Electronic Supplementary Material (ESI) for Chemical Science.

Supplementary Information

Synthesis of Ethanol from Aryl Methyl Ether/Lignin, CO_2 and H_2

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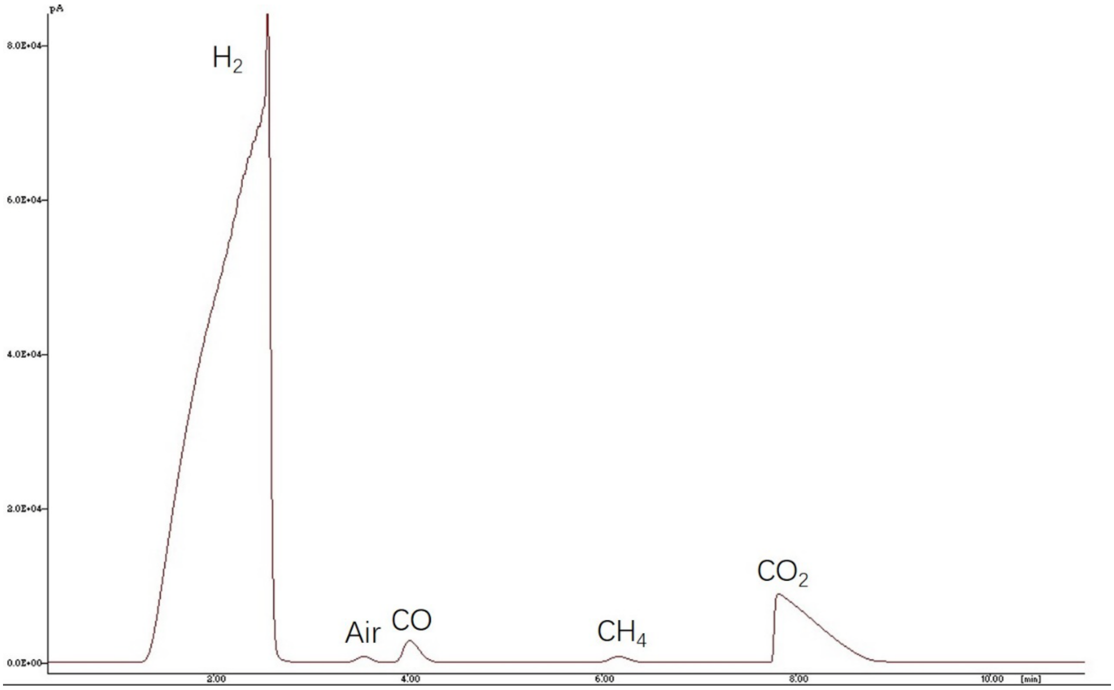


Fig. S1 GC graph of the gaseous sample after the reaction of CO_2 and H_2.

Reaction condition: 20 μmol $[RuCl_2(CO)_3]_2$ (based on the metal), 20 μmol triphos, 2.2 mmol LiI, 2 mL DMI , 3 MPa CO_2 and 5 MPa H_2 (at room temperature), 190 ^{o}C,10h.

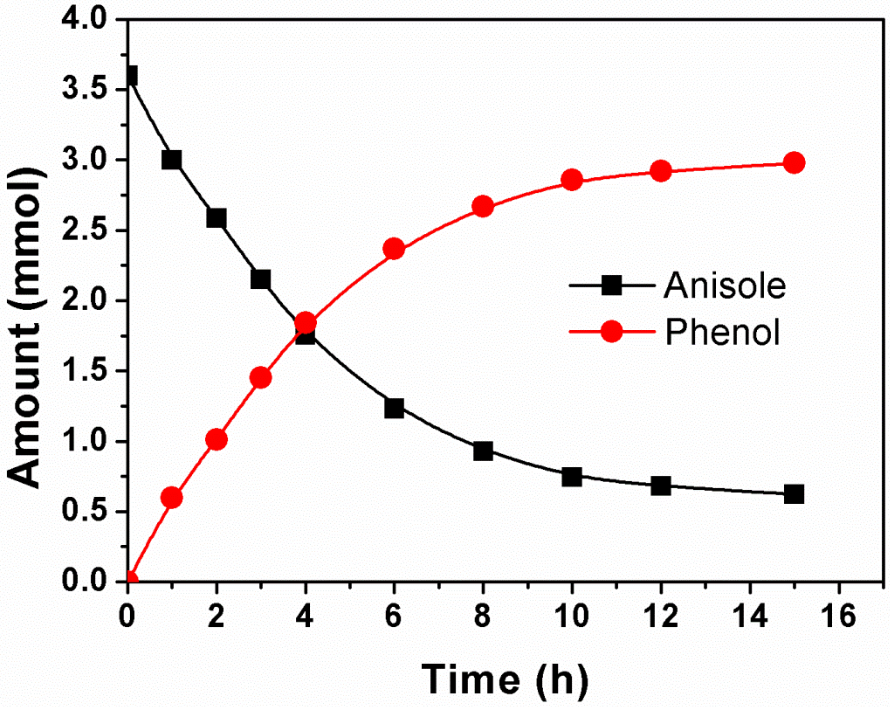
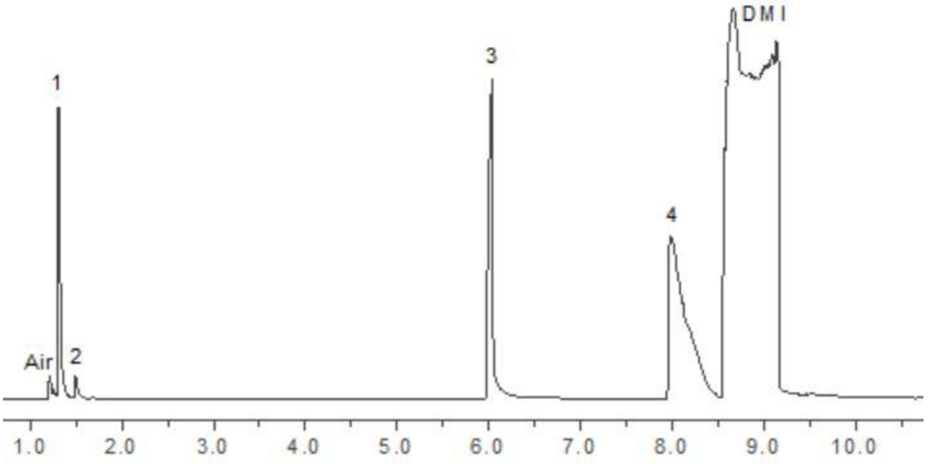


Fig. S2 Anisole decomposition and phenol generation during the reaction. Reaction conditions: 20 μmol $[RuCl_2(CO)_3]_2$ and 60 μmol $Co_2(CO)_8$ (based on the metal), 20 μmol triphos, 2.2 mmol LiI, 2 mL DMI, 3.6 mmol anisole, 3 MPa CO_2 and 5 MPa H_2 (at room temperature), 190 ^oC.



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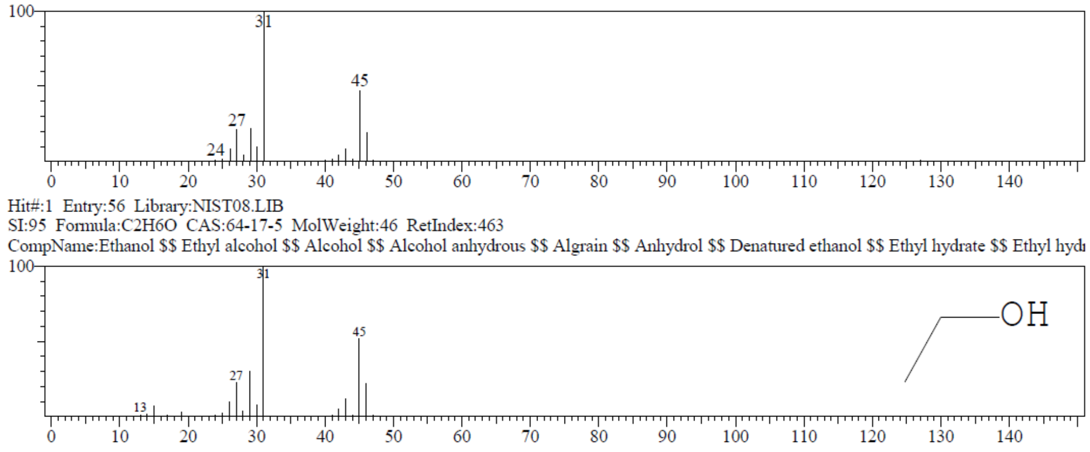

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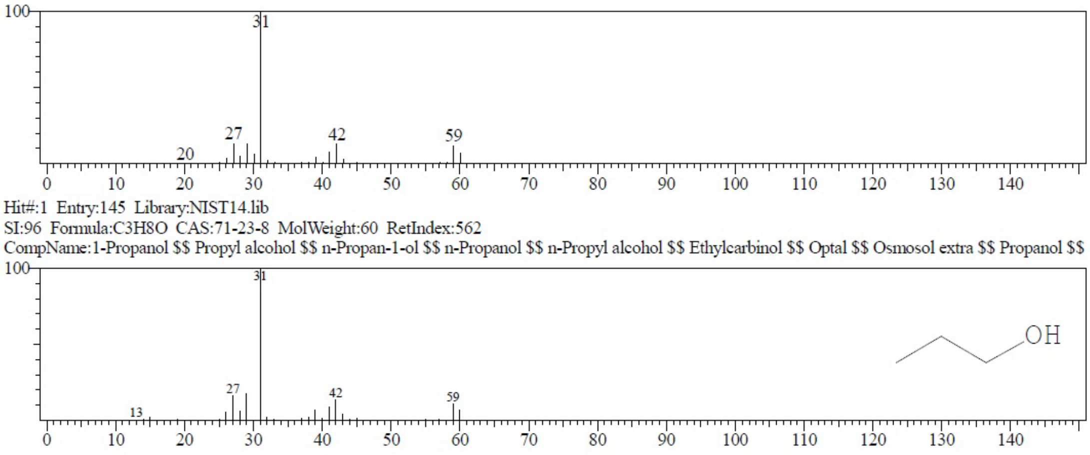
Target 2



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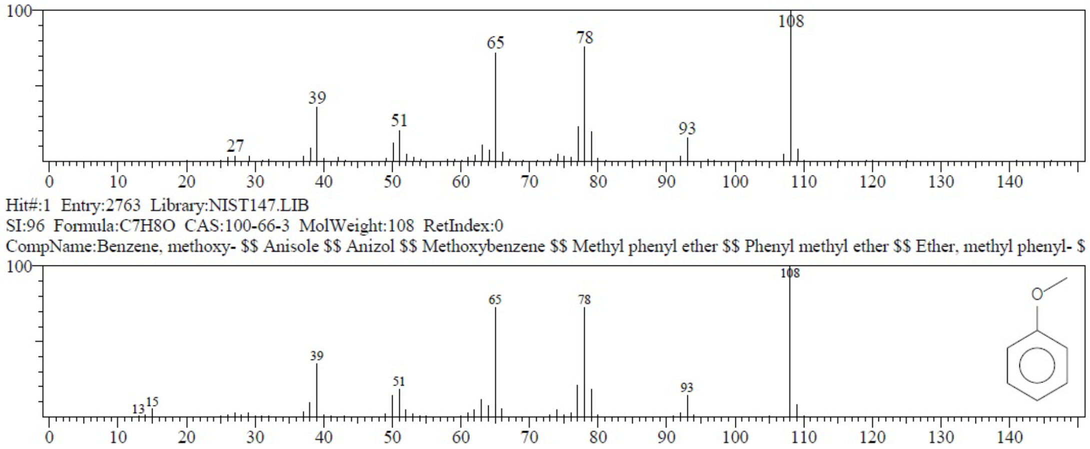
Target 3



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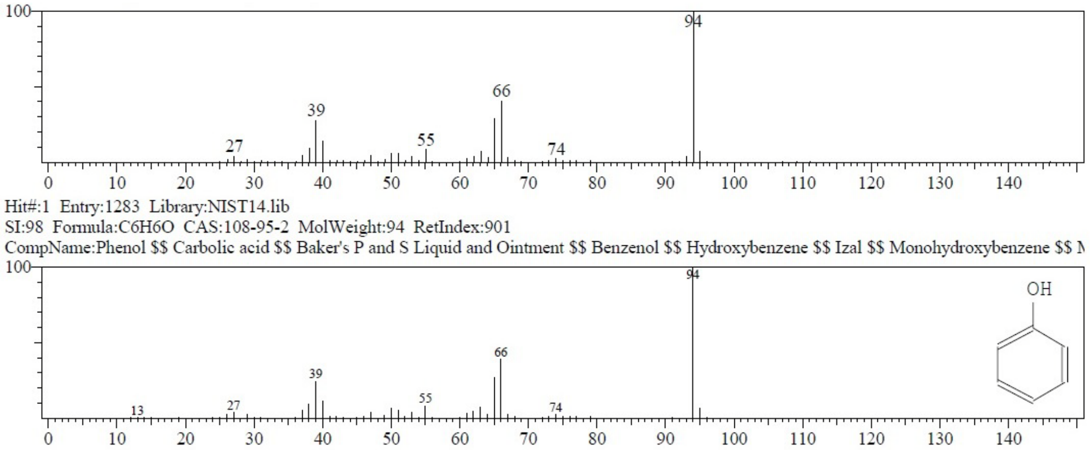
Target 4



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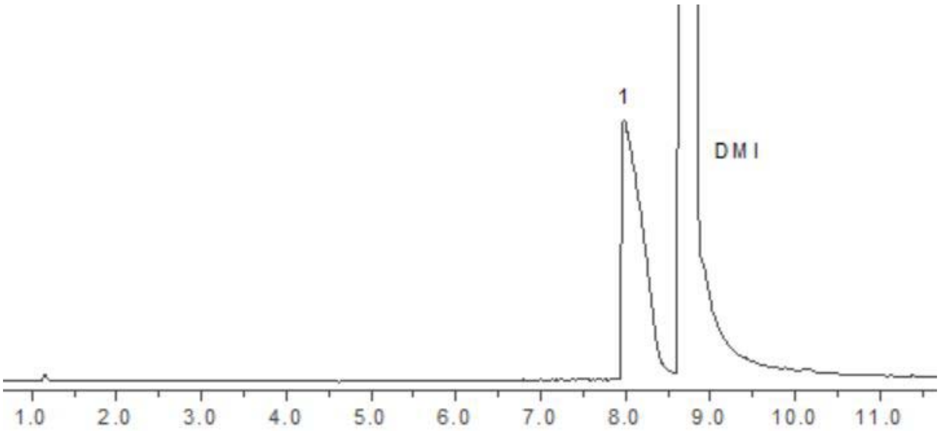
CompName:Phenol $$ Carbolic acid $$ Baker's P and S Liquid and Ointment $$ Benzenol $$ Hydroxybenzene $$ Izal $$ Monohydroxybenzene $$

Fig. S3 The GC-MS result of the reaction of entry 1 of Table 1. Reaction condition: 20 μmol $[RuCl_2(CO)_3]_2$ and 60 μmol $Co_2(CO)_8$ (based on the metal), 20 μmol triphos, 2.2 mmol LiI, 2 mL DMI, 3.6 mmol anisole, 3 MPa CO_2 and 5 MPa H_2 (at room temperature), 190 ^{o}C, 10 h.



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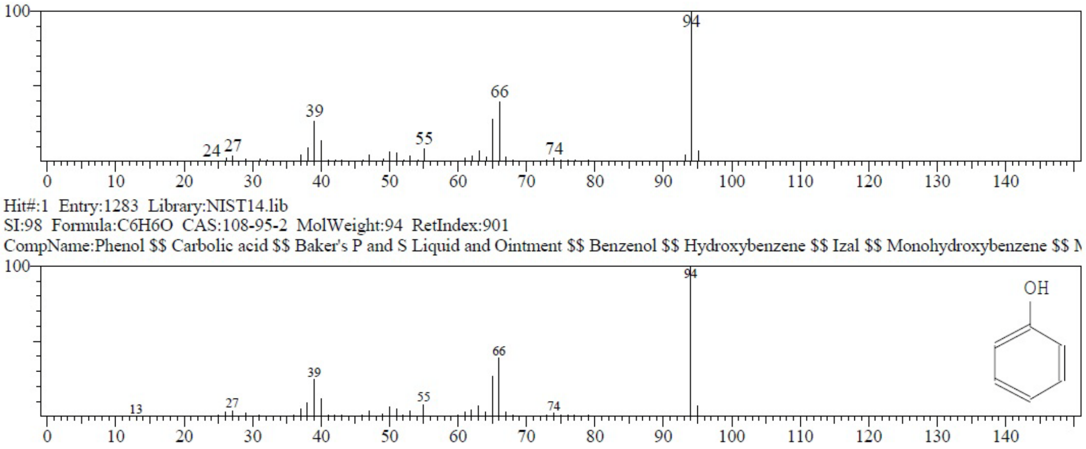

