Supplementary information for:

C(sp^3)–H Cyclizations of 2-(2-Vinyl)phenoxy-*tert*-anilines

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MW-assisted isomerization – optimization studies

1) Solvent screen

5 mg **14b** was dissolved in 0.5 mL solvent in a 10 mL MW vial. The solution was heated in a MW reactor for the indicated time points. At each time point 0.1 mL sample was taken, the solvent was distilled off and the residue was dissolved in 0.5 mL DMSO-d_6 for recording the ^{1}H NMR.

2) Concentration screen

5 or 50 mg **14b** was dissolved in 0.5 mL DMSO-d_6 in a 10 mL MW vial. The solution was heated in a MW reactor for the indicated time points. At each time point ^{1}H NMR was recorded.

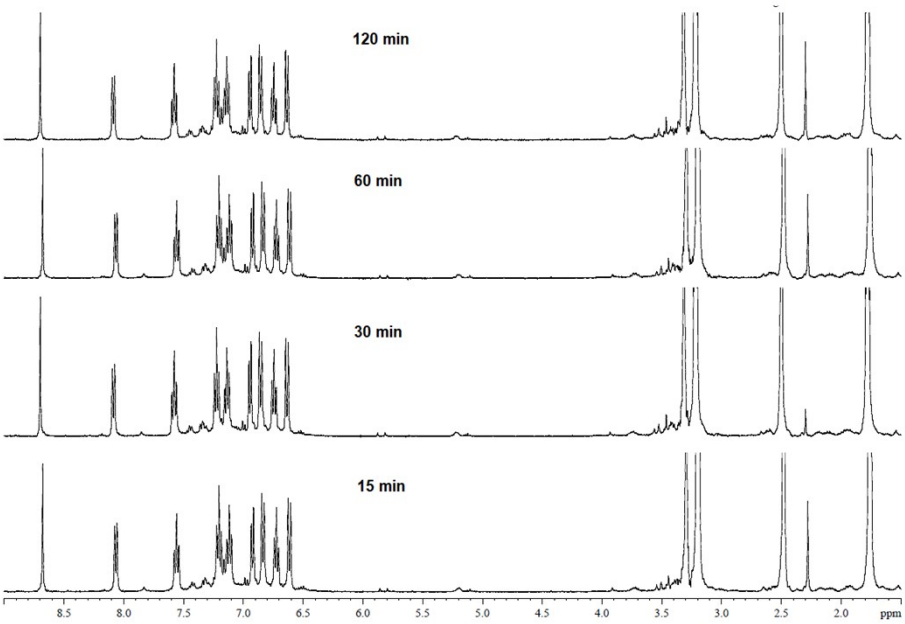


Figure S1. ^{1}H NMR monitoring of the cyclization in toluene.

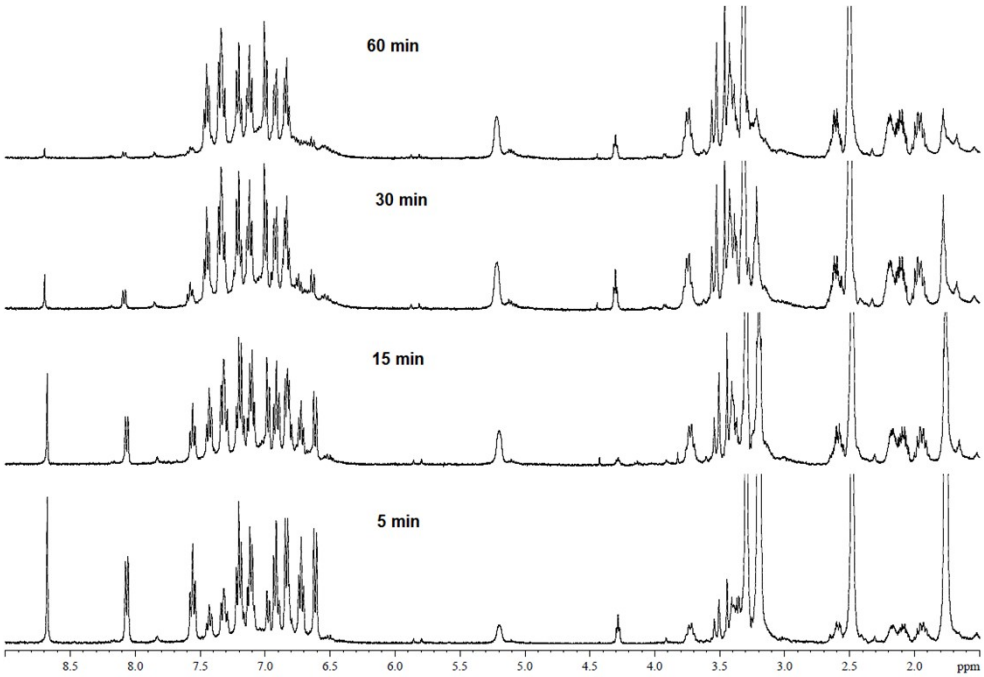


Figure S2. ^{1}H NMR monitoring of the cyclization in *n*-BuOH.

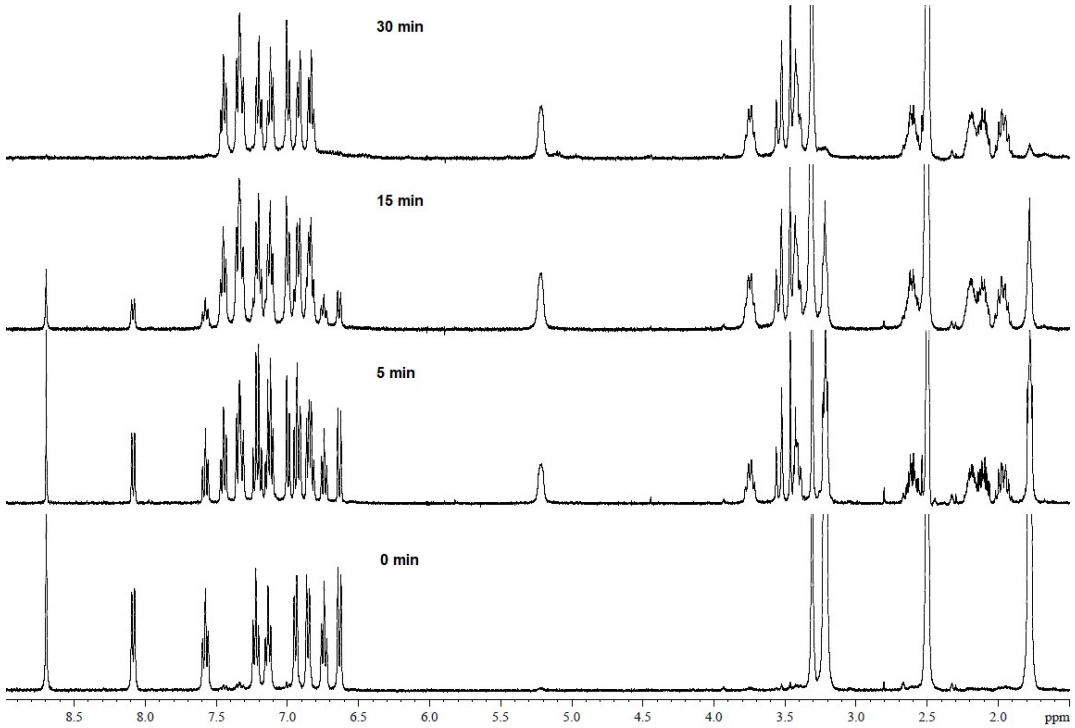


Figure S3. ^{1}H NMR monitoring of the cyclization in DMSO-d_6 (5 mg/0.5 mL).

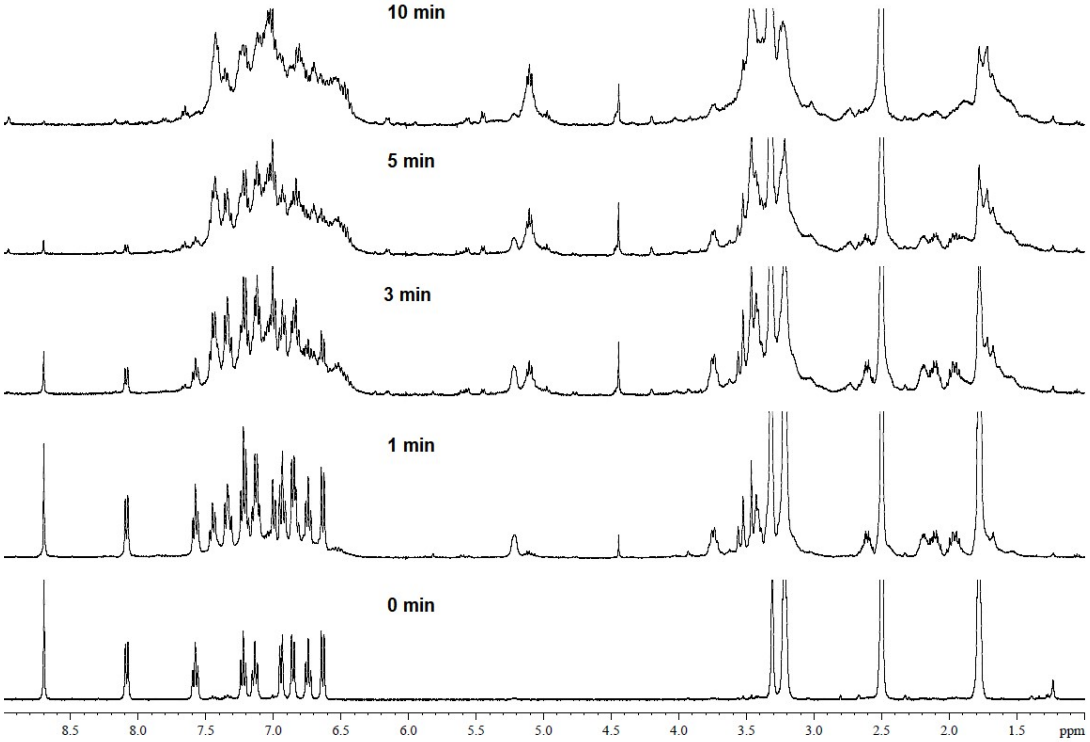
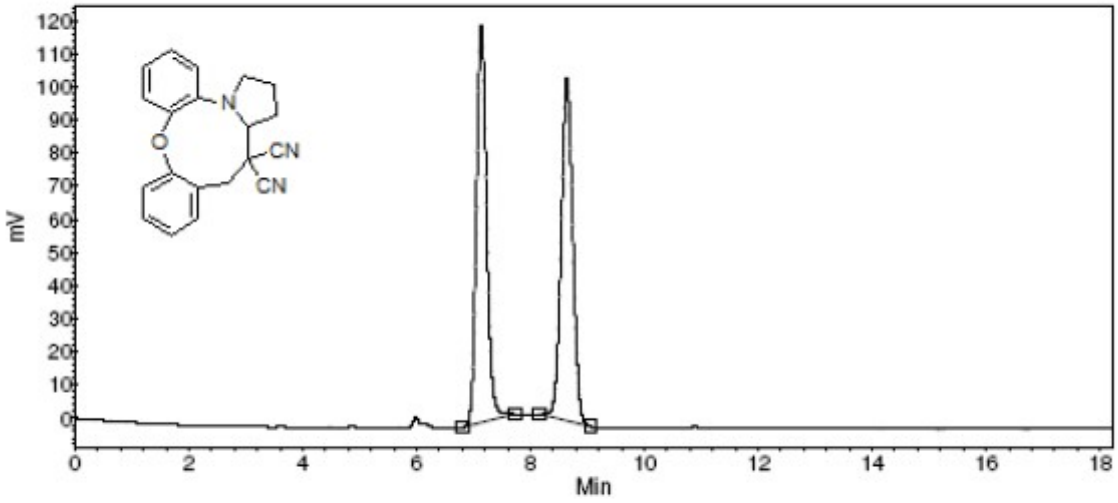


Figure S4. ^{1}H NMR monitoring of the cyclization in DMSO-d_6 (50 mg/0.5 mL).

DETECTION: UV 260 nm
COLUMN: Chiralcel AD 10 um 25 x 0.46
ELUENT: n-Hexane / Etanol 90 : 10

Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
7.135	50.34	119.9	24.8	50.339
9.639	49.66	103.2	24.5	49.661



DETECTION: UV 248 nm
COLUMN: Chiralcel AD 10 um 25 x 0.46
ELUENT: n-Hexane / Etanol 90 : 10

Time [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
6.132	49.57	772.4	125.7	49.570
6.929	50.43	687.3	127.9	50.430

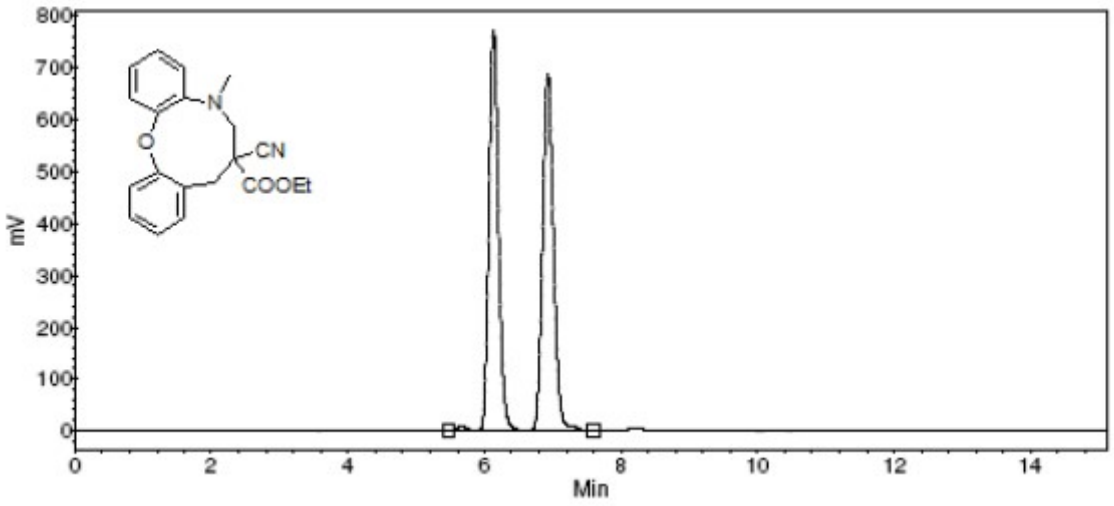
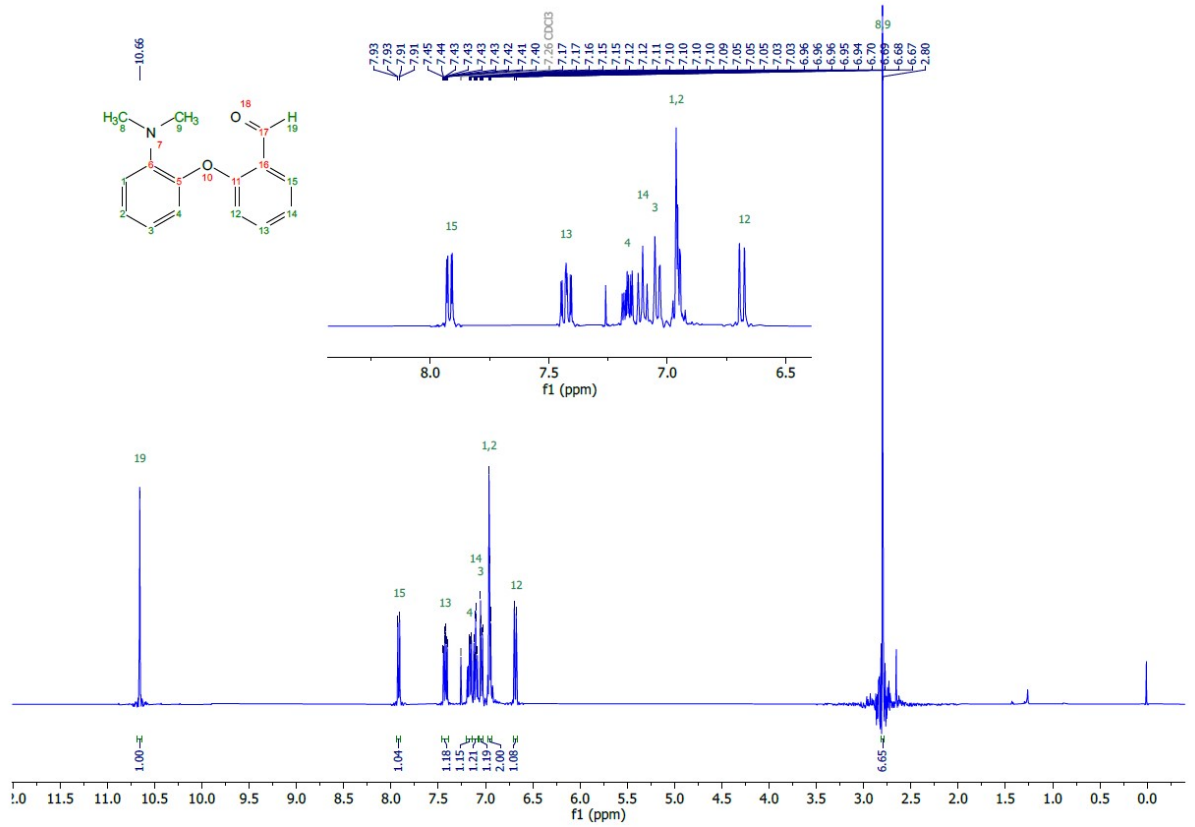
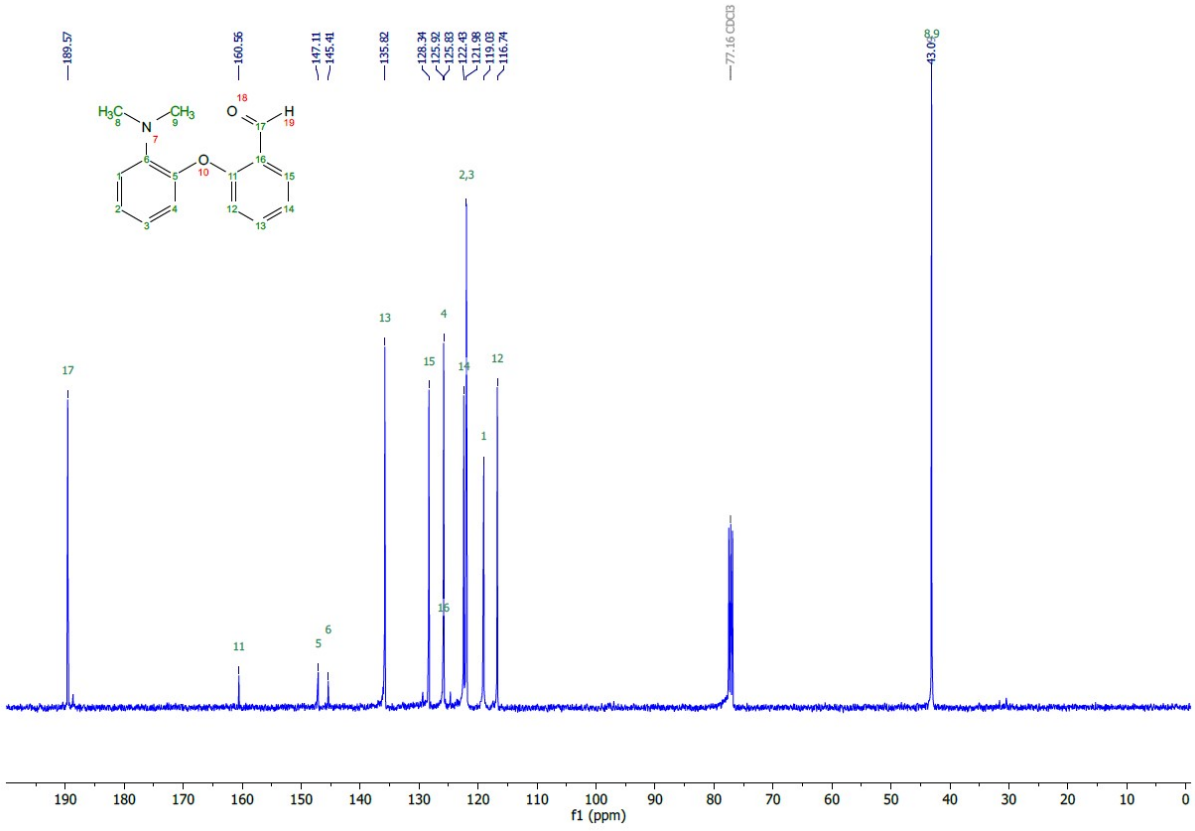


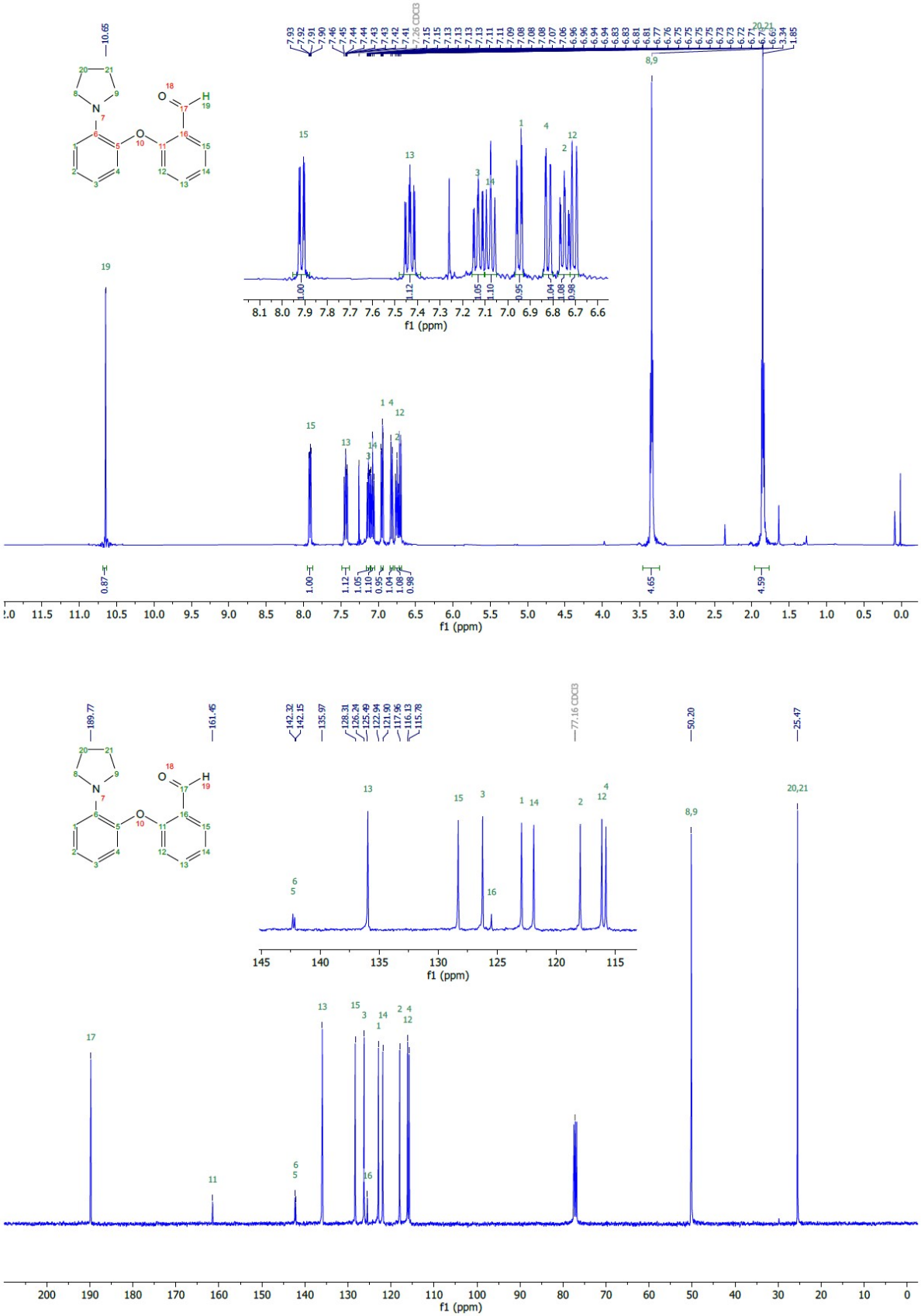
Figure S5. Chiral HPLC chromatogram of **15b** (upper chromatogram) and **15d** (lower chromatogram).

Copies of the ^{1}H and ^{13}C NMR spectra

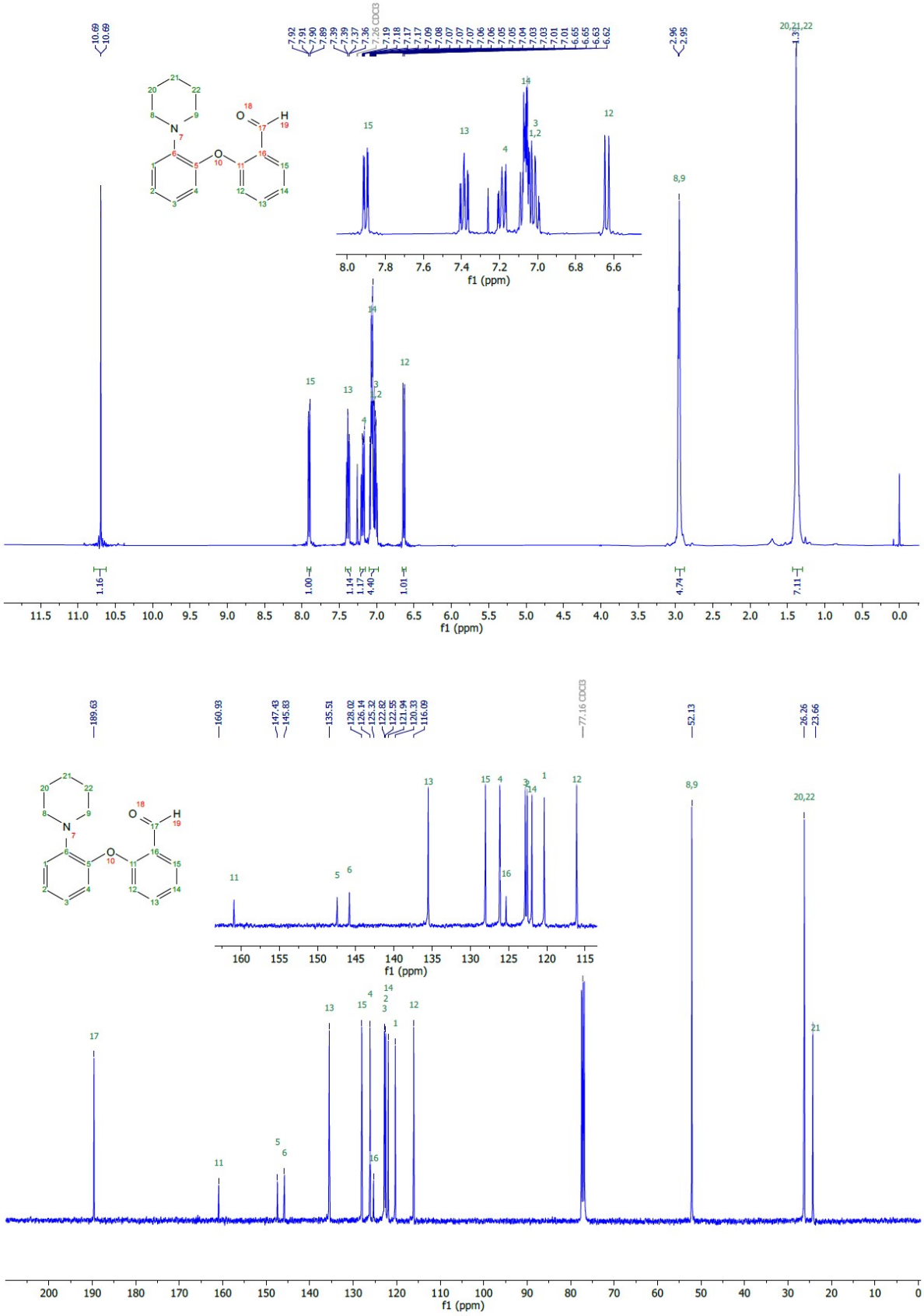




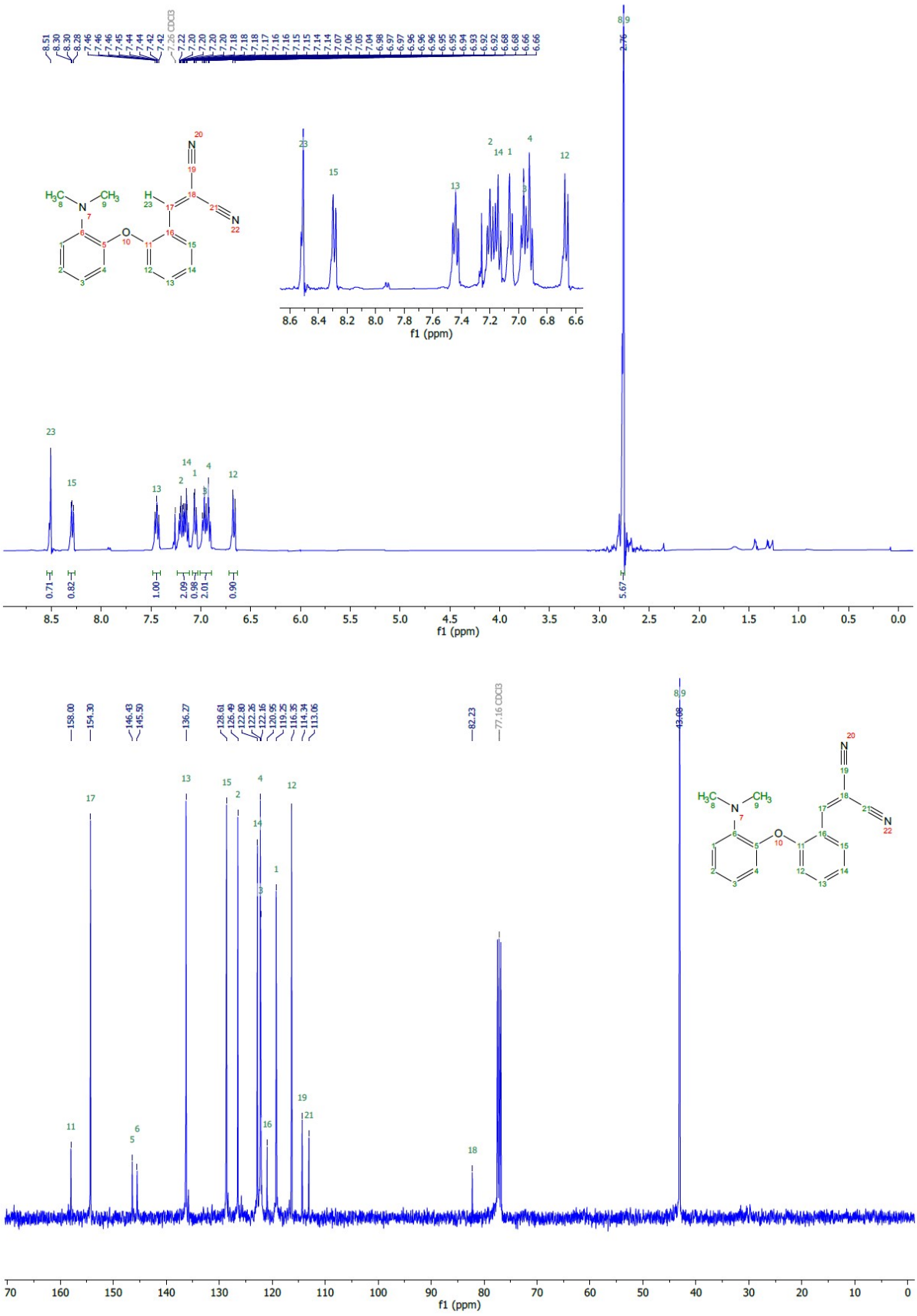
^{1}H and ^{13}C NMR spectrum of **22a**



