# METALATION OF TRIAZINES, II (1)
# SYNTHESIS OF BI-1,2,4-TRIAZINES AND 1,2,4-TRIAZINE-6-CARBALDEHYDES

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**Abstract**: 5-Methoxy-6H-1,2,4-triazines **1a** - **c**, 5H-1,2,4-triazine-6-diethylcarboxamides **7a**, **b** and 3,6-diphenyl-1,2,4-triazine 4-oxide **10** were lithiated with lithium 2,2,6,6-tetramethylpiperidide and the formed lithio-1,2,4-triazines **2a** - **c**, **8a**, **b**, **11** reacted with chlorotrimethylsilane and other reagents to give the bi-1,2,4-triazines **3a** - **c**, **4a**, **b**, **12**, **13**. 6-Lithio-1,2,4-triazines **2a**, **b** afforded **3a**, **b** and 5-methoxy-1,2,4-triazine-6-carbaldehydes **5a**, **b** when reacted with N-formylpiperidine or ethyl formate.

## Introduction

Lithio-substituted heterocycles are versatile intermediates in the synthesis of complex heterocyclic compounds (2). Lithiopyridines (3 - 6), lithiopyrazines (4, 7 - 9), lithiopyridazines (3, 4, 7, 10), and lithio-pyrimidines (3 - 7, 10 - 15) are known. Recently we reported the first synthesis of lithio-1,2,4-triazines (1) and their reactions with aldehydes and iodine.

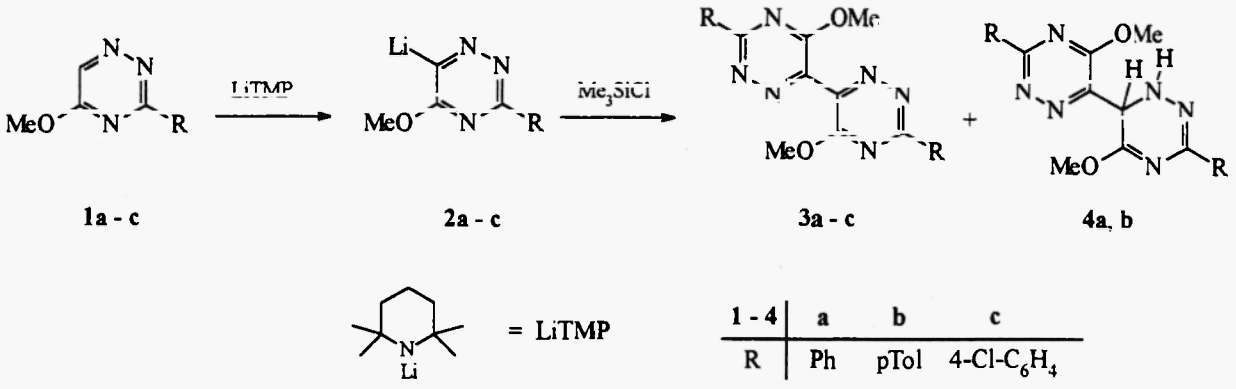
The *o*-directed metalation reaction involves deprotonation by a strong base in the *ortho*-position with respect to a directing metalating group containing a heteroatom. This leads to *o*-lithiated species which are converted into *o*-substituted products by treatment with an electrophilic reagent.

In addition to the 5-methoxy group (1) we used the 6-diethylcarboxamide group and the 4-N-oxide functionality as an *o*-directing group.

## Results and Discussion

*a) Synthesis of 6,6'-Bi-1,2,4-triazines*

Treatment of the 3-aryl-5-methoxy-1,2,4-triazines **1a** - **c** with four equivalents lithium 2,2,6,6-tetramethylpiperidide (LiTMP) in tetrahydrofurane (THF) at -100 °C and reaction of the formed 6-lithio derivatives **2a** - **c** with chlorotrimethylsilane by the *equilibrium shift procedure* (8) afforded unexpectedly not the 6-trimethylsilyl-1,2,4-triazines but the 5,5'-dimethoxy-6,6'-bi-1,2,4-triazines **3a** - **c** and the 1,6-dihydro-6,6'-bi-1,2,4-triazines **4a**, **b**. As described earlier (1), to shift the equilibrium **1** + LiTMP $\rightleftharpoons$ **2** + TMPH to the right side, getting the highest yield of **2**, one has to use a three- to fourfold excess of LiTMP.




