Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Efficient and selective copper-catalyzed organic solvent-free and biphasic oxidation of aromatic *gem*-disubstituted alkenes to carbonyl compounds by *tert*-butyl hydroperoxide at room temperature

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General

All chemicals were obtained from commercial sources and used without further purification. Phenanthroline, neocuproine, bipyridine, 4,4'-dimethyl-2,2'-bipyridine, α-methylstyrene, styrene, styrene oxide, 4-chloro-α-methylstyrene, α-4-dimethylstyrene, *cis*-stilbene, 1,1-diphenylethylene, 3-nitrostyrene, 3-nitrobenzaldehyde, 1,1-diphenylethylene oxide, valeraldehyde, benzaldehyde, 4-chloroacetophenone, acetophenone, 4-fluoroacetophenone, heptaldehyde, 1-octene and 2,6-di-*tert*-butyl-4-methylphenol were purchased from Across. Trans-5-decene, 3-methylstyrene, 4-fluoro-α-methylstyrene, 4-chloro-α-methylstyrene, 4-methylacetophenone, benzophenone, *tert*-butyl hydroperoxide 70% in aqueous solution (TBHP), 5-6 M TBHP solution in decane, *m*-tolualdehyde, cumene hydroperoxide (80%), 2,3-dihydrofuran, ammonium chloride, and cupric chloride dihydrate were purchased from Alfa Aesar. H_2O_2 (34.5-36.5 wt. % aqueous solution) and 2-methyl-1-1-heptene were purchased from Aldrich. $[(phen)Cu(\mu\text{-}Cl)(Cl)]_2$ and 2-hydroperoxytetrahydrofuran were synthesized according to literature.[1,2] Gas chromatographic analyses were performed on an Agilent 6890 instrument with a FID detector and an Aglient 30 m x 0.53 mm x 3.0 μm HP-1 capillary column. Product isolation was carried out by TLC (Merck, TLC silica gel 60 F_{254} 25 Aluminium sheets 20x20 cm). NMR spectra were recorded in $CDCl_3$ on a Bruker AV 300 MHz, at room temperature.

1. Md. M. Hossain and S.-G. Shyu, *Adv. Synth. Catal.,* 2010, **352**, 3061.
2. G. Liang, P. Gannett and B. Gold, *Nucleic Acids Research,* 1995, **23**, 713.

Typical procedure for alkene oxidation

A stock solution of $CuCl_2 \cdot 2H_2O$ in water (0.0171g/cc) was prepared (by dissolving 0.171 g in 10 mL H_2O). To 5 mL flask, catalyst **A** (100 μL of the stock solution, 0.01 mmol of $CuCl_2$) or **B** (100 μL of a stock solution; 0.01 mmol of $CuCl_2$, 2.1 mg, 0.01 mmol of neocuproine) was added. Then 700 μL of H_2O, 0.2 mmol of alkene, and *tert*-butyl hydroperoxide (200 μL, 1.55 mmol) were added in each case. The mixture was stirred vigorously at room temperature till to its reaction time specified in the Table 2. The reaction mixture was then diluted with ethyl acetate and the products dissolved in ethyl acetate layer were analysed by GC. For product separation, the aqueous phase was extracted with ethyl acetate (3x5 mL). The combined extracts were dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated and product isolation was carried out by TLC. Similar procedure was followed for the control reactions of styrene epoxide (23.0 μL, 0.2 mmol), 1,1-diphenylethylene oxide (39.4 mg, 0.2 mmol), and 2,6-di-*tert*-butyl-4-methylphenol (412 mg, 2 mmol). Products were characterized by ^1H NMR and ^{13}C NMR. For reaction without addition of H_2O, to a solid mixture of $CuCl_2 \cdot 2H_2O$ (1.71 mg, 0.01 mmol) and neocuporine (2.1 mg, 0.01 mmol), TBHP (200 uL, 1.55 mmol in 70 % aq. solution) and 1,1 diphenylethylene (35.7 uL, 0.2 mmol) were added and the reaction run as above. Similarly, a solution of TBHP (240 uL, 1.5 mmol in decane) and 1,1 diphenylethylene (35.7 uL, 0.2 mmol) were added to a solid mixture of $CuCl_2 \cdot 2H_2O$ (1.71 mg, 0.01 mmol) and neocuproine (2.1 mg, 0.01 mmol). Then the reaction was continued as above and products identified by GC diluting with ethyl acetate.

Benzaldehyde: TLC (hexane/ethyl acetate = 1:0.5) gave benzaldehyde as a colorless liquid; yield: 7.8 mg (37%). ^1H NMR (300 MHz, $CDCl_3$) δ ppm 9.79 (s, 1H), 7.67-7.24 (m, 5H); ^{13}C NMR (300 MHz, $CDCl_3$) δ ppm 192.0, 136.0, 134.1, 129.2, 128.6.

***m*-Tolualdehyde:** TLC (hexane/ethyl acetate = 1:0.5) gave *m*-tolualdehyde as a colorless liquid; yield: 5.8 mg (24%). ^1H NMR (300 MHz, $CDCl_3$) δ ppm 9.72 (s, 1H), 7.44-7.40 (m, 2H), 7.16-7.14 (m, 2H), 2.14 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ ppm 191.8, 138.4, 136.2, 134.7, 129.5, 128.4, 126.6, 20.5.

3-Nitrobenzaldehyde: TLC (hexane/dichloromethane = 1:1) gave 3-nitrobenzaldehyde as a colorless solid; yield: 6.9 mg (23%). ^1H NMR (300 MHz, $CDCl_3$) δ ppm 10.09 (s, 1H), 8.68-8.67 (m, 1H), 8.47-8.43 (m, 1H), 8.21 (d, J = 7.8, 1H), 7.75 (t, J = 7.8 Hz, 1H); ^{13}C NMR (300 MHz, $CDCl_3$) δ ppm 189.9, 148.9, 137.5, 134.8, 130.6, 128.7, 124.6.

Benzophenone: TLC (hexane/ethyl acetate = 1:0.5) gave benzophenone as a colorless solid; yield: 31.7 mg (87%). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.59-7.57 (m, 4H), 7.56-7.54 (m, 2H), 7.48-7.43 (m, 4H), ^{13}C NMR (300 MHz, $CDCl_3$) δ ppm 196.9, 137.8, 132.6, 130.2, 128.4.

Acetophenone: TLC (hexane/ethyl acetate = 1:0.5) gave acetophenone as a colorless liquid; yield: 21.8 mg (91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.68 (d, J = 7.5, Hz, 2H), 7.27 (t, J = 7.5, 1H), 7.16 (t, J = 8.1, 2H), 2.29 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ ppm 197.2, 136.6, 132.6, 128.1, 127.8, 26.0.

4-Methylacetophenone: TLC (hexane/ethyl acetate = 1:0.5) gave 4-methylcetophenone as a colorless liquid; yield: 23.9 mg (89%). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.57 (d, J = 8.4, Hz, 2H), 6.94 (d, J = 8.1, 2H), 2.26 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ ppm 196.8, 143.2, 134.2, 128.7, 127.9, 25.8, 20.9.

4-Fluoroacetophenone: TLC (hexane/ethyl acetate = 1:0.5) gave 4-fluoroacetophenone as a colorless liquid; yield: 23.7 mg (86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.88–7.83 (d,d, J = 5.4, 2H), 6.99 (t, J = 8.4, 2H), 2.46 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ ppm 196.3, 167.3, 164.0, 133.6, 133.5, 130.9, 130.8, 115.7, 115.4, 26.4.

4-Chloroacetophenone: TLC (hexane/ethyl acetate = 1:0.5) gave 4-chloroacetophenone as a colorless liquid; yield: 28.3 mg (92%). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.57 (d, J = 7.6, 2H), 7.09 (d, J = 8.4, 2H), 2.28 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ ppm 196.0, 138.8, 135.0, 129.3, 128.3, 25.9.

