

Supporting information for:

Total synthesis of phorbazole B

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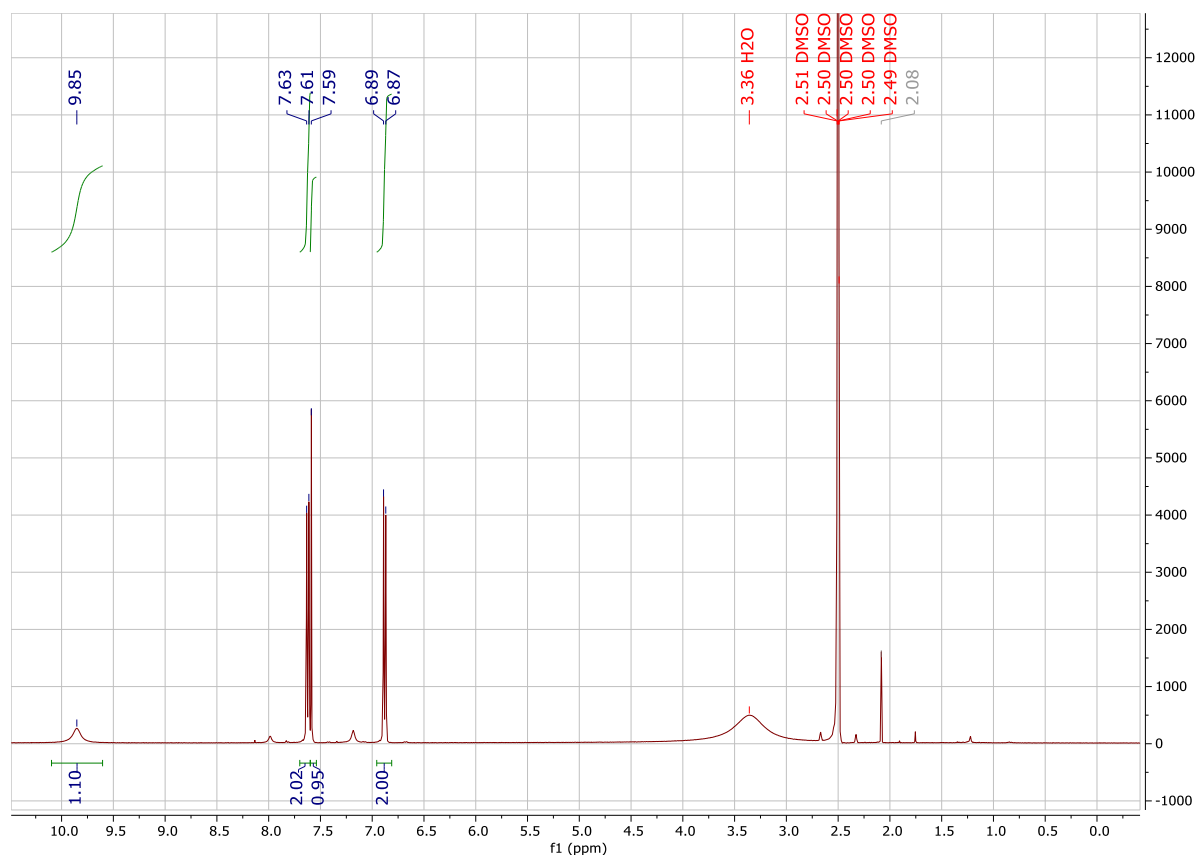


Figure S1. ^1H -NMR spectrum (400 MHz) of phorbazole B (**2**)

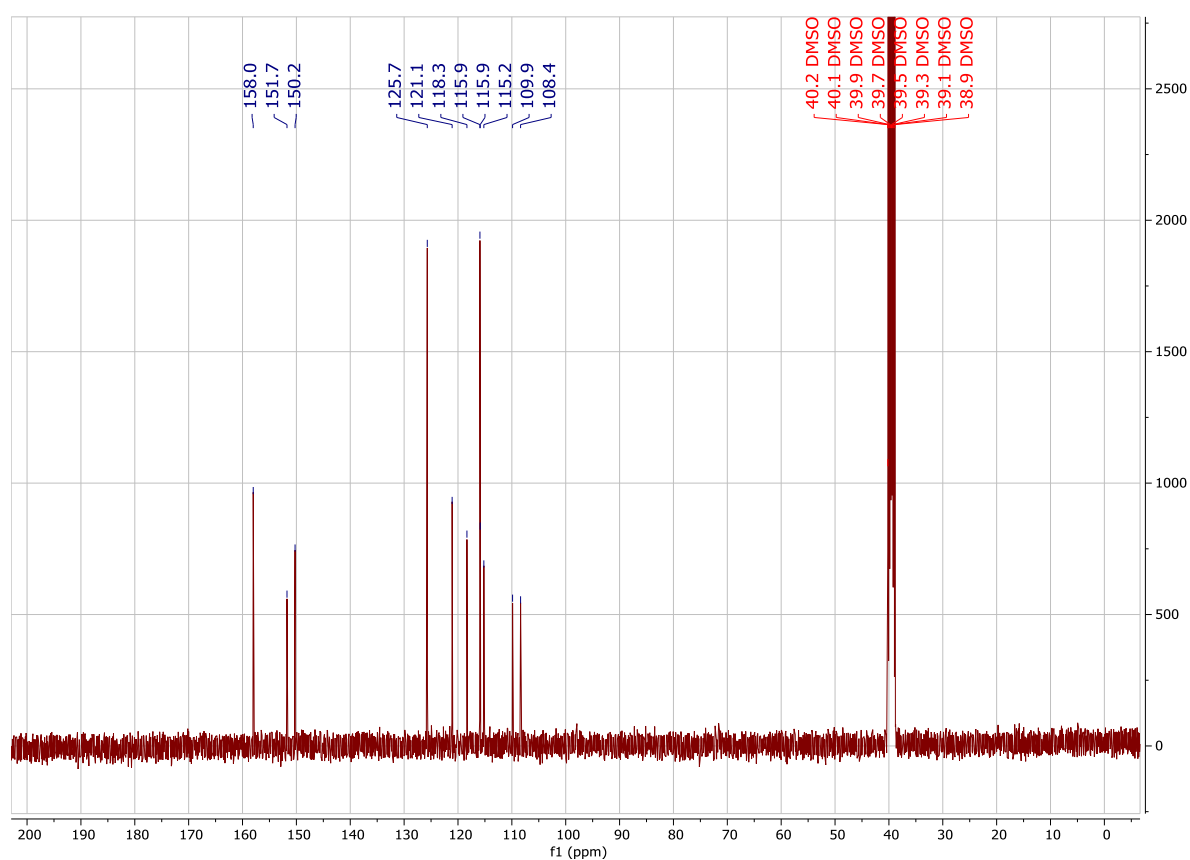


Figure S2. ^{13}C -NMR spectrum (101 MHz) of phorbazole B (**2**)

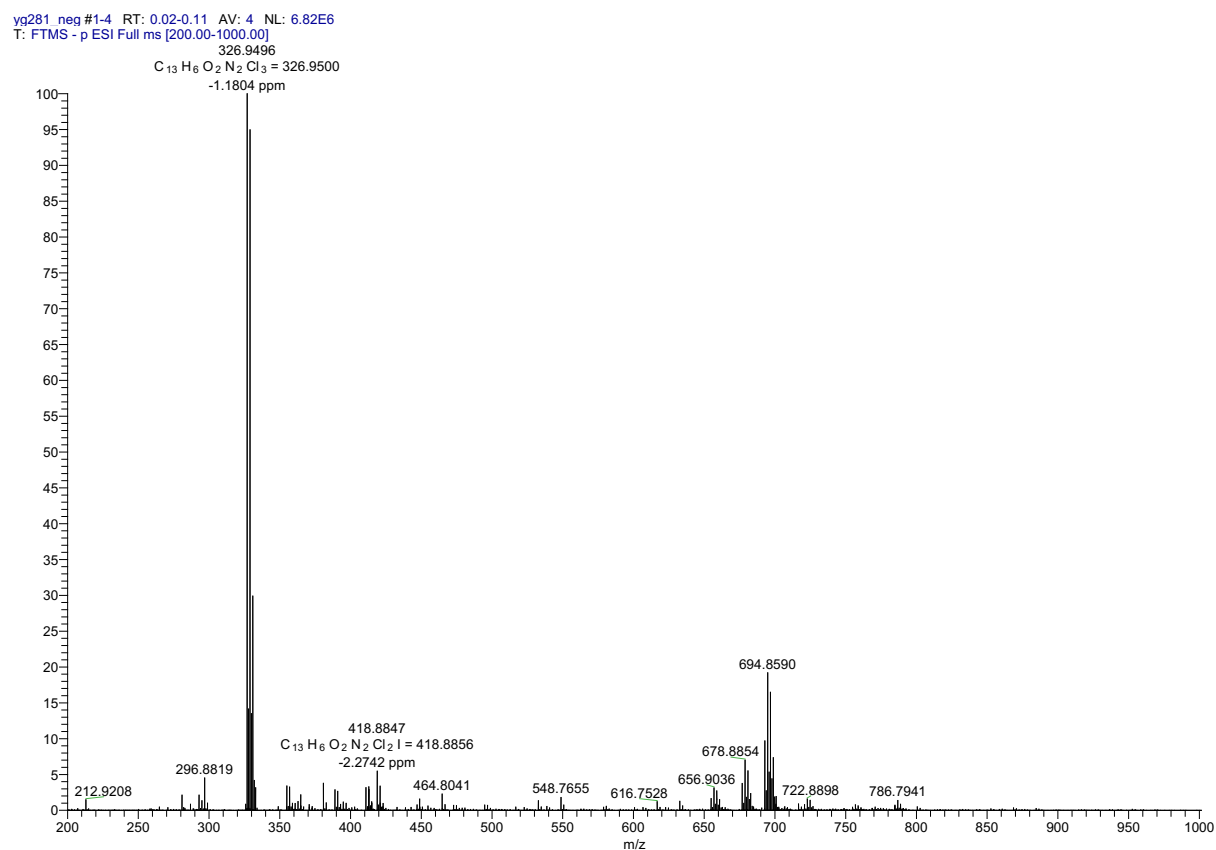
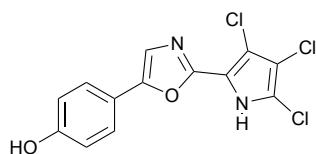


Figure S3. High resolution mass spectrum of phorbazole B (**2**)

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

Synthetic 2 ¹ H-NMR, 400 MHz, (CD ₃) ₂ SO	Isolated 2 ¹ H-NMR, 500 MHz, (CD ₃) ₂ SO
13.57 (s, 1H)	-
9.85 (s, 1H)	-
7.62 (d, <i>J</i> = 7.7 Hz, 2H)	7.63 (d, <i>J</i> = 8.0 Hz)
7.59 (s, 1H)	7.60 (s)
6.88 (d, <i>J</i> = 7.7 Hz, 2H)	6.88 (d, <i>J</i> = 8.0 Hz)
Synthetic 2 ¹³ C-NMR, 101 MHz, (CD ₃) ₂ SO	Isolated 2 ¹³ C-NMR, 150 MHz, (CD ₃) ₂ SO
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

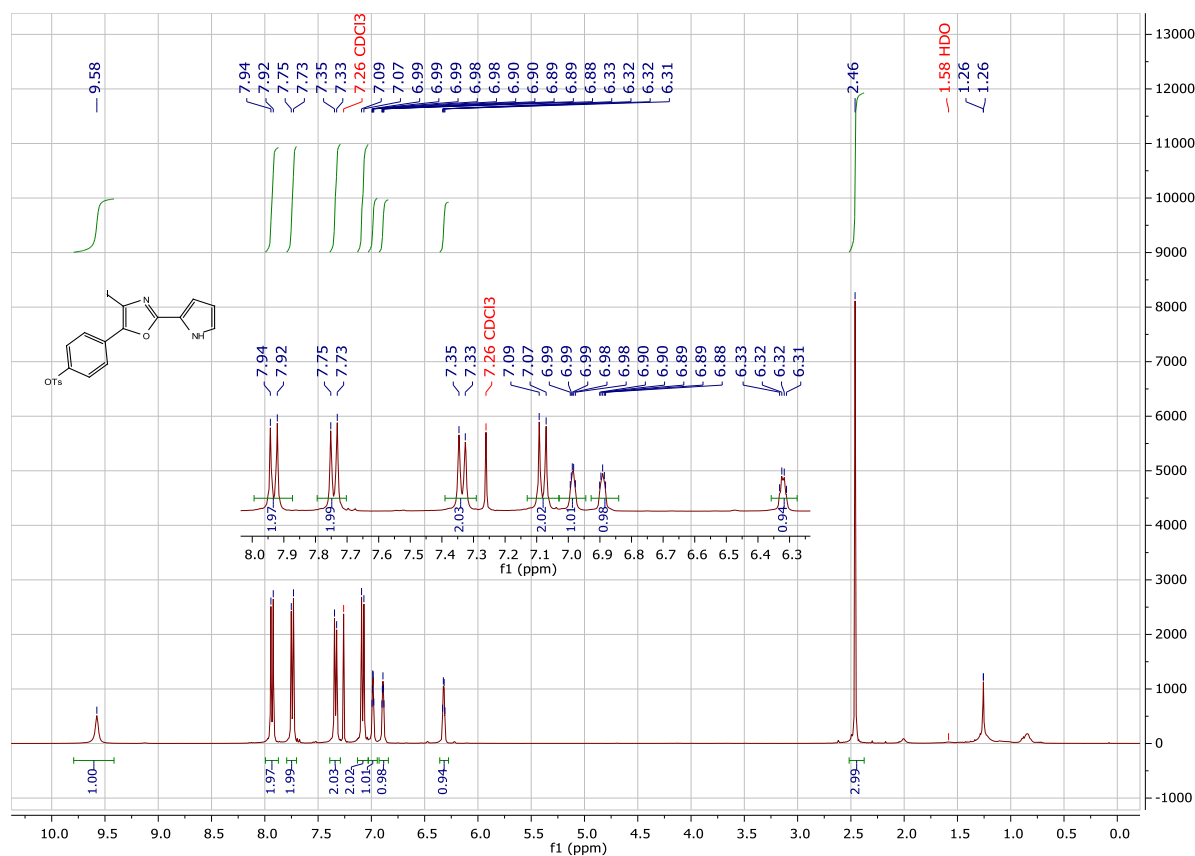


Figure S4. ¹H-NMR spectrum (400 MHz) of 13

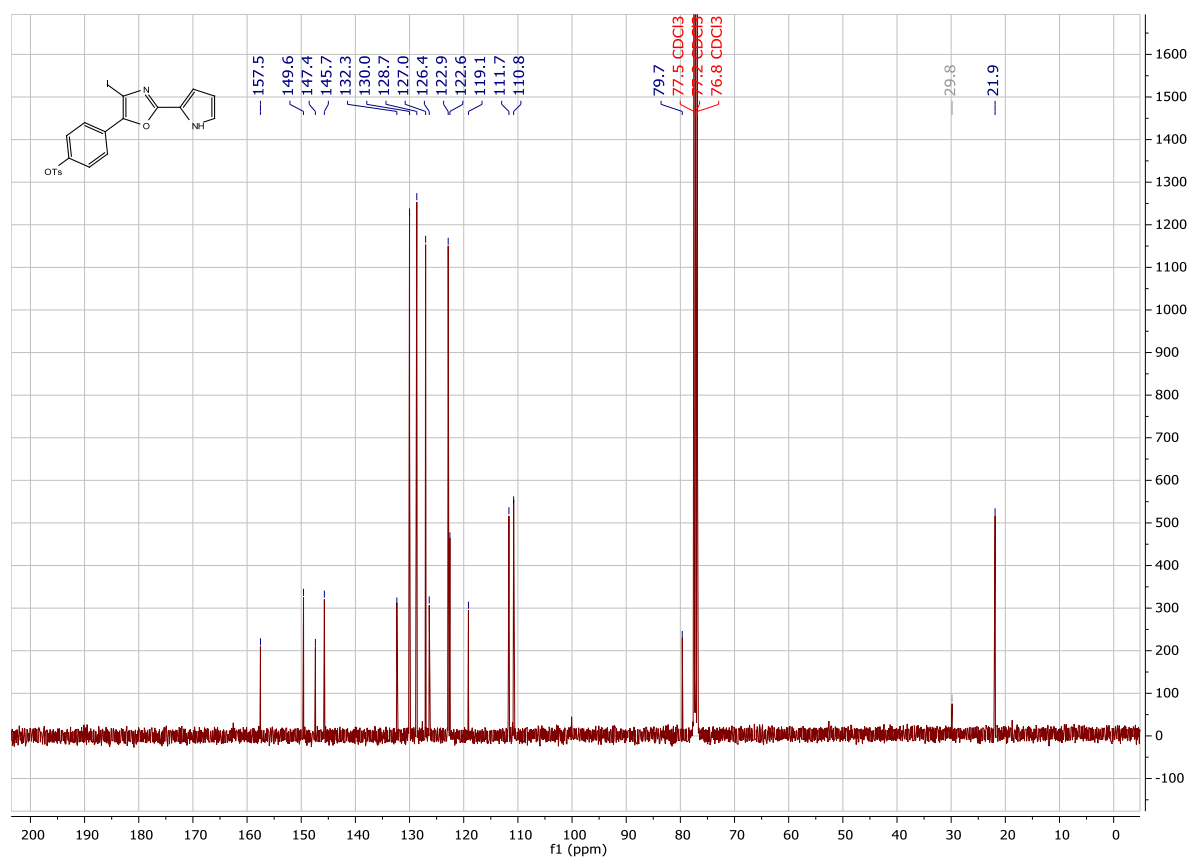


Figure S5. ¹³C-NMR spectrum (101 MHz) of 13

yg231on #1-4 RT: 0.02-0.11 AV: 4 NL: 1.26E7
T: FTMS + p ESI Full ms [200.00-700.00]

