Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

A Highly Efficient Synthesis of the DEFG-Ring System of Rubriflordilactone B

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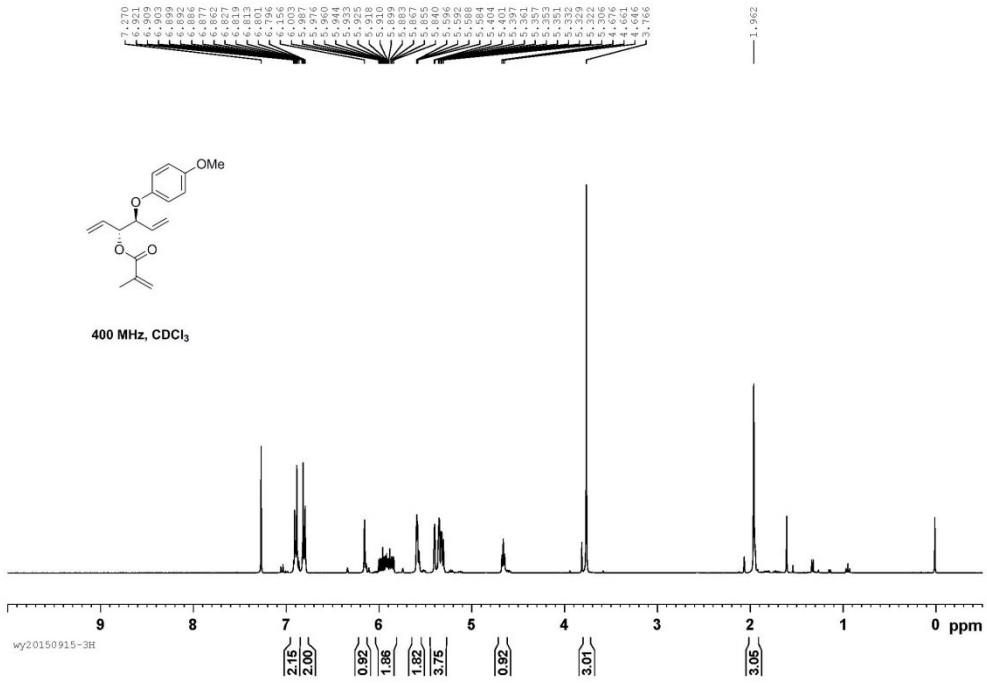
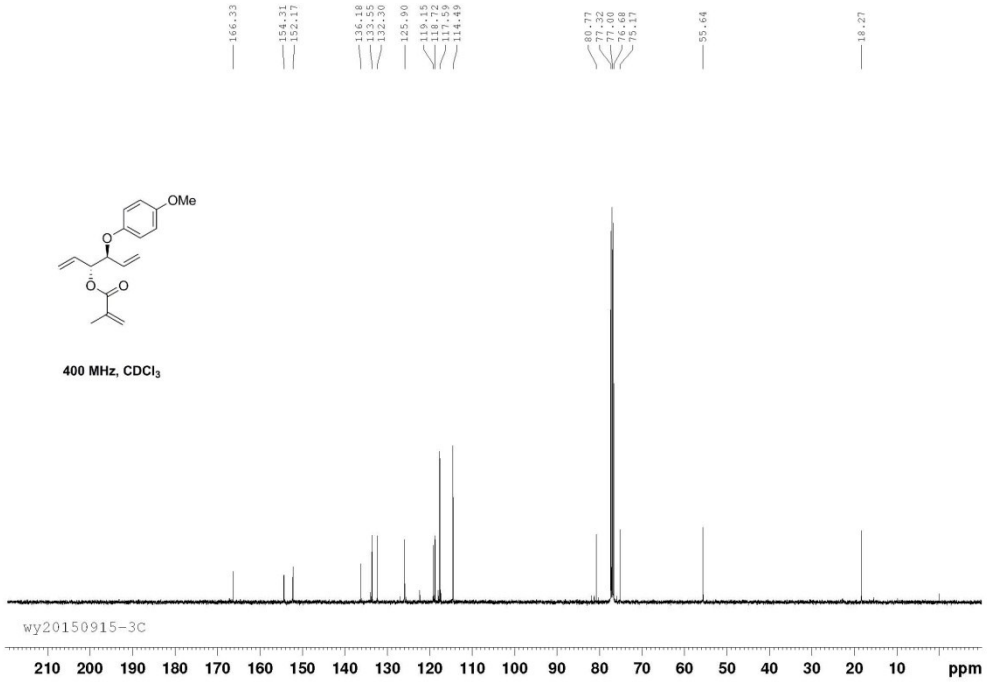
1. **General information:** Oxygen- and moisture-sensitive reactions were carried out under argon atmosphere. Solvents were purified and dried by standard methods prior to use. All commercially available reagents were used without further purification unless otherwise noted. Column chromatography was performed on silica gel (200-300 mesh). NMR spectra were recorded on Bruker 400 MHz and Oxford 600 MHz spectrometers in the $CDCl_3$ or acetone d_6. Chemical shifts are reported as δ values relative to internal chloroform (δ 7.27 for ^{1}H NMR and 77.00 for ^{13}C NMR) and acetone-d_6 (δ 2.05 for ^{1}H NMR and 29.92 for ^{13}C NMR). High resolution mass spectra (HRMS) were obtained on a 4G mass spectrometer by using electrospray ionization (ESI) analyzed by quadrupole time-of-flight (Q-TOF). Optical rotations were measured on a Rudolph Autoplo IV polarimeter.