NMR data

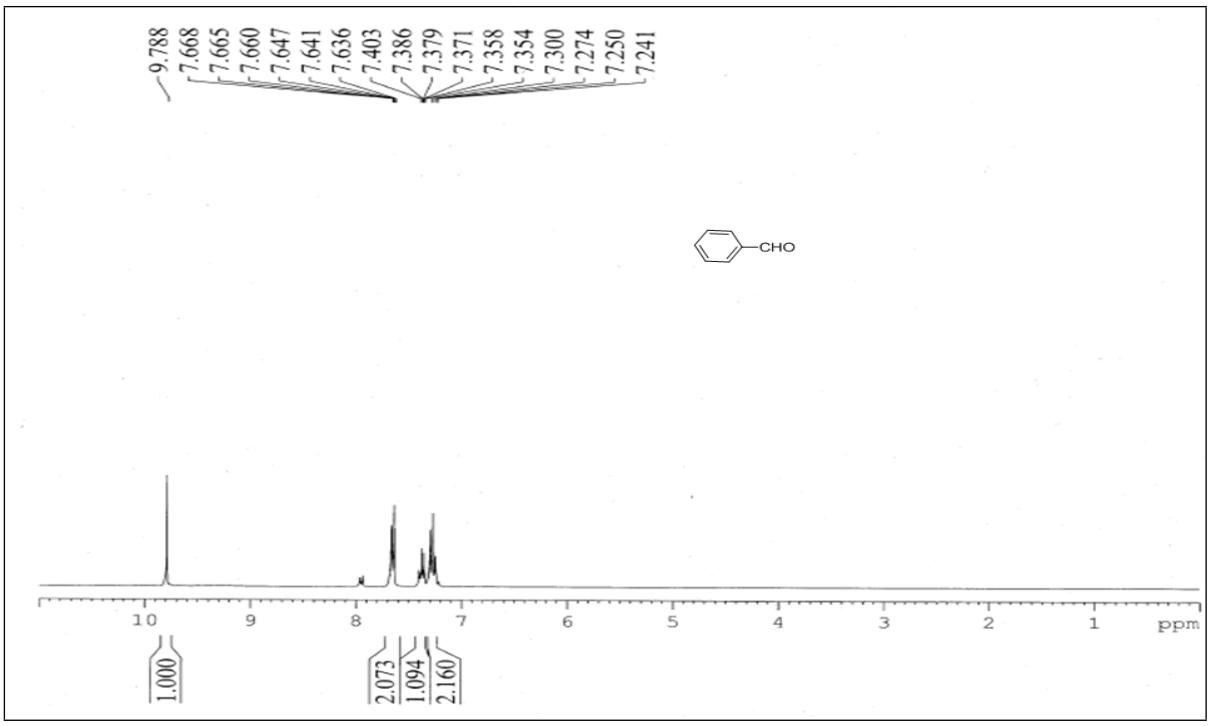


Fig. S1 ^{1}H NMR spectrum of Benzaldehyde

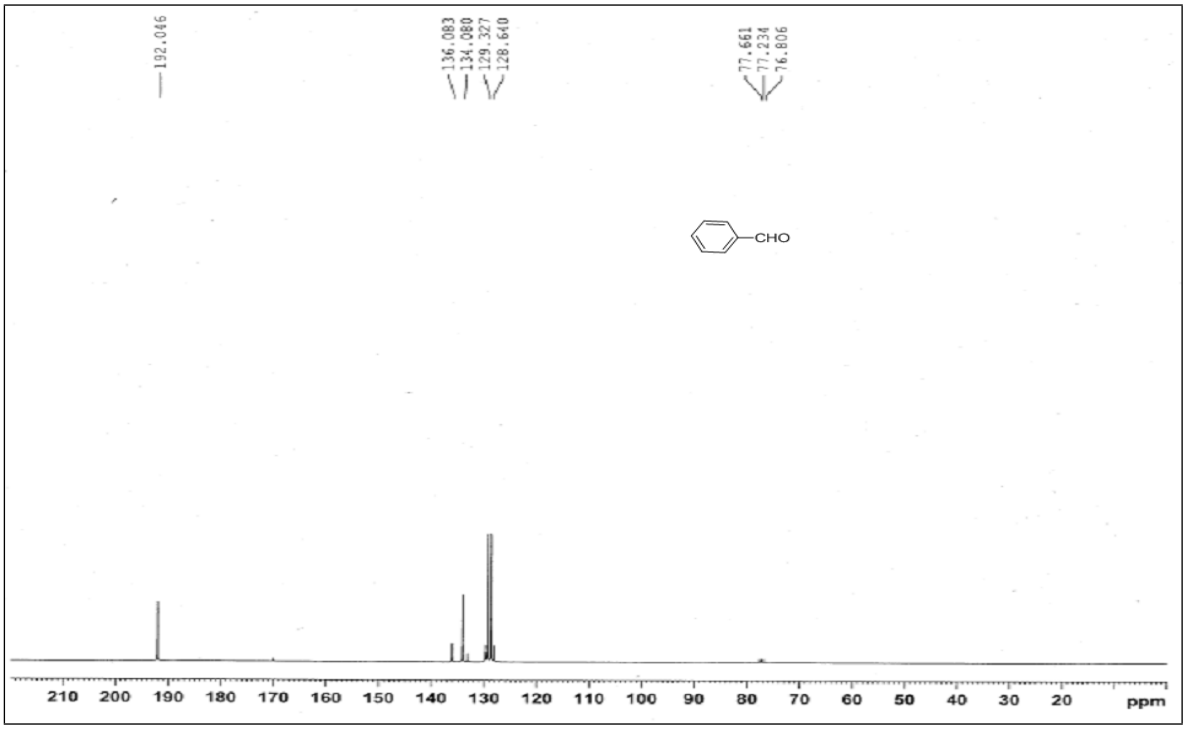


Fig. S2 ^{13}C NMR spectrum of Benzaldehyde

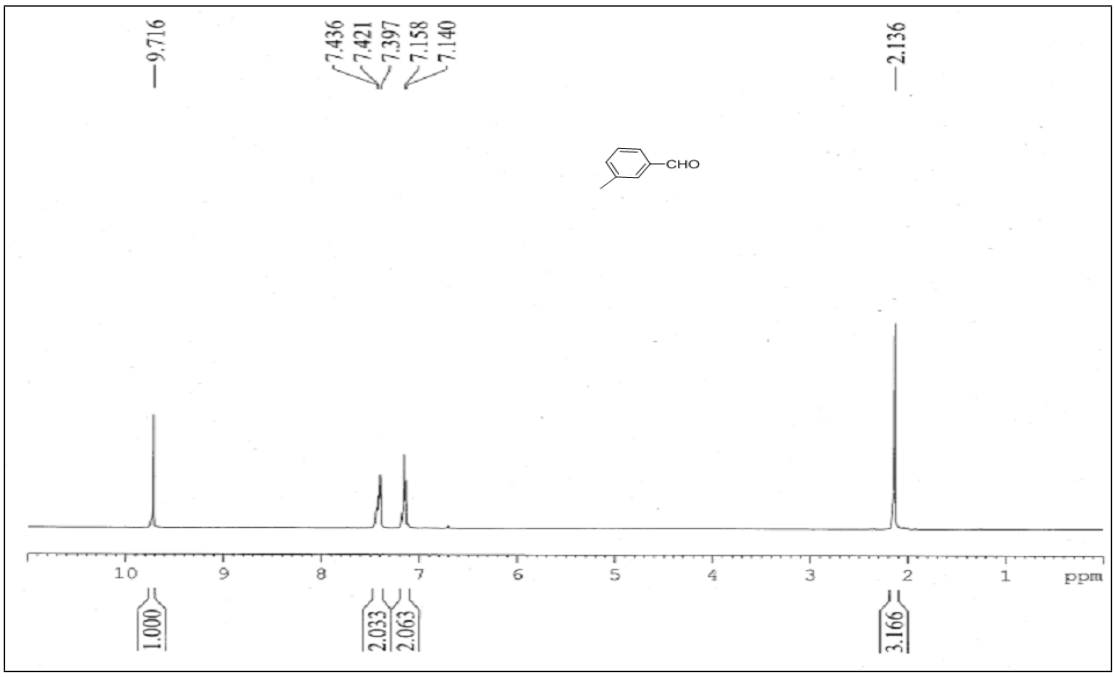


Fig. S3 ^{1}H NMR spectrum of *m*-Tolualdehyde

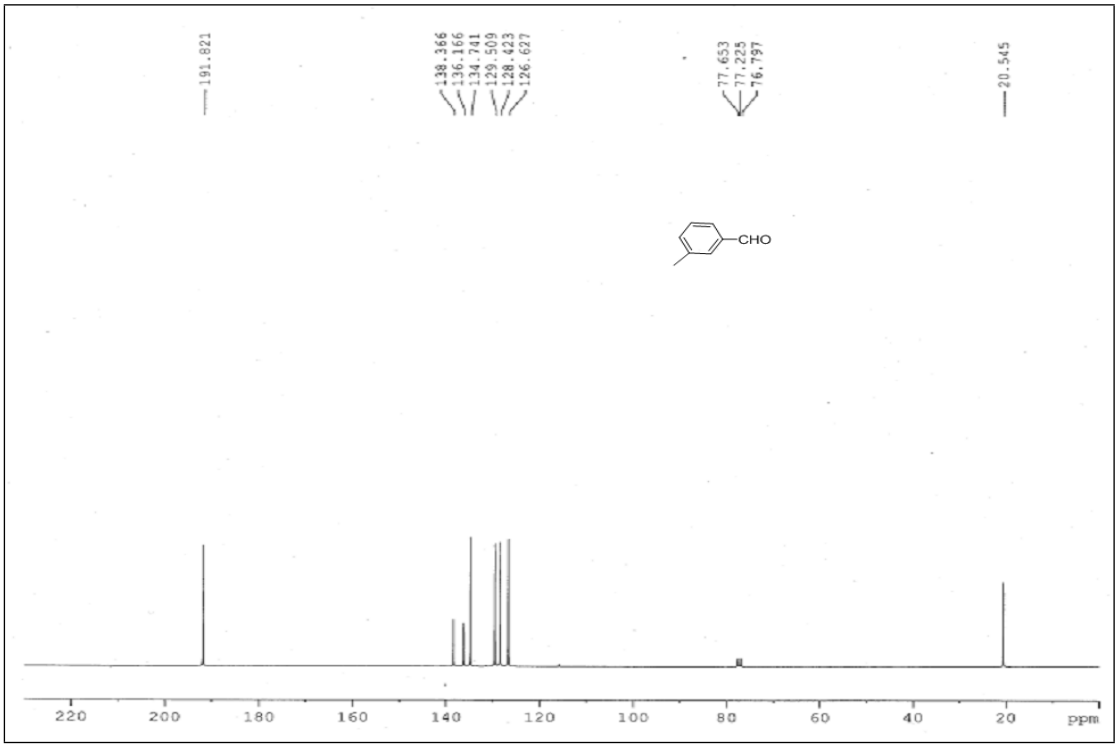


Fig. S4 ^{13}C NMR spectrum of *m*-Tolualdehyde

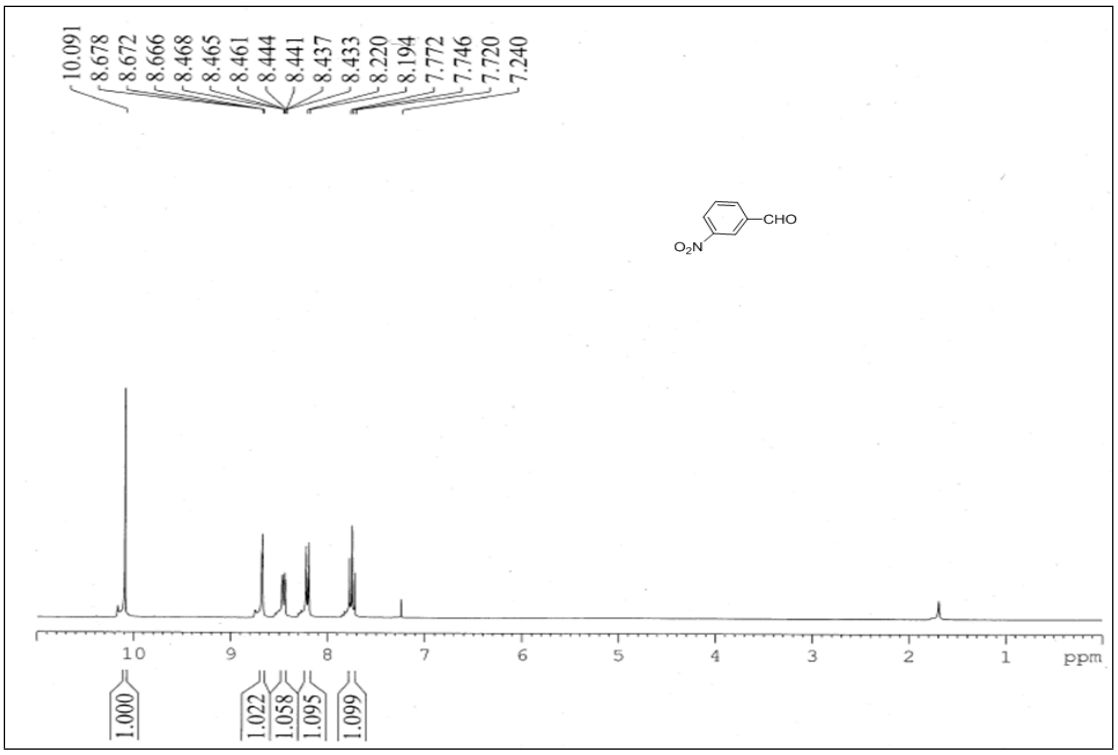


Fig. S5 ^{1}H NMR spectrum of 3-Nitrobenzaldedyde

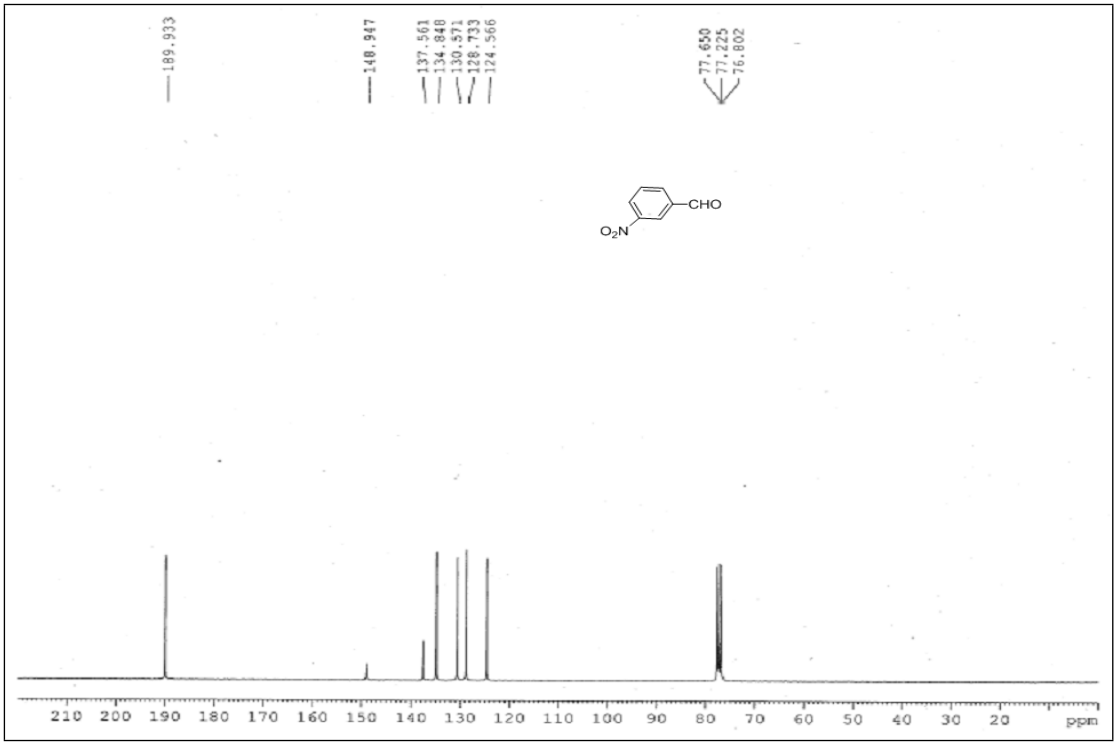


Fig. S6 ^{13}C NMR spectrum of 3-Nitrobenzaldehyde

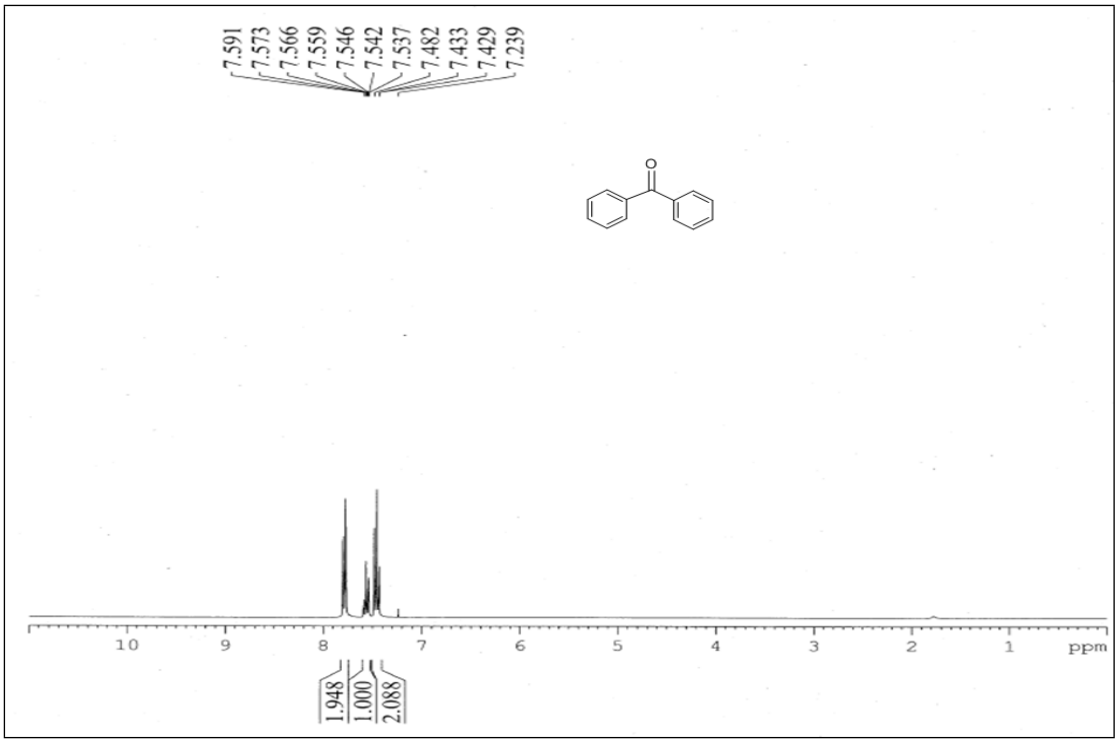


Fig. S7 ^{1}H NMR spectrum of Benzophenone

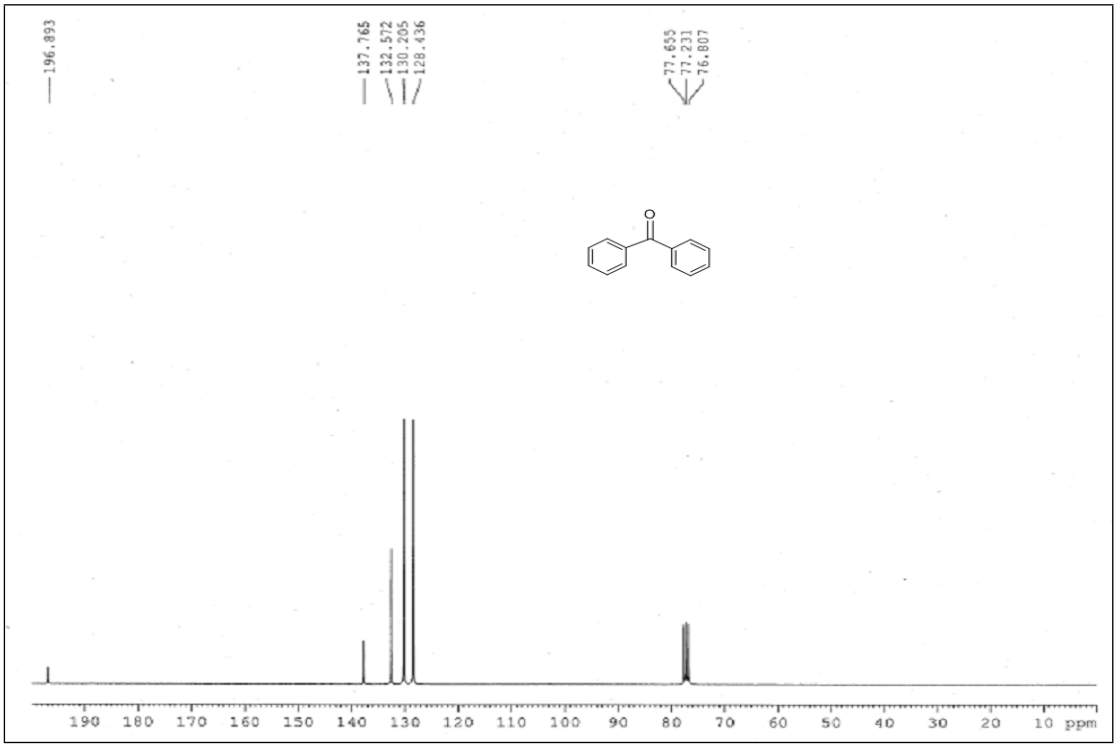


Fig. S8 ^{13}C NMR spectrum of Benzophenone

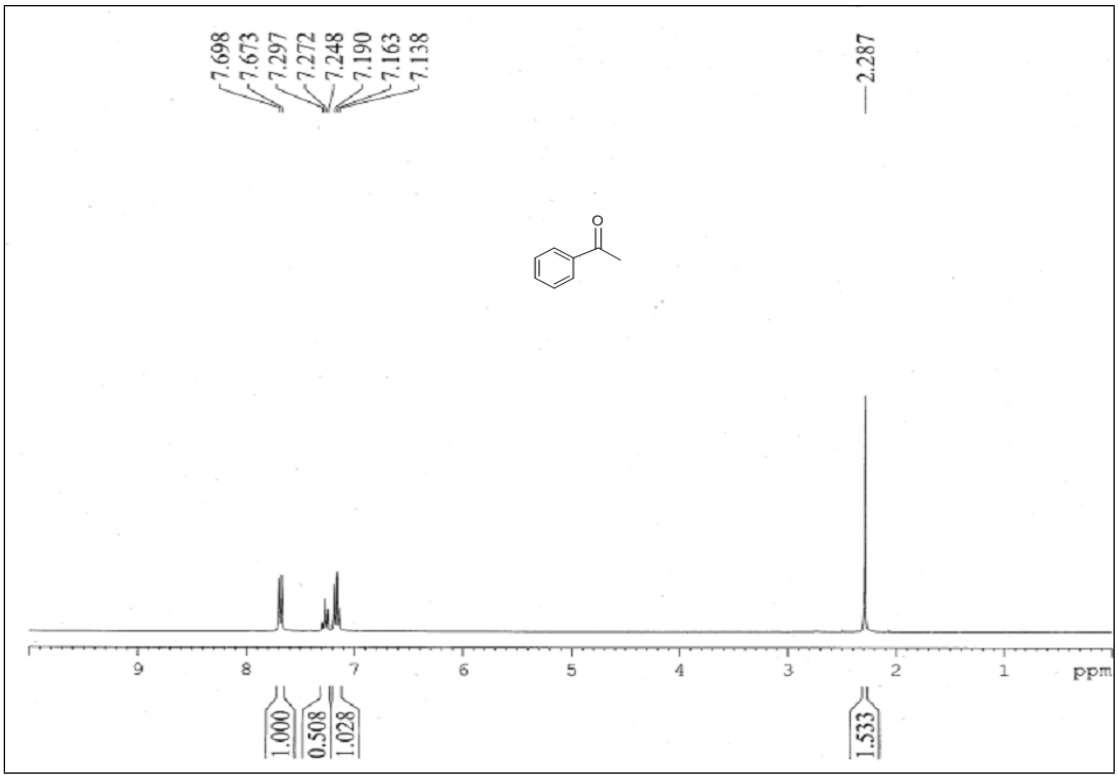


Fig. S9 ^{1}H NMR spectrum of Acetophenone

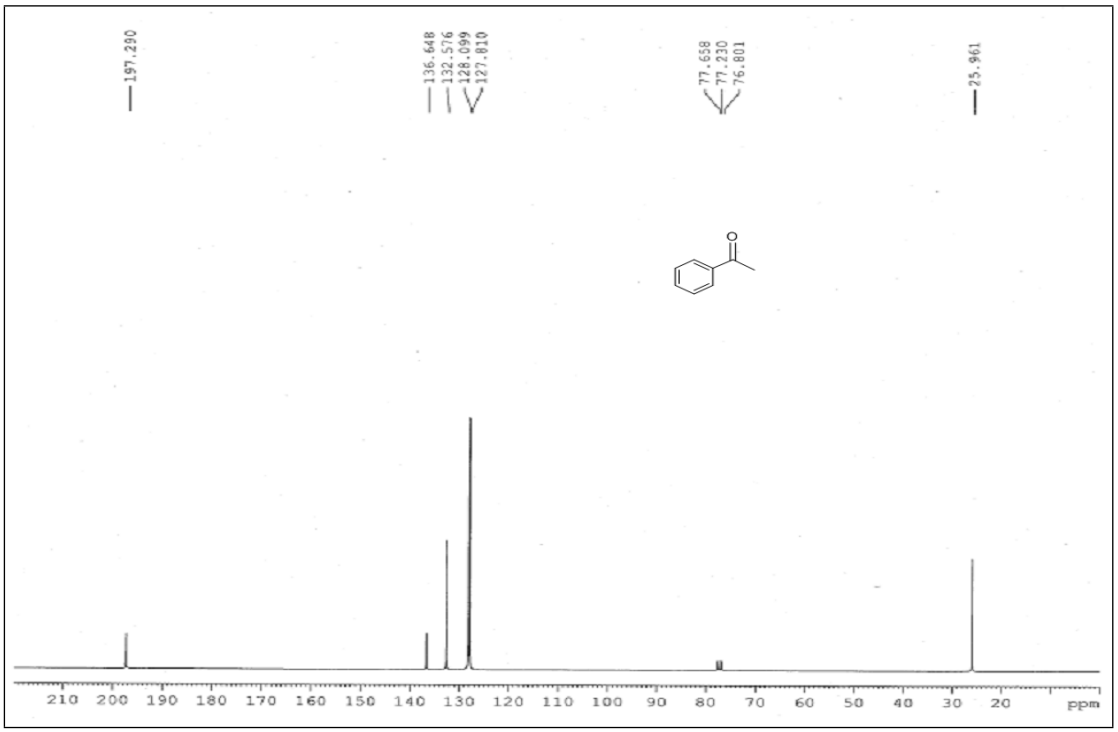


Fig. S10 ^{13}C NMR spectrum of Acetophenone

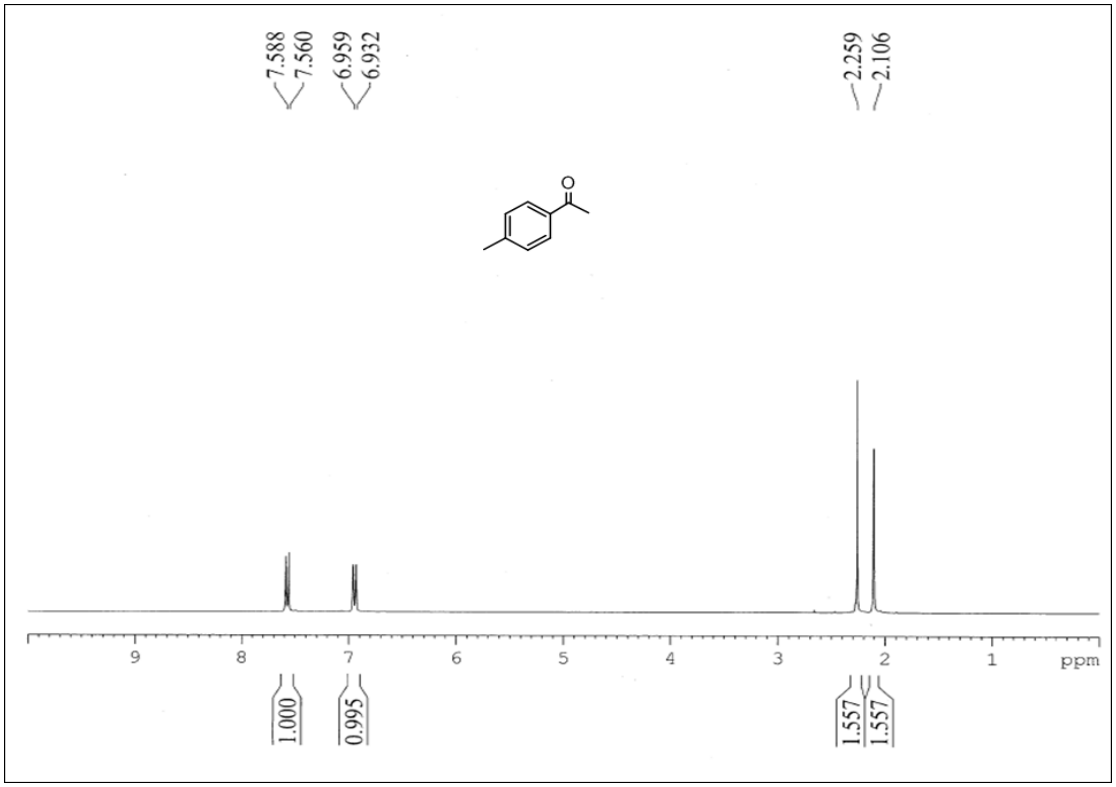


Fig. S11 ^{1}H NMR spectrum of 4-methylacetophenone

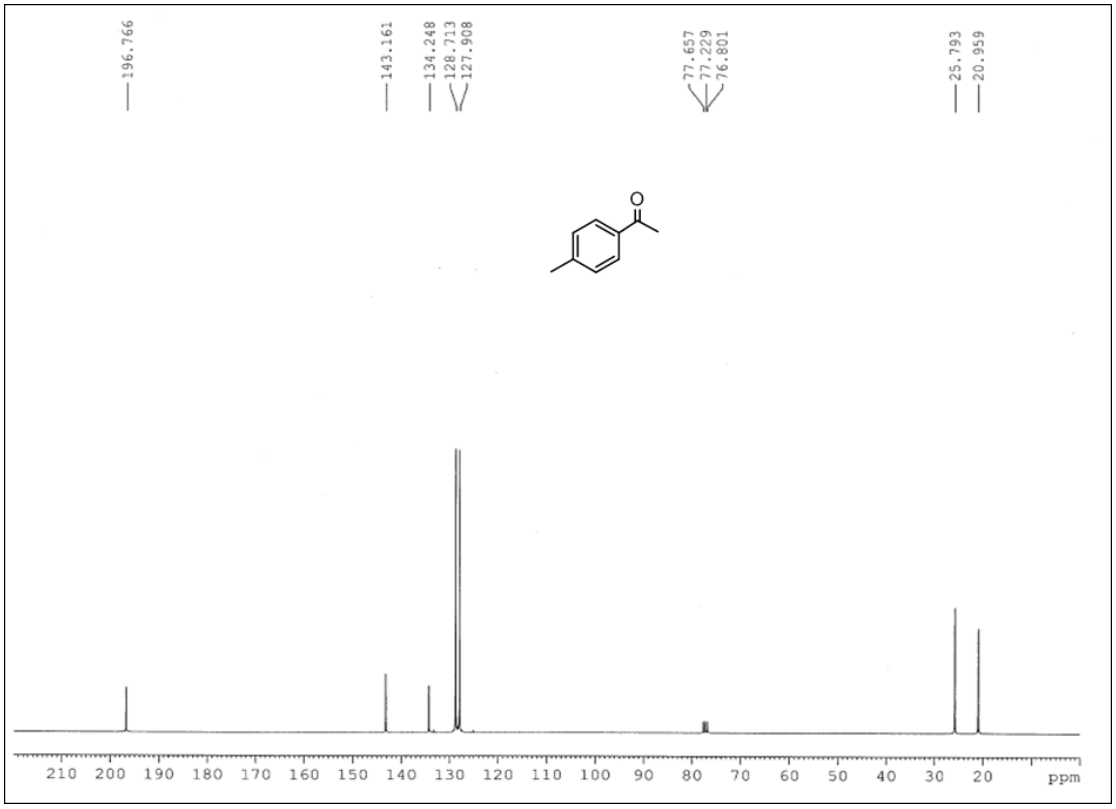


