Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

New Class of Rhodamine Luminophores: Design, Syntheses and Aggregation-Induced Emission Characetristics

Shinichiro Kamino,*[a] Yuka Horio,[b] Seiji Komeda,[c] Katsuhiko Minoura,[b] Hayato Ichikawa,[d] Jun Horigome,[e] Asana Tatsumi,[a] Shinya Kaji,[b] Takako Yamaguchi,[b] Yoshihide Usami,[b] Shun Hirota,[f] Shuichi Enomoto[a] and Yoshikazu Fujita[b]

[a] Laboratory of Multiple Molecular Imaging Research Center for Molecular Imaging Science RIKEN Kobe Institute, 650-0047, Kobe, Japan, Graduate School of Medicine, Dentistry and Pharmaceutical Sciences, Okayama University, 700-8530, Okayama, Japan. Fax: +81 862517953; Tel: +81 862517952; E-mail: skamino@riken.jp

[b] Osaka University of Pharmaceutical Sciences, 569-1094, Takatsuki, Japan.

[c] Suzuka University of Medical Science, 513-8670, Suzuka, Japan.

[d] College of Industrial Technology, Nihon University, 275-8575, Narashino, Japan.

[e] Hitachi High-Technologies Co., Ltd., 312-8504, Hitachinaka, Japan.

[f] Nara Institute of Science and Technology, 630-0192, Ikoma, Japan.

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1. General remarks

Reagents were purchased from Wako, Nacalai Tesque, or TCI Japan. All other solvents were used without further purification. Experiments were conducted under an atmosphere of dry nitrogen or using a guard tube.

^{1}H-NMR and ^{13}C-NMR spectra were recorded using 300 or 500 MHz spectrometers (Varian UNITY INOVA). Solvents used for NMR measurements were $CDCl_3$, DMSO-d_6 or TFA-d_8, with TMS as the internal standard. Mass spectra were acquired using a JMX-700 (2) (JEOL Co., Ltd.) MS instrument. Melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. Liquid column chromatography was conducted over silica gel (Merck Silica Gel 60 mesh 70-230). Developed TLC plates were visualized under a short-wave UV lamp, by staining with an I_2-SiO_2 mixture, and/or by heating plates that were dipped in ammonium phosphomolybdate sulfate solution. Dry THF was distilled over sodium benzophenone ketyl under argon atmosphere.

UV-vis spectra were collected on a SHIMADZU UV-1700 spectrophotometer at RT using a 1 cm or a 0.1 cm quartz cuvette. Emission spectra were collected on a HITACHI F-4500 fluorescence spectrophotometer. To obtain an accurate spectrum, spectrum correction was carried out with rhodamine B concentrated solution and a secondary-standard light source. In surface photometry, a cut filter was utilized to eliminate multiple lights, such as secondary light, due to the effects of light scattering. Fluorescence spectra of all samples were measured with excitation with 365 nm. Average particle size was measured by dynamic light scattering (ELSZ-2, Otsuka Electronics).

2. Syntheses

2-1. General Procedure for the synthesis of **2**

To a solution of phthalic anhydride (1 equiv) and anhydrous $AlCl_3$ (1.1 equiv) in CH_2Cl_2, **1** (1 equiv) was slowly added and the mixture was stirred under nitrogen at 0 ℃ for 4 hrs Then, the reaction mixture was poured into a mixture of water/6 M HCl, stirred for 10 min, and extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and evaporated to give the crude product. Recrystallization from MeOH/H_2O solution of **2a-2c** was carried out to obtain the pure product as a yellow solid, and **2d** was purified by silica gel column chromatography to obtain the pure product as yellow viscous oil.

2-[4-(Diethylamino)-2-methoxybenzoyl]benzoic acid 2a

^{1}H-NMR ($CDCl_3$, 500 MHz): δ 8.00 (dd, 1H, J = 7.8, 0.8 Hz), 7.65 (d, 1H, J = 8.9 Hz), 7.53 (td, 1H, J = 8.9 Hz), 7.41 (td, 1H, J = 7.8, 1.1 Hz), 7.27 (d, 1H, J = 7.3 Hz), 6.24 (dd, 1H, J = 8.9, 2.3 Hz), 5.99 (sd, 1H, J = 2.1 Hz), 3.55 (s, 3H), 3.40 (q, 4H, J = 7.1 Hz), 1.20 (t, 6H, J = 7.1 Hz). ^{13}C-NMR ($CDCl_3$, 500 MHz): δ 193.9, 170.7, 162.2, 153.1, 146.4, 134.4, 132.3, 130.4, 127.9, 127.4, 126.9, 114.3, 103.8, 93.6, 55.3, 44.6, 12.6. HRMS (EI) calcd for $C_{18}H_{19}NO_4$ (M^+): 327.1471, Found: 324.1471. Yield: 60 %.

2-[4-(Dipropylamino)-2-methoxybenzoyl]benzoic acid 2b

^{1}H-NMR ($CDCl_3$, 500 MHz): δ 8.00 (dd, 1H, J = 7.8, 0.92 Hz), 7.63 (d, 1H, J = 8.7 Hz), 7.52 (td, 1H, J = 7,3, 1.1 Hz), 7.40 (td, 1H, J = 7.6, 1.1 Hz), 7.26 (d, 1H, J = 6.6 Hz), 6.23 (dd, 1H, J = 9.2, 2.3 Hz), 5.97 (sd, 1H, J = 2.3 Hz), 3.54 (s, 3H), 3.28 (brs, 4H), 1.68-1.60 (m, 4H), 0.94 (t, 6H, J = 7.3 Hz). ^{13}C-NMR ($CDCl_3$, 500 MHz): δ 193.8, 170.9, 162.1, 153.5, 146.5, 134.3, 132.3, 130.3, 127.9, 127.4, 126.8, 114.3, 104.0, 93.9, 55.2, 52.8, 20.5, 11.4. HRMS (EI) calcd for $C_{21}H_{25}NO_4$ (M^+): 355.1779, Found: 355.1786. Yield: 24 %.

2-[4-(Dibutylamino)-2-methoxybenzoyl]benzoic acid 2c

^{1}H-NMR ($CDCl_3$, 500 MHz): δ 8.01 (dd, 1H, J = 7.8, 0.92 Hz), 7.63 (brs, 1H), 7.53 (td, 1H, J = 7,3, 1.1 Hz), 7.41 (td, 1H, J = 7.8, 1.1 Hz), 7.26 (d, 1H, J = 7.3 Hz), 6.22 (dd, 1H, J = 9.2, 2.3 Hz), 5.98 (sd, 1H, J = 1.8 Hz), 3.55 (s, 3H), 3.31 (brs, 4H), 1.63-1.57 (m, 4H), 1.40-1.32 (m, 4H), 0.96 (t, 6H, J = 7.3 Hz). ^{13}C-NMR ($CDCl_3$, 500 MHz): δ 193.9, 170.6, 164.7, 162.2, 153.5, 146.4, 134.4, 132.3, 130.4, 127.9, 127.4, 126.9, 114.2, 103.9, 93.8, 55.2, 50.8, 29.4, 20.2, 13.9. HRMS (EI) calcd for $C_{23}H_{29}NO_4$ (M^+): 383.2097, Found: 383.2093. Yield: 23 %.

2-[4-(Dihexylamino)-2-methoxybenzoyl]benzoic acid 2d

^{1}H-NMR ($CDCl_3$, 500 MHz): δ 8.02 (dd, 1H, J = 7.8, 0.92 Hz), 7.63 (brs, 1H), 7.53 (td, 1H, J = 7,6, 1.4 Hz), 7.42 (td, 1H, J = 7.8, 1.4 Hz), 7.27 (d, 1H, J = 8.7 Hz), 6.21 (dd, 1H, J = 8.9, 2.3 Hz), 5.97 (sd, 1H, J = 1.8 Hz), 3.56 (s, 3H), 3.23 (t, 4H, J = 7.8 Hz), 1.62-1.58 (m, 4H), 1.40-1.32 (m, 12H), 0.89 (t, 6H, J = 7.1 Hz). ^{13}C-NMR ($CDCl_3$, 500 MHz): 194.0, 170.4, 162.2, 153.5, 146.3, 134.4, 132.3, 131.9, 130.8, 130.5, 129.9, 128.6, 128.0, 127.5, 127.0, 114.2, 103.95, 93.8, 55.2, 52.8, 51.1, 31.6, 27.2, 26.7, 22.6, 14.0. HRMS (EI) calcd for $C_{27}H_{37}NO_4$ (M^+): 439.2723, Found: 439.2730.

2-2. General Procedure for the synthesis of **3**

To a stirred solution of **2** (1.0 equiv) in dry CH_2Cl_2 was added a solution of BBr_3 (1.9 equiv) in CH_2Cl_2 at -78 ℃. After 1 hrs, the mixture was warmed to -25 ℃. After completion of the reaction, the mixture was quenched with H_2O and evaporated to give the crude product. Recrystallization from MeOH/H_2O solution of **3a-3c** yielded the pure product as a yellow solid, and **3d** was purified by silica gel column chromatography to obtain the pure product as yellow viscous oil. .

2-[4-(Diethylamino)-2-hydroxybenzoyl]benzoic acid 3a

^{1}H-NMR ($CDCl_3$, 500 MHz): δ 12.65 (s, 1H), 8.07 (dd, 1H, J = 7.8, 0.9 Hz), 7.58 (td, 1H, J = 7.6, 1.4 Hz), 7.51 (td, 1H, J = 7.8, 1.4 Hz), 7.34 (dd, 1H, J = 7.6, 1.1 Hz), 6.91 (d, 1H, J = 8.9 Hz), 6.11 (sd, 1H, J = 2.5 Hz), 6.03 (dd, 1H, J = 9.2, 2.5 Hz), 3.37 (q, 4H, J = 7.1 Hz), 1.18 (t, 6H, J = 7.1 Hz). ^{13}C-NMR ($CDCl_3$, 500 MHz): δ 199.0, 167.5, 165.2, 153.6, 140.6, 134.6, 131.6, 130.4, 129.5, 128.9, 127.6, 110.1, 103.5, 96.7, 44.5, 12.5. HRMS (EI) calcd for $C_{19}H_{21}NO_4$ (M^+): 313.1314, Found: 313.1313. Yield: 65 %.

2-[4-(Dipropylamino)-2-hydroxybenzoyl]benzoic acid 3b

Yield: 1.0 g (52 %); ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 12.53 (s, 1H), 8.10 (d, 1H, J = 7.1 Hz), 7.62 (t, 1H, J = 7.3 Hz), 7.53 (t, 1H, J = 7.3 Hz), 7.36 (dd, 1H, J = 7.8, 1.1 Hz), 6.87 (d, 1H, J = 9.2 Hz), 6.12 (s, 1H), 6.03 (d, 1H, J = 8.9 Hz), 3.26 (t, 4H, J = 7.6 Hz), 1.65-1.59 (m, 4H), 0.92 (t, 6H, J = 7.3 Hz). ^{13}C-NMR ($CDCl_3$, 500 MHz): δ ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 198.1, 169.8, 165.4, 154.4, 141.2, 134.5, 132.7, 131.1, 129.1, 128.1, 127.6, 109.9, 104.0, 97.3, 52.8, 20.5, 11.3. HRMS (EI) calcd for $C_{20}H_{23}NO_4$ (M^+): 341.1630, Found: 341.1626.

2-[4-(Dibutylamino)-2-hydroxybenzoyl]benzoic acid 3c

^{1}H-NMR ($CDCl_3$, 500 MHz): δ 12.54 (s, 1H), 8.12 (d, 1H, J = 7.8 Hz), 7.63 (t, 1H, J = 7.3 Hz), 7.54 (t, 1H, J = 7.6 Hz), 7.36 (dd, 1H, J = 7.6, 0.92 Hz), 6.87 (d, 1H, J = 8.9 Hz), 6.11 (s, 1H), 6.03 (d, 1H, J = 8.5 Hz), 3.29 (t, 4H, J = 7.3 Hz), 1.58 (brs, 4H), 1.37-1.30 (m, 4H), 0.94 (t, 6H, J = 7.3 Hz). ^{13}C-NMR ($CDCl_3$, 500 MHz): δ 198.1, 169.5, 165.5, 154.4, 141.1, 134.5, 132.7, 131.1, 129.2, 128.1, 127.6, 109.8, 103.9, 97.2, 50.9, 29.4, 20.2, 13.9. HRMS (EI) calcd for $C_{22}H_{27}NO_4$ (M^+): 369.1940, Found: 369.1932. Yield: 49 %.

2-[4-(Dihexylamino)-2-hydroxybenzoyl]benzoic acid 3d

^{1}H-NMR ($CDCl_3$, 500 MHz): δ 12.55 (s, 1H), 8.10 (dd, 1H, J = 8.0, 0.92 Hz), 7.62 (dd, 1H, J = 7.6, 1.4 Hz), 7.53 (td, 1H, J = 7.8, 1.4 Hz), 7.34 (dd, 1H, J = 7.1, 0.92 Hz), 6.87 (d, 1H, J = 9.2 Hz), 6.11 (sd, 1H, J = 2.5 Hz), 6.02 (dd, 1H, J = 9.2, 2.5 Hz), 3.27 (brs, 4H), 1.59 (brs, 4H), 1.33-1.30 (m, 12H), 0.90-0.88 (m 6H). ^{13}C-NMR ($CDCl_3$, 500 MHz): δ 198.1, 169.0, 165.5, 154.4, 141.1, 134.5, 132.6, 131.1, 129.1, 128.1, 127.7, 109.8, 103.9, 97.2, 51.1, 31.59, 27.3, 26.7, 22.6, 14.0. HRMS (EI) calcd for $C_{26}H_{35}NO_4$ (M^+): 425.2563, Found: 425.2569.

2-3. General Procedure for the synthesis of **4**

3 (2.0 equiv) and resorcinol (1.0 equiv) were combined in methanesulfuric acid (2.0 mL) in a sealed tube and heated at 90 ℃ for 2 hrs. The reaction was poured into stirred ice water, its pH was adjusted to 11~12 with 1.0 M sodium hydroxide aqueous solution, and the mixture was stirred for 20 min. Then, the mixture was extracted with CH_2Cl_2 three times. The organic layers were dried over $MgSO_4$ and evaporated to give the crude product. This was purified by silica gel column chromatography and further recrystallized from acetonitrile solution to obtain the pure product as a white solid.

3',3"-Bis(oxospriroisobenzofuran)-3,7-bis(diethylamino)benzopyranoxanthene (ABPX01) 4a

δ^{1}H-NMR (THF-d_8, 500 MHz): δ 7.73-7.72 (m, 1H), 7.70 (dt, 1H, J = 7.6, 1.1 Hz), 7.61 (td, 1H, J = 7.6, 0.92 Hz), 7.52 (td, 1H, J = 7.3, 0.9 Hz), 7.47-7.43 (m, 2H), 7.16 (dt, 1H, J = 7.6, 0.9 Hz), 7.11 (s, 1H), 6.94-6.92 (m, 1H), 6.50-6.49 (m, 2H), 6.47 (d, 1H, J = 7.6 Hz), 6.45 (d, 1H, J = 7.6 Hz), 6.37-6.34 (m, 2H), 6.07 (s, 1H), 3.30-3.25 (m, 8H), 0.92 (t, 12H, J = 7.6 Hz). ^{13}C-NMR ($CDCl_3$, 500 MHz): δ 168.4, 168.3, 154.0, 153.9, 153.8, 153.7, 153.1, 153.0, 151.0, 150.9, 135.5, 134.8, 130.3, 130.0, 129.7, 129.4, 129.3, 128.8, 128.4, 128.1, 125.0, 124.9, 124.8, 124.4, 118.00, 117.8, 109.6, 106.6, 106.5, 104.4, 104.3, 98.6, 98.5, 83.0, 82.8, 53.4, 11.5. ^{13}C-NMR ($CDCl_3$, 500 MHz): δ HRMS (FAB) calcd for $C_{42}H_{37}N_2O_6$ (M+H): 665.2651, Found: 665.2654. Yield: 72 %.

3',3"-Bis(oxospriroisobenzofuran)-3,7-bis(dipropylamino)benzopyranoxanthene (ABPX02) 4b

^{1}H-NMR (THF-d_8, 500 MHz): δ 7.73-7.72 (m, 1H), 7.70 (dt, 1H, J = 7.6, 1.1 Hz), 7.61 (td, 1H, J = 7.6, 0.92 Hz), 7.52 (td, 1H, J = 7.3, 0.9 Hz), 7.47-7.43 (m, 2H), 7.16 (dt, 1H, J = 7.6, 0.9 Hz), 7.11 (s, 1H), 6.94-6.92 (m, 1H), 6.50-6.49 (m, 2H), 6.47 (d, 1H, J = 7.6 Hz), 6.45 (d, 1H, J = 7.6 Hz), 6.37-6.34 (m, 2H), 6.07 (s, 1H), 3.30-3.25 (m, 8H), 1.65-1.57 (m, 8H), 0.92 (t, 12H, J = 7.6 Hz). ^{13}C-NMR ($CDCl_3$, 500 MHz): δ 168.4, 168.3, 154.0, 153.9, 153.8, 153.7, 153.2, 153.0, 151.0, 150.9, 135.5, 134.8, 130.3, 130.0, 129.7, 129.4, 129.3, 128.8, 128.4, 128.1, 125.0, 124.9, 124.8, 124.4, 118.0. 117.8, 109.6, 106.6, 106.5, 104.4, 104.3, 98.6, 98.5, 83.0, 82.8, 53.4, 21.1, 11.5. HRMS (FAB) calcd for $C_{46}H_{45}N_2O_6$ (M+H): 721.3278, Found: 721.3276. Yield: 56 %.

