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Supporting Information

Towards the IR-limit of the Triplet-Triplet Annihilation Supported Upconversion: Tetraanthraporphyrin

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The synthesis of tetrakis-5,10,15,20-(p-methoxycarbonylphenyl)tetraanthra[2,3-b,g,l,q]porphyrin

All mentioned reagents except those prepared in the present work have been obtained from common commercial sources (Sigma-Aldrich, Acros, Fluka) and used as received. Solvents were purified according to standard procedures. NMR spectra were taken with Bruker Avance-400 instrument (^{1}H, 400 MHz, ^{13}C, 100 MHz), LDI-TOF spectra were taken with Brucker Daltonics Alphaflex II instrument, UV-Vis spectra were recorded on a Perkin Elmer Lambda 40 spectrometer (1cm glass cell).

Benzyne-furan adduct (1) was obtained according to literature procedure[1].

9,10-epoxy-1,4,4a,9,9a,10-hexahydroanthracene (2): Obtained according to Dehaen's procedure[2], modified to make it safer and more productive by using pyridine as solvent and $NaHCO_3$ as additive. This modification allows avoiding the danger of reaction vessel explosion by pressure of SO_2 when the mixture is being heated in the closed thick-wall vessel.

In freshly distilled (over NaOH) pyridine (30 mL) the adduct (**1**) was dissolved (7.2 g, 50 mmol), $NaHCO_3$ (2.5 g) were added, and the mixture was placed in thick-wall bulb stoppered by teflone threaded bushing. Sulfolene (6.5 g, 55 mmol) was added to the mixture in 7 portions, with each next portion being added after heating the mixture at 120 C for 10 h, cooling, and careful venting (***protective screen!, hood!***). After the reaction the mixture was filtered through Celite plug, evaporated on a rotary evaporator, and purified by column chromatography on a short silica column (eluent CH_2Cl_2). The resulting solid was twice recrystallized from MeOH in a freezer. Straw-colored crystals, 6.3 g (64%), m.p. 61-62 (lit. 64-66 C[2]); ^{1}H NMR (400 MHz, $CDCl_3$, 25 C, TMS): δ 7.38 (AA'BB', 2 H), 7.31 (AA'BB', 2 H), 6.12 (m, 2 H), 5.18 (s, 2 H), 2.67 (m, 2 H), 2.24 (m, 2 H), 2.10 ppm (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 C, TMS): δ 129.1, 126.4, 125.8, 118.7, 84.9, 42.3, 27.4 ppm.

1,4-Dihydroanthracene (3): Adduct (**2**) (4.96 g, 25 mmol) was dissolved in EtOH (100 mL). Conc. HCl (10 mL) was added to the solution and the reaction mixture was refluxed for 24 h under Ar. After cooling crystalline precipitate was filtered off, and twice recrystallized from MeOH. Colorless plates. yield 3.6 g (79%), m.p. 152-153 C (lit. 151 C [2]); ^{1}H NMR (400 MHz, $CDCl_3$, 25 C, TMS): δ 7.78 (AA'BB', 2 H), 7.65 (s, 2 H), 7.42 (AA'BB', 2 H), 6.07 (m, 2 H), 3.61 (s, 4 H).

2-chloro-3-(phenylsulfonyl)-1,2,3,4-tetrahydroanthracene (4): Thiophenol (1.7 mL, 1.76 g, 16 mmol) was added dropwise to a suspension of N-chlorosuccinimide (2.14 g, 16 mmol) in freshly distilled (over CaH_2) dichloromethane (20 mL). Deep orange color developed immediately. The mixture was stirred for 1 h, filtered from the white precipitate of succinimide. The orange filtrate was added drop wise at continuous stirring and cooling by ice bath to a solution of dihydroanthracene (**3**) (2.7 g, 15 mmol) in dichloromethane (50 mL). The mixture was stirred at room temperature for 2 h, evaporated to dryness on a rotary evaporator. The residue was dissolved in aqueous MeOH (60 mL, MeOH:H_2O = 2:1, v/v). Oxone® (10.2 g, 16 mmol) was added and the mixture was stirred at room temperature for 7 days (steady effective stirring is necessary), diluted with water (100 mL) and extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and evaporated to dryness. Solid residue was recrystallized from MeOH. White crystals, yield 4.2 g (78%), m.p. 159-162 C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 C, TMS): δ 7.99 (m, 2 H), 7.79 (m, 2 H), 7.72 (m, 1 H), 7.65 (s, 2 H), 7.63 (m, 2 H), 7.46 (m, 2 H), 4.96 (m, 1 H), 3.78 (m, 1 H), 3.57 (dd, J(H,H) = 15.7 Hz, J(H,H) = 4.5 Hz, 1 H), 3.43 (dd, J(H,H) = 16.0 Hz, J(H,H) = 6.7 Hz, 1 H), 3.32 (dd, J(H,H) = 16.2 Hz, J(H,H) = 8.2 Hz, 1 H), 3.27 ppm (dd, *J*(H,H) = 16.0 Hz, *J*(H,H) = 4.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 C, TMS): δ 137.69, 134.29, 132.85, 132.77, 131.27, 130.79, 129.49, 128.90, 127.36, 127.11, 126.37, 125.87, 67.57, 52.85, 37.74, 26.85 ppm.

