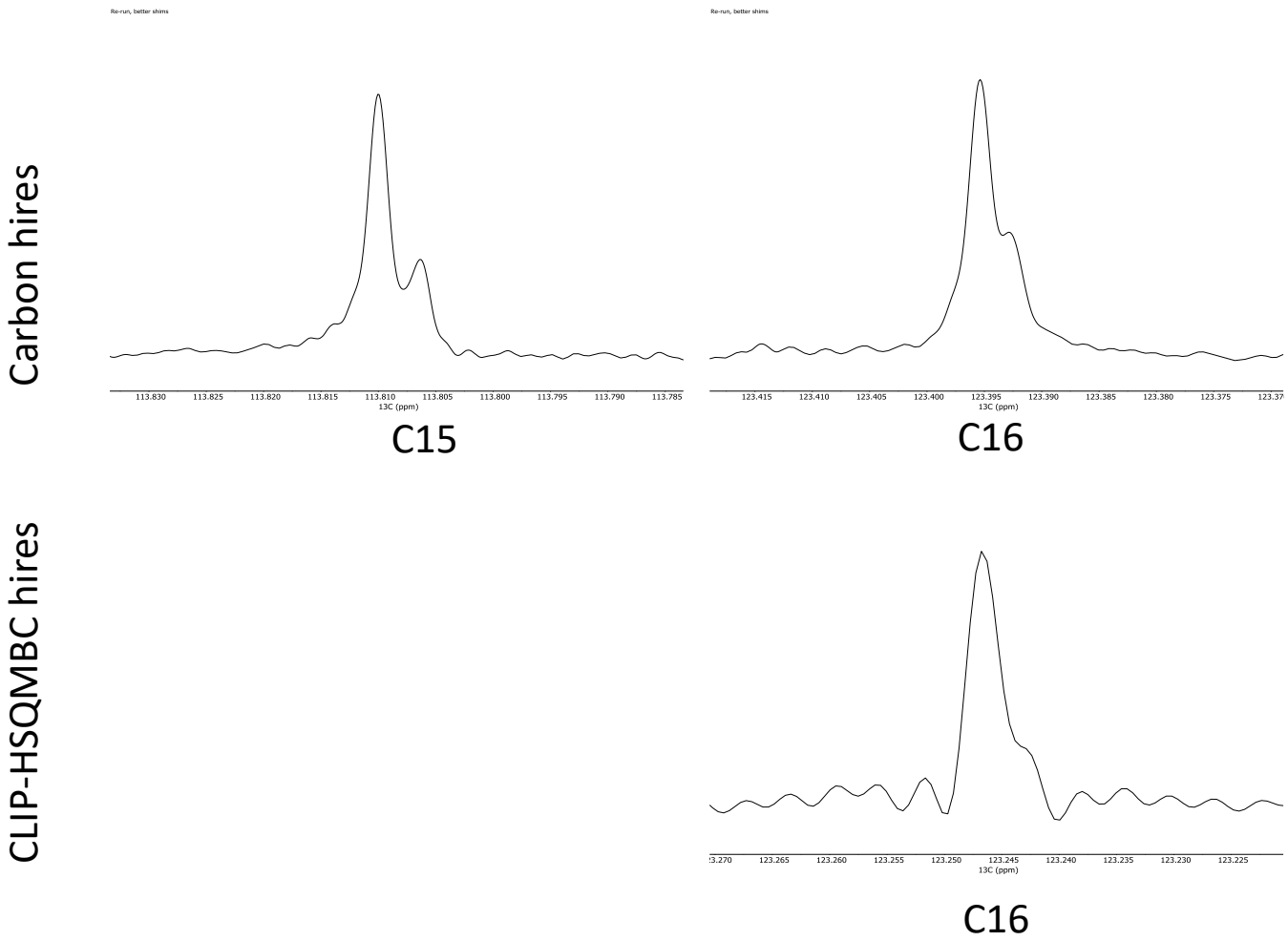


Figure S41. Hires ^{13}C (top panel) and hires selective CLIP-HSQMBC f1 projection (bottom panel) of **21**.

