

Supporting information

Iron(II) Bis-CNN Pincer Complex Catalyzed Cyclic Carbonate Synthesis at Room Temperature

Fei Chen, Ning Liu*, Bin Dai*

School of Chemistry and Chemical Engineering, Key Laboratory for Green Processing of
Chemical Engineering of Xinjiang Bingtuan, Shihezi University, North 4th Road, Shihezi,
Xinjiang 832003, China, E-mail: ninglau@163.com; ningliu@shzu.edu.cn; dbinly@126.com

Totals - 37 pages, and 64 figures

1. X-Ray Data of iron complex 1i	S2
2. H NMR spectra of the recycled catalyst.....	S3
3. NMR Spectra for the Iron Complexes 1a-1k	S4-S16
4. NMR Spectra for the Cycloaddition Products.....	S17-S32
5. HPLC Spectra for (<i>S</i>)- 2n , (<i>S</i>)- 2g , and (<i>R</i>)- 2g	S33-S37

1. X-Ray Data of iron complex 1i

CCDC 1511481 (**1i**) contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <https://www.ccdc.cam.ac.uk/>

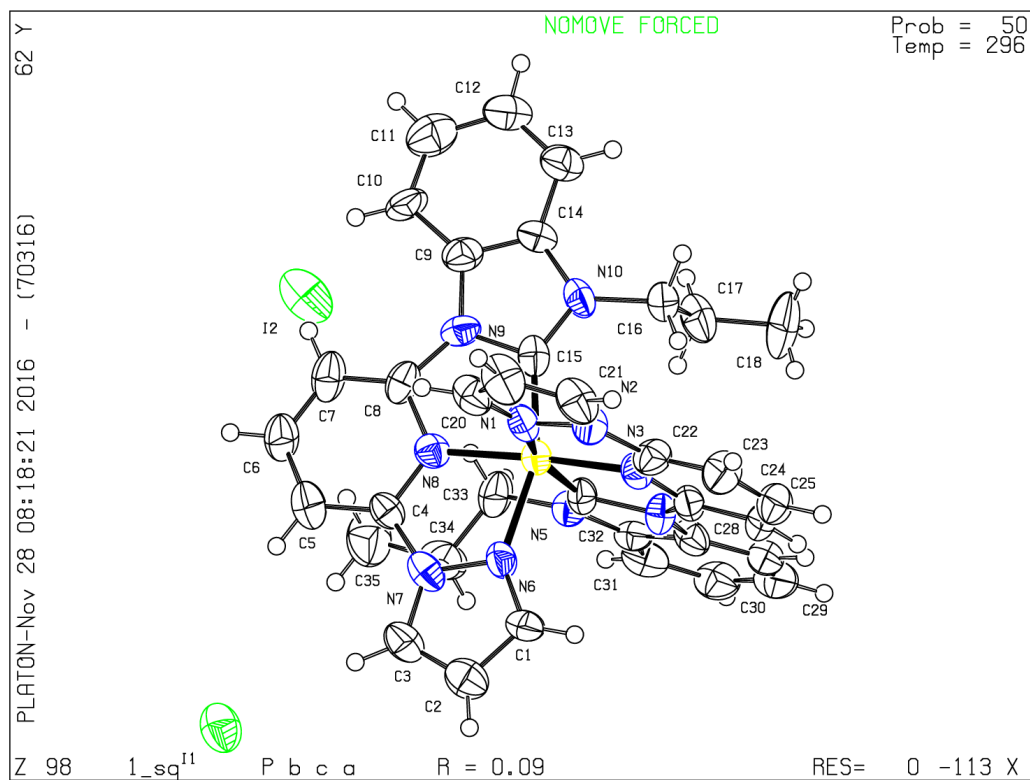


Figure S1. Thermal ellipsoid plots of **1i**.

cf-181

cf-125

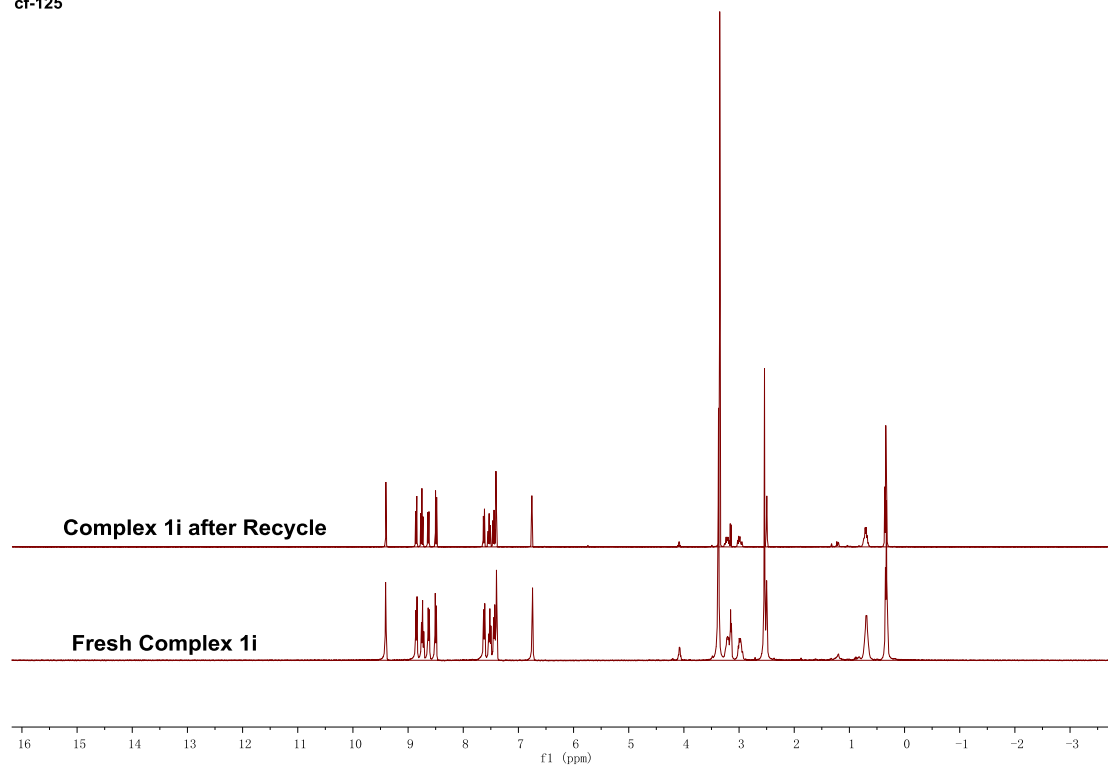


Figure S2. ^1H NMR(400 MHz, $\text{DMSO}-d_6$) spectra of the fresh and recycled catalyst **1i**.

2. NMR Spectra for the Iron Complexes

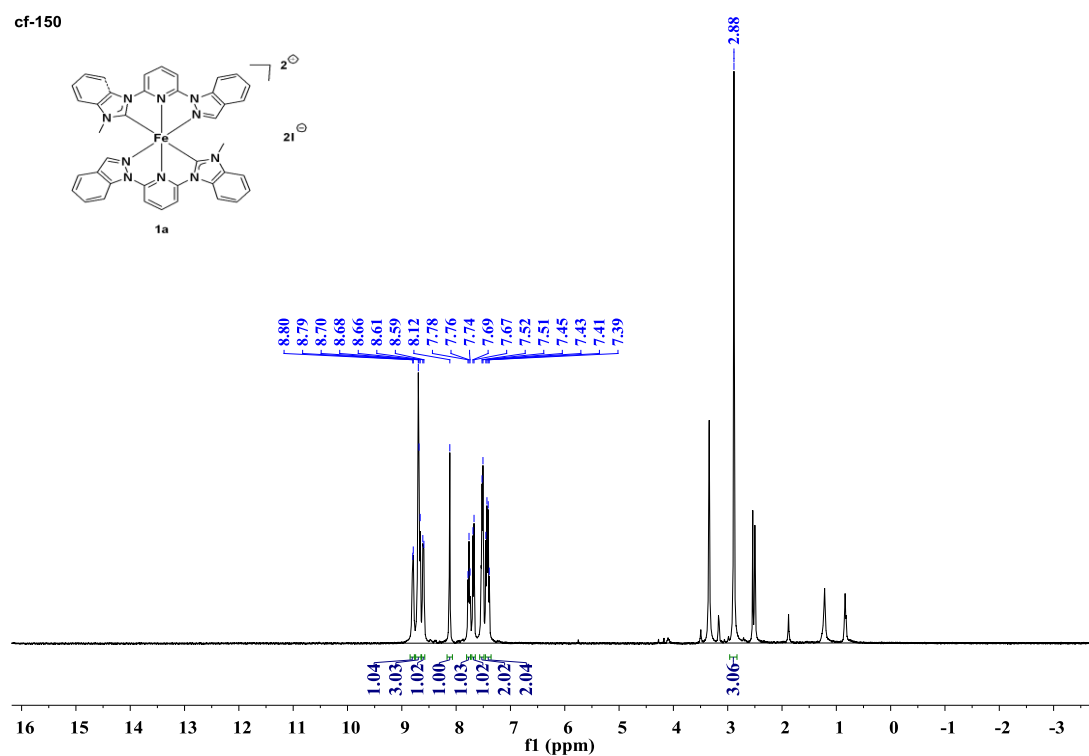


Figure S3. ¹H NMR spectra of Fe complex **1a**.

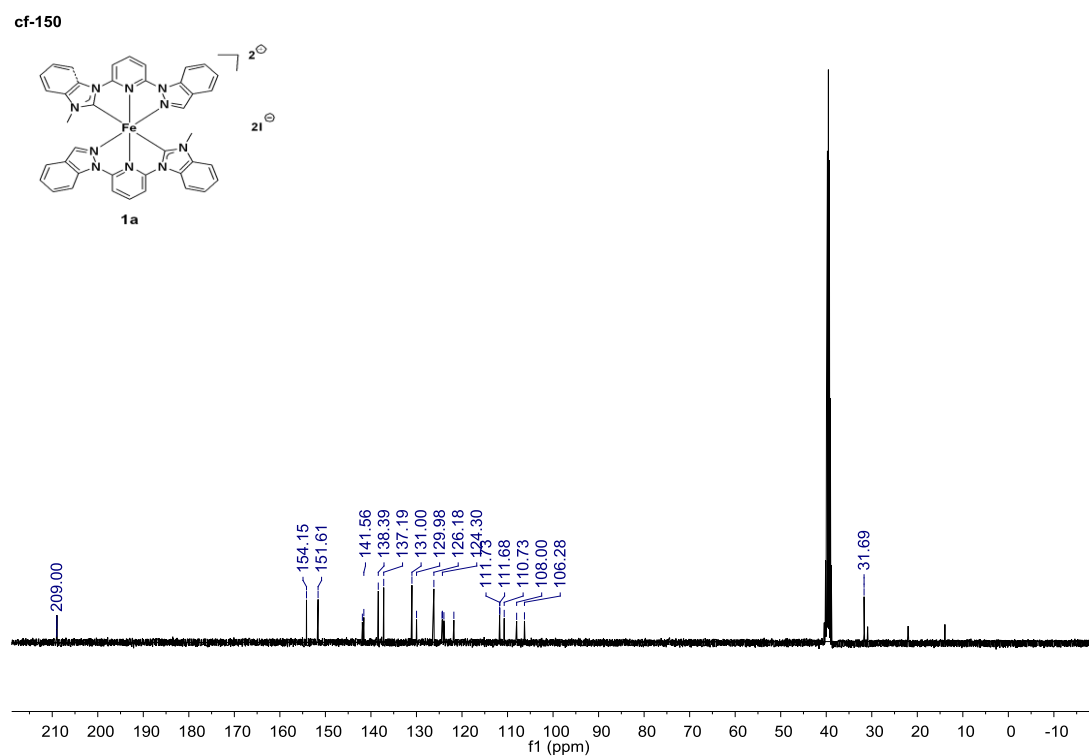


Figure S4. ¹³C NMR spectra of Fe complex **1a**.

cf-162

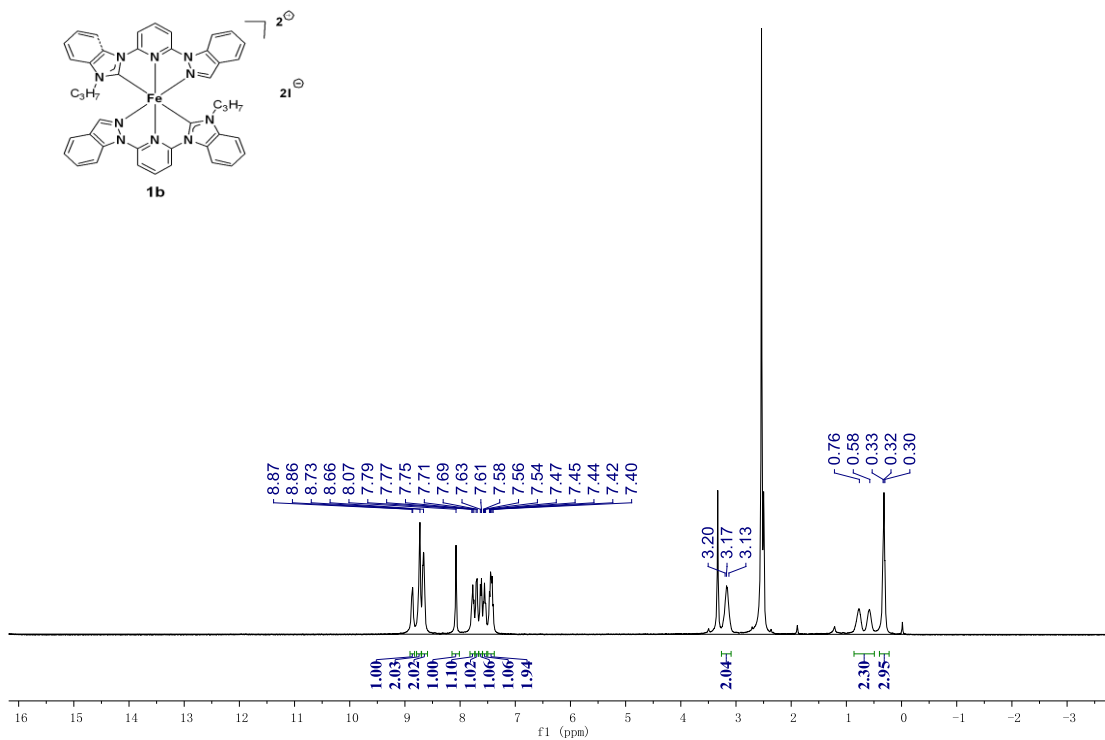


Figure S5. ^1H NMR spectra of Fe complex **1b**.

cf-162

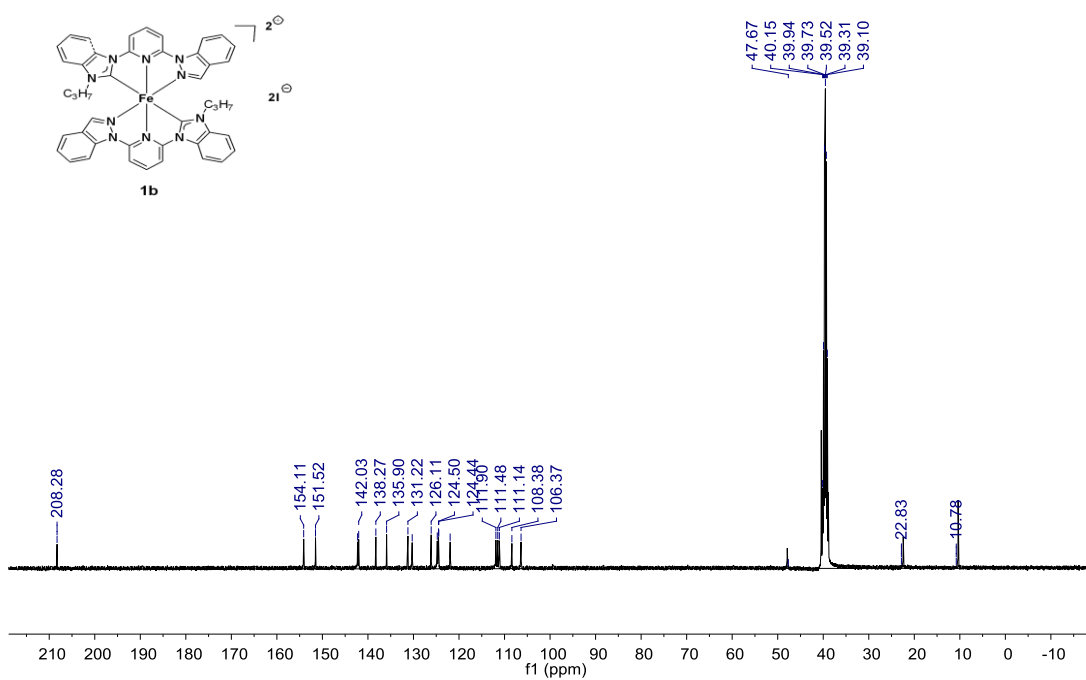


Figure S6. ^{13}C NMR spectra of Fe complex **1b**.

cf-148

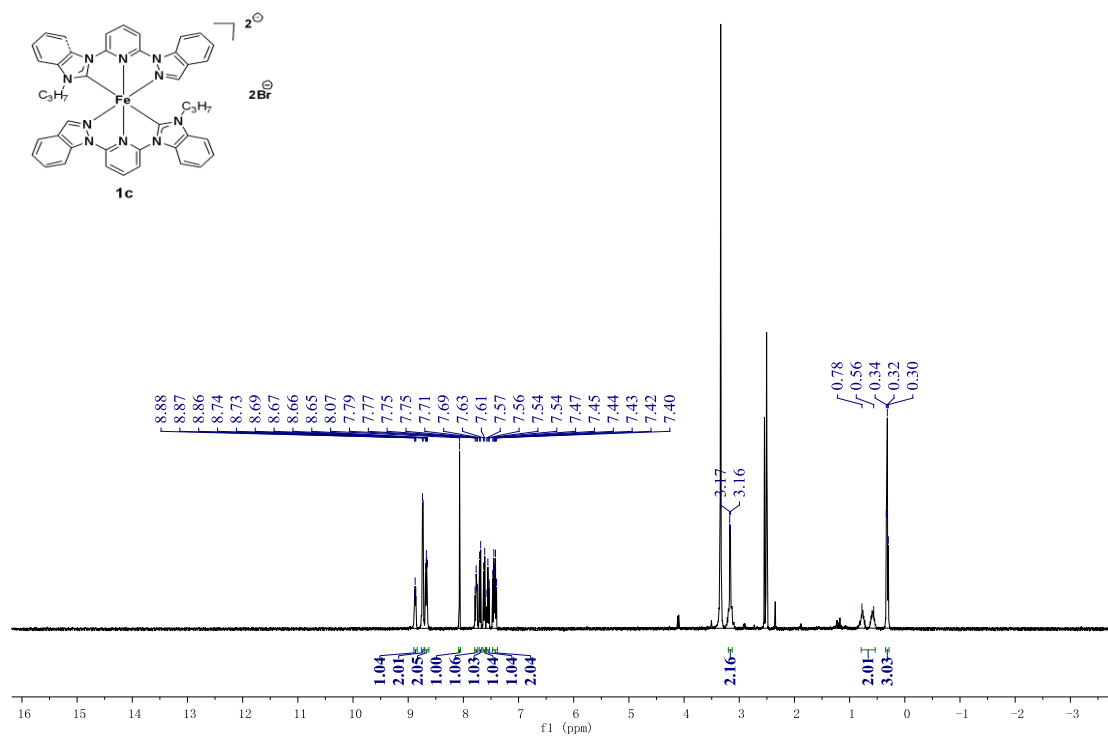


Figure S7. ¹H NMR spectra of Fe complex **1c**.

cf-148

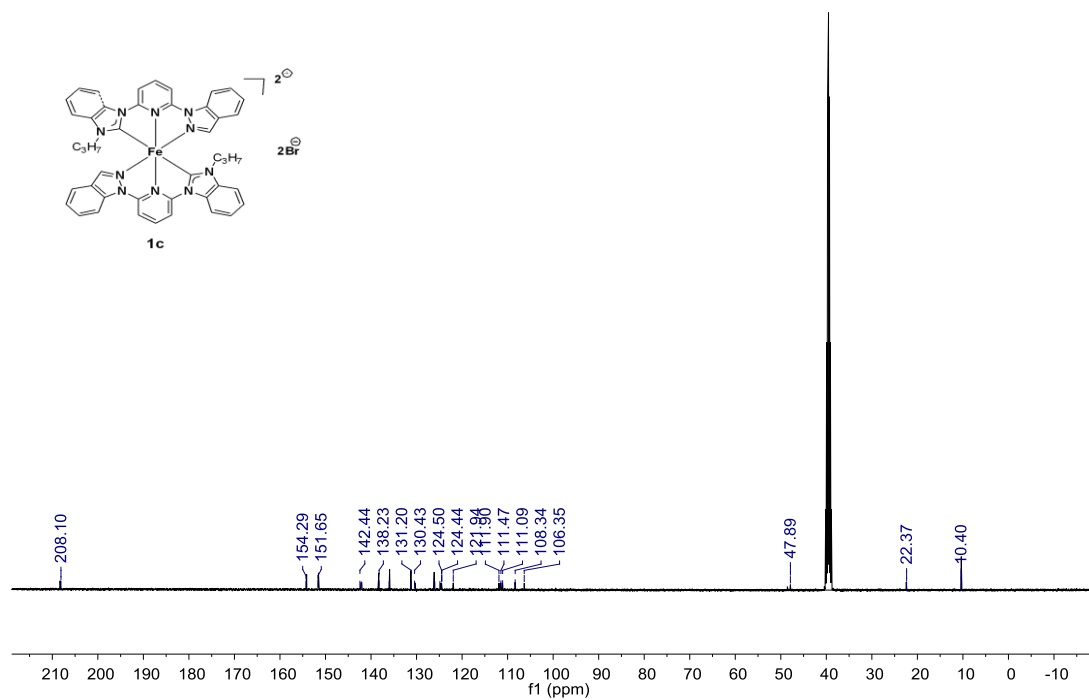


Figure S8. ¹³C NMR spectra of Fe complex **1c**.