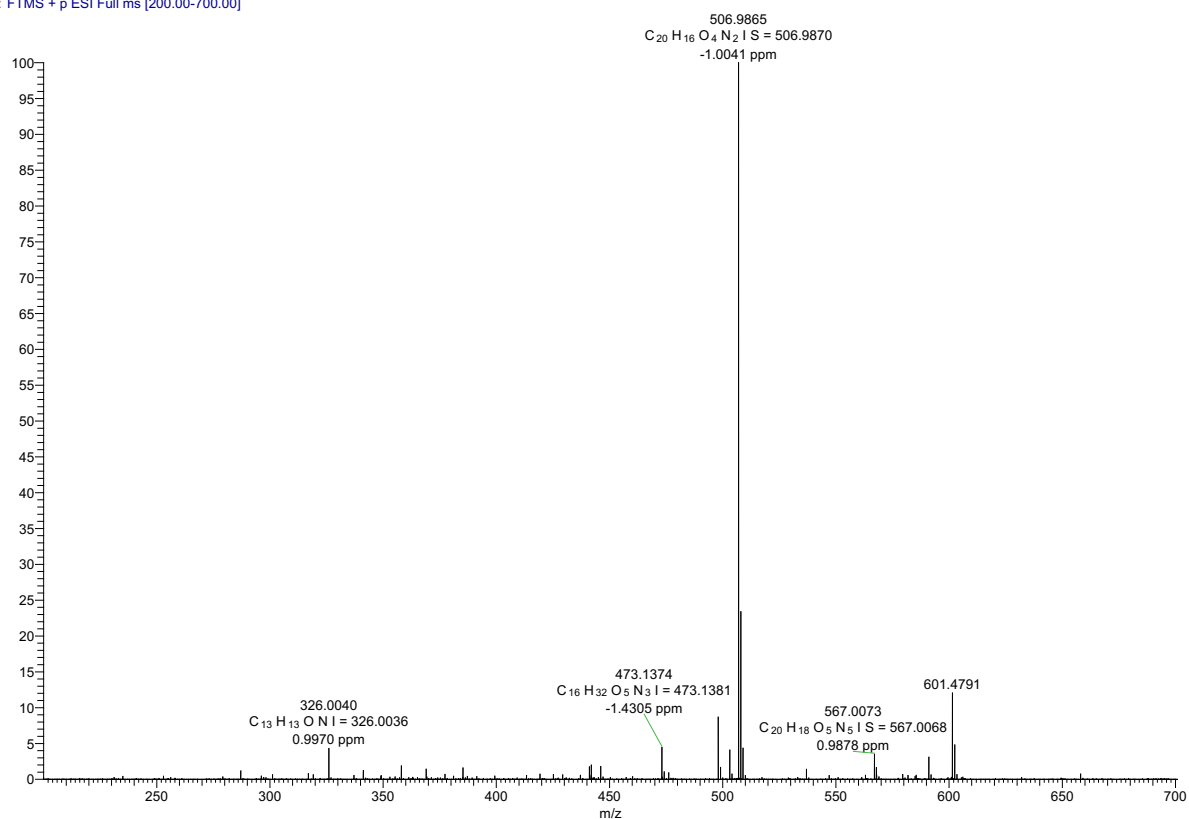


Figure S6. High resolution mass spectrum of **13**

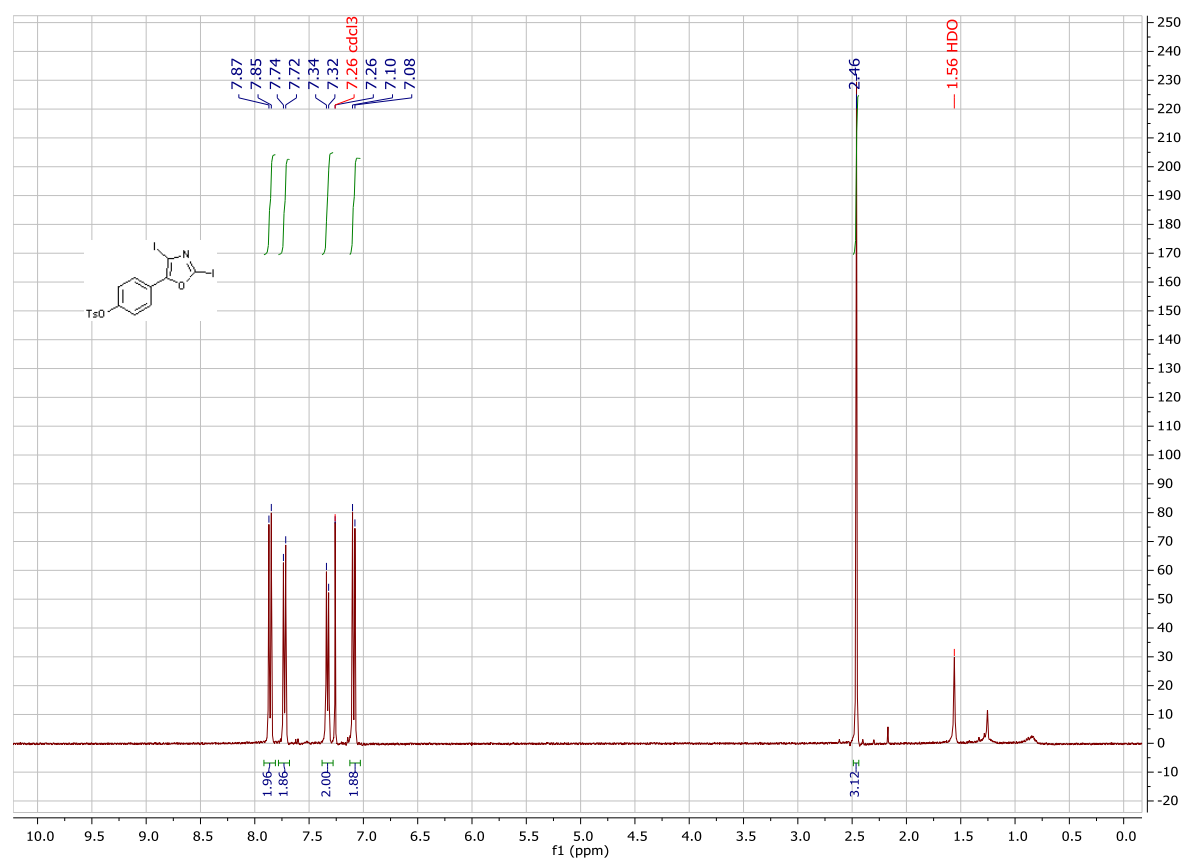
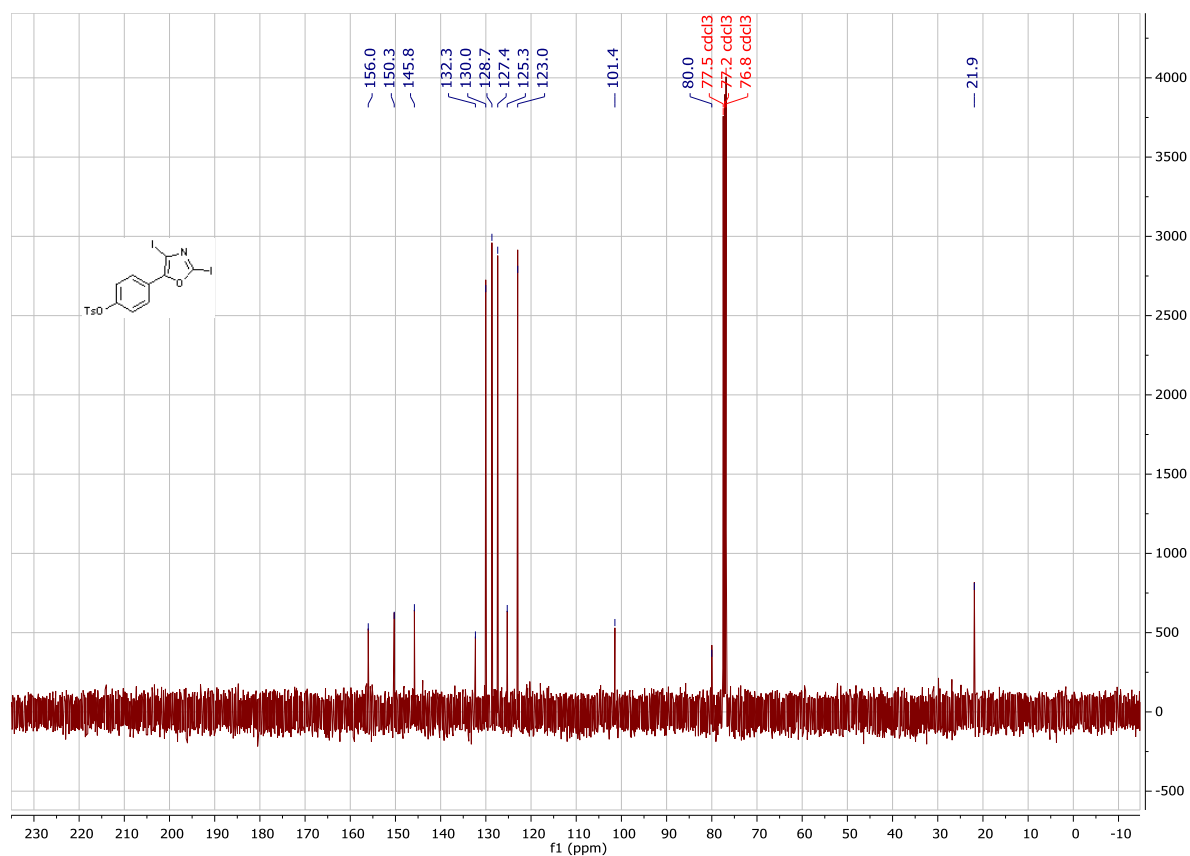
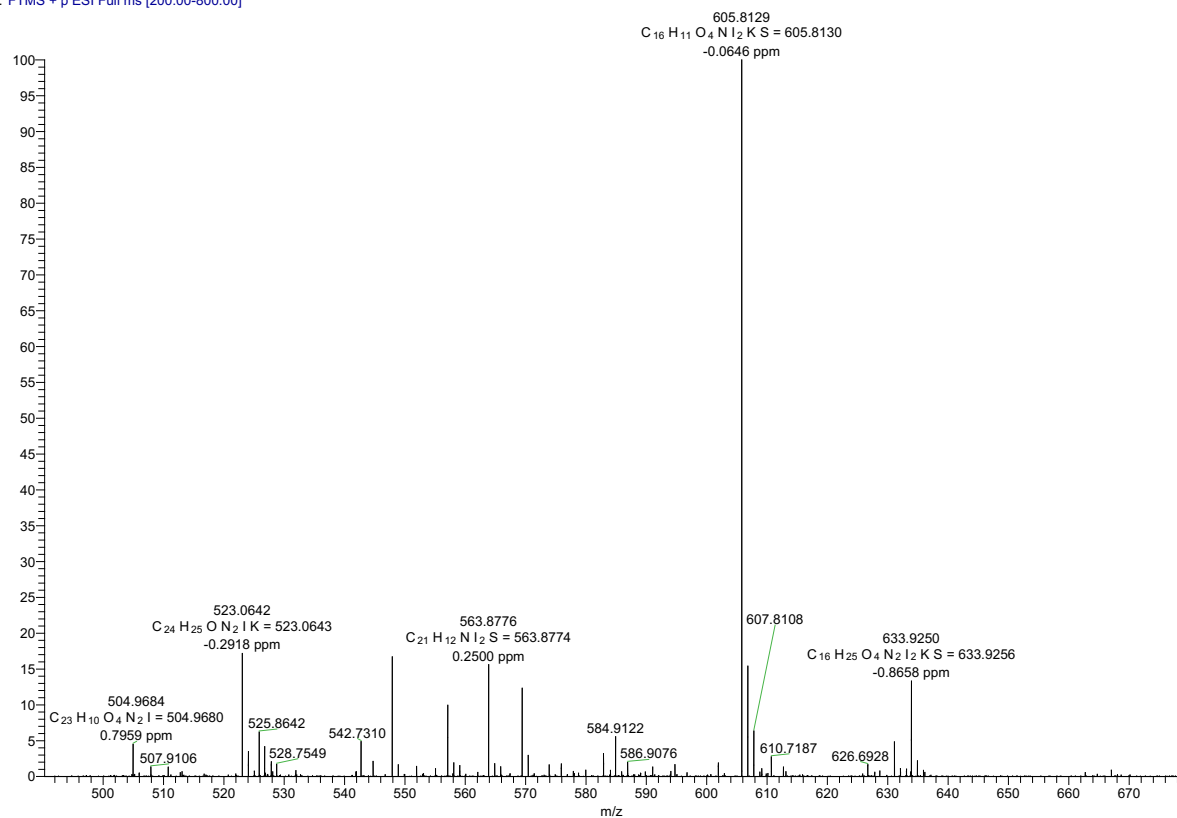


Figure S7. ¹H-NMR spectrum (400 MHz) of **14**

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

yg228A_pos #1-5 RT: 0.01-0.13 AV: 5 NL: 2.72E6
 T: FTMS + p ESI Full ms [200.00-800.00]

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

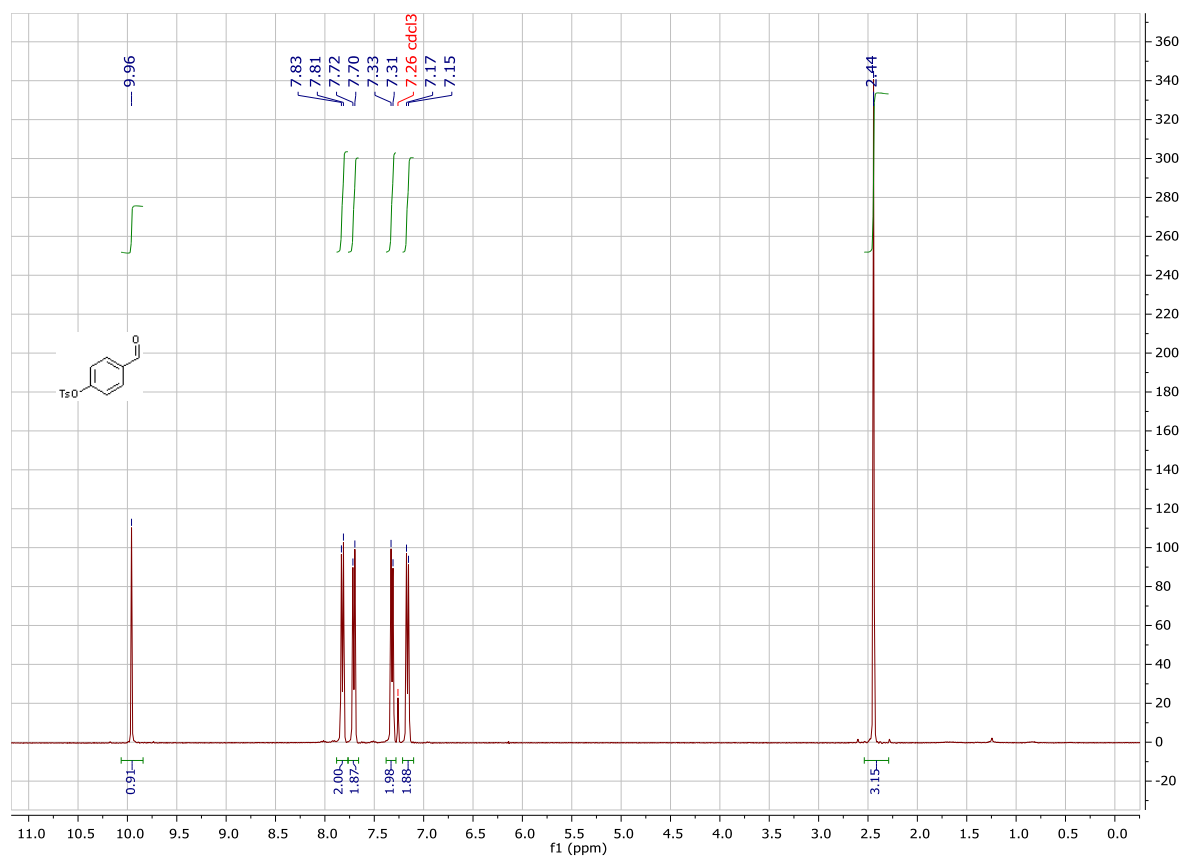


Figure S10. ¹H-NMR spectrum (400 MHz) of 15

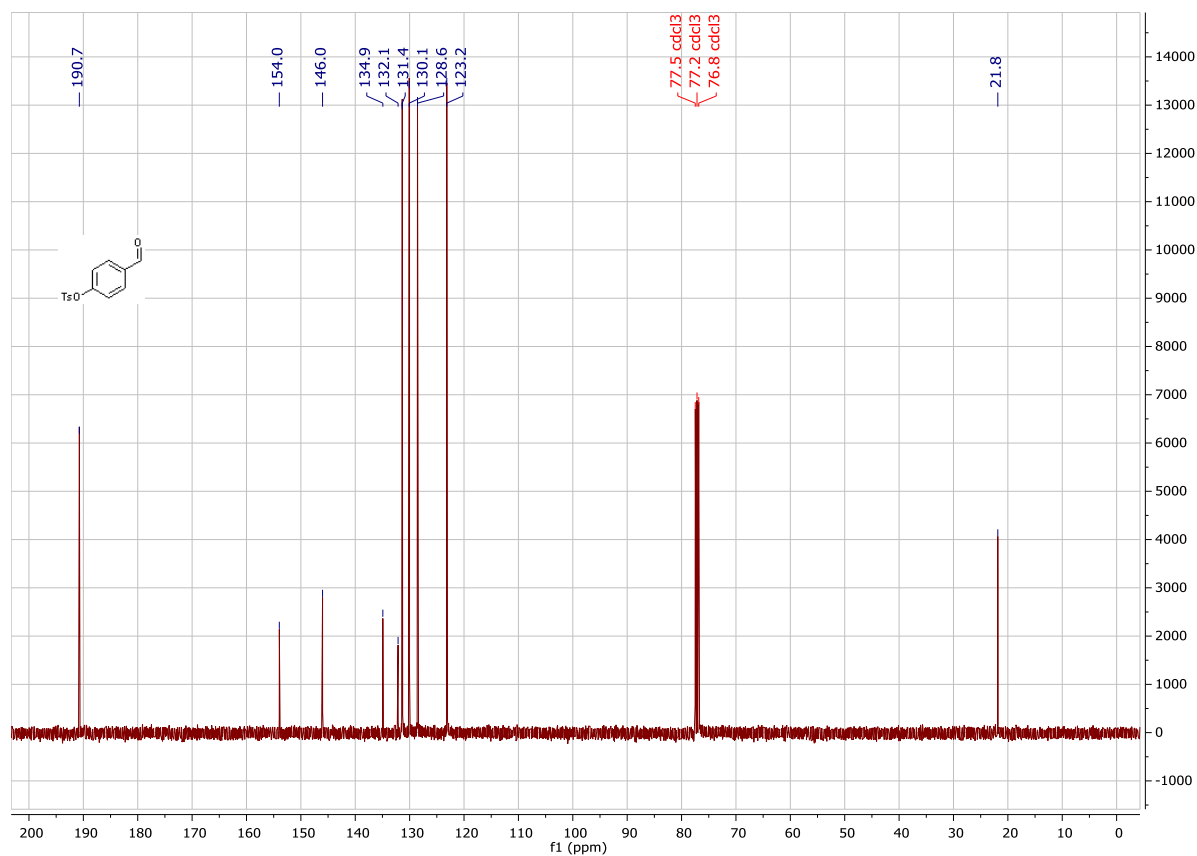
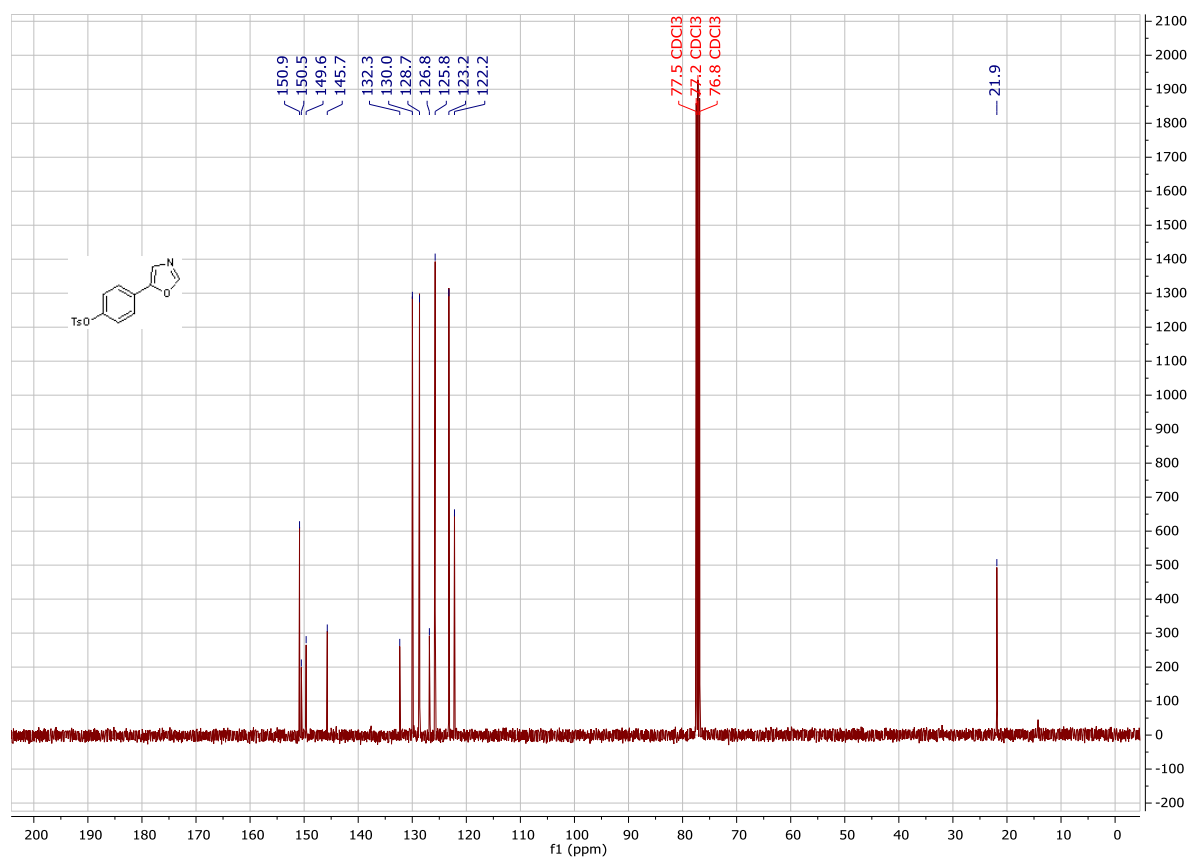
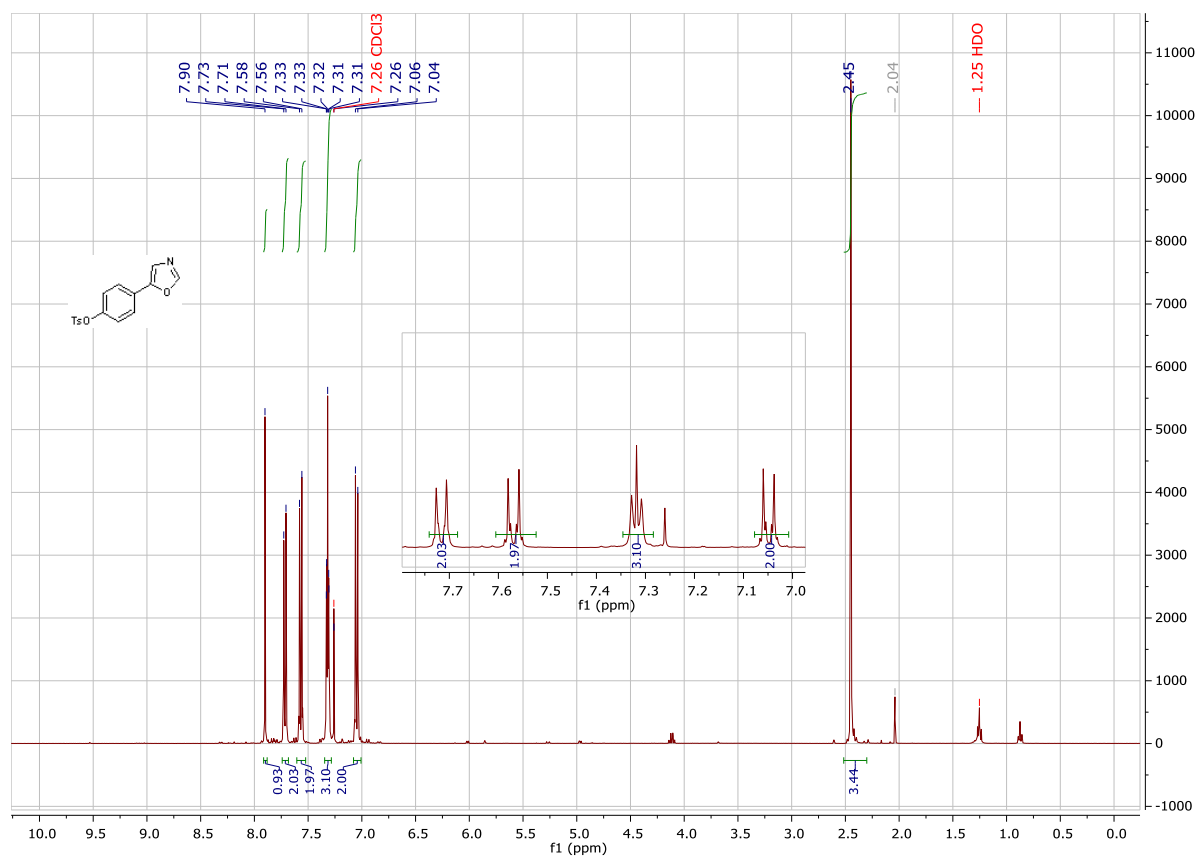


