Supporting Information

for

A Novel quinoline-based NNN-pincer Cu(II) complex as a superior catalyst for oxidative esterification of allylic C(sp^3)-H bonds

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General Procedure for gram-scale reaction:

Benzoic acid (**A**) and 4-hydroxybenzoic acid (**B**) have been used for exploring the gram-scale reaction.

A Schlenk flask equipped with a stir bar was charged with carboxylic acid derivative (1 g, 8.2 mmol (**A**)/ 7.2 mmol (**B**)) and catalyst (0.08 mmol, 85 mg (**A**)/ 0.07 mmol, 75 mg (**B**)). The Schlenk flask was then evacuated and back-filled with nitrogen. The process was repeated three times. Under nitrogen atmosphere, the Schlenk was charged with cyclohexene (8.2 mL, 82 mmol (**A**)/ 7.2 ml, 72 mmol (**B**)), TBHP (2.36 mL, 24.6 mmol (**A**)/ 2.07 ml, 21.6 mmol (**B**)), and DMF (10 mL) by syringe. The Schlenk flask was then placed in an oil bath preheated at 40 °C. After 1 h, the reaction mixture was cooled to room temperature and extracted with EtOAc and water. Organic phase was dried under reduced pressure. The crude product was purified by column chromatography on silica gel (5% EtOAc/pet ether) to afford the corresponding products **4a** and **4f** in 72% (1.2 g, 5.9 mmol) and 73% (1.14 g, 5.25 mmol) yields respectively.

Compound characterization Table

Known		Unknown
Compound name	**Reference**	**4g, 4l, 4m, 4o, 4s, 4t, 6b, 6d**
4a-4e, **4i**	1	
4n	2	
4h, **4p**, **4q**	3	
4k, **4r**, **4f**	4	
4j	5	
6a	6	
6c	7	

