Supporting Information
for

Energy Transfer in New D-π-A Conjugated Dendrimers: Their Synthesis and Photophysical Properties

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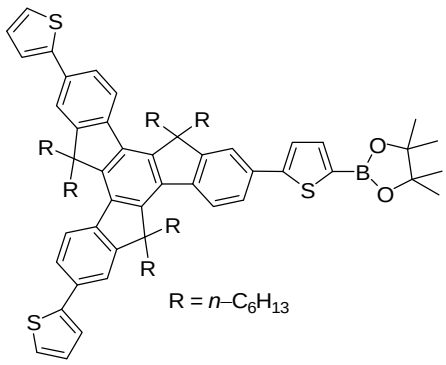
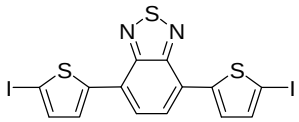
1. Experimental Section

General Methods. Chemicals were purchased and used as received. All air sensitive reactions were performed under nitrogen atmosphere unless stated otherwise. THF and Toluene were distilled from sodium. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Mercurry 300 (300 MHz), ARX400 (400 MHz) NMR instrument using $CDCl_3$ as solvent unless otherwise noted. Chemical shifts were reported in parts per million (ppm) relative to internal TMS (0 ppm) or residual $CHCl_3$ (7.26 ppm). UV-vis spectra were recorded on PerkinElmer Lambda 35 UV-vis Spectrometer. PL spectra were carried out on PerkinElmer LS55 Luminescence Spectrometer. MALDI-TOF MS spectra were recorded on a time-of-flight (TOF) mass spectrometer using a 337 nm nitrogen laser with dithranol as matrix. Elemental analyses were carried out on Elementar Vario EL (Germany).

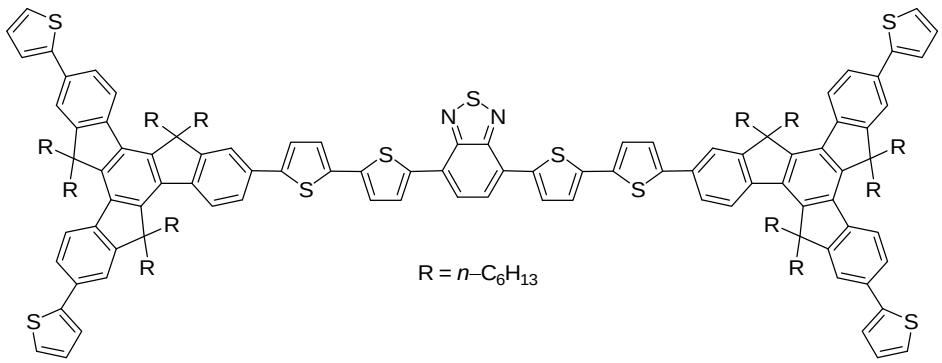


2. To a solution of **1** (1.1 g, 1.0 mmol) in 20 mL of THF at -78 ^{o}C was added dropwise *n*-BuLi in hexane solution (0.5 mL, 1.0 mmol) under nitrogen atmosphere. After the mixture was stirred at -78 ^{o}C for 1 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.23 g, 1.2 mmol) was added into at -78 ^{o}C. After it was stirred at -78 ^{o}C for 1 h, and then at room temperature for 12 h, the mixture was quenched with NH_4Cl solution. The aqueous layer was extracted with ethyl acetate, the combined organic extracts were washed with brine and dried over $MgSO_4$. After removal of solvents under reduced pressure, the residue was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate, 20:1) to give the product as a green solid (0.43 g, 36%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.35-8.37 (d, J = 8.4 Hz, 3H, Ar-H), 7.66-7.74 (m, 7H, Ar-H), 7.53-7.54 (d, J = 3.6 Hz, 1H, Ar-H), 7.46-7.47 (d, J = 3.6 Hz, 2H, Ar-H), 7.32-7.34 (d, J = 3.6 Hz, 2H, Ar-H), 7.14-7.16 (dd, J = 4.8，3.6 Hz, 2H,

Ar-H), 2.92-3.00 (m, 6H, CH_2), 2.11-2.16 (m, 6H, CH_2), 1.40 (s, 12H, CH_3), 0.83-0.94 (m, 36H, CH_2), 0.55-0.60 (m, 30H, CH_2, CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 154.4, 151.9, 145.2, 145.0, 140.2, 139.8, 138.2, 138.04, 137.97, 132.5, 132.3, 128.1, 124.9, 124.6, 124.3, 124.2, 122.9, 119.9, 119.4, 84.2, 55.8, 37.1, 31.5, 29.5, 24.8, 24.0, 22.3, 13.9, 13.8. MALDI-TOF MS (*m/z*): Calcd. for $C_{81}H_{107}BO_2S_3$: 1218.8. Found: 1219. Elemental Analysis: Calcd. for $C_{81}H_{107}BO_2S_3$: C, 79.76; H, 8.84. Found: C, 79.95; H, 8.68.

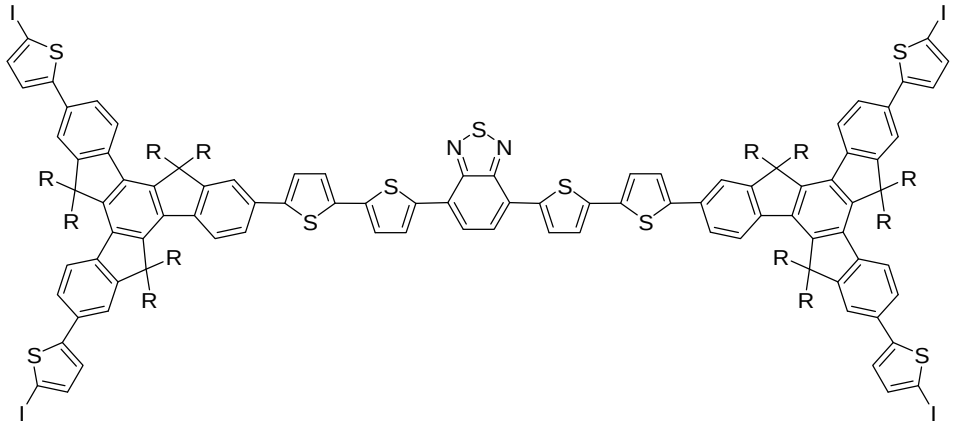


3. To a solution of diisopropylamine (0.29 g, 3.0 mmol) in 5 mL of THF at 0 °C was added dropwise *n*-BuLi in hexane solution (2.5 mmol, 1.0 mL) under nitrogen atmosphere. After the mixture was cooled to -78 °C, a solution of 4,7-bis(2-thienyl)-2,1,3-benzothiadiazole (1.0 mmol, 0.30 g) in THF was added dropwise. The mixture was stirred at -78 °C for 1 h. A solution of iodine (0.91 g, 3.6 mmol) in THF solution was added. The mixture was stirred at -78 °C for 1 h, and then quenched with NH_4Cl solution. The aqueous layer was extracted with ethyl acetate. The combined organic extracts were washed with brine, and then dried over $MgSO_4$. After removal of solvents under reduced pressure, the residue was washed with methanol to give the desired product as a red solid (0.48 g, 86%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.78 (s, 2H, Ar-H), 7.70-7.72 (d, J = 3.6 Hz, 2H, Ar-H), 7.33-7.34 (d, J = 3.6 Hz, 2H, Ar-H). ^{13}C NMR (THF-d_8, 75 MHz, 333 K, ppm): δ 154.3, 147.3, 139.8, 130.6, 127.33, 127.26, 79.0. EI-MS (*m/z*): Calcd. for $C_{14}H_6I_2N_2S_3$: 551.8. Found: 552. HRMS (*m/z*): Calcd. for $C_{14}H_6I_2N_2S_3$: 551.77827. Found: 551.77966. Elemental Analysis: Calcd. for $C_{14}H_6I_2N_2S_3$: C, 30.45; H, 1.10; N, 5.07. Found: C, 30.24; H, 0.90; N, 5.08.



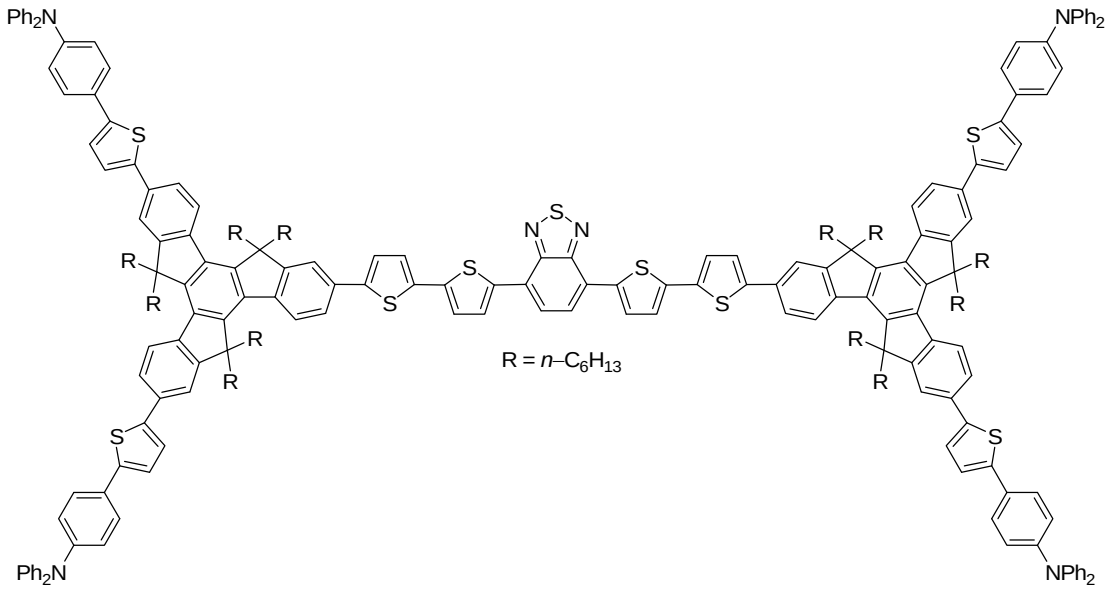
4. To a solution of **2** (0.15 g, 0.27 mmol) and **3** (0.82 g, 0.67 mmol) in 60 mL of THF was added 31 mg $Pd(PPh_3)_4$ and 1.5 mL of 2 M aqueous NaOH solution. After it was refluxed for

12 h under nitrogen atmosphere, the mixture was poured into NH_4Cl solution. The aqueous layer was extracted with ethyl acetate. The combined organic extracts were washed with brine and dried over $MgSO_4$. After removal of solvents under reduced pressure, the residue was purified by flash column chromatography (silica gel, petroleum ether/dichloromethane, 10:1) to give the product as a black solid (0.56 g, 84%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.36-8.38 (m, 6H, Ar-H), 8.12-8.13 (d, *J* = 3.6 Hz, 2H, Ar-H), 7.93 (s, 2H, Ar-H), 7.70 (m, 12H, Ar-H), 7.47-7.48 (d, *J* = 3.6 Hz, 4H, Ar-H), 7.44-7.45 (d, *J* = 3.6 Hz, 2H, Ar-H), 7.36-7.38 (m, 4H, Ar-H), 7.33-7.34 (d, *J* = 3.6 Hz, 4H, Ar-H), 7.15-7.17 (dd, *J* = 4.8，3.6 Hz, 4H, Ar-H), 2.98 (m, 12H, CH_2), 2.15 (m, 12H, CH_2), 0.88-0.93 (m, 72H, CH_2), 0.60-0.63 (m, 60H, CH_2, CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 154.5, 154.4, 152.5, 145.2, 145.14, 145.09, 144.9, 144.2, 140.1, 139.7, 139.1, 138.0, 137.9, 136.2, 132.5, 132.0, 128.4, 128.1, 125.5, 125.2, 125.1, 125.0, 124.6, 124.4, 124.2, 123.8, 122.9, 119.3, 119.1, 55.8, 37.1, 31.5, 29.5, 24.0, 22.3, 13.9. MALDI-TOF MS (*m/z*)：Calcd. for $C_{164}H_{196}N_2S_9$: 2481.3. Found: 2481. Elemental Analysis: Calcd. for $C_{164}H_{196}N_2S_9$: C, 79.30; H, 7.95; N, 1.13. Found: C, 79.34; H, 7.97; N, 1.01.



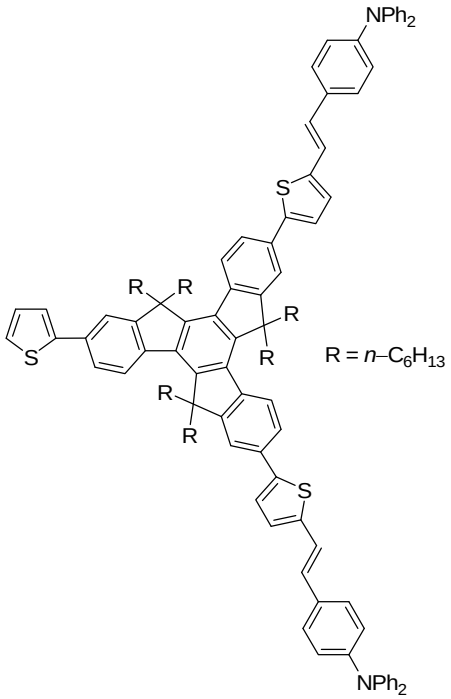
5. To a solution of **4** (0.25 g, 0.10 mmol) in 5 mL of dichloromethane was added 5 mL of acetic acid. The mixture was shielded from light and 99 mg (0.44 mmol) of NIS (*N*-iodosuccinimide) was added stepwise at 0 ^{o}C. After 2 h, the mixture was poured into aqueous Na_2CO_3 solution. The aqueous layers were extracted with ethyl acetate. The combined organic extracts were washed with brine and dried over $MgSO_4$. After removal of solvents under reduced pressure, the residue was purified by wash with ethanol to give the product as a black solid (0.27 g, 91%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.34-8.38 (m, 6H,

Ar-H), 8.12-8.13 (d, J = 3.6 Hz, 2H, Ar-H), 7.93 (s, 2H, Ar-H), 7.70-7.72 (m, 4H, Ar-H), 7.60-7.62 (m, 8H, Ar-H), 7.44-7.45 (d, J = 3.6 Hz, 2H, Ar-H), 7.36-7.39 (m, 4H, Ar-H), 7.29-7.30 (d, J = 3.6 Hz, 4H, Ar-H), 7.13-7.14 (d, J = 3.6 Hz, 4H, Ar-H), 2.93-2.97 (m, 12H, CH_2), 2.08-2.14 (m, 12H, CH_2), 0.88-0.93 (m, 72H, CH_2), 0.58-0.63 (m, 60H, CH_2, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 154.5, 152.5, 150.8, 145.4, 145.3, 144.1, 140.1, 139.9, 139.0, 138.0, 137.95, 137.89, 136.3, 132.1, 131.7, 128.4, 125.5, 125.2, 125.1, 125.0, 124.4, 124.3, 123.9, 123.86, 119.1, 119.0, 72.0, 55.8, 37.0, 31.5, 29.5, 23.9, 22.2, 13.9. MALDI-TOF MS (*m/z*): Calcd. for $C_{164}H_{192}I_4N_2S_9$: 2987.4. Found: 2987. Elemental Analysis: Calcd. for $C_{164}H_{192}I_4N_2S_9$: C, 65.93; H, 6.48; N, 0.94. Found: C, 65.63; H, 6.40; N, 0.85.



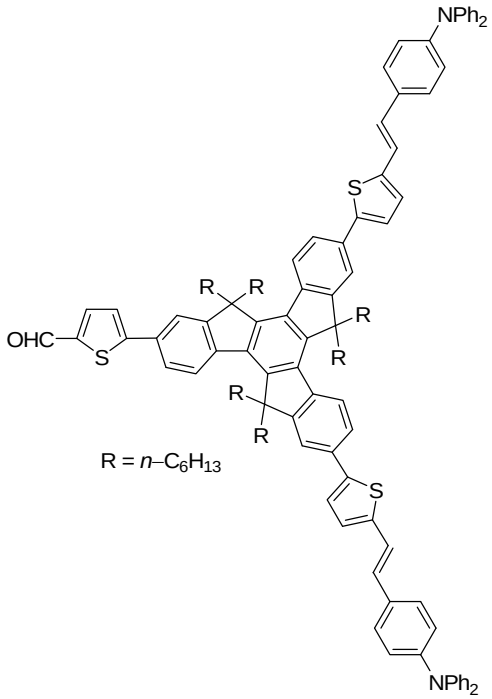
SBTTrTPA. To a solution of **5** (0.30 g, 0.10 mmol) and monoboronic pinacol ester of triphenylamine (0.30 g, 0.81 mmol) in 60 mL of THF was added 4 mg $Pd(PPh_3)_4$ and 1.5 mL of 2 M aqueous NaOH solution. After it was refluxed for 12 h under nitrogen atmosphere, the mixture was poured into NH_4Cl solution. The aqueous layer was extracted with ethyl acetate. The combined organic phases were washed with brine and dried over $MgSO_4$. After removal of solvents under reduced pressure, the residue was purified by flash column chromatography (silica gel, petroleum ether/dichloromethane, 4:1) to give the product as a black solid (0.26 g, 74%). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.37-8.39 (m, 6H, Ar-H), 8.12-8.13 (d, J = 3.6 Hz, 2H, Ar-H), 7.93 (s, 2H, Ar-H), 7.70 (m, 12H, Ar-H), 7.55-7.57 (d, J = 3.6 Hz, 8H, Ar-H), 7.44-7.45 (d, J = 3.6 Hz, 6H, Ar-H), 7.37-7.39 (m, 4H, Ar-H), 7.27-7.31 (m, 20H, Ar-H), 7.10-7.17 (m, 24H, Ar-H), 7.04-7.08 (m, 8H, Ar-H), 2.98 (m, 12H, CH_2), 2.15 (m, 12H, CH_2),

0.86-0.95 (m, 72H, CH_2), 0.60-0.63 (m, 60H, CH_2, CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 154.5, 154.4, 152.5, 147.5, 147.3, 145.2, 145.1, 145.0, 144.2, 143.3, 143.2, 140.1, 139.6, 139.1, 138.0, 137.9, 136.2, 132.5, 132.0, 129.3, 128.4, 126.4, 125.5, 125.2, 125.1, 125.0, 124.5, 123.9, 123.7, 123.2, 123.1, 119.0, 118.8, 55.8, 37.1, 31.5, 29.5, 24.0, 22.3, 13.9. MALDI-TOF MS (*m/z*): Calcd. for $C_{236}H_{248}N_6S_9$: 3457.1. Found: 3457. Elemental Analysis: Calcd. for $C_{236}H_{248}N_6S_9$: C, 81.99; H, 7.23; N, 2.43. Found: C, 81.76; H, 7.35; N, 2.23.



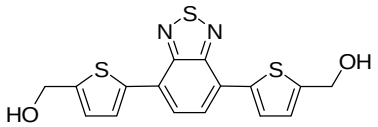
7. To a solution of diethyl 4-(diphenylamino)benzylphosphonate (2.13 g, 5.39 mmol) and the dialdehyde **6** (2.78 g, 2.42 mmol) in 80 mL dry THF was added a solution of *t*-BuOK (0.906 g, 8.09 mmol) in THF at –78 ºC under nitrogen atmosphere. After it was stirred 12 h at room temperature, the mixture was poured into NH_4Cl solution. The aqueous layer was extracted with ethyl acetate. The combined organic extracts were washed with brine and dried over $MgSO_4$. After removal of solvents under reduced pressure, the residue was purified by flash column chromatography (silica gel, petroleum ether/dichloromethane, 10:1) to give the product as a yellow solid (3.11g, 81%). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.35-8.37 (d, J = 8.4 Hz, 3H, Ar-H), 7.68-7.70 (m, 6H, Ar-H), 7.47-7.48 (d, J = 3.6 Hz, 1H, Ar-H), 7.37-7.39 (m, 5H, Ar-H), 7.33-7.34 (d, J = 3.6 Hz, 1H, Ar-H), 7.28-7.30 (m, 9H, Ar-H), 7.12-7.17 (m, 11H, Ar-H), 7.02-7.07 (m, 9H, Ar-H, *trans*-CH=CH), 6.93-6.97 (d, J = 16 Hz, 2H, *trans*-CH=CH), 2.97 (m, 6H, CH_2), 2.10-2.16 (m, 6H, CH_2), 0.85-0.97 (m, 36H, CH_2),

0.56-0.62 (m, 30H, CH_2, CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 154.4, 147.5, 147.3, 145.1, 144.9, 143.0, 142.5, 139.8, 139.7, 138.0, 132.5, 132.3, 131.1, 129.3, 128.1, 127.7, 127.2, 127.0, 124.9, 124.5, 124.1, 123.7, 123.5, 123.4, 123.1, 122.9, 120.3, 119.3, 118.9, 55.7, 37.1, 31.5, 29.5, 24.0, 22.3, 13.9. MALDI-TOF MS (*m/z*): Calcd. for $C_{115}H_{126}N_2S_3$: 1630.9. Found: 1631. Elemental Analysis: Calcd. for $C_{115}H_{126}N_2S_3$: C, 84.61; H, 7.78; N, 1.72. Found: C, 84.25; H, 7.86; N, 1.48.

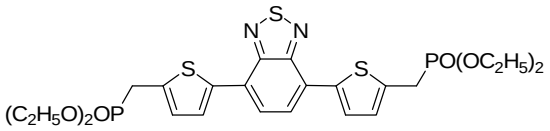


8. To a solution of **7** (2.43 g, 1.49 mmol) in 40 mL of THF at -78 °C was added dropwise *n*-BuLi in hexane solution (1.3 mL, 3.0 mmol) under nitrogen atmosphere. After 1 h at -78 °C, anhydrous DMF (0.27 g, 3.6 mmol) was added into the mixture. After it was stirred at -78 °C for 1 h, and then at room temperature for 12 h, the mixture was poured into NH_4Cl solution. The aqueous layer was extracted with ethyl acetate. The combined organic phases were washed with brine and dried over $MgSO_4$. After removal of solvents under reduced pressure, the residue was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate, 10:1) to give the product as a yellow solid (2.05 g, 83%). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 9.94 (s, 1H, CHO), 8.42-8.44 (d, *J* = 8.4 Hz, 1H, Ar-H), 8.35-8.38 (m, 2H, Ar-H), 7.81-7.82 (d, *J* = 3.6 Hz, 1H, Ar-H), 7.76-7.78 (m, 2H, Ar-H), 7.69-7.78 (m, 4H, Ar-H), 7.56-7.57 (d, *J* = 3.6 Hz, 1H, Ar-H), 7.37-7.40 (m, 5H, Ar-H), 7.26-7.30 (m, 8H, Ar-H), 7.12-7.17 (m, 10H, Ar-H), 7.03-7.08 (m, 9H, Ar-H), 6.93-6.97 (d, *J* = 16.0 Hz, 2H,

trans-CH=CH), 2.95-2.97 (m, 6H, CH_2), 2.15 (m, 6H, CH_2), 0.85-0.96 (m, 36H, CH_2), 0.54-0.62 (m, 30H, CH_2, CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 182.8, 154.9, 154.7, 154.4, 154.3, 147.5, 147.4, 145.8, 145.5, 145.2, 142.9, 142.6, 142.0, 141.8, 139.6, 139.5, 138.2, 138.1, 137.6, 137.5, 132.5, 131.0, 129.3, 127.8, 127.2, 127.0, 125.1, 125.0, 124.9, 124.7, 124.5, 123.8, 123.5, 123.1, 120.3, 119.8, 119.0, 55.84, 55.79, 37.0, 31.5, 29.5, 23.9, 22.2, 13.9. MALDI-TOF MS (*m/z*): Calcd. for $C_{116}H_{126}N_2OS_3$: 1658.9. Found: 1659. Elemental Analysis: Calcd. for $C_{116}H_{126}N_2OS_3$: C, 83.91; H, 7.65; N, 1.69. Found: C, 83.69; H, 7.67; N, 1.60.

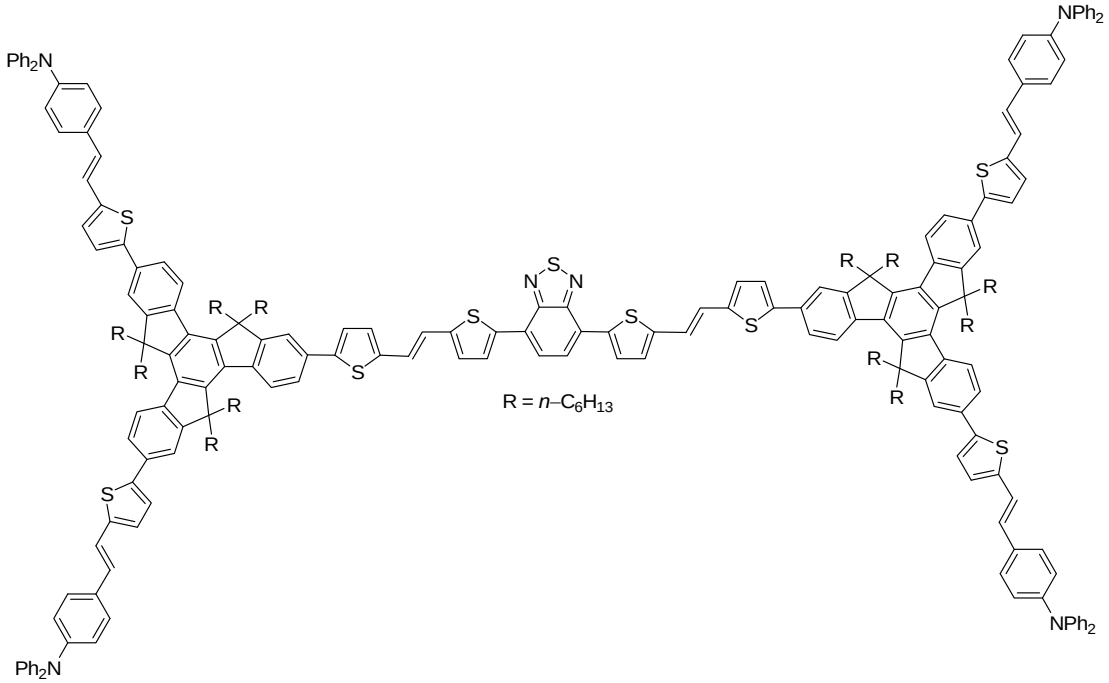


9. Sodium tetrahydroborate (0.42 g, 11 mmol) was added to a solution of 4,7-bis(5-formylthiophen-2-yl)-2,1,3-benzothiadiazole (0.80 g, 2.2 mmol) in 50 mL THF. After it was refluxed for 5 h, the mixture was poured into water. The precipitates were collected by filtration, washed with hexane and recrystallization from ethanol to give the product as a red solid (0.71 g, 88%). ^{1}H NMR (pyridine-d_5, 300 MHz, 333 K, ppm): δ 8.16-8.17 (d, J = 3.6 Hz, 2H, Ar-H), 7.89 (s, 2H, Ar-H), 7.24-7.25 (d, J = 3.6 Hz, 2H, Ar-H), 5.17 (s, 4H, Ar-H). ^{13}C NMR (pyridine-d_5, 75 MHz, 333K, ppm): δ 152.9, 138.6, 127.9, 126.3, 125.7, 125.2, 59.8. EI-MS (*m/z*): Calcd. for $C_{16}H_{12}N_2O_2S_3$: 360.0. Found: 360 (M^+). HRMS: Calcd. for $C_{16}H_{12}N_2O_2S_3$: 360.0061. Found: 360.0066. Elemental Analysis: Calcd. for $C_{16}H_{12}N_2O_2S_3$: C, 53.31; H, 3.36; N, 7.77. Found: C, 53.49; H, 3.28; N, 7.51.



