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Room temperature $Fe(NO_3)_3 \cdot 9H_2O$/TEMPO/NaCl-catalyzed aerobic oxidation of homopropargylic alcohols

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ABSTRACT

A practical and eco-friendly aerobic oxidation of homopropargylic alcohols using $Fe(NO_3)_3 \cdot 9H_2O$/TEMPO/NaCl as catalysts at room temperature under atmospheric pressure was developed affording corresponding homopropargylic ketones with moderate to good yields. Aryl, heteroaryl as well as alkyl 1,2-allenic ketones were obtained by the isomerization of corresponding terminal homopropargylic ketones through column chromatographic workup on silica gel.

1. Introduction

Numerous oxidation methods towards alcohols have been reported using at least a stoichiometric amount of oxidants, such as MnO_2, chromium oxides, DMSO as well as hypervalent iodine compounds in literature.[1] However, those conventional oxidants would produce almost the same amount of oxidant-derived waste causing serious environmental problems. As a mild and natural terminal oxidant, molecular oxygen would be the best alternative from the viewpoint of eco-friendly and economic advantages.[2] On the other hand, 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) has been reported as the catalyst to oxidize alcohols with various oxidants including molecular oxygen in literature.[3] Therefore, developing novel protocol for the oxidation of alcohols using molecular oxygen as terminal oxidant under mild conditions is highly required.

Homopropargylic ketones, which could be easily isomerized to allenic ketones, could be synthesized by the oxidation of corresponding alcohols, and there are few reports for this transformation using at least stoichiometric amount of oxidants.[4–7] In 1992, Marshall and co-workers reported the oxidation of homopropargylic alcohols by Dess–Martin reagent or Swern oxidation followed by a basic workup to afford corresponding allenic ketones in good yields;[4] In 1998, Hashmi and co-workers found that oxidation of homopropargylic alcohols by Dess–Martin reagent followed by a chromatographic workup on silica gel would also yield allenic ketones conveniently in good yields;[5] Fan's group have developed a $RuCl_3$-catalyzed protocol using TBHP as terminal oxidant in [bmin]PF_6 at 80 °C to afford allenic ketones in moderate yields;[6] Alsters[7a] and Fan[7b] have developed two different Cr-catalyzed protocols for the oxidation of homopropargylic alcohols affording corresponding allenic ketones with good yields independently. However, as far as we know, there is no catalytic aerobic oxidation protocol for such transformation reported in literature.

Recently, this group has established a general protocol for the aerobic oxidation of alcohols bearing a wide range of substrates especially for propargylic alcohols under mild conditions using $Fe(NO_3)_3 \cdot 9H_2O$/TEMPO/NaCl as catalyst, yielding corresponding aldehydes or ketones in good to excellent yields.[8] Therefore, we wish to investigate the application of this green and efficient protocol for the oxidation of homopropargylic alcohols (Scheme 1).

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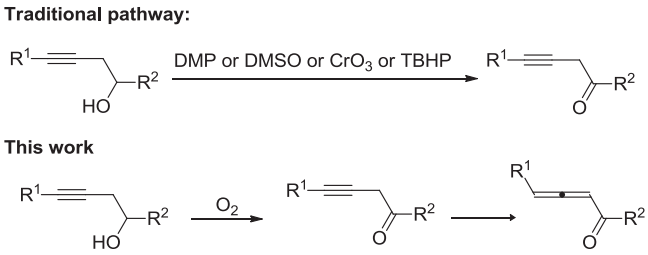
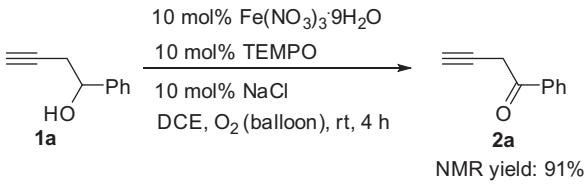


Scheme 1. Oxidation of homopropargylic alcohols.

2. Results and discussion

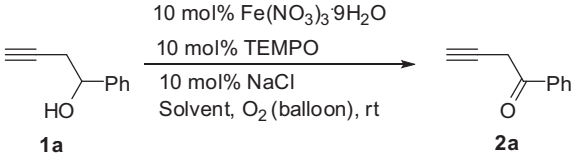
We have initially tried this aerobic oxidation of 1-phenyl-butyl-3-yl-1-ol (Scheme 2). To our surprise, when 10 mol % $Fe(NO_3)_3\cdot 9H_2O$, 10 mol % TEMPO, and 10 mol % NaCl (the role of Cl^- in this reaction is not quite clear yet, it is probably working as a ligand to Fe^{3+} to accelerate the oxidation[8a]) were used, this reaction could work smoothly at room temperature under atmospheric pressure of molecular oxygen affording corresponding homopropargylic ketone **2a** in 91% NMR yield.



Scheme 2. Initial trail of the iron-catalyzed aerobic oxidation of 1-phenyl-butyl-3-yl-1-ol.

Based on this observation, we tried to optimize the reaction conditions based on solvent effect, catalyst loading as well as different nitrate, the results were summarized in Table 1. Compared to toluene, ethyl acetate, and THF, the full conversion and highest NMR yield could be achieved when using DCE as solvent (Table 1, entries 1–4). Lowering the catalyst to 5 mol % each of $Fe(NO_3)_3\cdot 9H_2O$/TEMPO/NaCl, only 76% NMR yield of **2a** and 14% recovery of homopropargylic alcohol in 20 h was observed (Table 1, entry 5). When $Cu(NO_3)_2\cdot 3H_2O$ was used instead of $Fe(NO_3)_3\cdot 9H_2O$, the yield was obviously lower (Table 1, entry 6).

