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(*Z*)-3,4,4,4-TETRACHLOROBUT-2-ENOATES OF CERTAIN NATURAL ALCOHOLS, PHENOLS, AND OXIMES

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UDC 547.39+547.92

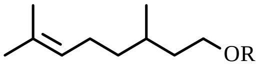
Previously unknown (Z)-3,4,4,4-tetrachlorobut-2-enoates ***1b-20b*** *were prepared in 77-88% yields by reaction in the presence of pyridine of 3,3,4,4,4-pentachlorobutanoic acid chloride with cetyl alcohol (****1a****), terpenols and terpenone oximes (****2a-13a****), sterols (****14a*** *and* ***15a****), diosgenin (****16a****), and plant phenols and their oximes (****17a-20a****).*

Key words: 3,3,4,4,4-pentachlorobutanoic acid chloride, (*Z*)-3,4,4,4-tetrachlorobut-2-enoates, esters, terpenols, terpenones, sterols, diosgenin, plant phenols, oximes, chemical modification.

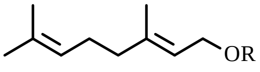
Our goal was to prepare new derivatives of natural compounds as esters of (*Z*)-3,4,4,4-tetrachlorobut-2-enoic acid. We expected that the biological activity of these compounds would be rather high because esters, especially of natural origin, are more active than chlorocarboxylic acids used in several pesticides with a wide spectrum of action, for example, derivatives of 2,2-dichloropropionic acid (algicide and herbicide dalapon), 2,2,3-trichloropropionic acid (herbicide TCP), 2,3,4,5,5-pentachloropentadien-2,4-oic acid (herbicide and defoliant pentadin), etc. [1, 2]. We selected natural alcohols and oximes of natrual aldehydes and ketones **1a-20a** for the synthesis.

$Me(CH_2)_{15}OR$

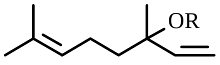
1a - b



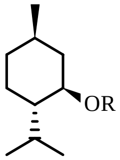
2a - b



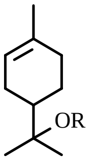
3a - b



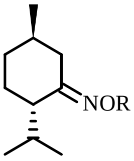
4a - b



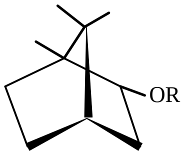
5a - b



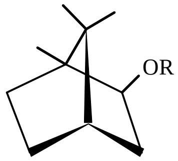
6a- b



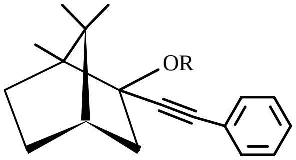
7a - b



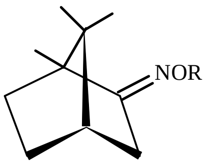
8a - b



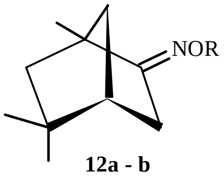
9a - b



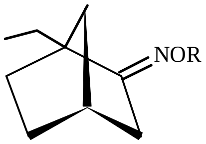
10a - b



11a - b



12a - b



13a - b

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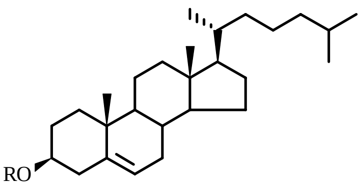
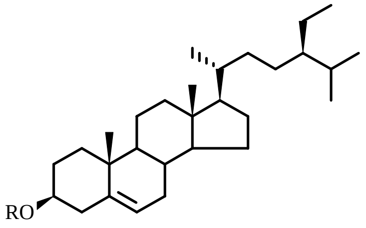
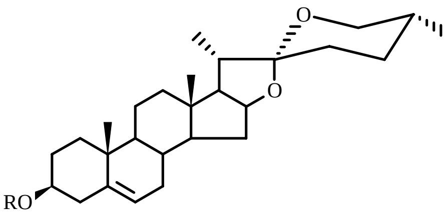


