

# Supporting Information

for

## Ruthenium-catalyzed C–H activation of thioxanthenes

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### Characterization data and spectra for compounds 2 and 3.

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## 1 Materials and methods

$^1\text{H}$  NMR spectra were recorded on a BRUKER Avance 400 (400 MHz) device at room temperature. Chemical shifts are expressed in parts per million (ppm,  $\delta$ ), downfield from tetramethylsilane (TMS) and referenced to residual solvent resonance (chloroform, 7.26 ppm) as internal standard. All coupling constants are absolute values and  $J$  values are expressed in Hertz (Hz). The spectra were analyzed according to first order and the descriptions of signals include: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet.  $^{13}\text{C}$  NMR spectra were recorded on a BRUKER Avance 400 (100 MHz) device at room temperature. Chemical shifts are expressed in parts per million (ppm,  $\delta$ ), downfield from tetramethylsilane (TMS) and referenced to residual solvent resonance ( $\text{CDCl}_3$ , 77.0 ppm) as internal standard. The signal structure was analyzed by DEPT and is described as follows: + = primary or tertiary C-atom (positive DEPT signal), - = secondary C-atom (negative DEPT signal), and  $\text{C}_q$  = quaternary C-atom (no DEPT signal).

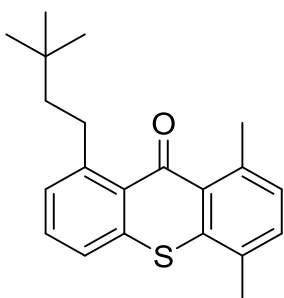
**EIMS** (electron ionization mass spectrometry) was performed using a *Finnigan* MAT 95 (70 eV). The molecular fragments are quoted as relation between mass and charge ( $m/z$ ), the intensities as percentage values relative to the intensity of the base signal (100%). The abbreviation  $[\text{M}]^+$  refers to the molecular ion.

**IR** (infrared spectroscopy) data were recorded on a *Bruker* Alpha FTIR spectrometer and are reported as follows: frequency of absorption ( $\text{cm}^{-1}$ ), intensity of absorption (vs = very strong (81–100%), s = strong (61–80%), m = medium (41–60%), w = weak (21–40%), vw = very weak (1–20%)).

Reactions were monitored by silica gel coated aluminium plates (*Merck*, silica gel 60,  $\text{F}_{254}$ ). Detection was performed by examination under UV light (254 nm). Solvents, reagents and chemicals were purchased from *Sigma-Aldrich* and *ABCR*. Toluene was distilled from sodium prior to use. All reactions were executed under argon atmosphere using oven-dried glassware. All other chemicals were used as purchased unless stated otherwise.

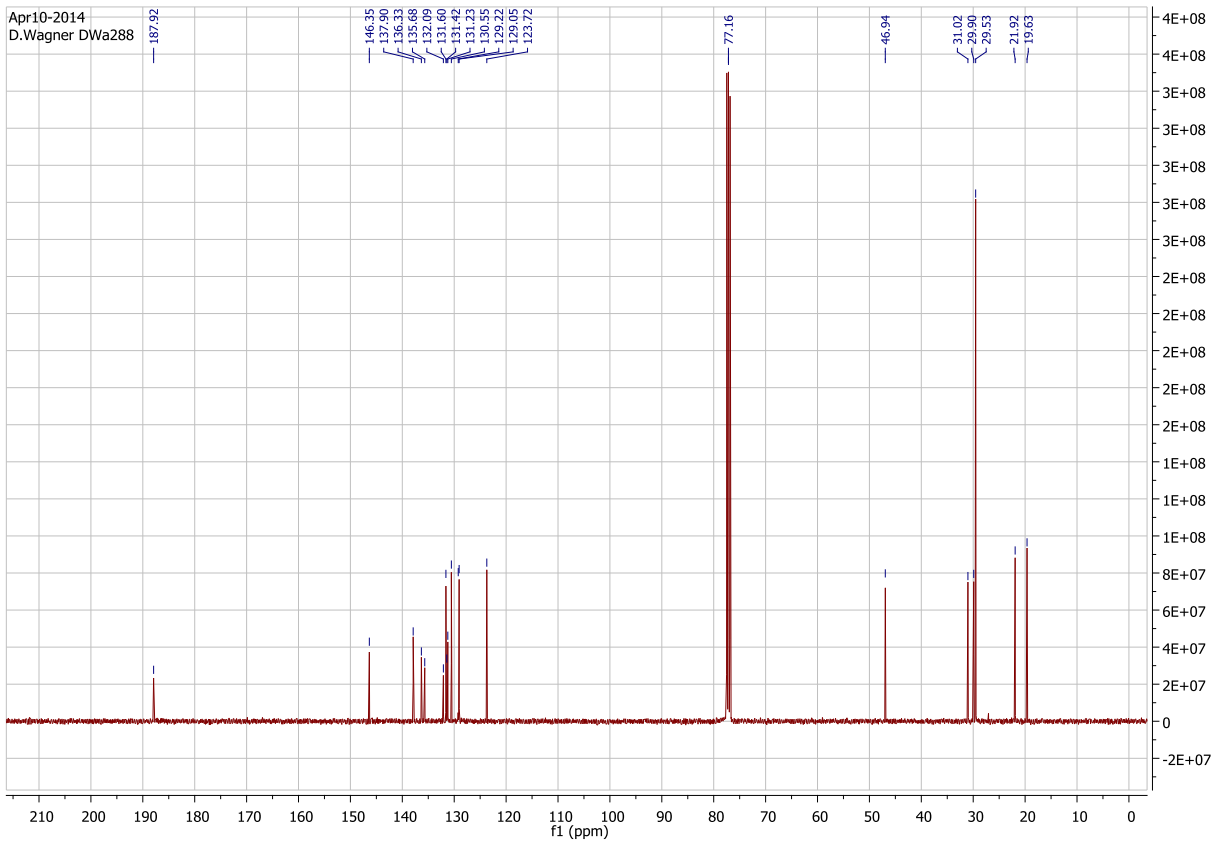
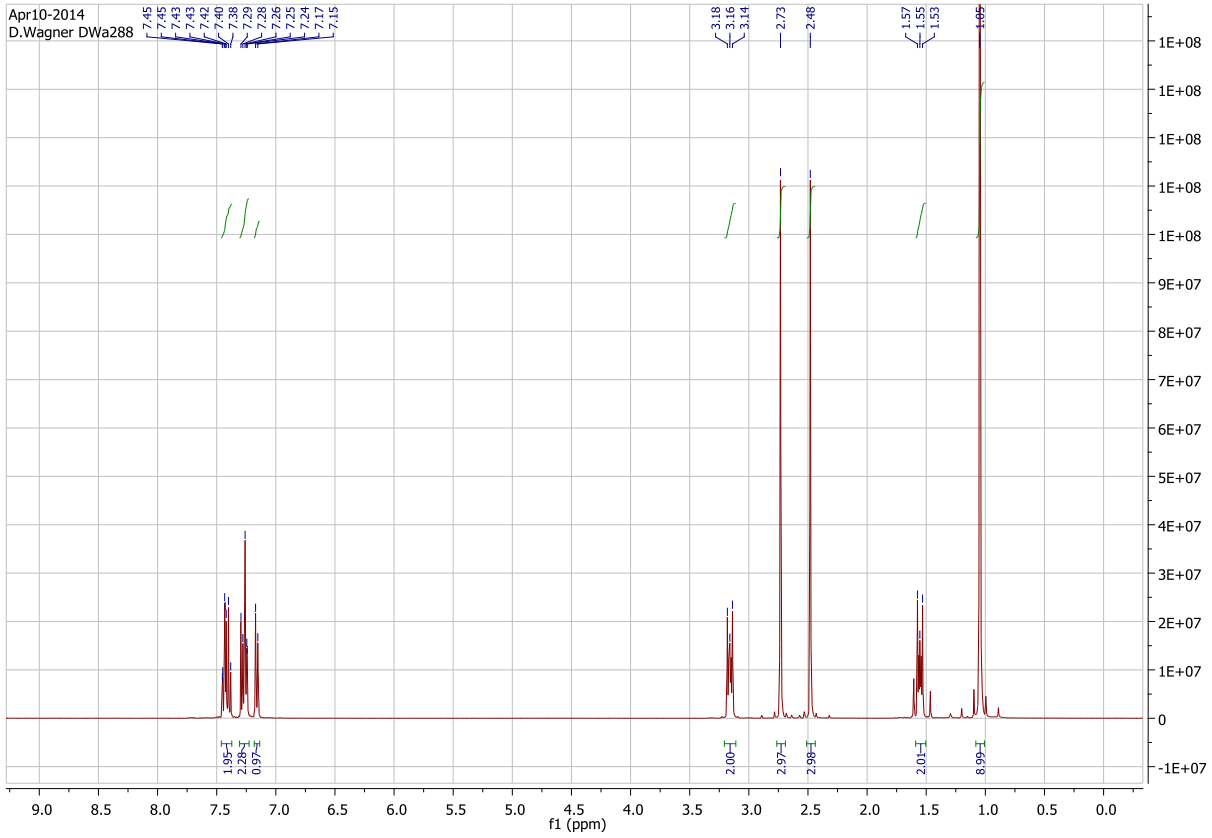
## 2 Analytical data

### 8-(3,3-Dimethylbutyl)-1,4-dimethyl-9H-thioxanthen-9-one (Iba)

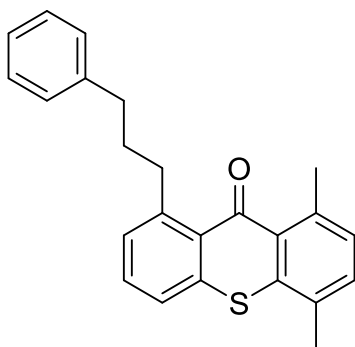


65% yield, clear oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.04 (s, 9 H,  $\text{C}(\text{CH}_3)_3$ ), 1.54 (dt, 2 H,  $\text{CH}_2$ ), 2.47 (s, 3 H,  $\text{CH}_3$  Thiox.), 2.72 (s, 3 H,  $\text{CH}_3$  Thiox.), 3.15 (dt, 2 H,  $\text{CH}_2$ ), 7.15 (d, 1 H,  $H_{\text{ar.}}$ ), 7.23 – 7.28 (m, 2 H,  $H_{\text{ar.}}$ ), 7.37 – 7.44 (m, 2 H,  $H_{\text{ar.}}$ ) –  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 19.5 (+,  $\text{CH}_3$  Thiox.), 21.8 (+,  $\text{CH}_3$  Thiox.), 29.4 (+,  $\text{C}(\text{CH}_3)_3$ ), 29.8 (-,  $\text{CH}_2$ ,  $\text{CH}_2$ ), 30.9 ( $\text{C}_q$ ,  $\text{C}(\text{CH}_3)_3$ ), 46.8 (-,  $\text{CH}_2$ ,  $\text{CH}_2$ ), 123.6 (+, CH, 5- $\text{CH}_{\text{TX}}$ ), 128.9 (+, CH, 7- $\text{CH}_{\text{TX}}$ ), 129.1 (+, CH, 2- $\text{CH}_{\text{TX}}$ ), 130.4 (+, CH, 6- $\text{CH}_{\text{TX}}$ ), 131.1 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 131.3 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 131.5 (+, CH, 3- $\text{CH}_{\text{TX}}$ ), 132.0 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 135.6 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 136.2 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 137.8 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 146.2 ( $\text{C}_q$ ,  $\text{CCH}_2$ ), 187.8 ( $\text{C}_q$ , CO) ppm. – MS (70 eV, EI),  $m/z$  (%): 324 (95)  $[\text{M}^+]$ , 267 (100)  $[\text{C}_{17}\text{H}_{15}\text{OS}^+]$ . – HRMS ( $\text{C}_{21}\text{H}_{24}\text{OS}$ ): calc. 324.1542; found 324.1542 – IR (ATR):  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 2945 (w), 1643 (m) (CO), 1564 (w), 1445 (w), 1390 (vw), 1378 (w), 1363 (w), 1292 (w), 1244 (w), 1207 (w), 1179 (vw), 1150 (vw), 1017 (vw), 953 (vw), 860 (w), 826 (w), 805 (w), 783 (m), 742 (w), 726 (vw), 707 (vw), 686 (w), 617 (vw), 556 (w), 495 (vw), 447 (vw). — EA: calc. for  $\text{C}_{21}\text{H}_{24}\text{OS}$ : C 77.73, H 7.46, S 9.88; found C 78.06, H 7.69, S 9.61.

