SUPPORTING INFORMATION

Rhodanine-Based Dyes Absorbing in the Entire Visible Spectrum

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Materials and Methods

Materials obtained from commercial suppliers were used without further purification. Solvents were dried and degassed following standard procedures. Air-sensitive reactions were carried out under argon atmosphere. Flash chromatography was performed using silica gel (Fluorochem, Silicagel 60A, 40-63 micron). Analytical thin layer chromatography (TLC) was performed using aluminum-coated Merck Kieselgel 60 F254 plates. NMR spectra were recorded on a Bruker Advance 300 (^{1}H: 400 MHz; ^{13}C: 101 MHz) spectrometer at 298 K using partially deuterated solvents as internal standards. Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet. FT-IR spectra were recorded on a Bruker Tensor 27 (ATR device) spectrometer. UV-Vis spectra were recorded in a Varian Cary 50 spectrophotometer. Mass spectra Matrix assisted Laser desorption ionization (coupled to a Time-of-Flight analyzer) experiments (MALDI-TOF) were recorded on a MAT 95 thermo spectrometer and a Bruker REFLEX spectrometer respectively. Cyclic voltammetry (CV) experiments were conducted in a 0.1 M solution of NBu$_4$PF$_6$ in DCM. Glassy carbon electrode was used as a working electrode and platinum wires were used as a counter and reference electrodes. Before each measurement, solutions were deoxygenated with N$_2$. Ferrocene was added as an internal standard; its oxidation potential in DCM was positioned at 0.7 V *vs.* NHE and materials redox potentials were recalculated in reference to NHE.
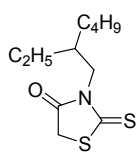
Synthesis

Compounds **1**,[1] **2**,[2] and **8**[3] were synthesized following previously reported procedures.

Scheme S1. Synthesis of the rhodanine fragments
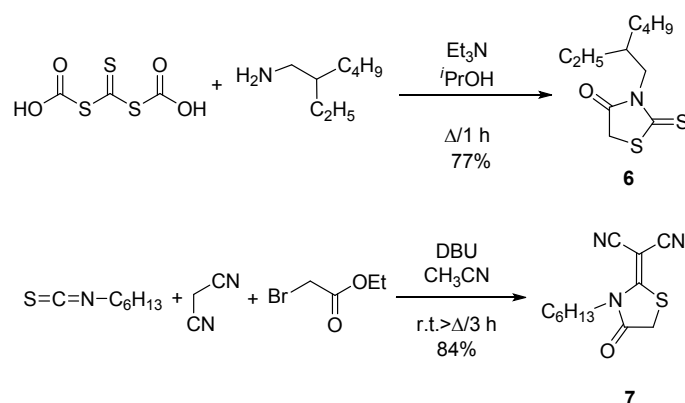
## *N*-(2-Ethylhexyl)rhodanine (6).

To a suspension of bis(carboxymethyl)trithiocarbonate (5 g, 22.09 mmol) in isopropanol (50 mL), 2-ethylhexylamine (3.6 mL, 22.09 mmol) and trimethylamine (13.5 mL, 22.50 mmol) were added. The resulting mixture was stirred and refluxed for 1 h. After cooling to room temperature, solvent was evaporated under reduced pressure. The

resulting oily crude was purified by flash chromatography (silica gel, hexane/DCM 1:1), providing title compound as colorless oil (3.87 g, 77%). ^{1}H NMR (400 MHz, CDCl3) δ: 3.97 (s, 2H), 3.90 (d, J = 7.4 Hz, 2H), 2.04–1.93 (m, 1H), 1.37–1.21 (m, 8H), 0.89 (t, J = 7.5 Hz, 3H), 0.88 (t, J = 6.8 Hz, 3H) ppm.