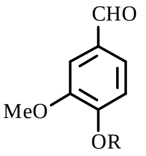
14a - b



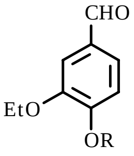
15a - b



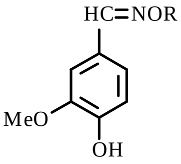
16a - b



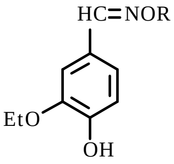
17a - b



18a- b

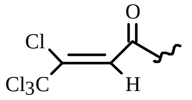


19a - b



20a - b

a: R = H; **b:** R =



We used the reaction of the appropriate alcohols, oximes, and phenols **1a-20a** with 3,3,4,4,4-pentachlorobutanoic acid chloride in absolute diethylether in the presence of pyridine to synthesize esters **1b-20b**. The esterification was accompanied by loss of HCl. Instead of the expected esters of 3,3,4,4,4-pentachlorobutanoic acid, derivatives of (*Z*)-3,4,4,4-tetrachlorobut-2-enoic acid were formed as the pure (*Z*)-isomers. This agrees with the literature [3, 4]. The optimum stoichiometric ratio of hydroxy compound, acyl chloride, and pyridine was 1:1:1. An excess of pyridine led to polymerization of the mixture and reduction of ester yield. The yields of **1b-20b** were 77-88%.

The structures of the synthesized esters were confirmed by elemental analyses, cryoscopic determination of the molecular weights, and PMR, IR, and UV spectra. It should be noted that the oxime hydroxyls of **19a** and **20a** are more reactive than those of the phenols. This was confirmed by the presence in the PMR spectra of **19b** and **20b** of signals for phenolic OH groups as broad singlets near 6.8 ppm whereas the signal for the oxime OH groups should appear near 9 ppm. The proton of the HC=N group in **19b** and **20b** appears as a singlet near 8.4 ppm.

The purity of the products was 98 ± 1% according to PMR spectroscopy. Analytical results for all compounds agreed with those calculated.

EXPERIMENTAL

IR spectra were recorded on a Protege-460 IR-Fourier spectrophotometer (Nicolet) as thin layers or in KBr; UV spectra, on a Specord UV-Vis instrument as solutions (10^{-4} M) in *n*-butanol. PMR spectra were obtained on a BS-587A spectrometer (100 MHz, Tesla) in $CDCl_3$ solutions (5%). Chemical shifts were determined relative to OMTS internal standard. Molecular weights (MW) were determined by cryoscopy in benzene. Column chromatography used neutral Al_2O_3 (L 40/250 μm, Brockman activity level II). The chloride of 3,3,4,4,4-pentachlorobutanoic acid was synthesized by boiling the carboxylic acid with a 2.5-fold excess of thionylchloride in CCl_4 [4].

Esters of (*Z*)-3,4,4,4-Tetrachlorobut-2-enoic Acid (1b-20b) (General Method). A solution of the appropriate compound (**1a-20a**, 10 mmol) in absolute diethylether (100 mL) was treated with absolute pyridine (10 mmol) and 3,3,4,4,4-pentachlorobutanoic acid chloride (10 mmol) in small portions with stirring and shaking of the reaction flask. The reaction mixture was left for 24-36 h at 20-23°C. The solid pyridinium chloride was filtered off. The filtrate was diluted with ether, washed three times each with water and aqueous $NaHCO_3$ solution (5%), and dried over $CaCl_2$. Solvent was distilled off. The solid was purified by low-temperature crystallization from 96% ethanol (**1b**, **11b**, **14b-16b**, **19b**, **20b**) or by column chromatography over Al_2O_3 (**2b-10b**, **12b**, **13b**, **17b**, **18b**) with elution by hexane.

This method produced:

1-Hexadecanol (*Z*)-3,4,4,4-Tetrachlorobut-2-enoate (1b). Yield 88%, mp 19-20°C. M: found 425.7, calc. 448.3. IR spectrum (ν, cm^{-1}): 3088 (=C–H); 2980, 2923, 2852 (CH_{Alk}); 1735 (C=O); 1632 (C=C); 1466 (CH_2); 1307, 1188 (C–O); 950, 822 (C–Cl); 778 (=C–H). UV spectrum (λ_{max}, nm, ε): 205 (6000), 245 (4000).

PMR spectrum (δ, ppm, J/Hz): 0.88 (t, CH_3), 1.15-1.90 [28H, m, $(CH_2)_{14}$], 4.23 (t, $^3J = 6.2$, CH_2O), 7.06 [s, C(O)CH].