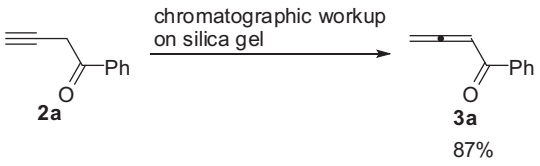
Table 1
Optimization of the aerobic oxidation of 1-phenyl-butyl-3-yl-1-ol (**1a**)



Entry	Solvent	Time (h)	Yield of **2a** (%, NMR)	Recovery of **1a** (%, NMR)
1	**DCE**	**4**	91	—
2	Toluene	20	89	4
3	Ethyl acetate	20	52	26
4	THF	20	25	73
5[a]	DCE	20	76	14
6[b]	DCE	20	52	36

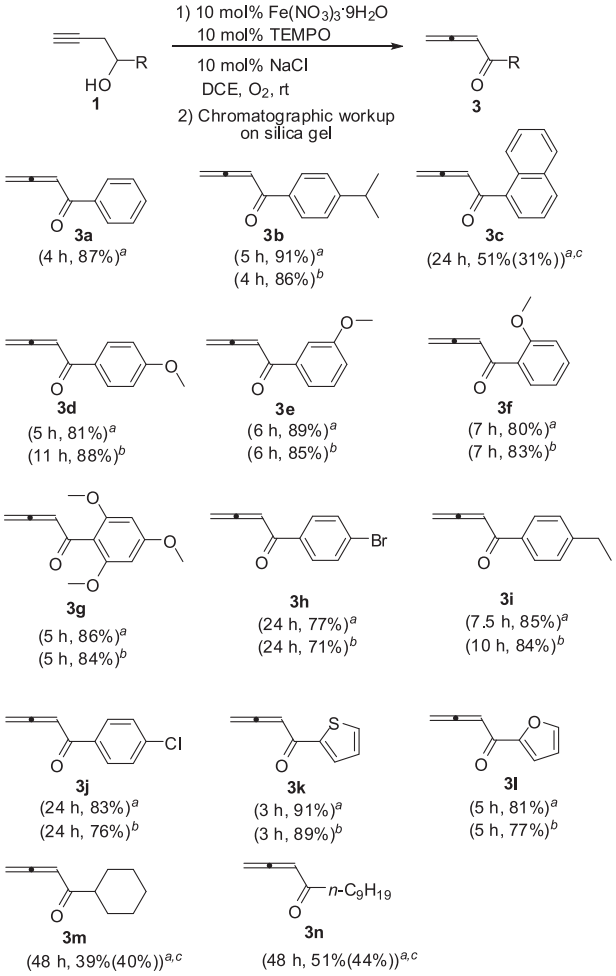
[a] 5 mol % each of the three catalysts were used here.
[b] $Cu(NO_3)_2\cdot 3H_2O$ was used instead of $Fe(NO_3)_3\cdot 9H_2O$.

Interestingly, after chromatographic workup procedure allenic ketone **3a** was isolated in 87% (Scheme 3).[4,5]



Scheme 3. Isomerization of the homopropargylic ketone.

We defined 10 mol % $Fe(NO_3)_3\cdot 9H_2O$, 10 mol % TEMPO, and 10 mol % NaCl in DCE at room temperature under atmospheric pressure for the aerobic oxidation of the homopropargylic alcohols followed by the chromatographic workup on silica gel as standard procedure for study on the substrate scope of various terminal homopropargylic alcohols. The results are summarized in Scheme 4. When R=Ph, *p*-$C_2H_5C_6H_4$, *p*-^{i}PrC$_6$H$_4$, *p*-ClC$_6$H$_4$, *p*-BrC$_6$H$_4$, *o*-MeO, *m*-MeO, *p*-MeO, or 2, 4, 6-$(MeO)_3$, the substrates were efficiently oxidized and isomerized to corresponding allenic ketones (**3a**, **b**, **d**–**j**). It was worth noting that when R=heteroaryl groups, such as 2-thienyl and 2-furyl, the corresponding allenic ketones could also be obtained with good yields (**3k** and **3l**). When

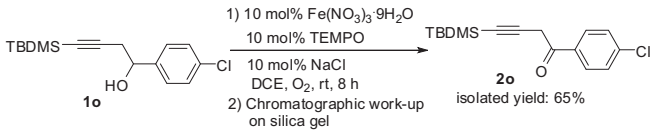


[a] 1 mmol of substrate, 10 mol% each of $Fe(NO_3)_3\cdot 9H_2O$, TEMPO and NaCl in DCE (4 mL); [b] 5 mmol of substrate, 10 mol% each of $Fe(NO_3)_3\cdot 9H_2O$, TEMPO and NaCl in DCE (5 mL); [c] Recovery of alcohol by NMR analysis in the parenthesis.

Scheme 4. The scope of aerobic oxidation of homopropargylic alcohols.

R=naphthyl, *c*-hexyl, and alkyl, moderate yields of the corresponding allenic ketones could be obtained (**3c**, **m**, and **n**).

We next investigated on the oxidation of non-terminal single-substituted homopropargylic alcohols (Scheme 5). TBDMS protected-homopropargylic alcohols **1o** could be oxidized to corresponding homopropargylic ketone **2o** in a moderate yield. Interestingly, there was no isomerized product observed after chromatographic workup on silica gel, this might be due to its steric hindrance of the protecting group.



Scheme 5. Aerobic oxidation of the TBDMS protected-homopropargylic alcohols.

3. Conclusions

In summary, we have developed a mild and eco-friendly protocol for the aerobic oxidation of homopropargylic alcohols using $Fe(NO_3)_3\cdot 9H_2O$/TEMPO/NaCl as catalysts to synthesize allenic ketones or homopropargylic ketones with moderate to good yields depending on the nature of substrate (sp-substitution).