Fig. S12 ^{13}C NMR spectrum of 4-methylacetophenone

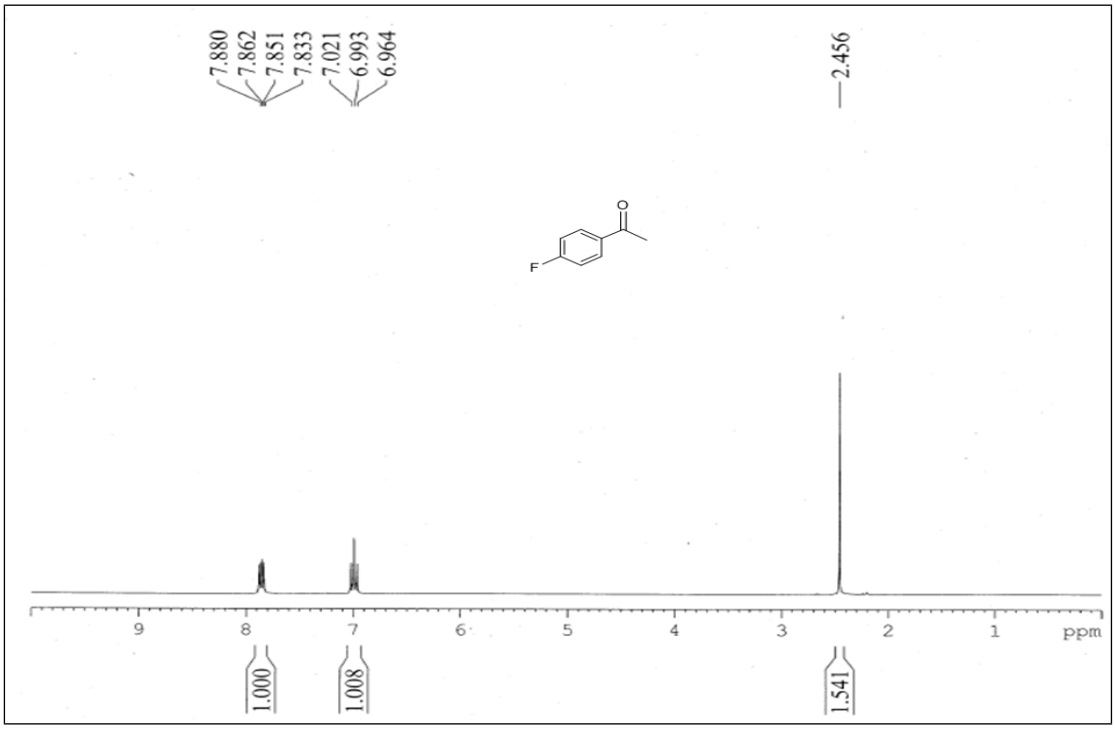


Fig. S13 ^{1}H NMR spectrum of 4-Fluoroacetophenone

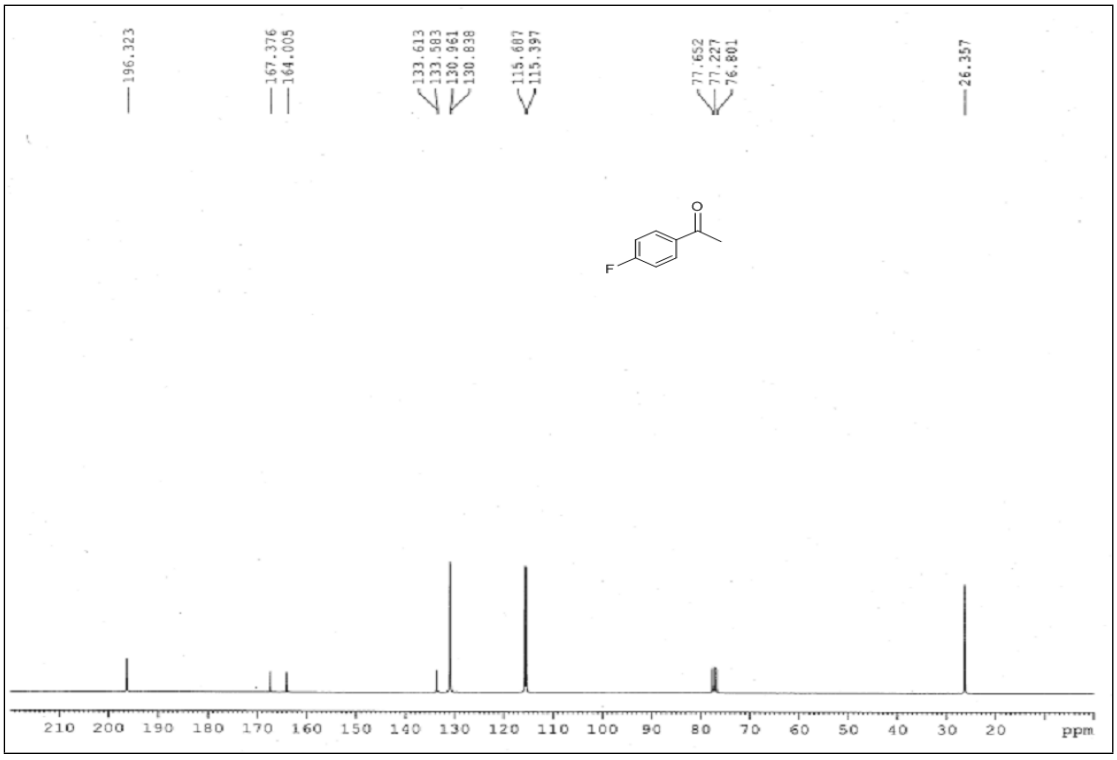


Fig. S14 ^{13}C NMR spectrum of 4-Fluoroacetophenone

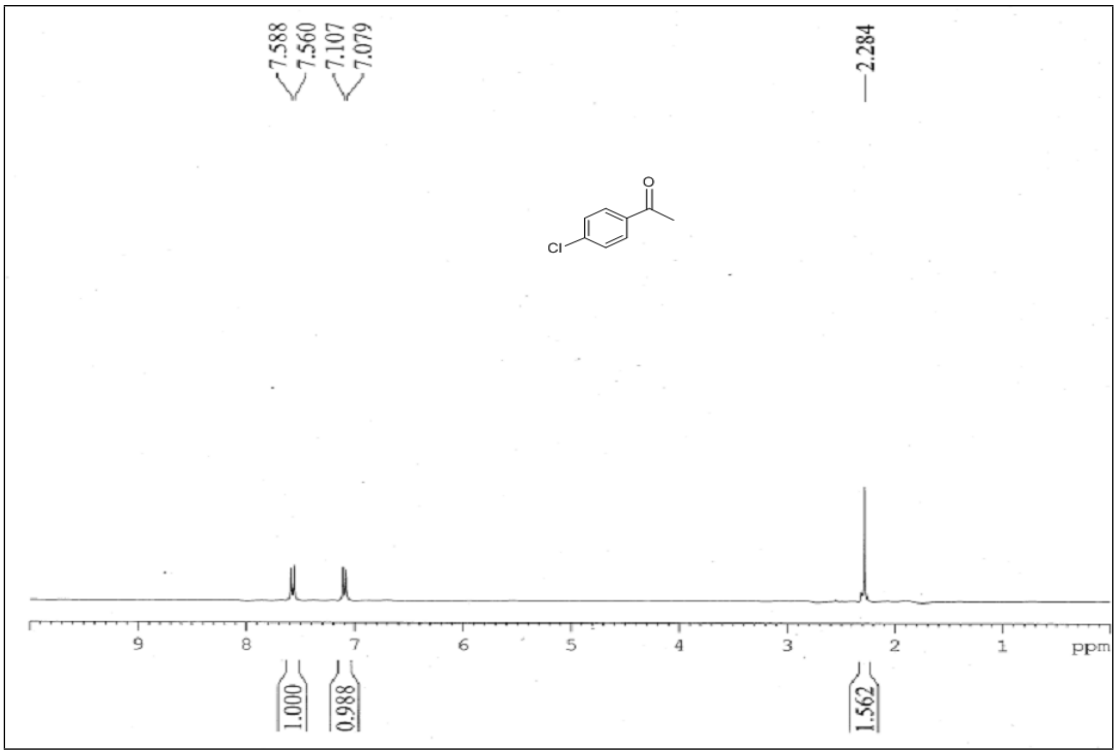


Fig. S15 ^{1}H NMR spectrum of 4-Chloroacetophenone

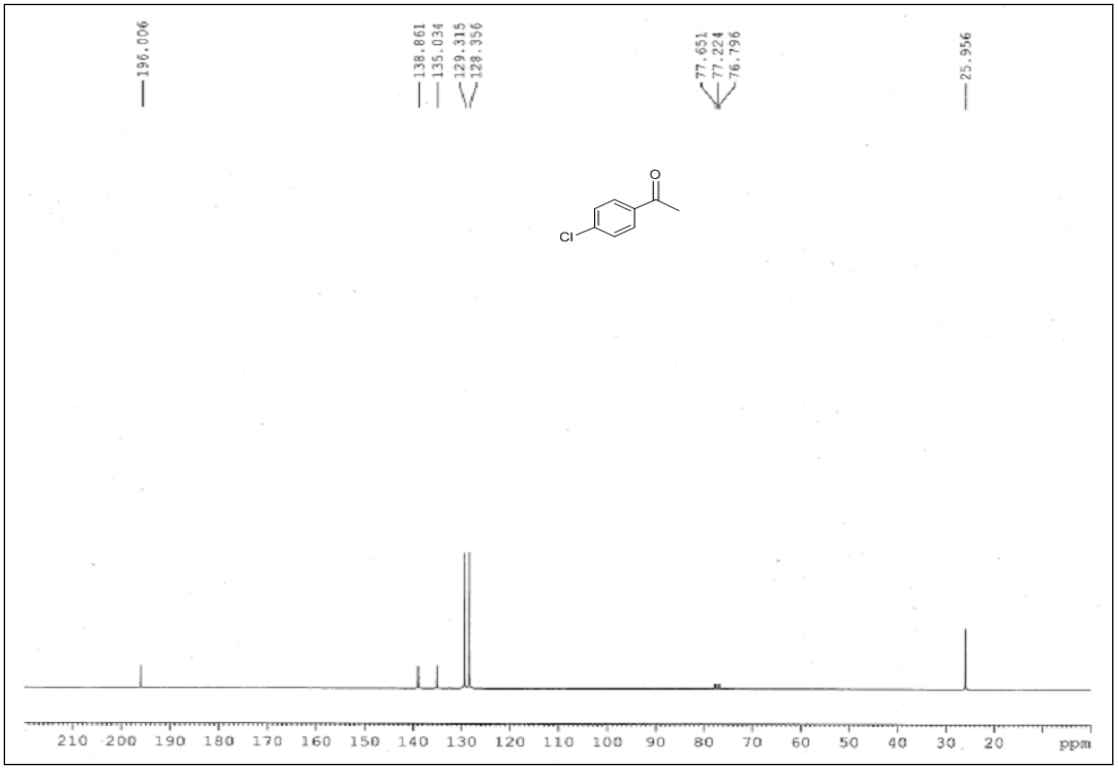


Fig. S16 ^{13}C NMR spectrum of 4-Chloroacetophenone

Alkene oxidation with water

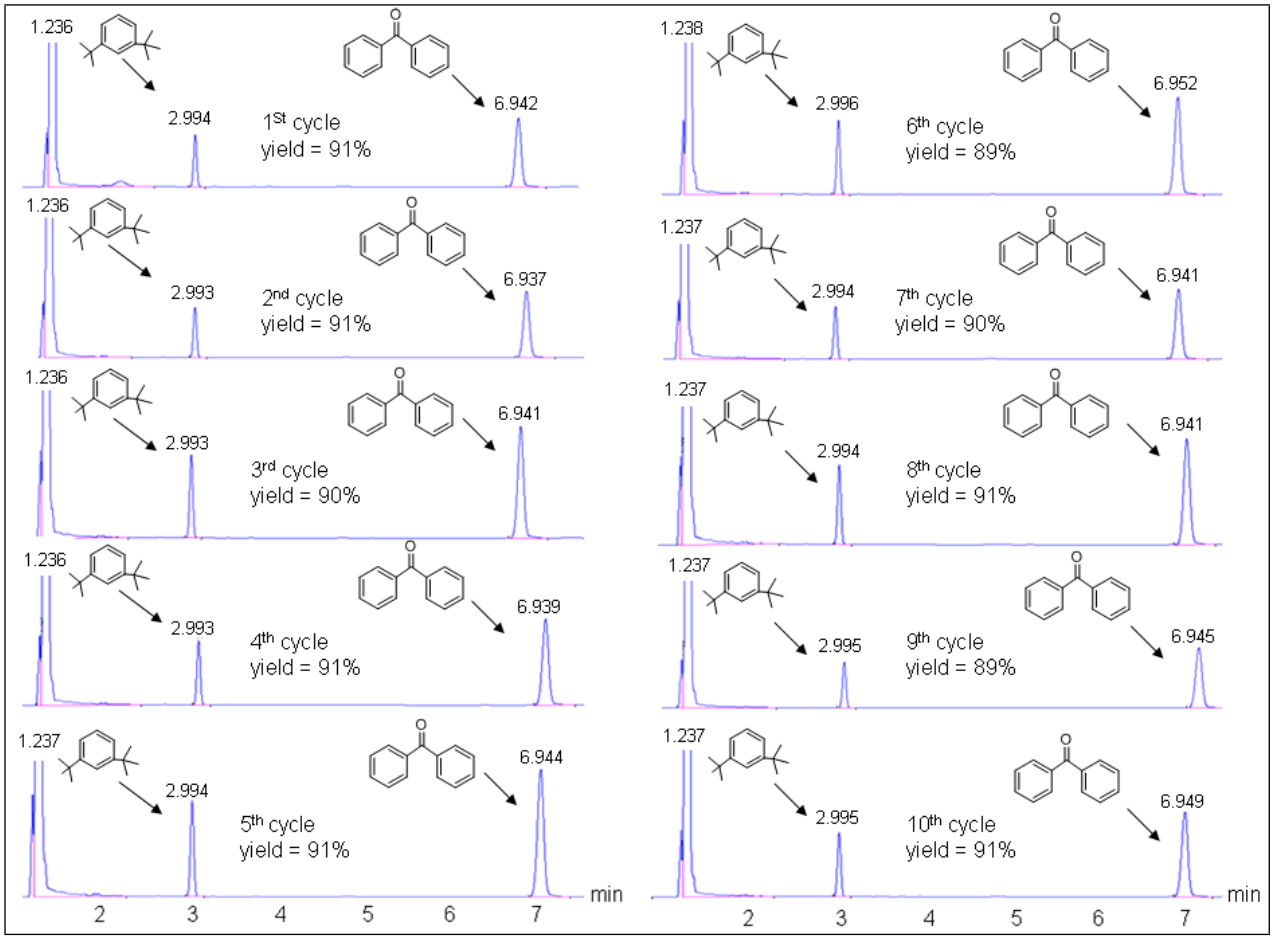
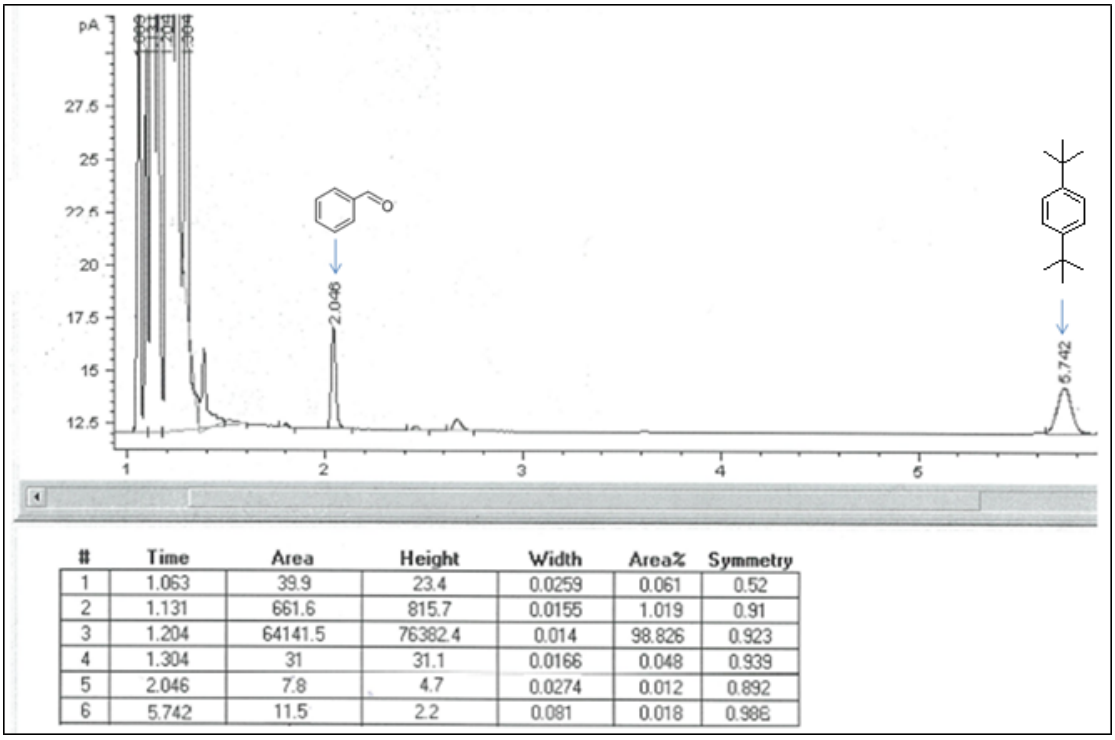
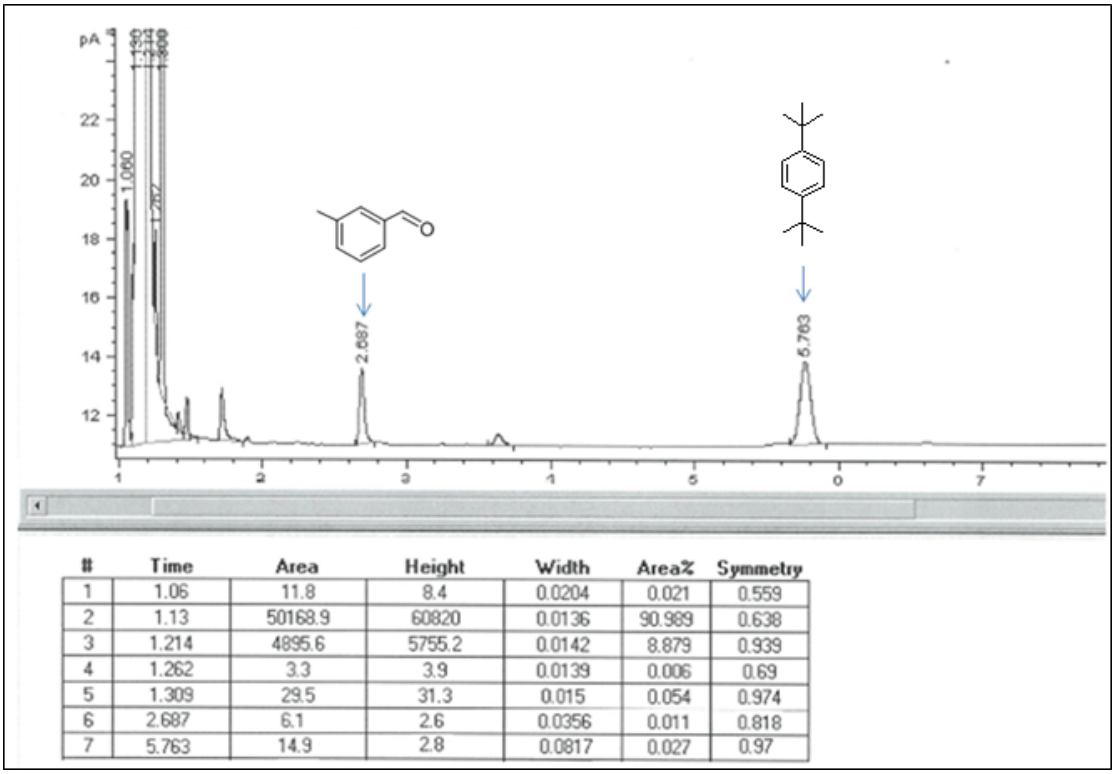


Fig. S17 GC Spectra of the catalytic cycles using 1,1-diphenylethylene



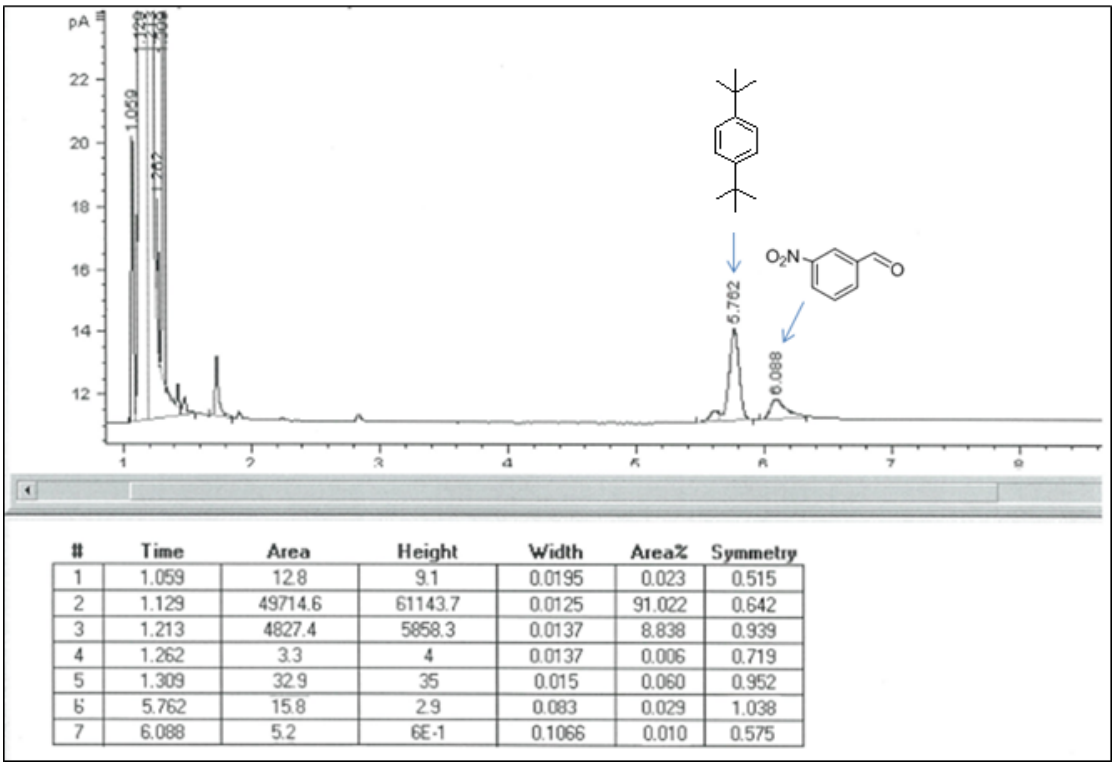
#	Time	Area	Height	Width	Area%	Symmetry
1	1.063	39.9	23.4	0.0259	0.061	0.52
2	1.131	661.6	815.7	0.0155	1.019	0.91
3	1.204	64141.5	76382.4	0.014	98.826	0.923
4	1.304	31	31.1	0.0166	0.048	0.939
5	2.046	7.8	4.7	0.0274	0.012	0.892
6	5.742	11.5	2.2	0.081	0.018	0.986

