Novel chromophores from alternated pyridine-ethylenedioxythiophene units oligomers: dramatic enhancement of photoluminescence properties in elongated derivatives

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Table of Contents

General Methods

All reactions were performed under argon atmosphere. THF was distilled over sodium/benzophenone. Liquid chromatography separations were achieved on silica gel Merck Geduran Si 60 (40–63 μm). Melting points were measured on a Kofler apparatus.

Nuclear magnetic resonance (NMR) spectra were recorded on Bruker ARX-200 (200 MHz and 50 MHz for ^{1}H and ^{13}C respectively) and Bruker AC-300 (300 MHz and 75 MHz for ^{1}H and ^{13}C respectively) spectrometers. ^{1}H chemical shifts (δ) are given in ppm relative to the solvent residual peak, and ^{13}C chemical shifts relative to the central peak of the solvent signal.[1] Coupling constants are given in Hz. *High resolution mass spectra* measurements and *elemental analyses* were performed at the CRMPO in Rennes (Centre Régional de Mesures Physiques de l'Ouest) using respectively a Micromass MS/MS ZABSpec TOF instrument in EI mode and a Thermo-Finnigan Flash EA 1112 CHNS analyzer.

UV/VIS spectra were recorded on a Jasco V-570 spectrophotometer.

Steady-state fluorescence measurements were performed at rt on dilute solutions (ca. 10^{-6} M) using an Edinburgh Instruments (FLS 920) spectrometer working in photon-counting mode, equipped with a calibrated quantum counter for excitation correction. Fully corrected emission spectra were obtained, for each compound, at $\lambda_{ex} = \lambda_{max}^{abs}$ with $A_{\lambda_{ex}} \leq 0.1$ to minimize internal absorption. Fluorescence quantum yields were measured using standard methods[2] on air-equilibrated samples at rt. The reported fluorescence quantum yields are within ± 10%.

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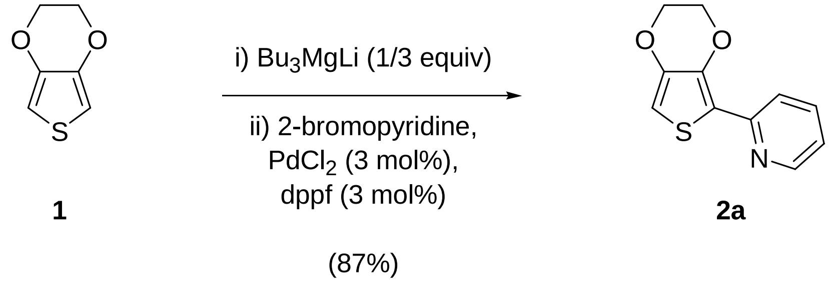
[1] H. E. Gottlieb, V. Kotlyar and A. Nudelman, *J. Org. Chem.,* 1997, **62**, 7512–7515.
[2] D. F. Eaton, *J. Photochem. Photobiol. B*, 1988, **2**, 523–531.

Fluorescence lifetimes were measured by time-correlated single photon counting (TCSPC) using the same FLS 920 fluorimeter. Excitation was achieved by a hydrogen-filled nanosecond flashlamp (repetition rate 40 kHz). The instrument response (FWHM ca. 1 ns) was determined by measuring the light scattered by a Ludox suspension. The TCSPC traces were analyzed by standard iterative reconvolution methods implemented in the software of the fluorimeter. All compounds displayed strictly monoexponential fluorescence decays ($\chi^2 < 1.1$).

Procedures and Characterization of Products



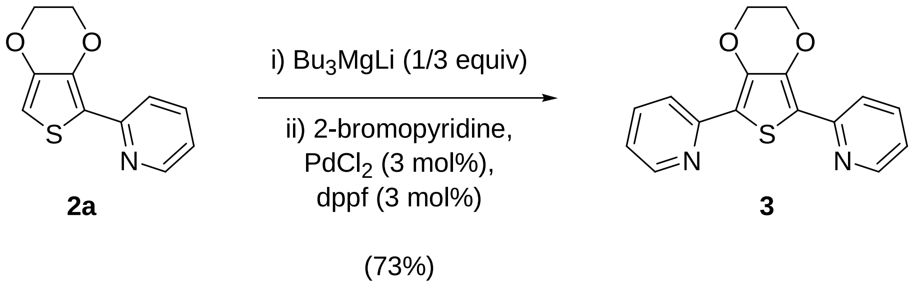
2-(3,4-Ethylenedioxythienyl)pyridine (2a). To a stirred suspension of Mg (24 mg, 1.0 mmol) in THF (5 mL) was added 1,2-dibromoethane (188 mg, 1.0 mmol) over 15 min. The reaction mixture was cooled to -10 °C before addition of *n*-BuLi (1.6 M hexanes solution, 3.00 mmol). After 1 h at the same temperature, 3,4-ethylenedioxythiophene (426 mg, 3.00 mmol) was added and the reaction mixture was stirred for 2 h at room temperature. $PdCl_2$ (16 mg, 3 mol %), dppf (50 mg, 3 mol %) and 2-bromopyridine (474 mg, 3.00 mmol) were successively added to the solution. The reaction mixture was stirred for 24 h at 60 °C, quenched with water (1 mL) and filtered over celite®. After addition of an aqueous saturated solution of NaCl (10 mL), the mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel (heptane/AcOEt: 9/1) gave **2a** (572 mg, 87%) as a white solid.

mp 54 °C.

^{1}H NMR ($CDCl_3$, 200 MHz) 4.22-4.37 (m, 4H), 6.43 (s, 1H), 7.05 (ddd, 1H, *J* = 1.1, 4.9 and 7.4), 7.63 (ddd, 1H, *J* = 1.8, 7.4 and 8.0), 7.92 (ddd, 1H, *J* = 1.1, 1.1 and 8.0), 8.51 (ddd, 1H, *J* = 1.1, 1.8 and 4.9).

^{13}C NMR ($CDCl_3$, 50 MHz) 64.4, 65.1, 101.4, 118.9, 120.4, 121.1, 136.4, 140.0, 142.1, 149.3, 151.7.

Anal. Calcd for $C_{11}H_9NO_2S$: C, 60.26; H, 4.14; N, 6.39; S, 14.62. Found: C, 60.24; H, 4.26; N, 6.31; S, 14.69.



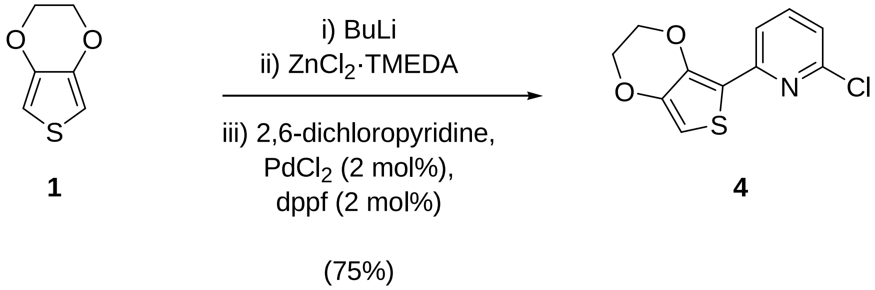
2,5-Bis(2-pyridyl)-3,4-ethylenedioxythiophene (3). To a stirred suspension of Mg (24 mg, 1.0 mmol) in THF (5 mL) was added 1,2-dibromoethane (188 mg, 1.0 mmol) over 15 min. The reaction mixture was cooled to -10 °C before addition of *n*-BuLi (1.6 M hexanes solution, 3.00 mmol). After 1 h at the same temperature, **2a** (658 mg, 3.00 mmol) was added and the reaction mixture was stirred for 2 h at room temperature. $PdCl_2$ (16 mg, 3 mol %), dppf (50 mg, 3 mol %) and 2-bromopyridine (474 mg, 3.00 mmol) were successively added to the solution. The reaction mixture was stirred for 24 h at 60 °C, quenched with water (1 mL) and filtered over celite®. After addition of an aqueous saturated solution of NaCl (10 mL), the mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel (heptane/AcOEt: 7/3) and crystallization in dichloromethane gave **3** (649 mg, 73%) as yellow crystals.

mp 189 °C.

^{1}H NMR ($CDCl_3$, 200 MHz) 4.29 (s, 4H), 6.95 (br dd, 2H, *J* = 4.8 and 7.4), 7.52 (br dd, 2H, *J* = 7.4 and 8.1), 7.81 (br d, 2H, *J* = 8.1), 8.44 (br d, 2H, *J* = 4.8).

^{13}C NMR ($CDCl_3$, 50 MHz) 64.8 (2C), 119.9 (2C), 121.0 (2C), 121.3 (2C), 136.3 (2C), 140.0 (2C), 149.4 (2C), 151.6 (2C).

Anal. Calcd for $C_{16}H_{12}N_2O_2S$: C, 64.85; H, 4.08; N, 9.45, S, 10.82. Found: C, 64.80; H, 4.10; N, 9.63, S, 11.27.