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SI:98  Formula:C6H6O  CAS:108-95-2  MolWeight:94  RetIndex:901
CompName:Phenol $$ Carbolic acid $$ Baker's P and S Liquid and Ointment $$ Benzenol $$ Hydroxybenzene $$ Izal $$ Monohydroxybenzene $$
```

Fig. S4 The GC-MS result of the reaction using 3 mmol phenol instead of 3.6mmol anisole. Reaction condition: 20 μmol $[RuCl_2(CO)_3]_2$ and 60 μmol $Co_2(CO)_8$ (based on the metal), 20 μmol triphos, 2.2 mmol LiI, 2 mL DMI, 3 mmol phenol, 3 MPa CO_2 and 5 MPa H_2 (at room temperature), 190 ^{o}C, 10 h.

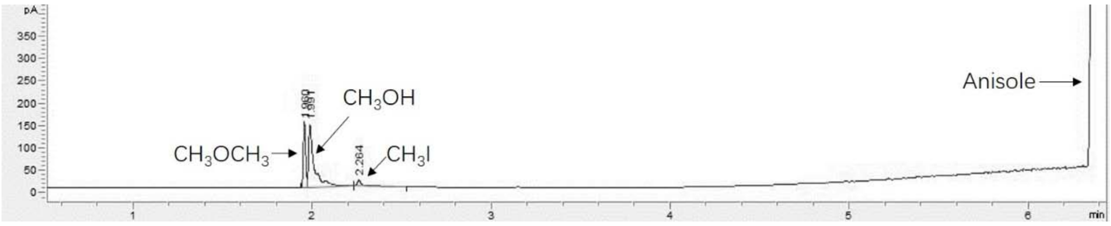


Fig. S5 GC graph of the liquid sample after the reaction of anisole and LiI.
Reaction condition: 2.2 mmol LiI, 2 mL DMI, 3.6 mmol anisole, 3 MPa CO_2 and 5 MPa H_2 (at room temperature), 190 ^{o}C, 10 h.

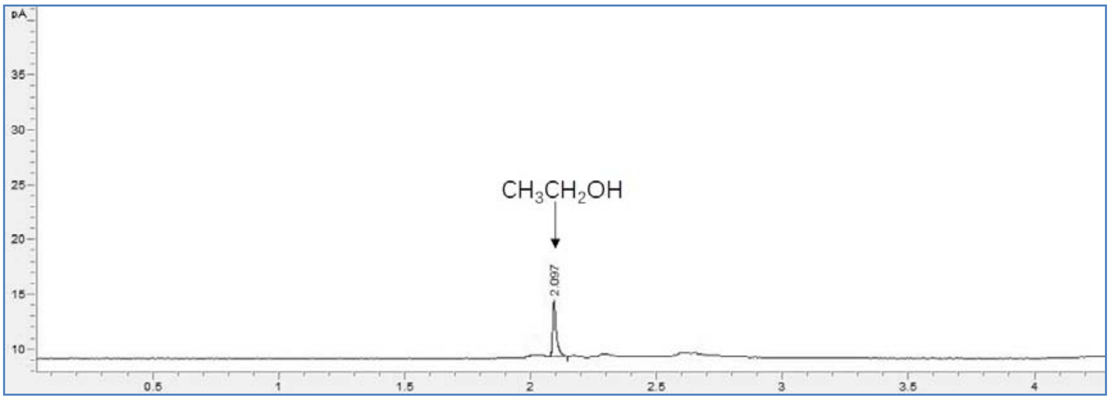
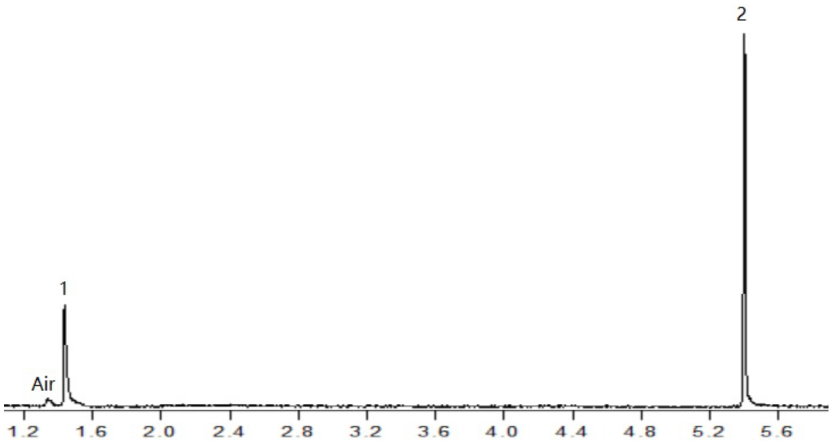


Fig. S6 GC graph of the liquid sample after the reaction of CH_3I, CO and H_2. Reaction condition: 20 μmol $[RuCl_2(CO)_3]_2$ and 60 μmol $Co_2(CO)_8$ (based on the metal), 20 μmol triphos, 2.2 mmol LiI, 2 mL DMI, 10 uL CH_3I, 0.8 MPa CO and 5 MPa H_2 (at room temperature), 190 ^oC,10 h.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1
Air
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2.4
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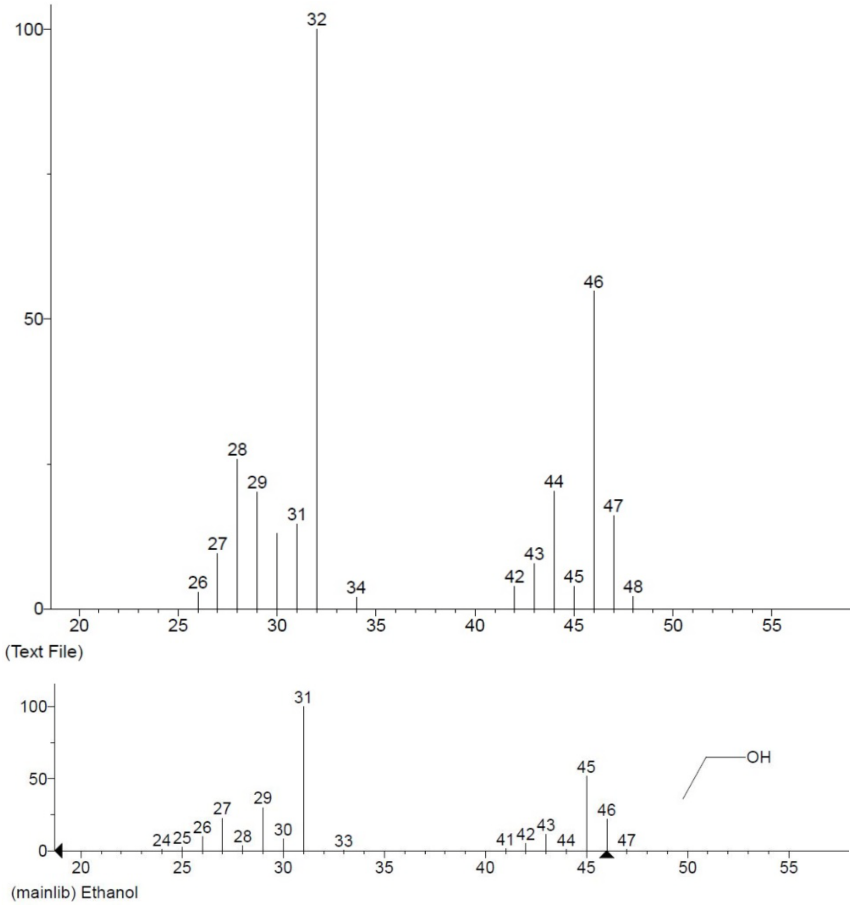
3.2
3.6
4.0
4.4
4.8
5.2
5.6

Target 1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48
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100
50
0
31
45
29
27
46
26
43
24
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45
50
55
(mainlib) Ethanol

Target 2

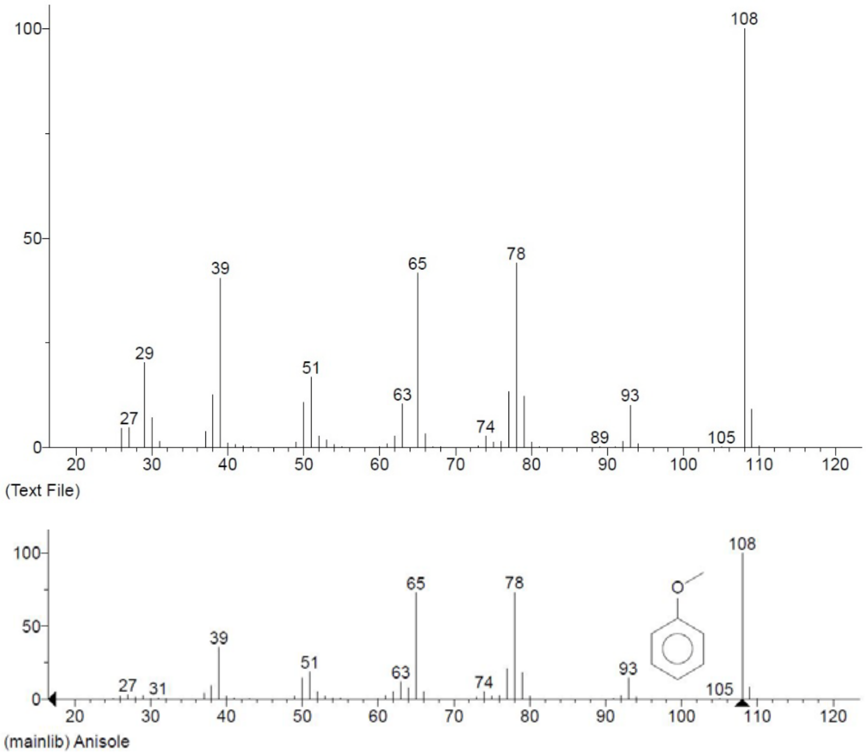


Fig. S7 The GC-MS result of the reaction using $^{13}CO_2$ instead of CO_2. Reaction condition: 20 μmol $[RuCl_2(CO)_3]_2$ and 60 μmol $Co_2(CO)_8$ (based on the metal), 20 μmol triphos, 2.2 mmol LiI, 2 mL DMI, 3.6 mmol anisole, 2 MPa $^{13}CO_2$ and 5 MPa H_2 (at room temperature), 190 ^{o}C,10 h.

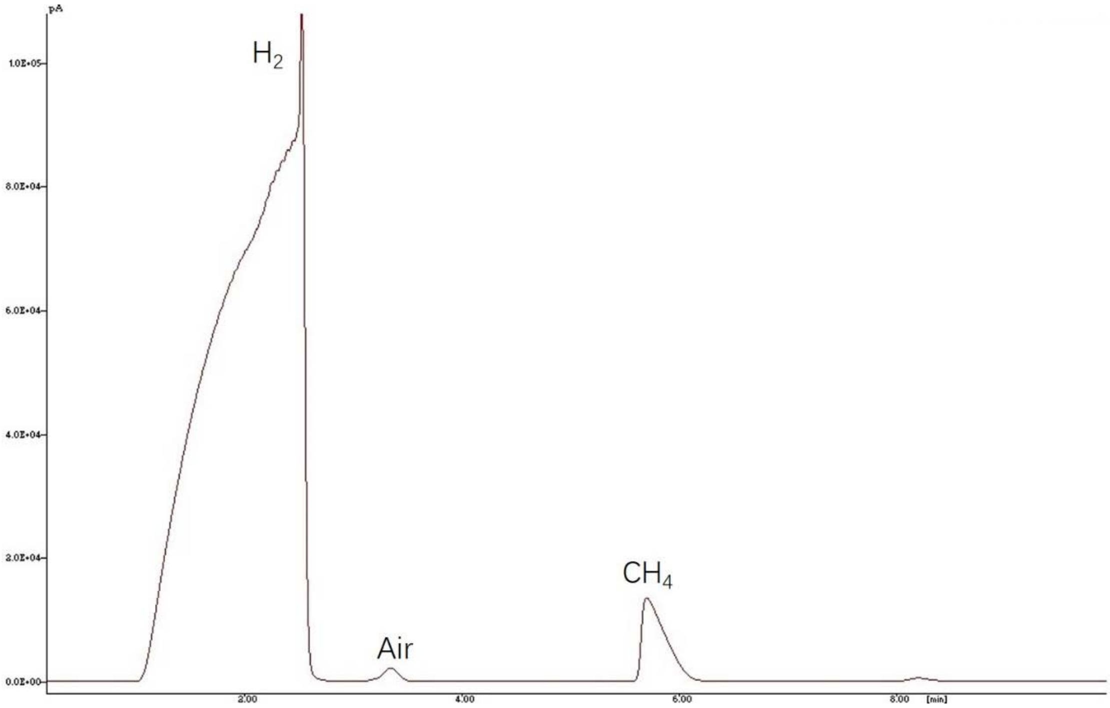


Fig. S8 GC graph of the gaseous sample after the reaction of CH_3I and H_2.
Reaction condition: 20 μmol $[RuCl_2(CO)_3]_2$ and 60 μmol $Co_2(CO)_8$ (based on the metal), 20 μmol triphos, 2.2 mmol LiI, 2 mL DMI, 40 uL CH_3I, 5 MPa H_2 (at room temperature), 190 ^oC, 10 h.

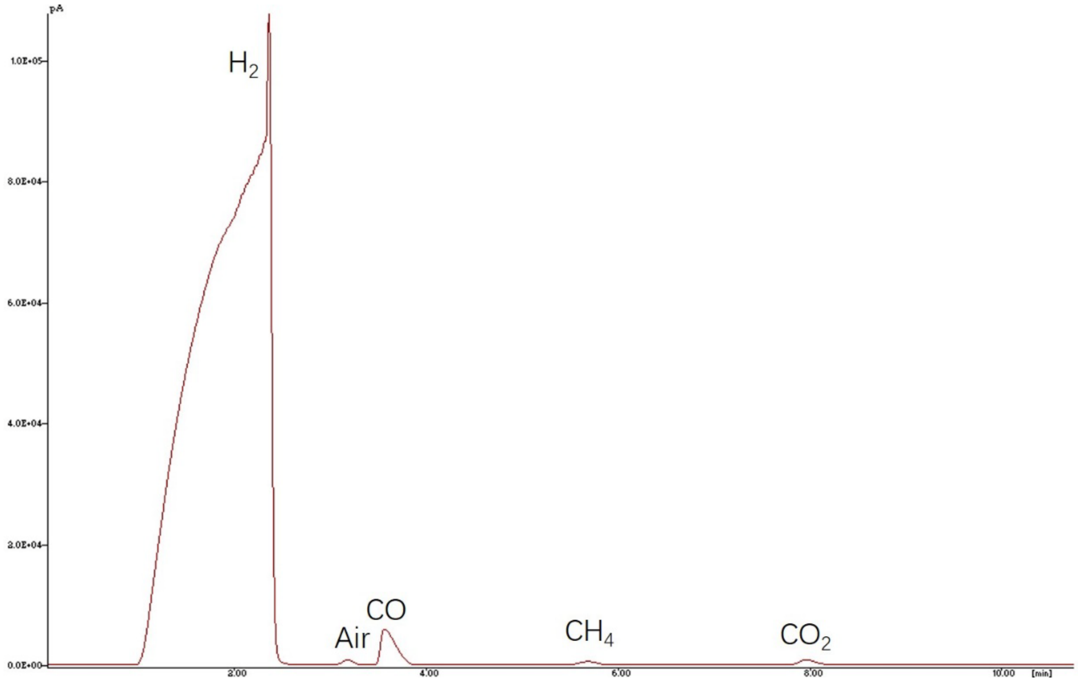
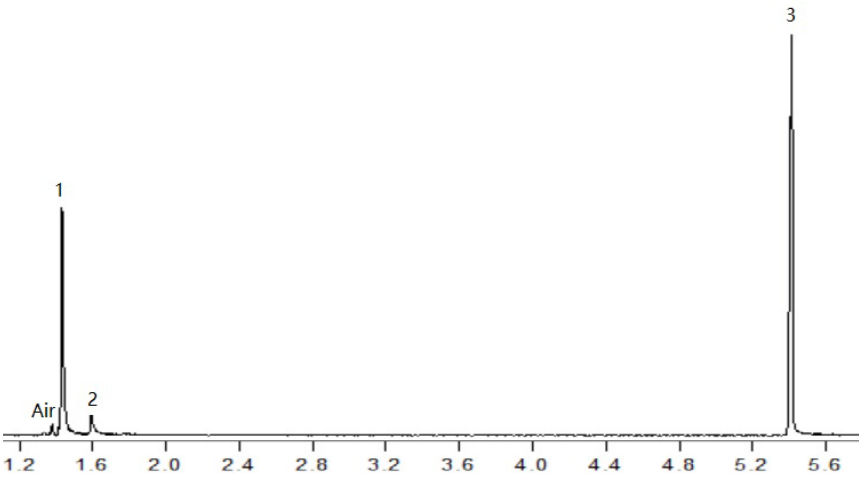
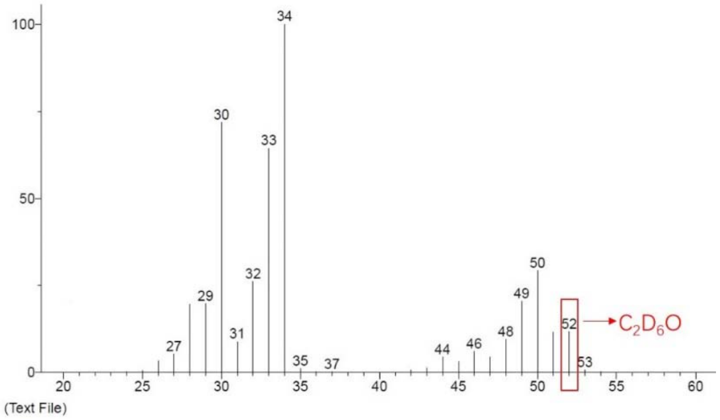


Fig. S9 GC graph of the gaseous sample after the reaction of CO and H_2.
Reaction condition: 20 μmol $[RuCl_2(CO)_3]_2$ and 60 μmol $Co_2(CO)_8$ (based on the metal), 20 μmol triphos, 2.2 mmol LiI, 2 mL DMI, 0.8 MPa CO and 5 MPa H_2 (at room temperature), 190 ^{o}C,10 h.

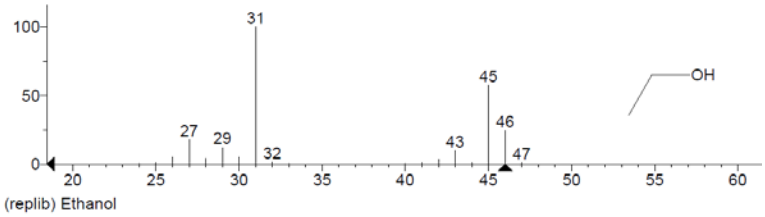
(a) Total ions chromatograph



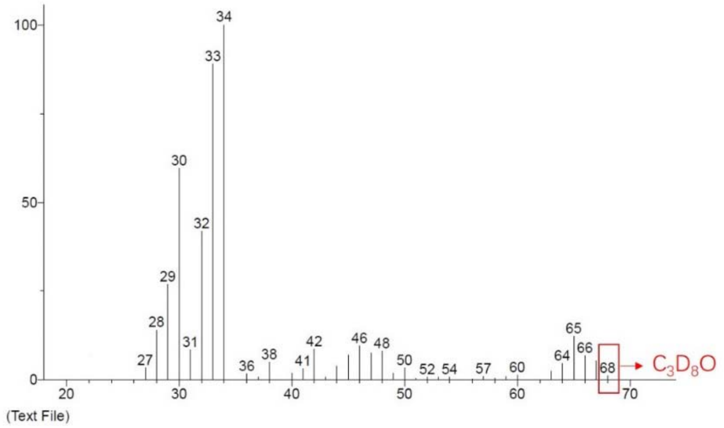
(b) deuterated ethanol



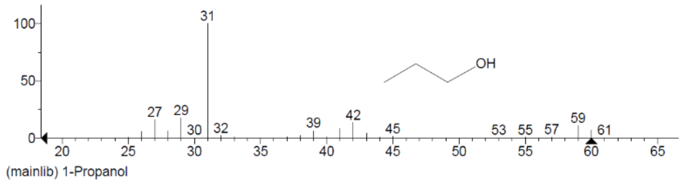
(c) standard ethanol



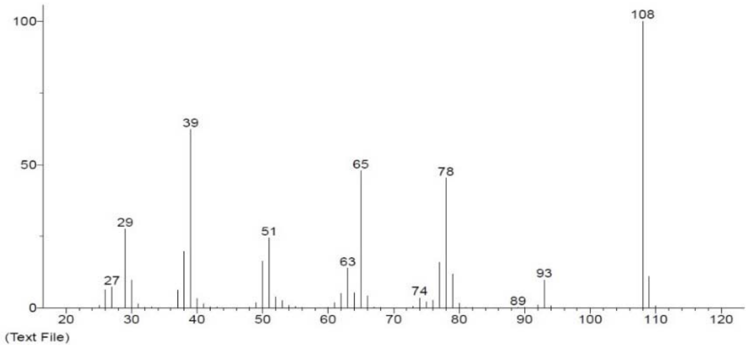
(d) deuterated propanol



(e) standard propanol



(f) unreacted anisole



(g) standard anisole

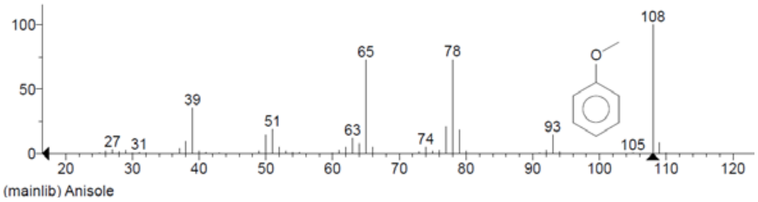


Fig. S10 The GC-MS result of the reaction using D_2 instead of H_2: (a) total ions chromatograph, (b) deuterated ethanol and (c) standard ethanol, (d) deuterated propanol and (e) standard propanol, (f) unreacted anisole and (g) standard anisole. Reaction condition: 20 μmol $[RuCl_2(CO)_3]_2$ and 60 μmol $Co_2(CO)_8$ (based on the metal), 20 μmol triphos, 2.2 mmol LiI, 2 mL DMI, 3.6 mmol anisole, 3 MPa CO_2 and 5 MPa D_2 (at room temperature), 190 ^{o}C, 10 h.

Notes:

Fig. S10b: One ethanol molecule could contain at most 6 D atoms, which suggests that the H atoms on the methyl group detached from the anisole substrate could be totally substituted by the D atoms.

Fig. S10d: One propanol molecule could contain at most 8 D atoms, which suggests that the H atoms on the methyl group detached from the anisole substrate could also be totally substituted by the D atoms.

Fig. S10f: No D atom entered the anisole molecule during the reaction. This indicates that the unreacted anisole did not experience H-D exchange.

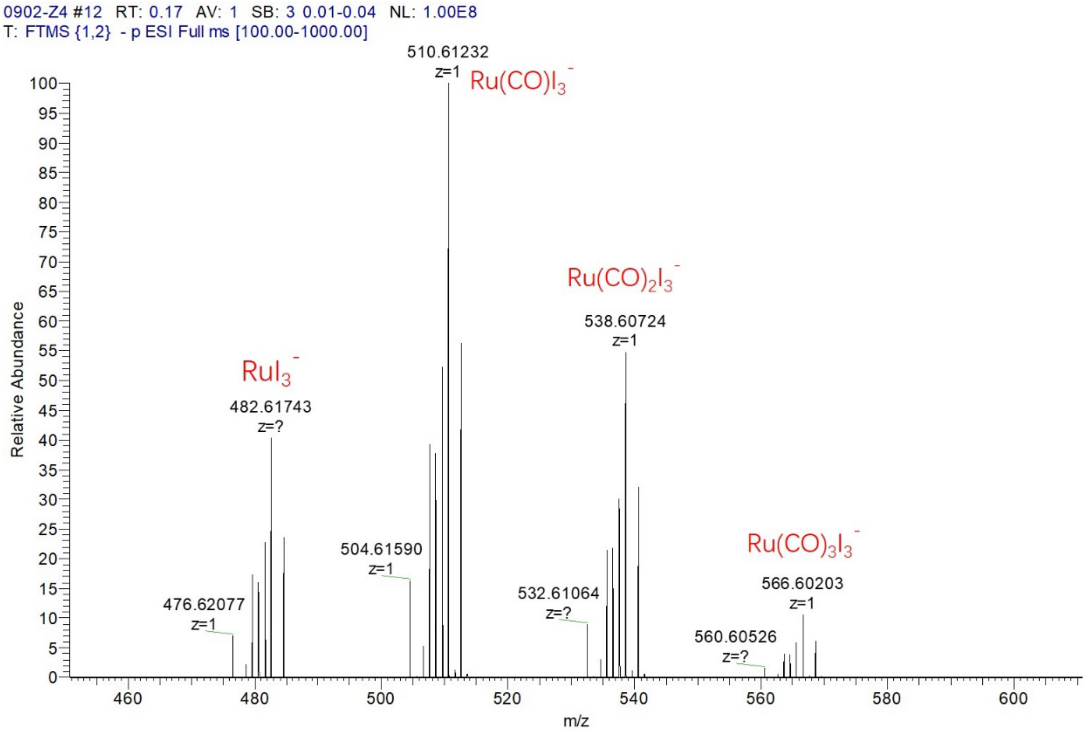
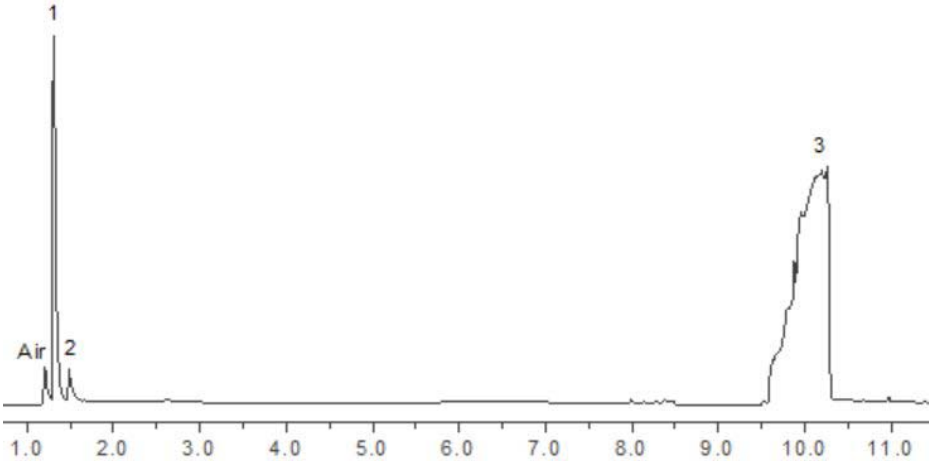


Fig. S11 The HR-ESI-MS (-) spectra of the reaction solution at condition of entry 1 of Table 1.

Notes: The HR-ESI-MS spectra revealed that the carbonyls of the Ru precursor were mainly retained in the catalyst after reaction. The Co catalyst after reaction could not be observed by HR-ESI-MS analysis, while in the literature cobalt complex with multi carbonyls were usually the active center at similar conditions[1].



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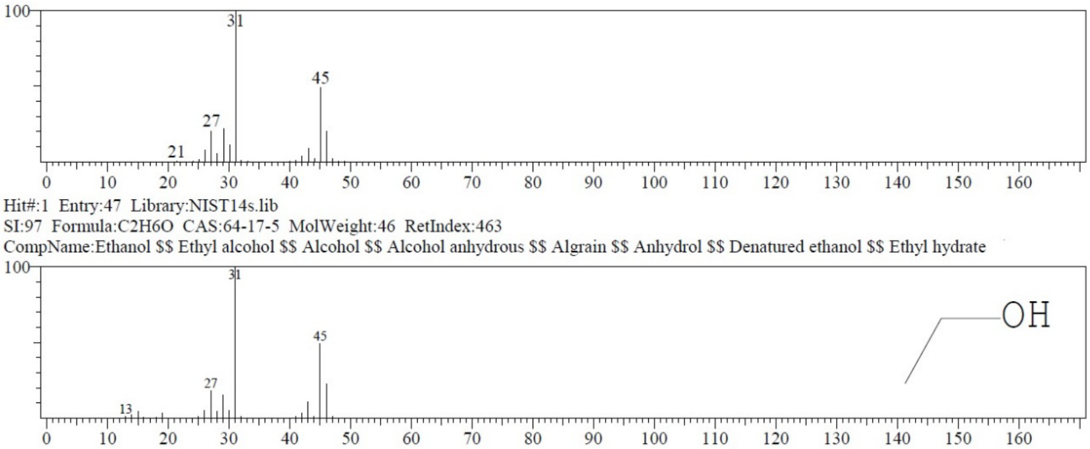

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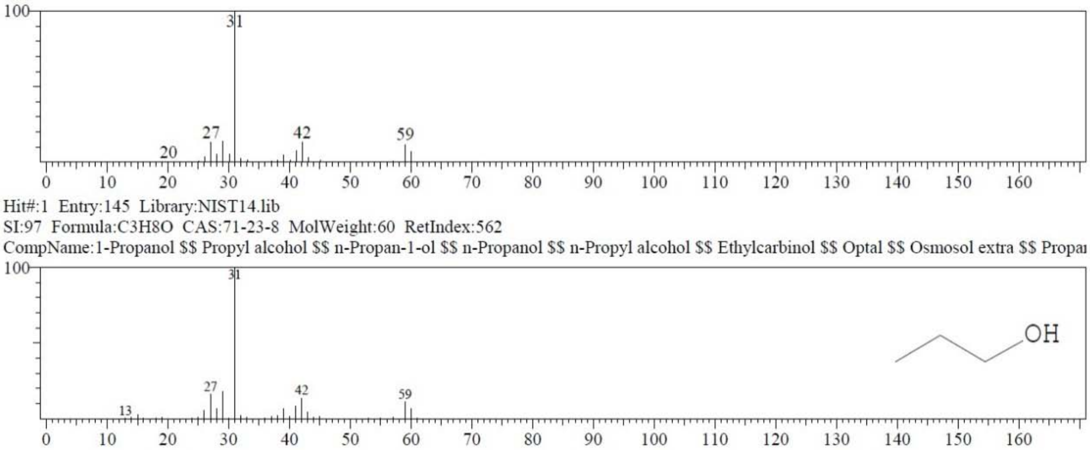
Target 2



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Target 3

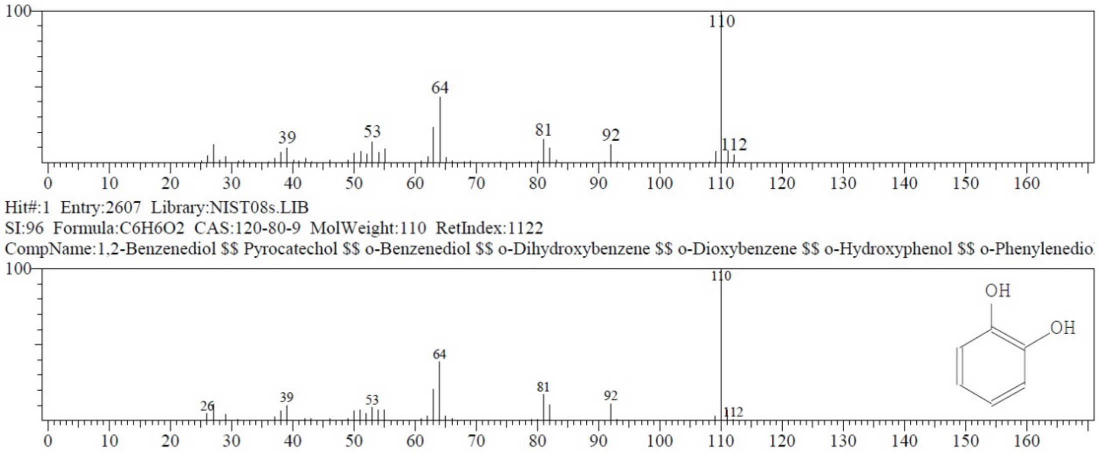

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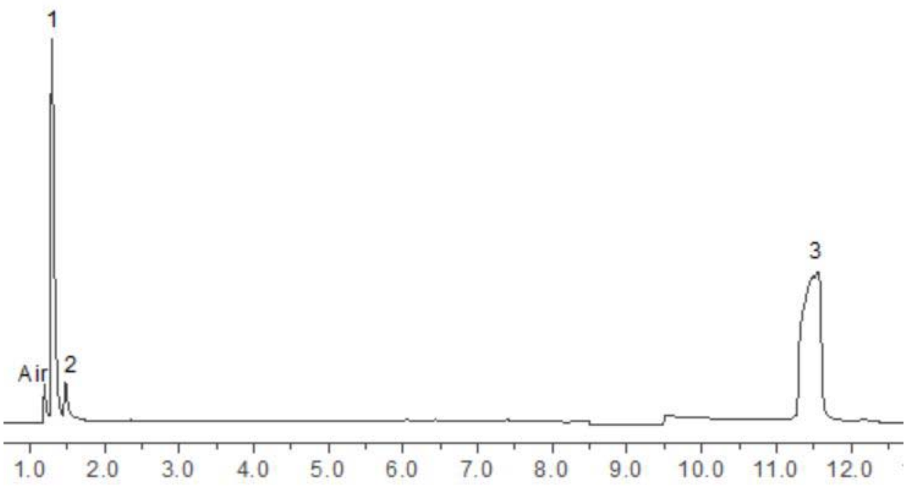
Fig. S12 The GC-MS spectra of the solution after the reaction in entry 1 of Table 2.

Note: To protect the detector of the MS, the solvent DMI (retention time 8.5min-9.5min) was cut during the analysis.



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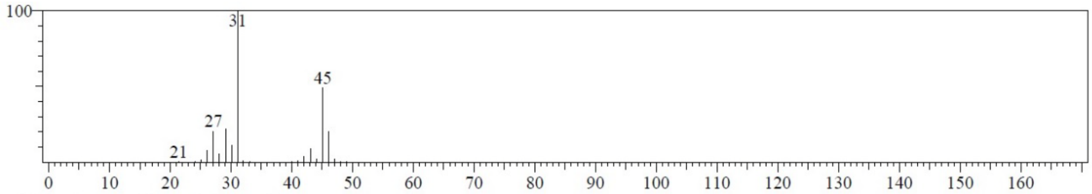

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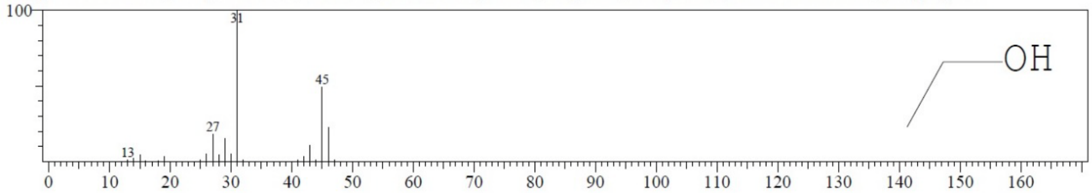

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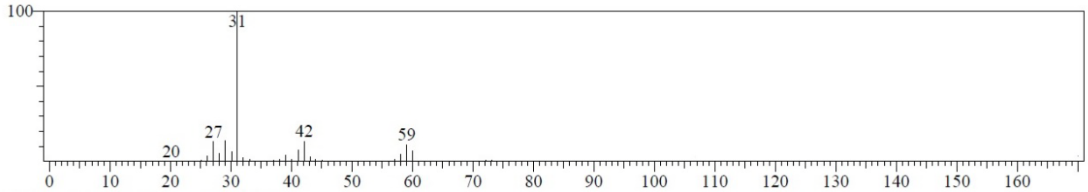

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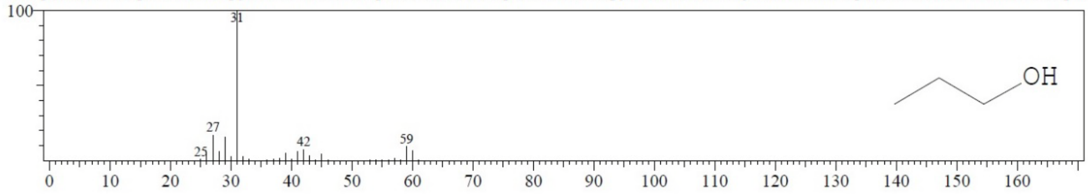

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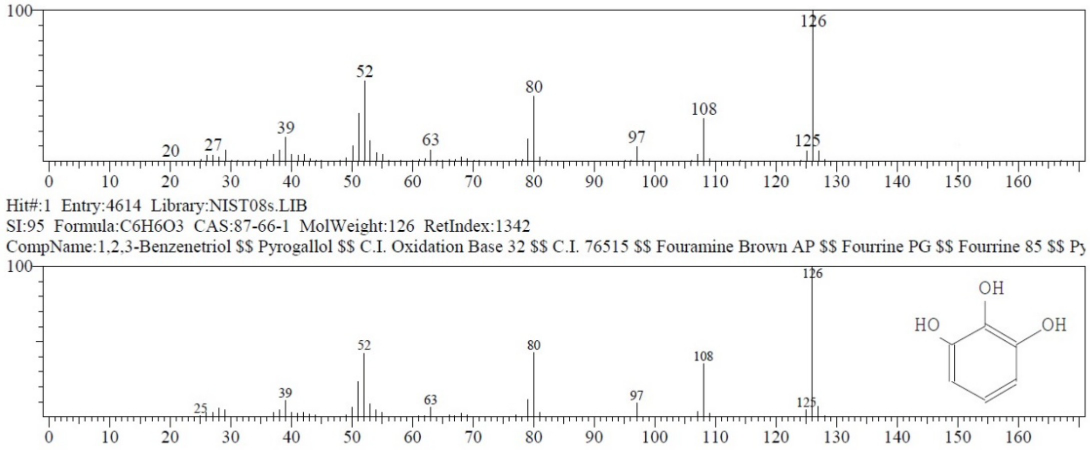

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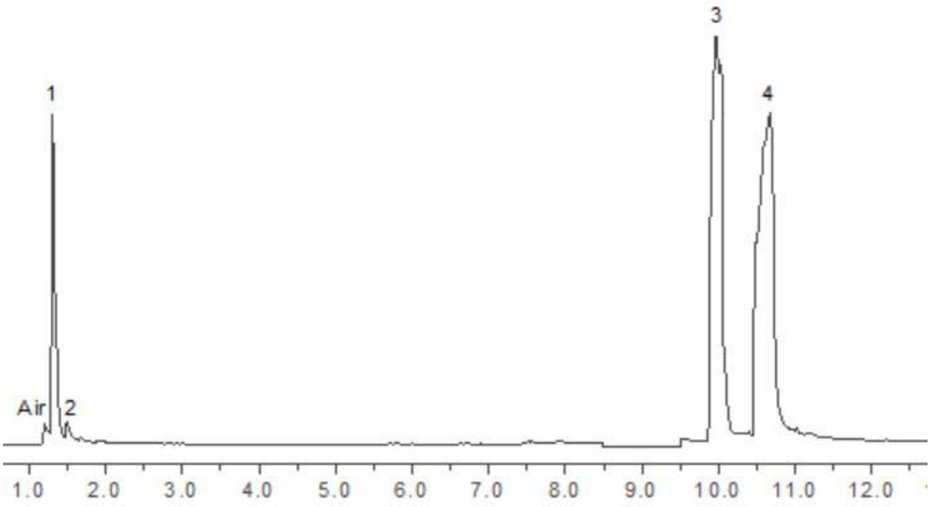
CompName:1,2,3-Benzenetriol $$ Pyrogallol $$ C.I. Oxidation Base 32 $$ C.I. 76515 $$ Fouramine Brown AP $$ Fourrine PG $$ Fourrine 85 $$ Py

Fig. S13 The GC-MS spectra of the solution after the reaction in entry 2 of Table 2.



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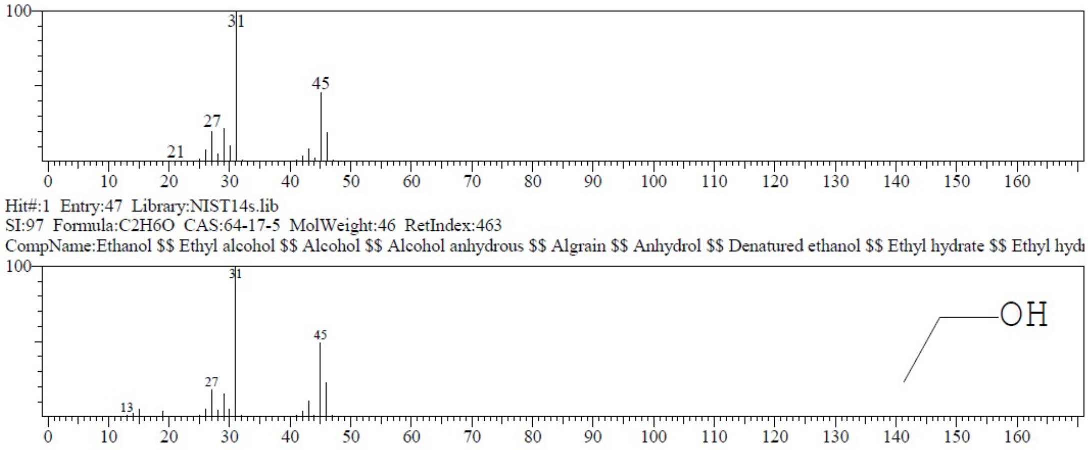

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CompName:Ethanol $$ Ethyl alcohol $$ Alcohol $$ Alcohol anhydrous $$ Algrain $$ Anhydrol $$ Denatured ethanol $$ Ethyl hydrate $$ Ethyl hyd
```
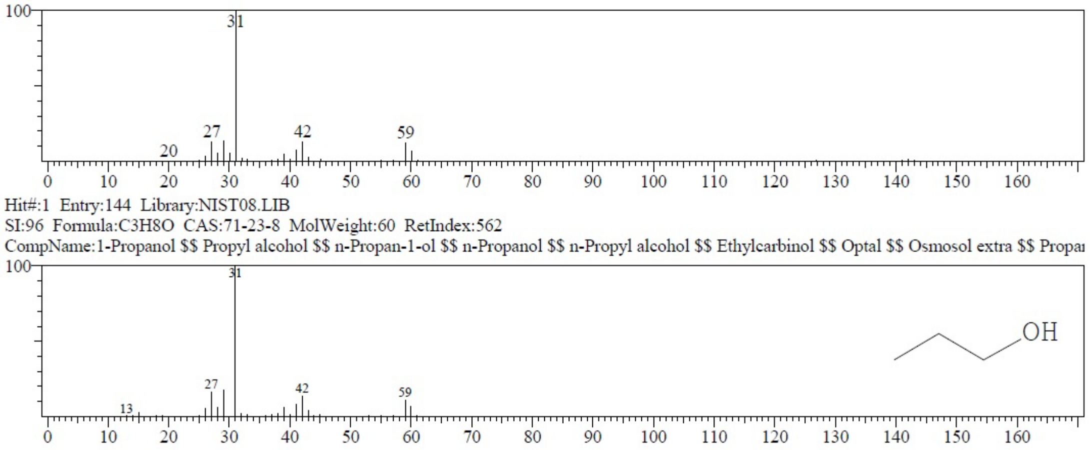