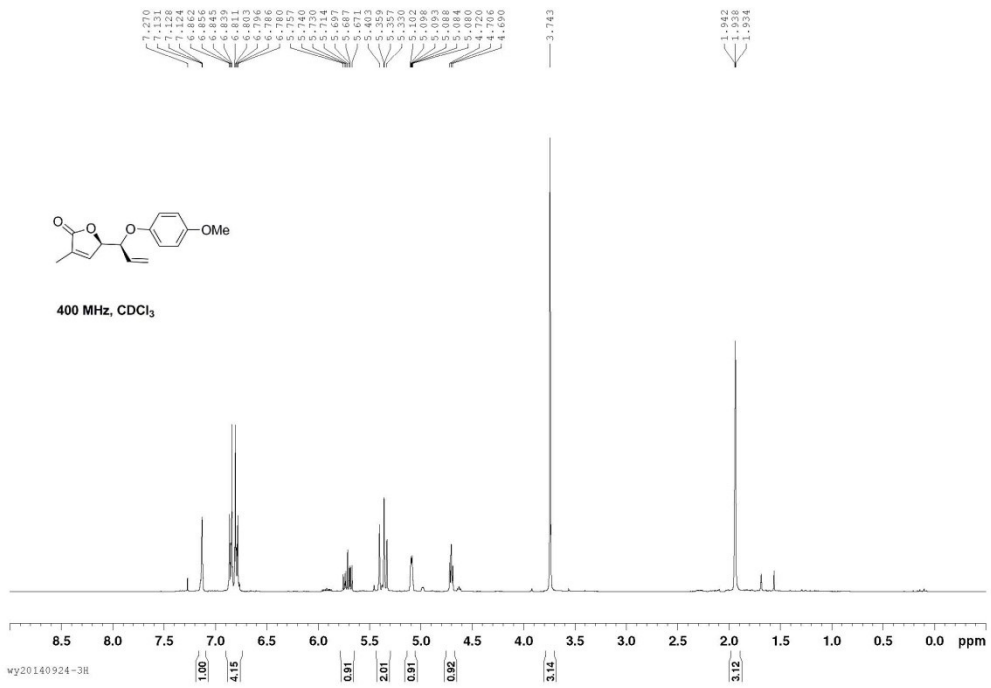
2. ^{1}H and ^{13}C NMR spectra of new compounds

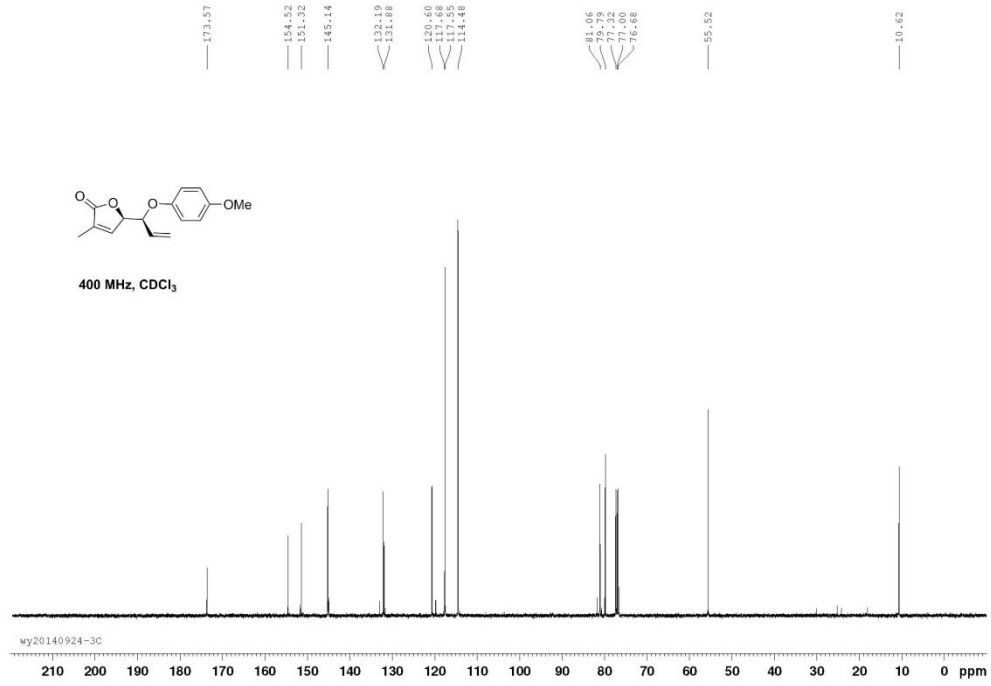
^{1}H and ^{13}C NMR spectra of compound **6**:



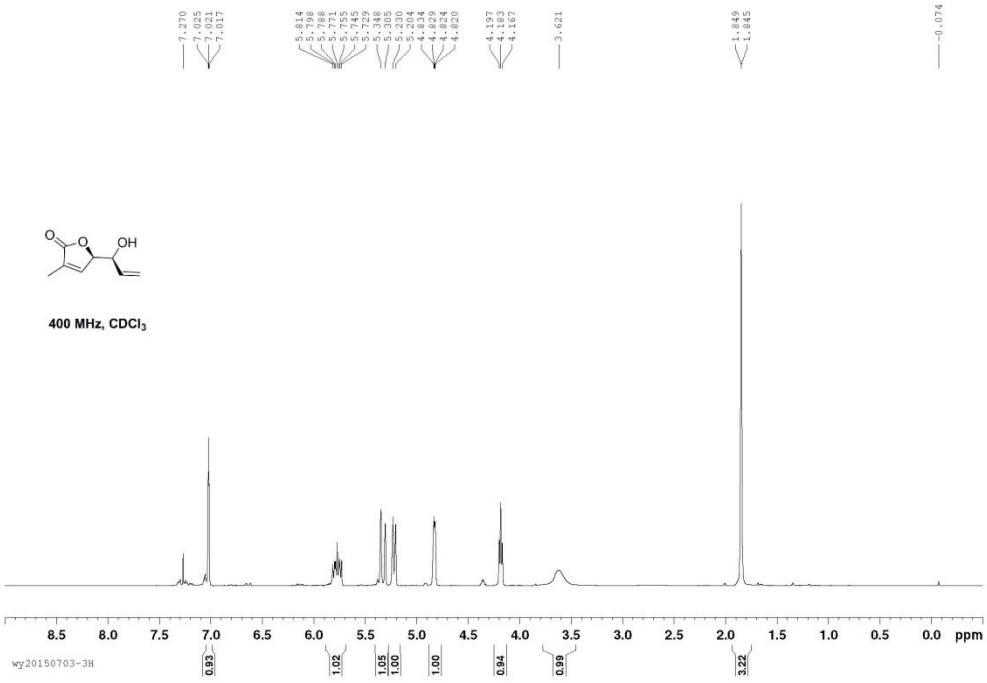


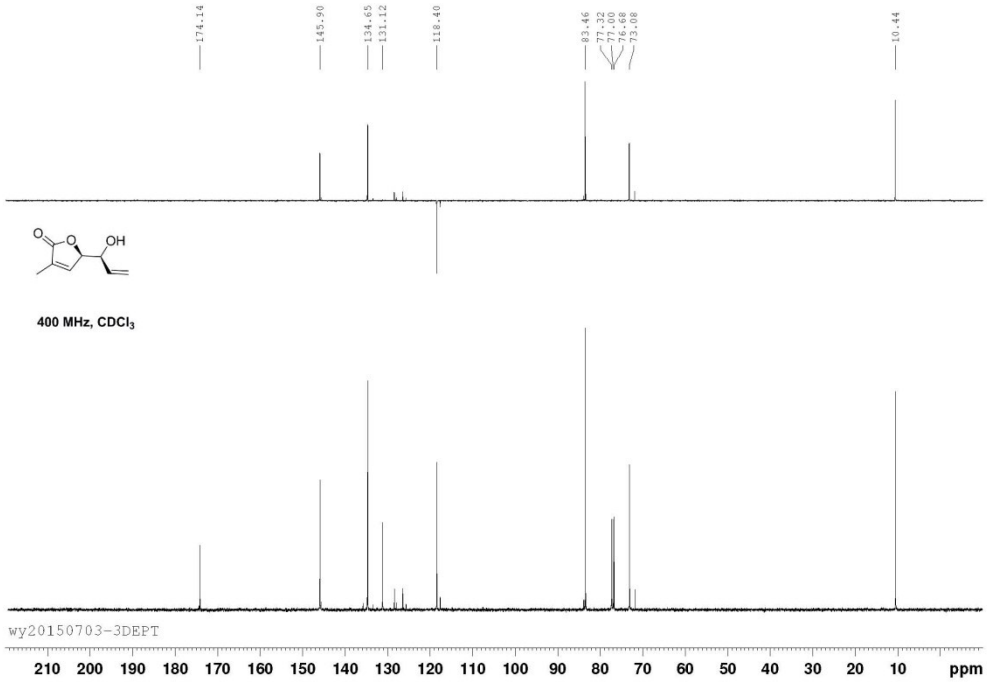
^{1}H and ^{13}C NMR spectra of compound **5**:



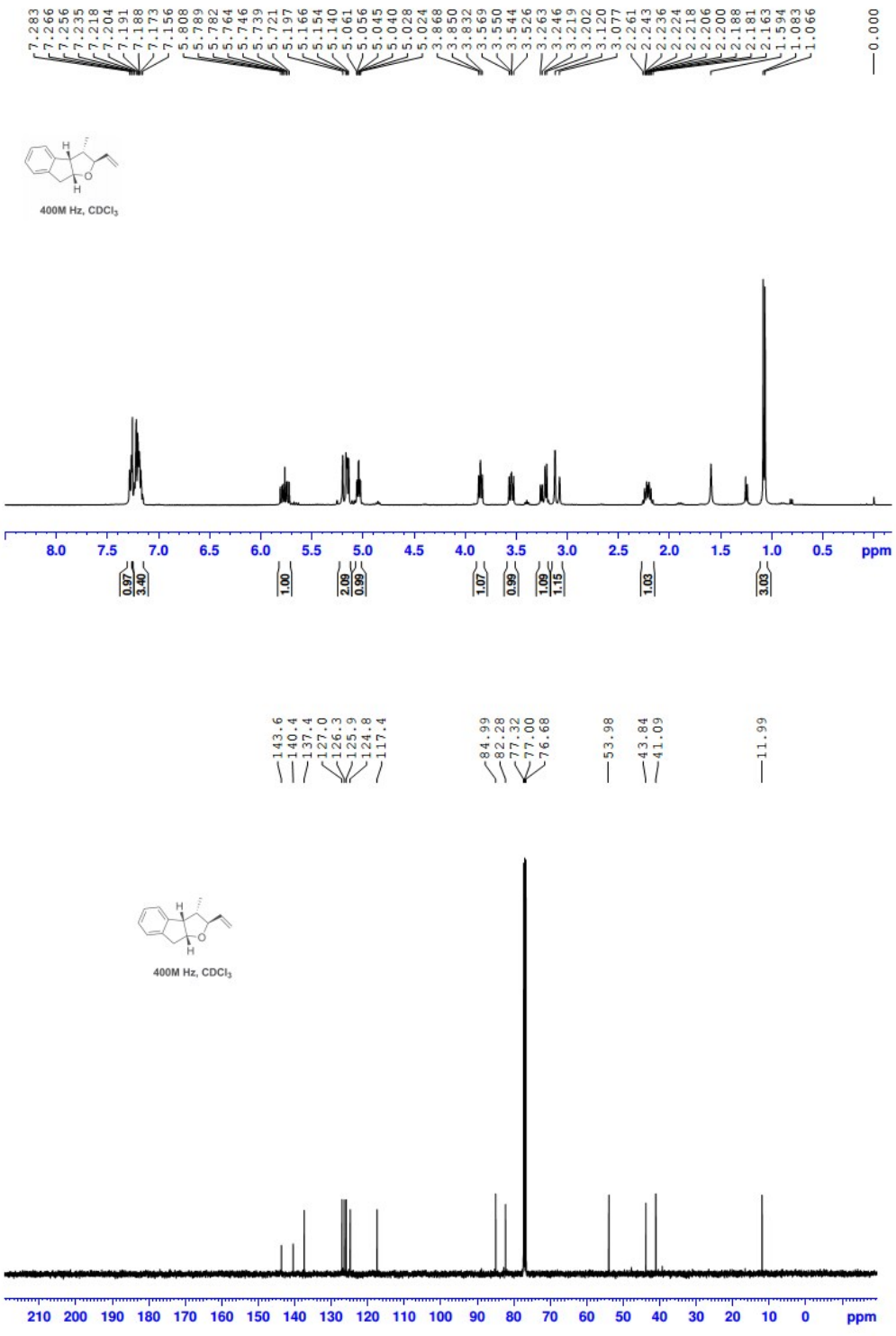


^{1}H and ^{13}C NMR spectra of compound **4**:

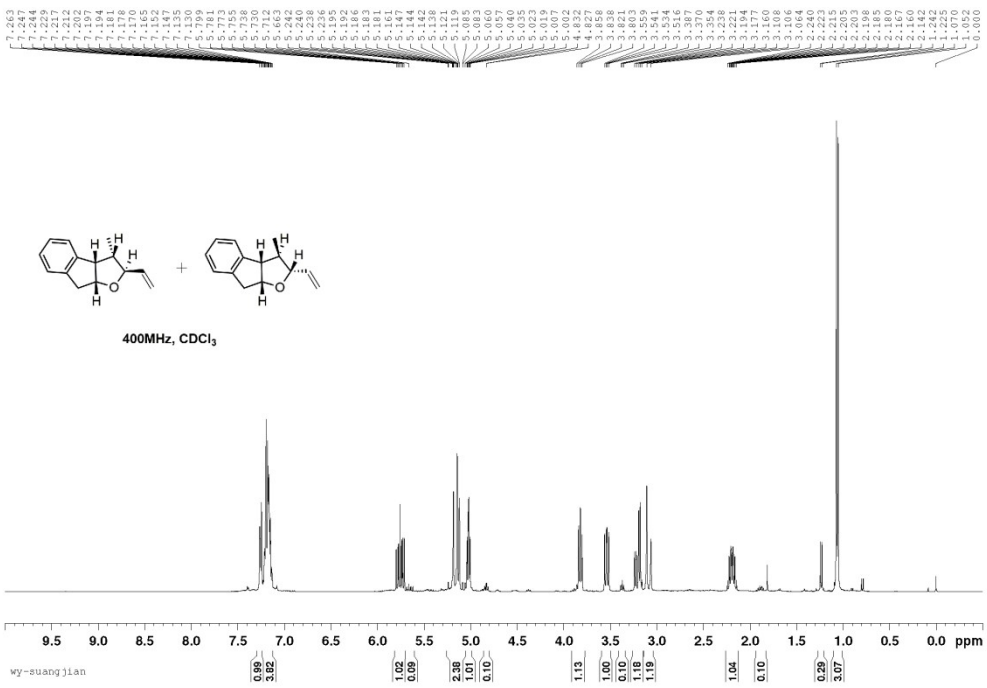


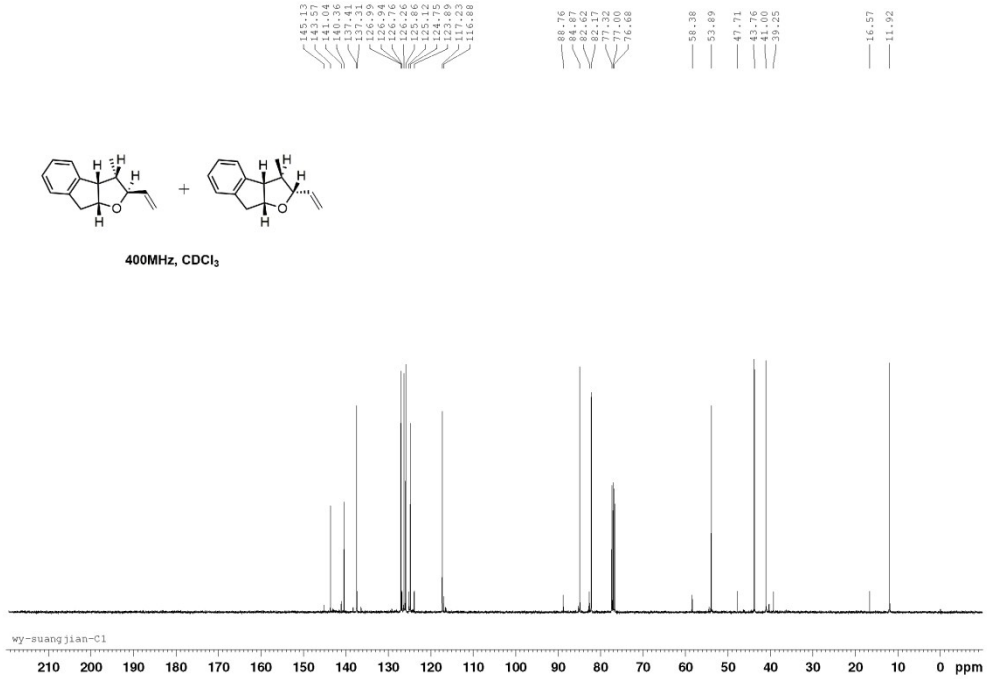


^{1}H and ^{13}C NMR spectra of compound **13**:

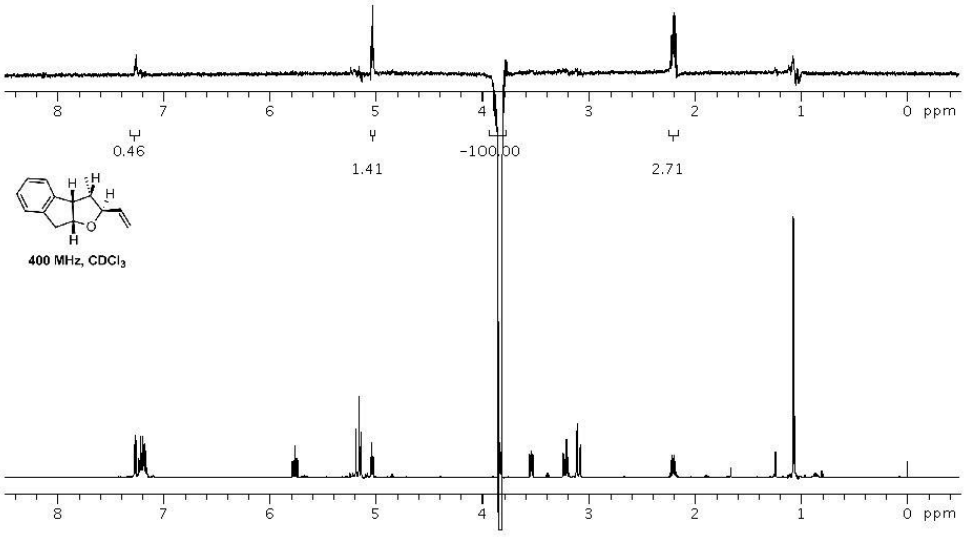


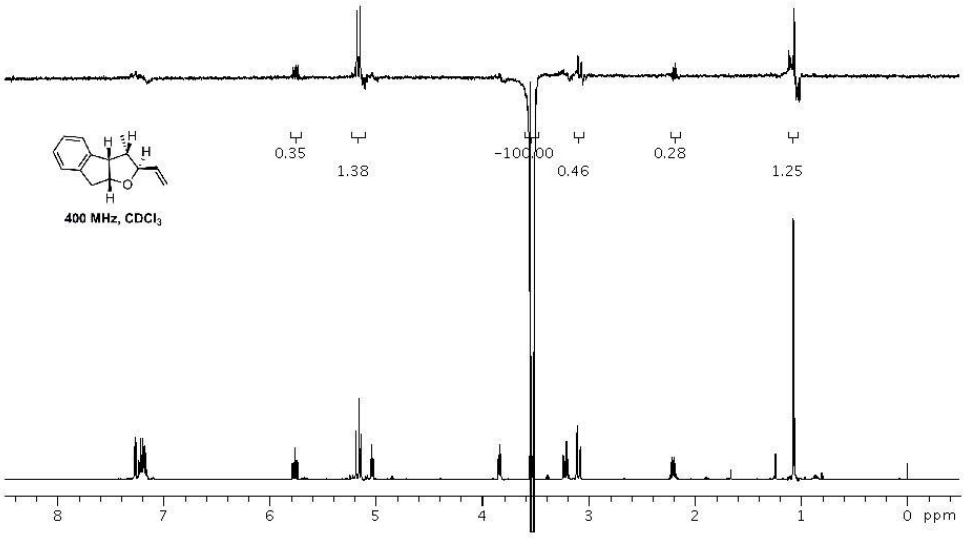
^{1}H and ^{13}C NMR spectra of compounds **13 and 13'**:



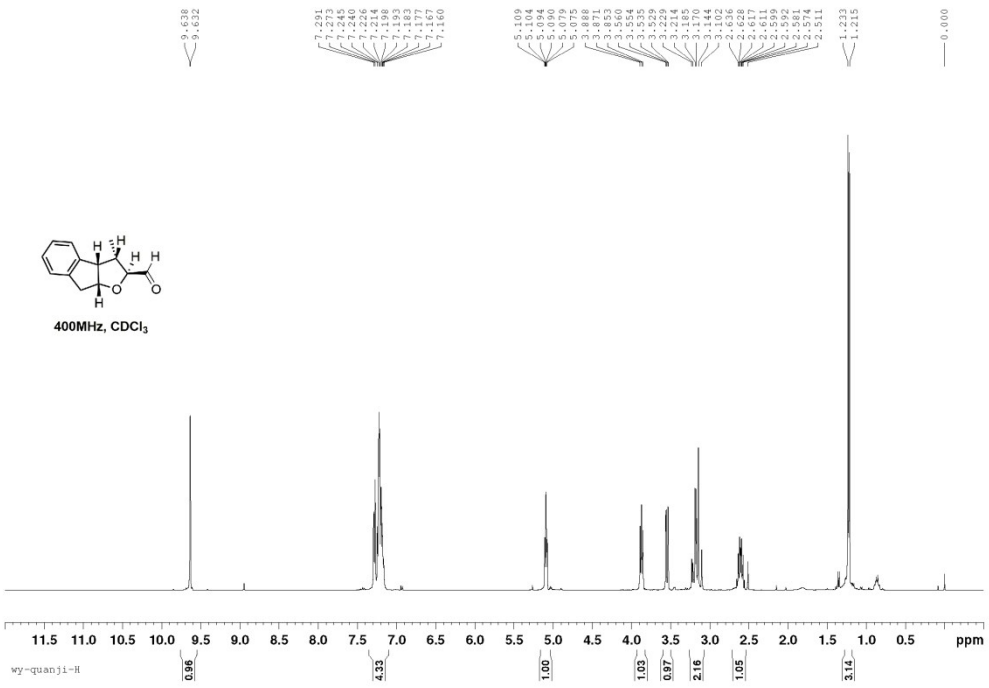


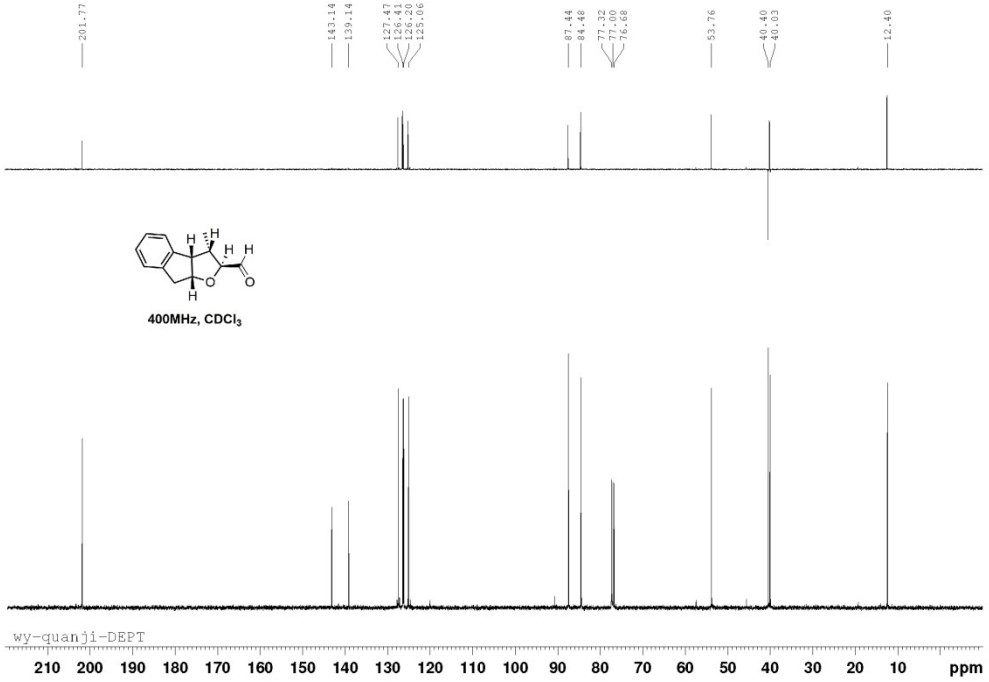
NOE of compound **13**:

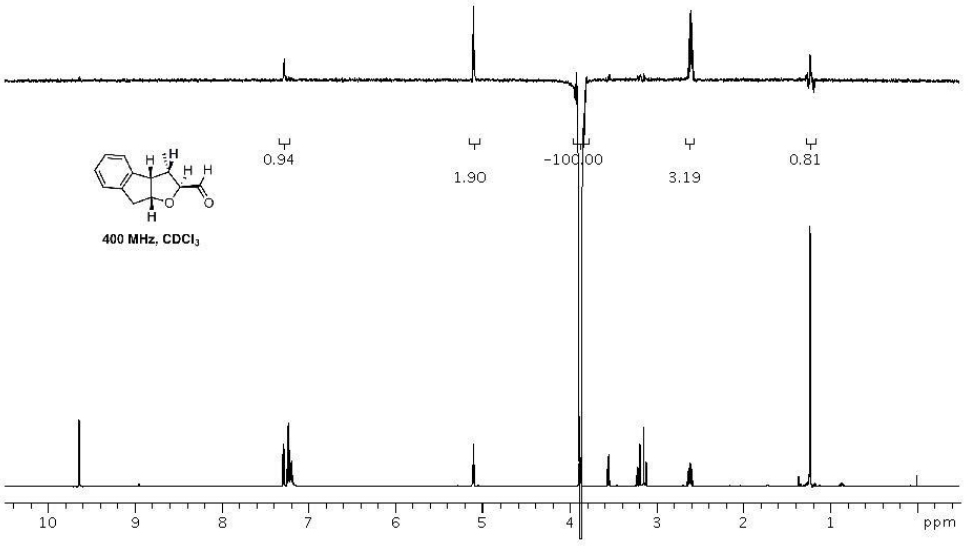




^{1}H and ^{13}C NMR spectra and NOE of compound **14**:



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1.90
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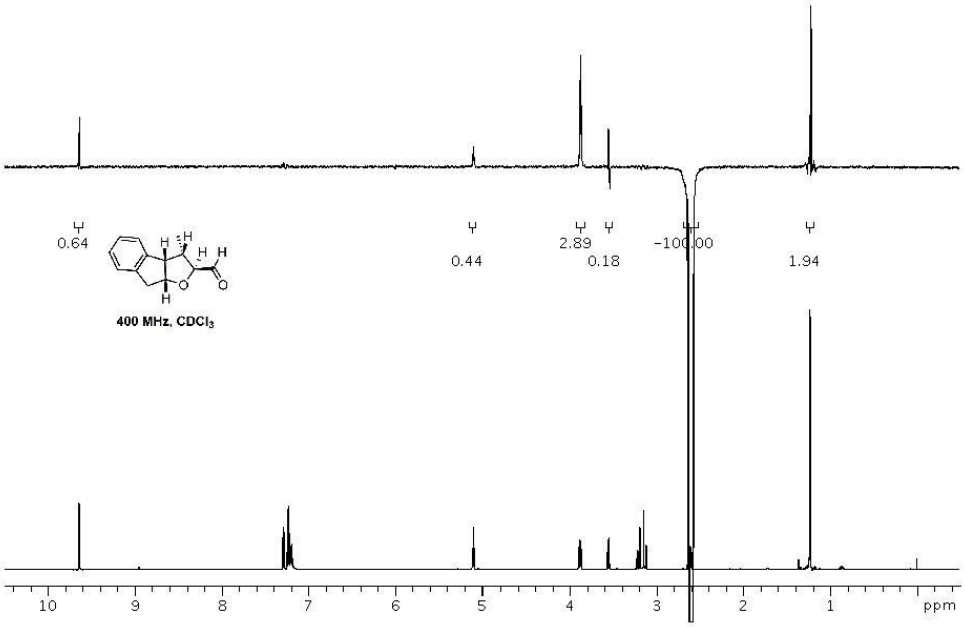
0.81
400 MHz, CDCl3
10
9
8
7
6
5
4
3
2
1
ppm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2.89
0.18
-100.00
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400 MHz, CDCl3
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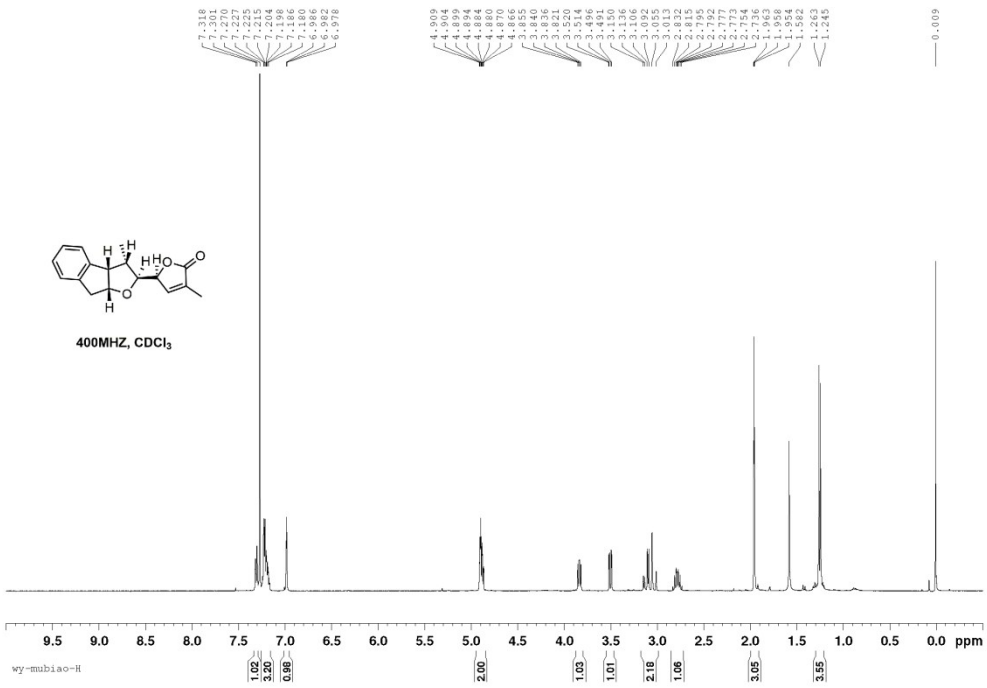
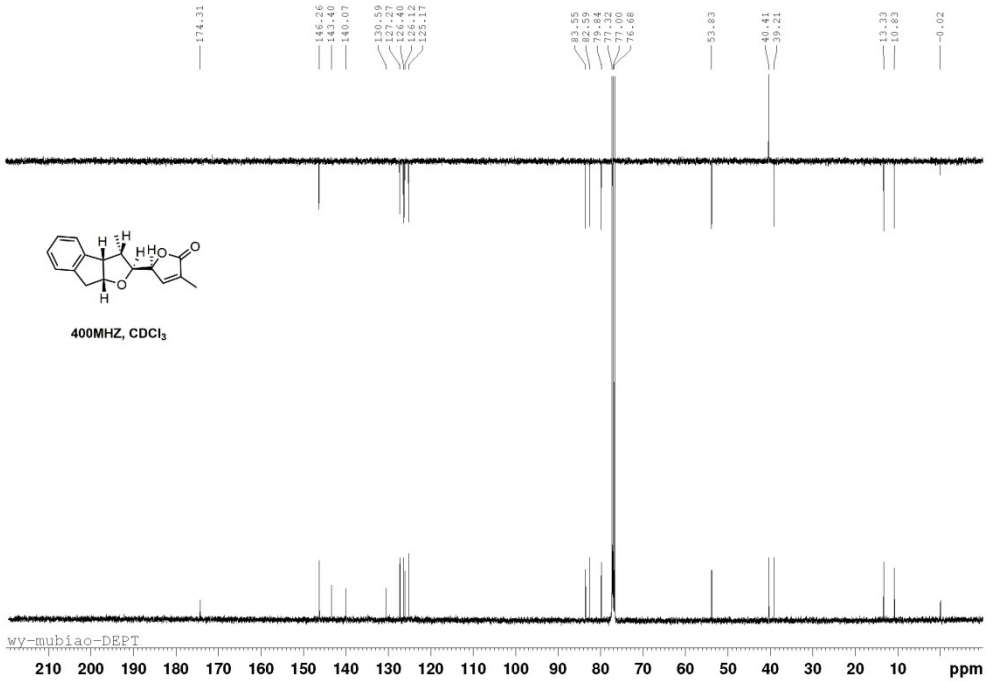
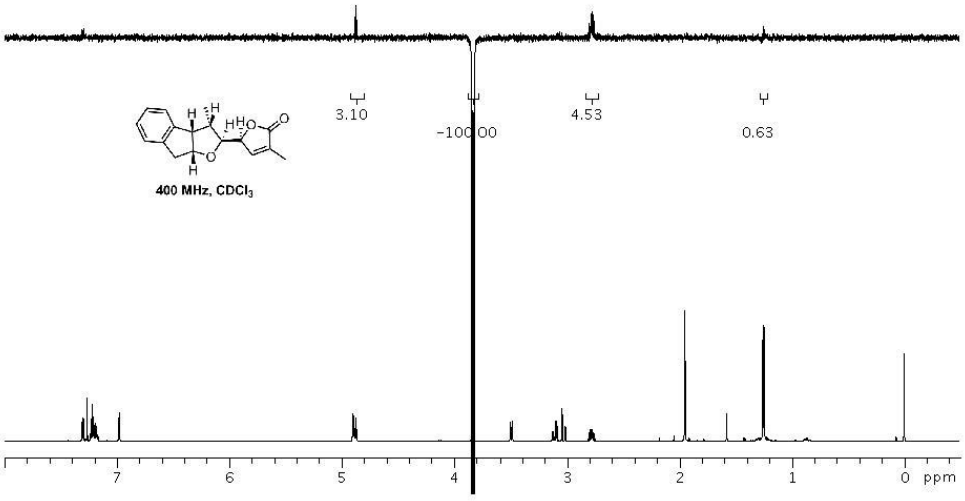
9
8
7
6
5
4
3
2
1
ppm