2-Chloro-6-(3,4-ethylenedioxy-2-thienyl)pyridine (4). To a stirred, cooled (-78 °C) solution of 3,4-ethylenedioxythiophene (426 mg, 3.00 mmol) in dry THF (5 mL) was slowly added *n*-BuLi (1.6 M hexanes solution, 3.00 mmol). The temperature was slowly raised to 0 °C before introduction $ZnCl_2$·TMEDA[3] (757 mg, 3.00 mmol). The mixture was stirred for 1 h at 0 °C and $PdCl_2$ (11 mg, 2 mol %), dppf (33 mg, 2 mol %), 2,6-dichloropyridine (444 mg, 3.00 mmol) were successively added. The reaction mixture was stirred for 48 h at 60 °C, quenched with water (1 mL) and filtered over celite®. After addition of an aqueous saturated solution of NaCl (10 mL), the mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel (heptane/CH_2Cl_2: 6/4) and crystallization in dichloromethane gave **4** (569 mg, 75%) as yellow crystals.

mp 168 °C.

^{1}H NMR ($CDCl_3$, 200 MHz) 4.25-4.36 (m, 4H), 6.45 (s, 1H), 7.06 (d, 1H, *J* = 7.7), 7.58 (dd, 1H, *J* = 7.7 and 7.7), 7.82 (d, 1H, *J* = 7.7).

^{13}C NMR ($CDCl_3$, 50 MHz) 64.4, 65.2, 102.5, 117.5, 118.6, 121.2, 139.1, 140.8, 142.0, 150.7, 152.3.

Anal. Calcd for $C_{11}H_8ClNO_2S$: C, 52.08; H, 3.18; N, 5.52; S, 12.64. Found: C, 52.00; H, 3.28; N, 5.92; S, 12.82.

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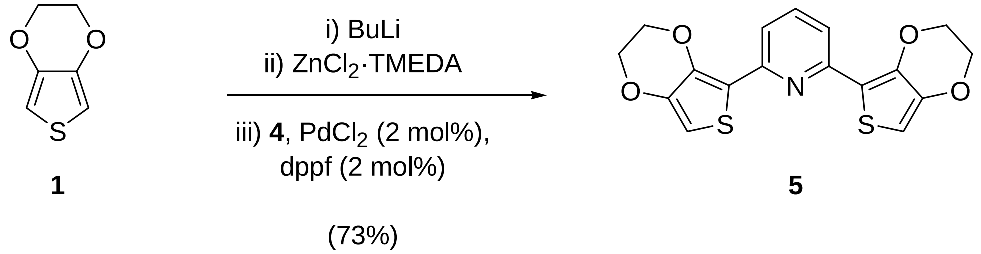
[3] For the synthesis of $ZnCl_2$·TMEDA, see: R. A. Kjonaas and R. K. Hoffer, *J. Org. Chem.*, 1988, **53**, 4133–4135. For Negishi coupling using $ZnCl_2$·TMEDA, see: I. Mutule and E. Suna, *Tetrahedron*, 2005, **61**, 11168–11176.



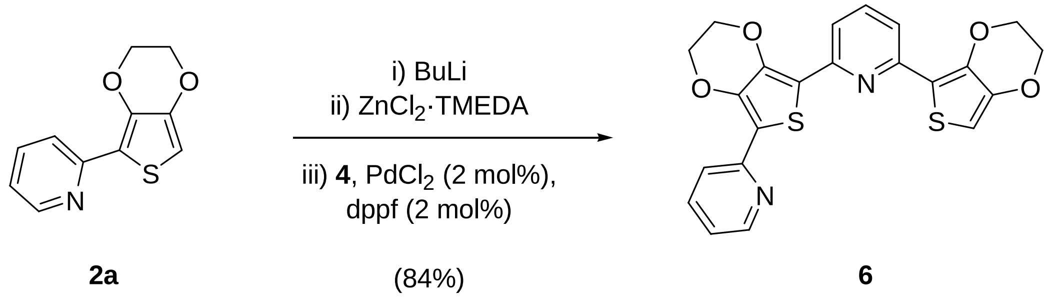
2,6-Bis(3,4-ethylenedioxy-2-thienyl)pyridine (5). To a stirred, cooled (-78 °C) solution of 3,4-ethylenedioxythiophene (426 mg, 3.00 mmol) in dry THF (5 mL) was slowly added *n*-BuLi (1.6 M hexanes solution, 3.00 mmol). The temperature was slowly raised to 0 °C before introduction $ZnCl_2$·TMEDA (757 mg, 3.00 mmol). The mixture was stirred for 1 h at 0 °C and $PdCl_2$ (11 mg, 2 mol %), dppf (33 mg, 2 mol %), **4** (761 mg, 3.00 mmol) were successively added. The reaction mixture was stirred for 48 h at 60 °C, quenched with water (1 mL) and filtered over celite®. After addition of an aqueous saturated solution of NaCl (10 mL), the mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel (heptane/CH_2Cl_2: 1/1) and crystallization in dichloromethane gave **5** (787 mg, 73%) as yellow crystals.

mp 266 °C.

^{1}H NMR ($CDCl_3$, 200 MHz) 4.25-4.37 (m, 8H), 6.43 (s, 2H), 7.68 (m, 3H).

^{13}C NMR ($CDCl_3$, 75 MHz) 34.7 (2C), 35.1 (2C), 101.8 (2C), 117.7 (2C), 118.8 (2C), 136.9, 140.0 (2C), 142.0 (2C), 150.7 (2C).

HRMS (EI): calcd for $C_{17}H_{13}NO_4S_2$ 359.0286, found 359.0272.



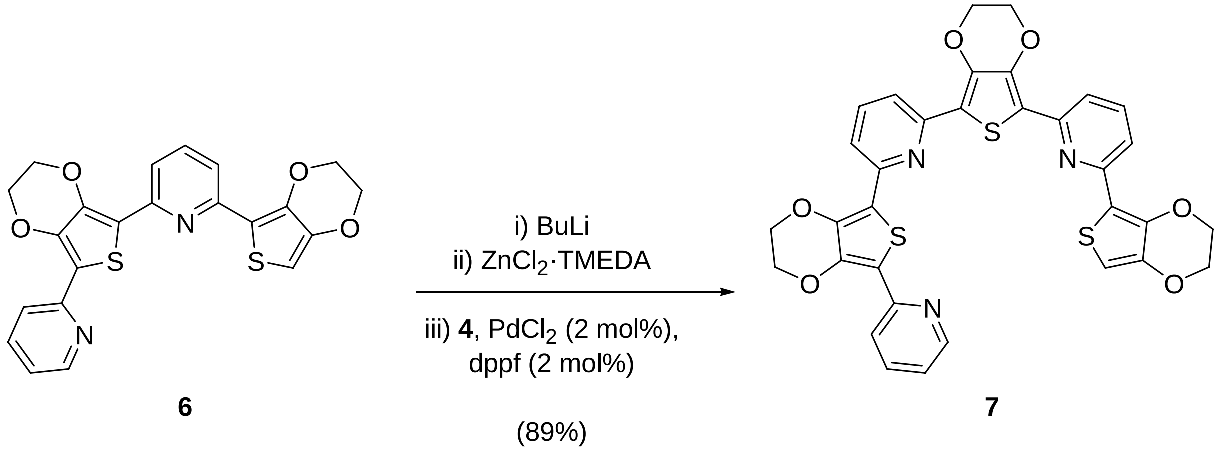
2-(6-(3,4-Ethylenedioxy-2-thienyl)-2-pyridyl)-5-(2-pyridyl)-3,4-ethylenedioxythiophene (6). To a stirred, cooled (-78 °C) solution of **2a** (329 mg, 1.50 mmol) in dry THF (3 mL) was slowly added *n*-BuLi (1.6 M hexanes solution, 1.50 mmol). The temperature was slowly raised to 0 °C before introduction $ZnCl_2$·TMEDA (378 mg, 1.50 mmol). The mixture was stirred for 1 h at 0 °C and $PdCl_2$ (5 mg, 2 mol %), dppf (17 mg, 2 mol %), **4** (380 mg, 1.50 mmol) were successively added. The reaction mixture was stirred for 48 h at 60 °C, quenched with water (1 mL) and filtered over celite®. After addition of an aqueous saturated solution of NaCl (5 mL), the mixture was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel (heptane/CH_2Cl_2: 1/1) gave **6** (550 mg, 84%) as a yellow solid.

mp 202 °C.

^{1}H NMR ($CDCl_3$, 200 MHz) 4.21-4.36 (m, 4H), 4.40 (s, 4H), 6.43 (s, 1H), 7.07 (dd, 1H, *J* = 4.8 and 7.3), 7.56-7.75 (m, 4H), 7.95 (d, 1H, *J* = 8.1), 8.59 (d, 1H, *J* = 4.8).

^{13}C NMR ($CDCl_3$, 50 MHz) 64.5, 64.7, 64.8, 65.1, 101.9, 118.0, 118.4, 119.4, 120.0, 120.5, 121.1, 121.2, 136.4, 136.7, 140.0 (2C), 140.1, 141.9, 149.4, 150.6, 150.9, 151.8.

Anal. Calcd for $C_{22}H_{16}N_2O_4S_2$: C, 60.53; H, 3.69; N, 6.42; S, 14.69. Found: C, 60.50; H, 3.75; N, 6.34; S, 14.52.



2-[6-[5-(2-Pyridyl)-3,4-ethylenedioxy-2-thienyl]-2-pyridyl]-5-[6-(3,4-ethylenedioxy-2-thienyl)-2-pyridyl]-3,4-ethylenedioxythiophene (7). To a stirred, cooled (-78 °C) solution of **6** (656 mg, 1.50 mmol) in dry THF (3 mL) was slowly added *n*-BuLi (1.6 M hexanes solution, 1.50 mmol). The temperature was slowly raised to 0 °C before introduction $ZnCl_2$·TMEDA (378 mg, 1.50 mmol). The mixture was stirred for 1 h at 0 °C and $PdCl_2$ (5 mg, 2 mol %), dppf (17 mg, 2 mol %), **4** (380 mg, 1.50 mmol) were successively added. The reaction mixture was stirred for 48 h at 60 °C, quenched with water (1 mL) and filtered over celite®. After addition of an aqueous saturated solution of NaCl (5 mL), the mixture was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel (heptane/CH_2Cl_2: 1/1) gave **7** (873 mg, 89%) as a yellow solid.