1d

2Cl^-

2Cl^-

C_3H_7

C_3H_7

8.95, 8.93, 8.81, 8.79, 8.75, 8.73, 8.71, 8.69, 8.08, 7.77, 7.75, 7.73, 7.69, 7.67, 7.64, 7.62, 7.55, 7.54, 7.52, 7.45, 7.43, 7.42, 7.41, 7.40, 7.38

0.82, 0.76, 0.71, 0.61, 0.57, 0.52, 0.32, 0.30, 0.28

3.23, 3.16, 3.11

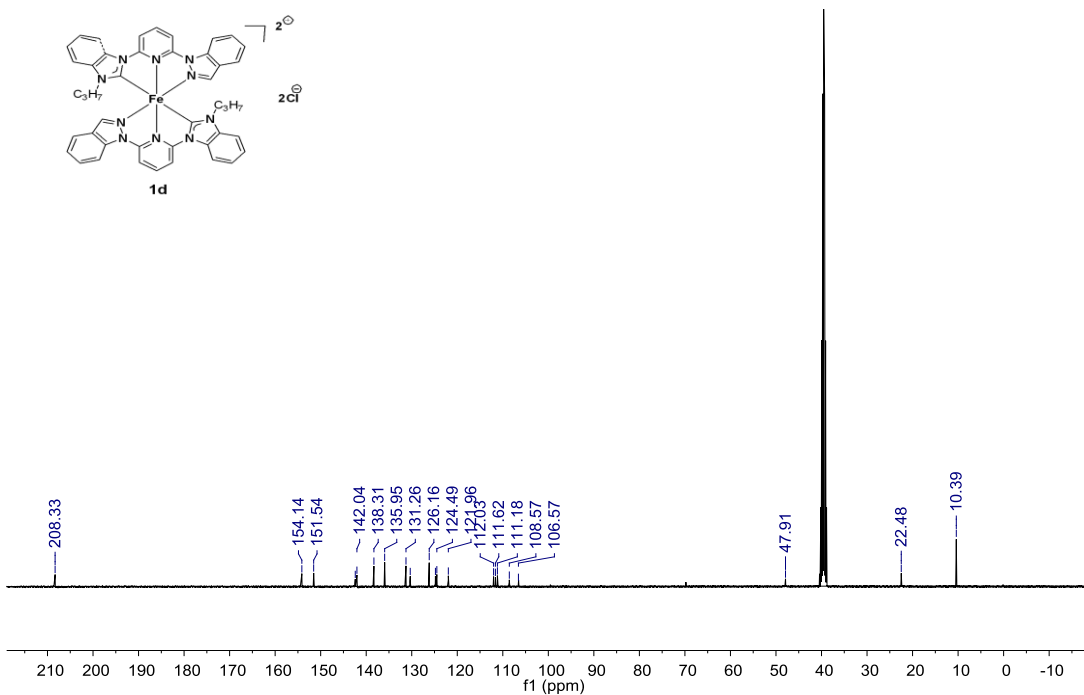
2.31

1.09, 1.12, 3.00, 1.11, 1.23, 1.17, 1.09, 1.09, 2.15

1.38, 1.22, 3.26

f1 (ppm)

cf-161



S7

cf-167

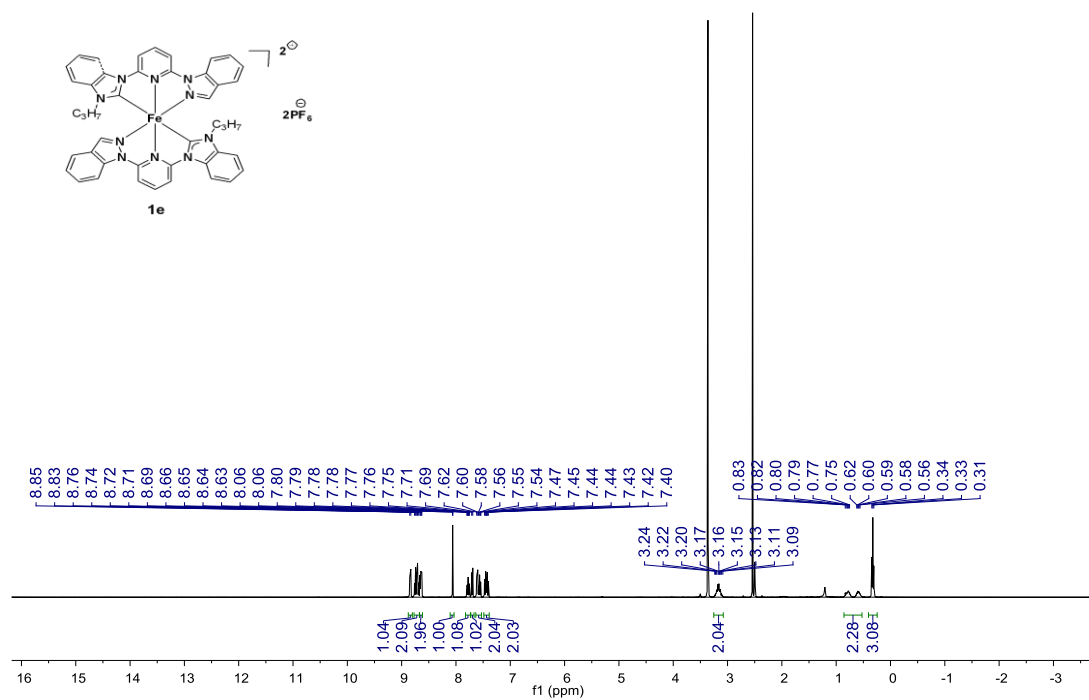


Figure S11. ^1H NMR spectra of Fe complex **1e**.

cf-167

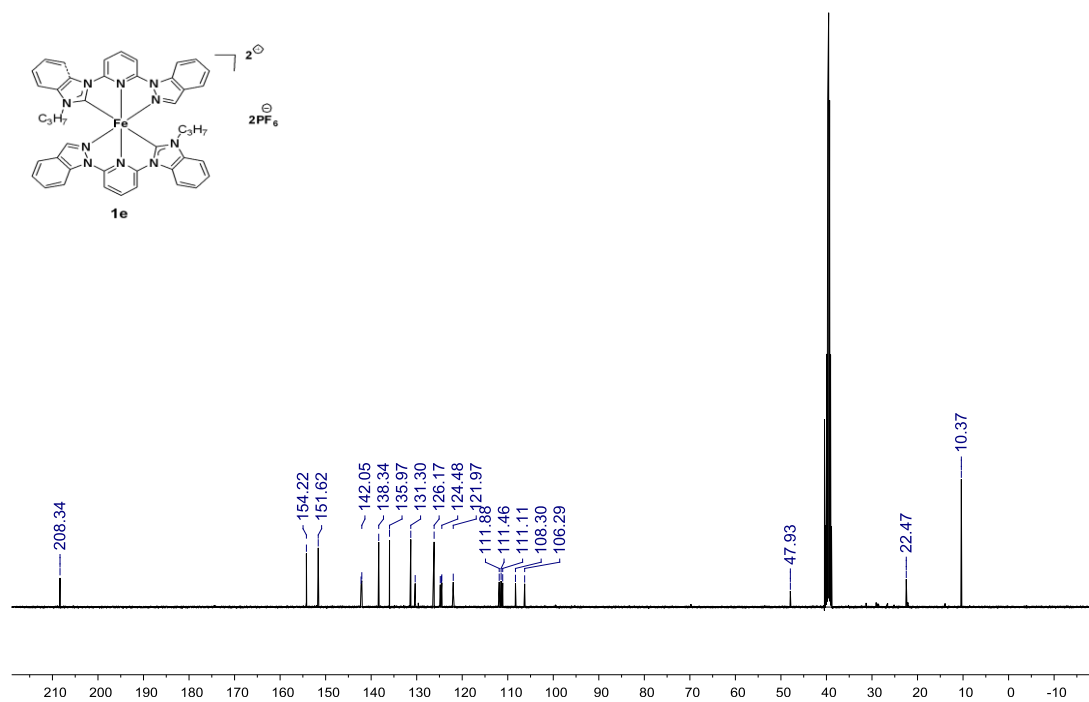


Figure S12. ^{13}C NMR spectra of Fe complex **1e**.

cf-167

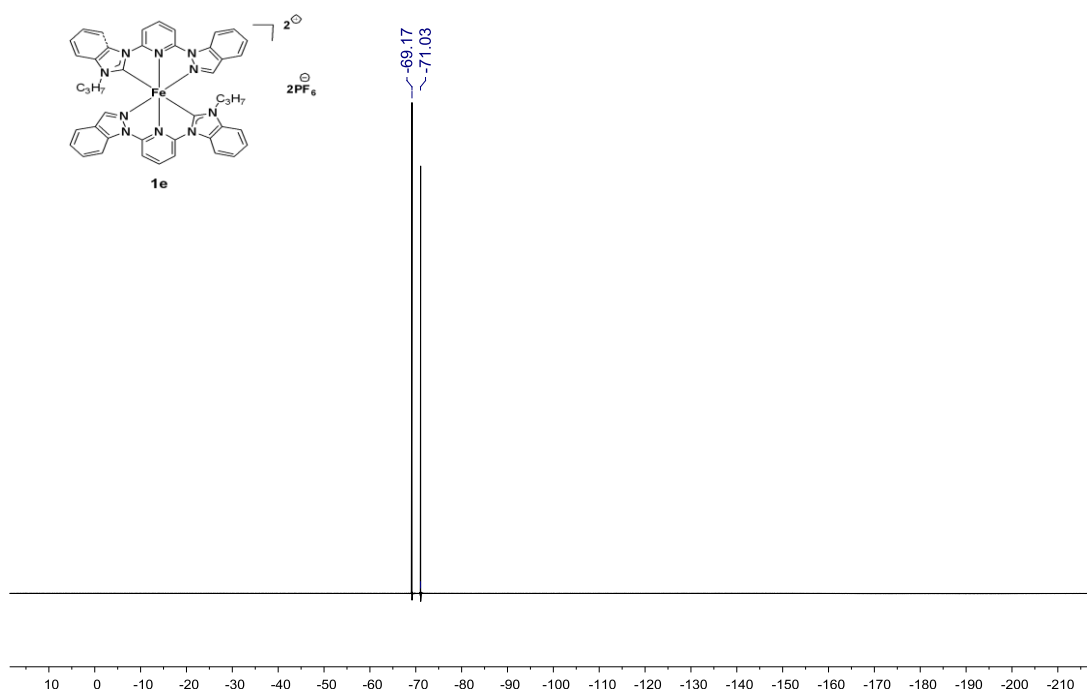


Figure S13. ^{19}F NMR spectra of Fe complex **1e**.

cf-163

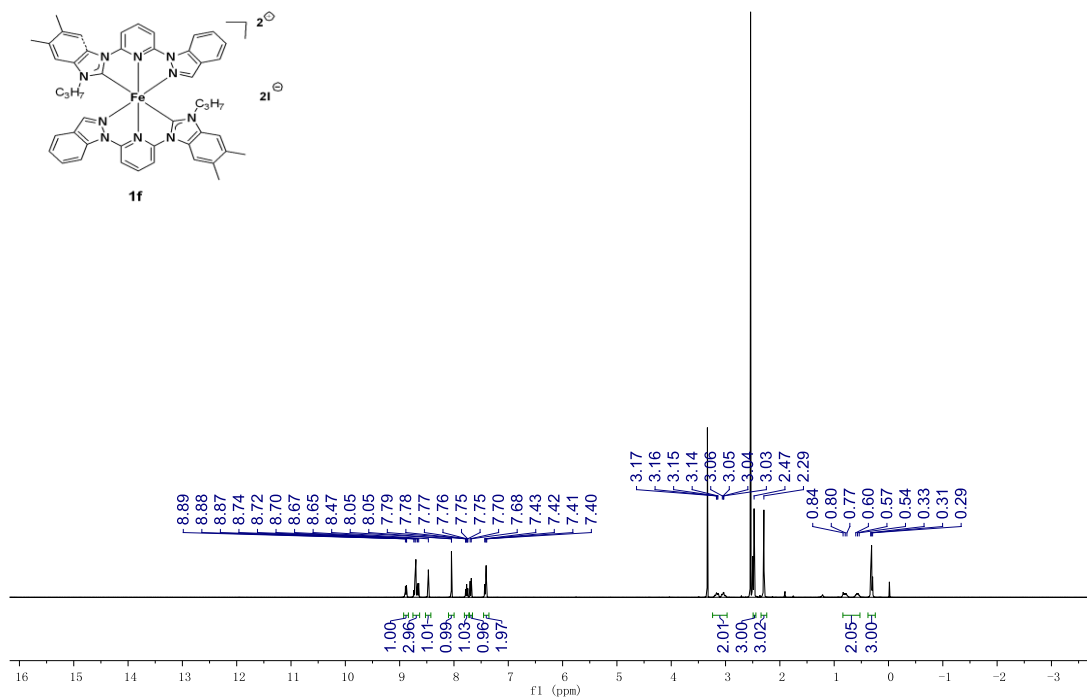


Figure S14. ^1H NMR spectra of Fe complex **1f**.

cf-163

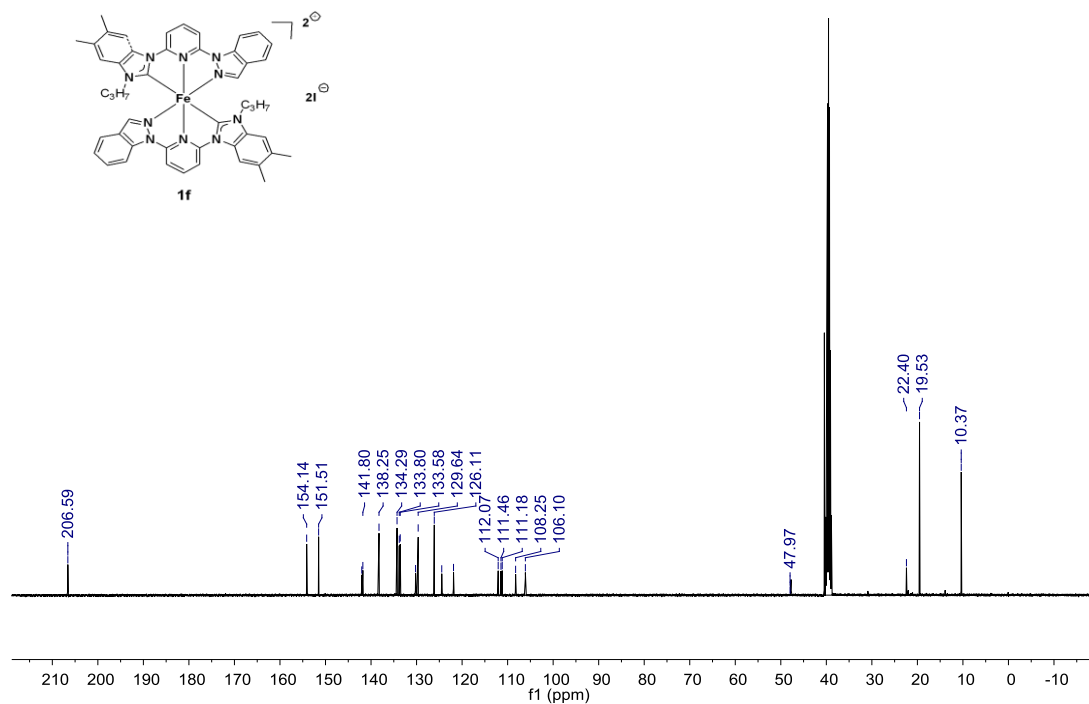


Figure S15. ^{13}C NMR spectra of Fe complex **1f**.

cf-129

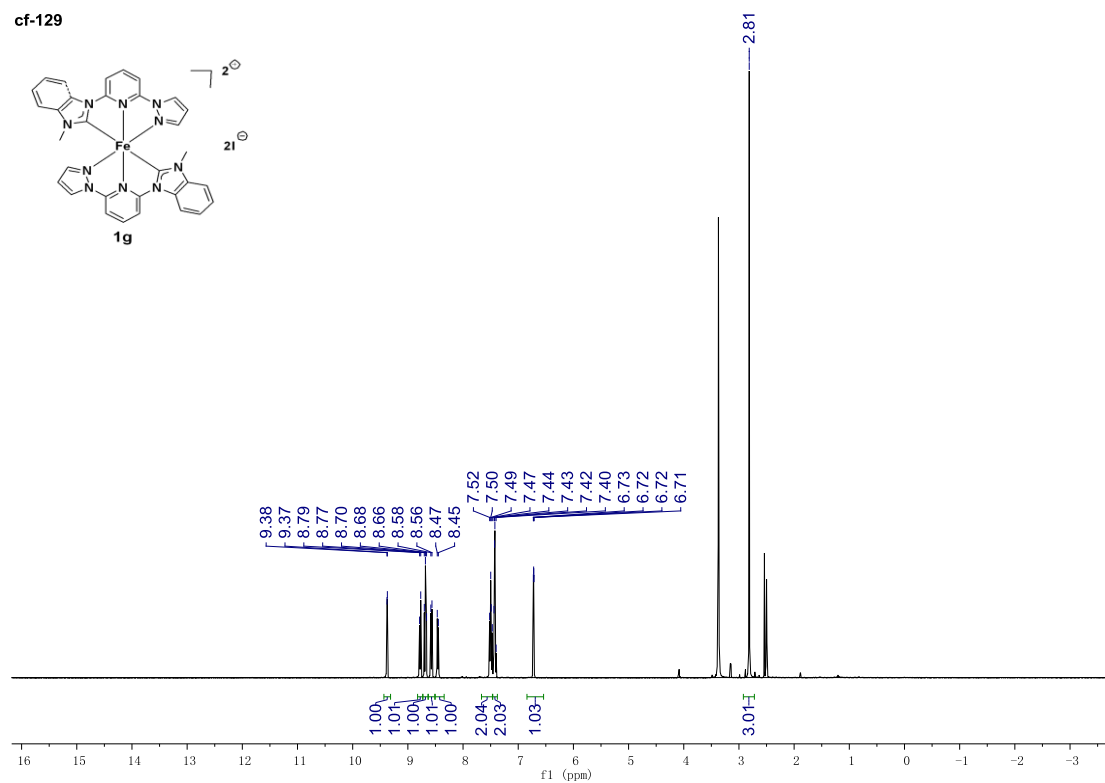


Figure S16. ^1H NMR spectra of Fe complex **1g**.

cf-129/2

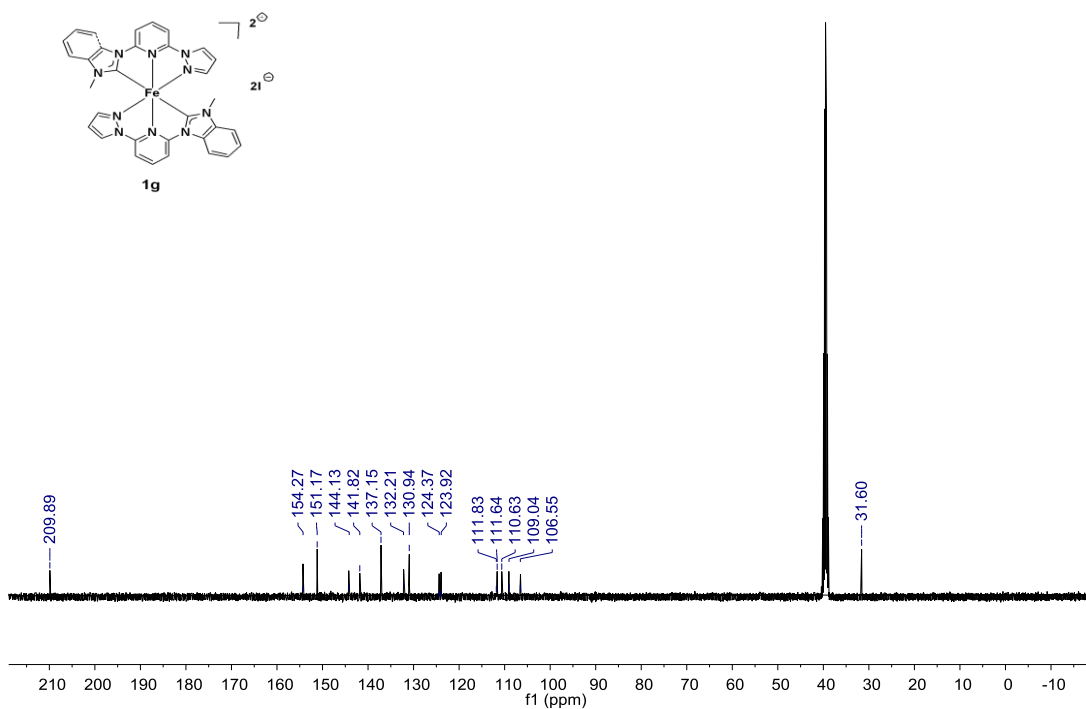


Figure S17. ^{13}C NMR spectra of Fe complex **1g**.

