

# Supplementary Materials

## Copper-catalyzed diboron-mediated *cis*-semihydrogenation of alkynes under facile conditions

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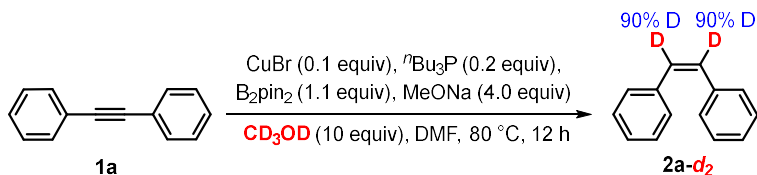
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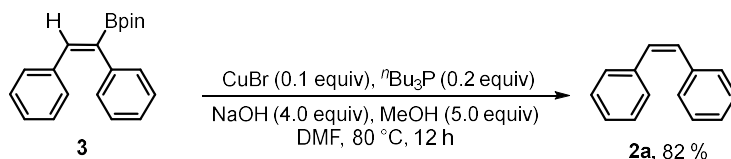
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## 1. Experimental procedures of mechanistic studies



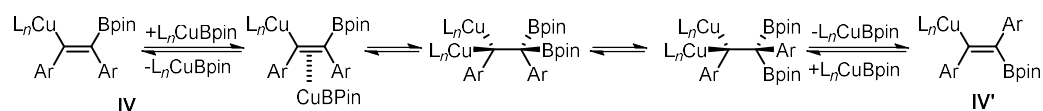
**Synthesis of (Z)-1,2-diphenylethene-1,2-*d*<sub>2</sub> (2a-*d*<sub>2</sub>).** To a mixture of **1a** (71.2 mg, 0.4 mmol, 1.0 equiv), CuBr (5.8 mg, 0.04 mmol, 0.1 equiv), <sup>t</sup>Bu<sub>3</sub>P (20 μL, 0.08 mmol, 0.2 equiv), B<sub>2</sub>pin<sub>2</sub> (111.7 mg, 0.44 mmol, 1.1 equiv), NaOMe (86.4 mg, 1.6 mmol, 4 equiv) and CD<sub>3</sub>OD (0.16 mL, 4 mmol, 10 equiv) was added 4.0 mL of DMF under argon. The reaction mixture was then placed in a preheated oil bath at 80 °C for 12 h. After the reaction was completed, the reaction was diluted with 8 mL of water then extracted with ethyl acetate (3 x 8 mL). The combined organic extracts were dried over anhydrous MgSO<sub>4</sub>, filtered, and then concentrated under reduced pressure and the residue was further purified by silica gel column chromatography (PE) to give the target product **2a-*d*<sub>2</sub>** (60.5 mg, 83% yield, 90% D by <sup>1</sup>H NMR). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.25 – 7.10 (m, 10H), 6.52 (s, 0.2H)



**Alcoholysis of (Z)-2-(1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3).** To a mixture of **3** (63.6 mg, 0.2 mmol, 1.0 equiv), CuBr (2.9 mg, 0.02 mmol, 0.1 equiv), <sup>t</sup>Bu<sub>3</sub>P (10 μL, 0.04 mmol, 0.2 equiv), NaOH (32.0 mg, 0.8 mmol, 4.0 equiv) and MeOH (40 μL, 2.0 mmol, 5.0 equiv) was added 4.0 mL of DMF under argon. The reaction mixture was then placed in a preheated oil bath at 80 °C for 12 h. After the reaction was completed, the reaction was monitored by GC analysis.

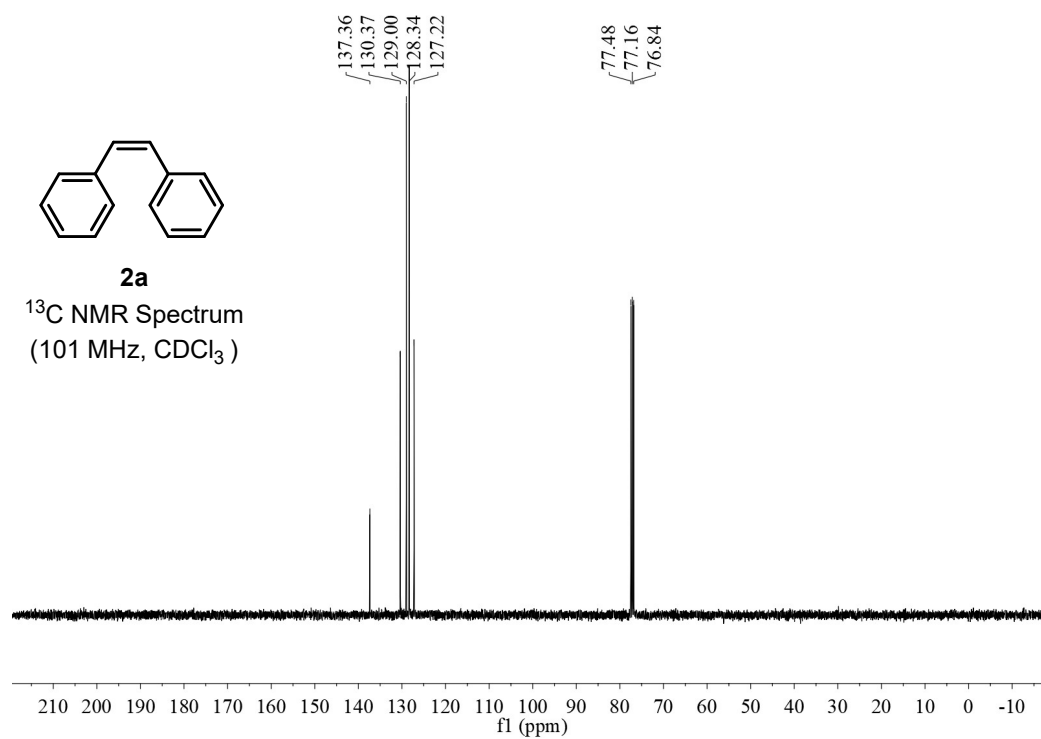
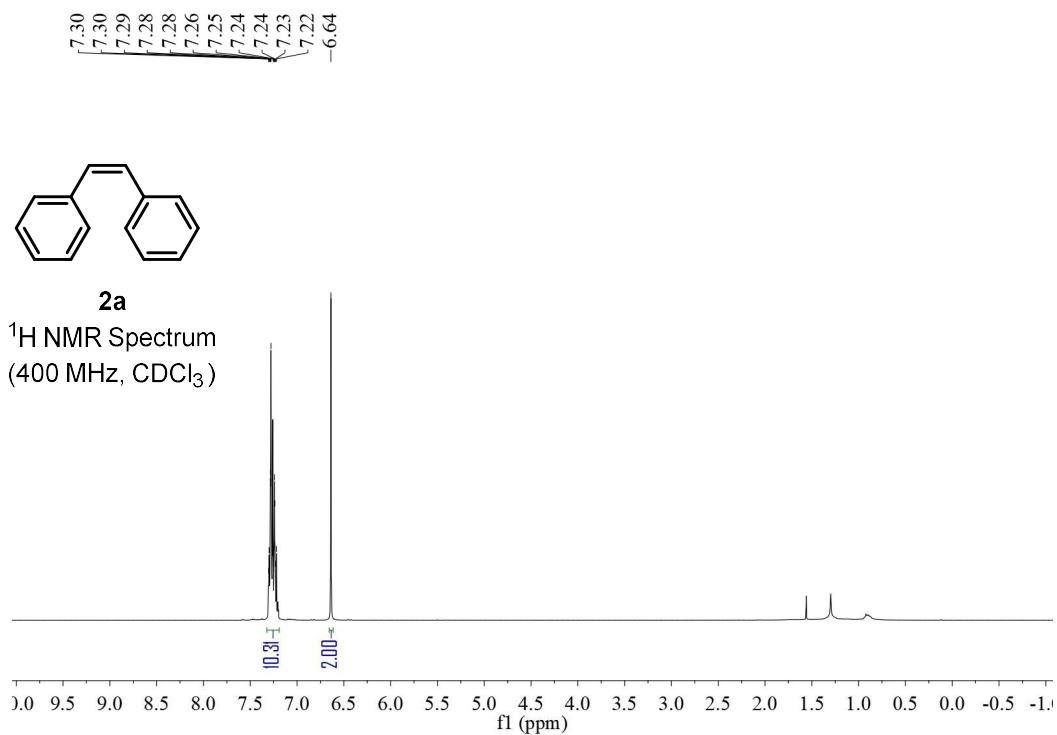
## 2. Possible explanation for reduced stereoselectivity in **2c**, **2d**, **2f**, and **2g** cases.

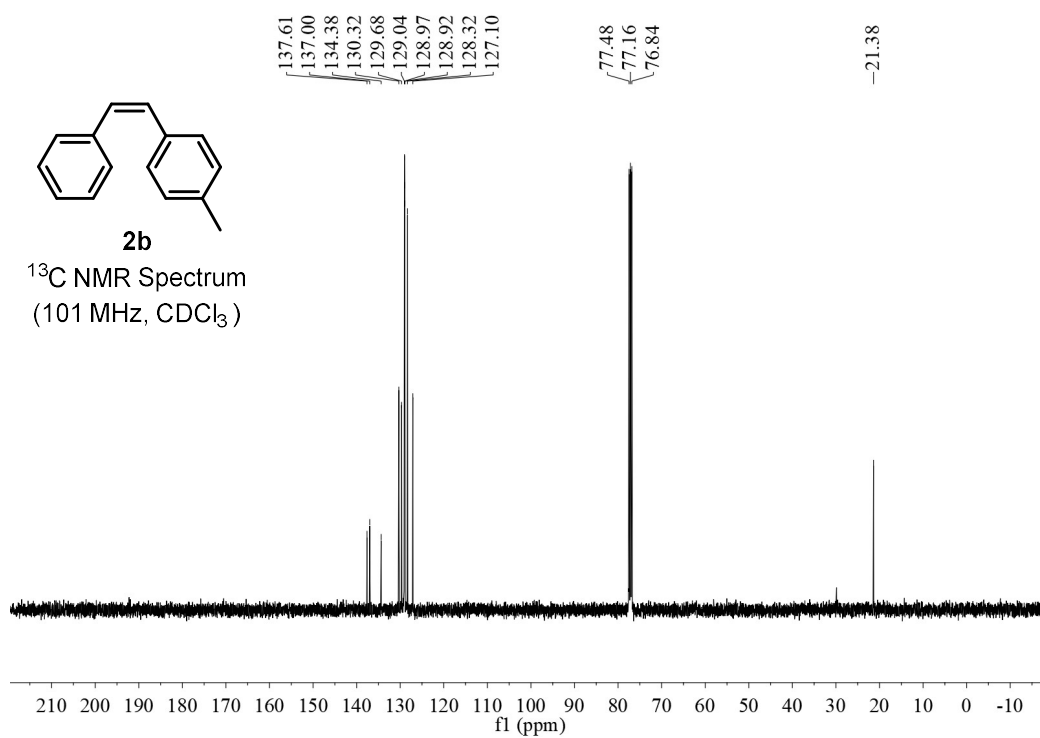
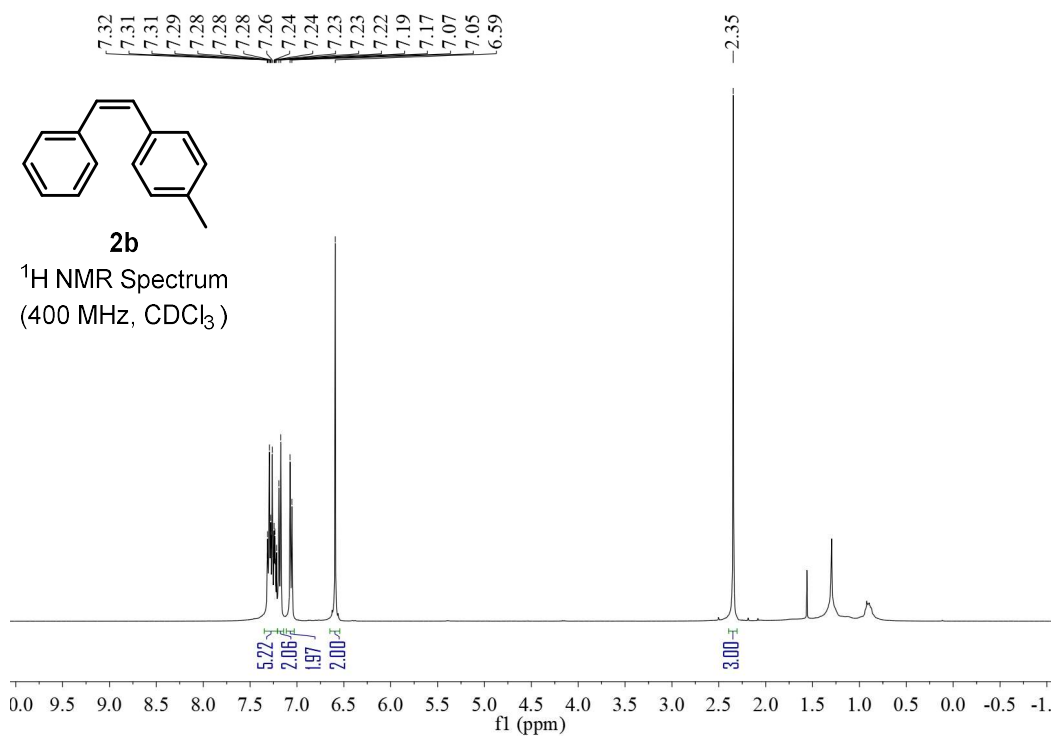
The reduced stereoselectivity of **2c** and **2d** might be due to the presence of electron donating group at *para*-position of arenes. These electron donating group might promote the isomerization through a reversible addition-elimination process as shown below. In the presence of electron donating group, the *in situ* generated olefin would be more labile to complex with another molecule of copper-boron species. Then addition of copper-boron species on double bond would lead to a saturated product, which could afford an isomerization product after elimination reaction. For the reduced stereoselectivity of **2f** and **2g**, we still have no convincing explanation. Actually, the stereoselectivity is the result of combination effects of steric hindrance and electronic effects of functional groups, making it difficult to predict which factor predominates.

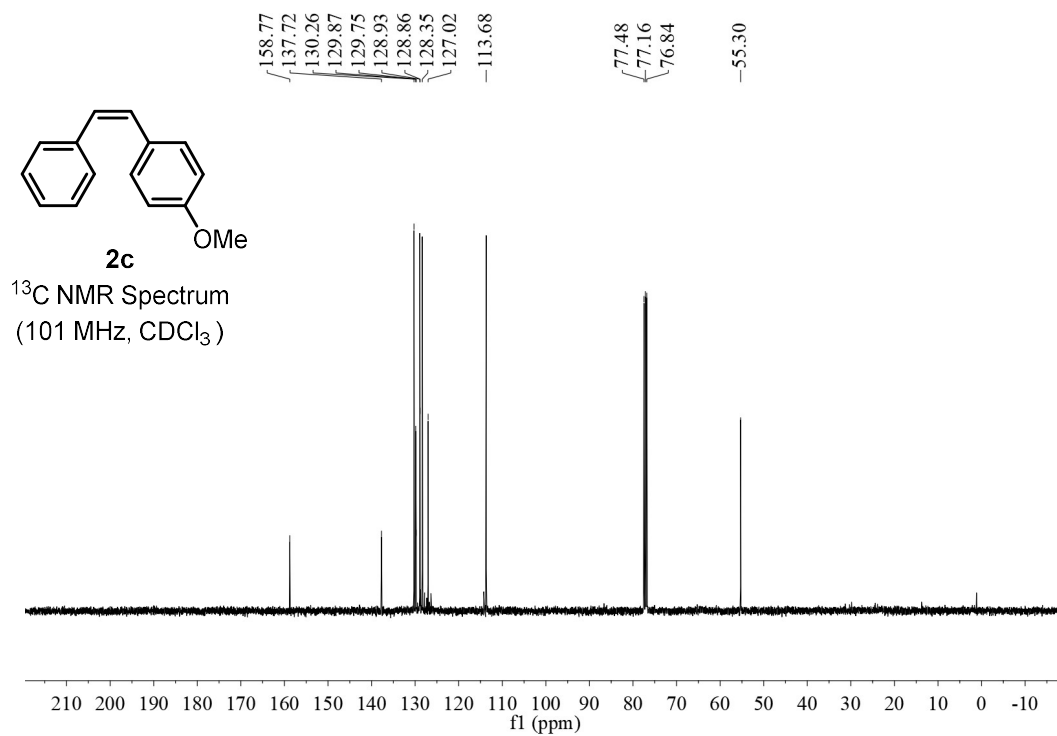
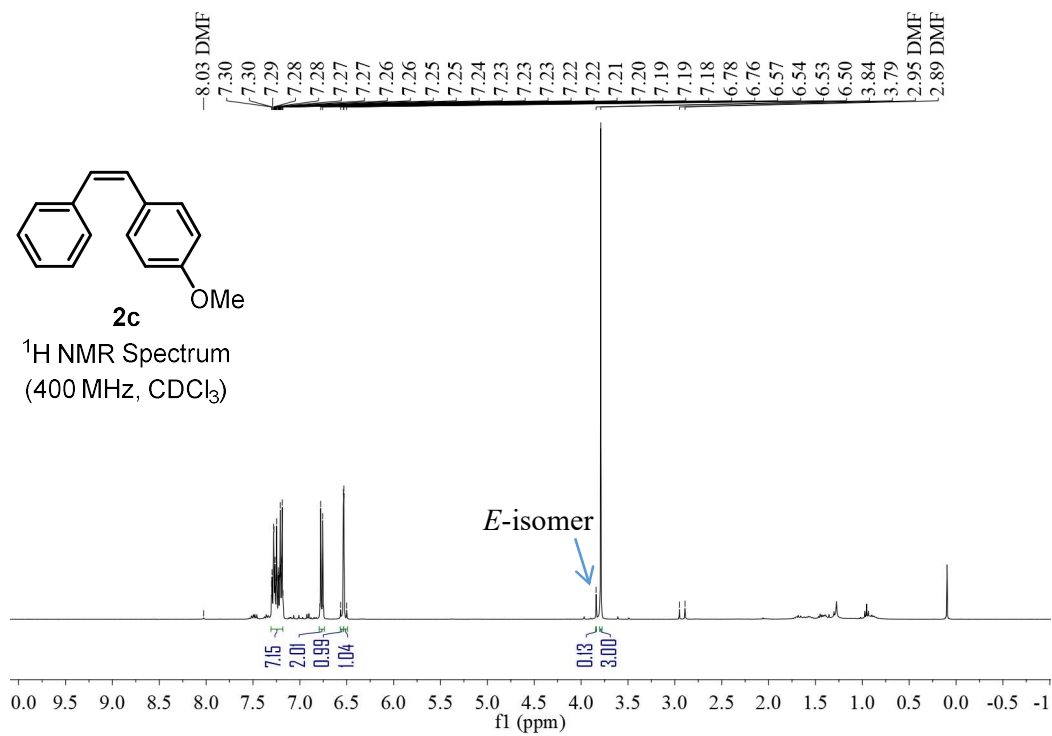