3',3"-Bis(oxospriroisobenzofuran)-3,7-bis(dibuthylamino)benzopyranoxanthene (ABPX03) 4c

^{1}H-NMR (THF-d_8, 500 MHz): δ 7.74-7.72 (m, 1H), 7.70 (dt, 1H, J = 7.6, 0.92 Hz), 7.62 (td, 1H, J = 7.6, 1.1 Hz), 7.52 (td, 1H, J = 7.3, 0.92 Hz), 7.47-7.43 (m, 2H), 7.16 (dt, 1H, J = 7.6, 0.92 Hz), 7.13 (s, 1H), 6.94-6.92 (m, 1H), 6.50-6.49 (m, 2H), 6.47 (d, 1H, J = 7.8 Hz), 6.45 (d, 1H, J = 7.8 Hz), 6.37-6.34 (m, 2H), 6.07 (s, 1H), 3.33-3.30 (m, 8H), 1.60-1.54 (m, 8H), 1.40-1.32 (m, 8H), 0.95 (t, 12H, J = 7.3 Hz). ^{13}C-NMR ($CDCl_3$, 500 MHz): δ 168.4, 168.3, 154.0, 153.9, 153.8, 153.7, 153.2, 153.0, 151.0, 150.9, 135.4, 134.8, 130.3, 130.0, 129.7, 130.0, 129.4, 128.8, 128.5, 128.1, 125.0, 124.9, 124.8, 124.4, 118.0, 117.8, 109.6, 106.6, 106.5, 104.5, 104.4, 98.6, 98.5, 83.0, 82.8, 51.4, 30.2, 21.0, 14.3. HRMS (FAB) calcd for $C_{50}H_{53}N_2O_6$ (M+H): 777.3903, Found: 777.3911. Yield: 52 %.

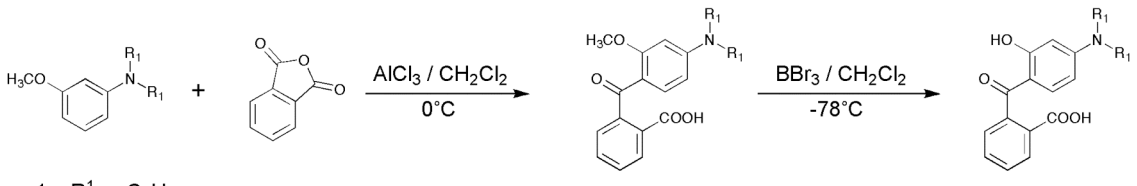
3',3"-bis(oxospriroisobenzofuran)-3,7-bis(dihexylamino)benzopyranoxanthene (ABPX04) 4d

^{1}H-NMR (THF-d_8, 500 MHz): δ 7.74-7.72 (m, 1H), 7.70 (d, 1H, J = 7.8 Hz), 7.62 (td, 1H, J = 7.6, 0.92 Hz), 7.52 (td, 1H, J = 7.6, 0.92 Hz), 7.47-7.44 (m, 2H), 7.16 (d, 1H, J = 7.6 Hz), 7.12 (s, 1H), 6.94-6.92 (m, 1H), 6.49-6.48 (m, 2H), 6.47 (d, 1H, J = 8.7 Hz), 6.45 (d, 1H, J = 8.0 Hz), 6.36-6.34 (m, 2H), 6.06 (s, 1H), 3.31 (brs, 8H), 1.59 (brs, 8H), 1.33 (brs, 24H), 0.90 (brs, 12H). ^{13}C-NMR ($CDCl_3$, 500 MHz): δ 168.4, 168.3, 154.0, 154.0, 153.9, 153.8, 153.7, 153.2, 153.0, 151.0, 150.9, 150.8, 135.4, 134.8, 130.3, 130.0, 129.7, 129.4, 129.3, 128.7, 128.5, 128.1, 125.0, 125.9, 124.8, 124.4, 118.0, 117.8, 109.6, 106.6, 106.5, 104.5, 104.4, 98.6, 98.5, 83.0, 82.8, 51.7, 32.7, 28.0, 27.6, 23.6, 14.4. HRMS (FAB) calcd for $C_{58}H_{69}N_2O_6$ (M+H): 889.5155, Found: 889.5165

3. Crystal data and experimental data of ABPX01^0

Crystal and experimental data: $C_{42}H_{37}N_2O_6$, M = 665.76, orthorhombic, Fdd2, a = 17.5837 (11), b = 23.2759 (11), c = 18.2237 (9) Å, α, β, γ = 90°, V = 7458.5 (7) Å^3, Z = 8, Dx = 1.186 g cm^{-3}, F(000) = 2808, μ (Mo Kα) = 0.079 mm^{-1}. The data were collected on a Rigaku RAXIS-RAPID area detector using graphite-monochromated MoKα radiation at 293.1 K. A total of 17,587 reflections were measured up to θ_{max} = 27.46° (0.85 Å resolution) and merged to 14,495 reflections with R_{int} = 0.034. The structure was solved using CrystalStructure 3.8 and refined with CrystalStructure 3.8. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated at the ideal positions and isotropically included in the calculations of the structure factors. The structure was converted at goodness of fit = 1.232, $(\Delta/\sigma)_{max}$ = 0.0088, $\Delta\rho_{max}$ = 2.50 e Å^{-3}, $\Delta\rho_{min}$ = -2.27 e Å^{-3}, R = 0.0589, and wR = 0.0772. Crystallographic data (excluding structure factors) for the structure of ABPX01^0 reported in this paper are deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-779022. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

4. Scheme and figures



1a: R^1 = $-C_2H_5$
1b: R^1 = $-C_3H_7$
1c: R^1 = $-C_4H_9$
1d: R^1 = $-C_6H_{13}$

Scheme S1 Synthetic routes of benzophenone derivatives.

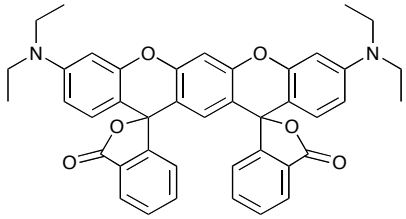


Fig. S1 Chemical structure of ABPX01^0.

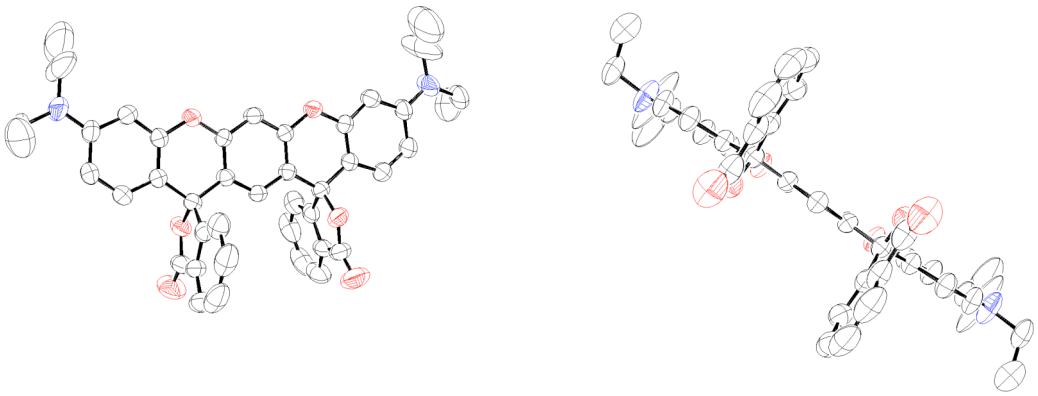


Fig. S2 ORTEP drawing of ABPX01^0. The trans-ABPX01^0 was confirmed in solids, of which five rings had a high degree of planarity.

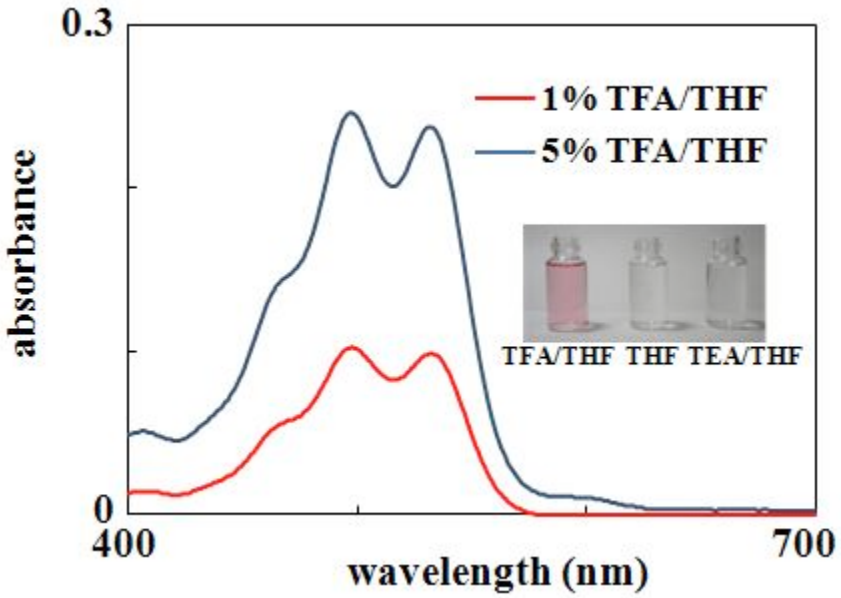


Fig. S3 Effect of protolytic reaction on absorption spectra of ABPX01 in TFA/THF solutions. TFA: trifluoroacetic acid, TEA: triethylamine. Inset: photograph of the solutions under room light. In strong acid solution, the absorbance spectra having two peaks at 490 nm and 540 nm should be attributable to the cationic species $ABPX01^{+}$. In THF and alkaline solutions, the spectra had no peaks that were attributable to the neutral lactonoid species $ABPX01^{0}$.

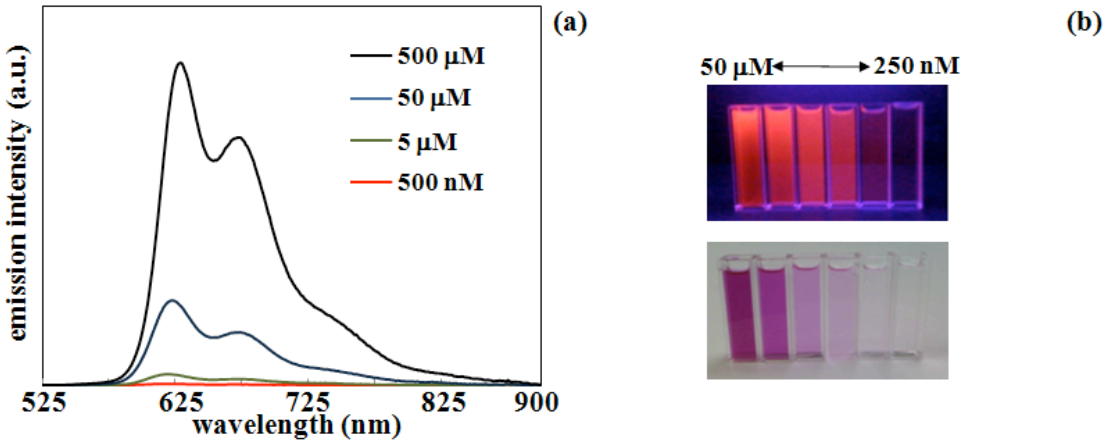


Fig. S4 (a) Emission at various concentrations of ABPX01^{+}. (b) photograph of the solutions, top: under 365 nm irradiation, bottom: under room light irradiation.

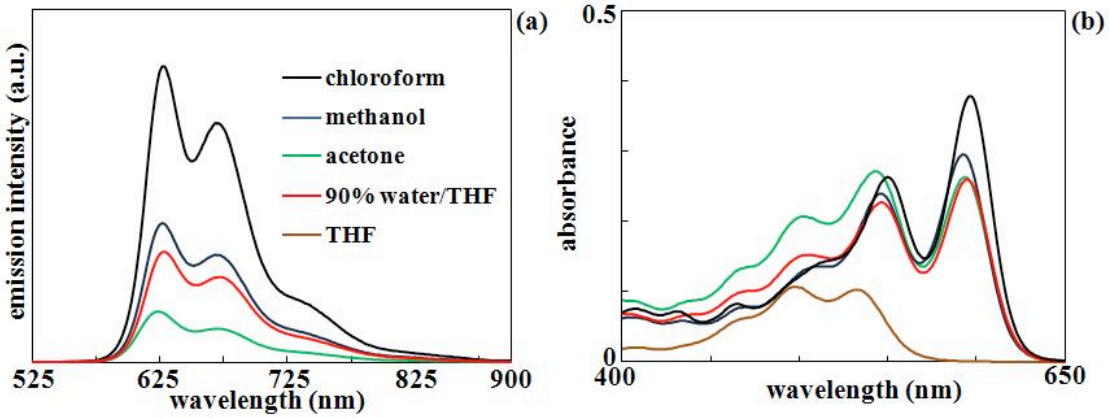


Fig. S5 (a) Emission spectra of 500 μM of ABPX01$^+$ and (b) absorption spectra of 5 μM of ABPX01$^+$ in various solvents. The emission spectrum in THF was not observed. 1.0% TFA was added to ensure protonation and prevent pseudobase formation during measurement.

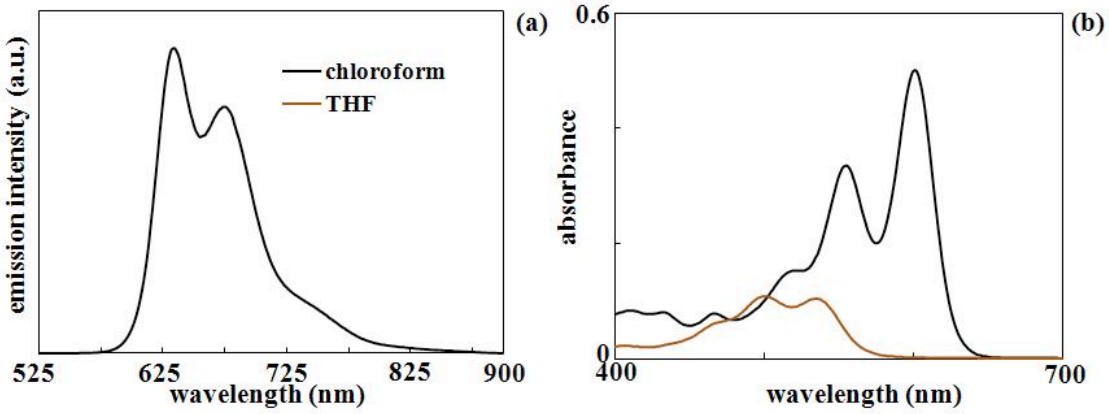


Fig. S6 (a) Emission spectra of 500 μM of ABPX02$^+$ and (b) absorption spectra of 5 μM of ABPX02$^+$ in various solvents. The emission spectrum in THF was not observed. 1.0% TFA was added to ensure protonation and prevent pseudobase formation during measurement.

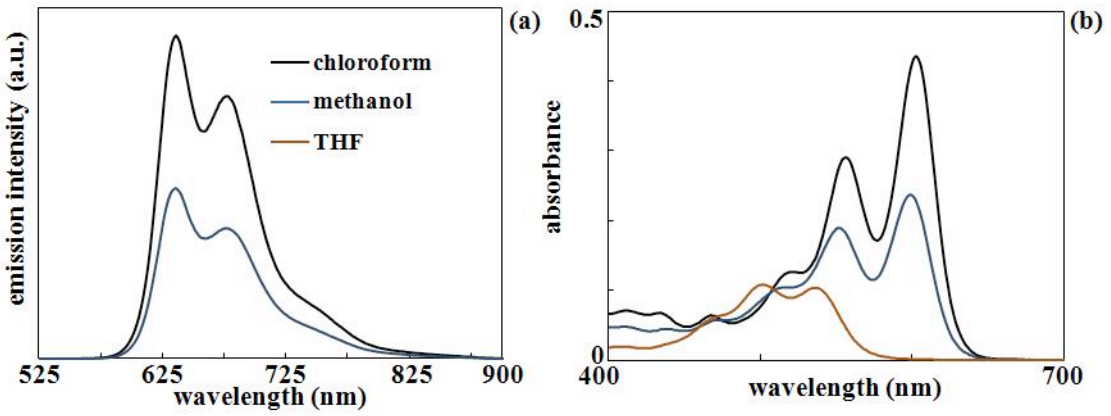


Fig. S7 (a) Emission spectra of 500 μM of ABPX03$^+$ and (b) absorption spectra of 5 μM of ABPX03$^+$ in various solvents. The emission spectrum in THF was not observed. 1.0% TFA was added to ensure protonation and prevent pseudobase formation during measurement.

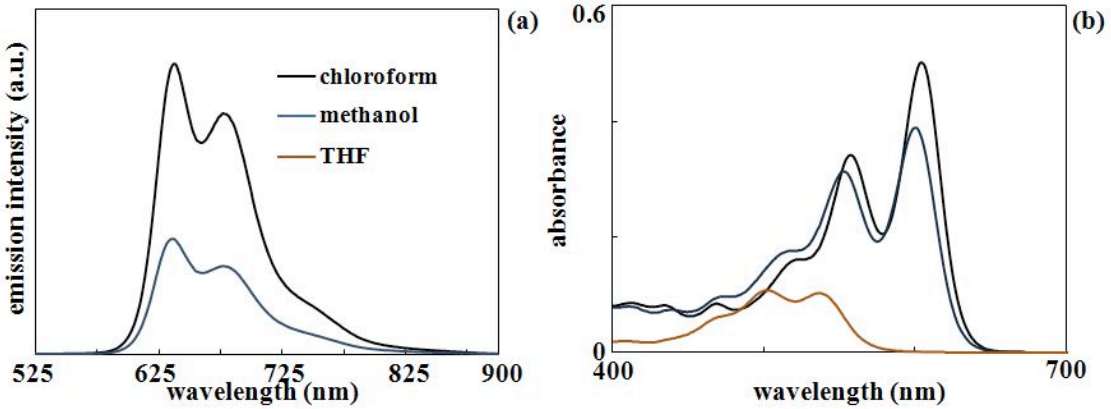


Fig. S8 (a) Emission spectra of 500 μM of ABPX04$^+$ and (b) absorption spectra of 5 μM of ABPX04$^+$ in various solvents. The emission spectrum in THF was not observed. 1.0% TFA was added to ensure protonation and prevent pseudobase formation during measurement.

