Transition-Metal-Catalyzed Oxidations, 5[1]

Oxygenation of *ortho*-Alkylated α- and ß-Naphthols to α-Ketols

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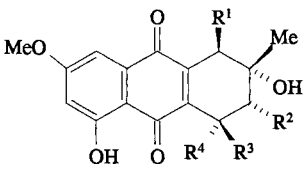
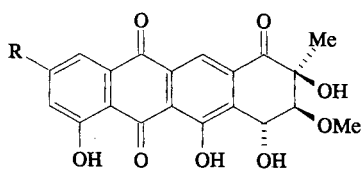
The α- and ß-naphthols **7a–7d**, **8a** and **8b** are converted into the corresponding α-ketols **9a–9c**, **10a**, **10b** and **10d** with concomitant dearomatization of ring A and partial shift of the alkyl group by reaction with *tert*-butyl hydroperoxide in the presence of $Ti(OiPr)_4$, $Zr(acac)_2$ or $[MoO(O_2)_2]$ py HMPT.

We have recently described the specific oxygenation of phenols to *ortho*-quinones[1,2]. In this reaction phenol and *tert*-butyl hydroperoxide (TBHP) are coordinated at the same metal atom, and the oxygen is therefore transferred exclusively to the neighboring carbon atom. In a second step the intermediate oxygenation product is *dehydrogenated* with cleavage of a H–C bond to yield *ortho*-quinones. The question arose which reaction occurs if no hydrogen is available, viz. when the neighboring position is blocked by an *alkyl* group. The transformation of a phenolic paracyclophane to an instable α-ketol intermediate was a first indication that oxygenation of phenols to α-ketols might still occur with *ortho*-substituted phenols[3]. However, dearomatization of the paracyclophane benzene ring by reaction at the highly strained brigdeheads is a facile and well-known reaction[4] and the general reactivity of *ortho*-alkylated phenols under the new oxygenation conditions remained to be explored.

α-Ketols resulting from the oxygenation of phenols are interesting intermediates in microbial degradation[5] and are assumed to be of considerable preparative value as building blocks in natural product synthesis[6]. For example, many polyketide-derived antibiotics such as the tricyclic quinones altersolanol A[7,8] (**1**) (identical with stemphylin[9]), altersolanol B[7,8] (**2**), dactylariol[10] (**3**), austrocortilutein[11] (**4**) or the tetracyclic compounds steffimycinone[12] (**5**) and arianciamycinone[13] (**6**) have an α-ketol structure.



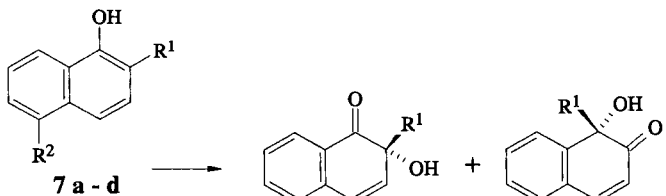
	R^1	R^2	R^3	R^4
1	OH	OH	OH	OH
2	H	OH	OH	H
3	OH	OH	H	H
4	H	H	H	OH



	R
5	OMe
6	H

In previous investigations Wessely et al.[14] have treated alkylated phenols (mainly cresols) with lead(IV) acetate and obtained acetoxycyclohexadienones that have been used in a number of modern syntheses[15–18]. However, the process is not entirely *ortho*-selective. A more selective process is the thermal rearrangement of 6-acyloxycyclohexadienones investigated by Barton et al.[19]. The use of other oxidants such as nitrogen dioxide[20], persulfuric acid/magnesium carbonate[21], hypervalent iodine compounds[22] or the rearrangement of aromatic hydroxylamines[23] predominantly affords the corresponding *para*-quinol derivatives.

We now disclose the results of an investigation of the reaction of *ortho*-substituted naphthols with the oxygenation systems TBHP and various transition metal alkoxides $[Ti(OiPr)_4, Zr(OnPr)_4, Zr(acac)_2]$ and the Mimoun molybdenum oxodiperoxo complex $[MoO(O_2)_2]$ · py · HMPT[24]. A selected number of commercially available or known substituted *ortho*-alkylated α-naphthols **7a**, **7b**[25], **7c**[26], **7d**[27] and the ß-naphthols **8a**[28] and **8b**[29] are chosen as targets for our initial studies.