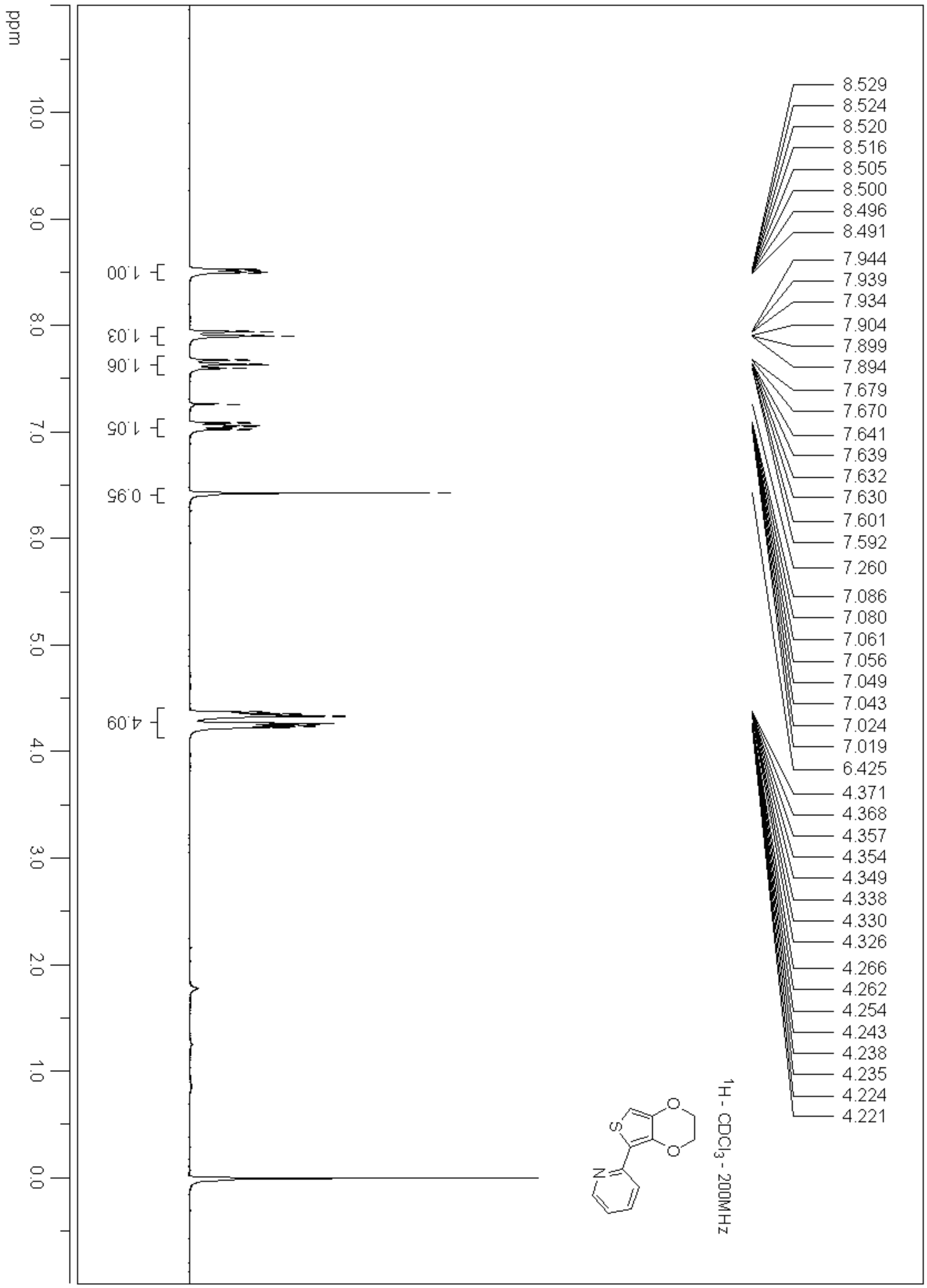
mp 238 °C.

^{1}H NMR ($CDCl_3$, 200 MHz) 4.27 (m, 2H), 4.43 (m, 10H), 6.45 (s, 1H), 7.09 (br dd, 1H, *J* = 4.6 and 7.1), 7.58-7.76 (m, 7H), 7.95 (br d, 1H, *J* = 8.0), 8.59 (br d, 1H, *J* = 4.6).

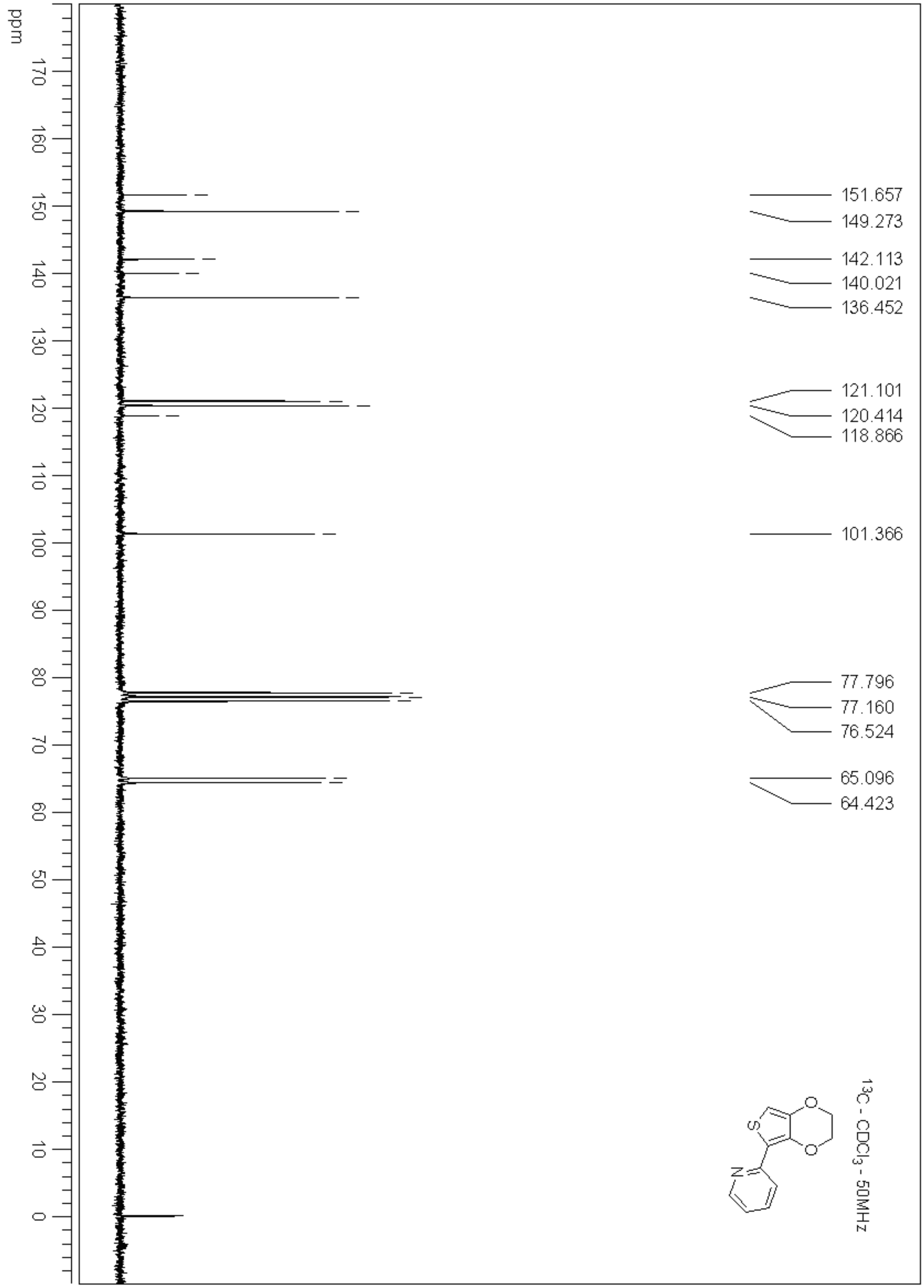
Anal. Calcd for $C_{33}H_{23}N_3O_6S_3$: C, 60.63; H, 3.55; N, 6.43; S, 14.71. Found: C, 60.61; H, 3.83; N, 6.28; S, 14.42.

