Electronic Supplementary Information

Regioselective condensation of hydroxyaromatic compounds with 2,5-dimethoxytetrahydrofuran: Facile one-pot synthesis of new substituted diaryl-fused 2,8-dioxabicyclo[3.3.2] nonanes comprising central ketal moieties

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General experimental methods (Materials and instruments): Unless otherwise stated, solvents and all reagents were commercially purchased and used without further purification. Melting points were determined with a Buchi 535 melting point apparatus. UV spectra were recorded on a Pharmacia Biotech Ultraspec 3000 model 80-2106-20 spectrometer. IR and FTIR spectra were recorded using a Perkin-Elmer781and Unicam Matteson 1000 spectrometers, respectively.^{1}HNMR and ^{13}CNMR spectra were recorded on a 250 MHz Bruker Avance DPX-250 spectrometer using tetramethyl silane (TMS) as an internal standard at 25 ^{o}C with frequencies of 250 and 62.9 MHz for the ^{1}H and ^{13}C NMR spectra, respectively ($CDCl_3$ or DMSO as a solvent). Mass spectra were recorded on GCMS-Trio1000 (Fisons) and Shimadzo

GCMS-Qp1000 EX instruments at 70 eV. Elemental analysis was performed on a Heraeus CHN-O-Rapid system.

Typical experimental procedure for 4d:

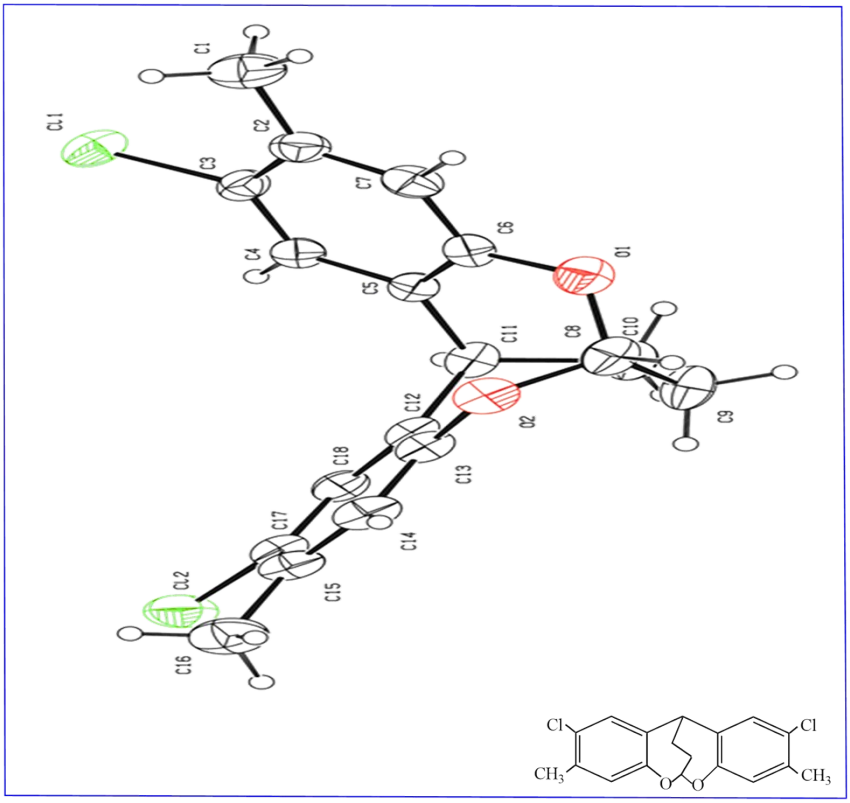
Phenolic compound **1d** (2.0 mmol), 2,5-dimethoxytetrahydrofuran (**2**, 1equiv.), and *p*-TSA (34 mg, 0.1 mmol) were dissolved in CH_2Cl_2 (20 mL) under nitrogen atmosphere. The resulting mixture was stirred at room temperature for 3 h. The reaction mixture was then transferred to a separatory funnel containing water and extracted with CH_2Cl_2 (2 × 20 mL). The combined organic extracts were dried over Na_2SO_4, and solvent was removed in *vacuo*. The crude product **4d** thus obtained were found to be clean upon TLC examination. The crude product was purified by recrystallizing from acetic acid. Yield 80%.

Synthetic procedure for 4d using TFA system:

Phenolic compound (**1d**, 2 mmol) was dissolved in CH_2Cl_2 (10 mL) and TFA (10 mL). 2,5-dimethoxytetrahydrofuran (**2**, 1 mmol) was added over 0.5 h while stirring was continued for an additional 3 h, after which the reaction was quenched with excess saturated aqueous Na_2CO_3. The organic layer was extracted with CH_2Cl_2, dried with $MgSO_4$, and the solvent was evaporated in *vacuo*. The crude product **4d** thus obtained were found to be clean upon TLC examination. The crude product was purified by recrystallization. Yield 75%.