SCHEME 1

Reaction of **1c** with LiTMP and chlorotrimethylsilane led only to the formation of **3c**, we did not isolate any 3,3'-bis-(4-chlorophenyl)-1,6-dihydro-5,5'-dimethoxy-6,6'-bi-1,2,4-triazine **4c**.

To our knowledge, besides our communication of the structure of 5,5'-dimethoxy-3,3'-diphenyl-6,6'-bi-1,2,4-triazine **3a** (16), no 6,6'-bi-1,2,4-triazines have been published so far. Lee synthesized 6,6'-bi-1,2,4-triazines starting from 6-ethinyl-1,2,4-triazines (17).

As shown in Table 1 the yields of **3a** and **4a** depend on the presence of chlorotrimethylsilane or other chlorosilanes and on the reaction time of **1a** with LiTMP. The use of reagents being sterically more hindered and at the same time less electrophilic than chlorotrimethylsilane gave lower yields of **3a** and **4a**.

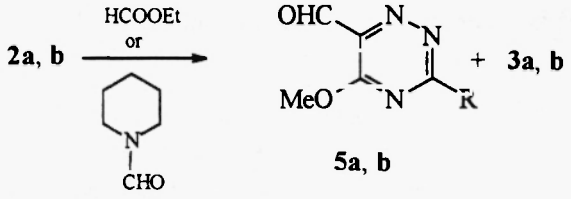
Table 1: Reaction conditions for the lithiation of 5-methoxy-3-phenyl-1,2,4-triazine **1a**.

| reaction-time [min] | electrophile | yield [%] **3a** | yield [%] **4a** | recovered [%] **1a** |
|---|---|---|---|---|
| 40 | none | 0 | 0 | 54 |
| 90 | none | 5 | 0 | 48 |
| 90 | $Me_3SiCl$ | 24 | 5 | 33 |
| 120 | $Me_3SiCl$ | 46 | 17 | < 1 |
| 180 | $Me_3SiCl$ | 18 | 62 | < 1 |
| 120 | $Et_3SiCl$ | 19 | 7 | < 1 |
| 120 | *n*-$Pr_3SiCl$ | 17 | 6 | < 1 |
| 120 | $Ph_3SiCl$ | 0 | 0 | 83 |

Quéguiner et al. (18) obtained 2,2'-biquinoxalines by *o*-directed metalation of 2-chloro and 2-methoxy-quinoxaline in the presence of chlorotrimethylsilane. The authors propose a carbanionic mechanism. Grignon-Dubois et al. (19) synthesized 2,2'-bis-(trimethylsilyl)-1,1',2,2'-tetrahydro-bi-1,1'-isoquinolines when they reacted isoquinoline with chlorotrimethylsilane and lithium or magnesium. A radical mechnism is suggested.

*b) Synthesis of 1,2,4-Triazine-6-carbaldehydes*

When we reacted the 6-lithio-3-aryl-5-methoxy-1,2,4-triazines **2a**, **b** with N-formylpiperidine or ethyl formate by the *procedure of accumulation* (8) we obtained together with the expected 3-aryl-5-methoxy-1,2,4-triazine-6-carbaldehydes **5a**, **b** the 6,6'-bi-1,2,4-triazines **3a**, **b** (Scheme 2). The use of N-formylpiperidine as formylating agent gave better yields both of **5** and **3** (see Table 2).