^{1}H and ^{13}C NMR Spectra

2a



2a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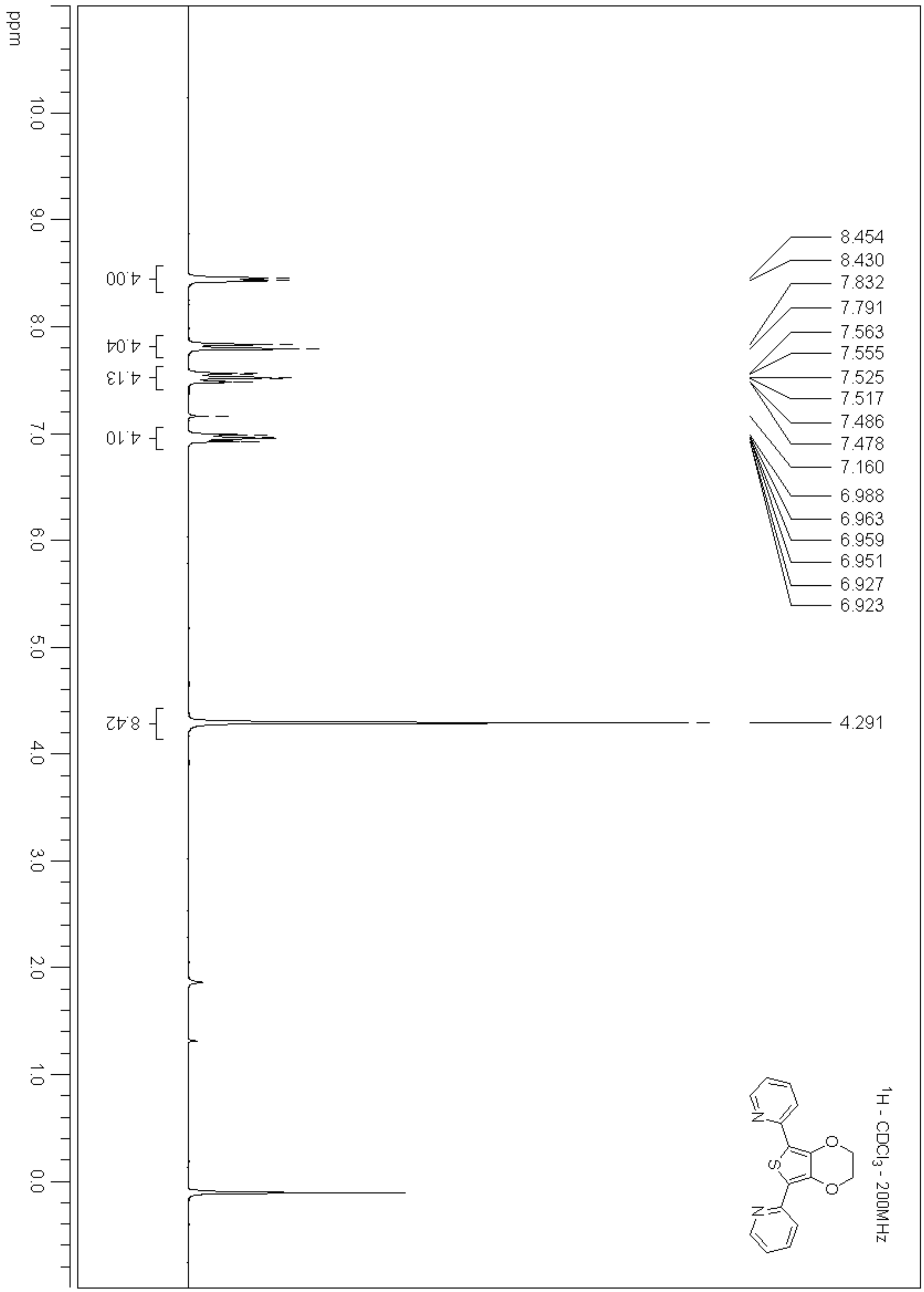
3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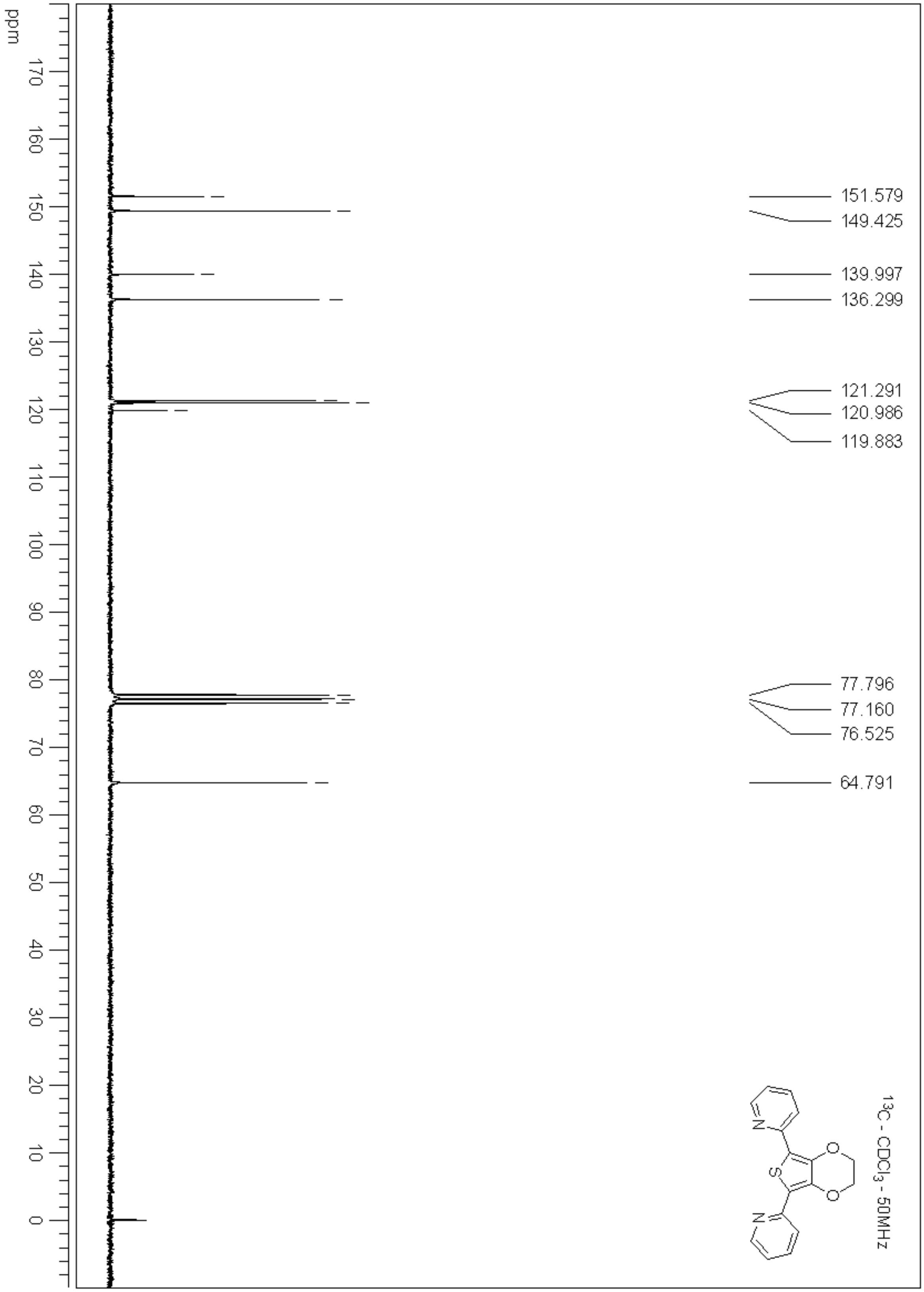
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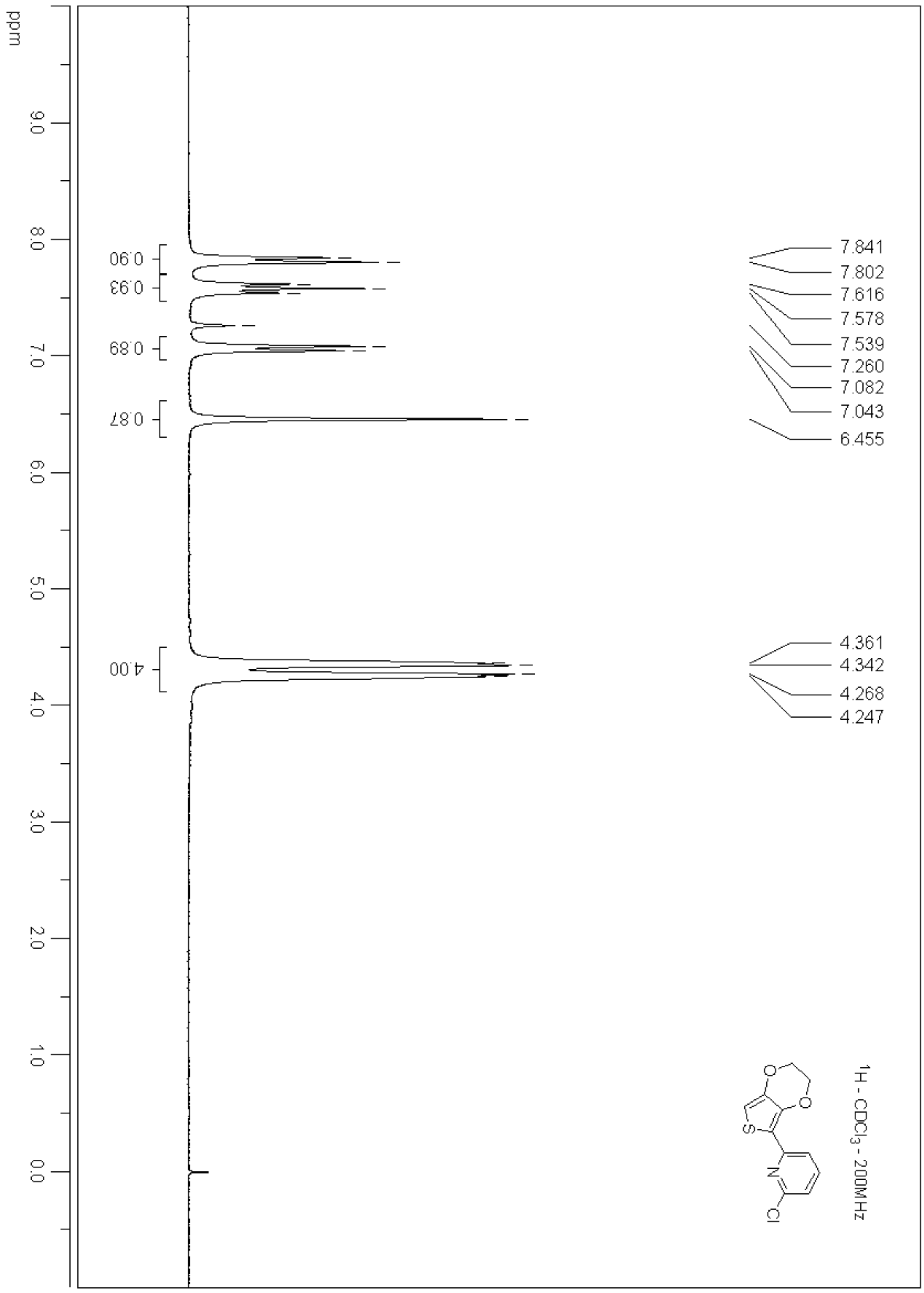