Fig. S18 The reaction was carried out using styrene (23.2 μL, 0.2 mmol) and catalyst **A** (100 μL stock solution, 0.01 mmol of $CuCl_2$) following the above typical procedure. The compound benzaldehyde was identified by GC with standard sample. The yield (43%) of cleavage product benzaldehyde was calculated with the internal standard 1,4-di-*tert*-butylbenzene (conversion factor = 2.15).



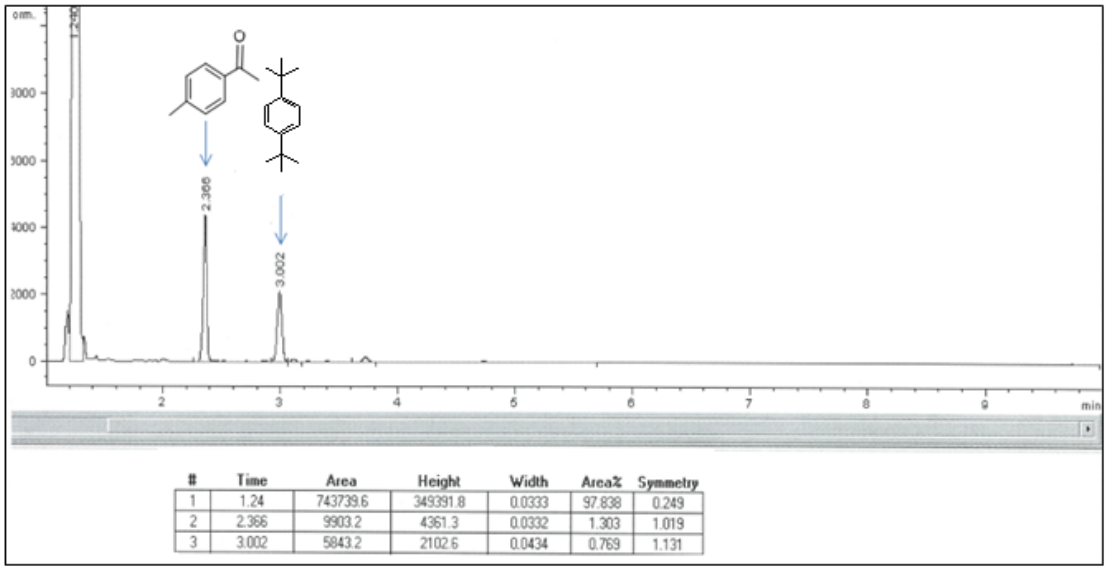
#	Time	Area	Height	Width	Area%	Symmetry
1	1.06	11.8	8.4	0.0204	0.021	0.559
2	1.13	50168.9	60820	0.0136	90.989	0.638
3	1.214	4895.6	5755.2	0.0142	8.879	0.939
4	1.262	3.3	3.9	0.0139	0.006	0.69
5	1.309	29.5	31.3	0.015	0.054	0.974
6	2.687	6.1	2.6	0.0356	0.011	0.818
7	5.763	14.9	2.8	0.0817	0.027	0.97

Fig. S19 The reaction was carried out using 3-methylstyrene (26.8 μL, 0.2 mmol) and catalyst **A** (100 μL stock solution, 0.01 mmol of $CuCl_2$) following the above typical procedure. The compound 3-methylbenzaldehyde was identified by GC with standard sample. The yield (30%) of cleavage product *m*-tolualdehyde was calculated with the internal standard 1,4-di-*tert*-butylbenzene (conversion factor = 2.4).