Synthetic procedure for 8 using TFA system:

2,7-dihydroxynaphthalene (**7**, 2 mmol) and 2,5-dimethoxytetrahydrofuran (**2**, 2 mmol, 1/1 mole ratio) and trifluoroacetic acid, TFA (10 mL) in CH_2Cl_2 (10 mL) were mixed in a round-bottomed flask at room temperature. The reaction mixture was then stirred at room temperature for 5 h and then the reaction mixture was quenched with excess saturated aqueous Na_2CO_3. The organic layer was extracted with CH_2Cl_2, dried with $MgSO_4$, and the solvent was evaporated in *vacuo*. The crude product was washed with water several times and boiled with water to remove unreacted diphenol. The residue was purified by recrystallizing from ethanol-water (5/1,v/v) mixture to afford **8** as white solid in 71% yield.



Crystal data

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Mr = 696 F000

Z, Calculated density 4, 1.407 Mg/m^3

Temperature 298(2) K

a = 22.398(5) Aº

b = 9.4469(19) Aº

c = 7.4776(15) Aº θ = 1.8–28.0º

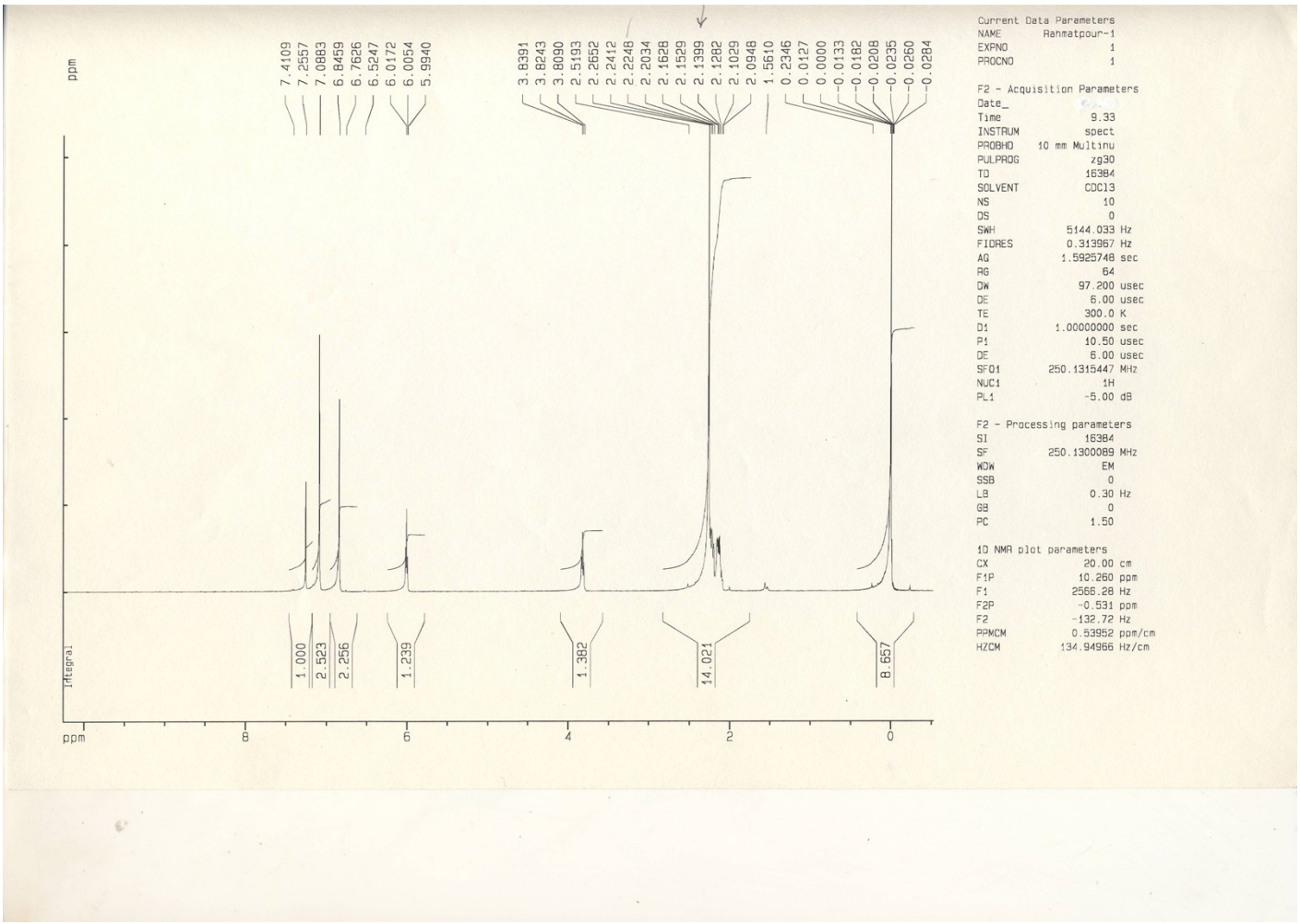
alpha = 90 deg μ = 0.07 mm−1

beta = 90

gamma = 90

Crystal size 0.50 x 0.45 x 0.40 mm

λ, Wavelength 0.71073 A



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PROCNO 1

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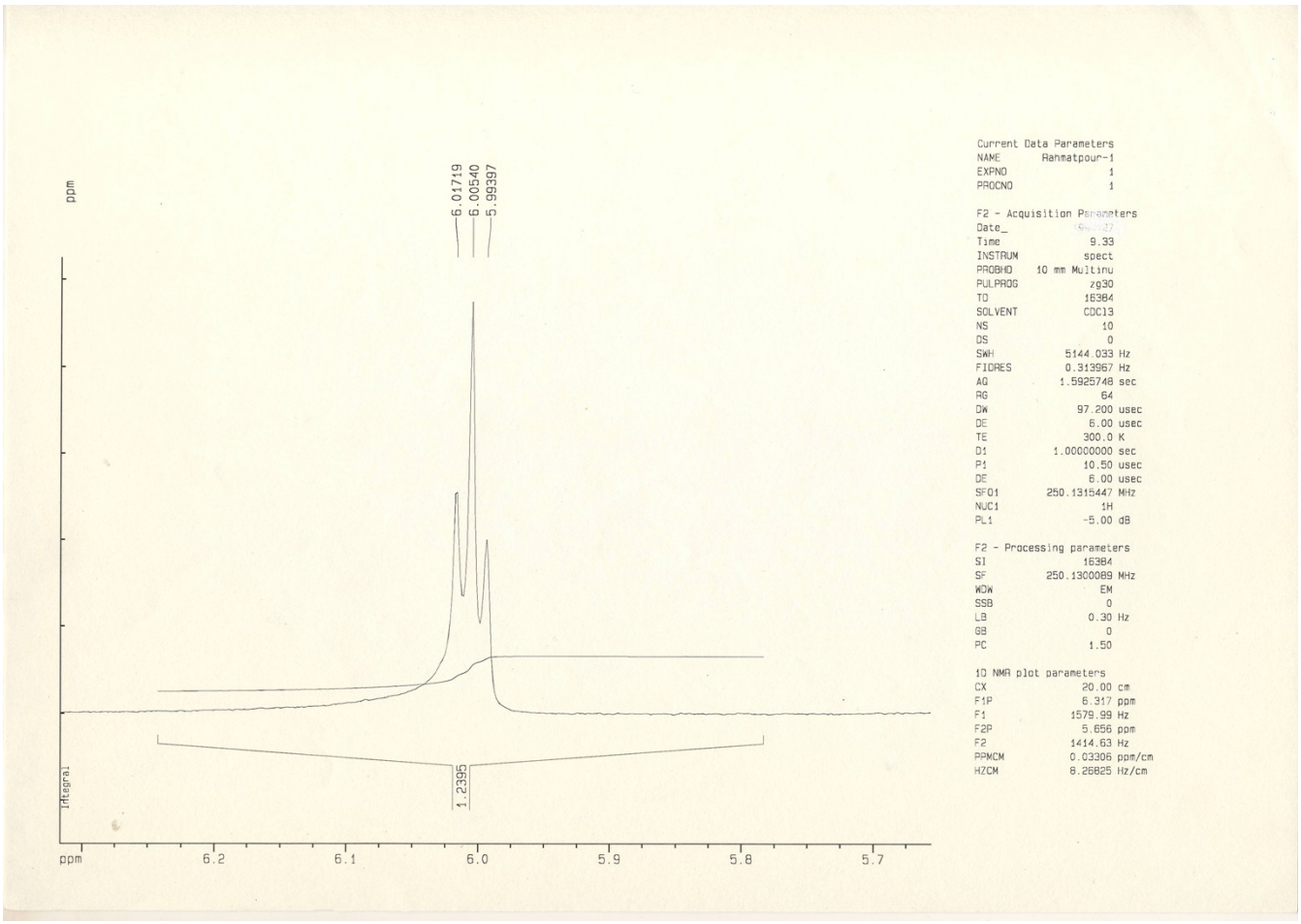

