

## Supplementary Material

### Generation and reversible cyclisation of furfurylic radicals

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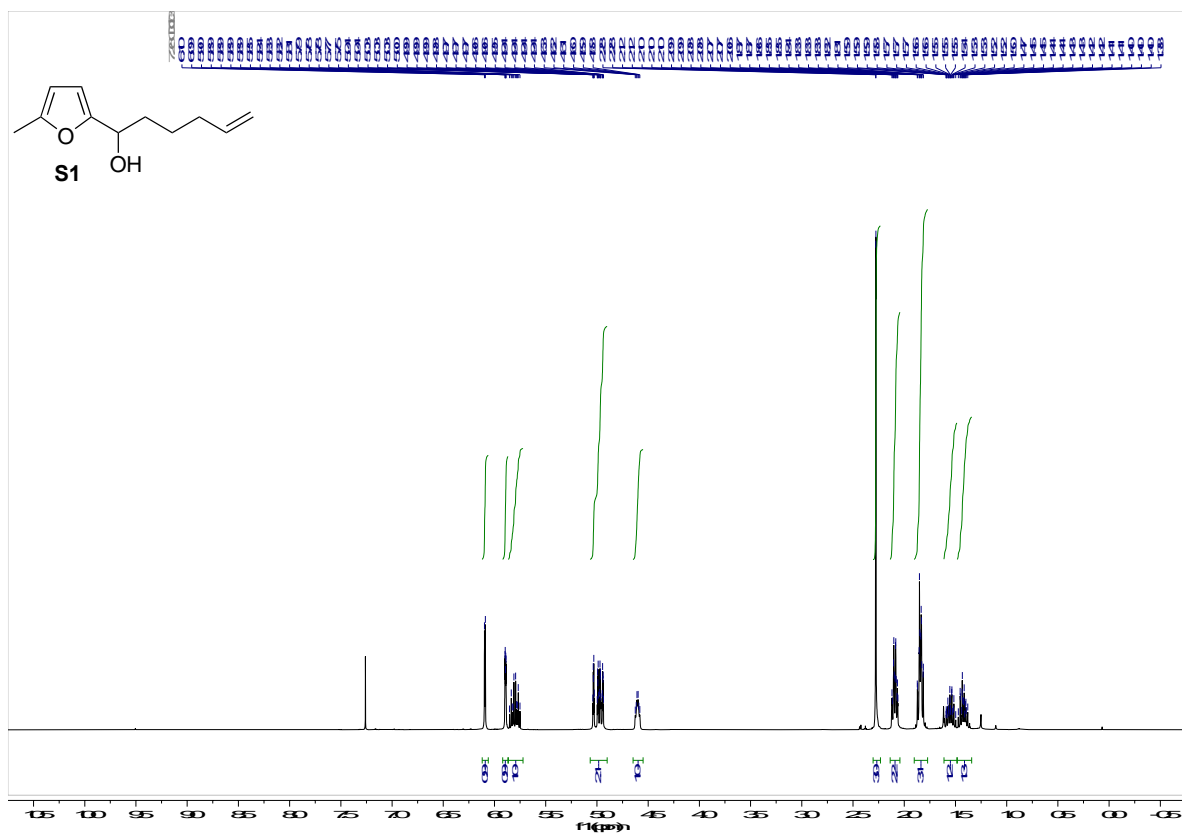
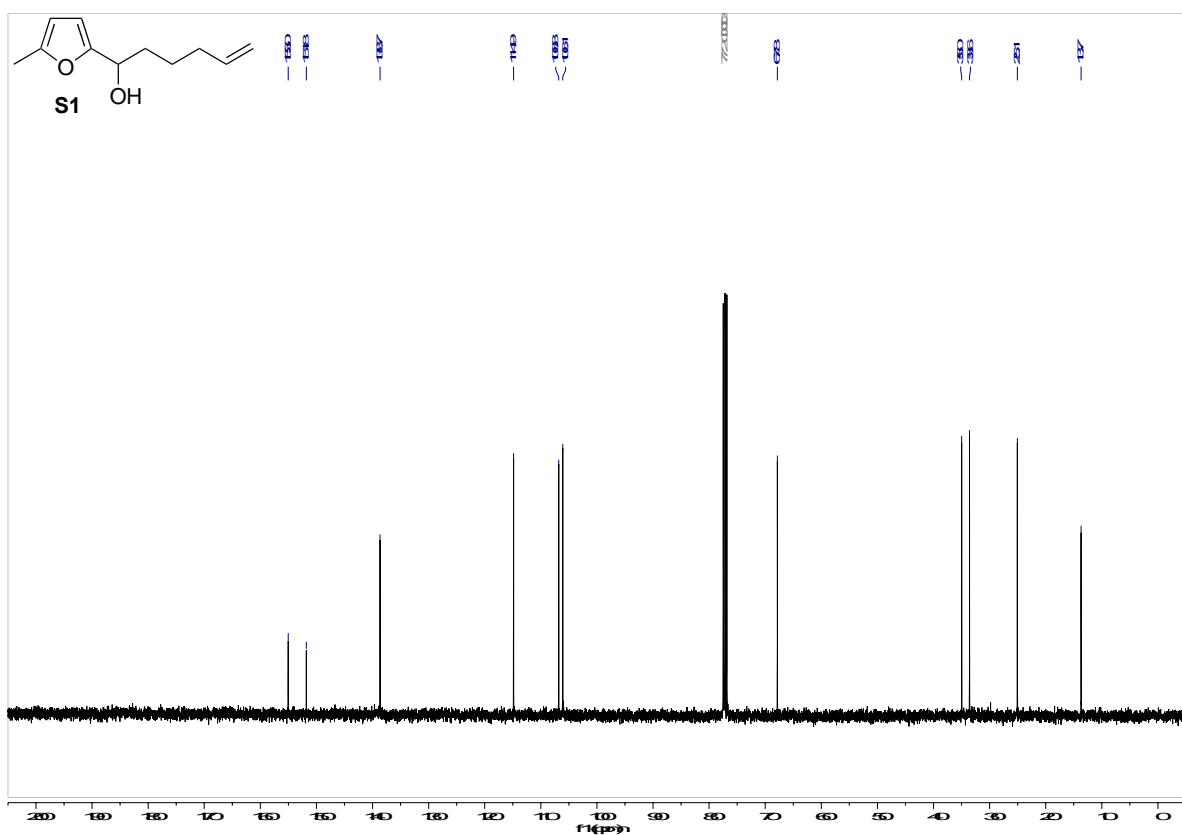


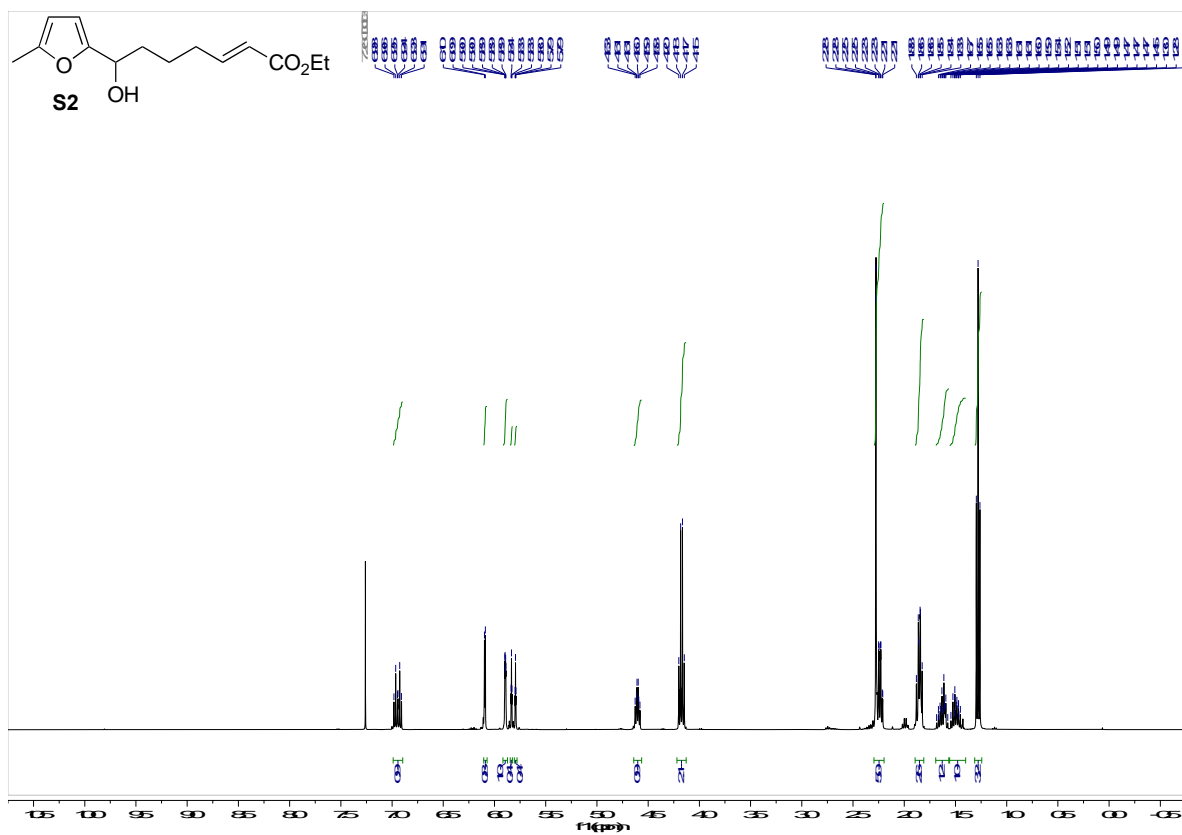
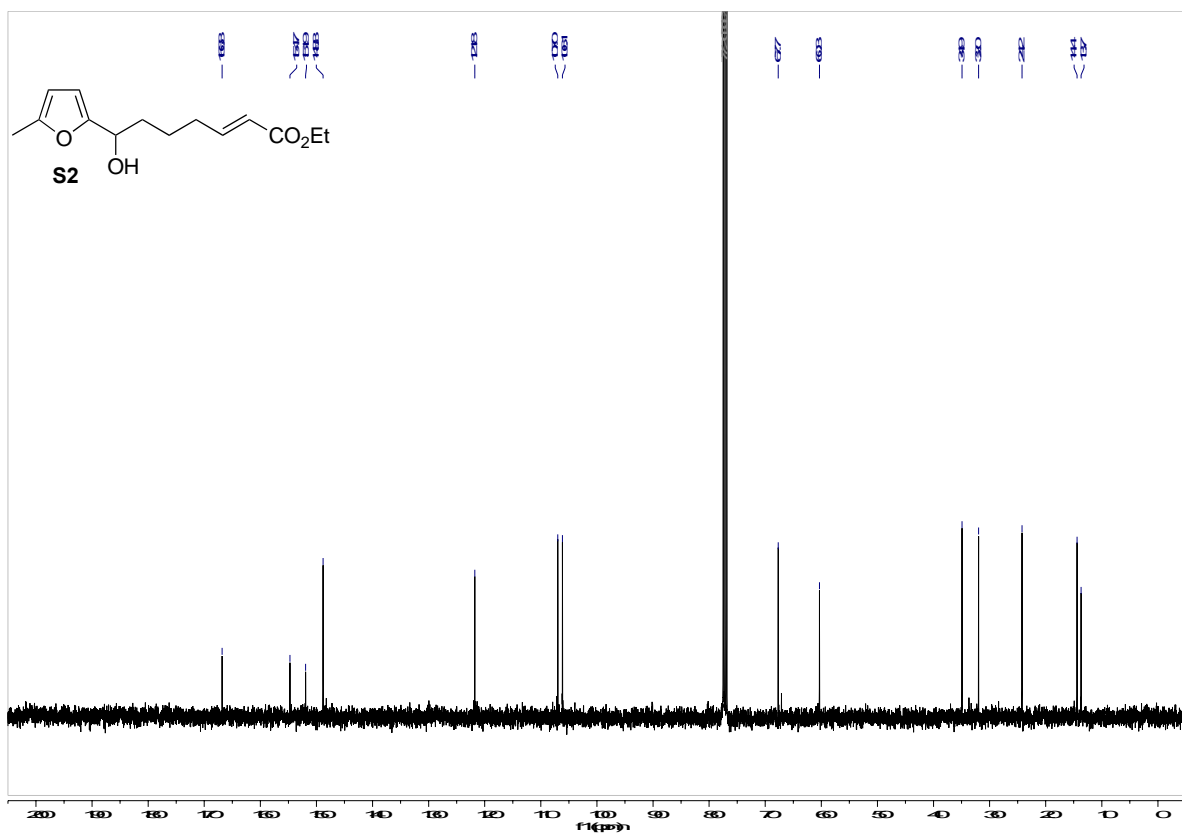








