Supporting Information

for

A convenient and practical synthesis of β-diketones bearing linear perfluorinated alkyl groups and a 2-thienyl moiety

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General information

2-Acetylthiophene, sodium hydride (60% dispersion in mineral oil) and other common chemicals were purchased from Acros Organics (Belgium). Ethyl or methyl esters of perfluorinated carboxylic acids were purchased from SIA “P&M-Invest” Ltd. (Moscow, Russia). Diethyl ether or THF were distilled over sodium metal/benzophenone under Ar atmosphere just before use. Ethyl acetate (for condensation) and esters of perfluorinated carboxylic acids were kept over 4 Å molecular sieves. Oven-dried glassware was used in the condensation step and manipulations were conducted under dry Ar blanket.

Caution! Dry or oil-free sodium hydride is highly pyrophoric and reacts violently with water. It should never be exposed to air during the washing procedure. It must be wetted by a solvent all the time and an inert atmosphere must be maintained during the manipulations. Traces of NaH in hexane after the washing procedure must be decomposed by careful addition of anhydrous ethanol followed by 96% ethanol before collecting it in a waste container.

NMR spectra were recorded at ambient temperature on a Bruker AM-300 instrument operating at 300, 282.5 and 75.5 MHz for $^1$H, $^{19}$F and $^{13}$C nuclei respectively. Chemical shifts were referenced to CHCl$_3$ (7.26 ppm), CDCl$_3$ (77.2 ppm) and CFCl$_3$ (0.00 ppm) for $^1$H, $^{13}$C and $^{19}$F spectra, respectively. $^{13}$C NMR spectra were also recorded on a Bruker DXR-500 and AV-600 instruments operated at 125.8 and MHz respectively. FTIR spectra were obtained on a Perkin-Elmer system Spectrum One 100 FTIR spectrometer in KBr pellets. GC–MS analysis and LRMS were performed on a Thermo DSQ II/Thermo Trace instrument; the ionization energy was 70 eV. HRMS was performed on a Bruker MicroTOF instrument with an ESI ionization source in the positive ion detection mode. Melting points were measured on a Büchi Melting Point M-560 apparatus and are uncorrected. Elemental microanalysis was performed in the
Laboratory of microanalysis of Nesmeyanov Institute of Organoelement Compounds, Moscow, Russia.

$^{13}$C-NMR spectra for fluorinated diketones are considerably less informative and more difficult to acquire and to interpret. Due to numerous C–F spin-spin interactions, the lines in a spectrum are repeatedly splitted and their intensities are very low, especially for quaternary carbon atoms in long-chain radicals. Out attempts to improve the quality of $^{13}$C-NMR spectra by utilizing high-field NMR spectrometers (Bruker DXR-500 and AV-600) also failed. With very long acquisition time, spectra became too complicated due to numerous signals of minor products and impurities, while with short acquisition times, only signals of carbon atoms that are not connected to fluorine atoms were recorded. The next problem is the high multiplicity of the signals – for long-chain fluorinated substituents it was impossible to resolve all multiplets even on the 600 MHz instrument. Therefore, these spectra are not fully described in the experimental section.

**General method for the preparation of fluorinated β-diketones (3a–g)**

Sodium hydride (4.0 g, 100 mmol, 60% dispersion in mineral oil) was placed in a 500 mL round-bottom flask and 50 mL of dry hexane was added. The suspension was stirred for a short time with a magnetic stirring bar and kept until the hexane layer became clear (20–30 min). Hexane was cautiously removed with a glass pipette until a wet paste of NaH remained. This procedure was repeated twice. After that, THF (150 mL) was added with vigorous stirring. Anhydrous EtOH (0.5 mL) was added in one portion at 0 °C, followed by the dropwise addition of a solution of 2-acetylthiophene (6.3 g, 50 mmol, 5.42 mL) and methyl or ethyl ester of the respective perfluorinated carboxylic acid (50.5 mmol) in 30 mL of THF. The white suspension rapidly turns pink and then reddish-brown. **Caution !** Hydrogen evolved during the addition and notable effervescence was observed. The rate of addition was maintained to control the evolution of hydrogen; usually the addition takes 60–80 min. When gas evolution
ceased, the cooling bath was removed and the reaction mixture was stirred for 5 h. After that, the dark brown solution with a small amount of precipitate was re-cooled to 0 °C, 10 mL of anhydrous EtOH was added slowly to decompose traces of NaH, and the resulting solution was stirred for 30 min. The solvent was removed by evaporation under reduced pressure (100 Torr, bath temperature 40 °C), then EtOAc (40 mL) and subsequently a mixture of conc. HCl (20 mL) and crushed ice (80 mL) were added to the residue. The resulting turbid liquid was shaken by hand until two clear layers formed. The organic phase was separated and the aqueous phase was then extracted with EtOAc (3 x 50 mL). The combined organic fractions were washed with brine (50 mL), dried over MgSO₄ and evaporated to dryness. The resulting brown oil was distilled in vacuo (2–3 Torr). The main fraction is pure enough. Additional portions of pure diketone can be separated from low-boiling fractions by precipitation as a copper salt. Decomposition should be performed with HCl (procedure A).

