

Supplementary Information for

Organocatalysts for the Synthesis of Cyclic Carbonates Under the Conditions of Ambient Temperature and Atmospheric CO₂ Pressure

Yeongju Seong, † Sanghun Lee, † Seungyeon Cho, Yoseph Kim* and Youngjo Kim*

Department of Chemistry, Chungbuk National University, Cheongju, Chungbuk 28644, Republic of Korea

† These authors contributed equally to this work

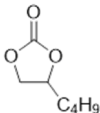
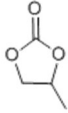
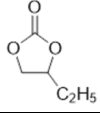
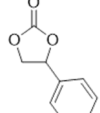
* Correspondence: armadajo@gmail.com, ykim@chungbuk.ac.kr; Tel.: +82-43-261-3395

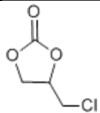
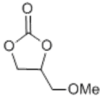
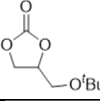
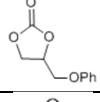
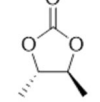
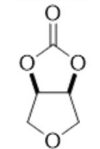
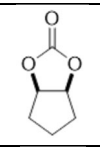
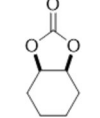
Table of Contents

1. Lists of Known Compounds	2
2. Crystallographic Data	4
3. ¹H-, ¹³C-NMR and HRMS Spectra for the Synthesized Compounds	6

1. Lists of Known Compounds

Table S1. List of known compounds

	2-(1H-1,2,4-triazol-3-yl)phenol (CAT-1) [28]
	2-(1H-pyrazol-3-yl)phenol (CAT-2) [30]
	2-(1H-tetrazol-5-yl)pyridine (CAT-3) [30]
	2-(2-methyl-2H-tetrazol-5-yl)phenol (CAT-4) [31]
	2-(1-phenyl-1H-imidazol-5-yl)phenol (CAT-1) [32]
	4-butyl-1,3-dioxolan-2-one (2a) [33]
	4-methyl-1,3-dioxolan-2-one (2b) [34]
	4-ethyl-1,3-dioxolan-2-one (2c) [35]
	4-phenyl-1,3-dioxolan-2-one (2d) [36]

	4-(chloromethyl)-1,3-dioxolan-2-one (2e) [34]
	4-(methoxymethyl)-1,3-dioxolan-2-one (2f) [37]
	4-[(1,1-dimethylethoxy)methyl]-1,3-dioxolan-2-one (2g) [34]
	4-(phenoxymethyl)-1,3-dioxolan-2-one (2h) [34]
	<i>trans</i> -4,5-dimethyl-1,3-dioxolan-2-one (<i>trans</i> - 2i) [38]
	tetrahydro-furo[3,4- <i>d</i>]-1,3-dioxol-2-one (<i>cis</i> - 2j) [39]
	tetrahydro-4 <i>H</i> -cyclopenta[<i>d</i>][1,3]dioxol-2-one (<i>cis</i> - 2k) [40]
	hexahydrobenzo[<i>d</i>][1,3]dioxol-2-one (<i>cis</i> - 2l) [41]

2. Crystallographic Data

Table S2. Crystallographic data for **CAT-6**

Compound	CAT-6
Chemical formula	C ₁₄ H ₁₂ N ₄ O
Crystal system	Monoclinic
Space group	P 21
<i>a</i> (Å)	8.7410(18) Å
<i>b</i> (Å)	12.941(3) Å
<i>c</i> (Å)	11.695(2) Å
α (deg)	90°
β (deg)	107.85(3)°
γ (deg)	90°
<i>V</i> (Å ³)	1259.2(5) Å ³
<i>Z</i>	4
<i>d</i> _{calcd} (g/cm ³)	1.331 Mg/m ³
<i>F</i> (000)	528
Reflections collected	12436
# of independent reflections	5208 [R(int) = 0.0359]
# of parameters	345
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>)) ^a	0.0491
<i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>)) ^b	0.1119
GOF(<i>I</i> > 2σ(<i>I</i>))	1.010

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}.$$

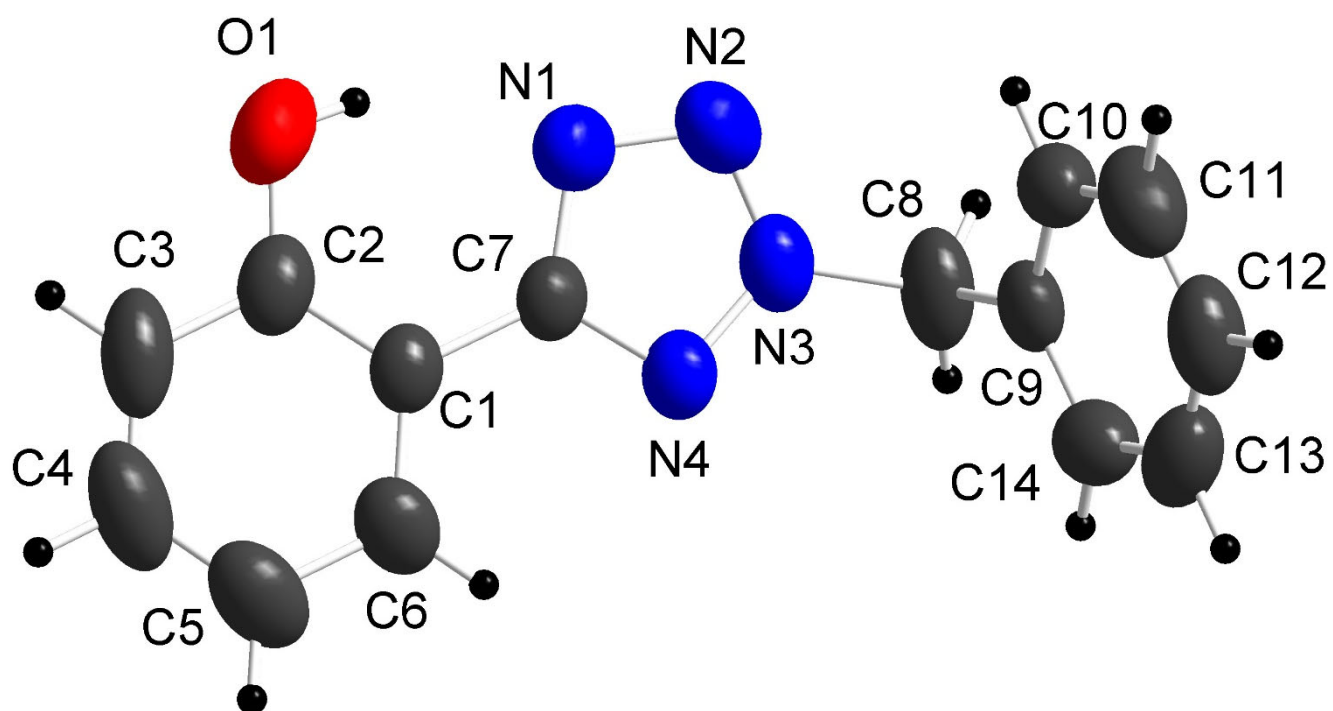


Figure S1. X-ray structure for 2-(2-benzyl-2*H*-tetrazol-5-yl)phenol(CAT-6).

3. ^1H -, ^{13}C -NMR and HRMS Spectra for the Synthesized Catalysts

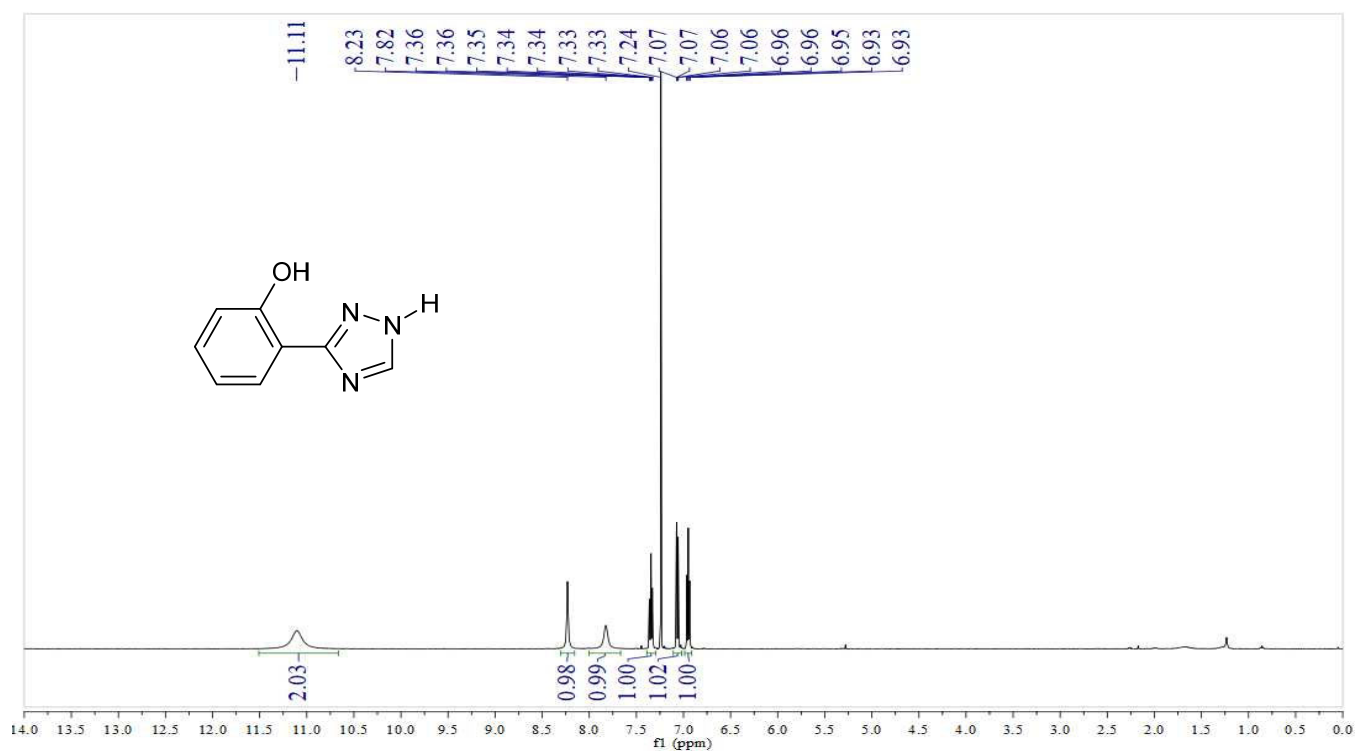


Figure S2. ^1H NMR spectrum of 2-(1H-1,2,4-triazol-3-yl)phenol (CAT-1) in CDCl₃.

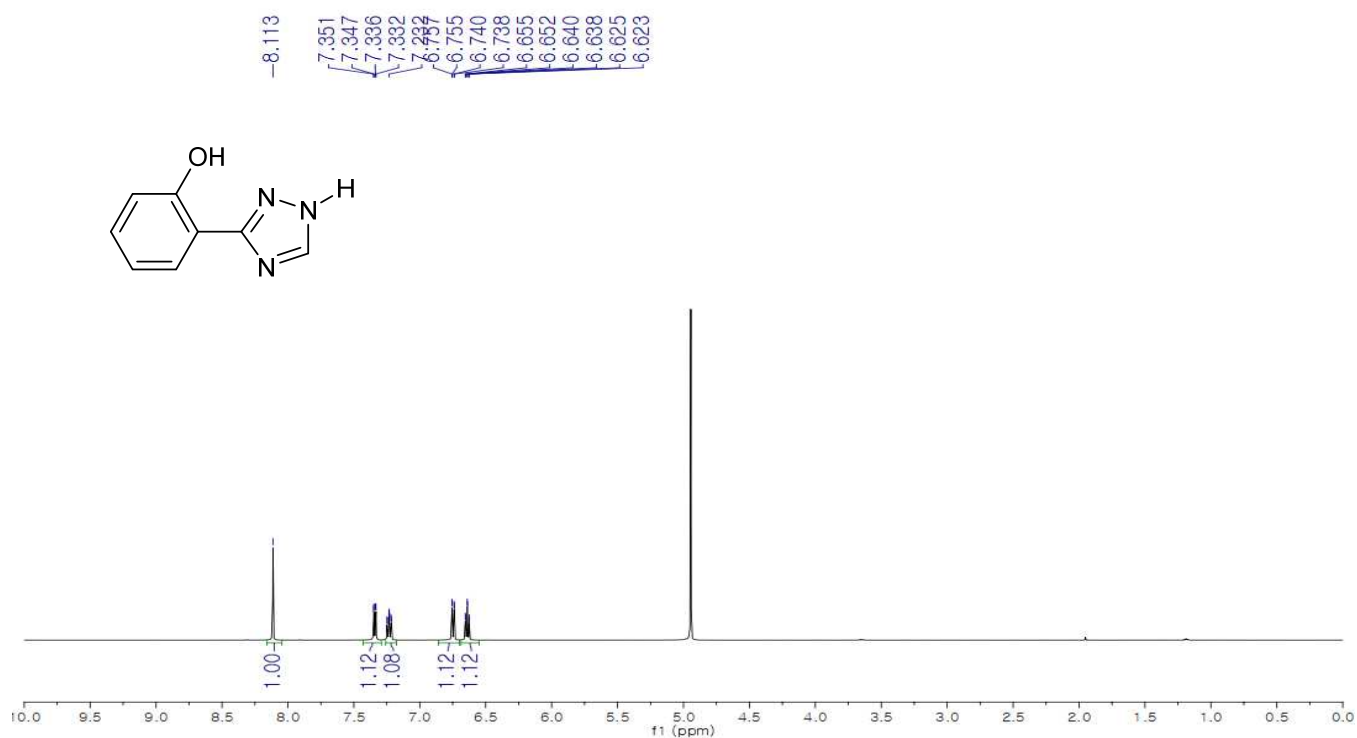


Figure S3. ^1H NMR spectrum of 2-(1H-1,2,4-triazol-3-yl)phenol (CAT-1) in D₂O.

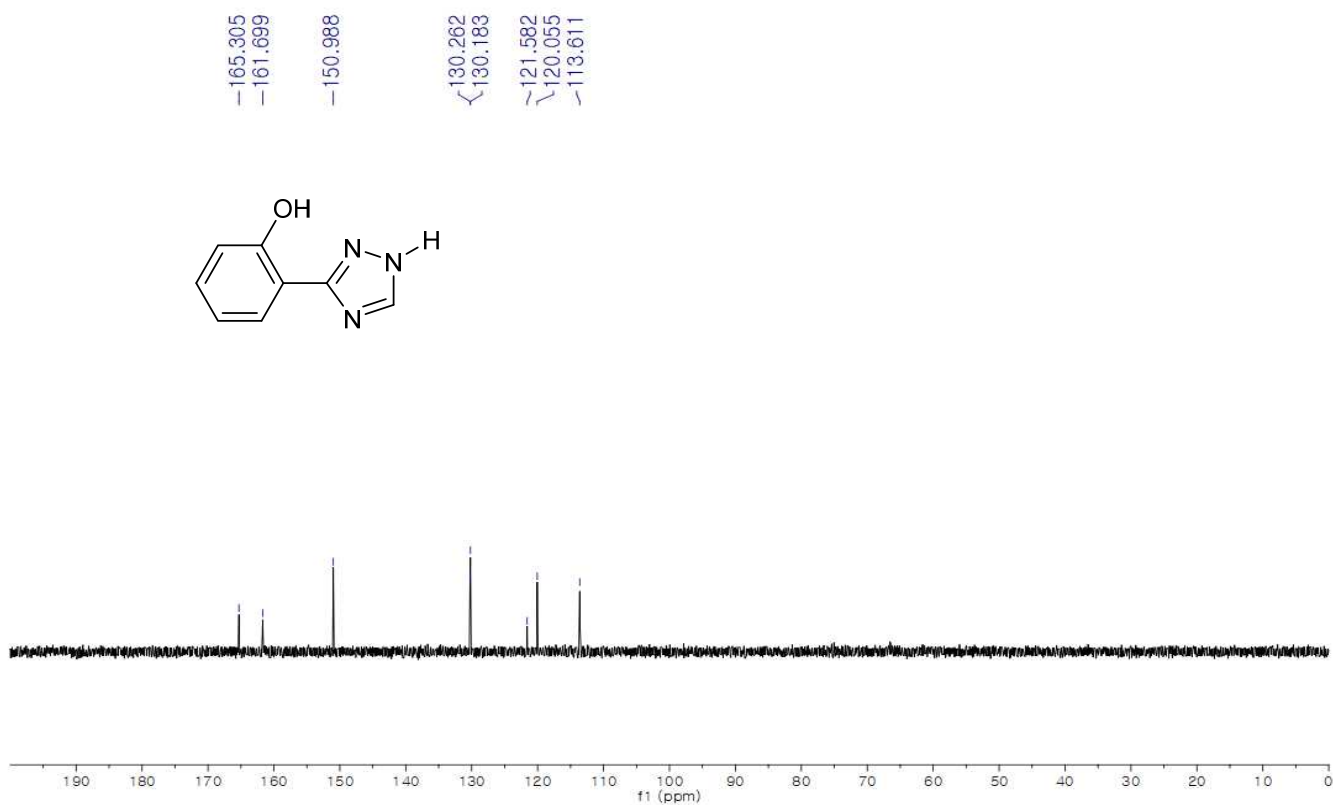
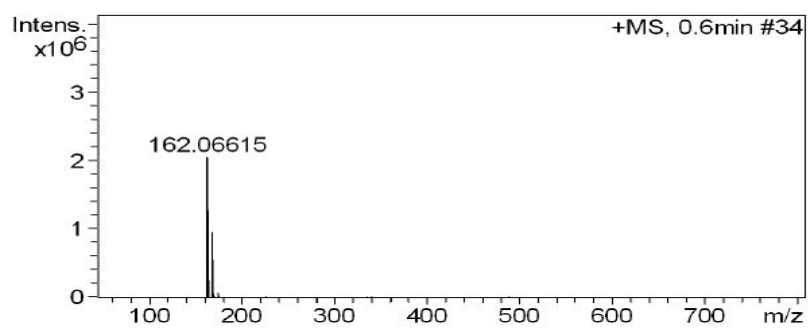


Figure S4. ¹³C NMR spectrum of 2-(1H-1,2,4-triazol-3-yl)phenol (CAT-1) in D₂O.

+MS, 0.6min #34



C₈H₇N₃O, M+nH ,162.07

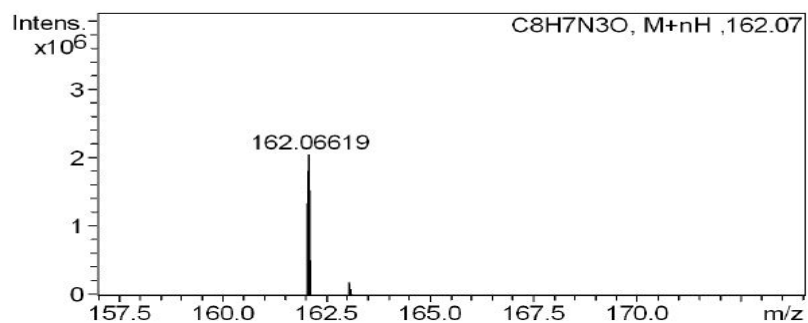


Figure S5. HR-MS spectrum of 2-(1H-1,2,4-triazol-3-yl)phenol (CAT-1).



Figure S6. COSY spectrum of 2-(1*H*-1,2,4-triazol-3-yl)phenol (CAT-1) in D₂O.

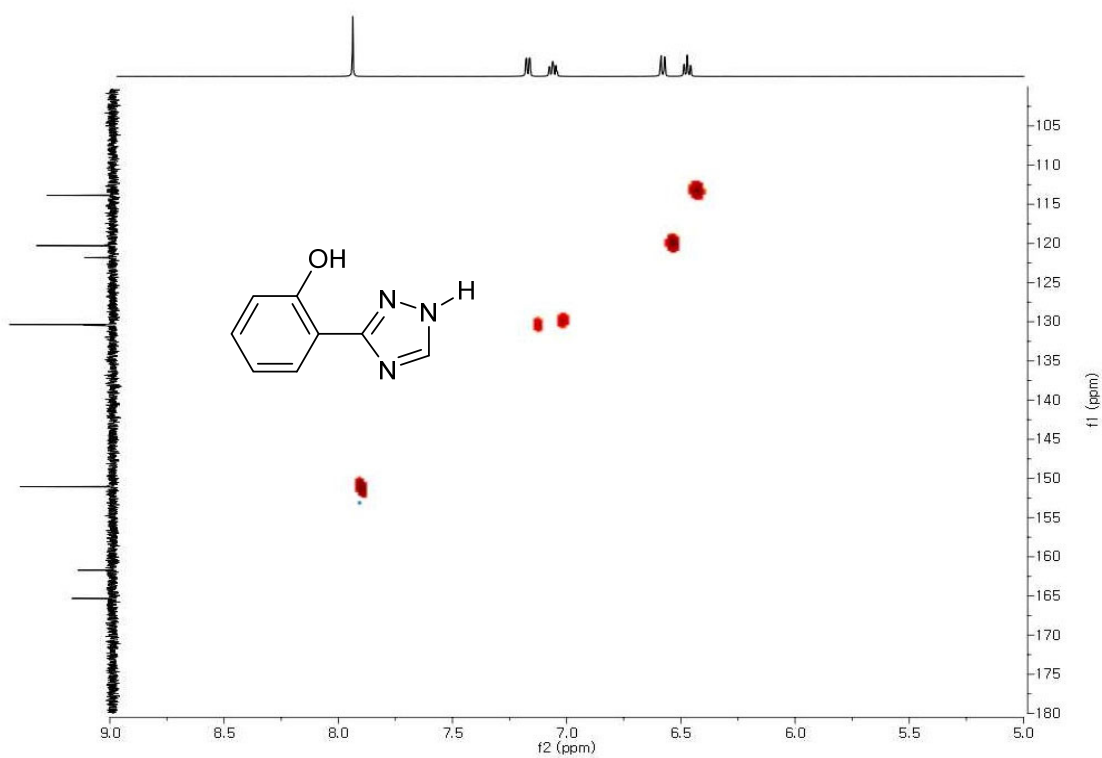


Figure S7. HSQC spectrum of 2-(1*H*-1,2,4-triazol-3-yl)phenol (CAT-1) in D₂O.

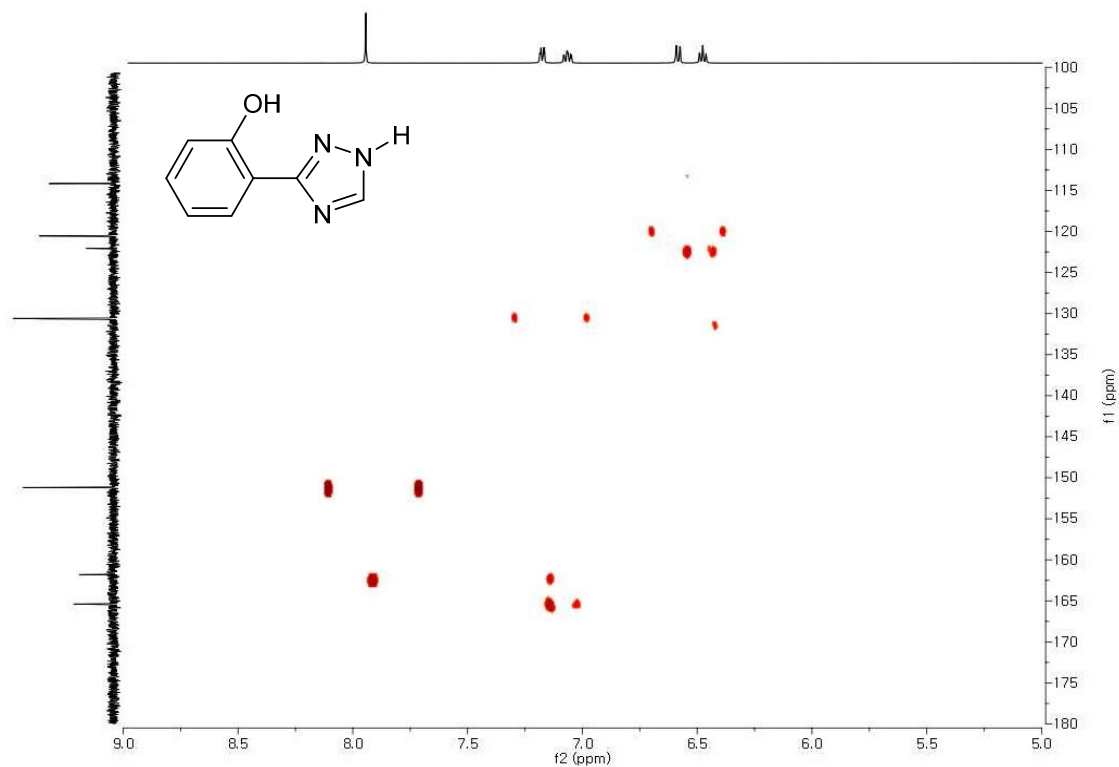


Figure S8. HMBC spectrum of 2-(1H-1,2,4-triazol-3-yl)phenol (CAT-1) in D₂O.

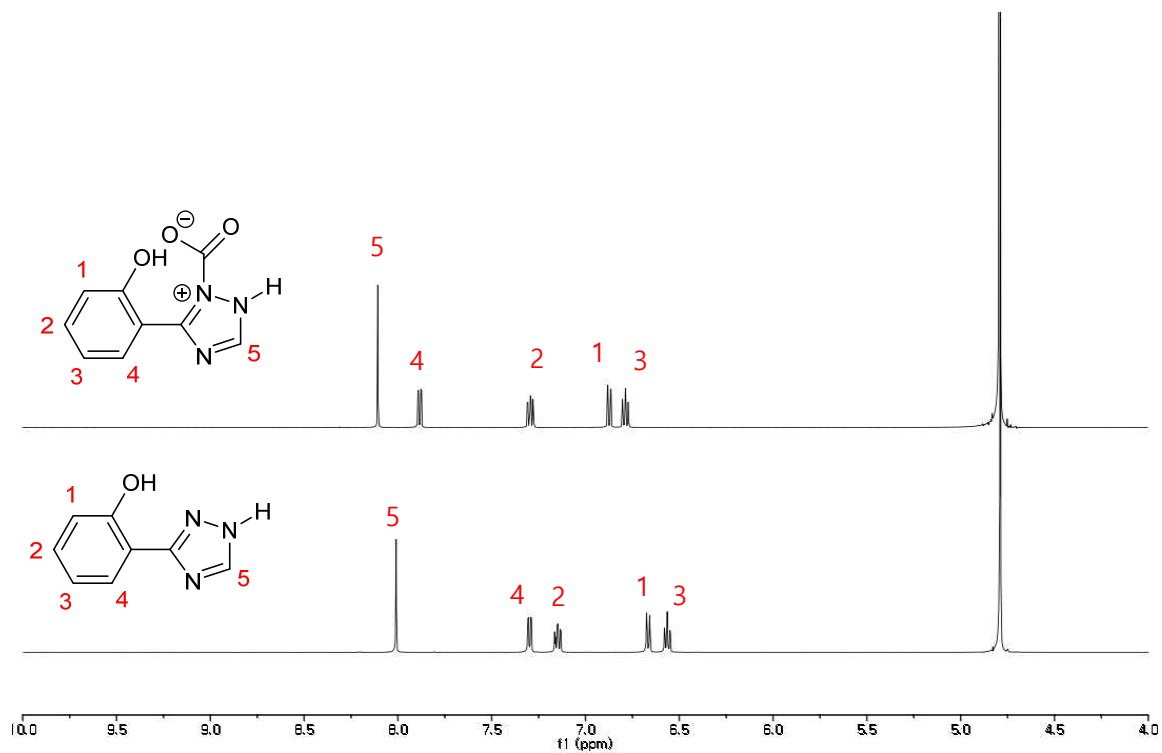


Figure S9. ^1H NMR spectrum of CAT-1 before (bottom) and after (top) bubbling CO₂ in D₂O.