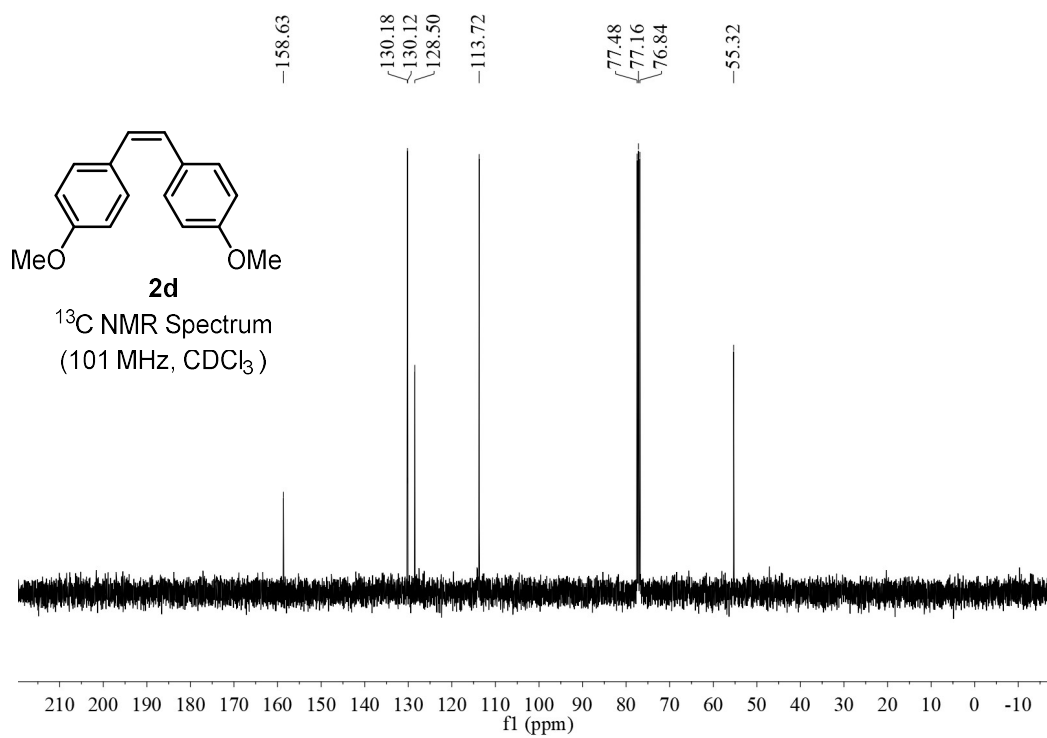
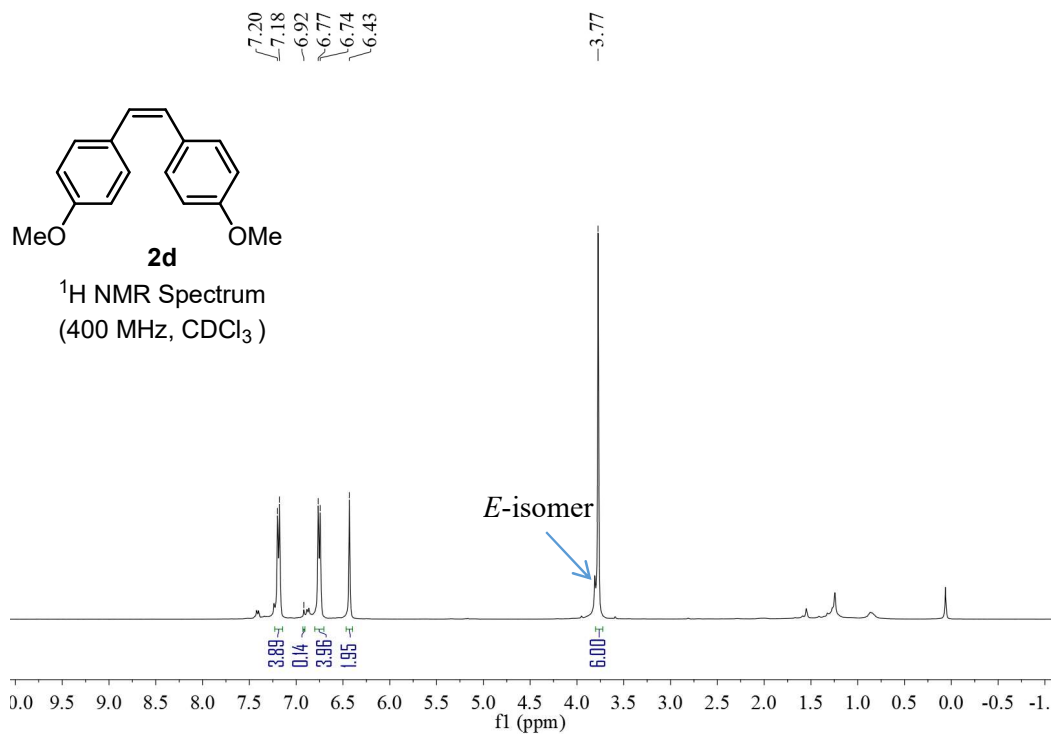
### 3. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra for all compounds

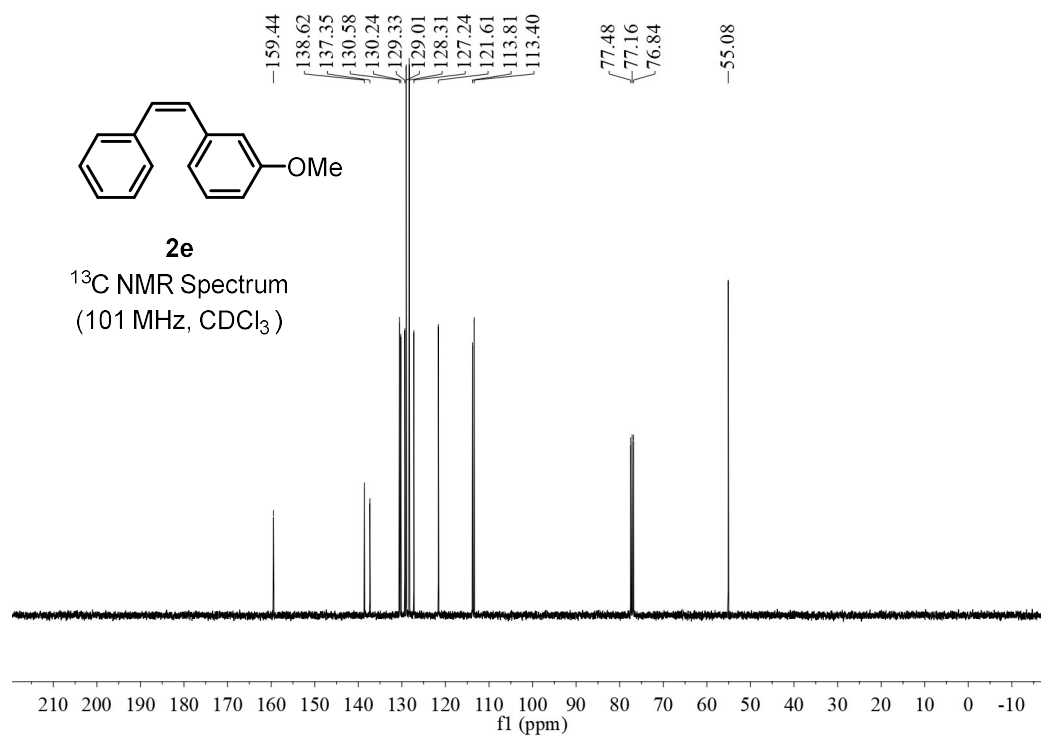
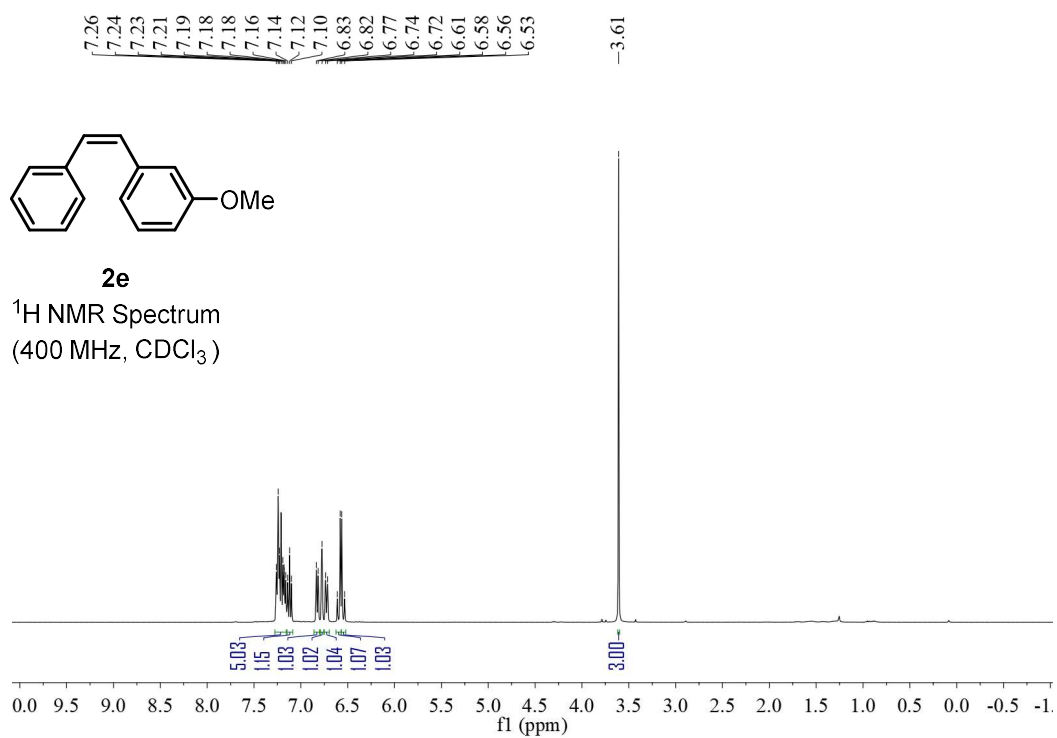
(a)  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{19}\text{F}$  NMR and HRMS spectra of 2a-2w.



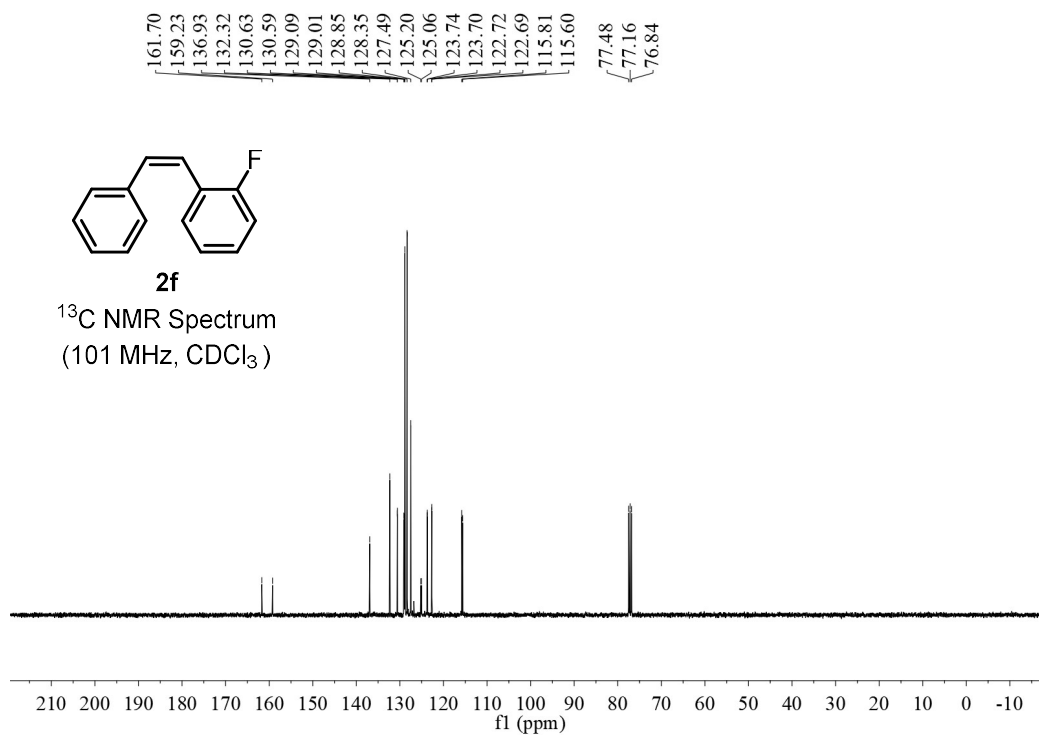
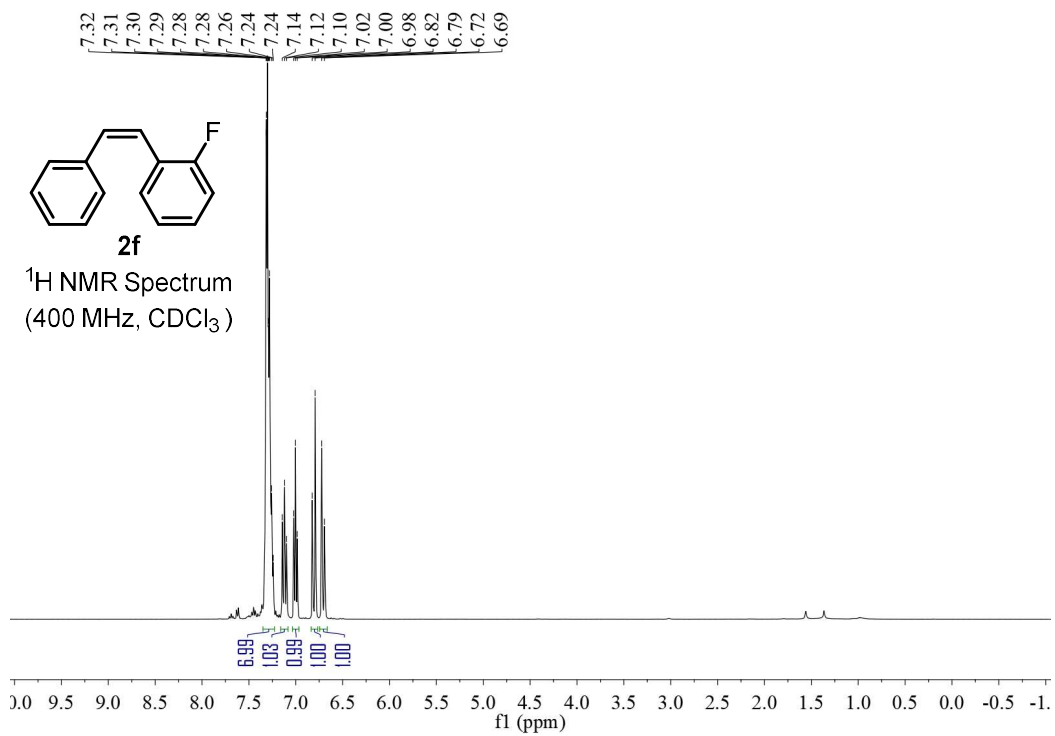


