

Supporting Information

Aqueous Phase C-H Bond Oxidation Reaction of Arylalkanes Catalyzed by a Water-Soluble Cationic Ru(III) Complex [(pymox-Me₂)₂RuCl₂]⁺BF₄⁻

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General Information. All operations were carried out in an inert-atmosphere glove box or by using standard high vacuum and Schlenk techniques unless otherwise noted. Tetrahydrofuran, benzene, hexanes and Et₂O were distilled from purple solutions of sodium and benzophenone immediately prior to use. The NMR solvents were dried from activated molecular sieves (4 Å). All organic substrates were received from commercial sources and used without further purification. The ¹H and ¹³C NMR spectra were recorded on a Varian 400 MHz FT-NMR spectrometer. UV-vis spectra were recorded on a Shimadzu UV-1600/1700 instrument. Electrochemical measurements were collected with a BAS CV-50V instrument. The product yields were measured from a Hewlett-Packard HP 6890 GC spectrometer. The elemental analyses were performed at the Midwest MicroLab, Indianapolis, IN.

Synthesis of (pymox-Me₂)Ru(COD)Cl₂ (1). In a glove box, 4,4-dimethyl-2-(2-pyridyl)oxazoline (0.21 g, 1.2 mmol) and [Ru(COD)Cl₂]_x (0.16 g, 0.5 mmol) were dissolved in ClCH₂CH₂Cl (15 mL) in a 25 mL Schlenk tube equipped with a magnetic stirring bar and Teflon stopcock. The reaction tube was brought out of the box, and was stirred in an oil bath at 50 °C for 24 h. After the reaction tube was cooled to room temperature, the volatiles were removed under vacuum, and the residue was recrystallized in CH₂Cl₂/*n*-hexanes to obtain a crude product mixture. The mixture was further purified by flash column chromatography (*n*-hexanes/EtOAc = 4:1) to afford analytically pure product **1** (0.15 g, 65% yield). Single crystals of **1** suitable for X-ray crystallographic analysis were obtained from slow evaporation of CH₂Cl₂ solution.

For **1**: ¹H NMR (400 MHz, CDCl₃) δ 8.05 (ddd, *J* = 5.3, 1.0, 0.7 Hz, py-6-H), 7.86-7.96 (m, 2H, py-3 and 4-H), 7.50 (ddd, *J* = 12.6, 5.3, 2.0 Hz, py-5-H), 5.03 (t, *J* = 2.5 Hz, =CH), 4.52 (t, *J* = 2.6 Hz, =CH), 4.46 (s, 2H, OCH₂), 2.61-2.78 (m, 4H, CH₂), 2.03-2.21 (m, 4H, CH₂), 1.52 (s, 6H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 166.6 (N=CO), 150.0, 148.0, 138.2, 128.0 and 126.2 (py), 89.5 and 89.2 (=CH), 82.5 (OCH₂), 70.3 (CCH₃), 30.5 and 29.0 (CH₂), 27.5 (CCH₃); Anal. Calcd for C₁₈H₂₄Cl₂N₂ORu: C, 47.37; H, 5.30. Found: C, 47.13; H, 5.22.

Synthesis of (pymox-Me₂)₂RuCl₂ (2). In a glove box, [Ru(COD)Cl₂]_x (0.20 g, 0.44 mmol) and 4,4-dimethyl-2-(2-pyridyl)oxazoline (0.34 g, 1.94 mmol) were dissolved in ClCH₂CH₂Cl (15 mL) in a 25 mL Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar. The reaction mixture was stirred in an oil bath at 100 °C for 24 h. After cooling to room temperature, the solvent was removed under vacuum. The residue was recrystallized in CH₂Cl₂/*n*-hexanes to obtain a crude product mixture. The product mixture was further purified by flash chromatography (*n*-hexanes/EtOAc = 4:1) to afford analytically pure product **2** (0.30 g, 65% yield). Alternatively, complex **1** (0.20 g, 0.44 mmol) and pymox-Me₂ (0.34 g, 1.94 mmol) were dissolved in ClCH₂CH₂Cl (15 mL) in a 25 mL Schlenk tube. The reaction mixture was stirred in an oil bath at 100 °C for 24 h. After cooling to room temperature, the solvent was removed under vacuum. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 4:1) to afford pure product **2** (0.25 g, 55% yield). Single crystals of **2** suitable for X-ray crystallographic analysis were obtained from CH₂Cl₂/*n*-hexanes solution.

For **2**: ¹H NMR (400 MHz, CDCl₃) δ 10.01 and 10.12 (s, py-6-H), 7.83-7.88 and 7.90-7.95 (m, 2H, py-3 and 4-H), 7.53-7.63 and 7.25-7.39 (m, py-5-H), 4.62 and 4.53 (s, OCH₂), 1.15 and 0.65 (s, CCH₃); ¹³C NMR (100 MHz, CDCl₃) δ 166.8 and 166.5 (N=CO), 156.2, 155.2, 151.6, 151.01, 133.1, 132.9, 132.8, 132.6, 126.1 and 124.9 (py), 83.4 and 82.7 (OCH₂), 70.6 and 70.3 (CCH₃), 28.2 and 27.1 (CCH₃); Anal. Calcd for C₂₀H₂₄Cl₂N₄O₂Ru: C, 45.81; H, 4.61. Found C, 44.92; H, 4.54.

Synthesis of [(pymox-Me₂)₂RuCl₂]⁺BF₄⁻ (3). In a 25 mL Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar, the complex **2** (100 mg, 0.19 mmol), NaBF₄ (90 mg, 0.95 mmol) and *t*-BuOOH (5.5 M in decane, 0.42 mL, 1.9 mmol) were dissolved in CH₂Cl₂ (5 mL). The reaction mixture was stirred for 5 h at room temperature. The solvent was removed under vacuum. The residue was recrystallized in CH₂Cl₂/*n*-hexanes to obtain the product **3** (85 mg, 73% yield). Single crystals of complex **3** suitable for X-ray crystallographic analysis were obtained from CH₂Cl₂/*n*-hexanes solution. The Evans NMR method was used to measure the

magnetic moment of the complex by following the experimental procedure described in: Girolami, G. S.; Rauchfuss, T. B.; Angelici, R. J. *Synthesis and Technique in Inorganic Chemistry: A Laboratory Manual*, University Science Books: Sausalito, CA, 1999, pp. 125-126.

For **3**: Anal. Calcd for C₂₀H₂₄BCl₂F₄N₄O₂Ru: C, 39.30; H, 3.96. Found C, 38.70; H, 3.77. $\mu_{eff} = 1.55 B_M$ at 293 K.

General Procedure of the Catalytic Reaction. In air, the complex **3** (6 mg, 10 μ mol), an alkane substrate (1.0 mmol) and *t*-BuOOH (70 wt% in H₂O, 0.43 mL, 3.0 mmol) were dissolved in water (3 mL) in a 25 mL Schlenk tube equipped with a magnetic stirring bar. The reaction mixture was stirred at 20 °C for 2-24 h. The reaction tube was opened to air and the solution was extracted with CH₂Cl₂ (10 mL). The solution was filtered through a small pad of silica gel. An internal standard (C₆Me₆, 20 mg) was added to the solution, and the product yield was determined by GC. The ketone product was readily isolated by a column chromatography on silica gel (hexane/EtOAc).

Catalytic Oxidation Reaction of Ethylbenzene with TEMPO. In air, complex **3** (6 mg, 10 μ mol) was charged with ethylbenzene (0.12 mL, 1.0 mmol), *t*-BuOOH (70 wt% in H₂O, 0.43 mL, 3.0 mmol), TEMPO (16 mg, 0.1 mmol), H₂O (1.5 mL) and *n*-hexanes (1.0 mL) in a thick-walled 25 mL Schlenk tube equipped with a magnetic stirring bar. The reaction mixture was stirred for 24 h at 20 °C. After the reaction was completed, the reaction tube was opened to air. The solution was extracted with CH₂Cl₂ (10 mL) and organic solution was filtered through a small pad of silica gel. The product yield as determined by GC was 34% (without TEMPO, 40% conversion). It should be noted that *n*-hexanes was added to dissolve TEMPO, and under these biphasic conditions, the reaction rate was considerably lower than in pure water.

Catalyst Recycling Experiment. The complex **3** (6 mg, 10 μ mol) was charged with ethylbenzene (0.12 mL, 1.0 mmol), *t*-BuOOH (70 wt% in H₂O, 0.43 mL, 3.0 mmol) and H₂O

(2.5 mL) in a thick-walled 25 mL Schlenk tube equipped with a magnetic stirring bar. The reaction mixture was stirred for 16 h at 20 °C. After the reaction was completed, the reaction tube was opened to air and the solution was extracted with CH₂Cl₂ (10 mL). The extracted solution was filtered through a small pad of silica gel and analyzed by GC. The second and third runs were repeated by using the same aqueous solution. The product yield as determined by GC: 1st run (90%), 2nd run (71%), 3rd run (61%).

Isotope Effect Study. In two separate tubes, complex **3** (6 mg, 10 μmol) was charged with ethylbenzene and ethylbenzene-*d*₁₀ (0.12 mL, 1.0 mmol), *t*-BuOOH (70 wt% in H₂O, 0.43 mL, 3.0 mmol), H₂O (1.5 mL) and *n*-hexanes (1.0 mL) in a 25 mL Schlenk tube equipped with a magnetic stirring bar in air. The reaction tube was stirred at 20 °C. A small portion of the aliquot was drawn periodically from the organic layer, and the product conversion was determined by GC. The *k*_{obs} was obtained from a first-order plot of $-\ln([\text{ethylbenzene}]_t/[\text{ethylbenzene}]_0)$ vs time.

