This ESI replaces the version published on 3rd November 2010, which contained an error in the experimental for compound 17, page 4.

Electronic Supplementary Information for the paper

New Stable Donor-Acceptor Dyads for Molecular Electronics

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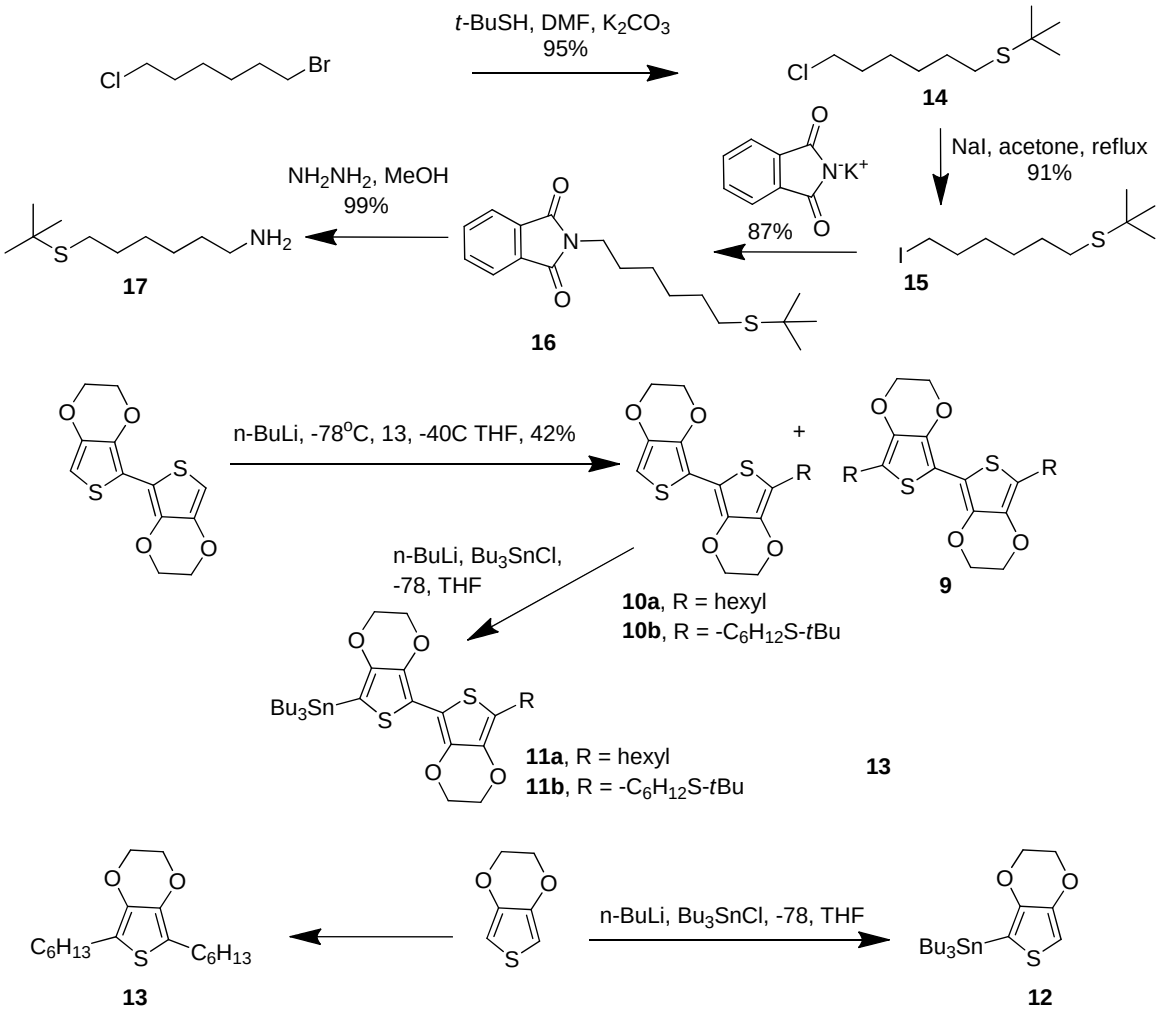
Synthesis of auxiliary reagents



***N*-2-Ethylhexyl-1,4,5,8-naphthalenetetracarboxyimide anhydride (6a).** Monoimide **6a** was prepared following a literature procedure,[47] from commercially available 1,4,5,8-naphthalenetetracarboxylic dianhydride **5 (**10.0 g, 37.3 mmol) and 2-ethyl-1-hexylamine (5.35 g, 41.3 mmol). The product was purified by column chromatography (silica; hexane/ethylacetate gradient) to afford the desired product **6a** as yellowish solid (first fraction) (6.1g, 43%) along with symmetric diimide **7** as a side product (second fraction) (5.9g, 32%). **6a**: m.p. 166–169 °C; δ_H (400 MHz, $CDCl_3$) 8.81 (4H, s), 4.15 (2H, m),

1.92 (1H, t, *J* 6.0 Hz), 1.33 (8H, m), 0.95 (3H, t, *J* 7.4 Hz), 0.89 (3H, t, *J* 7.2 Hz); δ_C (125.0 MHz, $CDCl_3$) 162.3, 158.8, 133.2, 131.3, 128.9, 127.9, 126.9, 122.8, 44.8, 37.9, 30.6, 28.6, 24.0, 23.0, 14.1, 10.6. **7:** m.p. 203-204 °C, δ_H (500 MHz, $CDCl_3$) 8.75 (4H, s), 4.15 (4H, m), 1.94 (2H, t, *J* 6.0 Hz), 1.43-1.22 (16H, m), 0.95 (6H, t, *J* 7.4 Hz), 0.89 (6H, t, *J* 7.2 Hz).

N-(2-Ethylhexyl)-N'-p-bromophenyl 1,4,5,8-naphthalenetetracarboxydiimide (8a). Compound **6a** (6.1 g, 16.1 mmol) and p-bromoaniline (2.80 g, 16.1 mmol) were dissolved in dry DMF (150 ml) and the reaction mixture was stirred at reflux overnight under nitrogen atmosphere. After cooling to room temperature, the solvent was removed under reduced pressure. After column chromatography on silica (CH2Cl2:EtOAc eluent, gradient), afforded the desired diimide 8a (6.5 g, 76%). M.p.: 213–214 _C; dH (400 MHz, CDCl3) 8.82 (4H, s), 7.72 (2H, d, J 8.8 Hz), 7.21 (2H, d, J 8.8 Hz), 4.16 (2H, m), 1.96 (1H, m), 1.36 (8H, m), 0.95 (3H, t, J 7.4 Hz), 0.89 (3H, t, J 7.2 Hz); dC (75.0 MHz, CDCl3) 163.1, 162.8, 133.5, 132.8, 131.5, 131.1, 130.2, 127.1, 126.4, 123.3, 44.7, 37.9, 30.7, 28.6, 24.0, 23.0, 14.1, 10.6; HR-MS (ESI): calculated for C28H25BrN2O4 533.1070, found 533.1058.

N-(6-(*tert*-butylsulfanyl)hexyl-1,4,5,8-naphthalenetetra-carboxyimide anhydride (6b). To a solution of **5** (1.0 g, 3.7mmol) in dry DMF (150 ml) was slowly added (during 3 h) a solution of amine **17** (0.65 g, 3.5 mmol) in dry DMF (40 ml) under nitrogen atmosphere and reaction mixture was refluxed overnight. After cooling to room temperature, reaction mixture was placed in the fridge for 2-3 h (–10°C). Precipitate (corresponding diimide side product) was filtered out and then the solvent was removed under reduced pressure. Crude product was dissolved in acetone and resulted solution was kept in the fridge overnight to precipitate more of diimide. The filtrate was concentrated and resulted solid was purified by column chromatography on silica (CH_2Cl_2:EtOAc eluent, gradient) resulting in desired monoimide **6b** as a yellow solid (0.88 g, 59%). M.p. 218–220°C; δ_H (400 MHz, $CDCl_3$) 8.81 (4H, s), 4.21 (2H, t, *J* 7.6), 2.53 (2H, t, *J* 7.2), 1.77 (2H, t, br), 1.7–1.4 (6H, m), 1.31 (9H, s); δ_C (75.0 MHz, $CDCl_3$) 162.1, 158.8, 133.1, 131.2, 128.8, 127.9, 122.7, 41.7, 41.1, 30.9, 29.7, 29.1, 28.2, 27.9, 26.9.

N-(6-(*tert*-butylsulfanyl)hexyl-N'-*p*-bromophenyl-1,4,5,8-naphthalenetetracarboxydiimide (8b). NDI **6b** (0.88 g, 2.0 mmol) and *p*-bromoaniline (1.0 g, 5.8 mmol) were dissolved in dry DMF (100 mL) and the reaction mixture was stirred under nitrogen atmosphere at reflux overnight. After cooling to room temperature, the solvent was removed under reduced pressure and the crude product was dried under vacuum. After column chromatography on silica (CH_2Cl_2:EtOAc eluent, gradient), desired diimide **8b** was obtained as dark yellow solid (0.75 g, 63%). M.p.: 237–239°C; δ_H (400 MHz, $CDCl_3$) 8.81 (4H, s), 7.72 (2H, d, *J* 8.8 Hz), 7.23 (2H, d, *J* 8.8 Hz), 4.21 (2H, m,), 2.53 (2H, t, *J* 7.2), 1.77 (2H, m), 1.62-1.39 (6H, m), 1.32 (9H, s); δ_C (75.0 MHz, $CDCl_3$) 163.1, 162.8, 131.5, 131.0, 130.2, 127.1, 126.4, 123.3, 41.5, 40.3, 31.0, 29.2, 28.9, 28.2, 27.3, 26.8; HR-MS (ESI): calculated for $C_{30}H_{29}BrN_2O_4S$ 592.1026, found 592.1033.

5-Hexyl-bisEDOT (10a). Compound **10a** was prepared according to literature procedure[49] from bis-EDOT (2 g) and 1-iodohexane (1.17 g, 7.1 mmol) Purification was performed by column chromatography on silica using hexanes:EtOAc (5:1) as eluent resulting in final product **10a** as a yellow powder (0.95 g, 37 %) and **9**

as a by-product (26%). **10a**: M.p. 118-120 °C (lit[49] 120 °C); δ_H (400 MHz, $CDCl_3$) 6.22 (s, 1H), 4.3-4.19 (m, 8H), 2.63 (t, 2H, *J* 7.6Hz), 1.6-1.61 (m, 4H), 1.4-1.36 (m, 4H), 0.88 (t, 3H, *J* 7.2 Hz). **9**: δ_H (400 MHz, $CDCl_3$) 4.3-4.19 (m, 8H), 2.63 (t, 2H, *J* 7.6Hz), 1.6-1.61 (m, 4H), 1.4-1.36 (m, 4H), 0.88 (t, 3H, *J* 7.2 Hz). The NMR suggests some impurities of the disubstituted bisEDOT, which, however, are easier to remove at the later stage.

***6-(tert*-butylsulfanyl)hexyl-bisEDOT (10b).** To a solution of bis-EDOT (1.0 g, 3.54 mmol) in dry THF (100 ml) at -78 °C a 2.5 M solution of *t*-BuLi (1.45 ml, 3.6 mmol) was added dropwise and reaction mixture was stirred at –40 °C for 2h under nitrogen atmosphere. Then reaction mixture was cooled to –78 °C and compound **15** (1.06 g, 3.54 mmol) was slowly added Mixture was stirred at –40 °C overnight (at the end the temperature raised to -10 °C). Then reaction was quenched with water, diluted with EtOAc and organic phase was washed sequentially with water and brine, dried with $MgSO_4$. Solution was filtered and concentrated under reduced pressure affording crude brown oil as a mixture of starting bisEDOT, monoalkylated and dialkylated bis-EDOT. Purification was performed by column chromatography on silica (hexanes:EtOAc eluent, gradient) resulted in product **10b** as a yellowish greasy solid (0.68g, 42%). δ_H (400 MHz, $CDCl_3$) 6.22 (s, 1H), 4.3-4.19 (m, 8H), 2.6 (2H, J 7.5Hz), 2.51 (t, 2H, 7.6Hz), 1.6-1.55 (m, 4H), 1.4-1.36 (m, 4H), 1.31 (s, 9H). The NMR suggests some impurities of the disubstituted bisEDOT, which, however, are easier to remove at the later stage.

5-Tributylstannyl-5'-hexyl-bisEDOT (11a). To a solution of **10a** (0.27g, 0.74 mmol) in dry diethyl ether (150 mL) at –78°C a solution of 1.7 M *n*-BuLi (0.52 mL, 0.88 mmol) was slowly added and reaction mixture was warmed up to -40 °C and stirred for 3–4 h under nitrogen atmosphere. After cooling the reaction mixture to –78°C tributylstannyl chloride (0.24 g, 0.74 mmol) was added and reaction mixture was slowly (overnight) warmed to room temperature. After quenching reaction with water organic phase was extracted with diethyl ether, washed with water, brine and dried over $MgSO_4$. Crude product (0.46 g) was used without further purification for synthesis of **2a** and **3a**. δ_H (400 MHz, $CDCl_3$) 4.3-4.19 (m, 8H), 2.62 (t, 2H, *J* 7.6Hz), 1.65-1.45 (m, 8H), 1.2-1.4 (m, 12H),1.15-1.0 (m, 6H) 0.88 (m, 12H).

5-tributylstannyl-5'-*(6-(tert*-butylsulfanyl)hexyl)-bisEDOT (11b). To a solution of **10b** (0.46 g, 1.0 mmol) in dry THF(150 mL) at –78°C was slowly added a solution of 2.5 M *n*-BuLi (0.4 mL, 1.0 mmol). Then reaction mixture was warmed up to –40 °C and stirred for 3–4 h. After cooling the reaction mixture to –78°C tributylstannyl chloride (0.33 g, 1.0 mmol) was added and reaction mixture was slowly (overnight) warmed to room temperature. After quenching reaction with water resulted solution was extracted with ethyl acetate, organic phase was washed with water, brine and dried over $MgSO_4$. Crude product (0.7 g) was used without further purification for the next step. δ_H (400 MHz, $CDCl_3$) 4.3-4.19 (m, 8H), 2.6 (2H, t, J 7.5), 2.51 (t, 2H, J 7.6Hz), 1.68-1.55 (m, 10H), 1.45-1.25 (m, 19H), 1.2-1.0 (m, 6H), 0.88 (t, 9H, *J* 7.2 Hz).

2-Tributylstannyl-EDOT (12). To a solution of EDOT (5.0 g, 35.2 mmol) in dry diethyl ether (300 mL) at –78°C was slowly added a solution of 2.5 M *n*-BuLi (14.1 mL, 35.2 mmol) reaction mixture was warmed up to room temperature and stirred for 1.2 h . After cooling the reaction mixture to –78°C tributylstannyl chloride (11.5 g, 35.2 mmol) was added and reaction mixture was slowly (overnight) warmed to room temperature. After quenching reaction with water resulted solution was extracted with diethyl ether, organic phase was washed with water, brine and dried over $MgSO_4$. Crude product was filtered through short pad

silica gel and used without further purification for the next step (10.1 g, 67%). δ_H (400 MHz, $CDCl_3$) 6.6 (s, 1H), 4.2-4.14 (m, 4H), 1.65-1.40 (m, 6H), 1.4-1.2 (m, 6H), 1.2-1.0 (m, 6H), 0.88 (t, 9H, *J* 7.2 Hz)

***tert*-Butylsulfanylhexyl-6-chloride (14).** To a solution of 1-bromo-2-chlorohexane (8.4 g, 42.1 mmol) and *tert*-butyl mercaptane (3.8 g, 41.2 mmol) in DMF well-grounded potassium carbonate (6.0 g, 55.6 mmol) was added and the reaction mixture was stirred at room temperature overnight. After all starting 6-bromohexyl chloride was consumed, reaction mixture was diluted with water and resulted solution was extracted with EtOAc, washed with water and brine. Organic phase was dried over $MgSO_4$. Evaporation of the solvent gave desired product as colorless oil (8.37g. 95%), which had sufficient purity (GC-MS) to use it for further transformation. δ_H (400 MHz, $CDCl_3$) 3.52 (t, 2H, *J* 6.8Hz), 2.52 (t, 2H, *J* 7.2Hz), 1.86 (2H, m), 1.57 (m, 2H), 1.50-1.38 (m, 4H), 1.37 (s, 9H). δ_C (75.0 MHz, $CDCl_3$) 44.9, 41.7, 32.4, 30.9, 29.6, 28.4, 28.0, 26.5. HRMS (APCI) calculated for $C_{10}H_{22}ClS$ 209.1125 found 209.1128

***tert*-Butyl-(6-iodohexyl)sulfane (15).** To a solution of *tert*-butylsulfanyl-6-chloride (**14**) (8.37g, 40.2 mmol) from previous step in acetone was added NaI (7.0 g, 47 mmol) and the reaction mixture was stirred at reflux overnight. Completion of the reaction was followed by ^1H NMR and GC-MS analysis. Then reaction mixture was diluted with water and resulted solution was extracted with EtOAc. Organic phase was washed with water, brine, and then was dried over $MgSO_4$. Solvent was evaporated resulting in desired product as a yellow oil (11.0 g, 91%); δ_H (400 MHz, $CDCl_3$) 3.18 (t, 2H, 6.9 Hz), 2.52 (t, 2H, 7.2 Hz), 1.94-1.80 (m, 2H), 1.6-1.57 (m, 2H), 1.45-1.38 (m, 4H), 1.37 (s, 9H); δ_C (125.0 MHz, $CDCl_3$) 41.9, 33.3, 30.9, 30.1, 29.5, 28.2, 28.1, 7.0. HRMS (APCI) calculated for $C_{10}H_{22}IS$ 301.0481 found 301.0477.