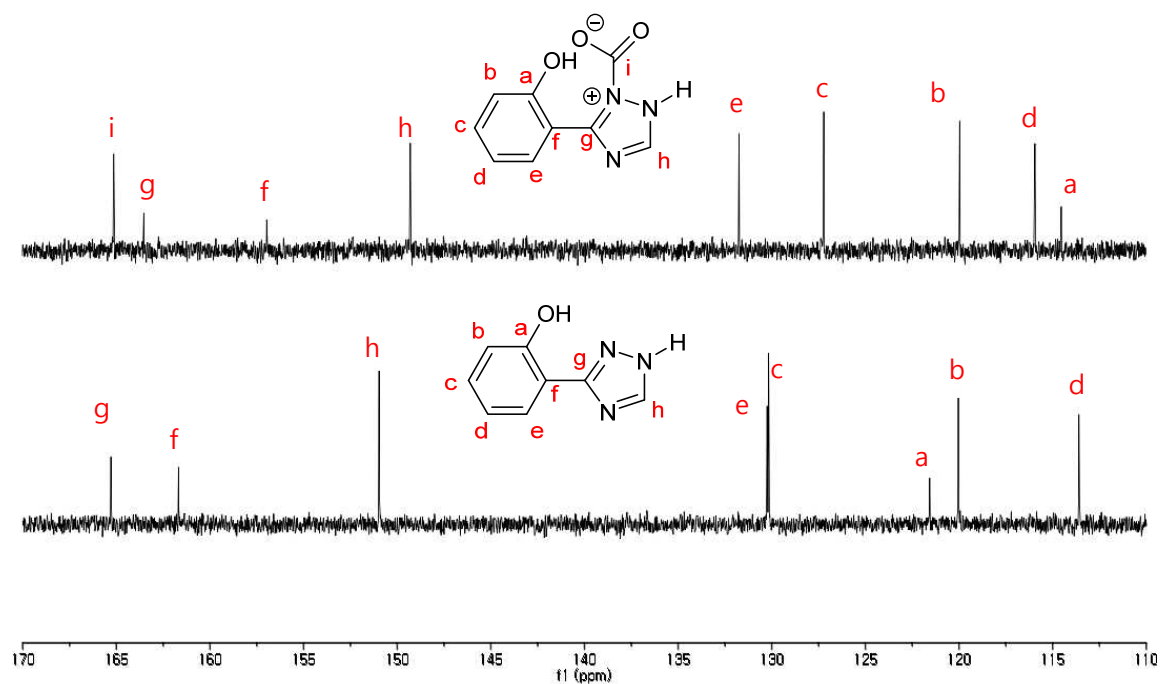


Figure S10. ^{13}C NMR spectrum of CAT-1 before (bottom) and after (top) bubbling CO_2 in D_2O .

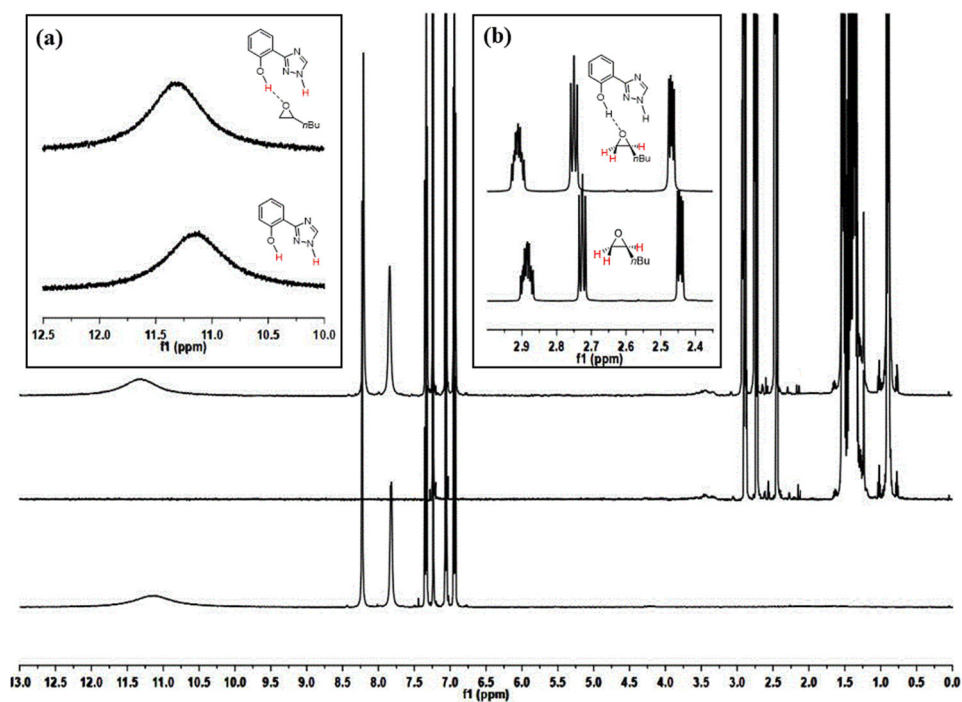


Figure S11. ^1H NMR spectrum of **CAT-1** (bottom), **1a** (middle), and a mixture of **CAT-1** and **1a** (top) in CDCl_3 . (a) O-H and N-H peaks in the ^1H NMR spectrum of **CAT-1** before (bottom) and after (top) adding **1a** in CDCl_3 ; (b) The methine proton and methylene protons on the three-membered ring carbons in the ^1H NMR spectrum of **1a** before (bottom) and after (top) adding **CAT-1** in CDCl_3 .

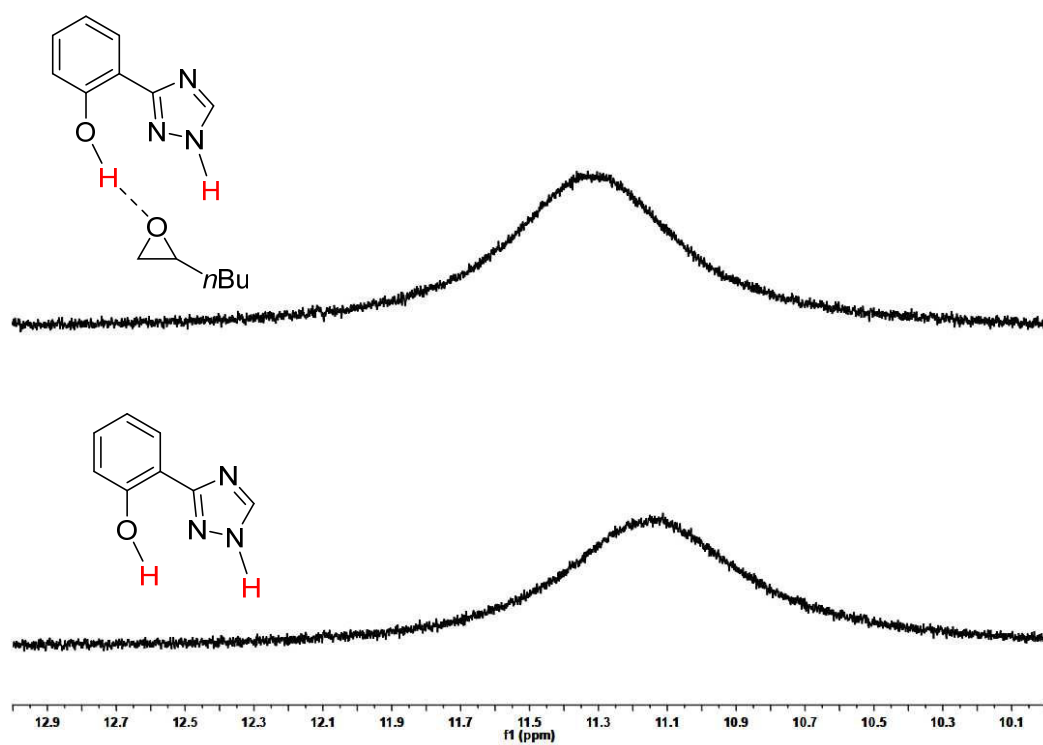


Figure S12. O–H and N–H peaks in the ^1H NMR spectrum of CAT–1 before (bottom) and after (top) adding **1a** in CDCl_3 .

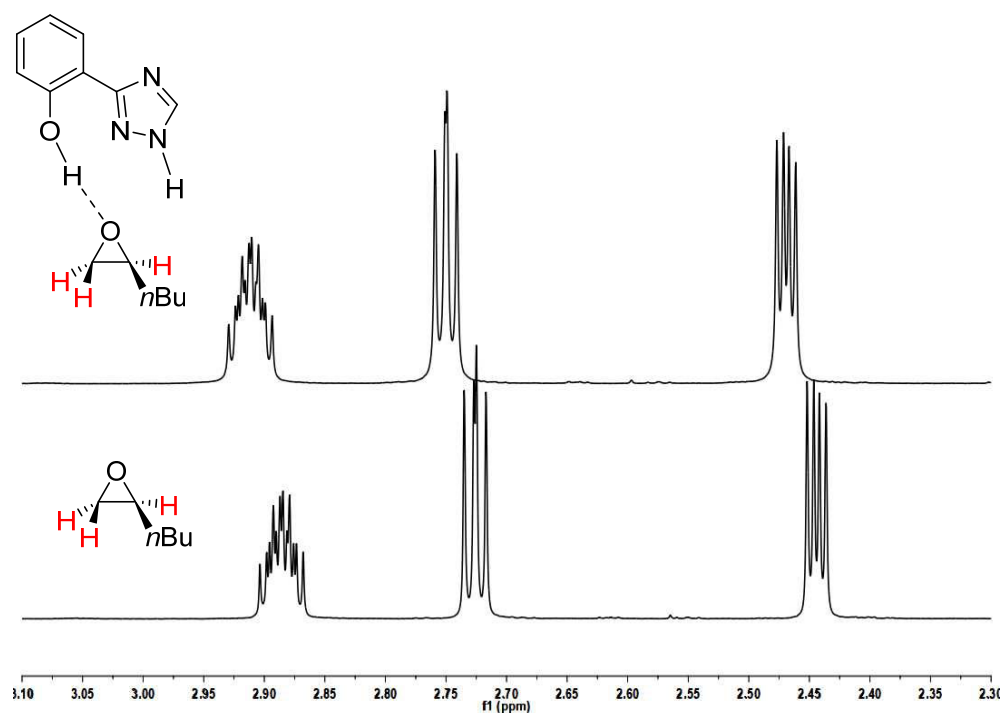


Figure S13. The methine proton and methylene protons on the three-membered ring carbons in the ^1H NMR spectrum of **1a** before (bottom) and after (top) adding **CAT-1** in CDCl_3 .

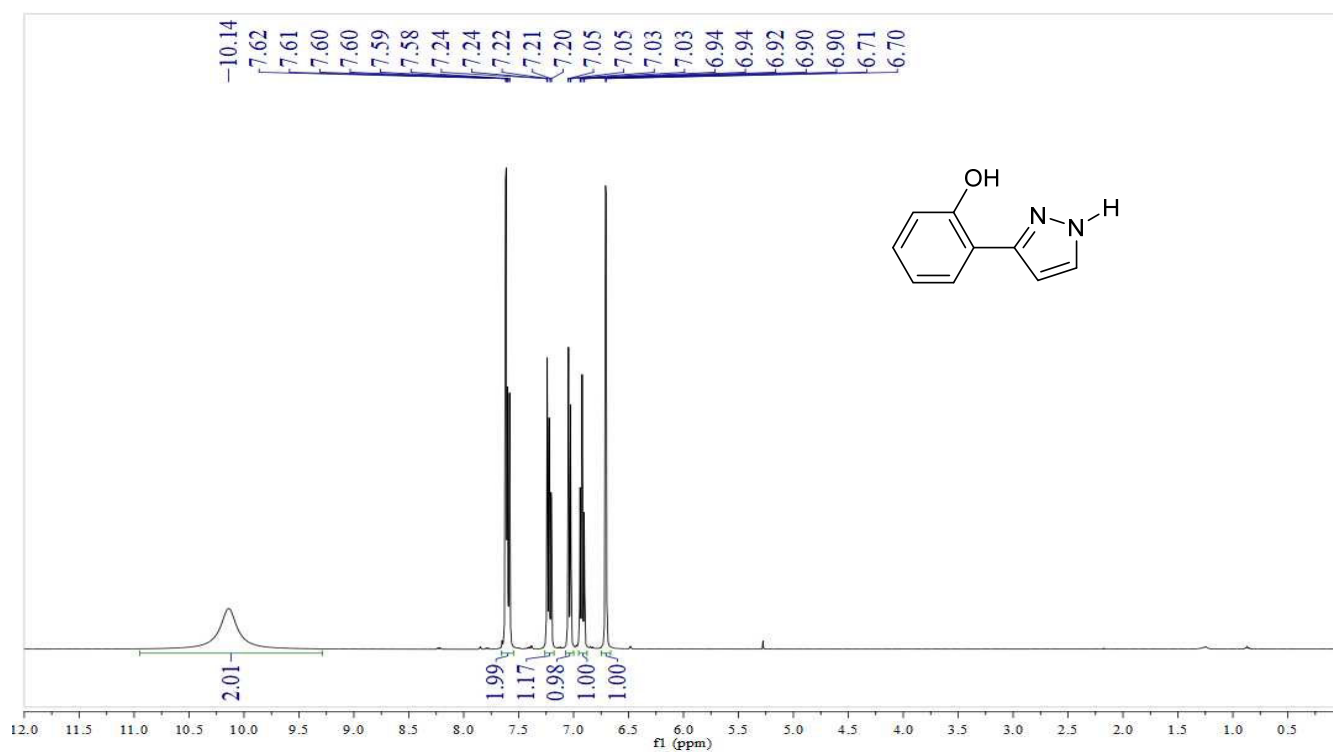


Figure S14. ¹H NMR spectrum of 2-(1*H*-pyrazol-3-yl)phenol (**CAT-2**) in CDCl₃.

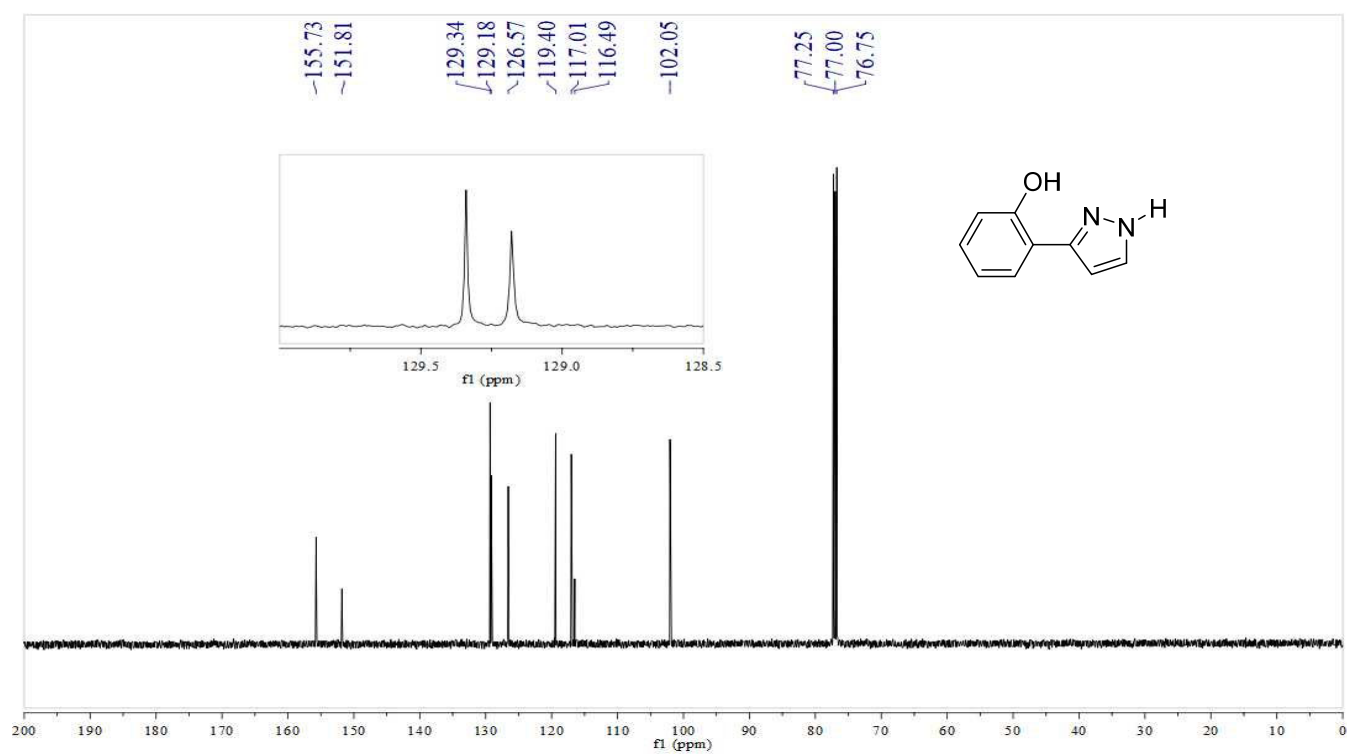


Figure S15. ¹³C NMR spectrum of 2-(1*H*-pyrazol-3-yl)phenol (**CAT-2**) in CDCl₃.

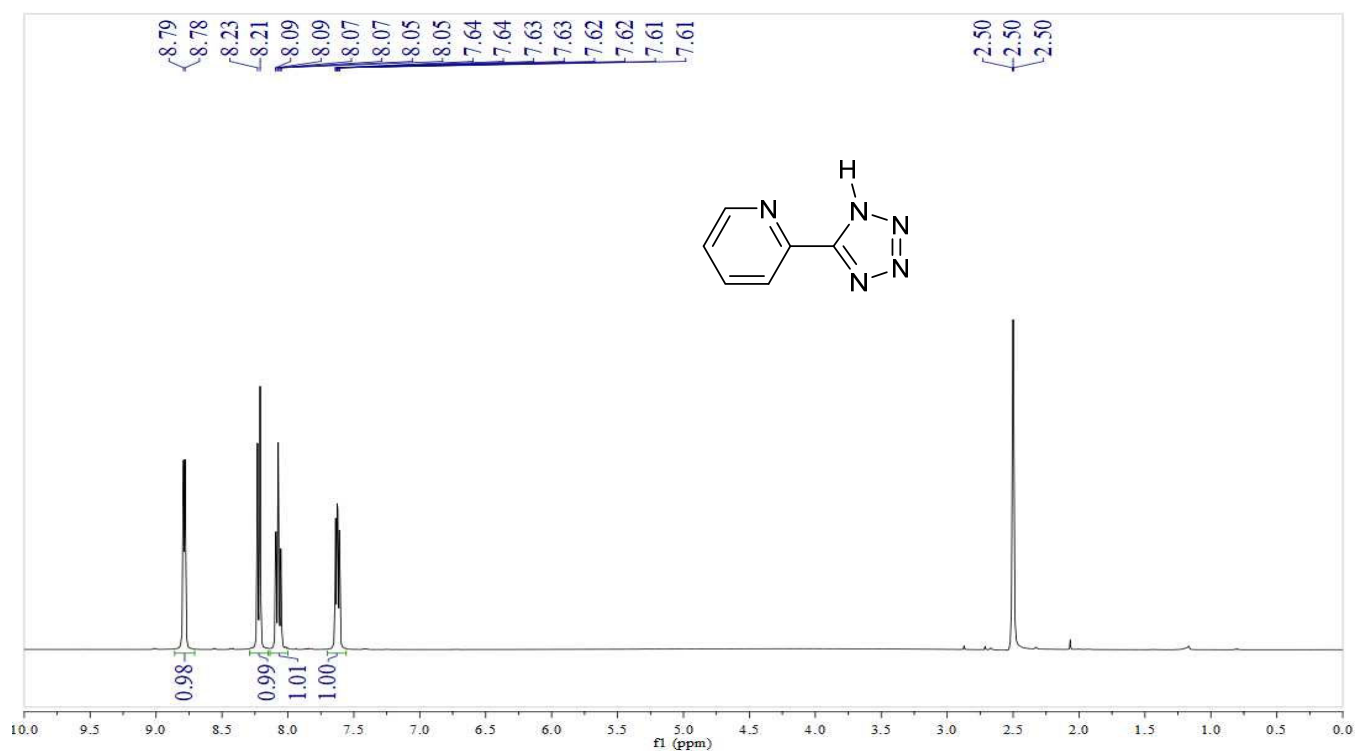


Figure S16. ¹H NMR spectrum of 2-(1*H*-tetrazol-5-yl)pyridine (CAT-3) in DMSO-*d*₆.

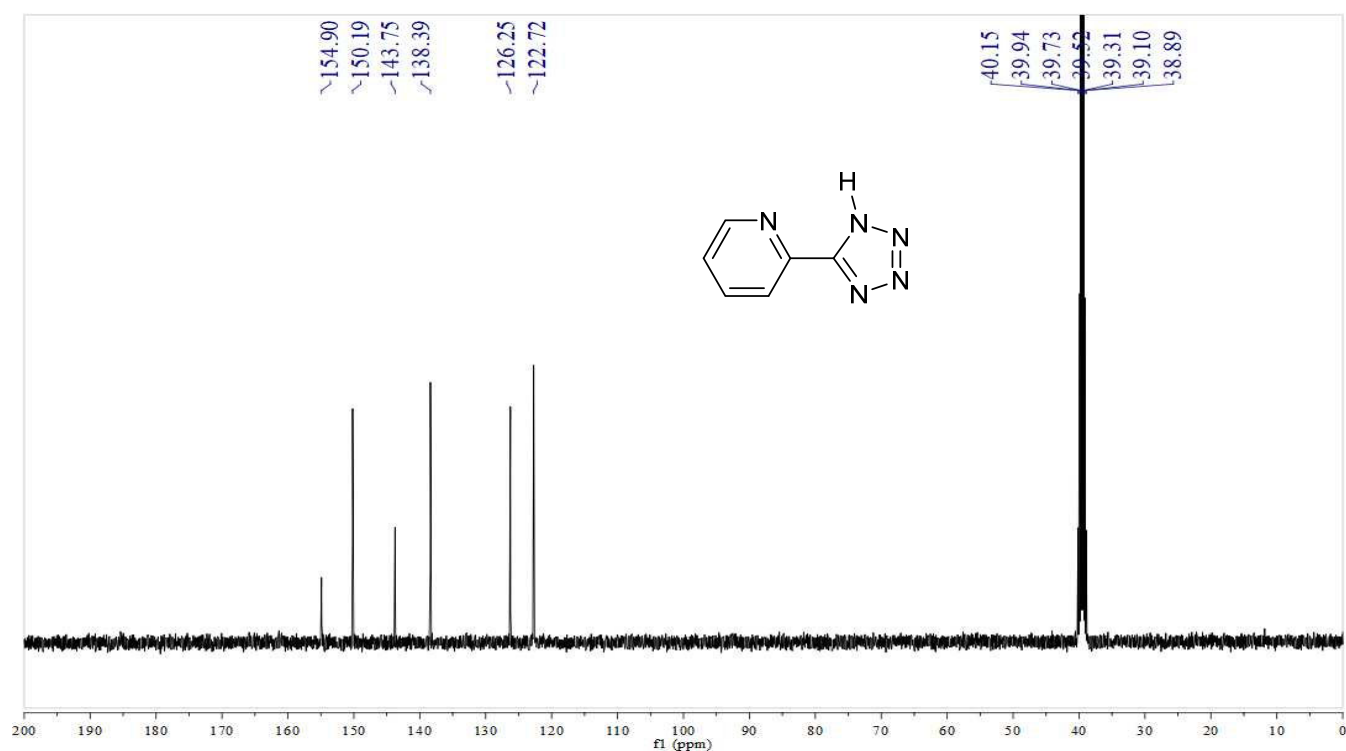


Figure S17. ¹³C NMR spectrum of 2-(1*H*-tetrazol-5-yl)pyridine (CAT-3) in CDCl₃.

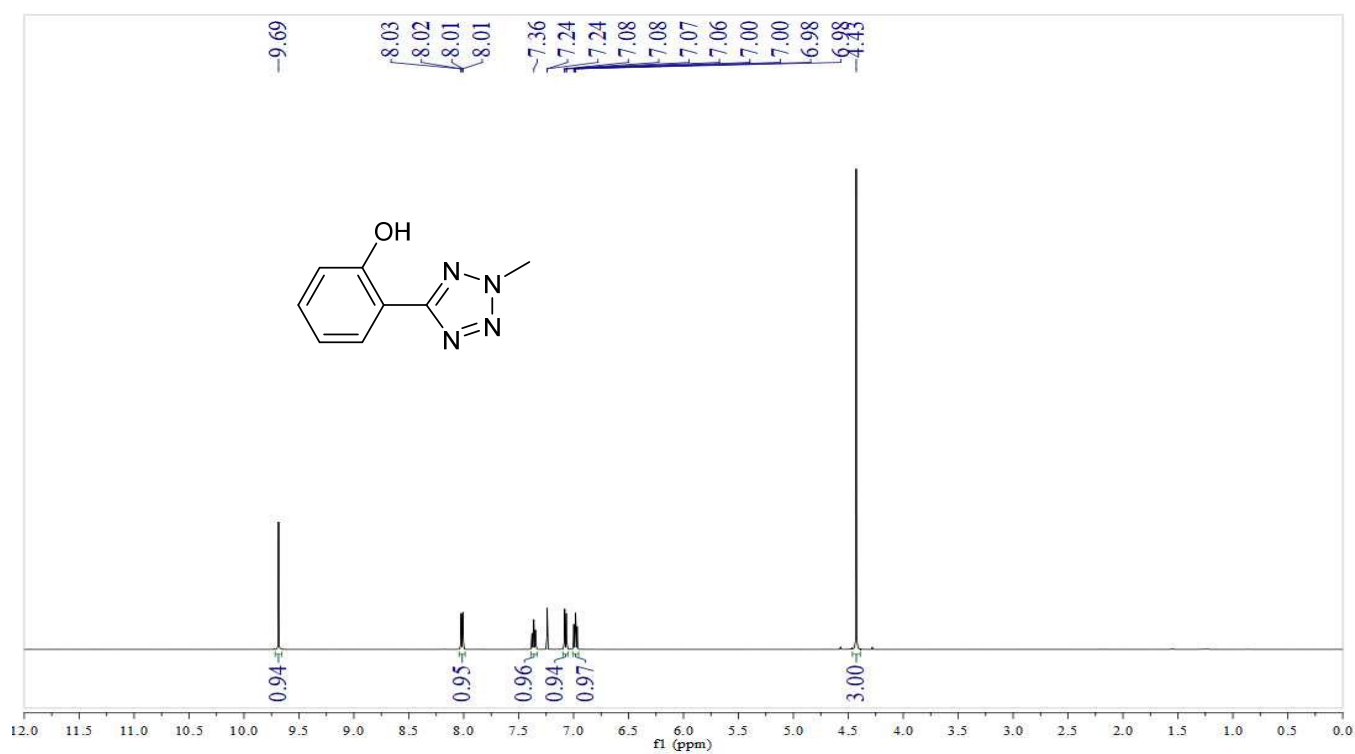


Figure S18. ¹H NMR spectrum of 2-(2-methyl-2H-tetrazol-5-yl)phenol (CAT-4) in CDCl₃.

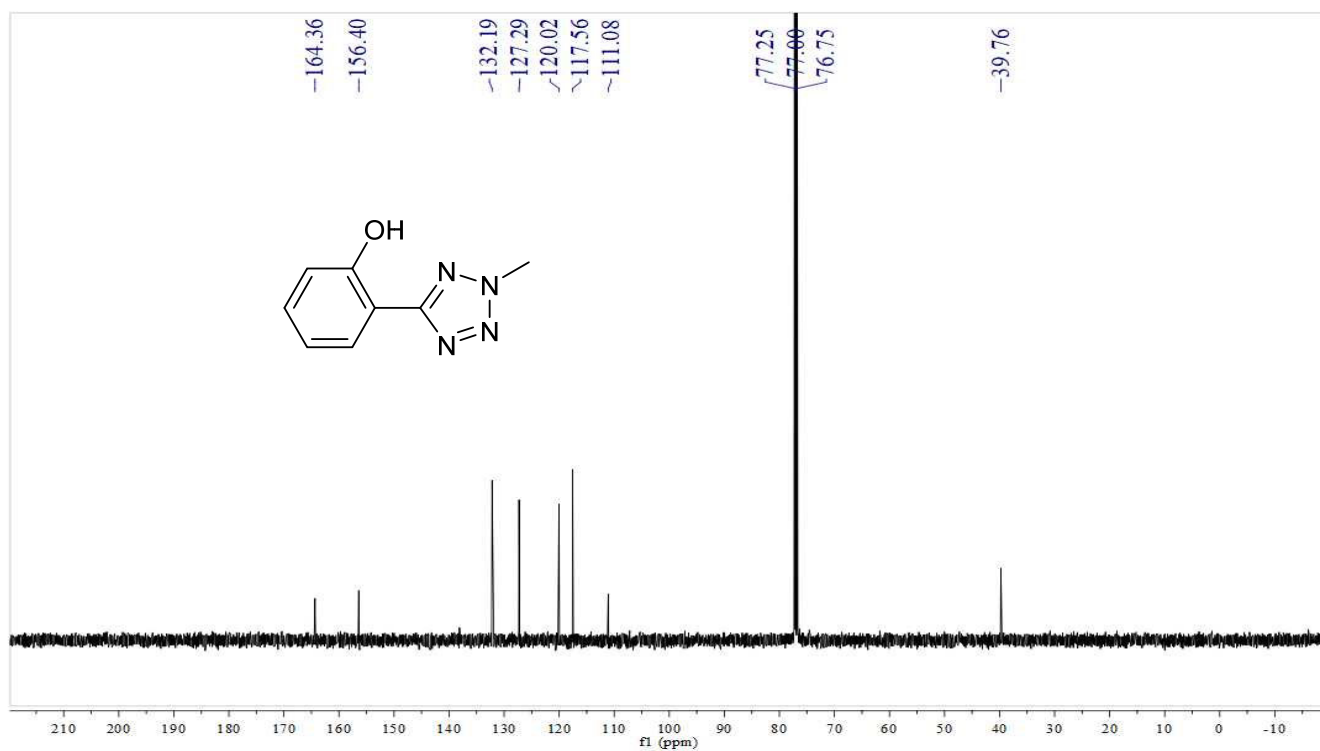


Figure S19. ¹³C NMR spectrum of 2-(2-methyl-2H-tetrazol-5-yl)phenol (CAT-4) in CDCl₃.