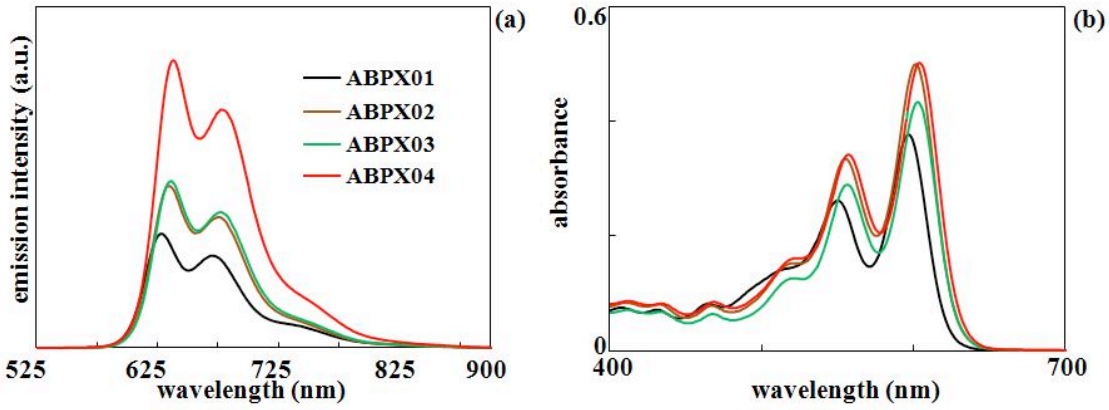


Fig. S9 (a) Emission and (b) absorption spectra of ABPX01^{+}-04^{+} in chloroform. A slightly continuous red shift was observed with an increase in *N*-alkyl chain length. 1.0% TFA was added to ensure protonation and prevent pseudobase formation during measurement.

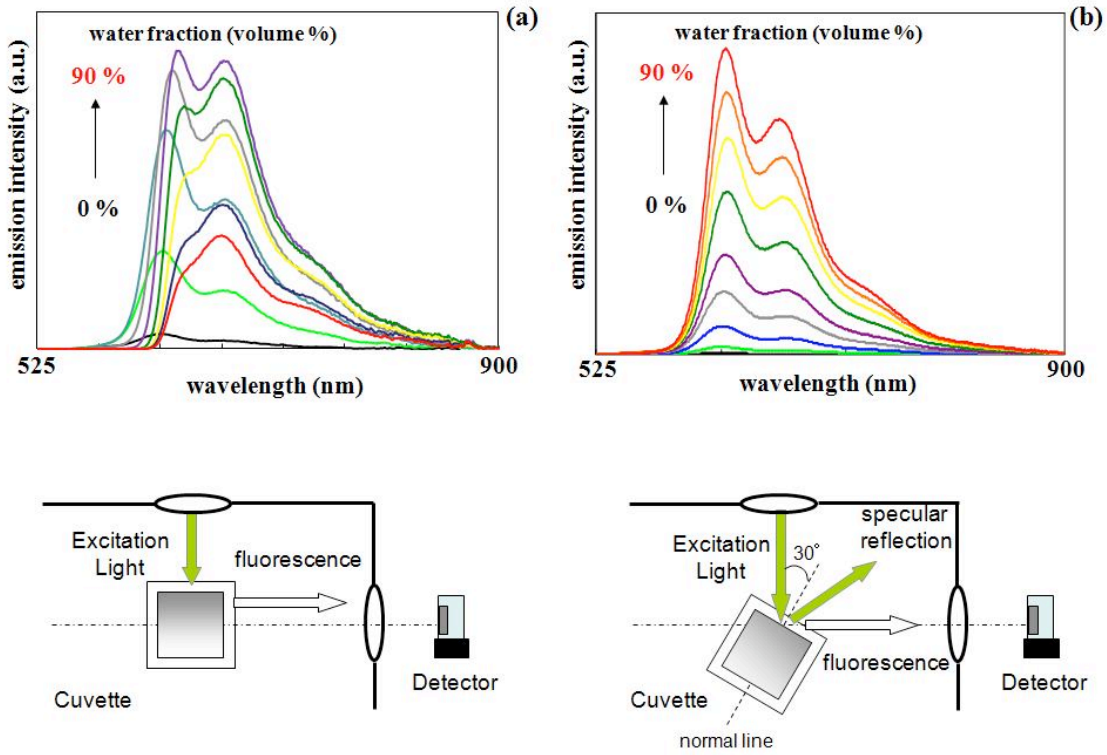


Fig. S10 Emission spectra of ABPX01 by (a) conventional photometric method and (b) surface photometric method. Shown below are the respective equipment configurations. The emission spectra by the conventional photometric method showed random shifts of the maximum wavelengths, which were caused by the internal filter effect when measurement of $ABPX01^{+}$ was conducted at a high concentration. The problem was solved by using the surface photometric method. The sample holder was set at an angle of 30° with respect to the excitation light. However, attention should be paid to the linearity of the emission intensity against the concentration for the accurate evaluation of high-concentration sample solutions, such as AIEE molecules. In addition, the relative quantum yields of ABPX in solution could not be determined because of the lack of a standard compound. We are now developing an apparatus for the measurement of the absolute fluorescence quantum yields of high-concentration solutions.

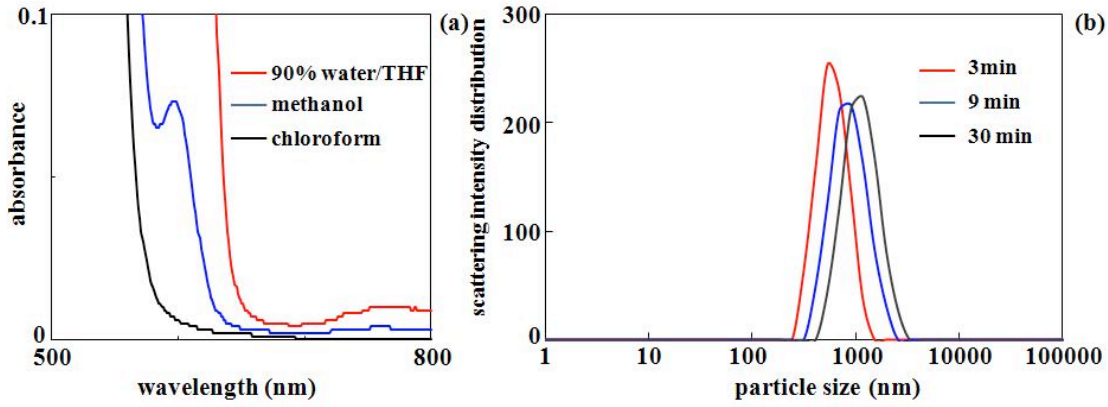


Fig. S11 (a) Level-off tails of 500 μM of ABPX01$^+$ were observed in chloroform, methanol, and 90% water/THF mixture solutions. In comparison, level-off tails of 500 μM of ABPX01$^+$ in chloroform could not be observed. (b) Dynamic laser scattering (time dependence of particle size distributions of 500 μM of ABPX01$^+$ in 90% water/THF mixtures). The nanoaggregate size of ABPX01$^+$ in solutions was increased as a time-dependent change. 1.0% TFA was added to ensure protonation and prevent pseudobase formation during measurement.

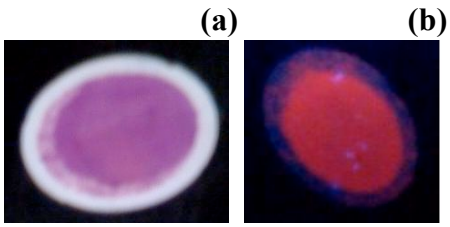


Fig. S12 Membrane filter photographs of ABPX01$^+$ in 90% water/THF mixtures (containing 1% TFA) under (a) room light and (b) 365 nm irradiation.

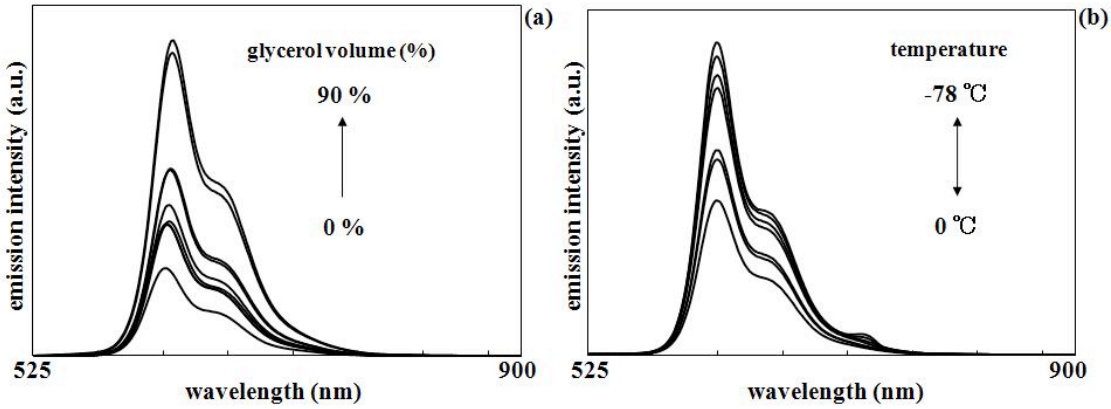
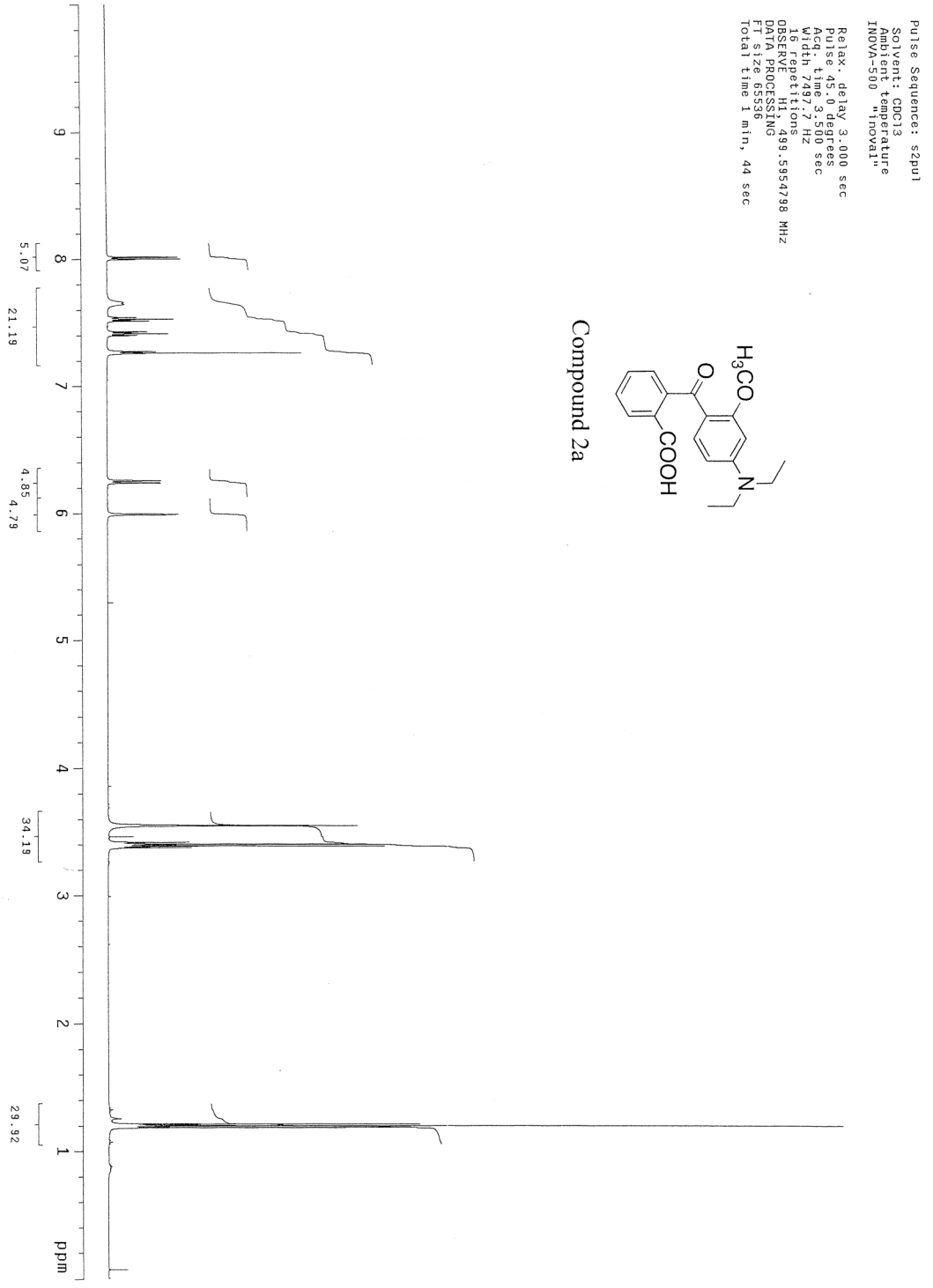
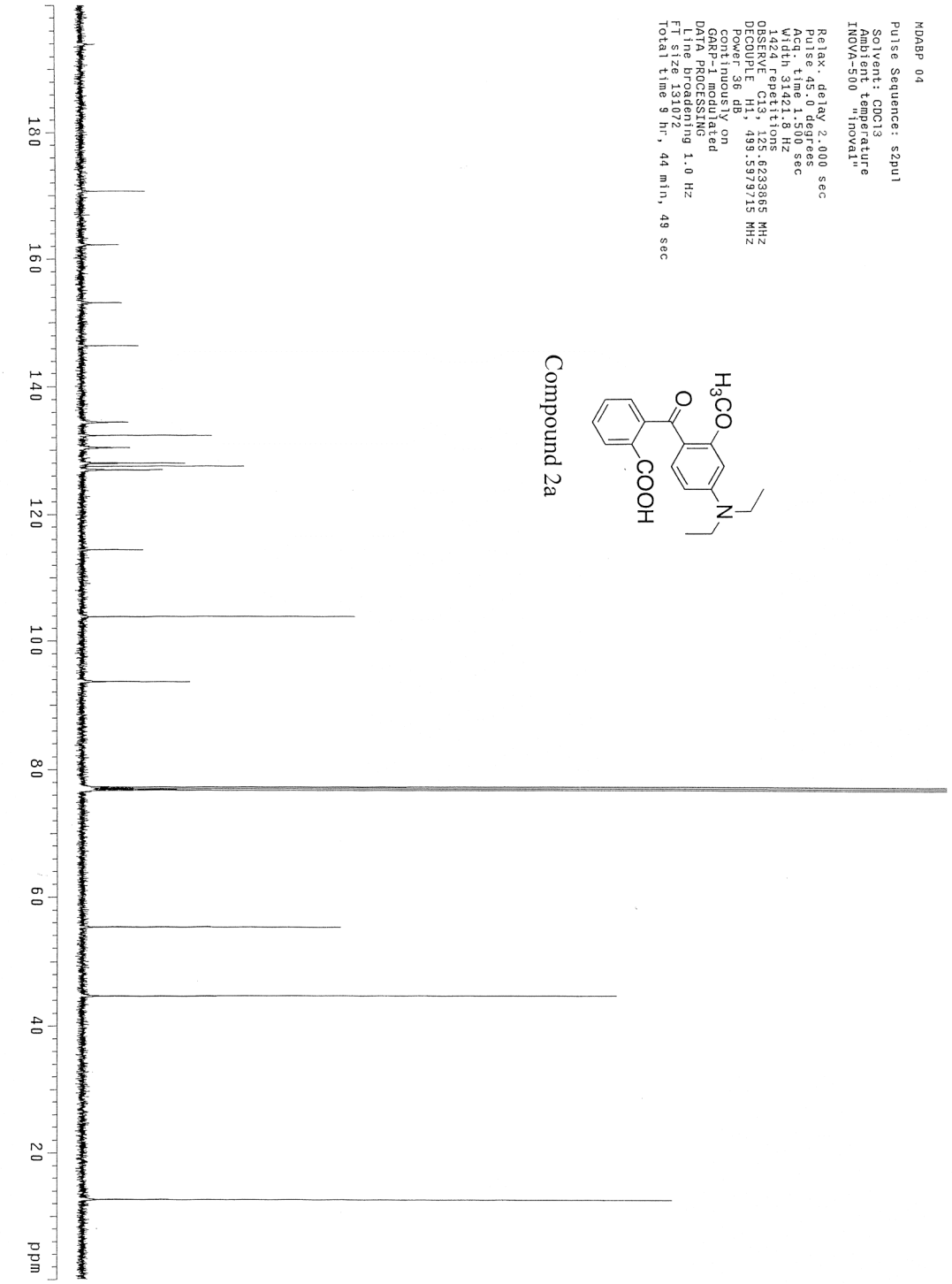
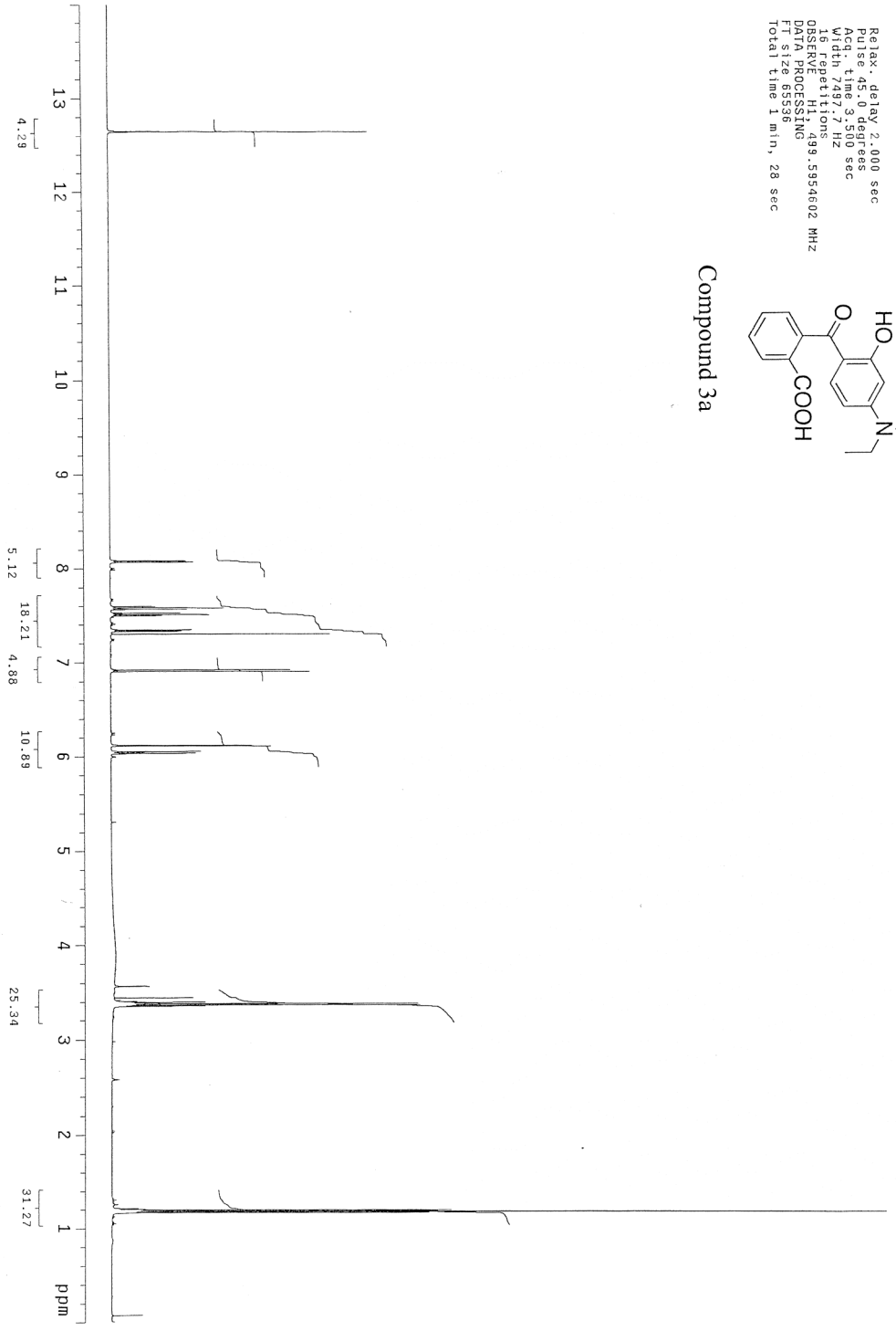