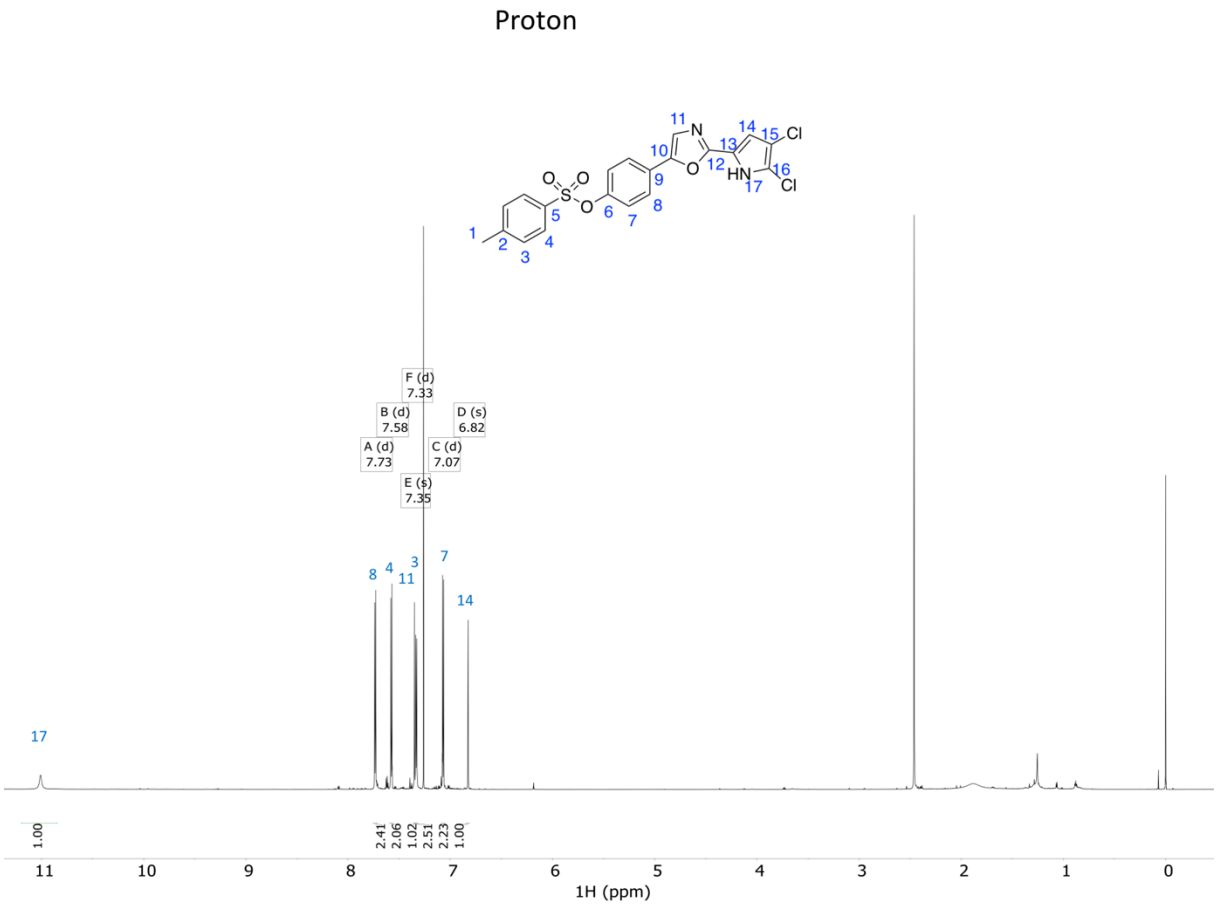


Figure S42. ^{1}H-NMR (850 MHz) spectrum of **24**.

