

## Supplementary Information

### **Metavanadate-mediated hydroxyl activation enhances reaction efficiency in the carboxylative cyclization of propargyl alcohol with CO<sub>2</sub>**

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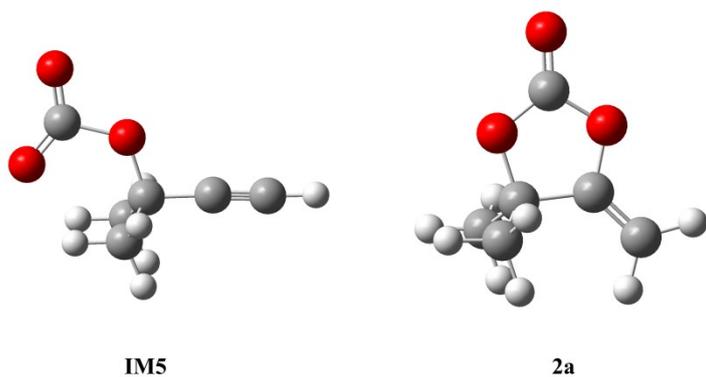
## Computational Method

DFT geometric and energy calculations were performed with Gaussian 16 C01.<sup>52</sup> TPSSH functional was used.<sup>53</sup> The def2-TZVP basis sets were used for the V and Ag atoms. The ma-def2-SVP basis sets were used for O and N. The def2-SVP basis sets were used for C and H.<sup>54</sup> Grimme's dispersion correction<sup>55</sup> with Becke-Johnson damping<sup>56</sup> was applied. Grimme's quasi-harmonic approximation<sup>57</sup> was applied to correct the entropy contribution from low-frequency vibrational modes to the Gibbs free energies. Implicit solvent corrections were applied by calculating single-point energies on the optimized gas phase geometries at the M05-2X<sup>58</sup>/6-31G\*<sup>59</sup> level with the Model based on Density (SMD).<sup>60</sup> 1-hexanol was selected as the continuum due to its similar molecular structure and dielectric constant with the reactant (which acts as the solvent). The electronic energies were further corrected with a single-point gas phase calculation at the wb97X2-D3BJ<sup>61</sup>/ma-def2-TZVPP level using ORCA 5.0.4.<sup>62</sup> Resolution of identity (RI) approximation was applied to accelerate the computation, and the def2-TZVPP/C auxiliary basis sets<sup>63</sup> were used. A  $-1.89$  kcal/mol molar correction on the Gibbs free energy was applied to each solvated species.

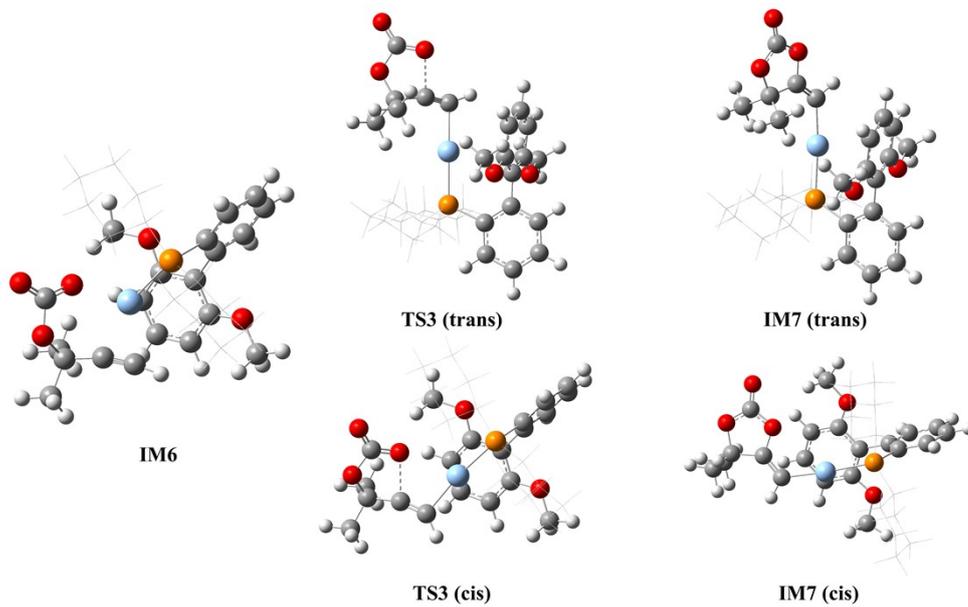
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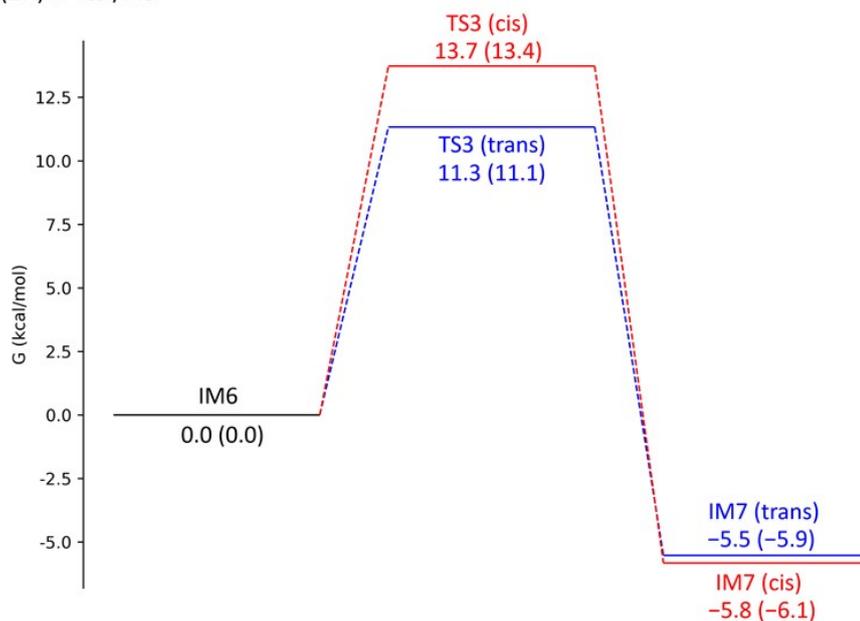


**Figure S1.** The DFT calculated structures of **IM5** and **2a**.



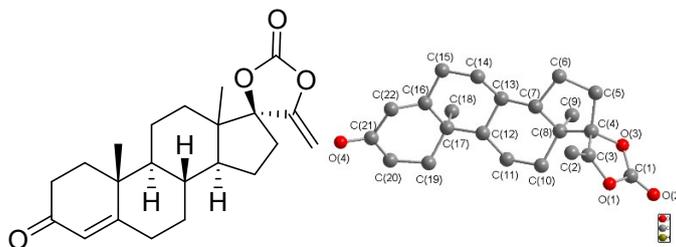
**Figure S2.** The DFT calculated structures of **IM6**, **TS3(trans)**, **TS3(cis)**, **IM7(trans)** and **IM7(cis)**.

$\omega$ B97X-2-D3/ma-def2-TZVPP//TPSSh-D3/def2-TZVP for Ag, ma-def2-SVP for O, def2-SVP for P, C, H  
 $\Delta G$  ( $\Delta H$ ) in kcal/mol



**Figure S3.** DFT calculated reaction energy profile for the Ag-catalyzed ring formation step. **IM6**: the structure of carbonate-Ag/Sphos complex. **TS3(trans)** and **TS3(cis)**: the trans/cis transition states from **IM6** to **IM7**. **IM7(trans)** and **IM7(cis)**: the trans/cis isomers of silver-substituted alkene structure. The DFT calculated structures of **IM6**, **TS3(trans)**, **TS3(cis)**, **IM7(trans)** and **IM7(cis)** are depicted in Figure S2.

### 1. The crystallographic information of **5a**.



**Table S1.** Crystal data and structure refinement.

Entry	
Empirical formula	C <sub>22</sub> H <sub>28</sub> O <sub>4</sub>
Formula weight	356.44
Space group	P 1 21 1(4)

$a$ , Å	8.1152(16)
$b$ , Å	10.943(2)
$c$ , Å	10.445(2)
$\alpha$ , deg	90
$\beta$ , deg	92.743(7)
$\gamma$ , deg	90
$V$ , Å <sup>3</sup>	926.5(3)
$Z$	2
temp, K	293
$\lambda$ (Mo $K\alpha$ ), Å	0.71073
$D$ , g cm <sup>-3</sup>	1.278

*Final R indices [I > 2sigma(I)]* R1 = 0.0465, wR2 = 0.1070

*R indices (all data)* R1 = 0.0602, wR2 = 0.1157

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**Table S2.** Bond lengths [Å] and angles [deg].

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Entry	Bond Distances (Å)
O1—C1	1.361(4)
O1—C3	1.390(4)
O2—C1	1.184(4)
O3—C1	1.335(4)
O3—C4	1.464(3)
O4—C21	1.220(4)

C2—C3	1.317(5)
C3—C4	1.506(4)
C4—C5	1.541(4)
C4—C8	1.553(4)
C5—C6	1.543(4)
C6—C7	1.532(4)
C7—C8	1.546(4)
C7—C13	1.529(4)
C8—C9	1.543(4)
C8—C10	1.521(4)
C10—C11	1.539(4)
C11—C12	1.543(4)
C12—C13	1.543(4)
C12—C17	1.563(3)
C13—C14	1.529(4)
C14—C15	1.523(4)
C15—C16	1.495(5)
C16—C17	1.523(4)
C16—C22	1.350(4)
C17—C18	1.549(4)
C17—C19	1.532(4)
C19—C20	1.517(4)
C20—C21	1.495(5)
C21—C22	1.457(5)

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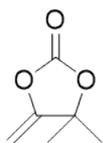
Entry	Bond Angles (°)
C1—O1—C3	109.0(2)
C1—O3—C4	110.4(2)
O2—C1—O1	123.6(3)
O2—C1—O3	125.9(3)
O3—C1—O1	110.5(3)
O1—C3—C4	106.8(3)
C2—C3—O1	121.0(3)
C2—C3—C4	132.2(3)
O3—C4—C3	100.7(2)
O3—C4—C5	112.1(2)
O3—C4—C8	110.7(2)
C3—C4—C5	113.6(3)
C3—C4—C8	116.4(2)
C5—C4—C8	103.7(2)
C4—C5—C6	105.7(2)
C7—C6—C5	104.7(2)
C6—C7—C8	104.1(2)
C13—C7—C6	119.1(2)
C13—C7—C8	113.8(2)
C7—C8—C4	98.6(2)
C9—C8—C4	108.5(2)
C9—C8—C7	112.7(2)
C10—C8—C4	116.9(2)

C10—C8—C7	108.9(2)
C10—C8—C9	110.8(3)
C8—C10—C11	109.8(2)
C10—C11—C12	113.0(2)
C11—C12—C17	113.4(2)
C13—C12—C11	112.5(2)
C13—C12—C17	112.6(2)
C7—C13—C12	108.8(2)
C7—C13—C14	110.1(2)
C14—C13—C12	109.0(2)
C15—C14—C13	112.0(3)
C16—C15—C14	112.8(3)
C15—C16—C17	117.2(2)
C22—C16—C15	120.5(3)
C22—C16—C17	122.3(3)
C16—C17—C12	108.3(2)
C16—C17—C18	108.3(2)
C16—C17—C19	109.7(2)
C18—C17—C12	111.6(2)
C19—C17—C12	108.6(2)
C19—C17—C18	110.3(3)
C20—C19—C17	113.9(3)
C21—C20—C19	111.6(3)
O4—C21—C20	122.5(3)

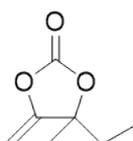
O4—C21—C22	121.4(3)
C22—C21—C20	116.0(3)
C16—C22—C21	124.1(3)

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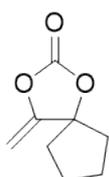
## 2. Characterization Data for Substrates and Products:



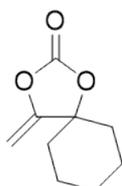
**4,4-dimethyl-5-methylene-1,3-dioxolan-2-one (2a):** colorless liquid, 92.7% yield. IR: 1823, 1683, 1264, 1090 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.76 (d, *J* = 4.0 Hz, 1H), 4.33 (d, *J* = 3.9 Hz, 1H), 1.61 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.71, 151.28, 85.31, 84.67, 27.54. HRMS (ESI): calcd. for C<sub>6</sub>H<sub>8</sub>O<sub>3</sub>: 128.0468 [M<sup>+</sup>]; found: 128.0470.



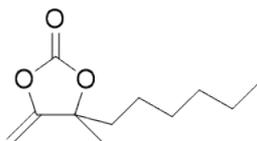
**4-ethyl-4-methyl-5-methylene-1,3-dioxolan-2-one (2b):** colorless liquid, 84.4% yield. IR: 1830, 1687, 1233 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.79 (d, *J* = 3.9 Hz, 1H), 4.26 (d, *J* = 3.9 Hz, 1H), 1.94 – 1.84 (m, 1H), 1.79 – 1.70 (m, 1H), 1.57 (s, 3H), 0.97 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 157.53, 151.66, 87.70, 85.68, 33.49, 26.06, 7.43. HRMS (ESI): calcd for C<sub>7</sub>H<sub>10</sub>NaO<sub>3</sub> [M + Na]<sup>+</sup>: 165.0528, found: 165.0530.



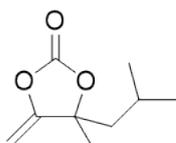
**4-methylene-1,3-dioxaspiro [4.4] nonan-2-one (2c):** colorless liquid, 87.2% yield. IR: 1833, 1687 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.79 (d, *J* = 3.9 Hz, 1H), 4.35 (d, *J* = 4.0 Hz, 1H), 2.28 – 2.18 (m, 2H), 1.99 – 1.79 (m, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 157.75, 151.49, 94.24, 85.36, 40.66, 24.26.



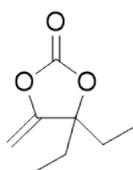
**4-methylene-1,3-dioxaspiro [4.5] decan-2-one (2d):** colorless liquid, 83% yield. IR: 1832, 1686 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.77 (d, *J* = 3.8 Hz, 1H), 4.30 (d, *J* = 3.9 Hz, 1H), 2.02 (d, *J* = 12.0 Hz, 2H), 1.73 – 1.58 (m, 6H), 1.39 – 1.27 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 158.75, 151.51, 86.42, 85.51, 36.52, 24.36, 21.62.



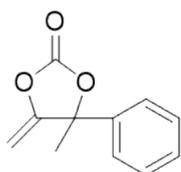
**4-methyl-5-methylene-4-phenyl-1,3-dioxolan-2-one(2e):** yellow liquid, 83%. IR: 1830, 1685, 1233  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.80 (d,  $J = 3.9$  Hz, 1H), 4.28 (d,  $J = 3.9$  Hz, 1H), 1.87 (ddd,  $J = 14.5, 11.1, 5.2$  Hz, 1H), 1.71 (ddd,  $J = 14.5, 11.3, 4.4$  Hz, 1H), 1.45 – 1.35 (m, 2H), 1.31 (dtdd,  $J = 12.6, 9.4, 6.8, 3.0$  Hz, 6H), 0.94 – 0.85 (m, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  157.79, 87.28, 85.46, 40.42, 31.48, 28.91, 26.31, 22.90, 22.46, 13.98 .



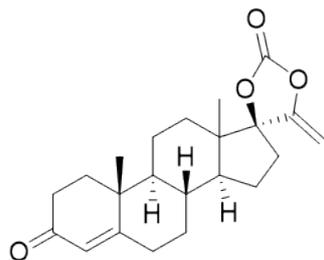
**4-hexyl-4-methyl-5-methylene-1,3-dioxolan-2-one (2f):** colorless liquid, 86.7% yield. IR: 1830, 1688, 1235  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.80 (d,  $J = 3.9$  Hz, 1H), 4.28 (d,  $J = 3.9$  Hz, 1H), 1.91 – 1.77 (m, 2H), 1.71 – 1.63 (m, 1H), 1.59 (s, 3H), 0.98 (dd,  $J = 6.5, 3.6$  Hz, 6H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.32, 87.34, 85.59, 48.53, 27.01, 24.29, 23.98, 23.68.



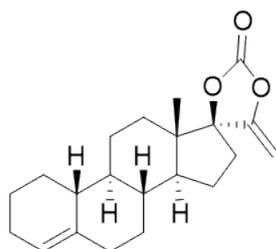
**4-isobutyl-4-methyl-5-methylene-1,3-dioxolan-2-one (2g):** colorless liquid, 85.7% yield. IR: 1834, 1689, 1234  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.87 (d,  $J = 3.9$  Hz, 1H), 4.24 (d,  $J = 3.8$  Hz, 1H), 1.94 (dq,  $J = 14.7, 7.3$  Hz, 2H), 1.73 (dq,  $J = 14.7, 7.4$  Hz, 2H), 0.99 (t,  $J = 7.4$  Hz, 6H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.78, 151.87, 90.87, 85.82, 31.90, 7.11.



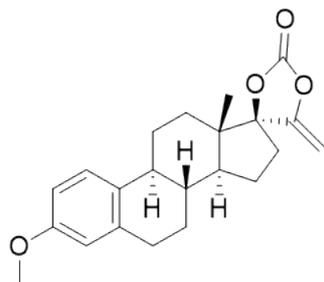
**4,4-diethyl-5-methylene-1,3-dioxolan-2-one (2h):** colorless liquid, 88.5% yield. IR : 1830, 1687, 1580, 1230  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 – 7.48 (m, 2H), 7.48 – 7.37 (m, 3H), 4.97 (dd,  $J = 4.0, 0.7$  Hz, 1H), 4.49 (dd,  $J = 4.0, 0.7$  Hz, 1H), 2.00 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  157.48, 139.26, 129.20, 128.94, 124.71, 88.19, 87.16, 27.52.