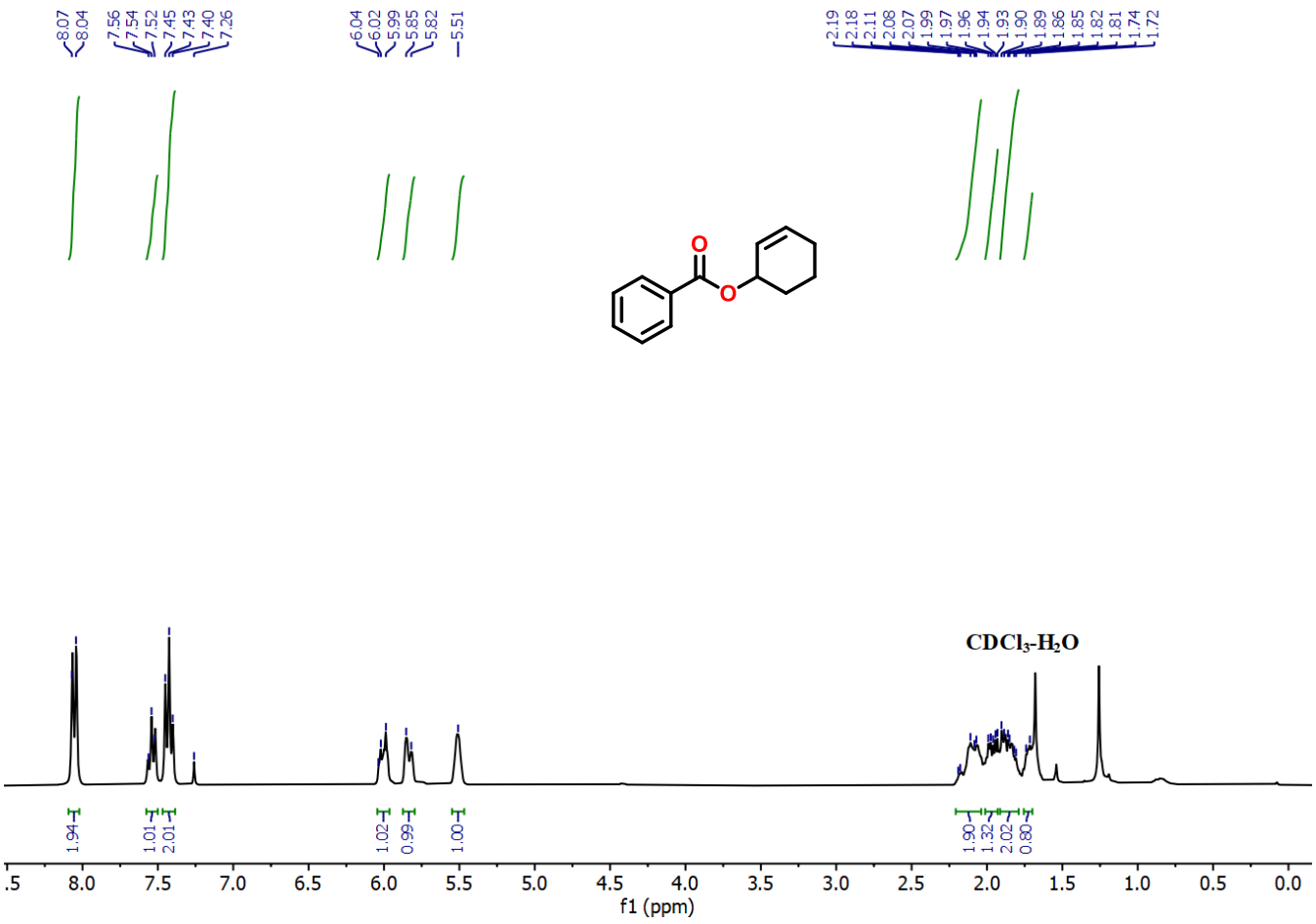

Fig. S1. ^{1}H NMR spectra of compound **4a**

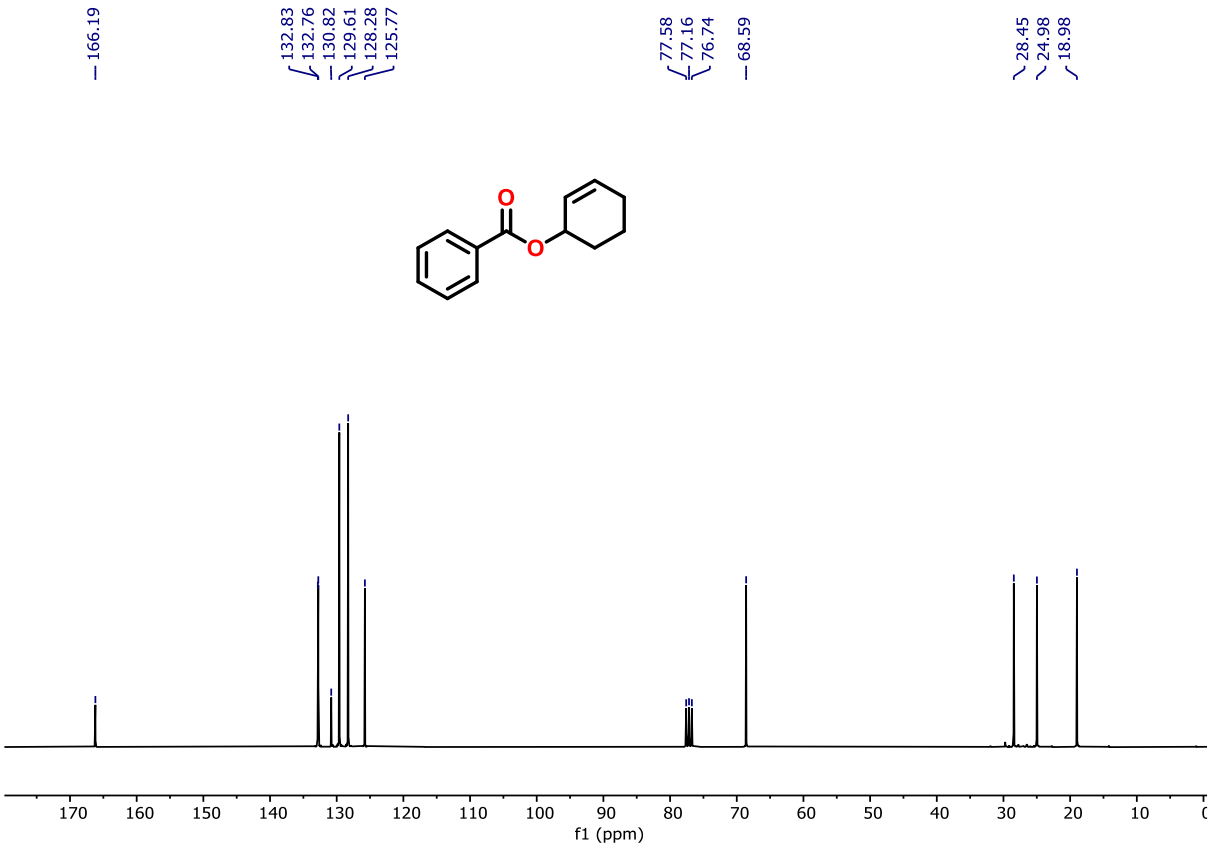

Fig. S2. ^{13}C NMR spectra of compound **4a**

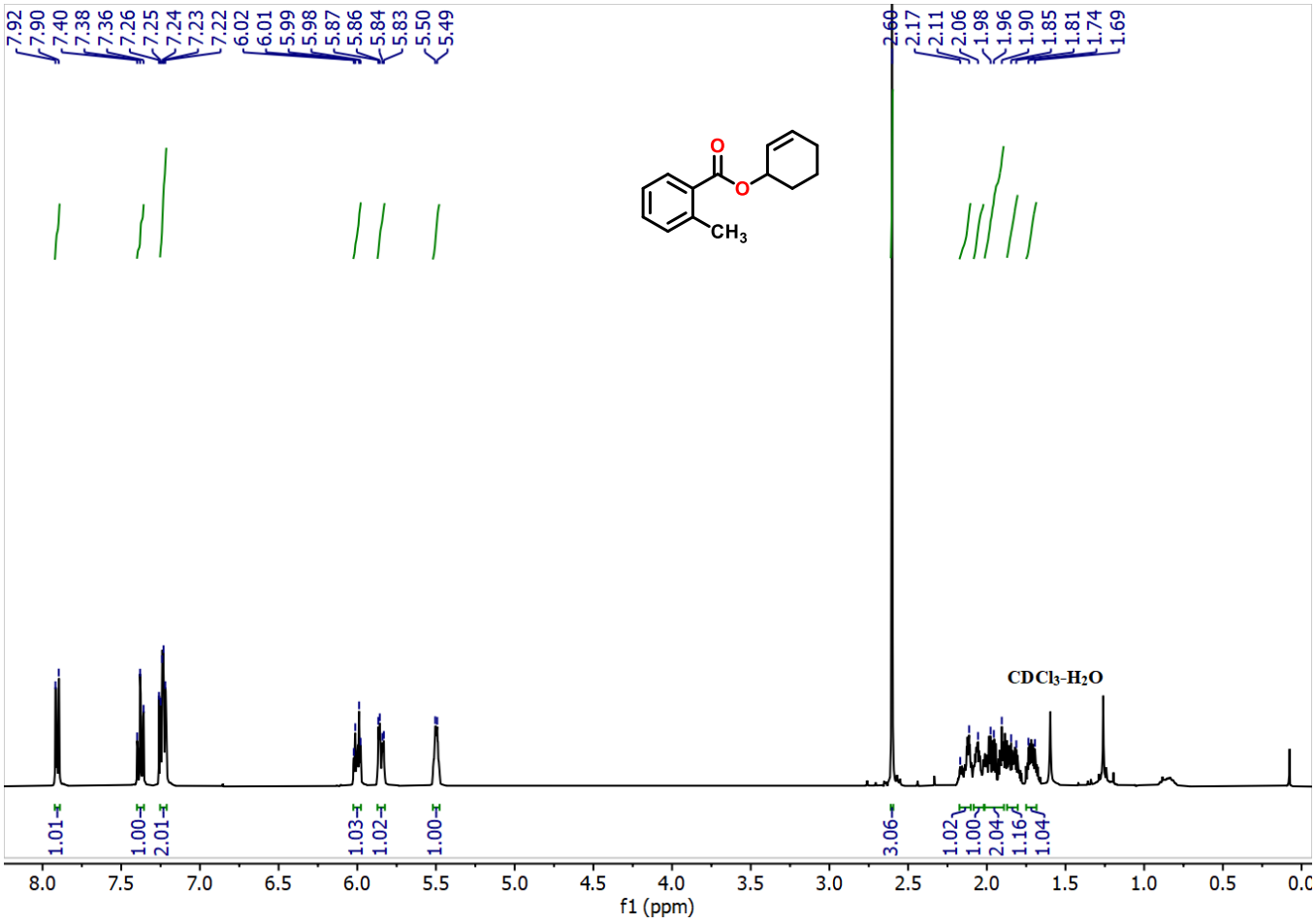

Fig. S3. ^{1}H NMR spectra of compound **4b**

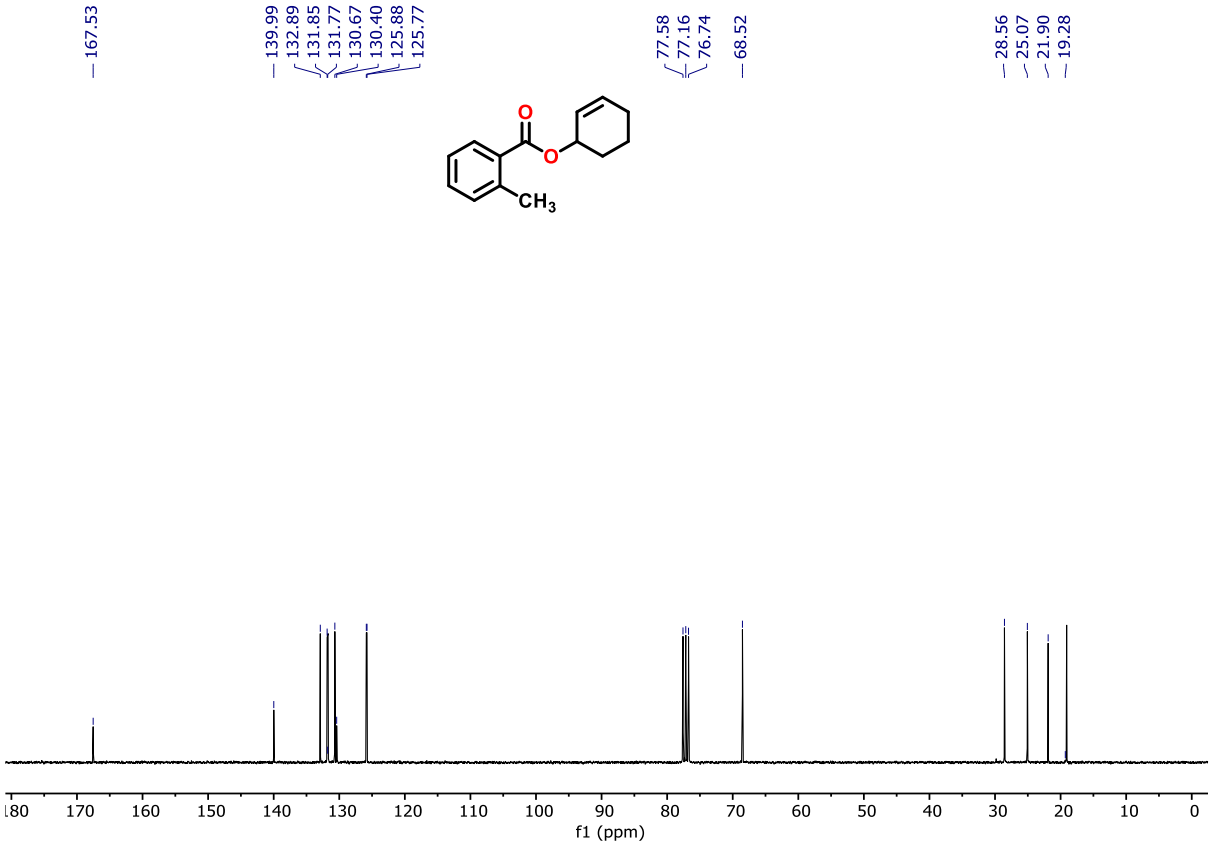

Fig. S4. ^{13}CNMR spectra of compound **4b**

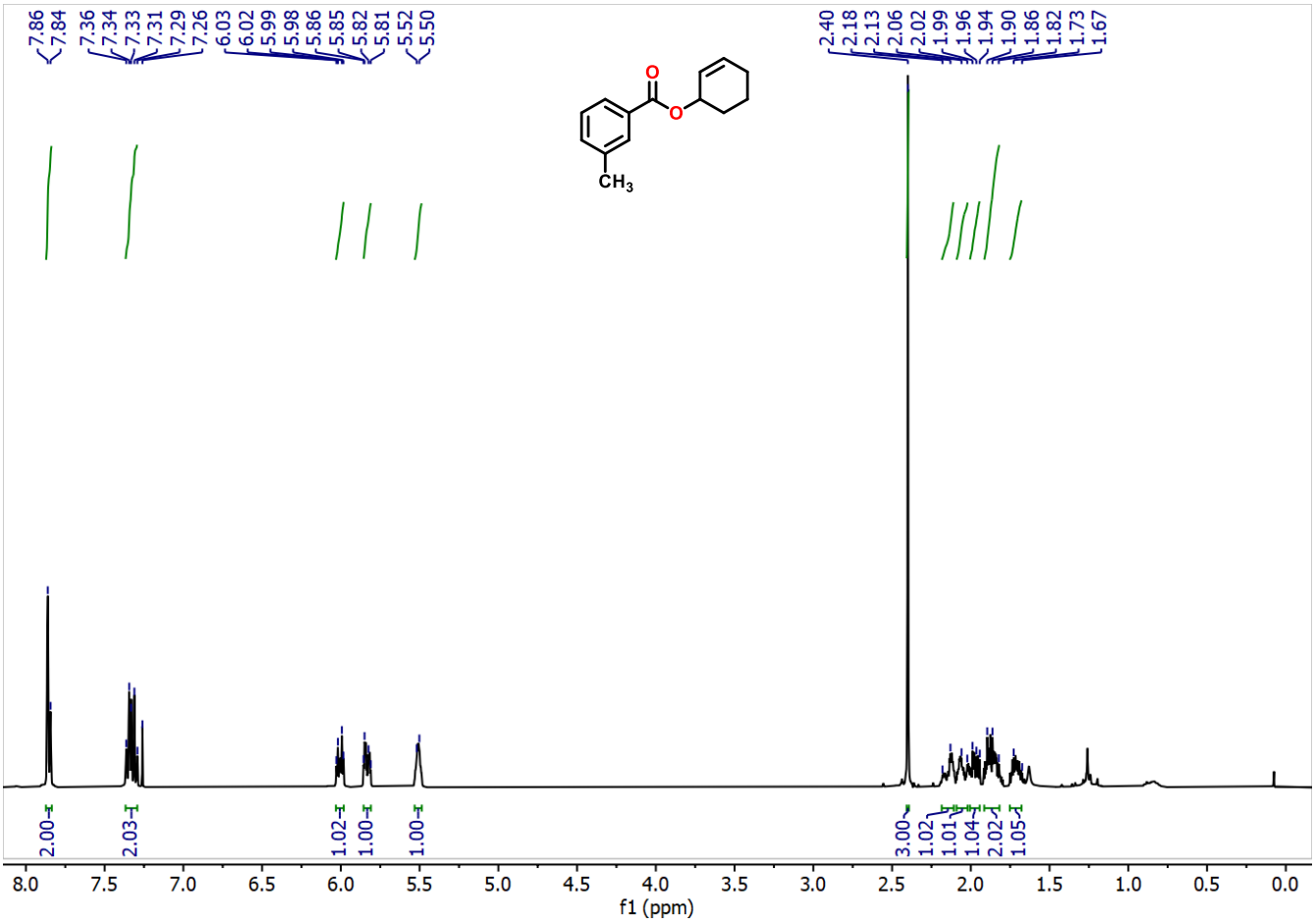

Fig. S5. ^{1}H NMR spectra of compound **4c**

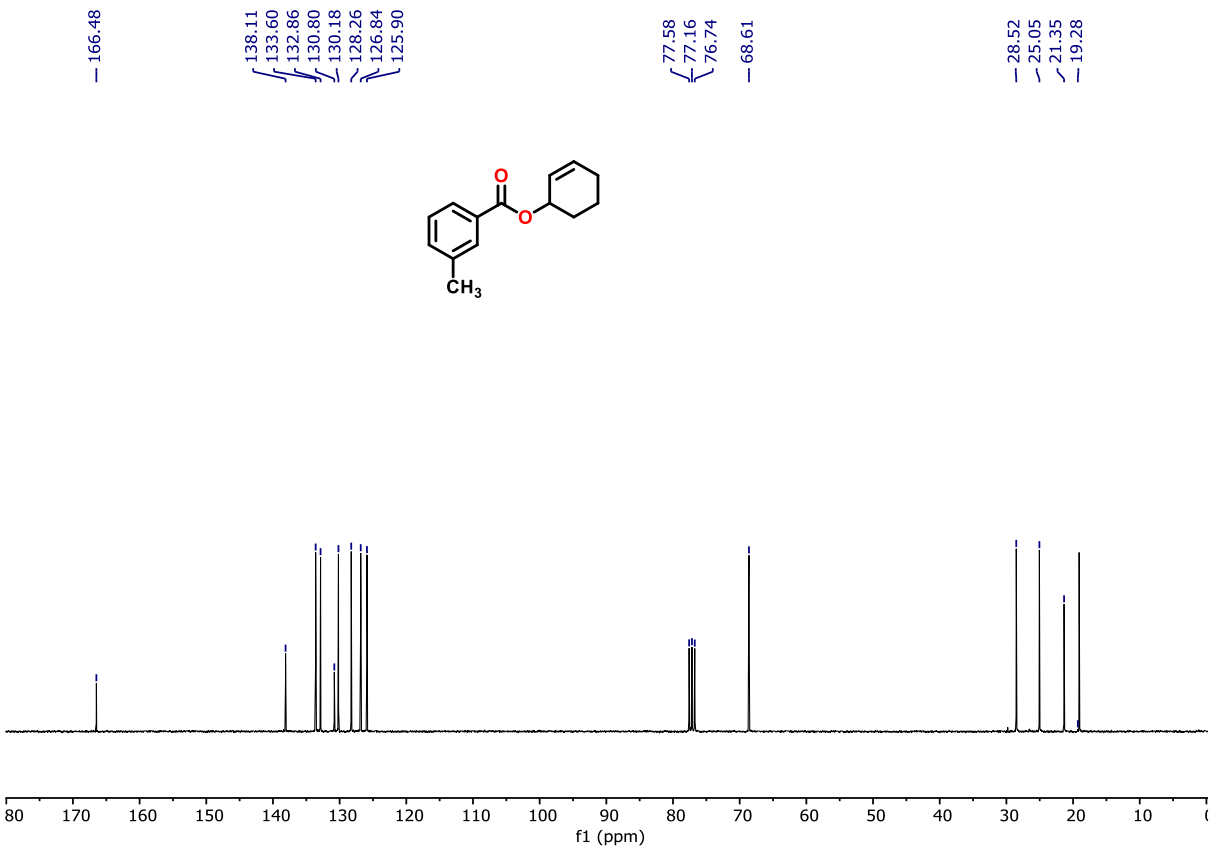

Fig. S6. ^{13}C NMR spectra of compound **4c**

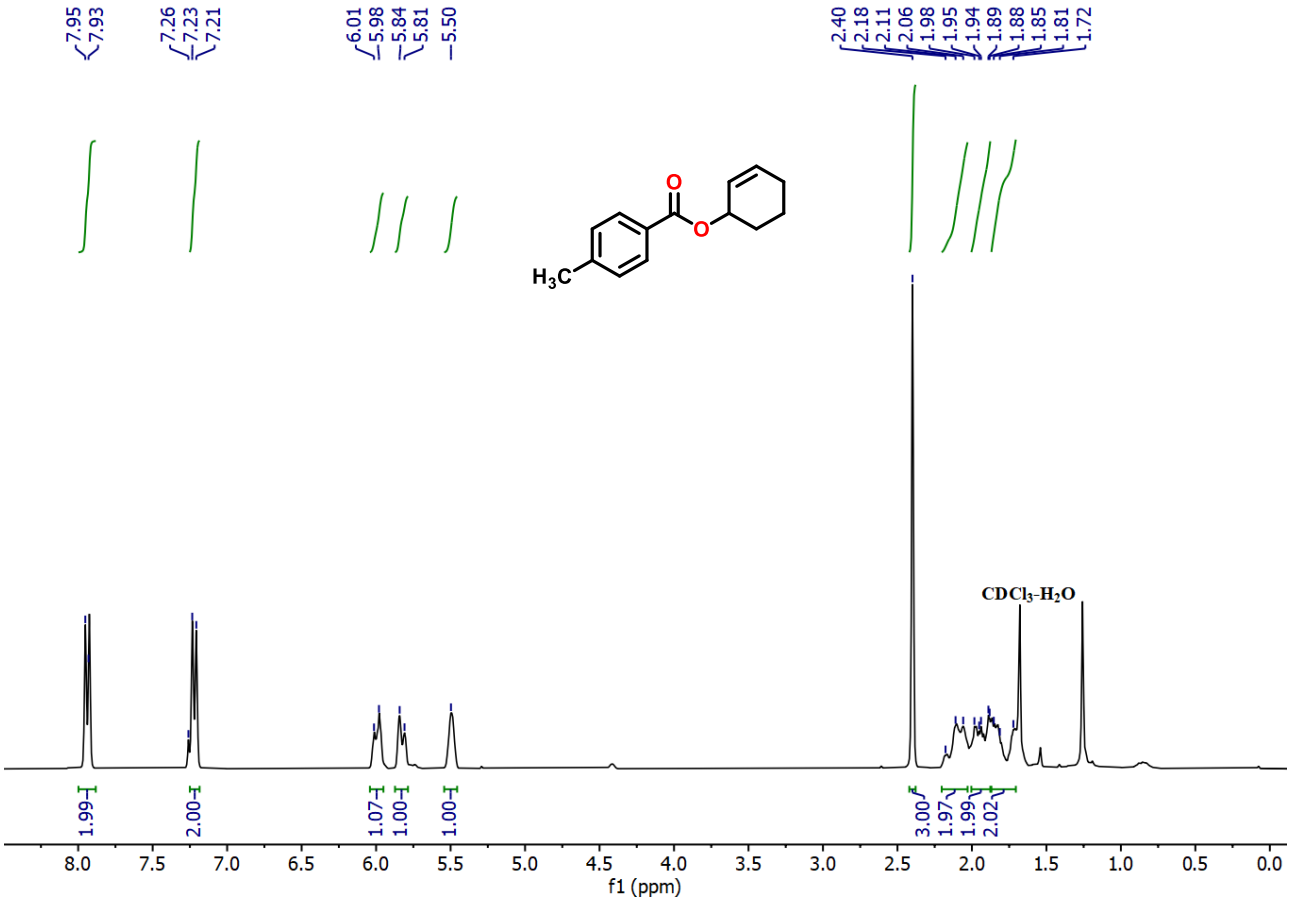

Fig. S7. ^{1}H NMR spectra of compound **4d**

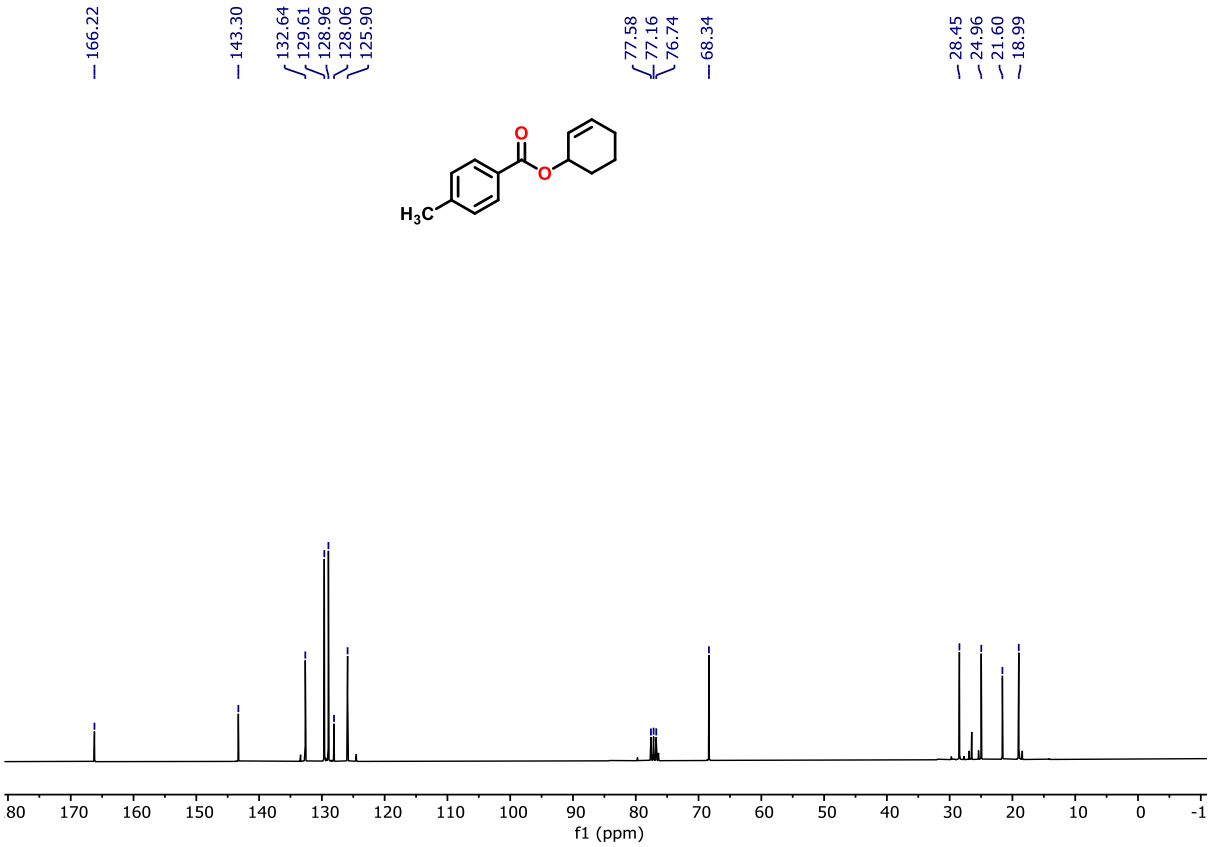

Fig. S8. ^{13}C NMR spectra of compound **4d**

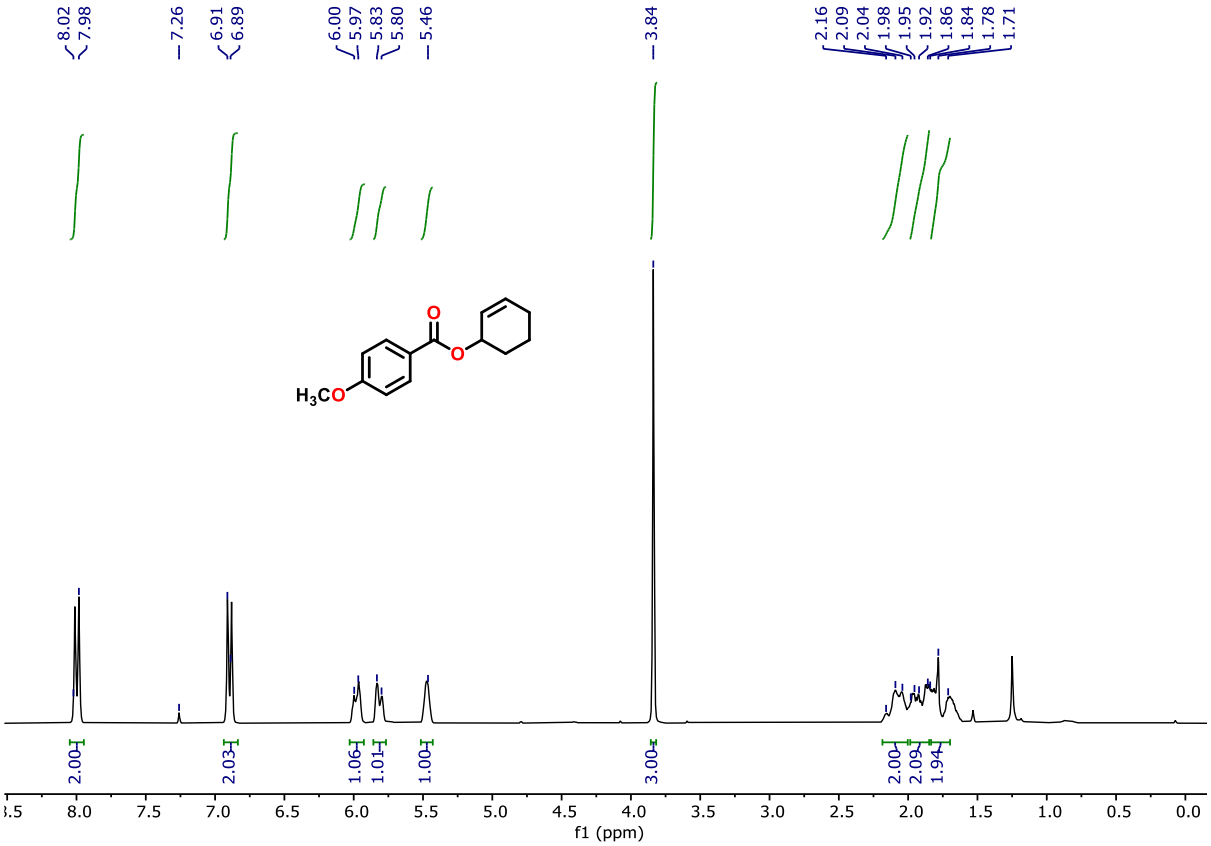

Fig. S9. ^{1}H NMR spectra of compound **4e**

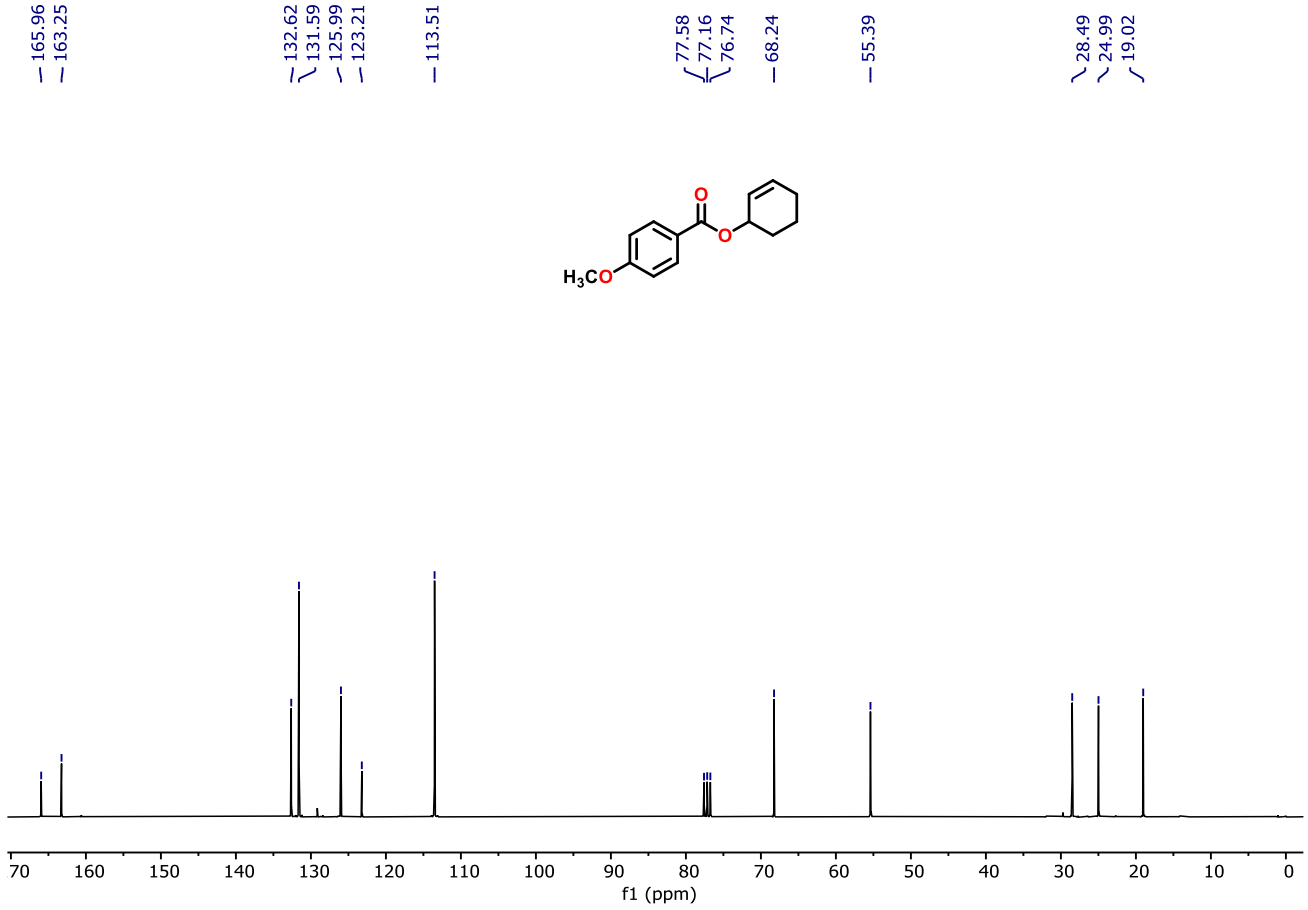

Fig. S10. ^{13}C NMR spectra of compound **4e**

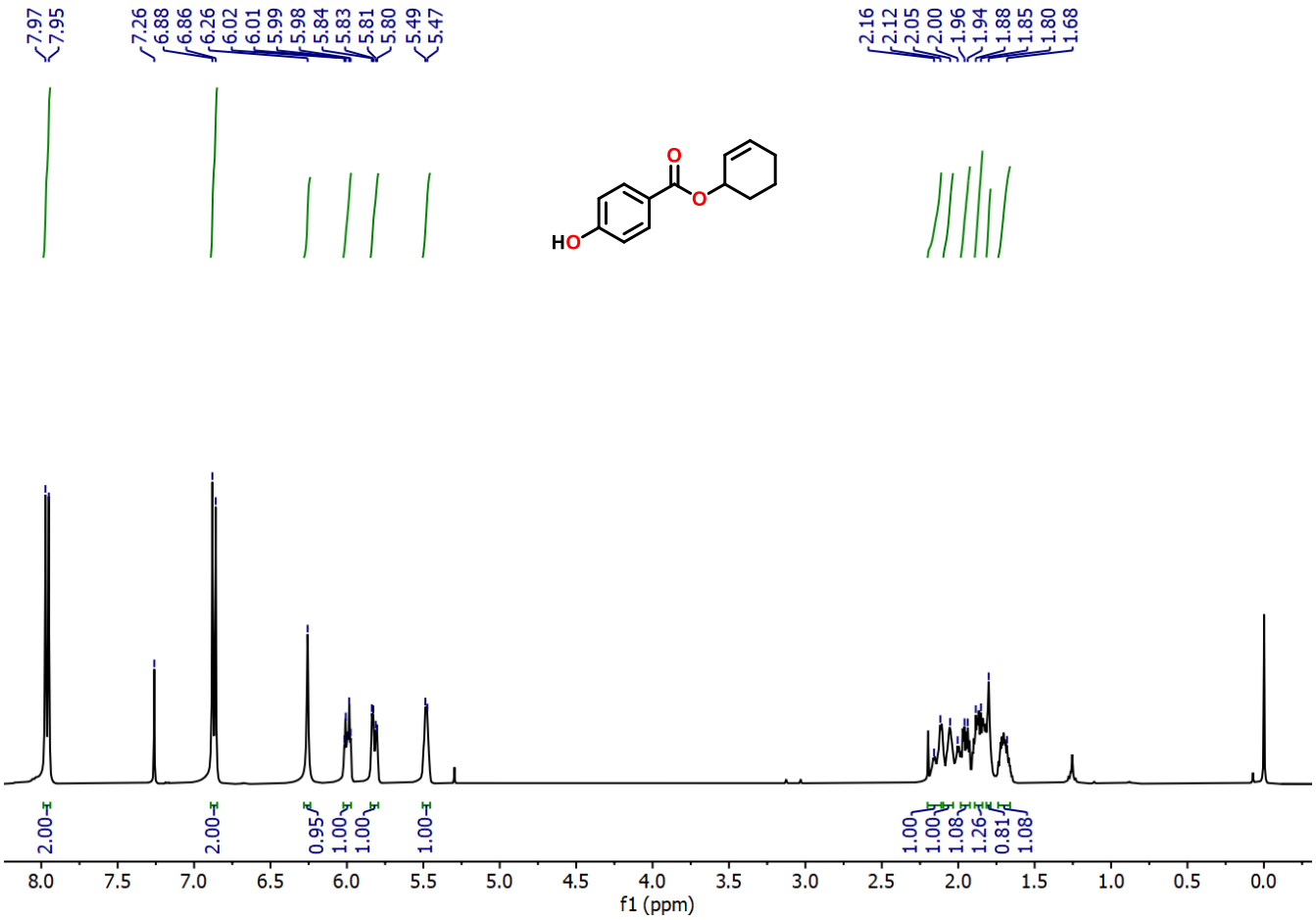

Fig. S11. ^{1}H NMR spectra of compound **4f**

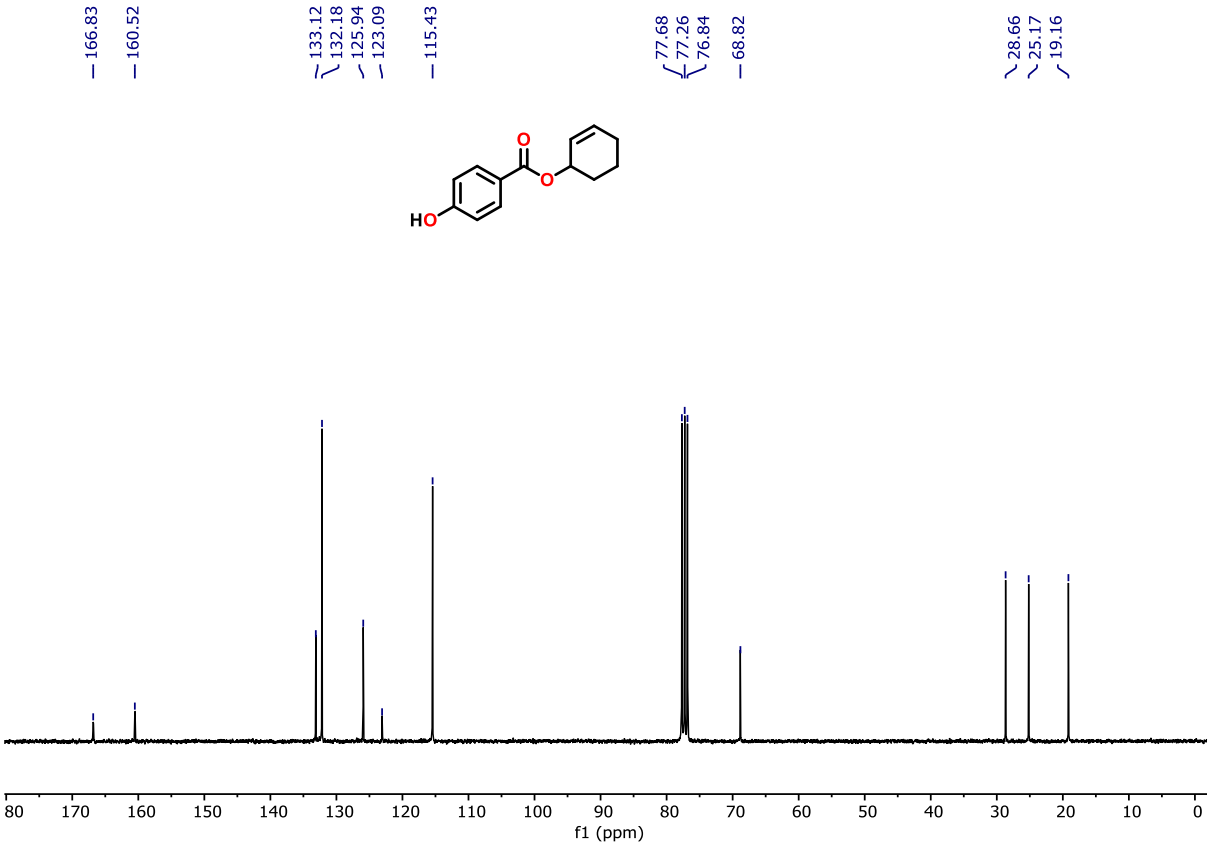

Fig. S12. ^{13}C NMR spectra of compound **4f**

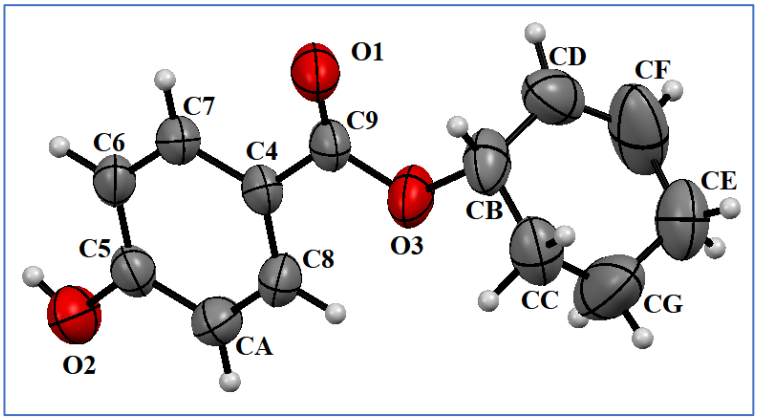

Fig. S13. ORTEP representation of the molecular structure of **4f** with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg) for **4f**: O3-CB 1.481(4), C9-O3 1.334(4), CB-CD 1.488(5), CD-CF 1.339(8), CF-CE 1.44(1), CE-CG 1.464(7), CG-CC 1.396(9), CC-CB 1.498(7); C9-O3-CB 118.8(3), O3-CB-CD 108.4(3), O3-CB-CC 106.1(3), O3-C9-C4 111.6(2), CB-CD-CF 120.4(5), CB-CC-CG 115.0(4), CG-CE-CF 111.0(5).

Table S1: Crystallographic details of compound **4f**

Empirical formula	$C_{13}H_{14}O_3$
Formula weight	218.24
Crystal size (mm)	0.32 X 0.22 X 0.12
Crystal system	monoclinic
Space group	*P21/c*
a [Å]	a=10.8811(2)
b [Å]	b=10.233(2)
c [Å]	c=11.017(2)
α [°]	90
β [°]	108.43(3)
γ [°]	90
volume [$Å^3$]	1163.7(4)
Z	4
F(000)	464
μ MoK_α [mm^{-1}]	0.088
Temperature [K]	293(2)
R_{int}	0.4013
Range of h, k, l	–13/13, –13/13, –14/14
$\theta_{min/max}$ (°)	1.973/27.290
GOF on F^2	1.048
Final R indices [I > 2σ(I)]	*R*1 = 0.0565 *wR*2 = 0.1555
R indices [all data]	*R*1 = 0.0776 *wR*2 = 0.1735