Target 2



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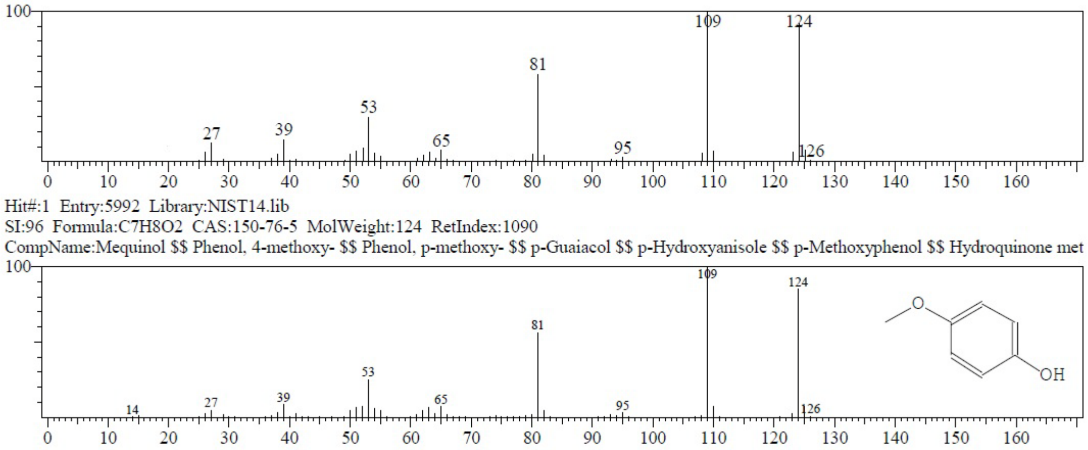
```

Target 3



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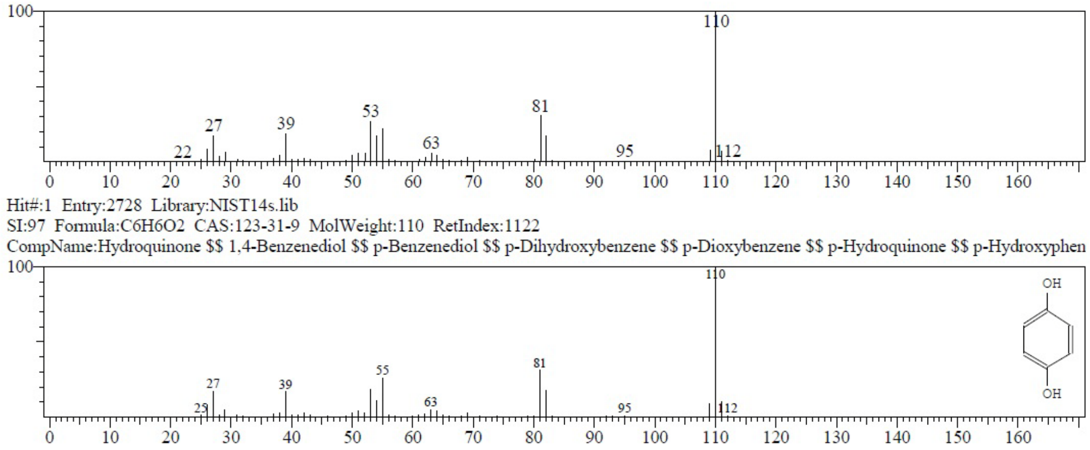
CompName:Mequinol $$ Phenol, 4-methoxy- $$ Phenol, p-methoxy- $$ p-Guaiacol $$ p-Hydroxyanisole $$ p-Methoxyphenol $$ Hydroquinone met

Target 4



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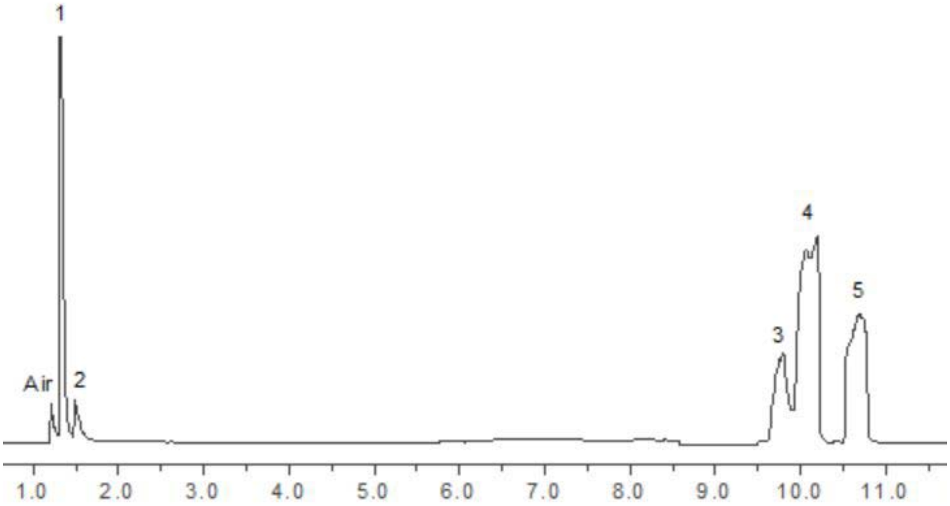
CompName:Hydroquinone $$ 1,4-Benzenediol $$ p-Benzenediol $$ p-Dihydroxybenzene $$ p-Dioxybenzene $$ p-Hydroquinone $$ p-Hydroxyphen

Fig. S14 The GC-MS spectra of the solution after the reaction in entry 3 of Table 2.

Note: White powder was observed after the reaction because of the limited solubility of hydroquinone in DMI.



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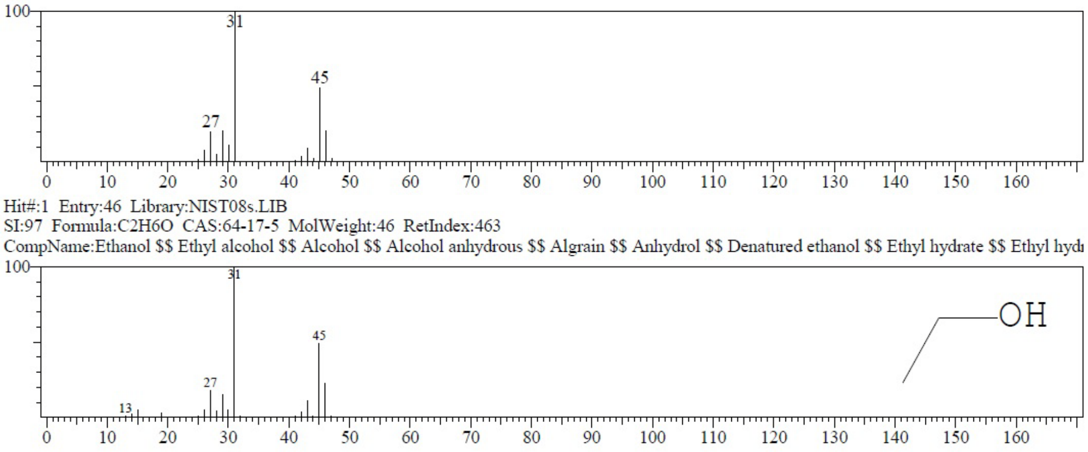
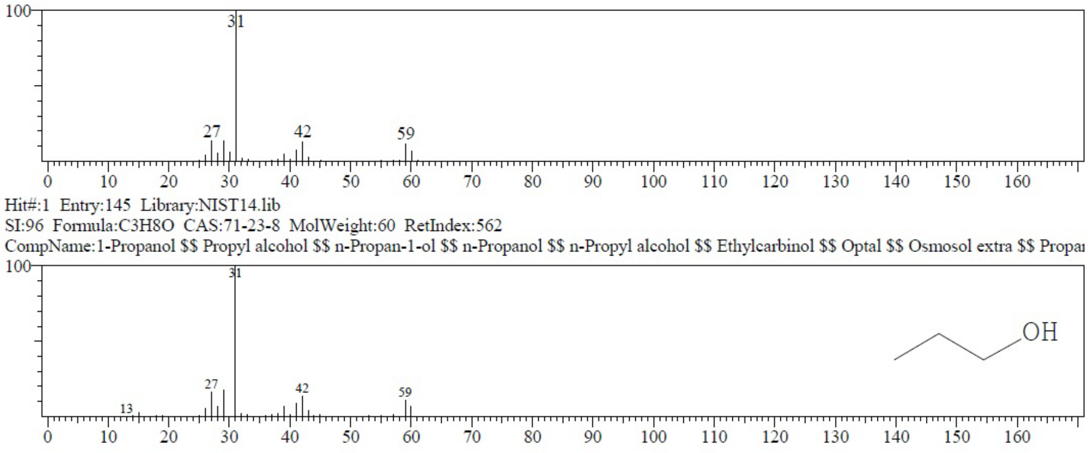


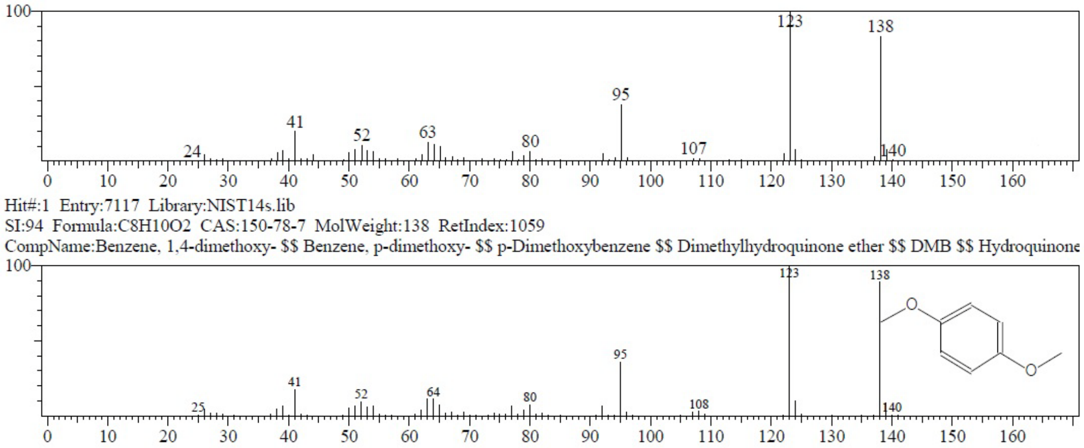
Hit#:1 Entry:46 Library:NIST08s.LIB
SI:97 Formula:C2H6O CAS:64-17-5 MolWeight:46 RetIndex:463
CompName:Ethanol $$ Ethyl alcohol $$ Alcohol $$ Alcohol anhydrous $$ Algrain $$ Anhydrol $$ Denatured ethanol $$ Ethyl hydrate $$ Ethyl hyd

Target 2

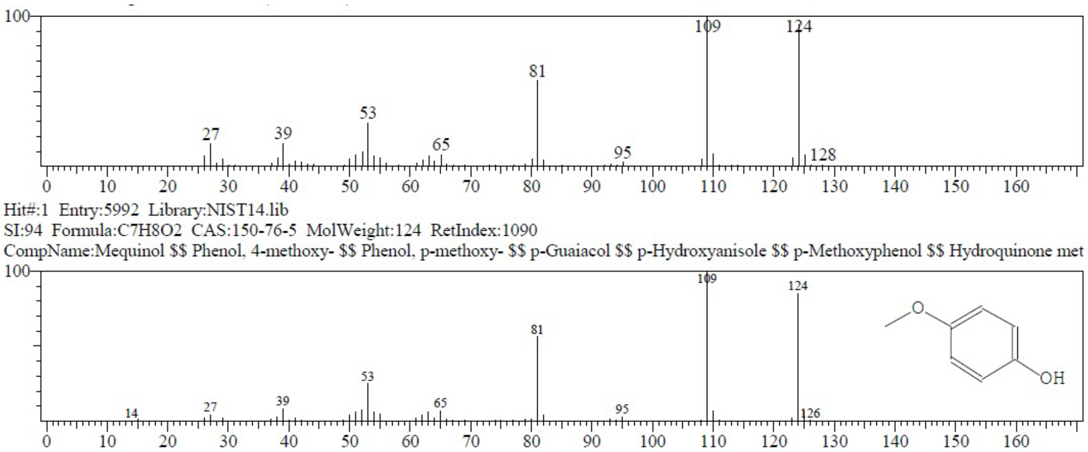


Hit#:1 Entry:145 Library:NIST14.lib
SI:96 Formula:C3H8O CAS:71-23-8 MolWeight:60 RetIndex:562
CompName:1-Propanol $$ Propyl alcohol $$ n-Propan-1-ol $$ n-Propanol $$ n-Propyl alcohol $$ Ethylcarbinol $$ Optal $$ Osmosol extra $$ Propa

Target 3


Hit#:1 Entry:7117 Library:NIST14s.lib
SI:94 Formula:C8H10O2 CAS:150-78-7 MolWeight:138 RetIndex:1059
CompName:Benzene, 1,4-dimethoxy- $$ Benzene, p-dimethoxy- $$ p-Dimethoxybenzene $$ Dimethylhydroquinone ether $$ DMB $$ Hydroquinone

Target 4


Hit#:1 Entry:5992 Library:NIST14.lib
SI:94 Formula:C7H8O2 CAS:150-76-5 MolWeight:124 RetIndex:1090
CompName:Mequinol $$ Phenol, 4-methoxy- $$ Phenol, p-methoxy- $$ p-Guaiacol $$ p-Hydroxyanisole $$ p-Methoxyphenol $$ Hydroquinone met

Target 5

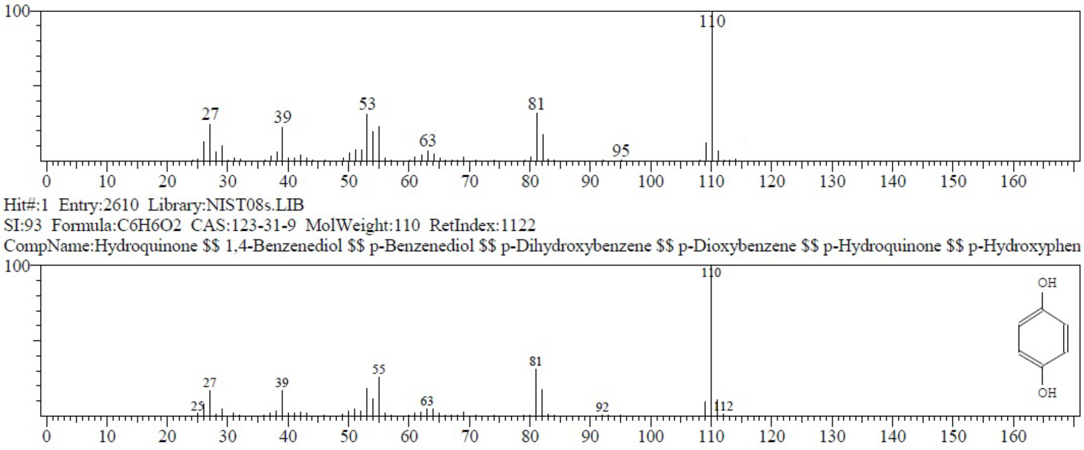
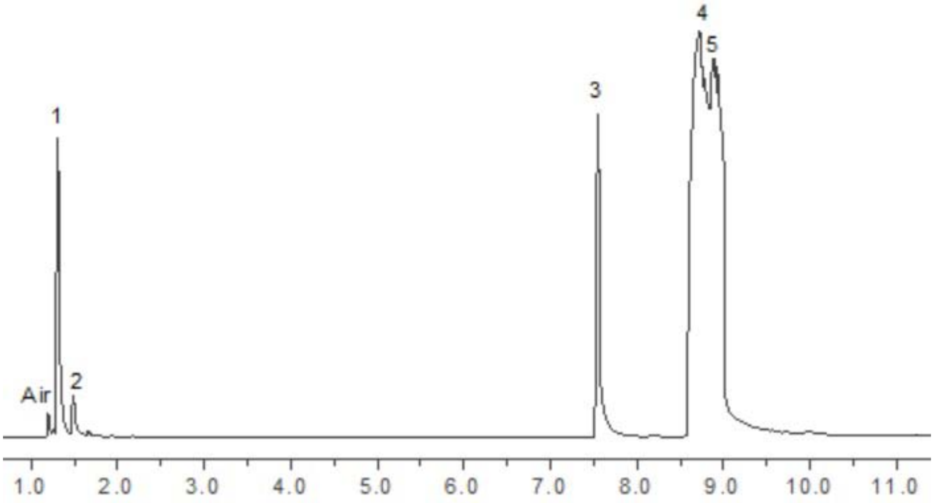
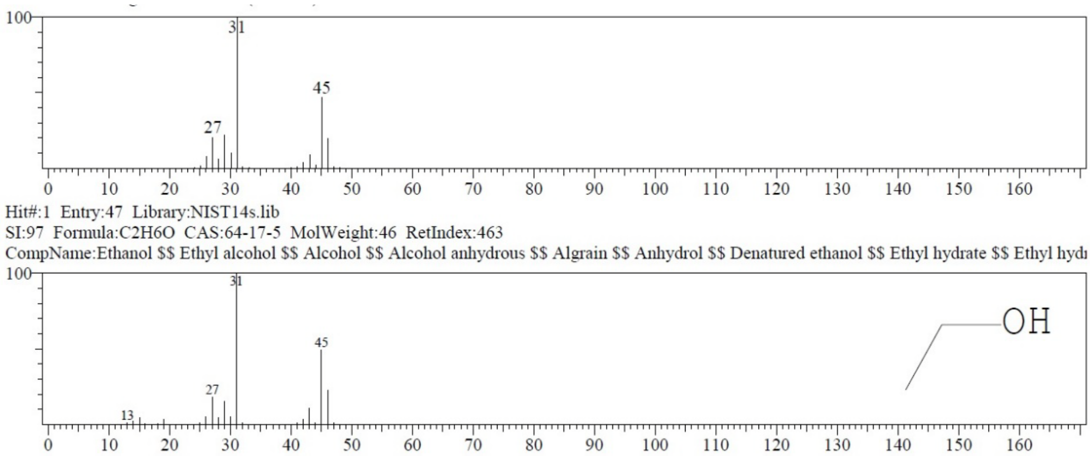

Hit#:1 Entry:2610 Library:NIST08s.LIB
SI:93 Formula:C6H6O2 CAS:123-31-9 MolWeight:110 RetIndex:1122
CompName:Hydroquinone $$ 1,4-Benzenediol $$ p-Benzenediol $$ p-Dihydroxybenzene $$ p-Dioxybenzene $$ p-Hydroquinone $$ p-Hydroxyphen

Fig. S15 The GC-MS spectra of the solution after the reaction in entry 4 of Table 2.

Note: White powder was observed after the reaction because of the limited solubility of hydroquinone in DMI.

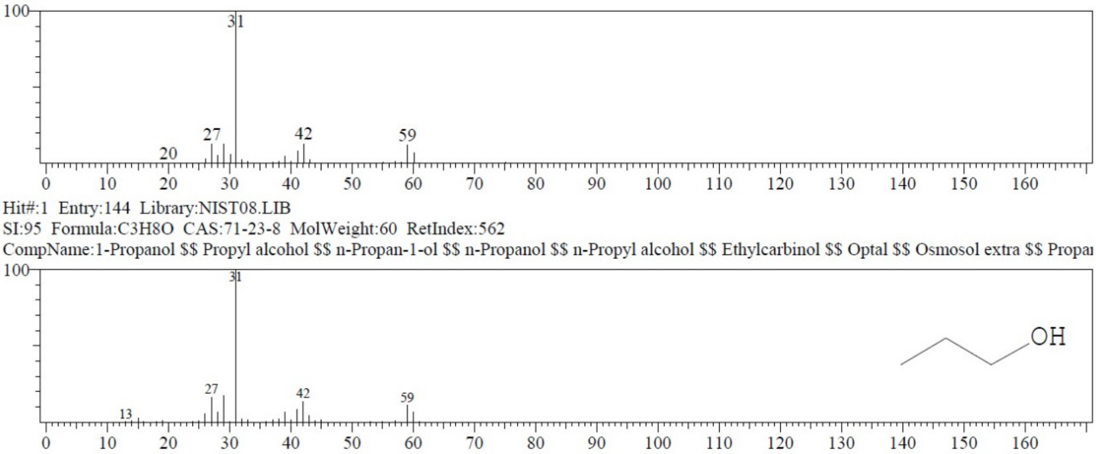


Target 1



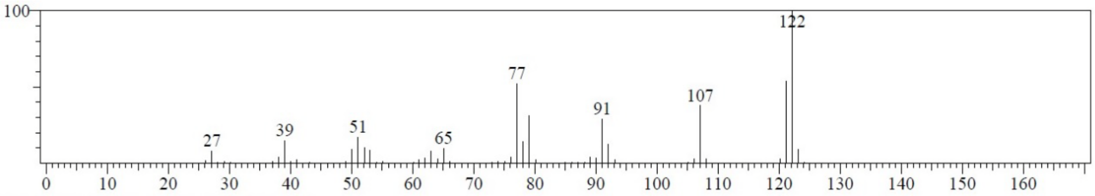
Hit#:1 Entry:47 Library:NIST14s.lib
SI:97 Formula:C2H6O CAS:64-17-5 MolWeight:46 RetIndex:463
CompName:Ethanol $$ Ethyl alcohol $$ Alcohol $$ Alcohol anhydrous $$ Algrain $$ Anhydrol $$ Denatured ethanol $$ Ethyl hydrate $$ Ethyl hyd

Target 2

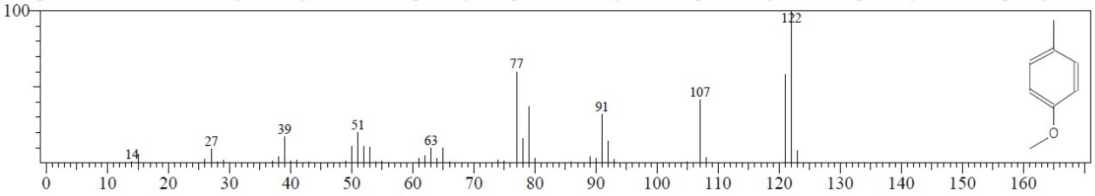


Hit#:1 Entry:144 Library:NIST08.LIB
SI:95 Formula:C3H8O CAS:71-23-8 MolWeight:60 RetIndex:562
CompName:1-Propanol $$ Propyl alcohol $$ n-Propan-1-ol $$ n-Propanol $$ n-Propyl alcohol $$ Ethylcarbinol $$ Optal $$ Osmosol extra $$ Propa

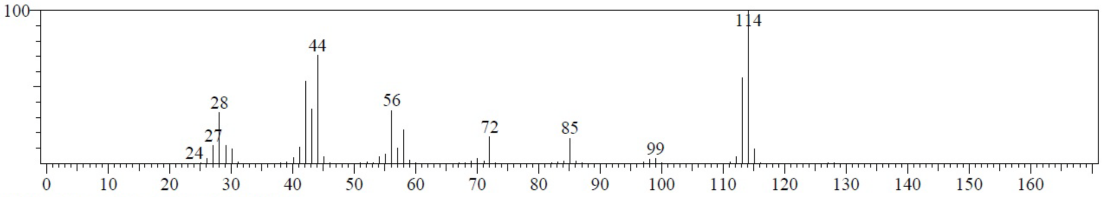
Target 3



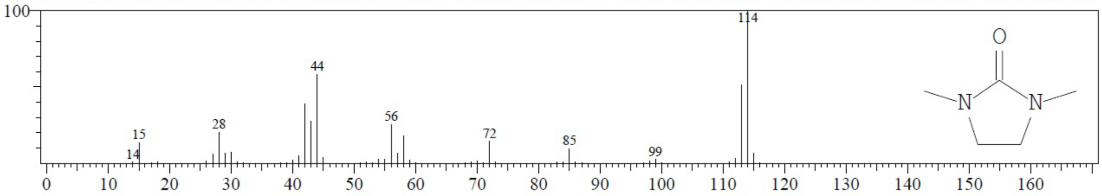
Hit#:1 Entry:4246 Library:NIST08s.LIB
SI:97 Formula:C8H10O CAS:104-93-8 MolWeight:122 RetIndex:983
CompName:Benzene, 1-methoxy-4-methyl- $$ Anisole, p-methyl- $$ p-Cresol methyl ether $$ p-Methoxytoluene $$ p-Methylanisole $$ p-Tolyl met



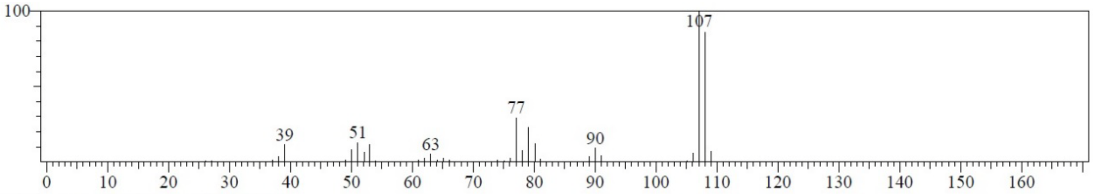