Figure S11. ¹³C-NMR spectrum (101 MHz) of 15



yg214_pos #1-5 RT: 0.02-0.13 AV: 5 NL: 4.06E7
T: FTMS + p ESI Full ms [200.00-800.00]

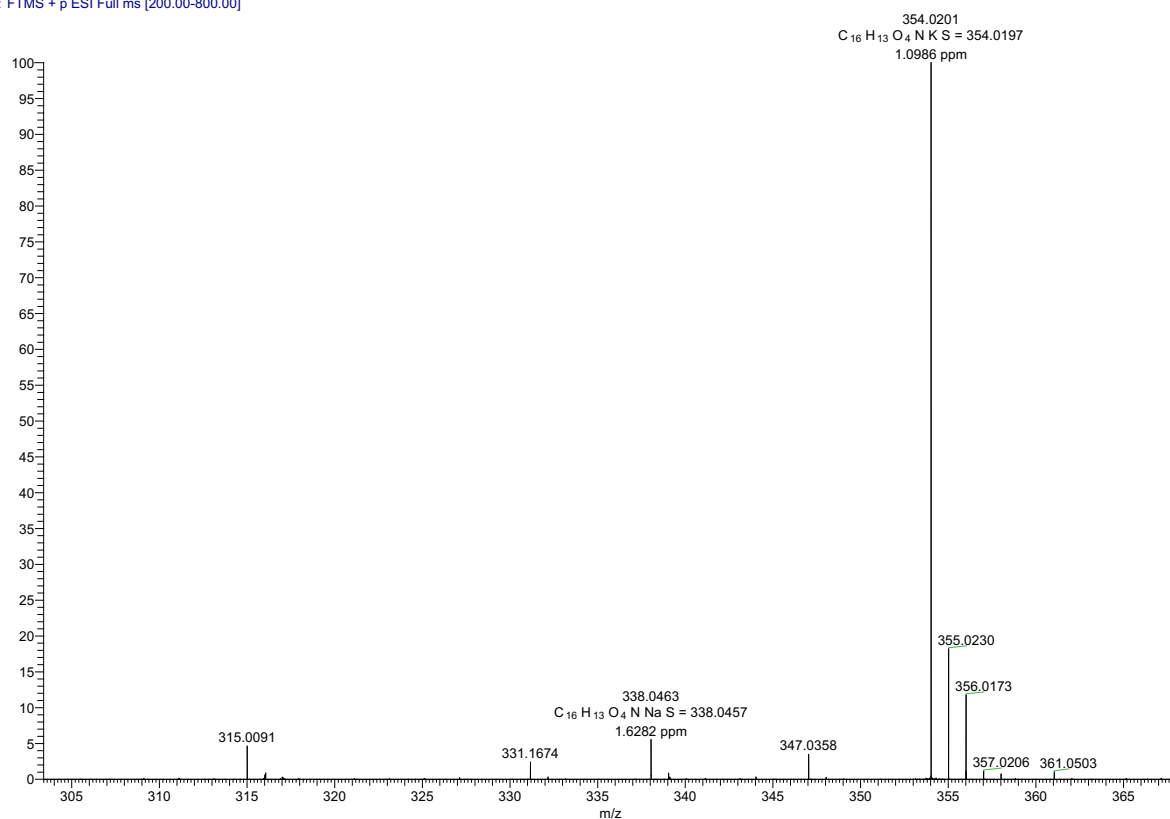


Figure S14. High resolution mass spectrum of 16.

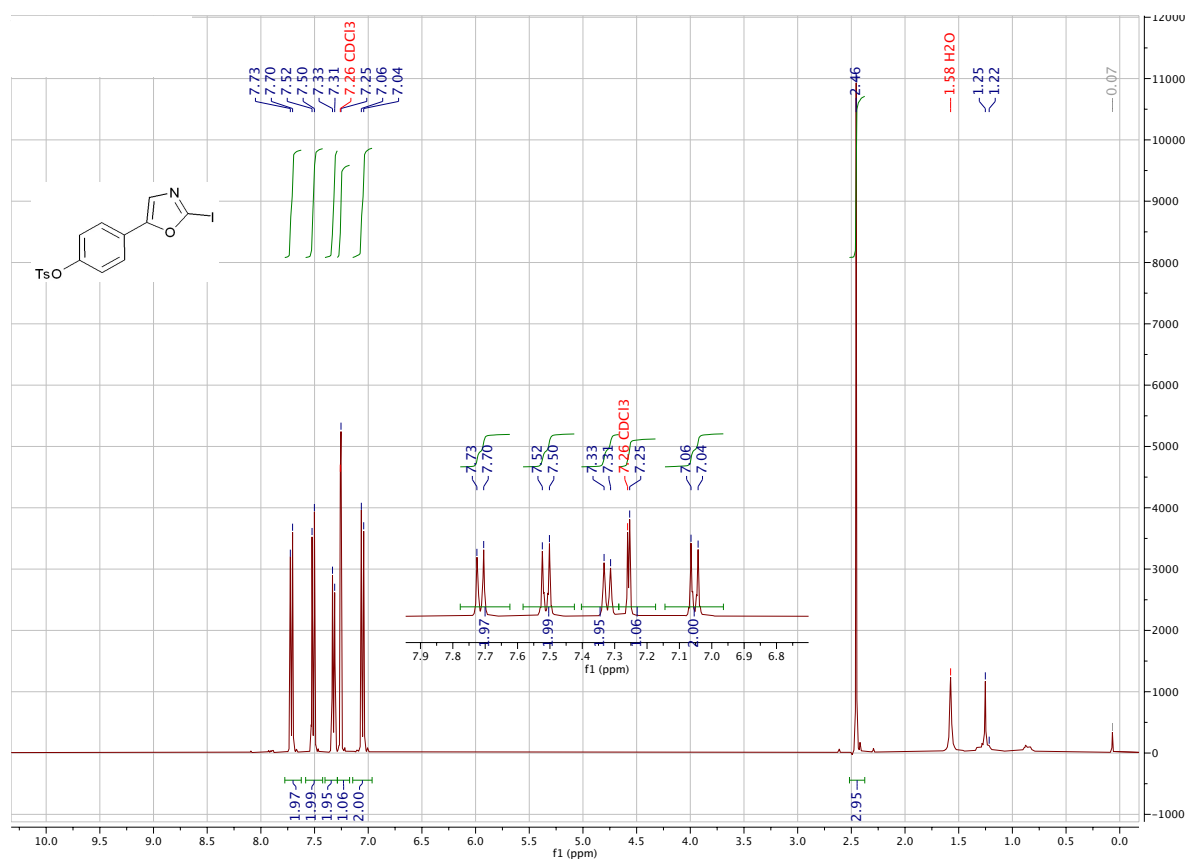
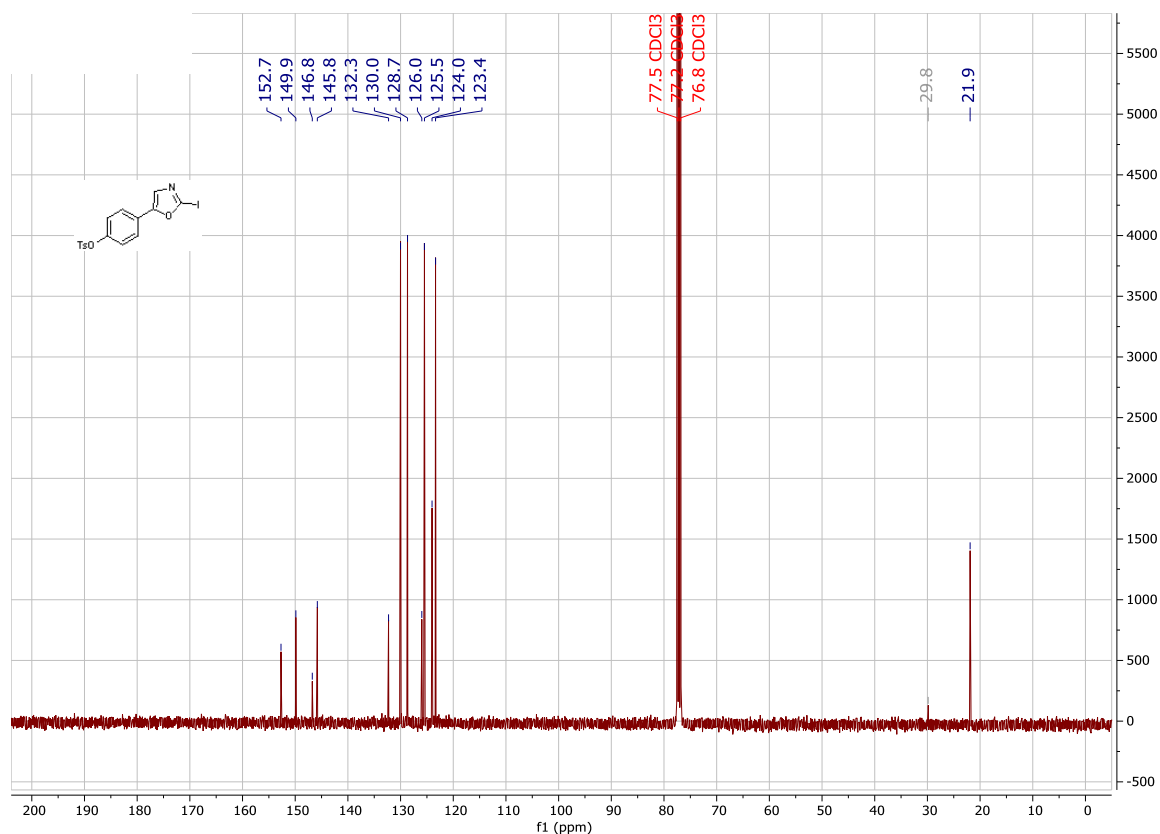
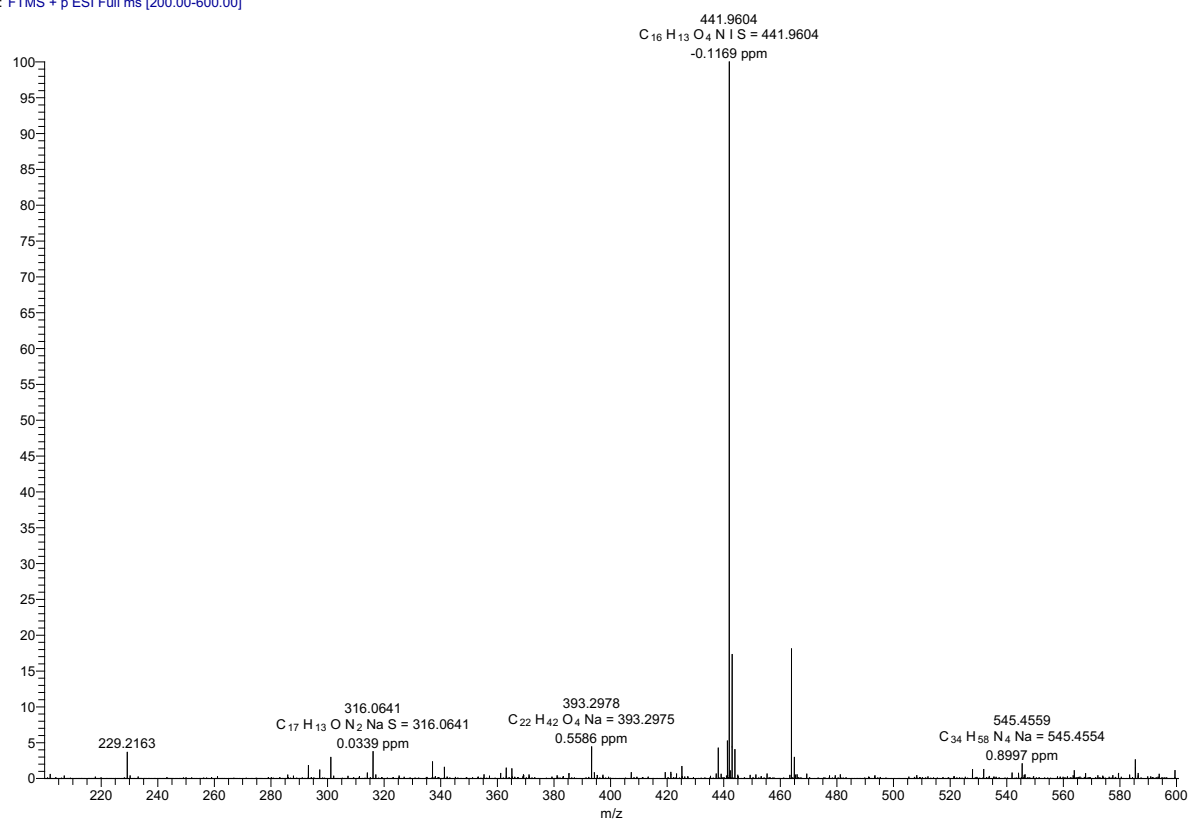


Figure S15. 1H -NMR spectrum (400 MHz) of 17

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

yg228B #1-5 RT: 0.02-0.13 AV: 5 NL: 1.44E7
T: FTMS + p ESI Full ms [200.00-600.00]

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

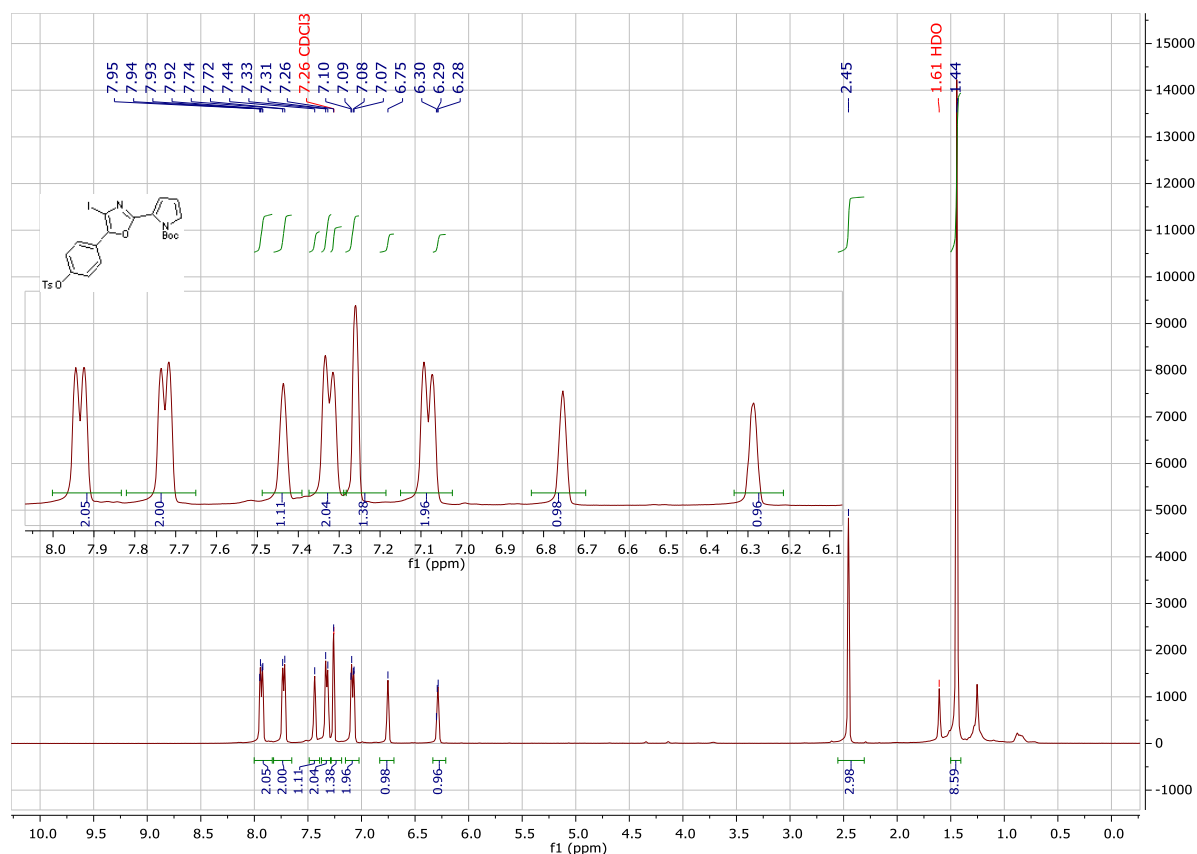


Figure S18. ¹H-NMR spectrum (400 MHz) of **18**

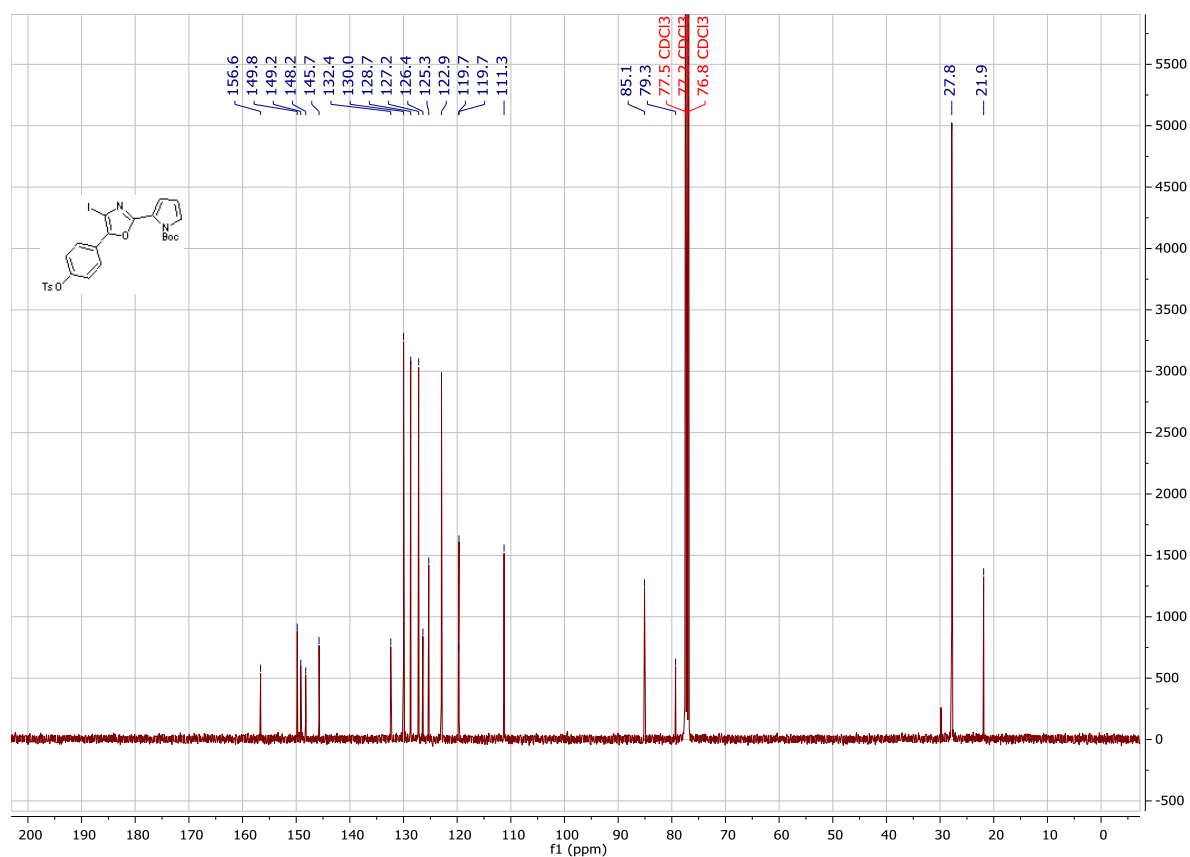


Figure S19. ¹³C-NMR spectrum (101 MHz) of **18**

yg230 #1-5 RT: 0.00-0.11 AV: 5 NL: 7.56E6
T: FTMS + p ESI Full ms [200.00-700.00]