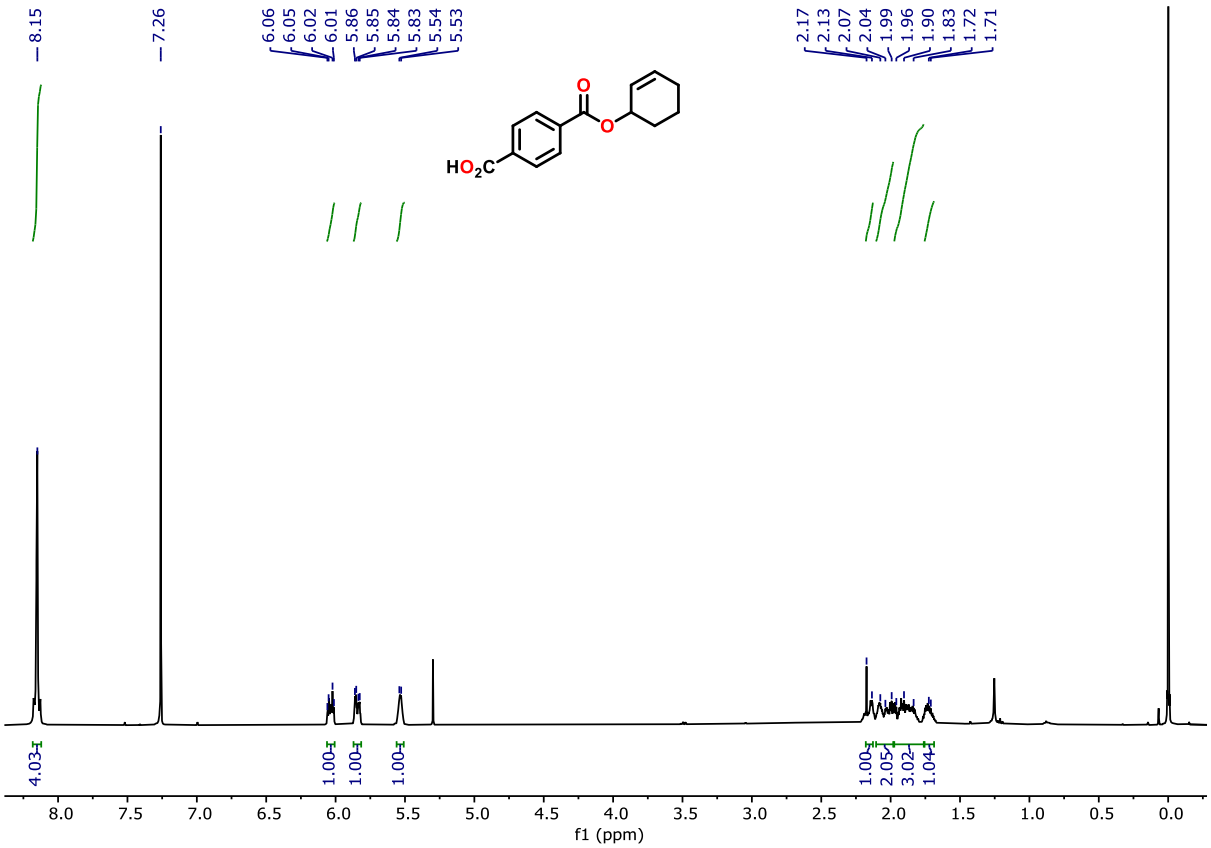

Fig. S14. ^{1}H NMR spectra of compound **4g**

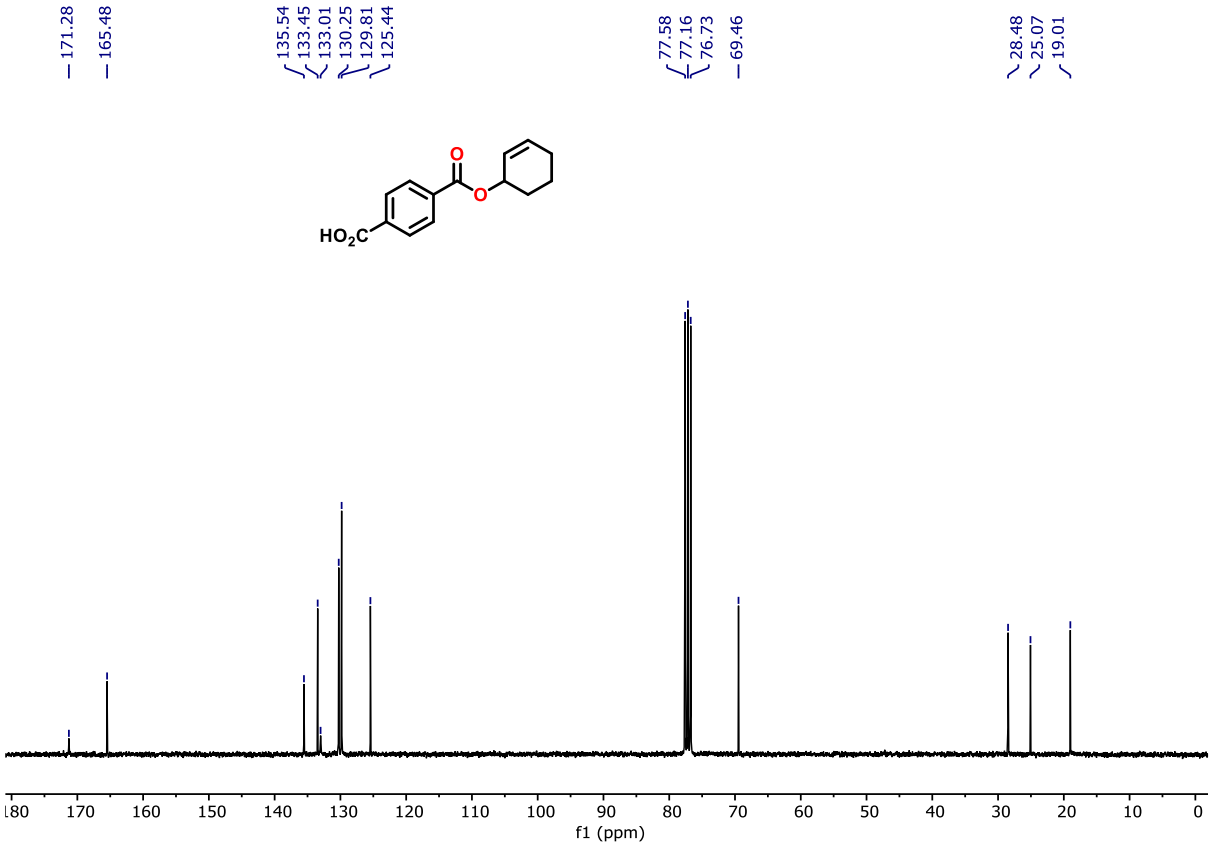

Fig. S15. ^{13}C NMR spectra of compound **4g**

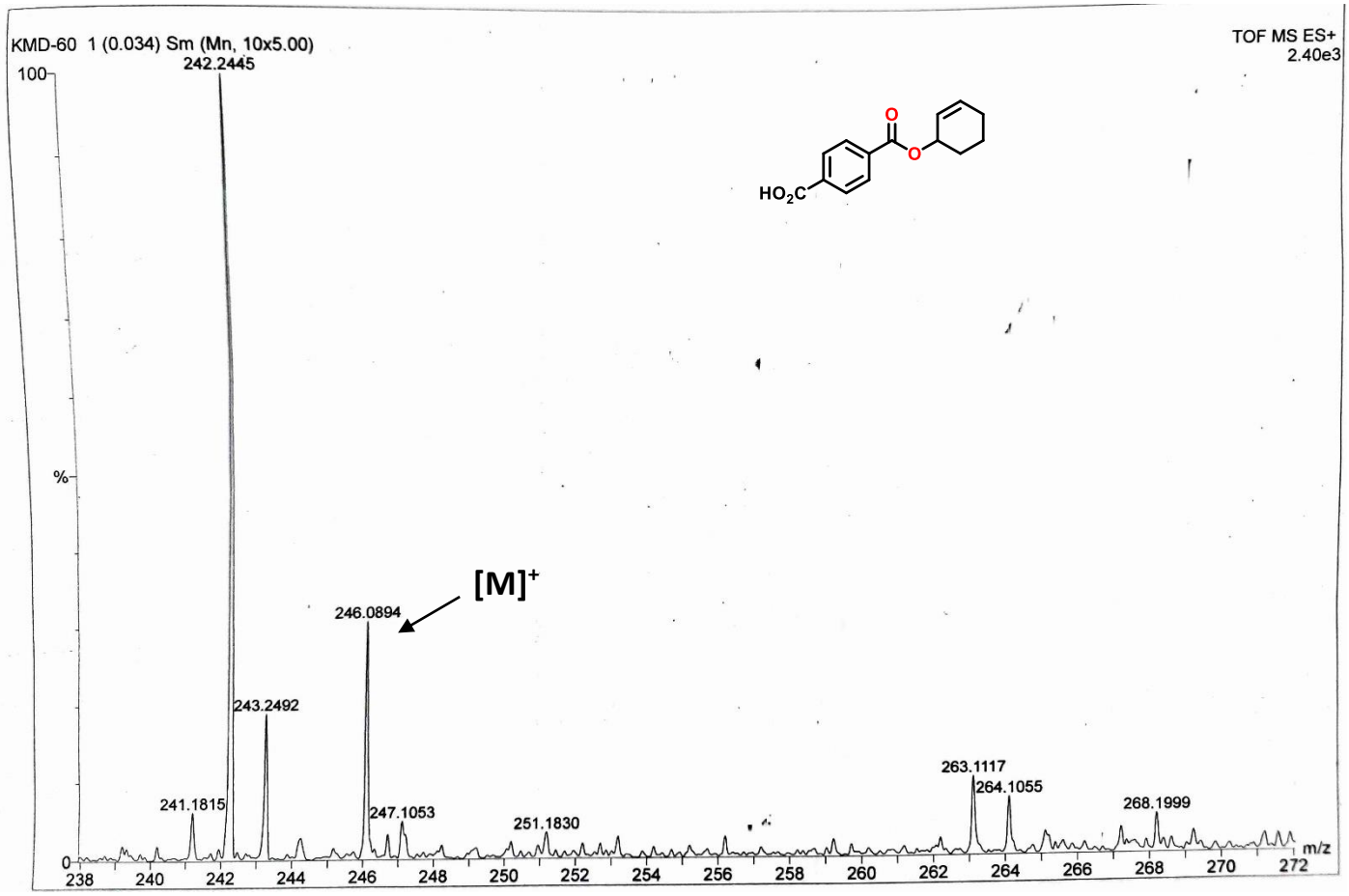

Fig. S16. HRMS of compound **4g**

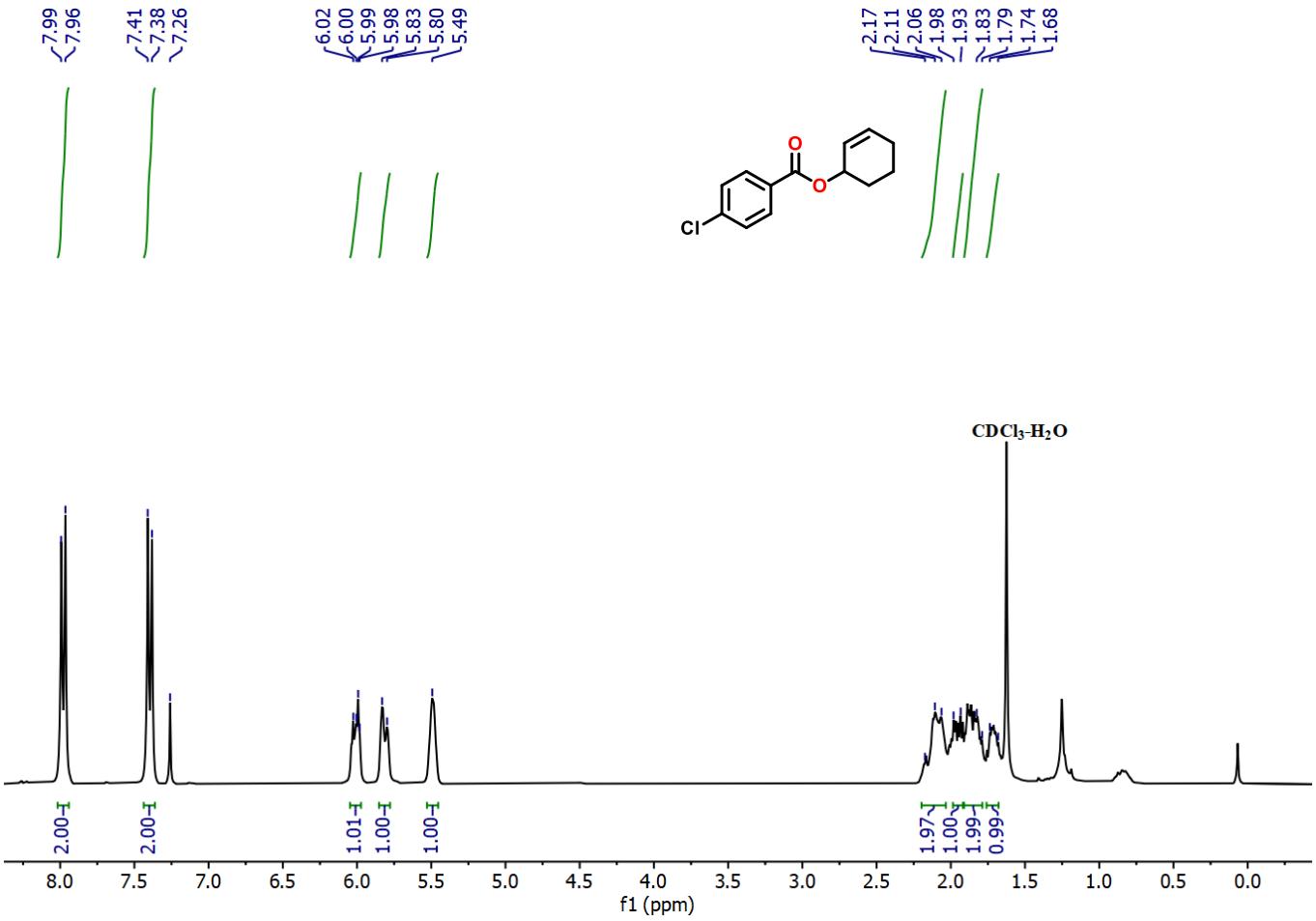

Fig. S17. ^{1}H NMR spectra of compound **4h**

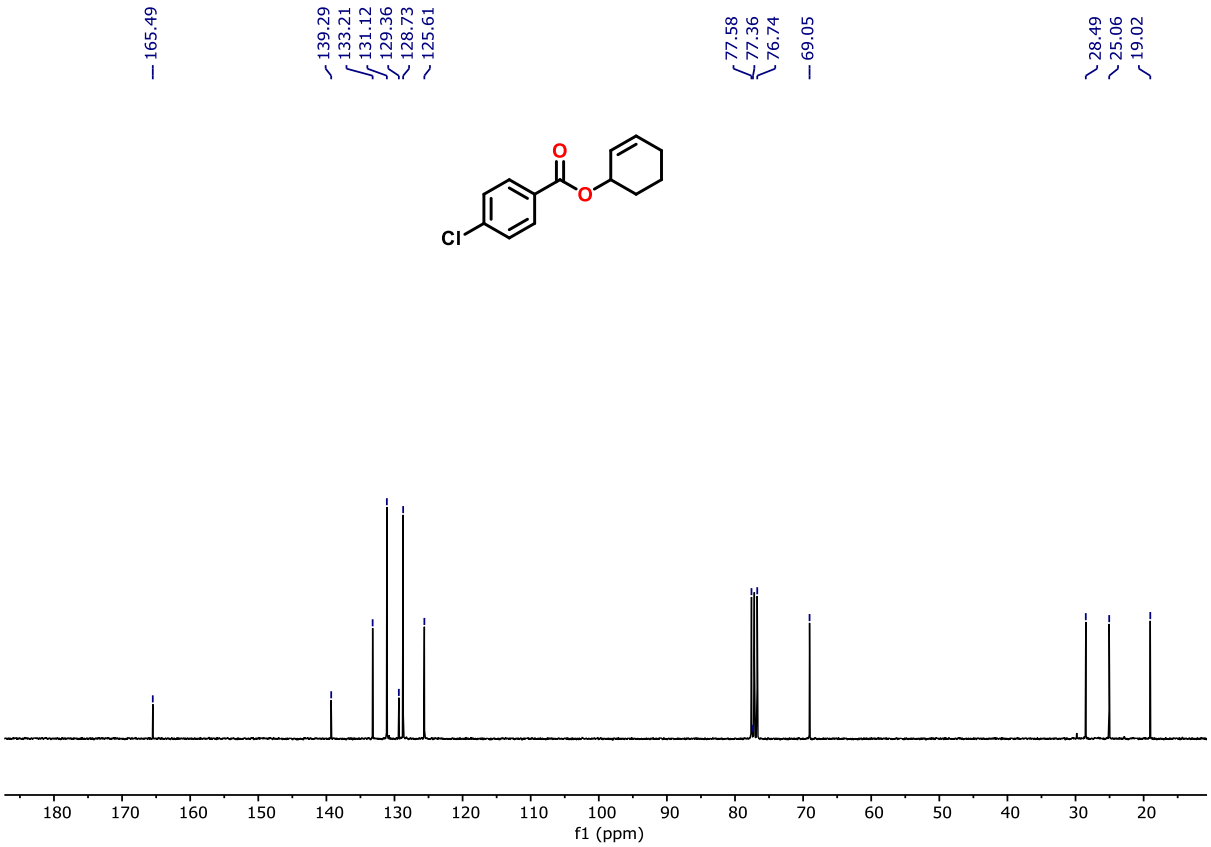

Fig. S18. ^{13}C NMR spectra of compound **4h**

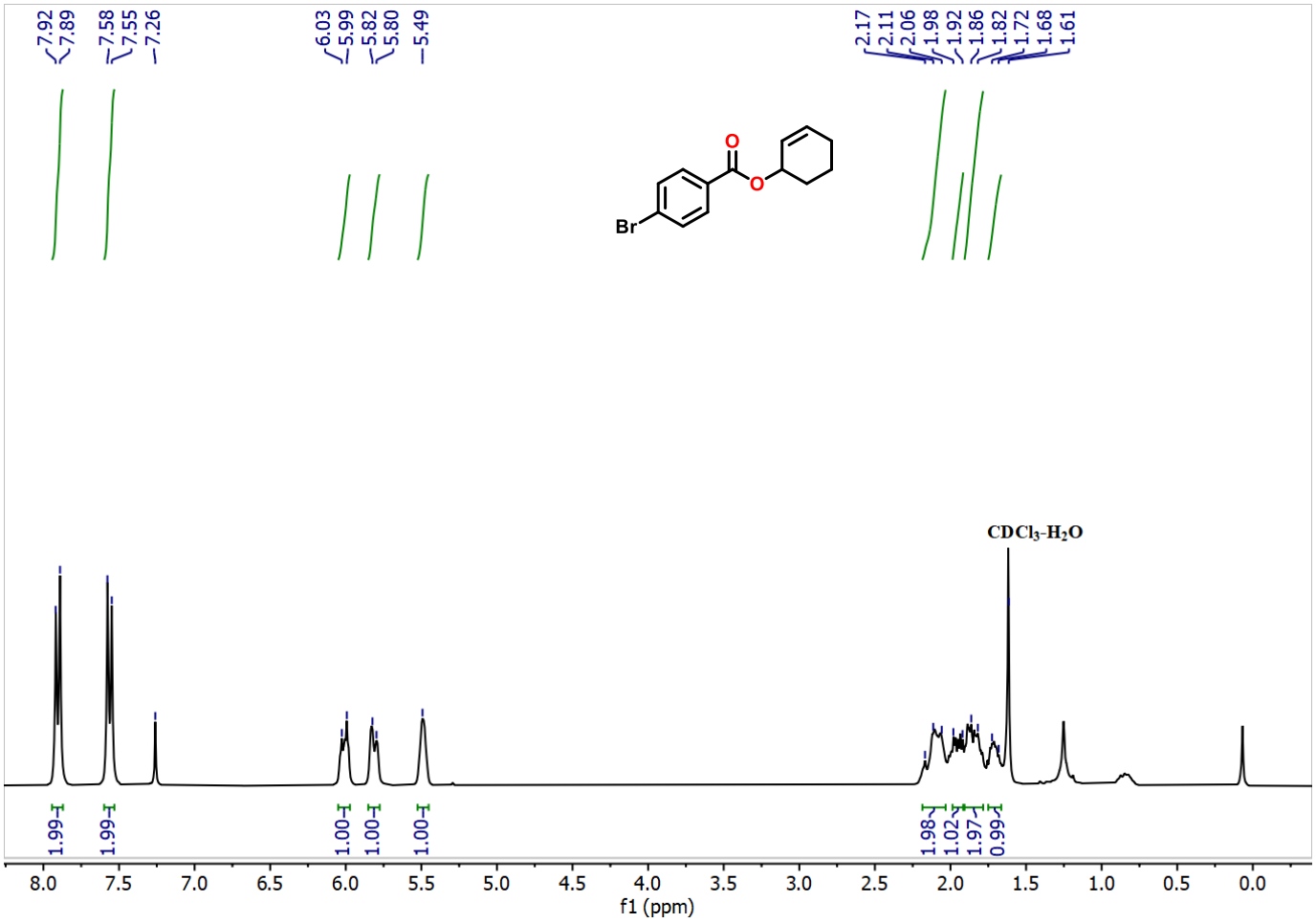

Fig. S19. ^{1}H NMR spectra of compound **4i**

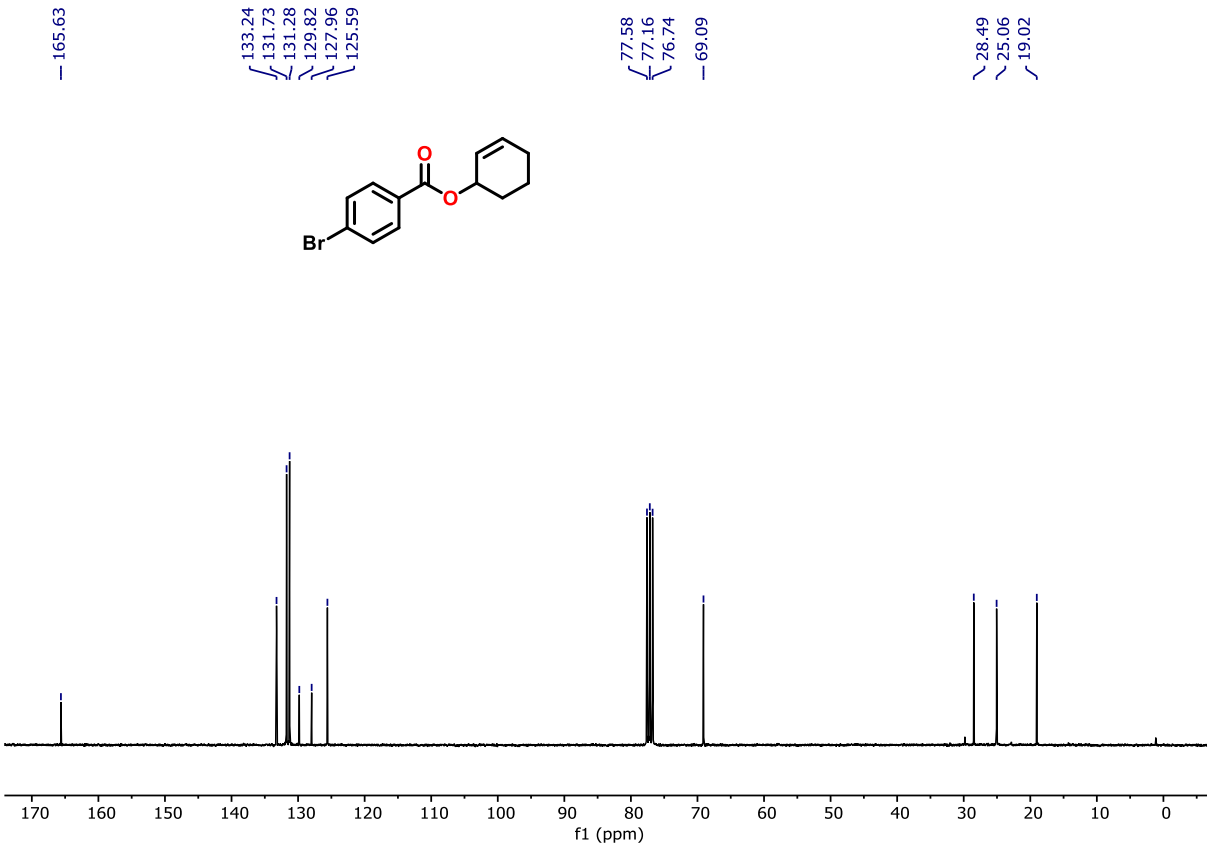

Fig. S20. ^{13}C NMR spectra of compound **4i**

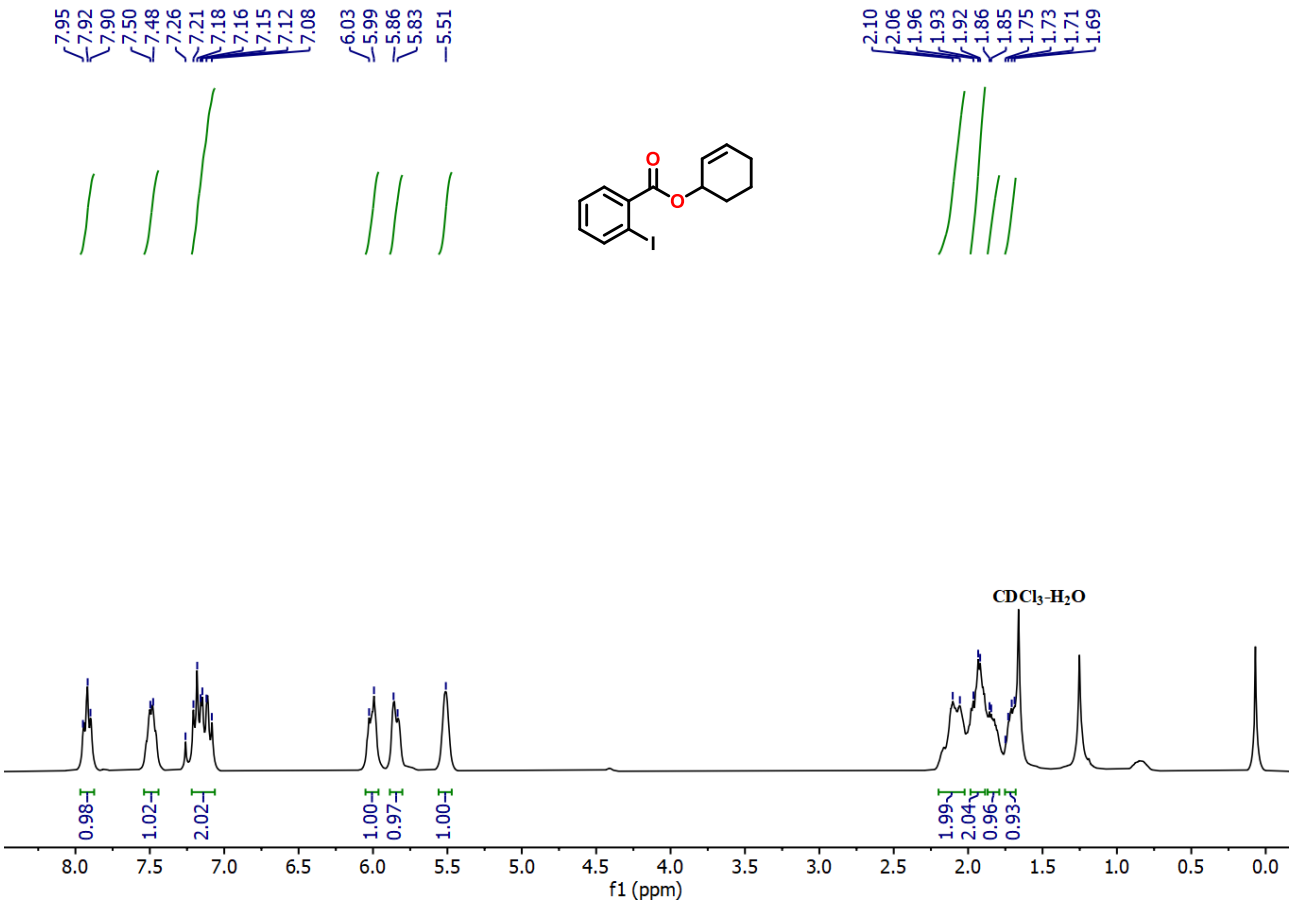

Fig. S21. ^{1}H NMR spectra of compound **4j**

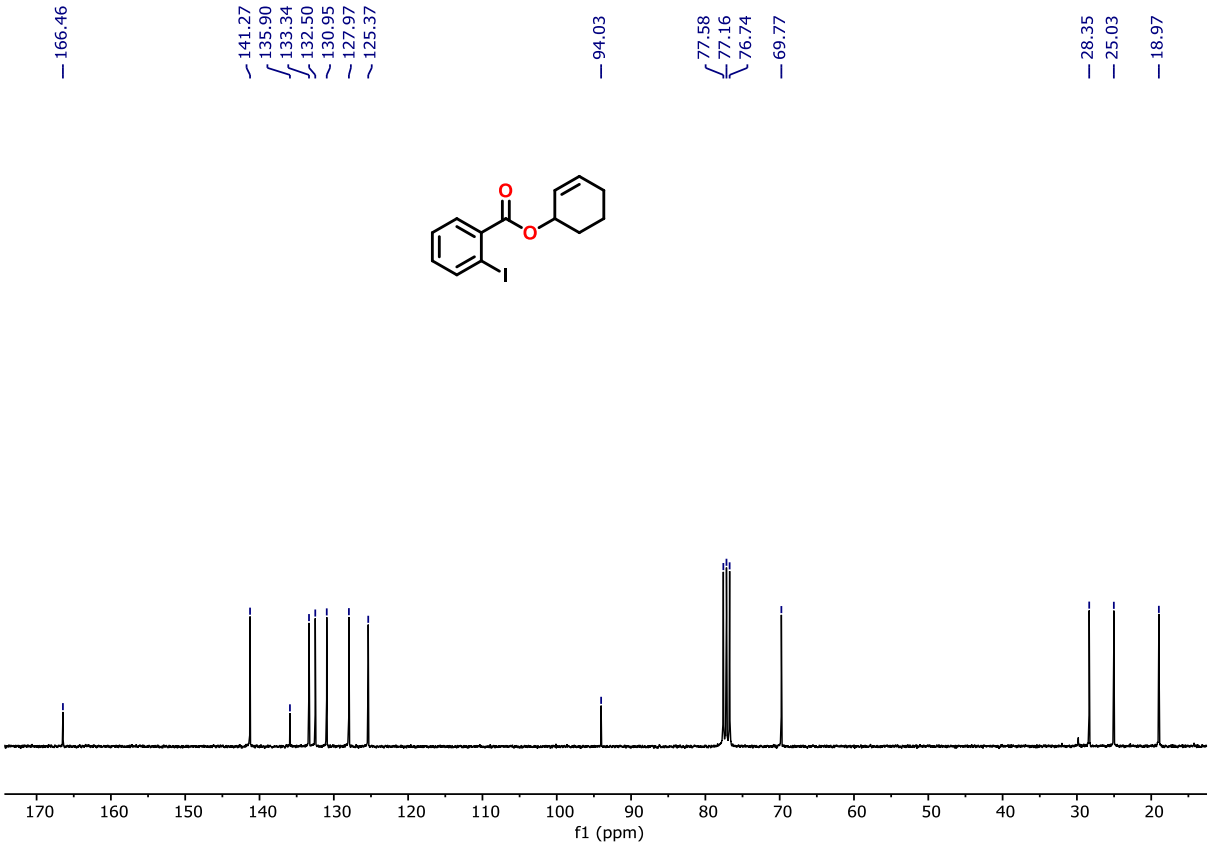