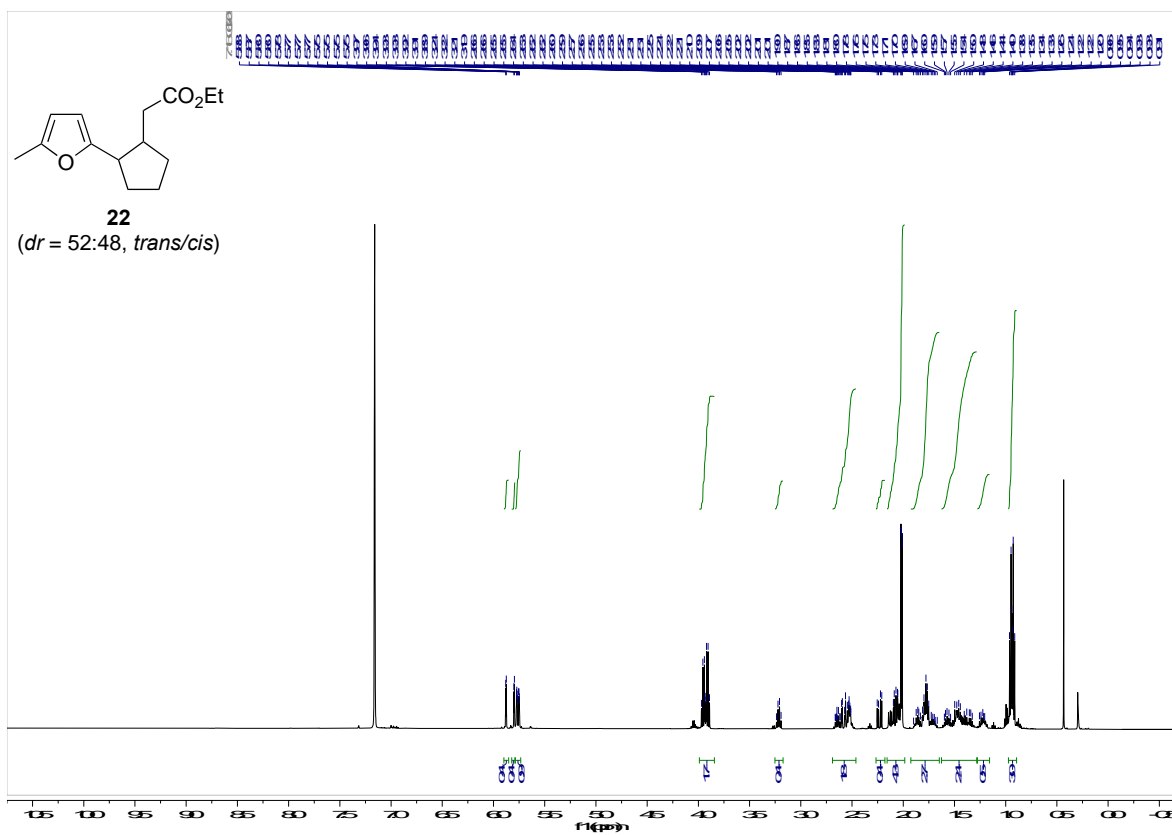
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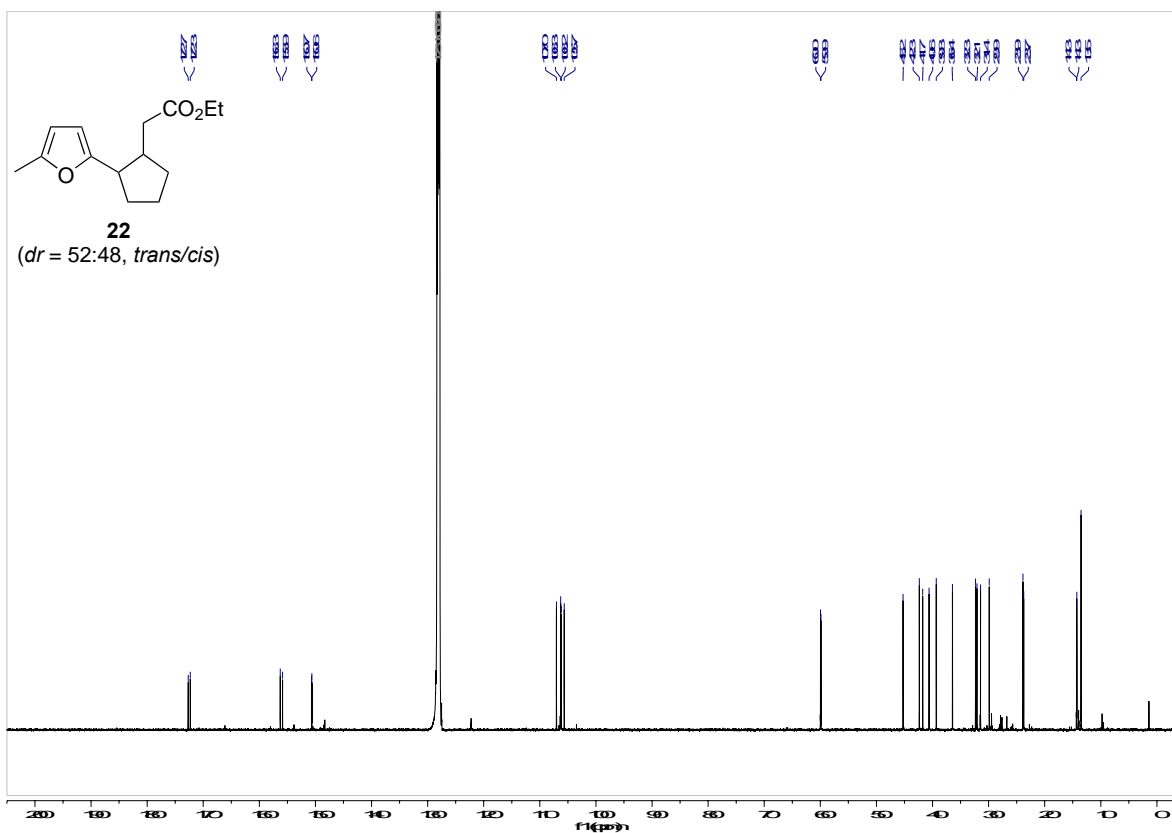