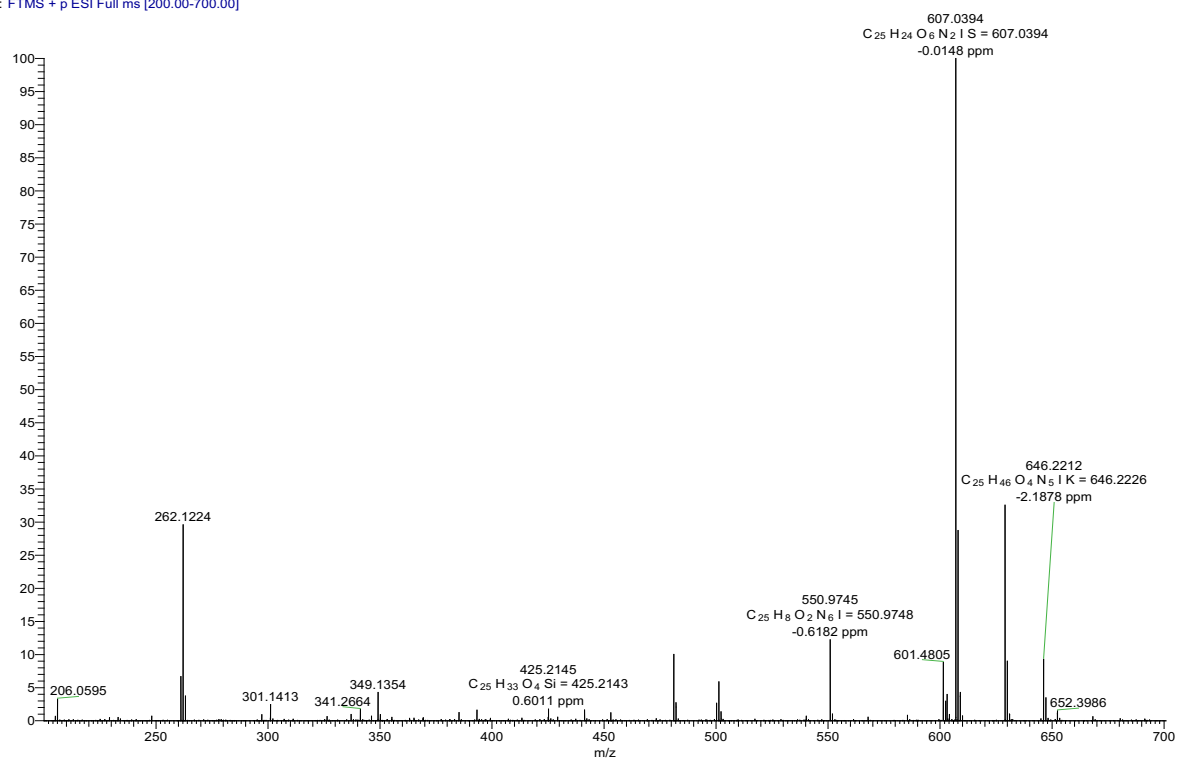


Figure S20. High resolution mass spectrum of 18.

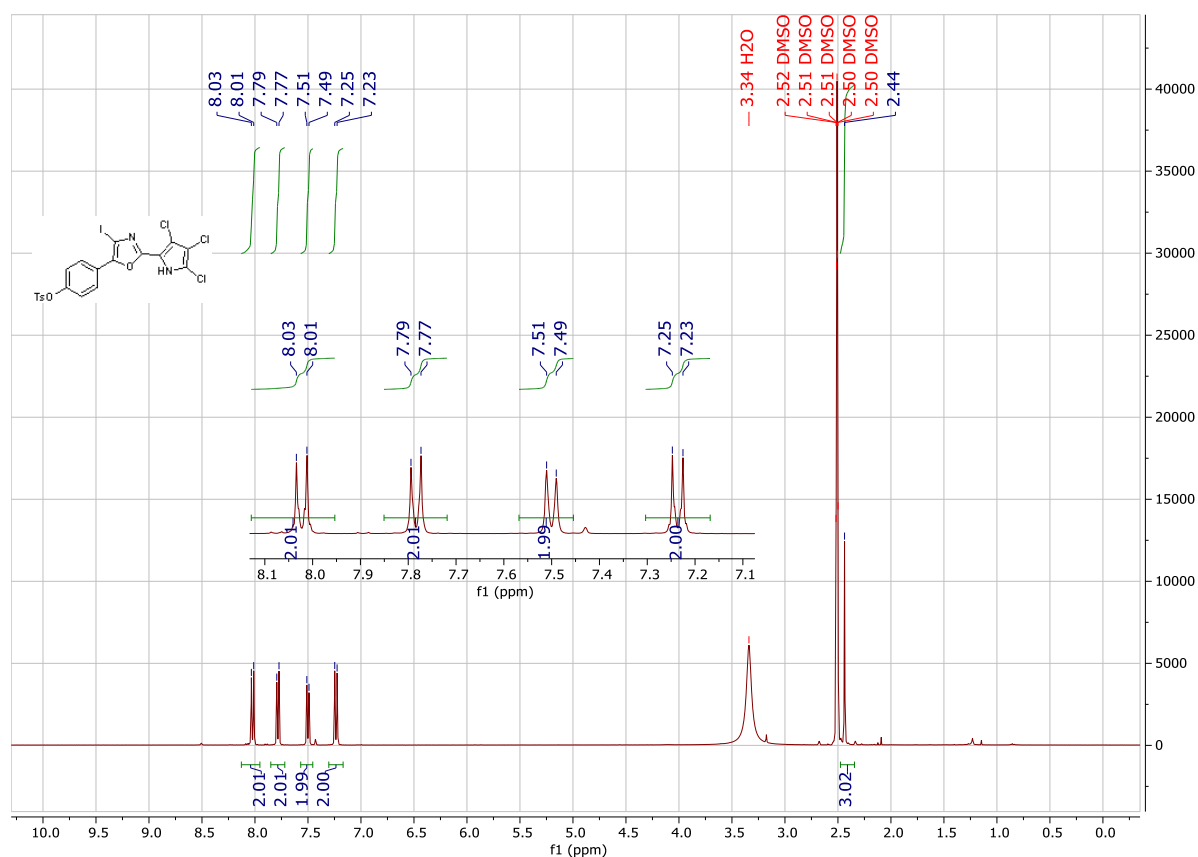
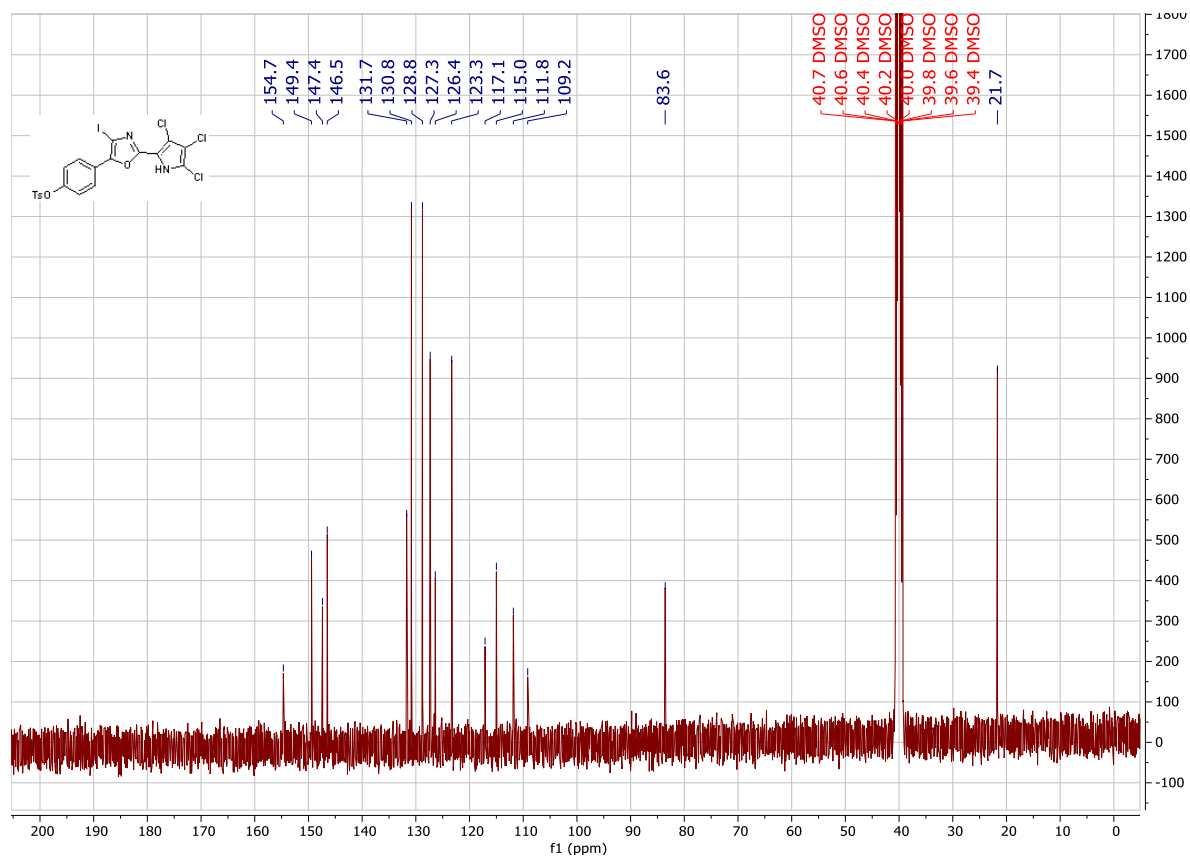


Figure S21. ¹H-NMR spectrum (400 MHz) of 19.

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

yg251pure_Neg #1-4 RT: 0.02-0.14 AV: 4 NL: 1.49E6
T: FTMS - p ESI Full ms [300.00-800.00]

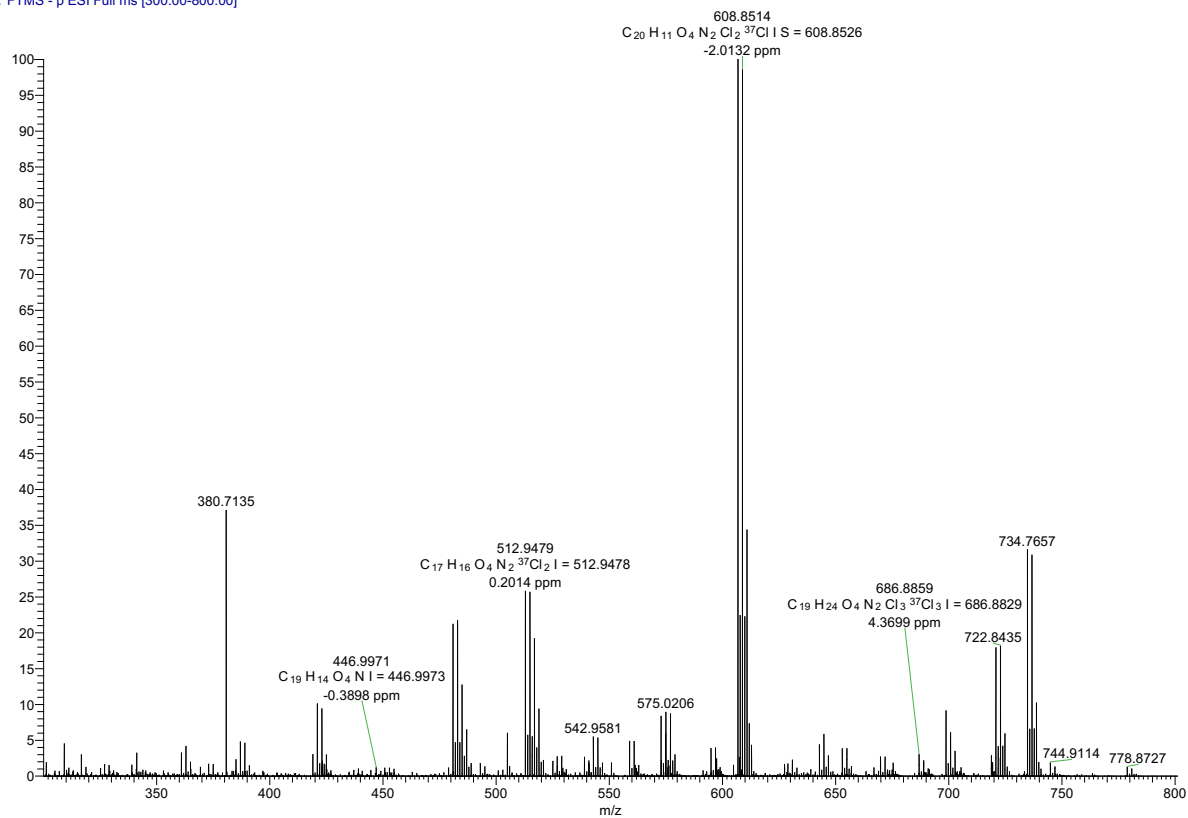
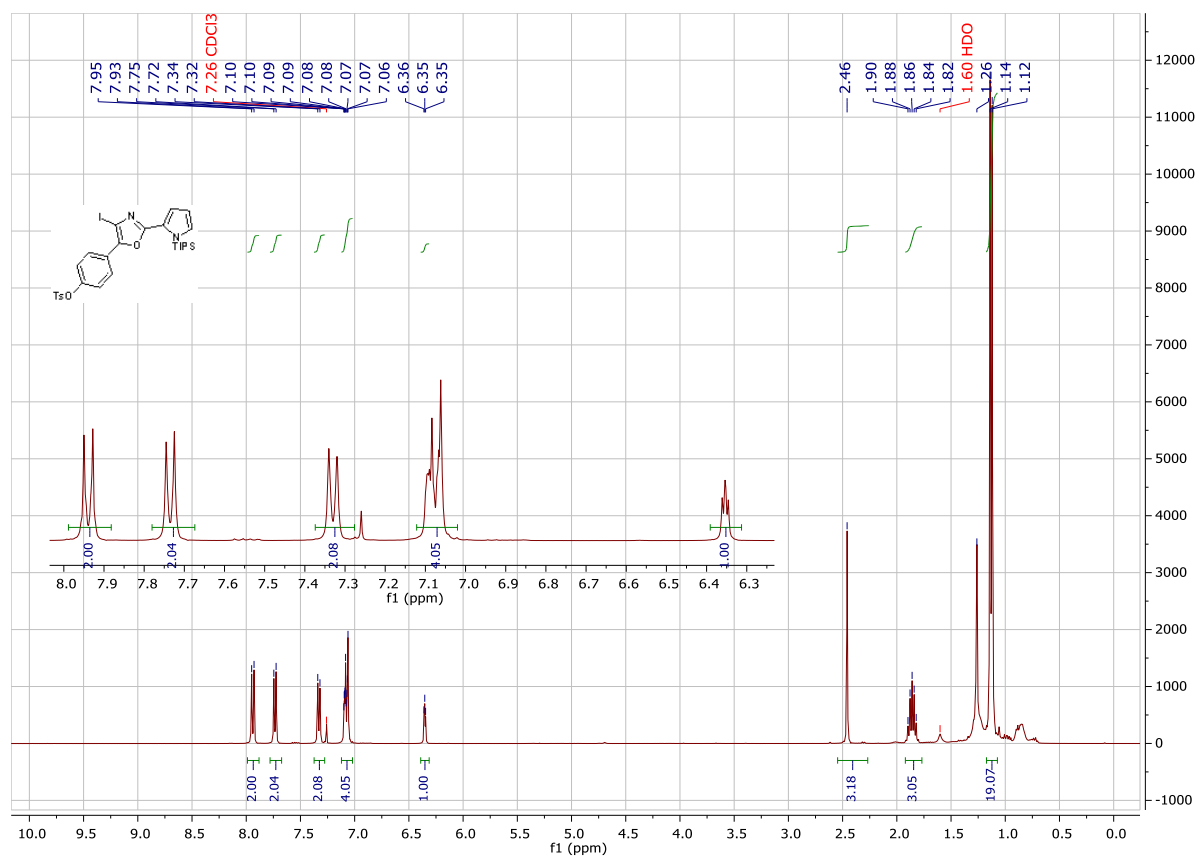


Figure S23. High resolution mass spectrum of 19.



yg246pure_Posb #1-5 RT: 0.02-0.13 AV: 5 NL: 9.70E6
T: FTMS + p ESI Full ms [200.00-800.00]