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1D NMR plot parameters

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F1	1579.99 Hz
F2P	5.656 ppm
F2	1414.63 Hz
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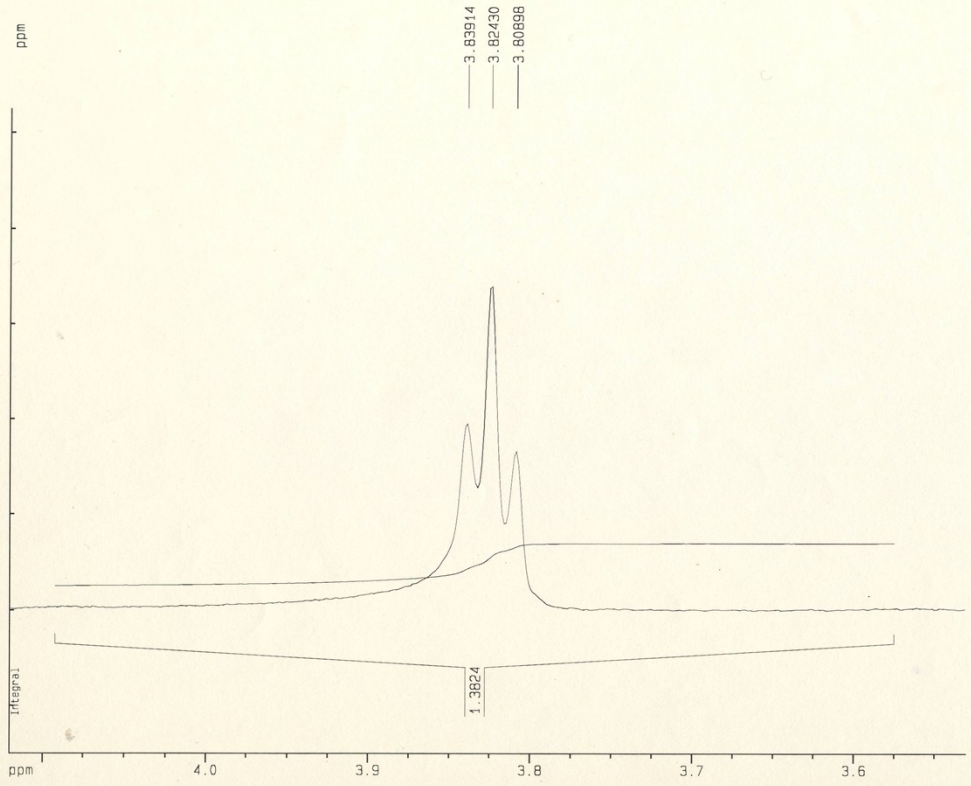

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1D NMR plot parameters

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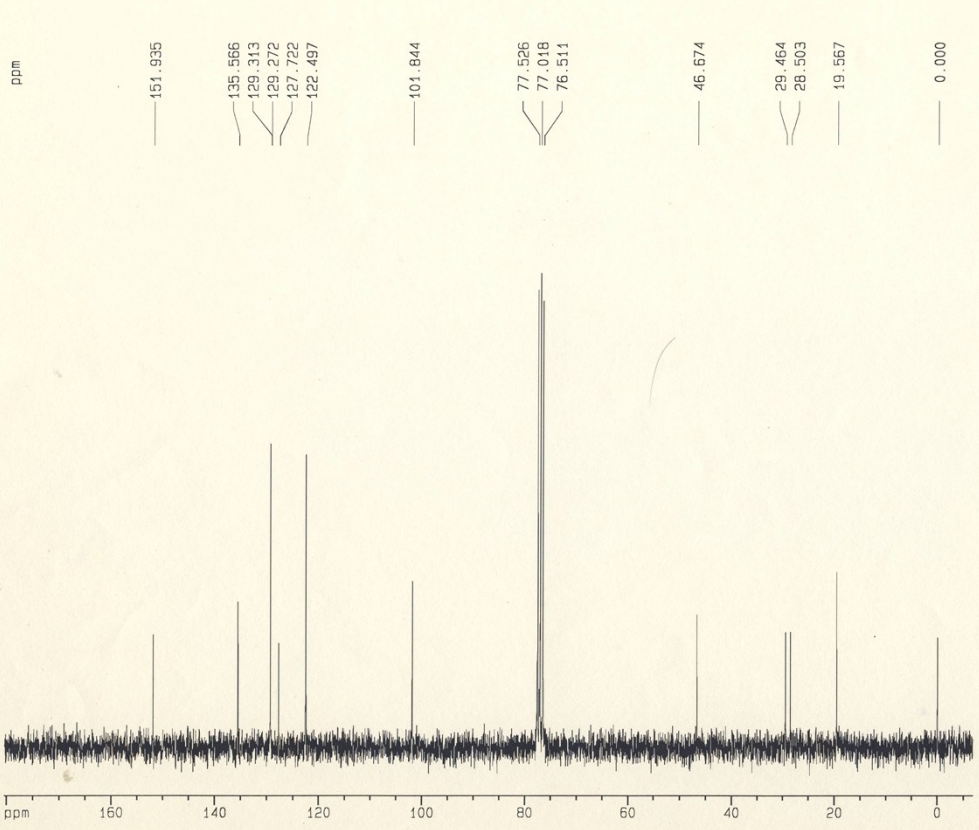


