Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

TBHP-promoted direct oxidation reaction of Benzylic C_{sp3}-H bond to Ketones

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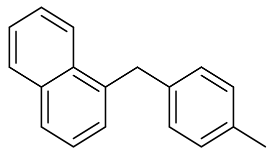
I. General Methods.

All reactions were carried out in pressure tubes. The reactions were monitored either by thin-layer chromatography on silica gel 60-F254 coated 0.2 mm plates (Yantai Chemical Industry Research Institute) or GC-MS (Thermo Fisher Trace 1300-ISQ). Visualization was accomplished by UV light (254 nm). The crude product were purified either using a preparative thin-layer chromatography (TLC) plate or flash column chromatography using silica gel (normal phase, 200-300 mesh, Branch of Qingdao Haiyang Chemical). ^{1}H NMR spectra was recorded on a 400/500 MHz spectrometer at ambient temperature. Data are reported as follows: (1) chemical shift in parts per million (δ, ppm) from $CDCl_3$ (7.26 ppm), MeOH-d^4 (3.31 ppm), DMSO-d^6 (2.50 ppm), and acetone-d^6 (2.05 ppm); (2) multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, and m = multiplet); (3) coupling constants (Hz). ^{13}C NMR spectra were recorded on a 100/125 MHz spectrometer at ambient temperature. Chemical shifts are reported in ppm from $CDCl_3$ (77.16 ppm), MeOH-d^4 (49.15 ppm), DMSO-d^6 (39.51 ppm), and acetone-d^6 (29.92 ppm). HRMS data were obtained on a QTOF mass spectrometer. All commercial materials were used as received unless otherwise noted.

II. Substrate Preparation

All substrates were commercially available except **1n** and **1p**. Substrate **1n** could be synthesized according to the literature procedures: Z.-C. Cao, D.-G. Yu, R.-Y. Zhu, J.-B. Wei and Z.-J. Shi, *Chem. Commun.*, 2015, **51**, 2683.). Substrate **1p** could be synthesized according to the procedure in P. Boggu, E. Venkateswararao, M. Manickam, D. Kwak and Y. Kim, *Bioorg. Med. Chem.* 2016, **24**, 1872.

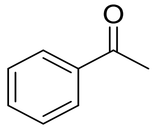


1-(4-methylbenzyl)naphthalene (1n)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.99 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.88−7.82 (m, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.48−7.38 (m, 3H), 7.28 (d, *J* = 6.9 Hz, 1H), 7.08 (s, 4H), 4.41 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 137.55,136.91,135.53, 133.94, 132.16, 129.15, 128.62, 128.65, 127.15, 125.94, 125.55, 125.53, 124.29, 38.62, 21.01. GC-MS (m/z)： calcd for $[C_{18}H_{16}]^+$,232.113; found 232.16. For characterization data, also see: M. Tobisu, A. Yasutome, H. Kinuta, K. Nakamura and N. Chatani, *Org. Lett.,* 2014, **16**, 5572.

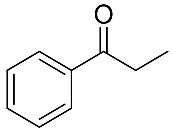
III. General Procedure for reaction & Products Data

A) General Procedure for oxidation reaction: The pressure tube was charged with alkylarene or diarylmethane (1.0 mmol), and the hexane solution of TBHP (2 ml, ~12 mmol) was added. Then, the pressure tube was sealed and heated at 130 ˚C. After the reaction was completed (typical reaction time: 10h), the reaction mixture was cooled to room temperature. The mixture was diluted by ethyl acetate, washed with water and saturated sodium chloride solution, dried over sodium sulfate, and the organic solvent was evaporated under reduced pressure. The resulting residue was purified by flash chromatography over a short plug of silica gel (petroleum ether/EtOAc) to obtained the desired product. (The hexane solution of TBHP was prepared by the extraction of 70% TBHP water solution with hexane, then dried over sodium sulfate. The excess hexane was evaporated via rotovap at reduced pressure using ice water bath. The concentration of TBHP was determined by ^{1}H NMR. For a similar procedure, also see: Y. Gao, R. M. Hanson, J. M. Klunder, S. Y. Ko, H. Masamune and K. B. Sharpless, *J. Am. Chem. Soc.*, 1987, **109**, 5765.)



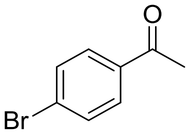
Acetophenone (2a)

Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93-7.81 (m, 2H), 7.51-7.42 (m, 1H), 7.41-7.31 (m, 2H), 2.53-2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.96, 133.03, 128.51, 128.23, 26.46. GC-MS(m/z)：calcd for$[C_8H_8O]^+$,120.06; found 120.09. For characterization data, also see: J. Ruan, X. Li, O. Saidi and J. Xiao, *J. Am. Chem. Soc.*, 2008, **130**, 2424.



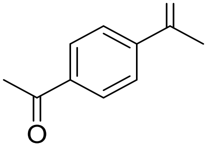
Propiophenone (2b)

Yield: 89%. For characterization data, also see: J. Ruan, X. Li, O. Saidi and J. Xiao, *J. Am. Chem. Soc.*, 2008, **130**, 2424.



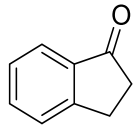
Bromoacetophenone (2c)

Yield: 92%. For characterization data, also see: D. T. Genna and G. H. Posner, *Org. Lett.*, 2011, **13**, 5358.



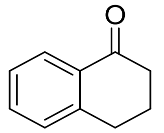
1,4-Diacetylbenzene (2d)

Yield: 81%. For characterization data, also see: J. Ruan, X. Li, O. Saidi and J. Xiao, *J. Am. Chem. Soc.*, 2008, **130**, 2424.