cf-169

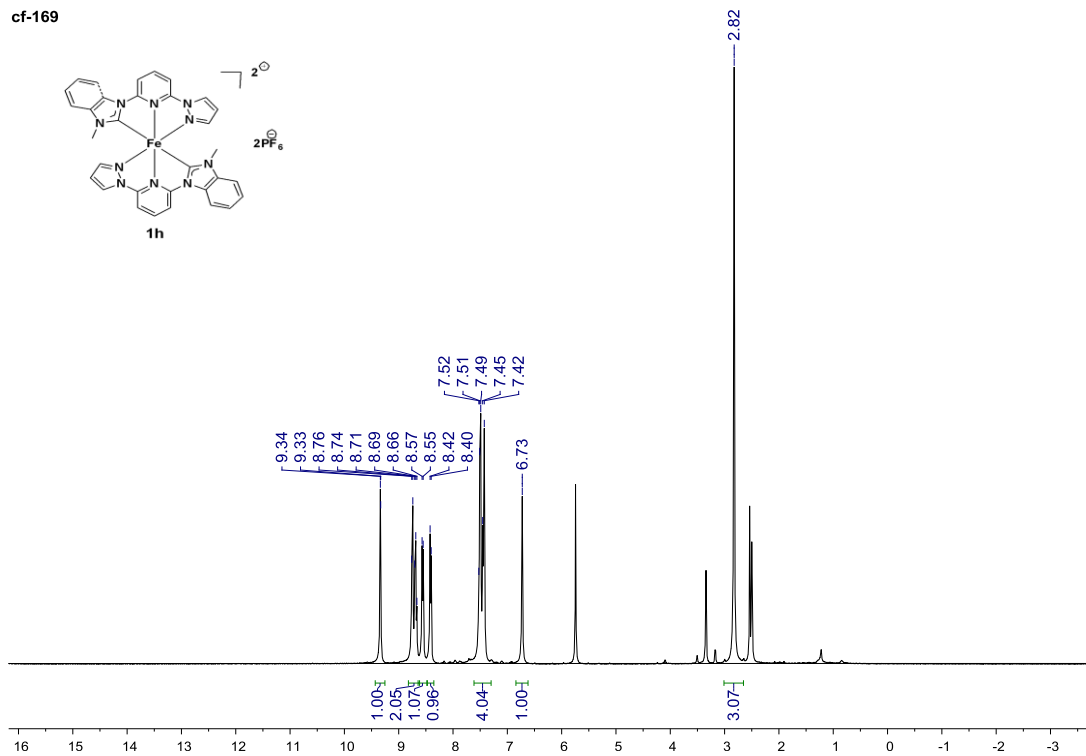
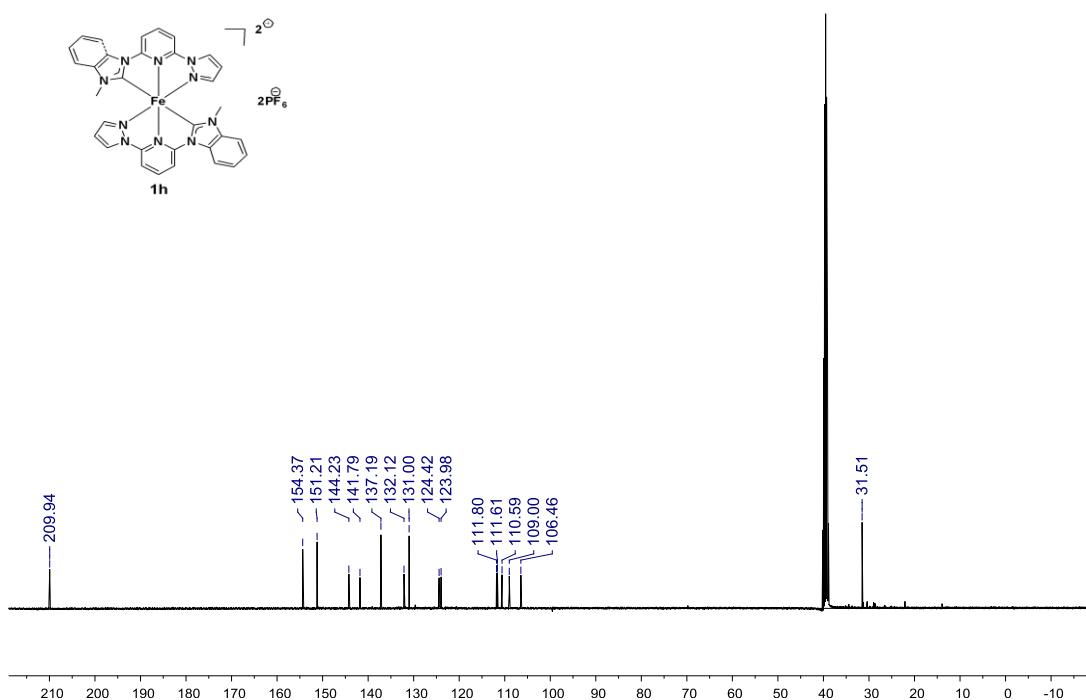
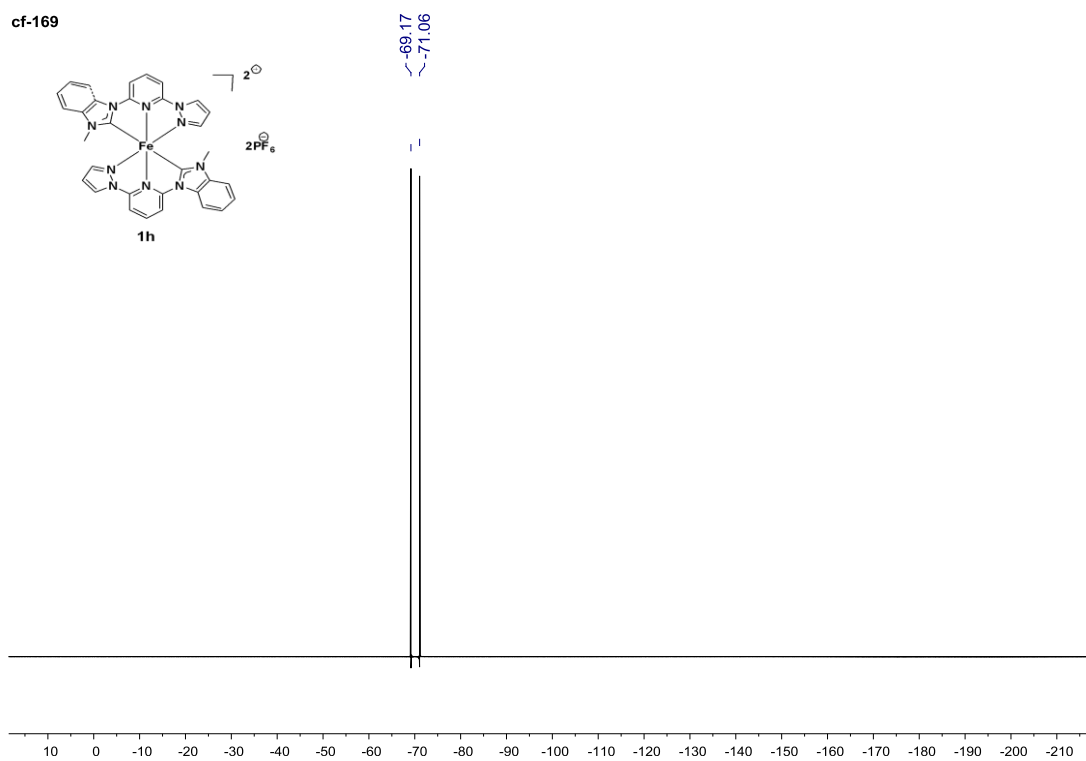


Figure S18. ^1H NMR spectra of Fe complex **1h**.

cf-169



cf-169



cf-125/1

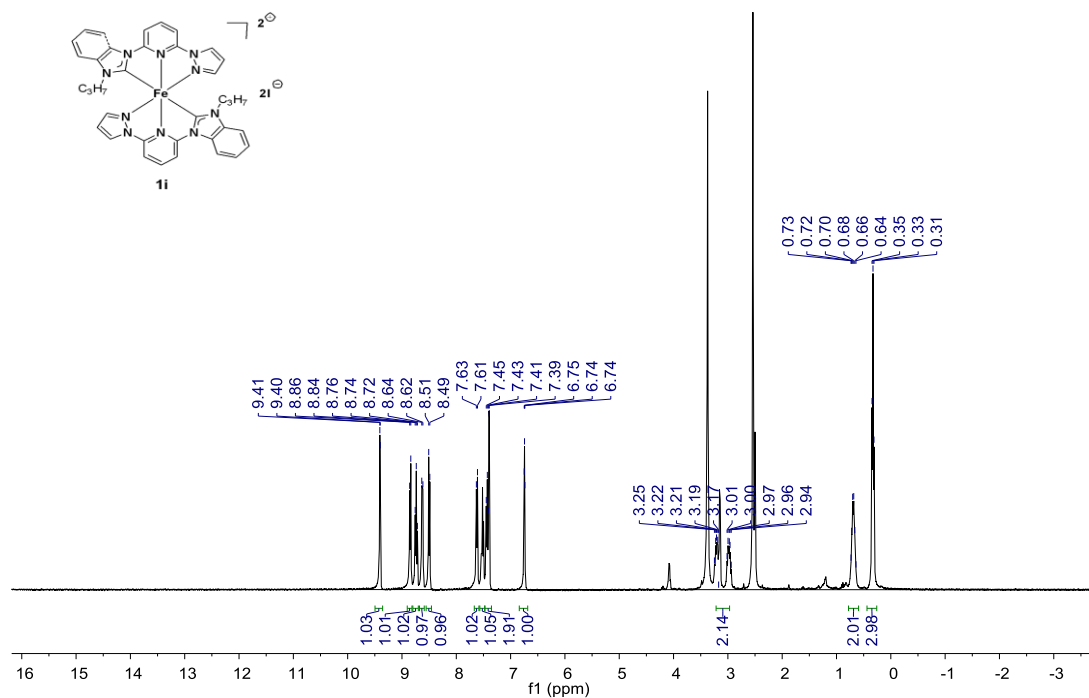


Figure S21. ¹H NMR spectra of Fe complex **1i**.

cf-145/2

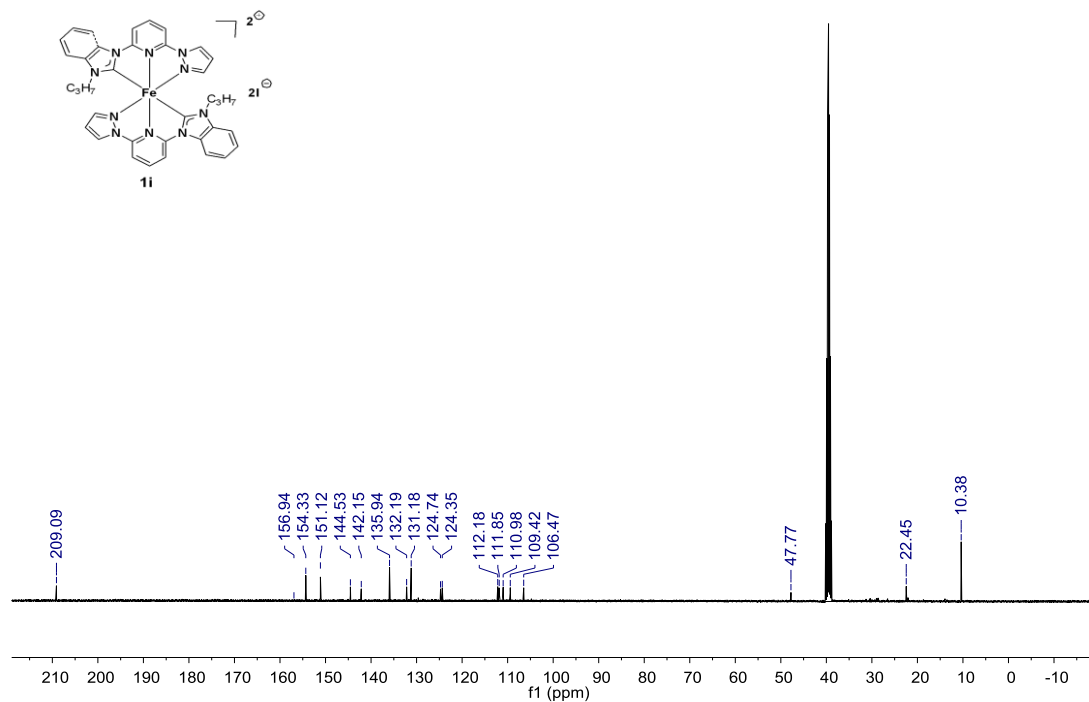


Figure S22. ¹³C NMR spectra of Fe complex **1i**.

cf-155

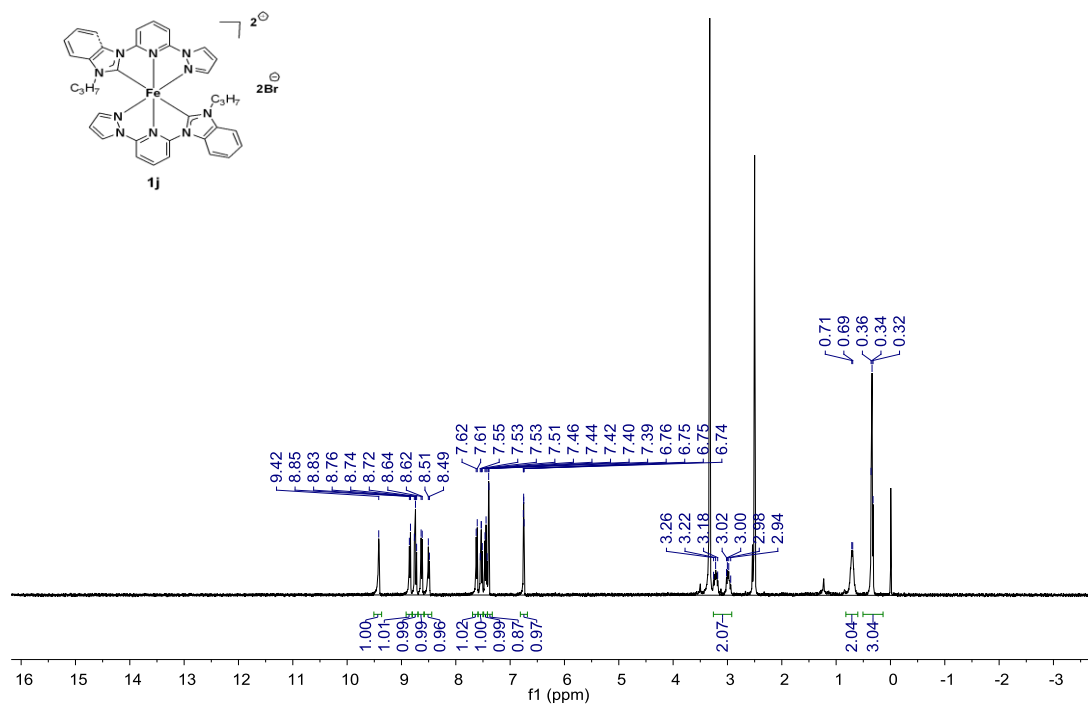


Figure S23. ¹H NMR spectra of Fe complex **1j**.

cf-155

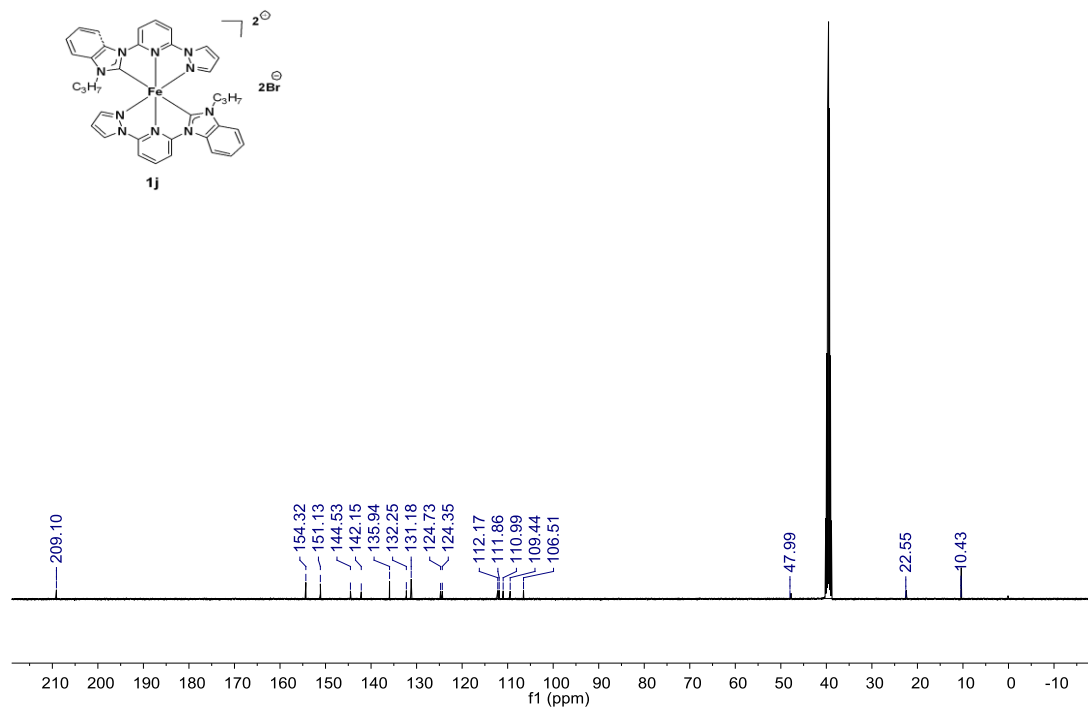


Figure S24. ¹³C NMR spectra of Fe complex **1j**.

cf-164

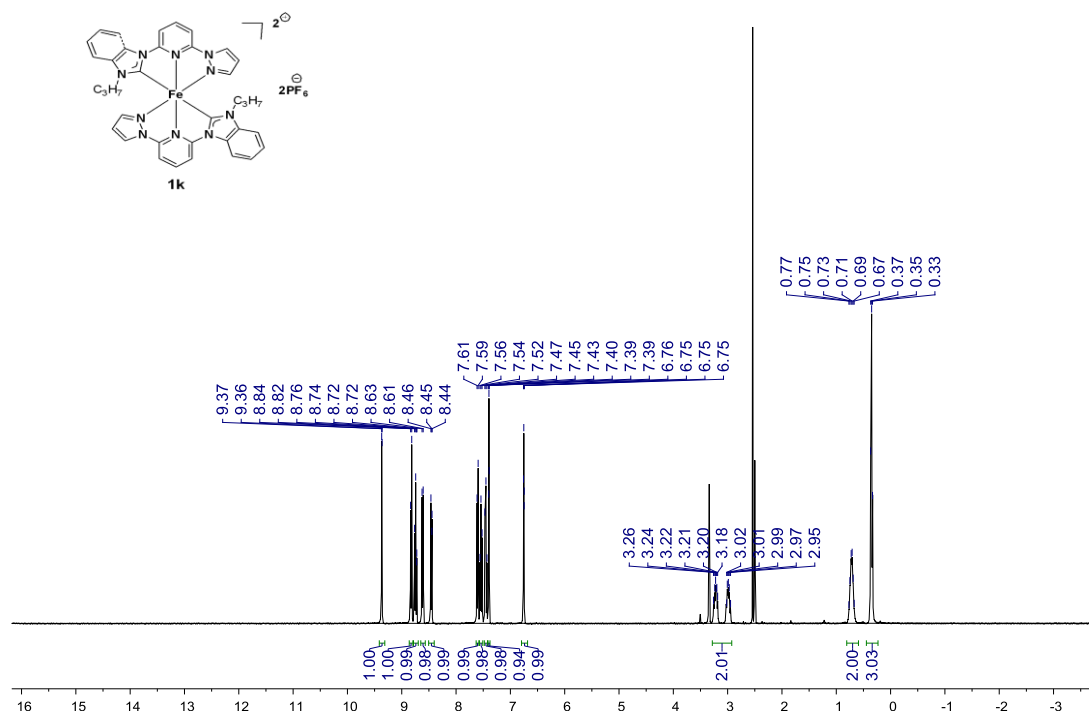


Figure S25. ^1H NMR spectra of Fe complex **1k**.

cf-164

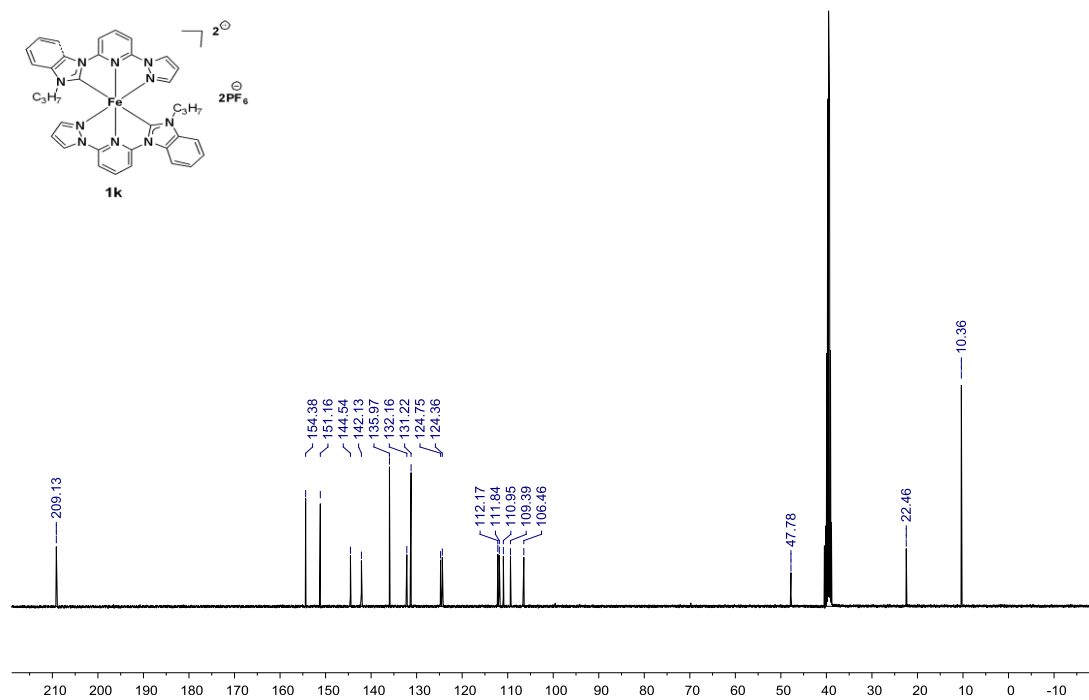


Figure S26. ^{13}C NMR spectra of Fe complex **1k**.