**3a:** white solid, 94% yield. IR: 2970, 1820, 1679, 1458, 1291, 1037, 1027, 864  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.77 – 5.70 (m, 1H), 4.94 (d,  $J = 3.9$  Hz, 1H), 4.36 (d,  $J = 3.9$  Hz, 1H), 2.50 – 2.41 (m, 2H), 2.41 – 2.35 (m, 2H), 2.35 – 2.24 (m, 1H), 2.21 – 1.99 (m, 2H), 1.91 (dtd,  $J = 11.3, 5.5, 4.5, 2.6$  Hz, 1H), 1.84 – 1.23 (m, 10H), 1.21 (s, 3H), 1.18 – 1.02 (m, 4H), 0.95 (tdd,  $J = 10.9, 8.8, 5.4$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.25, 157.74, 124.14, 96.76, 89.16, 53.12, 48.53, 47.34, 38.52, 35.67, 35.62, 34.22, 33.89, 32.53, 31.44, 30.99, 22.95, 20.24, 17.40, 14.30. HRMS (ESI): 356.1988, calcd. for  $\text{C}_{22}\text{H}_{28}\text{NaO}_4^+$   $[\text{M}+\text{Na}]^+$ : 379.1881.

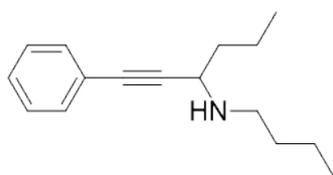


**3b:** white solid, 91%. IR: 2972, 1821, 1681, 1502, 1030, 868  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.75 (d,  $J = 8.0$  Hz, 1H), 5.41 (t,  $J = 1.9$  Hz, 1H), 3.01 – 2.75 (m, 2H), 2.31 – 2.17 (m, 1H), 2.13 – 1.81 (m, 8H), 1.81 – 1.65 (m, 3H), 1.53 – 1.19 (m, 7H), 1.18 – 1.08 (m, 2H), 0.90 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  192.33, 139.88, 120.35, 119.36, 52.19, 50.30, 46.70, 41.93, 40.62, 35.38, 34.92, 31.90, 28.78, 27.64, 26.08, 25.45, 24.13, 22.05, 18.21. HRMS (ESI): 328.2038, calcd. for  $\text{C}_{21}\text{H}_{28}\text{NaO}_3^+$   $[\text{M}+\text{Na}]^+$ : 351.1932.

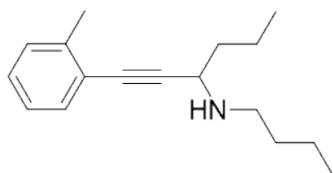


**3c:** white solid, 83% yield. IR: 2979, 1825, 1681, 1562, 1052, 878  $\text{cm}^{-1}$ . NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.93 (d,  $J = 7.9$  Hz, 1H), 7.24 (d,  $J = 8.6$  Hz, 1H), 6.75 (dd,  $J = 8.6, 2.8$  Hz, 1H), 6.67 (d,  $J = 2.8$

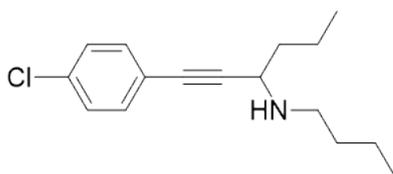
Hz, 1H), 5.84 (d,  $J = 8.3$  Hz, 1H), 3.81 (s, 3H), 3.08 – 2.94 (m, 2H), 2.92 (d,  $J = 7.2$  Hz, 1H), 2.36 (d,  $J = 56.9$  Hz, 2H), 2.14 – 1.90 (m, 3H), 1.56 (td,  $J = 12.1, 10.9, 6.7$  Hz, 5H), 1.44 – 1.34 (m, 1H), 0.94 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  192.32, 180.06, 157.60, 137.81, 132.13, 126.32, 119.45, 113.88, 111.58, 55.23, 52.20, 46.80, 43.90, 38.50, 34.96, 29.77, 27.76, 27.61, 26.44, 24.04, 18.25. HRMS (ESI): 354.1831, calcd. for  $\text{C}_{22}\text{H}_{26}\text{NaO}_4^+$   $[\text{M}+\text{Na}]^+$ : 377.1728.



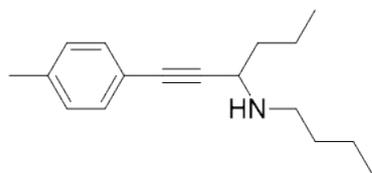
**N-butyl-1-phenylhex-1-yn-3-amine(4a):** yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 – 7.41 (m, 2H), 7.31 (dd,  $J = 5.0, 2.0$  Hz, 3H), 3.61 (dd,  $J = 7.9, 5.7$  Hz, 1H), 2.95 (ddd,  $J = 11.2, 8.3, 6.4$  Hz, 1H), 2.68 (ddd,  $J = 11.2, 8.3, 5.9$  Hz, 1H), 1.71 (dtd,  $J = 9.0, 7.4, 5.3$  Hz, 2H), 1.62 – 1.37 (m, 6H), 0.98 (dt,  $J = 14.4, 7.3$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  131.65, 128.22, 127.82, 123.53, 91.39, 83.51, 50.63, 47.34, 38.34, 32.27, 20.56, 19.45, 14.04, 13.95.



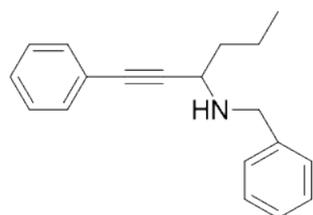
**N-butyl-1-(o-tolyl)hex-1-yn-3-amine (4b):** yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 – 7.37 (m, 1H), 7.26 – 7.07 (m, 3H), 3.66 (dd,  $J = 8.0, 5.6$  Hz, 1H), 2.98 (ddd,  $J = 11.2, 8.4, 6.4$  Hz, 1H), 2.70 (ddd,  $J = 11.1, 8.3, 5.8$  Hz, 1H), 1.72 (tdd,  $J = 9.0, 7.6, 5.2$  Hz, 2H), 1.64 – 1.36 (m, 6H), 0.98 (dt,  $J = 16.0, 7.3$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.91, 131.95, 129.34, 127.83, 125.47, 123.30, 95.44, 82.36, 50.77, 47.36, 38.48, 32.28, 20.82, 20.59, 19.49, 14.05, 13.95.



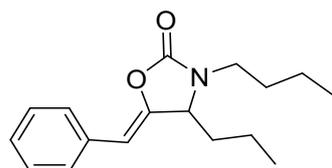
**N-butyl-1-(4-chlorophenyl)hex-1-yn-3-amine(4c):** yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 (d,  $J = 8.2$  Hz, 2H), 7.12 (d,  $J = 7.9$  Hz, 2H), 3.60 (dd,  $J = 7.9, 5.7$  Hz, 1H), 2.95 (ddd,  $J = 11.2, 8.2, 6.3$  Hz, 1H), 2.68 (ddd,  $J = 11.1, 8.2, 5.9$  Hz, 1H), 2.36 (s, 3H), 1.75 – 1.65 (m, 2H), 1.58 – 1.37 (m, 6H), 0.97 (dt,  $J = 13.4, 7.2$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.82, 131.52, 128.96, 120.43, 90.58, 83.57, 50.64, 47.32, 38.37, 32.26, 21.43, 20.56, 19.45, 14.04, 13.96.



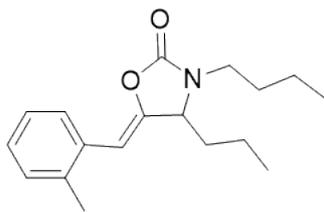
**N-butyl-1-(p-tolyl)hex-1-yn-3-amine(4d):** yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (d,  $J = 8.6$  Hz, 2H), 7.28 (d,  $J = 8.6$  Hz, 2H), 3.60 (dd,  $J = 7.9, 5.8$  Hz, 1H), 2.92 (ddd,  $J = 11.2, 8.2, 6.4$  Hz, 1H), 2.67 (ddd,  $J = 11.2, 8.2, 6.0$  Hz, 1H), 1.78 – 1.64 (m, 2H), 1.58 – 1.38 (m, 6H), 0.97 (dt,  $J = 14.3, 7.3$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  133.79, 132.87, 128.53, 121.98, 92.36, 82.47, 50.62, 47.32, 38.18, 32.20, 20.54, 19.42, 14.02, 13.92.



**N-benzyl-1-phenylhex-1-yn-3-amine(4e):** yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 – 7.38 (m, 5H), 7.38 – 7.29 (m, 5H), 4.14 (d,  $J = 12.8$  Hz, 1H), 3.94 (d,  $J = 12.9$  Hz, 1H), 3.65 (dd,  $J = 7.6, 6.1$  Hz, 1H), 1.75 (ddd,  $J = 13.4, 6.9, 4.0$  Hz, 2H), 1.65 – 1.55 (m, 2H), 1.00 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  133.79, 132.87, 128.53, 121.98, 92.36, 82.47, 50.62, 47.32, 38.18, 32.20, 20.54, 19.42, 14.02, 13.92.

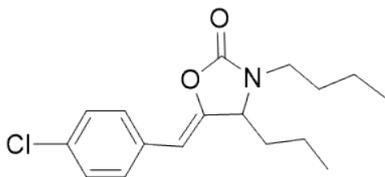


**(Z)-5-benzylidene-3-butyl-4-propyloxazolidin-2-one (5a):** yellow oil, 92% yield. IR: 3024, 2933, 1766, 1514, 1080, 1063  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 – 7.58 (m, 2H), 7.40 – 7.31 (m, 3H), 5.49 (d,  $J = 1.8$  Hz, 1H), 4.55 (p,  $J = 2.3$  Hz, 1H), 3.75 – 3.53 (m, 2H), 1.88 (ddt,  $J = 14.4, 11.5, 4.8$  Hz, 1H), 1.78 – 1.67 (m, 2H), 1.64 – 1.53 (m, 3H), 0.98 (t,  $J = 7.4$  Hz, 7H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  147.01, 133.63, 128.50, 128.29, 126.78, 58.39, 41.13, 34.41, 29.26, 19.94, 15.83, 13.94, 13.72.



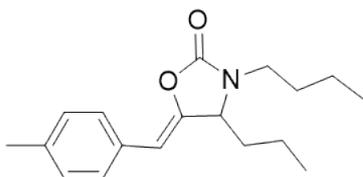
**(Z)-3-butyl-5-(2-methylbenzylidene)-4-propyloxazolidin-2-one(5b):** yellow oil, 91.4% yield.

IR: 3028, 2923, 1766, 1506, 1266, 1088  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (dd,  $J = 7.8, 1.3$  Hz, 1H), 7.22 – 7.13 (m, 3H), 5.63 (d,  $J = 1.9$  Hz, 1H), 4.58 (s, 1H), 3.62 (ddd,  $J = 14.1, 8.6, 7.4$  Hz, 1H), 3.05 (ddd,  $J = 13.9, 8.3, 5.2$  Hz, 2H), 2.34 (s, 3H), 1.90 (ddt,  $J = 14.5, 11.4, 4.9$  Hz, 1H), 1.77 – 1.54 (m, 5H), 1.49 – 1.32 (m, 5H), 0.99 (td,  $J = 7.4, 4.4$  Hz, 7H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.11, 134.89, 132.03, 129.97, 128.92, 126.89, 126.14, 99.43, 58.42, 41.14, 34.65, 29.29, 20.19, 19.94, 15.86, 13.99, 13.71.



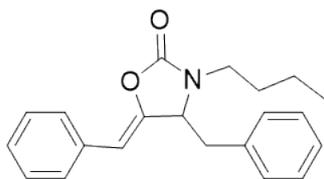
**(Z)-3-butyl-5-(4-chlorobenzylidene)-4-propyloxazolidin-2-one (5c):** yellow oil, 87.2% yield. IR:

3026, 2911, 1766, 1532, 1265, 1080, 1065  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 – 7.48 (m, 2H), 7.16 (d,  $J = 7.9$  Hz, 2H), 5.46 (d,  $J = 1.9$  Hz, 1H), 4.53 (dd,  $J = 4.9, 2.5$  Hz, 1H), 3.63 (ddd,  $J = 14.2, 8.6, 7.3$  Hz, 1H), 3.04 (ddd,  $J = 14.0, 8.3, 5.3$  Hz, 1H), 1.60 (dddd,  $J = 18.7, 9.1, 5.4, 2.0$  Hz, 4H), 1.39 (td,  $J = 10.1, 8.9, 6.3$  Hz, 4H), 0.98 (td,  $J = 7.3, 2.8$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.23, 136.56, 129.18, 128.20, 58.36, 41.11, 34.46, 29.26, 21.22, 19.93, 15.83, 13.92, 13.71.



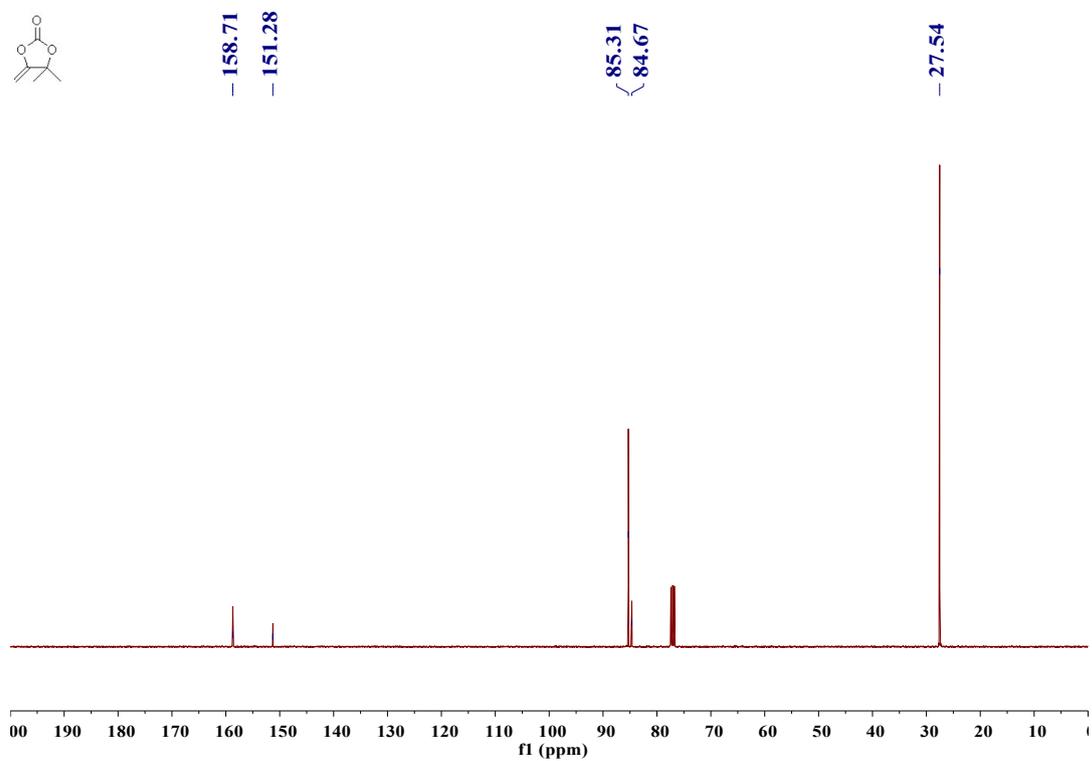
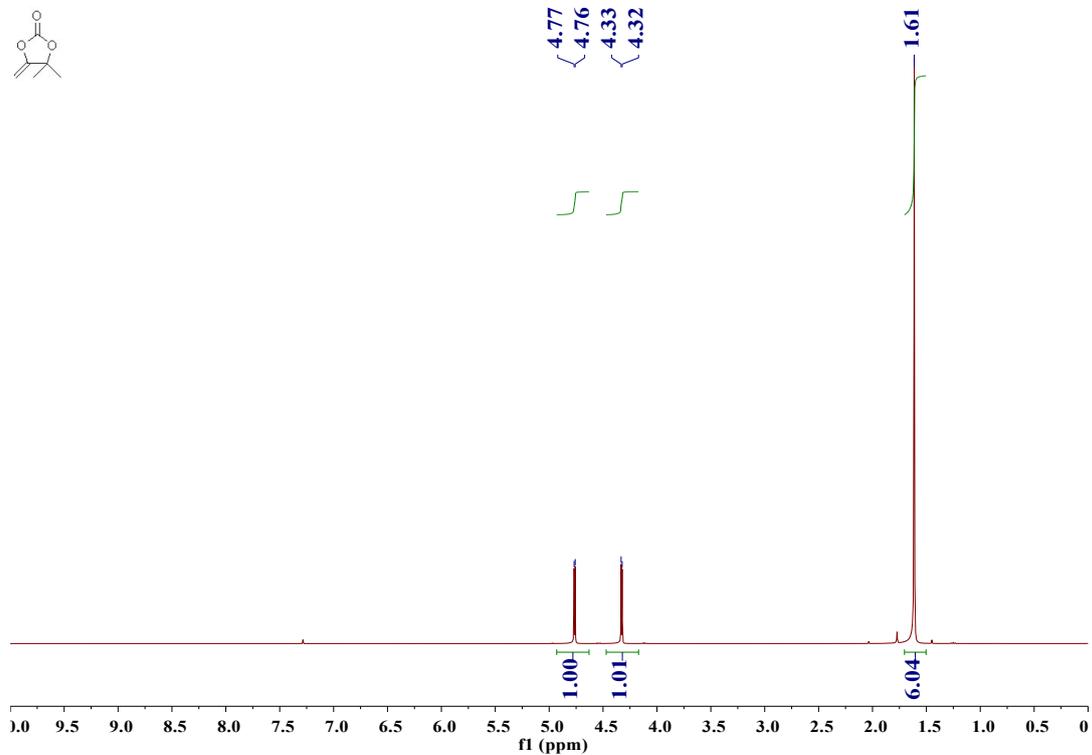
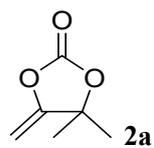
**(Z)-3-butyl-5-(4-methylbenzylidene)-4-propyloxazolidin-2-one(5d):** yellow oil, 90.5% yield.