Citronellol (*Z*)-3,4,4,4-Tetrachlorobut-2-enoate (2b). Yield 88%, d_{20}^{20} 1.1656, n_D^{20} 1.5080. M: found 344.5, calc. 362.1. IR spectrum (ν, cm^{-1}): 3090 (=C–H); 2964, 2926, 2915, 2873, 2855 (CH_{Alk}); 1737 (C=O); 1633 (C=C); 1456 (CH_2); 1303, 1180 (C–O); 950, 822 (C–Cl); 775, 731 (=C–H). UV spectrum (λ_{max}, nm, ε): 205 (10000), 245 (4000).

PMR spectrum (δ, ppm, J/Hz): 0.95 (d, $^3J = 6.2$, CH_3-3), 1.61 and 1.69 [s and s, $(CH_3)_2$-7], 4.28 (t, $^3J = 6.5$, 2H-1), 5.00-5.20 (m, H-6), 7.05 [s, C(O)CH].

Geraniol (*Z*)-3,4,4,4-Tetrachlorobut-2-enoate (3b). Yield 87%, d_{20}^{20} 1.1694, n_D^{20} 1.5160. M: found 348.3, calc. 360.1. IR spectrum (ν, cm^{-1}): 3082 (=C–H); 2966, 2927, 2856 (CH_{Alk}); 1736 (C=O); 1680, 1633 (C=C); 1448 (CH_2); 1302, 1179 (C–O); 940, 822 (C–Cl); 775, 732 (=C–H). UV spectrum (λ_{max}, nm, ε): 205 (14000), 245 (5000).

PMR spectrum (δ, ppm, J/Hz): 1.60 (s, CH_3-3), 1.68 and 1.75 [s and s, $(CH_3)_2$-7], 1.80-2.15 (m, H_2-4 and H_2-5), 4.72 (d, $^3J = 7.5$, 2H-1), 5.06 (t, $^3J = 6.2$, H-6), 5.40 (t, $^3J = 7.3$, H-2), 7.06 [s, C(O)CH].

Linalool (*Z*)-3,4,4,4-Tetrachlorobut-2-enoate (4b). Yield 77%, d_{20}^{20} 1.1233, n_D^{20} 1.5115. M: found 345.0, calc. 360.1. IR spectrum (ν, cm^{-1}): 3090, 3085, 3020 (=C–H); 2970, 2930, 2875, 2855 (CH_{Alk}); 1736 (C=O); 1680, 1633, 1610 (C=C); 1450 (CH_2); 1305, 1180 (C–O); 950, 822 (C–Cl); 860, 775 (=C–H). UV spectrum (λ_{max}, nm, ε): 208 (12000), 245 (5000).

PMR spectrum (δ, ppm): 1.54 (s, $2CH_3$-7), 1.65 (s, CH_3-3), 1.55-2.10 (m, 2H-4 and 2H-5), 4.95-6.15 (m, 2H-1, H-2, and H-6), 7.05 [s, C(O)CH].

(-)-1*R*,2*S*,5*R*-Menthol (*Z*)-3,4,4,4-Tetrachlorobut-2-enoate (5b). Yield 88%, d_{20}^{20} 1.2747, n_D^{20} 1.5145. M: found 347.8, calc. 362.1. IR spectrum (ν, cm^{-1}): 3088 (=C–H); 2955, 2930, 2870 (CH_{Alk}); 1733 (C=O); 1632 (C=C); 1456 (CH_2); 1301, 1185 (C–O); 953, 823 (C–Cl); 775 (=C–H). UV spectrum (λ_{max}, nm, ε): 205 (6000), 245 (4000).

PMR spectrum (δ, ppm, J/Hz): 0.83 (d, $^3J = 6.4$, CH_3-5), 0.94 [d, $^3J = 6.7$, $(CH_3)_2CH$–], 4.88 (dt, $^3J_{aa} = 10.0$, $^3J_{ae} = 4.6$, H-1), 7.06 [s, C(O)CH].

Terpineol (*Z*)-3,4,4,4-Tetrachlorobut-2-enoate (6b). Yield 77%, d_{20}^{20} 1.1745, n_D^{20} 1.5135. M: found 348.4, calc. 360.1. IR spectrum (ν, cm^{-1}): 3088, 3050 (=C–H); 2958, 2927, 2890, 2836 (CH_{Alk}); 1730 (=O); 1633 (C=C); 1455, 1445 (CH_2); 1303, 1188 (C–O); 950, 816 (C–Cl); 777, 734 (=C–H). UV spectrum (λ_{max}, nm, ε): 206 (10000), 245 (4000).

