Supporting Information

Highly efficient hydrogenation of levulinic acid to 2-methyltetrahydrofuran over Ni-Cu/Al_2O_3-ZrO_2 bifunctional catalysts

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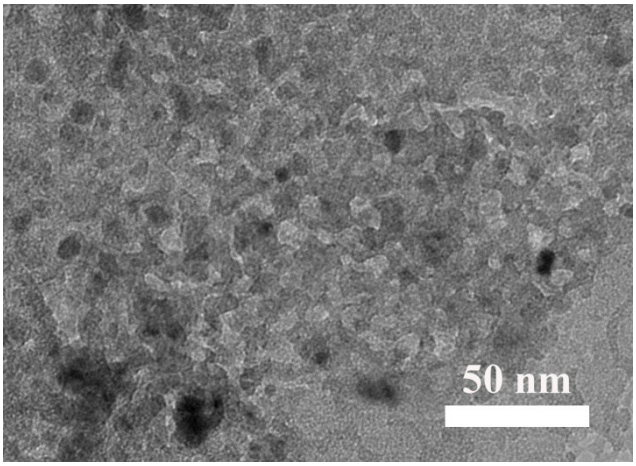


Fig. S1 TEM image of Cu-Ni/Al_2O_3.

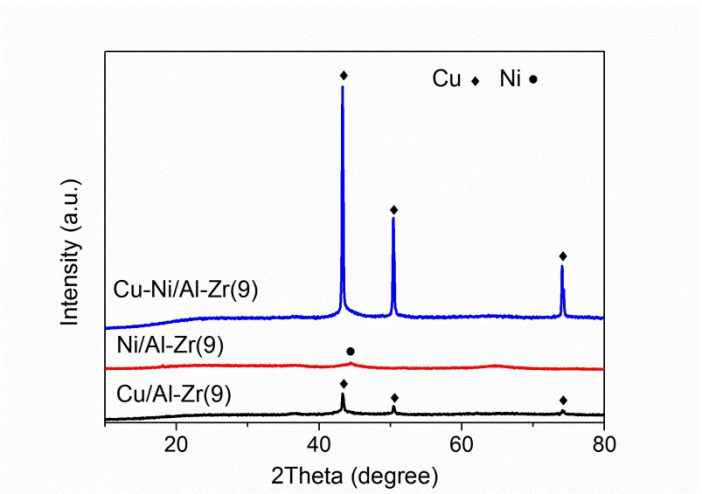


Fig. S2 XRD patterns of the as-prepared monometallic and bimetallic catalysts.

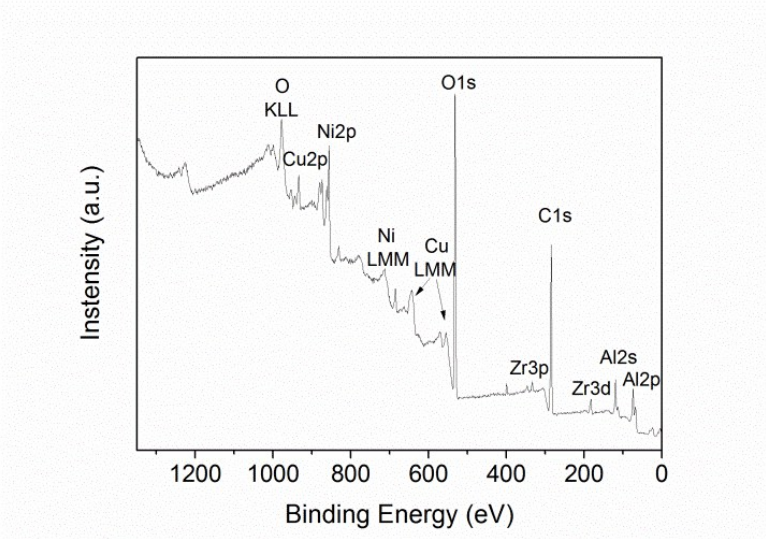


Fig. S3 XPS survey spectrum of the as-prepared Cu-Ni/Al-Zr(9) catalyst.

Table S1 The catalytic performances of Cu-Ni supporting on the as-prepared different carriers[a].