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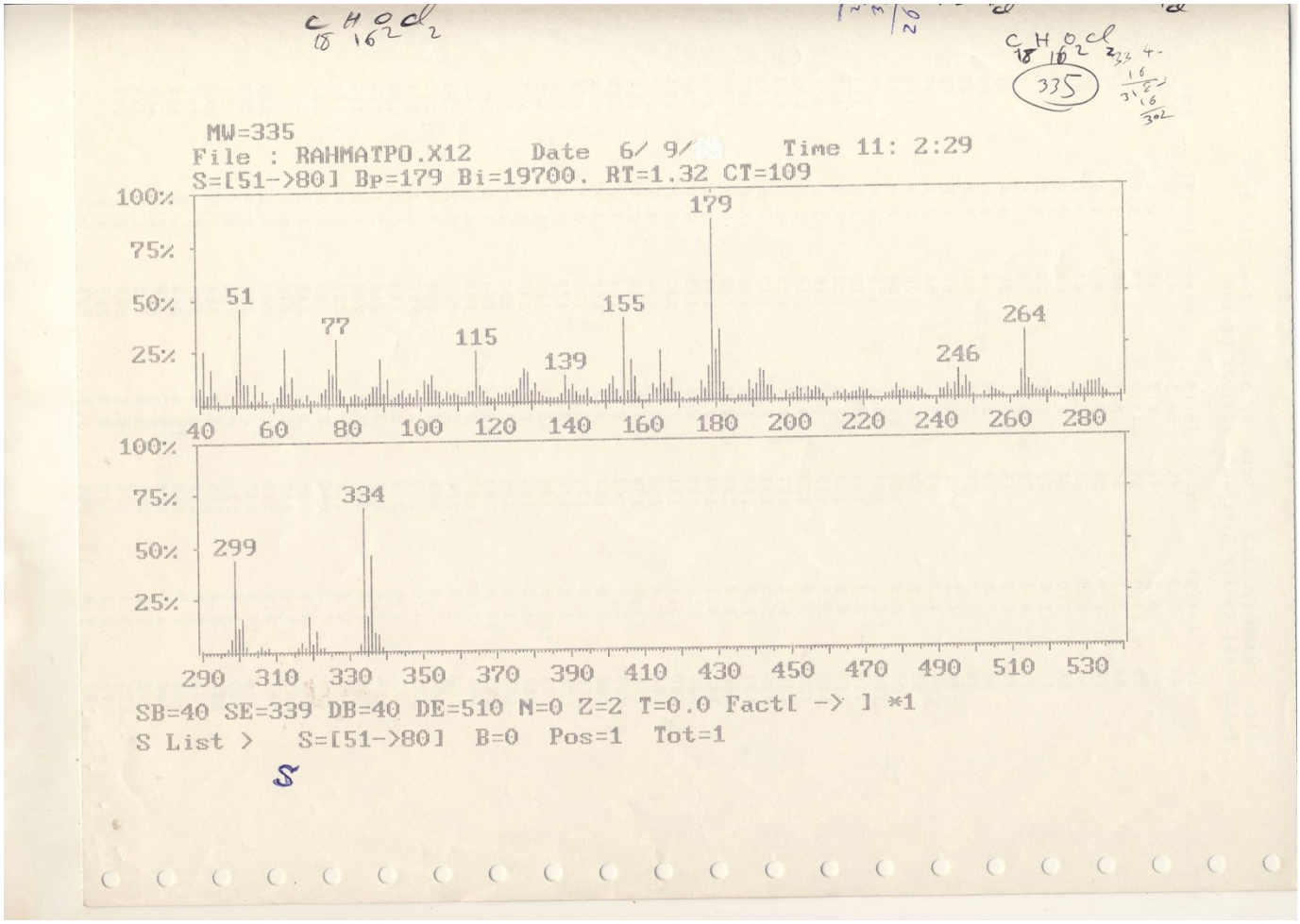
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155
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264
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100%
75%
50%
25%
334
299
290 310 330 350 370 390 410 430 450 470 490 510 530