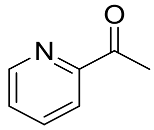
2,3-dihydro-1H-inden-1-one (2e)

Yield: 81%. For characterization data, also see: S. Gűlcemal, D. Gűlcemal, G. F. S. Whitehead and J. Xiao, *Chem. Eur. J.*, 2016, **22**, 10513.



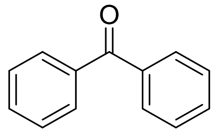
3,4-Dihydronaphthalen-1(2H)-one (2f)

Yield: 87%. For characterization data, also see: S. Gűlcemal, D. Gűlcemal, G. F. S. Whitehead and J. Xiao, *Chem. Eur. J.*, 2016, **22**, 10513.



2-Acetylpyridine (2g)

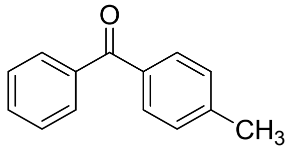
Yield: 79%. For characterization data, also see: D. T. Genna and G. H.Posner, *Org. Lett.*, 2011, **13**, 5358.



Benzophenone (2h)

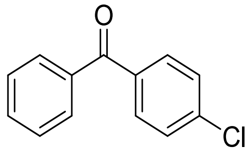
Yield: 93%. White solid, M.P. 48-49 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.91-7.72 (m, 2H), 7.65-7.59 (m, 1H), 7.54-7.47 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 196.76, 137.63, 132.42, 130.07, 128.29. GC-MS(m/z): calcd for $[C_{13}H_{10}O]^+$: 182.07; found: 182.11. For characterization data, also see: H. Wang, Z. Wang, H. Huang, J.

Tan and K. Xu, *Org. Lett.*, 2016, **18**, 5680.



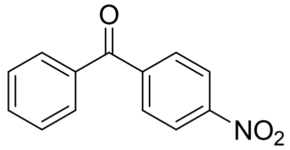
4-Methylbenzophenone (2i)

Yield: 91%. For characterization data, also see: H. Wang, Z. Wang, H. Huang, J. Tan and K. Xu, *Org. Lett.*, 2016, **18**, 5680.



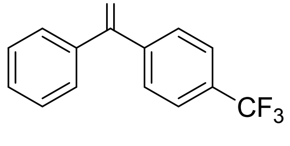
4-Chlorobenzophenone (2j)

Yield: 78%. For characterization data, also see: H. Wang, Z. Wang, H. Huang, J. Tan and K. Xu, *Org. Lett.*, 2016, **18**, 5680.



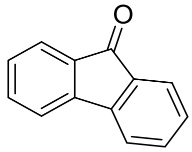
4-Chlorobenzophenone (2k)

Yield: 93%. For characterization data, also see: C. Liu, G. Meng, Y. Liu, R. Liu, R. Lalancette, R. Szostak and M. Szostak, *Org. Lett.,* 2016, **18**, 4194



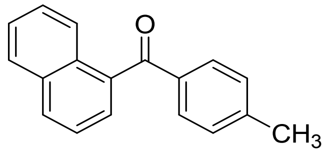
4-(Trifluoromethyl)benzophenone (2l)

Yield: 81%. For characterization data, also see: H. Wang, Z. Wang, H. Huang, J. Tan and K. Xu, *Org. Lett.*, 2016, **18**, 5680.



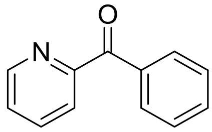
9-Fluorenone (2m)

Yield: 81%. For characterization data, also see: H. Wang, Z. Wang, H. Huang, J. Tan and K. Xu, *Org. Lett.*, 2016, **18**, 5680.



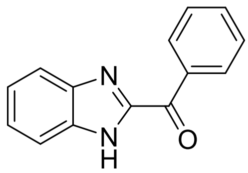
Naphthalen-1-yl(p-tolyl)methanone (2n)

Yield: 78%. For characterization data, also see: H. Wang, Z. Wang, H. Huang, J. Tan and K. Xu, *Org. Lett.*, 2016, **18**, 5680.



2-Benzoylpyridine (2o)

Yield: 82%. For characterization data, also see: H. Wang, Z. Wang, H. Huang, J. Tan and K. Xu, *Org. Lett.*, 2016, **18**, 5680.

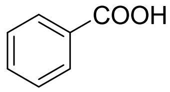


2-Benzoyl-1H-benzimidazole (2p)

Yield=70%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.57 (s, 1H), 8.71 (d, *J* = 7.6 Hz, 2H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.58 (dd, *J* = 14.5, 7.2

Hz, 3H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.96, 147.77, 144.01, 135.39, 133.91, 133.14, 131.33, 128.56, 126.48, 123.79, 122.34, 111.95. GC-MS(m/z) calcd for $[C_{14}H_{10}N_2O]^+$,222.08 ; found 222.16.

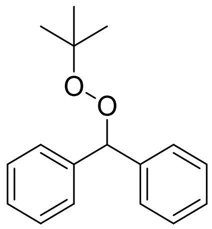
B) General Procedure for diphenylmethanol/2-phenylacetophenone oxidation: The pressure tube was charged with diphenylmethanol or 2-phenylacetophenone (1.0 mmol), and the hexane solution of TBHP (2 ml, ~6 mol/L) was added. Then, the pressure tube was sealed and heated at 130 ˚C. After the reaction was completed, the reaction mixture was cooled to room temperature. The mixture was diluted by ethyl acetate, washed with water and saturated sodium chloride solution, dried over sodium sulfate, and the organic phase was evaporated under reduced pressure. The resulting residue was purified by flash chromatography over silica gel (petroleum ether/EtOAc) to obtained the desired product.



benzoic acid (2q)

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.53 (s, 1H), 8.13 (d, *J* = 7.3 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, CDCl3) δ 172.49, 133.84, 130.24, 129.38, 128.51. GC-MS(m/z): calcd for $[C_7H_6O_2]^+$: 122.04; found 122.06.