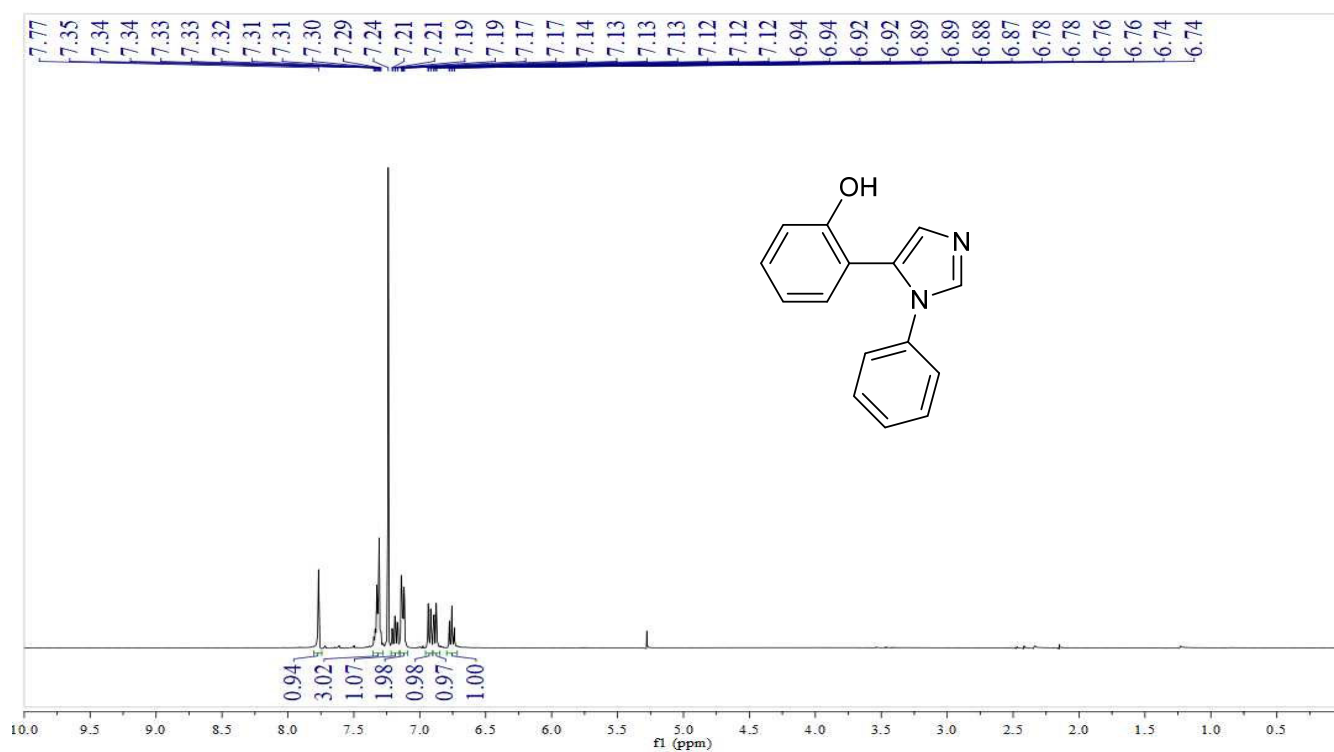


Figure S20. ¹H NMR spectrum of 2-(1-phenyl-1*H*-imidazol-5-yl)phenol (CAT-5) in CDCl₃.

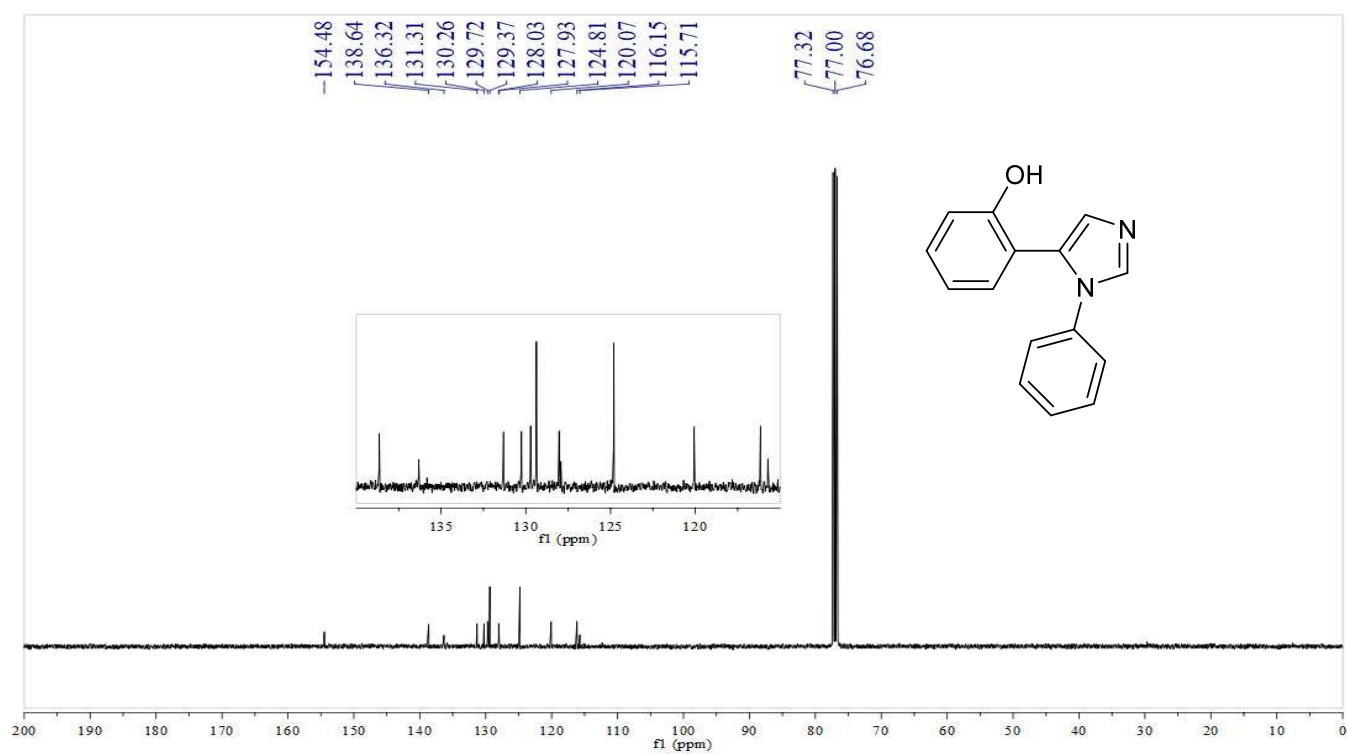


Figure S21. ¹³C NMR spectrum of 2-(1-phenyl-1*H*-imidazol-5-yl)phenol (CAT-5) in CDCl₃.

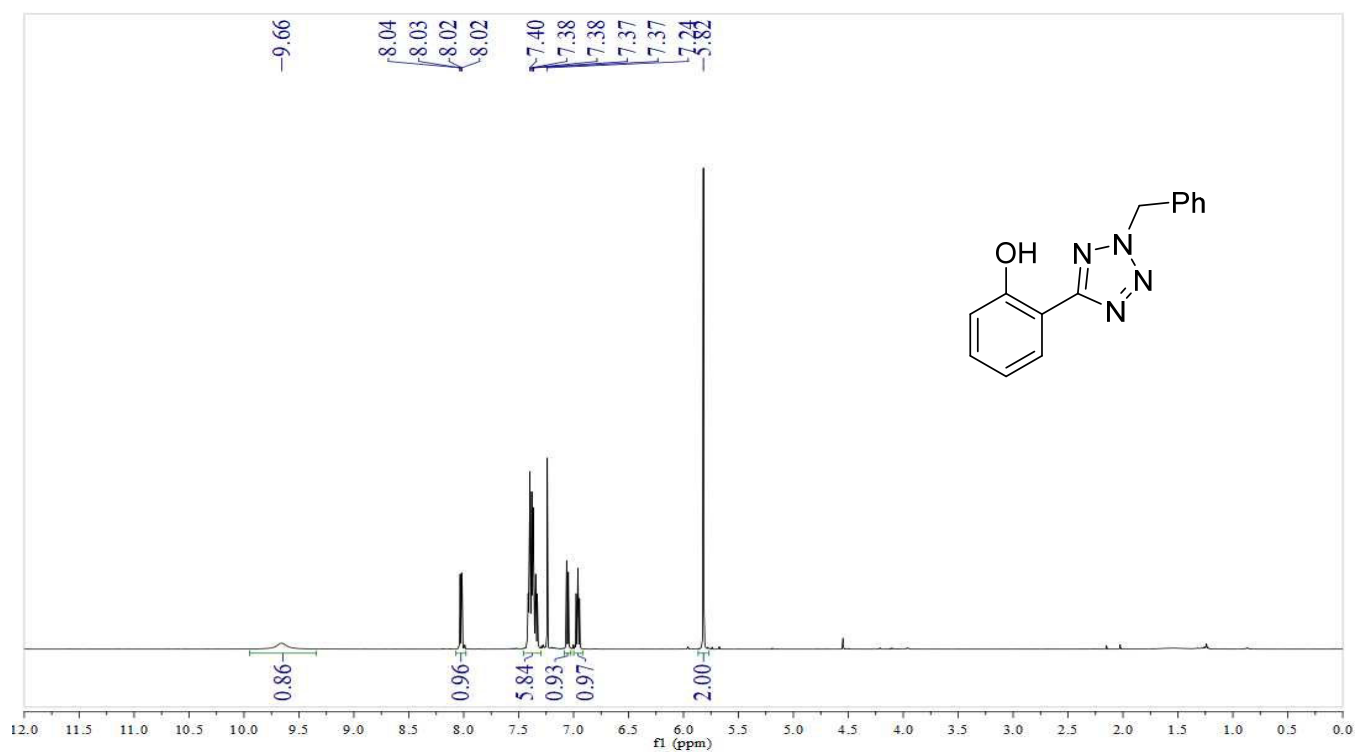


Figure S22. ¹H NMR spectrum of 2-(2-benzyl-2*H*-tetrazol-5-yl)phenol (**CAT-6**) in CDCl₃.

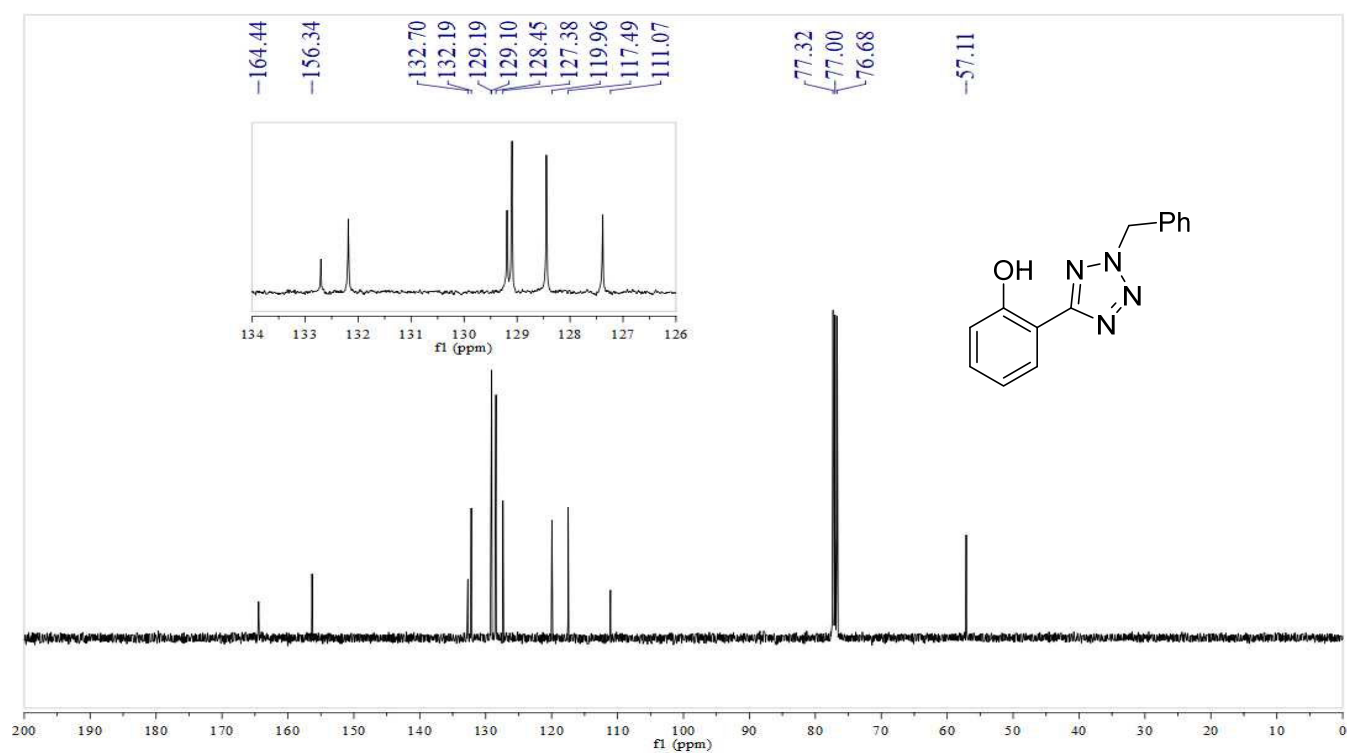
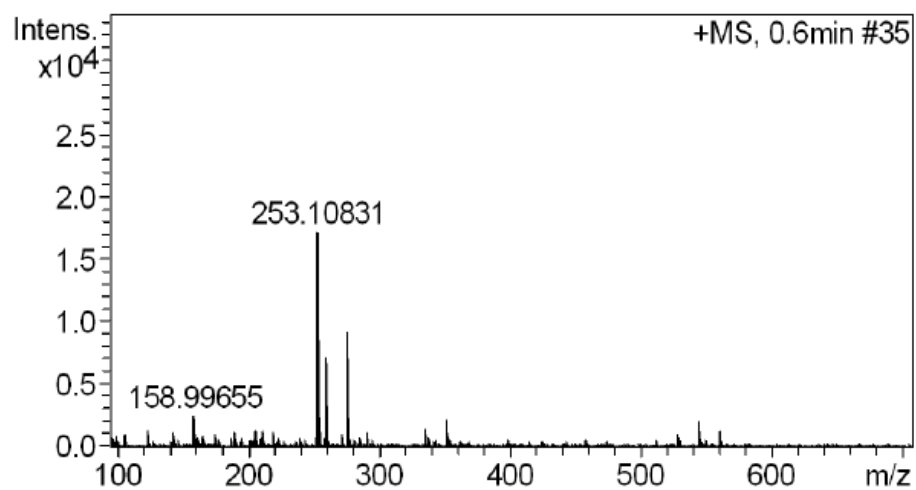


Figure S23. ¹³C NMR spectrum of 2-(2-benzyl-2*H*-tetrazol-5-yl)phenol (**CAT-6**) in CDCl₃.

+MS, 0.6min #35



C₁₄H₁₂N₄O, M+nH ,253.11

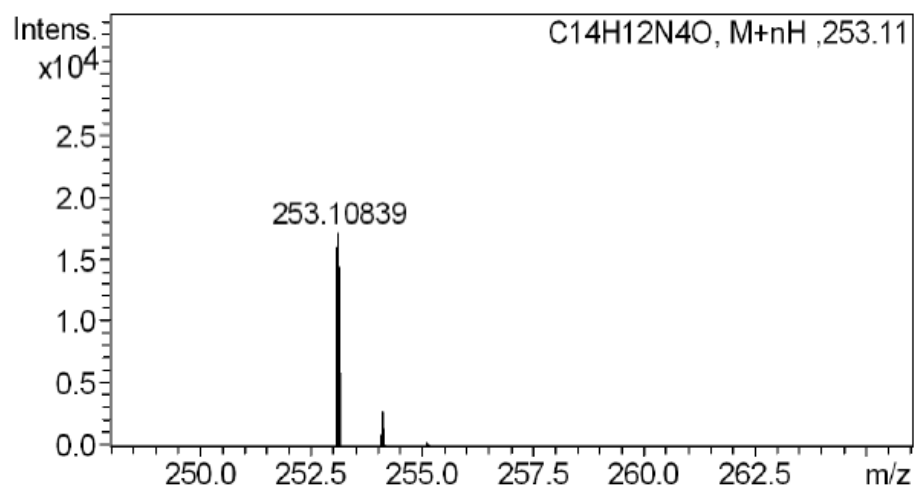


Figure S24. HR-MS spectrum of 2-(2-benzyl-2*H*-tetrazol-5-yl)phenol (CAT-6).

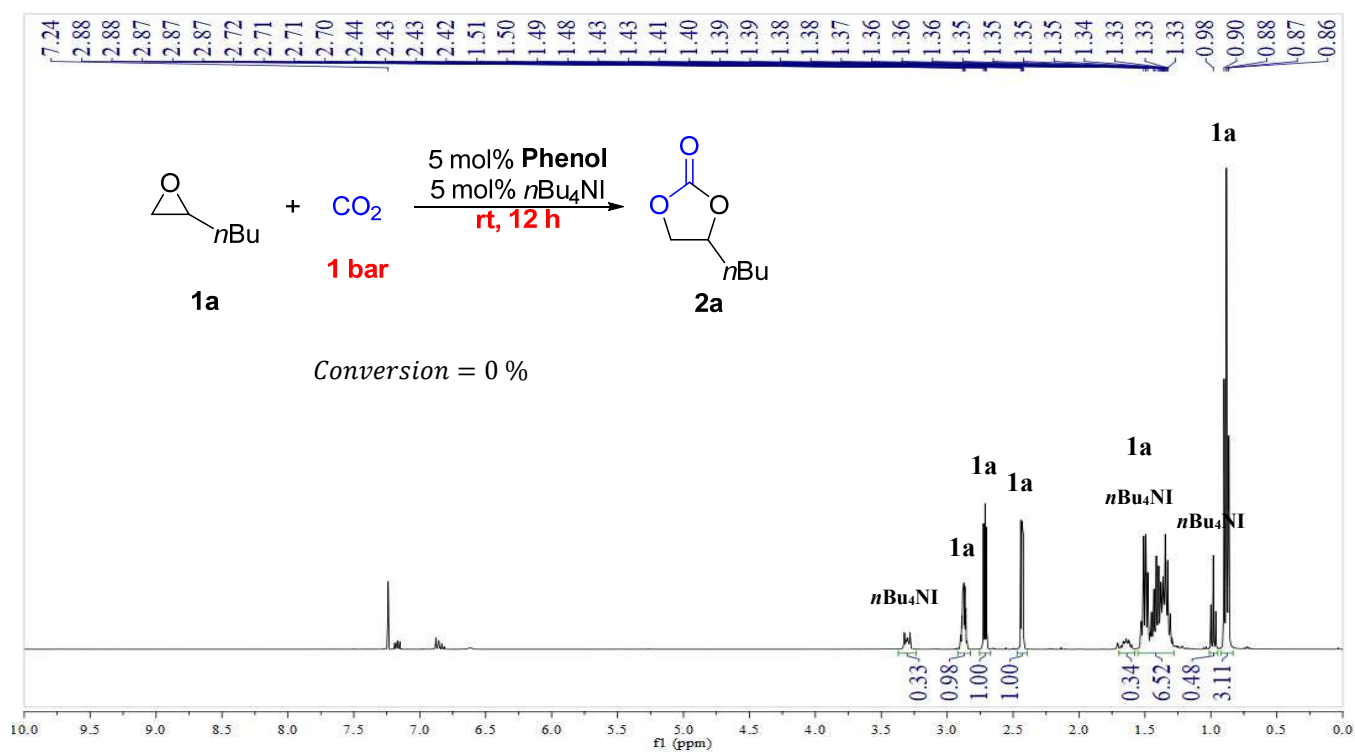


Figure S25. ^1H NMR spectrum for an aliquot of the reaction mixture after reaction in Table 1, entry 1.

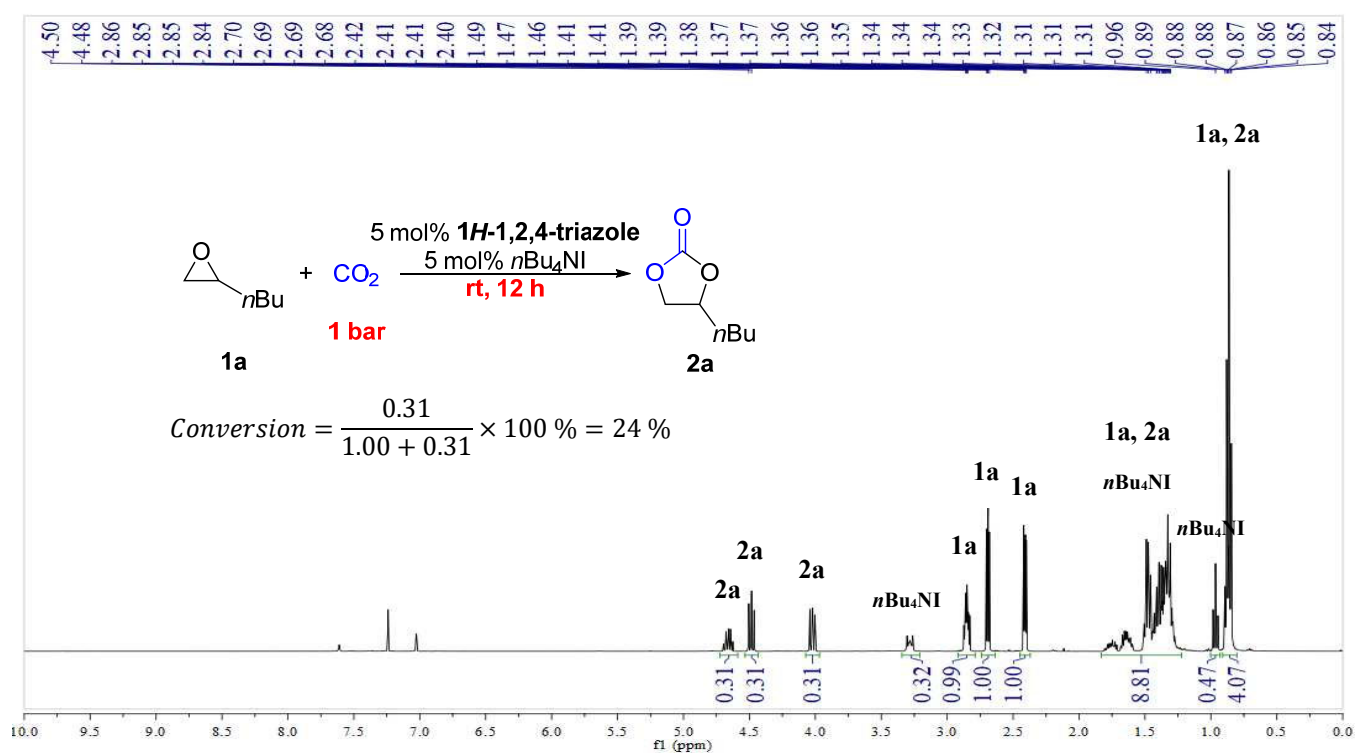


Figure S26. ^1H NMR spectrum for an aliquot of the reaction mixture after reaction in Table 1, entry 2.

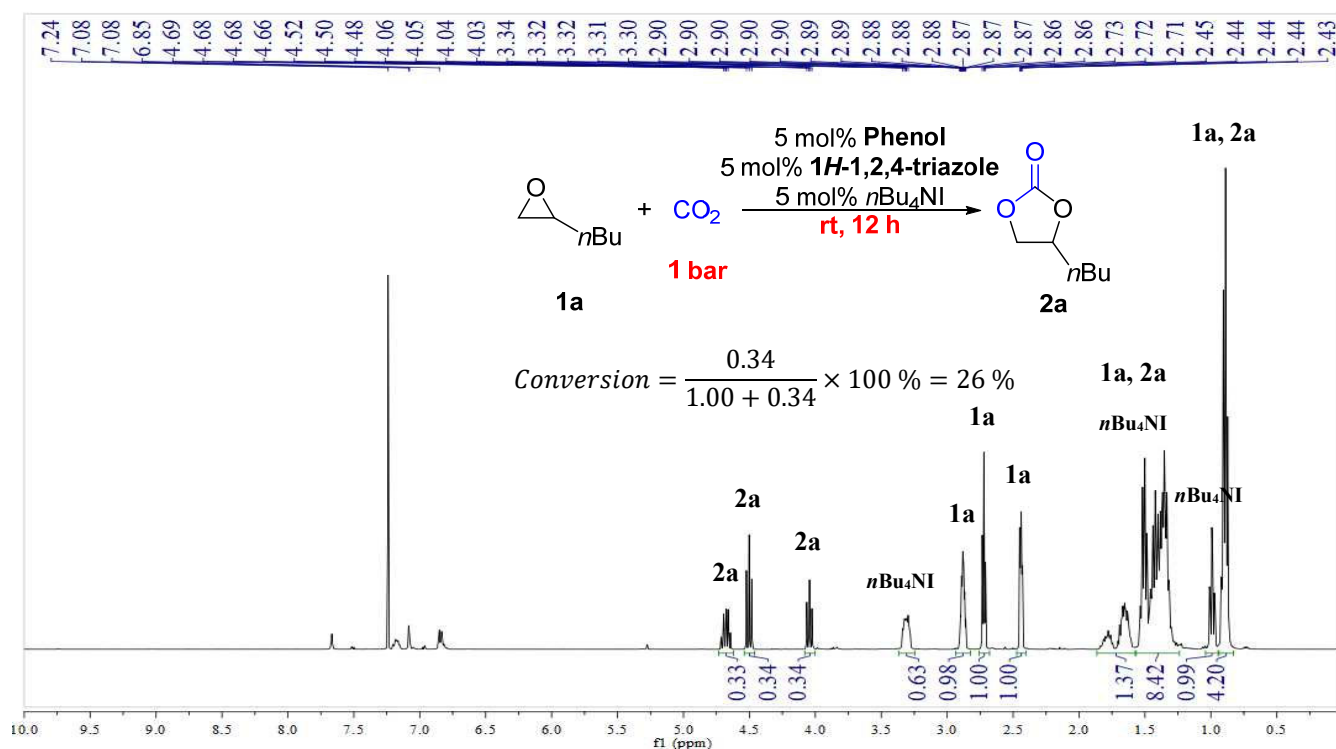


Figure S27. ¹H NMR spectrum for an aliquot of the reaction mixture after reaction in Table 1, entry 3.