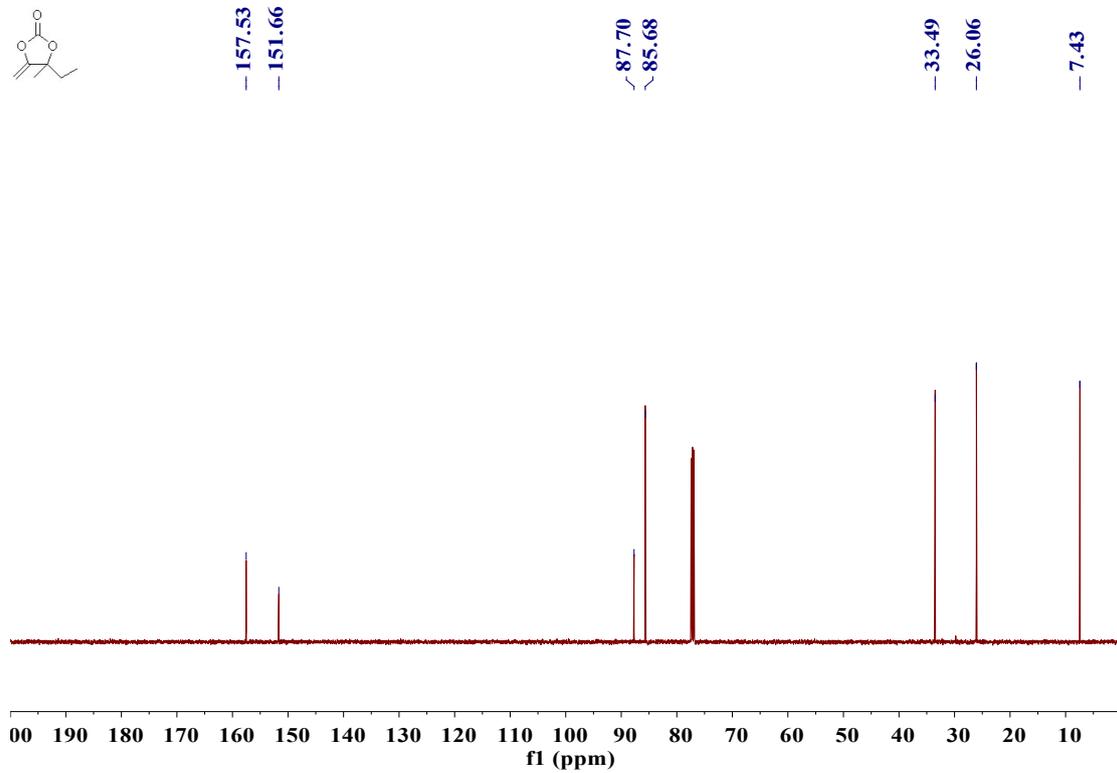
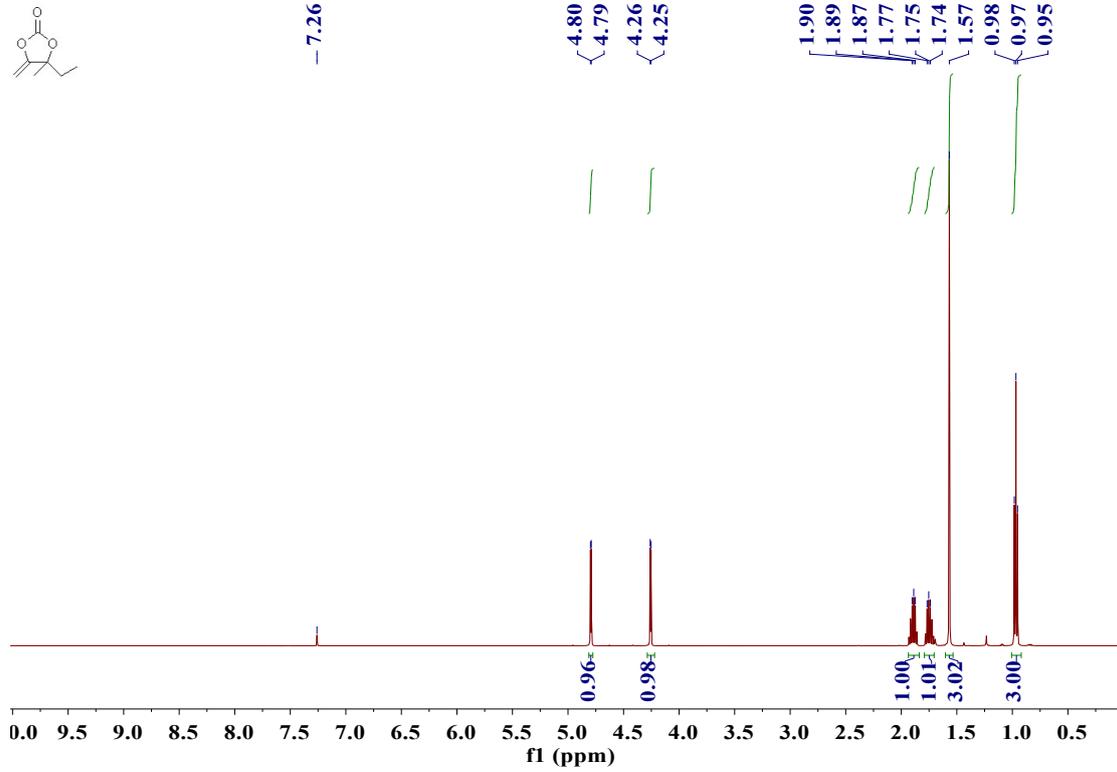
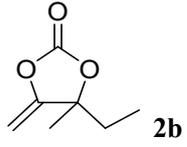
IR: 3028, 2924, 1768, 1512, 1269, 1084, 1065  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (d,  $J = 8.2$  Hz, 2H), 5.43 (d,  $J = 1.9$  Hz, 1H), 4.51 (s, 0H), 3.59 (dd,  $J = 13.6, 8.0$  Hz, 1H), 3.06 – 2.97 (m, 1H), 2.33 (s, 3H), 1.58 (tdd,  $J = 12.1, 7.9, 5.7$  Hz, 2H), 1.36 (d,  $J = 7.7$  Hz, 4H), 0.96 (dd,  $J = 7.2, 2.9$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.57, 146.49, 136.83, 131.03, 129.68, 129.45, 128.46, 124.80, 58.62, 41.37, 34.72, 29.52, 21.48, 20.19, 16.09, 14.19, 13.97.

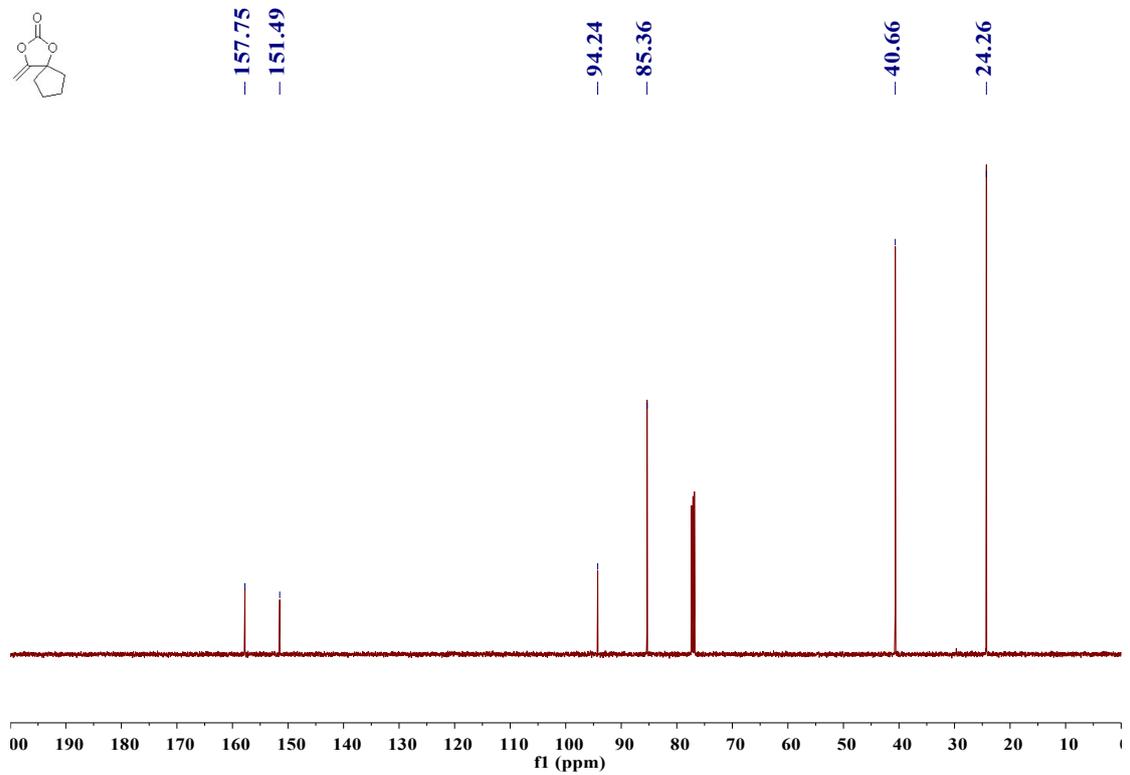
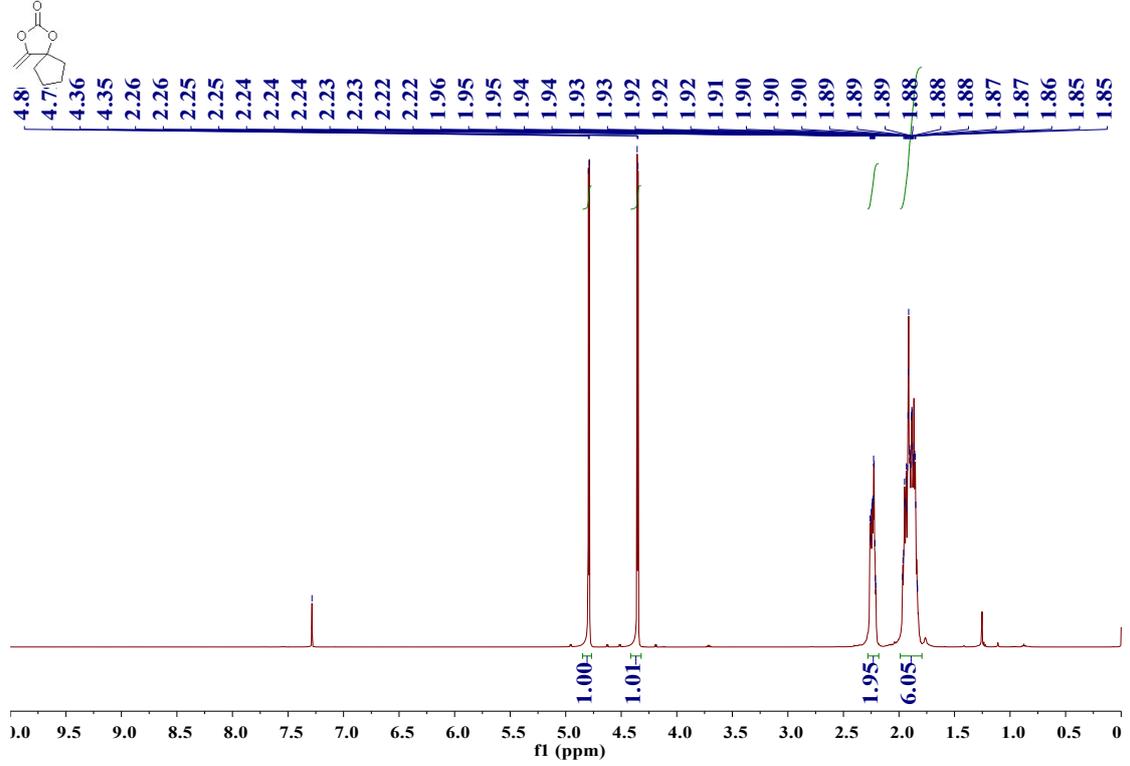
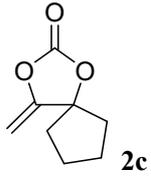


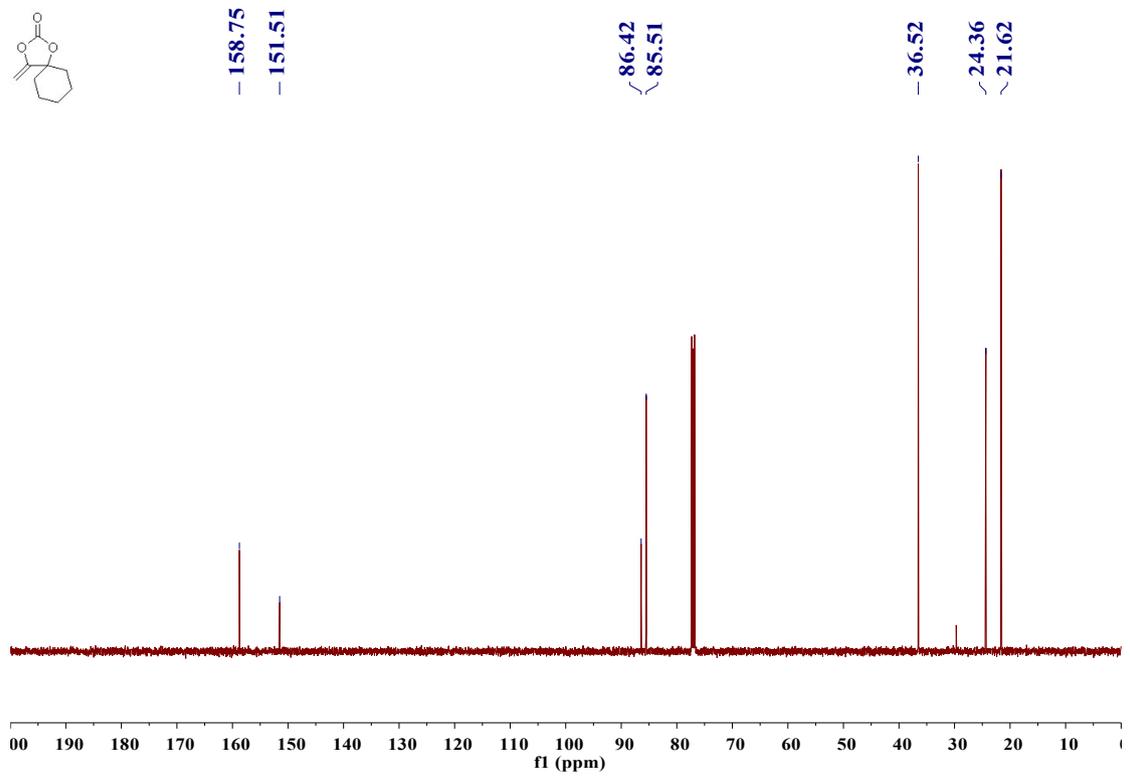
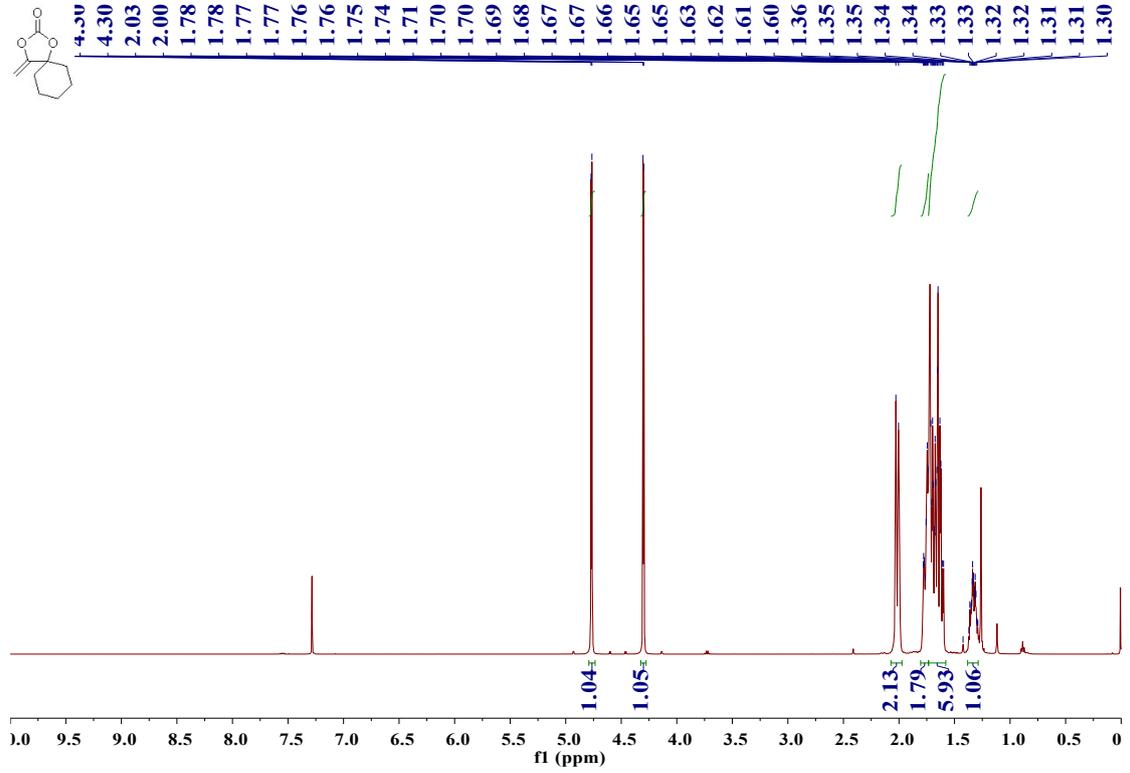
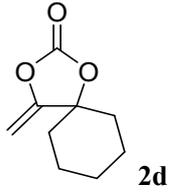
**(Z)-3-benzyl-5-benzylidene-4-propyloxazolidin-2-one (5e):** yellow oil, 83.7% yield. IR: 1770, 1694, 1492, 1270, 1072, 925  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 – 7.57 (m, 2H), 7.42 – 7.32 (m, 8H), 5.44 (d,  $J = 1.9$  Hz, 1H), 4.97 (d,  $J = 15.3$  Hz, 1H), 4.41 – 4.08 (m, 2H), 1.46 – 1.28 (m, 4H), 0.93 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.49, 146.75, 135.09, 133.50, 128.99, 128.52, 128.31, 128.23, 126.86, 57.88, 45.60, 34.00, 15.75, 13.91.

