

Supporting Information

Direct surface modification of graphitic C₃N₄ with porous organic polymer and silver nanoparticles for promoting CO₂ conversion

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Total number of pages: 17

Total number of figures: 27

Total number of tables: 1

1. Segmental figures and tables

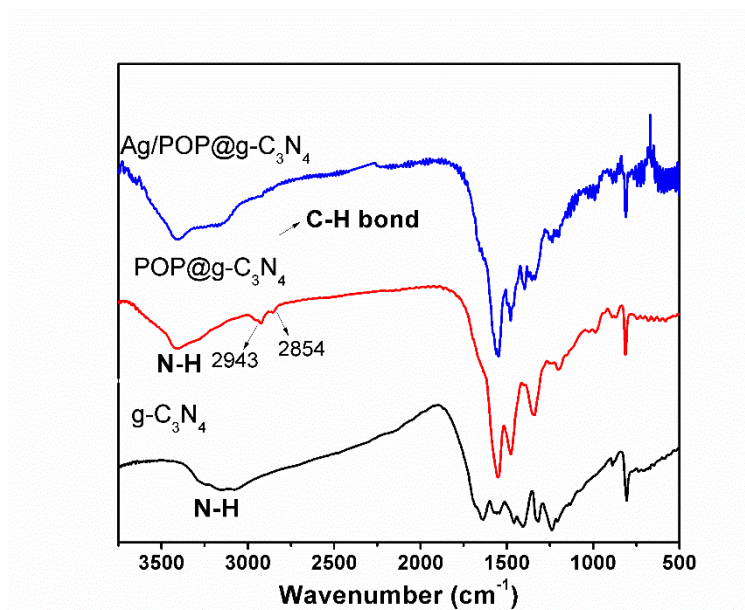


Figure S1. FT-IR spectra of $\text{g-C}_3\text{N}_4$, $\text{POP@g-C}_3\text{N}_4$ and $\text{Ag/POP@g-C}_3\text{N}_4$.

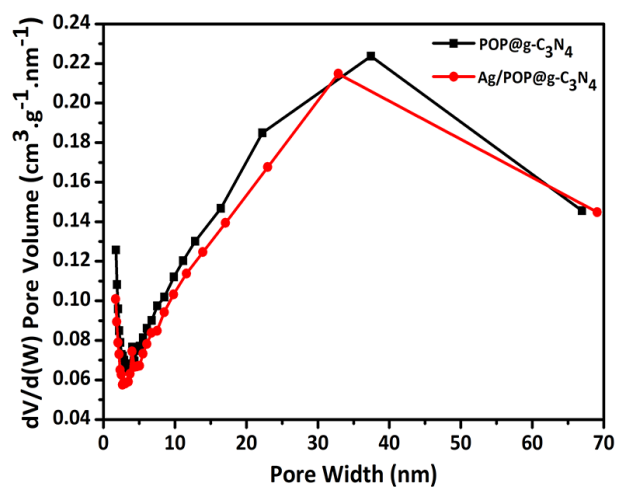


Figure S2. Pore size distributions of $\text{POP@g-C}_3\text{N}_4$ and $\text{Ag/POP@g-C}_3\text{N}_4$.

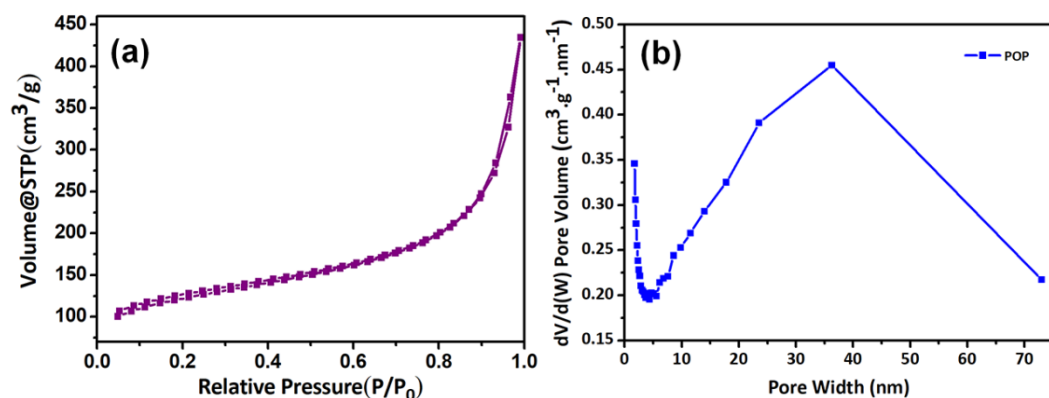


Figure S3. (a) N₂ adsorption-desorption isotherms of POP. (b) Pore size distributions of POP.

Table S1. Physicochemical properties of the catalyst

Sample	$S_{\text{BET}}^{\text{a}}$ (m ² /g)	V_{t}^{b} (cm ³ /g)	$V_{\text{micro}}^{\text{c}}$ (cm ³ /g)	$V_{\text{meso}}^{\text{d}}$ (cm ³ /g)
g-C ₃ N ₄	1.54	0.0326	0.00641	0.0326
POP	408.63	0.672	0.0794	0.620
POP@g-C ₃ N ₄	110.54	0.286	0.00873	0.287
Ag/POP@g-C ₃ N ₄	98.55	0.269	0.00722	0.265

^a S_{BET} : BET surface areas. ^b V_{t} : total pore volume at $P/P_0 = 0.99$. ^c V_{micro} : micropore volume, calculated by HK method. ^d V_{meso} : mesopore volume.

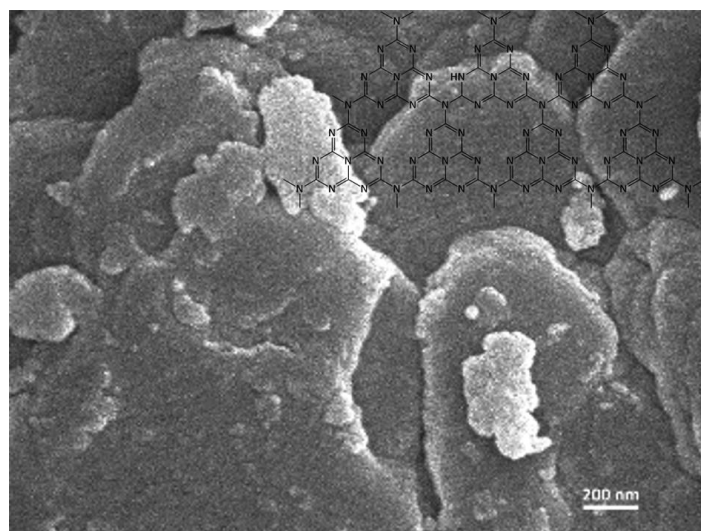


Figure S4. SEM image of g-C₃N₄.