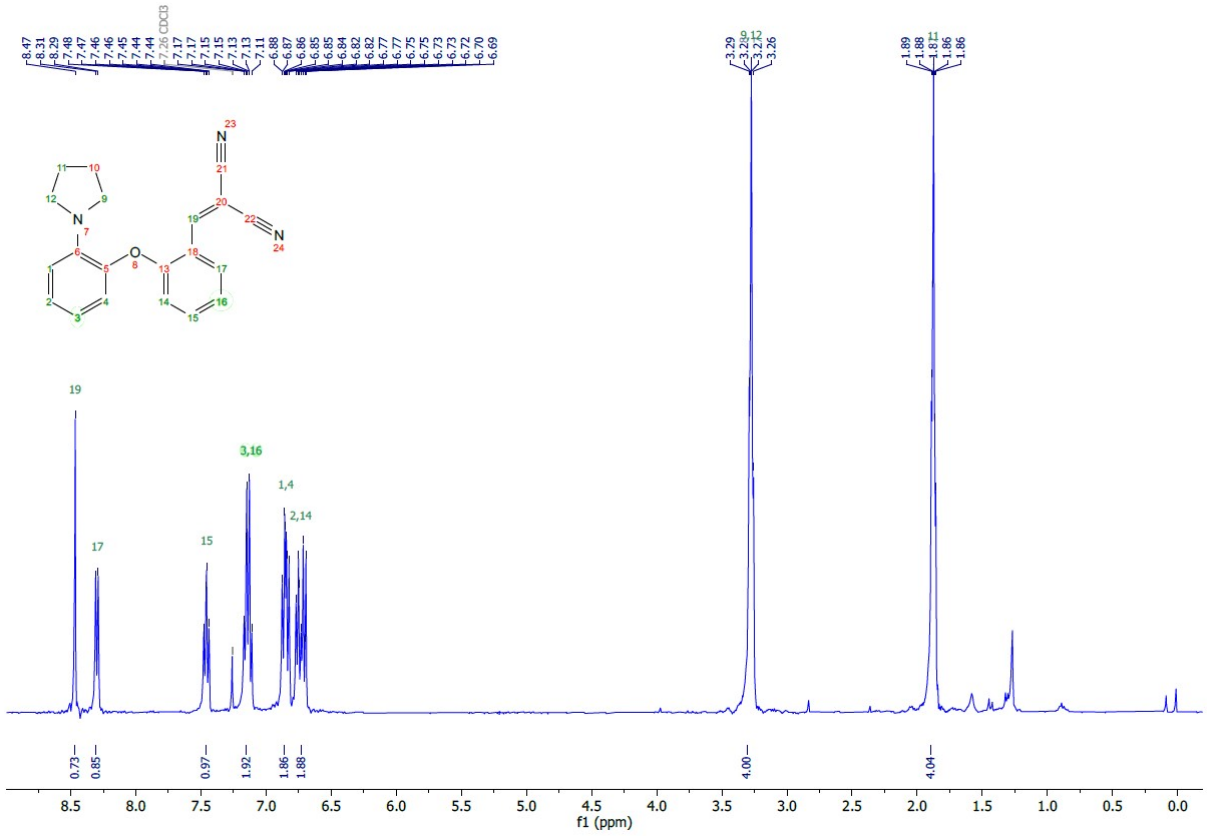
^{1}H and ^{13}C NMR spectrum of **22b**

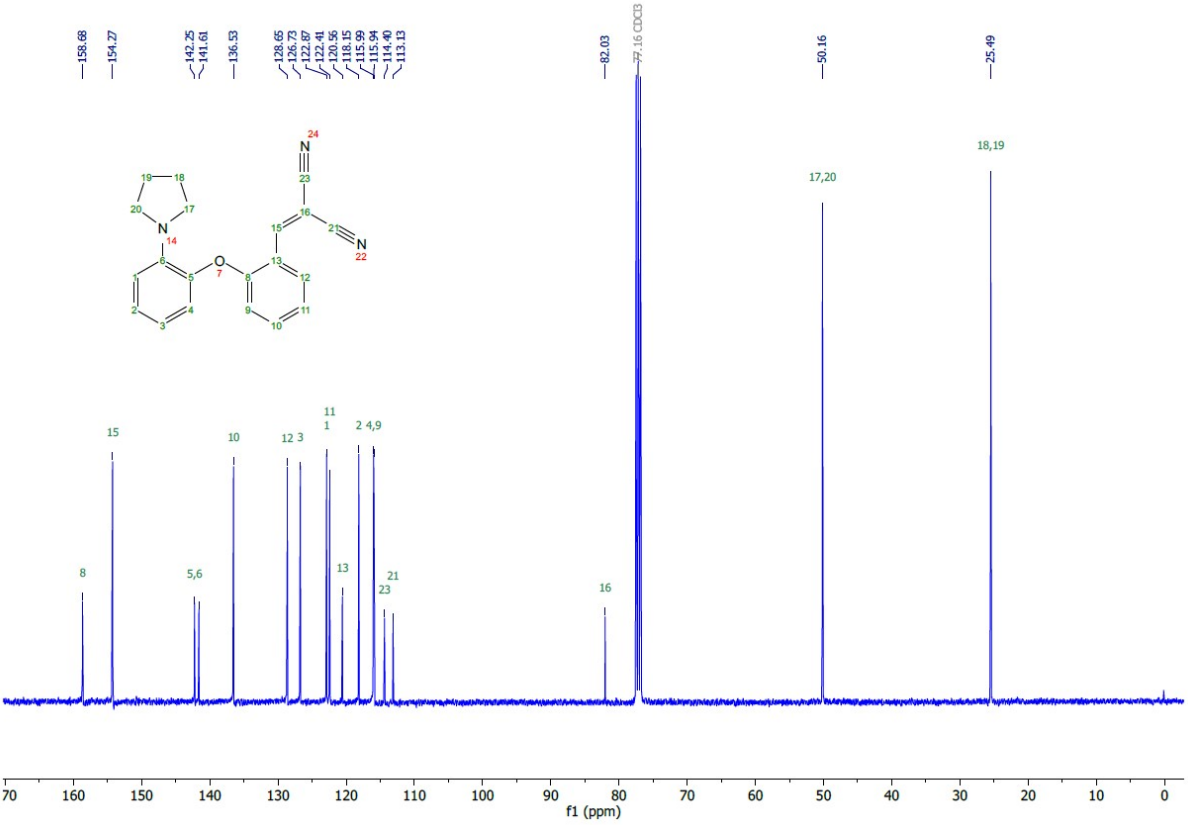


^{1}H and ^{13}C NMR spectrum of **22c**

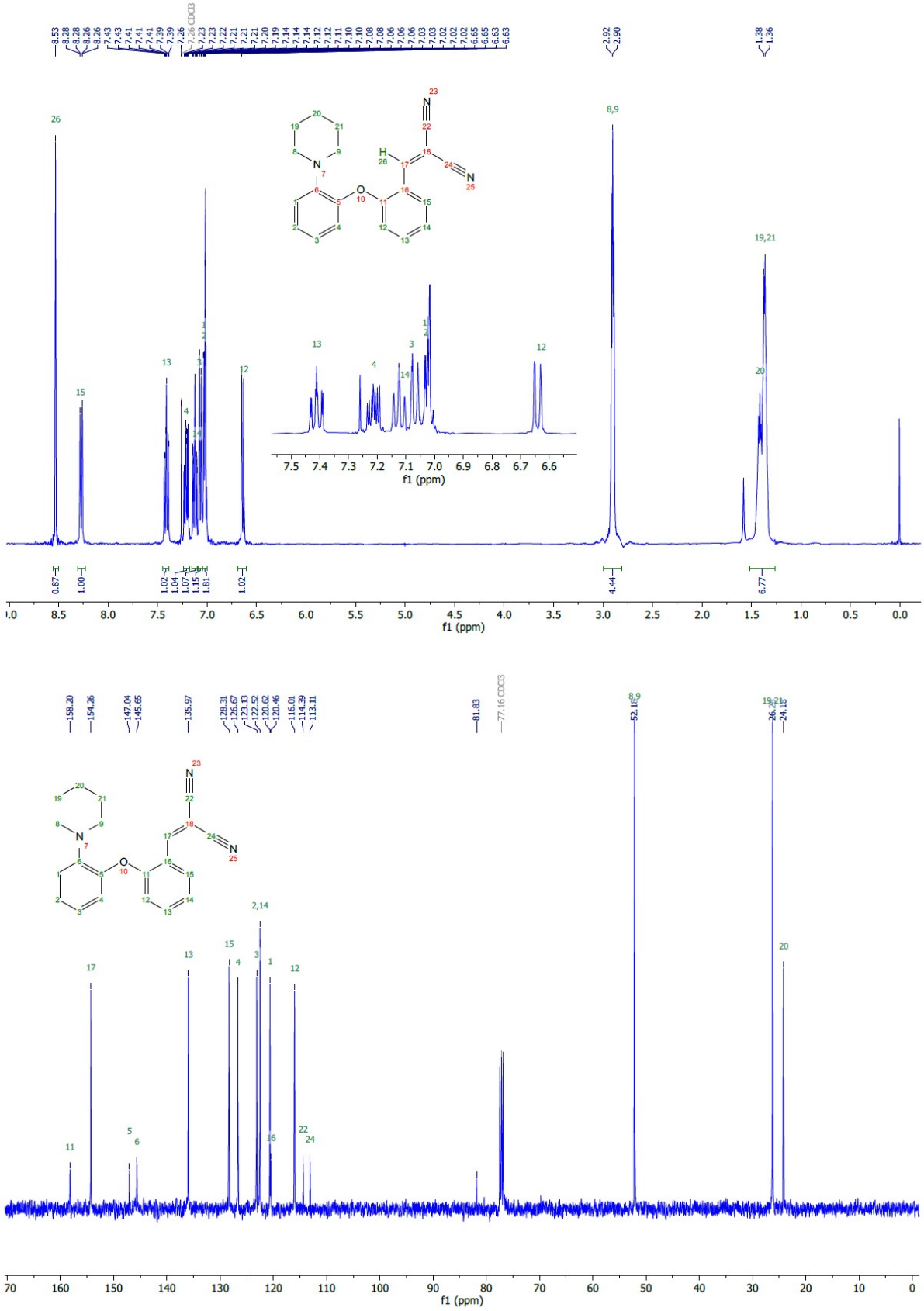


^{1}H and ^{13}C NMR spectrum of **14a**

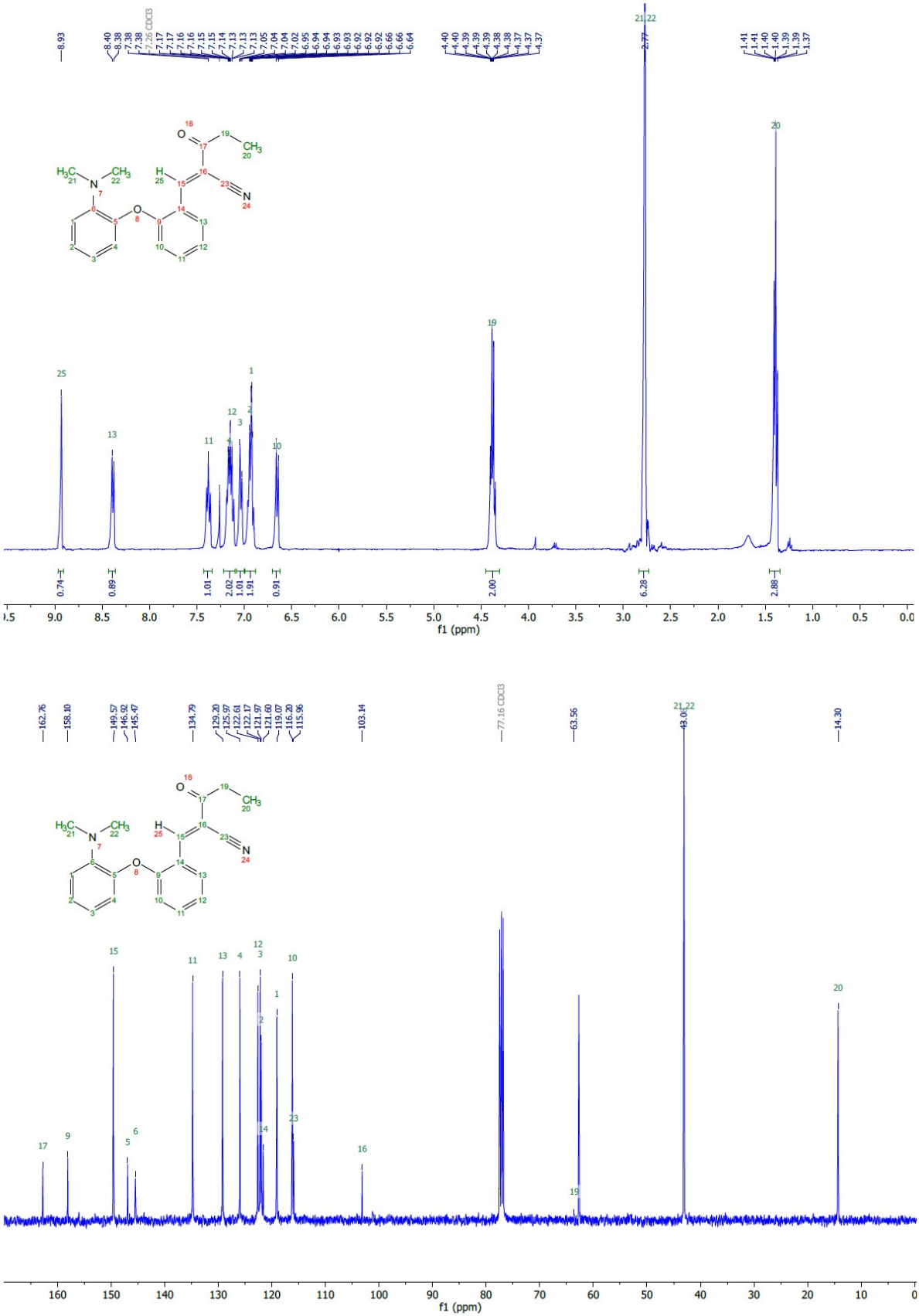




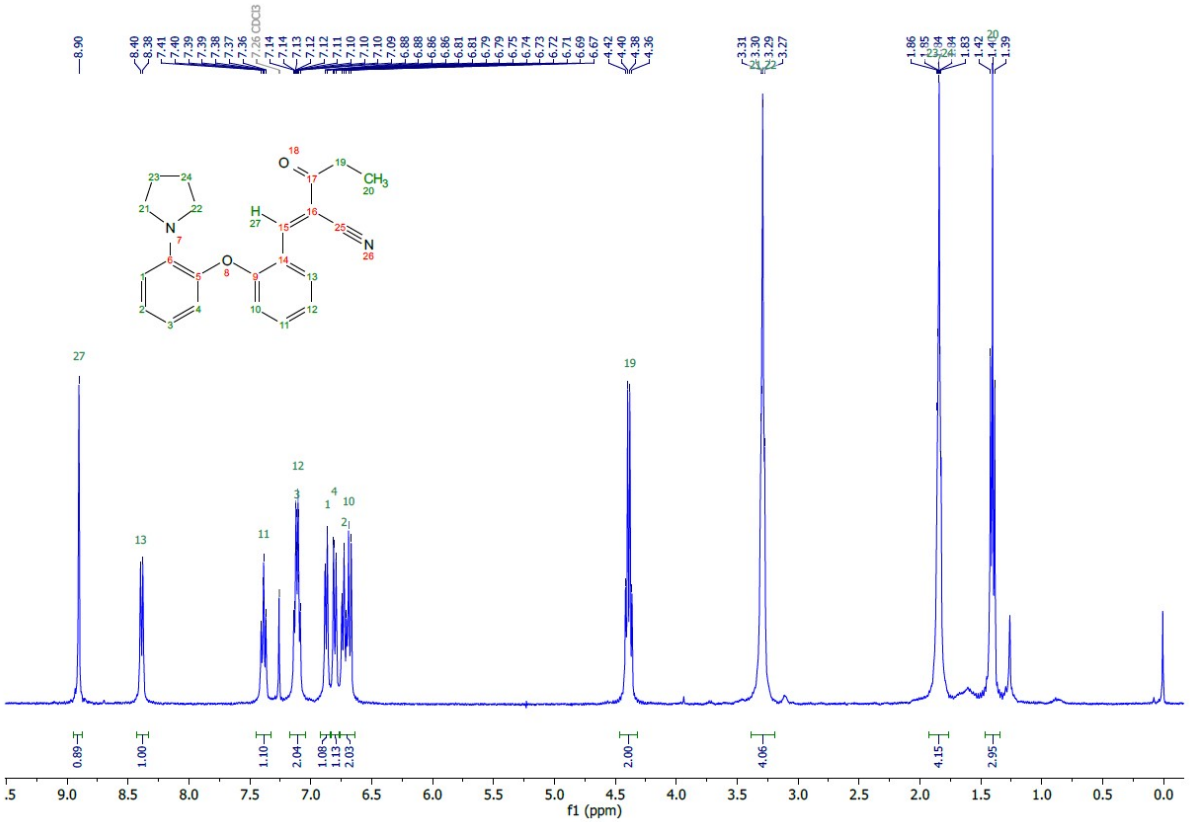
^{1}H and ^{13}C NMR spectrum of **14b**

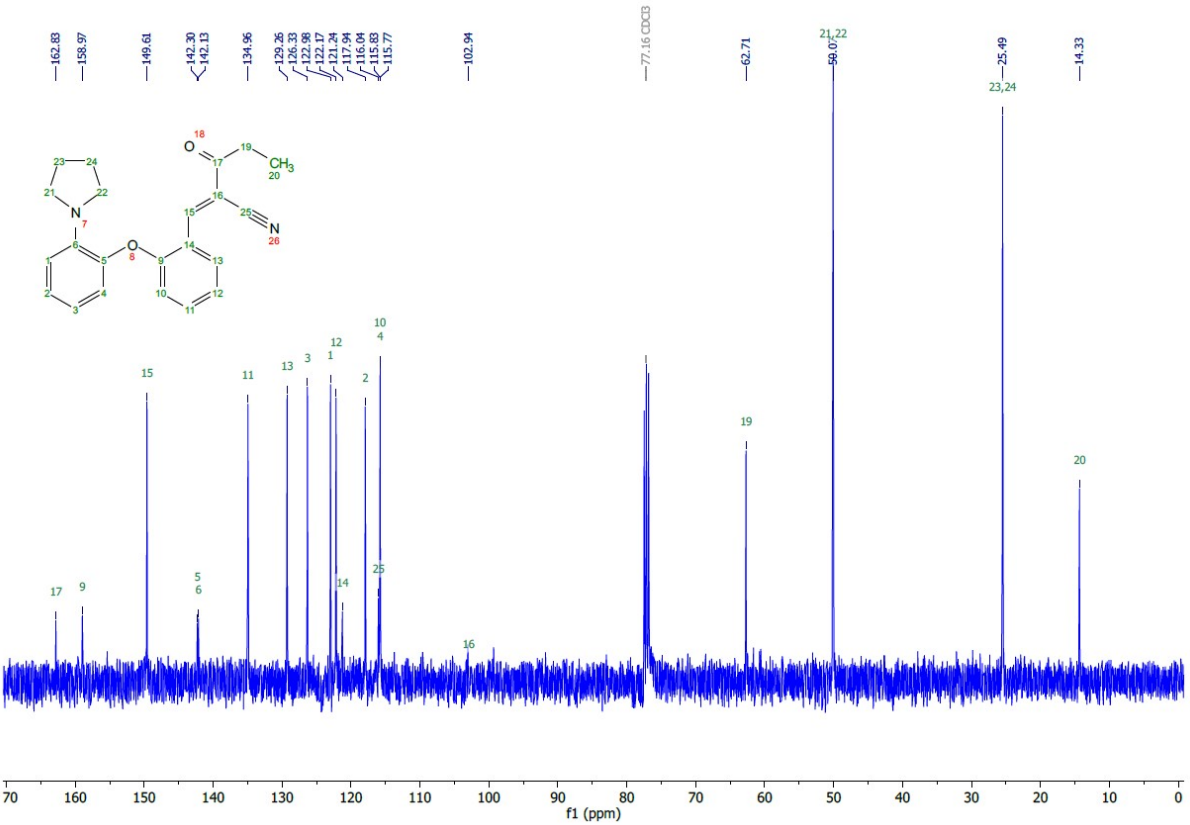


^{1}H and ^{13}C NMR spectrum of **14c**

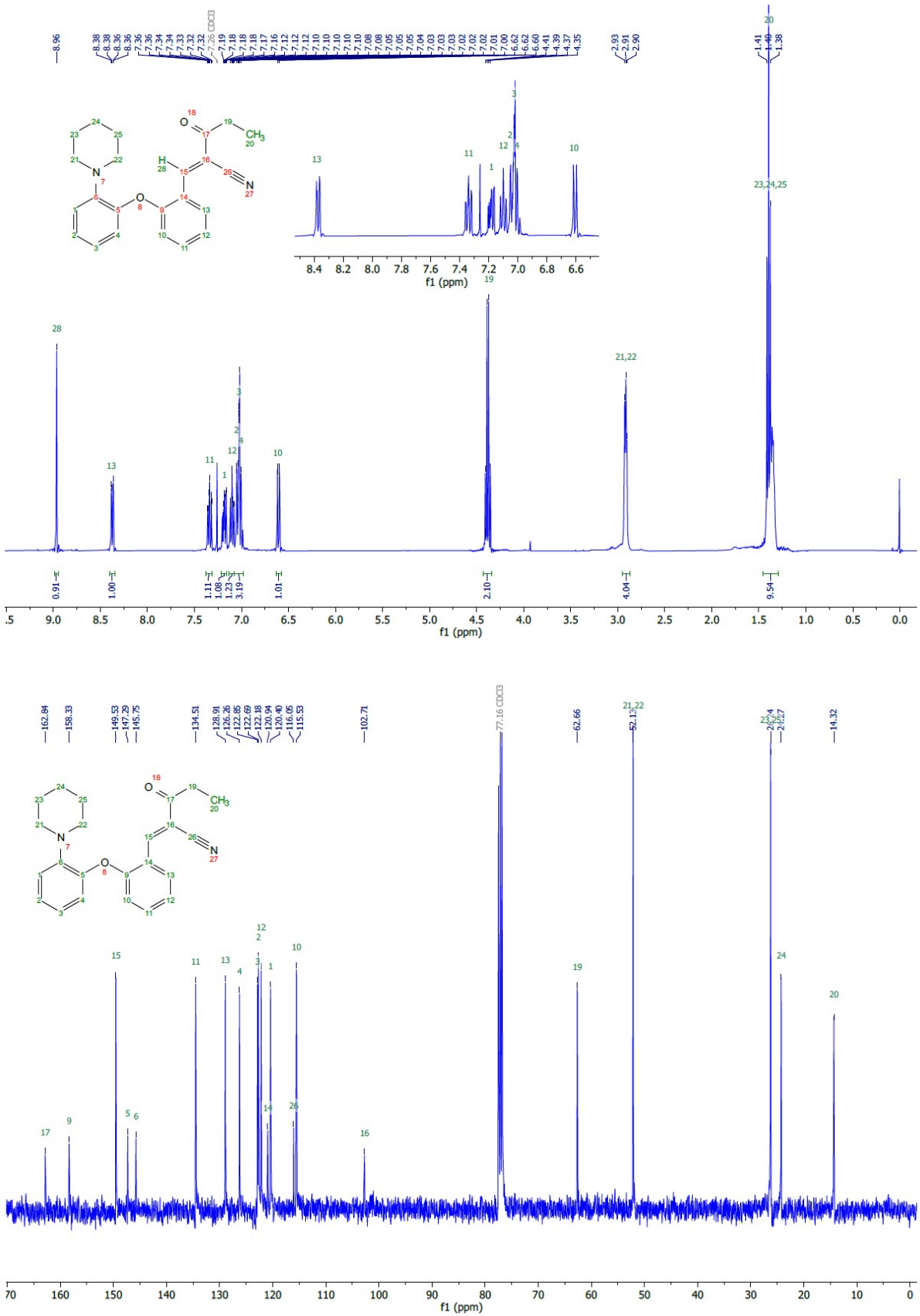


^{1}H and ^{13}C NMR spectrum of **14d**

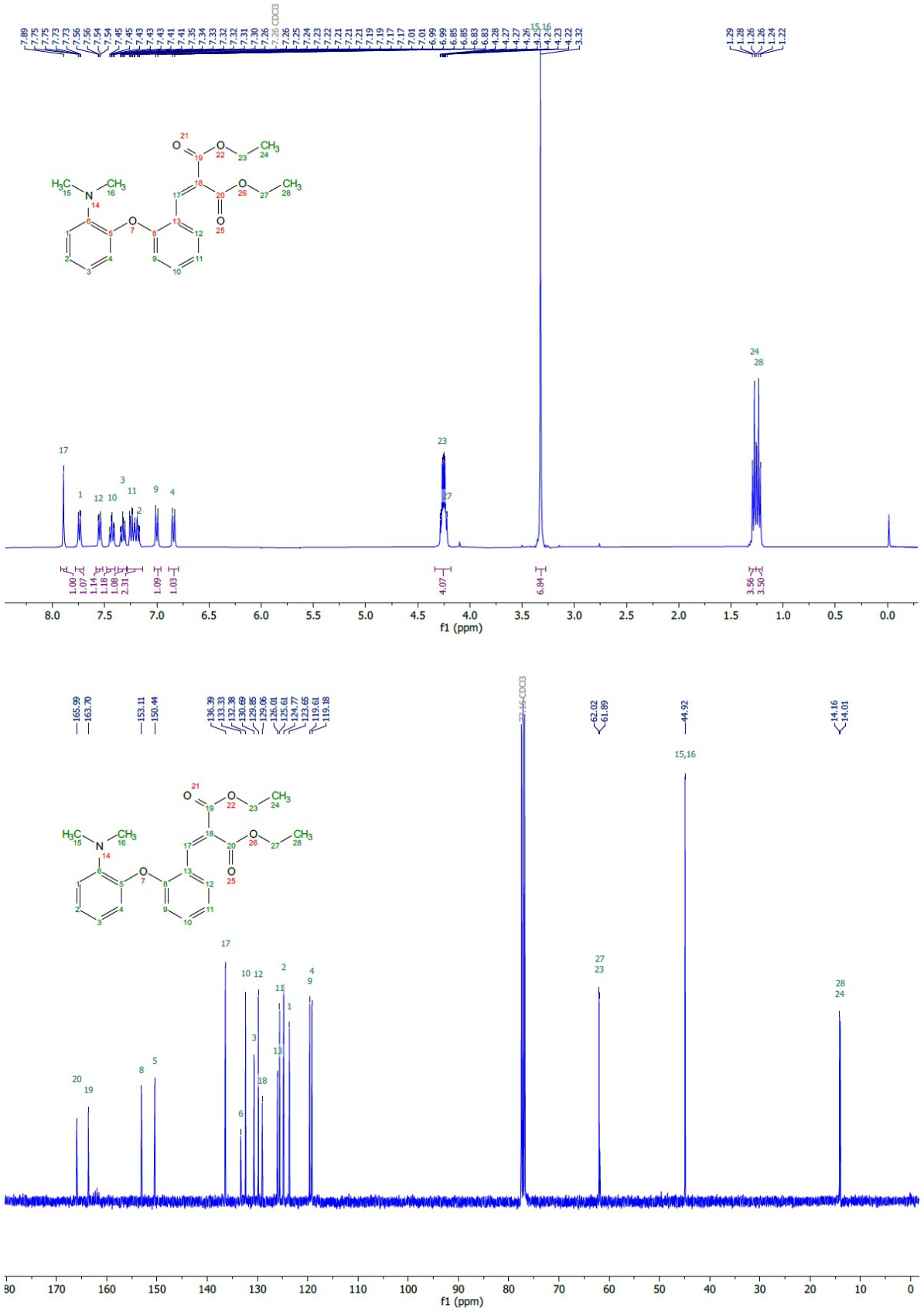




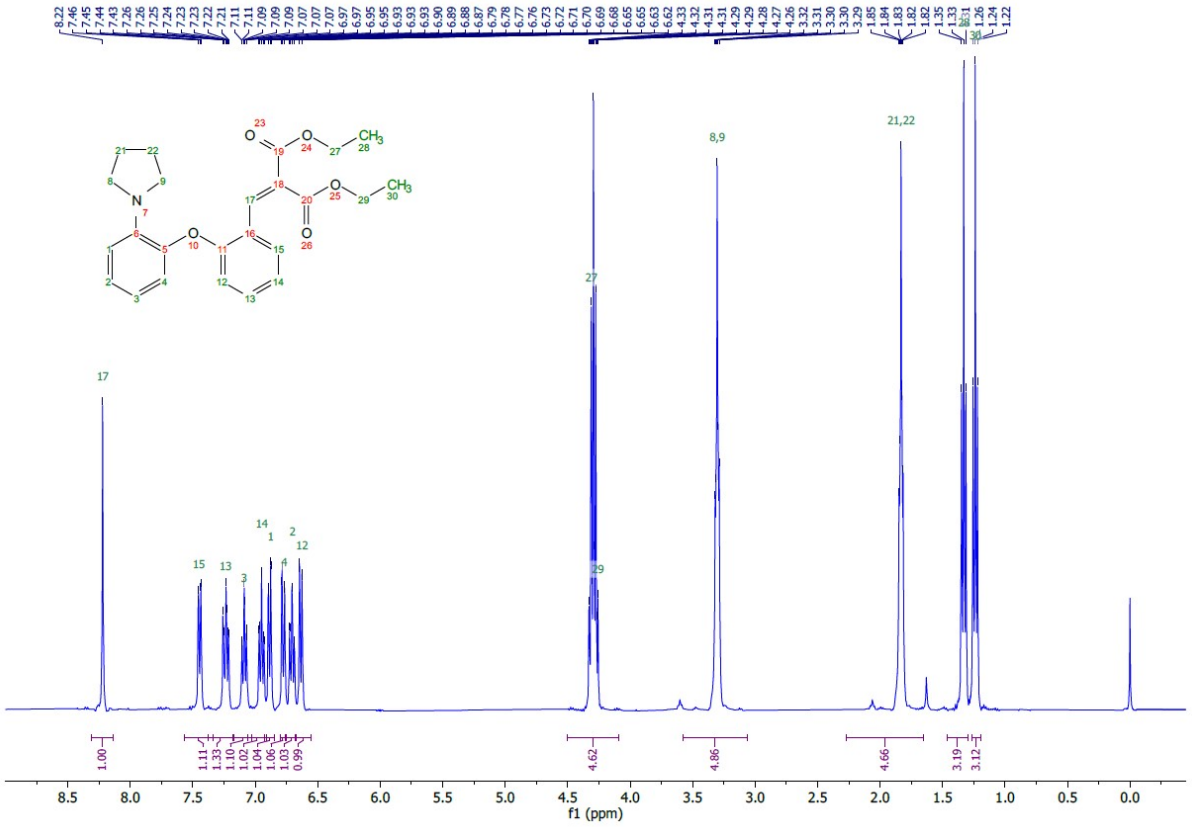
^{1}H and ^{13}C NMR spectrum of **14e**

