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Supplementary Information

Ligand Free Copper(I)-Catalyzed Synthesis of Diaryl Ether by Cs_2CO_3 via Free Radical Path

Hong-Jie Chen,[a,b] Mei-Chun Tseng,[a] Hsu I-Jui,[c] Wei-Ting Chen,[a,c] Chien-Chung Han*[b] and Shin-Guang Shyu*[a]

[a] Institute of Chemistry, Academia Sinica, 128 Academia Road Sec. 2, Nankang Taipei 115 Taiwan, R.O.C.
[b] Department of Chemistry, National Tsing Hua University, 101, Sec 2, Kuang-Fu Rd., Hsinchu 30013, Taiwan, R.O.C.
[c] Department of Molecular Science and Engineering, National Taipei University of Technology, 1,Sec. 3, Zhongxiao E Road, Taipei 10608, Taiwan, R.O.C.

E-mail: sgshyu@chem.sinica.edu.tw; Fax: +886-2-2783-1237; Tel: +886-2-2789-8593

CONTENT

Experimental Section

All reagents were purchased from commercial sources and used without further purification. Copper(I) iodide (fine grey powder), 2,4-dimethylphenol, 4-bromotoluene, 1-bromonaphthalene, 2-bromo-1,4-dimethylbenzene, 1,4-di-*tert*-butylbenzene and Cs_2CO_3 were purchased from ACROS. Toluene (dried, seccoSolv®) was purchased from Merck and purged with argon for 15 min before use. Reagents were transferred to the reaction vessel (Pyrex tube with a Teflon screw cap) in a glove box. GC experiments were performed on an Agilent 6890N gas chromatograph equipped with a 30 m X 0.53 mm X 3.0 m HP-1 capillary column and a FID detector. 1,4-di-*tert*-butylbenzene was used as the internal standard in the quantitative GC analyses.

Typical procedure of copper-catalyzed C–O coupling reaction.

2,4-Dimethylphenol (0.147 mL, 1.2 mmol), aryl bromide (1.0 mmol) were added to a Pyrex tube with a septum. The tube was evacuated and backfilled with nitrogen through needle for 3 cycles, then sealed with parafilm before it was put into the dry box. CuI (4.8 mg, 0.025 mmol, 2.5 mol%), 1,4-di-*tert*-butylbenzene (19.0 mg, 0.1 mmol), Cs_2CO_3 (978.0 mg, 3.0 mmol) and toluene (2 mL) were added to the tube in dry box at RT, and capped with a Teflon screwcap. The reaction mixture was stirred at 120 °C for 8 h. Quantitative GC analysis with 1,4-di-*tert*-butylbenzene as the internal standard was carried out to obtain the GC yield.

Aryl bromides and their correponding yields: 1. 4-bromotoluene (0.123 mL, 1.0 mmol), *68%*; 1-(bromonaphthalene 0.140 mL, 1.0 mmol), 23%; 2-bromo-1,4-dimethylbenzene 0.138 mlL, 1.0 mmol), 41%. 1,4-di-*tert*-butylbenzene was used as the internal standard, response factor : 1.1325 (4-bromotoluene), 0.392 (1-bromonaphthalene), 0.970 (2-bromo-1,4-dimethylbenzene).

Typical procedure of copper-catalyzed C–O coupling reaction with radical scavenger.

2,4-Dimethylphenol (0.147 mL, 1.2 mmol), aryl bromide (1.0 mmol) were added to a Pyrex tube with a septum. The tube was evacuated and backfilled with nitrogen through needle for 3 cycles, then sealed with parafilm before it was put into dry box. CuI (4.8 mg, 0.025 mmol, 2.5 mol%), 1,4-di-*tert*-butylbenzene (19.0 mg, 0.1 mmol), Cs_2CO_3 (978.0 mg, 3.0 mmol), cumene (50 mol% 0.690 mL) and toluene (2 mL) were added to the tube in dry box at RT, and capped with a Teflon screwcap. The reaction mixture was stirred at 120 °C for 8 h. Quantitative GC analysis with 1,4-di-*tert*-butylbenzene as the internal standard was carried out to obtain the GC yield.

Aryl bromides and their correponding yields: 1. 4-bromotoluene (0.123 mL, 1.0 mmol), 33%; 1-(bromonaphthalene 0.140 mL, 1.0 mmol), 0%; 2-bromo-1,4-dimethylbenzene 0.138 mlL, 1.0 mmol), 24%. 1,4-di-*tert*-butylbenzene was used as the internal standard, response factor : 1.1325 (4-bromotoluene), 0.392 (1-bromonaphthalene), 0.970 (2-bromo-1,4-dimethylbenzene).

Typical procedure of C–O coupling reaction with $CuCl_2$.

2,4-Dimethylphenol (0.147 mL, 1.2 mmol), 4-bromotoluene (0.123 mL, 1.0 mmol) were added to a Pyrex tube with a septum. The tube was evacuated and backfilled with nitrogen through needle for 3 cycles, then sealed with parafilm before it was put into dry box. $CuCl_2$ (3.5 mg, 0.025 mmol, 2.5 mol%), 1,4-di-*tert*-butylbenzene (19.0 mg, 0.1 mmol), Cs_2CO_3 (978.0 mg, 3.0 mmol) and toluene (2 mL) were added to the tube in dry box at RT, and capped with a Teflon screwcap. The reaction mixture was stirred at 120 °C for 8 h. GC yield 60%; 1,4-di-*tert*-butylbenzene was used as the internal standard, response factor : 1.1325.

Typical procedure of C–O coupling reaction with $CuCl_2$ and radical scavenger.

2,4-Dimethylphenol (0.147 mL, 1.2 mmol), 4-bromotoluene (0.123 mL, 1.0 mmol) were added to a Pyrex tube with a septum. The tube was evacuated and backfilled with nitrogen through needle for 3 cycles, then sealed with parafilm before it was put into dry box. $CuCl_2$ (3.5 mg, 0.025 mmol, 2.5

mol%), 1,4-di-*tert*-butylbenzene (19.0 mg, 0.1 mmol), Cs_2CO_3 (978.0 mg, 3.0 mmol), cumene (50 mol% 0.690 mL) and toluene (2 mL) were added to the tube in dry box at RT, and capped with a Teflon screwcap. The reaction mixture was stirred at 120 °C for 8 h. GC yield 49%; 1,4-di-*tert*-butylbenzene was used as the internal standard, response factor : 1.1325.

C–O coupling reaction of 2,4-dimethylphenol with 4-bromotoluene catalyzed by *in situ* prepared 2.5 mol% Cs[Cu(2,4-dimethylphenoxy)$_2$].

CuI (4.8 mg, 0.025 mmol, 2,5 mol%), Cs(2,4-dimethylphenoxy) (18.75 mg, 0.05 mmol, 5 mol%) and toluene (1 mL) were added to the Pyrex tube in dry box at RT, and sealed with a Teflon screwcap. The mixture was stirred at 120 °C for 8 h. Then the tube was transferred to the dry box and 2,4-dimethylphenol (0.147 mL, 1.2 mmol), 4-bromotoluene (0.123 mL, 1.0 mmol), 1,4-di-*tert*-butylbenzene (19.0 mg, 0.1 mmol) and toluene (1 mL) were added and the mixture was stirred at 120 °C for 8 h. GC yield 64%; 1,4-di-*tert*-butylbenzene was used as the internal standard, response factor : 1.1325.

C–O coupling reaction of 2,4-dimethyl phenol with 4-bromotoluene catalyzed by *in situ* prepared 2.5 mol% Cu(2,4-dimethylphenoxy)$_2$.

$CuCl_2$ (3.5 mg, 0.025 mmol, 2,5 mol%), Cs(2,4-dimethylphenoxy) (18.75 mg, 0.05 mmol, 5 mol%) and toluene (1 mL) were added to the Pyrex tube in a dry box at RT, and sealed with a Teflon screwcap. The mixture was stirred at 120 °C for 8 h. Then the tube was transferred to the dry box and 2,4-dimethylphenol (0.147 mL, 1.2 mmol), 4-bromotoluene (0.123 mL, 1.0 mmol), 1,4-di-*tert*-butylbenzene (19.0 mg, 0.1 mmol) and toluene (1 mL) was added and the mixture was stirred at 120 °C for 8 h. GC yield 67%; 1,4-di-*tert*-butylbenzene was used as the internal standard, response factor : 1.1325.

Stoichiometric reaction between *in situ* prepared 50 mol% Cs[Cu(2,4-dimethylphenoxy)$_2$] and 4-bromotoluene.

4-bromotoluene (0.123 mL, 1 mmol) was added to a Pyrex tube with a septum. The tube was evacuated and backfilled with nitrogen through needle for 3 cycles and then sealed with parafilm before it was put into dry box. CuI (95.2 mg, 0.5 mmol), Cs(2,4-dimethylphenoxy) (0.375 mg, 1.0 mmol), 1,4-di-*tert*-butylbenzene (19.0 mg, 0.1 mmol) and toluene (2 mL) were added to the tube in dry box at RT, and the tube was capped with a Teflon screwcap. The reaction mixture was stirred at 120 °C for 8 h. GC yield 84%; 1,4-di-*tert*-butylbenzene was used as the internal standard, response factor : 1.1325.

C–O coupling reaction without copper catalyst

2,4-Dimethylphenol (0.147 mλ, 1.2 mmol), 4-iodotoluene (218 mg, 1.0 mmol) were added to a Pyrex tube with a septum. The tube was evacuated and backfilled with nitrogen through needle for 3 cycles and was then sealed with parafilm before it was put into dry box. 1,4-di-*tert*-butylbenzene (19.0 mg, 0.1 mmol), Cs_2CO_3 (978.0 mg, 3.0 mmol) and toluene (2 mL) were added to the tube in dry box at RT, and the tube was capped with a Teflon screwcap. The reaction mixture was stirred at 120 °C for 48 h. GC yield: 22%; 1,4-di-*tert*-butylbenzene was used as the internal standard, response factor: 1.032.

Synthesis of cesium 2,4-dimethylphenoxide.

Potasium 2,4-dimethylphenoxide (800 mg, 5 mmol), cesium floride (760 mg, 5 mmol) and 20 ml tetrahydrofuran were added to a flask and the mixture was stirred at RT for 3 h in dry box. The solution was then filtrated under nitrogen and the filtrate was allowed to react with cesium floride (760 mg, 5 mmol) at RT for 3 h. After this procedure was repeated 3 times, solvent was removed from the filtrate and we obtained 0.48 g purple powder of cesium 2,4-dimethylphenoxide (yield: 38%).

NMR of cesium 2,4-dimethylphenoxide (see **Figure S32**)

^{1}H NMR (300 MHz, d^6-DMSO) δ ppm 6.449 (s, H), 6.325 (d, J = 7.8, H), 5.776 (d, J = 7.8, H), 1.973

(s,3H), 1.813 (s, 3H).

Elementary analysis of cesium 2,4-dimethylphenoxide (see **Figure S33**)

Cs[($OC_6H_3(CH_3)(CH_3)$)]: calcd C: 37.82, H: 3.57, O 6.30; found C 37.82, H 3.52, O 6.20

C–O coupling reaction with cesium 2,4-dimethylphenoxide.

Cesium 2,4-dimethylphenoxide (50.7 mg, 0.2 mmol), 4-iodotoluene (36.6 mg, 0.17 mmol) were added to a Pyrex tube with a septum. The tube was evacuated and backfilled with nitrogen through needle for 3 cycles and was then sealed with parafilm before it was put into dry box. 1,4-di-*tert*-butyl benzene (19.0 mg, 0.1 mmol) and toluene (0.4 mL) were added to the tube in dry box at RT, and the tube was capped with a Teflon screwcap. The reaction mixture was stirred at 120 °C for 48 h. GC yield: 10%; 1,4-di-*tert*-butylbenzene was used as the internal standard, response factor: 1.032.

ESI-MS analysis.

High-resolution ESI-MS were measured with a Waters LCT Premier XE with a Z-spray atmospheric pressure ionization source for ESI in the Mass Spectrometry Facility in the Institute of Chemistry, Academia Sinica. Leucine Enkephalin m/z 556.277 $[M+H]^+$ was used as a reference standard. Samples were injected 10 μL using a model Agilent 1100 autosampler system with flow injection analysis (FIA). The mobile phase was 100% acetonitrile at a flow rate of 50 μL/min.

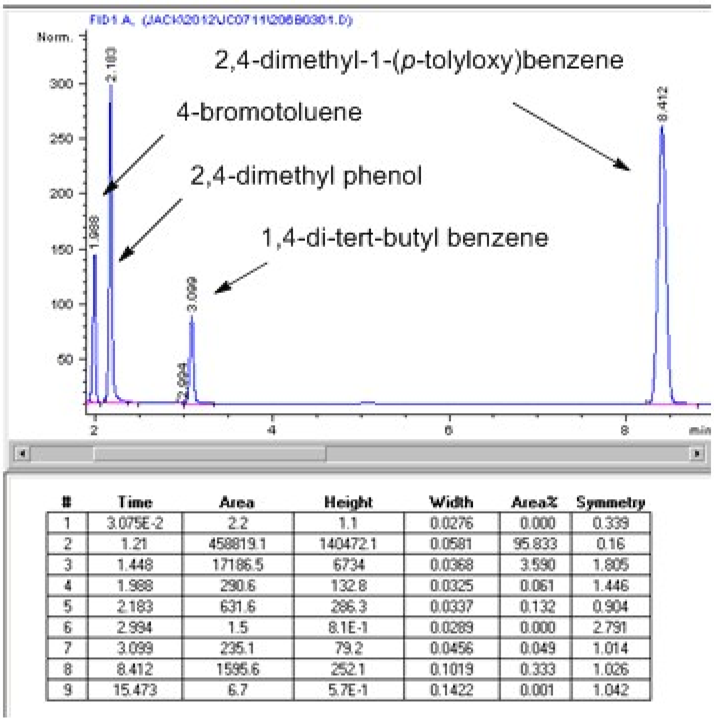
EPR Measurement.

EPR measurements were performed at the X-band using a Bruker E580 spectrometer equipped with a Bruker ELEXSYS super-high-sensitivity cavity in National Tsing Hua University. X-band EPR spectra of toluene reaction solution in a 4 mm EPR tube at 373K were obtained with a microwave power of

15.000 mW, frequency at 9.6589 GHz, ADC conversion time of 20.39 ms, receiver gain of 30, and modulation amplitude of 0.16 G at 100 kHz with phase of 0.0 deg. EPR spectra were examined by the program WINEPR. Simulations were carried by the EasySpin toolbox in Matlab.

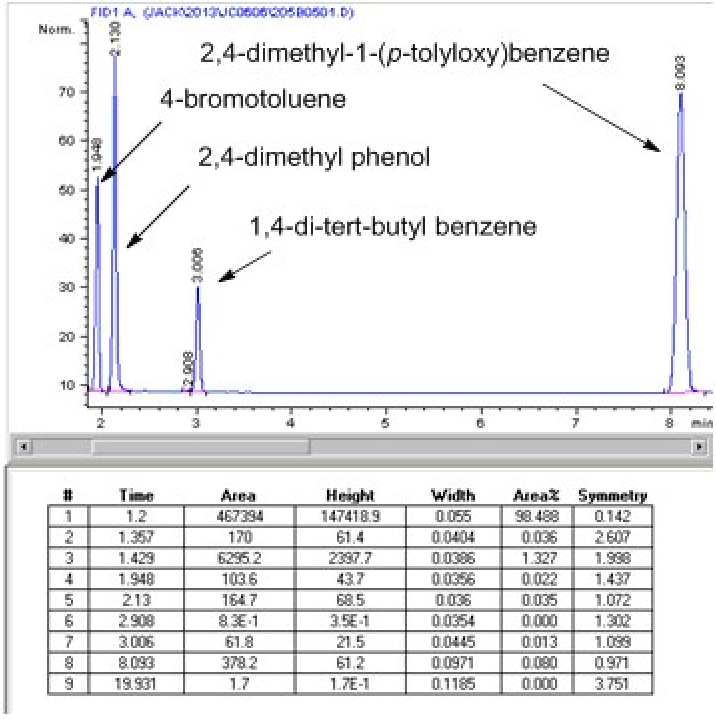
GC data for Copper-Catalyzed C-O Cross-Coupling Reaction

1. Copper-catalyzed C–O coupling reaction of 2,4-dimethyl phenol with 4-bromotoluene by CuI/Cs_2CO_3. (Table 1, entry 1)



#	Time	Area	Height	Width	Area%	Symmetry
1	3.075E-2	2.2	1.1	0.0276	0.000	0.339
2	1.21	458819.1	140472.1	0.0581	95.833	0.16
3	1.448	17186.5	6734	0.0368	3.590	1.805
4	1.988	290.6	132.8	0.0325	0.061	1.446
5	2.183	631.6	286.3	0.0337	0.132	0.904
6	2.994	1.5	8.1E-1	0.0289	0.000	2.791
7	3.099	235.1	79.2	0.0456	0.049	1.014
8	8.412	1595.6	252.1	0.1019	0.333	1.026
9	15.473	6.7	5.7E-1	0.1422	0.001	1.042

