

**Access to Functionalized Quaternary Stereocenters via the Copper-Catalyzed  
Conjugate Addition of Monoorganozinc Bromide Reagents Enabled by  
*N,N*-Dimethylacetamide**

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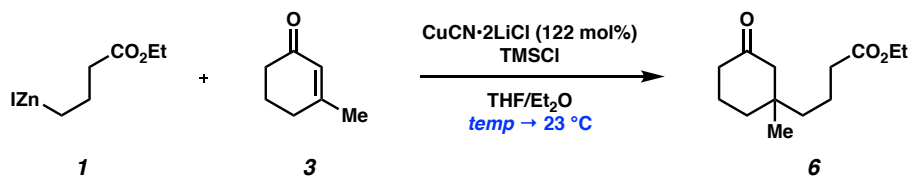
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## Preliminary Screening Data

Early optimization studies did not reveal a dependence on temperature (for the addition of the enone/Lewis acid solution to the cuprate reagent) or the equivalence of **1** with respect to yield (Table S1). We therefore chose 2 equiv RZnX at 0 °C for convenience, as well as the ability to mitigate any potential mild reaction exotherm.

Table S1. Preliminary Optimization of Temperature and Equivalence of **1** in the Production of **6**.



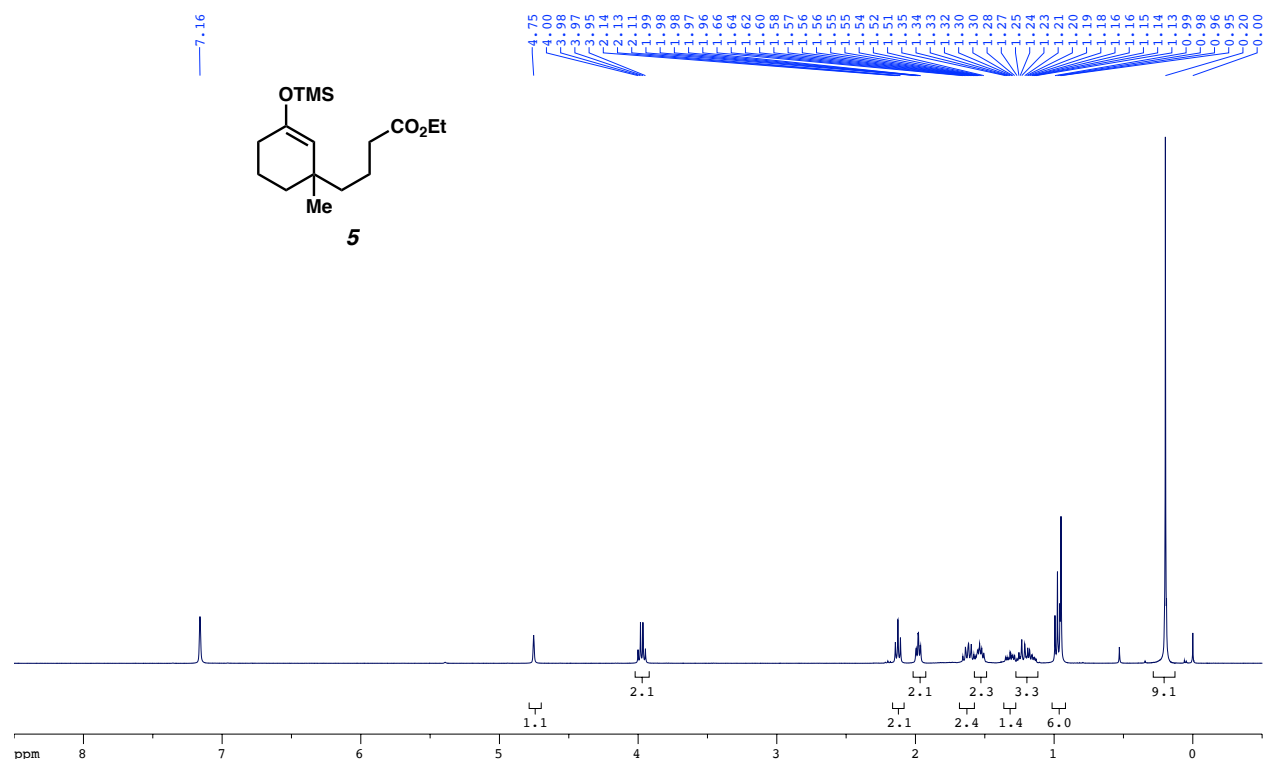
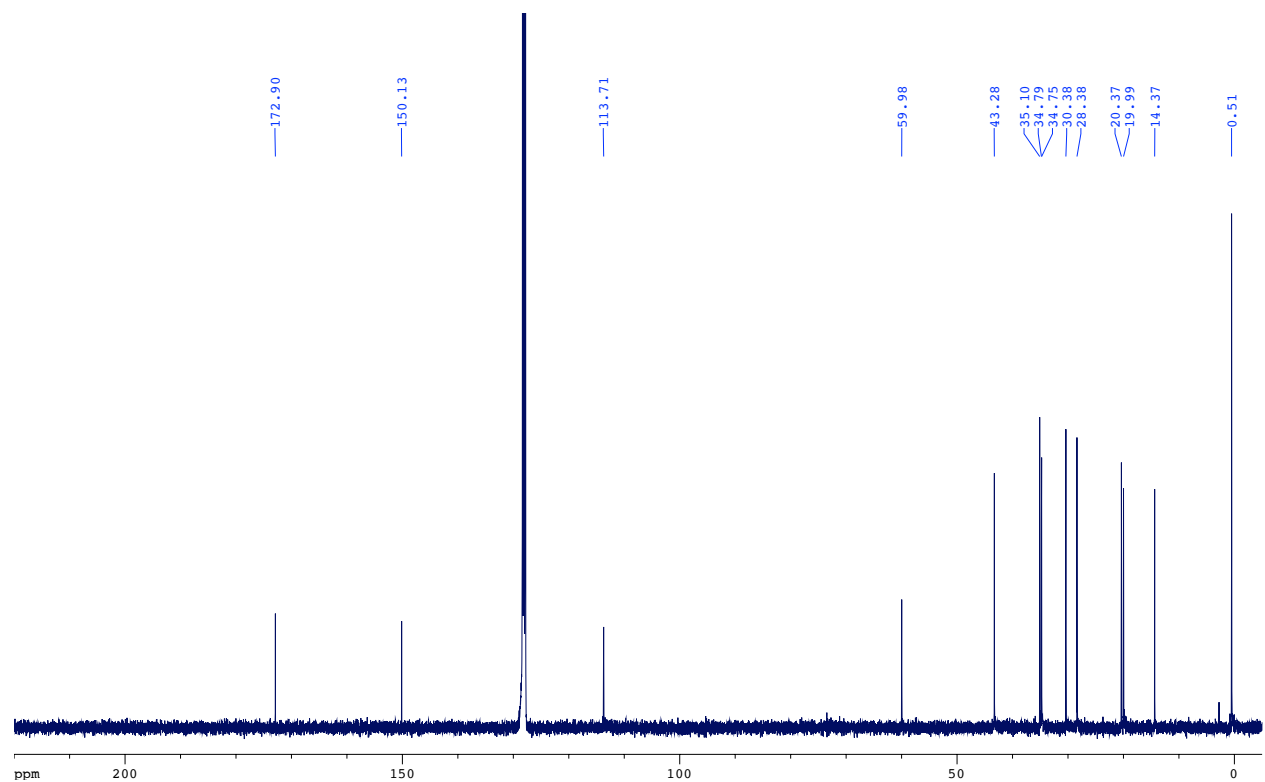
entry <sup>a</sup>	equiv <b>1</b>	initial temp (°C)	yield (%) <sup>b</sup>
1	1.4	-78	43
2	1.4	-10	47
3	1.4	0	48
4	2.0	0	48
5	1.4	23	49
6	2.0	23	48

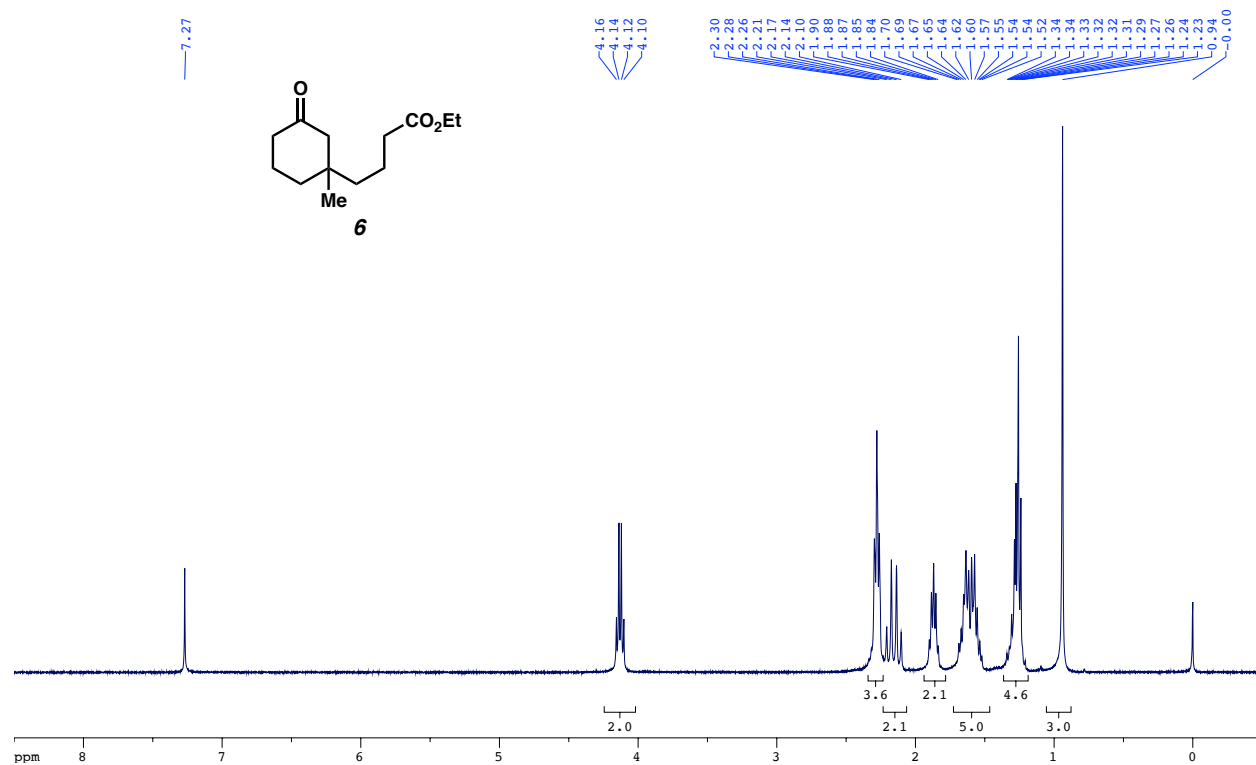
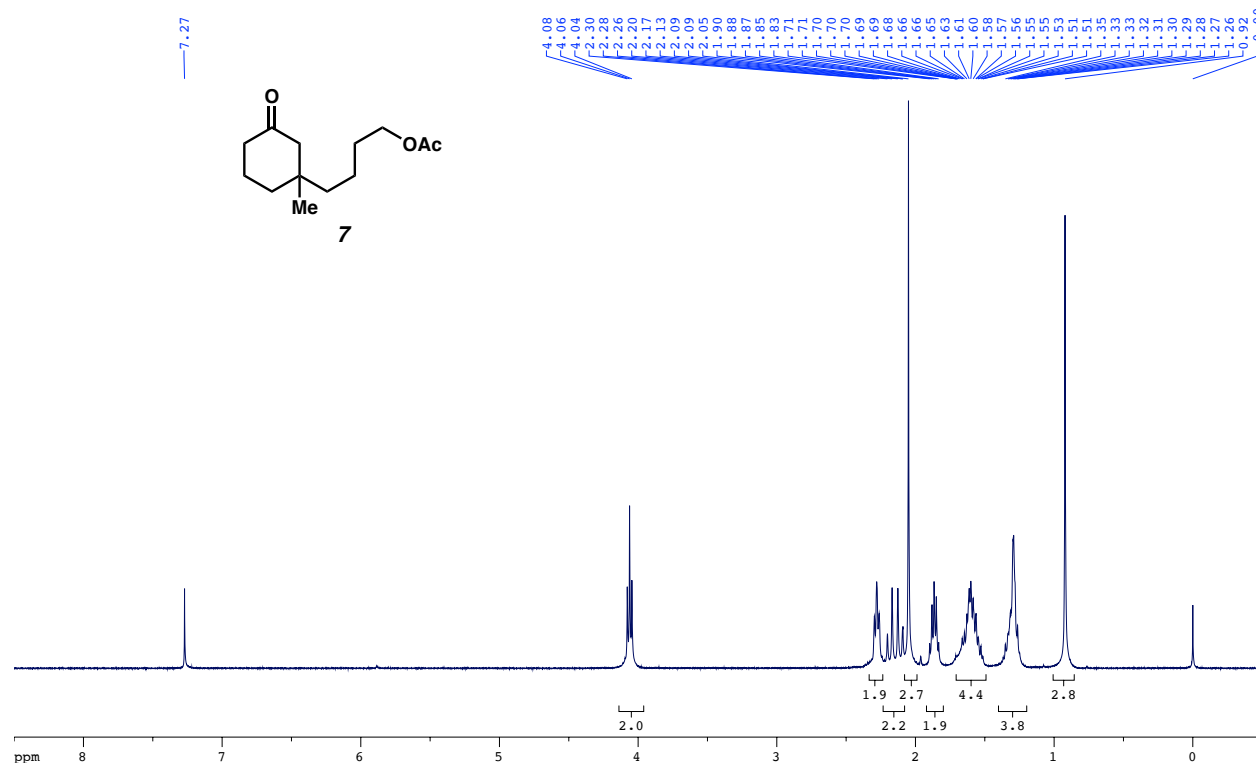
<sup>a</sup> 1.00 mmol scale **3** and 2.4 TMSCl for up to 24 h. <sup>b</sup> Isolated yields.