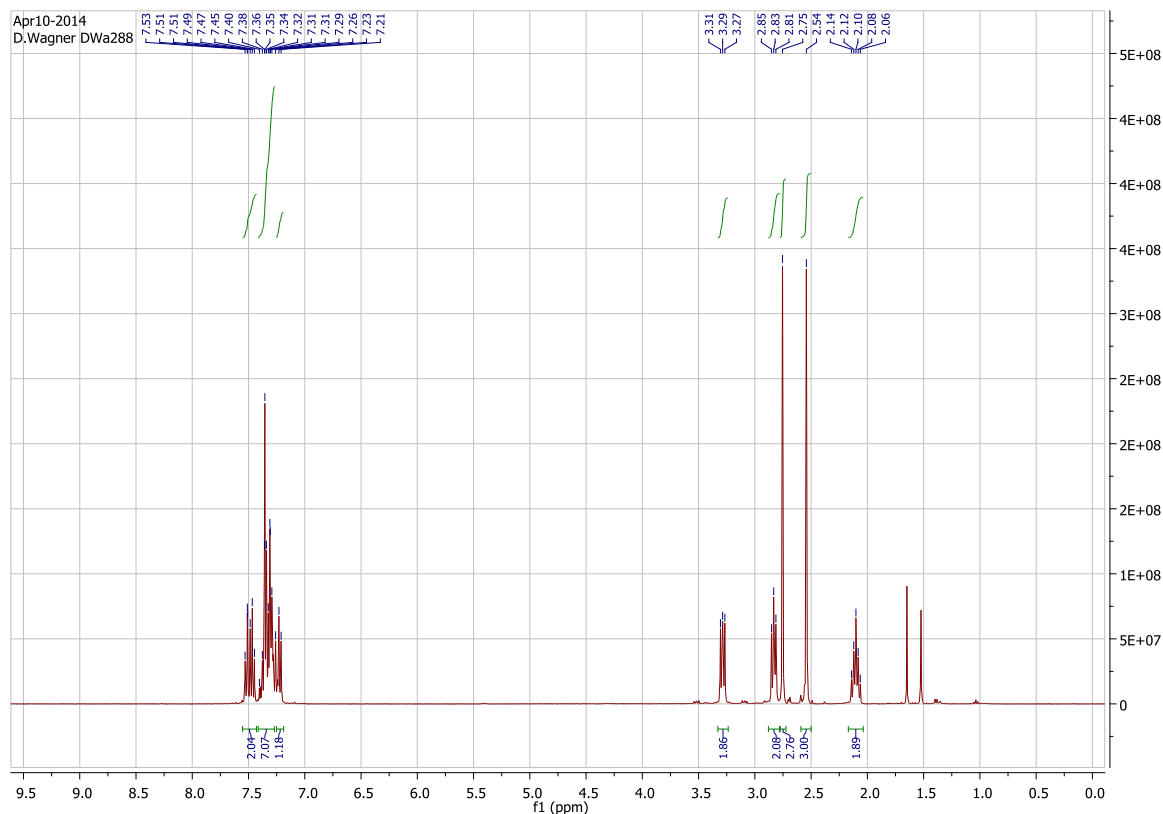


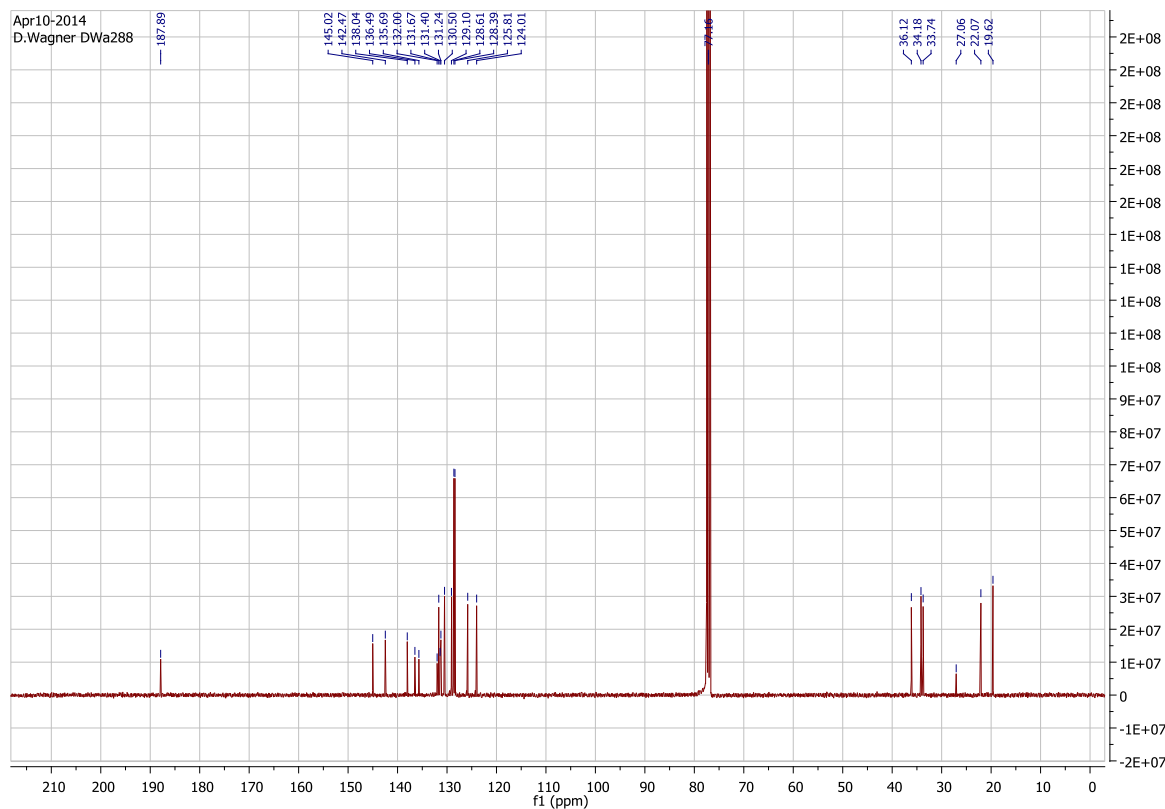
**1,4-Dimethyl-8-(3-phenylpropyl)-9H-thioxanthen-9-one (1bc)**



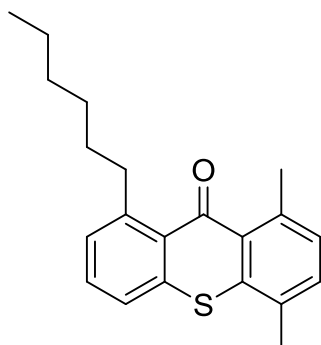
27% yield, clear oil.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.04 (dq, 2 H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 2.48 (s, 3 H,  $\text{CH}_3$  Thiox.), 2.69 (s, 3 H,  $\text{CH}_3$  Thiox.), 2.77 (t, 2 H,  $\text{CH}_2\text{C}_6\text{H}_5$ ), 3.22 (t, 2 H,  $\text{CH}_2$  Thiox.), 7.15 – 7.25 (m, 5 H,  $H_{\text{ar.}}$ ), 7.28 – 7.47 (m, 5 H,  $H_{\text{ar.}}$ ) –  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 19.62 (+,  $\text{CH}_3$  Thiox.), 22.07 (+,  $\text{CH}_3$  Thiox.), 33.7 (-,  $\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 34.2 (-,  $\text{CH}_2$ ,  $\text{CH}_2$  Thiox.), 36.1 (-,  $\text{CH}_2$ ,  $\text{CH}_2\text{Ph}$ ), 124.0 (+, CH, 5- $\text{CH}_{\text{TX}}$ ) 125.8 (+, CH, 4'-CH), 128.4 (+, CH, 2'-CH, 6'-CH), 128.6 (+, CH, 3'-CH, 5'-CH), 129.08 (+, CH, 2- $\text{CH}_{\text{TX}}$ ), 129.1 (+, CH, 7- $\text{CH}_{\text{TX}}$ ), 130.5 (+, CH, 3- $\text{CH}_{\text{TX}}$ ), 131.2 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 131.4 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 131.7 (+, CH, 6- $\text{CH}_{\text{TX}}$ ), 132.0 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 135.7 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 136.5 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 138.0 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 142.5 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 145.0 ( $\text{C}_q$ ,  $\text{C}_{\text{Ph}}$ ), 187.9 ( $\text{C}_q$ , CO) ppm. – MS (70 eV, EI),  $m/z$  (%): 358 (85) [ $\text{M}^+$ ], 267 (65) [ $\text{C}_{17}\text{H}_{15}\text{OS}^+$ ], 254 (100) [ $\text{C}_{16}\text{H}_{14}\text{OS}^+$ ]. – HRMS ( $\text{C}_{24}\text{H}_{22}\text{OS}$ ): calcd. 358.1386; found 358.1388 – IR (ATR):  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 2922 (vw), 2852 (vw), 1648 (w) (CO), 1562 (w), 1494 (vw), 1444 (w), 1378 (vw), 1281 (w), 1254 (vw), 1204 (vw), 1177 (vw), 1083 (vw), 1032 (vw), 958 (vw), 905 (vw), 862 (vw), 814 (w), 804 (w), 782 (w), 749 (w), 727 (w), 697 (w), 621 (vw), 587 (vw), 554 (vw), 483 (vw), 445 (vw). — EA: calcd. for  $\text{C}_{24}\text{H}_{22}\text{OS}$ : C 80.41, H 6.19, S 8.94; found C 80.52, H 6.39, S 8.61.