Target 4



Hit#:1 Entry:3943 Library:NIST08.LIB
SI:94 Formula:C5H10N2O CAS:80-73-9 MolWeight:114 RetIndex:1033
CompName:2-Imidazolidinone, 1,3-dimethyl- $$ Dimethylethyleneurea $$ N,N'-Dimethyl-2-imidazolidinone $$ N,N'-Dimethylethyleneurea $$ Rhon



Target 5



Hit#:1 Entry:2875 Library:NIST14.lib
SI:96 Formula:C7H8O CAS:106-44-5 MolWeight:108 RetIndex:1014
CompName:p-Cresol $$ Phenol, 4-methyl- $$ p-Hydroxytoluene $$ p-Kresol $$ p-Methylhydroxybenzene $$ p-Methylphenol $$ p-Oxytoluene $$ p-

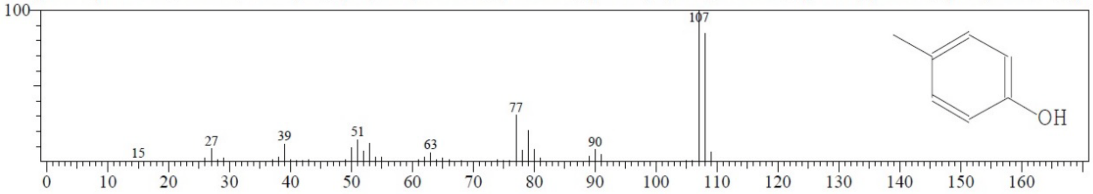
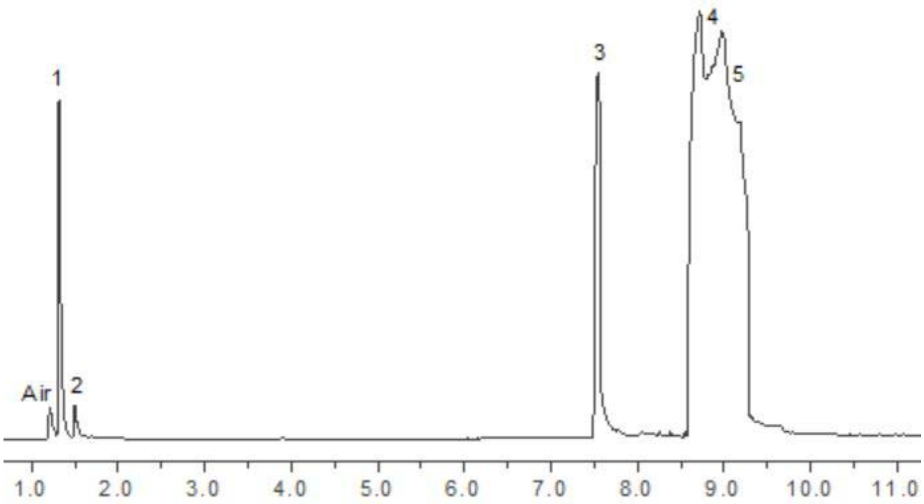
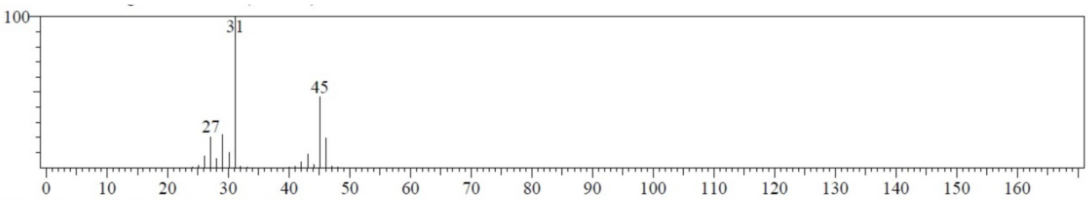


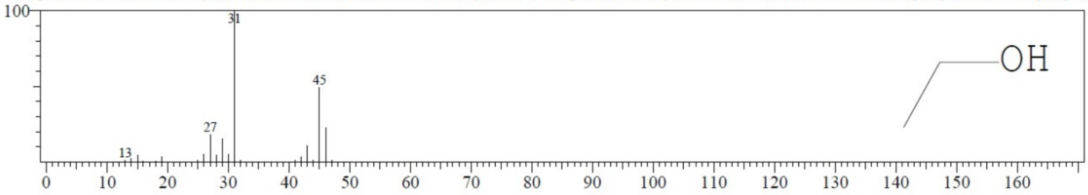
Fig. S16 The GC-MS spectra of the solution after the reaction in entry 5 of Table 2.



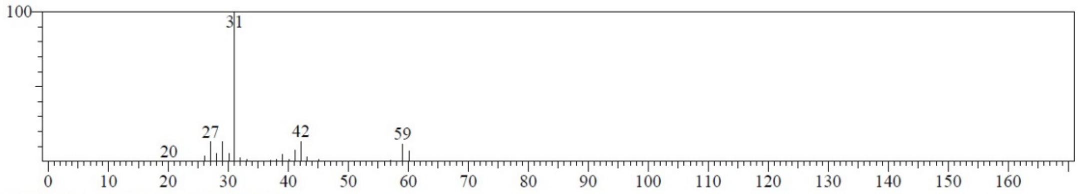
Target 1



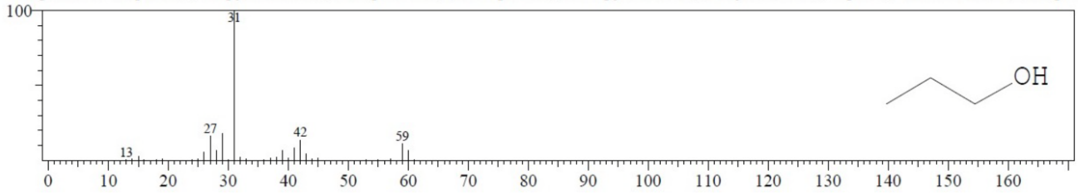
Hit#:1 Entry:47 Library:NIST14s.lib
SI:97 Formula:C2H6O CAS:64-17-5 MolWeight:46 RetIndex:463
CompName:Ethanol $$ Ethyl alcohol $$ Alcohol $$ Alcohol anhydrous $$ Algrain $$ Anhydrol $$ Denatured ethanol $$ Ethyl hydrate $$ Ethyl hyd



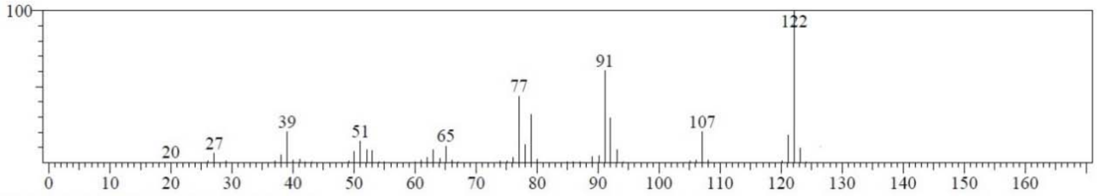
Target 2



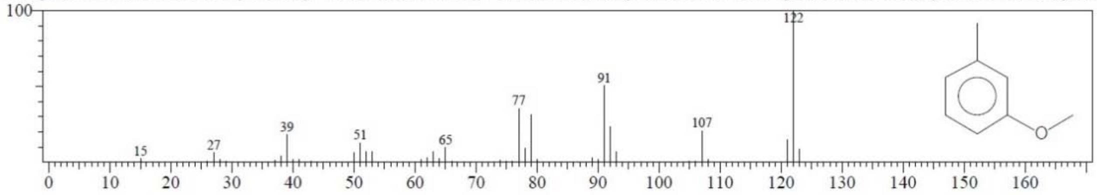
Hit#:1 Entry:145 Library:NIST14.lib
SI:97 Formula:C3H8O CAS:71-23-8 MolWeight:60 RetIndex:562
CompName:1-Propanol $$ Propyl alcohol $$ n-Propan-1-ol $$ n-Propanol $$ n-Propyl alcohol $$ Ethylcarbinol $$ Optal $$ Osmosol extra $$ Propa



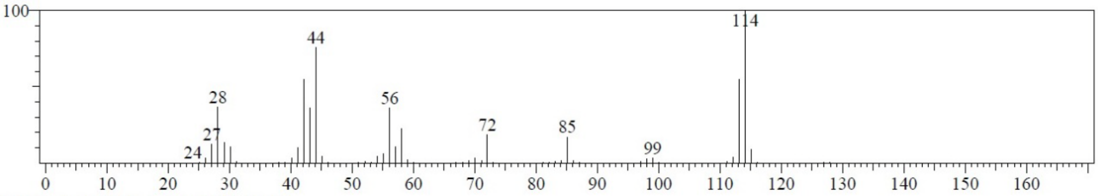
Target 3



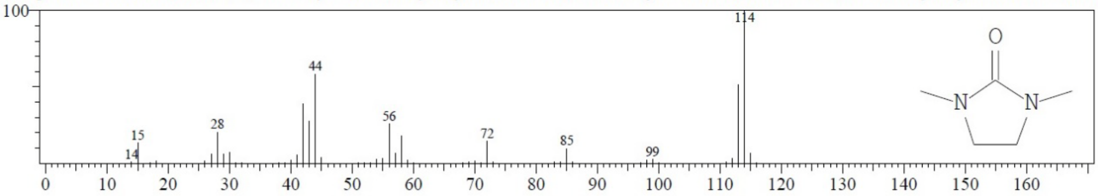
Hit#:1 Entry:5488 Library:NIST147.LIB
SI:97 Formula:C8H10O CAS:100-84-5 MolWeight:122 RetIndex:0
CompName:Benzene, 1-methoxy-3-methyl- $$ Anisole, m-methyl- $$ m-Cresol methyl ether $$ m-Methoxytoluene $$ m-Methylanisole $$ Methyl m



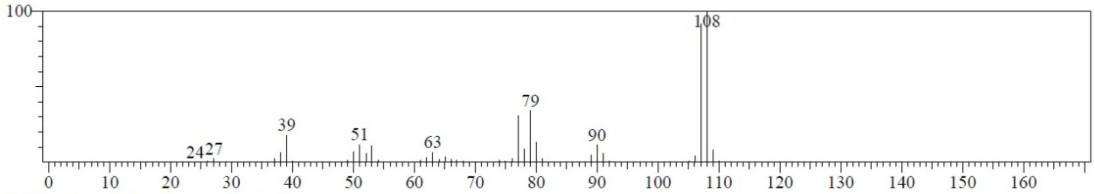
Target 4



Hit#:1 Entry:4015 Library:NIST14.lib
SI:93 Formula:C5H10N2O CAS:80-73-9 MolWeight:114 RetIndex:1033
CompName:2-Imidazolidinone, 1,3-dimethyl- $$ Dimethylethyleneurea $$ N,N'-Dimethyl-2-imidazolidinone $$ N,N'-Dimethylethyleneurea $$ Rhon



Target 5



Hit#:1 Entry:2878 Library:NIST14.lib
SI:96 Formula:C7H8O CAS:108-39-4 MolWeight:108 RetIndex:1014
CompName:Phenol, 3-methyl- $$ m-Cresol $$ m-Cresole $$ m-Cresylic acid $$ m-Hydroxytoluene $$ m-Kresol $$ m-Methylphenol $$ m-Oxytoluer

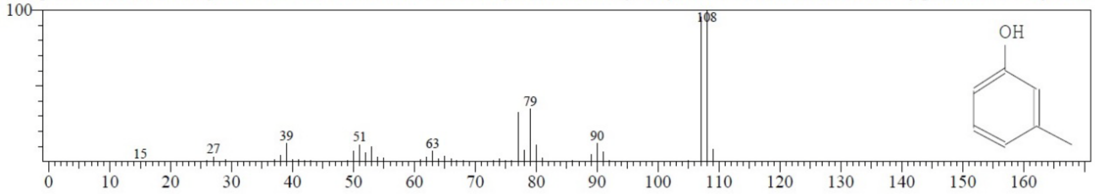
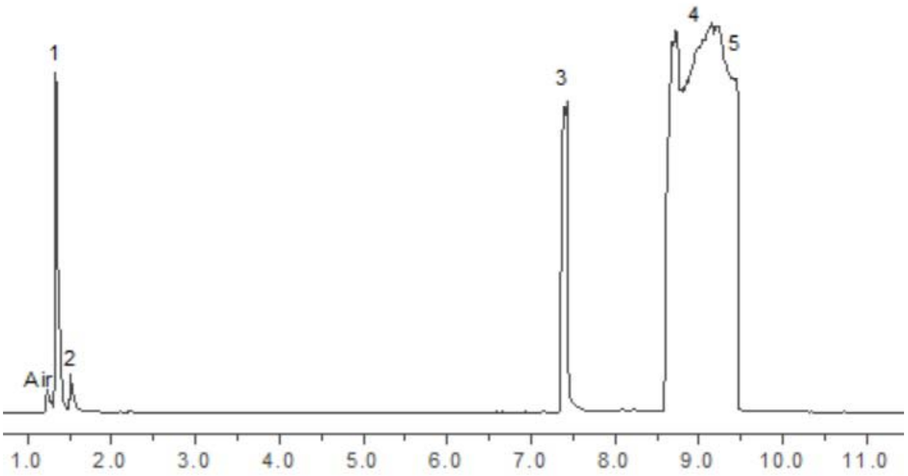
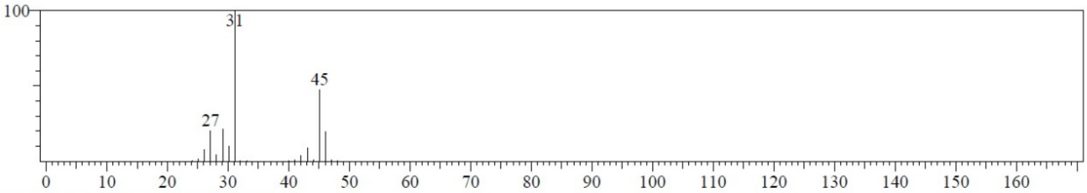


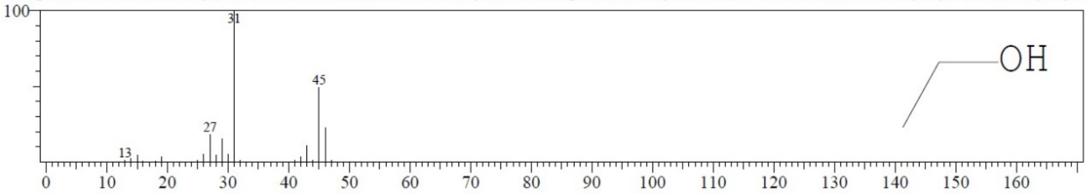
Fig. S17 The GC-MS spectra of the solution after the reaction in entry 6 of Table 2.



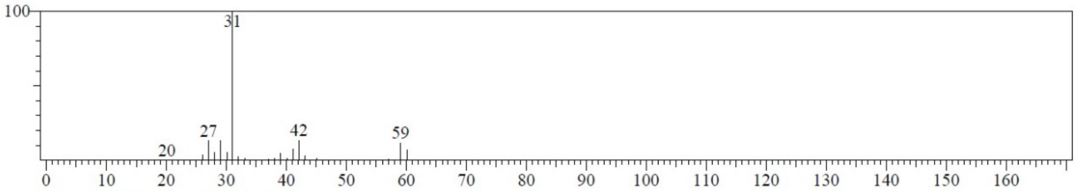
Target 1



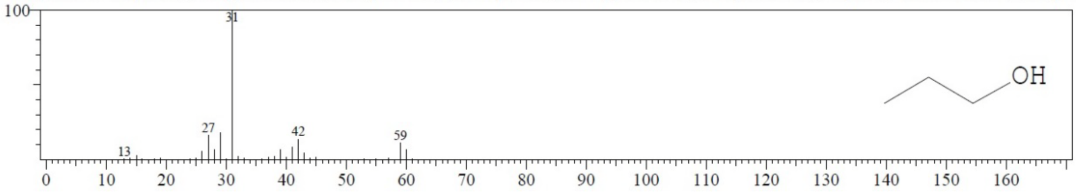
Hit#:1 Entry:47 Library:NIST14s.lib
SI:97 Formula:C2H6O CAS:64-17-5 MolWeight:46 RetIndex:463
CompName:Ethanol $$ Ethyl alcohol $$ Alcohol $$ Alcohol anhydrous $$ Algrain $$ Anhydrol $$ Denatured ethanol $$ Ethyl hydrate $$ Ethyl hyd



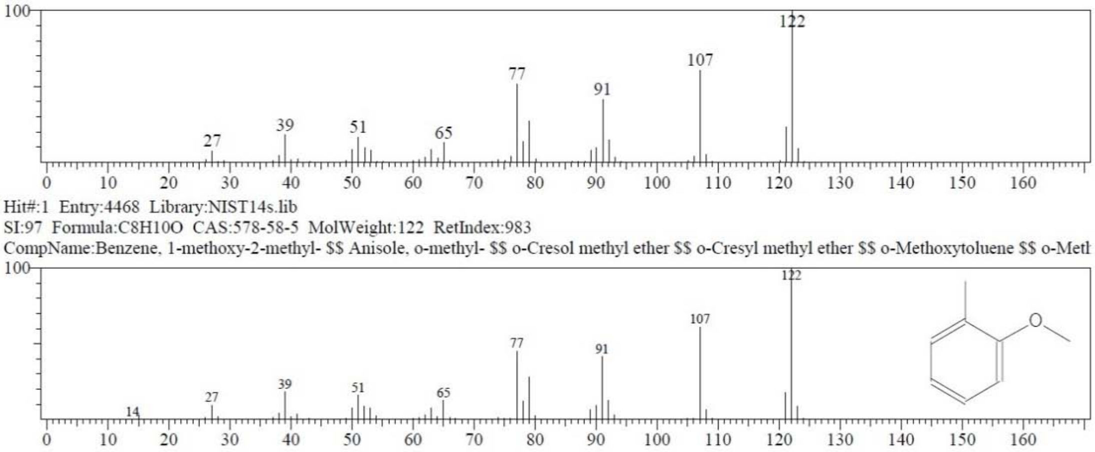
Target 2



Hit#:1 Entry:145 Library:NIST14.lib
SI:97 Formula:C3H8O CAS:71-23-8 MolWeight:60 RetIndex:562
CompName:1-Propanol $$ Propyl alcohol $$ n-Propan-1-ol $$ n-Propanol $$ n-Propyl alcohol $$ Ethylcarbinol $$ Optal $$ Osmosol extra $$ Propa

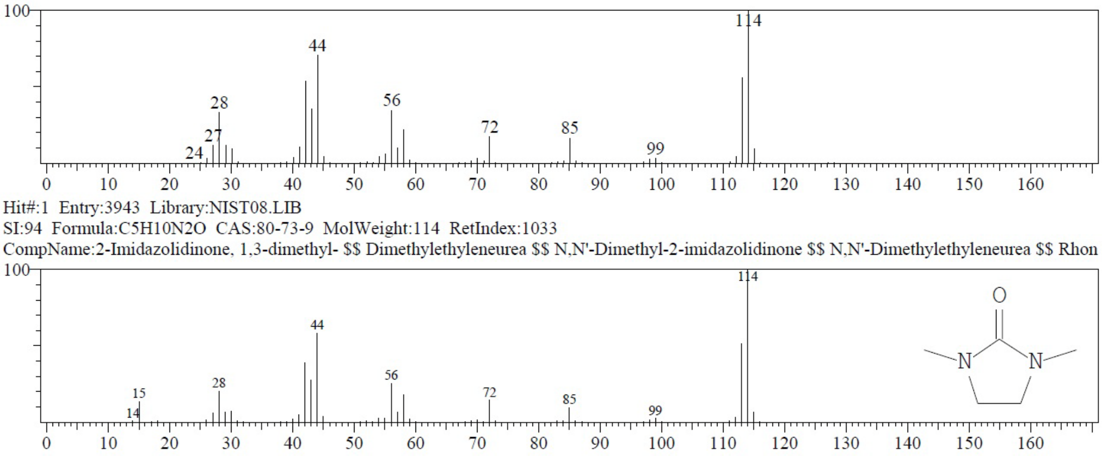


Target 3



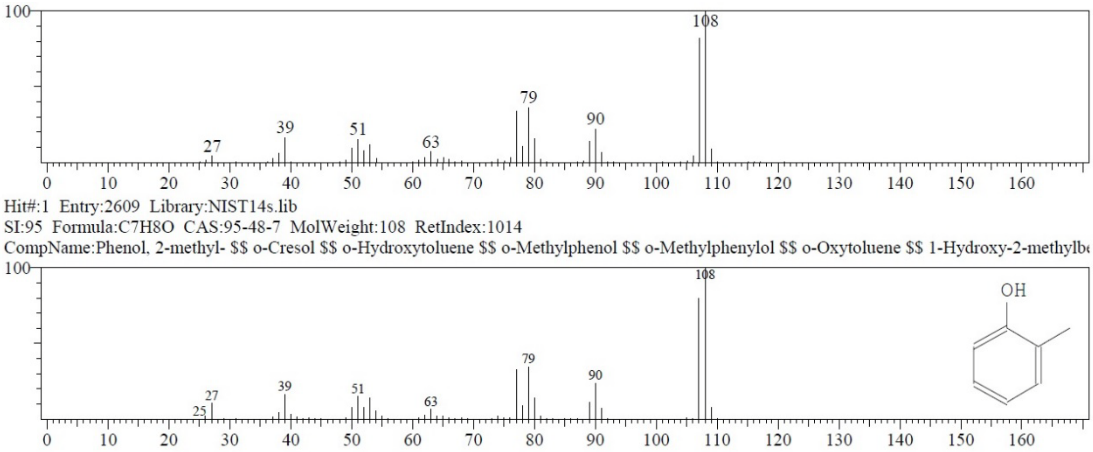
```
Hit#:1  Entry:4468  Library:NIST14s.lib
SI:97  Formula:C8H10O  CAS:578-58-5  MolWeight:122  RetIndex:983
CompName:Benzene, 1-methoxy-2-methyl- $$ Anisole, o-methyl- $$ o-Cresol methyl ether $$ o-Cresyl methyl ether $$ o-Methoxytoluene $$ o-Met
```

Target 4