C) General Procedure for reaction intermediate study: The reaction was performed following the standard conditions, except the reaction was stopped after 5 hours in order to study the potential reaction intermediate. **2h** was obtained 66% yield while reaction intermediate **4** was obtained with 30% yield. Intermediate **4** was then submitted to the standard oxidation reaction conditions again, the desired product was obtained with 91% yield.

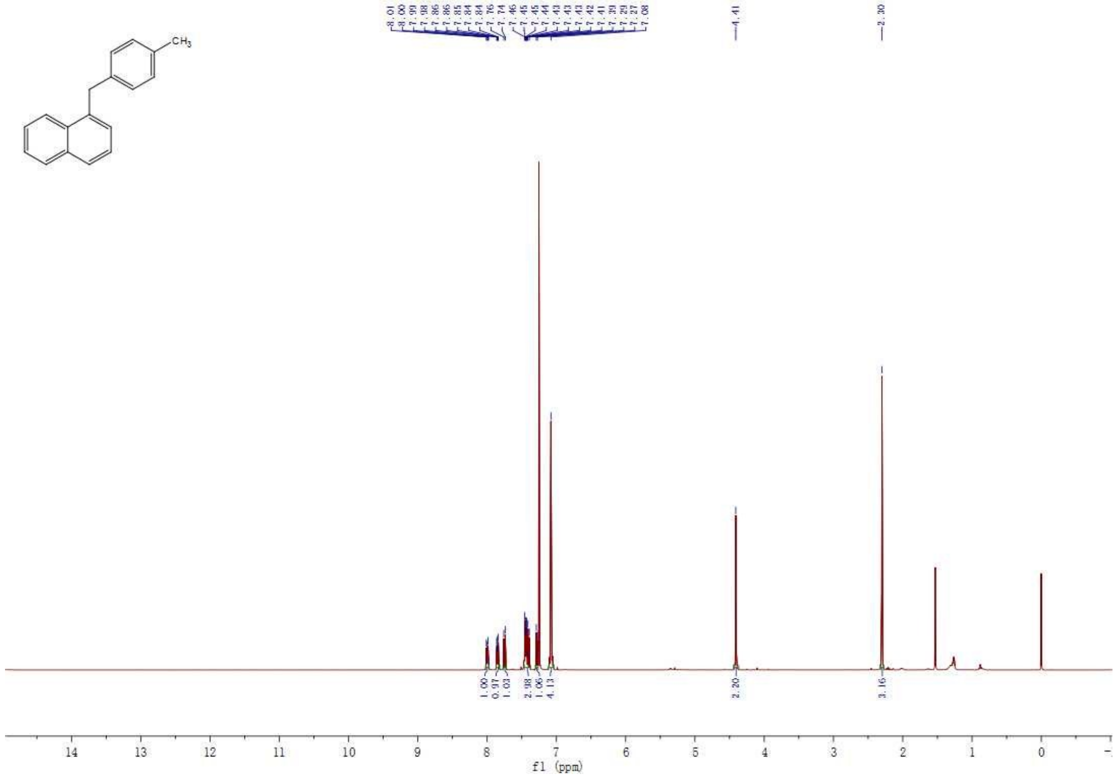


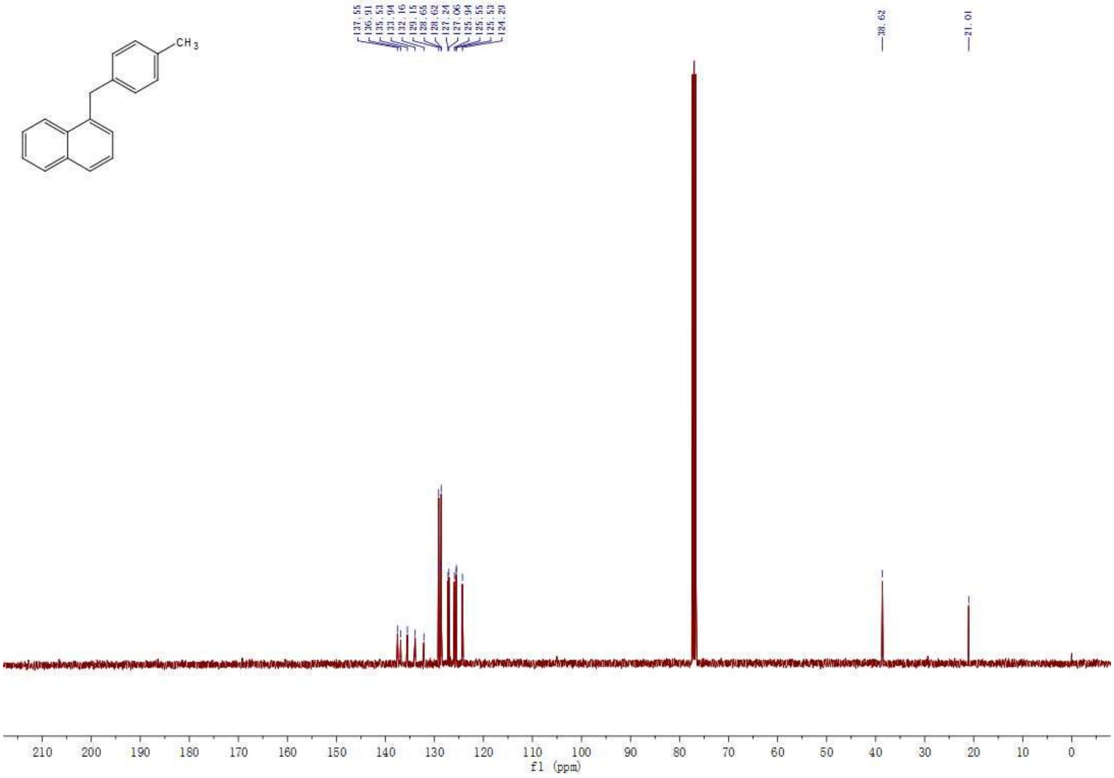
((tert-butylperoxy)methylene)dibenzene (4)

Yield: 30%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.22 (m, 10H), 5.97 (s, 1H), 1.26 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.41, 128.96，128.26, 127.68, 87.36, 80.62, 26.58. calcd for$[C_{17}H_{20}NaO_2]^+$: 279.13; found 279.16.

