

# **Supporting Information**

## *Anti-Selective Organocatalytic Michael Addition between Phenylacetaldehyde and Nitrostyrene*

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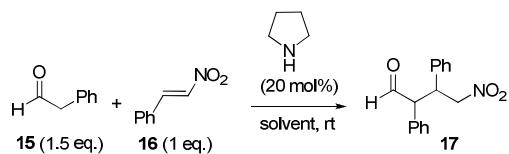
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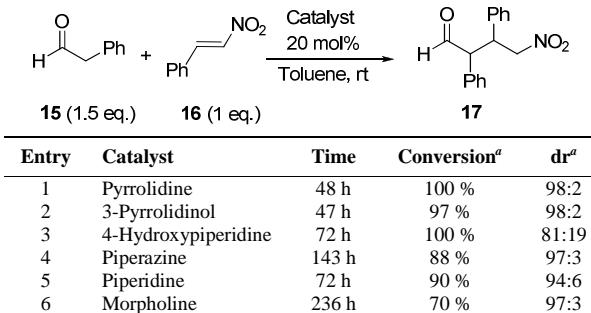
**Table S1: Michael addition between 15 and 16 in different solvents.**



Entry	Solvent <sup>a</sup>	time	Conversion <sup>b</sup>	dr <sup>b</sup>
1	Toluene	48 h	100 %	98:2
2	CH <sub>2</sub> Cl <sub>2</sub>	27 h	100 %	90:10
3	CHCl <sub>3</sub>	27 h	100 %	93:7
4	DMF	48 h	100 %	95:5
5	CH <sub>3</sub> CN	44 h	100 %	97:3
6	THF	118 h	100 %	93:7
7	iPrOH	25 h	96 %	97:3

<sup>a</sup>Anhydrous solvent were used. <sup>b</sup>Determined by <sup>1</sup>H NMR of crude product.

**Table S2. Michael addition between 15 and 16 catalyzed by secondary amines.**



Entry	Catalyst	Time	Conversion <sup>a</sup>	dr <sup>a</sup>
1	Pyrrolidine	48 h	100 %	98:2
2	3-Pyrrolidinol	47 h	97 %	98:2
3	4-Hydroxypiperidine	72 h	100 %	81:19
4	Piperazine	143 h	88 %	97:3
5	Piperidine	72 h	90 %	94:6
6	Morpholine	236 h	70 %	97:3

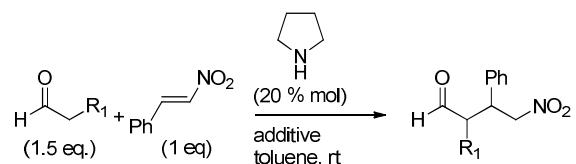
<sup>a</sup>Determined by <sup>1</sup>H NMR of crude mixtures.

**Table S3. Michael addition between 15 and 16 with varying pyrrolidine loadings.**

Entry	Mol [%]	Time	Conversion <sup>a</sup>	dr <sup>a</sup>
1	5	48 h	21 %	37:62
2	10	48 h	86 %	79:21
3	15	48 h	100 %	87:13
4	20	48 h	100 %	98:2

<sup>a</sup>Determined by <sup>1</sup>H NMR of crude mixtures.

**Table S4. Effect of Acetic Acid addition in the Michael Addition.<sup>a</sup>**



Entry	$\text{R}_1$	HAcO [mol %]	Time [h]	Conversion <sup>b</sup> [%]	dr <sup>b</sup>
1	Ph	---	23	87	96:4
2	Ph	5	23	72	97:3
3	$(\text{CH}_2)_3\text{CH}_3$	----	3.5	100	38:62
4	$(\text{CH}_2)_3\text{CH}_3$	5	0.8	100	39:61

<sup>a</sup>The same general experimental procedure was followed except the addition of 5 mol% of HAcO. <sup>b</sup>Determined by <sup>1</sup>H NMR of crude mixtures.

## X-ray Crystallography

A single crystal of **13a** and **17a** were submitted to X-ray data collections by using a Xcalibur, Sapphire3 (Oxford Diffraction Ltd., U.K.) four-circle diffractometer with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda=0.71073\text{\AA}$ ). The structures were solved by direct methods implemented in SHELXS-2013 program. The refinement was carried out by full-matrix anisotropic least-squares on F<sup>2</sup> for all reflections for non-H atoms by using the SHELXL-2013 program.

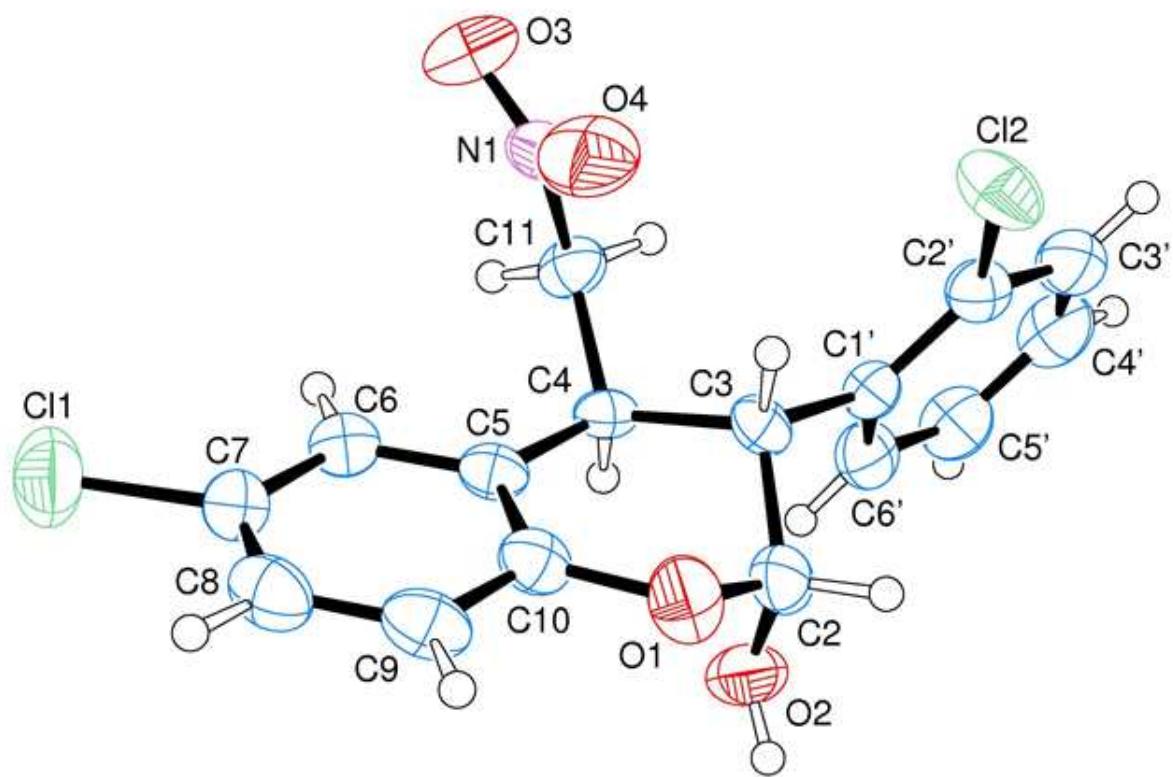
### **13a:**

C<sub>16</sub>H<sub>13</sub>Cl<sub>2</sub>NO<sub>4</sub>, M=354.17, Orthorhombic, a = 5.8820(3), b = 14.7971(9), c = 17.7539(13) Å U = 1545.24(17) Å<sup>3</sup>, T= 293 K, space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (no. 19), Z = 4, 3446 reflections measured, 1420 unique (I > 2σ<sub>(I)</sub> Rint = 0.042). The final wR<sub>2</sub> was 0.056 (all data).

### **17a:**

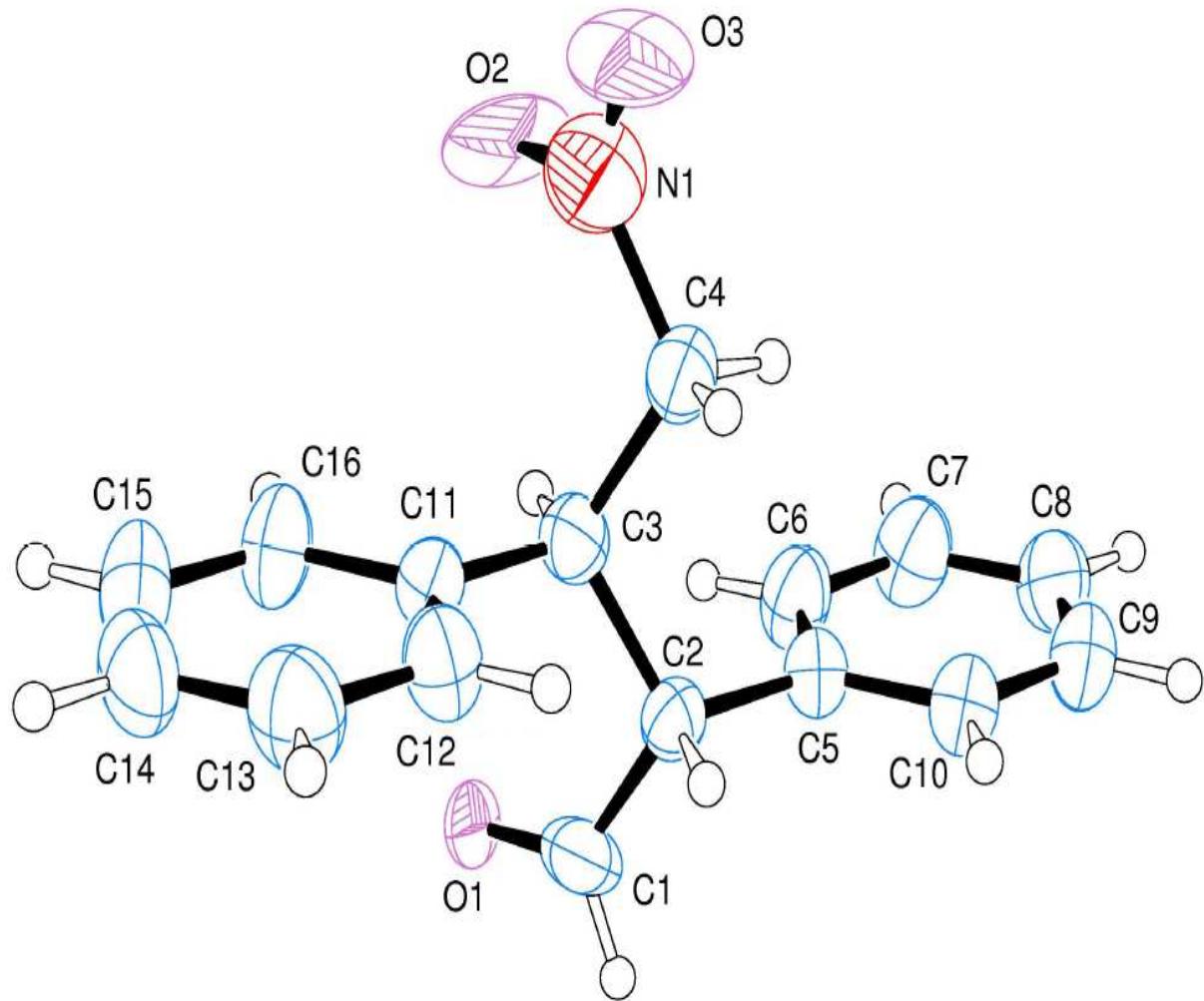
C<sub>16</sub>H<sub>15</sub>NO<sub>3</sub>, M=269.29, Monoclinic, a=5.8149(7), b=7.7454(9), c=15.5132(13)Å, β=95.543(8), U = 695.43(13)Å<sup>3</sup>, T= 293 K, space group Pn (no. 7), Z = 2, 2779 reflections measured, 1274 unique (I > 2σ<sub>(I)</sub> Rint = 0.028). The final wR<sub>2</sub> was 0.067 (all data).

Crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no.CCDC 1462871 (**17a**) and 1462872 (**13a**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

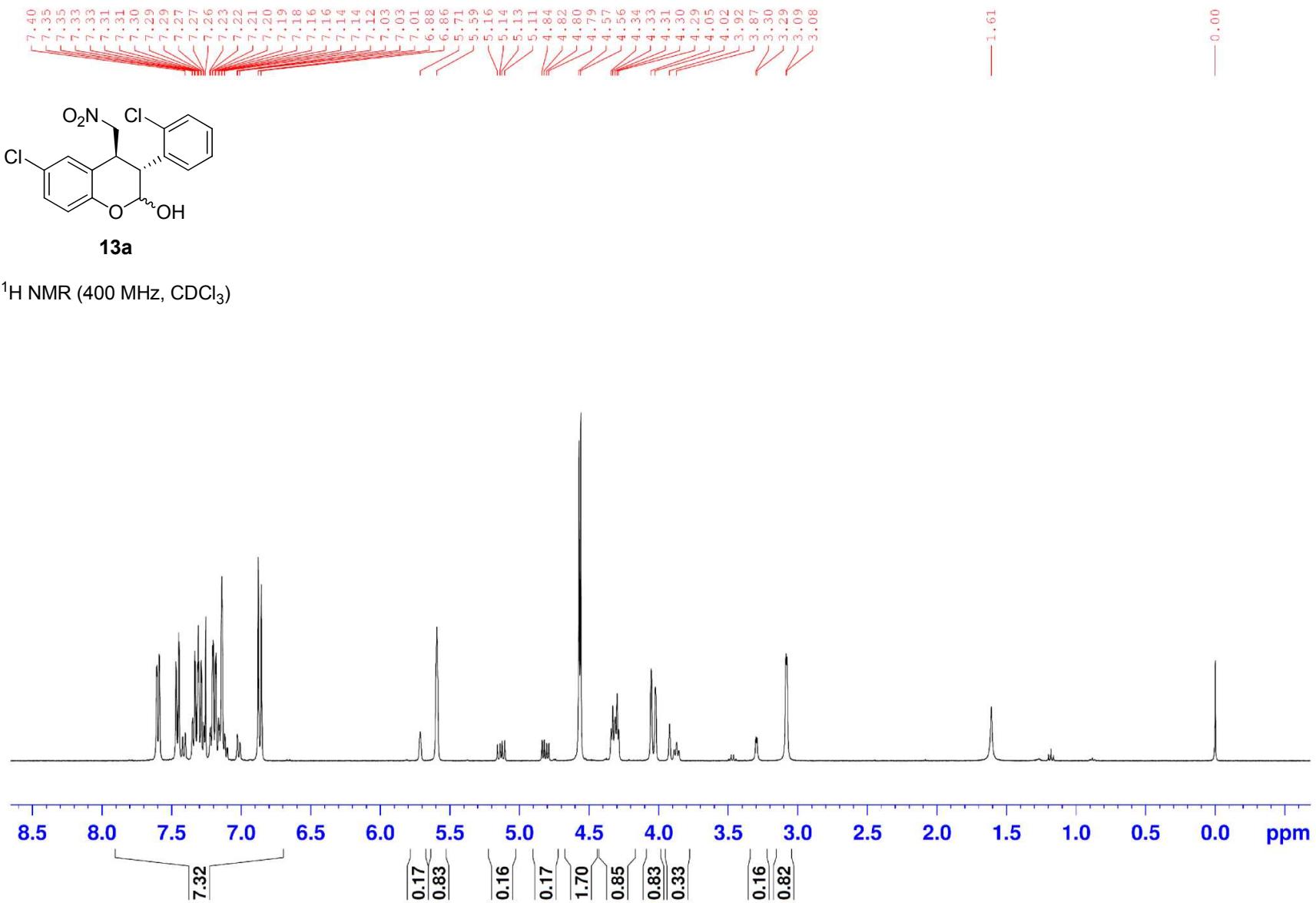


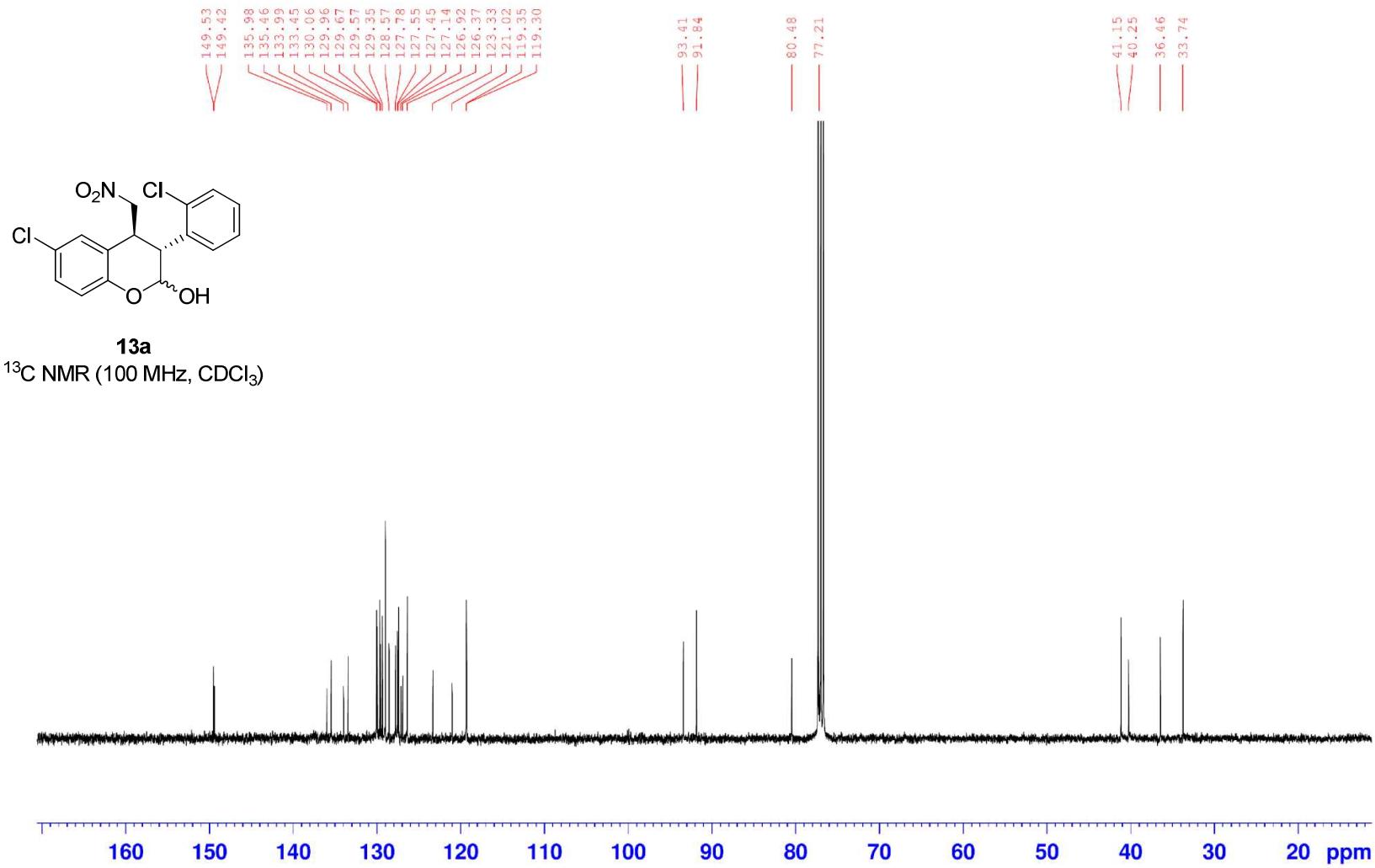
**Figure S1.** X-ray structure of **13a**. Ellipsoids enclose 50% probability.