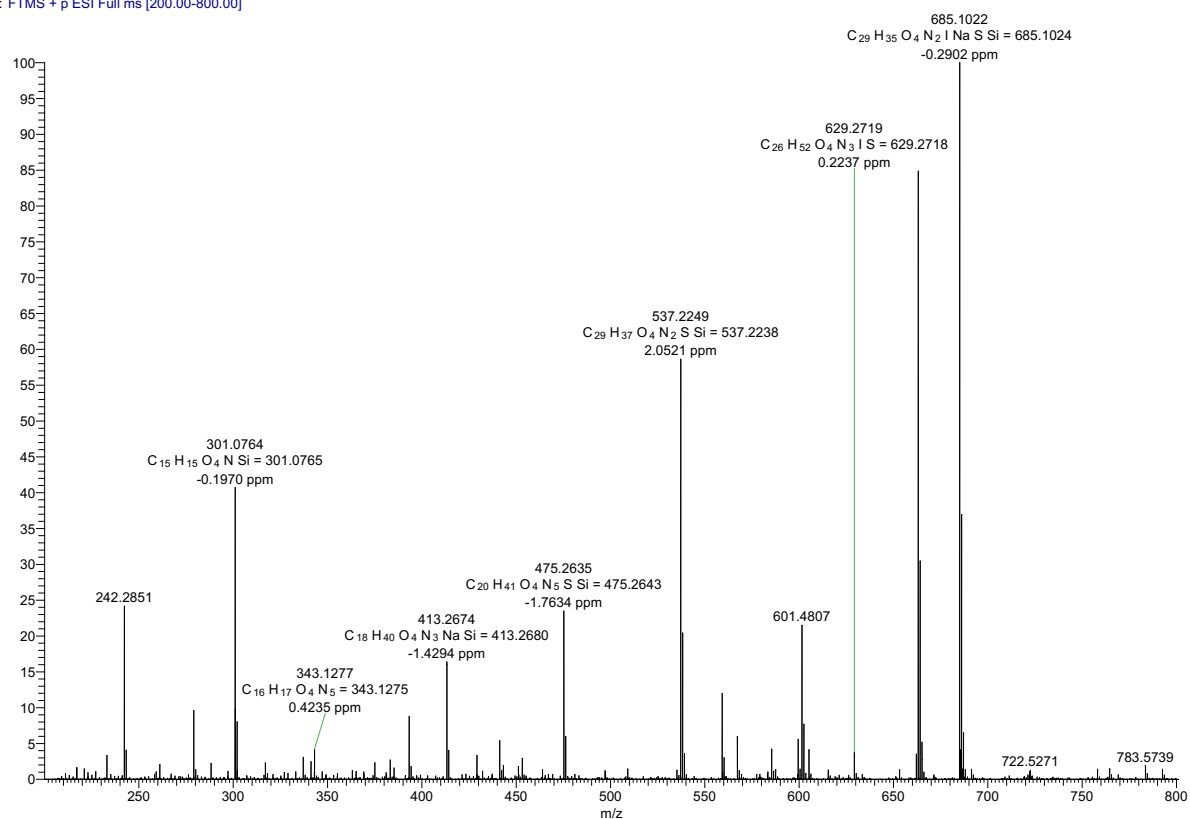


Figure S26. High resolution mass spectrum of **20b**

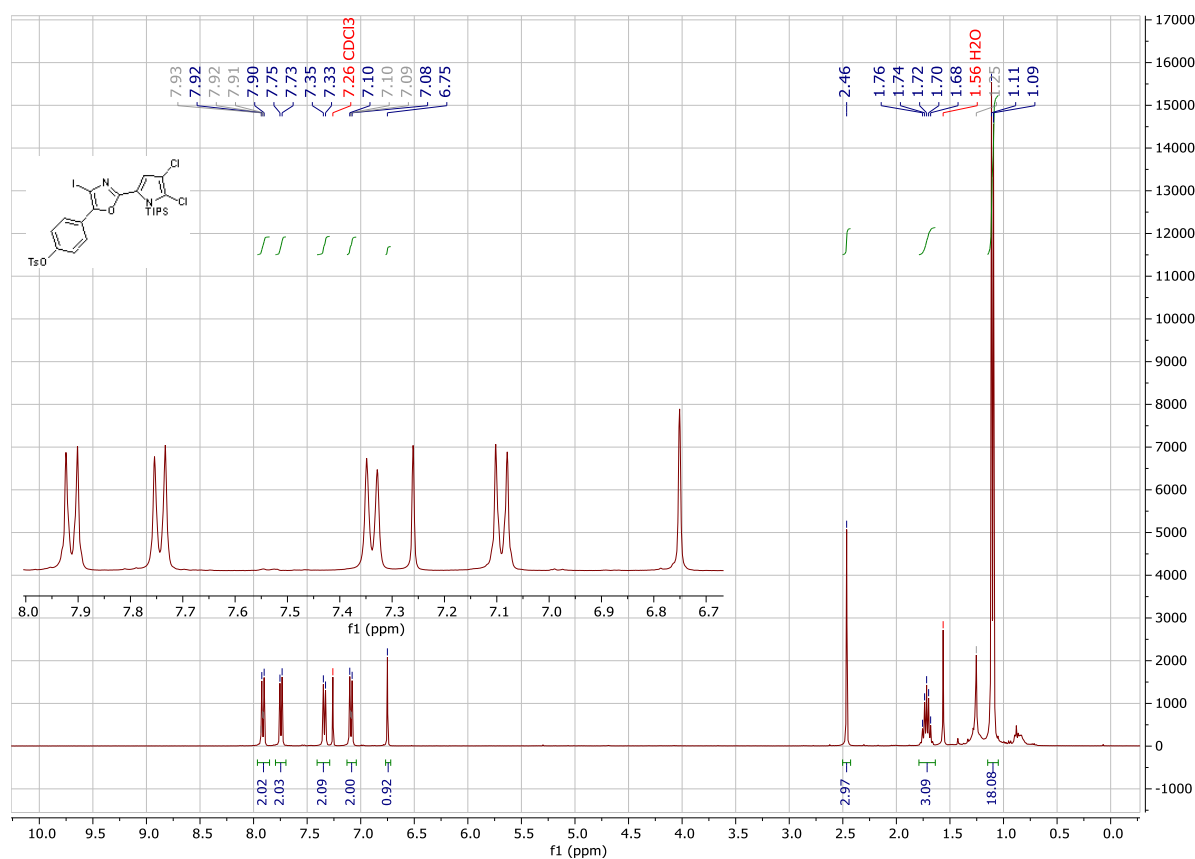


Figure S27. ¹H-NMR (400 MHz) spectrum of **21**.

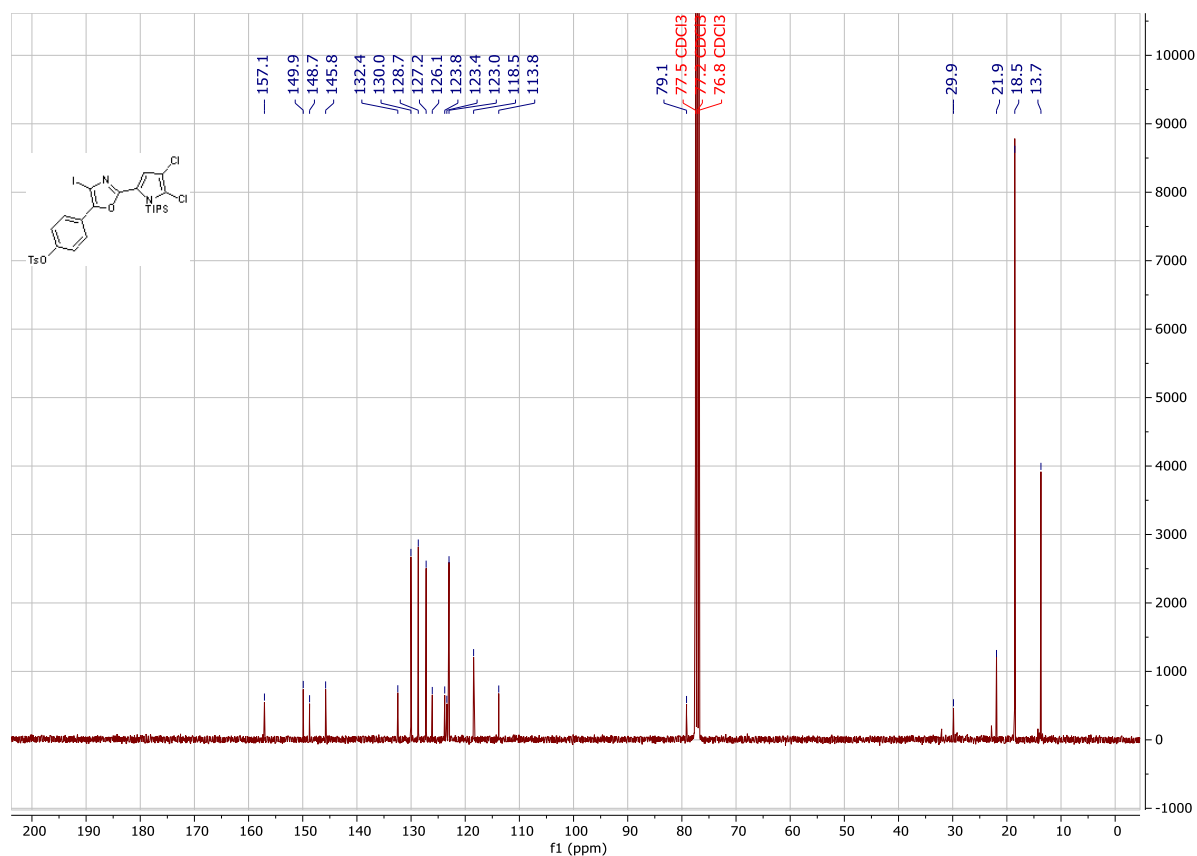


Figure S28. ^{13}C -NMR (101 MHz) spectrum of **21**.

yg285-10min-reset_pos #1-5 RT: 0.00-0.11 AV: 5 NL: 1.81E7
T: FTMS + p ESI Full ms [200.00-1000.00]

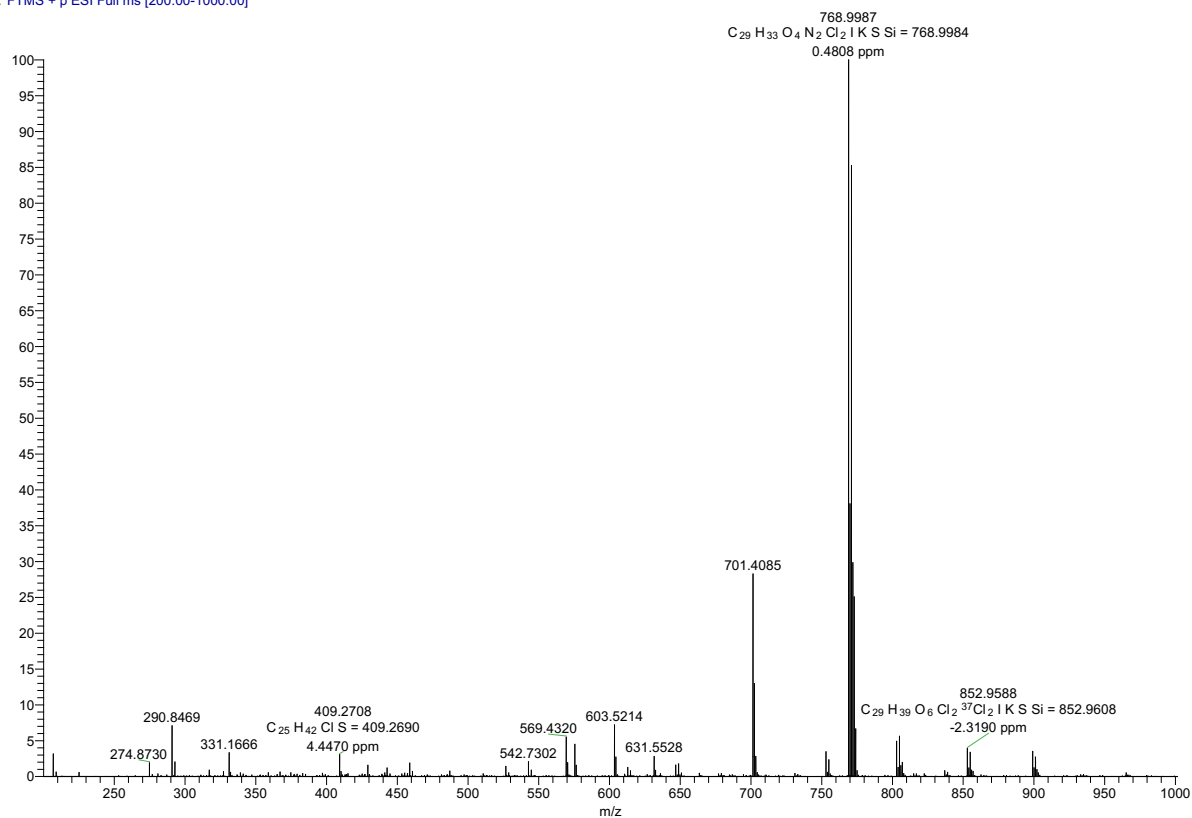


Figure S29. High resolution mass spectrum of **21**.

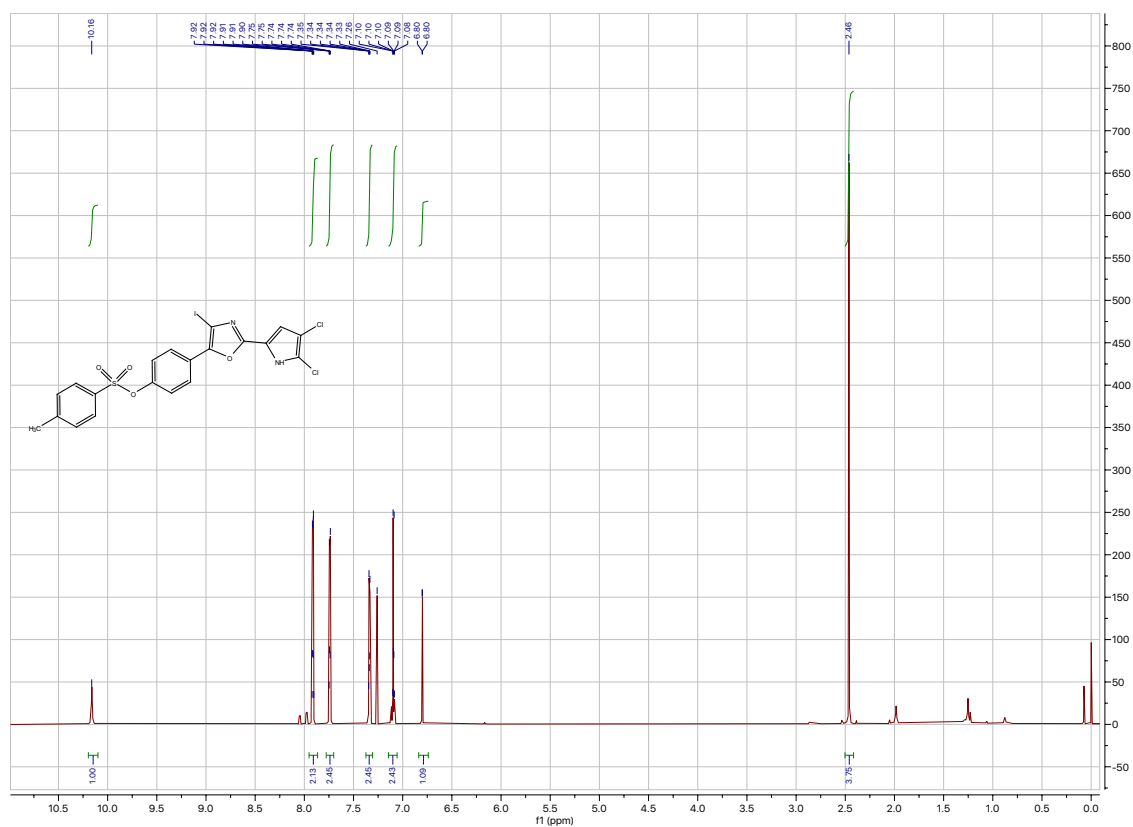


Figure S30. ¹H-NMR (850 MHz) spectrum of **22**.

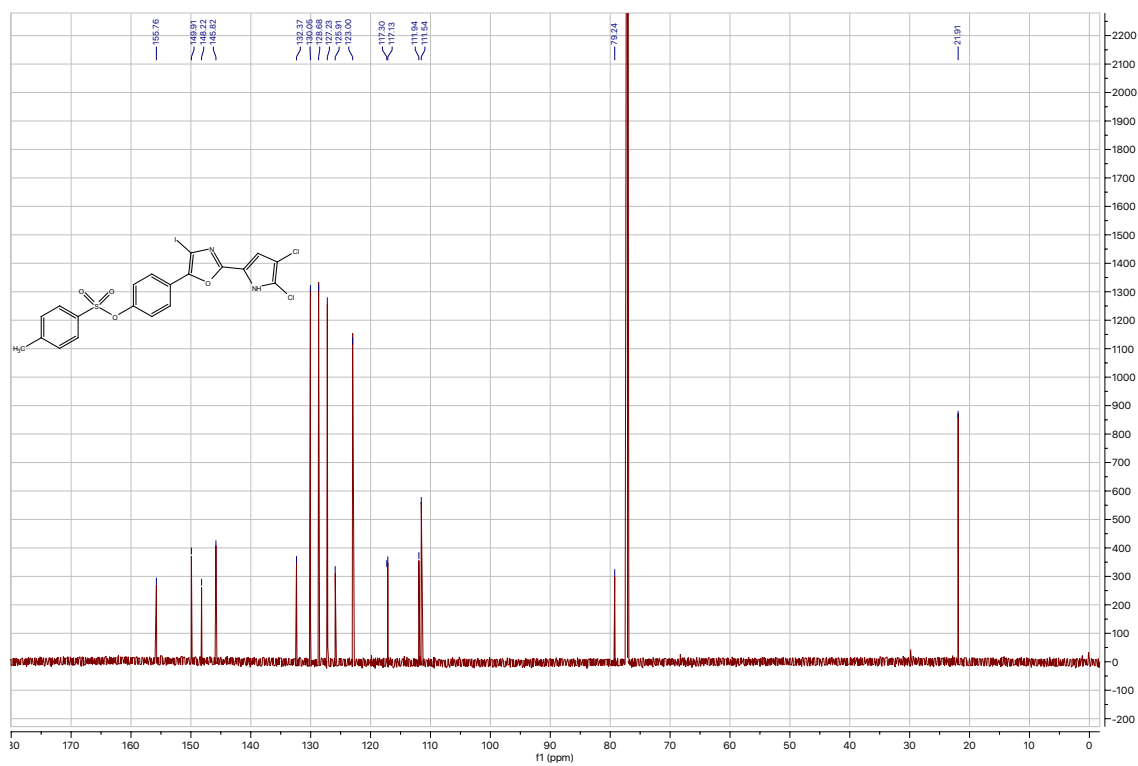


Figure S31. ¹³C-NMR (126 MHz) spectrum of **22**.

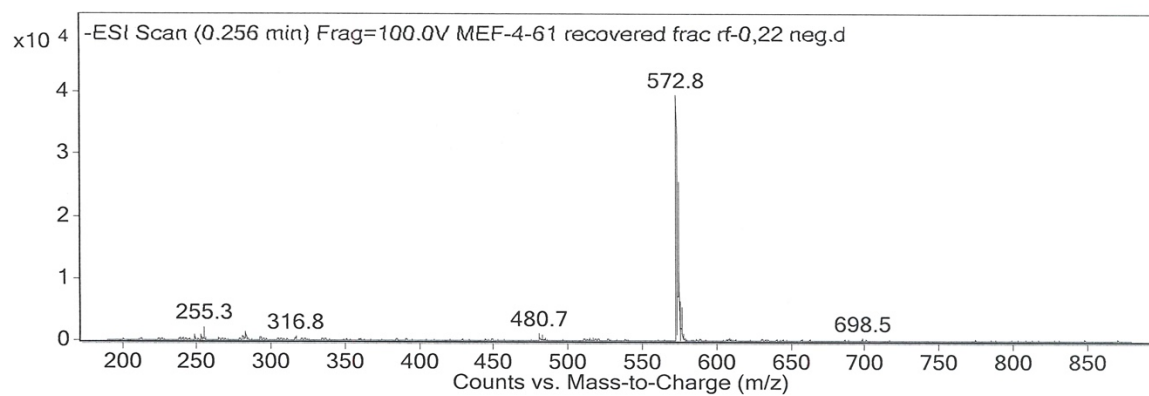


Figure S32. Low resolution MS of **22**.

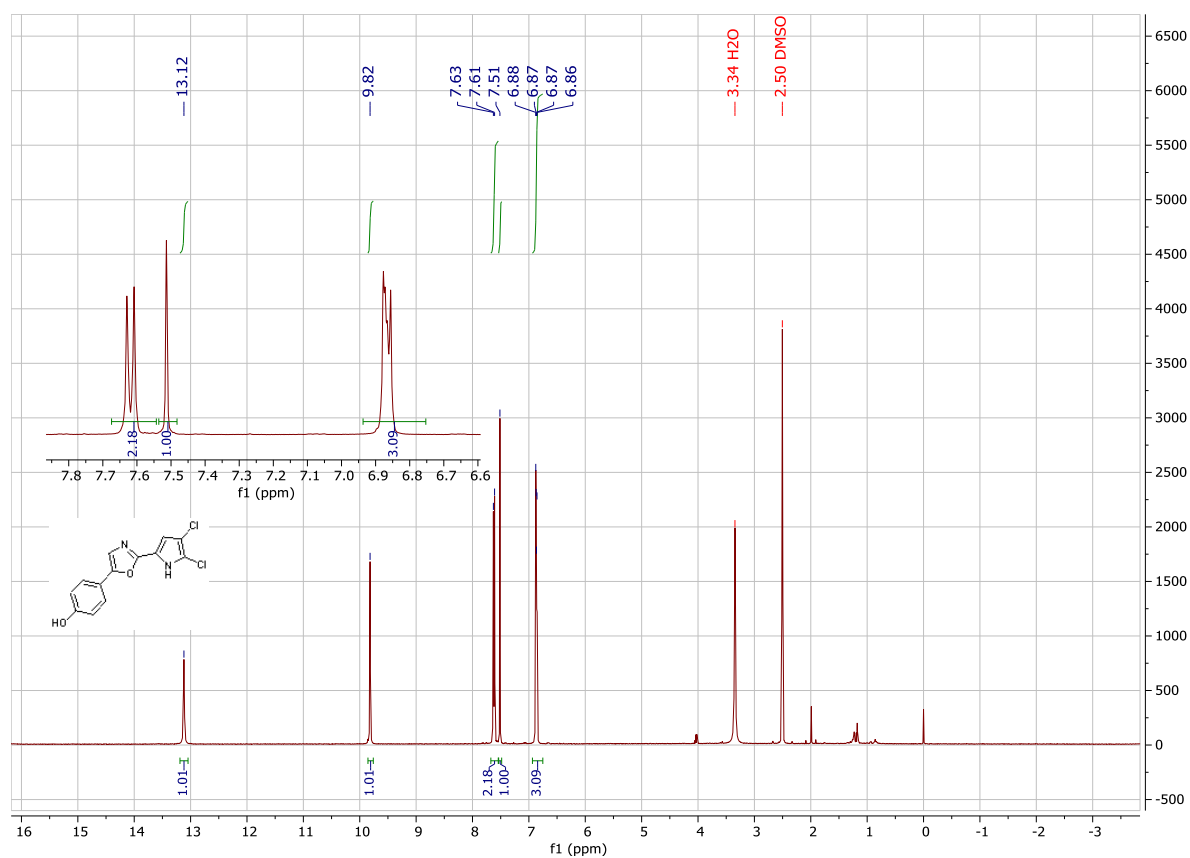


Figure S33. ^1H -NMR (400 MHz) spectrum of **23**.