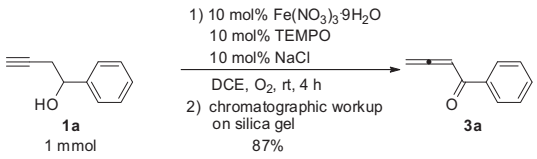
4. Experimental section

4.1. General information

^1H and ^{13}C NMR spectra were recorded with an instrument operated at 300 MHz for ^1H NMR and 75 MHz for ^{13}C NMR in $CDCl_3$. Chemical shifts (δ) are given in parts per million (ppm). Infrared spectra were recorded on an FTIR spectrometer. Mass spectra were recorded in EI mode. HRMS spectra were recorded in EI mode. The starting materials **1a**–**o** were synthesized according to the literature.[9]

4.2. Synthesis of 3a–n and 2o

4.2.1. 1-Phenylbuta-2,3-dien-1-one (*3a*).

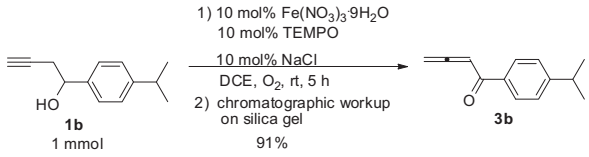


Typical procedure: To a 10 mL three-necked flask were added $Fe(NO_3)_3\cdot 9H_2O$ (40.2 mg, 0.1 mmol), TEMPO (15.8 mg, 0.1 mmol), NaCl (6.0 mg, 0.1 mmol), and DCE (4 mL). 1-Phenylbut-3-yn-1-ol **1a** (144.7 mg, 1.0 mmol) was then added to the suspension and the resulting mixture was placed under the atmosphere of oxygen from a balloon and stirred at room temperature until the reaction was complete as monitored by TLC (eluent: petroleum ether/ethyl acetate=10:1). Mesitylene (46 μl) was added for crude NMR analysis. The resulting mixture was purified by column chromatography on silica gel (petroleum ether/diethyl ether=10/1) to afford 1-phenylbuta-2,3-dien-1-one[10] **3a** (124.7 mg, 87%) (eluent: petroleum ether/diethyl ether=20/1) as an oil.

^1H NMR (300 MHz, $CDCl_3$) δ 7.93–7.86 (m, 2H, Ar–H), 7.58–7.52 (m, 1H, Ar–H), 7.44 (t, J=7.5 Hz, 2H, Ar–H), 6.44 (t, J=6.5 Hz, 1H, HC=C=C), 5.25 (d, J=6.6 Hz, 2H, C=C=CH_2); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 217.1, 191.0, 137.4, 132.8, 128.7, 128.3, 93.2, 79.2; IR (neat) 2987, 1960, 1932, 1649, 1596, 1578, 1448, 1416, 1348, 1276, 1214 cm^{-1}; MS (EI) m/z 144 (M^+, 9.33), 105 (100).

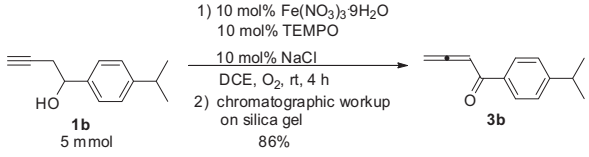
The following compounds (**3b**–**n**, **2o**) were prepared according to **3a**.

4.2.2. 1-(4-Isopropylphenyl)buta-2,3-dien-1-one (*3b*).



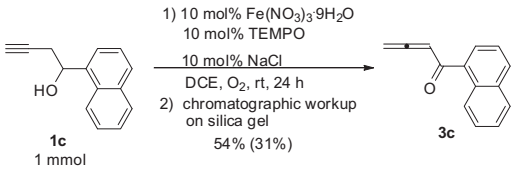
The reaction of 1-(4-isopropylphenyl)but-3-yn-1-ol **1b** (187.1 mg, 1.0 mmol), $Fe(NO_3)_3\cdot 9H_2O$ (40.6 mg, 0.1 mmol), TEMPO (15.5 mg, 0.1 mmol), and NaCl (5.8 mg, 0.1 mmol) in DCE (4 mL) afforded 1-(4-isopropylphenyl)buta-2,3-dien-1-one **3b** (167.7 mg, 91%) (eluent: petroleum ether/diethyl ether=10/1) as an oil.

^1H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, J=8.1 Hz, 2H, Ar–H), 7.30 (d, J=8.4 Hz, 2H, Ar–H), 6.45 (t, J=6.6 Hz, 1H, HC=C=C), 5.25 (d, J=6.6 Hz, 2H, C=C=CH_2), 3.20–2.89 (m, 1H, CH), 1.27 (d, J=6.6 Hz, 6H, CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 216.8, 190.4, 154.4, 135.2, 128.9, 126.5, 93.1, 79.1, 34.2, 23.6; IR (neat) 2962, 1961, 1933, 1650, 1606, 1568, 1463, 1419, 1350, 1277, 1221, 1186, 1094, 1056 cm^{-1}; MS (EI) m/z 186 (M^+, 6.61), 147 (100); HRMS calcd for $C_{13}H_{14}O$ (M^+): 186.1045; found: 186.1046.



The reaction of 1-(4-isopropylphenyl)but-3-yn-1-ol **1b** (943.8 mg, 5.0 mmol), $Fe(NO_3)_3\cdot 9H_2O$ (202.7 mg, 0.5 mmol), TEMPO (78.5 mg, 0.5 mmol), and NaCl (28.4 mg, 0.5 mmol) in DCE (5 mL) afforded 1-(4-isopropylphenyl)buta-2,3-dien-1-one **3b** (800.8 mg, 86%) (eluent: petroleum ether/diethyl ether=10/1) as an oil.

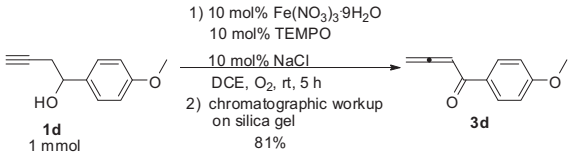
4.2.3. 1-(Naphth-1-yl)buta-2,3-dien-1-one (*3c*).