7 a - d

8a - b

9a - c

10 a - d

	R^1	R^2
a	Me	H
b	Et	H
c	Me	OMe
d	Et	OMe

The naphthols **7a–7d**, **8a** and **8b** are treated with a catalytic amount (0.2 to 0.4 equivalents) of the transition metal alkoxide and two equivalents of TBHP or two equivalents of $[MoO(O_2)_2]$ · py · HMPT in dichloromethane in the

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presence of 3 Å molecular sieves. No water is formed during the oxygenation process but the elimination of traces of water by the addition of molecular sieves slows down the decomposition of the transition-metal catalyst. This observation was also made in the catalytic variation of the Sharpless epoxidation[30]. The α-naphthols **7** and the ß-naphthols **8** react under surprisingly mild conditions at room temperature and even at −23 °C. The only exception is observed with 5,8-dimethoxy-2-methyl-1-naphthol, which shows no conversion due to chelate formation[1]. The first product isolated in the crystalline state in 89% yield is the oxidation product of the α-naphthol **7d**. There was some ambiguity in the assignment of the ^{13}C-NMR data to the initially presumed ketol structure of type **9**. Unfortunately, no spectroscopic data are available for a comparison with the α-ketol **10a** described in the patent literature[31]. To settle this problem we elucidated the structure by X-ray analysis. The structure of the rearranged 2-oxo compound **10d** (Figure 1) confirms that it is the only reaction product derived from naphthol **7d**.

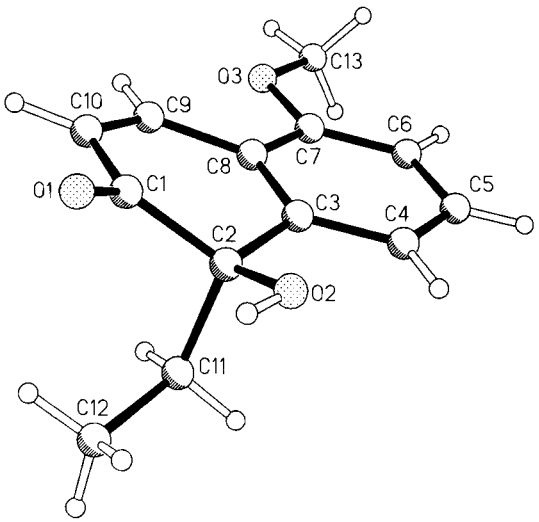

Figure 1. Molecule of compound **10d** in the crystal; radii are arbitrary

The NMR data of the unambiguously assigned structure **10d** allowed the structure determination of the other reaction products. Mixtures of the ketols **9** and **10** are produced in the oxygenation of some other naphthols. The influence of the substrate structure and the transition metal catalyst or molybdenum reagent is subsequently investigated in a series of experiments; the results are shown in Table 1. The product ratio of the ketols **9** and **10** is independently determined by HPLC and ^{1}H-NMR analysis using the distinct vinylic proton at C-4 and C-3.

The nature of the alkyl side chain in the starting naphthol is of major influence on the product composition. In all experiments, the ethyl side chain has shown a much greater migratory aptitude. As already mentioned, 2-ethyl-5-methoxy-1-naphthol (**7d**) produces only the rearranged product **10d** (entries 9 and 10). On the other hand, no rearrangement is observed in the reaction of **7a** and **8a** (with methyl side chains) and the pure α-ketols **9a** or **10a** can be isolated in excellent yields (entries 1 and 11; 93 and 80 % respectively). Similarly, only small amounts of the byproduct **10c** are detected in the conversion of the preparatively interesting 5-methoxy-2-methyl-1-naphthol (**7c**) to **9c** in the oxidation with the Mimoun complex (entry 7) or in even higher yield (85%) with the zirconium catalyst (entry 8). As expected, the electron-donating methoxy groups in the naphthols **7c** and **7d** accelerate the oxygen transfer (entries 7 and 9, 10).