Figure S1. Reaction for 8 h. GC yield : 68% (1,4-di-*tert*-butylbenzene was used as the internal standard, response factor : 1.1325)



#	Time	Area	Height	Width	Area%	Symmetry
1	1.2	467394	147418.9	0.055	98.488	0.142
2	1.357	170	61.4	0.0404	0.036	2.607
3	1.429	6295.2	2397.7	0.0386	1.327	1.998
4	1.948	103.6	43.7	0.0356	0.022	1.437
5	2.13	164.7	68.5	0.036	0.035	1.072
6	2.908	8.3E-1	3.5E-1	0.0354	0.000	1.302
7	3.006	61.8	21.5	0.0445	0.013	1.099
8	8.093	378.2	61.2	0.0971	0.080	0.971
9	19.931	1.7	1.7E-1	0.1185	0.000	3.751

Figure S2. Reaction with 2.69 ml toluenen for 8 h. GC yield : 60% (1,4-di-*tert*-butylbenzene was used as the internal standard, response factor : 1.1325)

2. Copper-catalyzed C–O coupling reaction of 2,4-dimethyl phenol with 4-bromotoluene by CuI/Cs_2CO_3/Cumene. (Table 1, entry 2)

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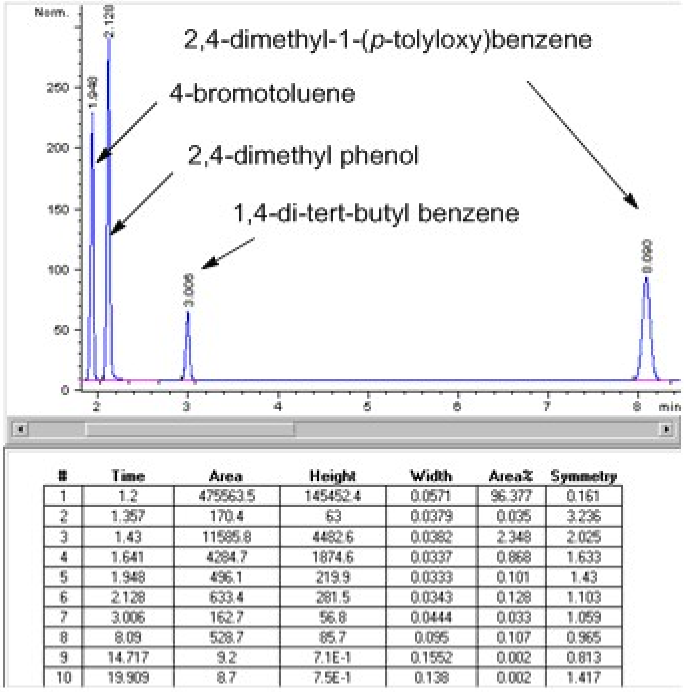
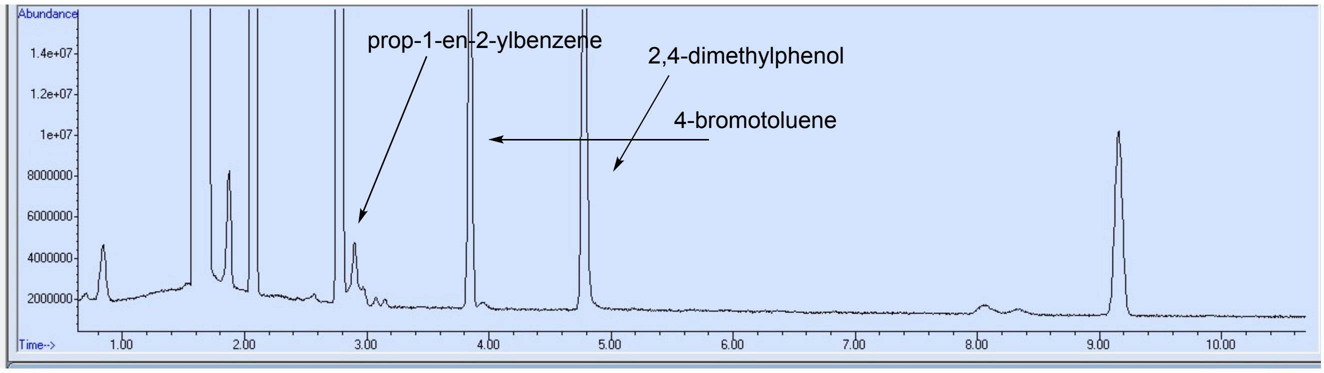
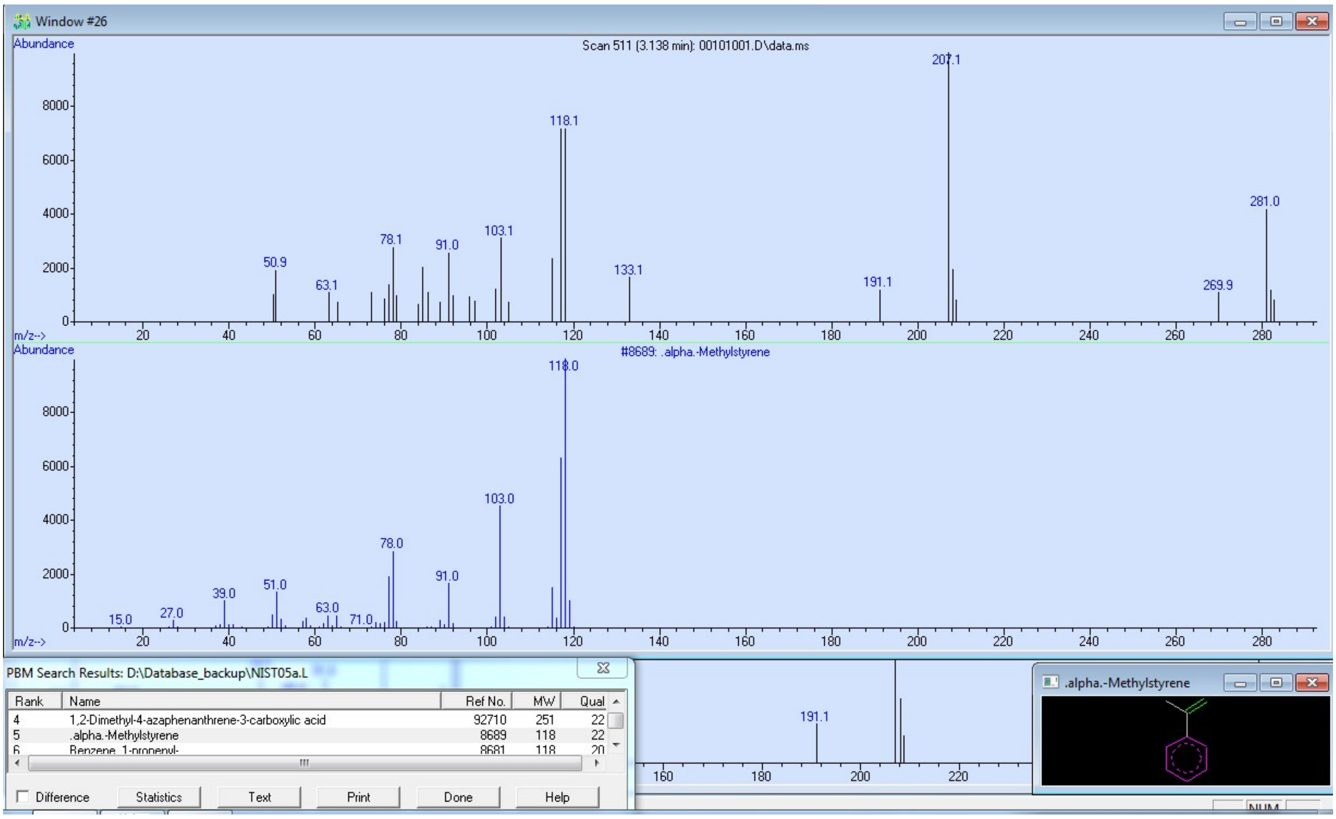


#	Time	Area	Height	Width	Area%	Symmetry
1	1.2	475563.5	145452.4	0.0571	96.377	0.161
2	1.357	170.4	63	0.0379	0.035	3.236
3	1.43	11585.8	4482.6	0.0382	2.348	2.025
4	1.641	4284.7	1874.6	0.0337	0.868	1.633
5	1.948	496.1	219.9	0.0333	0.101	1.43
6	2.128	633.4	281.5	0.0343	0.128	1.103
7	3.006	162.7	56.8	0.0444	0.033	1.059
8	8.09	528.7	85.7	0.095	0.107	0.965
9	14.717	9.2	7.1E-1	0.1552	0.002	0.813
10	19.909	8.7	7.5E-1	0.138	0.002	1.417

Figure S3. Reaction with 50 mol% of cumene for 8 h. GC yield : 33% (1,4-di-*tert*-butylbenzene was used as the internal standard, response factor : 1.1325)



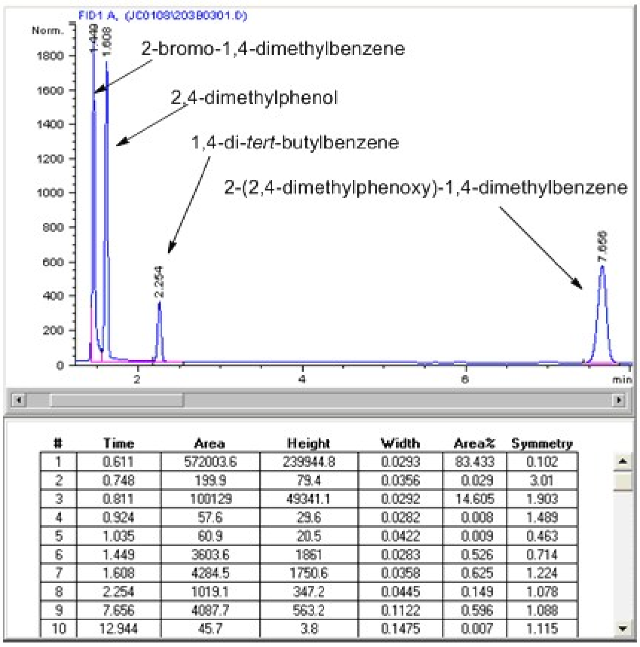


PBM Search Results: D:\Database_backup\NIST05a.L

Rank	Name	Ref No.	MW	Qual
4	1,2-Dimethyl-4-azaphenanthrene-3-carboxylic acid	92710	251	22
5	.alpha.-Methylstyrene	8689	118	22
6	Benzene, 1-propenyl-	8681	118	20

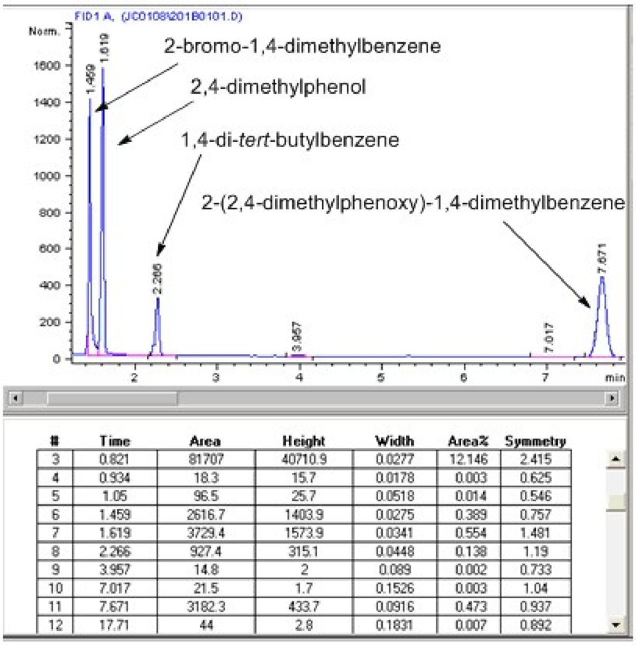
Figure S4. GC-MS data of prop-1-en-2-ylbenzene.

3. Copper-catalyzed C–O coupling reaction of 2,4-dimethyl phenol with 2-bromo-1,4-dimethylbenzene by CuI/Cs_2CO_3. (Table 1, entry 6)



#	Time	Area	Height	Width	Area%	Symmetry
1	0.611	572003.6	239944.8	0.0293	83.433	0.102
2	0.748	199.9	79.4	0.0356	0.029	3.01
3	0.811	100129	49341.1	0.0292	14.605	1.903
4	0.924	57.6	29.6	0.0282	0.008	1.489
5	1.035	60.9	20.5	0.0422	0.009	0.463
6	1.449	3603.6	1861	0.0283	0.526	0.714
7	1.608	4284.5	1750.6	0.0358	0.625	1.224
8	2.254	1019.1	347.2	0.0445	0.149	1.078
9	7.656	4087.7	563.2	0.1122	0.596	1.088
10	12.944	45.7	3.8	0.1475	0.007	1.115

Figure S5. Reaction or 8 h. GC yield : 41% (1,4-di-*tert*-butylbenzene was used as the internal standard, response factor : 0.970)

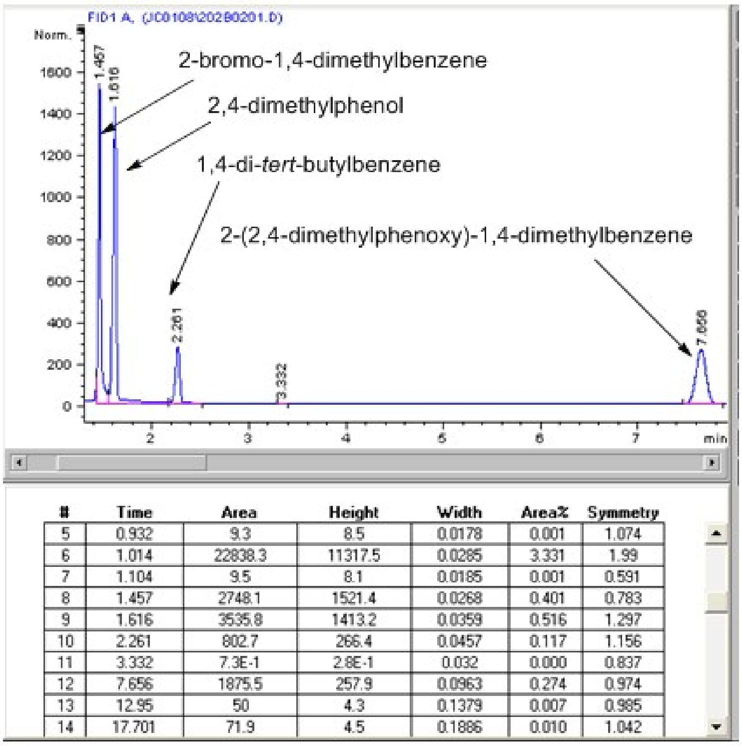


#	Time	Area	Height	Width	Area%	Symmetry
3	0.821	81707	40710.9	0.0277	12.146	2.415
4	0.934	18.3	15.7	0.0178	0.003	0.625
5	1.05	96.5	25.7	0.0518	0.014	0.546
6	1.459	2616.7	1403.9	0.0275	0.389	0.757
7	1.619	3729.4	1573.9	0.0341	0.554	1.481
8	2.266	927.4	315.1	0.0448	0.138	1.19
9	3.957	14.8	2	0.089	0.002	0.733
10	7.017	21.5	1.7	0.1526	0.003	1.04
11	7.671	3182.3	433.7	0.0916	0.473	0.937
12	17.71	44	2.8	0.1831	0.007	0.892

Figure S6. Reaction with 2.69 ml toluenen for 8 h. GC yield : 31% (1,4-di-*tert*-butylbenzene was used as the internal standard, response factor : 0.970)

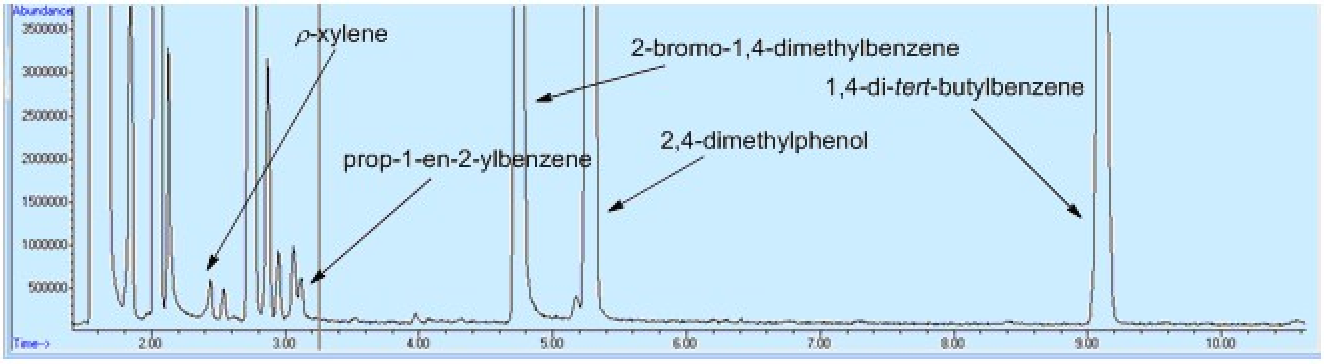
4. Copper-catalyzed C–O coupling reaction of 2,4-dimethyl phenol with 2-bromo-1,4-dimethylbenzene by CuI/Cs_2CO_3/Cumene. (Table 1, entry 7)