The reaction of 1-(naphthalen-1-yl)but-3-yn-1-ol **1c** (196.6 mg, 1.0 mmol), $Fe(NO_3)_3\cdot 9H_2O$ (41.0 mg, 0.1 mmol), TEMPO (15.5 mg, 0.1 mmol), and NaCl (6.0 mg, 0.1 mmol) in DCE (4 mL) afforded 1-(naphthalen-1-yl)buta-2,3-dien-1-one[11] **3c** (105.2 mg, 54%) (eluent: petroleum ether/diethyl ether=10/1) as an oil (31% of the starting material by NMR analysis).

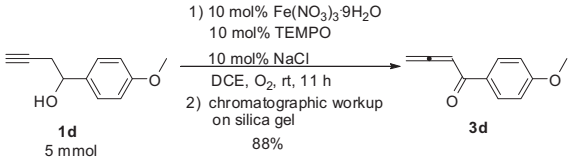
^1H NMR (300 MHz, $CDCl_3$) δ 8.35 (d, J=8.4 Hz, 1H, Ar–H), 7.94 (d, J=8.4 Hz, 1H, Ar–H), 7.90–7.83 (m, 1H, Ar–H), 7.72 (dd, J_1=7.1 Hz, J_2=1.1 Hz, 1H, Ar–H), 7.60–7.42 (m, 3H, Ar–H), 6.38 (t, J=6.5 Hz, 1H, HC=C=C), 5.08 (d, J=6.3 Hz, 2H, C=C=CH_2); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 217.8, 194.9, 135.6, 133.6, 131.6, 130.2, 128.2, 127.4, 127.3, 126.2, 125.3, 124.0, 97.1, 79.2; IR (neat) 1958, 1932, 1649, 1508, 1282, 1247, 1191, 1132 cm^{-1}; MS (EI) m/z 194 (M^+, 28.97), 127 (100).

*4.2.4. 1-(4-Methoxyphenyl)buta-2,3-dien-1-one (**3d**).*



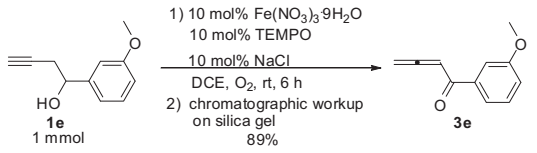
The reaction of 1-(4-methoxyphenyl)but-3-yn-1-ol **1d** (176.7 mg, 1.0 mmol), $Fe(NO_3)_3\cdot 9H_2O$ (40.4 mg, 0.1 mmol), TEMPO (15.7 mg, 0.1 mmol), and NaCl (5.6 mg, 0.1 mmol) in DCE (4 mL) afforded 1-(4-methoxyphenyl)buta-2,3-dien-1-one[11] **3d** (142.1 mg, 81%) (eluent: petroleum ether/diethyl ether=10/1) as a white solid: mp 54–55 °C (*n*-hexane/ethyl acetate).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (dt, J_1=9.2 Hz, J_2=2.5 Hz, 2H, Ar–H), 6.93 (dt, J_1=9.4 Hz, J_2=2.4 Hz, 2H, Ar–H), 6.44 (t, J=6.6 Hz, 1H, C=C=CH), 5.24 (d, J=6.6 Hz, 2H, C=C=CH_2), 3.86 (s, 3H, CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 216.5, 189.0, 163.4, 131.0, 130.3, 113.6, 92.8, 79.0, 55.4; IR (neat) 2976, 1957, 1924, 1642, 1591, 1508, 1421, 1351, 1260, 1220, 1170, 1094, 1026 cm^{-1}; MS (EI) *m*/*z* 174 (M^+, 2.82), 63 (100).



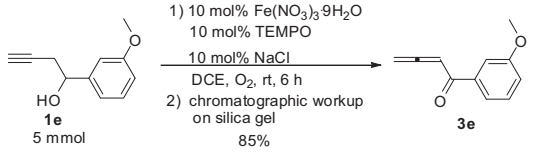
The reaction of 1-(4-methoxyphenyl)but-3-yn-1-ol **1d** (881.5 mg, 5.0 mmol), $Fe(NO_3)_3\cdot 9H_2O$ (202.0 mg, 0.5 mmol), TEMPO (78.9 mg, 0.5 mmol), and NaCl (29.2 mg, 0.5 mmol) in DCE (5 mL) afforded 1-(4-methoxyphenyl)buta-2,3-dien-1-one **3d** (768.1 mg, 88%) (eluent: petroleum ether/diethyl ether=10/1) as a white solid.

*4.2.5. 1-(3-Methoxyphenyl)buta-2,3-dien-1-one (**3e**).*



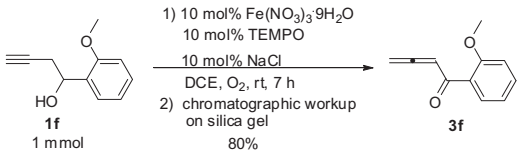
The reaction of 1-(3-methoxyphenyl)but-3-yn-1-ol **1e** (174.8 mg, 1.0 mmol), $Fe(NO_3)_3\cdot 9H_2O$ (40.6 mg, 0.1 mmol), TEMPO (15.4 mg, 0.1 mmol), and NaCl (6.0 mg, 0.1 mmol) in DCE (4 mL) afforded 1-(3-methoxyphenyl)buta-2,3-dien-1-one[5b] **3e** (153.1 mg, 89%) (petroleum ether/diethyl ether=10/1) as an oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, J=7.8 Hz, 1H, Ar–H), 7.41 (t, J=2.0 Hz, 1H, Ar–H), 7.34 (t, J=7.8 Hz, 1H, Ar–H), 7.09 (dd, J_1=8.1 Hz, J_2=2.4 Hz, 1H, Ar–H), 6.43 (t, J=6.6 Hz, 1H, HC=C=C), 5.25 (d, J=6.9 Hz, 2H, C=C=CH_2), 3.83 (s, 3H, OCH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 217.0, 190.6, 159.6, 138.7, 129.3, 121.2, 119.2, 113.0, 93.2, 79.2, 55.3; IR (neat) 1959, 1933, 1654, 1595, 1581, 1486, 1452, 1429, 1286, 1259, 1037 cm^{-1}; MS (EI) *m*/*z* 174 (M^+, 51.12), 135 (100).