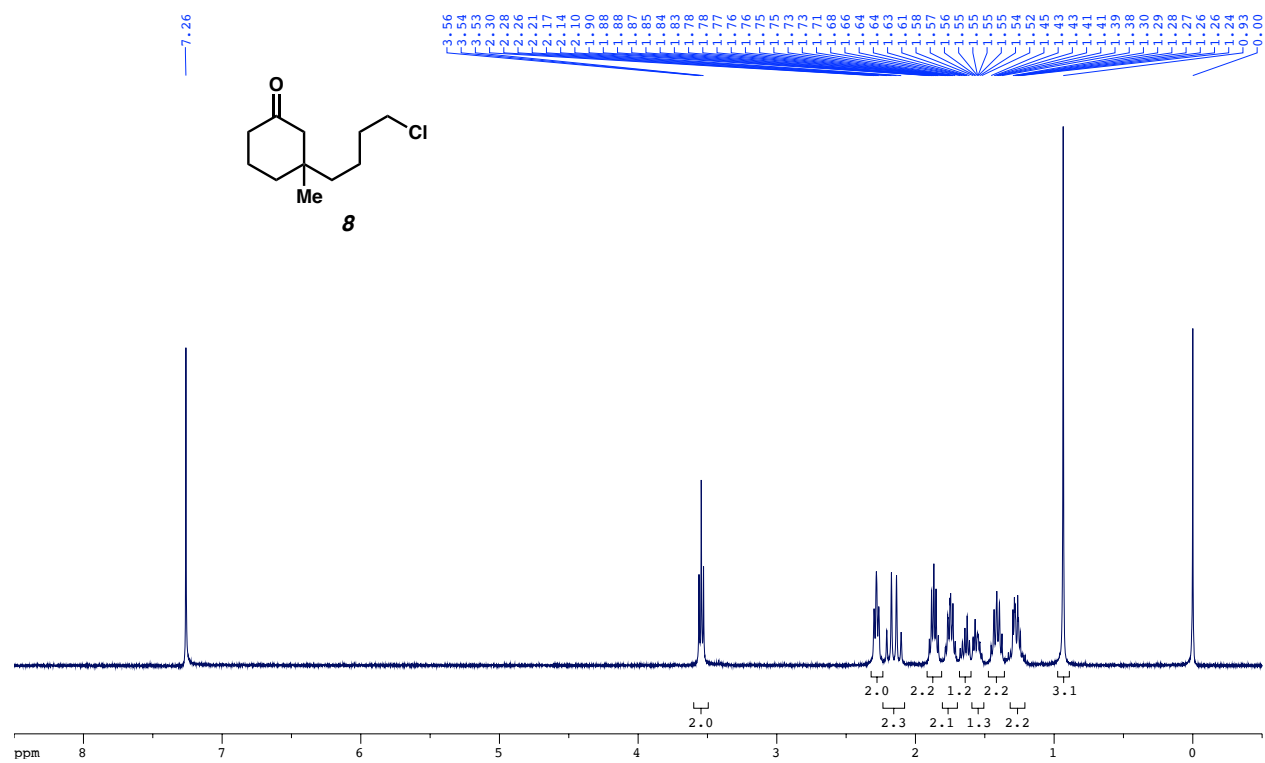
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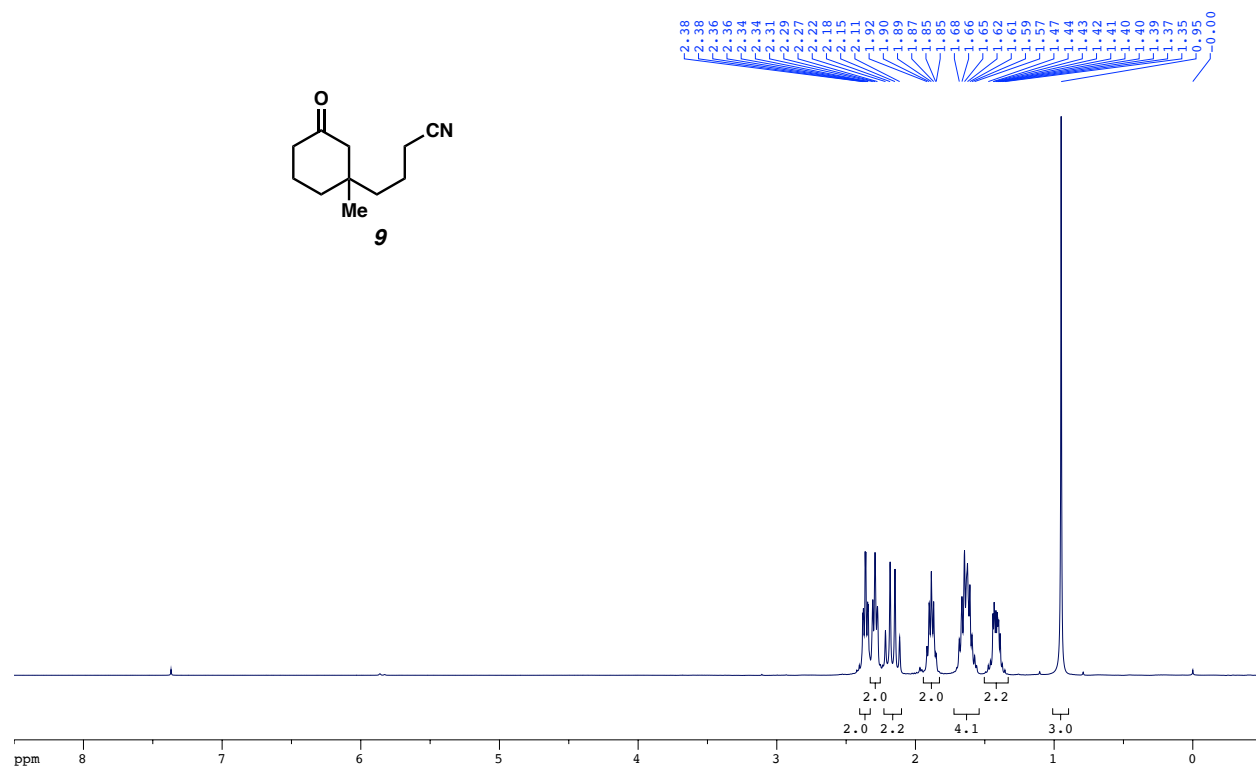
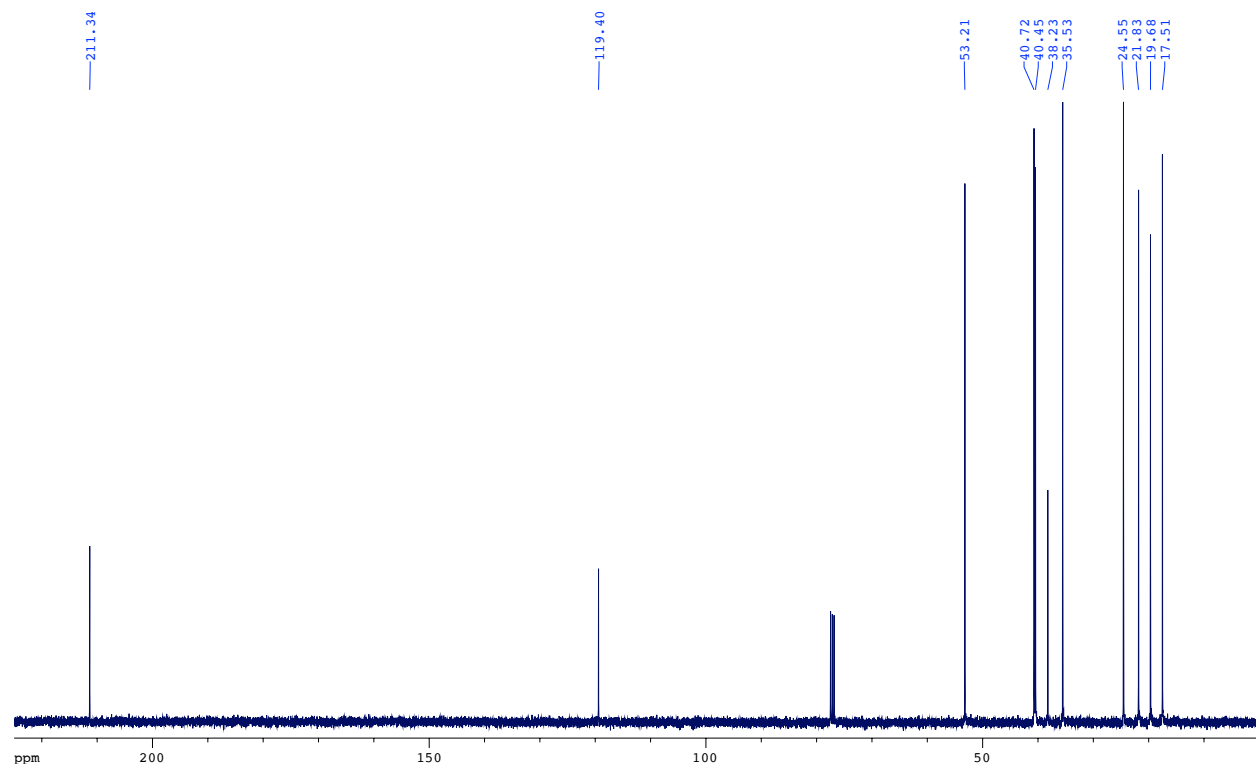
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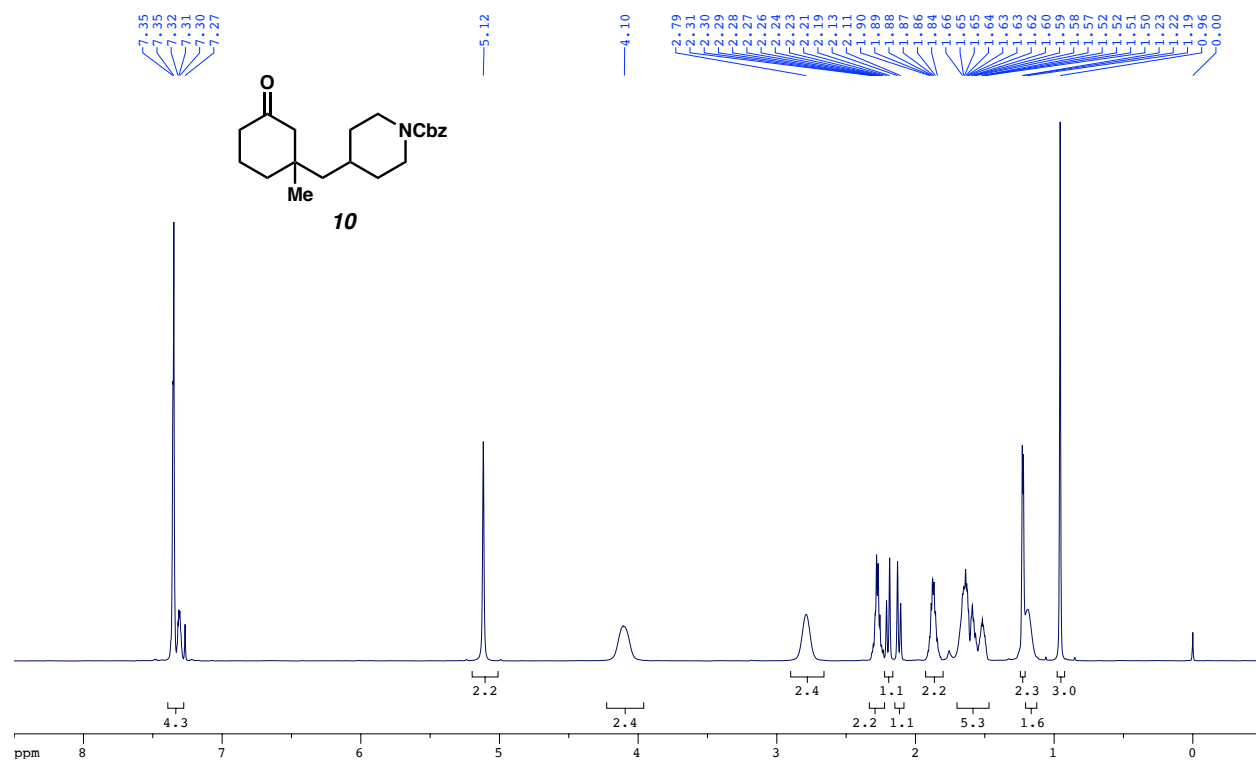
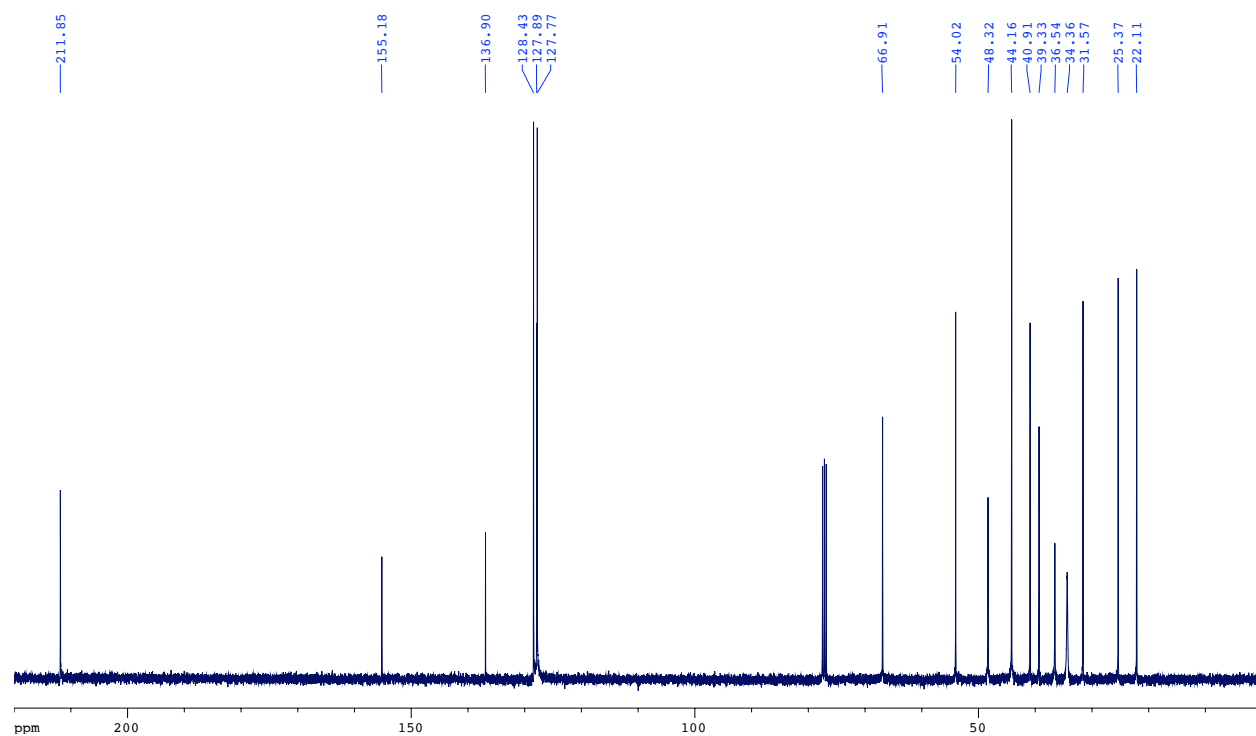
Figure S1. <sup>1</sup>H NMR spectrum (400 MHz, C<sub>6</sub>D<sub>6</sub>) of **5**.Figure S2. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (101 MHz, C<sub>6</sub>D<sub>6</sub>) of **5**.

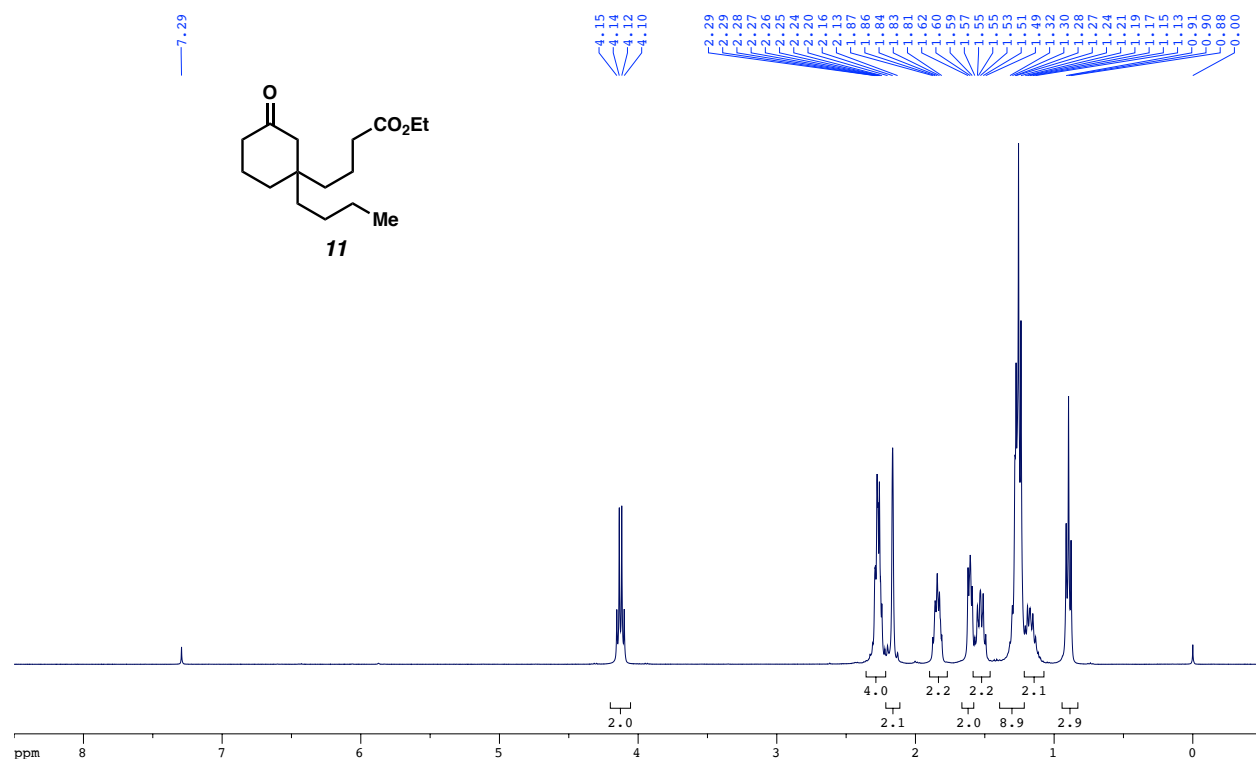
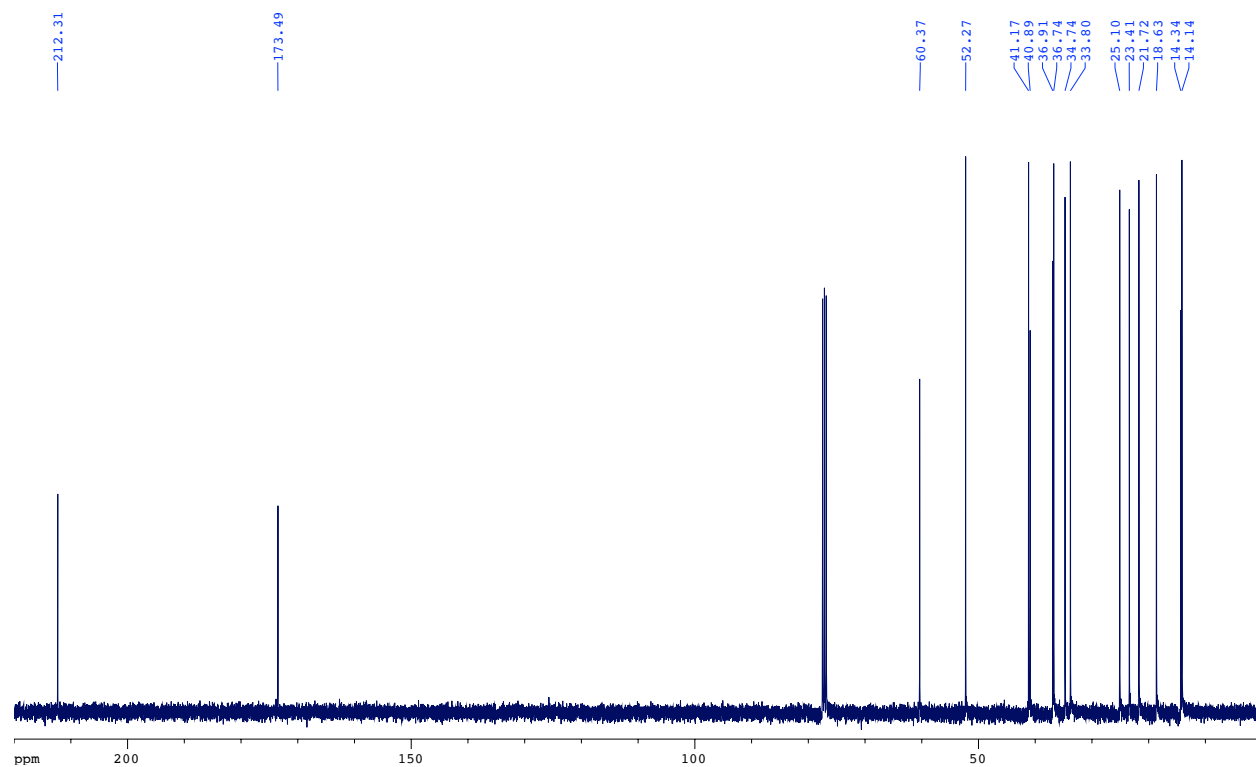
Figure S3. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **6**.Figure S4. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **7**.

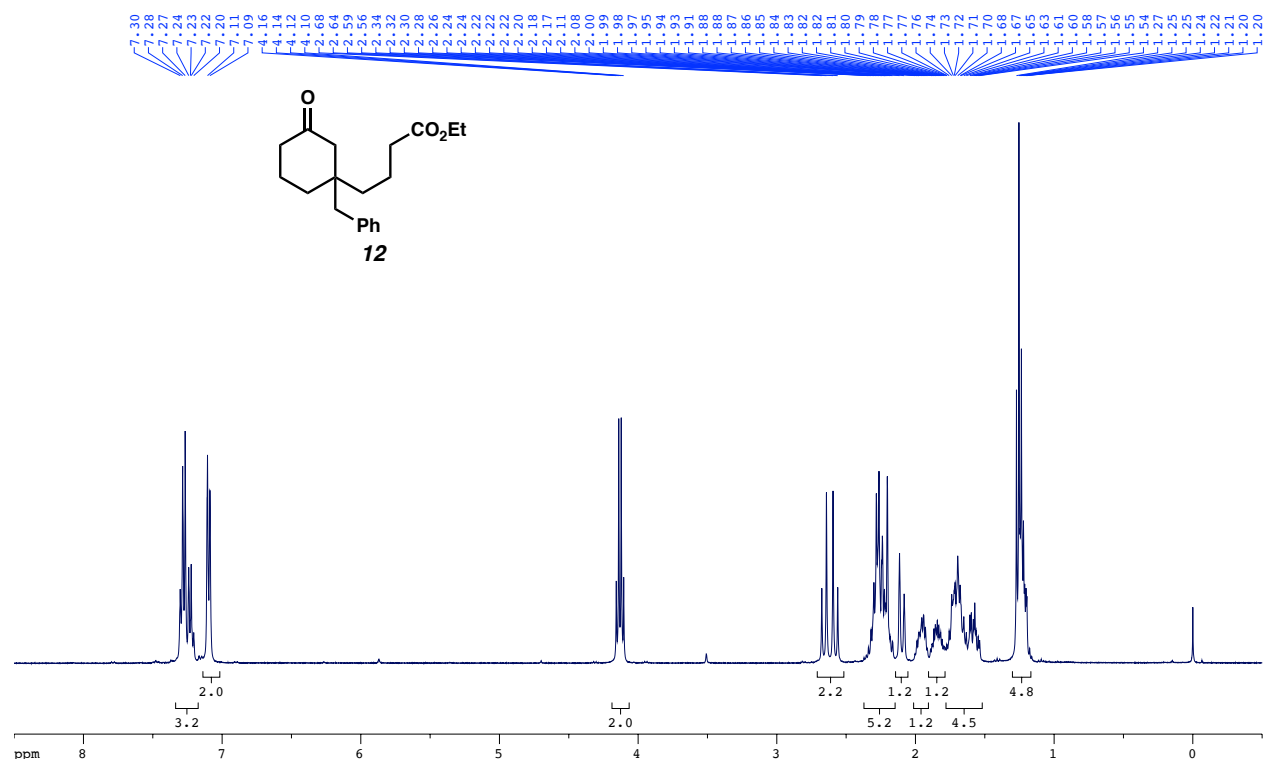
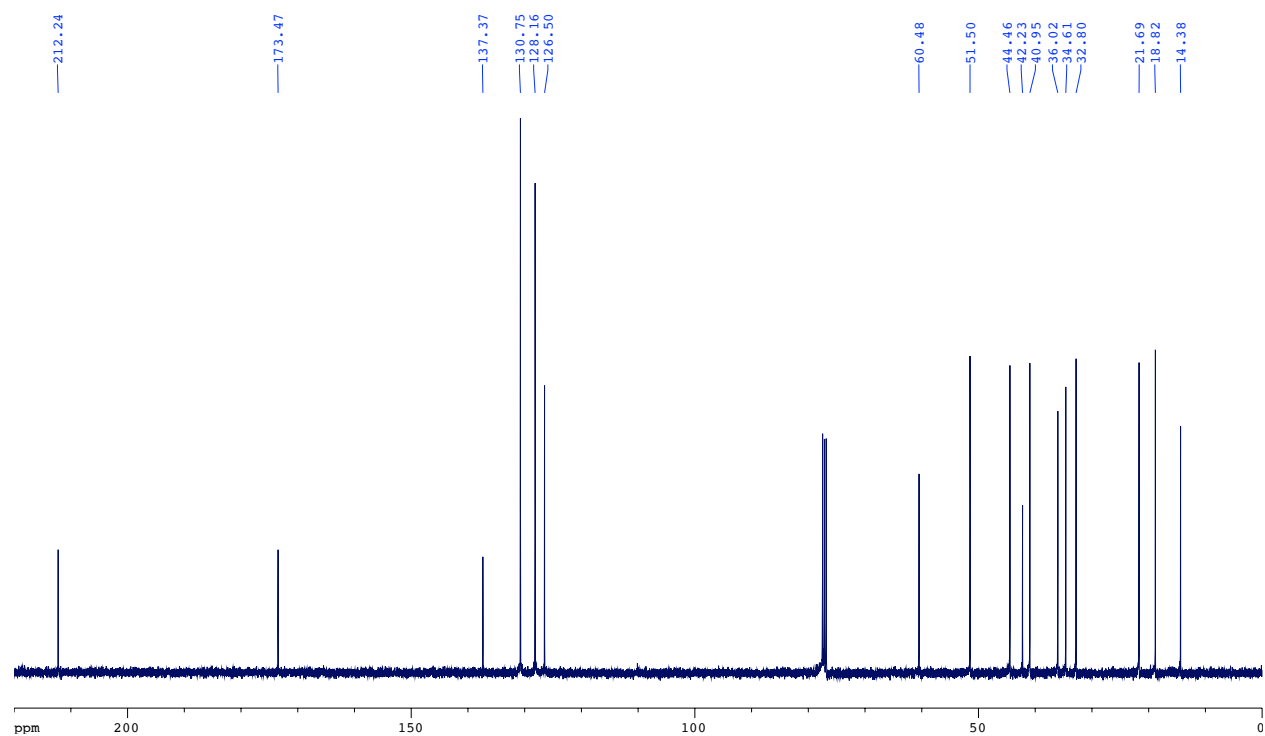
Figure S5. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **8**.