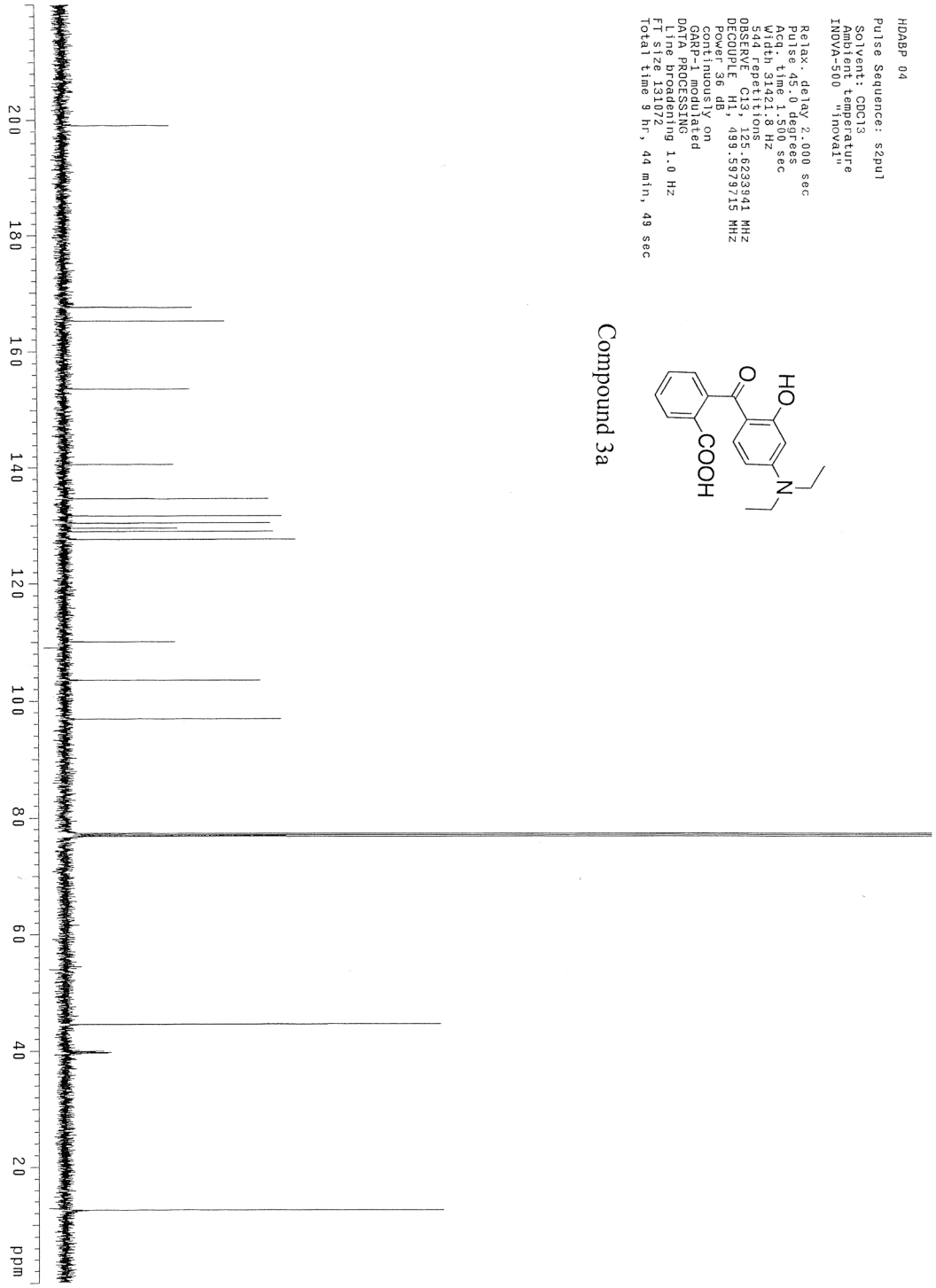
Fig S13. (a) Effects of composition of glycerol-methanol mixture on emission intensity of ABPX01. In the mixtures with glycerol fractions > 80%, the emission intensity rapidly increased due to the viscosity effect (viscochromism). (b) Effects of temperature on emission intensity of ABPX01 in methanol. When a methanol solution of ABPX01 was cooled, its emission intensity was increased due to thermochromism. The above results suggested that RIR caused AIEE. 1.0% TFA was added to ensure protonation and prevent pseudobase formation during measurement.

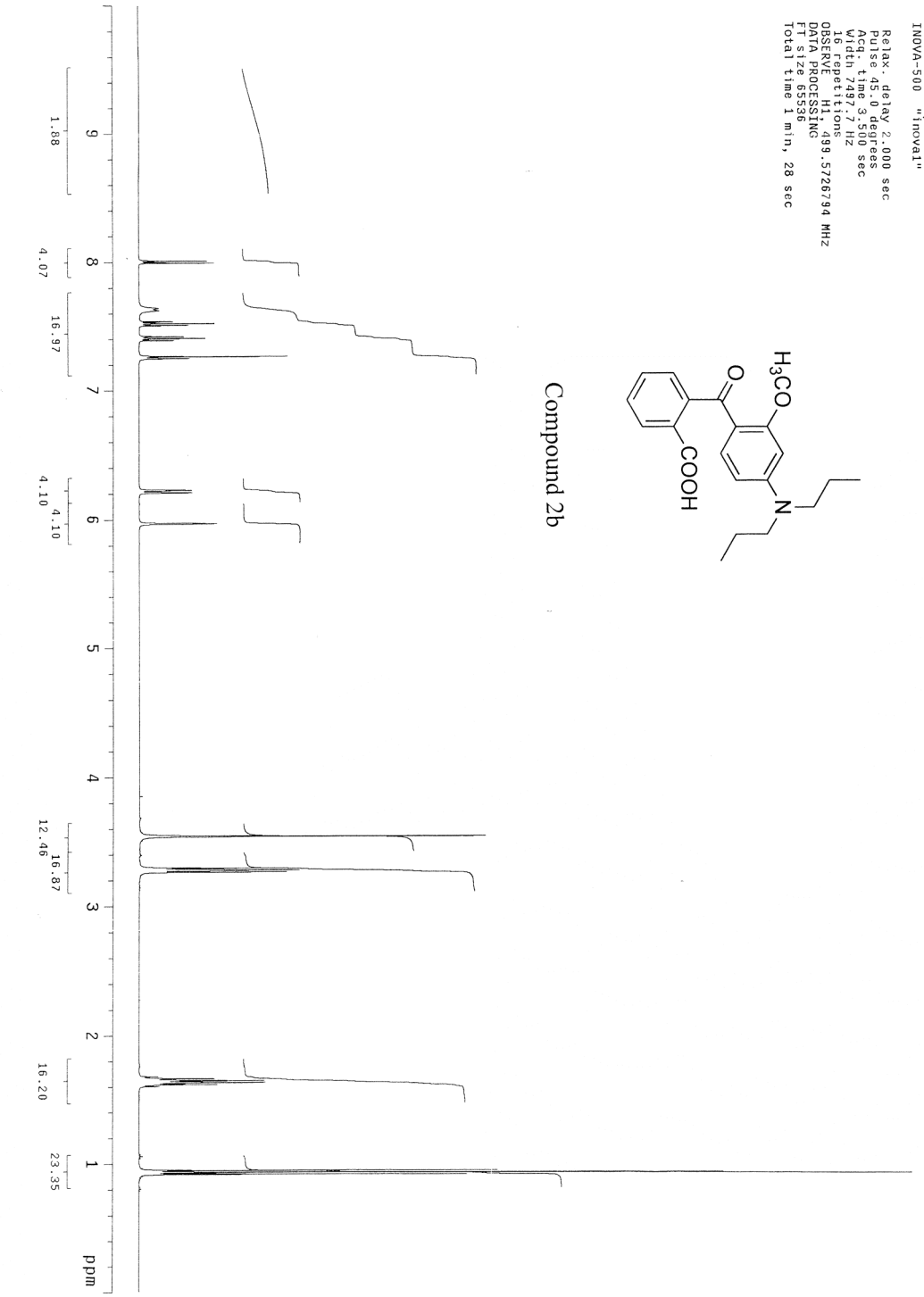
5. NMR data of benzophenone derivatives and ABPX01-04

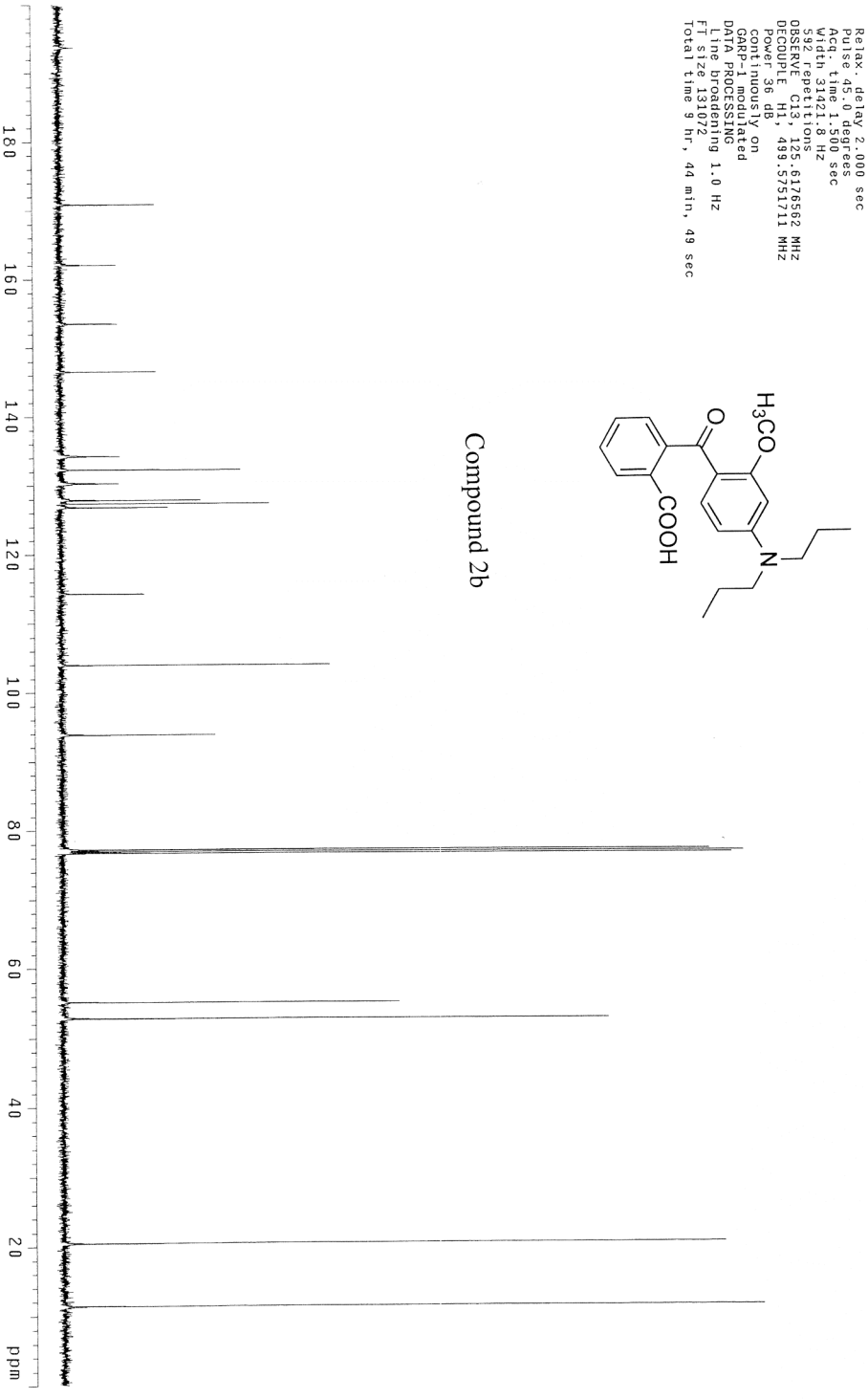


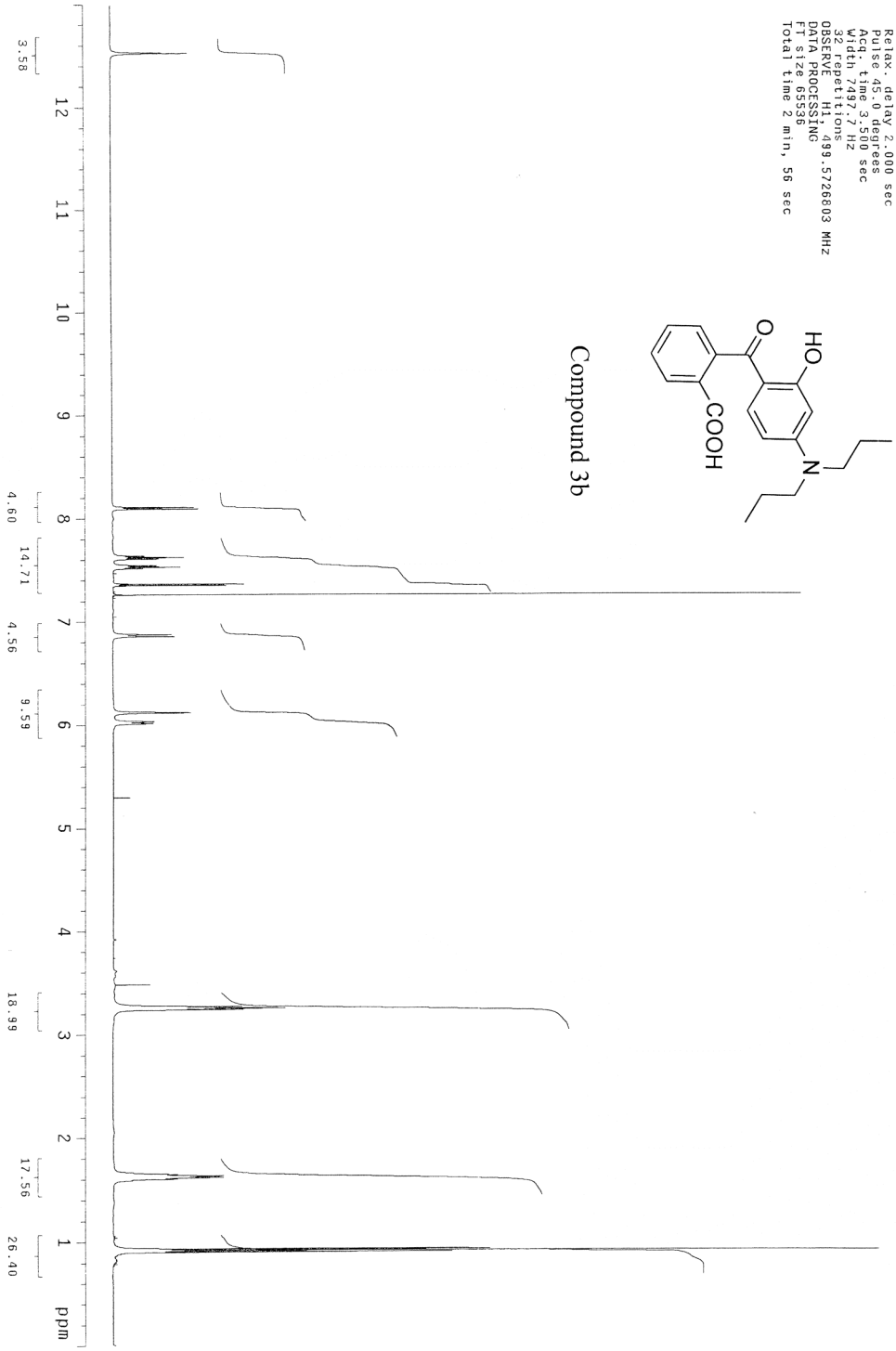

MDABP 04
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "inova1"
Relax. delay 2.000 sec
Pulse 45.0 degree
Acq. time 1.500 sec
Width 31421.8 Hz
1424 repetitions
OBSERVE C13, 125.623865 MHz
DECOUPLE H1, 499.5979715 MHz
Power 56 dB
continuously on
GARP-1 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 9 hr, 44 min, 49 sec
H3CO
O
COOH
N
Compound 2a
180
160
140
120
100
80
60
40
20
ppm