4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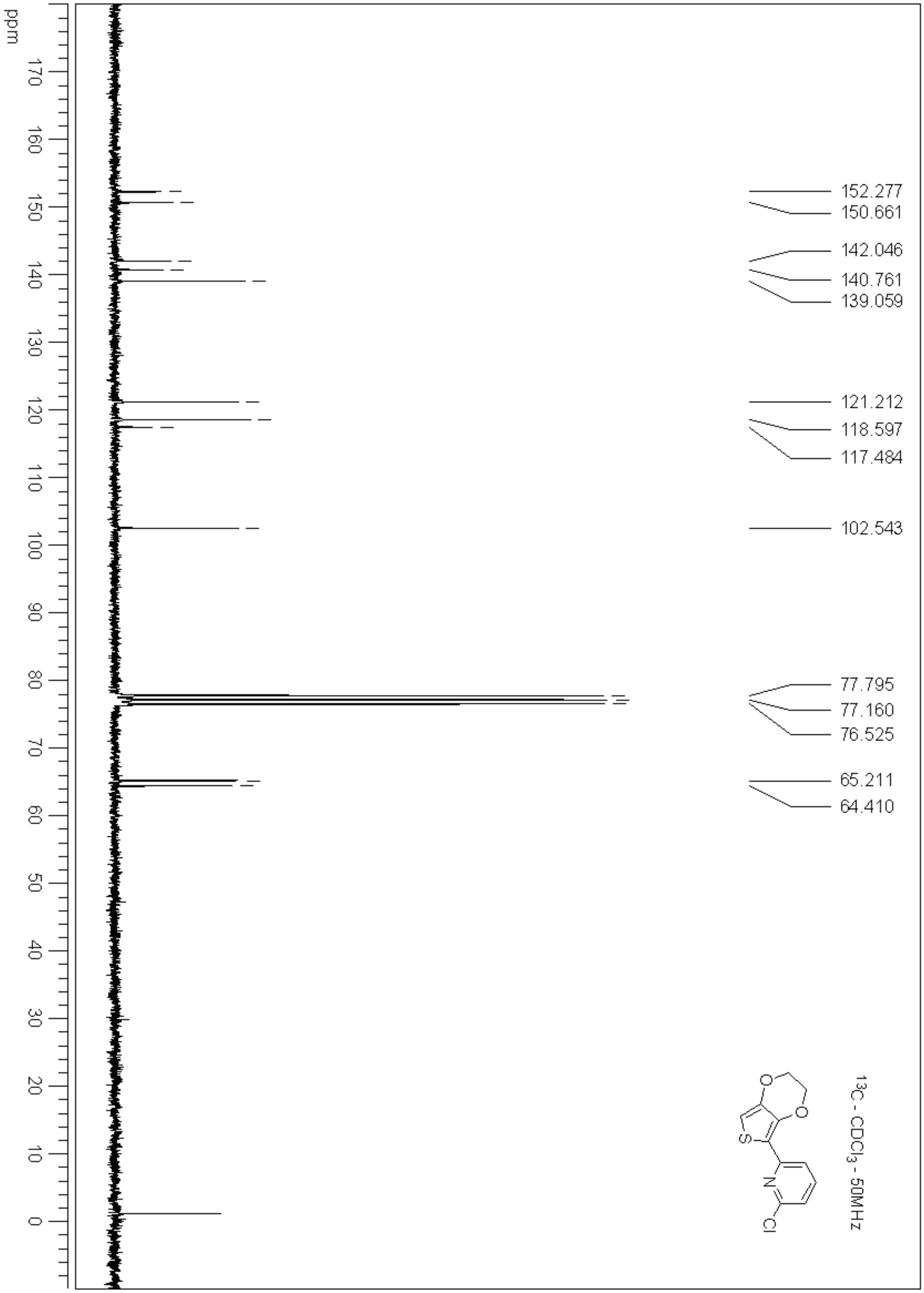
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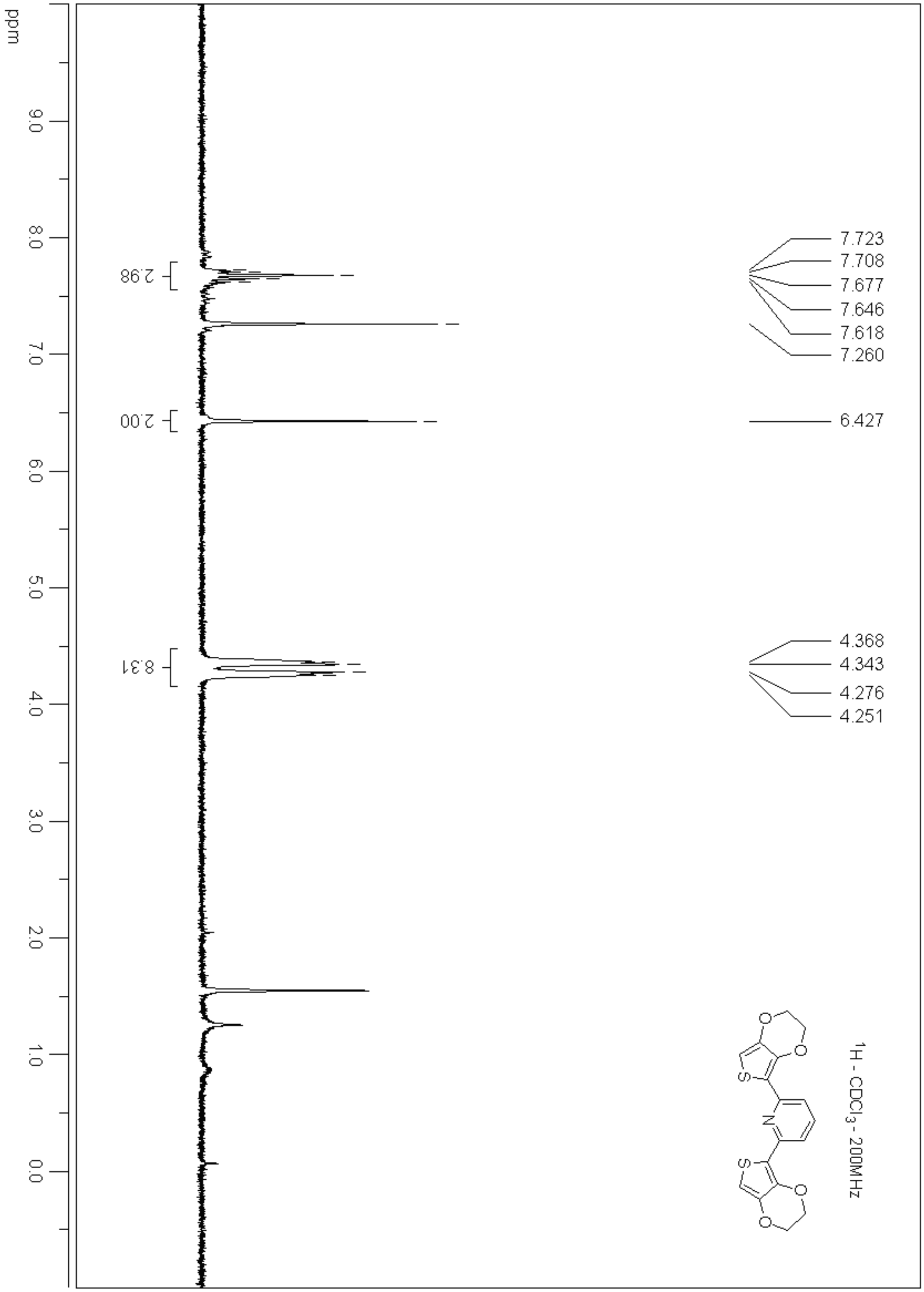
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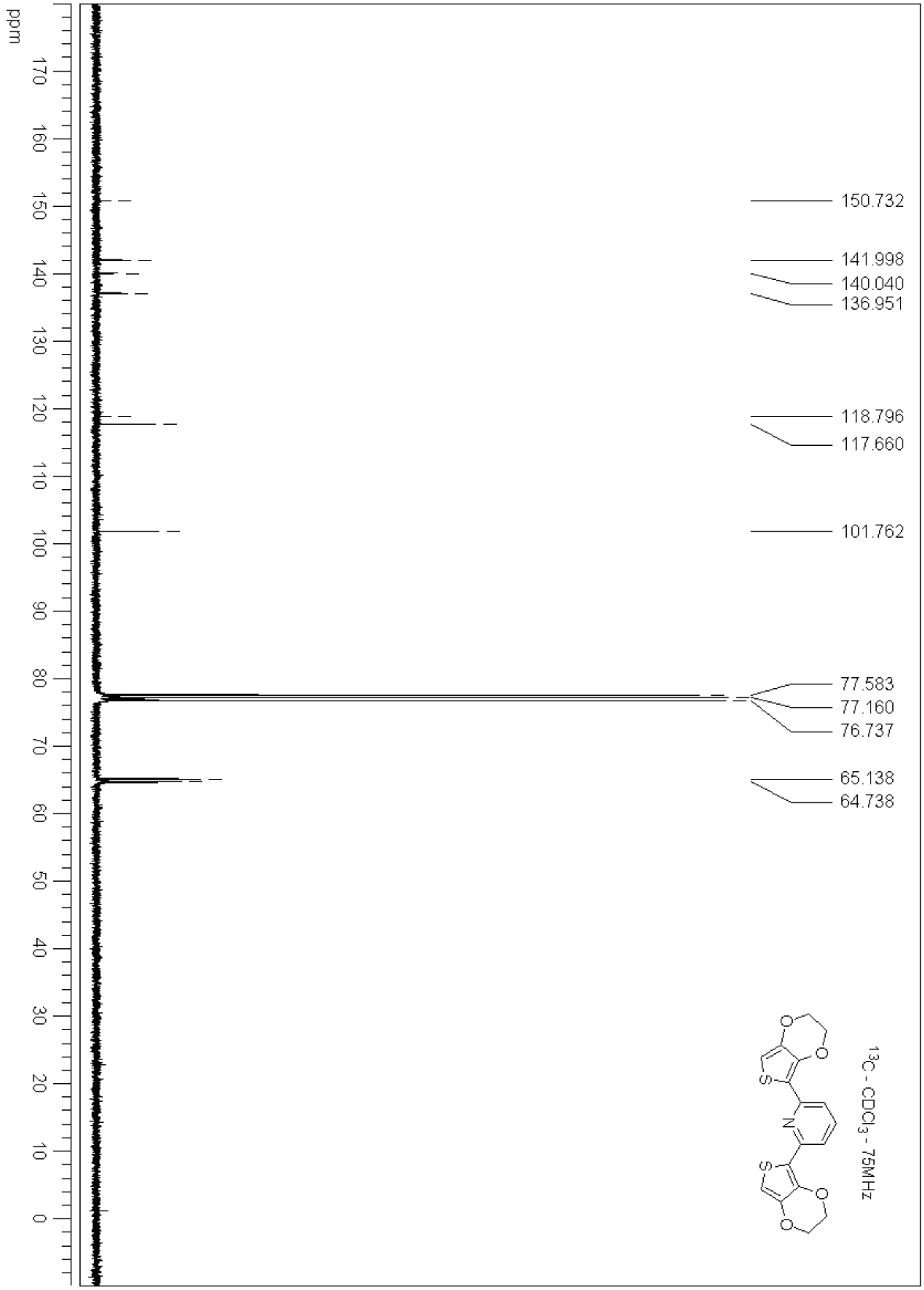
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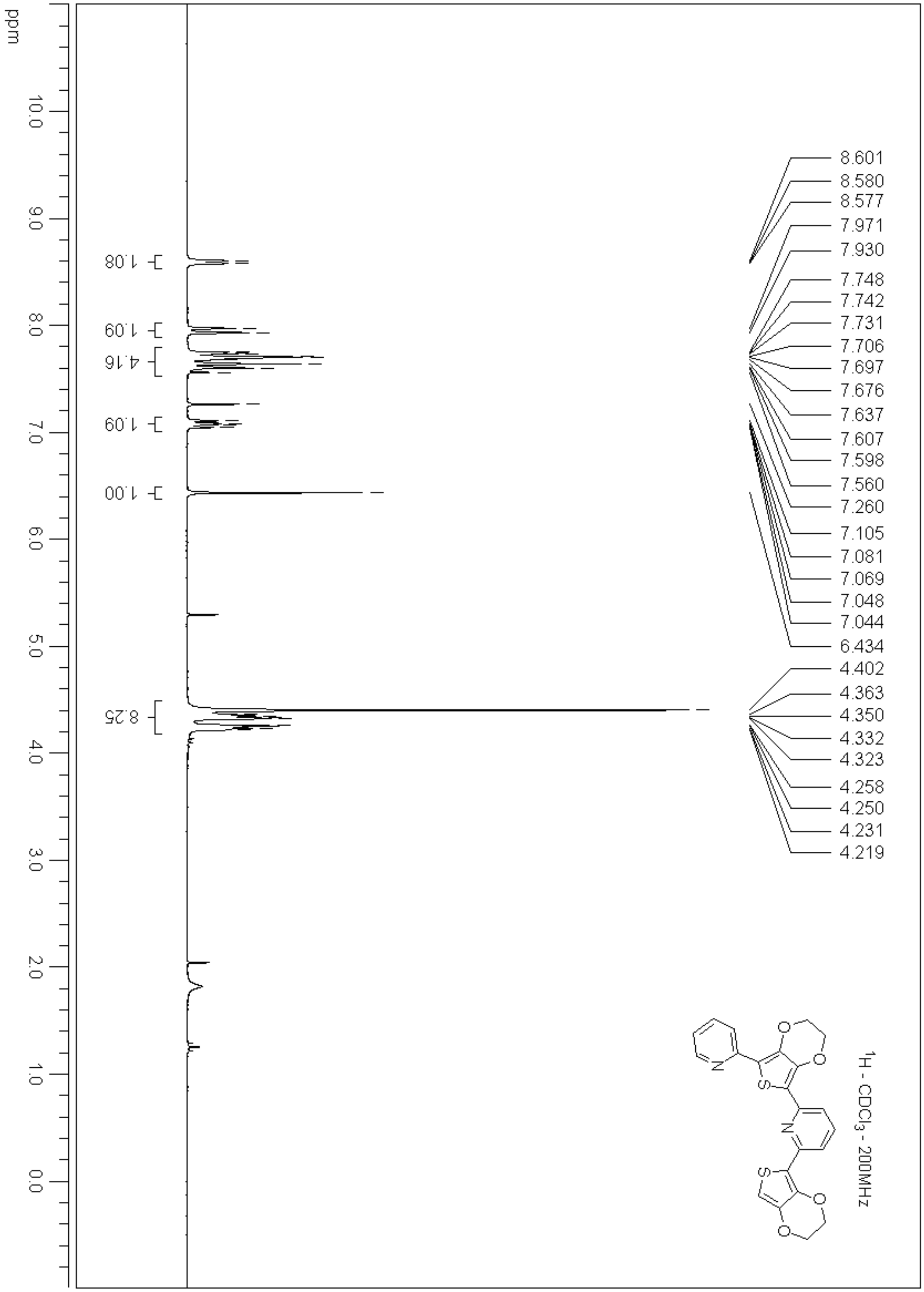
13C - CDCl3 - 75MHz