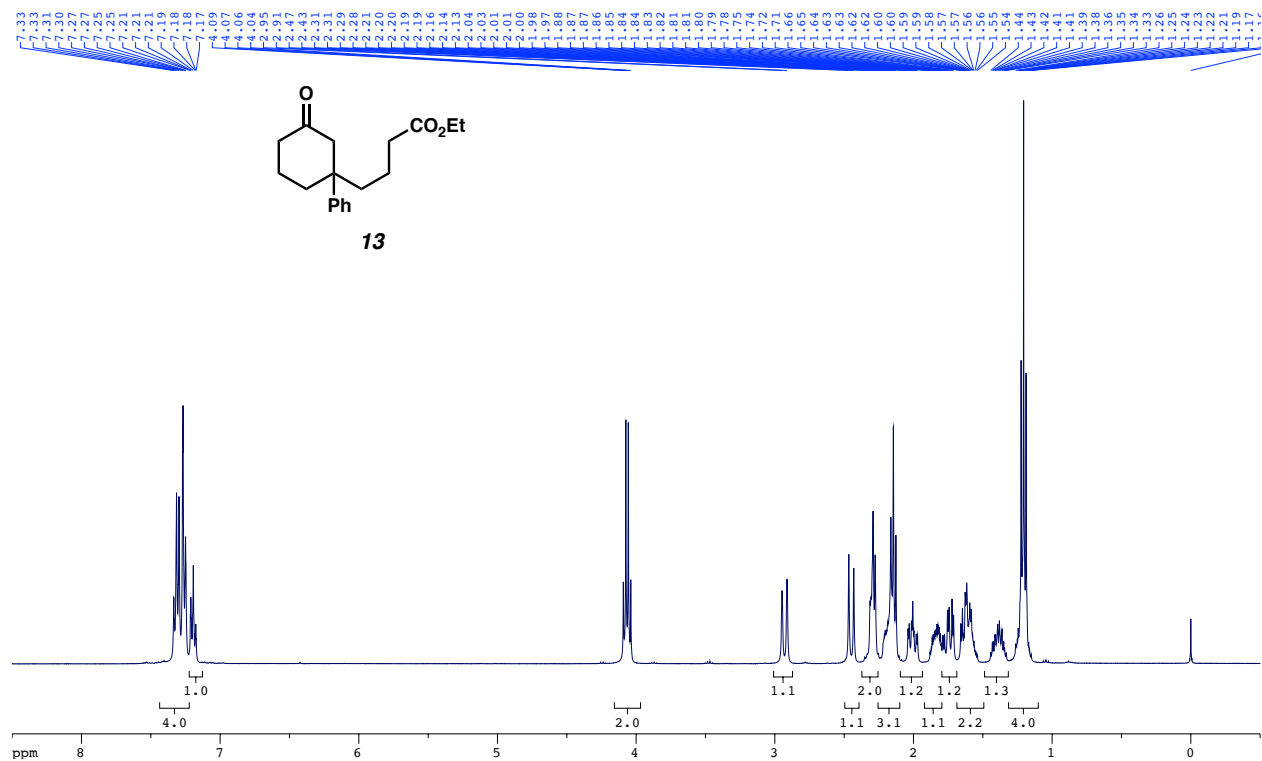
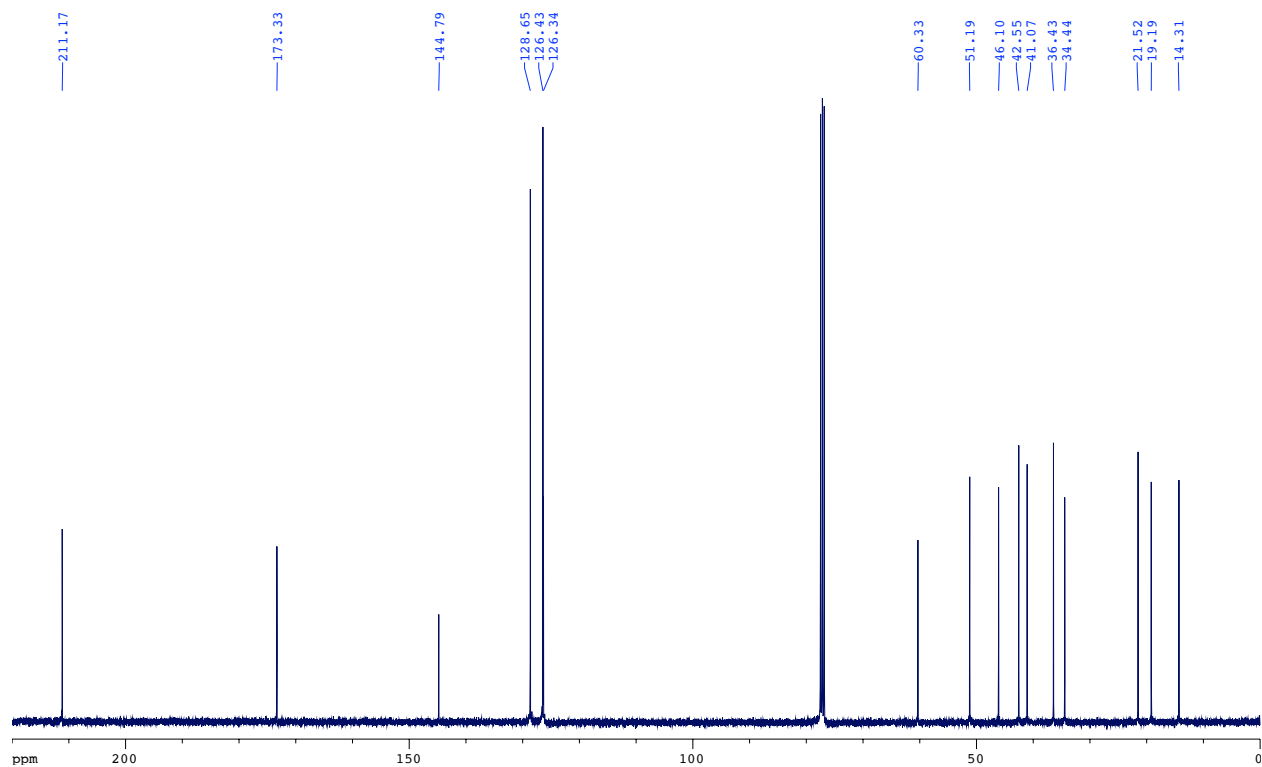
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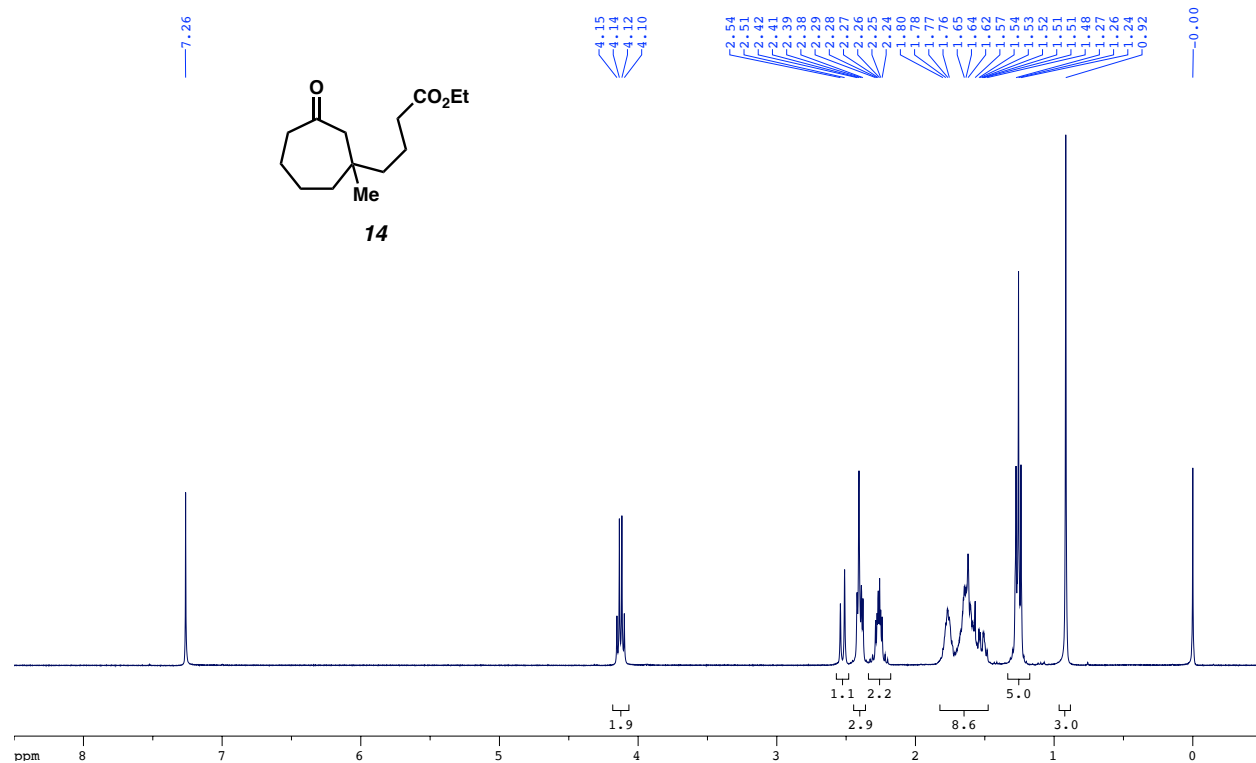
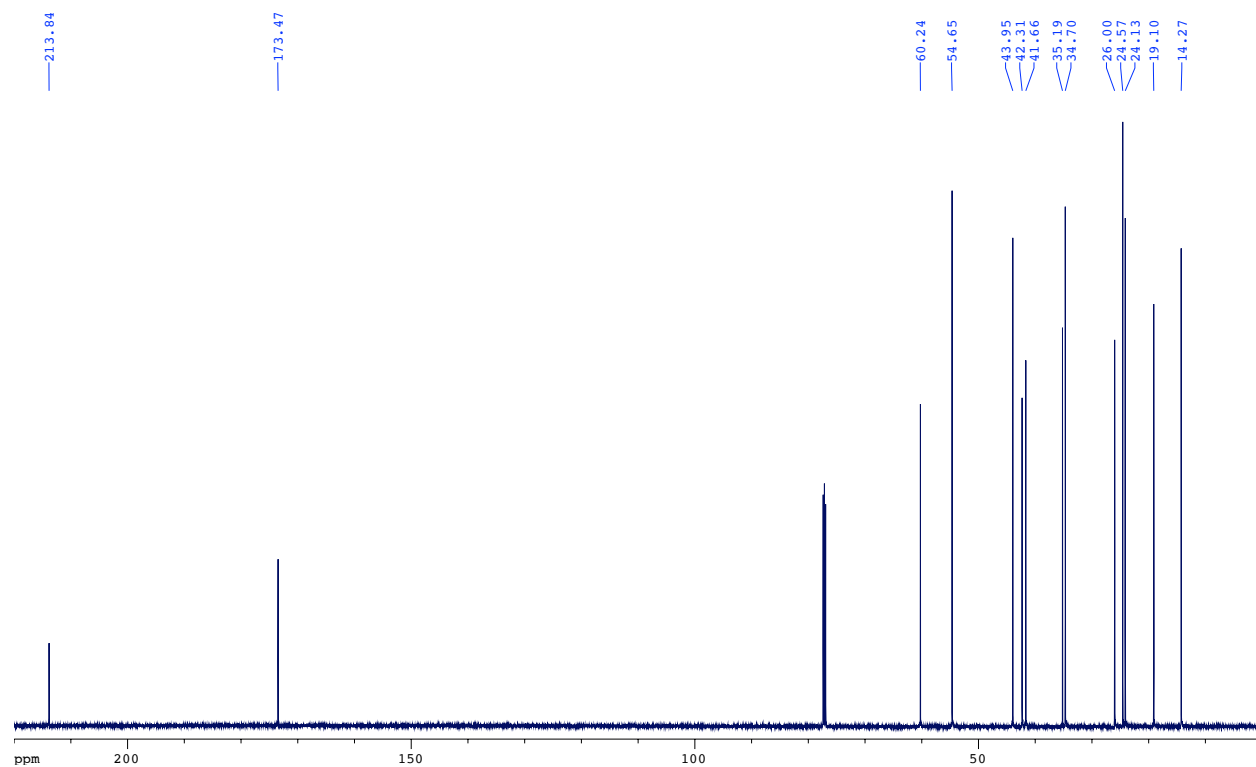


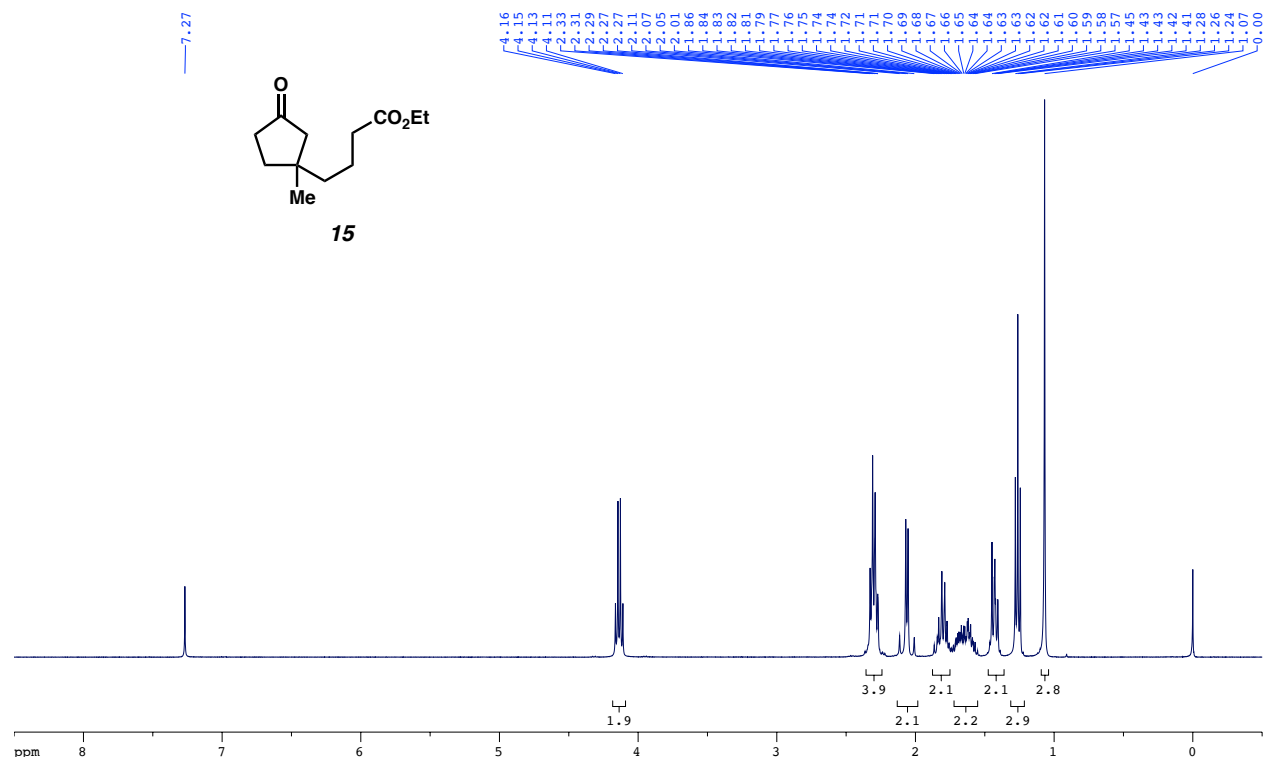
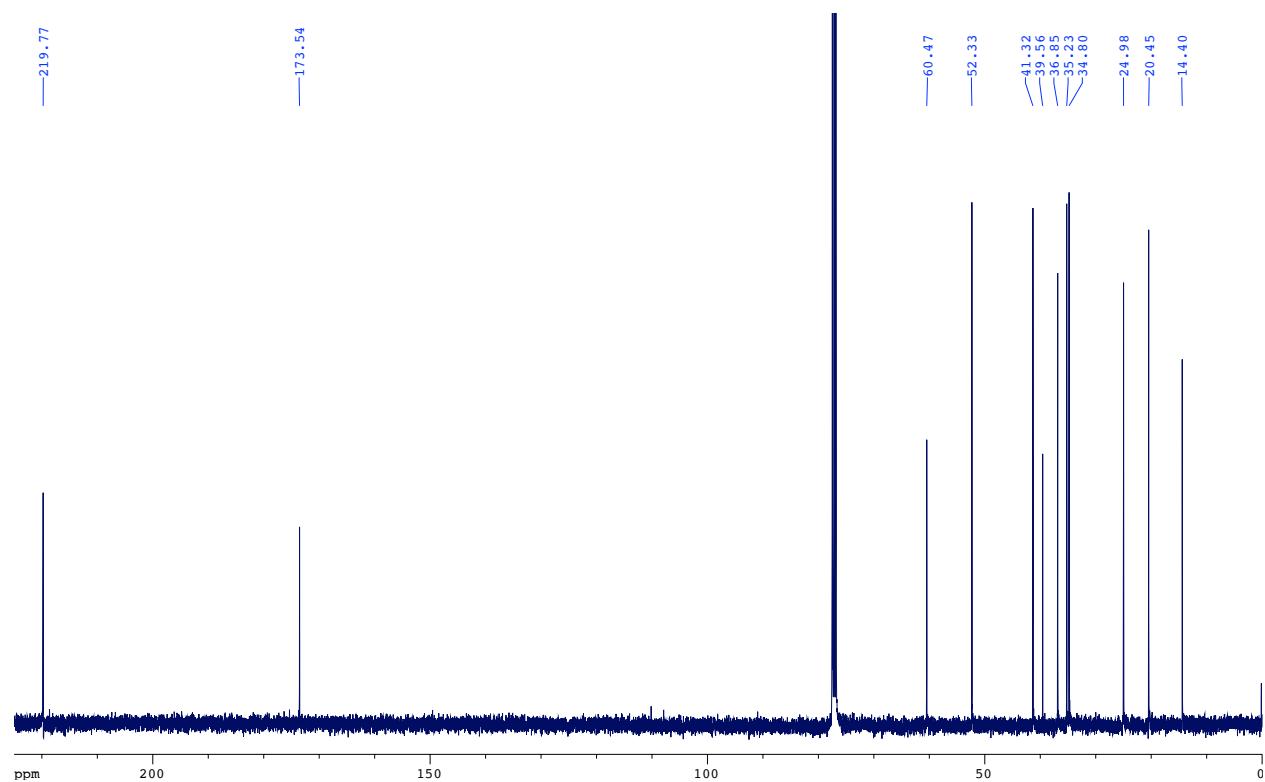
Figure S8. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of **10**.Figure S9. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **10**.