1-(2-Thienyl)butane-1,3-dione (5)

To a vigorously stirred suspension of NaH (2.4 g, 60 mmol, 60% dispersion in mineral oil) in 120 mL of THF, 0.2 mL of anhydrous EtOH was added in one portion. Stirring was continued and a mixture of 3.78 g (30 mmol) of 2-acetylthiophene and 36 mL (32.47 g, 368 mmol) of dry EtOAc was added dropwise at 0 °C. The resulting reddish-brown suspension was stirred at 0 °C for 5 h and left at a room temperature overnight. Caution! Hydrogen evolved during the addition and notable effervescence was observed. The reaction mixture was cooled to 0 °C again, 10 mL of anhydrous EtOH was added slowly to decompose traces of NaH, and the resulting solution was stirred for 30 min. The solvent was removed by evaporation under reduced pressure (100 Torr, bath temperature 40 °C) and EtOAc (40 mL), then a mixture of conc. HCl (20 mL) and crushed ice (80 mL) were added to the residue. The resulting turbid liquid was shaken
by hand until two clear layers formed. The organic phase was separated and the aqueous phase was extracted with EtOAc (3 × 50 mL). The combined organic fractions were washed with brine (50 mL), dried over MgSO₄ and evaporated to dryness. The resulting brown oil was distilled and the fraction with b.p. 105–115 °C/3 Torr (5.2 g) was collected. According to NMR data, it was not pure enough, and it was purified via the copper chelate (procedure B).

**Copper chelate preparation**

The weight of Cu(OAc)₂·H₂O was calculated assuming 100% purity of the diketone to be purified. To purify 100 mmol of a diketone, 40 g (200 mmol) of copper acetate monohydrate and 300 mL of 0.01 M aqueous AcOH were used. The salt was dissolved with stirring in the hot acid solution. The resulting dark greenish-blue solution was filtered hot through a loose cotton plug and the filtrate was re-heated to 90 °C. The diketone was added to the nearly boiling solution with vigorous mechanical stirring, after that the mixture was cooled to room temperature. The resulting precipitate was separated, washed thoroughly with warm 0.01 M aqueous AcOH, dried on a filter and washed several times with a sufficient amount of hexane. The copper chelate was dried in air to a constant weight.

**Copper chelate decomposition by HCl (highly acidic diketones, procedure A )**

A finely ground copper salt (50 mmol) was added in several portions with shaking to a two-phase mixture of EtOAc (50 mL) and 10% aqueous solution of HCl (50 mL) placed in a 250 mL separation funnel. The resulting mixture was vigorously shaken until all the chelate dissolved. The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 × 80 mL). The combined organic fractions were washed successively with 20 mL of 10% HCl and 50 mL of brine, dried over MgSO₄ and evaporated to dryness. The diketone was purified by vacuum distillation.
Copper chelate decomposition by Trilon B (low acidic diketones, procedure B)

A finely ground copper salt (50 mmol) was added in several portions with shaking to a two-phase mixture of EtOAc (100 mL) and saturated aqueous solution of Trilon B (150 mL) placed in a 500 mL separation funnel. The resulting mixture was vigorously shaken. After the separation of layers, the blue aqueous layer was discarded. Extraction was continued with 50 mL portions of the Trilon B solution until it remained colorless (2–4 times). The organic fraction was washed with brine (50mL), dried over MgSO₄ and evaporated to dryness. The diketone was purified by vacuum distillation.