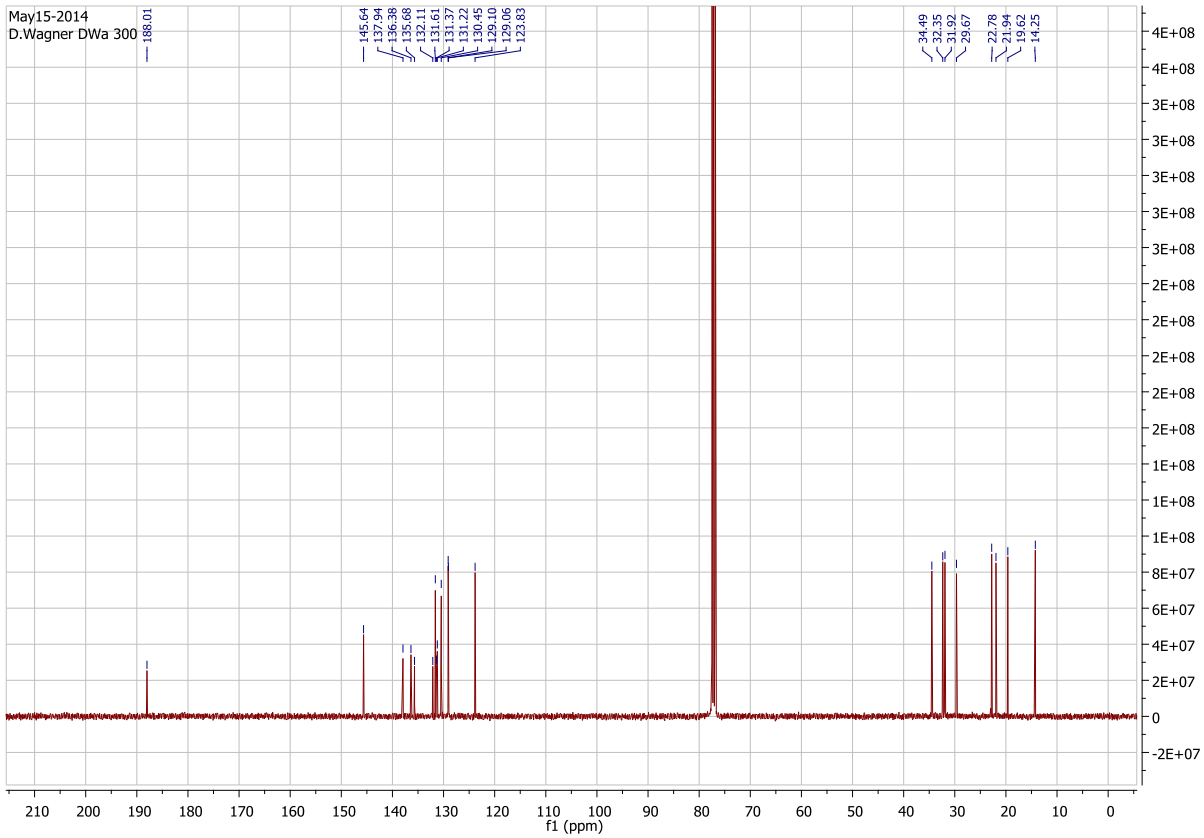
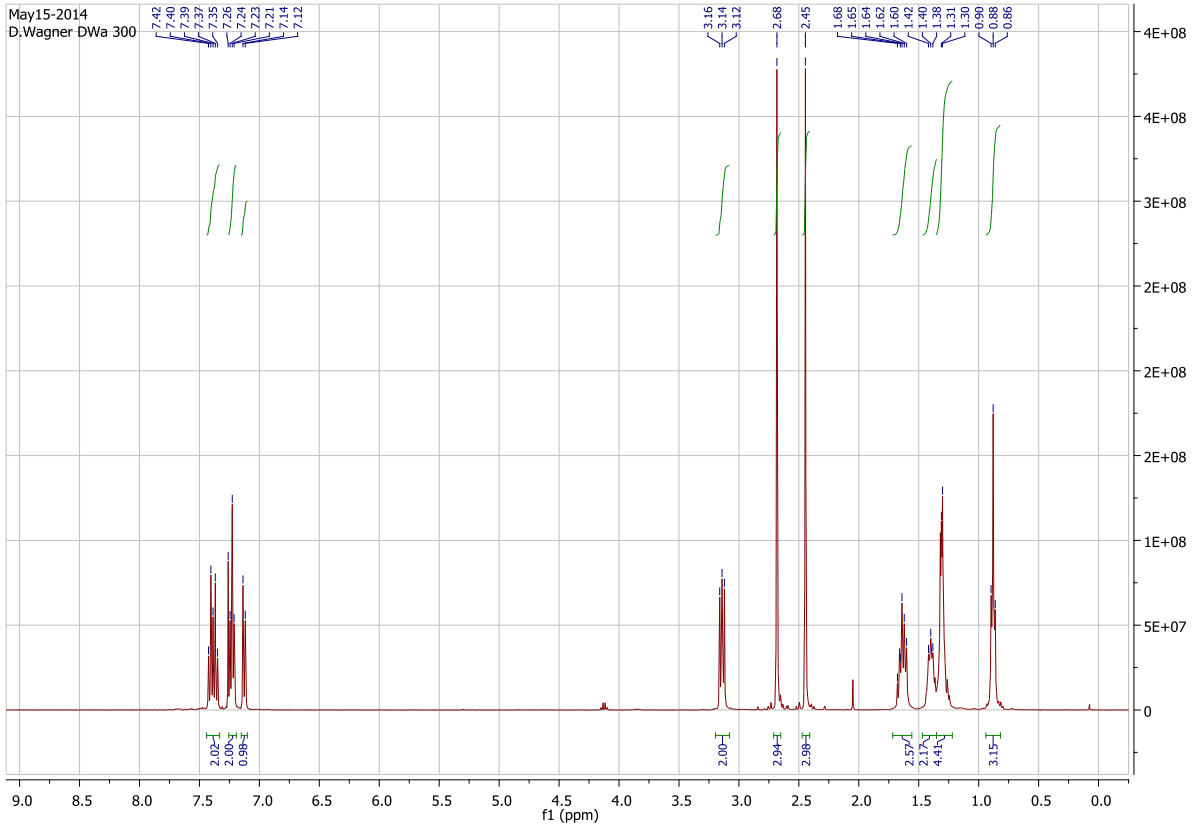


**8-Hexyl-1,4-dimethyl-9H-thioxanthen-9-one (1bb)**

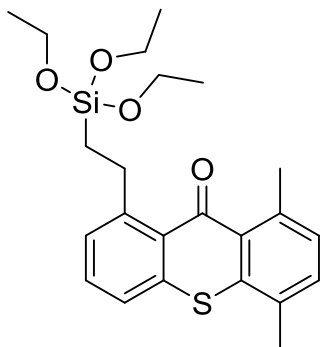


66% yield, clear oil.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.88 (t, 3 H,  $\text{CH}_2\text{CH}_3$ ), 1.21-1.46 (m, 6 H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 1.64 (m, 2 H,  $\text{CH}_2$ ), 2.45 (s, 3 H,  $\text{CH}_3$  Thiox.), 2.68 (s, 3 H,  $\text{CH}_3$  Thiox.), 3.14 (t, 2 H,  $\text{CH}_2$  Thiox.), 7.13 (d, 1 H,  $H_{\text{ar}}$ ), 7.21 – 7.25 (m, 2 H,  $H_{\text{ar}}$ ), 7.35 – 7.42 (m, 2 H,  $H_{\text{ar}}$ ) –  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 15.3 (+,  $\text{CH}_3$  Hex.), 19.6 (+,  $\text{CH}_3$  Thiox.), 21.9 (+,  $\text{CH}_3$  Thiox.), 22.8 (-,  $\text{CH}_2$ , Hex.), 29.7 (-,  $\text{CH}_2$ , Hex.), 32.0 (-,  $\text{CH}_2$ , Hex.), 32.4 (-,  $\text{CH}_2$ , Hex.), 34.5 (-,  $\text{CH}_2$ , Hex.), 123.8 (+, CH, 5- $\text{CH}_{\text{TX}}$ ), 129.0 (+, CH, 2- $\text{CH}_{\text{TX}}$ ), 129.1 (+, CH, 7- $\text{CH}_{\text{TX}}$ ), 130.5 (+, CH, 3- $\text{CH}_{\text{TX}}$ ), 131.2 ( $\text{C}_{\text{q}}$ ,  $\text{C}_{\text{TX}}$ ), 131.4 ( $\text{C}_{\text{q}}$ ,  $\text{C}_{\text{TX}}$ ), 131.6 (+, CH, 6- $\text{CH}_{\text{TX}}$ ), 132.1 ( $\text{C}_{\text{q}}$ ,  $\text{C}_{\text{TX}}$ ), 135.7 ( $\text{C}_{\text{q}}$ ,  $\text{C}_{\text{TX}}$ ), 136.4 ( $\text{C}_{\text{q}}$ ,  $\text{C}_{\text{TX}}$ ), 137.9 ( $\text{C}_{\text{q}}$ ,  $\text{C}_{\text{TX}}$ ), 145.6 ( $\text{C}_{\text{q}}$ ,  $\text{C}_{\text{TX}}$ ), 188.0 ( $\text{C}_{\text{q}}$ ,  $\text{CO}_{\text{TX}}$ ) ppm. – MS (70 eV, EI),  $m/z$  (%): 324 (90) [ $\text{M}^+$ ], 267 (90) [ $\text{C}_{17}\text{H}_{15}\text{OS}^+$ ], 254 (100) [ $\text{C}_{16}\text{H}_{14}\text{OS}^+$ ]. – HRMS ( $\text{C}_{21}\text{H}_{24}\text{OS}$ ): calcd. 324.1542; found 324.1543 – IR (ATR):  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 3446 (vw), 3054 (vw), 2927 (m), 2856 (m), 1715 (w), 1648 (s) (CO), 1569 (m), 1445 (m), 1380 (w), 1293 (m), 1206 (w), 1173 (vw), 1100 (vw), 1015 (vw), 957 (vw), 860 (w), 817 (w), 804 (w), 782 (w), 728 (vw), 686 (vw), 555 (vw), 439 (vw), 2737 (vw).— EA: calcd.  $\text{C}_{21}\text{H}_{24}\text{OS}$ : C 77.73, H 7.46, S 9.88; found C 77.67, H 7.71, S 9.62.