^{1}H and ^{13}C NMR spectra and NOE of compound **16**:



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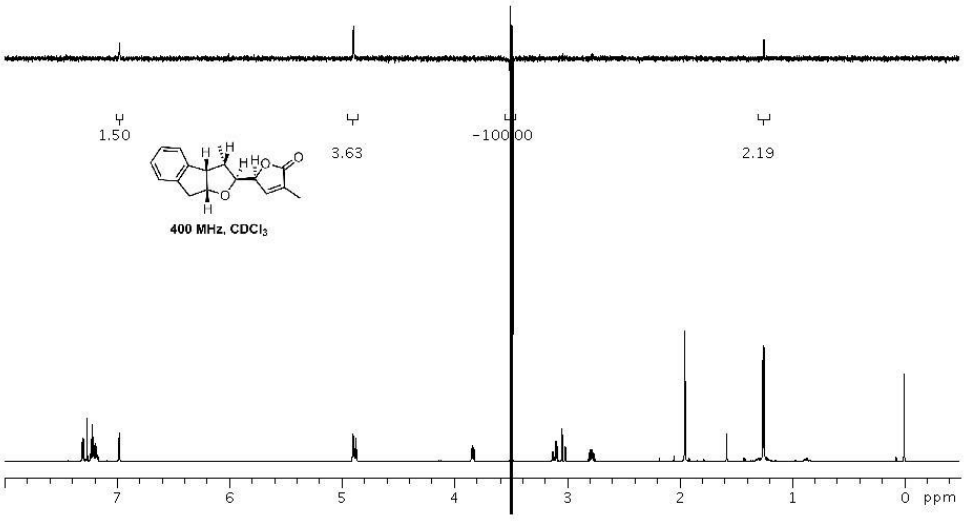
7
6
5
4
3
2
1
0 ppm


1.50
3.63
-100.00
2.19
400 MHz, CDCl3
7
6
5
4
3
2
1
0 ppm