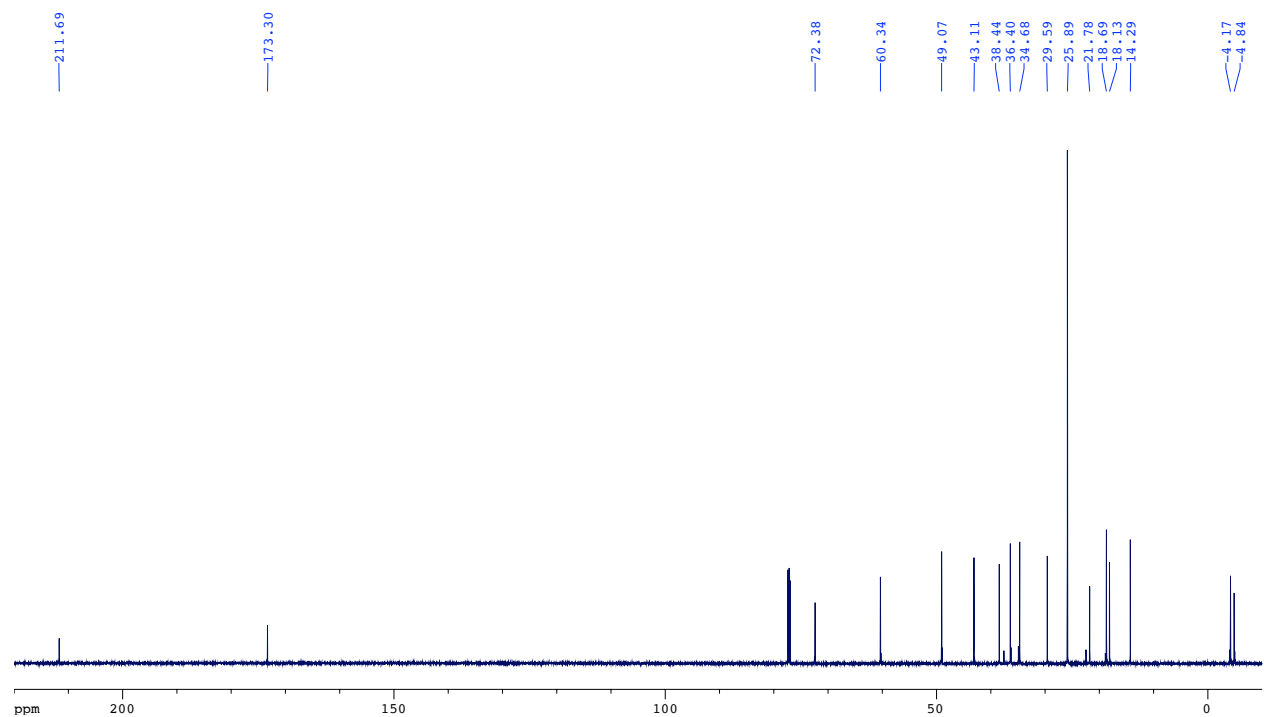
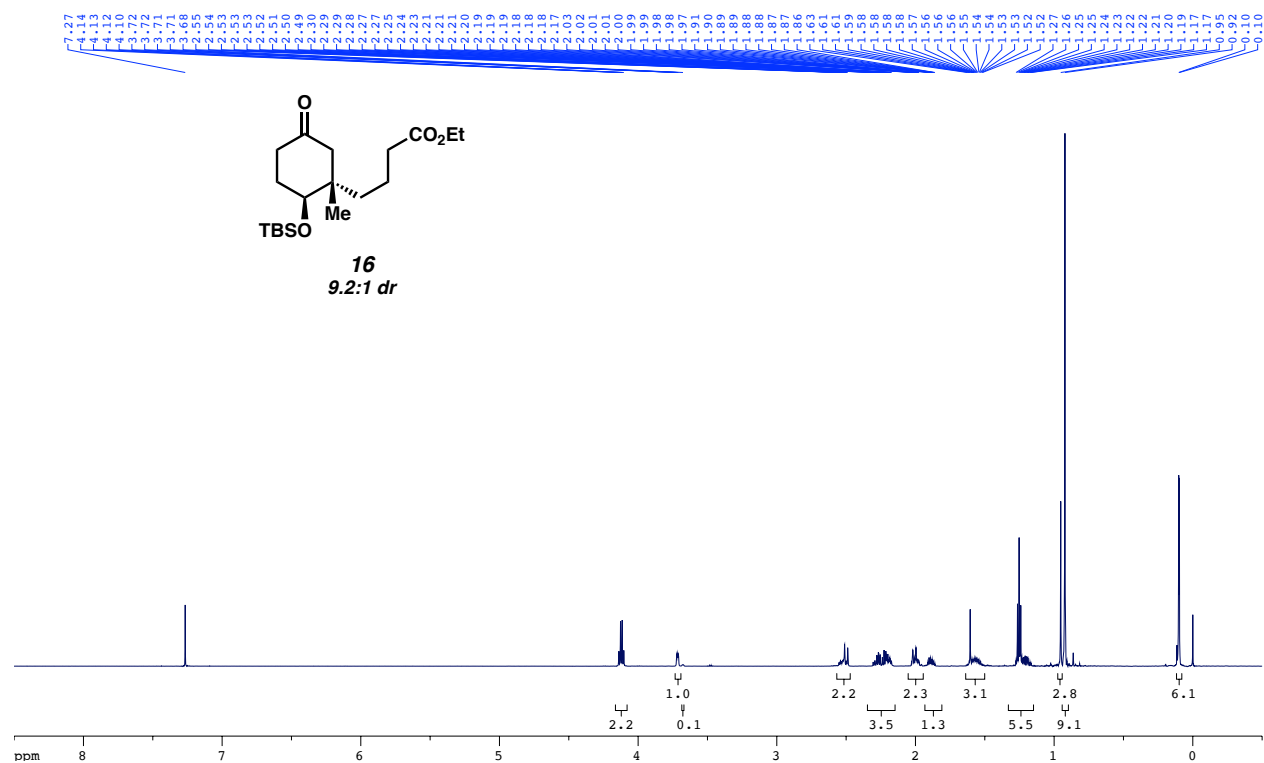
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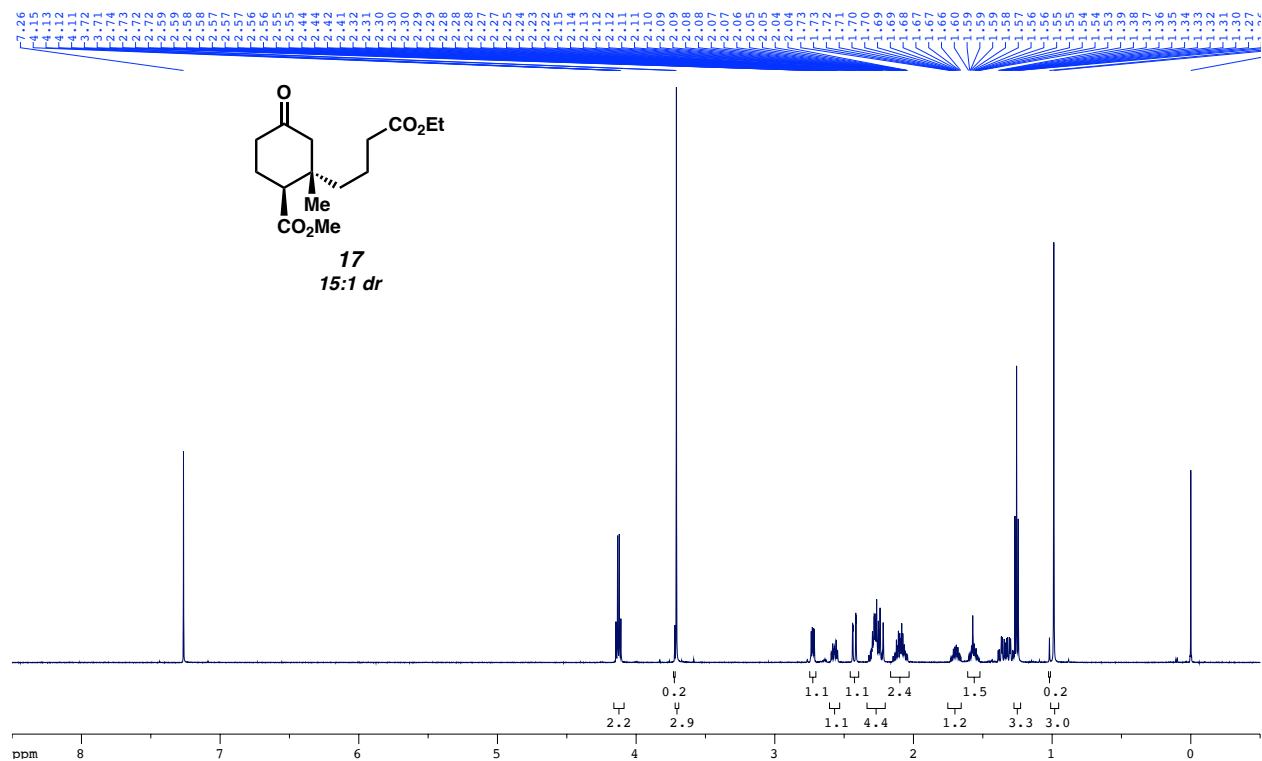
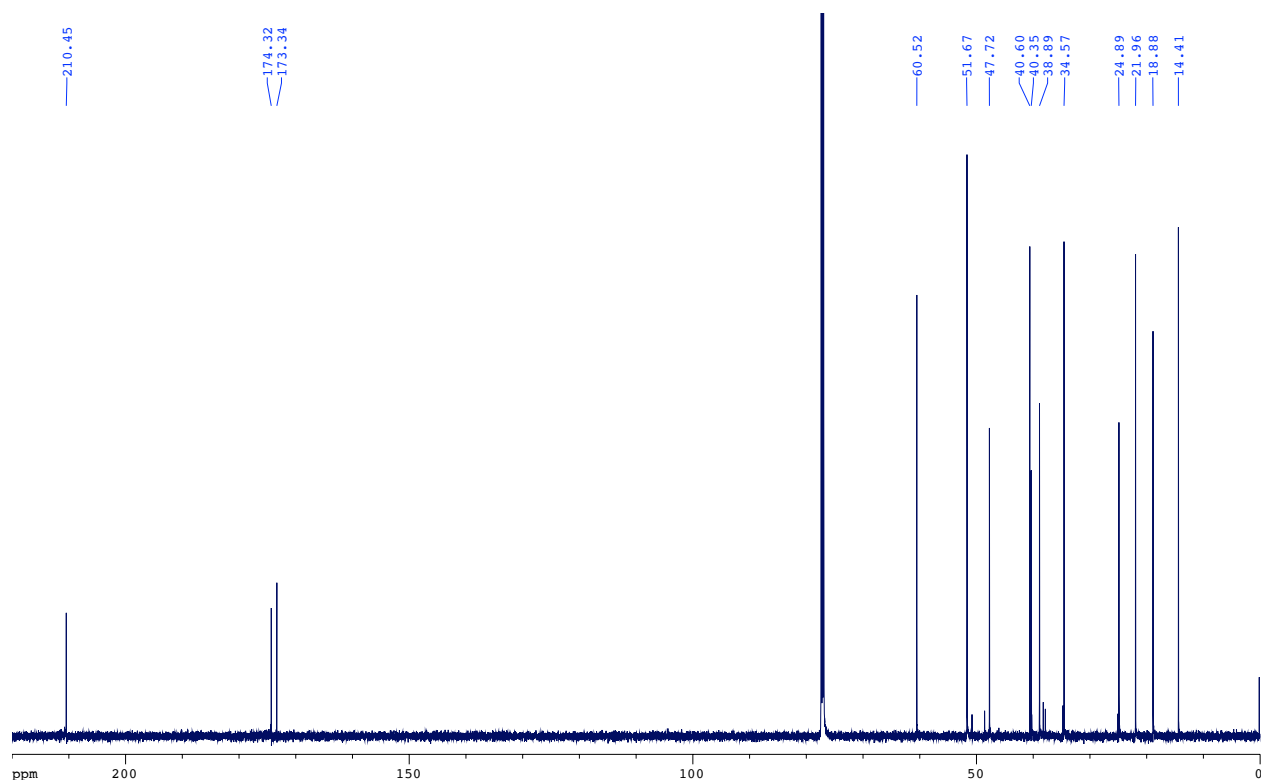
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Figure S14.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **13**.Figure S15.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **13**.

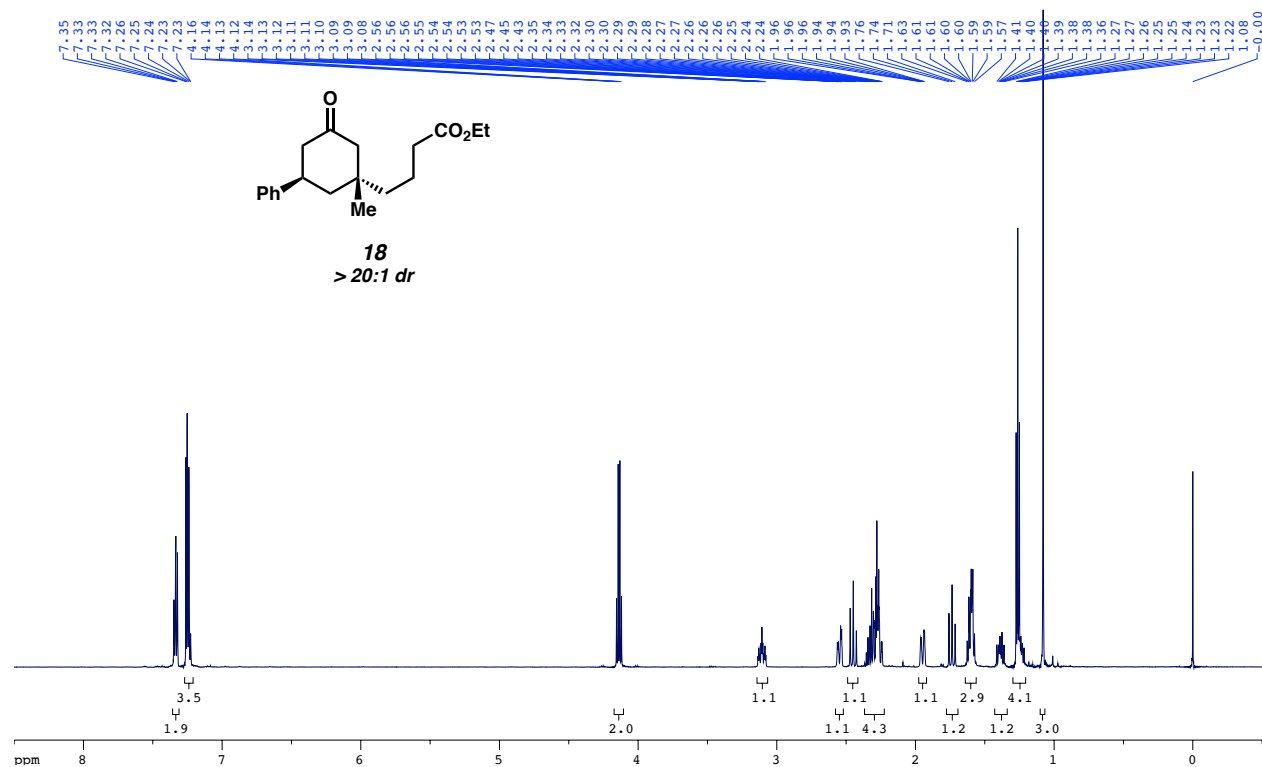
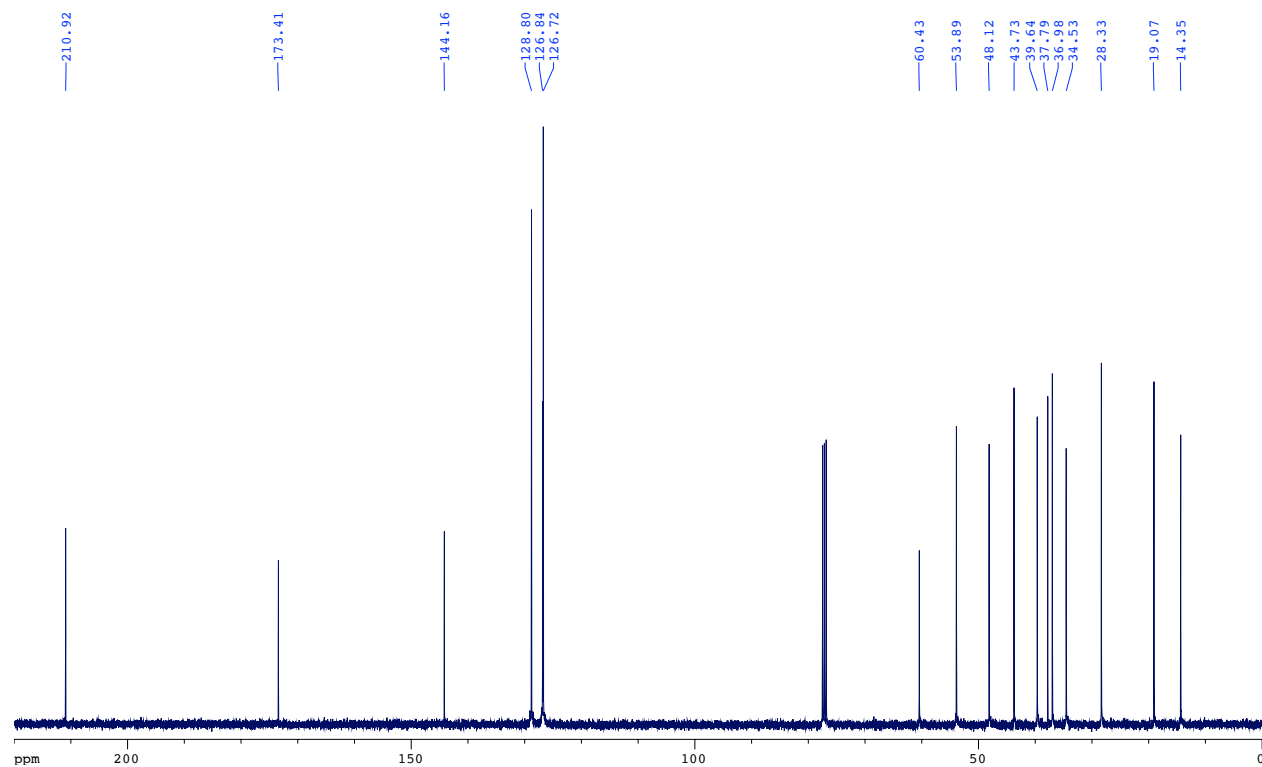
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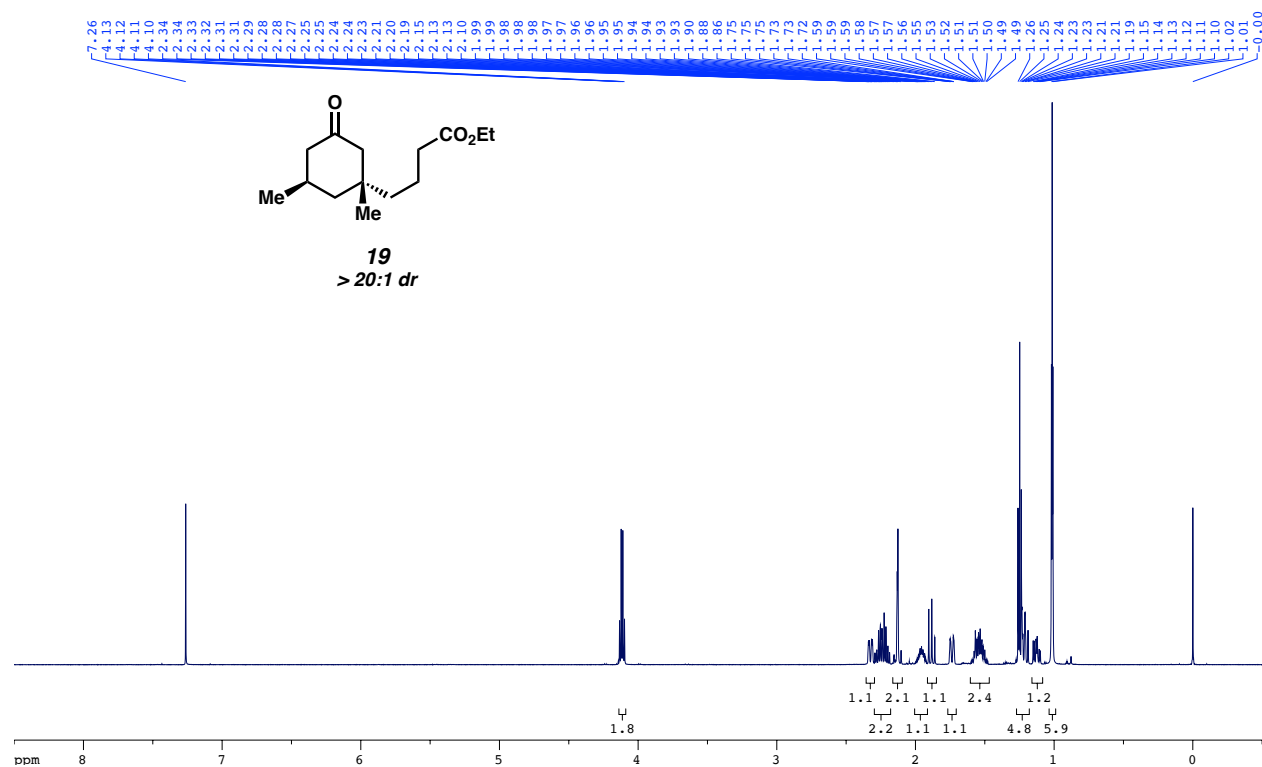
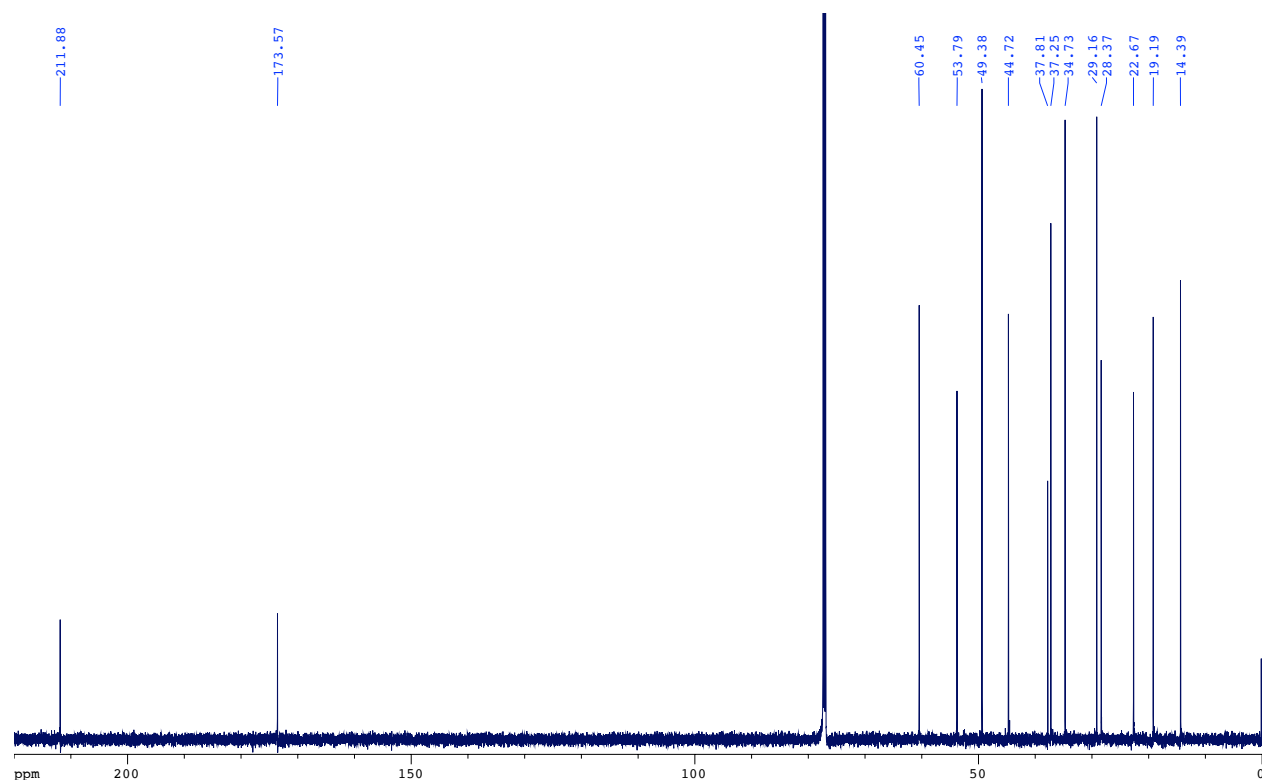
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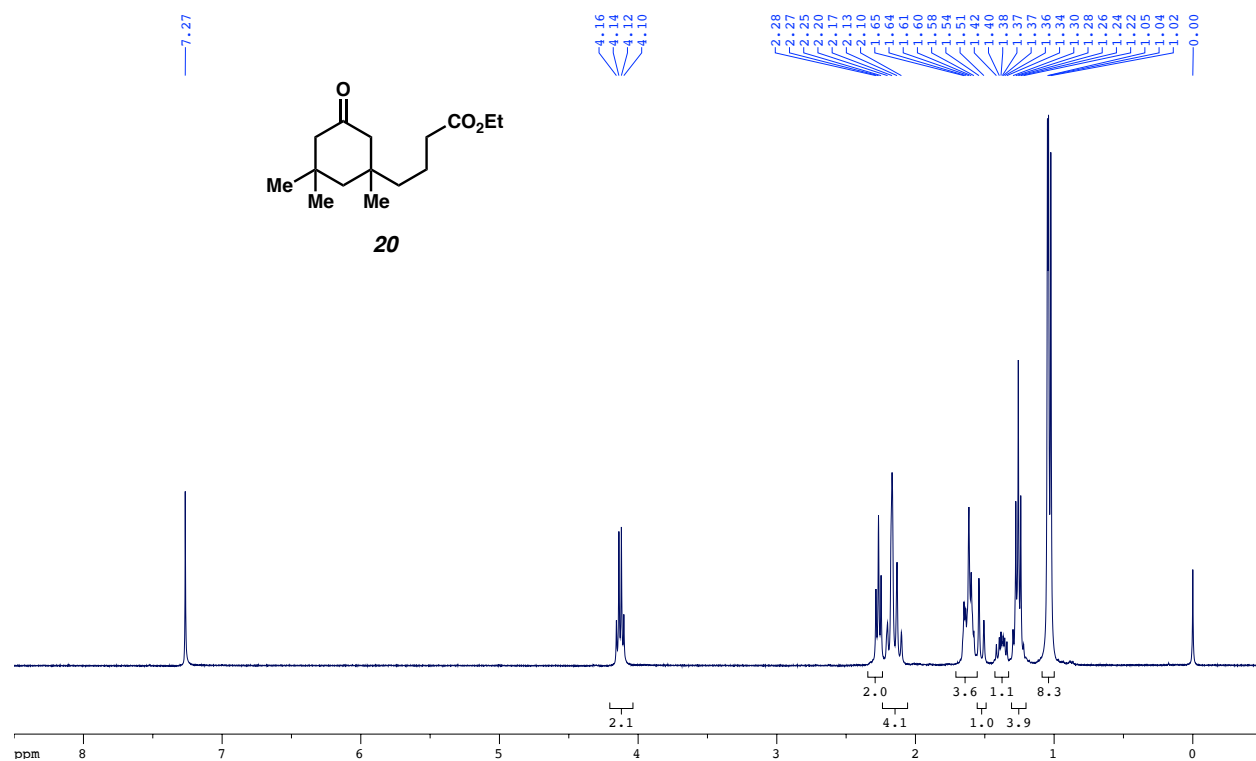
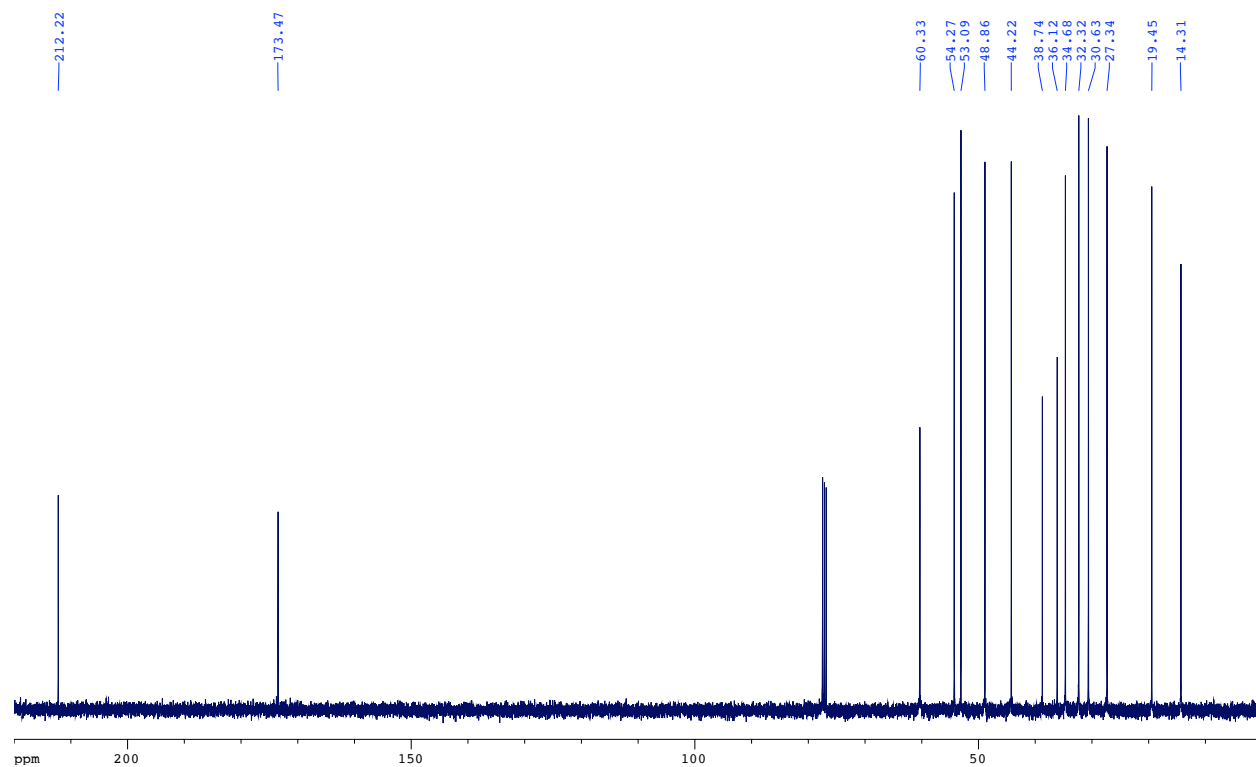