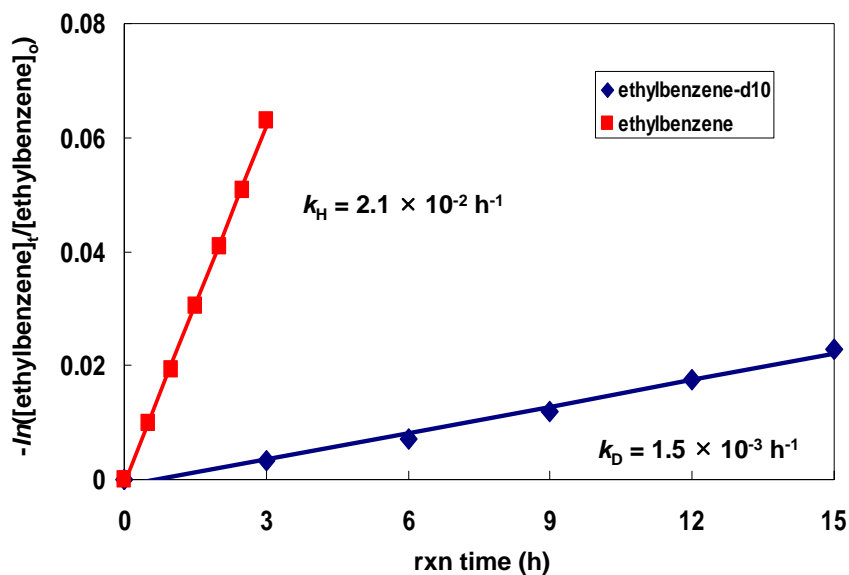


Figure S1. Pseudo first-order plots of $-\ln([\text{ethylbenzene}]_t/[\text{ethylbenzene}]_0)$ vs time.

Hammett Study. In five separate tubes, an equal amount of the complex **3** (6 mg, 10 μmol), *p*-X-C₆H₄CH₂CH₃ (X = OMe, Me, H, F, Cl) (0.12 mL, 1.0 mmol) and *t*-BuOOH (70 wt% in H₂O, 0.43 mL, 3.0 mmol) were dissolved in H₂O (1.5 mL) and *n*-hexanes (1.0 mL) in a 25 mL Schlenk tube equipped with a magnetic stirring bar in air. The reaction tubes were stirred at 20 °C. A small portion of the aliquot was drawn periodically from the organic layer, and the conversion was determined by GC. The k_{obs} was estimated from a first-order plot of $-\ln([\text{ArCH}_2\text{CH}_3]_t/[\text{ArCH}_2\text{CH}_3]_0)$ vs time.

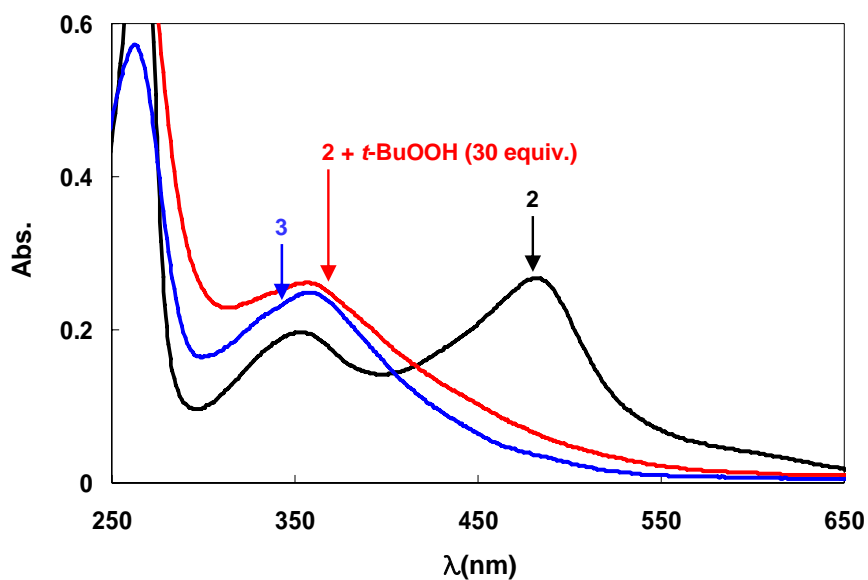


Figure S2. UV-vis spectra of **2** (20 μM), **2** (20 μM) and *t*-BuOOH (30 equiv), and **3** (20 μM) in water.

Cyclic Voltammetry of 3. In a volumetric flask, the sample solution was prepared by dissolving complex **3** (10 mg, 1.6 mM) and an electrolyte (0.25 M of Bu₄NPF₆) in 10 mL of CH₂Cl₂. Electrochemical measurements were collected at a scan rate of 200 mV/s from a three-electrode cell composed of a Ag/AgCl electrolyte, a platinum working electrode, and a glassy carbon counter electrode.

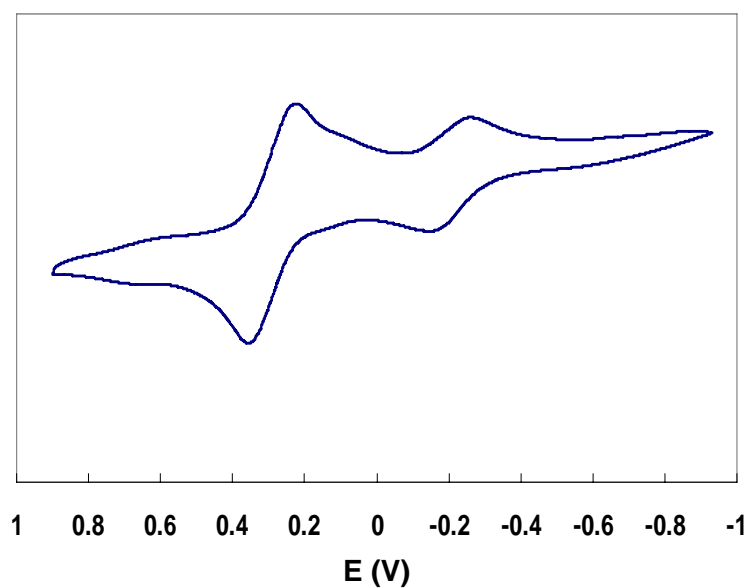


Figure S3. Cyclic voltammogram of **3** in CH₂Cl₂.

Table S1. Crystal data and structure refinement for **1**.

Empirical formula	$\text{C}_{18.5}\text{H}_{25}\text{C}_{13}\text{N}_2\text{ORu}$	
Formula weight	498.83	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	$a = 16.4410(4)$ Å	$\alpha = 90^\circ$
	$b = 9.8816(3)$ Å	$\beta = 110.3760(10)^\circ$
	$c = 12.8838(3)$ Å	$\gamma = 90^\circ$
Volume	$1962.17(9)$ Å ³	
Z	4	
Density (calculated)	1.689 Mg/m ³	
Absorption coefficient	10.305 mm ⁻¹	
F(000)	1012	
Crystal size	0.50 x 0.44 x 0.32 mm ³	
θ range for data collection	5.32 to 67.53°	
Index ranges	$-19 \leq h \leq 17, 0 \leq k \leq 11, 0 \leq l \leq 15$	
Reflections collected	16178	
Independent reflections	3383 [R(int) = 0.0305]	
Completeness to $\theta = 67.53^\circ$	95.6 %	
Absorption correction	Numerical	
Max. and min. transmission	0.1371 and 0.0791	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3383 / 0 / 332	
Goodness-of-fit on F ²	1.115	
Final R indices [I > 2 σ (I)]	$R_1 = 0.0211, wR_2 = 0.0516$	
R indices (all data)	$R_1 = 0.0212, wR_2 = 0.0517$	
Extinction coefficient	0.00074(5)	
Largest diff. peak and hole	0.639 and -0.452 e.Å ⁻³	

Table S2. Crystal data and structure refinement for **2**.