***N*–(6-(*tert*-Butylsulfanyl)hexyl)phthalimide (16).** To a solution of **15** (1.0 g, 4 mmol) in acetone (100 ml) at reflux, was added potassium phthalimide (1.0 g, 5.4 mmol) in small portions under nitrogen atmosphere. Reaction mixture was stirred at reflux for 4–6 h. Then it was cooled down to room temperature. Precipitate (formed KBr) was filtered off, and the solvent was evaporated under reduced pressure. Residue was purified by column chromatography on silica giving compound **16** as a white-beige greasy solid (1.15 g, 87% yield). δ_H (400 MHz, $CDCl_3$) 7.83 (m, 2H), 7.69 (m, 2H), 3.67 (t, 2H, *J* 7.2), 2.52 (t, 2H, *J* 6.6), 1.67 (m, 2H), 1.55 (m, 2H), 1.5-1.3 (m, 4H) , 1.35 (9H, s); δ_C (125.0 MHz, $CDCl_3$) 168.4, 133.8, 132.1, 123.1, 41.7, 37.9, 30.9, 29.7, 28.8, 28.5, 28.1, 26.5. HR-MS (CI) calculated for $C_{18}H_{25}O_2NSNa$ 342.1498 found 342.1508.

***tert*-Butylsulfanyl-6-hexylamine (17).** To a suspension of compound **16** (1.15 g, 3.60 mmol) in methanol (100 ml) was added hydrazine monohydrate (0.5 ml, 10 mmol) and reaction mixture was stirred at reflux for 2 h. Then solvent was evaporated and residue was dissolved in CH_2Cl_2, washed with 10% KOH, water and brine, dried over $MgSO_4$. Evaporation of CH_2Cl_2 under reduced pressure resulted in desired product **17** as a yellow oil (0.77 g, 100 %). δ_H (300 MHz, $CDCl_3$) 2.68 (t, 2H, *J* 7.5Hz), 2.52 (t, 2H, *J* 8 Hz), 1.57 (m, 2H), 1.5-1.26 (m, 6H), 1.31 (s, 9H), 1.19 (s, br, 2H). δ_C (125.0 MHz, $CDCl_3$) 42.2, 41.8, 33.7, 30.9, 29.8, 29.1, 28.2, 26.6; HR-MS (ESI) calculated for $C_{10}H_{23}NS$ (M+1) 190.1551, found 190.1607.

Cyclic voltammograms of dyads 3 and 4, in solution and in SAMs.

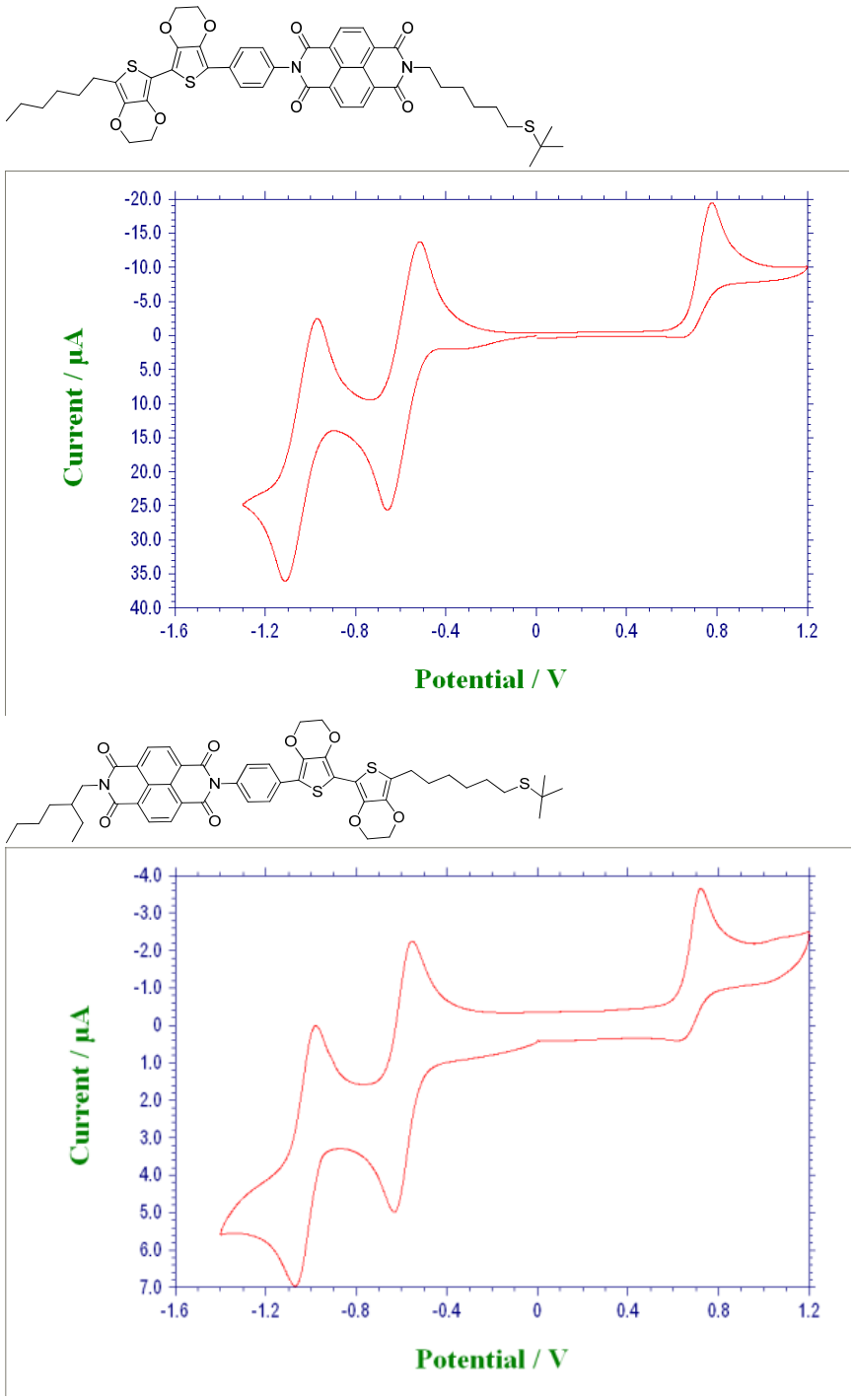


Figure S1. CV of dyads **3a** and **4a** (0.1 M Bu_4NPF_6 in DCM vs Ag/AgCl)

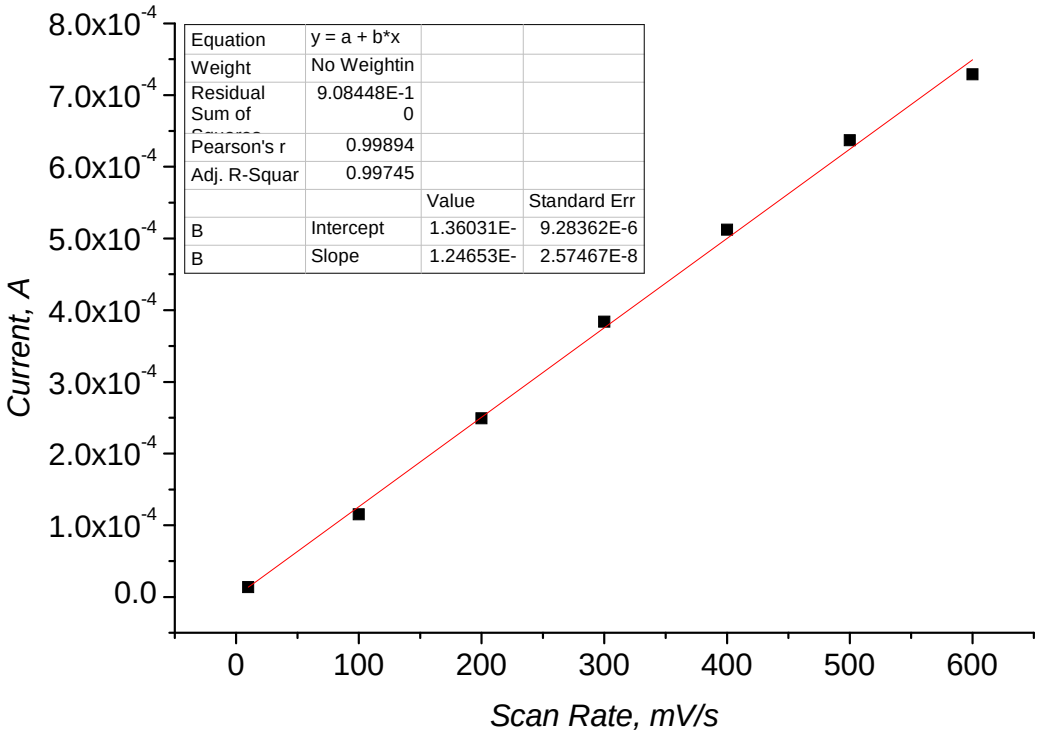


Figure S2. Linear dependence of the first reduction peak of the SAM of dyad **3** on the scan rate (on Au electrode).

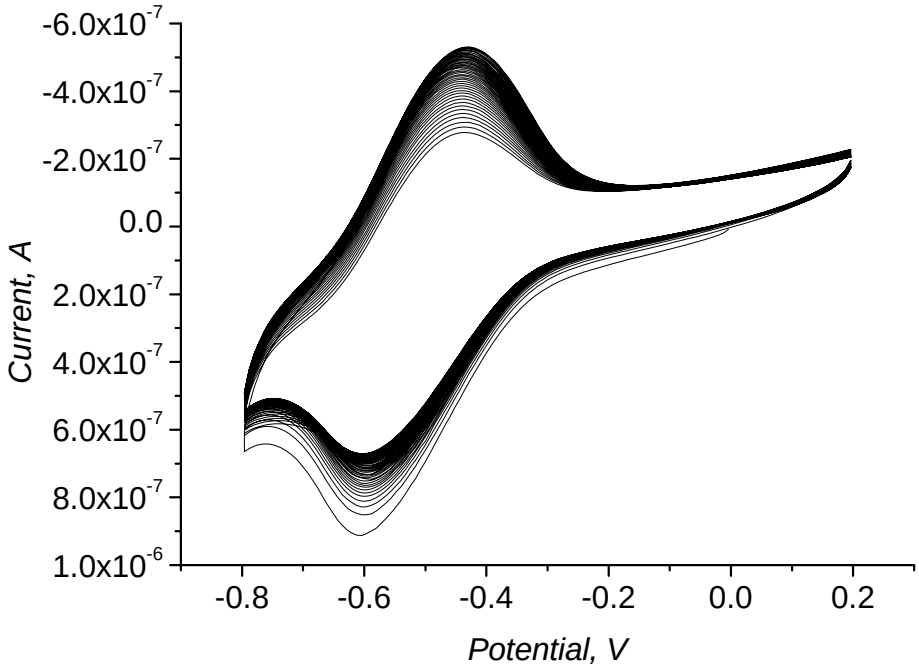


Figure S3. Multiple scanning of the SAM of the dyad **3**.

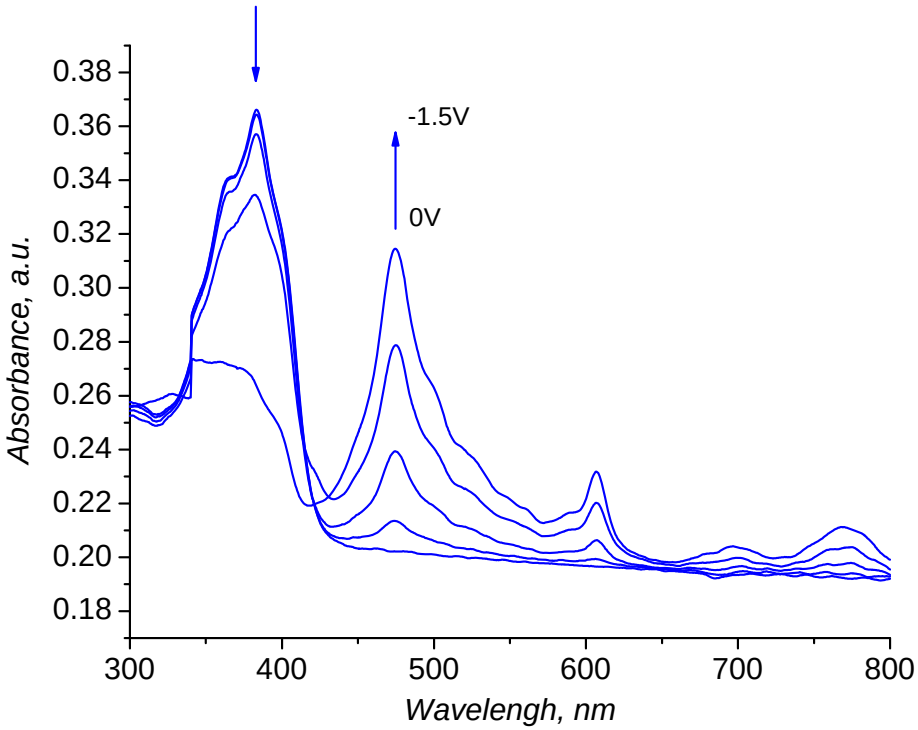


Figure S4. Spectroelectrochemistry of the dyad **2** (reduction of the NDI moiety) in DMF (0.1 M Bu_4NPF_6).

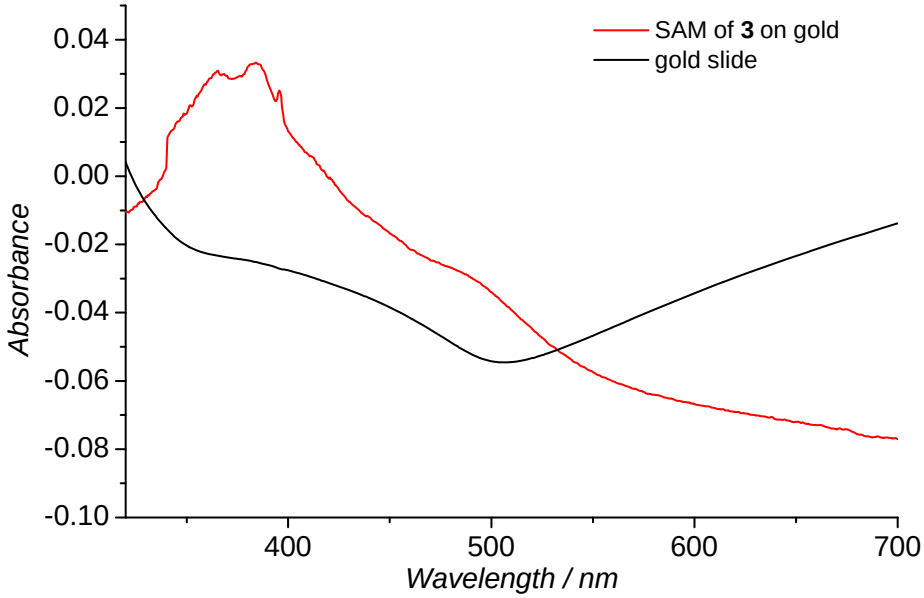


Figure S5. Absorption spectra of the dyad of dyad **3** in SAMs on semitransparent gold electrode (red) and differential absorbance between two gold slides showing a residual plasmonic band of gold nanoislands (a deep at ca 600 nm) (black).