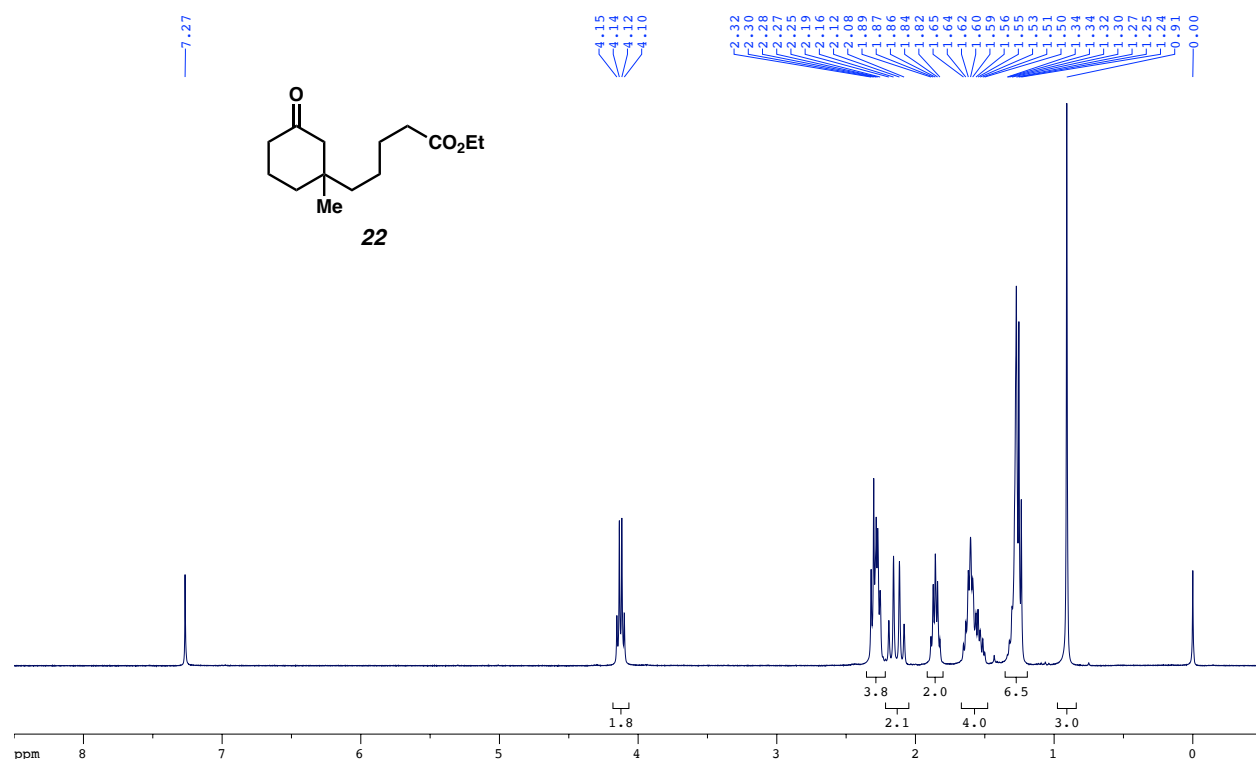
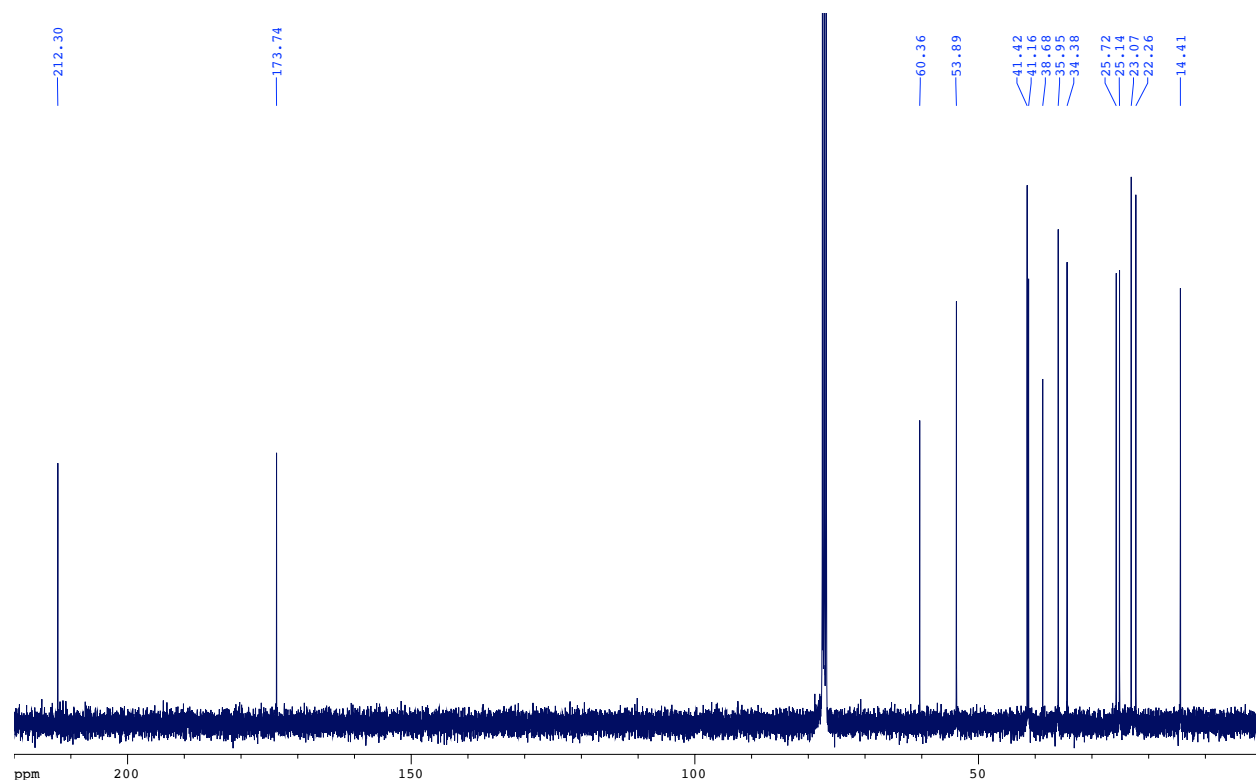
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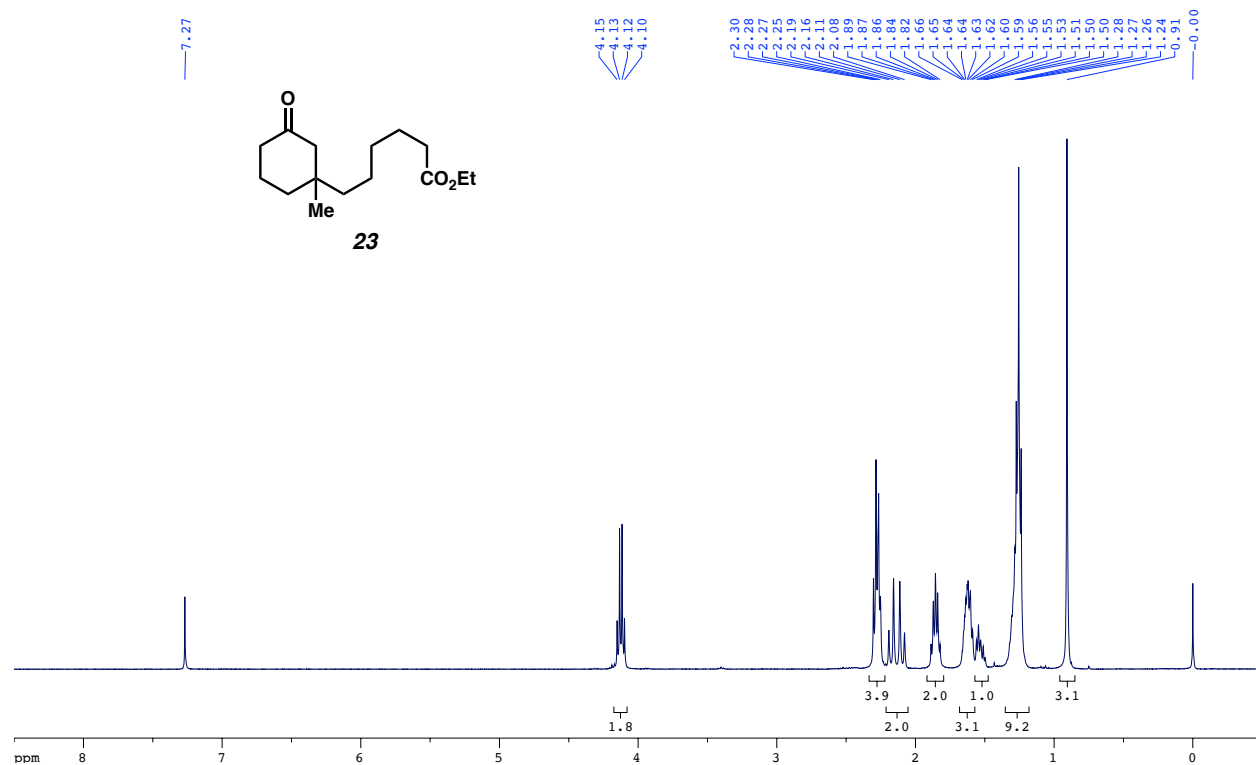
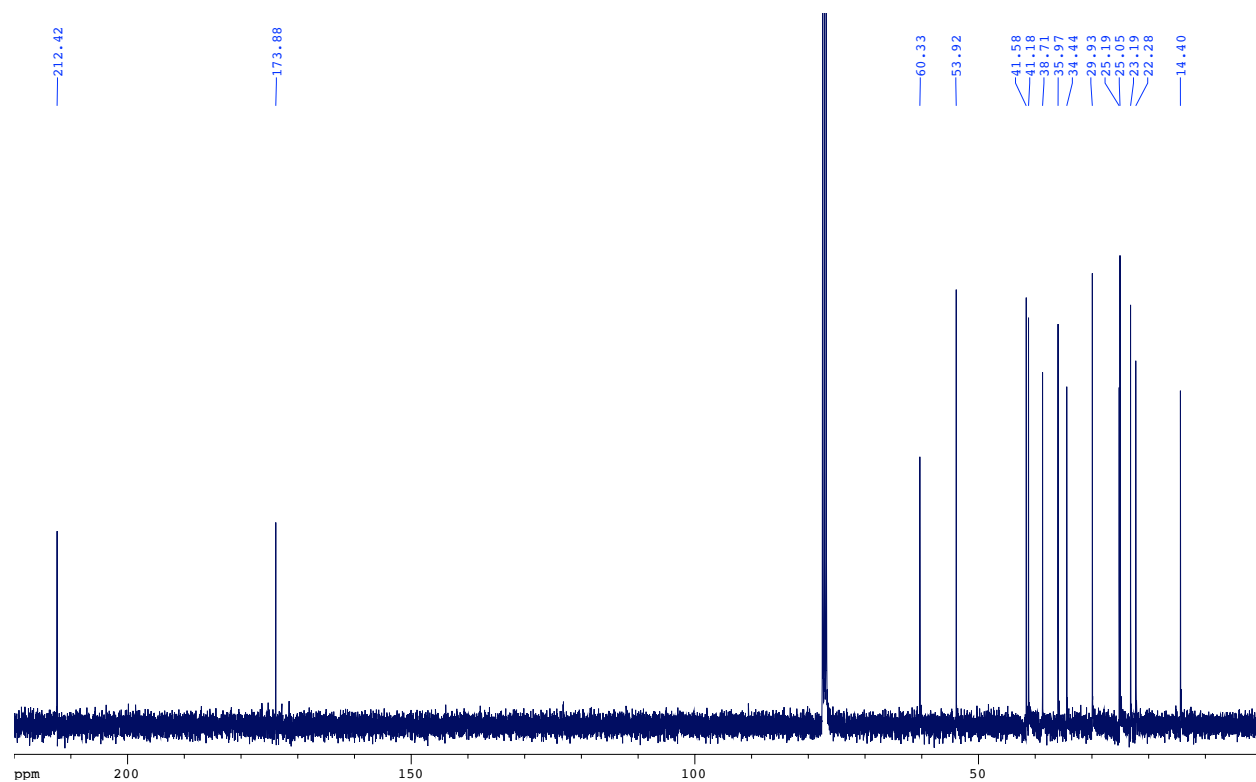


