

Supporting Information

Nucleophilic vinylic substitution in bicyclic methyleneaziridines: S_NV_π or S_NV_σ ?

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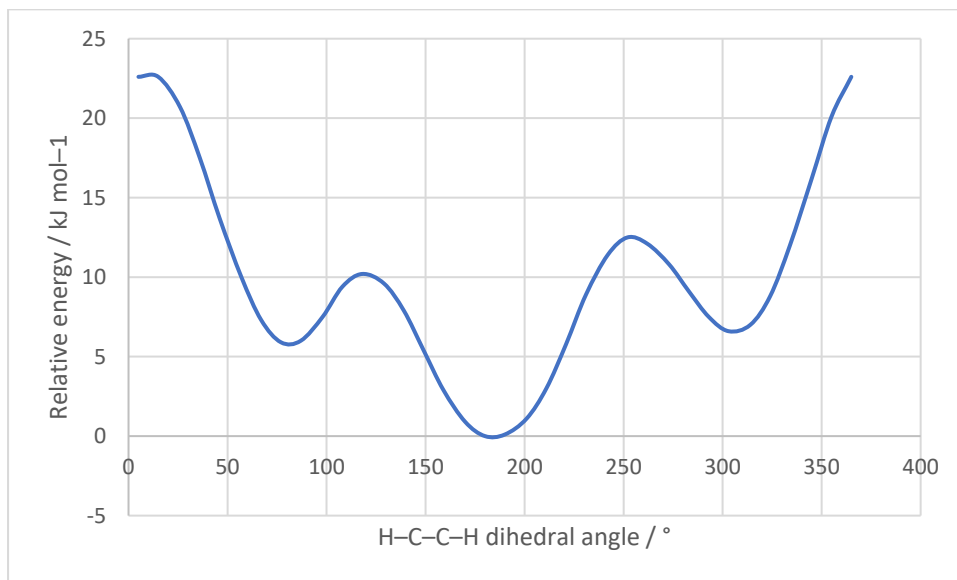
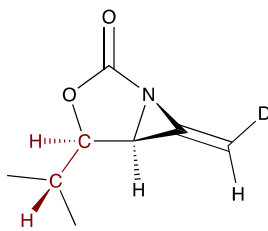
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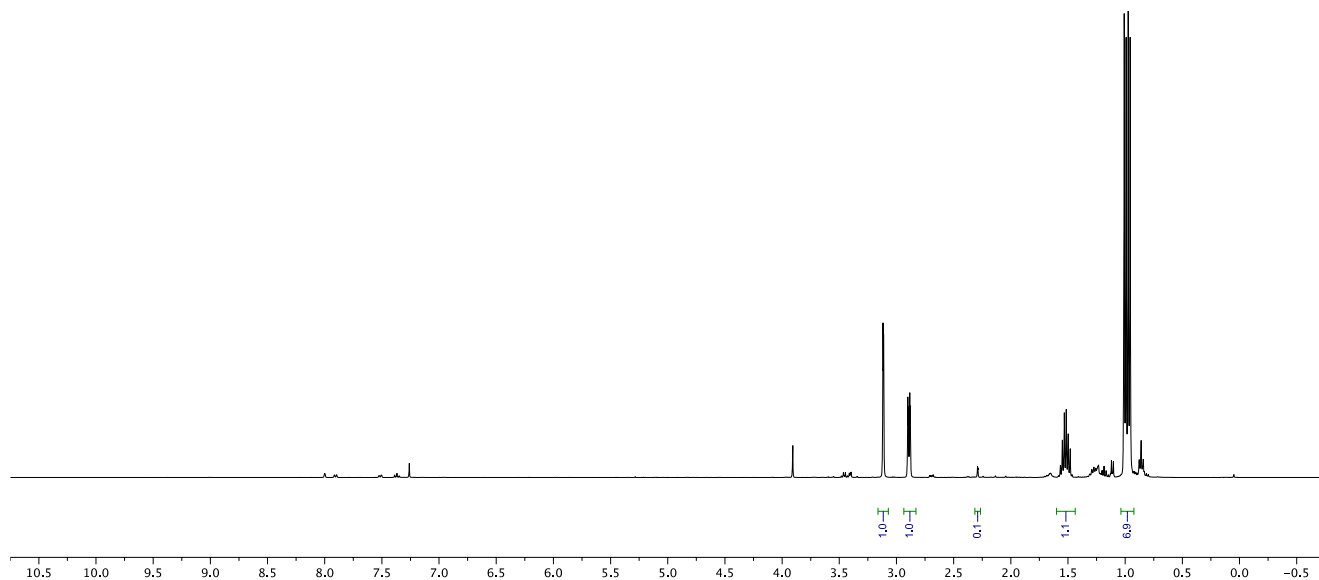
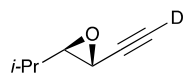
Contents

Conformational energy profile for compound 4	S2
Copies of ¹ H and ¹³ C NMR data	S3–S11
NOE data for compounds 4 , 11 , and 12	S12–S14

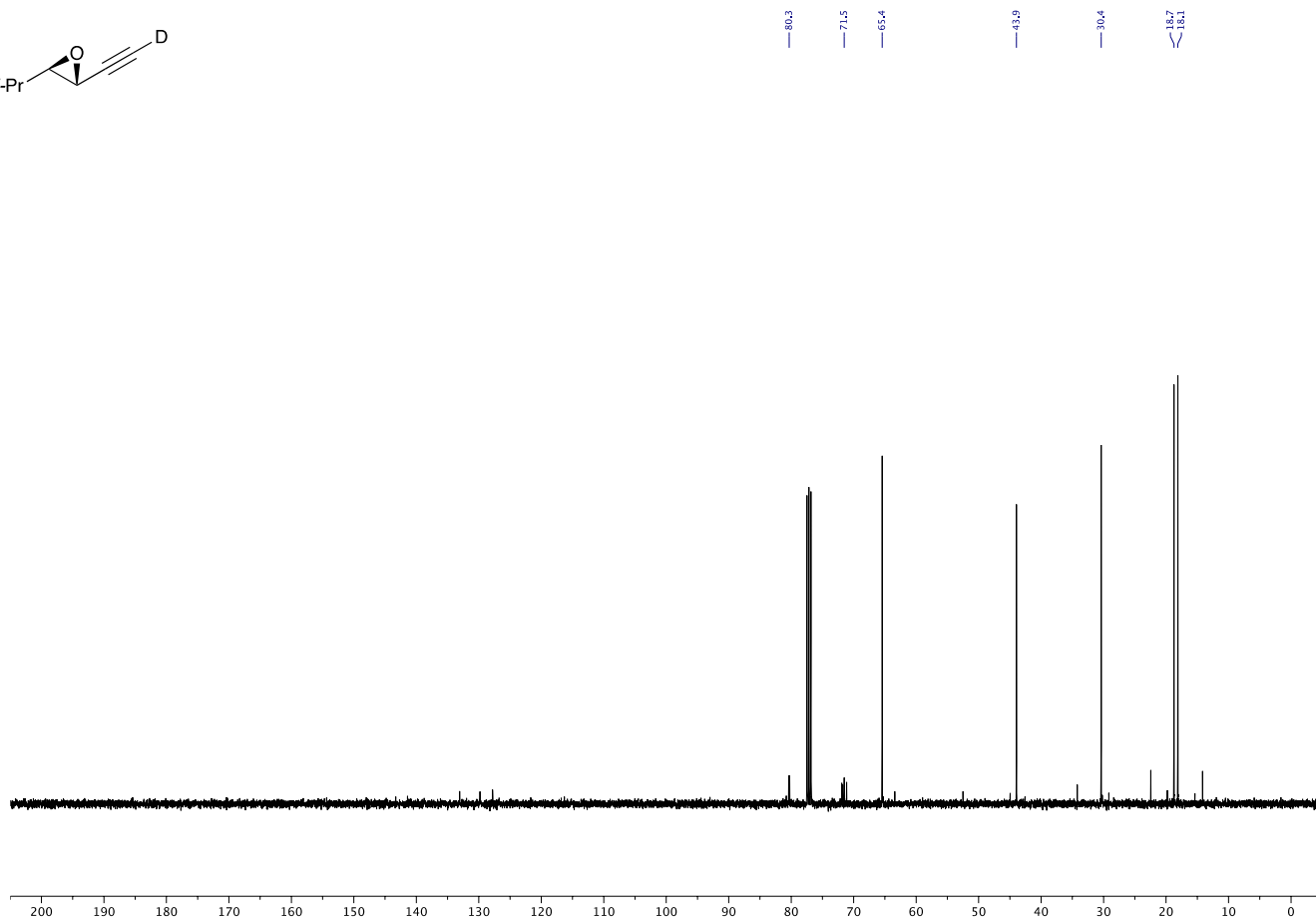
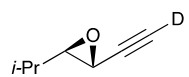
Energy profile for conformations obtained by rotating the C-*i*-Pr bond in methyleneaziridine 4