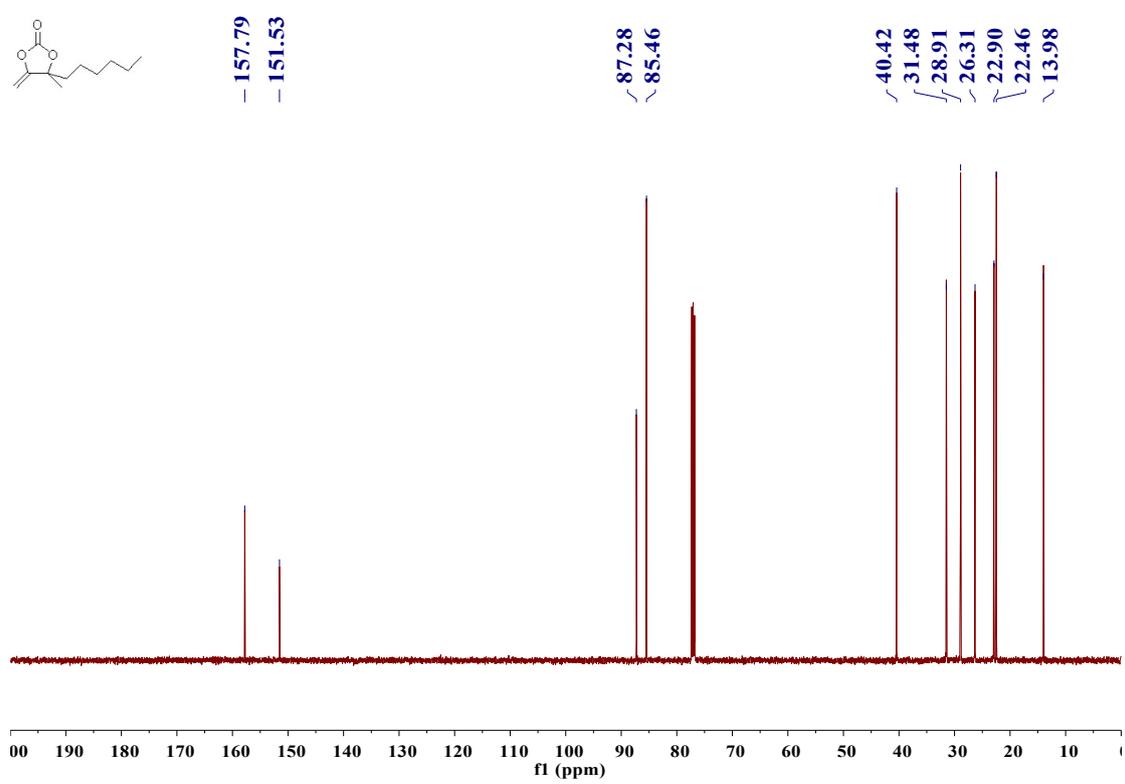
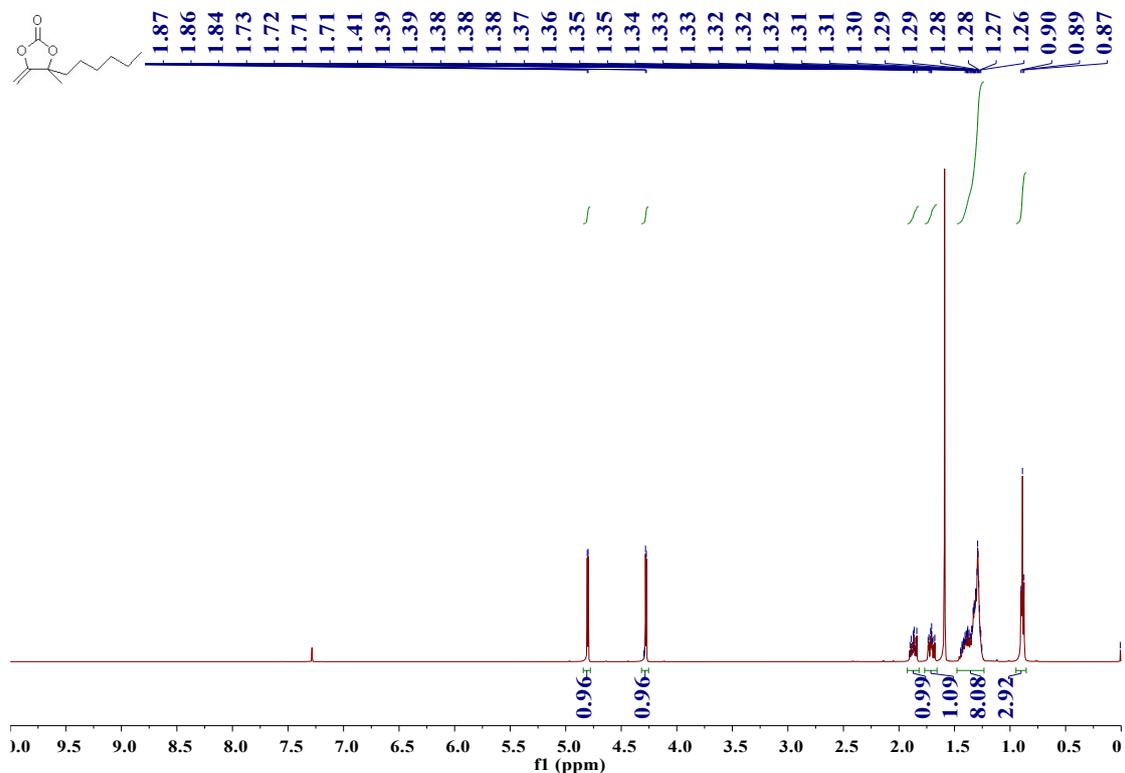
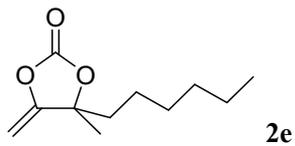
### 3. NMR Spectra of the Substrates and Products

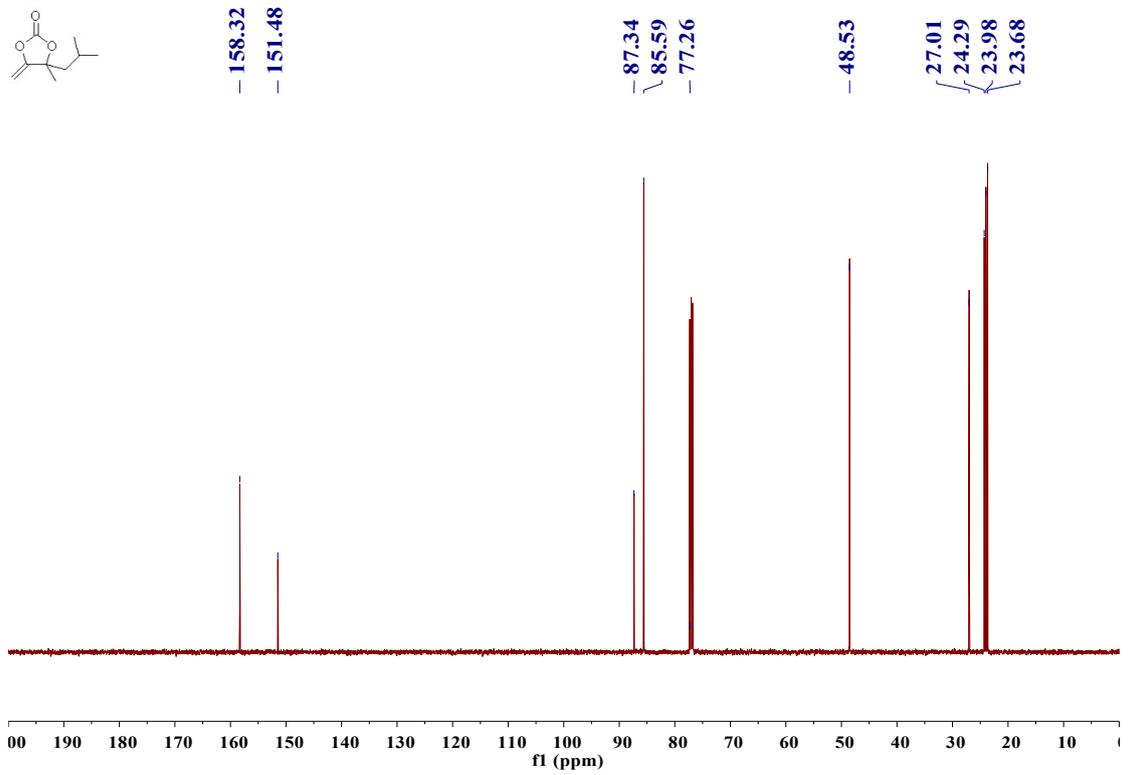
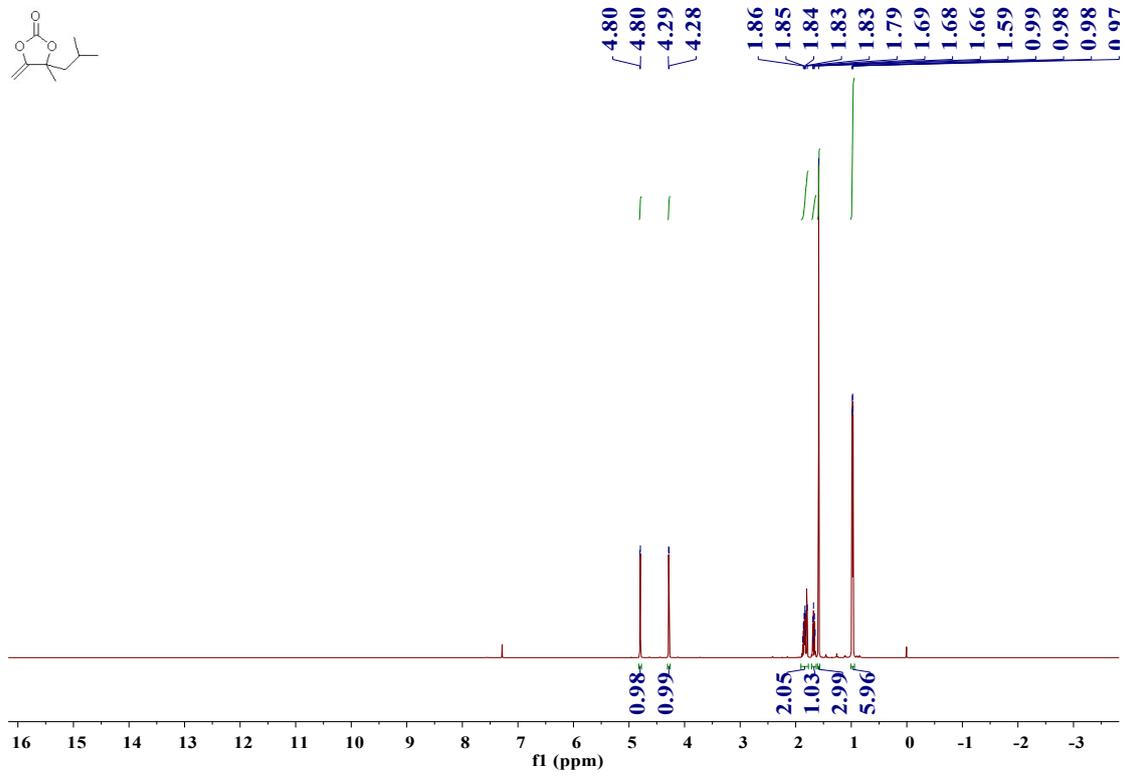
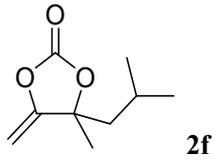


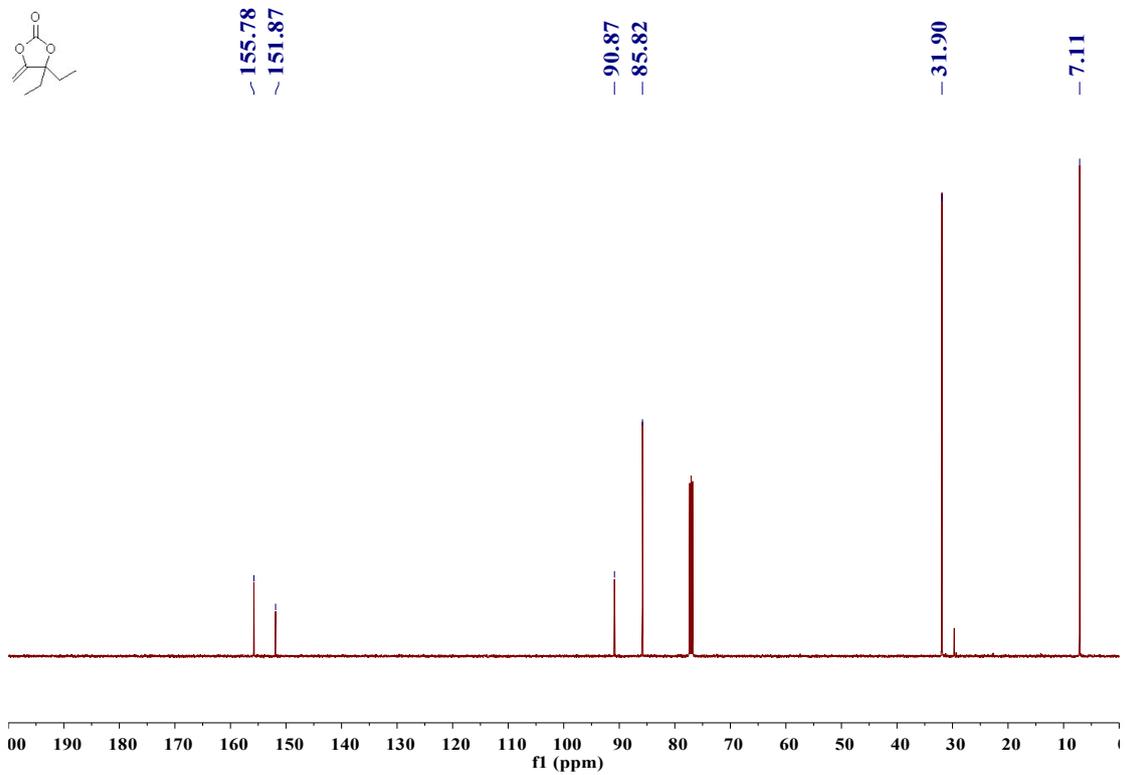
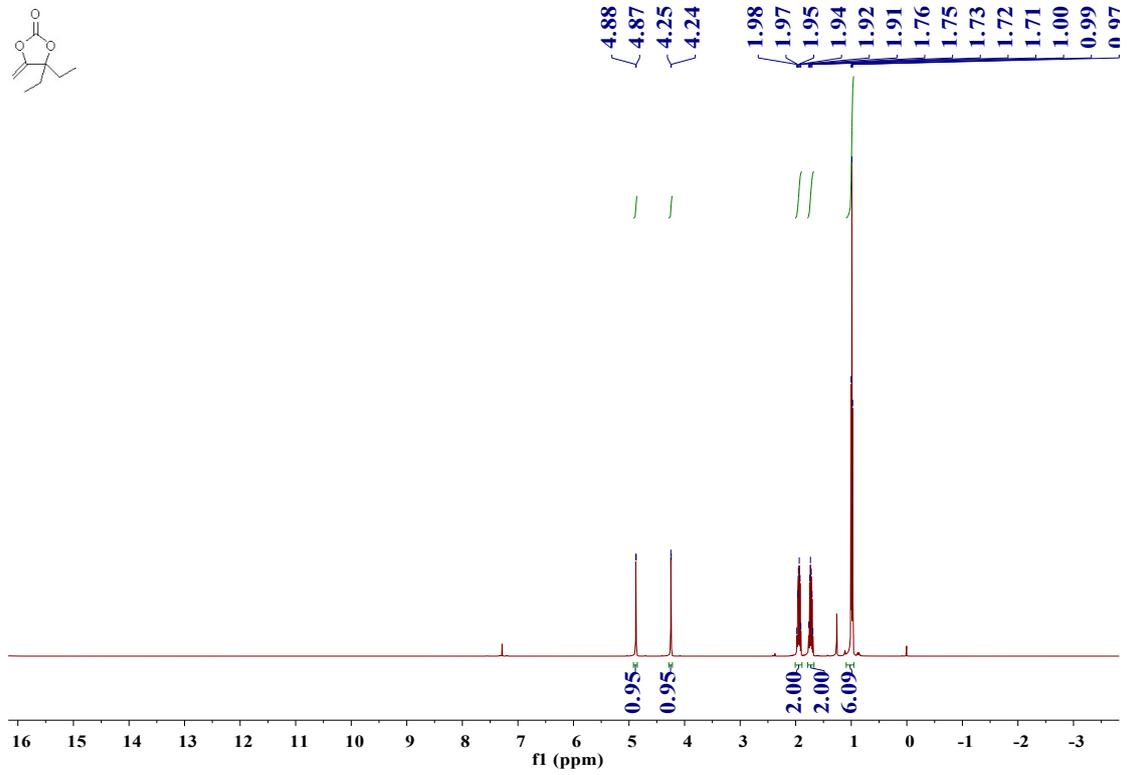
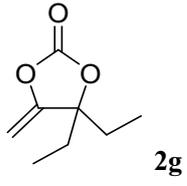