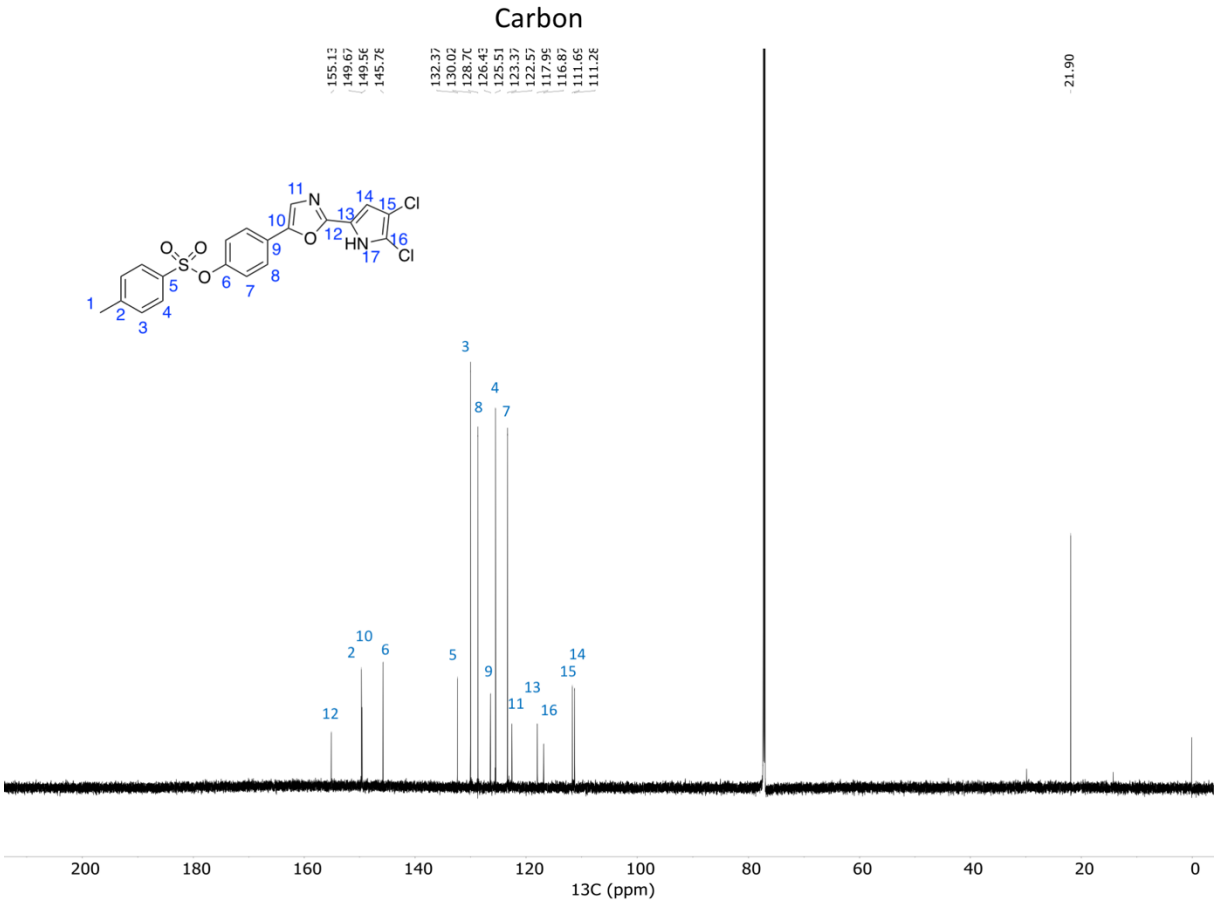


Figure S43. ^{13}C-NMR (214 MHz) spectrum of **24**.

