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Three powerful dinuclear metal-organic catalysts for converting CO_2 into organic carbonates

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Experimental section

Structure of the organic ligands HL, L2 and L3:

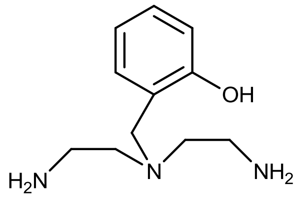


Chart S1 The organic ligand HL.

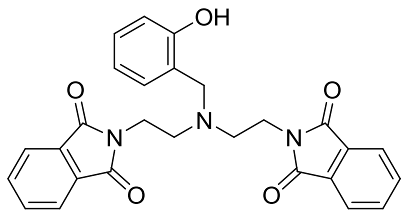


Chart S2 The structure of L2.

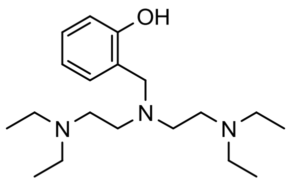


Chart S3 The structure of L3.

Crystallographic data and structure refinements:

Table S1 Crystallographic data for **L3-Zn**, **(*R*)-2a** and **(*S*)-2a**

	L3-Zn	**(*R*)-2a**	**(*S*)-2a**
formula	$C_{19}H_{38}N_3O_7ClZn$	$C_9H_8O_3$	$C_9H_8O_3$
fw	521.34	164.15	164.15
crystal system	Monoclinic	orthorhombic	Orthorhombic
space group	$P2_1$	$P2_12_12_1$	$P2_12_12_1$
T (K)	293(2)	173(2)	173(2)
a (Å)	9.7985(8)	6.1207(5)	6.1196(4)
b (Å)	13.1054(9)	7.5850(6)	7.5799(5)
c (Å)	9.8329(8)	16.9844(14)	16.9823(12)
β(°)	97.233(3)	90	90
V(Å^3)	1252.63(17)	788.51(11)	787.74(9)
Z	2	4	4
D_c (g cm^{-3})	1.382	1.383	1.384
F(000)	552	344	344
θ for data collection (°)	2.60 - 25.00	6.39 - 65.50	5.21 - 64.97
$R_1{}^a$, [$I > 2\sigma(I)$]	0.0677	0.0255	0.0262
$wR_2{}^b$ [$I > 2\sigma(I)$]	0.1872	0.0676	0.0667
GOF	1.077	1.079	1.065

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

Power X-ray diffraction (PXRD)

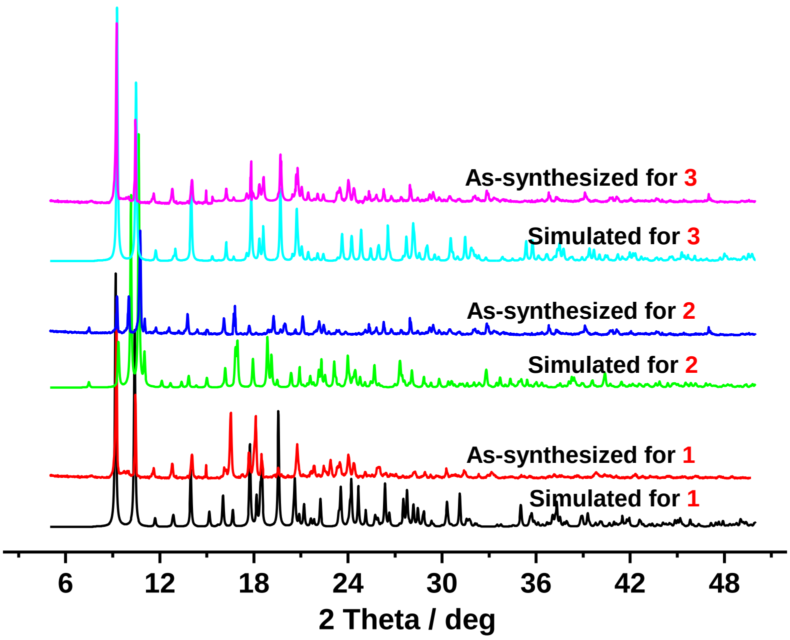


Figure S1 PXRD of **1 - 3**.

HPLC

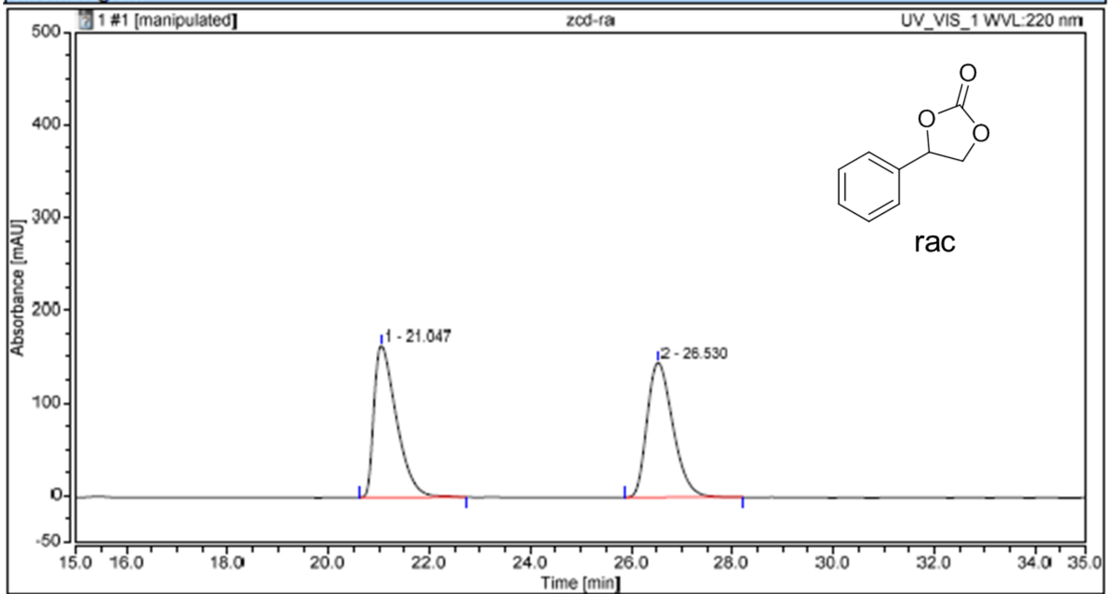
Styrene oxide was isolated as a colorless solid by flash chromatography using petroleum hexane/EtOAc (5:1) as eluent. R_f = 0.41; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.48 (m, 3H), 7.34-7.39 (m, 2H), 5.68 (t, J = 8.0 1H), 4.80 (t, J = 8.0 1H), 4.35 (t, J = 8.0 1H); The enantiomeric excess was determined by chiral HPLC using a Chiralcel OD column (4.6 mm x 250 mml) with hexane/isopropanol (90:10) as eluent and a flow rate of 1.0 mL/min. t_R=21.05 min, t_S=26.53 min. Detection wavelength: 220 nm.

Chromatogram and Results

Injection Details

Injection Name:	zcd-ra	*Run Time (min):*	40.00
Vial Number:	0	*Injection Volume:*	5.00
Injection Type:	Unknown	*Channel:*	UV_VIS_1
Calibration Level:		*Wavelength:*	220.0
Instrument Method:	zcd-1	*Bandwidth:*	4
Processing Method:	New Processing Method	*Dilution Factor:*	1.0000
Injection Date/Time:	24/二月/16 15:57	*Sample Weight:*	1.0000

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		21.047	85.106	163.856	49.70	52.98	n.a.
2		26.530	86.123	145.412	50.30	47.02	n.a.
Total:			**171.229**	**309.268**	**100.00**	**100.00**	

Chromatogram and Results

Injection Details

Injection Name:	**zcd-RorS**	*Run Time (min):*	**40.00**
Vial Number:	**1**	*Injection Volume:*	**5.00**
Injection Type:	**Unknown**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**220.0**
Instrument Method:	**zcd-1**	*Bandwidth:*	**4**
Processing Method:	**New Processing Method**	*Dilution Factor:*	**1.0000**
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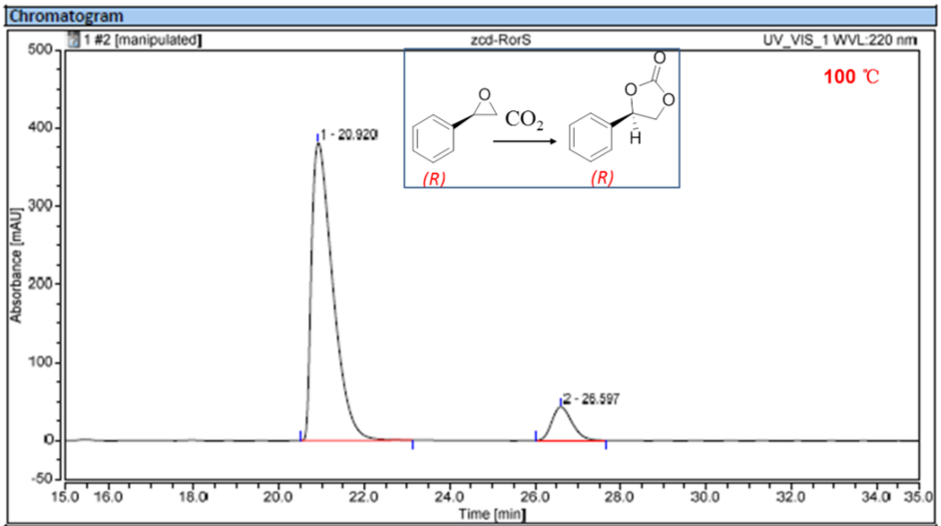
Chromatogram