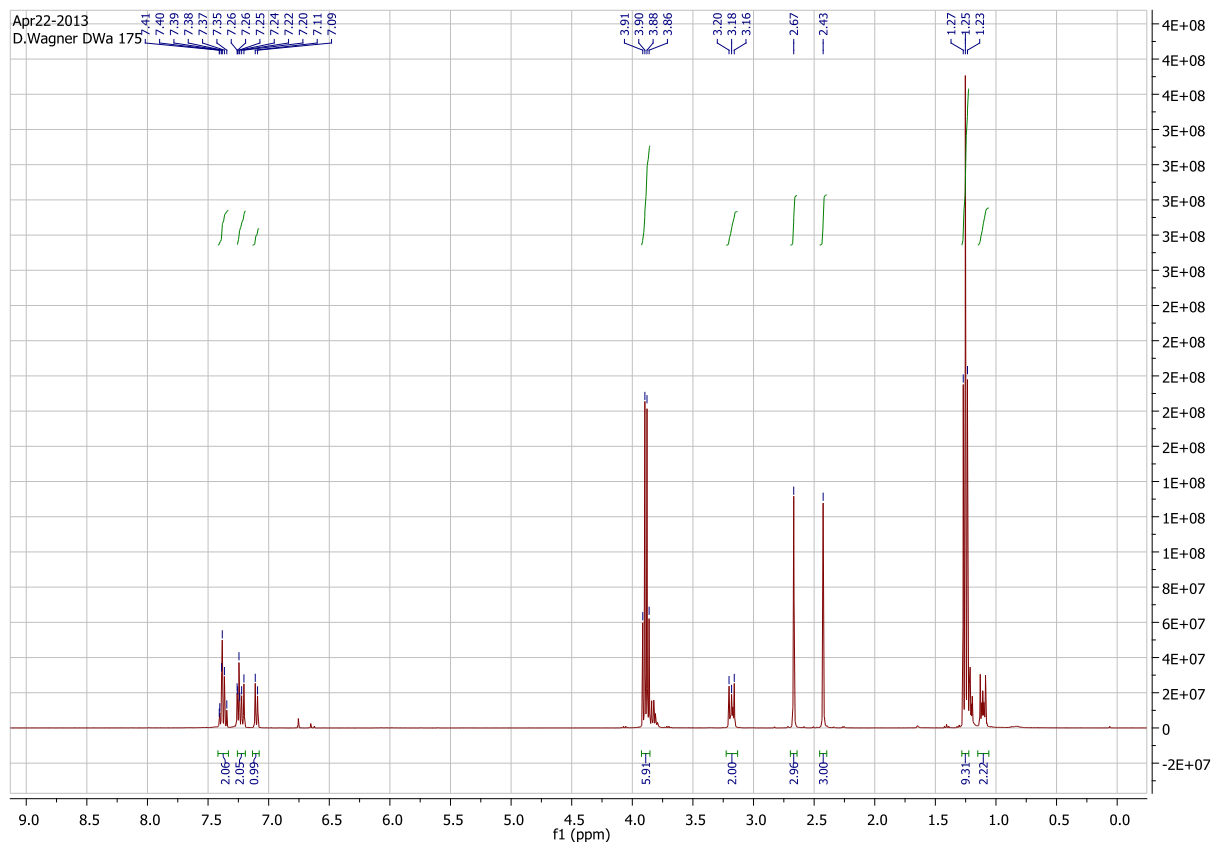


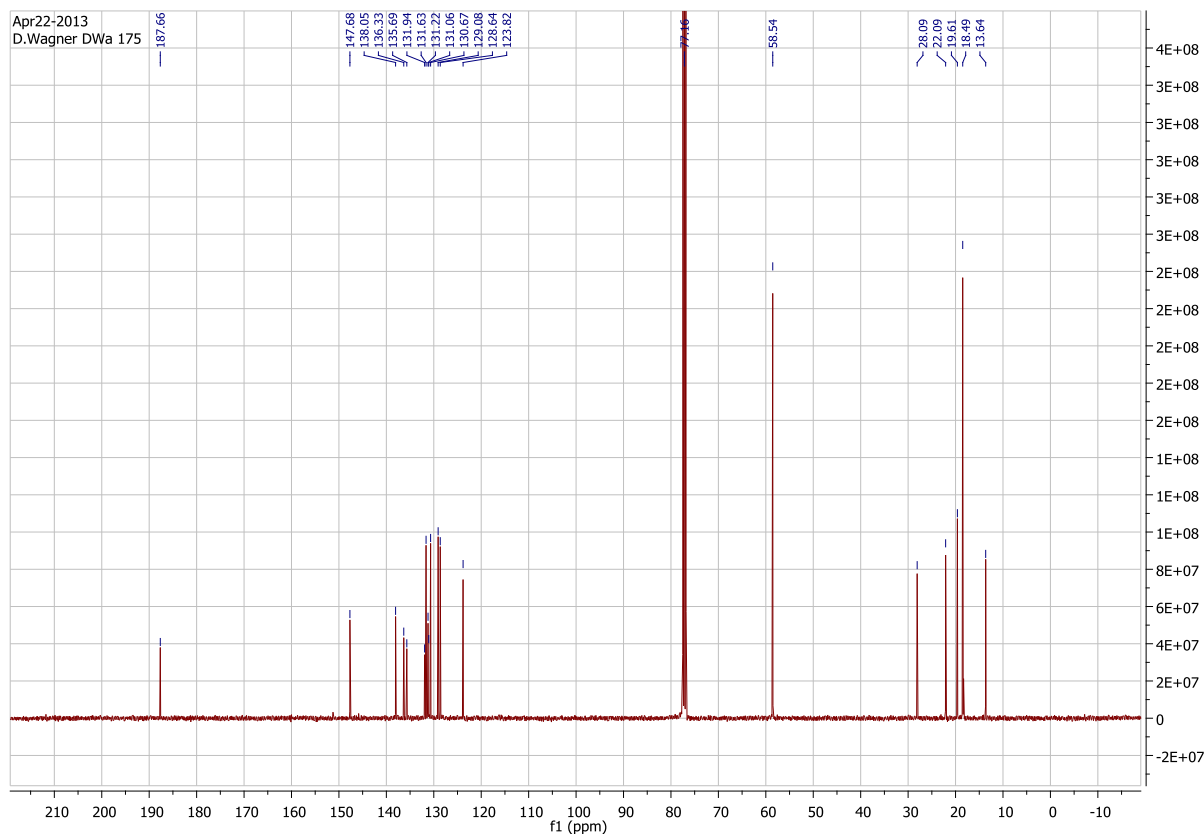
**1,4-Dimethyl-8-(2-(triethoxysilyl)ethyl)-9H-thioxanthen-9-one (1bd)**



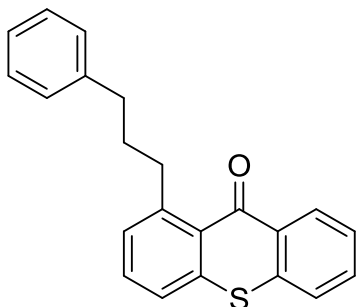
55% yield, clear oil.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.09 – 1.11 (m, 2 H,  $\text{SiCH}_2$ ), 1.25 (t, 9 H,  $\text{Si}(\text{OCH}_2\text{CH}_3)_3$ ), 2.43 (s, 3 H,  $\text{CH}_3$  Thiox.), 2.67 (s, 3 H,  $\text{CH}_3$  Thiox.), 3.16 – 3.20 (m, 2 H,  $\text{CH}_2$ ), 3.86 – 3.91 (q, 6 H,  $\text{Si}(\text{OCH}_2\text{CH}_3)_3$ ), 7.10 (d, 1 H,  $H_{\text{ar}}$ ), 7.20 – 7.25 (m, 2 H,  $H_{\text{ar}}$ ), 7.35 – 7.41 (m, 2 H,  $H_{\text{ar}}$ ) –  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 13.6 (+,  $\text{CH}_3$  Thiox.), 18.5 (-,  $\text{CH}_2$ ,  $\text{Si}(\text{OCH}_2\text{CH}_3)_3$ ), 19.6 (-,  $\text{CH}_2$ ,  $\text{SiCH}_2$ ), 22.1 (-,  $\text{CH}_2$ ,  $\text{CH}_2$  Thiox.), 28.1 (+,  $\text{CH}_3$  Thiox.), 58.5 (+,  $\text{CH}_3$ ,  $\text{Si}(\text{OCH}_2\text{CH}_3)_3$ ), 123.8 (+, CH, 5- $\text{CH}_{\text{TX}}$ ), 128.6 (+, CH, 7- $\text{CH}_{\text{TX}}$ ), 129.1 (+, CH, 2- $\text{CH}_{\text{TX}}$ ), 130.7 (+, CH, 6- $\text{CH}_{\text{TX}}$ ), 131.1 ( $\text{C}_{\text{q}}$ ,  $\text{C}_{\text{TX}}$ ), 131.2 ( $\text{C}_{\text{q}}$ ,  $\text{C}_{\text{TX}}$ ), 131.6 (+, CH, 3- $\text{CH}_{\text{TX}}$ ), 131.9 ( $\text{C}_{\text{q}}$ ,  $\text{C}_{\text{TX}}$ ), 135.7 ( $\text{C}_{\text{q}}$ ,  $\text{C}_{\text{TX}}$ ), 136.3 ( $\text{C}_{\text{q}}$ ,  $\text{C}_{\text{TX}}$ ), 138.1 ( $\text{C}_{\text{q}}$ ,  $\text{C}_{\text{TX}}$ ), 147.7 ( $\text{C}_{\text{q}}$ ,  $\text{C}_{\text{TX}}$ ), 187.7 ( $\text{C}_{\text{q}}$ , CO) ppm. – MS (70 eV, EI),  $m/z$  (%): 430 (95) [ $\text{M}^+$ ]. – HRMS ( $\text{C}_{23}\text{H}_{30}\text{SiSO}_4$ ): calcd. 430.1632; found 430.1634 – IR (ATR):  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 2970 (m), 2924 (w), 2889 (w), 1635 (m) (CO), 1573 (w), 1445 (m), 1380 (w), 1313 (w), 1298 (w), 1266 (vw), 1205 (vw), 1181 (m), 1071 (vs), 959 (s), 911 (w), 861 (w), 810 (w), 769 (s), 727 (w), 708 (w), 686 (w), 605 (w), 553 (w), 536 (vw), 508 (vw), 449 (w), 420 (w). — EA: calcd.  $\text{C}_{23}\text{H}_{30}\text{O}_4\text{SSi}$ : C 64.15, H 7.02, S 7.45; found C 63.82, H 7.56, S 6.60.





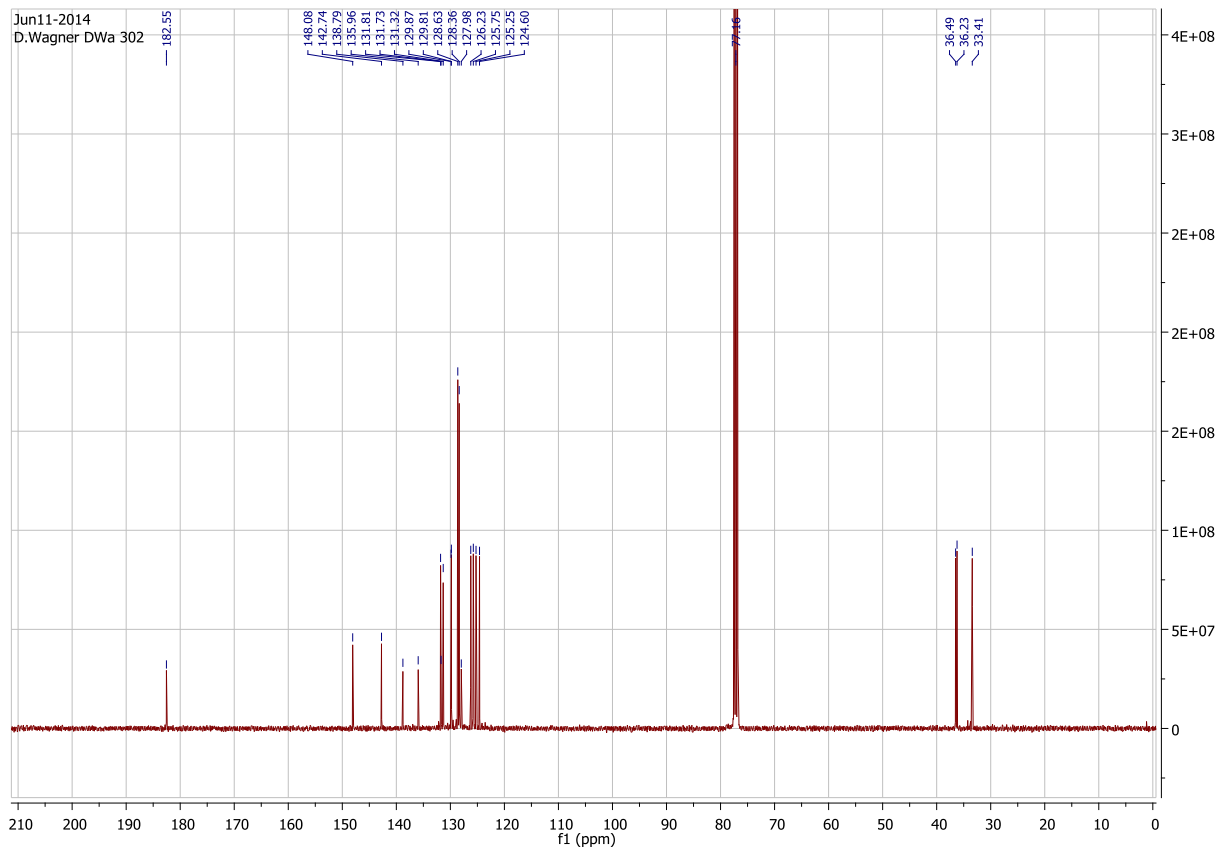
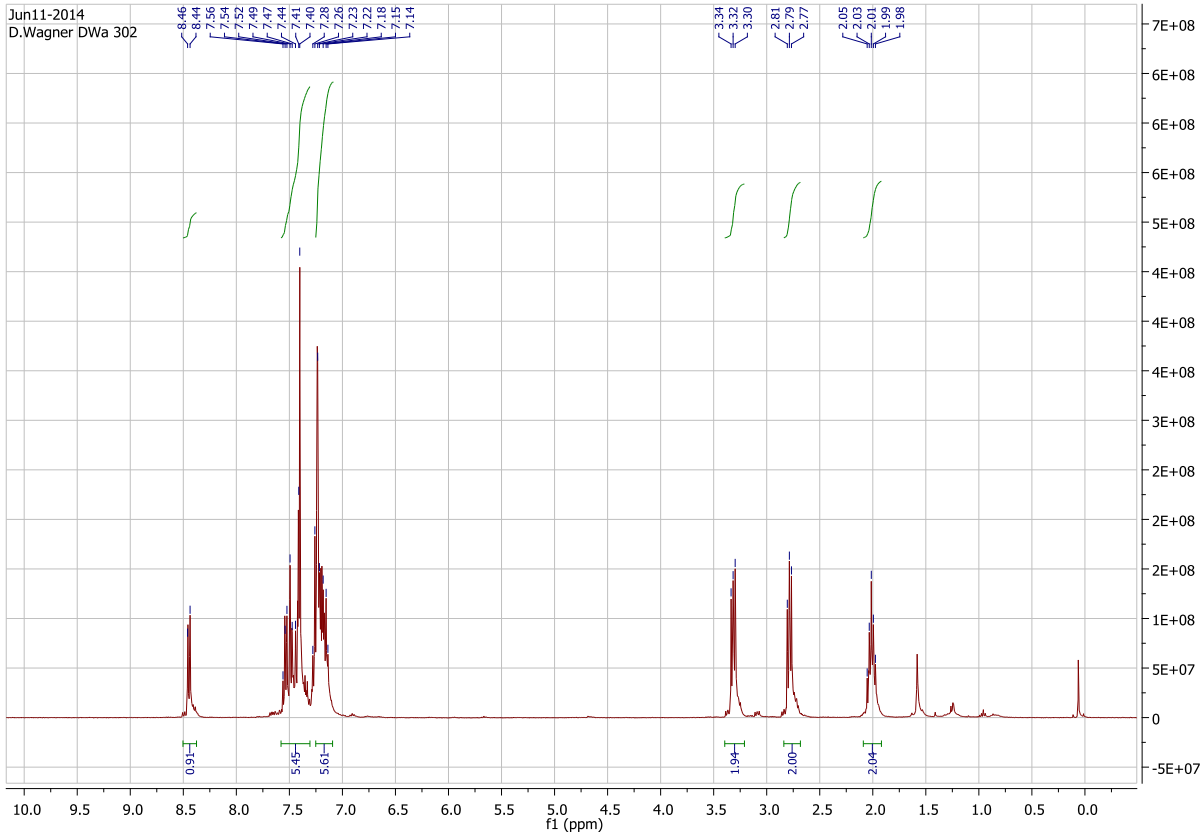
**1-(3-Phenylpropyl)-9H-thioxanthen-9-one (1ac)**



