

# Supporting Information

## Transition-Metal Catalyzed Benzyl Spirocyclization of *N*-Aryl Alkynamides with Methylarenes under Microwave Irradiation

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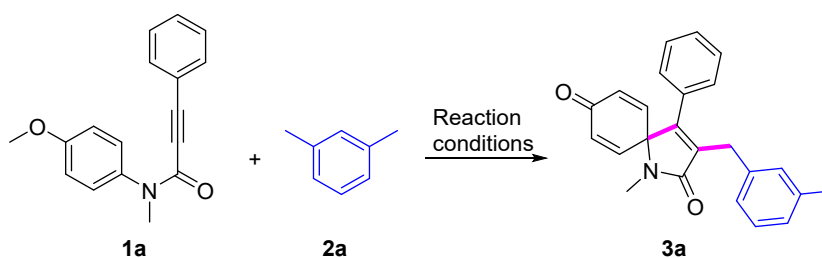
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## 1 General information

All chemicals were commercially available and used as received without further. Column chromatography was performed using 300-400 mesh silica. Nuclear magnetic resonance spectra were recorded on Bruker Avance 400 MHz spectrometer. Chemical shifts for  $^1\text{H}$  NMR spectra are recorded in parts per million from tetramethylsilane. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant in Hz and integration. Chemical shifts for  $^{13}\text{C}$  NMR spectra were recorded in parts per million from tetramethylsilane. Chemical shifts for  $^{19}\text{F}$  NMR spectra were recorded in parts per million with fluorobenzene as external standard. High resolution mass spectra (HR MS) were obtained on Thermo Scientific LTQ Orbitrap XL instrument using the ESI technique. IR spectra were recorded on WQF-510 Fourier transform infrared spectrophotometer. Melting points were measured on an XT4A microscopic apparatus uncorrected.

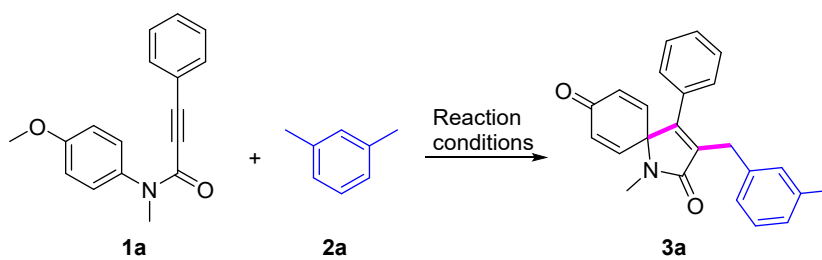
## 2 Screening the reaction conditions



**Table S1** Screening the ratio of **1a** and **2a**<sup>a</sup>

Entry	the ratio of <b>1a</b> (mmol) and <b>2a</b> (mL)	Yields (%) <sup>b</sup>
1	0.2 : 0.5	42
2	0.2 : 1.0	28
3	0.2 : 1.5	23
4	0.2 : 2.0	15

<sup>a</sup> Reaction conditions: *N*-(4-methoxyphenyl)-*N*-methyl-3-phenylpropionamide **1a** (0.2 mmol, 53.0 mg), *m*-xylene **2a**,  $\text{AgNO}_3$  (0.04 mmol, 6.8 mg),  $\text{CuBr}$  (0.03 mmol, 4.3 mg), and TBPB (0.4 mmol, 77.6 mg) at 130 °C under microwave irradiation for 30 mins. <sup>b</sup> Isolated yield.



**Table S2** Screening of different solvents<sup>a</sup>

Entry	Solvent	Yields (%) <sup>b</sup>
1	MeCN	0
2	DMSO	0
3	DMF	0
4	<i>m</i> -xylene	42

<sup>a</sup> Reaction conditions: *N*-(4-methoxyphenyl)-*N*-methyl-3-phenylpropionamide **1a** (0.2 mmol, 53.0 mg), *m*-xylene **2a** (0.5 mL), AgNO<sub>3</sub> (0.04 mmol, 6.8 mg), CuBr (0.03 mmol, 4.3 mg), and TBPB (0.4 mmol, 77.6 mg) at 130 °C under microwave irradiation for 30 mins. <sup>b</sup> Isolated yield.