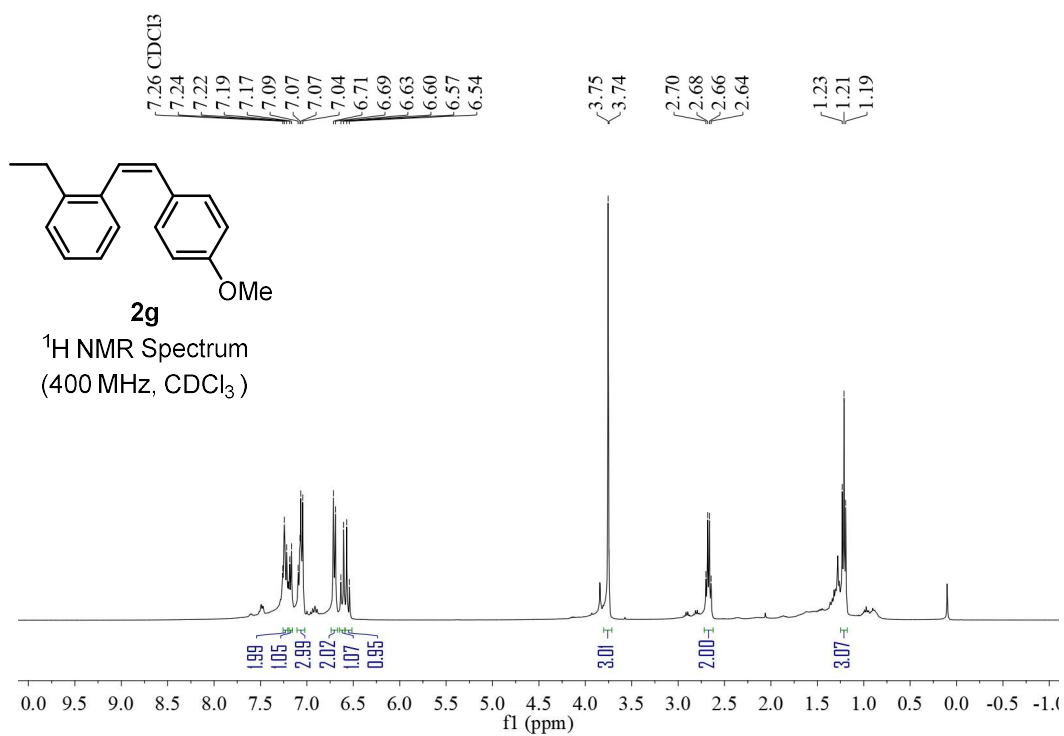
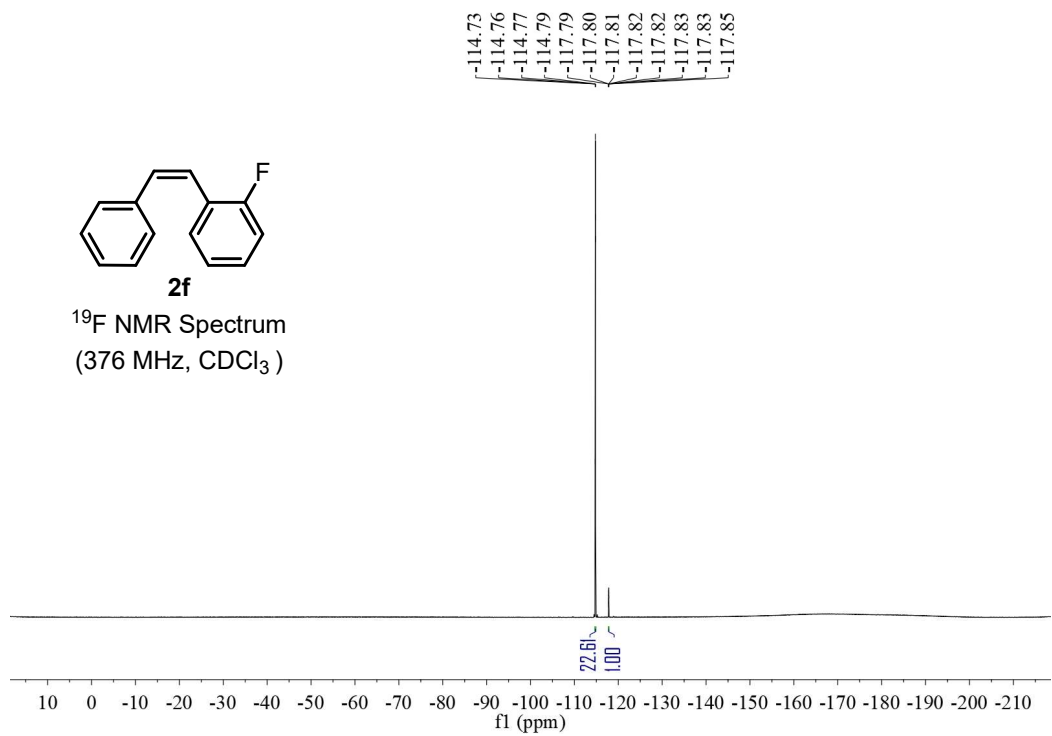


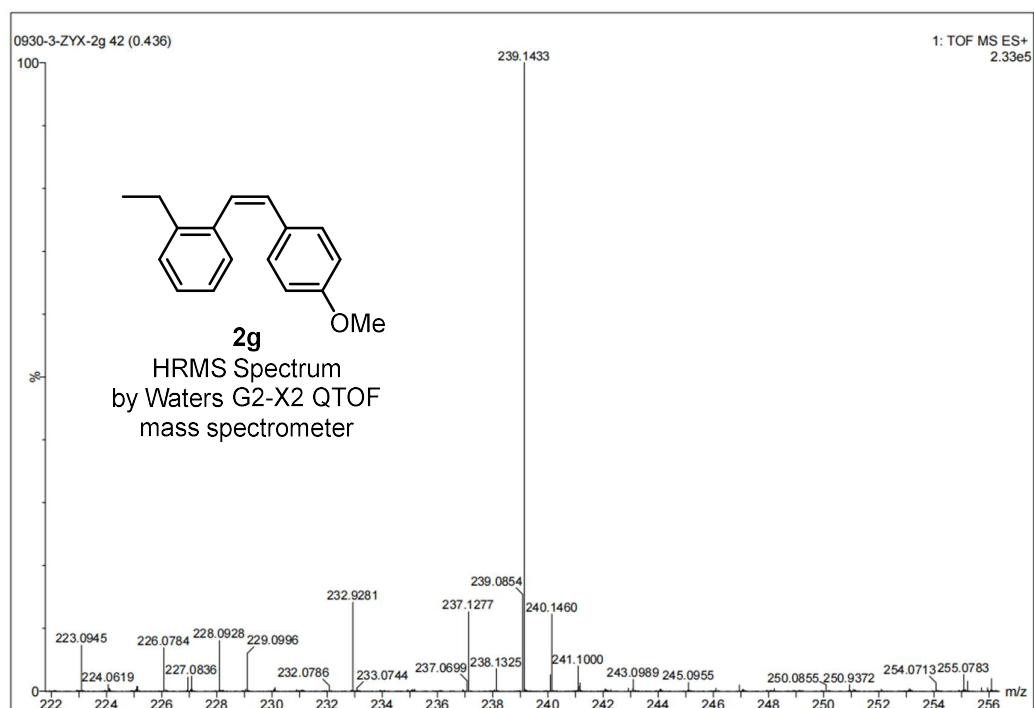
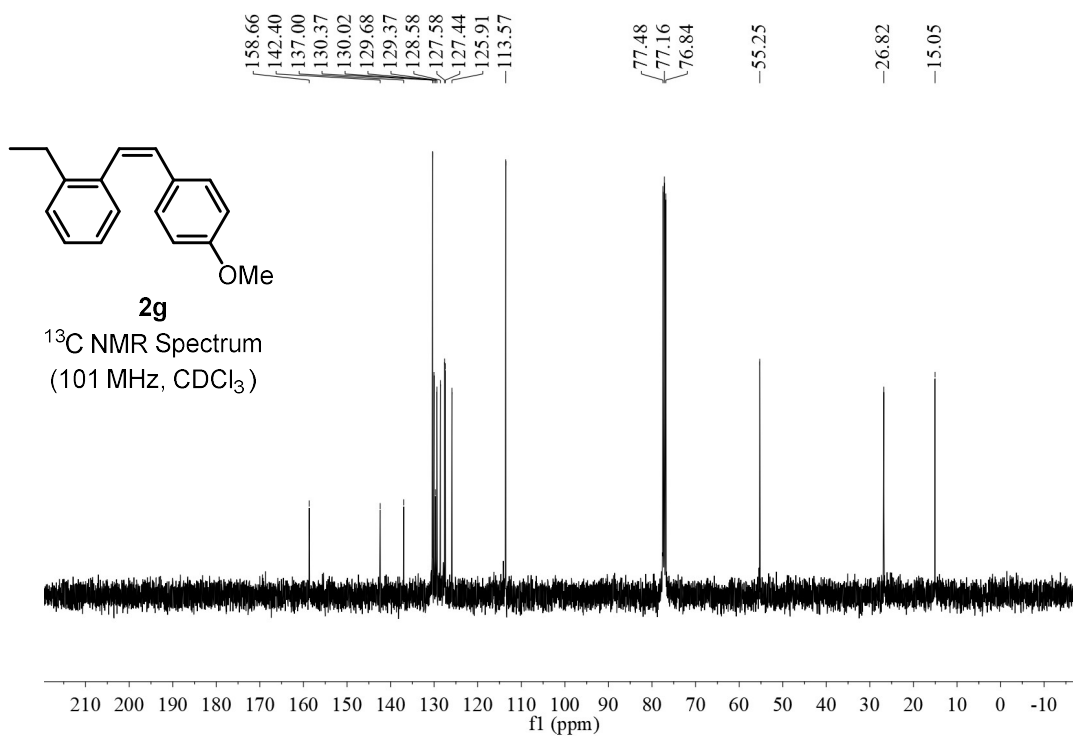


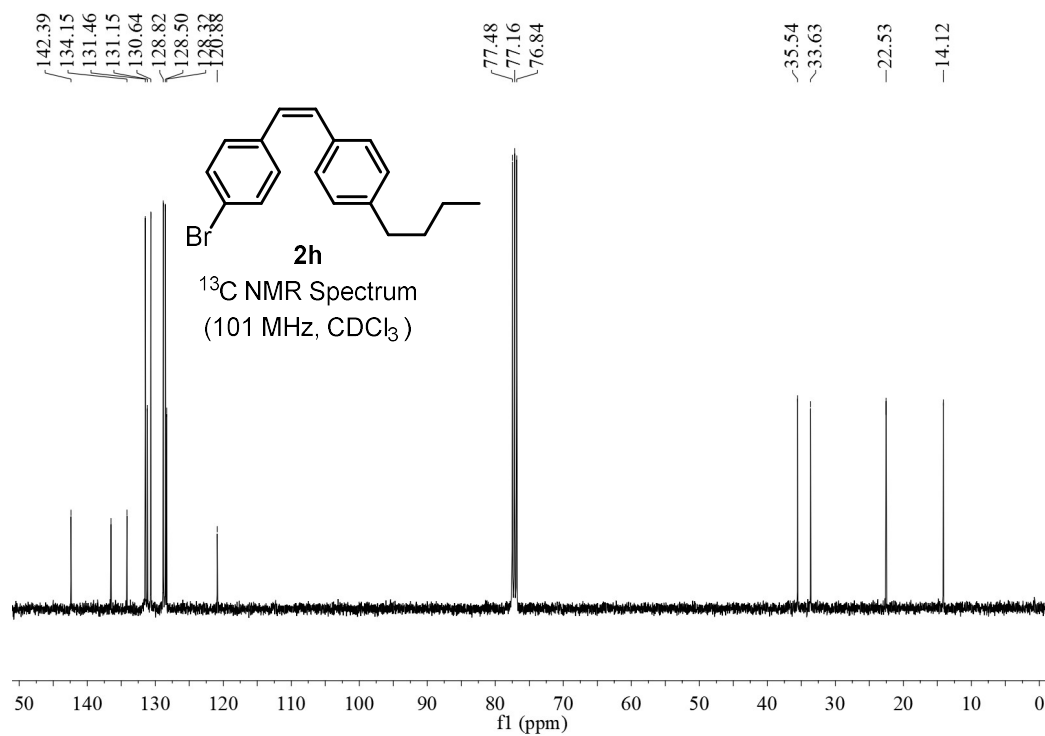
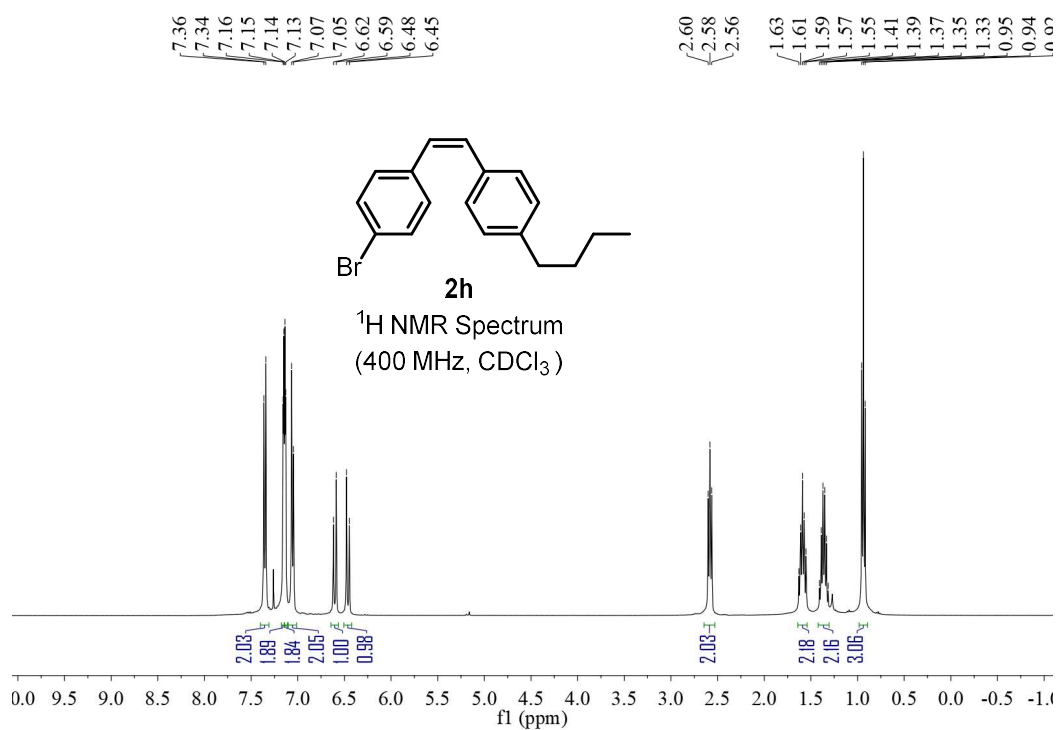