PMR spectrum (δ, ppm): 1.44 (s, $2CH_3$), 1.60 (s, CH_3), 5.34 (br.s, C=CH), 7.04 [s, C(O)CH].

(-)-1-(*Z*)-3,4,4,4-Tetrachlorobut-2-enyloxyimino)menthane (7b). Yield 79%, d_{20}^{20} 1.1784, n_D^{20} 1.5295. M: found 360.3, calc. 375.1. IR spectrum (ν, cm^{-1}): 3075 (=C–H); 2957, 2928, 2870 (CH_{Alk}); 1755 (C=O); 1632 (C=C); 1456 (CH_2), 1302, 1146 (C–O); 966, 816 (C–Cl); 770 (=C–H). UV spectrum (λ_{max}, nm, ε): 207 (9000), 245 (4000).

PMR spectrum (δ, ppm, J/Hz): 1.05 (d, $^3J = 6.0$, CH_3-5), 1.15 [d, $^3J = 6.0$, $(CH_3)_2CH$–], 7.22 [s, C(O)CH].

Borneol (*Z*)-3,4,4,4-Tetrachlorobut-2-enoate (8b). Yield 88%, d_{20}^{20} 1.2611, n_D^{20} 1.5295. M: found 351.8, calc. 360.1. IR spectrum (ν, cm^{-1}): 3082 (=C–H); 2980, 2956, 2881 (CH_{Alk}); 1733 (C=O); 1631 (C=C); 1473, 1454 (CH_2); 1306, 1185 (C–O); 967, 824 (C–Cl); 775 (=C–H). UV spectrum (λ_{max}, nm, ε): 205 (6000), 245 (4000).

PMR spectrum (δ, ppm): 0.92 (s, $2CH_3$), 0.98 (s, CH_3), 5.02 (m, H-2), 7.01 [s, C(O)CH].

Isoborneol (*Z*)-3,4,4,4-Tetrachlorobut-2-enoate (9b). Yield 86%, d_{20}^{20} 1.2544, n_D^{20} 1.5240. M: found 347.3, calc. 360.1. IR spectrum (ν, cm^{-1}): 3082 (=C–H); 3000, 2955, 2877 (CH_{Alk}); 1733 (C=O); 1631 (C=C); 1473, 1455 (CH_2); 1302, 1180 (C–O); 961, 822 (C–Cl); 775 (=C–H). UV spectrum (λ_{max}, nm, ε): 205 (6000), 245 (4000).

PMR spectrum (δ, ppm): 0.86 (s, CH_3), 0.90 (s, CH_3), 1.01 (s, CH_3), 4.80 (t, H-2), 7.00 [s, C(O)CH].

2-Phenylethynylisoborneol (*Z*)-3,4,4,4-Tetrachlorobut-2-enoate (10b). Yield 79%, d_{20}^{20} 1.2835, n_D^{20} 1.5690. M: found 442.6, calc. 460.2. IR spectrum (ν, cm^{-1}): 3090, 3040, 3025 (CH_{Ar}); 3080 (=C–H); 2954, 2872 (CH_{Alk}); 1736 (C=O); 1635 (C=C); 1600, 1489 (Ar); 1453, 1443 (CH_2); 1300, 1181 (C–O); 970, 823 (C–Cl); 777 (=C–H); 755, 691 (CH_{Ar}). UV spectrum (λ_{max}, nm, ε): 205 (32000), 244 (29000), 252 (20000).

PMR spectrum (δ, ppm): 0.92 (s, CH_3), 1.03 (s, CH_3), 1.12 (s, CH_3), 7.10 [s, C(O)CH], 7.35 (m, C_6H_5).

(1*S*)-(-)-(*E*)-2-(*Z*)-3,4,4,4-Tetrachlorobut-2-enyloxyimino)-1,7,7-trimethylbicyclo[2.2.1]heptane (11b). Yield 80%, mp 47-48°C. M: found 362.6, calc. 373.1. IR spectrum (ν, cm^{-1}): 3080 (=C–H); 2962, 2940, 2888, 2874 (CH_{Alk}); 1738 (C=O); 1632 (C=C); 1474, 1450 (CH_2); 1301, 1180 (C–O); 970, 813 (C–Cl); 774 (=C–H). UV spectrum (λ_{max}, nm, ε): 206 (10000), 244 (4000).