Table 1. Conditions and product ratio in the oxygenation of naphthols **7a**–**8b** to **9a**–**10d**[a]

Entry	Naphthol	Metal	Temp. [°C]	Time [h]	Product ratio **9**:**10**	Yield [%]
1	**7a**	Mo	22	3.5	only **9a**	93
2		Zr	22	5.25	only **9a**	91
3		Zr[b]	22	72	1:5	64
4		Ti	22	3.5	1:3.5	74
5	**7b**	Mo	22	2	1:1.2	90
6		Zr	22	20	1:1.2	87
7	**7c**	Mo	22	1	25:1	74
8		Zr	22	8	only **9c**	85
9	**7d**	Mo	22	1	only **10d**	89
10		Mo	-23	7	only **10d**	87
11	**8a**	Mo	22	22	only **10a**	80
12		Mo	22	22	1:23	85
13	**8b**	Mo	22	23	1:6	95
14		Zr[c]	22	42	1:4	87
15		Zr[c]	-23	48	1:4	89

[a] Mo: $[MoO(O_2)_2] \cdot py \cdot HMPT$; Ti: $Ti(OiPr)_4$; Zr: $Zr(acac)_2$. — [b] Catalyst is $Zr(OnPr)_4$. — [c] 0.4 equivalents of $Zr(acac)_2$.

The nature of the catalyst has also a certain influence and the use of titanium tetraisopropylate leads to more rearrangement (under comparable conditions) than the application of molybdenum or zirconium compounds (entries 4 and 11). The 2-naphthols **8a** and **8b** generally show less tendency to yield the rearranged 1-oxo compounds; **10a** and **10b** are the major products and the question arose whether the product ratio is the result of thermodynamic reaction control. In fact, the α-ketol rearrangement is a known process[32] and can be effected in our case by catalytic amounts of $Ti(OiPr)_4$ by starting with the pure ketol **9a** to give a ca. 1:4 mixture of **9a**:**10a** after 96 h of equilibration. Preliminary kinetic experiments show that only ca. 10% of **10a** are produced after 20 h in the $Ti(OiPr)_4$-catalyzed equilibration of **9a**. On the other hand, more than 70% of **10a** are formed in the oxygenation of **7a** within 3.5 h by using the same catalyst at the same concentration (entry 7). This result suggests that a much more rapid rearrangement of some intermediate (presumably an epoxide similar as in the NIH shift[33,34]) occurs and that subsequent equilibration of the products by α-ketol rearrangement plays only a minor role.

In summary, an operationally simple procedure is presented allowing the conversion of *ortho*-alkylated α- and ß-naphthols to the corresponding α-ketols, representing highly functionalized hydroaromatic starting materials for natural

product synthesis ("oxidative dearomatization"). Rearrangement can largely be suppressed in naphthols with methyl side chains by using zirconium catalysts or $[MoO(O_2)_2] \cdot py \cdot HMPT$. The thermodynamically more stable α-ketols of type **10** that are of interest in connection with photoresistors[31] are also easily prepared from 2-naphthols by the new procedure.

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Experimental

For general remarks see ref.[2]. For details of the X-ray measurement see ref.[35].

X-ray Structure Determination of Compound **10d**: *Crystal data:* $C_{13}H_{14}O_3$, M = 218.2. Monoclinic, space group $P2_1/n$, a = 852.2(3), b = 689.8(2), c = 1861.0(5) pm, β = 99.46(2)°, U = 1.0791 nm³, Z = 4, D_x = 1.343 Mg m⁻³, λ(MoKα) = 0.71069Å, μ = 0.09 mm⁻¹, T = 178 K, $F(000)$ = 464. Data collection and refinement: A yellow tablet 0.4 × 0.3 × 0.08 mm is mounted on a glass fiber in inert oil and transferred to the cold gas stream of the diffractometer (Siemens R3 with LT-2 low-temperature attachment). Data are collected to $2\theta_{max}$ 50° with monochromated MoKα radiation. Of 4097 reflections, 1912 are unique (R_{int} 0.024) and 1133 > 2σ(F) used for all calculations (program system Siemens SHELXTL PLUS). Structure solution and refinement: The structure is solved by direct methods and subjected to anisotropic full-matrix least-squares refinement on F. Hydrogen atoms are included by using a riding model, except for the hydroxyl H, which is refined freely. Refinement proceedes to R = 0.056, wR = 0.048. The weighting scheme is $w^{-1} = \sigma^2(F) + 0.0005F^2$; 154 parameters; S = 1.0; max. Δ/σ = 0.004; max. Δρ = 0.3 × 10⁻⁶ e pm⁻³. Final atomic coordinates are given in Table 2.