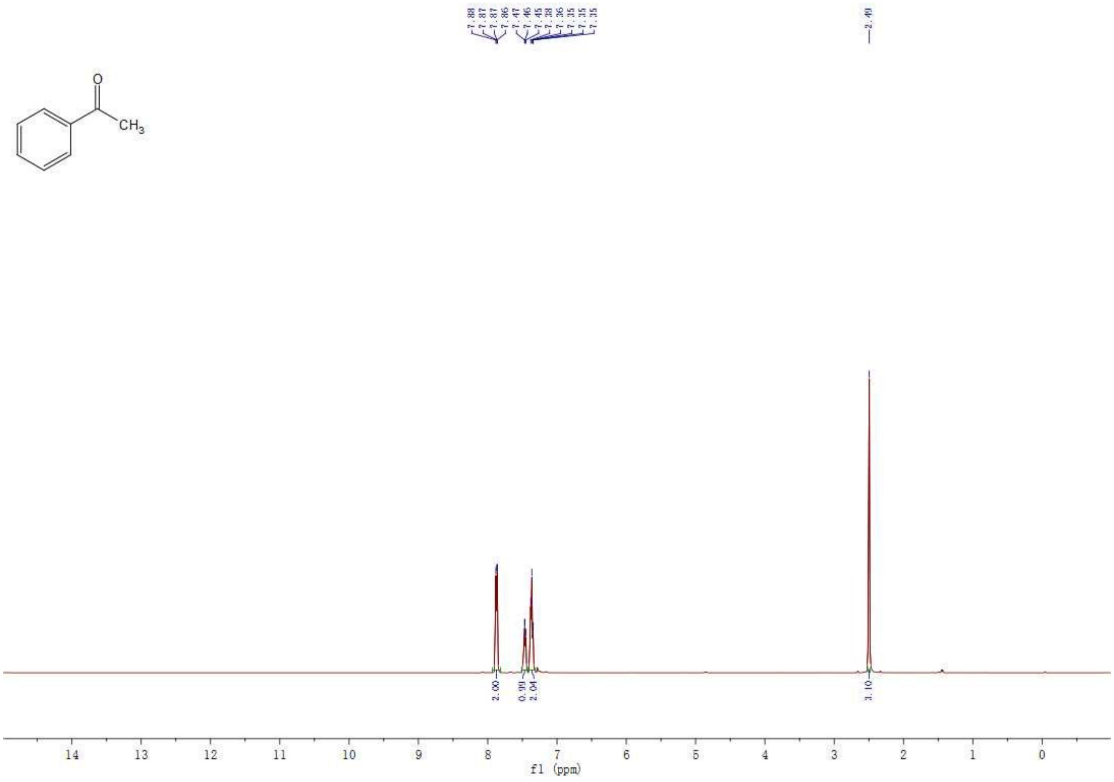
Ⅳ. Spectrum

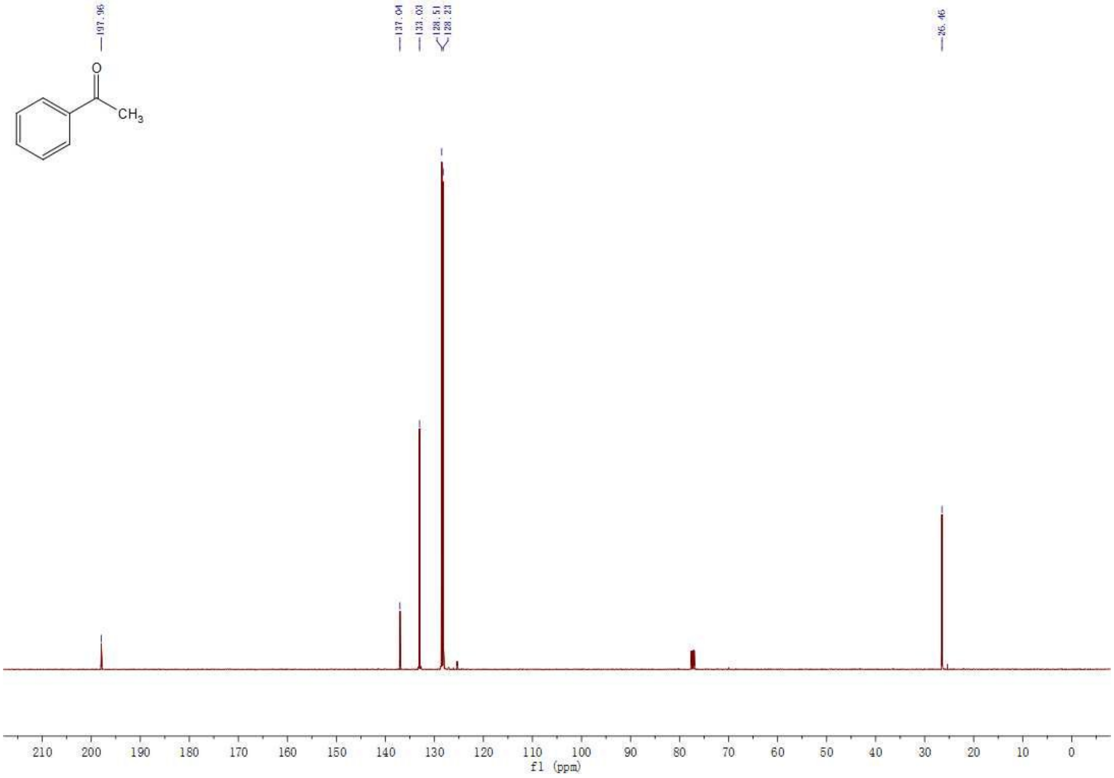
1-(4-methylbenzyl)naphthalene (1n)