2-(phenylsulfonyl)-1,2-dihydroanthracene (5): Chlorosulfone (**4**) (3.6 g, 10 mmol) was dissolved in freshly distilled CH_2Cl_2 (30 mL). To the solution DBU (1.6 mL, 10 mmol) was added drop wise under Ar. The mixture was stirred at r.t. for 1 h, treated by water (100 mL), layers were separated, and aqueous layer was extracted by CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and evaporated to dryness in vacuum. Solid residue was recrystallized from MeOH. White crystals, yield 3.1 g, 97%. M.p. 150-151 C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 C, TMS): δ 7.76 (m, 2 H), 7.68 (m, 2 H), 7.42 (m, 2 H), 7.40 (m, 1 H), 7.33 (m, 1 H), 7.28 (s, 1 H), 7.22 (m, 2 H), 6.81 (d, *J*(H,H) = 9.7 Hz), 6.12 (dd, *J*(H,H) = 9.7 Hz, *J*(H,H) = 5.0 Hz), 4.12 (m, 1 H), 3.60 (dd, *J*(H,H) = 16.9 Hz, *J*(H,H) = 4.8 Hz), 3.40 ppm (dd, *J*(H,H) = 16.9 Hz, *J*(H,H) = 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 25 C, TMS) δ 136.34, 134.04, 133.52, 133.43, 132.60, 129.82, 129.56, 129.20, 128.27, 127.79, 127.16, 126.39, 126.33, 125.85, 125.78, 119.77, 61.38, 28.53 ppm; elemental analysis calcd (%) for $C_{20}H_{16}O_2S$: C 74.97, H 5.03; found: C 74.77, H 4.80.

Ethyl 4,11-dihydro-2H-naphtho[2,3-*f*]isoindole-1-carboxylate (6): A solution of ethyl isocyanoacetate (0.8 mL, 7 mmol) in dry THF (10 mL) was added to a suspension of *t*-BuOK (85%, 0.9 g, 8 mmol) in THF (20 mL) at 0 C (ice bath). The mixture was stirred under Ar atmosphere for 1 h. Then a solution of sulfone (**5**) in THF (40 mL) was added dropwise, and the mixture was stirred at r.t. overnight. The mixture was evaporated on a rotary evaporator to ca. 10 mL volume, diluted with CH_2Cl_2 (50 mL), washed by water (2×100 mL) and brine, dried over Na_2SO_4 and evaporated to dryness in vacuum. The residue was recrystallized from MeOH.

Yellowish crystals, yield 1.4 g, 67%. M.p. 212-214 C; NMR (400 MHz, $CDCl_3$, 25 C, TMS): δ 8.96 (br. s, 1 H), 7.83 (s, 1 H), 7.80 (m, 2 H), 7.76 (s, 1 H), 7.44 (m, 2 H), 6.87 (d, J(H,H) = 2.15 Hz, 1 H), 4.42 (q, J(H,H) = 7.1 Hz, 2 H), 4.39 (m, 2 H), 4.08 (m, 2 H), 1.46 ppm (t, J(H,H) = 7.1 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$-[D_6]DMSO, 25 C, TMS): δ 161.45, 134.87, 132.17, 129.27, 128.61, 127.17, 126.91, 126.61, 126.18, 125.31, 120.08, 118.79, 117.21, 59.60, 28.89, 27.72, 14.83 ppm; elemental analysis calcd (%) for $C_{19}H_{17}NO_2$: C 78.33, H 5.88, N 4.81; found: C 78.15, H 6.14, N 4.55.

4,11-dihydro-2H-naphtho[2,3-*f*]isoindole (7): A suspension of ethyl ester (**6**) (1.46 g, 5 mmol) and NaOH (1 g, 25 mmol) in ethylene glycol (40 mL) was refluxed under Ar for 1 h. The reaction mixture was diluted by water (100 mL) and extracted by CH_2Cl_2 (3×30 mL). The combined organic layers were thoroughly washed by water (5×100 mL) and brine, dried over Na_2SO_4, passed through a short silica column, and evaporated in vacuum to dryness. Brownish solid, yield 0.8 g (73%); NMR (400 MHz, $CDCl_3$, 25 C, TMS): δ 8.04 (br. s, 1 H), 7.79 (AA'BB', 2 H), 7.77 (s, 2 H), 7.42 (AA'BB', 2 H), 6.72 (d, J(H,H) = 1.51 Hz, 2 H), 4.10 (s, 4 H). Due to high sensitivity of this compound, further purification to analytical purity was not undertaken, and the compound was used in porphyrin synthesis as is.

***Tetrakis*-5,10,15,20-(*p*-methoxycarbonylphenyl)tetraanthra[2,3-*b,g,l,q*]porphyrin (8fb)**: In a flask screened from daylight by aluminum foil, fitted with Ar inlet and outlet naphthoisoindole (**7**) (0.22 g, 1 mmol) was dissolved in freshly distilled CH_2Cl_2 (150 mL). P-methoxycarbonylbenzaldehyde (0.18 g, 1.1 mmol) was added, soon followed by $BF_3{\cdot}Et_2O$ (0,03 ml). The mixture was stirred at room temperature for 1 h, the DDQ (0.34 g, 1.5 mmol) was added as a solution in toluene (1 mL). The mixture was left stirring for 1 h, then washed by 10% aqueous solution of Na_2SO_3 (2×100 mL), 10% aqueous solution of Na_2CO_3 (1×100 mL), brine.