4,4,5,5,5-Pentafluoro-1-(thiophen-2-yl)pentane-1,3-dione (3a)

Colorless oil; yield: 7.0 g (52%) was obtained by direct distillation and 5.5 g was isolated from low-boiling fractions; yield: 12.5 g (92%); bp 77-78 °C (3 Torr) (lit. 95.5 °C /16 Torr) [1].

**IR (KBr):** 1639, 1592, 1330, 1203, 1069, 1003, 723 cm⁻¹.

**¹H NMR (CDCl₃, 300 MHz):** δ = 14.99 (broad s, 1H, OH), 7.87 (d, 1H, J=3.7Hz CH), 7.77(d, 1H, J=4.8Hz,CH), 7.22 (t, 1H, J=4.5Hz, CH), 6.52 (s, 1H, CH=C).

**¹⁹F NMR (CDCl₃, 282.5 MHz):** δ = -83.6 (s, 3F, CF₃), -124.57 (s, 2F,CF₂).

**¹³C NMR (CDCl₃, 75.5 MHz):** δ = 182.61 (s, 1C, C=O), 172.70 (t, 1C, J=26.6Hz, OH-C=), 139.41(s,1C, C₉H₅), 135.47 (s,1C, C₉H₅), 132.93 (s,1C, C₉H₅),128.97 (s,1C, C₉H₅), 123.97, 120.17, 116.37, 111.75, 108.31, 104.7 (m, 2C, CF₃-CF₂), 95.01 (t, 1C, J=3.7Hz, CH=).

**MS (EI, 70 eV):** m/z (%) = 272 (45) [M]⁺, 153(100) [M-C₂F₅]⁺, 111(44) [ThCO]⁺, 69(59) [CF₃]⁺.

**HRMS (ESI⁺):** m/z [M]⁺ calcd for C₉H₅F₅O₂S: 271.9930; found: 271.9934.
Anal. Calcd for C₉H₅F₅O₂S: C, 39.71; H, 1.85; F, 39.90. Found: C, 39.89; H, 1.73; F, 40.14.

4,4,5,5,6,6,6-Heptafluoro-1-(2-thienyl)hexane-1,3-dione (3b)

![Structure](image)

Yellow oil; yield: 10.7 g (66%) was obtained by direct distillation and 4.2 g was isolated from low-boiling fractions; yield: 14.9 g (93%); bp 87-88 °C (3 Torr) (lit. 99-102°C /5 Torr) [2].

IR (KBr): 1592, 1412, 1349, 1231, 1126, 1062, 872, 723 cm⁻¹.

¹H NMR (CDCl₃, 300 MHz): δ = 15.10 (broad s, 1H, OH), 7.88 (m, 1H, CH), 7.79(m, 1H, CH), 7.23 (m, 1H, CH), 6.50 (s, 1H, CH=CH).

¹⁹F NMR (CDCl₃, 282.5 MHz): δ = -81.40 (t, 3F, J= 8.3Hz, CF₃), -122.22 (d, 2F, J = 8.7Hz, CF₂), -127.63 (s, 2F, CF₂).

¹³C NMR (CDCl₃, 125.8 MHz): δ = 182.01 (s, 1C, C=O), 172.97 (t, 1C, J=26.6Hz, OH-C=), 139.14(s,1C, C₃Th), 135.32 (s,1C, C₃Th), 132.78 (s,1C, C₃Th),128.84 (s,1C, C₃Th), 128.05; 120.91; 118.93; 116.64; 111.58; 109.50; 108.58; 107.42 (m, 2C, C₃F₇) 95.05 (t, 1C, J=3.8Hz, CH=). Signals of CF₂ and CF₃ groups were not fully acquired and resolved.

MS (EI, 70 eV): m/z (%) = 322(18) [M]⁺, 153(100) [M-C₃F₇]⁺, 111(47) [Th-CO]⁺, 69(63) [CF₃]⁺.

HRMS (ESI⁺): m/z [M]⁺ calcd for C₁₀H₅F₇O₂S: 321.9898; found: 321.9901.

Anal. Calcd for C₁₀H₅F₇O₂S: C,37.28; H, 1.56; F, 41.28. Found: C, 37.11; H, 1.59; F, 41.36.
4,4,5,5,6,6,7,7,7-Nonafluoro-1-(2-thienyl)heptane-1,3-dione (3c)

Yellow solid; yield: 13.2 g (71%) was obtained by direct distillation and 2.1 g was isolated from low-boiling fractions; yield: 15.3 g (82%); bp 90-92 °C (3 Torr); mp 28–29 °C.