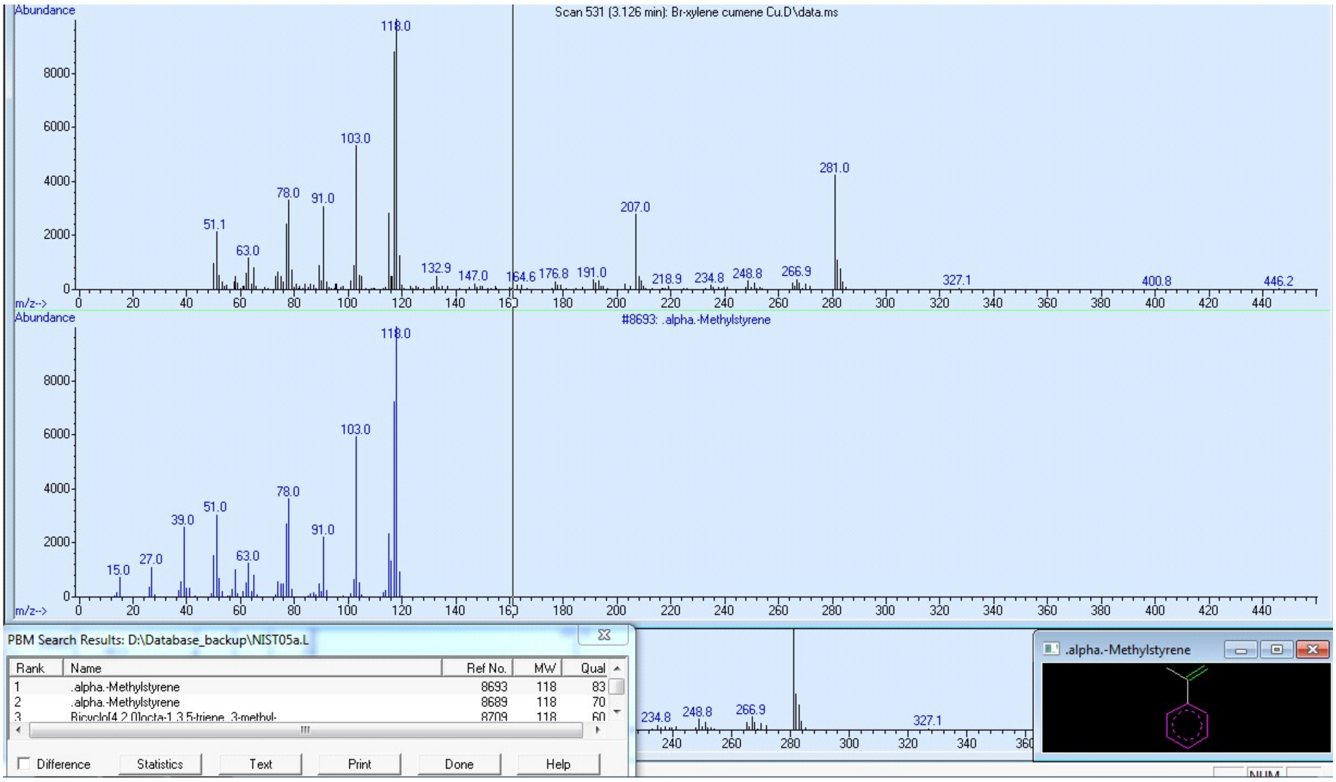
Cumene 50 mol%



#	Time	Area	Height	Width	Area%	Symmetry
5	0.932	9.3	8.5	0.0178	0.001	1.074
6	1.014	22838.3	11317.5	0.0285	3.331	1.99
7	1.104	9.5	8.1	0.0185	0.001	0.591
8	1.457	2748.1	1521.4	0.0268	0.401	0.783
9	1.616	3535.8	1413.2	0.0359	0.516	1.297
10	2.261	802.7	266.4	0.0457	0.117	1.156
11	3.332	7.3E-1	2.8E-1	0.032	0.000	0.837
12	7.656	1875.5	257.9	0.0963	0.274	0.974
13	12.95	50	4.3	0.1379	0.007	0.985
14	17.701	71.9	4.5	0.1886	0.010	1.042

Figure S7. Reaction with 50 mol% of cumene for 8 h. GC yield : 24% (1,4-di-*tert*-butylbenzene was used as the internal standard, response factor : 0.970)





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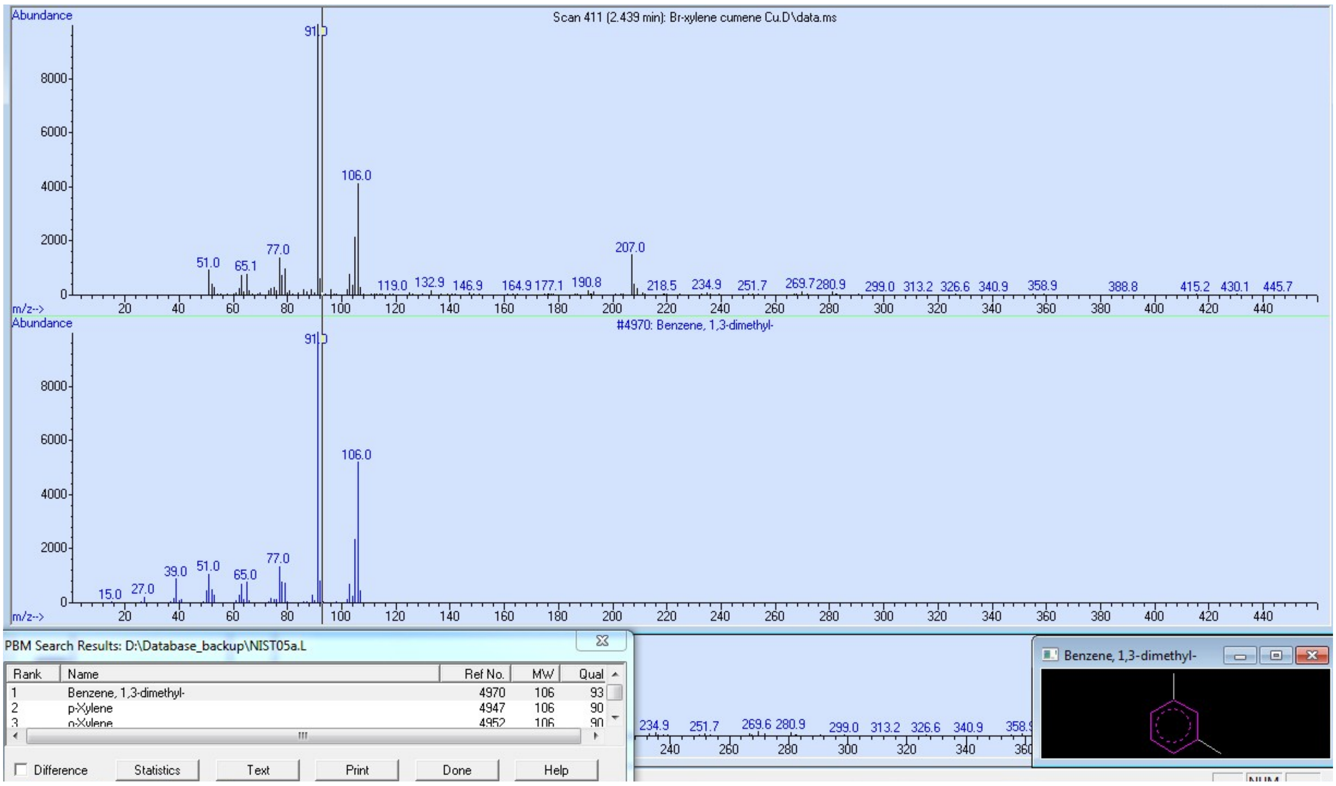
Rank	Name	Ref No.	MW	Qual
1	.alpha.-Methylstyrene	8693	118	83
2	.alpha.-Methylstyrene	8689	118	70
3	Bicyclo[4.2.0]octa-1,3,5-triene, 3-methyl-	8709	118	60

Figure S8. GC-MS data of prop-1-en-2-ylbenzene.



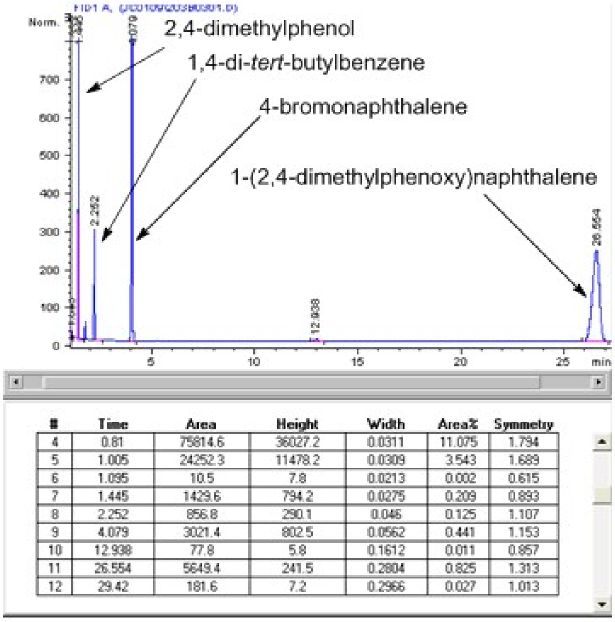
PBM Search Results: D:\Database_backup\NIST05a.L

Rank	Name	Ref No.	MW	Qual
1	Benzene, 1,3-dimethyl-	4970	106	93
2	p-Xylene	4947	106	90
3	o-Xylene	4952	106	90

Figure S9. GC-MS data of *ρ*-.xylene

5. Copper-catalyzed C–O coupling reaction of 2,4-dimethyl phenol with 1-bromonaphthalene by CuI/Cs_2CO_3. (Table 1, entry 8)

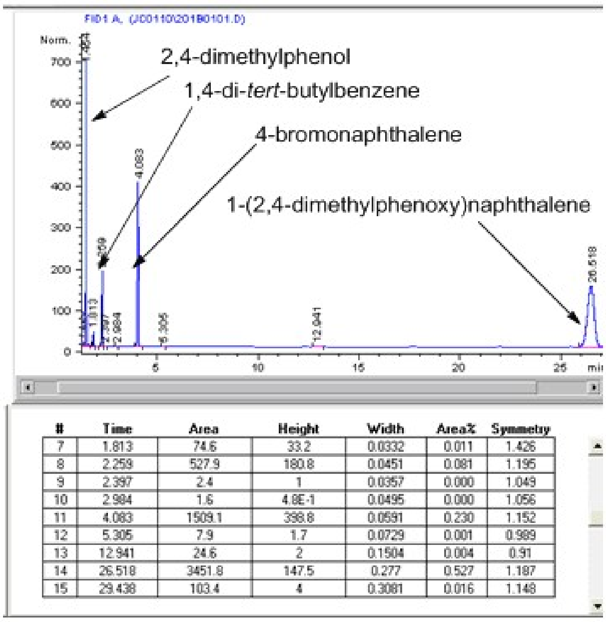
For 8 h



#	Time	Area	Height	Width	Area%	Symmetry
4	0.81	75814.6	36027.2	0.0311	11.075	1.794
5	1.005	24252.3	11478.2	0.0309	3.543	1.689
6	1.095	10.5	7.8	0.0213	0.002	0.615
7	1.445	1429.6	794.2	0.0275	0.209	0.893
8	2.252	856.8	290.1	0.046	0.125	1.107
9	4.079	3021.4	802.5	0.0562	0.441	1.153
10	12.938	77.8	5.8	0.1612	0.011	0.857
11	26.554	5649.4	241.5	0.2804	0.825	1.313
12	29.42	181.6	7.2	0.2966	0.027	1.013

Figure S10. Reaction for 8 h. GC yield : 23% (1,4-di-*tert*-butylbenzene was used as the internal standard, response factor : 0.392)

with 2.69 ml toluenen

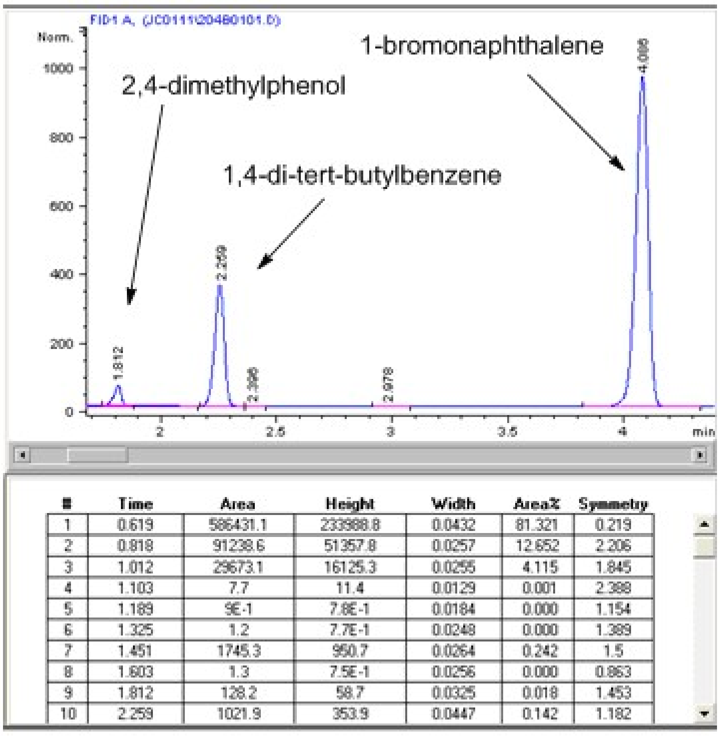


#	Time	Area	Height	Width	Area%	Symmetry
7	1.813	74.6	33.2	0.0332	0.011	1.426
8	2.259	527.9	180.8	0.0451	0.081	1.195
9	2.397	2.4	1	0.0357	0.000	1.049
10	2.984	1.6	4.8E-1	0.0495	0.000	1.056
11	4.083	1509.1	398.8	0.0591	0.230	1.152
12	5.305	7.9	1.7	0.0729	0.001	0.989
13	12.941	24.6	2	0.1504	0.004	0.91
14	26.518	3451.8	147.5	0.277	0.527	1.187
15	29.438	103.4	4	0.3081	0.016	1.148

Figure S11. Reaction with 2.69 ml toluenen for 8 h. GC yield : 21% (1,4-di-*tert*-butylbenzene was used as the internal standard, response factor : 0.392)

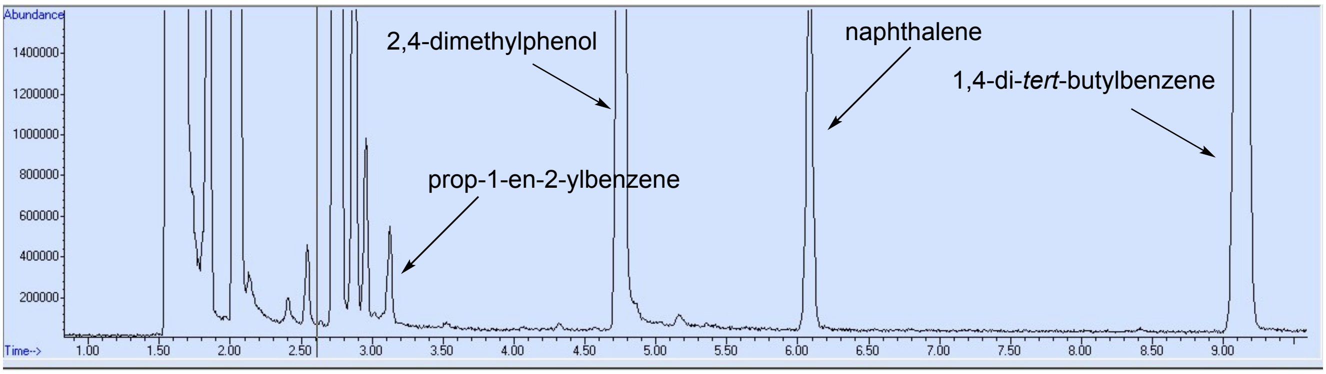
6. Copper-catalyzed C–O coupling reaction of 2,4-dimethyl phenol with 1-bromonaphthalene by CuI/Cs_2CO_3/Cumene. (Table 1, entry 9)