Entry	Catalyst	Zr: Al (mole ratio)	Con. (%)	Sel. (%)			MSR_{MTHF}[b] ($mmol_{MTHF}\ g_{cat.}^{-1}h^{-1}$)
				MTHF	GVL	Others	
1	$Cu\text{-}Ni/ZrO_2$	1:0	100	11.9	88.1	0	0.512
2	Cu-Ni/Al-Zr	1:1	100	42.3	57.7	0	1.821
3	Cu-Ni/Al-Zr	1:3	100	43.7	56.3	0	1.882
4	Cu-Ni/Al-Zr	1:6	100	65.0	25.8	9.2	2.799
5	Cu-Ni/Al-Zr	1:7	100	66.4	9.4	24.2	2.859
6	Cu-Ni/Al-Zr	1:8	100	94.5	0	5.5	4.069
7	Cu-Ni/Al-Zr	1:9	100	99.8	0	0	4.297
8	$Cu\text{-}Ni/Al_2O_3$	0:1	100	91.1	6.7	2.2	3.923

Reaction conditions: 0.1 g of LA, 0.02 g catalyst, 1.5 mL 2-butanol (solvent), 3 MPa H_2, 220 °C, 10 h; b) MSR: Mass-specific rate of MTHF production ($mmol_{MTHF}\ g_{cat.}^{-1}h^{-1}$) (defined as the moles of formed MTHF per gram of catalyst per hour).

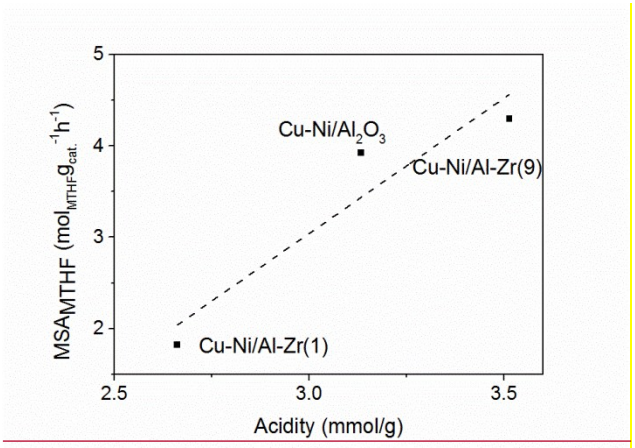


Fig. S4 Mass-specific rates of MTHF production as a function of the acid amount of the catalysts.

Table S1 The catalytic performance of Cu-Ni supporting on the commercial supports.

Entry	Catalyst	Con. (%)	Sel. (%)		
			MTHF	GVL	Others
1	$Cu\text{-}Ni/\alpha\text{-}Al_2O_3$	100	9.7	90.3	-
2	$Cu\text{-}Ni/\gamma\text{-}Al_2O_3$	100	8.8	91.2	-
3	$Cu\text{-}Ni/\ Al_2O_3$ (neutral)	100	10.1	85.4	4.5

a) Reaction conditions: 0.1 g of LA, 0.02 g catalyst, 1.5 mL 2-butanol (solvent), 3 MPa H_2, 220 °C, 10 h; b) $\alpha\text{-}Al_2O_3$, $\gamma\text{-}Al_2O_3$ and Al_2O_3 (neutral) were obtained from the Innochem Sci. &Tech. Co. Ltd. (Beijing, China), and the contents of both Cu and Ni in the catalysts were 10 wt.%.

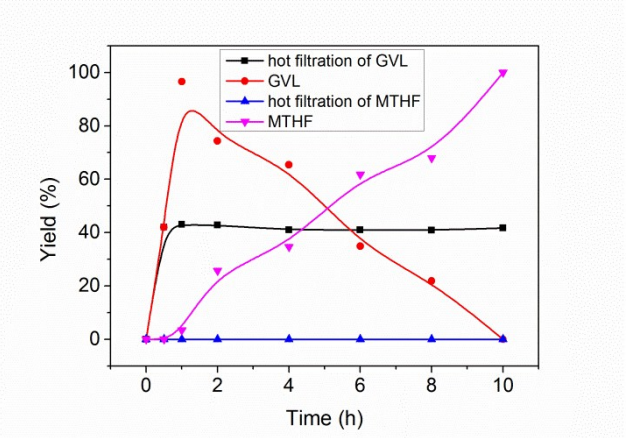


Fig. S4 Kinetic profiles (a) and hot filtration test results for the hydrogenation of levulinic acid with Cu-Ni/Al-Zr(9) catalyst. Hot filtration test condition: 0.1 g substrate, 1.5 mL 2-butanol, 20 mg Cu-Ni/Al-Zr(9), 220 °C; catalyst filtered after 30 minutes at 220 °C.