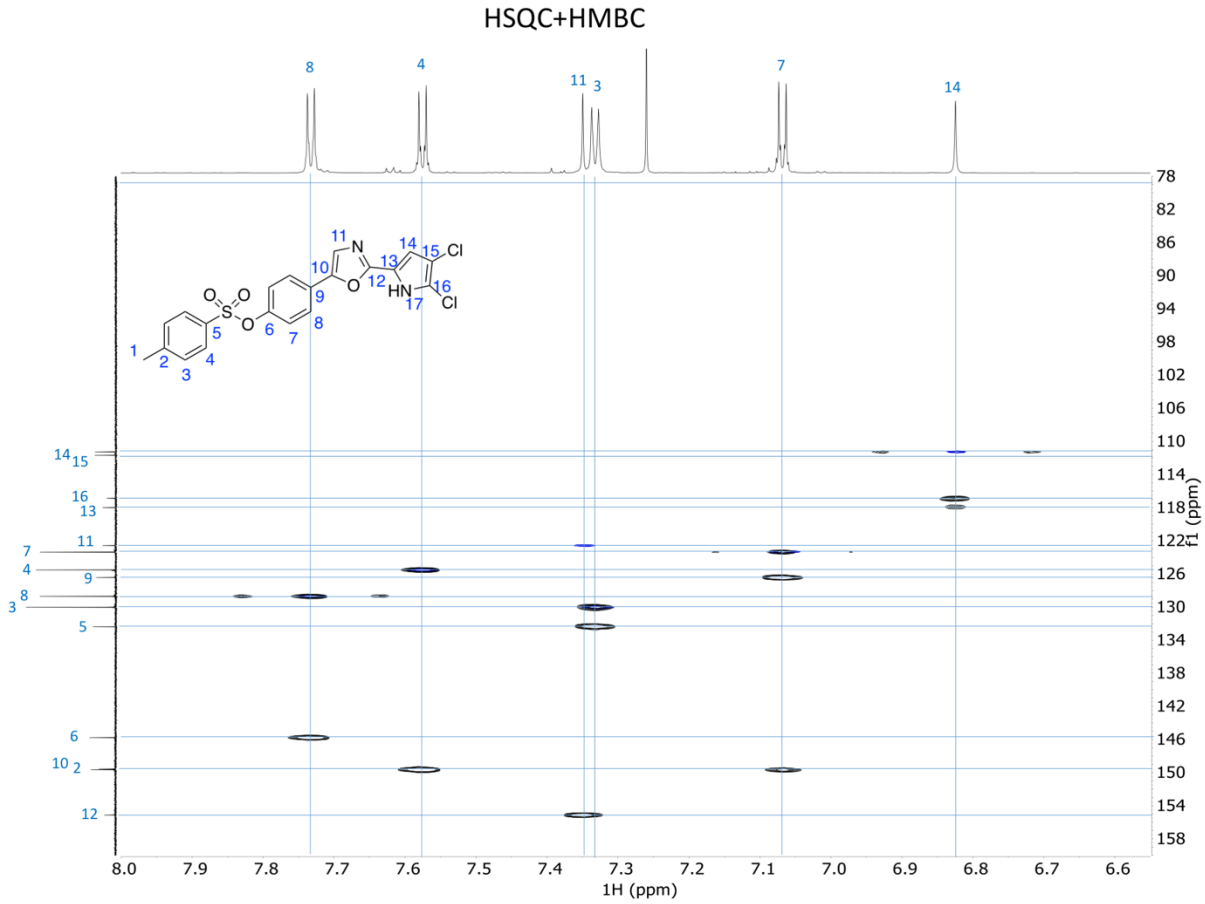


Figure S44. Superimposed HSQC and HMBC of **24**.