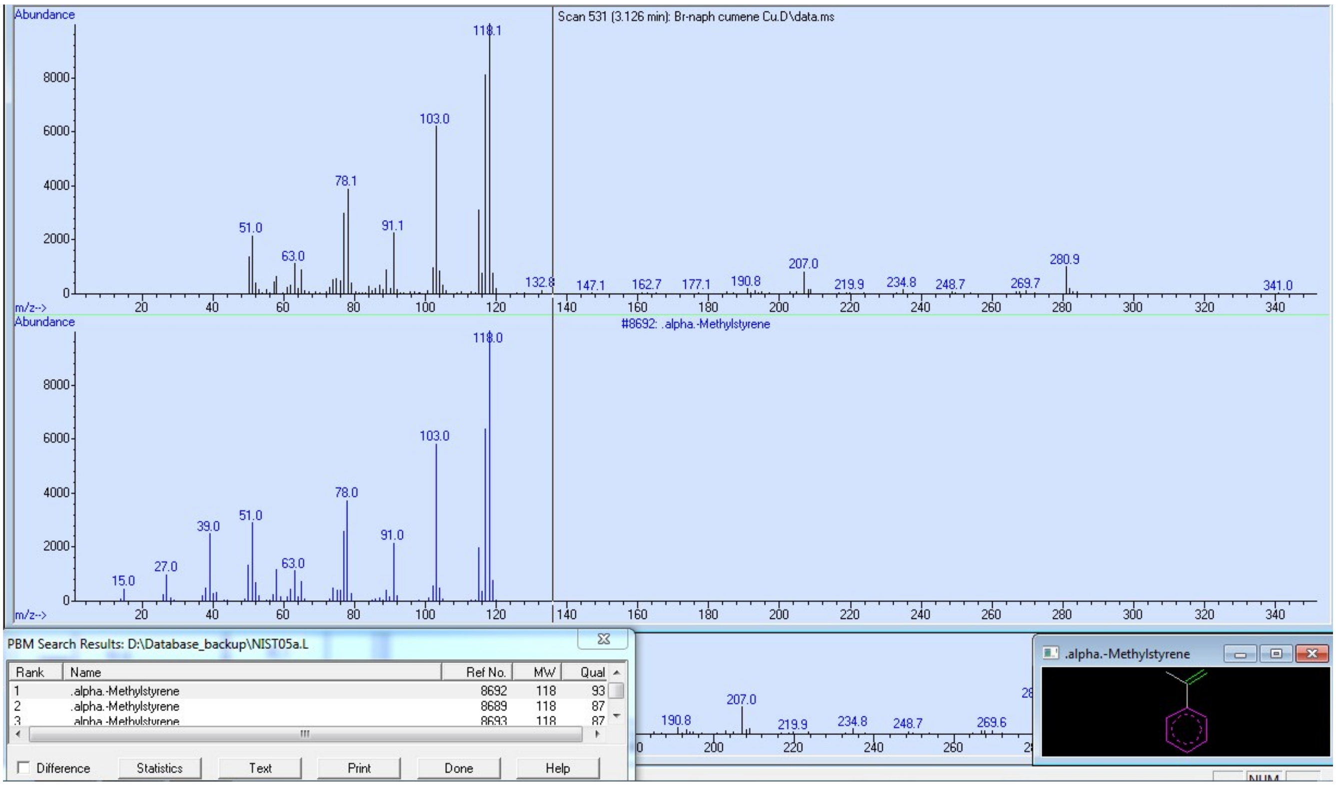
Cumene 50 mol%



#	Time	Area	Height	Width	Area%	Symmetry
1	0.619	586431.1	233988.8	0.0432	81.321	0.219
2	0.818	91238.6	51357.8	0.0257	12.652	2.206
3	1.012	29673.1	16125.3	0.0255	4.115	1.845
4	1.103	7.7	11.4	0.0129	0.001	2.388
5	1.189	9E-1	7.8E-1	0.0184	0.000	1.154
6	1.325	1.2	7.7E-1	0.0248	0.000	1.389
7	1.451	1745.3	950.7	0.0264	0.242	1.5
8	1.603	1.3	7.5E-1	0.0256	0.000	0.863
9	1.812	128.2	58.7	0.0325	0.018	1.453
10	2.259	1021.9	353.9	0.0447	0.142	1.182

Figure S12. Reaction with 50 mol% of cumene for 8 h. GC yield : 0% (1,4-di-*tert*-butylbenzene was used as the internal standard, response factor : 0.392)

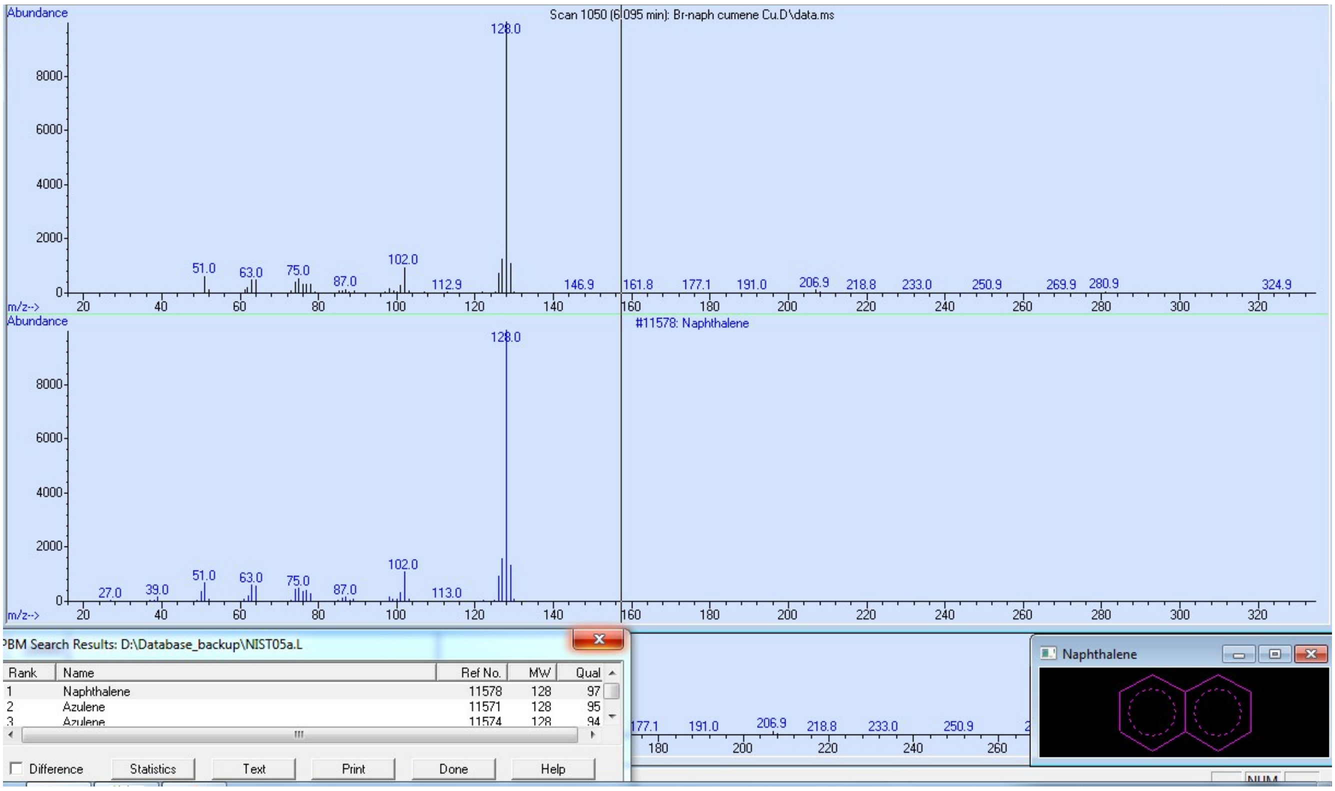




PBM Search Results: D:\Database_backup\NIST05a.L

Rank	Name	Ref No.	MW	Qual
1	.alpha.-Methylstyrene	8692	118	93
2	.alpha.-Methylstyrene	8689	118	87
3	.alpha.-Methylstyrene	8693	118	87

Figure S13. GC-MS data of prop-1-en-2-ylbenzene

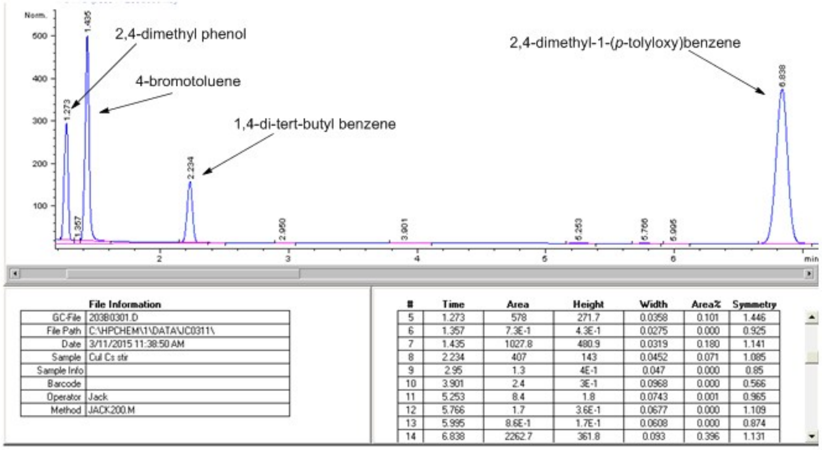


PBM Search Results: D:\Database_backup\NIST05a.L

Rank	Name	Ref No.	MW	Qual
1	Naphthalene	11578	128	97
2	Azulene	11571	128	95
3	Azulene	11574	128	94

Figue S14. GC-MS data of naphthalene

7. C−O coupling reaction of 2,4-dimethyl phenol with 4-bromotoluene by 2.5 mol% CuI stirred with 5 mol% Cs(2,4-dimethylphenoxy).



File Information

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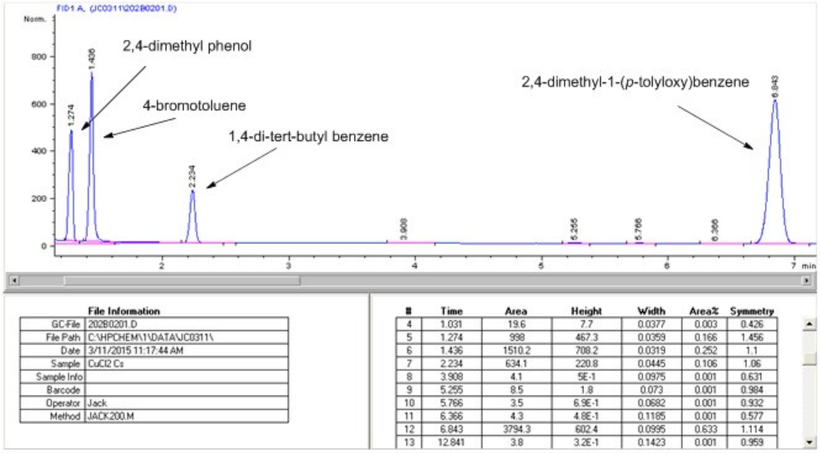
Date	3/11/2015 11:38:50 AM
Sample	CuI Cs stir
Sample Info	
Barcode	
Operator	Jack
Method	JACK200.M

#	Time	Area	Height	Width	Area%	Symmetry
5	1.273	578	271.7	0.0358	0.101	1.446
6	1.357	7.3E-1	4.3E-1	0.0275	0.000	0.925
7	1.435	1027.8	480.9	0.0319	0.180	1.141
8	2.234	407	143	0.0452	0.071	1.085
9	2.95	1.3	4E-1	0.047	0.000	0.85
10	3.901	2.4	3E-1	0.0968	0.000	0.566
11	5.253	8.4	1.8	0.0743	0.001	0.965
12	5.766	1.7	3.6E-1	0.0677	0.000	1.109
13	5.995	8.6E-1	1.7E-1	0.0608	0.000	0.874
14	6.838	2262.7	361.8	0.093	0.396	1.131

8. Copper-catalyzed C–O coupling reaction of 2,4-dimethyl phenol with 4-bromotoluene by $CuCl_2/Cs_2CO_3$.



File Information

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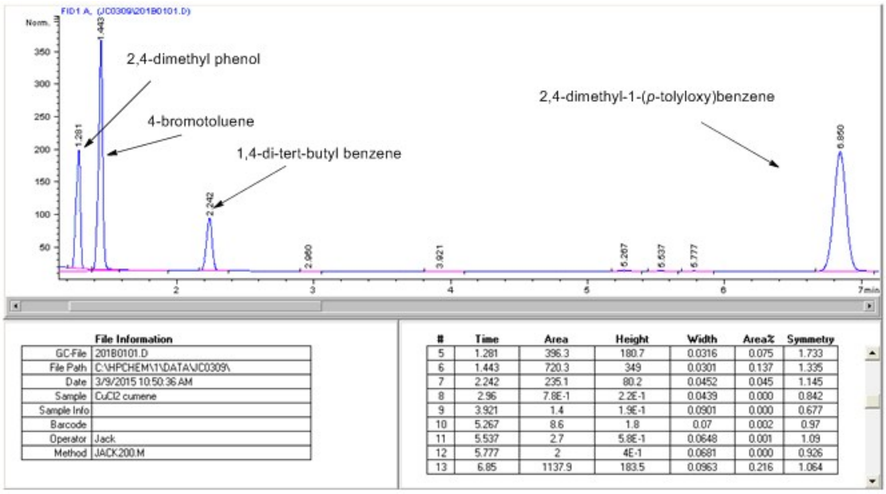
Date	3/11/2015 11:17:44 AM
Sample	CuCl2 Cs
Sample Info	
Barcode	
Operator	Jack
Method	JACK200.M

#	Time	Area	Height	Width	Area%	Symmetry
4	1.031	19.6	7.7	0.0377	0.003	0.426
5	1.274	998	467.3	0.0359	0.166	1.456
6	1.436	1510.2	708.2	0.0319	0.252	1.1
7	2.234	634.1	220.8	0.0445	0.106	1.06
8	3.908	4.1	5E-1	0.0975	0.001	0.631
9	5.255	8.5	1.8	0.073	0.001	0.984
10	5.766	3.5	6.9E-1	0.0682	0.001	0.932
11	6.366	4.3	4.8E-1	0.1185	0.001	0.577
12	6.843	3794.3	602.4	0.0995	0.633	1.114
13	12.841	3.8	3.2E-1	0.1423	0.001	0.959

9. Copper-catalyzed C–O coupling reaction of 2,4-dimethyl phenol with 4-bromotoluene by $CuCl_2/Cs_2CO_3$/Cumene.

50 mol%



File Information

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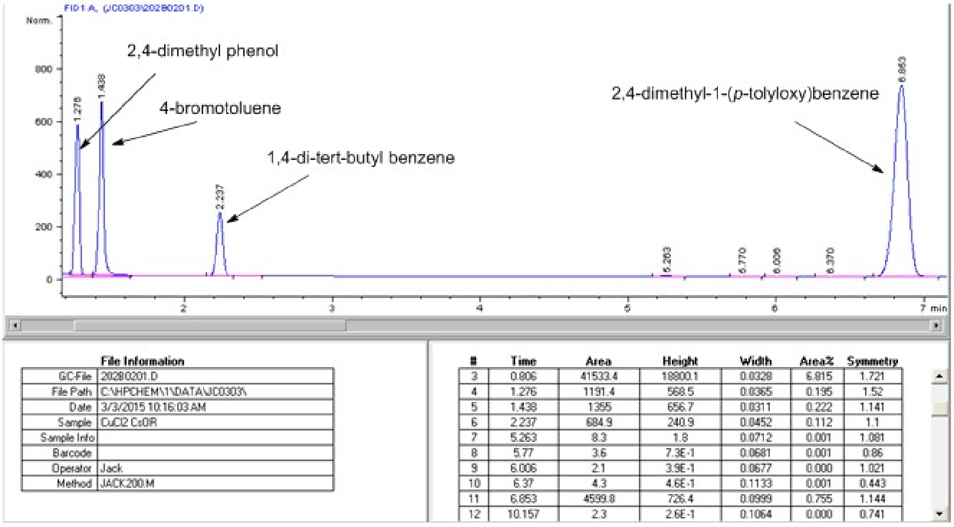
Date	3/9/2015 10:50:36 AM
Sample	CuCl2 cumene
Sample Info	
Barcode	
Operator	Jack
Method	JACK200.M

#	Time	Area	Height	Width	Area%	Symmetry
5	1.281	396.3	180.7	0.0316	0.075	1.733
6	1.443	720.3	349	0.0301	0.137	1.335
7	2.242	235.1	80.2	0.0452	0.045	1.145
8	2.96	7.8E-1	2.2E-1	0.0439	0.000	0.842
9	3.921	1.4	1.9E-1	0.0901	0.000	0.677
10	5.267	8.6	1.8	0.07	0.002	0.97
11	5.537	2.7	5.8E-1	0.0648	0.001	1.09
12	5.777	2	4E-1	0.0681	0.000	0.926
13	6.85	1137.9	183.5	0.0963	0.216	1.064

10. C–O coupling reaction of 2,4-dimethyl phenol with 4-bromotoluene by 2.5 mol% $CuCl_2$ stirred with 5 mol% Cs(2,4-dimethylphenoxy).