PMR spectrum (δ, ppm, J/Hz): 0.88 (s, CH_3), 0.99 (s, CH_3), 1.18 (s, CH_3), 7.17 [s, C(O)CH].

2-(*Z*)-3,4,4,4-Tetrachlorobut-2-enyloxyimino)-1,5,5-trimethylbicyclo[2.2.1]heptane (12b). Yield 82%, d_{20}^{20} 1.2010, n_D^{20} 1.5245. M: found 366.2, calc. 373.1. IR spectrum (ν, cm^{-1}): 3080 (=C–H); 2962, 2940, 2869 (CH_{Alk}); 1740 (C=O); 1632 (C=C); 1472, 1451 (CH_2), 1300, 1176 (C–O); 980, 811 (C–Cl); 771 (=C–H). UV spectrum (λ_{max}, nm, ε): 206 (10000), 244 (4000).

PMR spectrum (δ, ppm): 0.89 (s, CH_3), 1.01 (s, CH_3), 1.25 (s, CH_3), 7.06 [s, C(O)CH].

2-(*Z*-3,4,4,4-Tetrachlorobut-2-enyloxyimino)-1-ethylbicyclo[2.2.1]heptane (13b). Yield 87%, d_{20}^{20} 1.2138, n_D^{20} 1.5290. M: found 337.3, calc. 359.1. IR spectrum (ν, cm^{-1}): 3080 (=C–H); 2962, 2940, 2879 (CH_{Alk}); 1741 (C=O); 1632 (C=C); 1455 (CH_2); 1300, 1157 (C–O); 978, 809 (C–Cl); 771 (=C–H). UV spectrum (λ_{max}, nm, ε): 207 (10000), 244 (4000).

PMR spectrum (δ, ppm, J/Hz): 0.93 (t, $^3J = 7.0$, CH_3), 1.72 (q, $^3J = 7.0$, CH_2), 7.07 [s, C(O)CH].

Cholesterol (*Z*)-3,4,4,4-Tetrachlorobut-2-enoate (14b). Yield 88%, mp 110-111°C. M: found 577.8, calc. 592.5. IR spectrum (ν, cm^{-1}): 3080, 3040 (=C–H); 2960, 2934, 2900, 2867, 2852 (CH_{Alk}); 1733 (C=O); 1670, 1635 (C=C); 1467, 1440 (CH_2); 1301, 1192 (C–O); 960, 815 (C–Cl); 770, 740 (=C–H). UV spectrum (λ_{max}, nm, ε): 206 (10000), 245 (4000).

PMR spectrum (δ, ppm): 0.63 (s, CH_3-18), 1.06 (s, CH_3-19), 4.70 (m, H-3), 5.38 (m, H-6), 7.02 [s, C(O)CH].

***β*-Sitosterol (*Z*)-3,4,4,4-Tetrachlorobut-2-enoate (15b).** Yield 86%, mp 93-94°C. M: found 606.0, calc. 620.6. IR spectrum (ν, cm^{-1}): 3081, 3042 (=C–H); 2958, 2921, 2860, 2851 (CH_{Alk}); 1735 (C=O); 1672, 1633 (C=C); 1469 (CH_2); 1301, 1187 (C–O); 960, 814 (C–Cl); 770, 735 (=C–H). UV spectrum (λ_{max}, nm, ε): 206 (10000), 245 (4000).

PMR spectrum (δ, ppm): 0.67 (s, CH_3-18), 1.11 (s, CH_3-19), 4.60 (m, H-3), 5.35 (m, H-6), 7.03 [s, C(O)CH].

Diosgenin (*Z*)-3,4,4,4-Tetrachlorobut-2-enoate (16b). Yield 85%, mp 93-94°C. M: found 601.9, calc. 620.5. IR spectrum (ν, cm^{-1}): 3080, 3035 (=C–H); 2950, 2925, 2901, 2871, 2850 (CH_{Alk}); 1736 (C=O); 1670, 1632 (C=C); 1454 (CH_2); 1302, 1186, 1177, 1052 (C–O); 962, 810 (C–Cl); 770, 734 (=C–H). UV spectrum (λ_{max}, nm, ε): 206 (11000), 245 (4000).