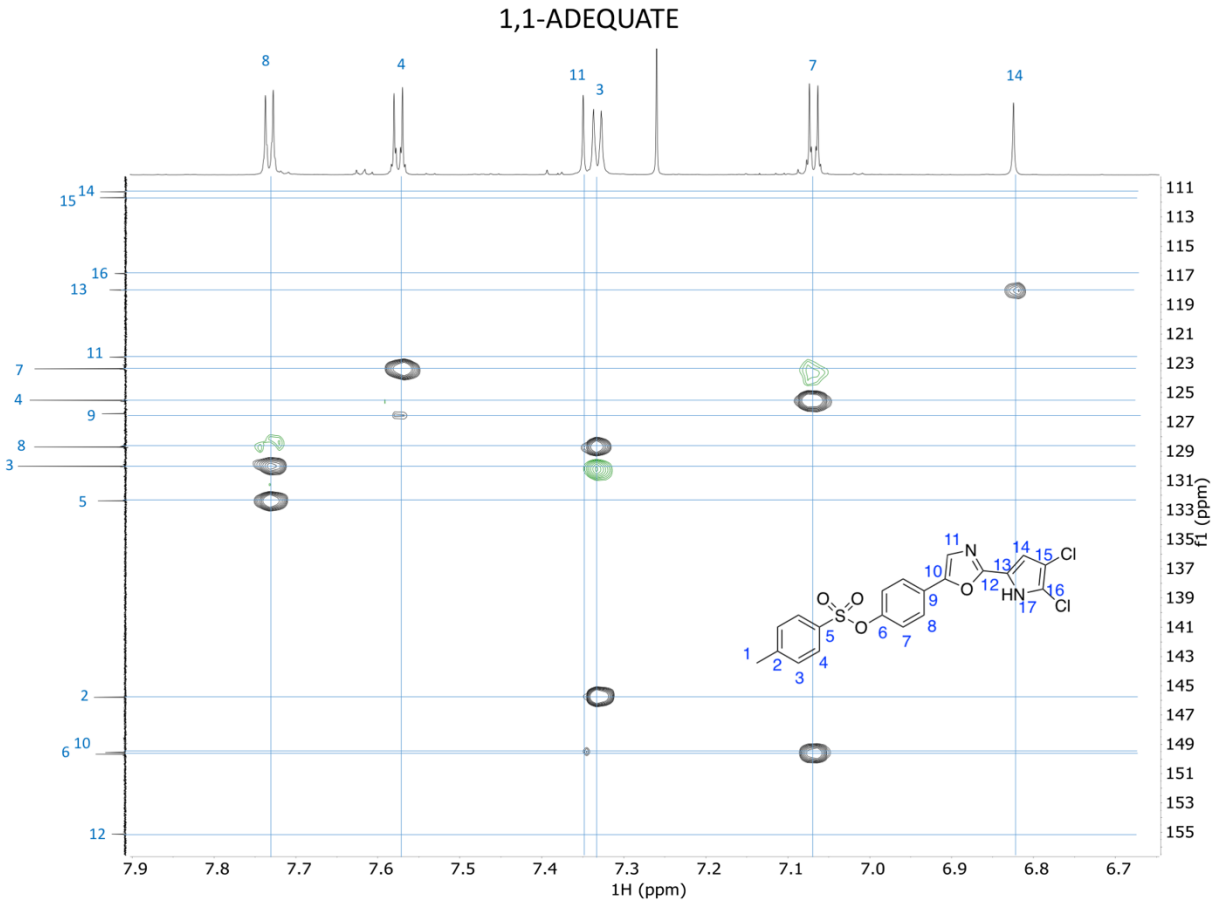


Figure S45. 1,1-ADEQUATE of **24**.