Fig. S22. ^{13}C NMR spectra of compound **4j**

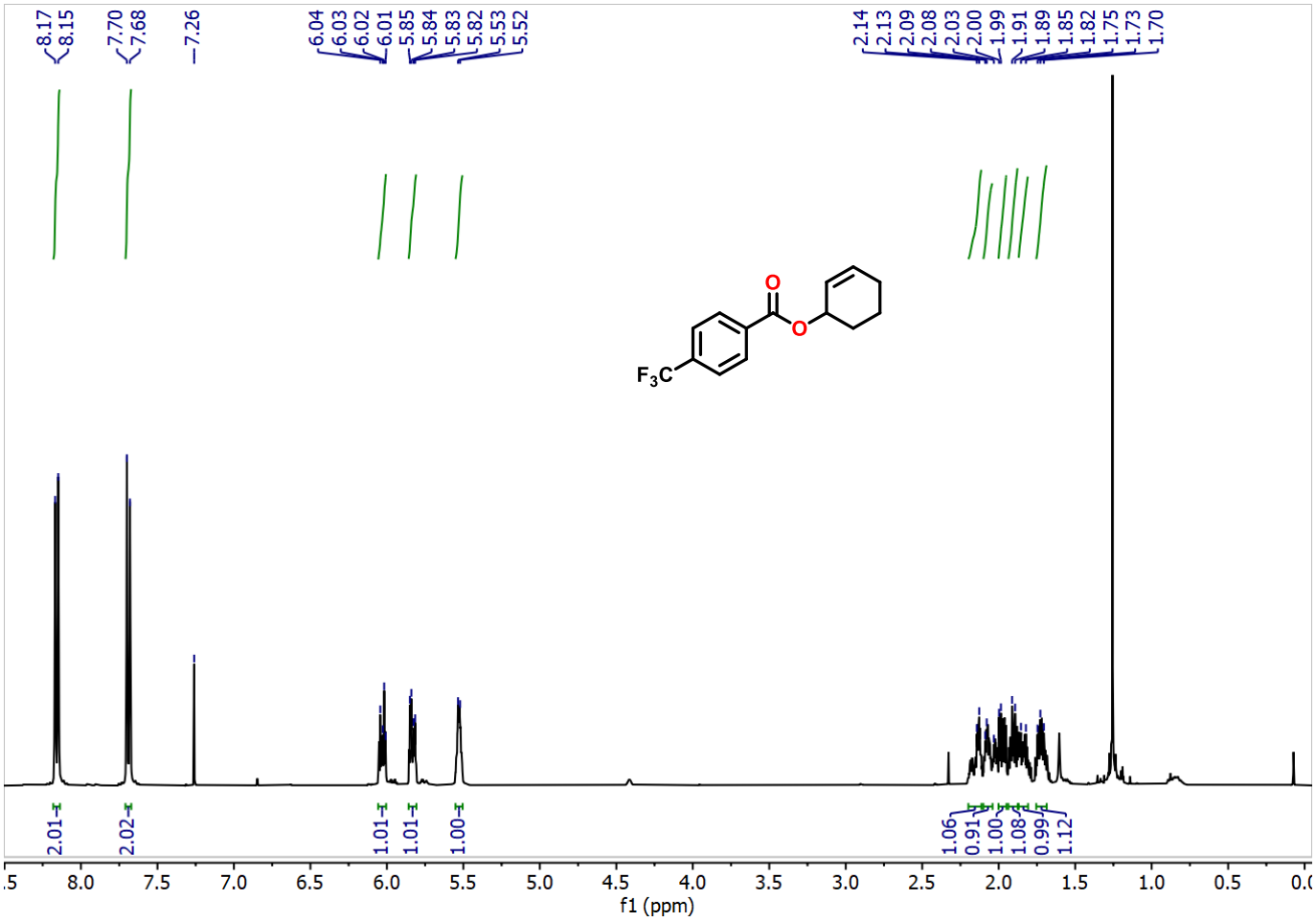

Fig. S23. ^{1}H NMR spectra of compound **4k**

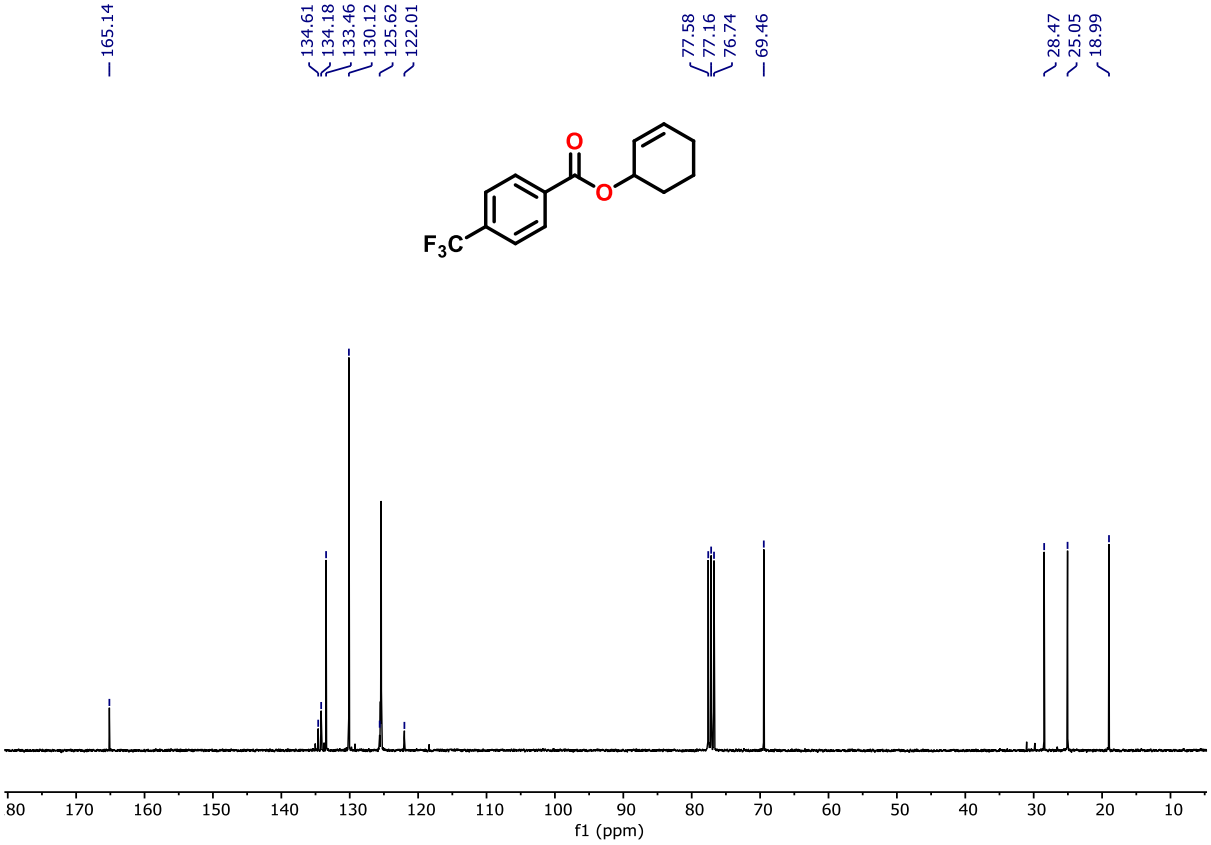

Fig. S24. ^{1}H NMR spectra of compound **4k**

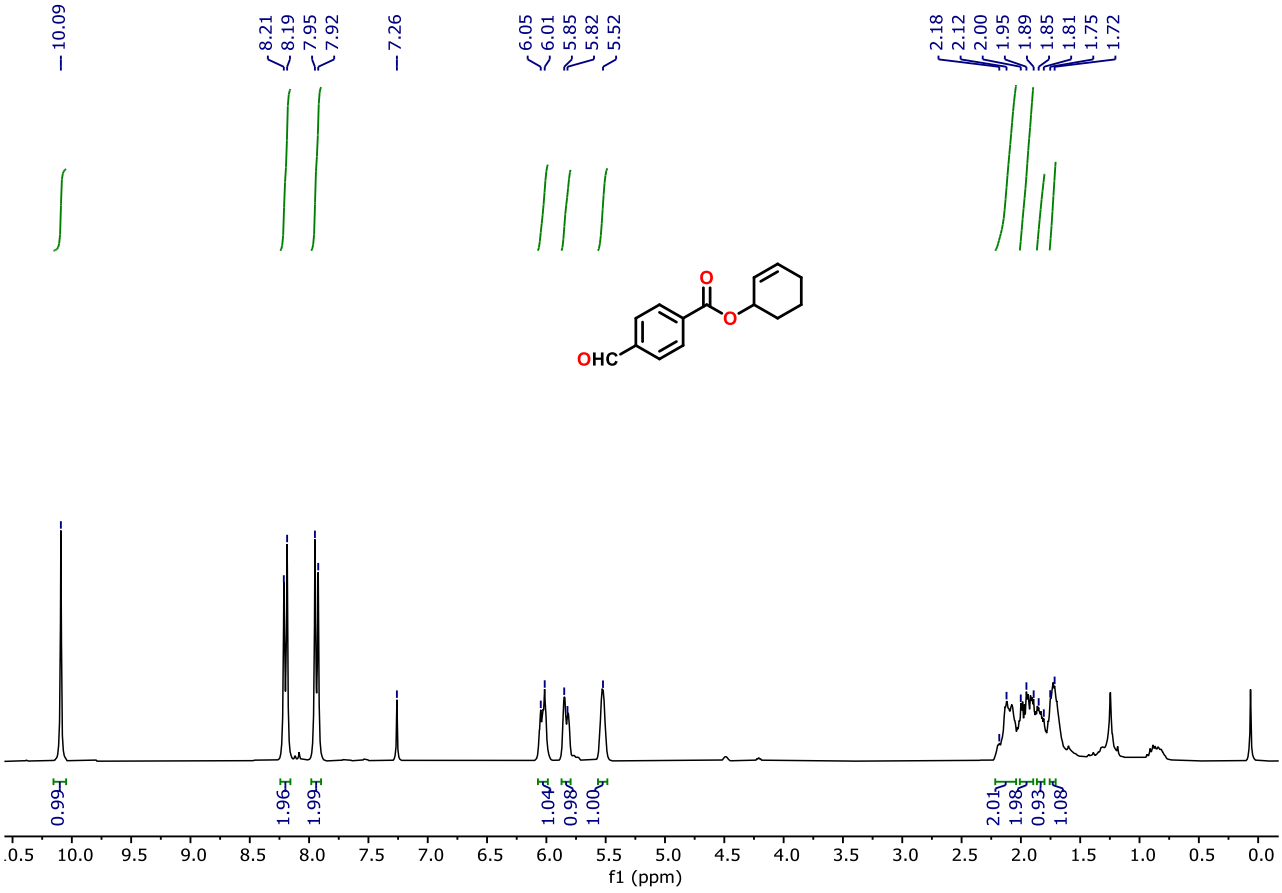

Fig. S25. ^{1}H NMR spectra of compound **4l**

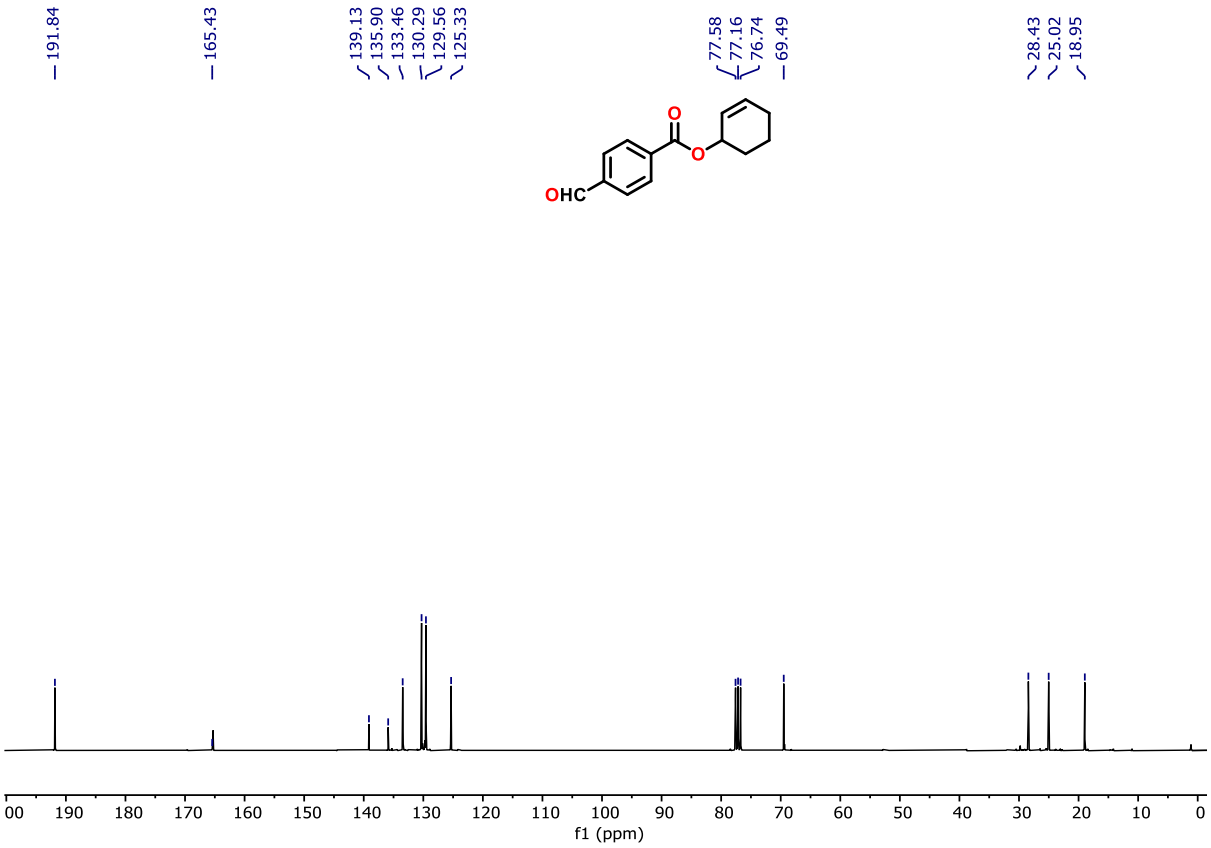

Fig. S26. ^{13}C NMR spectra of compound **4l**

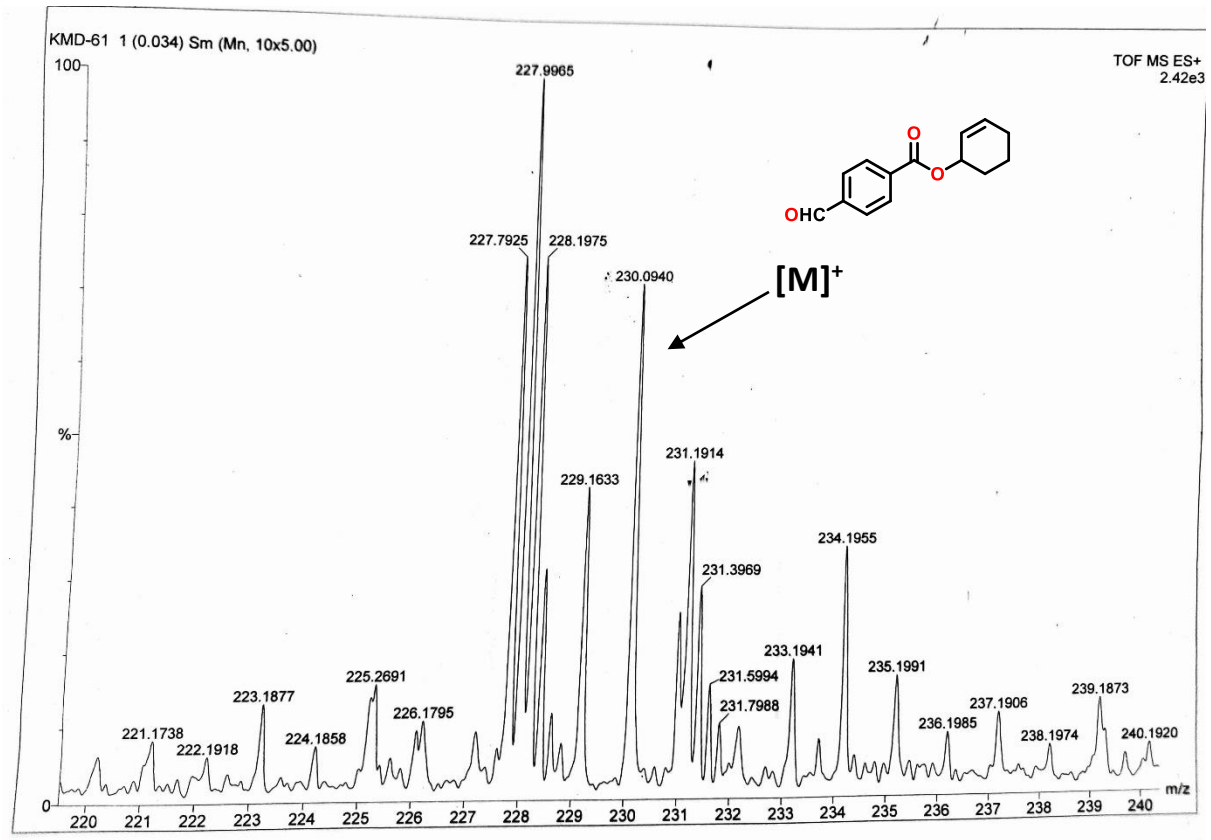

Fig. S27. HRMS of compound **4l**

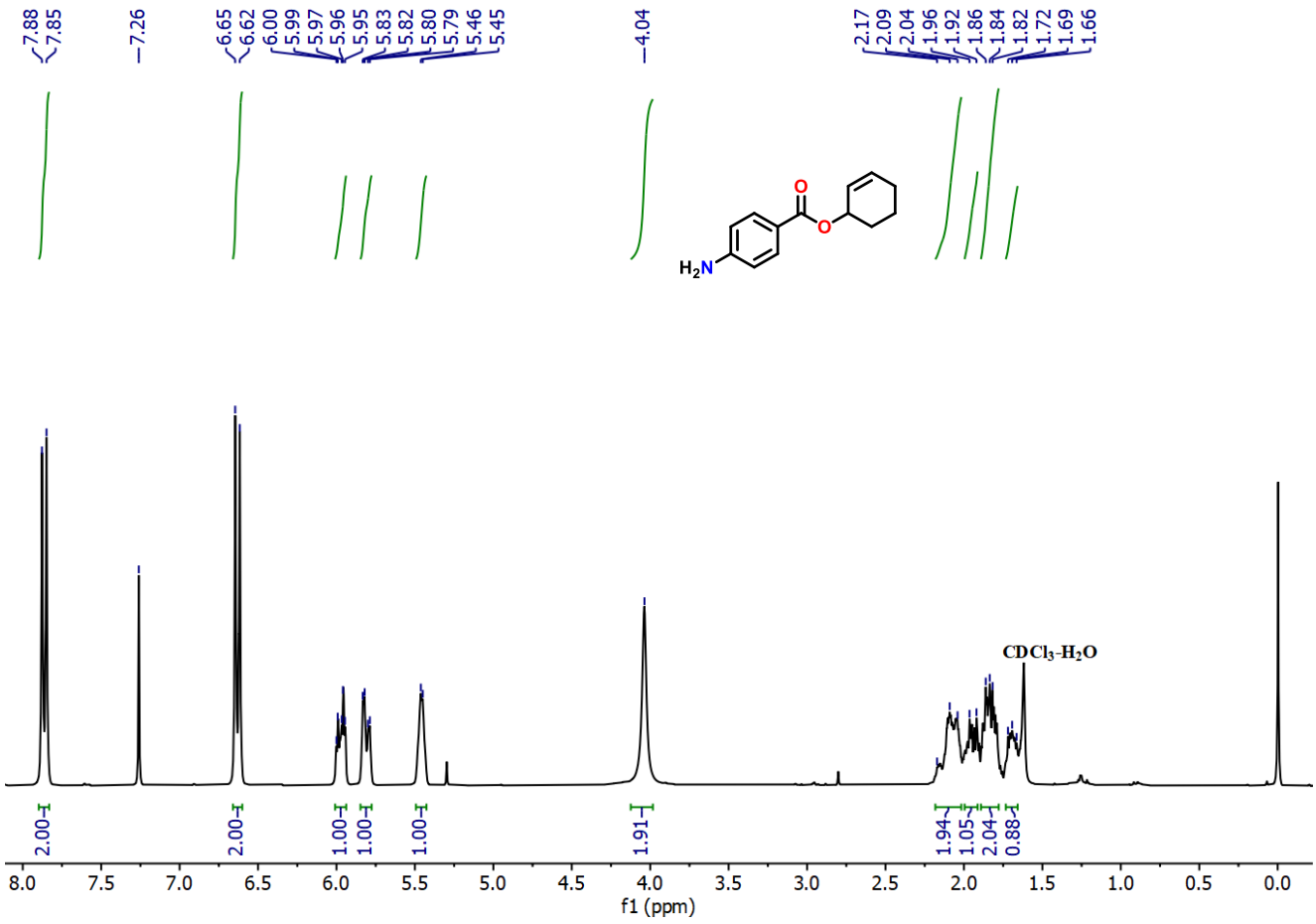

Fig. S28. ^{1}H NMR spectra of compound **4m**

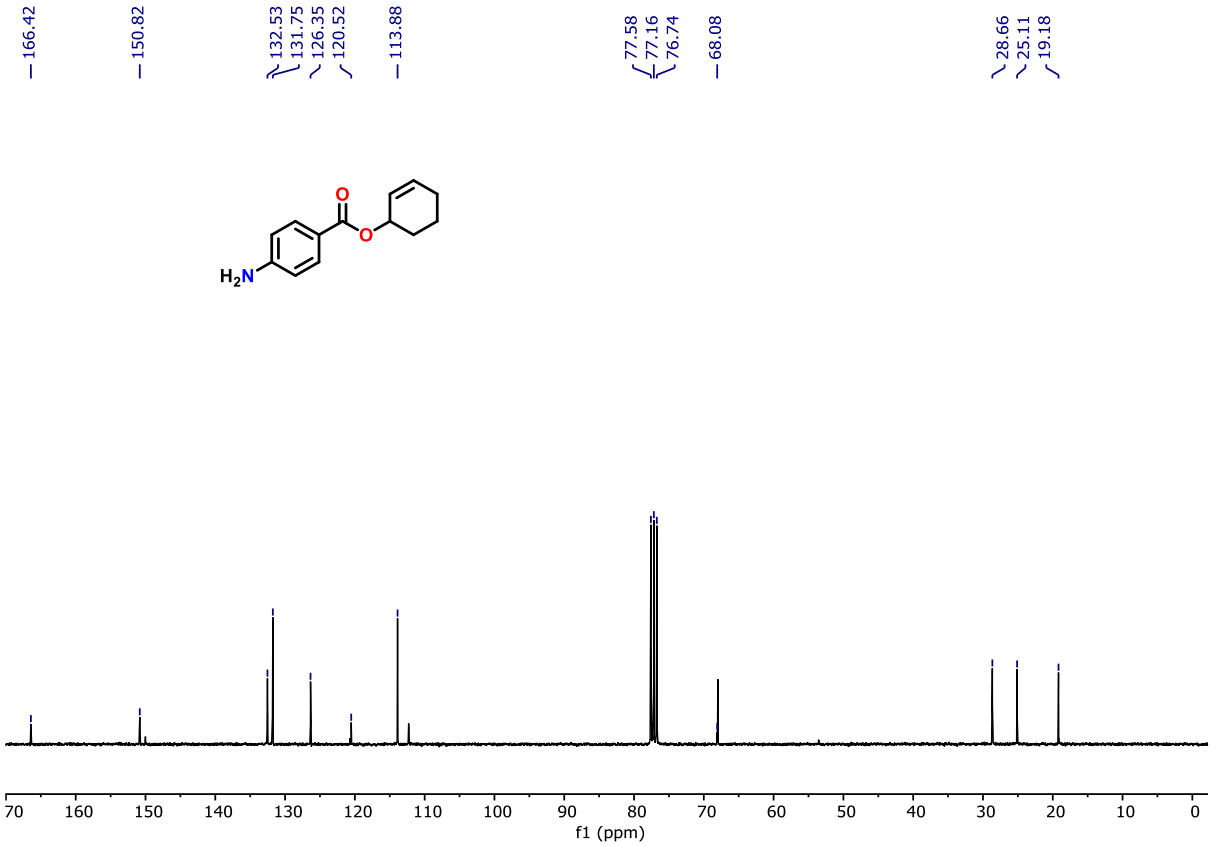

Fig. S29. ^{13}C NMR spectra of compound **4m**

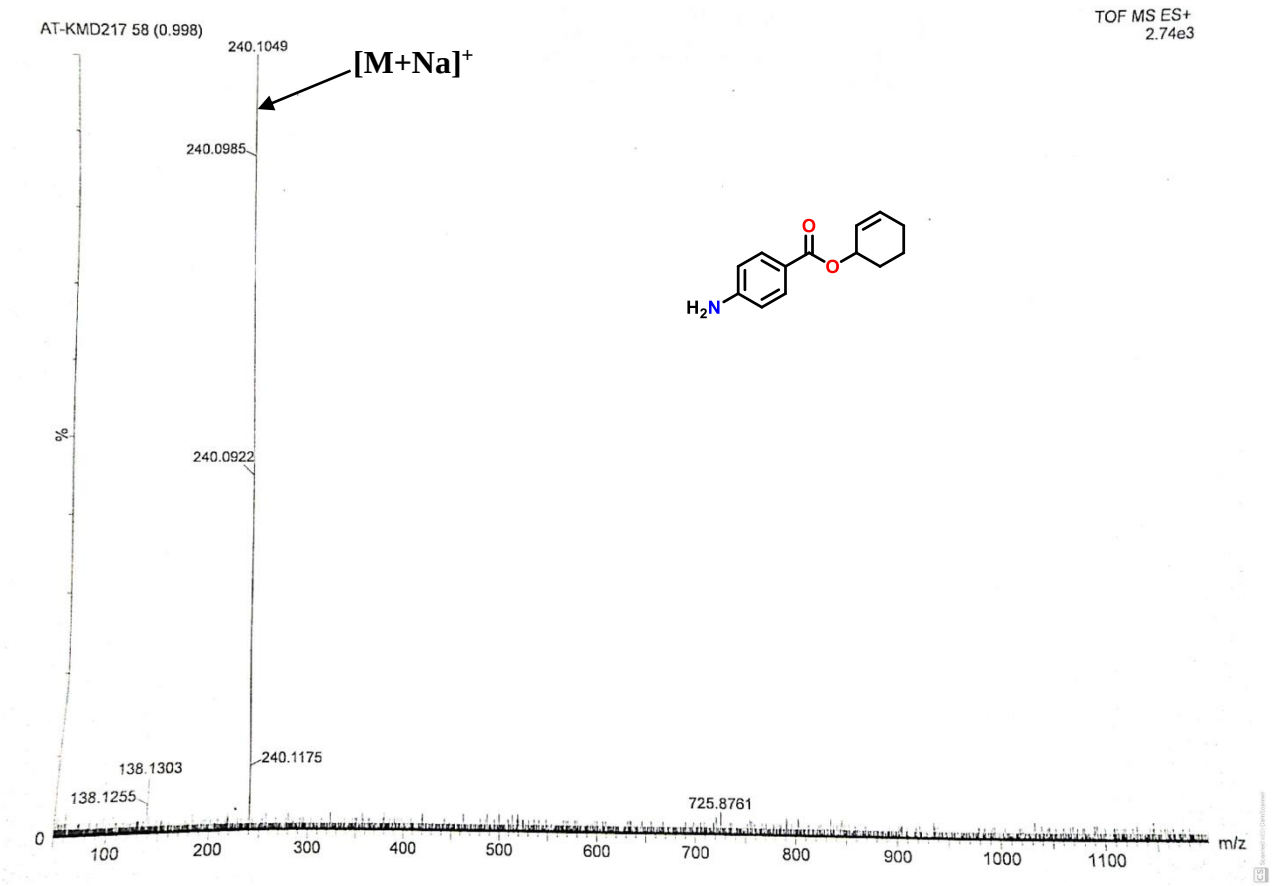

Fig. S30. HRMS of compound **4m**