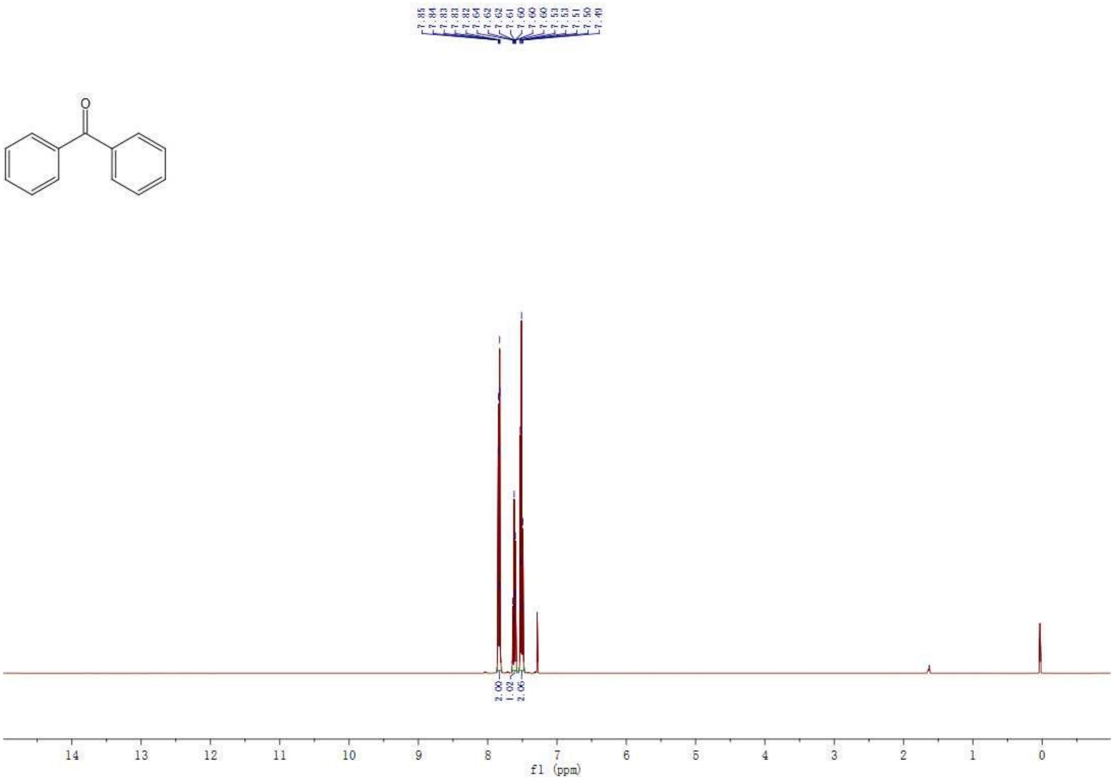


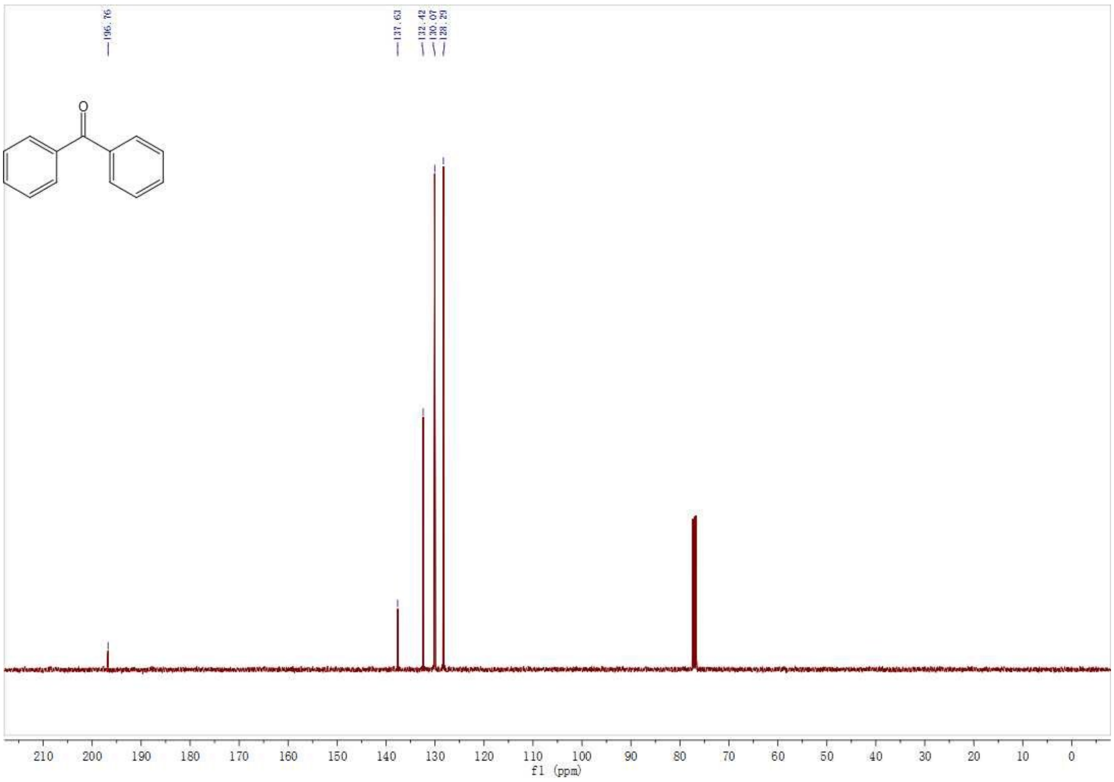
Acetophenone (2a)