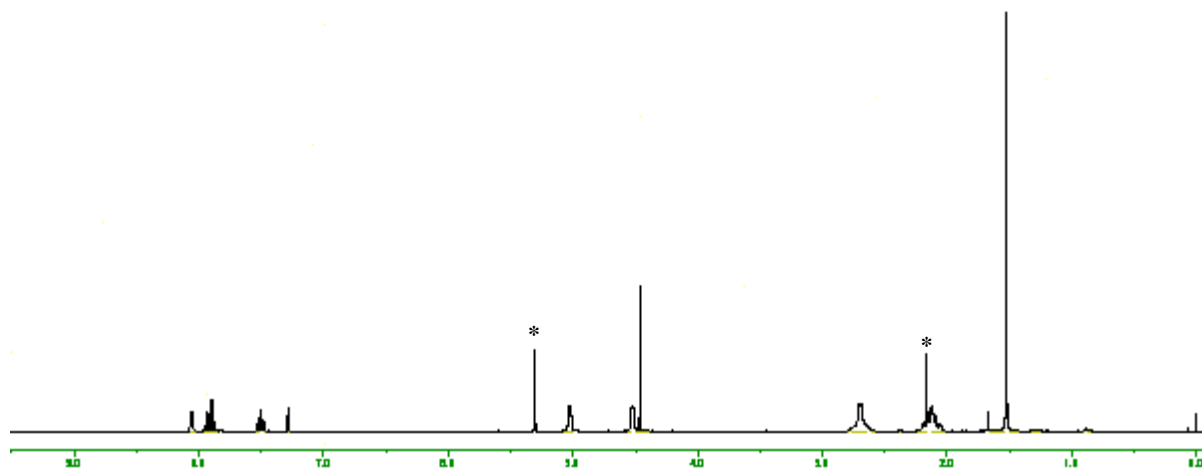
Empirical formula	$\text{C}_{20}\text{H}_{24}\text{C}_{12}\text{N}_4\text{O}_{2.14}\text{Ru}$	
Formula weight	526.68	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	$a = 10.72140(10)$ Å	$\alpha = 90^\circ$
	$b = 14.1607(2)$ Å	$\beta = 97.3240(10)^\circ$
	$c = 14.6702(2)$ Å	$\gamma = 90^\circ$
Volume	$2209.09(5)$ Å ³	
Z	4	
Density (calculated)	1.584 Mg/m ³	
Absorption coefficient	8.173 mm ⁻¹	
F(000)	1069	
Crystal size	0.29 x 0.15 x 0.10 mm ³	
θ range for data collection	4.16 to 68.00°	
Index ranges	$-12 \leq h \leq 12, 0 \leq k \leq 16, 0 \leq l \leq 17$	
Reflections collected	18294	
Independent reflections	3921 [R(int) = 0.0163]	
Completeness to $\theta = 68.00^\circ$	97.6 %	
Absorption correction	Numerical	
Max. and min. transmission	0.4954 and 0.2003	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3921 / 0 / 272	
Goodness-of-fit on F ²	0.981	
Final R indices [I > 2 σ (I)]	$R_1 = 0.0194, wR_2 = 0.0513$	
R indices (all data)	$R_1 = 0.0197, wR_2 = 0.0515$	
Extinction coefficient	0.00020(3)	
Largest diff. peak and hole	0.405 and -0.295 e.Å ⁻³	

Table S3. Crystal data and structure refinement for **3**.

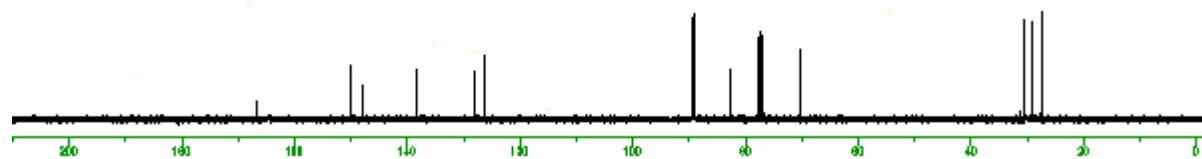
Empirical formula	$\text{C}_{21}\text{H}_{26}\text{BCl}_4\text{F}_4\text{N}_4\text{O}_2\text{Ru}$	
Formula weight	696.14	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	$a = 8.35260(10)$ Å	$\alpha = 90^\circ$
	$b = 28.1943(4)$ Å	$\beta = 108.2210(10)^\circ$
	$c = 12.6986(2)$ Å	$\gamma = 90^\circ$
Volume	$2840.52(7)$ Å ³	
Z	4	
Density (calculated)	1.628 Mg/m ³	
Absorption coefficient	8.407 mm ⁻¹	
F(000)	1396	
Crystal size	0.55 x 0.41 x 0.05 mm ³	
θ range for data collection	3.99 to 67.75°	
Index ranges	$-9 \leq h \leq 9, 0 \leq k \leq 33, 0 \leq l \leq 15$	
Reflections collected	23226	
Independent reflections	5024 [R(int) = 0.0211]	
Completeness to $\theta = 67.75^\circ$	97.6 %	
Absorption correction	Numerical	
Max. and min. transmission	0.6786 and 0.0905	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5024 / 9 / 370	
Goodness-of-fit on F ²	0.969	
Final R indices [I > 2 σ (I)]	$R_1 = 0.0478, wR_2 = 0.1237$	
R indices (all data)	$R_1 = 0.0489, wR_2 = 0.1245$	
Largest diff. peak and hole	1.507 and -1.065 e.Å ⁻³	

^1H and ^{13}C NMR Spectra of Complex **1**

^1H NMR (CDCl_3 , 400 MHz)

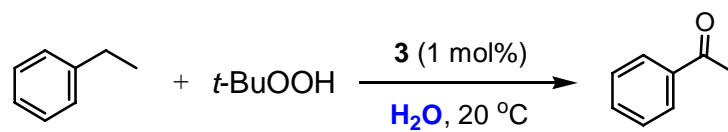


$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.6 MHz)

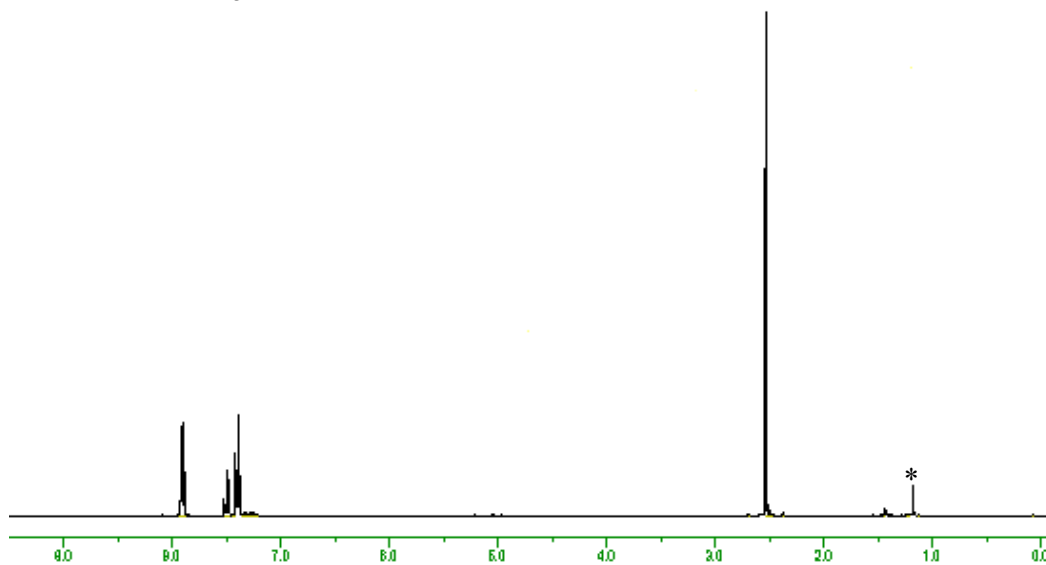


* denotes solvents.

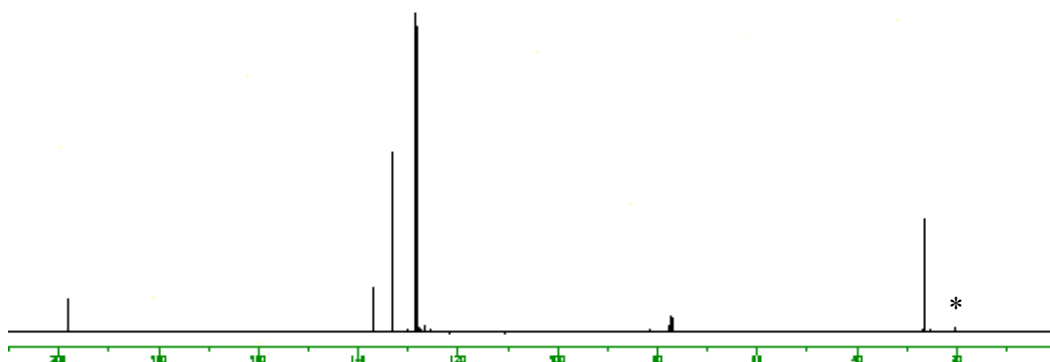
^1H and ^{13}C NMR Spectra of Selected Crude Organic Products



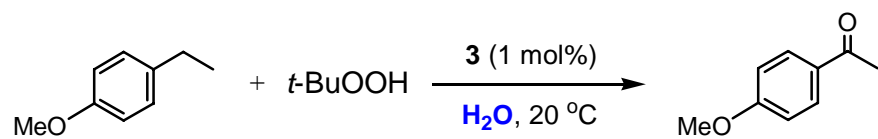
^1H NMR (CDCl_3 , 400 MHz)



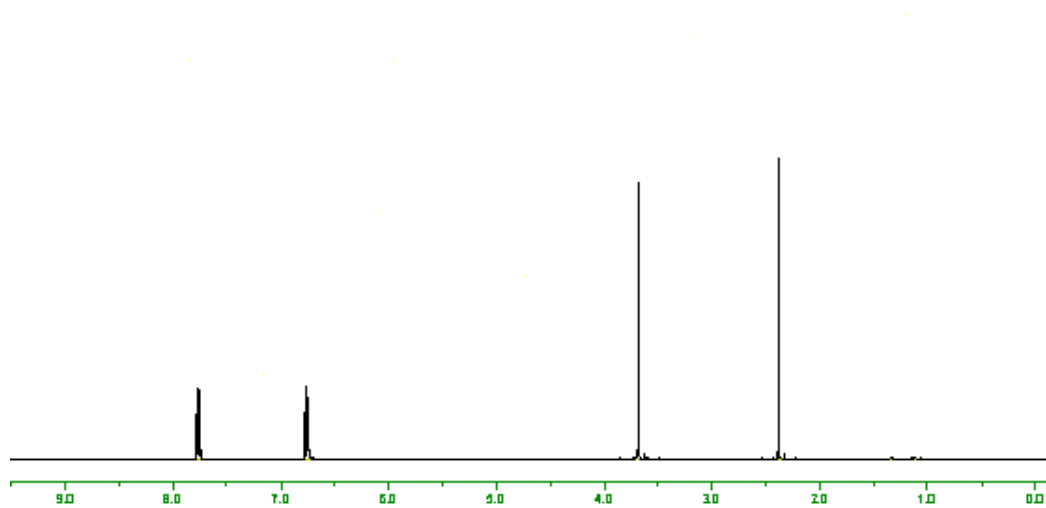
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.6 MHz)