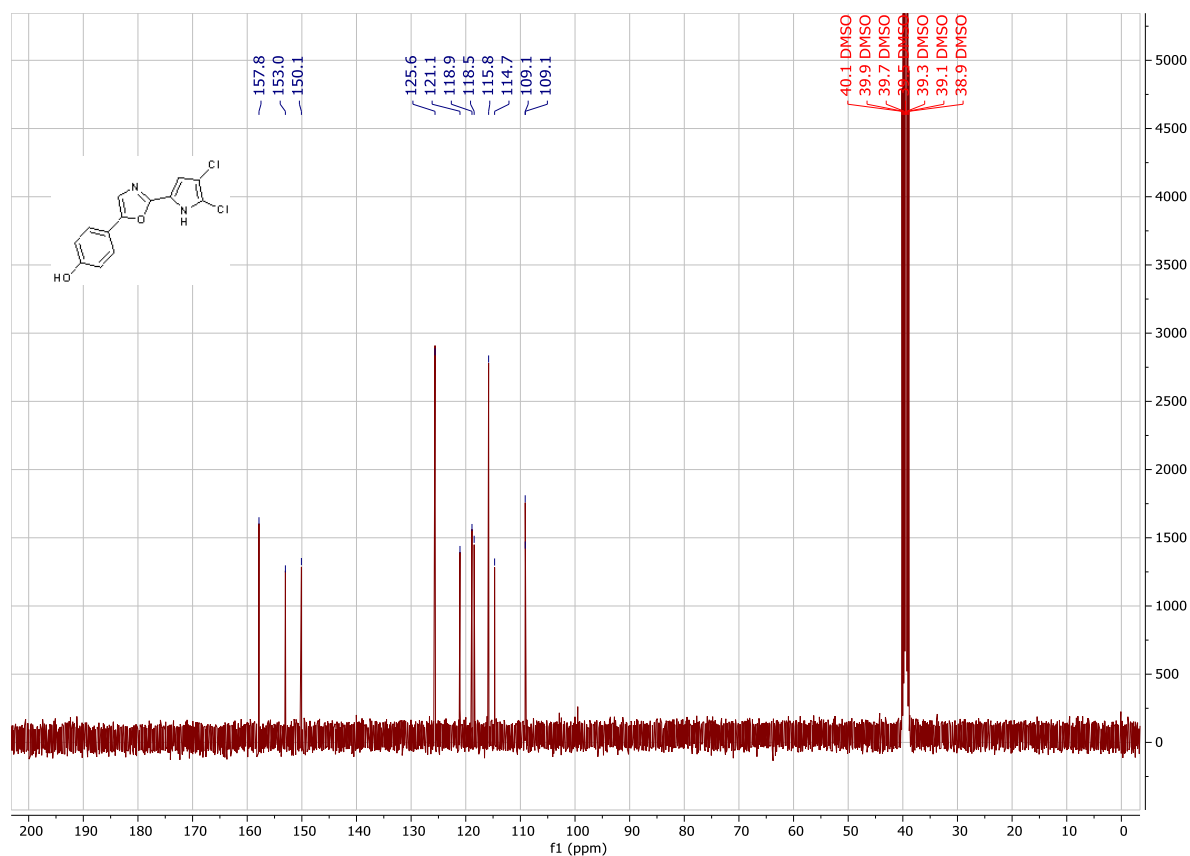


Figure S34. ¹³C-NMR (101 MHz) spectrum of **23**.

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T: FTMS + p ESI Full ms [200.00-600.00]

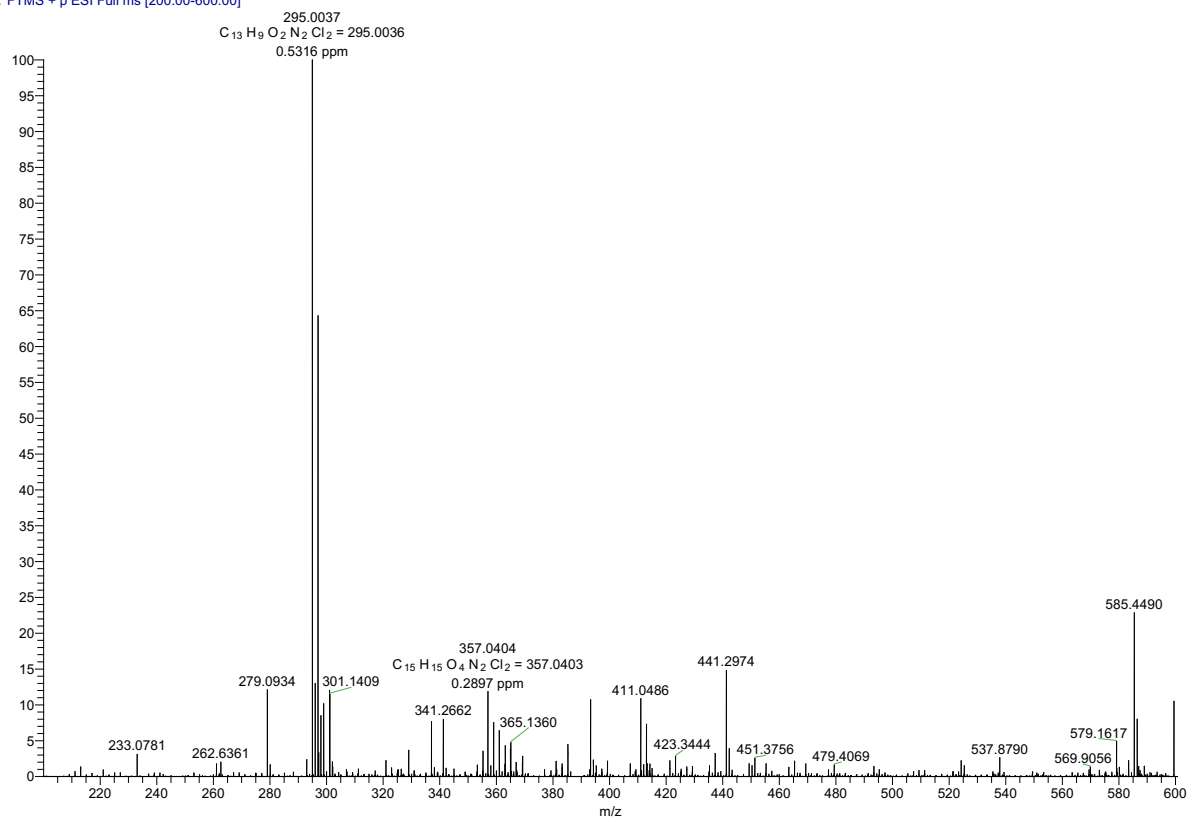
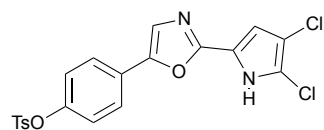


Figure S35. High resolution mass spectrum of **23**.

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); $^1\text{H-NMR}$ (400 MHz, $\text{SO}(\text{CD}_3)_2$) 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); $^{13}\text{C-NMR}$ (101 MHz, $\text{CO}(\text{CD}_3)_2$) 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 $\text{C}_{20}\text{H}_{13}\text{O}_4\text{N}_2\text{Cl}_2\text{S}$ [M-H] $^-$: 446.9973; found: 466.9969.

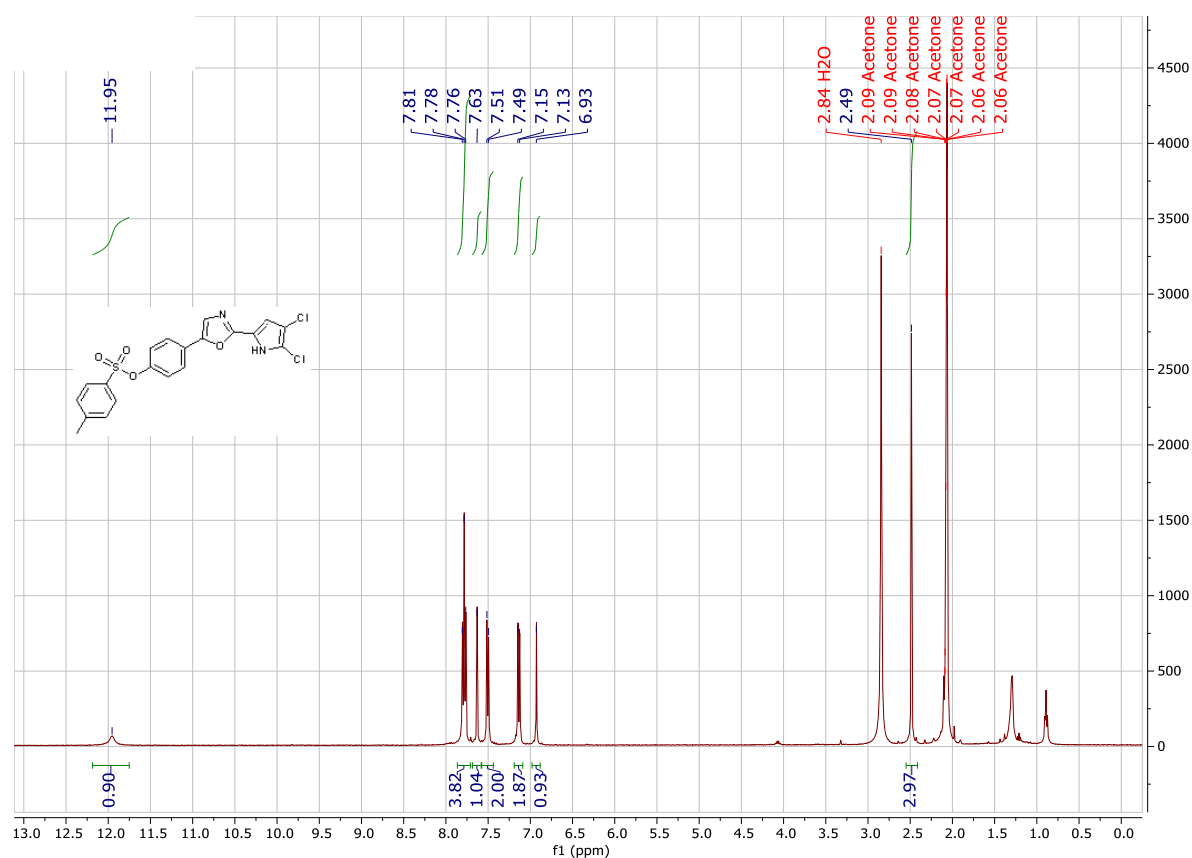
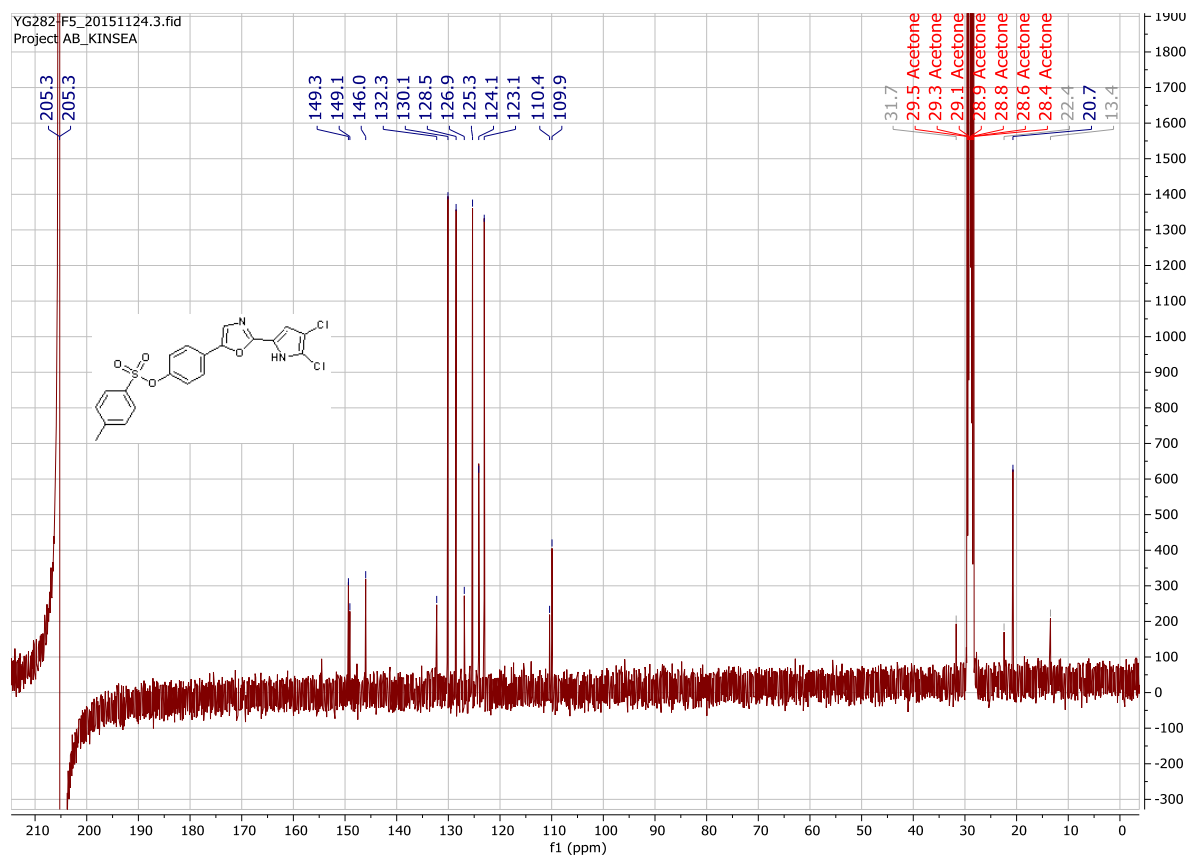
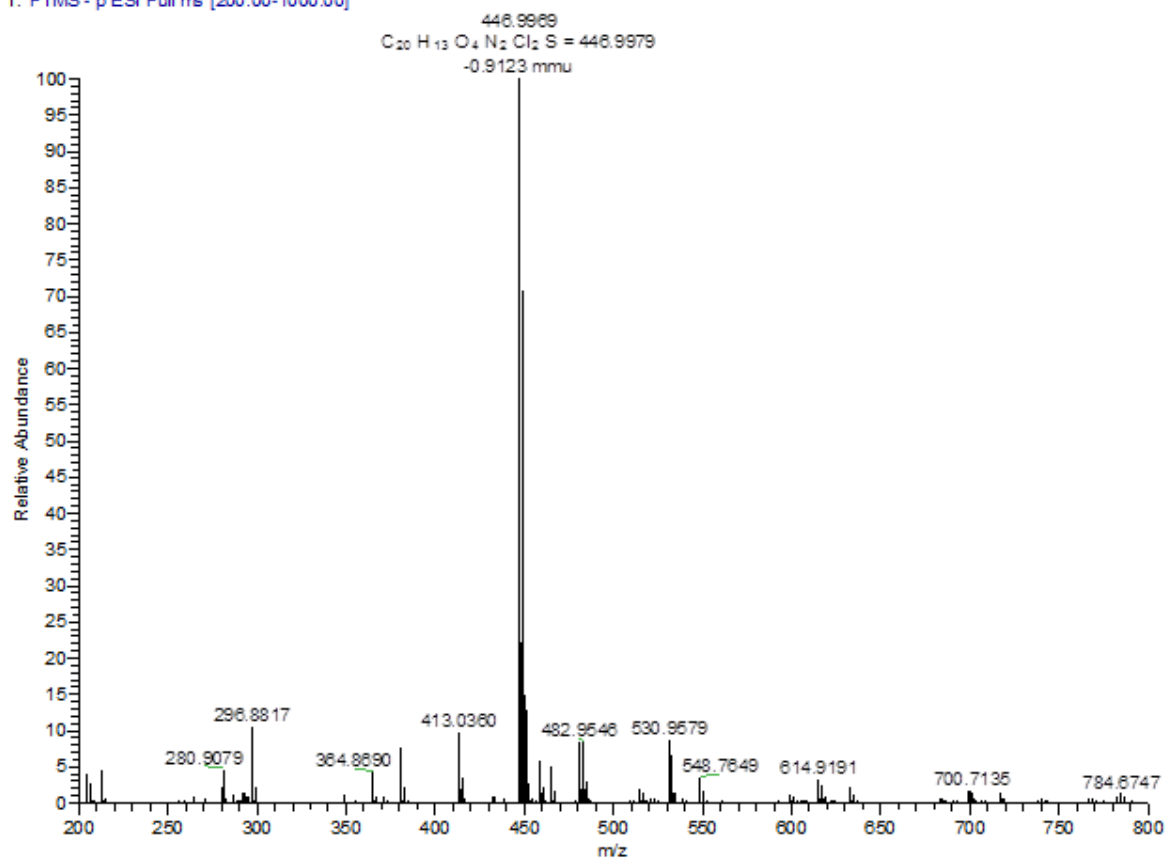


Figure S36. $^1\text{H-NMR}$ (400 MHz) spectrum of **24**.

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

vg282-f5 neg #1-5 RT: 0.01-0.13 AV: 5 NL: 3.70E6
T: FTMS - p ESI Full ms [200.00-1000.00]

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

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

Proton

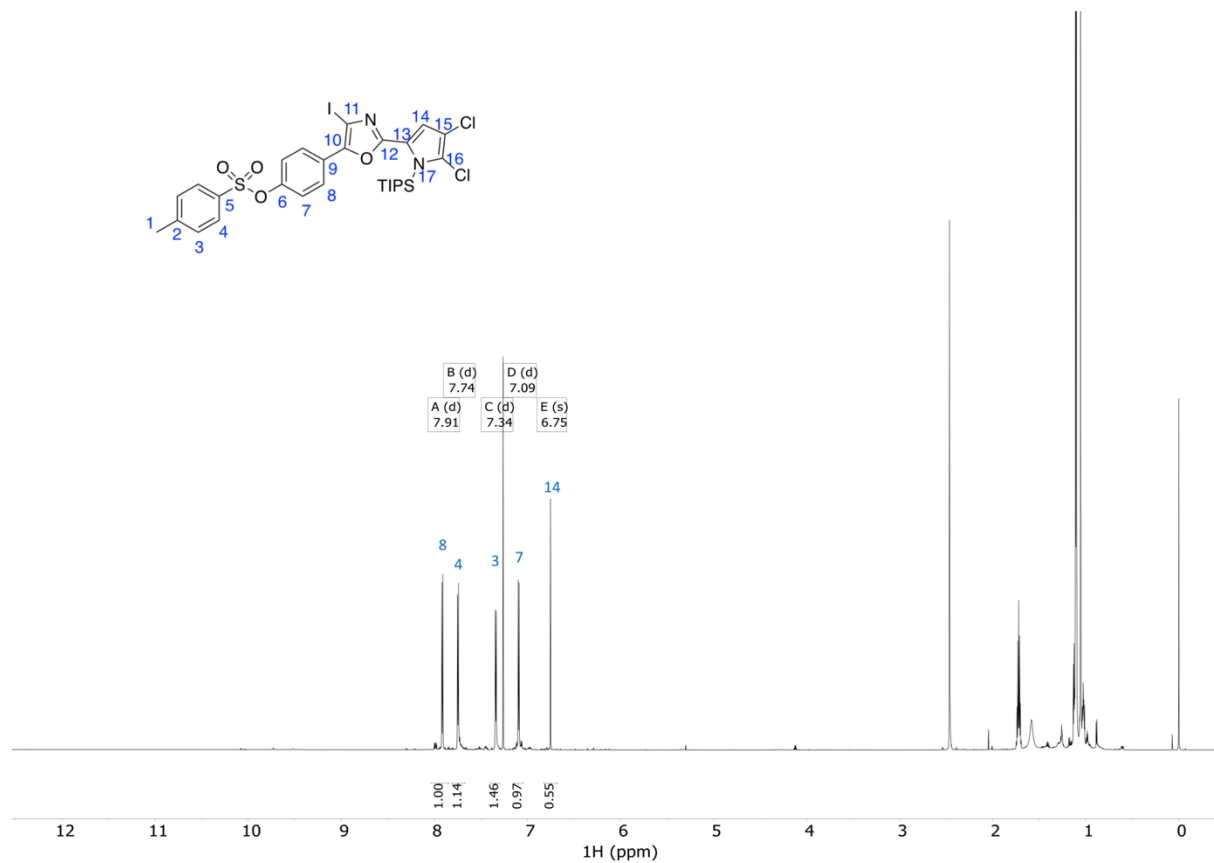


Figure S36. ¹H-NMR (850 MHz) spectrum of **21**.