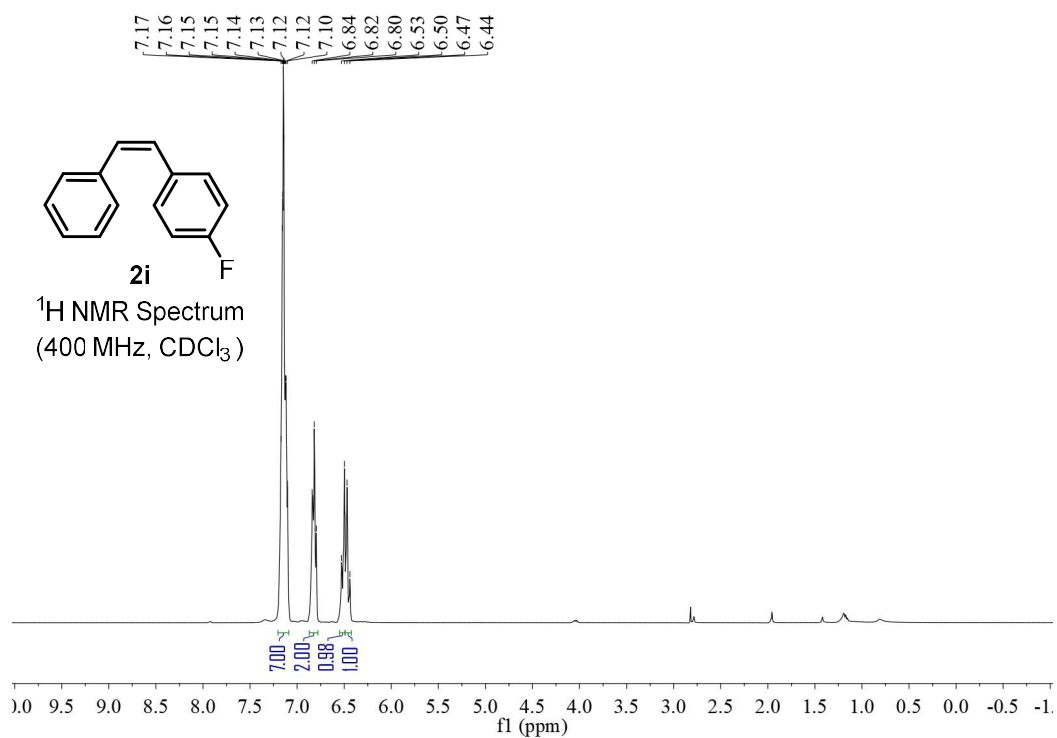
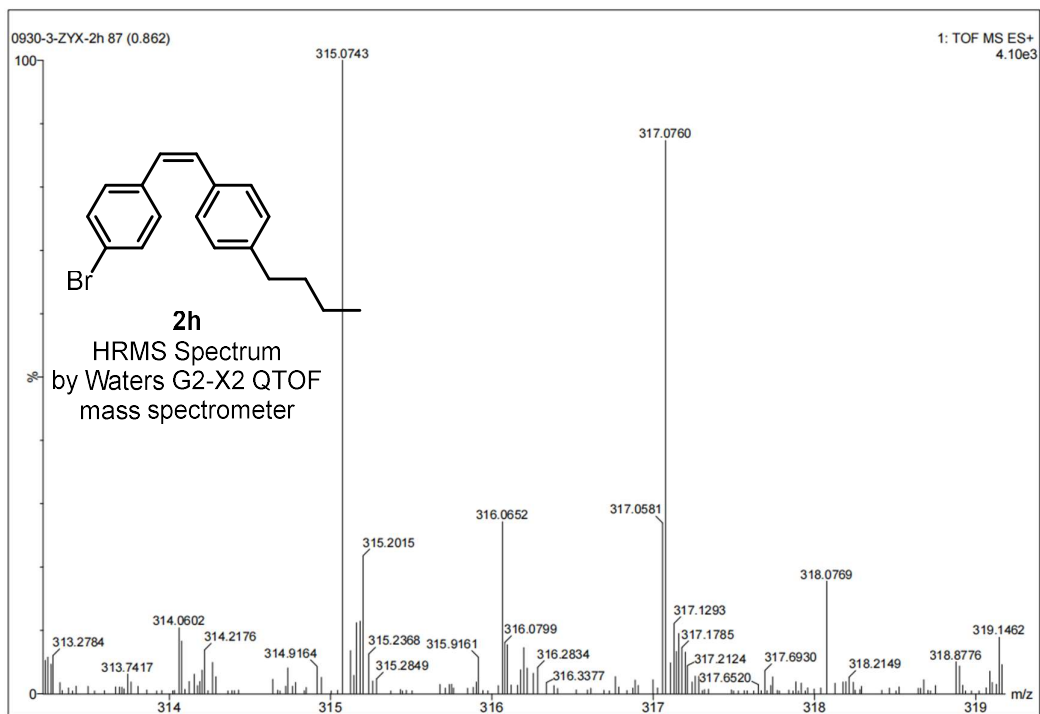


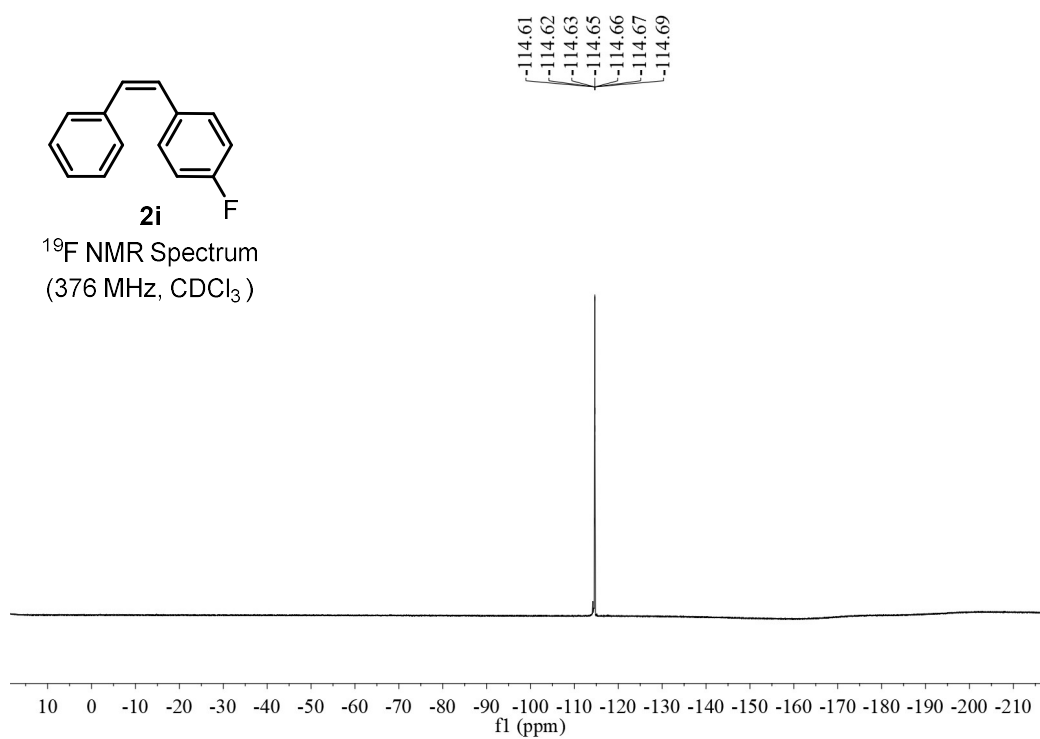
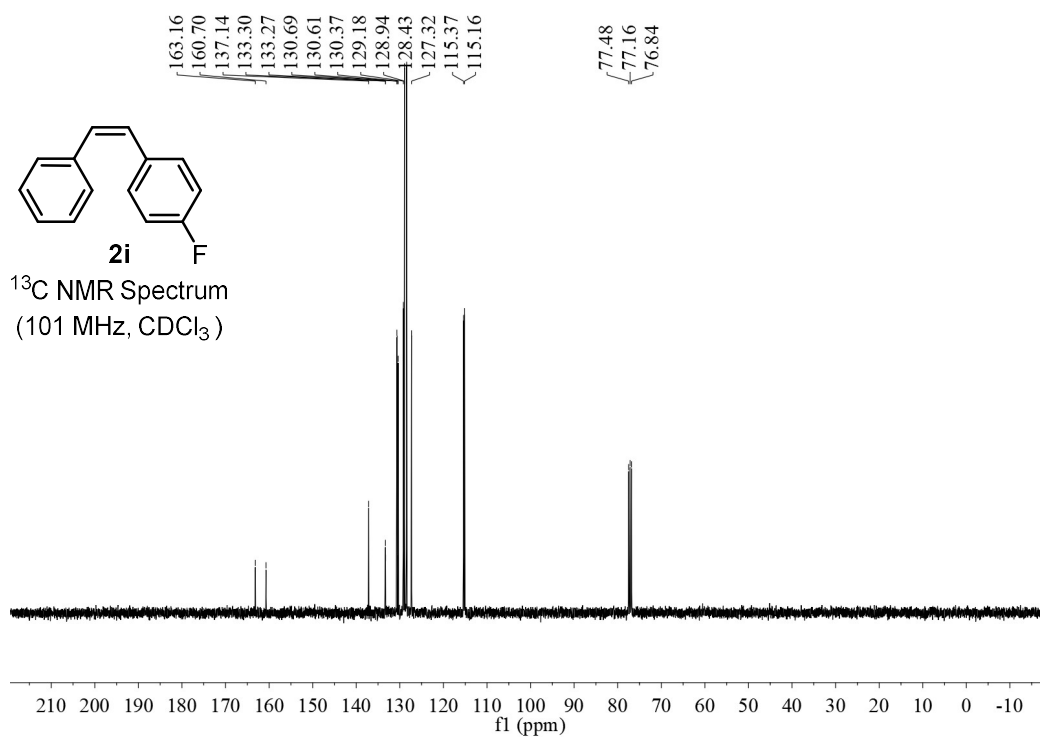


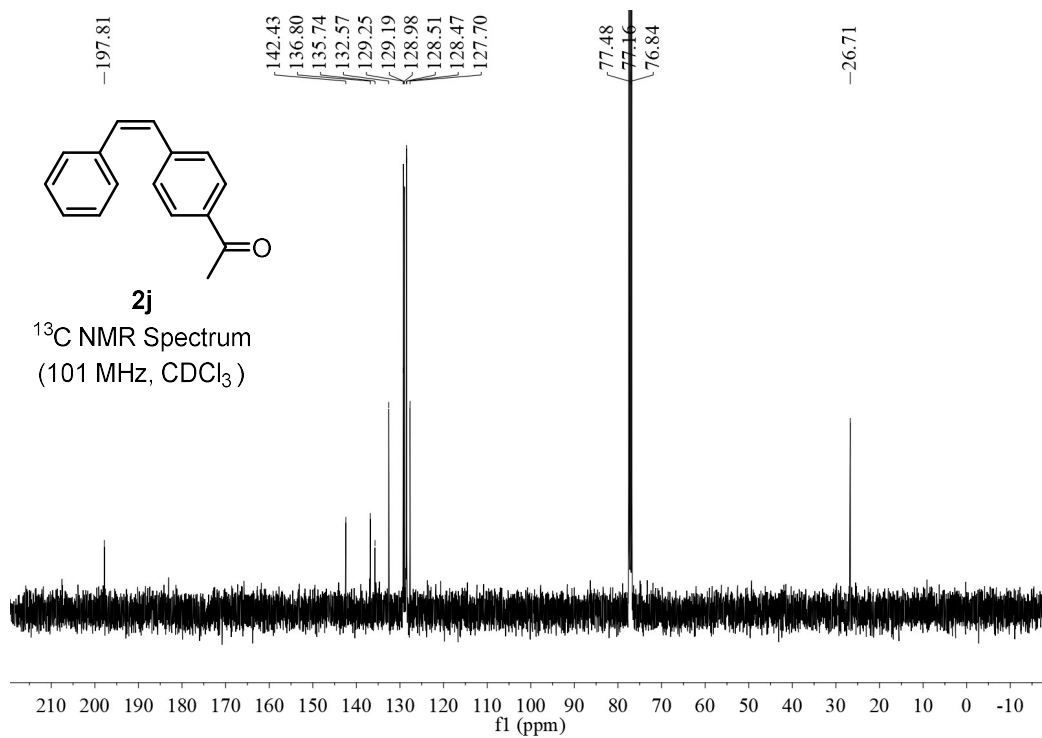
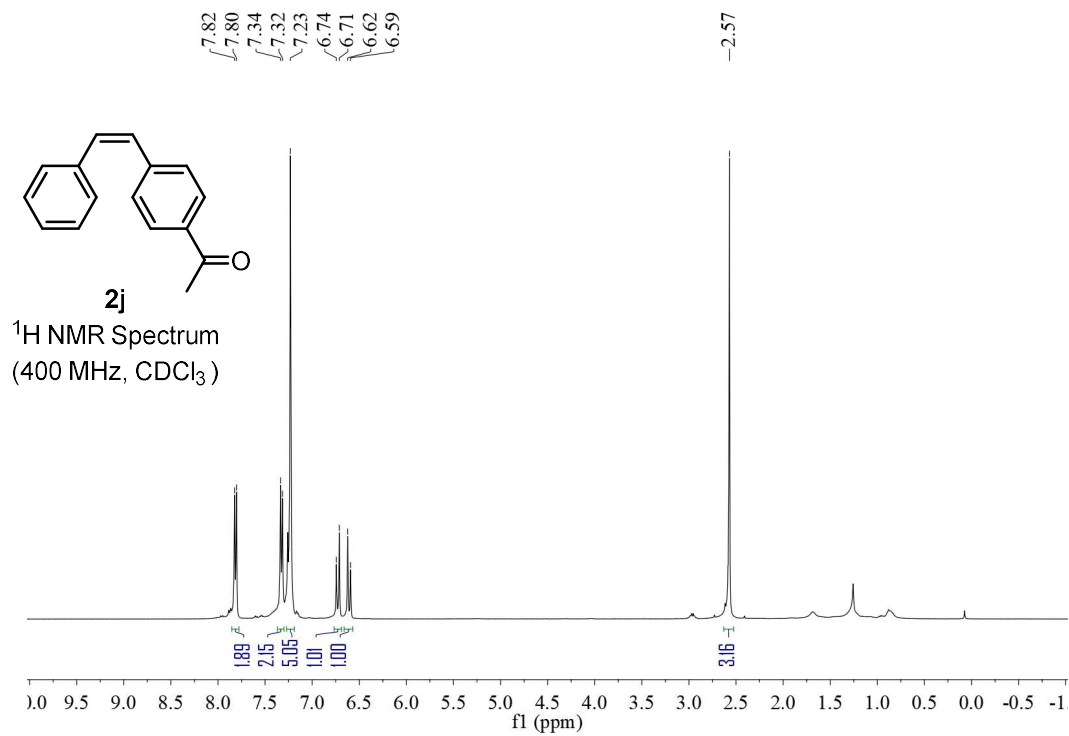


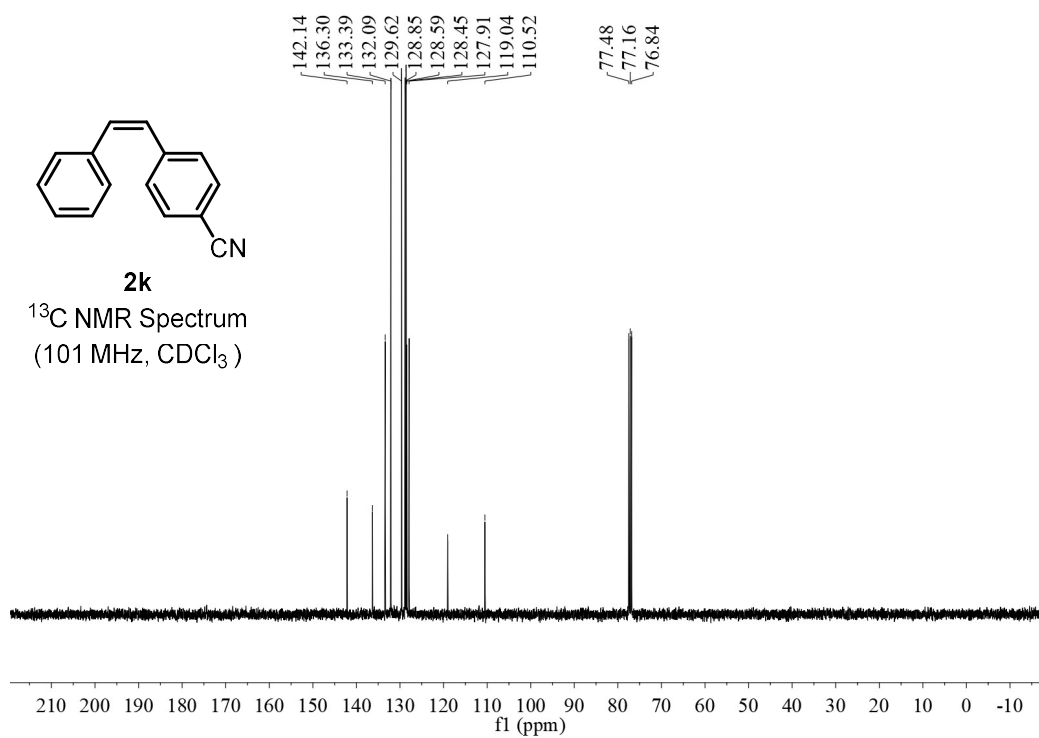
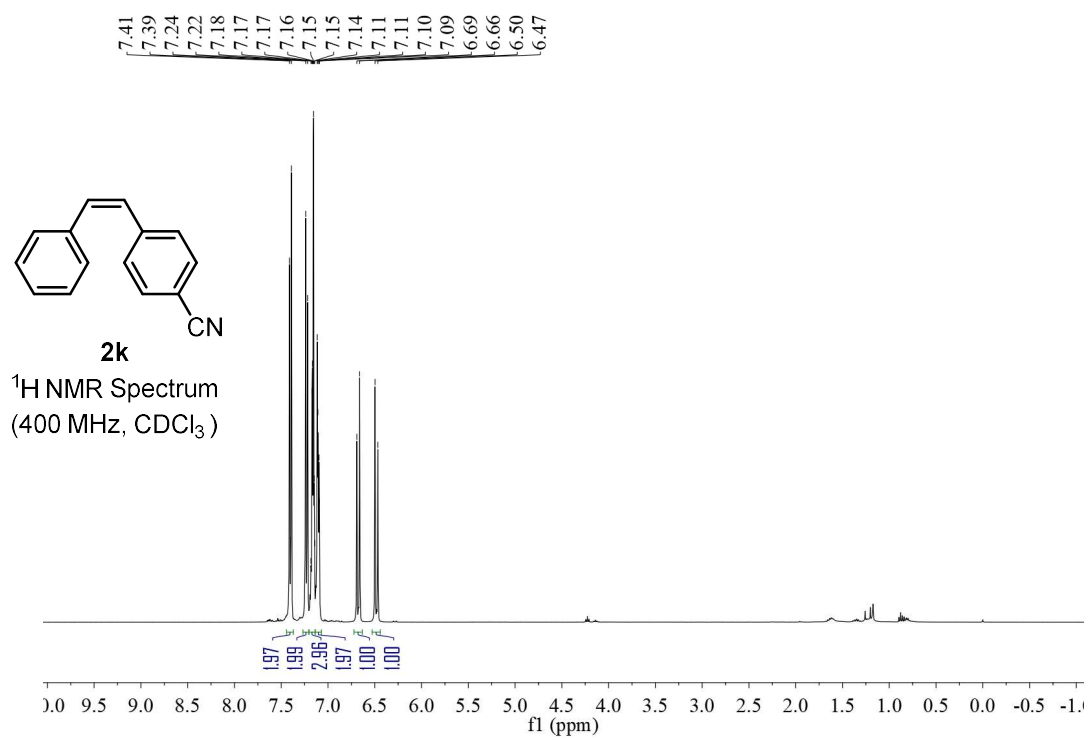