Organic phase was dried over Na_2SO_4, evaporated to dryness. The residue was recrystallized from CH_2Cl_2-Et_2O, the crystals were centrifuged, washed by ether until the washing liquid became colorless. All manipulations were performed either in the dark, or in vessels covered by aluminum foil. Brown crystalline powder (ether solvate), yield 0.13 g (36%). NMR (400 MHz, $CDCl_3$, 25 C, TMS): δ 8.62-8.71 (m, AA'XX', 16 H), 8.42 (br. s., 8 H), 8.02 (m, 8 H), 7.94 (br. s., 8 H), 7.45 (m, 8 H), 4.27 (s, 12 H), 3.67 (q, Et_2O), 2,24 (br. s., 2 H), 1.23 (t, Et_2O); UV/Vis for free base (toluene) λ_{max} (log ε) = 508 (4.65), 758 (3.5), 832 nm (4.40); diprotonated form (toluene, CF_3COOH) λ_{max} = 544; 800; 914 nm. MS LDI-TOF: *m/z*: found 1447.39, calcd. for [M^+] $C_{100}H_{62}N_4O_8$ 1447.46; elemental analysis calcd (%) for $C_{100}H_{62}N_4O_8 \cdot Et_2O$: C 82.09, H 4.77, N 3.68; found C 81,90, H 5.09, N 3.42.

(**8Zn**) Zinc complex, obtained by a treatment of solution of porphyrin (**8**) in CH_2Cl_2-pyridine by excess of $Zn(OAc)_2 \cdot 2H_2O$, with subsequent washing and crystallization. UV/Vis (toluene-pyridine) λ_{max} (log ε) = 510 (4.68); 732 (3.66); 810 nm (4.54); MS LDI-TOF: *m/z*: found 1510.15, calcd. for [M^+] $C_{100}H_{60}N_4O_8Zn$ 1509.37.

(**8Pd**) Palladium complex, obtained by a treatment of solution of porphyrin (**8**) in dioxane with a drop of Et_3N by $Pd(OAc)_2$ at room temperature for 5 h (control by UV-Vis spectroscopy), with subsequent washing and crystallization from CH_2Cl_2-Et_2O (by layering). UV/Vis (toluene) λ_{max} = 470, 704, 790 nm; MS LDI-TOF: *m/z*: found 1550.27, calcd. for [M^+] $C_{100}H_{60}N_4O_8Pd$ 1551.35.

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[1] *Org. Synth., Coll. Vol. 10, p.653 (2004);*

[2] W. Dehaen, D. Corens and G. L'Abbe, *Synthesis*, 1996, 201-203.

NMR spectra of new intermediate compounds.

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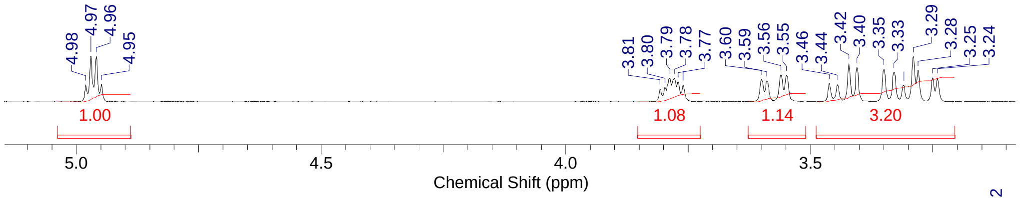