| 2 - 5 | a | b |
|---|---|---|
| R | Ph | pTol |

SCHEME 2

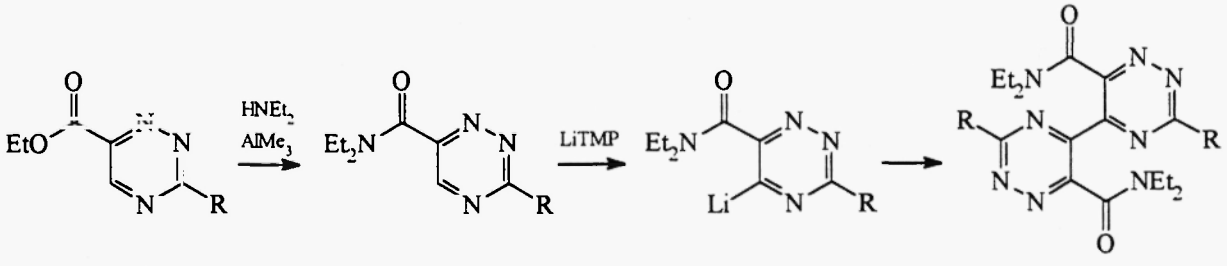
Table 2: Reagents for formylation of 6-lithio-5-methoxy-1,2,4-triazines **2a**, **b**

| electrophile | R | yield **5** [%] | yield **3** [%] |
|---|---|---|---|
| ethyl formate | Ph | 12 | 4 |
| N-formylpiperidine | Ph | 41 | 6 |
| ethyl formate | pTol | 14 | 5 |
| N-formylpiperidine | pTol | 39 | 21 |

*c) Synthesis and Metalation of 1,2,4-Triazine-6-diethylcarboxamides*

Similarly we obtained the 3,3'-diaryl-5,5'-bi-1,2,4-triazine-6,6'-bis-diethylcarboxamides **9a**, **b** in 30 % yield when we lithiated the 3-aryl-1,2,4-triazine-6-diethylcarboxamides **7a**, **b** with LiTMP and reacted the formed lithio-1,2,4-triazines **8a**, **b** with chlorotrimethylsilane by the *equilibrium shift procedure* (see Scheme 3).

When we added benzaldehyde to **8a**, **b**, we did not observe any reaction with this electrophile; we isolated the 5,5'-bi-1,2,4-triazines **9a**, **b** in 59 % yield. Finally we obtained **9a**, **b** in 70% yield when we did not add any electrophile to **8a**, **b**. This means that there is no effect of chlorotrimethylsilane on the formation of 5,5'-bi-1,2,4-triazines **9**, contrary to the formation of **3**.




| 6 - 9 | a | b |
|---|---|---|
| R | Ph | pTol |

SCHEME 3

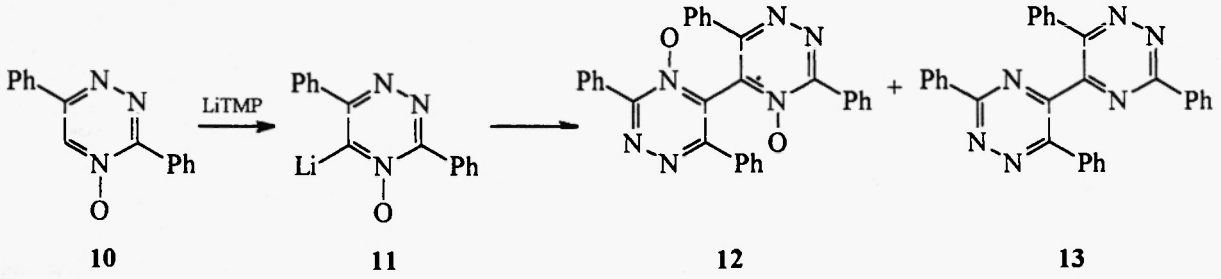
Reacting 6-lithio-5-methoxy-3-phenyl-1,2,4-triazine **2a** with 3-(4-tolyl)-1,2,4-triazine-6-diethylcarboxamide **7b** we obtained the 5,5'-bi-1,2,4-triazine **9b** in 68% yield and traces of the 6,6'-bi-1,2,4-triazine **3a**, no *mixed* 5,6'-bi-1,2,4-triazine could be isolated.