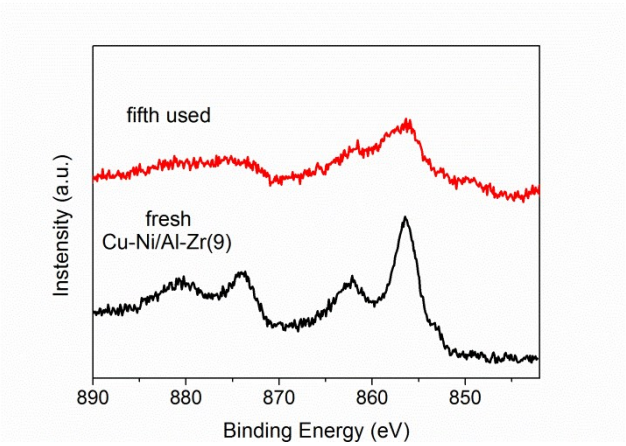


Fig. S5 Ni XPS spectra of the fresh and reused Cu-Ni/Al-Zr(9) catalyst containing 10 wt.% Cu and 10 wt.% Ni.

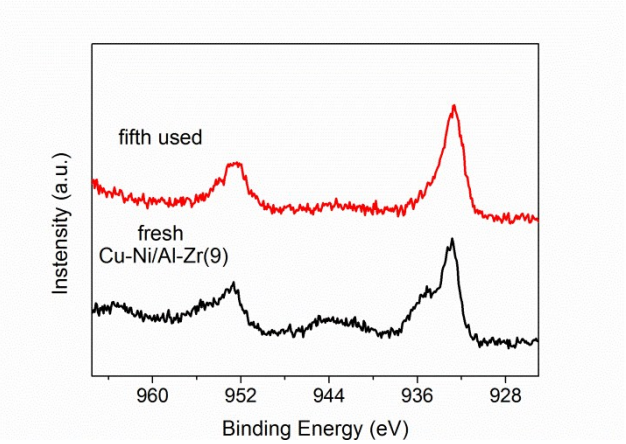


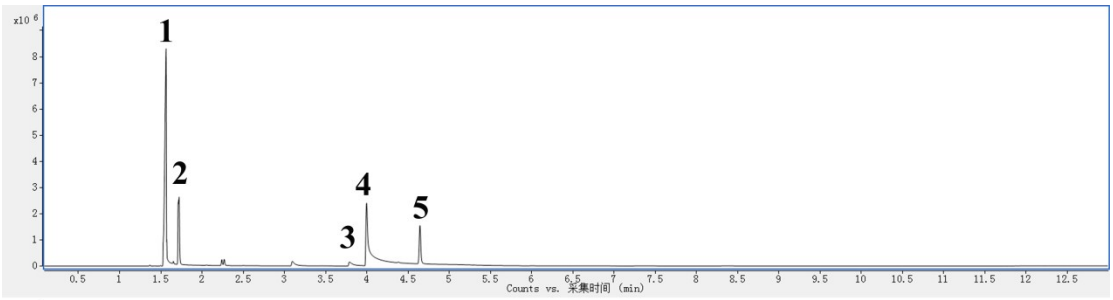
Fig. S6 Cu XPS spectra of the fresh and reused Cu-Ni/Al-Zr(9) catalyst containing 10 wt.% Cu and 10 wt.% Ni.

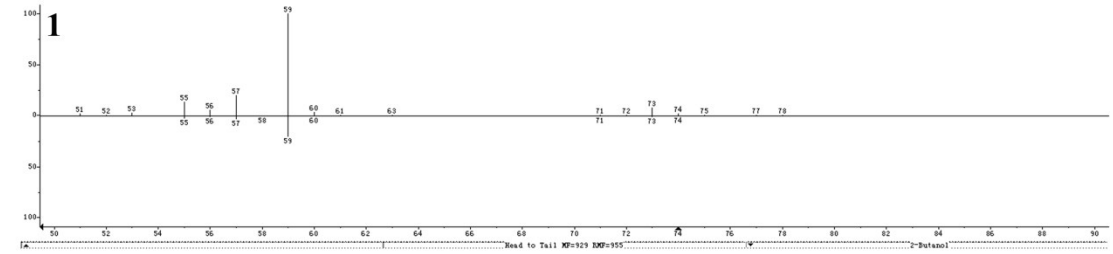
Table S2 Typically catalytic conversions of LA into MTHF.