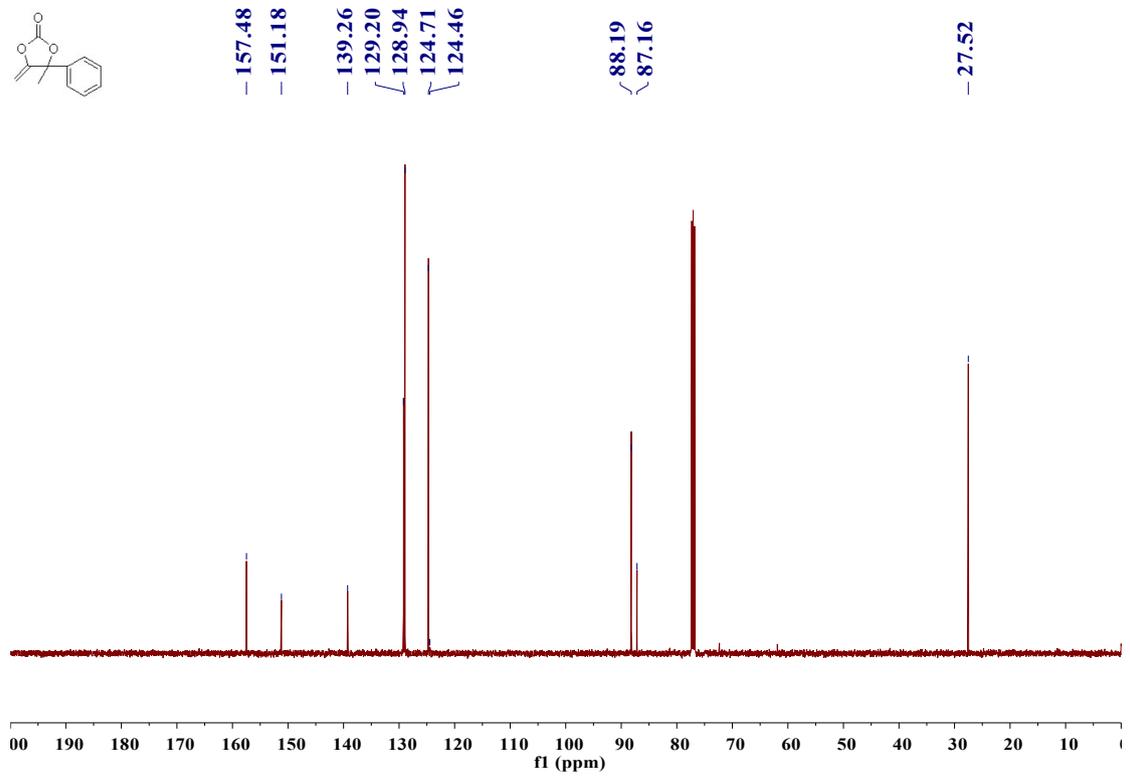
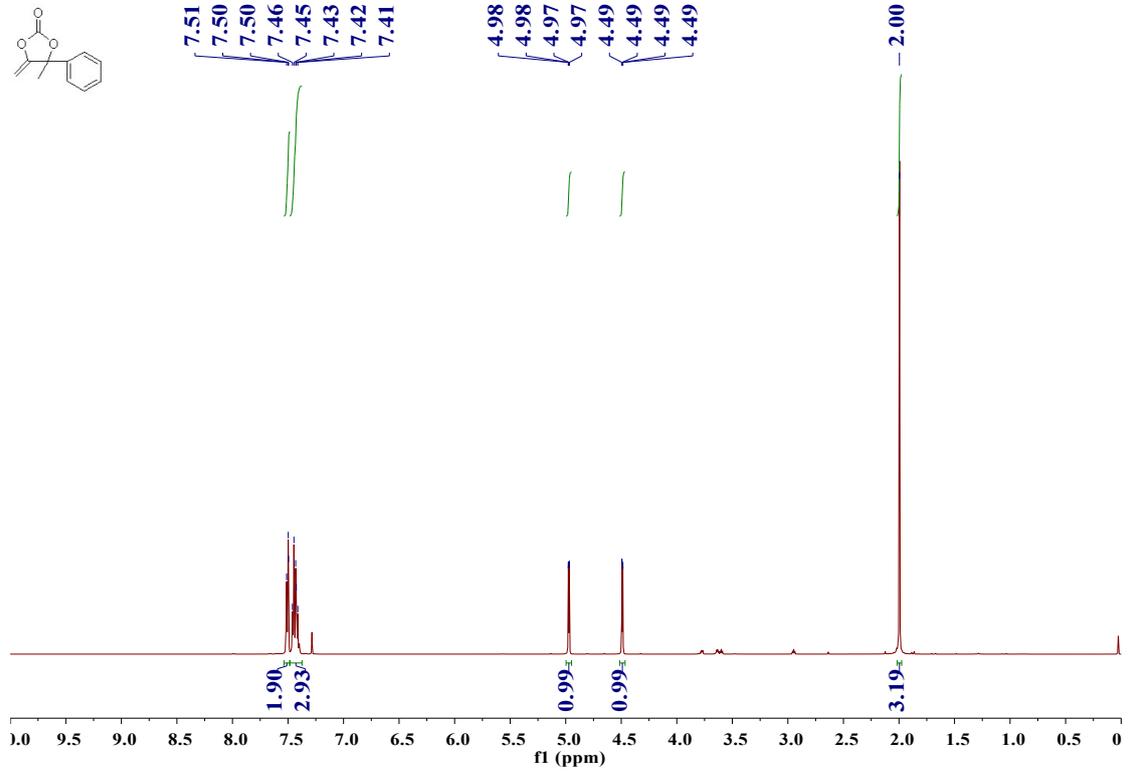
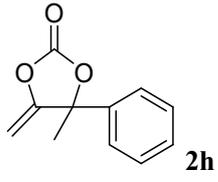


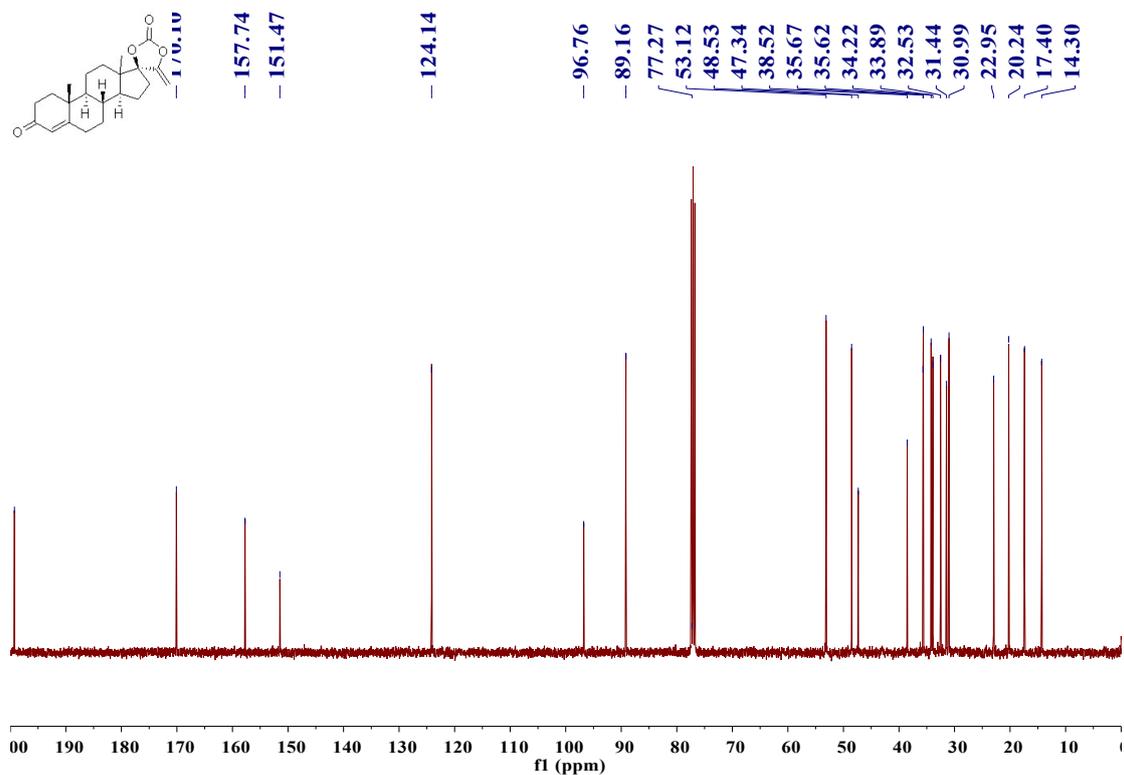
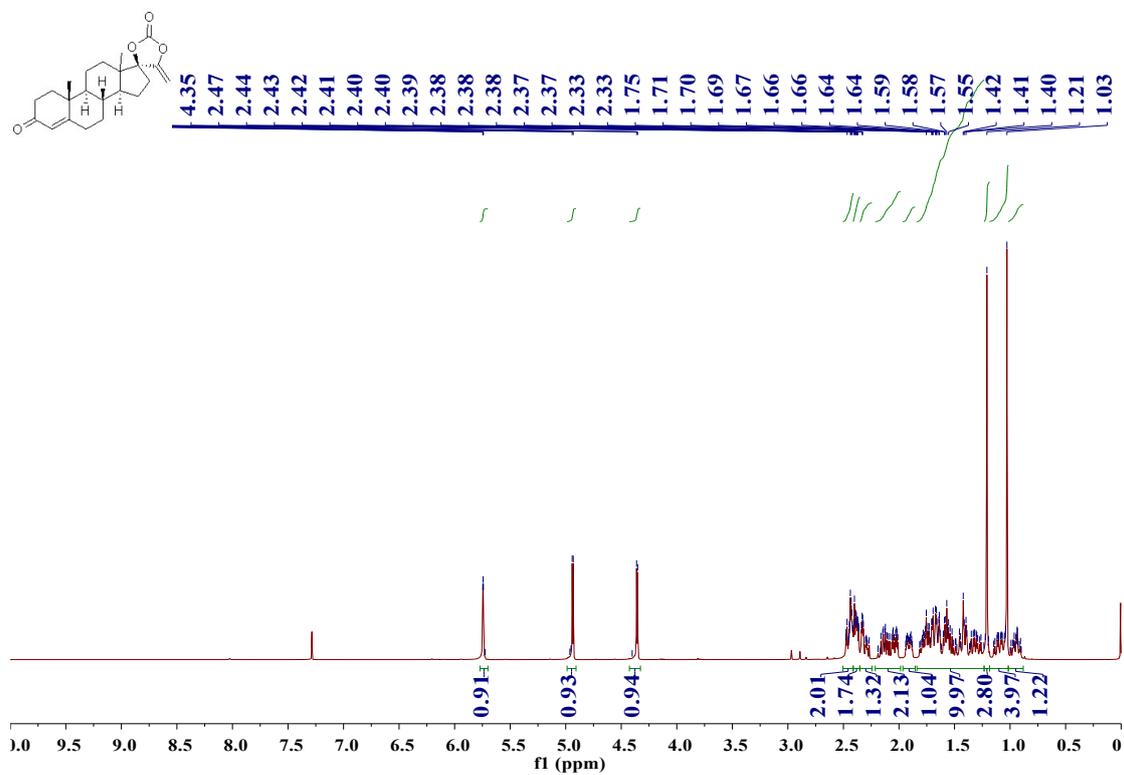
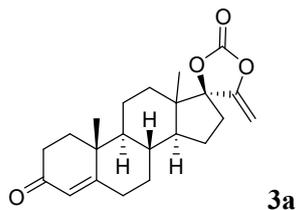


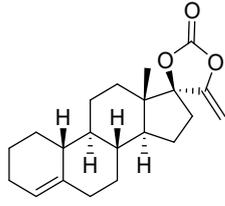




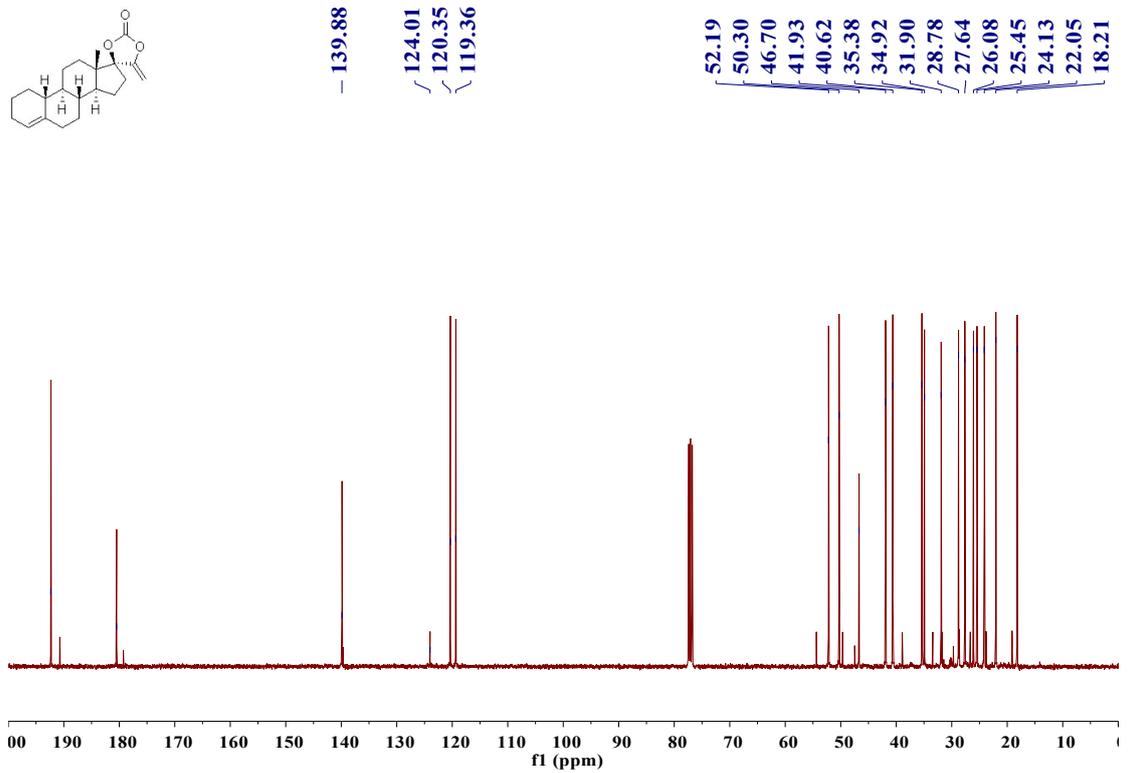
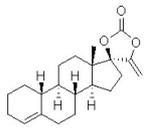
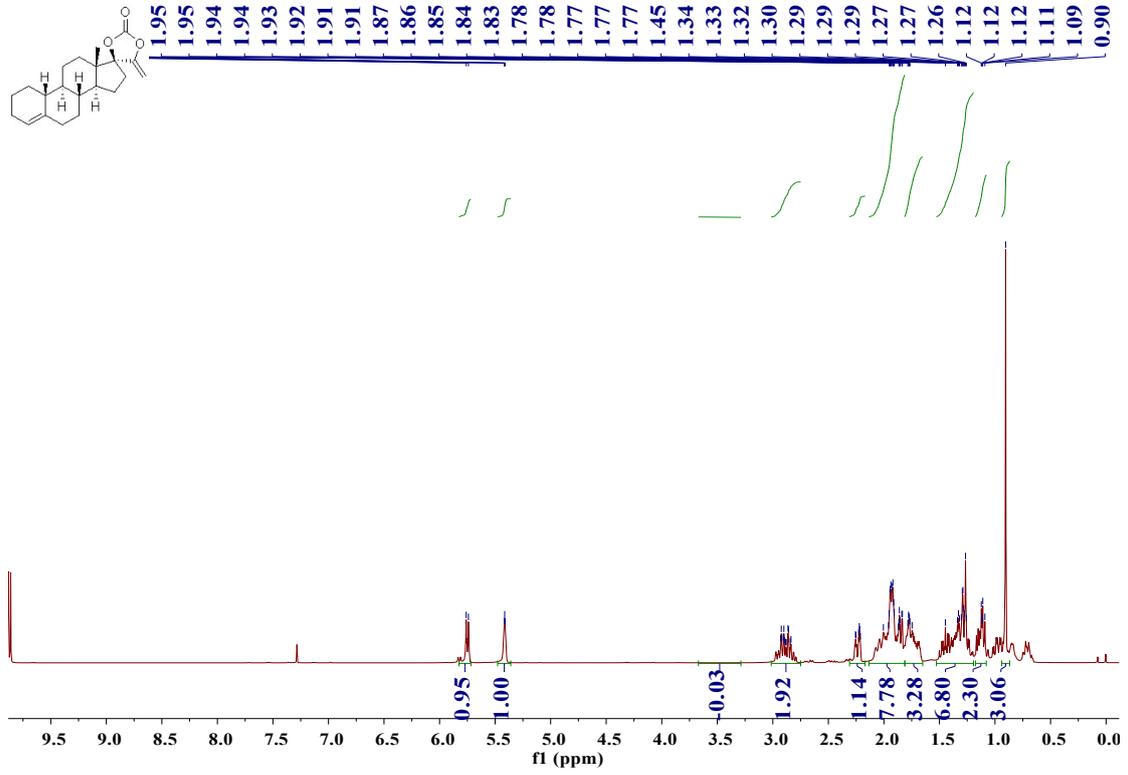