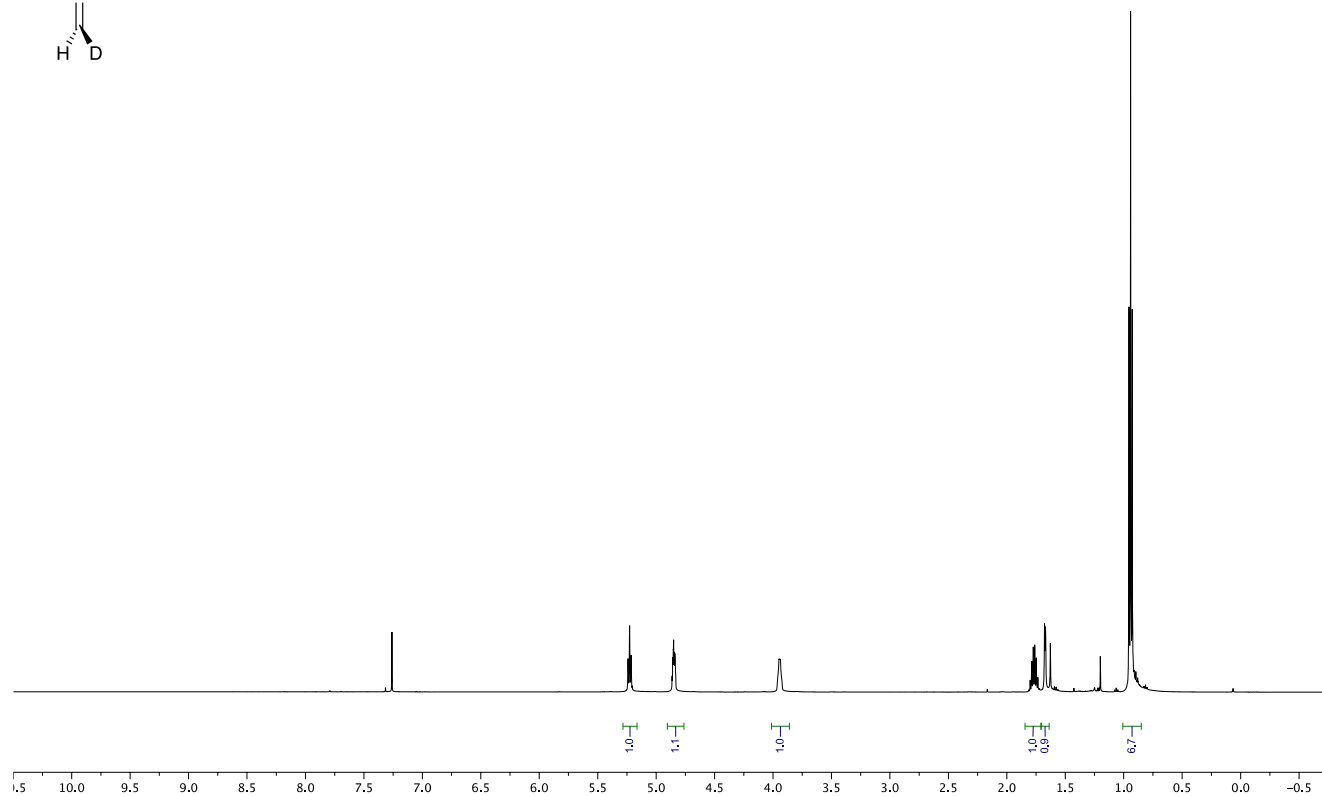
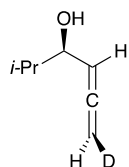
(7) ^1H NMR (400 MHz, CDCl_3) [volatile sample; contains a little PhCO_2Me and solvent]



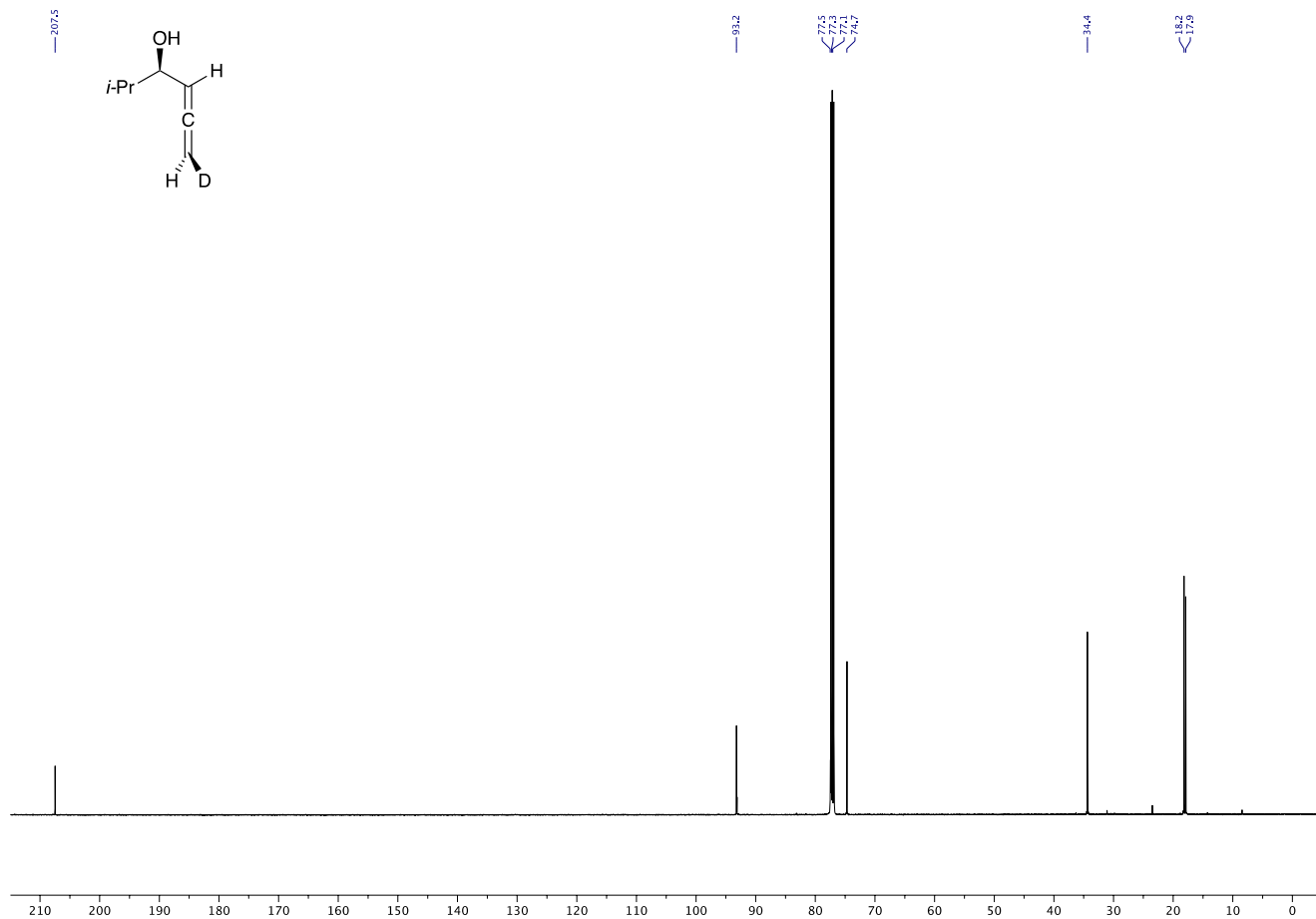
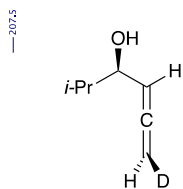
(7) ^{13}C NMR (100 MHz, CDCl_3)