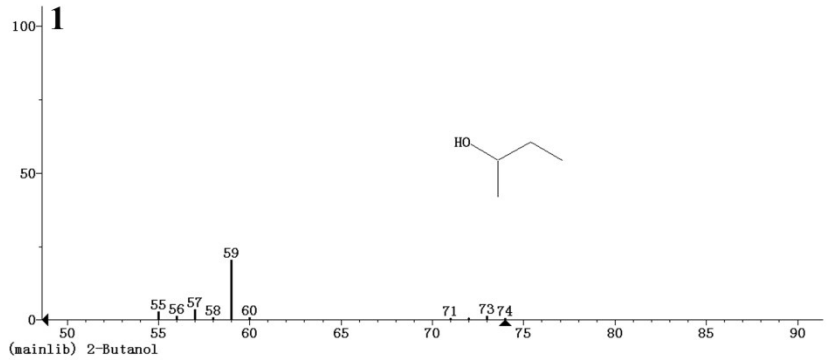
Ent.	Catalyst	Additive	T (°C)	H_2 (MPa)	t (h)	Con.(%) / Sel. (%)	References
1	Homogeneous catalyst 0.1 mol% $[Ru(acac)_3]$, 0.2 mol% triphos	1 mol% acidic ionic liquid& NH_4PF_6	160	10	18	100/92	W. Leitner et al, Angew. Chem. Int. Ed. 2010, 49, 5510-5514.
2	Homogeneous catalyst 0.5 mol% $[Ru(acac)_3]$ 0.5 mol% N-triphos^{Ph},	1.0mol % $HN(Tf)_2$	150	6.5	25	100/87	A. Phanopoulos, et al, ACS Catal. 2015, 5, 2500-2512.
3	Homogeneous catalyst 0.1 mol% $[Ru(acac)_3]$ 0.15 mol% N-triphos	0.25 mol% $Al(OTf)_3$	140	5.5	30	100/88	M. Beller, Angew. Chem. Int. Ed. 2015, 54, 5196-5200.
4	Heterogeneous catalyst Pd-Re/C (Pd: 5 wt.%, Re: 5 wt.%)	-	200 - 250	10	Continuous flow reator	100/ up to 90%	D. C. Elliott, J. G. Frye, US, 5883266, 1998.
5	Heterogeneous catalyst Cu-MINT (Cu: 0.51 wt.%)	-	150	30 min microwave irradiation, 300 W	0.5	90/75	J. M. Bermudez, et al, Green Chem., 2013, 15, 2786-2792.
6	Heterogeneous catalyst Ru/C (Ru: 5 wt.%)	-	two-step hydrogenation 1) H_2 1.2 MPa, 190 °C, 45 min 2) H_2 10 MPa, 190 °C, 4 h			90/61	M. G. Al-Shaal, et al, Green Chem., 2014, 16, 1358-1364.
7	Heterogeneous catalyst Cu/SiO_2 (Cu: 80 wt.%)	-	265	2.5	WHSV= 0.513 h^{-1}; molar ratio H_2/LA= 80; TOS= 100 h	100/64	P. P. Upare, et al, ChemSusChem, 2011, 4, 1749-1752.
8	Heterogeneou	-	250	7	5	100/75	I. Obregon, et al,