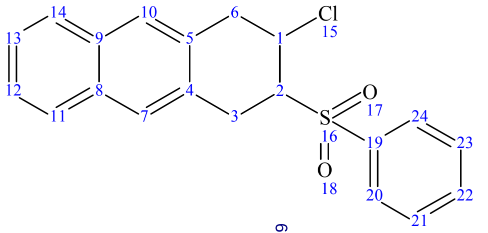

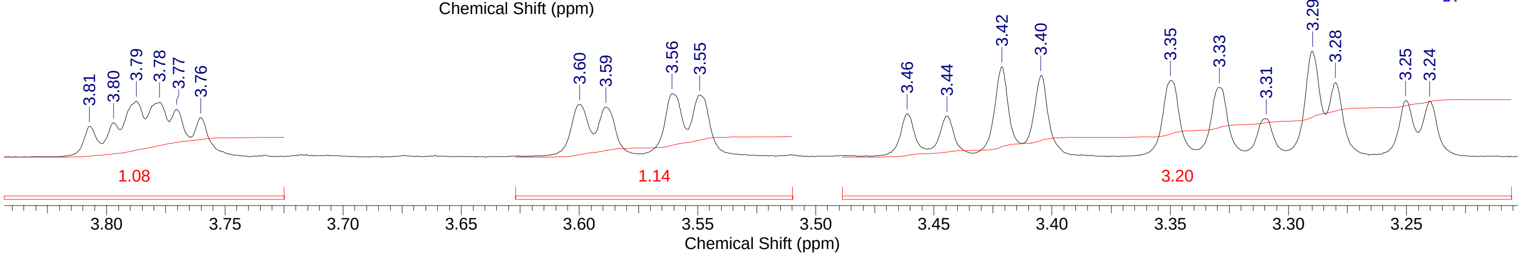

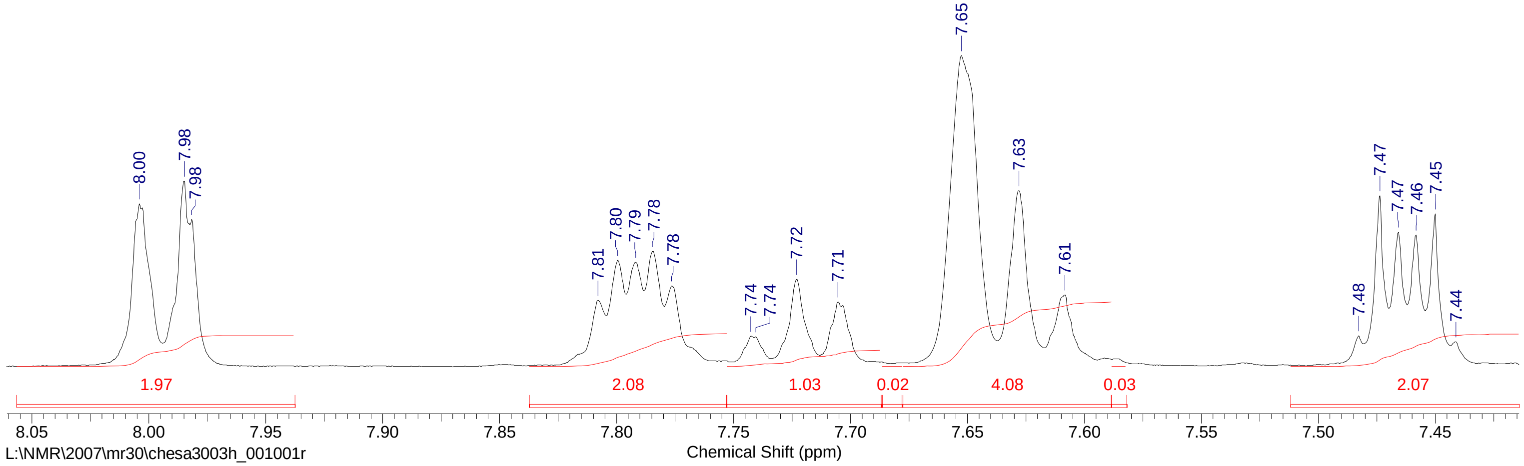

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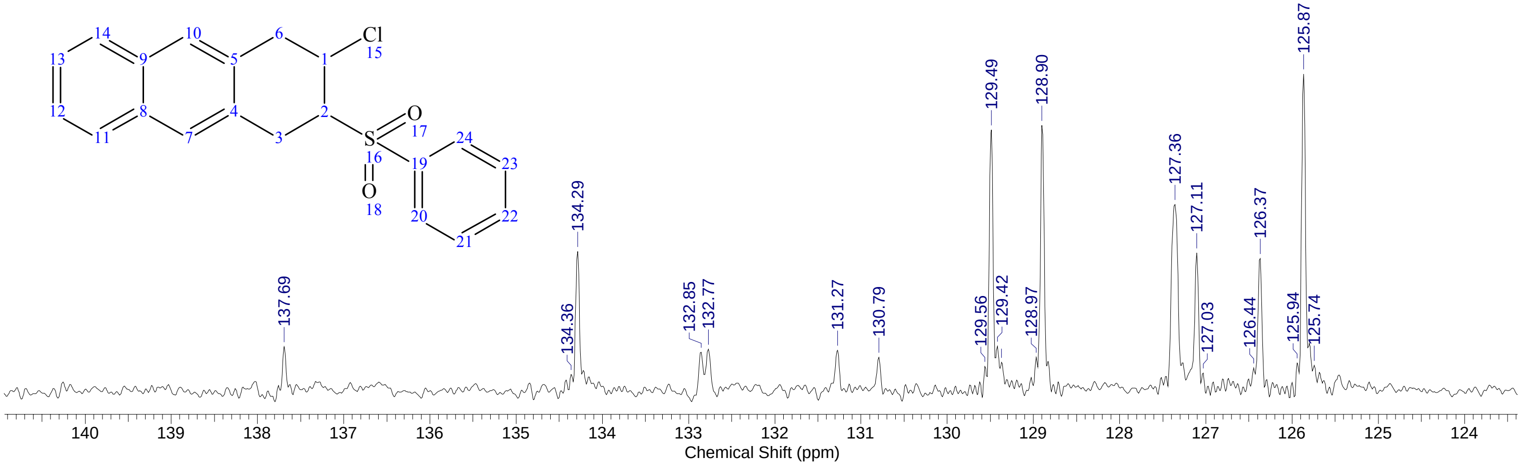