File Information

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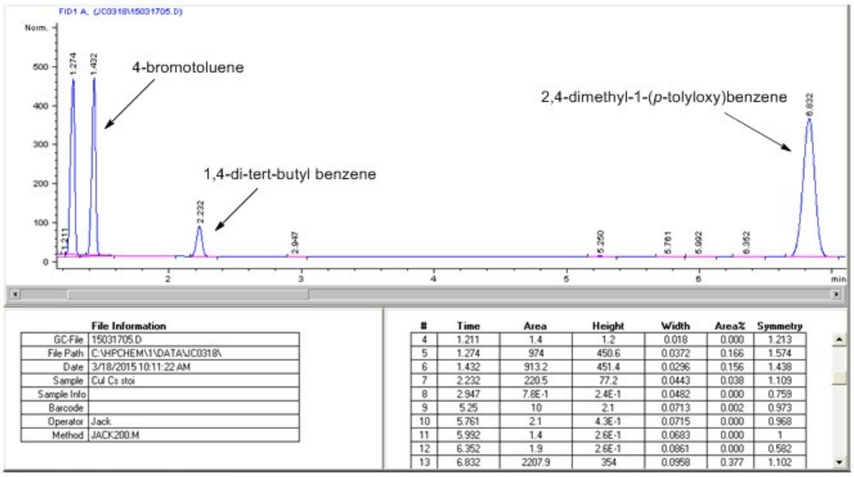
Date	3/3/2015 10:16:03 AM
Sample	CuCl2 CsOR
Sample Info	
Barcode	
Operator	Jack
Method	JACK200.M

#	Time	Area	Height	Width	Area%	Symmetry
3	0.806	41533.4	18800.1	0.0328	6.815	1.721
4	1.276	1191.4	568.5	0.0365	0.195	1.52
5	1.438	1355	656.7	0.0311	0.222	1.141
6	2.237	684.9	240.9	0.0452	0.112	1.1
7	5.263	8.3	1.8	0.0712	0.001	1.081
8	5.77	3.6	7.3E-1	0.0681	0.001	0.86
9	6.006	2.1	3.9E-1	0.0677	0.000	1.021
10	6.37	4.3	4.6E-1	0.1133	0.001	0.443
11	6.853	4599.8	726.4	0.0999	0.755	1.144
12	10.157	2.3	2.6E-1	0.1064	0.000	0.741

11. Stoichiometric C–O coupling reaction.



File Information

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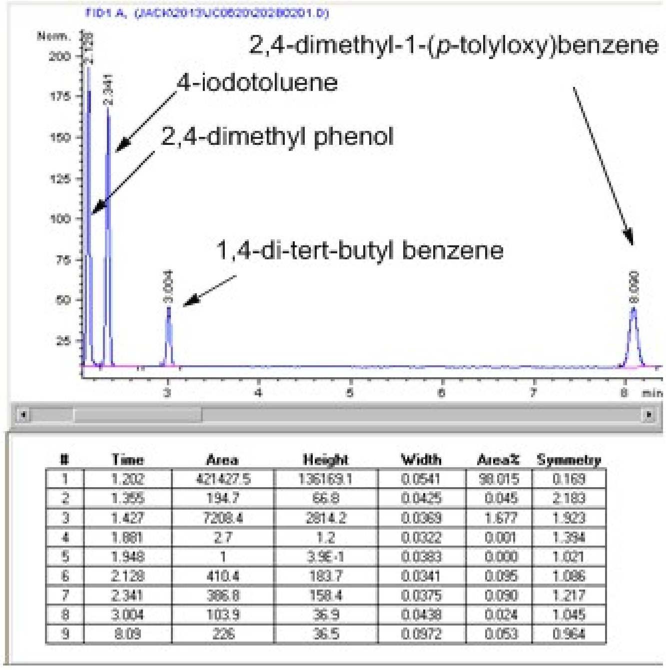
Date	3/18/2015 10:11:22 AM
Sample	Cul Cs stoi
Sample Info	
Barcode	
Operator	Jack
Method	JACK200.M

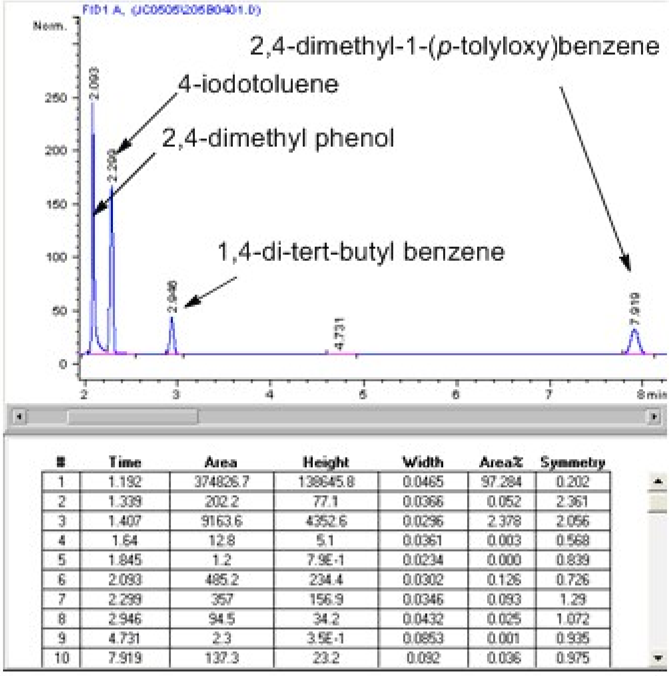
#	Time	Area	Height	Width	Area%	Symmetry
4	1.211	1.4	1.2	0.018	0.000	1.213
5	1.274	974	450.6	0.0372	0.166	1.574
6	1.432	913.2	451.4	0.0296	0.156	1.438
7	2.232	220.5	77.2	0.0443	0.038	1.109
8	2.947	7.8E-1	2.4E-1	0.0482	0.000	0.759
9	5.25	10	2.1	0.0713	0.002	0.973
10	5.761	2.1	4.3E-1	0.0715	0.000	0.968
11	5.992	1.4	2.6E-1	0.0683	0.000	1
12	6.352	1.9	2.6E-1	0.0861	0.000	0.582
13	6.832	2207.9	354	0.0958	0.377	1.102

12. C–O coupling reaction of 2,4-dimethyl phenol with 4-iodotoluene by Cs_2CO_3. (Table 1, entry 4)



#	Time	Area	Height	Width	Area%	Symmetry
1	1.202	421427.5	136169.1	0.0541	98.015	0.169
2	1.355	194.7	66.8	0.0425	0.045	2.183
3	1.427	7208.4	2814.2	0.0369	1.677	1.923
4	1.881	2.7	1.2	0.0322	0.001	1.394
5	1.948	1	3.9E-1	0.0383	0.000	1.021
6	2.128	410.4	183.7	0.0341	0.095	1.086
7	2.341	386.8	158.4	0.0375	0.090	1.217
8	3.004	103.9	36.9	0.0438	0.024	1.045
9	8.09	226	36.5	0.0972	0.053	0.964

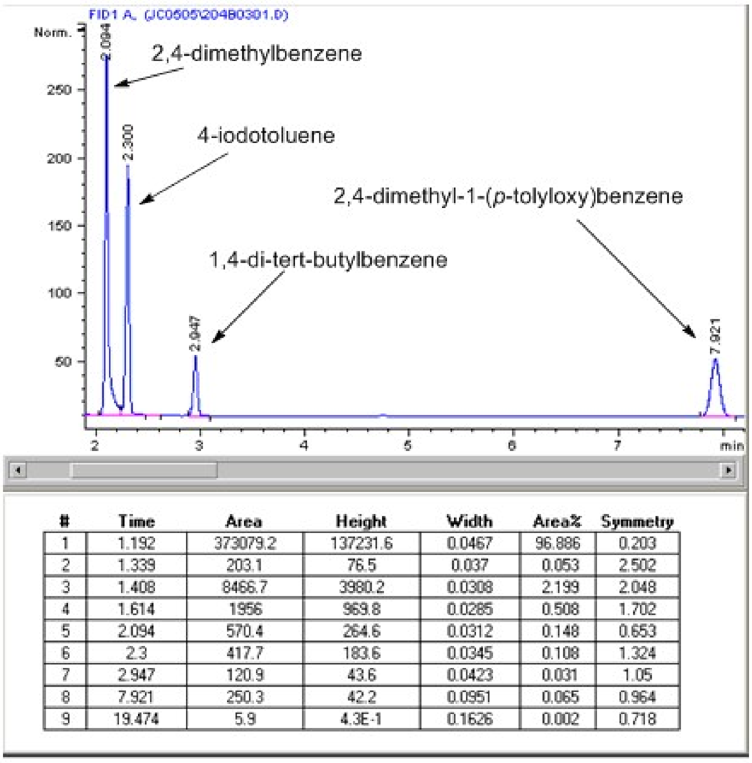
Figure S15. Reaction for 48 h. GC yield : 22% (1,4-di-*tert*-butylbenzene was used as the internal standard, response factor : 1.032)



#	Time	Area	Height	Width	Area%	Symmetry
1	1.192	374826.7	138645.8	0.0465	97.284	0.202
2	1.339	202.2	77.1	0.0366	0.052	2.361
3	1.407	9163.6	4352.6	0.0296	2.378	2.056
4	1.64	12.8	5.1	0.0361	0.003	0.568
5	1.845	1.2	7.9E-1	0.0234	0.000	0.839
6	2.093	485.2	234.4	0.0302	0.126	0.726
7	2.299	357	156.9	0.0346	0.093	1.29
8	2.946	94.5	34.2	0.0432	0.025	1.072
9	4.731	2.3	3.5E-1	0.0853	0.001	0.935
10	7.919	137.3	23.2	0.092	0.036	0.975

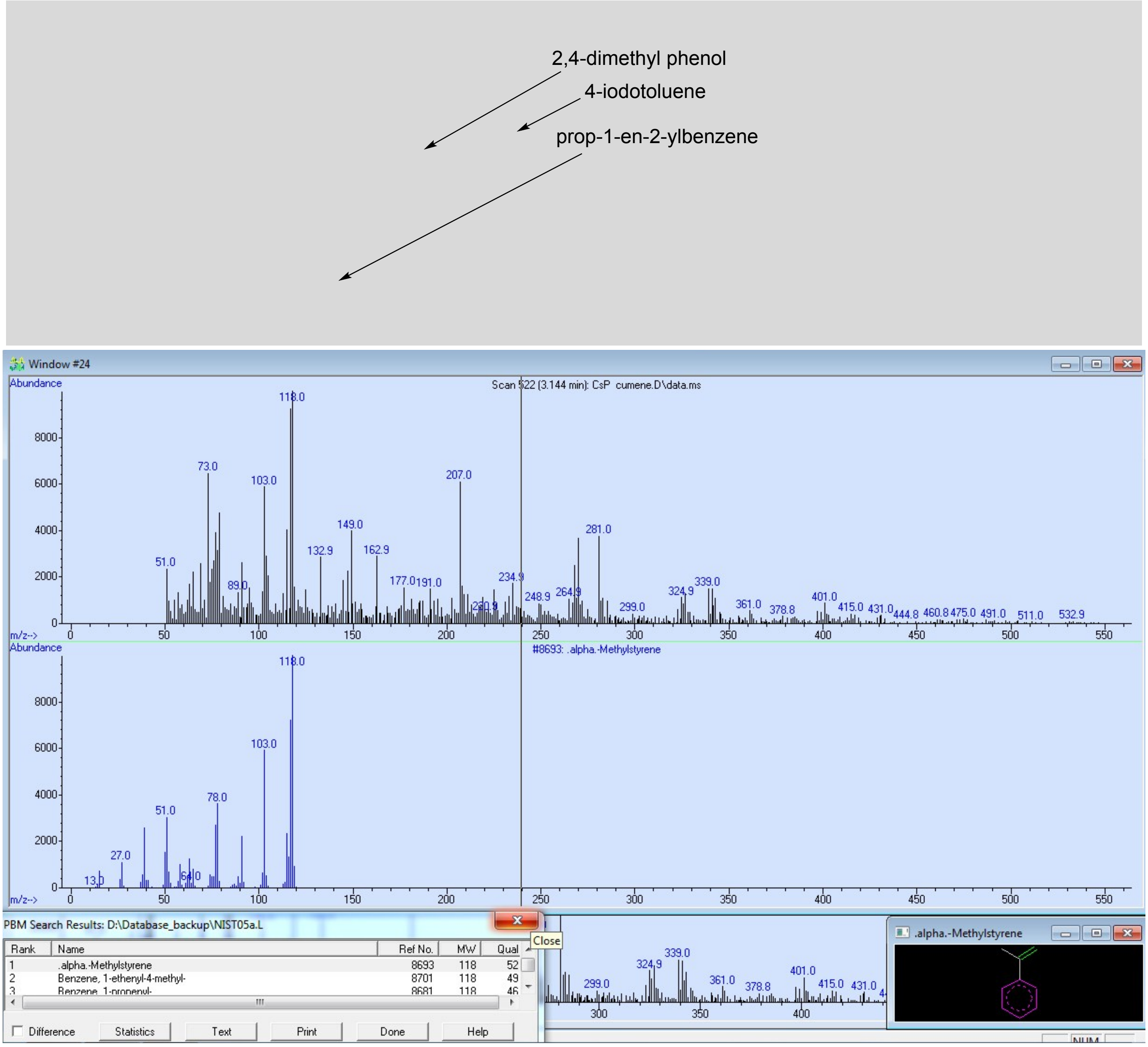
Figure S16. Reaction with 2.69 ml toluenen for 48 h. GC yield : 21% (1,4-di-*tert*-butylbenzene was used as the internal standard, response factor : 1.032)

13. C–O coupling reaction of 2,4-dimethyl phenol with 4-iodotoluene by Cs_2CO_3/Cumene. (Table 1, entry 5)



#	Time	Area	Height	Width	Area%	Symmetry
1	1.192	373079.2	137231.6	0.0467	96.886	0.203
2	1.339	203.1	76.5	0.037	0.053	2.502
3	1.408	8466.7	3980.2	0.0308	2.199	2.048
4	1.614	1956	969.8	0.0285	0.508	1.702
5	2.094	570.4	264.6	0.0312	0.148	0.653
6	2.3	417.7	183.6	0.0345	0.108	1.324
7	2.947	120.9	43.6	0.0423	0.031	1.05
8	7.921	250.3	42.2	0.0951	0.065	0.964
9	19.474	5.9	4.3E-1	0.1626	0.002	0.718

Figure S17. Reaction with 50 mol% of cumene for 8 h. GC yield : 21% (1,4-di-*tert*-butylbenzene was used as the internal standard, response factor : 1.032)

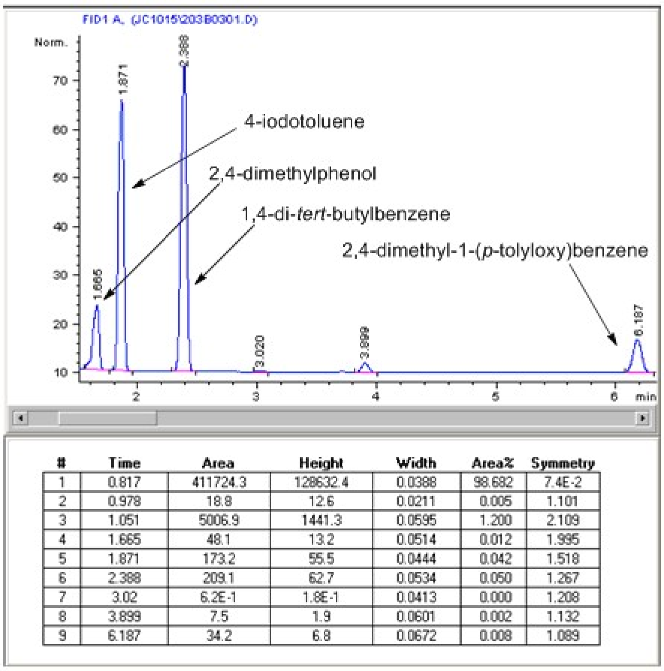


PBM Search Results: D:\Database_backup\NIST05a.L

Rank	Name	Ref No.	MW	Qual
1	.alpha.-Methylstyrene	8693	118	52
2	Benzene, 1-ethenyl-4-methyl-	8701	118	49
3	Benzene, 1-propenyl-	8681	118	46

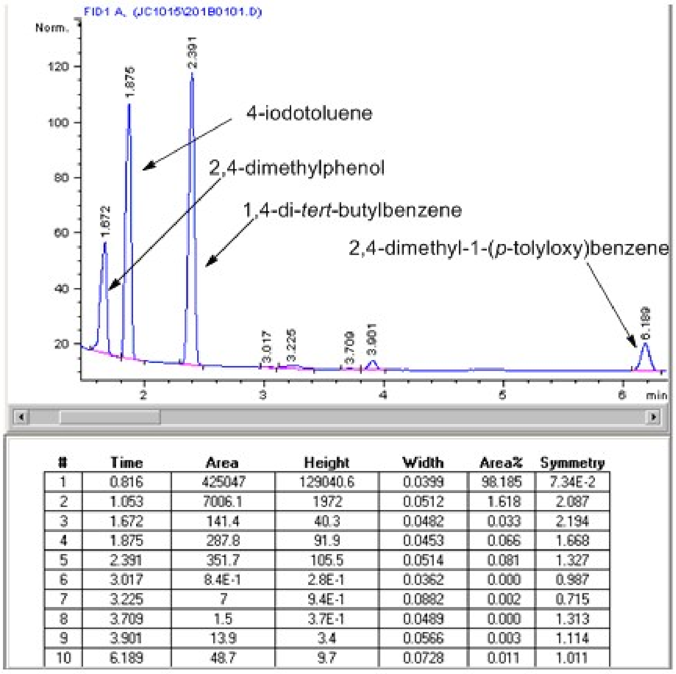
Figure S18. GC-MS data of prop-1-en-2-ylbenzene