10. To a solution of **9** (0.72 g, 2.0 mmol) in 6 mL of triethylphosphite was added iodine (1.0 g, 4.0 mmol) slowly at 0°C. After all iodine dissolved, 1,8-diazbicyclo[5.4.0.]undec-7-ene (DBU) (0.61 g, 4.0 mmol) was added dropwise. The mixture was heated to 125 °C for 12 h. After removal of trace triethyl phosphate under reduced pressure, the residue was purified by flash column chromatography (silica gel, ethyl acetate) to give the product as a red solid (0.49 g, 41%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.97-7.98 (dd, J = 3.6, 0.9 Hz, 2H, Ar-H), 7.78 (s,

2H, Ar-H), 7.07-7.09 (t, J = 3.6 Hz, 2H, Ar-H), 4.08-4.18 (dt, J = 15.3, 7.2 Hz, 8H, CH_2O), 3.40-3.47 (d, J = 21.3 Hz, 4H, CH_2), 1.30-1.35 (t, J = 7.2 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 152.4, 138.7, 134.3, 134.2, 128.4, 128.3, 127.6, 125.6, 125.3, 62.6, 62.5, 29.3, 27.4), (16.4, 16.3). EI-MS (*m/z*): Calcd. for $C_{24}H_{30}N_2O_6P_2S_3$: 600.1. Found: 600 (M^+). HRMS: Calcd. for $C_{24}H_{30}N_2O_6P_2S_3$: 600.0741. Found: 600.0746. Elemental Analysis: Calcd. for $C_{24}H_{30}N_2O_6P_2S_3$: C, 84.61; H, 7.78; N, 1.72. Found: C,85.01; H, 7.42 ; N, 1.68.

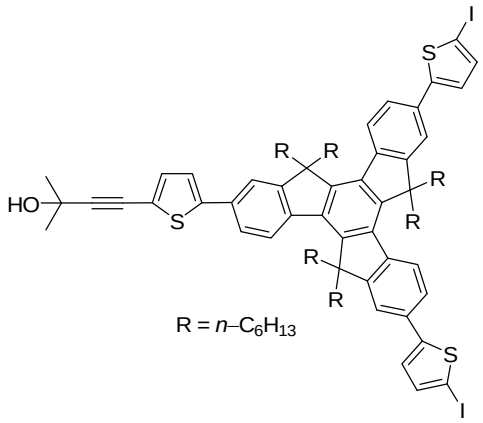


DBTTrTPA. To a solution of **10** (98 mg, 0.16 mmol) and **8** (0.60 g, 0.36 mmol) in 40 mL dry THF was added a solution of potassium *tert*-butoxide (61 mg, 0.54 mmol) in THF at -78 ºC under nitrogen atmosphere. After it was stirred at room temperature for 12 h, the mixture was poured into NH_4Cl solution. The aqueous layer was extracted with ethyl acetate, and the combined organic extracts were washed with brine and dried over $MgSO_4$. After removal of solvents under reduced pressure, the residue was purified by flash column chromatography (silica gel, petroleum ether/dichloromethane, 4:1) to give the product as a black solid (0.29 g, 51%). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.36-8.38 (m, 6H, Ar-H), 8.11-8.12 (d, J = 3.6 Hz, 2H, Ar-H), 7.91 (s, 2H, Ar-H), 7.69-7.70 (m, 12H, Ar-H), 7.38-7.40 (m, 14H, Ar-H), 7.26-7.30 (m, 20H, Ar-H), 7.17-7.22 (m, 6H, Ar-H), 7.12-7.14 (m, 20H, Ar-H), 7.03-7.08 (m, 20H, Ar-H), 6.93-6.97 (d, J = 16.0 Hz, 4H, *trans*-CH_2=CH_2), 2.98 (m, 12H, CH_2), 2.15 (m, 12H, CH_2), 0.85-0.96 (m, 72H, CH_2), 0.59-0.63 (m, 60H, CH_2, CH_3). ^{13}C NMR ($CDCl_3$, 75

MHz, ppm): δ 154.5, 154.4, 152.6, 147.5, 147.4, 145.24, 145.20, 145.16, 144.0, 143.0, 142.6, 141.6, 140.0, 139.8, 138.2, 138.1, 138.0, 132.5, 132.2, 131.1, 129.3, 128.4, 128.0, 127.8, 127.4, 127.2, 127.0, 125.6, 125.4, 125.0, 124.6, 123.8, 123.7, 123.5, 123.1, 122.5, 121.1, 120.3, 119.0, 55.8, 37.1, 31.5, 29.5, 24.0, 22.3, 13.9. MALDI-TOF MS (*m/z*): Calcd. for $C_{248}H_{260}N_6S_9$: 3609.8. Found: 3610. Elemental Analysis: Calcd. for $C_{248}H_{260}N_6S_9$: C, 82.43; H, 7.25; N, 2.33. Found: C, 82.06; H, 7.37; N, 2.14.

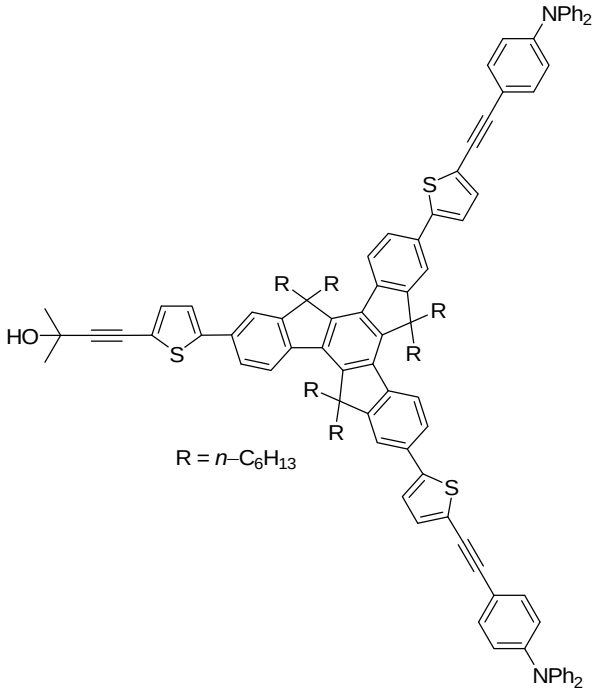
General Procedure for the Sonogashira Coupling Reaction:

A flask with a side arm was charged with acetylene derivatives (2.6 eq for synthesis of **13**, **TBTTrTPA**; 0.8 eq for synthesis of **12)**, aromatic iodides (1 eq.), $Pd_2(dba)_3$ or $PdCl_2(PPh_3)_2$ (0.02 eq.), triphenylphosphine (0.1 eq.), copper(I) iodide (0.02 eq.) and 20 mL of dry triethylamine and 10 mL of THF. The flask was stirred at 40 ^oC (for the synthesis of **13**, **TBTTrTPA**) or at room temperature (for the synthesis of **12**) under nitrogen atmosphere. The reaction mixture was quenched with NH_4Cl solution, the aqueous layer was extracted with dichloromethane. The combined organic extracts were washed with brine, and dried over. After removal of solvents under reduced pressure, the residue was purified by flash column chromatography to afford the desired product.



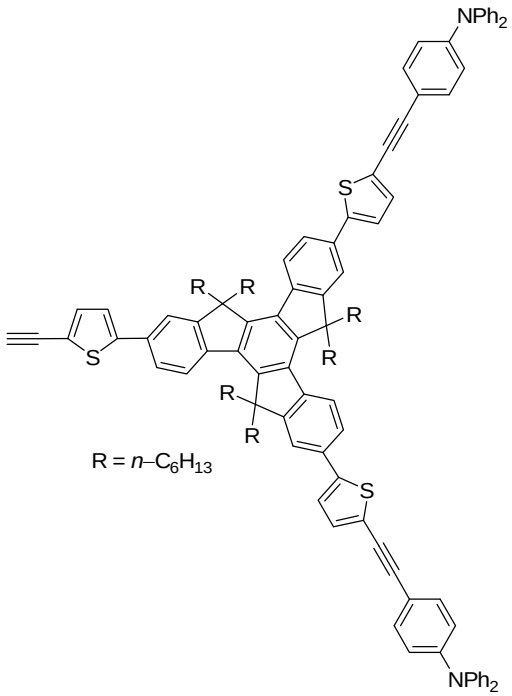
12. The general procedure for the Sonogashira coupling reaction between **11** and 2-methylbut-3-yn-2-ol was followed and purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate, 5:1) to afford the product as a white solid in 28% yield. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.34-8.37 (d, *J* = 8.4 Hz, 3H, Ar-H), 7.59-7.66 (m, 6H, Ar-H), 7.32-7.33 (d, *J* = 3.6 Hz, 1H, Ar-H), 7.29-7.31 (d, *J* = 3.6 Hz, 2H, Ar-H), 7.22-7.23 (d, *J* = 3.6 Hz, 1H, Ar-H), 7.13-7.14 (d, *J* = 3.6 Hz, 2H, Ar-H), 2.92-2.97 (m, 6H, CH_2), 2.05-2.12

(m, 6H, CH_2, OH), 1.66 (s, 6H, CH_3), 0.87-0.95 (m, 36H, CH_2), 0.53-0.62 (m, 30H, CH_2, CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 154.4, 150.8, 146.1, 145.3, 140.1, 140.0, 137.93, 137.87, 133.2, 131.8, 131.7, 125.0, 124.3, 124.1, 123.9, 122.7, 121.5, 119.2, 119.1, 98.2, 75.9, 72.1, 65.8, 55.8, 37.0, 31.42, 31.35, 29.4, 23.9, 22.2, 13.9. MALDI-TOF MS (*m/z*): Calcd. for $C_{80}H_{100}OI_2S_3$: 1427.6. Found: 1342 ($[M-C_6H_{13}]^+$). Elemental Analysis: Calcd. for $C_{80}H_{100}OI_2S_3$: C, 67.30; H, 7.06. Found: C, 67.70; H, 7.13.

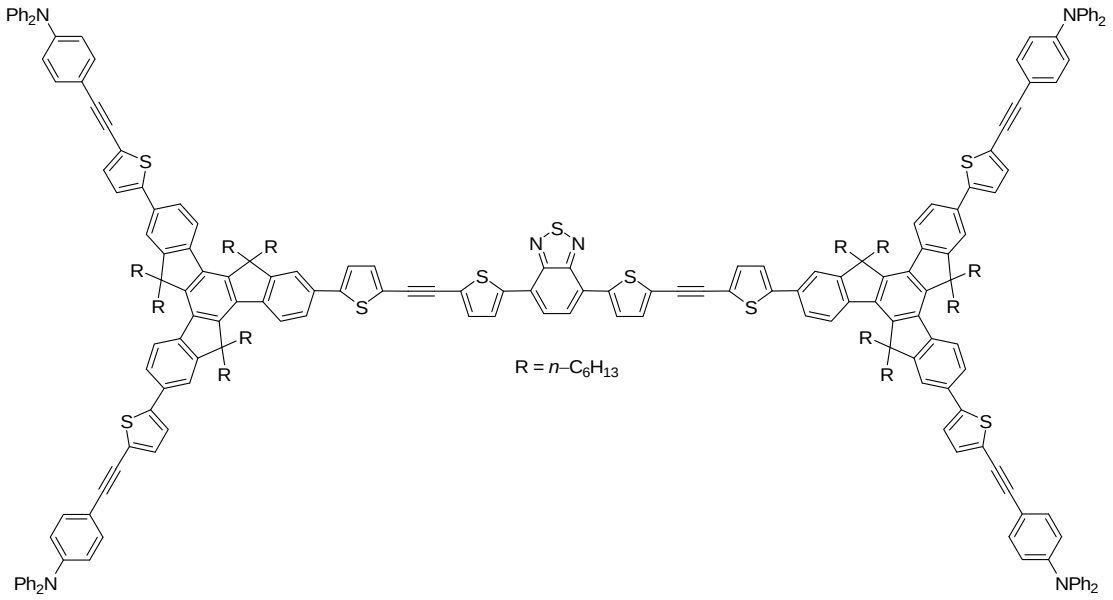


13. The general procedure for the Sonogashira coupling between **12** and 4-ethynyl-*N*,*N*-diphenylaniline was followed and purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate, 5:1) to afford the product as a yellow solid in 82% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.35-8.37 (d, J = 8.4 Hz, 3H, Ar-H), 7.63-7.67 (m, 6H, Ar-H), 7.36-7.40 (m, 6H, Ar-H), 7.26-7.32 (m, 11H, Ar-H), 7.21-7.22 (d, J = 3.6 Hz, 1H, Ar-H), 7.13-7.15 (m, 8H, Ar-H), 7.06-7.10 (m, 4H, Ar-H), 7.02-7.04 (m, 4H, Ar-H), 2.98-2.99 (m, 6H, CH_2), 2.05-2.16 (m, 6H, CH_2, OH), 1.66 (s, 6H, CH_3), 0.85-0.95 (m, 36H, CH_2), 0.55-0.62 (m, 30H, CH_2, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 154.5, 154.4, 148.1, 147.1, 146.2, 145.8, 145.39, 145.37, 145.32, 140.2, 140.1, 137.96, 137.89, 133.2, 132.6, 132.3, 132.0, 131.8, 129.45, 129.41, 129.38, 125.1, 125.07, 125.04, 125.02, 125.00, 124.1, 123.6, 122.9, 122.7, 122.1, 121.5, 119.2, 115.6, 98.2, 94.4, 82.3, 75.9, 65.8, 55.8, 37.1, 31.45, 31.37, 29.4, 23.9, 22.24, 22.20, 13.8. MALDI-TOF MS (*m/z*): Calcd. for $C_{120}H_{128}N_2OS_3$: 1708.9.

Found: 1709. Elemental Analysis: Calcd. for $C_{120}H_{128}N_2OS_3$: C, 84.26; H, 7.54; N, 0.94 Found: C, 84.22; H, 7.45; N, 1.39.



14. To a solution of **13** (1.75 g, 1.02 mmol) in toluene (100 mL) was added KOH (0.571 g, 10.2 mmol). After it was refluxed 0.5 h under nitrogen atmosphere, the mixture was quenched by NH_4Cl solution. The aqueous layer was extracted with dichloromethane. The combined organic extracts were washed with brine and then dried over $MgSO_4$. After removal of solvents under reduced pressure, the residue was purified by flash column chromatography (silica gel, petroleum ether/dichloromethane, 20:1) to provide the product as a yellow solid (1.28 g, 76%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.35-8.37 (d, *J* = 8.4 Hz, 3H, Ar-H), 7.65-7.67 (m, 6H, Ar-H), 7.35-7.40 (m, 6H, Ar-H), 7.27-7.31 (m, 12H, Ar-H), 7.12-7.14 (d, *J* = 3.6 Hz, 8H, Ar-H), 7.05-7.10 (m, 4H, Ar-H), 7.01-7.03 (d, *J* = 3.6 Hz, 4H, Ar-H), 3.43 (s, 1H, CCH), 2.94-2.97 (m, 6H, CH_2), 2.08-2.15 (m, 6H, CH_2), 0.84-0.95 (m, 36H, CH_2), 0.54-0.62 (m, 30H, CH_2, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 154.49, 154.46, 154.44, 148.1, 147.1, 146.7, 145.8, 145.45, 145.40, 145.3, 140.4, 140.0, 138.0, 137.9, 134.2, 132.6, 132.3, 132.0, 131.7, 129.4, 125.1, 124.2, 124.1, 123.6, 122.9, 122.7, 122.6, 122.1, 120.8, 119.3, 119.2, 115.6, 94.4, 82.3, 81.9, 76.8, 55.8, 37.1, 31.4, 29.4, 23.9, 22.2, 13.9. MALDI-TOF MS (*m/z*): Calcd. for $C_{117}H_{122}N_2S_3$: 1650.8. Found: 1651. Elemental Analysis: Calcd. for $C_{117}H_{122}N_2S_3$: C, 85.04; H, 7.44; N, 1.70. Found: C, 84.80; H, 7.67; N, 1.48.



TBTTrTPA. The general procedure for the Sonogashira coupling reaction between **1** and **14** was followed and purified by flash column chromatography (silica gel, petroleum ether /dichloromethane, 4:1) to afford the desired product as dark solid in 67% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.37-8.39 (m, 6H, Ar-H), 8.08-8.09 (d, *J* = 3.6 Hz, 2H, Ar-H), 7.94 (s, 1H, Ar-H), 7.67-7.70 (m, 12H, Ar-H), 7.36-7.42 (m, 18H, Ar-H), 7.28-7.32 (m, 20H, Ar-H), 7.13-7.16 (m, 16H, Ar-H), 7.07-7.11 (m, 8H, Ar-H), 7.02-7.05 (m, 8H, Ar-H), 2.97 (m, 12H, CH_2), 2.14 (m, 12H, CH_2), 0.86-0.97 (m, 72H, CH_2), 0.60-0.64 (m, 60H, CH_2, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 154.6, 154.5, 152.4, 148.1, 147.13, 147.06, 145.8, 145.5, 145.43, 145.38, 140.8, 140.4, 140.1, 138.0, 137.9, 133.5, 132.9, 132.6, 132.4, 132.0, 131.8, 129.4, 127.6, 125.7, 125.1, 124.9, 124.6, 124.2, 124.1, 123.7, 123.1, 122.9, 122.7, 122.1, 121.6, 119.1, 115.6, 94.4, 89.0, 87.6, 82.3, 76.7, 55.8, 37.1, 31.5, 29.5, 24.0, 22.3, 13.9. MALDI-TOF MS (*m/z*): Calcd. for $C_{248}H_{248}N_6S_9$: 3601.2. Found: 3601. Elemental Analysis: Calcd. for $C_{248}H_{248}N_6S_9$: C, 82.71; H, 6.94; N, 2.33. Found: C, 82.74; H, 6.92; N, 2.09.

2. **UV-vis and PL Spectra for dendrimers and model compounds.**

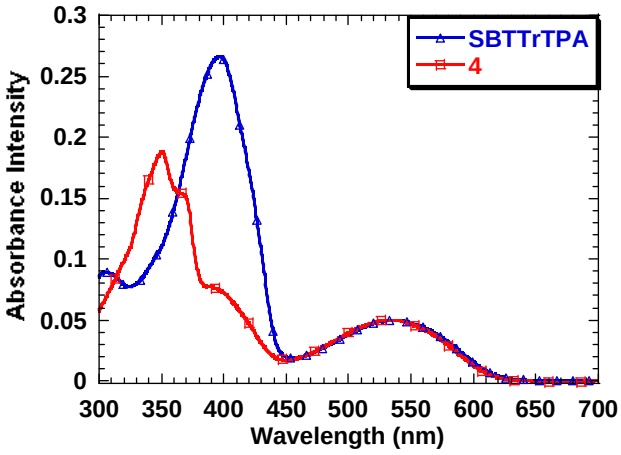


Figure S1. Absorption spectra of **4** and **SBTTrTPA** in dilute cyclohexane solution (10^{-6} M).

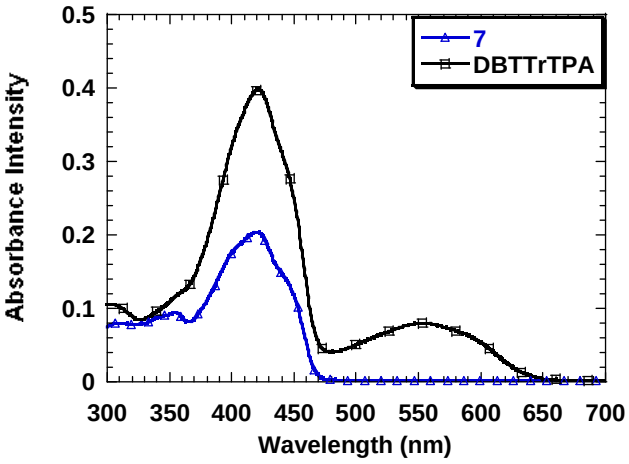


Figure S2. Absorption spectra of **7** and **DBTTrTPA** in dilute cyclohexane solution (10^{-6} M).

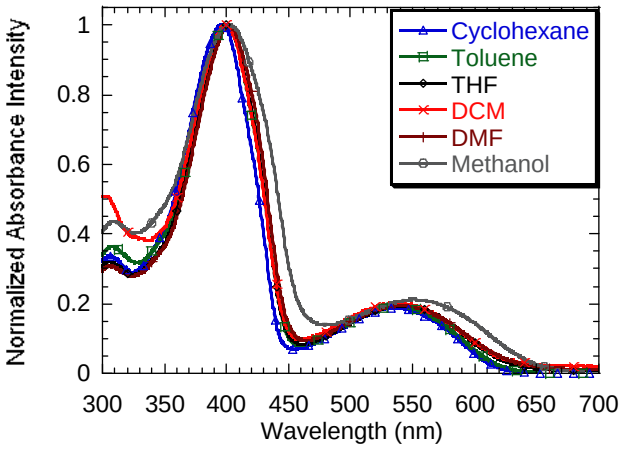


Figure S3. Absorption spectra of **SBTTrTPA** in various solvents at 10^{-6} M solution.

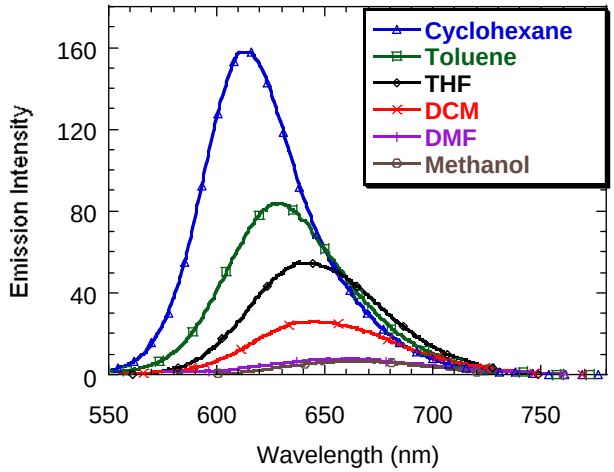


Figure S4. Emission spectra of the **SBTTrTPA** in various solvents at 10^{-6} M. Emission spectra were obtained upon excitation at 535 nm.

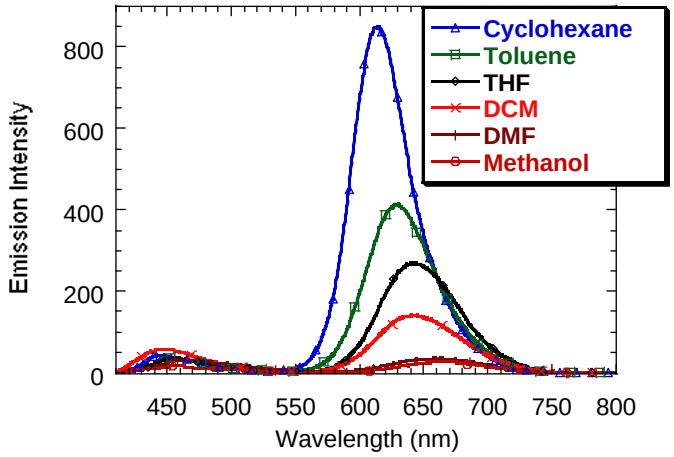


Figure S5. Emission spectra of **SBTTrTPA** in various solvents at 10^{-6} M. Emission spectra were obtained upon excitation at 396 nm.

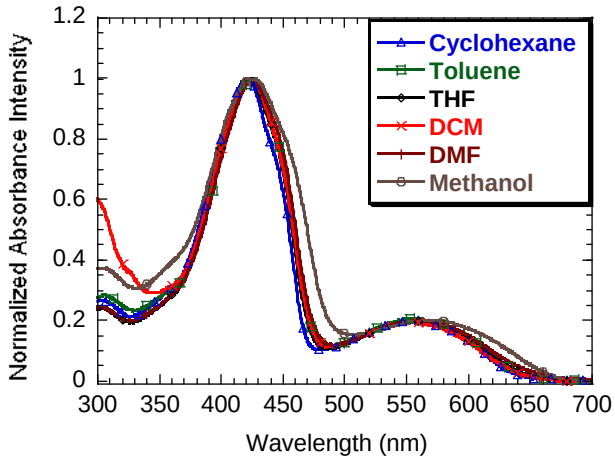


Figure S6. Absorption spectra of **DBTTrTPA** in various solvents at 10^{-6} M solution.

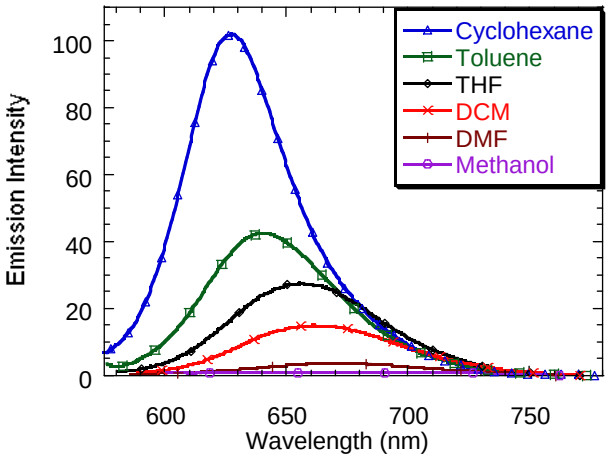


Figure S7. Emission spectra of **DBTTrTPA** in various solvents at 10^{-6} M. Emission spectra were obtained upon excitation at 552 nm.

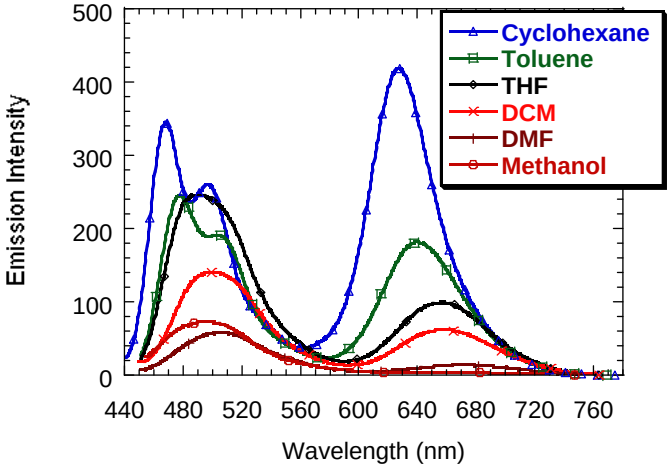


Figure S8. Emission spectra of the **DBTTrTPA** in various solvents at 10^{-6} M. Emission spectra were obtained upon excitation at 421 nm.

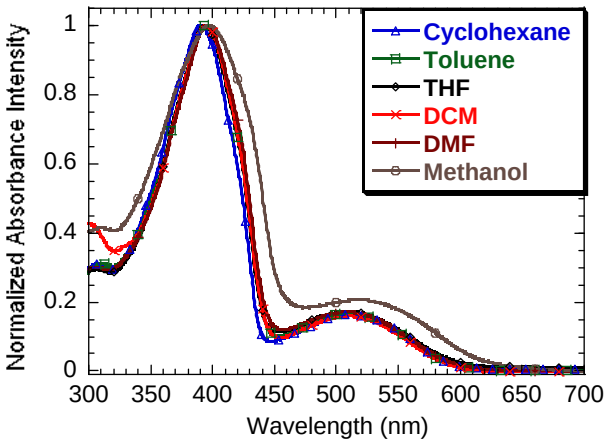


Figure S9. Absorption spectra of **TBTTrTPA** in various solvents at 10^{-6} M solution.

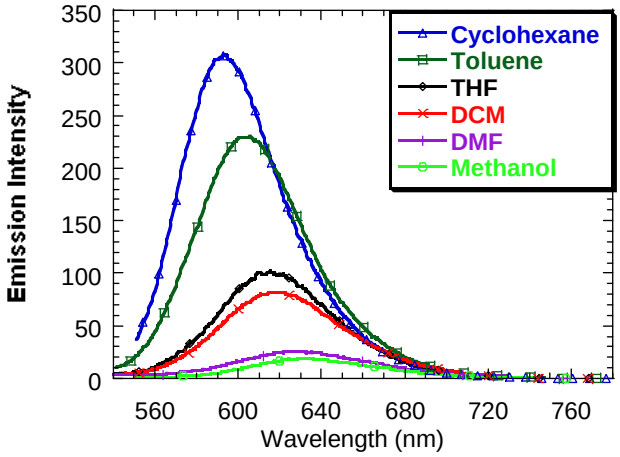


Figure S10. Emission spectra of the **TBTTrTPA** in various solvents at 10^{-6} M. Emission spectra were obtained upon excitation at 512 nm.

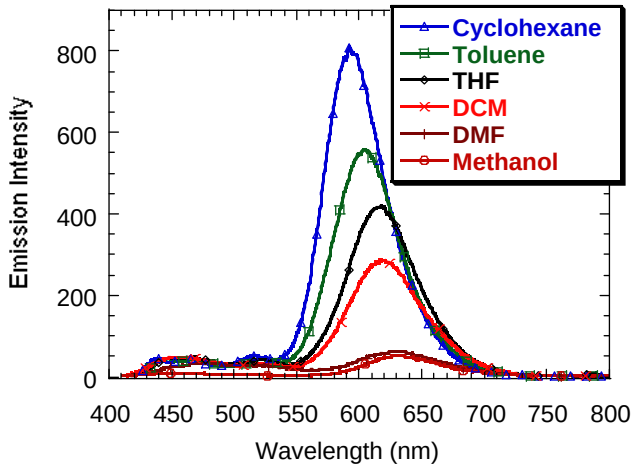


Figure S11. Emission spectra of **TBTTrTPA** in various solvents at 10^{-6} M. Emission spectra were obtained upon excitation at 391 nm.