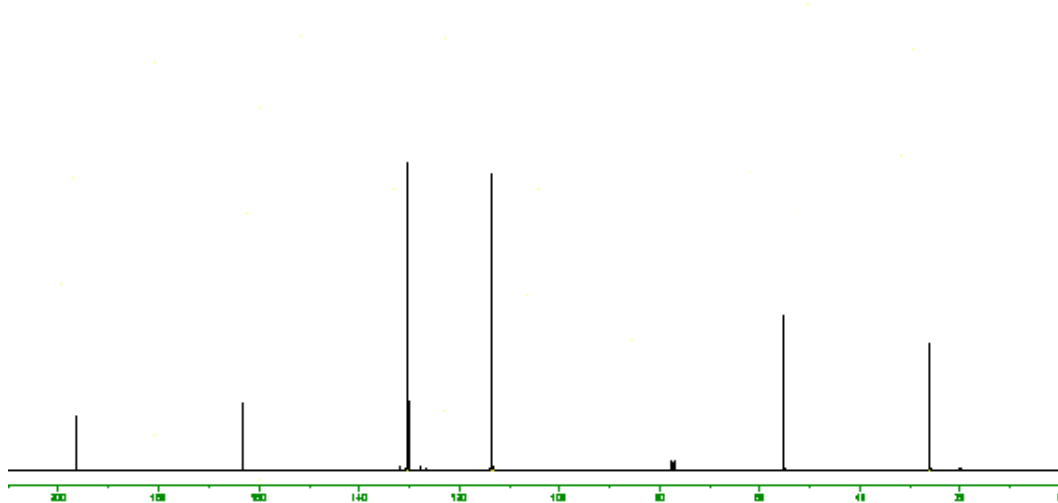
* denotes $t\text{-BuOH}$.

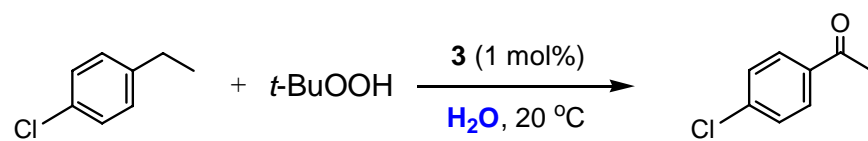


^1H NMR (CDCl_3 , 400 MHz)

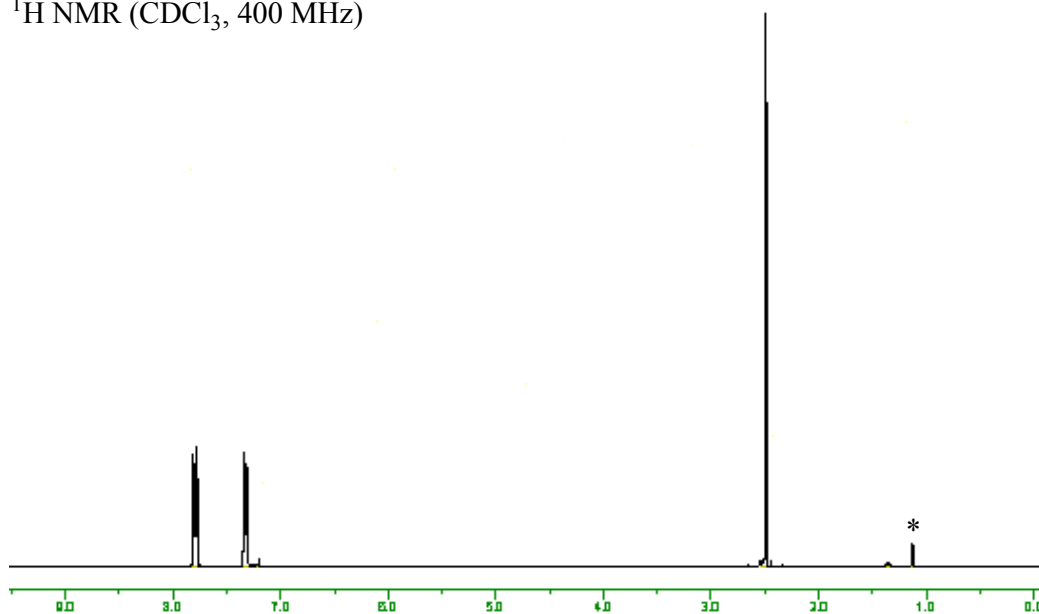


$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.6 MHz)

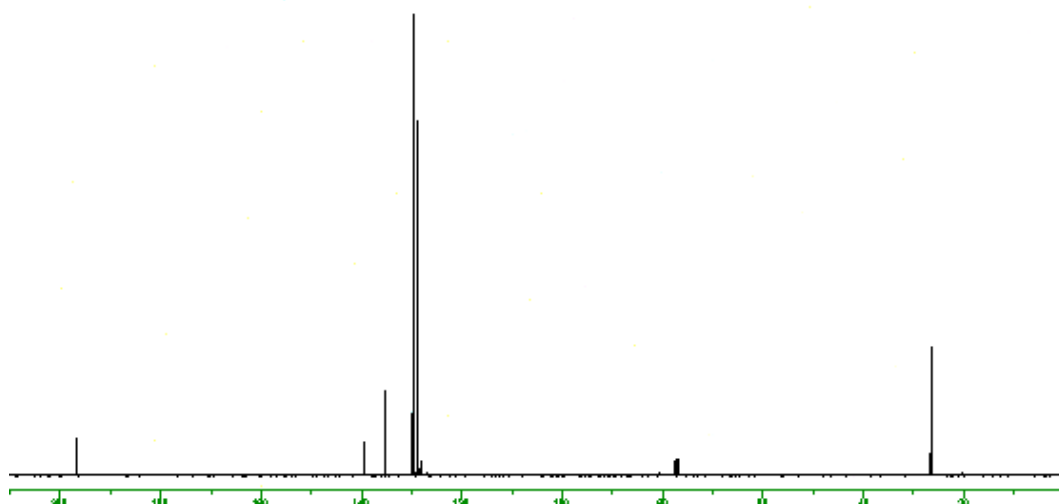




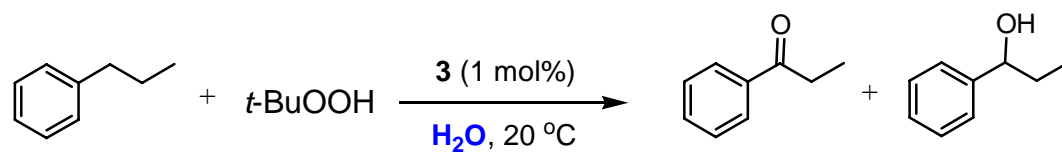
^1H NMR (CDCl_3 , 400 MHz)



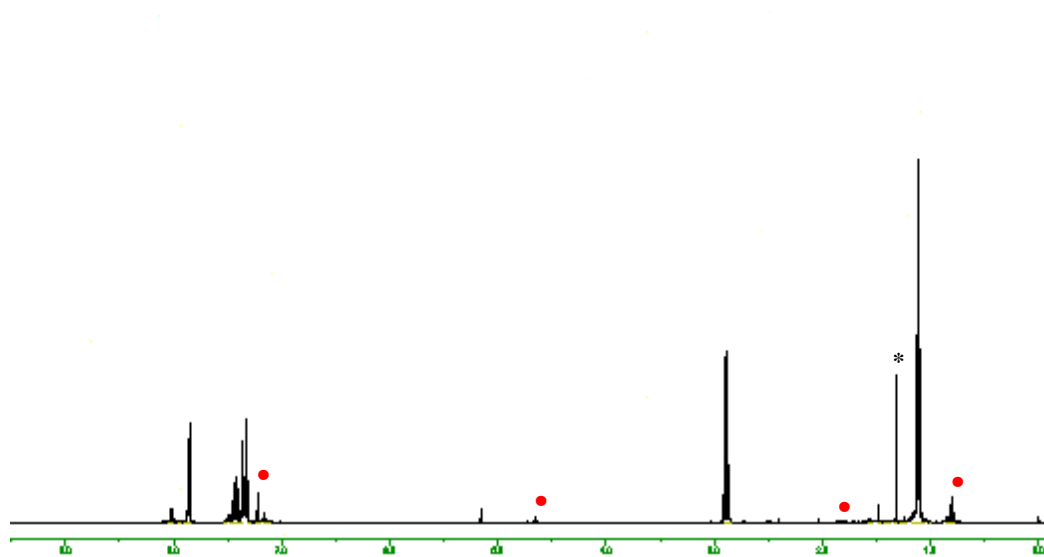
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.6 MHz)