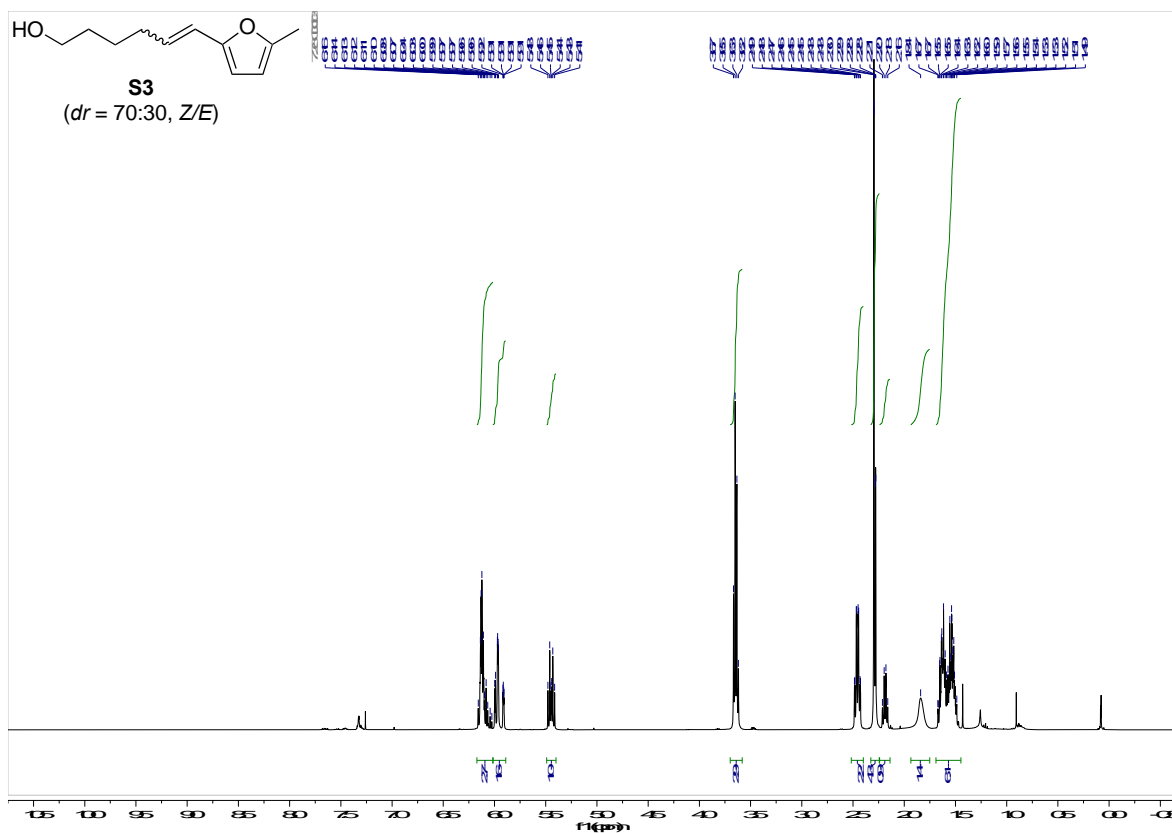
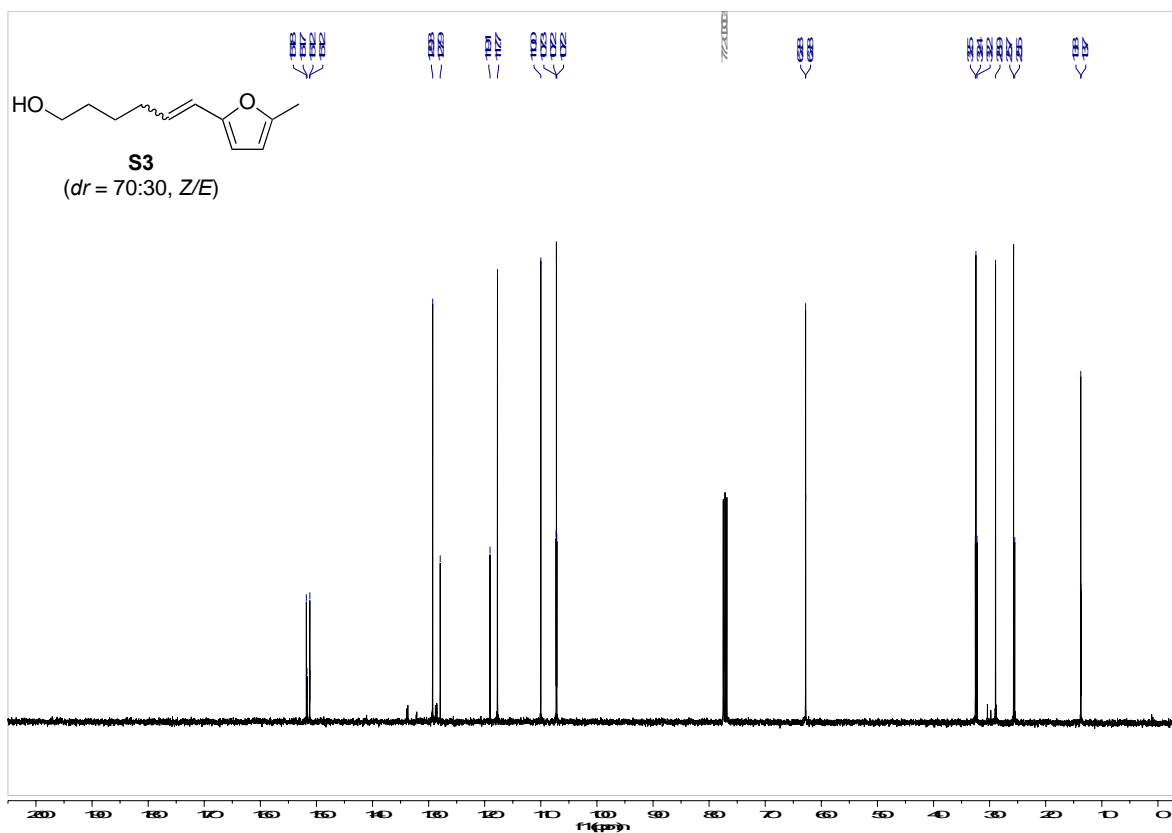


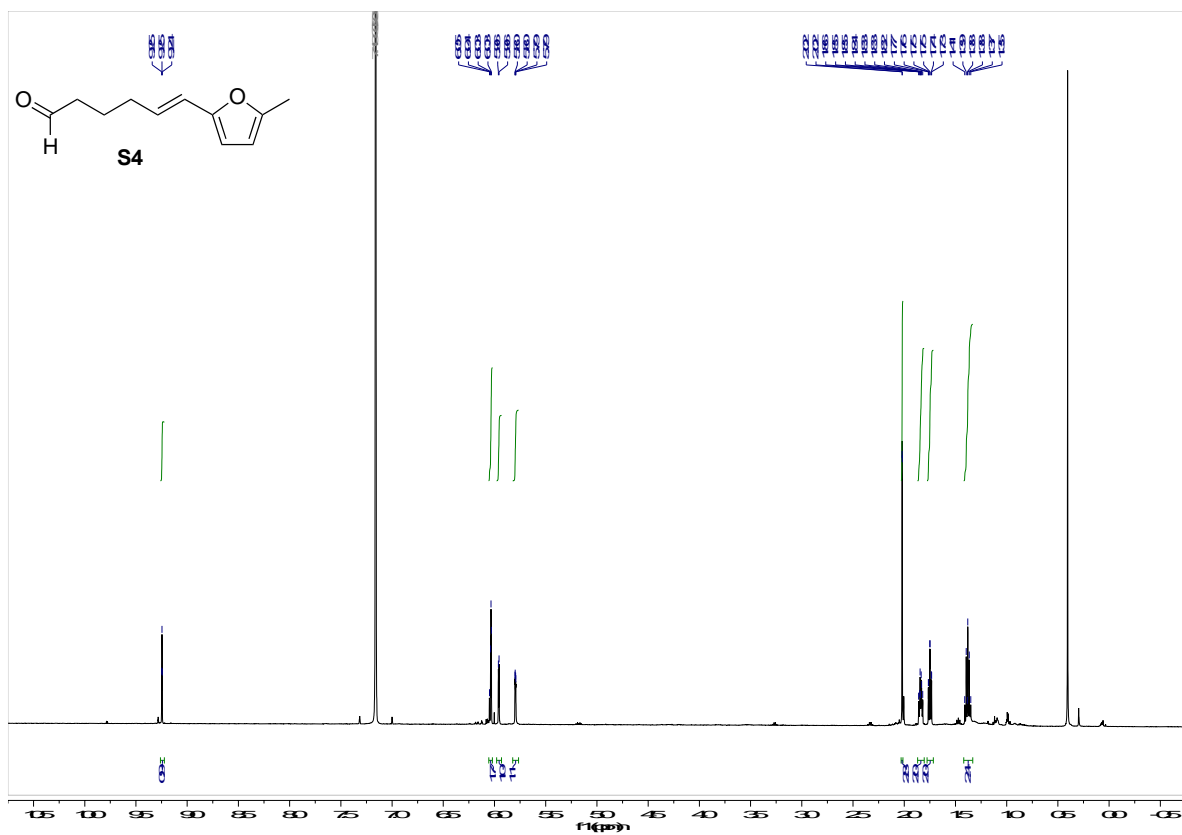
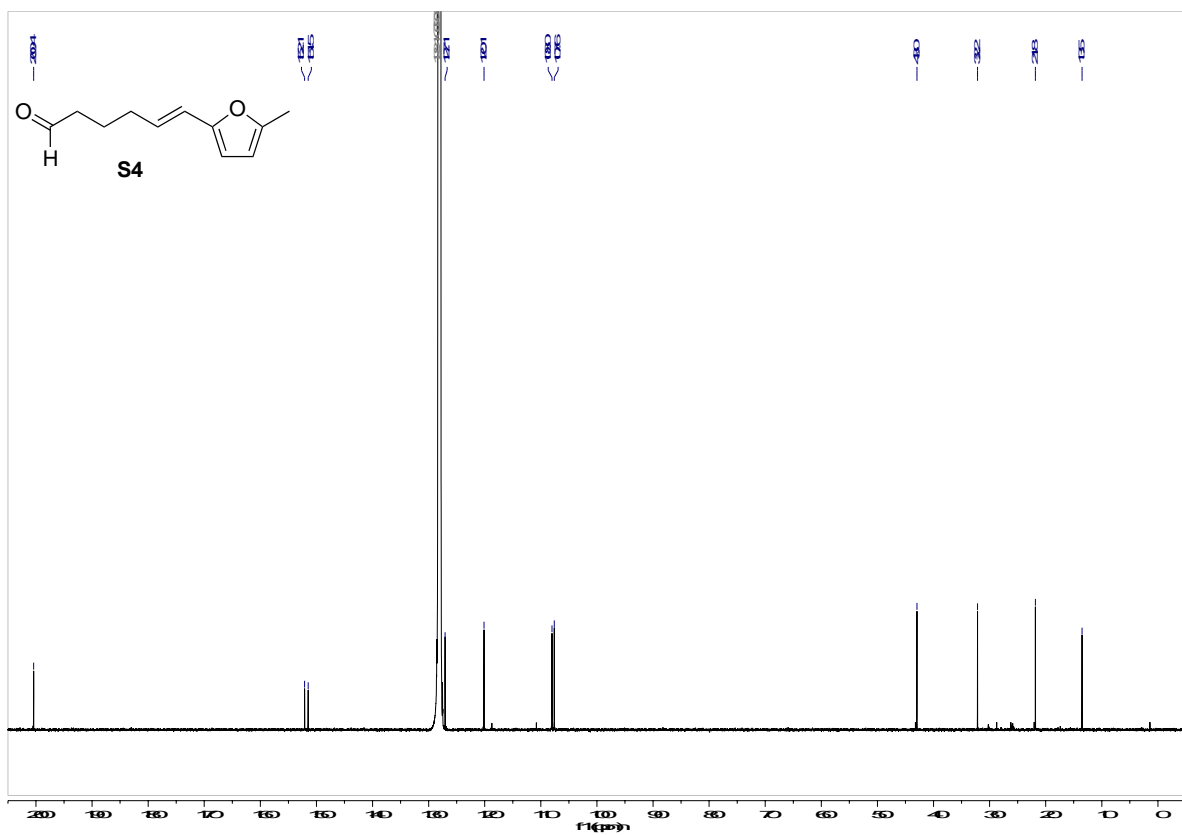
<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)