5,5'-Bi-1,2,4-triazines are already known; they were prepared by reaction of 5H-1,2,4-triazines with sodium methoxide (20), sodium cyanide (21, 22), potassium cyanide (18, 21) or potassium amide (20, 24, 25).

We obtained the unknown 3-aryl-1,2,4-triazine-6-diethylcarboxamides **7a**, **b** by reaction of 3-aryl-1,2,4-triazine-6-carboxylates **6a**, **b** (26) with diethylamine in the presence of triethylaluminum (27).

*d) Metalation of 3,6-Diphenyl-1,2,4-triazine-4-oxide*

3,6-Diphenyl-1,2,4-triazine 4-oxide **10** (28) can also be lithiated to give **11**. Reaction of **10** with chlorotrimethylsilane led to the isolation of 3,3',6,6'-tetraphenyl-5,5'-bi-1,2,4-triazine 4,4'-dioxide **12** and 3,3',6,6'-tetraphenyl-5,5'-bi-1,2,4-triazine **13** (29). This means that not only dimerization occured but also partial reduction of the N-oxide group. When we did not add any electrophile to **11**, we obtained the same yields of **12** and **13**. This result corresponds to the previous findings that there is no promoting effect of chlorotrimethylsilane on the formation of 5,5'-bi-1,2,4-triazines **9a**, **b**.




SCHEME 4

**Conclusion**

The mechanism - ionic or radical - of the reactions described is not yet completely evaluated. We suppose that the reactions giving 6,6'-bi-1,2,4-triazines **3**, **4** follow a radical pathway, whereas the dimerizations leading to 5,5'-bi-1,2,4-triazines **9**, **12**, **13** proceed by a carbanionic mechanism. Paudler et al. (20, 23) proposed both mechanisms for the dimerization of 5H-1,2,4-triazines under the influence of KCN, NaOMe or $K/NH_3$ yielding 5,5'-bi-1,2,4-triazines. A radical-anionic mechanism has been suggested by Newkome (30) for the synthesis of bipyridines by metalation of pyridine with lithium di*iso*propylamide.

Further work in this area is in progress, especially for getting insight into the mechanism of the reaction leading to 6,6'-bi-1,2,4-triazines and the influence of trialkylchlorosilanes in this reaction.

**Experimental**

All manipulations were carried out under argon. - THF was dried with a benzophenone-sodium mixture and distilled directly before use. - Melting points were determined with a melting point microscope (Fa. C. Reichert) and are uncorrected. - $^1$H-NMR spectra were recorded with a Bruker WM 300 instrument with

tetramethylsilane as internal standard. - Mass spectra were recorded with a Varian 311 A with data system Tecnivent 110. - For column chromatography (CC) silica gel (0.063-0.2 mm; Fa. Macherey-Nagel) was used.

*3-Aryl-1,2,4-triazine-diethylcarboxamides* **7a**, **b**: To a solution of diethylamine (140 µl, 1.35 mmol) in absol. dichloromethane (3.5 ml) triethyl aluminum (680 µl, 1.35 mmol in *n*-hexane) was added at 0 °C. The solution was warmed to 20 °C and stirred for 1 h. **6a**, **b** (26) (1.35 mmol) was added. After 12 h at 20 °C a mixture of 2 *N* hydrochloric acid (1.8 ml) and water (8.5 ml), and then a saturated sodium hydrogen carbonate solution was added (until pH = 9). The organic phase was separated and the aqueous phase extracted with dichloromethane (4 x 30 ml). The combined organic phases were dried with magnesium sulfate. The solvent was evaporated and the residue purified by CC on silica gel (ethyl acetate/cyclohexane 1:2). Results and physical data are listed in tables 3 and 4.