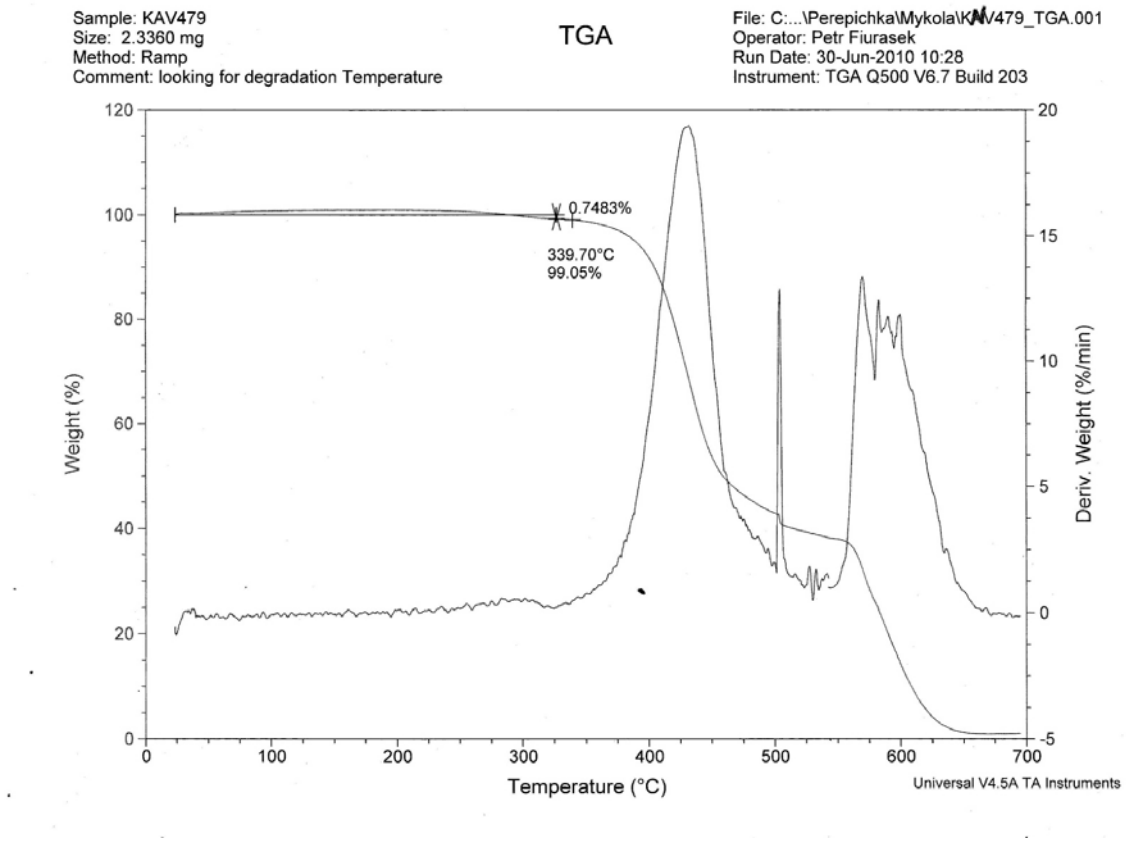


Figure S6. TGA analysis of the dyad **2.**

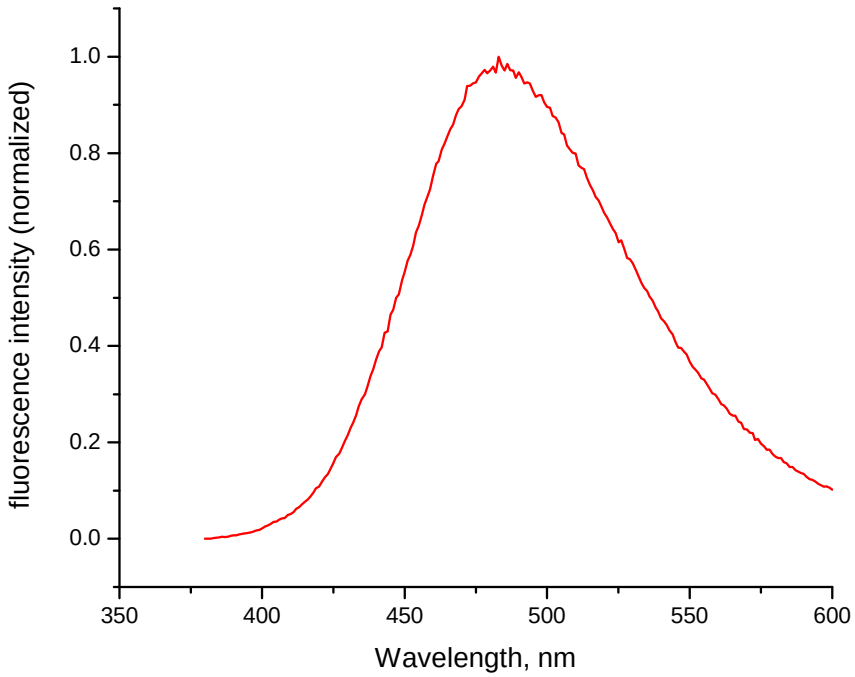
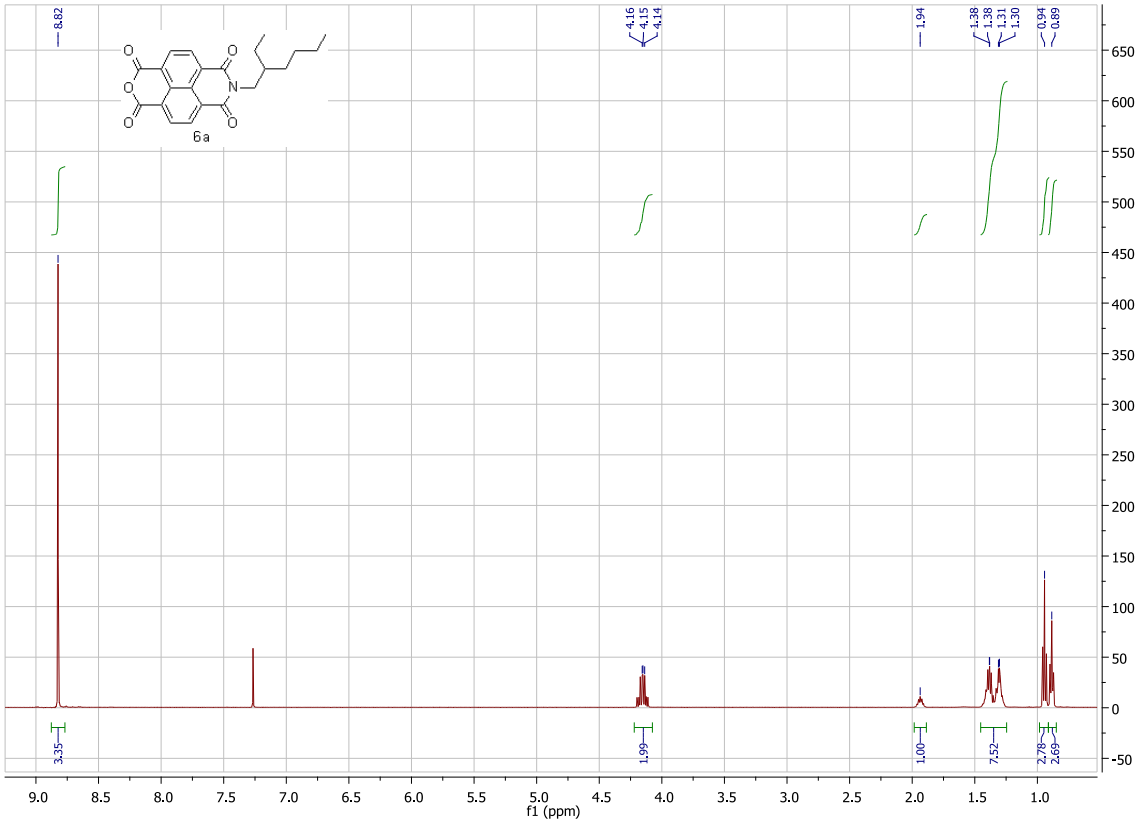
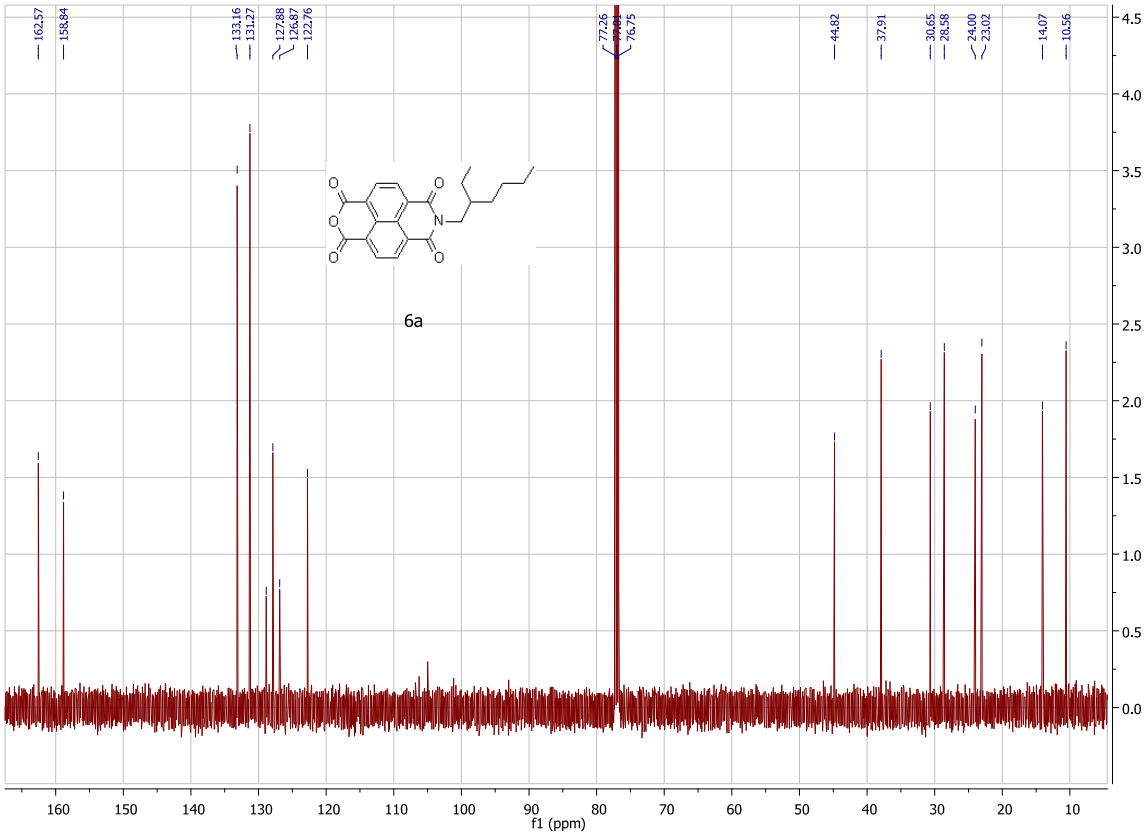
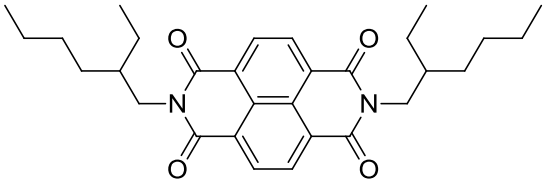


Figure S7. Fluorescence of the dyad **2** in toluene.







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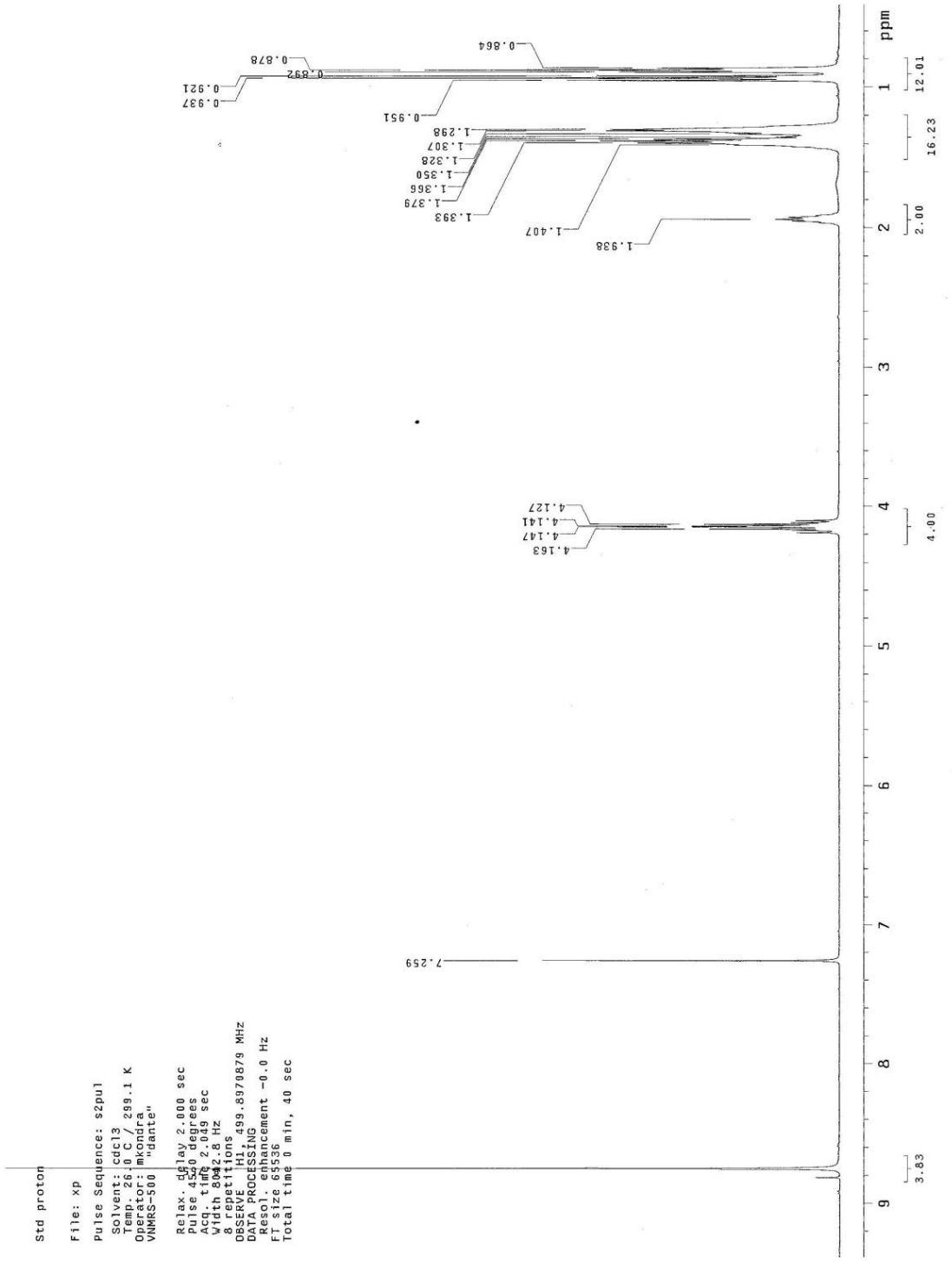