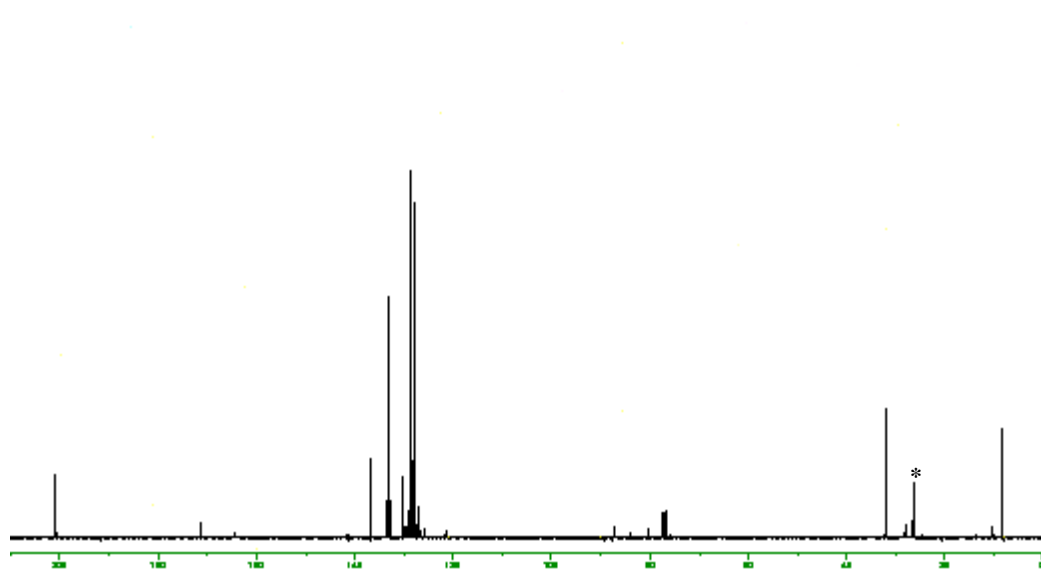
* denotes *t*-BuOH.



^1H NMR (CDCl_3 , 400 MHz)

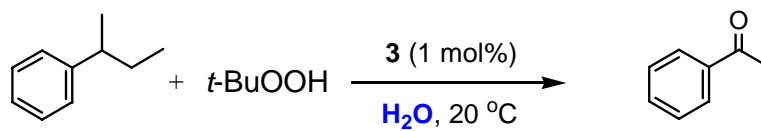


$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.6 MHz)

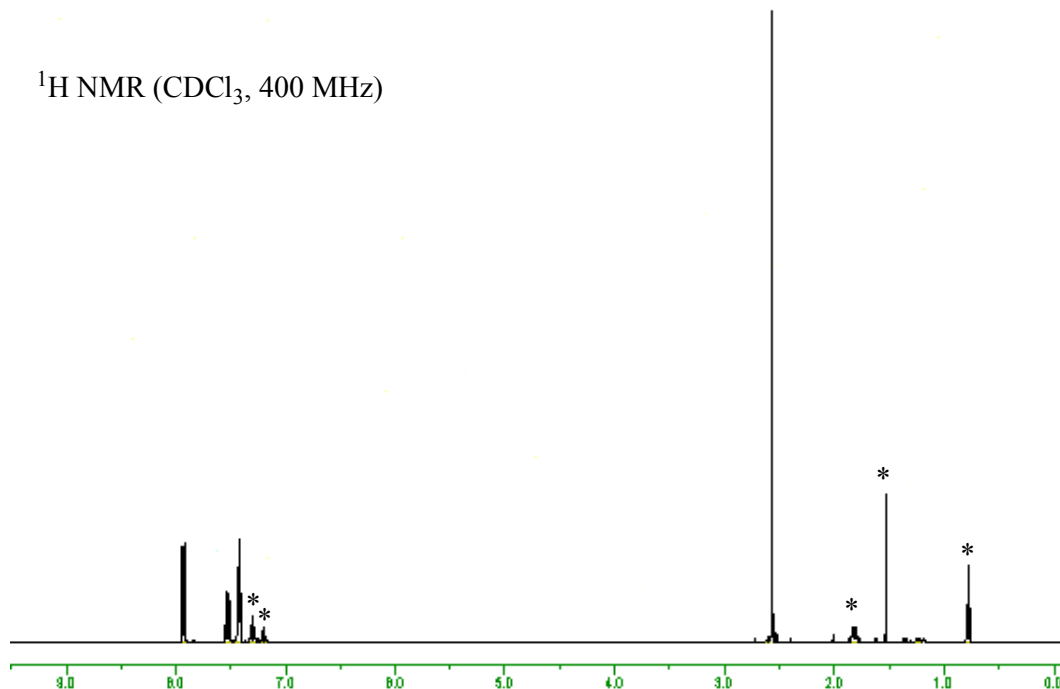


• denotes alcohol product.

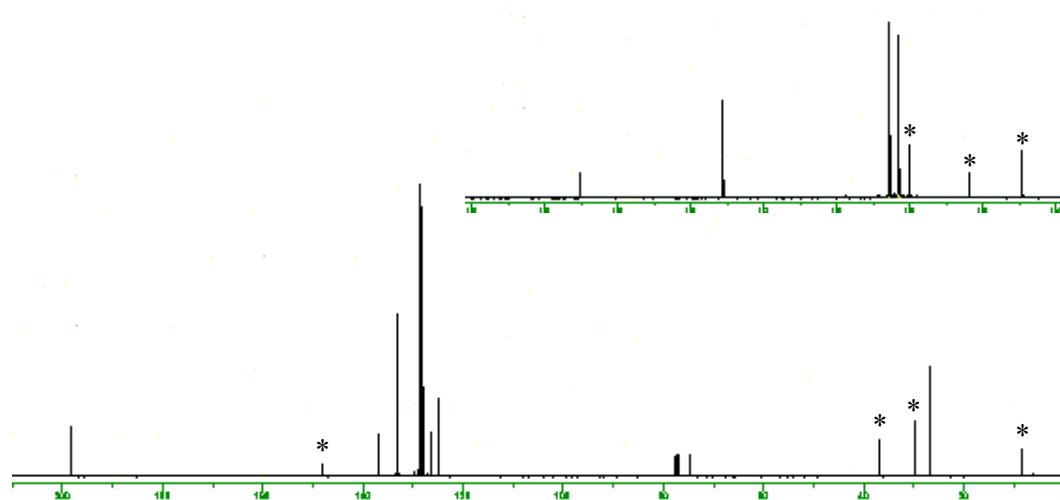
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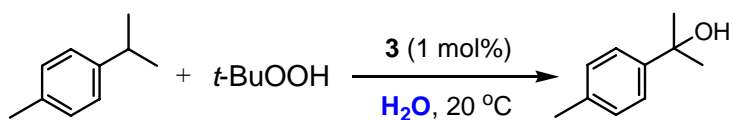
^1H NMR (CDCl_3 , 400 MHz)



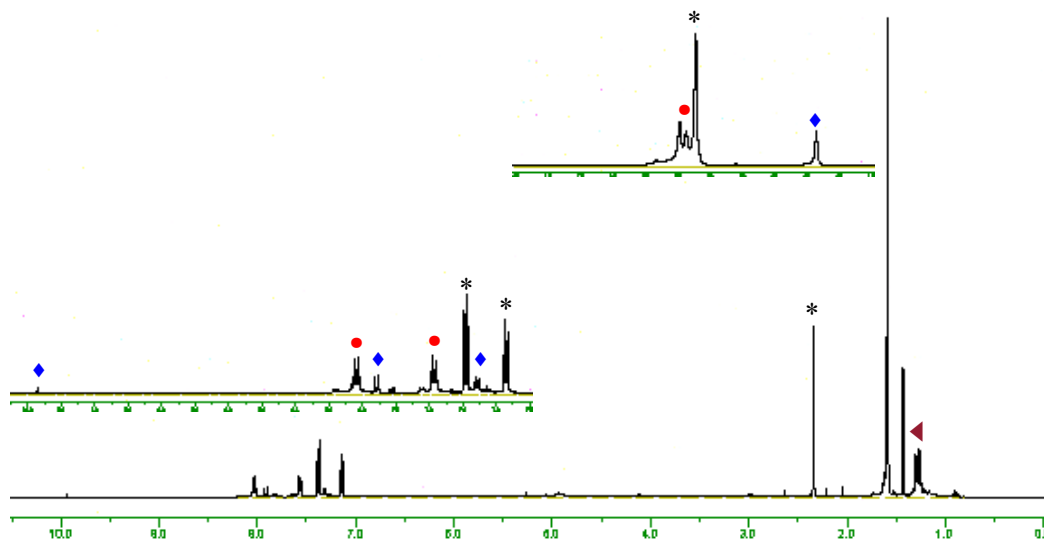
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.6 MHz)