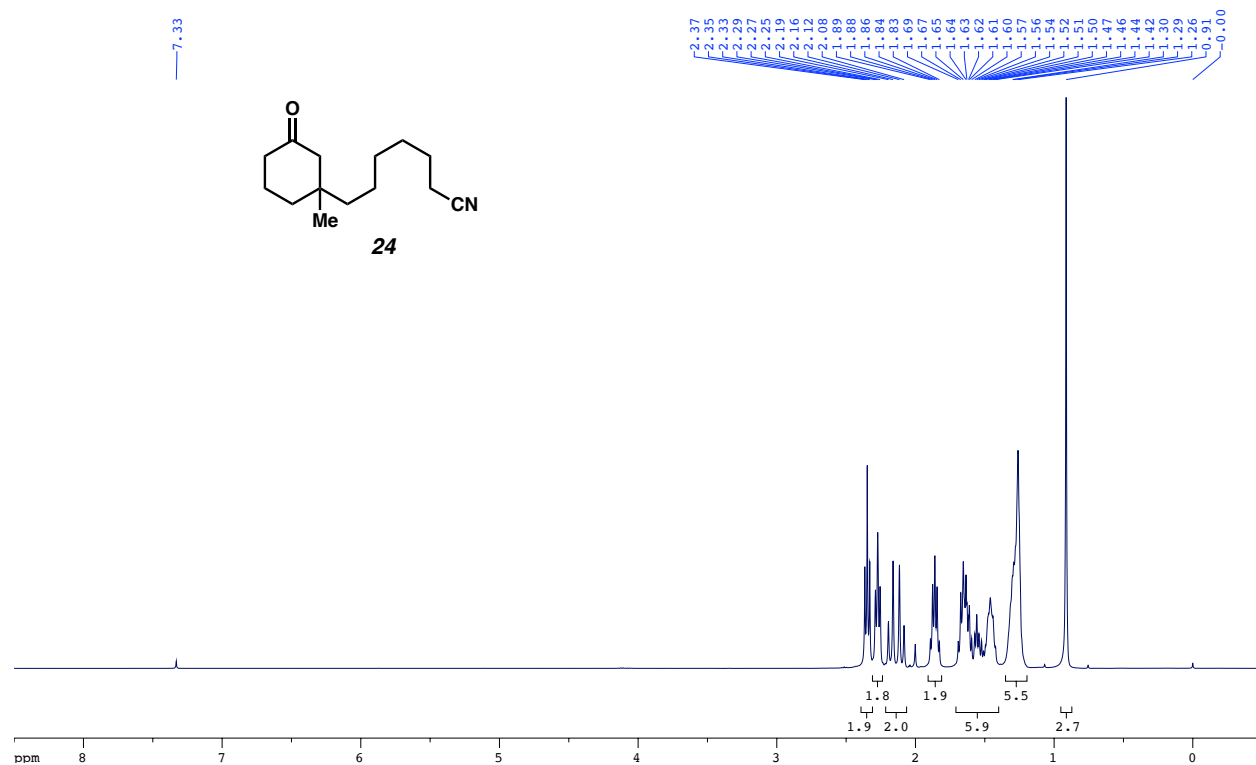
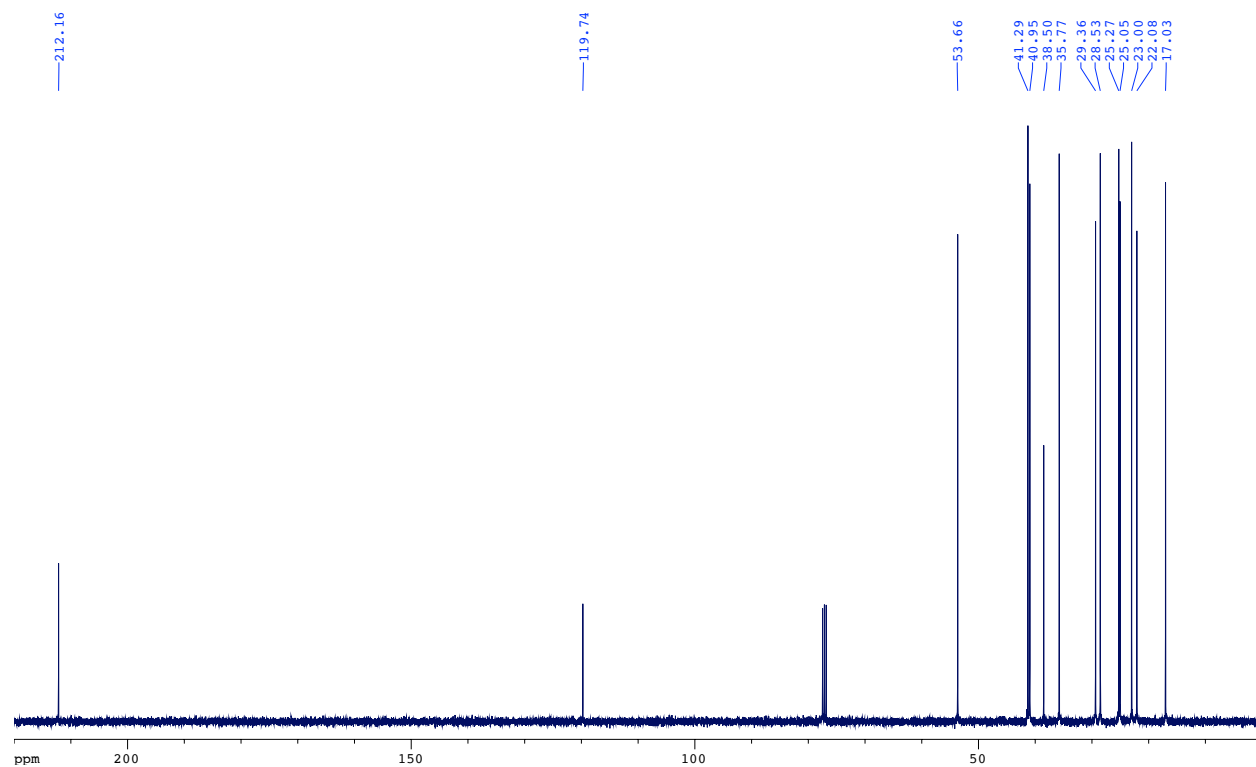
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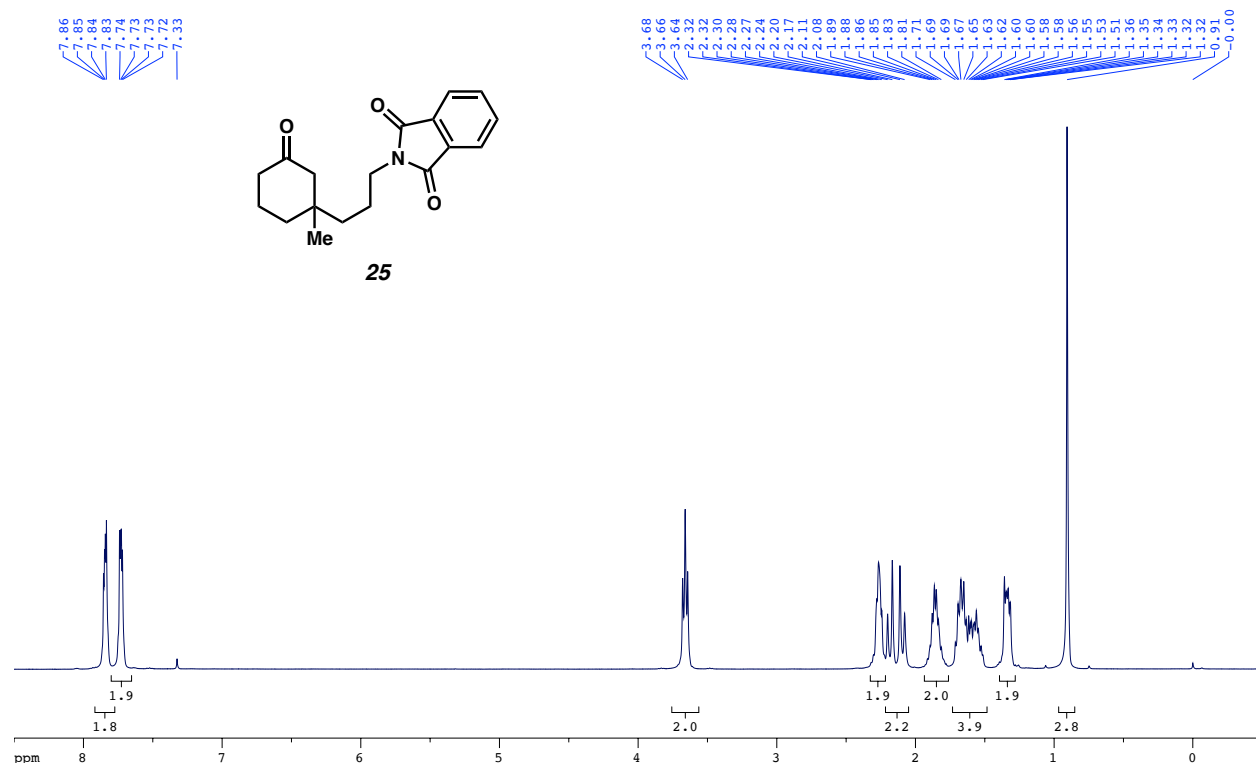
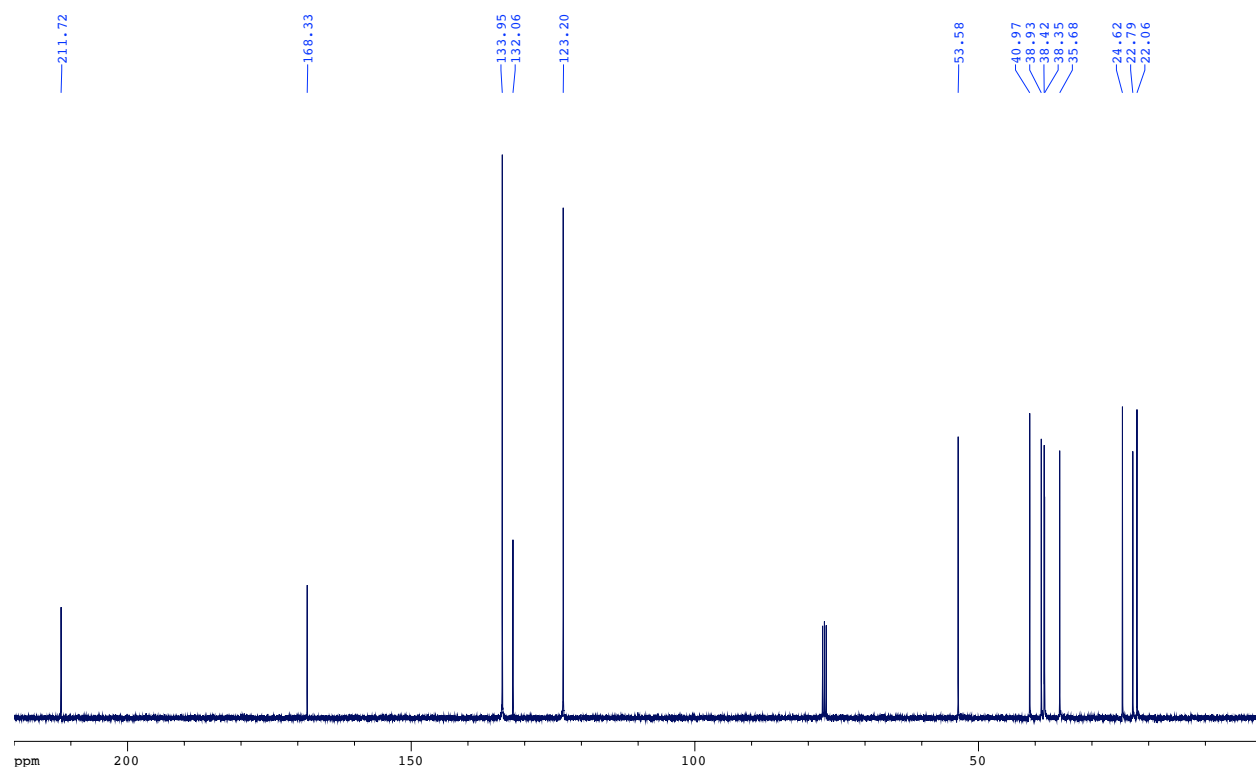
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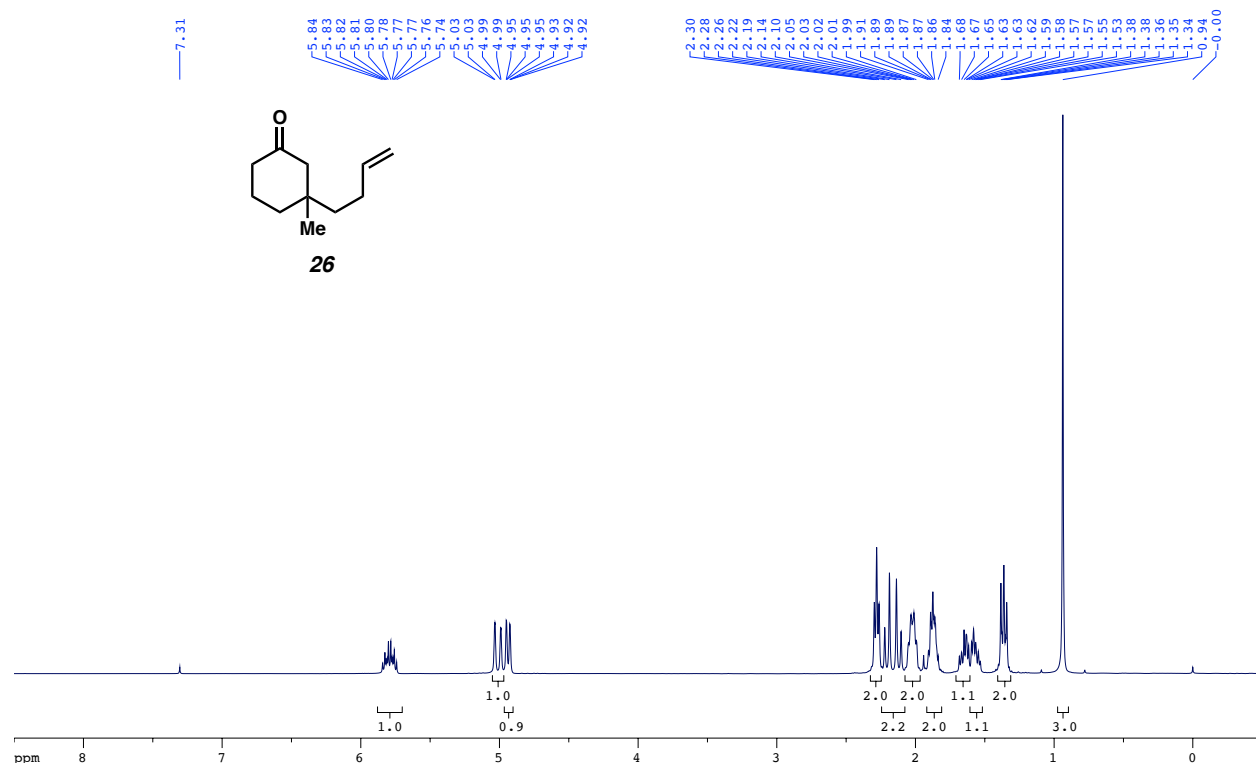
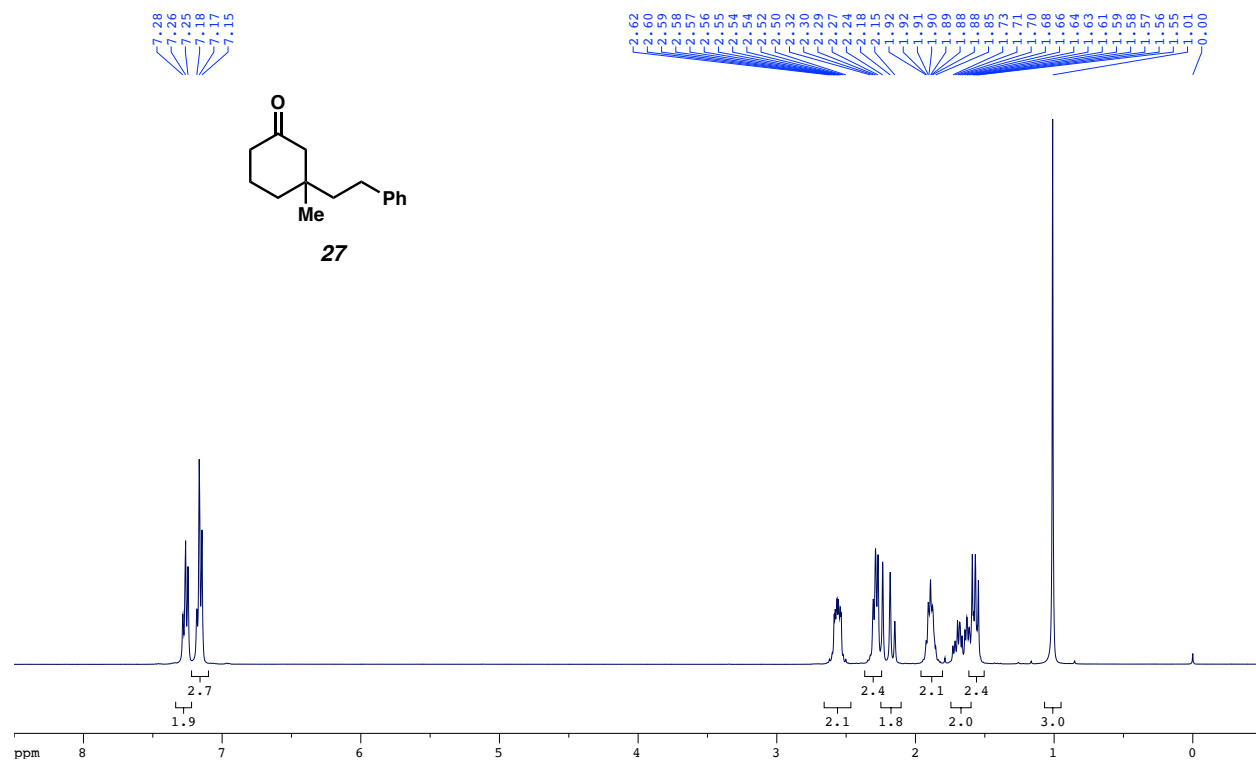
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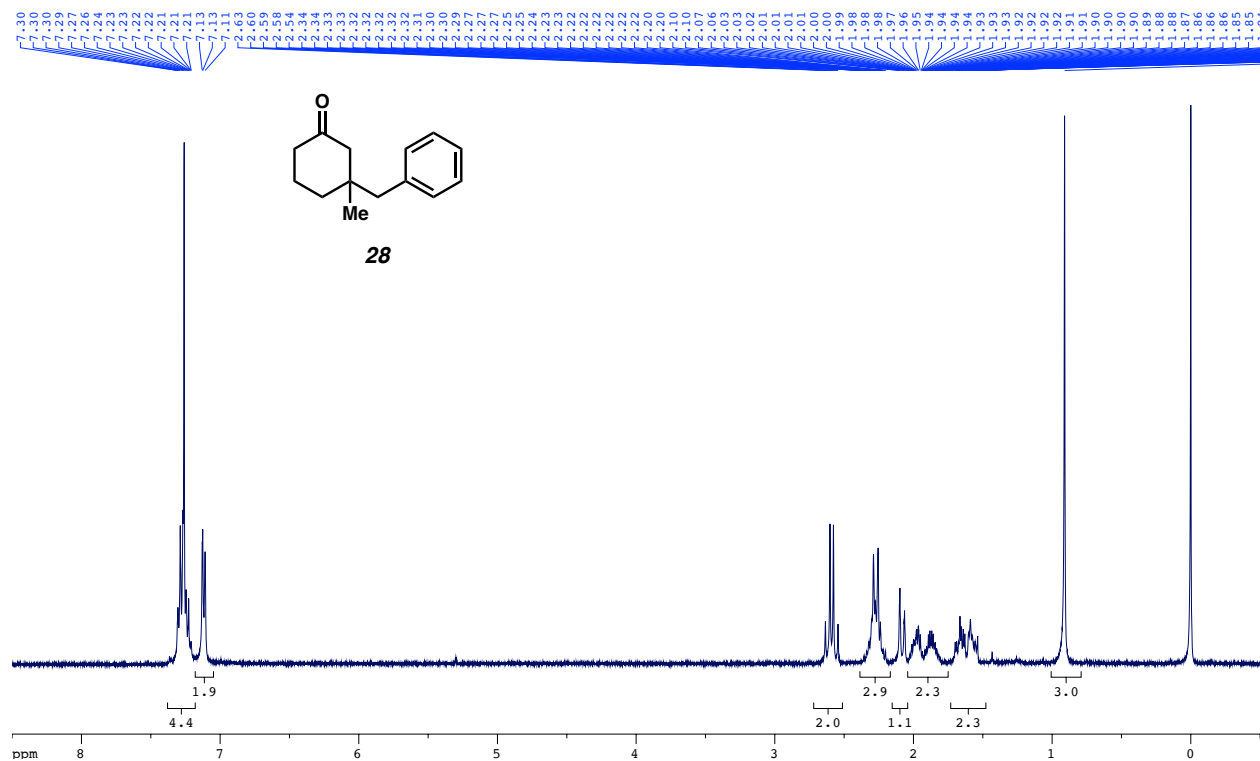
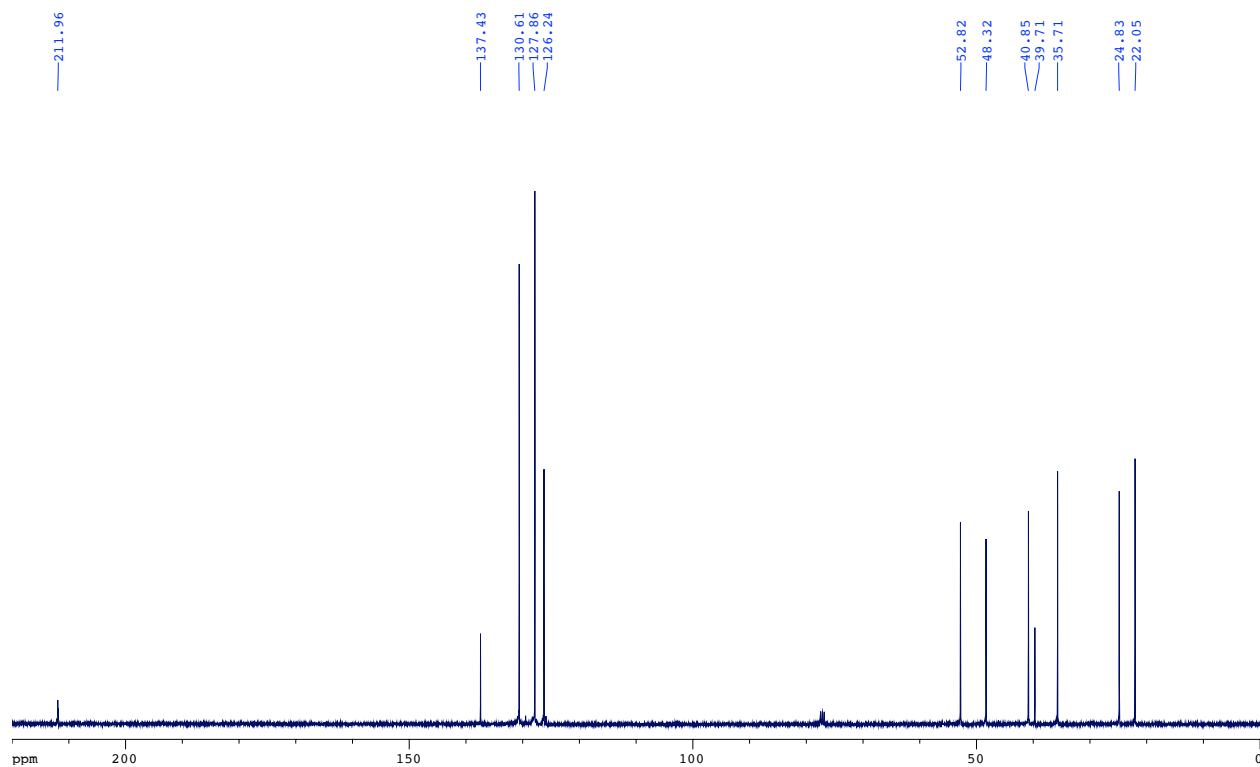
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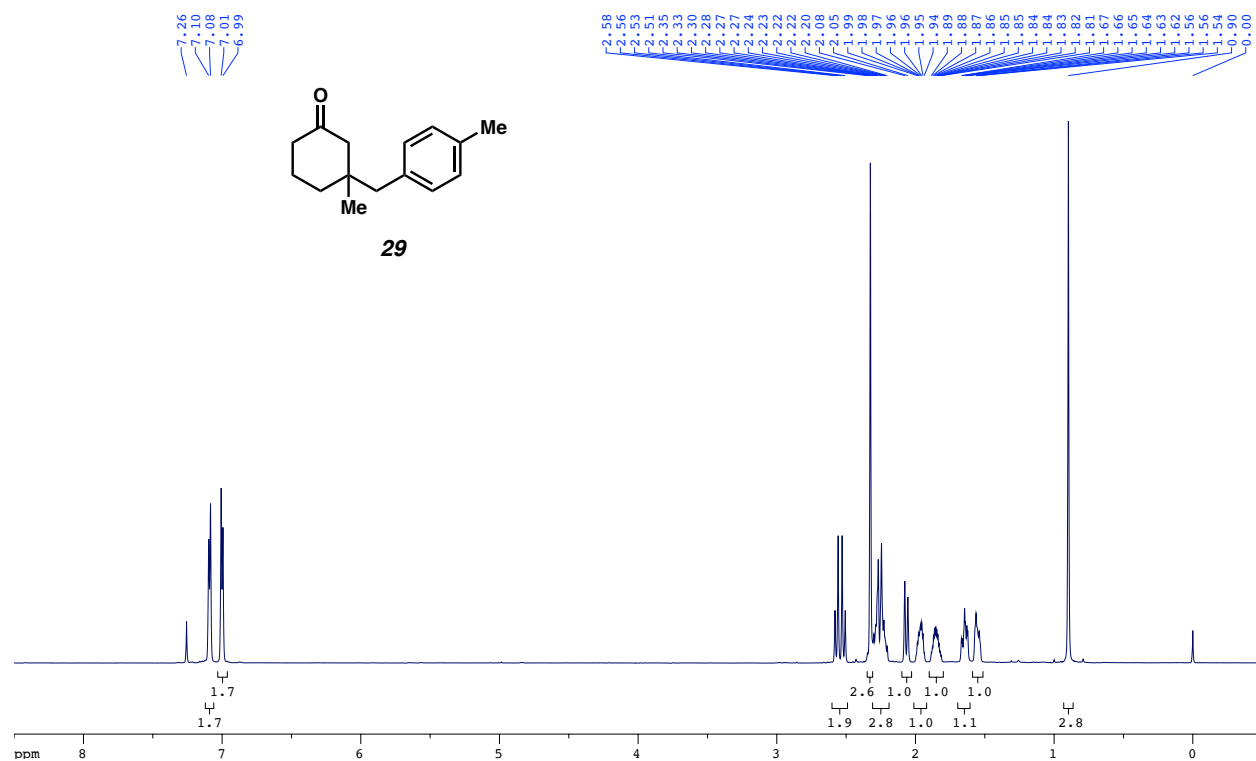
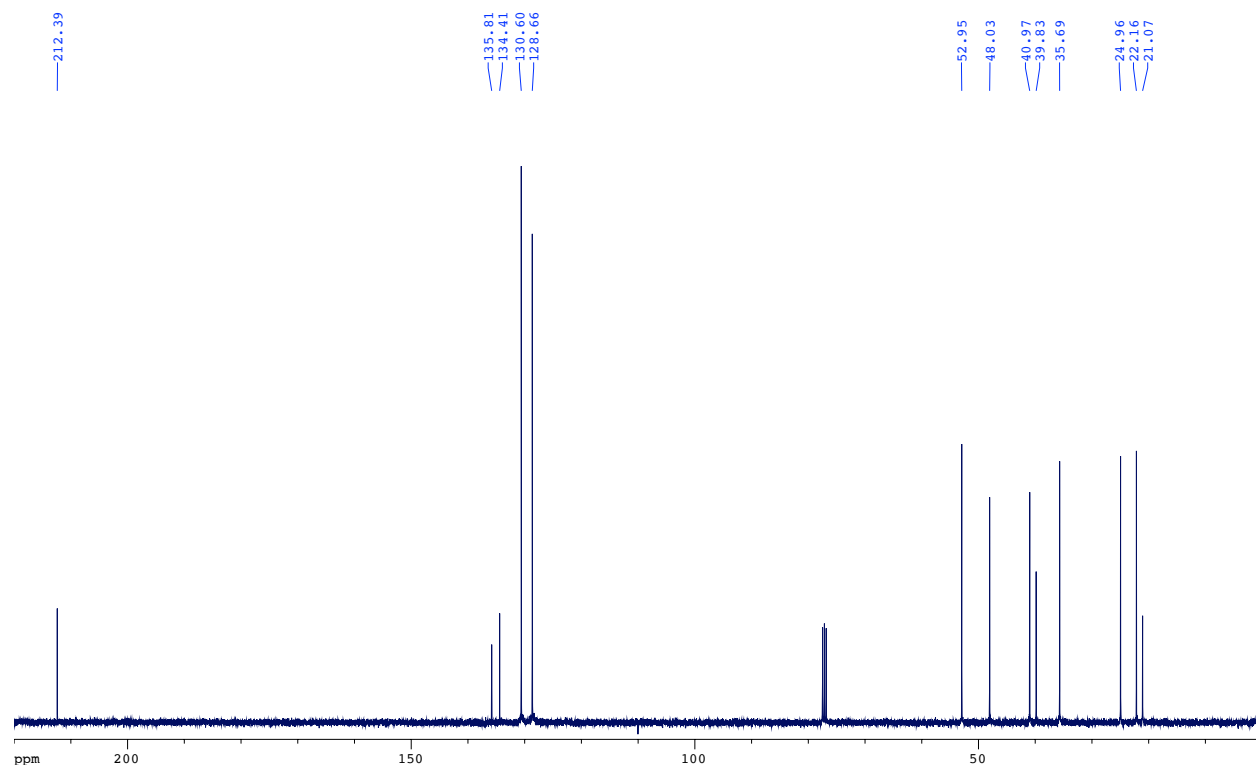
Figure S34.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **24**.Figure S35.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **24**.