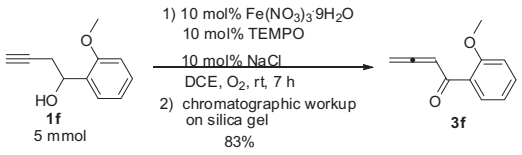
The reaction of 1-(3-methoxyphenyl)but-3-yn-1-ol **1e** (834.1 mg, 5.0 mmol), $Fe(NO_3)_3\cdot 9H_2O$ (201.5 mg, 0.5 mmol), TEMPO (77.6 mg, 0.5 mmol), and NaCl (28.5 mg, 0.5 mmol) in DCE (5 mL) afforded 1-(3-methoxyphenyl)buta-2,3-dien-1-one **3e** (703.3 mg, 85%) (eluent: petroleum ether/diethyl ether=10/1) as an oil.

*4.2.6. 1-(2-Methoxyphenyl)buta-2,3-dien-1-one (**3f**).*



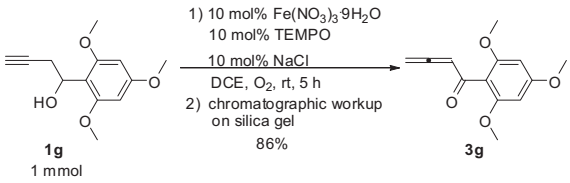
The reaction of 1-(2-methoxyphenyl)but-3-yn-1-ol **1f** (174.5 mg, 1.0 mmol), $Fe(NO_3)_3\cdot 9H_2O$ (41.0 mg, 0.1 mmol), TEMPO (15.4 mg, 0.1 mmol), and NaCl (6.0 mg, 0.1 mmol) in DCE (4 mL) afforded 1-(2-methoxyphenyl)buta-2,3-dien-1-one **3f** (137.3 mg, 80%) (eluent: petroleum ether/diethyl ether=5/1) as an oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (dd, J_1=7.7 Hz, J_2=2.0 Hz, 1H, Ar–H), 7.44–7.37 (m, 1H, Ar–H), 7.00–6.90 (m, 2H, Ar–H), 6.44 (t, J=6.3 Hz, 1H, HC=C=C), 5.14 (d, J=6.6 Hz, 2H, C=C=CH_2), 3.85 (s, 3H, OCH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 216.9, 192.6, 157.6, 132.7, 129.9, 128.4, 120.3, 111.3, 96.6, 78.9, 55.5; IR (neat) 1959, 1934, 1656, 1598, 1486, 1465, 1436, 1339, 1283, 1246, 1163, 1022 cm^{-1}; MS (EI) *m*/*z* 174 (M^+, 6.55), 135 (100); HRMS calcd for $C_{11}H_{10}O_2$ (M^+): 174.0681; found: 174.0682.



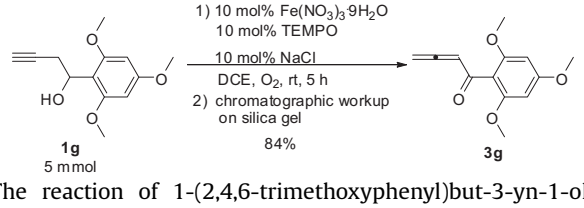
The reaction of 1-(2-methoxyphenyl)but-3-yn-1-ol **1f** (884.6 mg, 5.0 mmol), $Fe(NO_3)_3\cdot 9H_2O$ (202.0 mg, 0.5 mmol), TEMPO (77.9 mg, 0.5 mmol), and NaCl (29.5 mg, 0.5 mmol) in DCE (5 mL) afforded 1-(2-methoxyphenyl)buta-2,3-dien-1-one **3f** (722.0 mg, 83%) (eluent: petroleum ether/diethyl ether=10/1) as an oil.

*4.2.7. 1-(2,4,6-Trimethoxyphenyl)buta-2,3-dien-1-one (**3g**).*



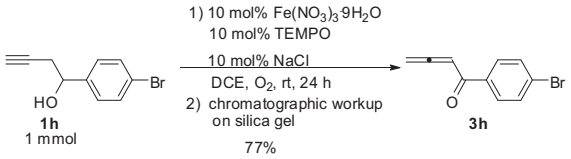
The reaction of 1-(2,4,6-trimethoxyphenyl)but-3-yn-1-ol **1g** (236.0 mg, 1.0 mmol), $Fe(NO_3)_3\cdot 9H_2O$ (39.4 mg, 0.1 mmol), TEMPO (15.5 mg, 0.1 mmol), and NaCl (5.8 mg, 0.1 mmol) in DCE (4 mL) afforded 1-(2,4,6-trimethoxyphenyl)buta-2,3-dien-1-one[11] **3g** (200.9 mg, 86%) (eluent: petroleum ether/diethyl ether=1/1) as a yellow solid: mp 73–74 °C (*n*-hexane/ethyl acetate).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (s, 2H, Ar–H), 6.42 (t, J=6.5 Hz, 1H, HC=C=C), 5.26 (d, J=6.3 Hz, 2H, C=C=CH_2), 3.911 (s, 3H), 3.909 (s, 3H), 3.90 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 216.6, 189.5, 152.9, 142.5, 132.5, 106.3, 93.0, 79.0, 60.9, 56.2; IR (neat) 1939, 1648, 1583, 1504, 1451, 1412, 1337, 1313, 1244, 1226, 1185, 1155, 1125 cm^{-1}; MS (EI) *m*/*z* 234 (M^+, 47.68), 195 (100).