Table 2. Atomic coordinates (× 10⁴) and equivalent isotropic displacement parameters (× 10⁻¹) [pm²][a] with estimated standard deviations in parentheses of **10d**

	x	y	z	U(eq)
O(1)	2972(3)	4943(3)	2664(1)	42(1)
C(1)	4238(4)	5119(5)	3090(2)	32(1)
C(2)	5026(4)	3336(4)	3461(2)	28(1)
O(2)	3931(3)	1839(3)	3522(1)	35(1)
C(11)	6244(4)	2667(5)	2956(2)	35(1)
C(12)	5515(4)	2226(6)	2178(2)	43(1)
C(3)	5979(4)	3752(5)	4205(2)	27(1)
C(4)	6269(4)	2310(5)	4725(2)	32(1)
C(5)	7274(4)	2691(5)	5378(2)	35(1)
C(6)	8020(4)	4473(5)	5505(2)	34(1)
C(7)	7731(4)	5907(5)	4985(2)	32(1)
O(3)	8397(3)	7717(3)	5059(1)	38(1)
C(13)	9520(4)	8078(6)	5704(2)	44(1)
C(8)	6666(4)	5592(4)	4331(2)	26(1)
C(9)	6188(4)	7142(5)	3814(2)	30(1)
C(10)	5053(4)	6948(5)	3236(2)	31(1)

[a] Equivalent istropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

General Procedure for the Oxidation of Naphthols to α-Ketols: A solution of ca. 1 mmol of the naphthol (**7a**, **7b**[25], **7c**[26], 7d[27], **8a**[28], **8b**[29]) in 10 ml of dry CH_2Cl_2 and 0.2 mmol of the transition-metal alkoxide Ti(O*i*Pr)₄, Zr(acac)₂ or Zr(O*n*Pr)₄ (see Table 1) are slowly added under Ar within 1 h to a solution of 2 mmol of *tert*-butyl hydroperoxide (TBHP) (4.35 M in 40 ml of dry CH_2Cl_2) (alternatively 2 mmol of $[MoO(O_2)_2] \cdot py \cdot HMPT$[24]) containing 100 mg of molecular sieves (3 Å). The reaction is monitored by TLC and the mixture is stirred for the time and at the temperatures given in Table 1. After complete conversion of the starting material the reaction is quenched by hydrolysis with 2 ml of 10% sulfuric acid. The mixture is stirred for 30 min, then 10 g of Na_2SO_4 is added, and stirring is continued for further 30 min. The solution is filtered, the filtrate evaporated to dryness at reduced pressure and the residue separated if required by layer chromatography on silica gel (dichloromethane) and crystallized from hexane.

2-Hydroxy-2-methyl-2H-naphthalene-1-one (**9a**): According to the general procedure 158 mg (1 mmol) of 2-methyl-1-naphthol (**7a**) is oxidized to afford 178 mg (93 %) of **9a**; m.p. 89–90°C. – IR (KBr): ν = 1684, 1647, 1601 cm⁻¹. – UV (CH_3OH): λ_{max} (lg ε) = 231 (4.513), 275 (sh), 325 nm (sh). – ¹H NMR (400 MHz, $CDCl_3$): δ = 1.45 (s; 3H, CH_3), 3.60 (br. s; 1H, OH), 6.32 (d, $J_{3,4}$ = 9.8 Hz; 1H, 3-H), 6.47 (d, $J_{3,4}$ = 9.8 Hz; 1H, 4-H), 7.20 (d, J = 7.6 Hz; 1H, Ar-H), 7.35 (t, J = 7.6 Hz; 1H, Ar-H), 7.58 (dt, J_{ortho} = 7.4 Hz, J_{meta} = 1.3 Hz; 1H, Ar-H), 7.97 (d, J = 7.4 Hz; 1 H, Ar-H). – ¹³C NMR ($CDCl_3$): δ = 28.43 (q), 75.30 (s), 124.22 (d), 127.21 (d), 127.47 (d), 128.11 (s), 128.17 (d), 135.16 (d), 137.05 (d), 137.82 (s), 204.23 (s). – MS: m/z (%) = 175 (3) [M^+ + 1H], 174 (25) [M^+], 146 (13) [M^+ – CO], 131 (100) [M^+ – CO – CH_3], 103 (24).