6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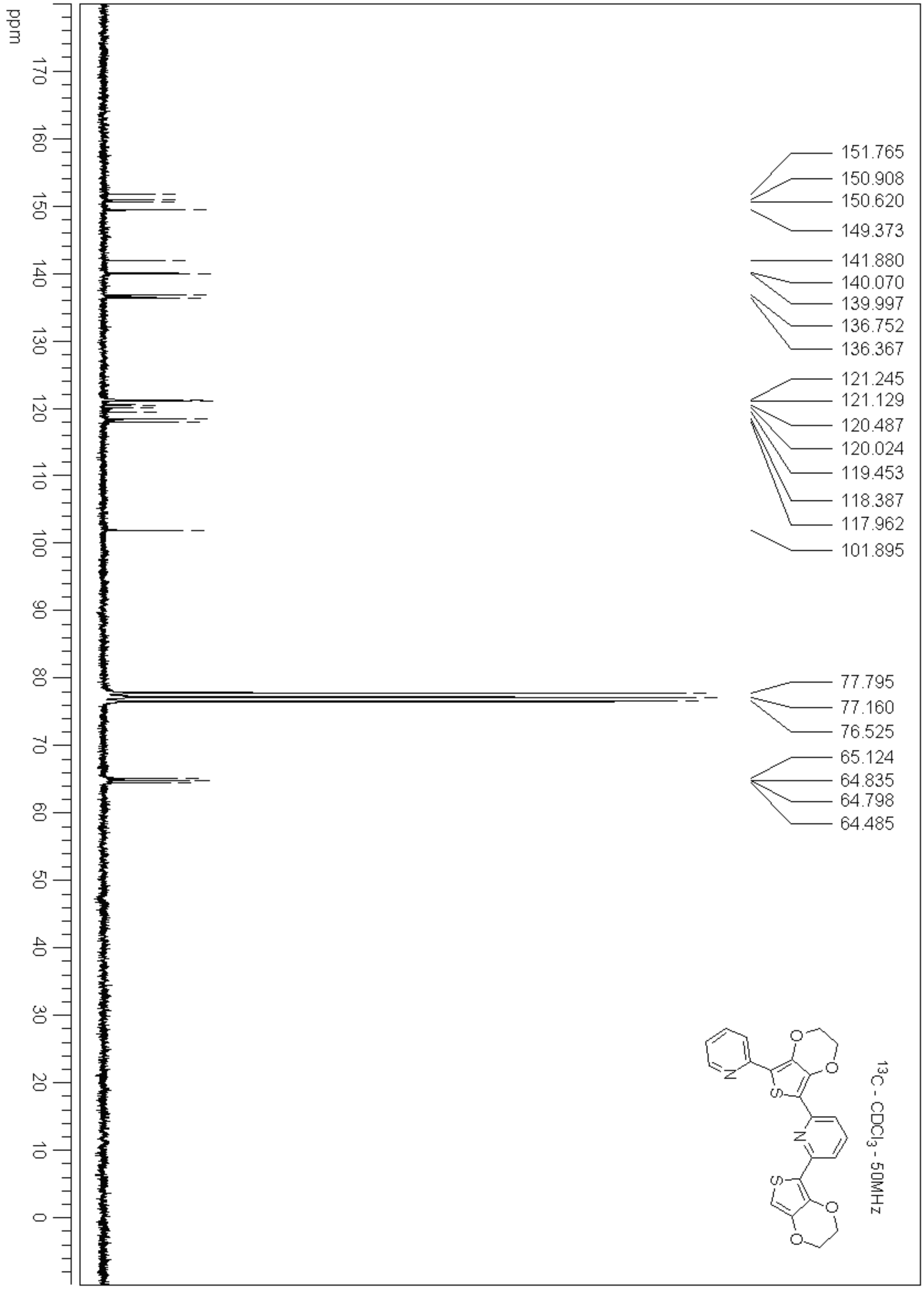
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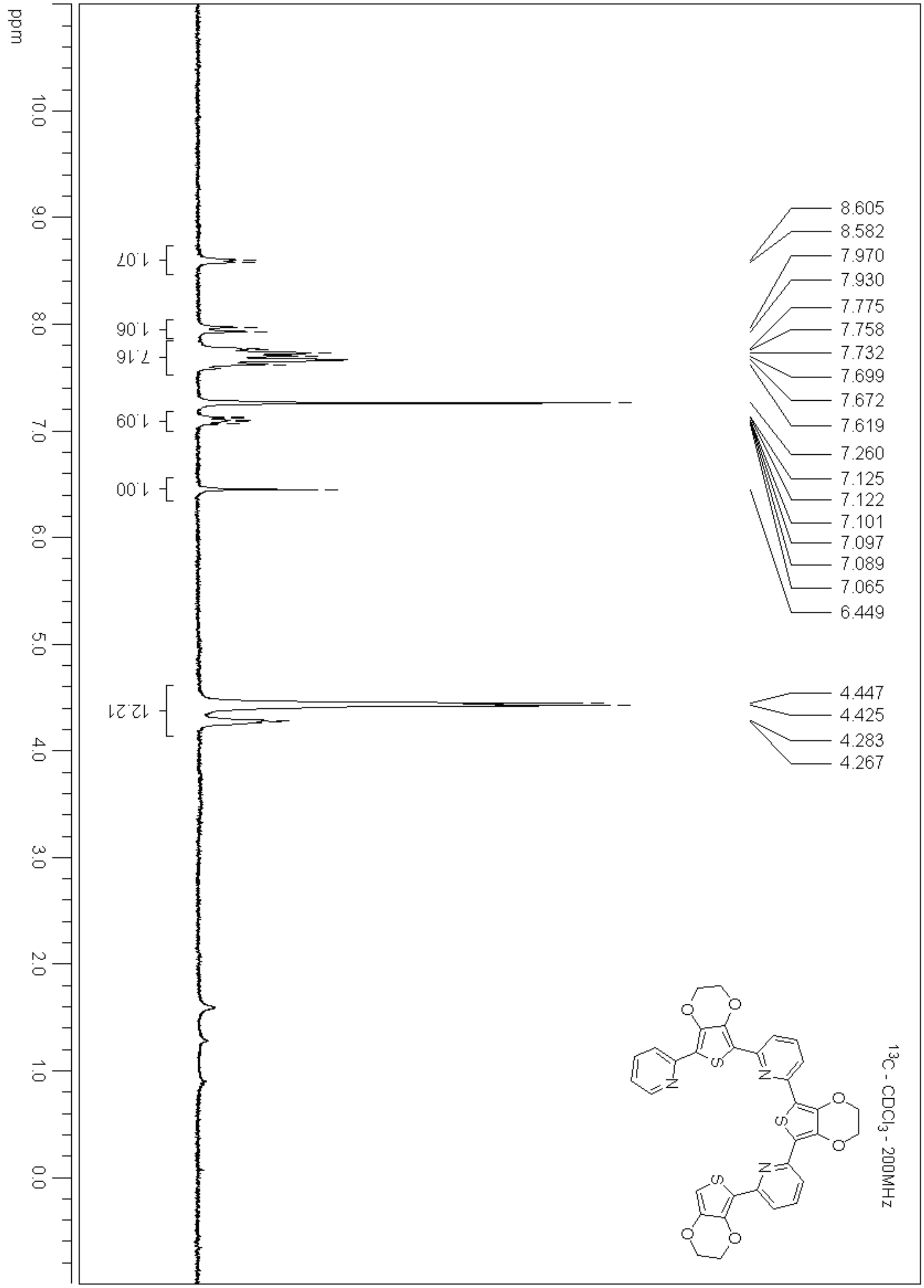
7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7.089
7.065
6.449
4.447
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O
S
N
^{13}C - $CDCl_3$ - 200MHz