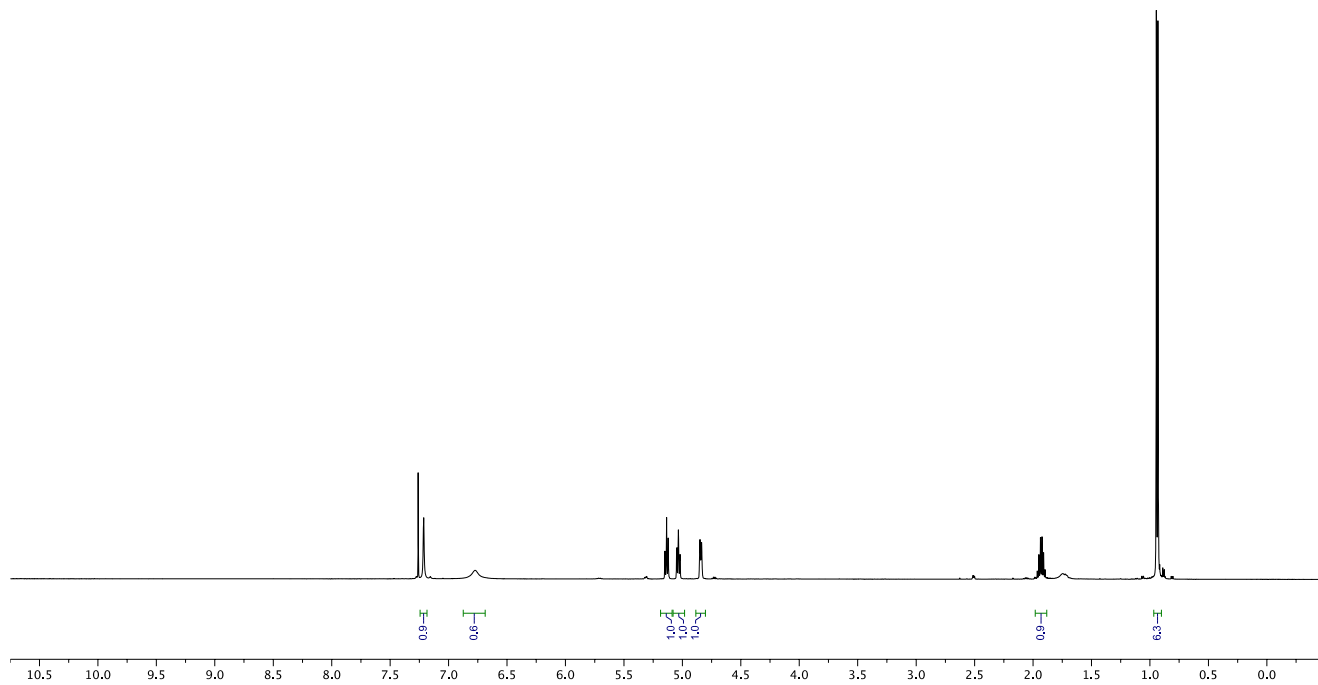
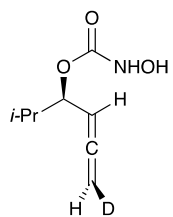
(8) ^1H NMR (500 MHz, CDCl_3)



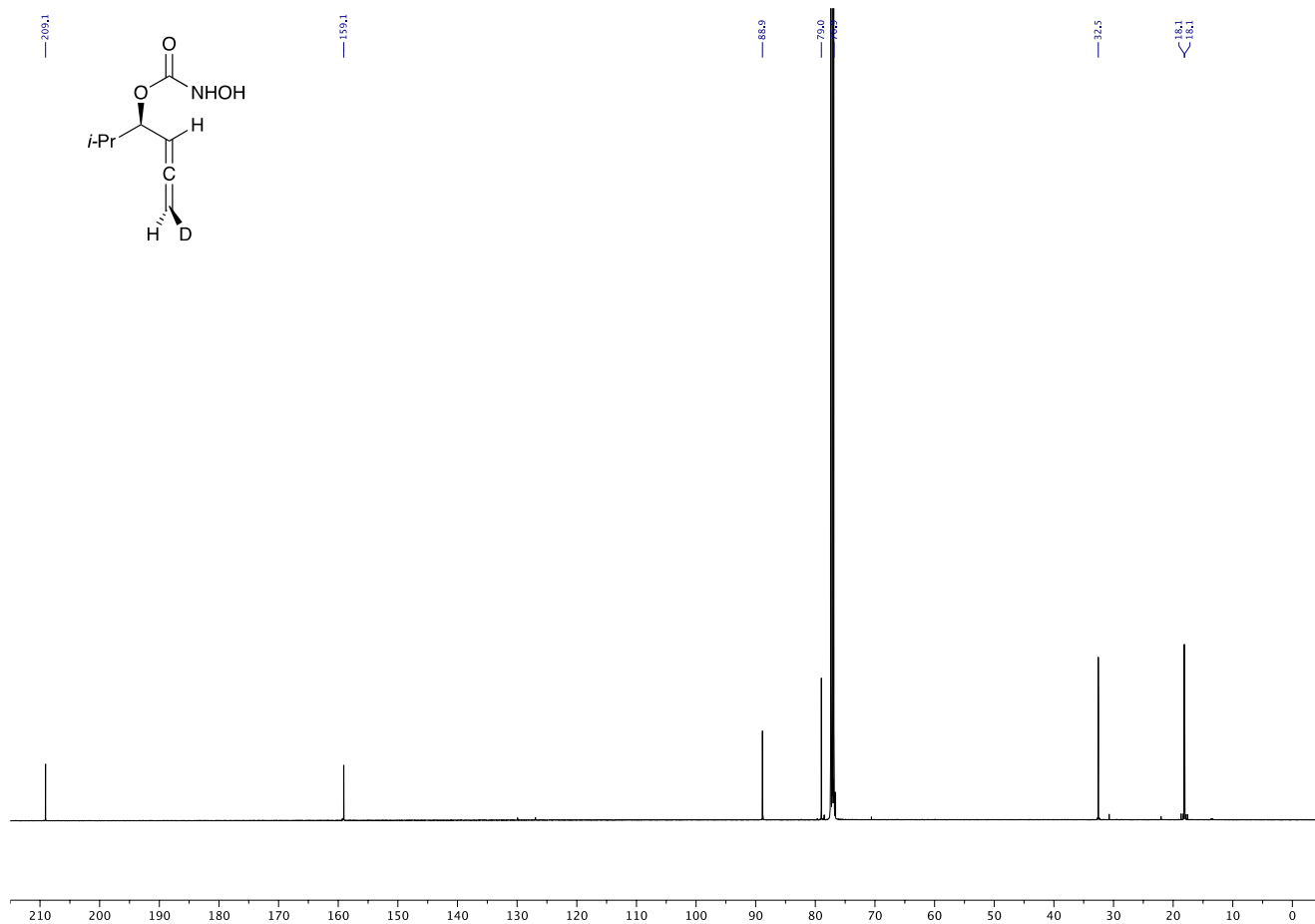
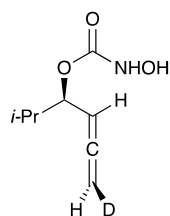
(8) ^{13}C NMR (125 MHz, CDCl_3)