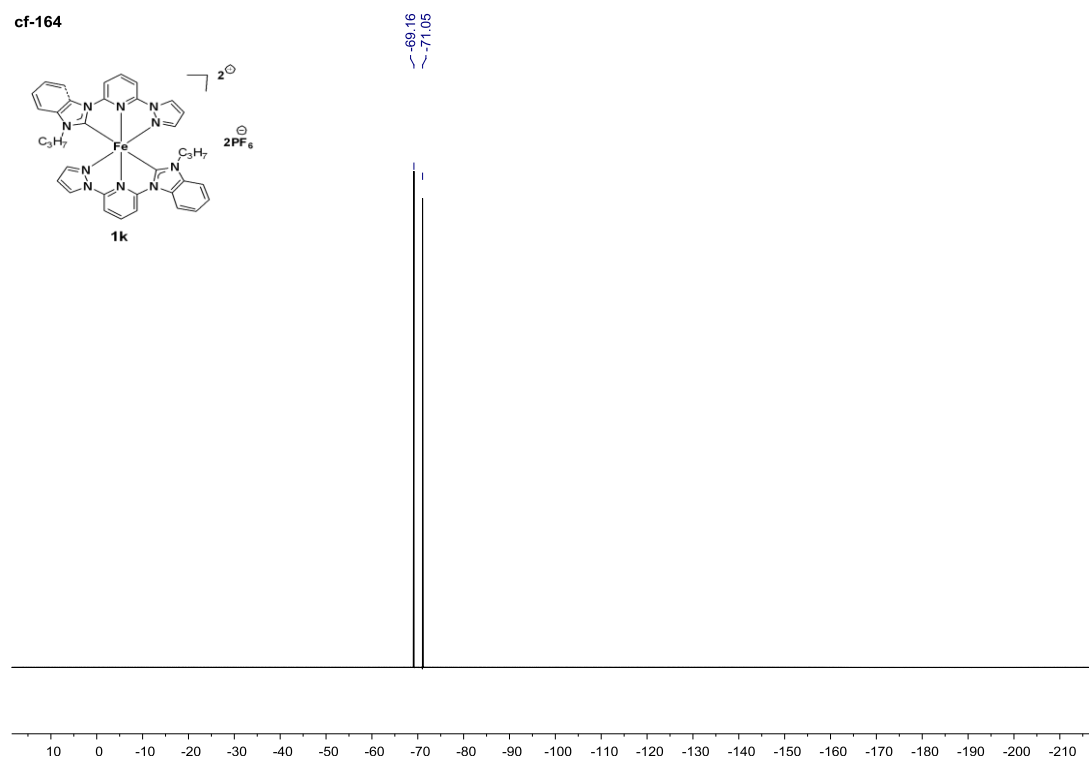


Figure S27. ¹⁹F NMR spectra of Fe complex **1k**.

3. NMR Spectra for the Cycloaddition Products

cf-12

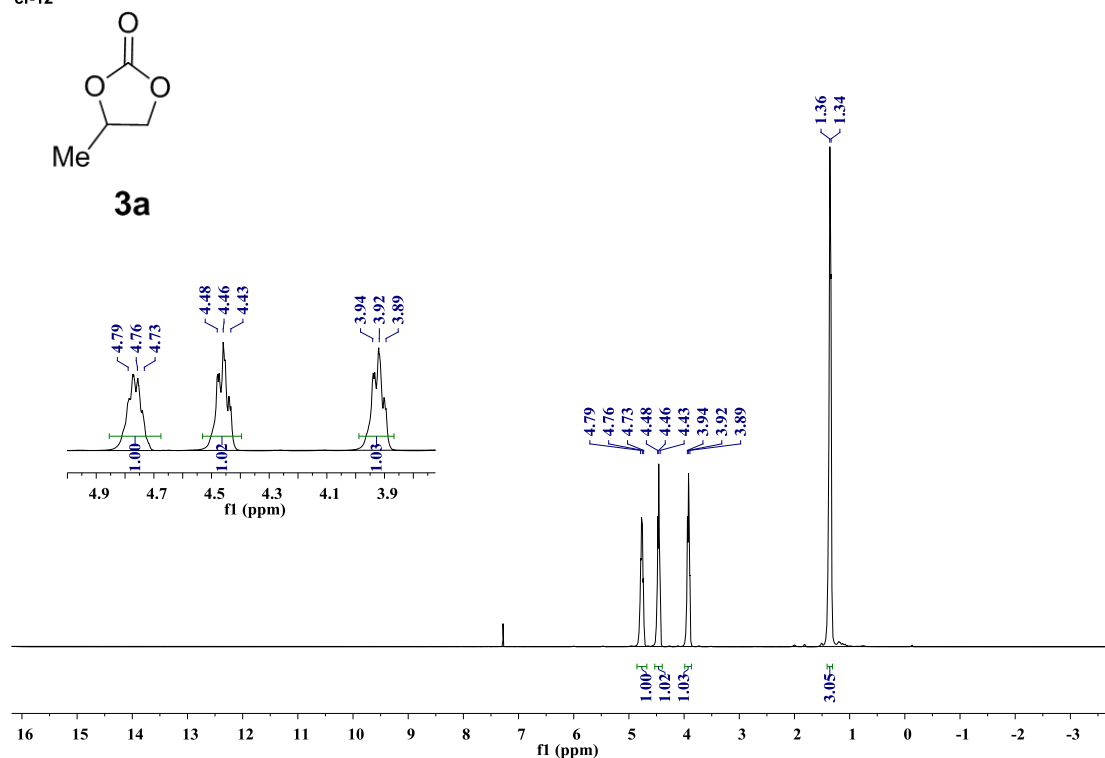


Figure S28. ^1H NMR spectra of cyclic carbonate **3a**.

cf-12

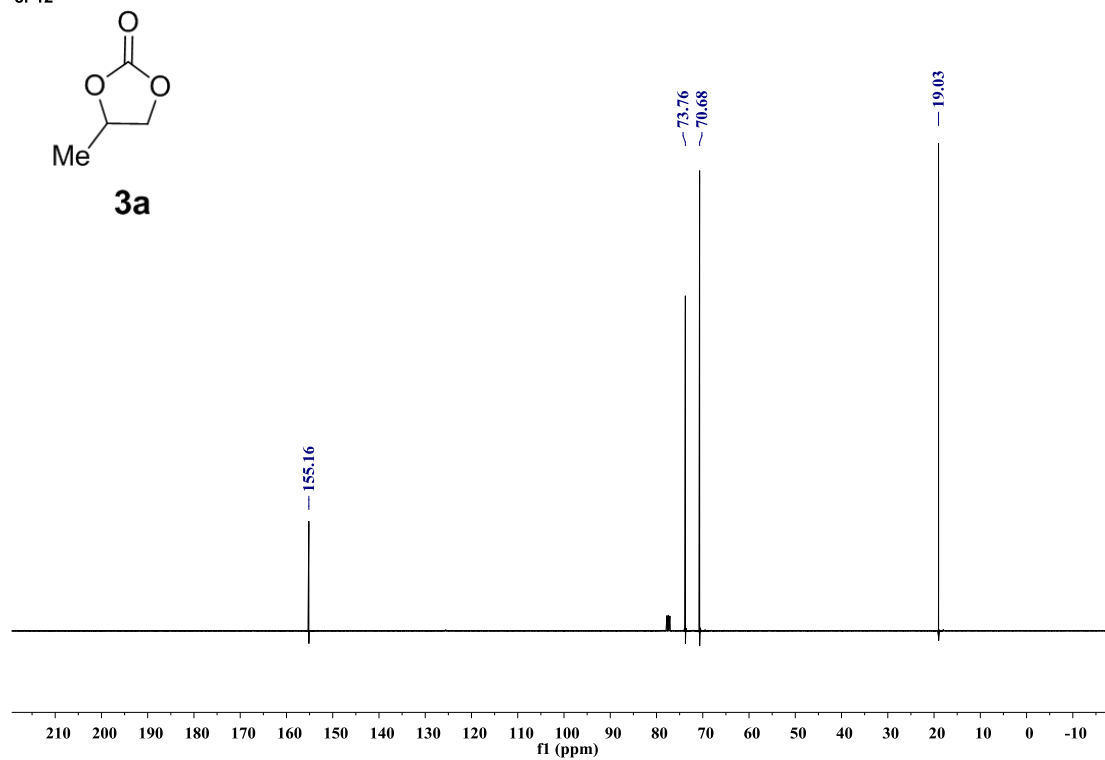
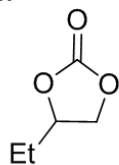
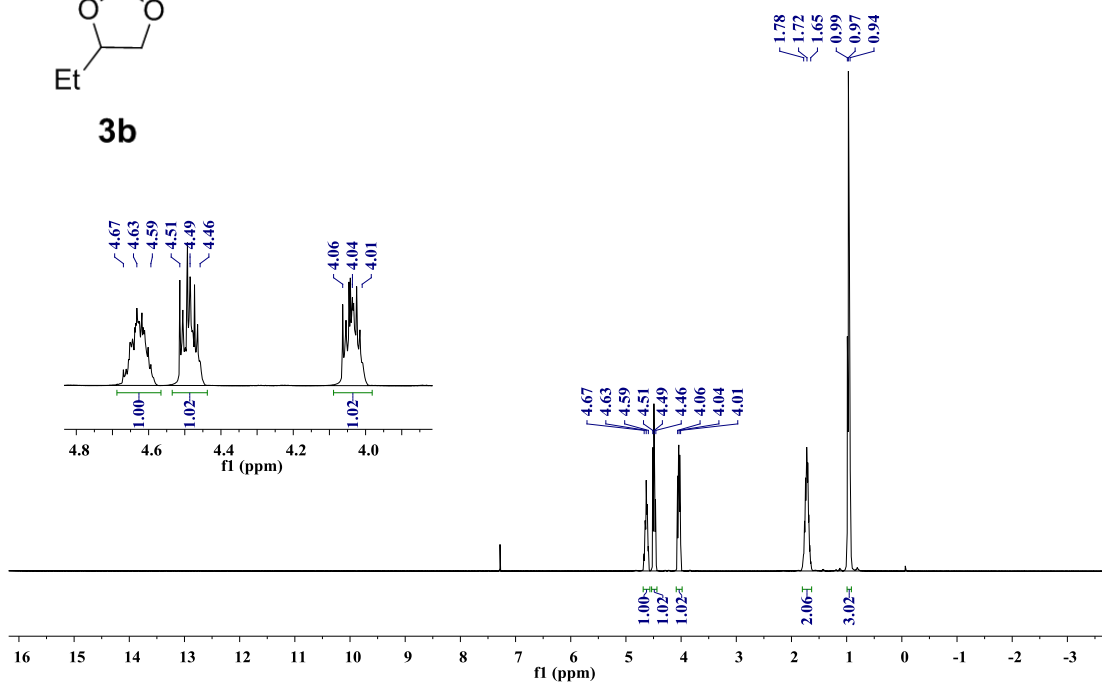
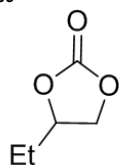
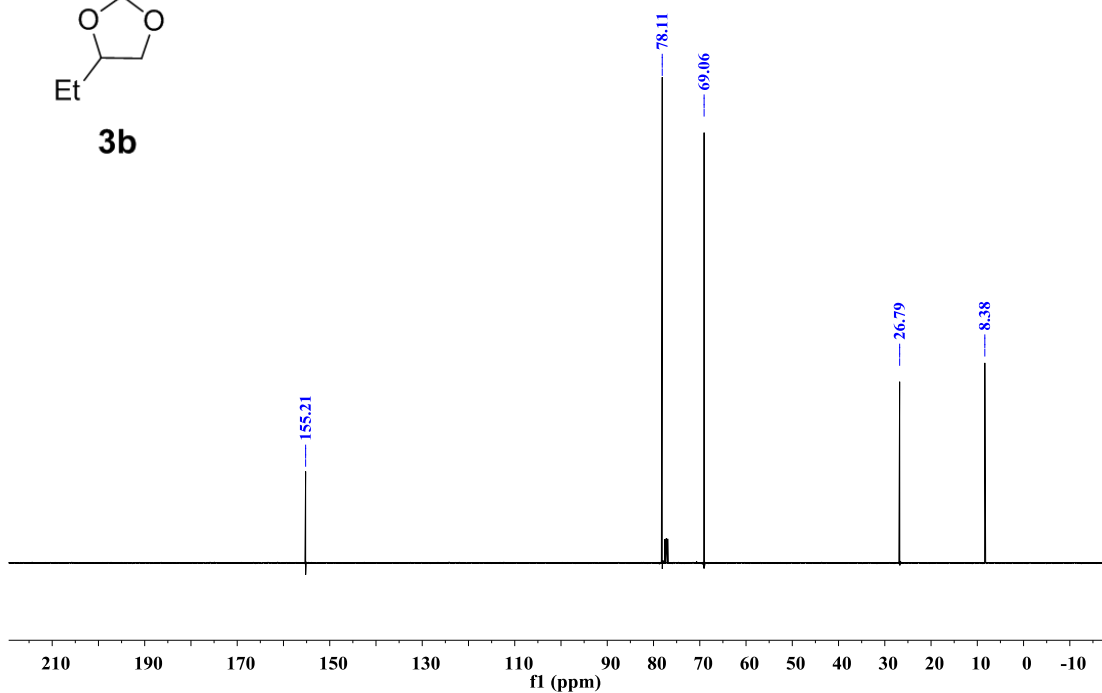


Figure S29. ^{13}C NMR spectra of cyclic carbonate **3a**.

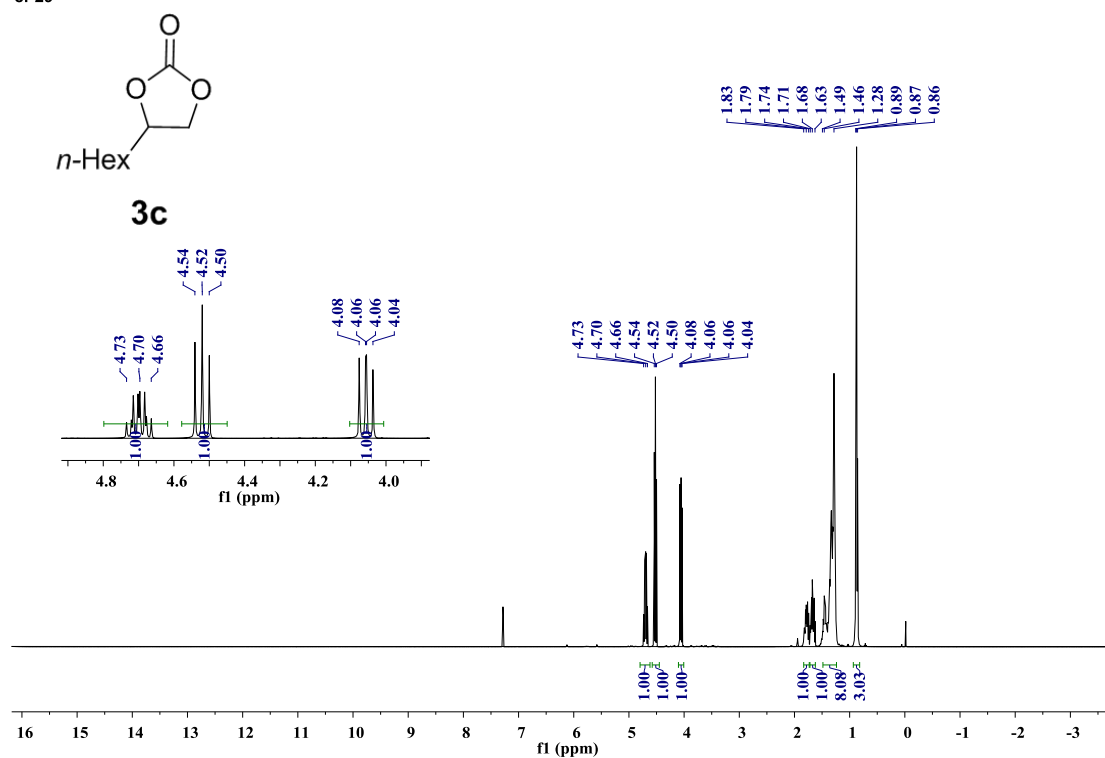
cf-109

**3b****Figure S30.** ¹H NMR spectra of cyclic carbonate **3b**.

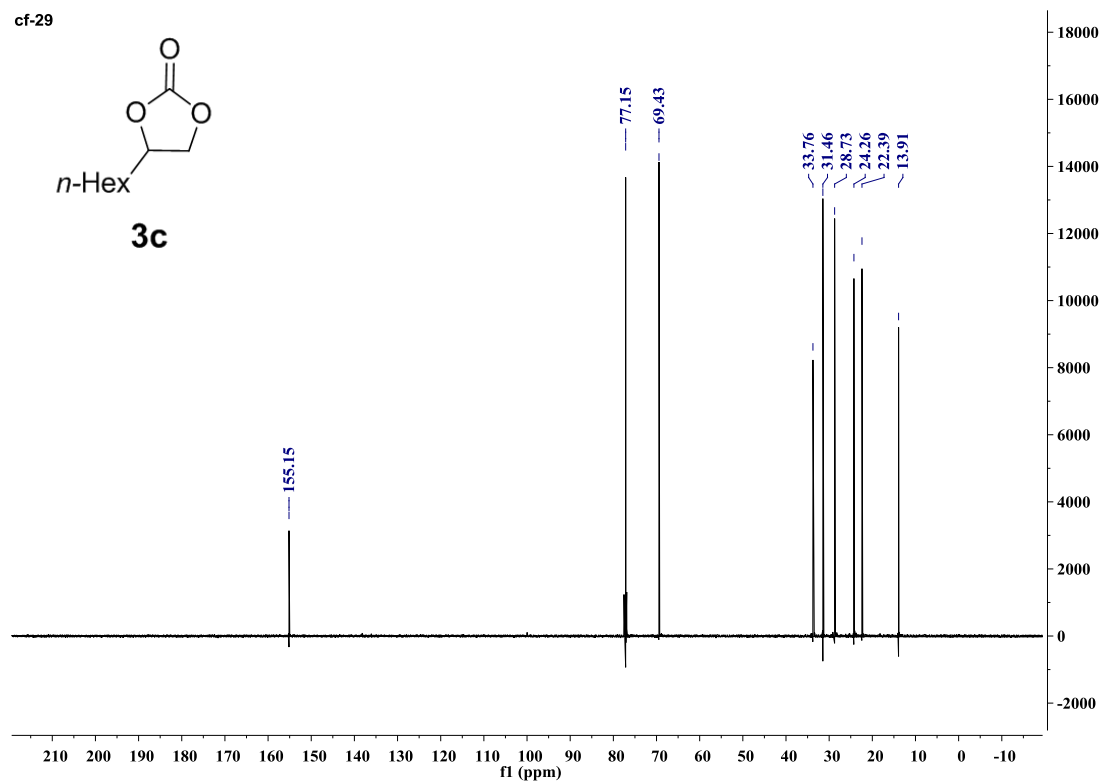
cf-109

**3b****Figure S31.** ¹³C NMR spectra of cyclic carbonate **3b**.

cf-29

Figure S32. ¹H NMR spectra of cyclic carbonate **3c**.