```
Hit#:1  Entry:3943  Library:NIST08.LIB
SI:94  Formula:C5H10N2O  CAS:80-73-9  MolWeight:114  RetIndex:1033
CompName:2-Imidazolidinone, 1,3-dimethyl- $$ Dimethylethyleneurea $$ N,N'-Dimethyl-2-imidazolidinone $$ N,N'-Dimethylethyleneurea $$ Rhon
```

Target 5



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Hit#:1  Entry:2609  Library:NIST14s.lib
SI:95  Formula:C7H8O  CAS:95-48-7  MolWeight:108  RetIndex:1014
CompName:Phenol, 2-methyl- $$ o-Cresol $$ o-Hydroxytoluene $$ o-Methylphenol $$ o-Methylphenylol $$ o-Oxytoluene $$ 1-Hydroxy-2-methylb
```
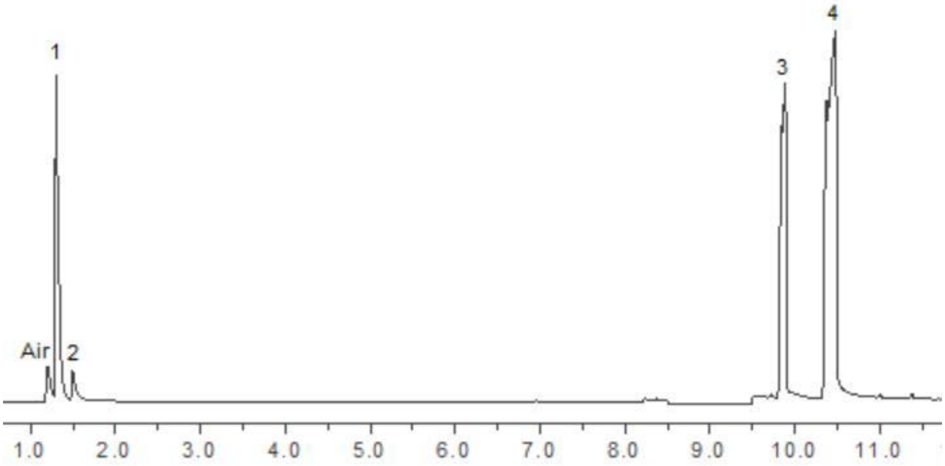
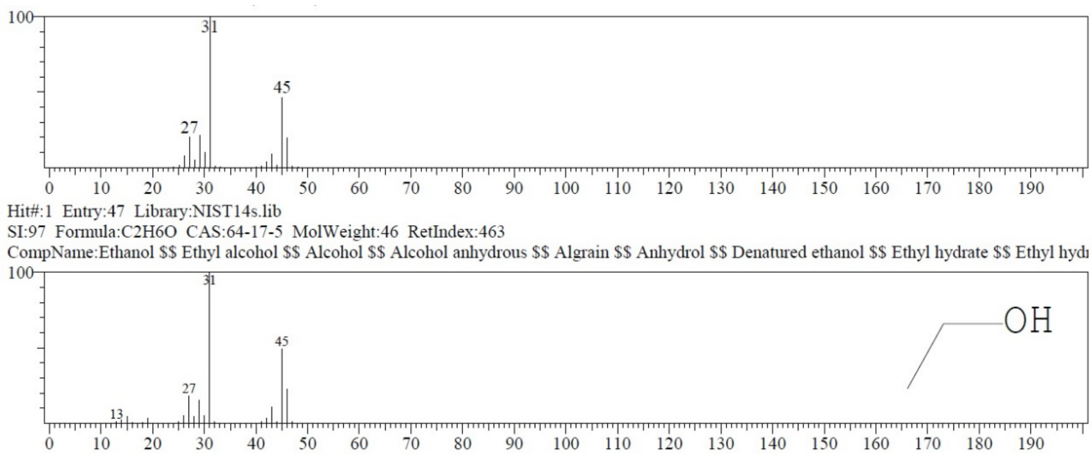

Fig. S18 The GC-MS spectra of the solution after the reaction in entry 7 of Table 2.