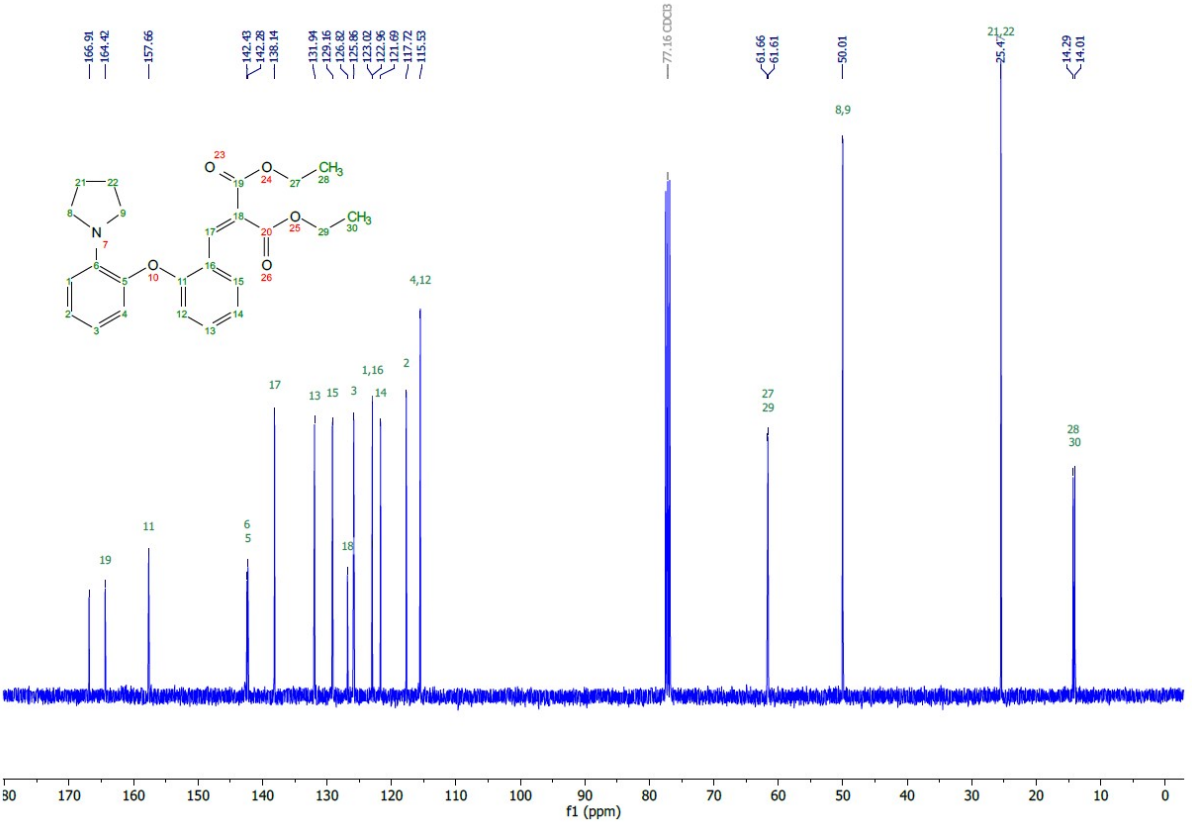


^{1}H and ^{13}C NMR spectrum of **14f**

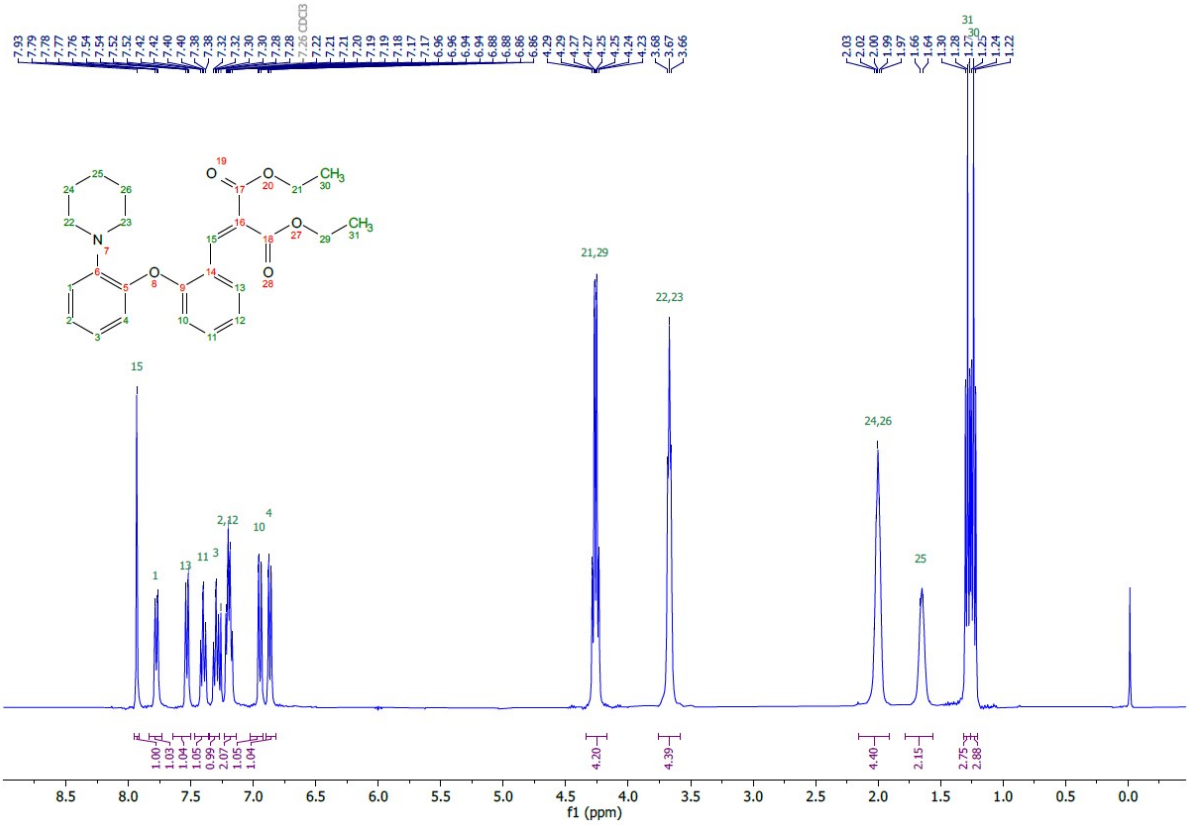


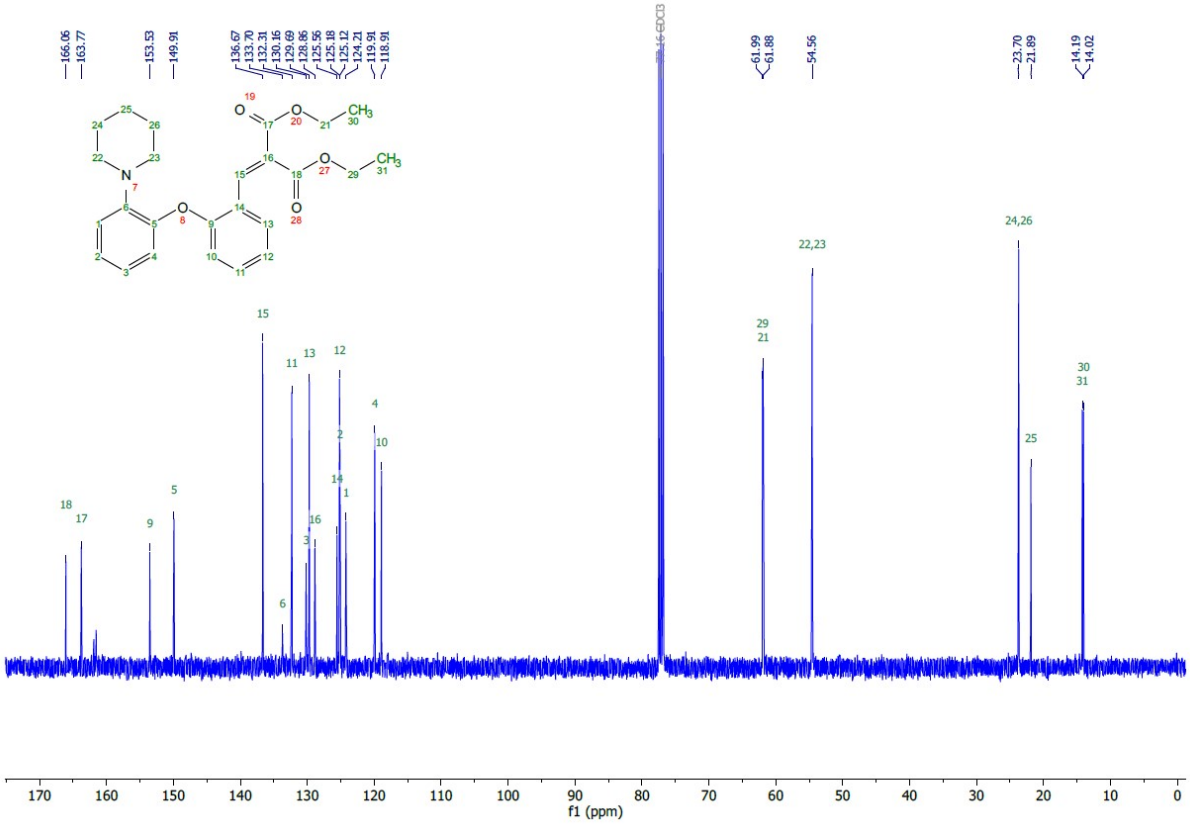
^{1}H and ^{13}C NMR spectrum of **14g**



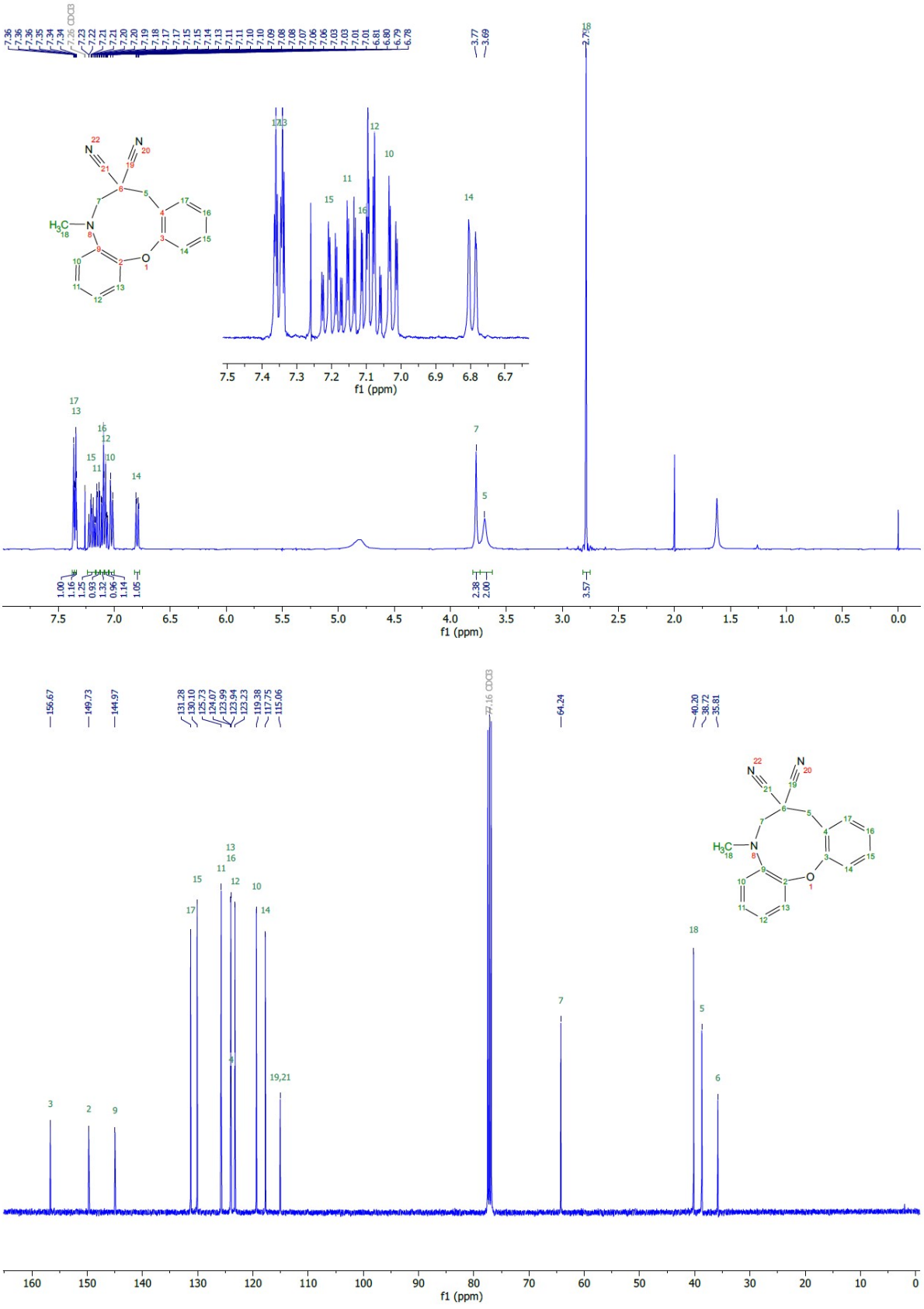


^{1}H and ^{13}C NMR spectrum of **14h**

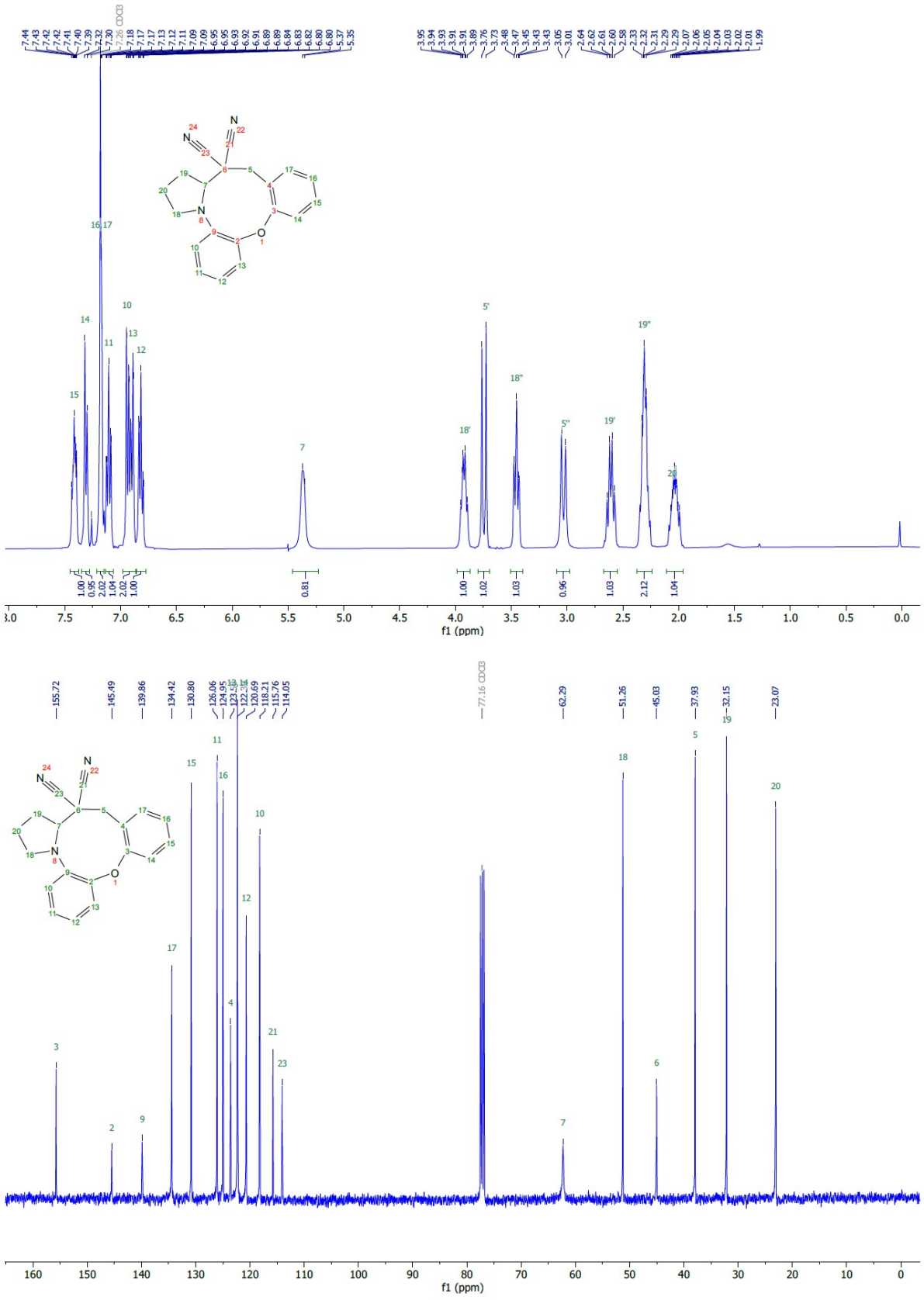




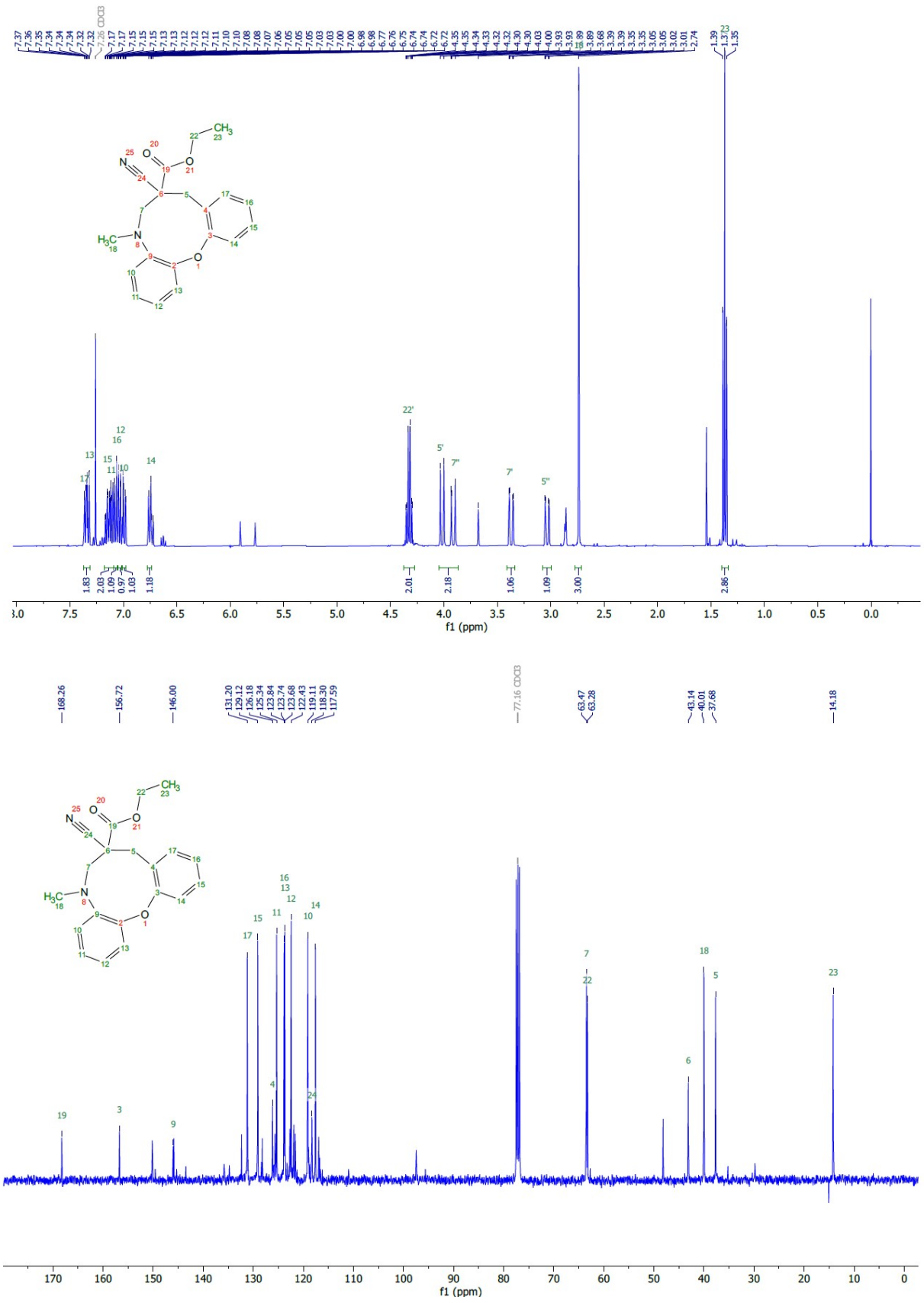
^{1}H and ^{13}C NMR spectrum of **14i**



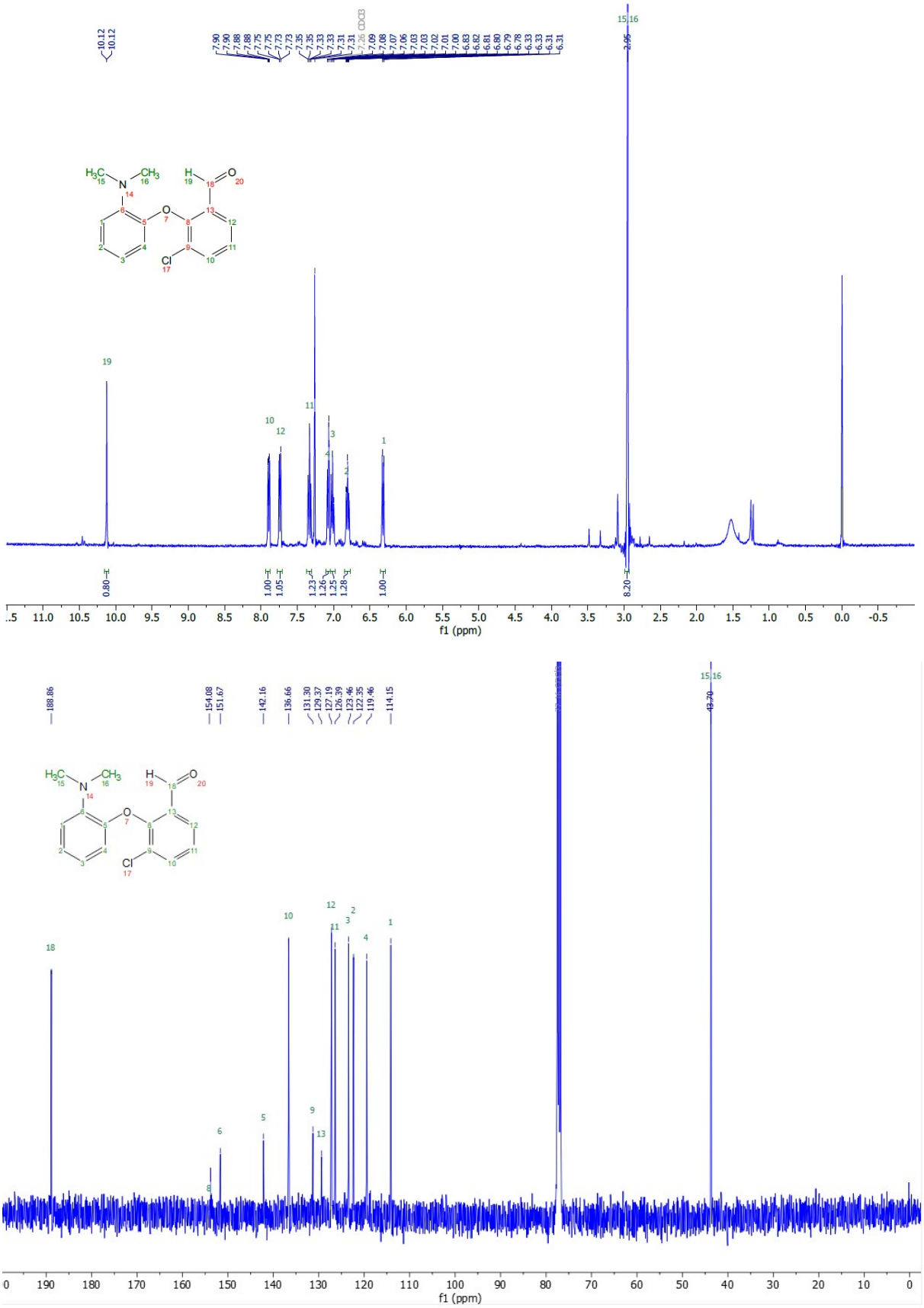
^{1}H and ^{13}C NMR spectrum of **15a**



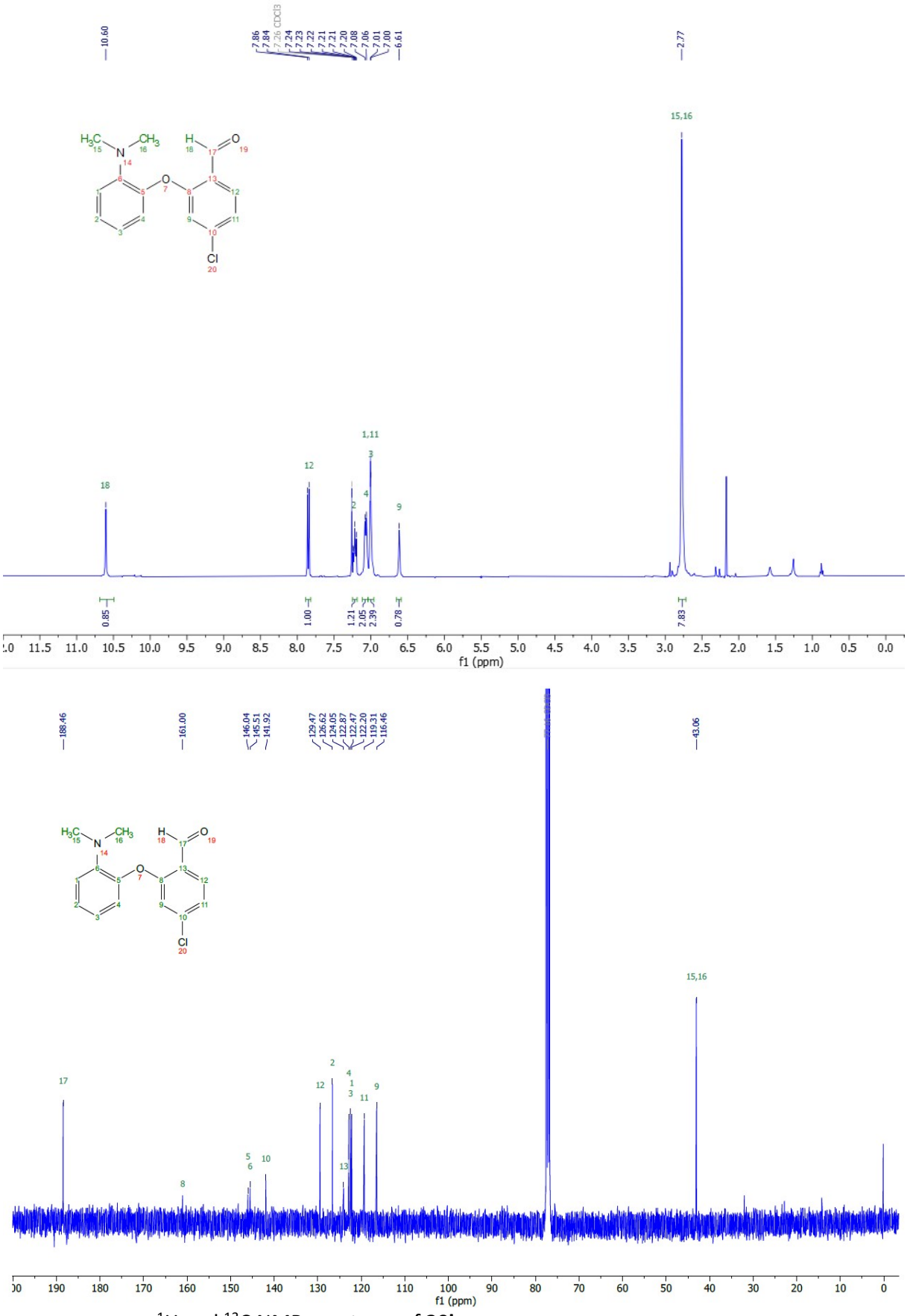
^{1}H and ^{13}C NMR spectrum of **15b**