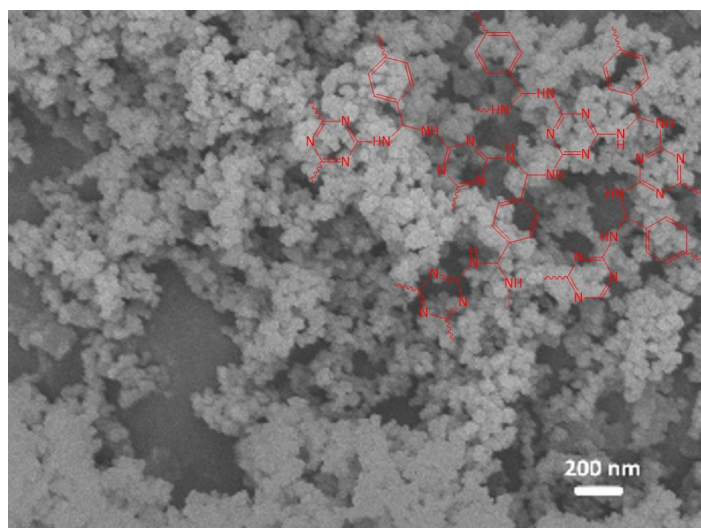


Figure S5. SEM image of POP.

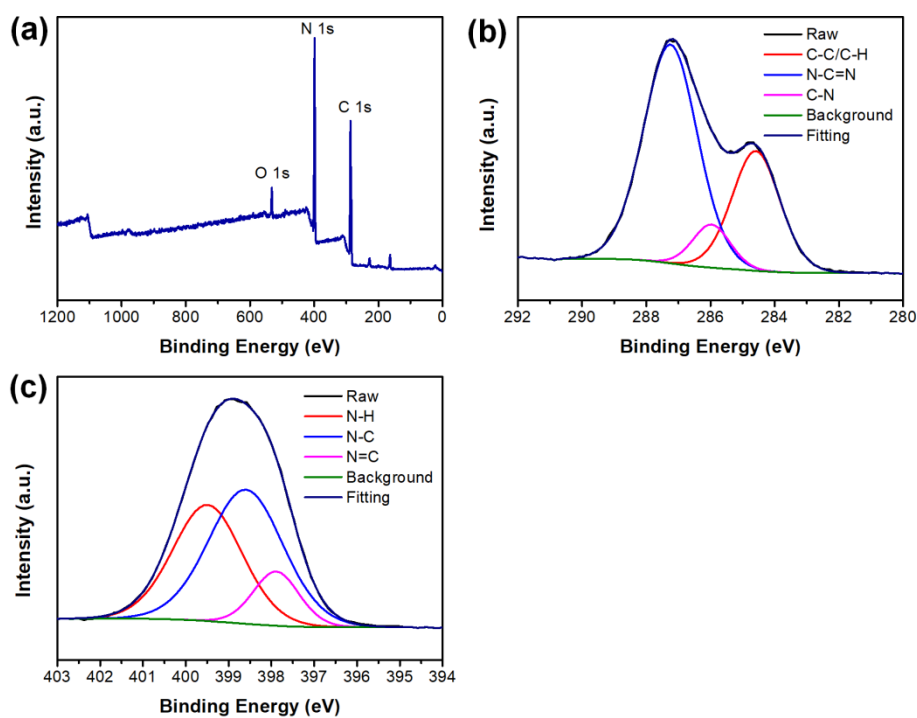
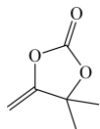


Figure S6. XPS spectra of POP@g-C₃N₄. (a) Survey spectrum, (b) C 1s, and (c) N 1s high-resolution spectra.

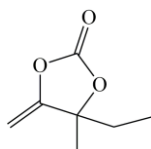
2. NMR and GC-MS data

4,4-dimethyl-5-methylene-1,3-dioxolan-2-one (1a):



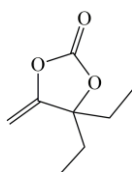
Colorless oil liquid. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 4.77 (d, $J = 4.00$ Hz, 1H), 4.31 (d, $J = 4.00$ Hz, 1H), 1.61 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 158.73, 151.27, 85.29, 84.83, 27.57. GC-MS calcd. for $\text{C}_6\text{H}_8\text{O}_3$ 128.05, found 128.10.

4-ethyl-4-methyl-5-methylene-1,3-dioxolan-2-one (1b):



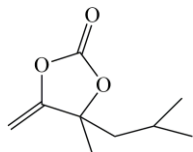
Colorless oil liquid. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 4.82 (d, $J = 4.00$ Hz, 1H), 4.26 (d, $J = 4.00$ Hz, 1H), 1.96-1.87 (m, 1H), 1.80-1.71 (m, 1H), 1.58 (s, 3H), 1.00-0.97 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 157.44, 151.57, 87.58, 85.57, 33.41, 25.99, 7.35. GC-MS calcd. for $\text{C}_7\text{H}_{10}\text{O}_3$ 142.06, found 142.08.

4,4-dieethyl-5-methylene-1,3-dioxolan-2-one (1c):



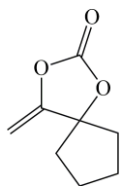
Colorless oil liquid. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 4.86 (d, $J = 4.00$ Hz, 1H), 4.23 (d, $J = 4.00$ Hz, 1H), 1.97-1.88 (m, 2H), 1.75-1.64 (m, 2H), 0.99- 0.95 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 155.78, 151.89, 90.86, 85.82, 31.90, 7.11. GC-MS calcd. for $\text{C}_8\text{H}_{12}\text{O}_3$ 156.08, found 156.07.

4-isobutyl-4-methyl-5-methylene-1,3-dioxolan-2-one (1d):



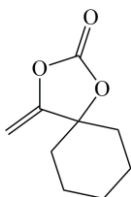
Colorless oil liquid. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 4.79 (d, $J = 4.00$ Hz, 1H), 4.27 (d, $J = 4.00$ Hz, 1H), 1.88-1.77 (m, 2H), 1.69-1.61 (s, 1H), 1.57 (s, 3H), 0.97-0.95 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 158.31, 151.49, 87.34, 85.59, 48.52, 27.01, 24.28, 23.98, 23.67. GC-MS calcd. for $\text{C}_8\text{H}_{12}\text{O}_3$ 170.21, found 170.16.

4-methylene-1,3-dioxaspiro[4.4]nonan-2-one (1e):



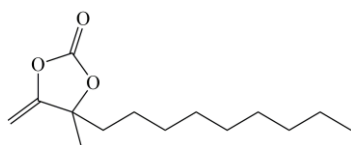
Colorless oil liquid. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 4.78 (d, $J = 4.00$ Hz, 1H), 4.33 (d, $J = 4.00$ Hz, 1H), 2.28-2.19 (m, 2H), 1.98-1.77 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 157.75, 151.51, 94.23, 85.34, 40.65, 24.25. GC-MS calcd. For $\text{C}_8\text{H}_{10}\text{O}_3$ 154.06, found 154.03.

4-methylene-1,3-dioxaspiro [4.5]decan-2-one (1f):



Colorless oil liquid. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 4.76 (d, $J = 4.00$ Hz, 1H), 4.28 (d, $J = 4.00$ Hz, 1H), 2.02-1.98 (d, 2H), 1.72-1.61 (m, 7H), 1.36-1.25 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 158.74, 151.50, 86.40, 85.49, 36.51, 24.35, 21.61. GC-MS calcd. for $\text{C}_9\text{H}_{12}\text{O}_3$ 168.08, found 168.06.

4-methyl-5-methylene-4-nonyl-1,3-dioxolan-2-one (1g):



Colorless solid. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 4.79 (d, $J = 4.00$ Hz, 1H), 4.26 (d, $J = 4.00$ Hz, 1H), 1.85 (m, 1H), 1.68 (m, 1H), 1.57 (s, 3H), 1.35-1.25 (m, 14H), 0.89-0.85 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 157.75, 151.58, 87.28, 85.47, 40.42, 31.82, 29.41, 29.31, 29.26, 29.23, 26.32, 22.93, 22.85, 14.09. GC-MS calcd. for $\text{C}_{14}\text{H}_{24}\text{O}_3$ 240.17, found 240.10.