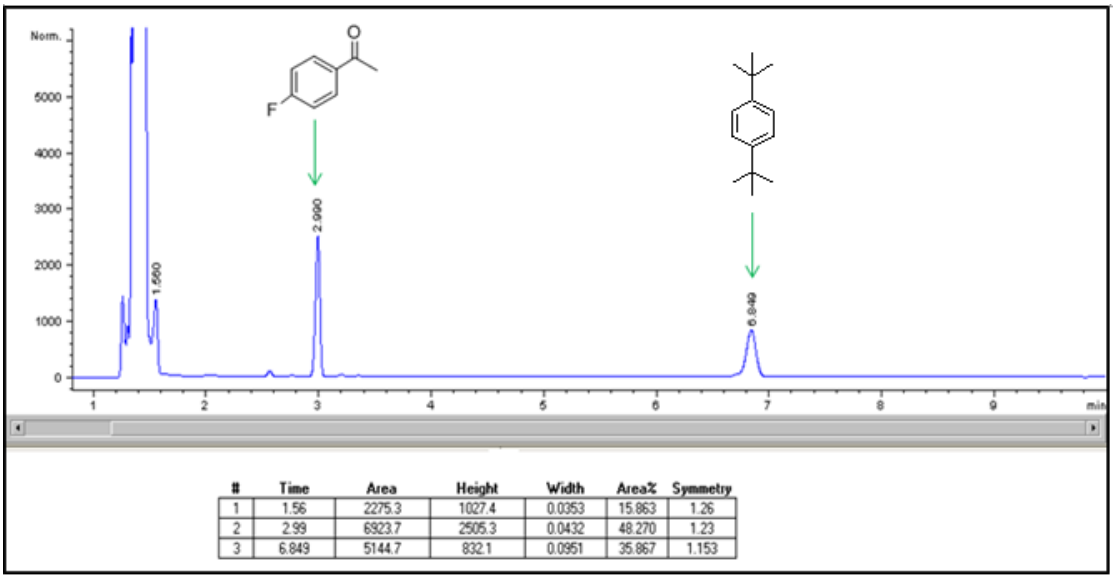
#	Time	Area	Height	Width	Area%	Symmetry
1	1.059	12.8	9.1	0.0195	0.023	0.515
2	1.129	49714.6	61143.7	0.0125	91.022	0.642
3	1.213	4827.4	5858.3	0.0137	8.838	0.939
4	1.262	3.3	4	0.0137	0.006	0.719
5	1.309	32.9	35	0.015	0.060	0.952
6	5.762	15.8	29	0.083	0.029	1.038
7	6.088	5.2	6E-1	0.1066	0.010	0.575

Fig. S20 The reaction was carried out using 3-nitrostyrene (28.7 μL, 0.2 mmol) and catalyst **A** (100 μL stock solution, 0.01 mmol of $CuCl_2$) following the above typical procedure. The compound benzaldehyde was identified by GC with standard sample. The yield (29%) of cleavage product 3-nitrobenzaldehyde was calculated with the internal standard 1,4-di-*tert*-butylbenzene (conversion factor = 2.9).



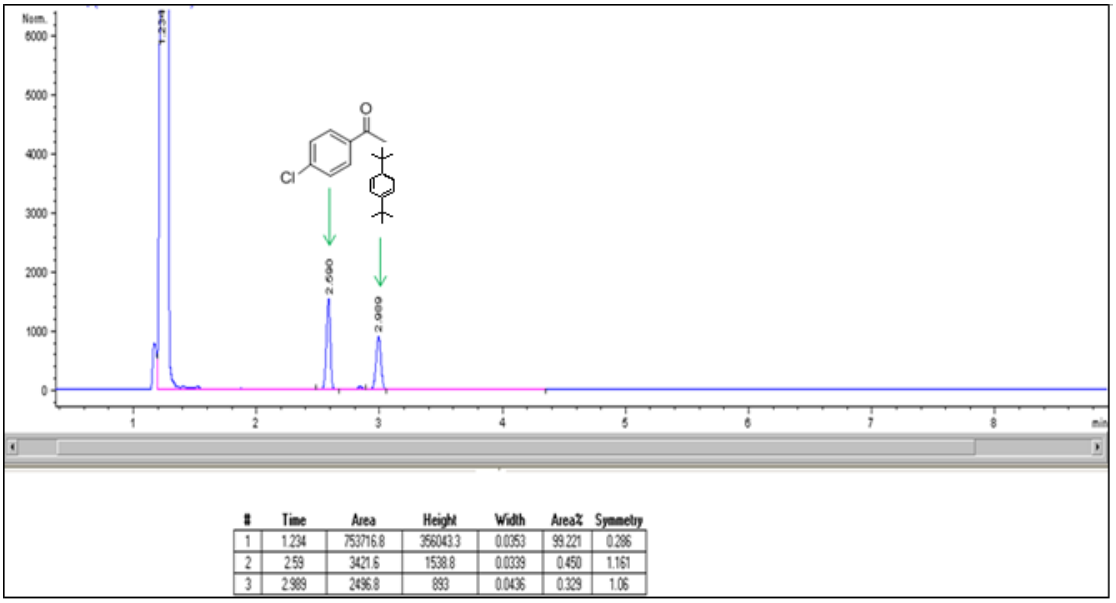
#	Time	Area	Height	Width	Area%	Symmetry
1	1.24	743739.6	349391.8	0.0333	97.838	0.249
2	2.366	9903.2	4361.3	0.0332	1.303	1.019
3	3.002	5843.2	2102.6	0.0434	0.769	1.131

Fig. S21 The reaction was carried out using α-4-dimethylstyrene (30.3 μL, 0.2 mmol) and catalyst **B** (100 μL stock solutions, 0.01 mmol of $CuCl_2$; 0.01 mmol, 2.1 mg of neocuproine) following the above typical procedure. The compound 4-methylacetophenone was identified by GC with standard sample. The yield (91%) of the cleavage product 4-methylacetophenone was calculated with the internal standard 1,4-di-*tert*-butylbenzene (conversion factor = 1.8).



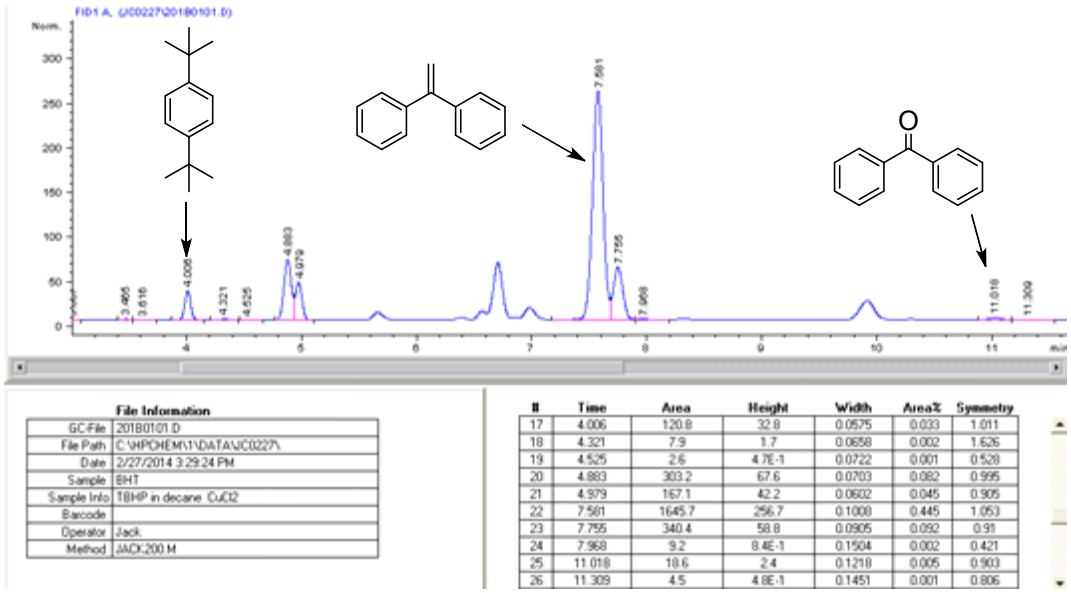
#	Time	Area	Height	Width	Area%	Symmetry
1	1.56	2275.3	1027.4	0.0353	15.863	1.26
2	2.99	6923.7	2505.3	0.0432	48.270	1.23
3	6.849	5144.7	832.1	0.0951	35.867	1.153

Fig. S22 The reaction was carried out using 4-fluoro-α-methylstyrene (28.4 μL, 0.2 mmol) and catalyst **B** (100 μL stock solution, 0.01 mmol of $CuCl_2$; 0.01 mmol, 2.1 mg of neocuproine) following the above typical procedure. The compound 4-fluoroacetophenone was identified by GC with standard sample. The yield (89%) of the cleavage product 4-fluoroacetophenone was calculated with the internal standard 1,4-di-tert-butylbenzene (conversion factor = 2.2).



#	Time	Area	Height	Width	Area%	Symmetry
1	1.234	753716.8	356043.3	0.0353	99.221	0.286
2	2.59	3421.6	1538.8	0.0339	0.450	1.161
3	2.989	2496.8	893	0.0436	0.329	1.06

Fig. S23 The reaction was carried out using 4-chloro-α-methylstyrene (29.6 μL, 0.2 mmol) and catalyst **B** (100 μL stock solutions, 0.01 mmol of $CuCl_2$; 0.01 mmol, 2.1 mg of neocuproine) following the above typical procedure. The compound 4-chloroacetophenone was identified by GC with standard sample. The yield (98%) of the cleavage product 4-chloroacetophenone was calculated with the internal standard 1,4-di-*tert*-butylbenzene (conversion factor = 2.26).



#	Time	Area	Height	Width	Area%	Symmetry
17	4.006	120.8	32.8	0.0575	0.033	1.011
18	4.321	7.9	1.7	0.0658	0.002	1.626
19	4.525	2.6	4.7E-1	0.0722	0.001	0.528
20	4.883	303.2	67.6	0.0703	0.082	0.995
21	4.979	167.1	42.2	0.0602	0.045	0.905
22	7.581	1645.7	256.7	0.1008	0.445	1.053
23	7.755	340.4	58.8	0.0905	0.092	0.91
24	7.968	9.2	8.4E-1	0.1504	0.002	0.421
25	11.018	18.6	2.4	0.1218	0.005	0.903
26	11.309	4.5	4.8E-1	0.1451	0.001	0.806

Fig. S24 The reaction was carried out using 1,1-diphenylethylene (35.7 μL, 0.2 mmol), neocuproine (2.1 mg, 0.01 mmol), and solid $CuCl_2{\cdot}2H_2O$ (1.71 mg, 0.01 mmol), *tert*-butyl hydroperoxide (200 μL, 1.55 mmol, 70% aqueous solution) and 2,6-di-*tert*-butyl-4-methylphenol (440.7 mg, 2 mmol) following the above typical procedure. The compound benzophenone was identified by GC with standard sample. The yield (2%) of the cleavage product benzophenone was calculated with the internal standard 1,4-di-*tert*-butylbenzene (conversion factor = 1.07).

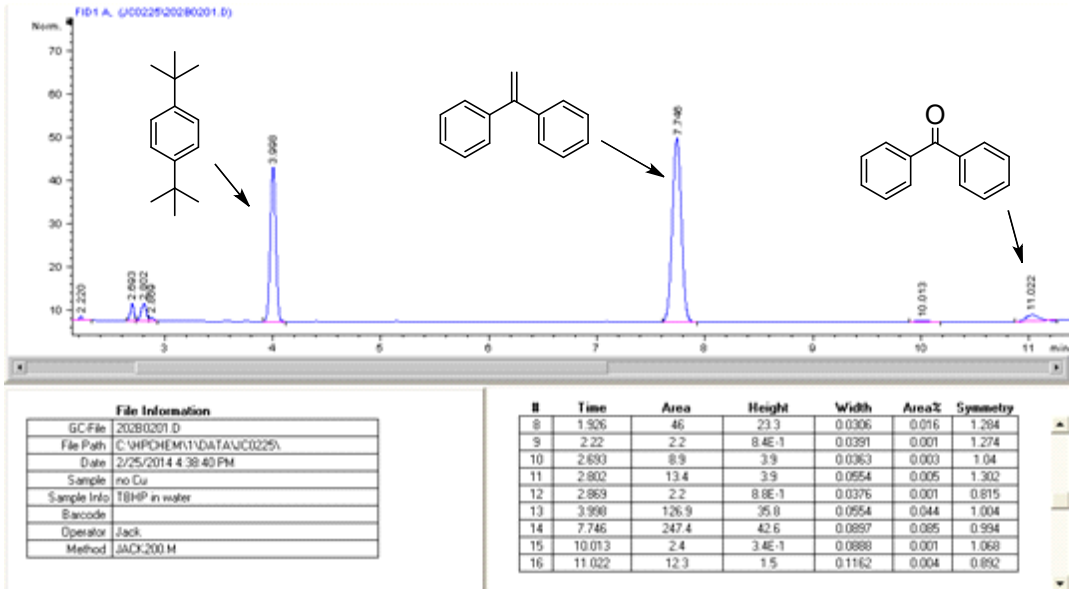
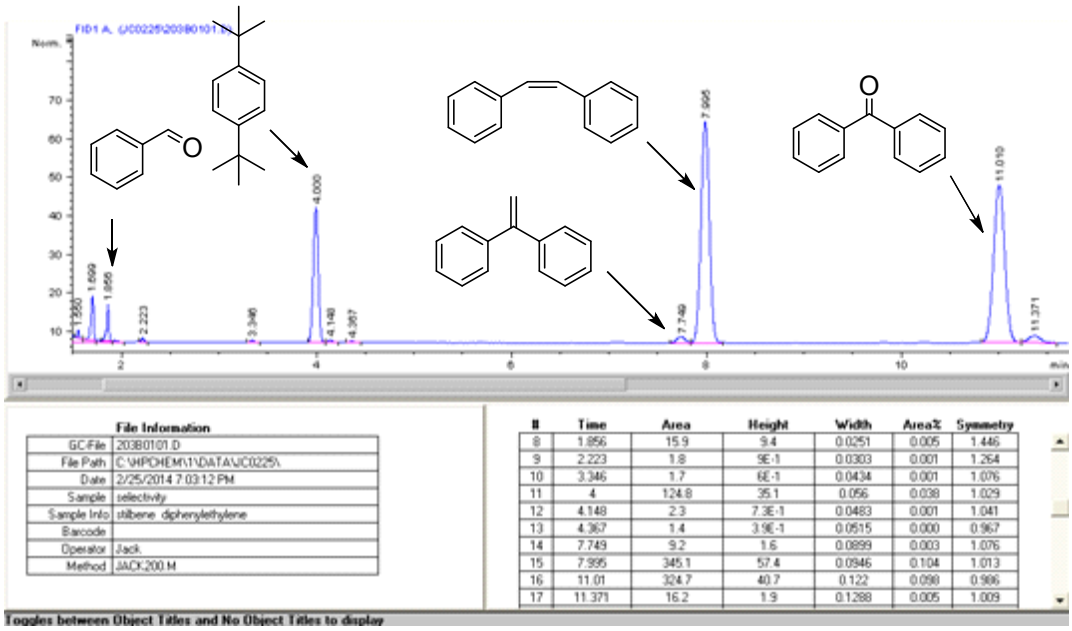


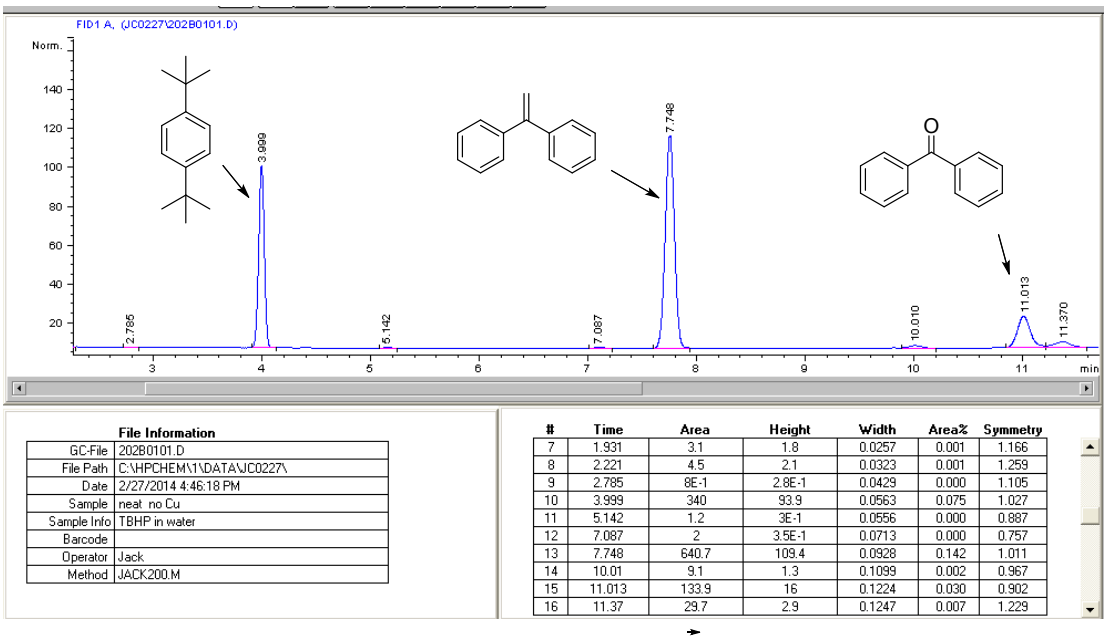
Fig. S25 The reaction was carried out using 1,1-diphenylethylene (35.7 μL, 0.2 mmol), Neocuporine (2.1 mg, 5 mol%), *tert*-butyl hydroperoxide (200 μL, 1.55 mmol, 70% aqueous solution) and H_2O (700 μL) following the above typical procedure. The compound benzophenone was identified by GC with standard sample. The yield (3%) of the cleavage product benzophenone was calculated with the internal standard 1,4-di-*tert*-butylbenzene (conversion factor = 1.07).