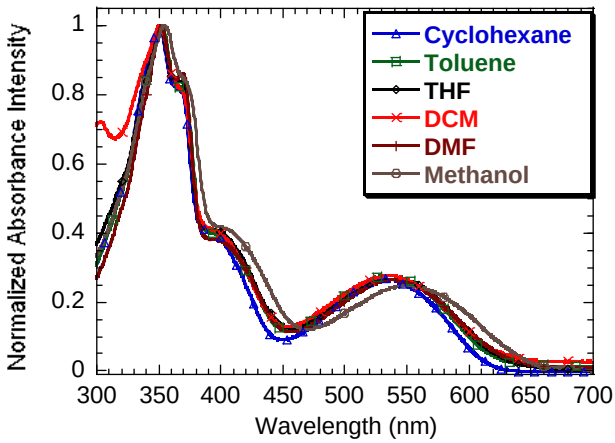


Figure S12. Absorption spectra of **4** in various solvents at 10^{-6} M solution.

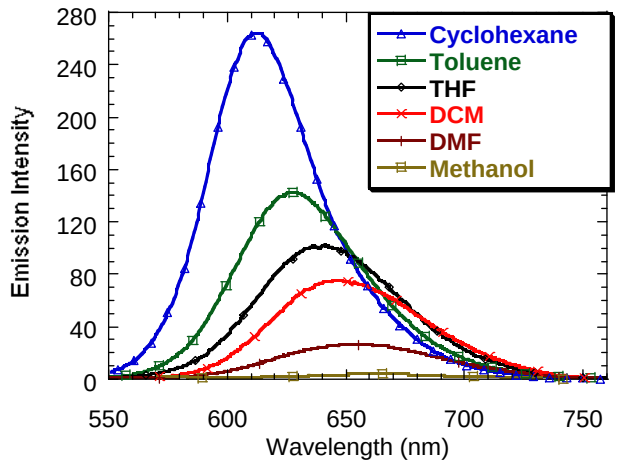


Figure S13. Emission spectra of **4** in various solvents at 10^{-6} M solution. Emission spectra were obtained upon excitation at 535 nm.

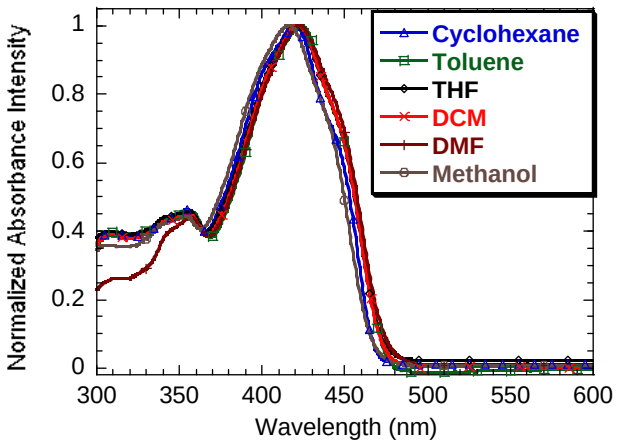


Figure S14. Absorption spectra of **7** in various solvents at 10^{-6} M solution.

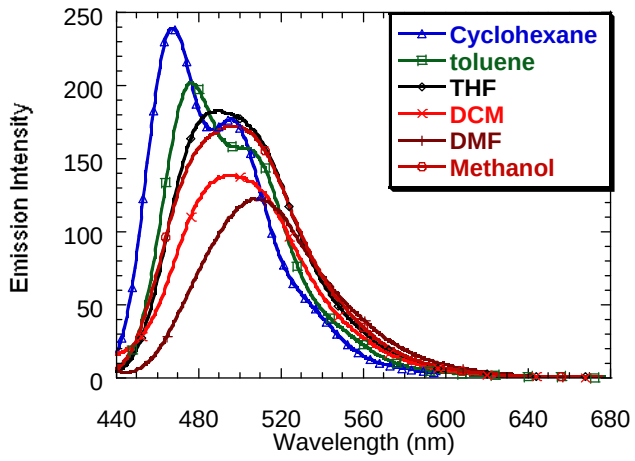


Figure S15. Emission spectra of **7** in various solvents at 10^{-6} M solution. Emission spectra were obtained upon excitation at 421 nm.

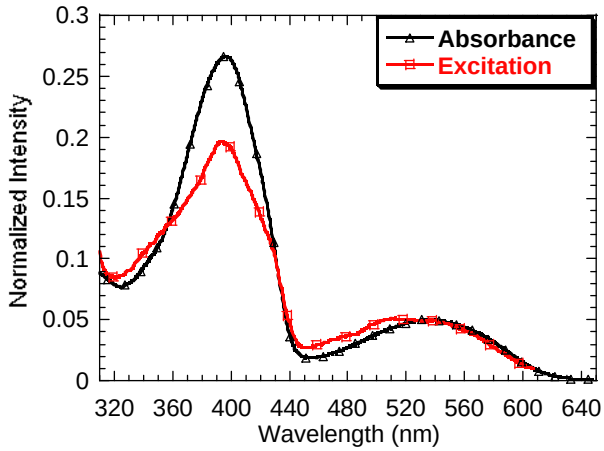


Figure S16. Comparison of absorption and excitation spectra of **SBTTrTPA** in 10^{-6} M cyclohexane solution. The spectra were normalized at longer wavelength absorption region.

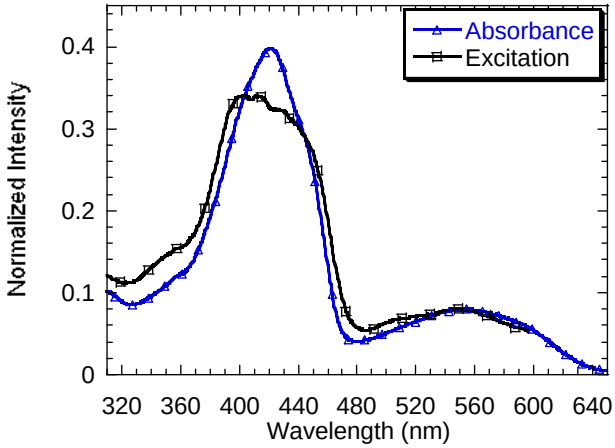


Figure S17. Comparison of absorption and excitation spectra of **DBTTrTPA** in 10^{-6} M cyclohexane solution. The spectra were normalized at longer wavelength absorption region.

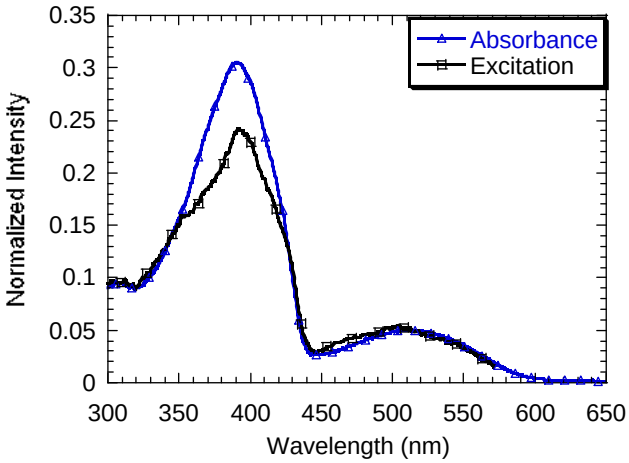


Figure S18. Comparison of absorption and excitation spectra of **TBTTrTPA** in 10^{-6} M cyclohexane solution. The spectra were normalized at longer wavelength absorption region.

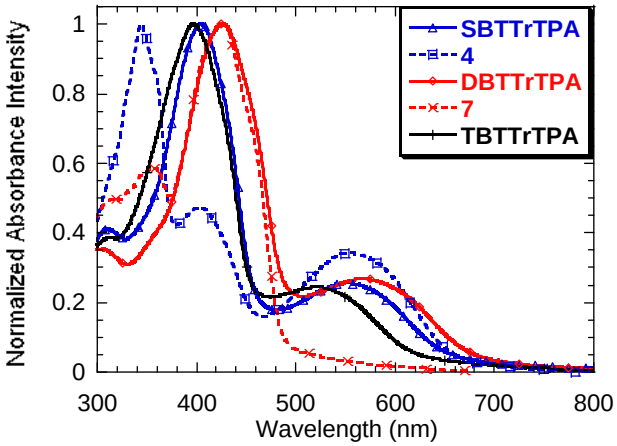


Figure S19. Absorption spectra of dendrimers and model compounds in thin films.

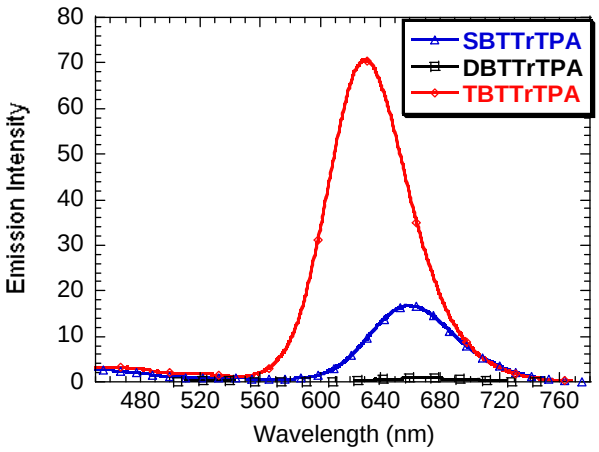
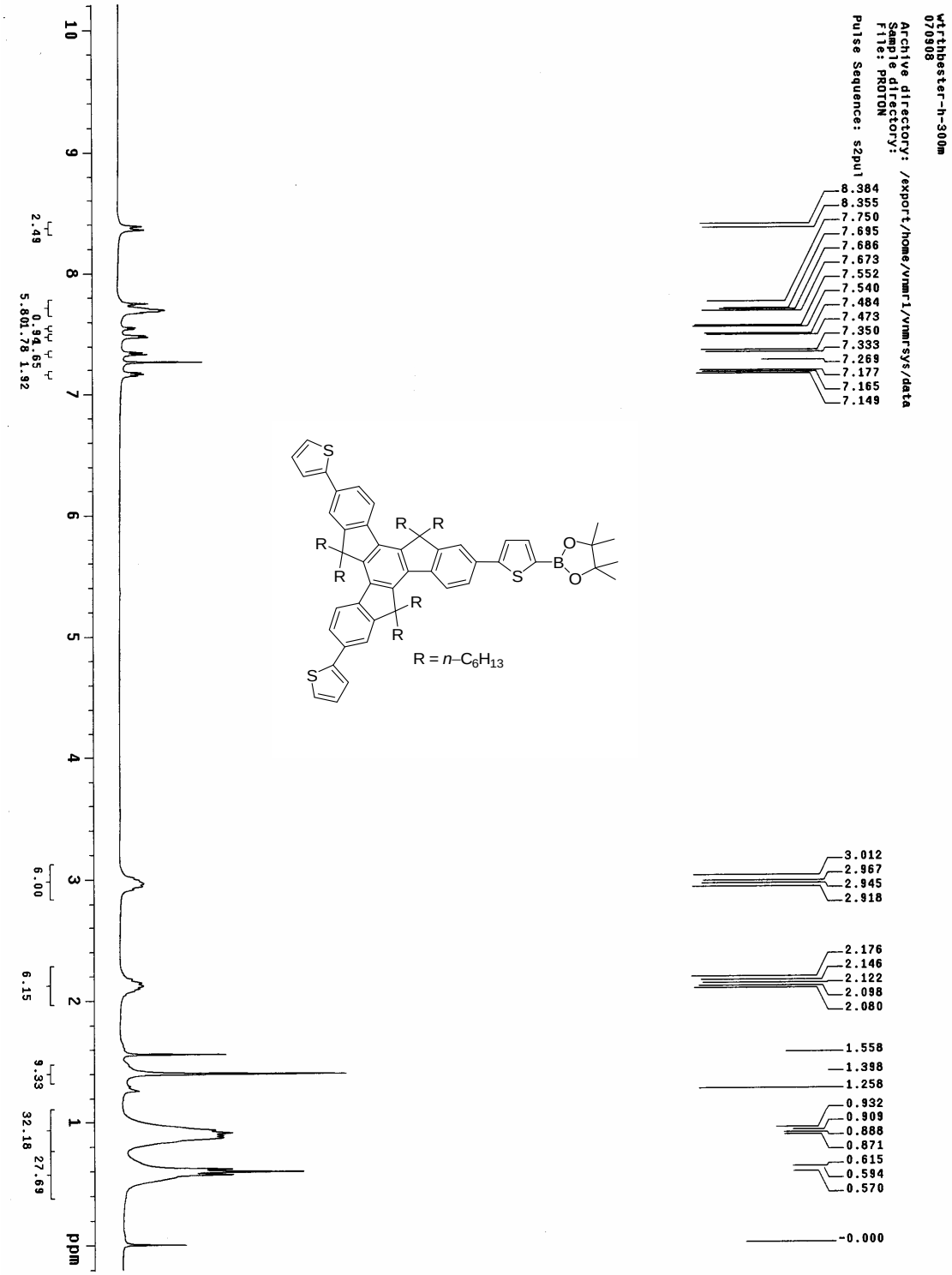


Figure S20. Comparison of emission spectra of dendrimers in thin films upon excitation at 405 nm for **SBTTrTPA**, 426 nm for **DBTTrTPA**, and 397 nm for **TBTTrTPA**, respectively.

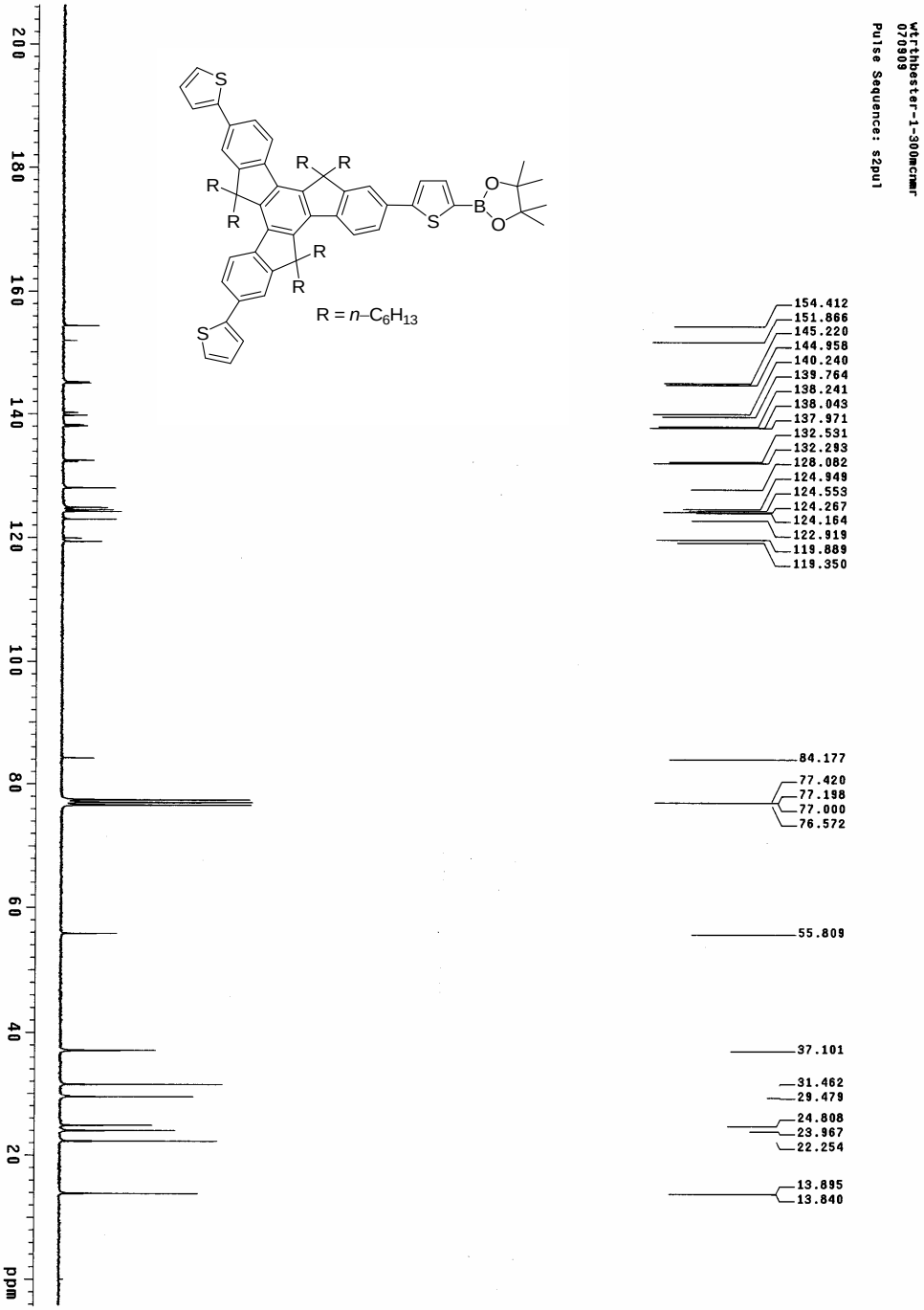
Table S1. Emission wavelength and intensity of dendrimers in different solvents upon excitation at 535 nm for **SBTTrTPA**, 552 nm for **DBTTrTPA**, 512 nm for **TBTTrTPA**, respectively.

Compounds	Cyclohexane (nm)	Toluene (nm)	THF (nm)	CH_2Cl_2 (nm)	DMF (nm)	CH_3OH (nm)
SBTTrTPA	614 (158)	628 (87)	642 (55)	647 (28)	658 (7)	662 (6)
DBTTrTPA	628 (102)	640 (42)	658 (27)	661 (14)	670 (3.5)	672 (1)
TBTTrTPA	592 (310)	604 (230)	617 (99)	618 (78)	628 (26)	633 (19)

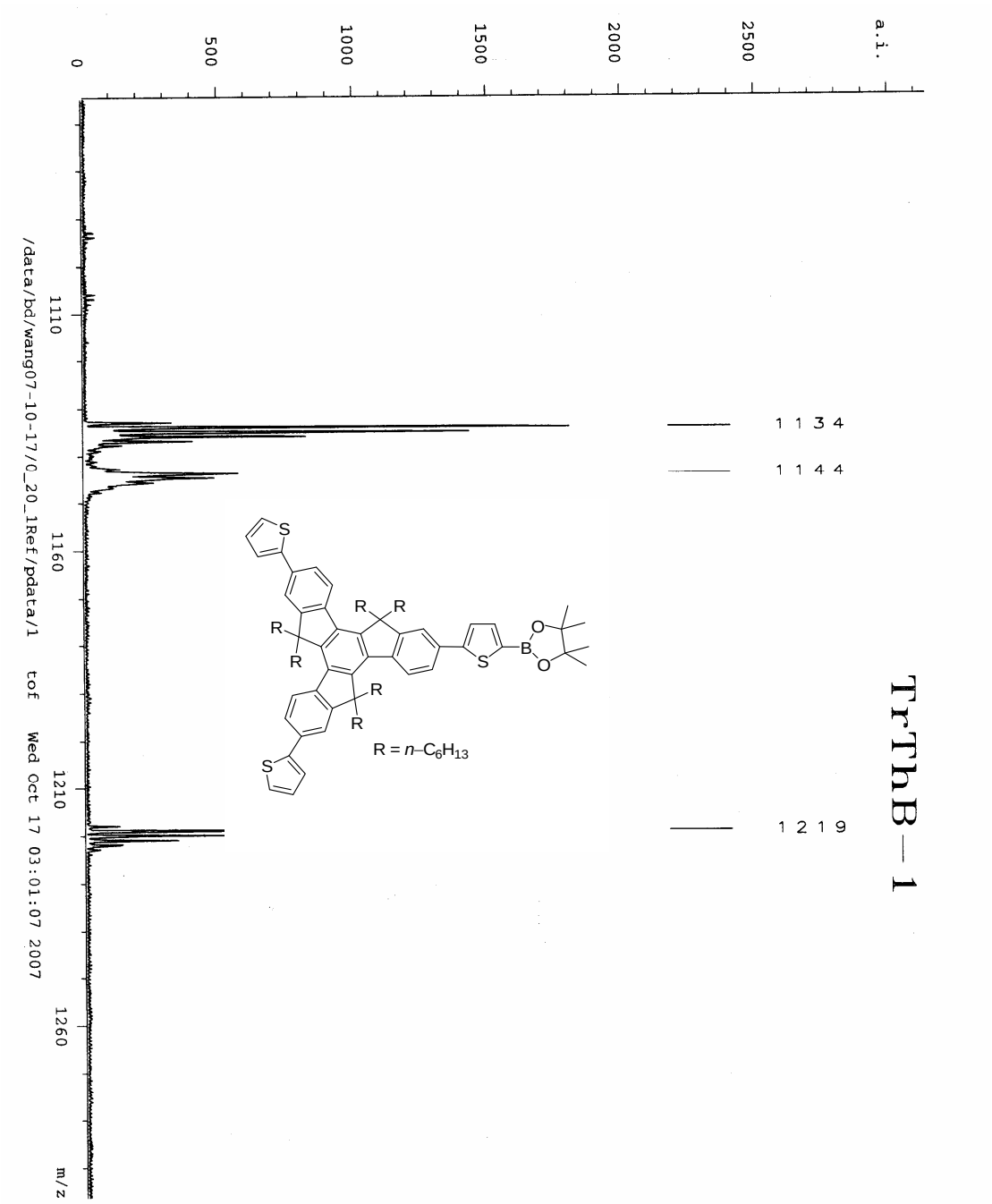
3. Copies of ^{1}H, ^{13}C NMR and MALDI-TOF MS spectra.



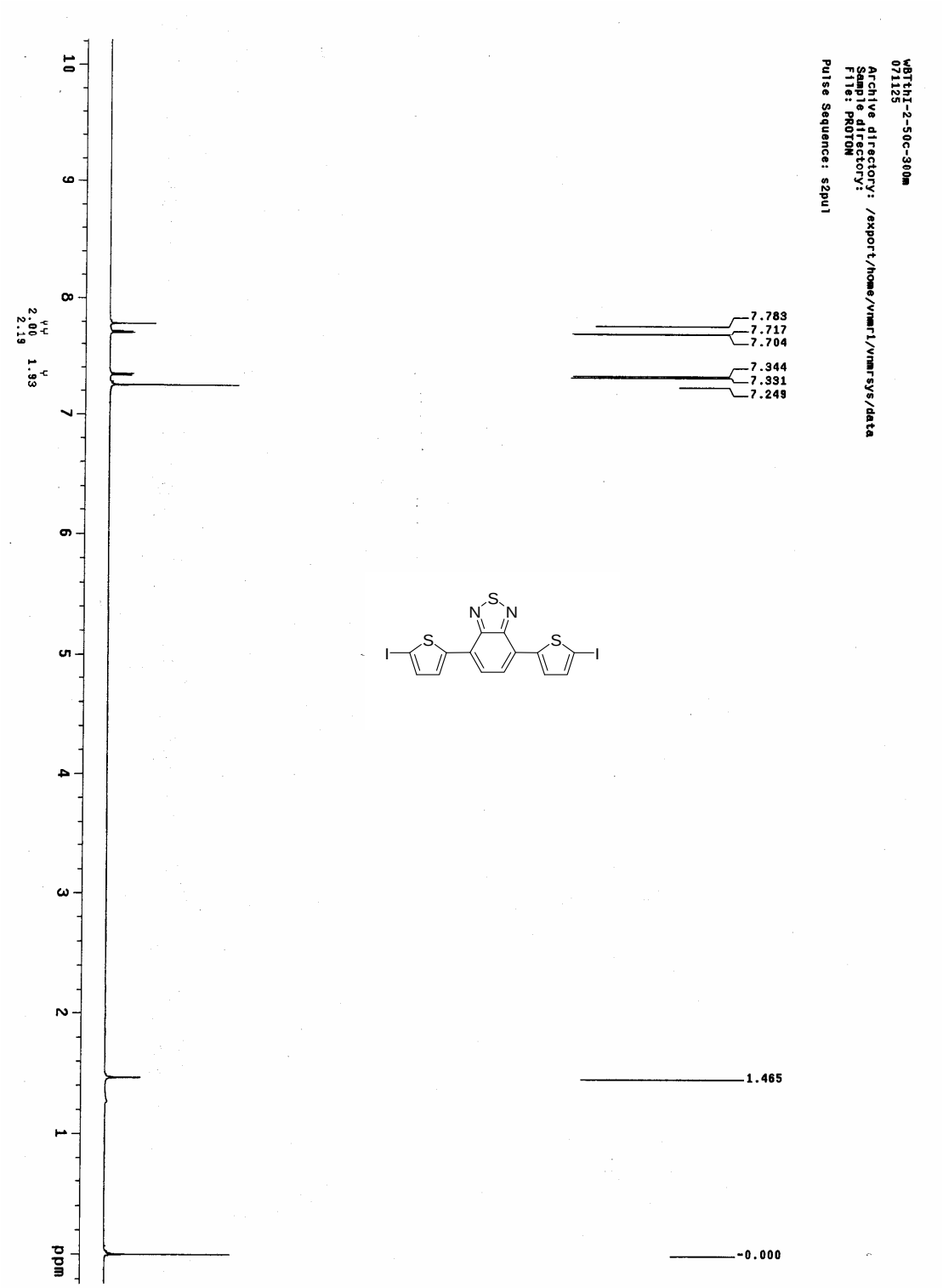
^{1}H NMR spectrum for compound **2**.



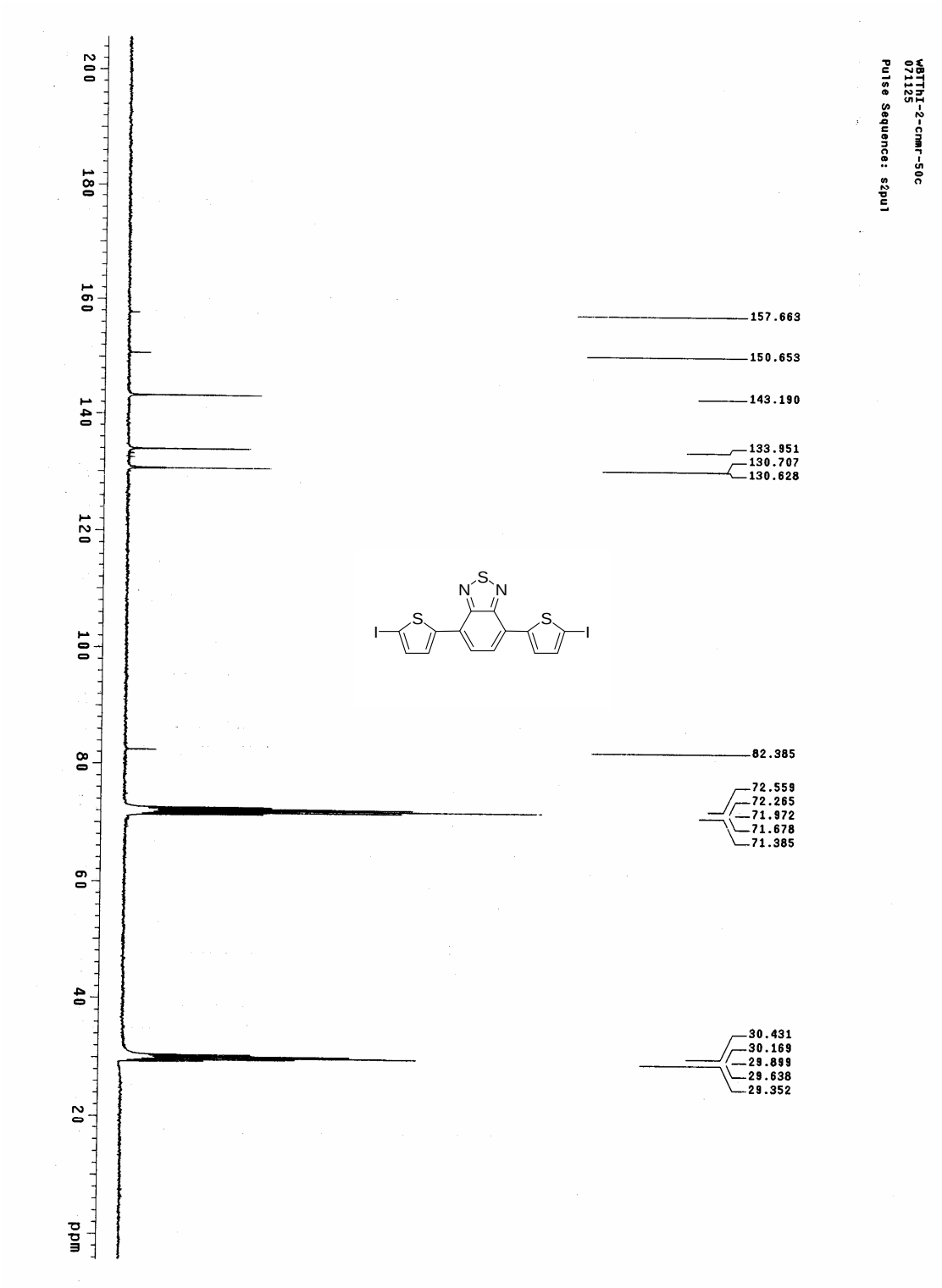
^{13}C NMR spectrum for compound **2**.