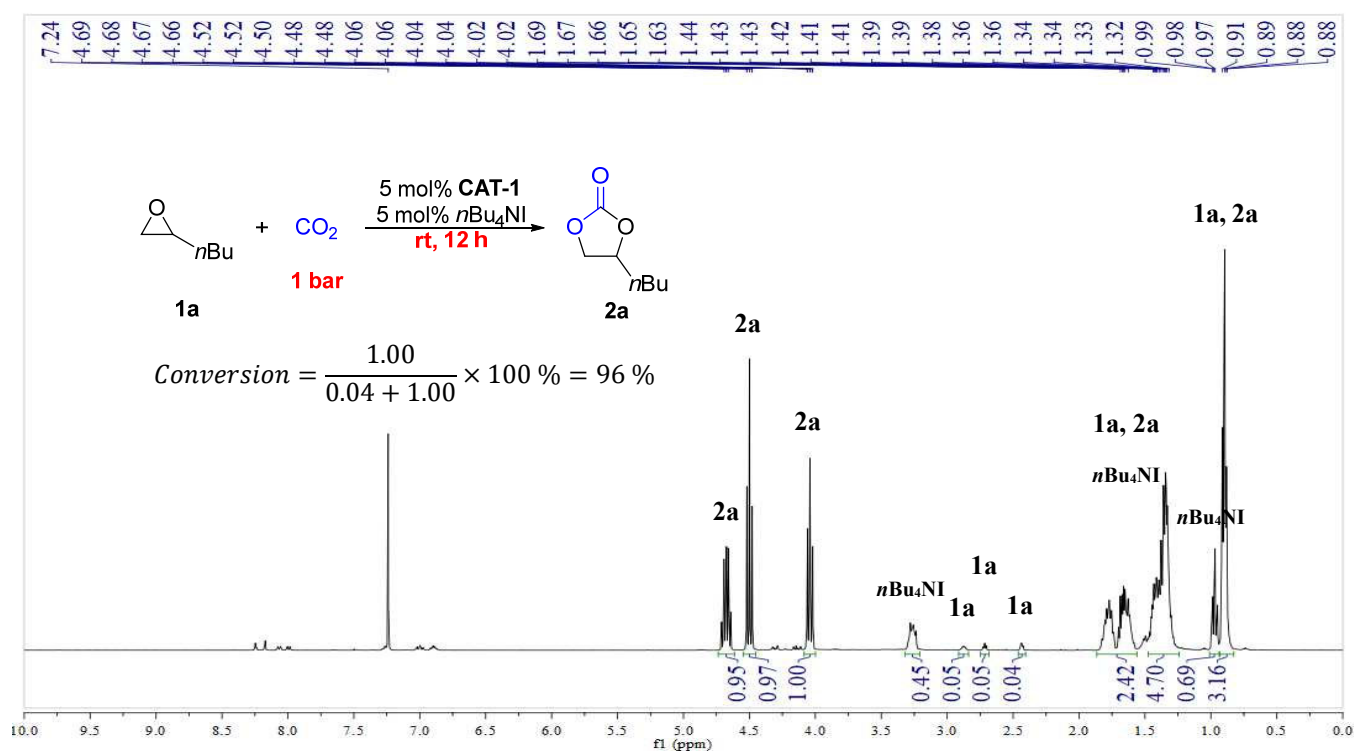


Figure S28. ¹H NMR spectrum for an aliquot of the reaction mixture after reaction in Table 1, entry 4.

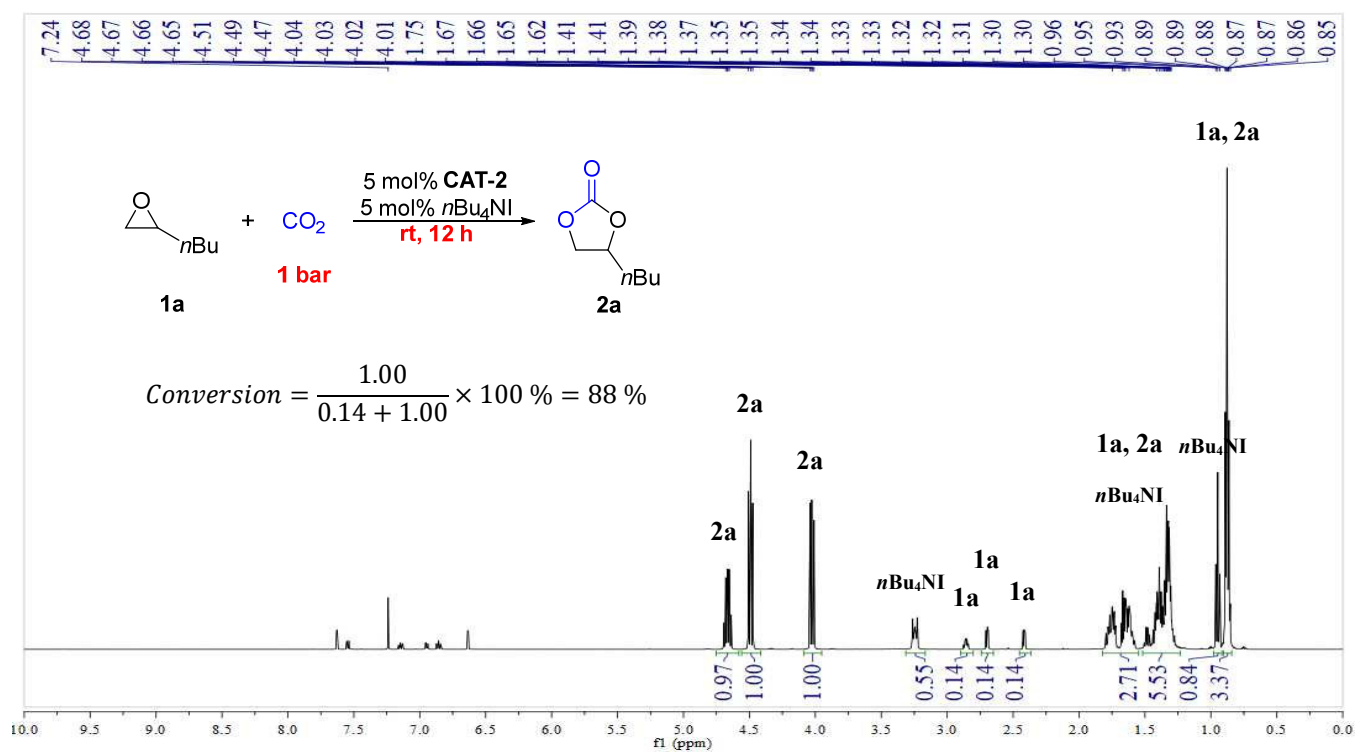


Figure S29. ^1H NMR spectrum for an aliquot of the reaction mixture after reaction in Table 1, entry 5.

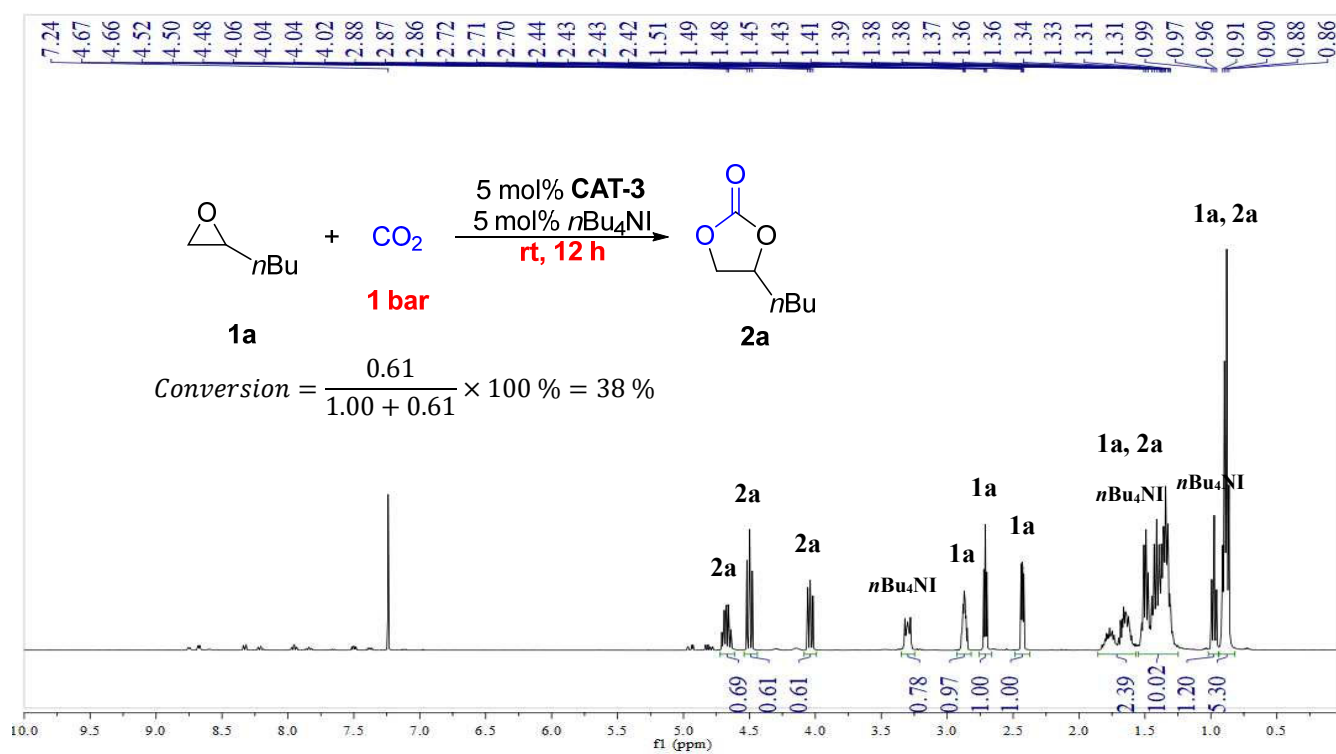


Figure S30. ^1H NMR spectrum for an aliquot of the reaction mixture after reaction in Table 1, entry 6.

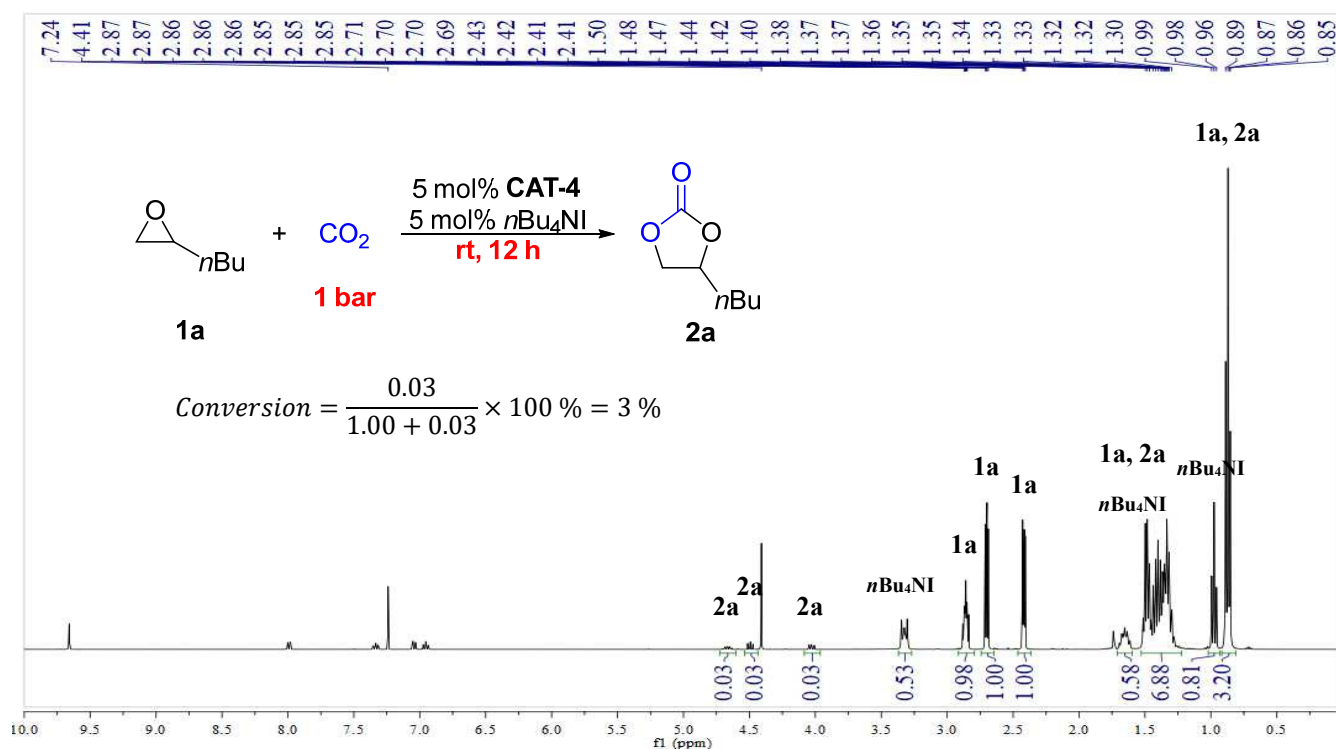


Figure S31. ^1H NMR spectrum for an aliquot of the reaction mixture after reaction in Table 1, entry 7.

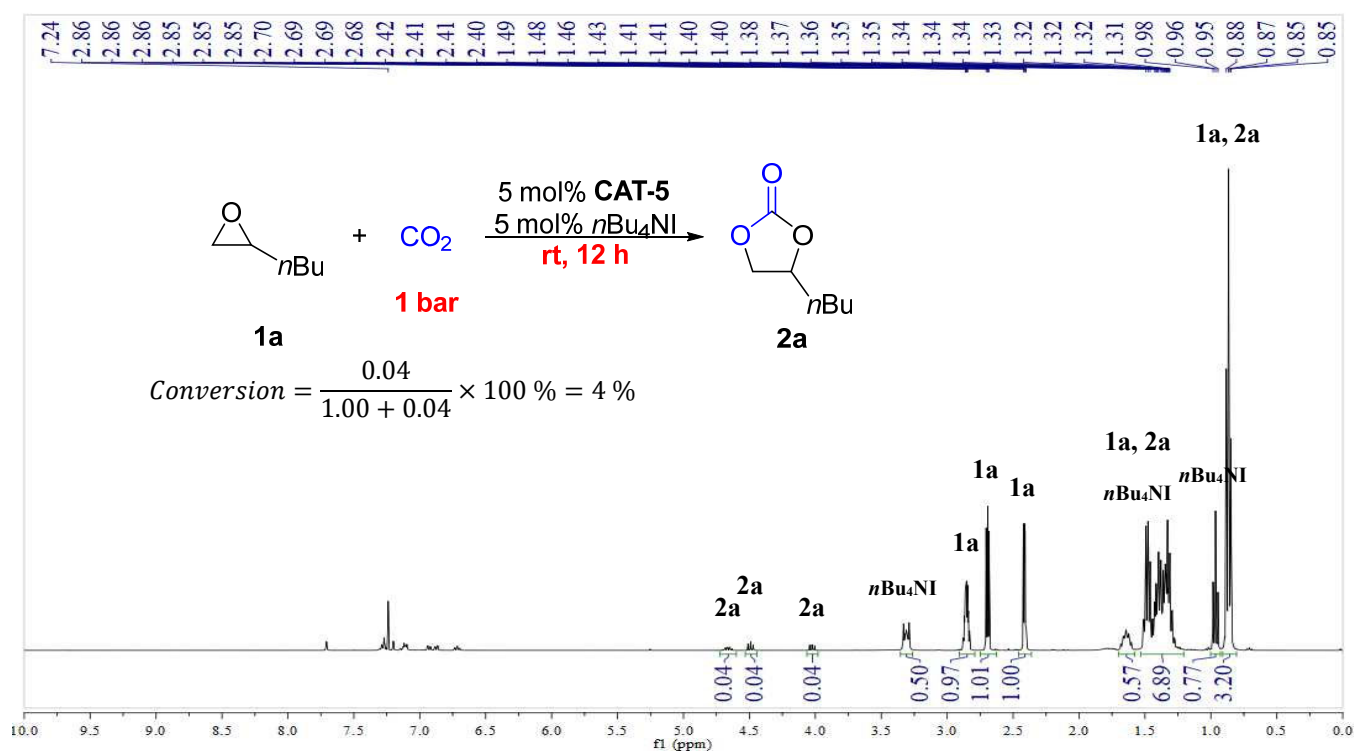


Figure S32. ^1H NMR spectrum for an aliquot of the reaction mixture after reaction in Table 1, entry 8.

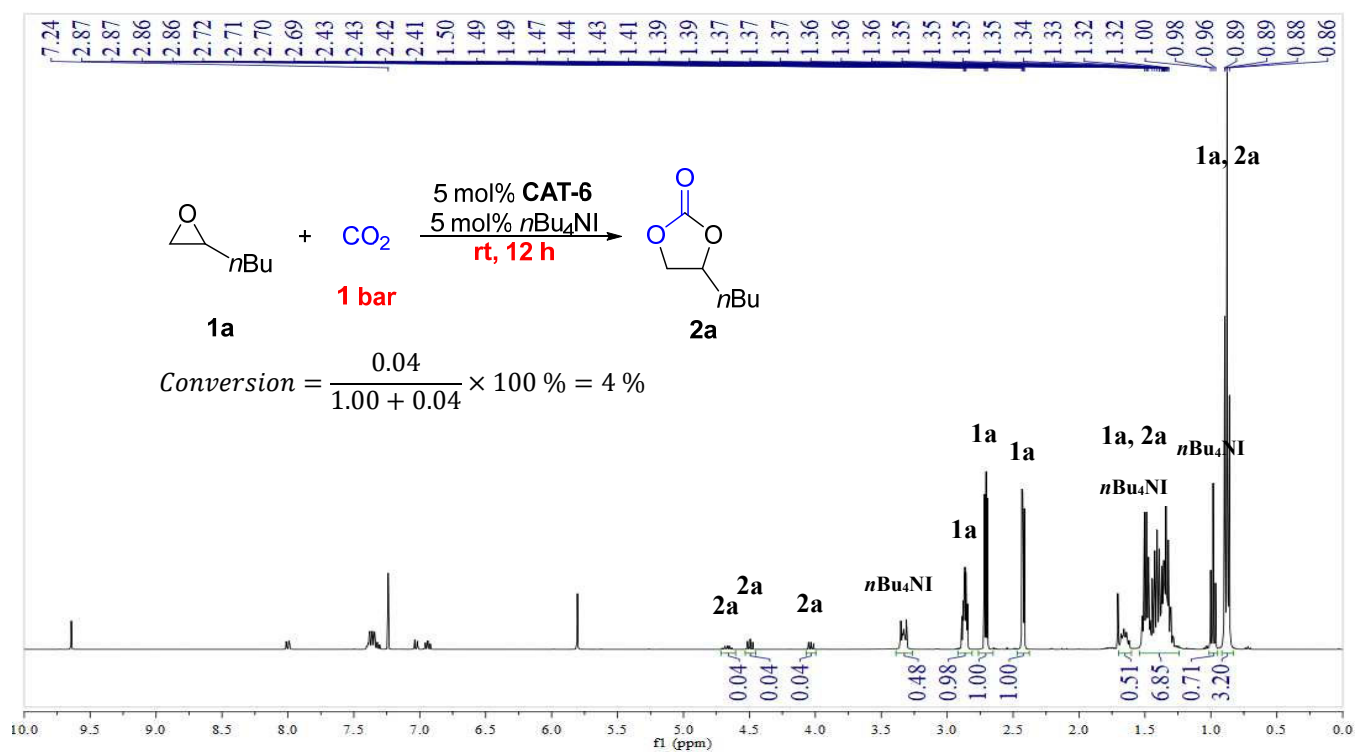


Figure S33. ^1H NMR spectrum for an aliquot of the reaction mixture after reaction in Table 1, entry 9.

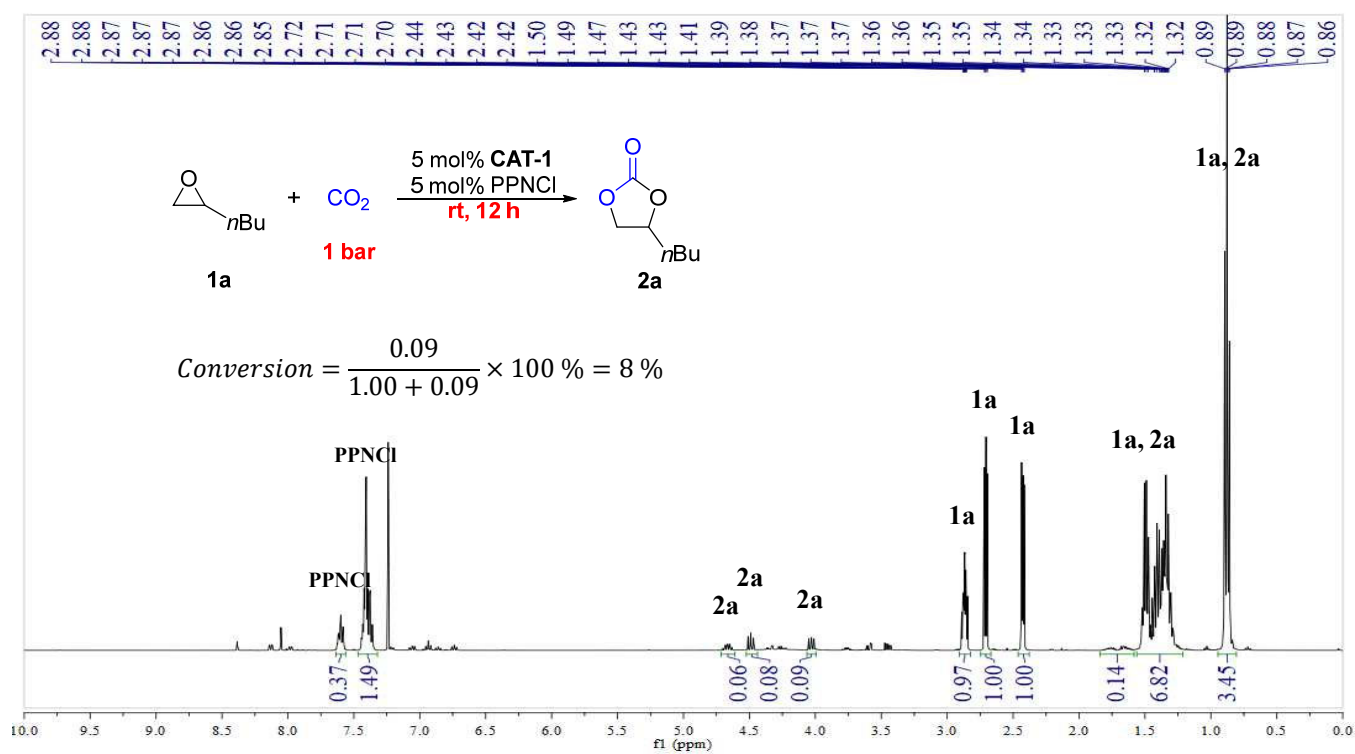


Figure S34. ^1H NMR spectrum for an aliquot of the reaction mixture after reaction in Table 2, entry 2.

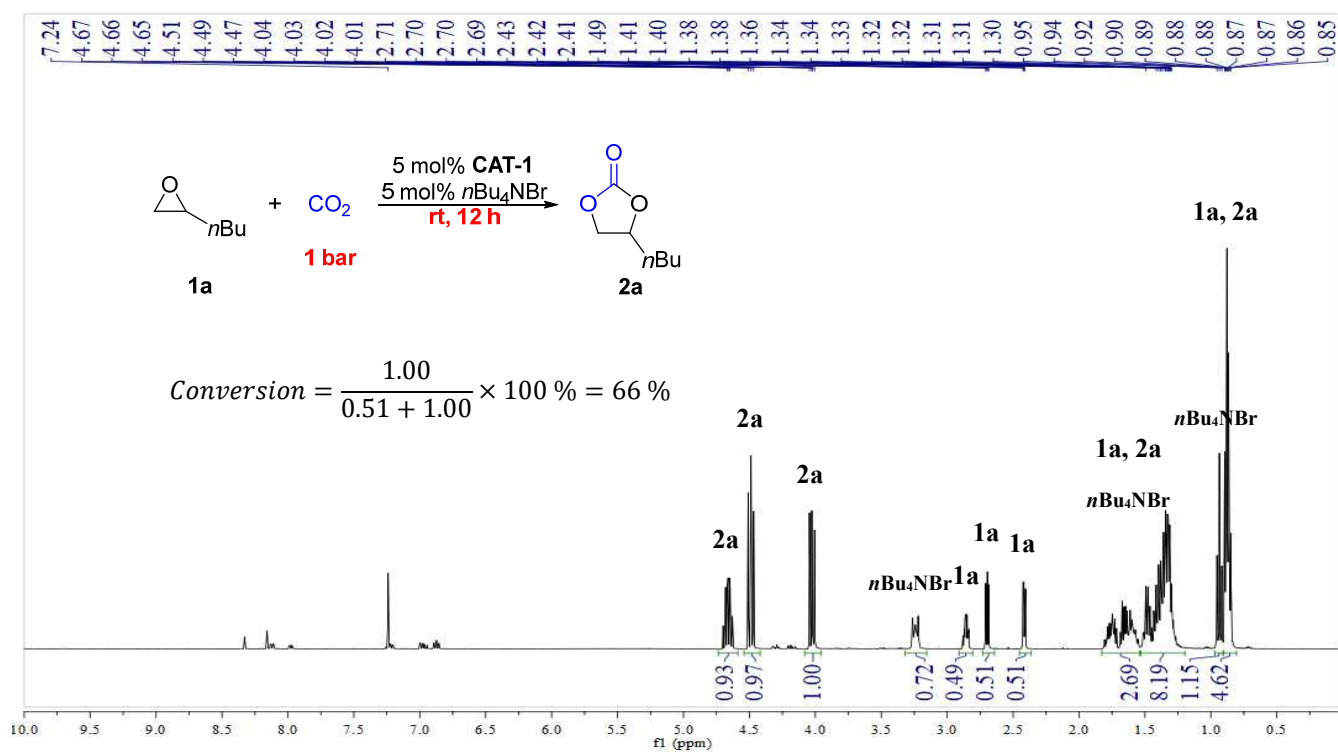


Figure S35. ^1H NMR spectrum for an aliquot of the reaction mixture after reaction in Table 2, entry 3.

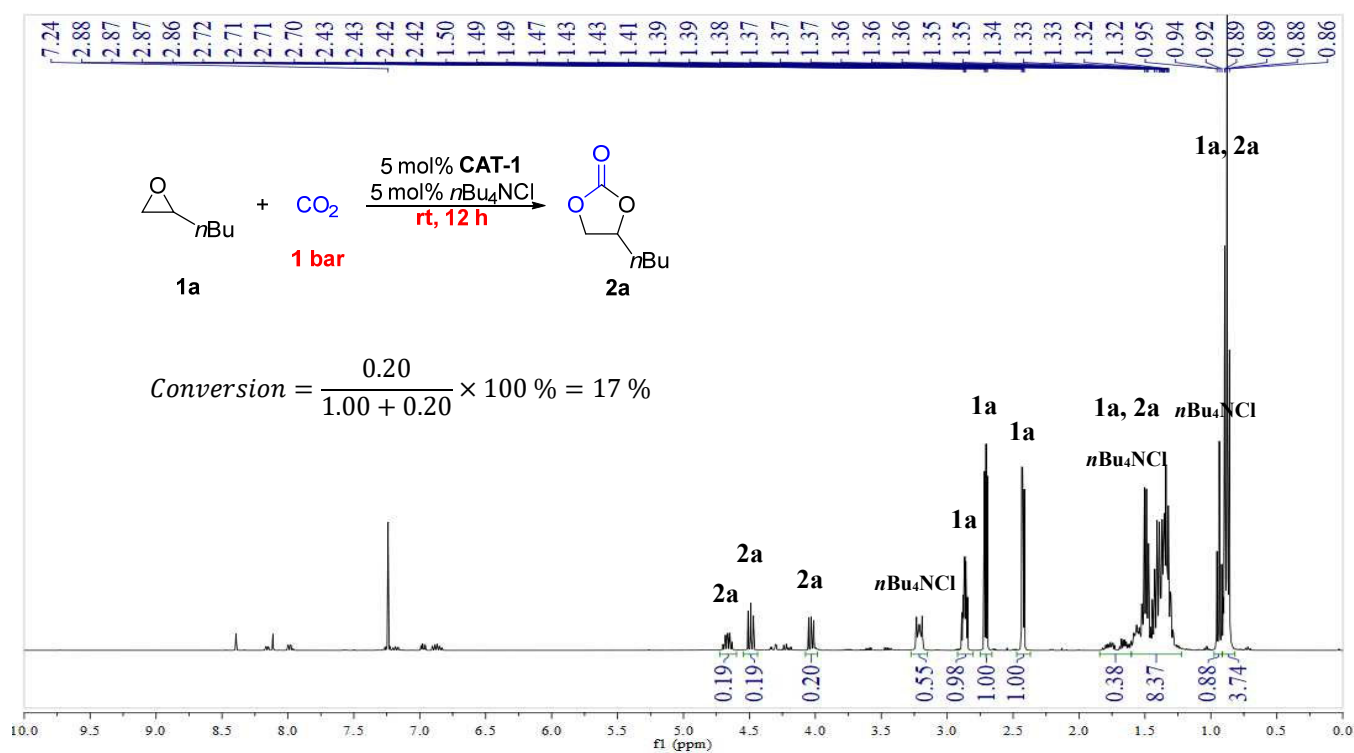


Figure S36. ^1H NMR spectrum for an aliquot of the reaction mixture after reaction in Table 2, entry 4.