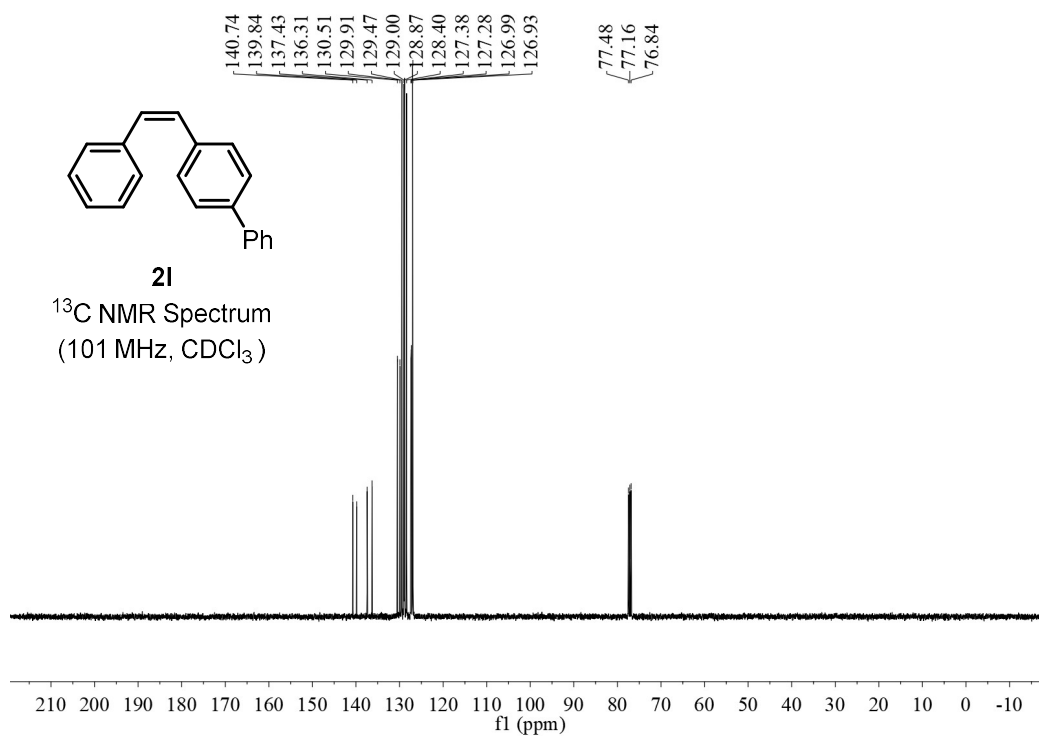
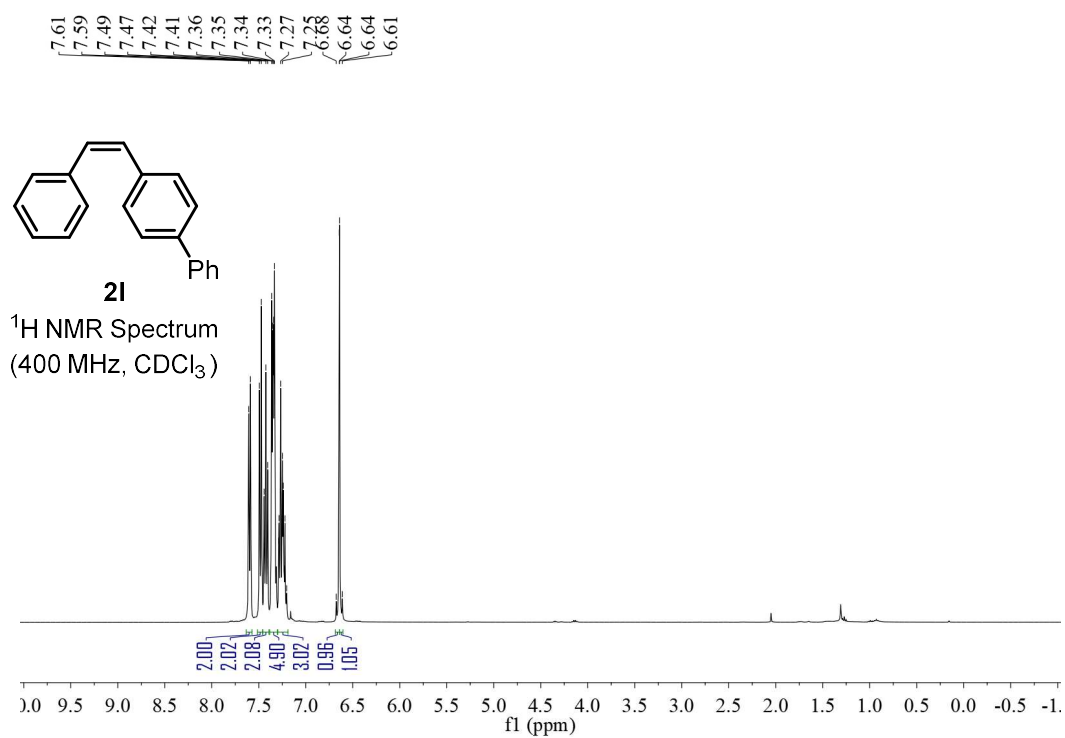


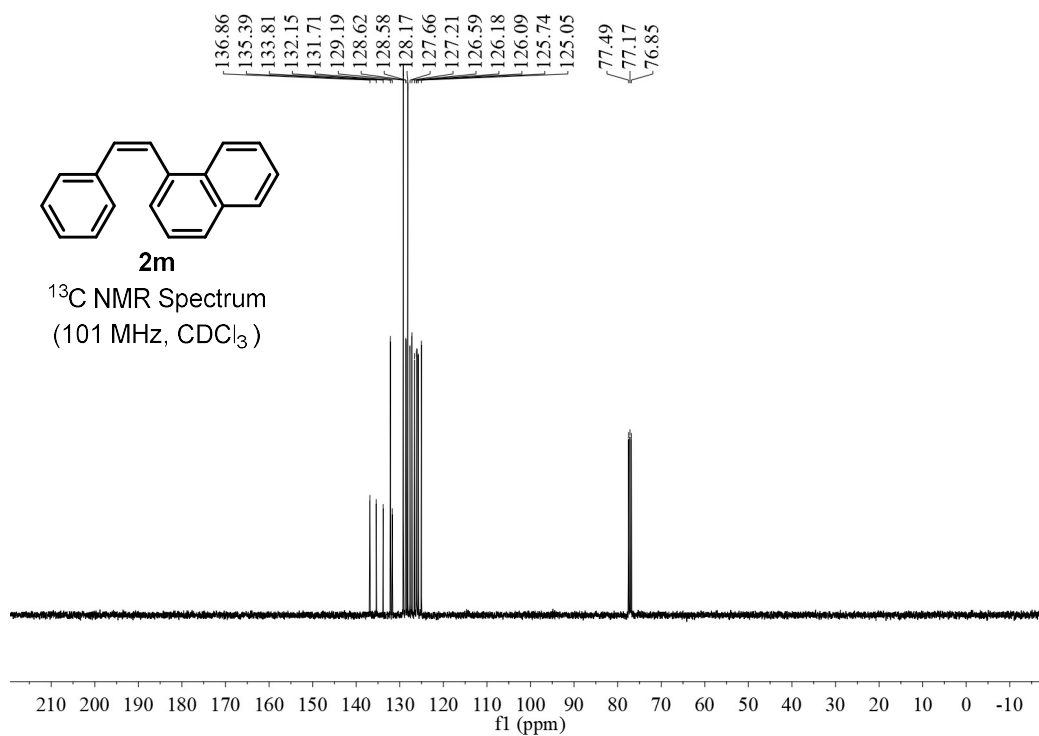
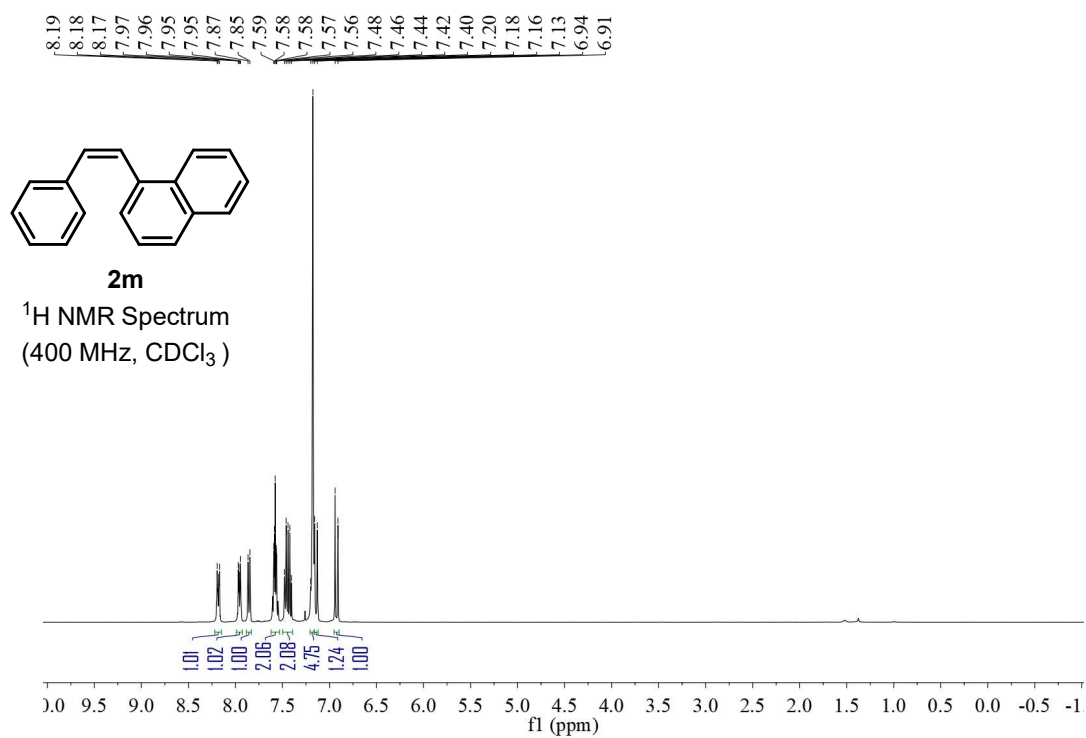


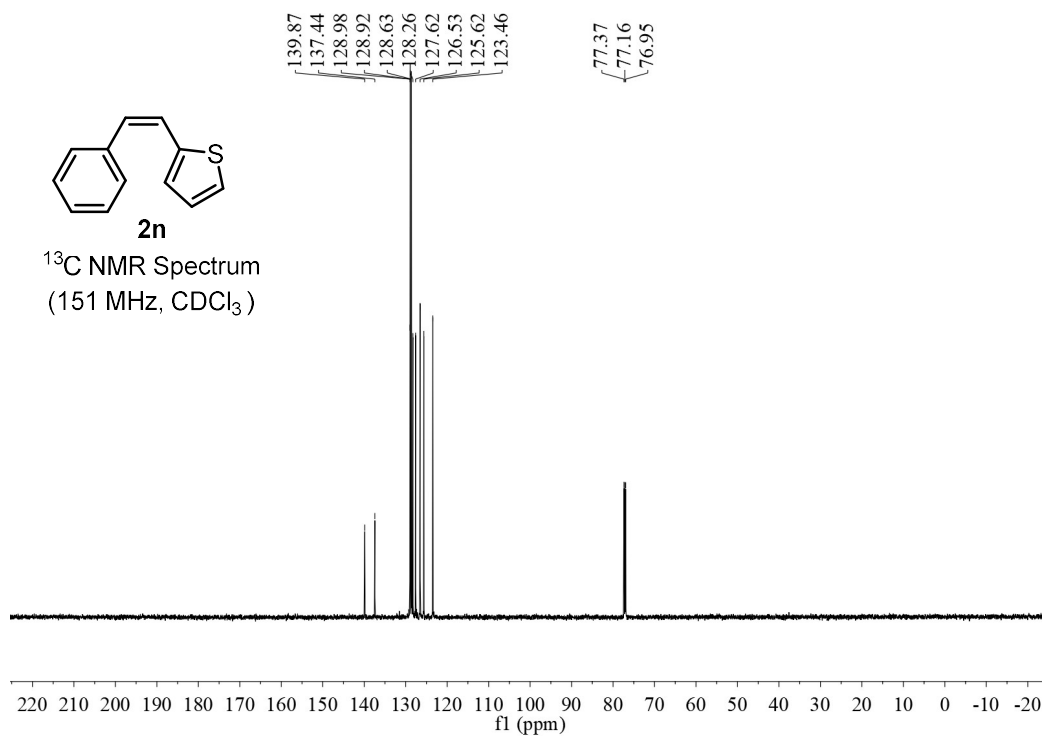
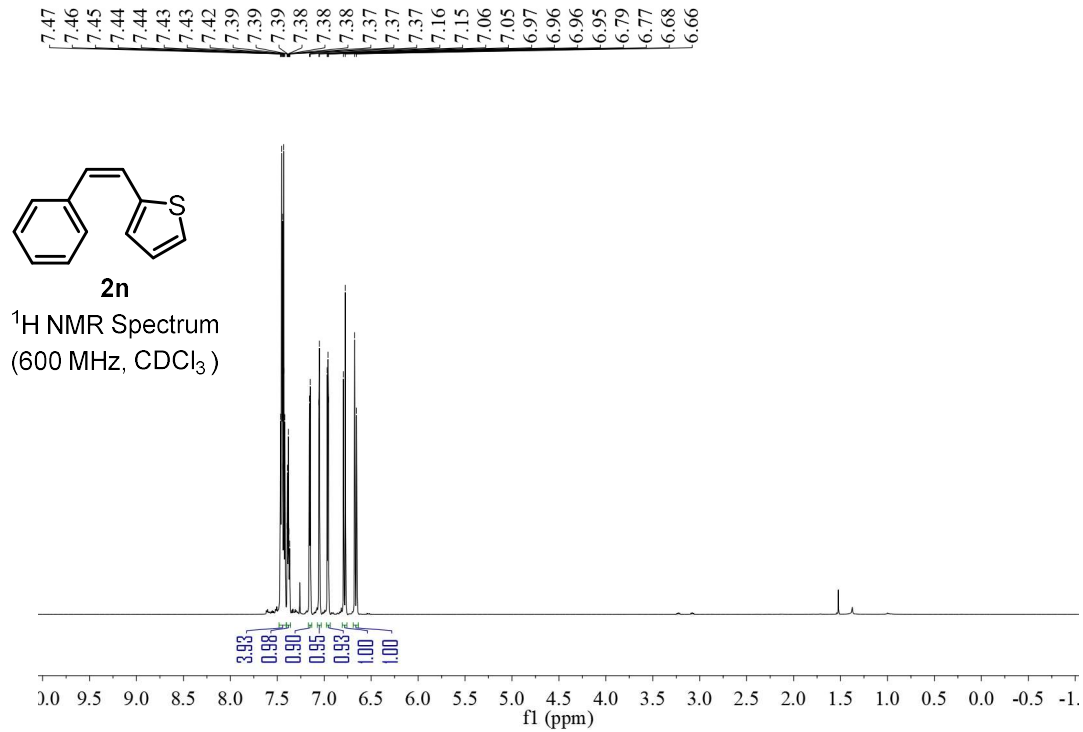