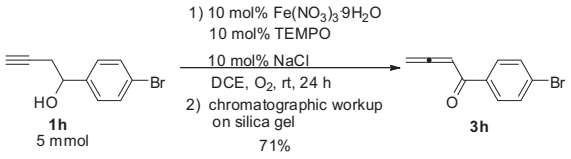
The reaction of 1-(2,4,6-trimethoxyphenyl)but-3-yn-1-ol **1g** (1.1825 g, 5.0 mmol), $Fe(NO_3)_3\cdot 9H_2O$ (200.4 mg, 0.5 mmol), TEMPO (77.7 mg, 0.5 mmol), and NaCl (29.6 mg, 0.5 mmol) in DCE (5 mL) afforded 1-(2,4,6-trimethoxyphenyl)buta-2,3-dien-1-one **3g** (989.9 mg, 84%) (eluent: petroleum ether/diethyl ether=1/1) as a yellow solid.

*4.2.8. 1-(4-Bromophenyl)buta-2,3-dien-1-one (**3h**).*



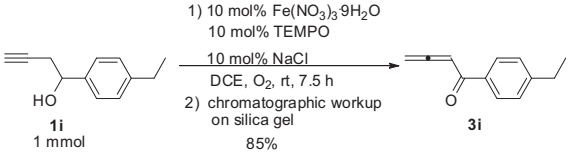
The reaction of 1-(4-bromophenyl)but-3-yn-1-ol **1h** (225.3 mg, 1.0 mmol), $Fe(NO_3)_3\cdot 9H_2O$ (40.7 mg, 0.1 mmol), TEMPO (15.9 mg, 0.1 mmol), and NaCl (6.0 mg, 0.1 mmol) in DCE (4 mL) afforded 1-(4-bromophenyl)buta-2,3-dien-1-one[6] **3h** (172.8 mg, 77%) (eluent: petroleum ether/diethyl ether=10/1) as an oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (dt, J_1=8.9 Hz, J_2=2.1 Hz, 2H, Ar–H), 7.58 (dt, J_1=8.9 Hz, J_2=2.1 Hz, 2H, Ar–H), 6.38 (t, J=6.6 Hz, 1H, HC=C=C), 5.26 (d, J=6.3 Hz, 2H, C=C=CH_2); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 217.2, 190.0, 136.1, 131.6, 130.2, 127.8, 93.2, 79.5; IR (neat) 1960, 1931, 1652, 1585, 1566, 1484, 1417, 1395, 1346, 1276, 1211, 1177, 1069, 1009 cm^{-1}; MS (EI) *m*/*z* 224 (M^+(^{81}Br), 0.72), 222 (M^+(^{79}Br), 1.32), 50 (100).



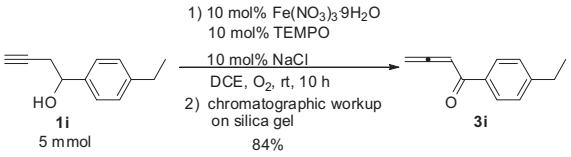
The reaction of 1-(4-bromophenyl)but-3-yn-1-ol **1h** (1.1338 g, 5.0 mmol), $Fe(NO_3)_3\cdot 9H_2O$ (199.2 mg, 0.5 mmol), TEMPO (78.5 mg, 0.5 mmol), and NaCl (28.9 mg, 0.5 mmol) in DCE (5 mL) afforded 1-(4-bromophenyl)buta-2,3-dien-1-one **3h** (797.0 mg, 71%) (eluent: petroleum ether/diethyl ether=10/1) as an oil.

*4.2.9. 1-(4-Ethylphenyl)buta-2,3-dien-1-one (**3i**).*



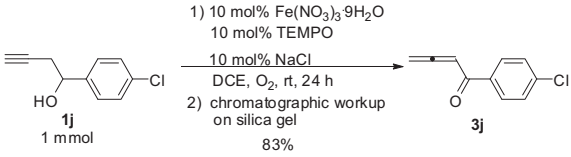
The reaction of 1-(4-ethylphenyl)but-3-yn-1-ol **1i** (174.0 mg, 1.0 mmol), $Fe(NO_3)_3\cdot 9H_2O$ (40.0 mg, 0.1 mmol), TEMPO (15.8 mg, 0.1 mmol), and NaCl (5.8 mg, 0.1 mmol) in DCE (4 mL) afforded 1-(4-ethylphenyl)buta-2,3-dien-1-one **3i** (145.8 mg, 85%) (eluent: petroleum ether/diethyl ether=10/1) as an oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, J=6.6 Hz, 2H, Ar–H), 7.26 (d, J=8.4 Hz, 2H, Ar–H), 6.44 (t, J=6.5 Hz, 1H, HC=C=C), 5.24 (d, J=6.6 Hz, 2H, C=C=CH_2), 2.69 (q, J=7.6 Hz, 2H, CH_2), 1.25 (t, J=7.5 Hz, 3H, CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 216.7, 190.3, 149.7, 135.0, 128.8, 127.8, 93.0, 79.0, 28.8, 15.0; IR (neat) 2970, 2878, 2831, 1961, 1933, 1650, 1606, 1578, 1508, 1417, 1347, 1276, 1220, 1181 cm^{-1}; MS (EI) *m*/*z* 172 (M^+, 2.14), 133 (100); HRMS calcd for $C_{12}H_{12}O$ (M^+): 172.0888; found: 172.0889.

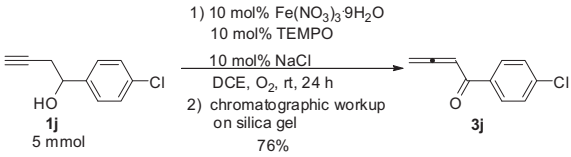


The reaction of 1-(4-ethylphenyl)but-3-yn-1-ol **1i** (869.1 mg, 5.0 mmol), $Fe(NO_3)_3\cdot 9H_2O$ (203.1 mg, 0.5 mmol), TEMPO (77.0 mg, 0.5 mmol), and NaCl (28.2 mg, 0.5 mmol) in DCE (5 mL) afforded 1-(4-ethylphenyl)buta-2,3-dien-1-one **3i** (724.0 mg, 84%) (eluent: petroleum ether/diethyl ether=10/1) as an oil.