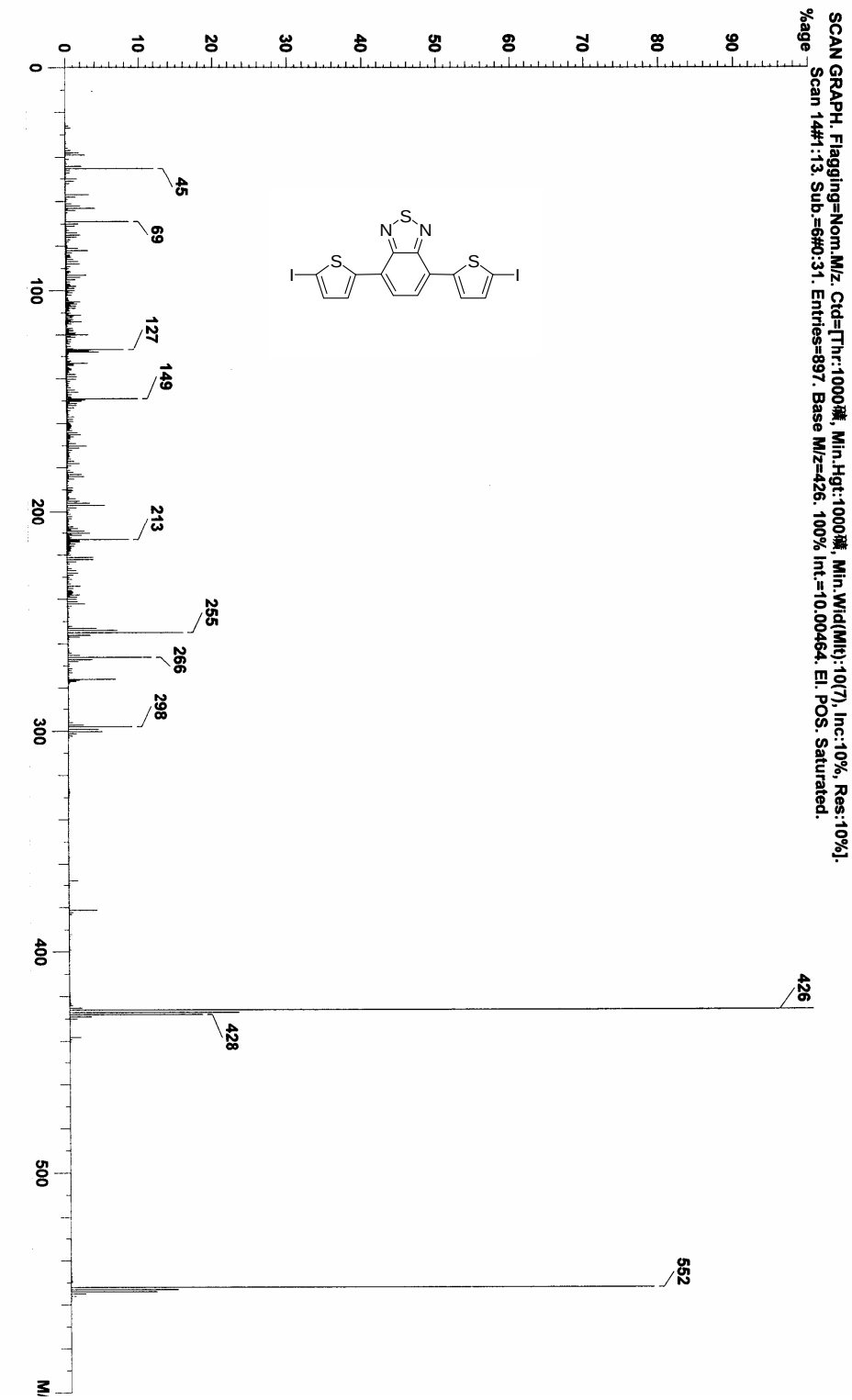
MALDI-TOF mass spectrum for compound **2**.



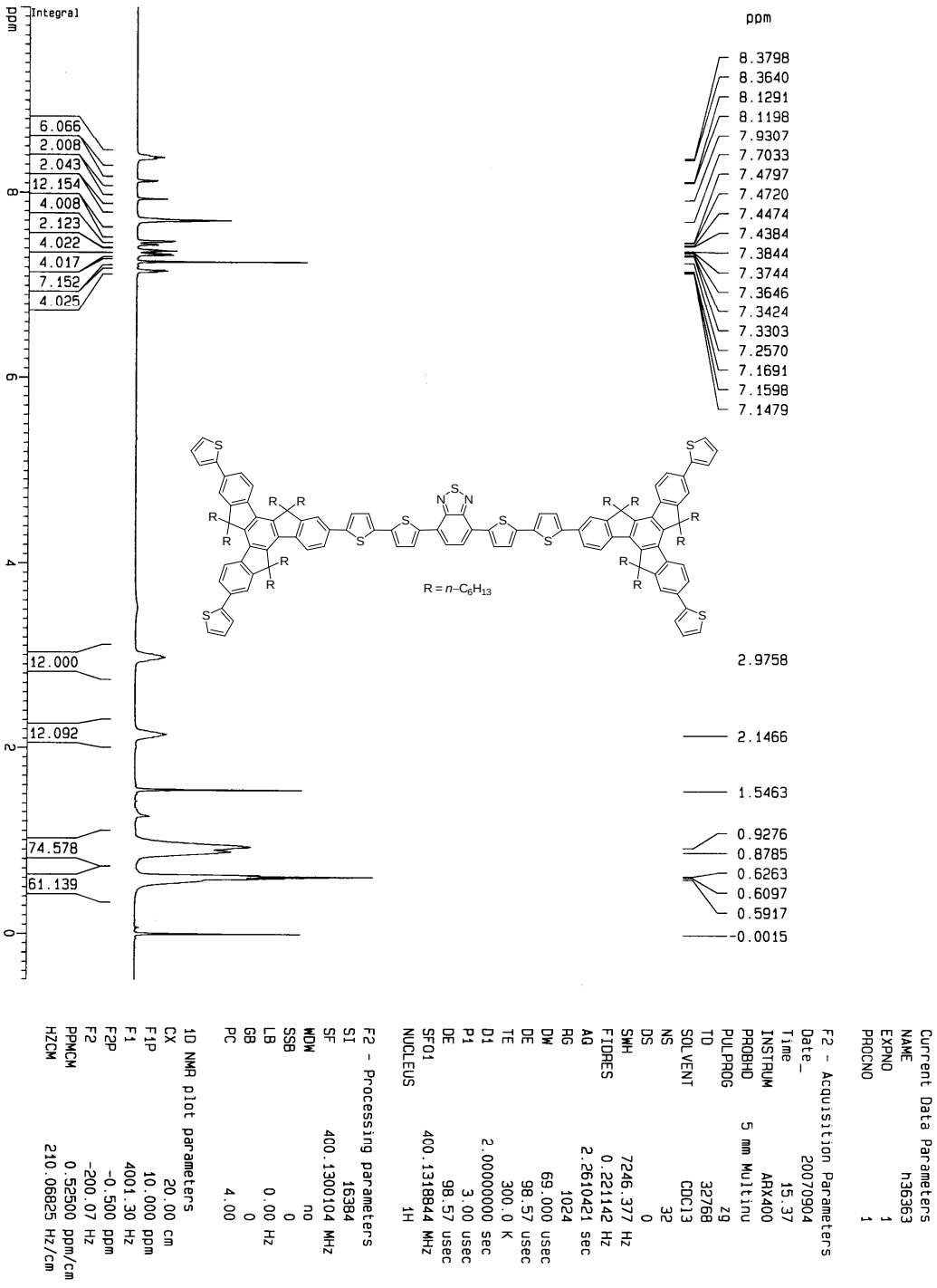
^{1}H NMR spectrum for compound **3**.



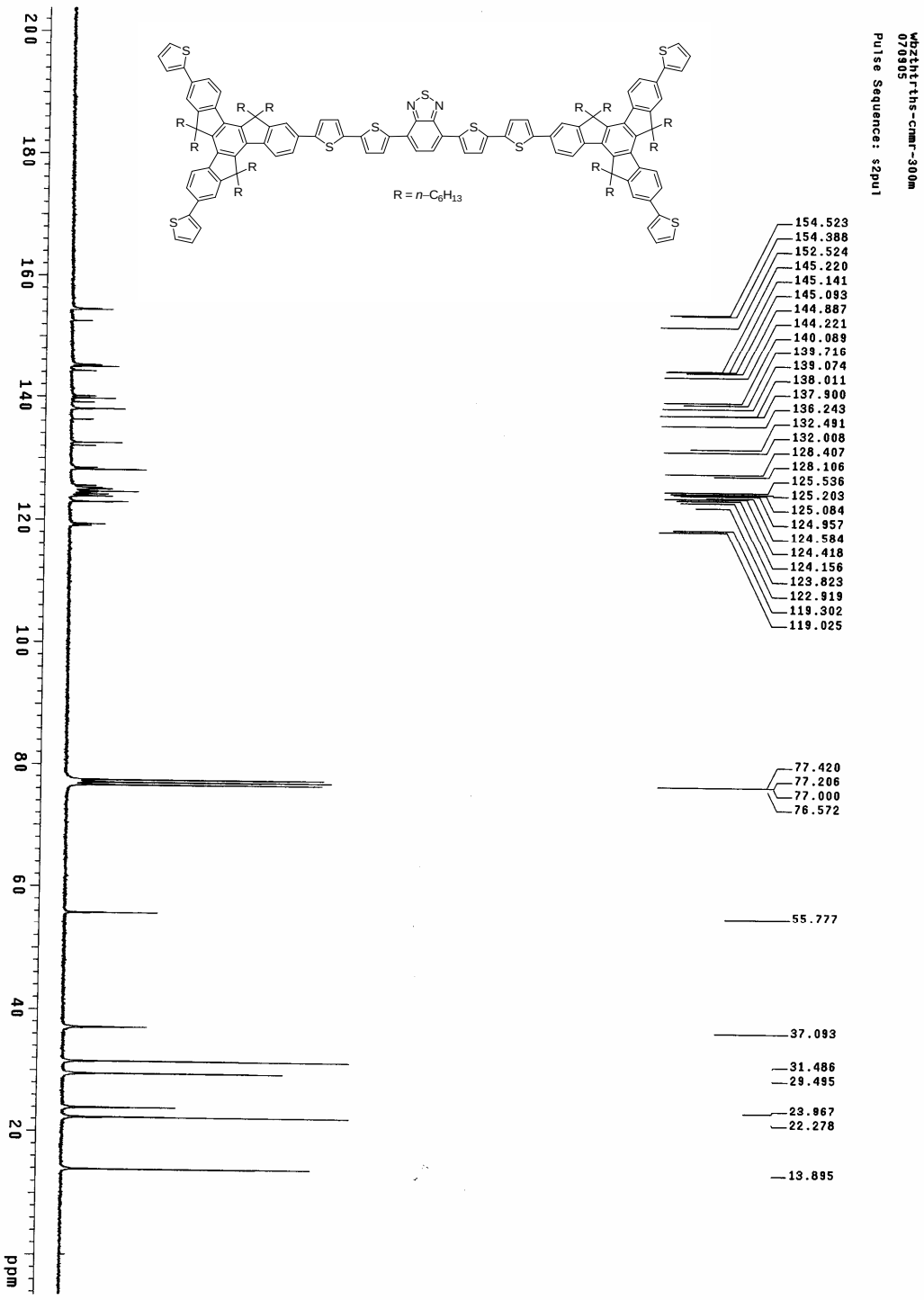
^{13}C NMR spectrum for compound **3**.



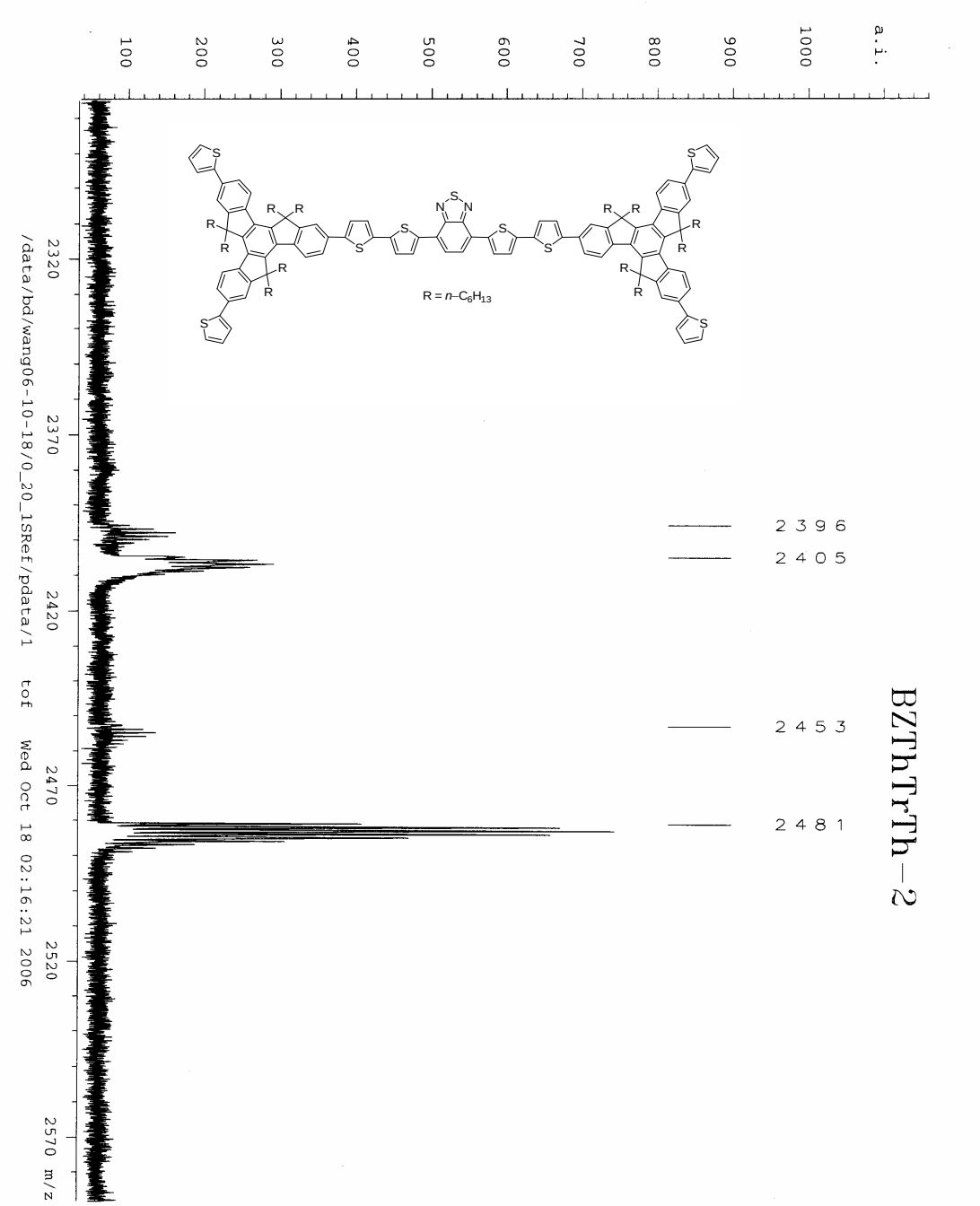
EI mass spectrum for compound **3**.



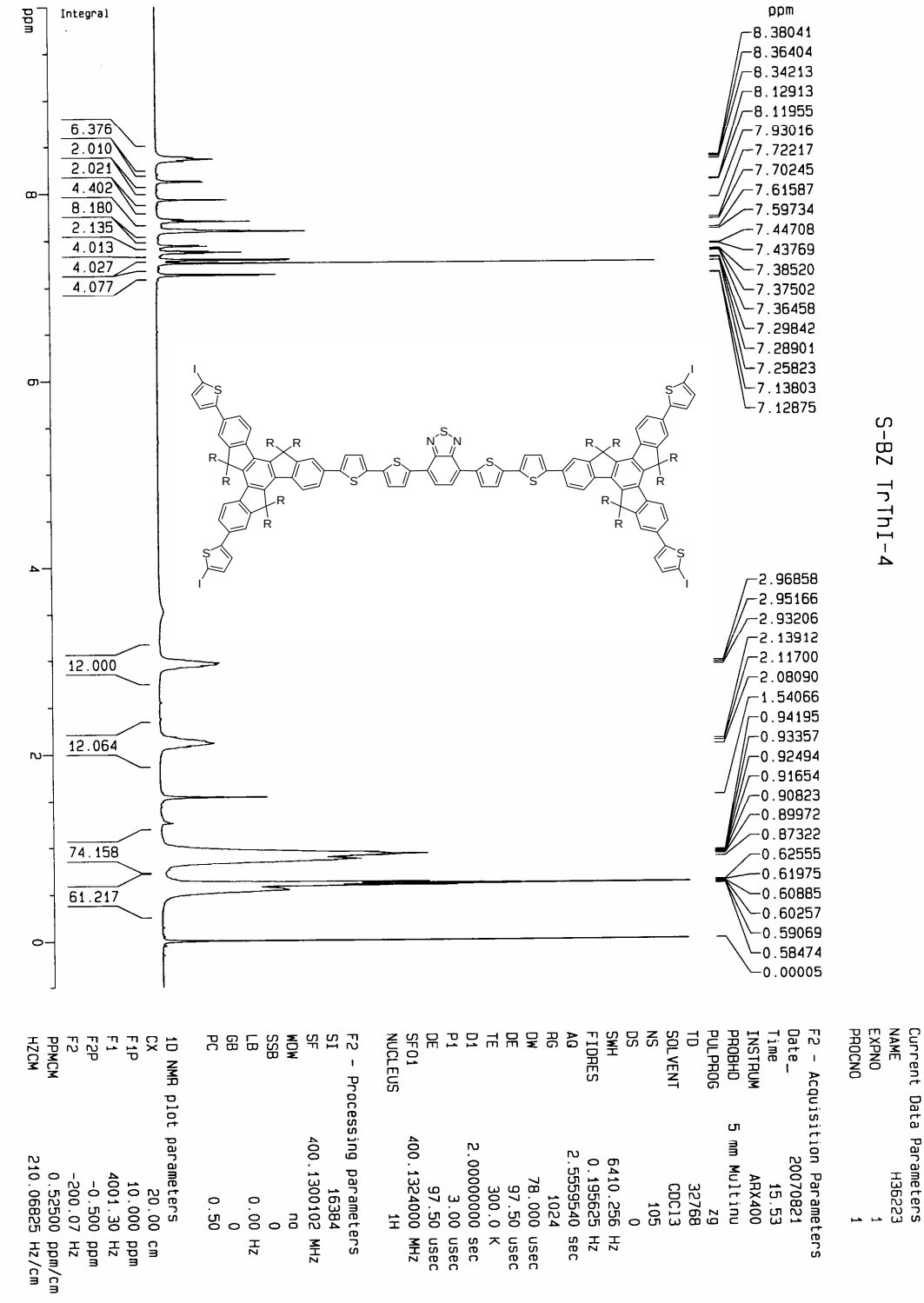
^{1}H NMR spectrum for compound **4**.



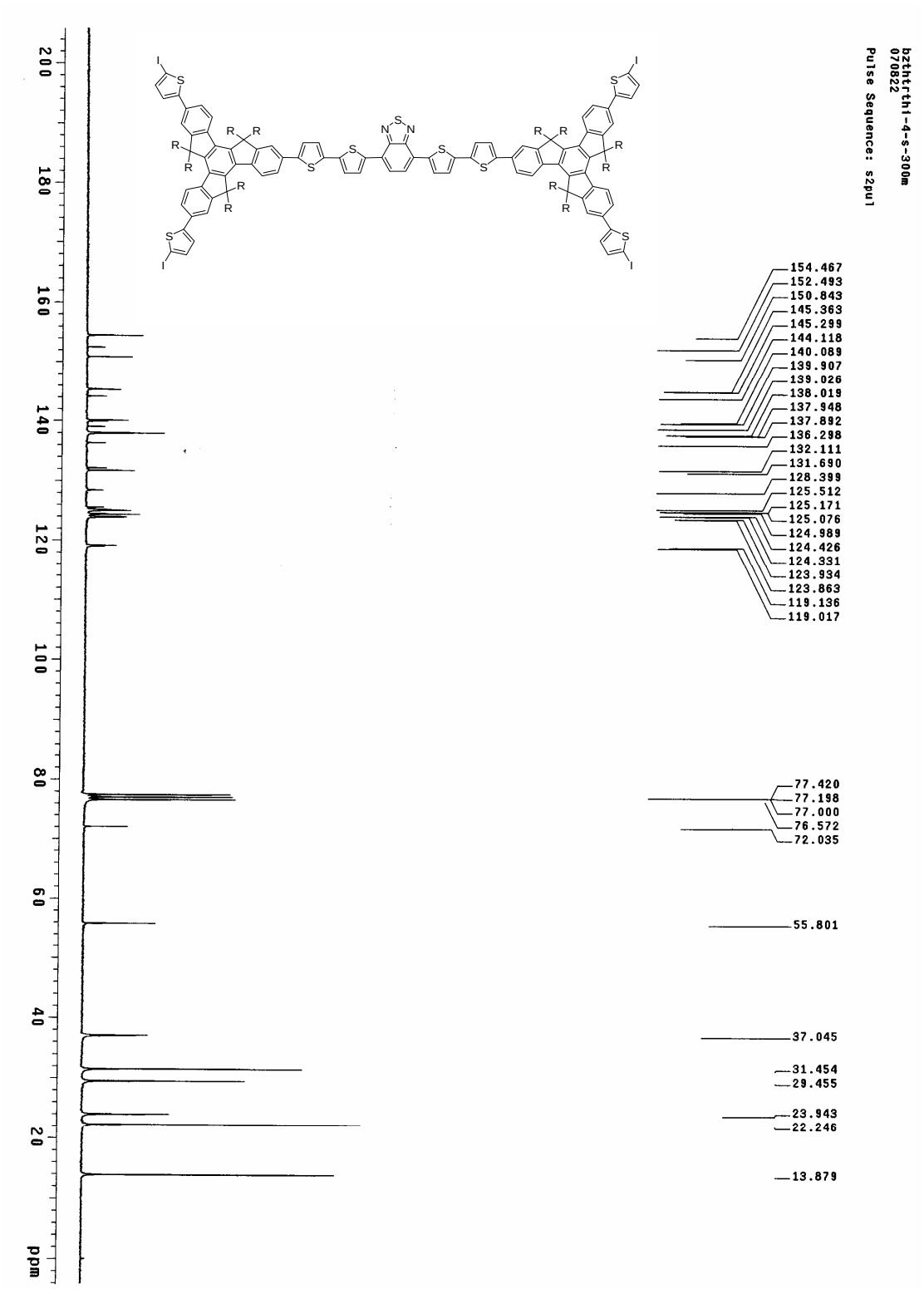
^{13}C NMR spectrum for compound **4**.



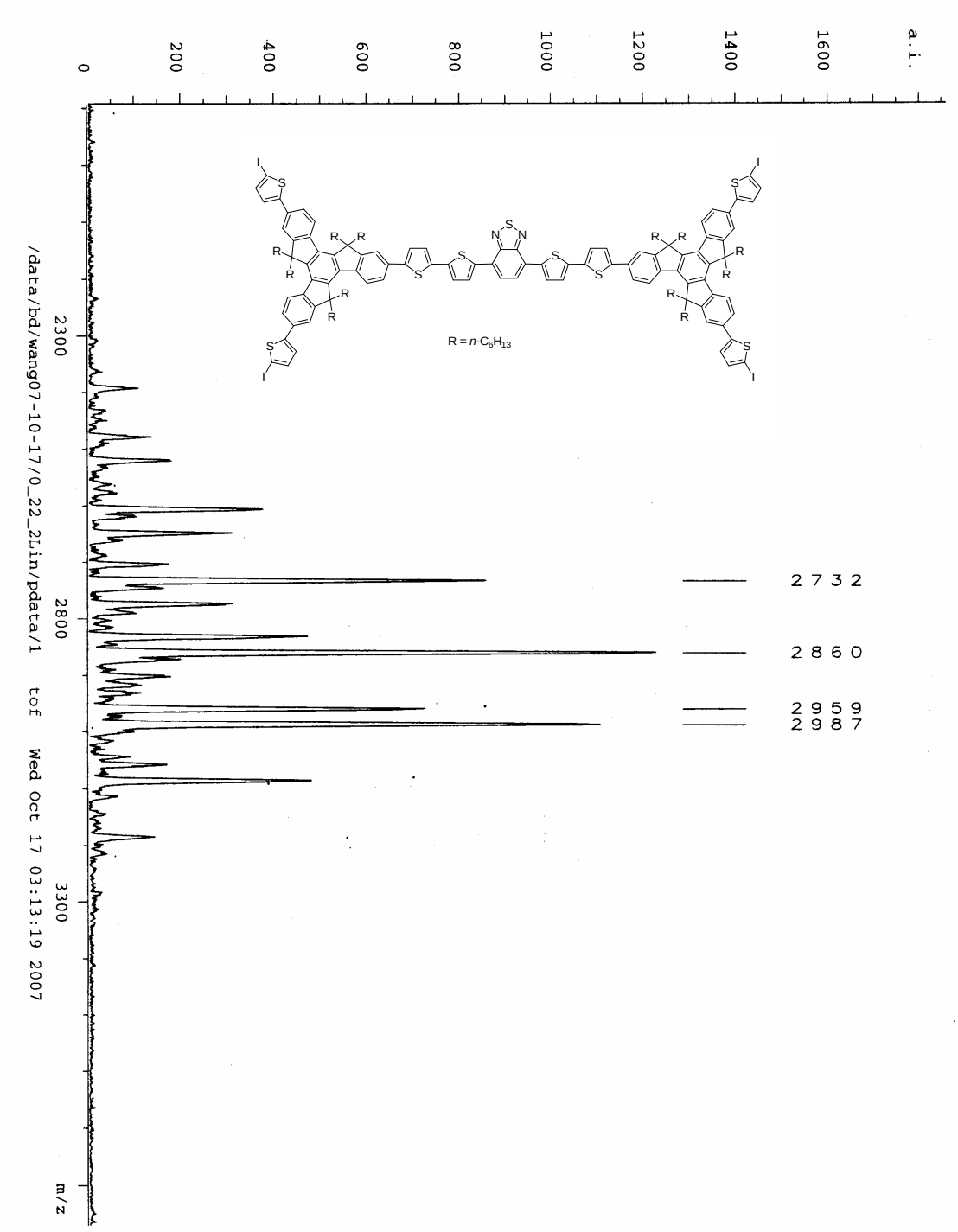
MALDI-TOF mass spectrum for compound **4**.