### 3 Copies of spectra of products

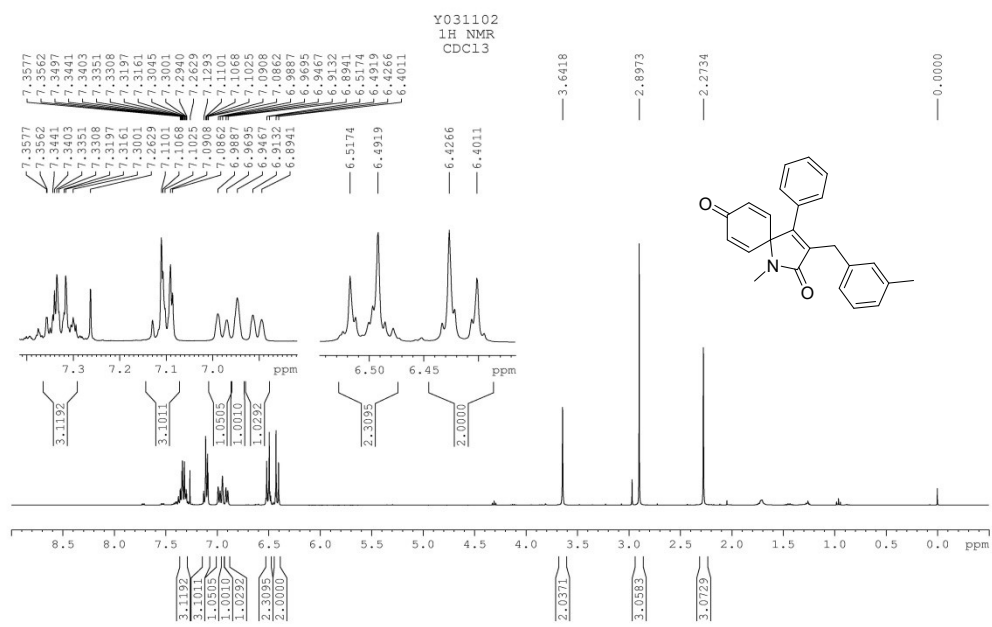


Fig. 1 <sup>1</sup>H NMR spectrum of compound 3a

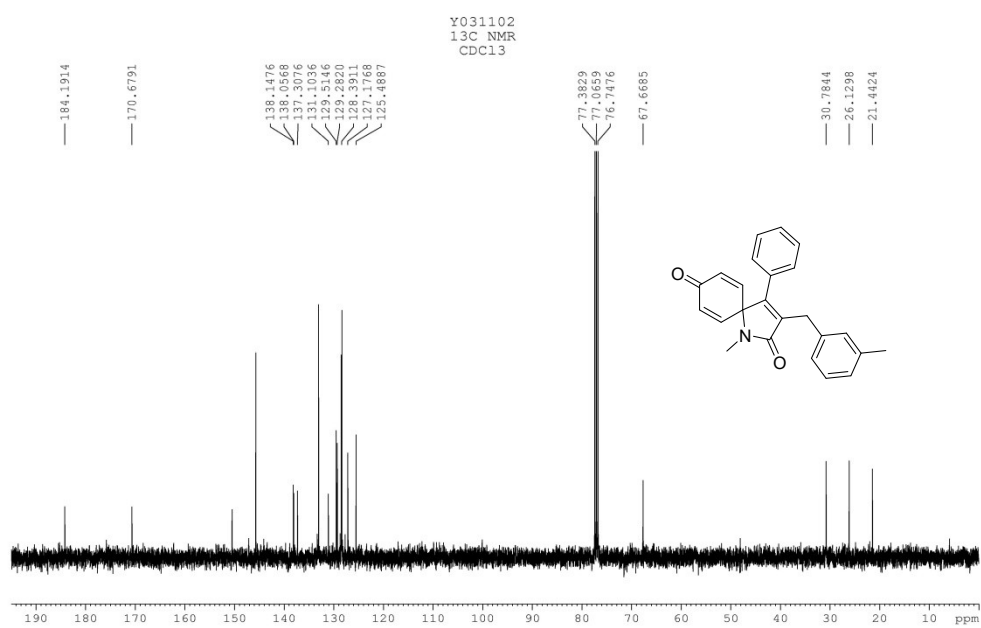


Fig. 2 <sup>13</sup>C NMR spectrum of compound 3a

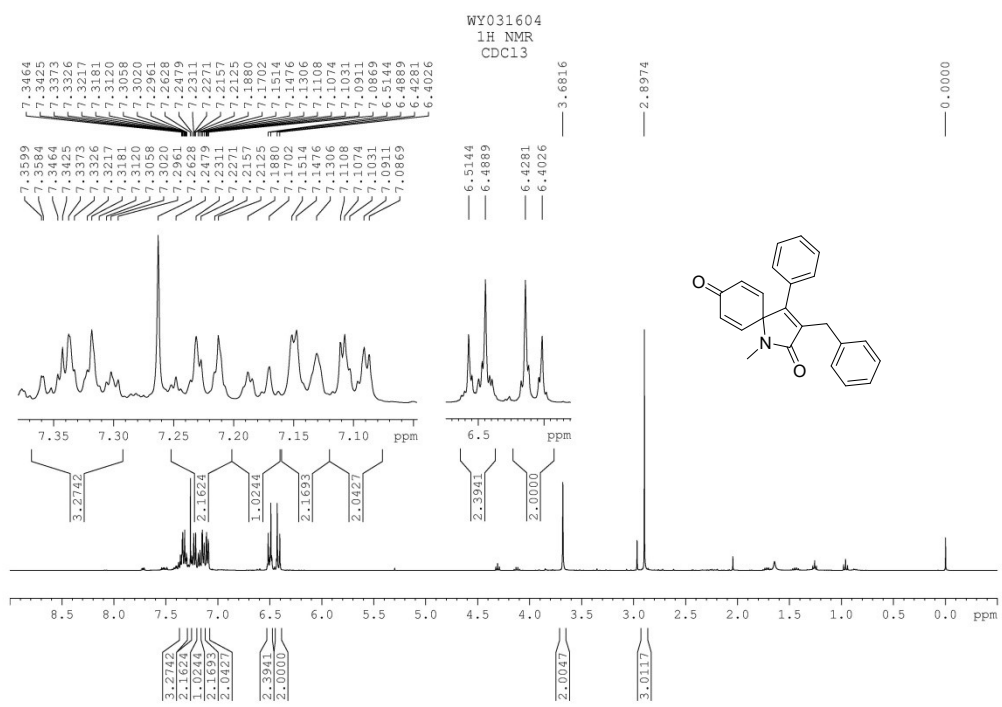


Fig. 3 <sup>1</sup>H NMR spectrum of compound 3b

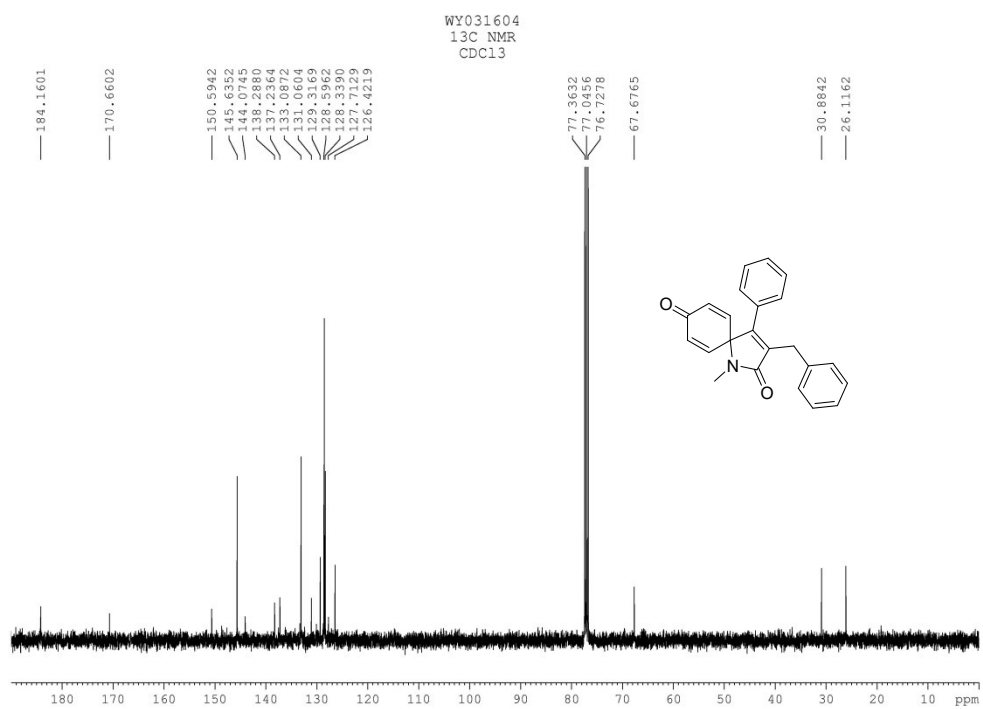


Fig. 4 <sup>13</sup>C NMR spectrum of compound 3b

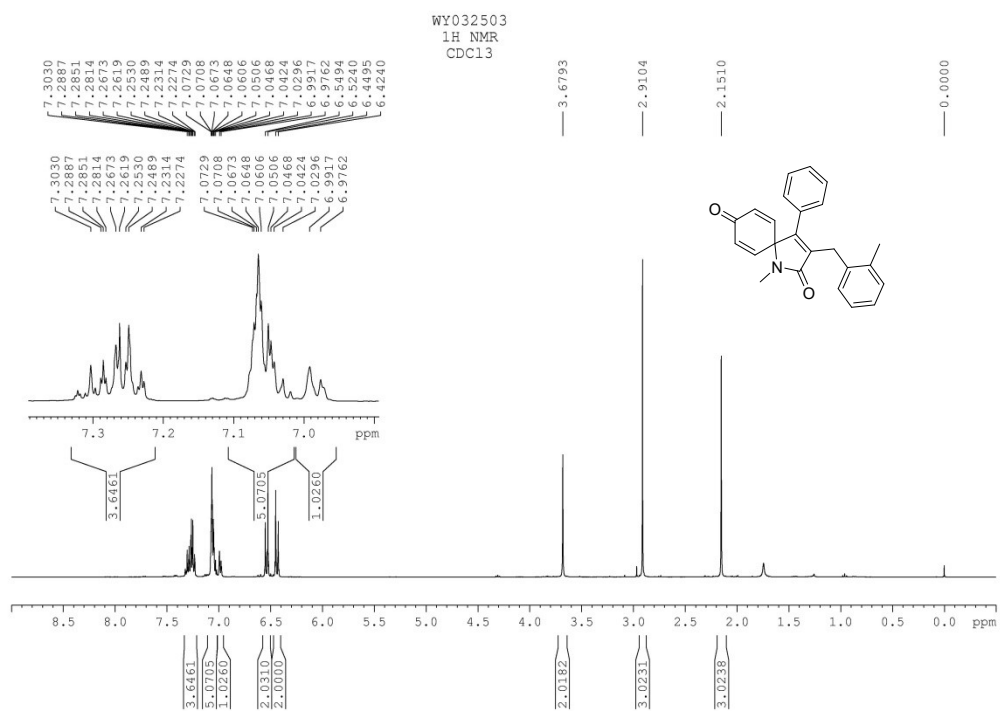


Fig. 5 <sup>1</sup>H NMR spectrum of compound 3c

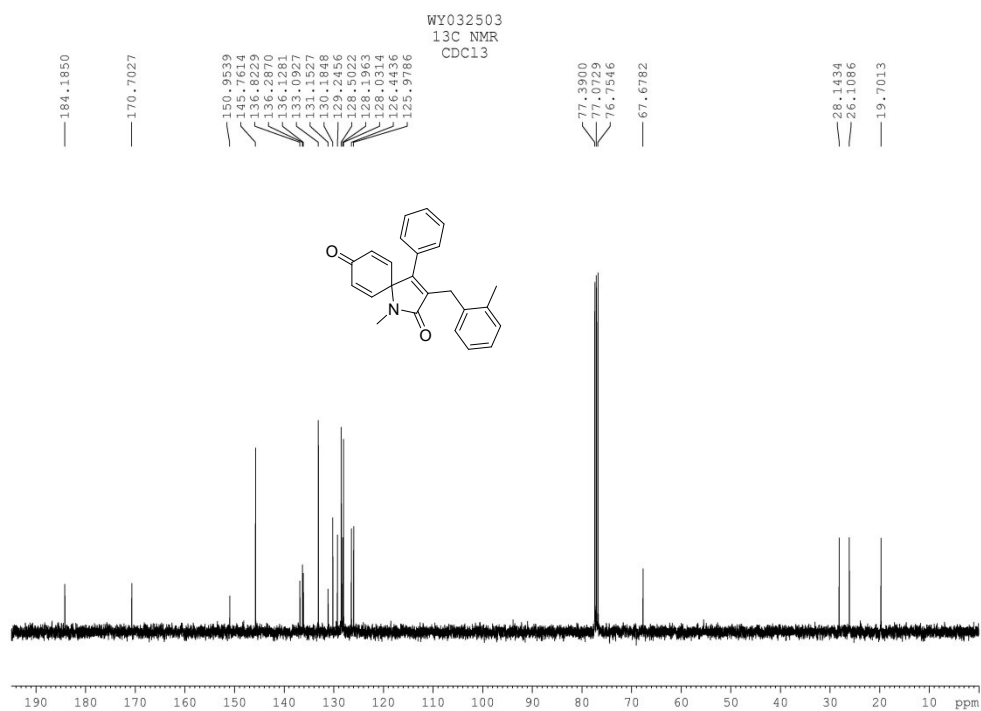


Fig. 6 <sup>13</sup>C NMR spectrum of compound 3c

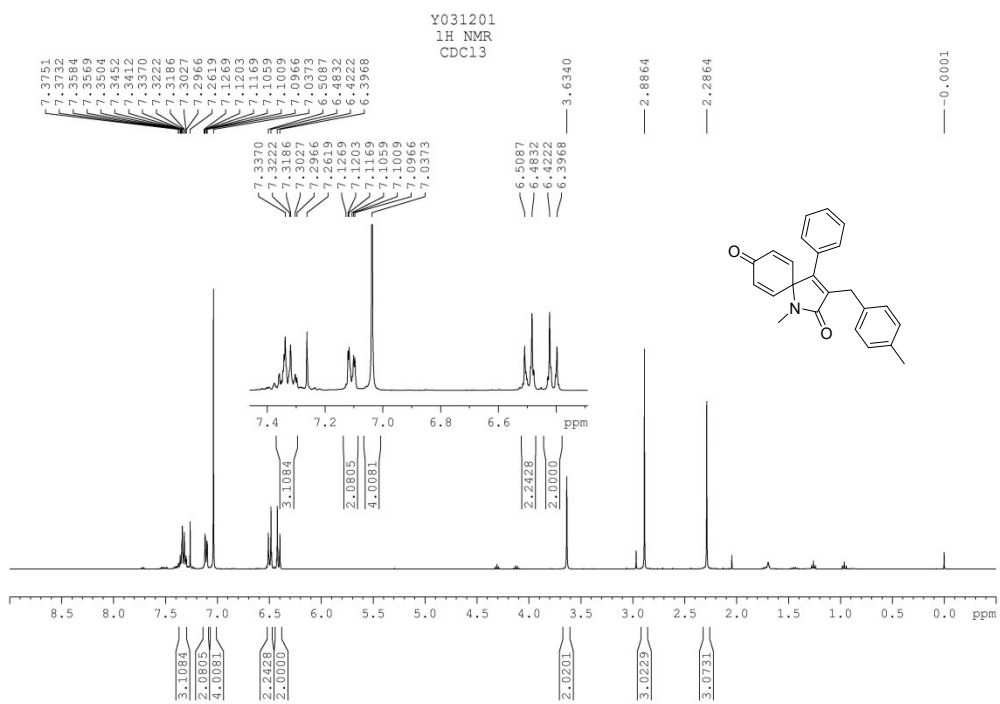


Fig. 7 <sup>1</sup>H NMR spectrum of compound 3d

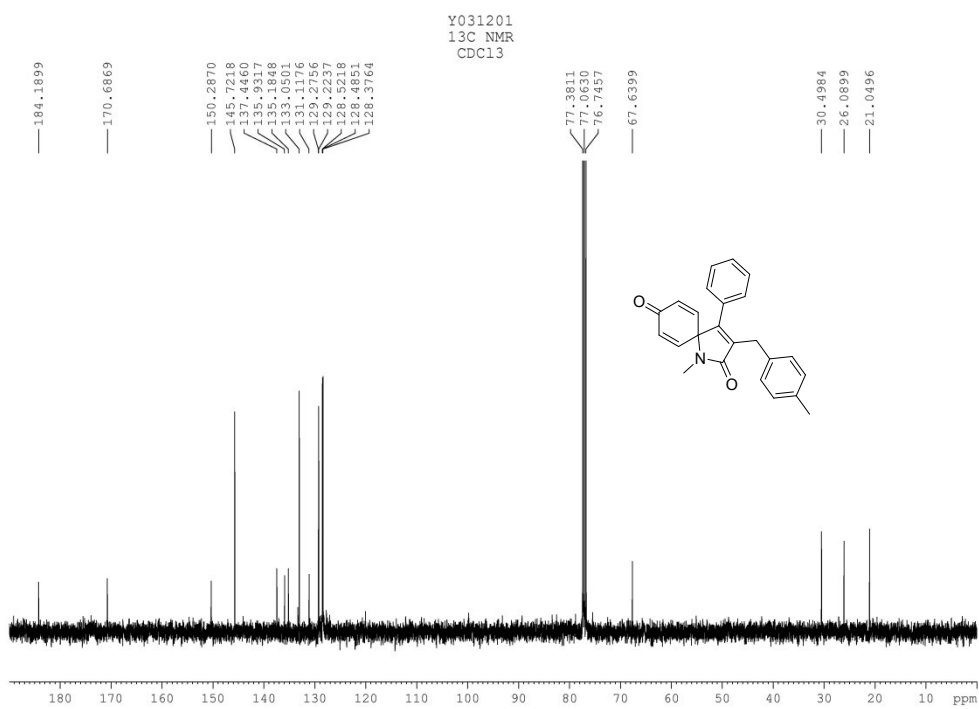


Fig. 8 <sup>13</sup>C NMR spectrum of compound 3d

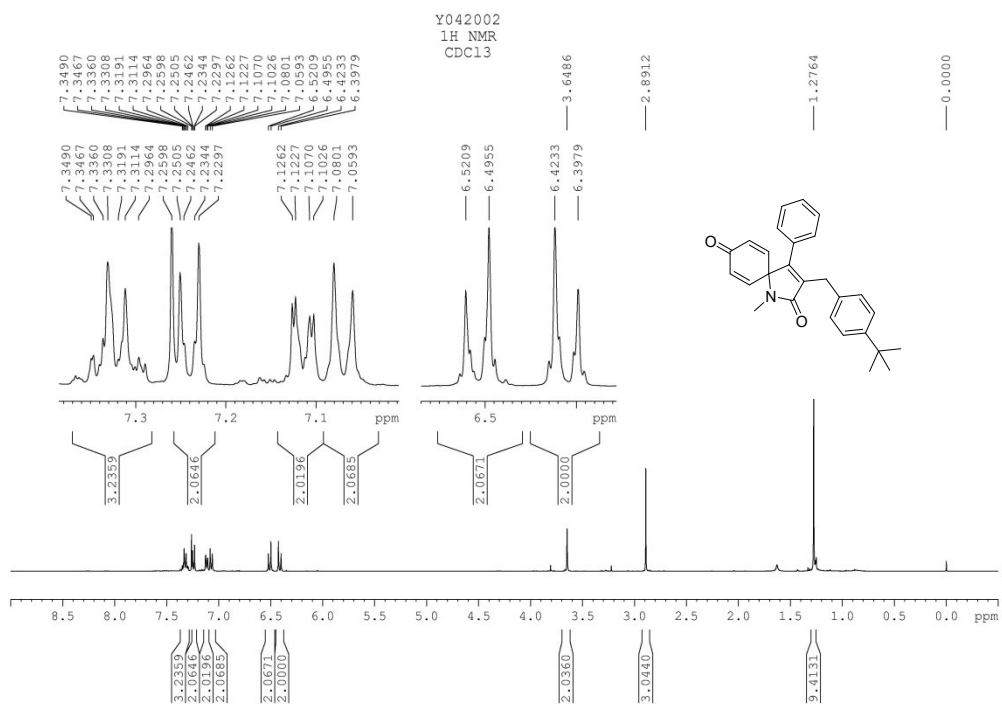


Fig. 9 <sup>1</sup>H NMR spectrum of compound 3e

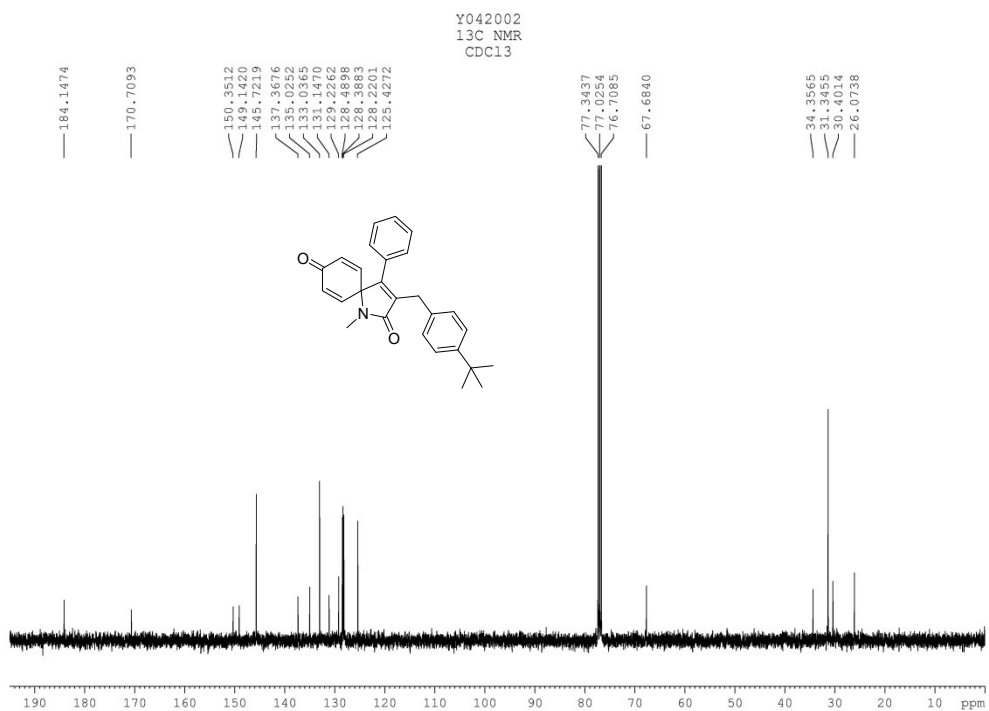


Fig. 10 <sup>13</sup>C NMR spectrum of compound 3e