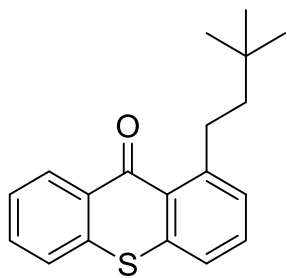
7% yield, clear oil.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.04 (dq, 2 H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 2.81 (t, 2 H,  $\text{CH}_2\text{C}_6\text{H}_5$ ), 3.34 (t, 2 H,  $\text{CH}_2$  Thiox.), 7.16 – 7.59 (m, 11 H,  $H_{\text{ar.}}$ ), 8.47 (dd, 1 H, 8- $H_{\text{TX}}$ ). –  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 33.4 (-,  $\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 36.2 (-,  $\text{CH}_2$ ,  $\text{CH}_2\text{TX}$ ), 36.5 (-,  $\text{CH}_2$ ,  $\text{CH}_2\text{Ph}$ ), 124.6 (+, CH, 4'- $\text{CH}_{\text{TX}}$ ), 125.3 (+, CH, 4' CH), 125.8 (+, CH, 7- $\text{CH}_{\text{TX}}$ ), 126.2 (+, CH, 8- $\text{CH}_{\text{TX}}$ ), 128.0 (Cq,  $\text{C}_{\text{TX}}$ ), 128.4 (+, CH, 2'-CH, 6'-CH), 128.6 (+, CH, 3'-CH, 5'-CH), 129.8 (+, CH, 5- $\text{CH}_{\text{TX}}$ ), 129.9 (+, CH, 2- $\text{CH}_{\text{TX}}$ ), 131.3 (+, CH, 6- $\text{CH}_{\text{TX}}$ ), 131.7 (Cq,  $\text{C}_{\text{TX}}$ ), 131.8 (Cq,  $\text{C}_{\text{TX}}$ ), 135.0 (Cq,  $\text{C}_{\text{TX}}$ ), 138.8 (Cq,  $\text{C}_{\text{TX}}$ ), 142.7 (Cq,  $\text{C}_{\text{TX}}$ ), 148.1 (Cq,  $\text{C}_{\text{Ph}}$ ), 182.5 (Cq, CO). MS (70 eV, EI),  $m/z$  (%): 330 (35) [ $\text{M}^+$ ], 239 (100) [ $\text{C}_{15}\text{H}_{11}\text{OS}^+$ ], 226 (95) [ $\text{C}_{14}\text{H}_9\text{OS}^+$ ]. – HRMS ( $\text{C}_{22}\text{H}_{18}\text{OS}$ ): calcd. 330.1073; found 330.1071 – IR (ATR):  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 3023 (vw) 2922 (w), 2849 (w), 1912 (vw), 1626 (m) (CO), 1584 (m), 1493 (w), 1432 (m); 1344 (vw), 1303 (m), 1182 (w), 1154 (w), 1081 (w), 1034 (w), 957 (vw), 928 (vw), 890 (vw), 873 (w), 806 (vw), 784 (w), 740 (m), 714 (m), 696 (m), 670 (m), 647 (w), 581 (vw), 541 (vw), 521 (vw), 484 (w).



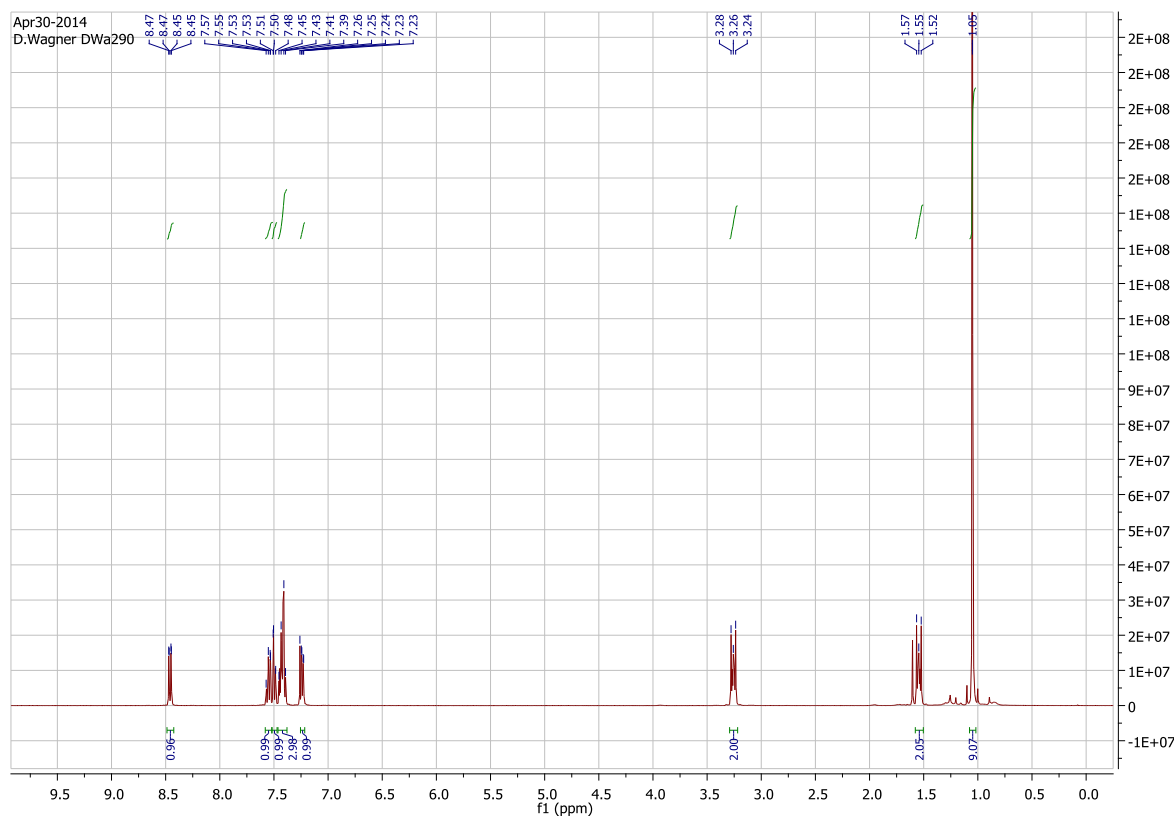


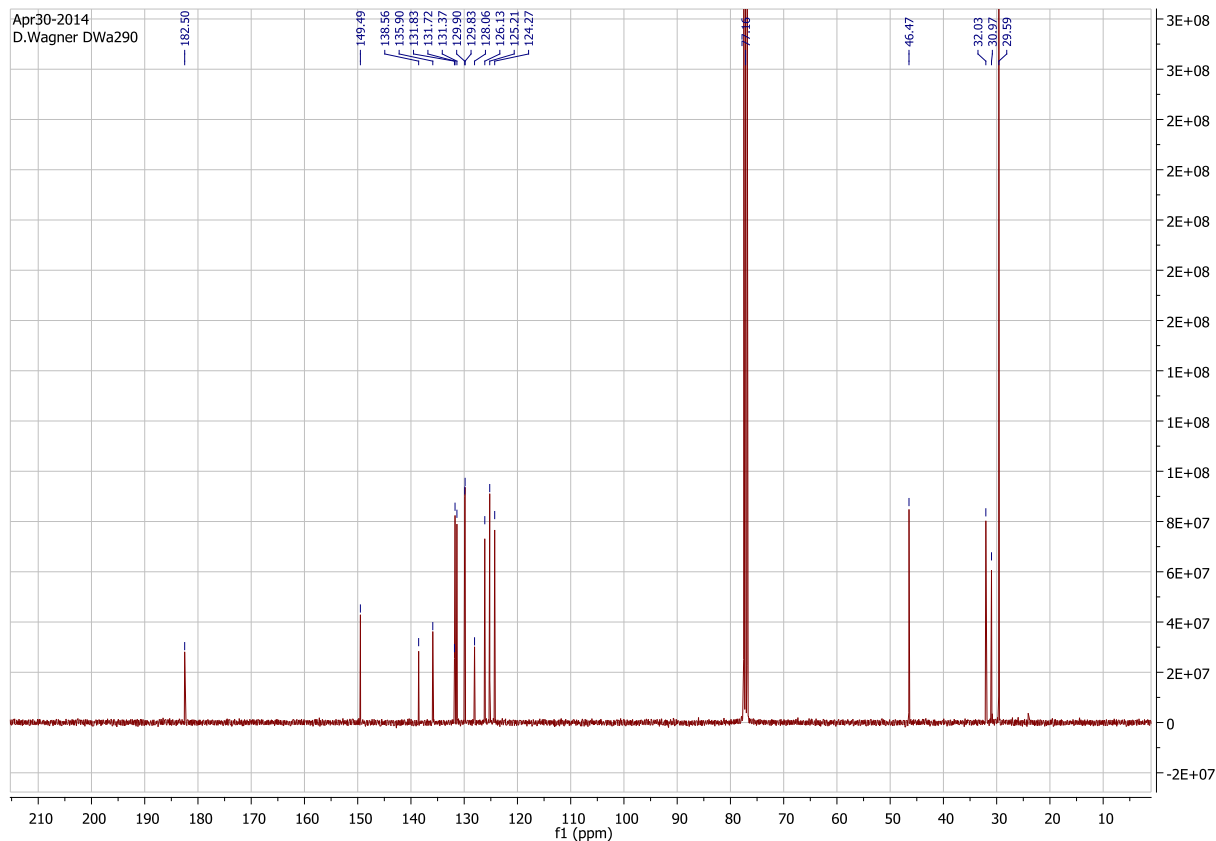
**1-(3,3-Dimethylbutyl)-9H-thioxanthen-9-one (1aa),**