Integration Results

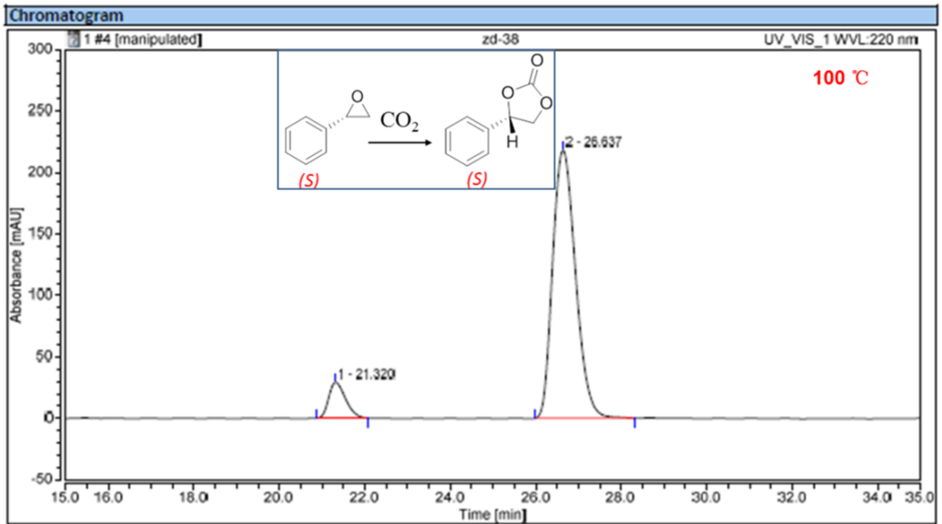
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.920	220.960	381.748	90.37	89.87	n.a.
2		26.597	23.547	43.050	9.63	10.13	n.a.
Total:			**244.508**	**424.798**	**100.00**	**100.00**	

Chromatogram and Results

Injection Details

Injection Name:	**zd-38**	*Run Time (min):*	**40.00**
Vial Number:	**3**	*Injection Volume:*	**5.00**
Injection Type:	**Unknown**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**220.0**
Instrument Method:	**zcd-1**	*Bandwidth:*	**4**
Processing Method:	**New Processing Method**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**02/三月/16 12:31**	*Sample Weight:*	**1.0000**

Chromatogram



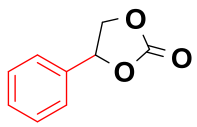
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		21.320	13.107	29.082	8.88	11.76	n.a.
2		26.637	134.474	218.201	91.12	88.24	n.a.
Total:			**147.581**	**247.283**	**100.00**	**100.00**	

Figure S2 The figures of HPLC

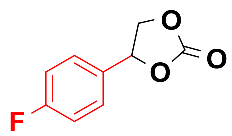
Characterization data of compounds

4-phenyl-1,3-dioxolan-2-one **2a**



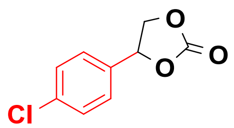
R_f = 0.7 (EA/Hexane = 1:5), Yield 79%, colorless crystalline. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49-7.42 (m, 3H), 7.40-7.33 (m, 2H), 5.68 (t, *J* = 8.1 Hz, 1H), 4.81(t, *J* = 8.4 Hz, 1H), 4.35 (dd, *J* = 8.1 Hz, 8.7 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.89, 135.82, 129.74, 129.24, 125.91, 78.03, 71.20 ppm. See also: J. Melendez, M. North and P. Villuendas, *Chem. Commun.*, 2009, **18**, 2577.

4-(4-fluorophenyl)-1,3-dioxolan-2-one **2b**



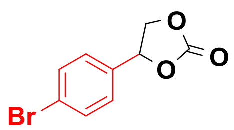
R_f = 0.6 (EA/Hexane = 1:6), Yield 80%, white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44-7.31 (m, 2H), 7.20-7.09 (m, 2H), 5.67 (t, *J* = 8.0 Hz, 1H), 4.80 (t, *J* = 8.4 Hz, 1H), 4.33 (dd, *J* = 8.7 Hz, 7.9 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.37 (d, *J* = 248.0 Hz), 154.65, 131.62 (d, *J* = 3.0 Hz), 128.09, 128.01, 116.45, 116.23, 77.45, 71.11 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -110.97 ppm. See also: C. William, H. Ross W, N. Michael and P. Riccardo, *Chem. Eur. J.*, 2010, **16**, 6828.

4-(4-chlorophenyl)-1,3-dioxolan-2-one **2c**



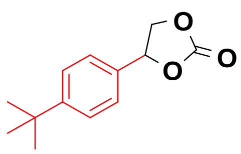
R_f = 0.8 (EA/Hexane = 1:3), Yield 80%, white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48-7.38 (m, 2H), 7.37-7.28 (m, 2H), 5.66 (t, *J* = 8.0 Hz, 1H), 4.81 (t, *J* = 8.4 Hz, 1H), 4.31 (dd, *J* = 8.7 Hz, 7.8 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.52, 135.79, 134.29, 129.52, 127.26, 77.24, 71.00 ppm.

4-(4-bromophenyl)-1,3-dioxolan-2-one **2d**



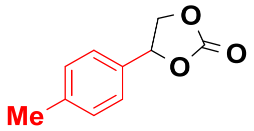
R_f = 0.7 (EA/Hexane = 1:5), Yield 78%, white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62-7.53 (m, 2H), 7.29-7.20 (m, 2H), 5.64 (t, *J* = 8.0 Hz, 1H), 4.80 (t, *J* = 8.4 Hz, 1H), 4.30 (dd, *J* = 8.7 Hz, 7.7 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.50, 134.82, 132.48, 127.48, 123.92, 77.25, 70.93 ppm.

4-(4-tert-butylphenyl)-1,3-dioxolan-2-one **2e**



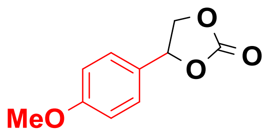
R_f = 0.8 (EA/Hexane = 1:5), Yield 71%, white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50-7.43 (m, 2H), 7.34-7.28 (m, 2H), 5.66 (t, *J* = 8.0 Hz, 1H), 4.78 (t, *J* = 8.4 Hz, 1H), 4.36 (dd, *J* = 8.6 Hz, 8.0 Hz, 1H), 1.33 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.91, 153.11, 132.64, 126.18, 125.83, 78.05, 71.11, 34.78, 31.22 ppm. HRMS (EI) m/z calcd for $C_{13}H_{16}O_3$ $[M+Na]^+$: 243.0997; found: 243.2875.

4-p-tolyl-1,3-dioxolan-2-one **2f**



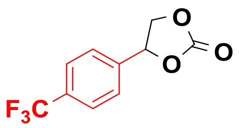
R_f = 0.6 (EA/Hexane = 1:8), Yield 75%, colorless crystalline. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25 (s, 4H), 5.64 (t, *J* = 8.0 Hz, 1H), 4.77 (t, *J* = 8.3 Hz, 1H), 4.34 (dd, *J* = 8.6 Hz, 7.9 Hz, 1H), 2.39 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.96, 139.87, 132.72, 129.87, 126.03, 78.14, 71.20 ppm. See also: J. Melendez, M. North and P. Villuendas, *Chem. Commun.*, 2009, **18**, 2577.

4-(4-methoxyphenyl)-1,3-dioxolan-2-one **2g**



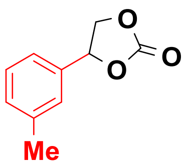
R_f = 0.7 (EA/Hexane = 1:10), Yield 76%, yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34-7.27 (m, 2H), 6.99-6.92 (m, 2H), 5.62 (t, *J* = 8.1 Hz, 1H), 4.75 (t, *J* = 8.4 Hz, 1H), 4.35 (dd, *J* = 8.7 Hz, 8.1 Hz, 3H), 3.83 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.74, 154.90, 127.81, 127.40, 114.59, 78.17, 71.11, 55.41 ppm. HRMS (EI) m/z calcd for $C_{10}H_{10}O_4$ $[M+Na]^+$: 217.0477; found: 217.0472.

4-(4-(trifluoromethyl)phenyl)-1,3-dioxolan-2-one **2h**



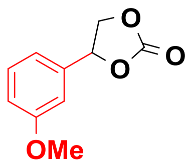
R_f = 0.7 (EA/Hexane = 1:5), Yield 72%, light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.7-7.56 (m, 3H), 7.54-7.41 (m, 1H), 6.11-5.93 (m, 1H), 4.81 (td, *J* = 8.7 Hz, 1.3 Hz, 1H), 4.14(dd, *J* = 8.8 Hz, 7.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 154.68, 139.98, 131.56 (q, *J* = 32.5 Hz), 126.20, 126.16, 126.13, 126.09, 123.71 (q, *J* = 270.7 Hz), 77.06, 70.98 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.96 ppm. HRMS (EI) m/z calcd for $C_{10}H_7F_3O_3$ $[M+Na]^+$: 255.0245; found: 255.0240.