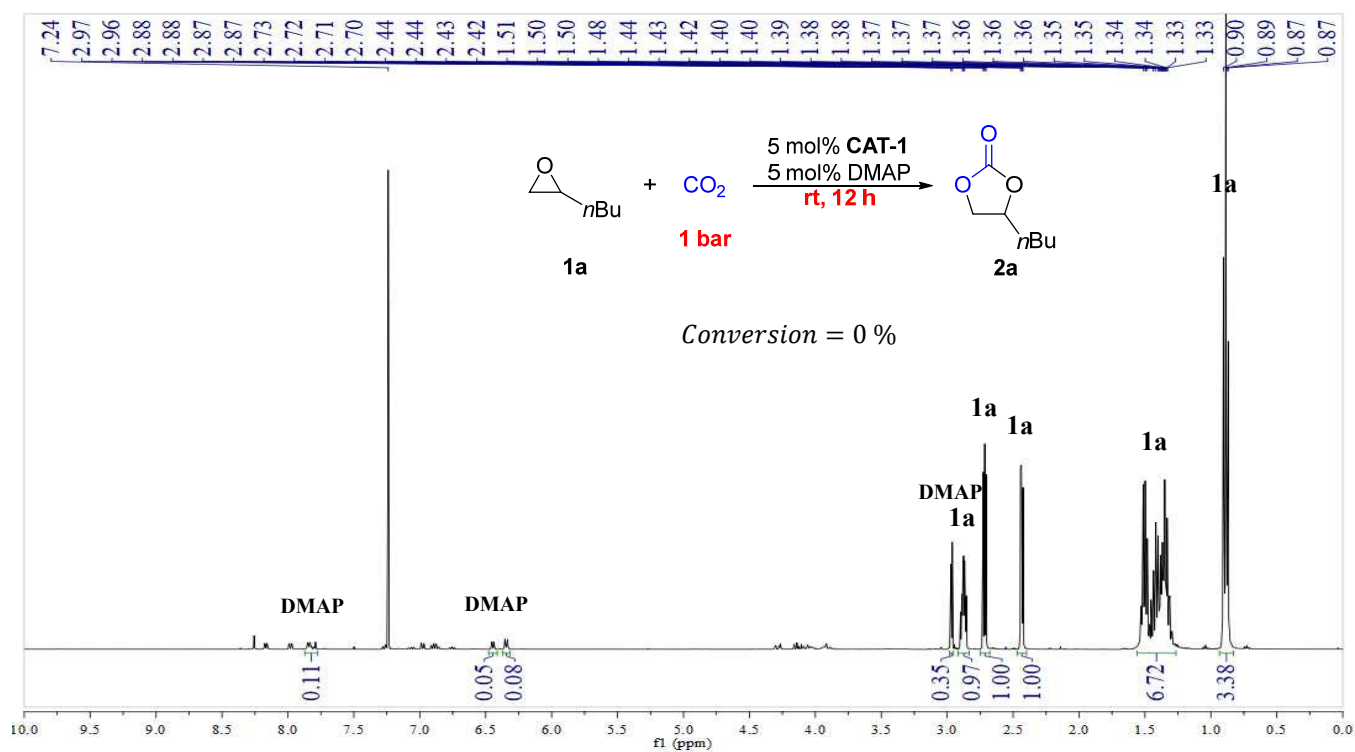


Figure S37. ¹H NMR spectrum for an aliquot of the reaction mixture after reaction in Table 2, entry 5.

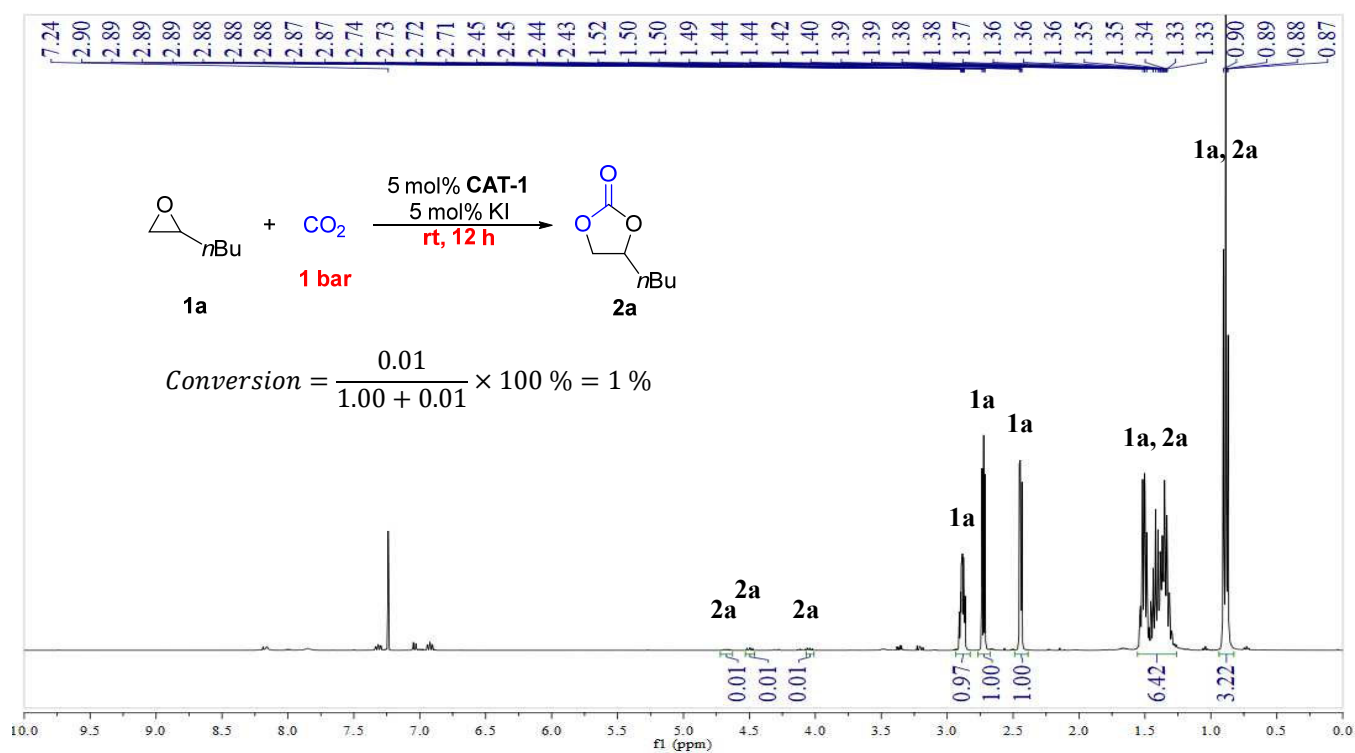


Figure S38. ¹H NMR spectrum for an aliquot of the reaction mixture after reaction in Table 2, entry 6.

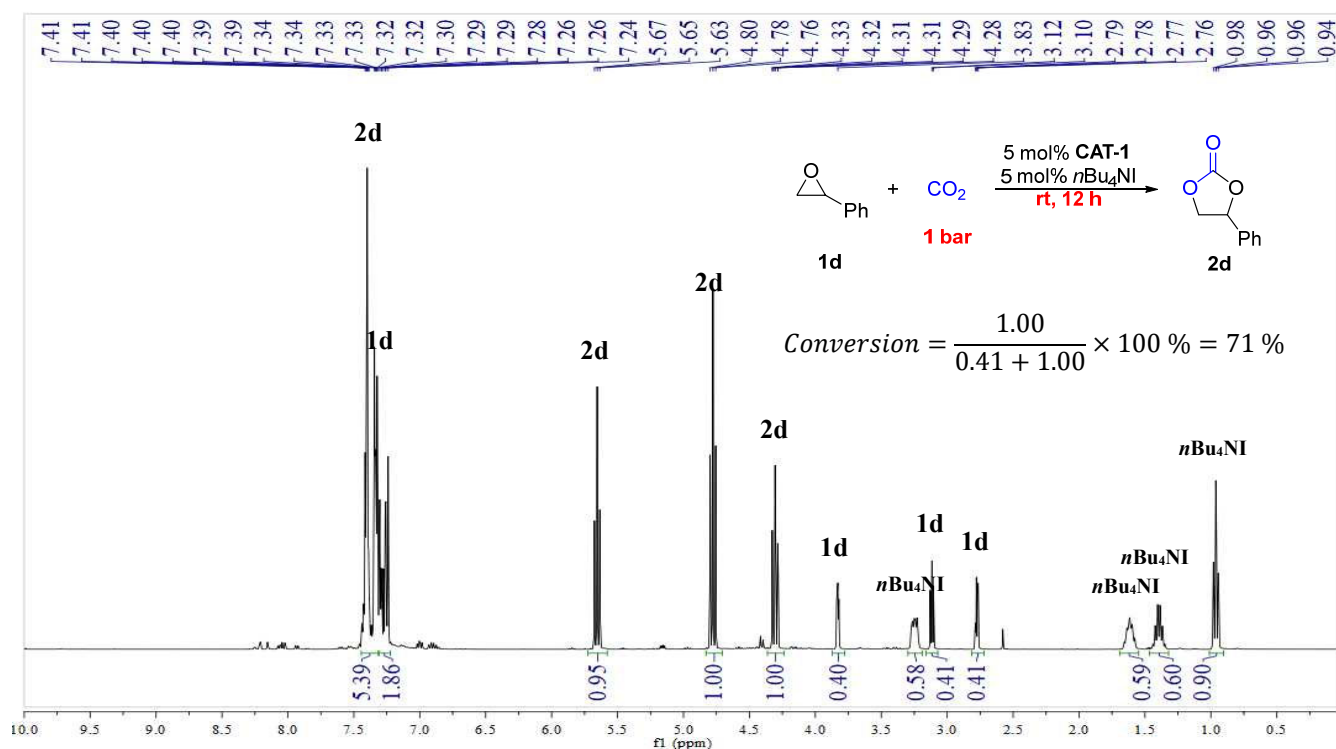


Figure S41. ¹H NMR spectrum for an aliquot containing mixtures after reaction for **2d** in Figure 3.

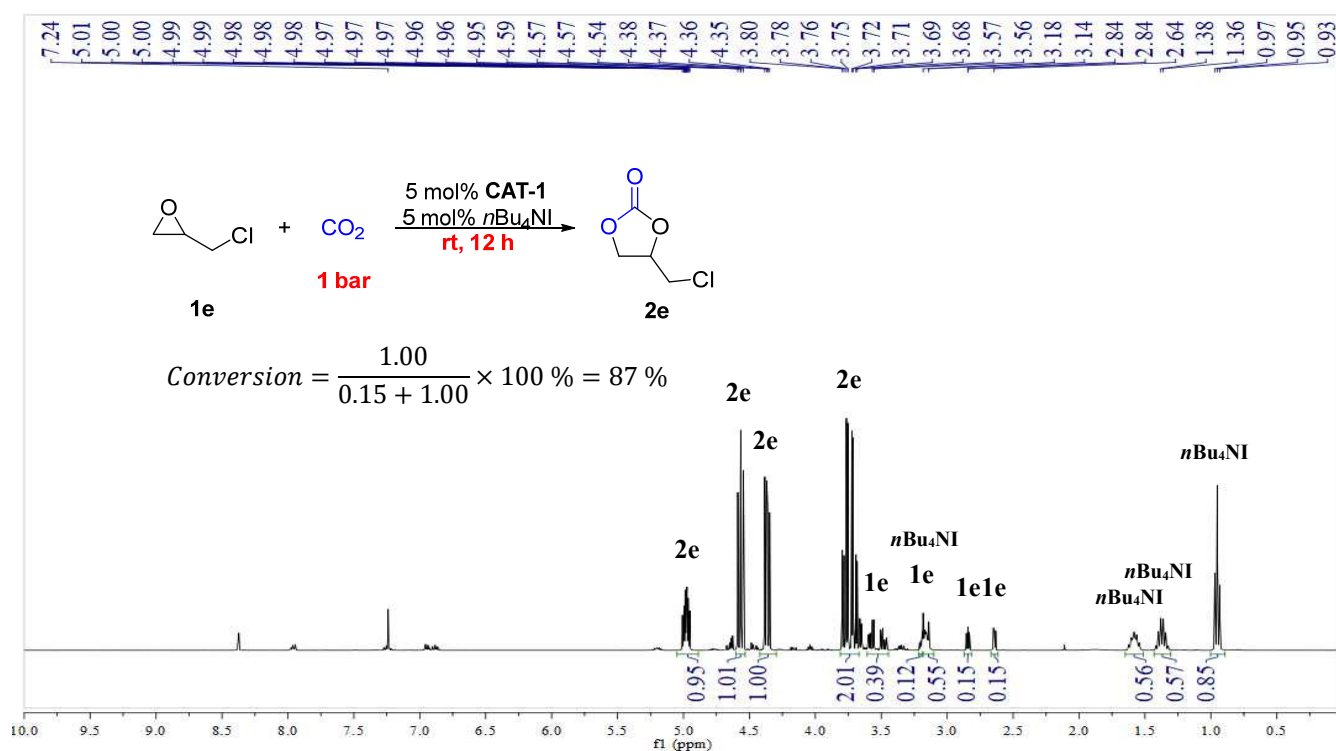


Figure S42. ¹H NMR spectrum for an aliquot containing mixtures after reaction for **2e** in Figure 3.

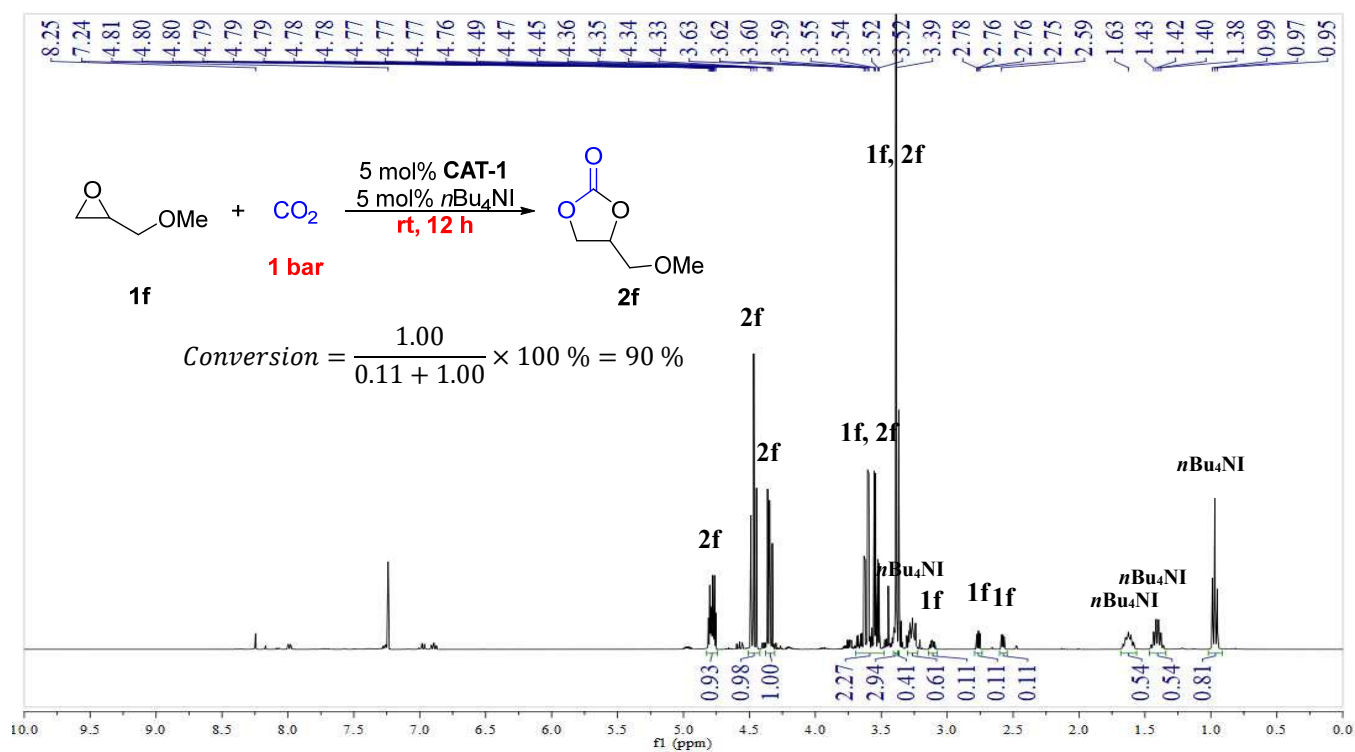


Figure S43. ^1H NMR spectrum for an aliquot containing mixtures after reaction for **2f** in Figure 3.

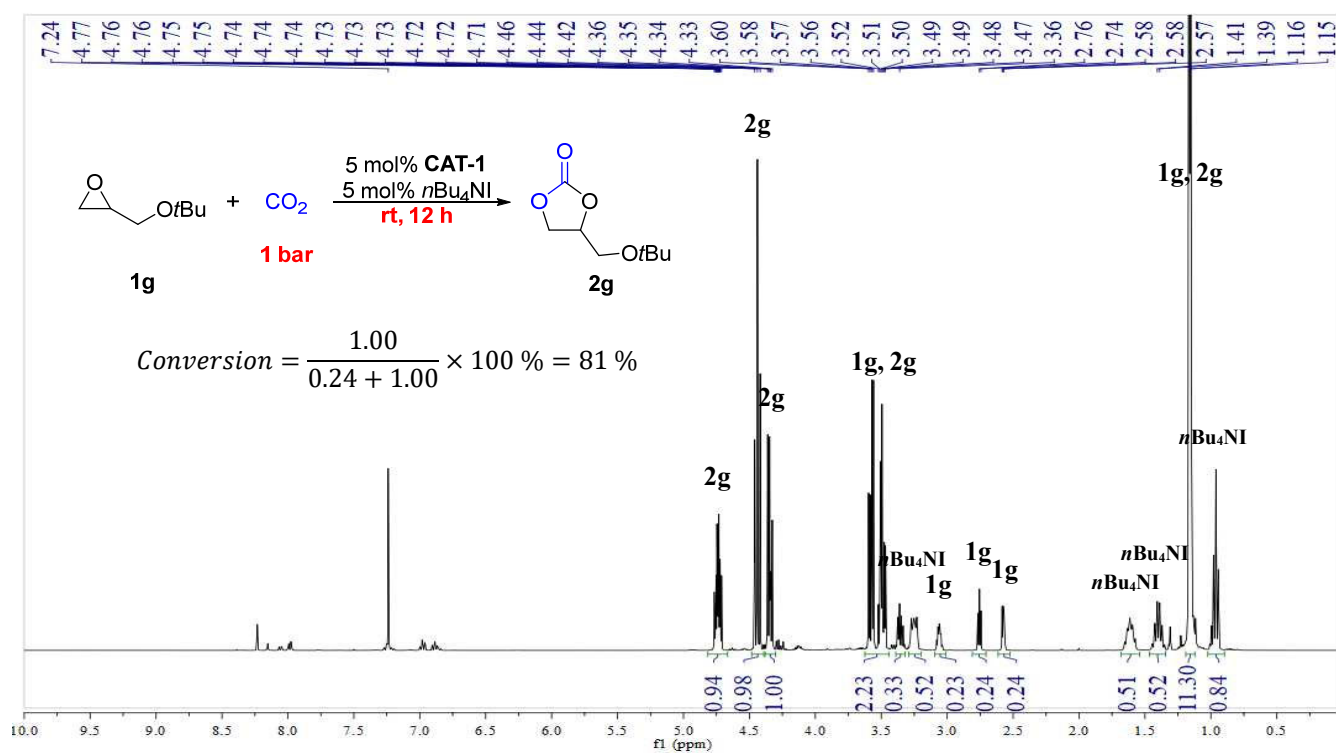


Figure S44. ^1H NMR spectrum for an aliquot containing mixtures after reaction for **2g** in Figure 3.

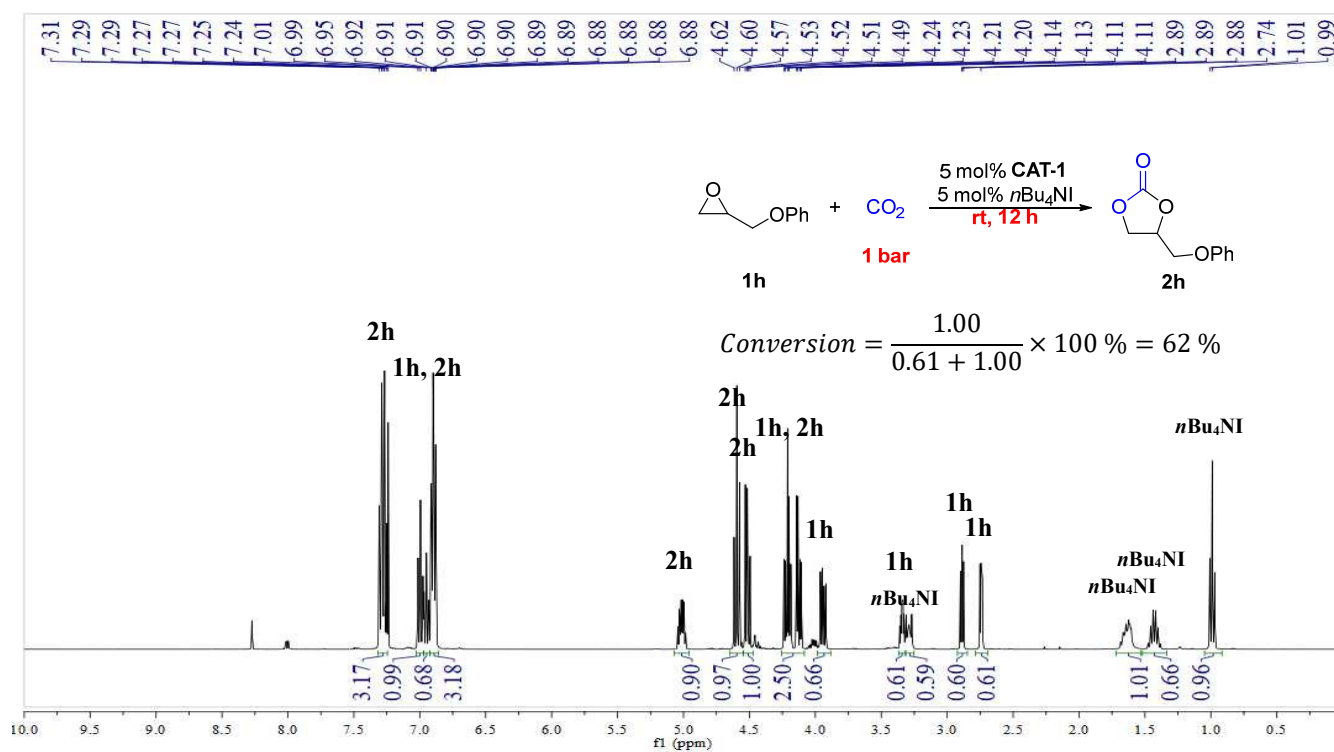


Figure S45. ^1H NMR spectrum for an aliquot containing mixtures after reaction for **2h** in Figure 3.

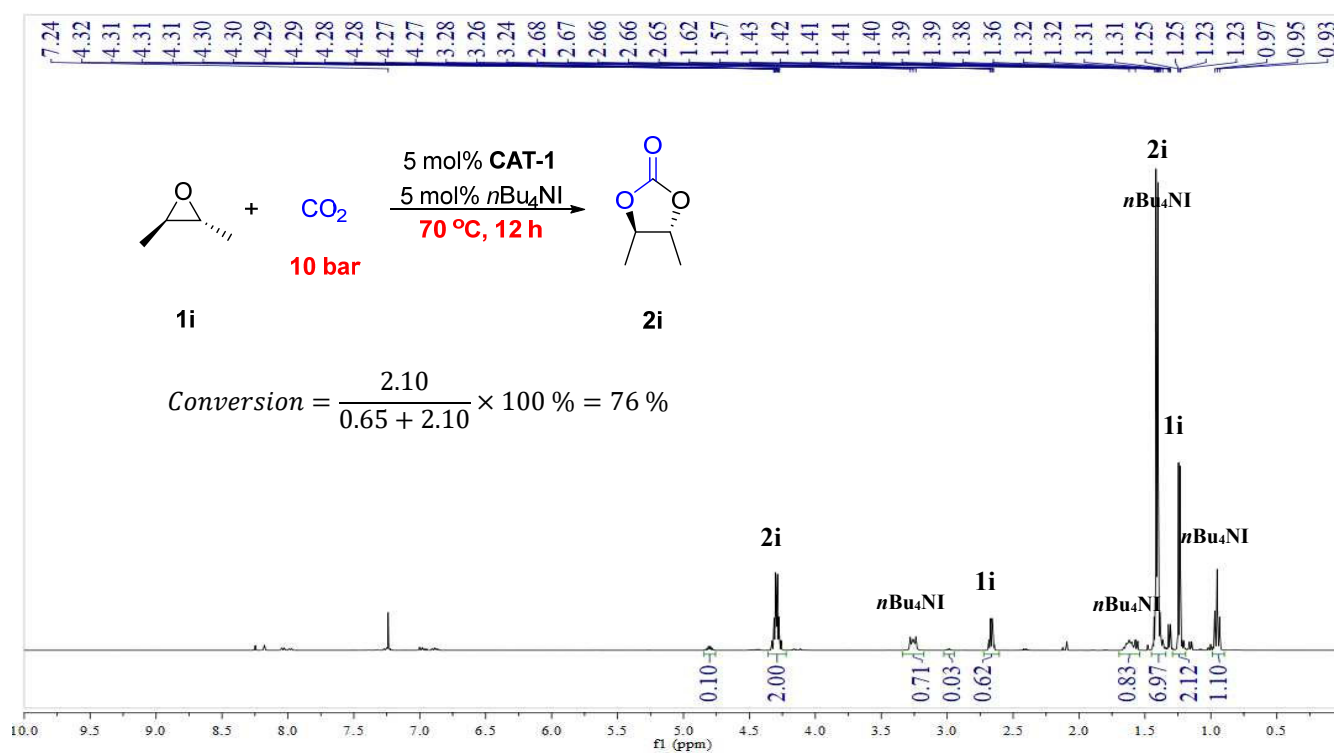


Figure S46. ^1H NMR spectrum for an aliquot containing mixtures after reaction for *trans*-**2i** in Figure 4.

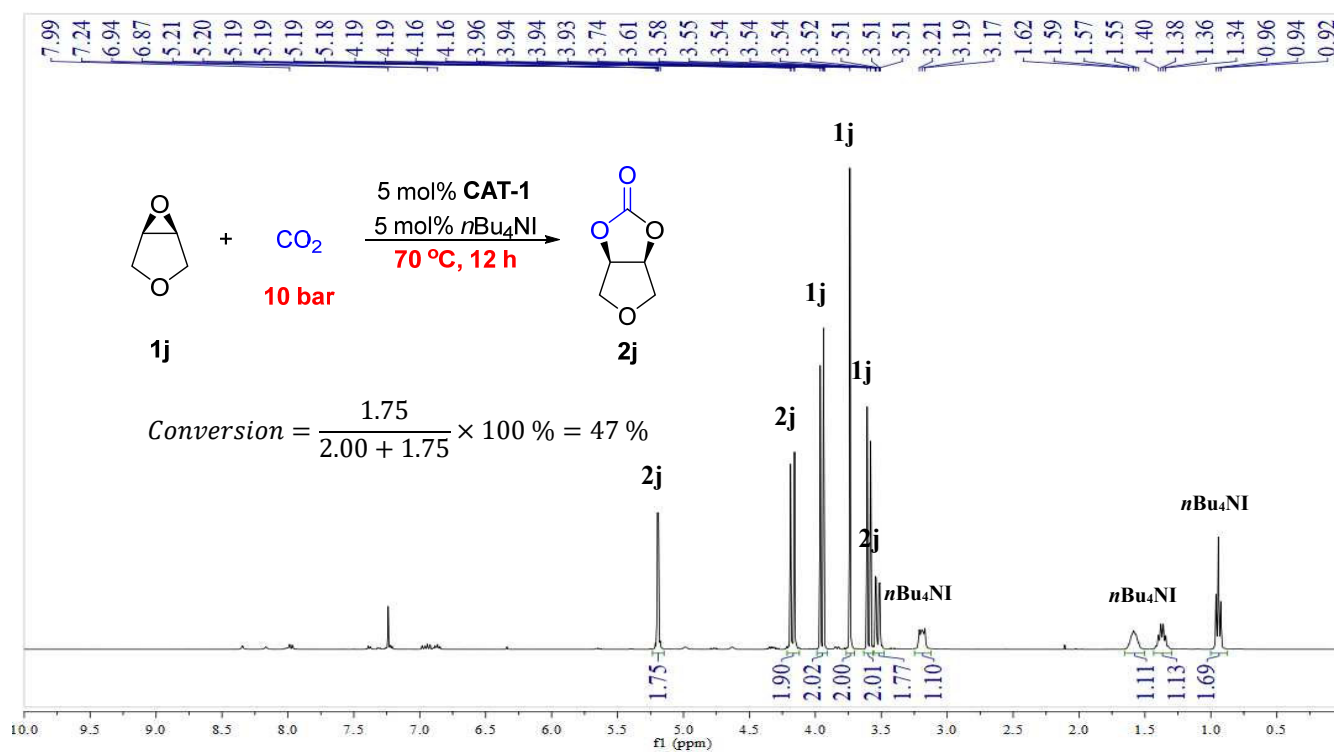


Figure S47. ^1H NMR spectrum for an aliquot containing mixtures after reaction for *cis*-**2j** in Figure 4.