IR (KBr): 1617, 1412, 1353, 1239, 1137, 866, 722 cm\(^{-1}\).

\(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta = 15.08\) (broad s, 1H, OH), 7.87 (s, 1H, CH), 7.79(s, 1H, CH), 7.23 (m, 1H, CH), 6.50 (s, 1H, CH=C).

\(^19\)F NMR (CDCl\(_3\), 282.5 MHz): \(\delta = -81.68\) (s, 3F, CF\(_3\)), -121.39 (t, 2F, J = 10.5Hz, CF\(_2\)), -124.06 (s, 2F, CF\(_2\)), -126.66 (s, 2F, CF\(_2\)).

\(^{13}\)C NMR (CDCl\(_3\), 125.8 MHz): \(\delta = 182.94\) (s, 1C, C=O), 173.22 (t, 1C, J=26.6Hz, OH-C=), 139.10(s,1C, C\(_{Th}\)), 135.27 (s,1C, C\(_{Th}\)), 132.74 (s,1C, C\(_{Th}\)),128.83 (s,1C, C\(_{Th}\)),118.34; 116.12; 112.27; 109.93; 108.16 (m, 4C, C\(_4\)F\(_9\)) 95.01 (s, 1C, CH=C). Signals of CF\(_2\) and CF\(_3\) groups were not fully acquired and resolved.

MS (EI, 70 eV): m/z (%) = 372(35) [M]\(^+\), 153(100) [M-C\(_4\)F\(_7\)]\(^+\), 111(35) [ThCO]\(^+\), 69(33) [CF\(_3\)]\(^+\).

HRMS (ESI\(^+\)): m/z [M]\(^+\) calcd for C\(_{11}\)H\(_5\)F\(_9\)O\(_2\)S: 371.9867; found: 371.9863.

Anal. Calcd for C\(_{11}\)H\(_5\)F\(_9\)O\(_2\)S: C,35.50; H, 1.35; F, 45.94. Found: C, 35.66; H, 1.31; F, 45.90.

4,4,5,5,6,6,7,7,8,8,8-Undecafluoro-1-(2-thienyl)octane-1,3-dione (3d)

Light-yellow oil; yield: 15.9 g (75%) was obtained by direct distillation and 2.9 g was isolated from low-boiling fractions; yield: 18.8 g (88%); bp 92-95 °C (2 Torr).
IR (KBr): 1598; 1412; 1359; 1240; 1202; 1143; 863; 723 cm$^{-1}$.

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ = 15.15 (broad s, 1H, OH), 7.88 (s, 1H, CH), 7.79 (s, 1H, CH), 7.23 (m, 1H, CH), 6.51 (s, 1H, CH=C).

$^{19}$F NMR (CDCl$_3$, 282.5 MHz): $\delta$ = -81.61 (s, 3F, CF$_3$), -121.23 (s, 2F, CF$_2$), -123.31 (s, 4F, CF$_2$), -126.97 (s, 2F, CF$_2$).

$^{13}$C NMR (CDCl$_3$, 125.8 MHz): $\delta$ = 181.90 (s, 1C, C=O), 173.33 (t, 1C, J=26.7Hz, OH-C=), 139.10 (s, 1C, C$_\text{Th}$), 135.27 (s, 1C, C$_\text{Th}$), 132.73 (s, 1C, C$_\text{Th}$), 118.31, 116.01, 112.49, 110.24, 108.17 (m, 5C, C$_5$F$_{11}$), 94.99 (s, 1C, CH=). The signals of CF$_2$ and CF$_3$ groups were not fully acquired and were not resolved.

MS (EI, 70 eV): m/z (%) = 422(28) [M]$^+$, 153(100) [M-C$_5$F$_{11}$]$^+$, 111(31) [ThCO]$^+$, 69(31) [CF$_3$]$^+$.

HRMS (ESI+): m/z [M]$^+$ calcd for C$_{12}$H$_5$F$_{11}$O$_2$S: 421.9835; found: 421.9838.

Anal. Calcd for C$_{12}$H$_5$F$_{11}$O$_2$S: C, 34.14; H, 1.19; F, 49.50. Found: C, 34.02; H, 1.26; F, 49.31.