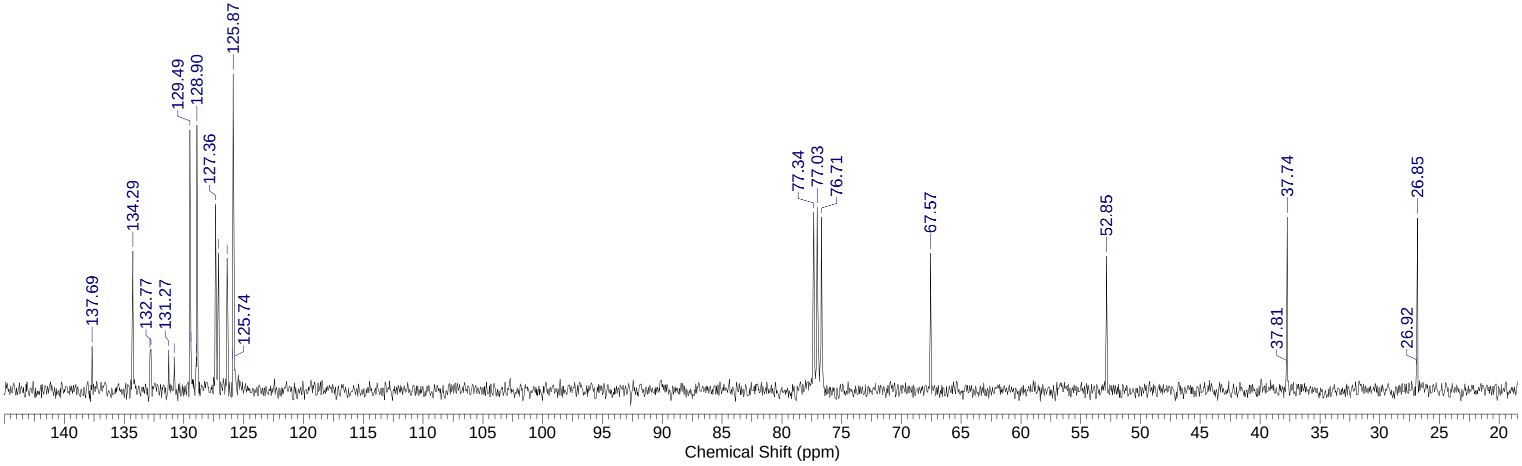

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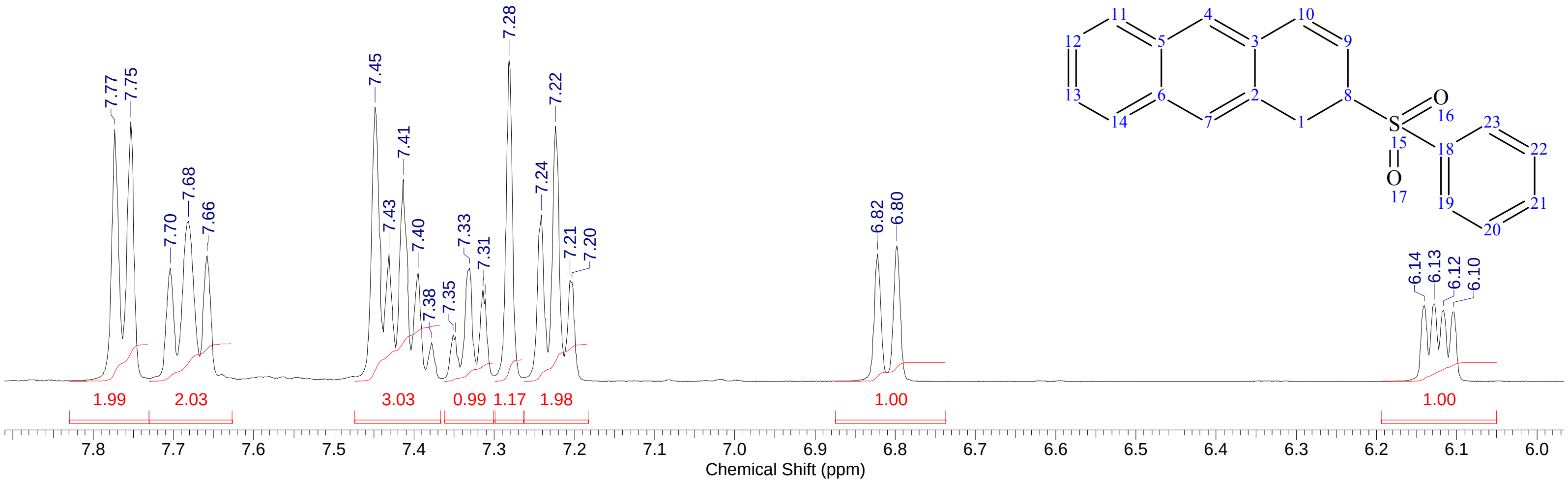