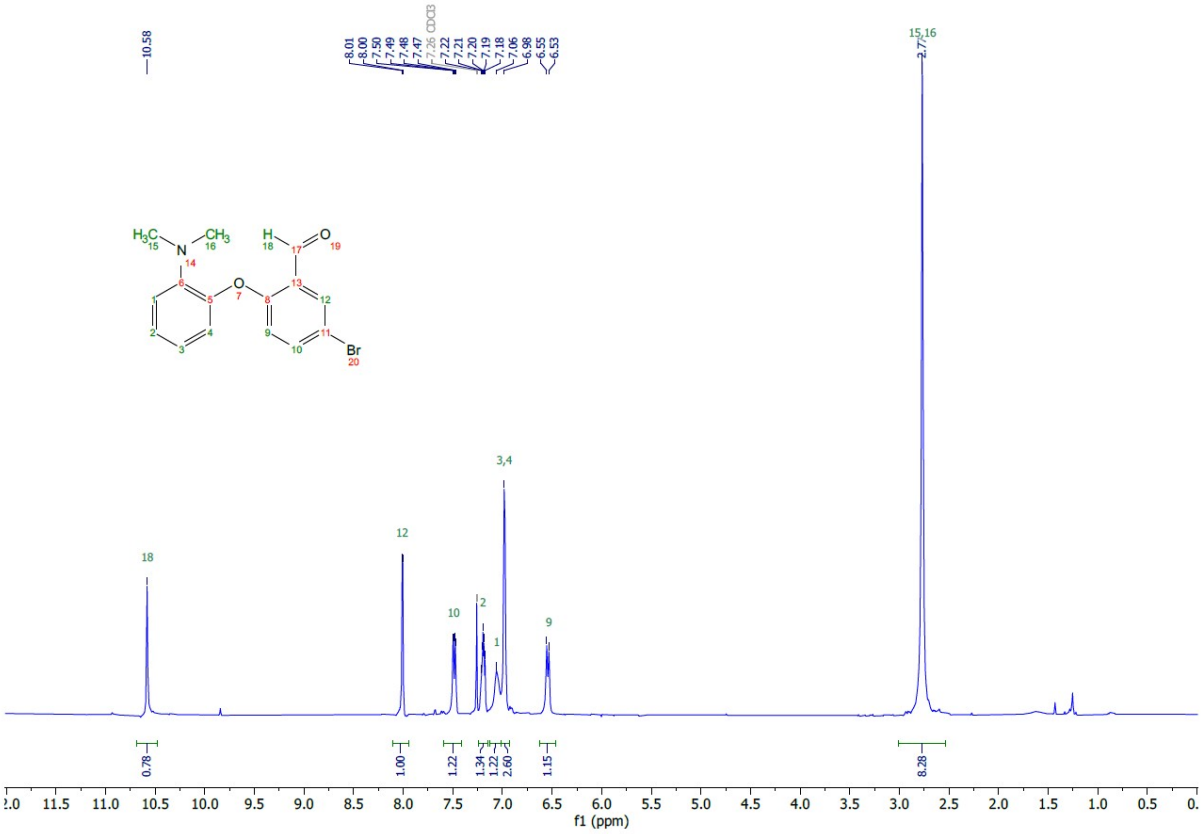
^{1}H and ^{13}C NMR spectrum of **15d**

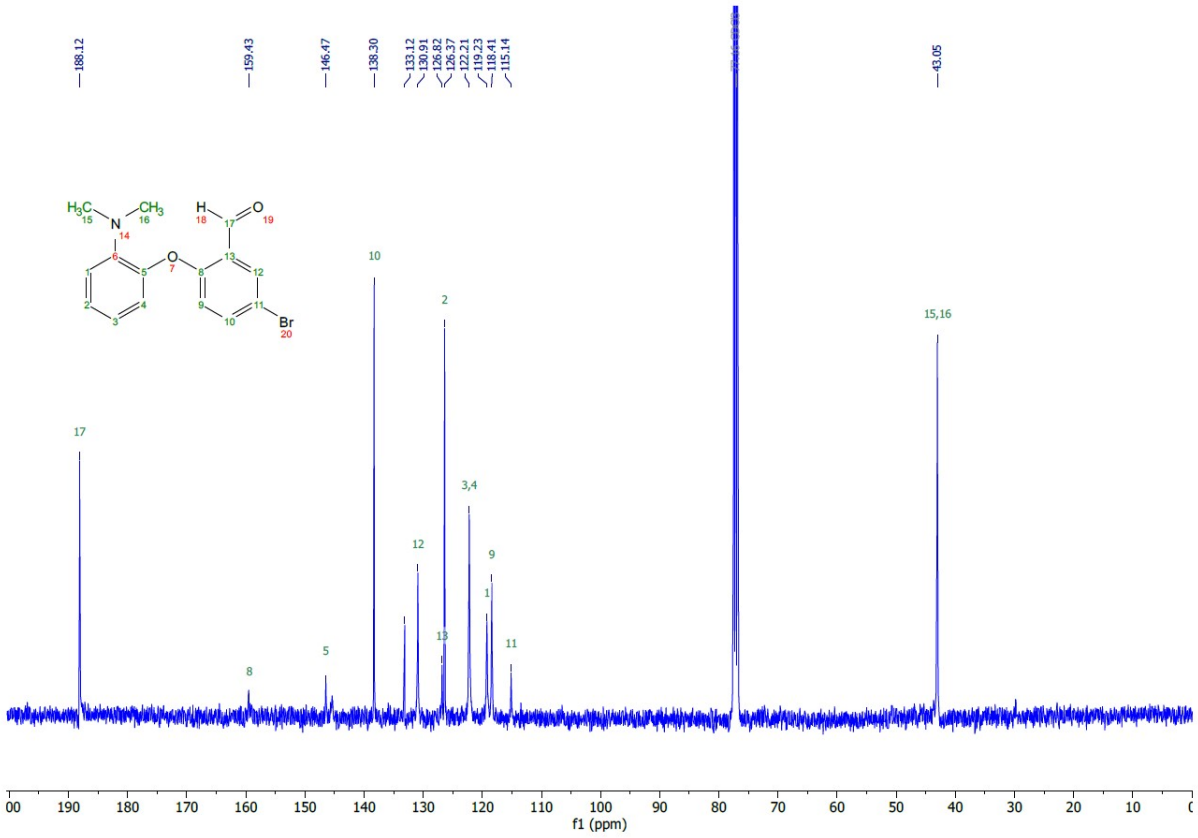


^{1}H and ^{13}C NMR spectrum of **30a**

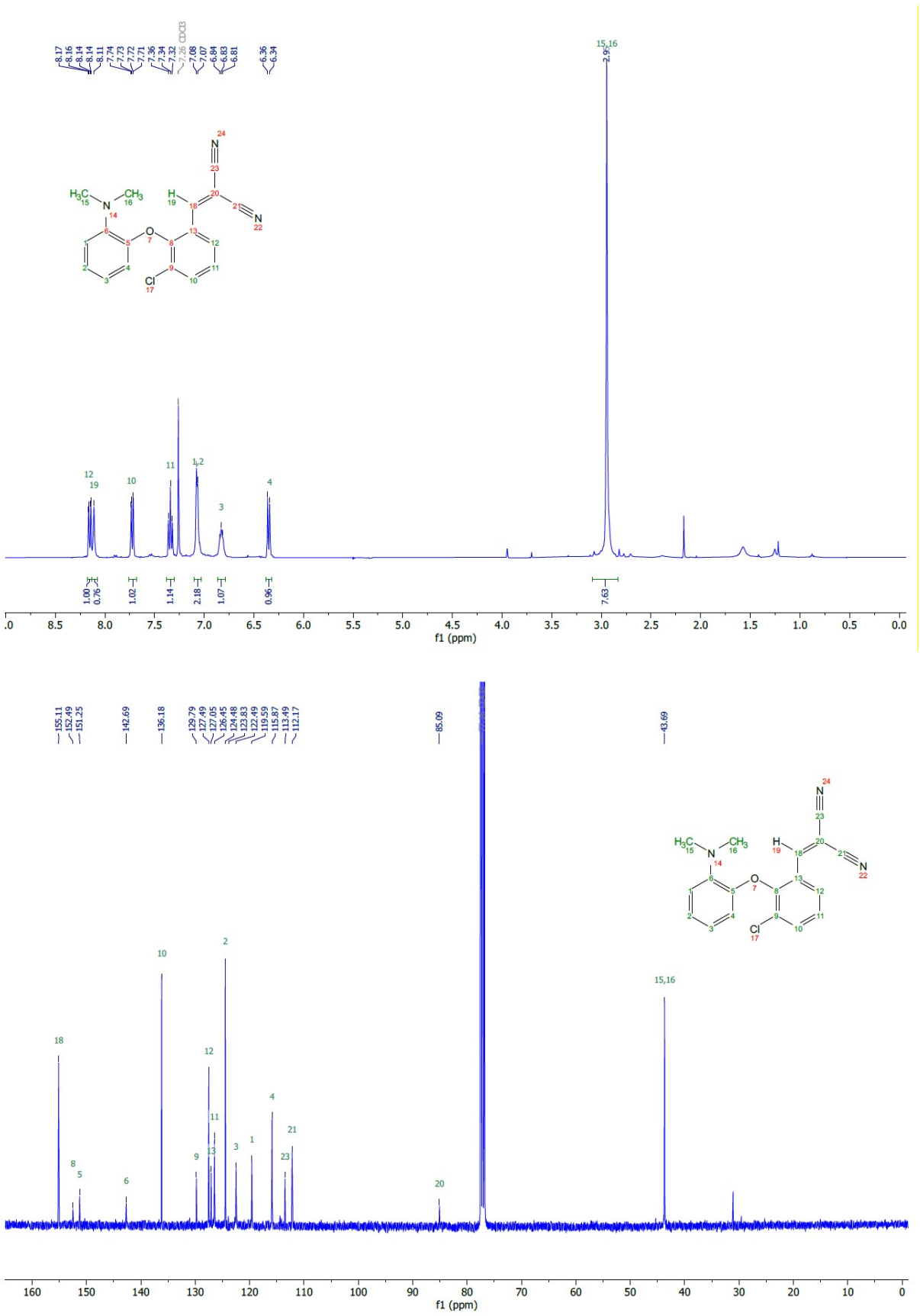


^{1}H and ^{13}C NMR spectrum of **30b**





^{1}H and ^{13}C NMR spectrum of **30c**



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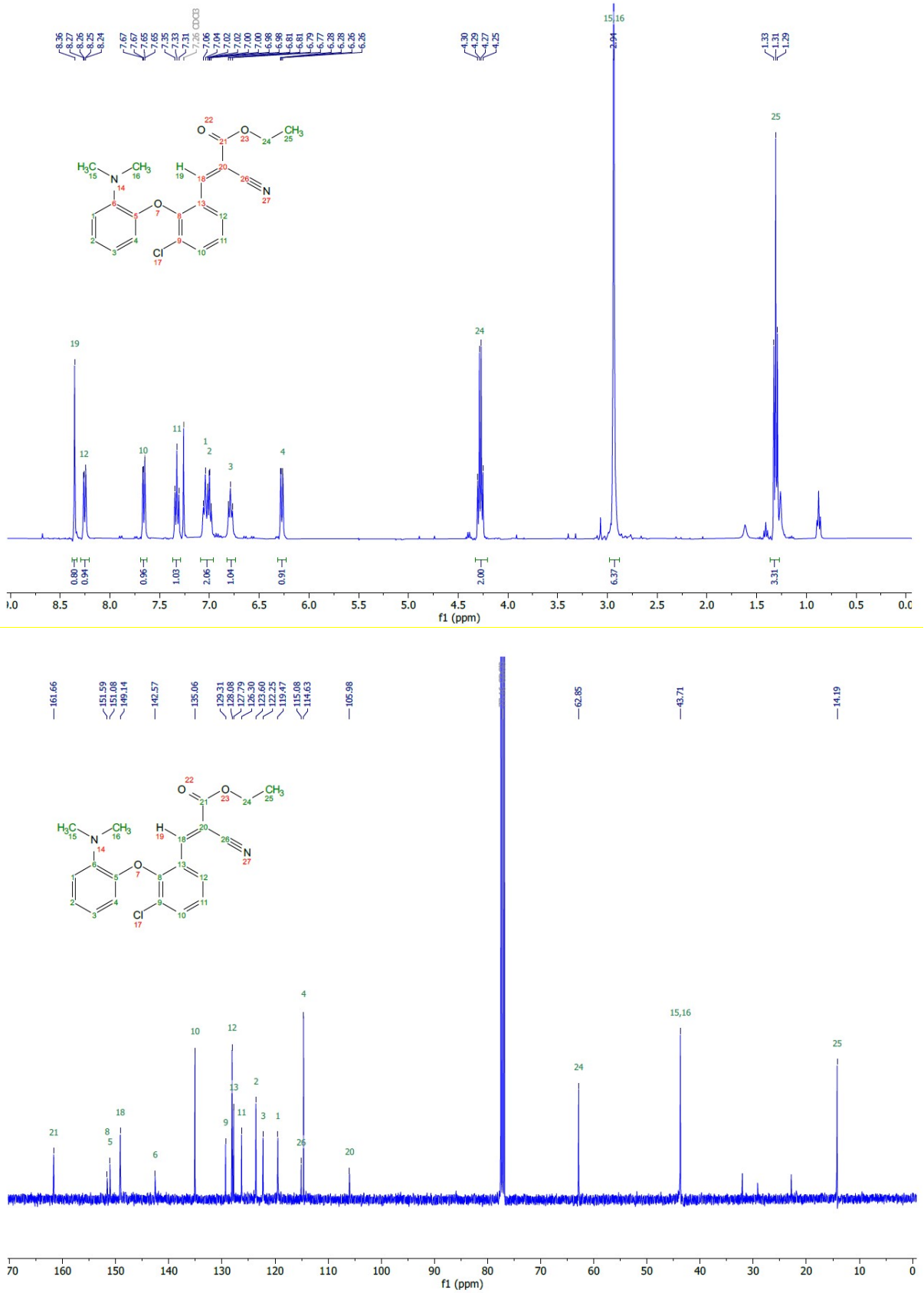
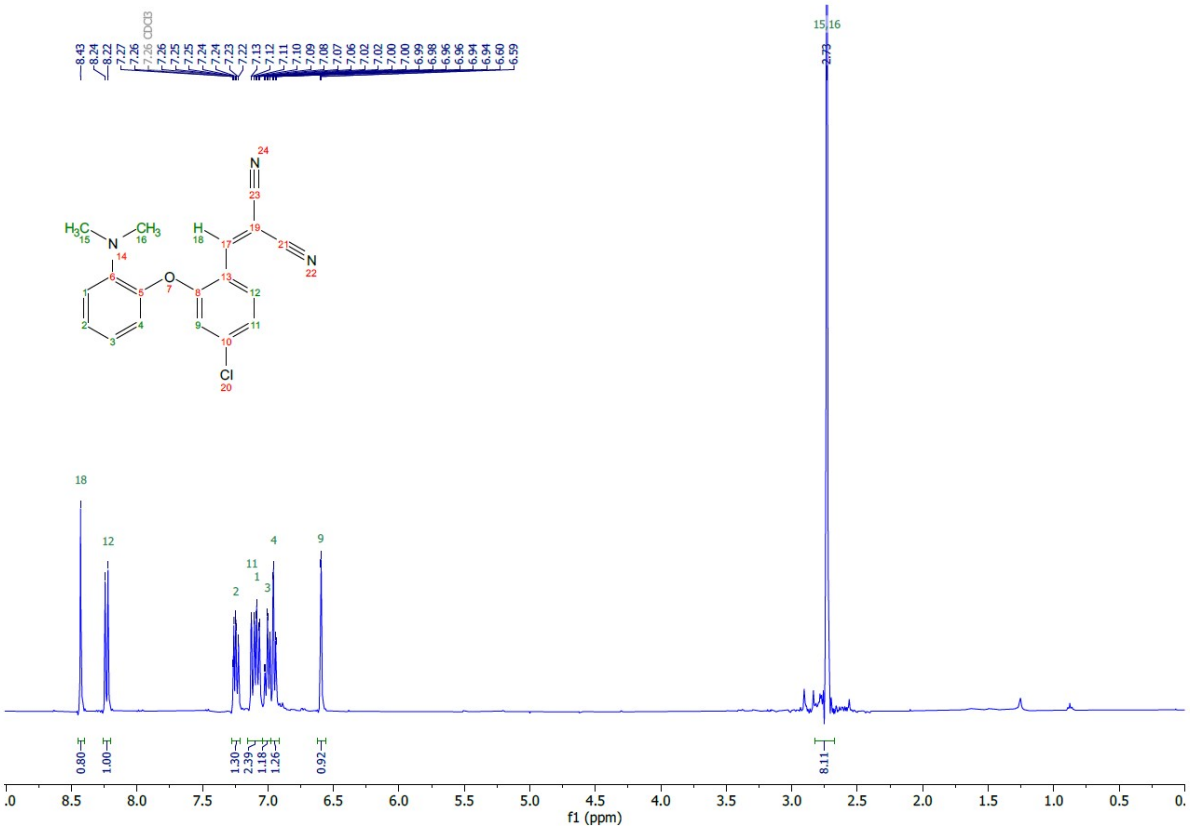
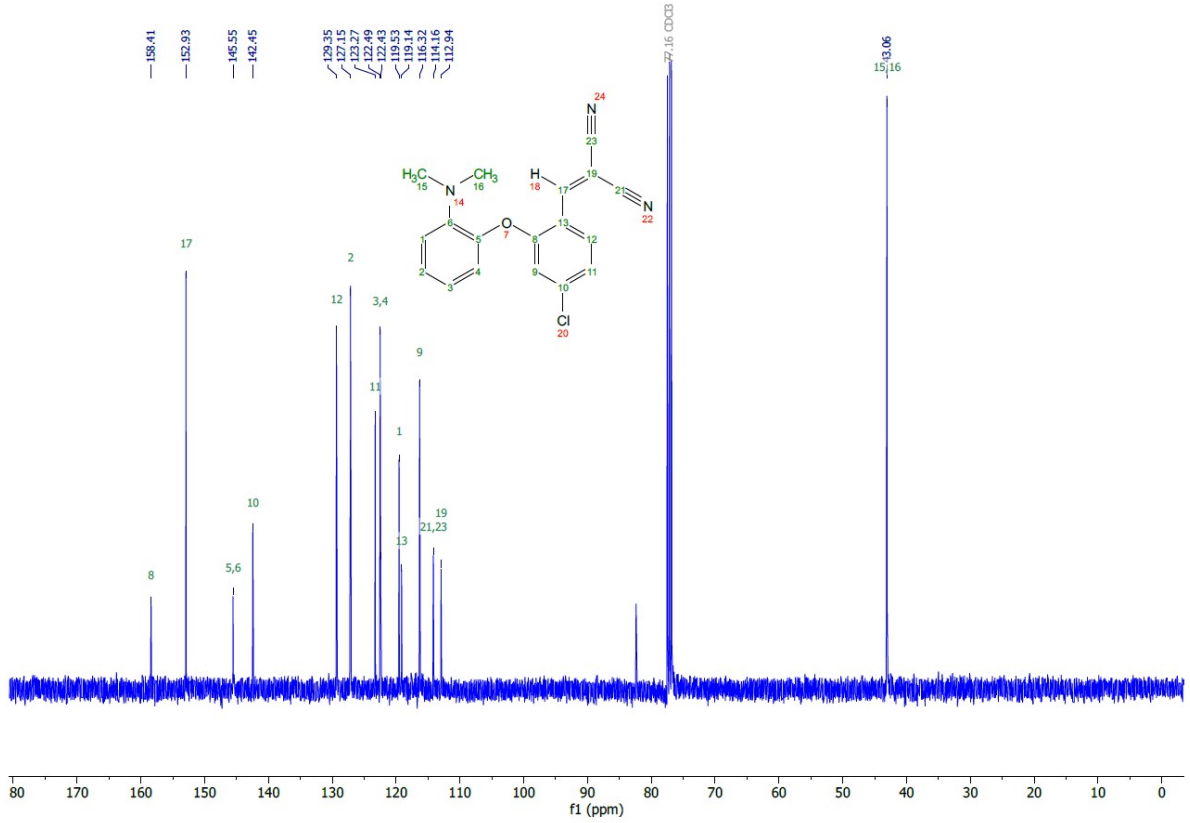
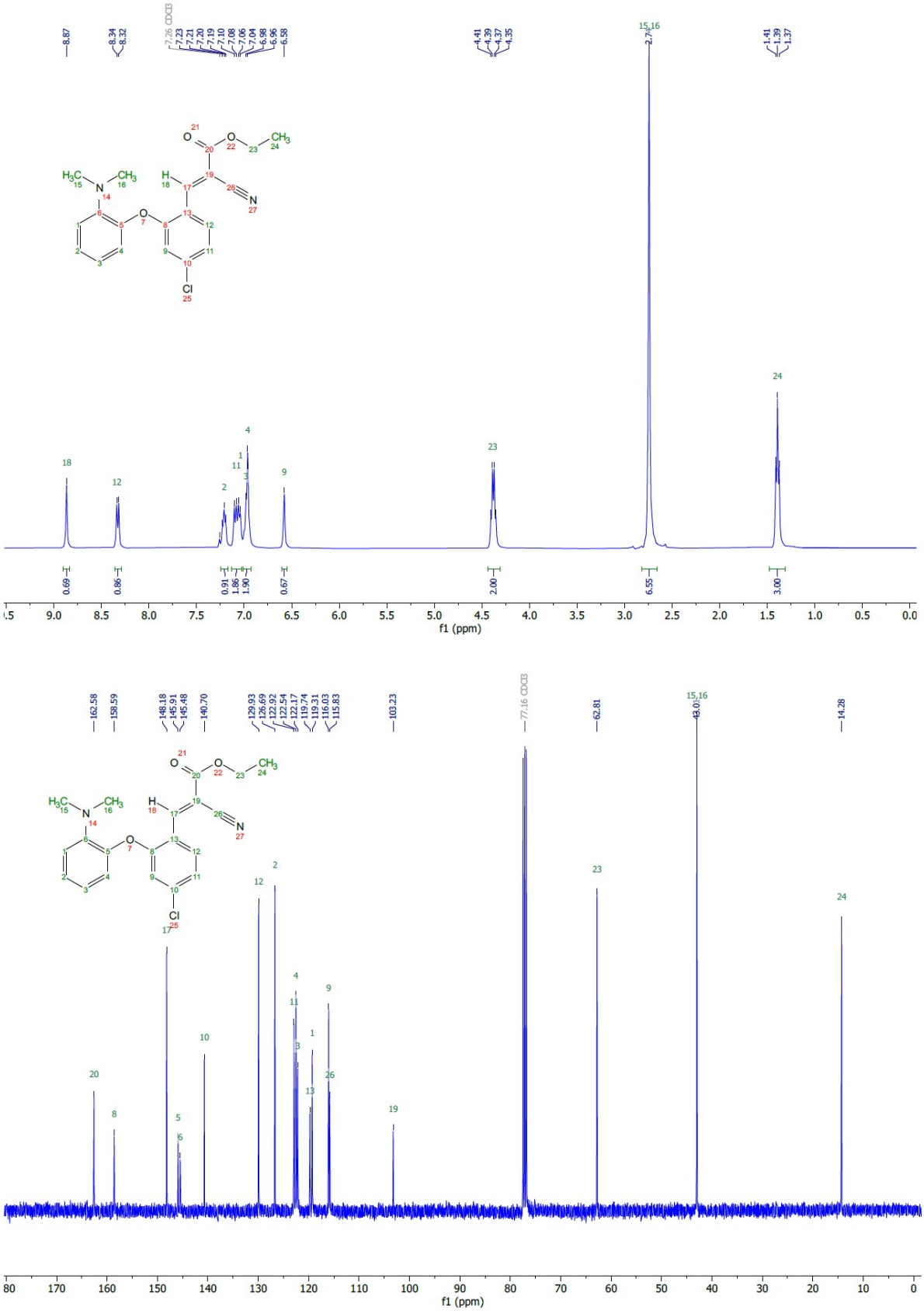