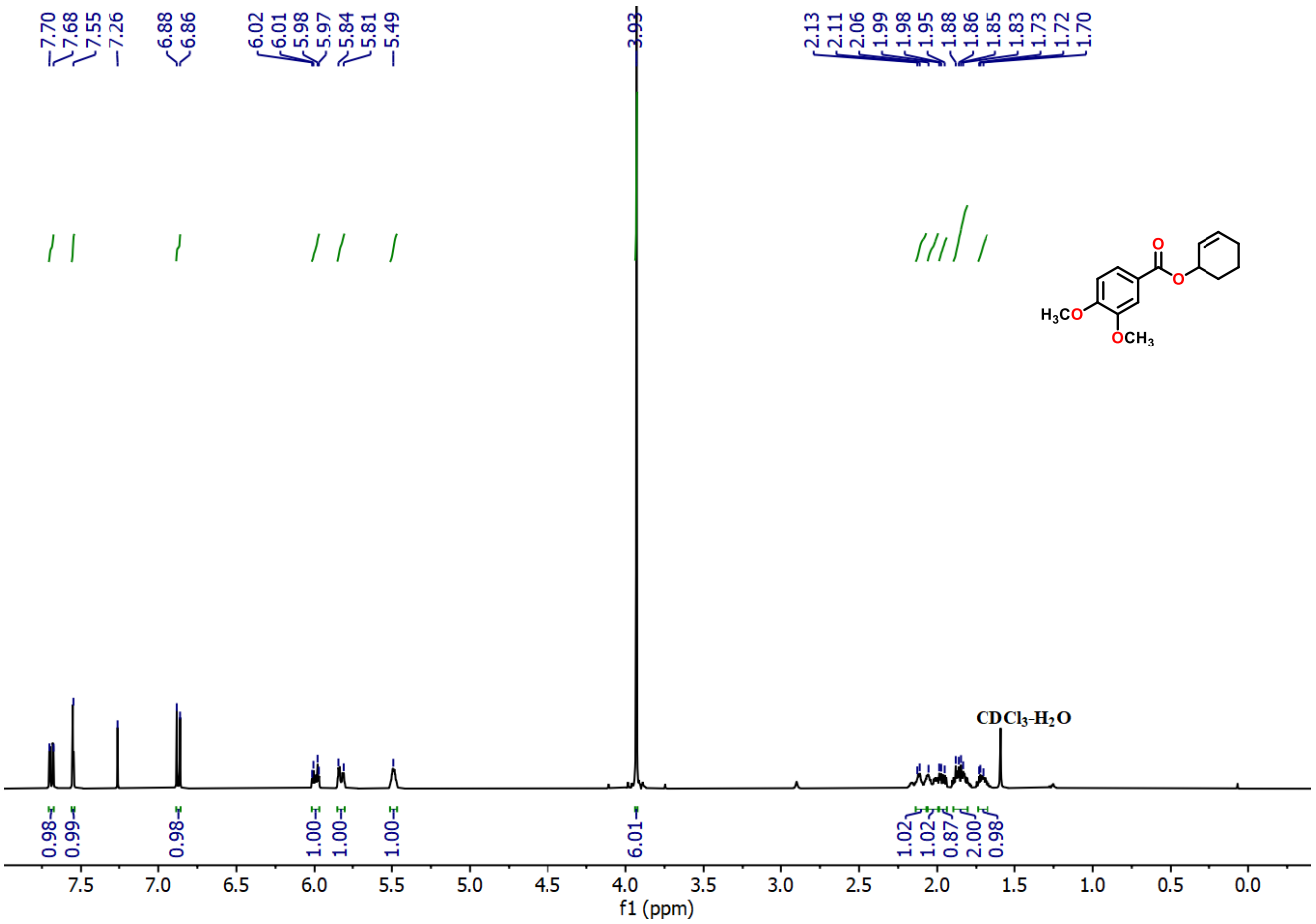

Fig. S31. ^{1}H NMR spectra of compound **4n**

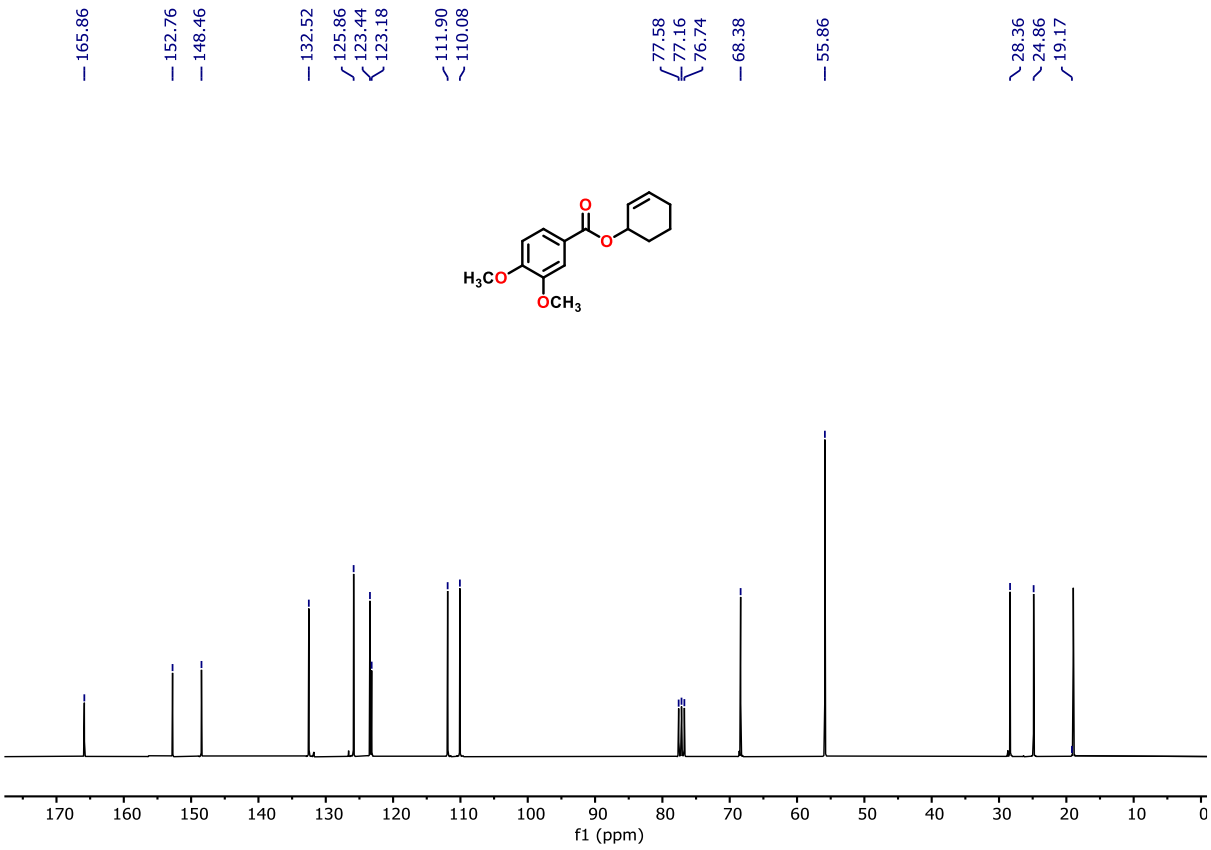

Fig. S32. ^{13}C NMR spectra of compound **4n**

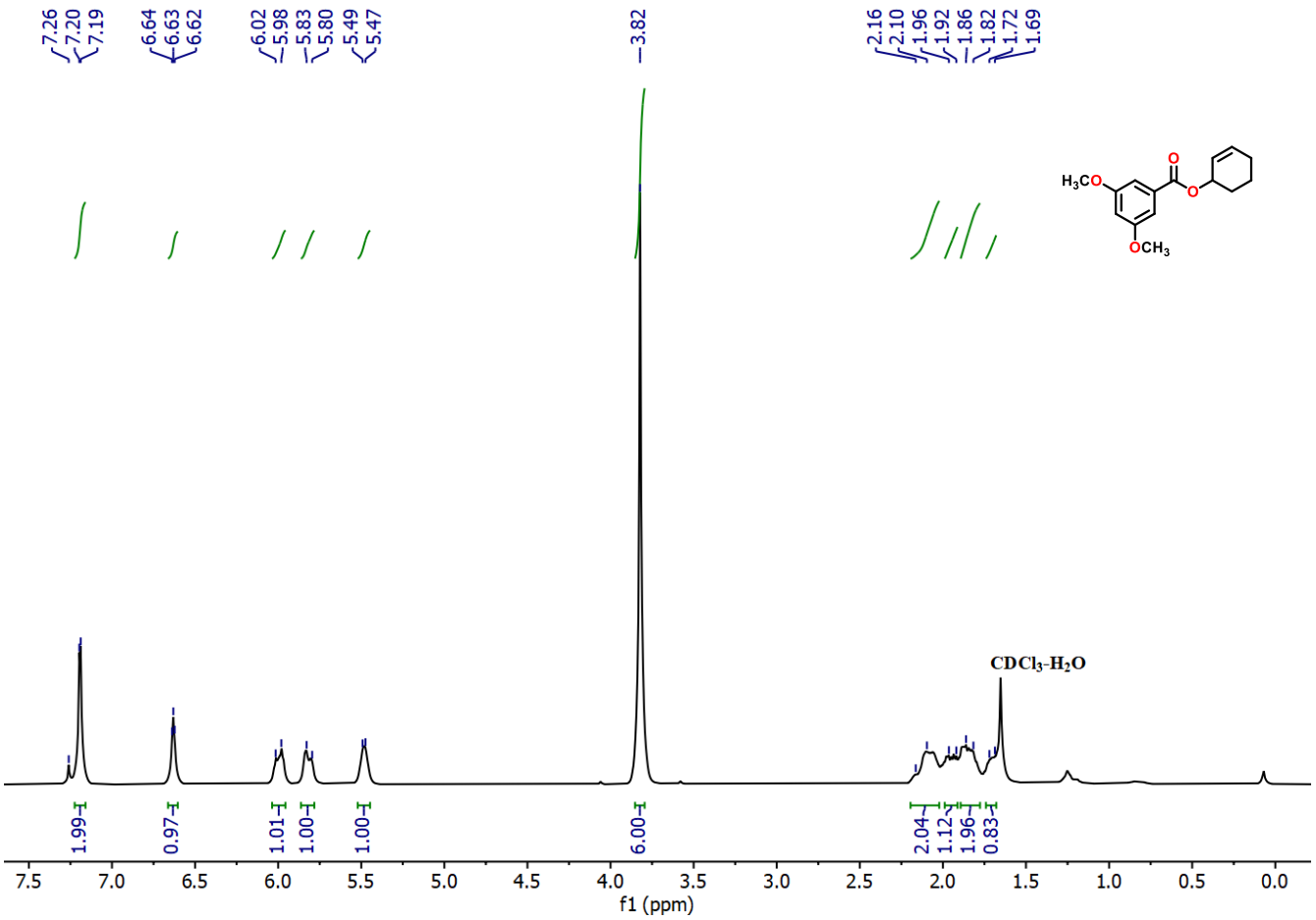

Fig. S33. ^{1}H NMR spectra of compound **4o**

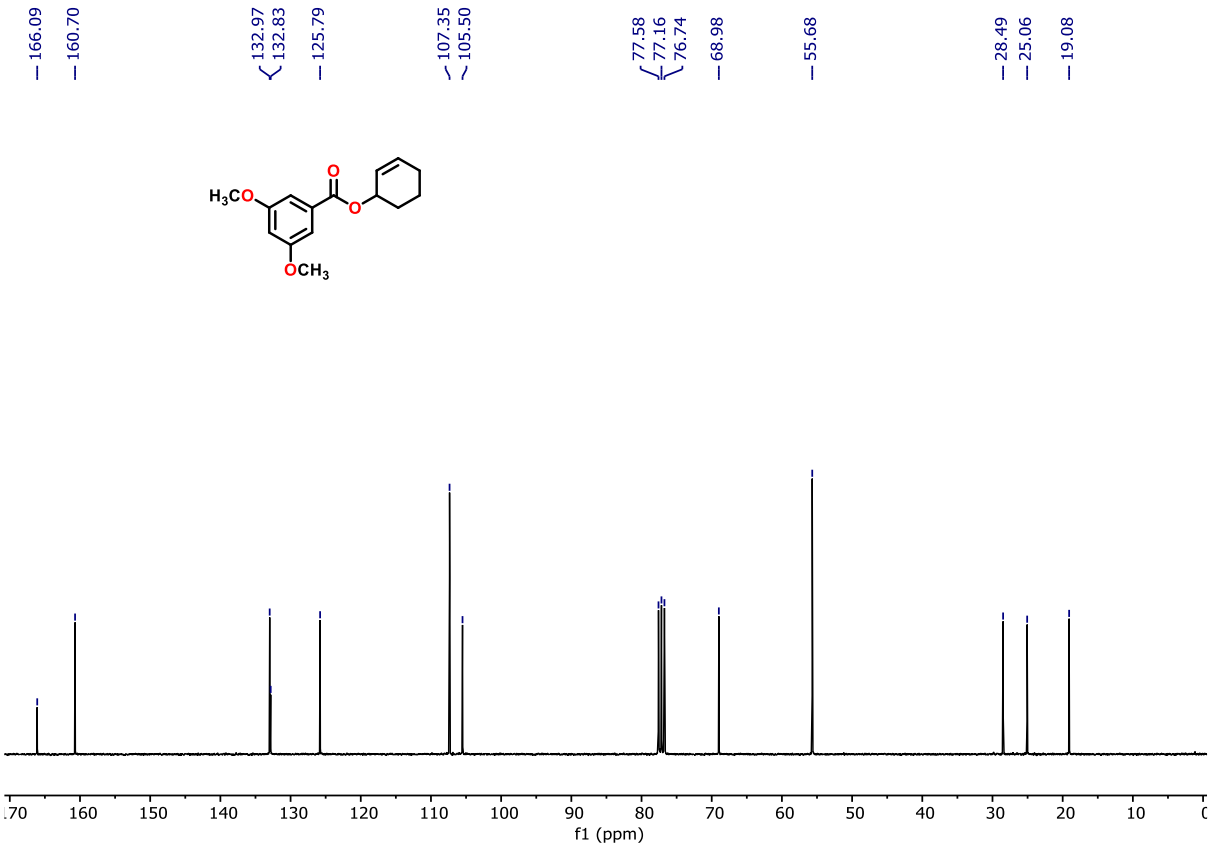

Fig. S34. ^{13}C NMR spectra of compound **4o**

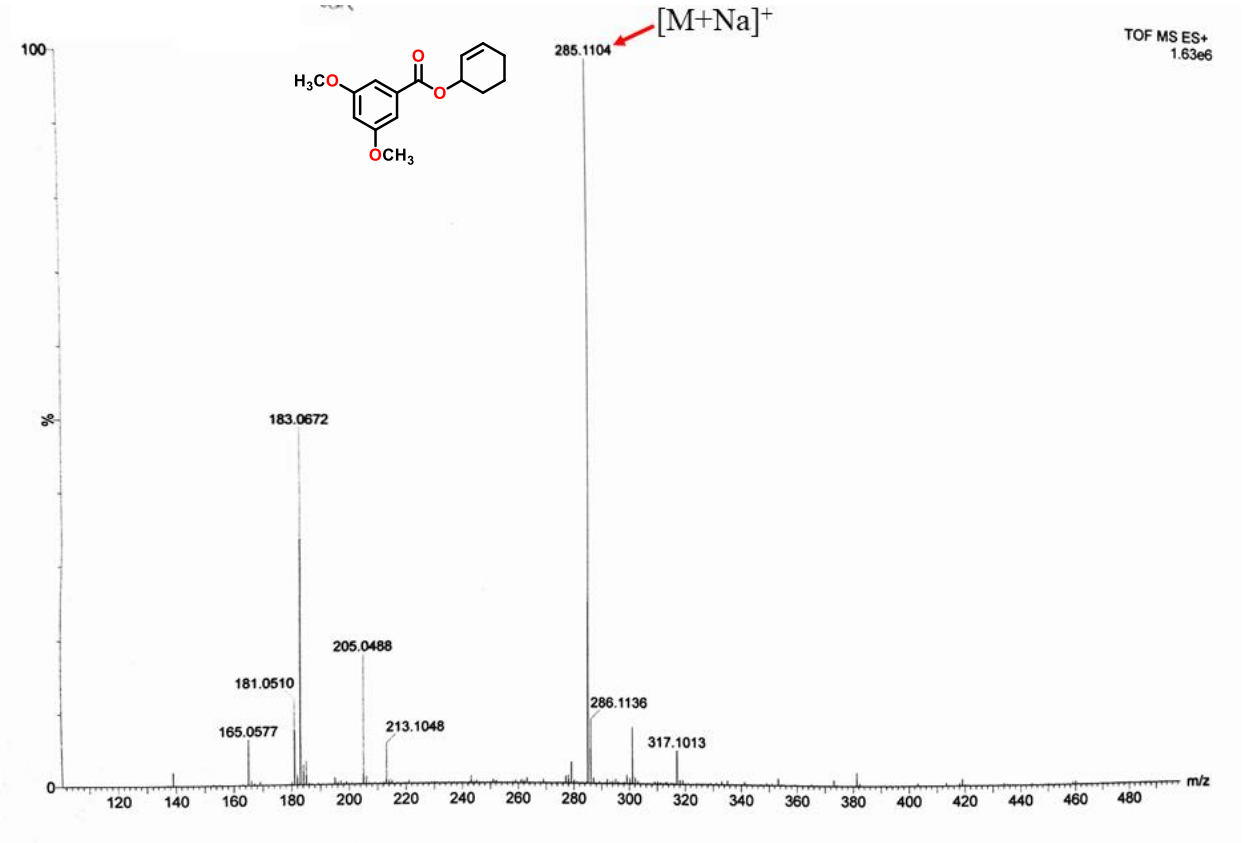

Fig. S35. HRMS of compound **4o**

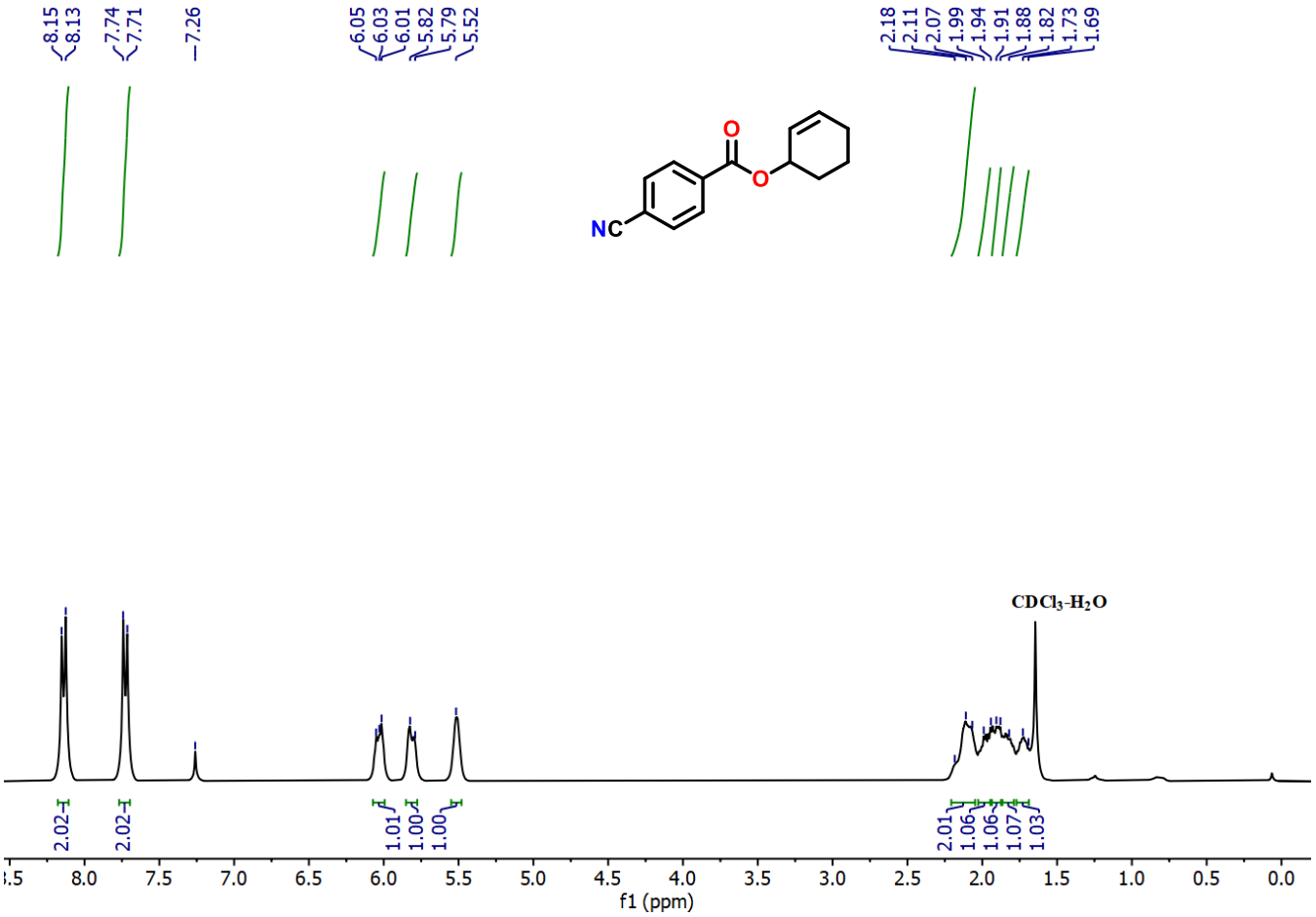

Fig. S36. ^{1}H NMR spectra of compound **4p**

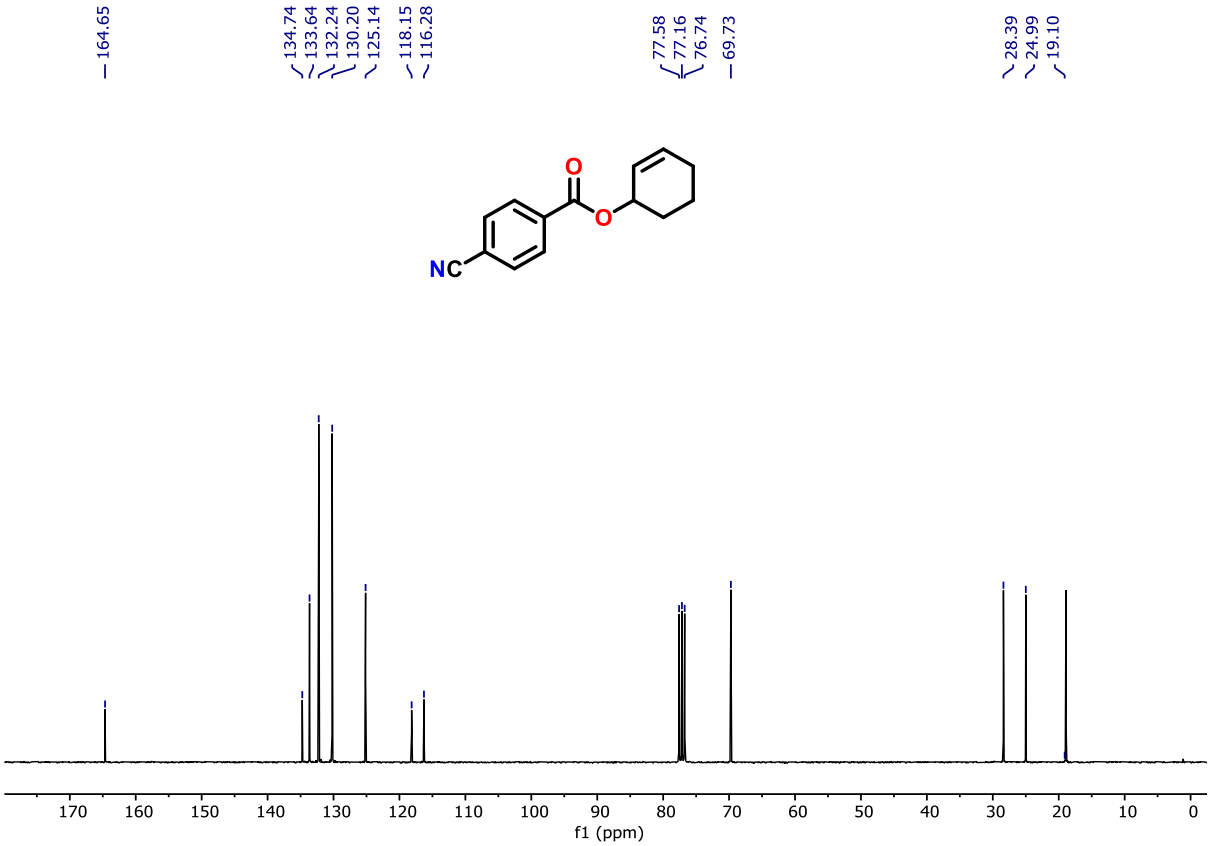

Fig. S37. ^{13}C NMR spectra of compound **4p**

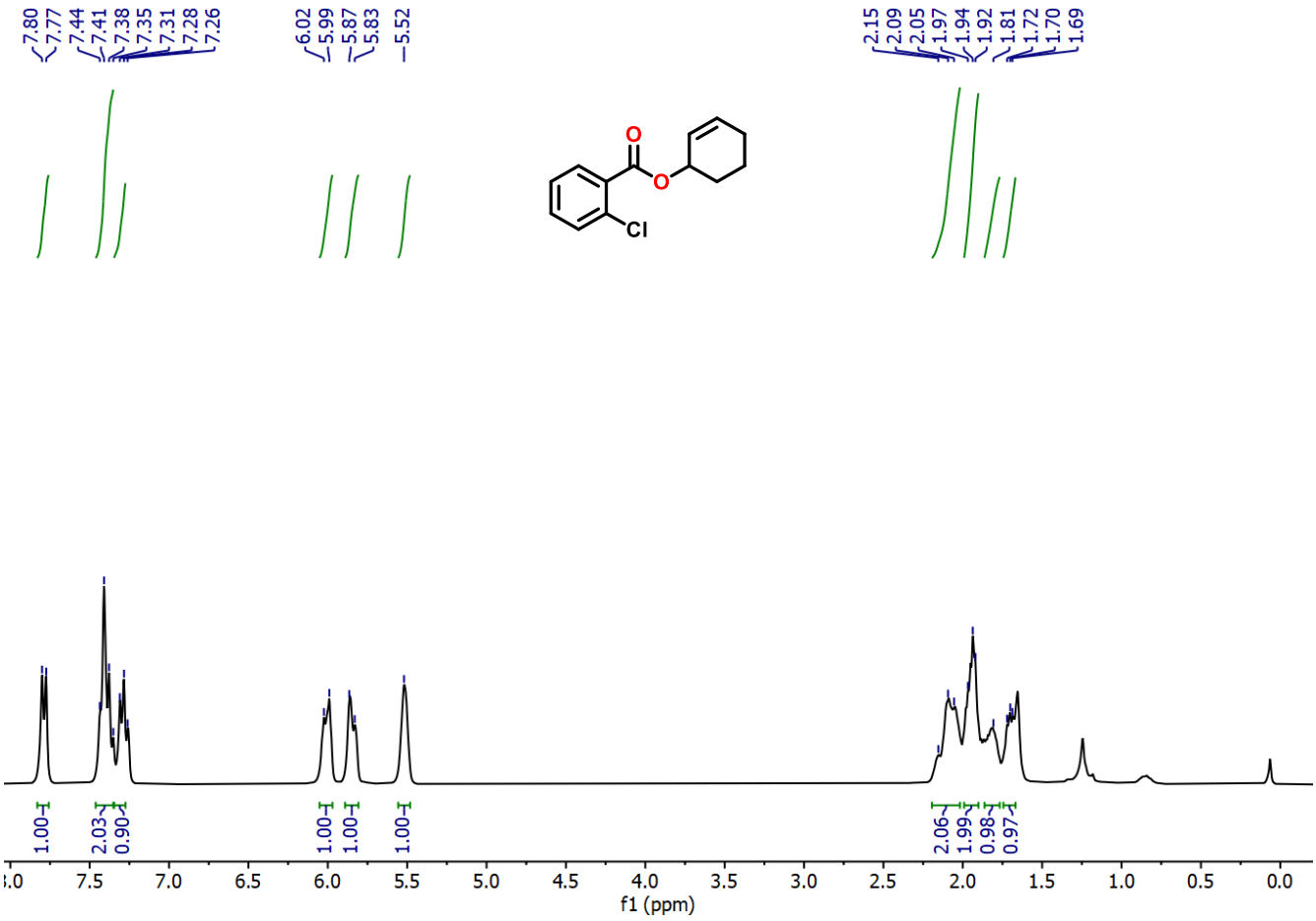

Fig. S38. ^{1}H NMR spectra of compound **4q**

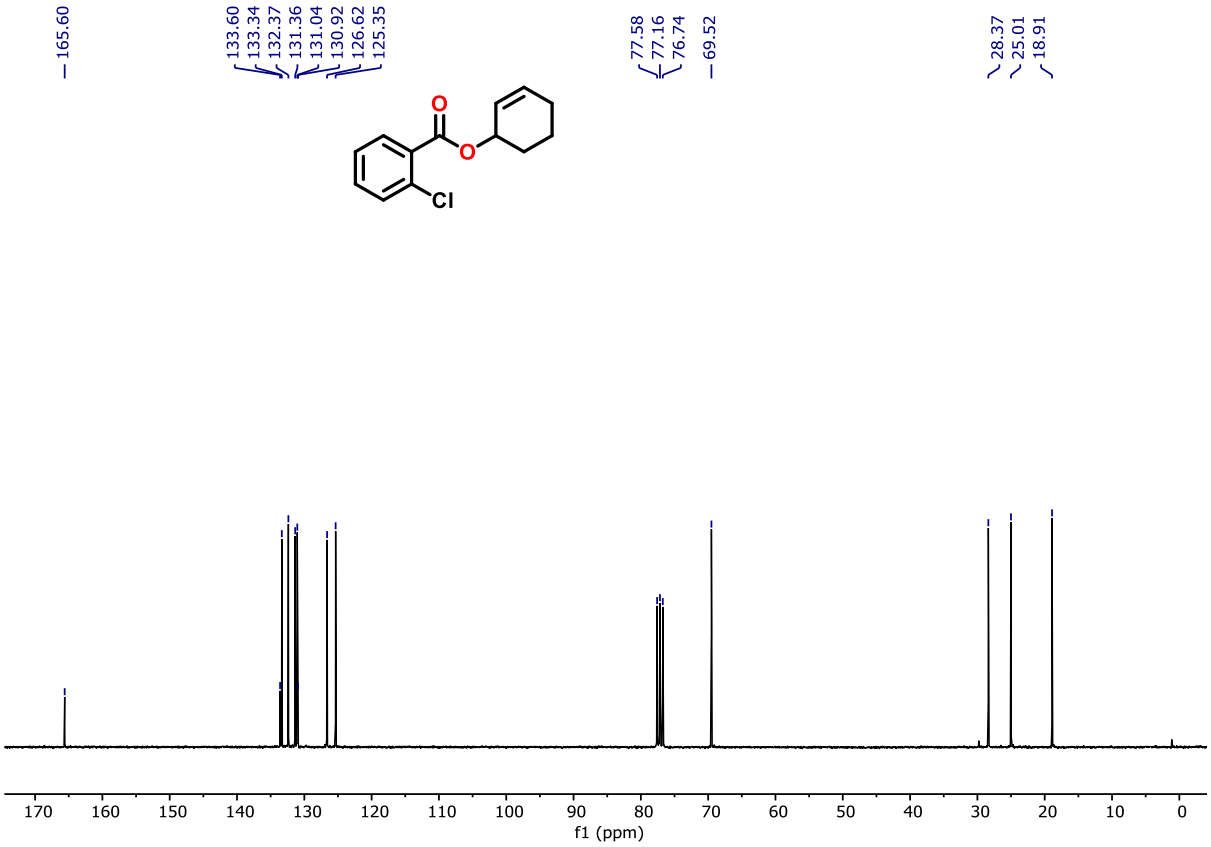