cf-29

Figure S33. ¹³C NMR spectra of cyclic carbonate **3c**.

cf-176

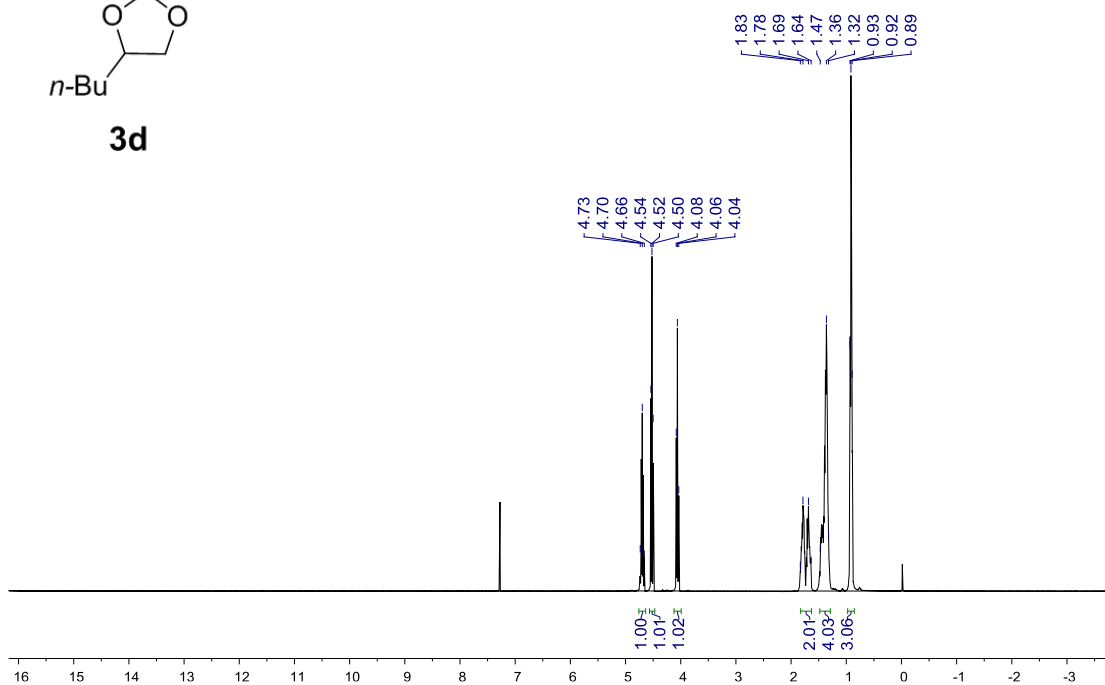
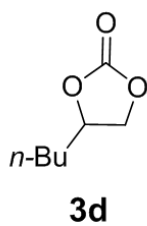


Figure S34. ¹H NMR spectra of cyclic carbonate **3d**.

cf-176

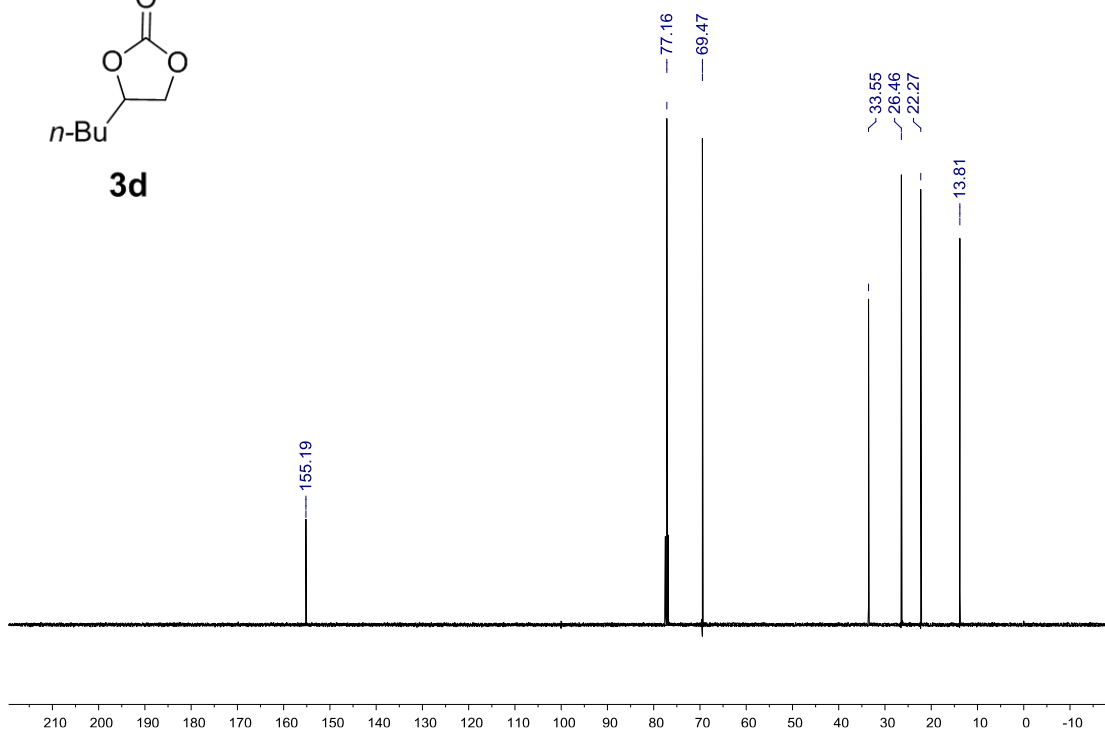
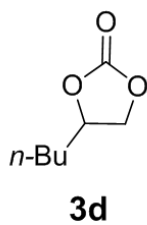


Figure S35. ¹³C NMR spectra of cyclic carbonate **3d**.

cf-27

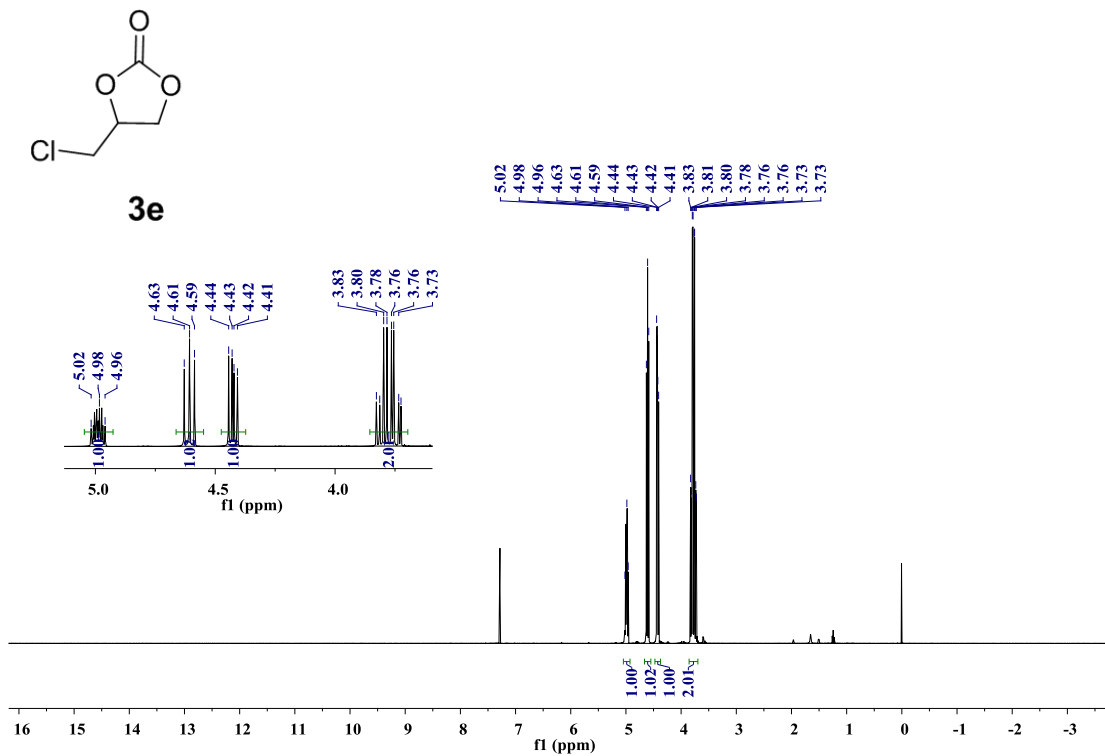


Figure S36. ¹H NMR spectra of cyclic carbonate **3e**.

cf-27

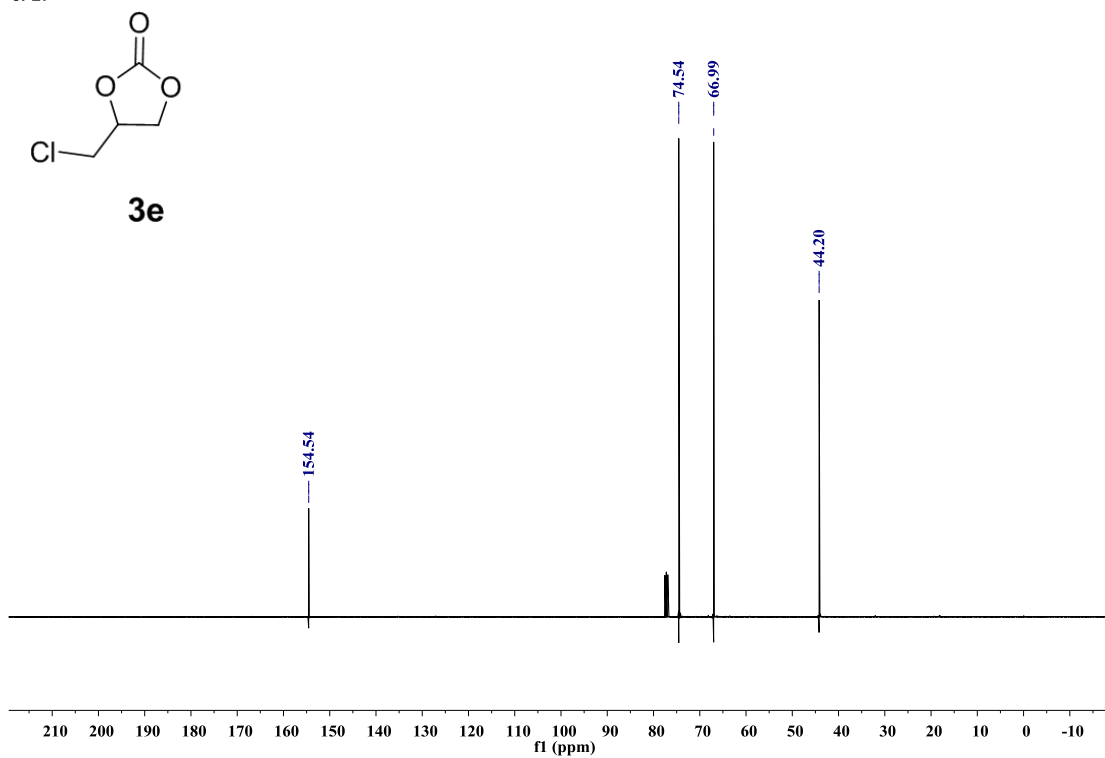


Figure S37. ¹³C NMR spectra of cyclic carbonate **3e**.

cf-68

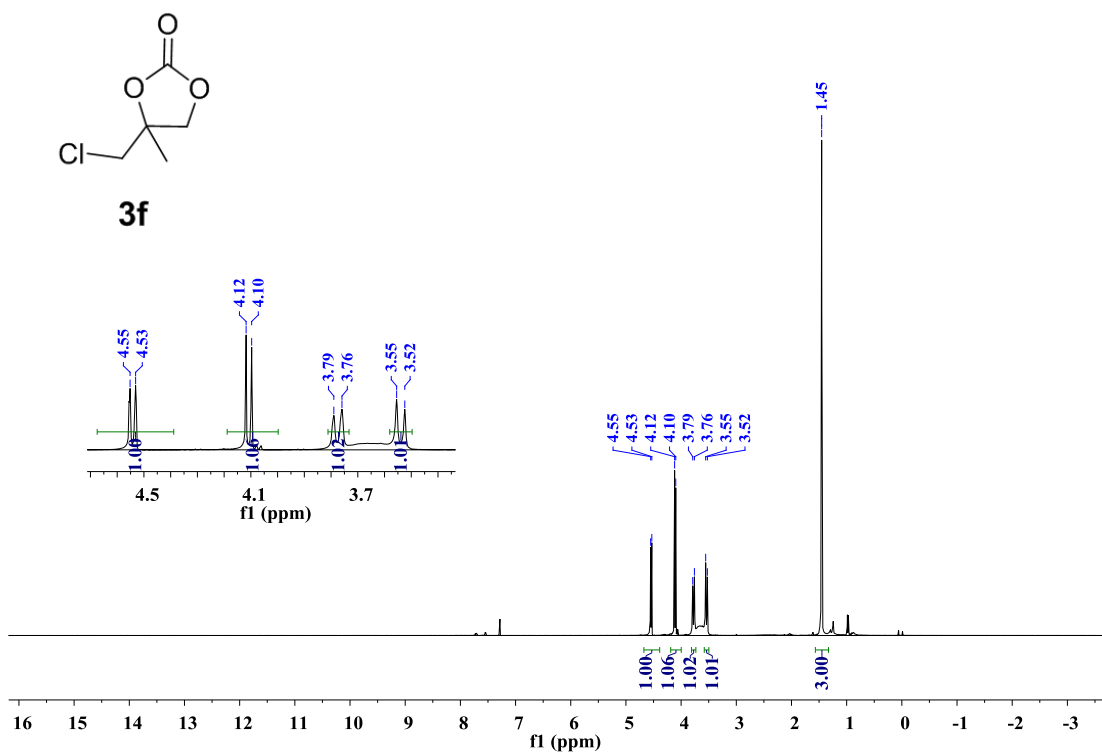


Figure S38. ¹H NMR spectra of cyclic carbonate **3f**.

cf-68

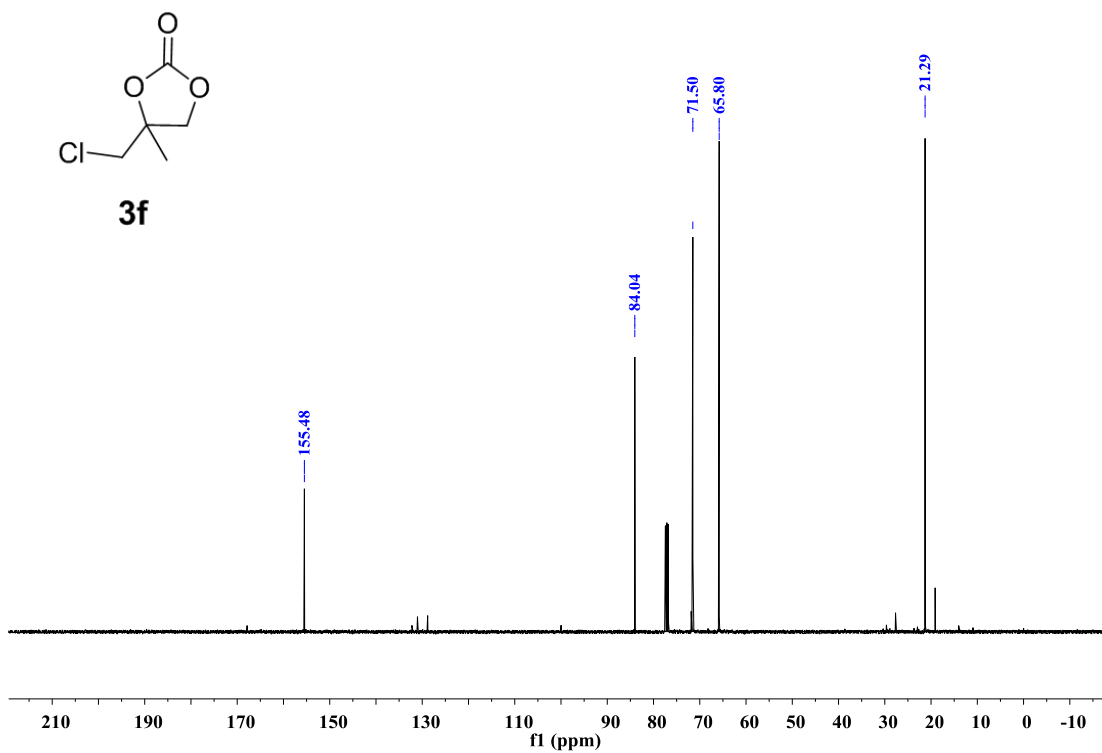


Figure S39. ¹³C NMR spectra of cyclic carbonate **3f**.

cf-108

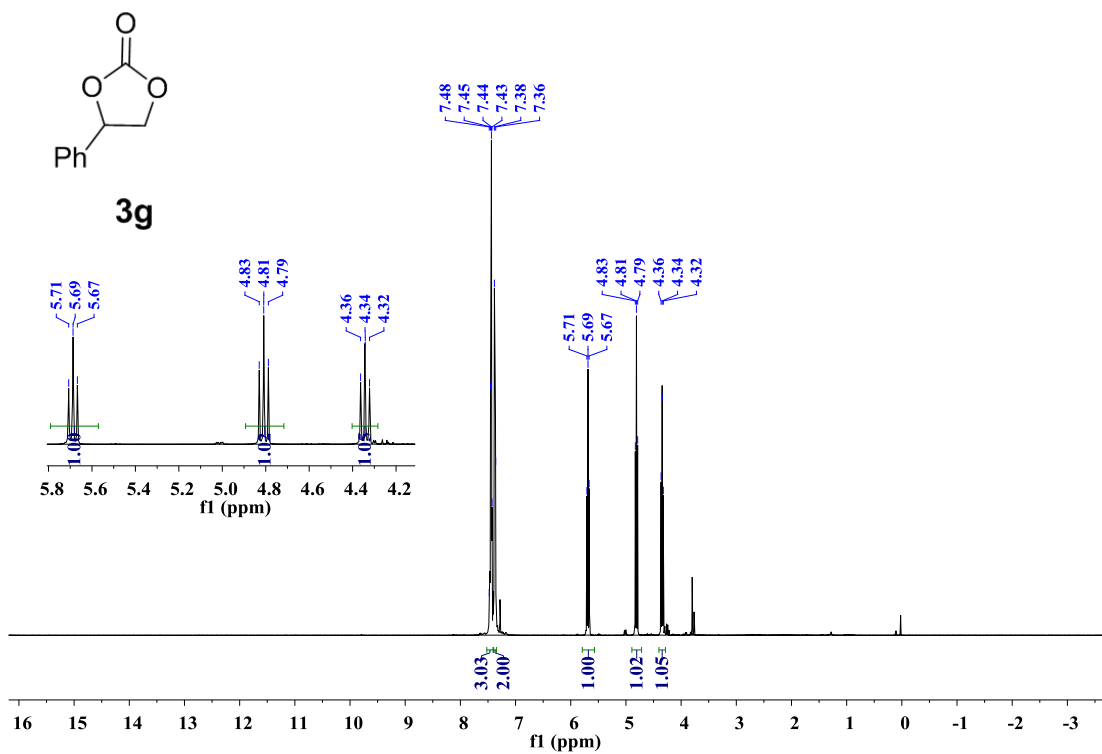


Figure S40. ¹H NMR spectra of cyclic carbonate **3g**.

