Supplementary Materials: Cyclometalated Iridium(III) Complexes Containing Benzoxazole Derivatives and Different Ancillary Ligands for Catalytic Oxidation of Toluene

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Table S1. Crystal data of complexes **1** and **2**.

	1	**2**
empirical formula	C31 H21 Cl Ir N3 O2	C32 H23 Cl Ir N3 O2
fw	695.16	709.18
temp [K]	110(2)	110(2)
cryst size [mm^3]	0.76 x 0.58 x 0.38	0.70 x 0.56 x 0.46
cryst syst	Monoclinic	Triclinic
space group	P 21/c	P -1
a [Å]	9.6077(2)	12.2515(4)
b [Å]	17.1133(3)	13.7904(4)
c [Å]	16.5835(3)	17.8219(5)
α [deg]	90	73.583(3)
β [deg]	99.796(2)	78.557(2)
γ [deg]	90	71.135(3)
V [$Å^3$], Z	2686.89(9), 4	2714.09(14), 4
ϱ_{calcd} [$g.cm^{-3}$]	1.718	1.736
μ [mm^{-1}]	5.102	5.053
F(000)	1352	1384
Scan mode	ω	ω
detector	Bruker-CCD	Bruker-CCD
θ_{max} [deg]	29.20	29.23
no. of total refins	13167	24208
no. of unique refins	6220	12516
R(int)	0.0276	0.0229
no. of params	343	697
GOF on F^2	0.977	1.018
R indices [$I>\sigma 2(I)$]	R1 = 0.0256	R1 = 0.0239
	wR2 = 0.0595	wR2 = 0.0462
R indices (all data)	wR2 = 0.0360	wR2 = 0.0365
	R1 = 0.0609	R1 = 0.0476
max diff. peak, hole ($e.Å^{-3}$)	1.296, -0.974	1.216, -0.987

Table S2. Crystal data of complexes **4**–**6**.

	4	**5**	**6**
empirical formula	$C_{31}H_{17}ClF_4IrN_3O_2$	$C_{32}H_{19}ClF_4IrN_3O_2$	$C_{32}H_{16}ClF_4IrN_4O_2$
fw	767.14	781.15	792.14
temp [K]	110(2) K	110(2) K	297(2)
cryst size [mm^3]	0.58 x 0.42 x 0.28	0.72 x 0.38 x 0.28	0.48 x 0.40 x 0.21
cryst syst	Monoclinic	Monoclinic	Monoclinic
space group	P 21/n	P 21/c	P 21/c
a [Å]	9.7170(2)	12.1130(2)	23.9090(12)
b [Å]	17.9672(4)	16.4385(3)	13.5257(7)
c [Å]	6.2161(3)	13.9655(2)	20.3311(10)
α [deg]	90	90	90
β [deg]	94.710(2)	103.533(2)	111.9160(10)
γ [deg]	90	90	90
V [$Å^3$], Z	2821.56(10), 2	2703.60(8), 4	6099.6(5), 2
ϱ_{calcd} [$g.cm^{-3}$]	1.906	1.919	1.759
μ [mm^{-1}]	4.984	5.102	4.529
F(000)	1564	1512	3124
Scan mode	ω	ω	ω
detector	Bruker-CCD	Bruker-CCD	Bruker-CCD
θ_{max} [deg]	29.22	29.26	26.03
no. of total refins	13859	25755	33780
no. of unique refins	6574	6538	11970
R(int)	0.0261	0.0299	0.0326
no. of params	412	388	829
GOF on F^2	0.953	0.996	1.070
R indices [$I>\sigma 2(I)$]	R1 = 0.0254	R1 = 0.0194	R1 = 0.0319
	wR2 = 0.0505	wR2 = 0.0399	wR2 = 0.0847
R indices (all data)	R1 = 0.0368	R1 = 0.0295	R1 = 0.0444
	wR2 = 0.0519	wR2 = 0.0408	wR2 = 0.0899
max diff. peak, hole ($e.Å^{-3}$)	1.719, -1.023	0.824, -0.824	1.448, -1.301

Table S3. Crystal data of complexes **8** and **9**.