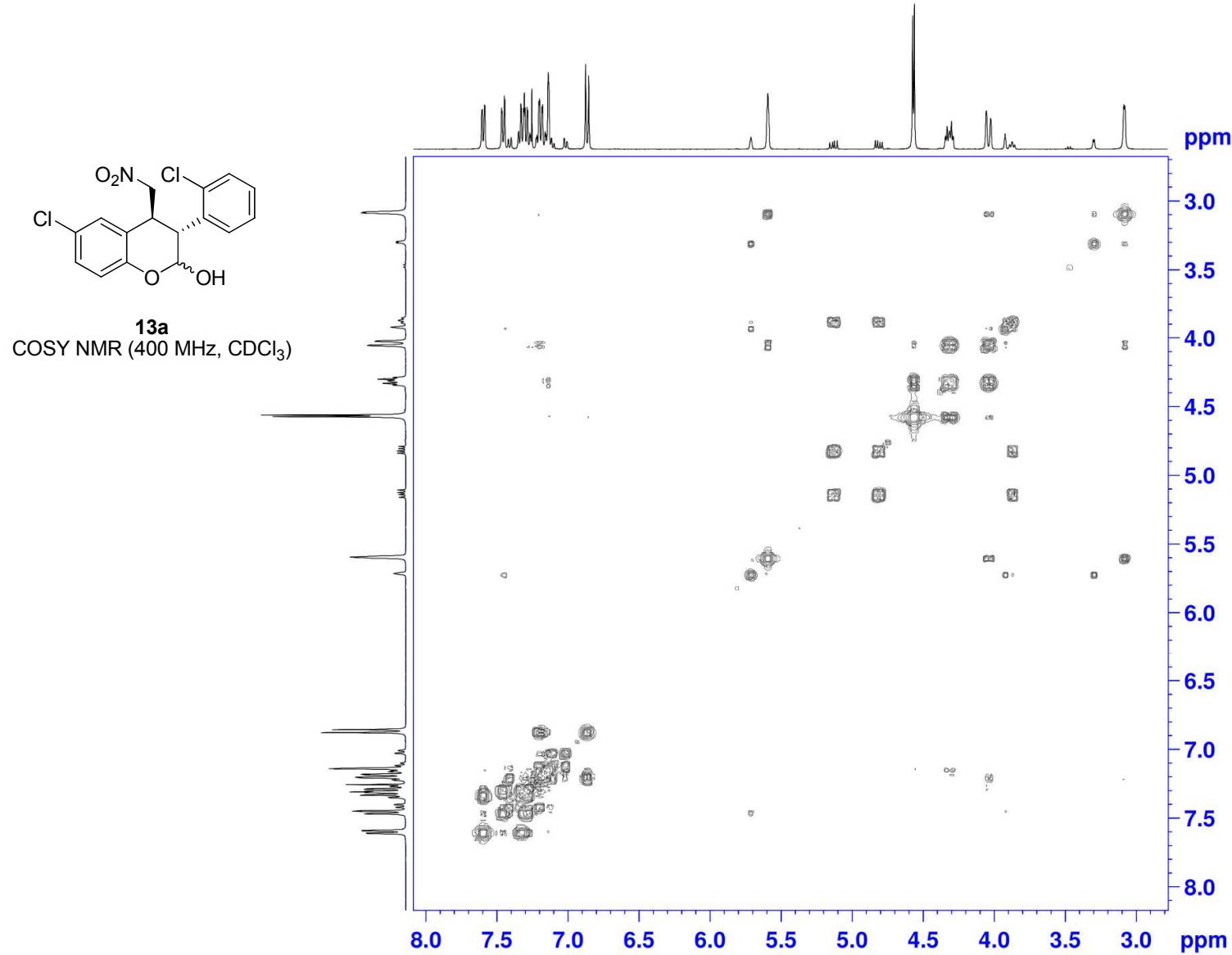
I

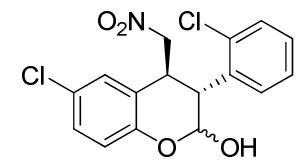


**Figure S2.** X-ray structure of **17a**. Ellipsoids enclose 50% probability.

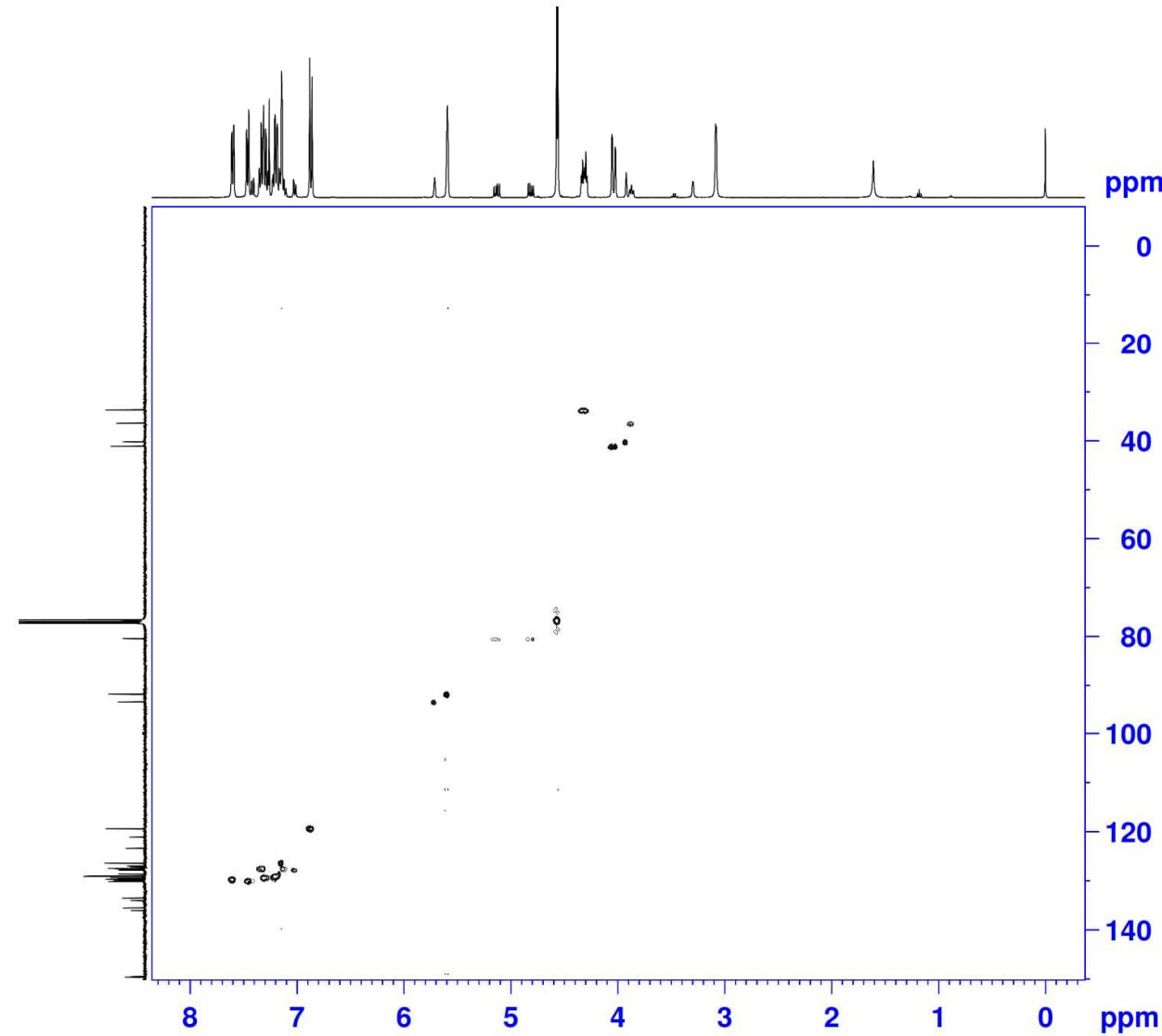


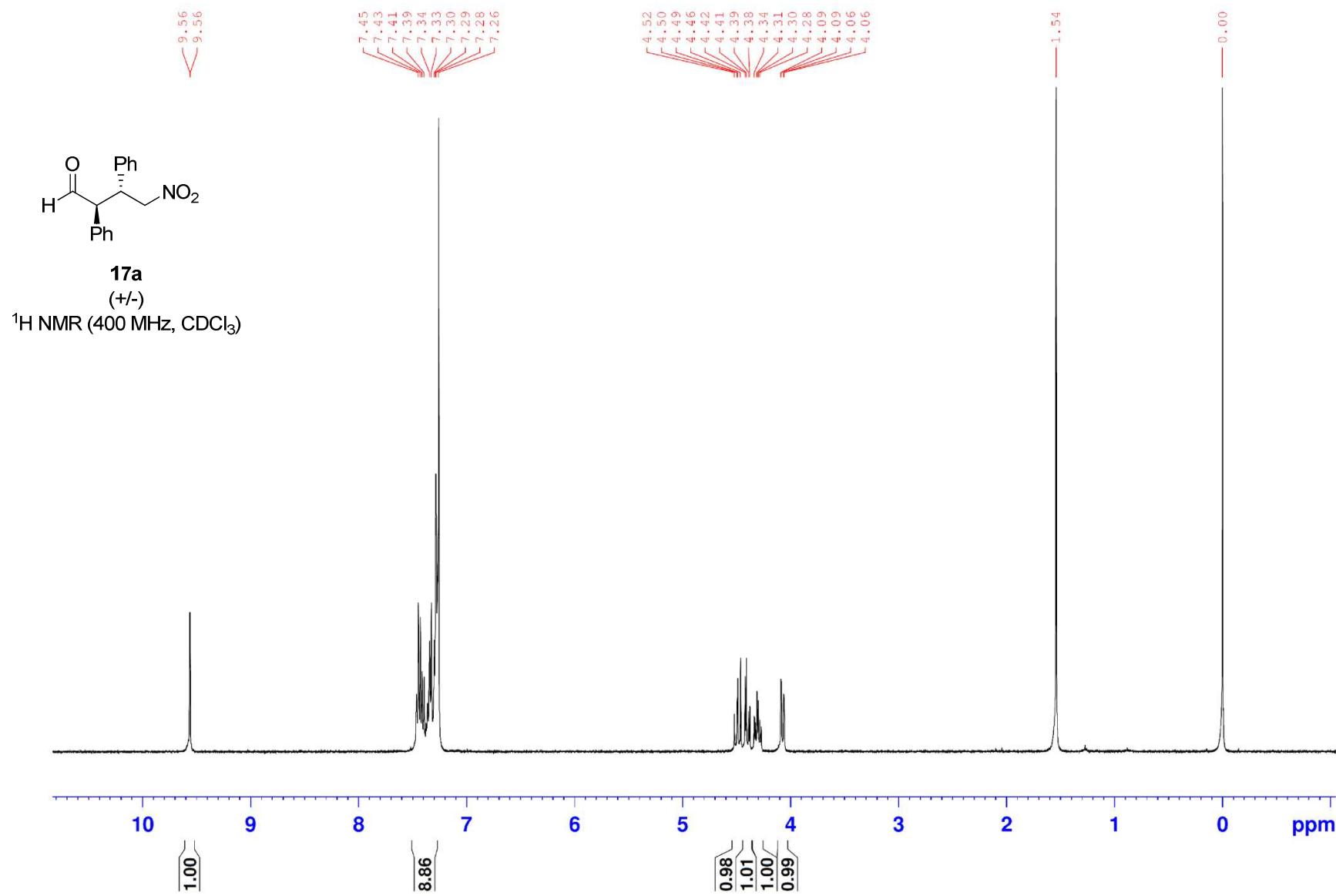