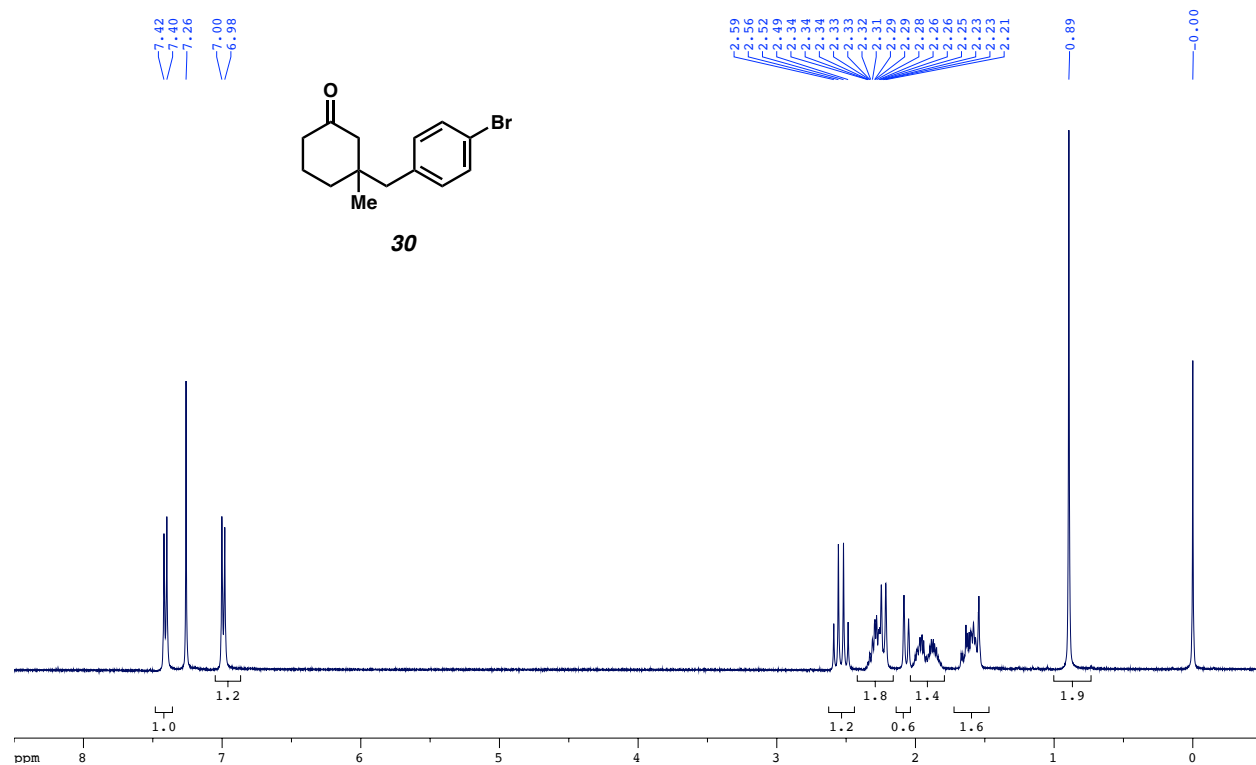
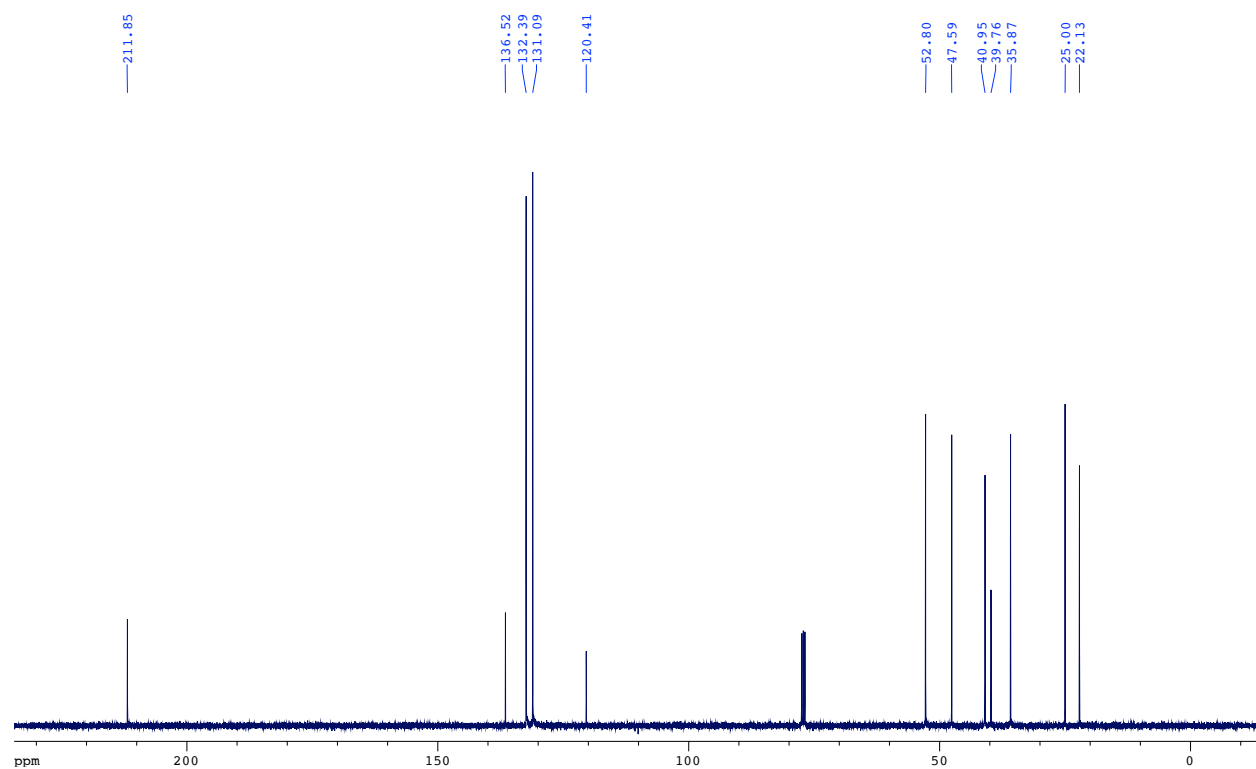
Figure S36.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **25**.Figure S37.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **25**.

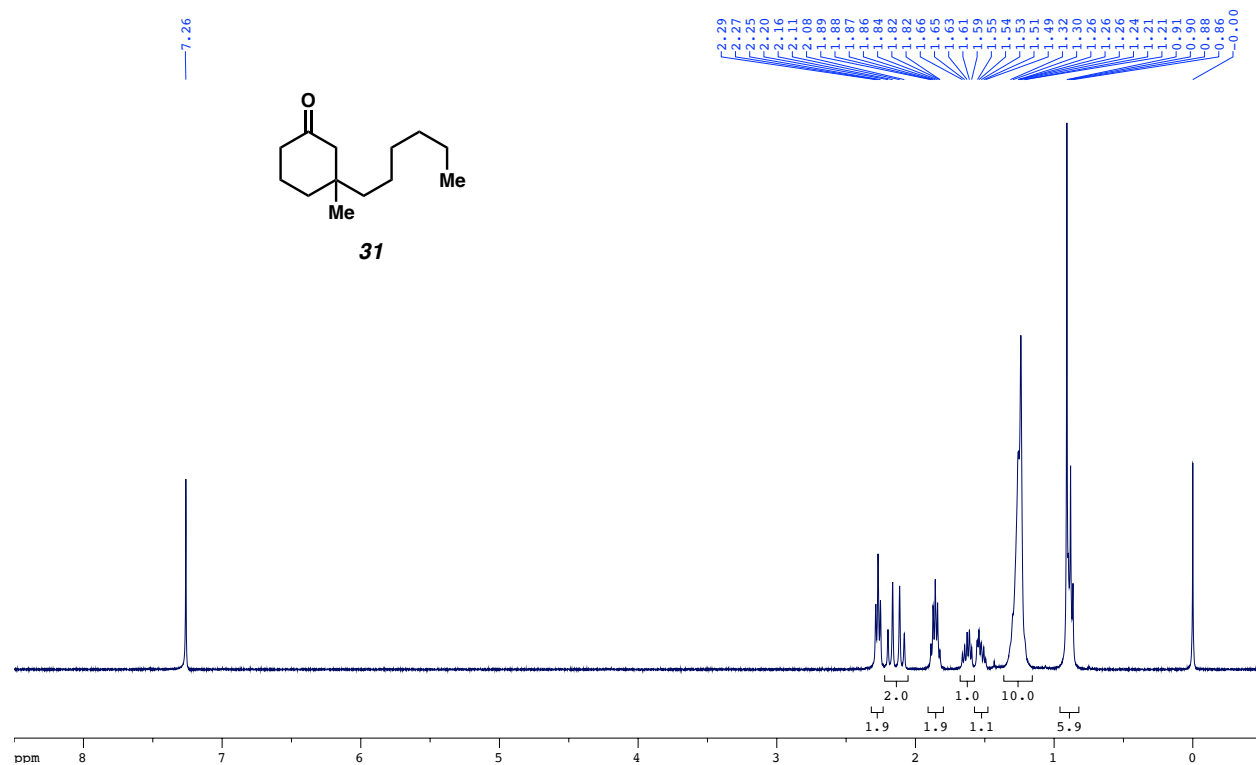
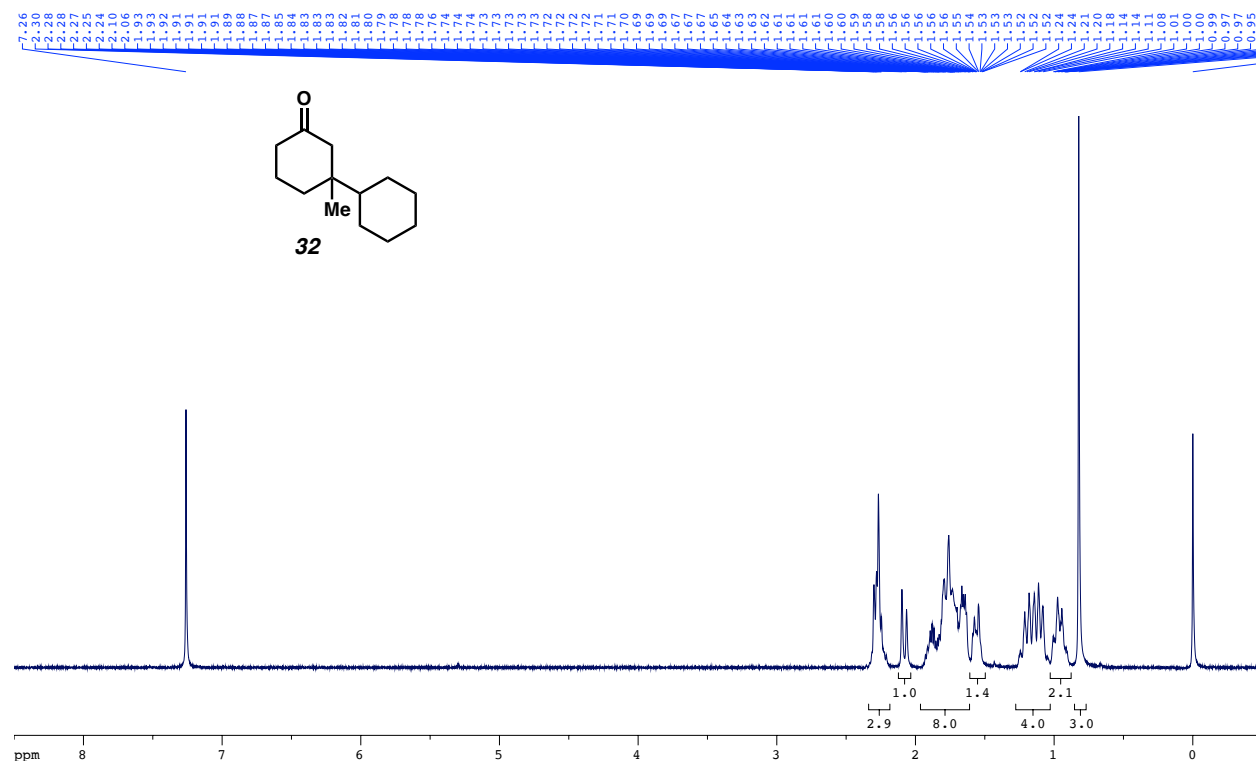
Figure S38. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **26**.Figure S39. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **27**.