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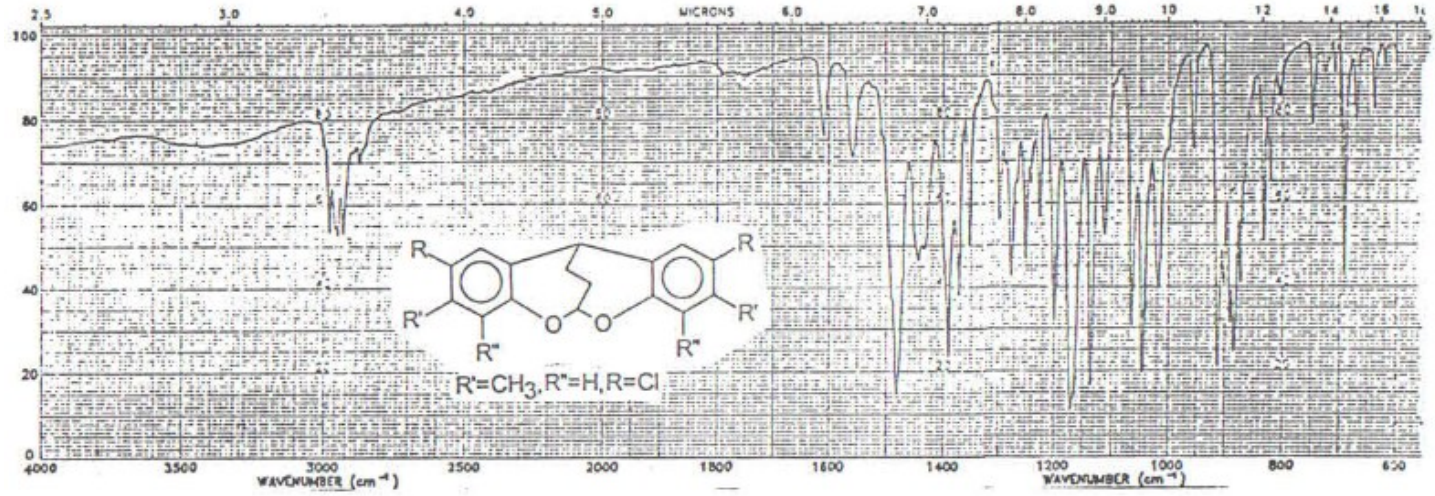
MICRONS
WAVENUMBER (cm⁻¹)
WAVENUMBER (cm⁻¹)
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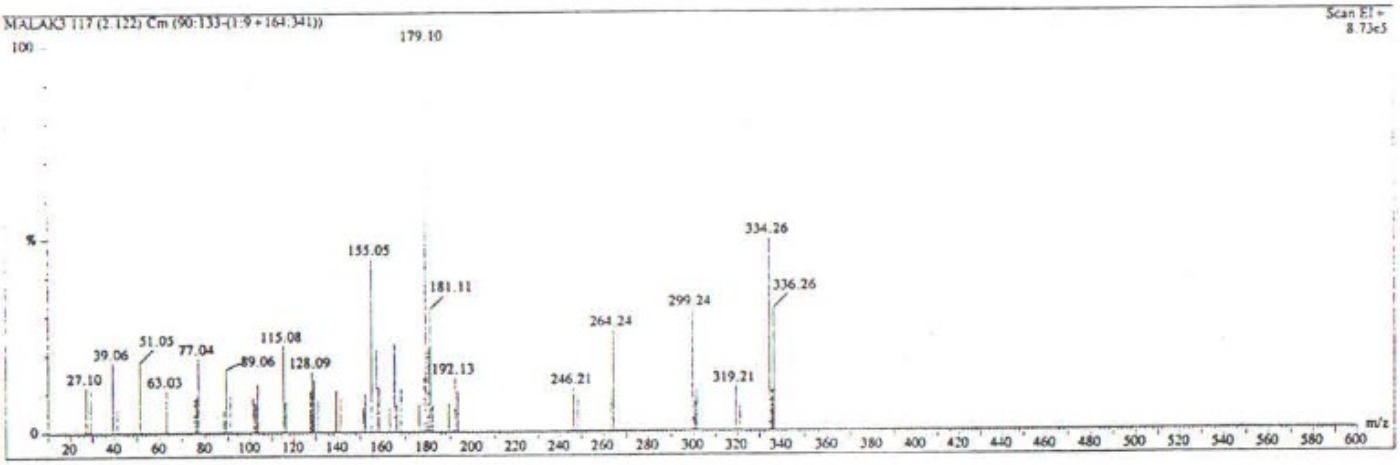
R'
R"
O
O
R"=CH3, R"=H, R=Cl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100
%