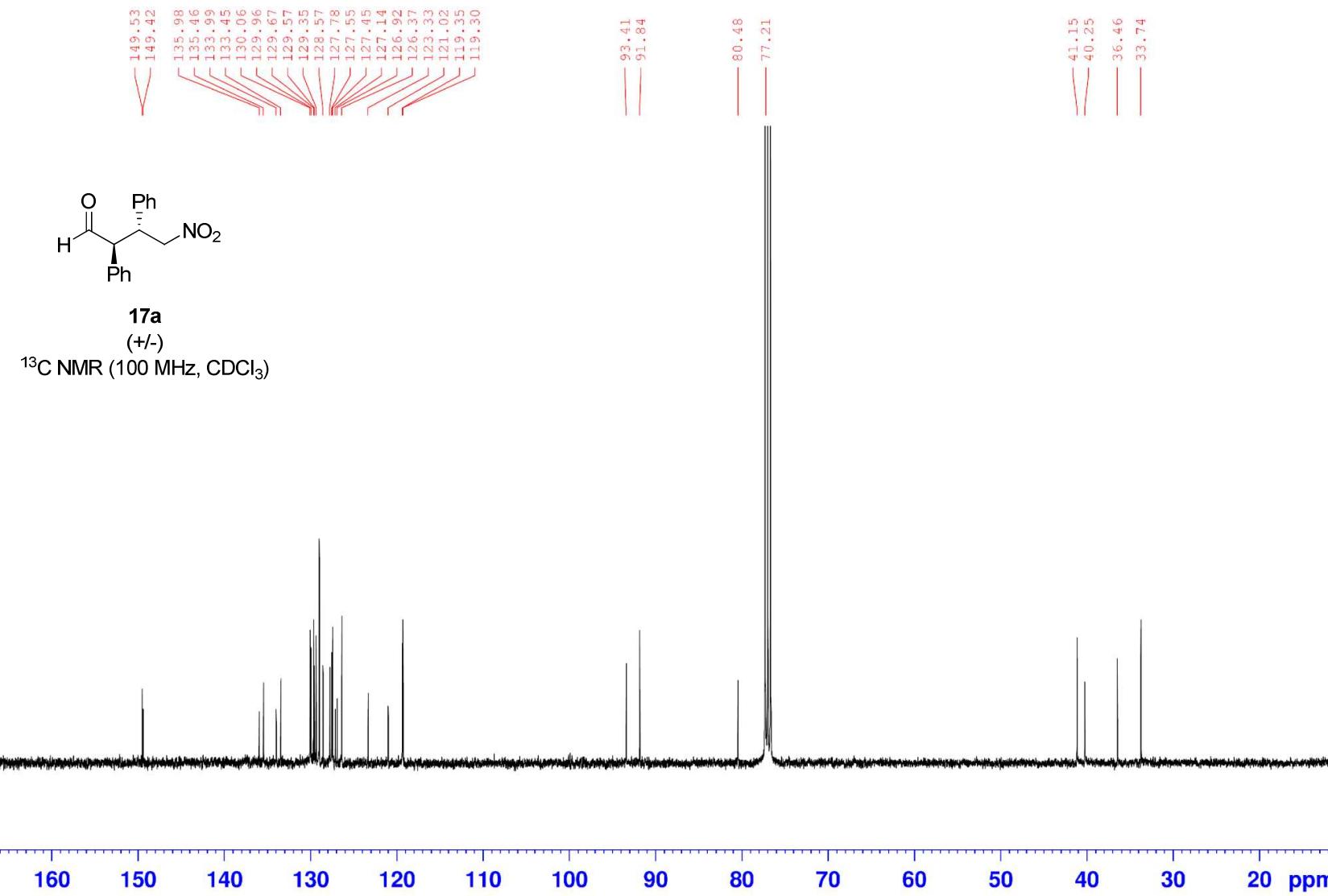


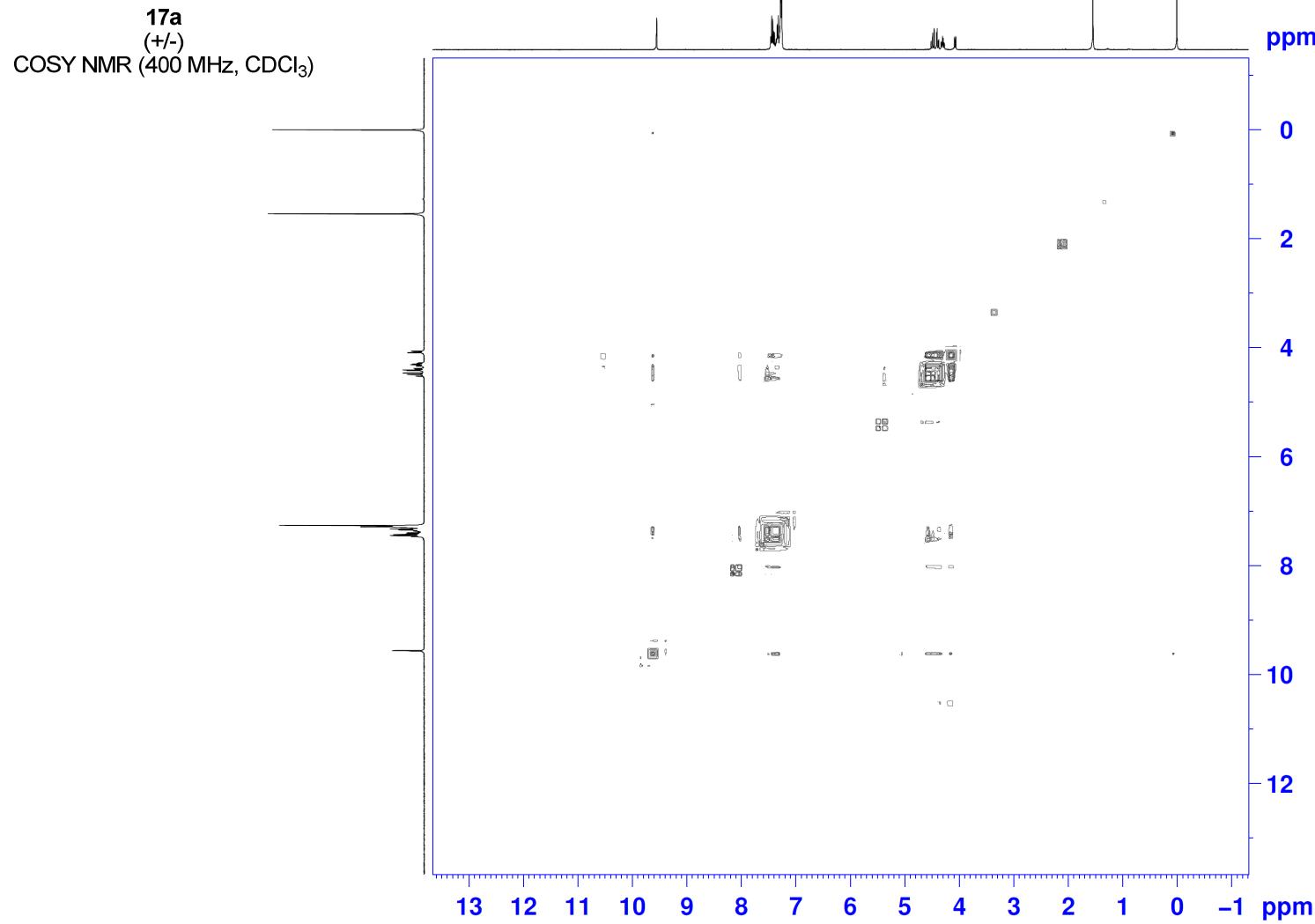
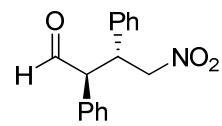


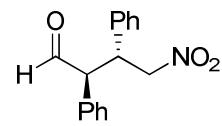
**13a**  
HSQC NMR (400 MHz,  $\text{CDCl}_3$ )