3. Copies of NMR and GC-MS spectra of all products

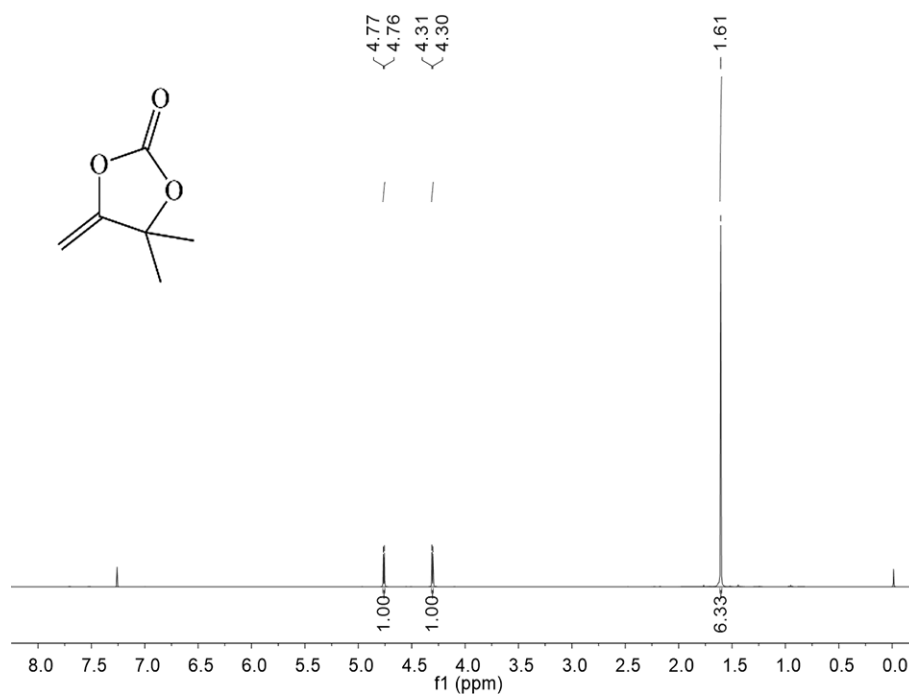


Figure S7. ¹H NMR spectrum of product *1a*

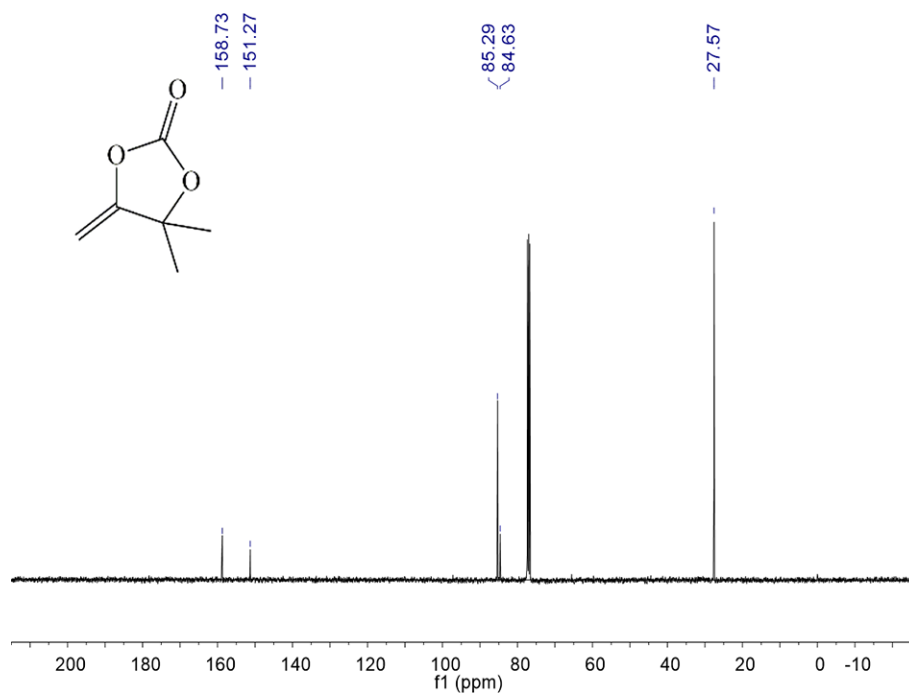


Figure S8. ¹³C NMR spectrum of product *1a*

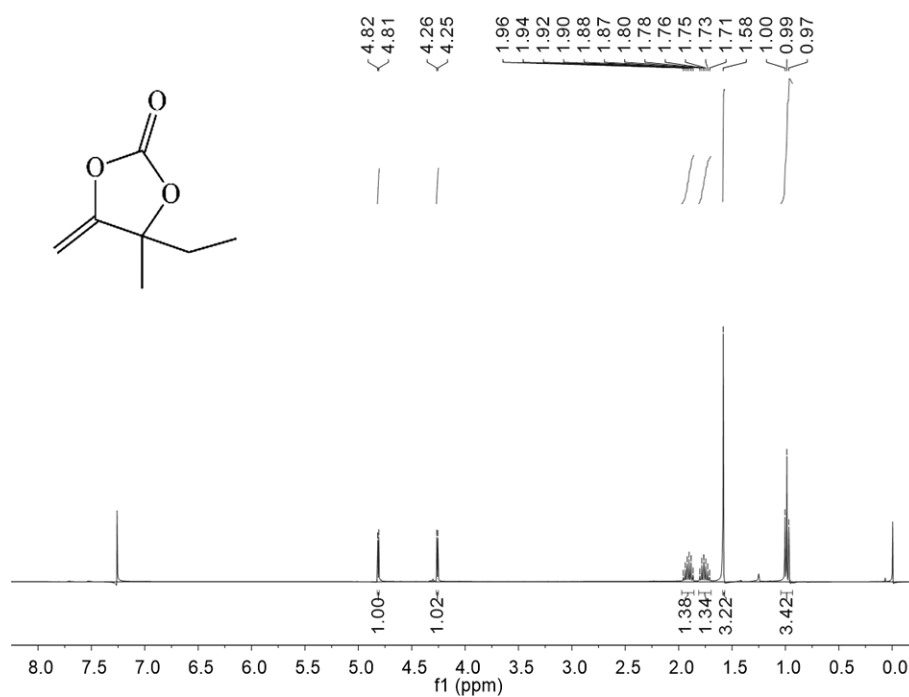