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155.05
181.11
334.26
336.26
299.24
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51.05
77.04
39.06
89.06
128.09
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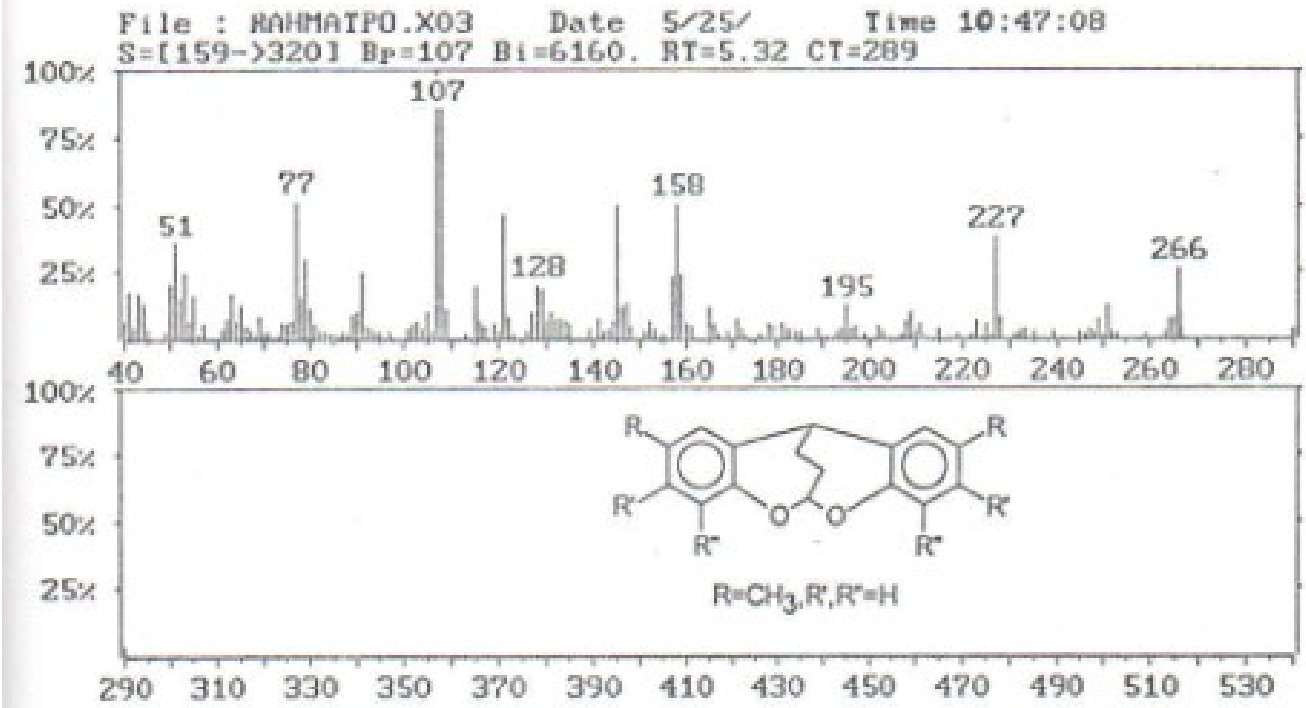
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158
195