^{1}H and ^{13}C NMR spectrum of **31b**

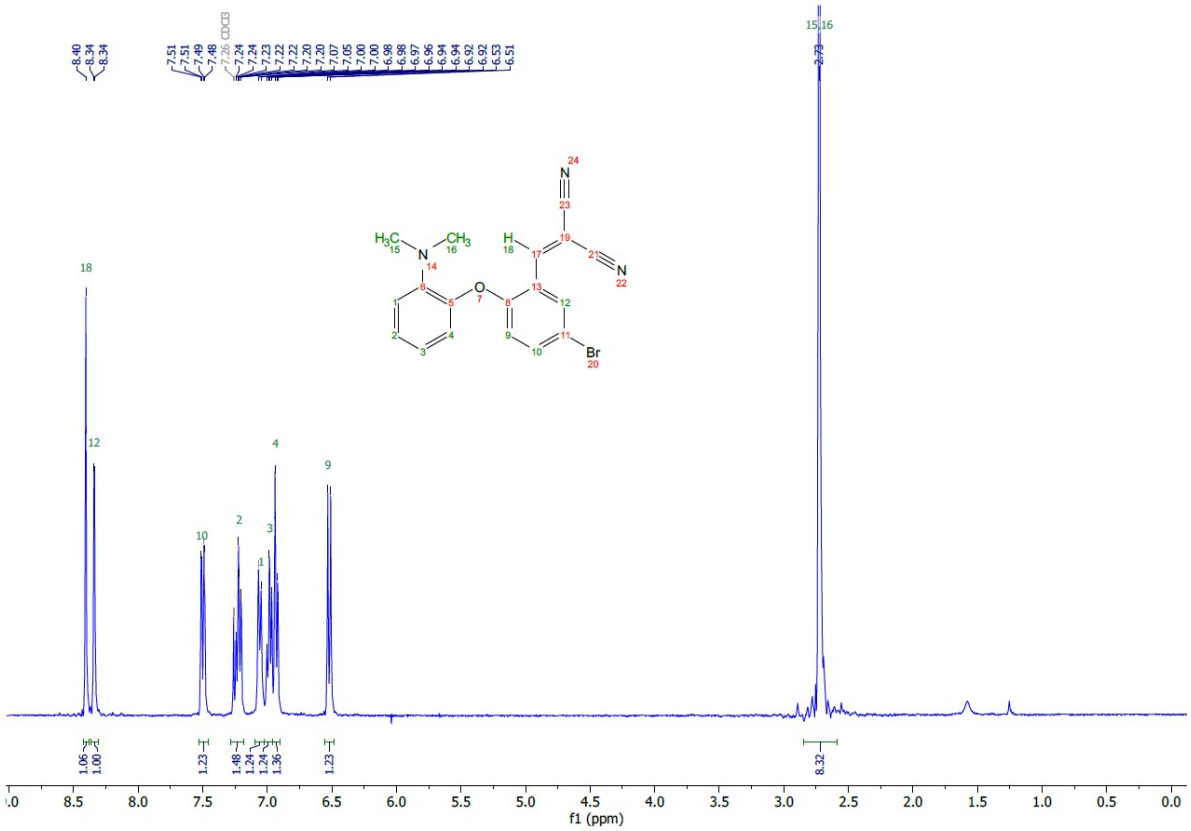


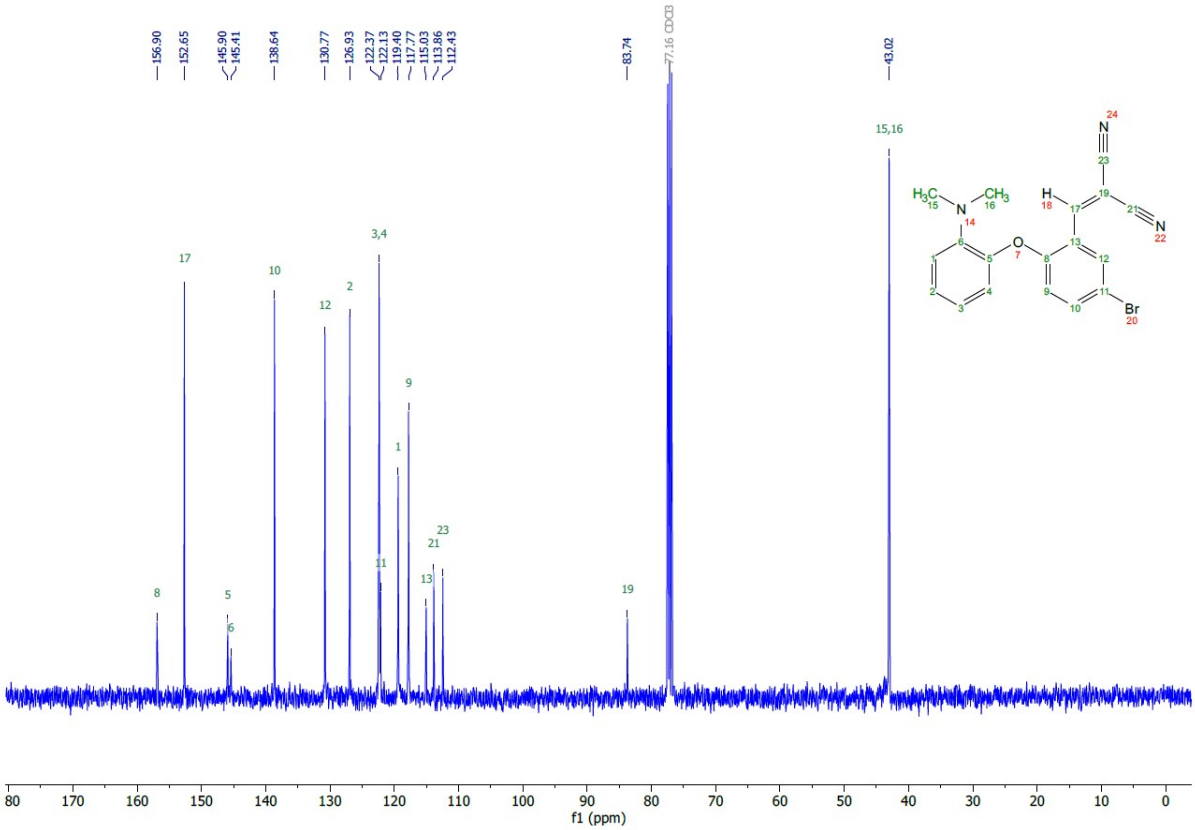


^{1}H and ^{13}C NMR spectrum of **31c**

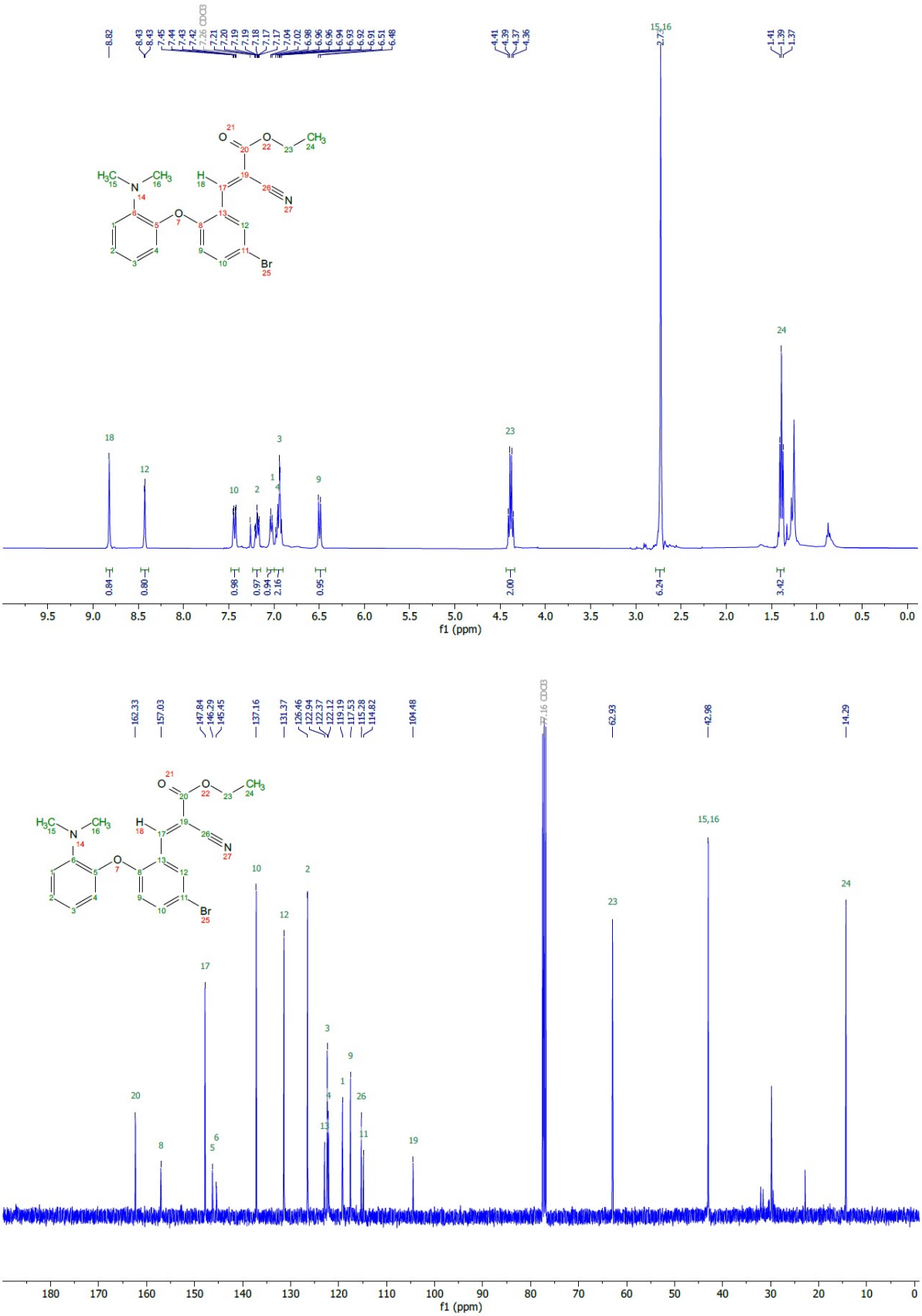


^{1}H and ^{13}C NMR spectrum of **31d**

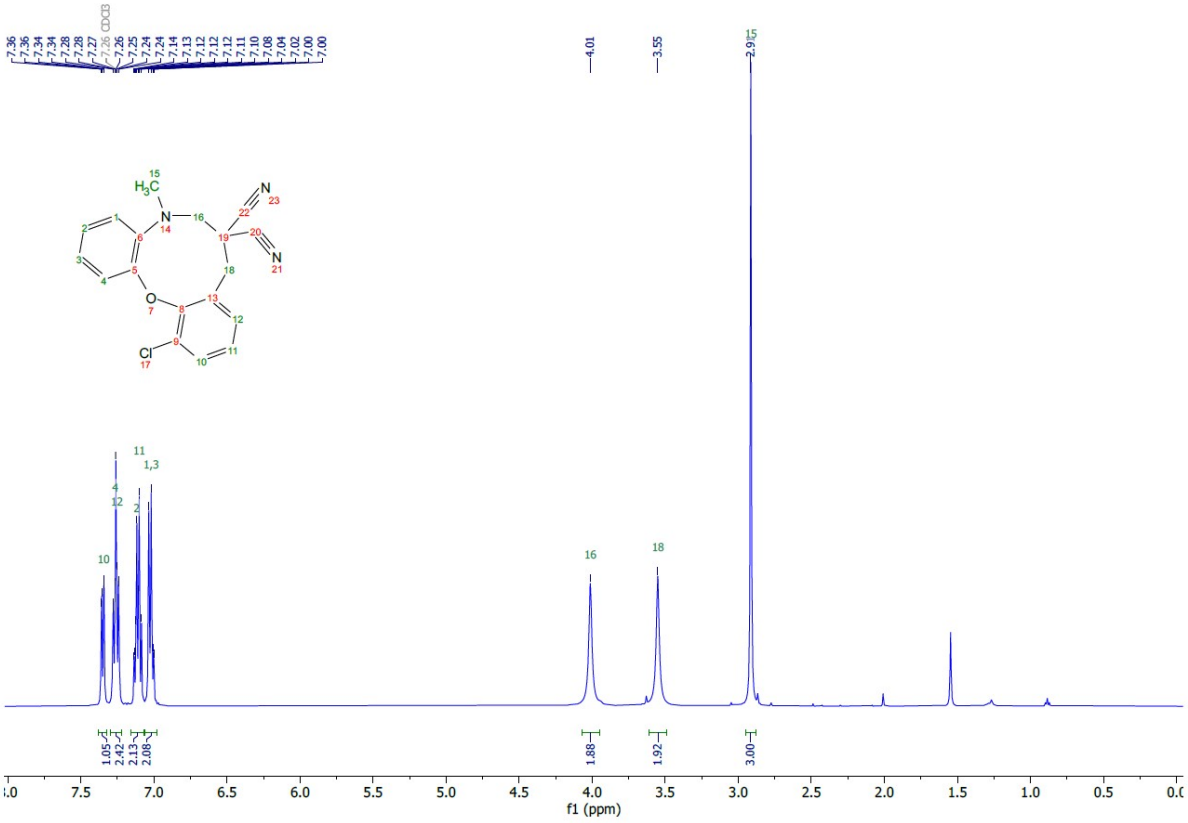


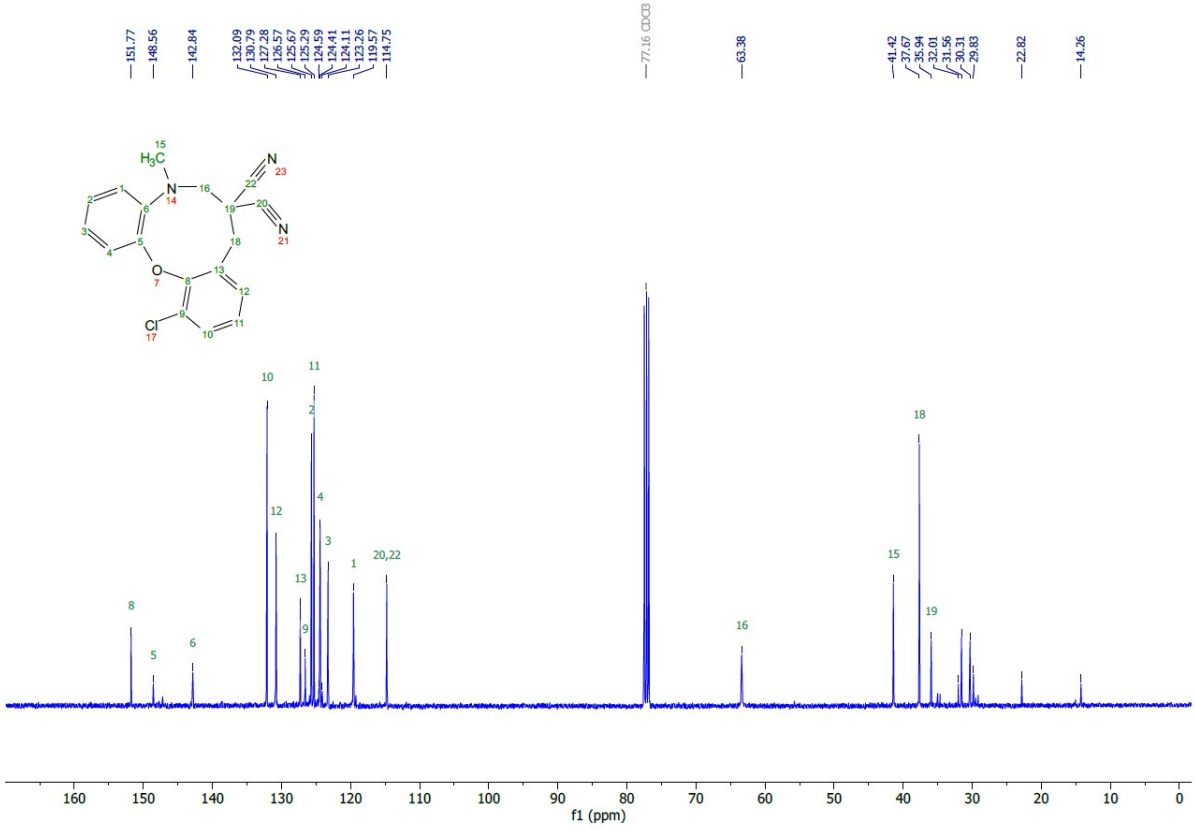


^{1}H and ^{13}C NMR spectrum of **31e**



^{1}H and ^{13}C NMR spectrum of **31f**





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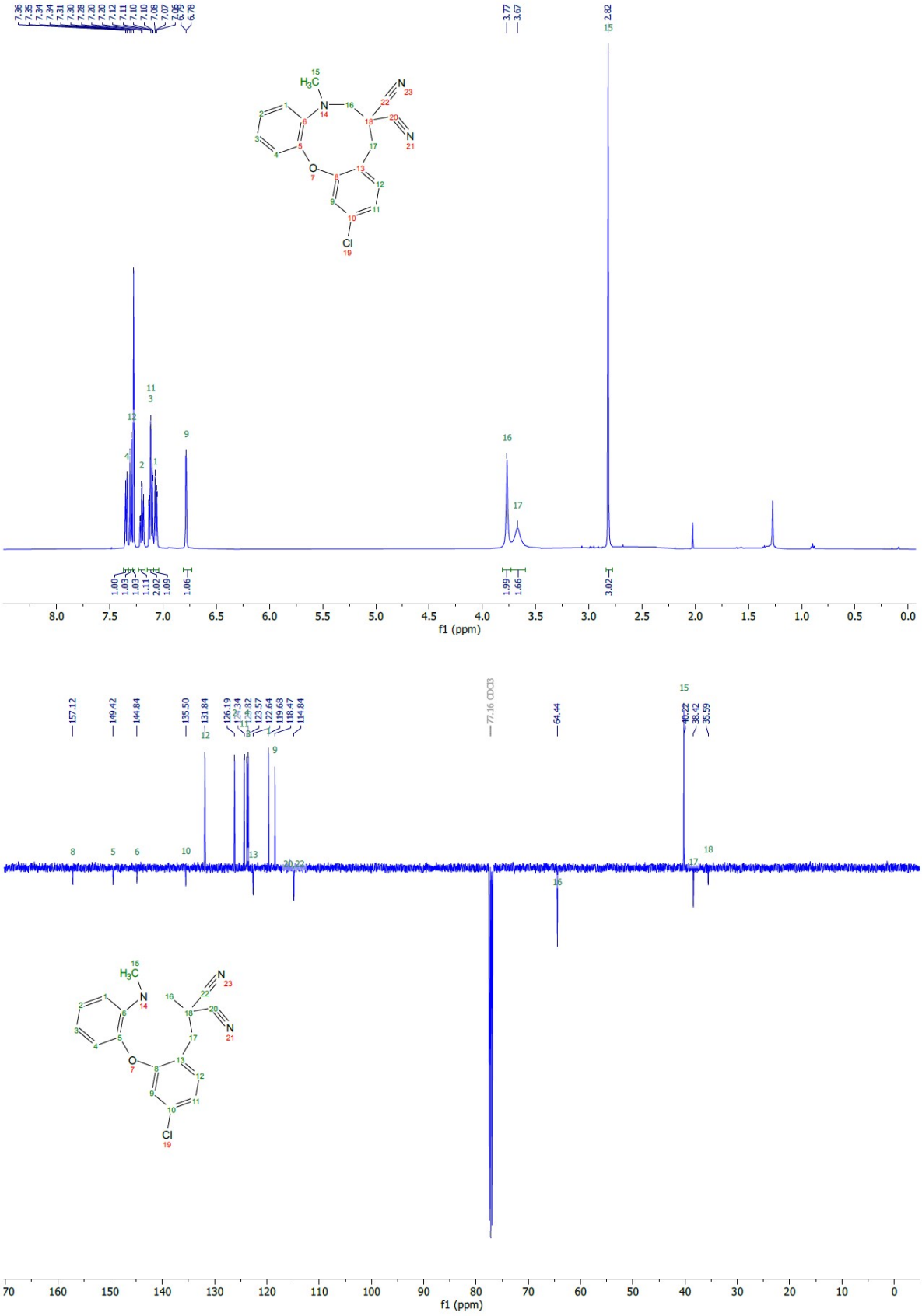
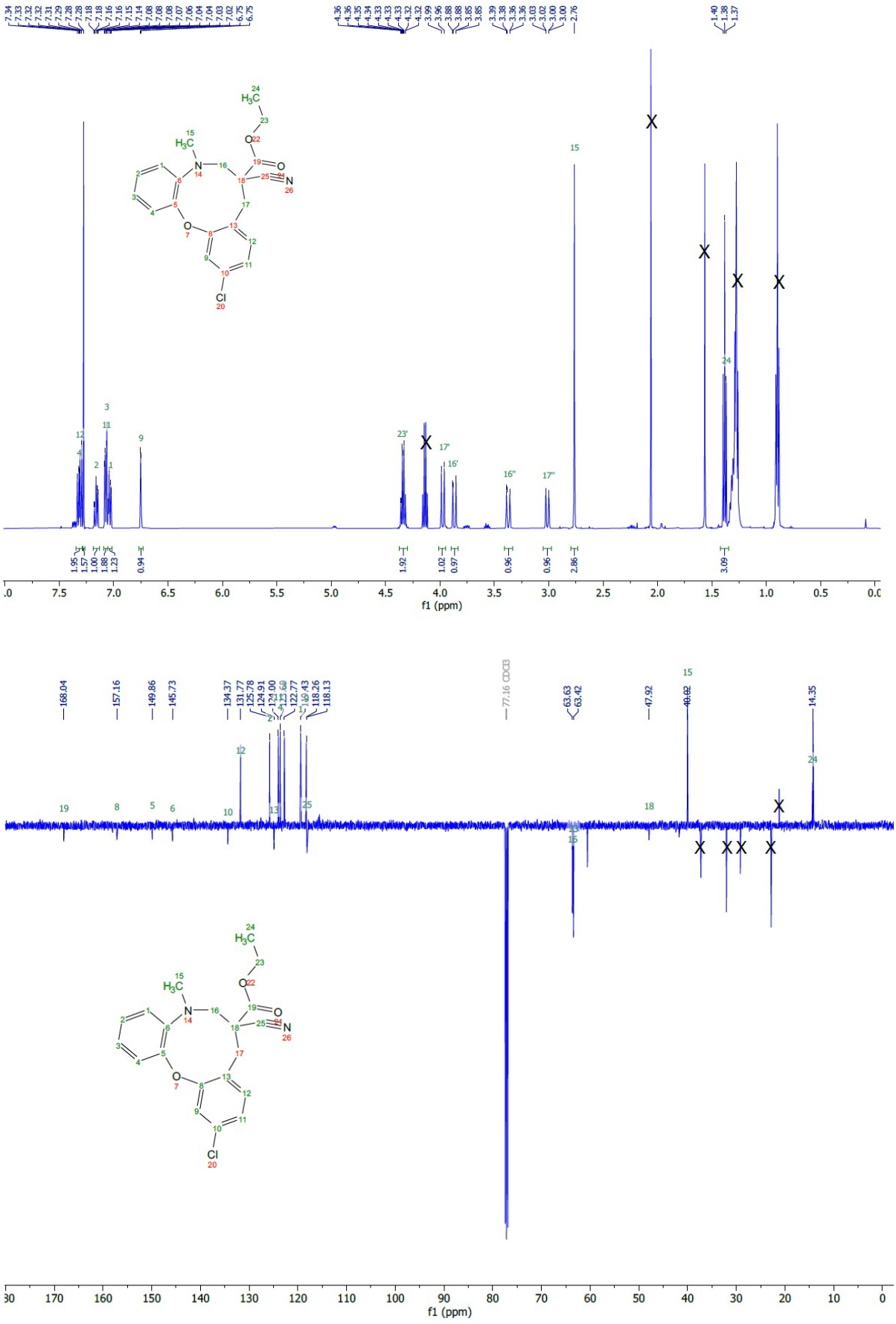
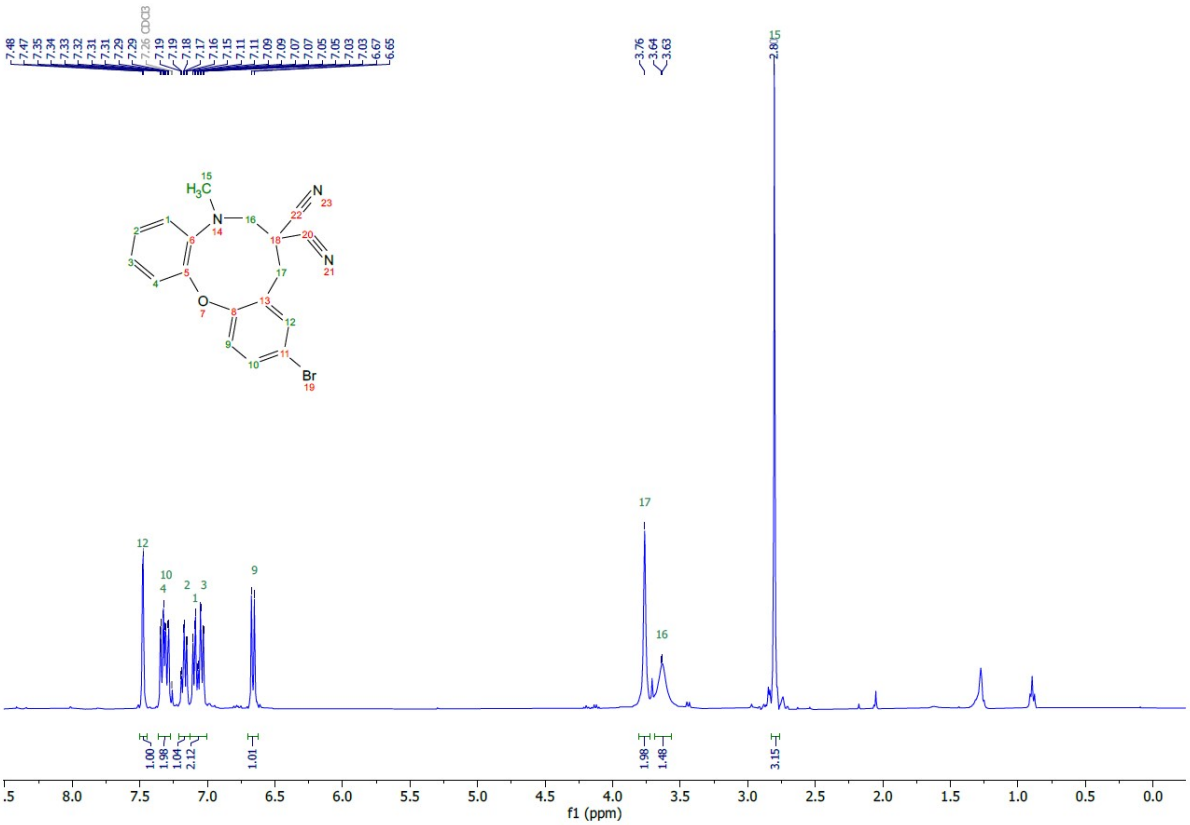
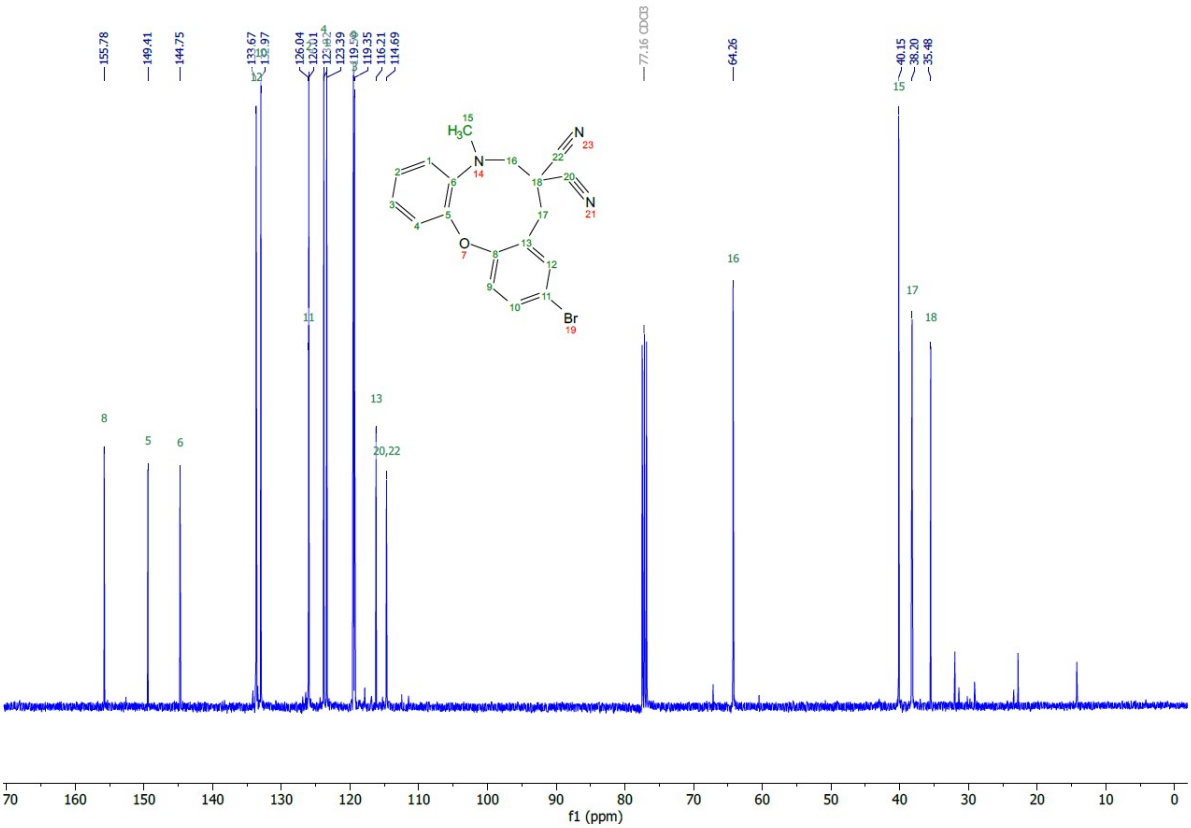