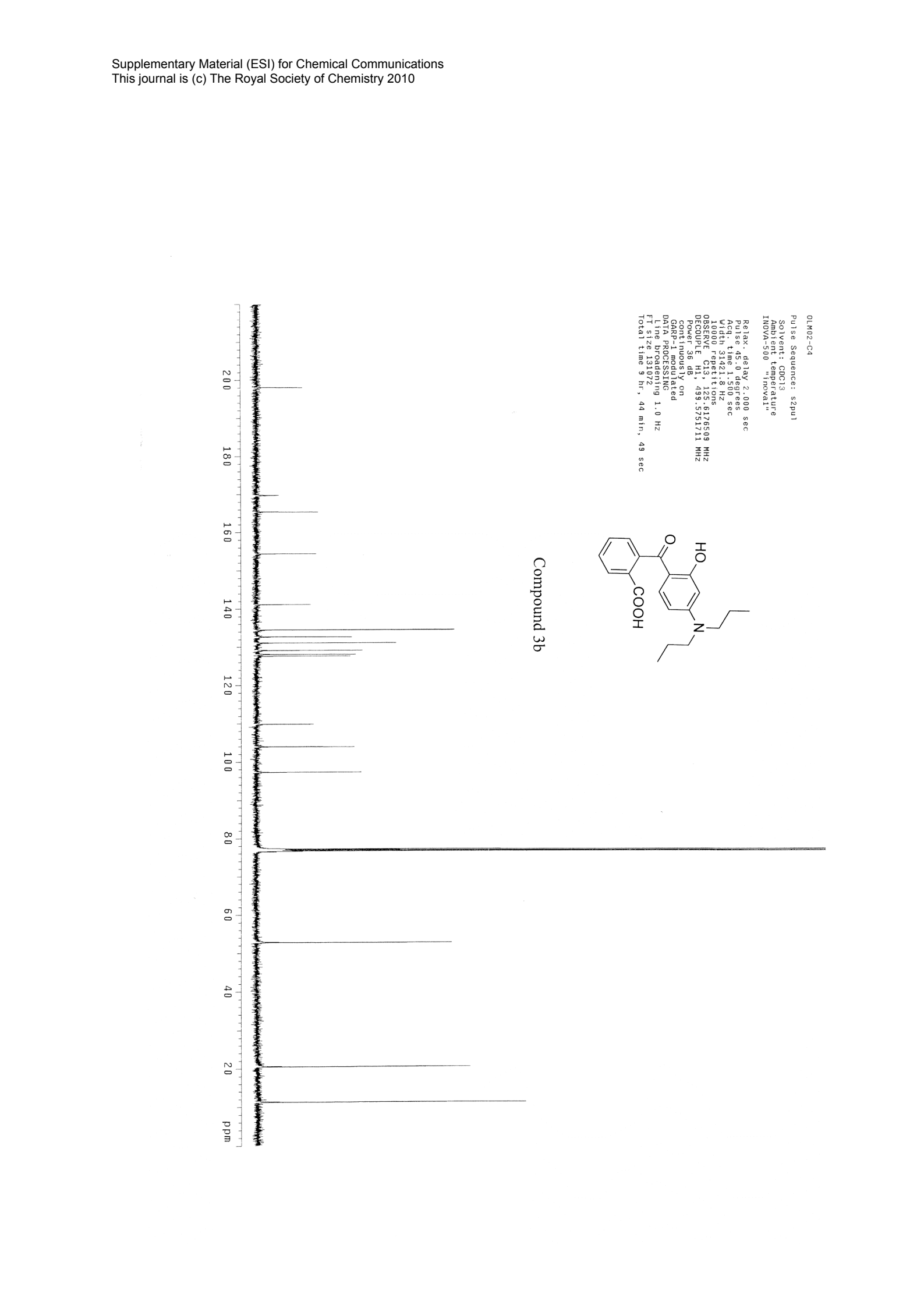

HDABP 04
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "inova1"
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 7497.7 Hz
16 repetitions
OBSERVE H1, 499.5954602 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 28 sec
HO
O
N
COOH
Compound 3a
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
4.29
5.12
18.21
4.88
10.89
25.34
31.27

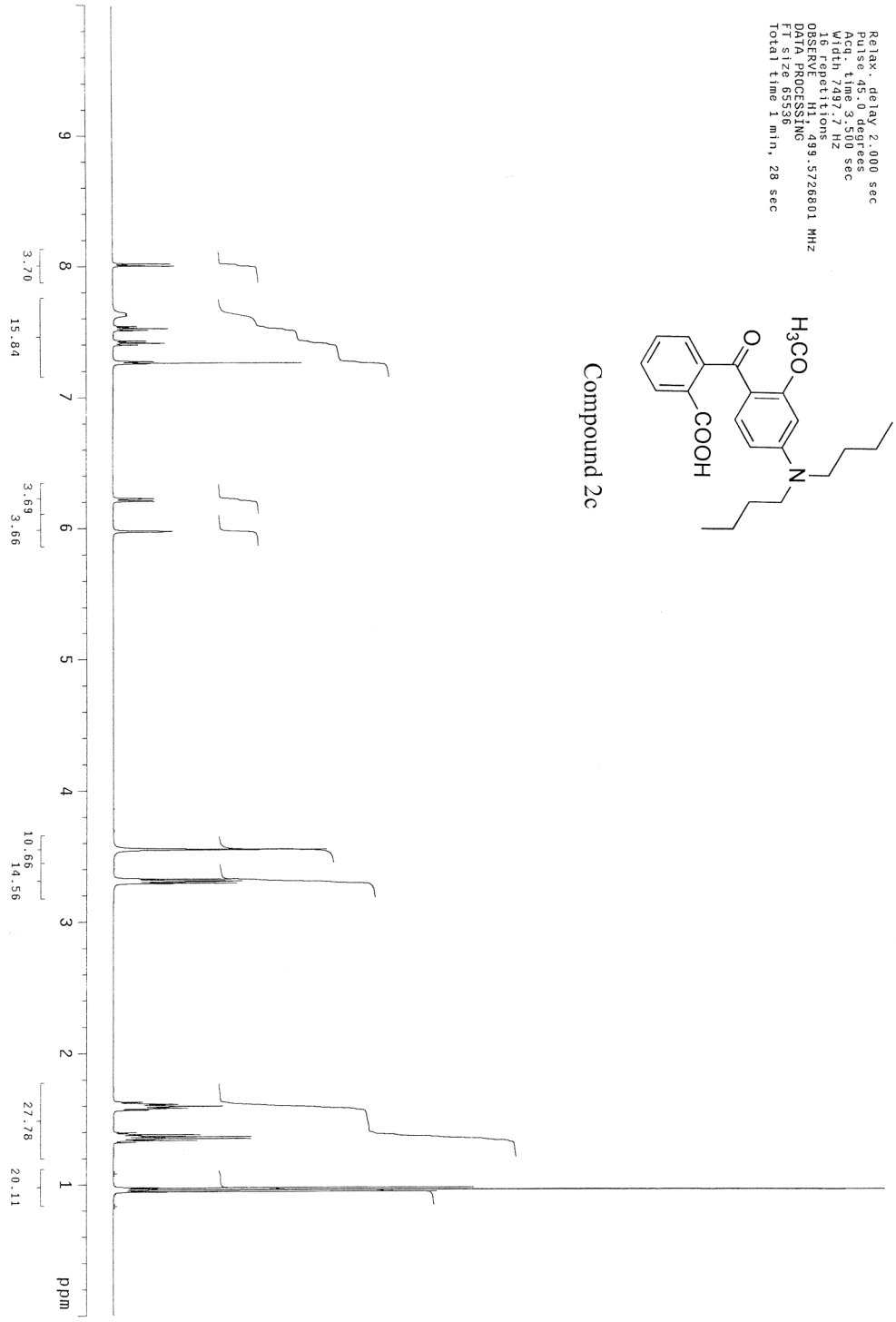

HDABP 04
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "inova1"
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.500 sec
Width 31421.8 Hz
544 repetitions
OBSERVE C13, 125.6233941 MHz
DECOUPLE H1, 499.5979715 MHz
Power 36 dB
continuously on
GARP-1 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 9 hr, 44 min, 49 sec
HO
O
N
COOH
Compound 3a
200
180
160
140
120
100
80
60
40
20
ppm


OLM02-C3
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "inova1"
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 7497.7 Hz
16 repetitions
OBSERVE H1, 499.5726794 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 28 sec
H3CO
O
N
COOH
Compound 2b
1.88
4.07
16.97
4.10
4.10
12.46
16.87
16.20
23.35
9
8
7
6
5
4
3
2
1
ppm


OLM02-C3
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "inova1"
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.500 sec
Width 31421.8 Hz
592 repetitions
OBSERVE C13, 125.6170562 MHz
DECOUPLE H1, 499.5751711 MHz
Power 36 dB
continuously on
GARP-1 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 9 hr, 44 min, 49 sec
H3CO
O
COOH
N
Compound 2b
180
160
140
120
100
80
60
40
20
ppm


OLM02-C4
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "inova1"
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
width 7497.7 Hz
32 repetitions
OBSERVE H1, 499.5726803 MHz
DATA PROCESSING
FT size 65536
Total time 2 min, 56 sec
HO
O
COOH
N
Compound 3b
3.58
4.60
14.71
4.56
9.59
18.99
17.56
26.40
12
11
10
9
8
7
6
5
4
3
2
1
ppm

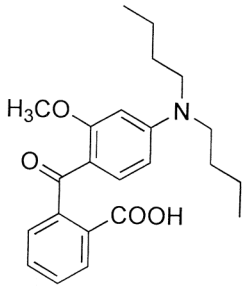

OLM02-C4
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "inova1"
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.500 sec
Width 31421.8 Hz
10000 repetitions
OBSERVE C13, 125.6176509 MHz
DECOUPLE H1, 499.5751711 MHz
Power 36 dB
continuously on
GARP-1 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 9 hr, 44 min, 49 sec
HO
O
COOH
N
Compound 3b
200
180
160
140
120
100
80
60
40
20
ppm


OlM03-C3
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "inova1"
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 7497.7 Hz
16 repetitions
OBSERVE H1, 499.5726801 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 28 sec
H3CO
O
COOH
N
Compound 2c
3.70
15.84
3.69
3.66
10.66
14.56
27.78
20.11
9
8
7
6
5
4
3
2
1
ppm

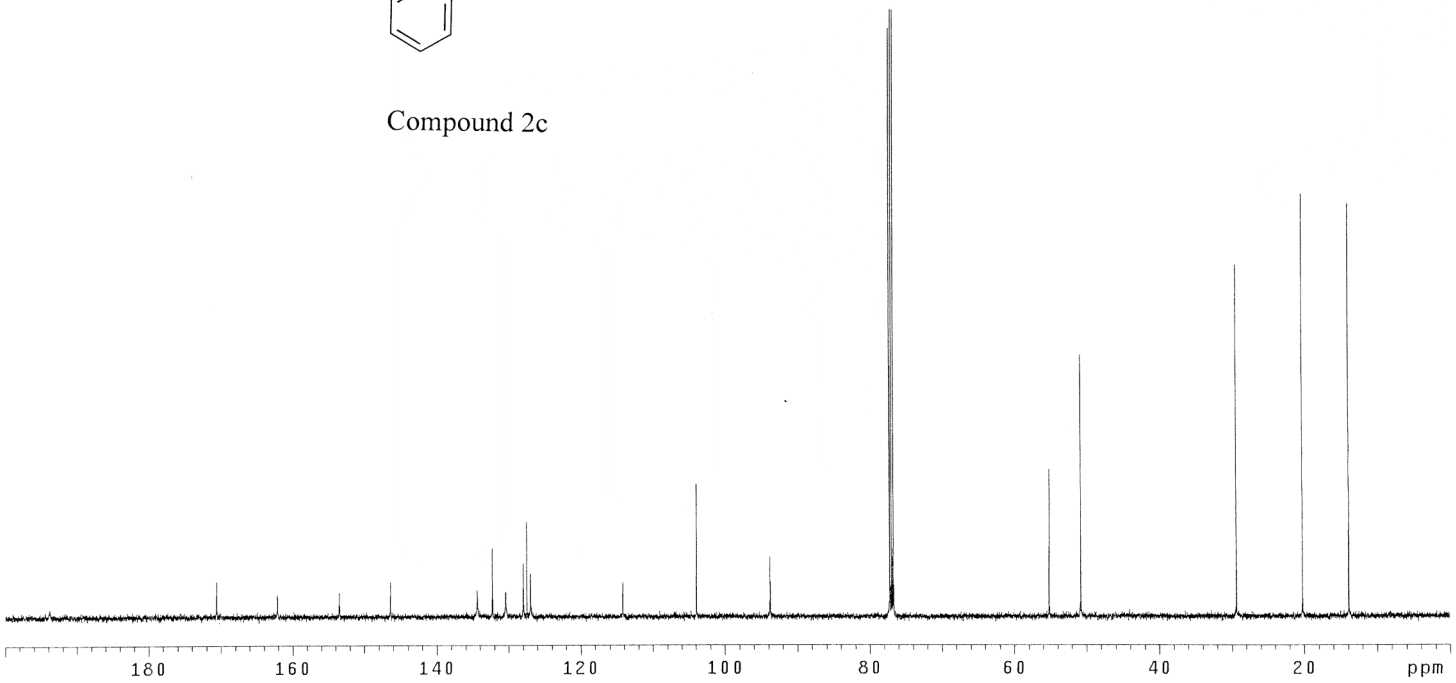
OLM03-C3

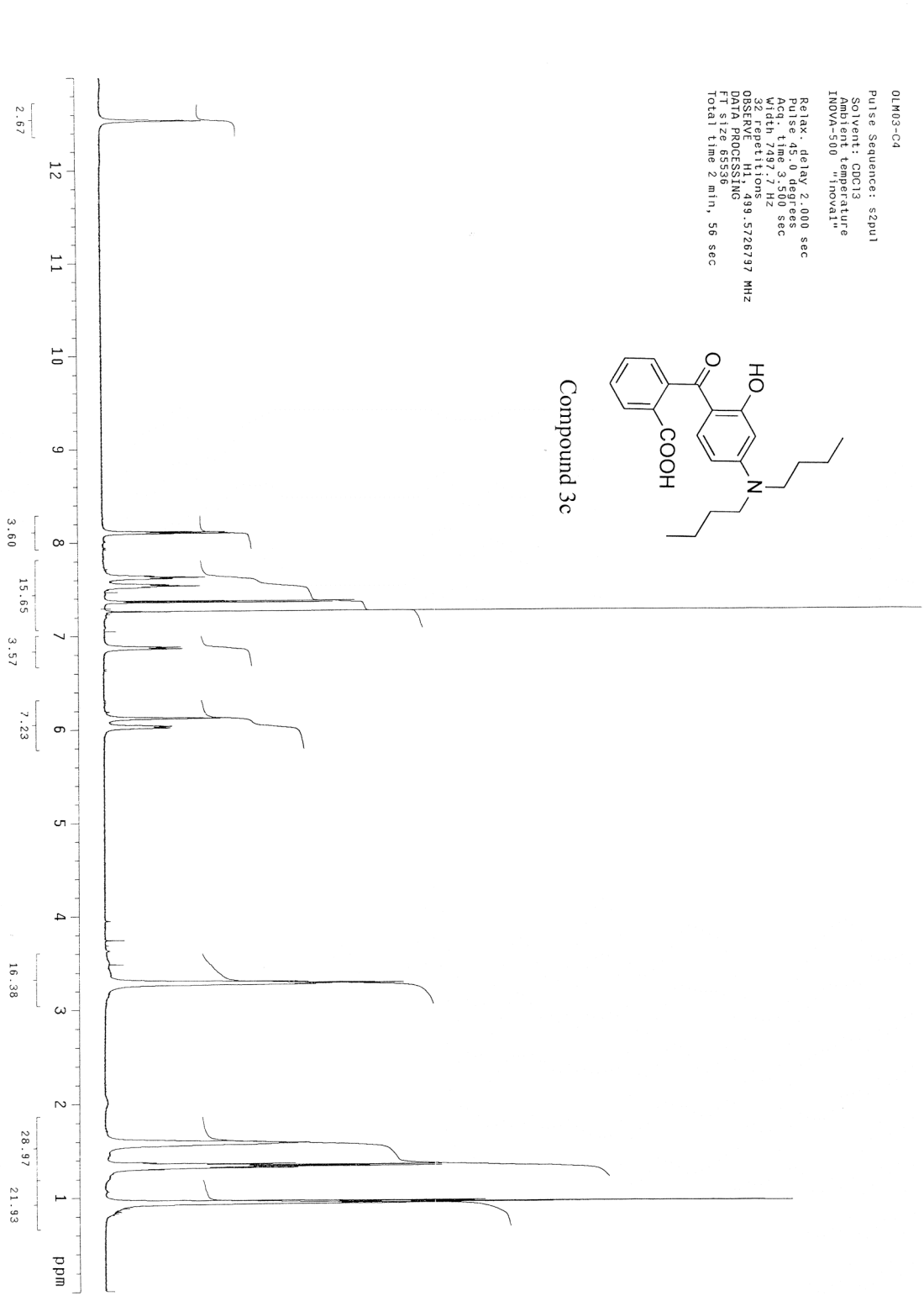
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "inova1"