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R
R'
R"
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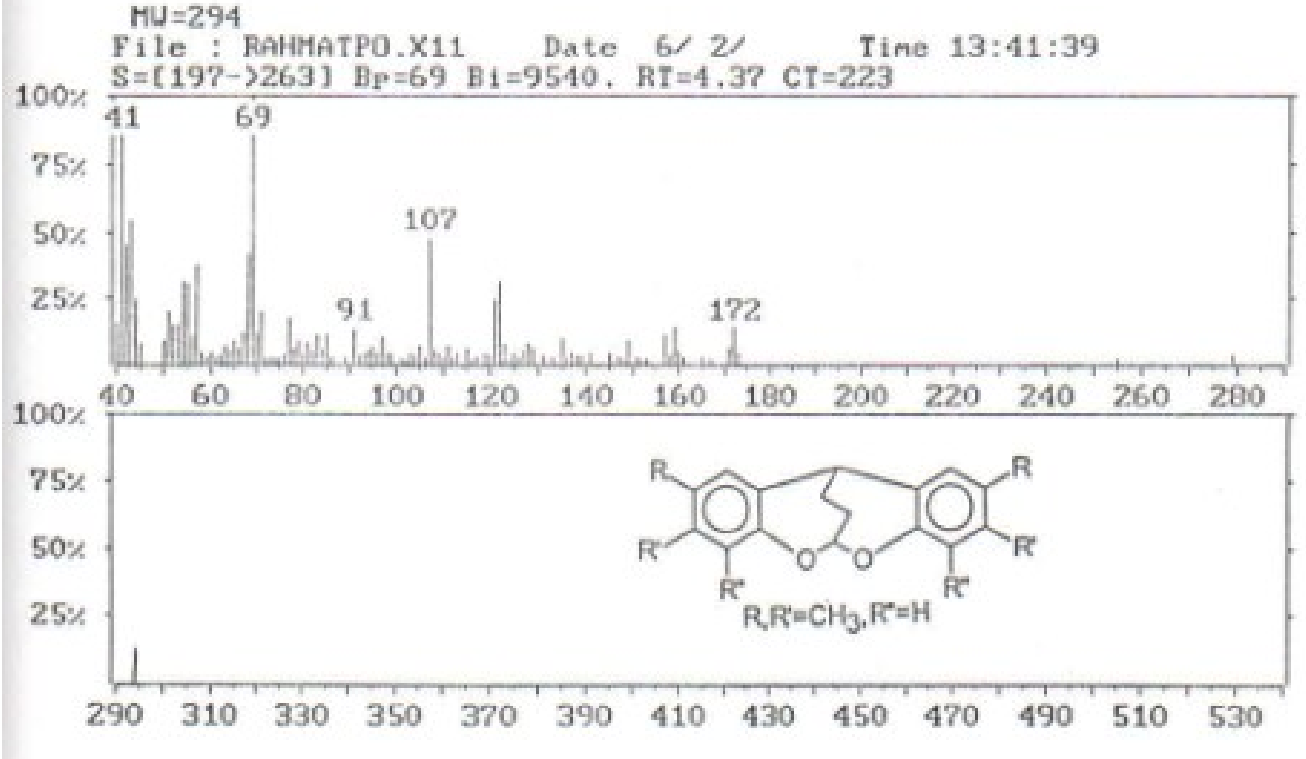
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R
R'
R"
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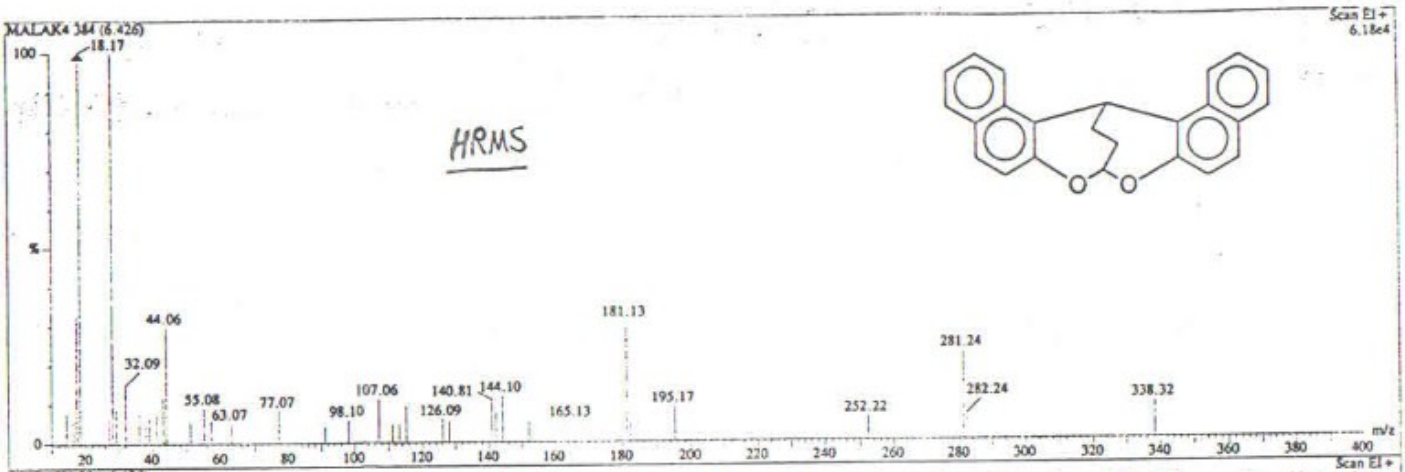

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