^{1}H and ^{13}C NMR spectrum of **32c**

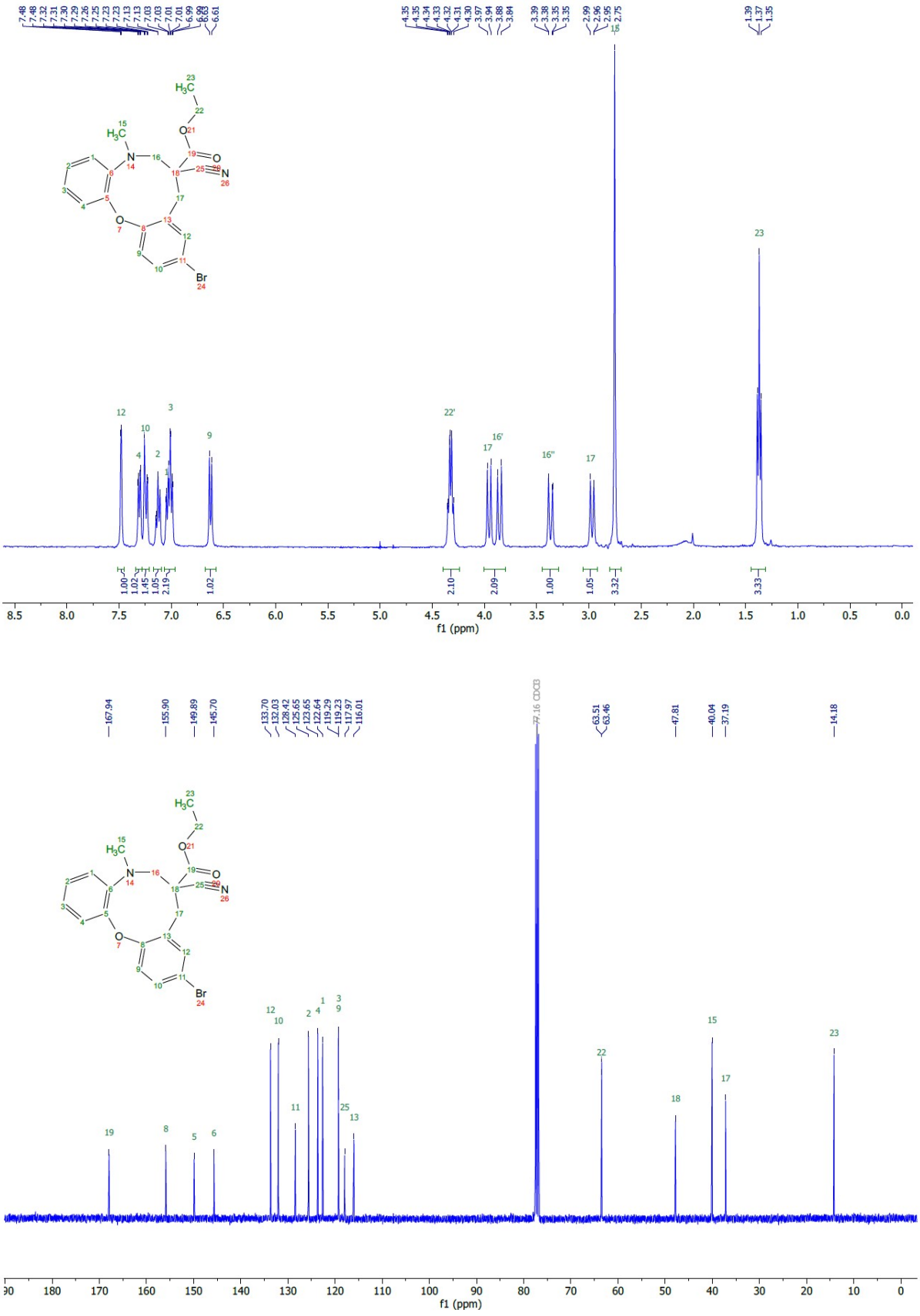


^{1}H and ^{13}C NMR spectrum of **32d**

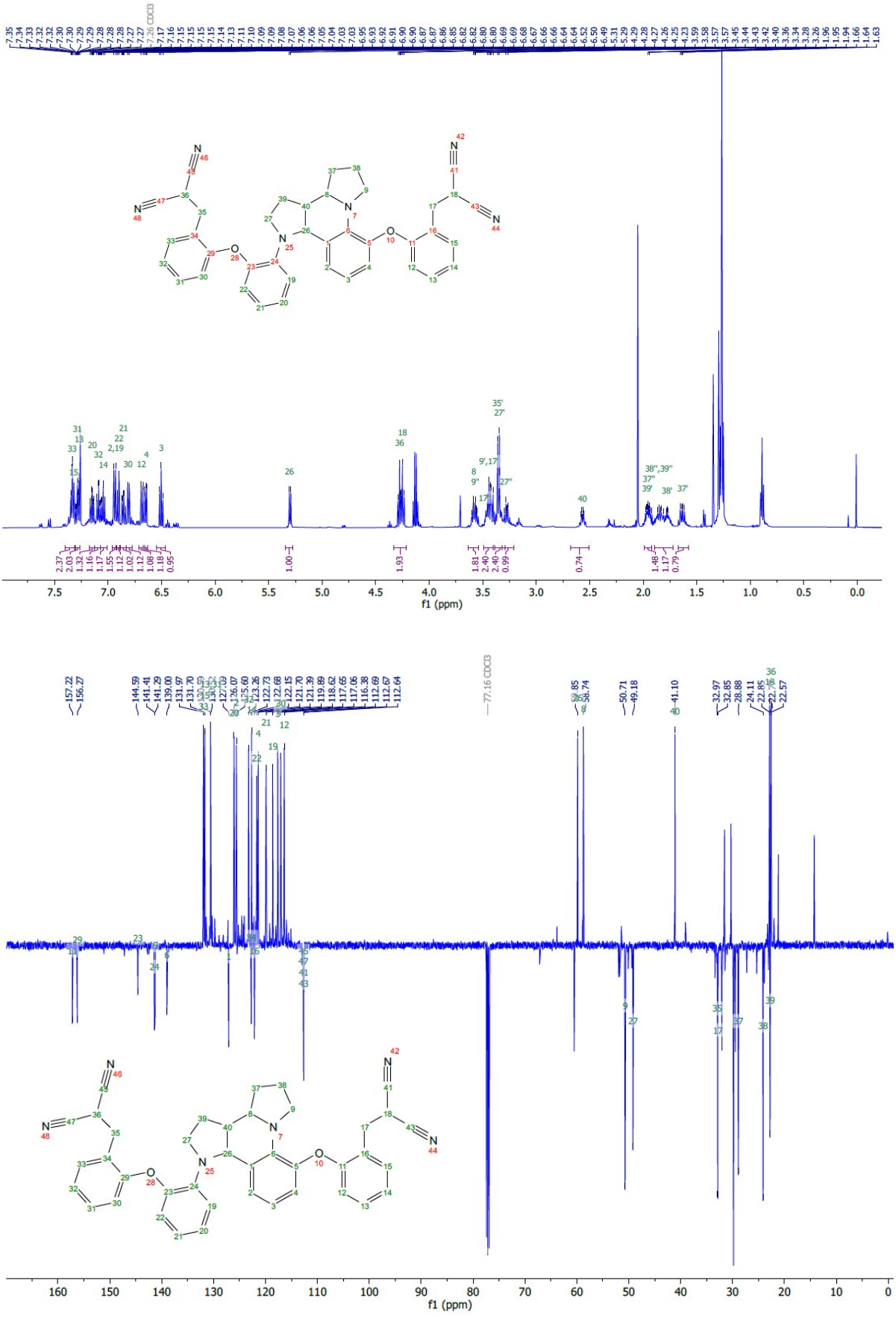




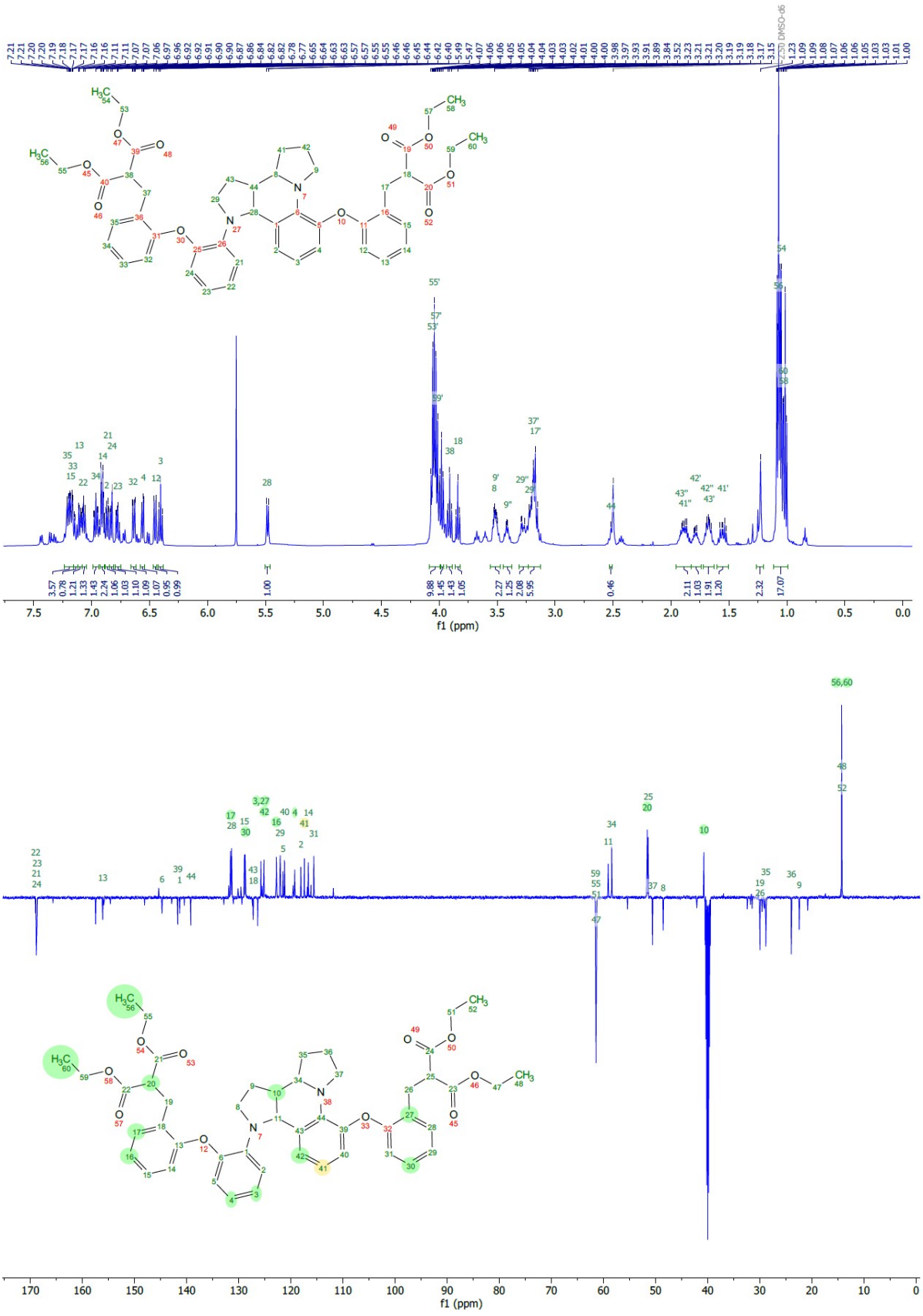
^{1}H and ^{13}C NMR spectrum of **32e**



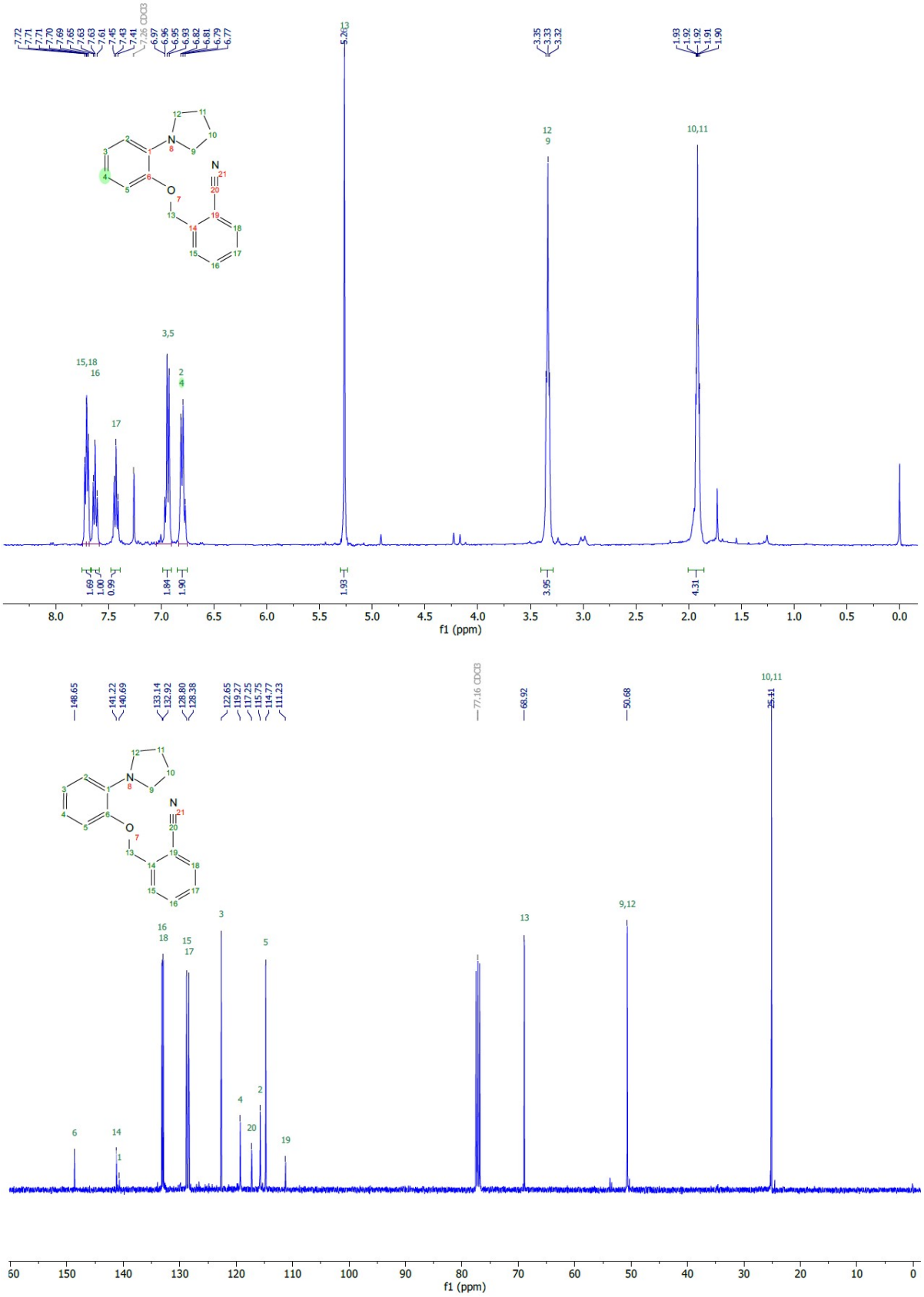
^{1}H and ^{13}C NMR spectrum of **32f**



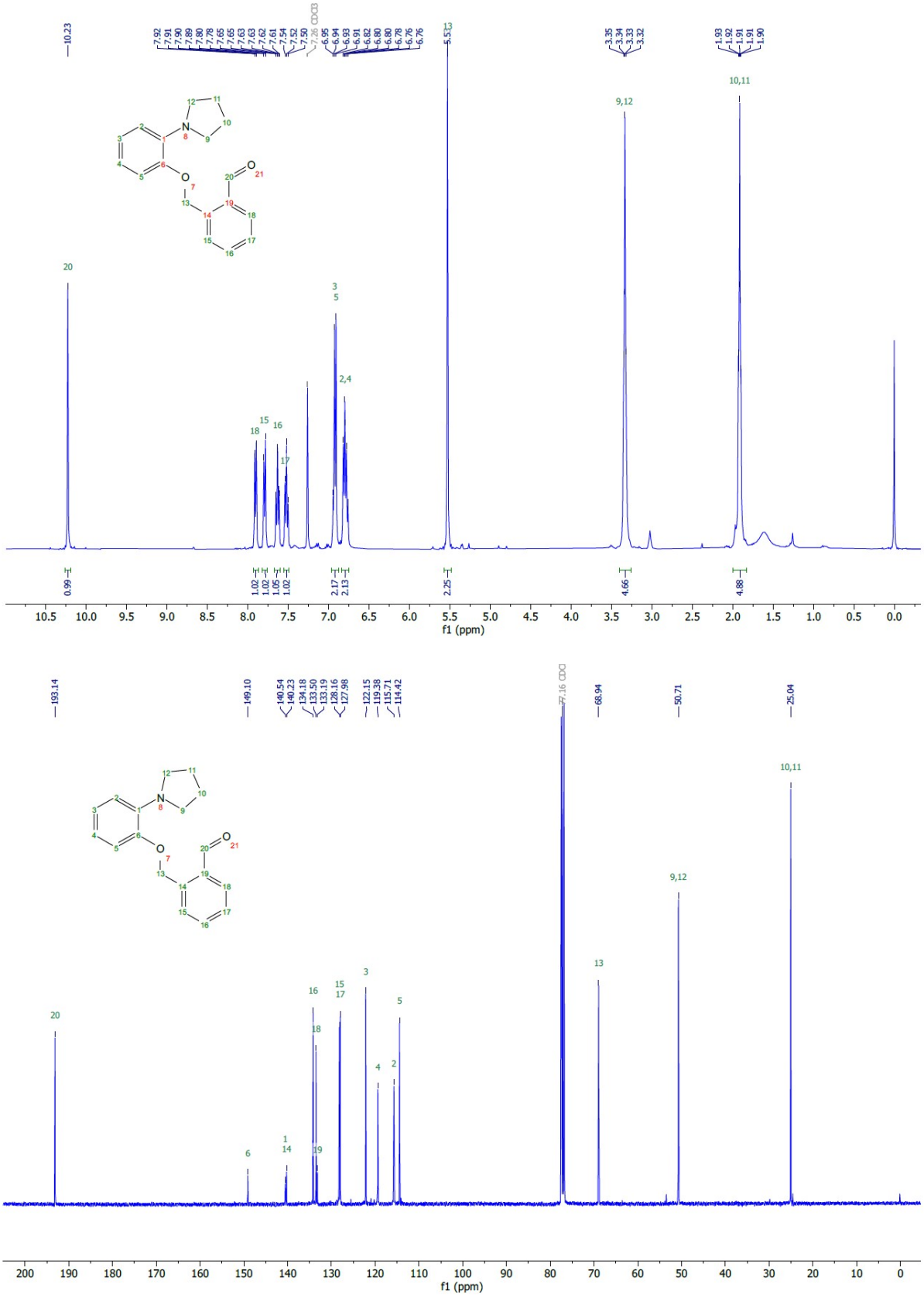
^{1}H and ^{13}C NMR spectrum of **23**



^{1}H and ^{13}C NMR spectrum of **24**



^{1}H and ^{13}C NMR spectrum of **33**



^{1}H and ^{13}C NMR spectrum of **34**

Crystallographic Data

For both structures, data collection: *CAD-4 EXPRESS* (Enraf Nonius, 1992); cell refinement: *CAD-4 EXPRESS* (Enraf Nonius, 1992); data reduction: PROFIT (Streltsov & Zavodnik, 1989); program(s) used to solve structure: *SIR92* (Giacovazzo *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999). Crystal data, data collection and structure refinement details are summarized in Table S1. Geometric parameters are summarized in Tables S2 and S3 for **14c** and **15a**, respectively. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.
Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

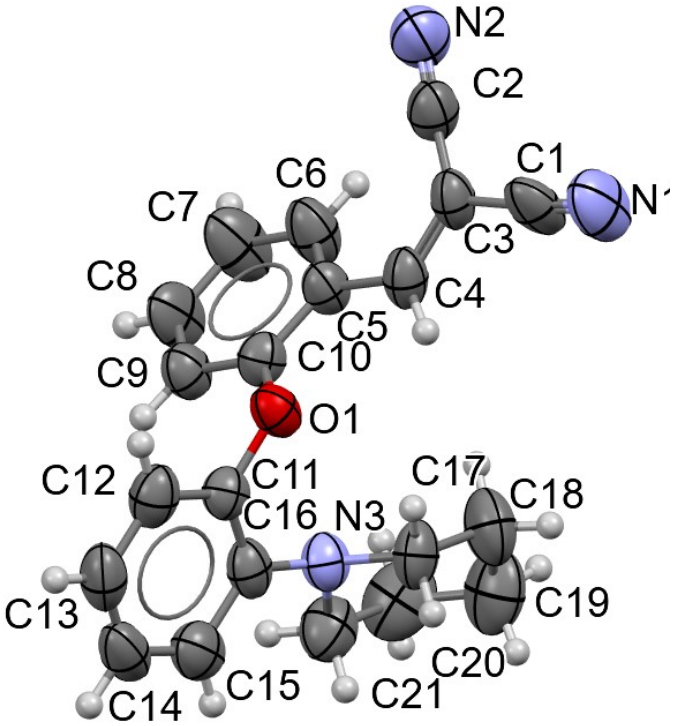


Figure S6 ORTEP view of **14c** at 50% probability level with numbering scheme.

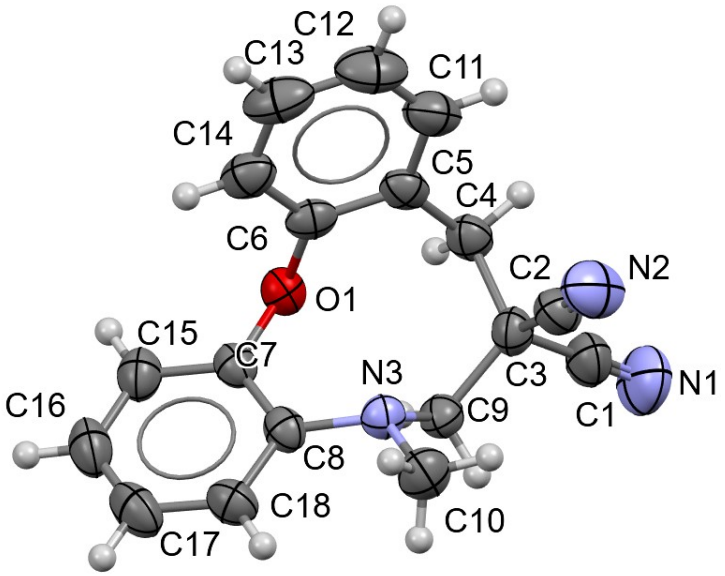


Figure S7 ORTEP view of **15a** at 50% probability level with numbering scheme.

Table S1 *Experimental details of X-ray diffraction studies*

	14c	**15a**
Crystal data		
Chemical formula	$C_{21}H_{19}N_3O$	$C_{18}H_{15}N_3O$
M_r	329.39	289.33
Crystal system, space group	Monoclinic, *C*2/*c*	Orthorhombic, $P2_12_12_1$
Temperature (K)	293	293
a, *b*, *c* (Å)	27.317 (5), 8.519 (5), 19.641 (5)	8.745 (1), 9.836 (1), 17.535 (1)
α, β, γ (°)	90.000 (5), 127.830 (5), 90.000 (5)	90, 90, 90
V (Å^3)	3610 (2)	1508.3 (2)
Z	8	4
Radiation type	Mo *K*α	Mo *K*α
μ (mm^{-1})	0.08	0.08
Crystal size (mm)	0.35 × 0.25 × 0.2	0.66 × 0.3 × 0.25
Data collection		
Diffractometer	Enraf Nonius CAD4	
Absorption correction	–	Ψ scan North A.C.T., Phillips D.C. & Mathews F.S. (1968) Acta. Cryst. A24, 351 Number of Ψ scan sets used was 2 Theta correction was applied. Averaged transmission function was used. Fourier

		smoothing - Window value 5
T_{min}, T_{max}	–	0.856, 0.946
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3725, 3725, 1955	1767, 1710, 1401
R_{int}	n.a.	0.024
$(\sin \Theta/\lambda)_{max}$ (Å^{-1})	0.606	0.616
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.073, 0.191, 1.06	0.056, 0.140, 1.10
No. of reflections	3725	1710
No. of parameters	226	200
H-atom treatment	H-atom parameters constrained	
	$w = 1/[\sigma^2(F_o^2) + (0.0586P)^2 + 19.9399P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 0.3772P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.27, -0.35	0.20, -0.21
Absolute structure	–	Flack H D (1983), Acta Cryst. A39, 876-881
Absolute structure parameter	–	-3 (4)

Computer programs: CAD-4 EXPRESS (Enraf Nonius, 1992), PROFIT (Streltsov & Zavodnik, 1989), SIR92 (Giacovazzo et al., 1993), SHELXL97 (Sheldrick, 2008), ORTEP-3 for Windows (Farrugia, 1997), WinGX publication routines (Farrugia, 1999).

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Document origin: publCIF [Westrip, S. P. (2010). J. Apply. Cryst., 43, 920-925].

Table S2. *X-ray experimental details and geometric parameters for* ***14c.***

Crystal data

$C_{21}H_{19}N_3O$	$F(000) = 1392$
$M_r = 329.39$	$D_x = 1.212$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å
Hall symbol: -C 2yc	Cell parameters from 25 reflections
$a = 27.317$ (5) Å	$\theta = 4.7–11.5°$
$b = 8.519$ (5) Å	$\mu = 0.08$ mm^{-1}
$c = 19.641$ (5) Å	$T = 293$ K
$\beta = 127.830$ (5)°	Prism, colourless
$V = 3610$ (2) Å^3	0.35 × 0.25 × 0.2 mm
$Z = 8$	

Data collection

Enraf Nonius CAD4 diffractometer	$\theta_{max} = 25.5°$, $\theta_{min} = 2.6°$
Radiation source: fine-focus sealed tube	$h = -6 \rightarrow 33$
Graphite monochromator	$k = -4 \rightarrow 10$
profiled $\omega/2\theta$ scans	$l = -23 \rightarrow 18$
3725 measured reflections	4 standard reflections every 102 reflections
3725 independent reflections	intensity decay: 4%
1955 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.073$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.191$	H-atom parameters constrained
$S = 1.06$	$w = 1/[\sigma^2(F_o^2) + (0.0586P)^2 + 19.9399P]$ where $P = (F_o^2 + 2F_c^2)/3$
3725 reflections	$(\Delta/\sigma)_{max} < 0.001$
226 parameters	$\Delta\square_{max} = 0.27$ e Å^{-3}
0 restraints	$\Delta\square_{min} = -0.35$ e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the

estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.
Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²) for (**14c**)*

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.4624 (4)	0.3095 (8)	-0.5300 (4)	0.077 (2)
C2	0.4442 (4)	0.0593 (9)	-0.4920 (4)	0.072 (2)
C3	0.4778 (3)	0.1998 (7)	-0.4631 (4)	0.0616 (17)
C4	0.5235 (3)	0.2395 (7)	-0.3806 (4)	0.0620 (17)
H4	0.5403	0.3393	-0.3713	0.074*
C5	0.5493 (3)	0.1421 (7)	-0.3046 (4)	0.0570 (16)
C6	0.5509 (4)	-0.0212 (8)	-0.3071 (4)	0.082 (2)
H6	0.5341	-0.0714	-0.3592	0.099*
C7	0.5774 (4)	-0.1102 (8)	-0.2329 (5)	0.100 (3)
H7	0.5779	-0.2191	-0.2352	0.12*
C8	0.6030 (4)	-0.0338 (8)	-0.1556 (4)	0.088 (3)
H8	0.6215	-0.0926	-0.1055	0.106*
C9	0.6018 (3)	0.1253 (8)	-0.1513 (4)	0.0634 (17)
H9	0.618	0.1744	-0.0991	0.076*
C10	0.5765 (3)	0.2130 (7)	-0.2245 (4)	0.0544 (15)
C11	0.6083 (3)	0.4527 (7)	-0.1473 (4)	0.0536 (15)
C12	0.5787 (3)	0.5188 (7)	-0.1161 (4)	0.0694 (18)
H12	0.536	0.5101	-0.1474	0.083*
C13	0.6137 (4)	0.5971 (8)	-0.0382 (5)	0.077 (2)
H13	0.5948	0.6406	-0.0162	0.093*
C14	0.6751 (4)	0.6099 (8)	0.0056 (4)	0.079 (2)
H14	0.6985	0.6608	0.0587	0.094*
C15	0.7048 (3)	0.5498 (8)	-0.0259 (4)	0.076 (2)
H15	0.7473	0.563	0.0048	0.091*
C16	0.6698 (3)	0.4682 (7)	-0.1049 (4)	0.0596 (16)
C17	0.6790 (3)	0.4867 (7)	-0.2195 (4)	0.072 (2)
H17A	0.6994	0.5881	-0.2036	0.087*
H17B	0.6346	0.5038	-0.2579	0.087*
C18	0.6980 (4)	0.3892 (10)	-0.2650 (5)	0.098 (3)
H18A	0.6741	0.2927	-0.2859	0.117*

H18B	0.6882	0.4471	-0.3145	0.117*
C19	0.7646 (4)	0.3502 (11)	-0.2083 (6)	0.111 (3)
H19A	0.7889	0.4452	-0.1931	0.133*
H19B	0.7738	0.2807	-0.2383	0.133*
C20	0.7815 (4)	0.2707 (10)	-0.1273 (6)	0.109 (3)
H20A	0.7608	0.1699	-0.142	0.131*
H20B	0.8259	0.2525	-0.0879	0.131*
C21	0.7625 (3)	0.3721 (9)	-0.0840 (4)	0.083 (2)
H21A	0.7732	0.3196	-0.0327	0.099*
H21B	0.7849	0.4707	-0.0666	0.099*
N1	0.4480 (4)	0.3873 (8)	-0.5854 (4)	0.109 (2)
N2	0.4149 (3)	-0.0502 (8)	-0.5195 (4)	0.096 (2)
N3	0.6969 (2)	0.4024 (6)	-0.1416 (3)	0.0614 (14)
O1	0.57169 (19)	0.3746 (4)	-0.2261 (2)	0.0585 (11)

*Atomic displacement parameters (Å²) for (**14c**)*

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.110 (6)	0.047 (4)	0.056 (4)	-0.003 (4)	0.042 (4)	-0.012 (3)
C2	0.103 (6)	0.055 (4)	0.073 (5)	-0.001 (4)	0.061 (5)	0.001 (4)
C3	0.091 (5)	0.051 (4)	0.056 (4)	0.007 (4)	0.051 (4)	0.008 (3)
C4	0.092 (5)	0.049 (4)	0.064 (4)	0.009 (3)	0.057 (4)	0.009 (3)
C5	0.076 (4)	0.042 (3)	0.052 (3)	0.004 (3)	0.039 (3)	0.004 (3)
C6	0.122 (6)	0.061 (4)	0.067 (4)	0.009 (4)	0.060 (5)	0.000 (4)
C7	0.149 (8)	0.052 (4)	0.069 (5)	0.020 (5)	0.051 (5)	0.020 (4)
C8	0.123 (7)	0.060 (4)	0.060 (4)	0.001 (4)	0.045 (5)	0.026 (4)
C9	0.076 (5)	0.056 (4)	0.053 (4)	0.005 (3)	0.037 (4)	0.008 (3)
C10	0.061 (4)	0.047 (3)	0.060 (4)	0.008 (3)	0.039 (3)	0.009 (3)
C11	0.056 (4)	0.049 (3)	0.052 (3)	0.008 (3)	0.032 (3)	0.011 (3)
C12	0.092 (5)	0.055 (4)	0.084 (5)	0.006 (4)	0.065 (4)	0.010 (4)
C13	0.120 (7)	0.065 (5)	0.078 (5)	0.004 (5)	0.076 (5)	0.005 (4)
C14	0.123 (7)	0.054 (4)	0.061 (4)	-0.012 (5)	0.058 (5)	-0.006 (3)
C15	0.092 (5)	0.065 (4)	0.064 (4)	-0.004 (4)	0.044 (4)	0.011 (4)
C16	0.081 (5)	0.050 (4)	0.054 (4)	0.011 (3)	0.045 (4)	0.012 (3)
C17	0.092 (5)	0.073 (4)	0.073 (4)	0.017 (4)	0.061 (4)	0.024 (4)
C18	0.118 (7)	0.118 (7)	0.087 (5)	0.018 (6)	0.078 (6)	0.005 (5)
C19	0.139 (8)	0.107 (7)	0.141 (8)	0.032 (6)	0.114 (8)	0.015 (6)
C20	0.107 (7)	0.090 (6)	0.151 (8)	0.034 (5)	0.090 (7)	0.026 (6)
C21	0.075 (5)	0.090 (5)	0.081 (5)	0.013 (4)	0.047 (4)	0.022 (4)
N1	0.149 (7)	0.082 (4)	0.069 (4)	-0.003 (5)	0.054 (4)	0.020 (4)
N2	0.132 (6)	0.075 (4)	0.089 (5)	-0.022 (4)	0.071 (5)	-0.007 (4)

N3	0.070 (4)	0.060 (3)	0.056 (3)	0.010 (3)	0.039 (3)	0.013 (3)
O1	0.070 (3)	0.050 (2)	0.048 (2)	0.004 (2)	0.032 (2)	0.0023 (19)

*Geometric parameters (Å, º) for (**14c**)*

C1—N1	1.119 (8)	C13—C14	1.342 (10)
C1—C3	1.449 (8)	C13—H13	0.93
C2—N2	1.128 (8)	C14—C15	1.385 (10)
C2—C3	1.400 (9)	C14—H14	0.93
C3—C4	1.347 (8)	C15—C16	1.410 (9)
C4—C5	1.457 (8)	C15—H15	0.93
C4—H4	0.93	C16—N3	1.425 (7)
C5—C6	1.394 (8)	C17—N3	1.477 (7)
C5—C10	1.398 (8)	C17—C18	1.525 (9)
C6—C7	1.388 (9)	C17—H17A	0.97
C6—H6	0.93	C17—H17B	0.97
C7—C8	1.384 (9)	C18—C19	1.474 (10)
C7—H7	0.93	C18—H18A	0.97
C8—C9	1.360 (9)	C18—H18B	0.97
C8—H8	0.93	C19—C20	1.517 (10)
C9—C10	1.373 (8)	C19—H19A	0.97
C9—H9	0.93	C19—H19B	0.97
C10—O1	1.382 (6)	C20—C21	1.509 (10)
C11—C16	1.348 (8)	C20—H20A	0.97
C11—O1	1.393 (7)	C20—H20B	0.97
C11—C12	1.400 (8)	C21—N3	1.440 (8)
C12—C13	1.380 (9)	C21—H21A	0.97
C12—H12	0.93	C21—H21B	0.97
N1—C1—C3	175.6 (8)	C14—C15—H15	120.4
N2—C2—C3	176.3 (9)	C16—C15—H15	120.4
C4—C3—C2	126.6 (6)	C11—C16—C15	118.4 (6)
C4—C3—C1	117.9 (6)	C11—C16—N3	119.0 (6)
C2—C3—C1	115.5 (6)	C15—C16—N3	122.6 (6)
C3—C4—C5	126.8 (6)	N3—C17—C18	109.1 (5)
C3—C4—H4	116.6	N3—C17—H17A	109.9
C5—C4—H4	116.6	C18—C17—H17A	109.9
C6—C5—C10	117.6 (6)	N3—C17—H17B	109.9
C6—C5—C4	122.5 (6)	C18—C17—H17B	109.9
C10—C5—C4	119.7 (5)	H17A—C17—H17B	108.3
C7—C6—C5	121.0 (6)	C19—C18—C17	112.7 (6)