cf-108

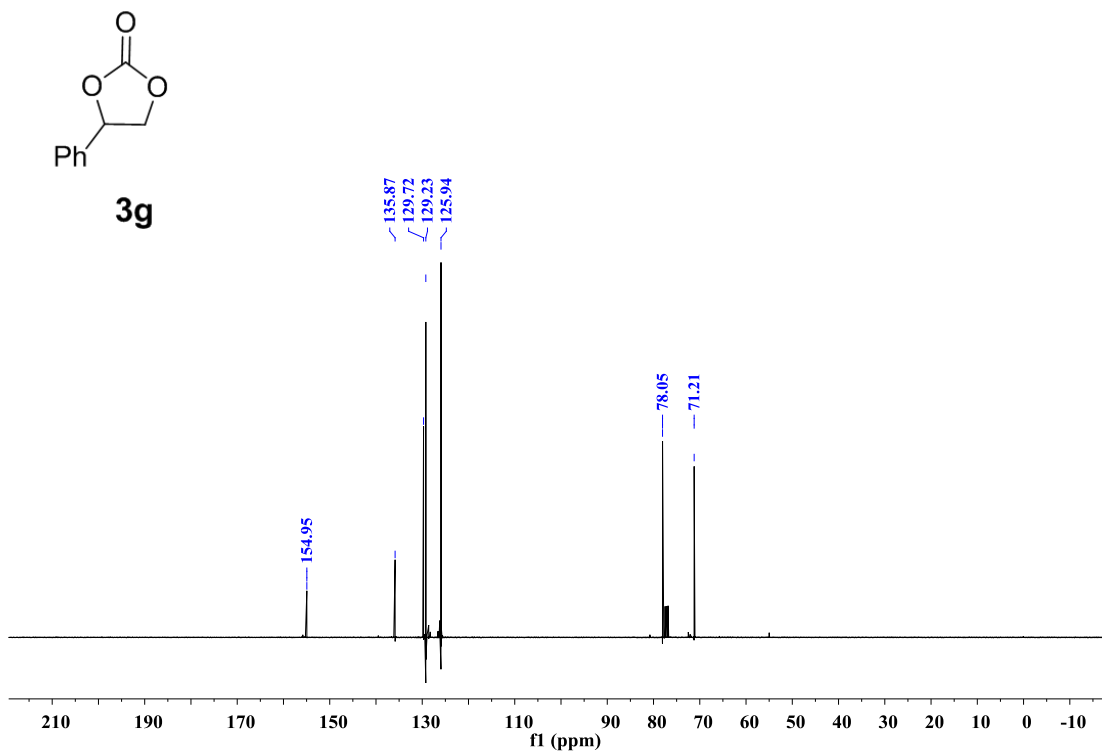
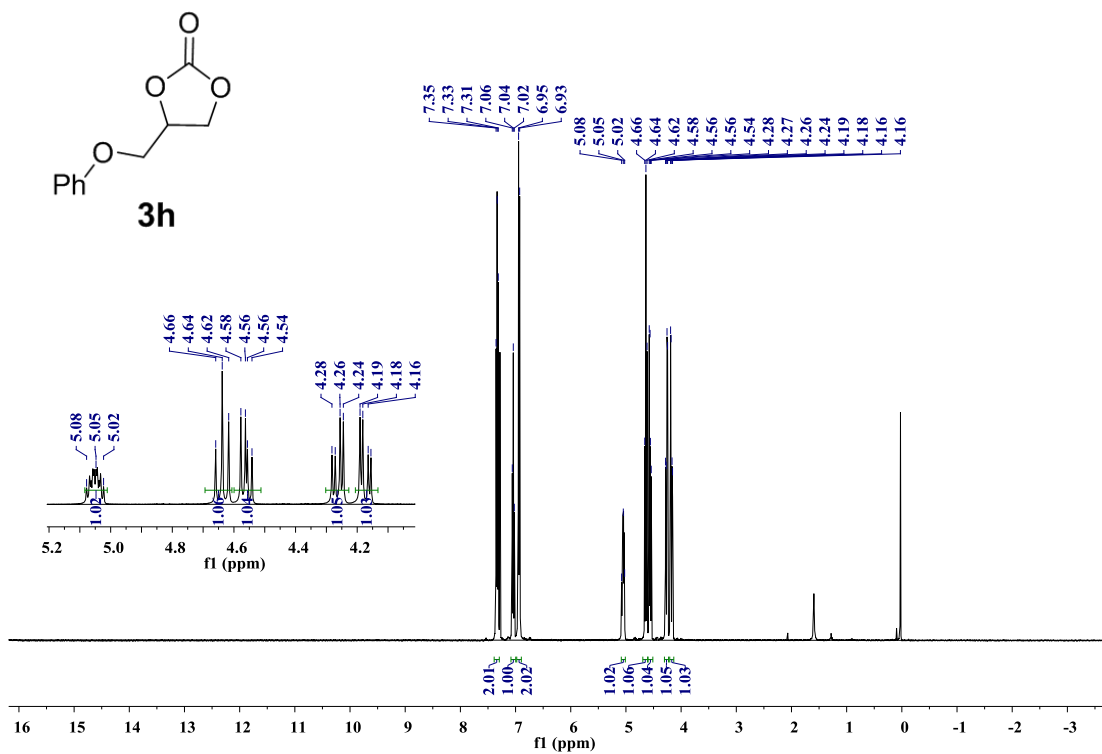
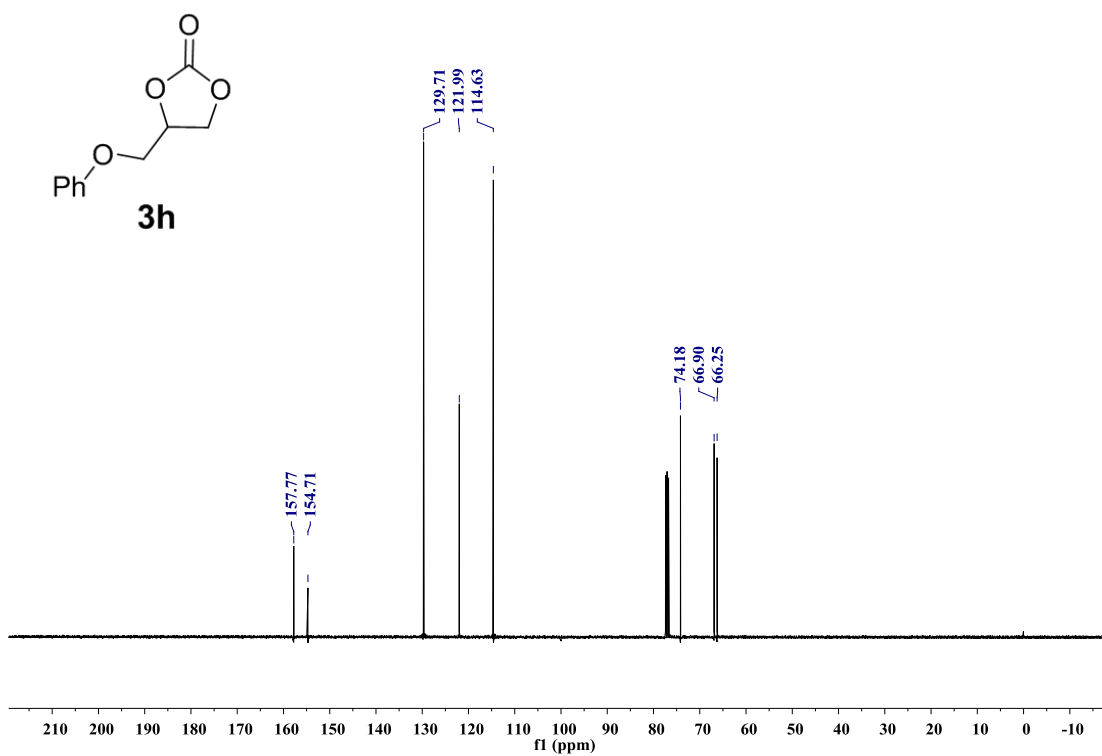


Figure S41. ¹³C NMR spectra of cyclic carbonate **3g**.

cf-17

Figure S42. ¹H NMR spectra of cyclic carbonate **3h**.

cf-17

Figure S43. ¹³C NMR spectra of cyclic carbonate **3h**.

cf-99

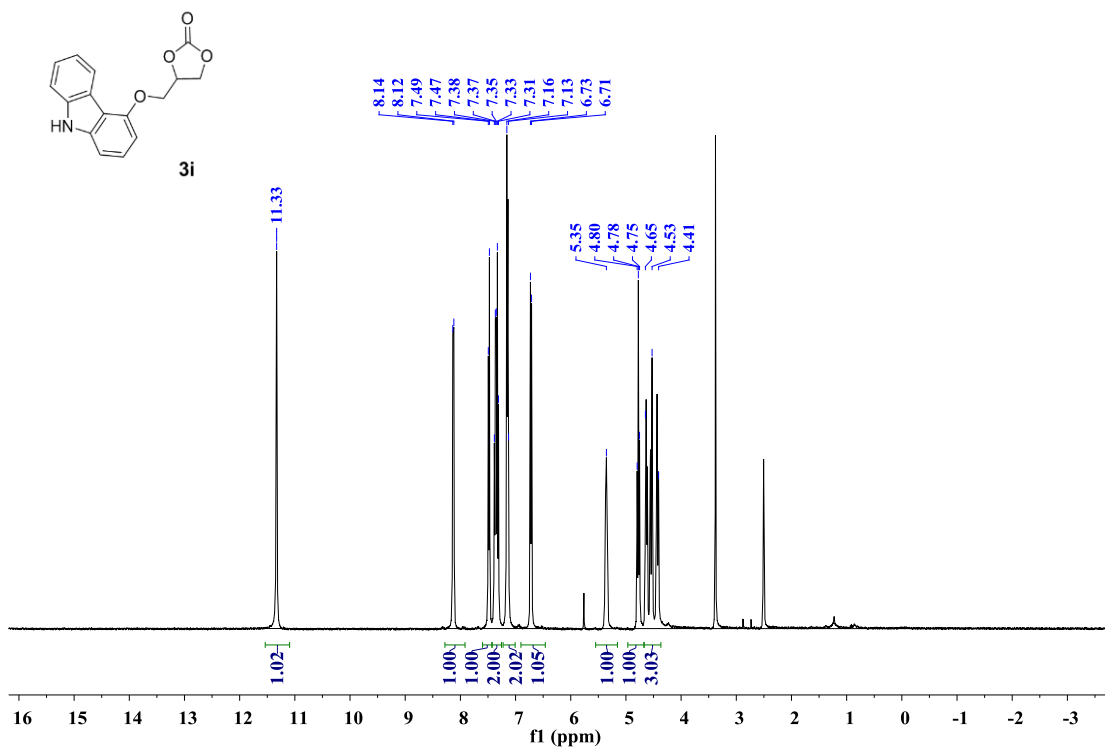


Figure S44. ¹H NMR spectra of cyclic carbonate **3i**.

cf-99

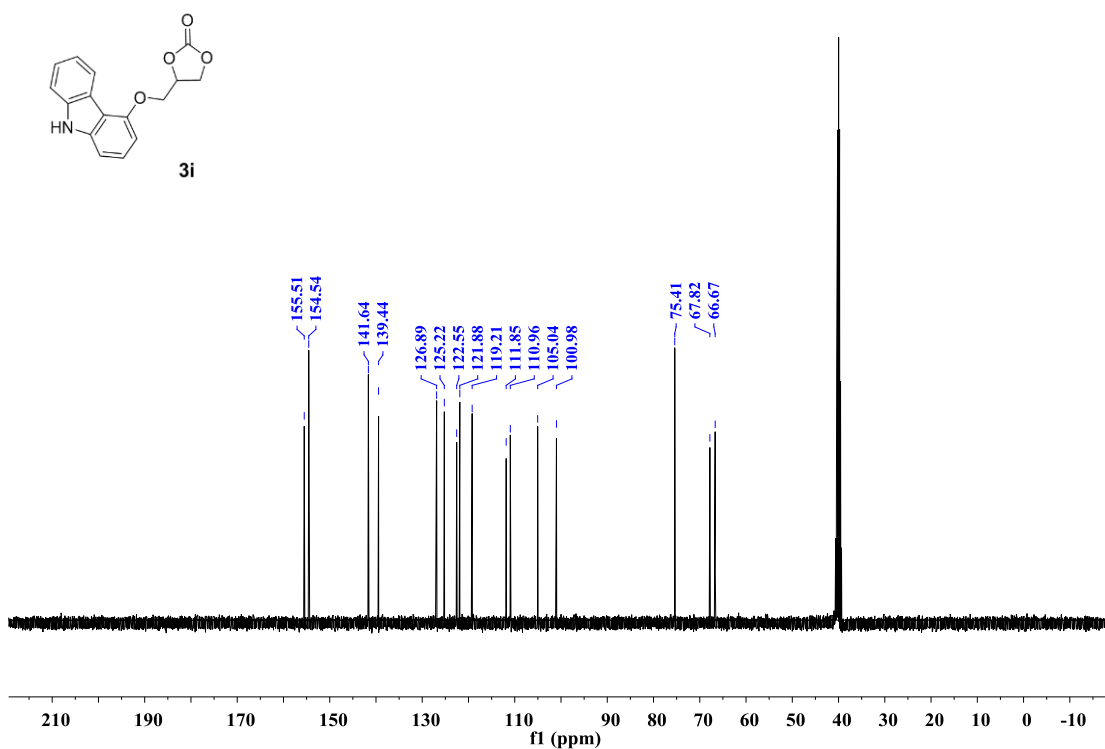


Figure S45. ¹³C NMR spectra of cyclic carbonate **3i**.

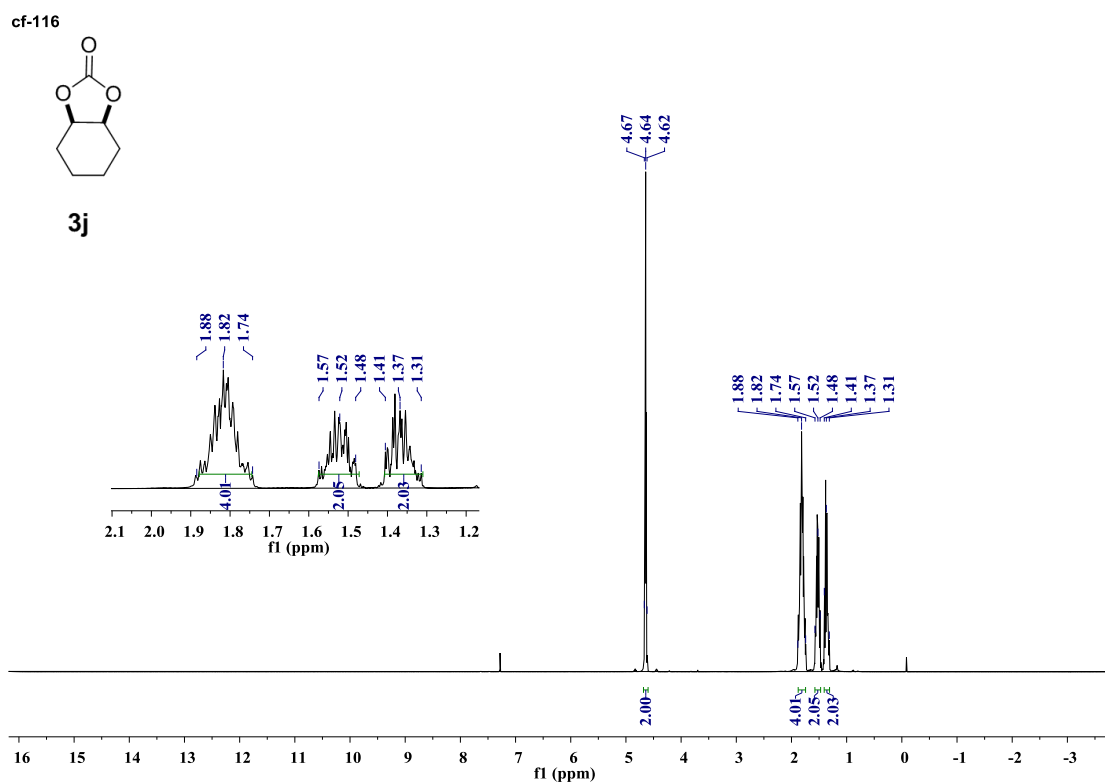


Figure S46. ¹H NMR spectra of cyclic carbonate **3j**.

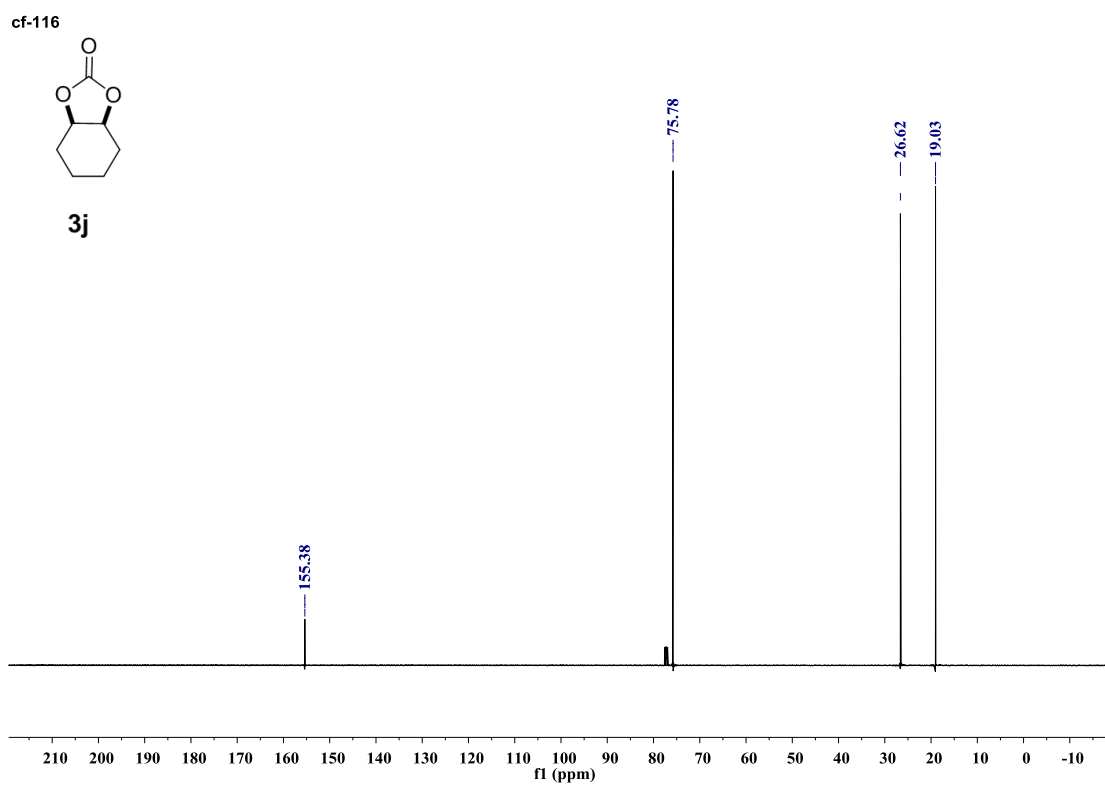


Figure S47. ¹³C NMR spectra of cyclic carbonate **3j**.

cf-100

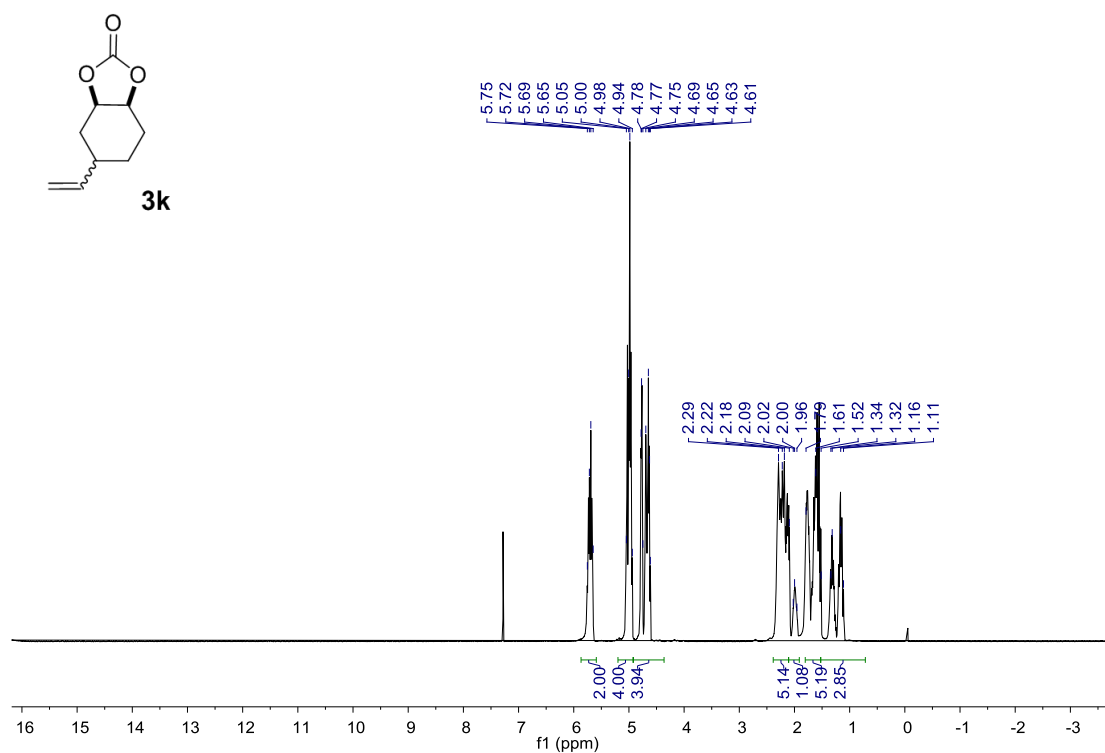


Figure S48. ¹H NMR spectra of cyclic carbonate **3k**.