4-m-tolyl-1,3-dioxolan-2-one **2i**



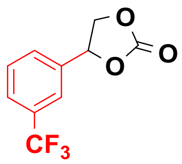
R_f = 0.6 (EA/Hexane = 1:8), Yield 84%, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.05 (m, 4H), 5.70-5.54 (m, 1H), 4.84-4.64 (m, 1H), 4.35-4.13 (m, 1H), 2.21 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.18, 139.01, 136.07, 130.32, 129.02, 126.70, 123.17, 78.17, 71.23, 21.23 ppm. HRMS (EI) m/z calcd for $C_{10}H_{10}O_3$ $[M+Na]^+$: 201.0528; found: 201.0523.

4-(3-methoxyphenyl)-1,3-dioxolan-2-one **2j**



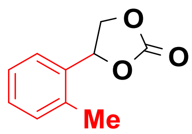
R_f = 0.7 (EA/Hexane = 1:10), Yield 84%, yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.38 (t, *J* = 7.9 Hz, 1H), 7.16-6.93 (m, 3H), 5.84 (t, *J* = 8.0 Hz, 1H), 4.89 (td, *J* = 8.2 Hz, 1.2 Hz, 1H), 4.43 (ddd, *J* = 8.8 Hz, 7.9 Hz, 1.0 Hz, 1H), 3.79 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.56, 154.71, 137.77, 130.03, 118.45, 114.81, 111.98,77.63, 70.77, 55.11 ppm. See also: C. William, W, H. Ross, N. Michael and P. Riccardo, *Chem. Eur. J.*, 2010, **16**, 6828.

4-(3-(trifluoromethyl)phenyl)-1,3-dioxolan-2-one **2k**



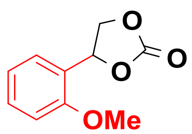
R_f = 0.7 (EA/Hexane = 1:5), Yield 74%, light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70-7.45 (m, 4H), 5.77 (t, *J* = 8.0 Hz, 1H), 4.92-4.78 (m, 1H), 4.37-4.20 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.75, 137.13, 131.29 (q, *J* = 32.4 Hz), 129.88, 129.31, 126.31 (q, *J* = 3.7 Hz), 123.72 (q, *J* = 270.7 Hz), 122.76 (q, *J* = 3.7 Hz), 77.52, 71.01 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.87 ppm. HRMS (EI) m/z calcd for $C_{10}H_7F_3O_3$ $[M+Na]^+$: 255.0245; found: 255.0241.

4-o-tolyl-1,3-dioxolan-2-one **2l**



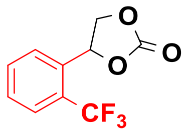
R_f = 0.6 (EA/Hexane = 1:8), Yield 64%, light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49-7.03 (m, 4H), 5.86 (td, *J* = 8.0 Hz, 6.8Hz, 3.1Hz, 1H), 4.79 (tdd, *J* = 8.4 Hz, 3.2 Hz, 1.6 Hz, 1H), 4.35-4.09 (m, 1H), 2.27 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.25, 135.03, 134.33, 131.01, 129.18, 126.72, 124.69, 75.66, 70.46, 18.84 ppm. HRMS (EI) m/z calcd for $C_{10}H_{10}O_3$ $[M+Na]^+$: 201.0528; found: 201.0524.

4-(2-methoxyphenyl)-1,3-dioxolan-2-one **2m**



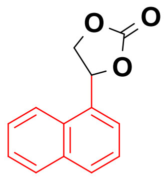
R_f = 0.7 (EA/Hexane = 1:10), Yield 78%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.25 (m, 2H), 7.00-6.87 (m, 2H), 5.75 (t, *J* = 7.8 Hz, 1H), 4.76 (t, *J* = 8.5 Hz, 1H), 4.21 (dd, *J* = 8.4 Hz, 7.1 Hz, 1H), 3.79 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.50, 155.37, 130.53, 126.51, 124.71, 120.66, 110.91, 75.23, 70.45, 55.48 ppm. HRMS (EI) m/z calcd for $C_{10}H_{10}O_4$ $[M+Na]^+$: 217.0477; found: 217.0473.

4-(2-(trifluoromethyl)phenyl)-1,3-dioxolan-2-one **2n**



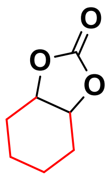
R_f = 0.7 (EA/Hexane = 1:5), Yield 31%, light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75-7.40 (m, 4H), 6.03 (m, 1H), 4.88-4.73 (m, 1H), 4.14 (dd, J = 8.8 Hz, 7.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.60, 135.01, 133.09, 129.34, 126.78(d, J = 31.0 Hz), 126.28 (q, J = 6.1 Hz), 125.86, 123.89 (q, J = 271.1 Hz), 73.88 (q, J = 2.8 Hz), 71.45 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -58.93 ppm. HRMS (EI) m/z calcd for $C_{10}H_7F_3O_3$ $[M+Na]^+$: 255.0245; found: 255.0242.

4-(naphthalen-1-yl)-1,3-dioxolan-2-one **2o**



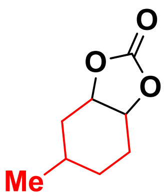
R_f = 0.7 (EA/Hexane = 1:5), Yield 76%, brown yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02-7.87 (m, 2H), 7.75-7.47 (m, 5H), 6.42 (t, J = 7.8 Hz, 1H), 5.06 (t, J = 8.4 Hz, 1H), 4.39 (dd, J = 8.5 Hz, 7.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.82, 133.81, 131.72, 129.75, 129.47, 129.20, 127.21, 126.37, 125.50, 122.33, 121.54, 75.55, 70.79 ppm. HRMS (EI) m/z calcd for $C_{13}H_{10}O_3$ $[M+Na]^+$: 237.0528; found: 237.0523.

hexahydrobenzo[d]-1,3-dioxolan-2-one **2p**



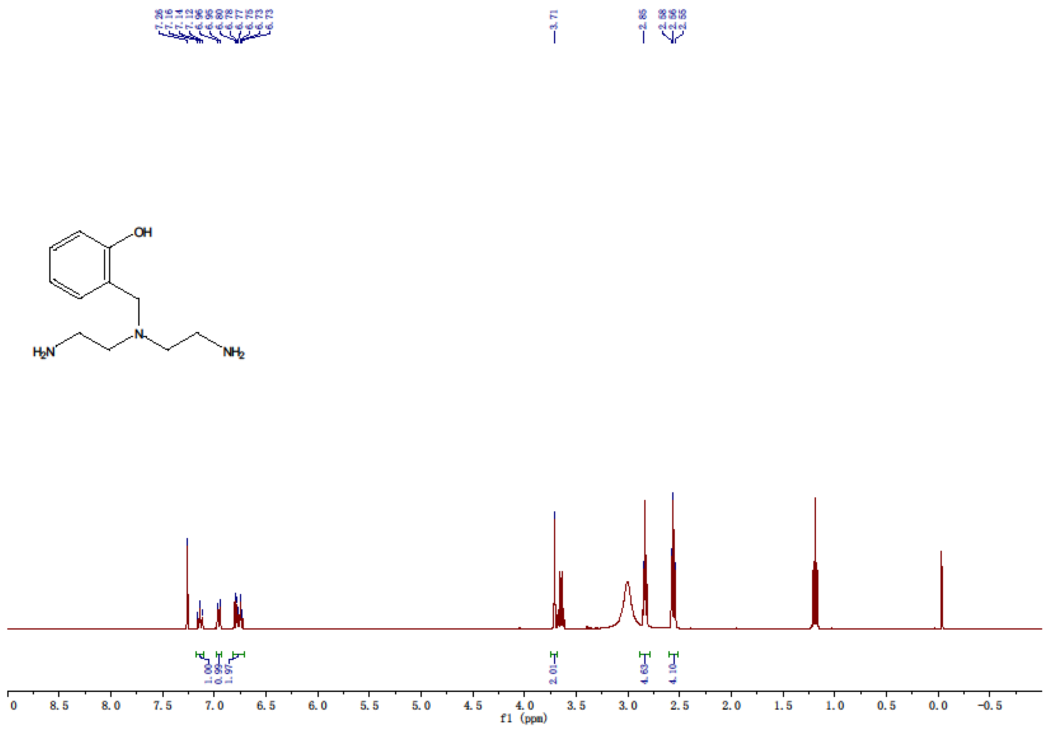
R_f = 0.6 (EA/Hexane = 1:10), Yield 61%, brown yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.05 (m, 2H), 2.04 (m, 2H), 1.72 (m, 4H) ppm ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.36, 81.75, 33.12, 21.46 ppm. See also: C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adán, E. Martin and A. W. Kleij, *J. Am. Chem. Soc.* 2013, **135**, 1228.