Figure S9. ¹H NMR spectrum of product *1b*

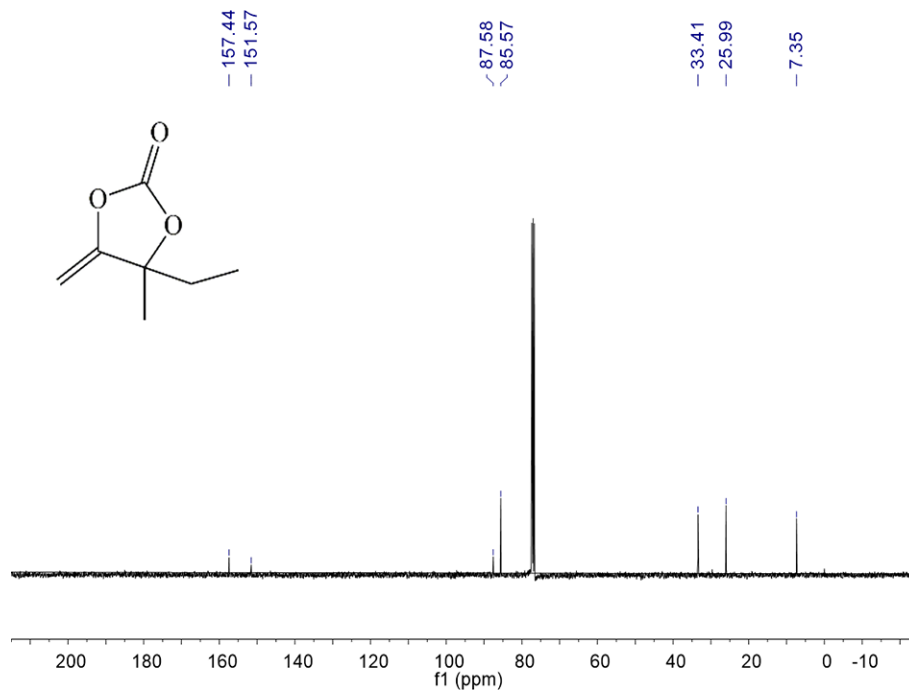


Figure S10. ¹³C NMR spectrum of product *1b*

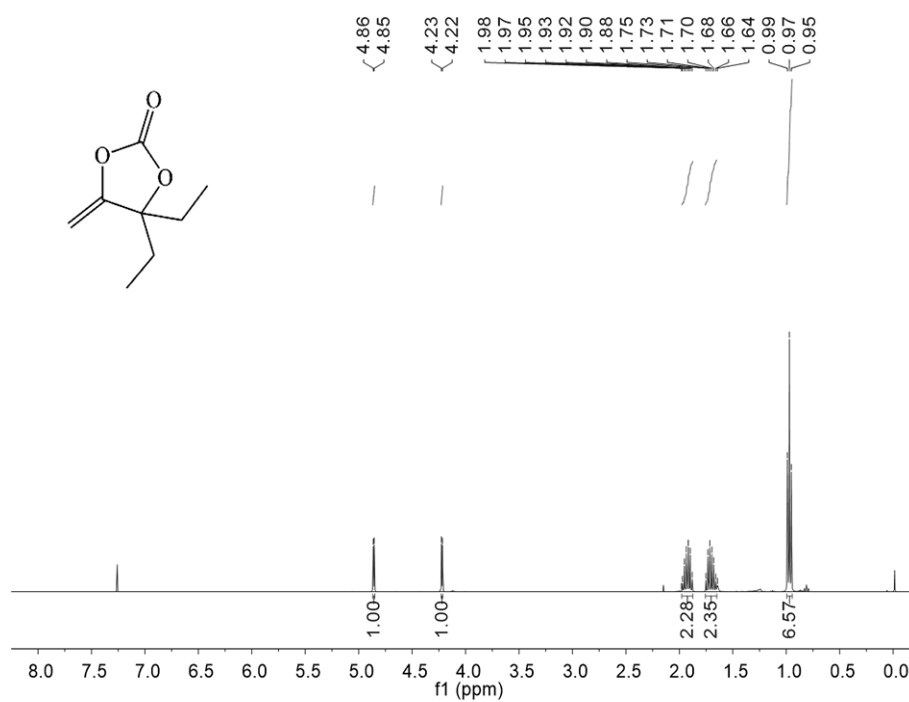


Figure S11. ¹H NMR spectrum of product *1c*

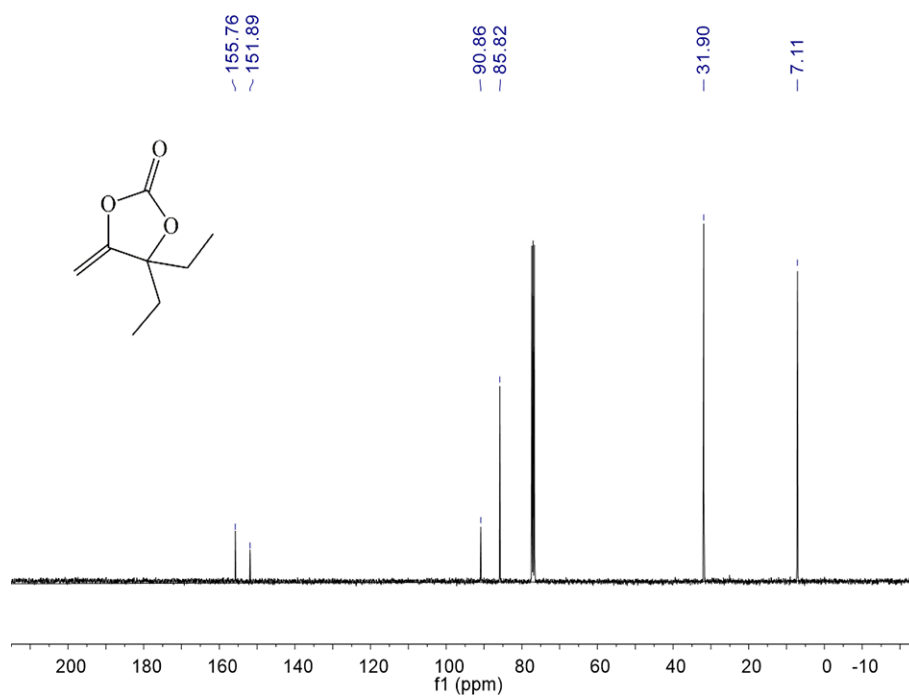