Fig. S39. ^{13}C NMR spectra of compound **4q**

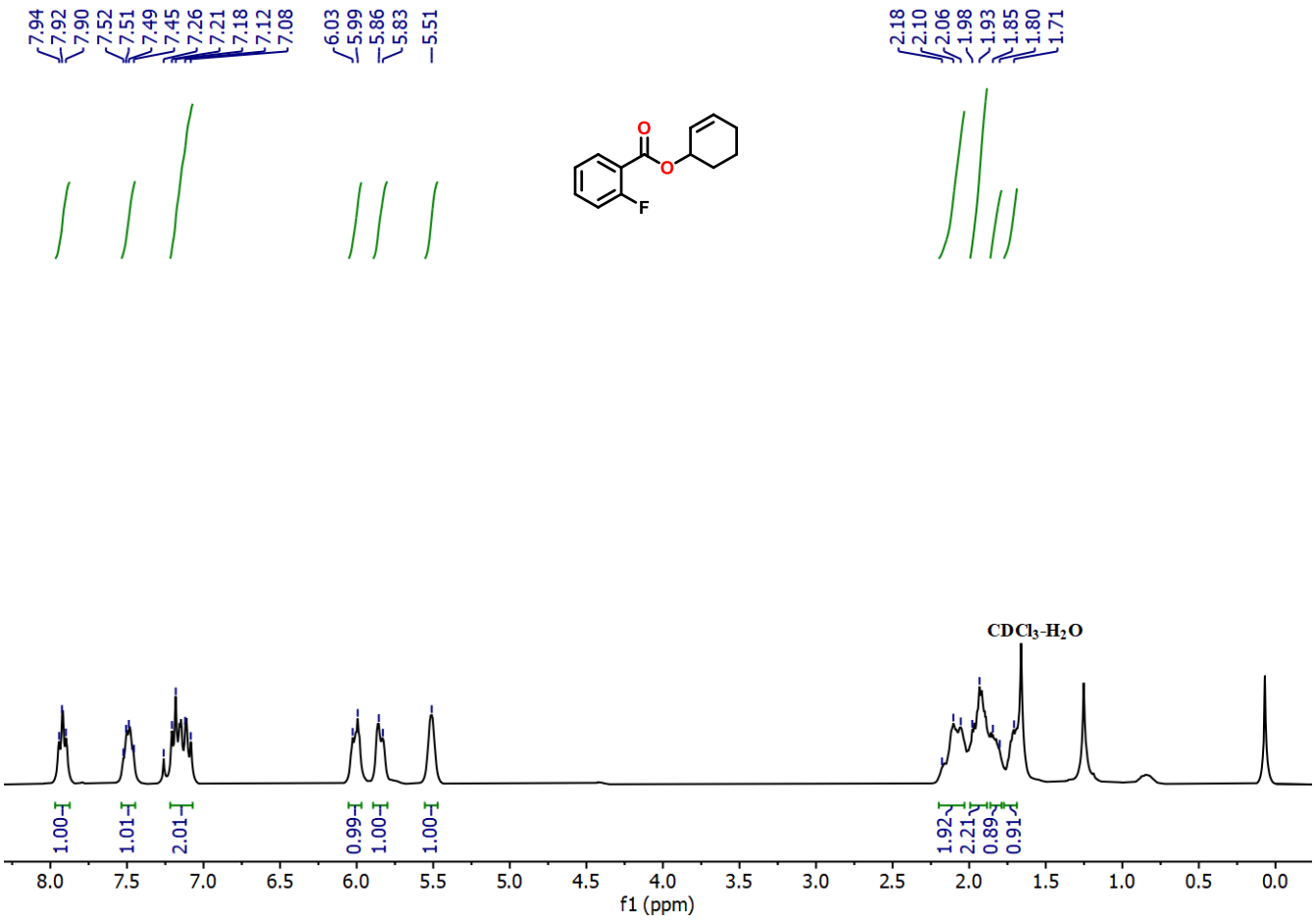

Fig. S40. ^{1}H NMR spectra of compound **4r**

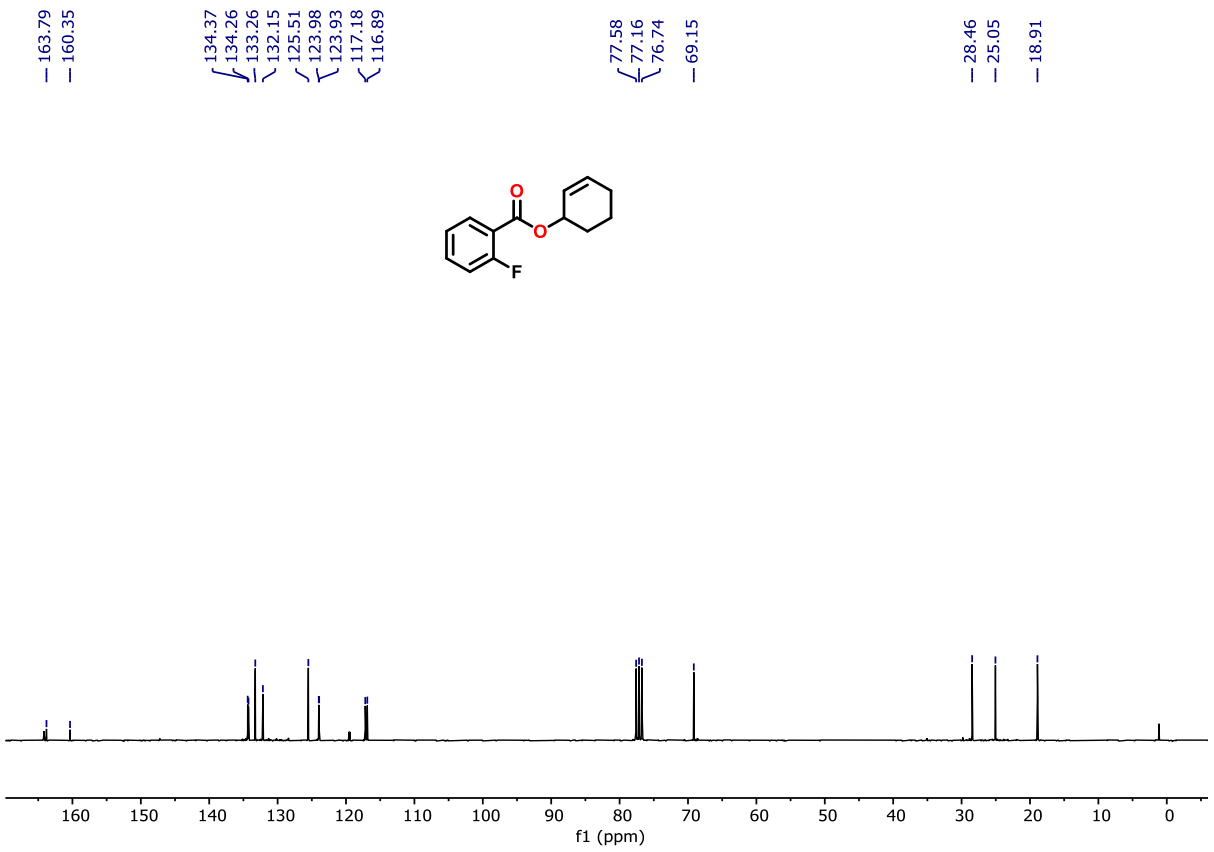

Fig. S41. ^{13}C NMR spectra of compound **4r**

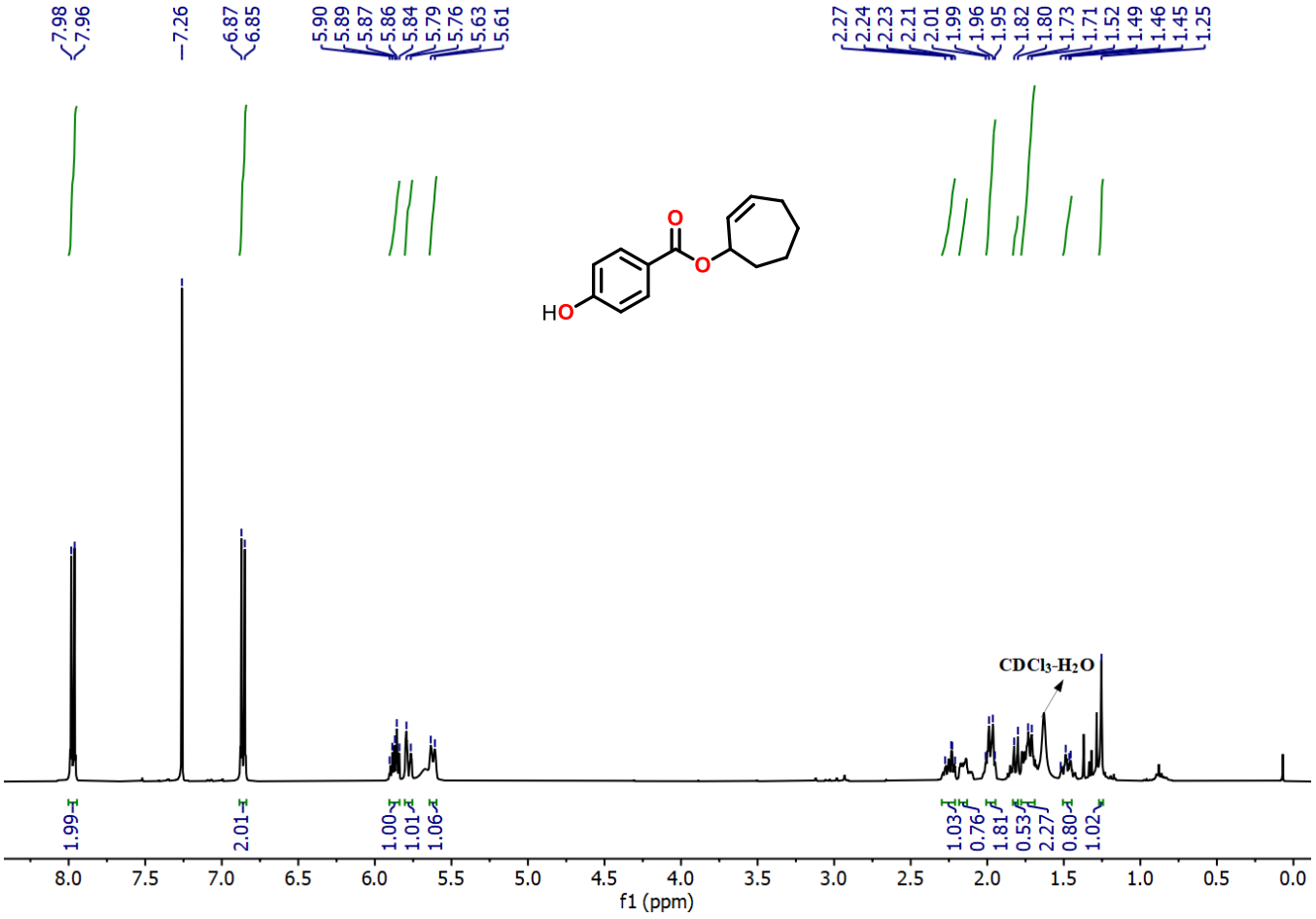

Fig. S42. ^{1}H NMR spectra of compound **4s**

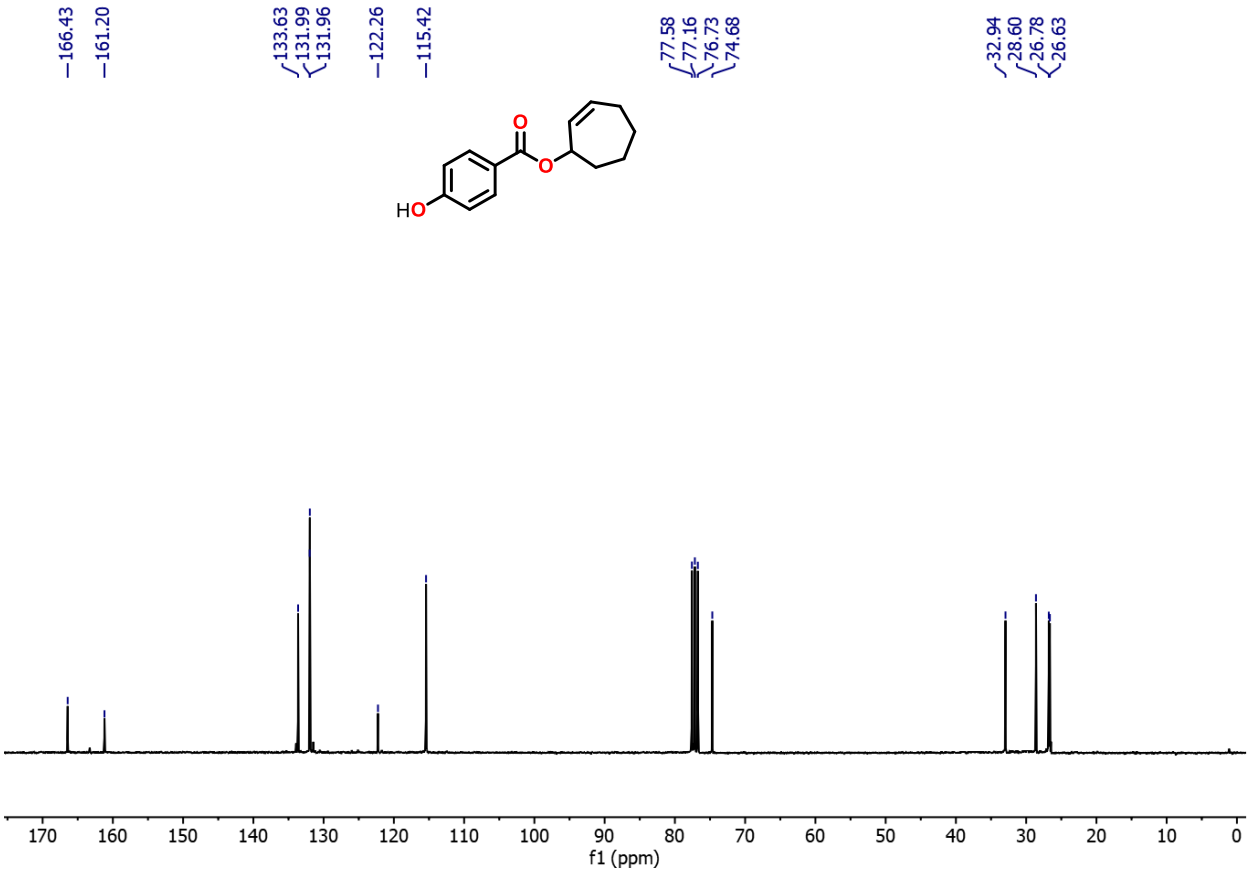

Fig. S43. ^{13}C NMR spectra of compound **4s**

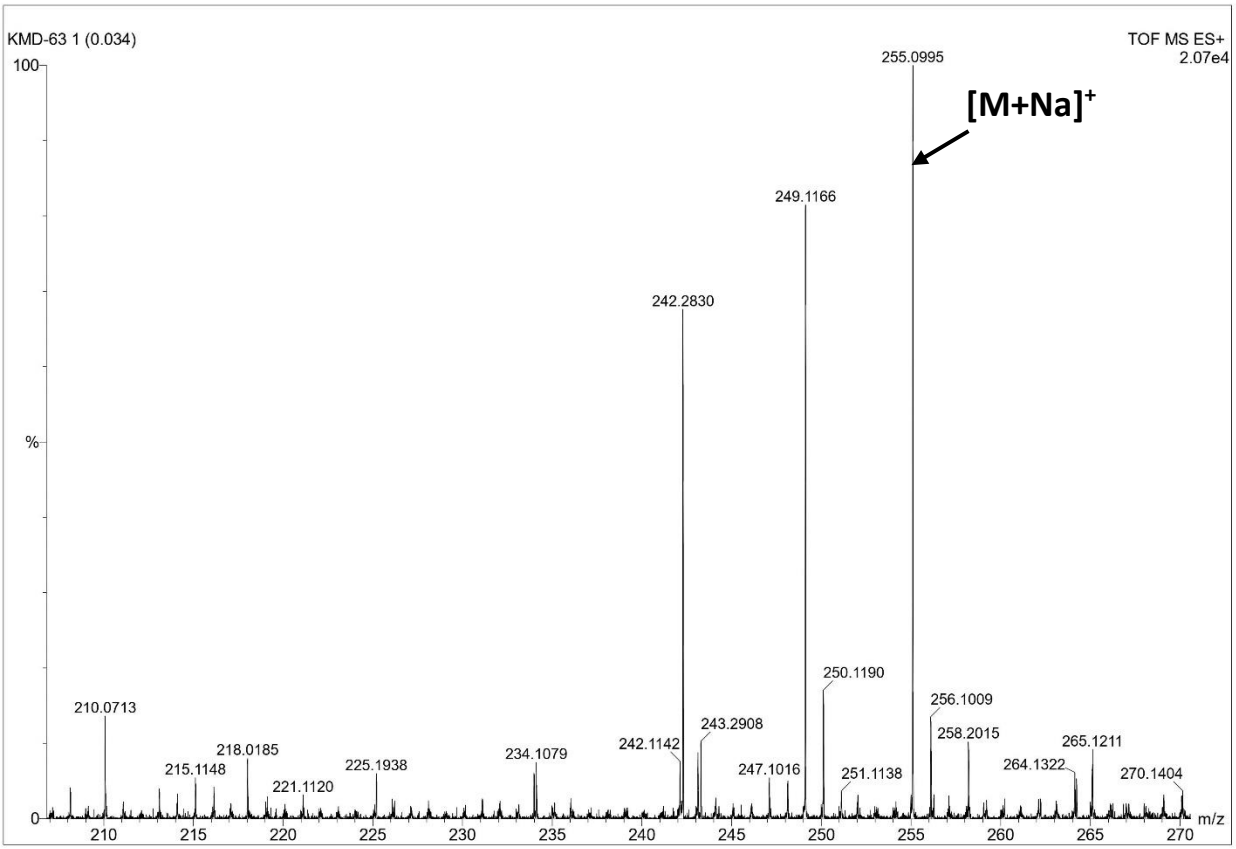

Fig. S44. HRMS of compound **4s**

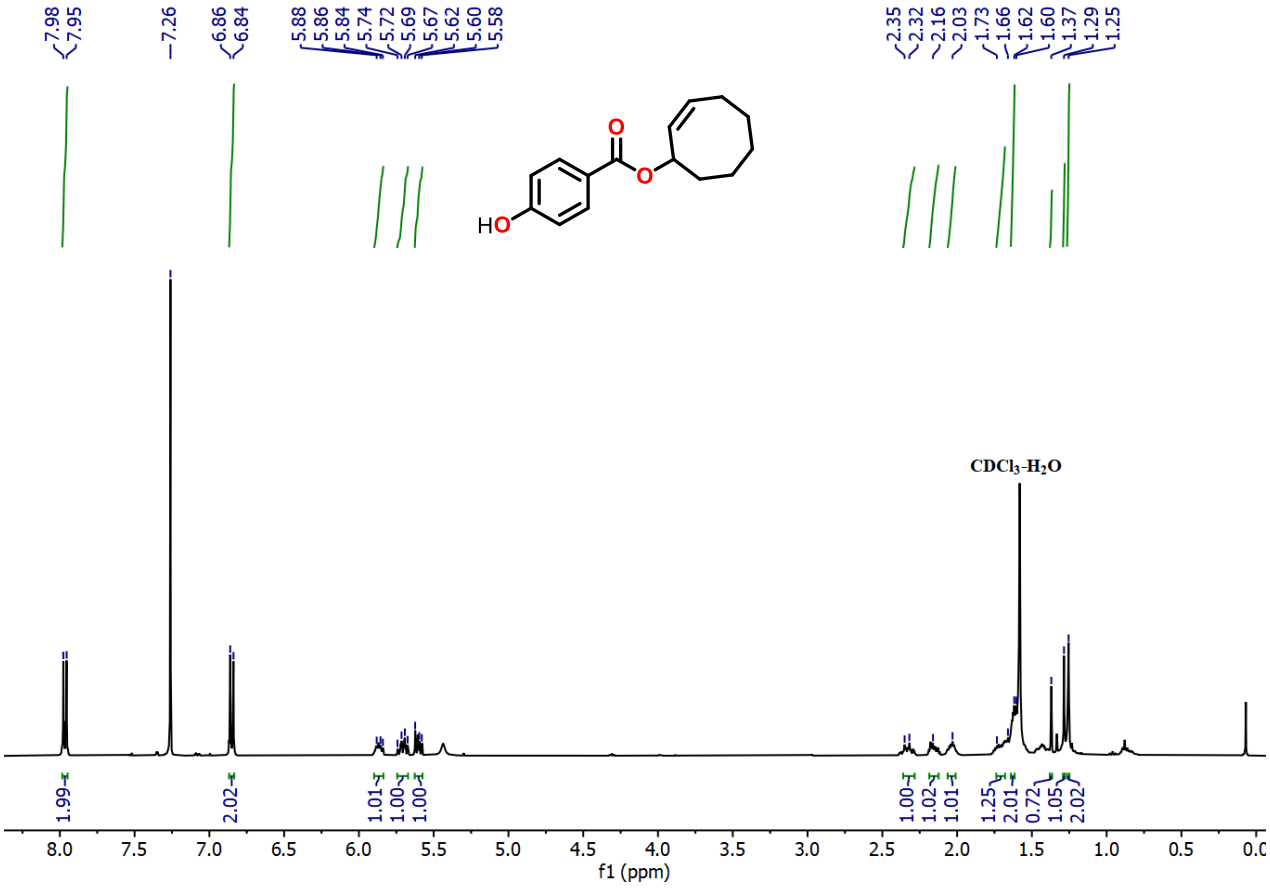

Fig. S45. ^{1}H NMR spectra of compound **4t**

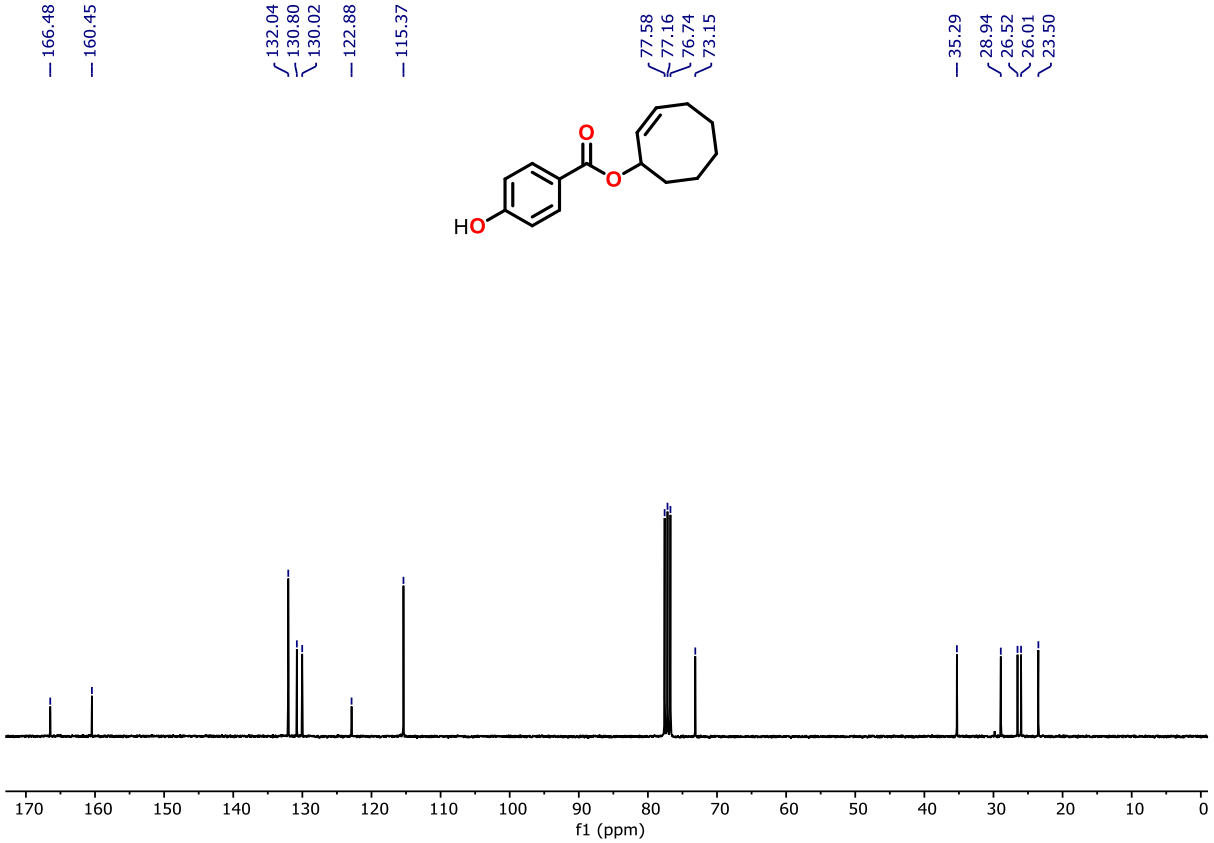

Fig. S46. ^{13}C NMR spectra of compound **4t**

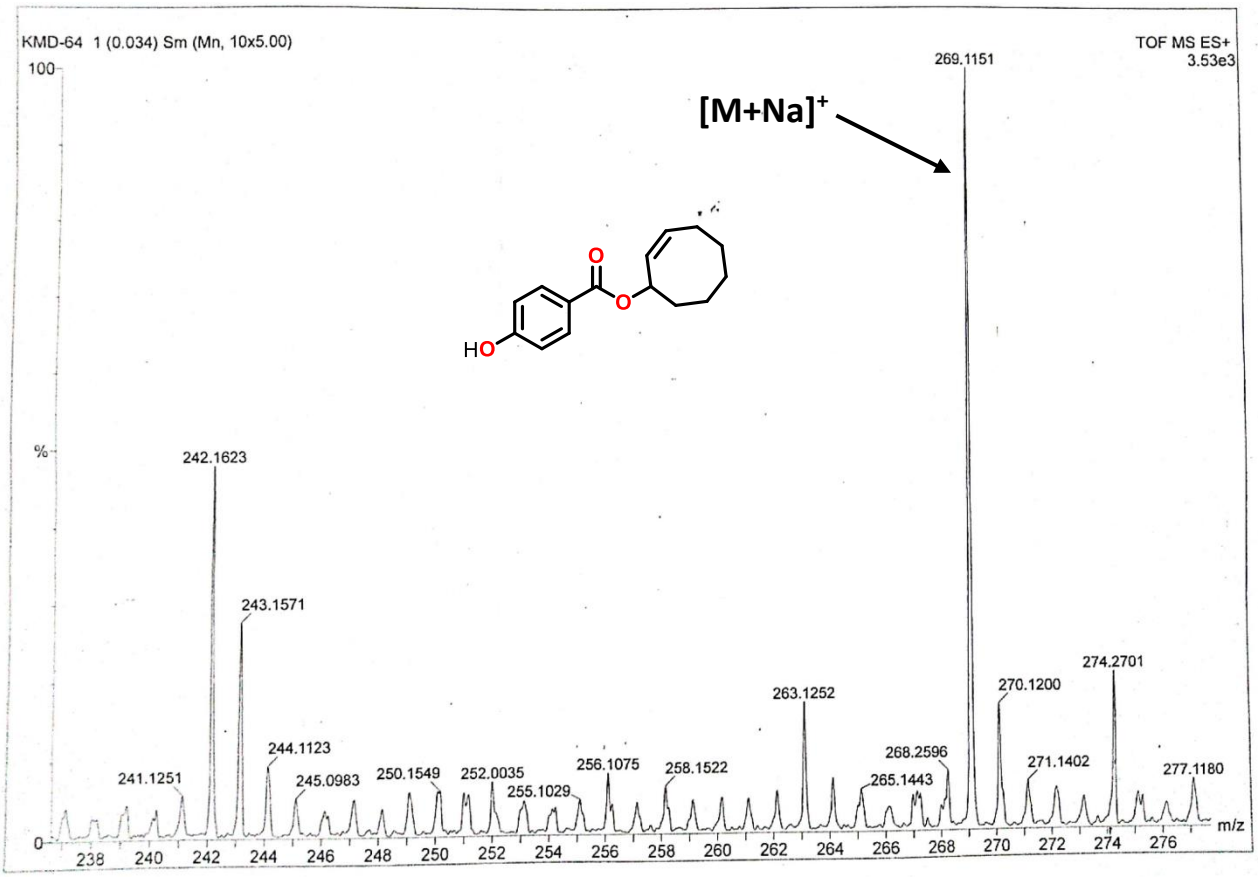

Fig. S47. HRMS of compound **4t.**

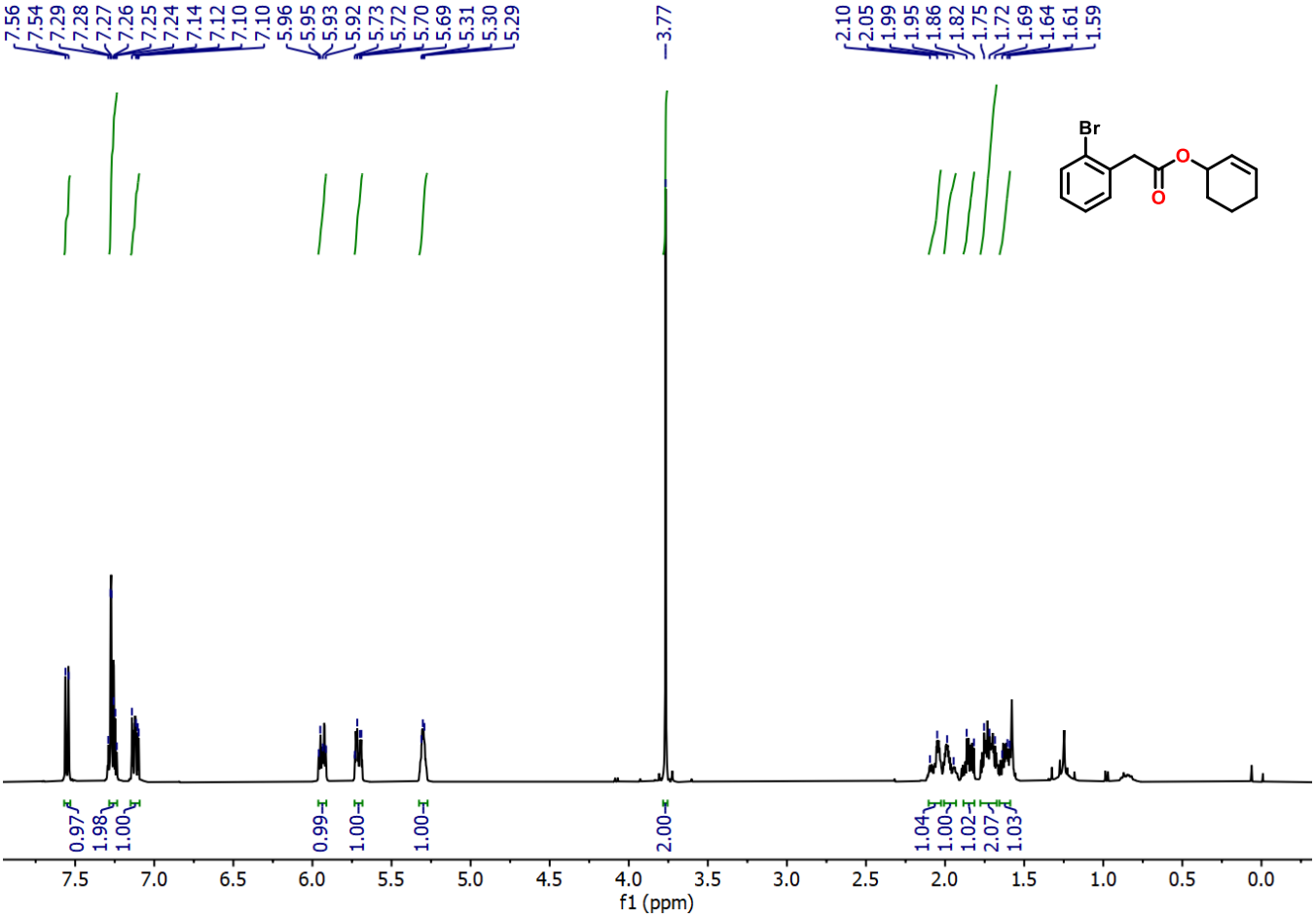