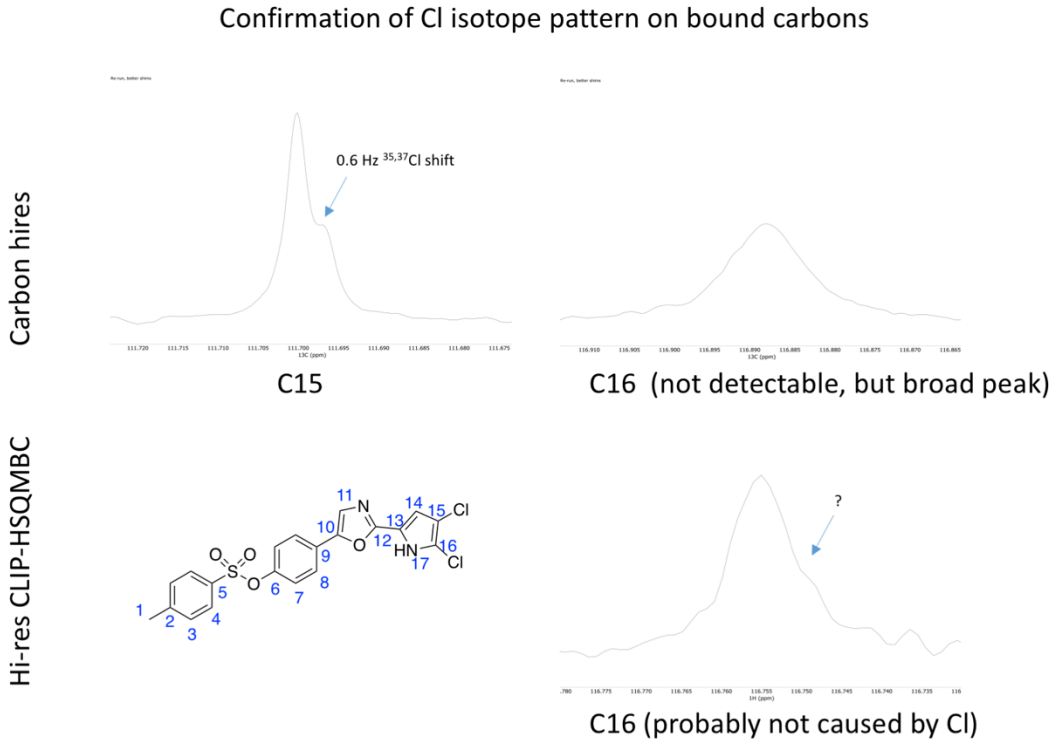


Figure S46. Hires ^{13}C (top panel) and hires selective CLIP-HSQMBC f1 (bottom panel) projection of **24**.