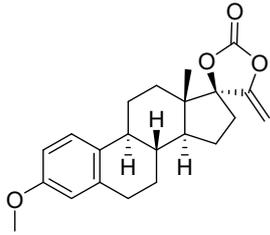




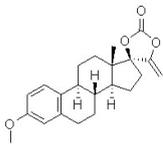
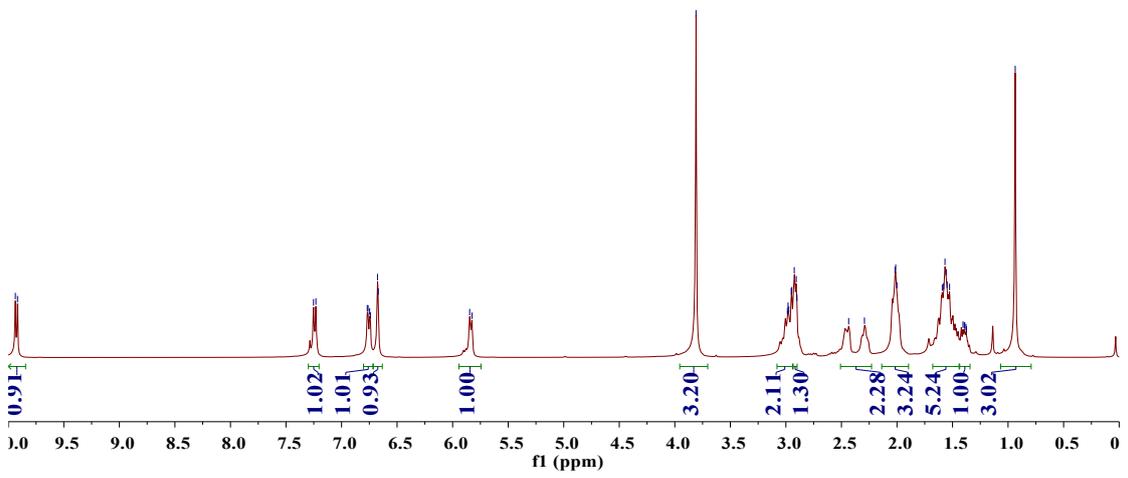
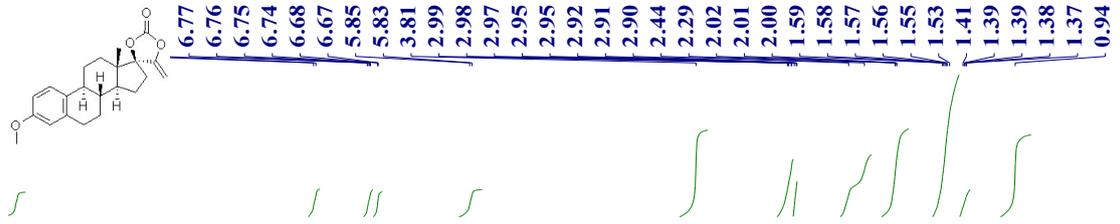


**3b**





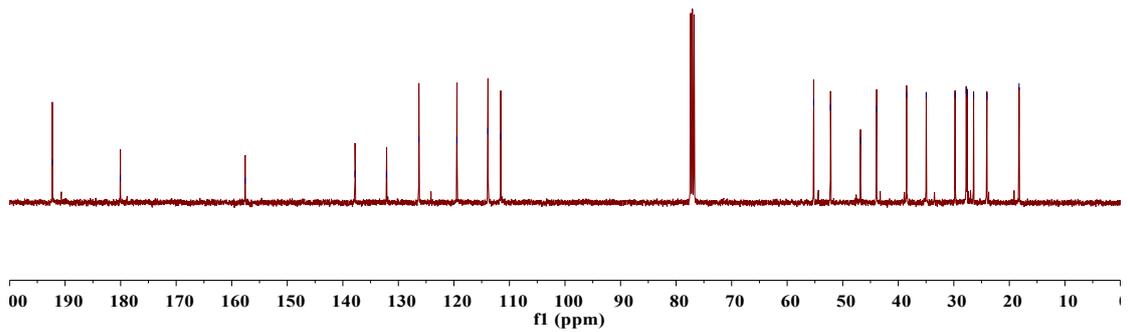
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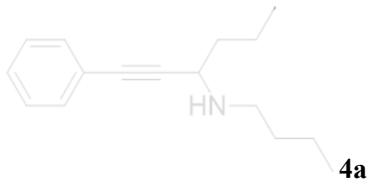


- 157.60

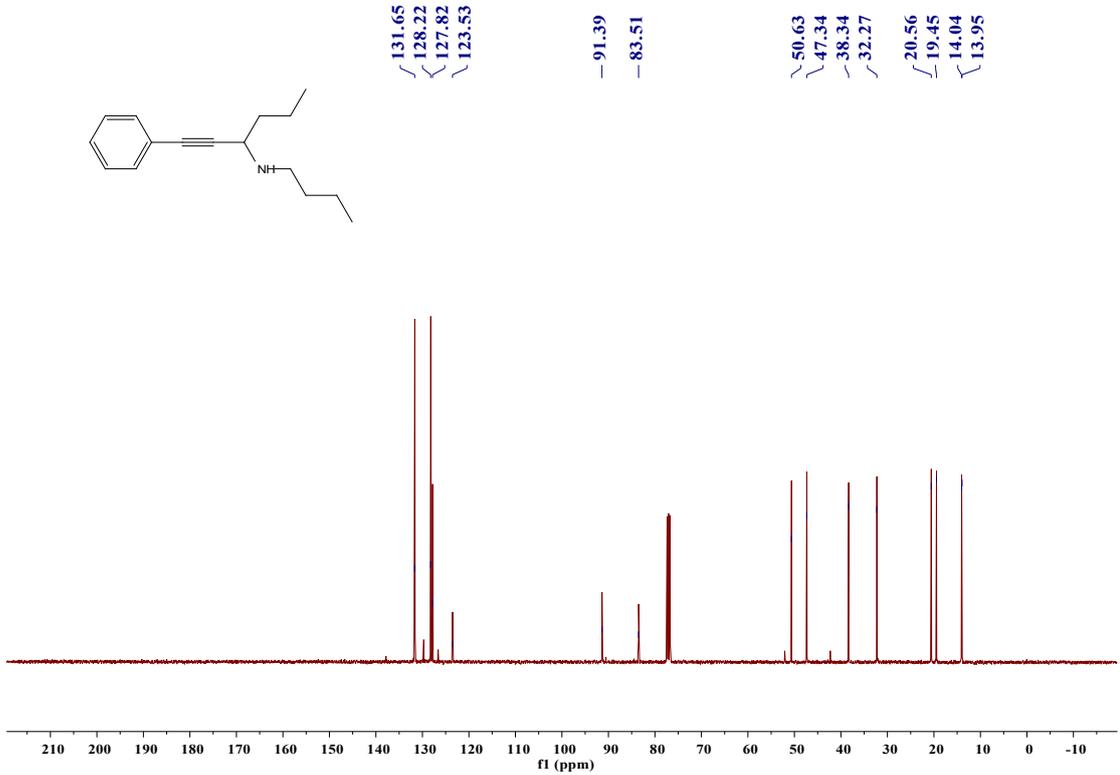
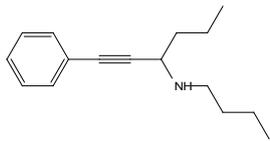
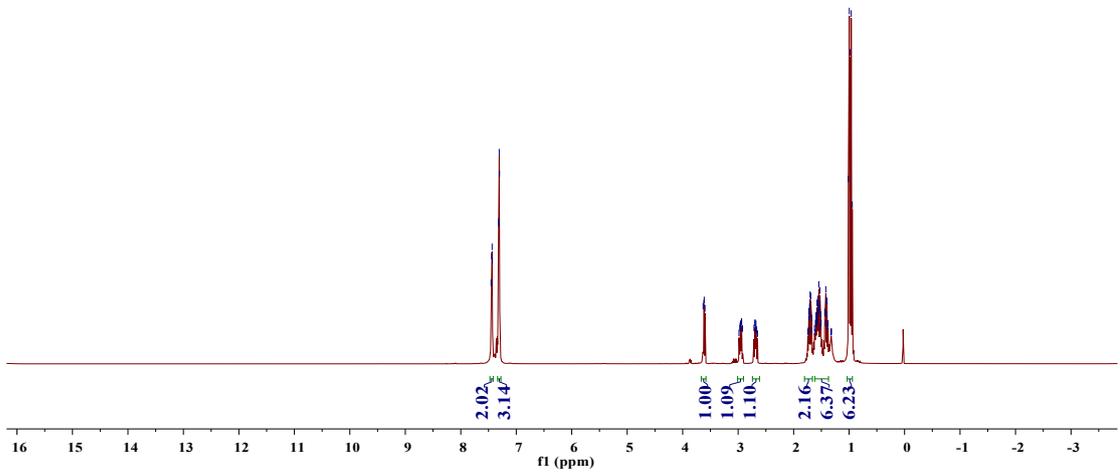
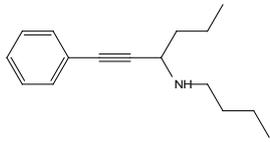
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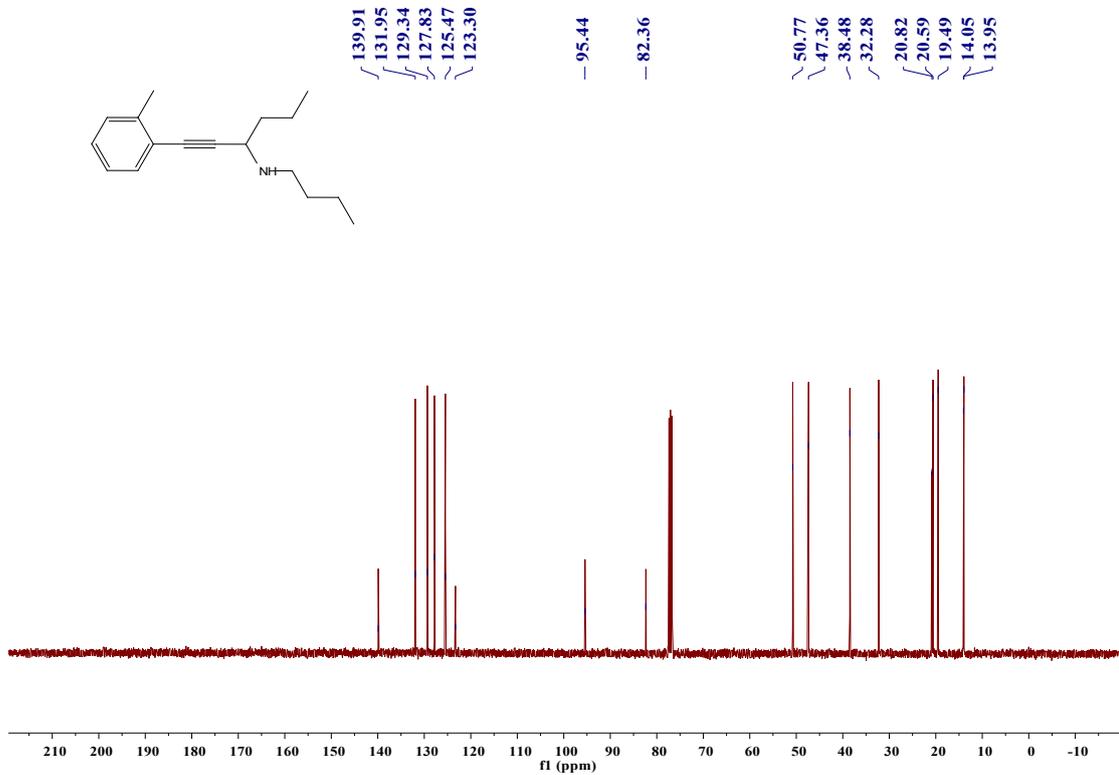
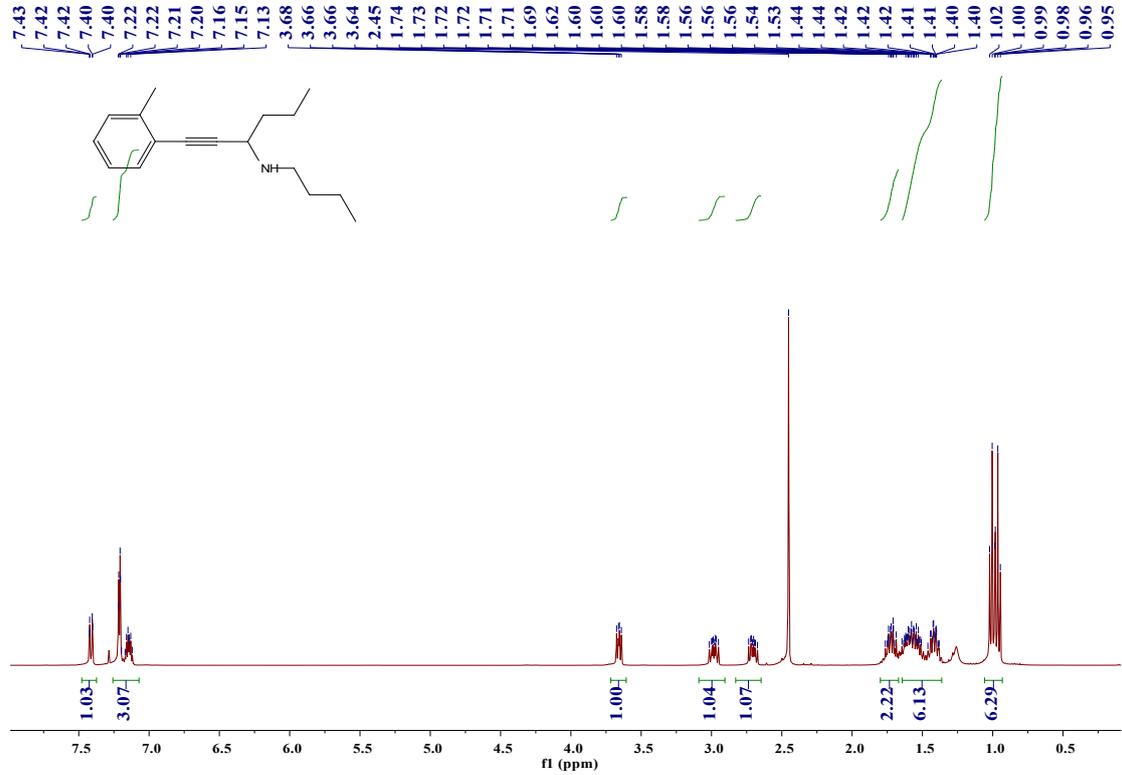
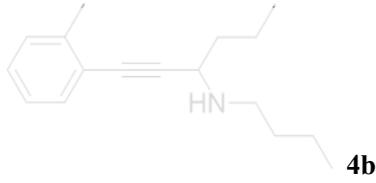
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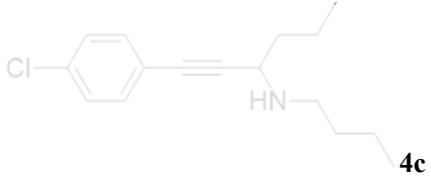




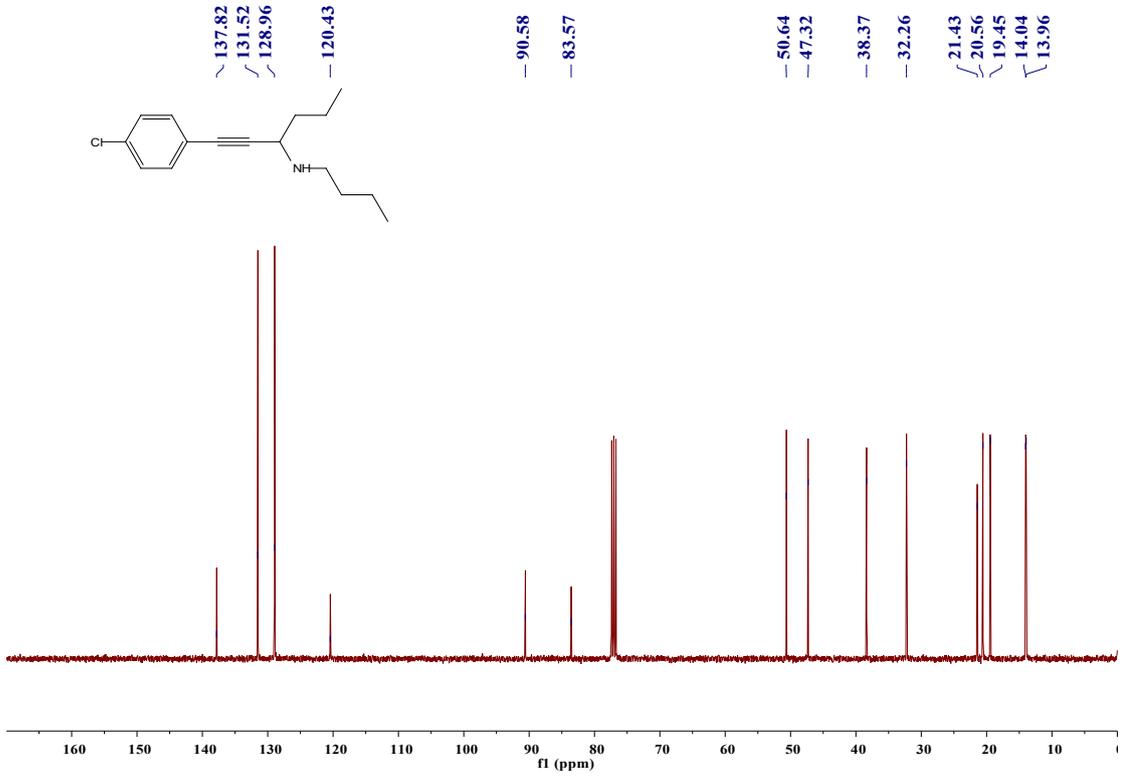
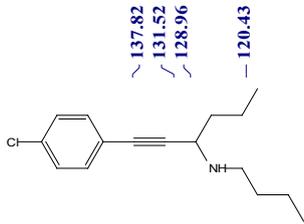
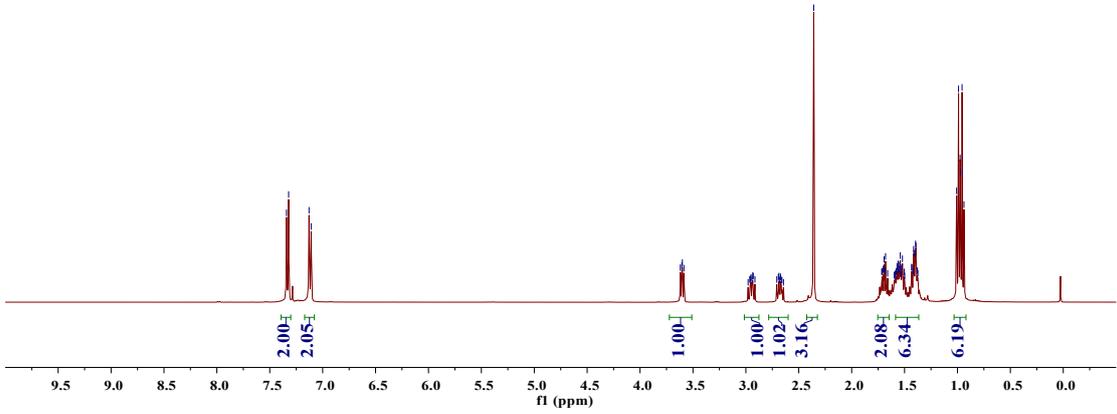
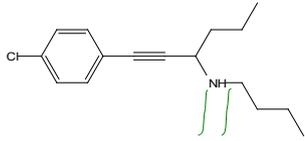
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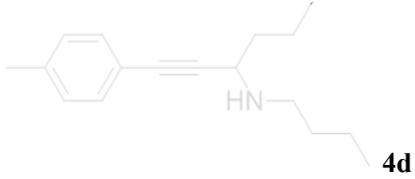