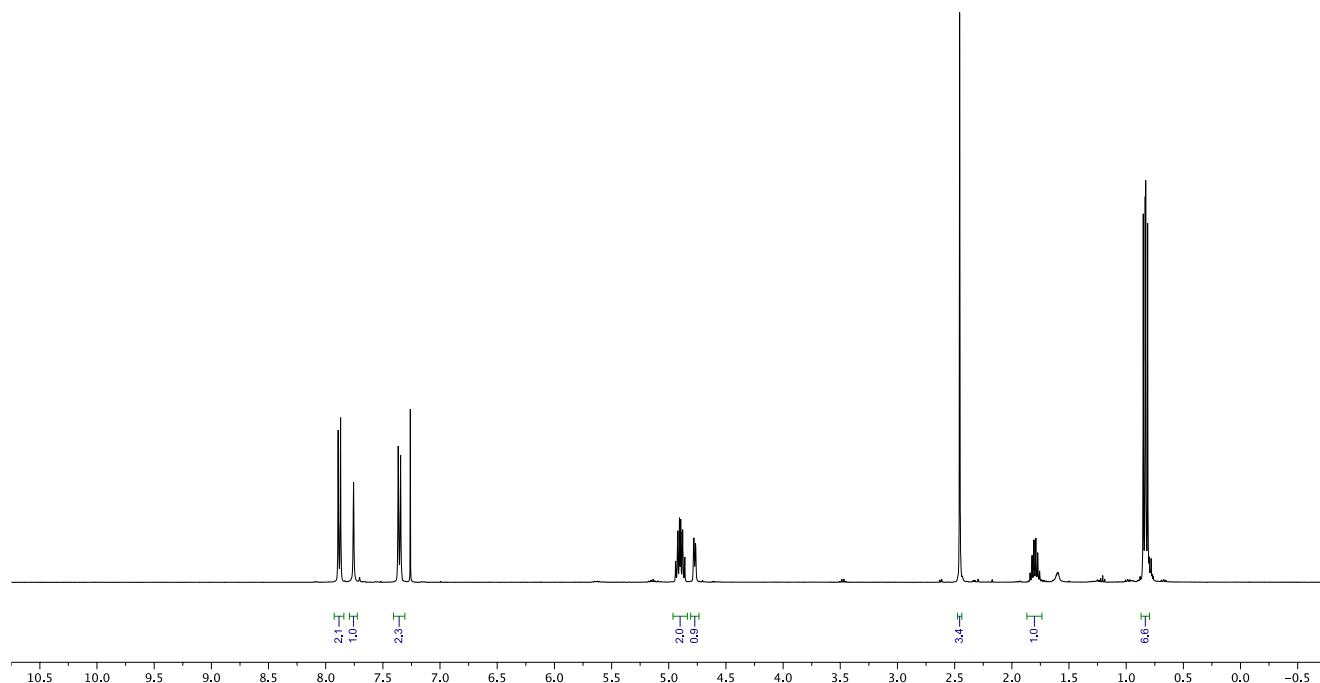
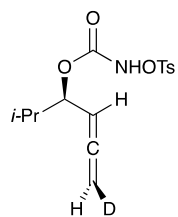
(S1) ^1H NMR (500 MHz, CDCl_3)



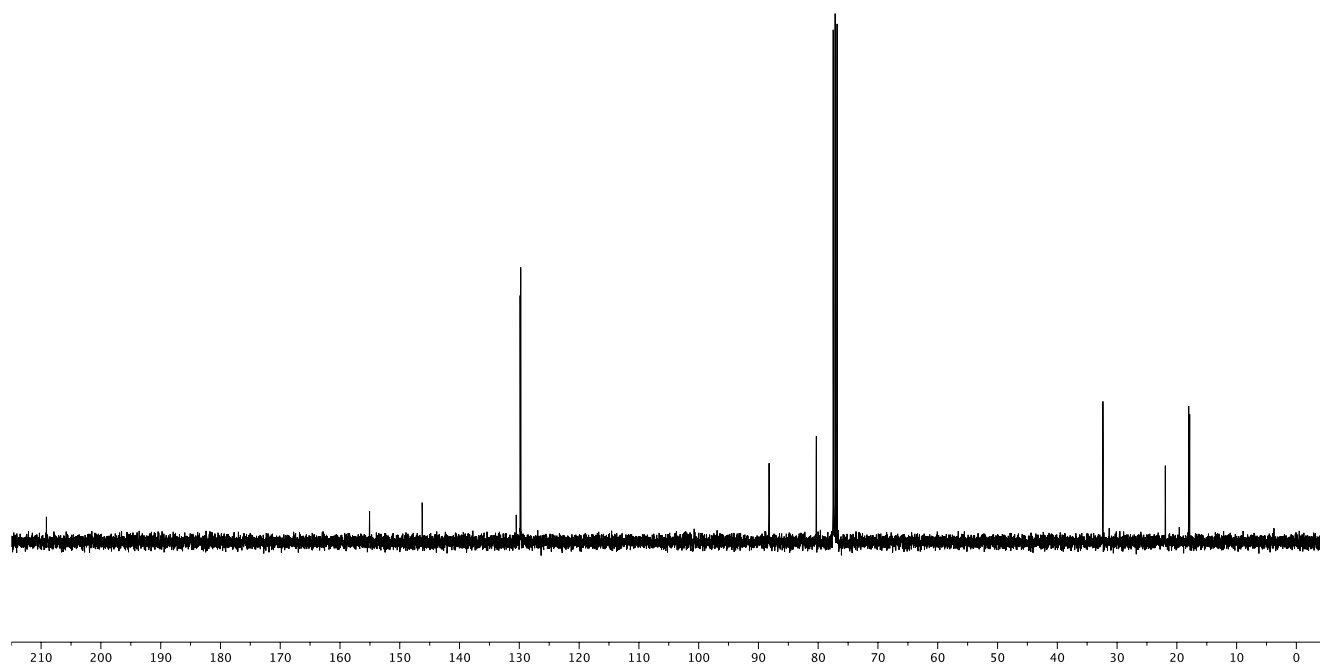
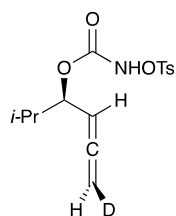
(S1) ^{13}C NMR (125 MHz, CDCl_3)



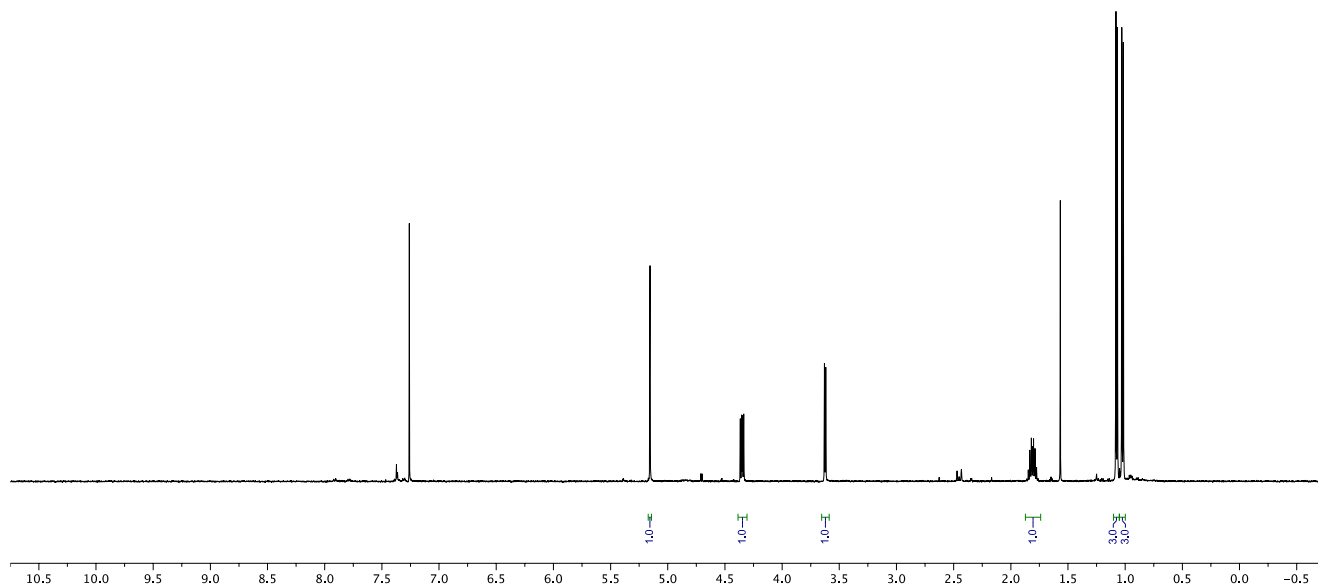
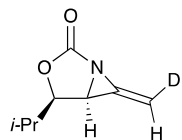
(9) ^1H NMR (400 MHz, CDCl_3)



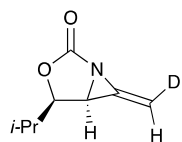
(9) ^{13}C NMR (100 MHz, CDCl_3)