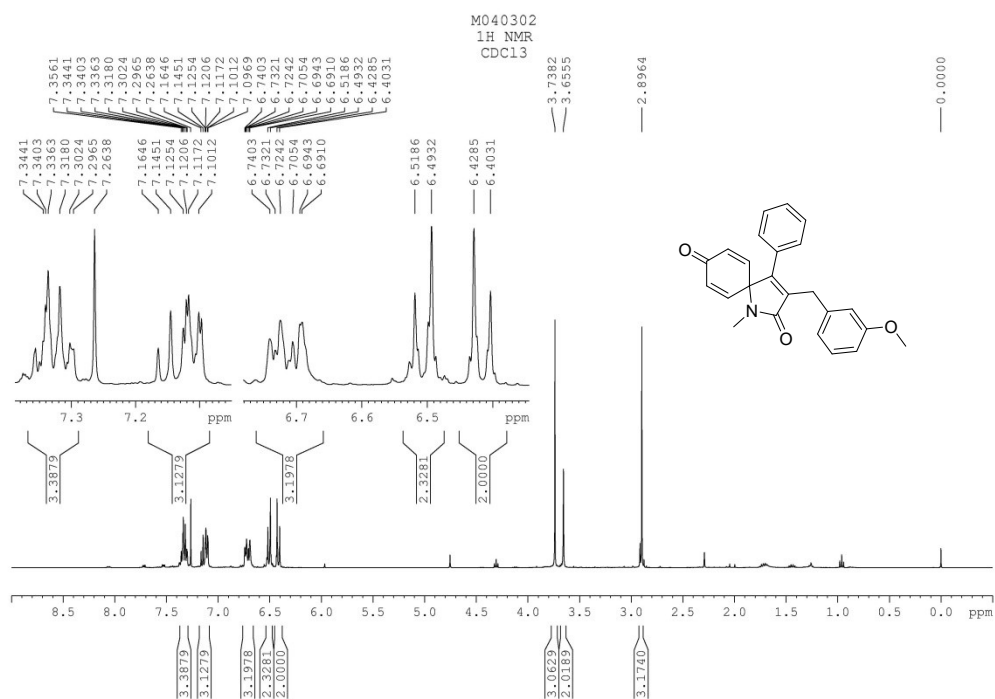


Fig. 11 <sup>1</sup>H NMR spectrum of compound 3f

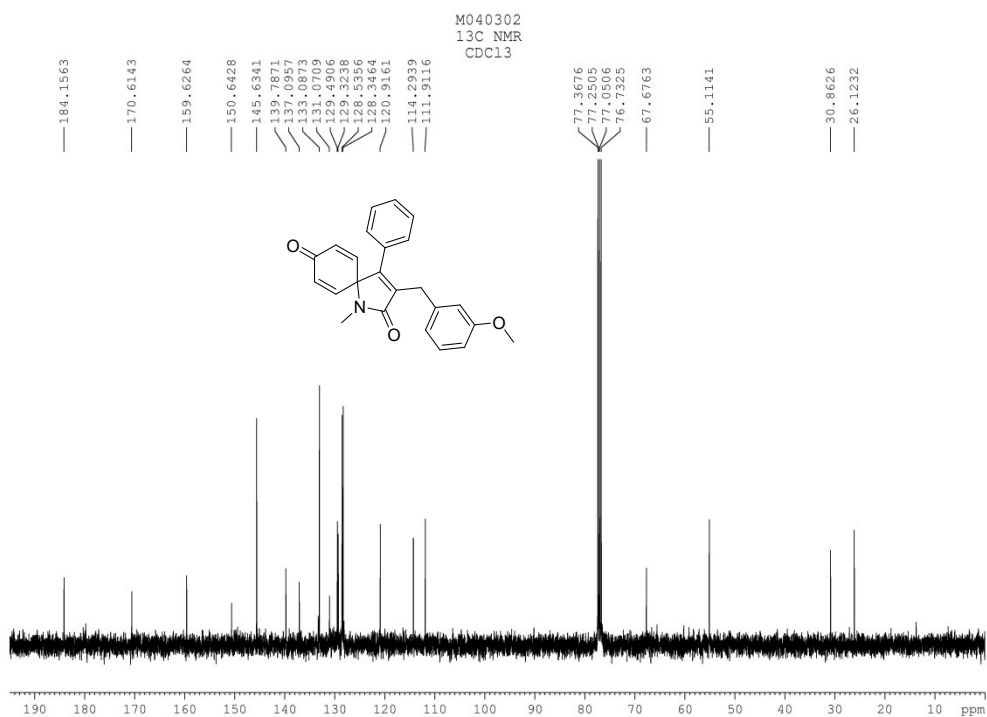


Fig. 12 <sup>13</sup>C NMR spectrum of compound 3f

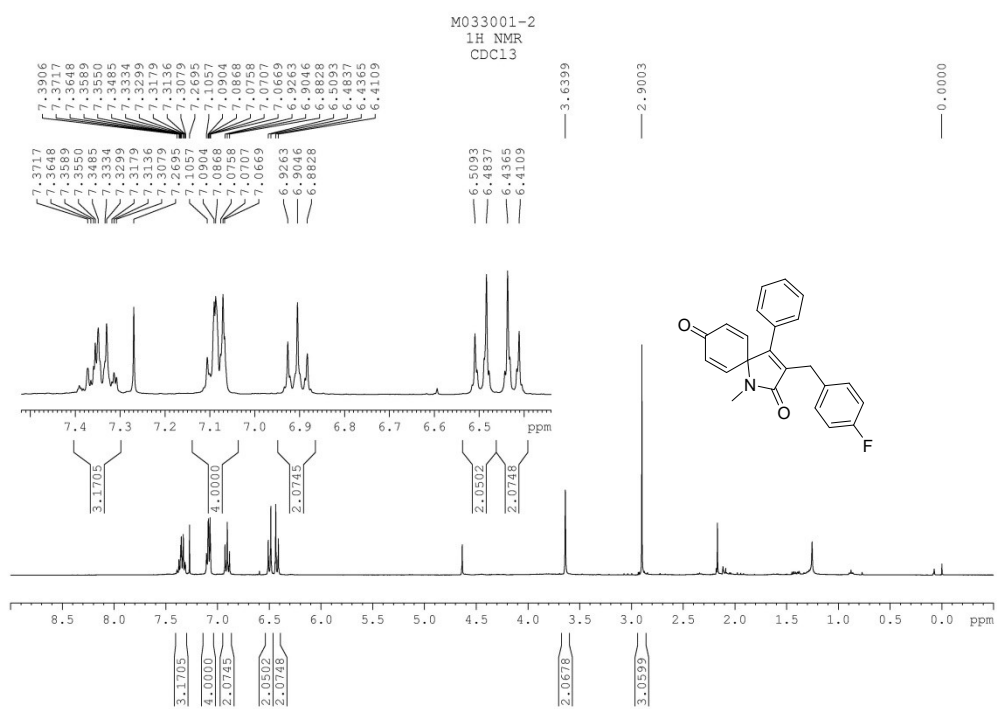


Fig. 13 <sup>1</sup>H NMR spectrum of compound **3g**

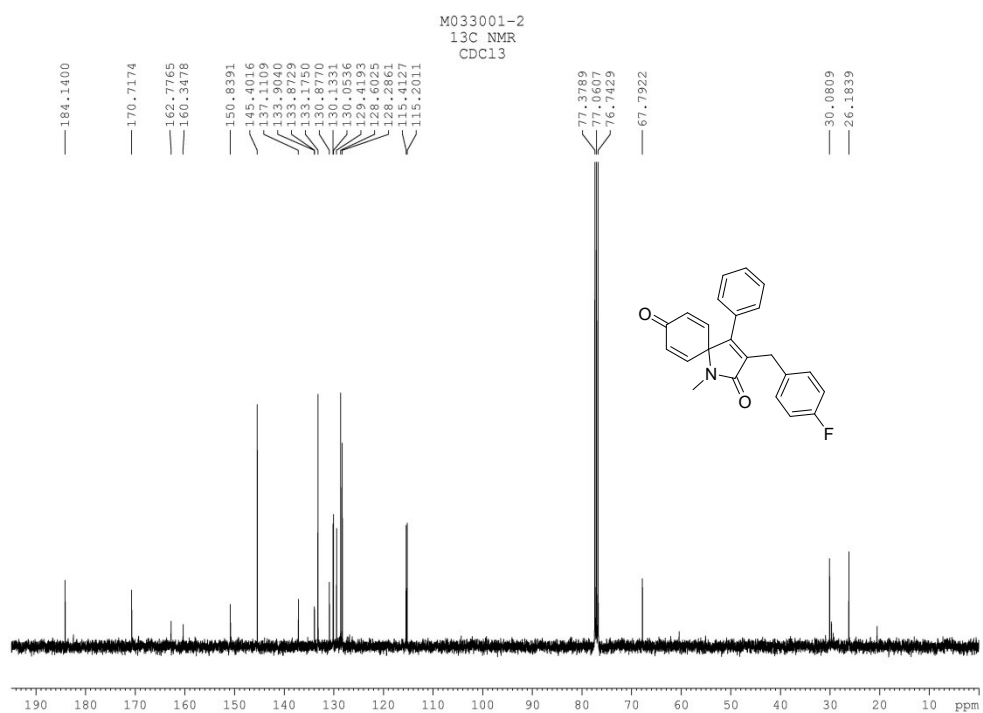


Fig. 14 <sup>13</sup>C NMR spectrum of compound **3g**

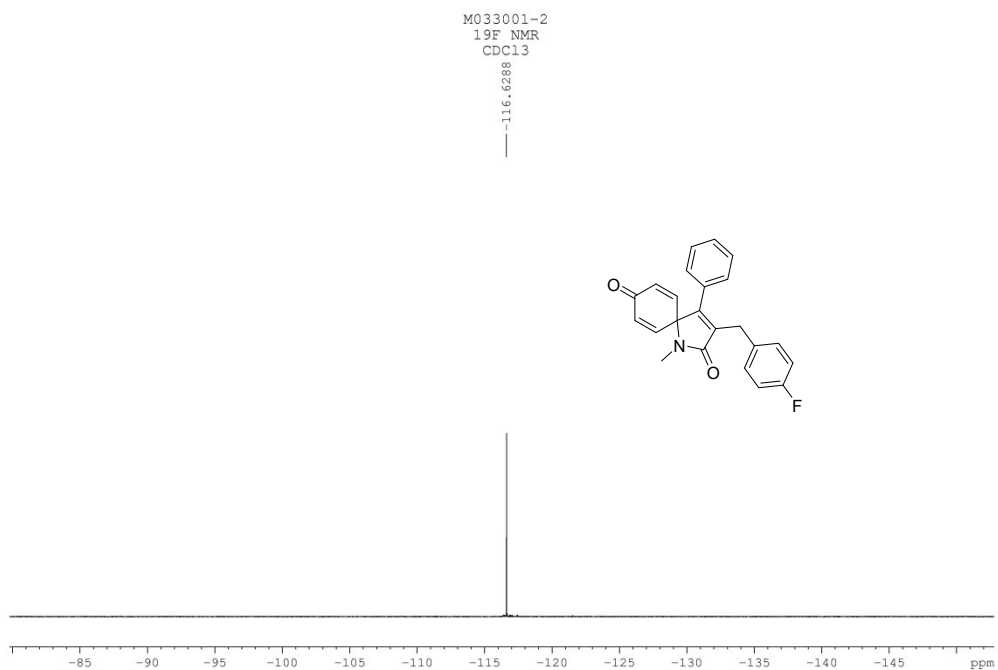


Fig. 15 <sup>19</sup>F NMR spectrum of compound 3g

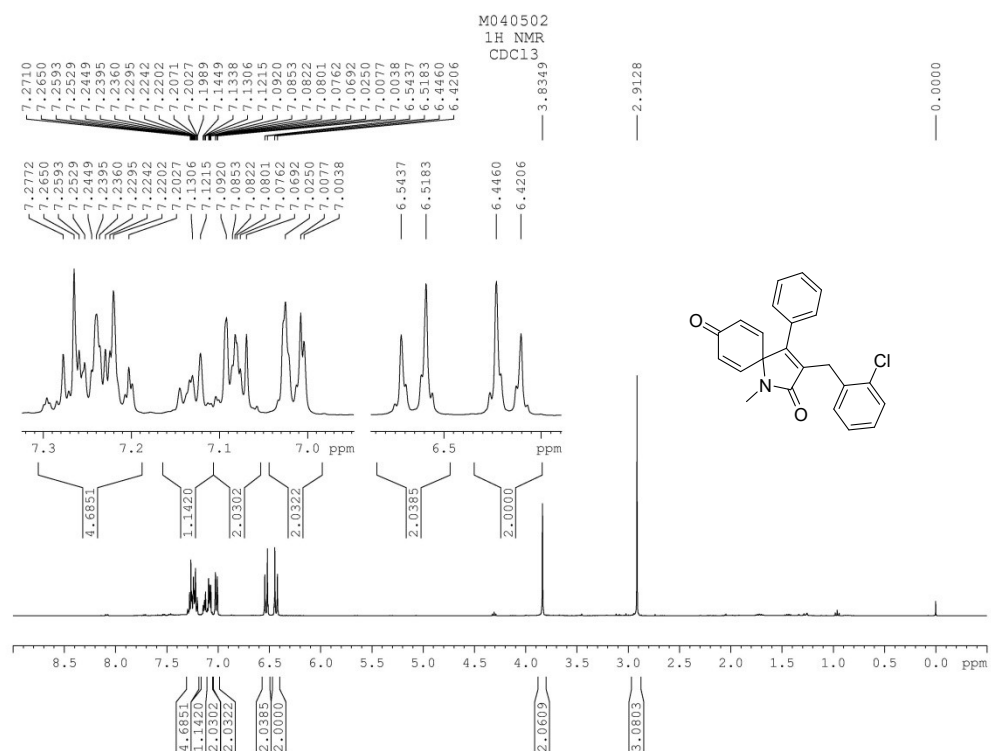


Fig. 16 <sup>1</sup>H NMR spectrum of compound 3h

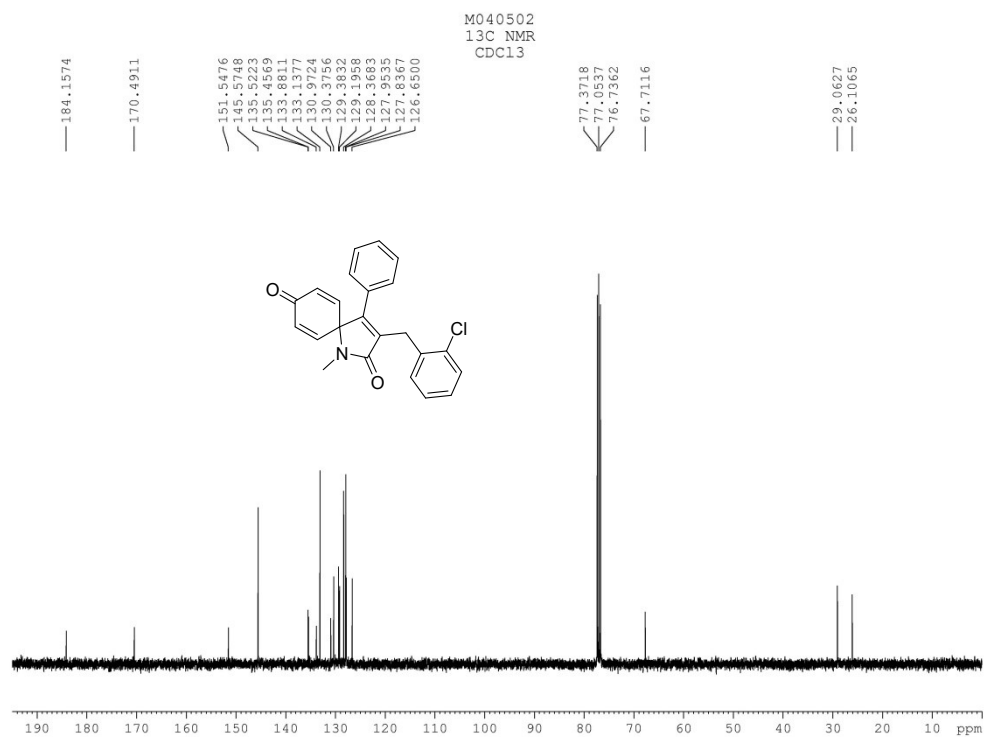


Fig. 17 <sup>13</sup>C NMR spectrum of compound 3h

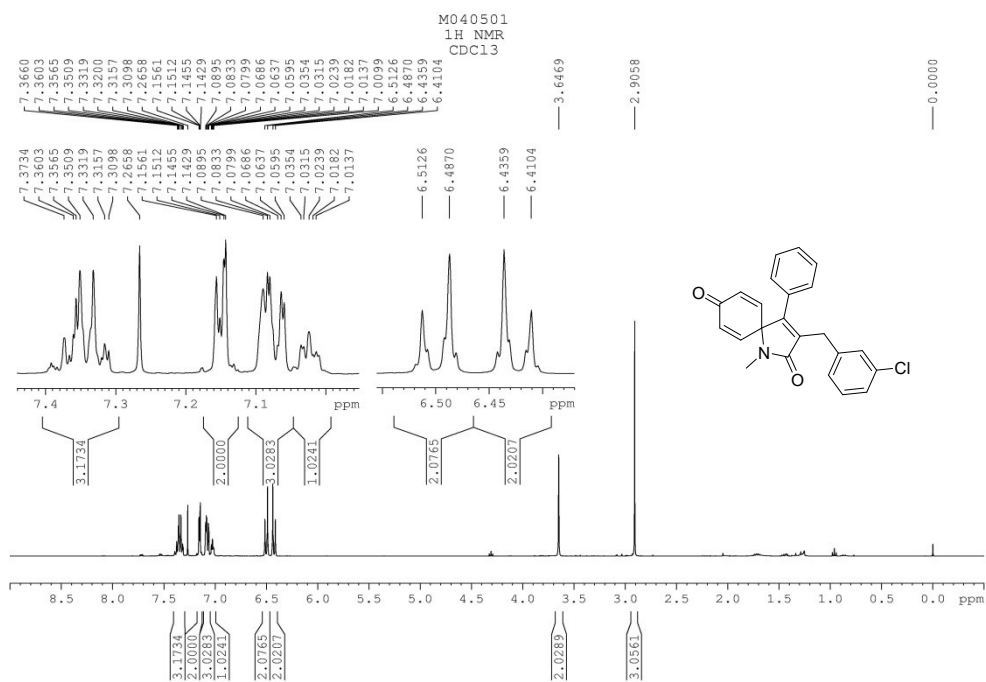


Fig. 18 <sup>1</sup>H NMR spectrum of compound 3i

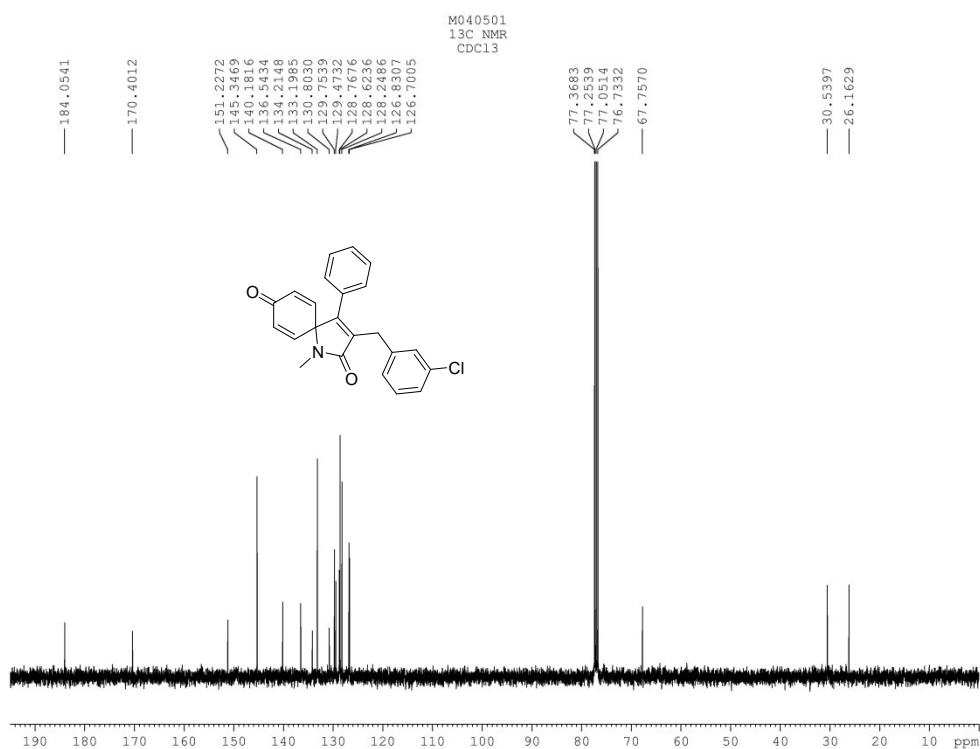


Fig. 19 <sup>13</sup>C NMR spectrum of compound 3i

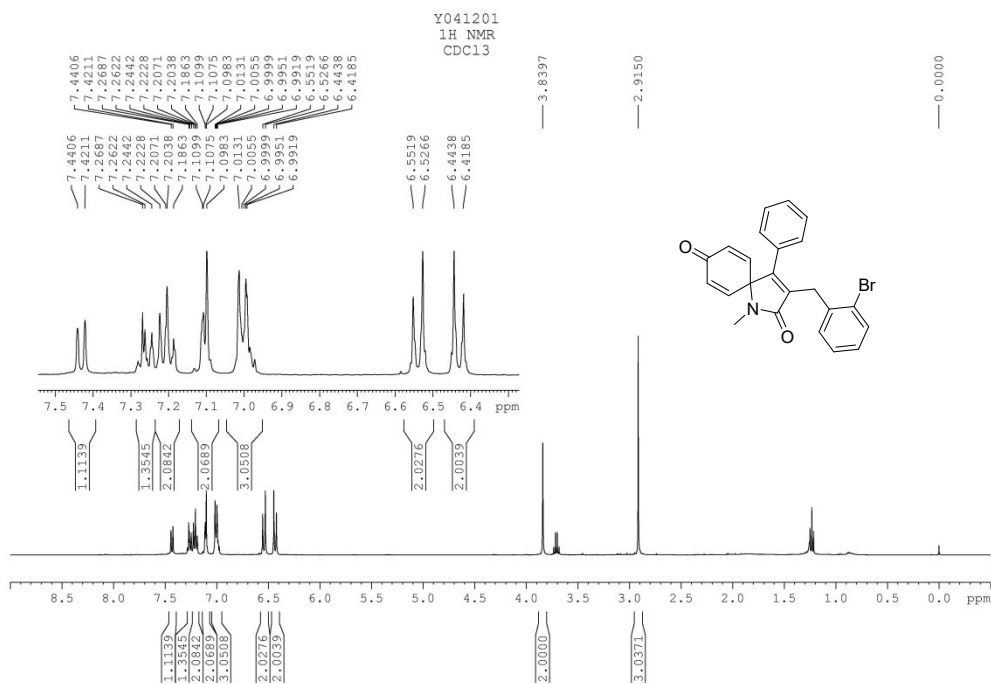


Fig. 20 <sup>1</sup>H NMR spectrum of compound 3j

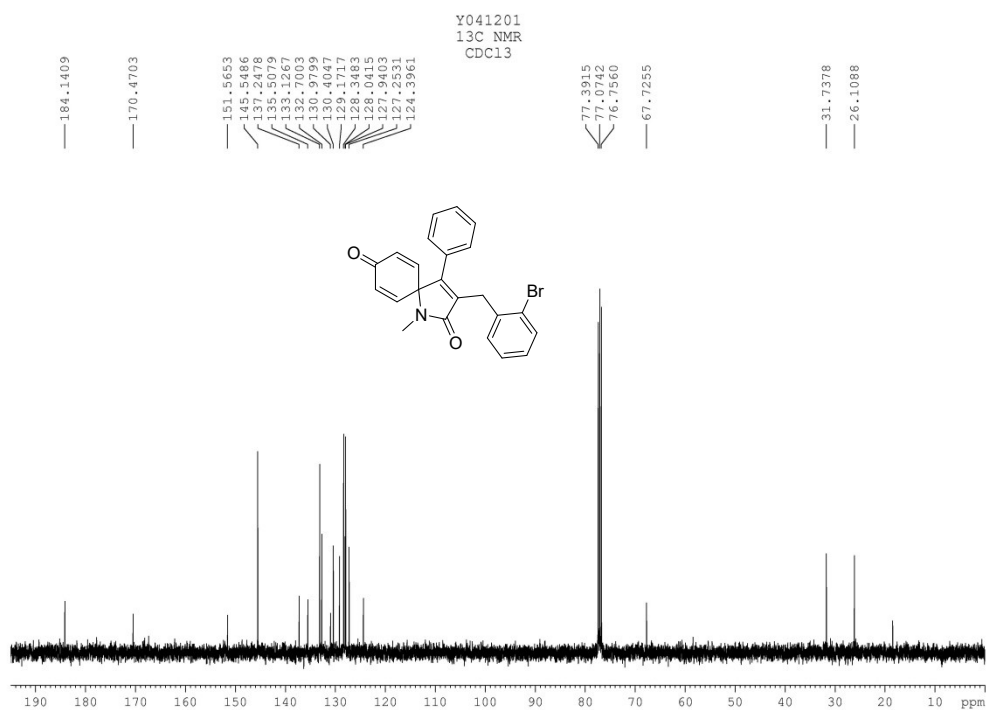