Figure S12. ¹³C NMR spectrum of product *1c*

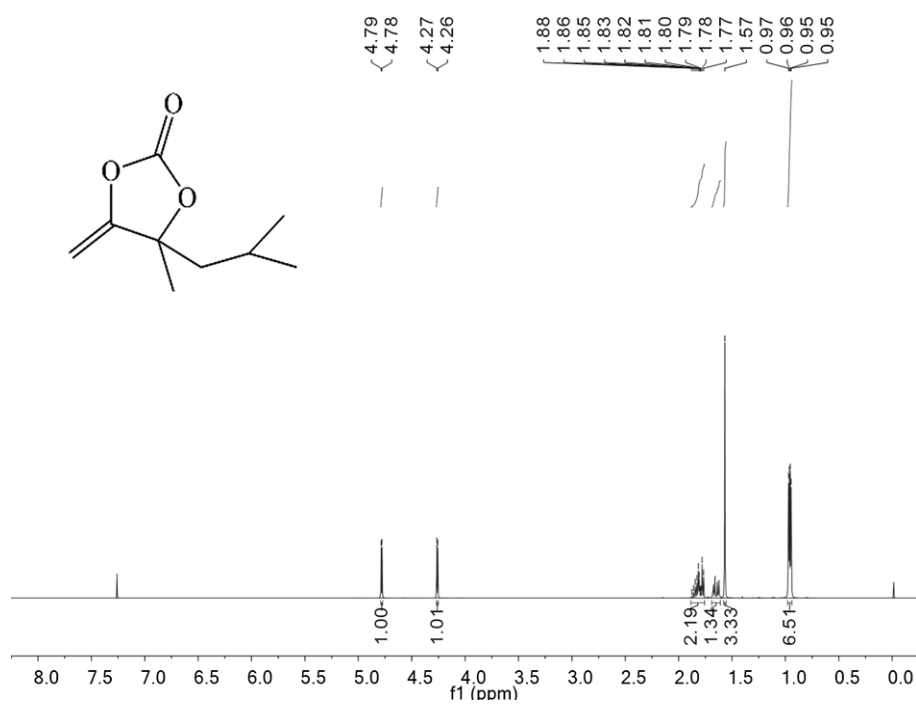


Figure S13. ^1H NMR spectrum of product *1d*

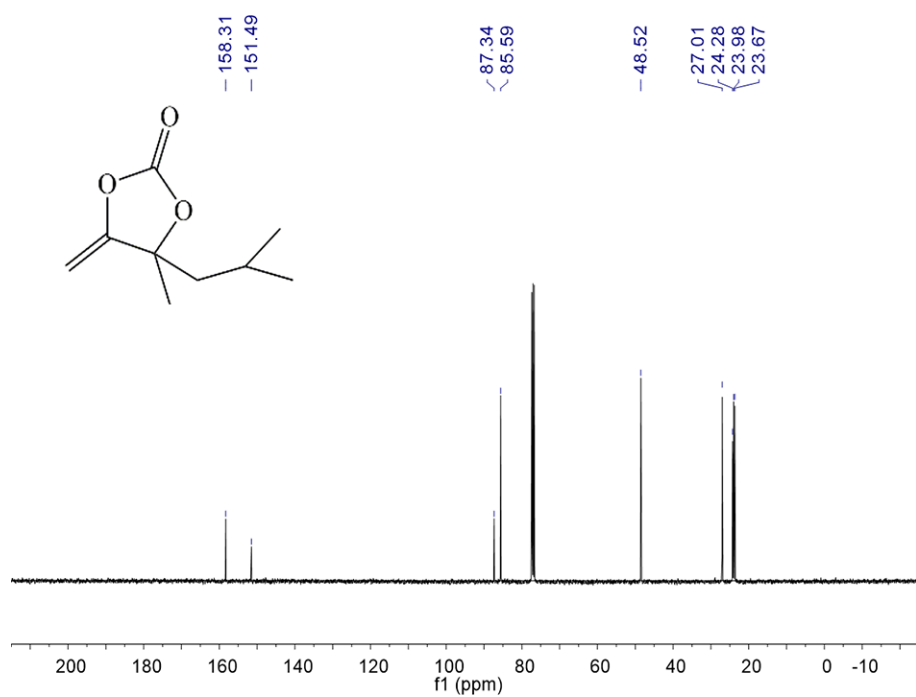
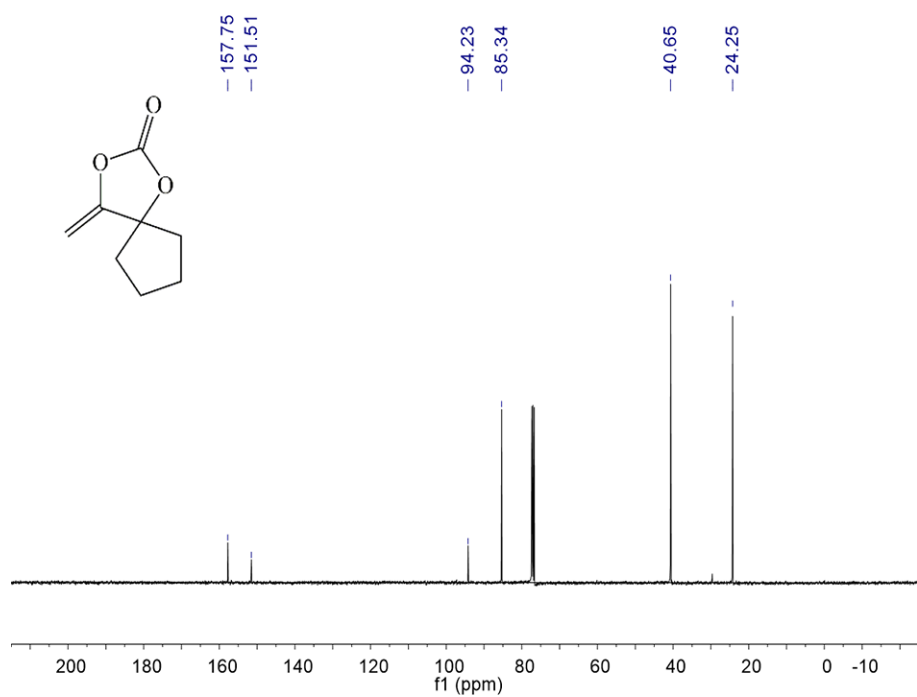
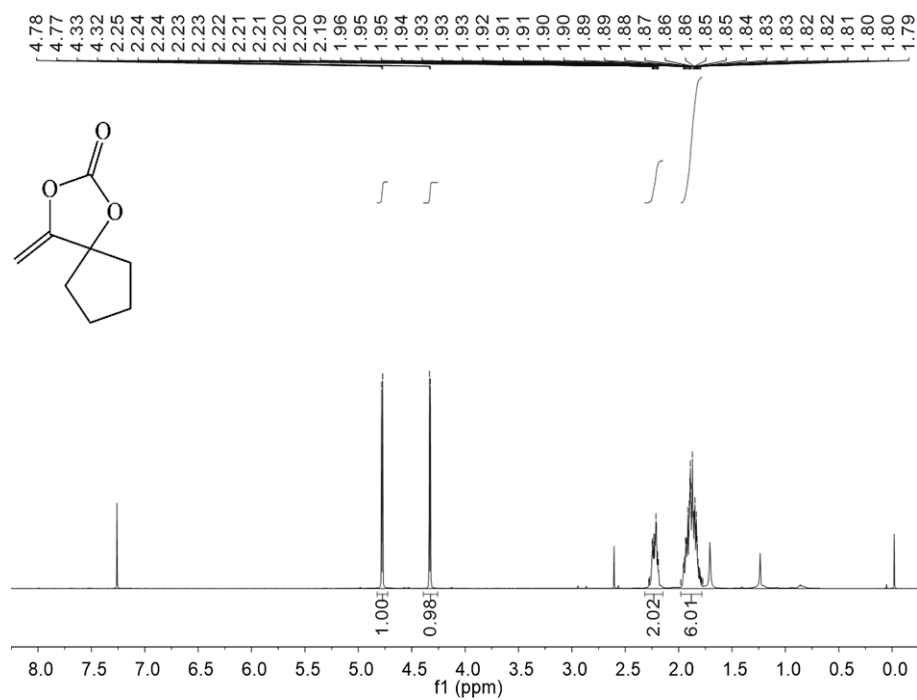