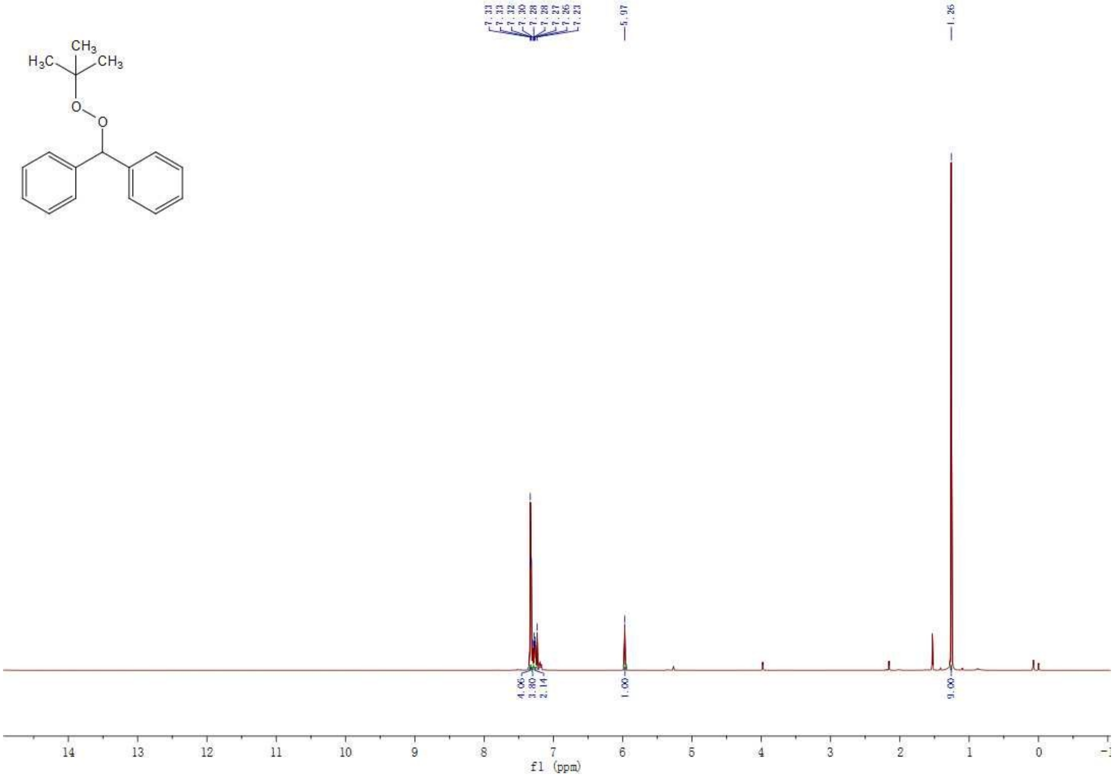


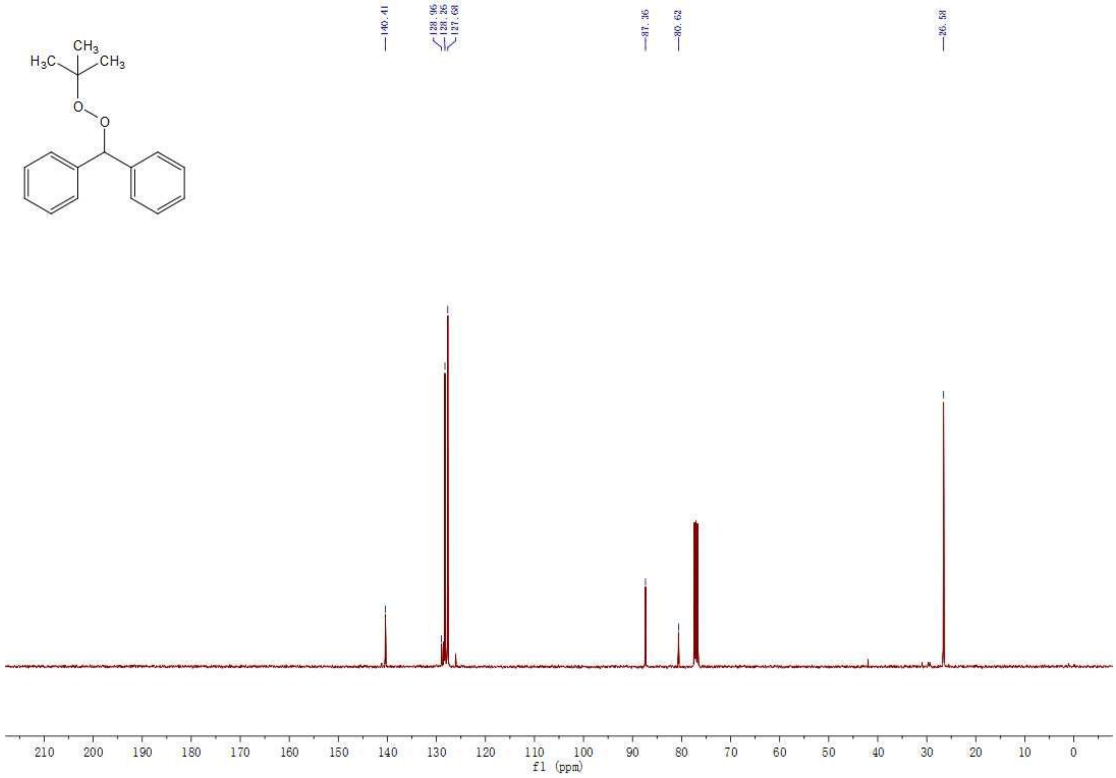
Benzophenone (2h)