## 2-(3-Hexyl-4-oxothiazolidin-2-ylidene)malononitrile (7).
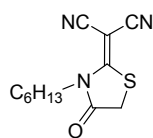
To an acetonitrile solution (70 mL) of hexyl isothiocyanate (3.4 mL, 22 mmol) and malononitrile (1.32 g, 20 mmol), DBU (3 mL, 20 mL) was added at room temperature. After stirring for 30 min, ethyl 2-bromoacetate (3.8 mL, 34 mmol) was added. Reaction was stirred at room temperature for 1 h and then stirred further 3 h at reflux. Upon completion, reaction was quenched with 2 M hydrochloric acid aqueous solution and extracted with DCM (3 x 50 mL), dried over Na_2SO_4, filtered and evaporated under vacuum. Purification was carried out by column chromatography (silica gel, DCM/hexane 3:1) yielding a tan solid (4.19 g, 84%). Further purification may be carried out by recrystallization from minimal amount of methanol at -20 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 4.10–4.06 (m, 2H), 3.99 (s, 2H), 1.72–1.64 (m, 2H), 1.40–1.30 (m, 6H), 0.89 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ: 171.7, 142.9, 113.0, 111.8, 56.8, 45.5, 32.4, 31.3, 28.6, 25.7, 22.5, 14.0 ppm. FTIR (neat): 2933, 2860, 2218, 1746, 1522, 1460, 1384, 1335, 1278, 1171, 1126, 1052, 893, 785 cm^{-1}. HRMS (MALDI-TOF): m/z calculated for $C_{12}H_{15}N_3OS$: 249.0936, found 249.0941.

Scheme S2. Synthesis of diphenylaminothiophene donating fragment.
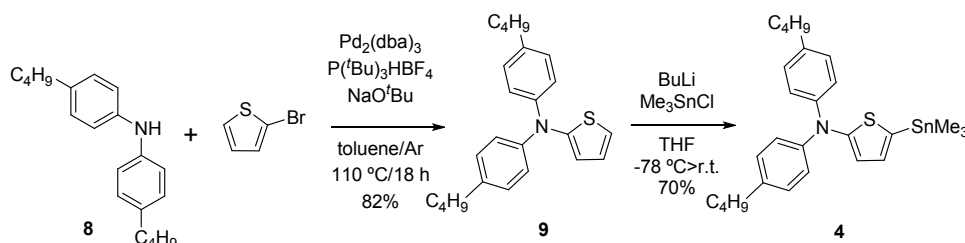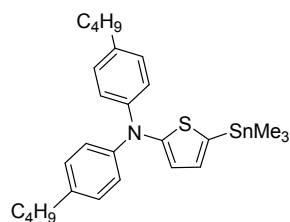

N,N-Bis(4-butylphenyl)thiophen-2-amine (9).
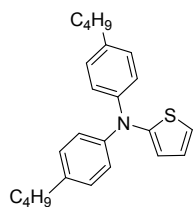
Into a 100mL 2-neck round flask 2-bromothiophene (0.24 g, 1.5 mmol), bis(4-butylphenyl)amine (0.42 g, 1.50 mmol), Pd$_2$(dba)$_3$ (18 mg, 0.04 mmol), and P(^{t}Bu)$_3$HBF$_4$ (44 mg, 0.15 mmol) were added. After purging the air with N$_2$, dry toluene (20mL) was introduced, and the resulting mixture was degassed by bubbling N$_2$ into the solvent over 30 minutes. Then, NaO^{t}Bu (0.43 g, 4.5 mmol) was added in one portion into the mixture, and degassed for further 10 min. Reaction was stirred at reflux for 18 h. After cooling down to room temperature, the mixture was diluted with toluene (100 mL) and washed with H$_2$O. Separated organic extracts were dried over anhydrous Na$_2$SO$_4$, filtered, and dried under reduced pressure. Product was purified by flash chromatography (silica gel, hexane/DCM 10:1) obtaining a yellow oil (0. 44g, 82%). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.10–6.99 (m, 8H), 6.93 (d, J = 5.6 Hz, 1H), 6.85 (dd, J = 5.5, 3.7 Hz,

1H), 6.66 (d, J = 3.6 Hz, 1H), 2.58–2.53 (m, 4H), 1.58 (m, 4H), 1.36 (m, 4H), 0.93 (t, J = 7.3 Hz, 6H) ppm.