C7—C6—H6	119.5	C19—C18—H18A	109.1
C5—C6—H6	119.5	C17—C18—H18A	109.1
C8—C7—C6	118.8 (6)	C19—C18—H18B	109.1
C8—C7—H7	120.6	C17—C18—H18B	109.1
C6—C7—H7	120.6	H18A—C18—H18B	107.8
C9—C8—C7	121.5 (6)	C18—C19—C20	109.5 (7)
C9—C8—H8	119.3	C18—C19—H19A	109.8
C7—C8—H8	119.3	C20—C19—H19A	109.8
C8—C9—C10	119.5 (6)	C18—C19—H19B	109.8
C8—C9—H9	120.2	C20—C19—H19B	109.8
C10—C9—H9	120.2	H19A—C19—H19B	108.2
C9—C10—O1	123.0 (5)	C21—C20—C19	110.3 (6)
C9—C10—C5	121.5 (5)	C21—C20—H20A	109.6
O1—C10—C5	115.3 (5)	C19—C20—H20A	109.6
C16—C11—O1	120.5 (5)	C21—C20—H20B	109.6
C16—C11—C12	121.8 (6)	C19—C20—H20B	109.6
O1—C11—C12	117.7 (6)	H20A—C20—H20B	108.1
C13—C12—C11	119.1 (7)	N3—C21—C20	110.7 (6)
C13—C12—H12	120.4	N3—C21—H21A	109.5
C11—C12—H12	120.4	C20—C21—H21A	109.5
C14—C13—C12	119.5 (7)	N3—C21—H21B	109.5
C14—C13—H13	120.2	C20—C21—H21B	109.5
C12—C13—H13	120.2	H21A—C21—H21B	108.1
C13—C14—C15	122.0 (6)	C16—N3—C21	117.2 (5)
C13—C14—H14	119	C16—N3—C17	112.9 (5)
C15—C14—H14	119	C21—N3—C17	111.2 (5)
C14—C15—C16	119.1 (7)	C10—O1—C11	117.2 (4)

Table S3. *X-ray experimental details and geometric parameters for* ***15a.***

Crystal data

$C_{18}H_{15}N_3O$	$F(000) = 608$
$M_r = 289.33$	$D_x = 1.274$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 25 reflections
$a = 8.745$ (1) Å	$\theta = 9.5–18.4°$
$b = 9.836$ (1) Å	$\mu = 0.08$ mm^{-1}
$c = 17.535$ (1) Å	$T = 293$ K
$V = 1508.3$ (2) Å^3	Prism, colourless
$Z = 4$	0.66 × 0.3 × 0.25 mm

Data collection

Enraf Nonius CAD4 diffractometer	1401 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.024$
Graphite monochromator	$\theta_{max} = 26.0°$, $\theta_{min} = 2.6°$
profiled $\omega/2\theta$ scans	$h = -1 \rightarrow 10$
Absorption correction: ψ scan North A.C.T., Phillips D.C. & Mathews F.S. (1968) Acta. Cryst. A24, 351 Number of ψ scan sets used was 2 Theta correction was applied. Averaged transmission function was used. Fourier smoothing - Window value 5	$k = 0 \rightarrow 12$
$T_{min} = 0.856$, $T_{max} = 0.946$	$l = -8 \rightarrow 21$
1767 measured reflections	3 standard reflections every 91 reflections
1710 independent reflections	intensity decay: 6%

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.056$	H-atom parameters constrained
$wR(F^2) = 0.140$	$w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 0.3772P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} < 0.001$
1710 reflections	$\Delta\rho_{max} = 0.20$ e Å^{-3}
200 parameters	$\Delta\rho_{min} = -0.21$ e Å^{-3}
0 restraints	Absolute structure: Flack H D (1983), Acta Cryst. A39, 876-881
Primary atom site location: structure-invariant	Absolute structure parameter: -3 (4)

direct methods	

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.
Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²) for (**15a**)*

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.8214 (5)	0.2694 (5)	0.3534 (2)	0.0615 (12)
C2	0.9261 (5)	0.1662 (4)	0.2429 (2)	0.0544 (10)
C3	0.7825 (4)	0.2152 (4)	0.2769 (2)	0.0458 (9)
C4	0.6751 (4)	0.0906 (4)	0.2888 (2)	0.0474 (9)
H4A	0.7191	0.0325	0.3277	0.057*
H4B	0.5774	0.123	0.3077	0.057*
C5	0.6478 (4)	0.0079 (4)	0.2192 (2)	0.0438 (9)
C6	0.5401 (4)	0.0496 (3)	0.1659 (2)	0.0427 (8)
C7	0.4483 (4)	0.2624 (4)	0.12592 (18)	0.0413 (8)
C8	0.5766 (4)	0.3406 (4)	0.10805 (18)	0.0409 (8)
C9	0.7104 (4)	0.3353 (4)	0.23006 (18)	0.0437 (8)
H9A	0.6043	0.3455	0.2451	0.052*
H9B	0.7632	0.4187	0.2434	0.052*
C10	0.8526 (5)	0.3816 (5)	0.1139 (2)	0.0585 (11)
H10A	0.8637	0.352	0.062	0.088*
H10B	0.9416	0.3559	0.1425	0.088*
H10C	0.8415	0.4787	0.1151	0.088*
C11	0.7241 (5)	-0.1121 (4)	0.2053 (3)	0.0616 (11)
H11	0.7959	-0.1426	0.2405	0.074*
C12	0.6969 (6)	-0.1872 (5)	0.1413 (3)	0.0751 (15)
H12	0.751	-0.2672	0.133	0.09*
C13	0.5892 (7)	-0.1447 (5)	0.0888 (3)	0.0717 (15)
H13	0.5704	-0.1962	0.0453	0.086*
C14	0.5095 (5)	-0.0252 (4)	0.1011 (2)	0.0566 (11)
H14	0.4364	0.0042	0.0663	0.068*

C15	0.3095 (5)	0.2800 (4)	0.0890 (2)	0.0532 (10)
H15	0.2254	0.2275	0.1026	0.064*
C16	0.2970 (5)	0.3756 (5)	0.0322 (2)	0.0623 (12)
H16	0.2038	0.3894	0.0078	0.075*
C17	0.4226 (6)	0.4506 (5)	0.0115 (2)	0.0647 (12)
H17	0.4148	0.5126	-0.0284	0.078*
C18	0.5611 (5)	0.4353 (4)	0.0492 (2)	0.0516 (10)
H18	0.6443	0.4886	0.0352	0.062*
N1	0.8454 (6)	0.3102 (5)	0.4121 (2)	0.0930 (15)
N2	1.0350 (5)	0.1192 (4)	0.2179 (3)	0.0802 (13)
N3	0.7169 (3)	0.3180 (3)	0.14753 (15)	0.0408 (7)
O1	0.4574 (3)	0.1658 (2)	0.18347 (12)	0.0428 (6)

*Atomic displacement parameters (Å²) for (**15a**)*

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.064 (3)	0.067 (3)	0.054 (2)	-0.007 (2)	-0.015 (2)	0.009 (2)
C2	0.045 (2)	0.047 (2)	0.071 (3)	0.0020 (19)	-0.003 (2)	0.007 (2)
C3	0.0375 (19)	0.052 (2)	0.0484 (19)	-0.0014 (18)	-0.0053 (17)	0.0013 (17)
C4	0.046 (2)	0.048 (2)	0.0484 (19)	-0.0026 (18)	0.0002 (17)	0.0105 (17)
C5	0.0411 (19)	0.0399 (18)	0.051 (2)	-0.0041 (16)	0.0071 (17)	0.0123 (16)
C6	0.0428 (19)	0.0378 (17)	0.0476 (19)	-0.0082 (17)	0.0121 (17)	0.0017 (15)
C7	0.0440 (19)	0.0430 (19)	0.0370 (16)	0.0058 (17)	-0.0023 (16)	0.0004 (15)
C8	0.044 (2)	0.0435 (18)	0.0352 (17)	0.0060 (17)	-0.0013 (16)	-0.0006 (16)
C9	0.043 (2)	0.0408 (17)	0.0470 (19)	0.0007 (17)	-0.0030 (17)	-0.0039 (16)
C10	0.049 (2)	0.063 (2)	0.064 (3)	-0.008 (2)	0.006 (2)	0.007 (2)
C11	0.059 (3)	0.044 (2)	0.082 (3)	0.001 (2)	0.007 (2)	0.010 (2)
C12	0.082 (4)	0.045 (2)	0.099 (4)	0.009 (3)	0.026 (3)	-0.003 (3)
C13	0.098 (4)	0.050 (2)	0.066 (3)	-0.016 (3)	0.021 (3)	-0.014 (2)
C14	0.069 (3)	0.050 (2)	0.050 (2)	-0.014 (2)	0.004 (2)	0.0024 (19)
C15	0.045 (2)	0.060 (2)	0.054 (2)	0.004 (2)	-0.0075 (18)	-0.007 (2)
C16	0.057 (3)	0.074 (3)	0.056 (2)	0.013 (3)	-0.018 (2)	-0.003 (2)
C17	0.083 (3)	0.066 (3)	0.045 (2)	0.017 (3)	-0.010 (2)	0.009 (2)
C18	0.059 (2)	0.049 (2)	0.047 (2)	0.002 (2)	0.001 (2)	0.0090 (18)
N1	0.115 (4)	0.104 (3)	0.060 (2)	-0.015 (3)	-0.032 (3)	-0.003 (3)
N2	0.048 (2)	0.070 (2)	0.122 (3)	0.009 (2)	0.012 (2)	0.009 (3)
N3	0.0379 (16)	0.0442 (16)	0.0401 (15)	-0.0027 (14)	0.0028 (13)	0.0026 (13)
O1	0.0392 (12)	0.0483 (13)	0.0409 (12)	0.0032 (12)	0.0040 (11)	0.0032 (11)

*Geometric parameters (Å, º) for (**15a**)*

C1—N1	1.124 (5)	C7—O1	1.388 (4)
C1—C3	1.483 (6)	C7—C8	1.396 (5)
C2—N2	1.146 (5)	C8—C18	1.397 (5)
C2—C3	1.471 (6)	C8—N3	1.426 (4)
C3—C4	1.558 (5)	C9—N3	1.458 (4)
C3—C9	1.571 (5)	C10—N3	1.466 (5)
C4—C5	1.486 (5)	C11—C12	1.365 (7)
C5—C11	1.377 (5)	C12—C13	1.381 (7)
C5—C6	1.389 (5)	C13—C14	1.383 (6)
C6—C14	1.379 (5)	C15—C16	1.375 (6)
C6—O1	1.387 (4)	C16—C17	1.372 (7)
C7—C15	1.387 (5)	C17—C18	1.388 (6)
N1—C1—C3	177.5 (5)	O1—C7—C8	119.6 (3)
N2—C2—C3	175.3 (4)	C7—C8—C18	117.1 (3)
C2—C3—C1	106.8 (3)	C7—C8—N3	119.8 (3)
C2—C3—C4	108.1 (3)	C18—C8—N3	123.1 (3)
C1—C3—C4	107.4 (3)	N3—C9—C3	114.6 (3)
C2—C3—C9	112.2 (3)	C12—C11—C5	121.6 (4)
C1—C3—C9	107.1 (3)	C11—C12—C13	120.2 (4)
C4—C3—C9	114.8 (3)	C12—C13—C14	119.7 (4)
C5—C4—C3	114.7 (3)	C6—C14—C13	119.0 (4)
C11—C5—C6	117.6 (4)	C16—C15—C7	119.6 (4)
C11—C5—C4	122.4 (4)	C17—C16—C15	119.7 (4)
C6—C5—C4	120.0 (3)	C16—C17—C18	120.9 (4)
C14—C6—O1	121.5 (4)	C17—C18—C8	120.6 (4)
C14—C6—C5	121.8 (4)	C8—N3—C9	115.5 (3)
O1—C6—C5	116.6 (3)	C8—N3—C10	115.8 (3)
C15—C7—O1	118.4 (3)	C9—N3—C10	112.4 (3)
C15—C7—C8	122.0 (3)	C6—O1—C7	115.6 (2)

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Cyclizations with LC-MS monitoring

1) 10 mg vinyl compound was dissolved in 1 mL DMSO and heated at the indicated temperature with conventional heating (16 h) or with microwave irradiation (15 or 30 min)
2) 10 mg vinyl compound was dissolved in 1 mL MeCN or 1 mL DMSO, 0.1 eq of the indicated catalyst was added and the mixture was heated at the indicated temperature with conventional heating (MeCN, 16 h) or with microwave irradiation (DMSO)

***Table S4**. Reaction conditions tested for the cyclization of vinyl derivatives.*

Entry	Vinyl compound	Solvent	Temp.	Heating method	Reaction time	Catalyst	Result
1	**14a**	DMSO	50˚C	conv.	16 h	-	20% conversion 5% aldehyde
2		DMSO	75°C	conv.	16 h	-	40% conversion 15% aldehyde 10% oxazonine
3		DMSO	100°C	conv.	16 h	-	50% conversion 20% aldehyde 20% oxazonine
4		DMSO	125°C	conv.	16 h	-	70% conversion 7% aldehyde 20% oxazonine
5		DMSO	125°C	MW	15 min	-	30% conversion 7% aldehyde 20% oxazonine
6		DMSO	125°C	MW	30 min	-	60% conversion 10% aldehyde 25% oxazonine
7		DMSO	150°C	MW	15 min	-	75% conversion 10% aldehyde 58% oxazonine
8		DMSO	150°C	MW	30 min	-	85% conversion 12% aldehyde 54% oxazonine
9		DMSO	175°C	MW	15 min	-	full conversion 98% oxazonine
10		DMSO	175°C	MW	30 min	-	full conversion 85% oxazonine
11	**14b***	DMSO	50°C	MW	15 min	-	20% conversion 15% oxazonine
12		DMSO	50°C	MW	30 min	-	35% conversion 20% oxazonine
13		DMSO	75°C	MW	15 min	-	60% conversion 20% oxazonine 15% dimer
14		DMSO	75°C	MW	30 min	-	65% conversion 20% oxazonine 20% dimer
15		DMSO	100°C	MW	15 min	-	full conversion 22% oxazonine 32% dimer
16		DMSO	100°C	MW	30 min	-	full conversion complex mixture
17	**14c***	DMSO	50°C	MW	15 min	-	no conversion
18		DMSO	50°C	MW	30 min	-	decomposition

19		DMSO	75°C	MW	15 min	-	decomposition
20		DMSO	75°C	MW	30 min	-	complex mixture
21		DMSO	100°C	MW	15 min	-	complex mixture
22		DMSO	100°C	MW	30 min	-	complex mixture
23	**14d**	DMSO	125°C	MW	15 min	-	60% conversion 25% aldehyde 10% oxazonine
24		DMSO	125°C	MW	30 min	-	50% conversion 20% aldehyde 8% oxazonine
25		DMSO	150°C	MW	15 min	-	35% conversion 7% aldehyde 15% oxazonine
26		DMSO	150°C	MW	30 min	-	70% conversion 20% aldehyde 40% oxazonine
27		DMSO	175°C	MW	15 min	-	60% conversion 15% aldehyde 30% oxazonine
28		DMSO	175°C	MW	30 min	-	80% conversion 35% oxazonine
29	**14e***	DMSO	50°C	MW	15 min	-	decomposition
30		DMSO	50°C	MW	30 min	-	decomposition
31		DMSO	75°C	MW	15 min	-	complex mixture
32		DMSO	75°C	MW	30 min	-	complex mixture
33		DMSO	100°C	MW	15 min	-	complex mixture
34		DMSO	100°C	MW	30 min	-	complex mixture
35	**14f**	DMSO	50°C	MW	15 min	-	30% conversion 9% oxazonine
36		DMSO	50°C	MW	30 min	-	30% conversion 9% oxazonine
37		DMSO	75°C	MW	15 min	-	20% conversion
38		DMSO	75°C	MW	30 min	-	no conversion
39		DMSO	100°C	MW	15 min	-	no conversion
40		DMSO	100°C	MW	30 min	-	35% conversion 5% oxazonine
41		ACN	80°C	conv.	16 h	$Yb(OTf)_3$	<5% conversion
42		ACN	80°C	conv.	16 h	$Gd(OTf)_3$	15% conversion 10% aldehyde
43		ACN	80°C	conv.	16 h	$FeCl_3 \times 6H_2O$	<5% conversion
44		ACN	80°C	conv.	16 h	$Mg(ClO_4)_2$	5% conversion 5% aldehyde
45		ACN	80°C	conv.	16 h	$AlCl_3$	no conversion
46		DMSO	125°C	MW	15 min		30% conversion 15% oxazonine
47		DMSO	125°C	MW	30 min		30% conversion 15% oxazonine
48		DMSO	150°C	MW	15 min		20% conversion
49		DMSO	150°C	MW	30 min		no conversion
50		DMSO	175°C	MW	15 min		no conversion
51		DMSO	175°C	MW	30 min		35% conversion 15% oxazonine
52		ACN	100°C	MW	1 h	$Gd(OTf)_3$	10% conversion 3% aldehyde
53		ACN	100°C	MW	2 h	$Gd(OTf)_3$	15% conversion

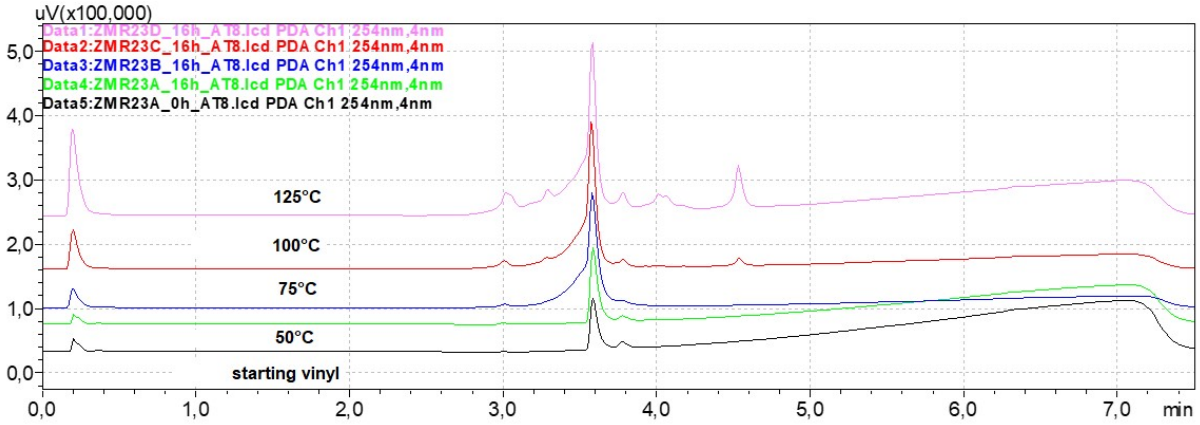
							5% aldehyde
54		ACN	100°C	MW	4 h	$Gd(OTf)_3$	20% conversion 10% aldehyde
55		ACN	100°C	MW	8 h	$Gd(OTf)_3$	15% conversion 10% aldehyde
56	**14g**	DMSO	125°C	MW	15 min		30% conversion decomposition
57		DMSO	125°C	MW	30 min		30% conversion decomposition
58		DMSO	150°C	MW	15 min		40% conversion decomposition
59		DMSO	150°C	MW	30 min		50% conversion decomposition
60		DMSO	175°C	MW	15 min		decomposition
61		DMSO	175°C	MW	30 min		decomposition
62		ACN	80°C	conv.	16 h	$Yb(OTf)_3$	full conversion peak 817, 819, 614
63		ACN	80°C	conv.	16 h	$Gd(OTf)_3$	full conversion peak 817, 819, 614
64		ACN	80°C	conv.	16 h	$FeCl_3 \times 6H_2O$	<5% conversion
65		ACN	80°C	conv.	16 h	$Mg(ClO_4)_2$	full conversion peak 817, 819, 614
66	**14h**	ACN	80°C	conv.	16 h	$Yb(OTf)_3$	full conversion 55% dimer
67		ACN	80°C	conv.	16 h	$Gd(OTf)_3$	full conversion 70% dimer
68		ACN	80°C	conv.	16 h	$FeCl_3 \times 6H_2O$	<5% conversion
69		ACN	80°C	conv.	16 h	$Mg(ClO_4)_2$	full conversion 40% dimer
70		ACN	80°C	conv.	16 h	$AlCl_3$	60% conversion 55% dimer
71		DMSO	125°C	MW	15 min	-	30% conversion
72		DMSO	125°C	MW	30 min	-	25% conversion
73		DMSO	150°C	MW	15 min	-	30% conversion
74		DMSO	150°C	MW	30 min	-	30% conversion
75		DMSO	175°C	MW	15 min	-	decomposition
76		DMSO	175°C	MW	30 min	-	decomposition
77	**14i**	DMSO	125°C	MW	15 min	-	20% conversion
78		DMSO	125°C	MW	30 min	-	20% conversion
79		DMSO	150°C	MW	15 min	-	10% conversion 5% oxazonine
80		DMSO	150°C	MW	30 min	-	5% conversion 5% oxazonine
81		DMSO	175°C	MW	15 min	-	15% conversion 5% oxazonine
82		DMSO	175°C	MW	30 min	-	30% conversion 5% oxazonine decomposition
83		ACN	80°C	conv.	16 h	$Yb(OTf)_3$	30% conversion
84		ACN	80°C	conv.	16 h	$Gd(OTf)_3$	70% conversion 50% M_w 687 20% M_w 884
85		ACN	80°C	conv.	16 h	$FeCl_3 \times 6H_2O$	complex mixture
86		ACN	80°C	conv.	16 h	$Mg(ClO_4)_2$	<5% conversion

*: due to high decomposition rate, no higher temperatures were tested

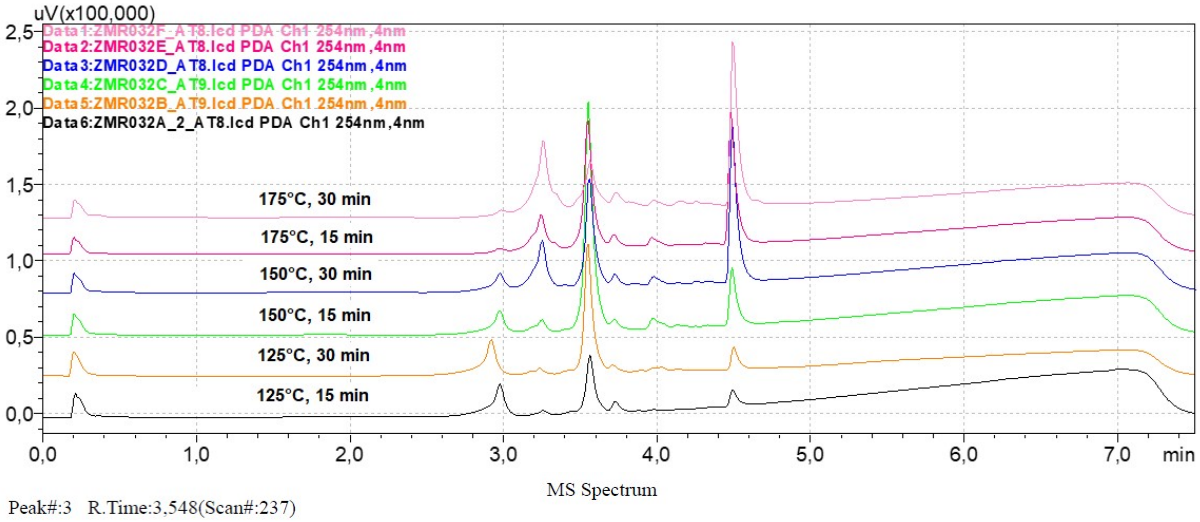
Representative reaction monitoring data (LC-MS)

Compound 14d

Conventional heating for 16 h at the indicated temperatures

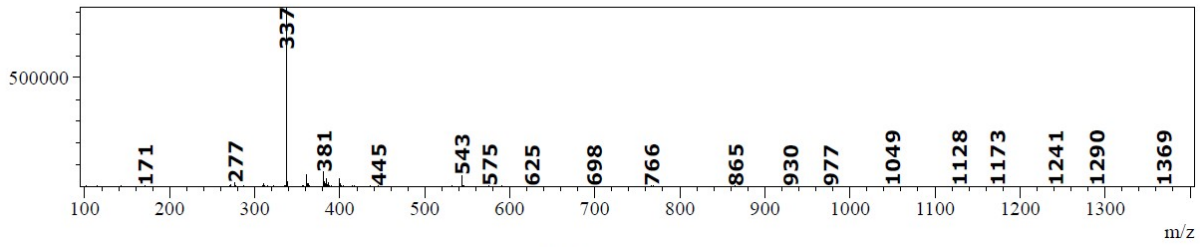


MW heating with the indicated conditions



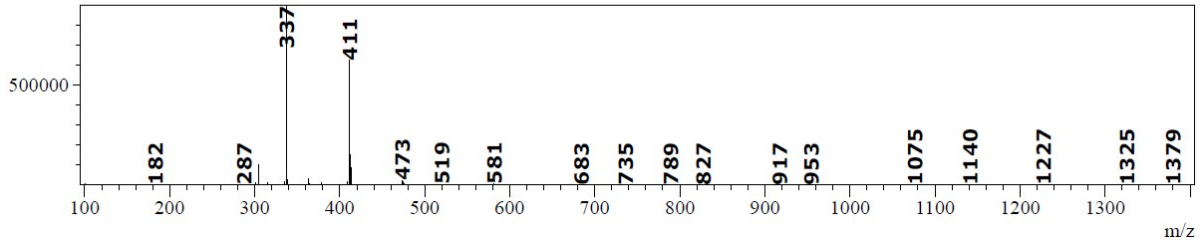
MS Spectrum

Peak#:3 R.Time:3.548(Scan#:237)



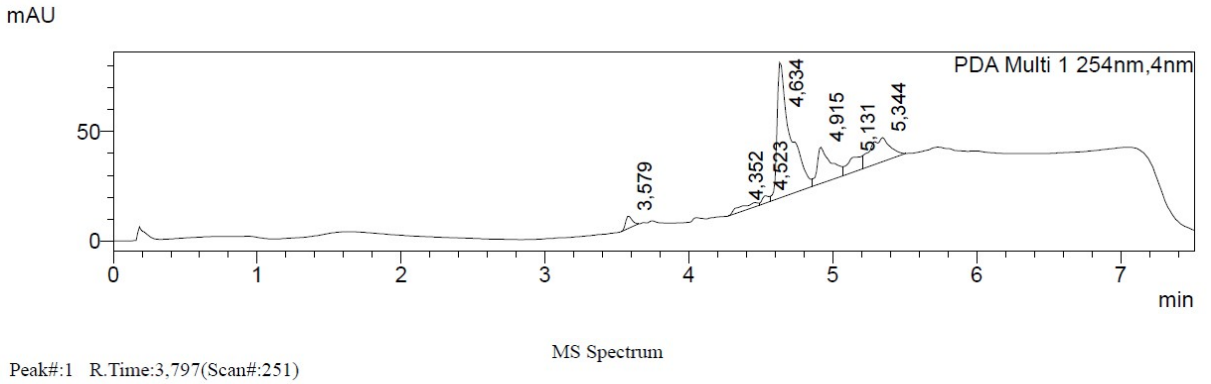
MS Spectrum

Peak#:4 R.Time:4.479(Scan#:293)



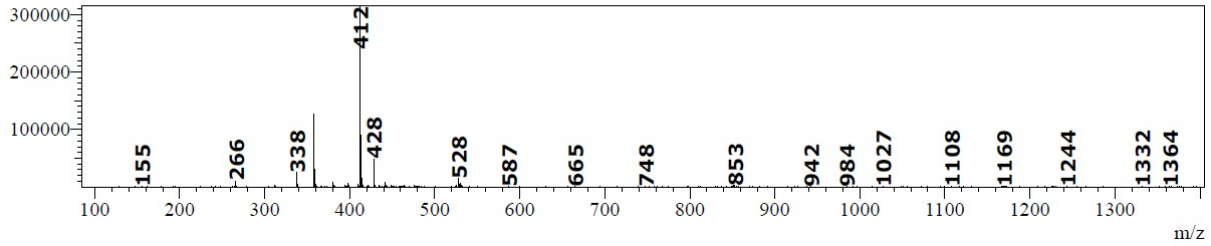
Compound 14h

Conventional heating in MeCN with $Gd(OTf)_3$



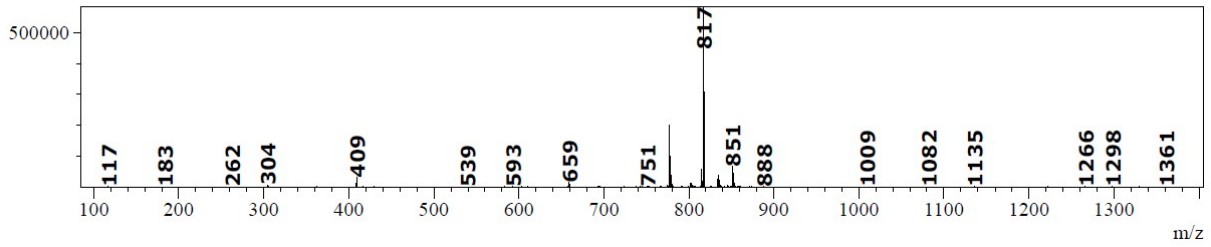
MS Spectrum

Peak#:1 R.Time:3,797(Scan#:251)