Fig. 21 <sup>13</sup>C NMR spectrum of compound 3j

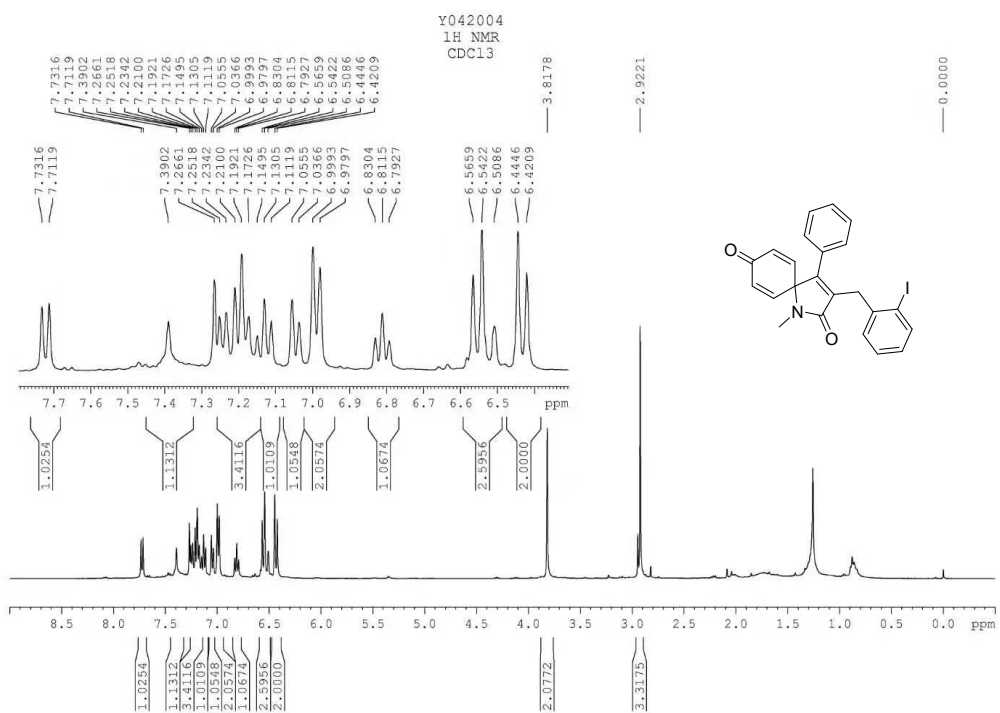


Fig. 22 <sup>1</sup>H NMR spectrum of compound 3k

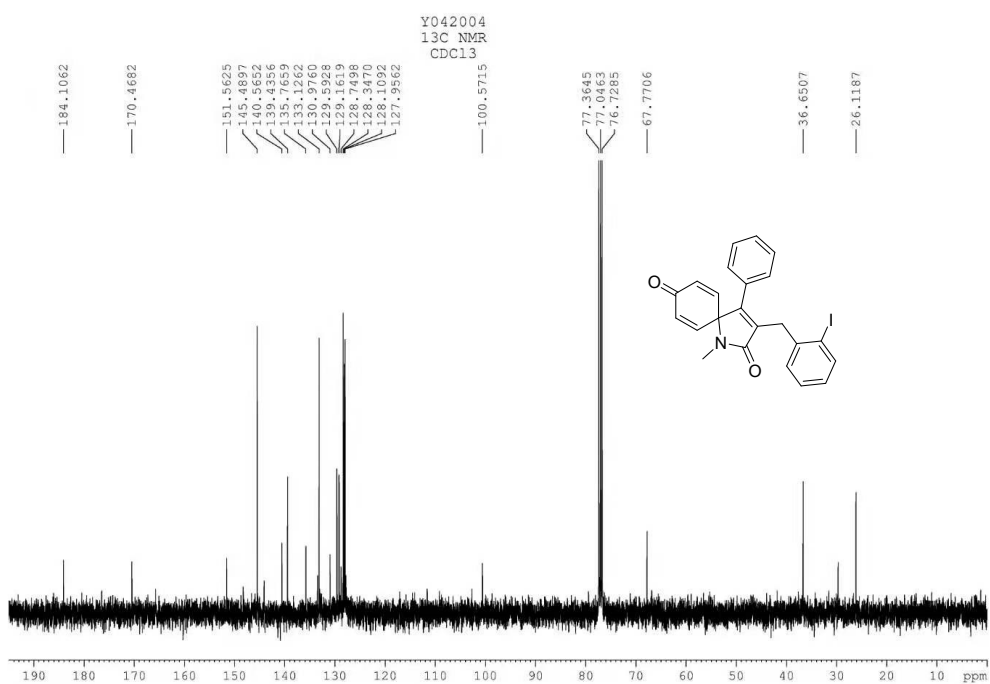


Fig. 23 <sup>13</sup>C NMR spectrum of compound 3k

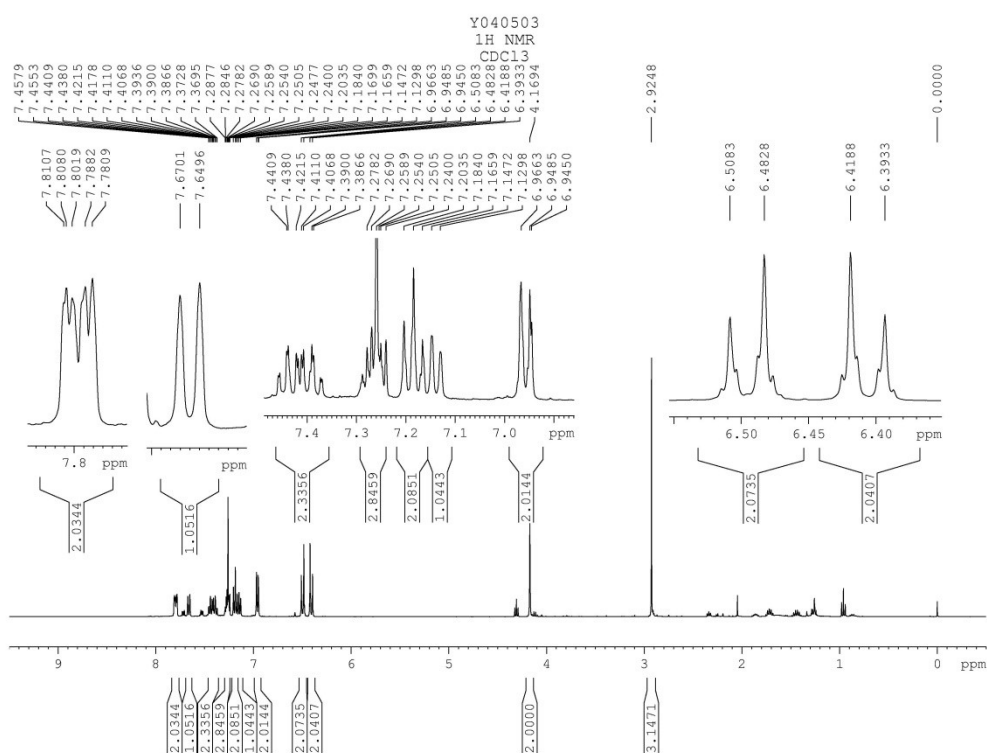


Fig. 24 <sup>1</sup>H NMR spectrum of compound 3l

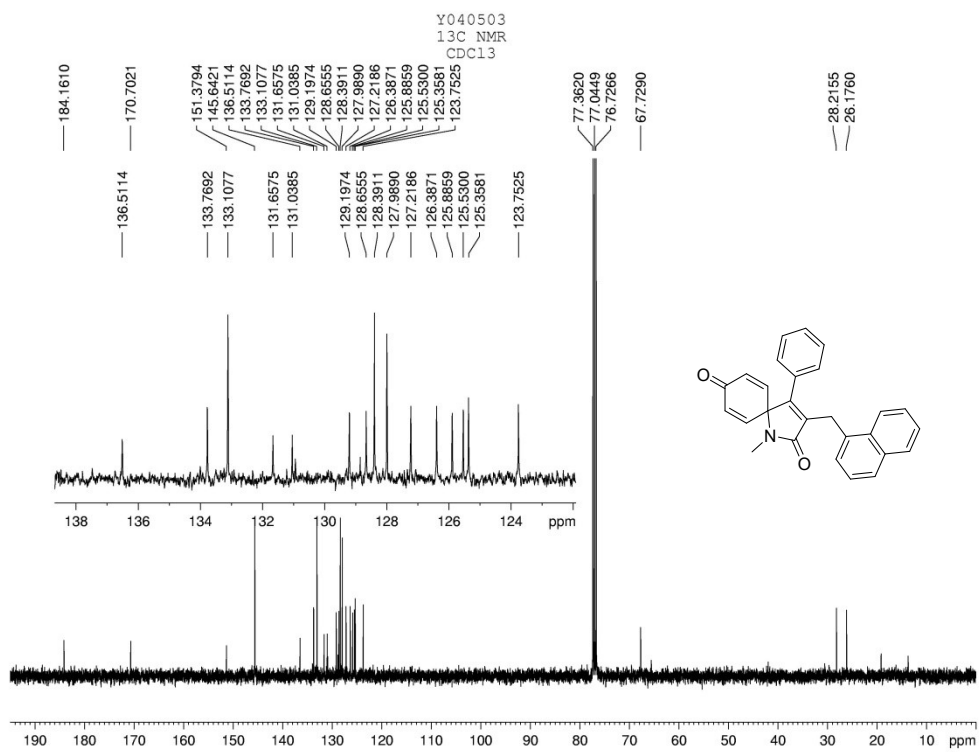


Fig. 25 <sup>13</sup>C NMR spectrum of compound 3l

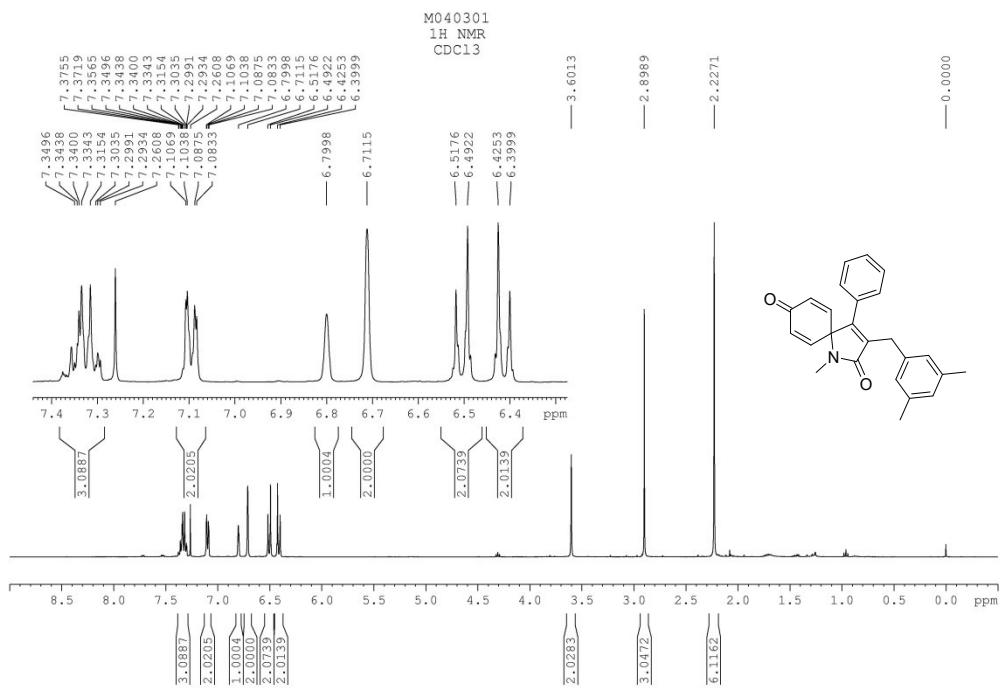


Fig. 26 <sup>1</sup>H NMR spectrum of compound 3m



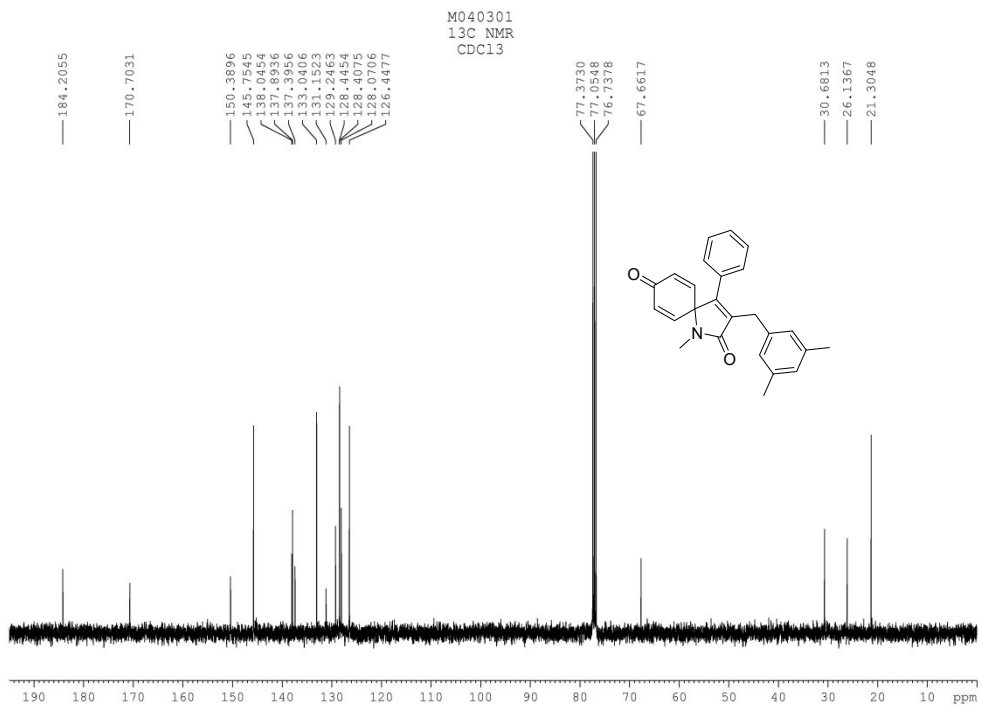


Fig. 27 <sup>13</sup>C NMR spectrum of compound 3m

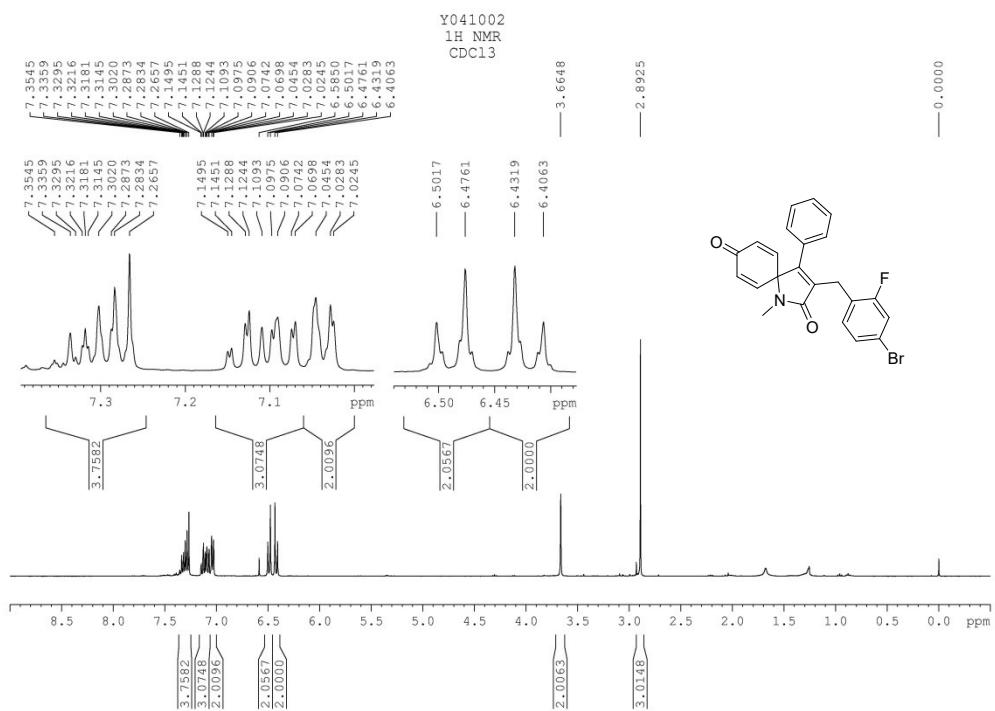


Fig. 28 <sup>1</sup>H NMR spectrum of compound 3n

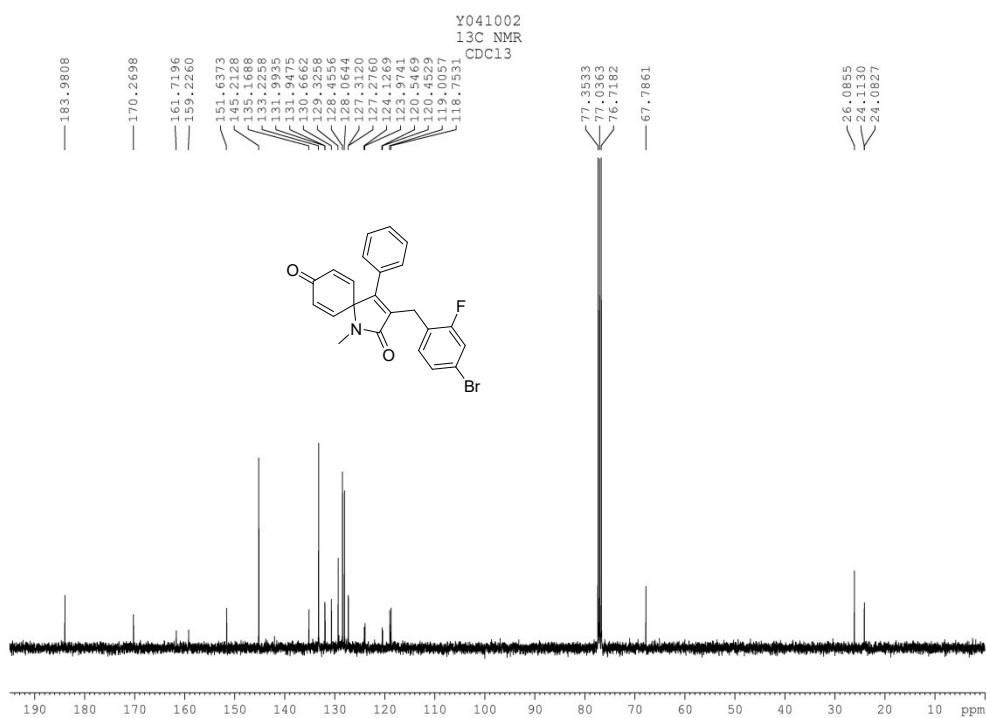


Fig. 29 <sup>13</sup>C NMR spectrum of compound 3n

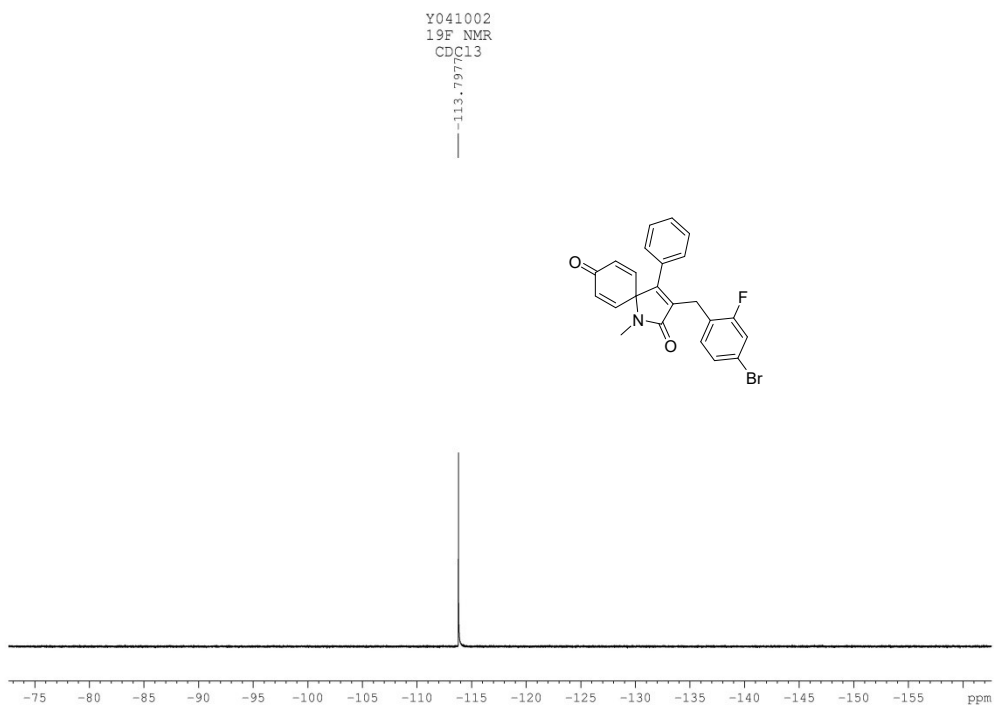


Fig. 30 <sup>19</sup>F NMR spectrum of compound 3n

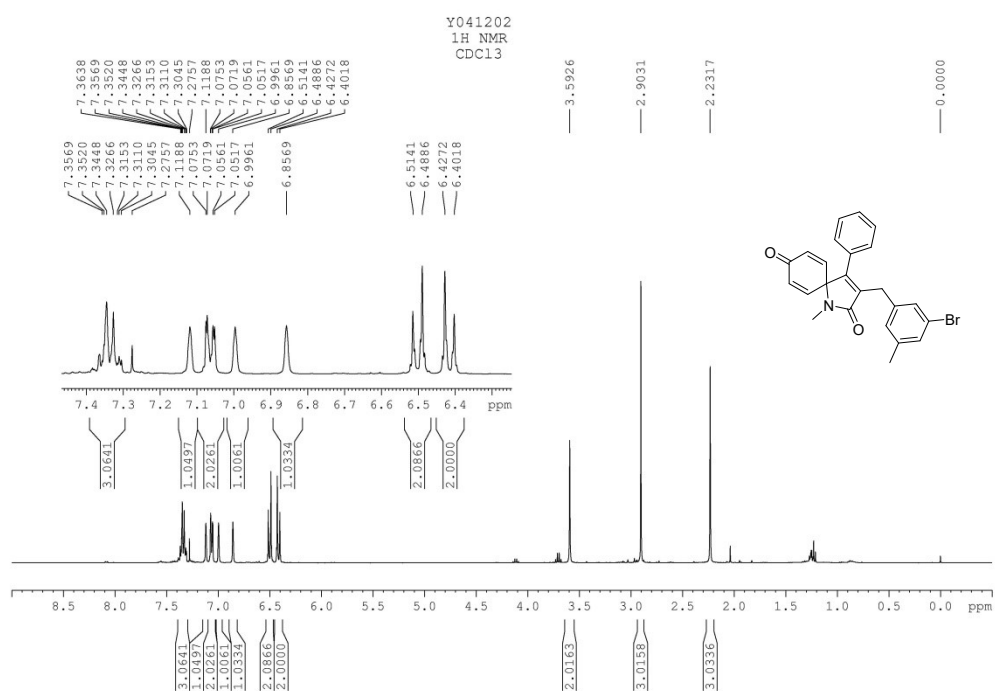