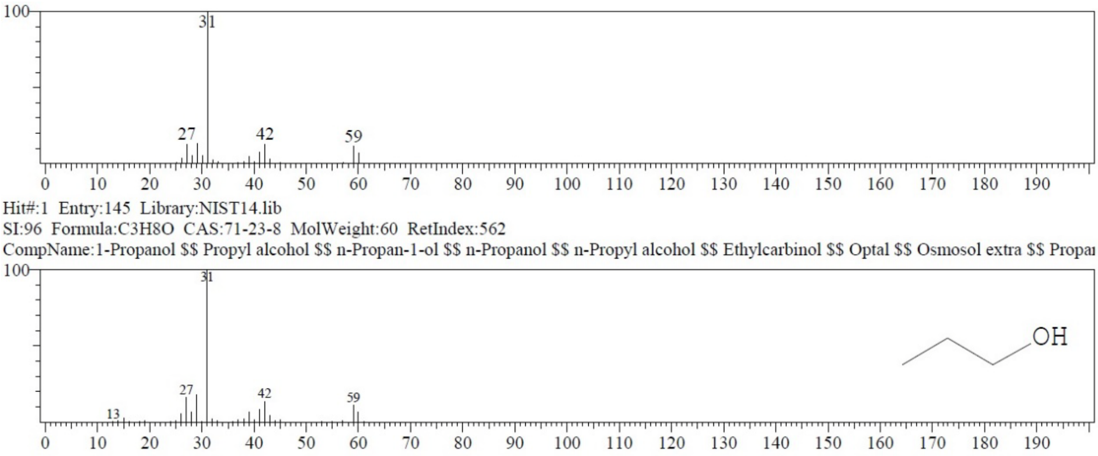


Target 1



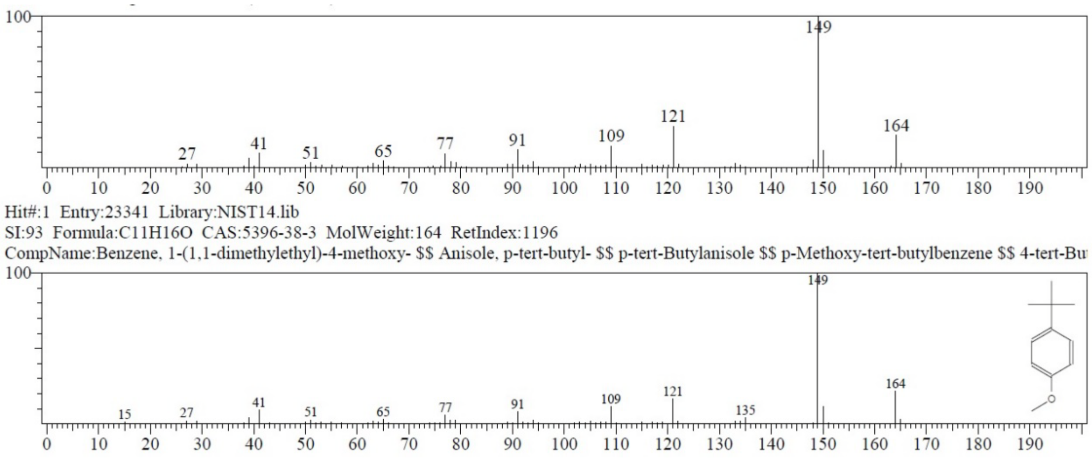
Hit#:1 Entry:47 Library:NIST14s.lib
SI:97 Formula:C2H6O CAS:64-17-5 MolWeight:46 RetIndex:463
CompName:Ethanol $$ Ethyl alcohol $$ Alcohol $$ Alcohol anhydrous $$ Algrain $$ Anhydrol $$ Denatured ethanol $$ Ethyl hydrate $$ Ethyl hyd

Target 2



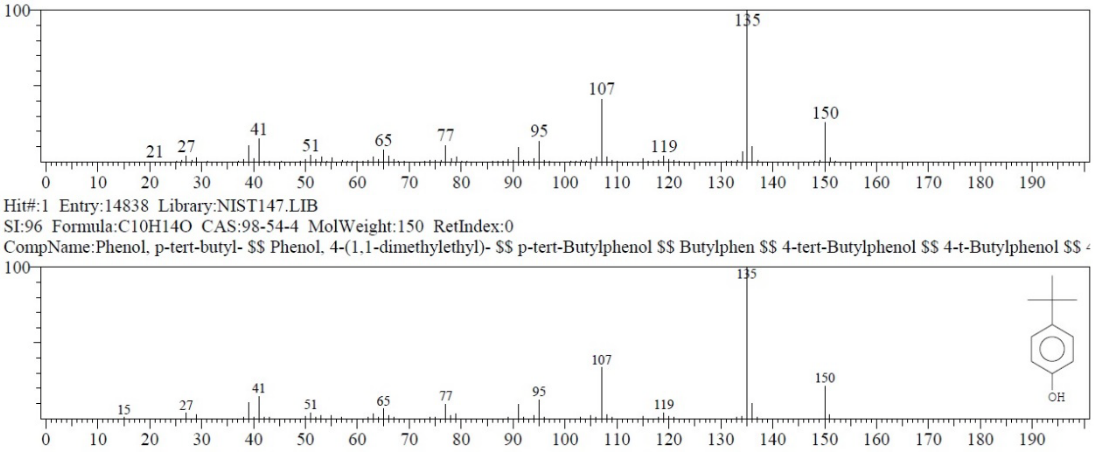
Hit#:1 Entry:145 Library:NIST14.lib
SI:96 Formula:C3H8O CAS:71-23-8 MolWeight:60 RetIndex:562
CompName:1-Propanol $$ Propyl alcohol $$ n-Propan-1-ol $$ n-Propanol $$ n-Propyl alcohol $$ Ethylcarbinol $$ Optal $$ Osmosol extra $$ Propa

Target 3



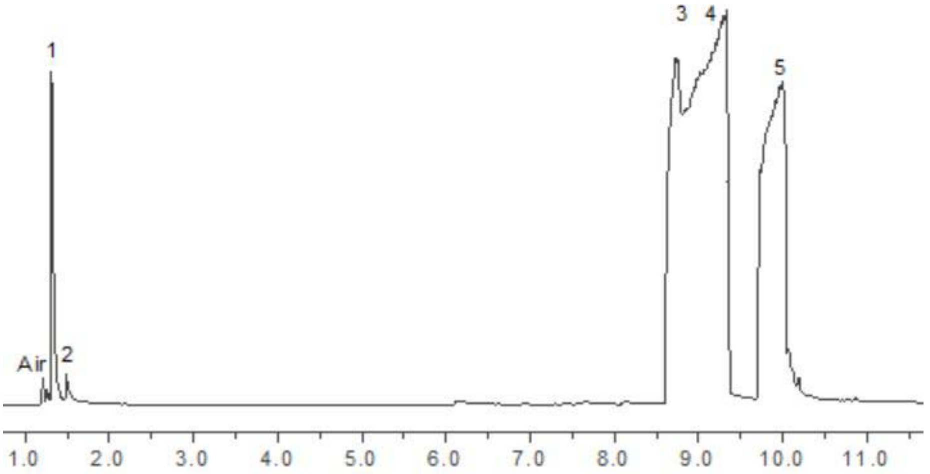
```
Hit#:1  Entry:23341  Library:NIST14.lib
SI:93  Formula:C11H16O  CAS:5396-38-3  MolWeight:164  RetIndex:1196
CompName:Benzene, 1-(1,1-dimethylethyl)-4-methoxy- $$ Anisole, p-tert-butyl- $$ p-tert-Butylanisole $$ p-Methoxy-tert-butylbenzene $$ 4-tert-Bu
```

Target 4

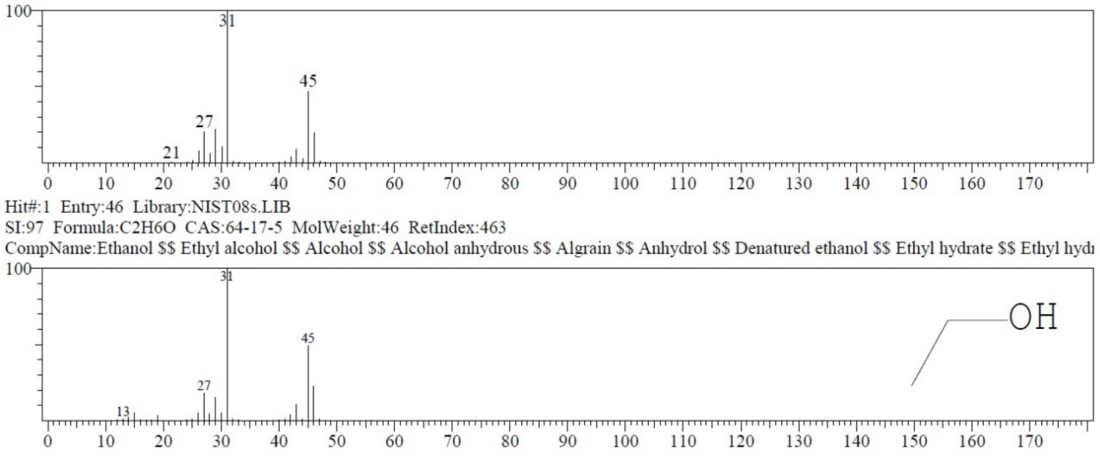


```
Hit#:1  Entry:14838  Library:NIST147.LIB
SI:96  Formula:C10H14O  CAS:98-54-4  MolWeight:150  RetIndex:0
CompName:Phenol, p-tert-butyl- $$ Phenol, 4-(1,1-dimethylethyl)- $$ p-tert-Butylphenol $$ Butylphen $$ 4-tert-Butylphenol $$ 4-t-Butylphenol $$
```

Fig. S19 The GC-MS spectra of the solution after the reaction in entry 8 of Table 2.

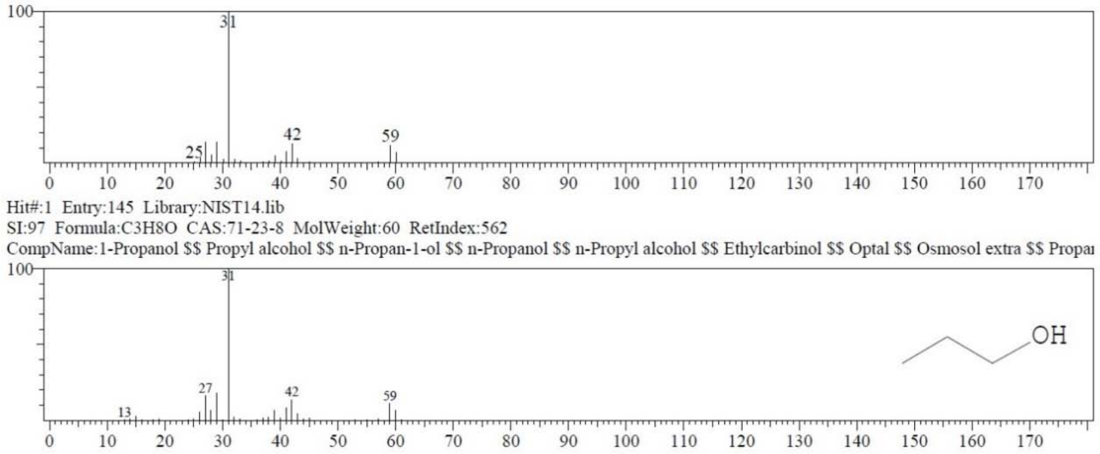


Target 1



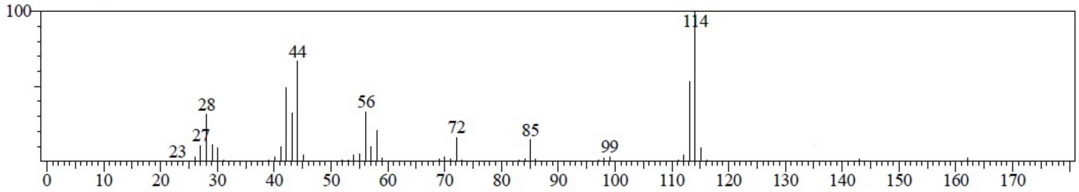
Hit#:1 Entry:46 Library:NIST08s.LIB
SI:97 Formula:C2H6O CAS:64-17-5 MolWeight:46 RetIndex:463
CompName:Ethanol $$ Ethyl alcohol $$ Alcohol $$ Alcohol anhydrous $$ Algrain $$ Anhydrol $$ Denatured ethanol $$ Ethyl hydrate $$ Ethyl hyd

Target 2

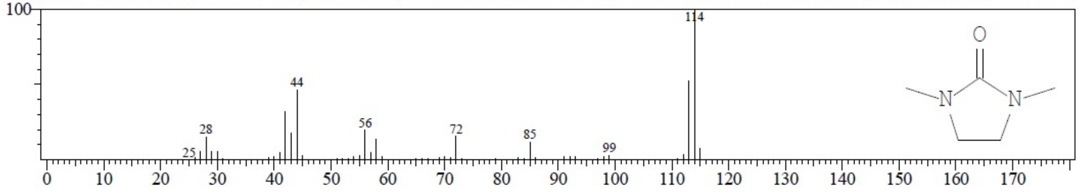


Hit#:1 Entry:145 Library:NIST14.lib
SI:97 Formula:C3H8O CAS:71-23-8 MolWeight:60 RetIndex:562
CompName:1-Propanol $$ Propyl alcohol $$ n-Propan-1-ol $$ n-Propanol $$ n-Propyl alcohol $$ Ethylcarbinol $$ Optal $$ Osmosol extra $$ Propa

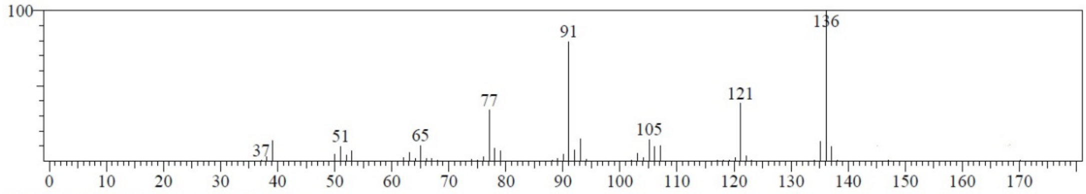
Target 3



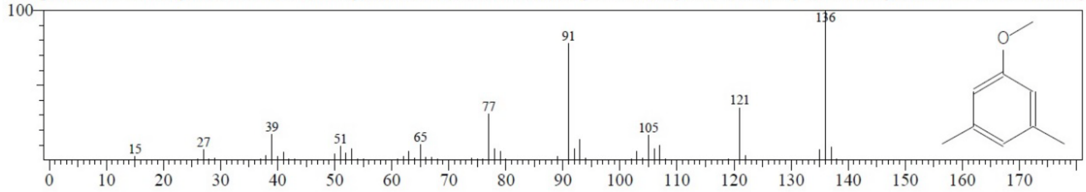
Hit#:1 Entry:3280 Library:NIST14s.lib
SI:91 Formula:C5H10N2O CAS:80-73-9 MolWeight:114 RetIndex:1033
CompName:2-Imidazolidinone, 1,3-dimethyl- $$ Dimethylethyleneurea $$ N,N'-Dimethyl-2-imidazolidinone $$ N,N'-Dimethylethyleneurea $$ Rhonite 1 $$



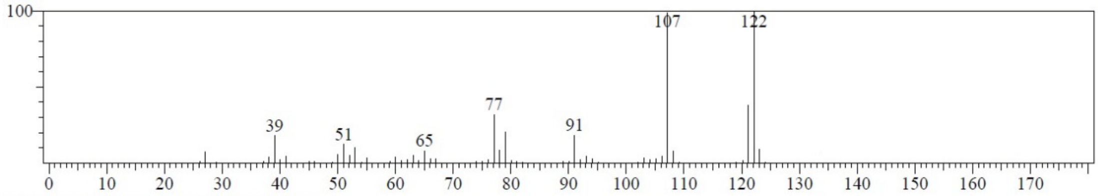
Target 4



Hit#:1 Entry:6762 Library:NIST14s.lib
SI:95 Formula:C9H12O CAS:874-63-5 MolWeight:136 RetIndex:1096
CompName:3,5-Dimethylanisole $$ 2,5-Dimethylanisole $$ Benzene, 1-methoxy-3,5-dimethyl- $$ 1-Methoxy-3,5-dimethylbenzene # $$ 3,5-Dimethy



Target 5



Hit#:1 Entry:4242 Library:NIST08s.LIB
SI:96 Formula:C8H10O CAS:108-68-9 MolWeight:122 RetIndex:1127
CompName:Phenol, 3,5-dimethyl- $$ 3,5-Xylenol $$ 1-Hydroxy-3,5-dimethylbenzene $$ 1,3,5-Xylenol $$ 3,5-Dimethylphenol $$ 1,3-Dimethyl-5-hy

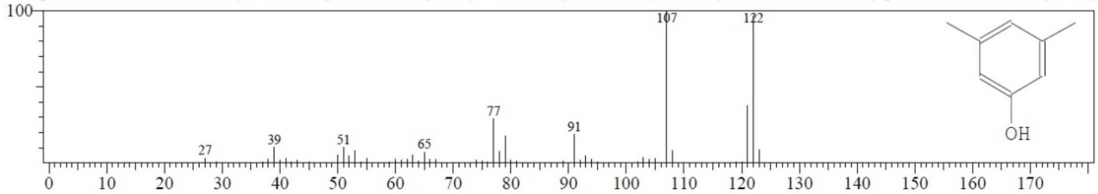
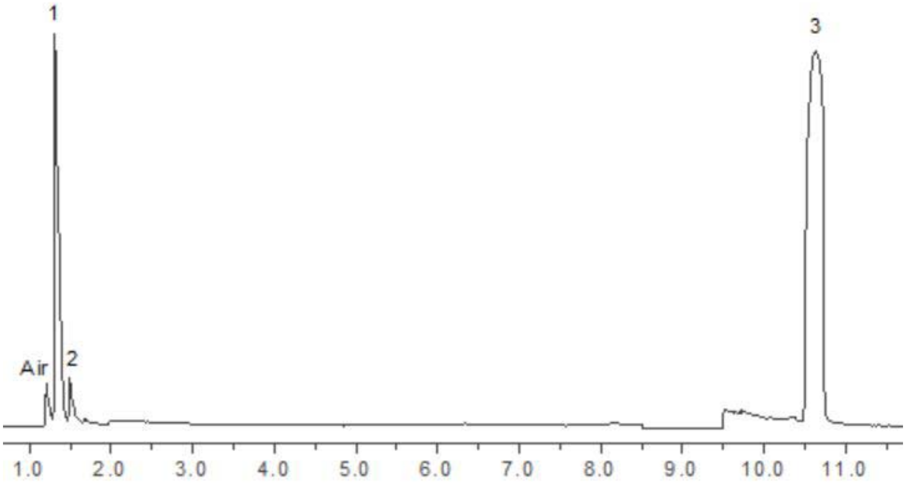
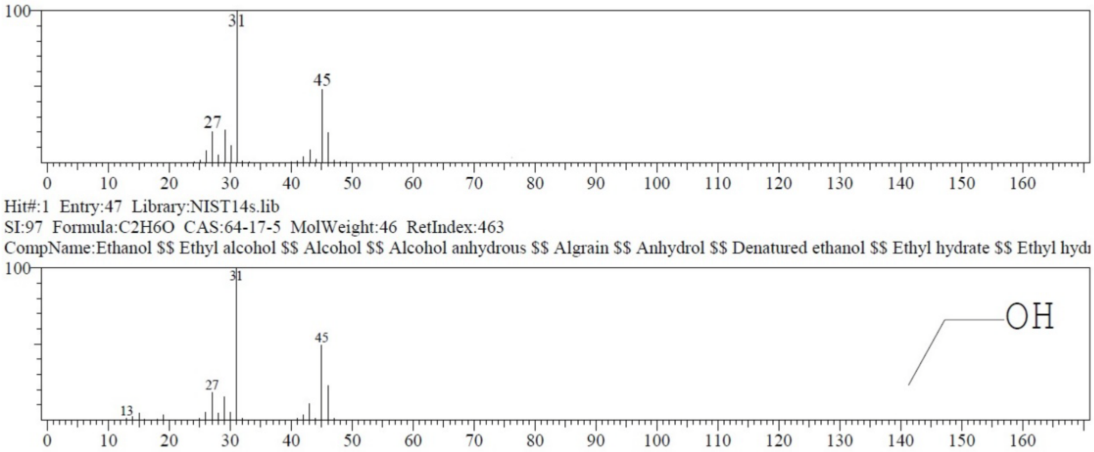


Fig. S20 The GC-MS spectra of the solution after the reaction in entry 9 of Table 2.