Crystal Data

Single crystals suitable for X-ray diffraction were grown after slow evaporation (several days at room temperature) of solutions of **3**, **5** and **6** in CH_2Cl_2.

The samples were studied with graphite monochromatized $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). X-ray diffraction data were collected at T = 100(2) K using KappaCCD diffractometer. The structure was solved by direct methods using the SIR97 program,[4] and then refined with full-matrix least-square methods based on F^2 (SHELX-97)[5] with the aid of the WINGX program.[6] All non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms were finally included in their calculated positions.

Compound **3**.[7]

$C_{16}H_{12}N_2O_2S$, M_r = 296.34, monoclinic; space group P21/n, a = 10.4925(3) Å, b = 9.8365(3) Å, c = 13.1153(4) Å, β = 97.7390(10)°, V = 1341.29(7) Å^3, Z = 4, ρ_{calcd} = 1.467 g.cm^{-3}, μ = 0.247 mm^{-1}. A final refinement on F^2 with 3044 unique intensities and 190 parameters converged at $\omega R(F^2)$ = 0.0745 (R(F) = 0.0294) for 2921 observed reflections with $I > 2\sigma(I)$.

Compound **5**.

$C_{17}H_{13}NO_4S_2$, M_r = 359.40, monoclinic; space group P21/n, a = 7.2617(9) Å, b = 6.9926(9) Å, c = 28.988(4) Å, β = 90.338(4)°, V = 1471.9(3) Å^3, Z = 4, ρ_{calcd} = 1.622 g.cm^{-3}, μ = 0.385 mm^{-1}. A final refinement on F^2 with 3148 unique intensities and 217 parameters converged at $\omega R(F^2)$ = 0.093 (R(F) = 0.037) for 2790 observed reflections with $I > 2\sigma(I)$.

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[4] A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.*, 1999, **32**, 115–119.

[5] SHELX97 - Programs for Crystal Structure Analysis (Release 97-2). G. M. Sheldrick, Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.

[6] L. J. Farrugia, *J. Appl. Cryst.*, 1999, **32**, 837–838.

[7] The crystal structure of compound **3** has been published while our paper was submitted: B. Djukic, L. E. Harrington, J; F. Britten, M. T. Lemaire, *Acta Cryst.*, **2008**, E64, o463.

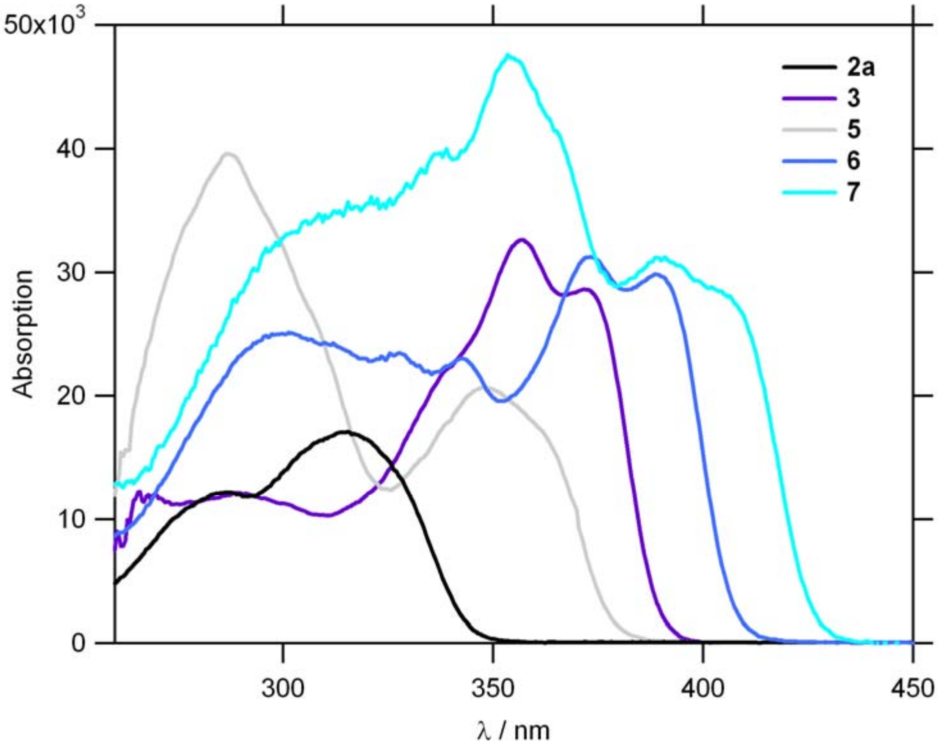
Compound **6**.