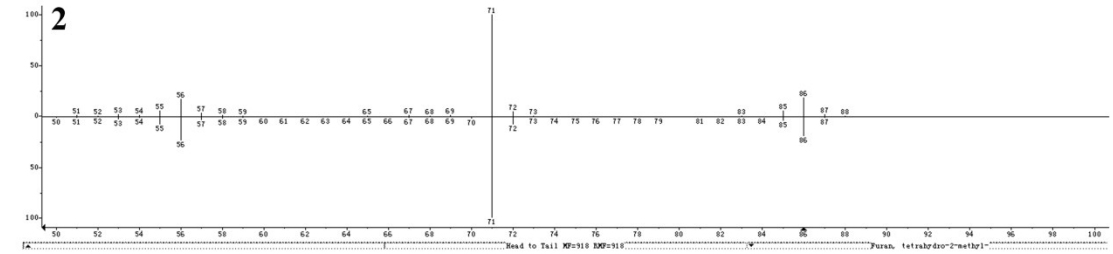
	s catalyst Cu-Ni/Al_2O_3 (Cu: 12 wt.% Ni: 23 wt.%)						ChemSusChem, 2015, 8, 3483-3488.
9	Heterogeneous catalyst Ni–Cu/Al_2O_3 (Cu: 12 wt.% Ni: 23 wt.%)	-	250	4	20	100/80	I. Obregjn, et al, ChemSusChem, 2016, 9, 2488-2495
10	Heterogeneous catalyst Pt−Mo/H-β (Pt: 2 mol %, Pt/Mo=15)		130	5	24	>99/86	T. Mizugaki, ACS Sustainable Chem. Eng., 2016, 4, 682-685
11	Heterogeneous catalyst Cu/Al_2O_3-SiO_2 (Cu: 20.3 wt.%)	-	250	fixed bed reactor WHSV of ethyl levulinate: 0.6 h^{-1} molar ratio of H_2 to EL: 50 (mol/mol)		99.9/65.2	J, Zheng, Sci. Rep., 2016, 6, 28898.
12	Heterogeneous catalyst Cu-Ni/Al-Zr(9) (Cu: 10 wt.%, Ni: 10 wt.%)	-	220	3	10	100/99.8	This work

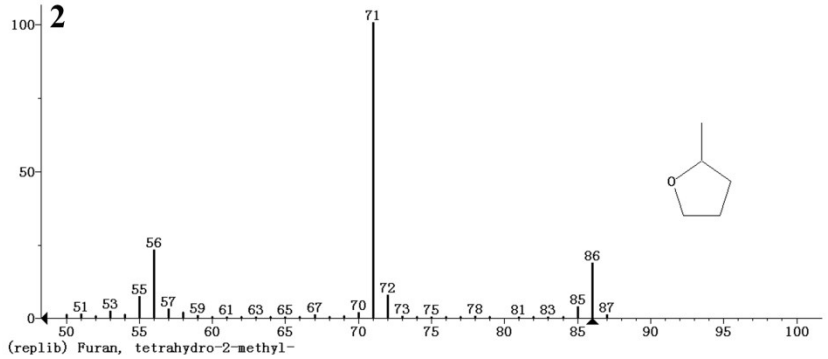
Fig. S7 GC-MS spectra of the reaction mixture with Cu-Ni/Al-Zr(9) catalyst.