	8	**9**
empirical formula	$C_{32}H_{19}N_3O_2IF_4Ir$	$C_{32}H_{16}N_4O_2IF_4Ir$
fw	873.01	883.61
temp [K]	110(2) K	110(2) K
cryst size [mm^3]	0.75 x 0.60 x 0.40	0.76 x 0.60 x 0.36
cryst syst	Triclinic	Triclinic
space group	P -1	P -1
a [Å]	8.5721(2)	11.8797(4)
b [Å]	10.9433(3)	12.1298(4)
c [Å]	16.9964(6)	12.8946(4)
α [deg]	95.019(2)	88.936(2)
β [deg]	97.165(2)	86.581(2)
γ [deg]	91.412(2)	68.125(3)
V [$Å^3$], Z	1574.85(8), 2	1721.22(10), 2
ρ_{calcd} [$g.cm^{-3}$]	1.931	2.033
μ [mm^{-1}]	5.280	5.147
F(000)	878	1004
Scan mode	ω	ω
detector	Bruker-CCD	Bruker-CCD
θ_{max} [deg]	29.20	29.25
no. of total refins	14010	15110
no. of unique refins	7249	7983
R(int)	0.0229	0.0210
no. of params	409	463
GOF on F^2	1.030	1.012
R indices [$I>\sigma 2(I)$]	R1 = 0.0317	R1 = 0.0236
	wR2 = 0.0703	wR2 = 0.0549
R indices (all data)	R1 = 0.0401	R1 = 0.0286
	wR2 = 0.0723	wR2 = 0.0558
max diff. peak, hole ($e.Å^{-3}$)	1.809, -2.395	1.530, -1.268

Table S4. Reaction rate (μM/s) of the catalytic oxidation for toluene.

Catalyst		**1**			**2**			**3**			**4**			**5**		
Temp.		T_1[e]	T_2[f]	T_3[g]	T_1	T_2	T_3	T_1	T_2	T_3	T_1	T_2	T_3	T_1	T_2	T_3
Conc. of Cat.	C_1[a]	0.32	0.86	7.01	0.29	0.76	6.56	0.27	0.70	7.41	0.48	1.49	8.58	0.48	1.44	8.50
	C_2[b]	0.56	1.47	11.5	0.55	1.45	8.13	0.51	1.39	10.1	0.90	2.90	15.2	0.91	2.70	16.2
	C_3[c]	0.24	0.60	6.45	0.23	0.61	3.81	0.23	0.59	4.69	0.41	1.35	8.55	0.43	1.32	8.27
	C_4[d]	0.39	1.21	7.71	0.46	1.13	5.77	0.45	0.92	5.75	0.80	2.40	14.2	0.64	2.34	15.1
Catalyst		**6**			**7**			**8**			**9**					
Temp.		T_1	T_2	T_3	T_1	T_2	T_3	T_1	T_2	T_3	T_1	T_2	T_3			
Conc. of Cat.	C_1	0.50	1.40	8.98	0.36	1.02	7.71	0.32	0.89	8.25	0.30	1.00	8.27			
	C_2	0.91	2.81	17.3	0.64	1.75	15.1	0.47	1.48	14.2	0.56	1.74	14.3			
	C_3	0.41	1.06	7.63	0.29	0.78	7.62	0.25	0.71	7.52	0.25	0.75	7.38			
	C_4	0.70	2.22	14.8	0.36	1.30	11.2	0.40	1.26	11.9	0.44	1.33	12.5			

[a] 0.1mM of catalyst in neat toluene ([toluene] = 9.39 M), [b] 0.2mM of catalyst in net toluene, [c] 0.1mM of catalyst in a reaction solution consisted of 80% of toluene and 20% of 1,2-dichlorobenzene (v/v) ([toluene]=7.51M); [d] 0. 2mM of catalyst in a reaction solution consisted of 80% of toluene and 20% of 1,2-dichlorobenzene, [e] at 333 K of reaction temperature, [f] at 353 K of reaction temperature, [g] at 373 K of reaction temperature.

Table S5. Rate constants and activation energy of the catalytic oxidation for toluene.

Catalyst		**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
k rate[a]	k_{333}	53	52	50	89	85	88	58	52	53
	k_{353}	144	135	126	278	273	255	171	153	168
	k_{373}	1183	1037	896	1675	1633	1661	1492	1451	1478
Ea[b]		27.7	28.1	30.8	22.91	23.2	24.3	26.8	29.2	27.3

[a] rate constant (s^{-1}) . [b] average of activation energy (kcal/mol).