4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluoro-1-(2-thienyl)nonane-1,3-dione (3e)

White solid; yield: 18.0 g (76%) was obtained by direct distillation and 1.6 g was isolated from low-boiling fractions; yield: 19.6 g (83%); bp 110-112 °C (2 Torr); mp 47–48 °C.

IR (KBr): 1591; 1411; 1237; 1209; 1147; 1071; 854; 723 cm$^{-1}$.

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ = 14.85(broad s, 1H, OH), 7.88 (d, 1H, J=3.8Hz, CH), 7.79(d, 1H, J=4.8Hz, CH), 7.23 (t, 1H, J=4.5Hz, CH), 6.51 (s, 1H, CH=C).

$^{19}$F NMR (CDCl$_3$, 282.5 MHz): $\delta$ = -81.62 (s, 3F, CF$_3$), -121.15 (s, 2F, CF$_2$), -122.47 (s, 2F, CF$_2$), -123.13 (s, 2F, CF$_2$), -123.53 (s, 2F, CF$_2$), -126.97 (s, 2F, CF$_2$).
\(^{13}\)C NMR (CDCl\(_3\), 125.8 MHz): \(\delta = 182.03\) (s, 1C, C=O), 173.61 (t, 1C, J=26.6Hz, OH-C=), 139.28(s,1C, C\(_{Th}\)), 135.37 (s,1C, C\(_{Th}\)), 132.87 (s,1C, C\(_{Th}\)), 128.96 (s,1C, C\(_{Th}\)), 95.14 (s, 1C, CH=). The signals of CF\(_2\) and CF\(_3\) groups were not fully acquired and were not resolved.

MS (EI, 70 eV): m/z (%) = 472(5.5) [M]\(^+\), 153(100) [M-C\(_6\)F\(_{13}\)]\(^+\), 111(35.5) [ThCO]\(^+\), 69(37.5) [CF\(_3\)]\(^+\).

HRMS (ESI\(^+\)): m/z [M]\(^+\) calcd for C\(_{13}\)H\(_5\)F\(_{13}\)O\(_2\)S: 471.9803; found: 471.9807.

**Anal. Calcd for C\(_{13}\)H\(_5\)F\(_{13}\)O\(_2\)S:** C,33.07; H, 1.07; F, 52.30. Found: C, 32.91; H, 1.28; F, 52.46.

**4,4,5,5,6,6,7,7,8,8,9,9,10,10-Pentadecafluoro-1-(2-thienyl)decane-1,3-dione (3f)**

![Chemical Structure](image)

Yellow solid; yield: 20.1 g (77%); bp 122-125 °C (2 Torr); mp 53.5–54.5 °C.

**IR (KBr):** 1643; 1411; 1201; 1146; 1061; 1025; 809; 722; 673; 554; 527 cm\(^{-1}\).

**\(^1\)H NMR (CDCl\(_3\), 300 MHz):** \(\delta = 14.95\) (broad s, 1H, OH), 7.88 (d, 1H, J=3.7Hz, CH), 7.79(d, 1H, J=4.9Hz, CH), 7.23 (t, 1H, J=4.2Hz, CH), 6.50 (s, 1H, CH=C).

**\(^19\)F NMR (CDCl\(_3\), 282.5 MHz):** \(\delta = -81.64\) (s, 3F, CF\(_3\)), -121.16 (t, 2F, J=11.3Hz, CF\(_2\)), -122.30 (s, 2F, CF\(_2\)), -122.76 (s, 2F, CF\(_2\)), -123.10 (s, 2F, CF\(_2\)), -123.51 (s, 2F, CF\(_2\)), -126.91 (s, 2F, CF\(_2\)).

**\(^13\)C NMR (CDCl\(_3\), 151 MHz):** \(\delta = 182.64\) (s, 1C, C=O), 177.12 (t, 1C, J=26.4Hz, OH-C=), 139.85(s,1C, C\(_{Th}\)), 136.05 (s,1C, C\(_{Th}\)), 132.51 (s,1C, C\(_{Th}\)), 129.60 (s,1C, C\(_{Th}\)), 118.79, 111.63,110.81 (m, 7C, C\(_7\)F\(_{13}\)), 95.75 (s, 1C, CH=). The signals of CF\(_2\) and CF\(_3\) groups were not fully acquired and were not resolved.