$C_{22}H_{16}N_2O_4S_2$, M_r = 436.49, monoclinic; space group C1c1, a = 49.259(5) Å, b = 4.9656(4) Å, c = 15.3119(13) Å, β = 90.604(6)°, V = 3745.1(6) Å^3, Z = 8, ρ_{calcd} = 1.548 g.cm^{-3}, μ = 0.320 mm^{-1}. A final refinement on F^2 with 6033 unique intensities and 541 parameters converged at ωR(F^2) = 0.1789 (R(F) = 0.0724) for 5081 observed reflections with I > 2σ(I).

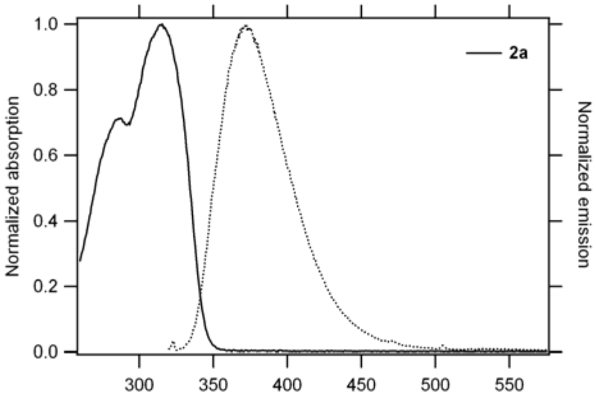
Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

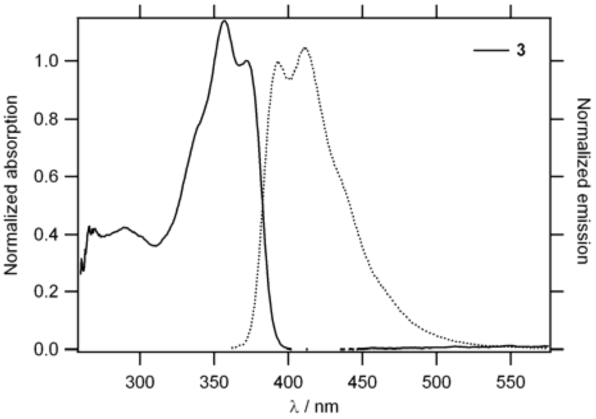
Absorption and Emission Data

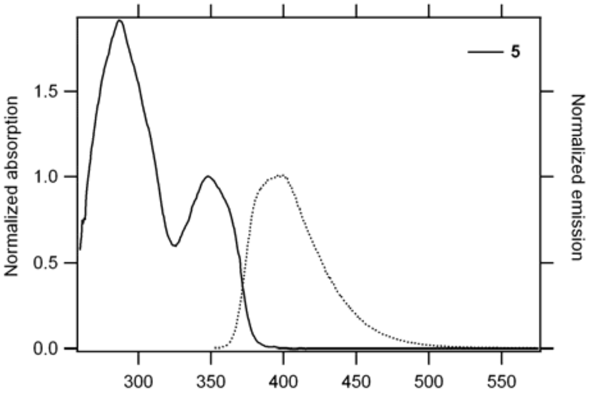
Absorption spectra of chromophores 2a**,** 3**,** 5**,** 6 **and** 7 **in chloroform.**

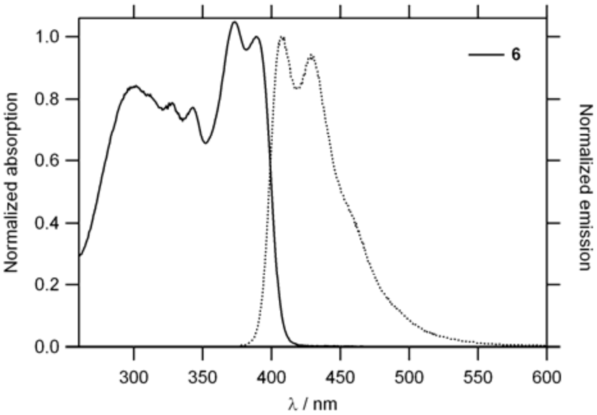


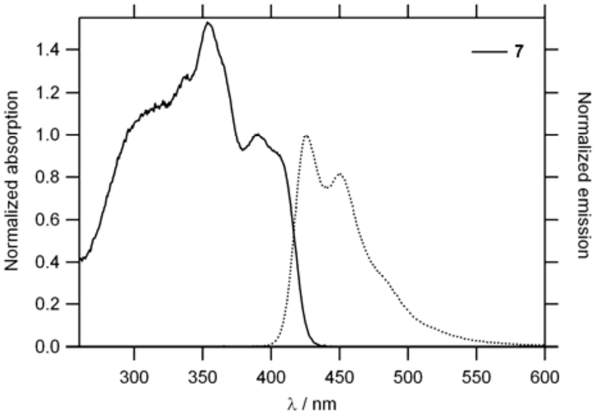
Normalized absorption and emission spectra of chromophores 2a, 3, 5, 6 and 7 in chloroform.











Solvatochromic data.

Solvent	λ_{max}^{abs} / λ_{max}^{em} [nm] **2a** (DA)	λ_{max}^{abs} / λ_{max}^{em} [nm] **3** (ADA)	λ_{max}^{abs} / λ_{max}^{em} [nm] **5** (DAD)	λ_{max}^{abs} / λ_{max}^{em} [nm] **6** ($(DA)_2$)	λ_{max}^{abs} / λ_{max}^{em} [nm] **7** ($(DA)_3$)
AcOEt	311 / 370	354, 370 / 386, 406	347 / 391	369, 387 / 398, 423	352, 388 / 420, 445
THF	313 / 371	355, 372 / 388, 408	348 / 392	371, 389 / 402, 425	353, 390 / 421, 447
Acetone	-	354, 370 / 387, 407	347 / 393	376, 388 / 403, 424	352, 389 / 422, 447
CH_3CN	312 / 377	353, 369 / 389, 407	347 / 393	371, 388 / 405, 426	353, 390 / 424, 449
DMSO	315 / 379	358, 375 / 394, 413	351 / 399	375, 393 / 410, 432	356, 395 / 423, 454

Computational Methods

Ground state optimized geometries have been obtained at the HF/6-31G level of theory using the Gaussian 03 package.[8] To optimize molecular geometries for the lowest excited state we used the TURBOMOLE package[9] at the TD-HF/SV level of theory. Thus absorption and fluorescence points were treated within consistent framework at TD-B3LYP/6-31G//HF/6-31G and TD-B3LYP/6-31G//TD-HF/SV levels, respectively, in conventional quantum chemical notation "single point//optimization level". Natural transition orbitals[10] and dipole moments were calculated at the TD-B3LYP/6-31G level of theory using the Gaussian 98 package.[8] Figures showing molecular geometries and natural transition orbitals were obtained with XcrySDen.[11]

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[8] Gaussian 98, Revision A.11 and Gaussian 03, Revision D.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

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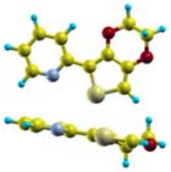
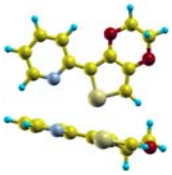
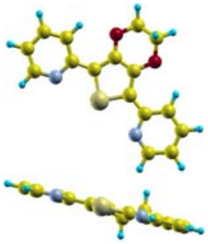
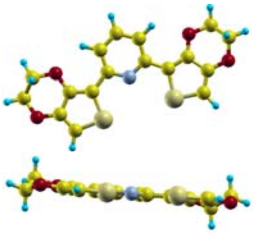
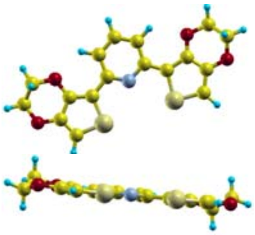
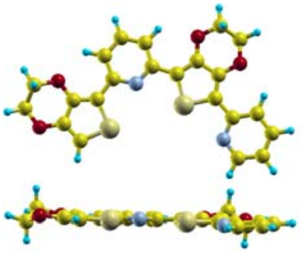
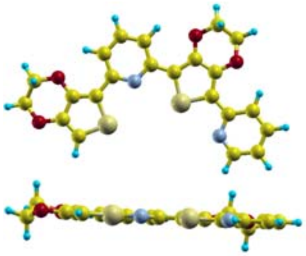
[10] R. L. Martin, *J. Chem. Phys.*, 2003, **118**, 4775–4777.

[11] A. Kokalj, *J. Mol. Graphics Modell.*, 2000, **17**, 176–179.

Ground state (absorption) and excited state (emission) optimized geometries

	Ground state	Excited state
2a		
3		
5		
6		
7