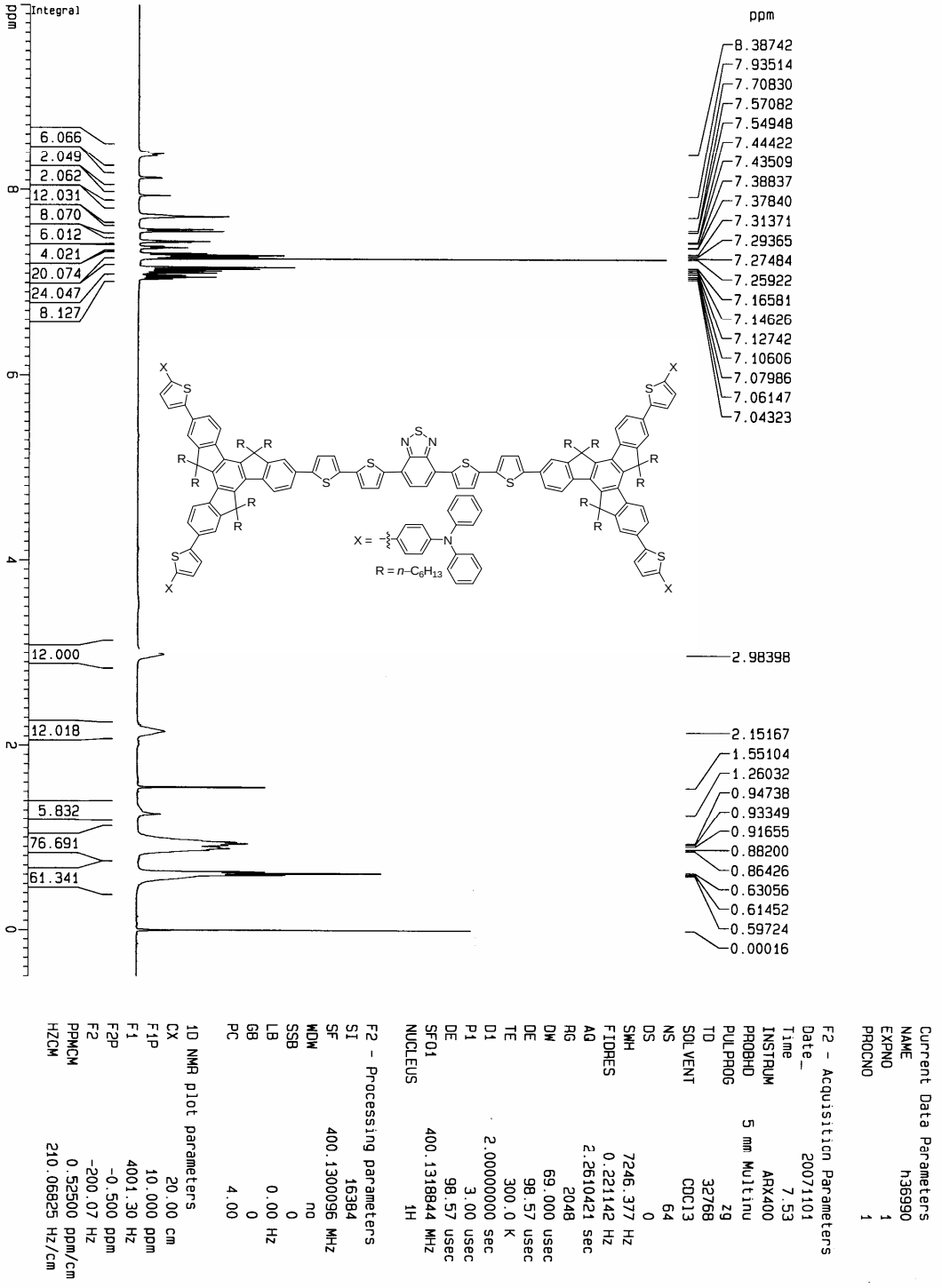
^{1}H NMR spectrum for compound **5**.



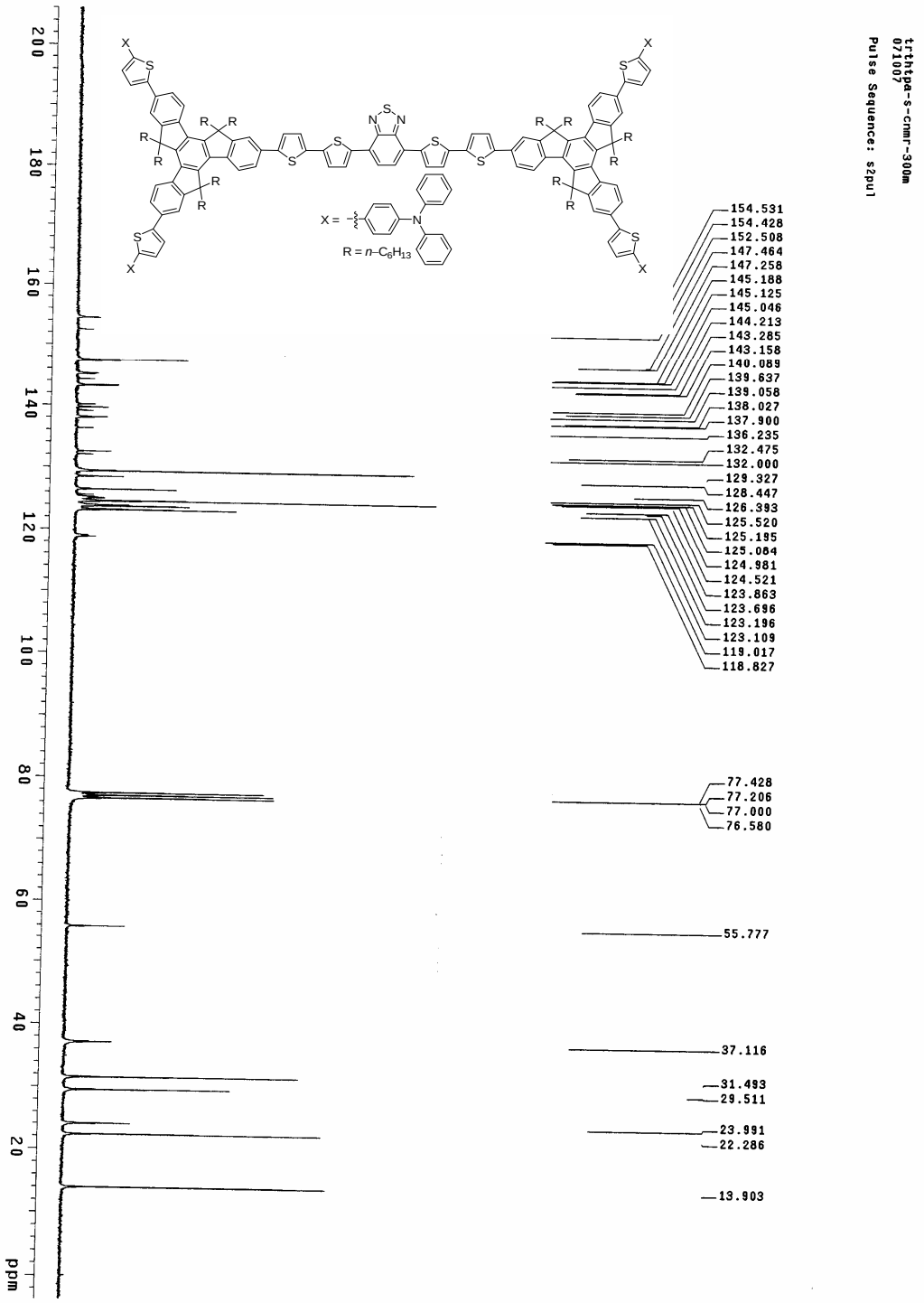
^{13}C NMR spectrum for compound **5**.



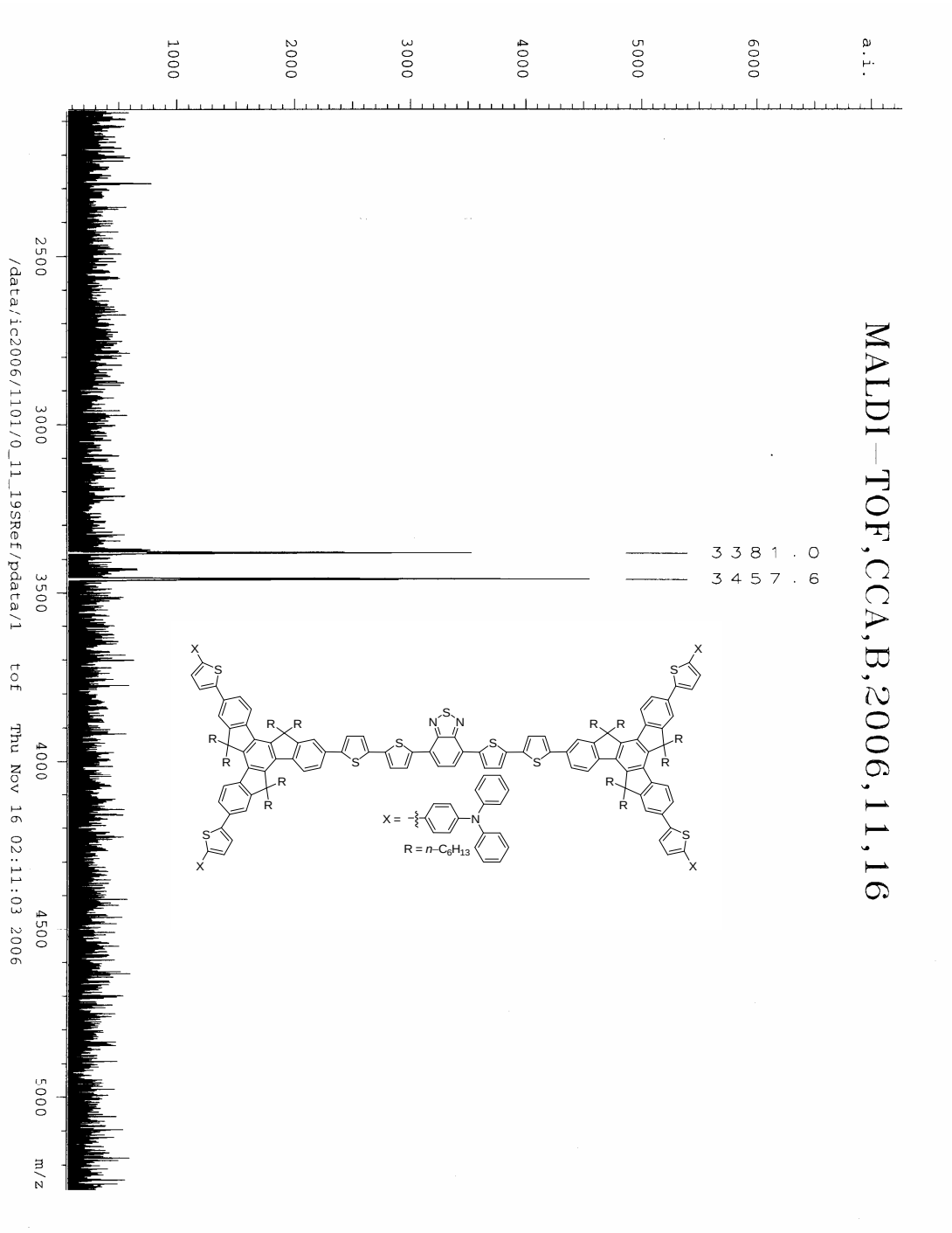
MALDI-TOF mass spectrum for compound **5**.



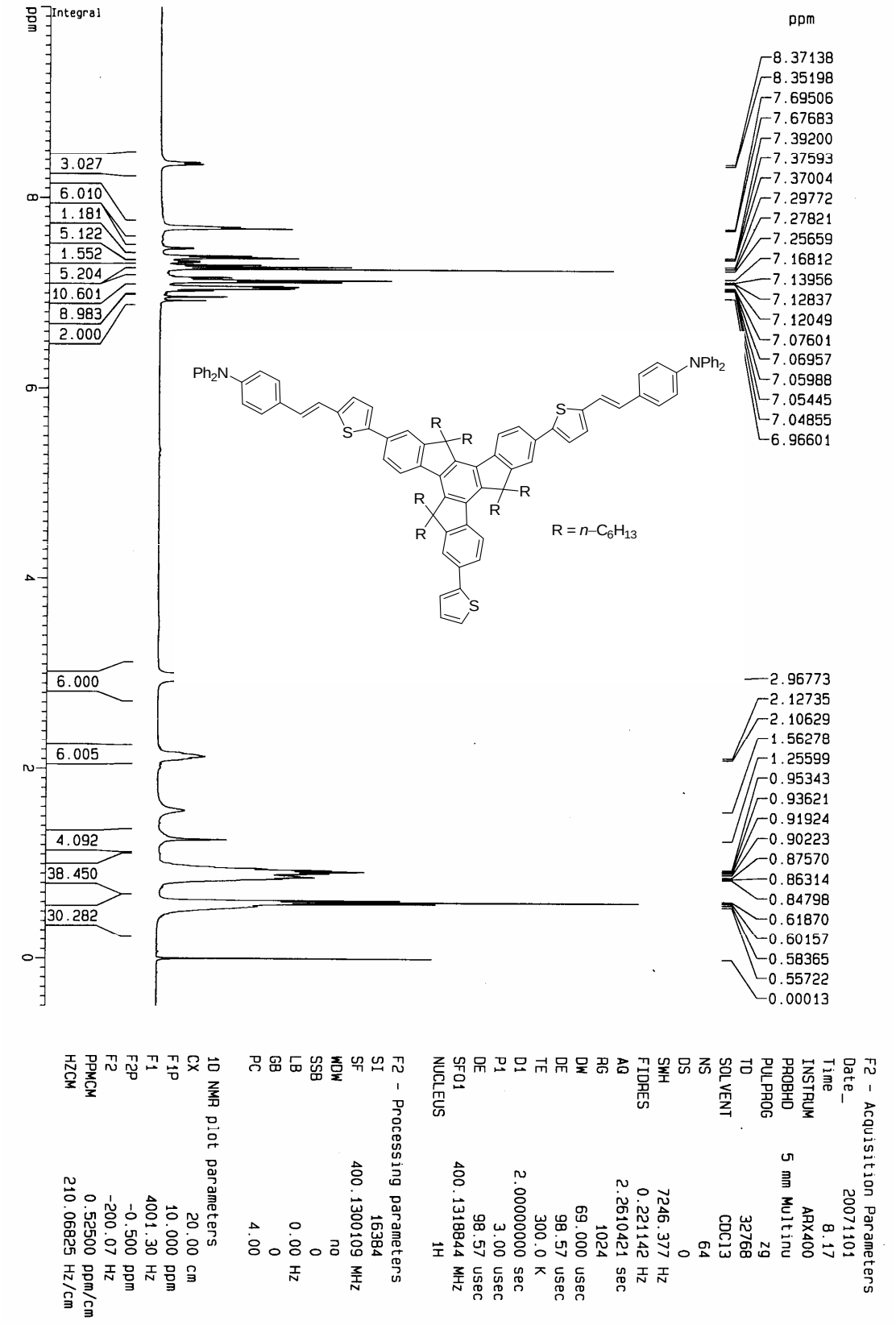
^{1}H NMR spectrum for **SBTTrTPA**.



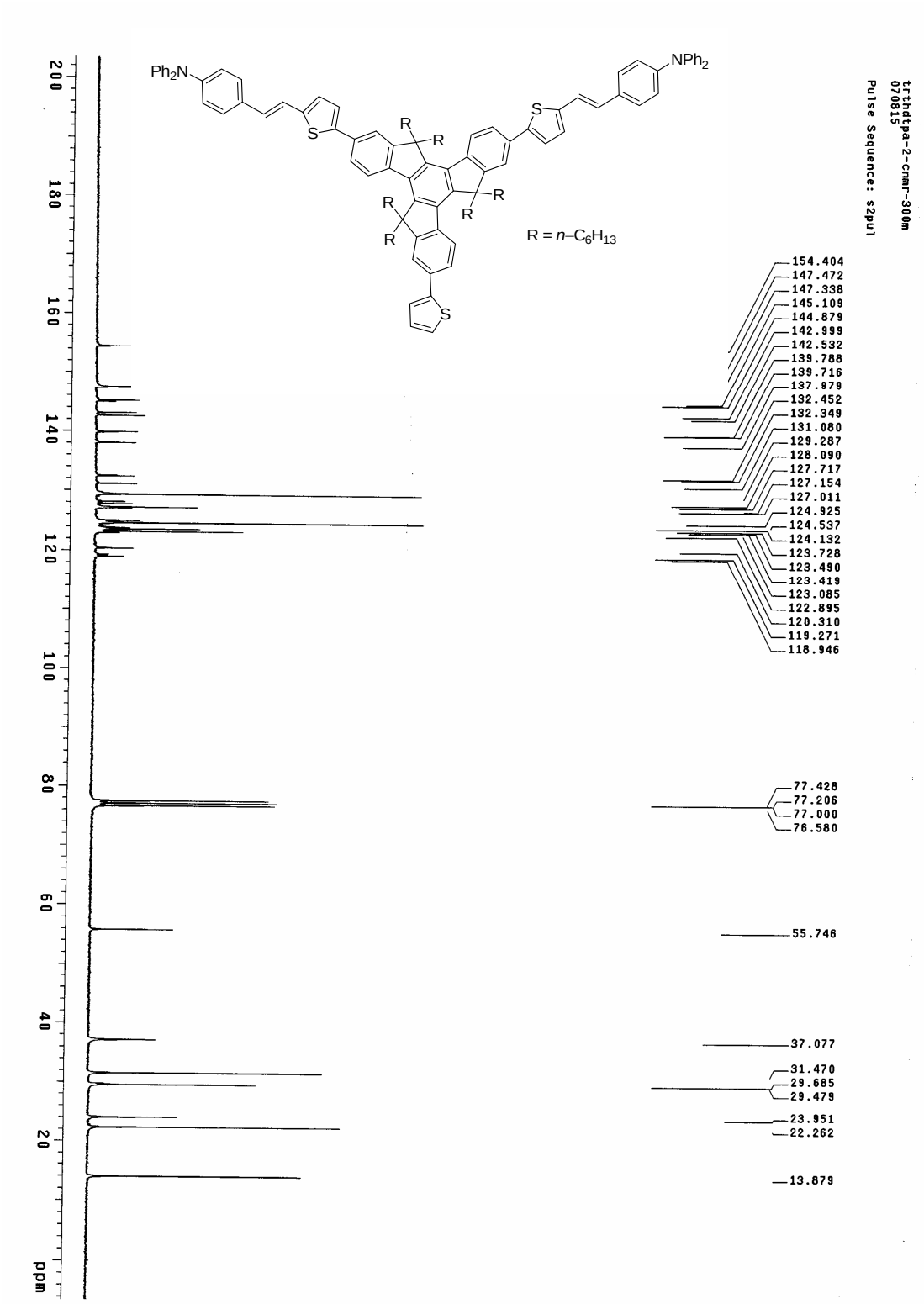
^{13}C NMR spectrum for **SBTTrTPA**.



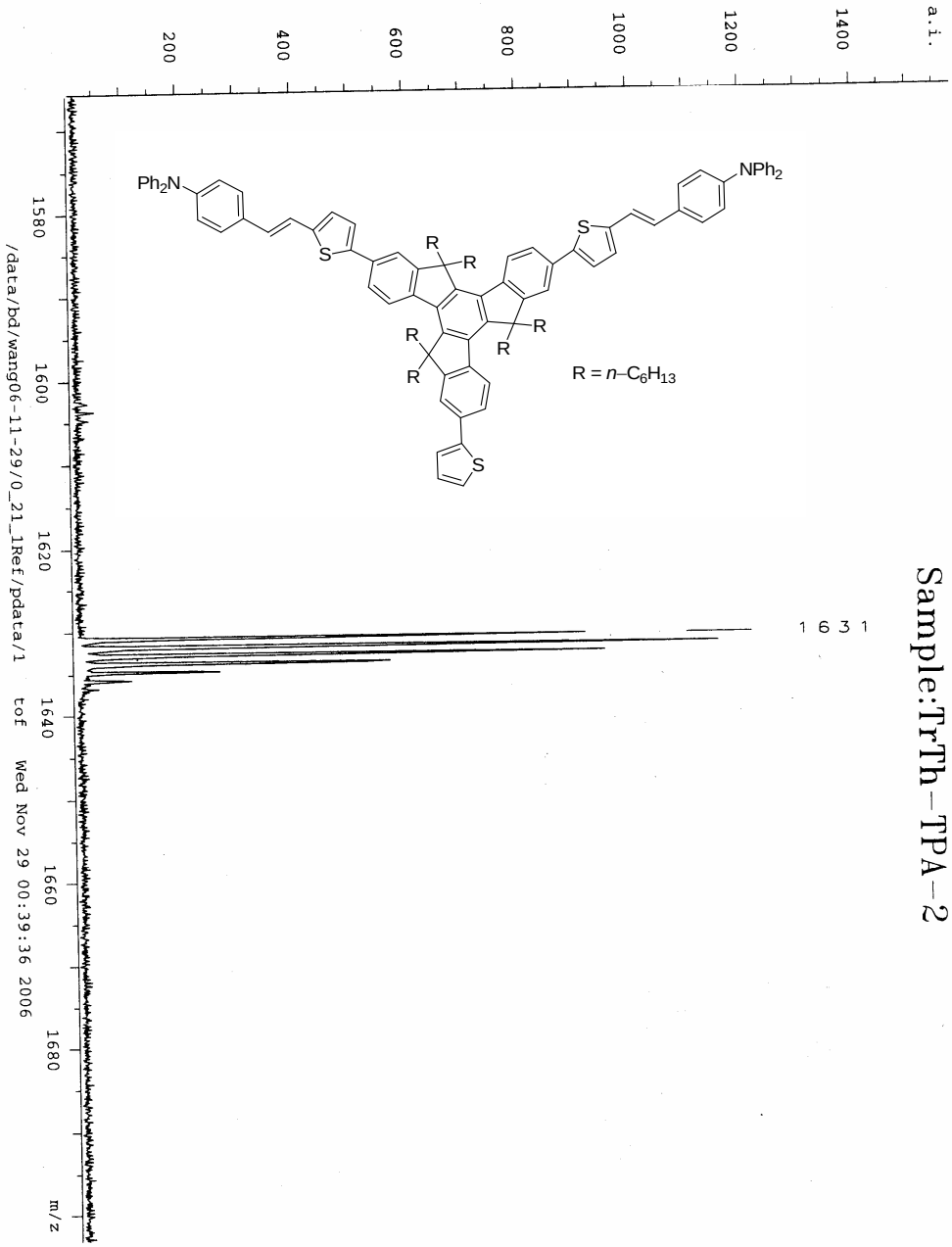
MALDI-TOF mass spectrum for **SBTTrTPA**.



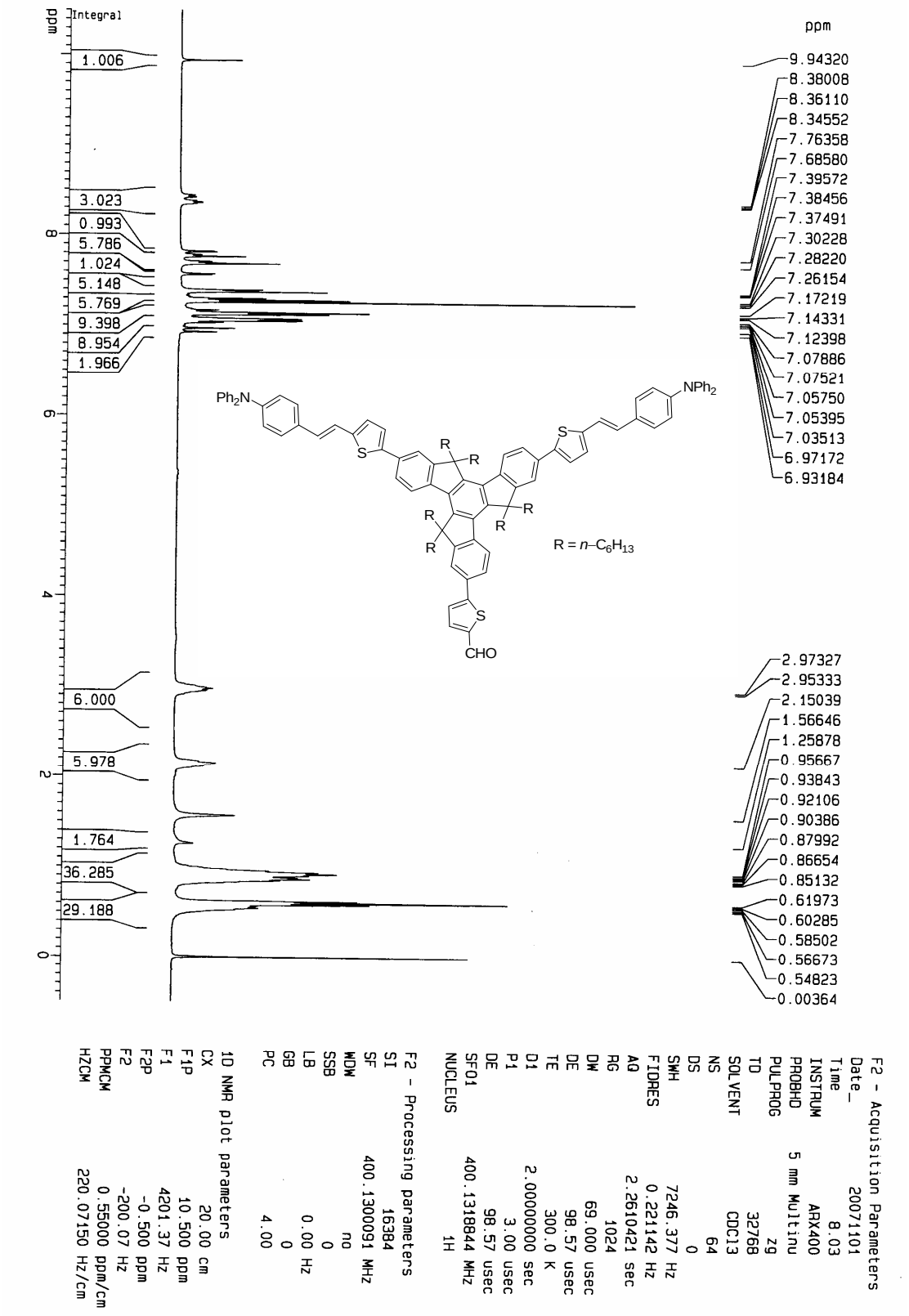
^{1}H NMR spectrum for compound **7**.



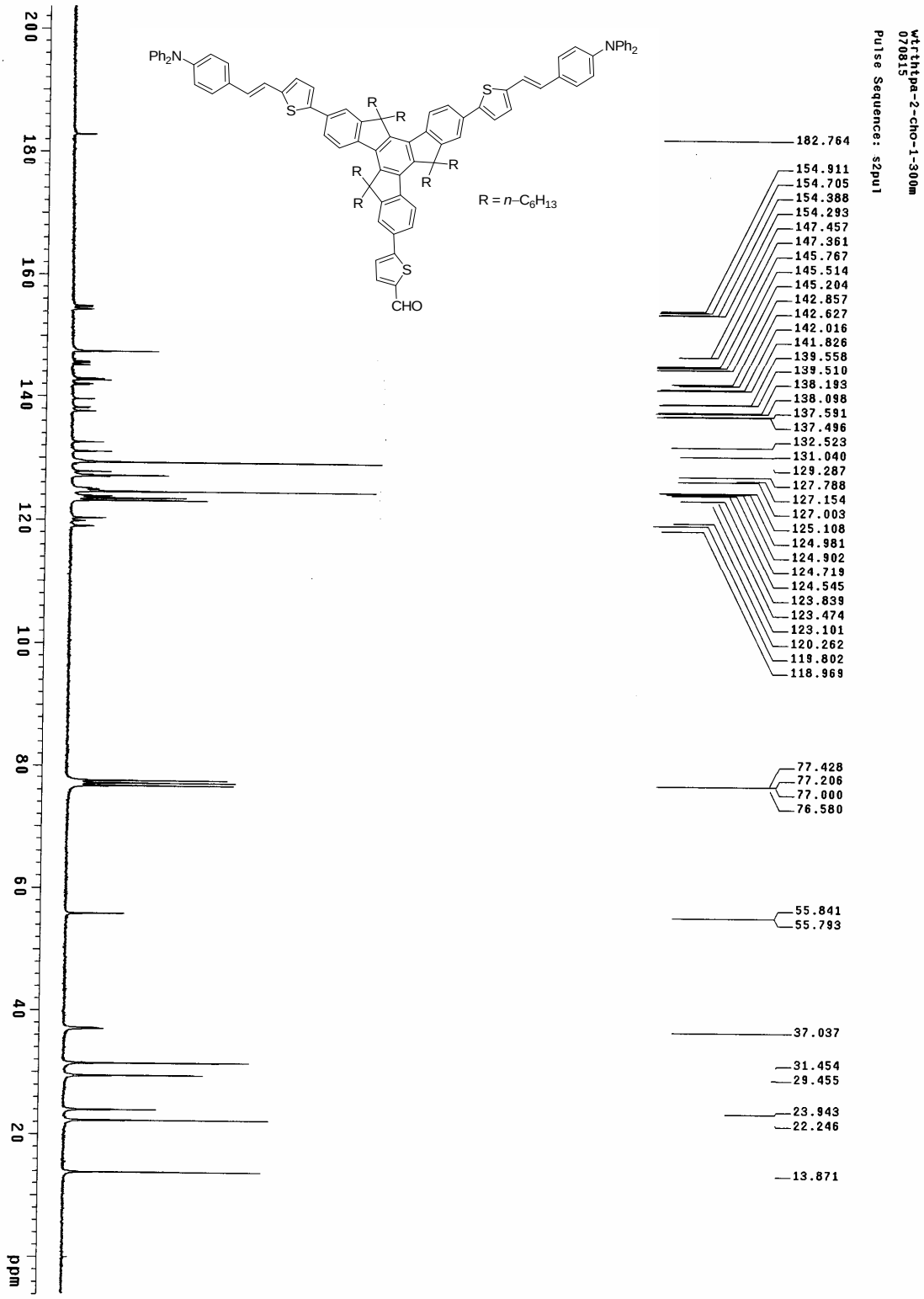
^{13}C NMR spectrum for compound **7**.