### *N,N*-Bis(4-butylphenyl)-5-(trimethylstannyl)-2-thiophenamine (4).

Inside a 100 mL flame-dried 2-neck round flask with nitrogen atmosphere *N,N*-bis(4-butylphenyl)thiophen-2-amine (**9**) (0.70 g, 1.92 mmol) was dissolved in dry THF (20 mL). After cooling to –78 °C, BuLi (2.5 M in hexanes, 1.15 mL, 2.90 mmol) was added dropwise over 10 min. The resulting mixture was warmed to 0 °C and stirred for 1h. Then, trimethyltin chloride (1.0 M in hexane, 3.85 mL, 3.85 mmol) was added in one portion and the mixture was allowed to warm to room temperature and stirred overnight. Saturated ammonium chloride solution (20 mL) was added to the reaction mixture and the product was extracted with diethyl ether. Combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and solvent removed under reduced pressure. Product **4** (0.70 g, 70%) was obtained as an oil and used in the next synthetic step without further purification. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.04 (d, J = 1.6 Hz, 8H), 6.93 (d, J = 3.4 Hz, 1H), 6.72 (d, J = 3.4 Hz, 1H), 2.59–2.52 (m, 4H), 1.64–1.55 (m, 4H), 1.36 (m, 4H), 0.93 (t, J = 7.3 Hz, 6H), 0.32 (s, 9H) ppm.

**Scheme S3. Synthetic routes to dyes RFTA-1−4.**
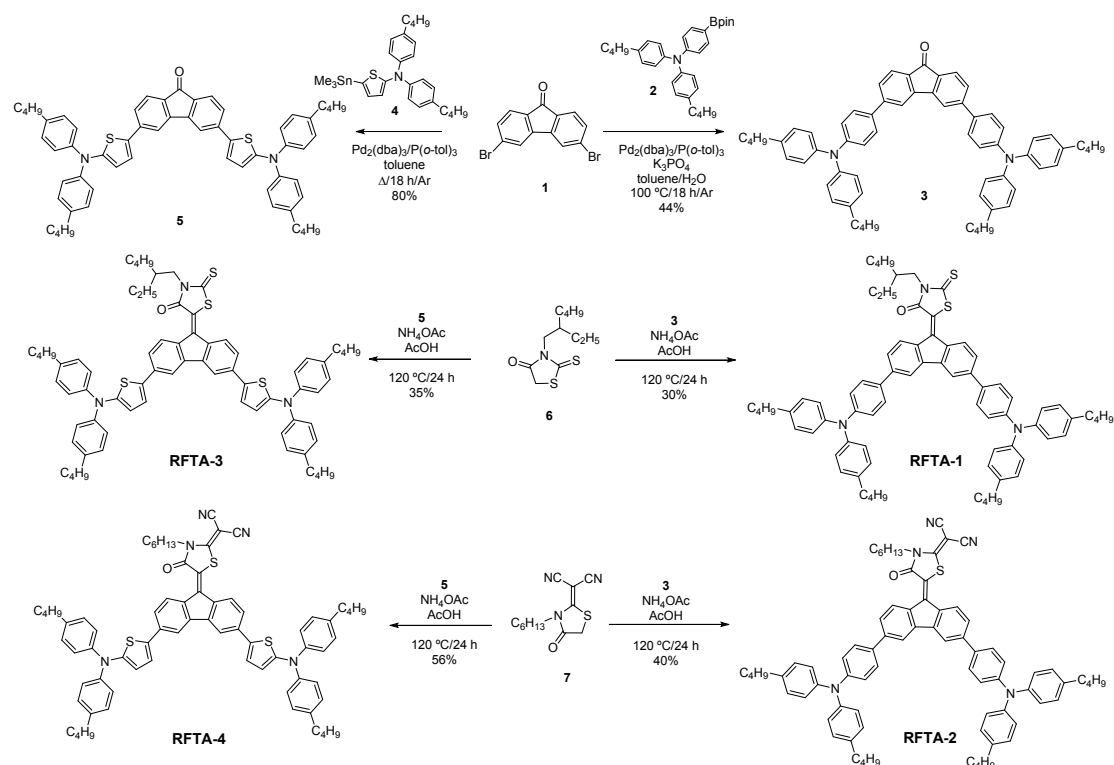
3,6-bis[di(4'-butylphenyl)aminophenylene]-9*H*-fluoren-9-one (3).
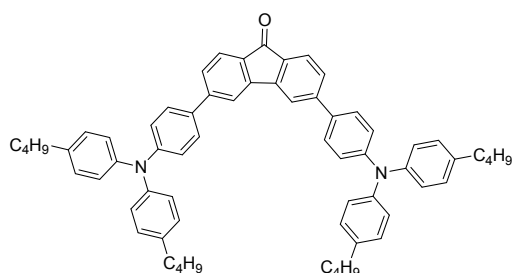
Into a 100 mL 2-neck round flask filled with dry toluene (20 mL) and nitrogen, 4-butyl-*N*-(4-butylphenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (0.68 g, 1.4 mmol), 3,6-dibromo-9*H*-fluoren-9-one (0.24 g, 0.70 mmol), $Pd_2(dba)_3$ (16 mg, 0.02 mmol), and P(*o*-tolyl)$_3$ (21 mg, 0.07 mmol) were dissolved. The mixture was degassed for 30 minutes. Then, a previously degassed K_3PO_4 (4.4 g, 21 mmol) DI water solution (7 mL) was added. The resulting mixture was stirred at 100 °C for 18 h. The mixture was cooled to room temperature and washed with H_2O. After extraction with DCM, combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and evaporated. The resulting crude was purified by flash chromatography (silica gel, hexane/dichloromethane 1:2) giving the title compound as an orange solid (0.3 g, 44%). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.75 (s, 2H), 7.69 (d, *J* = 7.7 Hz, 2H), 7.52 (d, *J* = 8.7 Hz, 4H), 7.47 (dd, *J* = 7.8, 1.3 Hz, 2H), 7.15–7.06 (m, 20H), 2.65–2.58 (m, 8H), 1.69–1.59 (m, 8H), 1.48–1.36 (m, 8H), 0.98 (t, *J* = 7.4 Hz, 12H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ: 193.0, 148.8, 147.2, 145.0, 144.9, 138.2, 133.0, 132.5, 129.3, 127.8, 126.9, 125.0, 124.6, 122.1, 122.0, 118.3, 35.1, 33.7, 22.5, 14.0 ppm. FTIR (neat): 3025, 2955, 2925, 2858, 1702, 1604, 1504, 1455, 1370, 1295, 1108, 914, 730 cm^{-1}. HRMS (MALDI-TOF): *m/z* calculated for $C_{65}H_{66}N_2O$: 890.5163, found 890.5170.