Fig. 31 <sup>1</sup>H NMR spectrum of compound 3o

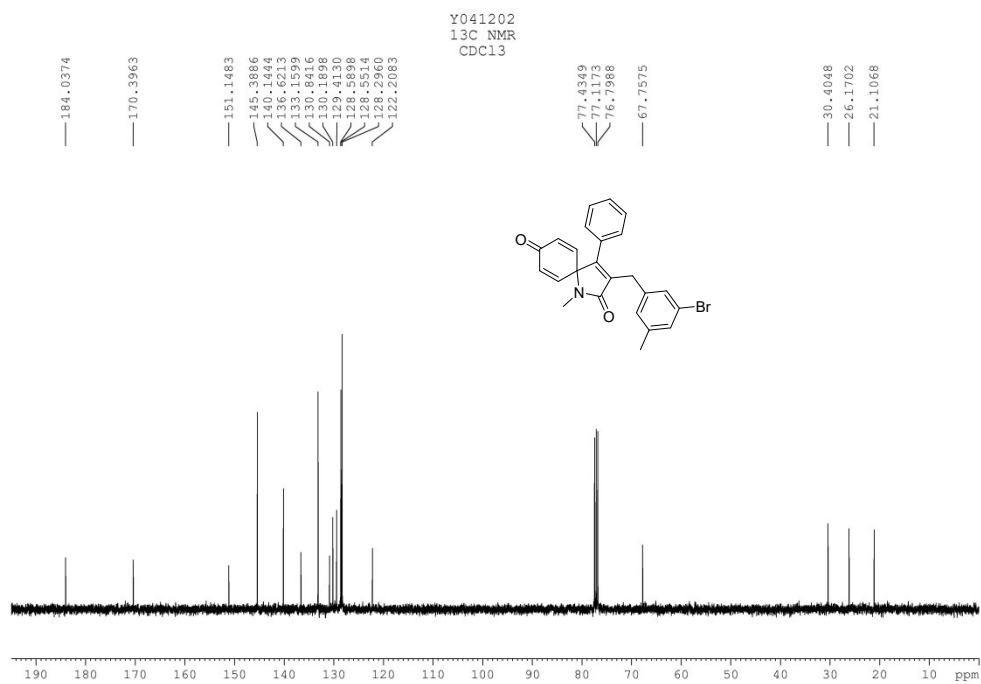


Fig. 32 <sup>13</sup>C NMR spectrum of compound 3o



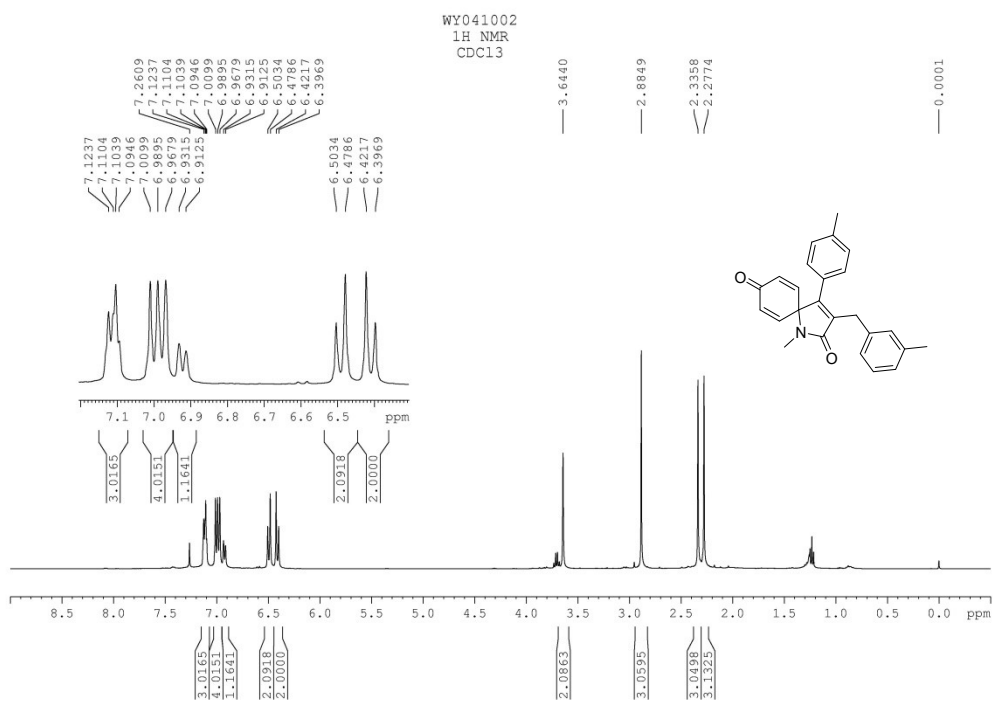


Fig. 35 <sup>1</sup>H NMR spectrum of compound 3s

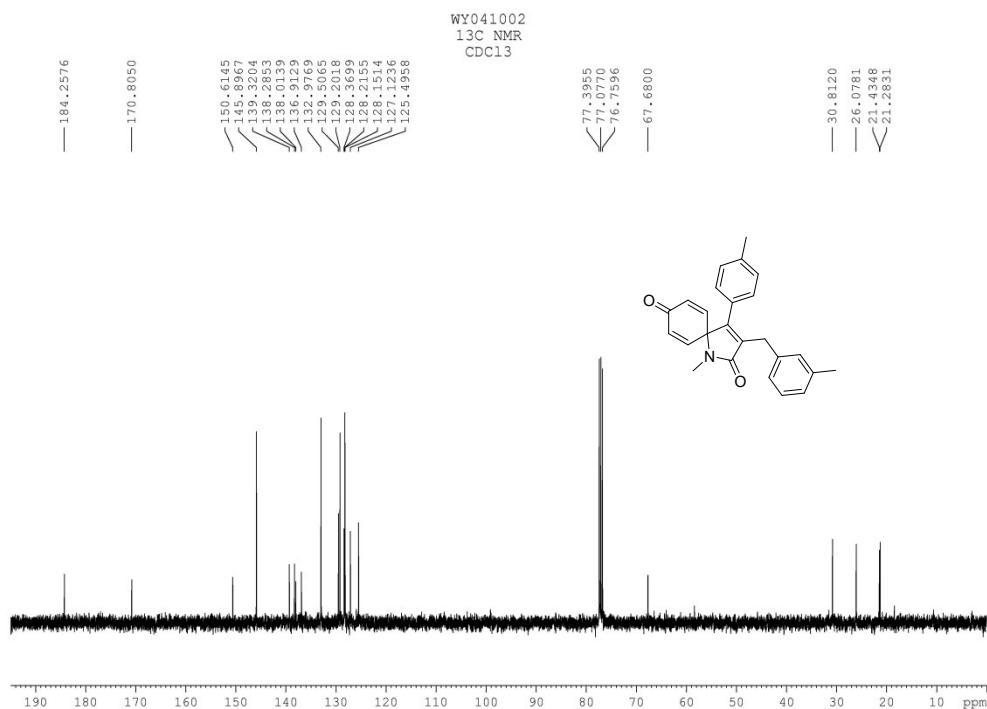


Fig. 36 <sup>13</sup>C NMR spectrum of compound 3s

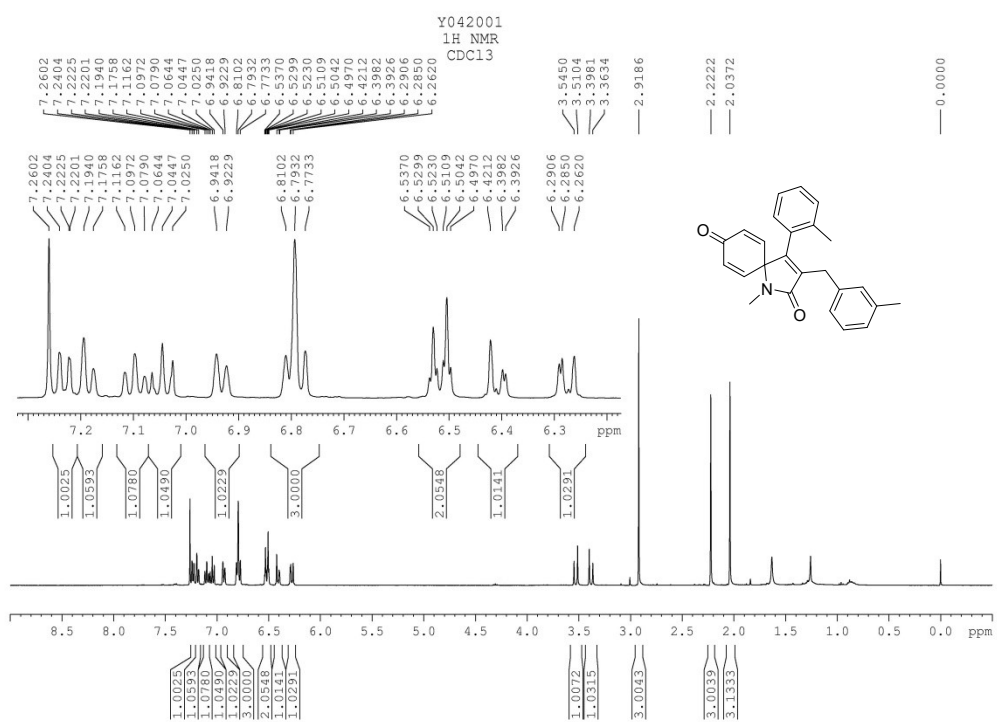


Fig. 37 <sup>1</sup>H NMR spectrum of compound 3t

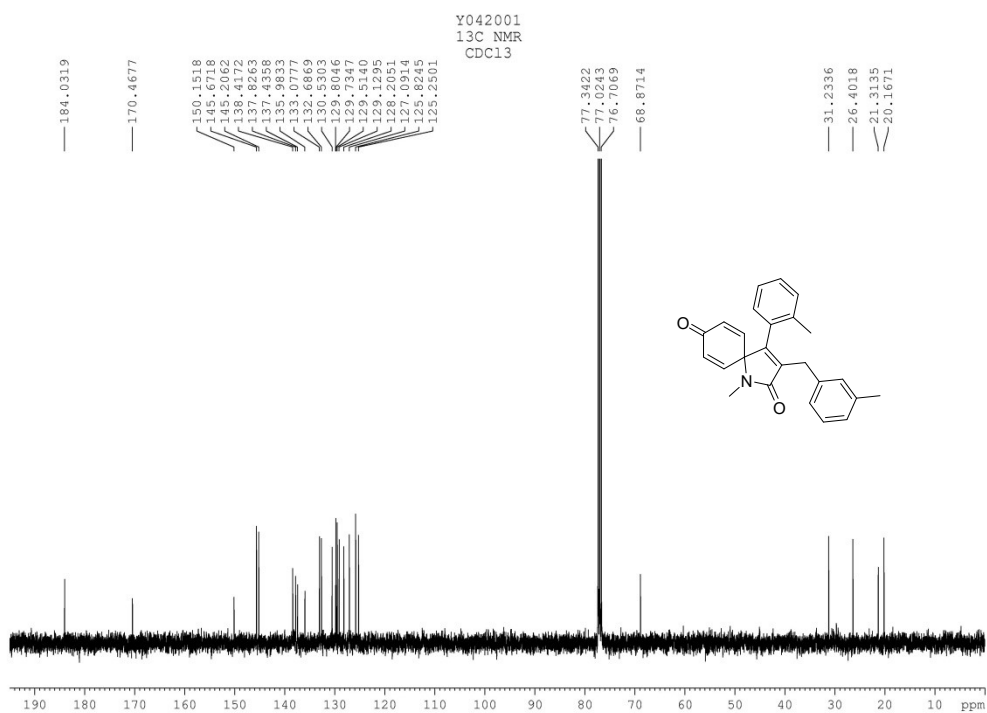


Fig. 38 <sup>13</sup>C NMR spectrum of compound 3t

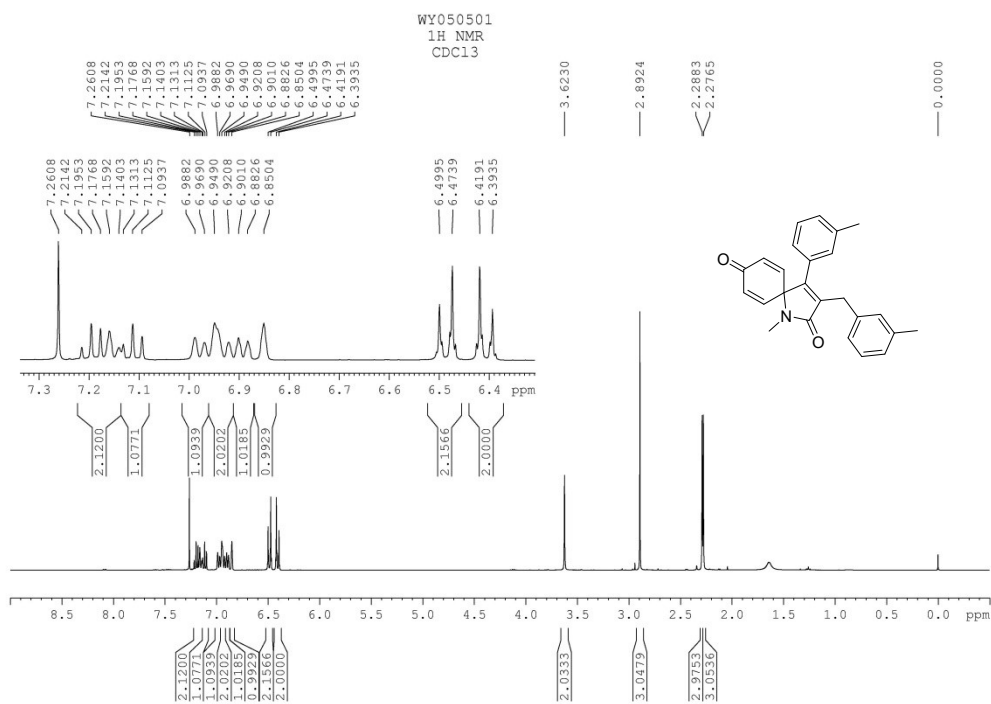


Fig. 39 <sup>1</sup>H NMR spectrum of compound 3u

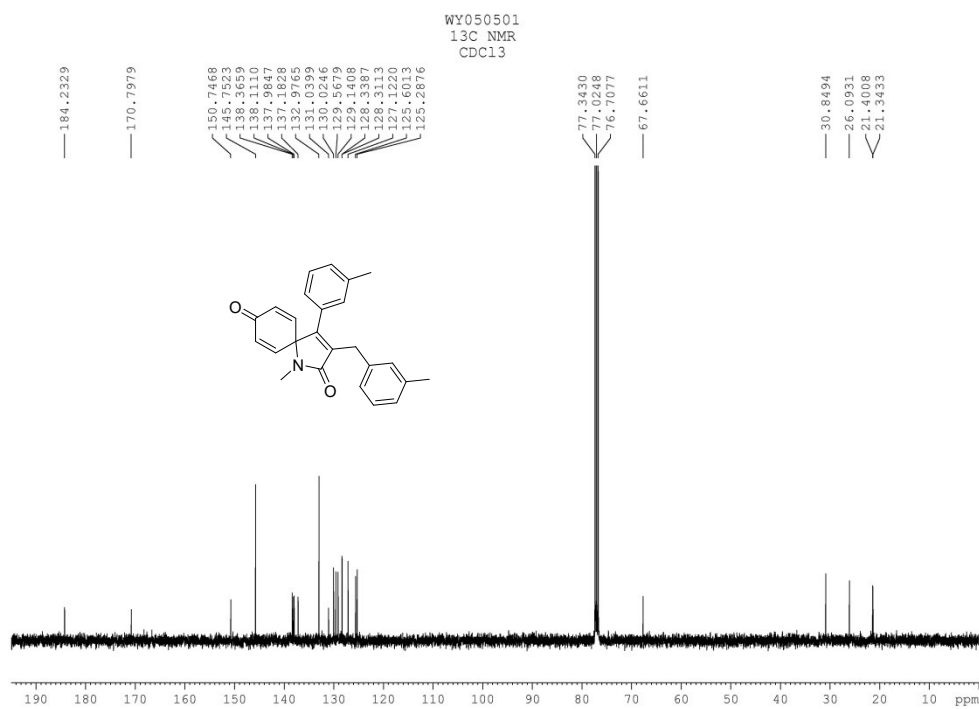


Fig. 40 <sup>13</sup>C NMR spectrum of compound 3u

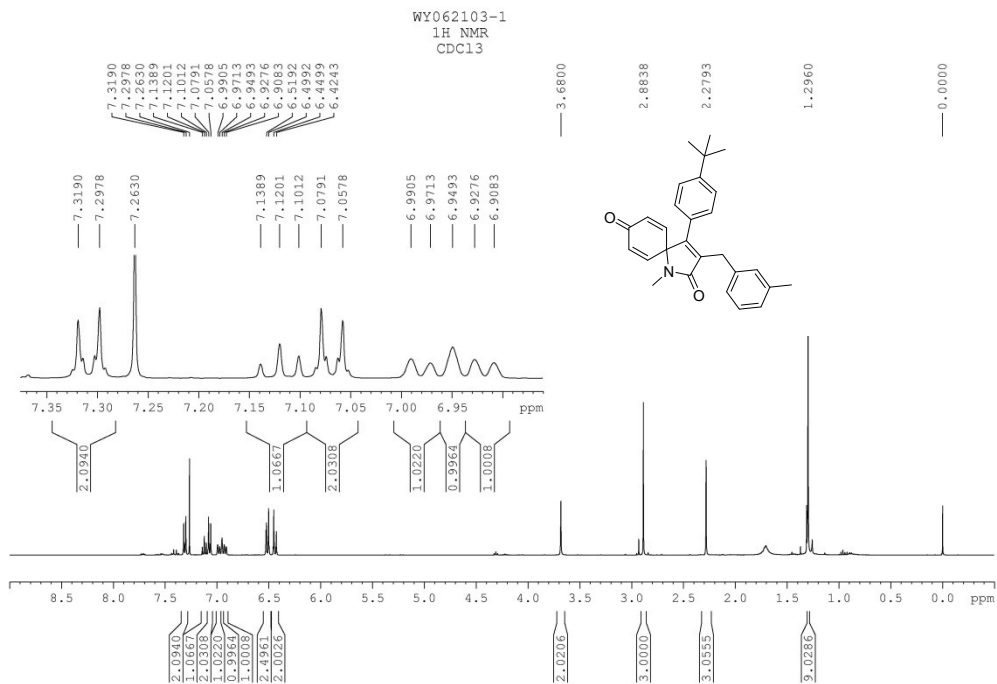


Fig. 41 <sup>1</sup>H NMR spectrum of compound 3v

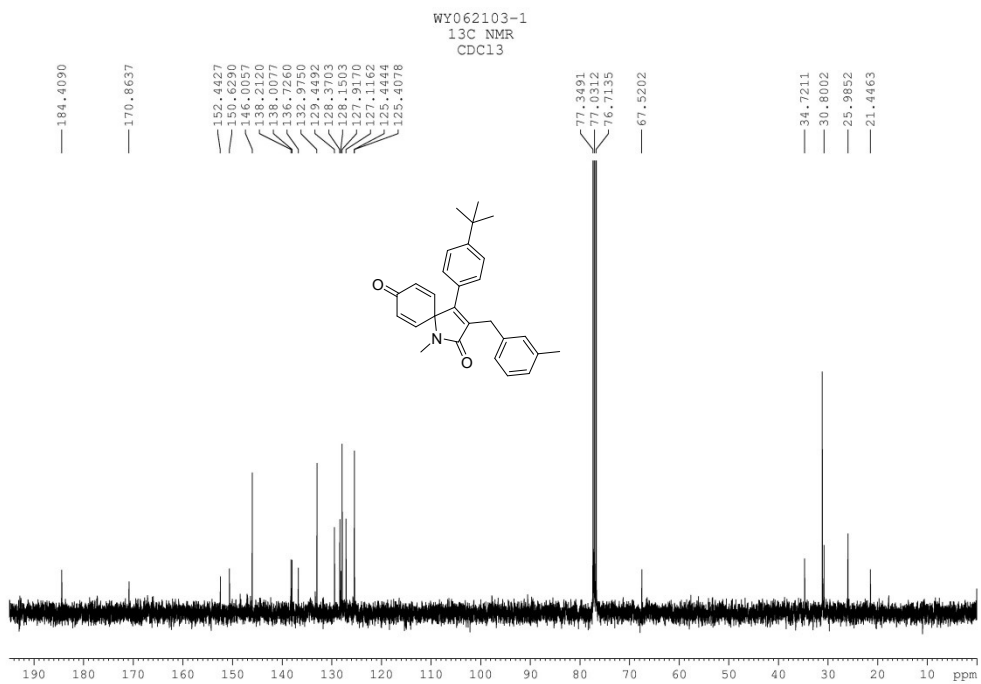




Fig. 42 <sup>13</sup>C NMR spectrum of compound 3v

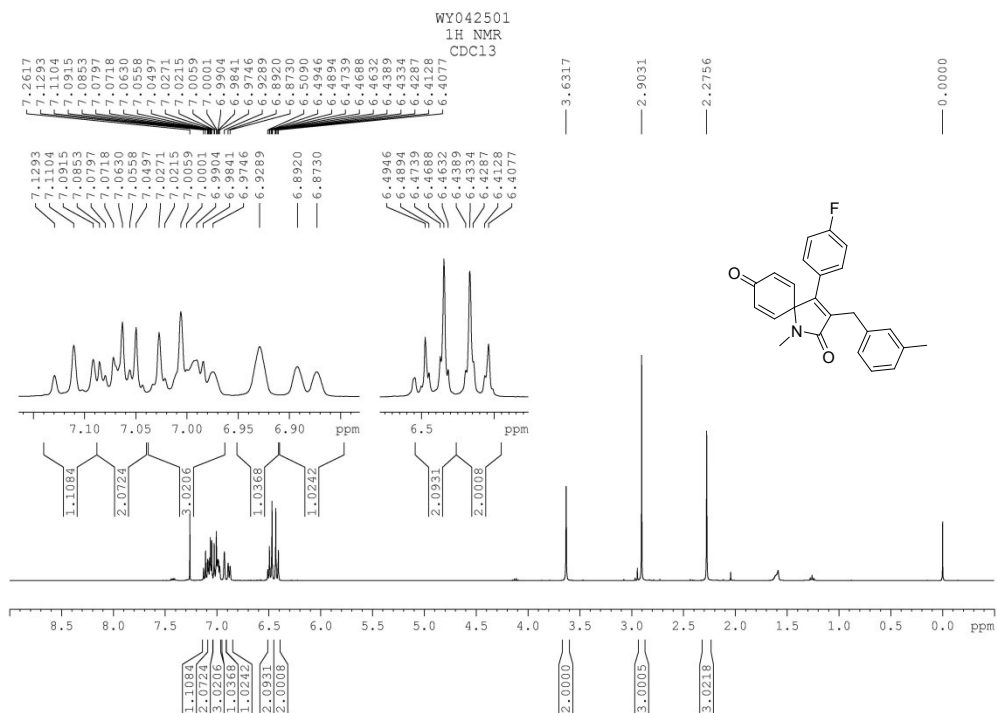
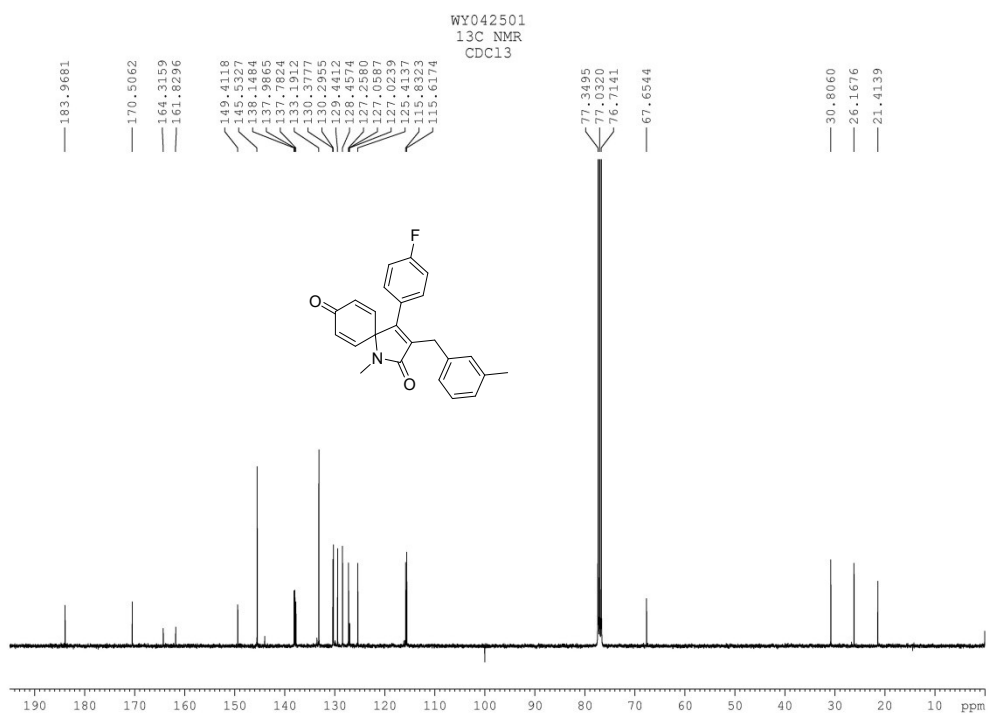