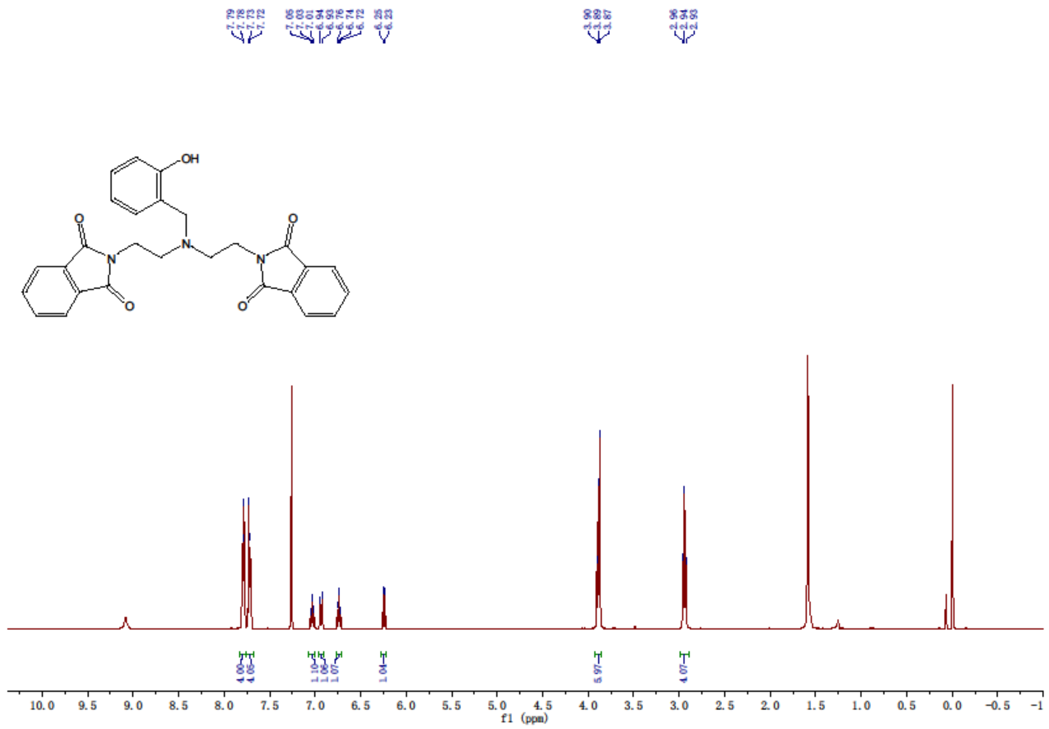
5-methylhexahydrobenzo[d]-1,3-dioxolan-2-one **2q**

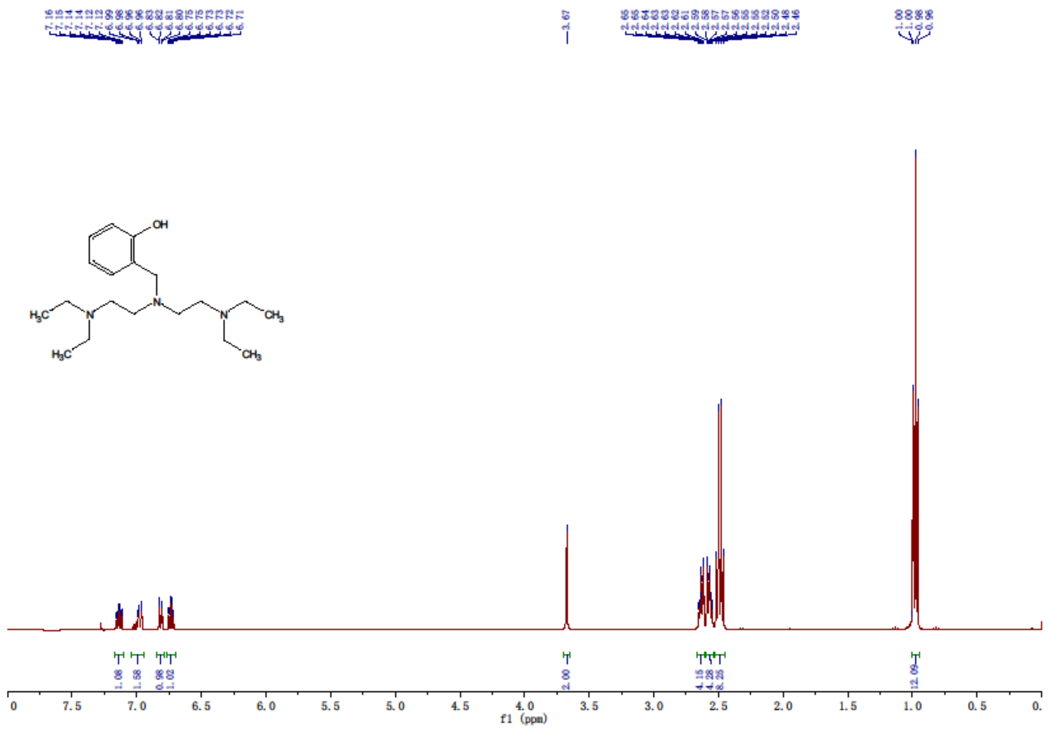


R_f = 0.7 (EA/Hexane = 1:8), Yield 52%, brown yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.71 (m, 4H), 2.34 (m, 1H), 2.27 (m, 1H), 2.14 (m, 2H), 1.77 (m, 3H), 1.66 (m, 3H), 1.38 (m, 2H), 1.22 (m, 2H), 1.00 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.24, 155.21, 76.49, 75.86, 75.60, 75.24, 36.32, 34.40, 28.36, 27.86, 27.42, 27.17, 26.04, 25.10, 21.87, 21.34 ppm. See also: V. Laserna, G. Fiorani, C. J. Whiteoak, E. Martin, E. Escudero-Adán and A. W. Kleij, *Angew. Chem. Int. Ed.*, 2014, **53**, 10416.