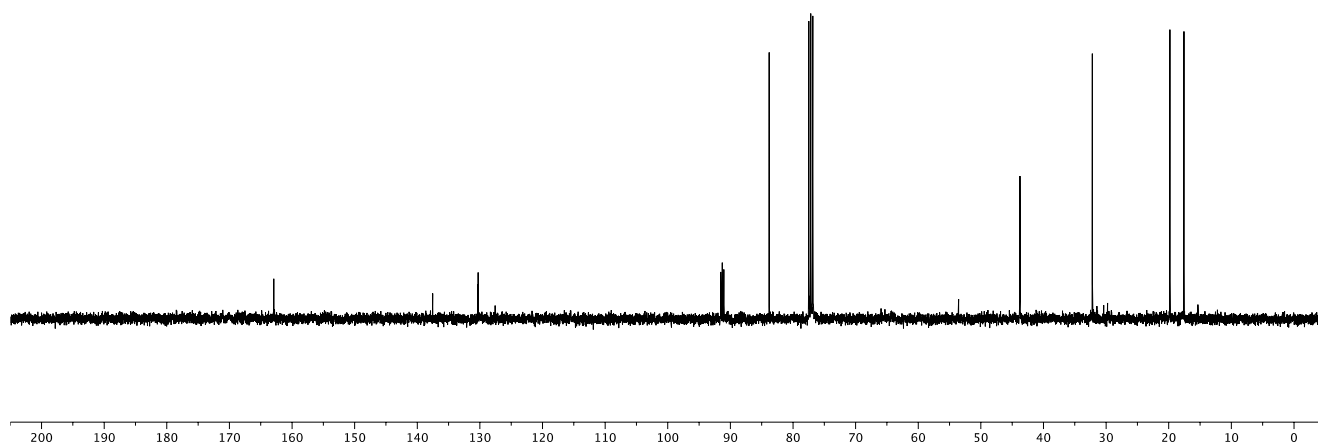
(4) ^1H NMR (500 MHz, CDCl_3)



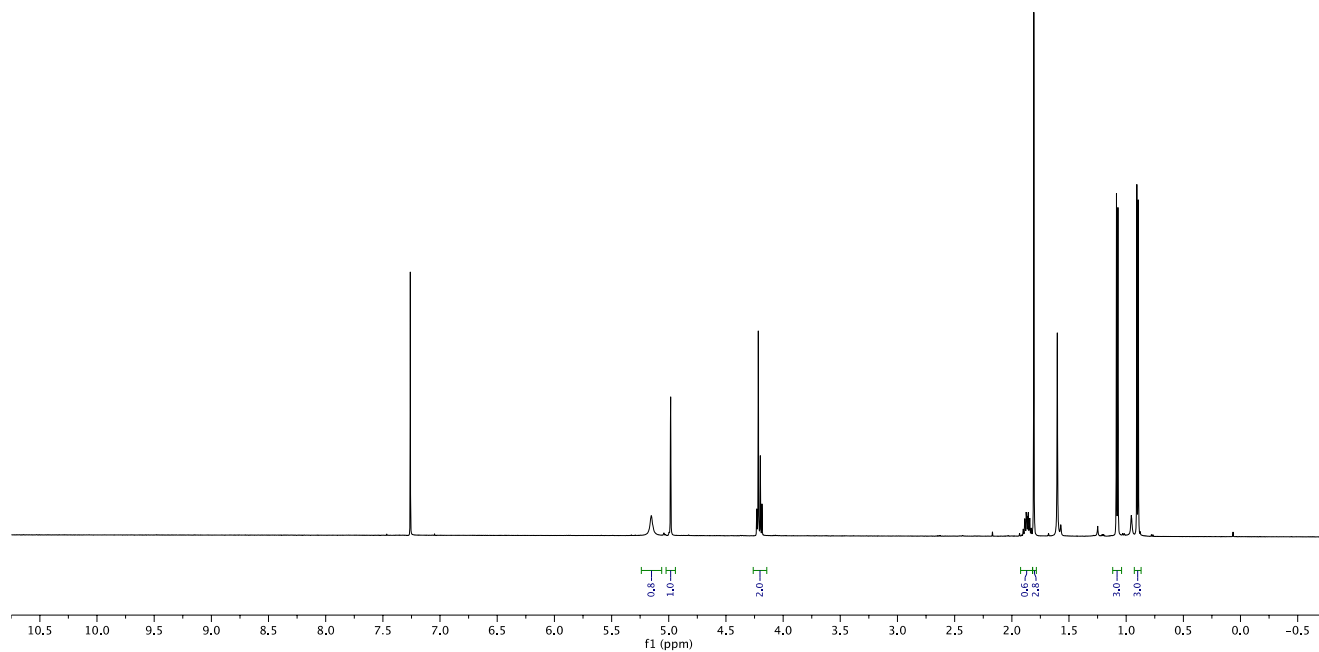
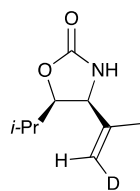
(4) ^{13}C NMR (100 MHz, CDCl_3)



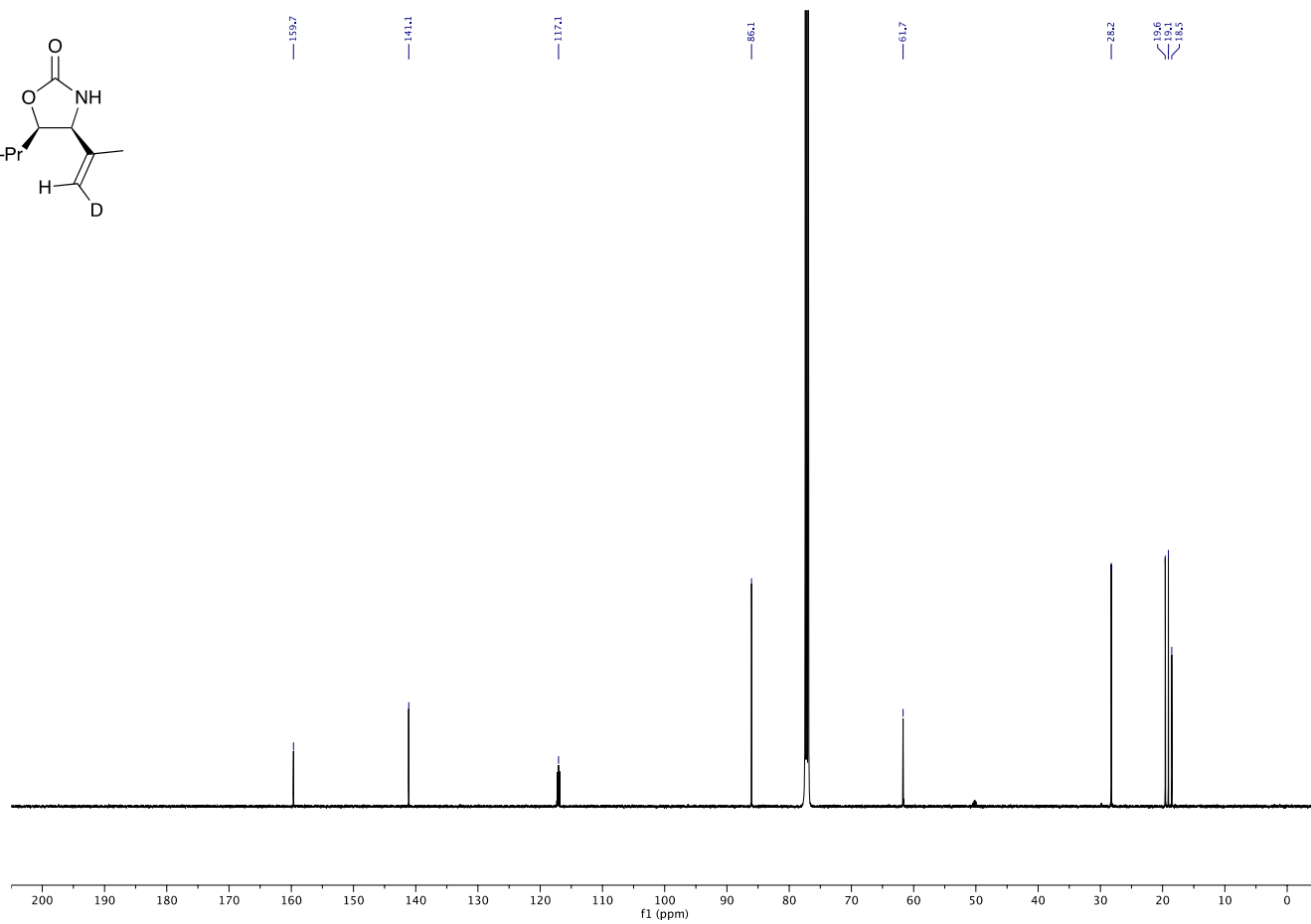
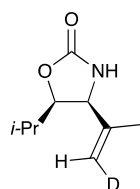
162.9, 130.3, 91.3, 83.8, 43.7, 32.2, 19.8, 17.6



(11) ^1H NMR (500 MHz, CDCl_3)