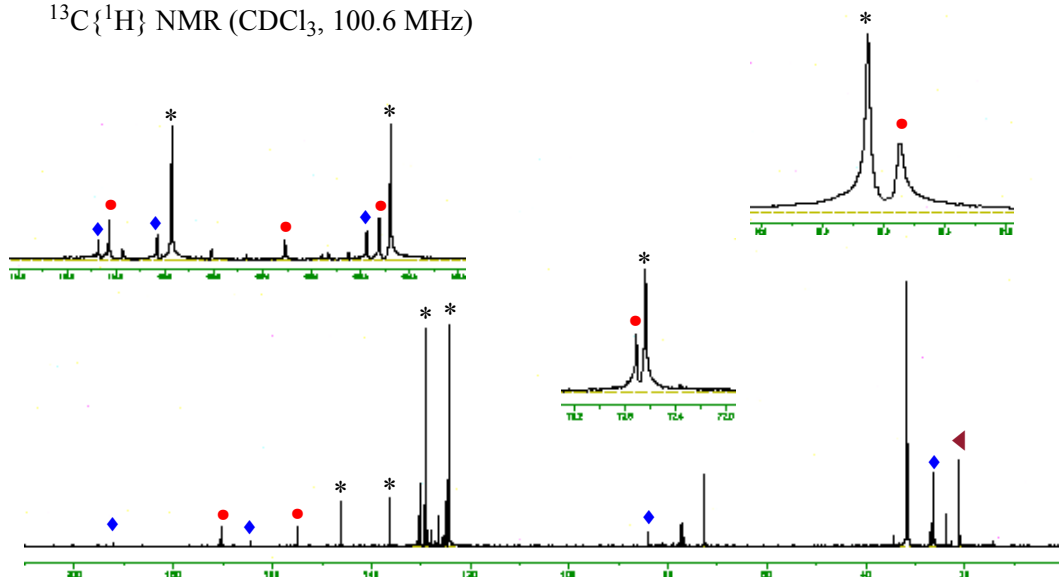
* denotes *sec*-Butylbenzene



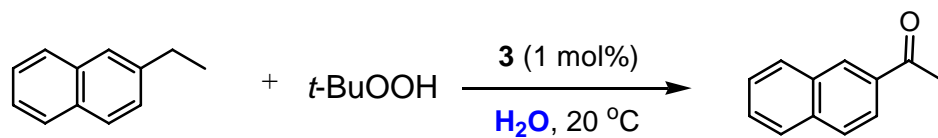
^1H NMR (CDCl_3 , 400 MHz)



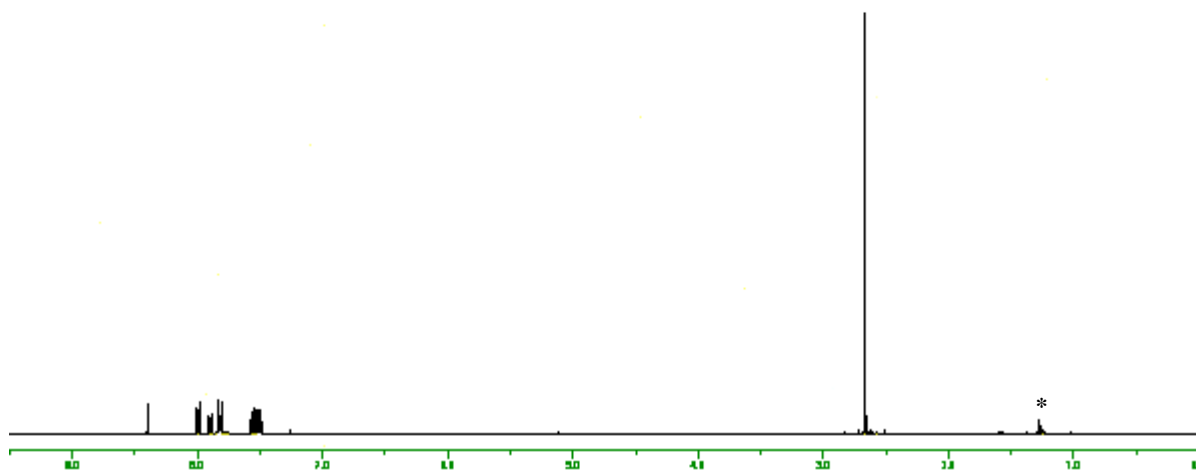
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.6 MHz)



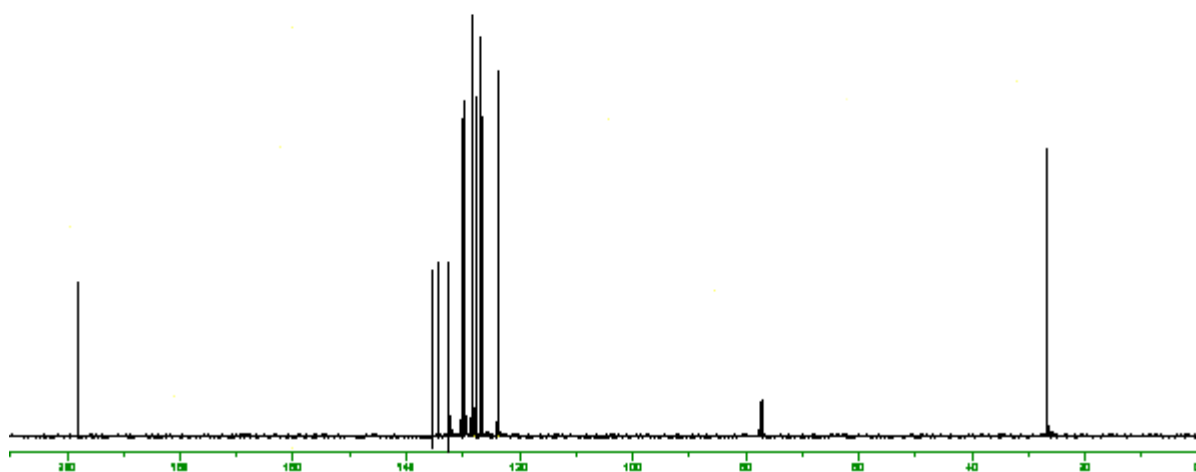
- * denotes *p*, α , α -trimethylbenzyl alcohol
- ♦ denotes 4-(1-hydroxy-1-methylethyl)benzaldehyde
- denotes 4-(1-hydroxy-1-methylethyl)benzoic acid
- ▲ denotes *t*-BuOH



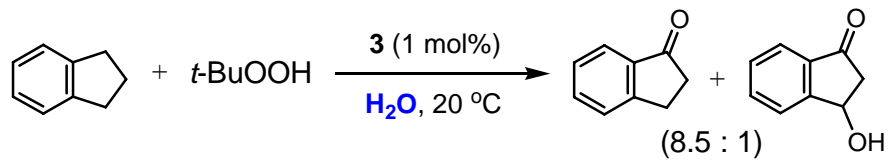
^1H NMR (CDCl_3 , 400 MHz)



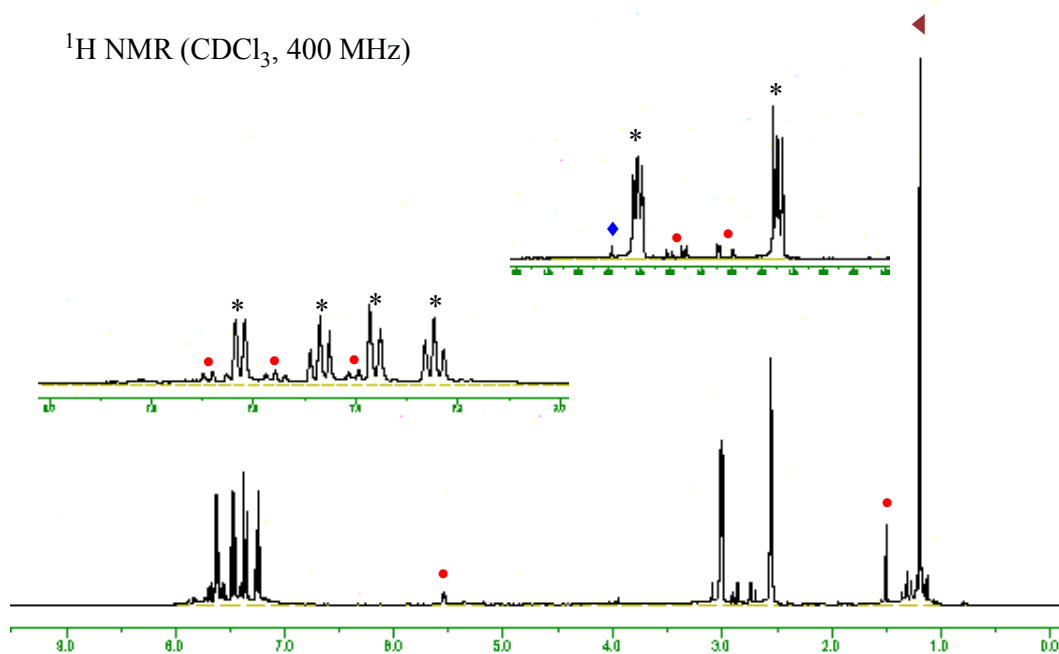
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.6 MHz)