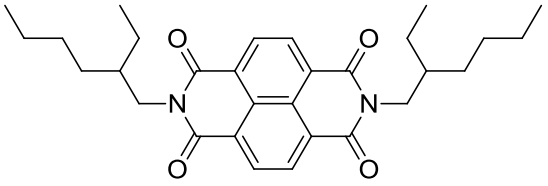

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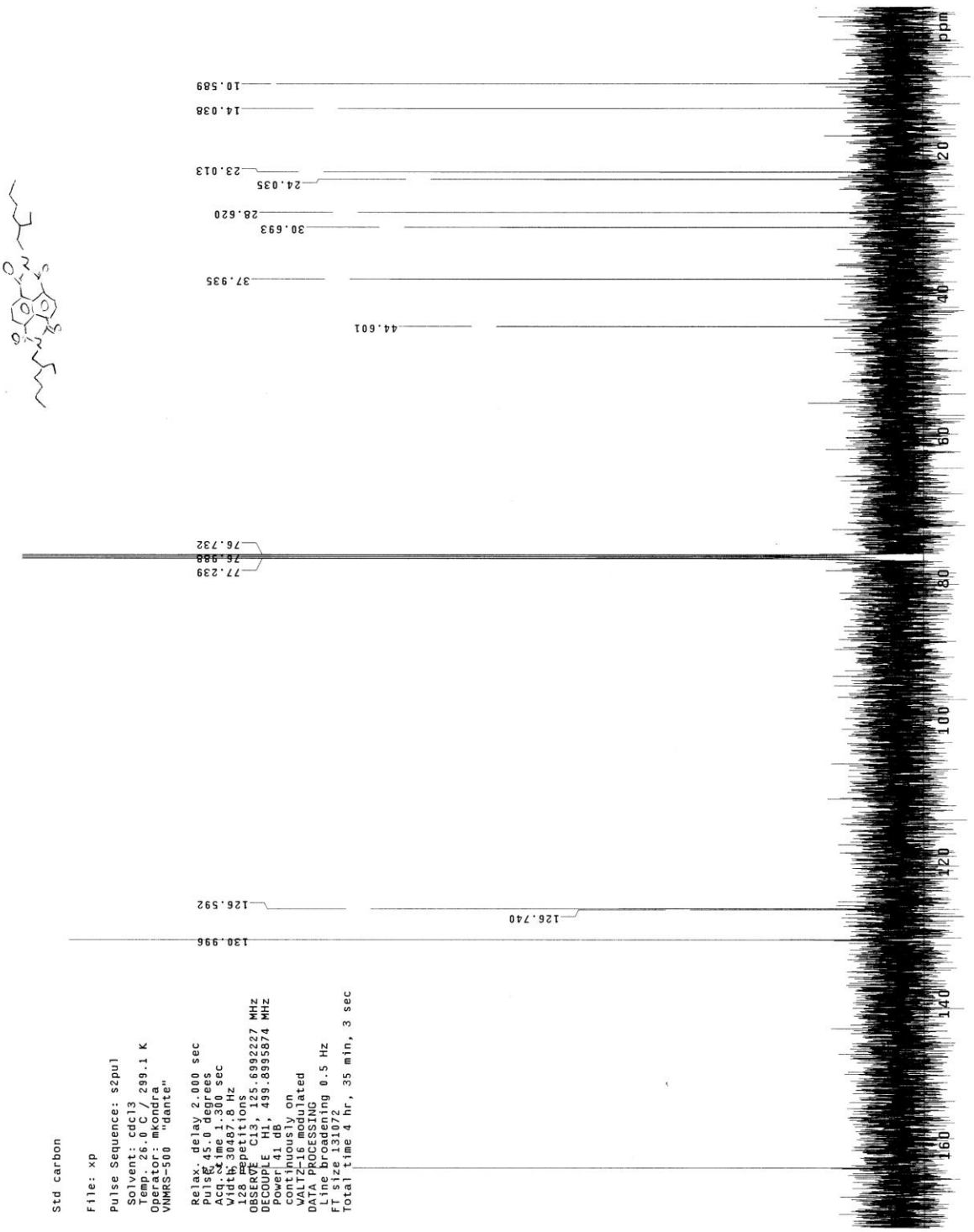
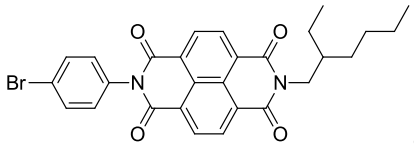
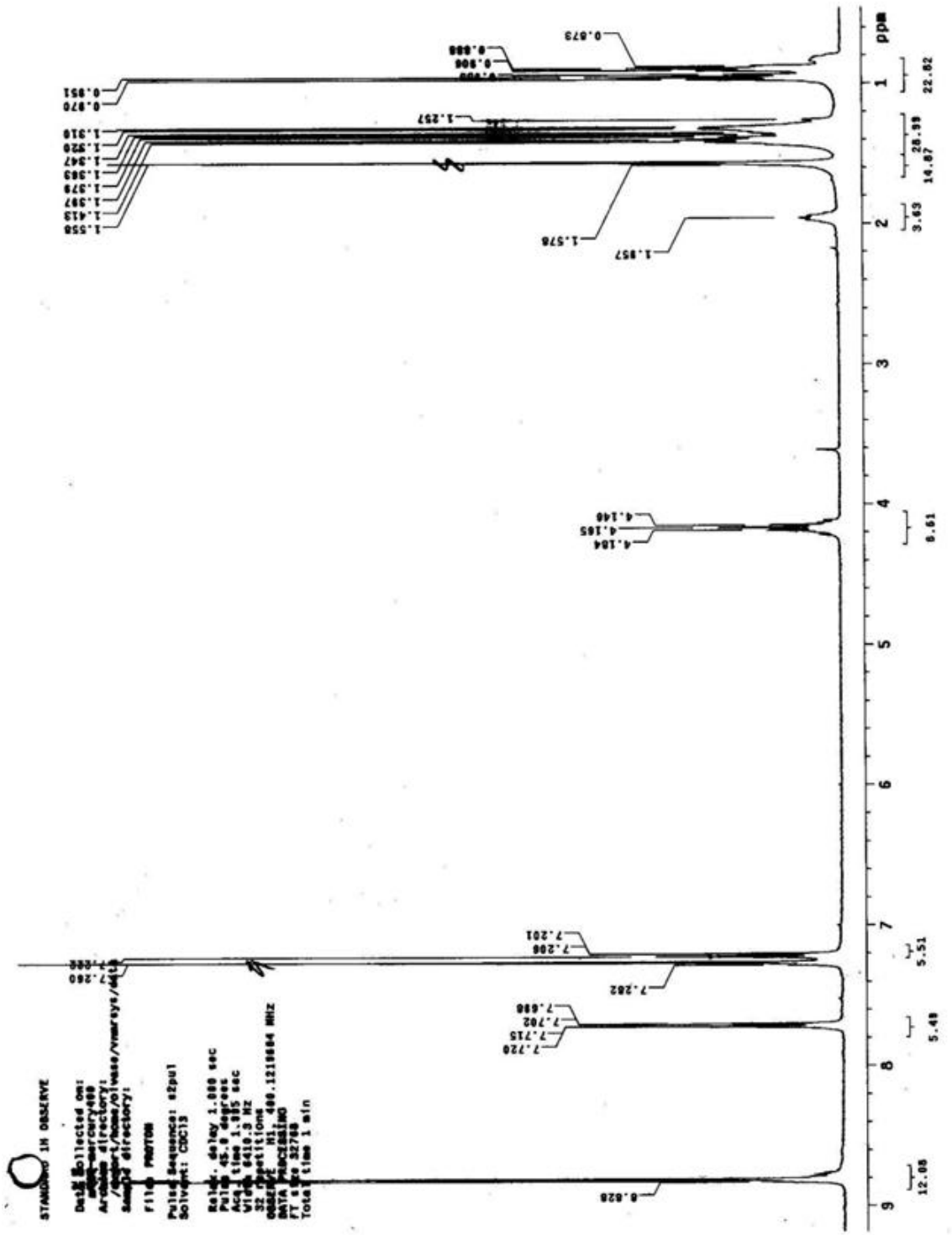
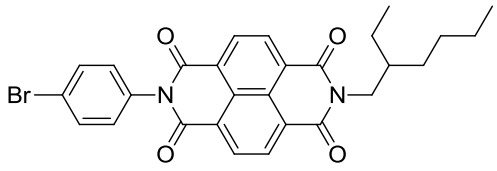




8a





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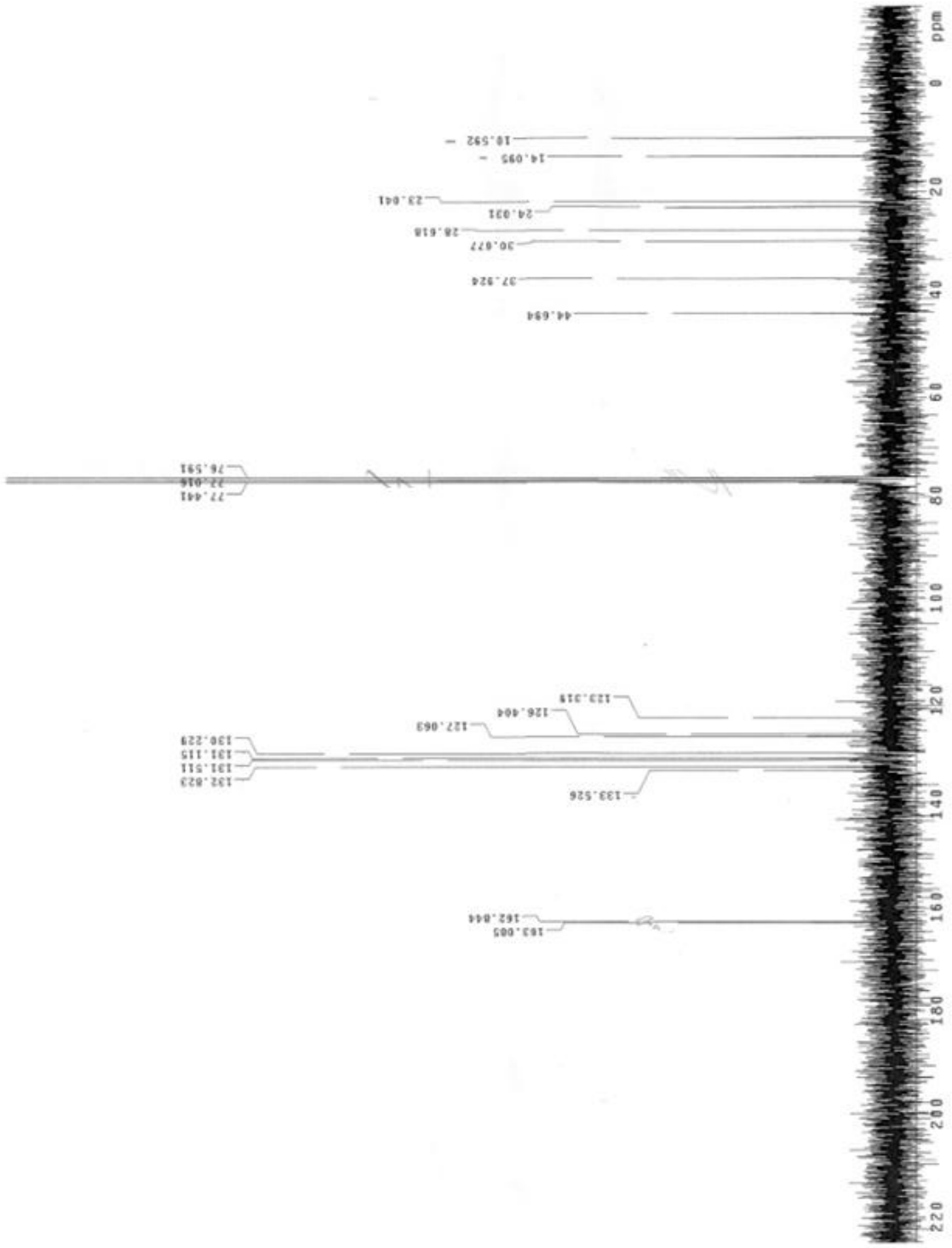
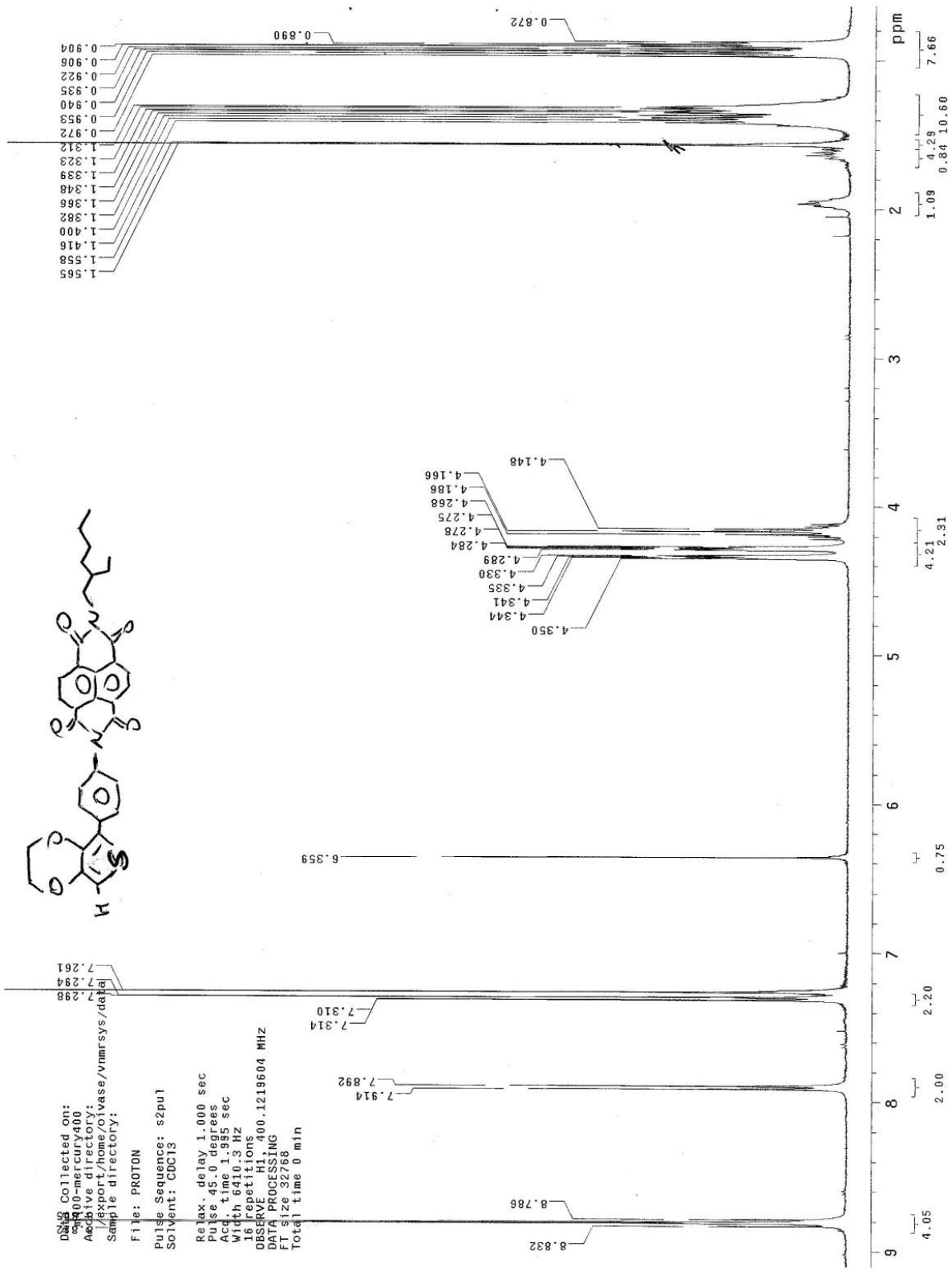
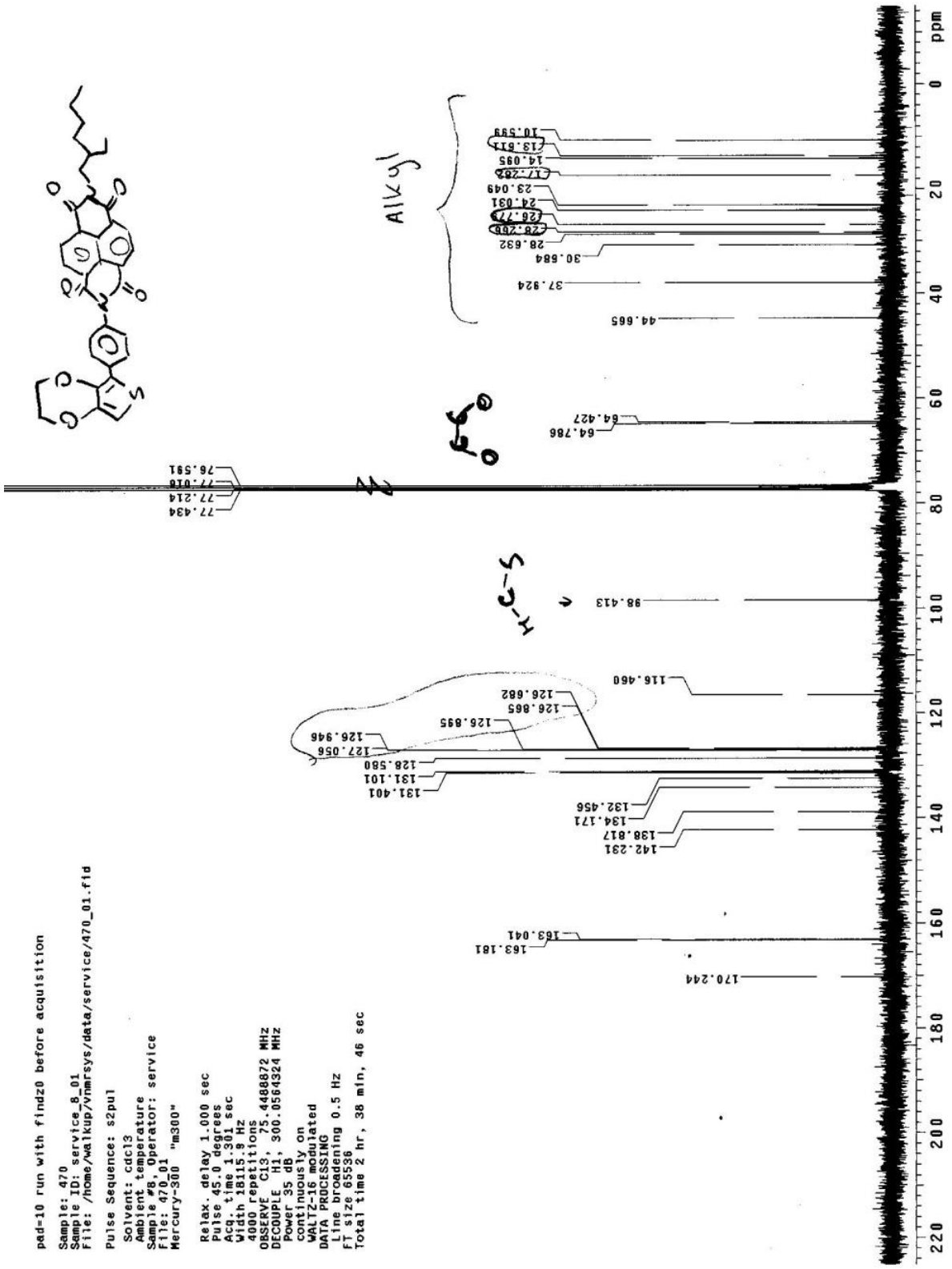


Dyad 1



Dyad 1



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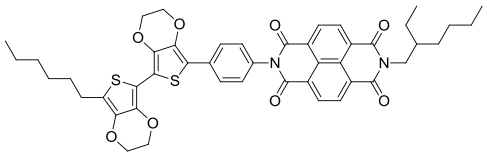