Figure S14. ^{13}C NMR spectrum of product *1d*



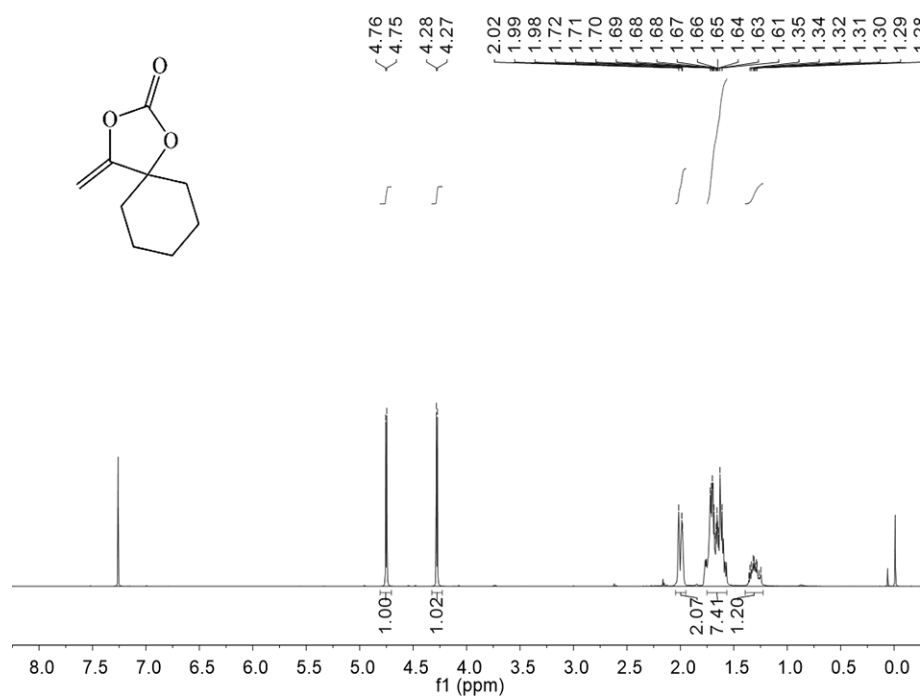


Figure S17. ¹H NMR spectrum of product *If*

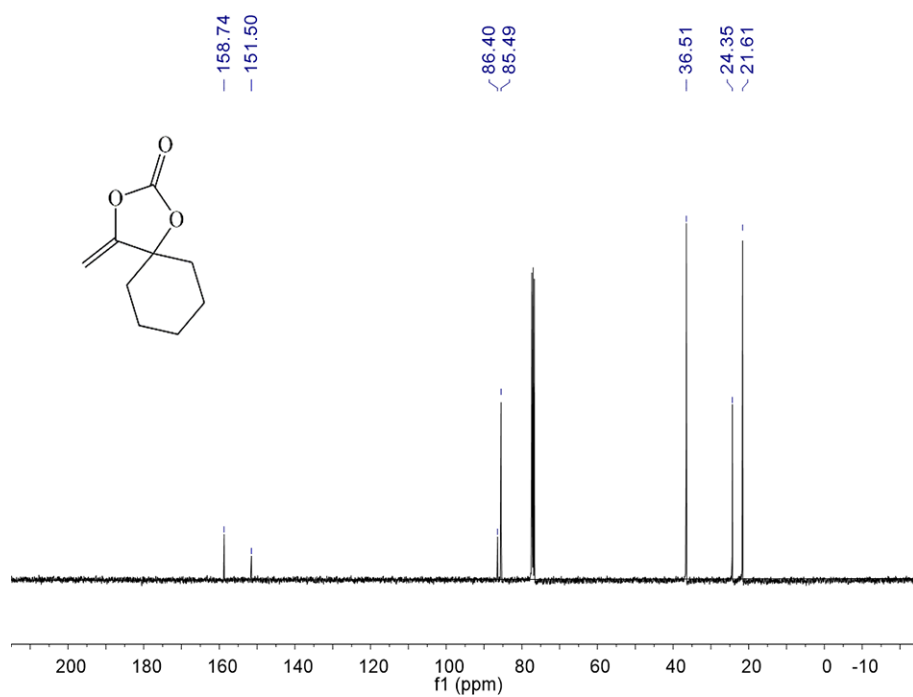


Figure S18. ¹³C NMR spectrum of product *If*

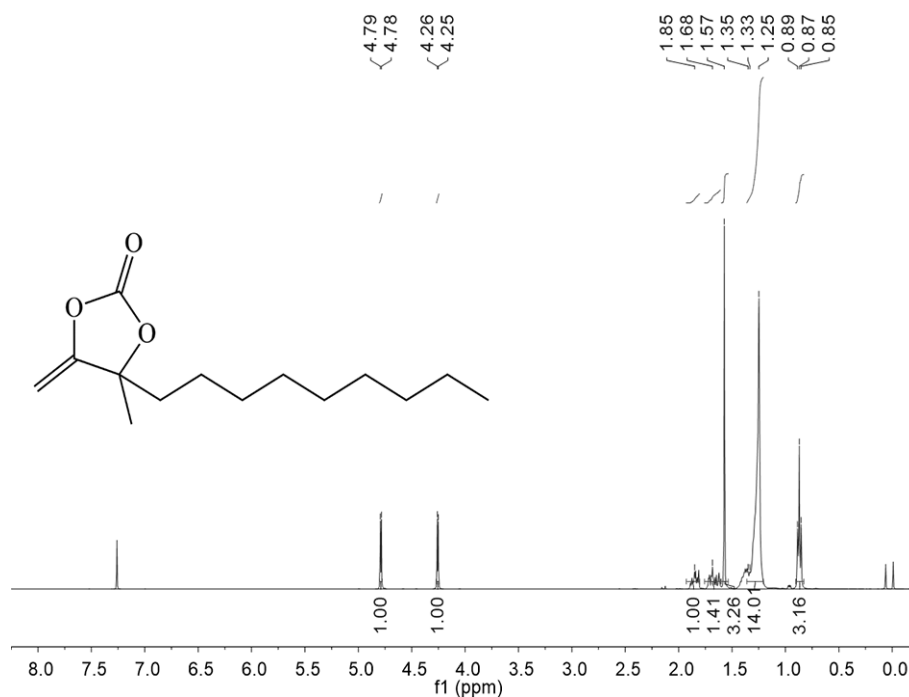


Figure S19. ¹H NMR spectrum of product *Ig*

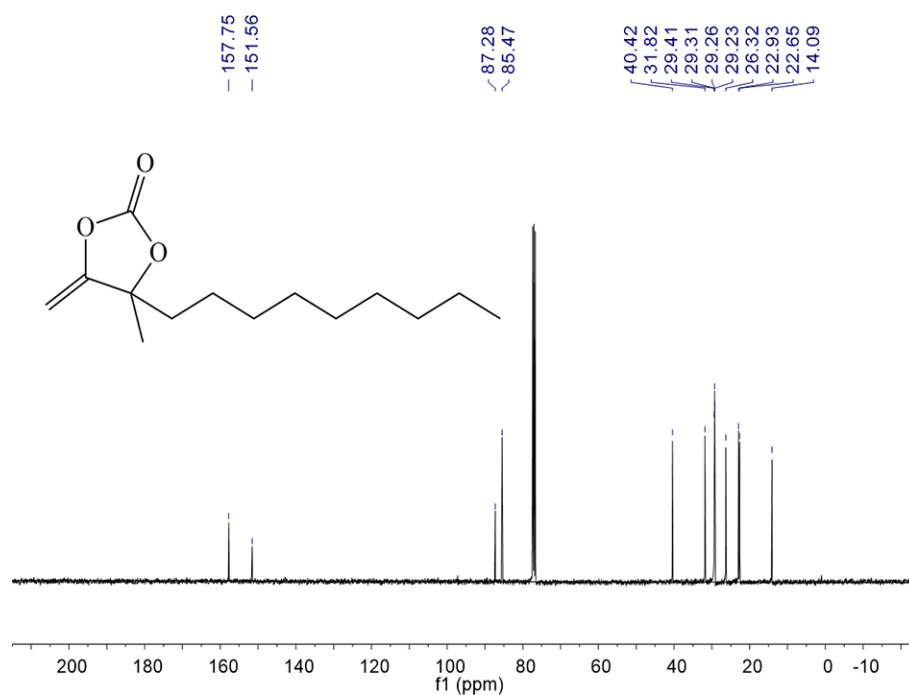


Figure S20. ¹³C NMR spectrum of product *Ig*

Copies of MS Spectra of All Products