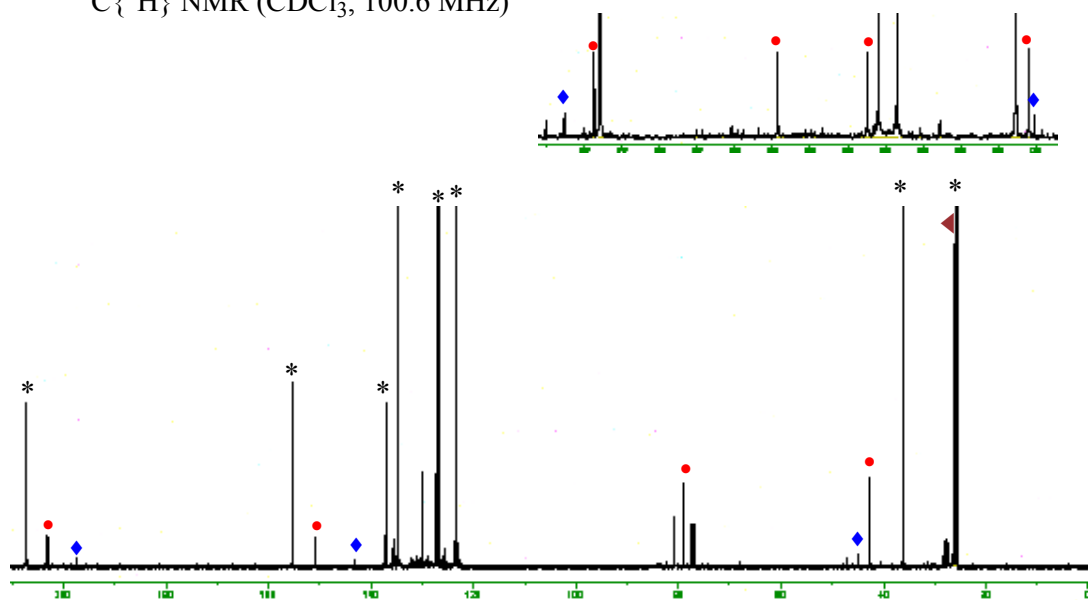
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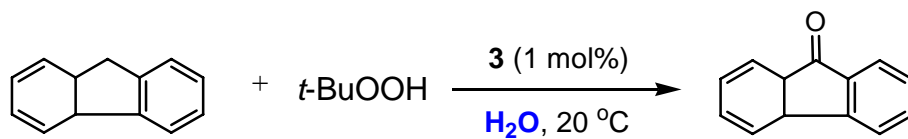
^1H NMR (CDCl_3 , 400 MHz)



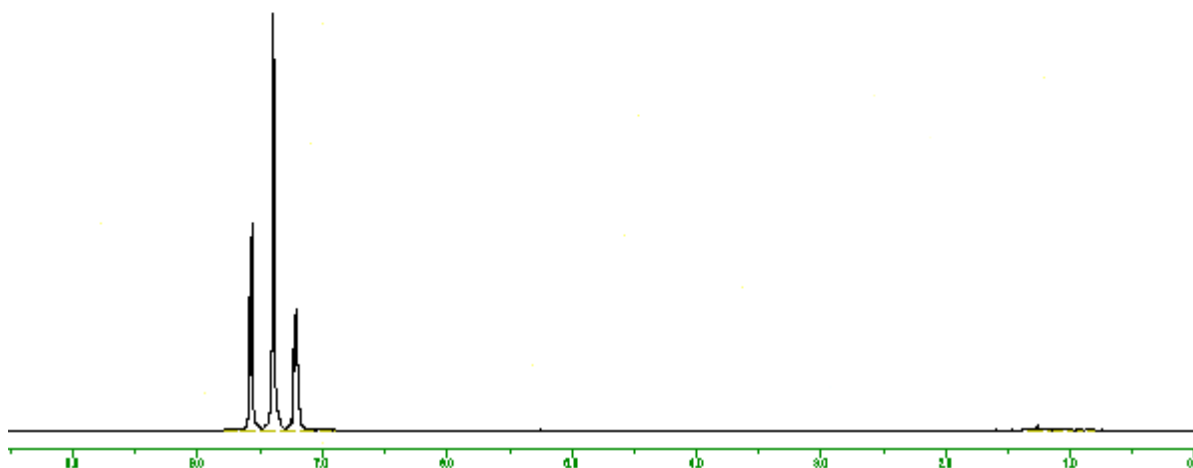
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.6 MHz)



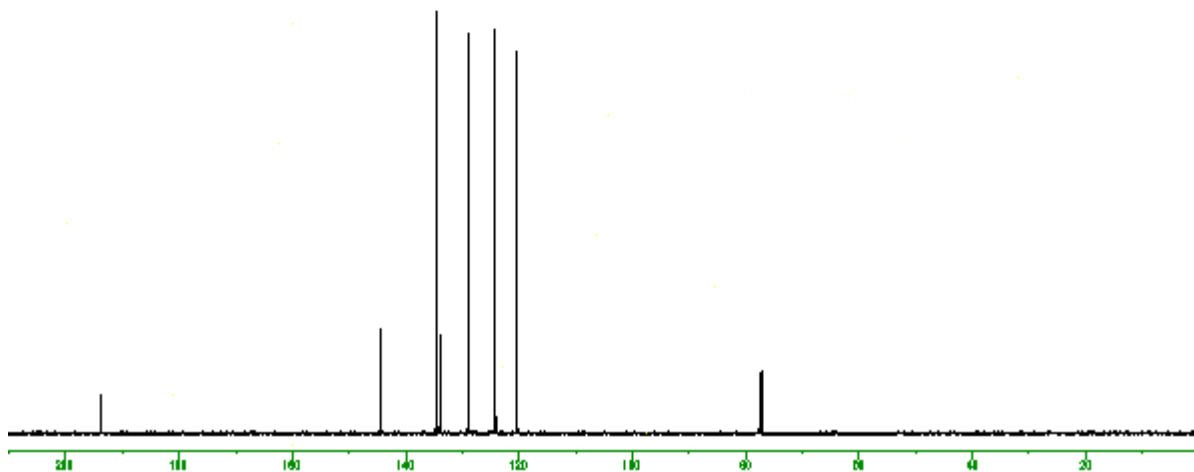
- * denotes 1-indanone
- denotes 3-hydroxy-1-indanone
- ♦ denotes 1,3-indandione
- ◄ denotes $t\text{-BuOH}$

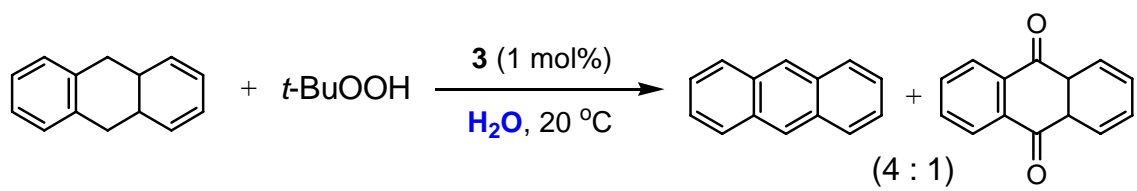


^1H NMR (CDCl_3 , 400 MHz)

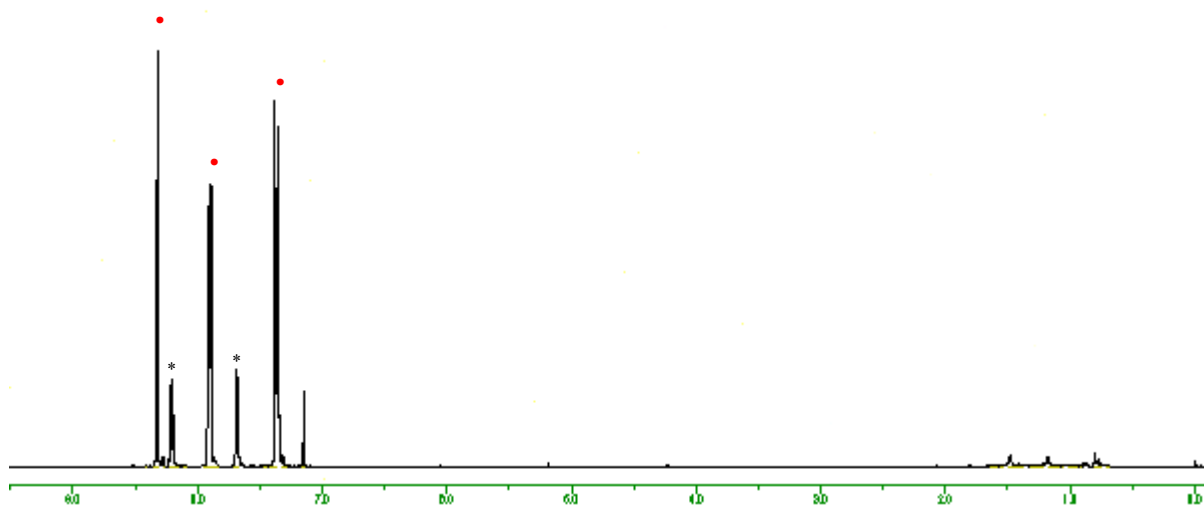


$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.6 MHz)