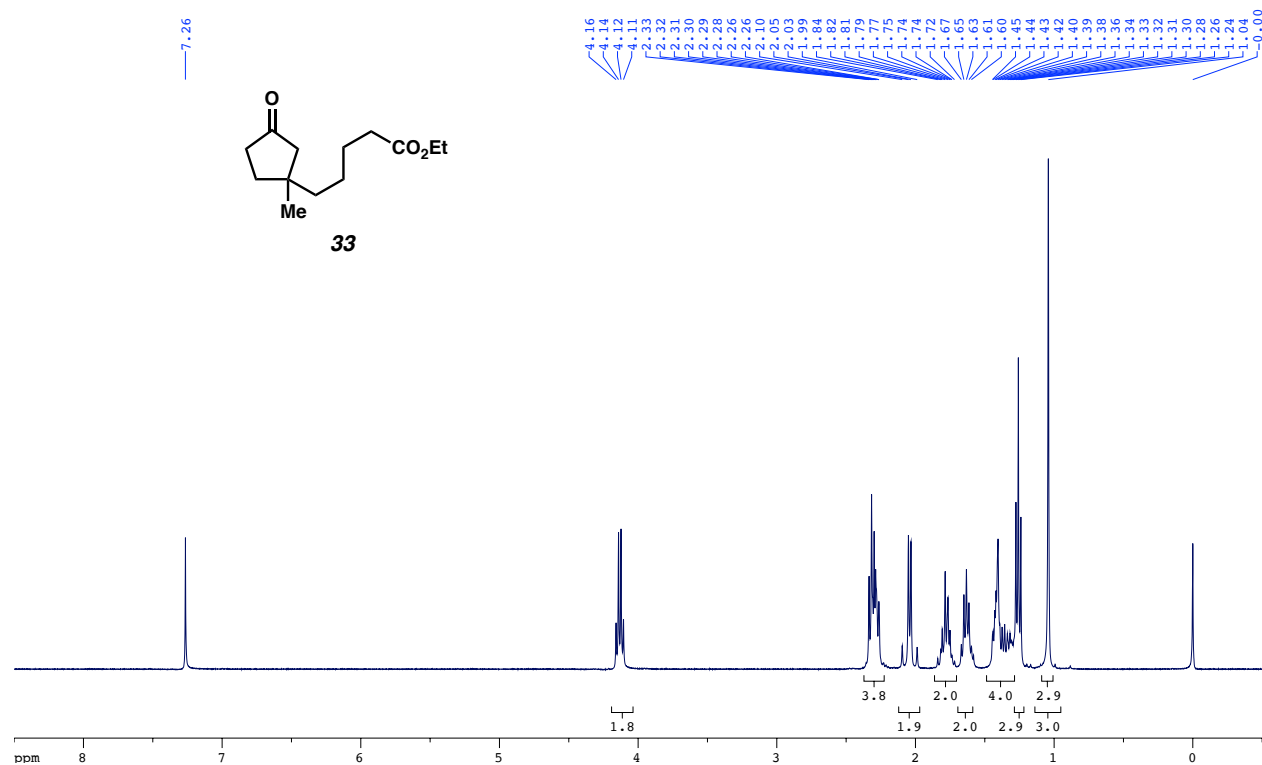
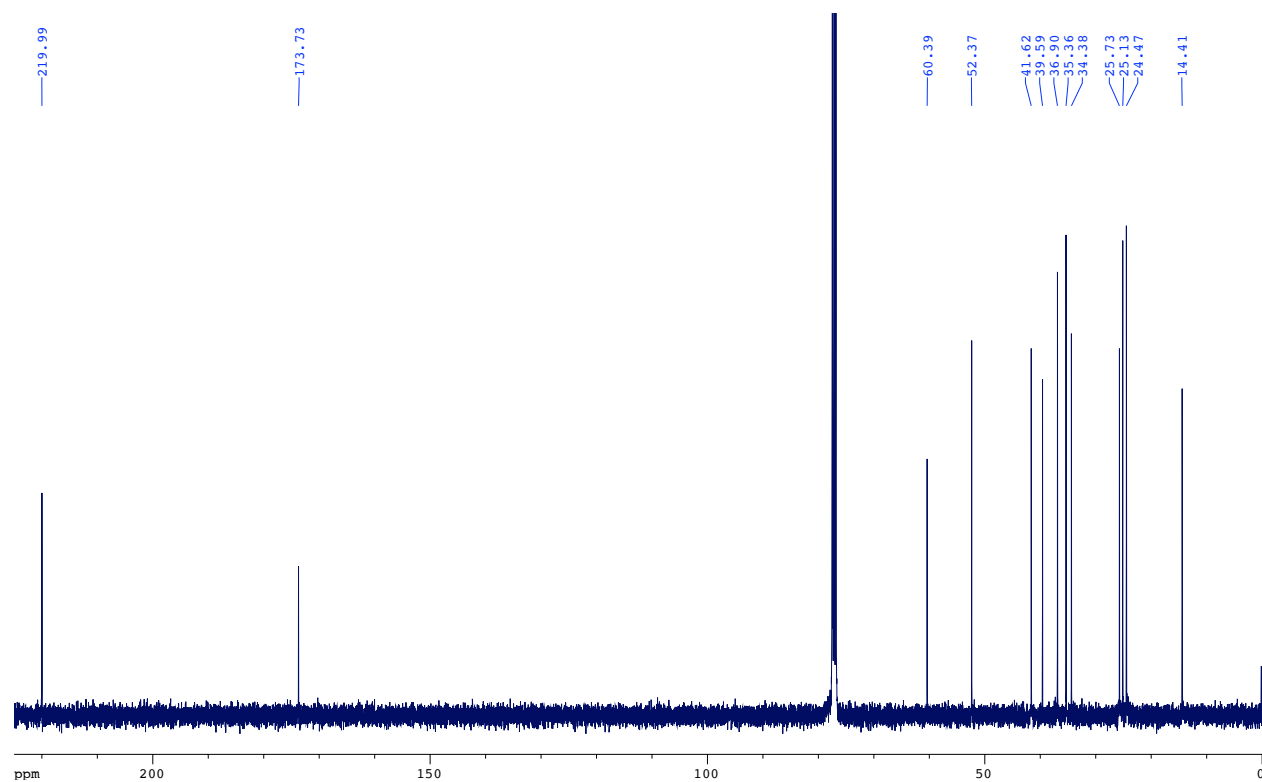


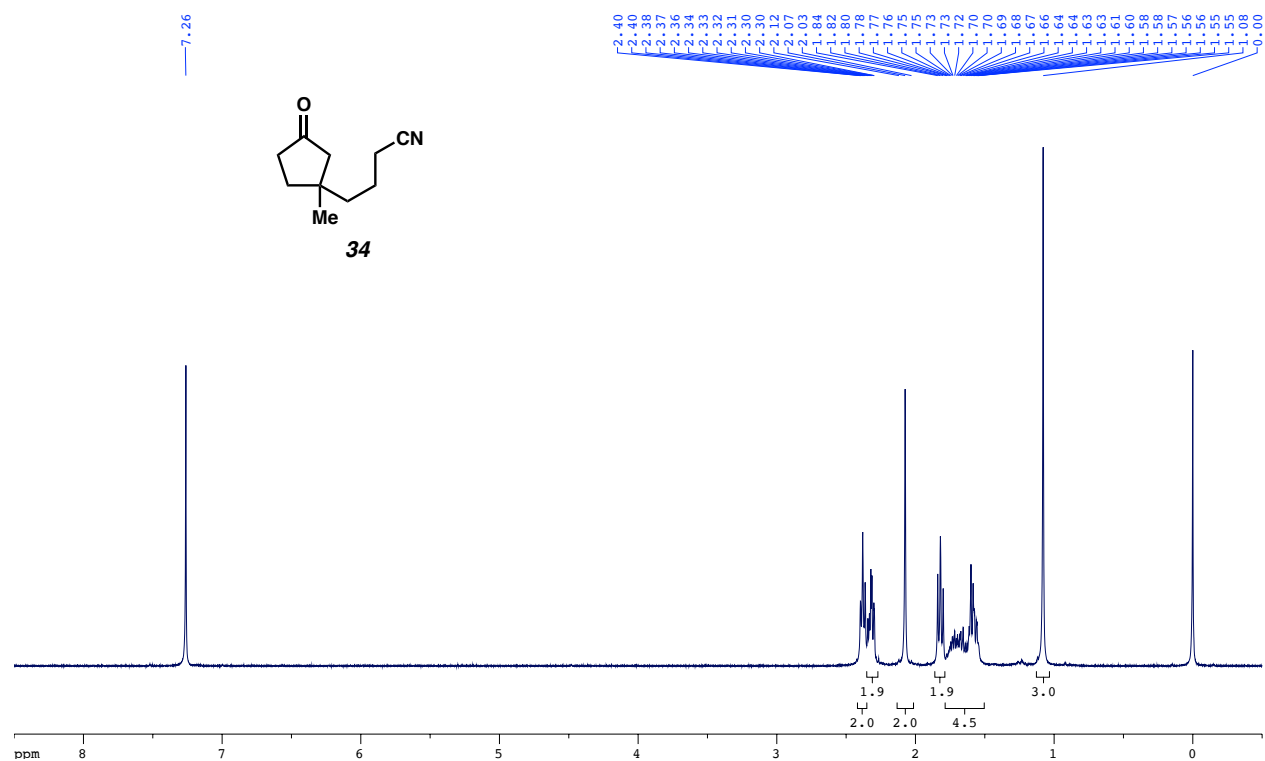
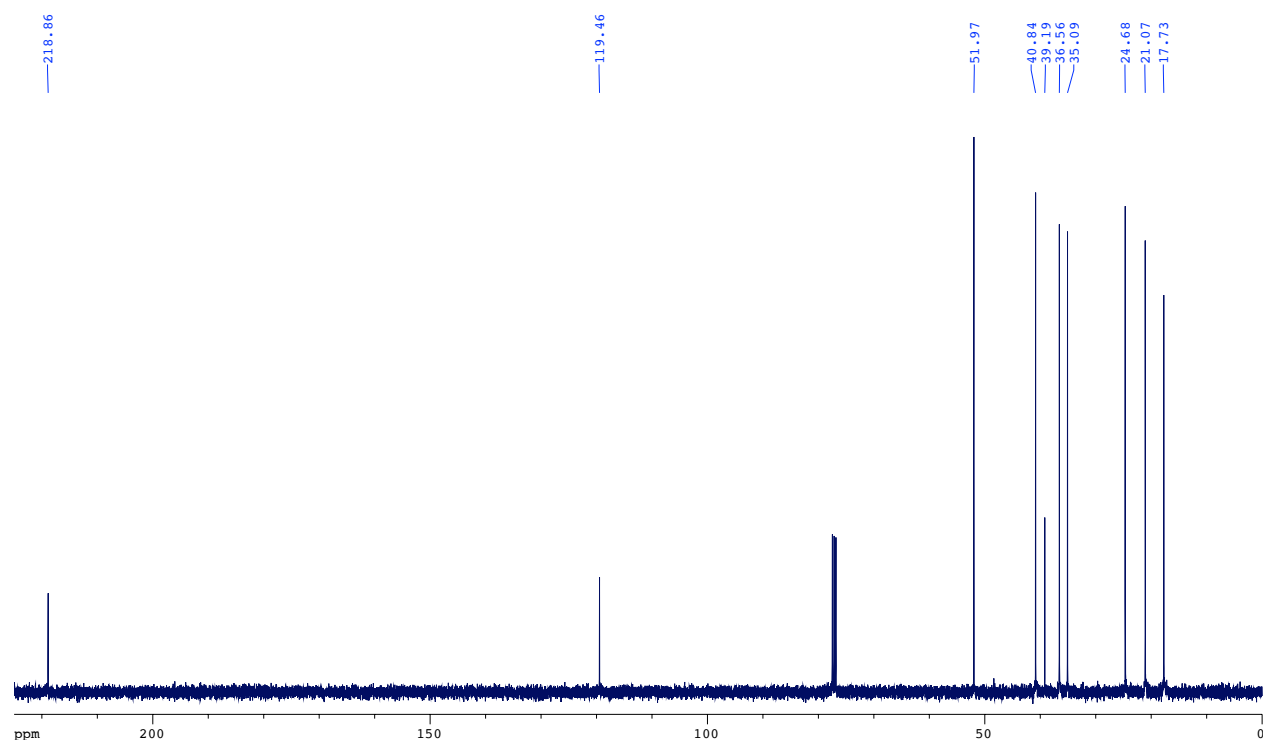
Figure S40. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **28**.Figure S41. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (101 MHz, CDCl<sub>3</sub>) of **28**.

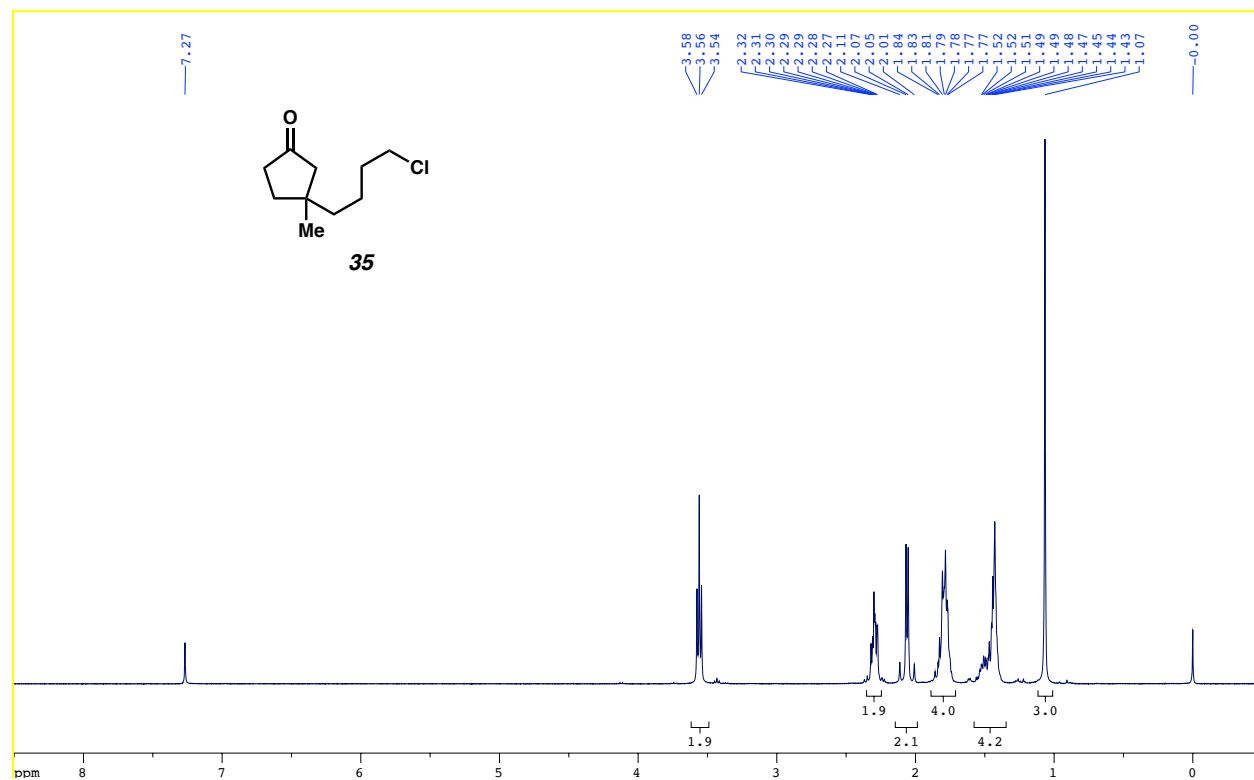
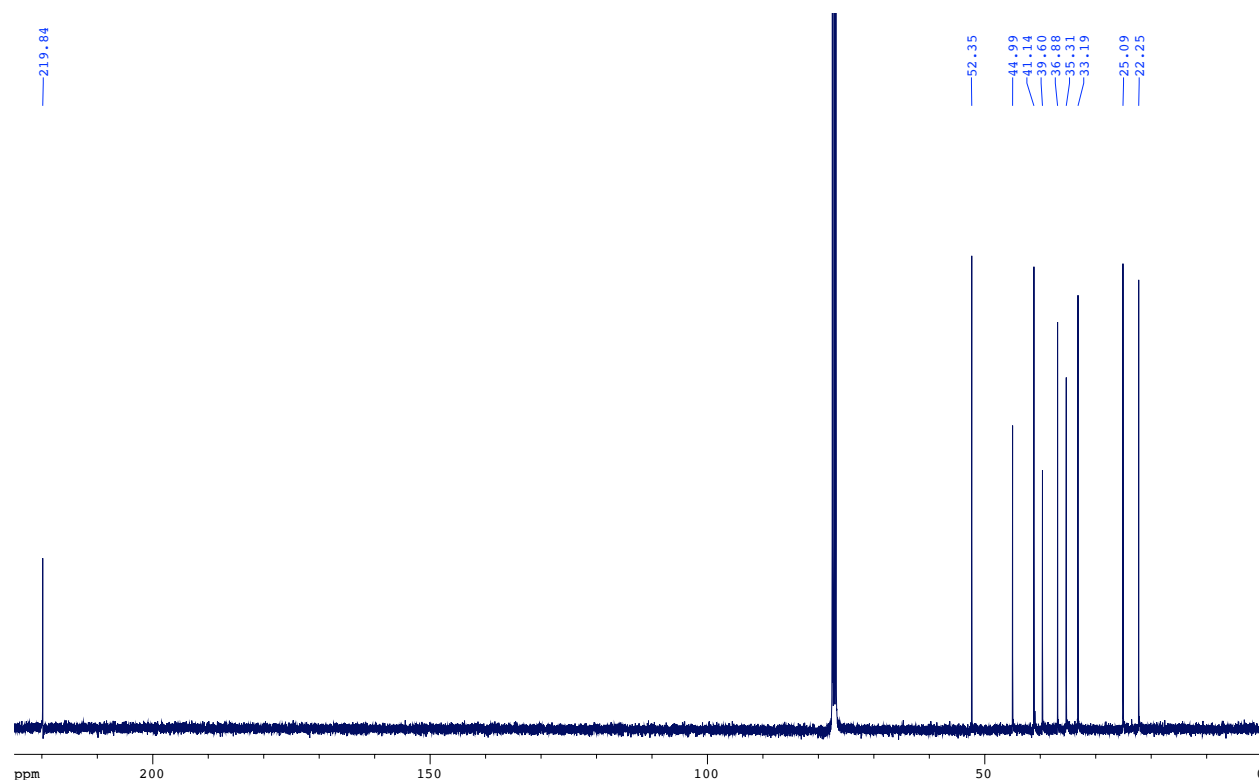
Figure S42.  $^1\text{H}$  NMR spectrum (600 MHz,  $\text{CDCl}_3$ ) of **29**.Figure S43.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **29**.

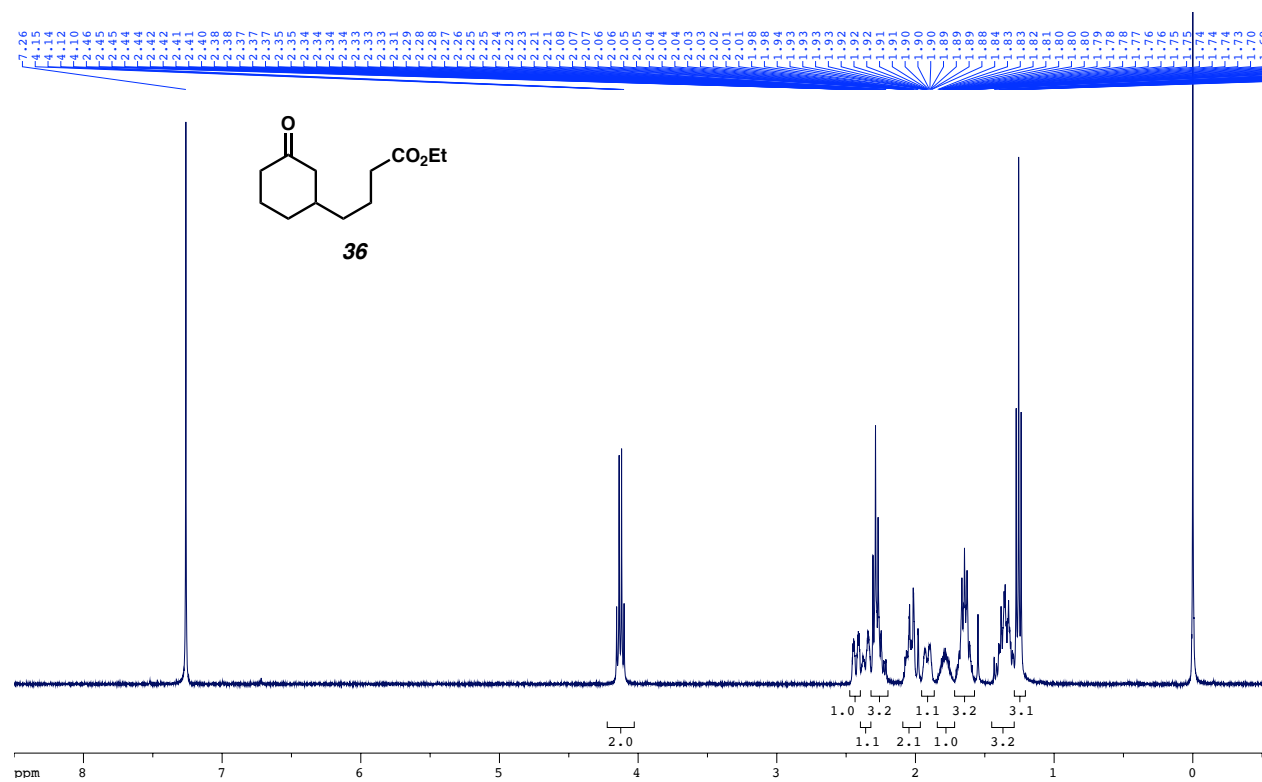
Figure S44.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **30**.Figure S45.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **30**.

Figure S46. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **31**.Figure S47. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of **32**.

Figure S48.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **33**.Figure S49.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **33**.

Figure S50.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **34**.Figure S51.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **34**.

Figure S52.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **35**.Figure S53.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of **35**.

Figure S54.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of **36**.