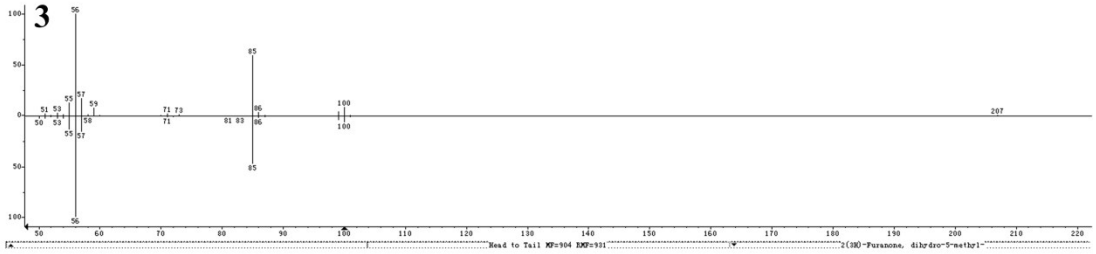








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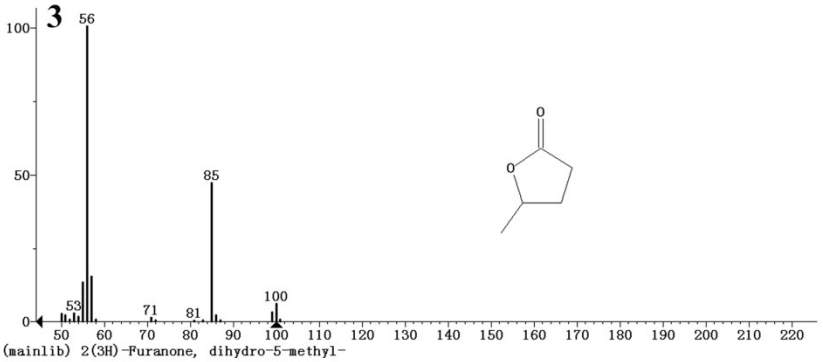
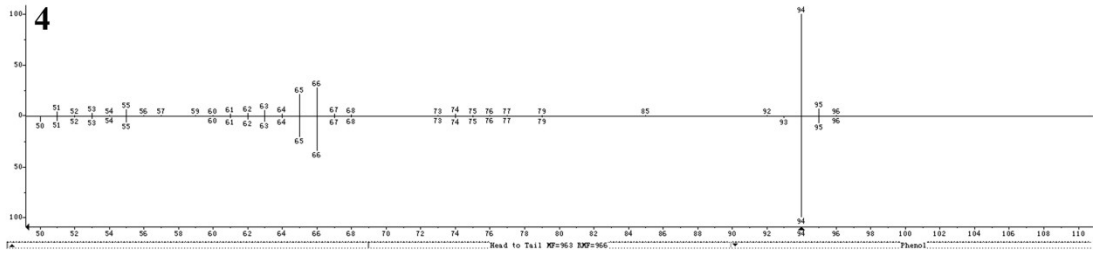
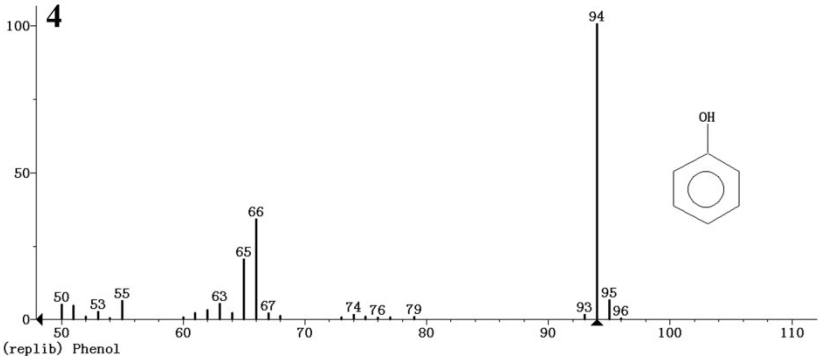
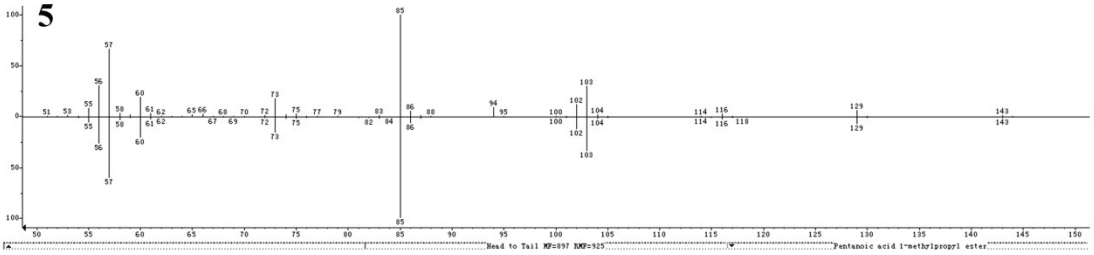
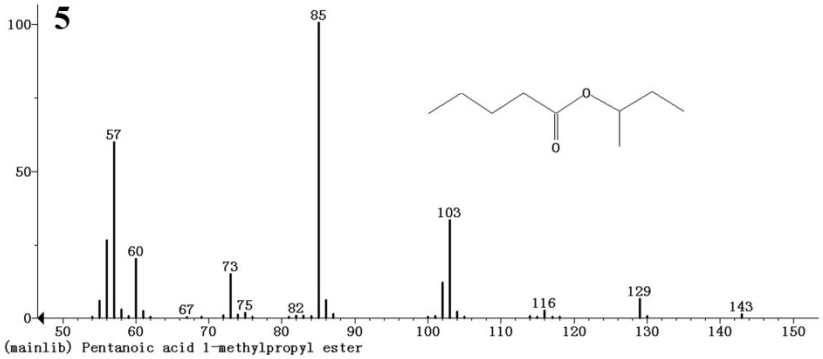
Head to Tail MF=904 RMF=931
2(3H)-Furanone, dihydro-5-methyl-


3
56
85
53
71
81
100
O
O
(mainlib) 2(3H)-Furanone, dihydro-5-methyl-


4
Head to Tail MF=963 RMF=966
Phenol


4
94
OH
66
65
50
53
55
63
67
74
76
79
93
95
96
(replib) Phenol


5
Head to Tail MF=897 RMF=925
Pentanoic acid 1-methylpropyl ester


5
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(mainlib) Pentanoic acid 1-methylpropyl ester