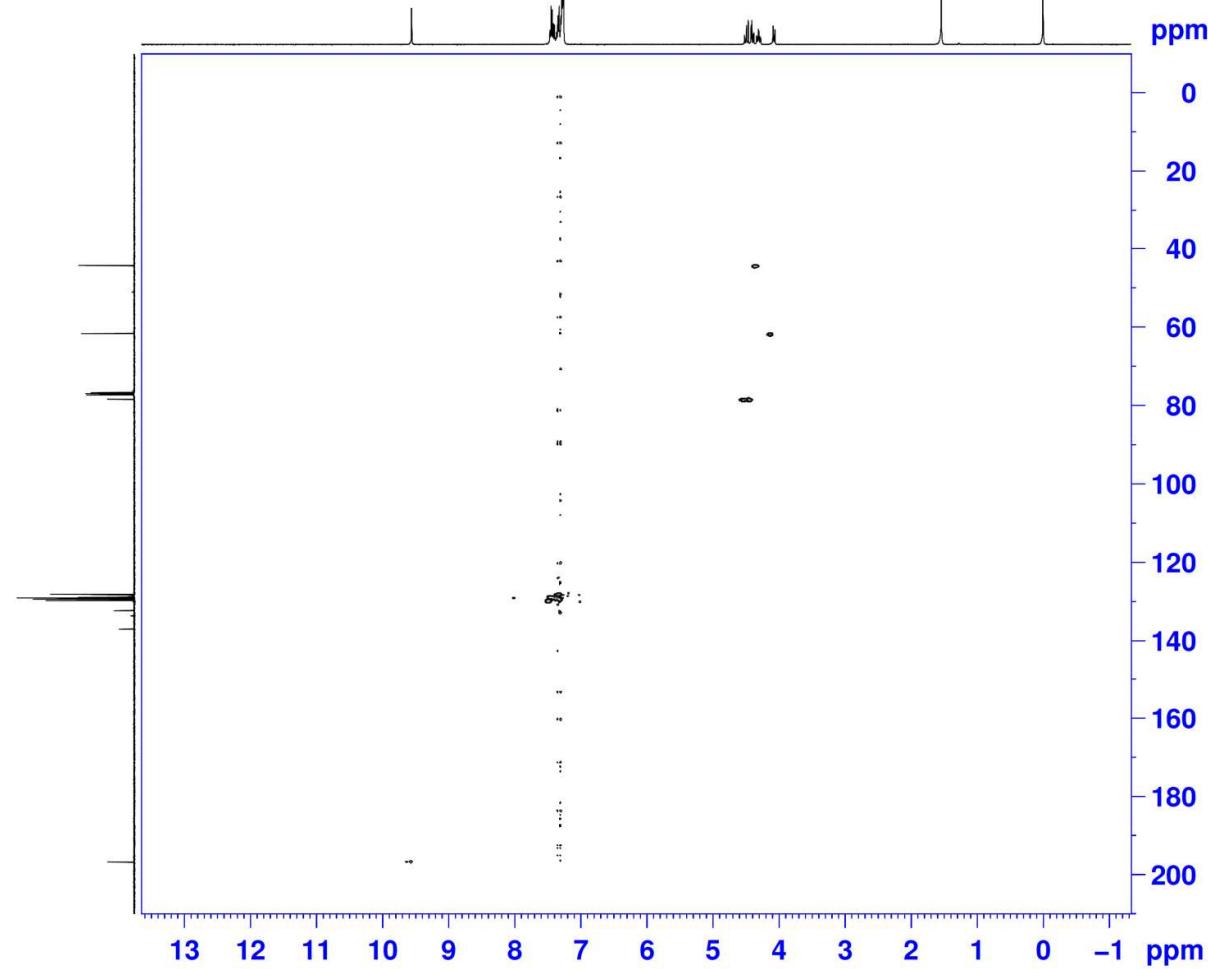


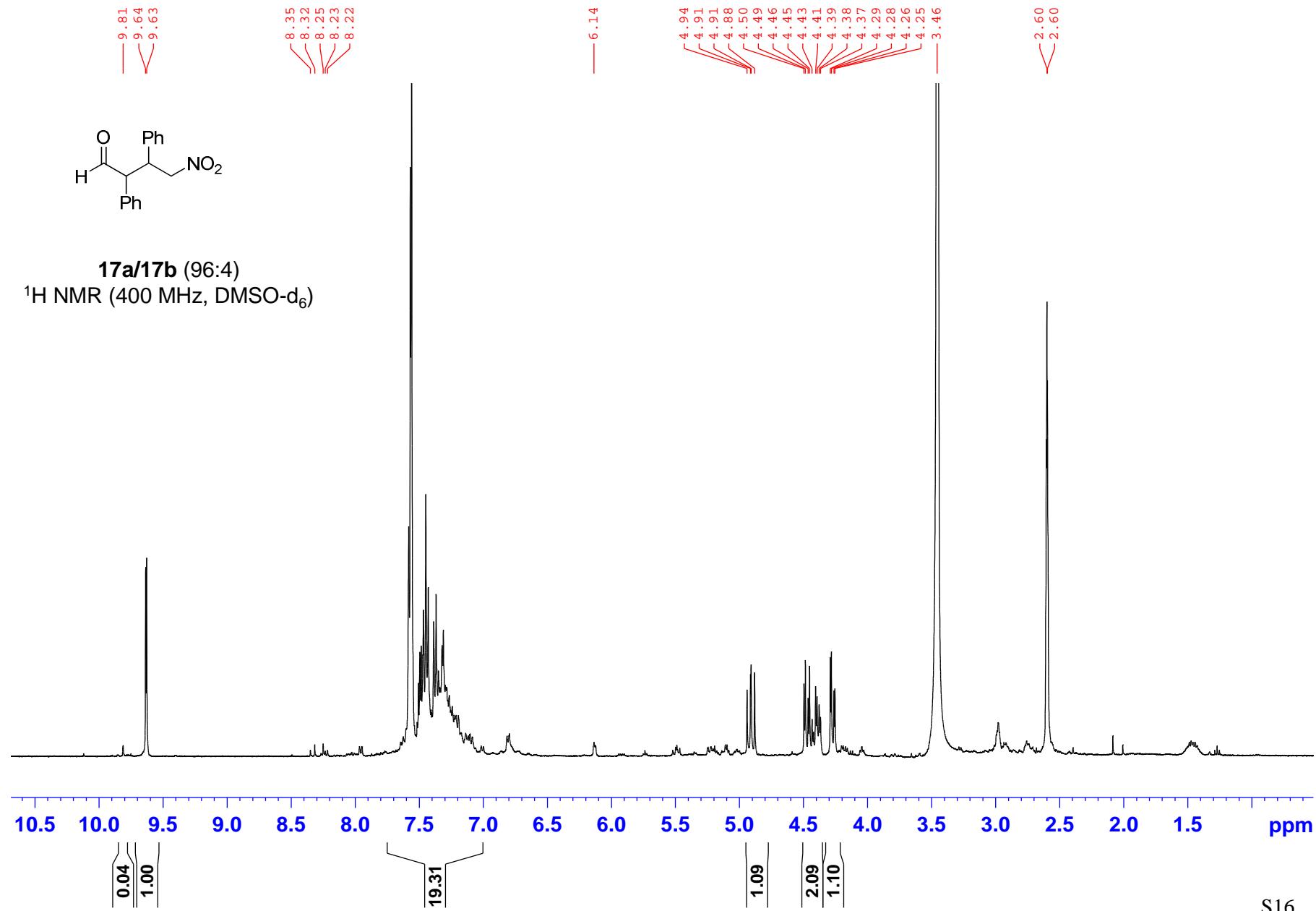




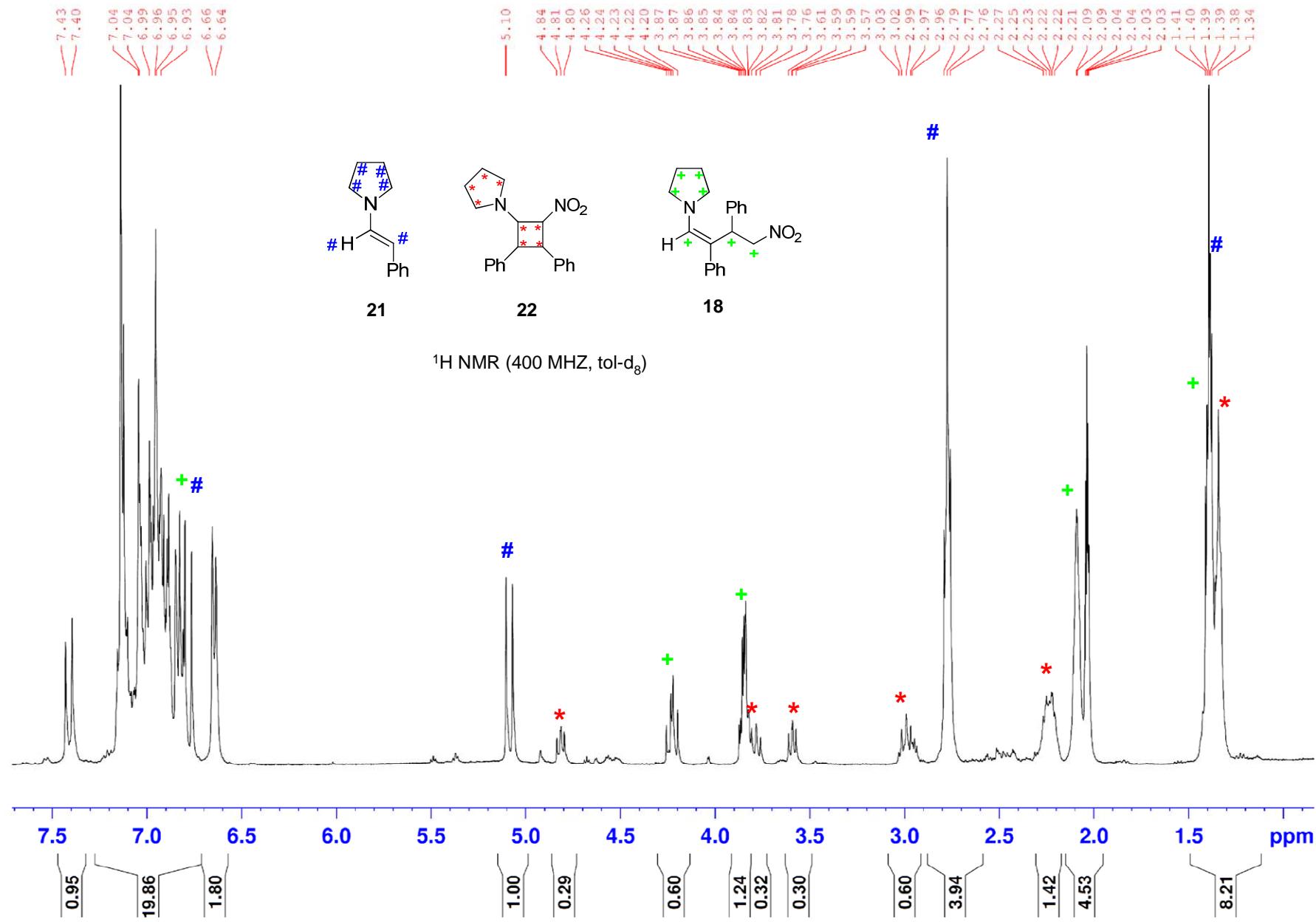


**17a**  
(+/-)  
HSQC NMR (400 MHz, CDCl<sub>3</sub>)

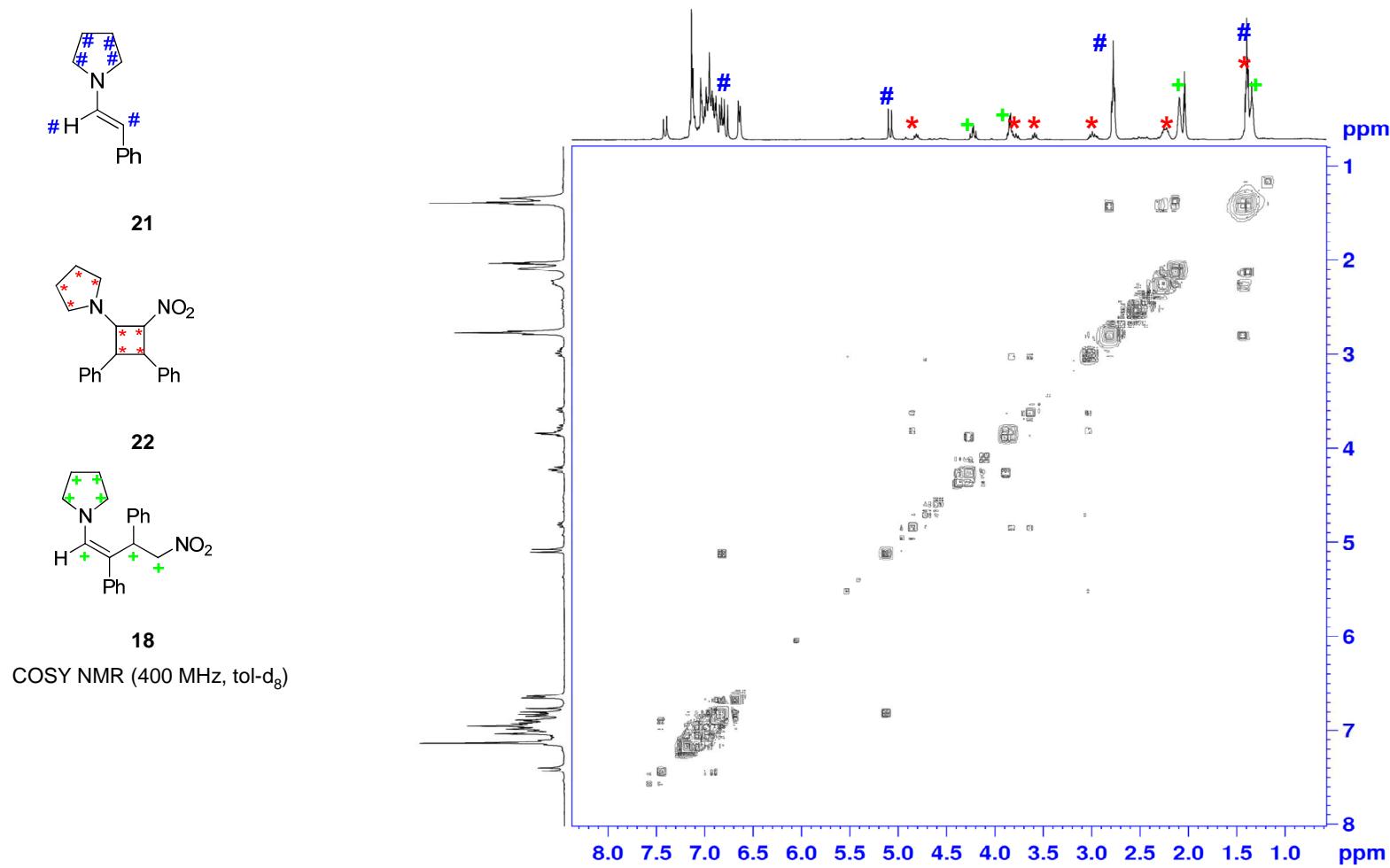




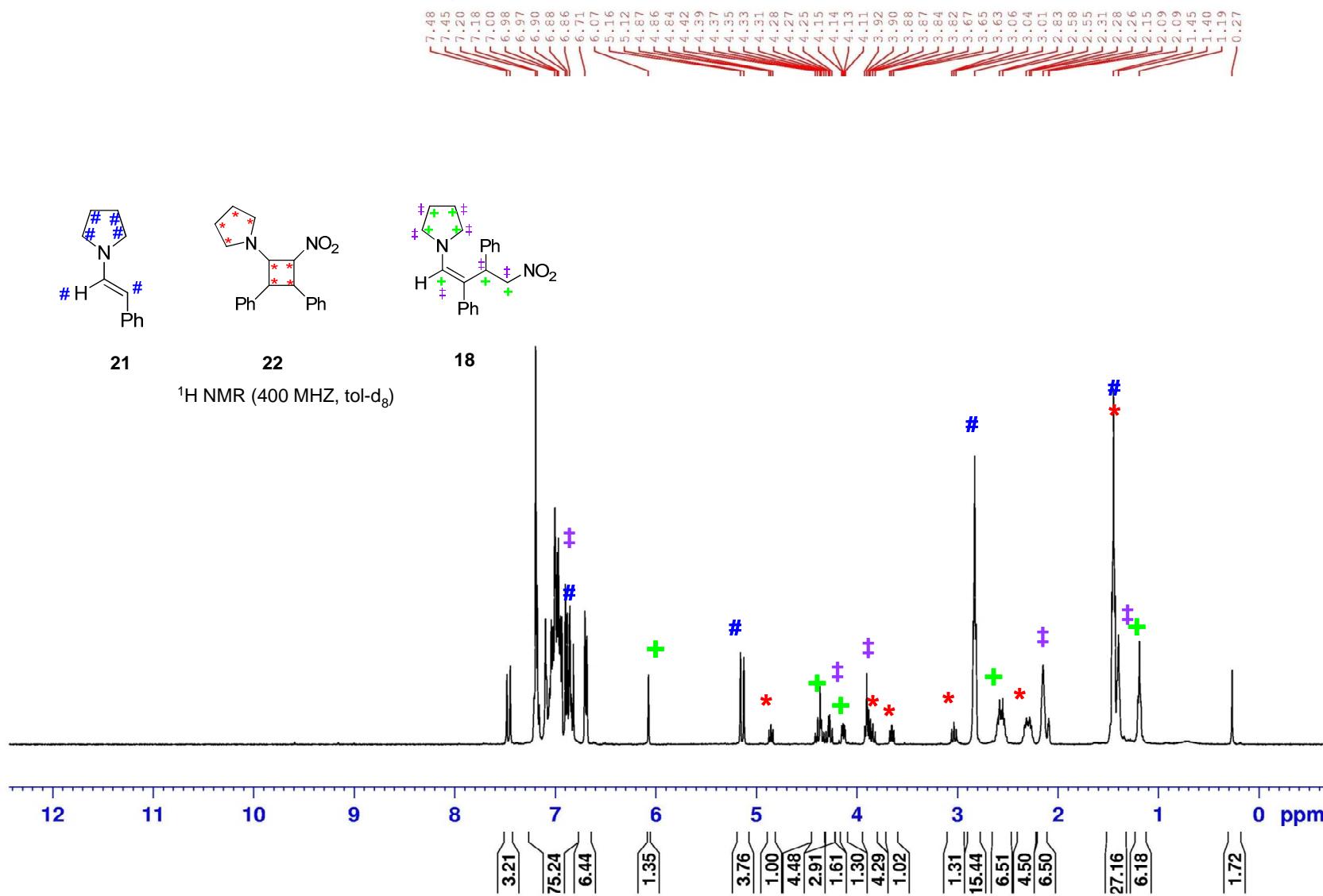
Michael addition of phenylacetaldehyde (**15**) to nitrostyrene (**16**) carried out in an NMR tube under