Compound RFTA-1.
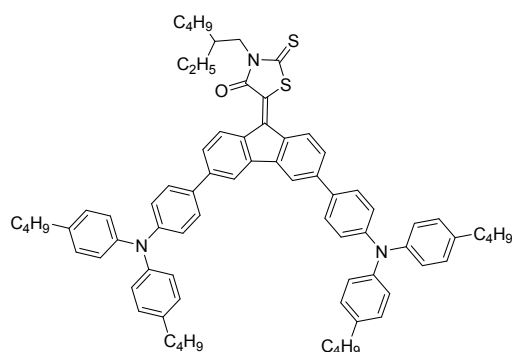
Into a 100 mL 2-neck round bottom flask equipped with a condenser, **3** (0.12 g, 0.14 mmol), 3-(2-ethylhexyl)-2-thioxothiazolidin-4-one (**6**) (0.17 g, 0.70 mmol), and NH_4OAc (75 mg, 0.9 mmol) were added to glacial acetic acid (10 mL). The mixture was stirred at 118 °C for 24 h. After cooling to room temperature, the reaction was diluted with chloroform and repeatedly washed with a $NaHCO_3$ saturated solution until no CO_2 generation is observed. Organic extracts were dried over anhydrous Na_2SO_4, filtered, and dried. Purification was carried out by flash chromatography (silica gel, hexane/dichloromethane 1:2) to give a dark purple solid (0.04 g, 30%). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 9.31 (d, *J* = 8.4 Hz, 1H), 7.88–7.79 (m, 3H), 7.55 (dd, *J* = 8.2, 6.3 Hz, 4H), 7.52–7.48 (m, 2H), 7.13–7.05 (m, 20H), 4.10 (d, *J* = 7.5 Hz, 2H), 2.63–2.55 (m, 8H), 2.14–2.11 (m, 1H), 1.67–1.58 (m, 10H), 1.44–1.35 (m, 14H), 0.96 (t, *J* = 7.3 Hz, 12H), 0.92–0.89 (m, 6H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ: 191.8, 148.6, 148.4, 145.1, 145.0, 143.7, 143.1,