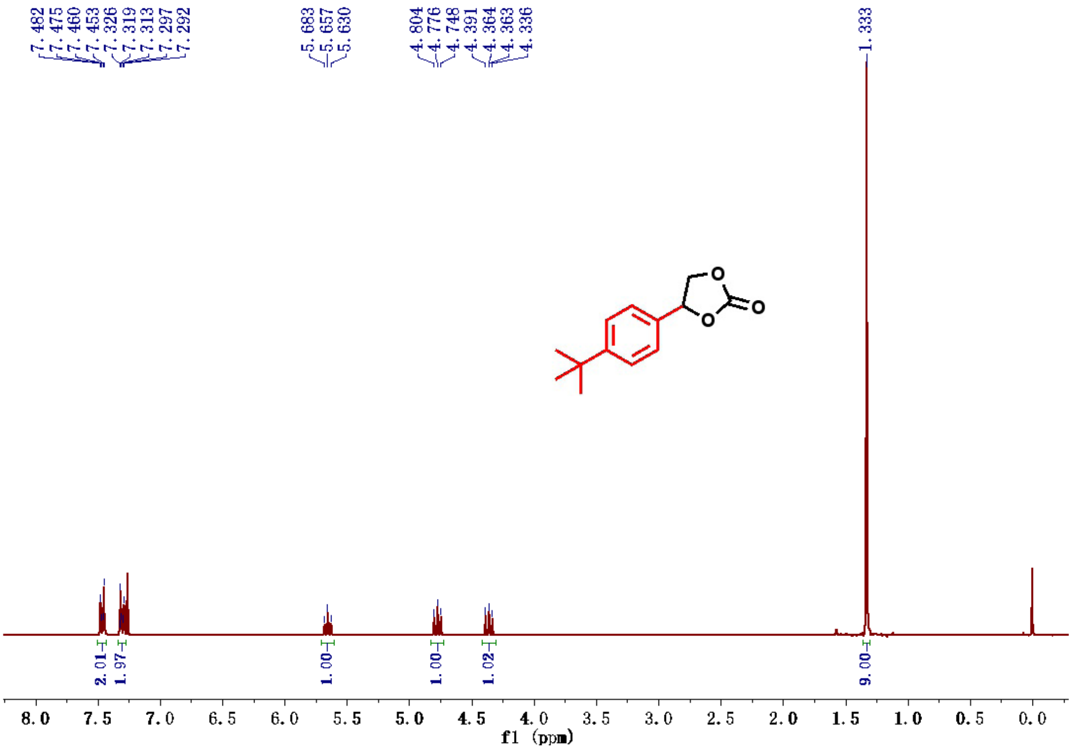
^{1}H- and ^{13}C-NMR spectra

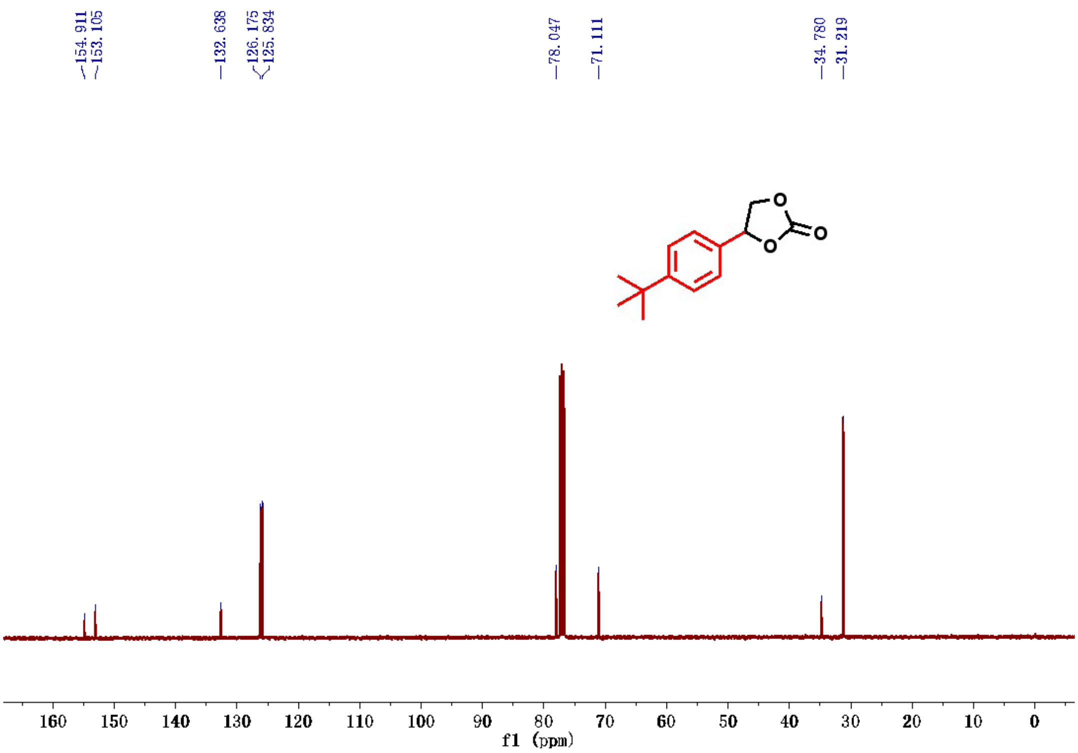




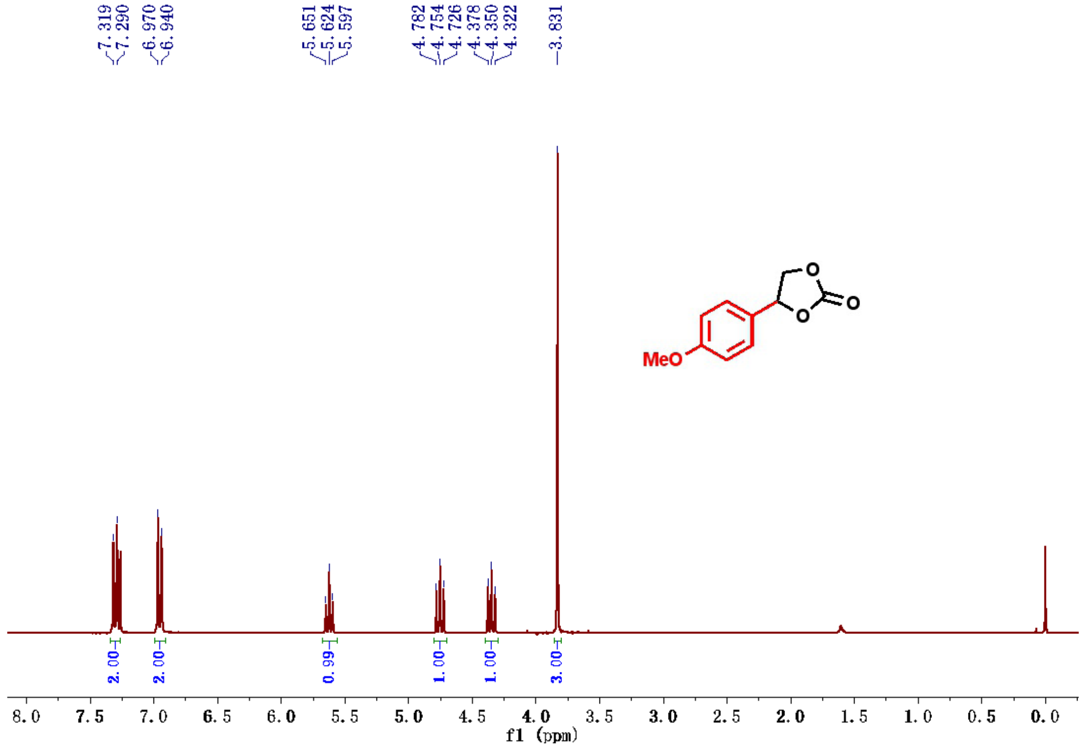


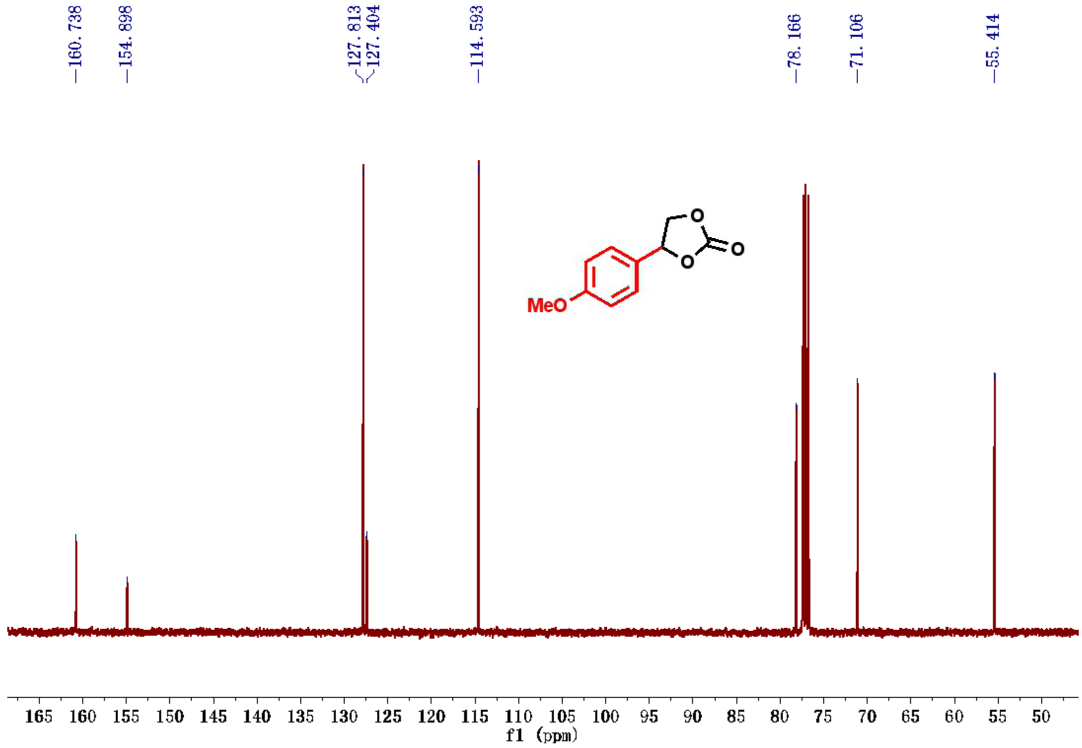
4-(4-tert-butylphenyl)-1,3-dioxolan-2-one **2e**