PMR spectrum (δ, ppm): 0.79 (s, CH_3-18), 1.03 (s, CH_3-19), 4.35 (m, H-3), 5.30 (m, H-6), 7.05 [s, C(O)CH].

Vanillin (*Z*)-3,4,4,4-Tetrachlorobut-2-enoate (17b). Yield 80%, d_{20}^{20} 1.2615, n_D^{20} 1.5780. M: found 342.4, calc. 358.0. IR spectrum (ν, cm^{-1}): 3075, 3010 (=C–H and CH_{Ar}); 2977, 2941, 2910, 2839, 2800, 2736 (CH_{Alk}); 1760, 1735, 1701 (C=O); 1631 (C=C); 1601, 1502, 1465, 1423 (Ar); 1299, 1274, 1140, 1031 (C–O); 973, 819 (C–Cl); 771, 733, 654 (=C–H and CH_{Ar}). UV spectrum (λ_{max}, nm, ε): 206 (14000), 224 (15000), 245 (5000), 261 (8000), 309 (3000).

PMR spectrum (δ, ppm): 3.93 (s, CH_3), 7.00-7.55 (m, C_6H_3), 7.37 [s, C(O)CH], 9.96 (s, CHO).

Vanillal (*Z*)-3,4,4,4-Tetrachlorobut-2-enoate (18b). Yield 77%, d_{20}^{20} 1.2406, n_D^{20} 1.5705. M: found 359.6, calc. 372.0. IR spectrum (ν, cm^{-1}): 3074, 3008 (=C–H and CH_{Ar}); 2984, 2938, 2902, 2833, 2790, 2732 (CH_{Alk}); 1761, 1736, 1698 (C=O); 1631 (C=C); 1601, 1503, 1442, 1390 (Ar); 1299, 1274, 1141, 1038 (C–O); 973, 820 (C–Cl); 772, 731, 654 (=C–H and CH_{Ar}). UV spectrum (λ_{max}, nm, ε): 206 (14000), 224 (15000), 245 (6000), 261 (8000), 309 (3000).

PMR spectrum (δ, ppm, J/Hz): 1.45 (t, $^3J = 7.4$, CH_3), 4.15 (q, $^3J = 7.4$, CH_2), 7.95-7.55 (m, C_6H_3), 7.37 [s, C(O)CH], 9.97 (s, CHO).

4-(N-*Z*-3,4,4,4-Tetrachlorobut-2-enyloxyiminomethyl)-2-methoxy-1-phenol (19b). Yield 84%, mp 92-93°C. M: found 357.3, calc. 373.0. IR spectrum (ν, cm^{-1}): 3407 (OH); 3081, 3070, 3030 (=C–H and CH_{Ar}); 2970, 2926, 2854 (CH_{Alk}); 1714 (C=O); 1631 (C=C); 1595, 1515, 1463, 1422, 1376 (Ar); 1285, 1185, 1030 (C–O); 980, 817 (C–Cl); 779, 734, 618, 600 (=C–H and CH_{Ar}). UV spectrum (λ_{max}, nm, ε): 210 (20000), 220 (12000), 245 (5000), 305 (6000).

PMR spectrum (δ, ppm): 3.92 (s, CH_3), 6.80 (s, OH), 7.00-7.40 (m, C_6H_3), 7.10 [s, C(O)CH], 8.40 (s, CHN).

4-(N-*Z*-3,4,4,4-Tetrachlorobut-2-enyloxyiminomethyl)-2-ethoxy-1-phenol (20b). Yield 81%, mp 88-89°C. M: found 360.7, calc. 387.0. IR spectrum (ν, cm^{-1}): 3410 (OH); 3080, 3070, 3035 (=C–H and CH_{Ar}); 2975, 2925, 2855 (CH_{Alk}); 1715 (C=O); 1630 (C=C); 1595, 1515, 1465, 1422, 1375 (Ar); 1285, 1185, 1030 (C–O); 980, 817 (C–Cl); 780, 735, 618, 600 (=C–H and CH_{Ar}). UV spectrum (λ_{max}, nm, ε): 210 (19000), 220 (12000), 245 (5000), 305 (6000).

PMR spectrum (δ, ppm, J/Hz): 1.41 (t, $^3J = 7.4$, CH_3), 4.11 (q, $^3J = 7.4$, CH_2), 6.75 (s, OH), 7.05-7.45 (m, C_6H_3), 7.08 [s, C(O)CH], 8.38 (s, CHN).

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