stoichiometric conditions in presence of molecular sieves. NMR analysis of reaction intermediates recorded at 0.25 h.



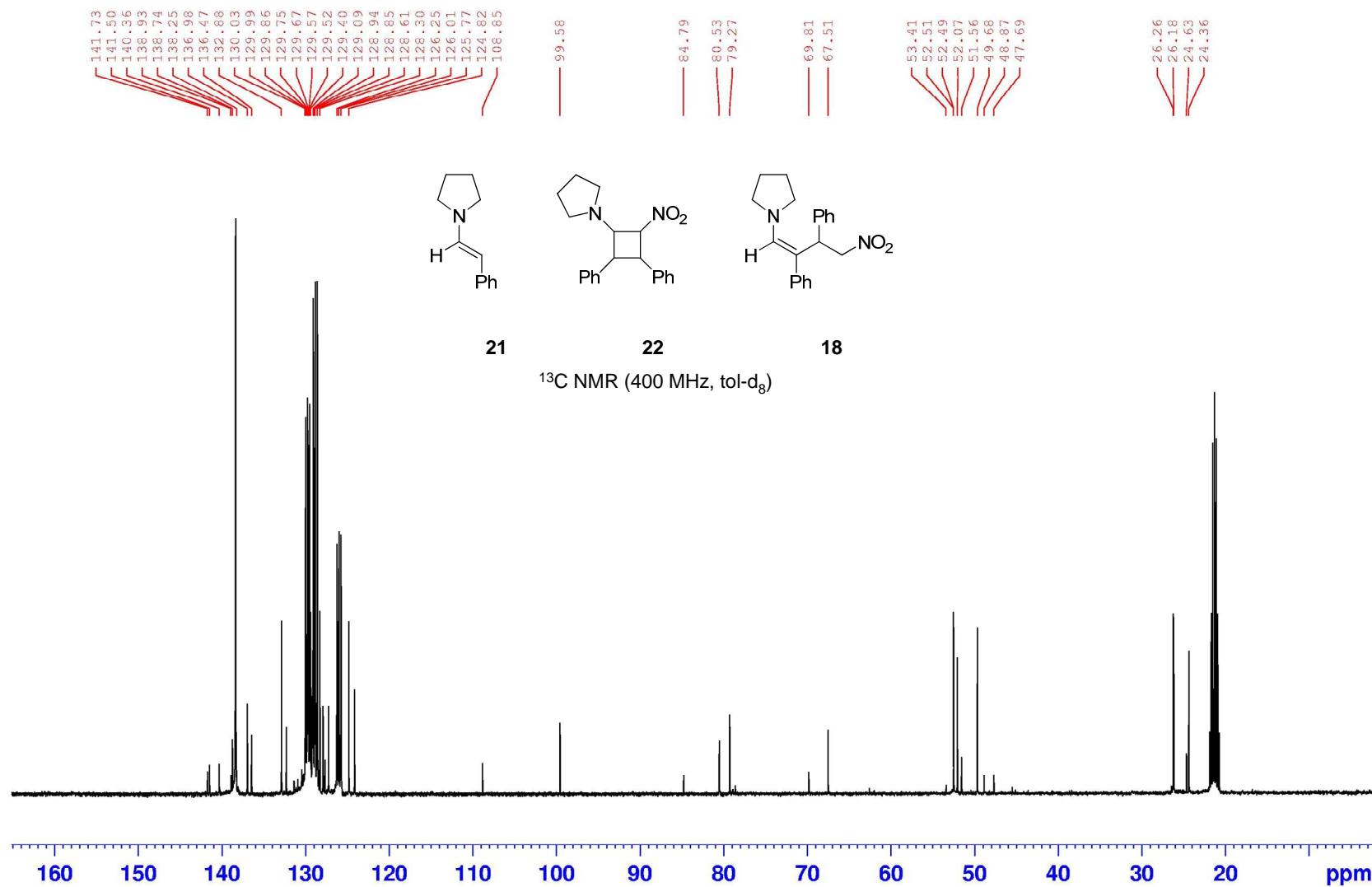
Michael addition of phenylacetaldehyde (**15**) to nitrostyrene (**16**) carried out in an NMR tube under stoichiometric conditions in presence of molecular sieves. NMR analysis of reaction intermediates recorded at 0.25 h.