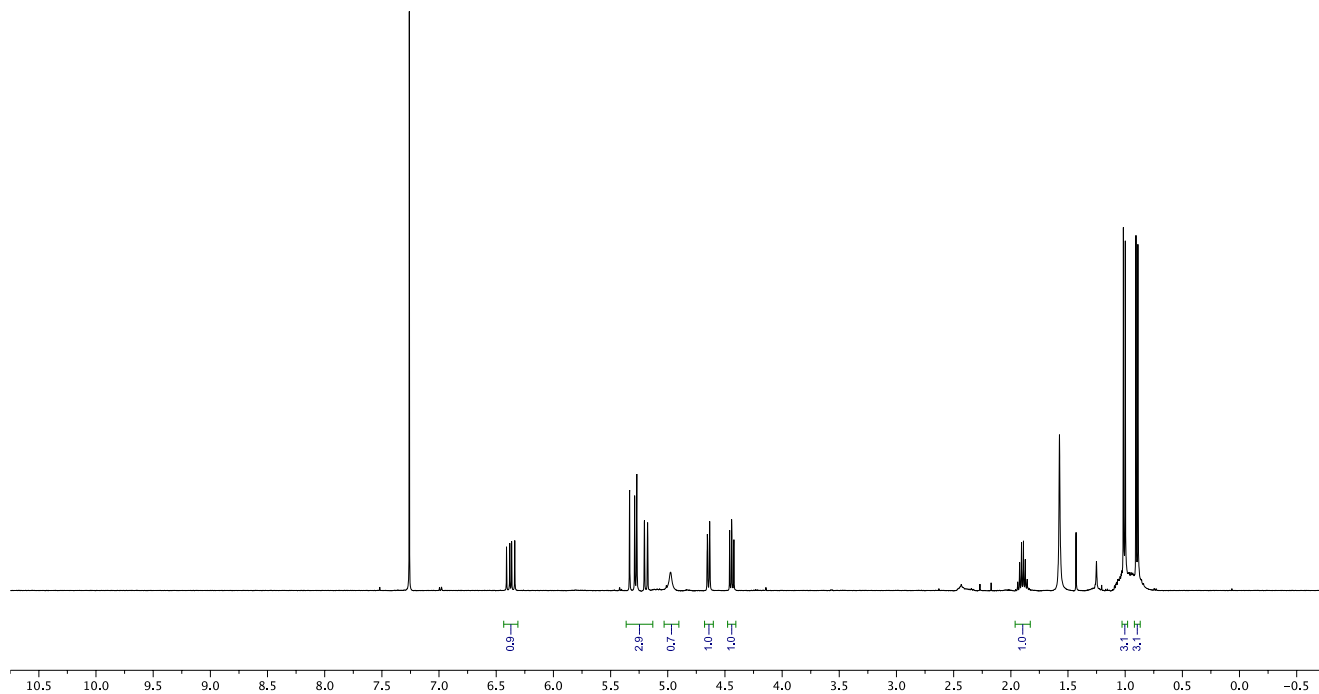
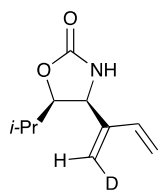


(11) ^{13}C NMR (125 MHz, CDCl_3)

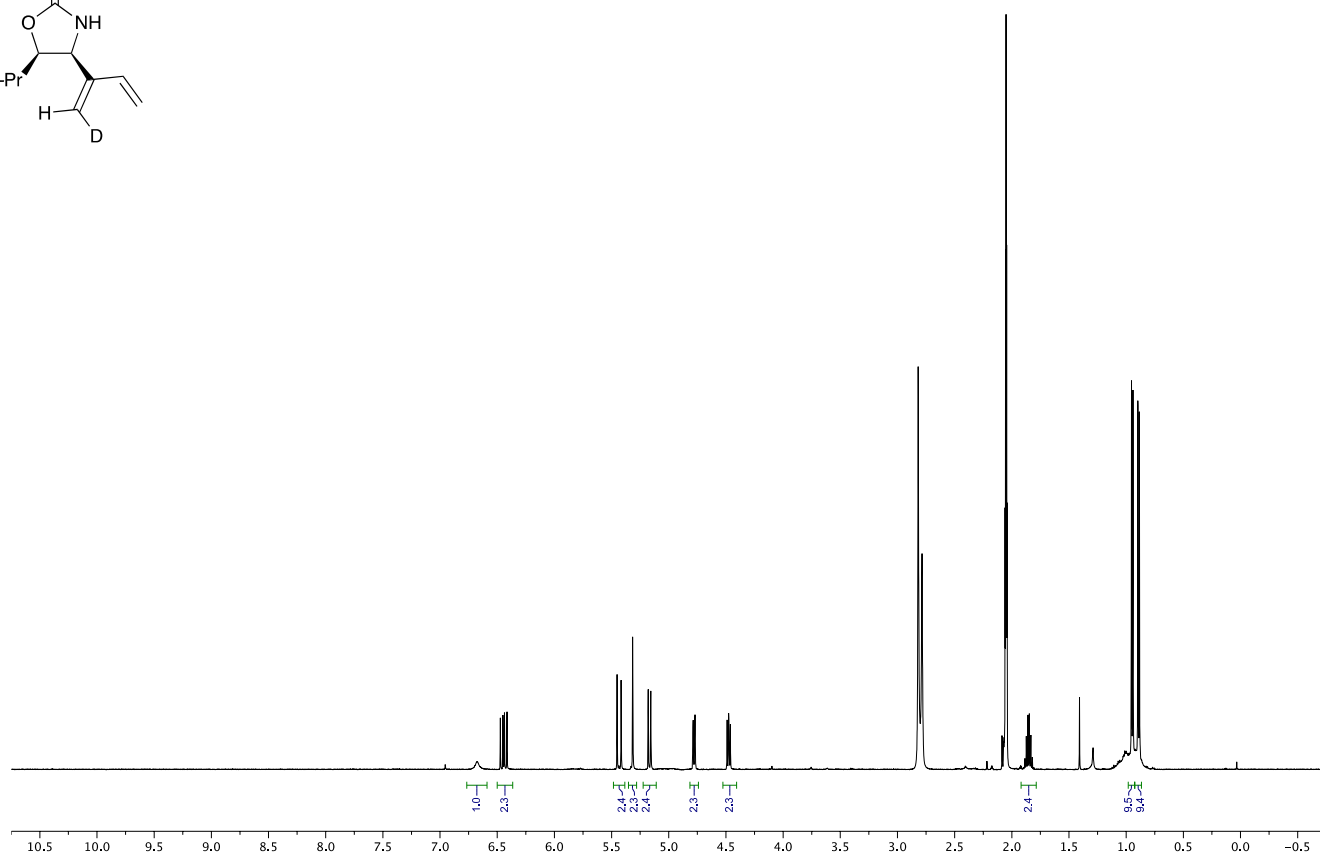
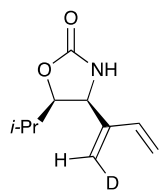


(12)