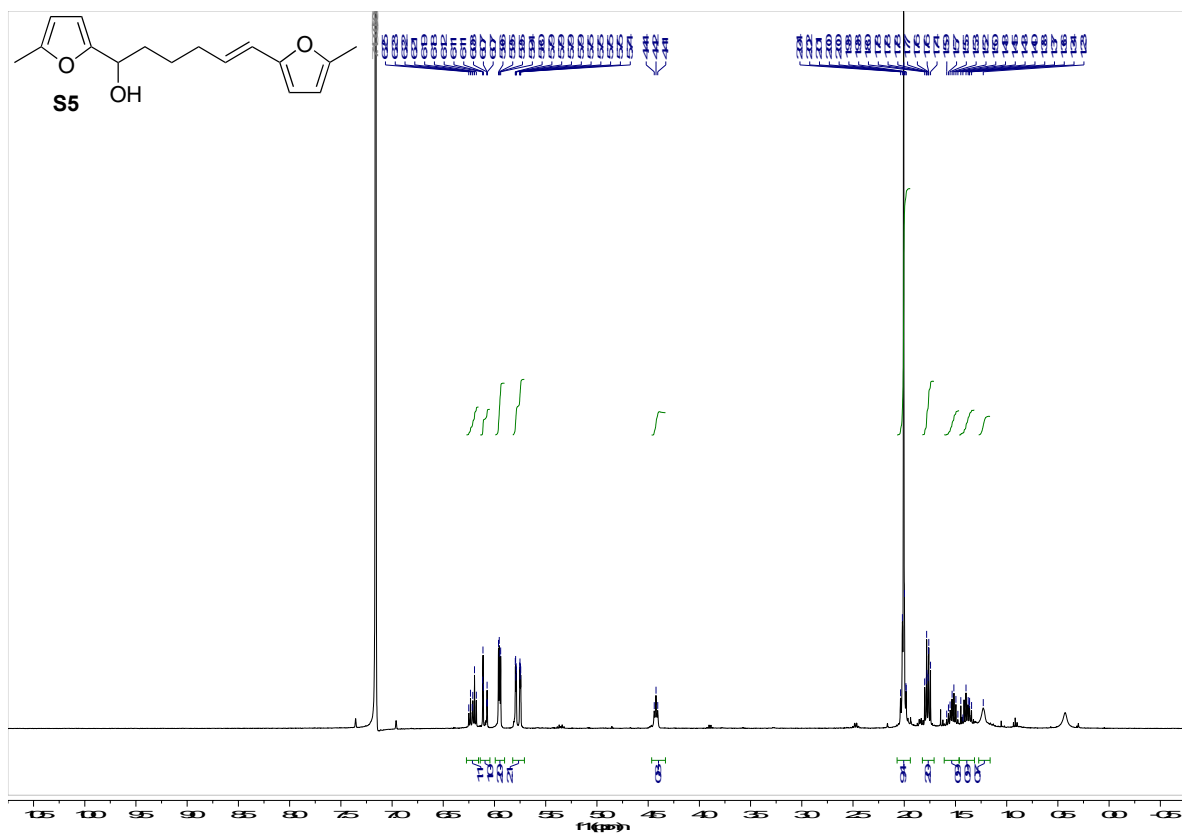
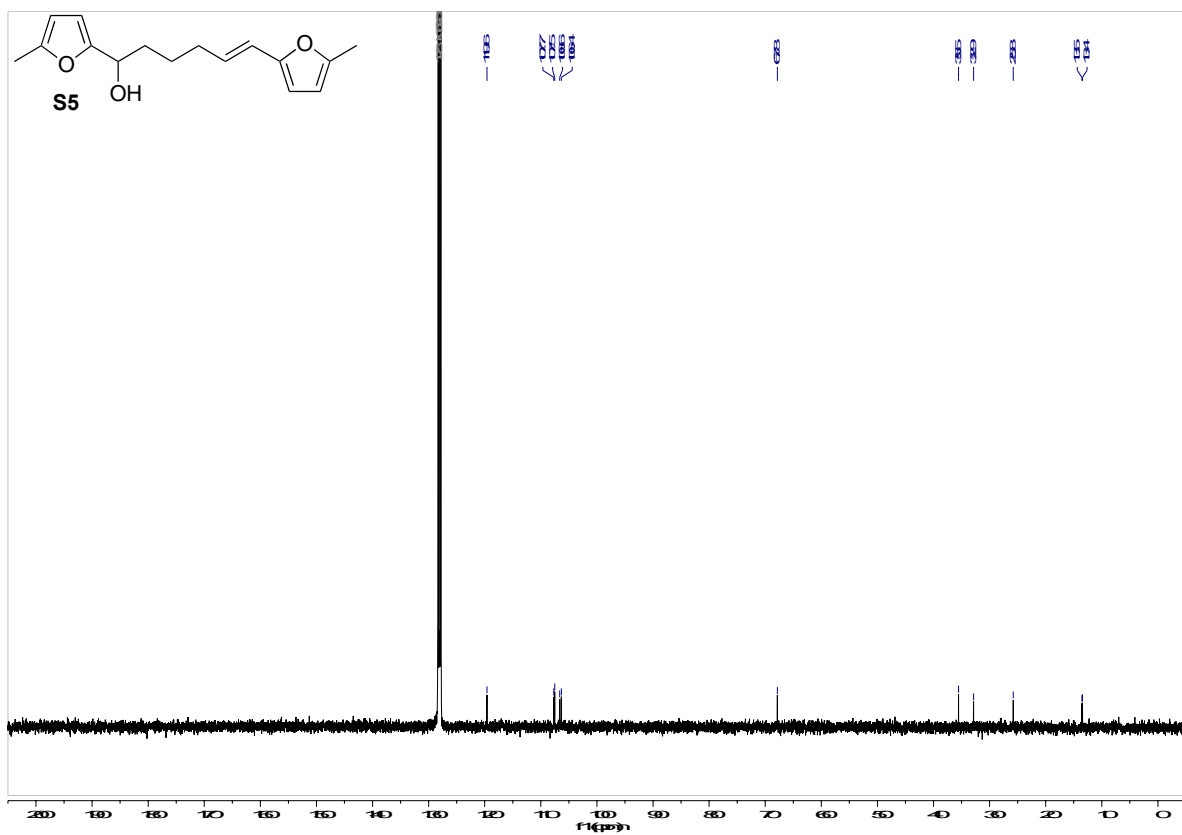


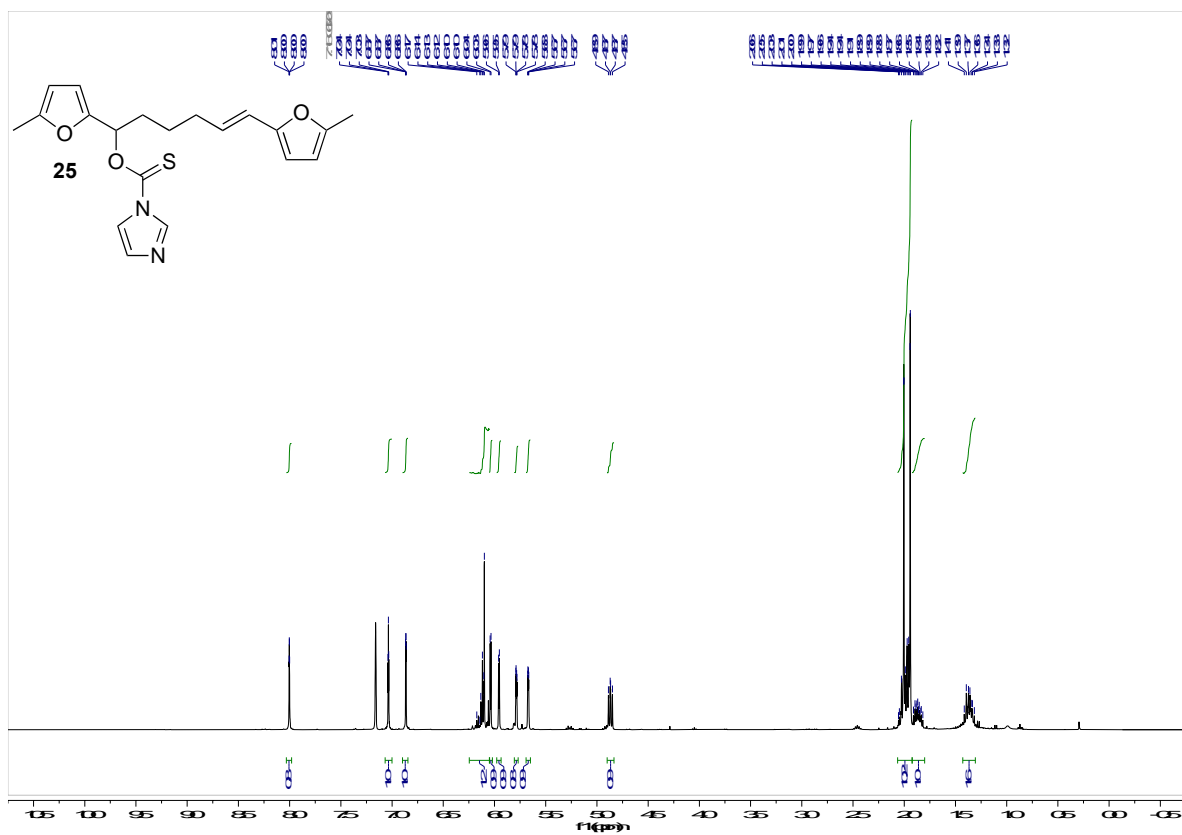
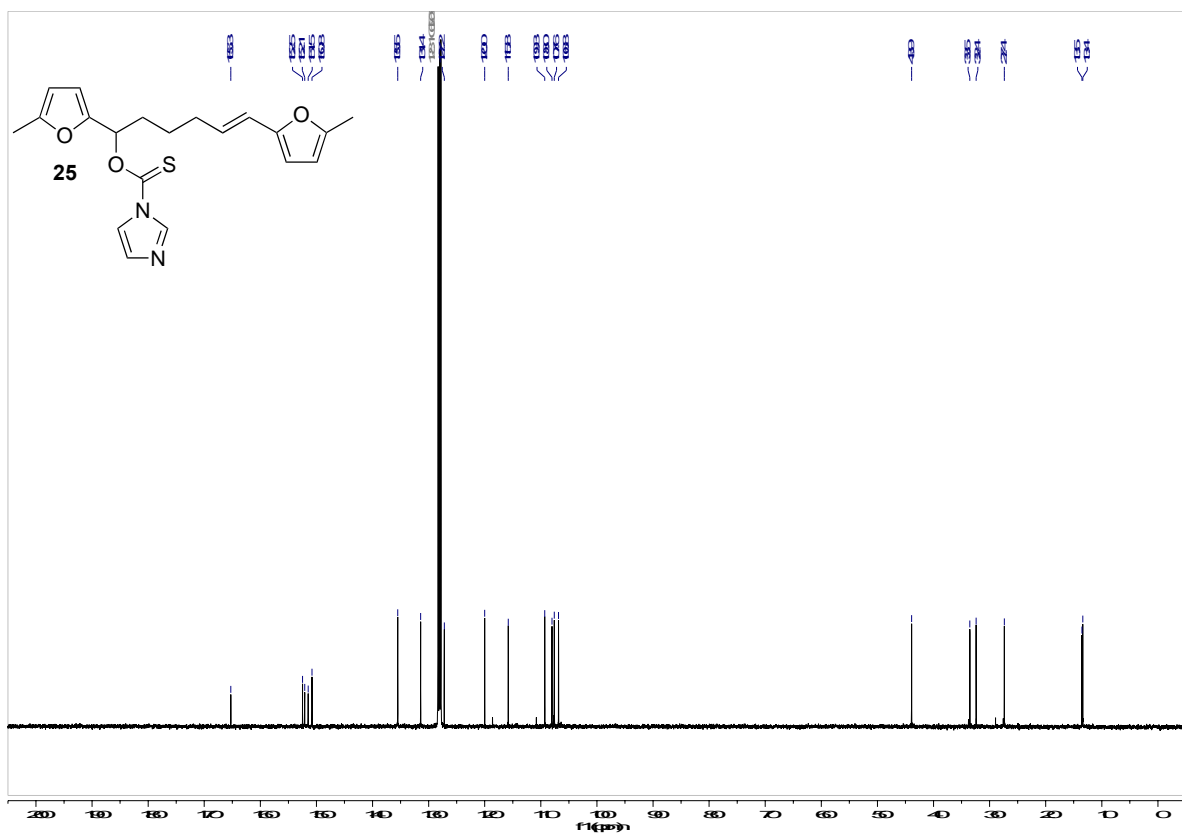
<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)