#	Time	Area	Height	Width	Area%	Symmetry
8	1.856	15.9	9.4	0.0251	0.005	1.446
9	2.223	1.8	9E-1	0.0303	0.001	1.264
10	3.346	1.7	6E-1	0.0434	0.001	1.076
11	4	124.8	35.1	0.056	0.038	1.029
12	4.148	2.3	7.3E-1	0.0483	0.001	1.041
13	4.367	1.4	3.9E-1	0.0515	0.000	0.967
14	7.749	9.2	1.6	0.0899	0.003	1.076
15	7.995	345.1	57.4	0.0946	0.104	1.013
16	11.01	324.7	40.7	0.122	0.098	0.986
17	11.371	16.2	1.9	0.1288	0.005	1.009

Fig. S26 The reaction was carried out using 1,1-diphenylethylene (35.7 µL, 0.2 mmol), *cis*-stilbene (36.8 µL, 0.2mmol), catalyst **B** (100 mL stock solution, 0.01 mmol of $CuCl_2$; 0.01 mmol, 2.1 mg of neocuproine), *tert*-butyl hydroperoxide (200 µL, 1.55 mmol, 70% aqueous solution) and H_2O (700 µL) following the above typical procedure. The compound benzophenone and benzaldehyde was identified by GC with standard sample. The yield (84%) of the cleavage product benzophenone was calculated with the internal standard 1,4-di-*tert*-butylbenzene (conversion factor = 1.07) and the yield (8%) of the cleavage product benzaldehyde was calculated with the internal standard 1,4-di-*tert*-butylbenzene (conversion factor = 1.99).

Alkene oxidation without water



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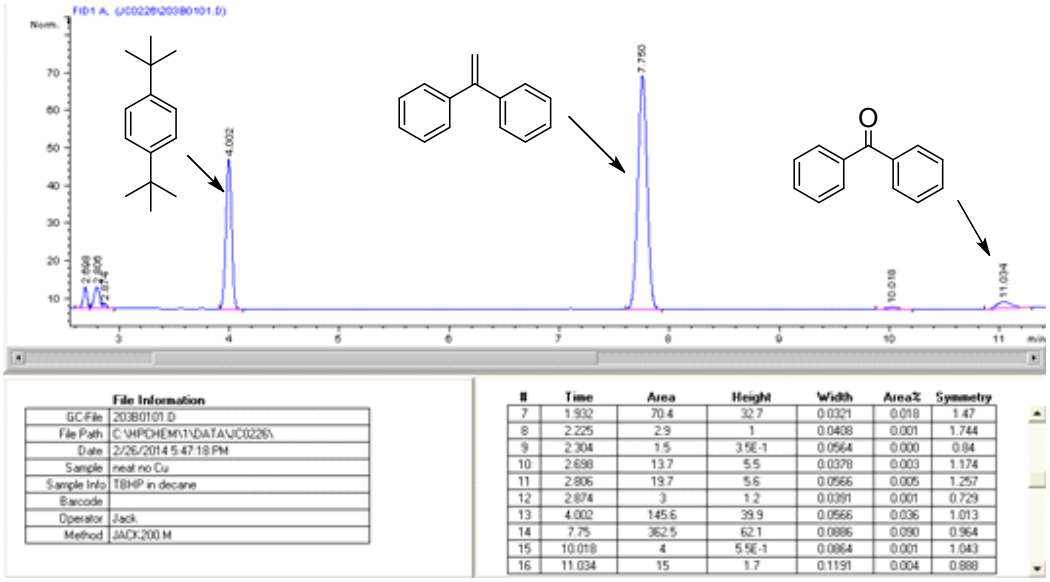
Date	2/27/2014 4:46:18 PM
Sample	neat no Cu
Sample Info	TBHP in water
Barcode	
Operator	Jack
Method	JACK200.M

#	Time	Area	Height	Width	Area%	Symmetry
7	1.931	3.1	1.8	0.0257	0.001	1.166
8	2.221	4.5	2.1	0.0323	0.001	1.259
9	2.785	8E-1	2.8E-1	0.0429	0.000	1.105
10	3.999	340	93.9	0.0563	0.075	1.027
11	5.142	1.2	3E-1	0.0556	0.000	0.887
12	7.087	2	3.5E-1	0.0713	0.000	0.757
13	7.748	640.7	109.4	0.0928	0.142	1.011
14	10.01	9.1	1.3	0.1099	0.002	0.967
15	11.013	133.9	16	0.1224	0.030	0.902
16	11.37	29.7	2.9	0.1247	0.007	1.229

Fig. S27 The reaction was carried out using 1,1-diphenylethylene (35.7 μL, 0.2 mmol), Neocuporine (2.1 mg, 5 mol%) and *tert*-butyl hydroperoxide (200 μL, 1.55 mmol, 70% aqueous solution) without addition of water following the above typical procedure. The compound benzophenone was identified by GC with standard sample. The yield (4%) of the cleavage product benzophenone was calculated with the internal standard 1,4-di-*tert*-butylbenzene (conversion factor = 1.07).



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Sample Info	TBHP in decane
Barcode	
Operator	Jack
Method	JACK200.M

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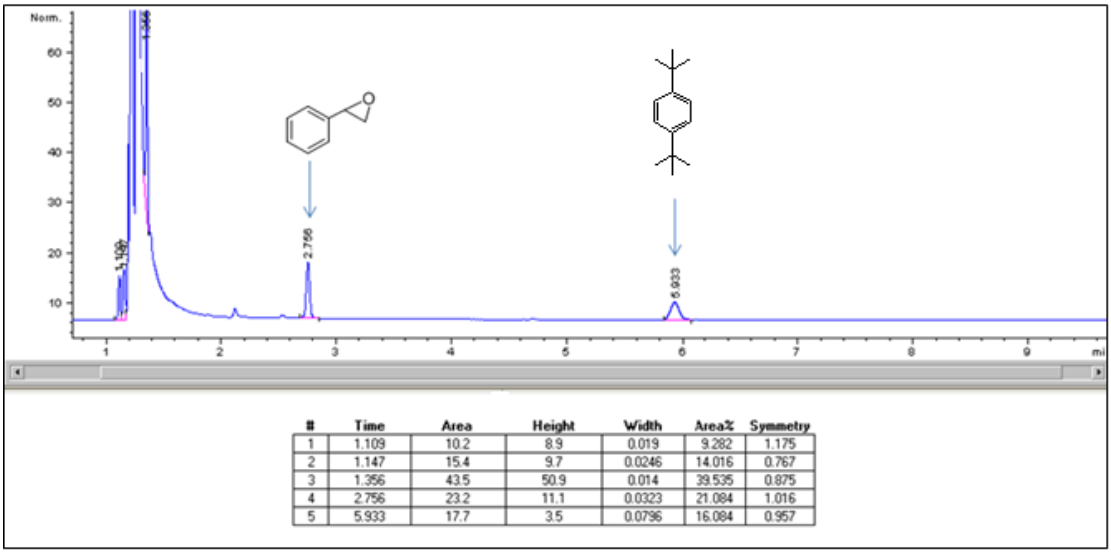
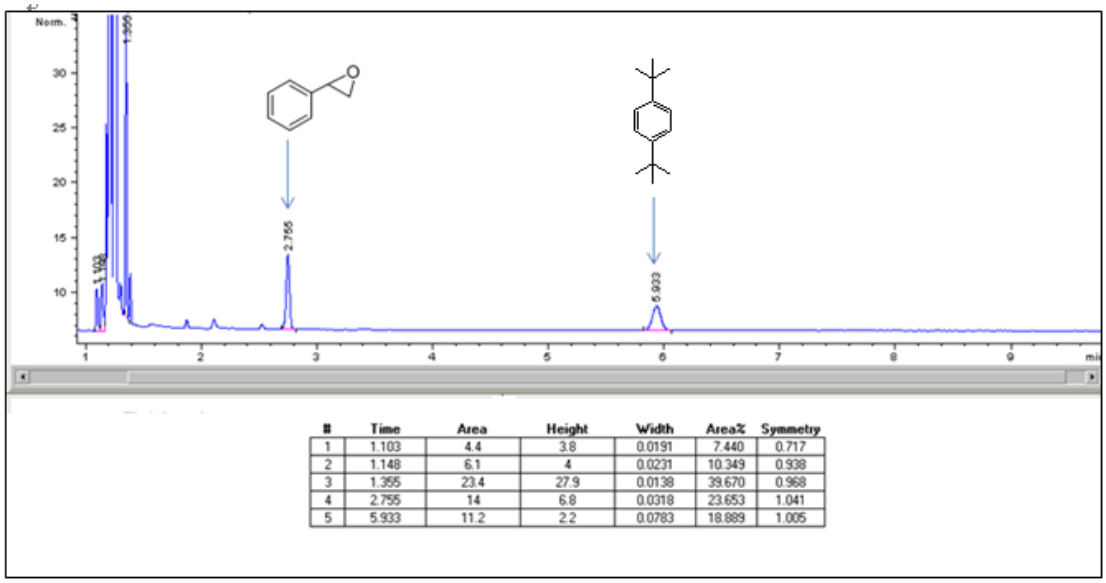
7	1.932	70.4	32.7	0.0321	0.018	1.47
8	2.225	2.9	1	0.0408	0.001	1.744
9	2.304	1.5	3.5E-1	0.0564	0.000	0.84
10	2.698	13.7	5.5	0.0378	0.003	1.174
11	2.806	13.7	5.6	0.0566	0.005	1.257
12	2.874	3	1.2	0.0391	0.001	0.729
13	4.002	145.6	39.9	0.0566	0.036	1.013
14	7.75	362.5	62.1	0.0886	0.090	0.964
15	10.018	4	5.5E-1	0.0864	0.001	1.043
16	11.034	15	1.7	0.1191	0.004	0.888

Fig. S28 The reaction was carried out using 1,1-diphenylethylene (35.7 µL, 0.2 mmol), Neocuporine (2.1 mg, 5 mol%) and *tert*-butyl hydroperoxide (240 µL, 1.55 mmol, 5M-6M decane solution) without addition of water following the above typical procedure. The compound benzophenone was identified by GC with standard sample. The yield (3%) of the cleavage product benzophenone was calculated with the internal standard 1,4-di-*tert*-butylbenzene (conversion factor = 1.07).



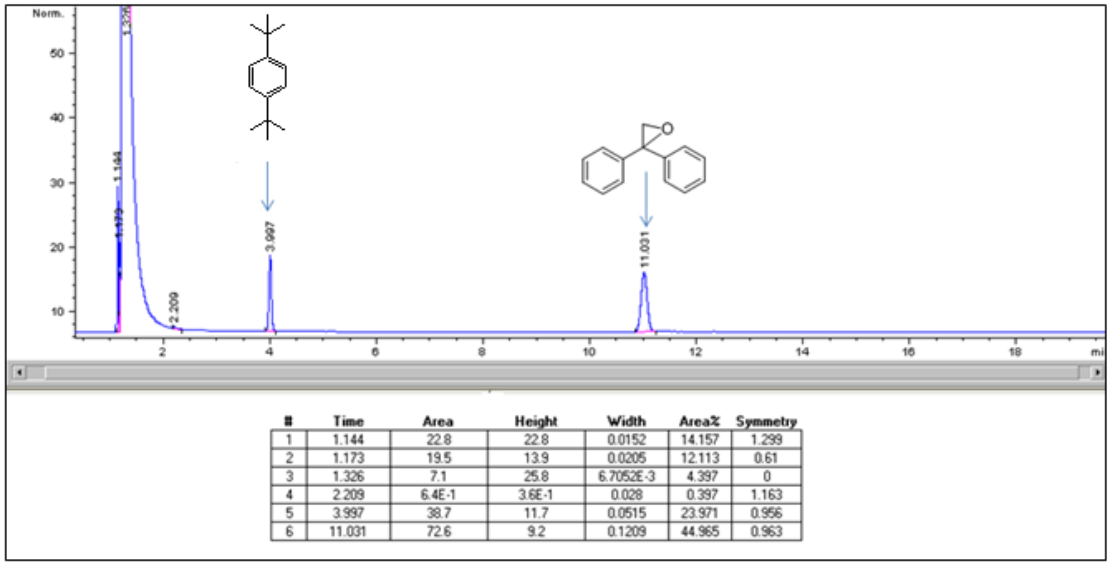
#	Time	Area	Height	Width	Area%	Symmetry
1	1.109	10.2	8.9	0.019	9.282	1.175
2	1.147	15.4	9.7	0.0246	14.016	0.767
3	1.356	43.5	50.9	0.014	39.535	0.875
4	2.756	23.2	11.1	0.0323	21.084	1.016
5	5.933	17.7	3.5	0.0796	16.084	0.957

Fig. S29 The reaction was carried out using styrene oxide (23.0 µL, 0.2 mmol) and catalyst **B** (100 µL stock solutions, 0.01 mmol of $CuCl_2$; 0.01 mmol, 2.1 mg of neocuproine) following the above typical procedure. The starting material styrene oxide was identified by GC with standard sample. The yield (96%) was calculated with the internal standard 1,4-di-*tert*-butylbenzene (conversion factor = 2.35).



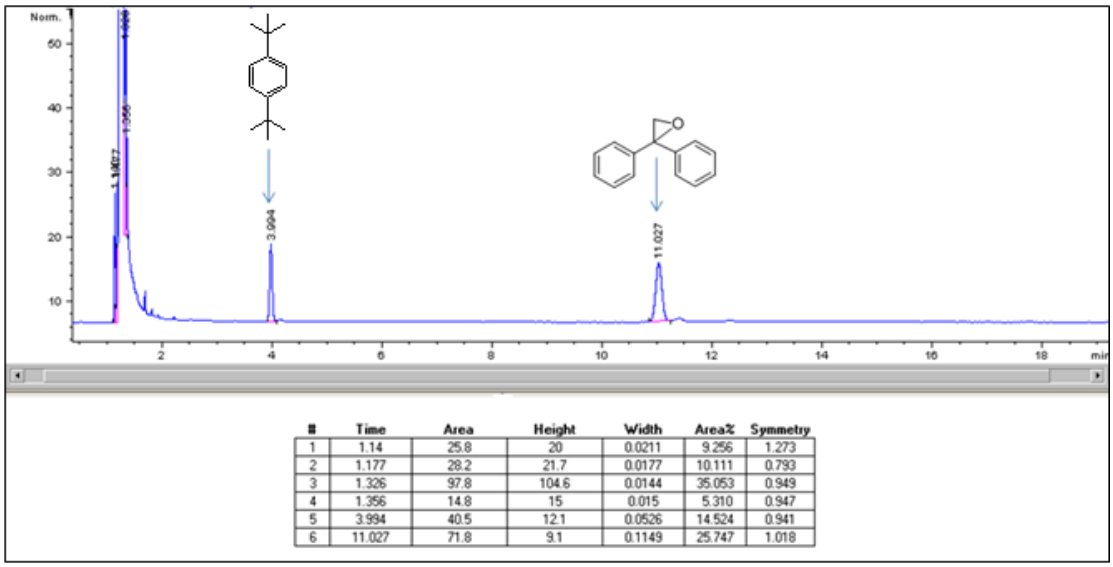
#	Time	Area	Height	Width	Area%	Symmetry
1	1.103	4.4	3.8	0.0191	7.440	0.717
2	1.148	6.1	4	0.0231	10.349	0.938
3	1.355	23.4	27.9	0.0138	39.670	0.968
4	2.755	14	6.8	0.0318	23.653	1.041
5	5.933	11.2	2.2	0.0783	18.889	1.005

Fig.30 The reaction was carried out using styrene oxide (23.0 μL, 0.2 mmol) and catalyst **A** (100 μL stock solution, 0.01 mmol of $CuCl_2$) following the above typical procedure. The starting material styrene oxide was identified by GC with standard sample. The yield (93%) was calculated with the internal standard 1,4-di-*tert*-butylbenzene (conversion factor = 2.35).