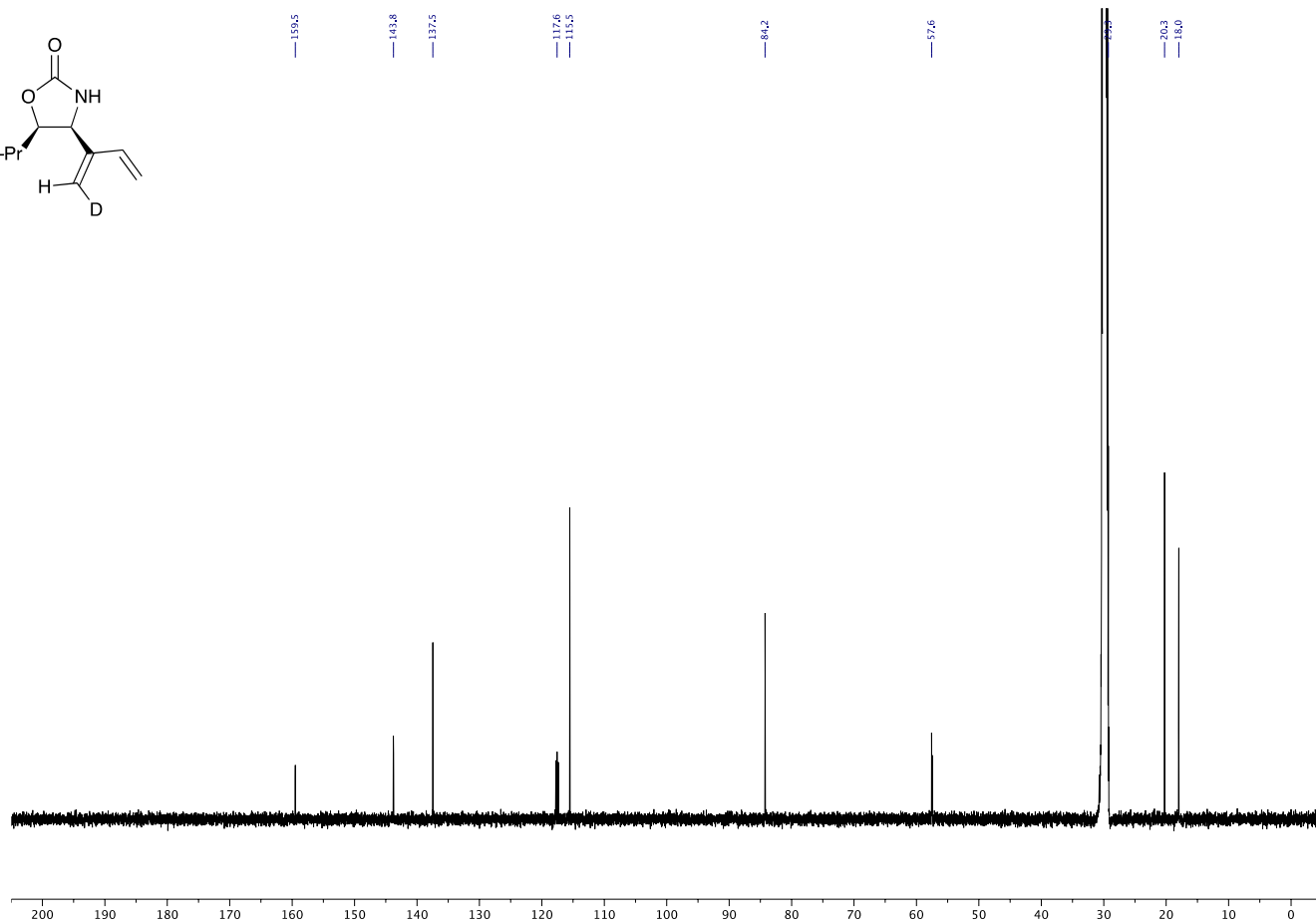
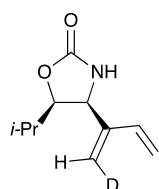
^1H NMR (500 MHz, CDCl_3)



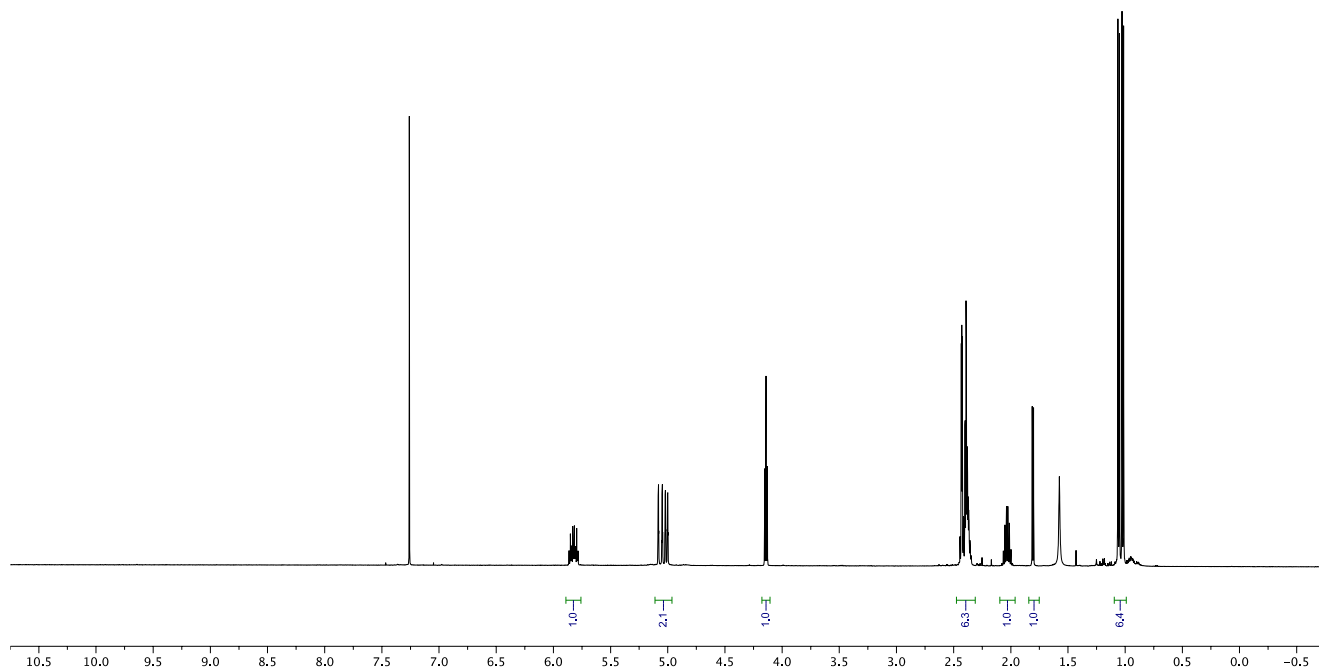
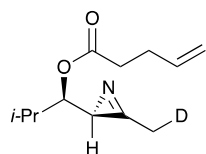
(12) ^1H NMR (500 MHz, acetone- d_6)



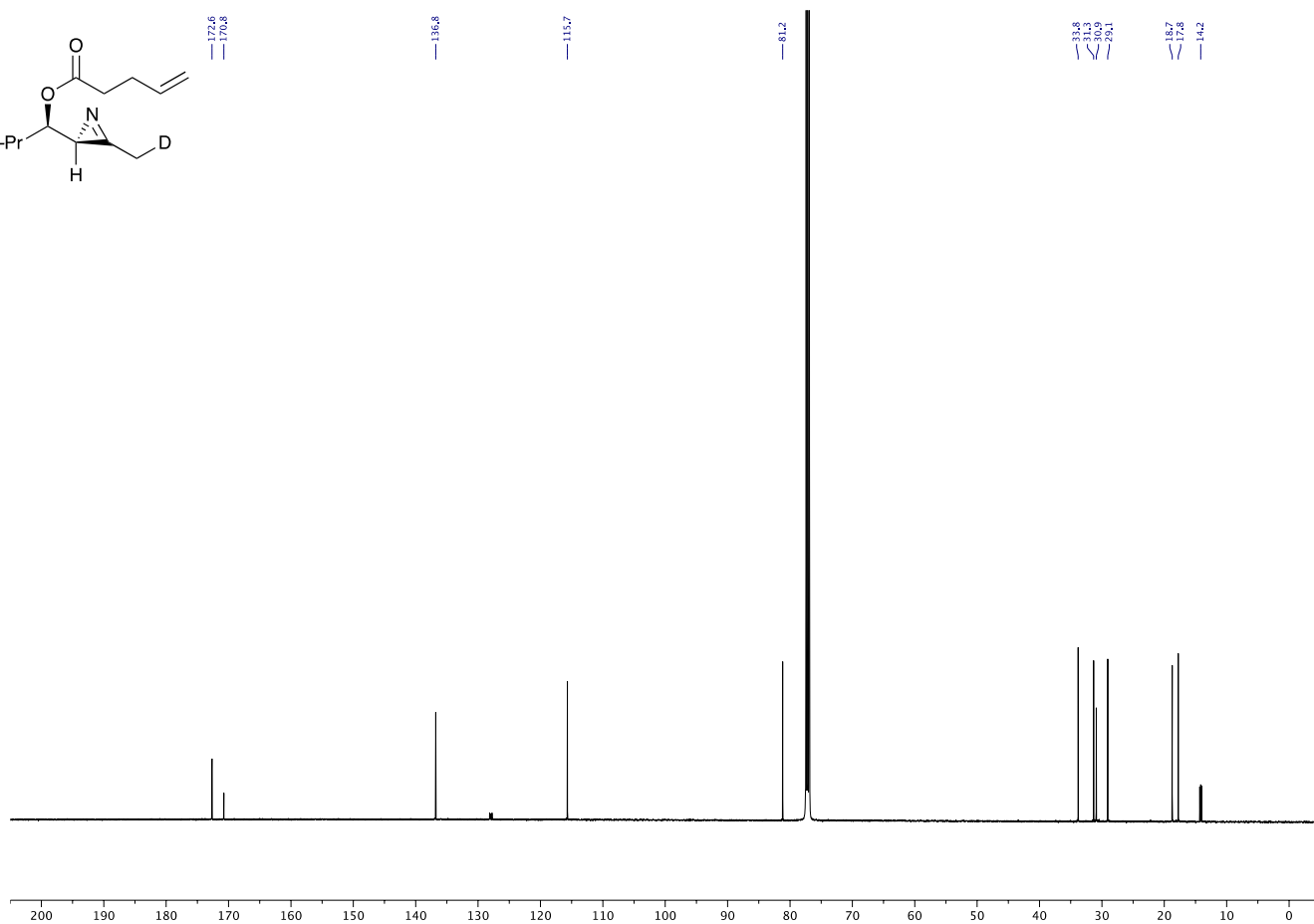
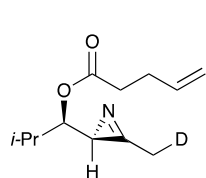
(12) ^{13}C NMR (125 MHz, acetone- d_6)