Table 3: Yields, melting points and elemental analyses of the 1,2,4-triazines **3** - **5**, **7**, **9**, **12**, **13**

| No. | Yield | M.p. [°C] | Formula Mol mass | Analysis: C | H | Calculated Found N |
|---|---|---|---|---|---|---|
| **3a** | 46 % | 230 | $C_{20}H_{16}N_6O_2$ | 64.51 | 4.33 | 22.57 |
| | | (ethanol) | (372.4) | 64.52 | 4.14 | 22.49 |
| **3b** | 9 % | 228 - 229 | $C_{22}H_{20}N_6O_2$ | 65.99 | 5.03 | 20.99 |
| | | (ethanol) | (400.4) | 65.79 | 5.05 | 20.95 |
| **3c** | 40 % | 246 | $C_{20}H_{14}Cl_2N_6O_2$ | 54.44 | 3.20 | 19.05 |
| | | (ethyl acetate) | (441.3) | 54.32 | 3.11 | 19.23 |
| **4a** | 17 % | 190 | $C_{20}H_{18}N_6O_2$ | 64.16 | 4.85 | 22.45 |
| | | (ethyl acetate) | (374.4) | 64.08 | 4.74 | 22.27 |
| **4b** | 51 % | 164 - 166 | $C_{22}H_{22}N_6O_2$ | 65.66 | 5.51 | 20.88 |
| | | (ethyl acetate) | (402.5) | 65.80 | 5.50 | 20.86 |
| **5a** | 41 % | 132 | $C_{11}H_9N_3O_2$ | 61.39 | 4.21 | 19.53 |
| | | (*n*-hexane) | (215.2) | 61.51 | 4.19 | 19.65 |
| **5b** | 39 % | 162 | $C_{12}H_{11}N_3O_2$ | 62.87 | 4.84 | 18.33 |
| | | (*n*-hexane) | (229.2) | 62.85 | 4.73 | 18.51 |
| **7a** | 65 % | 91 - 92 | $C_{14}H_{16}N_4O$ | 65.60 | 6.29 | 21.86 |
| | | (*n*-hexane) | (256.3) | 65.47 | 6.29 | 21.70 |
| **7b** | 72 % | 58 | $C_{15}H_{18}N_4O$ | 66.65 | 6.71 | 20.73 |
| | | (*n*-hexane) | (270.3) | 66.39 | 6.69 | 20.80 |
| **9a** | 70 % | 220 - 221 | $C_{28}H_{30}N_8O_2$ | 65.87 | 5.92 | 21.94 |
| | | (ethanol) | (510.6) | 65.86 | 5.97 | 22.13 |
| **9b** | 70 % | 255 | $C_{30}H_{34}N_8O_2$ | 66.90 | 6.36 | 20.80 |
| | | (ethyl acetate) | (538.7) | 66.89 | 6.45 | 20.88 |
| **12** | 21 % | 192 | $C_{30}H_{20}N_6O_2$ | 72.57 | 4.06 | 16.93 |
| | | (ethanol) | (496.5) | 72.58 | 3.90 | 17.07 |
| **13** | 24 % | 233 | $C_{30}H_{20}N_6$ | 77.57 | 4.34 | 18.09 |
| | | (ethyl acetate) | (464.5) | 77.44 | 4.30 | 18.19 |

*5,5'-Dimethoxy-6,6'-bi-1,2,4-triazines* **3a** - **c** and *1,6-dihydro-5,5'-dimethoxy-6,6'-bi-1,2,4-triazines* **4a**, **b**: To a solution of BuLi (12 mmol in *n*-hexane) in THF (50 ml) 2,2,6,6-tetramethylpiperidine (2.4 ml, 14 mmol) was

added at -30 °C. The solution was warmed to 0 °C and stirred for 30 min. After cooling to -100 °C **1a** (31), **1b** (1) or **1c** (32) (3 mmol) and chlorotrimethylsilane (1.7 ml, 12 mmol) were added simultaneously by two syringes, keeping the temperature below -95 °C. The mixture was stirred for 2 h at -100 °C , then a mixture of conc. hydrochloric acid (2 ml), methanol (2 ml) and THF (8 ml) was added and the solution warmed slowly to room temp. A saturated sodium hydrogen carbonate solution was added (until pH = 8), the organic solvents were removed under reduced pressure and the aqueous solution extracted with dichloromethane (3 x 30 ml). The combined organic phases were dried with magnesium sulfate, the solvent removed and the residue separated by CC (ethyl acetate/cyclohexane 1:2). **3a**: $R_f$ = 0.29, **4a**: $R_f$ = 0.23, **3b**: $R_f$ = 0.45, **4b**: $R_f$ = 0.37, **3c**: $R_f$ = 0.26. Results and physical data are listed in tables 3 and 4.