142.6, 141.6, 138.2, 138.1, 136.7, 134.7, 132.7, 132.3, 130.1, 129.3, 129.3, 127.6, 127.5, 124.9, 124.9, 122.2, 122.1, 48.8, 37.2, 35.1, 33.7, 29.7, 28.5, 24.0, 23.1, 22.4, 14.1, 14.0, 10.7 ppm. FTIR (neat): 2924, 2855, 2218, 1735, 1599, 1510, 1460, 1374, 1261, 1093, 1022, 801 cm^{-1}. HRMS (MALDI-TOF): m/z calculated for $C_{76}H_{83}N_3O_1S_2$: 1117.5972, found 1117.5955.

Compound RFTA-2.
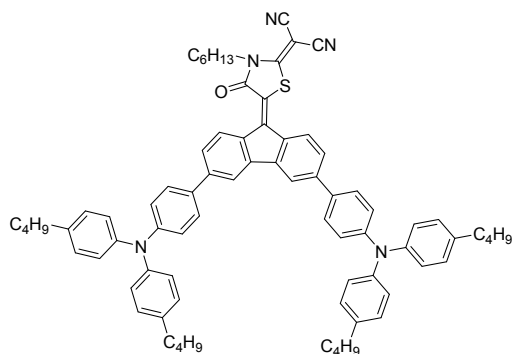
Into a 100 mL 2-neck round bottom flask equipped with a condenser, **3** (0.14 g, 0.16 mmol), 2-(3-hexyl-4-oxothiazolidin-2-ylidene)malononitrile (**7**) (0.21 g, 0.78 mmol), and NH_4OAc (86 mg, 1.12 mmol) were added to glacial acetic acid (10 mL). The mixture was stirred at 118 °C for 24 h. After cooling to room temperature, the reaction was diluted with chloroform and repeatedly washed with a $NaHCO_3$ saturated solution until no CO_2 generation is observed. Organic extracts were dried over anhydrous Na_2SO_4, filtered, and dried. Purification was carried out by flash chromatography (silica gel, hexane/dichloromethane 1:2) to give a dark purple solid (0.07 g, 40%). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 9.21 (d, J = 8.5 Hz, 1H), 7.87–7.83 (m, 3H), 7.55–7.49 (m, 6H), 7.12–7.06 (m, 20H), 4.28–4.25 (m, 2H), 2.59 (t, J = 7.6 Hz, 8H), 1.83–1.76 (m, 2H), 1.65–1.58 (m, 8H), 1.49–1.45 (m, 2H), 1.43–1.34 (m, 12H), 0.95 (t, J = 7.3 Hz, 12H), 0.91–0.88 (m, 3H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ: 164.8, 164.4, 149.0, 148.8, 145.2, 145.0, 144.9, 144.1, 144.0, 143.0, 142.2, 138.4, 138.2, 135.6, 134.1, 131.6, 131.2, 130.6, 129.4, 129.3, 127.5, 127.4, 125.2, 125.1, 121.9, 121.7, 117.8, 117.1, 114.7, 113.4, 112.3, 54.5, 45.3, 35.2, 33.7, 31.2, 29.7, 28.6, 25.8, 22.5, 14.0 ppm. FTIR (neat): 3030, 2924, 2855, 2215, 1713, 1595, 1539, 1509, 1470, 1451, 1321, 1279, 1101, 826 cm^{-1}. HRMS (MALDI-TOF): m/z calculated for $C_{77}H_{79}N_5OS$: 1121.6003, found 1121.6000.