Fig. S48. ^{1}H NMR spectra of compound **6b**

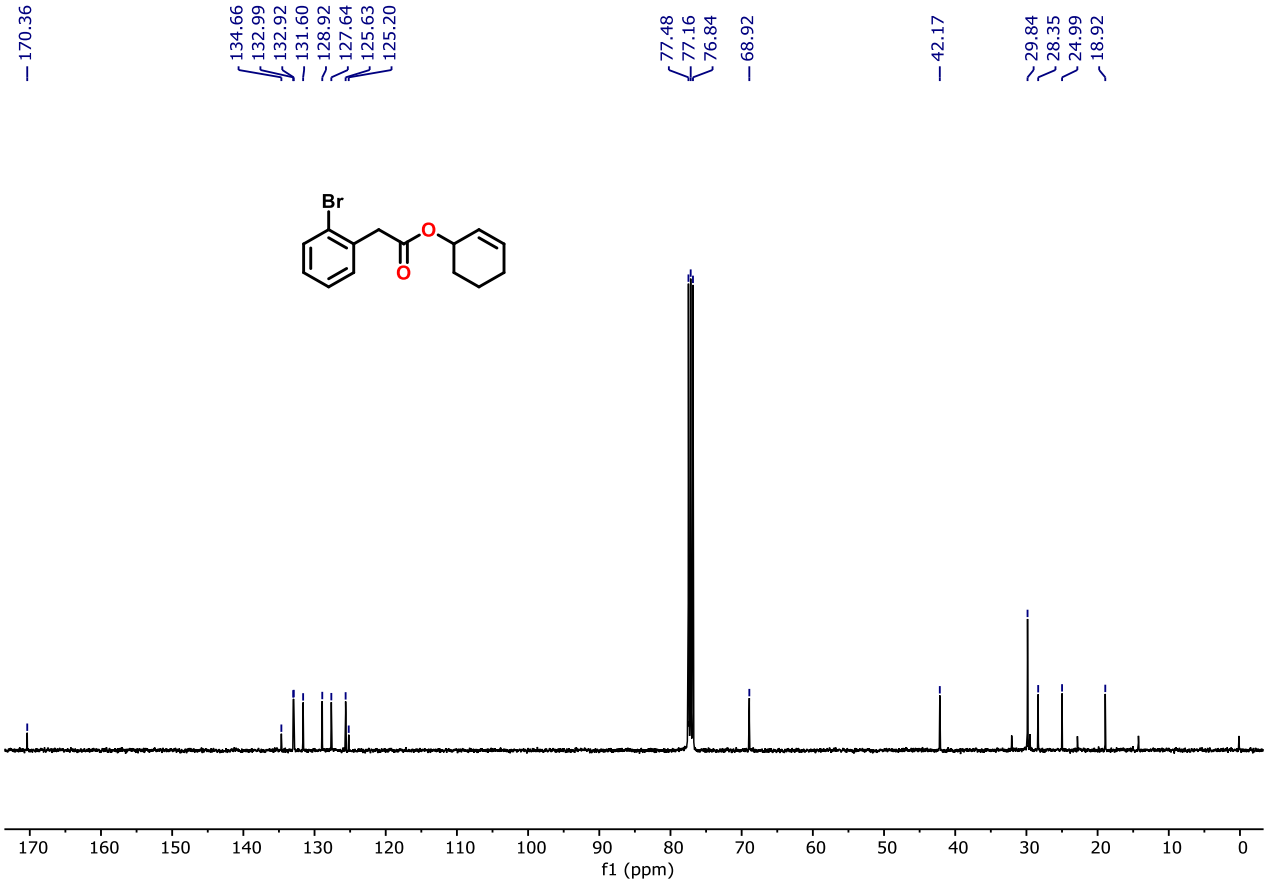

Fig. S49. ^{13}C NMR spectra of compound **6b**

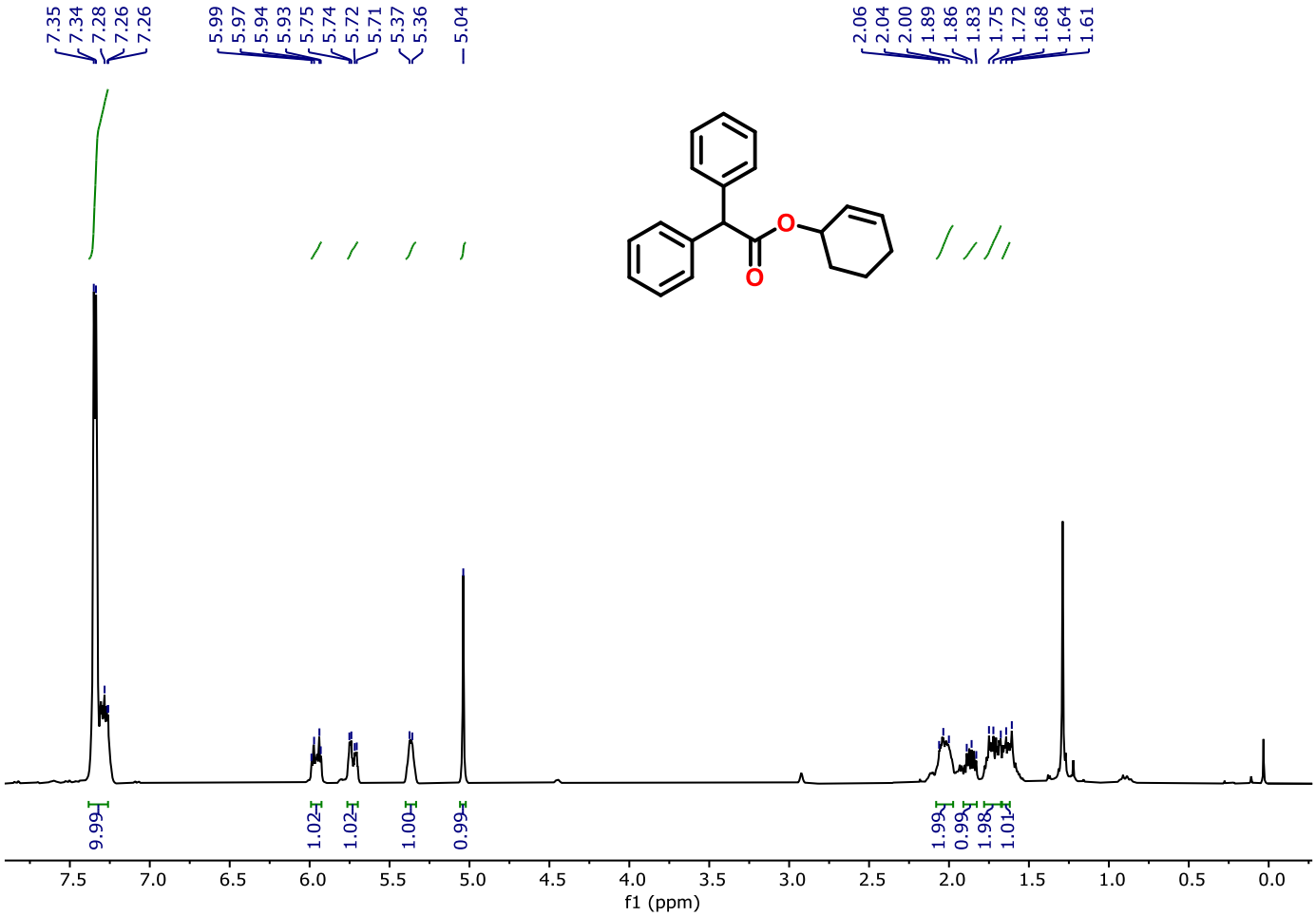

Fig. S50. ^{1}H NMR spectra of compound **6c**

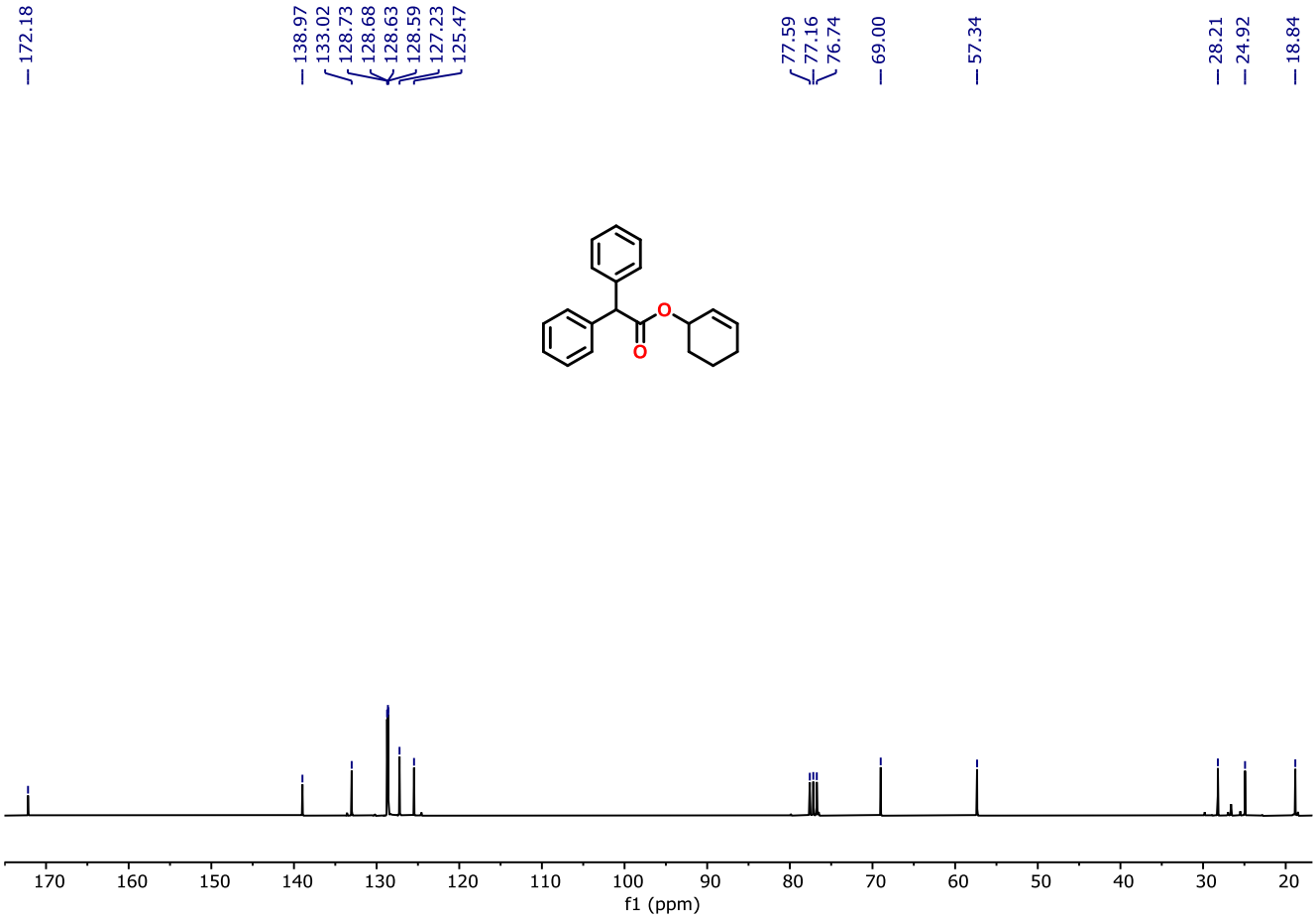

Fig. S51. ^{13}C NMR spectra of compound **6c**

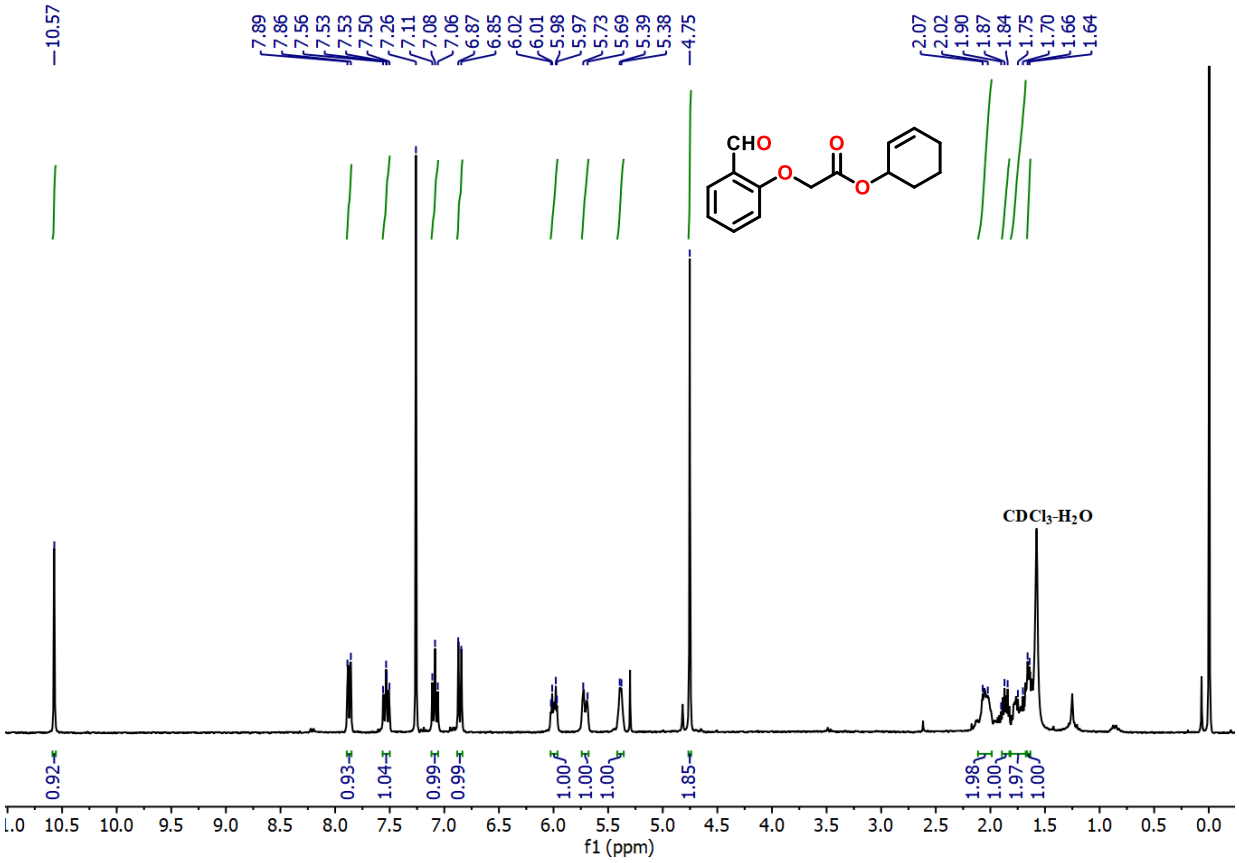

Fig. S52. ^{1}H NMR spectra of compound **6d**

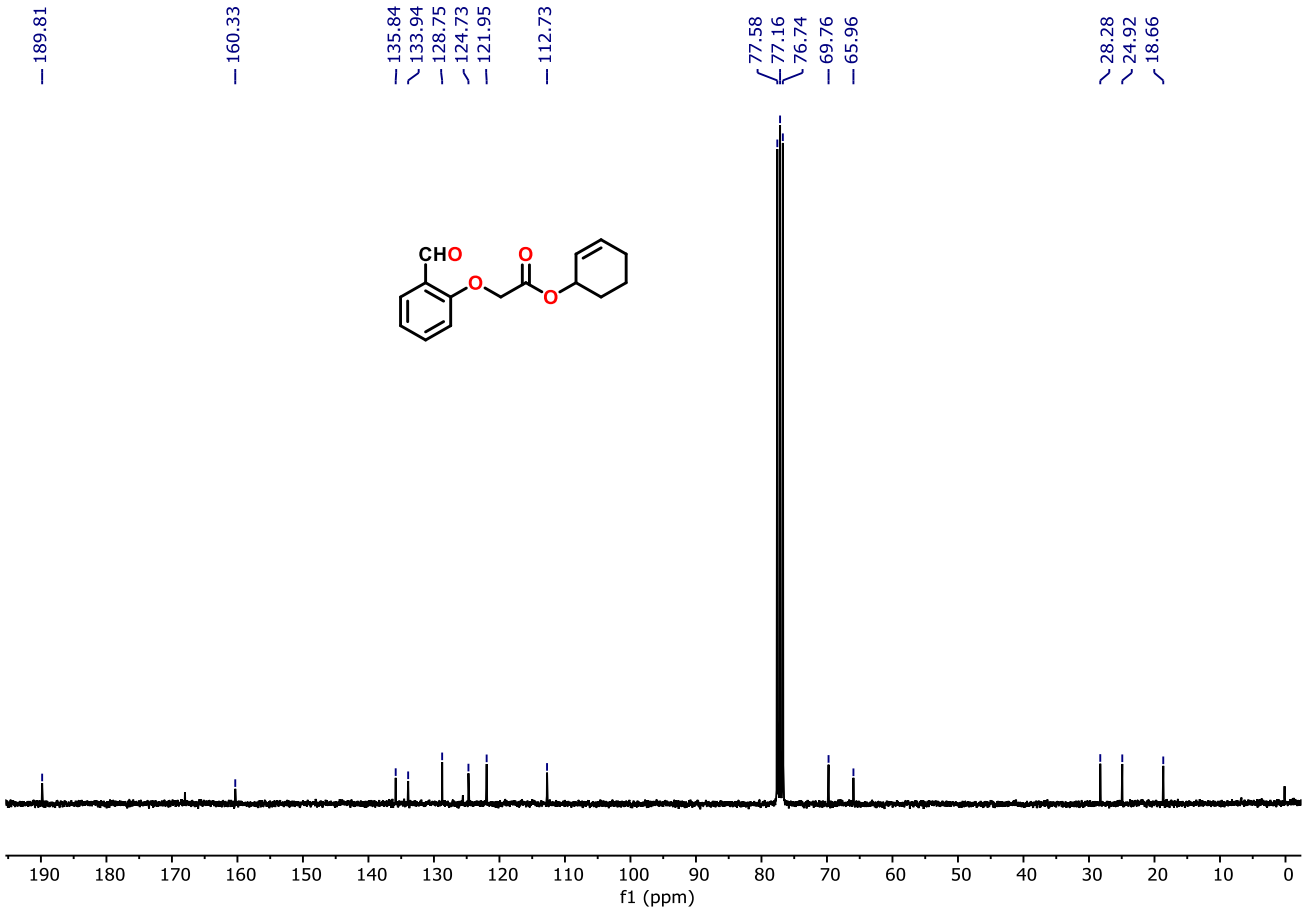

Fig. S53. ^{13}C NMR spectra of compound **6d**

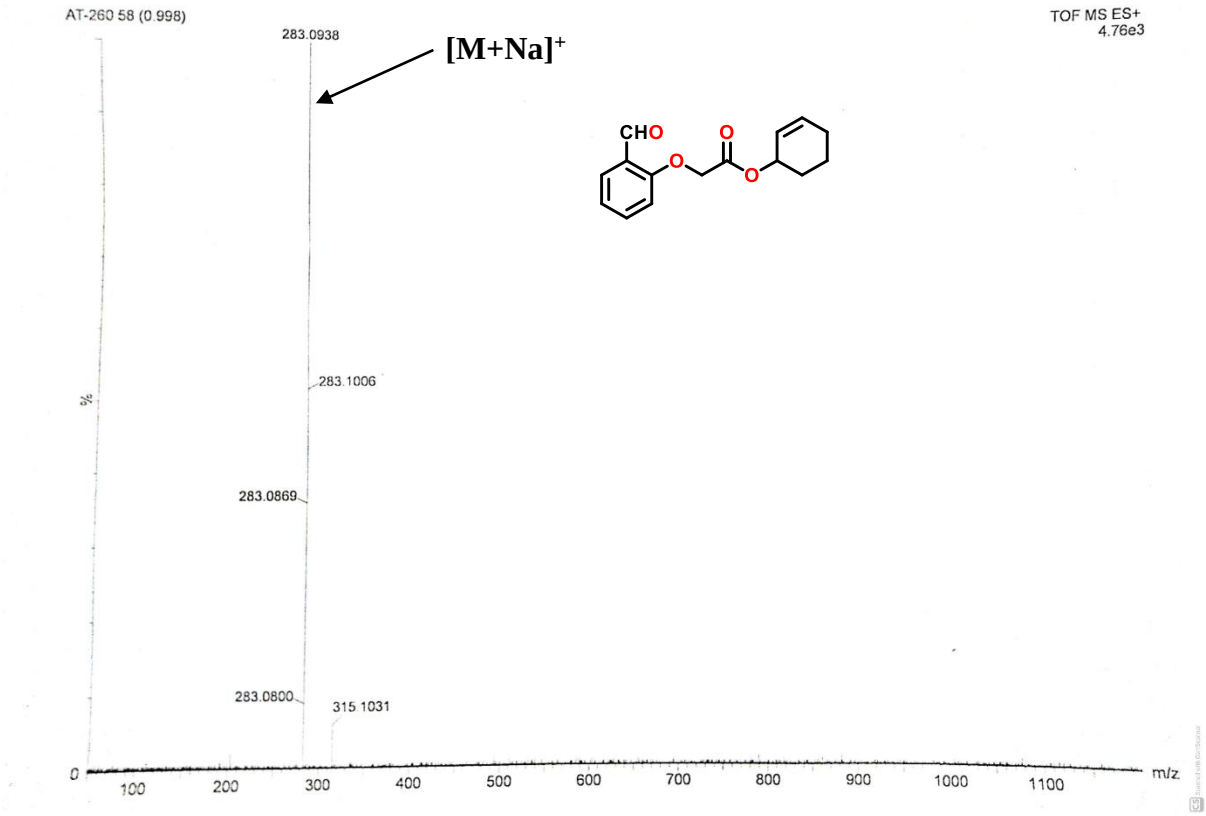

Fig. S54. HRMS spectra of compound **6d**

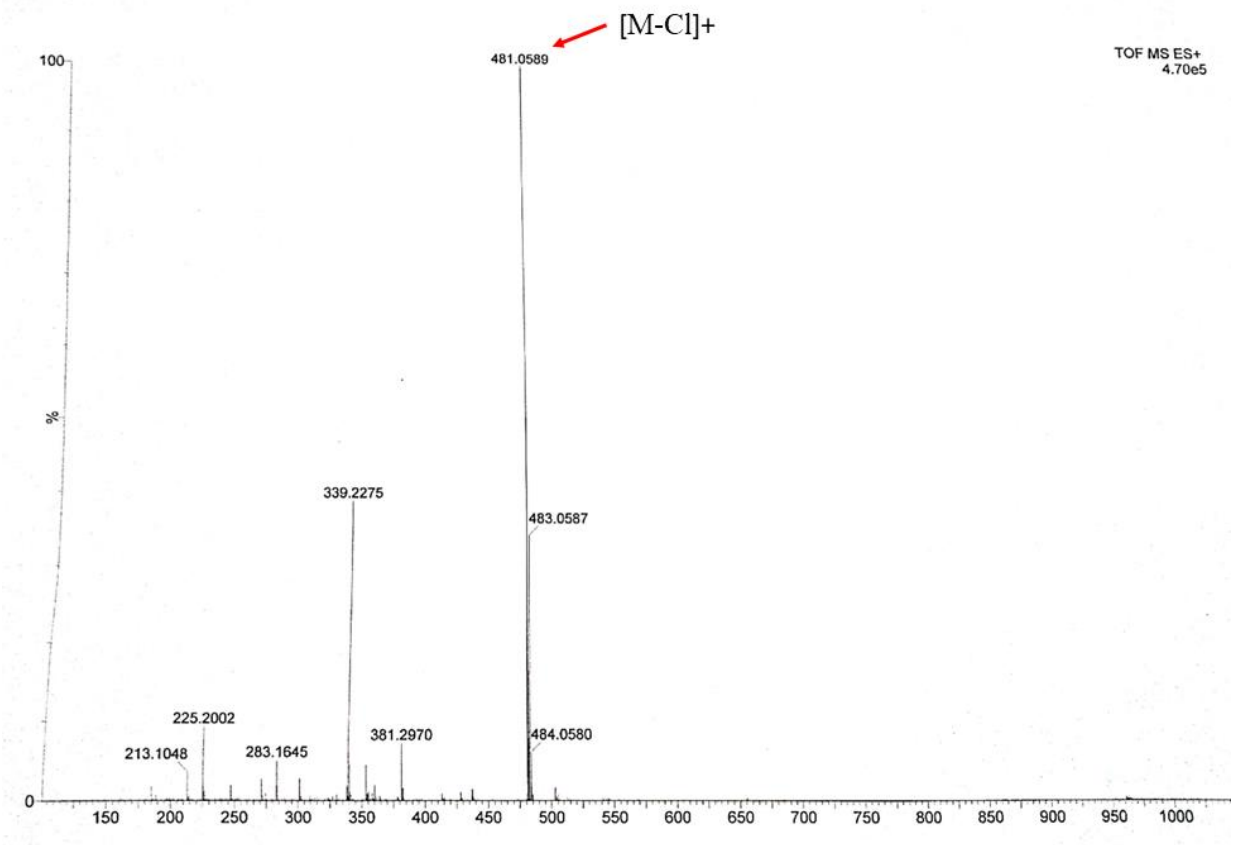

Fig. S55. HRMS of copper complex **1**

Table S2: Crystallographic details of complex **1**