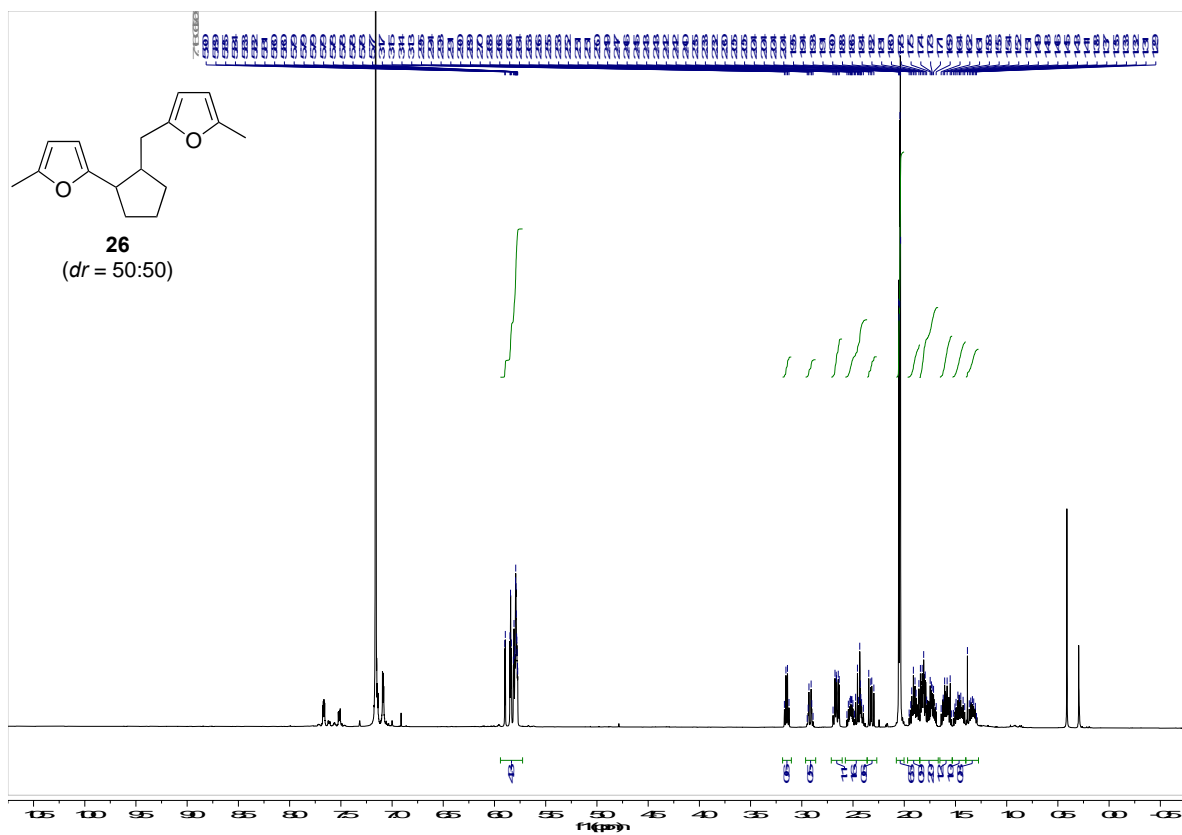
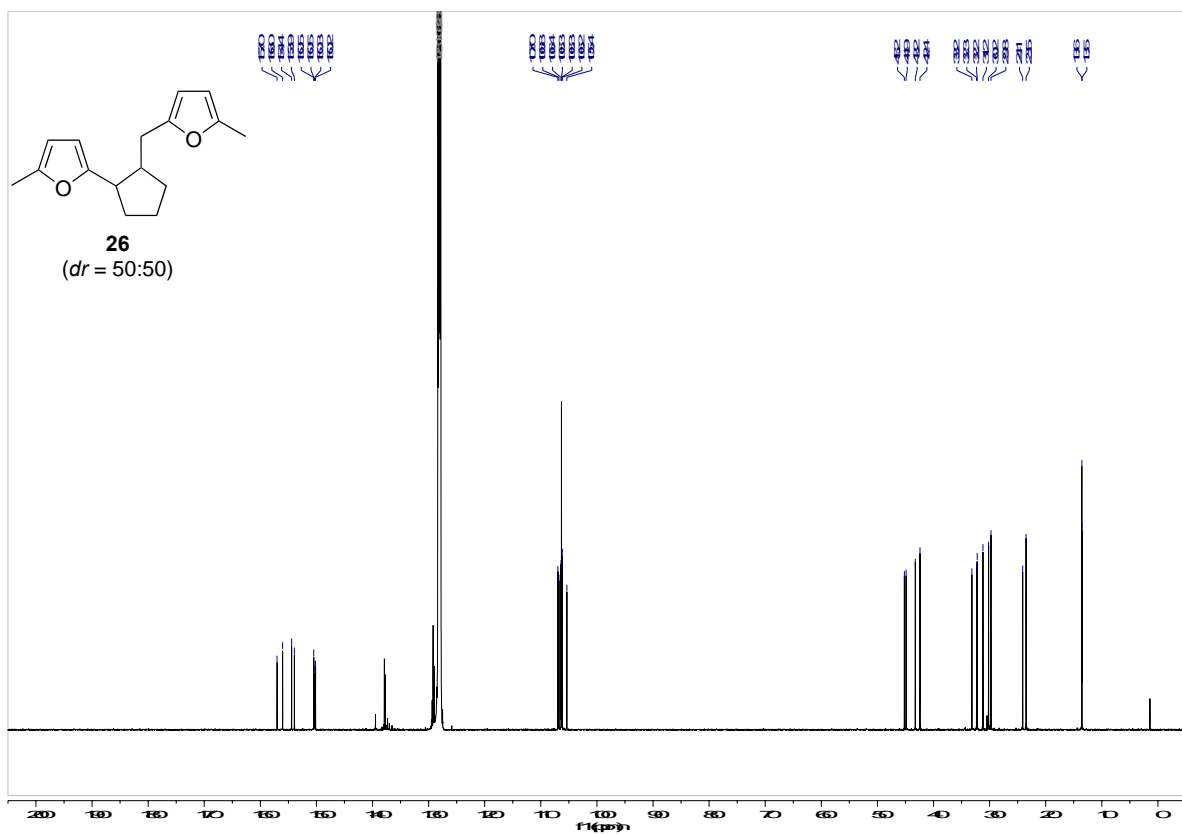


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ) $^{13}\text{C}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ )

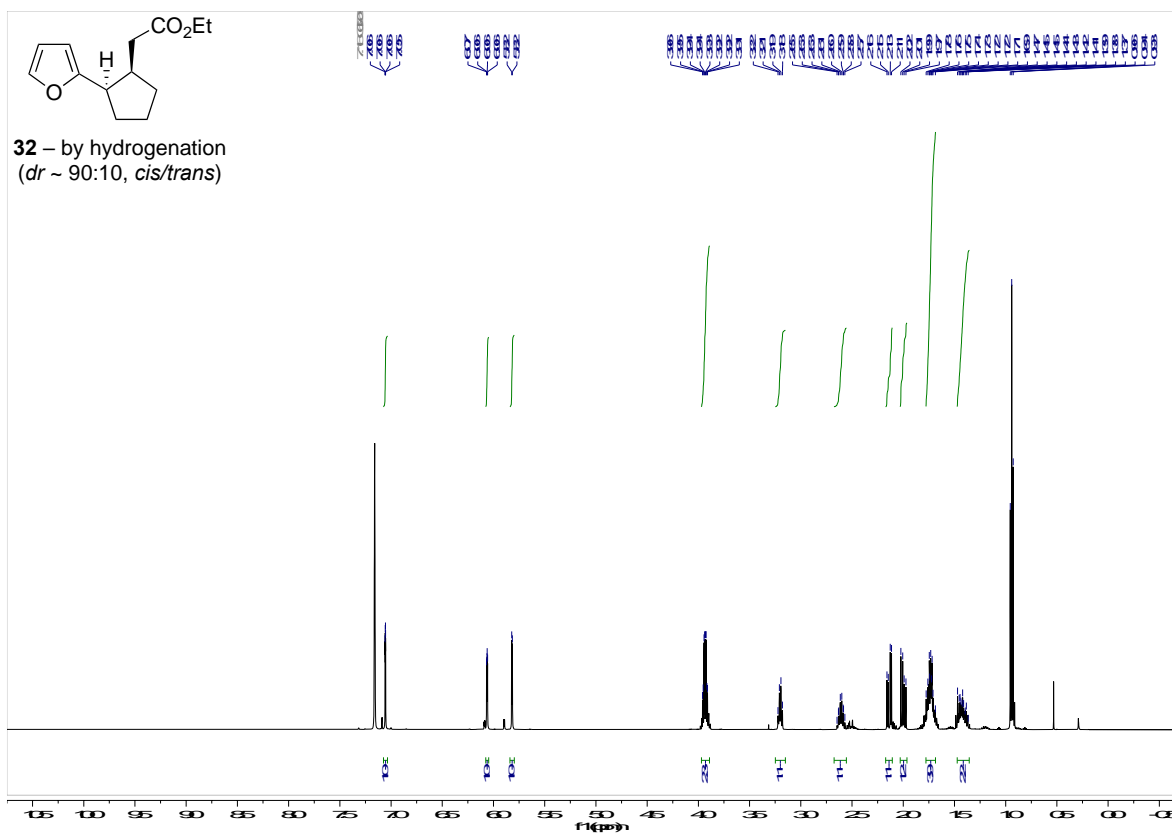
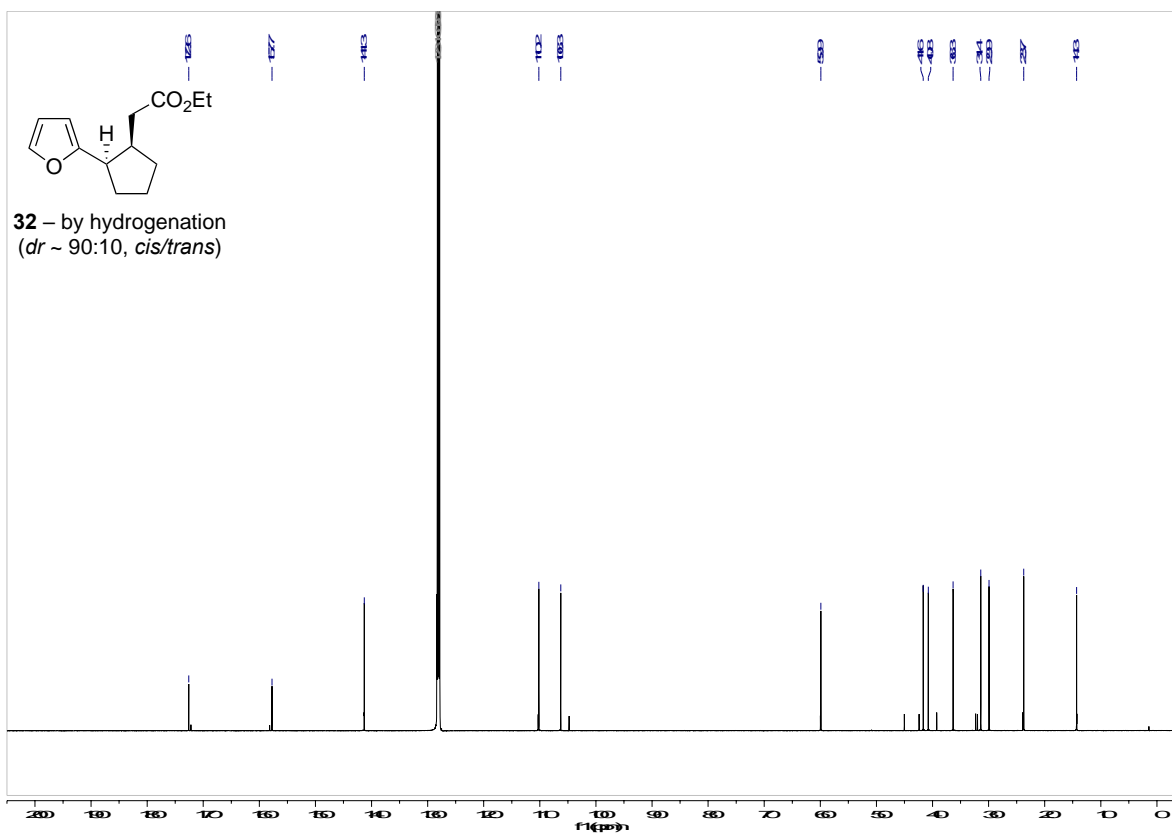
$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ) $^{13}\text{C}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ )

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ) $^{13}\text{C}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ )

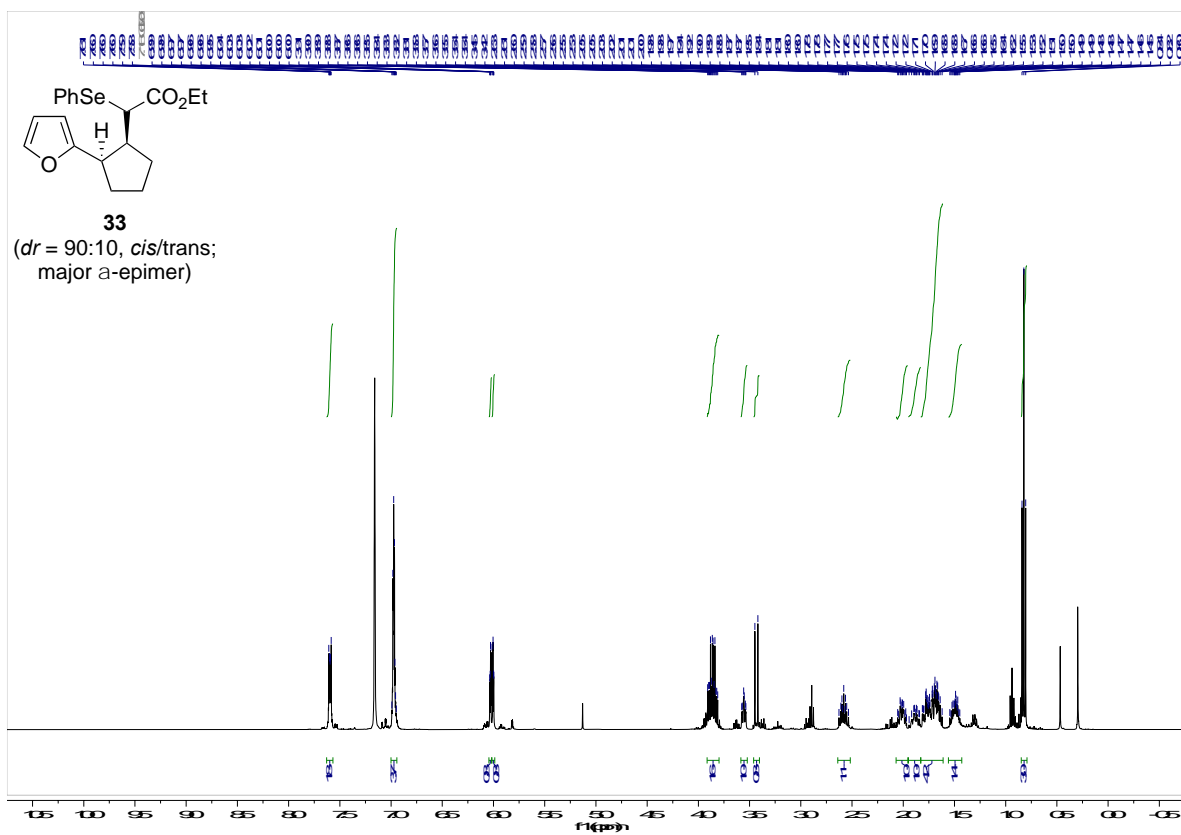
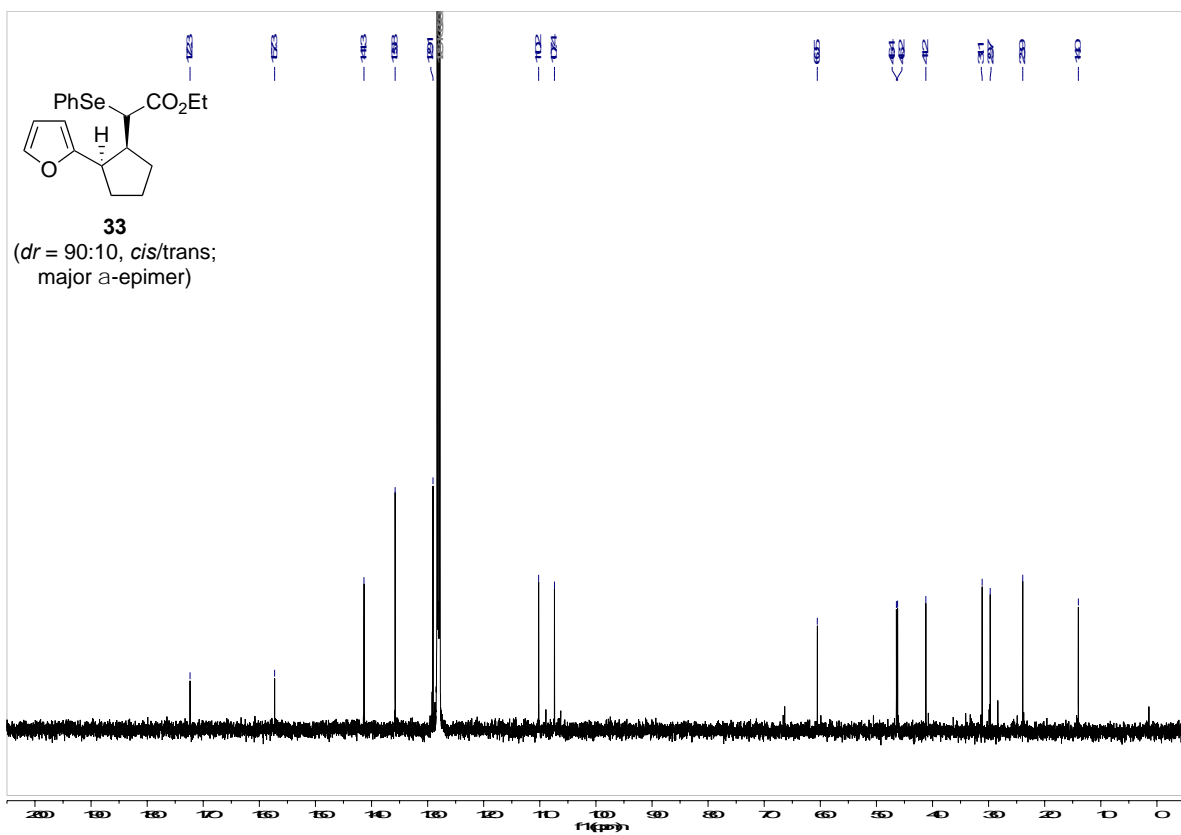
$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ) $^{13}\text{C}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ )



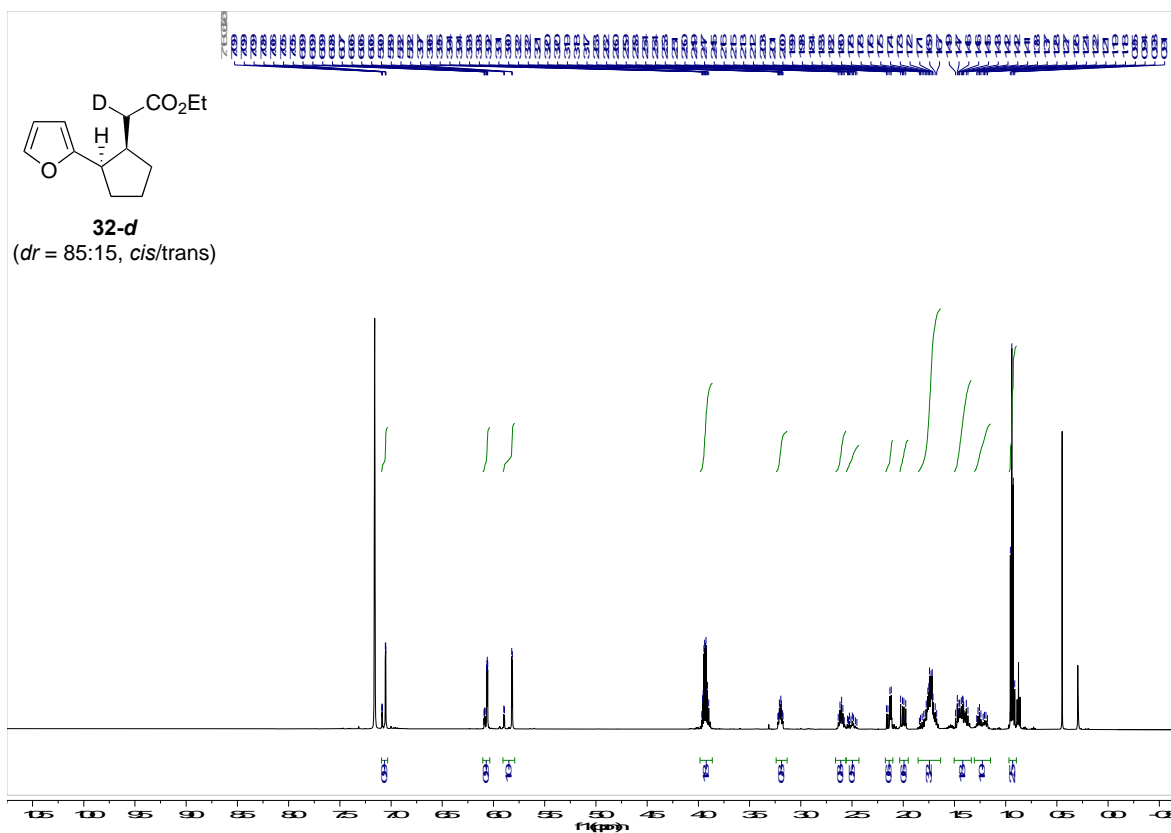
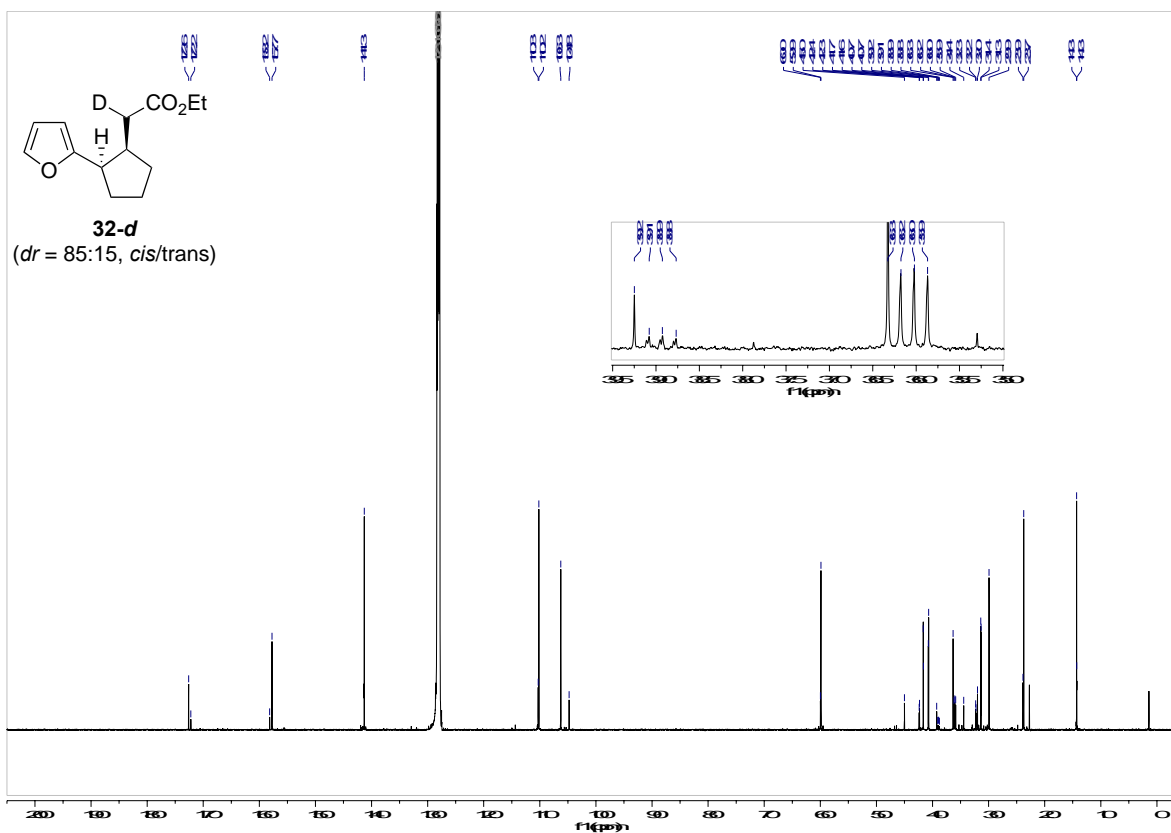


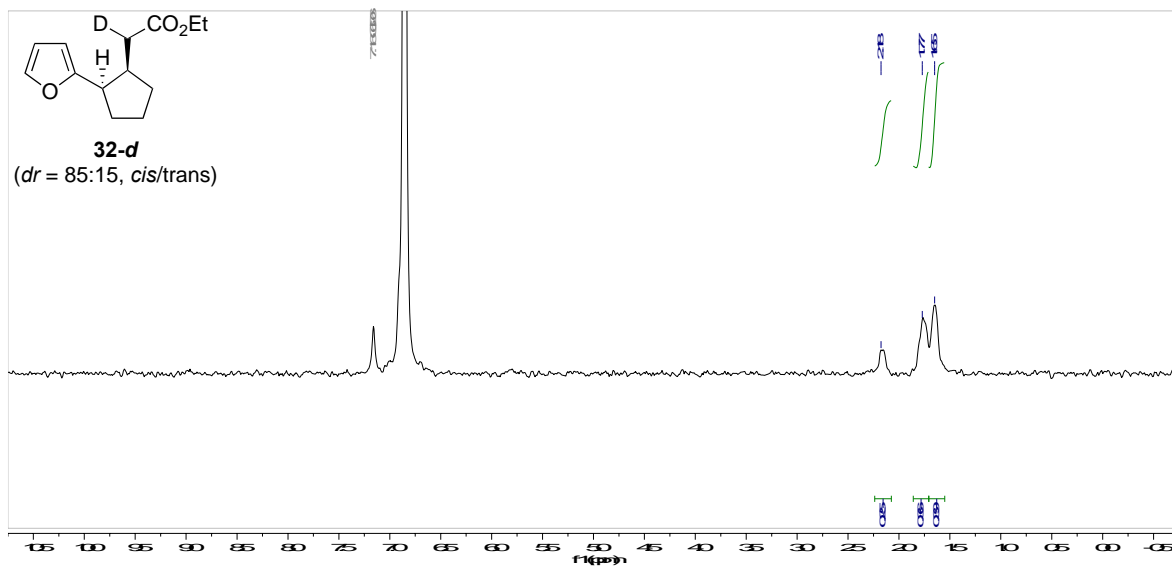
<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)