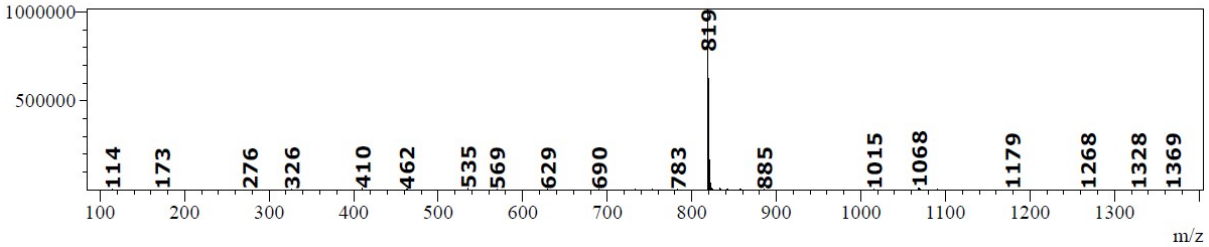
MS Spectrum

Peak#:2 R.Time:4,693(Scan#:305)

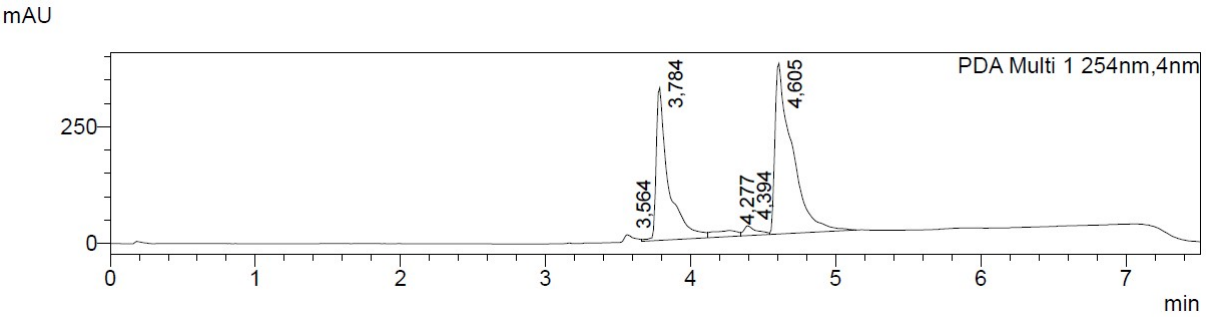


MS Spectrum

Peak#:3 R.Time:4,959(Scan#:321)

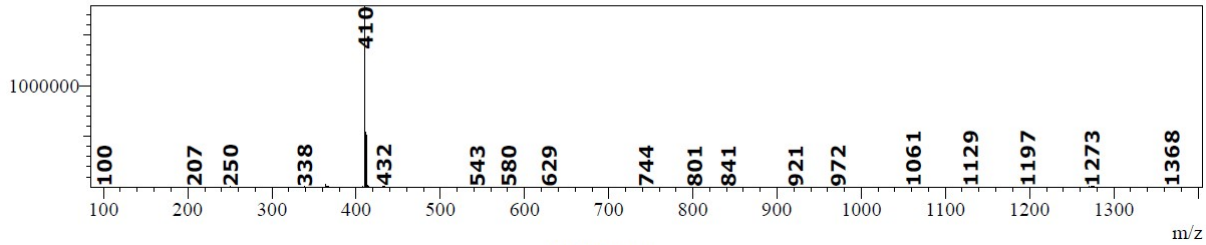


Conventional heating in MeCN with $AlCl_3$



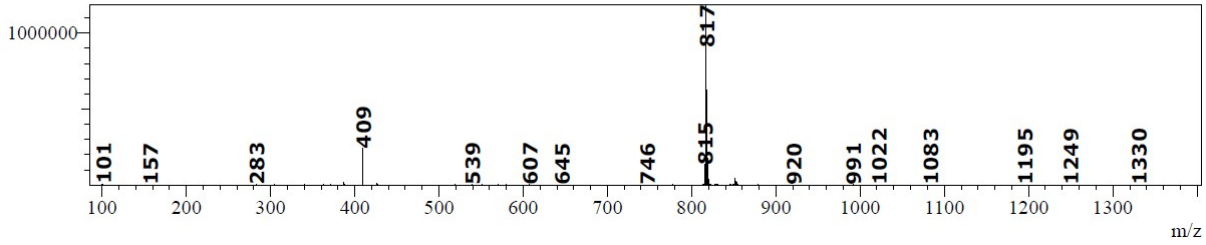
MS Spectrum

Peak#:1 R.Time:3,781(Scan#:251)

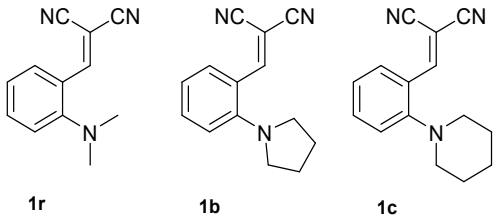


MS Spectrum

Peak#:2 R.Time:4,627(Scan#:301)



Cyclization studies with photoirradiation



I) Measurement of UV/VIS Spectra and the Molar Extinction Coefficients (ε)

Spectroscopic characterization has been performed on a Shimadzu UV-1900i spectrophotometer (quartz cell, Hellma, path length: 1.0 cm).

UV−VIS spectra were measured for a 0.05 mM solution of the compounds in DMSO or acetonitrile. A blank solution of the solvents were used to subtract baseline absorption. The spectra were recorded between 260 and 800 nm. ε values were calculated using the Beer−Lambert law: $\varepsilon = A(cl)^{-1}$, where *A* is the absorbance value measured at each wavelength, *c* is the concentration of the sample, and *l* is the cuvette length.

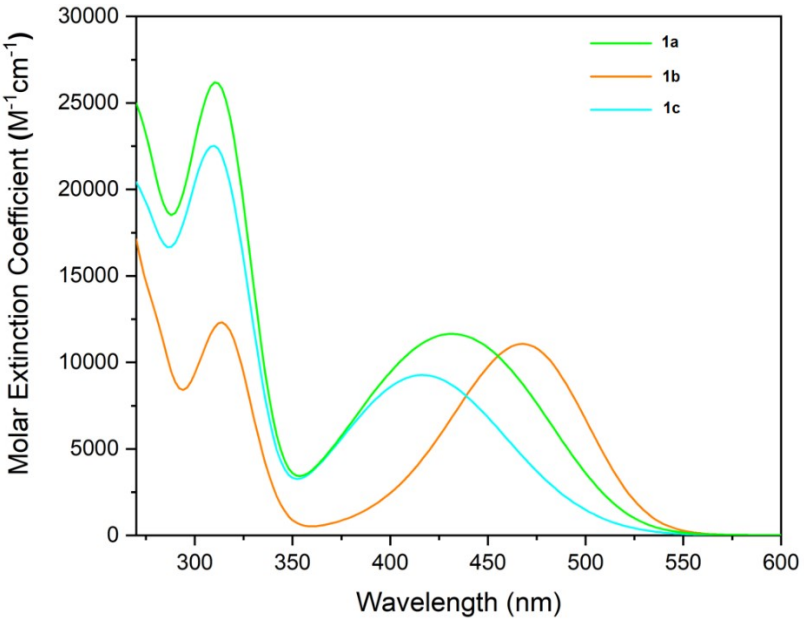


Figure S8. UV-VIS spectra in DMSO of compounds **1r**, **1b** and **1c**.

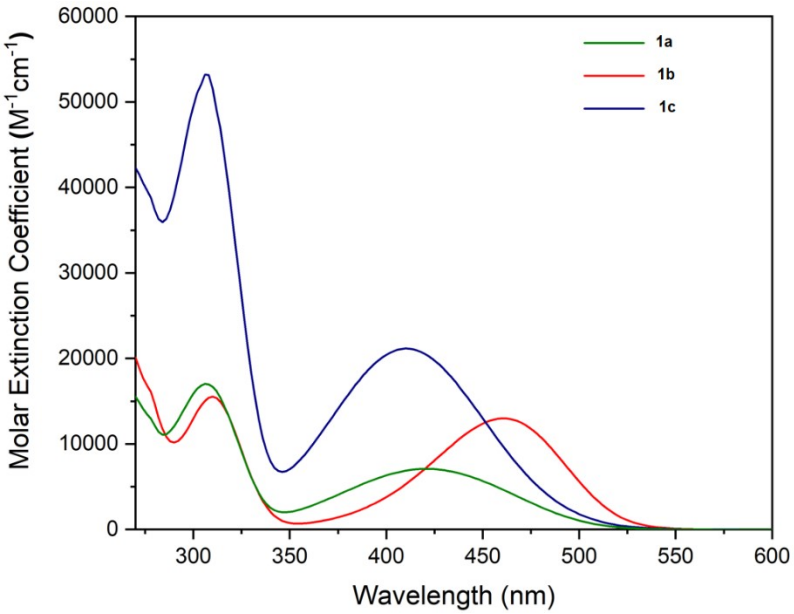


Figure S9. UV-VIS spectra in MeCN of compounds **1r**, **1b** and **1c**.

	MeCN	DMSO	Irradiated at:
1r	420 nm	432 nm	395 nm
1b	460 nm	468 nm	500 nm
1c	410 nm	416 nm	395 nm

Absorption maxima and irradiation wavelengths.

II) Photoirradiation experiments in PhotoCube

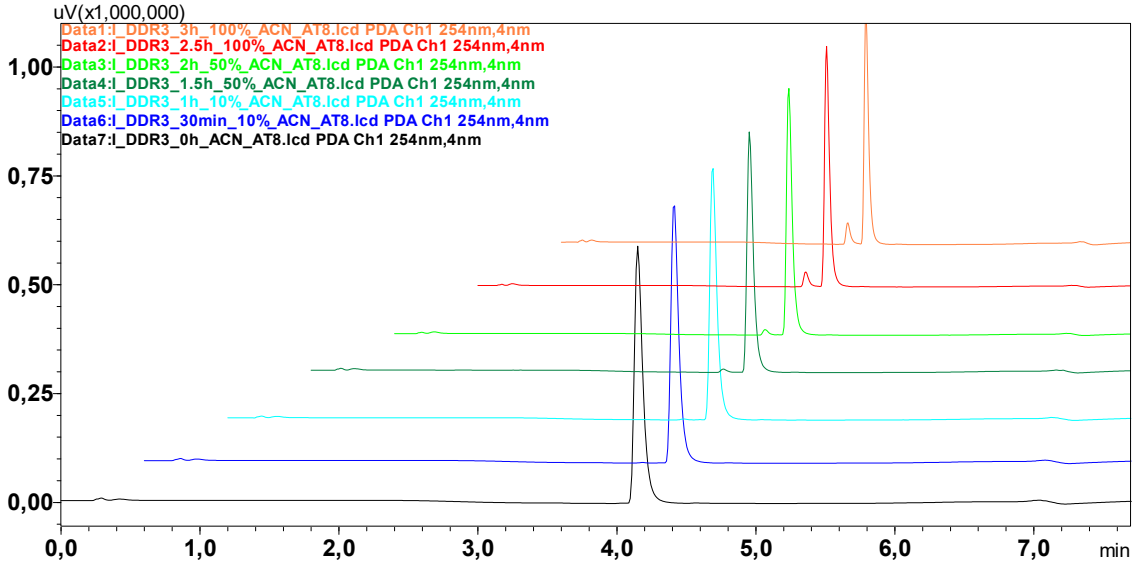
Irradiation power	**Irradiation time**	**1r** DMSO	**1r** MeCN	**1b** DMSO	**1b** MeCN	**1c** DMSO	**1c** MeCN
		Ratio of vinyl derivative and cyclized product					
10%	30 min	99:0	100:0	80:19*	90:9	93:5	98:1
10%	1 h	98:0	100:0	80:19**	90:10**	93:5	98:1
50%	30 min	98:1	99:1	72:27	86:13	90:8	98:2
50%	1 h	96:2	98:2	70:29	85:15	89:9	97:3
100%	30 min	94:5	94:6	62:37	78:21	86:12	96:4
100%	1 h	91:8	91:9	53:45	72:28	84:14	94:6

*in a control experiment, the reaction proceeded at rt, under ambient light

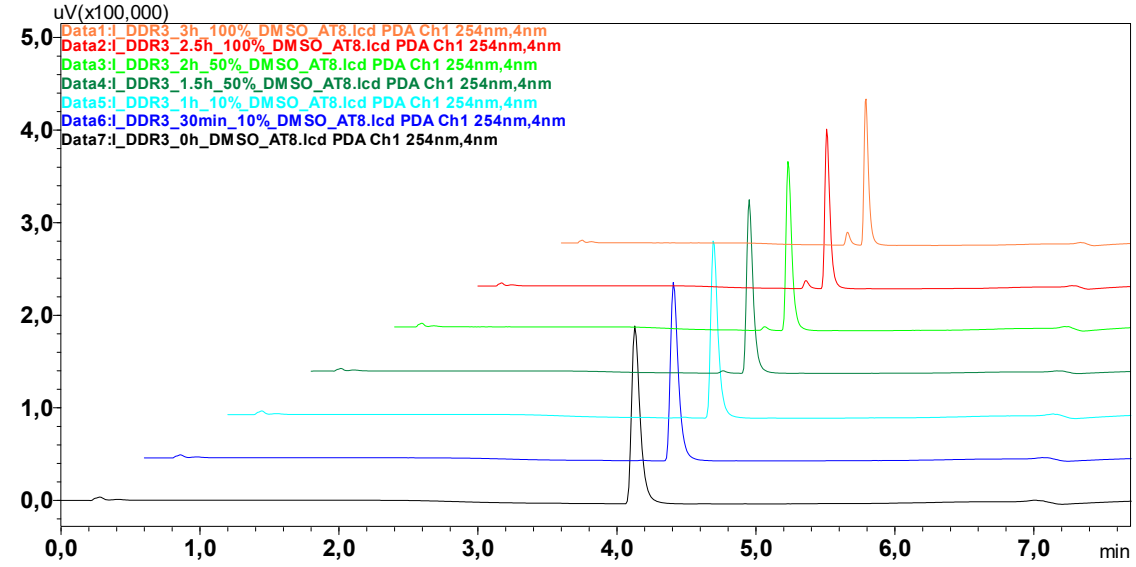
**in a control experiment, the reaction proceeded at rt, under dark conditions

LC-MS monitoring of the photoirradiation experiments

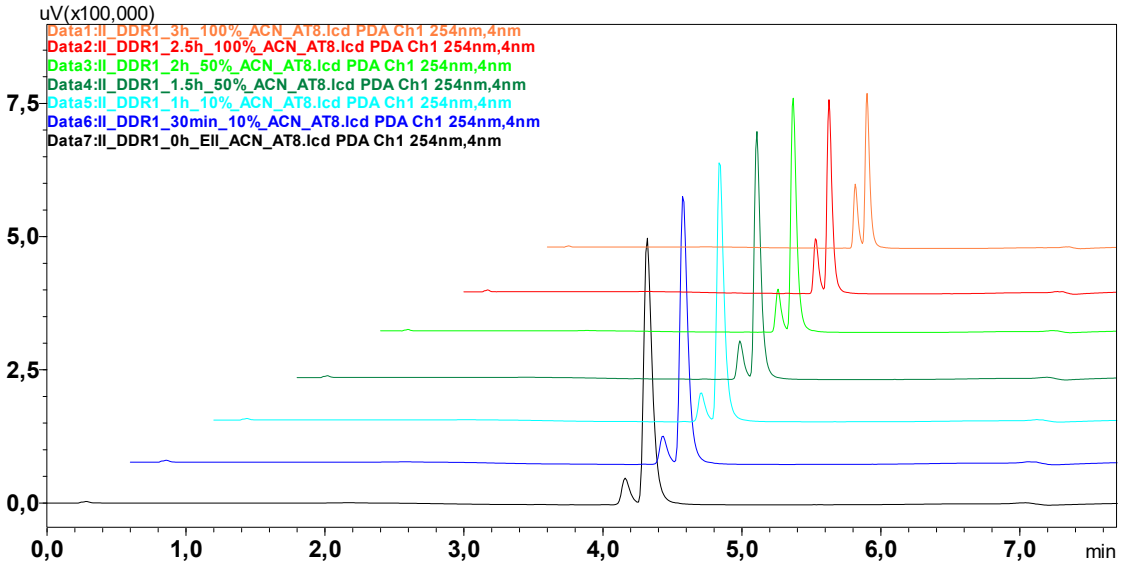
1r (ACN)



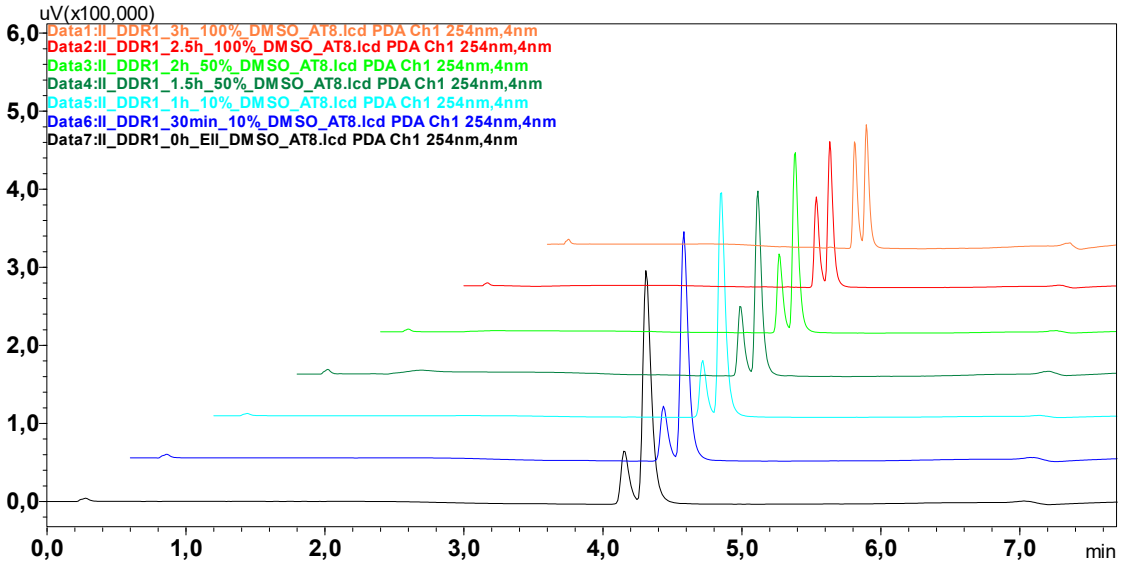
1r (DMSO)



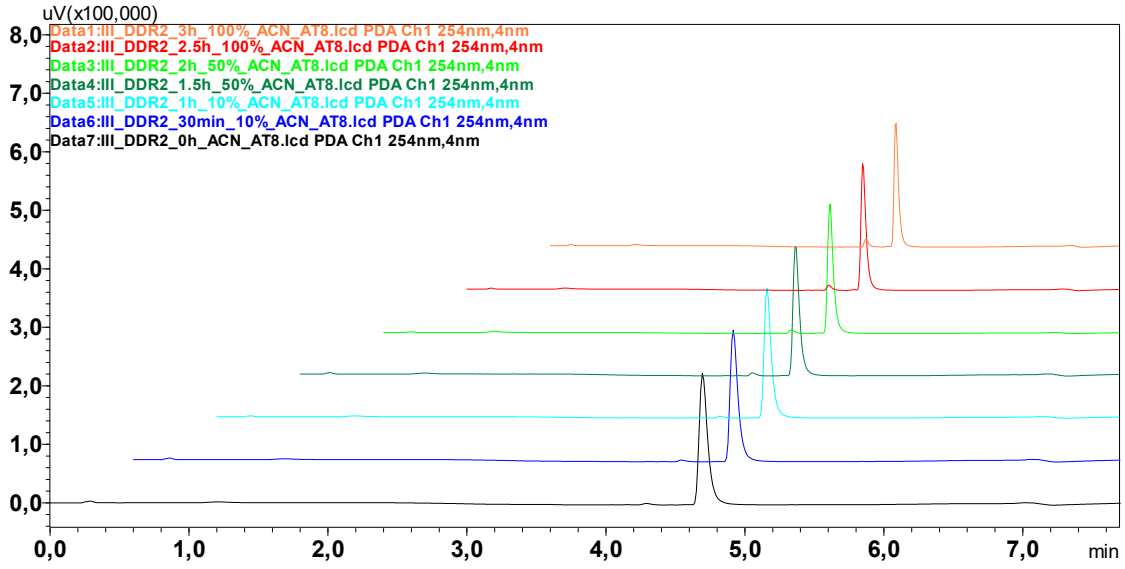
1b (ACN)



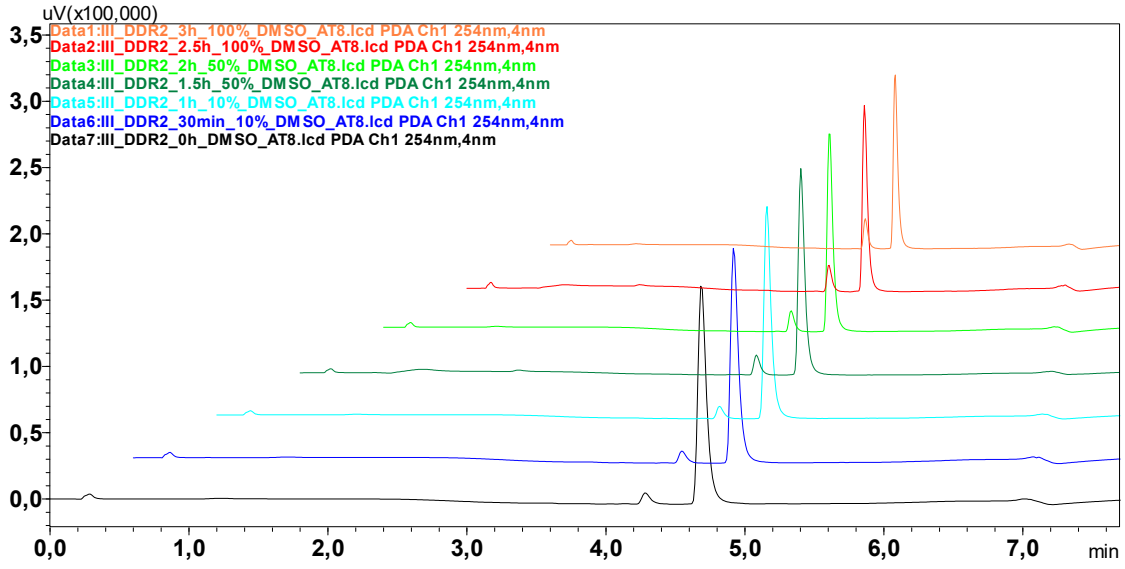
1b (DMSO)



1c (ACN)



1c (DMSO)



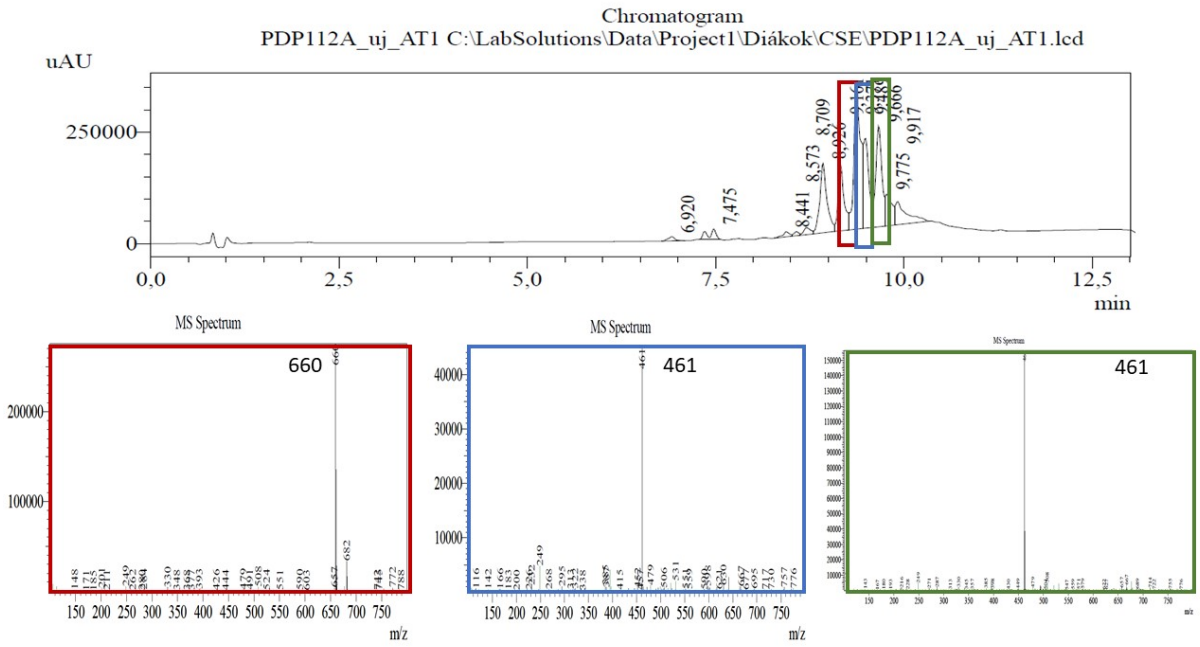
Cyclization studies on 35

Table S5*. Reaction conditions tested for the cyclization of vinyl derivative* ***35****.*

Entry	Solvent	Temperature	Time	Catalyst
1	MeCN	80°C	16 h	$Gd(OTf)_3$
2	MeCN	80°C	16 h	$Yb(OTf)_3$
3	MeCN	80°C	16 h	$Mg(ClO_4)_2$
4	DMSO	100°C (MW)	30 min	-
5	DMSO	75°C (MW)	30 min	-
6	DMSO	50°C (MW)	30 min	-
7	MeCN	80°C (MW)	1 h	-
8	MeCN	80°C (MW)	1 h	$Gd(OTf)_3$
9	MeCN	80°C (MW)	1 h	$Gd(OTf)_3$

For entries 1-7 mainly decomposition was observed. For entry 8, the formation of 3 novel products was detected. Entry 9 was a scale-up experiment, using the same conditions as for entry 8.

LC-MS results obtained for entry 9:



Cyclization studies on 38a,b[1]

Table S6*. Reaction conditions tested for the cyclization of vinyl derivatives* ***38a,b****.*

Entry	Solvent	Temperature	Time	Catalyst
1	DMSO	50°C	1 h	-
2	DMSO	50°C	5 h	-
3	DMSO	75°C	30 min	-
4	DMSO	75°C	1 h	-
5	DMSO	100°C	15 min	-
6	DMSO	100°C	30 min	-
7	DMSO	125°C	30 min	-
8	DMSO	150°C	1 h	-
9	neat	75°C	30 min	-
10	neat	75°C	1 h	-
11	neta	100°C	30 min	-
12	neat	120°C	30 min	-
13	neat	150°C	30 min	-
14	neat	200°C	2 min	-
15	neat	120°C	2 h	Al_2O_3
16	MeCN	60°C	2 h	$Gd(OTf)_3$

Under all the conditions tested only decomposition was observed and the corresponding cyclized products could not be isolated.

[1]P. Bottino, Studies on extensions of tert-amino effect: Ring-fusion to bridged biaryls and steroids, PhD Thesis, 2012, Universitá degli Studi di Catania, http://archivia.unict.it/handle/10761/1349 (accessed Dec 2023).

Theoretical methods

Theoretical calculations were carried out by Gaussian16 software [1], using the standard convergence criteria given as default. Optimization and vibrational frequencies were carried out by the B3LYP method [2,3] using the 6-31G(d,p) basis set and the IEFPCM method for implicit solvent model. Thermodynamic functions were computed at 298.15 K.

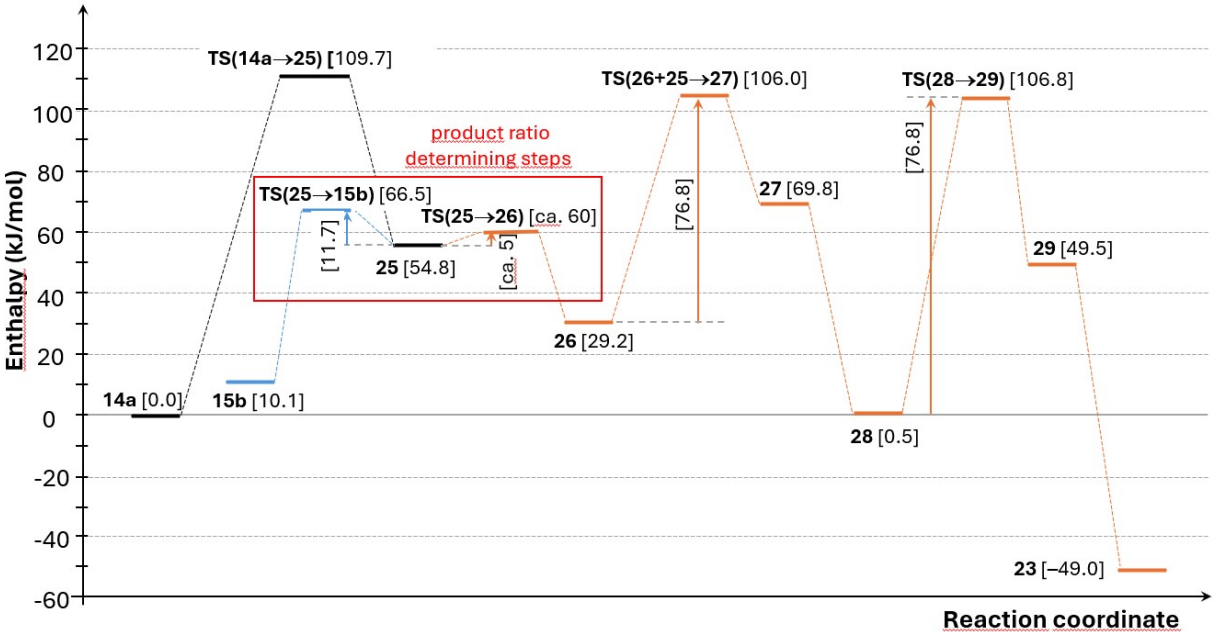


Figure S10. Calculated enthalpies for the two possible reaction pathways branching from the common **25** intermediate.

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4. J. Tomasi, B. Mennucci and R. Cammi, Chem. Rev., 2005, 105, 2999–3094.