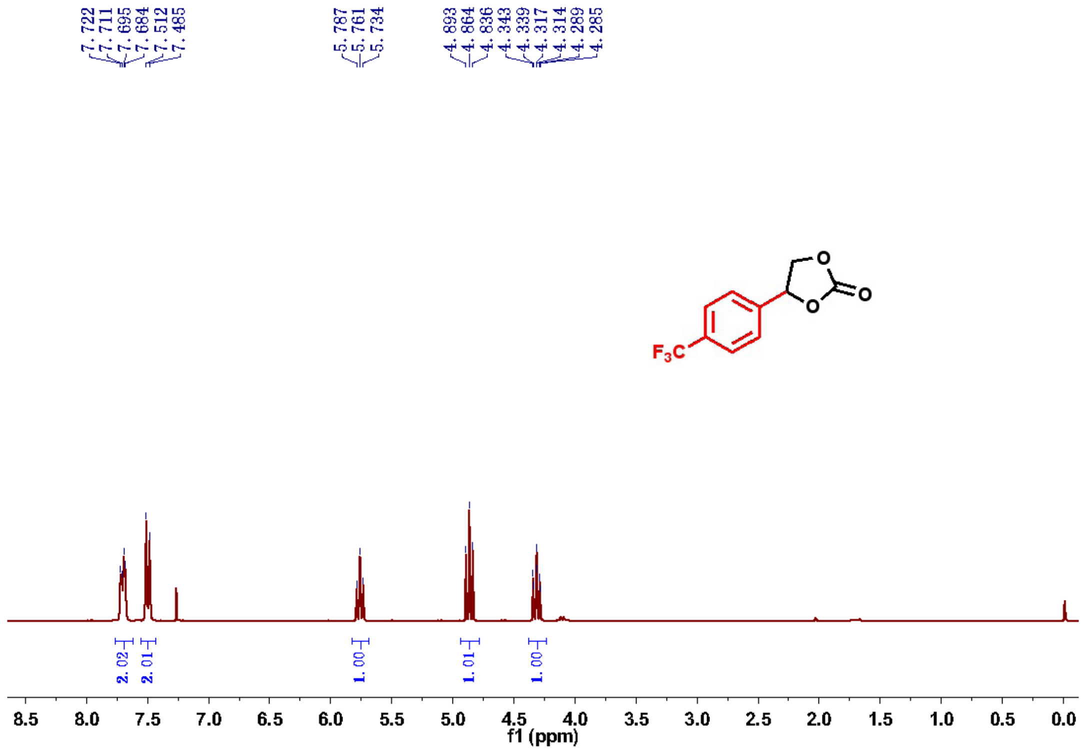


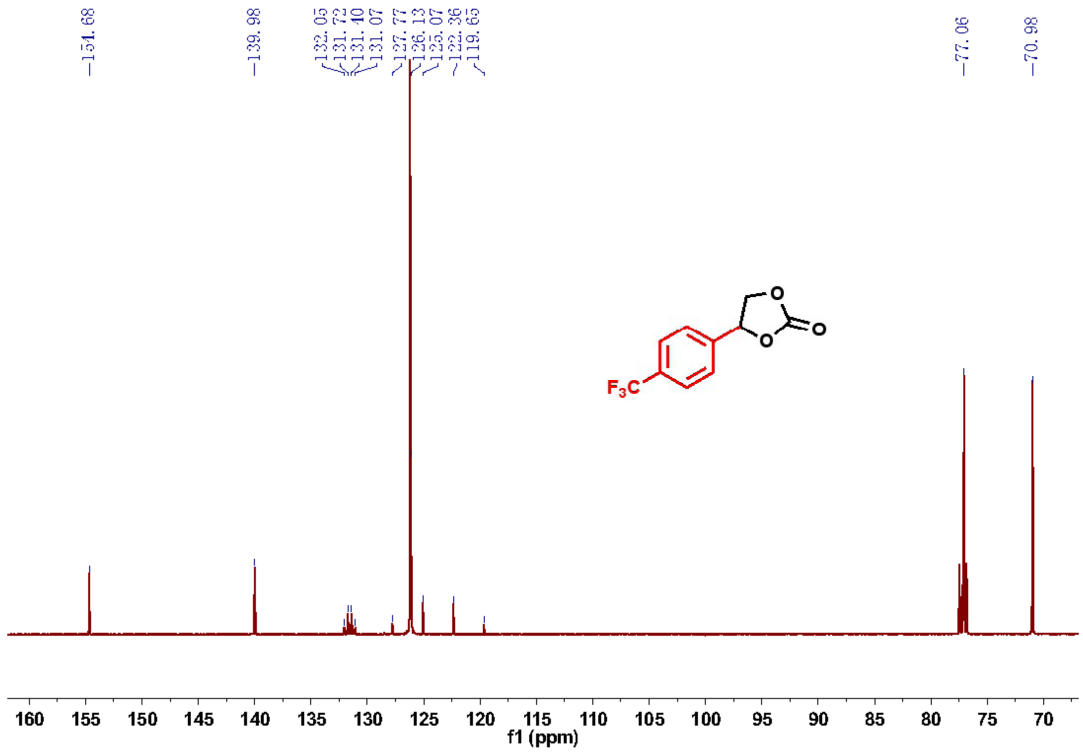
4-(4-methoxyphenyl)-1,3-dioxolan-2-one **2g**



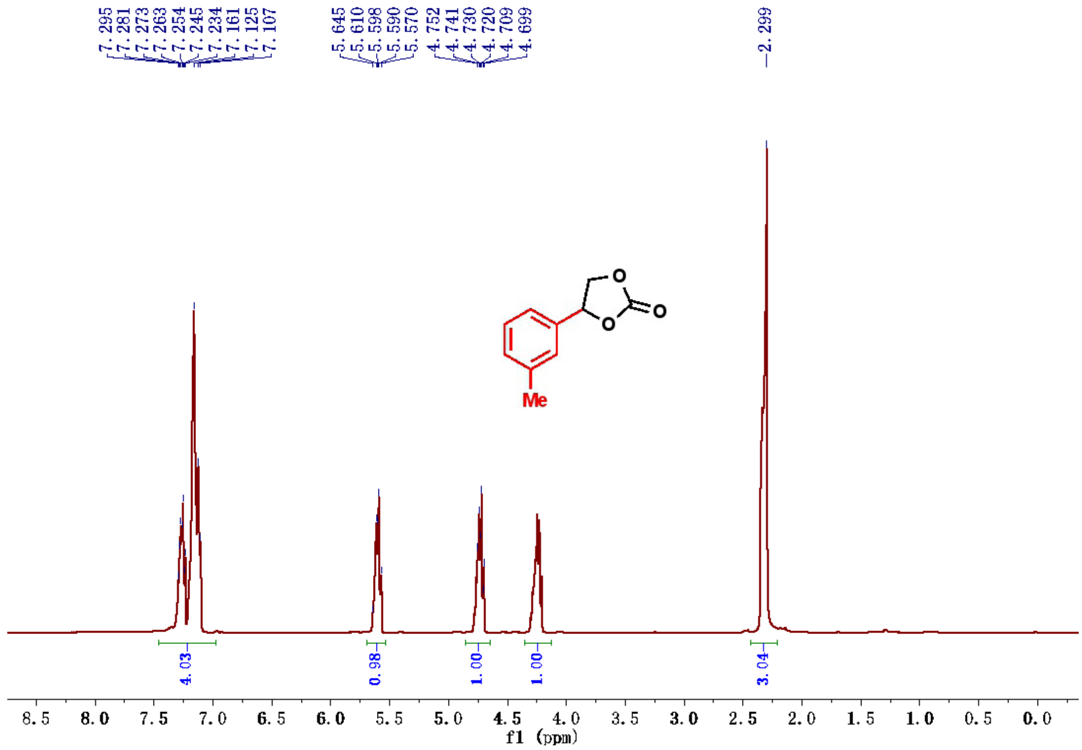


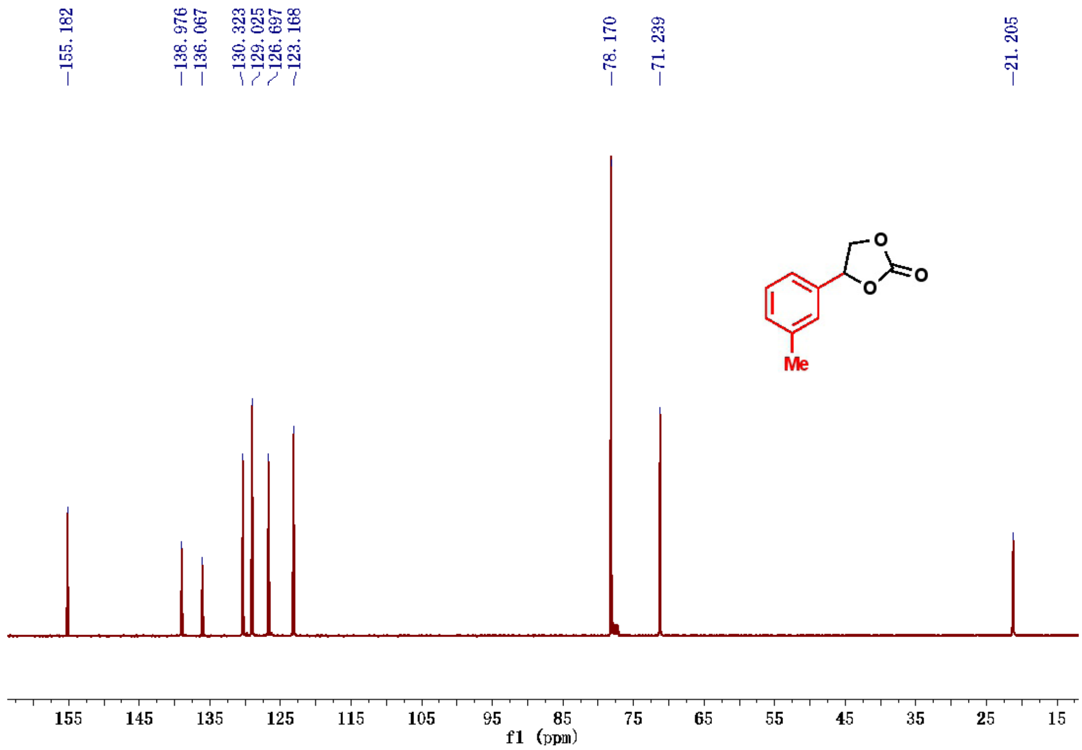
4-(4-(trifluoromethyl)phenyl)-1,3-dioxolan-2-one **2h**