Fig. 43 <sup>1</sup>H NMR spectrum of compound 3w





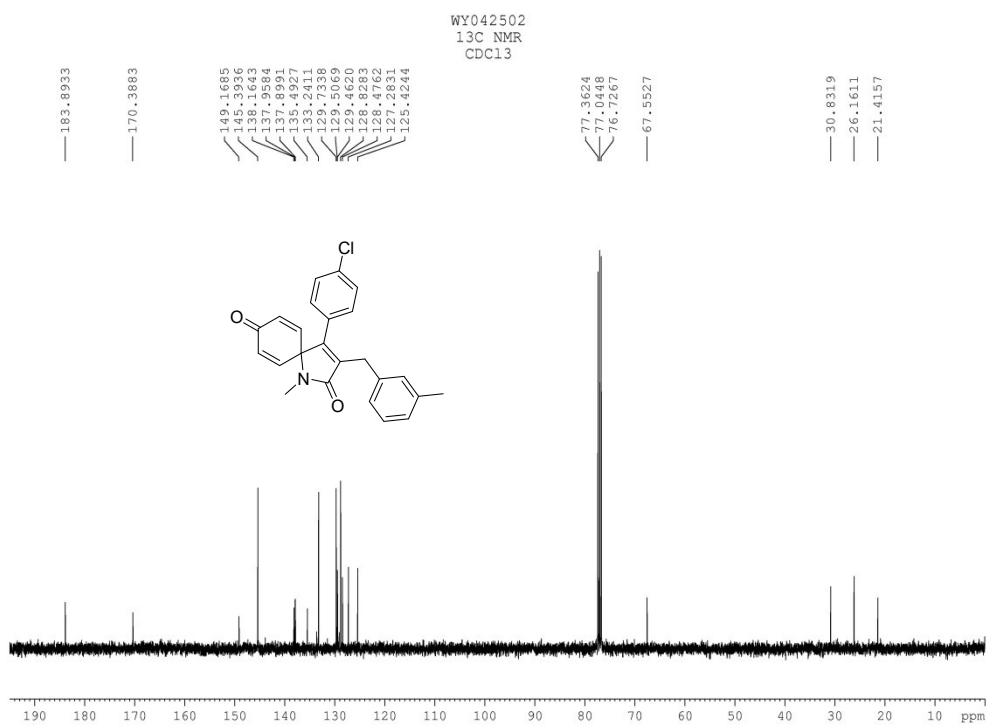


Fig. 47 <sup>13</sup>C NMR spectrum of compound 3x

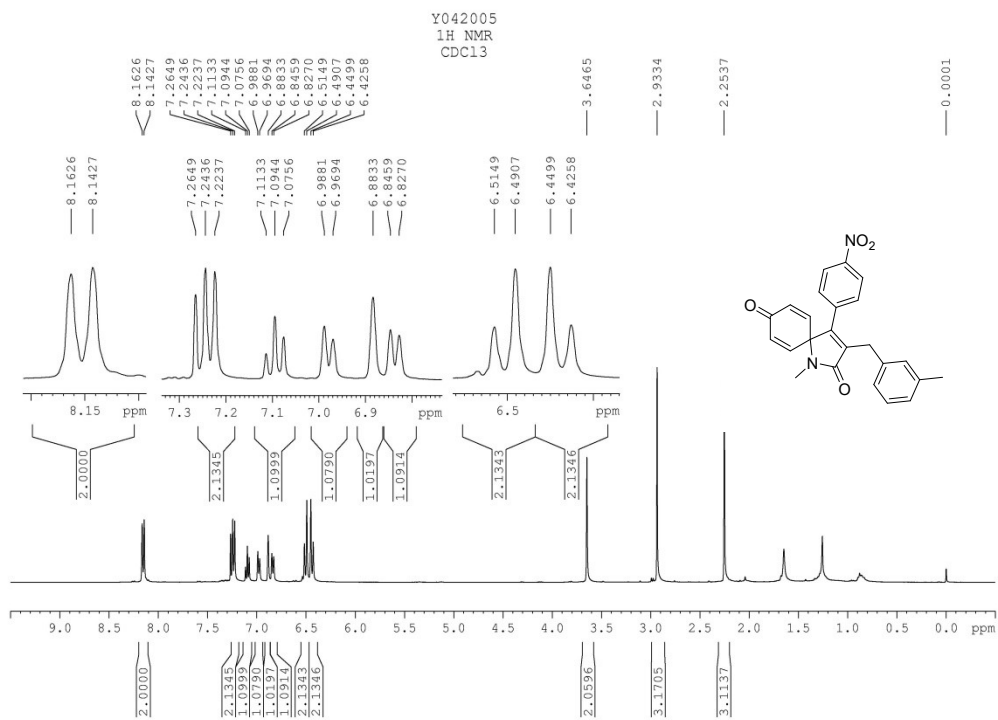


Fig. 48 <sup>1</sup>H NMR spectrum of compound 3y

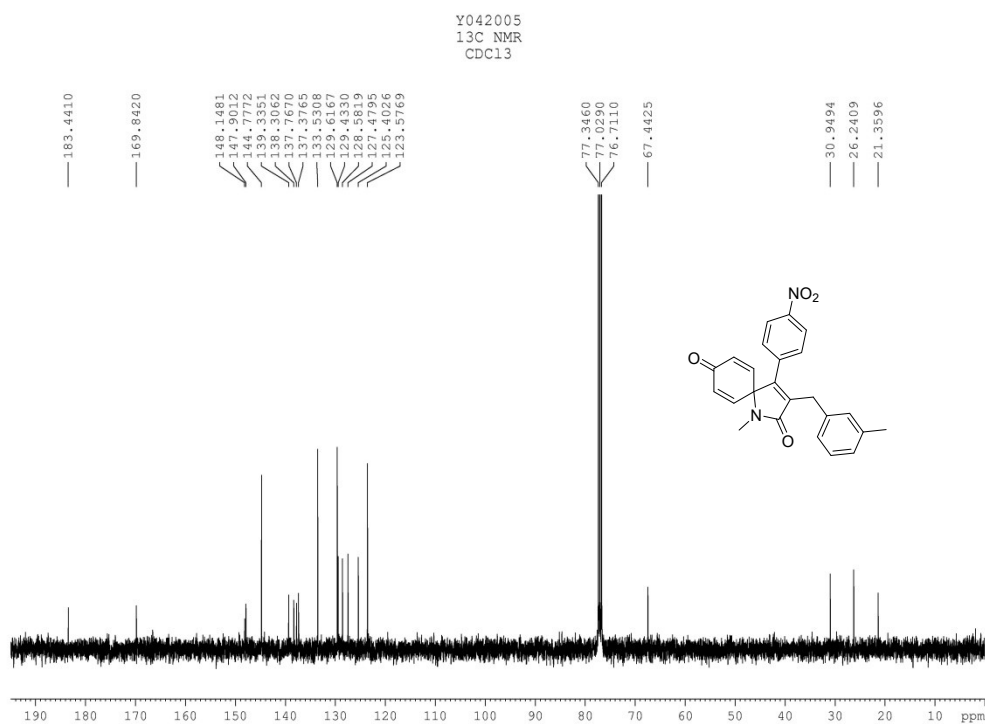


Fig. 49 <sup>13</sup>C NMR spectrum of compound 3y

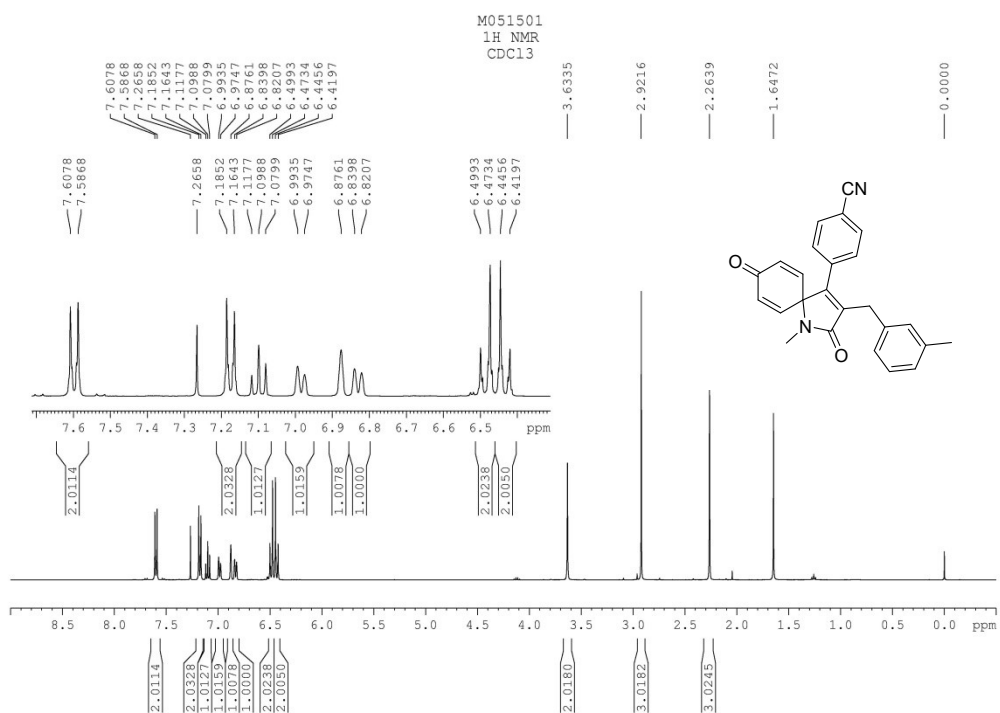


Fig. 50 <sup>1</sup>H NMR spectrum of compound 3z

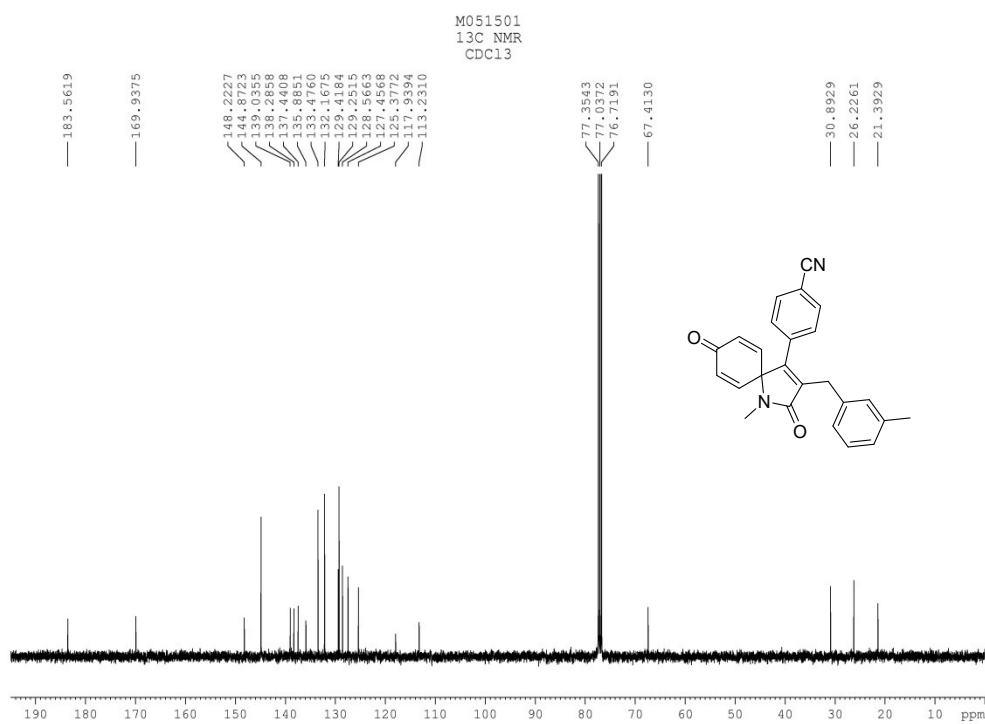


Fig. 51 <sup>13</sup>C NMR spectrum of compound 3z

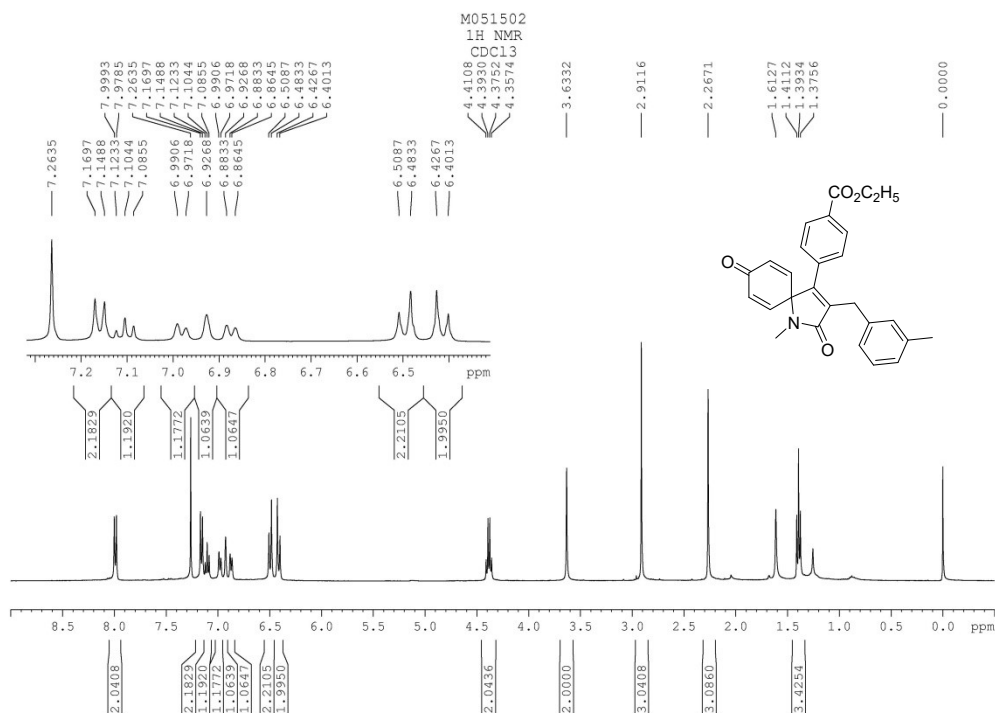


Fig. 52 <sup>1</sup>H NMR spectrum of compound 3aa

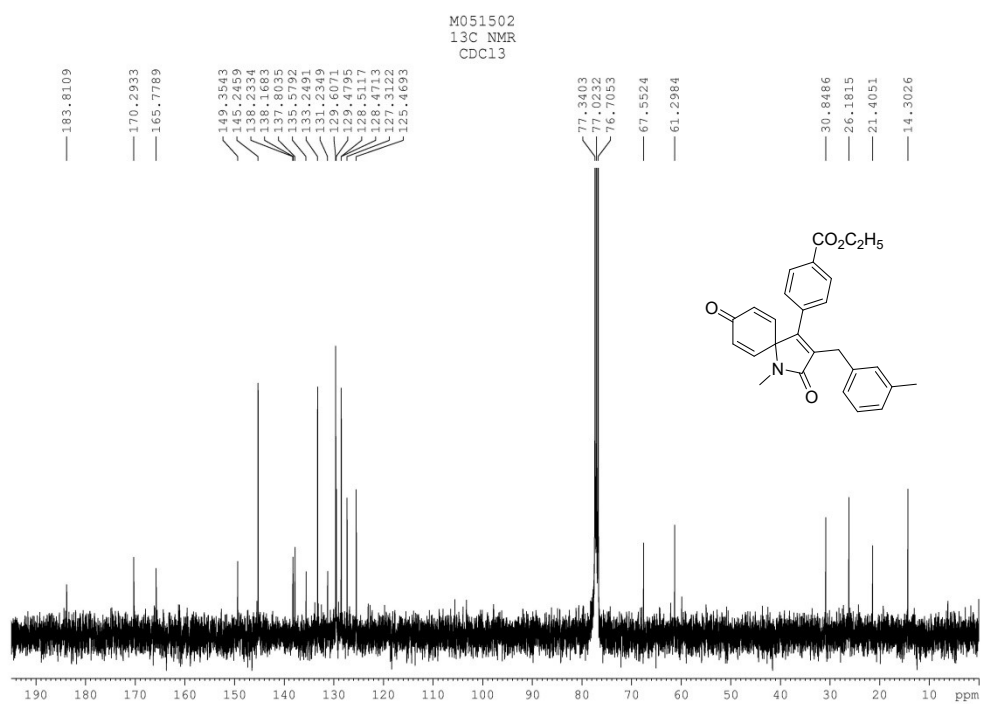


Fig. 53 <sup>13</sup>C NMR spectrum of compound 3aa

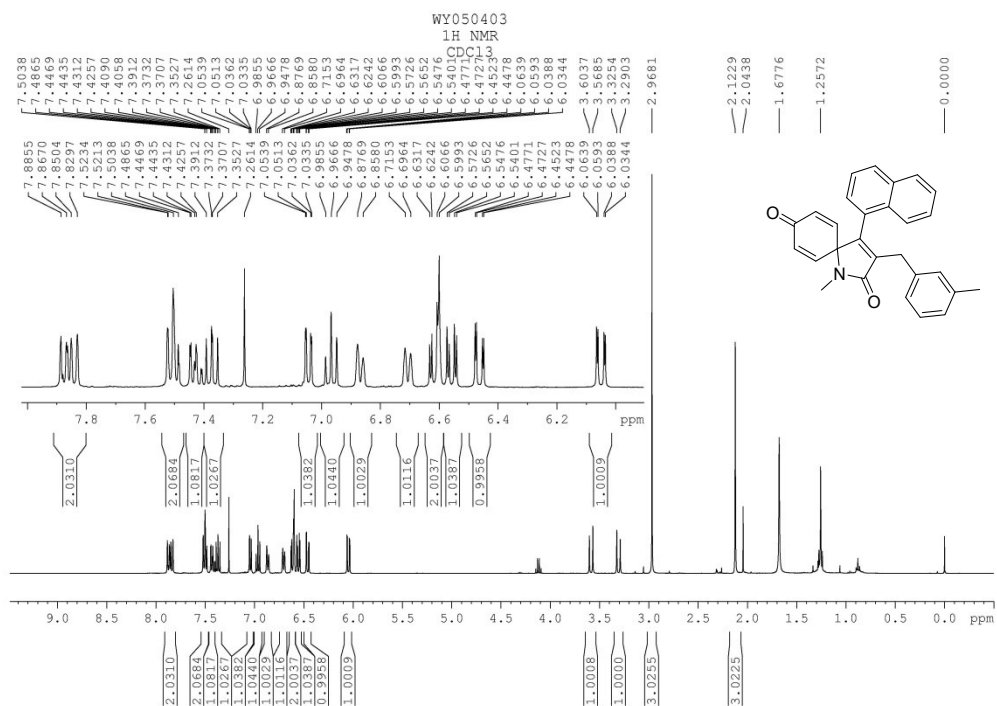


Fig. 54 <sup>1</sup>H NMR spectrum of compound 3ab

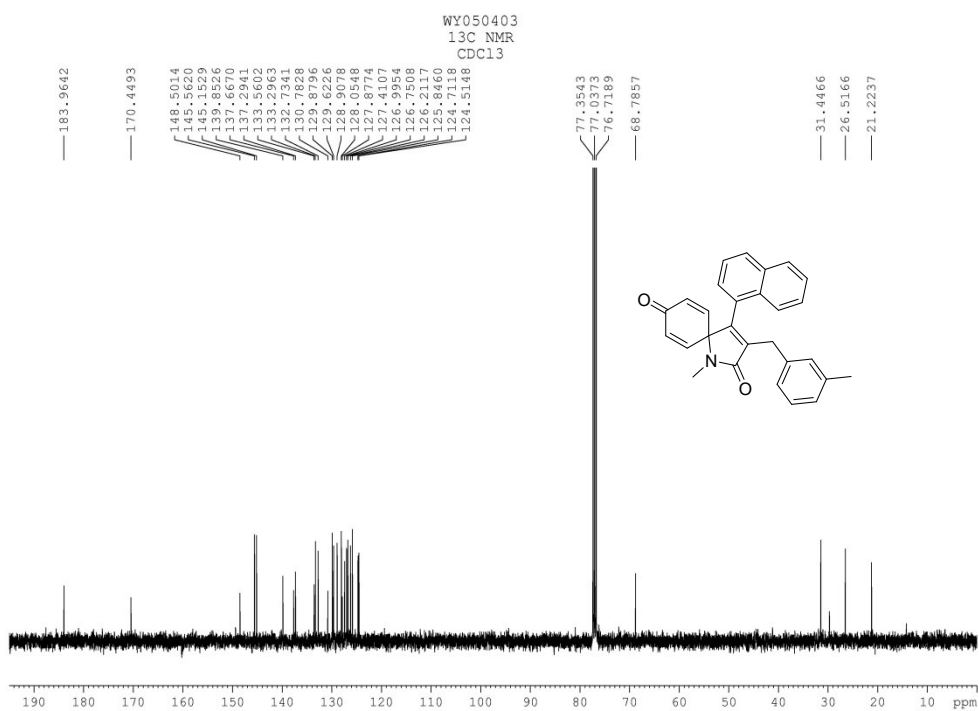


Fig. 55 <sup>13</sup>C NMR spectrum of compound 3ab

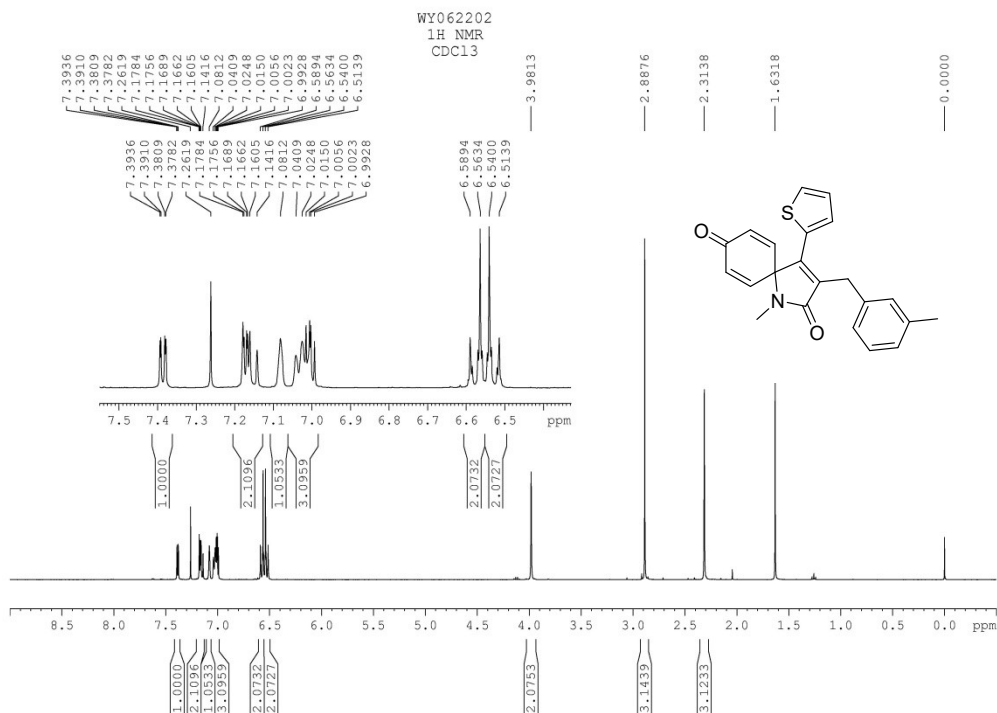


Fig. 56 <sup>1</sup>H NMR spectrum of compound 3ac

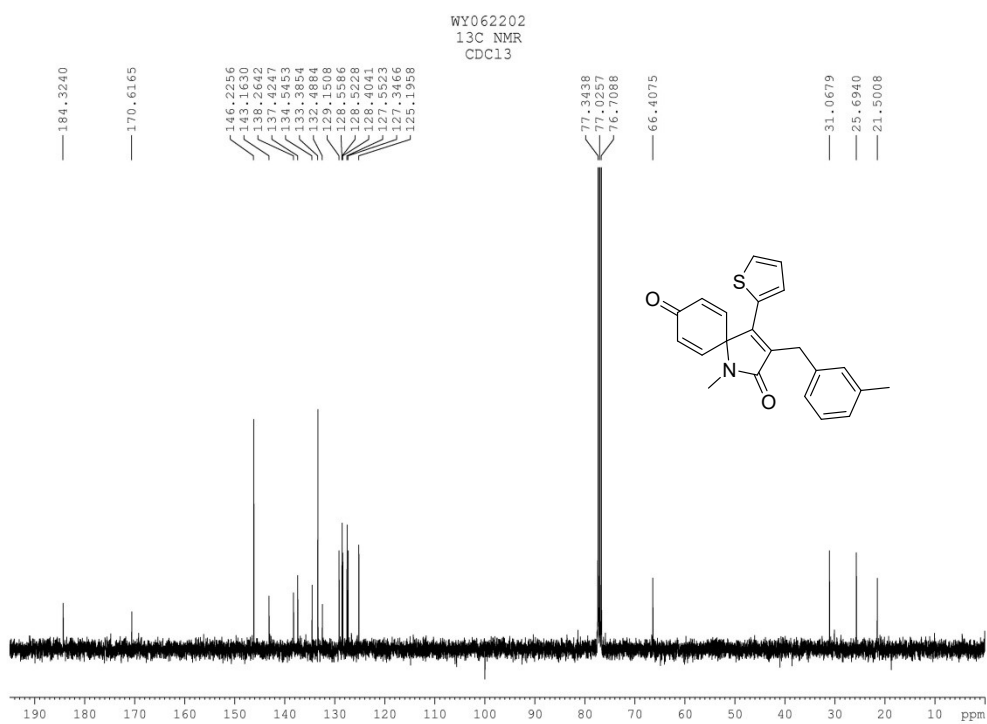