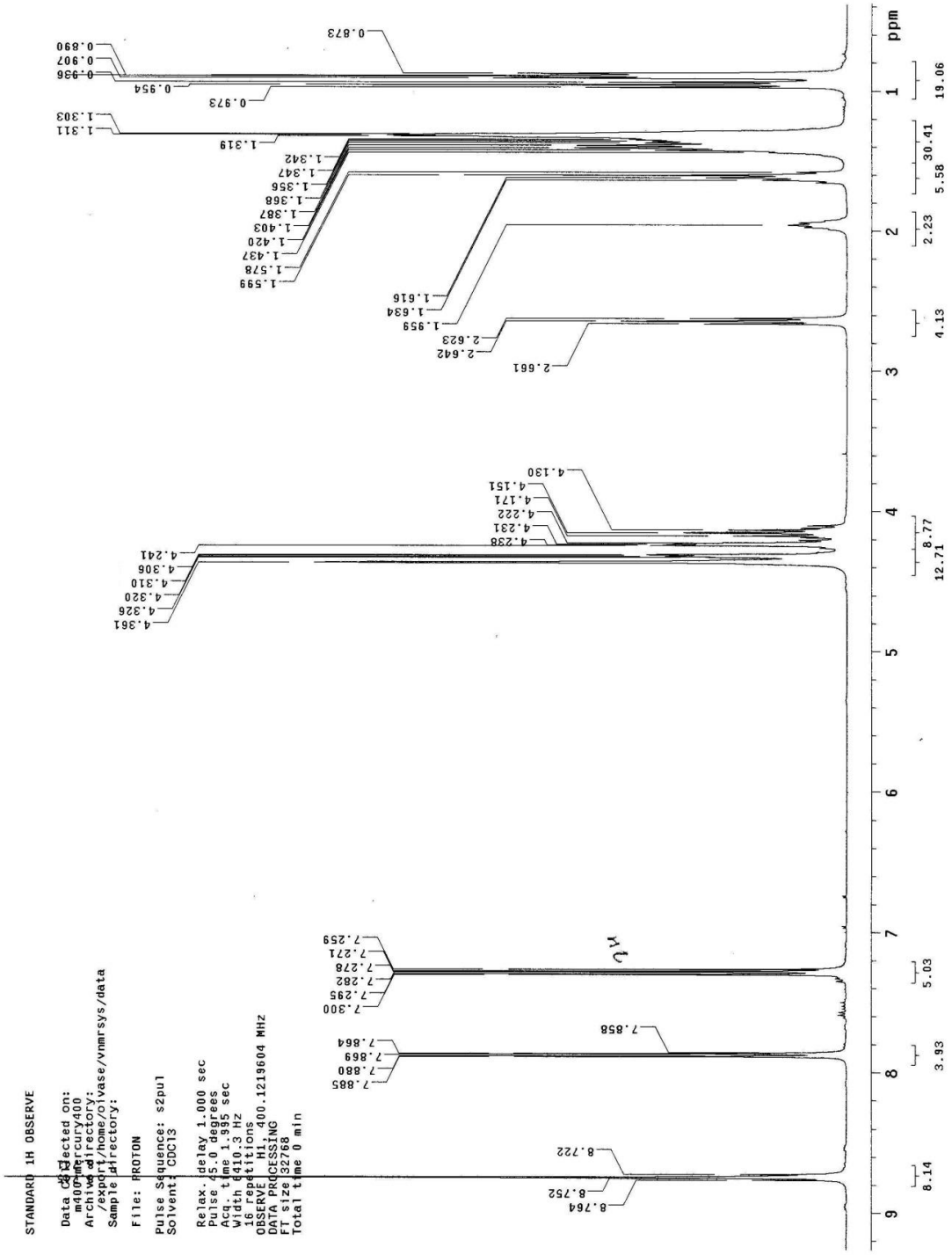

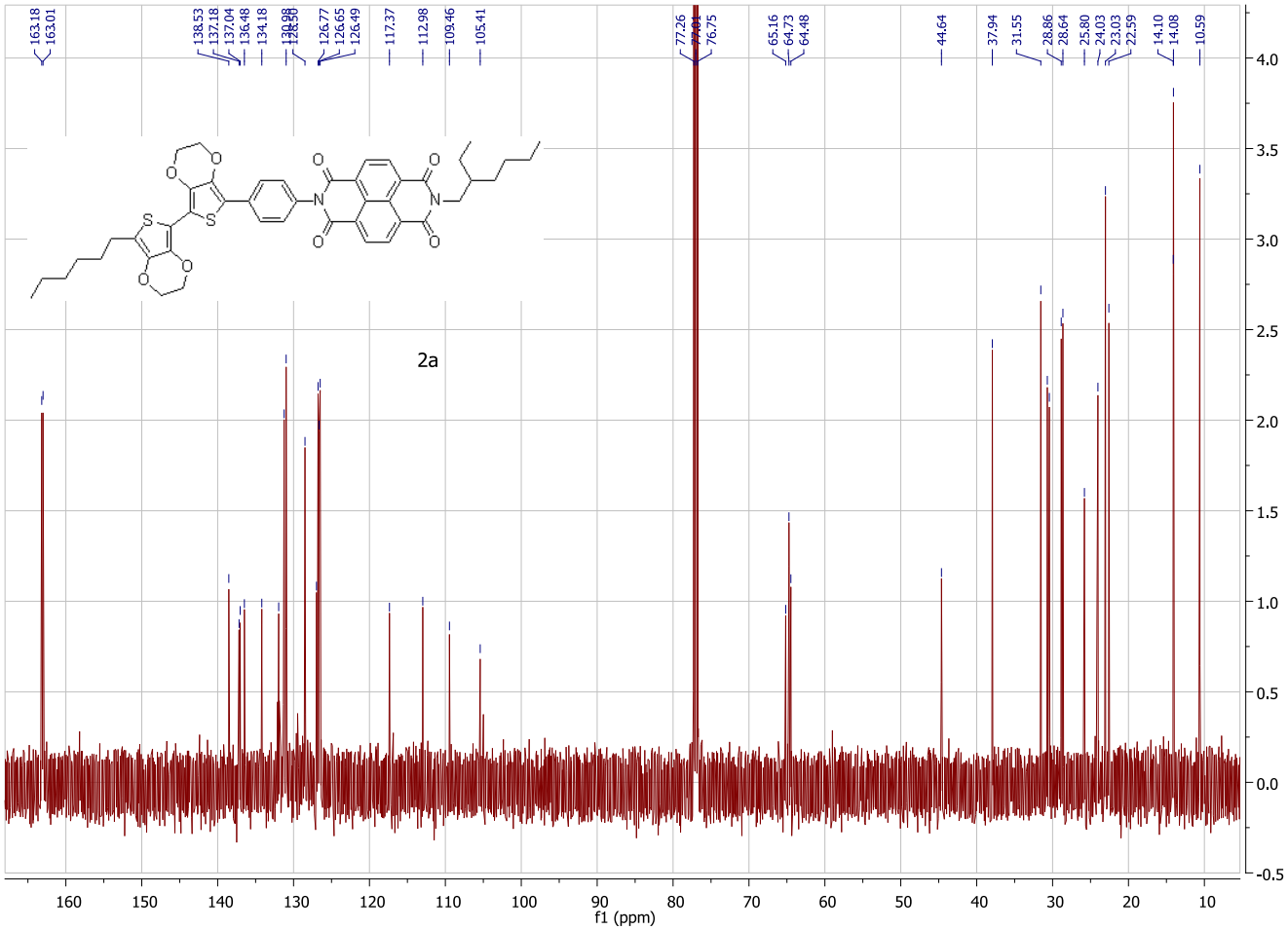

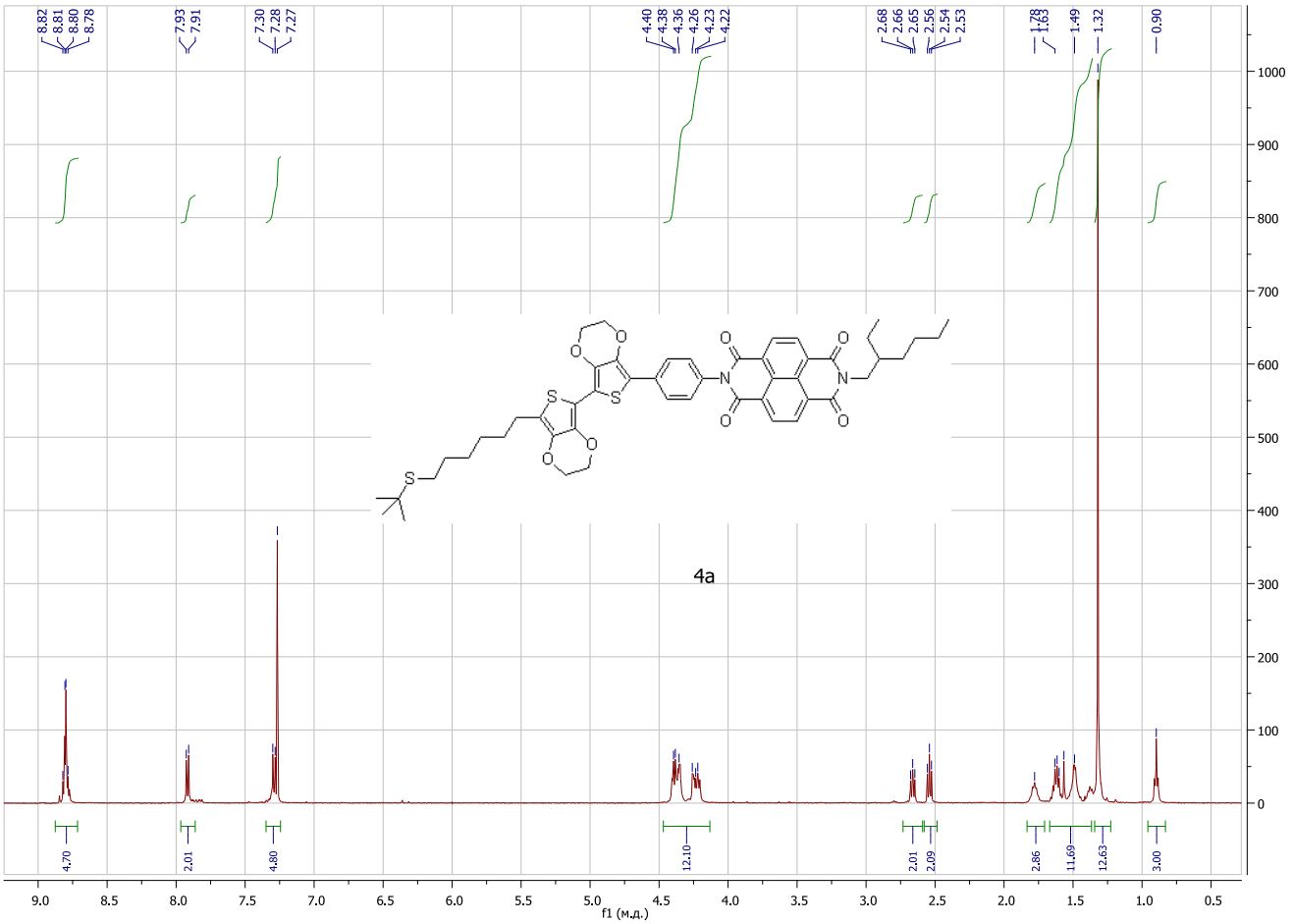

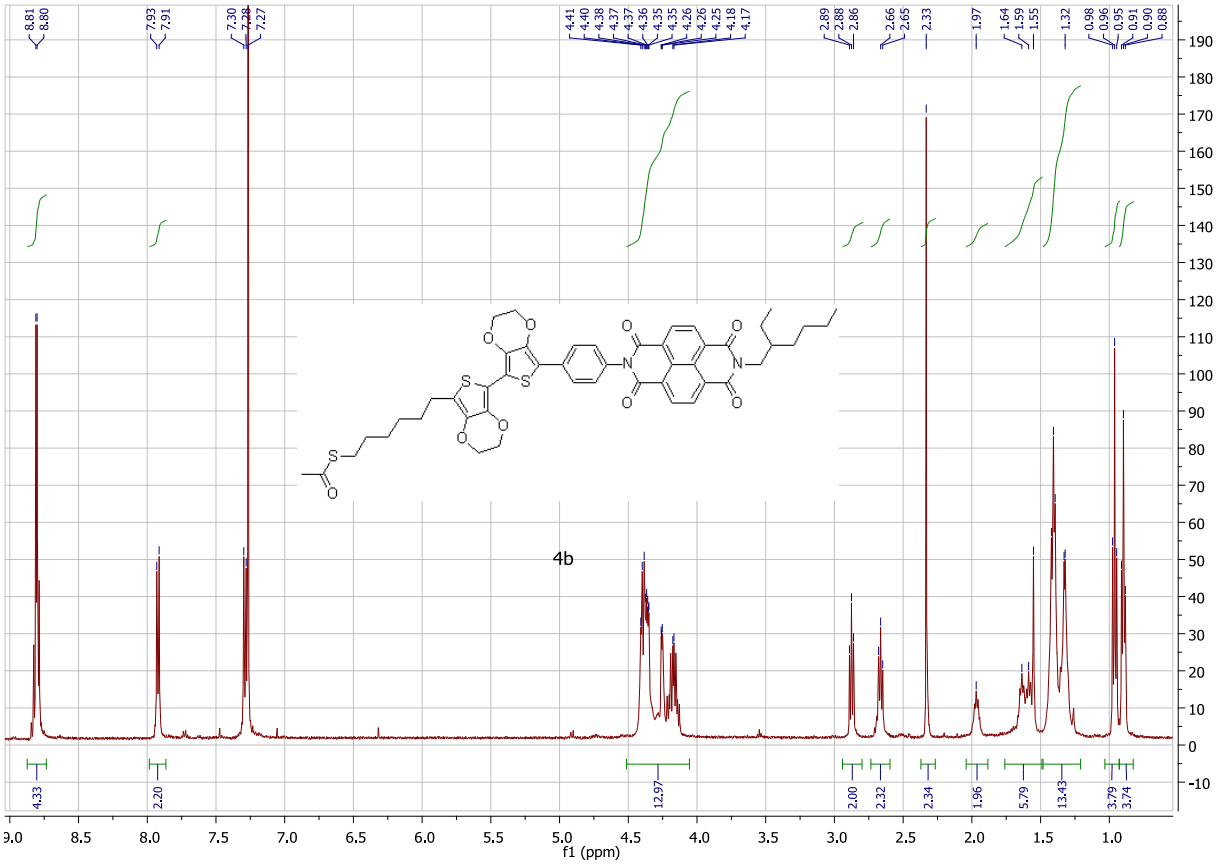

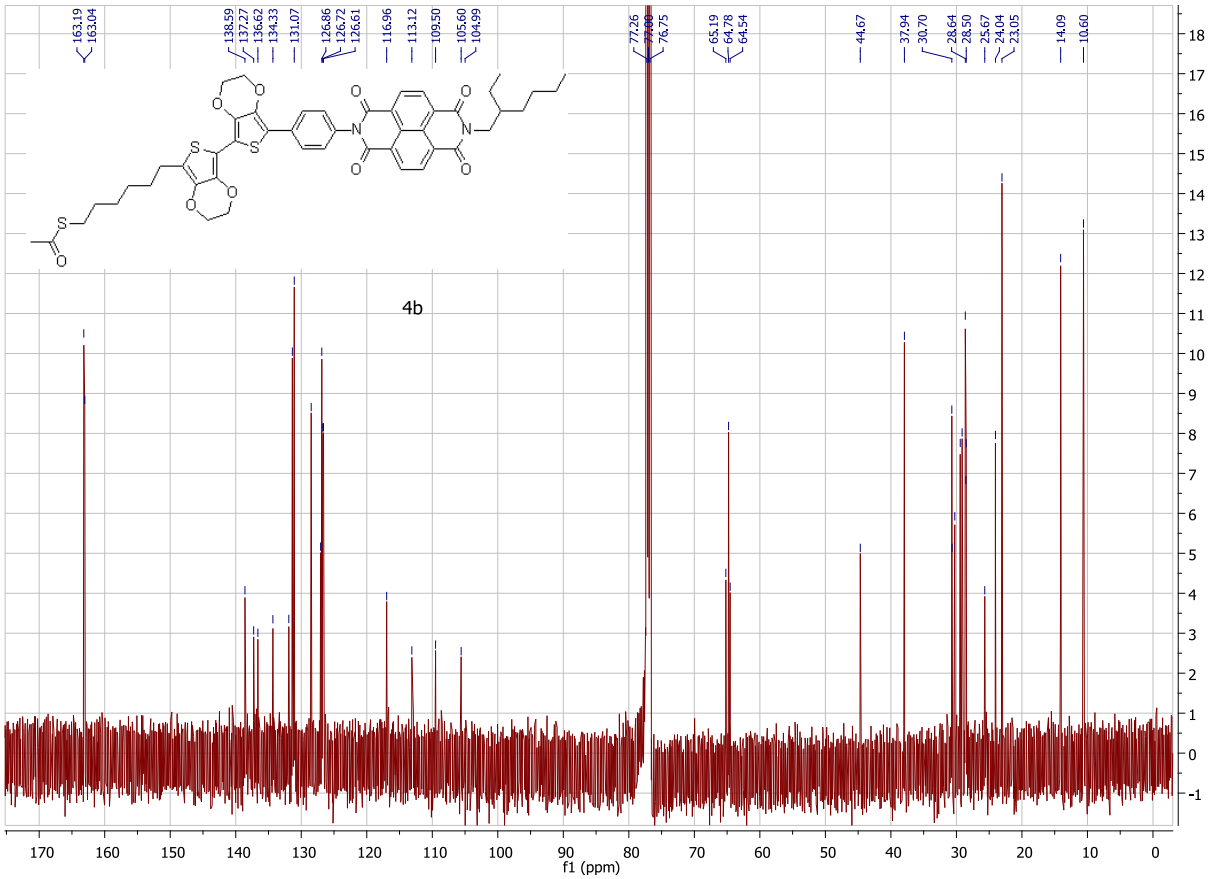

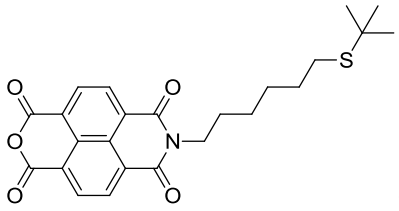