(13) ^1H NMR (500 MHz, CDCl_3)



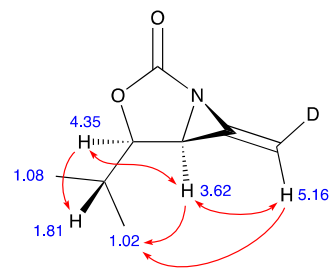
(S1) ^{13}C NMR (125 MHz, CDCl_3)



NOE experiments for compound 4

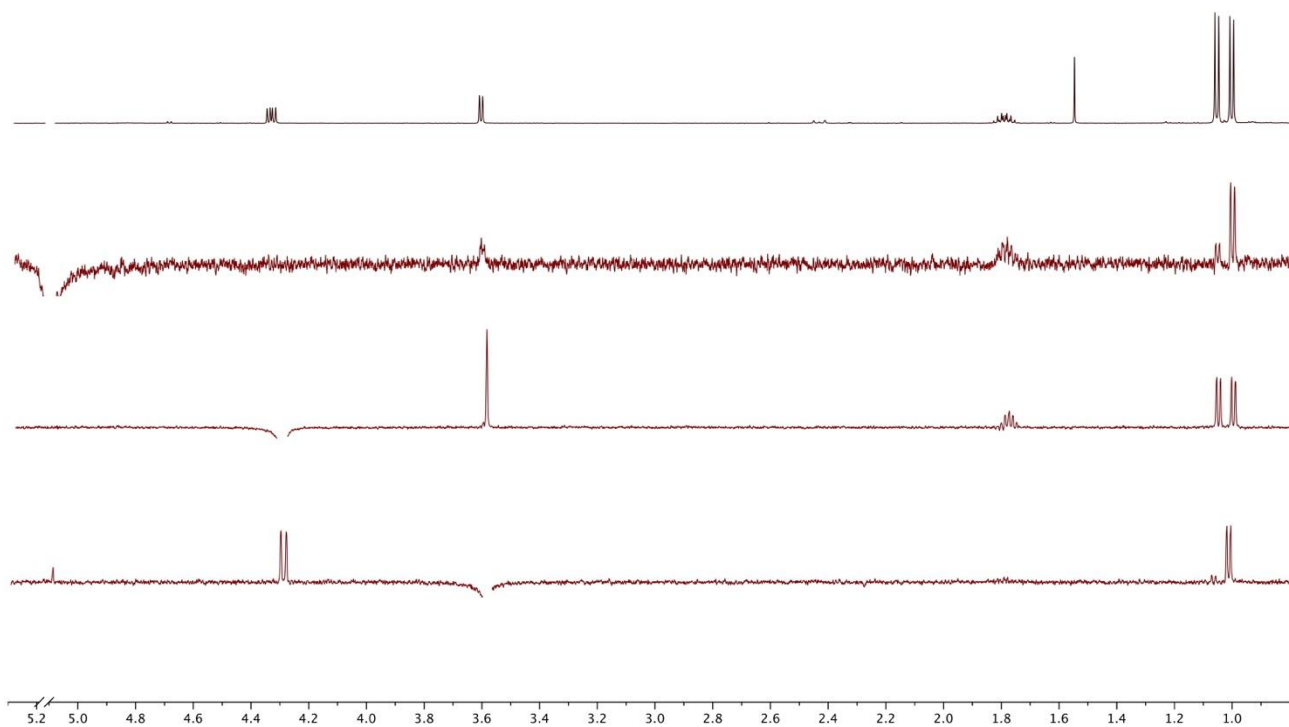
Top trace: full spectrum*

Lower traces: NOE experiment with irradiation of:

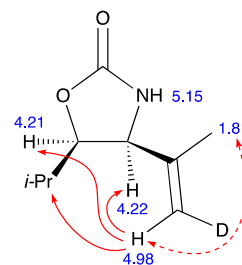


- (a) =CHD resonance at δ 5.16 (1H, s) • weak correlations with CHN and *i*-Pr support its *trans*-disposition with respect to the alkene–N bond;
- (b) =CHO resonance at δ 4.35 (1H, dd) • expected correlations to CHN and *i*-Pr only;
- (c) CHN resonance at δ 3.62 (1H, d) • in addition to the expected CHO correlation, weak correlation to =CHD is consistent with observation (a); correlation to one only of the *i*-Pr methyls (*cf.* (a)).

(* first irradiated region in this spectrum deleted to maintain the correspondence of peaks in the stack)



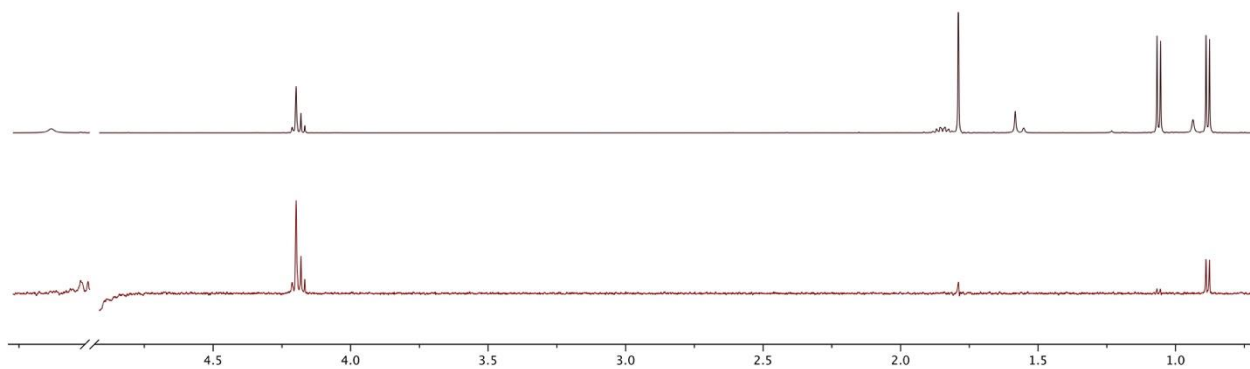
NOE experiment for compound 11



Upper trace: full spectrum*

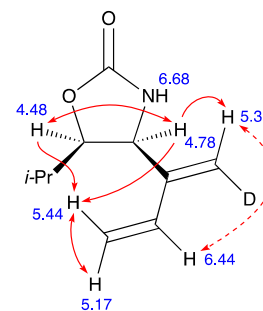
Lower trace: NOE experiment with irradiation of =CHD resonance at δ 4.98 (1H, s)

(*irradiated region in this spectrum deleted to maintain the correspondence of peaks in the stack)



- Strong correlations to the CHNH and CHO protons at 4.18–4.24 (2H, m) and one of the *i*-Pr methyls at 0.90 (3H, d) support a *cis*- disposition of the =CHD proton and the heterocycle; a very weak correlation to the vinyl methyl resonance at 1.81 ppm supports their *trans*- disposition across the alkene double bond.

NOE experiments for compound 12



Top trace: full spectrum

Lower traces: NOE experiment with irradiation of:

- (a) =CHZHE resonance at δ 5.44 (1H, d) • no correlation with =CHD consistent with D and vinyl group *cis*-disposed;
- (b) =CHD resonance at δ 5.32 (1H, s) • no significant correlations;
- (c) =CHZHE resonance at δ 5.17 (1H, d) • correlation only to its *geminal* methylene proton;
- (d) CHN resonance at δ 4.78 (1H, d) • in addition to the expected CHO correlation, weak correlations to =CHZHE and =CHD support their overall *cis*-relationship to the heterocycle;
- (e) CHO resonance at δ 4.48 (1H, dd) • in addition to the expected CHN correlation, a weak correlation to =CHZHE supports the observation in (d).

(* first irradiated region in this spectrum deleted to maintain the correspondence of peaks in the stack)