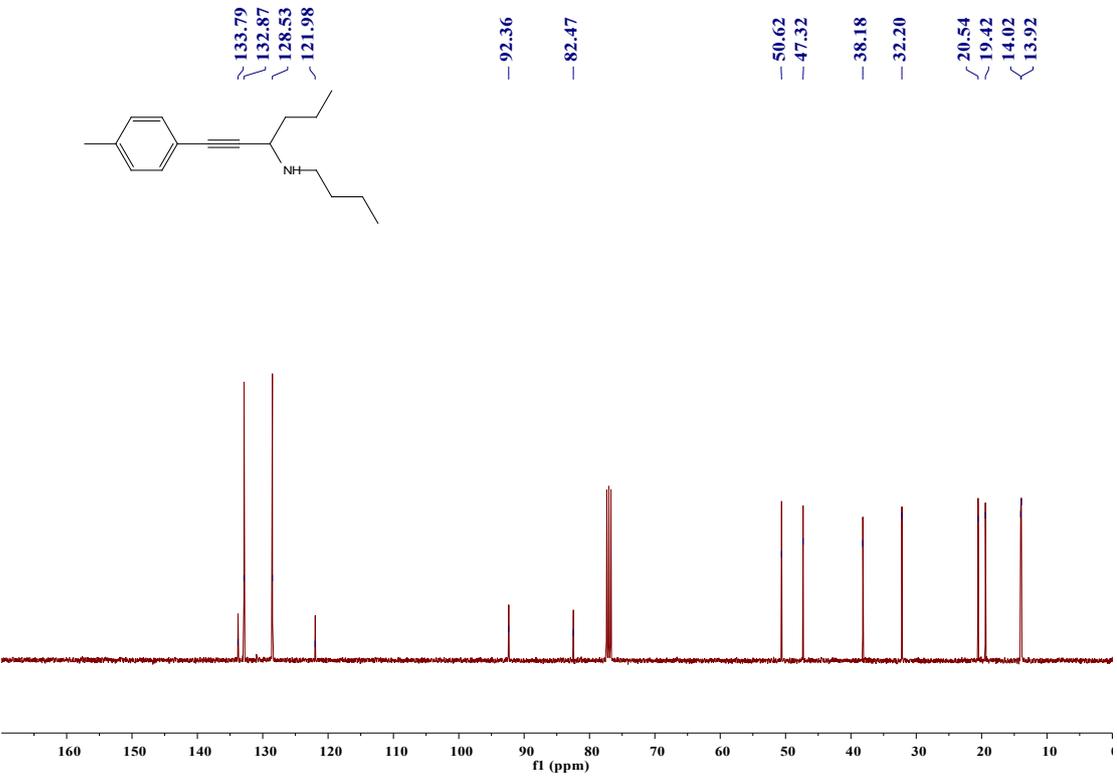
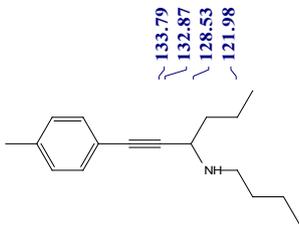
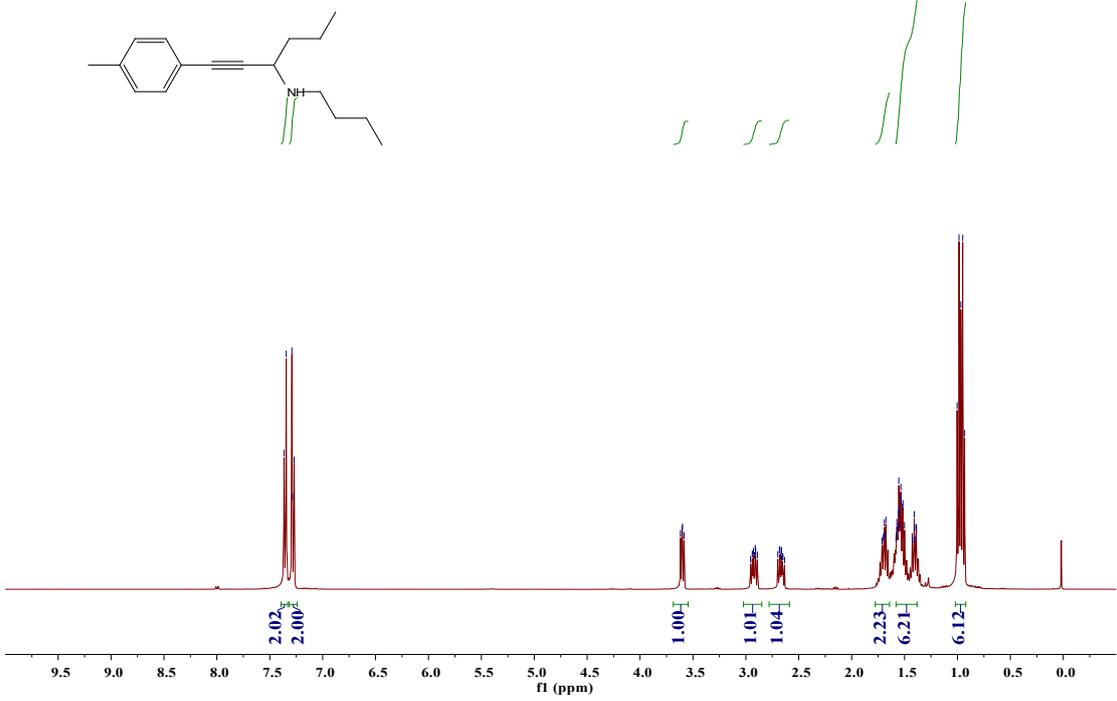


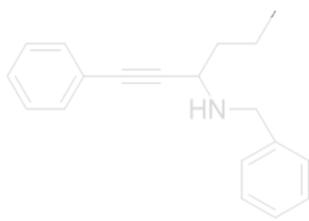
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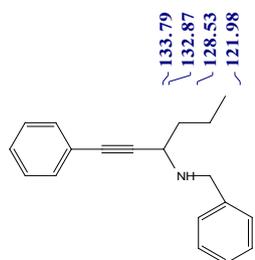
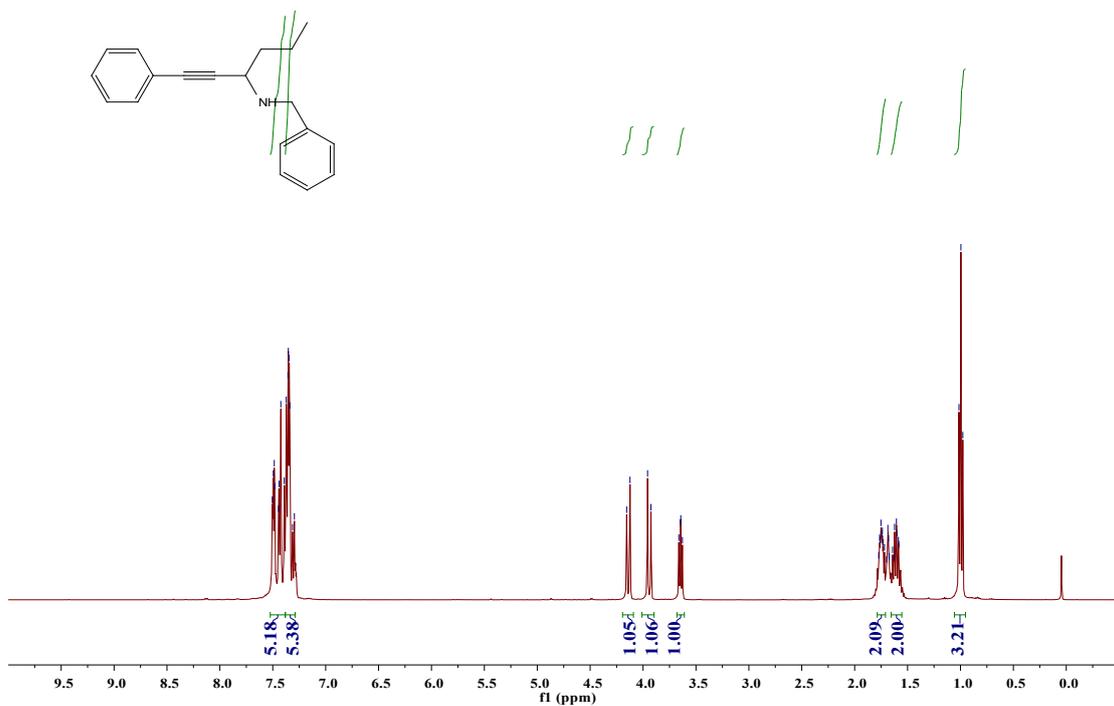
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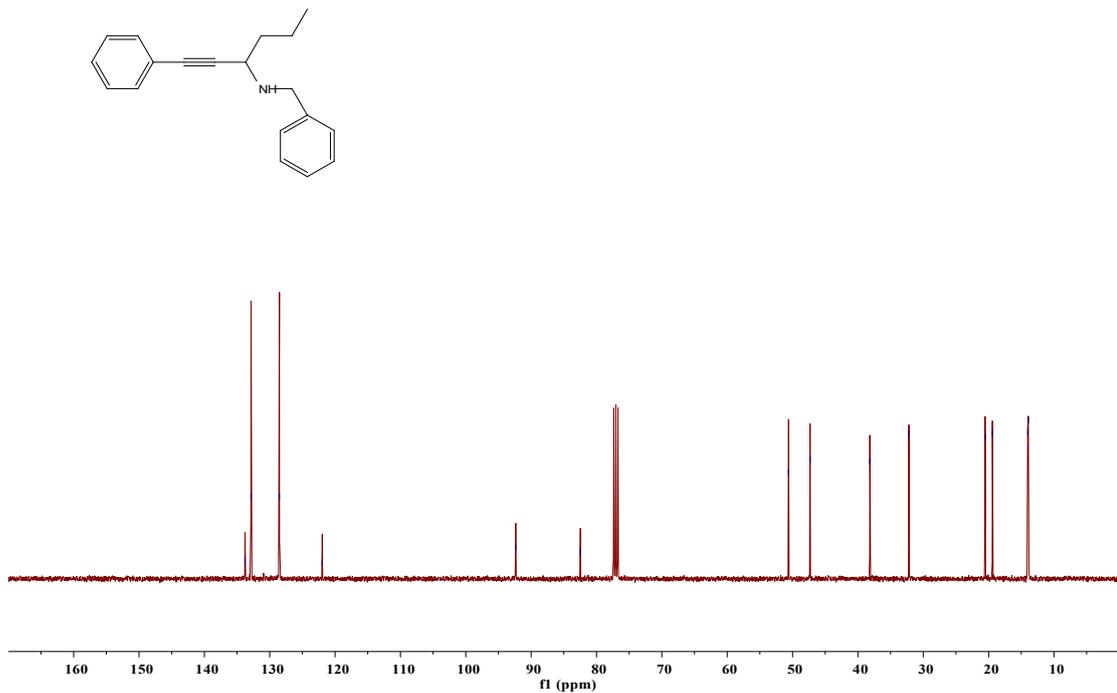
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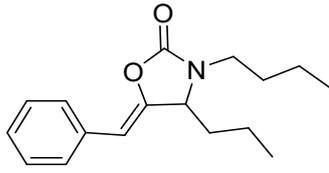
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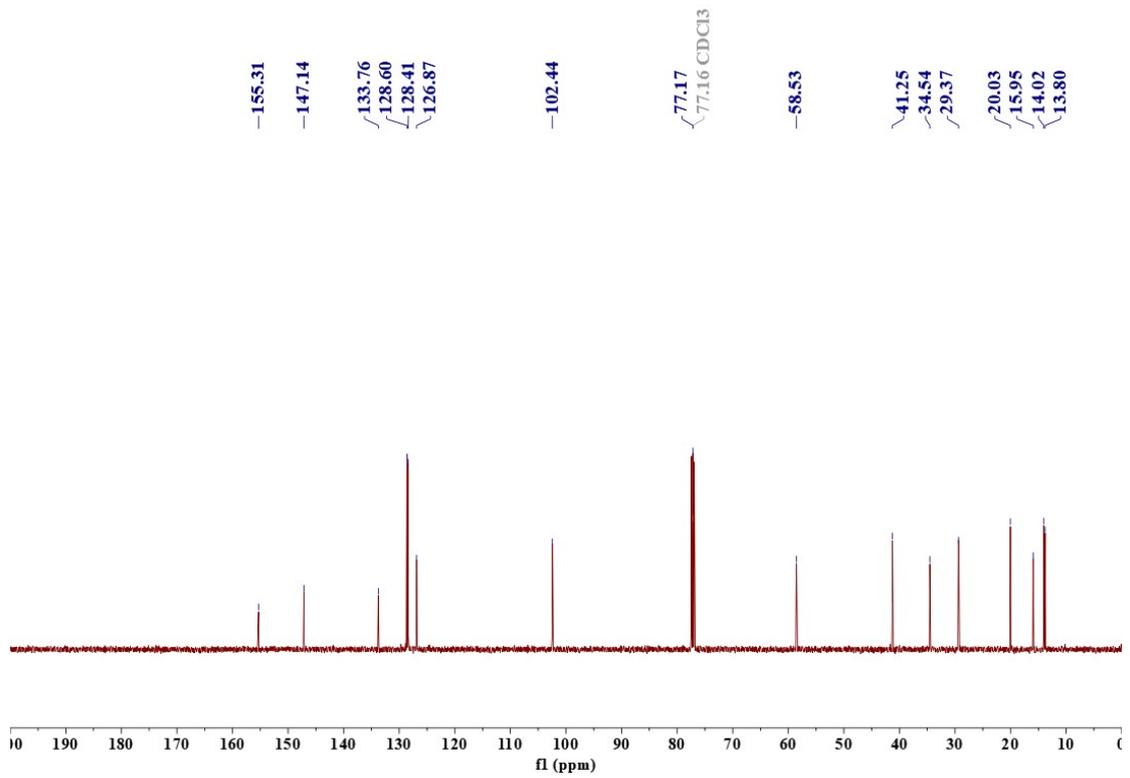
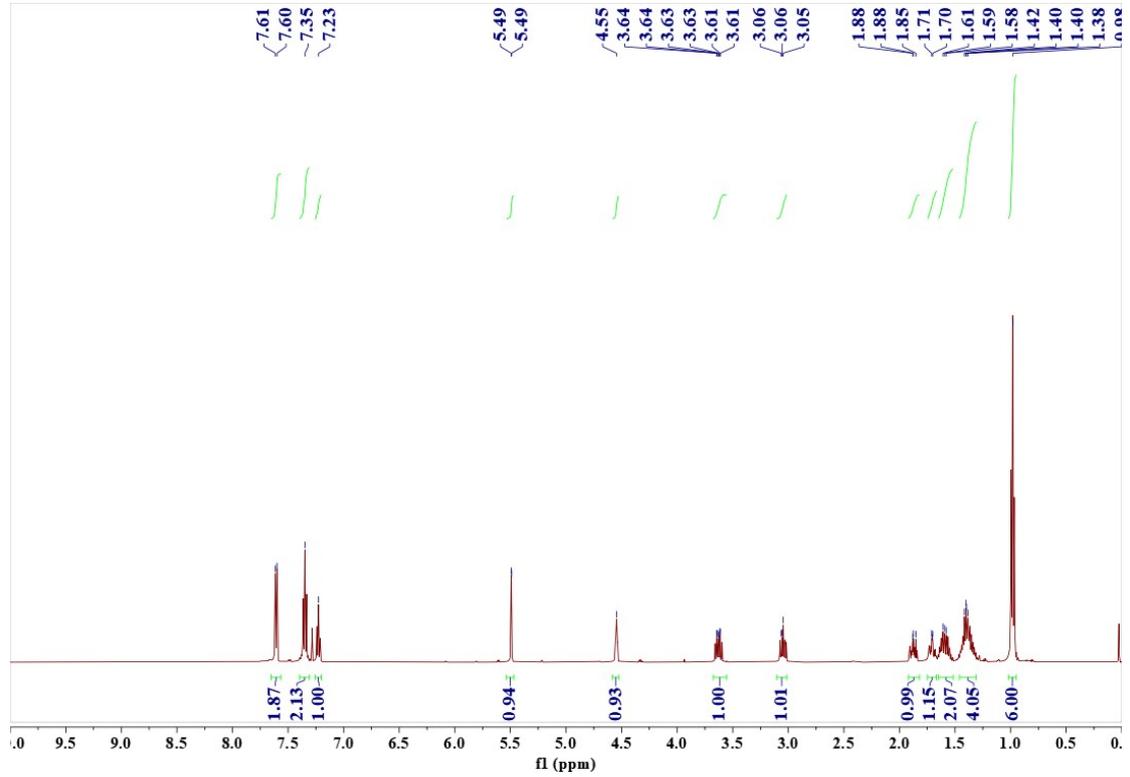
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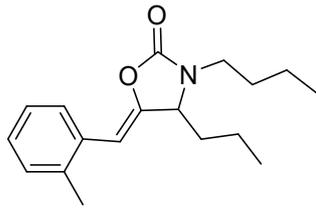
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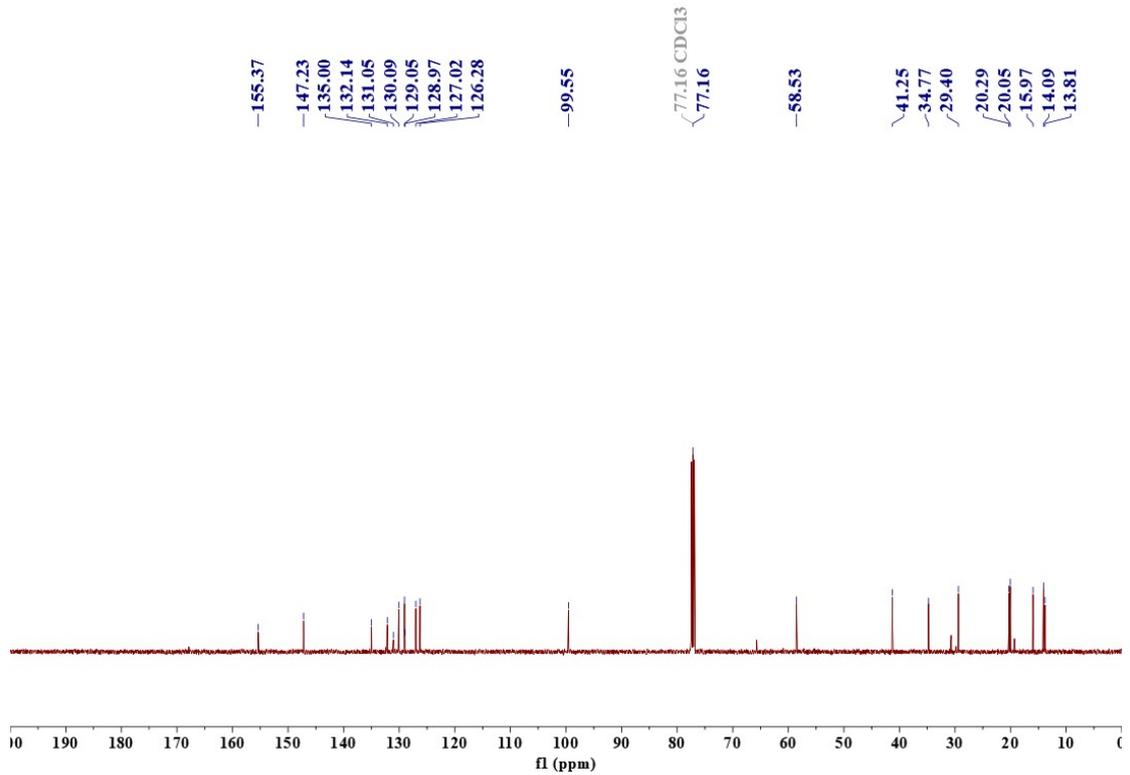
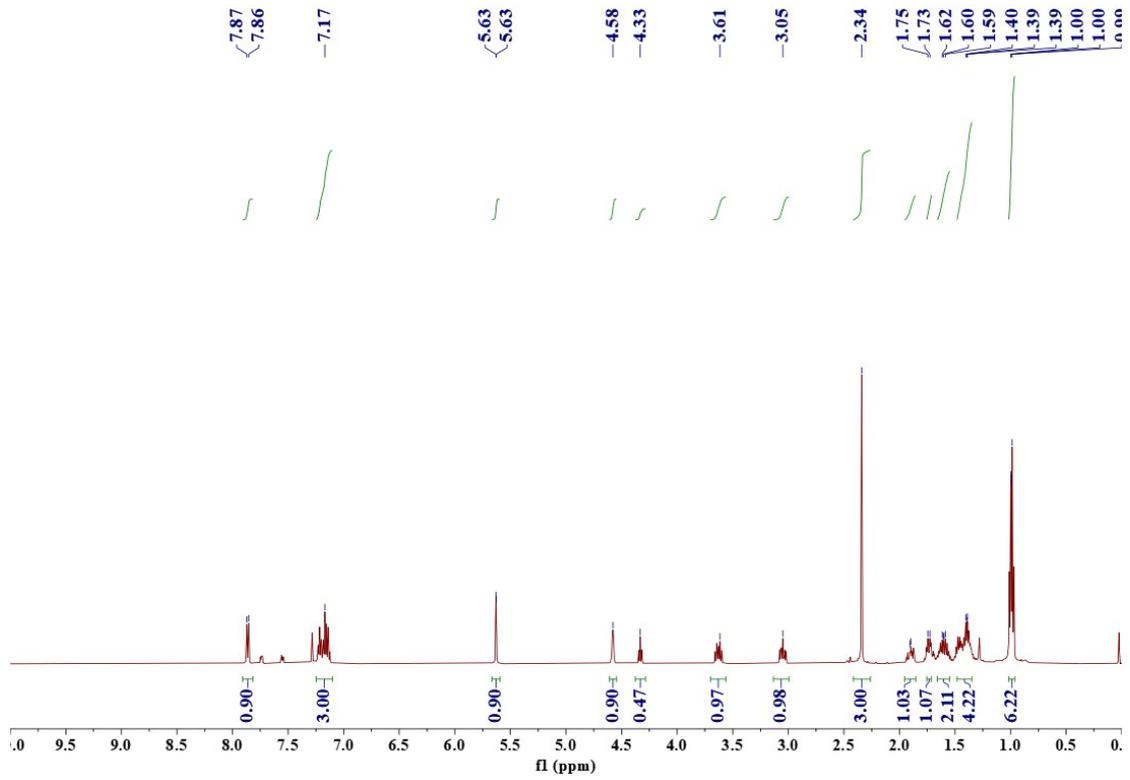