*6-Lithio-5-methoxy-1,2,4-triazines* **2a**, **b** and *5-Lithio-1,2,4-triazine-6-diethylcarboxamides* **8a**, **b**: According to the precedure described previously (1), to a solution of BuLi (8 mmol in *n*-hexane) in THF (40 ml) 2,2,6,6-tetramethylpiperidine (1.6 ml, 9.3 mmol) was added at -30 °C. The solution was warmed to 0 °C and stirred for 30 min. After cooling to -100 °C **1a** (31), **1b** (1), **7a**, **b** (8 mmol) in THF (5 ml) was added, keeping the temp. below -95 °C. The mixture was stirred for 60 min at -100 °C and used for the following reactions.

*5-Methoxy-1,2,4-triazine-6-carbaldehydes* **5a**, **b**: To a solution of **2a**, **b** (2.0 mmol) in THF N-formyl-piperidine (0.9 ml, 8 mmol) was added with stirring at -100 °C. After 2 h stirring at -100 °C the mixture was hydrolyzed and worked up as described for **3a**, **b**. CC: ethyl acetate/cyclohexane 2:3; **3a**: $R_f$ = 0.38, **5a**: $R_f$ = 0.25; **3b**: $R_f$ = 0.47, **5b**: $R_f$ = 0.35. Results and physical data in tables 3 and 4.

*5,5'-Bi-1,2,4-triazine-6,6'-bis-diethylcarboxamides* **9a**, **b**: a.) The solution of **8a**, **b** in THF was stirred at -100 °C. After 1 h at -100 °C the mixture was hydrolyzed and worked-up as described for **3a**, **b**. Purification by CC on silica gel with ethyl acetate/cyclohexane (1:2). Results and physical data are listed in tables 3 and 4.

b) To a solution of BuLi (4.0 mmol in *n*-hexane) in THF (25 ml) 2,2,6,6-tetramethylpiperidine (0.85 ml, 4.7 mmol) was added at -30 °C. The solution was warmed to 0 °C and stirred for 30 min. After cooling to -100 °C, **7b** (24) (272 mg, 1.0 mmol) and chlorotrimethylsilane (0.5 ml, 4.0 mmol) were added simultaneously by two syringes, keeping the temperature below -95 °C. Hydrolysis and work-up as before yielded 30 % **9b**.

c) To a solution of **8a**, **b** (2.0 mmol) in THF benzaldehyde (0.86 ml, 8 mmol) was added with stirring at -100 °C for 1 h. Hydrolysis and work up as before yielded 59 % **9b** and 59 % **9b**.

*3,3',6,6'-Tetraphenyl-5,5'-bi-(1,2,4-triazine) 4,4'-dioxide* **12** and *3,3',6,6'-tetraphenyl-5,5'-bi-1,2,4-triazine* **13**: a) To a solution of BuLi (4 mmol in *n*-hexane) in THF (25 ml) 2,2,6,6,-tetramethylpiperidine (0.85 ml, 4.7 mmol) was added at -30 °C. The solution was warmed to 0 °C and stirred for 30 min. After cooling to -100 °C 3,6-diphenyl-1,2,4-triazine 4-oxide **10** (26) (498 mg, 2 mmol) and chlorotrimethylsilane (0.5 ml, 4 mmol) were added simultaneously by two syringes, keeping the temperature below -95 °C. Hydrolysis and work-up as described for **3a**, **b**. CC: ethyl acetate/cyclohexane (1:2); **12**: $R_f$ = 0.26, **13**: $R_f$ = 0.38. Results and physical data are listed in tables 3 and 4.

b) The same procedure as described above, but without adding chlorotrimethylsilane gave the same result.