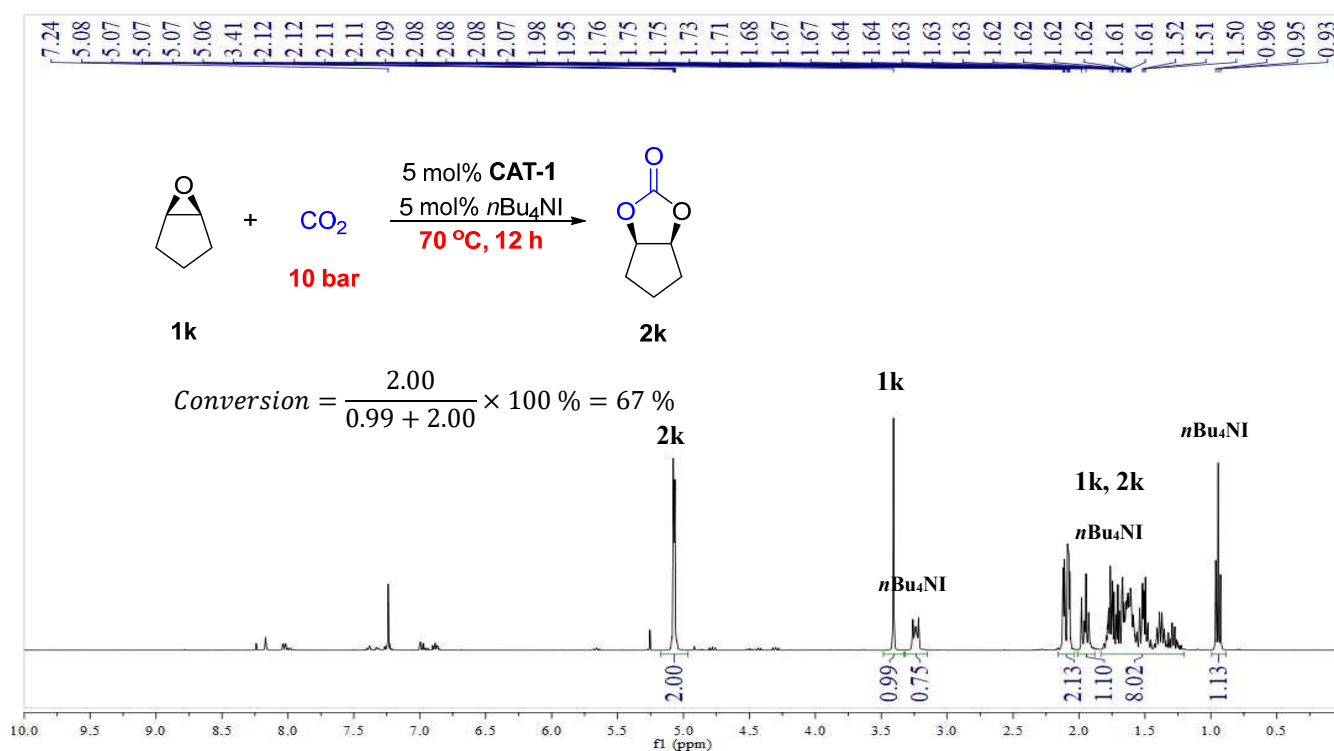


Figure S48. ^1H NMR spectrum for an aliquot containing mixtures after reaction for *cis*-**2k** in Figure 4.

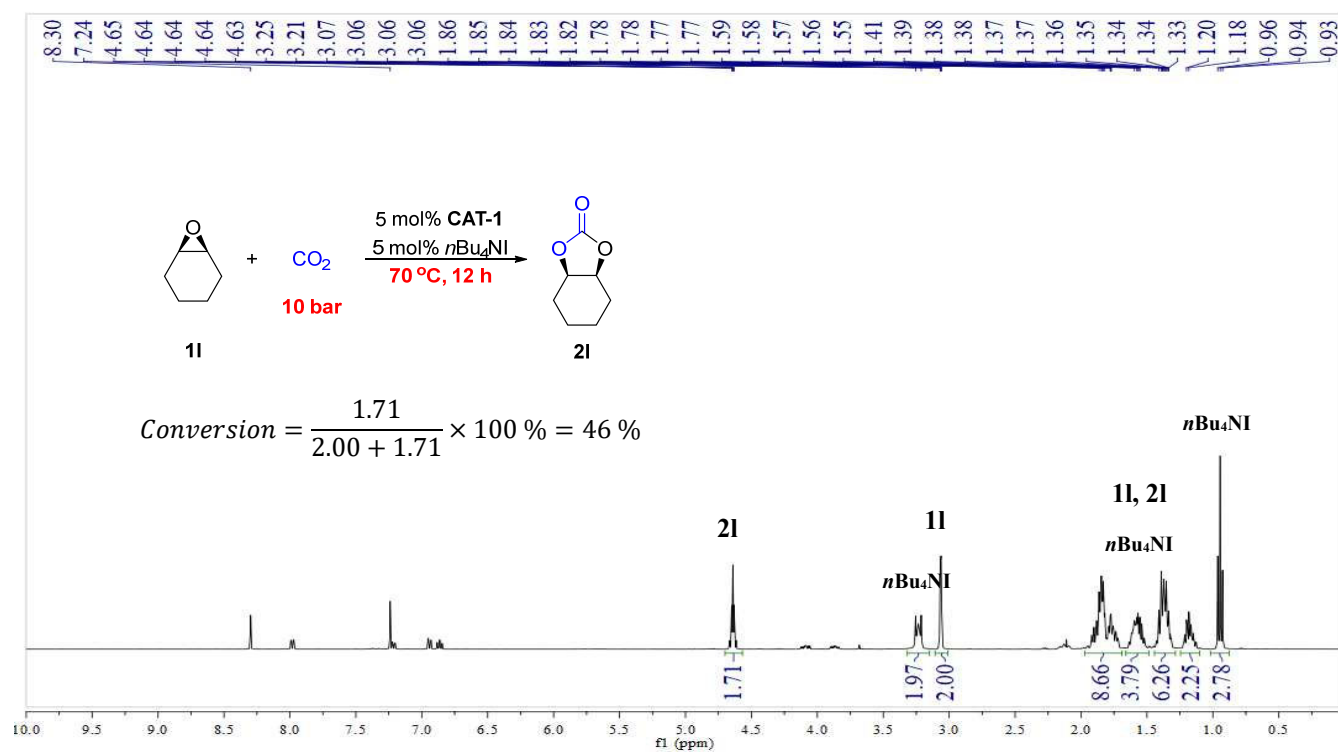


Figure S49. ¹H NMR spectrum for an aliquot containing mixtures after reaction for *cis*-**21** in Figure 4.

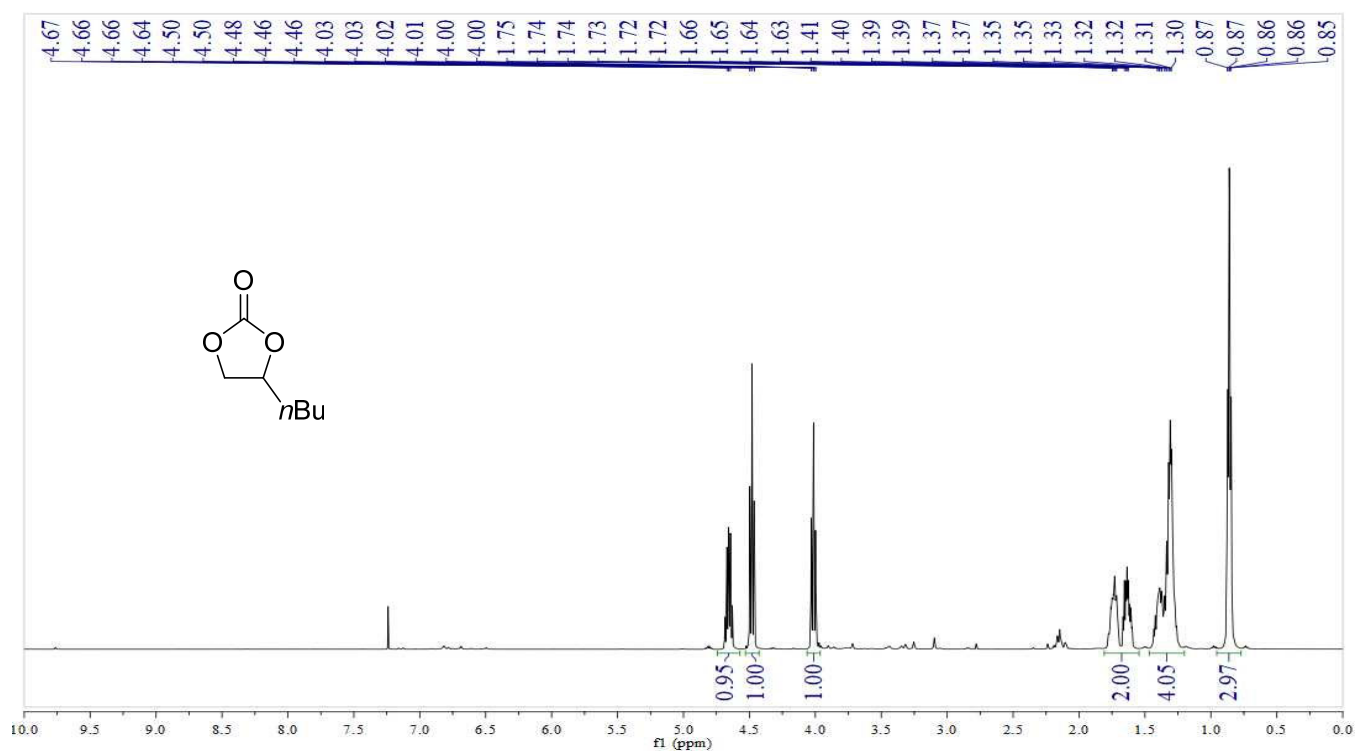


Figure S50. ¹H NMR spectrum of purified 4-butyl-1,3-dioxolan-2-one (**2a**) in CDCl₃.

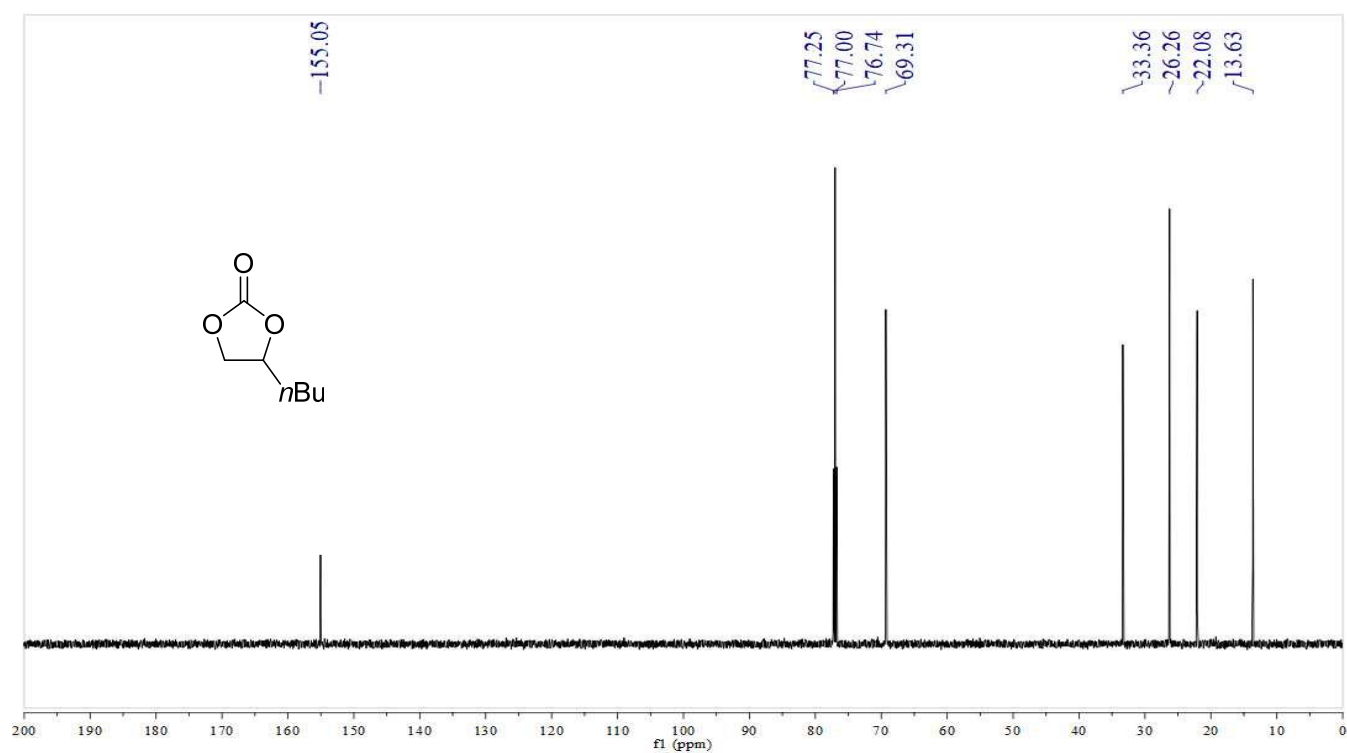


Figure S51. ¹³C NMR spectrum of purified 4-butyl-1,3-dioxolan-2-one (**2a**) in CDCl₃.

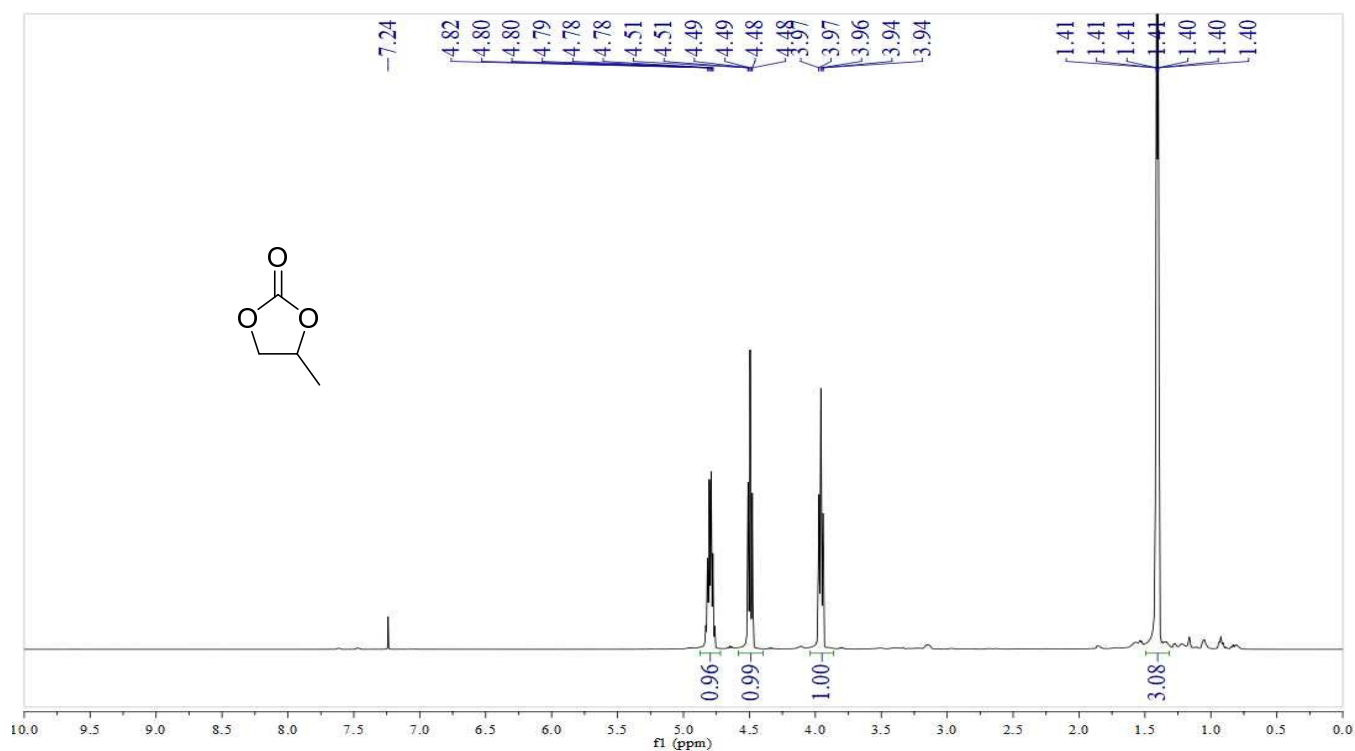


Figure S52. ^1H NMR spectrum of purified 4-methyl-1,3-dioxolan-2-one (**2b**) in CDCl_3 .

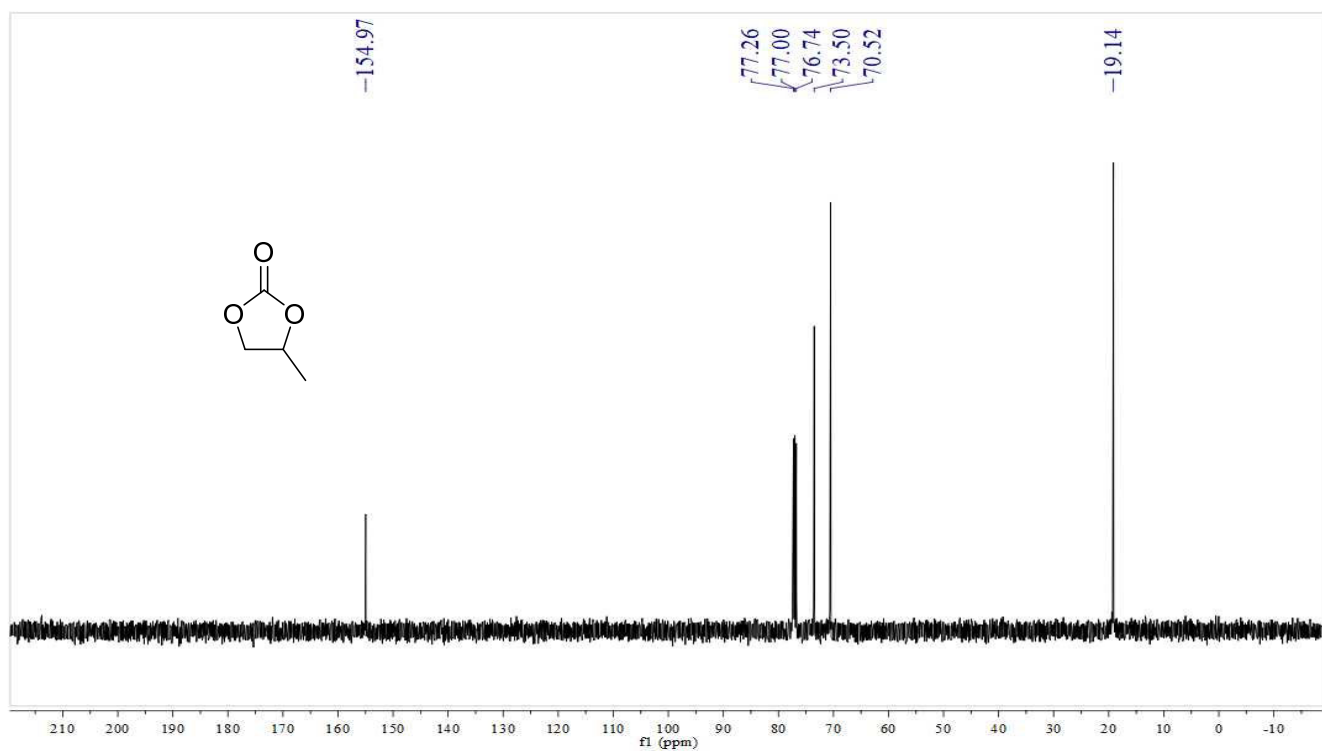


Figure S53. ^{13}C NMR spectrum of purified 4-methyl-1,3-dioxolan-2-one (**2b**) in CDCl_3 .

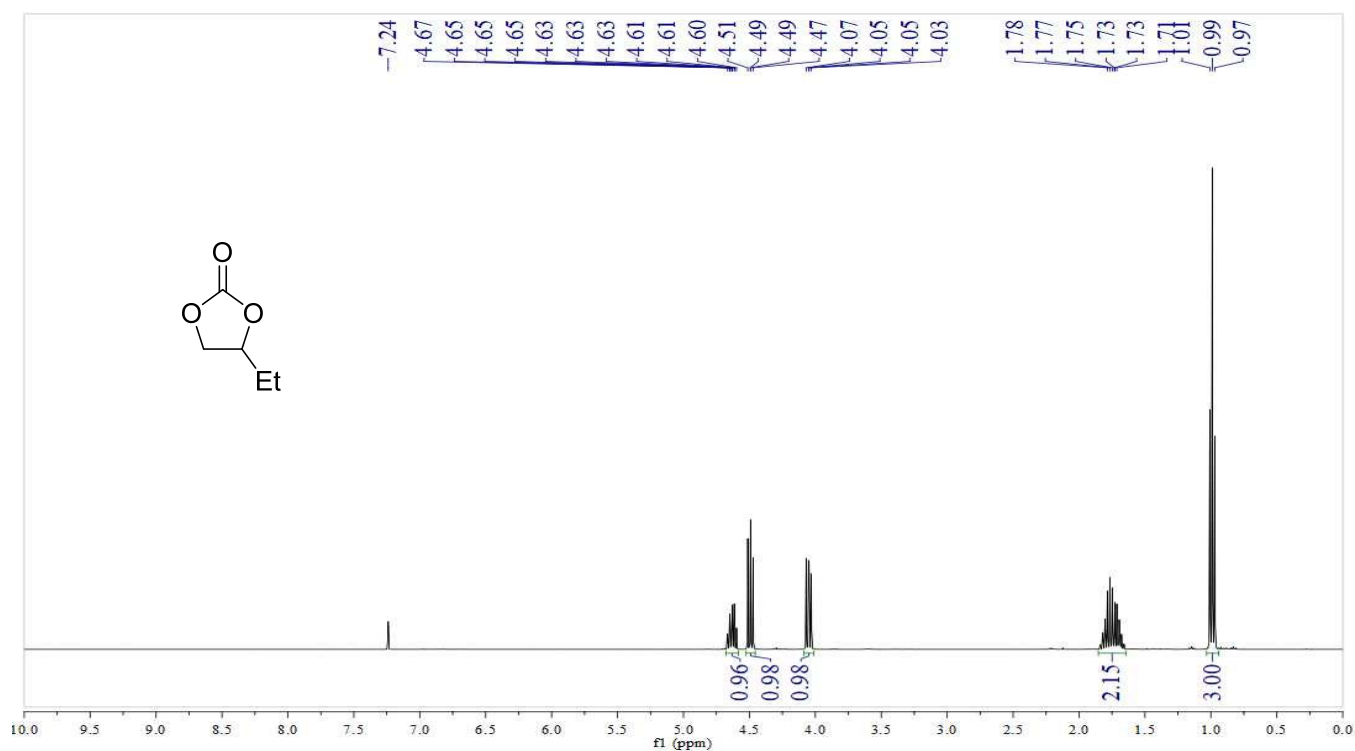


Figure S54. ¹H NMR spectrum of purified 4-ethyl-1,3-dioxolan-2-one(2c) in CDCl₃.

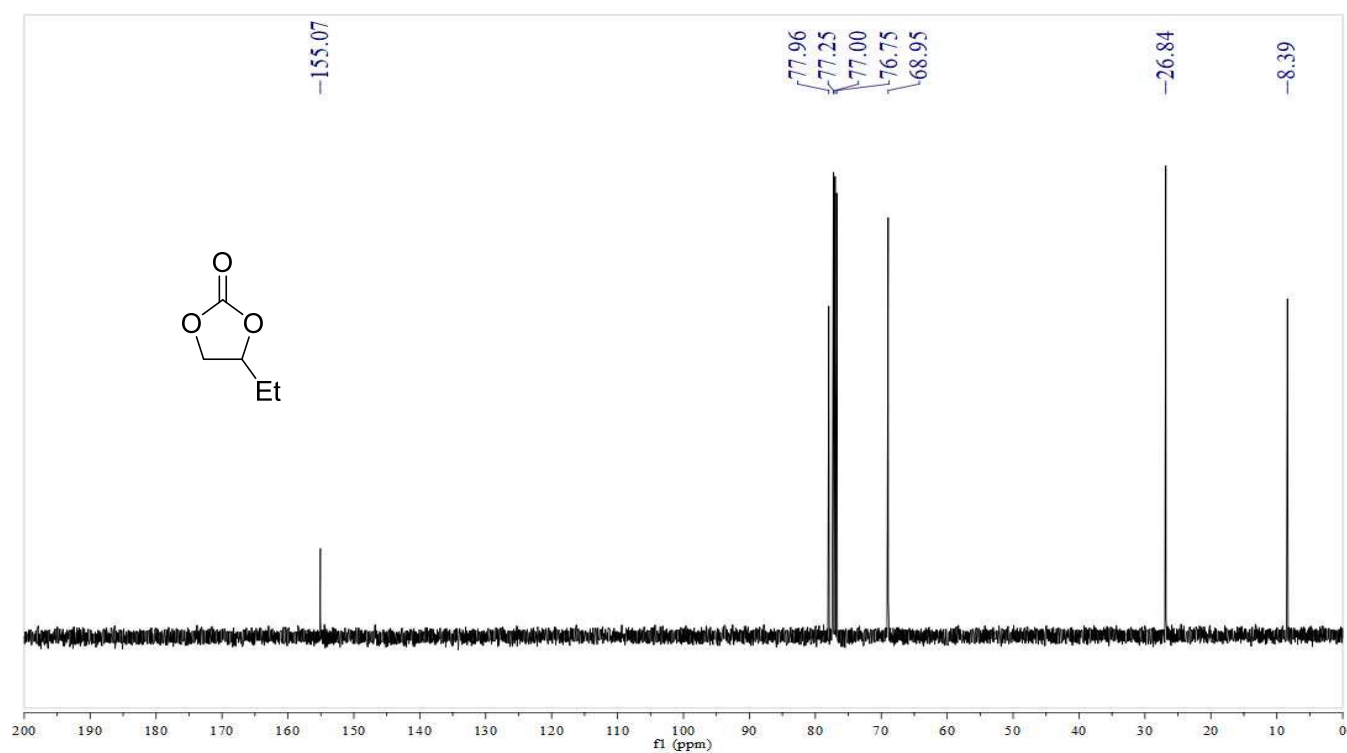


Figure S55. ¹³C NMR spectrum of purified 4-ethyl-1,3-dioxolan-2-one(2c) in CDCl₃.

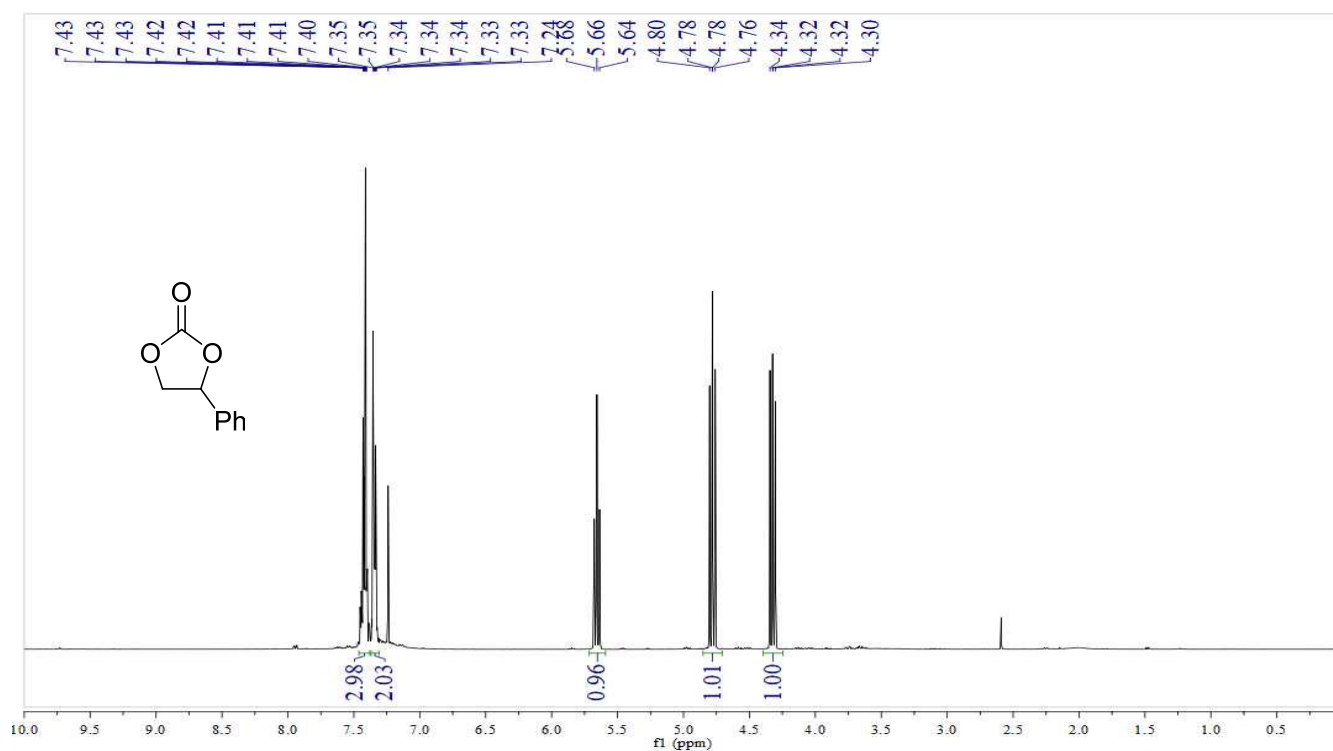


Figure S56. ¹H NMR spectrum of purified 4-phenyl-1,3-dioxolan-2-one(**2d**) in CDCl₃.