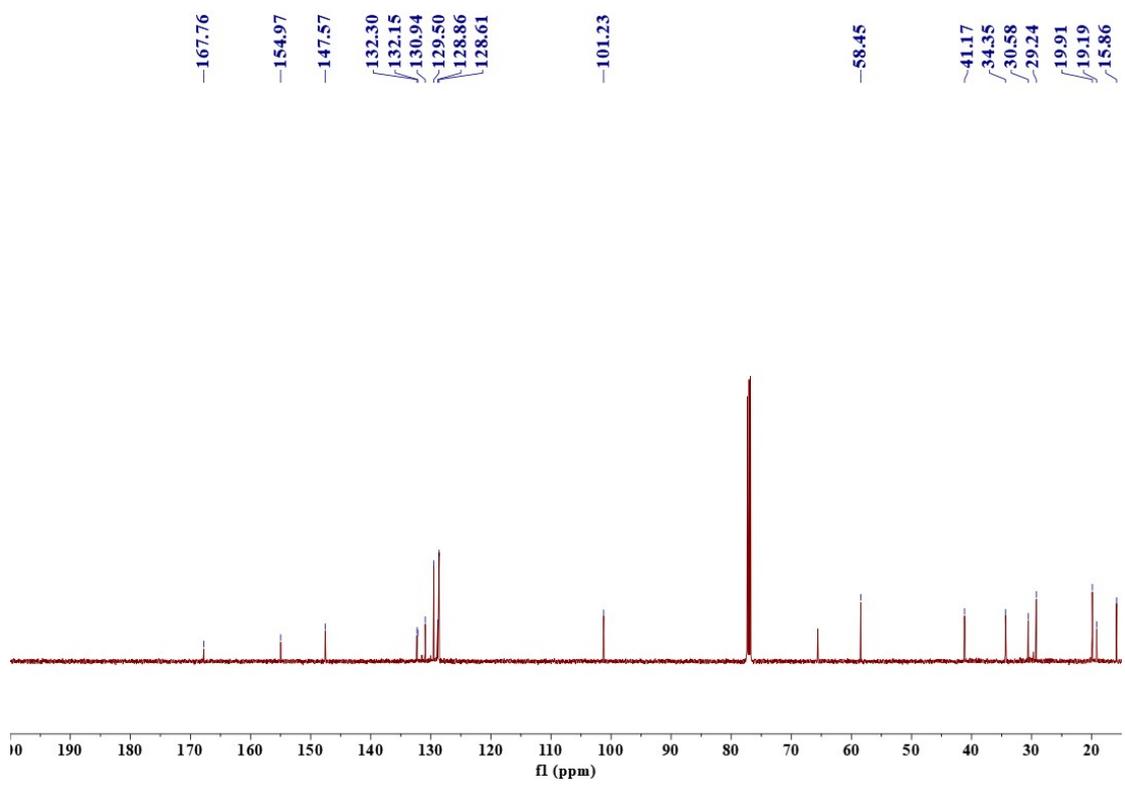
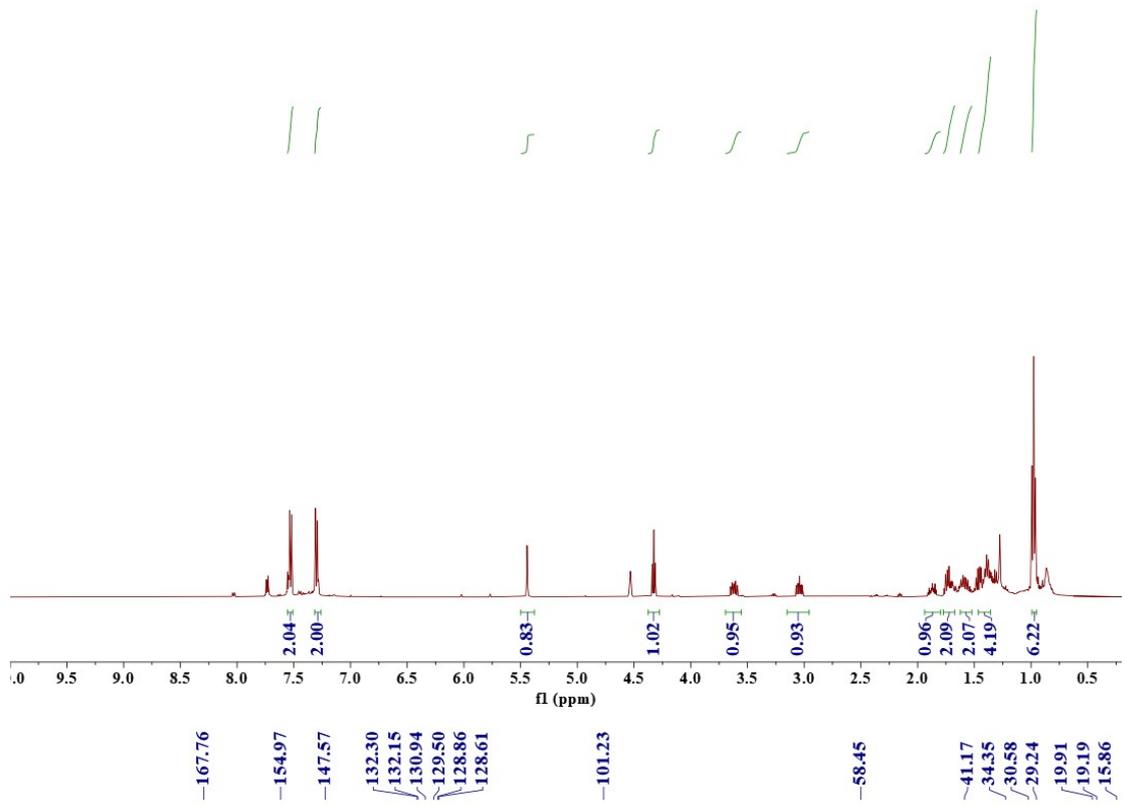
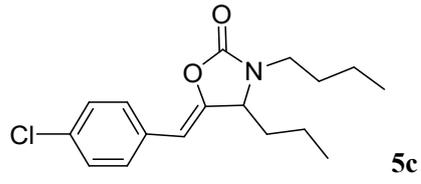
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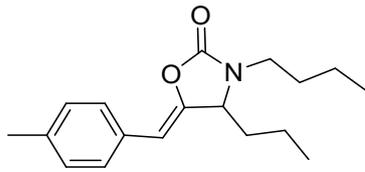




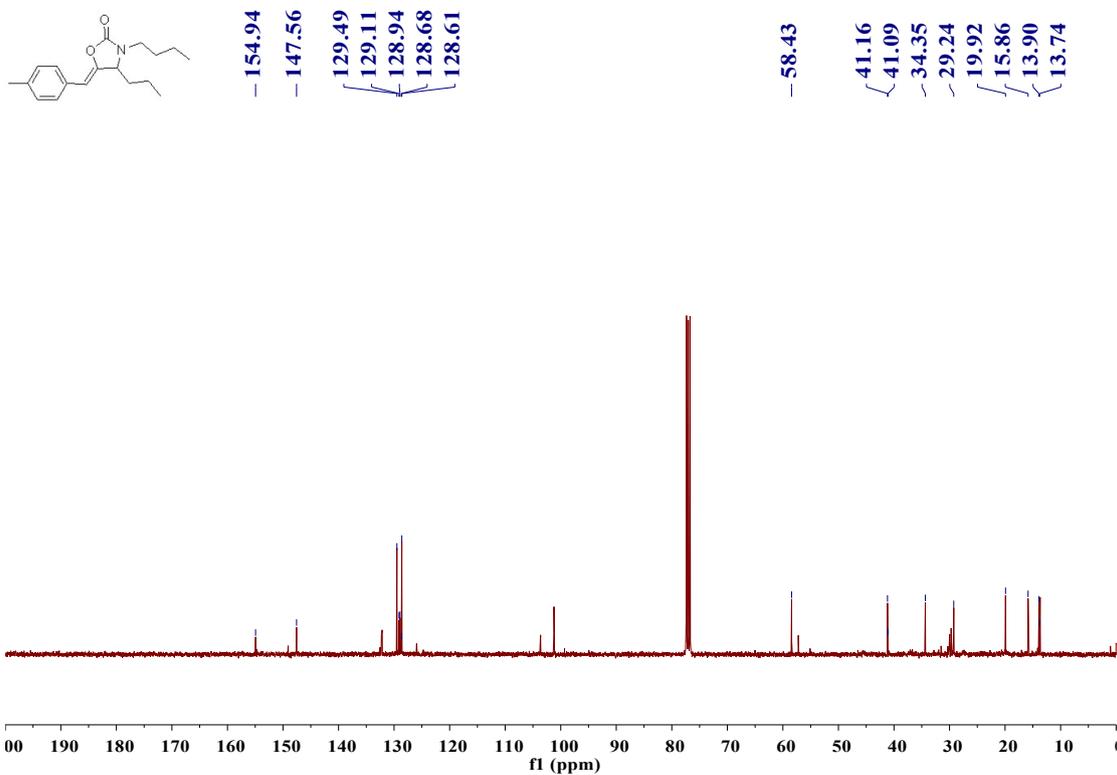
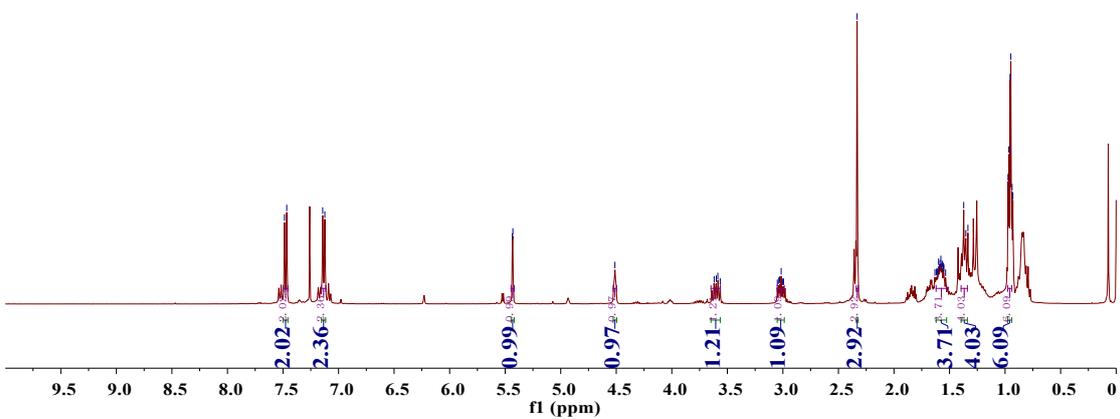
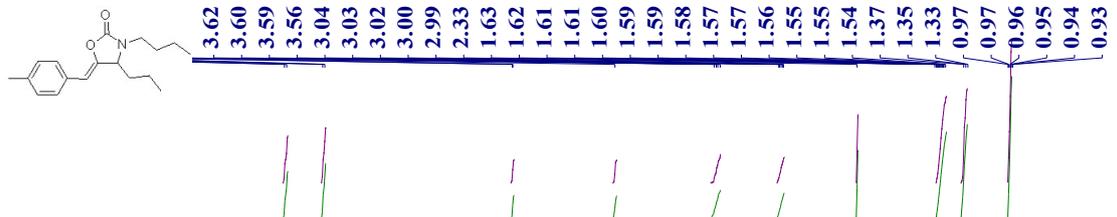
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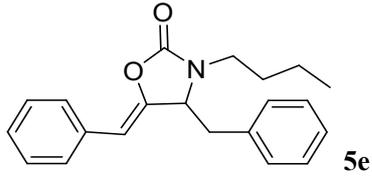






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