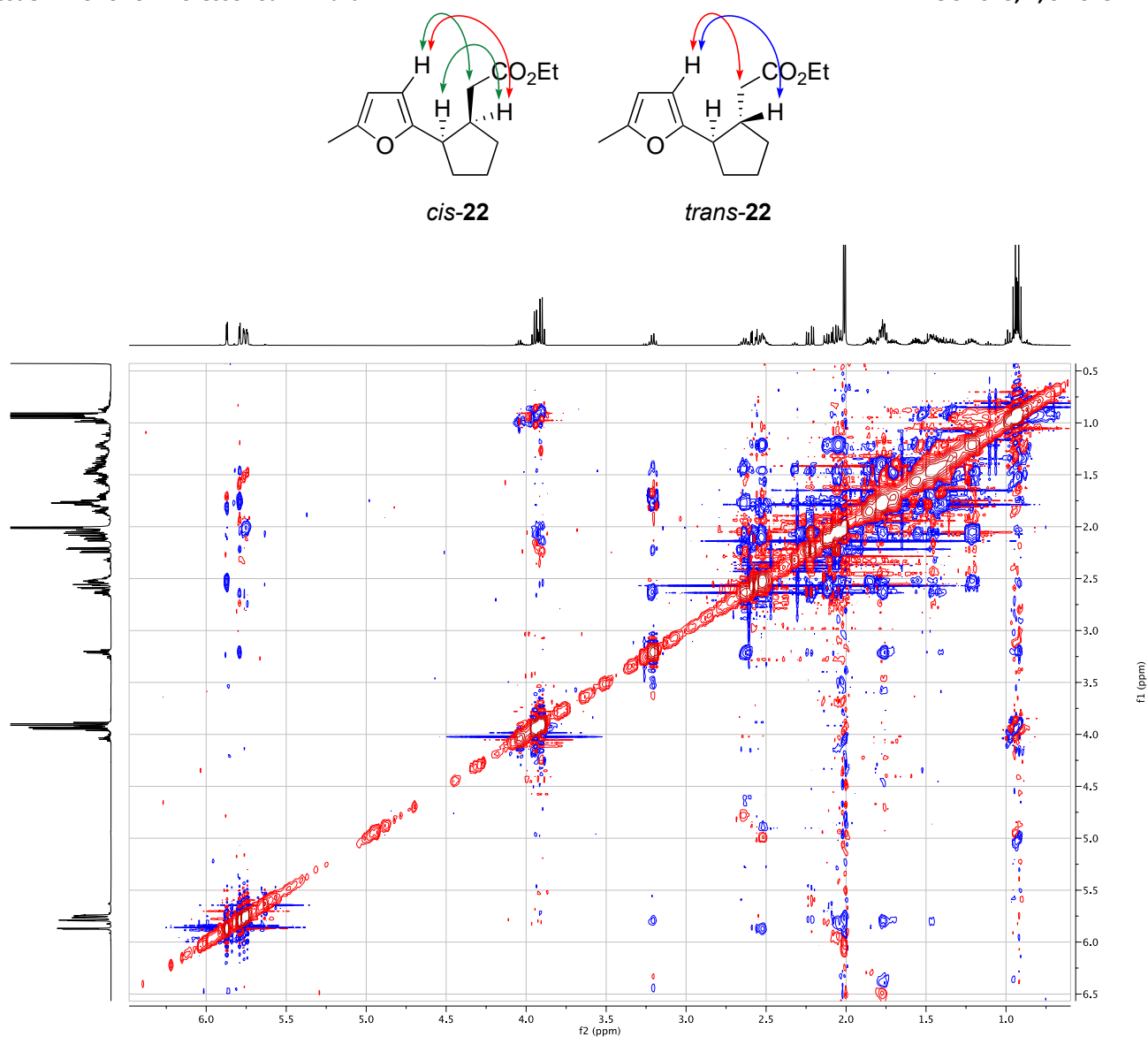


$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ) $^{13}\text{C}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ )

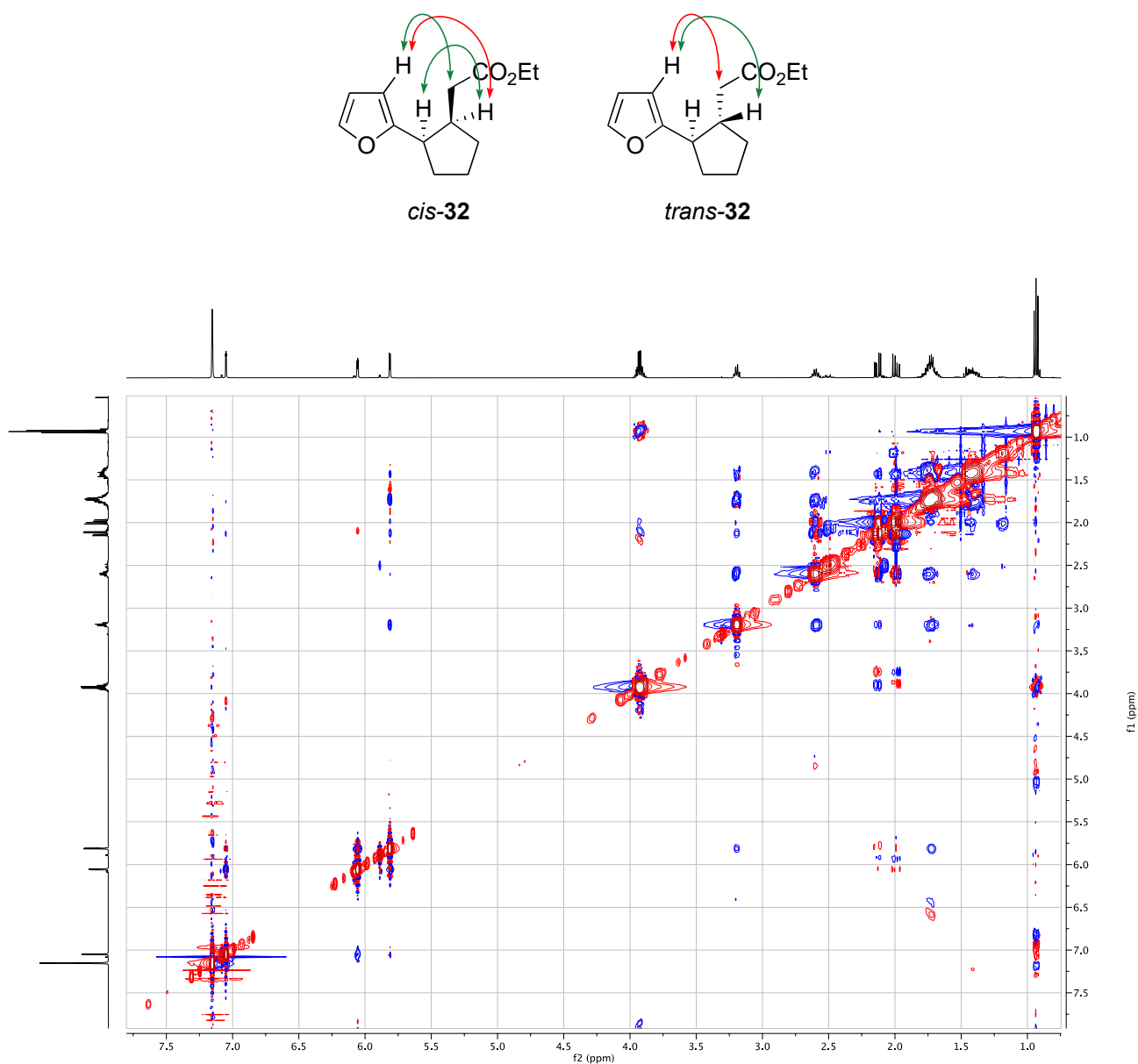


$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ) $^{13}\text{C}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ )

$^2\text{H}$  NMR (92 MHz,  $\text{C}_6\text{H}_6$  spiked with  $\text{C}_6\text{D}_6$ )



**Figure S1** <sup>1</sup>H-<sup>1</sup>H NOESY (500 MHz, C<sub>6</sub>D<sub>6</sub>) spectrum of compound **22** (*dr* = 52:48, *trans/cis*) from radical cyclisation. Green arrows indicate observed correlations; red arrows indicate those not observed; blue arrow is an ambiguous correlation.



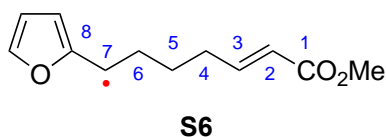
**Figure S2** <sup>1</sup>H–<sup>1</sup>H NOESY (500 MHz, C<sub>6</sub>D<sub>6</sub>) spectrum of compound **32** (*dr* = 90:10, *cis/trans*) prepared by hydrogenation. Green arrows indicate observed correlations; red arrows indicate those not observed.



## DFT calculations

Energy calculations for *trans*- and *cis*-**22'**

- A conformer distribution was obtained within *Spartan'20* using molecular mechanics (MMFF, MonteCarlo) to generate 38 conformations for *trans*-**22'** and 24 for *cis*-**22'**; the methyl ester was used here to keep the number of conformations to a manageable level.
- The low-lying conformations, representing ~95% of the conformational space, were retained: 17 for *trans*-**22'**, 13 for *cis*-**22'**.
- DFT (B3LYP/6-31G\*) equilibrium geometry calculations of the 30 separate conformations were used to obtain a Boltzmann-weighted average energy for each diastereomer leading to the values presented in Figure 1 of the main text.

Transition state calculations for the cyclisation of methyl (*E*)-7-(2-furyl)hept-2-enoate (7-yl radical) (**S6**)

- Transition states were computed within *Spartan'20* for the cyclisation of 6-hexenyl radical in both *anti* ('chair') and *gauche* ('boat') conformations as defined in Table 1 of the main text.
- These were then used to build the substituted radical **S6** in *anti* and *gauche* conformations, each configured to lead to either *cis* or *trans* disubstituted cyclopentane.
- For each of the four so-generated transition state approximations, a conformer distribution was obtained (MMFF, MonteCarlo) with the hexenyl radical core frozen (Table S1).
- DFT (B3LYP/6-31G\*) equilibrium geometry calculations of the 28 separate radical conformations, with the cores unfrozen, were used to obtain an energy-weighted conformer distribution within each parent.
- In all cases, based on the Boltzmann weightings, just one or two low-lying conformations accounted for 83–90% of the conformational space; these were selected for DFT (B3LYP/6-31G\*) transition state calculations with all constraints removed, leading to the energies presented in Table 1 of the main text.

**Table S1.** Numbers of conformations taken through each stage of the transition state calculations.

Conformation	MMFF conformers	Number selected for TS calcns
<i>anti-cis</i>	4	1 (83%)
<i>anti-trans</i>	5	2 (83%)
<i>gauche-cis</i>	9	1 (86%)
<i>gauche-trans</i>	10	2 (90%)