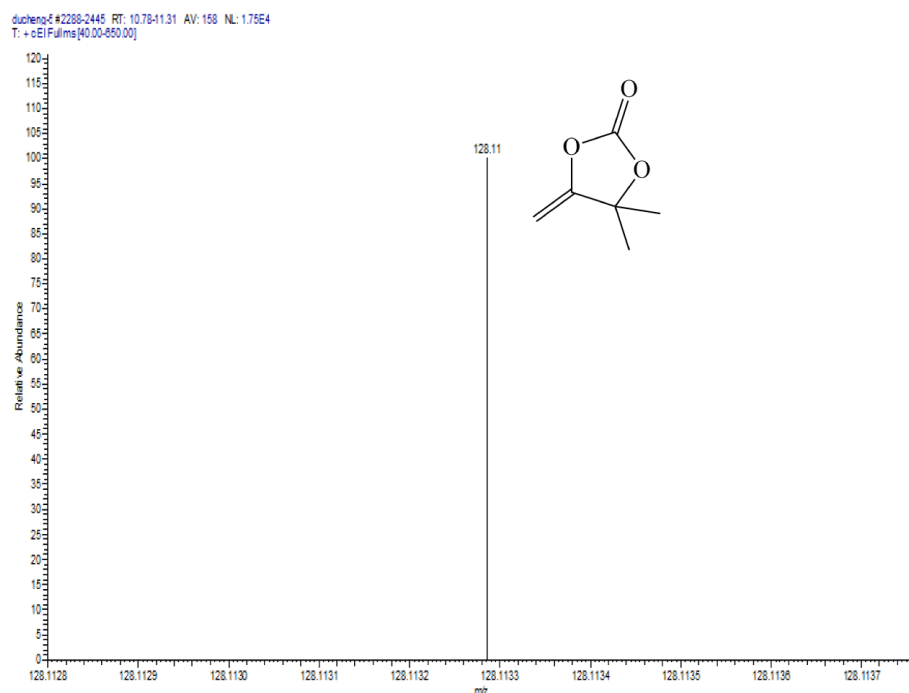


Figure S21. MS spectrum of product *1a*

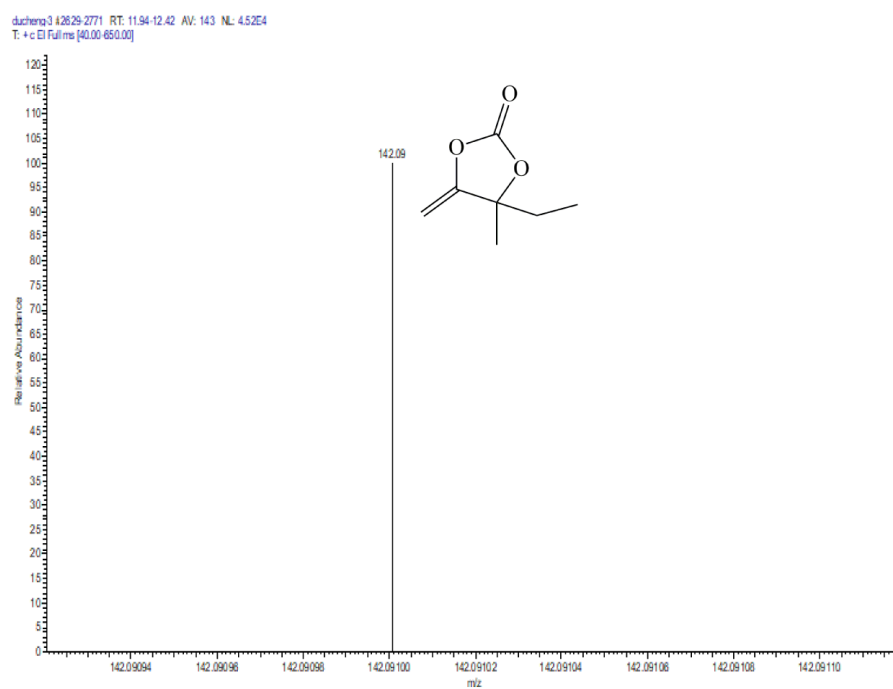


Figure S22. MS spectrum of product *1b*

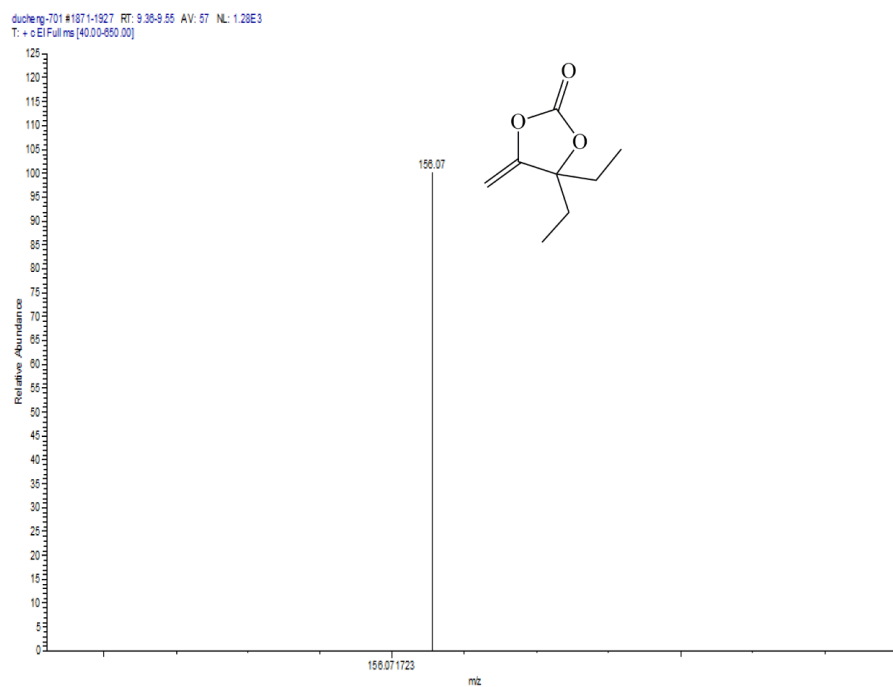


Figure S23. MS spectrum of product *1c*

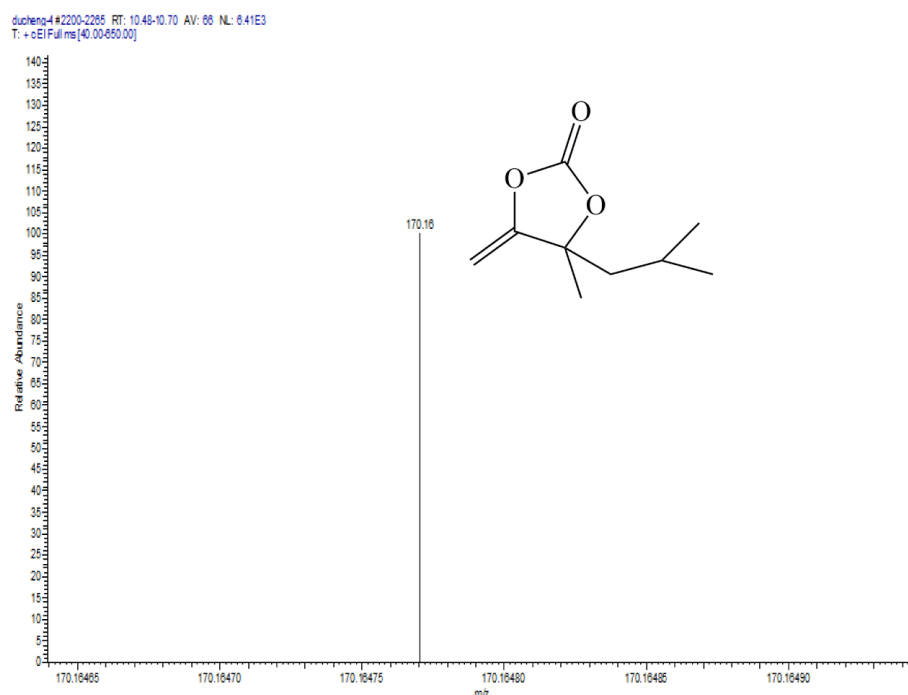


Figure S24. MS spectrum of product *1d*

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T: + e EI Full ms [40.00-650.00]