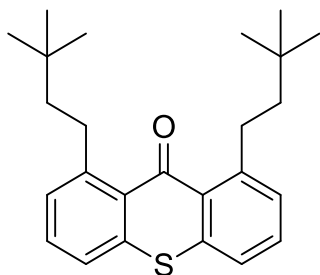
47% yield, clear oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.05 (s, 9 H,  $\text{C}(\text{CH}_3)_3$ ), 1.54 (dt, 2 H,  $\text{CH}_2$ ), 3.26 (dt, 2 H,  $\text{CH}_2$ ), 7.23 – 7.26 (dd, 1 H,  $H_{\text{ar}}$ ), 7.39 – 7.45 (m, 3 H,  $H_{\text{ar}}$ ), 7.48 – 7.57 (m, 2 H,  $H_{\text{ar}}$ ), 8.46 (dd, 1 H,  $H_{\text{ar}}$ ) –  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 29.6 (+,  $\text{CH}_3$ ,  $\text{C}(\text{CH}_3)_3$ ), 31.0 ( $\text{C}_q$ ,  $\text{C}(\text{CH}_3)_3$ ), 32.0 (-,  $\text{CH}_2$ ,  $\text{CH}_{2\text{TX}}$ ), 46.5 (-,  $\text{CH}_2$ ,  $\text{CH}_2$ ), 124.3 (+, CH, 4- $\text{CH}_{\text{TX}}$ ), 125.2 (+, CH, 7- $\text{CH}_{\text{TX}}$ ), 126.1 (+, CH, 8- $\text{CH}_{\text{TX}}$ ), 128.1 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 129.8 (+, CH, 5- $\text{CH}_{\text{TX}}$ ), 129.9 (+, CH, 2- $\text{CH}_{\text{TX}}$ ), 131.4 (+, CH, 6- $\text{CH}_{\text{TX}}$ ), 131.7 (+, CH, 3- $\text{CH}_{\text{TX}}$ ), 131.8 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 135.9 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 138.6 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 149.5 ( $\text{C}_q$ , 1- $\text{C}_{\text{TX}}$ ), 182.5 ( $\text{C}_q$ , CO). MS (70 eV, EI),  $m/z$  (%): 296 (35) [ $\text{M}^+$ ], 239 (100) [ $\text{C}_{15}\text{H}_{11}\text{OS}^+$ ]. – HRMS ( $\text{C}_{19}\text{H}_{20}\text{OS}$ ): calcd. 296.1229; found 296.1228. – IR (ATR):  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 2950 (w), 2859 (w), 1630 (m) (CO), 1583 (m), 1556 (w), 1462 (w), 1443 (m), 1361 (w), 1291 (m), 1235 (w), 1181 (w), 1153 (w), 1126 (w), 1083 (w), 1050 (vw), 1035 (vw), 1009 (vw), 957 (vw), 930 (vw), 872 (w), 811 (vw), 787 (m), 760 (w), 746 (m), 716 (w), 670 (w), 651 (w), 614 (w), 556 (vw). – EA: calcd. for  $\text{C}_{19}\text{H}_{20}\text{OS}$ : C 76.99, H 6.80, S 10.82; found C 77.12, H 7.07, S 10.42



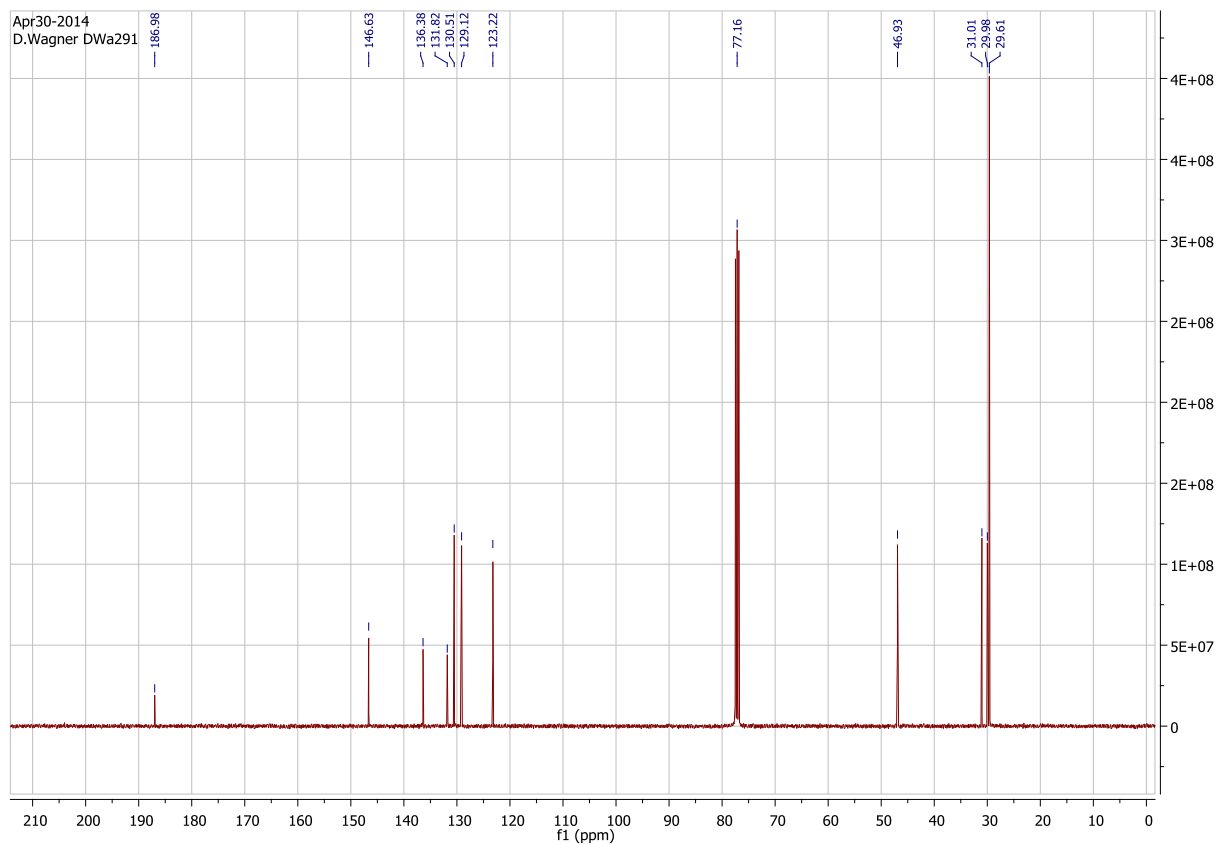
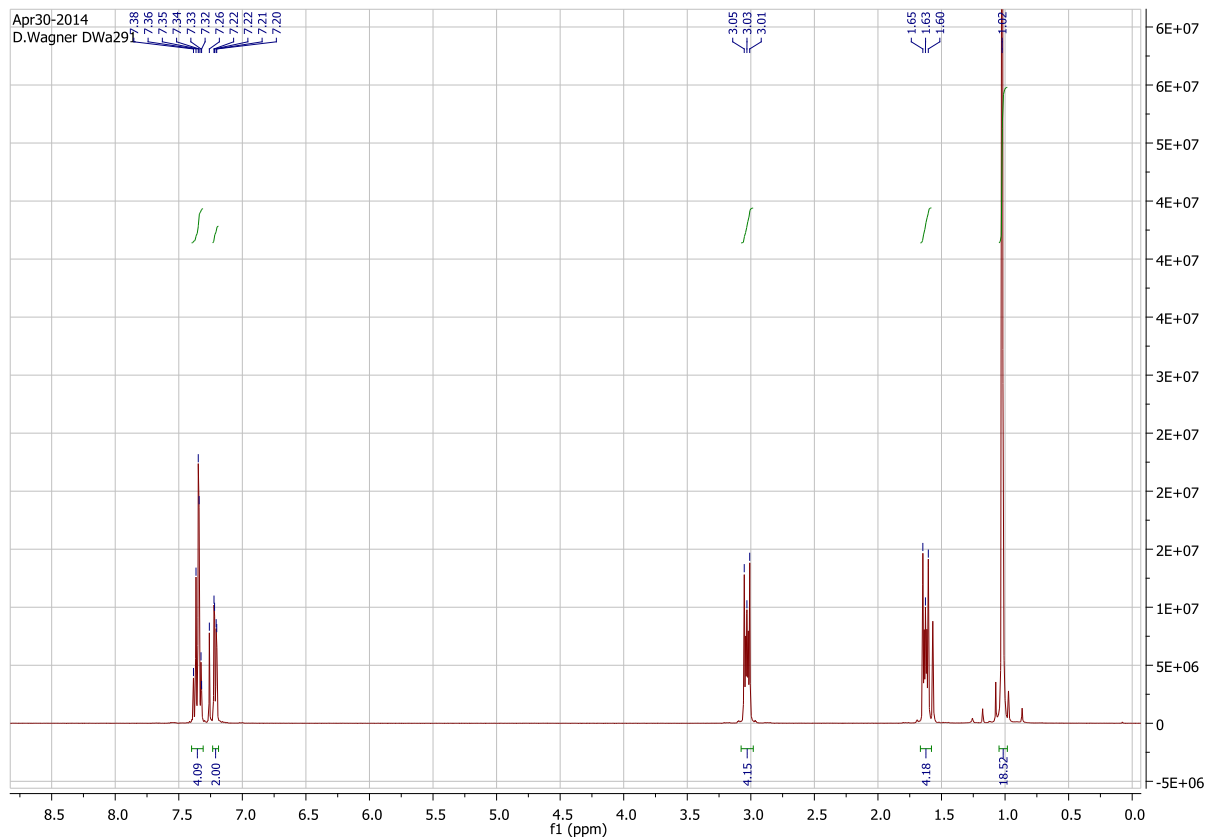


**1,8-Bis(3,3-dimethylbutyl)-9H-thioxanthen-9-one (1aa<sub>bis</sub>)**

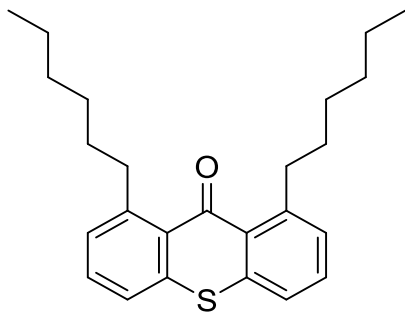


20% yield, clear oil.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.02 (s, 18 H, 2  $\times$   $\text{C}(\text{CH}_3)_3$ ), 1.63 (dt, 4 H, 2  $\times$   $\text{CH}_2$ ), 3.03 (dt, 4 H, 2  $\times$   $\text{CH}_2$ ), 7.20 – 7.22 (dd, 2 H, 2,6- $H_{\text{TX}}$ ), 7.32 – 7.38 (m, 4 H, 3,4,5,6- $H_{\text{TX}}$ ).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 29.6 (+,  $\text{CH}_3$ ,  $\text{C}(\text{CH}_3)_3$ ), 30.0 (-,  $\text{CH}_2$ ,  $\text{CH}_{2\text{TX}}$ ), 31.0 ( $\text{C}_q$ ,  $\text{C}(\text{CH}_3)_3$ ), 46.9 (-,  $\text{CH}_2$ ,  $\text{CH}_2$ ), 123.2 (+, CH, 4,5- $\text{CH}_{\text{TX}}$ ), 129.1 (+, CH, 2,7- $\text{CH}_{\text{TX}}$ ), 130.5 (+, CH, 3,6- $\text{CH}_{\text{TX}}$ ), 131.8 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 136.4 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 146.6 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 187.0 ( $\text{C}_q$ , CO). MS (70 eV, EI),  $m/z$  (%): 380 (70) [ $\text{M}^+$ ], 323 (100) [ $\text{C}_{21}\text{H}_{23}\text{OS}^+$ ]. – HRMS ( $\text{C}_{25}\text{H}_{32}\text{OS}$ ): calcd. 380.2168; found 380.2167. – IR (ATR):  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 2943 (vw), 2860 (vw), 1656 (w) (CO), 1577 (vw), 1560 (vw), 1445 (w), 1361 (vw), 1314 (vw), 1284 (w), 1235 (vw), 1181 (vw), 1151 (vw), 1049 (vw), 918 (vw), 863 (vw), 814 (vw), 779 (w), 750 (vw), 686 (vw), 601 (vw), 552 (vw), 450 (vw). EA: calcd. for  $\text{C}_{25}\text{H}_{32}\text{OS}$ : C 78.90, H 8.48, S 8.42; found C 78.91, H 8.68, S 8.12