Fig. 57 <sup>13</sup>C NMR spectrum of compound 3ac

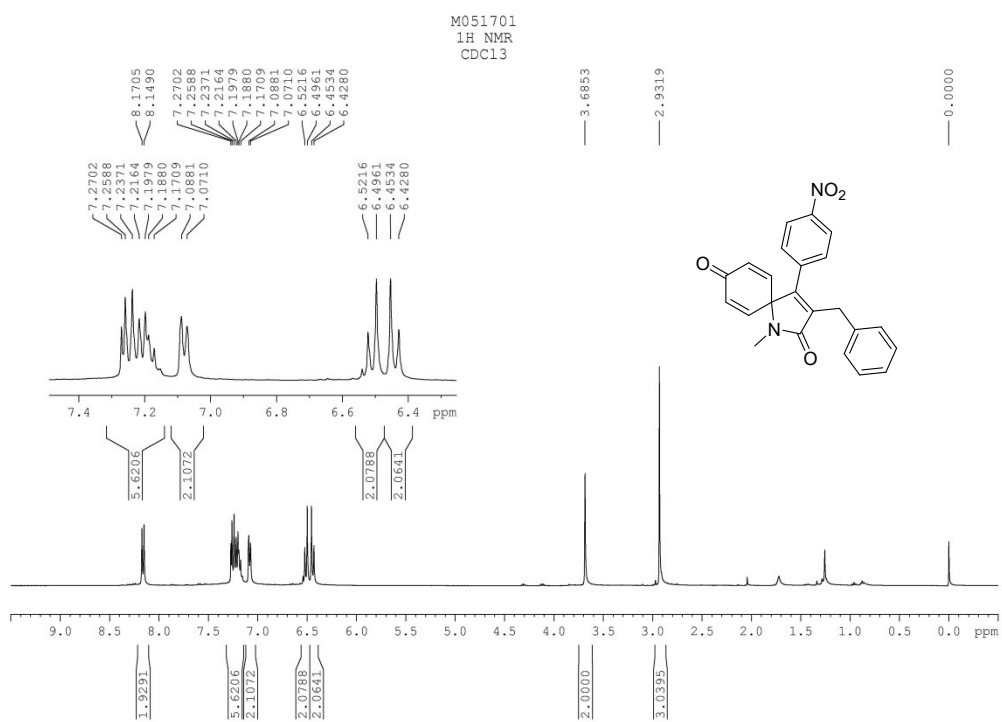


Fig. 58 <sup>1</sup>H NMR spectrum of compound 3ad



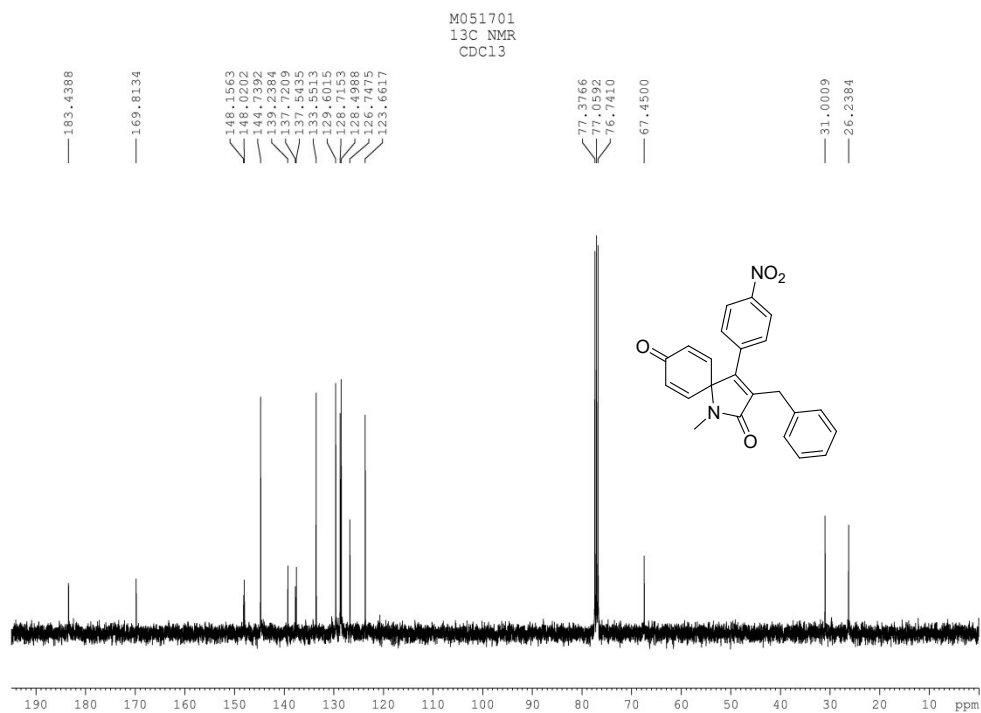


Fig. 59 <sup>13</sup>C NMR spectrum of compound 3ad

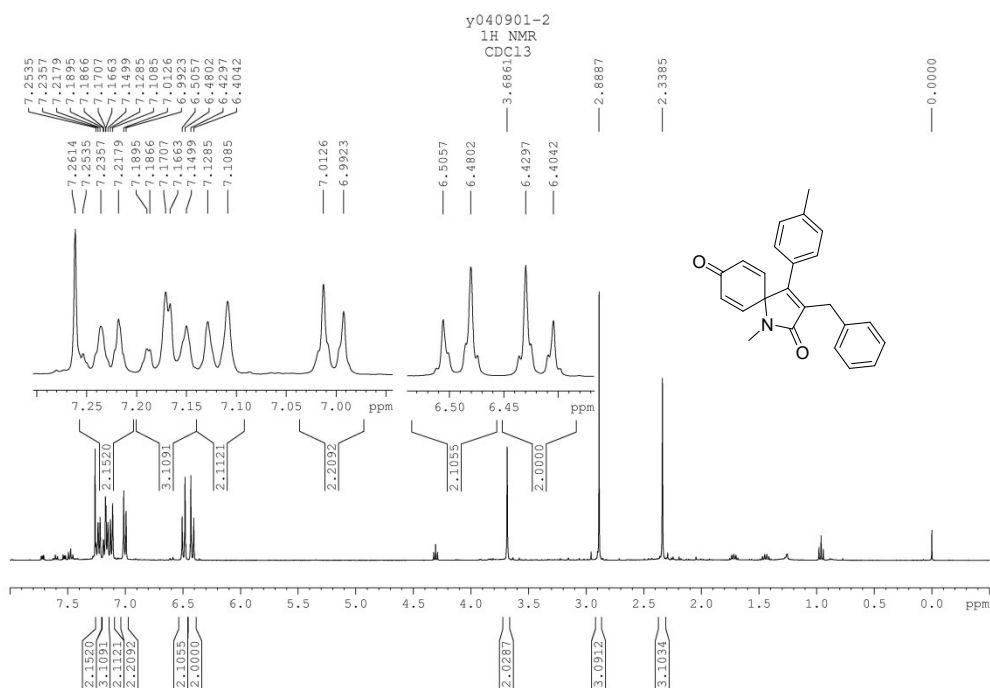


Fig. 60 <sup>1</sup>H NMR spectrum of compound 3ae

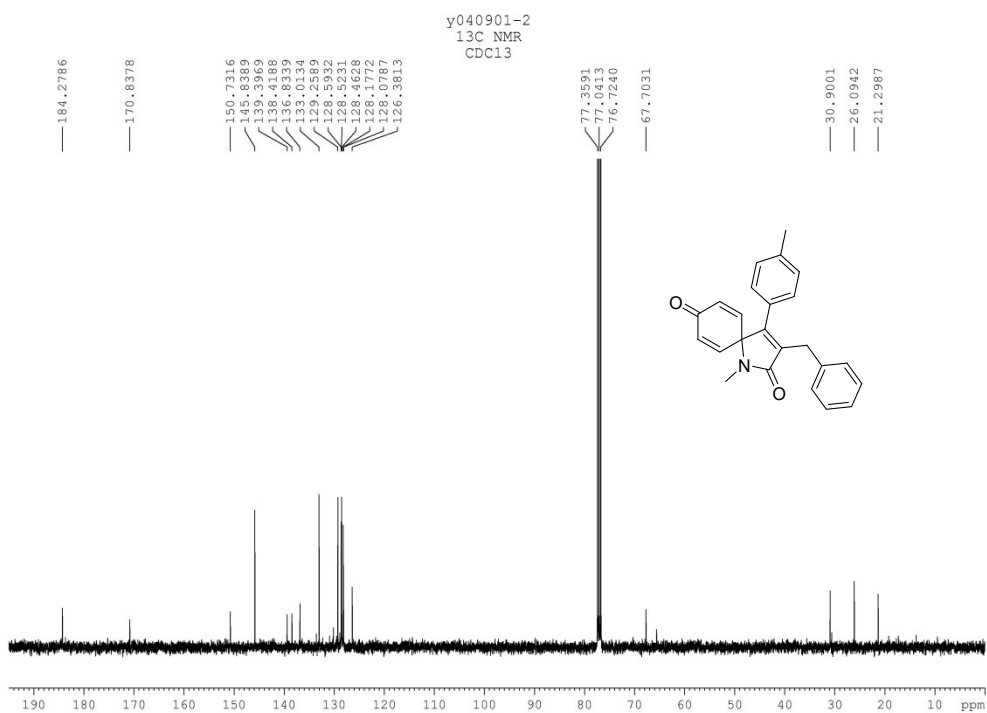


Fig. 61 <sup>13</sup>C NMR spectrum of compound 3ae

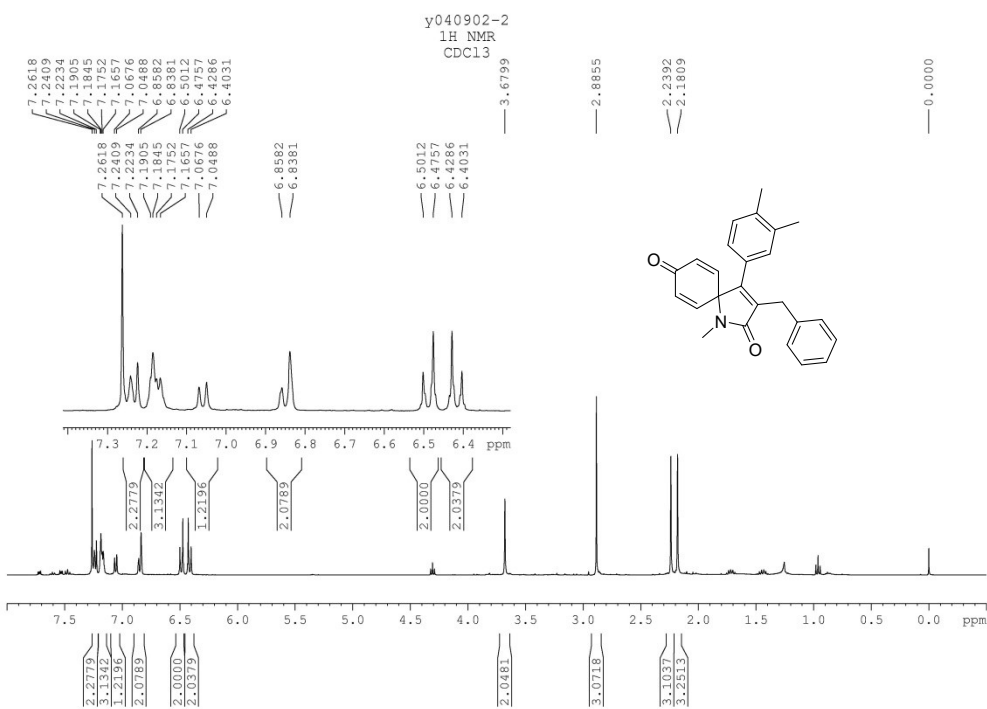


Fig. 62 <sup>1</sup>H NMR spectrum of compound 3af

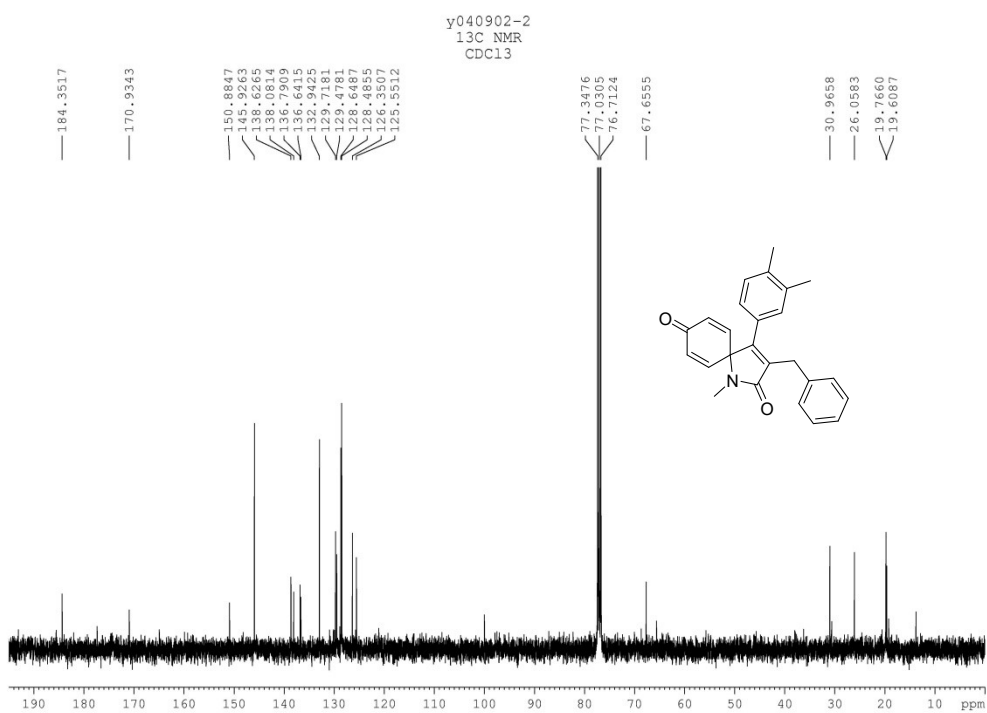


Fig. 63 <sup>13</sup>C NMR spectrum of compound 3af

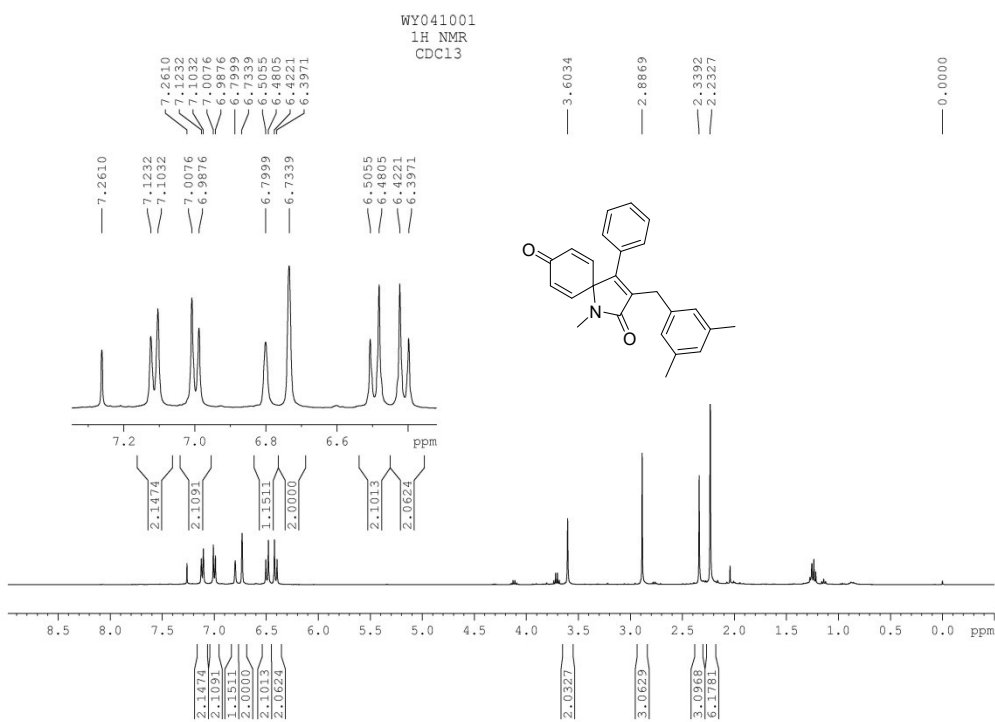


Fig. 64 <sup>1</sup>H NMR spectrum of compound 3ag

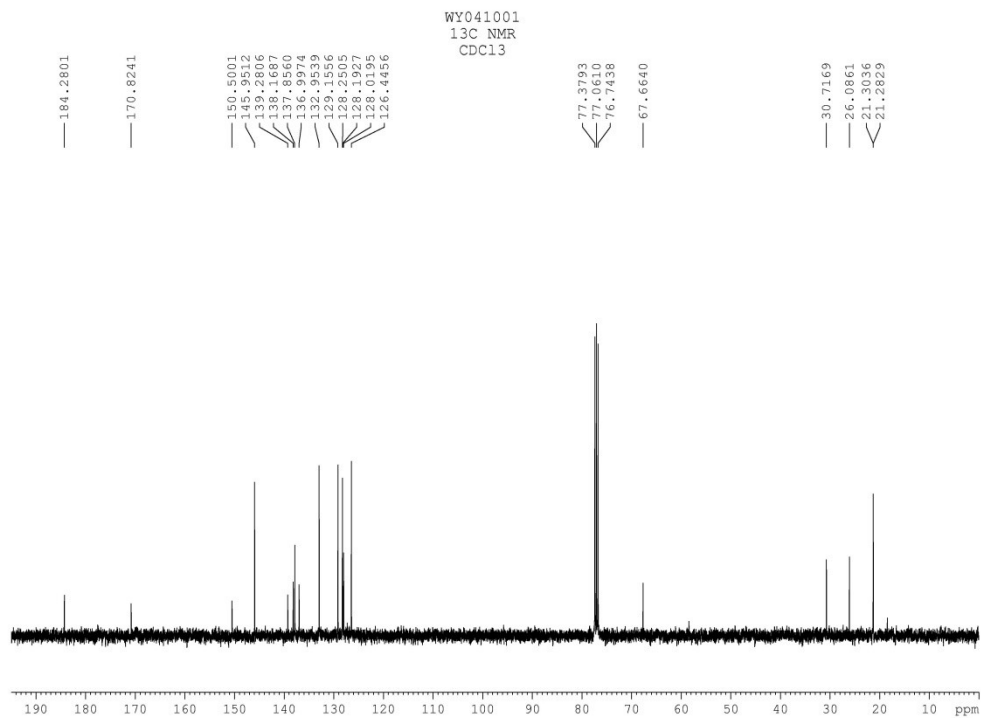


Fig. 65 <sup>13</sup>C NMR spectrum of compound 3ag

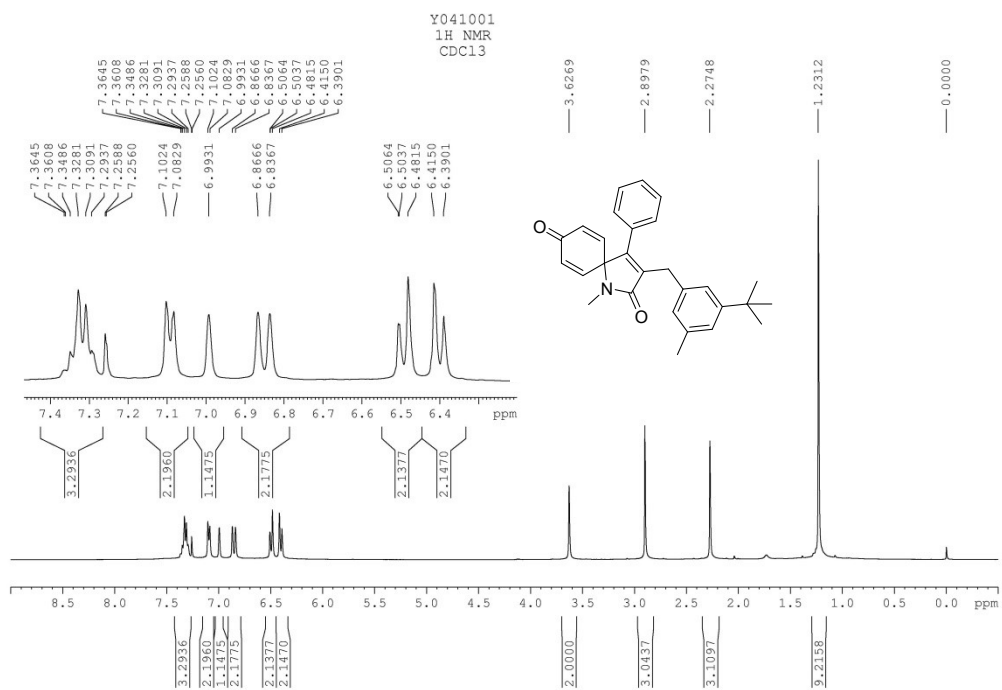


Fig. 66 <sup>1</sup>H NMR spectrum of compound 3af

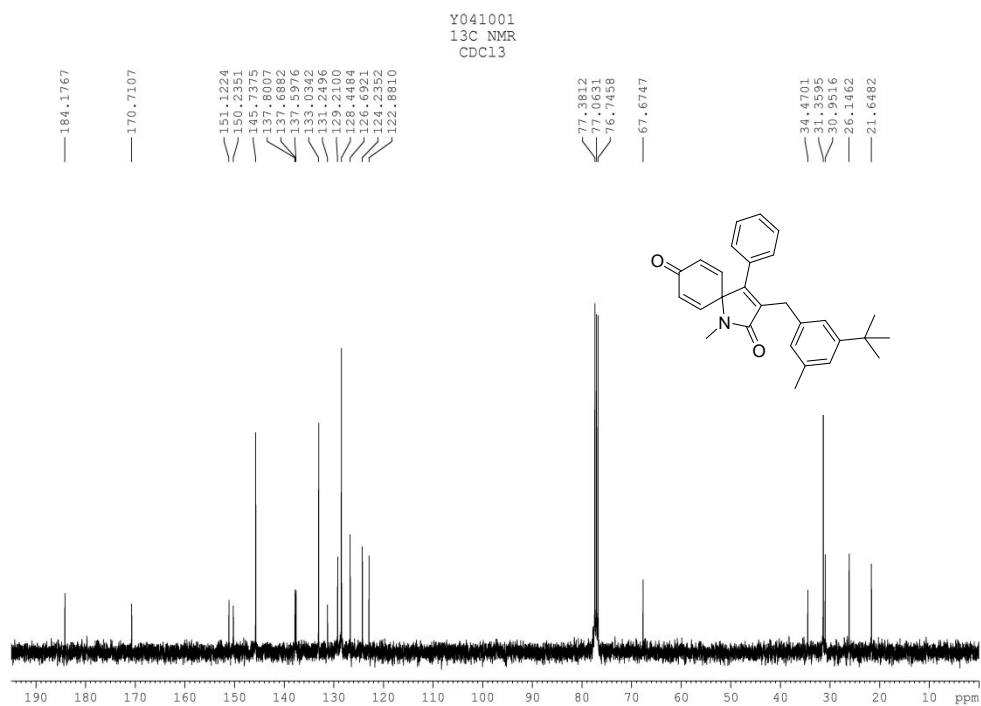


Fig. 67 <sup>13</sup>C NMR spectrum of compound 3af

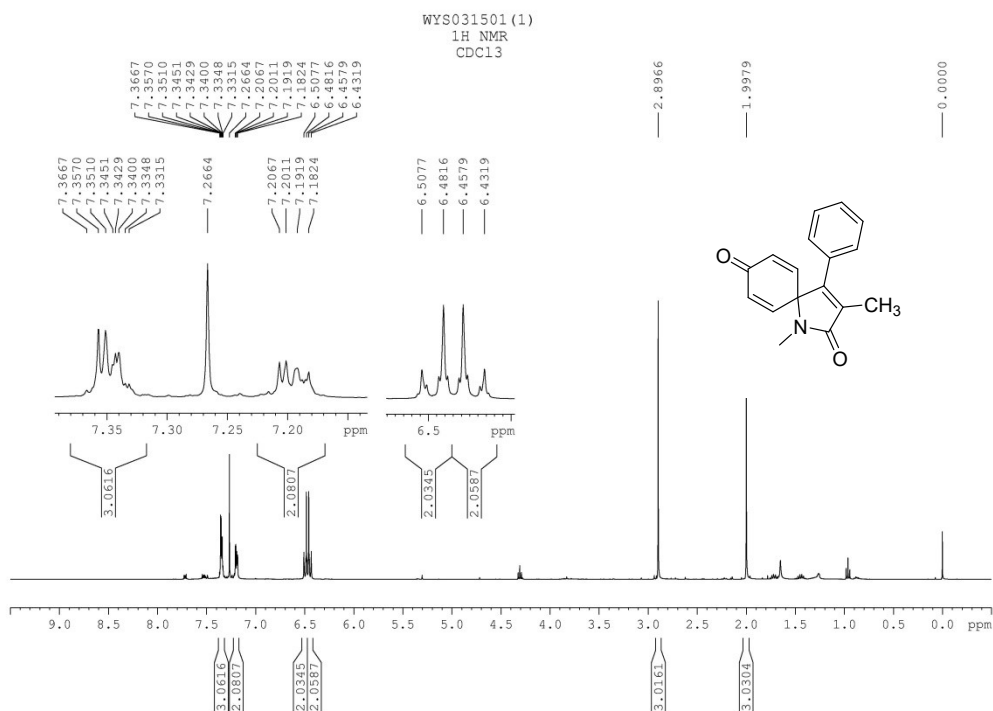