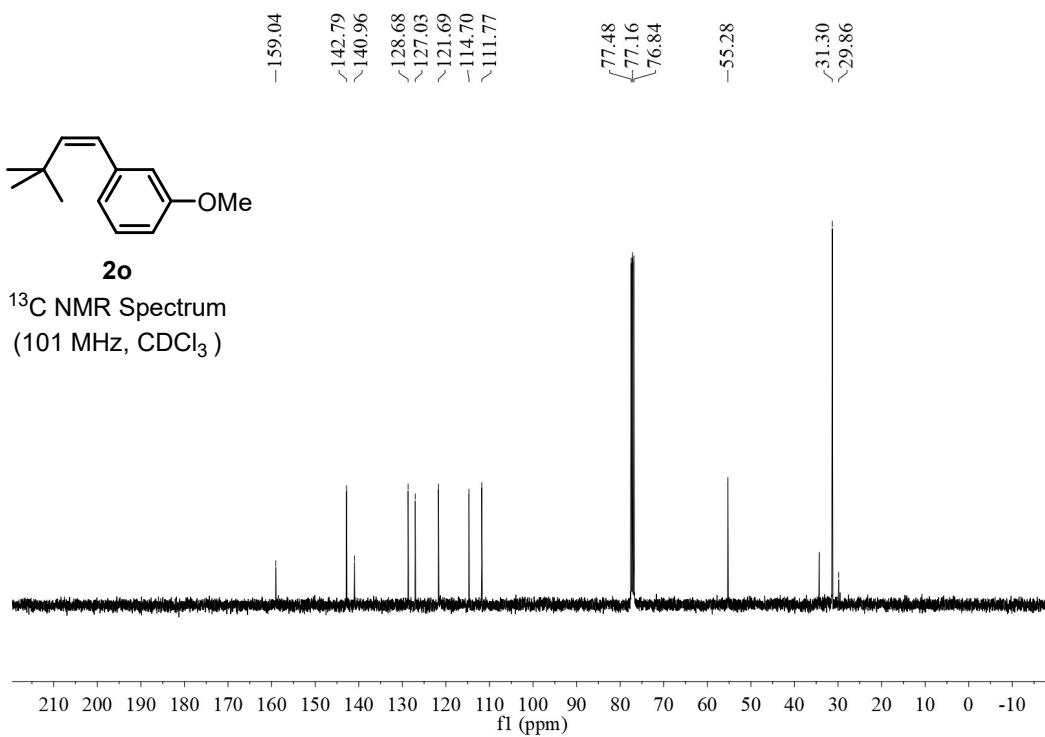
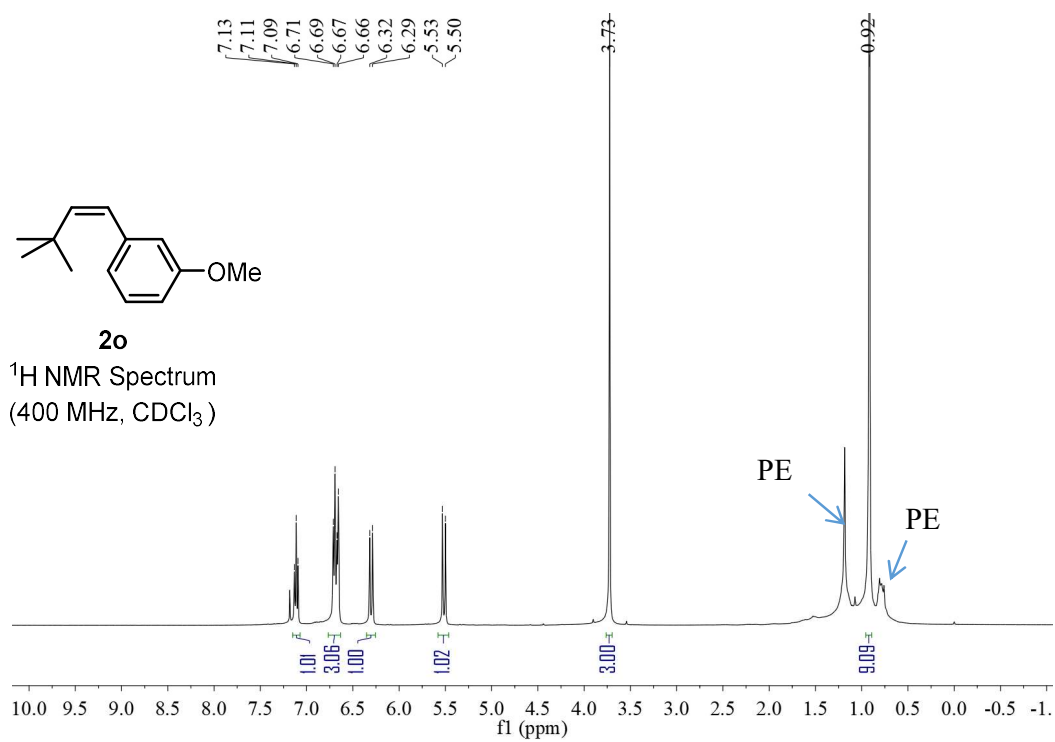


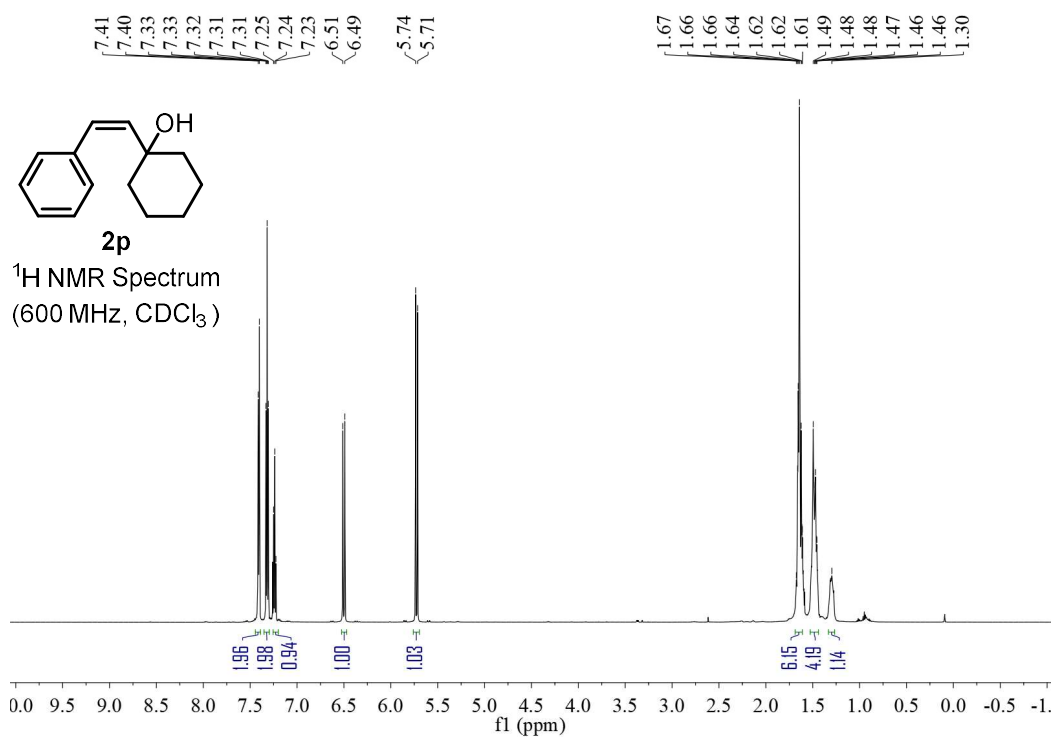
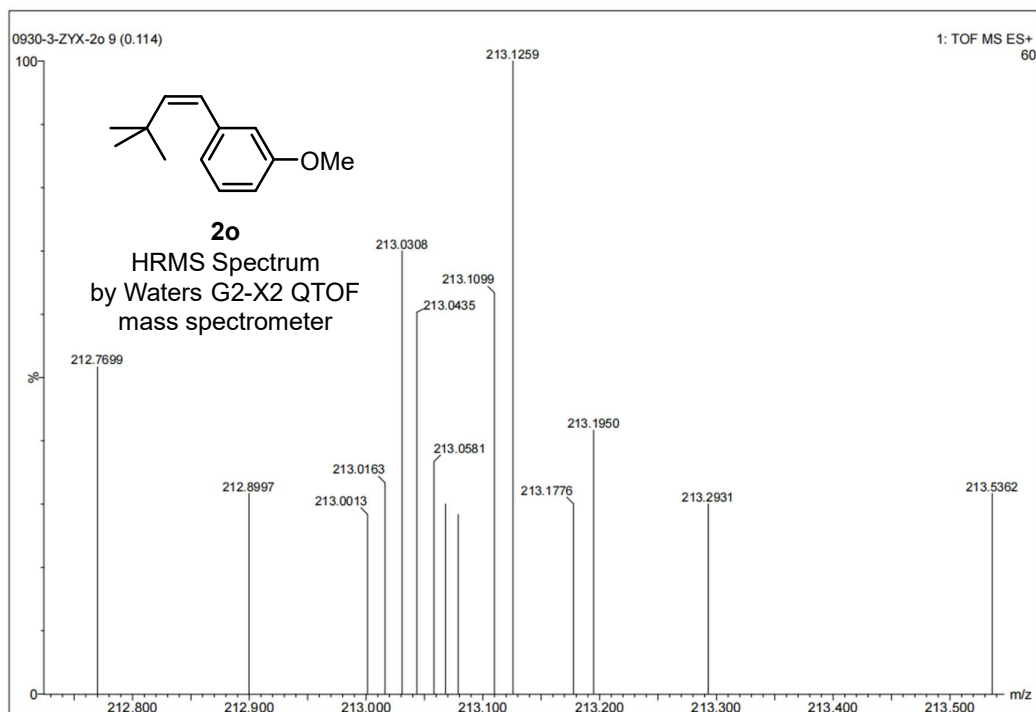


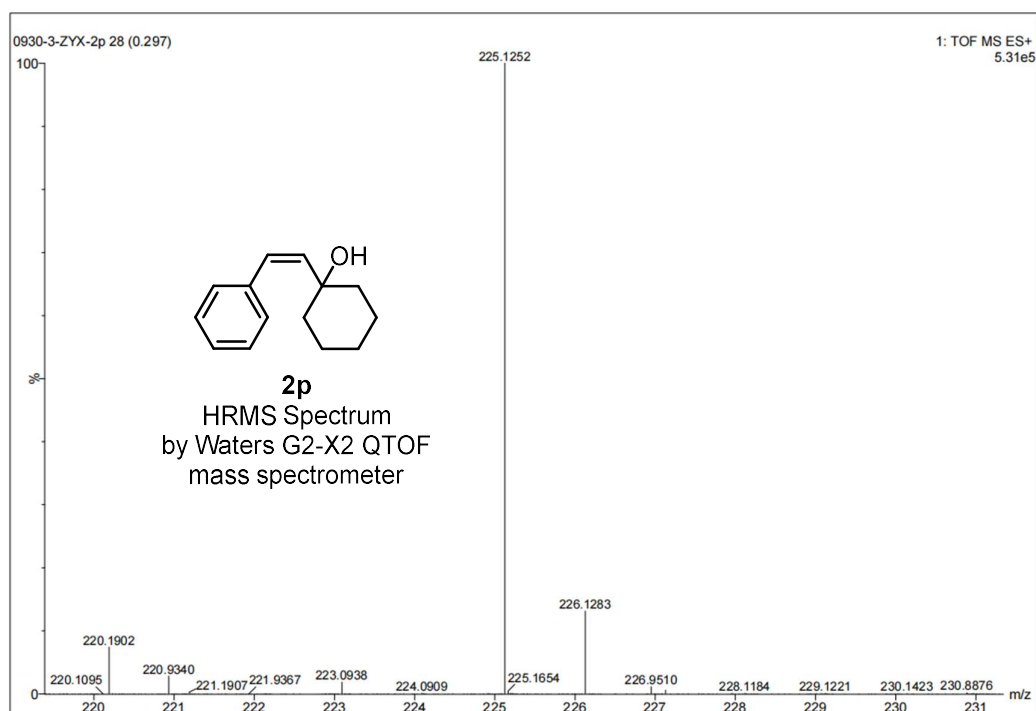
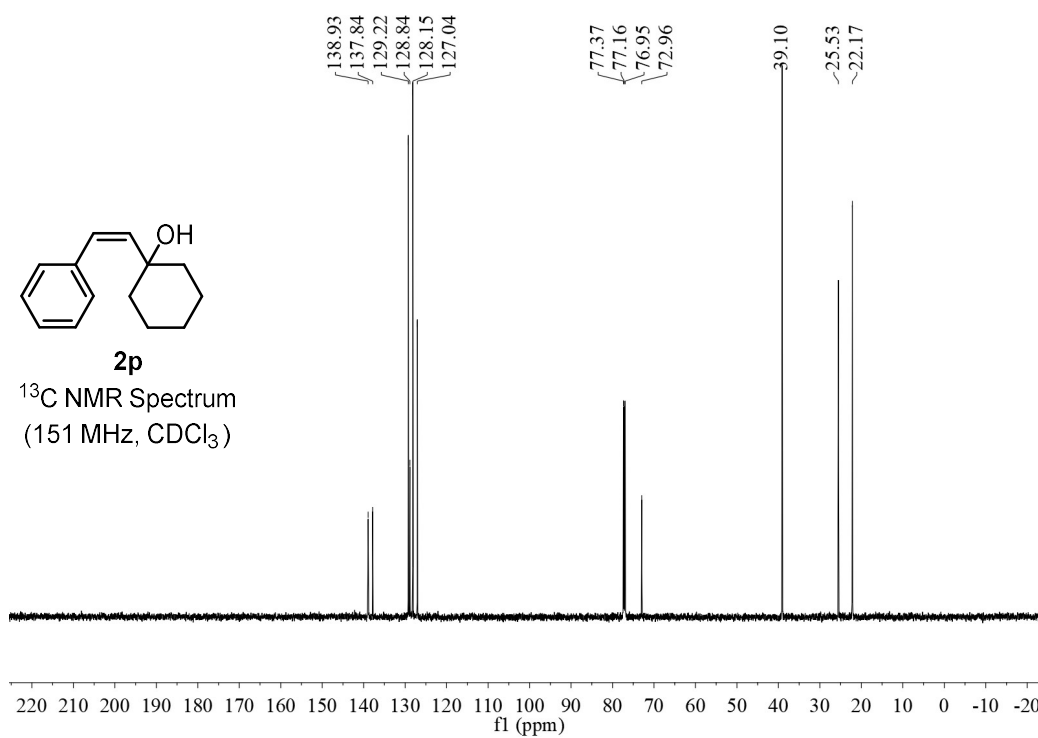