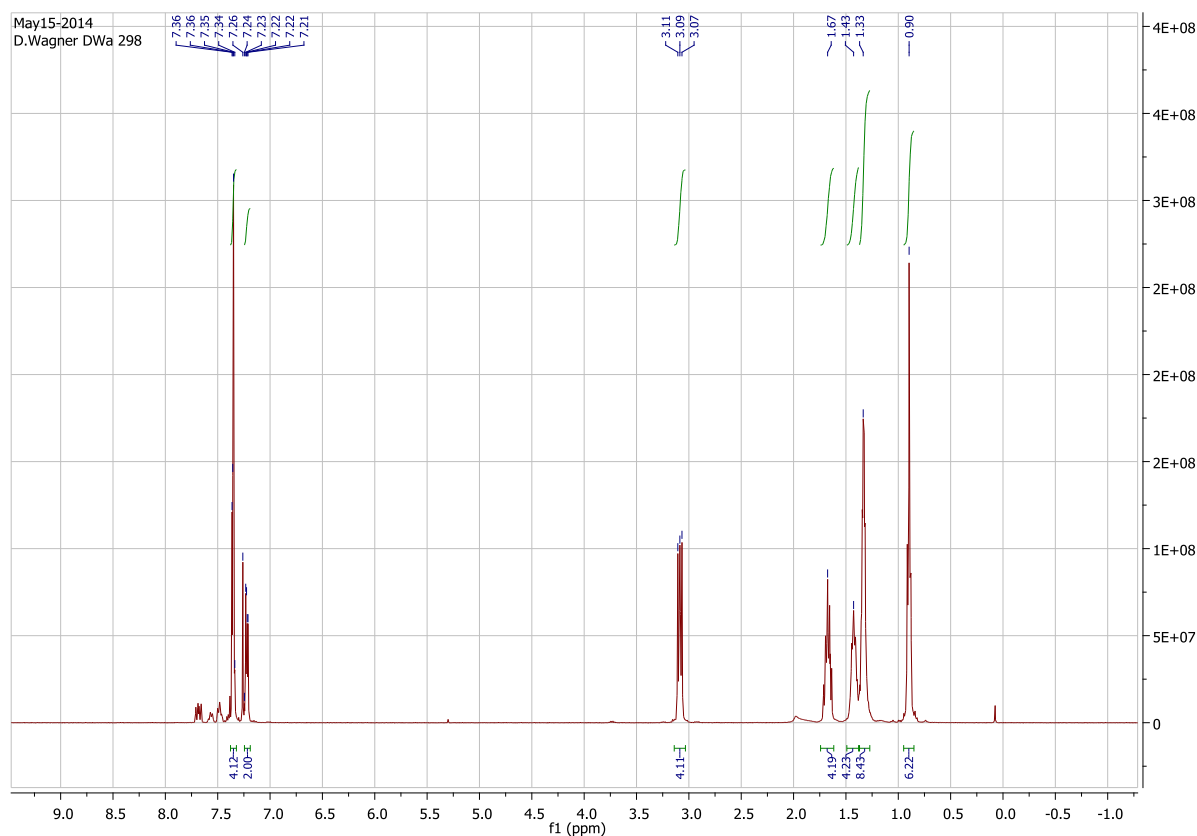


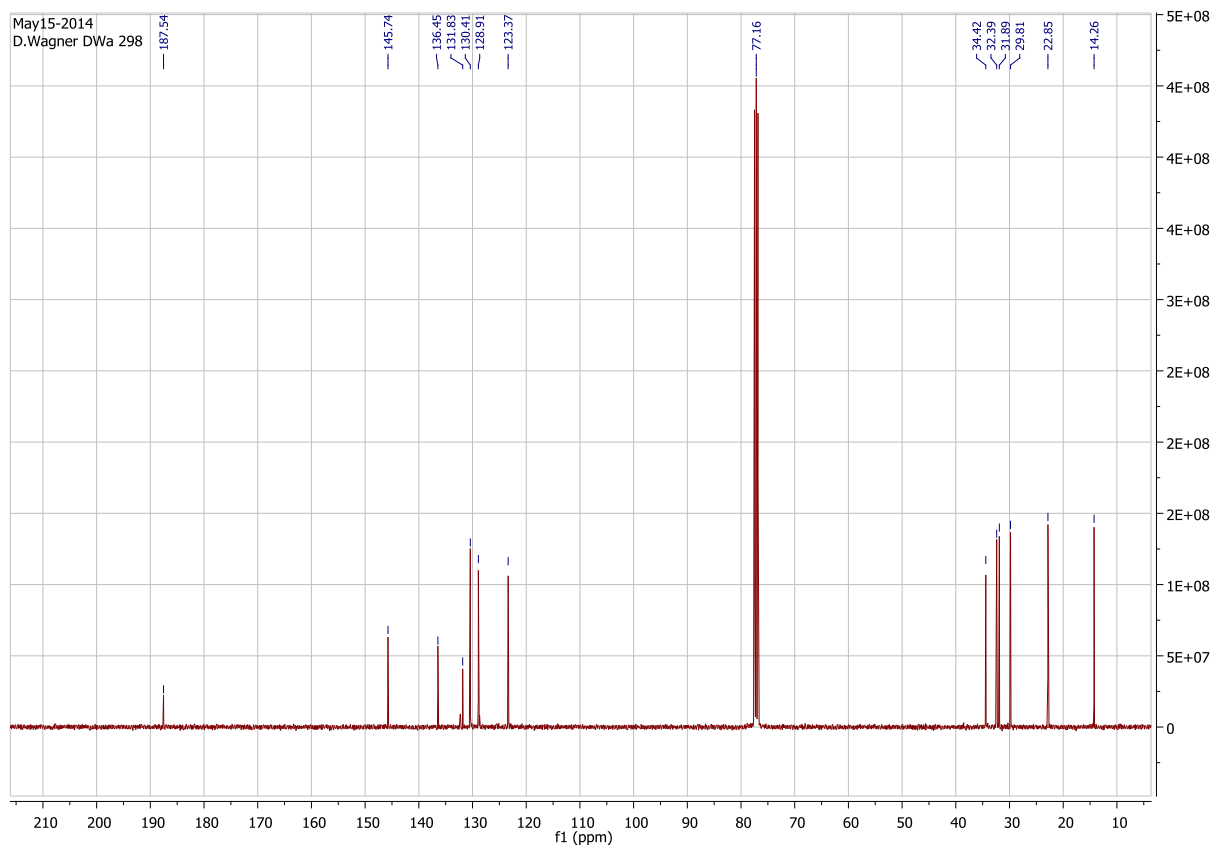
**1,8-Dihexyl-9H-thioxanthen-9-one (1ab<sub>bis</sub>)**



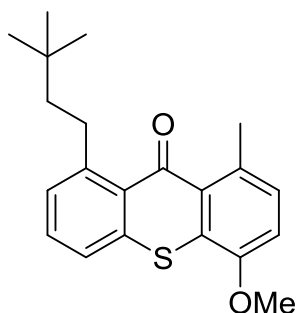
43% yield, clear oil.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.90 (t, 6 H, 2 x  $\text{CH}_3$ ), 1.33 – 1.43 (m, 12 H, 2 x  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.67 (m, 2 H,  $\text{C}_4\text{H}_9\text{CH}_2\text{CH}_2$ ), 3.09 (dt, 2 H,  $\text{C}_5\text{H}_{11}\text{CH}_2$ ), 7.21 – 7.24 (m, 2 H, 2,7- $\text{CH}_{\text{TX}}$ ), 7.33 – 7.36 (m, 4 H, 3,4,5,6- $\text{C}_{\text{TX}}$ ).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 14.3 (+,  $\text{CH}_3$ ,  $\text{CH}_3$ ), 22.9 (-,  $\text{CH}_2$ ,  $\text{CH}_3\text{CH}_2$ ), 29.8 (-,  $\text{CH}_2$ ,  $\text{C}_2\text{H}_5\text{CH}_2$ ), 31.9 (-,  $\text{CH}_2$ ,  $\text{C}_3\text{H}_7\text{CH}_2$ ), 32.4 (-,  $\text{CH}_2$ ,  $\text{C}_4\text{H}_9\text{CH}_2$ ), 34.4 (-,  $\text{CH}_2$ ,  $\text{C}_5\text{H}_{11}\text{CH}_2$ ), 123.4 (+, CH, 4- $\text{CH}_{\text{TX}}$ ), 128.9 (+, CH, 2-CH), 130.4 (+, CH, 3-CH), 131.8 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 136.5 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 145.7 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 187.5 ( $\text{C}_q$ , CO). – MS (70 eV, EI),  $m/z$  (%): 380 (100) [ $\text{M}^+$ ]. – HRMS ( $\text{C}_{25}\text{H}_{32}\text{OS}$ ): calcd. 380.2168; found 380.2168. – IR (ATR):  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 3444 (vw), 3055 (vw), 2956 (w), 2926 (w), 2855 (w), 1653 (w) (CO), 1581 (w), 1560 (vw), 1445 (w), 1378 (vw), 1288 (vw), 1174 (vw), 1118 (vw), 861 (vw), 779 (w), 722 (vw), 687 (vw), 542 (vw). – EA: calcd. for  $\text{C}_{25}\text{H}_{32}\text{OS}$ : C 78.90, H 8.48, S 8.42; found C 79.40, H 8.09, S 7.67.