$C_{11}H_{10}O_2$ Calcd. 174.06808 Found 174.0681 (± 2 ppm) (MS)
$C_{11}H_{10}O_2$ (174.2) Calcd. C 75.84 H 5.79
Found C 75.79 H 5.67

2-Ethyl-2-hydroxy-2H-naphthalene-1-one (**9b**): According to the general procedure 172 mg (1.00 mmol) of 7**b** is oxidized to afford 169 mg (90%) of an oil; **9b** and **10b** are separated in small amounts by reverse-phase HPLC. – ¹H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.4 Hz; 3H, CH_2CH_3), 1.60–1.69 (m; 2H, CH_2CH_3), 3.55 (br. s; 1H, OH), 6.30 (d, $J_{3,4}$ = 9.9 Hz; 1H, 3-H), 6.52 (d, $J_{3,4}$ = 9.9 Hz; 1H, 4-H), 7.20 (d, J = 7.7 Hz; 1H, Ar-H), 7.34 (dt, J_{ortho} = 7.7 Hz, J_{meta} = 1.0 Hz; 1H, Ar-H), 7.57 (dt, J_{ortho} = 7.8 Hz, J_{meta} = 1.3 Hz; 1H, Ar-H), 7.93 (d, J = 7.8 Hz; 1 H, Ar-H). – ¹³C NMR ($CDCl_3$): δ = 7.64 (q), 34.98 (t), 78.29 (s), 124.99 (d), 126.83 (d), 127.39 (d), 128.16 (d), 128.35 (s), 135.05 (d), 136.33 (d), 137.94 (s), 204.52 (s).

2-Hydroxy-5-methoxy-2-methyl-2H-naphthalene-1-one (**9c**): According to the general procedure 172 mg (0.91 mmol) of 7**c** is oxidized to afford 160 mg (85%) of **9c**; m.p. 76°C (diethyl ether). – IR (KBr): ν̃ = 1717, 1686, 1593, 1574, 1489 cm⁻¹. – UV (CH_3OH): λ_{max} (lgε) = 206 (4.118), 232 (4.274), 295 nm (sh). – ¹H NMR (300 MHz, $CDCl_3$): δ = 1.41 (s; 3H, CH_3), 3.85 (s; 3H, OCH_3), 3.86 (s; 1H, OH), 6.25 (d, $J_{3,4}$ = 10.1 Hz; 1H, 3-H), 6.87 (d, $J_{3,4}$ = 10.1 Hz; 1H, 4-H), 7.08 (d, $J_{6,7}$ = 8.2 Hz; 1H, 6-H), 7.27 (t, $J_{6,7}$ = 8.2 Hz, $J_{7,8}$ = 7.7 Hz; 1H, 7-H), 7.53 (d, $J_{7,8}$ = 7.7 Hz; 1H, 8-H). – ¹³C NMR ($CDCl_3$): δ = 28.32 (q), 55.78 (q), 75.23 (s), 116.65 (d), 117.82 (d), 118.74 (d), 126.59 (s), 128.70 (d), 128.77 (s), 135.73 (d), 154.80 (s), 204.62 (s).

$C_{12}H_{12}O_3$ Calcd. 204.07865 Found 204.0786 (± 2 ppm) (MS)
$C_{12}H_{12}O_3$ (204.3) Calcd. C 70.58 H 5.92
Found C 70.81 H 6.12

1-Hydroxy-1-methyl-1H-naphthalene-2-one (**10a**): According to the general procedure 158 mg (1 mmol) of 1-methyl-2-naphthol (**8a**) is oxidized to afford 140 mg (80 %) of **10a**; m.p. 85°C (ref.[36] m.p. 87–89°C). – IR (KBr): ν̃ = 1656, 1625, 1614, 1600 cm⁻¹. – UV (CH_3OH): λ_{max} (lg ε) = 208 (4.025), 233 (4.143), 236 (sh), 309 nm (3.954). – ¹H NMR (400 MHz, $CDCl_3$): δ = 1.55 (s; 3H, CH_3), 3.76 (s; 1H, OH), 6.20 (d, $J_{3,4}$ = 9.8 Hz; 1H, 3-H), 7.28–7.34 (m; 2H, Ar-H), 7.43 (d, $J_{3,4}$ = 9.8 Hz; 1H, 4-H), 7.42–7.46 (m; 1H, Ar-

H), 7.72 (d, J = 8.1 Hz; 1H, Ar-H). – ^{13}C NMR ($CDCl_3$): δ = 33.15 (q), 77.13 (s), 122.39 (d), 125.55 (d), 127.83 (d), 128.29 (s), 129.42 (d), 130.66 (d), 145.11 (s), 145.95 (d), 205.26 (s). – MS: m/z (%) = 175 (4) [M^+ + 1], 174 (28) [M^+] 146 (100) [M^+ – CO], 145 (51), 131 (77) [M^+ – CO – CH_3], 103 (20).