Empirical formula	$C_{25}H_{13}ClN_5O_2$
Formula weight	517.42
Crystal size (mm)	0.2 X 0.2 X 0.1
Crystal system	triclinic
Space group	P -1
a [Å]	a=8.1305(7)
b [Å]	b=9.2545(8)
c [Å]	c=14.7289(13)
α [°]	96.831(3)
β [°]	98.583(3)
γ [°]	104.865(3)
volume [Å^3]	1044.74(16)
Z	2
F(000)	526.0
μ MoK$_\alpha$ [mm^{-1}]	1.21
Temperature [K]	273(2)
R_{int}	0.0589
Range of h, k, l	–10/10, –12/12, –19/14
$\theta_{min/max}$ (°)	2.308/28.358
GOF on F^2	1.133
Final R indices [I > 2σ(I)]	$R1$ = 0.0785 $wR2$ = 0.2316
R indices [all data]	$R1$ = 0.0828 $wR2$ = 0.2338

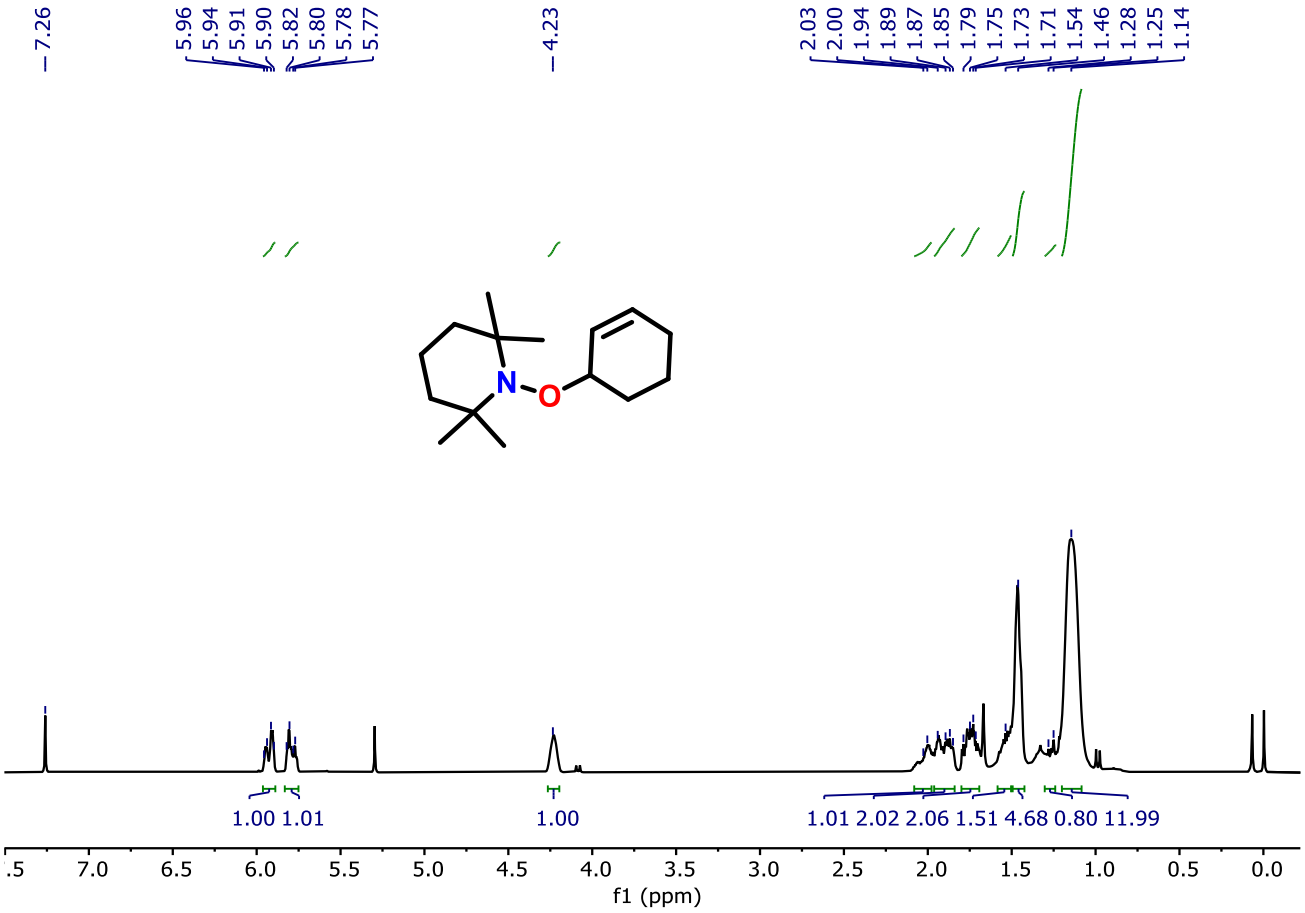

Fig. S56. ^{1}H NMR spectra of the TEMPO-based alkoxyamine compound 1-(cyclohex-2-en-1-yloxy)-2,2,6,6-tetramethylpiperidine.

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