3,6-bis(5-(bis(4-butylphenyl)amino)thiophen-2-yl)-9H-fluoren-9-one (5).
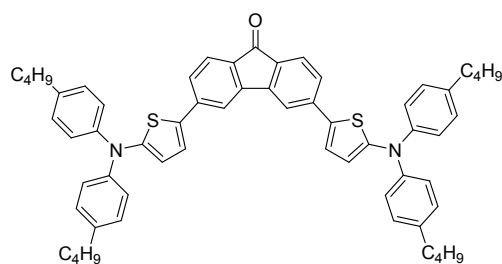
Into a 100 mL 2-neck round bottom flask equipped with a condenser, N,N-bis(4-butylphenyl)-5-(trimethylstannyl)thiophen-2-amine (**4**) (0.70 g, 1.34 mmol), 3,6-dibromo-9H-fluoren-9-one (0.20 g, 0.60 mmol), Pd$_2$(dba)$_3$ (0.014 g, 0.014 mmol), and P(o-tolyl)$_3$ (0.018 g, 0.06 mmol) were added to dry toluene (15 mL) under nitrogen atmosphere. The reaction mixture was degassed for 30 min, and then stirred and refluxed for 18h. Upon cooling, Et$_2$O (50 mL) was added and then washed with H$_2$O (2 x 50 mL). The organic layer was extracted, dried over anhydrous Na$_2$SO$_4$, filtered, and evaporated to dryness. Purification by column chromatography (silica gel, hexane/DCM 1:2) gave rise to a dark red solid (0.44 g, 80%). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.62 (d, J = 1.1 Hz, 2H), 7.58 (d, J = 7.8 Hz, 2H), 7.39 (dd, J = 7.8, 1.5 Hz, 2H), 7.27 (d, J = 4.0 Hz, 2H), 7.17 (m, 16H), 6.55 (d, J = 4.0 Hz, 2H),

2.63–2.55 (m, 8H), 1.66–1.56 (m, 8H), 1.44–1.32 (m, 8H), 0.94 (t, J = 7.3 Hz, 12H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ: 192.1, 154.5, 145.2, 144.6, 140.7, 138.6, 133.7, 132.7, 129.2, 129.2, 124.8, 124.7, 124.1, 123.5, 123.5, 123.1, 118.1, 116.2, 35.1, 33.6, 22.4, 14.0 ppm. FTIR (neat): 3052, 2955, 2926, 2859, 1707, 1596, 1508, 1473, 1435, 1318, 1280, 1183, 828, 743, 694 cm^{-1}. HRMS (MALDI-TOF): m/z calculated for C$_{61}$H$_{62}$N$_2$O$_1$S$_2$: 902.4298, found 902.4295.