$C_{11}H_{10}O_2$ (174.2) Calcd. C 75.84 H 5.79
Found C 75.79 H 5.67

1-Ethyl-1-hydroxy-1H-naphthalene-2-one (**10b**): According to the general procedure 172 mg (1 mmol) of 1-ethyl-2-naphthol (**8b**) is oxidized to afford 109 mg (58%) of **10b**; m.p. 85°C (diethyl ether; ref.[31]: 84.5–87.5°C). – IR (KBr): $\tilde{\nu}$ = 1663, 1610, 1600, 1561 cm^{-1}. – UV (CH_3OH): λ_{max} (lg ε) = 209 (4.064), 236 (4.138), 311 (3.913), 348 nm (sh). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.82 (t, J = 7,4 Hz; 3H, CH_2CH_3), 1.74–1.90 (m; 2H, CH_2CH_3), 3.77 (br. s; 1H, OH), 6.12 (d, $J_{3,4}$ = 9.9 Hz; 1H, 3-H), 7.27–7.31 (m; 2H, Ar-H), 7.40 (d, $J_{3,4}$ = 9.9 Hz; 1H, 4-H), 7.42 (dt, J_{ortho} = 7.5 Hz, J_{meta} = 1.8 Hz; 1H, Ar-H), 7.65 (d, $J_{5,6}$ = 7.0 Hz; 1H, 5-H). – ^{13}C NMR ($CDCl_3$): δ = 8.06 (q), 38.54 (t), 80.21 (s), 122.76 (d), 126.09 (d), 127.23 (d), 128.95 (s), 129.33 (d), 130.15 (d), 144.35 (s), 145.86 (d), 205.46 (s). – MS: m/z (%) = 189 (4) [M^+ + 1], 188 (30) [M^+], 160 (68) [M^+ – CO], 131 (100) [M^+ – CO – C_2H_5].

1-Ethyl-1-hydroxy-5-methoxy-1H-naphthalene-2-one (**10d**): According to the general procedure 158 mg (0.78 mmol) of **7d** is oxidized to afford 155 mg (89%) of **10d**; m.p. 73°C (ethyl ether). – IR (KBr): $\tilde{\nu}$ = 3430, 2971, 2938, 2916, 1662, 1604, 1592, 1562 cm^{-1}. – UV (CH_3OH): λ_{max} (lg ε) = 207 (4.185), 237 (sh), 266 (sh), 302 (sh), 351 nm (3.827). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.81 (t, J = 7.5 Hz; 3H, CH_2CH_3), 1.72–1.87 (m; 2H, CH_2CH_3), 3.88 (s; 3H, OCH_3), 3.89 (s; 1H, OH), 6.11 (d, $J_{3,4}$ = 10.2 Hz; 1H, 3-H), 6.82 (dd, $J_{7,8}$ = 8.2 Hz, $J_{6,8}$ = 0.8 Hz; 1H, 8-H), 7.23 (dd, $J_{6,7}$ = 7.8 Hz, $J_{6,8}$ = 0.8 Hz; 1H, 6-H), 7.37 (dd, $J_{7,8}$ = 8.2 Hz, $J_{6,7}$ = 7.8 Hz; 1H, 7-H), 7.93 (d, $J_{3,4}$ = 10.2 Hz; 1H, 4-H). – ^{13}C NMR ($CDCl_3$): δ = 8.08 (q), 38.67 (t), 55.74 (q), 80.31 (s), 109.67 (d), 118.03 (s), 118.35 (d), 121.06 (d), 131.51 (d), 139.68 (d), 146.42 (s), 156.74 (s), 205.44 (s). – MS: m/z (%) = 219 (6) [M^+ + 1], 218 (38) [M^+], 190 (66) [M^+ – CO], 161 (100) [M^+ – CO – C_2H_5], 131 (28).

$C_{13}H_{14}O_3$ (218.3) Calcd. C 71.54 H 6.47
Found C 71.10 H 6.50

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