*4.2.10. 1-(4-Chlorophenyl)buta-2,3-dien-1-one (**3j**).*



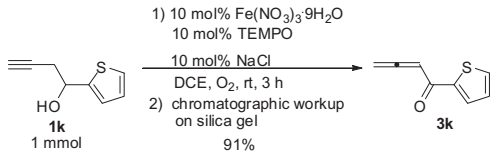
The reaction of 1-(4-chlorophenyl)but-3-yn-1-ol **1j** (179.8 mg, 1.0 mmol), $Fe(NO_3)_3\cdot 9H_2O$ (39.8 mg, 0.1 mmol), TEMPO (15.7 mg, 0.1 mmol), and NaCl (5.6 mg, 0.1 mmol) in DCE (4 mL) afforded 1-(4-chlorophenyl)buta-2,3-dien-1-one **3j** (147.0 mg, 83%) (eluent: petroleum ether/diethyl ether=10/1) as an oil.



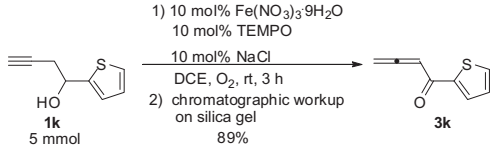
The reaction of 1-(4-chlorophenyl)but-3-yn-1-ol **1j** (901.9 mg, 5.0 mmol), $Fe(NO_3)_3\cdot 9H_2O$ (202.0 mg, 0.5 mmol), TEMPO (79.0 mg, 0.5 mmol), and NaCl (29.6 mg, 0.5 mmol) in DCE (5 mL) afforded 1-(4-chlorophenyl)buta-2,3-dien-1-one[8a] **3j** (674.8 mg, 76%) as an oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (dt, J_1=8.9 Hz, J_2=2.1 Hz, 2H, Ar–H), 7.41 (dt, J_1=8.7 Hz, J_2=2.3 Hz, 2H, Ar–H), 6.38 (t, J=6.5 Hz, 1H, HC=C=C), 5.26 (d, J=6.6 Hz, 2H, C=C=CH_2); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 217.1, 189.8, 139.1, 135.6, 130.1, 128.6, 93.2, 79.4.

*4.2.11. 1-(2-Thienyl)buta-2,3-dien-1-one (**3k**).*



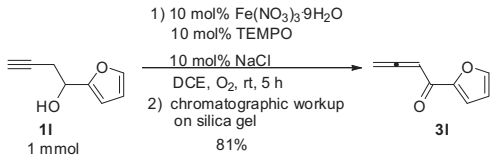
The reaction of 1-(2-thienyl)but-3-yn-1-ol **1k** (151.6 mg, 1.0 mmol), $Fe(NO_3)_3\cdot 9H_2O$ (40.7 mg, 0.1 mmol), TEMPO (15.9 mg, 0.1 mmol), and NaCl (5.8 mg, 0.1 mmol) in DCE (4 mL) afforded 1-(2-thienyl)buta-2,3-dien-1-one **3k** (136.0 mg, 91%) (eluent: petroleum ether/diethyl ether=10/1) as an oil.



The reaction of 1-(2-thienyl)but-3-yn-1-ol **1k** (759.6 mg, 5.0 mmol), $Fe(NO_3)_3\cdot 9H_2O$ (204.9 mg, 0.5 mmol), TEMPO (77.2 mg, 0.5 mmol), and NaCl (28.8 mg, 0.5 mmol) in DCE (5 mL) afforded 1-(2-thienyl)buta-2,3-dien-1-one **3k** (664.5 mg, 89%) (eluent: petroleum ether/diethyl ether=10/1) as an oil.

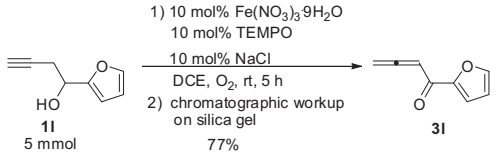
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, J=3.6 Hz, 1H, heteroaryl-H), 7.63 (d, J=4.8 Hz, 1H, heteroaryl-H), 7.11 (t, J=4.4 Hz, 1H, heteroaryl-H), 6.37 (t, J=6.6 Hz, 1H, HC=C=C), 5.33 (d, J=6.6 Hz, 2H, C=C=CH_2); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 215.8, 181.8, 143.5, 133.7, 132.4, 127.8, 93.2, 79.8; IR (neat) 1961, 1933, 1630, 1516, 1412, 1357, 1279, 1236, 1219 cm^{-1}; MS (EI) *m*/*z* 150 (M^+, 20.34), 111 (100); HRMS calcd for $C_8H_6O_4S$ (M^+): 150.0139; found: 150.0138.

*4.2.12. 1-(2-Furyl)buta-2,3-dien-1-one (**3l**).*



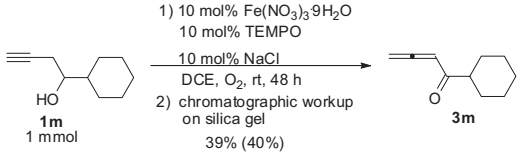
The reaction of 1-(2-furyl)but-3-yn-1-ol **1l** (135.4 mg, 1.0 mmol), $Fe(NO_3)_3\cdot 9H_2O$ (40.3 mg, 0.1 mmol), TEMPO (15.9 mg, 0.1 mmol), and NaCl (5.5 mg, 0.1 mmol) in DCE (4 mL) afforded 1-(2-furyl)buta-2,3-dien-1-one **3l** (107.4 mg, 81%) (eluent: petroleum ether/diethyl ether=10/1) as an oil.