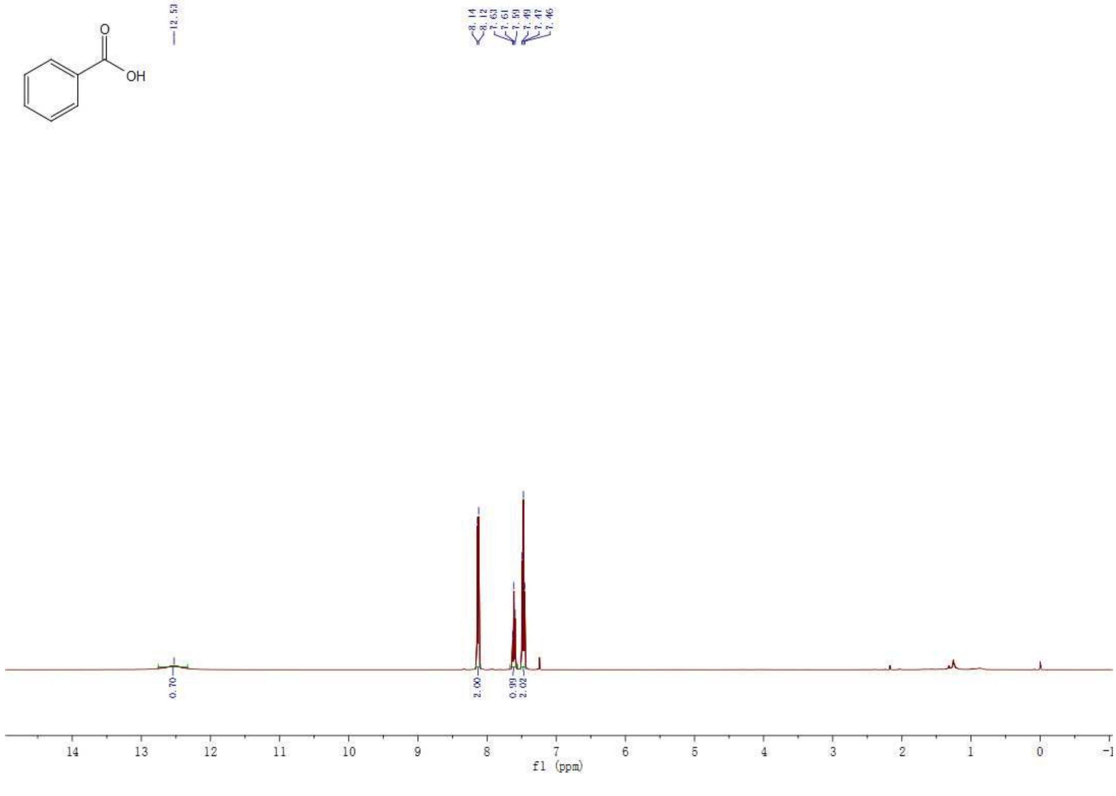


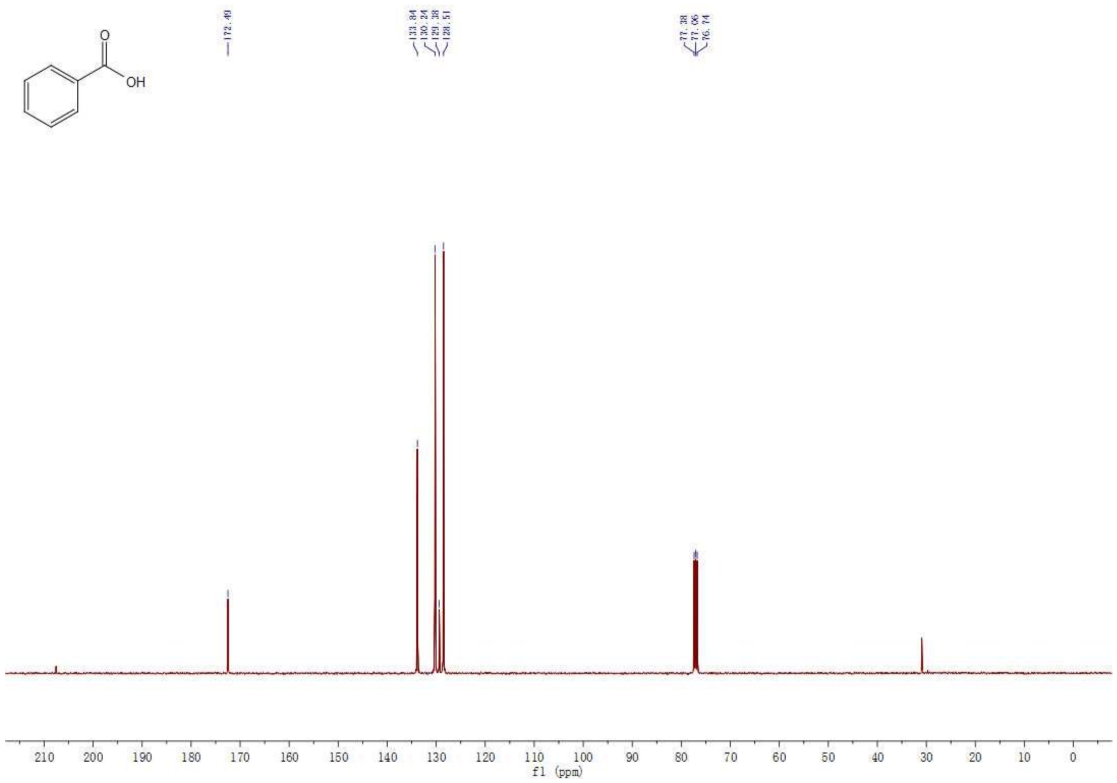
((tert-butylperoxy)methylene)dibenzene (4)