Compound RFTA-3.
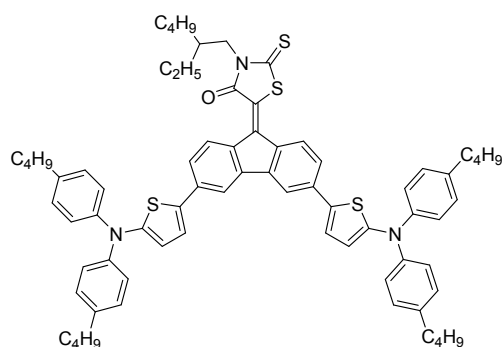
Into a 100 mL 2-neck round bottom flask equipped with a condenser, **5** (0.10 g, 0.11 mmol), 3-(2-ethylhexyl)-2-thioxothiazolidin-4-one (**6**) (0.14 g, 0.35 mmol), and NH$_4$OAc (60 mg, 0.77 mmol) were added to glacial acetic acid (10 mL). The mixture was stirred at 118 °C for 24 h. After cooling to room temperature, the reaction was diluted with chloroform and repeatedly washed with a NaHCO$_3$ saturated solution until no CO$_2$ generation is observed. Organic extracts were dried over anhydrous Na$_2$SO$_4$, filtered, and dried. Purification was carried out by flash chromatography (silica gel, pentane/dichloromethane 10:1) to yield a dark green solid (0.03 g, 35%). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 9.11 (d, J = 8.5 Hz, 1H), 7.59–7.54 (m, 3H), 7.31 (d, J = 8.7 Hz, 1H), 7.28 (dd, J = 8.4, 1.6 Hz, 1H), 7.22 (d, J = 3.9 Hz, 1H), 7.21 (d, J = 3.9 Hz, 1H), 7.18–7.06 (m, 16H), 6.54 (d, J = 3.9 Hz, 2H), 4.00 (d, J = 7.4 Hz, 2H), 2.62–2.59 (m, 8H), 2.10–2.04 (m, 1H), 1.66–1.59 (m, 8H), 1.45–1.28 (m, 16H), 0.96 (t, J = 7.3 Hz, 12H), 0.94–0.88 (m, 6H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ: 191.4, 166.5, 154.1, 153.7, 145.3, 145.3, 142.6, 142.1, 140.7, 138.5, 138.4, 137.2, 137.0, 136.1, 134.3, 133.9, 130.1, 129.3, 129.2, 127.5, 124.3, 123.8, 123.7, 123.5, 123.3, 121.0, 118.8, 118.4, 115.9, 115.5, 48.7, 37.2, 35.1, 33.7, 30.6, 28.5, 24.0, 23.1, 22.5, 14.1, 14.0, 10.7 ppm. FTIR (neat): 3030, 2956, 2925, 2857, 1702, 1655, 1605, 1507, 1457, 1371, 1292, 1192, 1128, 828, 791 cm^{-1}. HRMS (MALDI-TOF): m/z calculated for C$_{72}$H$_{79}$N$_3$O$_1$S$_4$: 1129.5100, found 1129.5071.
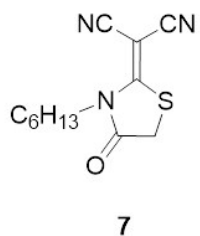
Compound RFTA-4.
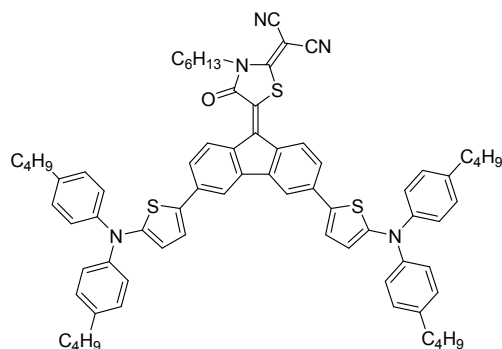