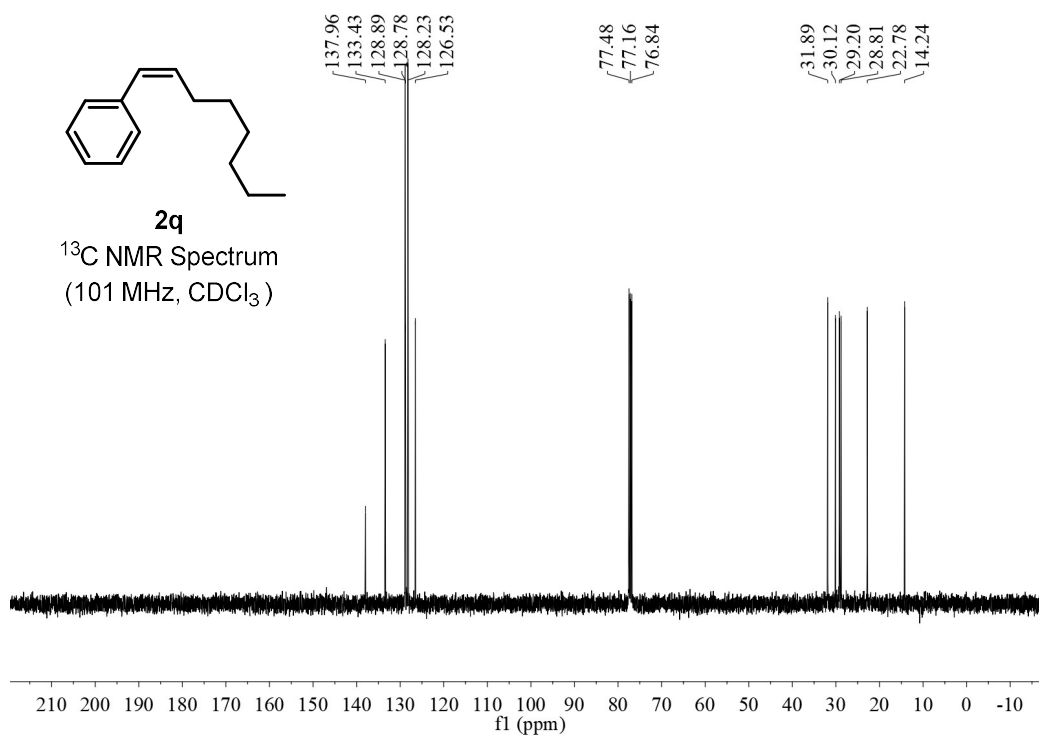
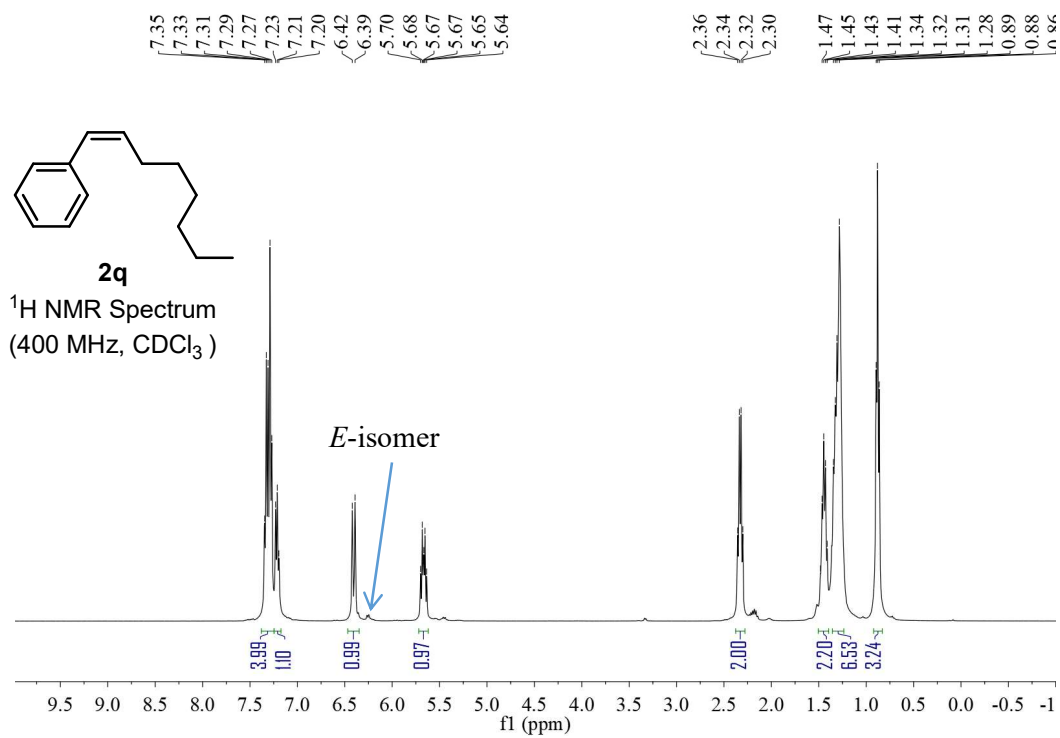


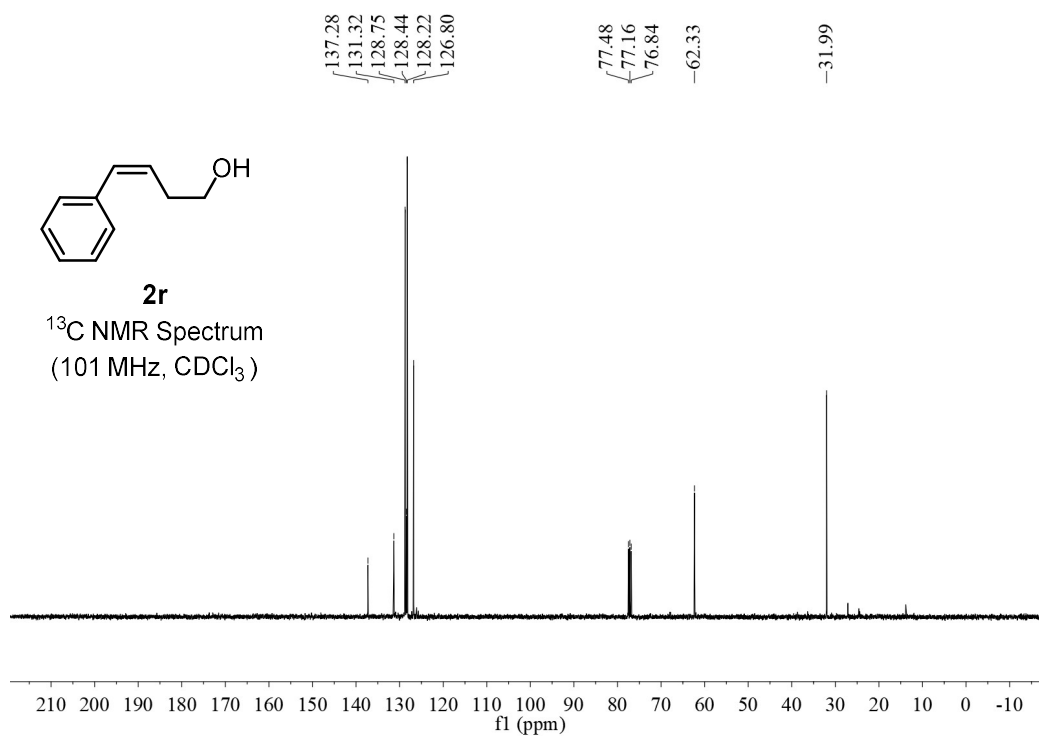
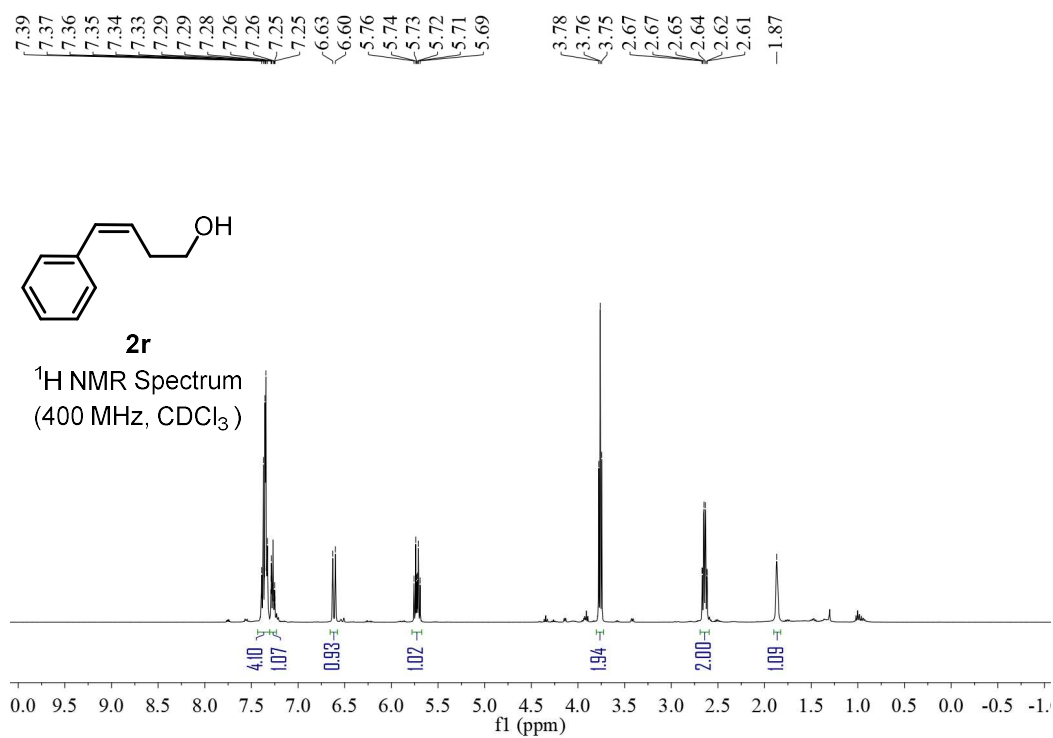




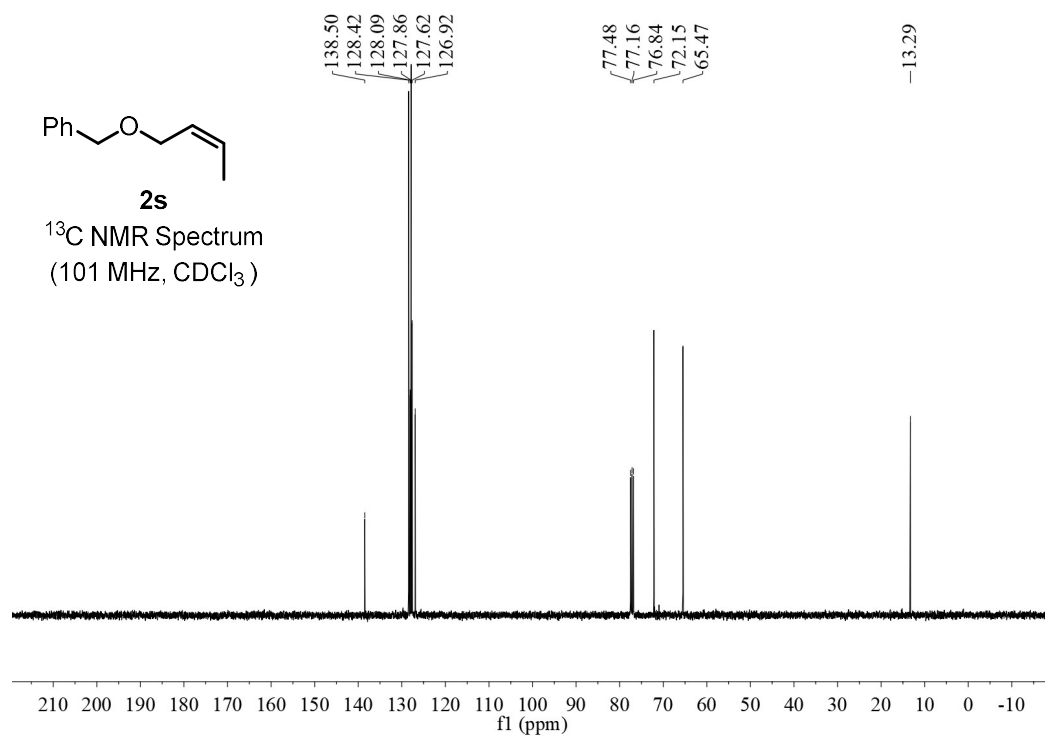
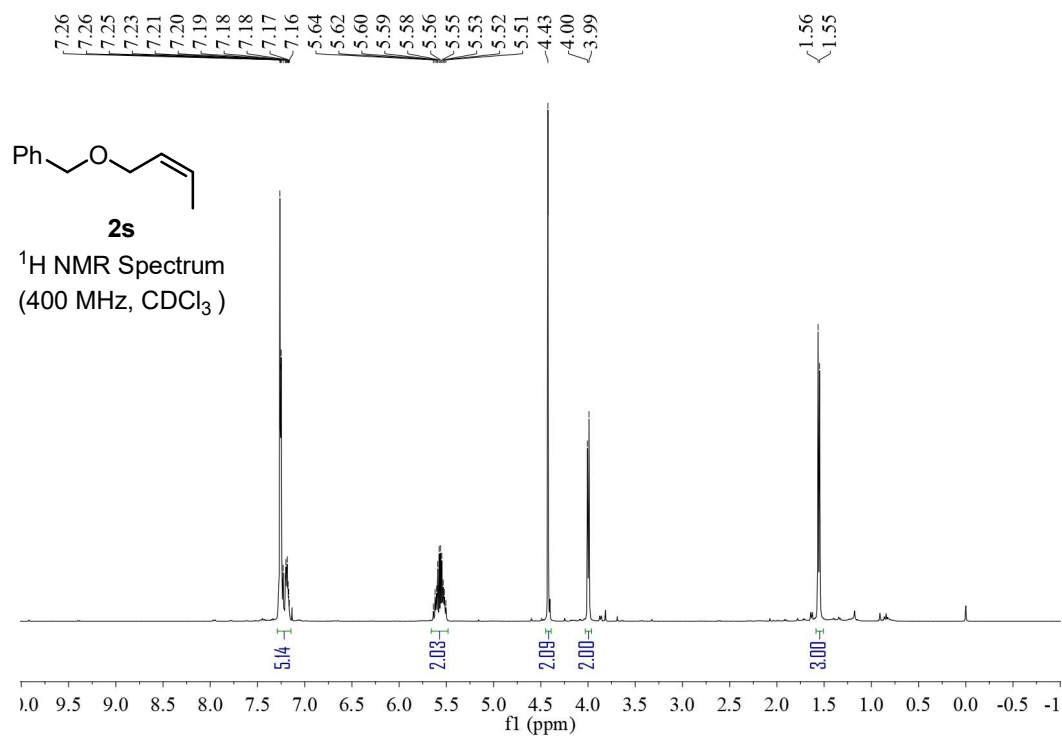


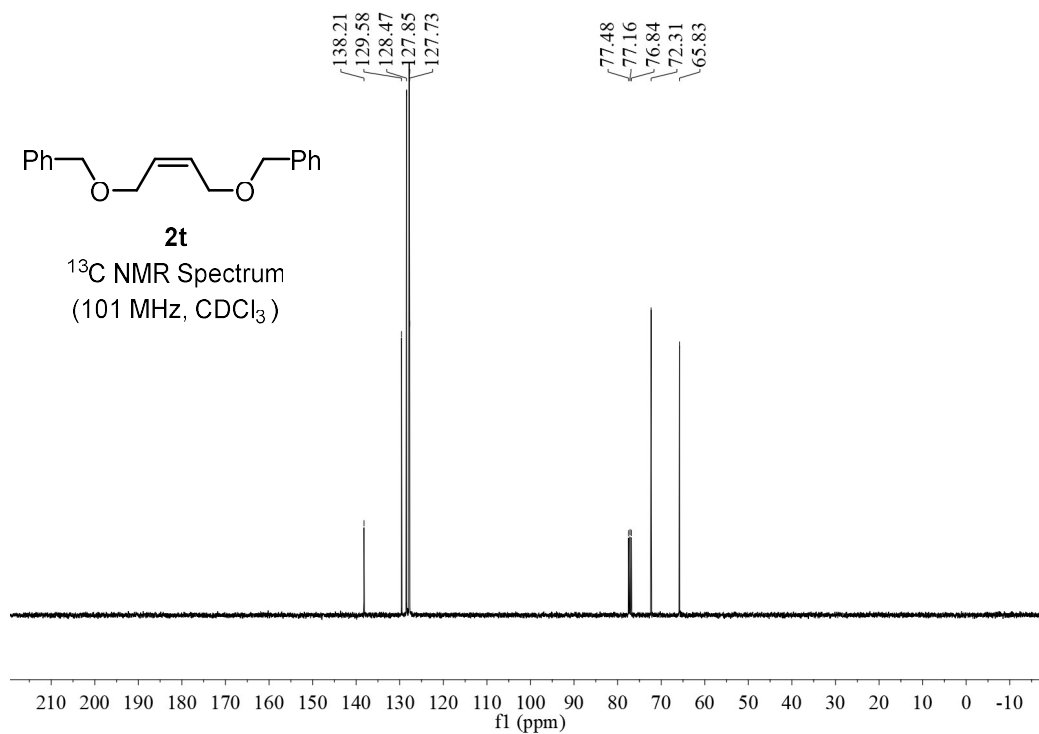
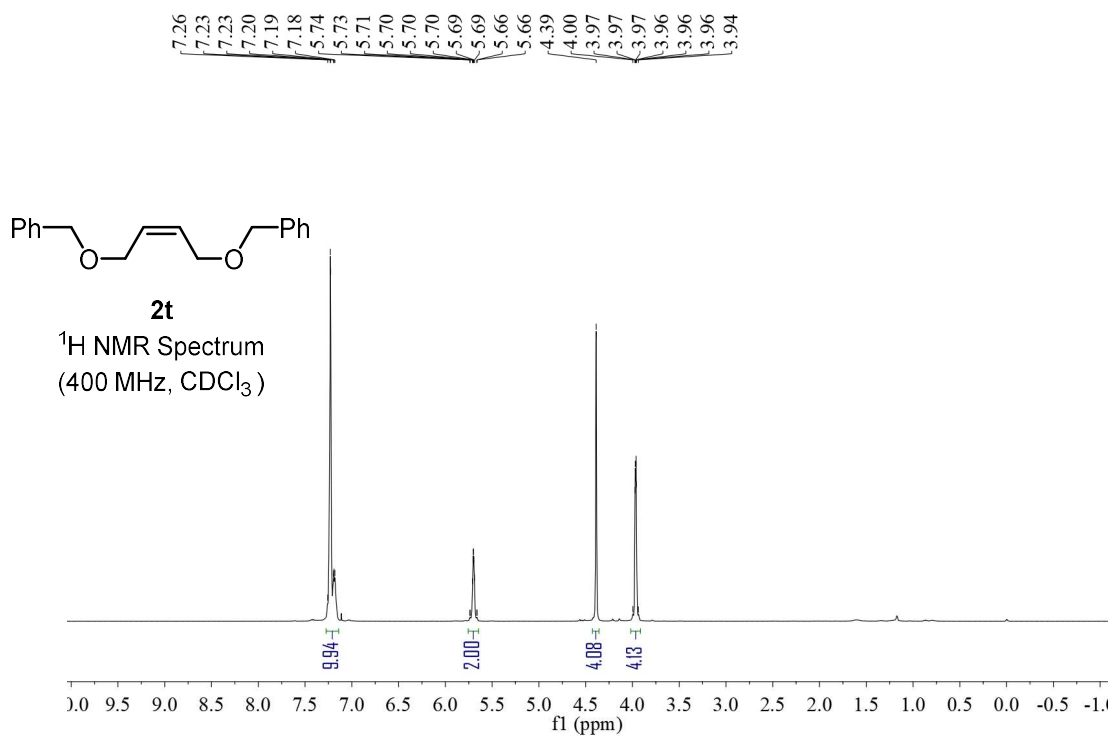