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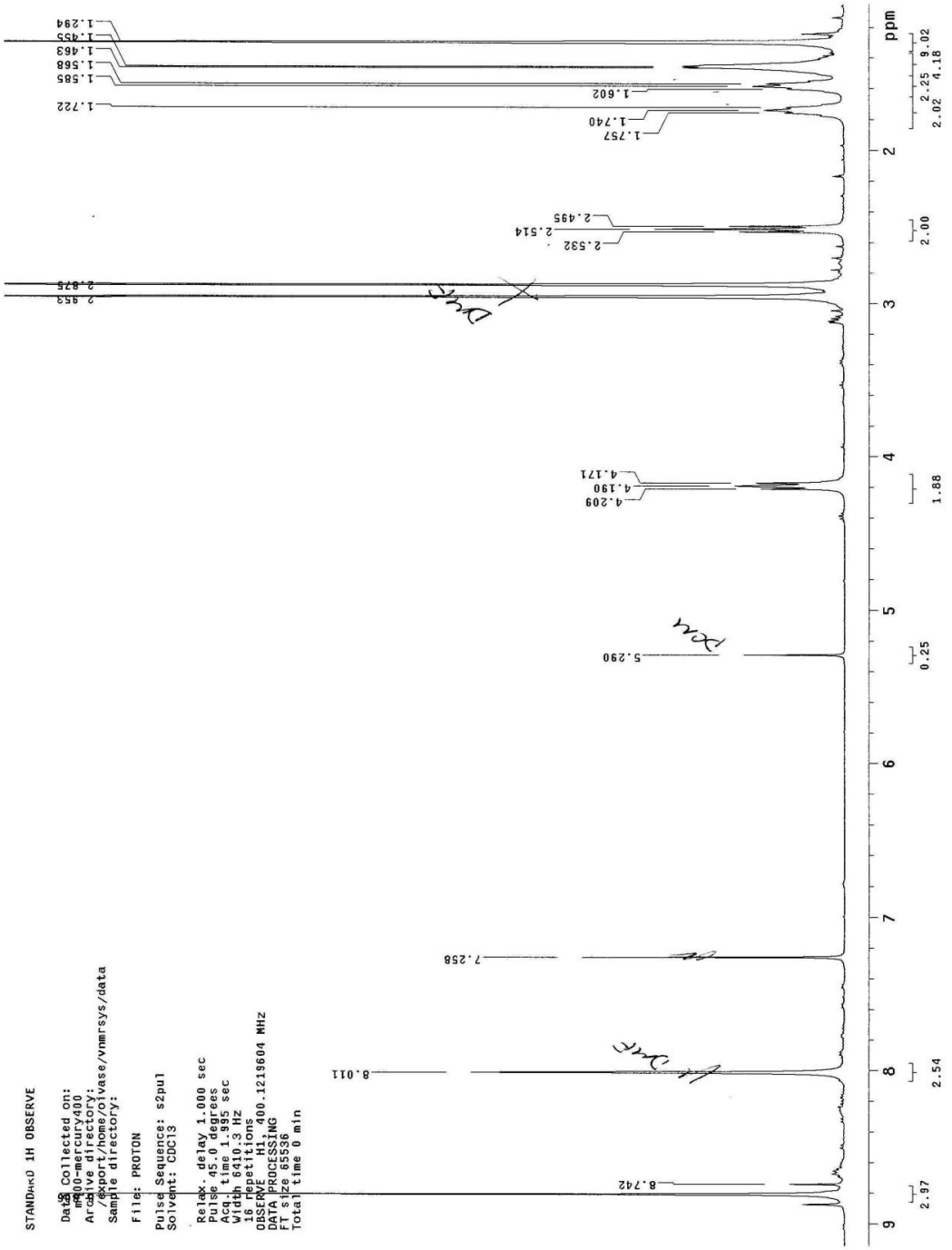

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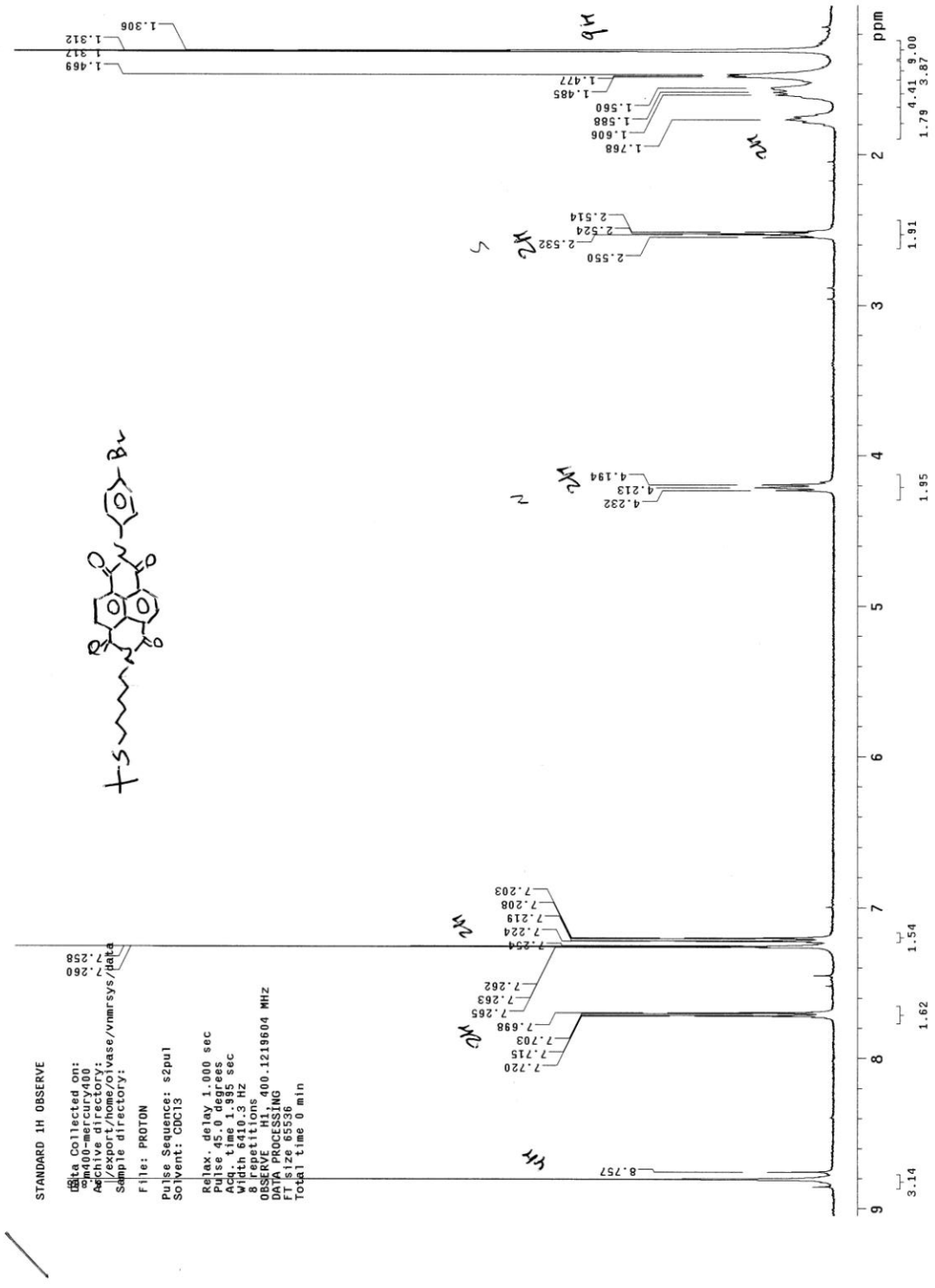

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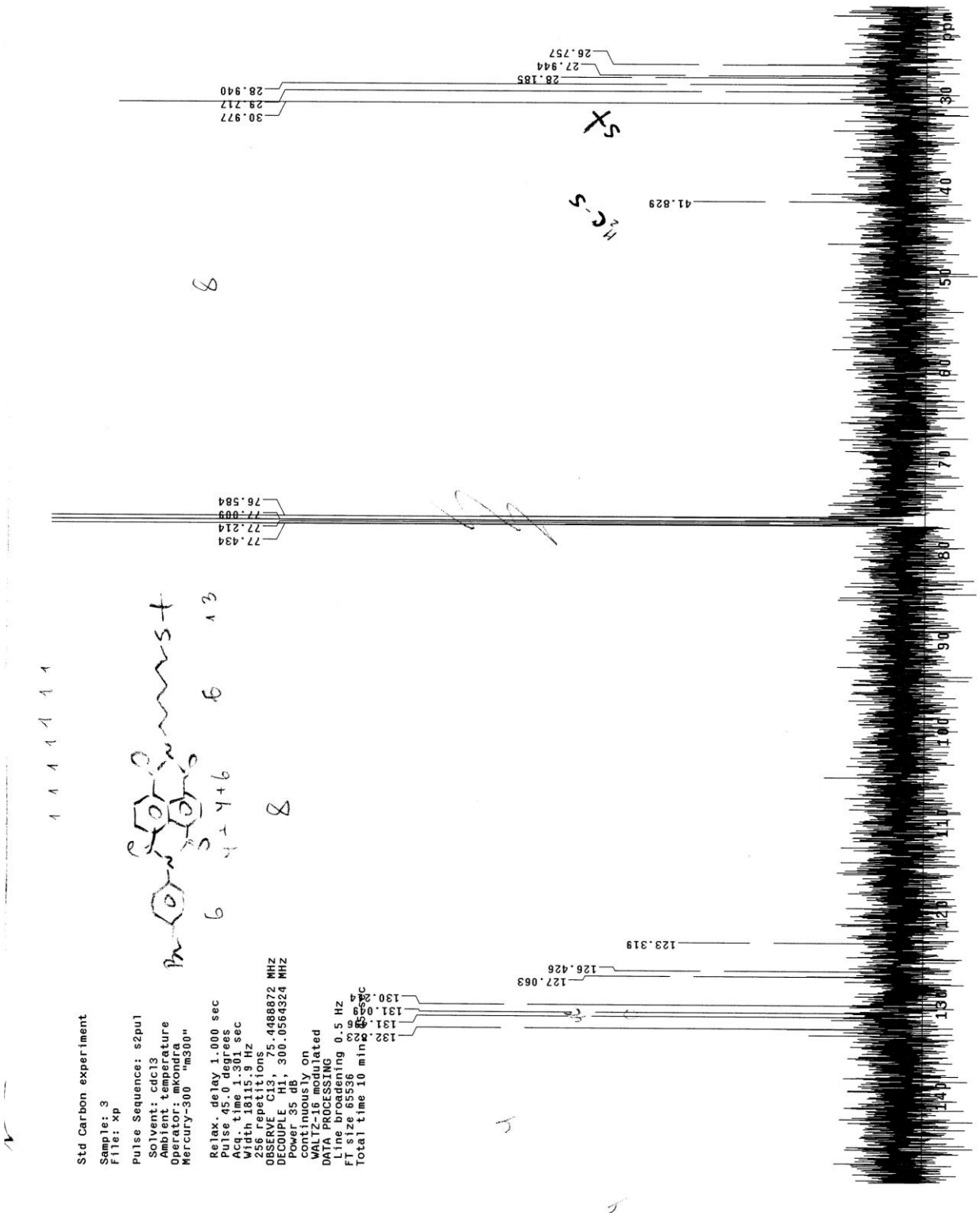