14. C–O coupling reaction of cesium 2,4-dimethylphenoxide with 4-iodotoluene . (Scheme 2)



#	Time	Area	Height	Width	Area%	Symmetry
1	0.817	411724.3	128632.4	0.0388	98.682	7.4E-2
2	0.978	18.8	12.6	0.0211	0.005	1.101
3	1.051	5006.9	1441.3	0.0595	1.200	2.109
4	1.665	48.1	13.2	0.0514	0.012	1.995
5	1.871	173.2	55.5	0.0444	0.042	1.518
6	2.388	209.1	62.7	0.0534	0.050	1.267
7	3.02	6.2E-1	1.8E-1	0.0413	0.000	1.208
8	3.899	7.5	1.9	0.0601	0.002	1.132
9	6.187	34.2	6.8	0.0672	0.008	1.089

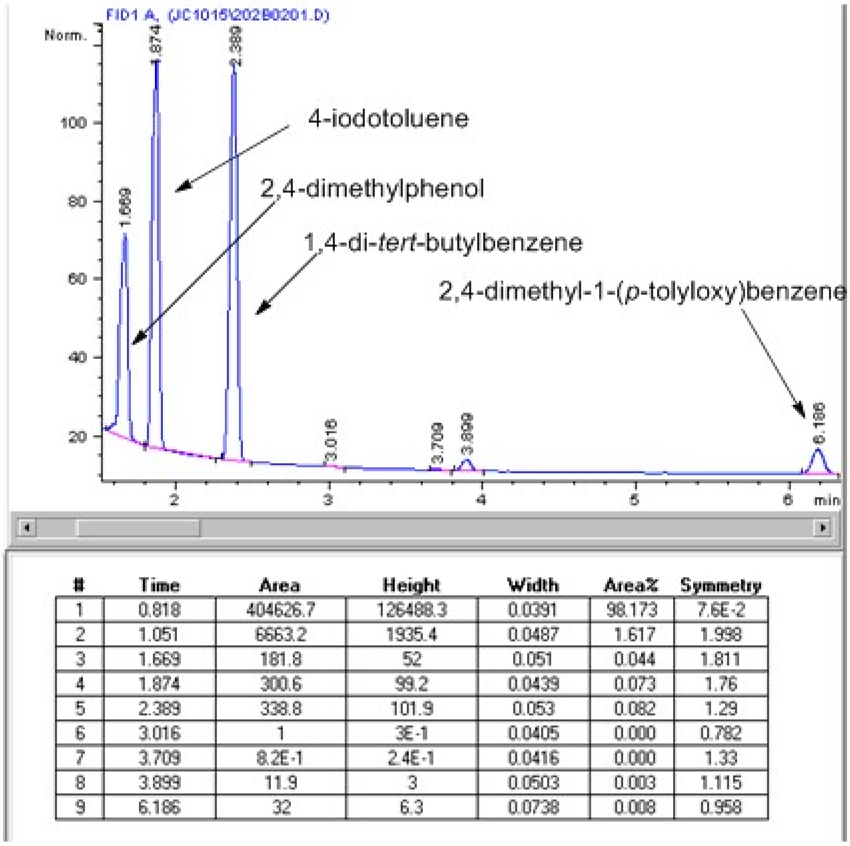
Figure S19. Reaction for 48 h. GC yield : 10% (1,4-di-*tert*-butylbenzene was used as the internal standard, response factor : 1.032)



#	Time	Area	Height	Width	Area%	Symmetry
1	0.816	425047	129040.6	0.0399	98.185	7.34E-2
2	1.053	7006.1	1972	0.0512	1.618	2.087
3	1.672	141.4	40.3	0.0482	0.033	2.194
4	1.875	287.8	91.9	0.0453	0.066	1.668
5	2.391	351.7	105.5	0.0514	0.081	1.327
6	3.017	8.4E-1	2.8E-1	0.0362	0.000	0.987
7	3.225	7	9.4E-1	0.0882	0.002	0.715
8	3.709	1.5	3.7E-1	0.0489	0.000	1.313
9	3.901	13.9	3.4	0.0566	0.003	1.114
10	6.189	48.7	9.7	0.0728	0.011	1.011

Figure S20. Reaction with 2.69 ml toluenen for 48 h. GC yield : 3% (1,4-di-*tert*-butylbenzene was used as the internal standard, response factor : 1.032)

15. C–O coupling reaction of cesium 2,4-dimethylphenoxide with 4-iodotoluene by Cumene (Scheme 2)



#	Time	Area	Height	Width	Area%	Symmetry
1	0.818	404626.7	126488.3	0.0391	98.173	7.6E-2
2	1.051	6663.2	1935.4	0.0487	1.617	1.998
3	1.669	181.8	52	0.051	0.044	1.811
4	1.874	300.6	99.2	0.0439	0.073	1.76
5	2.389	338.8	101.9	0.053	0.082	1.29
6	3.016	1	3E-1	0.0405	0.000	0.782
7	3.709	8.2E-1	2.4E-1	0.0416	0.000	1.33
8	3.899	11.9	3	0.0503	0.003	1.115
9	6.186	32	6.3	0.0738	0.008	0.958

Figure S21. Reaction with 50 mol% of cumene for 8 h. GC yield : 8% (1,4-di-*tert*-butylbenzene was used as the internal standard, response factor : 1.032)

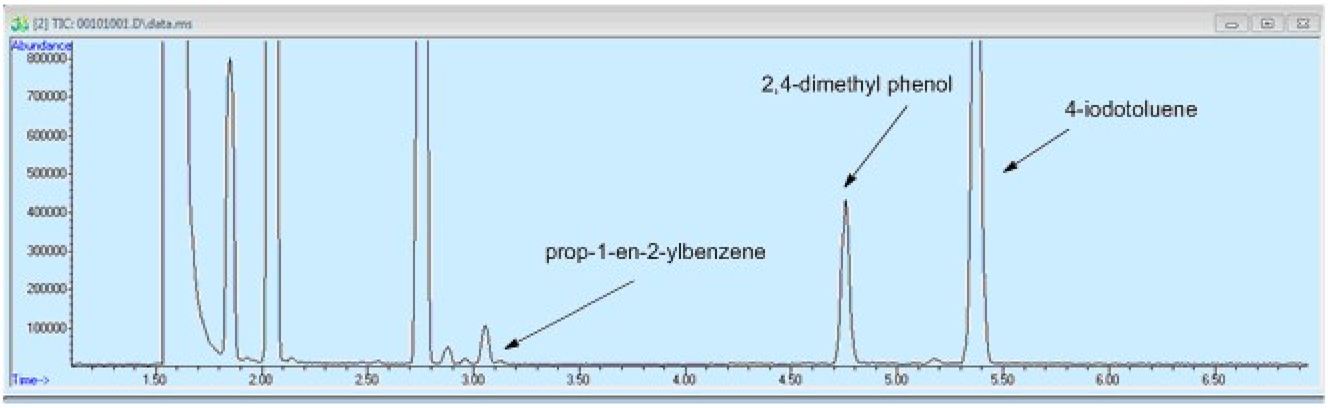


Figure S22. GC-MS data of prop-1-en-2-ylbenzene.

In situ ESI-MS Spectra and Isotope Distributions of Intermediates

1. Experimental and simulated isotopic distributions of [Cs$_2$(2,4-dimethylphenoxy)]$^+$, [Cu(I)(2,4-dimethylphenoxy)$_2$]$^-$ and [Cs(2,4-dimethylphenoxy)$_2$]$^-$ (from the ESI-MS spectra of the C-O coupling reaction mixxture of 2,4-dimethyl phenol and 4-bromotoluene catalyzed by CuI/Cs$_2$CO$_3$ in toluene at 120 ^{o}C)

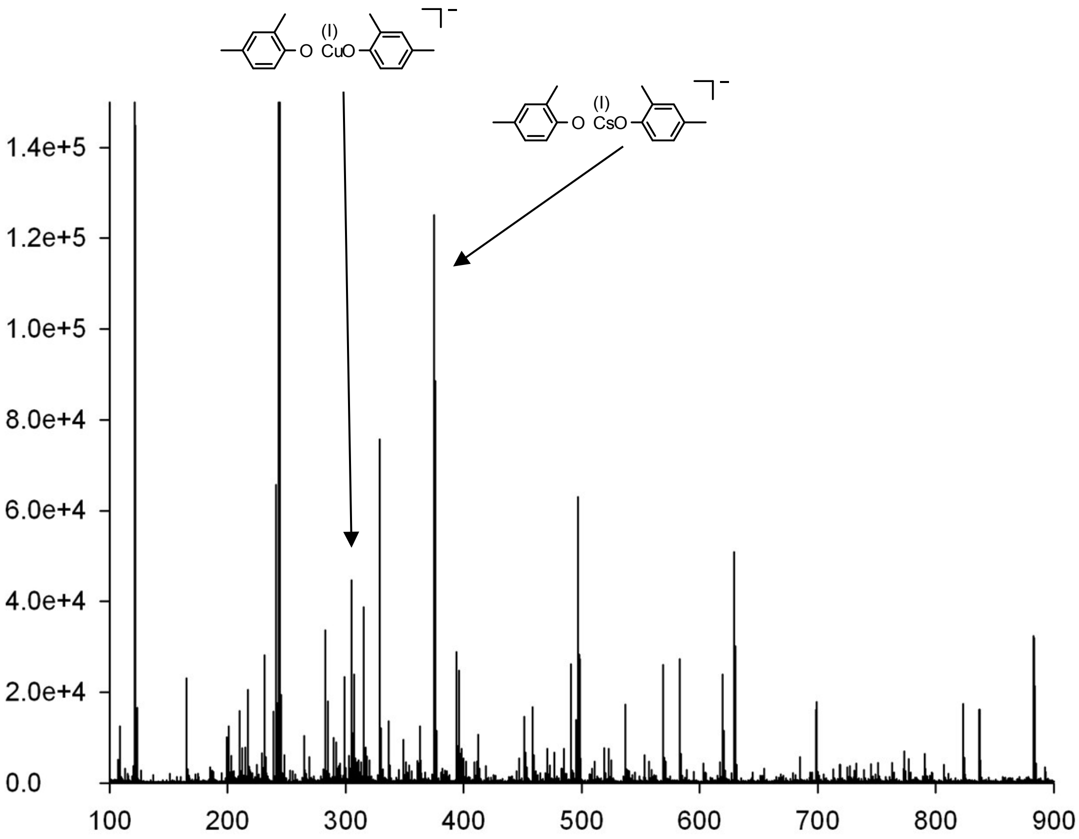


Figure S23.ESI-MS(-) full mass of m/z = 305 and 375.

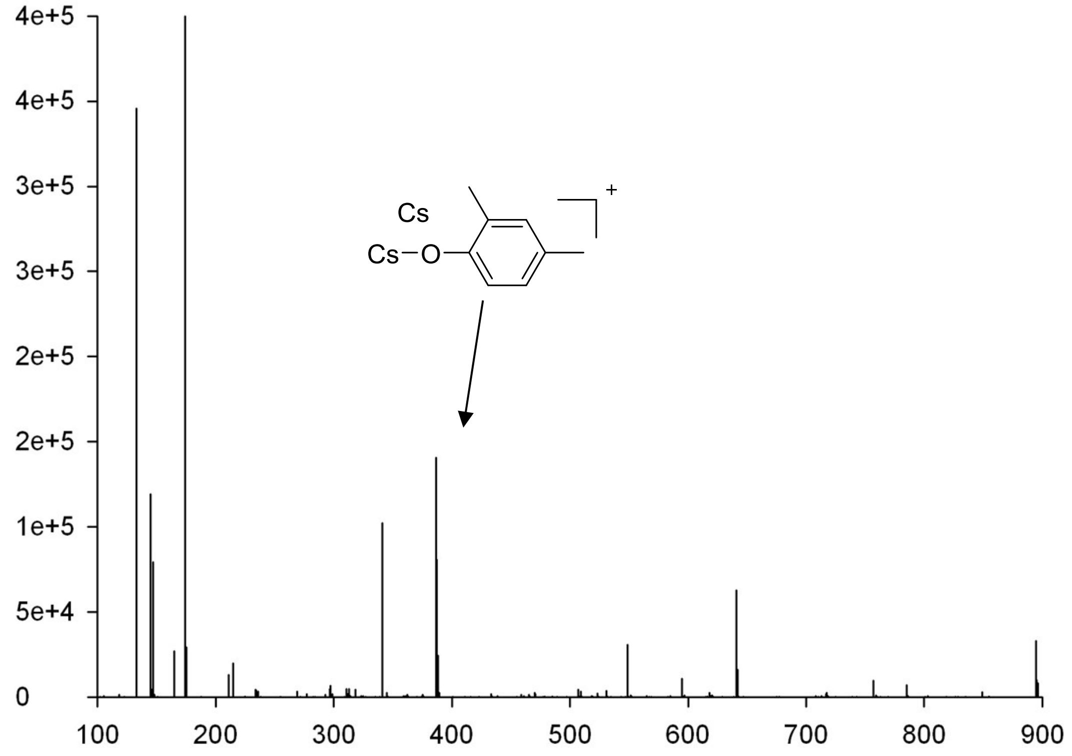
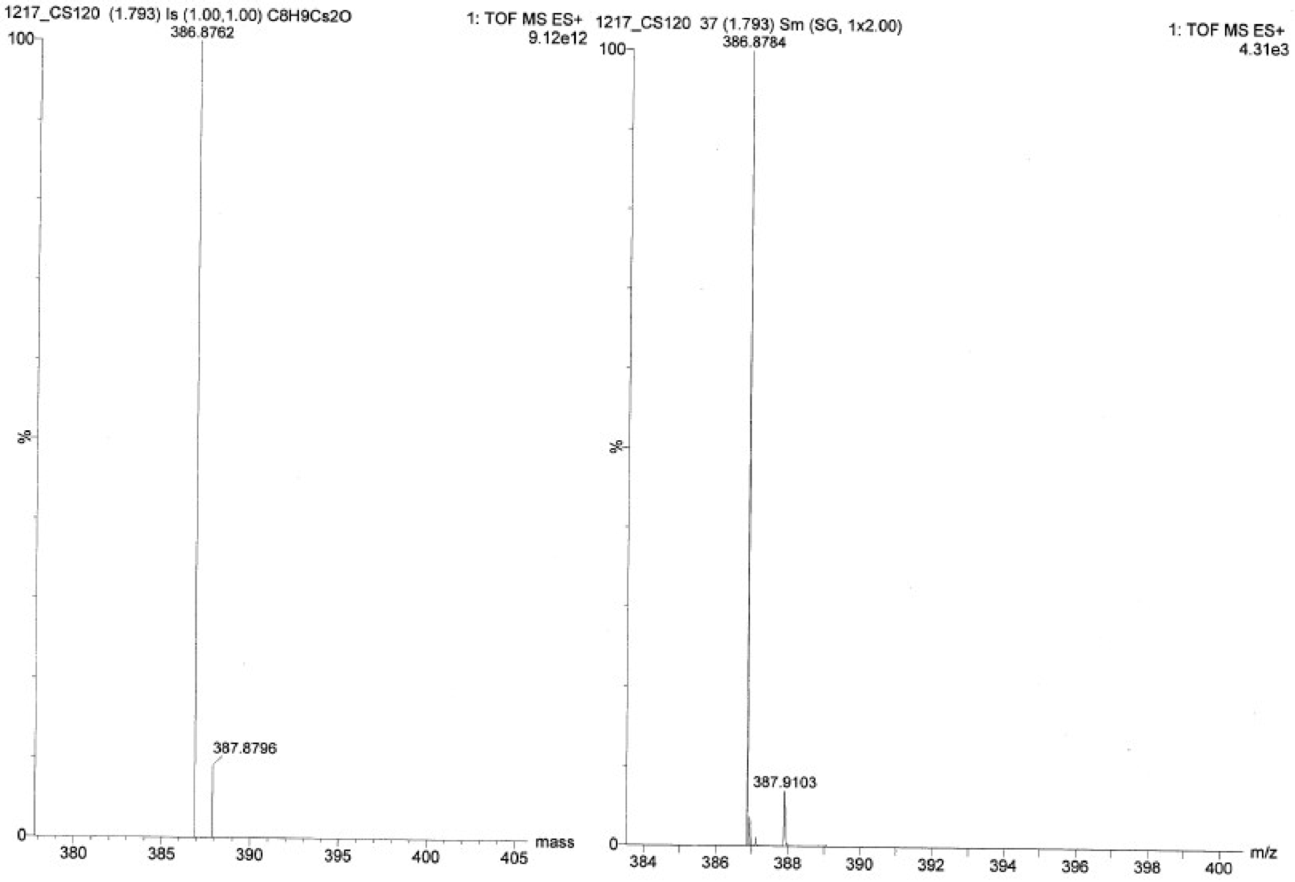