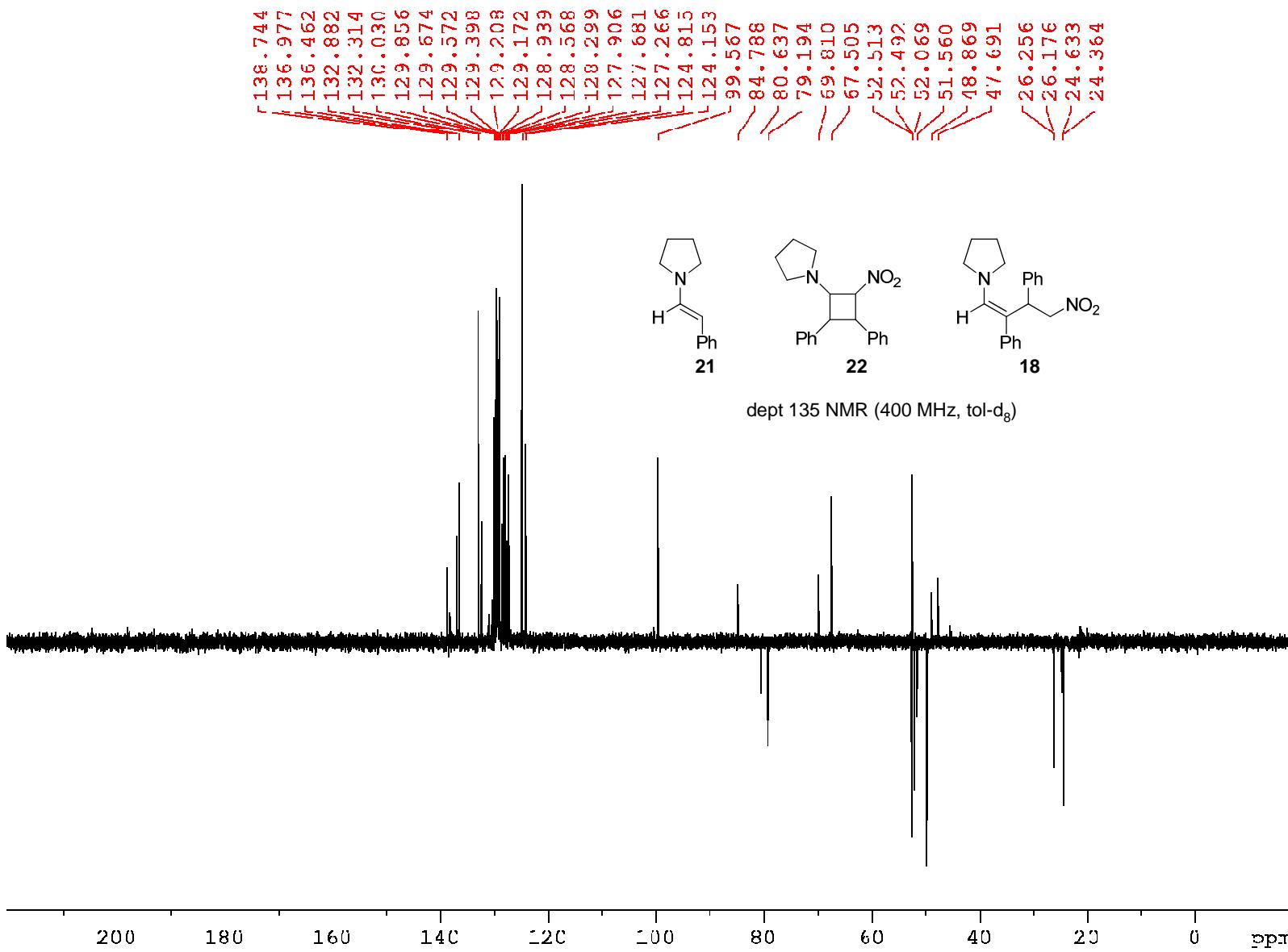
Michael addition of phenylacetaldehyde (**15**) to nitrostyrene (**16**) carried out in an NMR tube under stoichiometric conditions in presence of molecular sieves. NMR analysis of reaction intermediates recorded at 22 h.



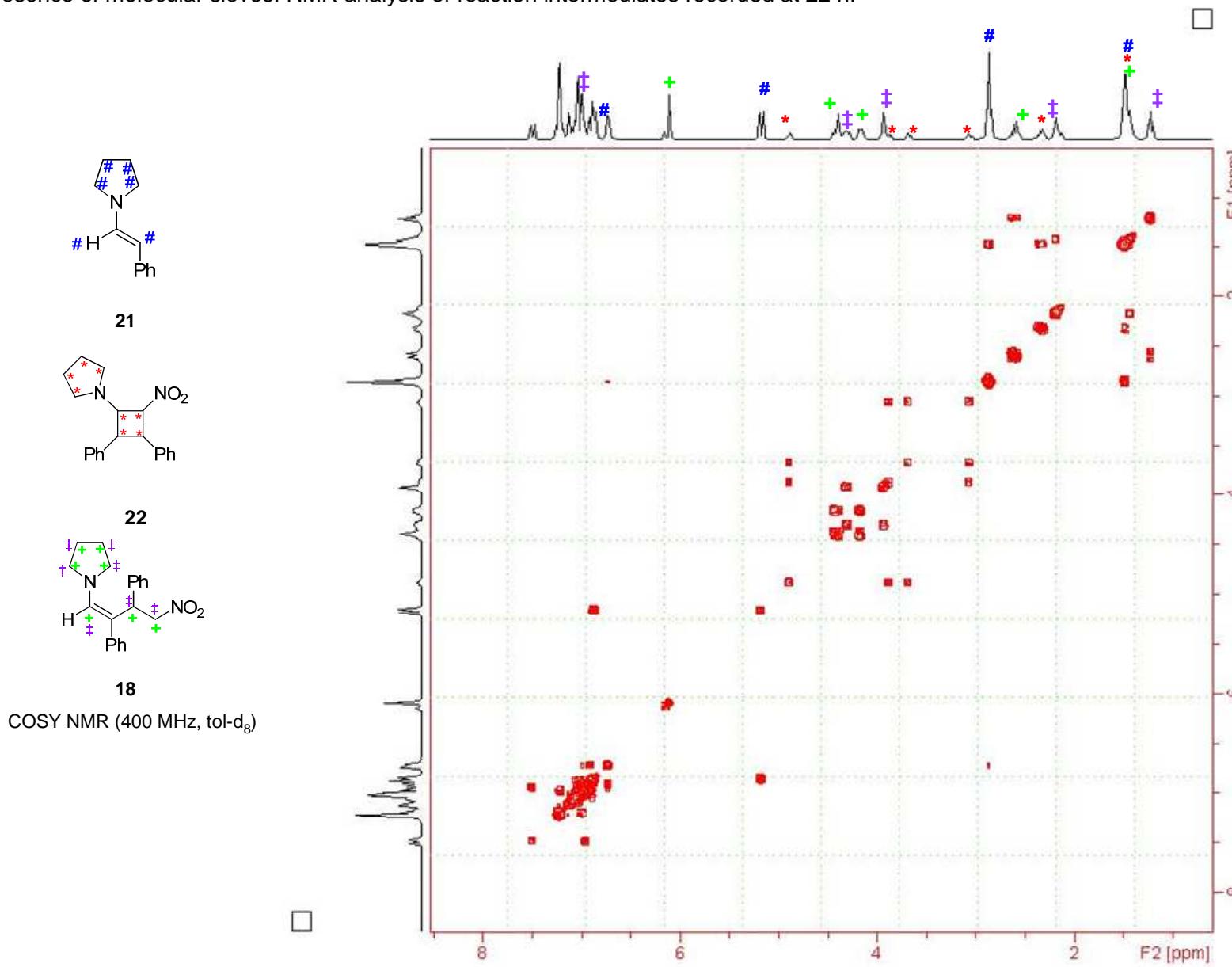
Michael addition of phenylacetaldehyde (**15**) to nitrostyrene (**16**) carried out in an NMR tube under stoichiometric conditions in presence of molecular sieves. NMR analysis of reaction intermediates recorded at 22 h.