cf-100

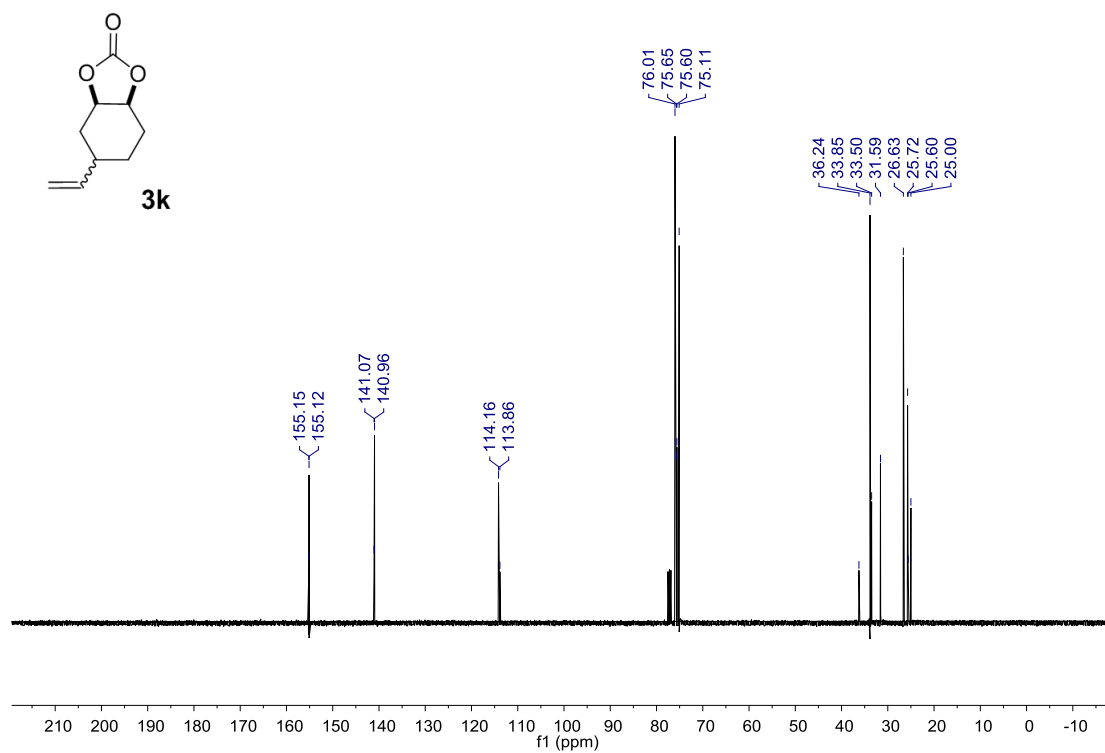
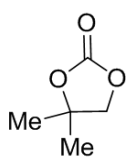
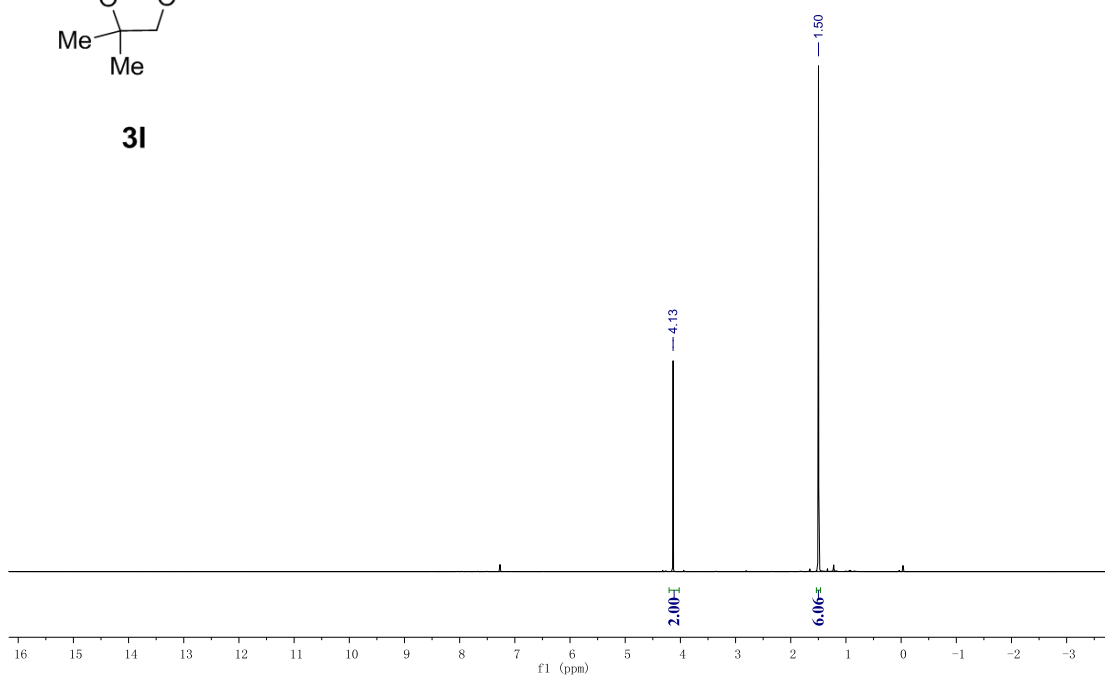
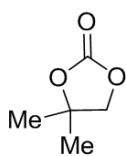
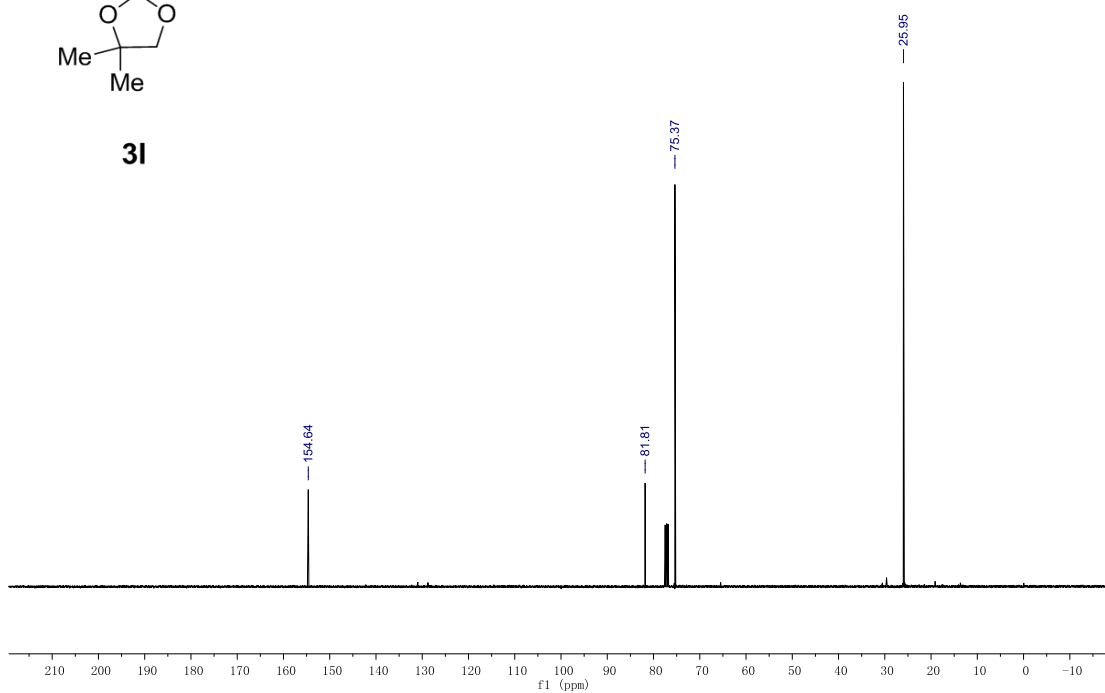


Figure S49. ¹³C NMR spectra of cyclic carbonate **3k**.

cf-182

**3l****Figure S50.** ¹H NMR spectra of cyclic carbonate **3l**.

cf-182

**3l****Figure S51.** ¹³C NMR spectra of cyclic carbonate **3l**.

氢谱

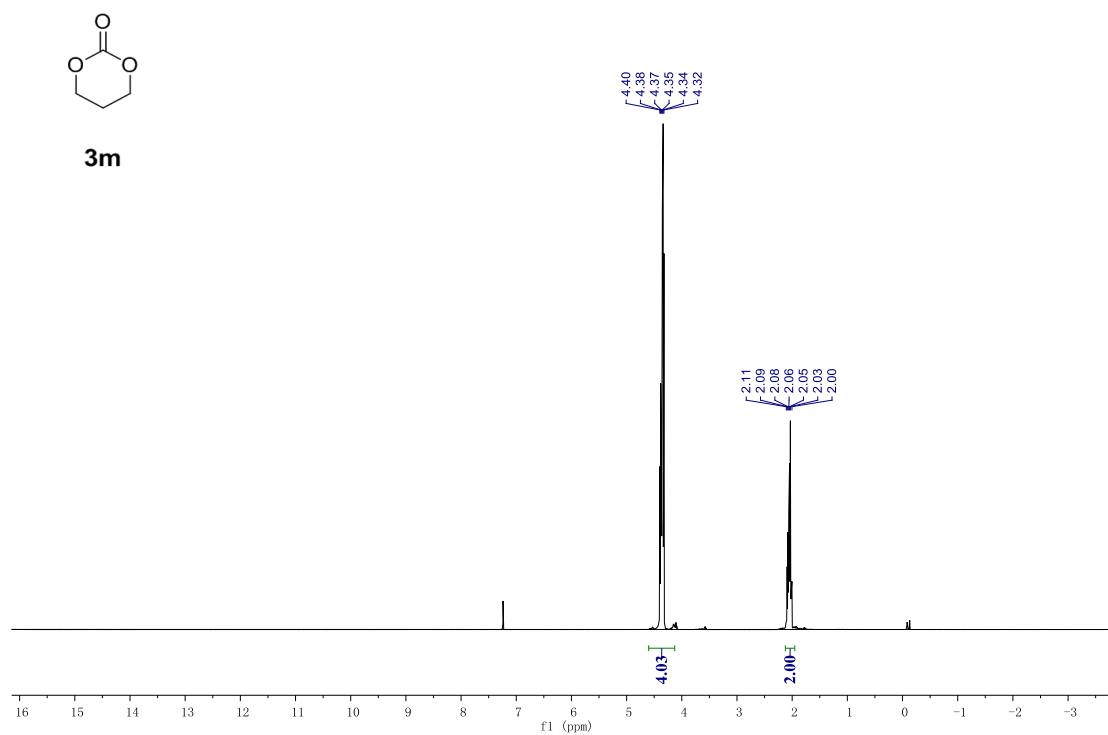


Figure S52. ^1H NMR spectra of cyclic carbonate **3m**.

cf-196

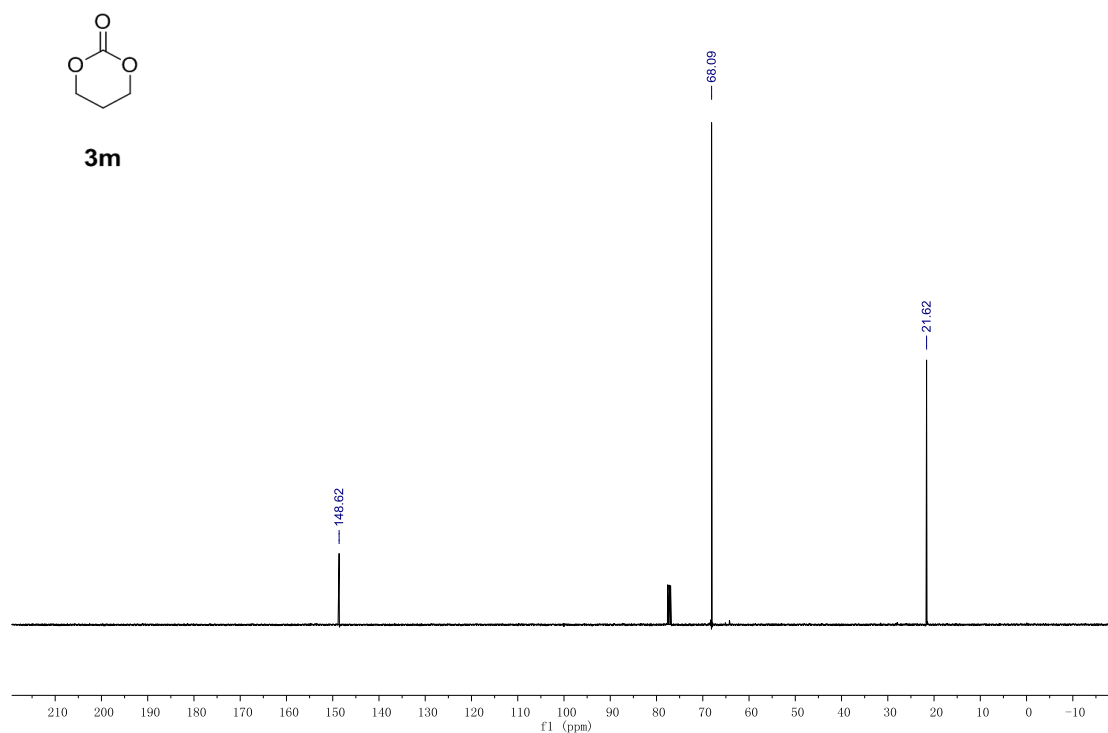
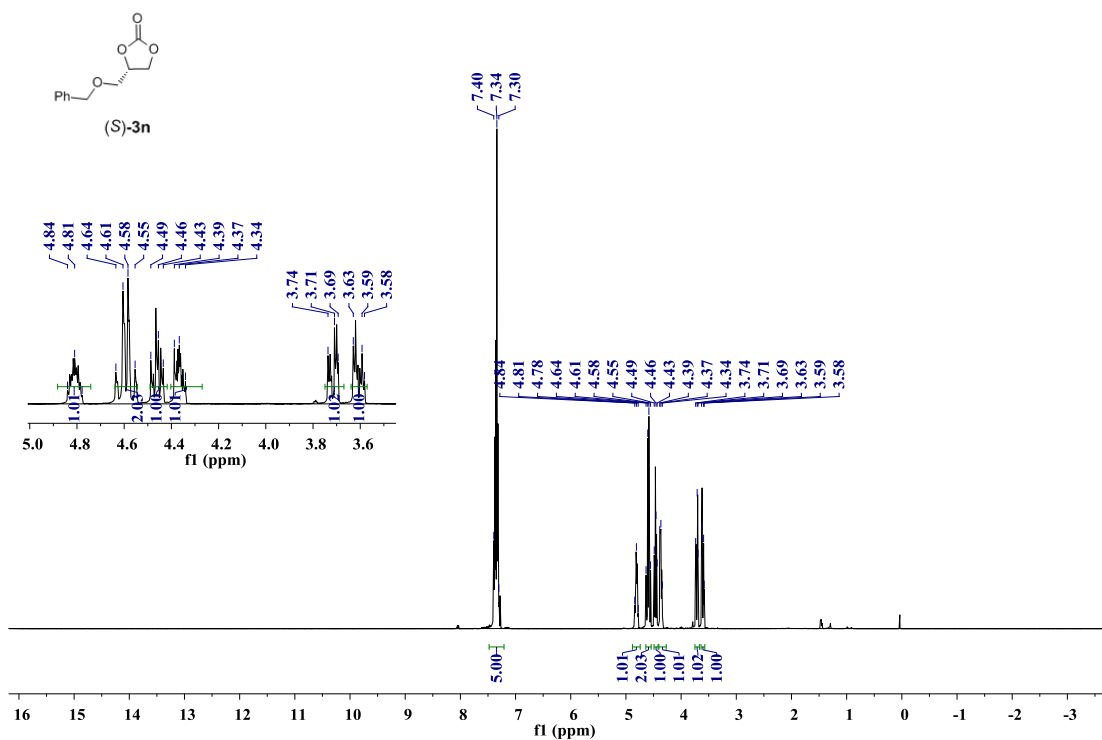
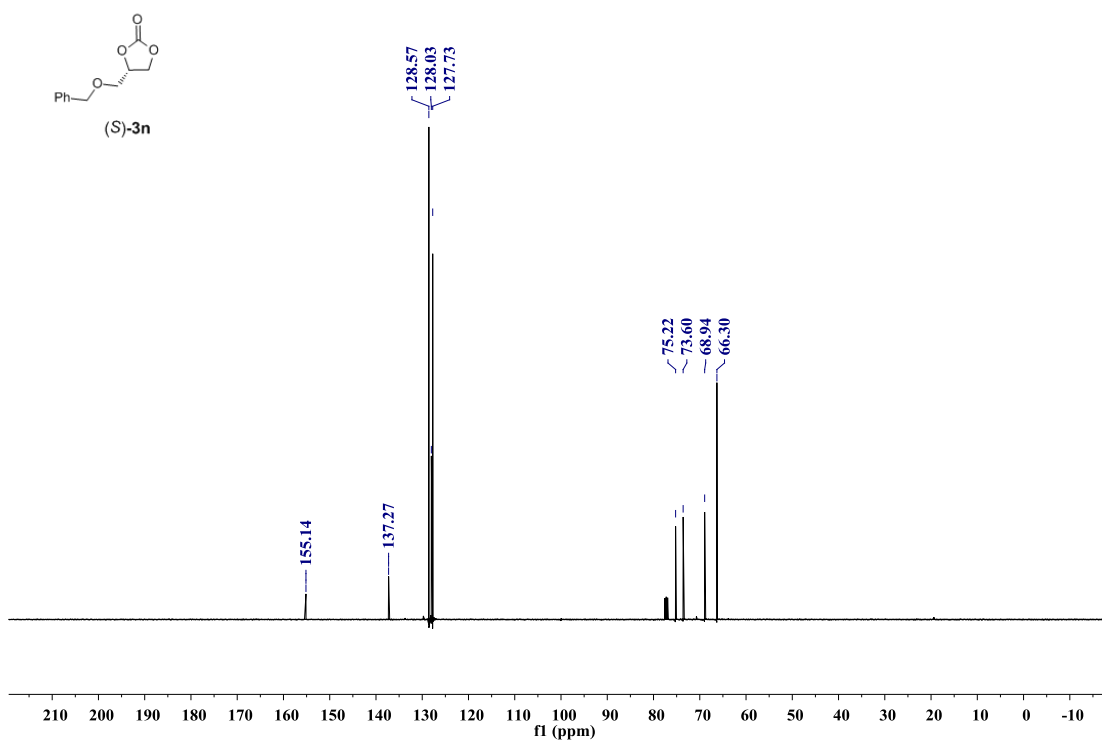


Figure S53. ^{13}C NMR spectra of cyclic carbonate **3m**.

cf-115

Figure S54. ¹H NMR spectra of cyclic carbonate (*S*)-**3n**.

cf-115

Figure S55. ¹³C NMR spectra of cyclic carbonate (*S*)-**3n**.

cf-276

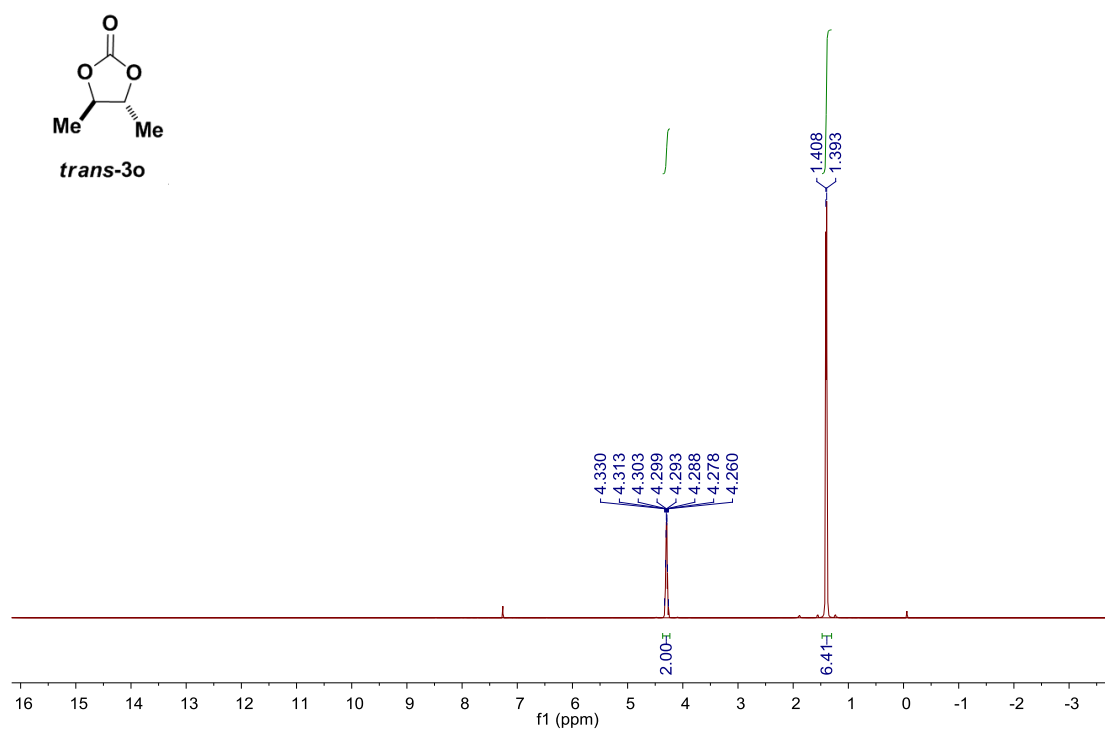


Figure S56. ^1H NMR spectra of cyclic carbonate *trans*-**3o**.