Fig. 68 <sup>1</sup>H NMR spectrum of compound 5

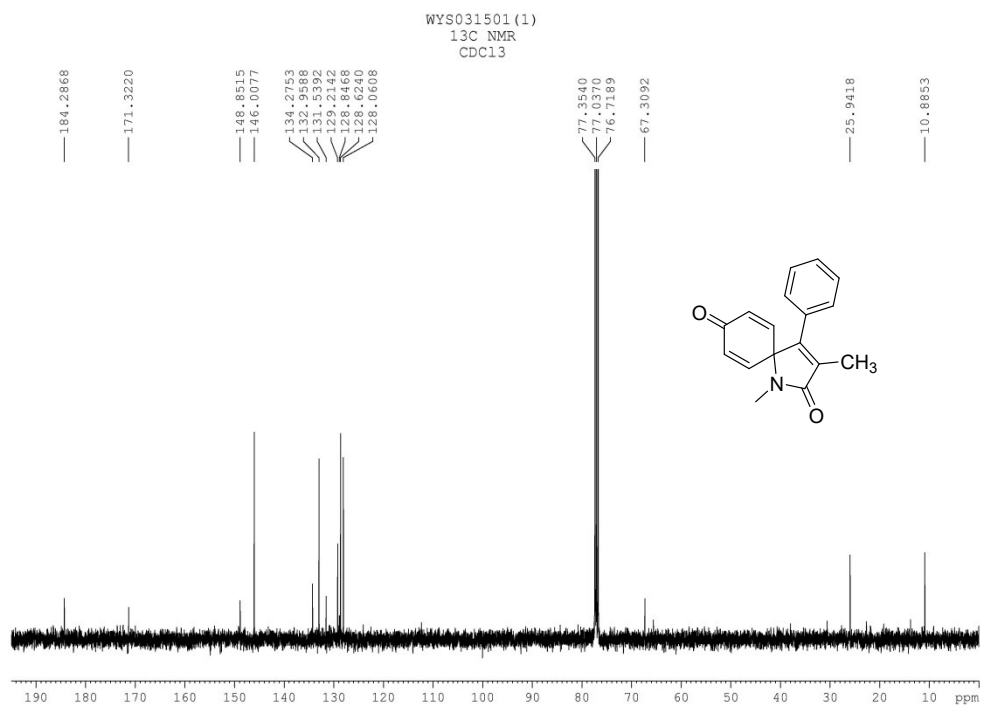


Fig. 69 <sup>13</sup>C NMR spectrum of compound 5

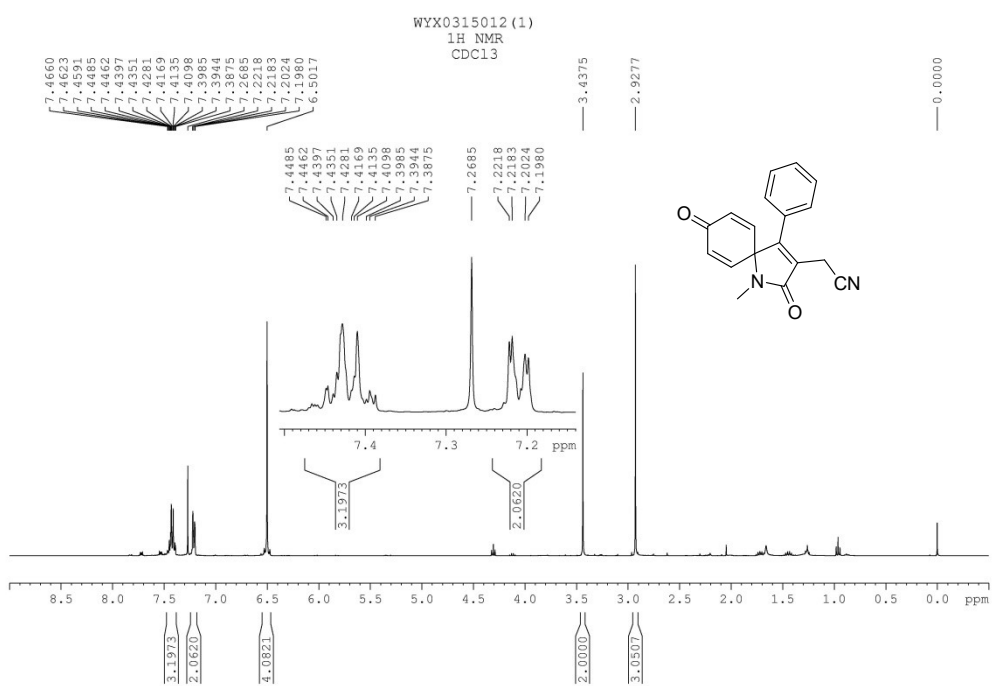


Fig. 70 <sup>1</sup>H NMR spectrum of compound 6

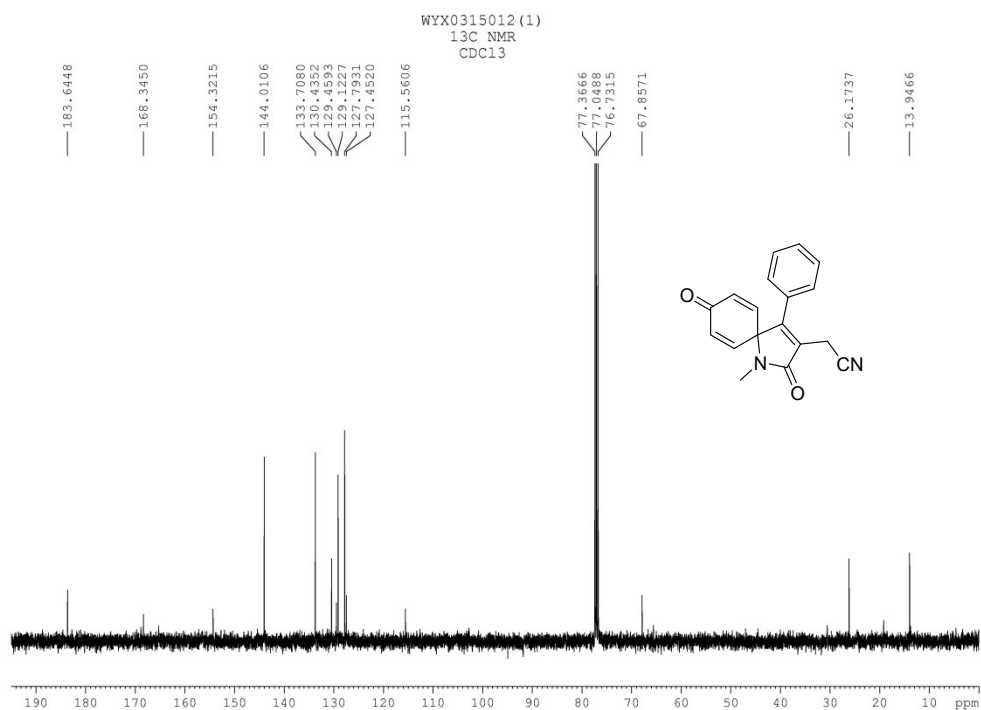


Fig. 71 <sup>13</sup>C NMR spectrum of compound 6

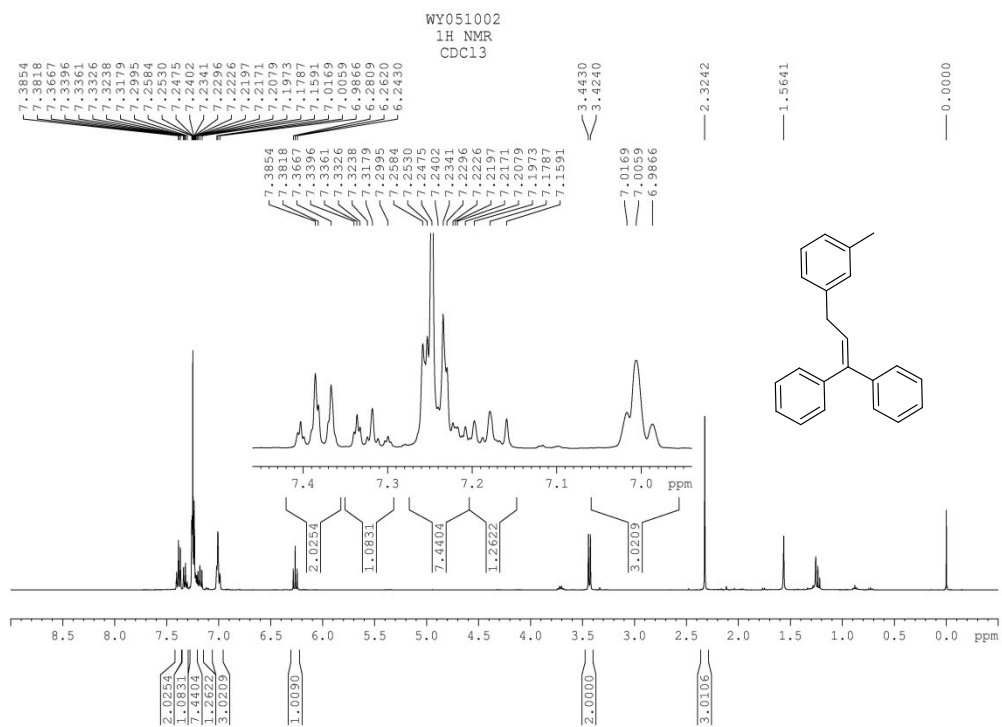


Fig. 72 <sup>1</sup>H NMR spectrum of compound 8

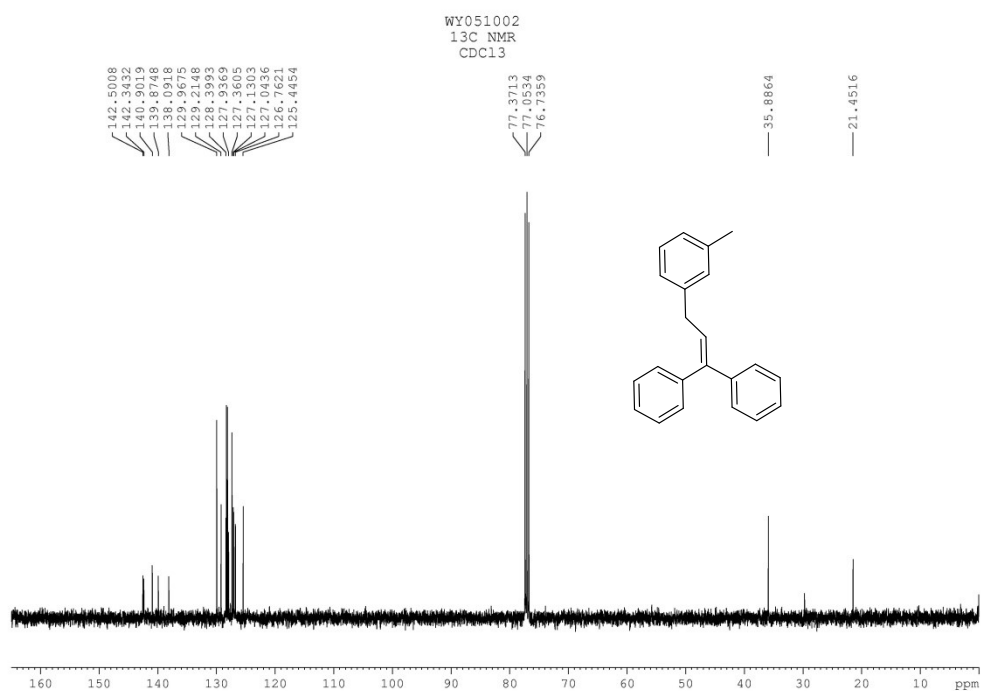


Fig. 73  $^{13}\text{C}$  NMR spectrum of compound 8

#### 4 HR MS spectrum of the adduct 7 of TEMPO and benzyl radical

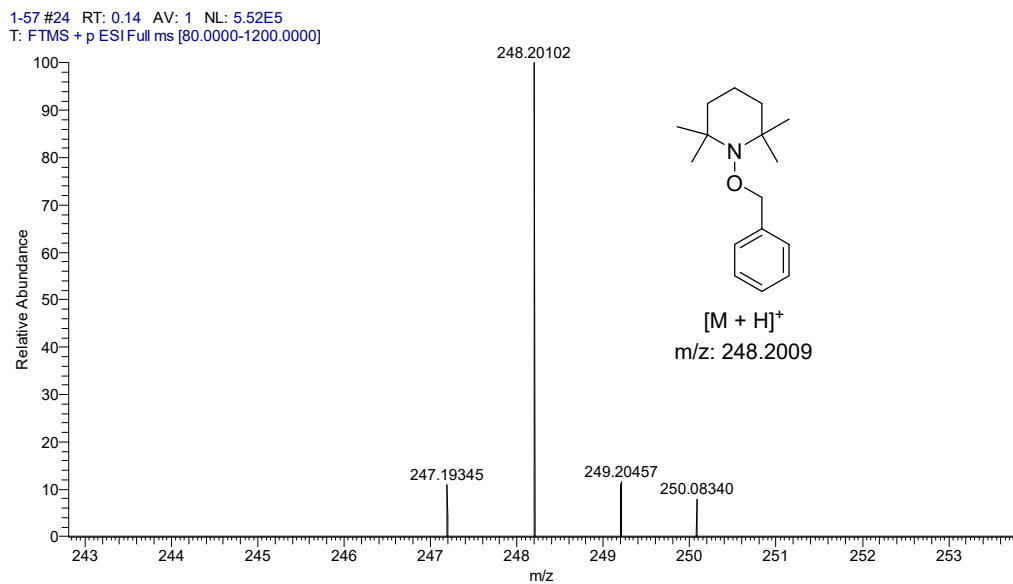


Fig. 74 HR MS spectrum of the adduct 7



## 5 HR MS spectrum of the adduct 8 of ethene-1,1-diyldibenzene and *m*-methyl benzyl radical

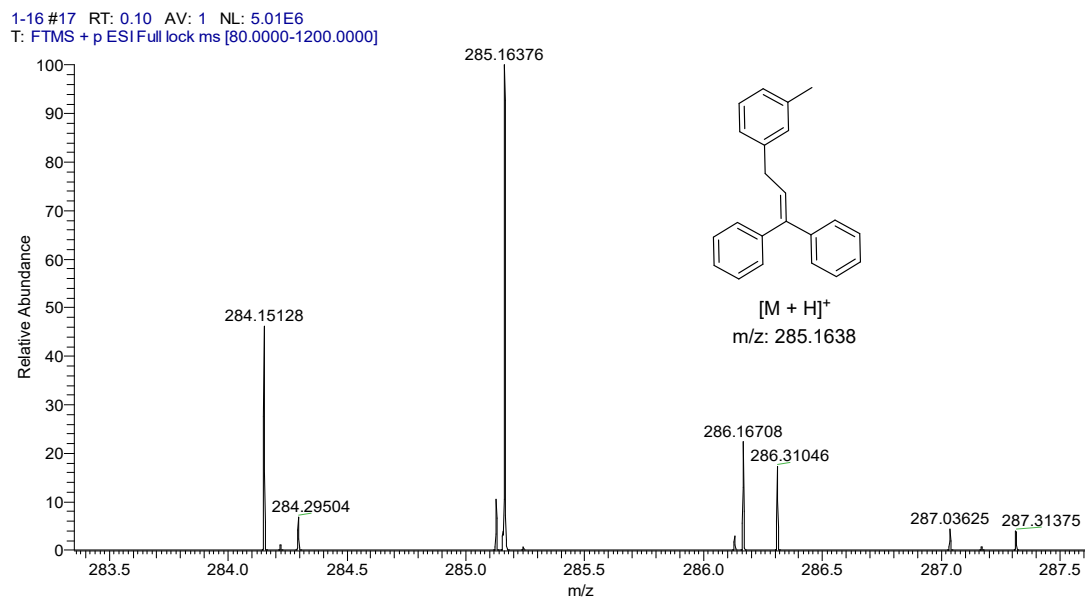


Fig. 75 HR MS spectrum of the adduct 8

## 6 Kinetic isotope effect experiments

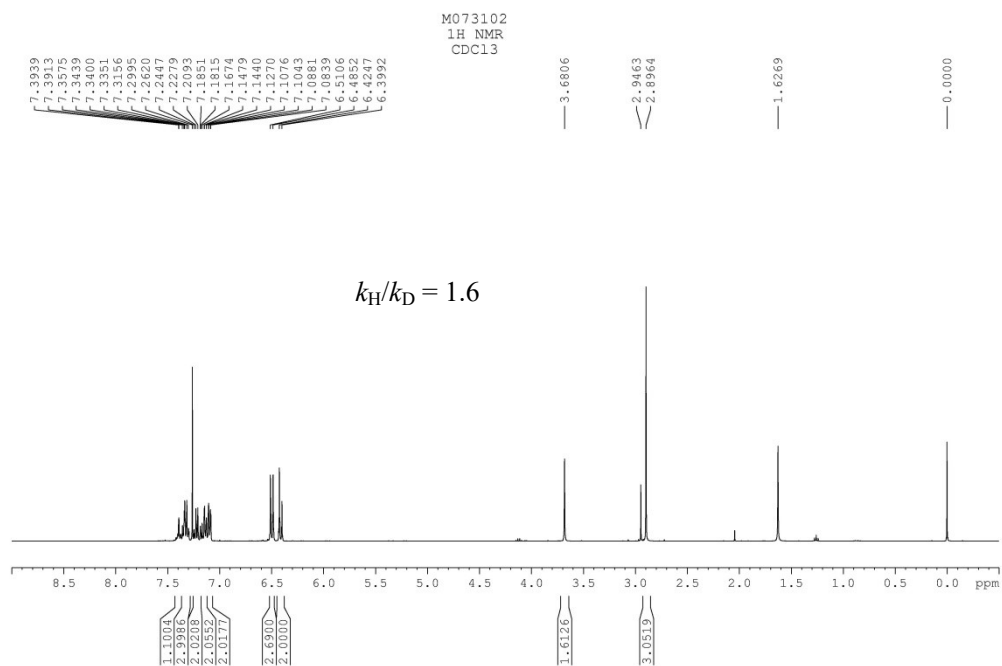
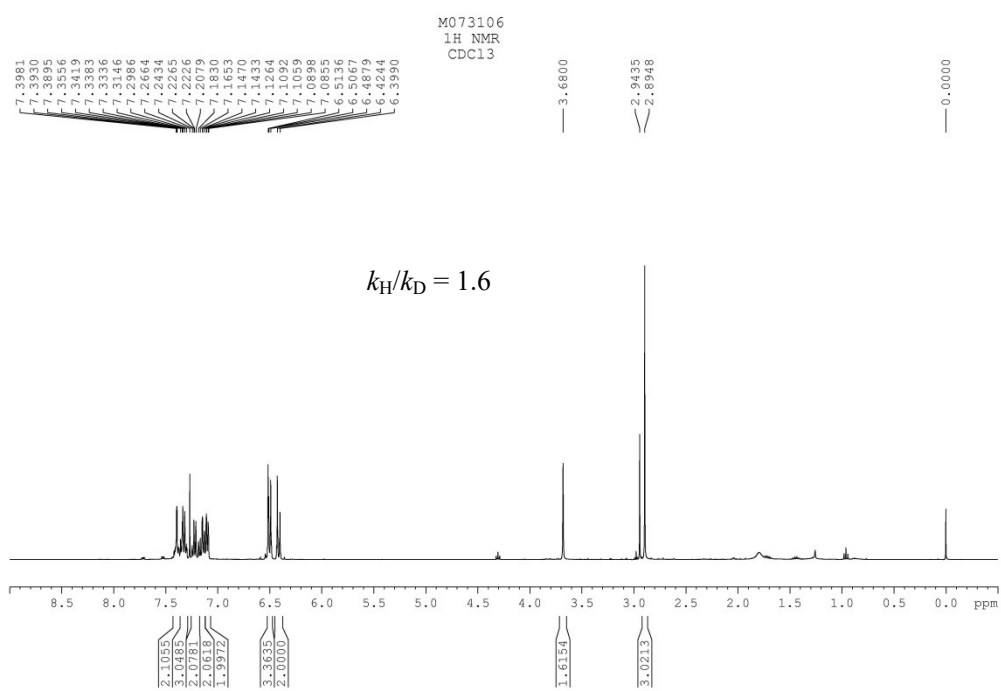


Fig. 76 Kinetic isotope effect experiment 1



**Fig. 77** Kinetic isotope effect experiment 2