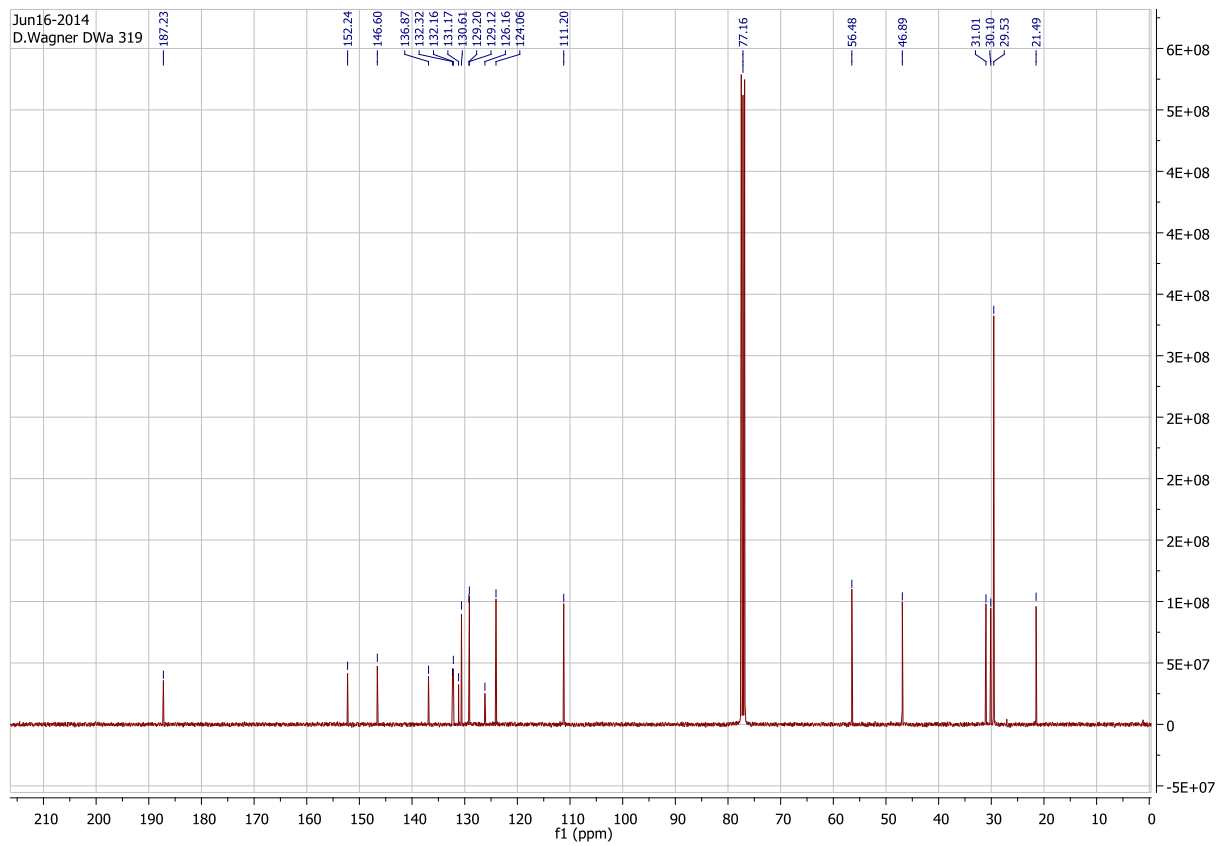
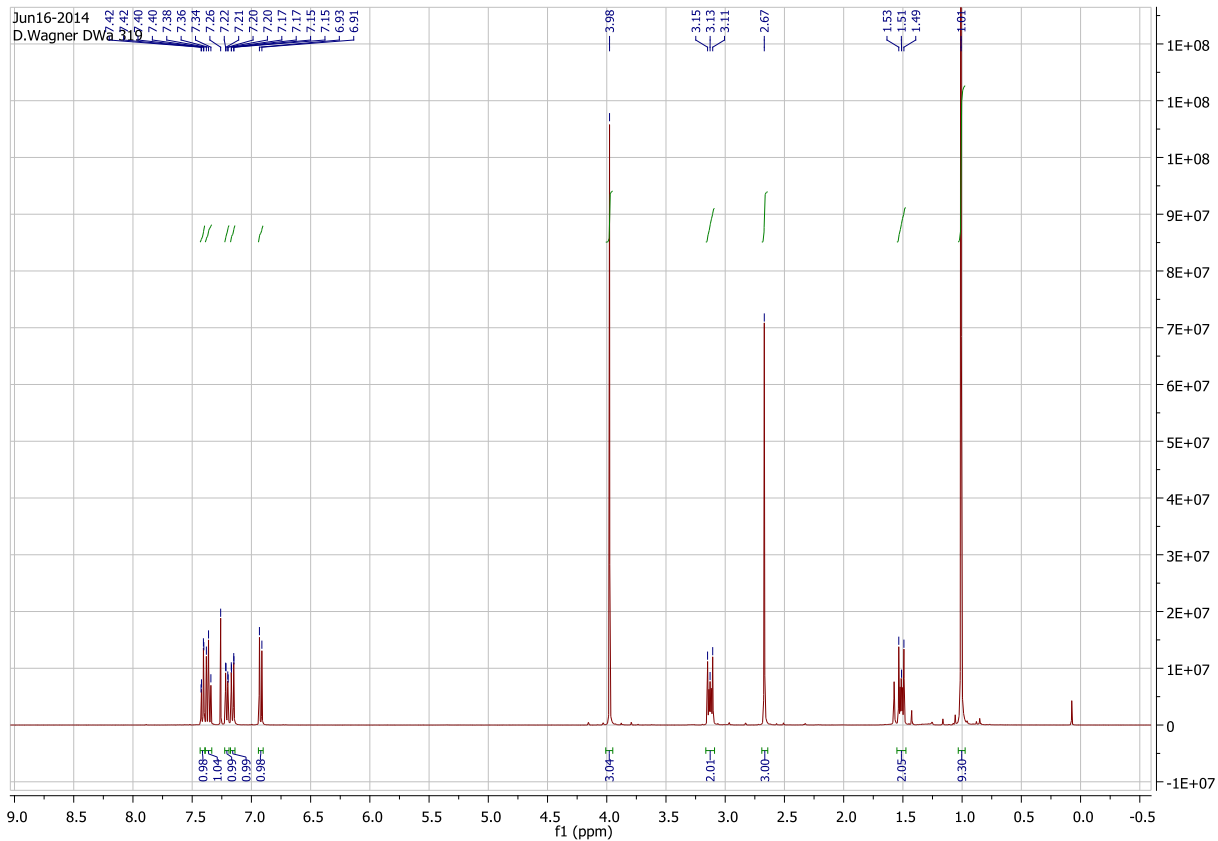


**8-(3,3-Dimethylbutyl)-4-methoxy-1-methyl-9H-thioxanthen-9-one (1ha)**

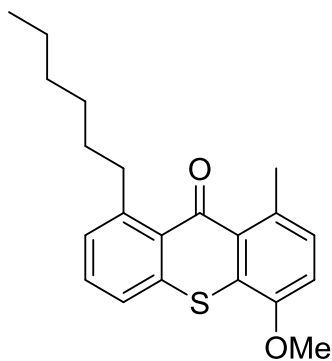


83%, clear oil

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.01 (s, 9 H,  $\text{C}(\text{CH}_3)_3$ ), 1.51 (dt, 2 H,  $\text{CH}_2$ ), 2.67 (s, 3 H,  $\text{CH}_3$ ), 3.13 (dt, 2 H,  $\text{CH}_2$ ), 3.98 (s, 3 H,  $\text{OCH}_3$ ), 6.92 (d, 1 H,  $H_{\text{ar}}$ ), 7.15 – 7.22 (m, 2 H,  $H_{\text{ar}}$ ), 7.34 – 7.42 (m, 2 H,  $H_{\text{ar}}$ ).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 21.5 (+,  $\text{CH}_3$  Thiox.), 29.4 (+,  $\text{C}(\text{CH}_3)_3$ ), 30.1 (-,  $\text{CH}_2$ ,  $\text{CH}_2$ ), 31.0 ( $\text{C}_{\text{q}}$ ,  $\text{C}(\text{CH}_3)_3$ ), 46.9 (-,  $\text{CH}_2$ ,  $\text{CH}_2$ ), 56.6 (+,  $\text{CH}_3$ ,  $\text{OCH}_3$ ), 111.2 (+, CH, 3- $\text{CH}_{\text{TX}}$ ), 124.1 (+, CH, 5- $\text{CH}_{\text{TX}}$ ), 126.2 ( $\text{C}_{\text{q}}$ ,  $\text{C}_{\text{TX}}$ ), 129.1 (+, CH, 2- $\text{CH}_{\text{TX}}$ ), 129.2 (+, CH, 7- $\text{CH}_{\text{TX}}$ ), 130.6 (+, CH, 6- $\text{CH}_{\text{TX}}$ ), 131.2 ( $\text{C}_{\text{q}}$ ,  $\text{C}_{\text{TX}}$ ), 132.2 ( $\text{C}_{\text{q}}$ ,  $\text{C}_{\text{TX}}$ ), 132.3 ( $\text{C}_{\text{q}}$ ,  $\text{C}_{\text{TX}}$ ), 136.9 ( $\text{C}_{\text{q}}$ ,  $\text{C}_{\text{TX}}$ ), 146.6 ( $\text{C}_{\text{q}}$ ,  $\text{C}_{\text{TX}}$ ), 152.2 ( $\text{C}_{\text{q}}$ ,  $\text{C}_{\text{TX}}$ ), 187.2 ( $\text{C}_{\text{q}}$ , CO). ppm. MS (70 eV, EI),  $m/z$  (%): 283 (100) [ $\text{C}_{17}\text{H}_{15}\text{O}_2\text{S}^+$ ], 340 (50) [ $\text{M}^+$ ]. – HRMS ( $\text{C}_{21}\text{H}_{24}\text{O}_2\text{S}$ ): calcd. 340.1492; found 340.1491. – IR (ATR):  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 2954 (w), 1646 (w), 1560 (w), 1444 (w), 1392 (w), 1363 (vw), 1293 (w), 1259 (w), 1244 (w), 1216 (w), 1183 (w), 1063 (w), 954 (w), 859 (w), 813 (w), 802 (w), 786 (w), 752 (vw), 724 (vw), 689 (w), 634 (vw), 617 (vw), 565 (vw), 547 (vw), 442 (vw). EA: calcd. for  $\text{C}_{21}\text{H}_{24}\text{O}_2\text{S}$ : C 74.08, H 7.11, S 9.42; found C 74.29, H 7.19, S 9.33



**8-Hexyl-4-methoxy-1-methyl-9H-thioxanthen-9-one (1hb)**



65%, clear oil.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.88 (t, 3 H,  $\text{CH}_2\text{CH}_3$ ), 1.29-1.40 (m, 6 H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 1.64 (m, 2 H,  $\text{CH}_2$ ), 2.66 (s, 3 H,  $\text{CH}_3$  Thiox.), 3.14 (t, 2 H,  $\text{CH}_2$  Thiox.), 3.98 (s, 3 H,  $\text{OCH}_3$ ), 6.92 (d, 1 H,  $H_{\text{ar.}}$ ), 7.15 – 7.22 (m, 2 H,  $H_{\text{ar.}}$ ), 7.35 -7.43 (m, 2 H,  $H_{\text{ar.}}$ ) –  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 14.2 (+,  $\text{CH}_3$  Hex.), 21.5 (+,  $\text{CH}_3$  Thiox.), 22.8 (-,  $\text{CH}_2$ , Hex.), 29.7 (-,  $\text{CH}_2$ , Hex.), 31.9 (-,  $\text{CH}_2$ , Hex.), 32.3 (-,  $\text{CH}_2$ , Hex.), 34.7 (-,  $\text{CH}_2$ , Hex.), 56.5 (+,  $\text{CH}_3$ ,  $\text{OCH}_3$ ), 111.2 (+, CH, 5- $\text{CH}_{\text{TX}}$ ), 124.2 (+, CH, 2- $\text{CH}_{\text{TX}}$ ), 126.2 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 129.0 (+, CH, 7- $\text{CH}_{\text{TX}}$ ), 129.1 (+, CH, 3- $\text{CH}_{\text{TX}}$ ), 130.5 (+, CH, 3- $\text{CH}_{\text{TX}}$ ), 131.1 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 132.2 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 132.3 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 136.9 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 145.9 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 152.2 ( $\text{C}_q$ ,  $\text{C}_{\text{TX}}$ ), 187.3 ( $\text{C}_q$ ,  $\text{CO}_{\text{TX}}$ ) ppm. – MS (70 eV, EI),  $m/z$  (%): 340 (100) [ $\text{M}^+$ ], 283 (75) [ $\text{C}_{17}\text{H}_{15}\text{O}_2\text{S}^+$ ]. – HRMS ( $\text{C}_{21}\text{H}_{24}\text{O}_2\text{S}$ ): calcd. 340.1492; found 340.1493 – IR (ATR):  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 2923 (w), 2853 (w), 1642 (m), 1573 (w), 1560 (w), 1433 (m), 1380 (vw), 1286 (w), 1257 (m), 1215 (m), 1064 (m), 958 (w), 858 (w), 801 (w), 780 (w), 725 (w), 692 (w), 570 (vw), 437 (vw). – EA: calcd. for  $\text{C}_{21}\text{H}_{24}\text{O}_2\text{S}$ : C 74.08, H 7.11, S 9.42; found C 74.65, H 7.27, S 9.44