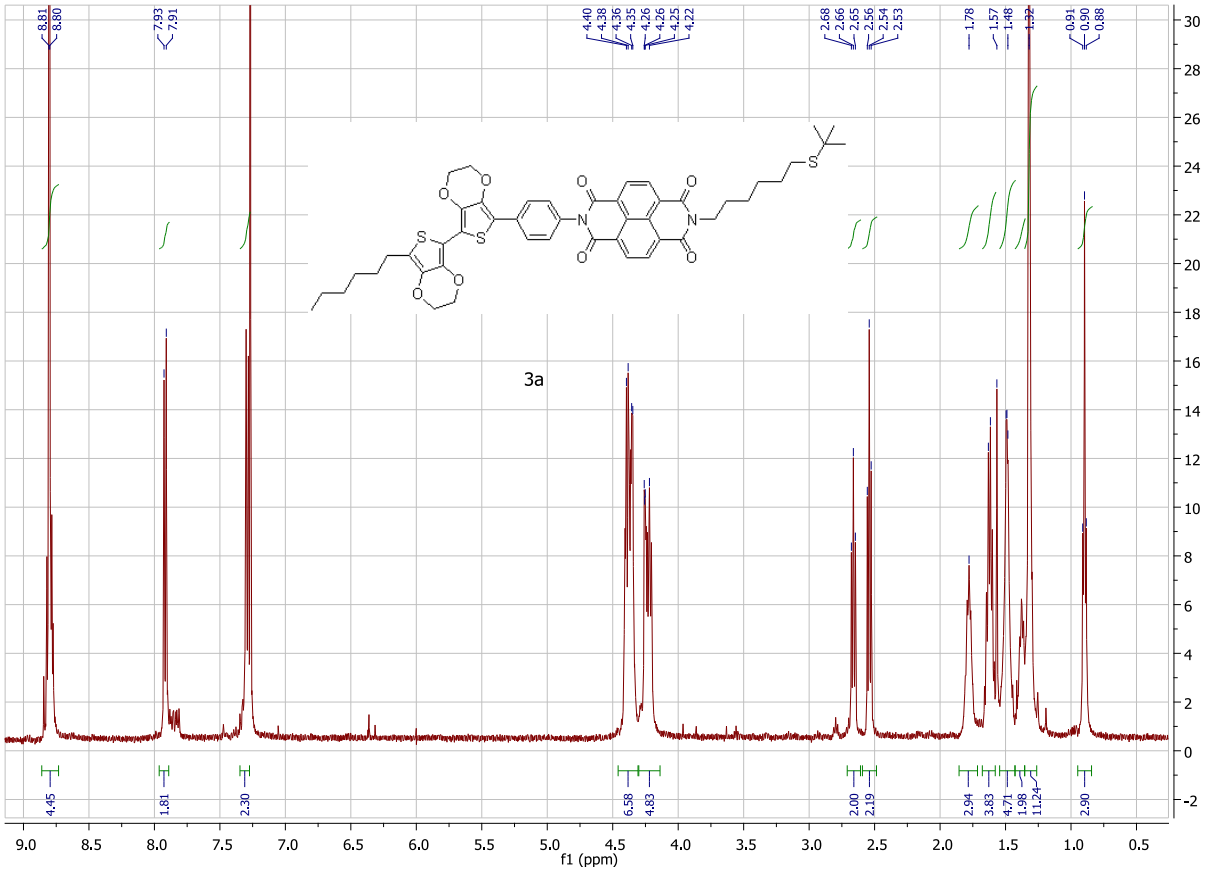

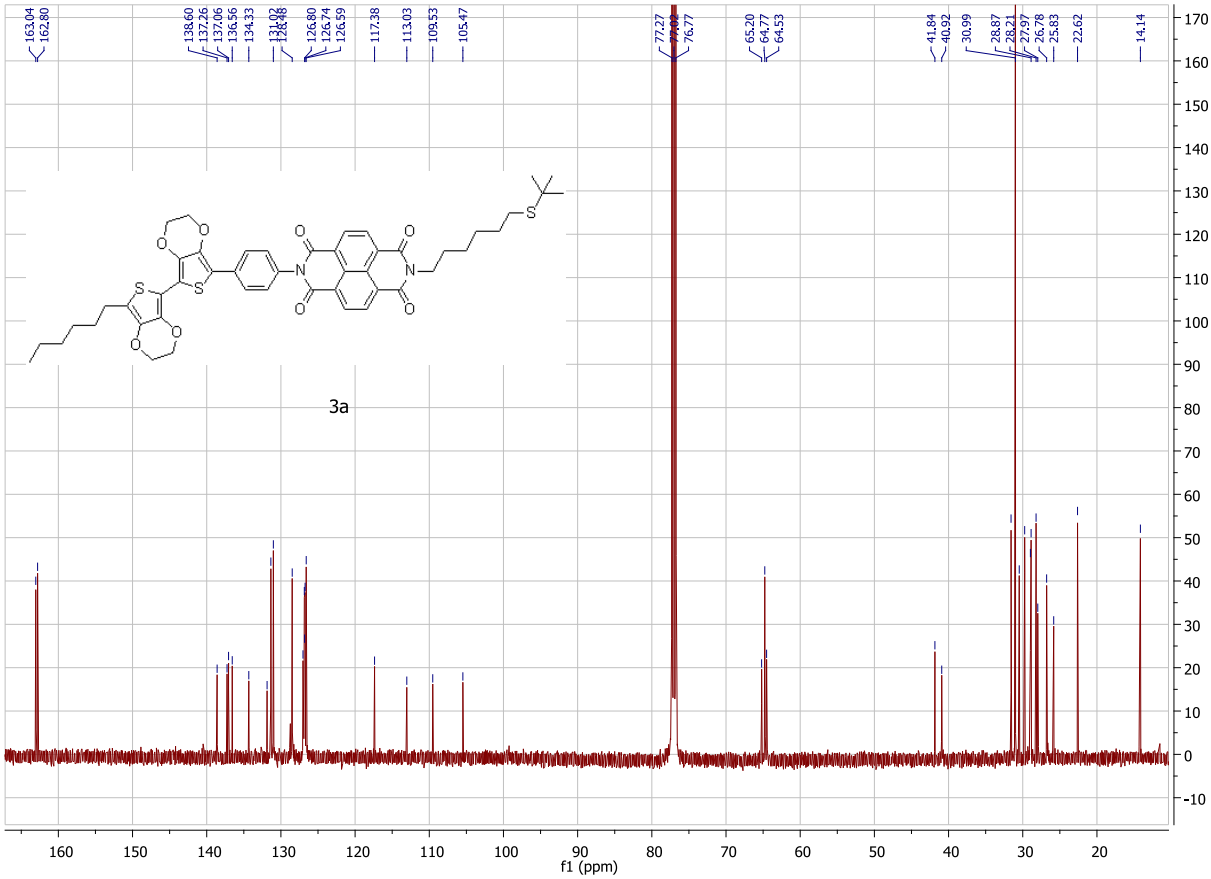

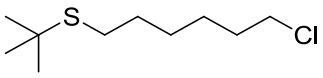

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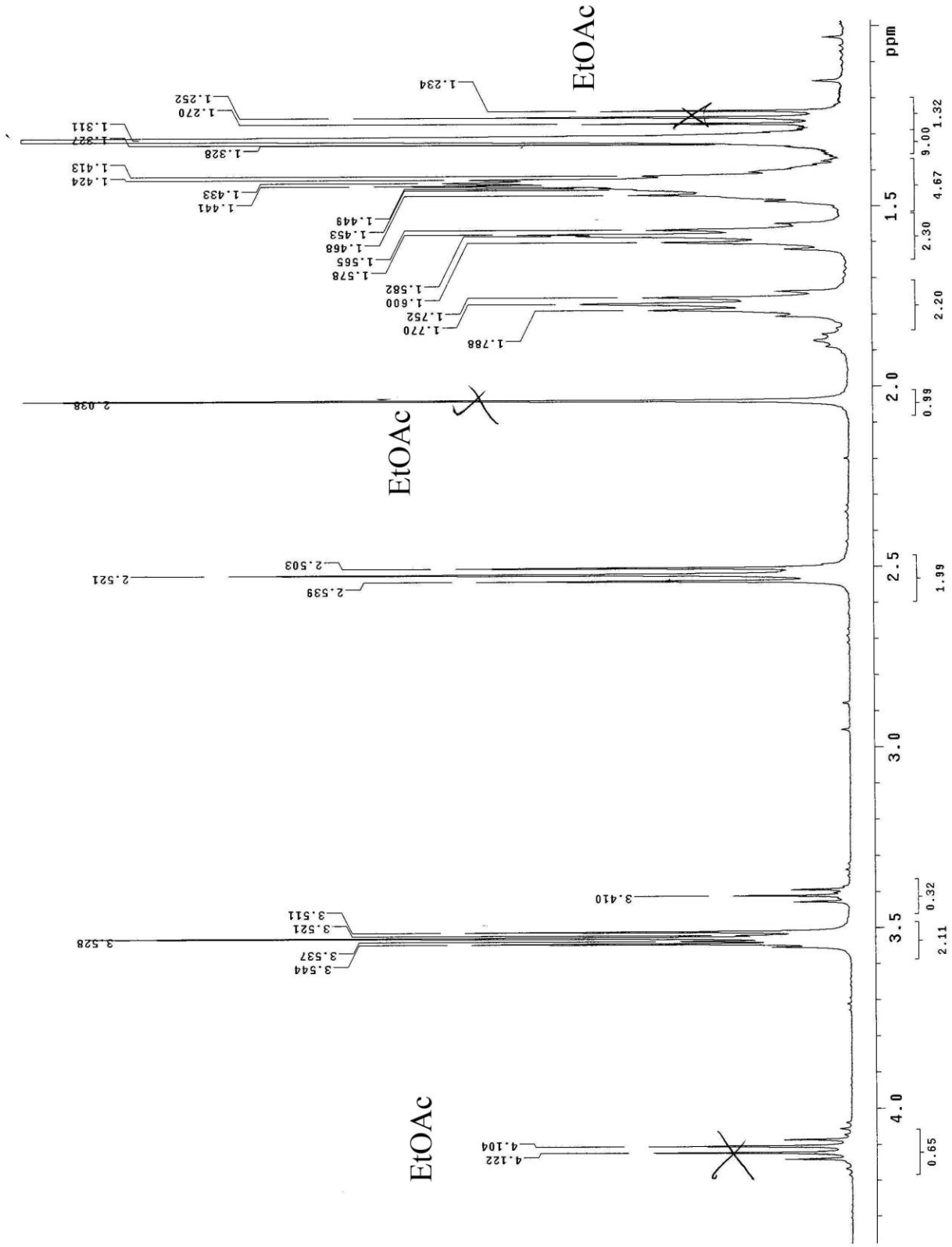

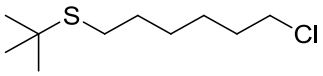

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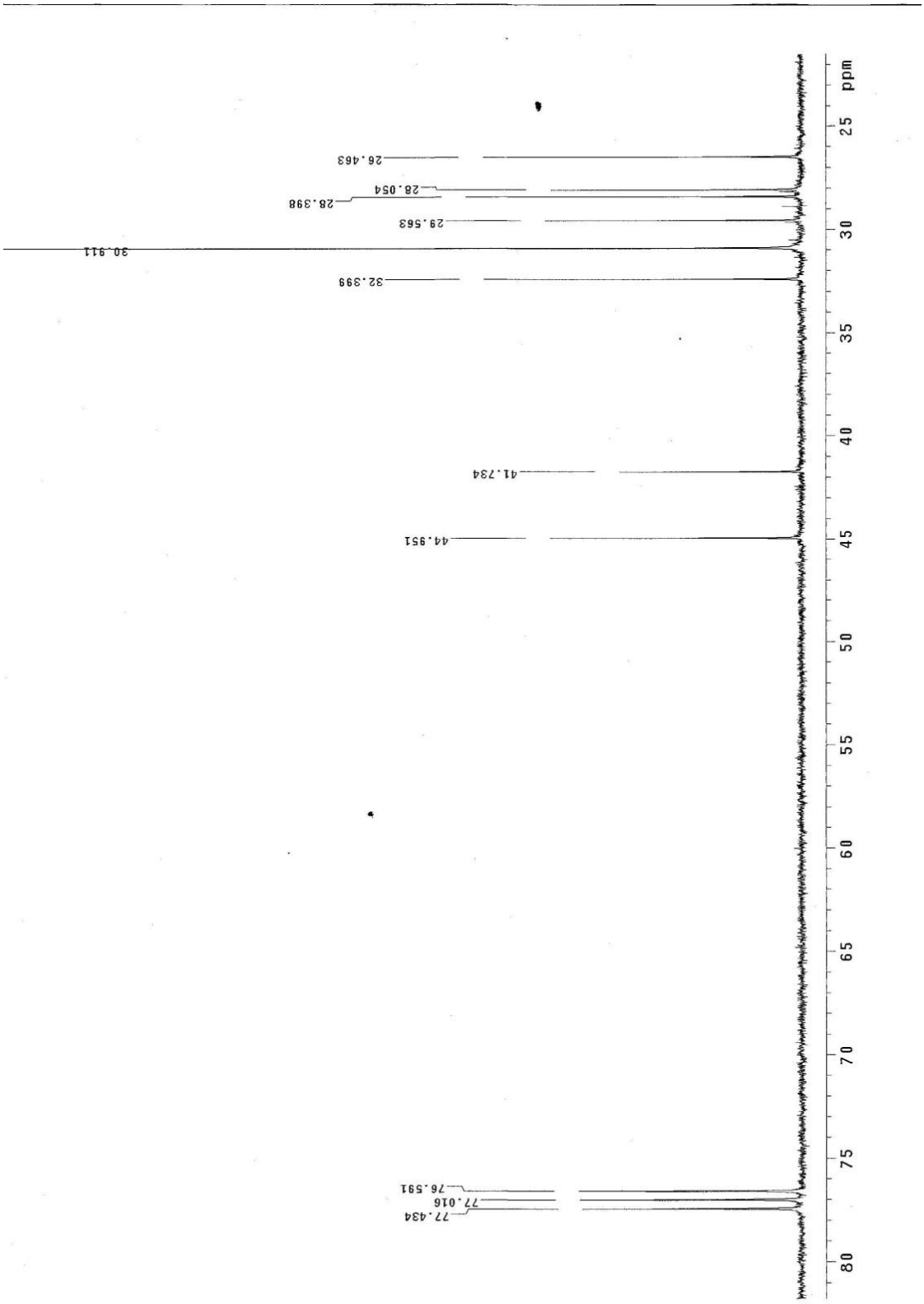

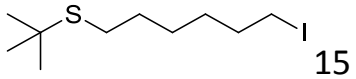

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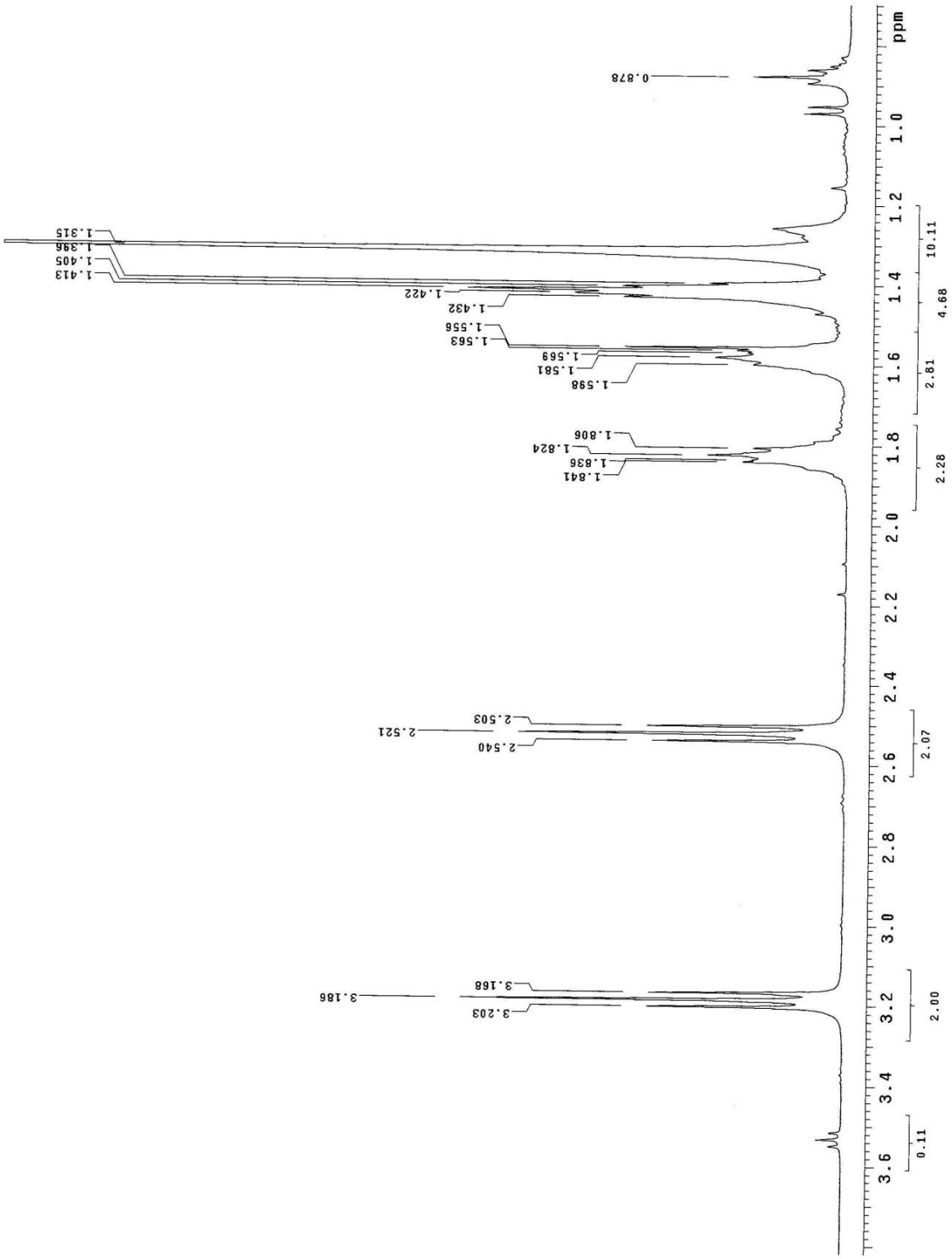