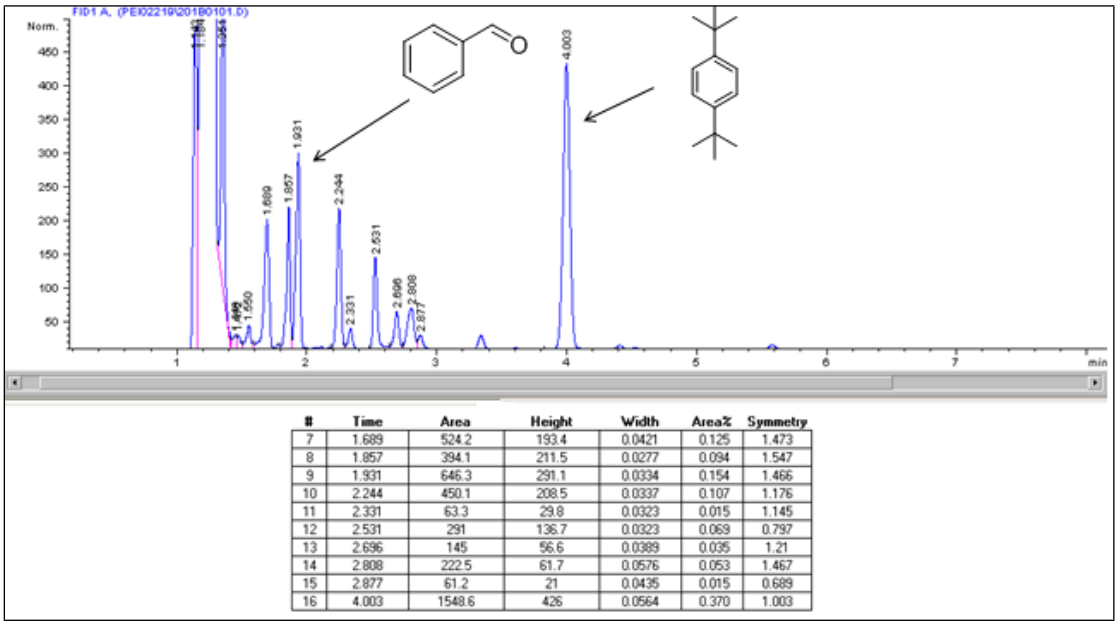
#	Time	Area	Height	Width	Area%	Symmetry
1	1.144	22.8	22.8	0.0152	14.157	1.299
2	1.173	19.5	13.9	0.0205	12.113	0.61
3	1.326	7.1	25.8	6.7052E-3	4.397	0
4	2.209	6.4E-1	3.6E-1	0.028	0.397	1.163
5	3.997	38.7	11.7	0.0515	23.971	0.956
6	11.031	72.6	9.2	0.1209	44.965	0.963

Fig. S31 The reaction was carried out using 1,1-diphenylethylene oxide (39.4 mg, 0.2 mmol) and catalyst **B** (100 μL stock solutions, 0.01 mmol of $CuCl_2$; 0.01 mmol, 2.1 mg of neocuproine) following the above typical procedure. The starting material 1,1-diphenylethylene oxide was identified by GC with standard sample. The yield (95%) was calculated with the internal standard 1,4-di-*tert*-butylbenzene (conversion factor = 1.6).



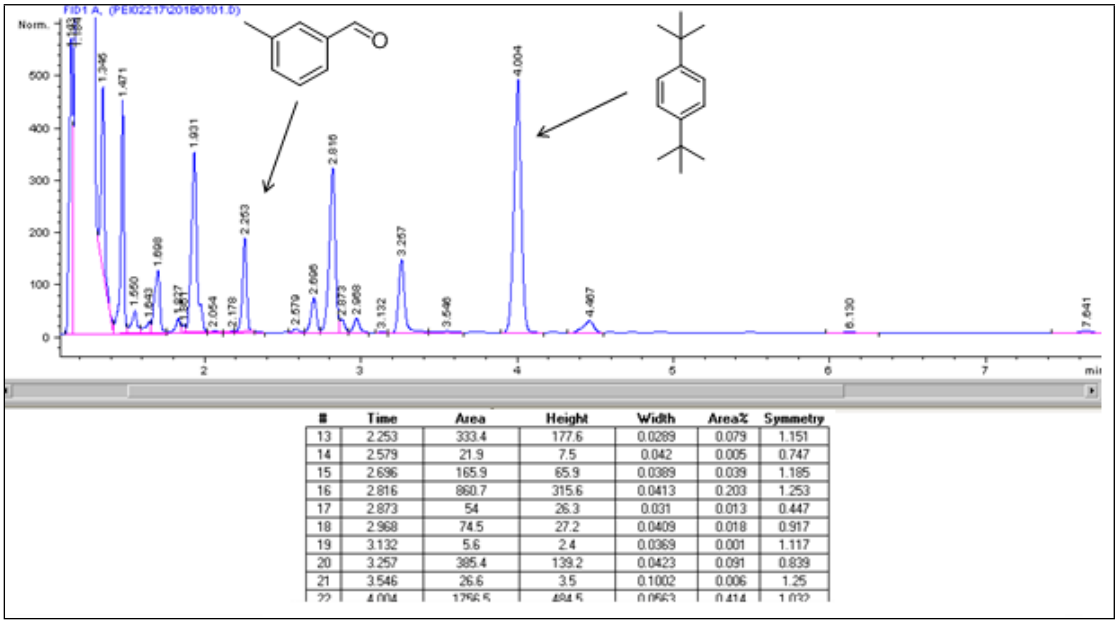
#	Time	Area	Height	Width	Area%	Symmetry
1	1.14	25.8	20	0.0211	9.256	1.273
2	1.177	28.2	21.7	0.0177	10.111	0.793
3	1.326	97.8	104.6	0.0144	35.053	0.949
4	1.356	14.8	15	0.015	5.310	0.947
5	3.994	40.5	12.1	0.0526	14.524	0.941
6	11.027	71.8	9.1	0.1149	25.747	1.018

Fig. S32 The reaction was carried out using 1,1-diphenylethylene oxide (39.4 mg, 0.2 mmol) and catalyst **A** (100 μL stock solution, 0.01 mmol of $CuCl_2$) following the above typical procedure. The starting material 1,1-diphenylethylene oxide was identified by GC with standard sample. The yield (90%) was calculated with the internal standard 1,4-di-*tert*-butylbenzene (conversion factor = 1.6).



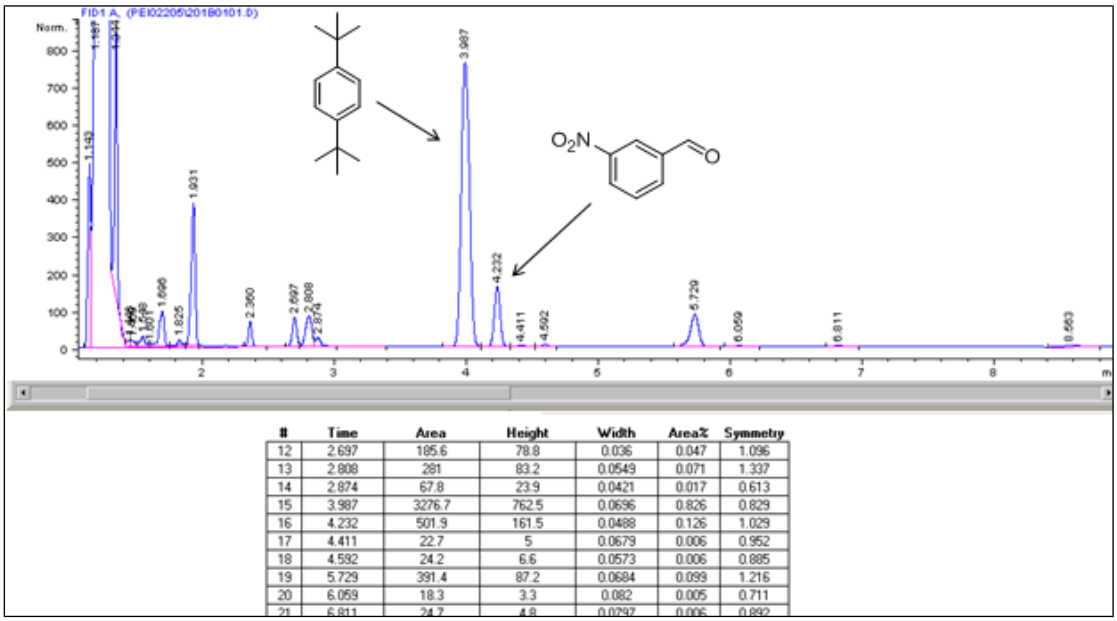
#	Time	Area	Height	Width	Area%	Symmetry
7	1.689	524.2	193.4	0.0421	0.125	1.473
8	1.857	394.1	211.5	0.0277	0.094	1.547
9	1.931	646.3	291.1	0.0334	0.154	1.466
10	2.244	450.1	208.5	0.0337	0.107	1.176
11	2.331	63.3	29.8	0.0323	0.015	1.145
12	2.531	291	136.7	0.0323	0.069	0.797
13	2.696	145	56.6	0.0389	0.035	1.21
14	2.808	222.5	61.7	0.0576	0.053	1.467
15	2.877	61.2	21	0.0435	0.015	0.689
16	4.003	1548.6	426	0.0564	0.370	1.003

Fig. S33 The reaction was carried out using styrene (23.2 μL, 0.2 mmol) neocuproine (2.1 mg, 0.01 mmol), and solid $CuCl_2 \cdot 2H_2O$ (1.71 mg, 0.01 mmol) without addition of water following the above typical procedure. The compound benzaldehyde was identified by GC with standard sample. The yield (16.9%) of the cleavage product benzaldehyde was calculated with the internal standard 1,4-di-*tert*-butylbenzene (conversion factor = 1.99).



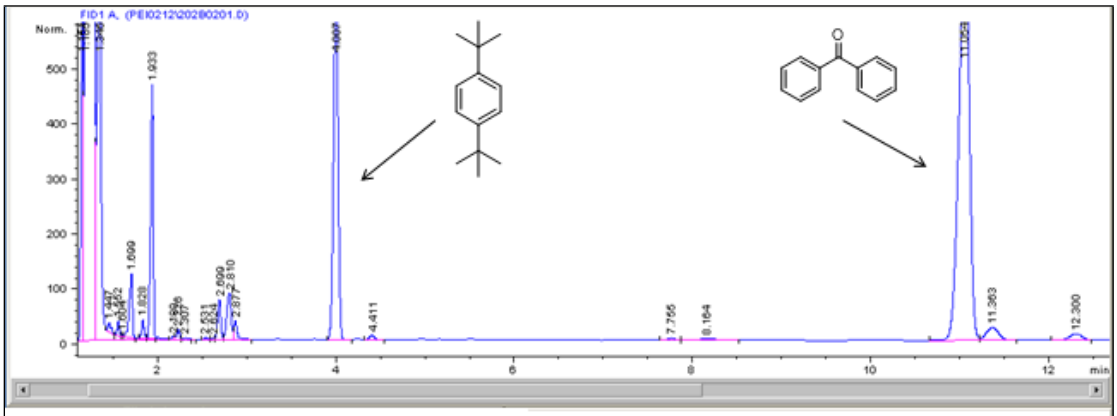
#	Time	Area	Height	Width	Area%	Symmetry
13	2.253	333.4	177.6	0.0289	0.079	1.151
14	2.579	21.9	7.5	0.042	0.005	0.747
15	2.696	165.9	65.9	0.0389	0.039	1.185
16	2.816	860.7	315.6	0.0413	0.203	1.253
17	2.873	54	26.3	0.031	0.013	0.447
18	2.968	74.5	27.2	0.0409	0.018	0.917
19	3.132	5.6	2.4	0.0369	0.001	1.117
20	3.257	385.4	139.2	0.0423	0.091	0.839
21	3.546	26.6	3.5	0.1002	0.006	1.25

Fig. S34 The reaction was carried out using 3–methylstyrene (27.1 μL, 0.2 mmol) neocuproine (2.1 mg, 0.01 mmol), and solid $CuCl_2{\cdot}2H_2O$ (1.71 mg, 0.01 mmol) without addition of water following the above typical procedure. The compound *m*-tolualdehyde was identified by GC with standard sample. The yield (12.4%) of the cleavage product *m*-tolualdehyde was calculated with the internal standard 1,4-di-*tert*-butylbenzene (conversion factor = 1.97).



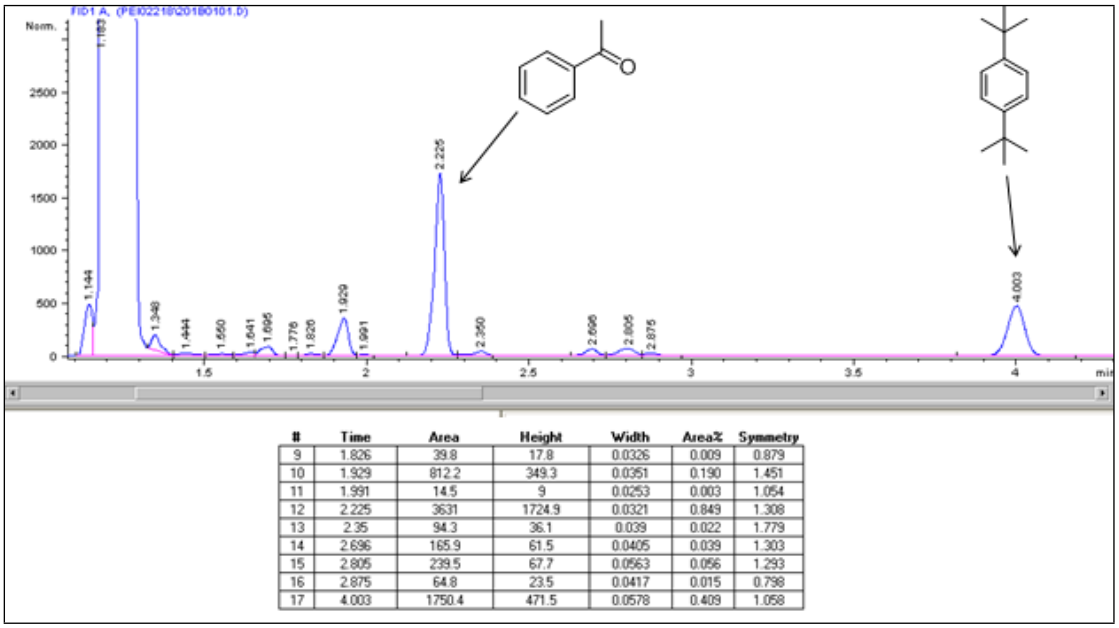
#	Time	Area	Height	Width	Area%	Symmetry
12	2.697	185.6	78.8	0.036	0.047	1.096
13	2.808	281	83.2	0.0549	0.071	1.337
14	2.874	67.8	23.9	0.0421	0.017	0.613
15	3.987	3276.7	762.5	0.0696	0.826	0.829
16	4.232	501.9	161.5	0.0488	0.126	1.029
17	4.411	22.7	5	0.0679	0.006	0.952
18	4.592	24.2	6.6	0.0573	0.006	0.885
19	5.729	391.4	87.2	0.0684	0.099	1.216
20	6.059	18.3	3.3	0.082	0.005	0.711
21	6.811	24.7	4.8	0.0797	0.006	0.892

Fig. S35 The reaction was carried out using 3-nitrostyrene (28.7 μL, 0.2 mmol) neocuproine (2.1 mg, 0.01 mmol), and solid $CuCl_2{\cdot}2H_2O$ (1.71 mg, 0.01 mmol) without addition of water following the above typical procedure. The compound 3-nitrobenzaldehyde was identified by GC with standard sample. The yield (11.5%) of the cleavage product 3-nitrobenzaldehyde was calculated with the internal standard 1,4-di-*tert*-butylbenzene (conversion factor = 2.26).



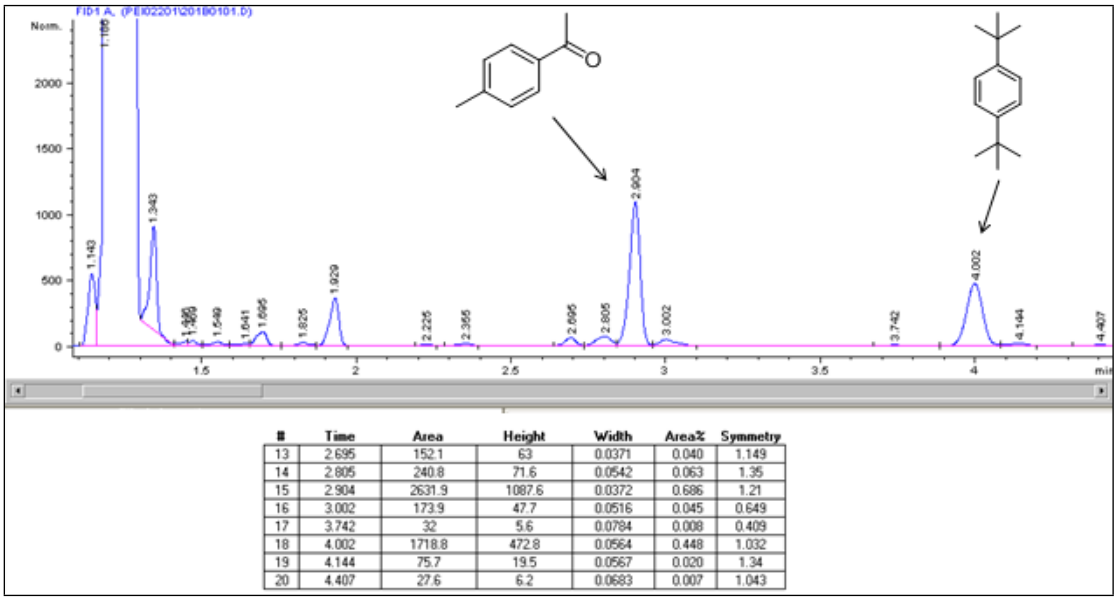
#	Time	Area	Height	Width	Area%	Symmetry
16	2.81	285.5	85.4	0.0535	0.066	1.43
17	2.877	96.7	33.5	0.0432	0.022	0.656
18	4.007	2272.8	639.6	0.0555	0.527	1.061
19	4.411	36.7	8.9	0.0635	0.009	1.07
20	7.755	24.3	4	0.0943	0.006	0.936
21	8.164	49.2	2.2	0.2768	0.011	0.844
22	11.054	6035.7	737.3	0.1295	1.399	1.318
23	11.363	225.1	23.2	0.1541	0.052	1.016
24	12.3	118.6	11.7	0.1519	0.027	1.102

Fig. S36 The reaction was carried out using 1,1-diphenylethylene (35.7 μL, 0.2 mmol) neocuproine (2.1 mg, 0.01 mmol), and solid $CuCl_2 \cdot 2H_2O$ (1.71 mg, 0.01 mmol) without addition of water following the above typical procedure. The compound benzophenone was identified by GC with standard sample. The yield (95.2%) of the cleavage product benzophenone was calculated with the internal standard 1,4-di-*tert*-butylbenzene (conversion factor = 1.07).