Figure S24. ESI-MS(+) full mass of m/z = 385



Simulated isotopic distributions of [Cs_2(2,4-dimethylphenoxy)]$^+$

Experimental isotopic distributions of [Cs_2(2,4-dimethylphenoxy)]$^+$

Figure S25. Isotopic distributions of [Cs_2(2,4-dimethylphenoxy)]$^+$

Simulated isotopic distributions of $[Cu(I)(2,4\text{-dimethylphenoxy})_2]^-$

Experimental isotopic distributions of $[Cu(I)(2,4\text{-dimethylphenoxy})_2]^-$

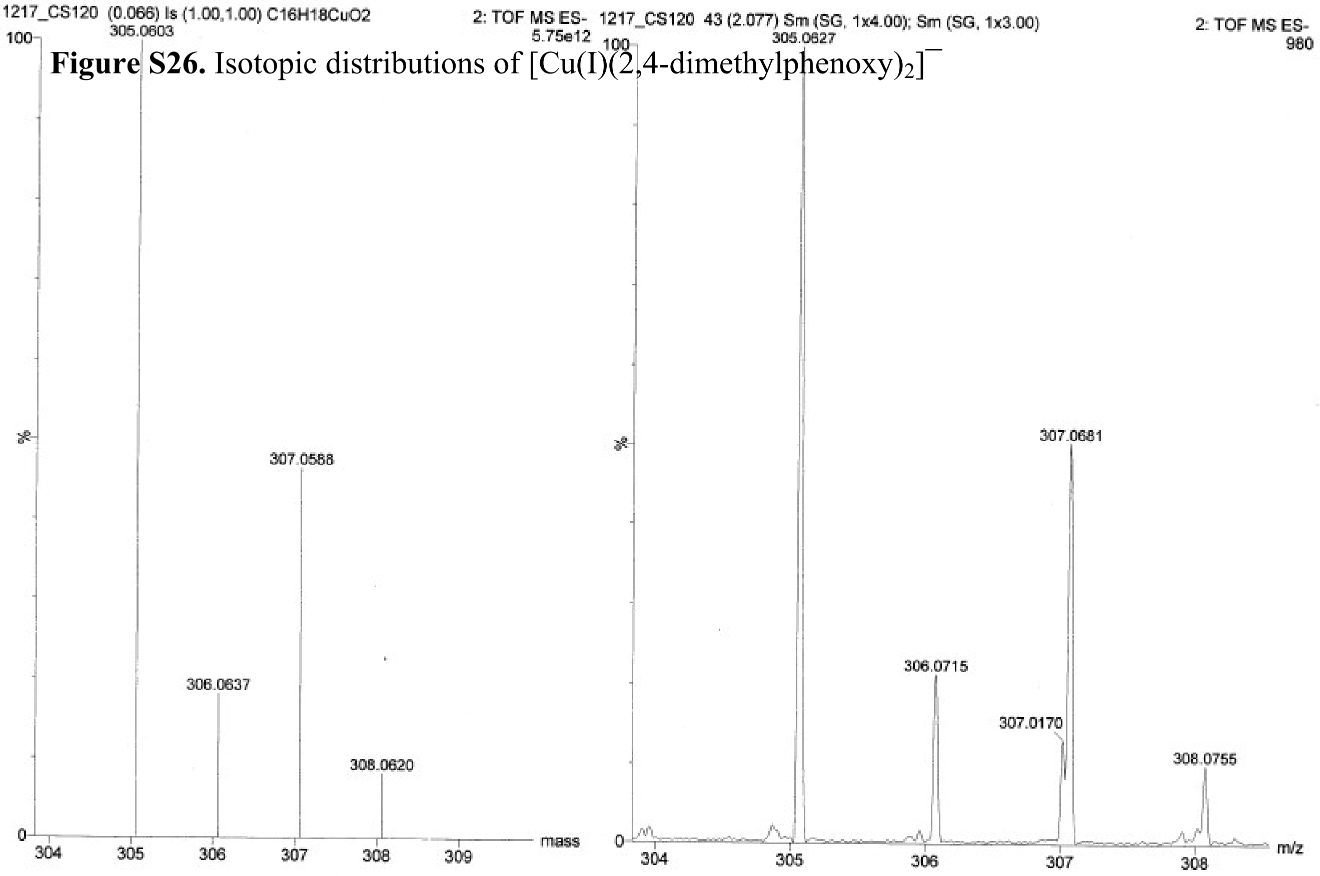
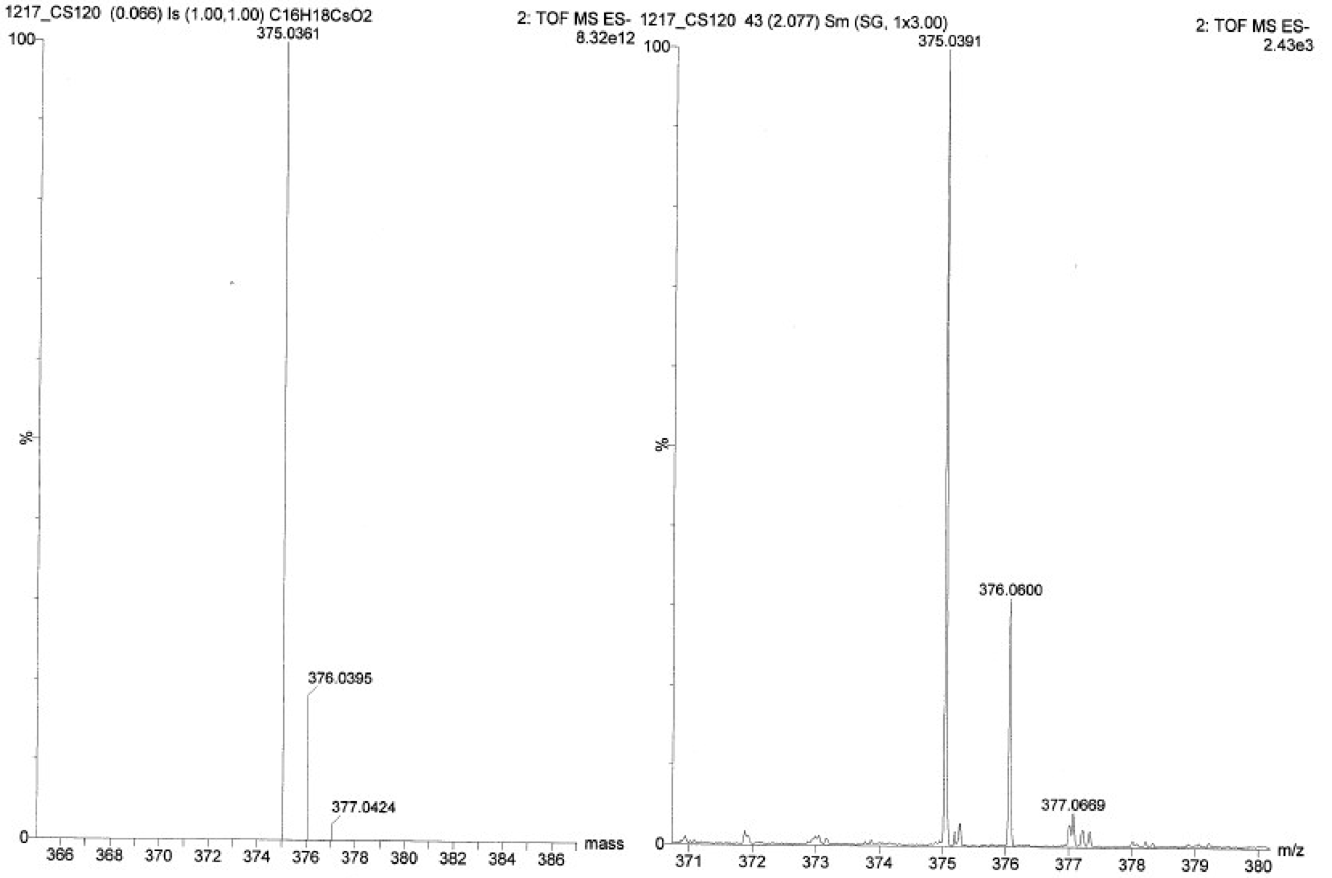


Figure S26. Isotopic distributions of $[Cu(I)(2,4\text{-dimethylphenoxy})_2]^-$



Simulated isotopic distributions of [Cs(2,4-dimethylphenoxy)$_2$]$^-$

Experimental isotopic distributions of [Cs(2,4-dimethylphenoxy)$_2$]$^-$

Figure S27. Isotopic distributions of [Cs(2,4-dimethylphenoxy)$_2$]$^-$

2. Experimental and simulated isotopic distributions [Cu(II)(2,4-dimethylphenoxy)$_2$(ρ-tolyl)]$^-$ or [Cu(0)(2,4-dimethylphenoxy)(1-(2,4-dimethylphenoxy)-4-methylbenzene)]$^-$ (from the ESI-MS spectra of the C-O coupling reaction mixxture of 2,4-dimethyl phenol and 4-bromotoluene catalyzed by CuI/Cs$_2$CO$_3$ in toluene at 120 ^{o}C)

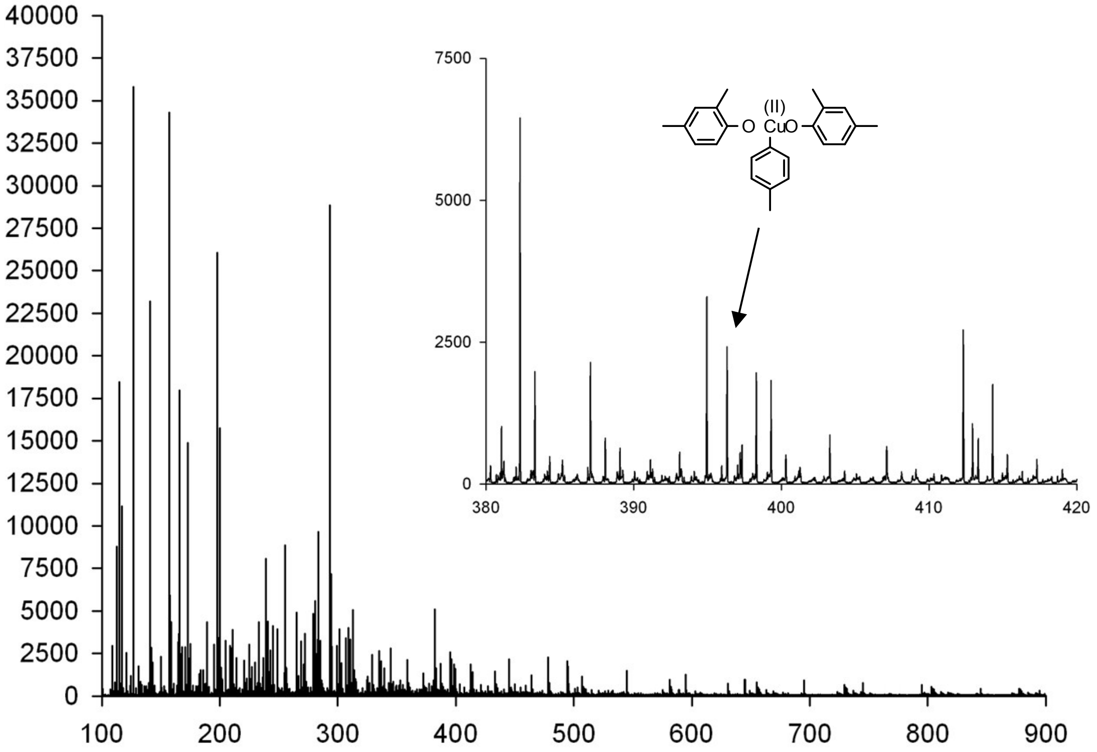
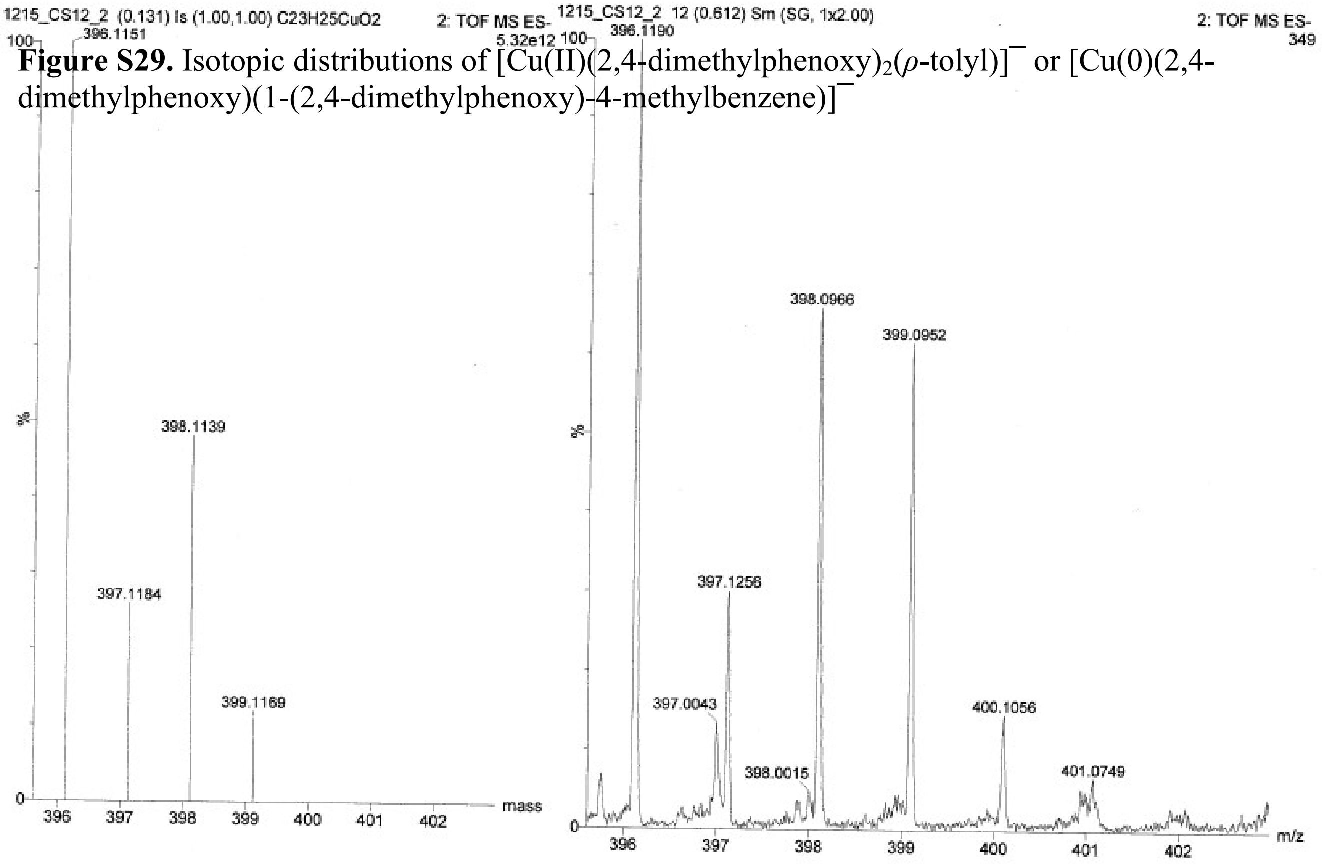


Figure S28. ESI-MS(-) full mass of m/z = 396



Simulated isotopic distributions of [Cu(II)(2,4-dimethylphenoxy)$_2$(ρ-tolyl)]$^-$ or [Cu(0)(2,4-dimethylphenoxy)(1-(2,4-dimethylphenoxy)-4-methylbenzene)]$^-$

Experimental isotopic distributions of [Cu(II)(2,4-dimethylphenoxy)$_2$(ρ-tolyl)]$^-$ or [Cu(0)(2,4-dimethylphenoxy)(1-(2,4-dimethylphenoxy)-4-methylbenzene)]$^-$

Figure S29. Isotopic distributions of [Cu(II)(2,4-dimethylphenoxy)$_2$(ρ-tolyl)]$^-$ or [Cu(0)(2,4-dimethylphenoxy)(1-(2,4-dimethylphenoxy)-4-methylbenzene)]$^-$

3. Experimental and simulated isotopic distributions of [Cu(II)(2,4-dimethylphenoxy)$_2$(ρ-tolyl)]$^-$ or [Cu(0)(2,4-dimethylphenoxy)(1-(2,4-dimethylphenoxy)-4-methylbenzene)]$^-$ (from the ESI-MS spectra of the C-O coupling reaction mixxture of 2,4-dimethyl phenol and 4-bromotoluene catalyzed by CuI/Cs$_2$CO$_3$ in toluene at 120 °C)