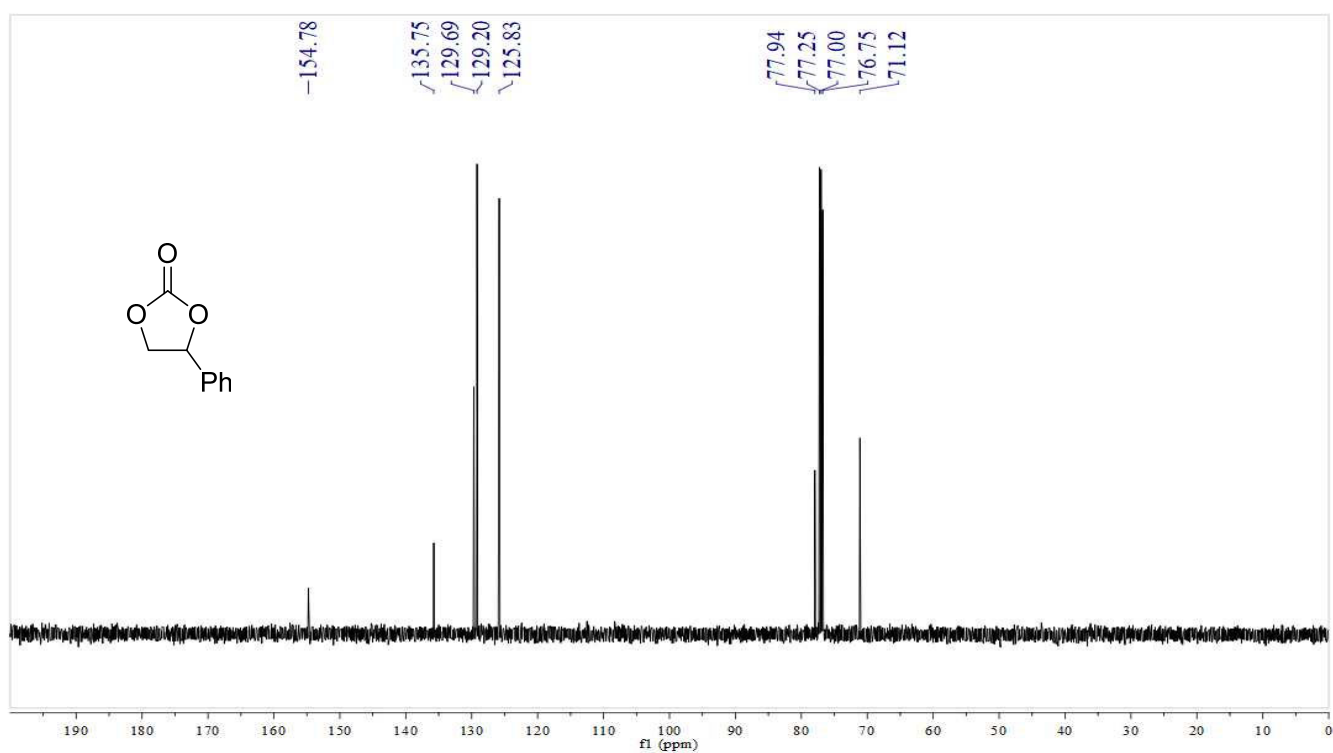


Figure S57. ¹³C NMR spectrum of purified 4-phenyl-1,3-dioxolan-2-one(**2d**) in CDCl₃.

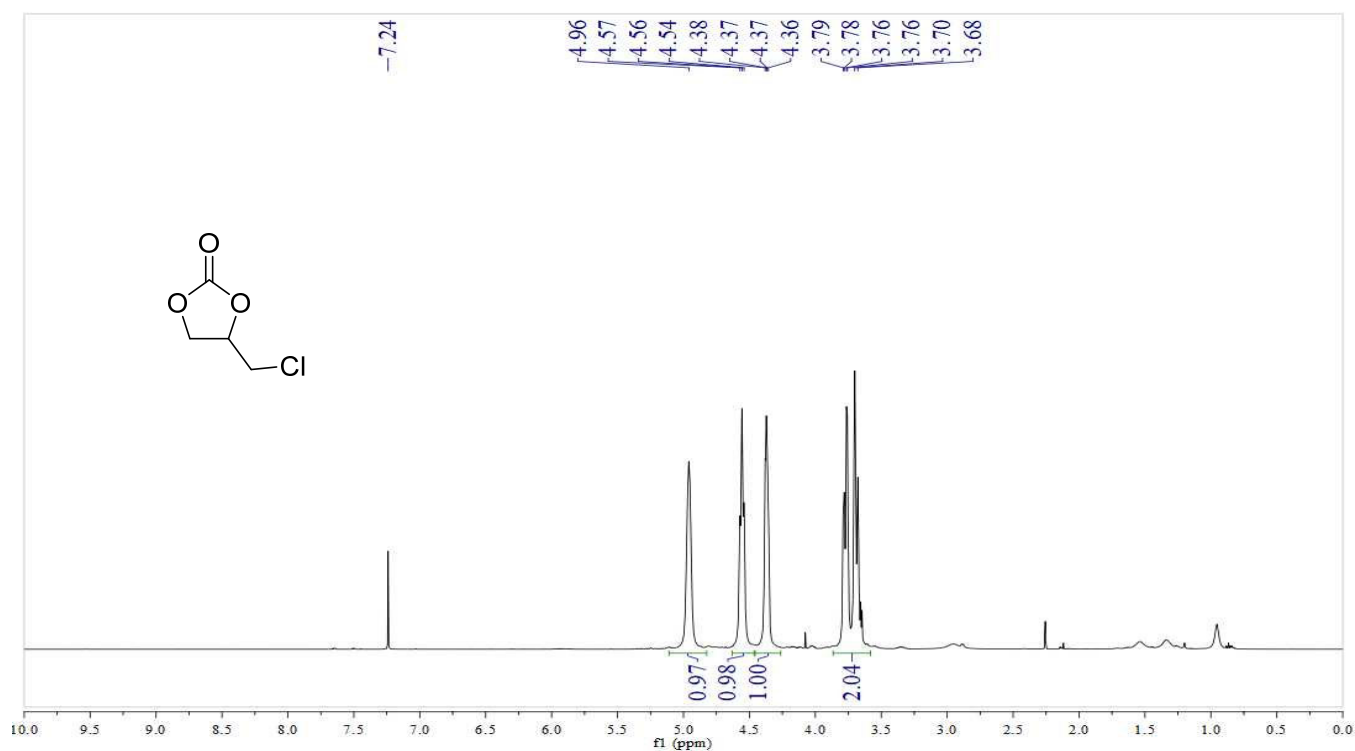


Figure S58. ¹H NMR spectrum of purified 4-(chloromethyl)-1,3-dioxolan-2-one(**2e**) in CDCl₃.

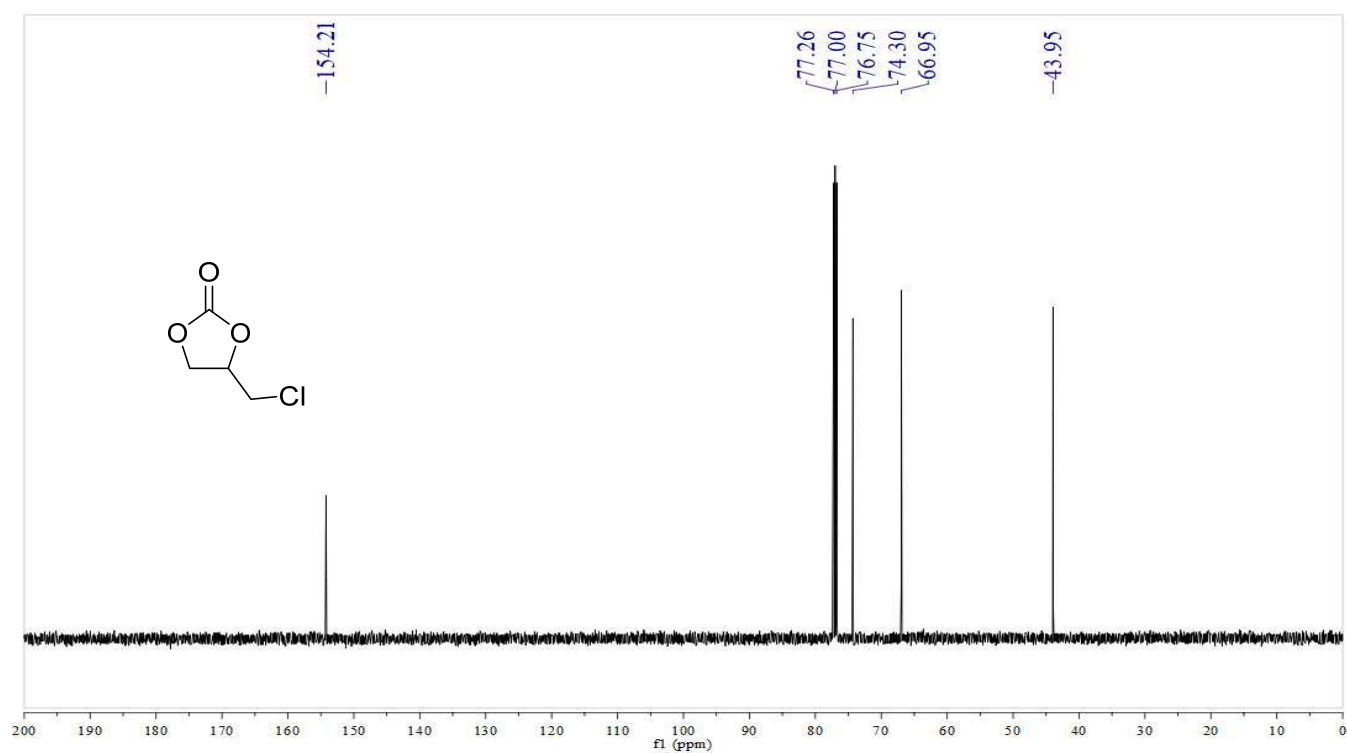


Figure S59. ¹³C NMR spectrum of purified 4-(chloromethyl)-1,3-dioxolan-2-one(**2e**) in CDCl₃.

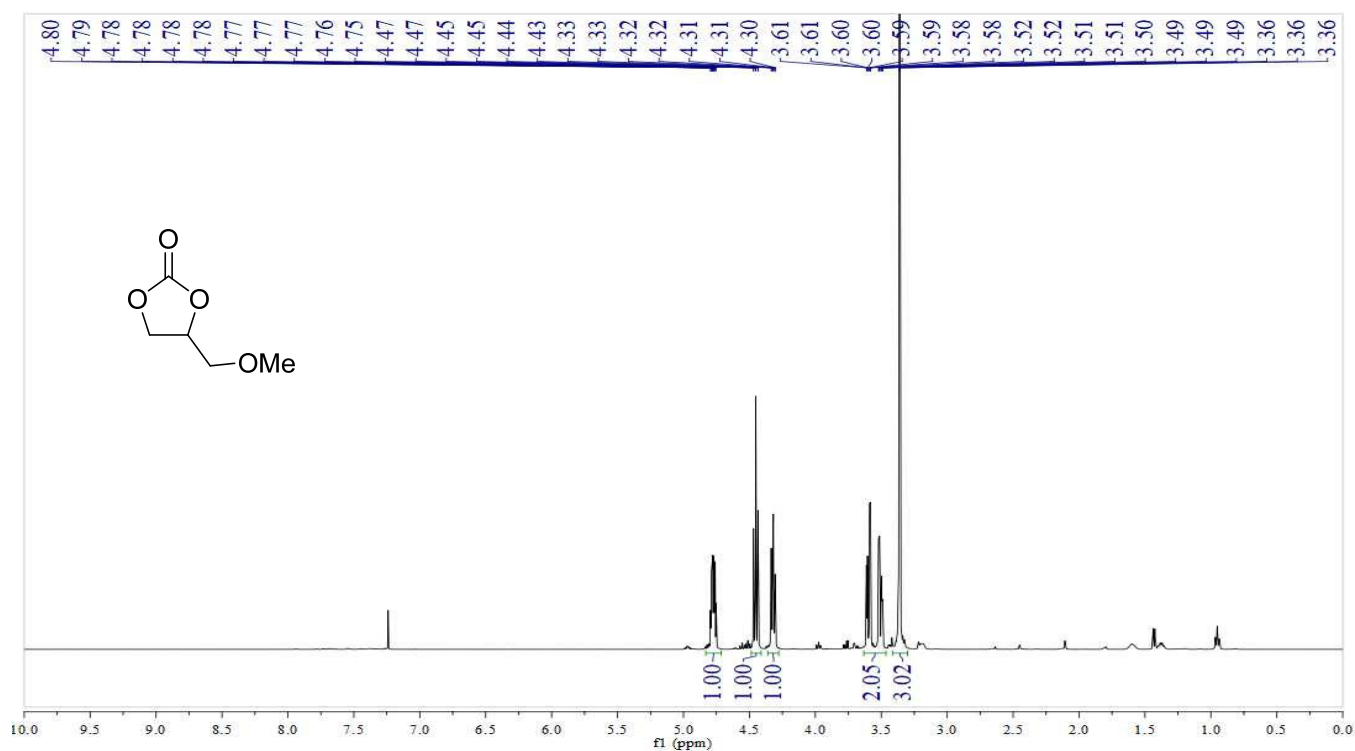


Figure S60. ¹H NMR spectrum of purified 4-(methoxymethyl)-1,3-dioxolan-2-one(**2f**) in CDCl₃.

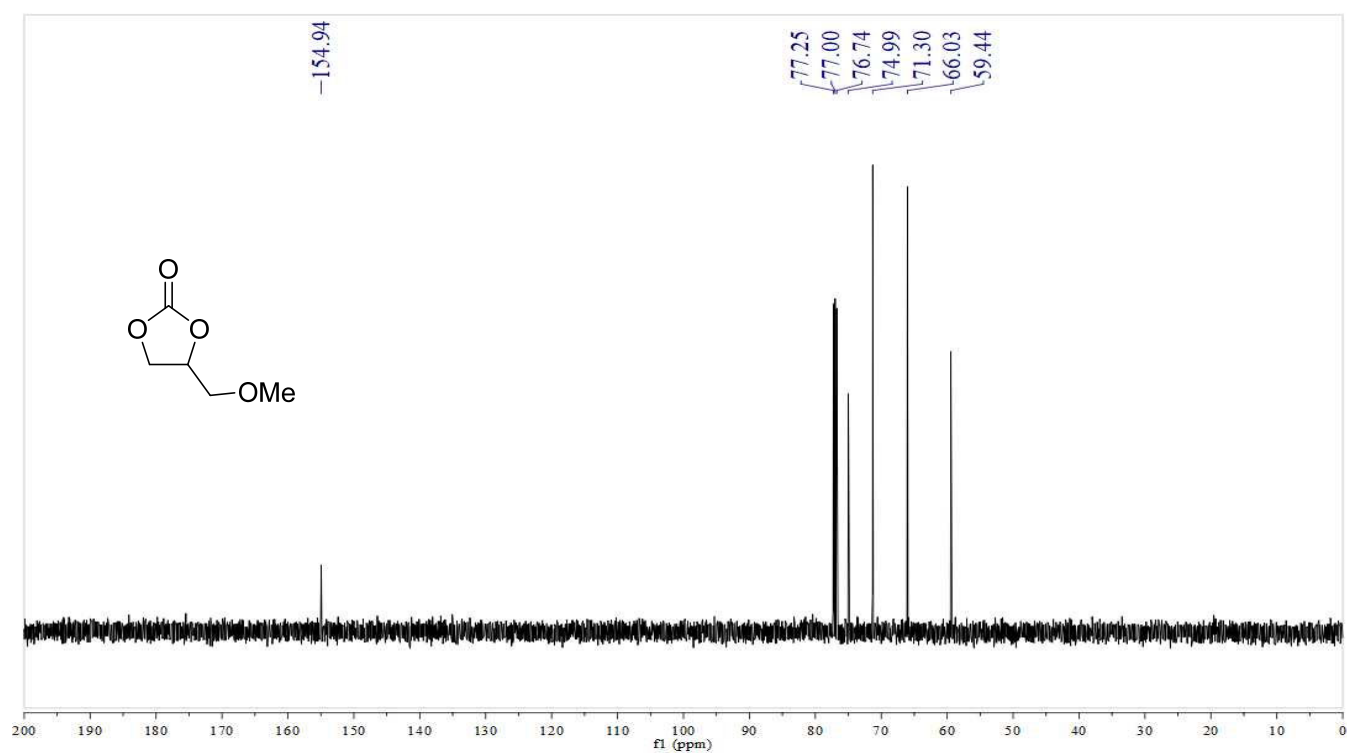


Figure S61. ¹³C NMR spectrum of purified 4-(methoxymethyl)-1,3-dioxolan-2-one(**2f**) in CDCl₃.

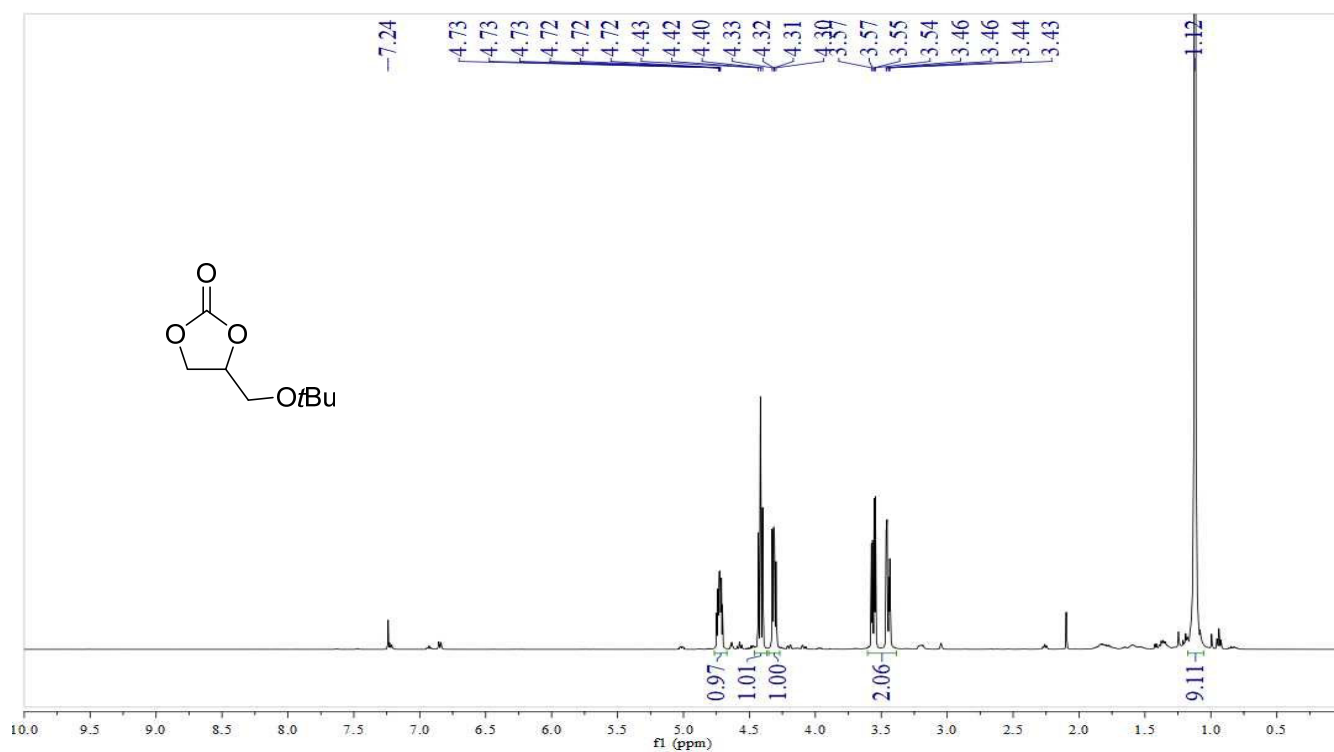


Figure S62. ¹H NMR spectrum of purified 4-[(1,1-dimethylethoxy)methyl]-1,3-dioxolan-2-one(**2g**) in CDCl₃.

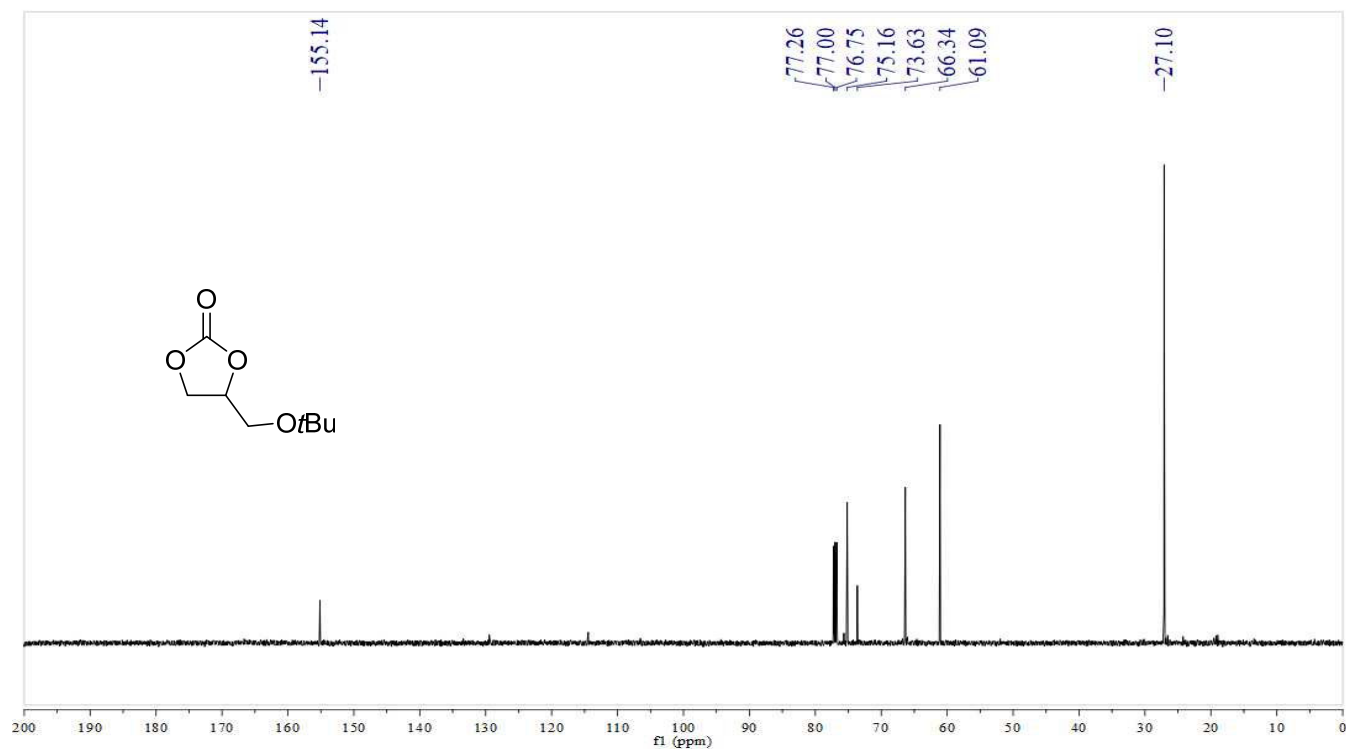


Figure S63. ¹³C NMR spectrum of purified 4-[(1,1-dimethylethoxy)methyl]-1,3-dioxolan-2-one(**2g**) in CDCl₃.

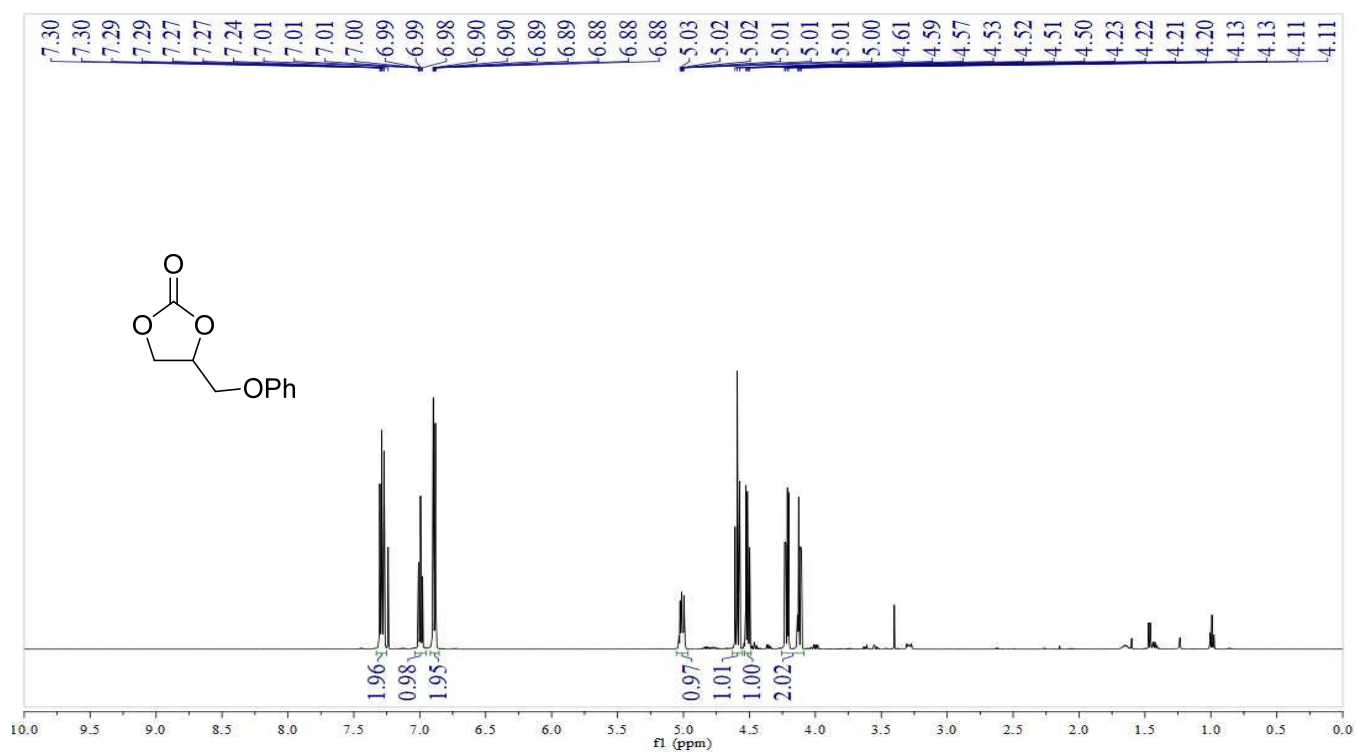


Figure S64. ¹H NMR spectrum of purified 4-(phoxymethyl)-1,3-dioxolan-2-one(**2h**) in CDCl₃.