cf-276

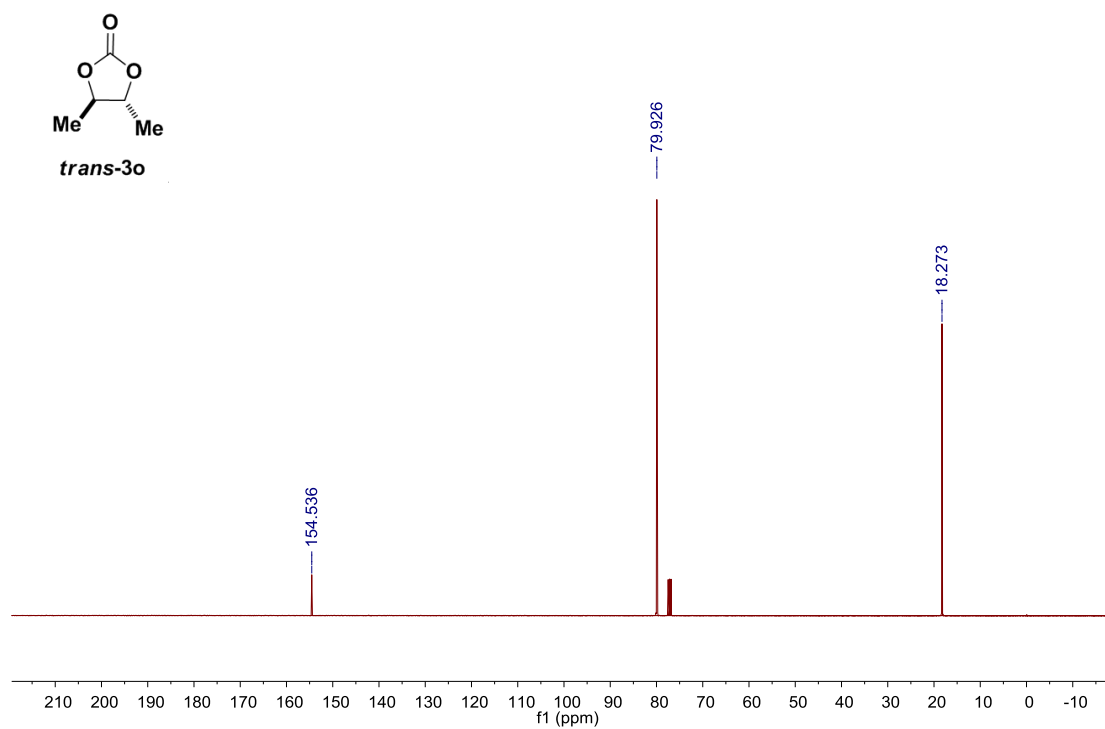


Figure S57. ^{13}C NMR spectra of cyclic carbonate *trans*-**3o**.

cf-272

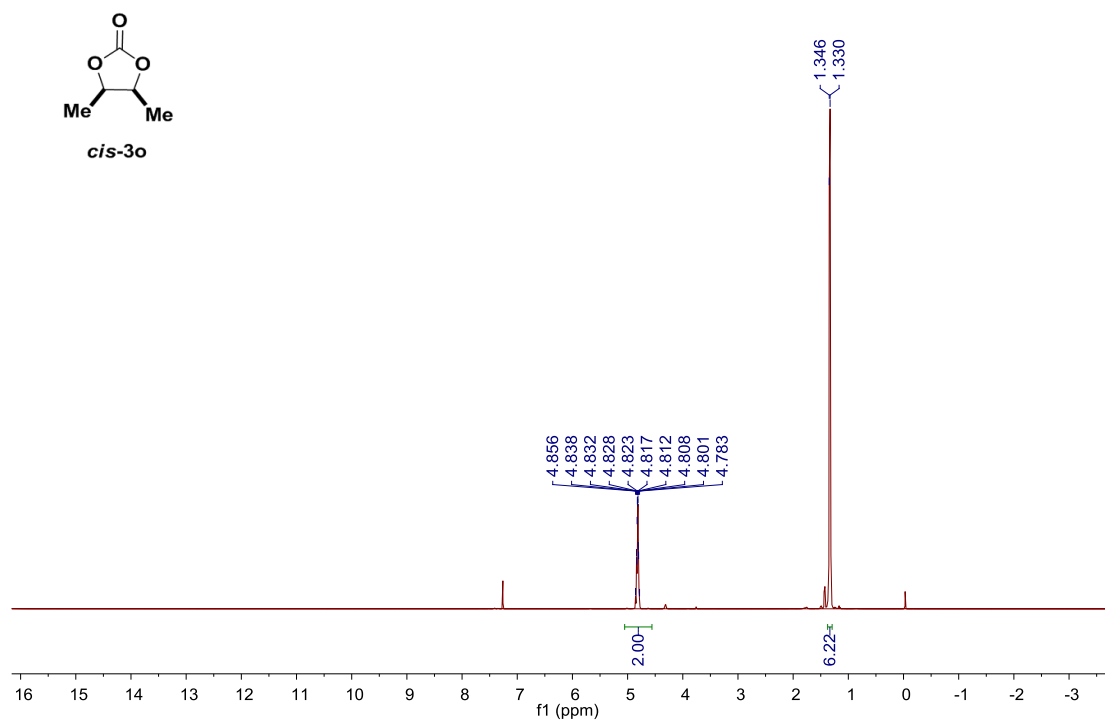


Figure S58. ^1H NMR spectra of cyclic carbonate *cis*-**3o**.

cf-272

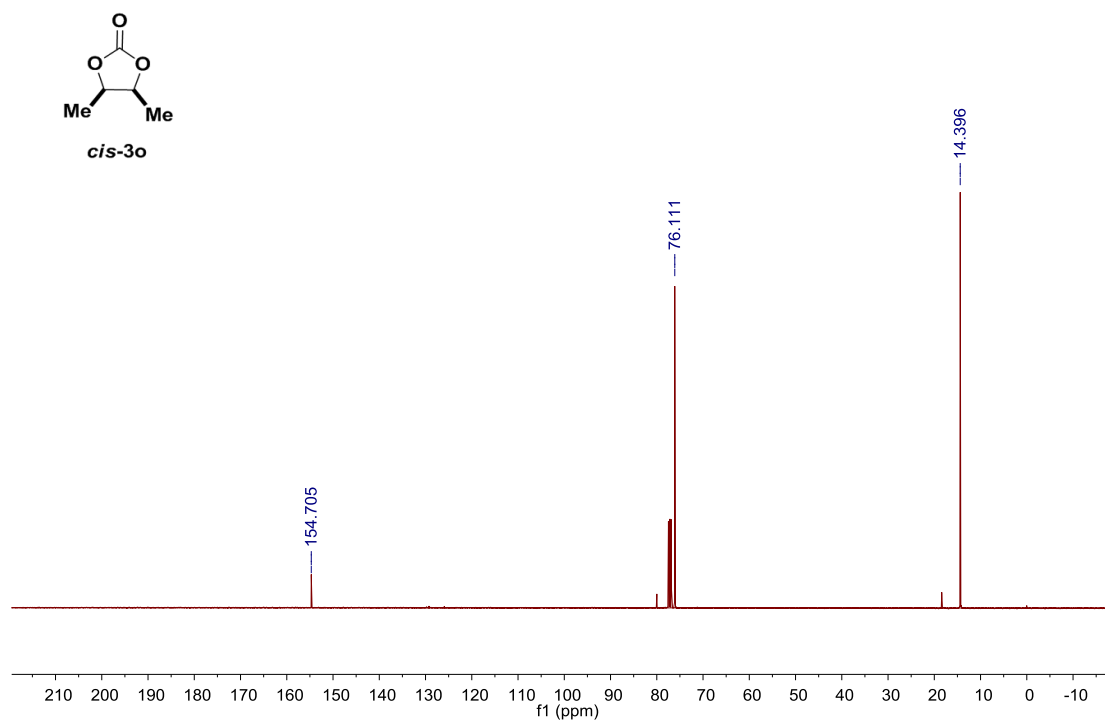


Figure S59. ^{13}C NMR spectra of cyclic carbonate *cis*-**3o**.

Figure S60. HPLC spectrum of *racemic 3n-ol*.



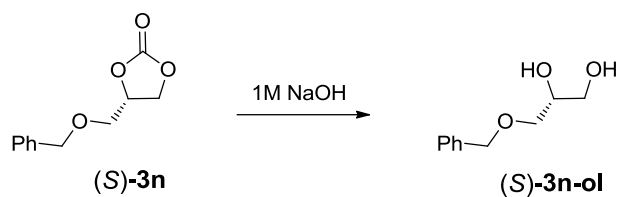
Breeze

Report Method: Untitled

Printed 6:36:54 PM 1/22/2016

Page: 1 of 1

(*S*)-4-((benzyloxy)methyl)-1,3-dioxolan-2-one: The ee of the resulting 4-((benzyloxy)methyl)-1,3-dioxolan-2-one was determined by chiral HPLC analysis of the diol derived from hydrolysis with 1M NaOH (OD-H, hexane:*i*-PrOH = 95:5, t_R (major) = 5.928 min, t_R (minor) = 8.953 min). (Reference: Ren, W. M.; Liu, Y.; Lu, X.-B. *J. Org. Chem.* **2014**, 79, 9771-9777.)



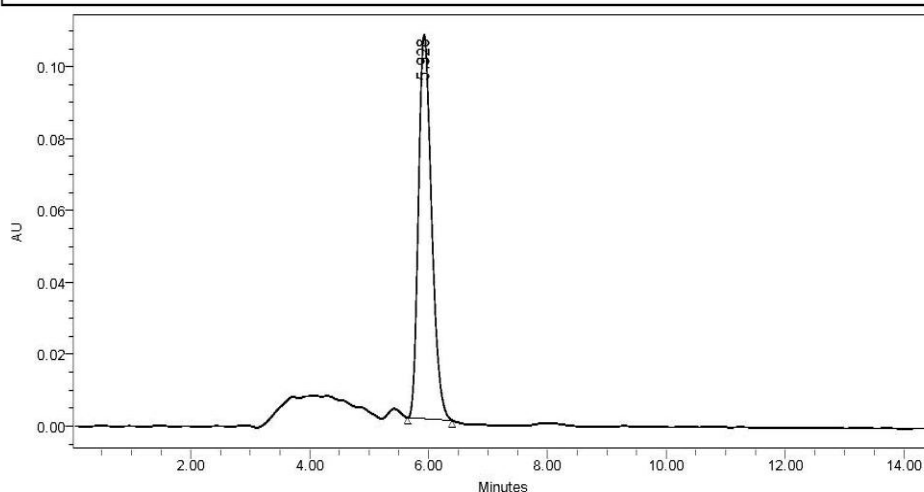
shzu

Project Name: Defaults
Reported by User: System

Breeze

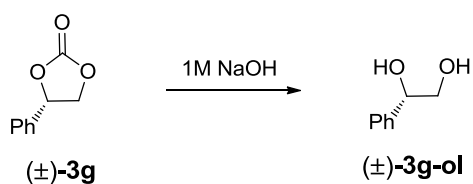
SAMPLE INFORMATION

Sample Name: cf20160121-2	Acquired By: System
Sample Type: Unknown	Date Acquired: 1/21/2016 8:24:37 PM
Vial: 1	Acq. Method: w y8020
Injection #: 2	Date Processed: 1/21/2016 8:39:25 PM
Injection Volume: 20.00 ul	Channel Name: 2487Channel 1
Run Time: 60.00 Minutes	Sample Set Name:



	RT (min)	Area ($\mu V \cdot sec$)	% Area	Height (μV)	% Height
1	5.928	1641377	100.00	107039	100.00

Figure S61. HPLC spectrum of (*S*)-3n-ol.



XJTIPC

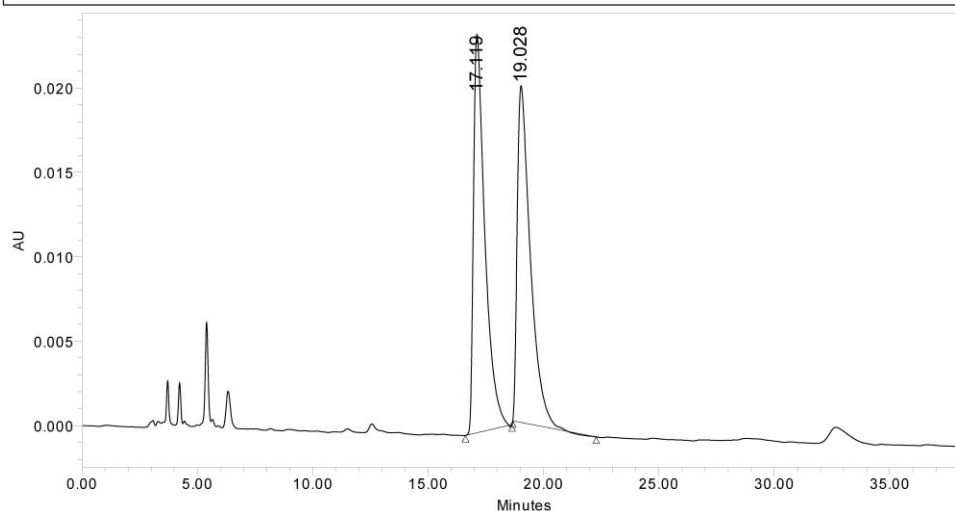
Project Name Lu

Reported by User: Breeze user (Breeze)

Breeze²
HPLC System

SAMPLE INFORMATION

Sample Name:	CF-108	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	9/11/2017 1:47:41 AM CST
Vial:	999	Acq. Method:	20170816955254
Injection #:	1	Date Processed:	9/11/2017 5:11:38 AM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	100.00 Minutes	Sample Set Name	



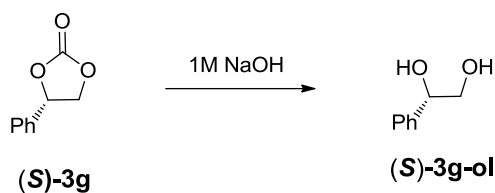
	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	17.119	810275	50.55	23598	54.19
2	19.028	792764	49.45	19949	45.81

Report Method: Untitled
Page: 1 of 1

Printed: 9/11/2017
5:20:16 AM PRC

Figure S62. HPLC spectrum of *racemic 3g-ol*.

(S)-3-phenoxy-1,2-propylene carbonate: The ee of the resulting phenyl(ethylene carbonate) was determined by chiral HPLC analysis of the diol derived from hydrolysis with 1M NaOH (OD-H, hexane:*i*-PrOH = 95:5, $t_R(\text{major}) = 18.167 \text{ min}$, $t_R(\text{minor}) = 16.739 \text{ min}$).



XJTIPC

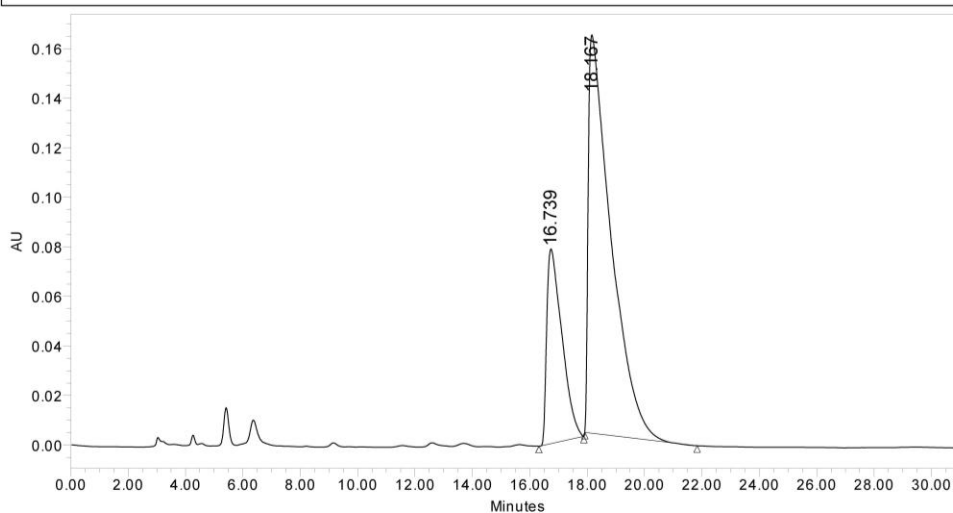
Project Name Lu

Reported by User: Breeze user (Breeze)

Breeze²
HPLC System

SAMPLE INFORMATION

Sample Name: 279-3	Acquired By: Breeze
Sample Type: Unknown	Date Acquired: 9/11/2017 4:05:30 AM CST
Vial: 1	Acq. Method: 20170816955254
Injection #: 1	Date Processed: 9/11/2017 5:24:51 AM CST
Injection Volume: 10.00 ul	Channel Name: W2489 ChA
Run Time: 100.00 Minutes	Sample Set Name



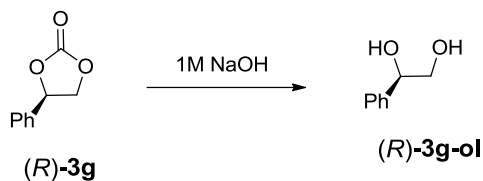
	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	16.739	2884345	24.67	78514	32.82
2	18.167	8809682	75.33	160698	67.18

Report Method: Untitled
Page: 1 of 1

Printed: 9/11/2017
5:25:45 AM PRC

Figure S63. HPLC spectrum of (S)-3g-ol.

(R)-3-phenoxy-1,2-propylene carbonate: The ee of the resulting phenyl(ethylene carbonate) was determined by chiral HPLC analysis of the diol derived from hydrolysis with 1M NaOH (OD-H, hexane:*i*-PrOH = 95:5, $t_R(\text{major}) = 18.426 \text{ min}$, $t_R(\text{minor}) = 15.982 \text{ min}$).



XJTIPC

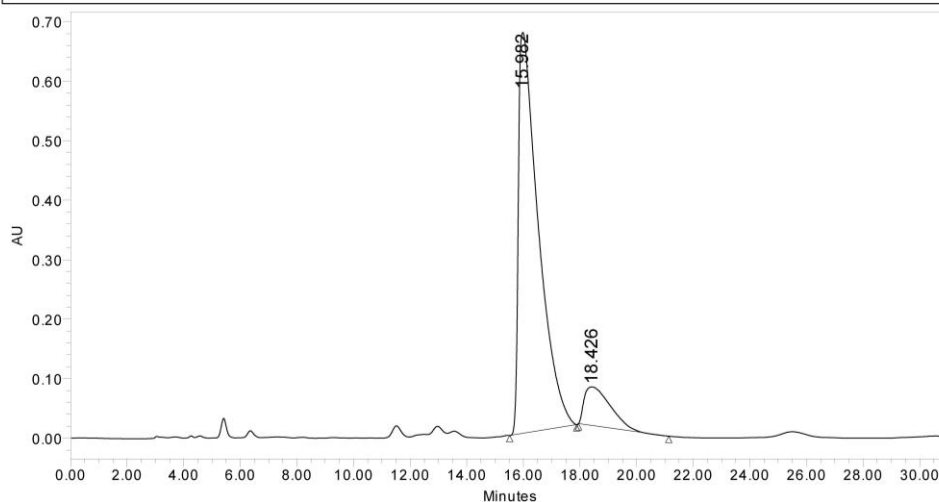
Project Name Lu

Reported by User: Breeze user (Breeze)

Breeze²
HPLC System

SAMPLE INFORMATION

Sample Name: CF-278	Acquired By: Breeze
Sample Type: Unknown	Date Acquired: 9/11/2017 4:38:14 AM CST
Vial: 2	Acq. Method: 20170816955254
Injection #: 1	Date Processed: 9/11/2017 5:27:21 AM CST
Injection Volume: 10.00 μl	Channel Name: W2489 ChA
Run Time: 100.00 Minutes	Sample Set Name



	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	15.982	32988908	88.73	673825	91.24
2	18.426	4191791	11.27	64686	8.76

Report Method: Untitled

Page: 1 of 1

Printed: 9/11/2017

5:28:11 AM PRC

Figure S64. HPLC spectrum of (R)-3g-o.