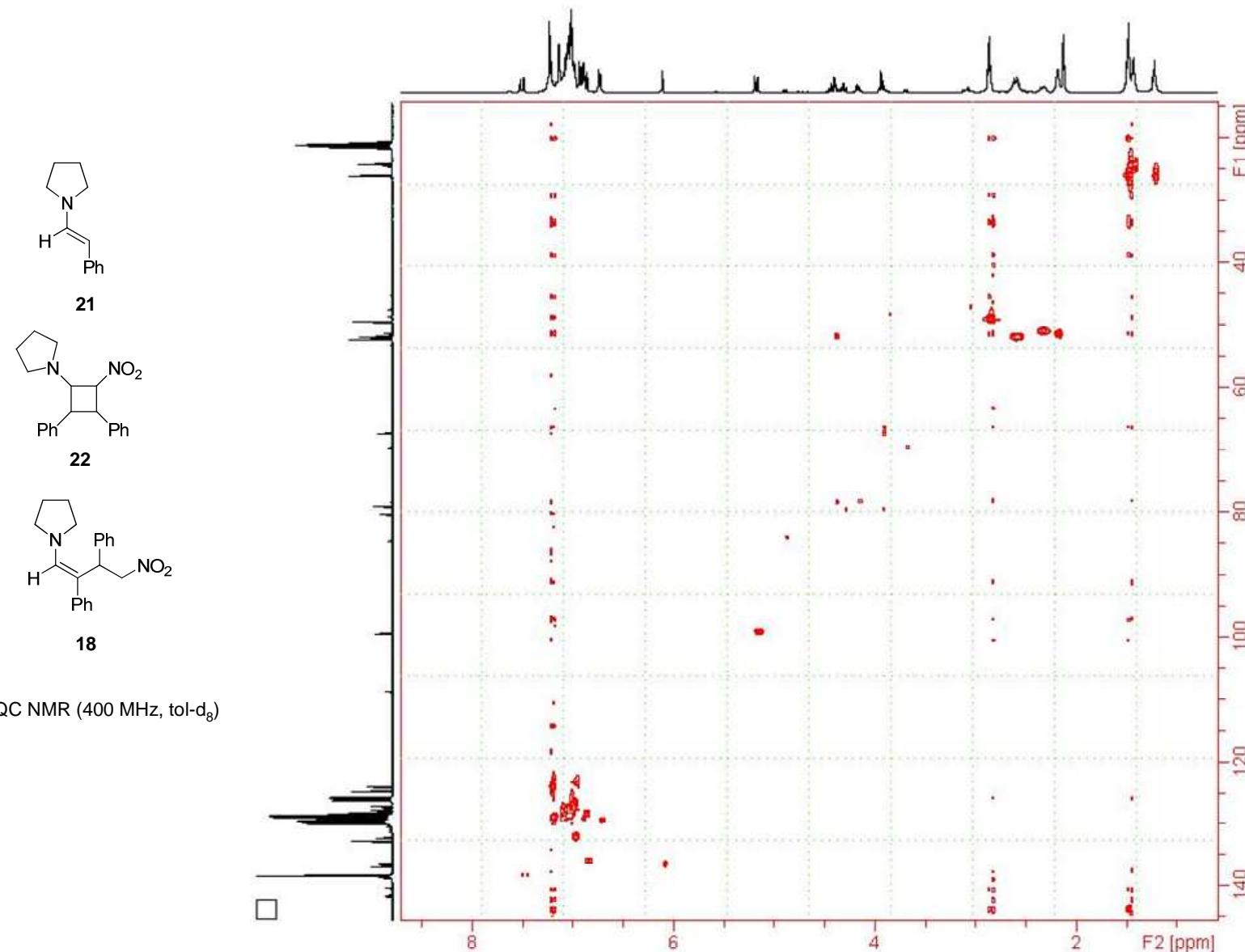
Michael addition of phenylacetaldehyde (**15**) to nitrostyrene (**16**) carried out in an NMR tube under stoichiometric conditions in presence of molecular sieves. NMR analysis of reaction intermediates recorded at 22 h.

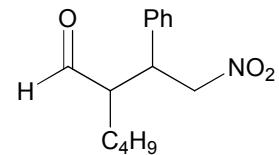


Michael addition of phenylacetaldehyde (**15**) to nitrostyrene (**16**) carried out in an NMR tube under stoichiometric conditions in presence of molecular sieves. NMR analysis of reaction intermediates recorded at 22 h.

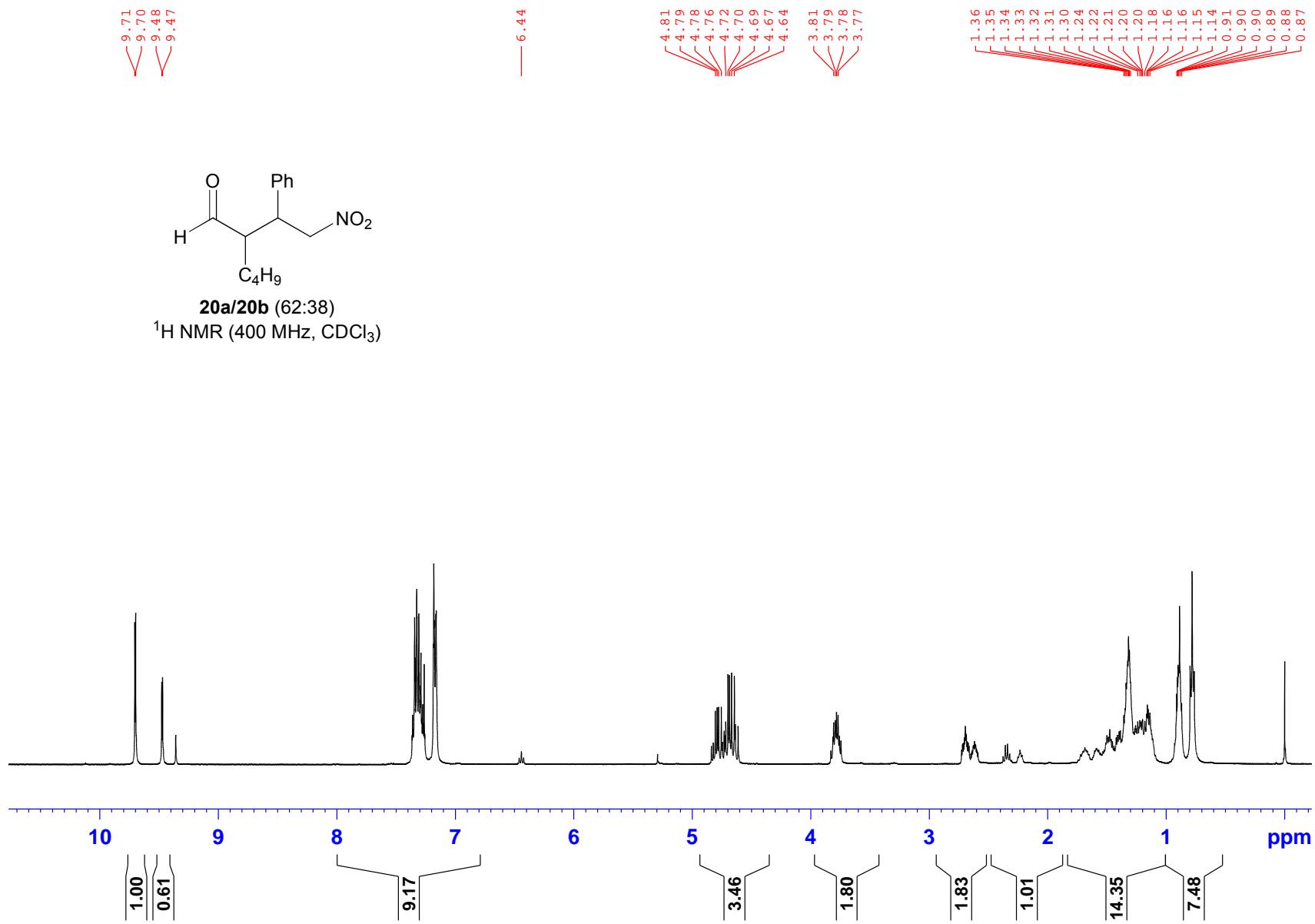


Michael addition of phenylacetaldehyde (**15**) to nitrostyrene (**16**) carried out in an NMR tube under stoichiometric conditions in presence of molecular sieves. NMR analysis of reaction intermediates recorded at 22 h.

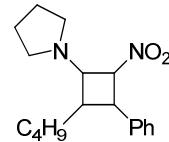




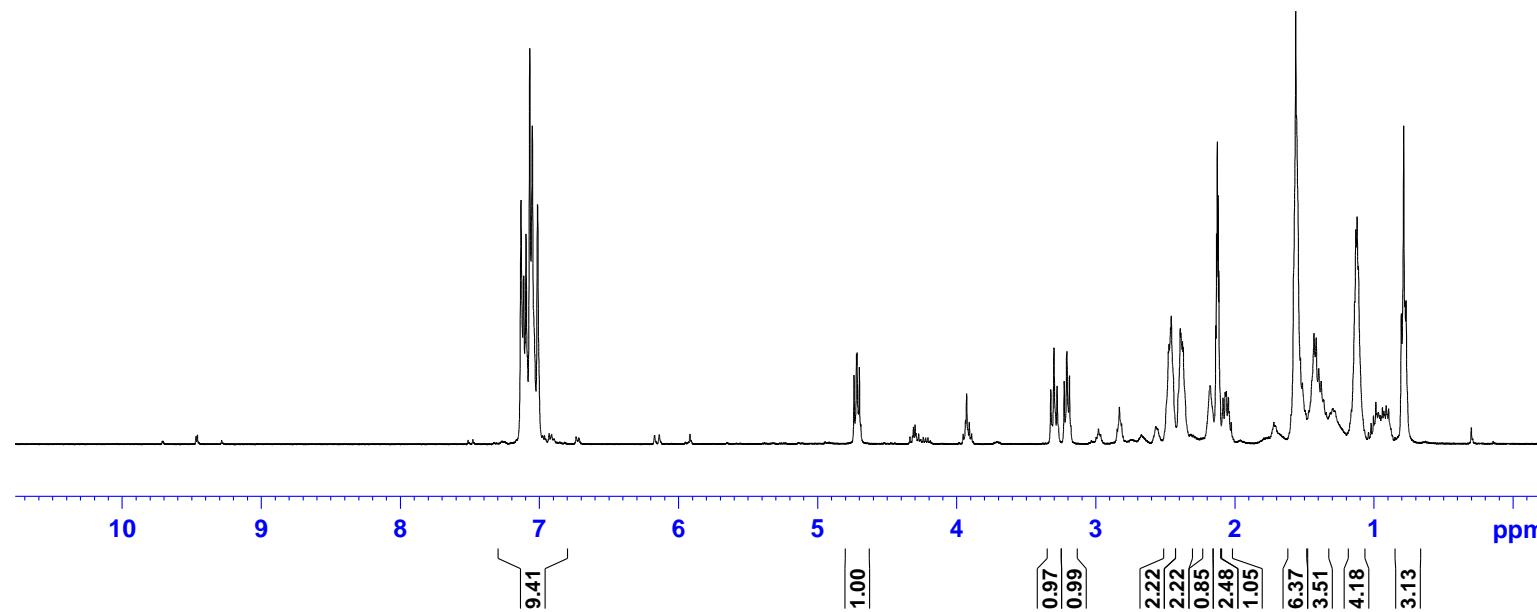
**20a/20b** (62:38)  
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



Michael addition of hexanal (**19**) to nitrostyrene (**16**) carried out in an NMR tube under stoichiometric conditions in presence of molecular sieves. NMR analysis of reaction intermediates recorded at 0.25 h under.



**24**  
 $^1\text{H}$  NMR (400 MHz, tol-d<sub>8</sub>)



Michael addition of hexanal (**19**) to nitrostyrene (**16**) carried out in an NMR tube under stoichiometric conditions in presence of molecular sieves. NMR analysis of reaction intermediates recorded at 0.25 h under.