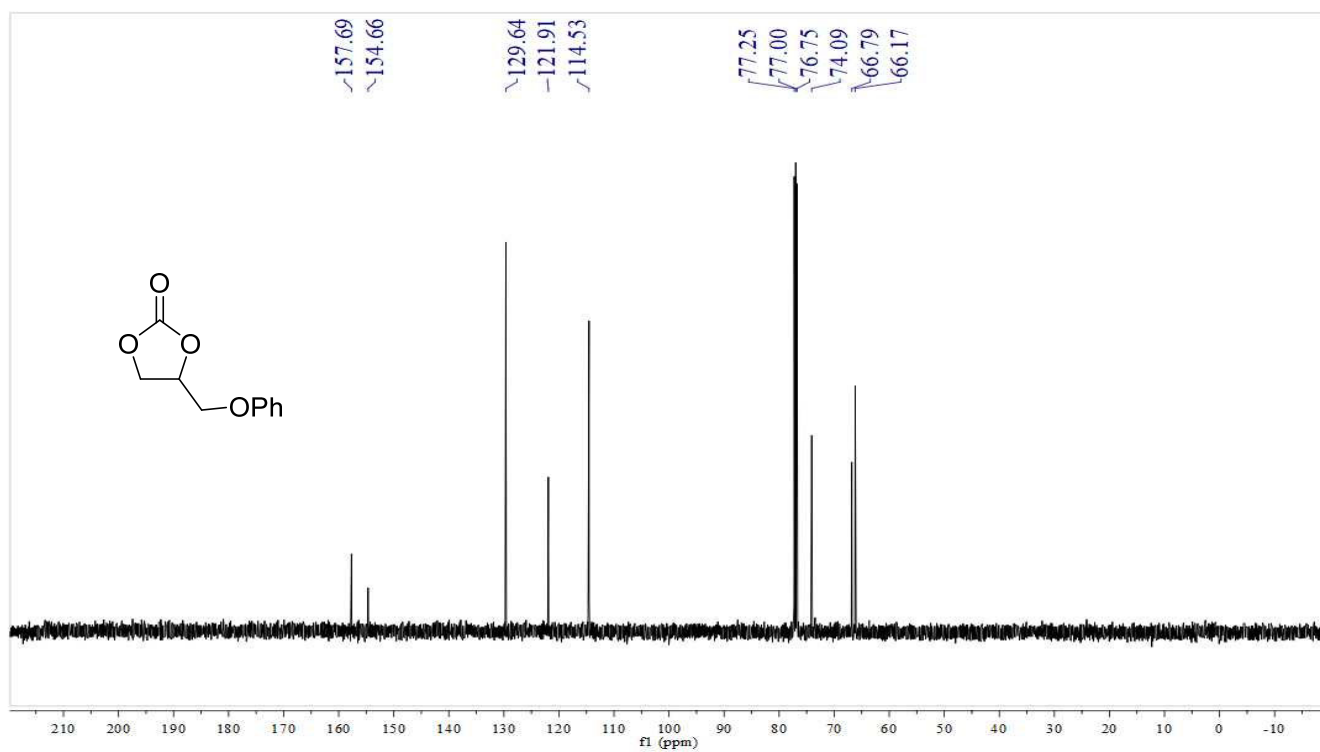


Figure S65. ¹³C NMR spectrum of purified 4-(phoxymethyl)-1,3-dioxolan-2-one(**2h**) in CDCl₃.

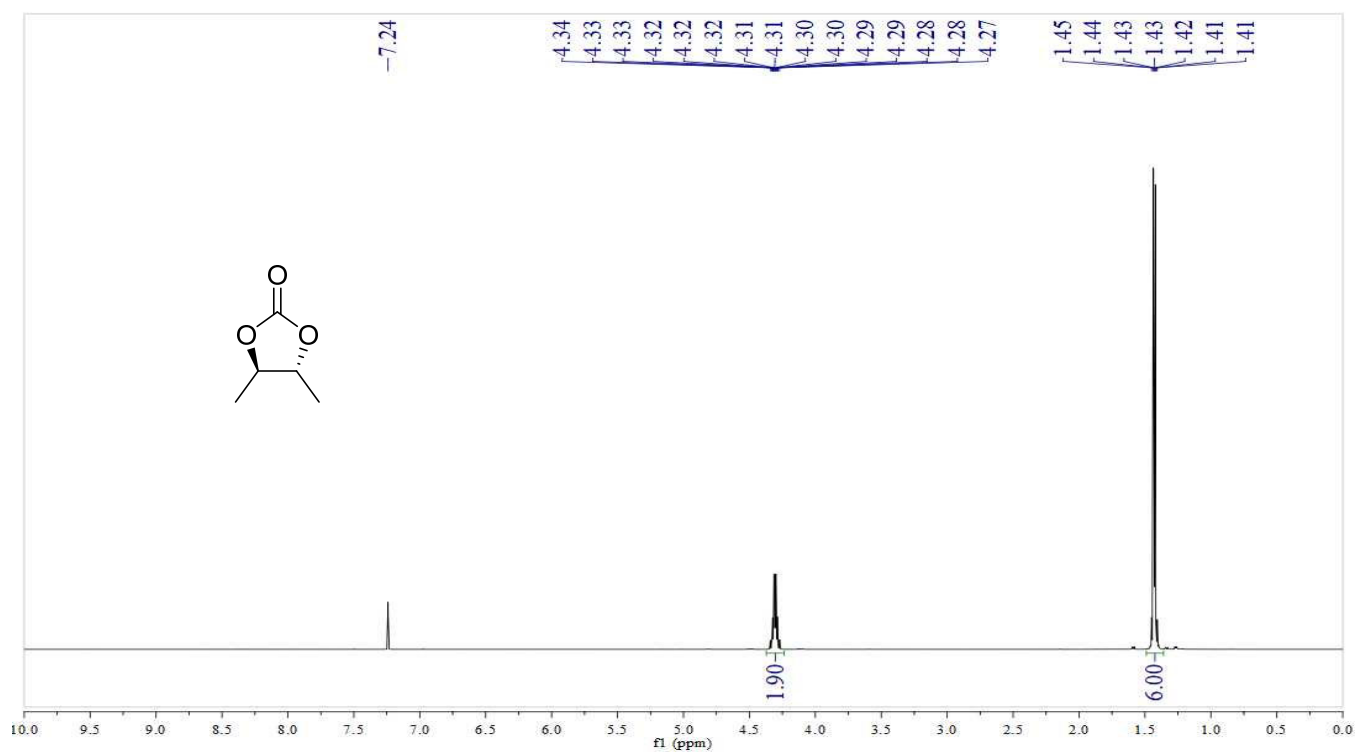


Figure S66. ¹H NMR spectrum of purified *trans*-4,5-dimethyl-1,3-dioxolan-2-one(*trans*-**2i**) in CDCl₃.

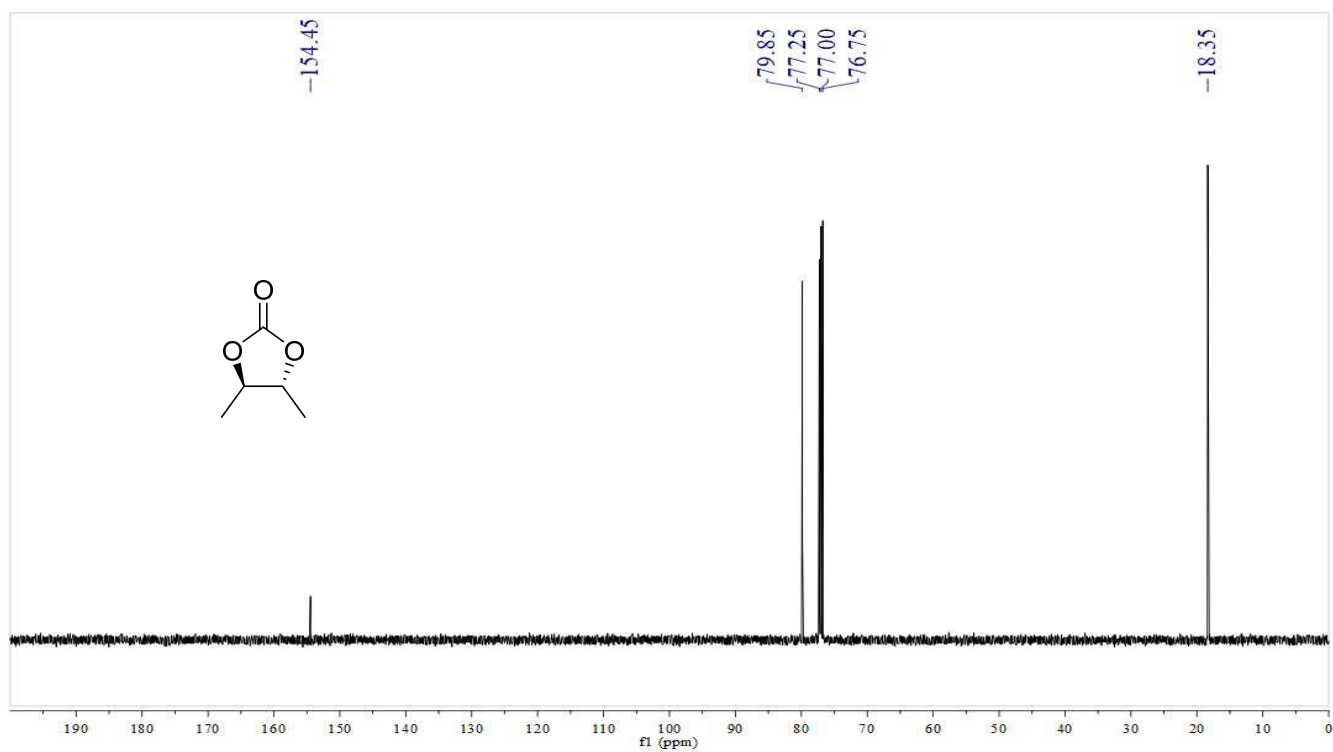


Figure S67. ¹³C NMR spectrum of purified *trans*-4,5-dimethyl-1,3-dioxolan-2-one(*trans*-**2i**) in CDCl₃.

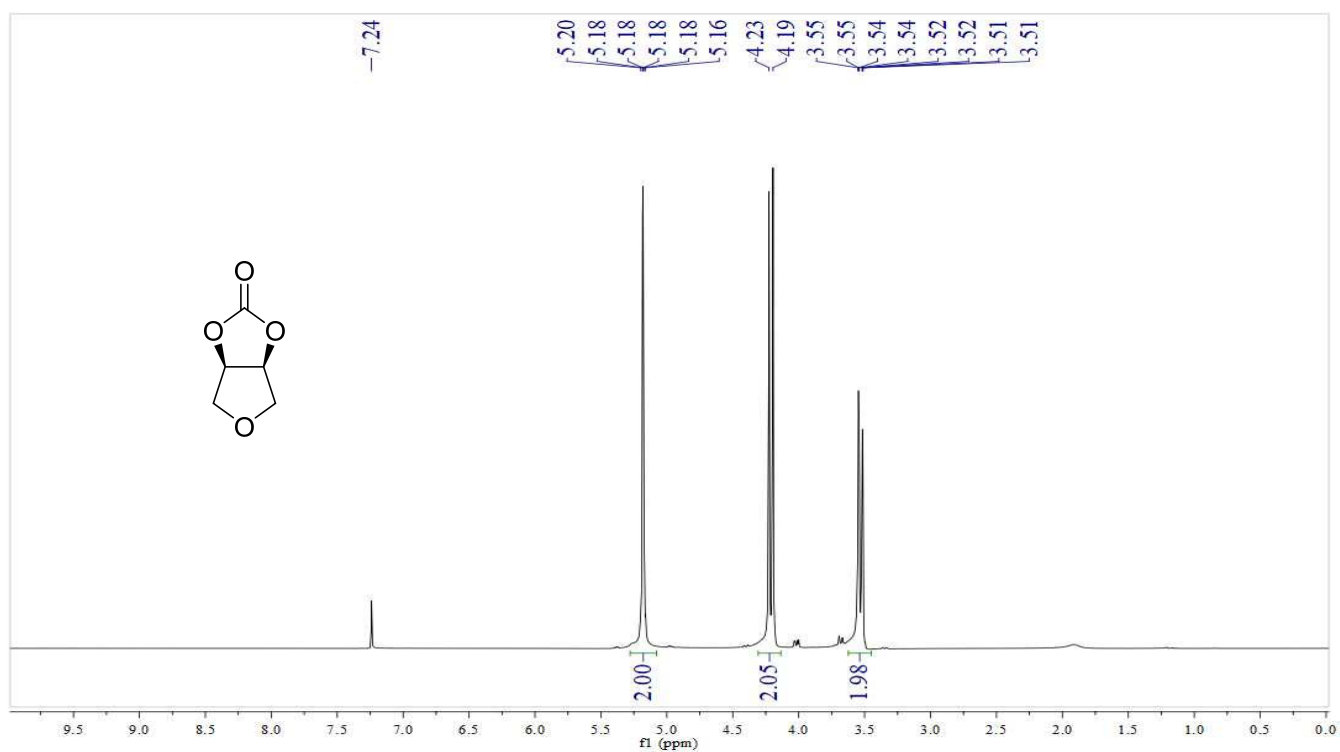


Figure S68. ¹H NMR spectrum of purified *cis*-tetrahydrofuro[3,4-*d*][1,3]dioxol-2-one (*cis*-**2j**) in CDCl₃.

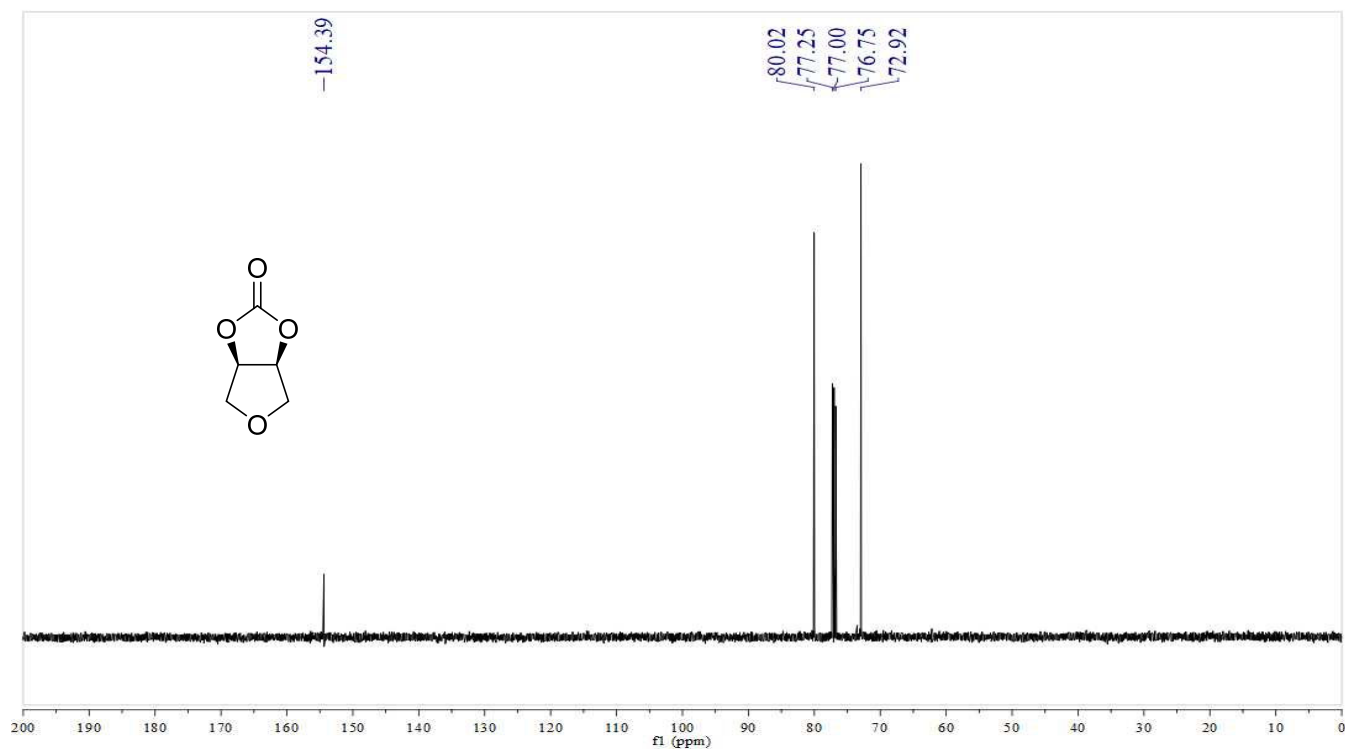


Figure S69. ¹³C NMR spectrum of purified *cis*-tetrahydrofuro[3,4-*d*][1,3]dioxol-2-one (*cis*-**2j**) in CDCl₃.

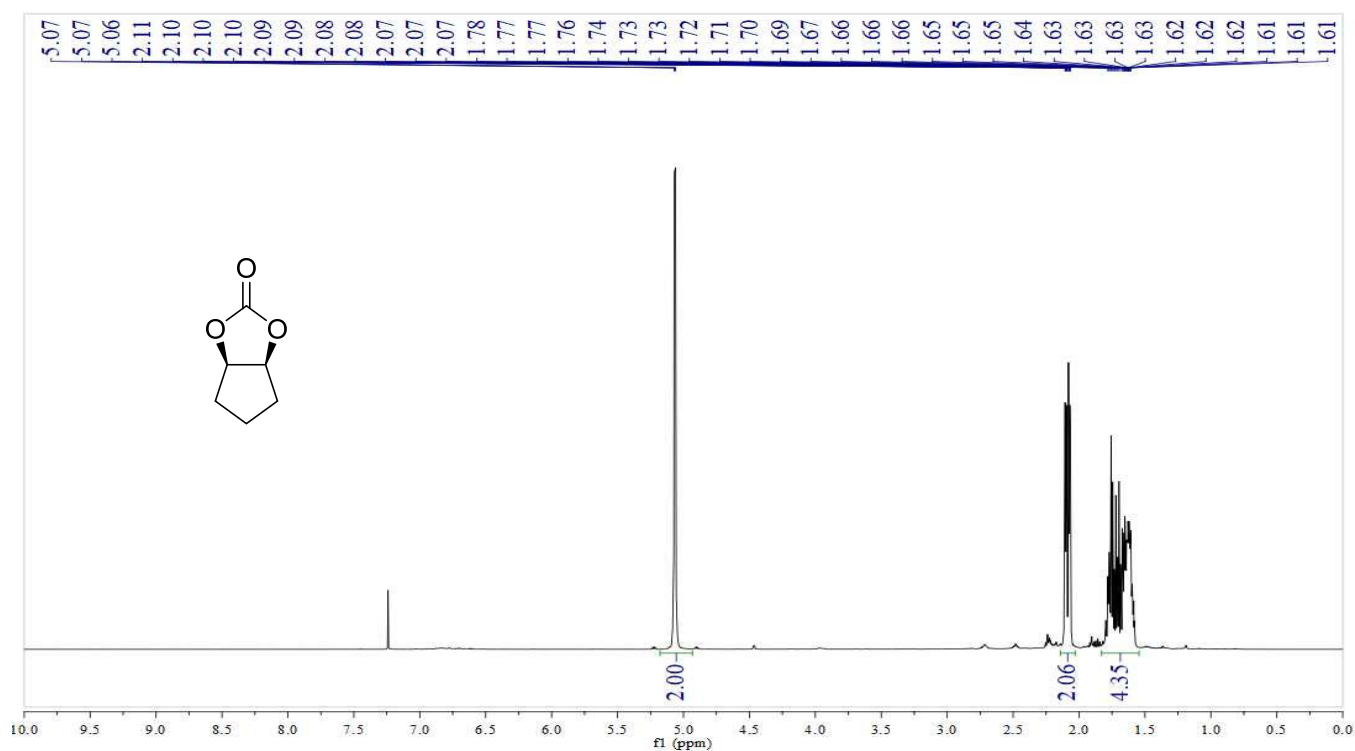


Figure S70. ¹H NMR spectrum of purified *cis*-tetrahydro-4*H*-cyclopenta[*d*][1,3]dioxol-2-one (*cis*-2k) in CDCl₃.

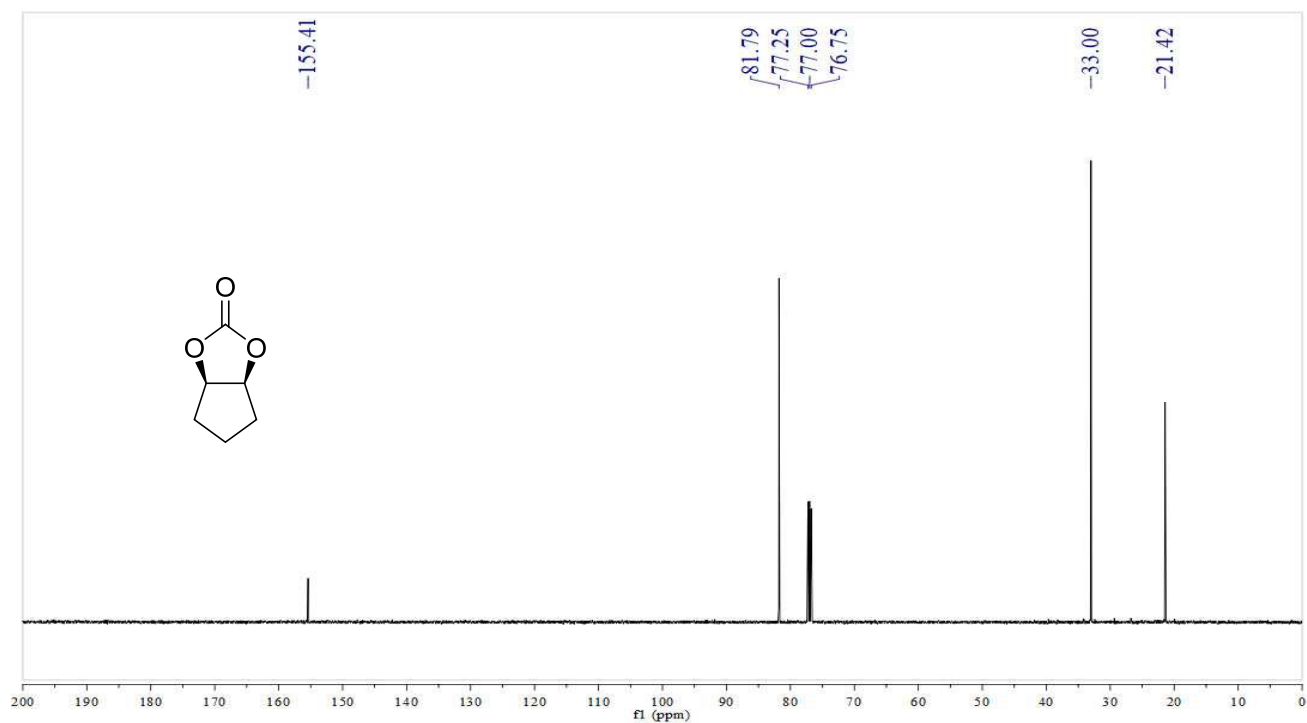


Figure S71. ¹³C NMR spectrum of purified *cis*-tetrahydro-4*H*-cyclopenta[*d*][1,3]dioxol-2-one (*cis*-2k) in CDCl₃.

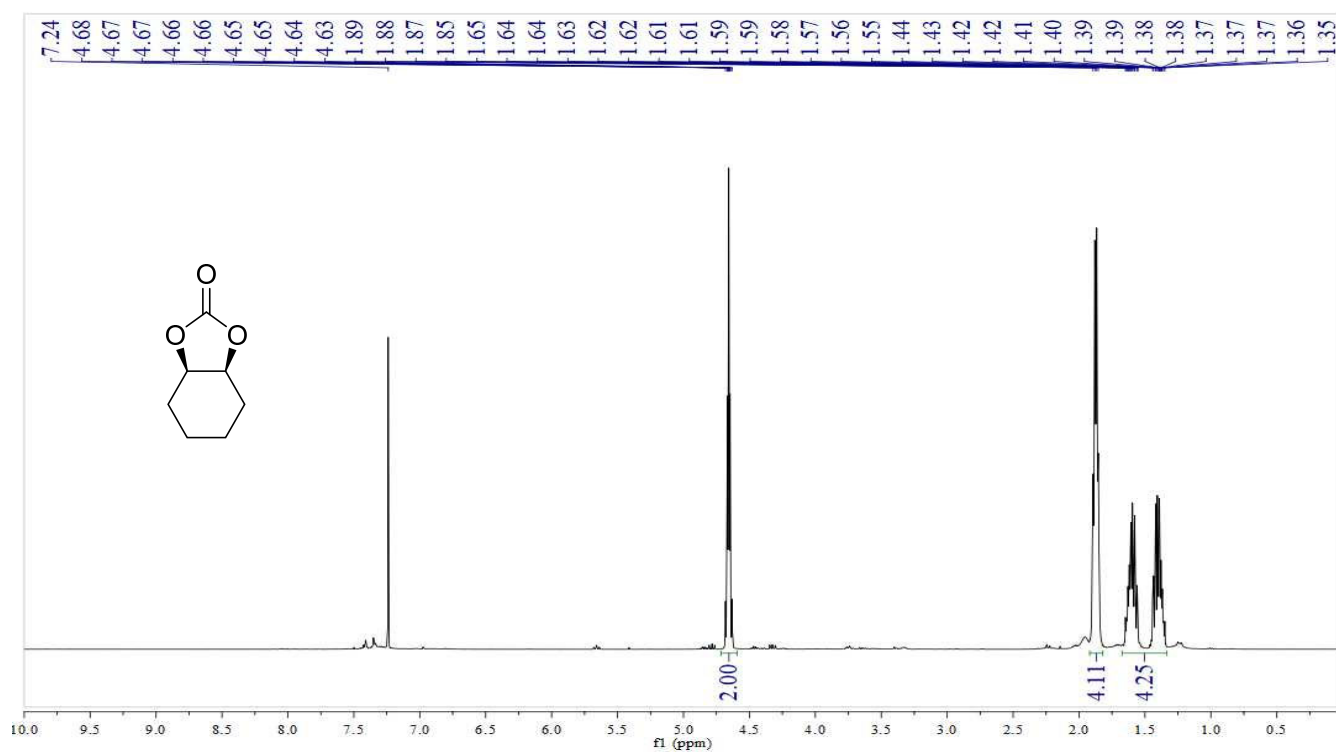


Figure S72. ¹H NMR spectrum of purified *cis*-hexahydrobenzo[*d*][1,3]dioxol-2-one (*cis*-**21**) in CDCl₃.

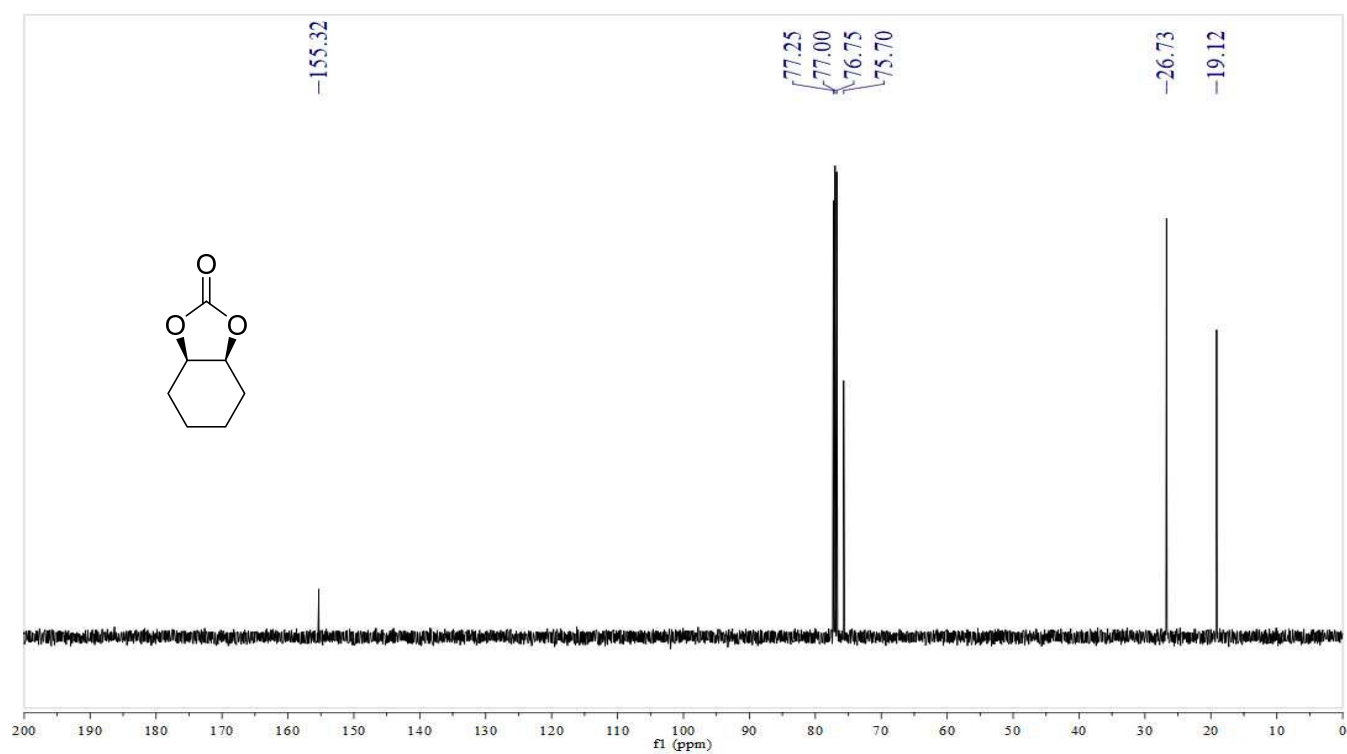


Figure S73. ¹³C NMR spectrum of purified *cis*-hexahydrobenzo[*d*][1,3]dioxol-2-one (*cis*-**21**) in CDCl₃.