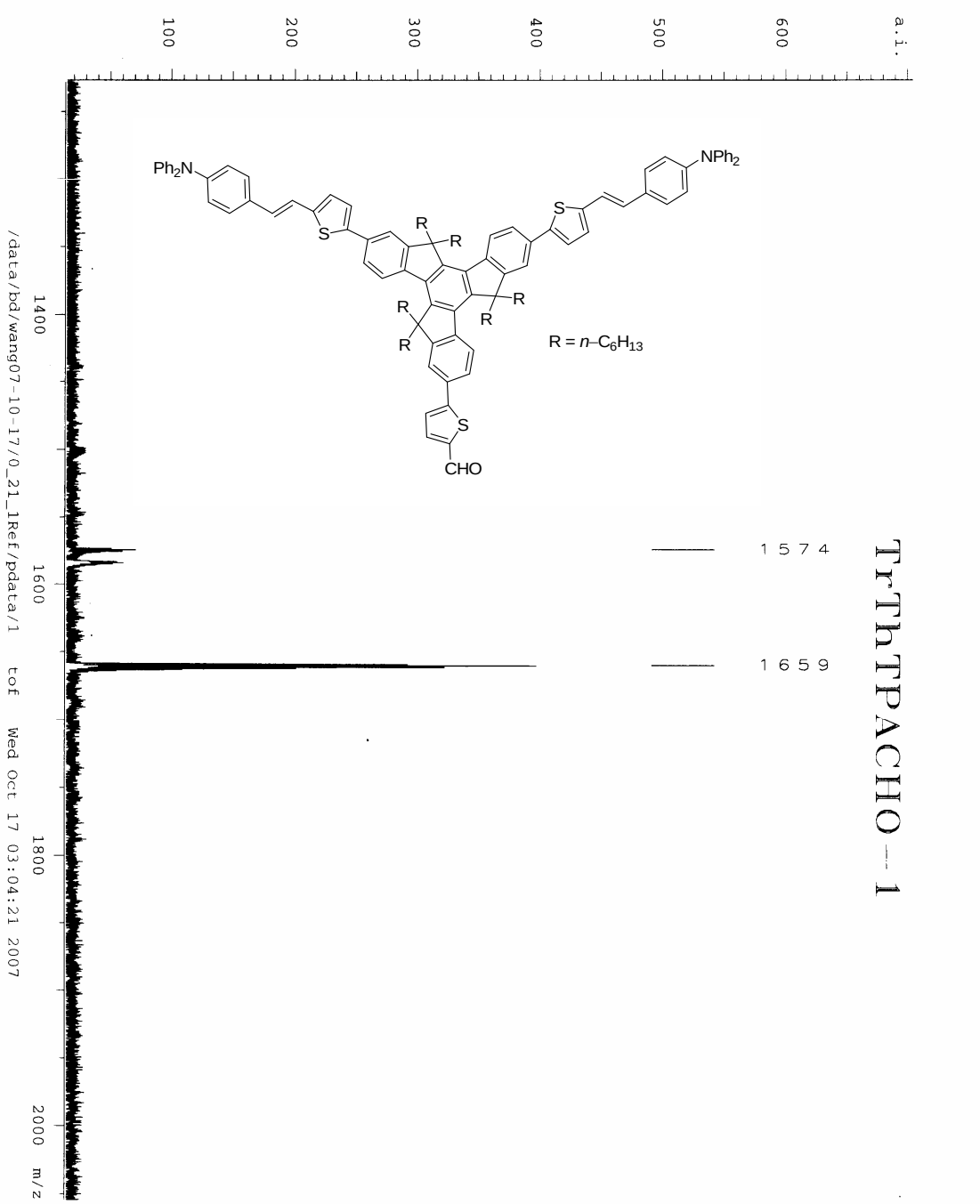
MALDI-TOF mass spectrum for compound **7**.



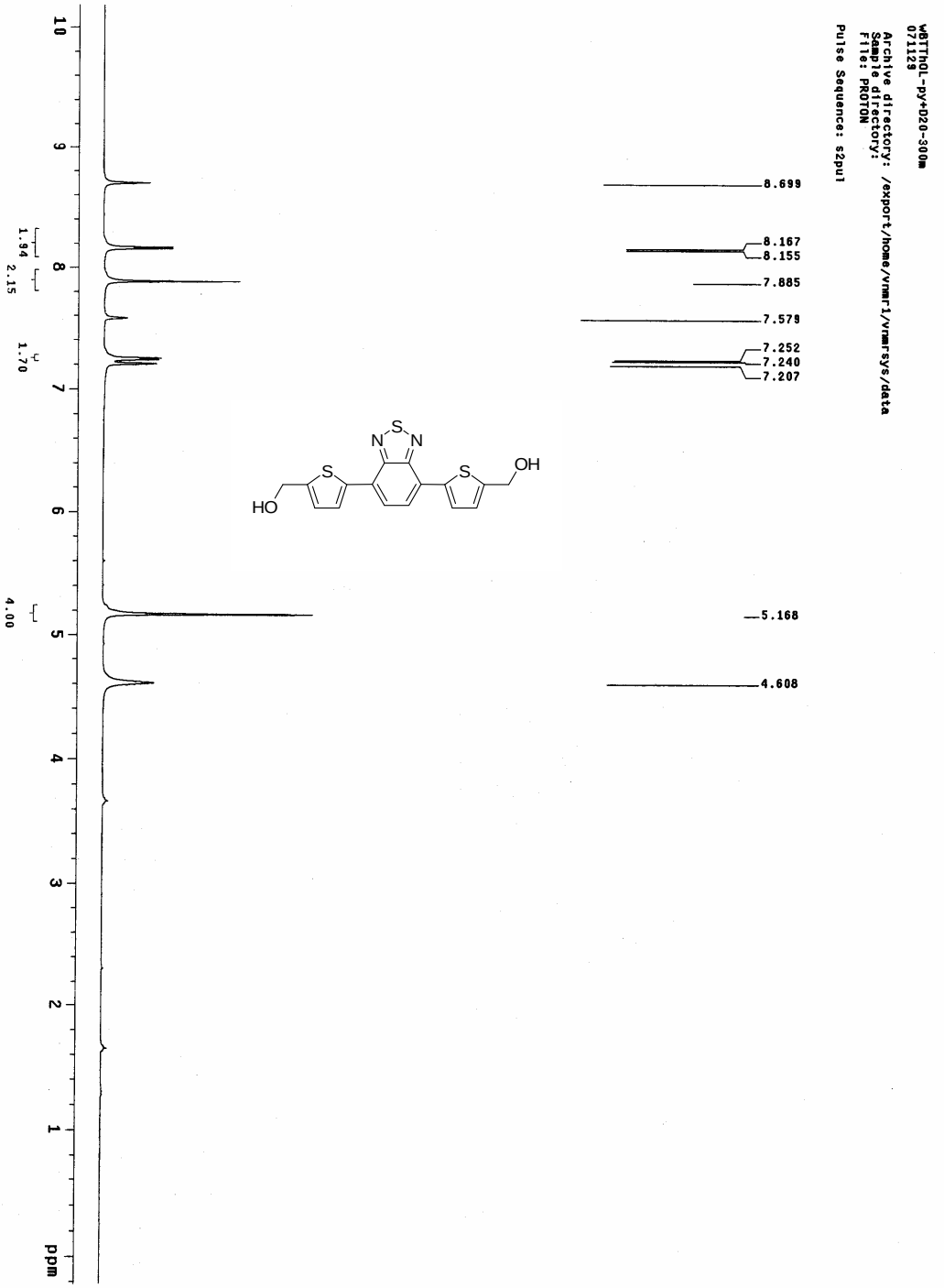
^{1}H NMR spectrum for compound **8**.



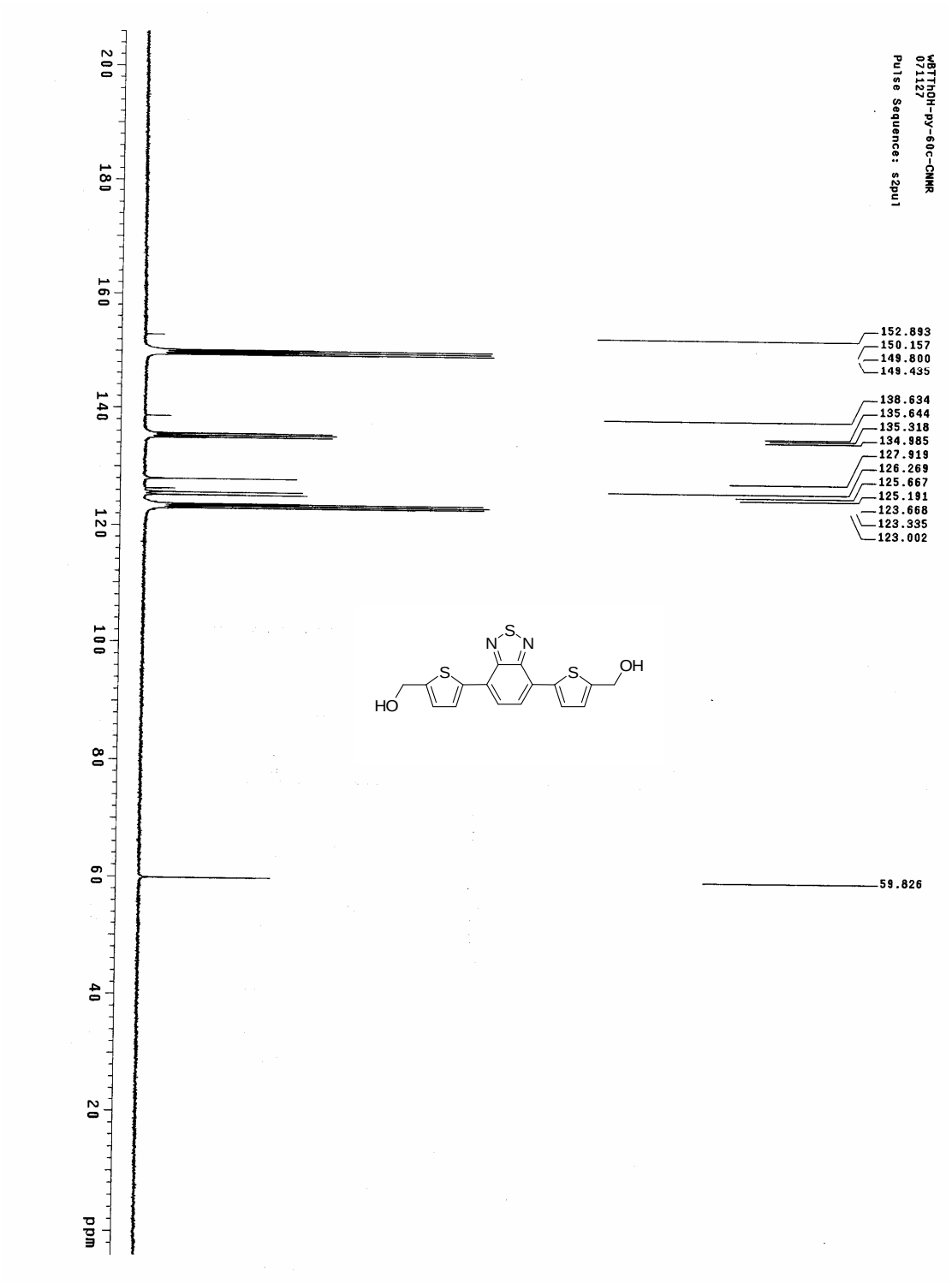
^{13}C NMR spectrum for compound **8**.



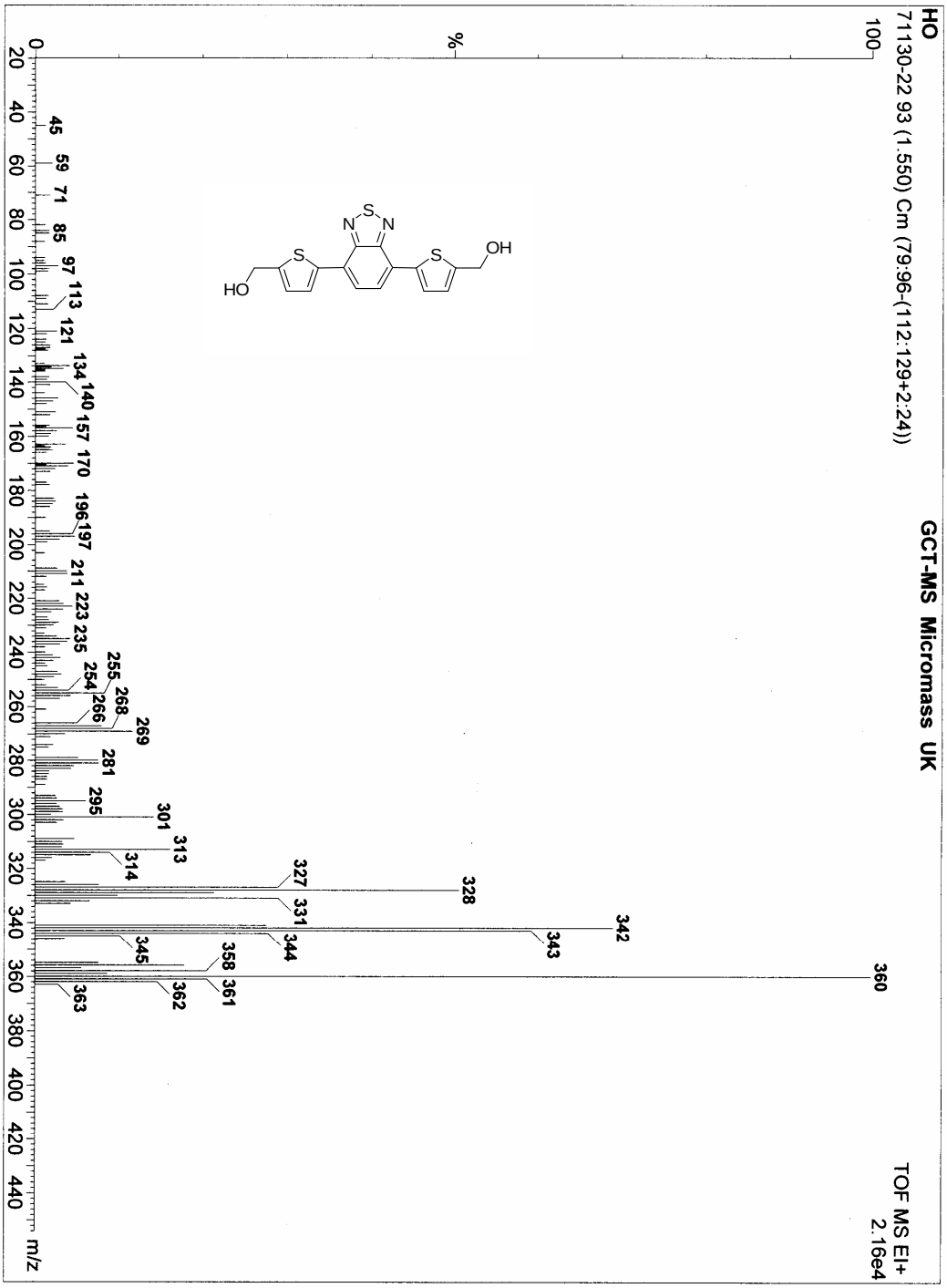
MALDI-TOF mass spectrum for compound **8**.



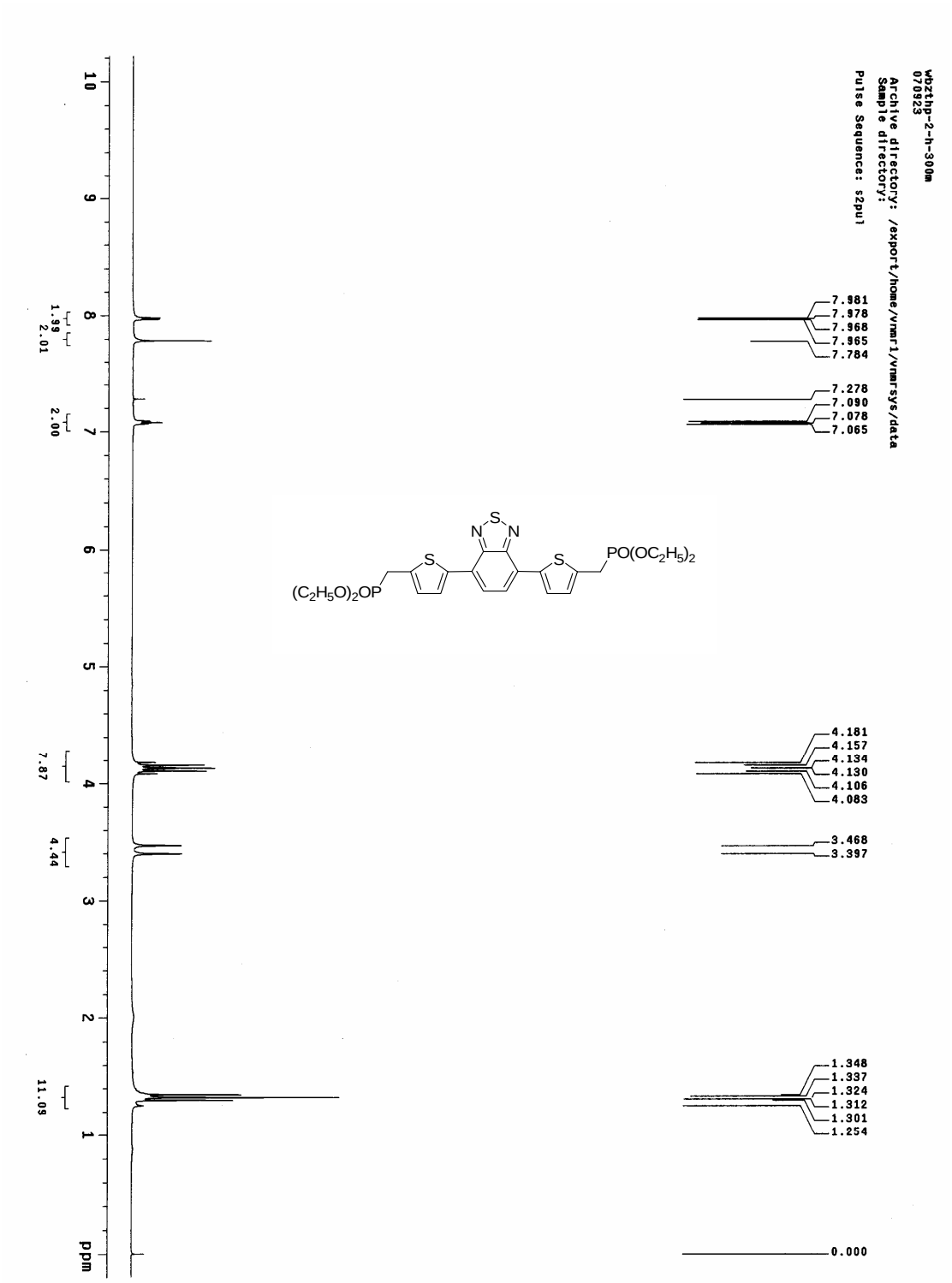
^{1}H NMR spectrum for compound **9**.



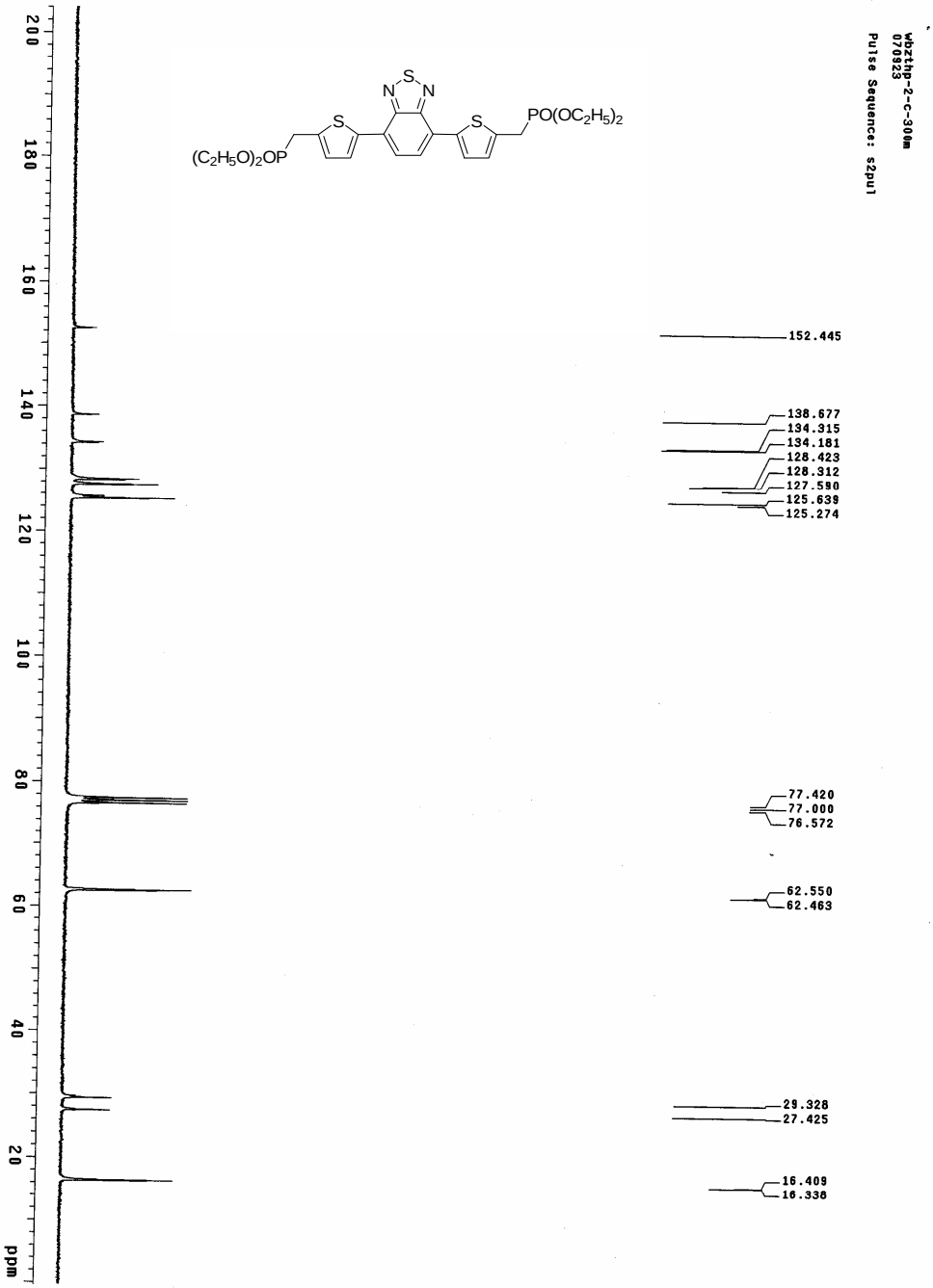
^{13}C NMR spectrum for compound **9**.



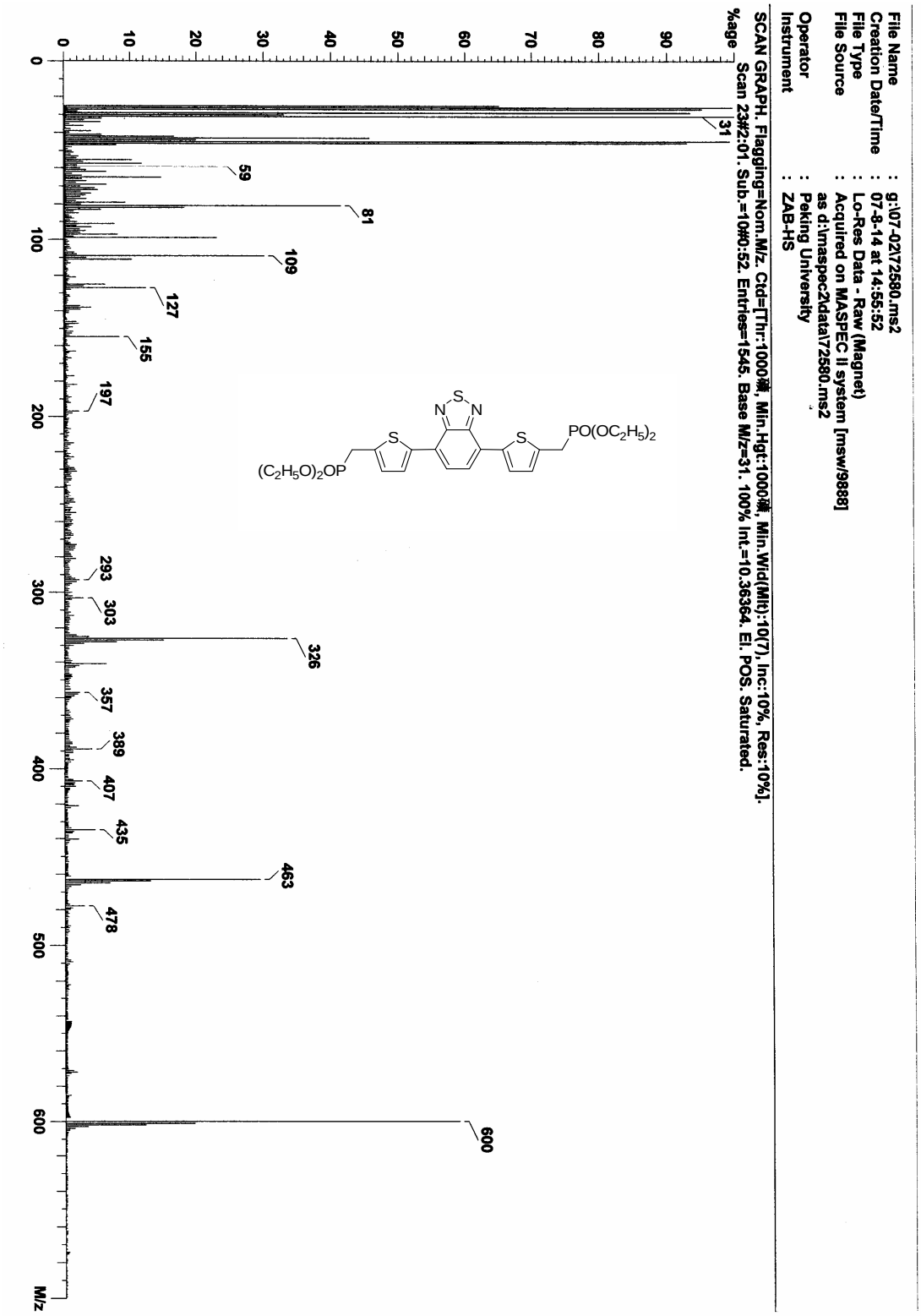
EI mass spectrum for compound **9**.