Table S6. Reaction rates, catalytic frequencies, concentration of the product and turnover number of catalytic oxidation of toluene with various concentrations of complexes as catalysts.

Cat. \ para. (mM)		rate [a]	TOF [b]	CP_6 [c]	TON_6 [d]	selectivity (%) [e]
1	1	4.72	17	102	102	89
	0.1	7.50	270	162	1620	90
	0.01	4.72	1700	102	10200	89
	0.001	1.09	3900	23	23400	86
2	1	4.46	16	96	97	89
	0.1	7.28	262	157	1580	90
	0.01	4.00	1440	86	8620	88
	0.001	0.97	3480	21	20900	86
3	1	4.41	16	95	96	89
	0.1	6.77	244	146	1460	90
	0.01	3.88	1400	84	8380	86
	0.001	0.84	3050	18	18400	88
4	1	19.0	68	411	410	96
	0.1	19.4	698	419	4180	96
	0.01	12.0	4300	258	25800	95
	0.001	2.81	10100	61	60700	95
5	1	20.3	73	438	437	97
	0.1	15.4	553	332	3320	96
	0.01	11.6	4180	251	25000	96
	0.001	2.75	9940	60	59600	95
6	1	15.0	54	323	323	96
	0.1	13.0	468	281	2810	96
	0.01	9.00	3240	194	19400	95
	0.001	2.75	9900	59	59500	95
7	1	6.08	22	131	131	94
	0.1	9.67	349	209	2090	95
	0.01	4.99	1800	108	10800	94
	0.001	1.35	4880	29	29200	93
8	1	5.76	21	124	124	93
	0.1	8.56	308	185	1850	94
	0.01	4.94	1780	107	10700	92
	0.001	1.27	4570	27	27500	92
9	1	5.62	20	121	121	92
	0.1	8.46	304	183	1830	93
	0.01	4.50	1620	97	9750	91
	0.001	1.05	3780	23	22600	90

[a] catalytic rate of complexes for the catalytic oxidation of toluene (μM s^{-}), [b] catalytic frequencies of the complexes (h^{-1}); [c] the concentration of the product after 6 hours of reaction time (mM); [d] the turnover number after 6 hours of reaction time. [e] the chemoselectivity to benzaldehyde