The reaction of 1-(2-furyl)but-3-yn-1-ol **1l** (681.3 mg, 5.0 mmol), $Fe(NO_3)_3\cdot 9H_2O$ (204.0 mg, 0.5 mmol), TEMPO (78.7 mg, 0.5 mmol), and NaCl (28.8 mg, 0.5 mmol) in DCE (5 mL) afforded 1-(2-furyl)buta-2,3-dien-1-one[11] **3l** (516.2 mg, 77%) (eluent: petroleum ether/diethyl ether=10/1) as an oil.



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (dd, J_1=1.5 Hz, J_2=0.8 Hz, 1H, heteroaryl-H), 7.28 (dd, J_1=3.6 Hz, J_2=0.6 Hz, 1H, heteroaryl-H), 6.54 (dd, J_1=3.6 Hz, J_2=1.8 Hz, 1H, heteroaryl-H), 6.44 (t, J=6.5 Hz, 1H, HC=C=C), 5.34 (d, J=6.6 Hz, 2H, C=C=CH_2); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 216.1, 177.7, 152.3, 146.5, 118.0, 112.3, 92.4, 79.7; IR (neat) 1960, 1933, 1645, 1567, 1465, 1418, 1392, 1164, 1016 cm^{-1}; MS (EI) *m*/*z* 134 (M^+, 19.84), 95 (100).

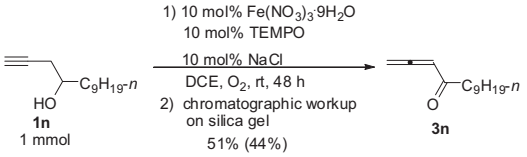
*4.2.13. 1-Cyclohexylbuta-2,3-dien-1-one (**3m**).*



The reaction of 1-cyclohexylbut-3-yn-1-ol **1m** (152.9 mg, 1.0 mmol), $Fe(NO_3)_3\cdot 9H_2O$ (40.9 mg, 0.1 mmol), TEMPO (15.5 mg, 0.1 mmol), and NaCl (5.4 mg, 0.1 mmol) in DCE (4 mL) afforded 1-cyclohexylbuta-2,3-dien-1-one[10] **3m** (59.3 mg, 39%) as an oil (40% of the starting material by NMR analysis).

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.74 (t, J=6.6 Hz, 1H, HC=C=C), 5.22 (d, J=6.6 Hz, 2H, C=C=CH_2), 2.80–2.49 (m, 1H, CH), 1.82–1.60 (m, 5H, CH_2), 1.45–1.10 (m, 5H, CH_2); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 216.1, 203.8, 95.4, 79.1, 47.0, 29.0, 25.7, 25.5; IR (neat) 2932, 2855, 1961, 1934, 1677, 1450, 1165, 1126 cm^{-1}; MS (EI) *m*/*z* 150 (M^+, 8.19), 55 (100).

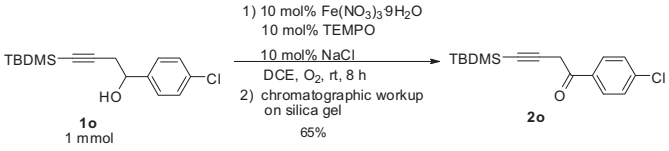
*4.2.14. Trideca-1,2-dien-4-one (**3n**).*



The reaction of tridec-1-yn-4-ol **1n** (196.1 mg, 1.0 mmol), $Fe(NO_3)_3\cdot 9H_2O$ (41.0 mg, 0.05 mmol), TEMPO (15.6 mg, 0.05 mmol), and NaCl (6.0 mg, 0.05 mmol) in DCE (4 mL) afforded trideca-1,2-dien-4-one[8a] **3n** (98.3 mg, 51%) (eluent: petroleum ether/diethyl ether=10/1) as an oil (44% of the starting material by NMR analysis).

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.76 (t, J=6.6 Hz, 1H, HC=C=C), 5.22 (d, J=6.3 Hz, 2H, C=C=CH_2), 2.59 (t, J=7.5 Hz, 2H, CH_2), 1.62–1.50 (m, 2H, CH_2), 1.35–1.08 (m, 12H, CH_2), 0.87 (t, J=6.8 Hz, 3H, CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 216.6, 201.0, 96.7, 79.2, 39.2, 31.8, 29.4, 29.3, 29.22, 29.17, 24.6, 22.6, 14.1.

*4.2.15. 4-(tert-Butyldimethylsilyl)-1-(4-chlorophenyl)but-3-yn-1-one (**2o**).*



The reaction of 4-(*tert*-butyldimethylsilyl)-1-(4-chlorophenyl) but-3-yn-1-ol **1o** (293.1 mg, 1.0 mmol), $Fe(NO_3)_3\cdot 9H_2O$ (40.5 mg, 0.1 mmol), TEMPO (15.7 mg, 0.1 mmol), and NaCl (6.0 mg, 0.1 mmol) in DCE (4 mL) afforded 4-(*tert*-butyldimethylsilyl)-1-(4-chlorophenyl)but-3-yn-1-one **2o** (187.9 mg, 65%) (eluent: petroleum ether/diethyl ether=10/1) as an oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (dt, J_1=8.8 Hz, J_2=2.1 Hz, 2H, Ar–H), 7.44 (dt, J_1=8.9 Hz, J_2=2.3 Hz, 2H, Ar–H), 3.83 (s, 2H, CH_2), 0.88 (s, 9H, $C(CH_3)_3$), 0.07 (s, 6H, CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 191.8, 139.9, 133.5, 130.2, 128.8, 98.5, 89.2, 32.1, 25.9, 16.5, −4.8; IR (neat) 2178, 1694, 1590, 1489, 1471, 1400, 1208, 1093, 1010 cm^{-1}; MS (EI) *m*/*z* 294 (M^+(^{37}Cl), 0.15), 292 (M^+(^{35}Cl), 0.44), 111 (100); HRMS calcd for $C_{16}H_{21}OSi^{35}Cl$ (M^+): 292.1050; found: 292.1053.

Acknowledgements

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.08.082.

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