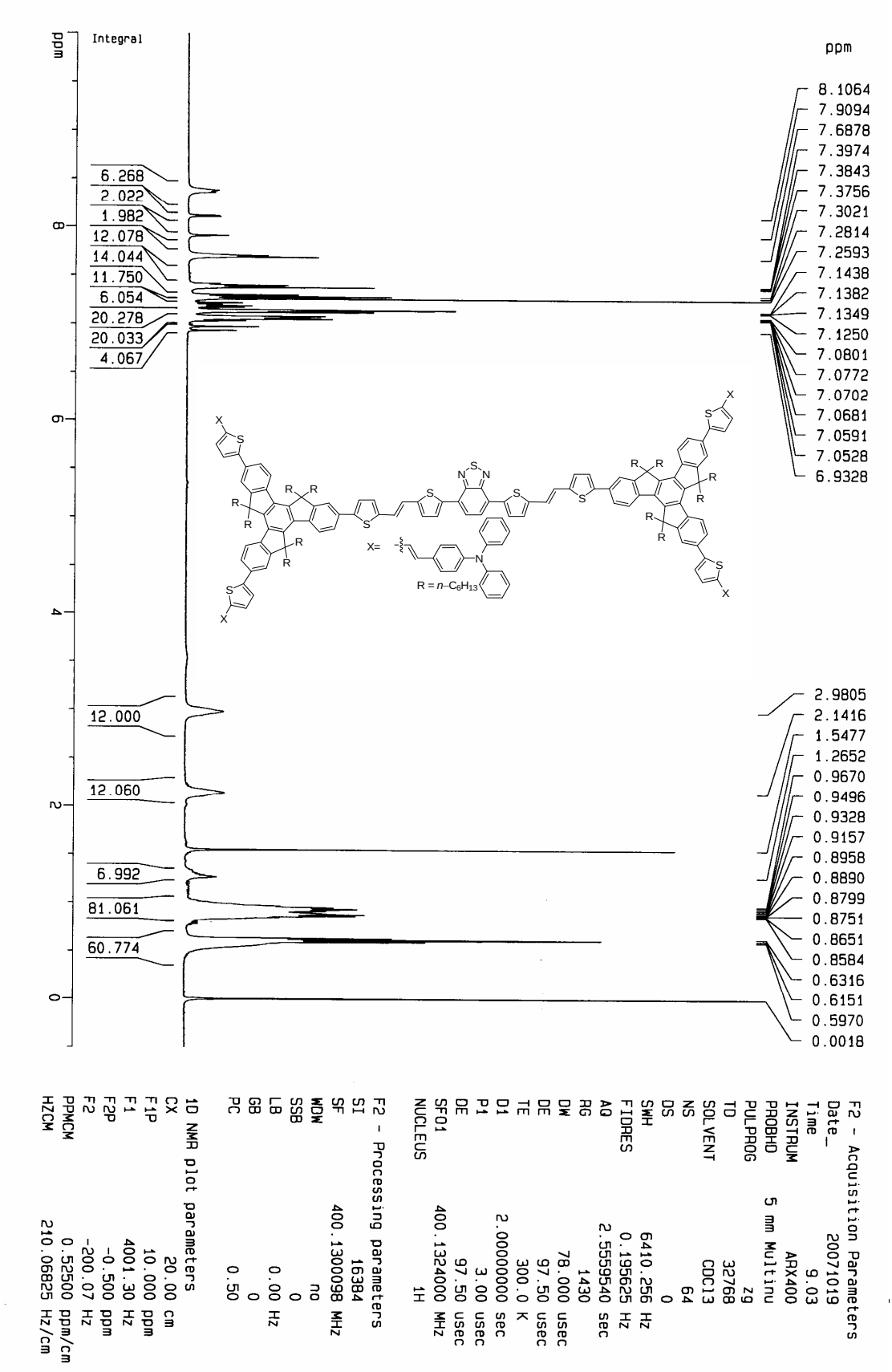
^{1}H NMR spectrum for compound **10**.



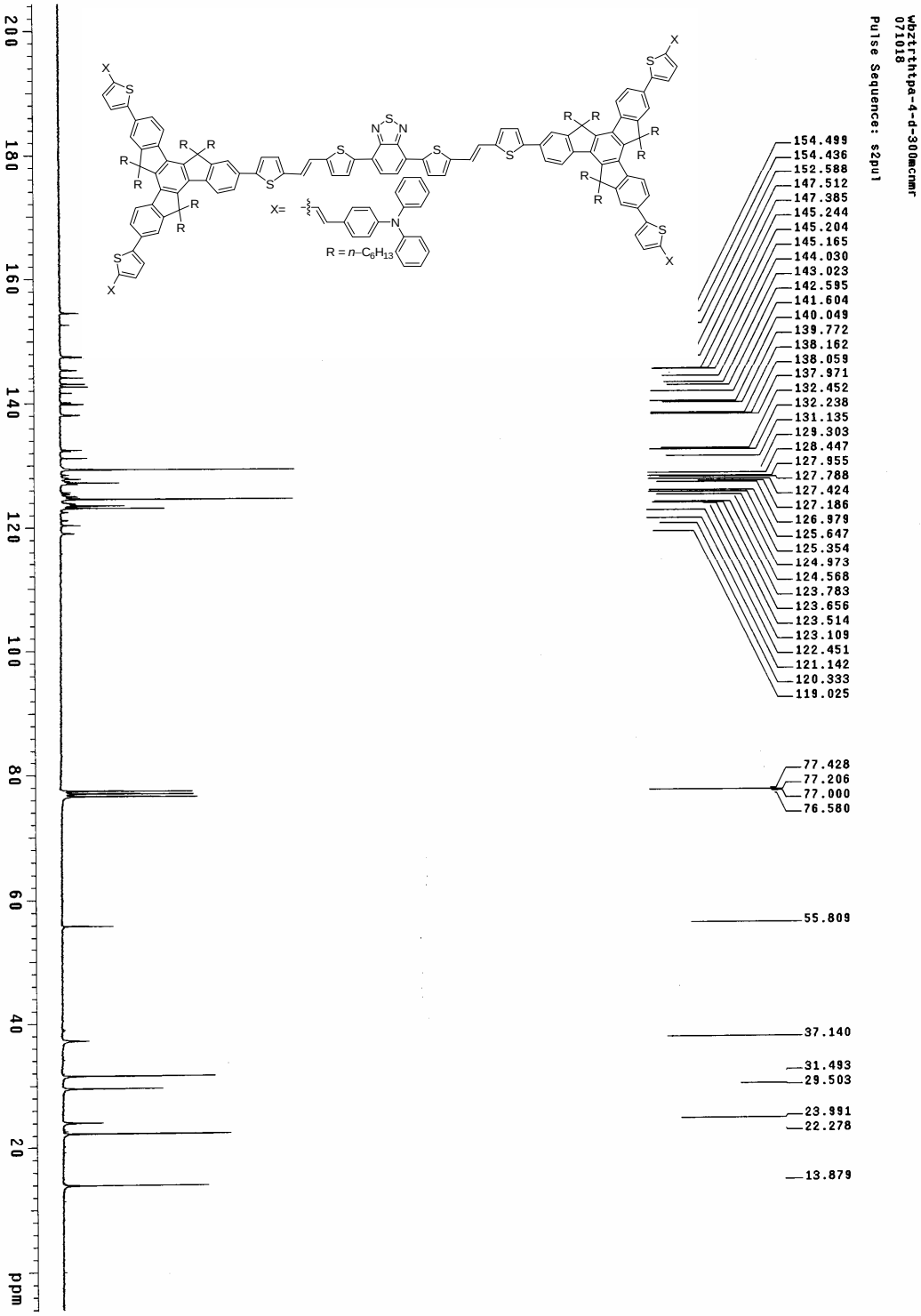
^{13}C NMR spectrum for compound **10**.



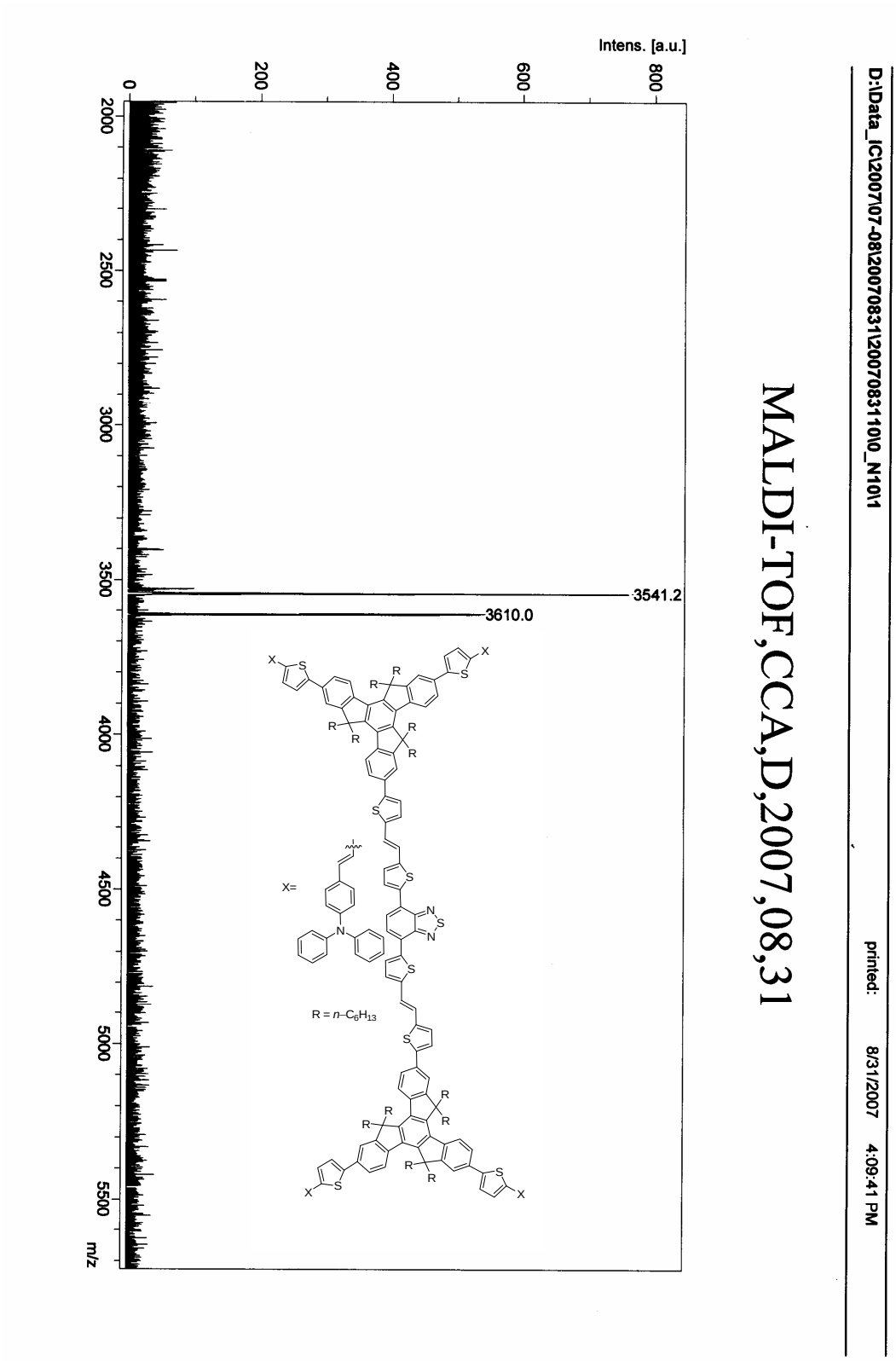
EI mass spectrum for compound **10**.



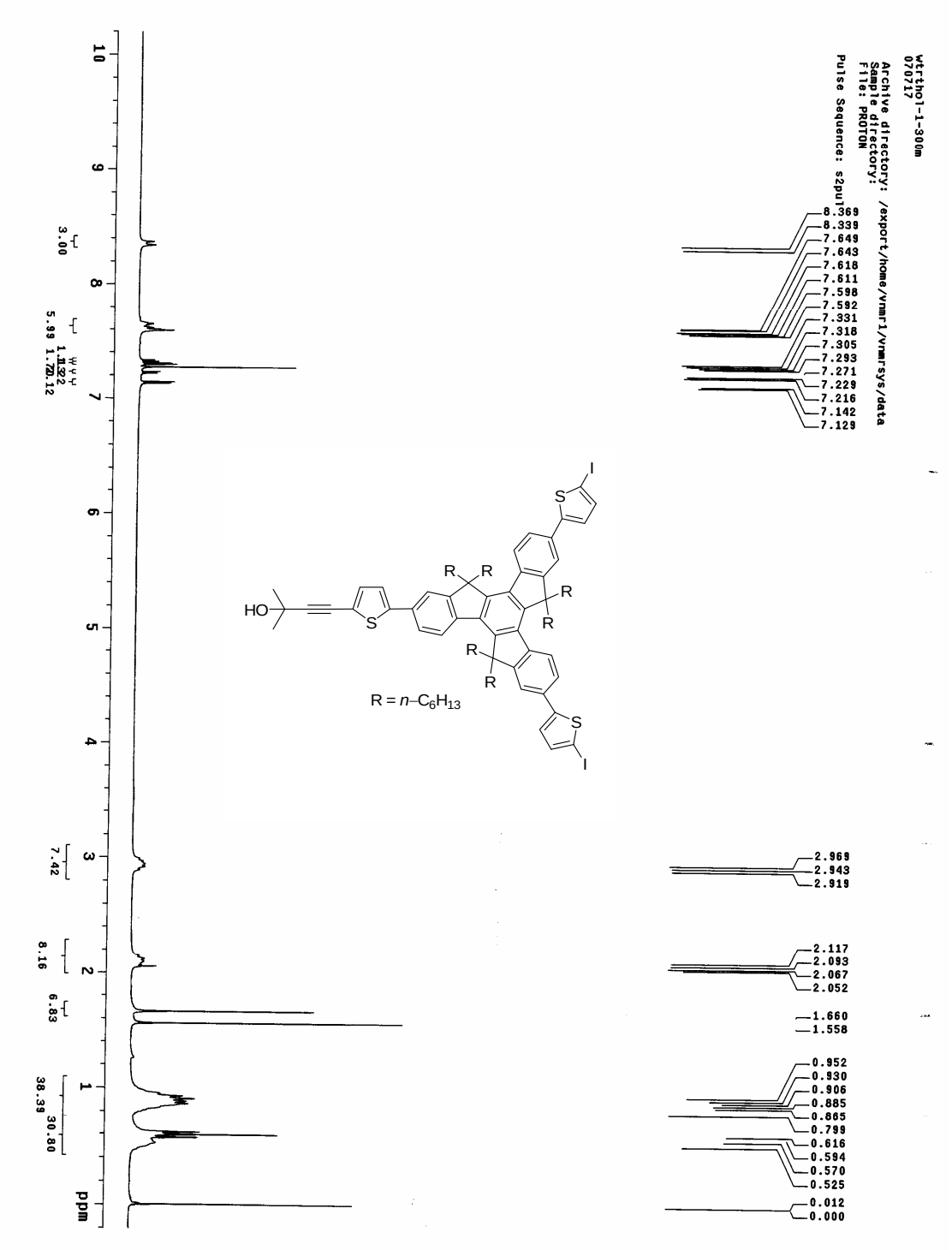
^{1}H NMR spectrum for **DBTTrTPA**.



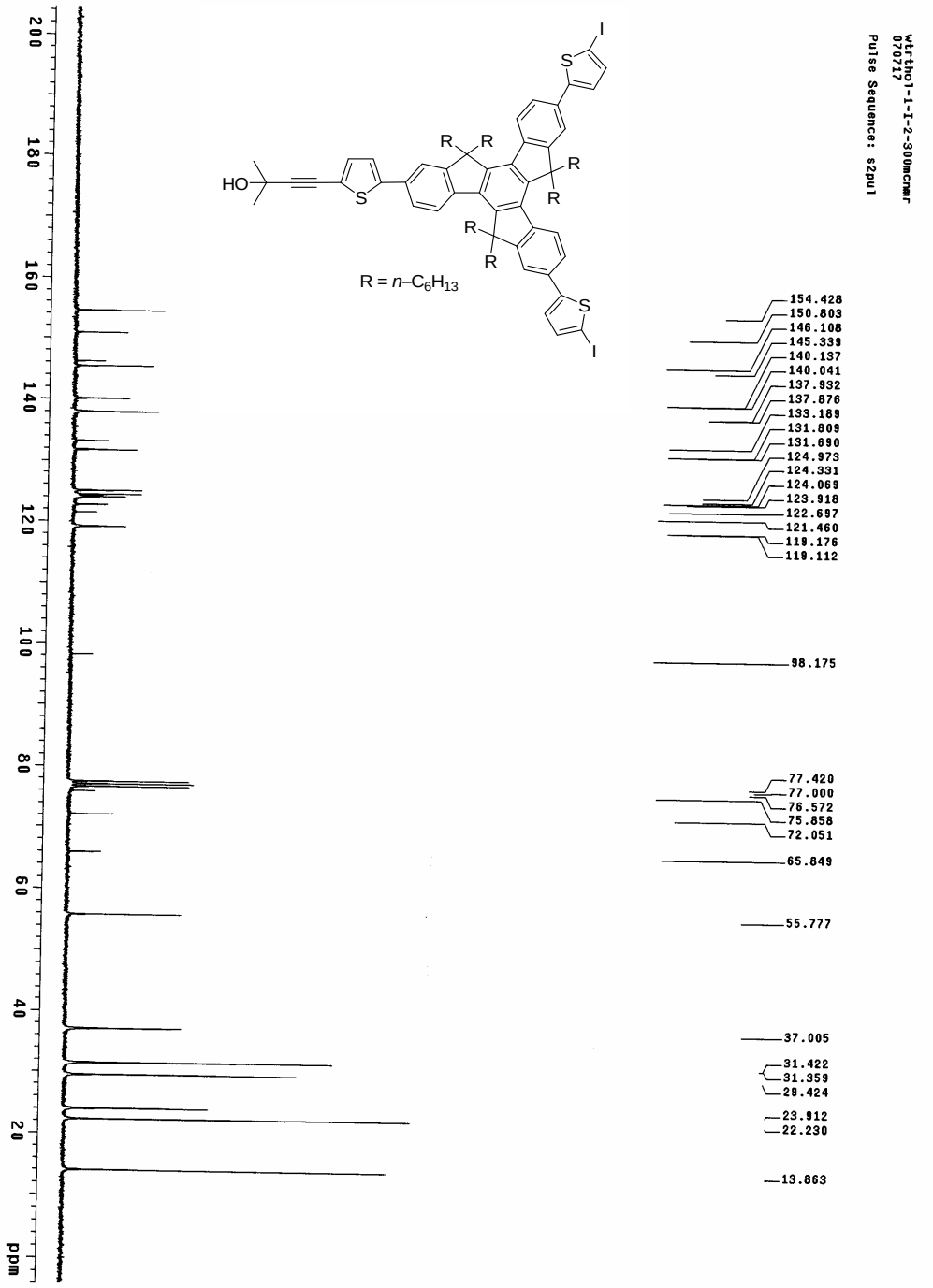
^{13}C NMR spectrum for **DBTTrTPA**.



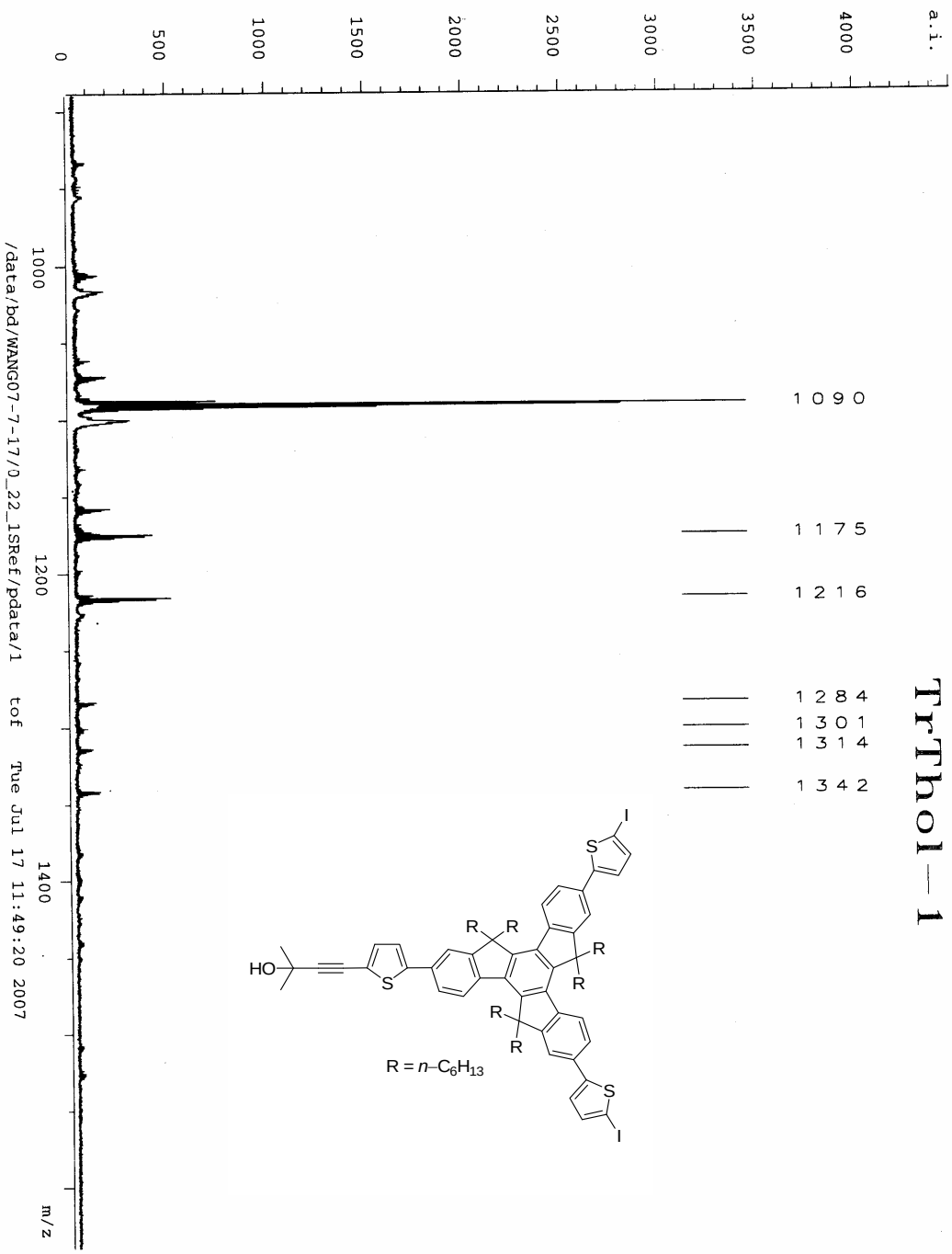
MALDI-TOF mass spectrum for **DBTTrTPA**.



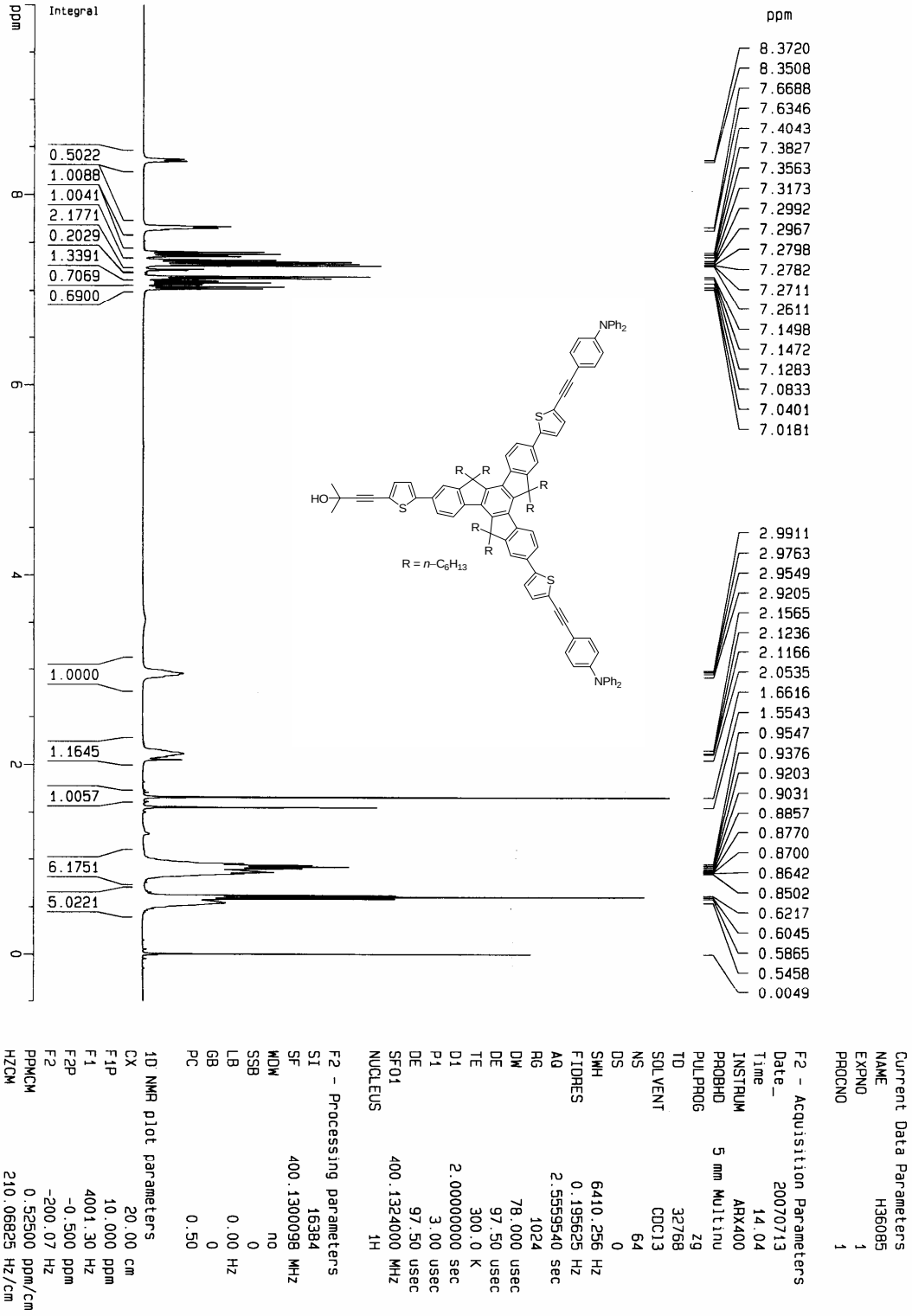
^{1}H NMR spectrum for compound **12**.



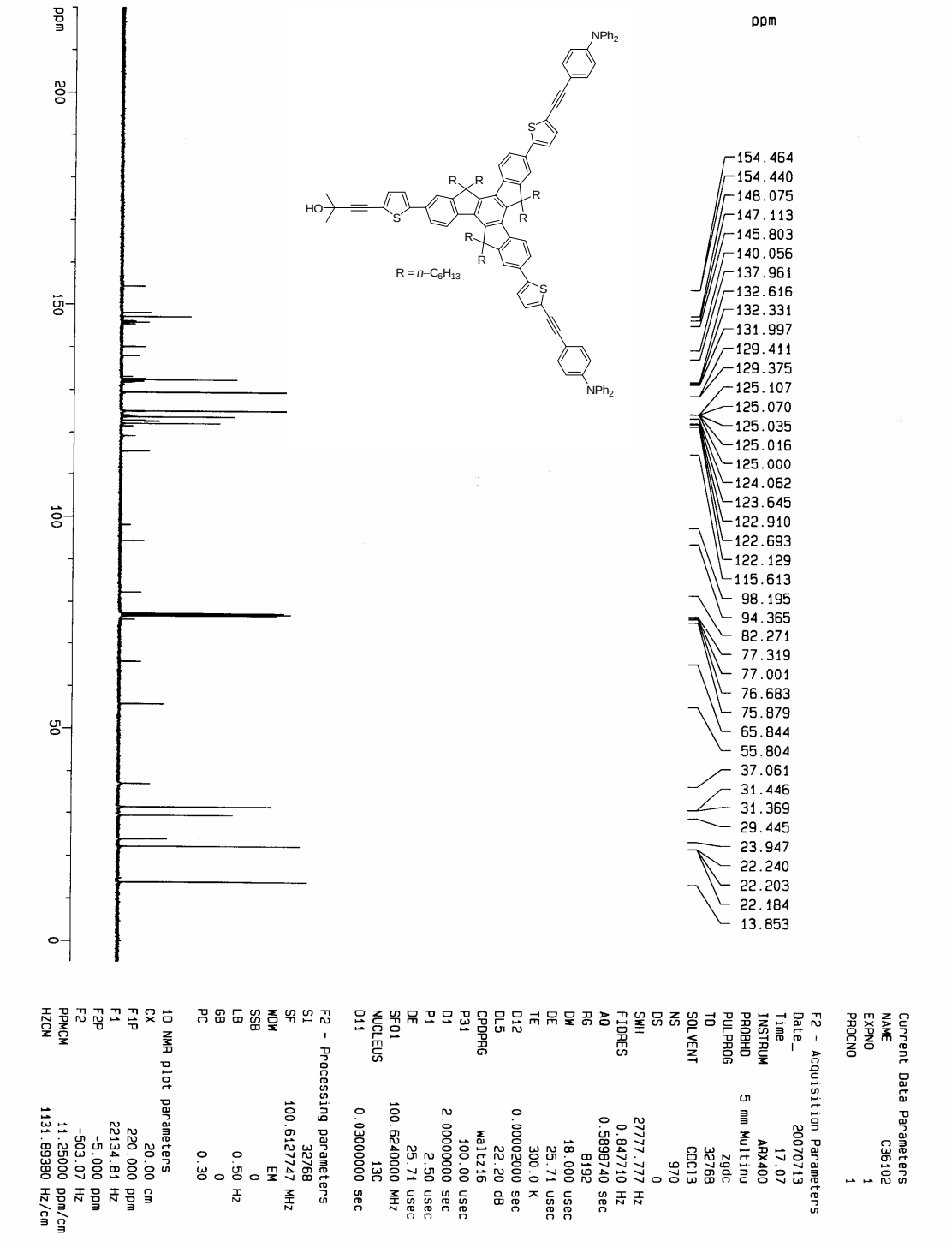
^{13}C NMR spectrum for compound **12**.