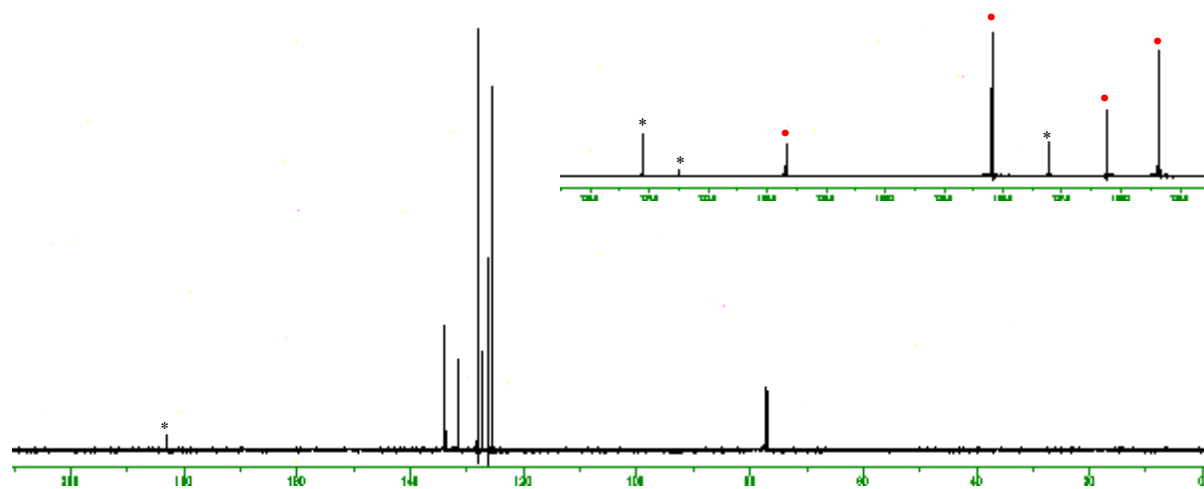




^1H NMR (CDCl_3 , 400 MHz)

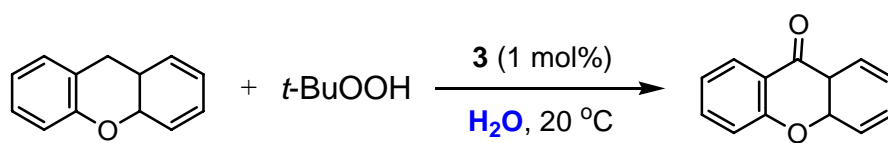


$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.6 MHz)

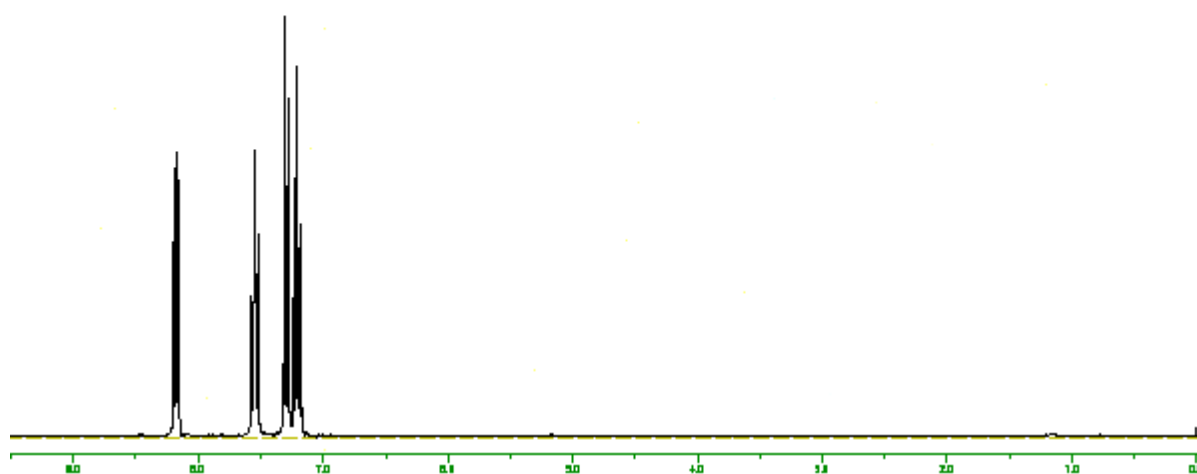


• denotes anthracene

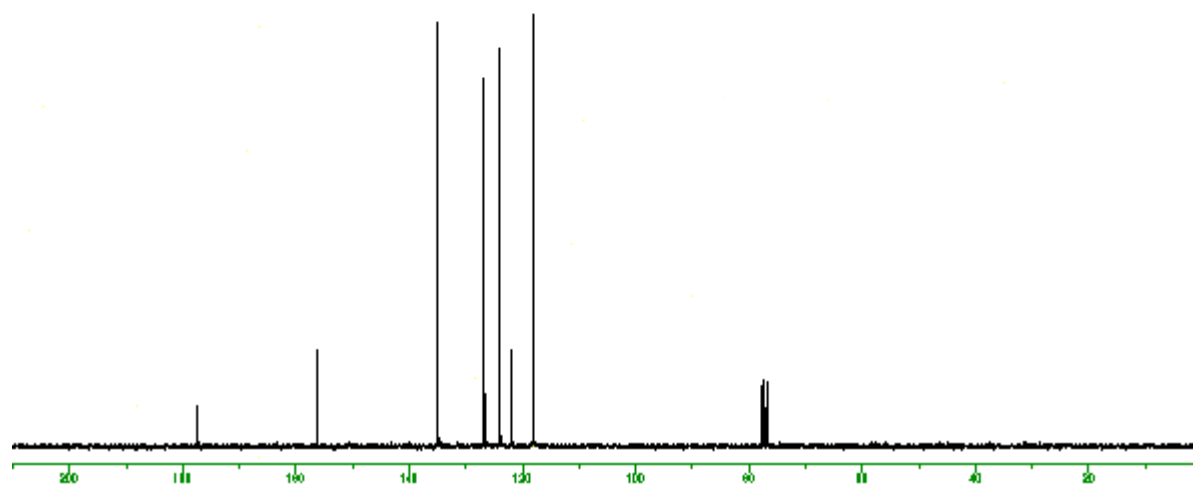
* denotes 1,4-dihydroanthraquinone

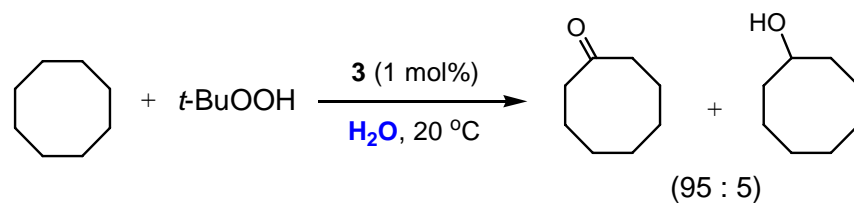


^1H NMR (CDCl_3 , 400 MHz)

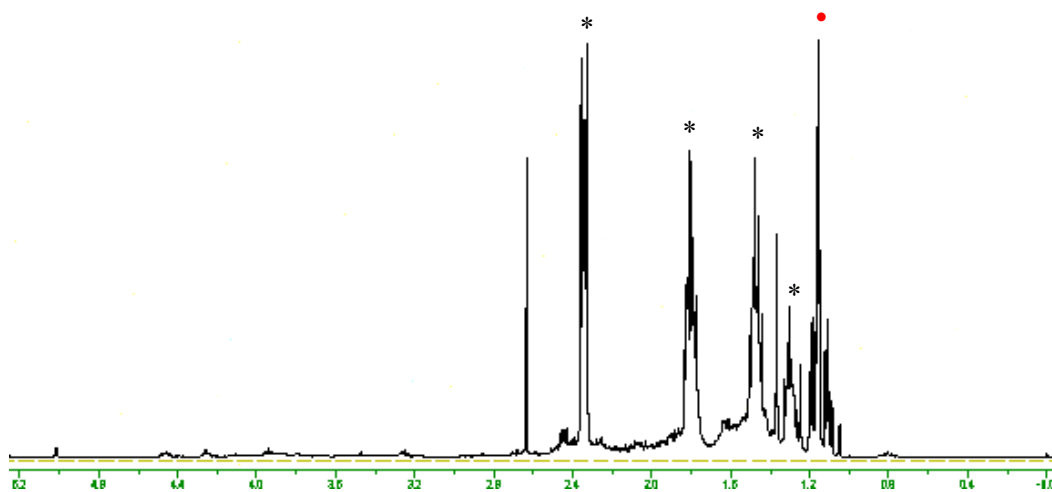


$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.6 MHz)

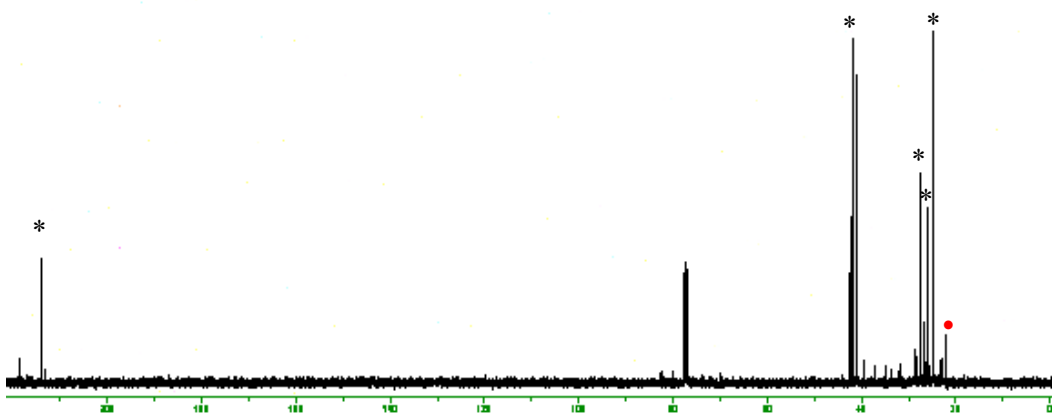




^1H NMR (CDCl_3 , 400 MHz)



$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.6 MHz)



* denotes cyclooctanone

• denotes $t\text{-BuOH}$

contains cyclooctanol and diketons