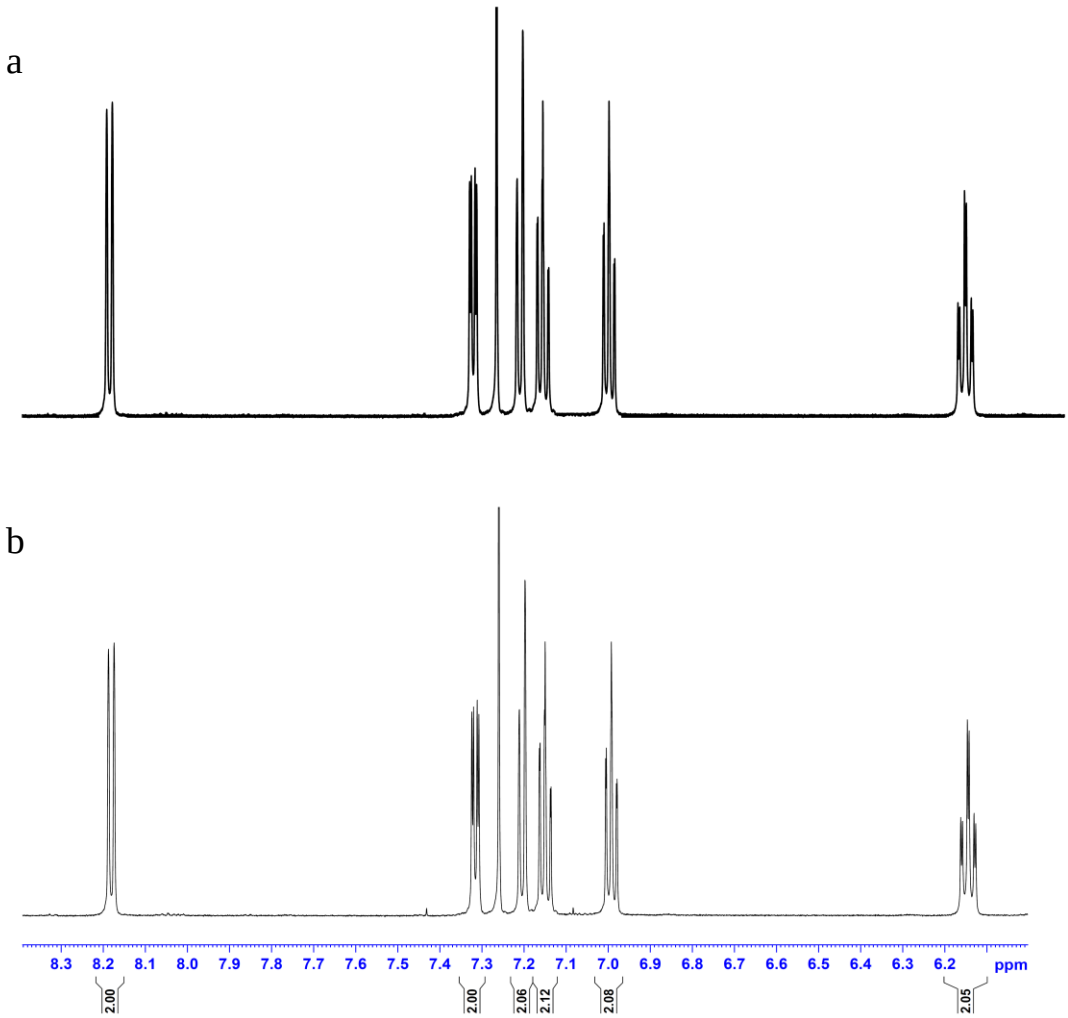

Figure S1. (a) NMR spectrum of precipitate formed from solution when a higher concentration of complex **4** was used, and (b) NMR spectrum of **D2**.

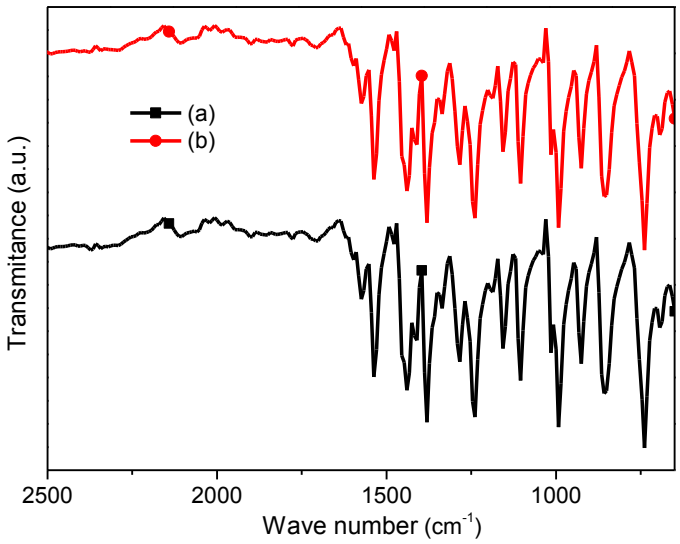

Figure S2. (a) IR spectrum of precipitate formed from solution when a higher concentration of complex **4** was used, and (b) IR spectrum of **D2**.