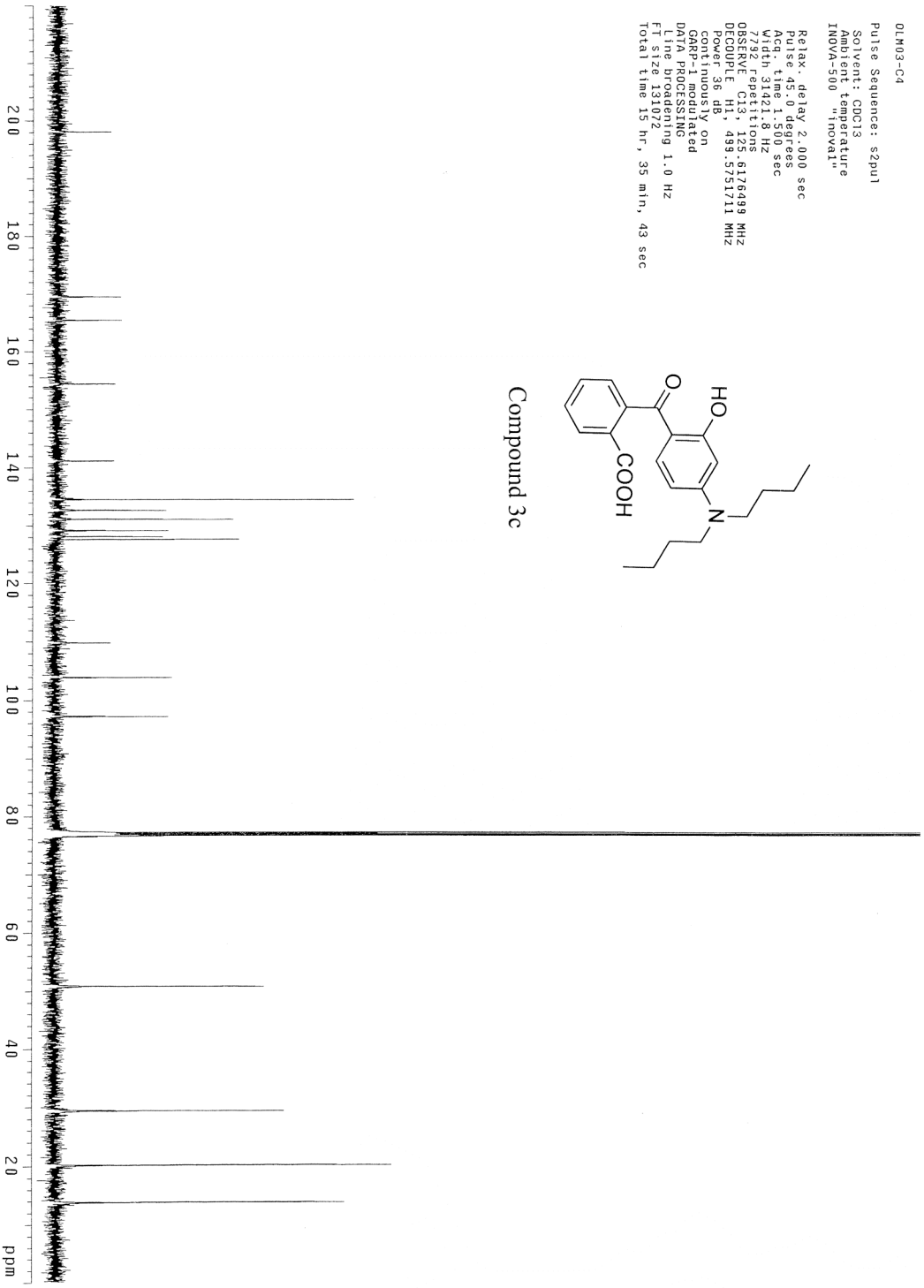
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.500 sec
Width 31421.8 Hz
944 repetitions
OBSERVE C13, 125.6176533 MHz
DECOUPLE H1, 499.5751711 MHz
Power 36 dB
continuously on
GARP-1 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 9 hr, 44 min, 49 sec

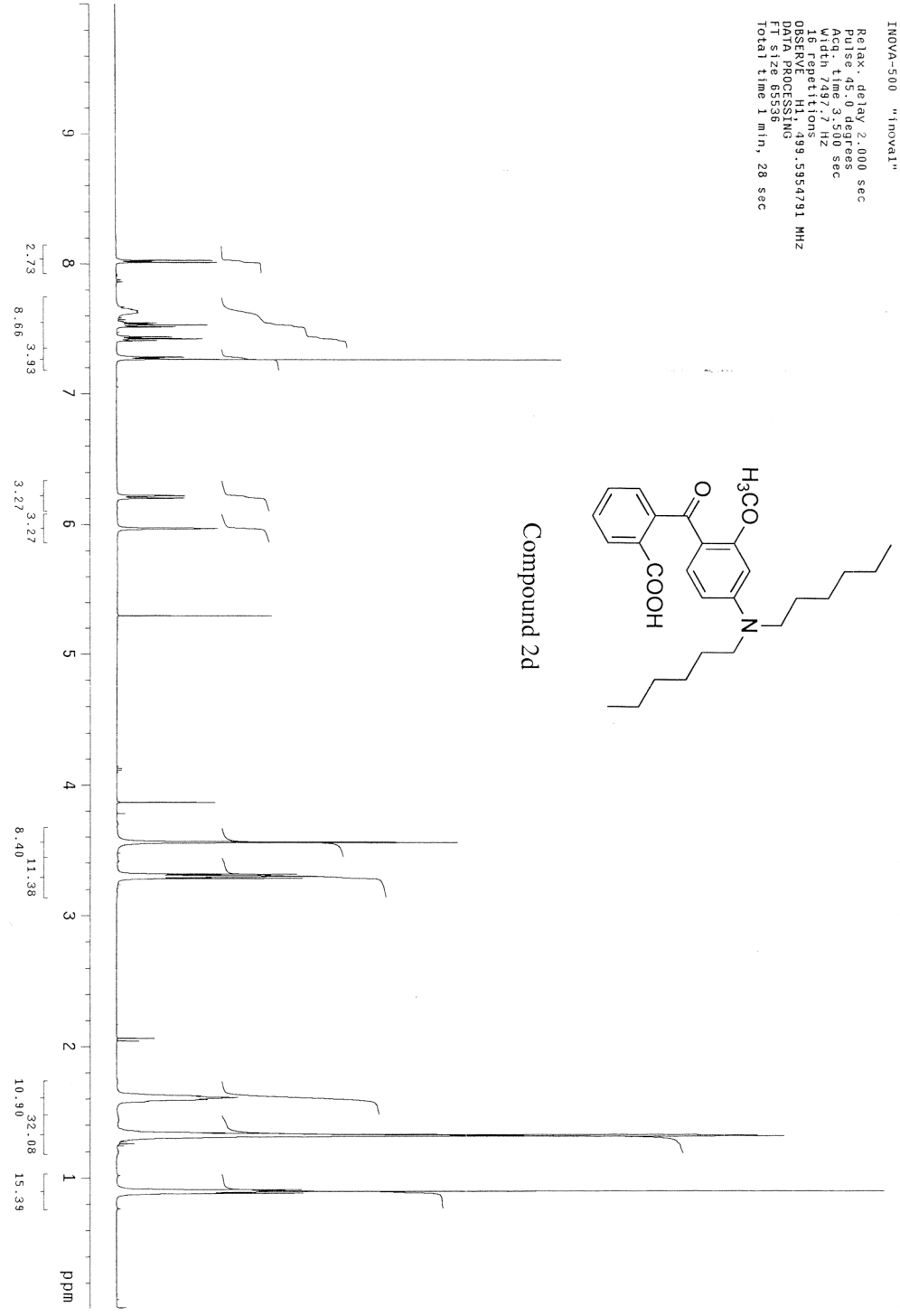


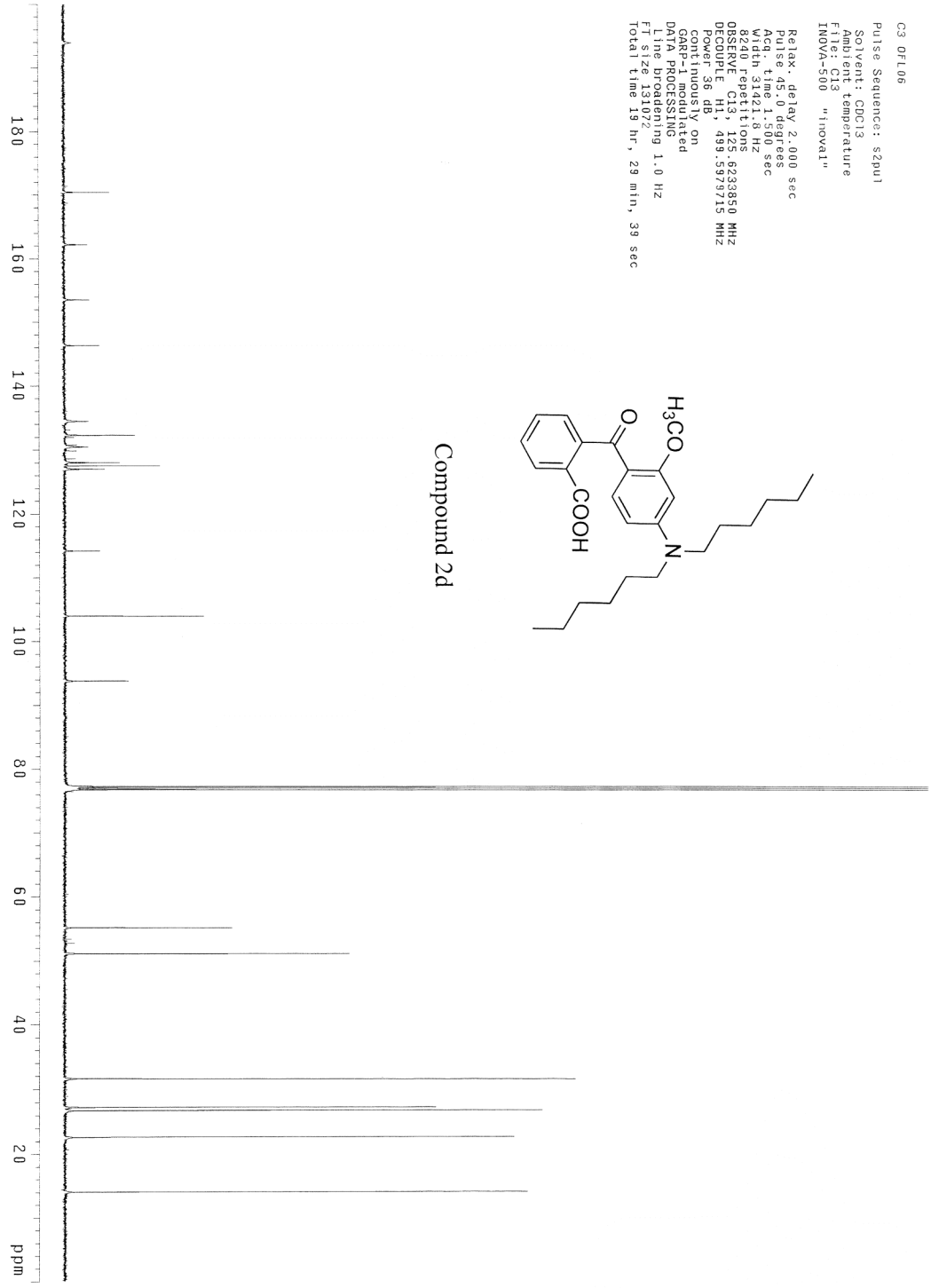
Compound 2c

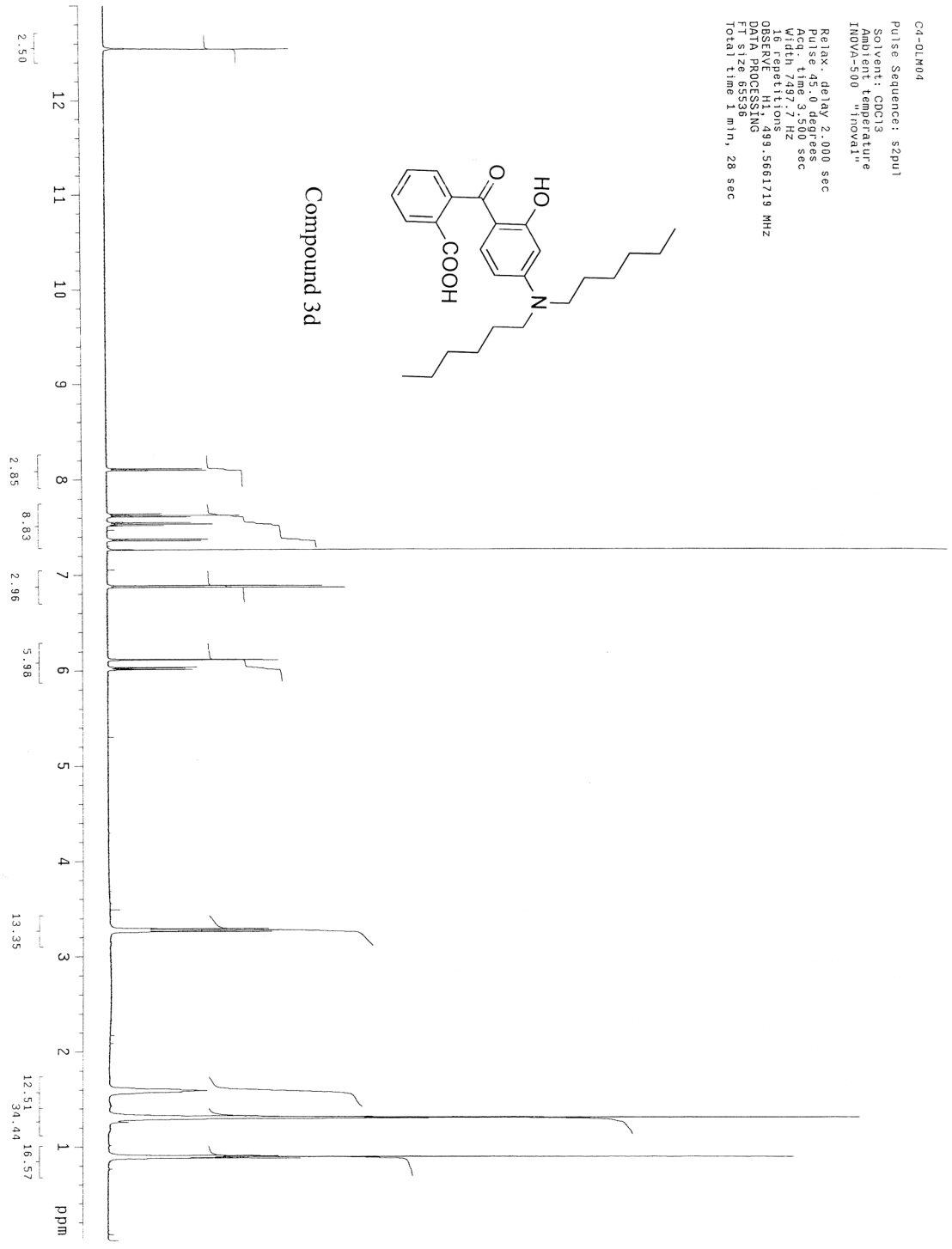


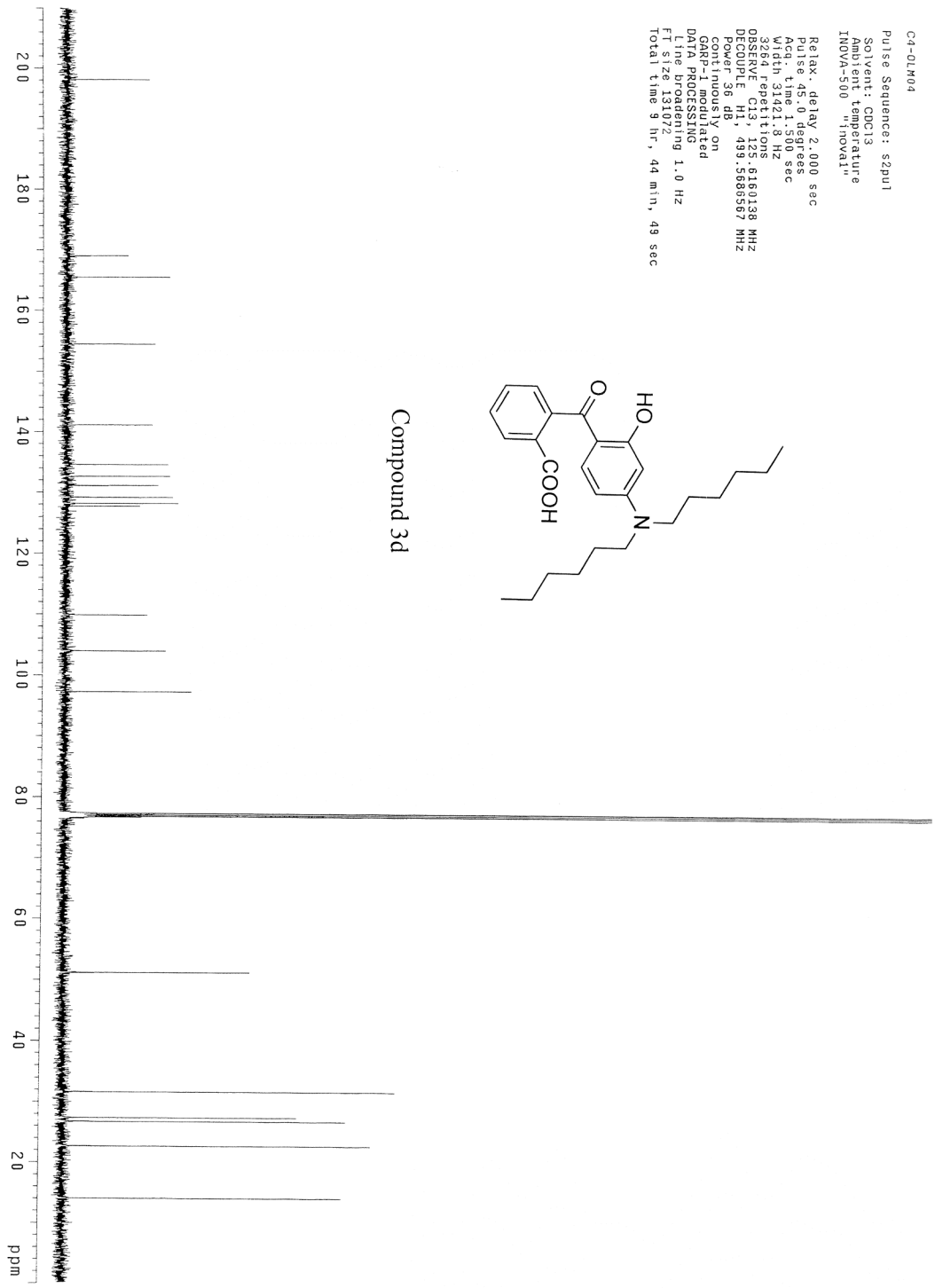

OLM03-C4
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "inova1"
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 7497.7 Hz
32 repetitions
OBSERVE H1, 499.5726797 MHz
DATA PROCESSING
FT size 65536
Total time 2 min, 56 sec
HO
O
COOH
N
Compound 3c
2.67
3.60
15.65
3.57
7.23
16.38
28.97
21.93
12
11
10
9
8
7
6
5
4
3
2
1
ppm