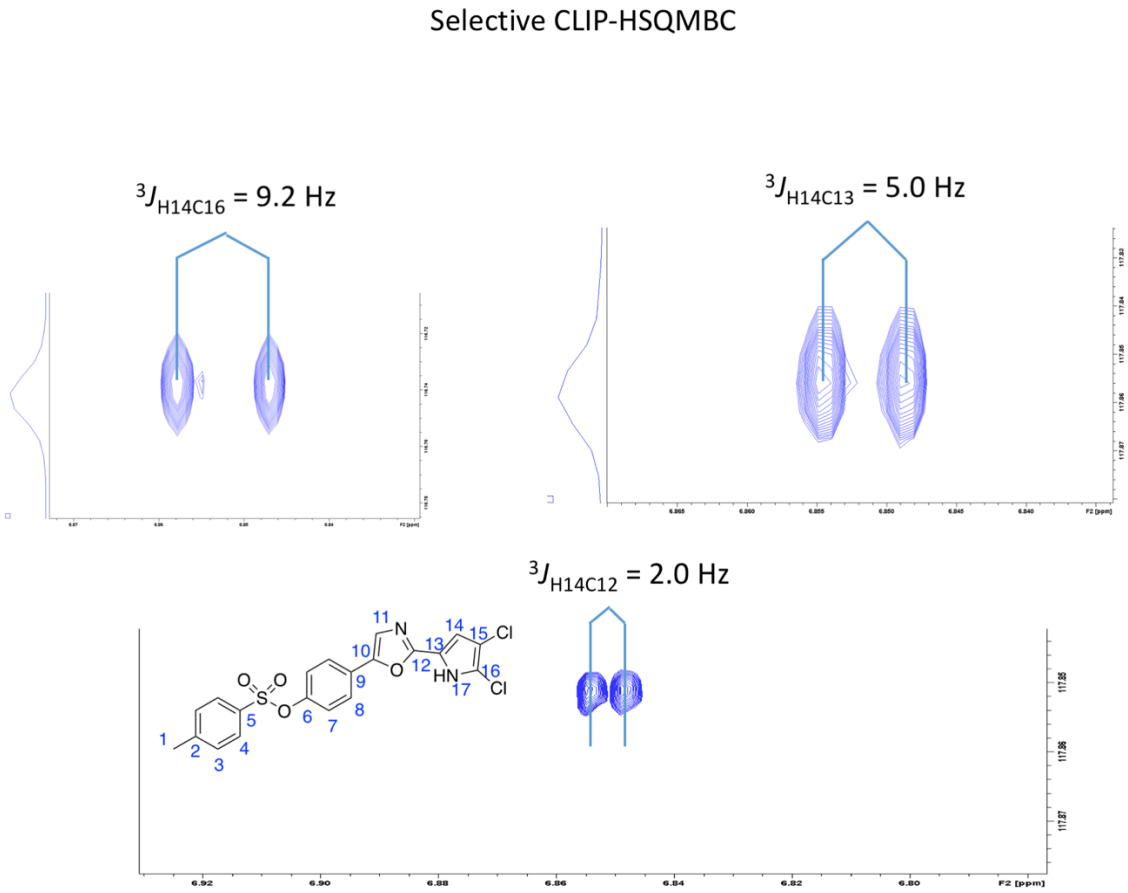


Figure S47. Selective CLIP-HSQMBC of **24**.

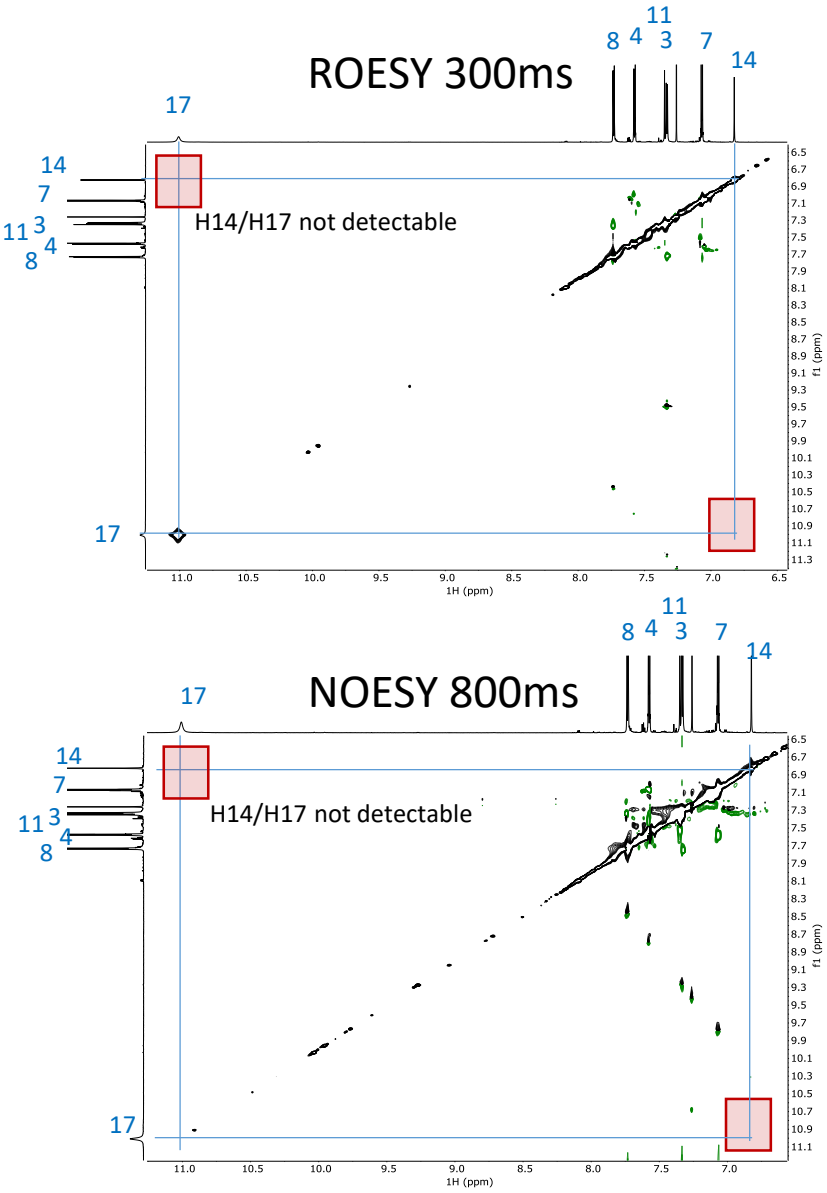


Figure S48. NOESY and ROESY of **24**.

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