a

b

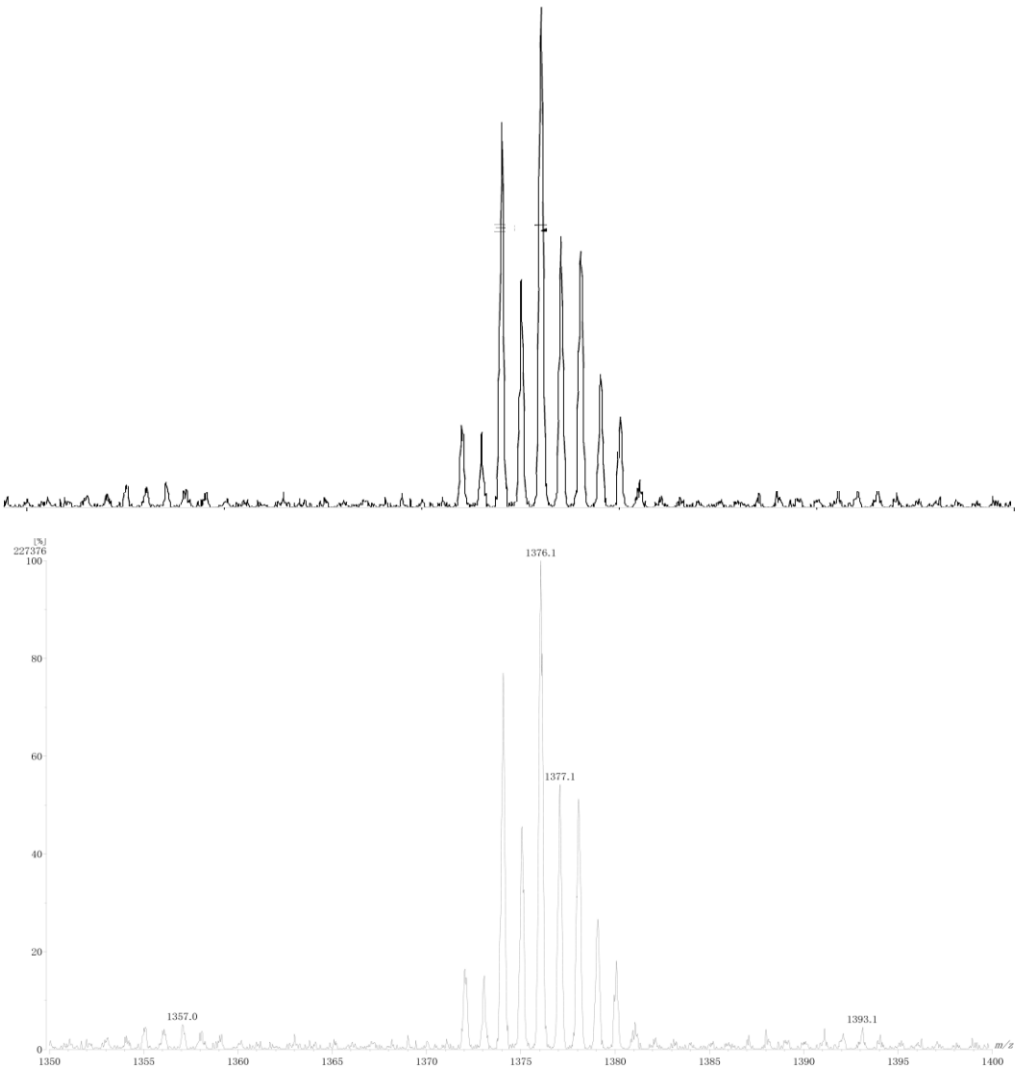

Figure S3. (a) MS spectrum of precipitate formed from solution when a higher concentration of complex **4** was used, and (b) MS spectrum of **D2**.

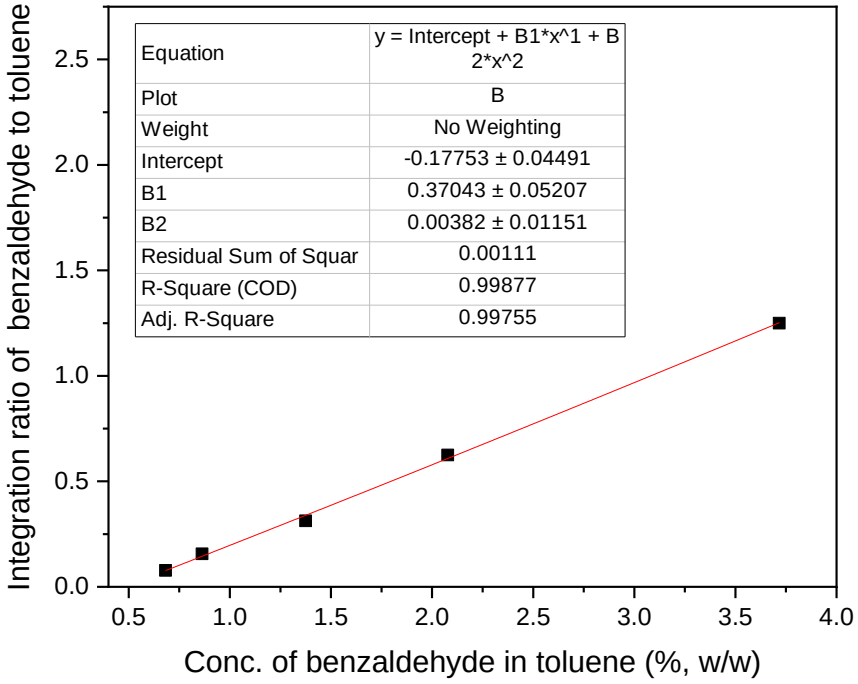

Figure S4. The calibration curve of the standard solutions containing toluene and benzaldehyde.