OLM03-C4
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "inova1"
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.500 sec
Width 31421.8 Hz
77927 repetitions
OBSERVE C13, 125.6176499 MHz
DECOUPLE H1, 499.5751711 MHz
Power 36 dB
continuously on
GARP-1modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 15 hr, 35 min, 43 sec
HO
O
COOH
N
Compound 3c
200
180
160
140
120
100
80
60
40
20
ppm

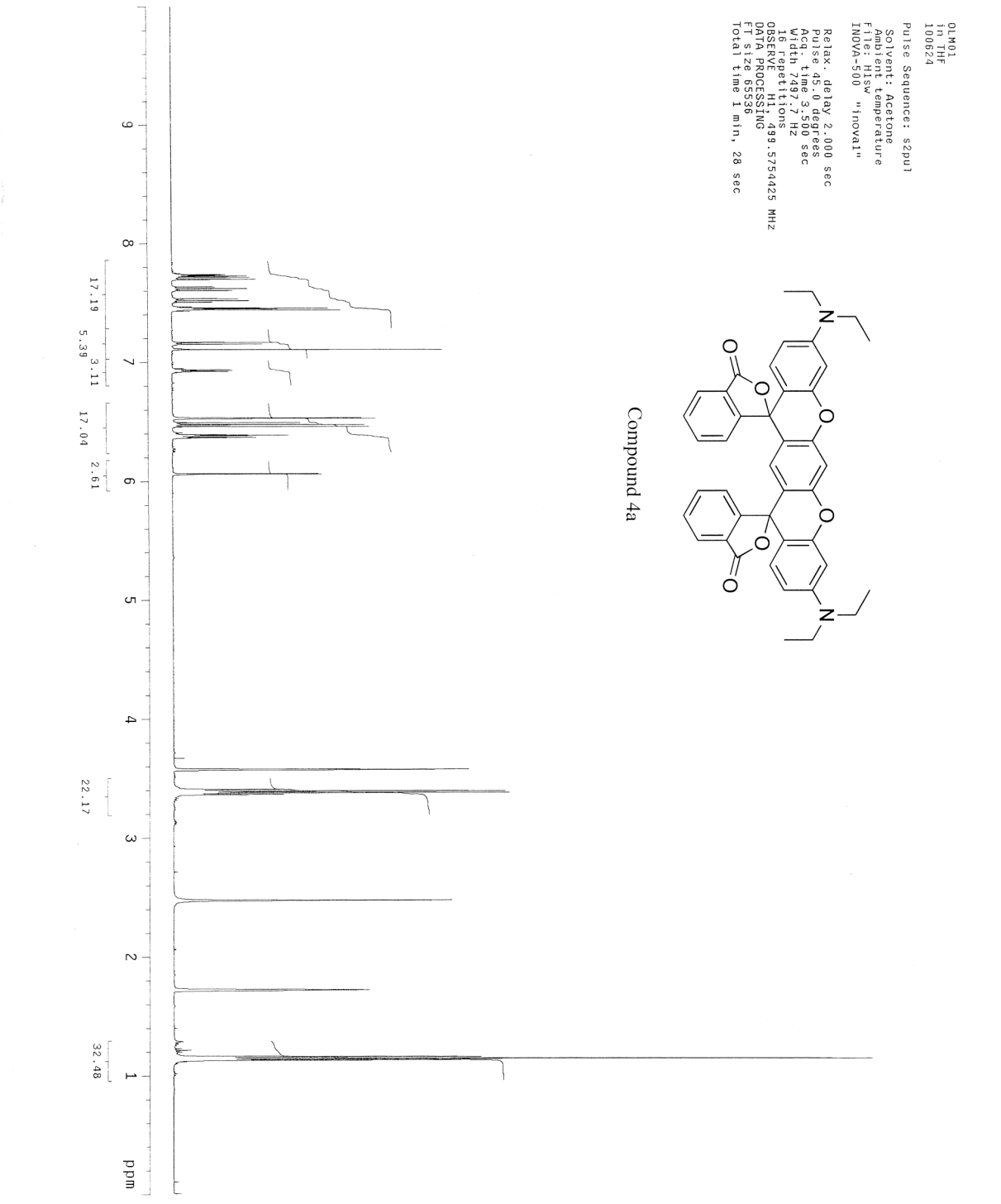

C3 OFL06
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: H1sw
INOVA-500 "inova1"
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 7497.7 HZ
16 repetitions
OBSERVE H1, 499.5954791 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 28 sec
H3CO
O
COOH
N
Compound 2d
2.73
8.66
3.93
3.27
3.27
8.40
11.38
10.90
32.08
15.39
9
8
7
6
5
4
3
2
1
ppm

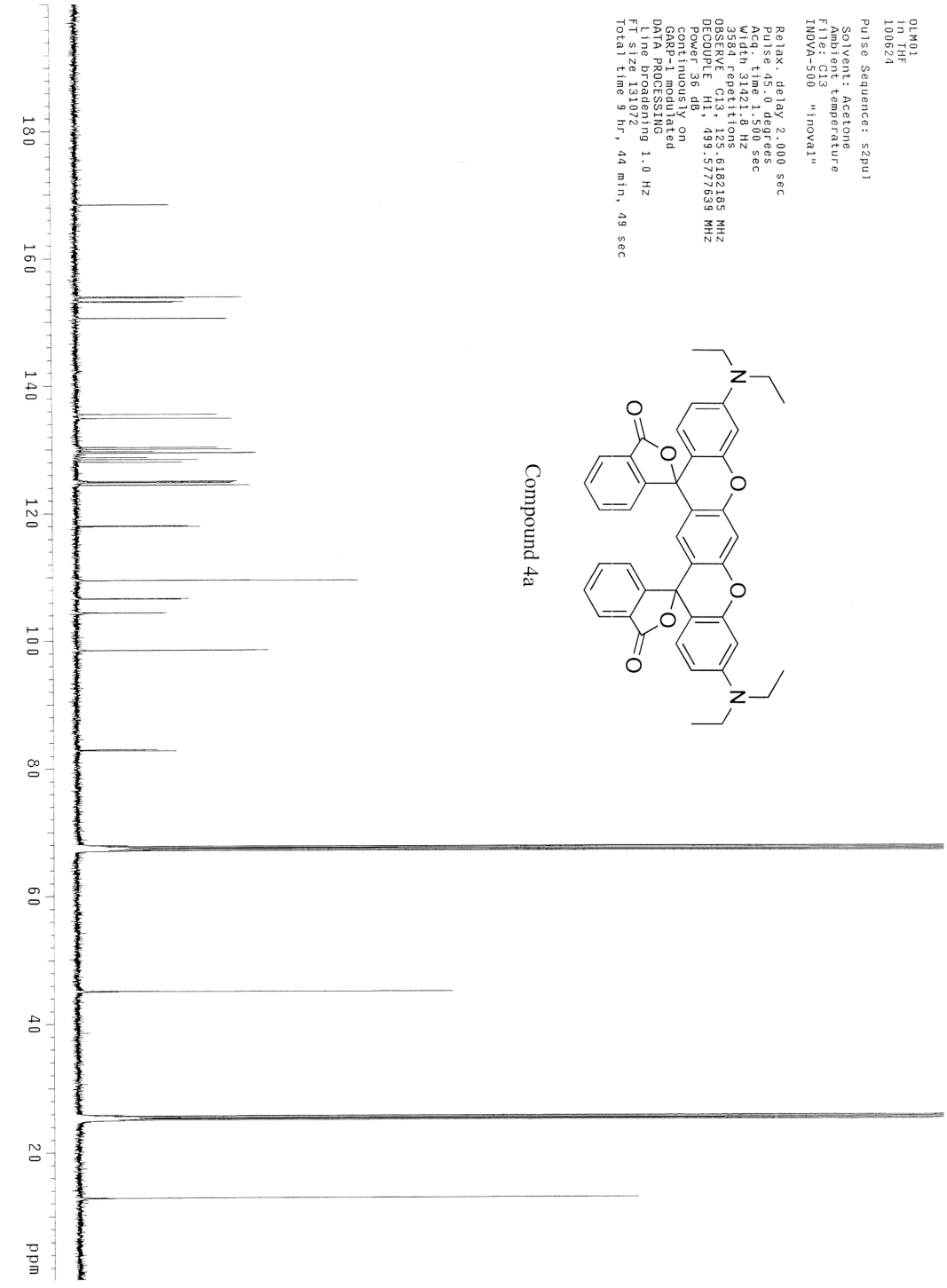

C3 OFL06
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: C13
INOVA-500 "inova1"
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.500 sec
Width 31421.8 Hz
8240 repetitions
OBSERVE C13, 125.623850 MHz
DECOUPLE H1, 499.597715 MHz
Power 36 dB
continuously on
GARP-1 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 19 hr, 29 min, 39 sec
H3CO
O
COOH
N
Compound 2d
180
160
140
120
100
80
60
40
20
ppm

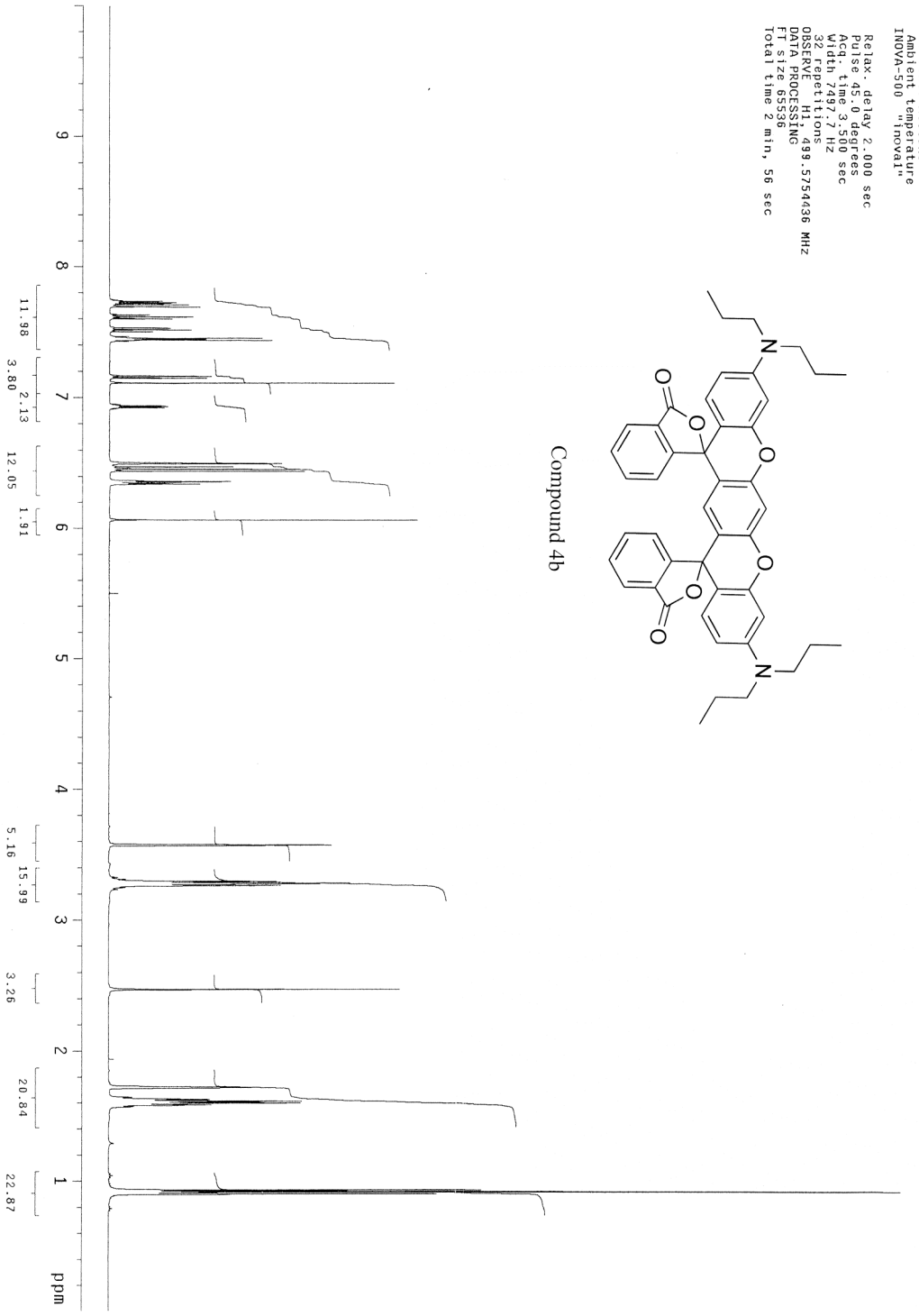

C4-OLM04
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "inova1"
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 7497.7 Hz
16 repetitions
OBSERVE H1, 499.5661719 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 28 sec
Compound 3d
HO
O
COOH
N
2.50
2.85
8.83
2.96
5.98
13.35
12.51
34.44
16.57
12
11
10
9
8
7
6
5
4
3
2
1
ppm

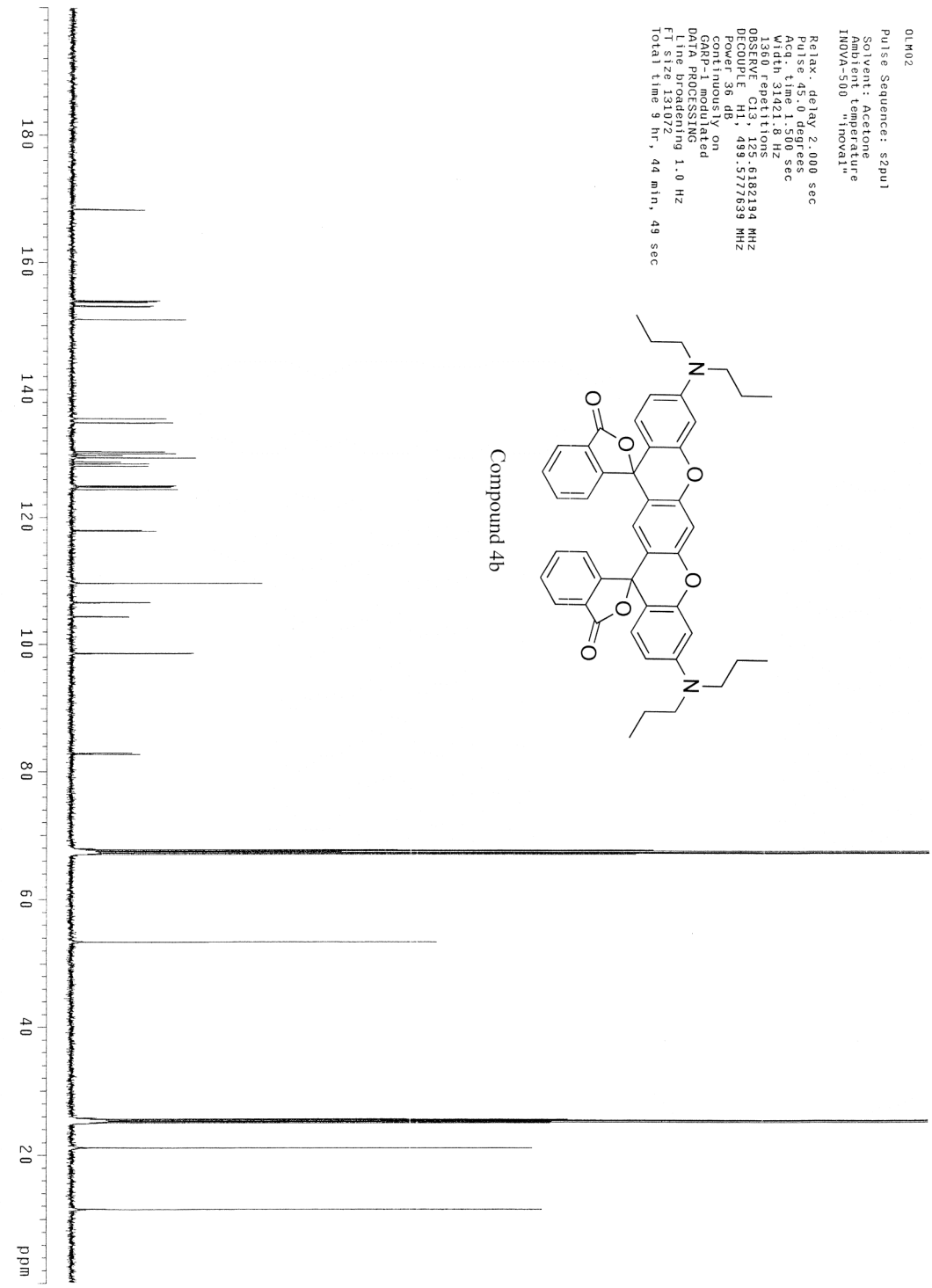

C4-OLM04
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "inova1"
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.500 sec
Width 31421.8 Hz
32641 repetitions
OBSERVE C13, 125.6160138 MHz
DECOUPLE H1, 499.5686567 MHz
Power 36 dB
continuously on
GARP-1 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 9 hr, 44 min, 49 sec
HO
O
COOH
N
200
180
160
140
120
100
80
60
40
20
ppm