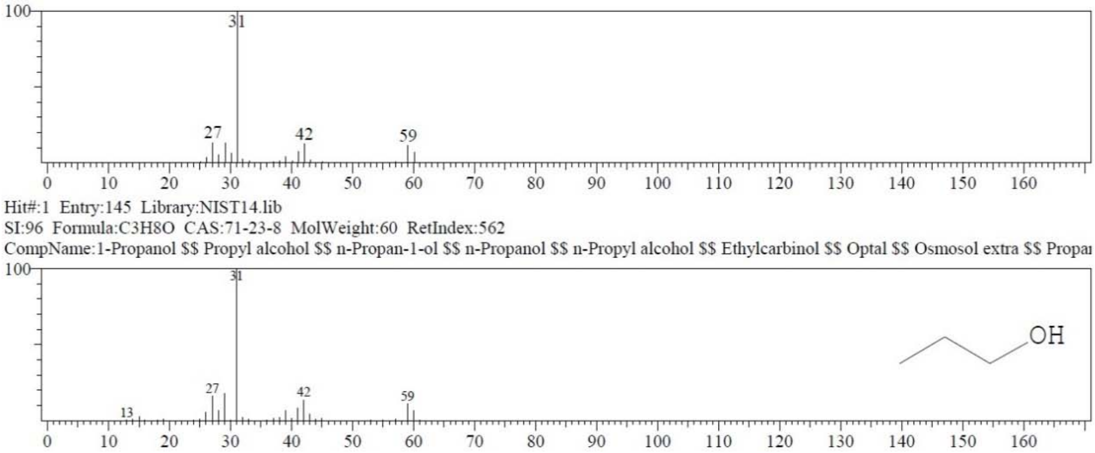


Target 1



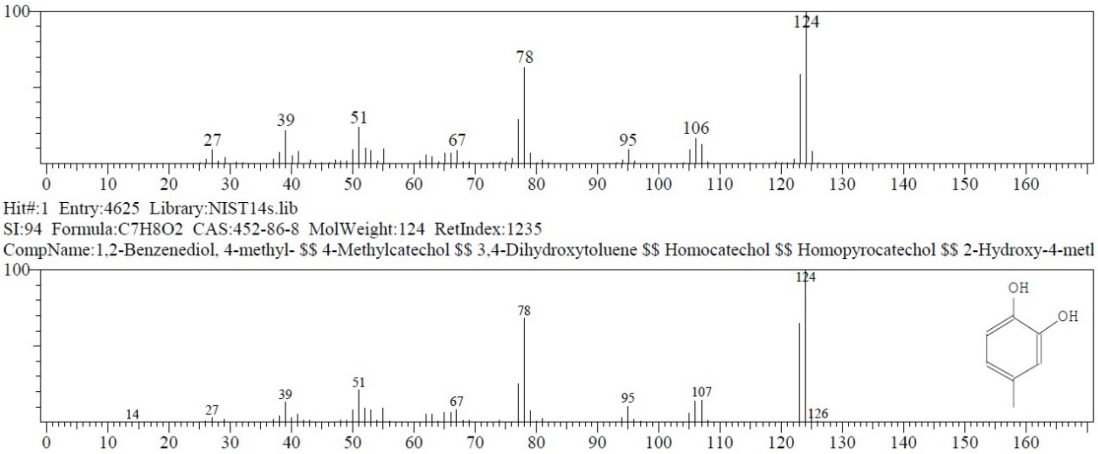
Hit#:1 Entry:47 Library:NIST14s.lib
SI:97 Formula:C2H6O CAS:64-17-5 MolWeight:46 RetIndex:463
CompName:Ethanol $$ Ethyl alcohol $$ Alcohol $$ Alcohol anhydrous $$ Algrain $$ Anhydrol $$ Denatured ethanol $$ Ethyl hydrate $$ Ethyl hyd

Target 2



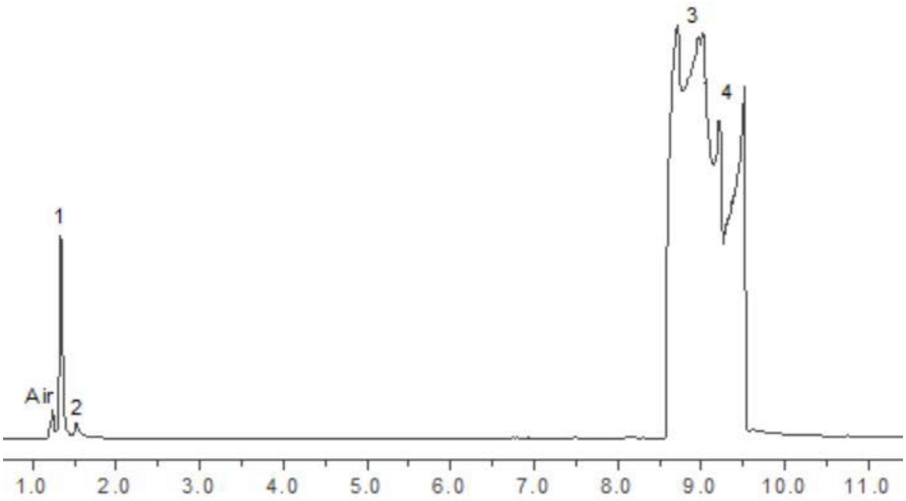
Hit#:1 Entry:145 Library:NIST14.lib
SI:96 Formula:C3H8O CAS:71-23-8 MolWeight:60 RetIndex:562
CompName:1-Propanol $$ Propyl alcohol $$ n-Propan-1-ol $$ n-Propanol $$ n-Propyl alcohol $$ Ethylcarbinol $$ Optal $$ Osmosol extra $$ Propa

Target 3

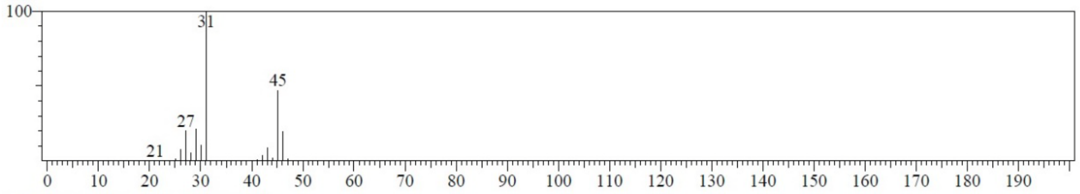


```
Hit#:1  Entry:4625  Library:NIST14s.lib
SI:94  Formula:C7H8O2  CAS:452-86-8  MolWeight:124  RetIndex:1235
CompName:1,2-Benzenediol, 4-methyl- $$ 4-Methylcatechol $$ 3,4-Dihydroxytoluene $$ Homocatechol $$ Homopyrocatechol $$ 2-Hydroxy-4-met
```

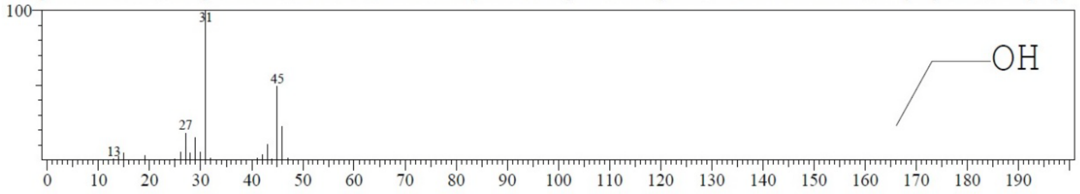
Fig. S21 The GC-MS spectra of the solution after the reaction in entry 10 of Table 2.



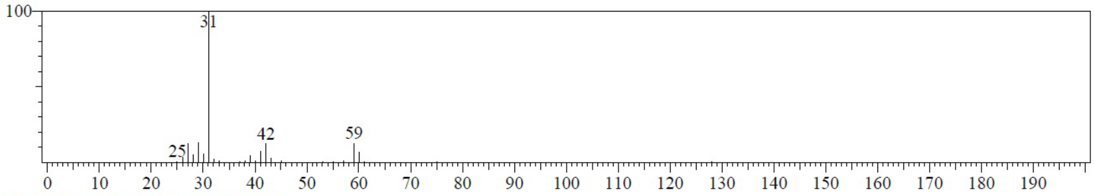
Target 1



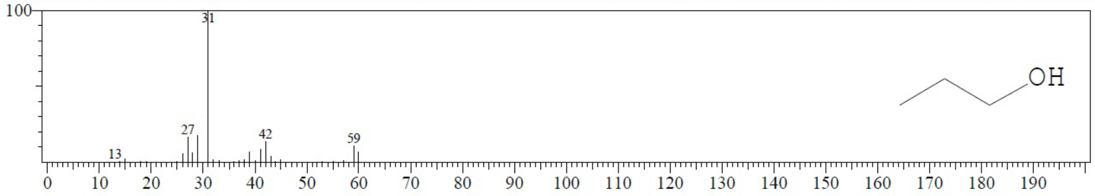
```
Hit#:1  Entry:47  Library:NIST14s.lib
SI:97  Formula:C2H6O  CAS:64-17-5  MolWeight:46  RetIndex:463
CompName:Ethanol $$ Ethyl alcohol $$ Alcohol $$ Alcohol anhydrous $$ Algrain $$ Anhydrol $$ Denatured ethanol $$ Ethyl hydrate $$ Ethyl hyd
```



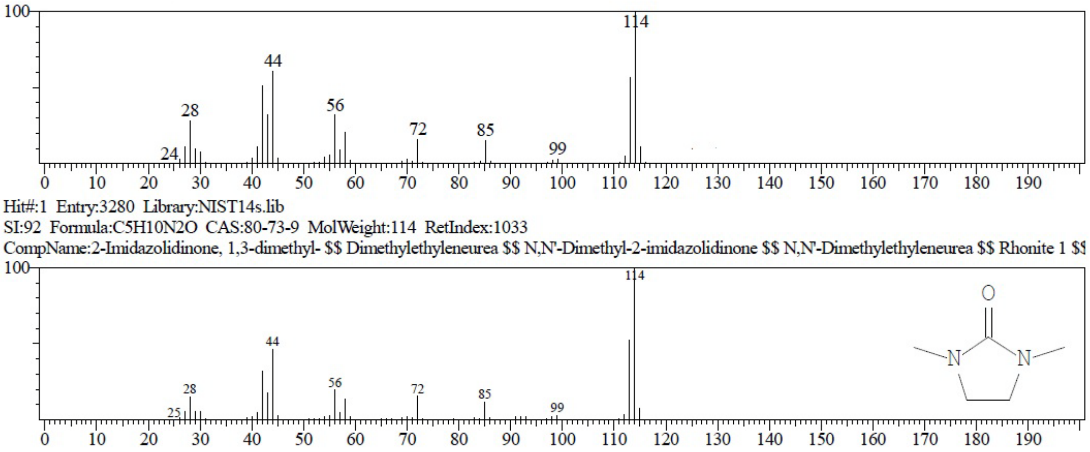
Target 2



```
Hit#:1  Entry:145  Library:NIST14.lib
SI:96  Formula:C3H8O  CAS:71-23-8  MolWeight:60  RetIndex:562
CompName:1-Propanol $$ Propyl alcohol $$ n-Propan-1-ol $$ n-Propanol $$ n-Propyl alcohol $$ Ethylcarbinol $$ Optal $$ Osmosol extra $$ Propa
```



Target 3


Hit#:1 Entry:3280 Library:NIST14s.lib
SI:92 Formula:C5H10N2O CAS:80-73-9 MolWeight:114 RetIndex:1033
CompName:2-Imidazolidinone, 1,3-dimethyl- $$ Dimethylethyleneurea $$ N,N'-Dimethyl-2-imidazolidinone $$ N,N'-Dimethylethyleneurea $$ Rhonite 1 $$

Target 4

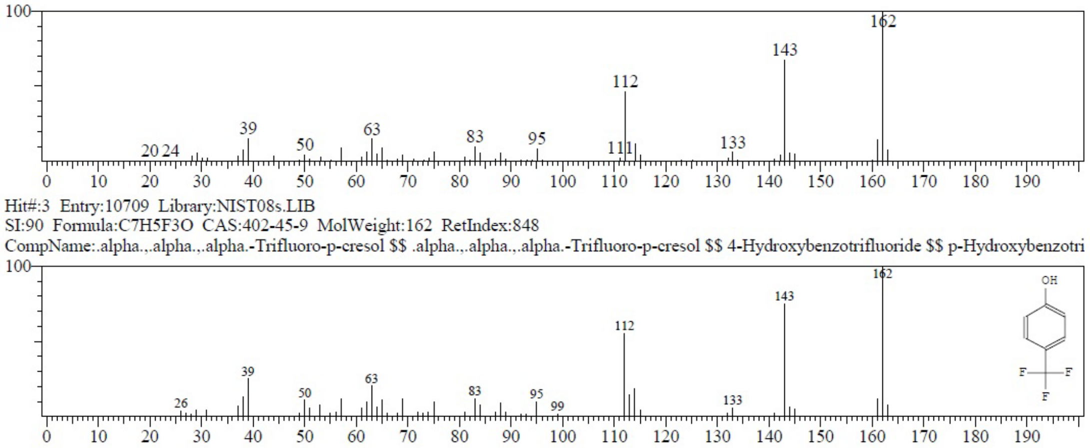
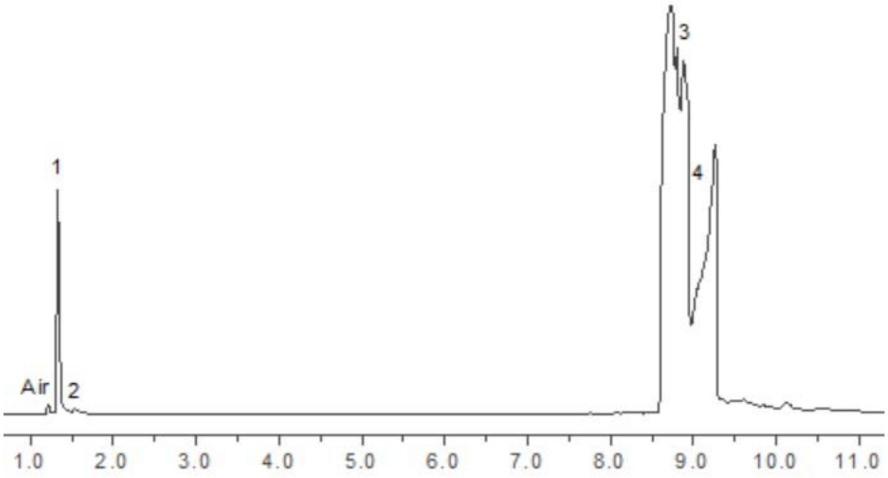
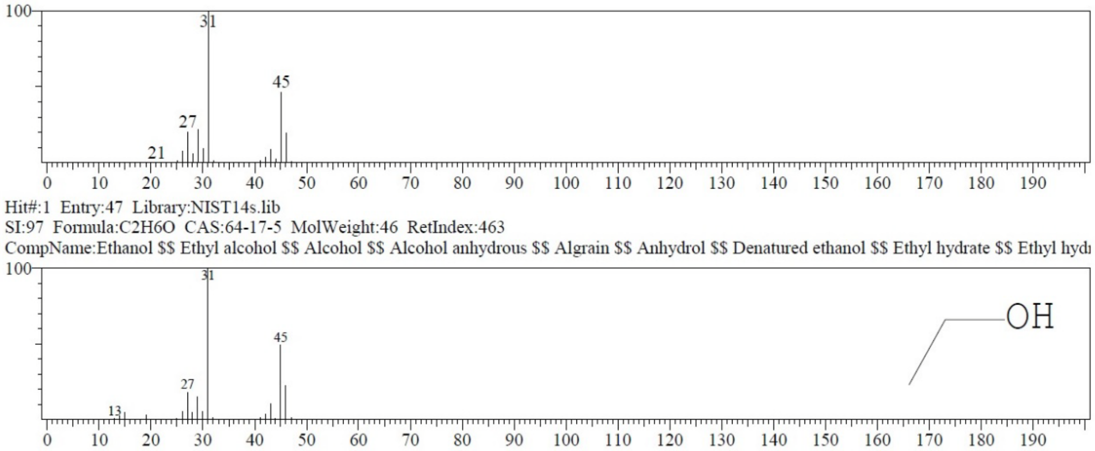

Hit#:3 Entry:10709 Library:NIST08s.LIB
SI:90 Formula:C7H5F3O CAS:402-45-9 MolWeight:162 RetIndex:848
CompName:.alpha.,.alpha.,.alpha.-Trifluoro-p-cresol $$ .alpha.,.alpha.,.alpha.-Trifluoro-p-cresol $$ 4-Hydroxybenzotrifluoride $$ p-Hydroxybenzotri

Fig. S22 The GC-MS spectra of the solution after the reaction in entry 11 of Table 2.

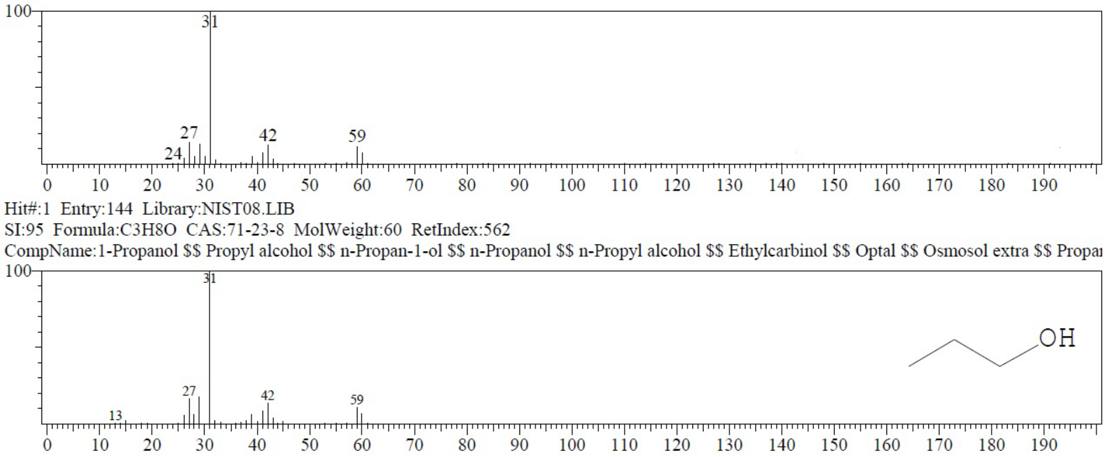


Target 1



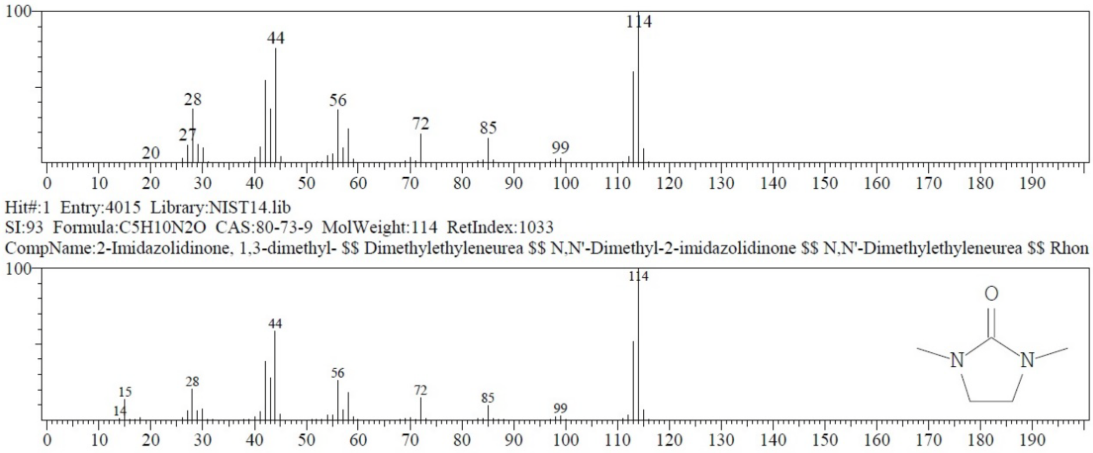
Hit#:1 Entry:47 Library:NIST14s.lib
SI:97 Formula:C2H6O CAS:64-17-5 MolWeight:46 RetIndex:463
CompName:Ethanol $$ Ethyl alcohol $$ Alcohol $$ Alcohol anhydrous $$ Algrain $$ Anhydrol $$ Denatured ethanol $$ Ethyl hydrate $$ Ethyl hyd

Target 2



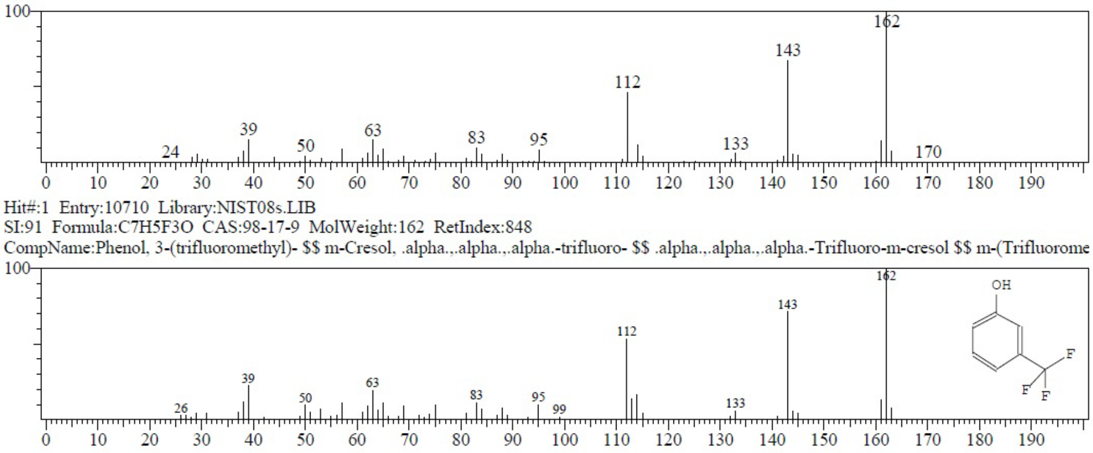
Hit#:1 Entry:144 Library:NIST08.LIB
SI:95 Formula:C3H8O CAS:71-23-8 MolWeight:60 RetIndex:562
CompName:1-Propanol $$ Propyl alcohol $$ n-Propan-1-ol $$ n-Propanol $$ n-Propyl alcohol $$ Ethylcarbinol $$ Optal $$ Osmosol extra $$ Propa

Target 3



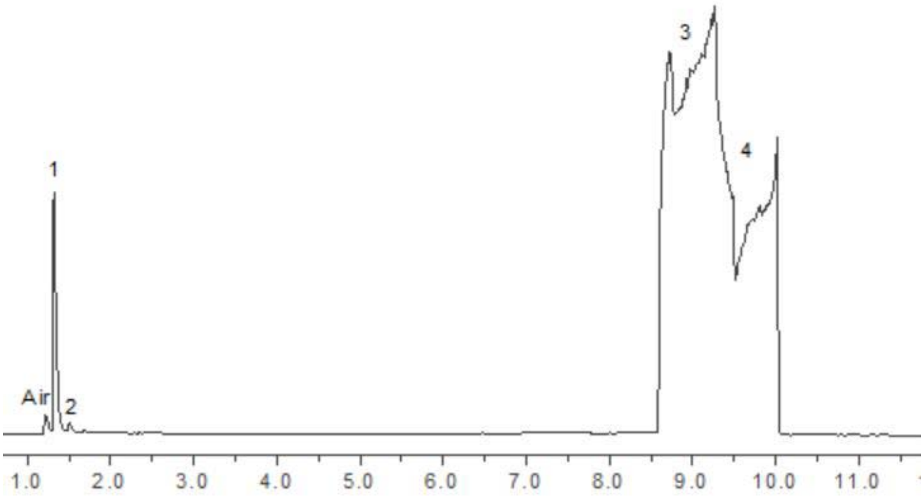
Hit#:1 Entry:4015 Library:NIST14.lib
SI:93 Formula:C5H10N2O CAS:80-73-9 MolWeight:114 RetIndex:1033
CompName:2-Imidazolidinone, 1,3-dimethyl- $$ Dimethylethyleneurea $$ N,N'-Dimethyl-2-imidazolidinone $$ N,N'-Dimethylethyleneurea $$ Rhon

Target 4

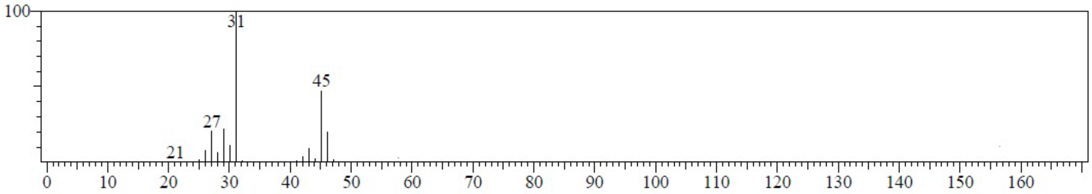


Hit#:1 Entry:10710 Library:NIST08s.LIB
SI:91 Formula:C7H5F3O CAS:98-17-9 MolWeight:162 RetIndex:848
CompName:Phenol, 3-(trifluoromethyl)- $$ m-Cresol, .alpha.,.alpha.,.alpha.-trifluoro- $$ .alpha.,.alpha.,.alpha.-Trifluoro-m-cresol $$ m-(Trifluorome

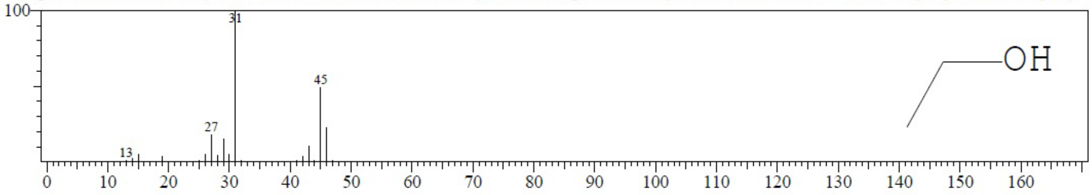
Fig. S23 The GC-MS spectra of the solution after the reaction in entry 12 of Table 2.