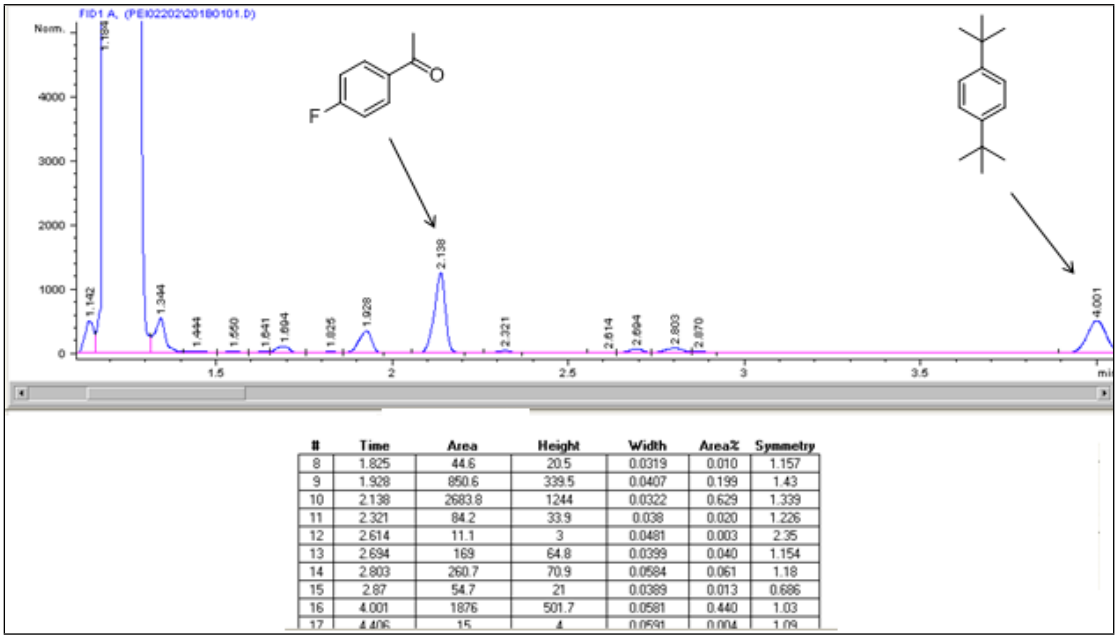
#	Time	Area	Height	Width	Area%	Symmetry
9	1.826	39.8	17.8	0.0326	0.009	0.879
10	1.929	812.2	349.3	0.0351	0.190	1.451
11	1.991	14.5	9	0.0253	0.003	1.054
12	2.225	3631	1724.9	0.0321	0.849	1.308
13	2.35	94.3	36.1	0.039	0.022	1.779
14	2.696	165.9	61.5	0.0405	0.039	1.303
15	2.805	239.5	67.7	0.0563	0.056	1.293
16	2.875	64.8	23.5	0.0417	0.015	0.798
17	4.003	1750.4	471.5	0.0578	0.409	1.058

Fig. S37 The reaction was carried out using isopropenylbenzene (26.3 μL, 0.2 mmol) neocuproine (2.1 mg, 0.01 mmol), and solid $CuCl_2 \cdot 2H_2O$ (1.71 mg, 0.01 mmol) without addition of water following the above typical procedure. The compound acetophenone was identified by GC with standard sample. The yield (99.5%) of the cleavage product acetophenone was calculated with the internal standard 1,4-di-*tert*-butylbenzene (conversion factor = 1.44).



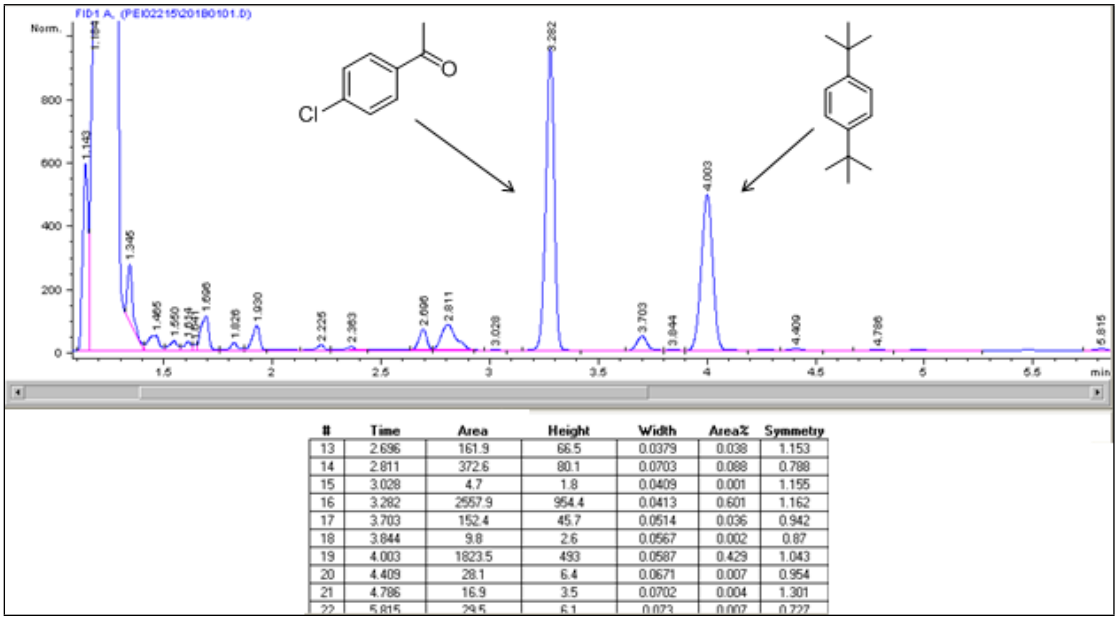
#	Time	Area	Height	Width	Area%	Symmetry
13	2.695	152.1	63	0.0371	0.040	1.149
14	2.805	240.8	71.6	0.0542	0.063	1.35
15	2.904	2631.9	1087.6	0.0372	0.686	1.21
16	3.002	173.9	47.7	0.0516	0.045	0.649
17	3.742	32	5.6	0.0784	0.008	0.409
18	4.002	1718.8	472.8	0.0564	0.448	1.032
19	4.144	75.7	19.5	0.0567	0.020	1.34
20	4.407	27.6	6.2	0.0683	0.007	1.043

Fig. S38 The reaction was carried out using 1-isopropenyl-4-methylbenzene (26.3 μL, 0.2 mmol) neocuproine (2.1 mg, 0.01 mmol), and solid $CuCl_2 \cdot 2H_2O$ (1.71 mg, 0.01 mmol) without addition of water following the above typical procedure. The compound 4-methylacetophenone was identified by GC with standard sample. The yield (84.1%) of the cleavage product 4-methylacetophenone was calculated with the internal standard 1,4-di-*tert*-butylbenzene (conversion factor = 1.65).



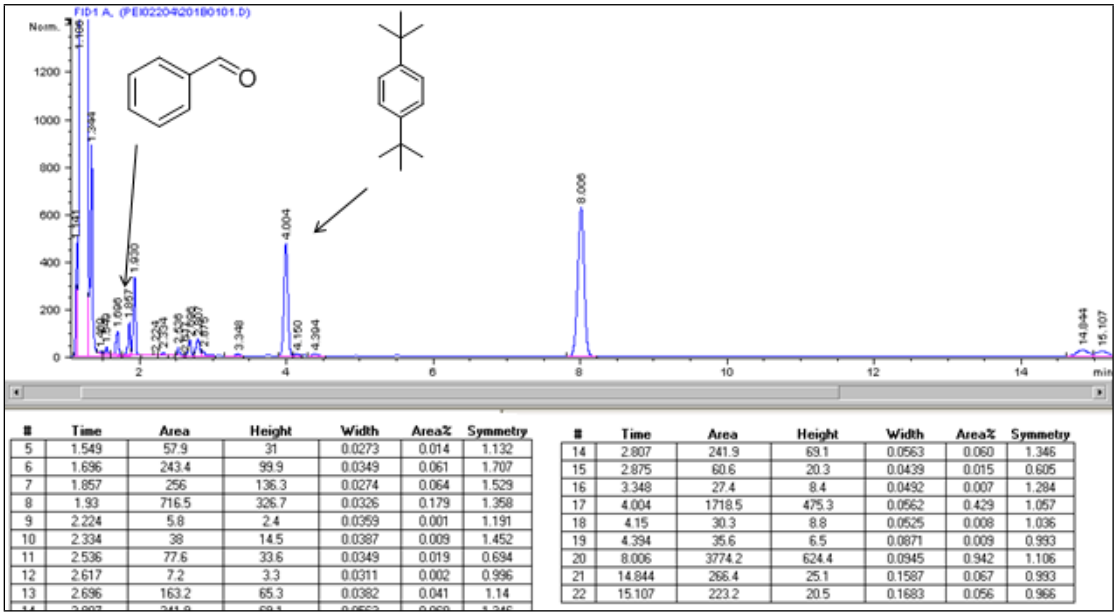
#	Time	Area	Height	Width	Area%	Symmetry
8	1.825	44.6	20.5	0.0319	0.010	1.157
9	1.928	850.6	339.5	0.0407	0.199	1.43
10	2.138	2683.8	1244	0.0322	0.629	1.339
11	2.321	84.2	33.9	0.038	0.020	1.226
12	2.614	11.1	3	0.0481	0.003	2.35
13	2.694	169	64.8	0.0399	0.040	1.154
14	2.803	260.7	70.9	0.0584	0.061	1.18
15	2.87	54.7	21	0.0389	0.013	0.686
16	4.001	1876	501.7	0.0581	0.440	1.03
17	4.406	15	4	0.0591	0.004	1.09

Fig. S39 The reaction was carried out using 1-fluoro-4-isopropenylbenzene (25.19 μL, 0.2 mmol) neocuproine (2.1 mg, 0.01 mmol), and solid $CuCl_2 \cdot 2H_2O$ (1.71 mg, 0.01 mmol) without addition of water following the above typical procedure. The compound 4-fluoroacetophenone was identified by GC with standard sample. The yield (93.4%) of the cleavage product 4-fluoroacetophenone was calculated with the internal standard 1,4-di-*tert*-butylbenzene (conversion factor = 1.96).



#	Time	Area	Height	Width	Area%	Symmetry
13	2.696	161.9	66.5	0.0379	0.038	1.153
14	2.811	372.6	80.1	0.0703	0.088	0.788
15	3.028	4.7	1.8	0.0409	0.001	1.155
16	3.282	2557.9	954.4	0.0413	0.601	1.162
17	3.703	152.4	45.7	0.0514	0.036	0.942
18	3.844	9.8	2.6	0.0567	0.002	0.87
19	4.003	1823.5	493	0.0587	0.429	1.043
20	4.409	28.1	6.4	0.0671	0.007	0.954
21	4.786	16.9	3.5	0.0702	0.004	1.301
22	5.815	29.5	6.1	0.073	0.007	0.722

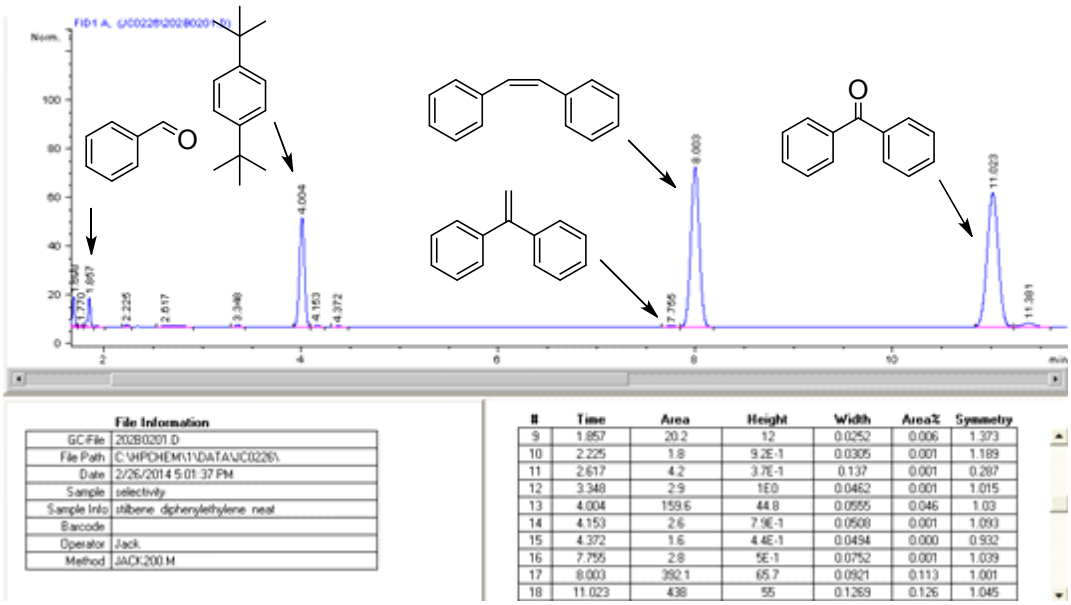
Fig. S40 The reaction was carried out using 1-chloro-4-isopropenylbenzene (29.9 μL, 0.2 mmol) neocuproine (2.1 mg, 0.01 mmol), and solid $CuCl_2 \cdot 2H_2O$ (1.71 mg, 0.01 mmol) without addition of water following the above typical procedure. The compound 4-chloroacetophenone was identified by GC with standard sample. The yield (93.0%) of the cleavage product 4-chloroacetophenone was calculated with the internal standard 1,4-di-*tert*-butylbenzene (conversion factor = 1.99).



#	Time	Area	Height	Width	Area%	Symmetry
5	1.549	57.9	31	0.0273	0.014	1.132
6	1.696	243.4	99.9	0.0349	0.061	1.707
7	1.857	256	136.3	0.0274	0.064	1.529
8	1.93	716.5	326.7	0.0326	0.179	1.358
9	2.224	5.8	2.4	0.0359	0.001	1.191
10	2.334	38	14.5	0.0387	0.009	1.452
11	2.536	77.6	33.6	0.0349	0.019	0.694
12	2.617	7.2	3.3	0.0311	0.002	0.996
13	2.696	163.2	65.3	0.0382	0.041	1.14

#	Time	Area	Height	Width	Area%	Symmetry
14	2.807	241.9	69.1	0.0563	0.060	1.346
15	2.875	60.6	20.3	0.0439	0.015	0.605
16	3.348	27.4	8.4	0.0492	0.007	1.284
17	4.004	1718.5	475.3	0.0562	0.429	1.057
18	4.15	30.3	8.8	0.0525	0.008	1.036
19	4.394	35.6	6.5	0.0871	0.009	0.993
20	8.006	3774.2	624.4	0.0945	0.942	1.106
21	14.844	266.4	25.1	0.1587	0.067	0.993
22	15.107	223.2	20.5	0.1683	0.056	0.966

Fig. S41 The reaction was carried out using cis-stilbene (36.8 μL, 0.2 mmol) neocuproine (2.1 mg, 0.01 mmol), and solid $CuCl_2 \cdot 2H_2O$ (1.71 mg, 0.01 mmol) without addition of water following the above typical procedure. The compound benzaldehyde was identified by GC with standard sample. The yield (9.9%) of the cleavage product benzaldehyde was calculated with the internal standard 1,4-di-*tert*-butylbenzene (conversion factor = 1.99).



#	Time	Area	Height	Width	Area%	Symmetry
9	1.857	20.2	12	0.0252	0.006	1.373
10	2.225	1.8	9.2E-1	0.0305	0.001	1.189
11	2.617	4.2	3.7E-1	0.137	0.001	0.287
12	3.348	2.9	1E0	0.0462	0.001	1.015
13	4.004	159.6	44.8	0.0555	0.046	1.03
14	4.153	2.6	7.9E-1	0.0508	0.001	1.093
15	4.372	1.6	4.4E-1	0.0494	0.000	0.932
16	7.755	2.8	5E-1	0.0752	0.001	1.039
17	8.000	392.1	65.7	0.0921	0.113	1.001
18	11.023	438	55	0.1269	0.126	1.045

Fig. S42 The reaction was carried out using 1,1-diphenylethylene (35.7 μL, 0.2 mmol), *cis*-stilbene (36.8 μL, 0.2mmol), neocuproine (2.1 mg, 0.01 mmol), solid $CuCl_2 \cdot 2H_2O$ (1.71 mg, 0.01 mmol) and *tert*-butyl hydroperoxide (200 μL, 1.55 mmol, 70% aqueous solution) without addition of water following the above typical procedure. The compound benzophenone and benzaldehyde was identified by GC with standard sample. The yield (88%) of the cleavage product Benzophenone was calculated with the internal standard 1,4-di-*tert*-butylbenzene (conversion factor = 1.07) and the yield (8%) of the cleavage product benzaldehyde was calculated with the internal standard 1,4-di-*tert*-butylbenzene (conversion factor = 1.99).