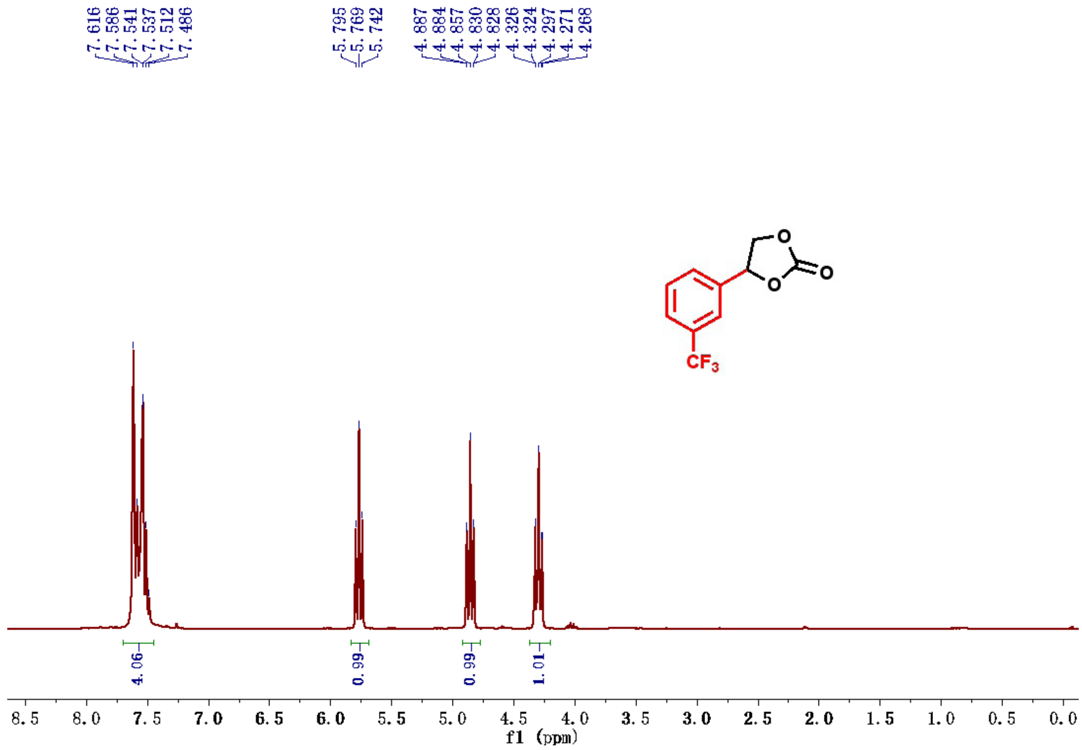


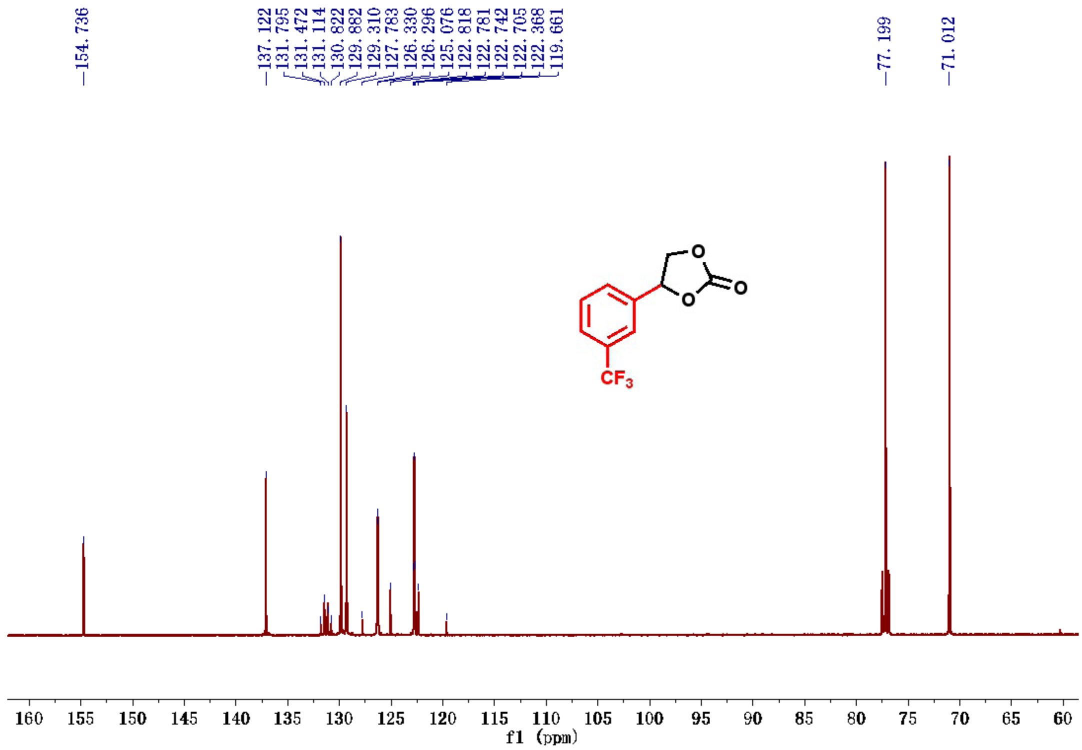
4-m-tolyl-1,3-dioxolan-2-one **2i**



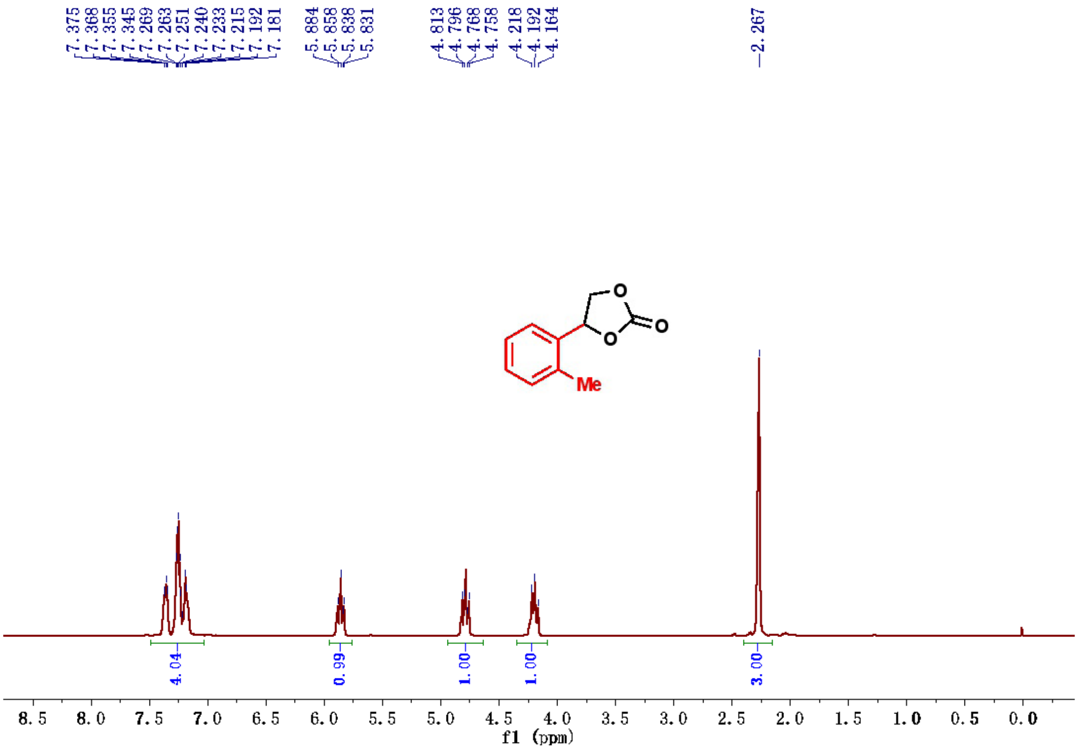


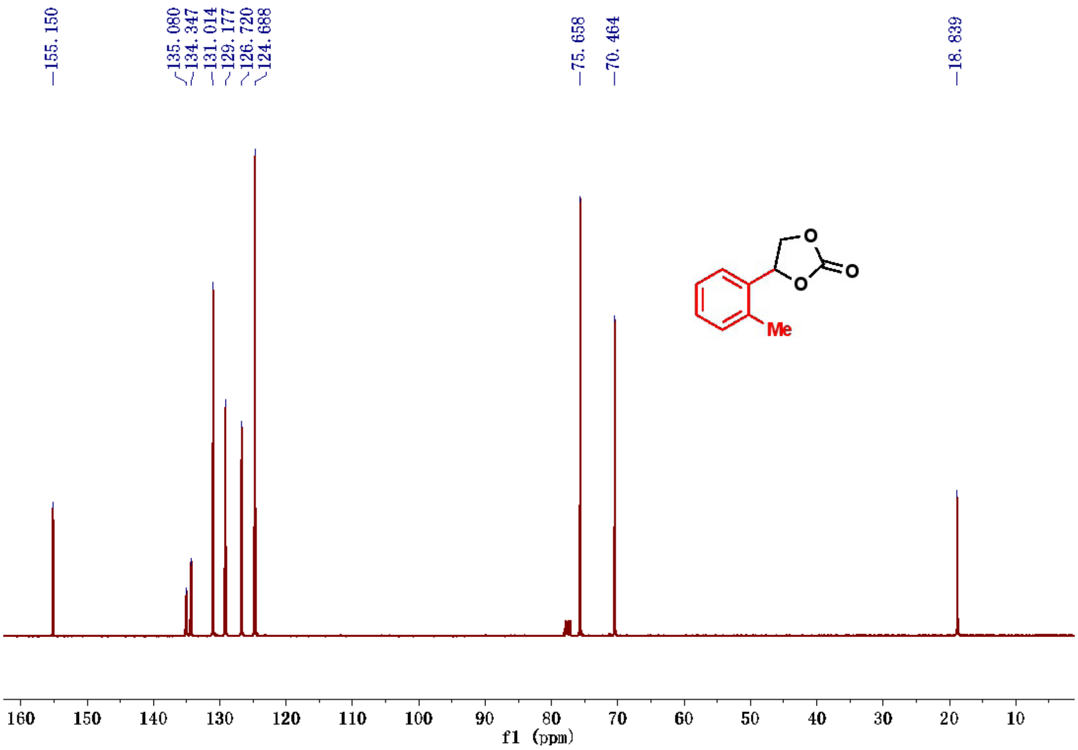
4-(3-(trifluoromethyl)phenyl)-1,3-dioxolan-2-one **2k**