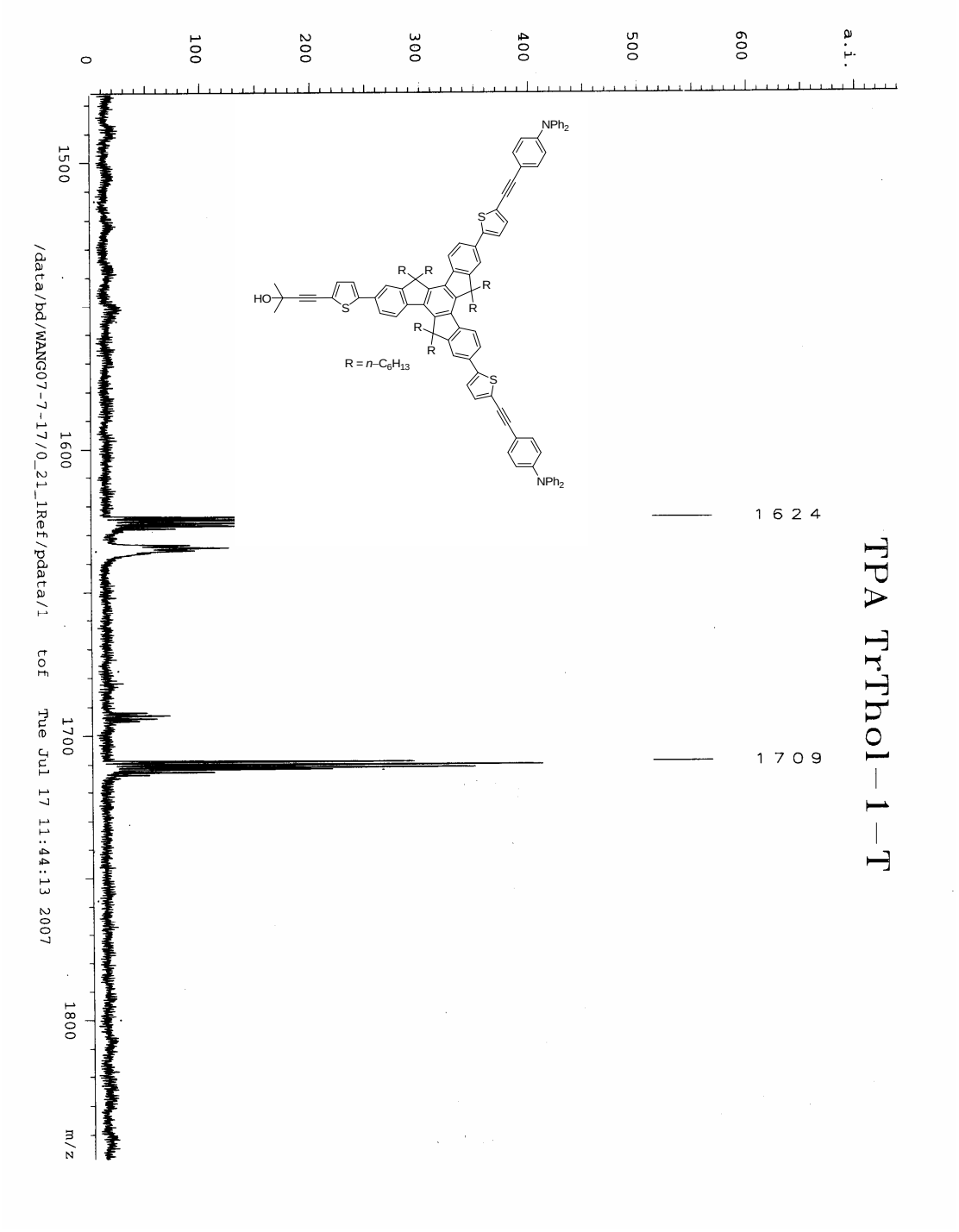
MALDI-TOF mass spectrum for compound **12**.



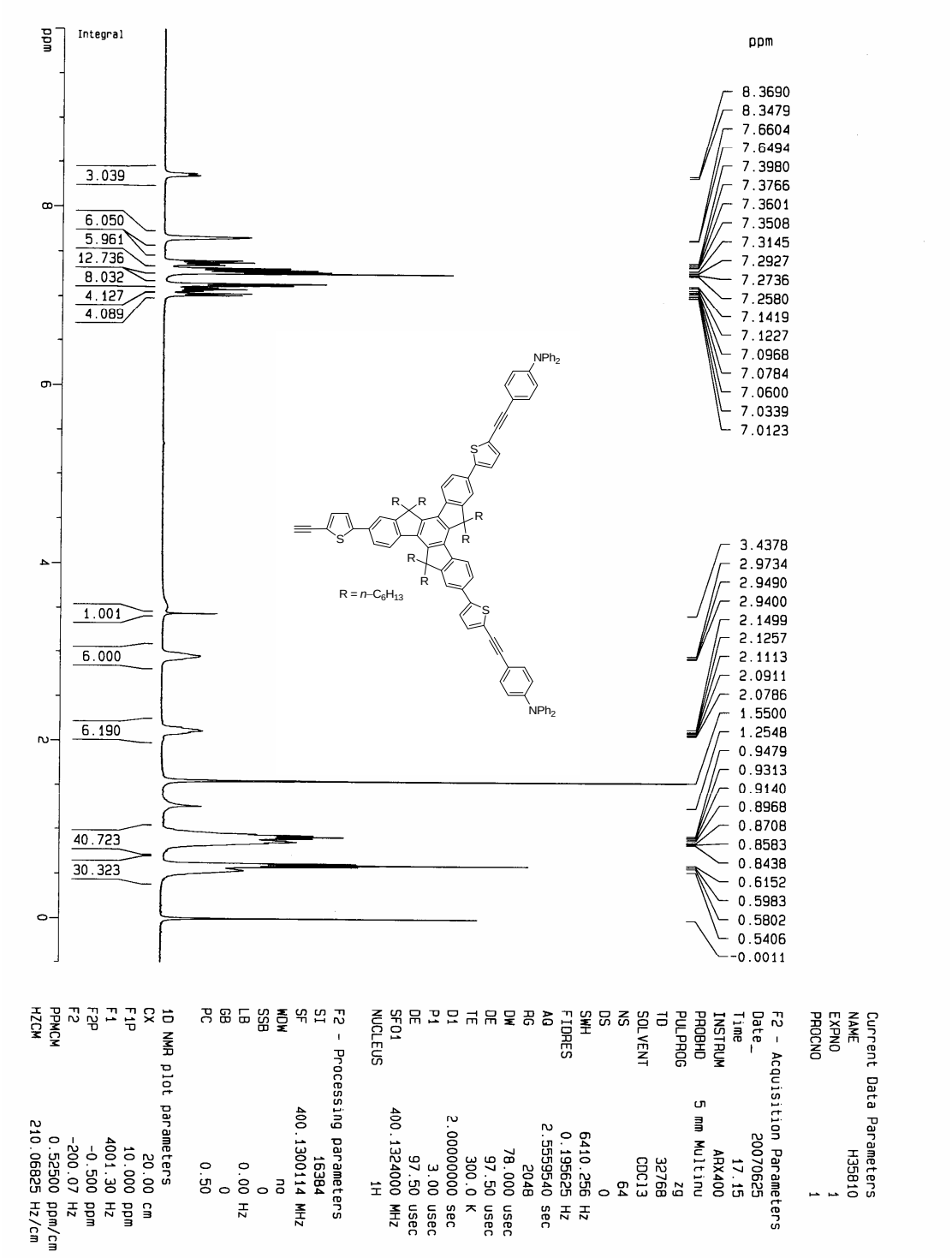
^{1}H NMR spectrum for compound **13**.



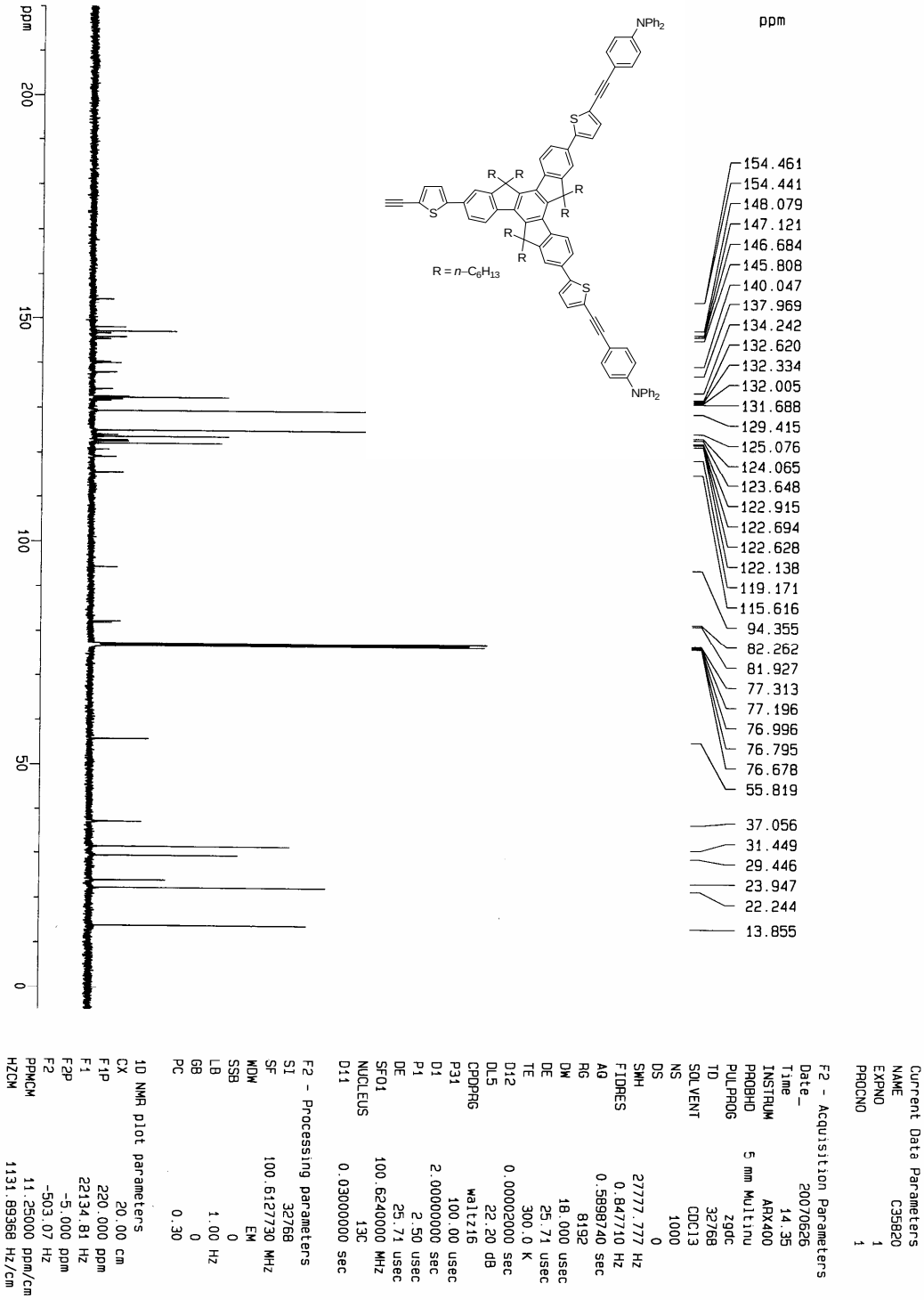
^{13}C NMR spectrum for compound **13**.



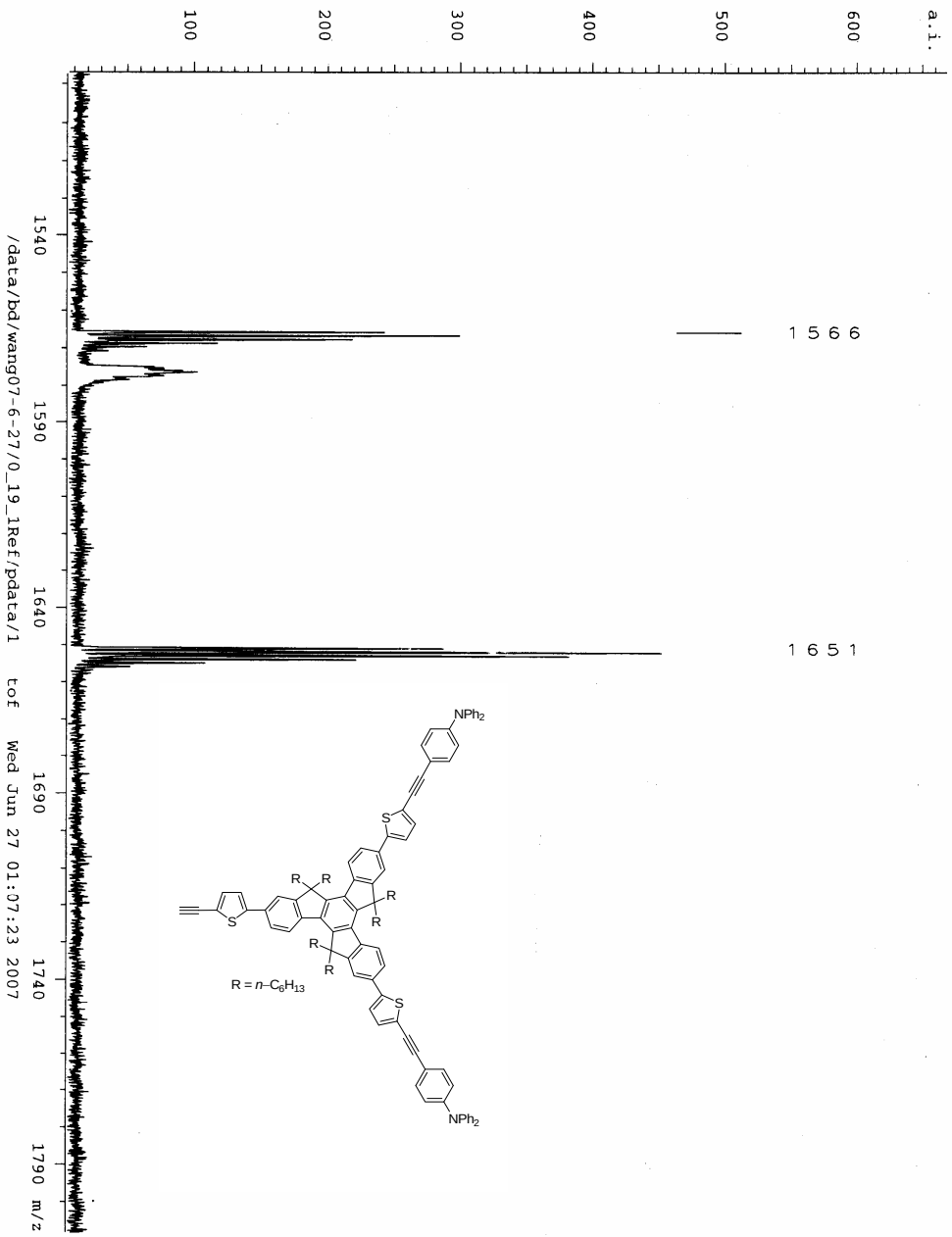
MALDI-TOF mass spectrum for compound **13**.



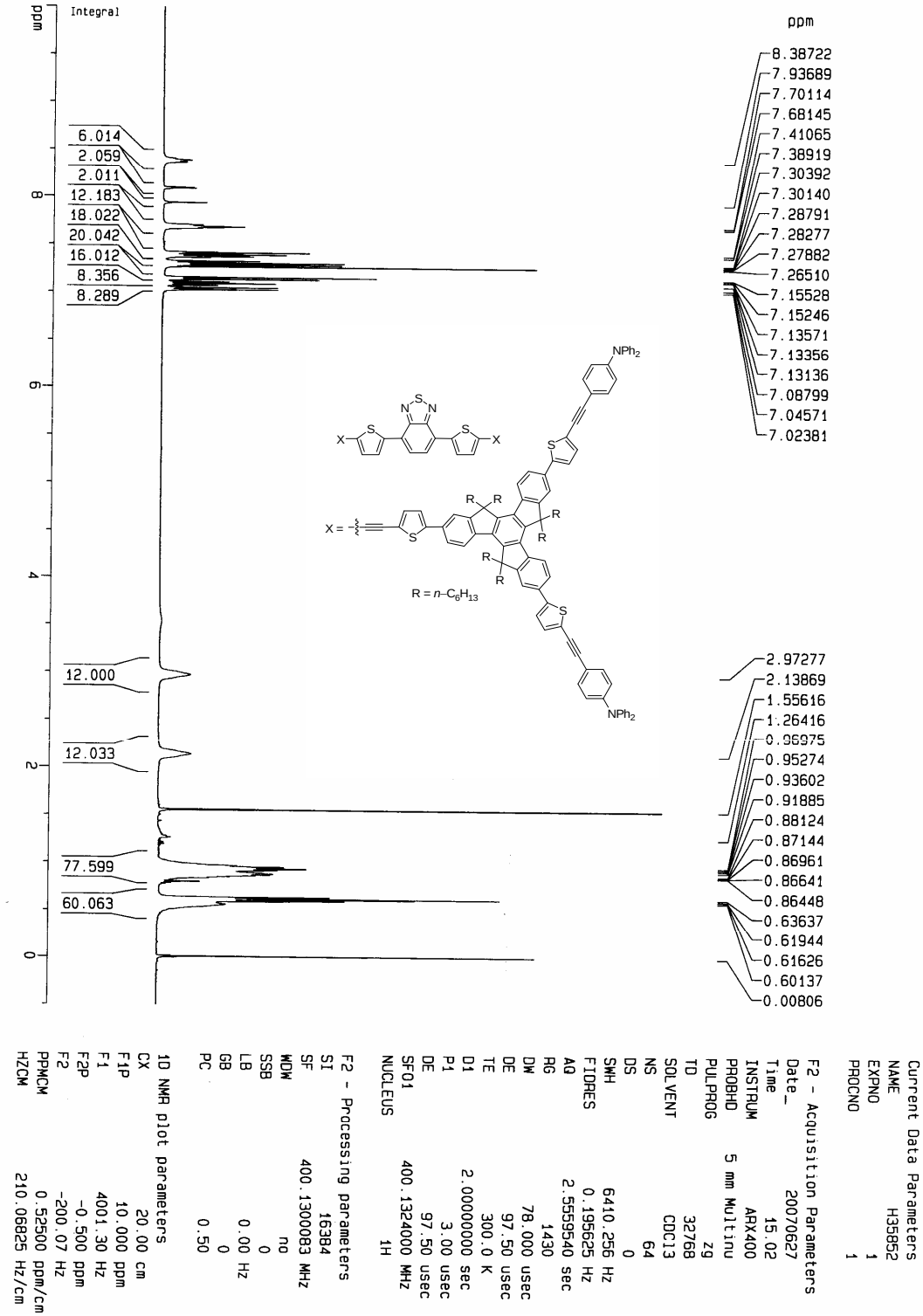
^{1}H NMR spectrum for compound **14**.



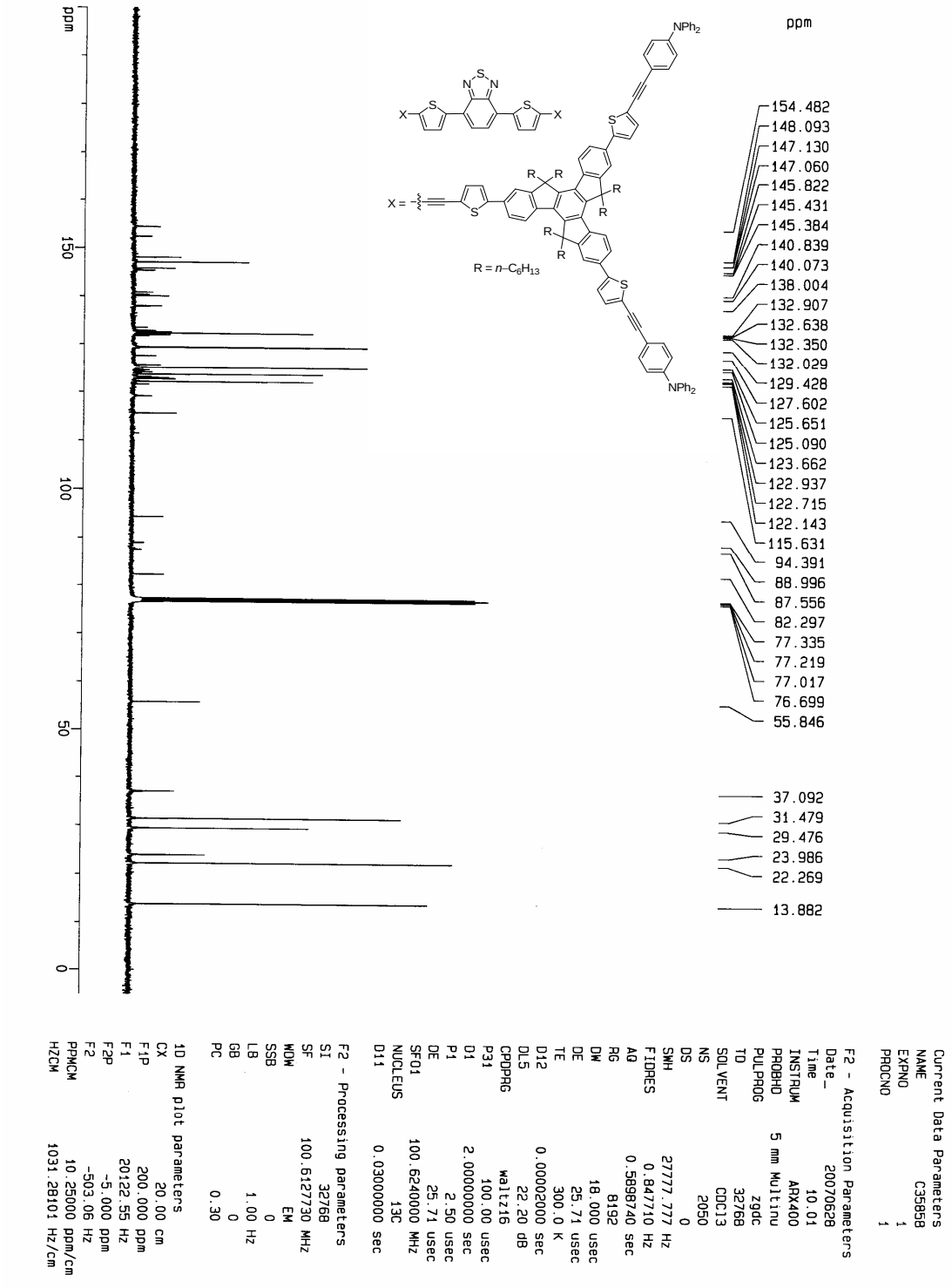
^{13}C NMR spectrum for compound **14**.



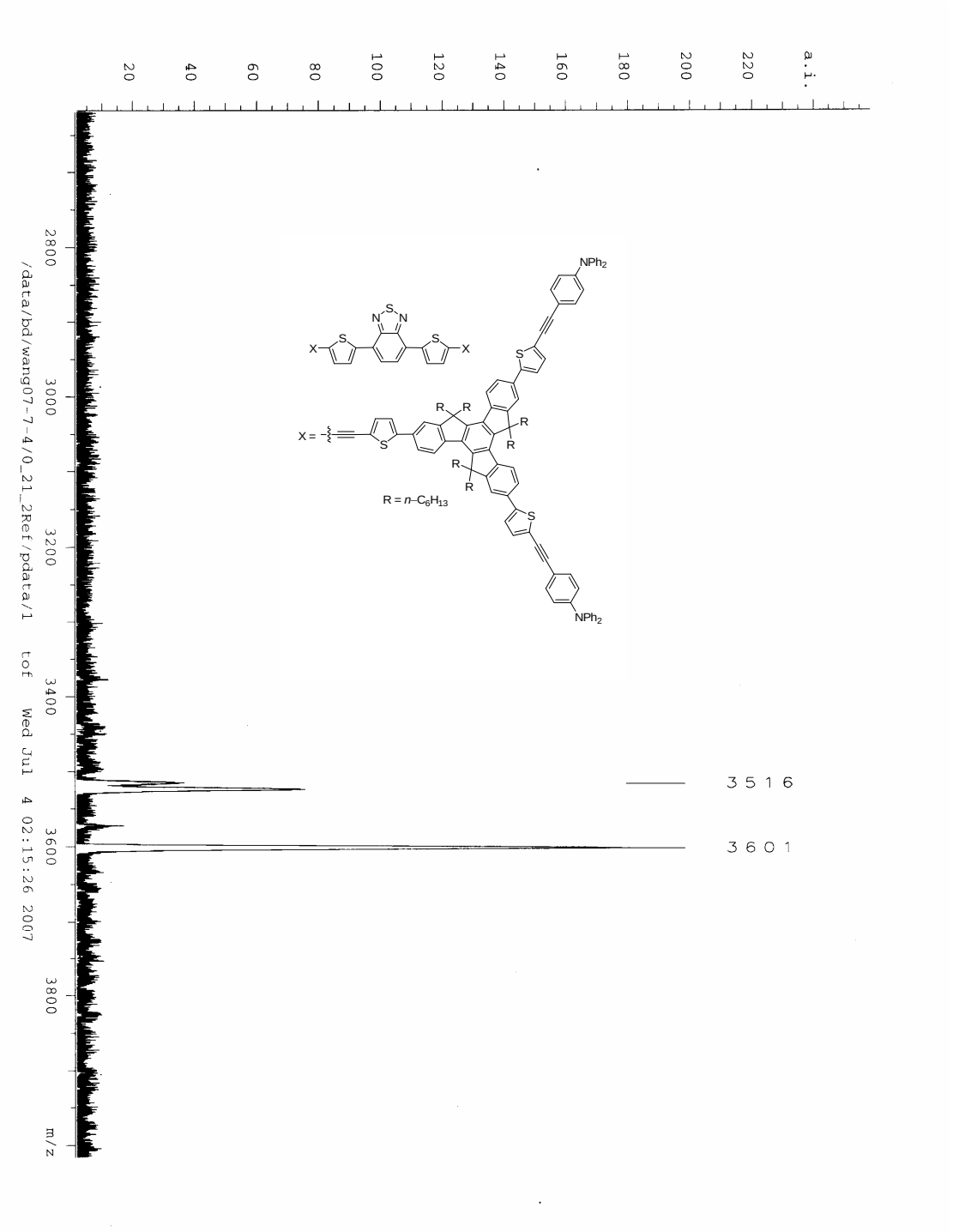
MALDI-TOF mass spectrum for compound **14**.



^{1}H NMR spectrum for **TBTTrTPA**.



^{13}C NMR spectrum for **TBTTrTPA**.



MALDI-TOF mass spectrum for **TBTTrTPA**.