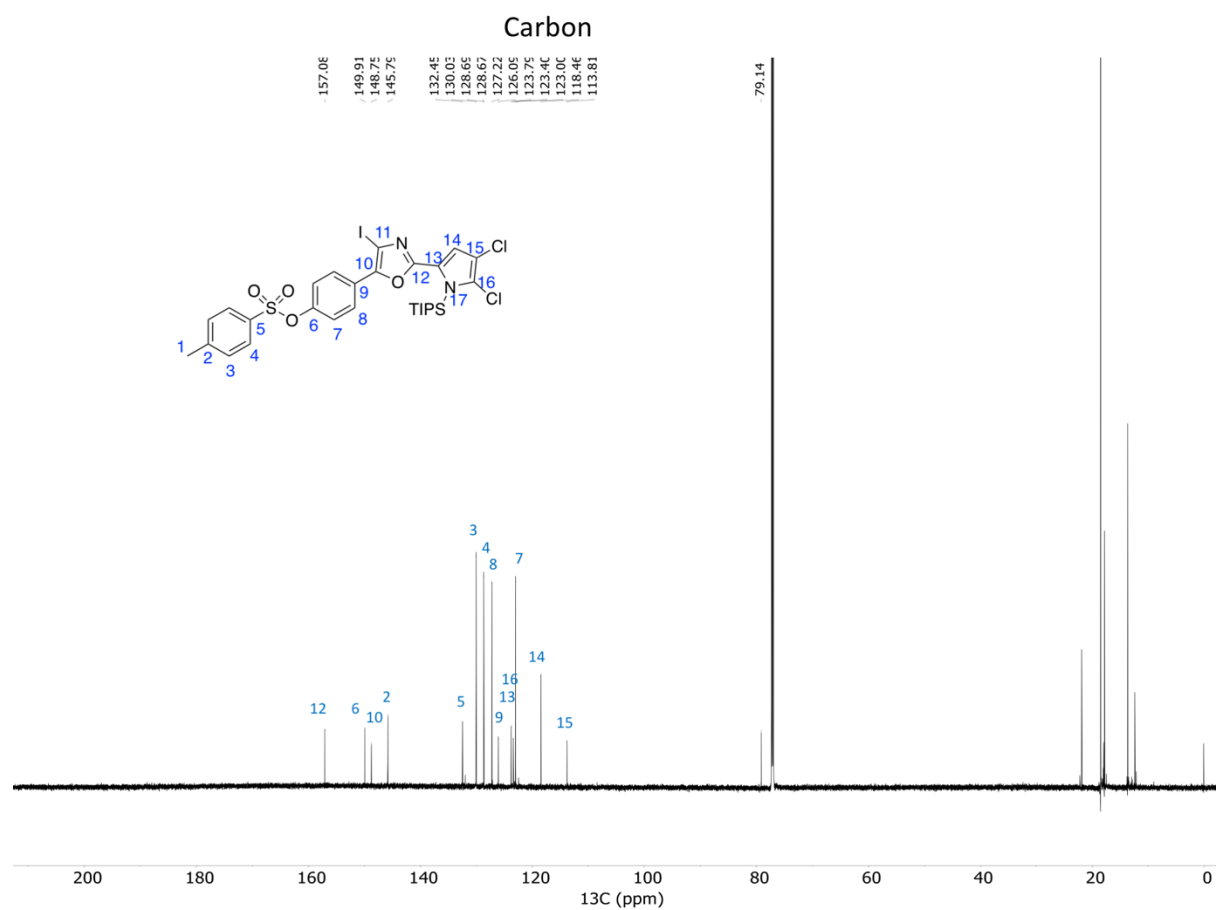


Figure S37. ^{13}C -NMR (214 MHz) spectrum of **21**.

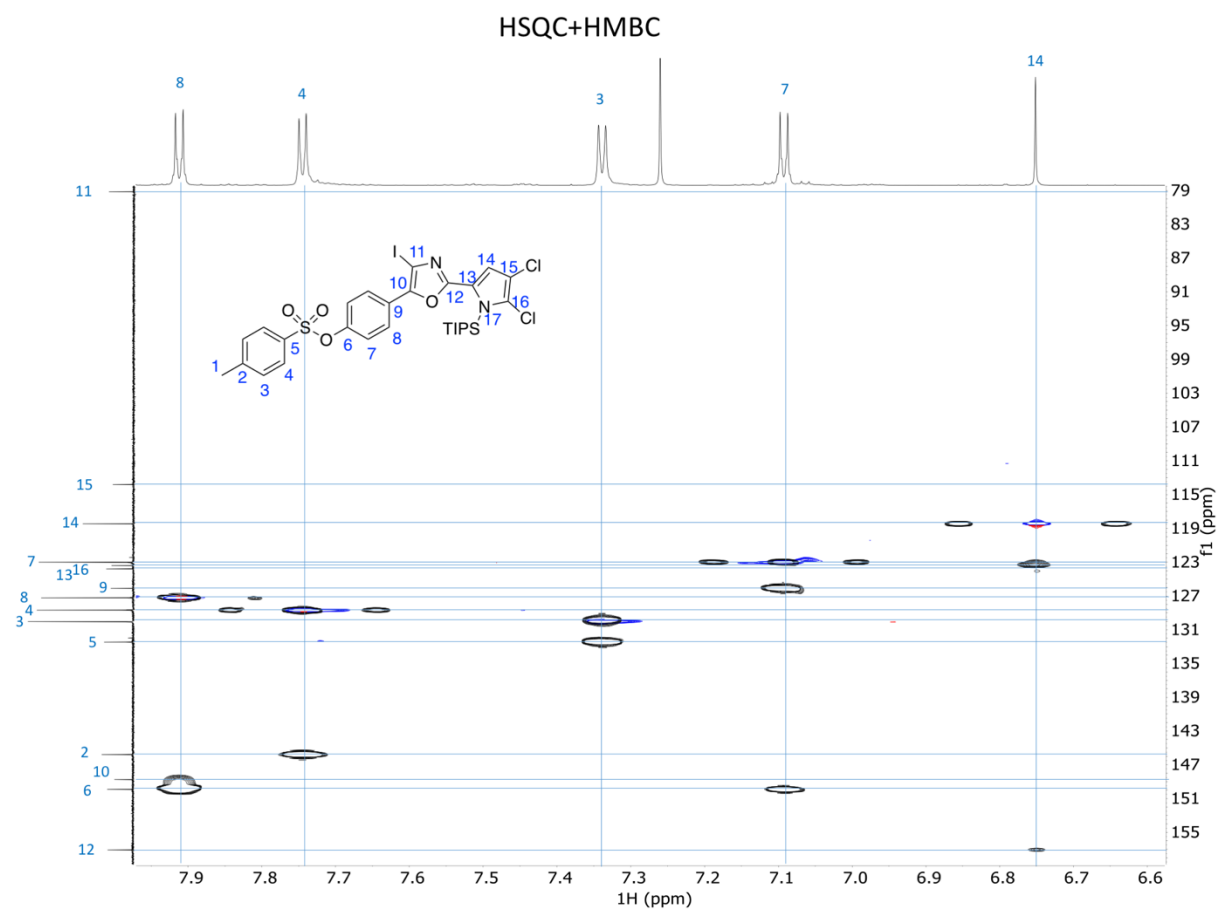


Figure S38. Superimposed HSQC and HMBC of **21**.

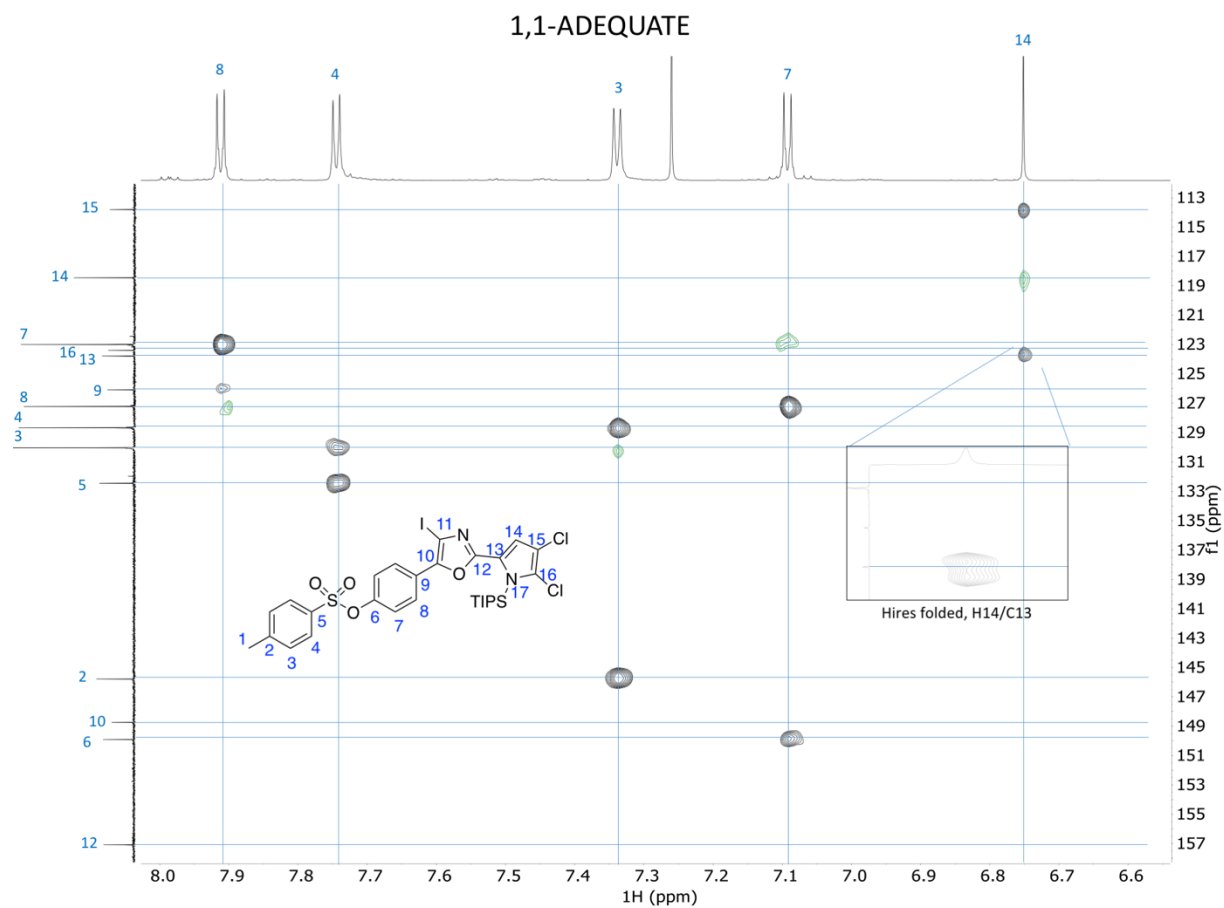


Figure S39. 1,1-ADEQUATE of **21**.

Selective CLIP-HSQMBC

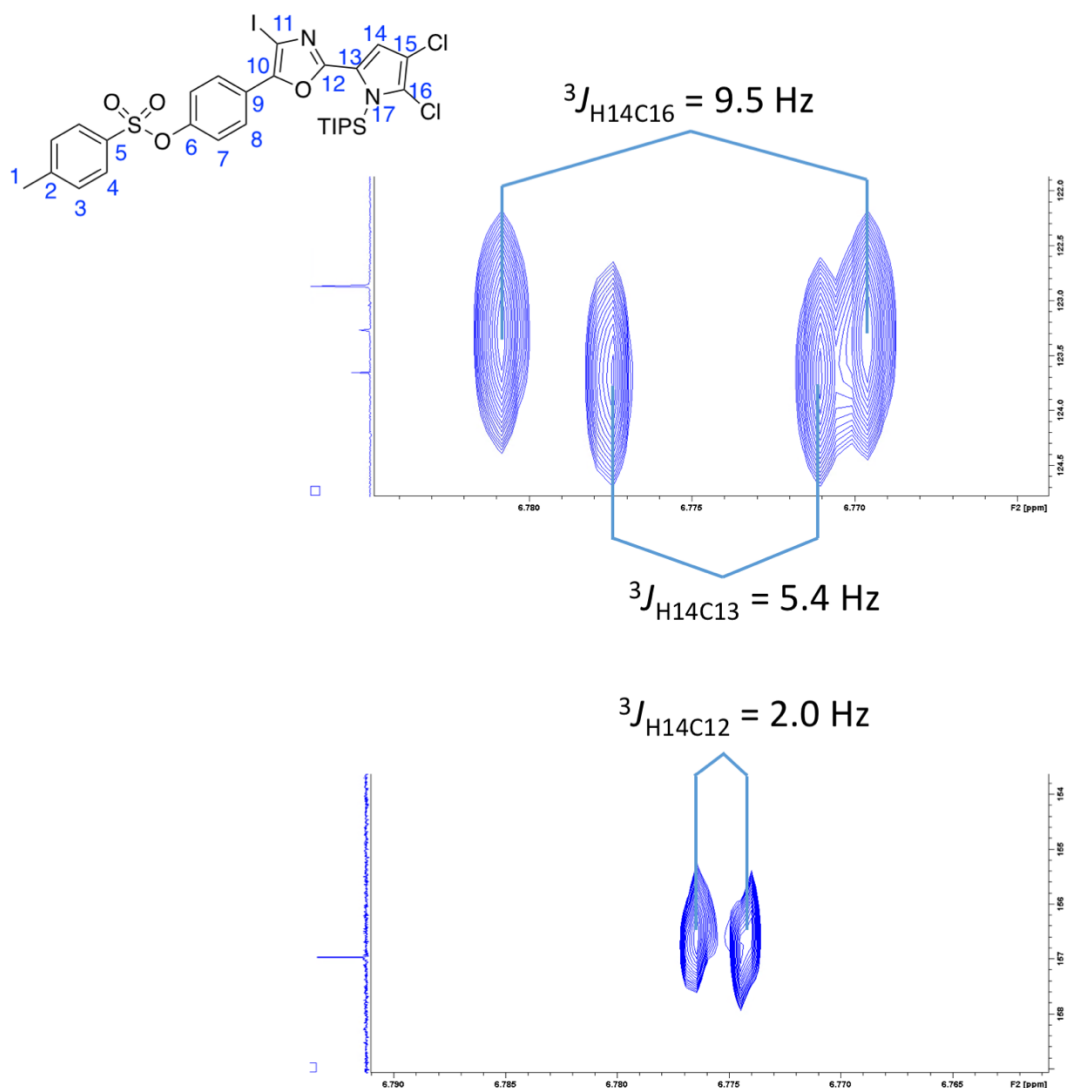
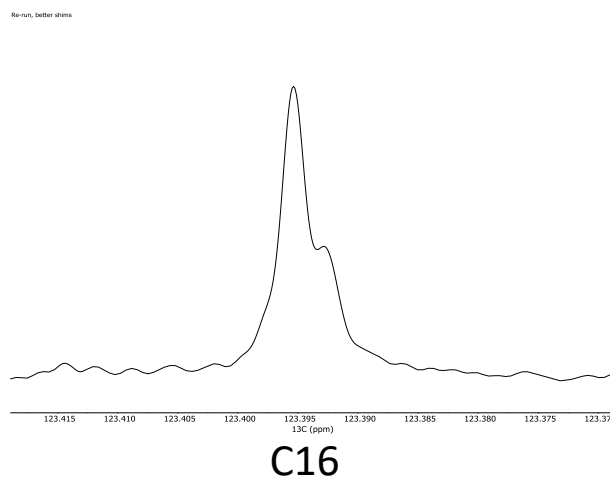
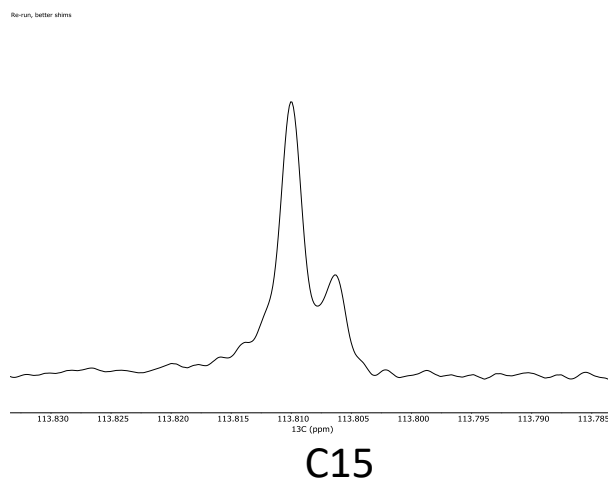


Figure S40. Selective CLIP-HSQMBC spectra of **21**.

Carbon hires



CLIP-HSQMBC hires

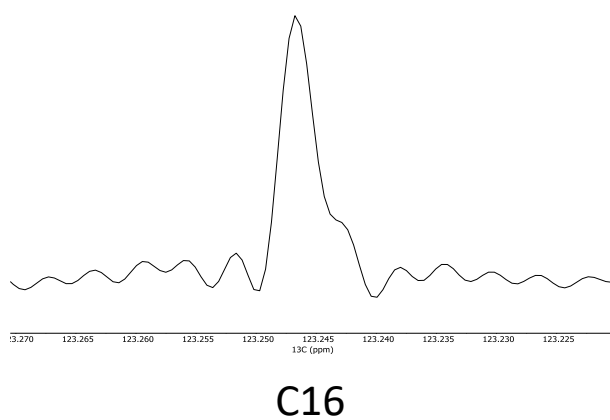


Figure S41. Hires ^{13}C (top panel) and hires selective CLIP-HSQMBC f1 projection (bottom panel) of **21**.

Proton

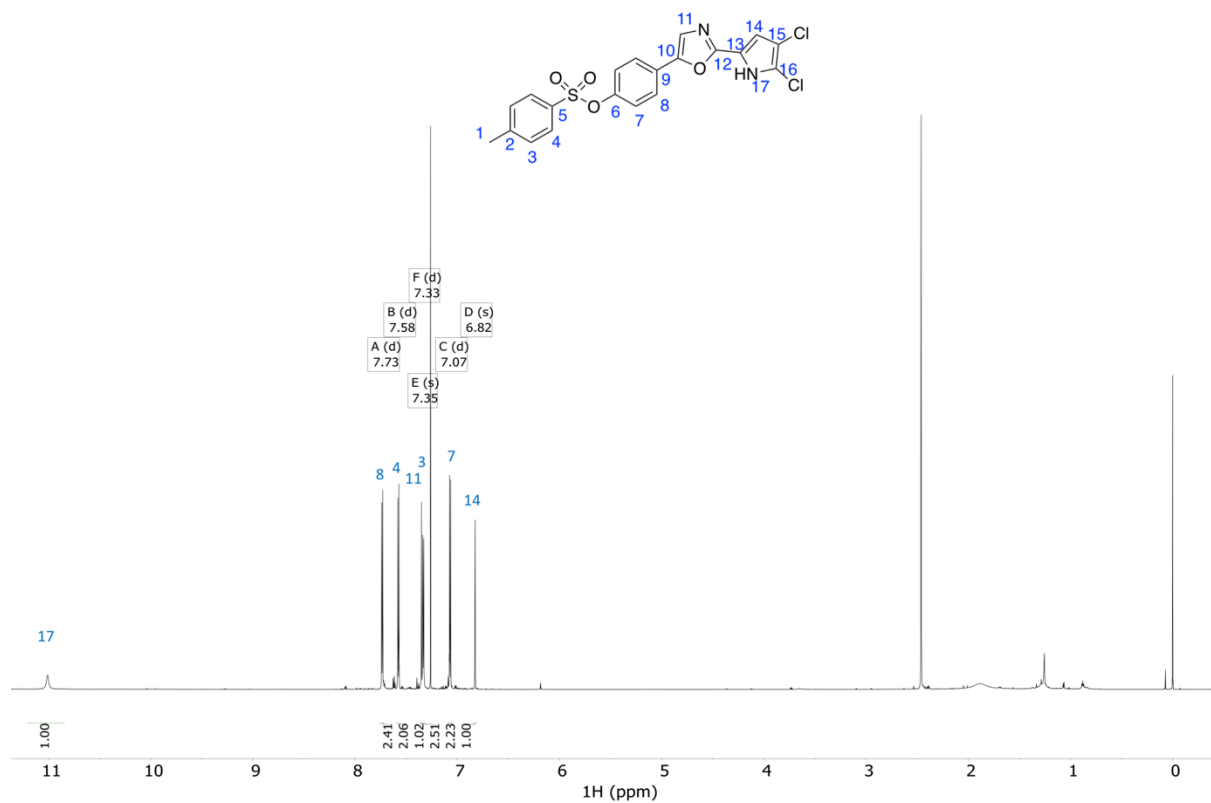


Figure S42. ¹H-NMR (850 MHz) spectrum of **24**.