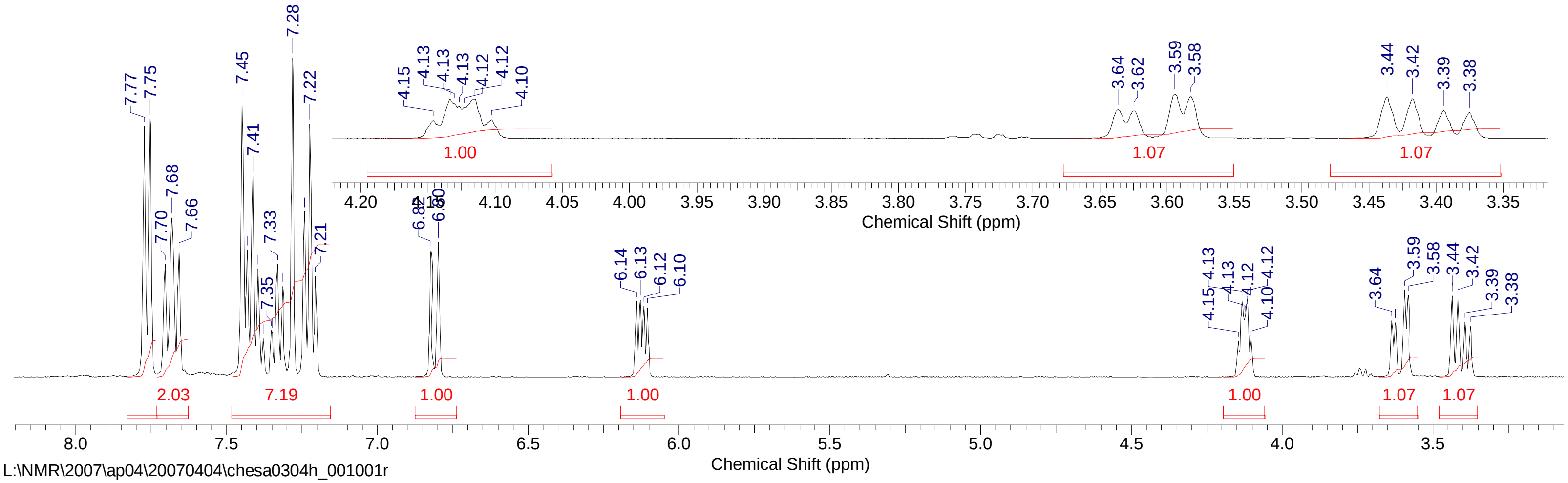

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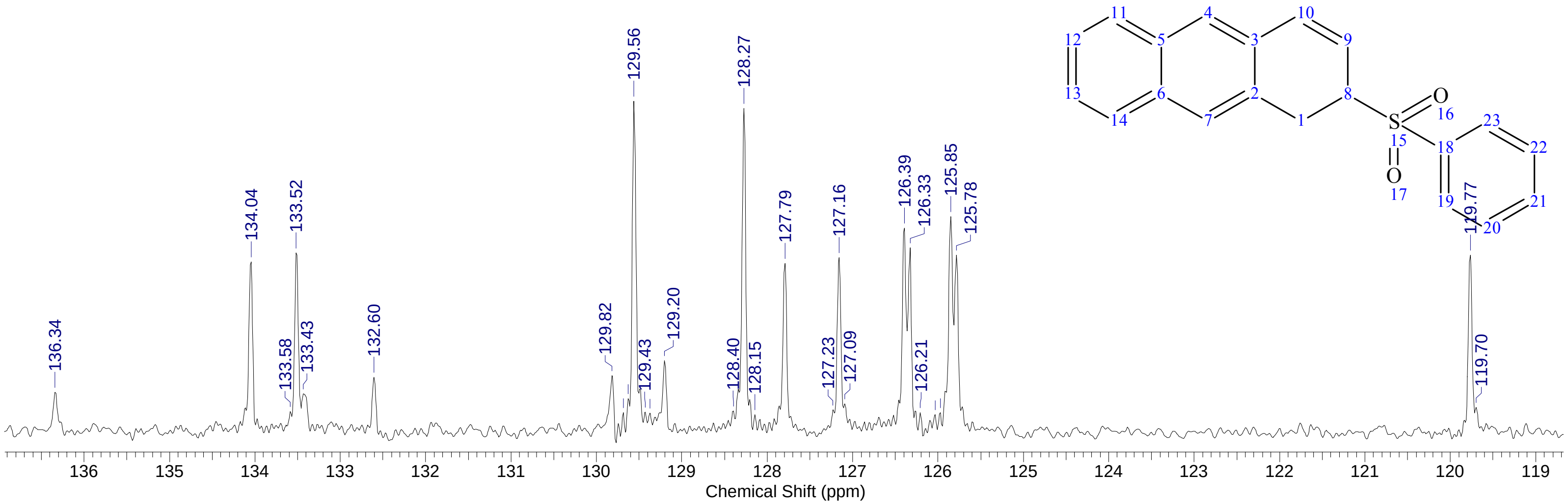