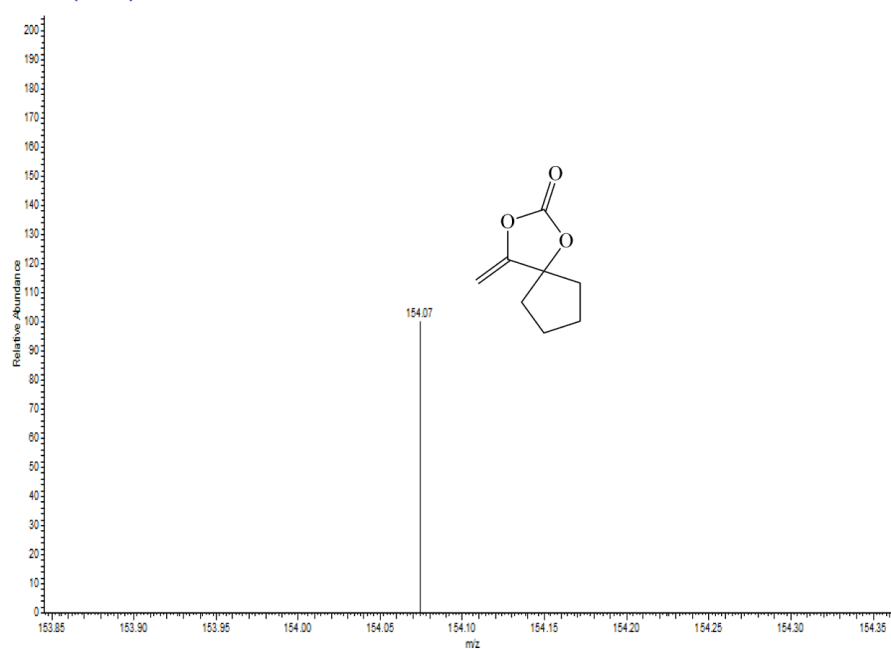


Figure S25. MS spectrum of product *1e*

achemo-2 #2582-2645 RT: 11.71-11.99 AV: 94 NL: 1.54E5
+ e EI Full ms [40.00-650.00]

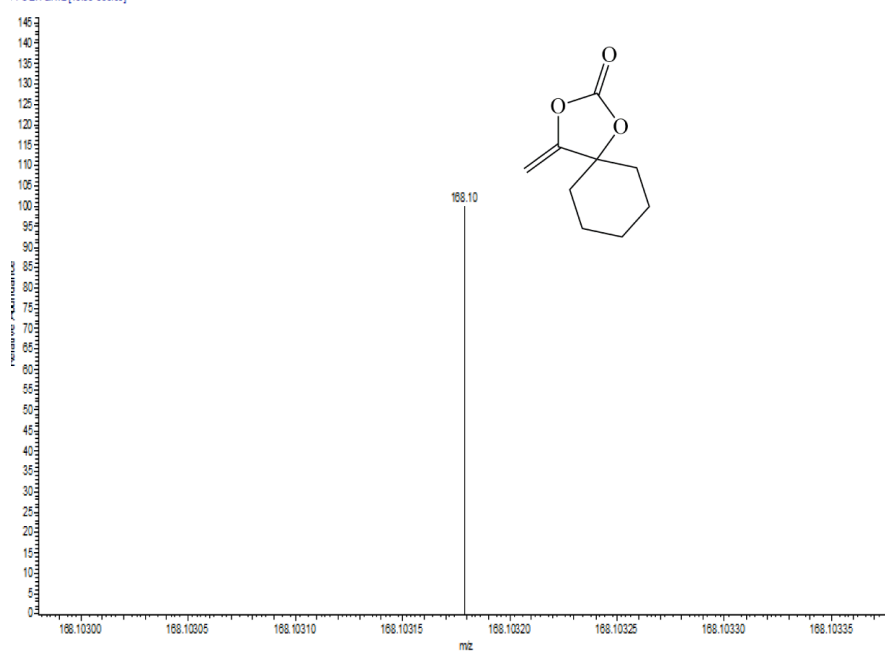


Figure S26. MS spectrum of product *1f*

duchong-#3079-3143 RT: 13.47-13.69 AV: 65 NL: 488E3
T: • cEI Full ms [40.00-650.00]

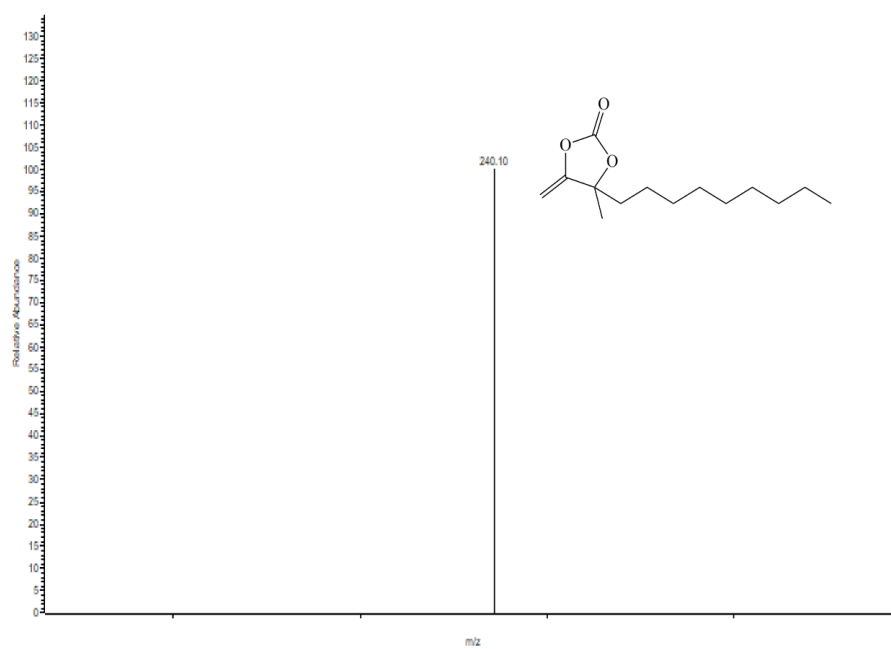


Figure S27. MS spectrum of product *1g*