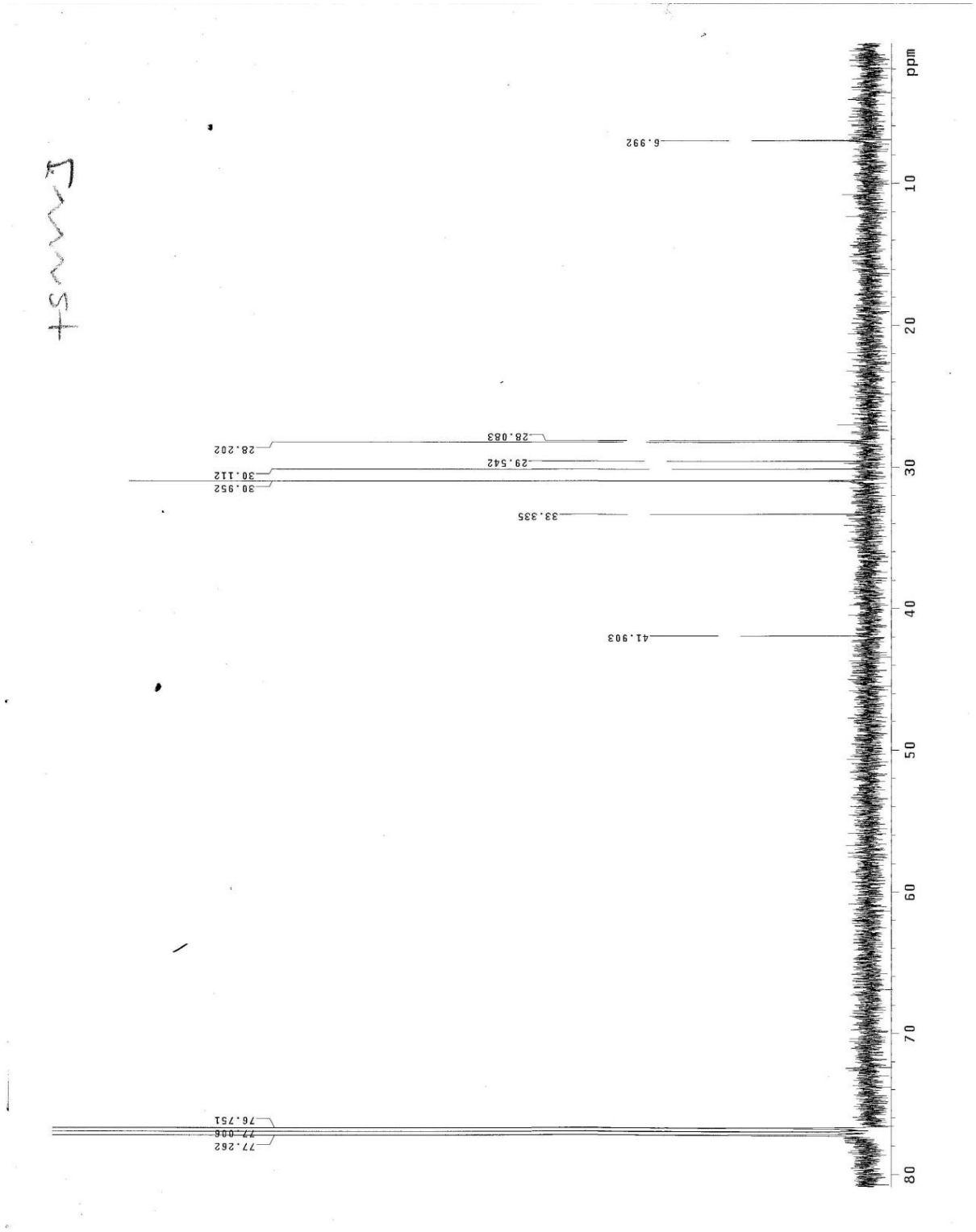

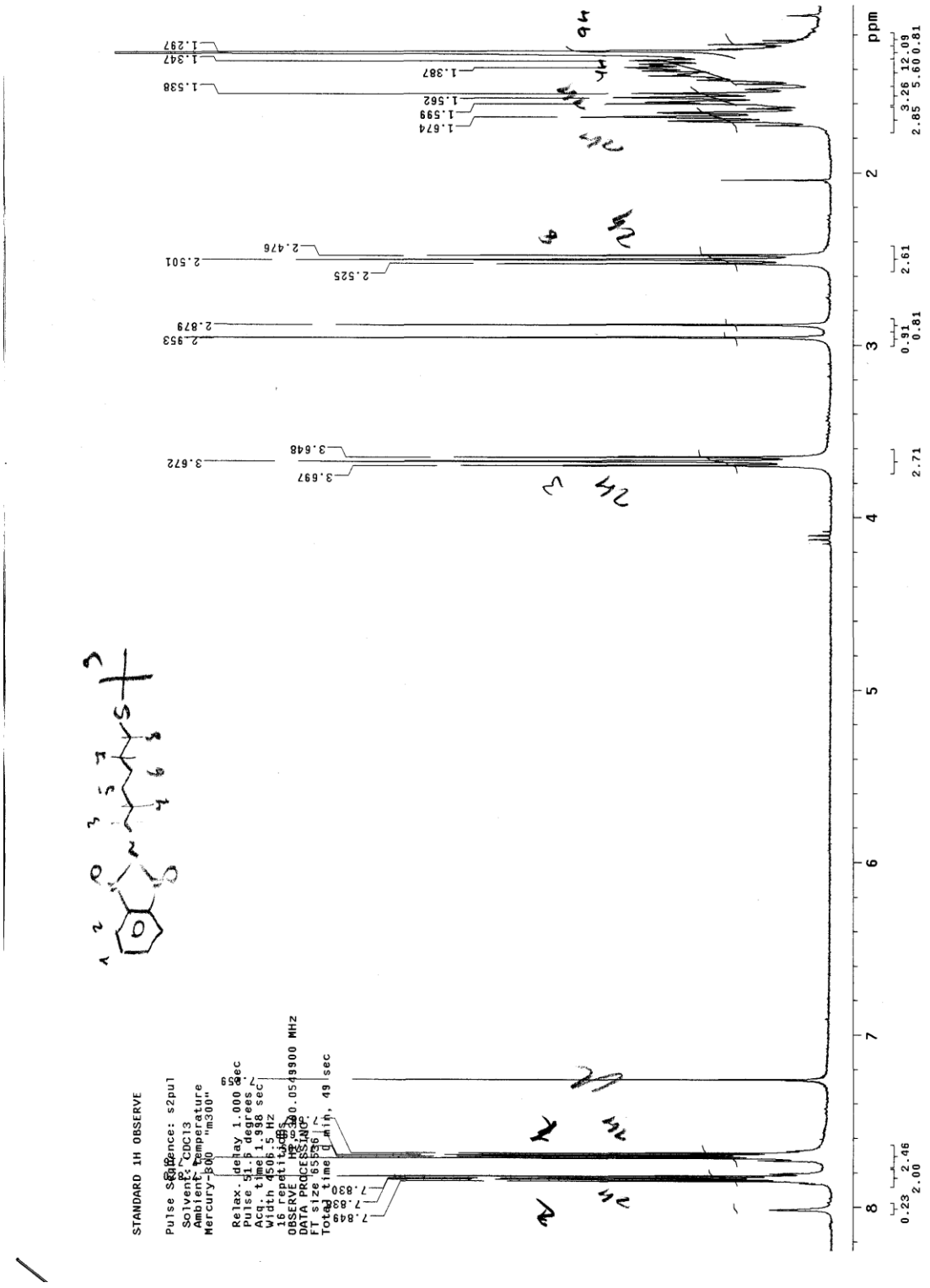

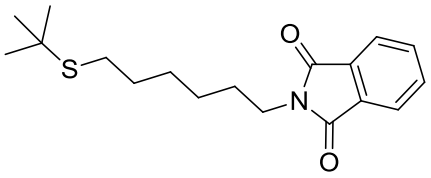

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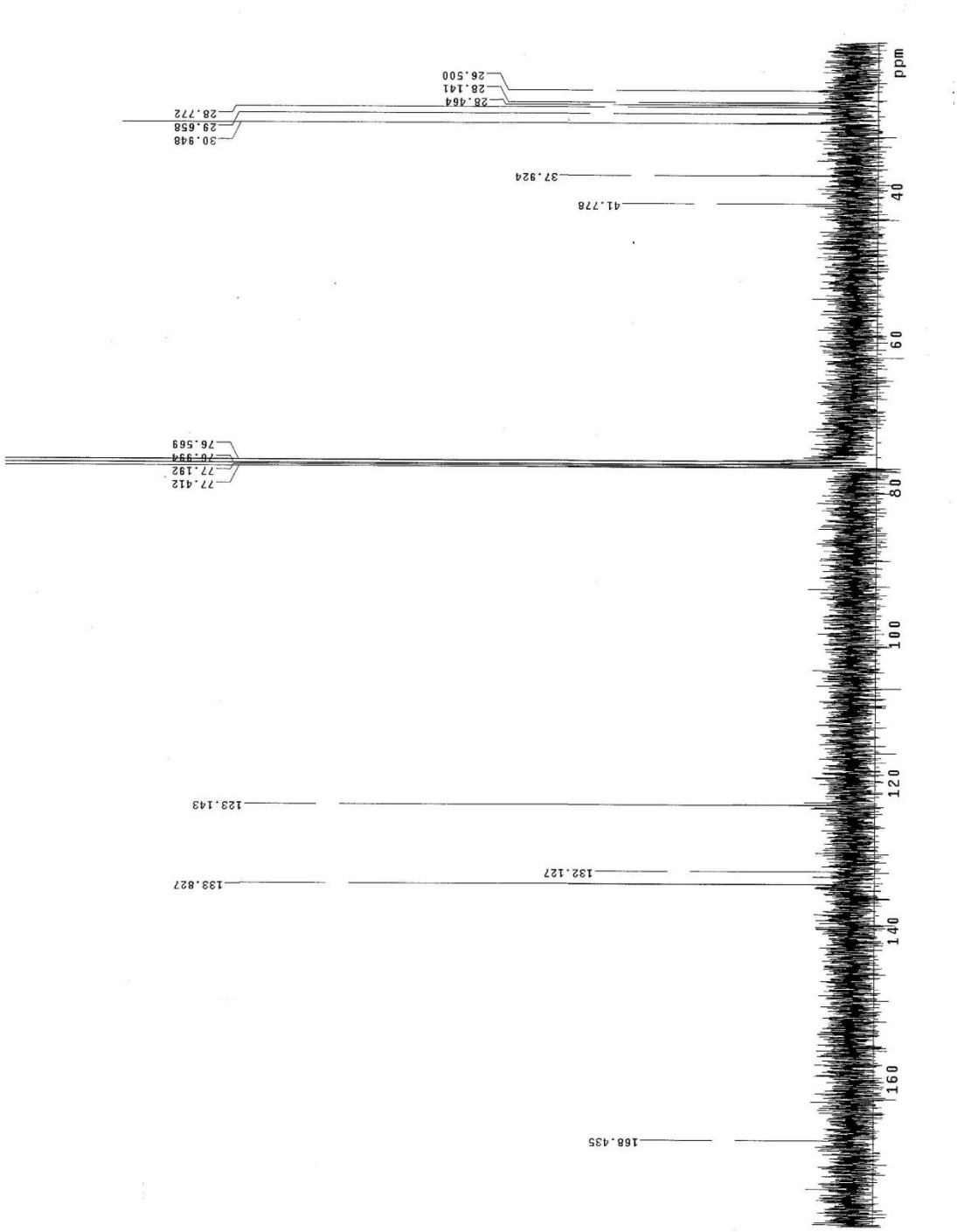

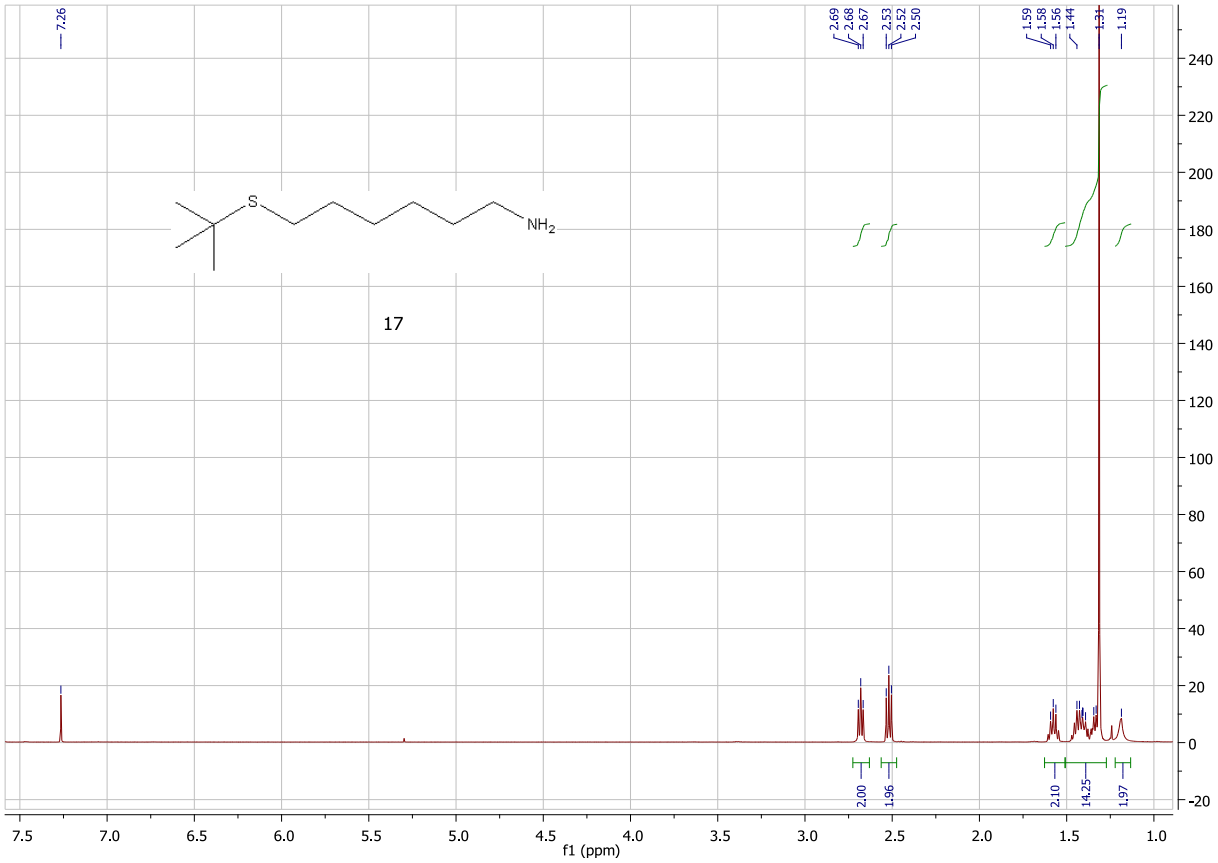

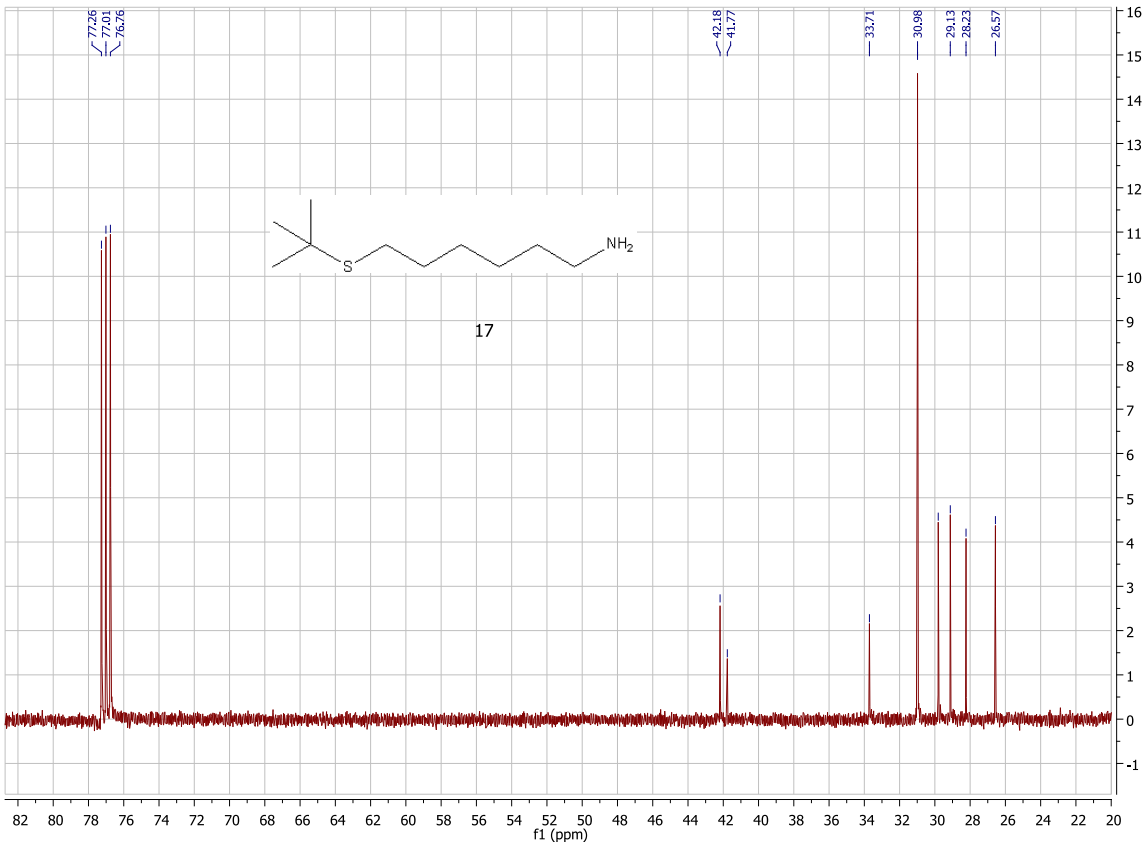

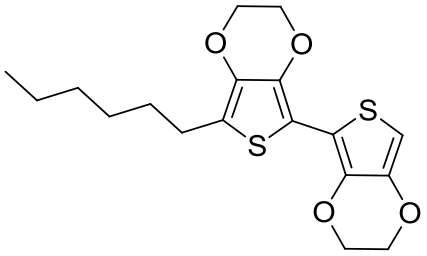

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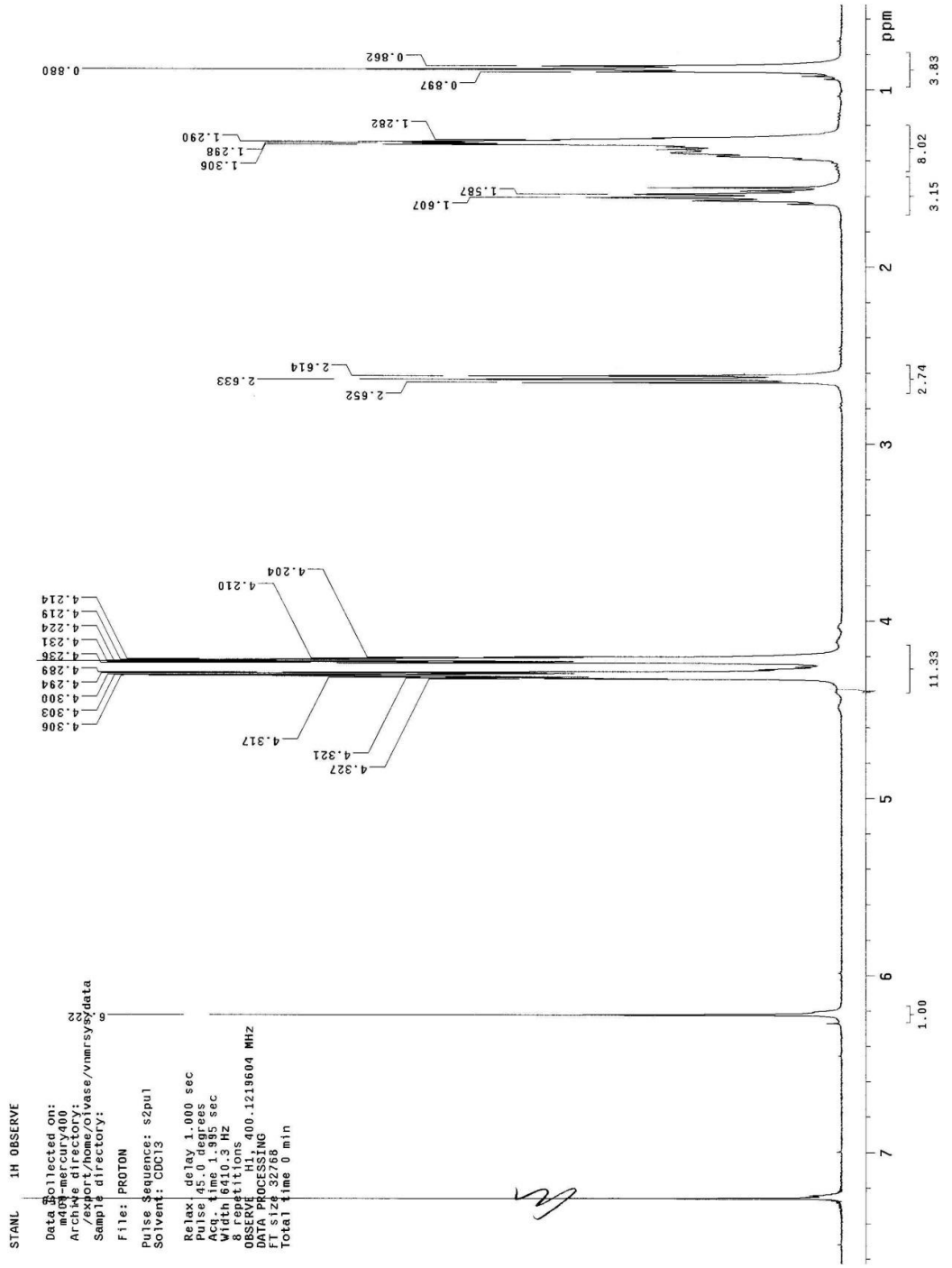

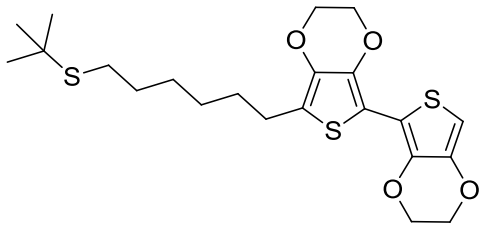

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