**MS (EI, 70 eV):** m/z (%) = 2.5(5.5) [M]\(^+\), 153(100) [M-C\(_7\)F\(_{13}\)]\(^+\), 111(36) [ThCO]\(^+\), 69(32) [CF\(_3\)]\(^+\).
HRMS (ESI+): m/z [M]^+ calcd for C_{14}H_{5}F_{15}O_{2}S: 521.9771; found: 521.9775.

Anal. Calcd for C_{14}H_{5}F_{15}O_{2}S: C, 32.20; H, 0.97; F, 54.57. Found: C, 32.34; H, 0.91; F, 54.69.

4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11-Leptadecafluoro-1-(2-thienyl)undecane-1,3-dione (3g)

White solid; yield: 23.7 g (83%); bp 142-145 °C (2 Torr); mp 75–76 °C.

IR (KBr): 1611; 1409; 1202; 1151; 966; 794; 734; 672; 527 cm⁻¹.

¹H NMR (CDCl₃, 300 MHz): δ = 15.05 (broad s, 1H, OH), 7.92 (d, 1H, J=3.7Hz, CH), 7.82 (d, 1H, J=4.8Hz, CH), 7.23 (t, 1H, J=4.4Hz, CH), 6.51 (s, 1H, CH=C).

¹⁹F NMR (CDCl₃, 282.5 MHz): δ = -81.64 (s, 3F, CF₃), -121.16 (t, 2F, J=11.3Hz, CF₂), -122.26 (s, 2F, CF₂), -122.64 (s, 4F, CF₂), -123.09 (s, 2F, CF₂), -123.50 (s, 2F, CF₂), -126.91 (s, 2F, CF₂).

¹³C NMR (CDCl₃, 151 MHz): δ = 182.67 (s, 1C, C=O), 174.13 (m, 1C, OH-C=), 139.86 (s, 1C, C_{Th}), 136.04 (s, 1C, C_{Th}), 133.50 (s, 1C, C_{Th}), 129.60 (s, 1C, C_{Th}), 119.96, 114.91, 111.54, 108.57 (m, 7C, C_{7F_{15}}), 95.75 (s, 1C, CH=). The signals of CF₂ and CF₃ groups were not fully acquired and were not resolved.

MS (EI, 70 eV): m/z (%) = 572(1.5) [M]^+, 153(100) [M-C₆F₁₇]^+, 111(30.5) [ThCO]^+, 69(30) [CF₃]^+.

HRMS (ESI+): m/z [M]^+ calcd for C_{15}H_{5}F_{17}O_{2}S: 571.9739; found: 571.97736.

Anal. Calcd for C_{15}H_{5}F_{17}O_{2}S: C, 31.48; H, 0.88; F, 56.44. Found: C, 31.26; H, 0.81; F, 56.09.
1-(2-Thienyl)butane-1,3-dione (5)

Yellow solid; yield: 3.6 g (71%); bp 105-106 °C (3 Torr); mp 35–36 °C (lit. 35-37)[3].

IR (KBr): 1721, 1614, 1520, 1411, 1325, 1277, 1235, 793, 721, 621 cm⁻¹.

¹H NMR (CDCl₃, 300 MHz, a mixture of keto- and enol forms): δ = 16.65 (broad s, 1H, OH), 7.69 (m, 1.31 H, CH), 7.61 (m, 0.92 H, CH), 7.17 (m, 1.13 H, CH), 6.03(s, 1 H, CH=С enol form), 4.03(s, 0.40 H, CH₂, keto form), 2.31(s, 0.64 H, CH₃ enol form), 2.14 (s, 3 H, CH₃ keto form).

¹³C NMR (CDCl₃, 75.5 MHz, mixture of keto- and enol forms): δ = 201.41, 187.43, 186.14, 181.71, 143.68, 141.74, 135.12 (keto form), 133.75 (keto form), 132.31, 130.20, 128.53 (keto form), 128.23, 96.41, 55.44 (keto form), 30.42, 23.64 (keto form).

MS (El, 70 eV): m/z (%) = 168 (100) [M]⁺, 135(32) [M-SH]⁺, 111(68) [ThCO]⁺, 43(26) [CH₃-CO]⁺.

HRMS (ESI+): m/z [M + Na]⁺ calcd for C₈H₆O₂S: 191.0143; found: 191.0146.

References

1. Moore, R.A.; Levine, R. J. Org. Chem. 1964, 29, 1439.
2. Barkley, L. B.; Levine, R. JACS 1951, 73, 4625.
3. Sneed, J. K.; Levine, R. JACS 1950, 72, 5219.