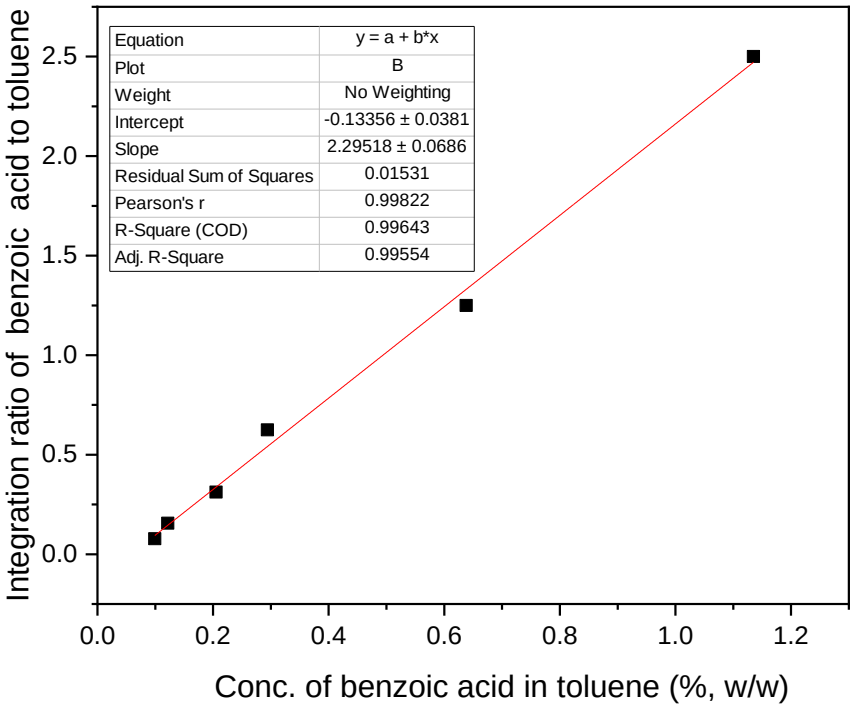

Figure S5. The calibration curve of the standard solutions containing toluene and benzoic acid.

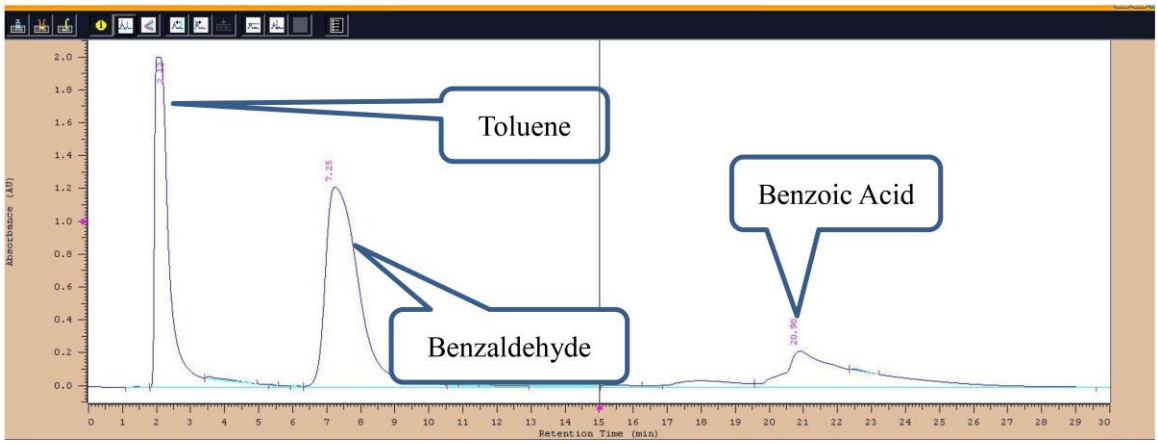

Figure S6. A picture of HPLC containing toluene, benzaldehyde, and benzoic acid, the integration ratio of benzaldehyde to toluene is1.44 (0.38 % of benzaldehyde in toluene), the integration ratio of benzoic acid to toluene is 0.12 (0.16 % of benzaldehyde in toluene).