Table 4: Selected spectroscopic data of the 1,2,4-triazines **3** - **5**, **7**, **9**, **12**, **13**

| No. | $^1$H-NMR data ($CDCl_3$) 300 MHz, $\delta$ values | MS: m/z (%) (70 eV)[a] |
|---|---|---|
| **3a** | 8.53, 7.47 (m, 10 H); 4.12 (s, 6 H) | 372 (73) [$M^+$], 110 (100) |
| **3b** | 8.43, 7.28 (m, 8 H); 4.09 (s, 6 H); 2.39 (s, 6 H) | 400 (33) [$M^+$], 110 (100) |
| **3c** | 8.47, 7.45 (m, 8 H); 4.10 (s, 6H) | 440 (51) [$M^+$, $^{35}Cl$, $^{35}Cl$] 442 (36) [$M^+$, $^{35}Cl$, $^{37}Cl$] 444 (5) [$M^+$, $^{37}Cl$, $^{37}Cl$], 110 (100) |
| **4a** | 8.35, 7.90, 7.43, 7.25 (m, 10 H); 6.40 (br. s, 1 H); 5.15 (s, 1 H); 4.11 (s, 3 H); 4.07 (s, 3 H) | 374 (100) [$M^+$] |
| **4b** | 8.24, 7.79, 7.19, 7.06 (m, 8 H); 6.34 (s, 1 H); 5.12 (s, 1 H); 4.10 (s, 3 H); 4.06 (s, 3 H); 2.33 (s, 3 H); 2.25 (s, 3 H) | 402 (100) [$M^+$] |
| **5a** | 10.39 (s, 1 H); 8.62, 7.58 (m, 5 H); 4.29 (s, 3 H) | 215 (100) [$M^+$] |
| **5b** | 10.36 (s, 1 H), 8.50, 7.37 (m, 4 H); 4.28 (s, 3 H), 2.47 (s, 3 H) | 229 (81) [$M^+$], 117 (100) |
| **7a** | 9.02 (s, 1 H); 8.55, 7.56 (m, 5 H); 3.63 (q, $J$ = 7.1 Hz, 2 H); 3.62 (q, $J$ = 7.1 Hz, 2 H), 1.32 (t, $J$ = 7.1 Hz, 3 H); 1.31 (t, $J$ – 7.1 Hz, 3 H) | 256 (10) [$M^+$], 72 (100) |
| **7b** | 9.01 (s, 1 H); 8.46, 7.36 (m, 4 H); 3.64 (q, $J$ = 7.1 Hz, 4 H); 2.45 (s, 3 H); 1.33 (t, $J$ = 7.1 Hz, 3 H); 1.32 (t, $J$ = 7.1 Hz, 3 H) | 270 (31) [$M^+$], 72 (100) |
| **9a** | 8.49, 7.53 (m, 10 H); 3.52 (q, $J$ = 7.1 Hz, 4 H); 3.42 (q, $J$ = 7.1 Hz, 4 H); 1.18 (t, $J$ = 7.1 Hz, 3 H); 1.03 (t, $J$ = 7.1 Hz, 3 H) | 510 (44) [$M^+$], 72 (100) |
| **9b** | 8.37, 7.29 (m, 8 H), 3.51 (q, $J$ = 7.1 Hz, 4 H); 3.41 (q, $J$ = 7.1 Hz, 4 H); 2.39 (s, 6 H); 1.17 (t, $J$ = 7.1 Hz, 6 H); 1.04 (t, $J$ = 7.1 Hz, 6 H) | 538 (36) [$M^+$], 72 (100) |
| **12** | 8.55, 8.42, 7.58, 7.43, 7.29, 7.11 (m, 20 H) | 496 (33) [$M^+$] 464 (100) |
| **13** | 8.63, 7.60, 7.36, 7.22, 7.03 (m, 20 H) | 464 (100) [$M^+$] |

[a] **4a**, **b**, **12**, **13**: FD-spectra

**References and Notes**


# Dedicated to Professor **Miha Tisler** on the occasion of his 70th birthday.

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