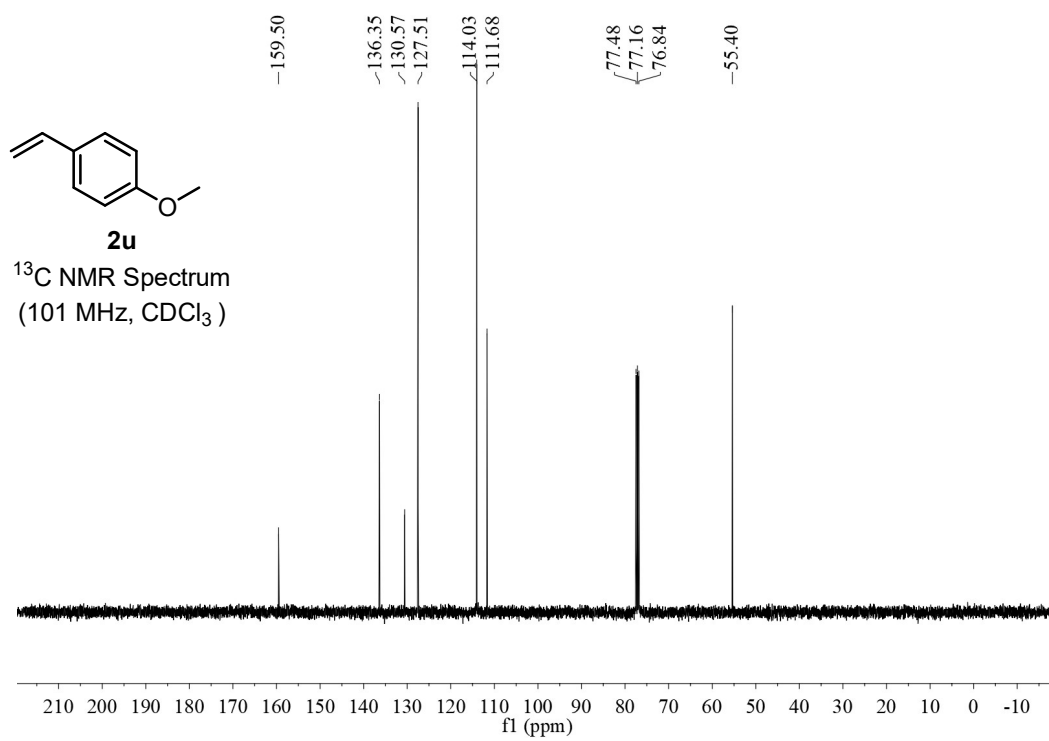
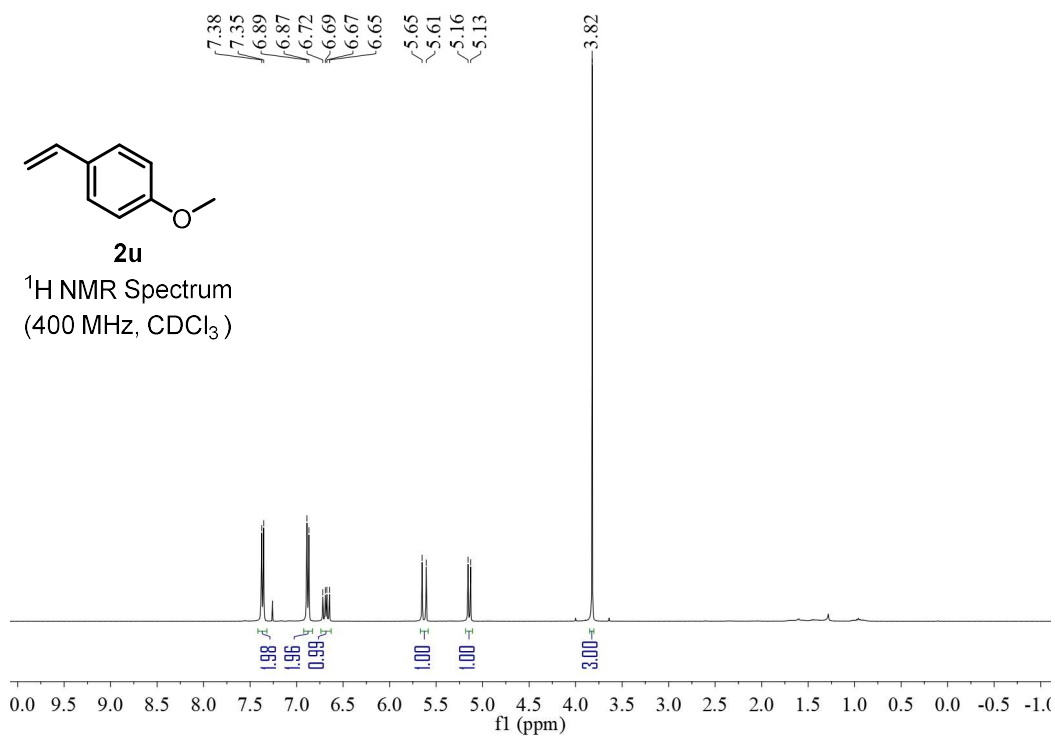


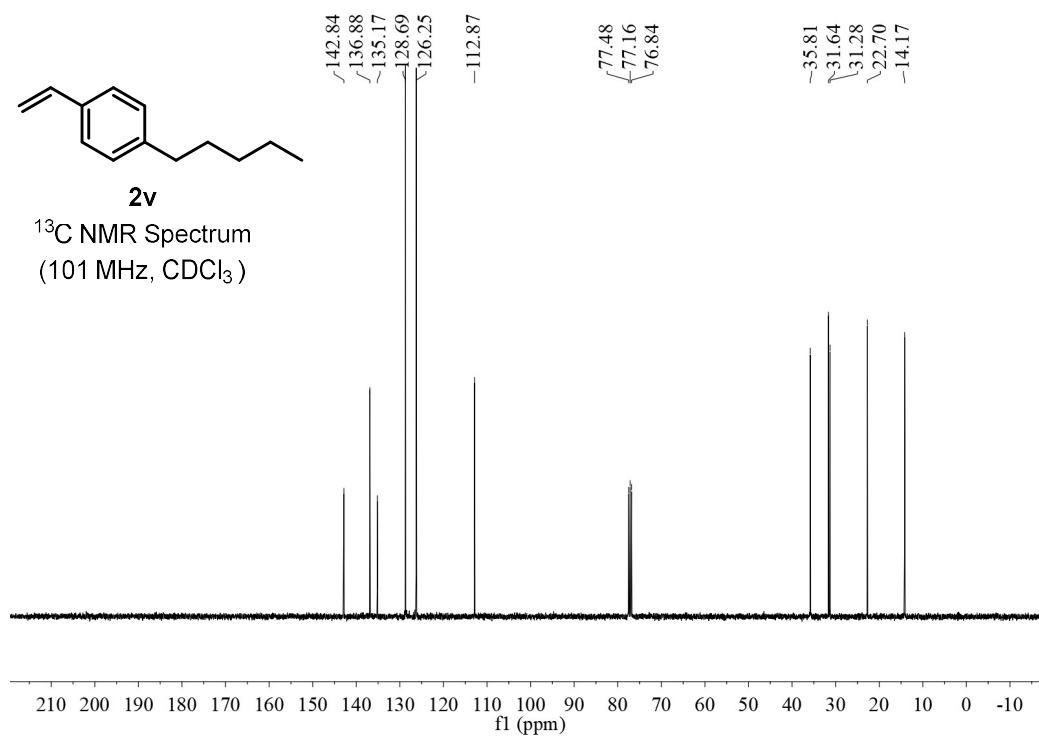
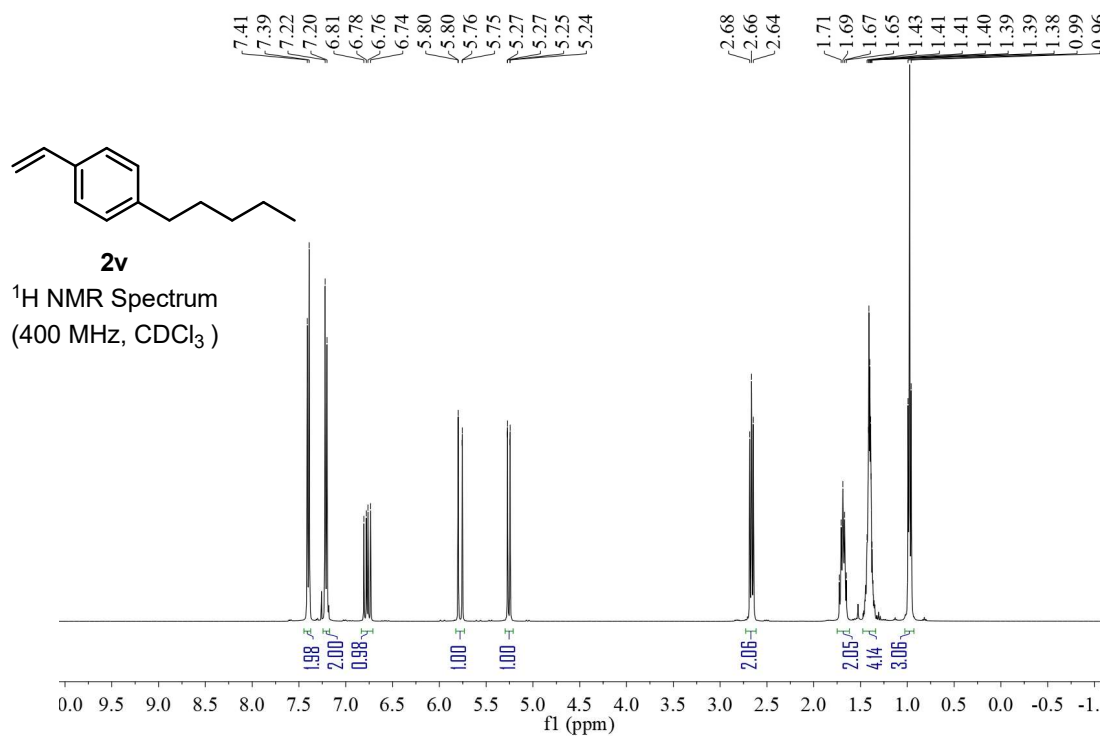


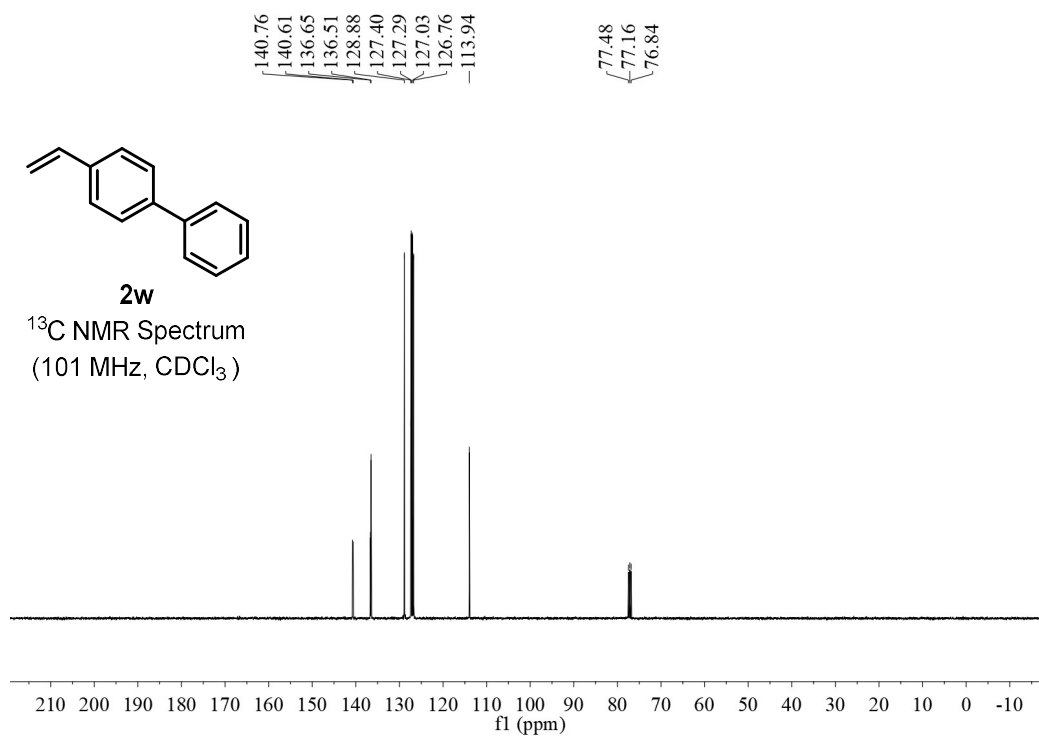
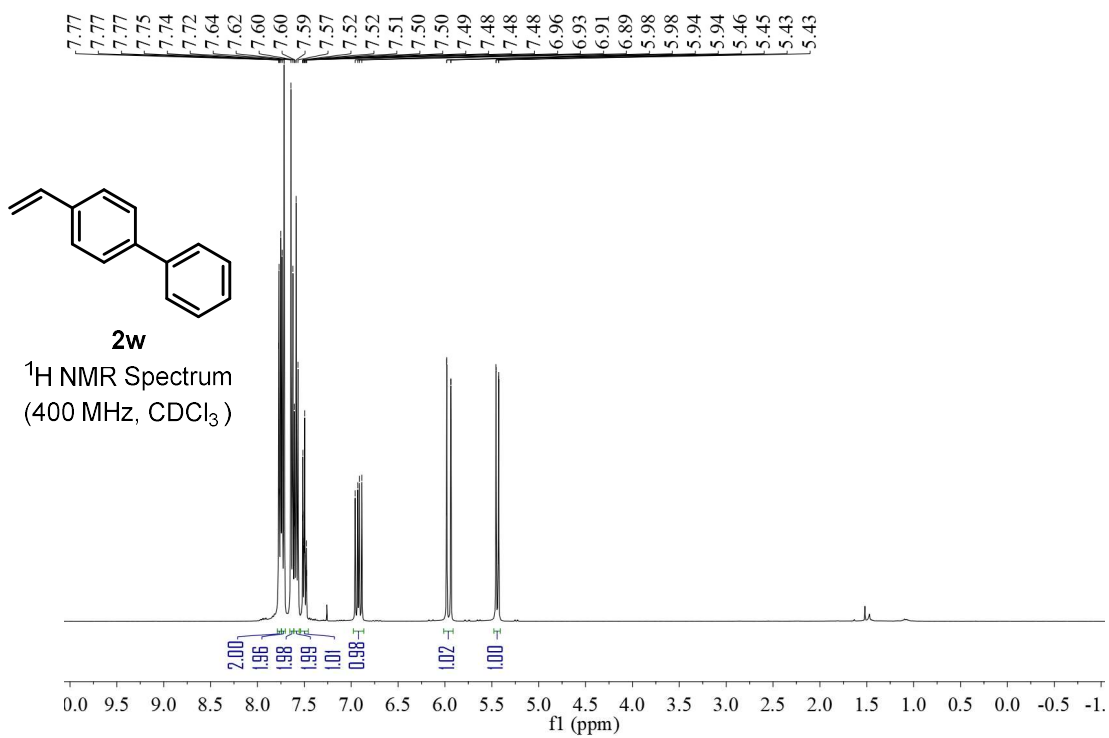












**(b)  $^1\text{H}$  NMR spectrum of  $2a\text{-}d_2$**