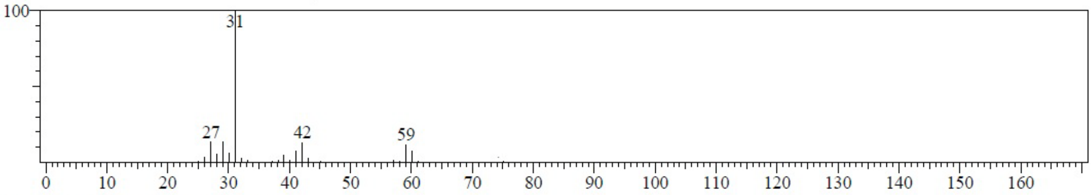
Target 1



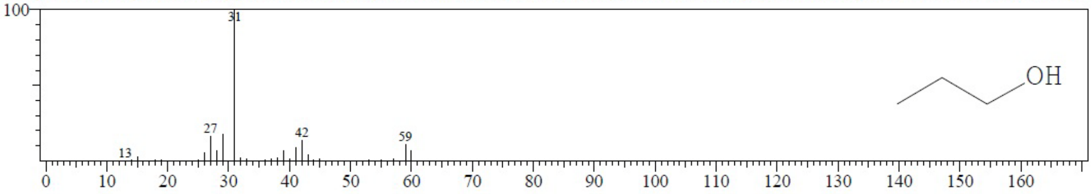
Hit#:1 Entry:47 Library:NIST14s.lib
SI:97 Formula:C2H6O CAS:64-17-5 MolWeight:46 RetIndex:463
CompName:Ethanol $$ Ethyl alcohol $$ Alcohol $$ Alcohol anhydrous $$ Algrain $$ Anhydrol $$ Denatured ethanol $$ Ethyl hydrate $$ Ethyl hyd



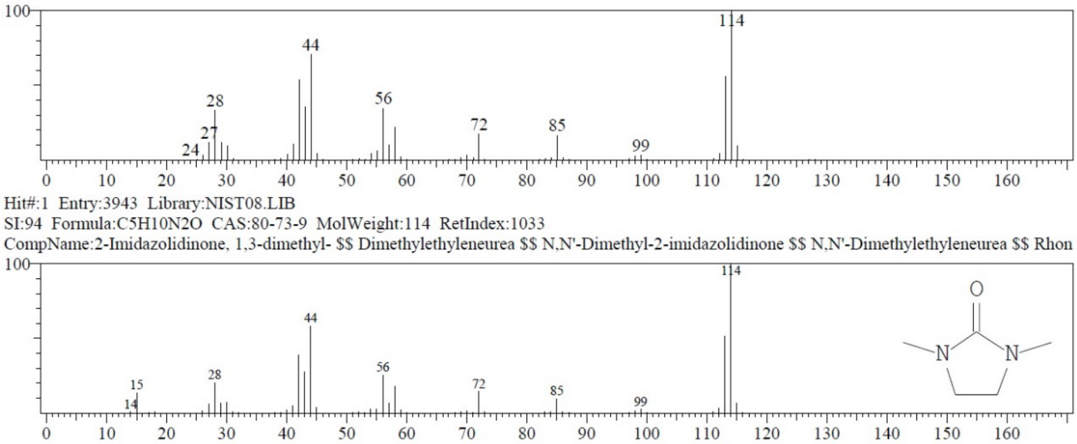
Target 2



Hit#:1 Entry:145 Library:NIST14.lib
SI:96 Formula:C3H8O CAS:71-23-8 MolWeight:60 RetIndex:562
CompName:1-Propanol $$ Propyl alcohol $$ n-Propan-1-ol $$ n-Propanol $$ n-Propyl alcohol $$ Ethylcarbinol $$ Optal $$ Osmosol extra $$ Propa



Target 3



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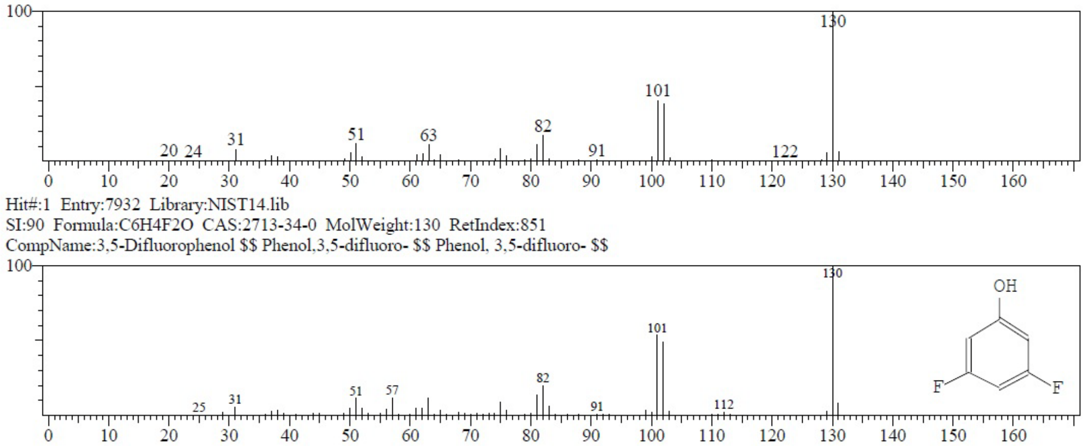
Hit#:1  Entry:3943  Library:NIST08.LIB
SI:94  Formula:C5H10N2O  CAS:80-73-9  MolWeight:114  RetIndex:1033
CompName:2-Imidazolidinone, 1,3-dimethyl- $$ Dimethylethyleneurea $$ N,N'-Dimethyl-2-imidazolidinone $$ N,N'-Dimethylethyleneurea $$ Rhon
```

Target 4



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Hit#:1  Entry:7932  Library:NIST14.lib
SI:90  Formula:C6H4F2O  CAS:2713-34-0  MolWeight:130  RetIndex:851
CompName:3,5-Difluorophenol $$ Phenol,3,5-difluoro- $$ Phenol, 3,5-difluoro- $$
```
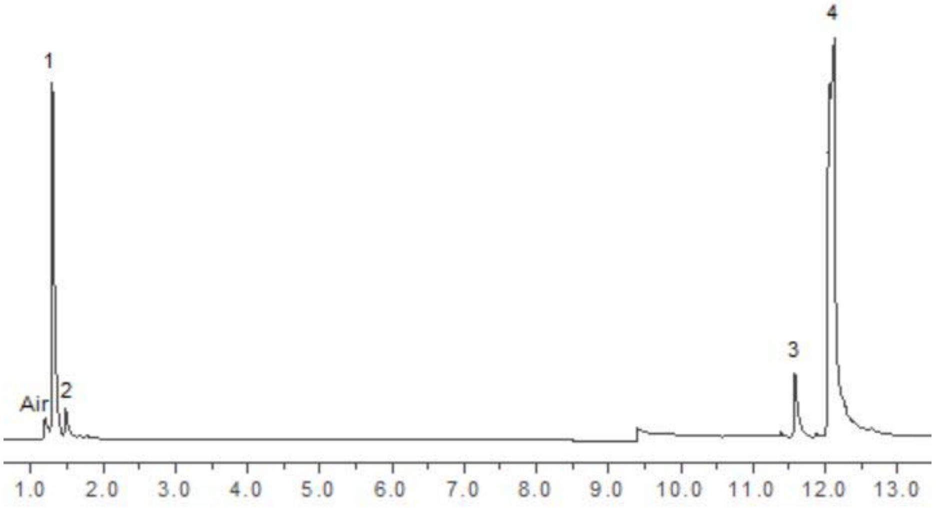
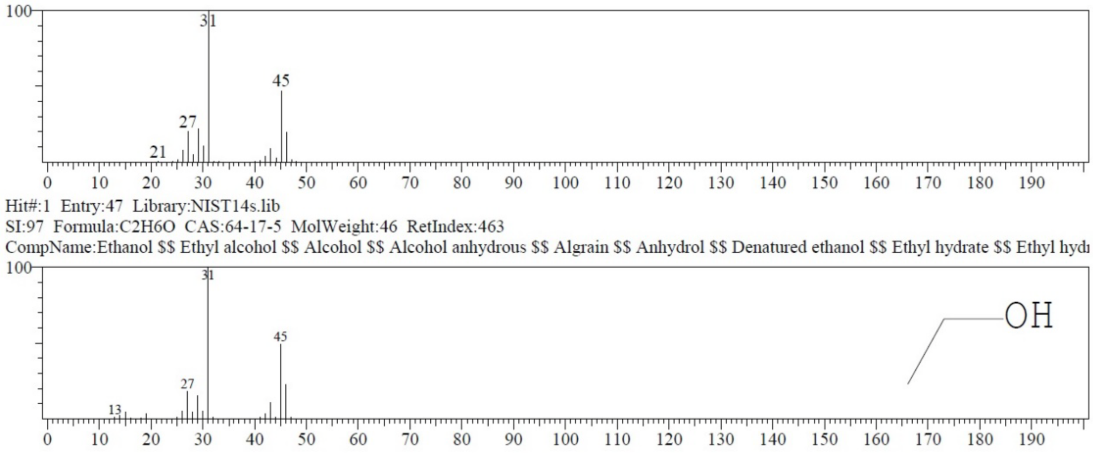

Fig. S24 The GC-MS spectra of the solution after the reaction in entry 13 of Table 2.

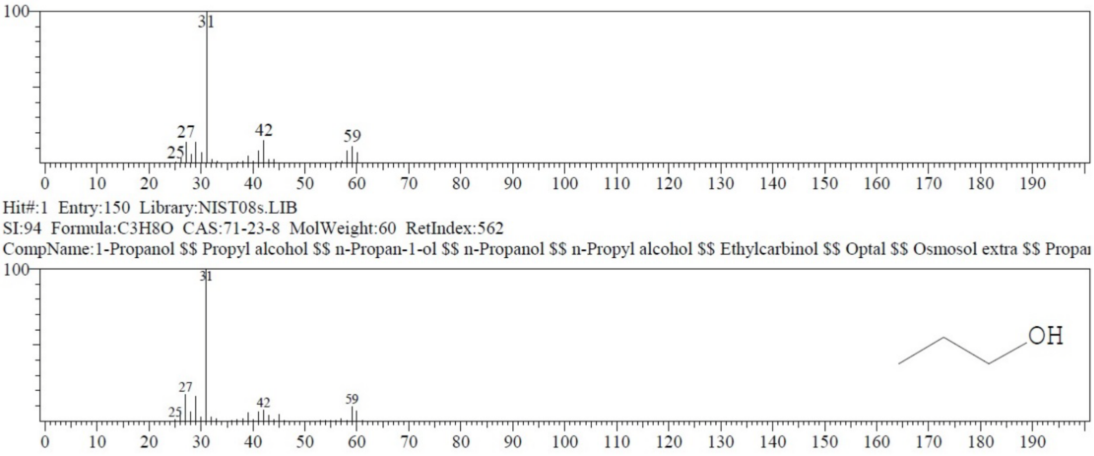


Target 1



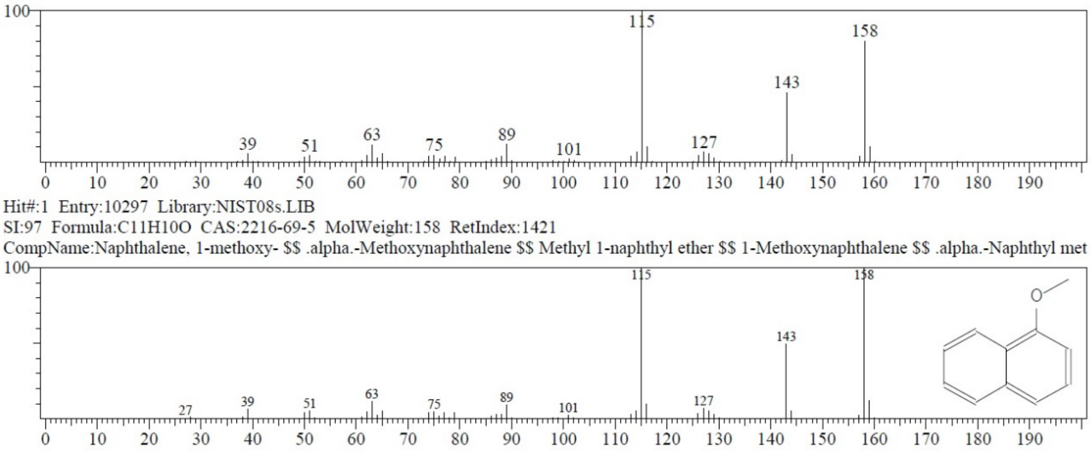
```
Hit#:1  Entry:47  Library:NIST14s.lib
SI:97  Formula:C2H6O  CAS:64-17-5  MolWeight:46  RetIndex:463
CompName:Ethanol $$ Ethyl alcohol $$ Alcohol $$ Alcohol anhydrous $$ Algrain $$ Anhydrol $$ Denatured ethanol $$ Ethyl hydrate $$ Ethyl hyd
```

Target 2



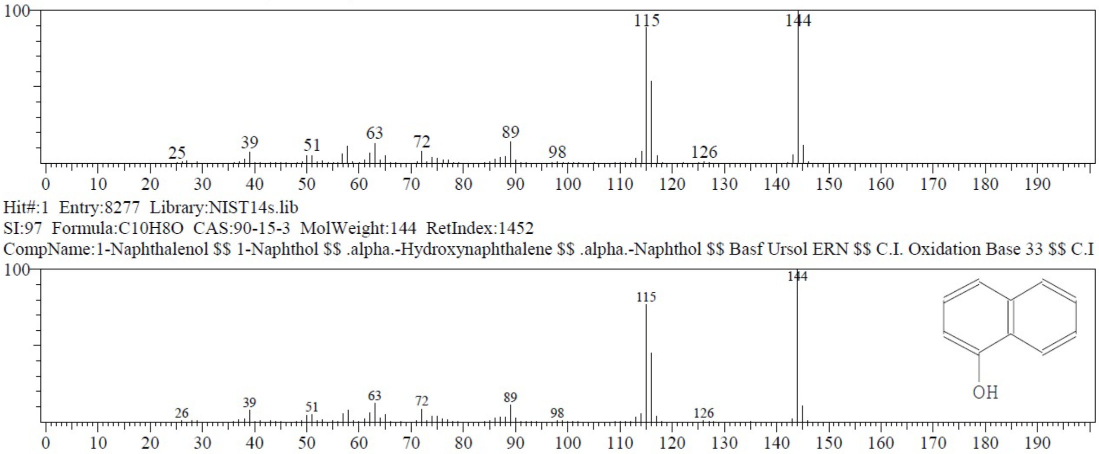
```
Hit#:1  Entry:150  Library:NIST08s.LIB
SI:94  Formula:C3H8O  CAS:71-23-8  MolWeight:60  RetIndex:562
CompName:1-Propanol $$ Propyl alcohol $$ n-Propan-1-ol $$ n-Propanol $$ n-Propyl alcohol $$ Ethylcarbinol $$ Optal $$ Osmosol extra $$ Propa
```

Target 3



```
Hit#:1  Entry:10297  Library:NIST08s.LIB
SI:97  Formula:C11H10O  CAS:2216-69-5  MolWeight:158  RetIndex:1421
CompName:Naphthalene, 1-methoxy- $$ .alpha.-Methoxynaphthalene $$ Methyl 1-naphthyl ether $$ 1-Methoxynaphthalene $$ .alpha.-Naphthyl met
```

Target 4



```
Hit#:1  Entry:8277  Library:NIST14s.lib
SI:97  Formula:C10H8O  CAS:90-15-3  MolWeight:144  RetIndex:1452
CompName:1-Naphthalenol $$ 1-Naphthol $$ .alpha.-Hydroxynaphthalene $$ .alpha.-Naphthol $$ Basf Ursol ERN $$ C.I. Oxidation Base 33 $$ C.I
```

Fig. S25 The GC-MS spectra of the solution after the reaction in entry 14 of Table 2.

Table S1 Effect of reaction parameters on the reaction.[a]

Entry	Ru (μmol)	Co (μmol)	LiI (mmol)	Triphos (μmol)	CO_2	H_2	TON
1	10	30	2.2	20	3	5	63
2	20	60	2.2	20	3	5	73
3	30	90	2.2	20	3	5	48
4	10	70	2.2	20	3	5	65
5	30	50	2.2	20	3	5	46
6	50	30	2.2	20	3	5	11
7	20	60	1.1	20	3	5	33
8	20	60	3.3	20	3	5	60
9	20	60	2.2	10	3	5	59
10	20	60	2.2	30	3	5	62
11[b]	20	60	2.2	20	3	5	1
12	20	60	2.2	20	0	5	0
13	20	60	2.2	20	3	0	0
14	20	60	2.2	20	0.75	1.25	9
15	20	60	2.2	20	1.5	2.5	43
16	20	60	2.2	20	2.25	3.75	53
17	20	60	2.2	20	3.75	6.25	74
18	20	60	2.2	20	1	7	63
19	20	60	2.2	20	2	6	69
20	20	60	2.2	20	4	4	69
21	20	60	2.2	20	5	3	61
22	20	60	2.2	20	6	2	40
23[c]	20	60	2.2	20	1	5	68

[a]Reaction conditions: $[RuCl_2(CO)_3]_2/Co_2(CO)_8$ were used as the catalyst and their dosages were based on the metal, 2 mL DMI, 3.6 mmol anisole, 190 °C, 10 h. [b]No anisole was added before the reaction. [c] 0.8MPa CO was used instead of 3MPa CO_2.

Note: At fixed Ru/Co ratio of 1/3, the reaction rate initially increased and then dropped with elevating catalyst dosages, and the highest TON was obtained at 20 μmol Ru and 60 μmol Co (entries 1-3). When the total Ru-Co dosage was fixed at 80 μmol, the suitable Ru/Co ratio was 1/3 (entries 2, 4-6). After testing the catalytic rate at different LiI dosages, we found that 2.2 mmol was appropriate (entries 2, 7, 8). The impact of triphos dosge was also studied and the suitable dosage was 20 μmol (entries 2, 9, 10). The anisole, CO_2 and H_2 were all essential to the reaction, because ethanol could hardly be observed without anyone of them (entries 11-13). With the rising gas pressure, the TON of ethanol increased remarkably, while the increase became minor when the pressure was high enough (entries 2, 14-17). We fixed the total pressure at 8 MPa and changed the CO_2/H_2 ratio, and found that 3 MPa CO_2 and 5 MPa H_2 were fit for the reaction (entries 2, 18-22). In short, the optimized reaction conditions were 20 μmol Ru and 60 μmol Co catalysts, 2.2 mmol LiI, 20 μmol triphos, 3 MPa CO_2 and 5 MPa H_2, 190 °C.

Table S2 Impact of the catalytic components and reactant gases on the decomposition of anisole at 190 °C.

Entry	Catalyst 20 µmol Ru/60 µmol Co	Promoter 2.2 mmol	Ligand 20 µmol	CO_2 MPa	H_2 MPa	Anisole decomposition%
1	-	LiI	-	0	0	3.9
2	$[RuCl_2(CO)_3]_2$, $Co_2(CO)_8$	-	triphos	3	5	0
3	$[RuCl_2(CO)_3]_2$, $Co_2(CO)_8$	LiI	triphos	3	5	79.3
4	-	LiI	-	3	5	43.1
5	$Co_2(CO)_8$	LiI	triphos	3	5	46.2
6	$[RuCl_2(CO)_3]_2$,	LiI	triphos	3	5	76.2
7	$[RuCl_2(CO)_3]_2$, $Co_2(CO)_8$	LiI	-	3	5	68.2
8	$[RuCl_2(CO)_3]_2$, $Co_2(CO)_8$	LiI	$LiBF_4$	3	5	100

References

1. M. Röper, H. Loevenich and J. Korff, J. Mol. Catal., 1982, **17**, 315–322.