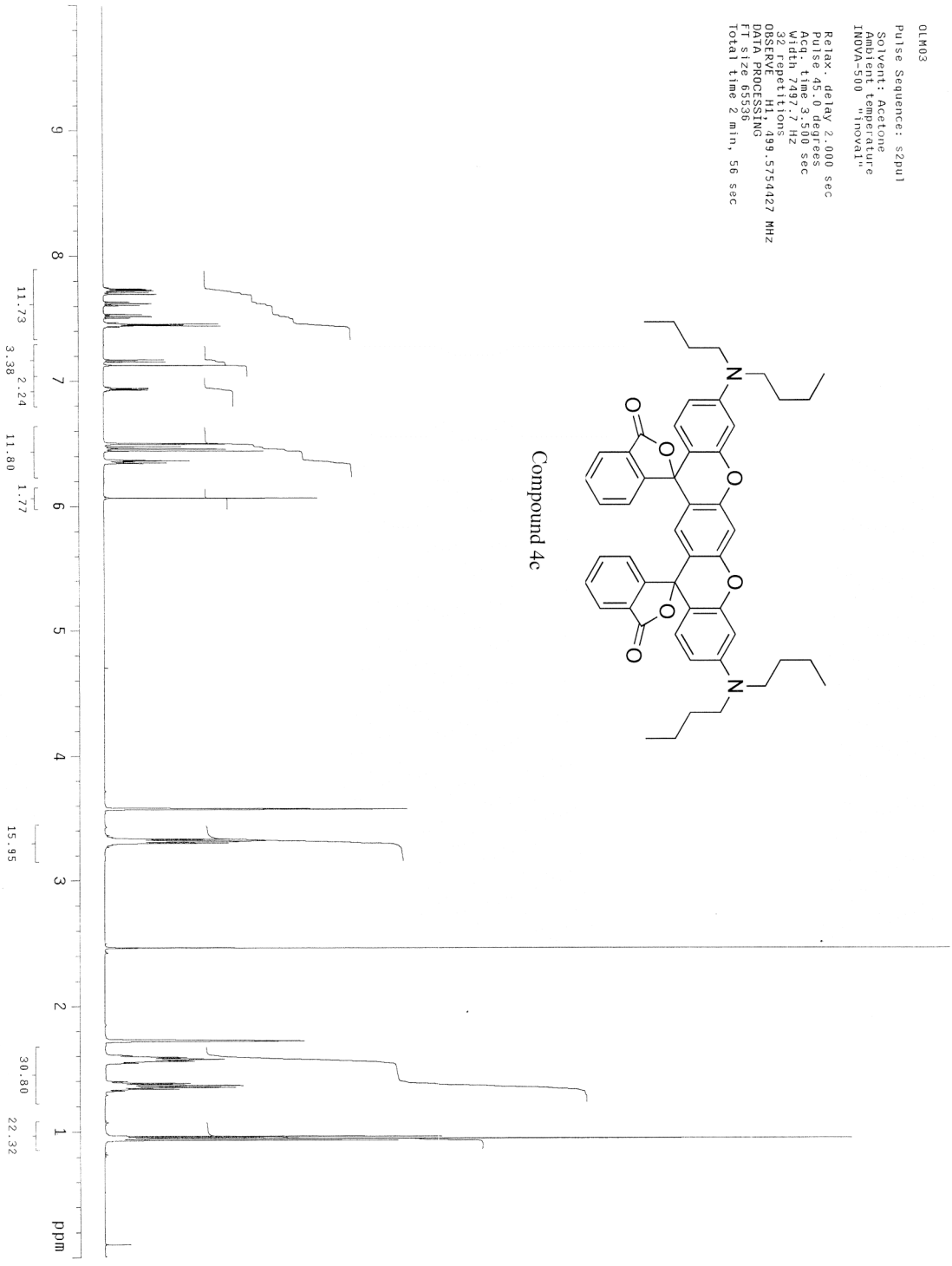
Compound 3d


OLM01
in THF
100624
Pulse Sequence: s2pul
Solvent: Acetone
Ambient temperature
Flow Flow
INOVA-500 "inova1"
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 7497.7 Hz
16 repetitions
OBSERVE H1, 499.5754425 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 28 sec
Compound 4a
9
8
7
6
5
4
3
2
1
ppm
17.19
5.39
3.11
17.04
2.61
22.17
32.48

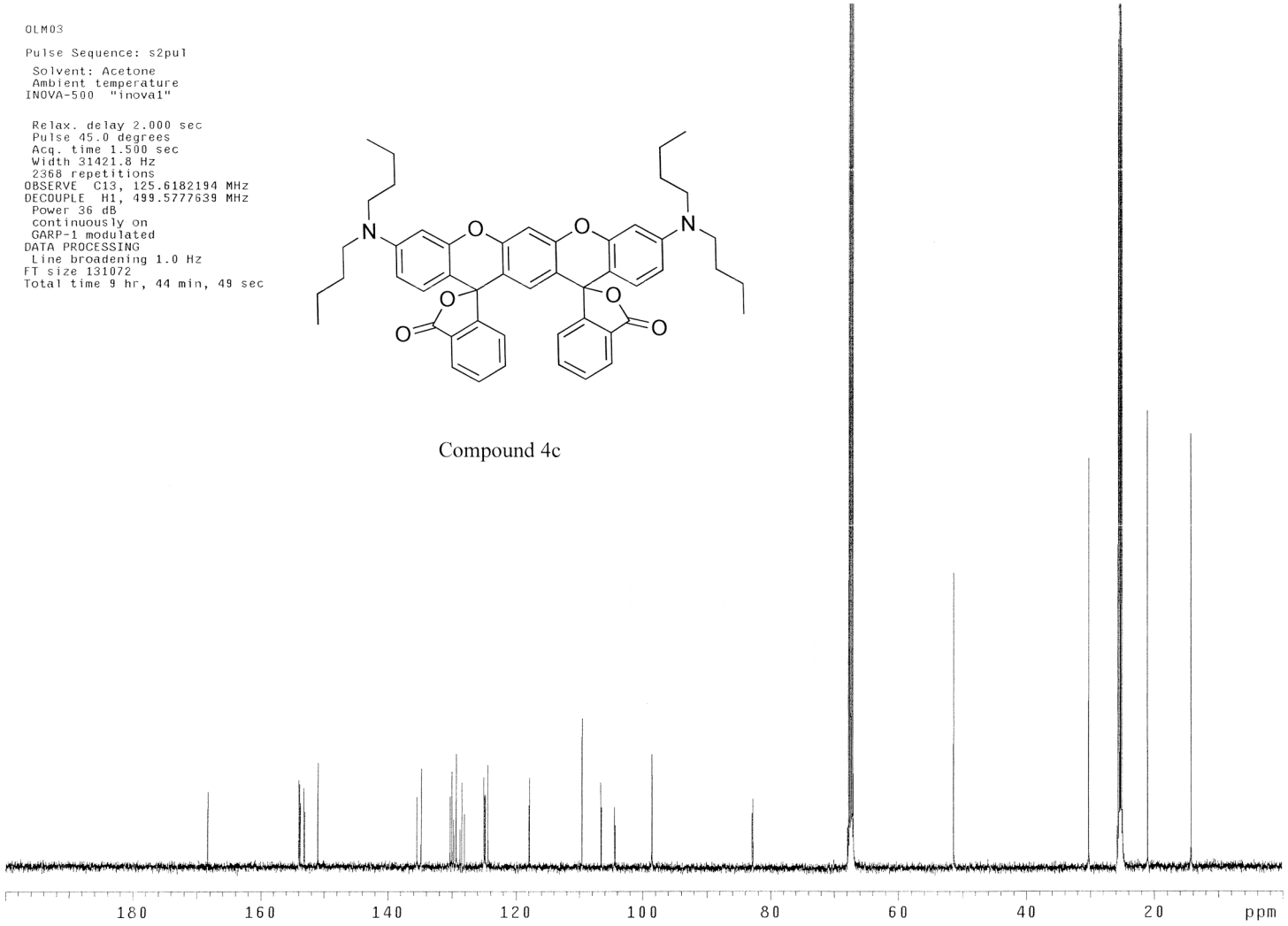

QLM01
in THF
100624
Pulse Sequence: s2pul
Solvent: Acetone
Ambient temperature
File: C13
INOVA-500 "inova1"
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.500 sec
Width 31421.8 Hz
3584 repetitions
OBSERVE C13, 125.6182185 MHz
DECOUPLE H1, 499.5777639 MHz
Power 36 dB
continuously on
GARP-1 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 9 hr, 44 min, 49 sec
Compound 4a
180
160
140
120
100
80
60
40
20
ppm


OLM02
Pulse Sequence: s2pul
Solvent: Acetone
Ambient temperature
INOVA-500 "inova1"
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 7497.7 Hz
32 repetitions
OBSERVE H1, 499.5754436 MHz
DATA PROCESSING
FT size 65536
Total time 2 min, 56 sec
Compound 4b
11.98
3.80
2.13
12.05
1.91
5.16
15.99
3.26
20.84
22.87
9
8
7
6
5
4
3
2
1
ppm

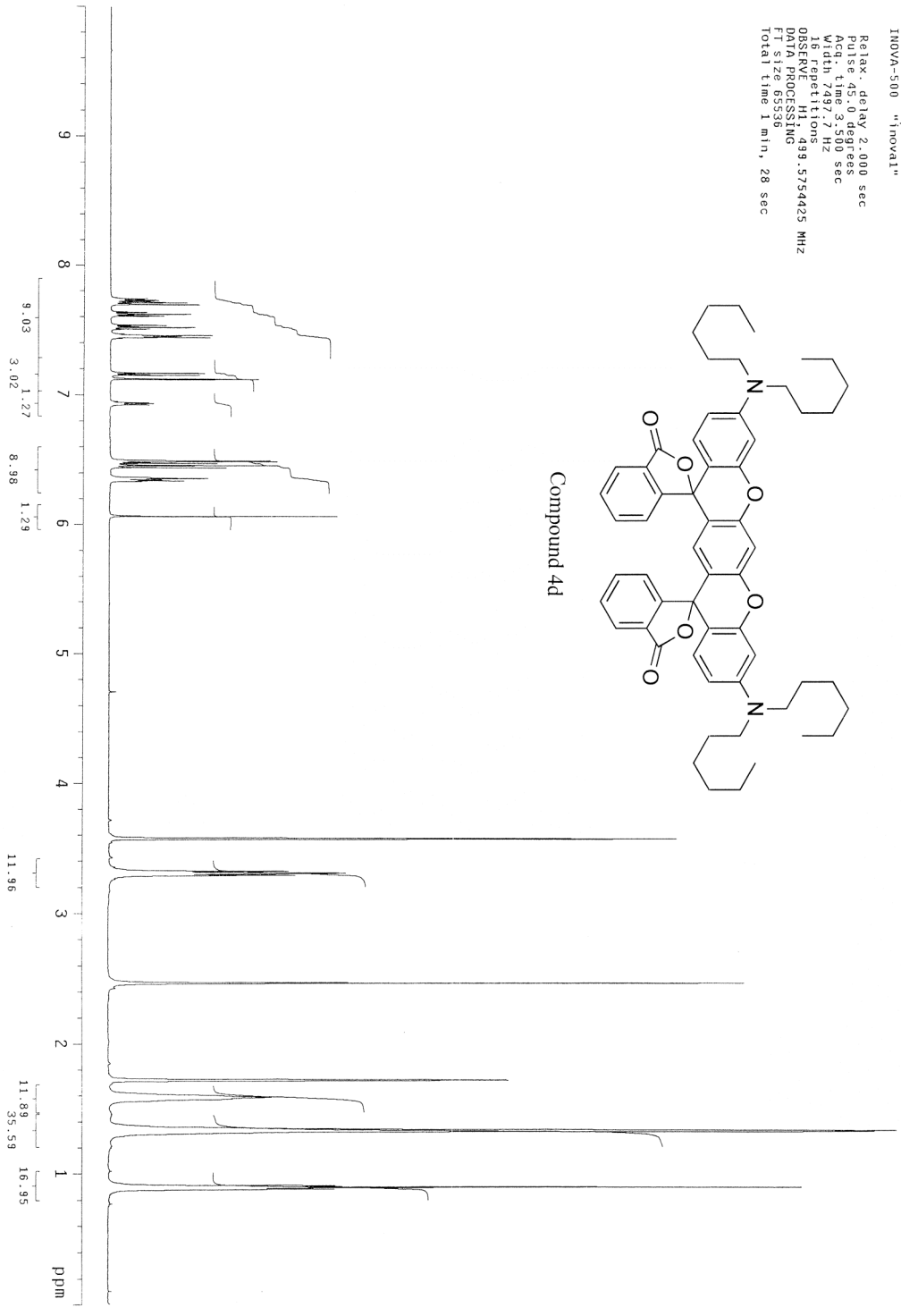

OLM02
Pulse Sequence: s2pul
Solvent: Acetone
Ambient temperature
INOVA-500 "inova1"
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.500 sec
Width 31421.8 Hz
1360 repetitions
OBSERVE C13, 125.6182194 MHz
DECOUPLE H1, 499.5777639 MHz
Power 36 dB
continuously on
GARP-1 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 9 hr, 44 min, 49 sec
Compound 4b
180
160
140
120
100
80
60
40
20
ppm

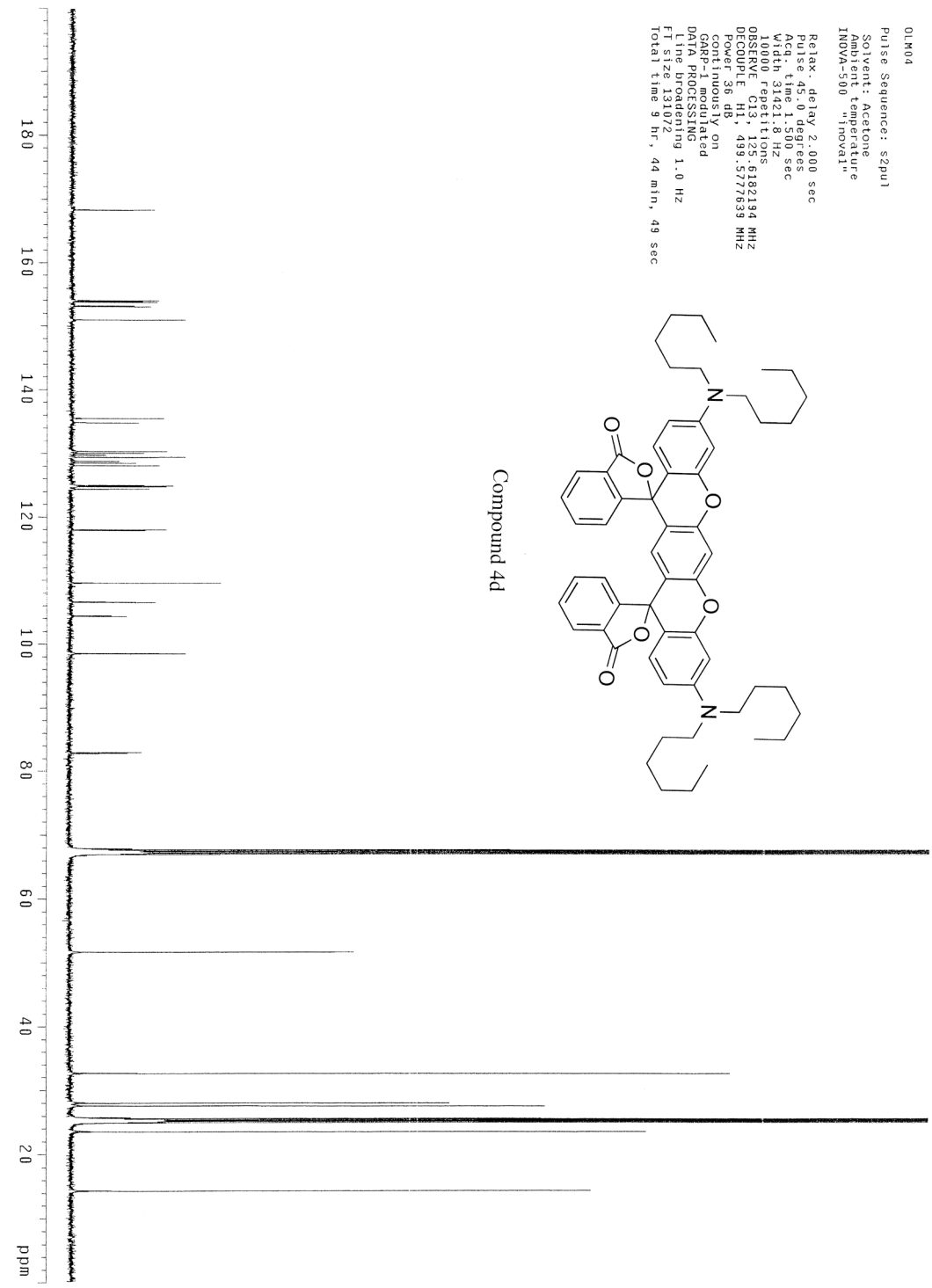

OLM03
Pulse Sequence: s2pul
Solvent: Acetone
Ambient temperature
INOVA-500 "inova1"
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
width 7497.7 Hz
32 repetitions
OBSERVE H1, 499.5754427 MHz
DATA PROCESSING
FT size 65536
Total time 2 min, 56 sec
11.73
3.38
2.24
11.80
1.77
15.95
30.80
22.32
9
8
7
6
5
4
3
2
1
ppm

Compound 4c



Compound 4c


OLM04
Pulse Sequence: s2pul
Solvent: Acetone
Ambient temperature
INOVA-500 "inova1"
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 7497.7 Hz
1 repetitions
OBSERVE H1, 499.5754425 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 28 sec
Compound 4d
9.03
3.02
1.27
8.98
1.29
11.96
11.89
35.59
16.95
ppm


OLM04
Pulse Sequence: s2pul
Solvent: Acetone
Ambient temperature
INOVA-500 "inova1"
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.500 sec
Width 31421.8 Hz
10000 repetitions
OBSERVE C13, 125.6182194 MHz
DECOUPLE H1, 499.5777639 MHz
Power 36 dB
continuously on
GARP-1 modulated
DATA PROCESSING
FT size 131072
Total time 9 hr, 44 min, 49 sec
Compound 4d
180
160
140
120
100
80
60
40
20
ppm