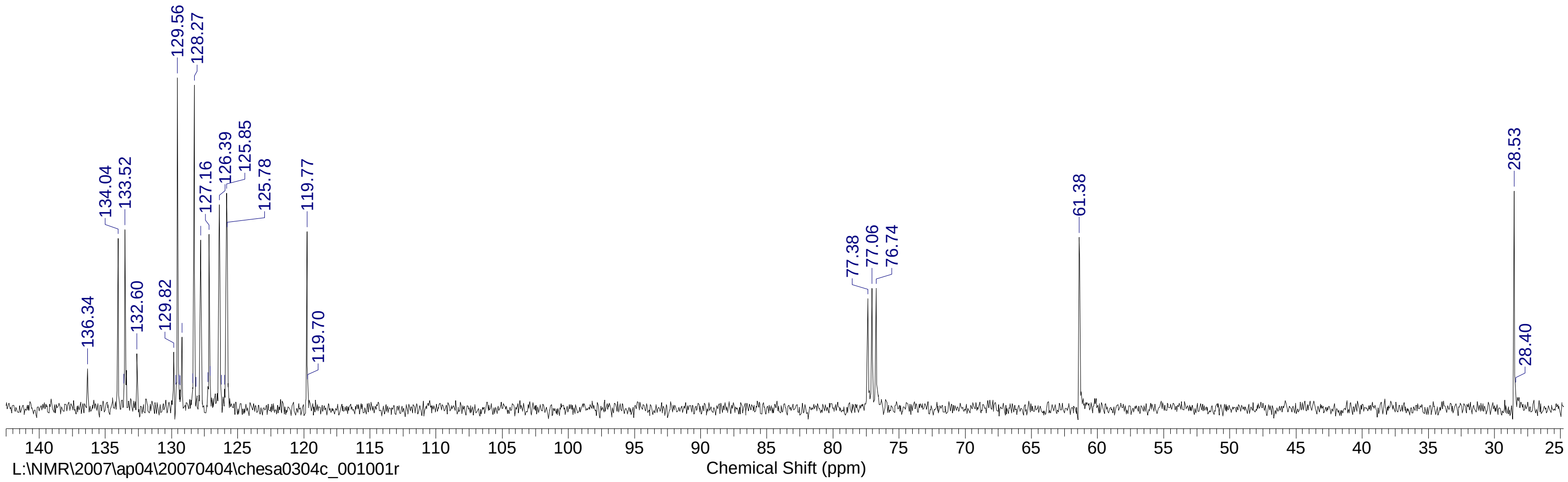

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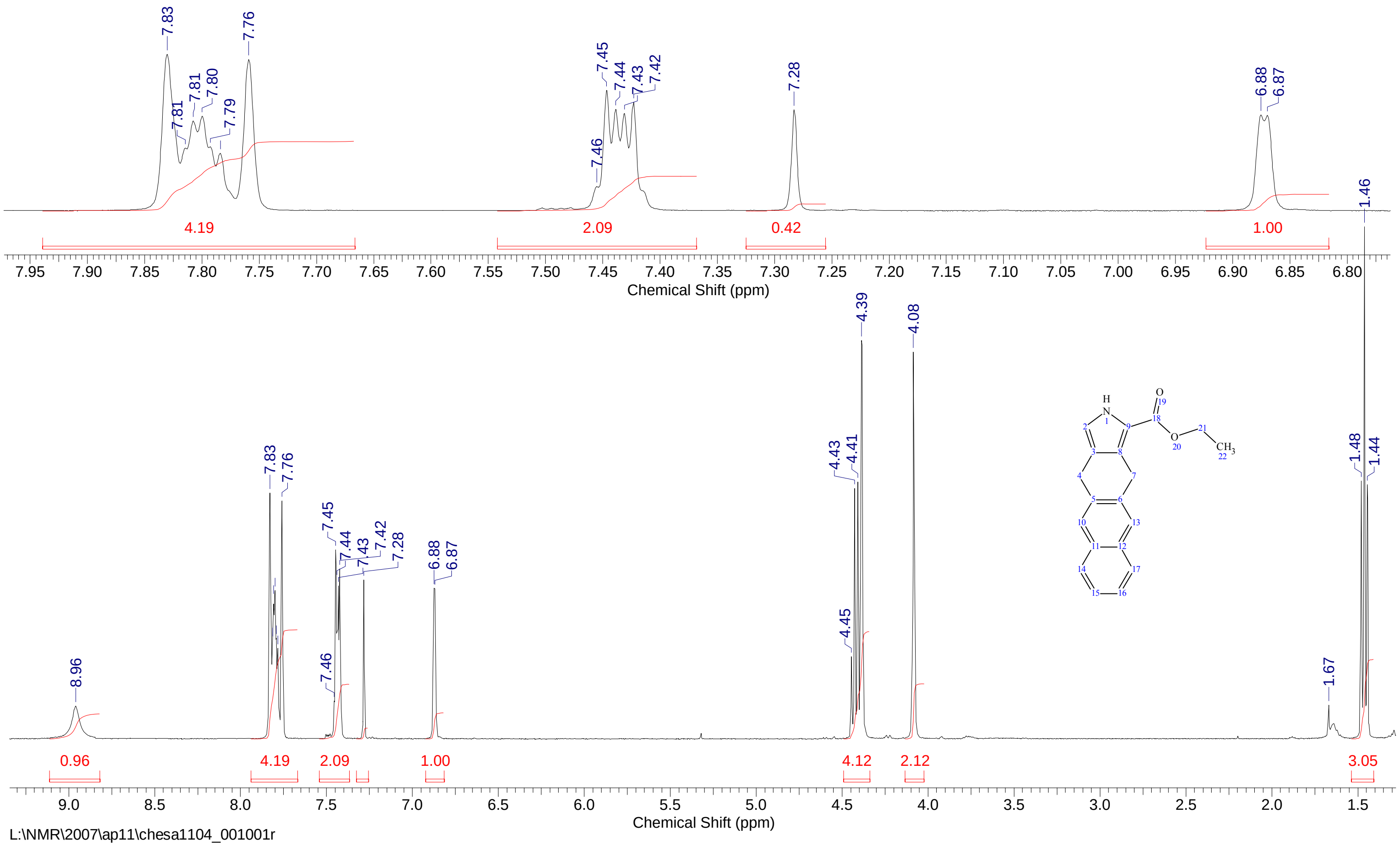

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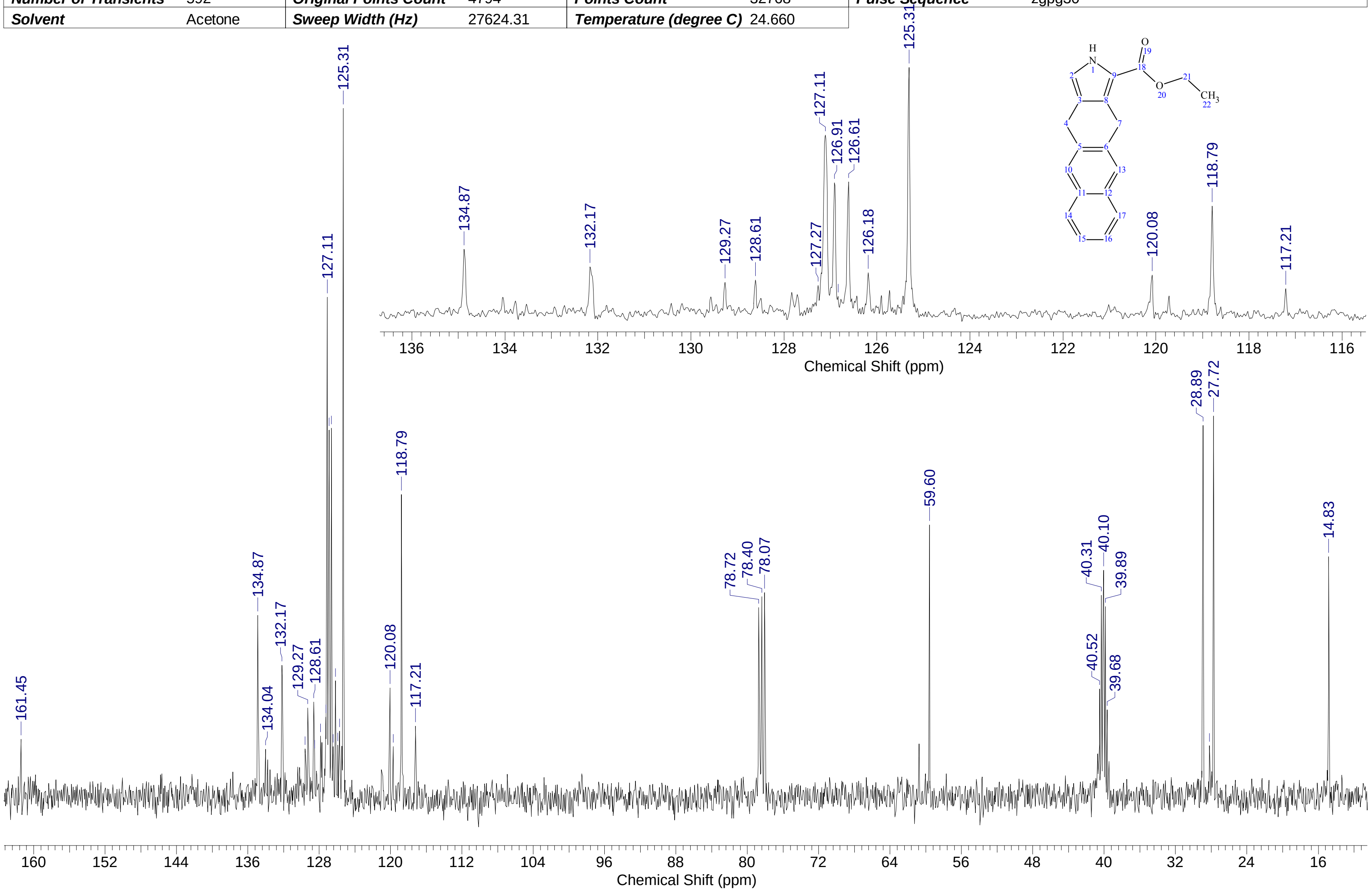