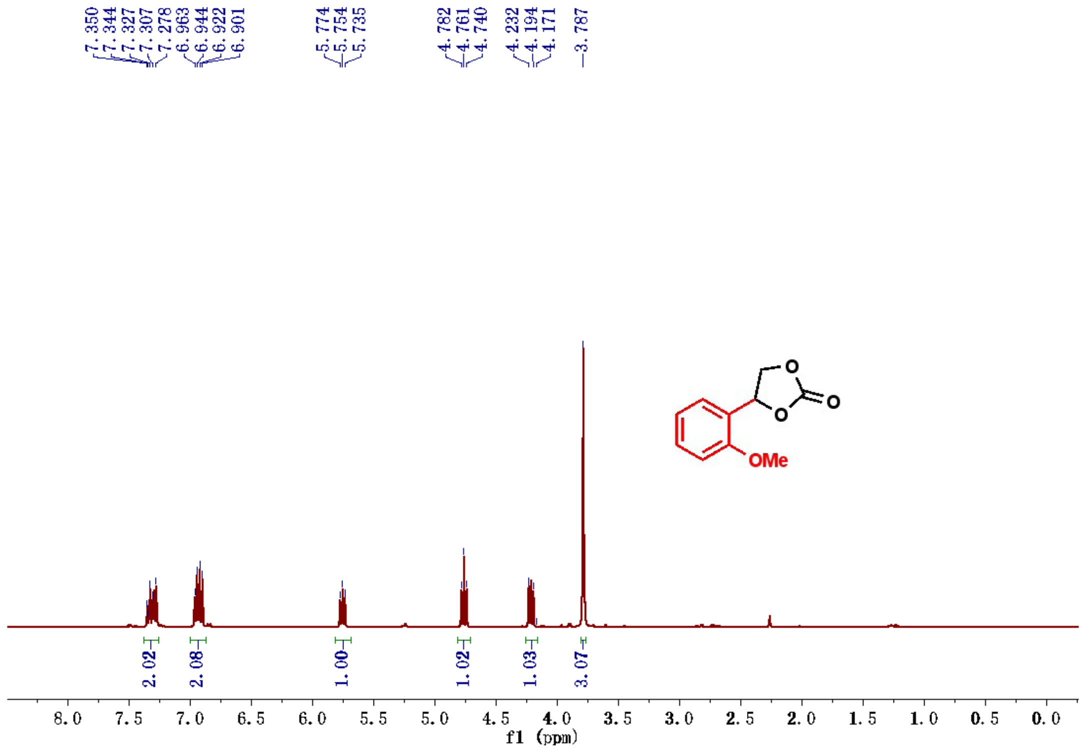


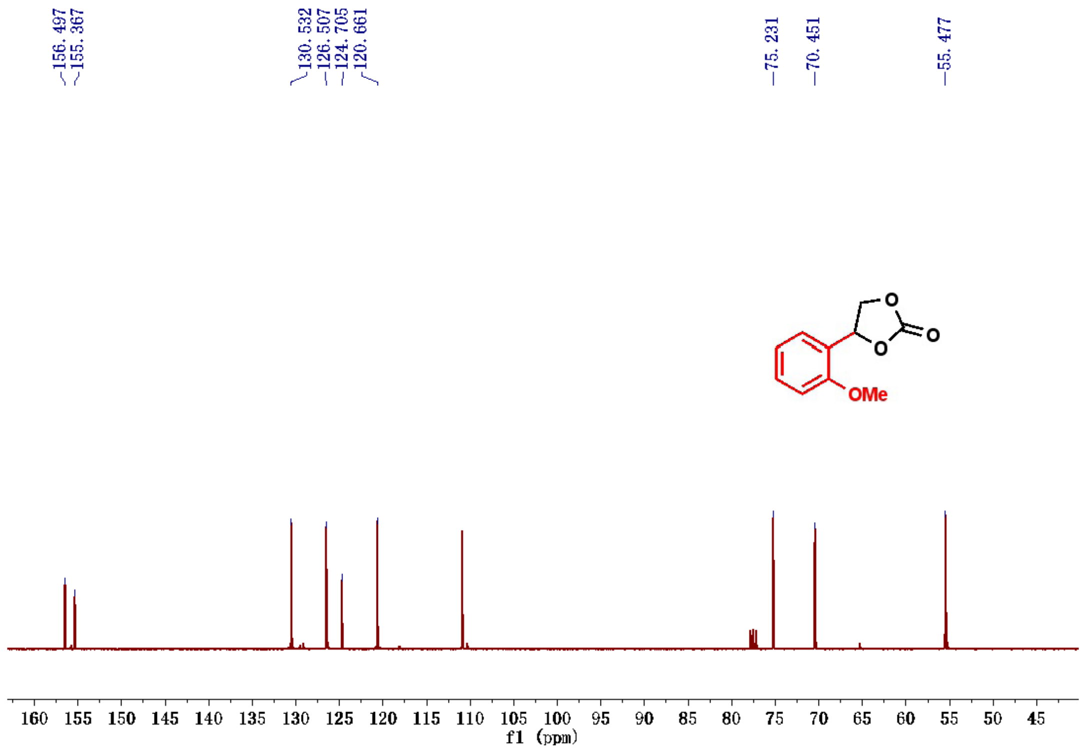
4-o-tolyl-1,3-dioxolan-2-one **2l**



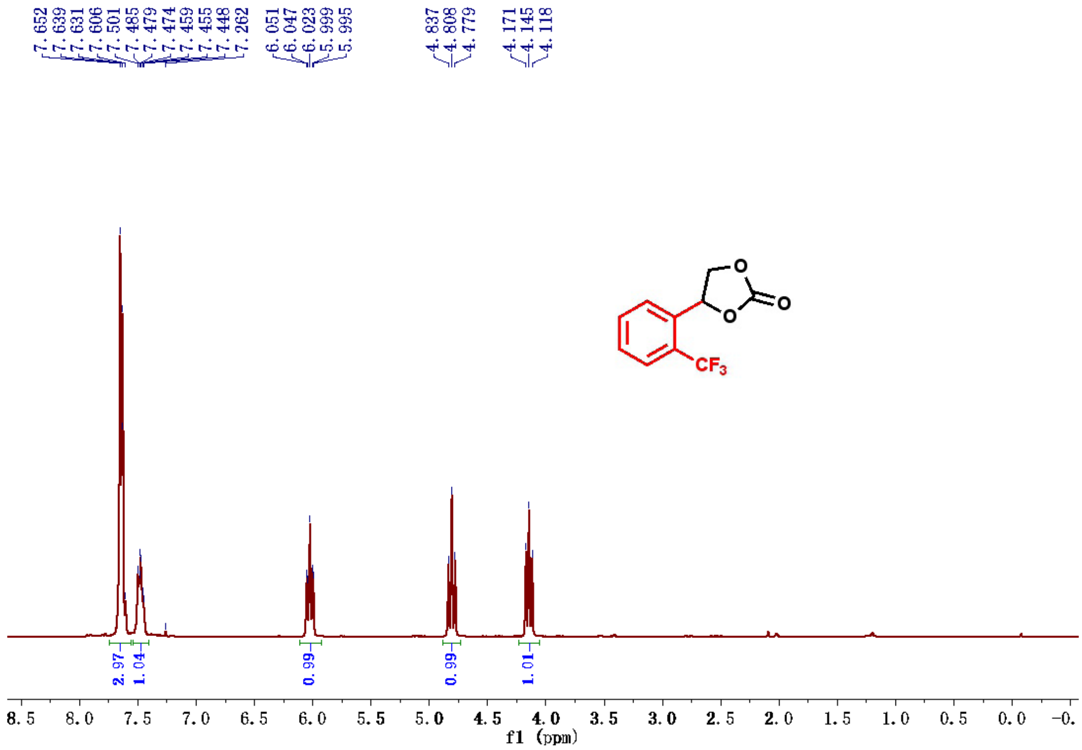


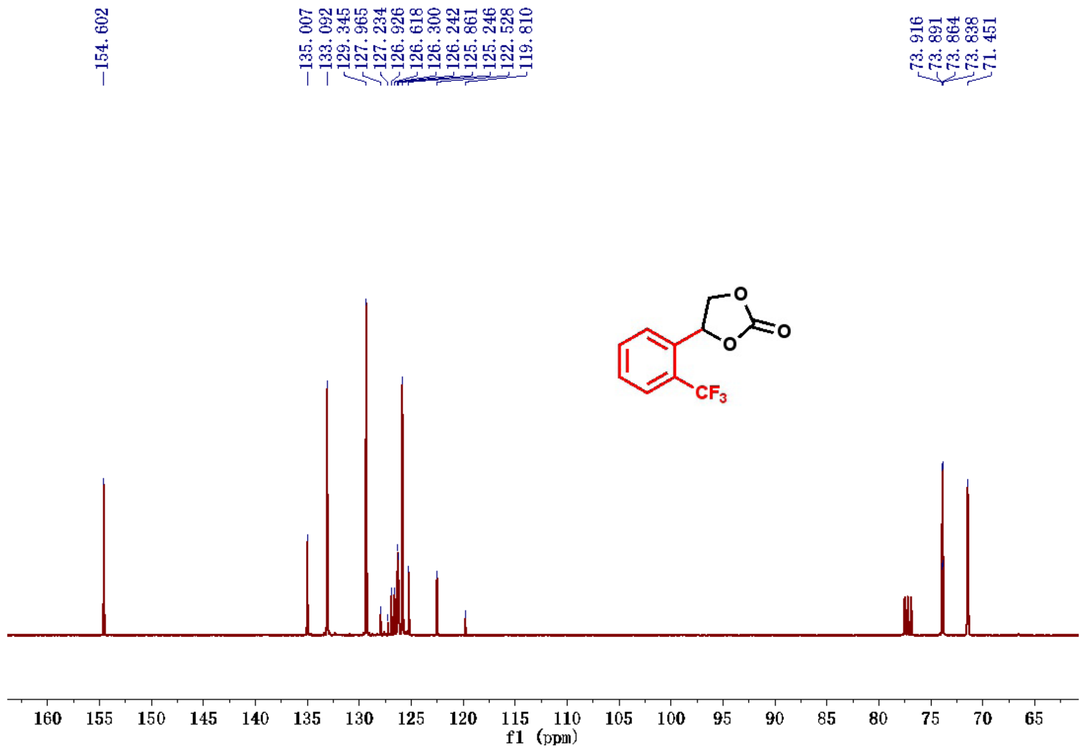
4-(2-methoxyphenyl)-1,3-dioxolan-2-one **2m**





4-(2-(trifluoromethyl)phenyl)-1,3-dioxolan-2-one **2n**





4-(naphthalen-1-yl)-1,3-dioxolan-2-one **2o**