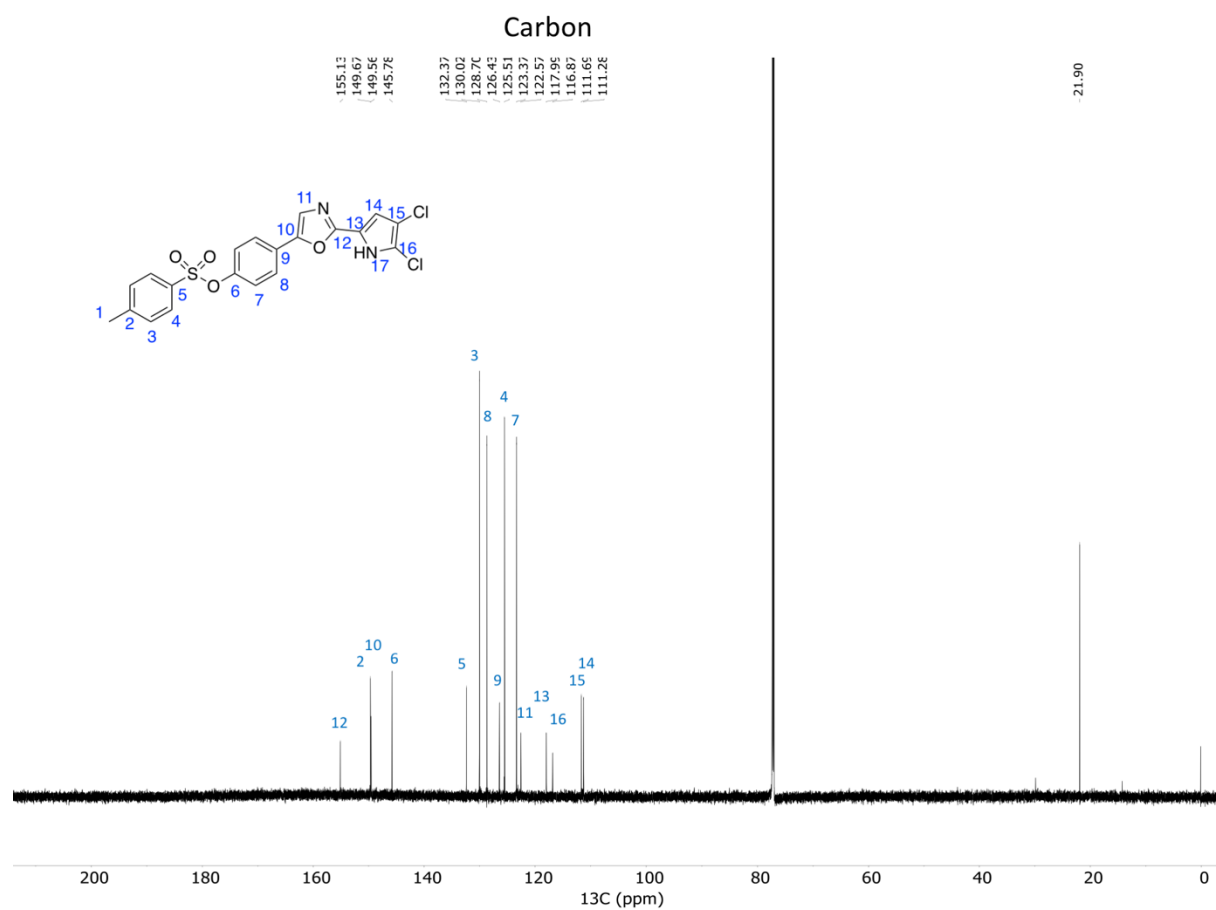


Figure S43. ^{13}C -NMR (214 MHz) spectrum of **24**.

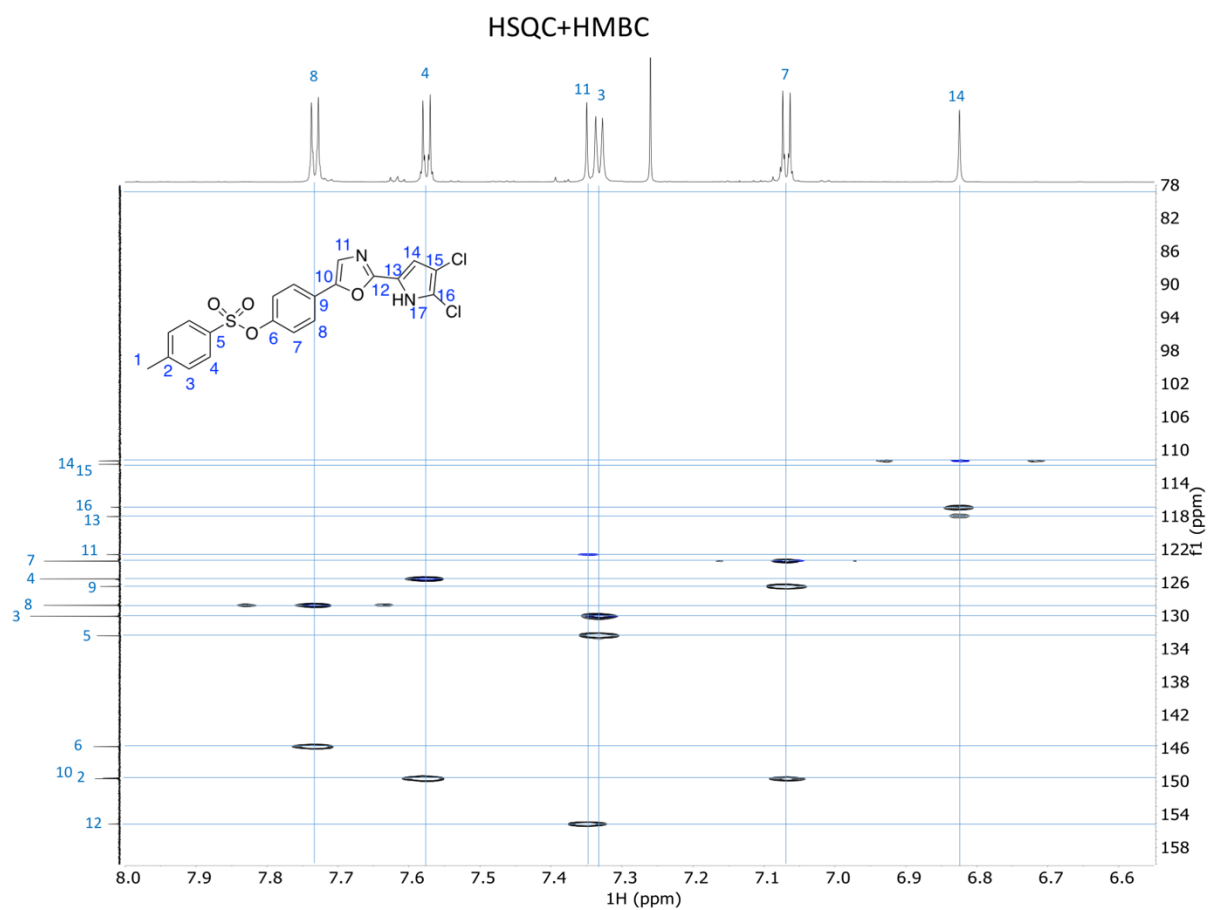


Figure S44. Superimposed HSQC and HMBC of **24**.

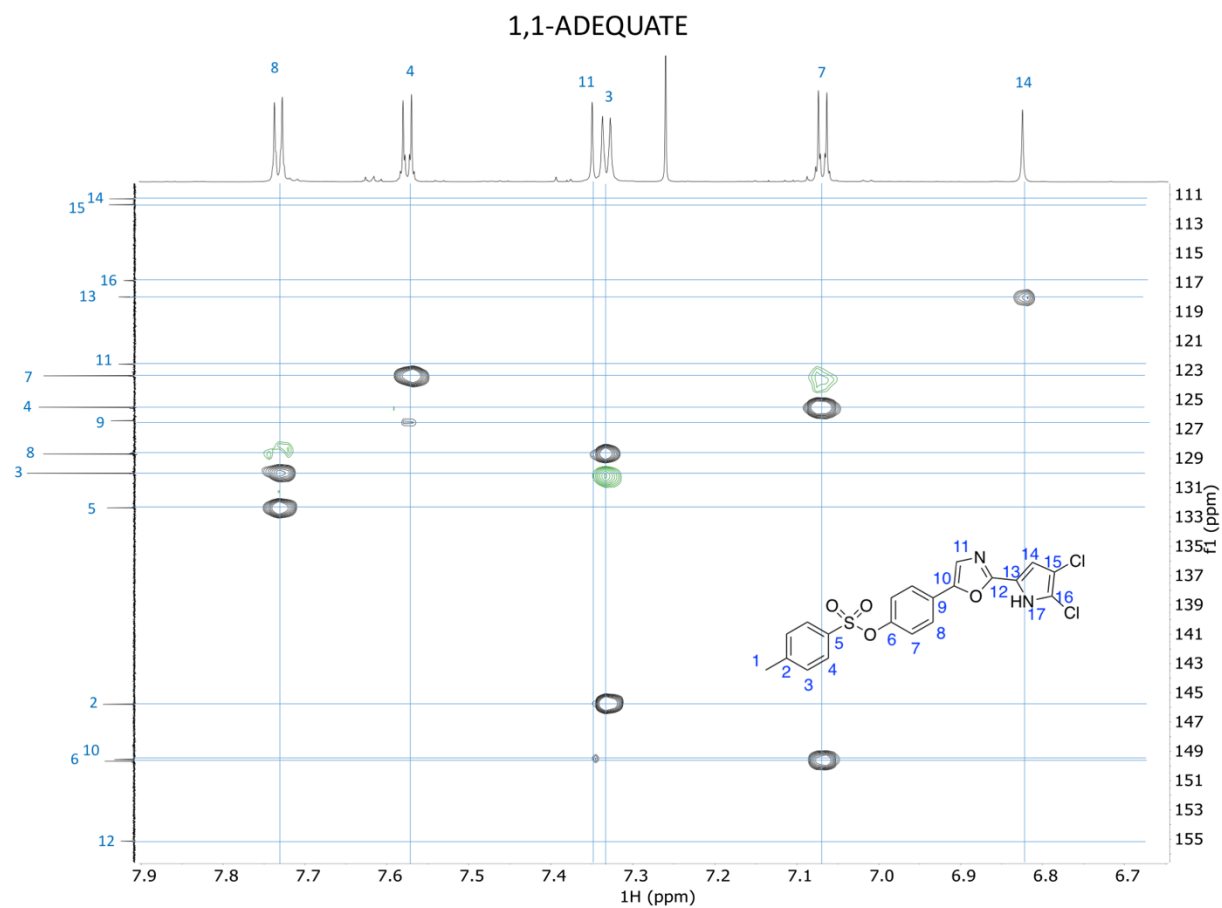


Figure S45. 1,1-ADEQUATE of **24**.

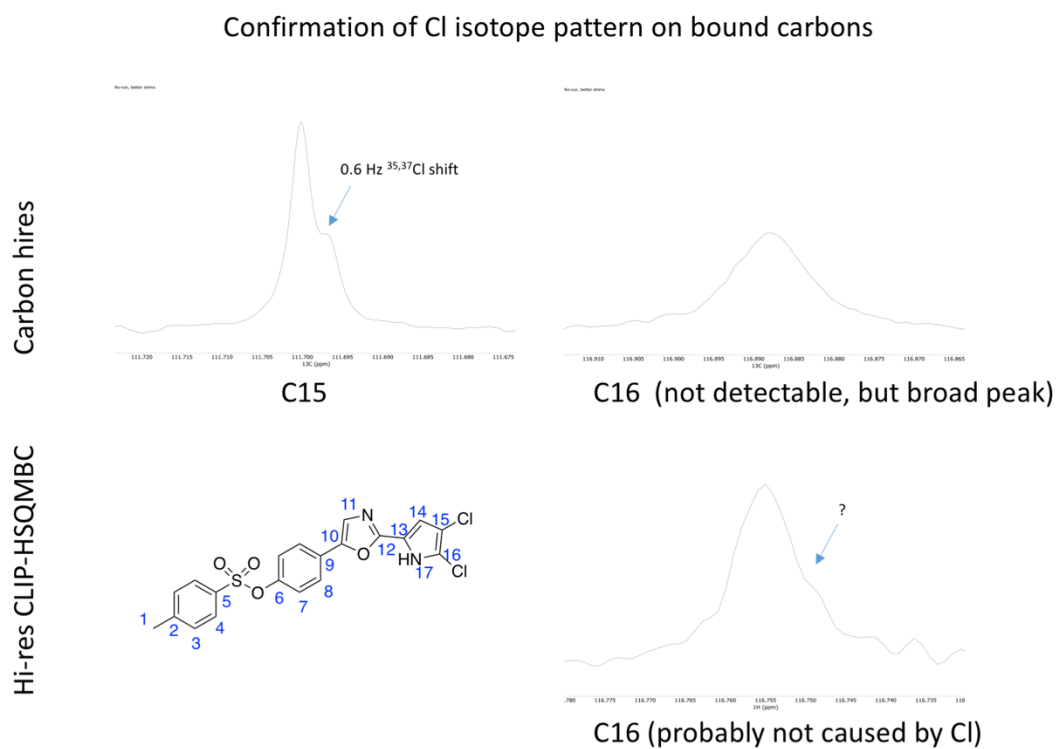


Figure S46. Hires ^{13}C (top panel) and hires selective CLIP-HSQMBC f1 (bottom panel) projection of **24**.

Selective CLIP-HSQMBC

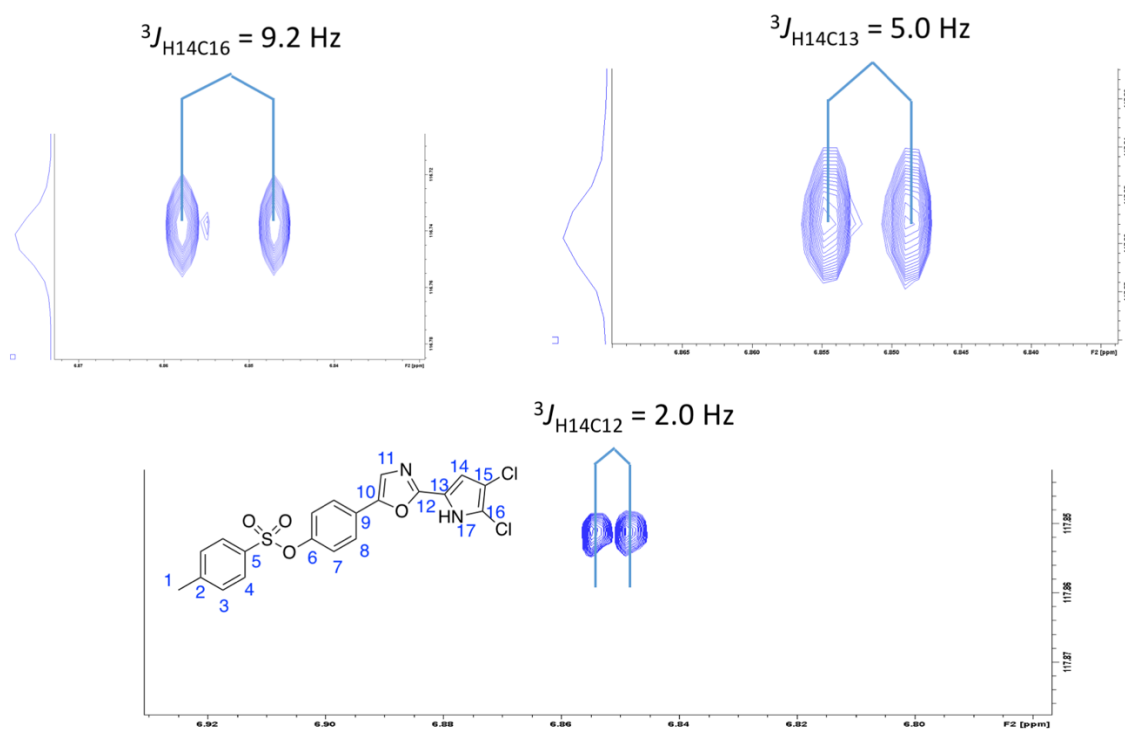


Figure S47. Selective CLIP-HSQMBC of **24**.

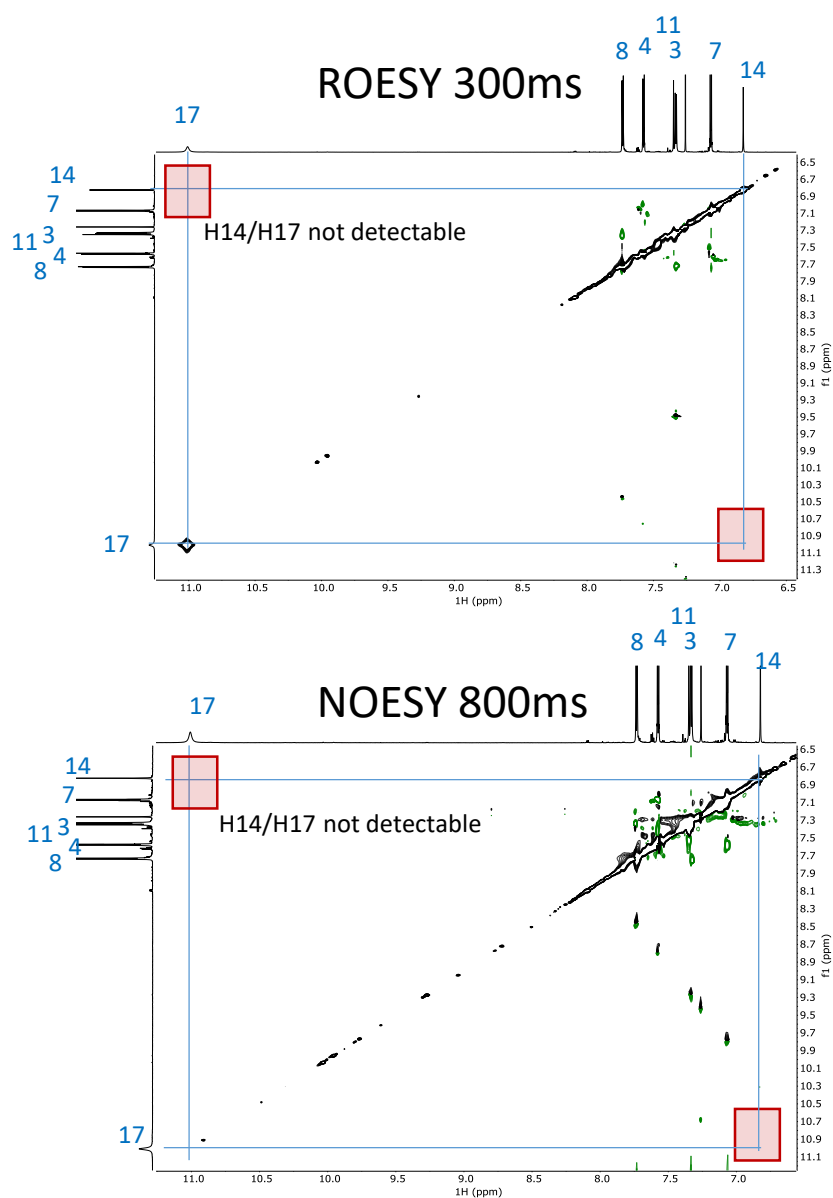


Figure S48. NOESY and ROESY of **24**.

References

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