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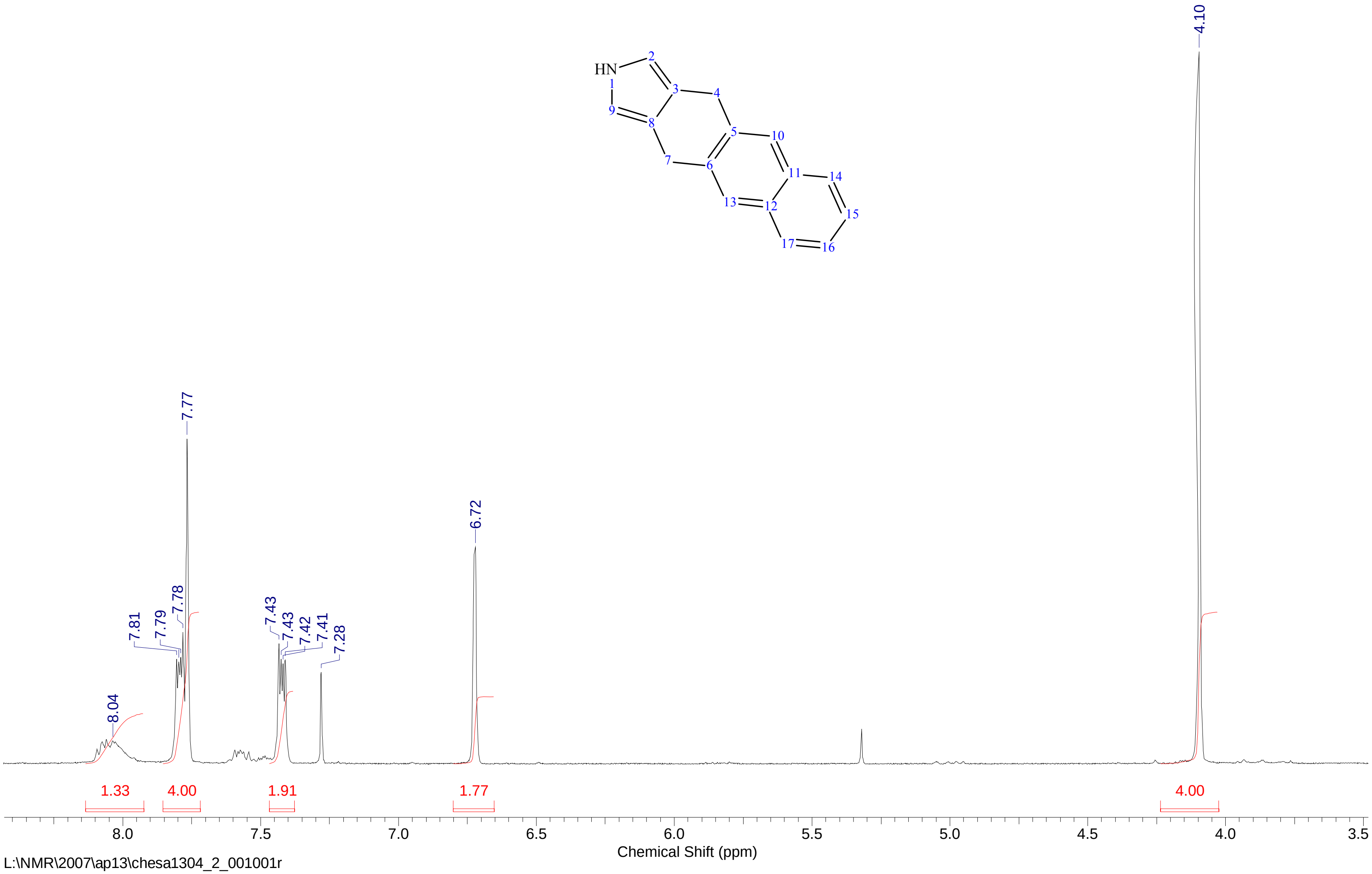

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