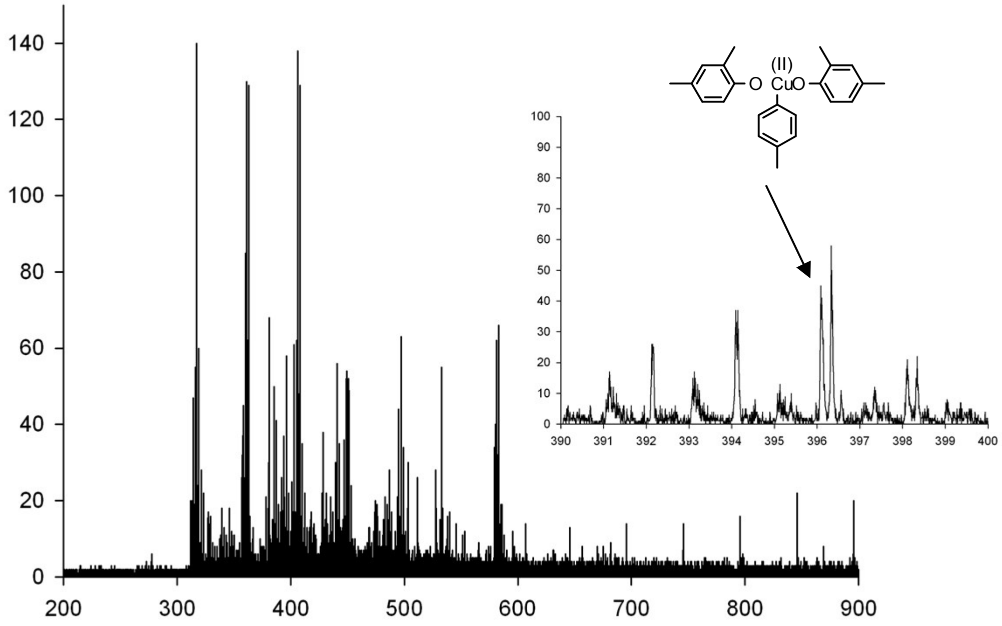
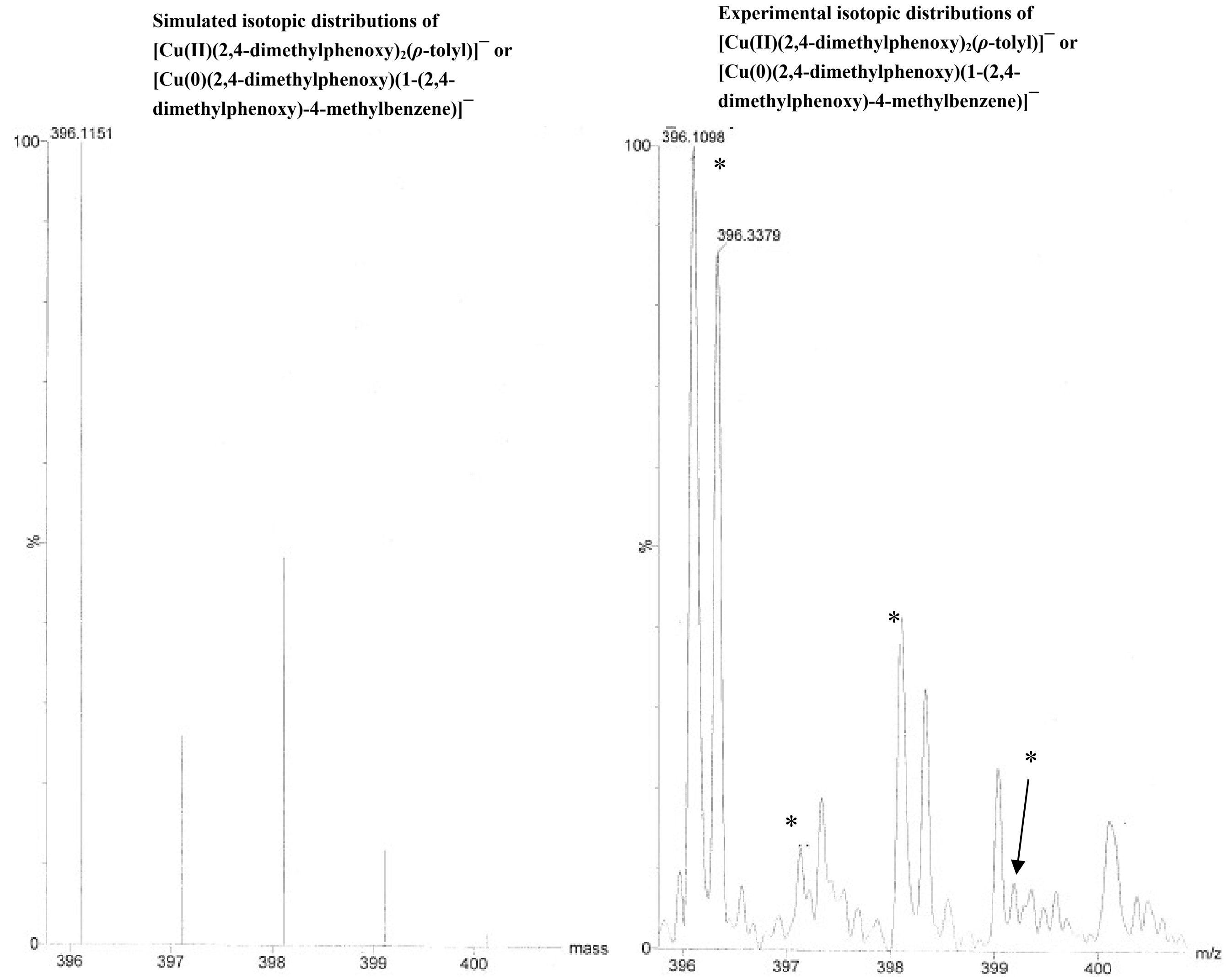


Figure S30. ESI-MS(-) full mass of m/z = 396


Simulated isotopic distributions of $[Cu(II)(2,4\text{-dimethylphenoxy})_2(\rho\text{-tolyl})]^-$ or $[Cu(0)(2,4\text{-dimethylphenoxy})(1\text{-}(2,4\text{-dimethylphenoxy})\text{-}4\text{-methylbenzene})]^-$

Experimental isotopic distributions of $[Cu(II)(2,4\text{-dimethylphenoxy})_2(\rho\text{-tolyl})]^-$ or $[Cu(0)(2,4\text{-dimethylphenoxy})(1\text{-}(2,4\text{-dimethylphenoxy})\text{-}4\text{-methylbenzene})]^-$

*Signals of the compound

Figure S31. Isotopic distributions of $[Cu(II)(2,4\text{-dimethylphenoxy})_2(\rho\text{-tolyl})]^-$ or $[Cu(0)(2,4\text{-dimethylphenoxy})(1\text{-}(2,4\text{-dimethylphenoxy})\text{-}4\text{-methylbenzene})]^-$

NMR data of cesium 2,4-dimethylphenoxide

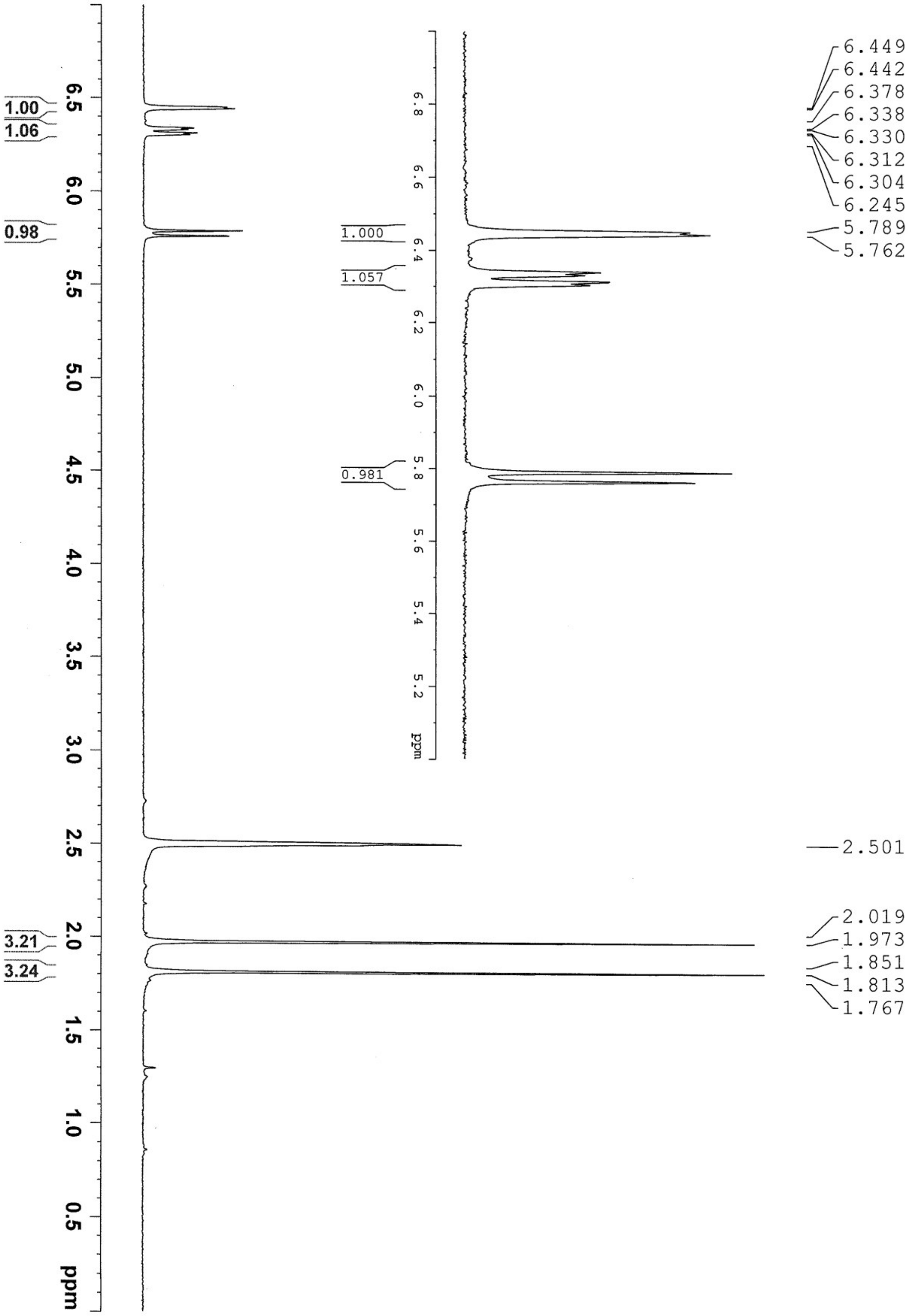
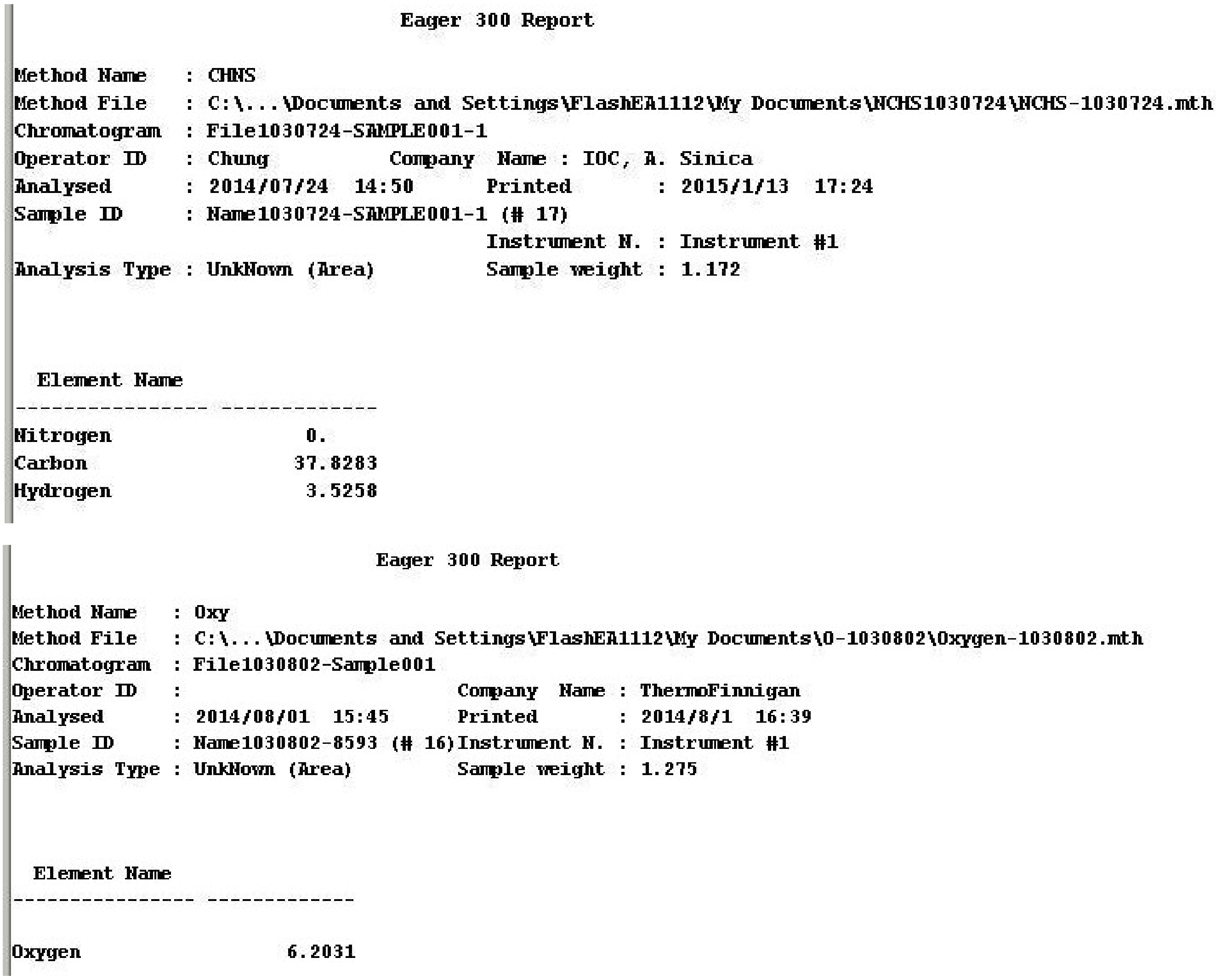


Figure S32. NMR data of cesium 2,4-dimethylphenoxide.

Elementary analysis of cesium 2,4-dimethylphenoxide



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                                Eager 300 Report

Method Name    : CHNS
Method File    : C:\...\Documents and Settings\FlashEA1112\My Documents\NCHS1030724\NCHS-1030724.mth
Chromatogram   : File1030724-SAMPLE001-1
Operator ID    : Chung           Company  Name : IOC, A. Sinica
Analysed       : 2014/07/24  14:50      Printed       : 2015/1/13  17:24
Sample ID      : Name1030724-SAMPLE001-1 (# 17)
                                        Instrument N. : Instrument #1
Analysis Type : UnkNown (Area)          Sample weight : 1.172



  Element Name
---------------- -------------
Nitrogen                 0.
Carbon                 37.8283
Hydrogen                3.5258
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                                Eager 300 Report

Method Name    : Oxy
Method File    : C:\...\Documents and Settings\FlashEA1112\My Documents\O-1030802\Oxygen-1030802.mth
Chromatogram   : File1030802-Sample001
Operator ID    :                        Company  Name : ThermoFinnigan
Analysed       : 2014/08/01  15:45      Printed       : 2014/8/1  16:39
Sample ID      : Name1030802-8593 (# 16)Instrument N. : Instrument #1
Analysis Type : UnkNown (Area)          Sample weight : 1.275



  Element Name
---------------- -------------

Oxygen                  6.2031
```

Figure S33. Elementary analysis of cesium 2,4-dimethylphenoxide

EPR spectra for Copper-Catalyzed C–O Cross-Coupling Reaction without phen

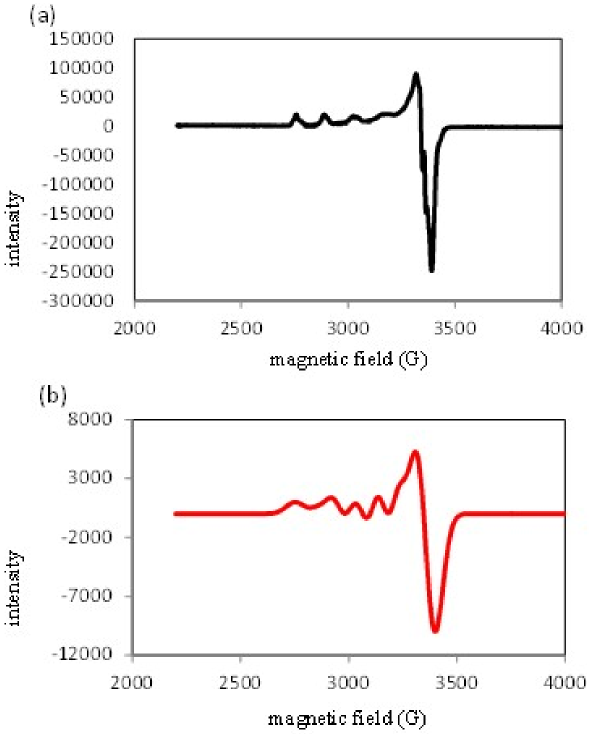

Figure S34. (a) Experimental (b) Simulated EPR spectra for the reaction of 2,4-dimethyl phenol and 4-bromotoluene with Cs_2CO_3 in the presence of CuI in toluene at 298K.