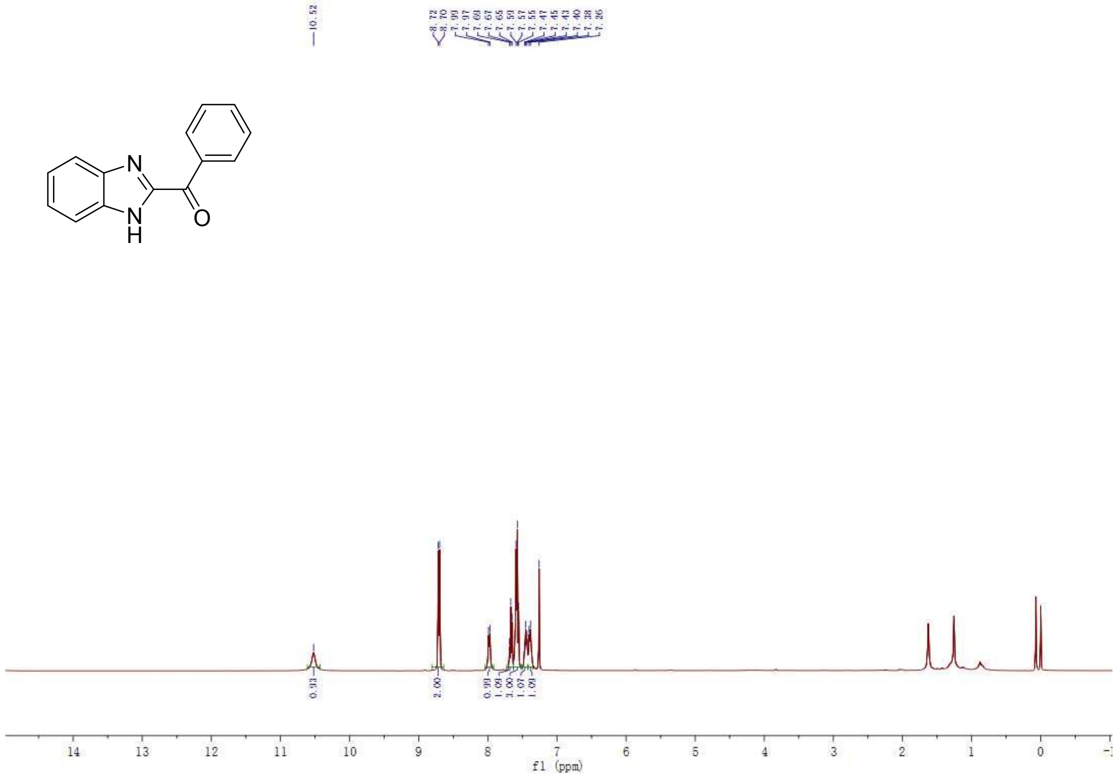


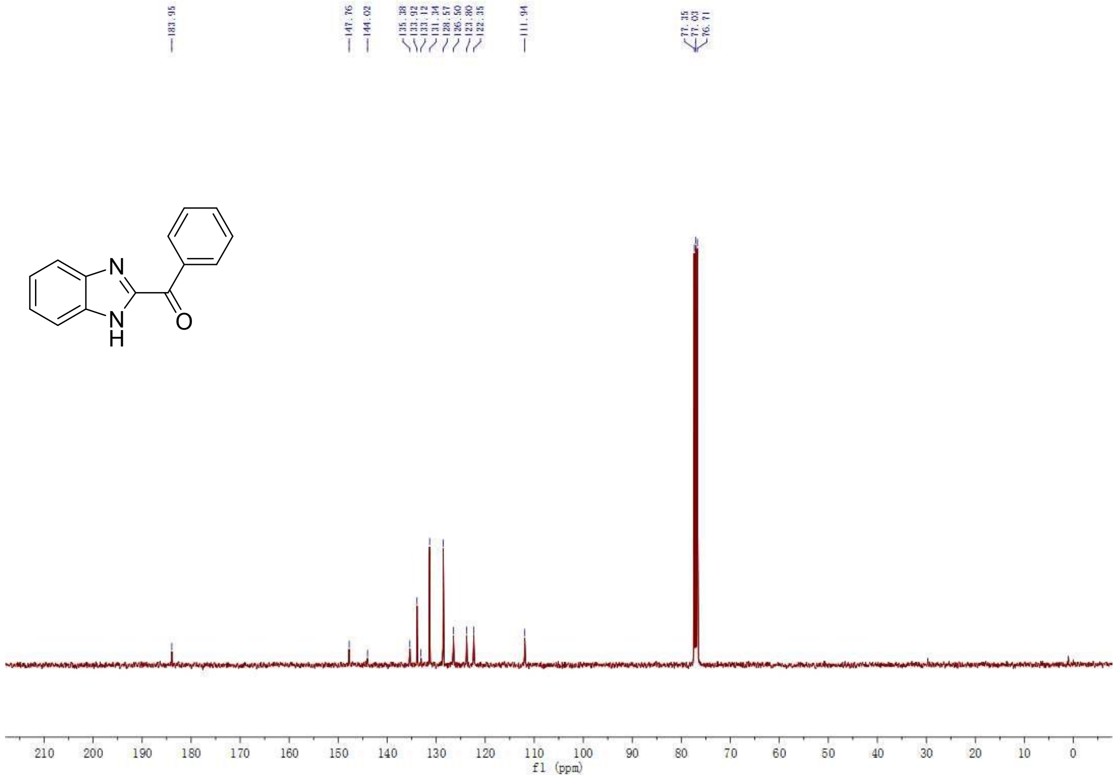
benzoic acid (3p)





2-Benzoyl-1H-benzimidazole (2p)

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