Into a 100 mL 2-neck round bottom flask equipped with a condenser, **5** (0.18 g, 0.20 mmol), 2-(3-hexyl-4-oxothiazolidin-2-ylidene)malononitrile (**7**) (0.27 g, 1.02 mmol), and NH$_4$OAc (0.11 g, 1.43 mmol) were added to glacial acetic acid (10 mL). The mixture was stirred at 118 °C for 24 h. After cooling to room temperature, the reaction was diluted with chloroform and repeatedly washed with a NaHCO$_3$ saturated solution until no CO$_2$ generation was observed. Organic extracts were
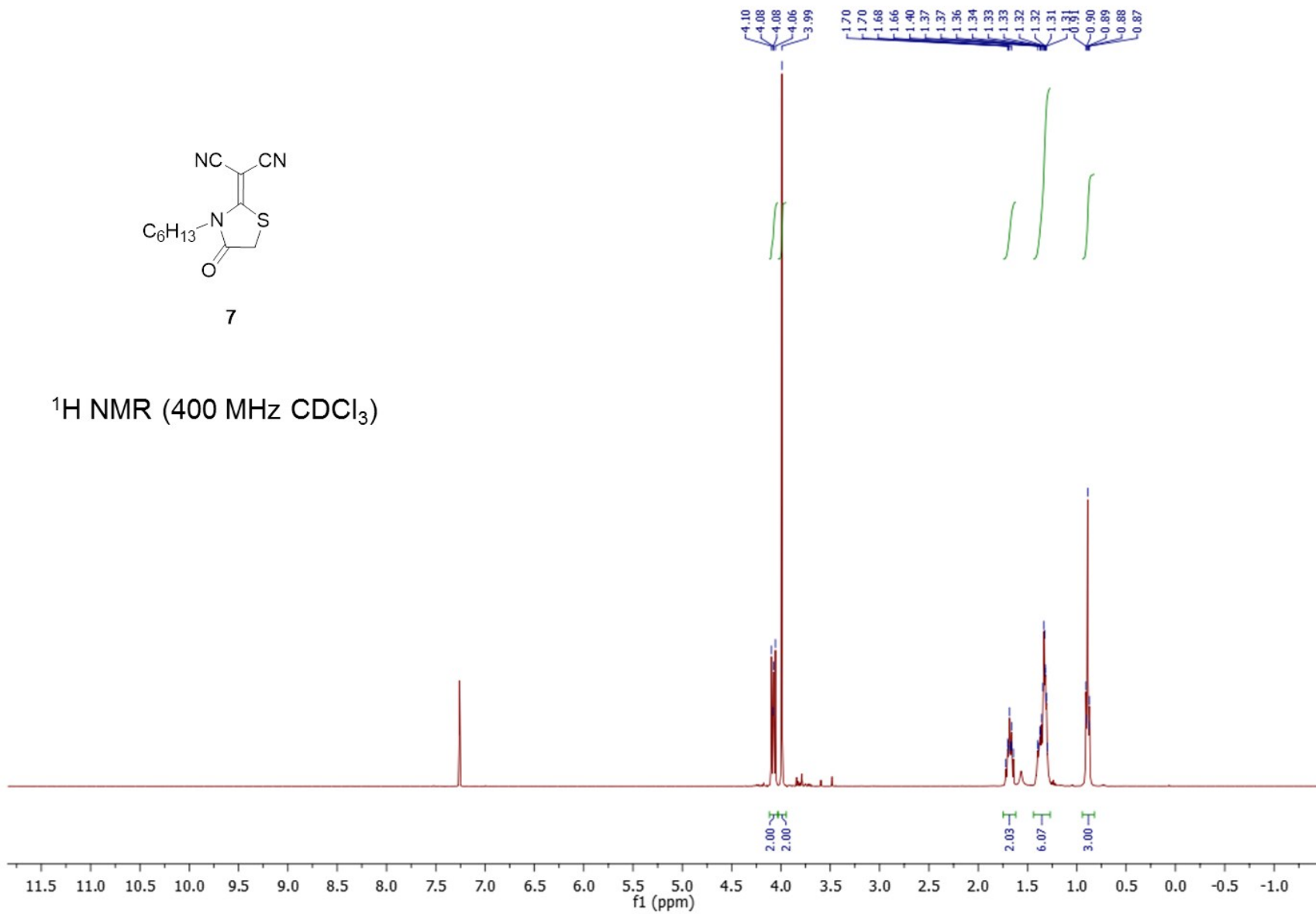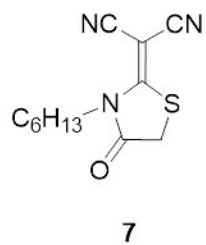
dried over anhydrous Na$_2$SO$_4$, filtered, and dried. Purification was carried out by flash chromatography (silica gel, hexane/dichloromethane 1:2) to give a deep blue solid (0.13 g, 56%). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 9.09 (d, J = 8.6 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.68 (d, J = 1.8 Hz, 1H), 7.66 (d, J = 1.9 Hz, 1H),   7.42 (dd, J = 8.4, 1.8 Hz, 1H), 7.37 (dd, J = 8.6, 1.9 Hz, 1H), 7.29 (d, J = 4.1 Hz, 1H), 7.28 (d, J = 4.1 Hz, 1H), 7.18–7.10 (m, 16H), 6.56 (d, J = 4.1 Hz, 1H), 6.55 (d, J = 4.1 Hz, 1H), 4.26–4.20 (m, 2H), 2.63–2.56 (m, 8H), 1.82–1.71 (m, 2H), 1.67–1.56 (m, 8H), 1.49–1.44 (m, 2H), 1.43–1.32 (m, 12H), 0.94 (t, J = 7.3 Hz, 12H), 0.90 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (126 MHz, CDCl$_3$) δ: 164.7, 164.3, 154.9, 154.8, 145.1, 145.0, 144.6, 142.6, 141.9, 138.8, 138.8, 137.9, 135.1, 133.7, 133.2, 132.7, 130.5, 129.3, 129.3, 129.2, 127.3, 124.5, 124.2, 124.0, 123.7, 123.6, 117.6, 115.9, 115.2, 113.6, 113.5, 112.5, 54.2, 45.2, 35.1, 33.6, 31.3, 29.7, 28.7, 25.7, 22.5, 22.4, 14.0 ppm. FTIR (neat): 2923, 2854, 2215, 1714, 1651, 1604, 1545, 1510, 1454, 1375, 1275, 755 cm^{-1}. HRMS (MALDI-TOF): m/z calculated for C$_{73}$H$_{75}$N$_5$O$_1$S$_3$: 1133.5128, found 1133.5116.
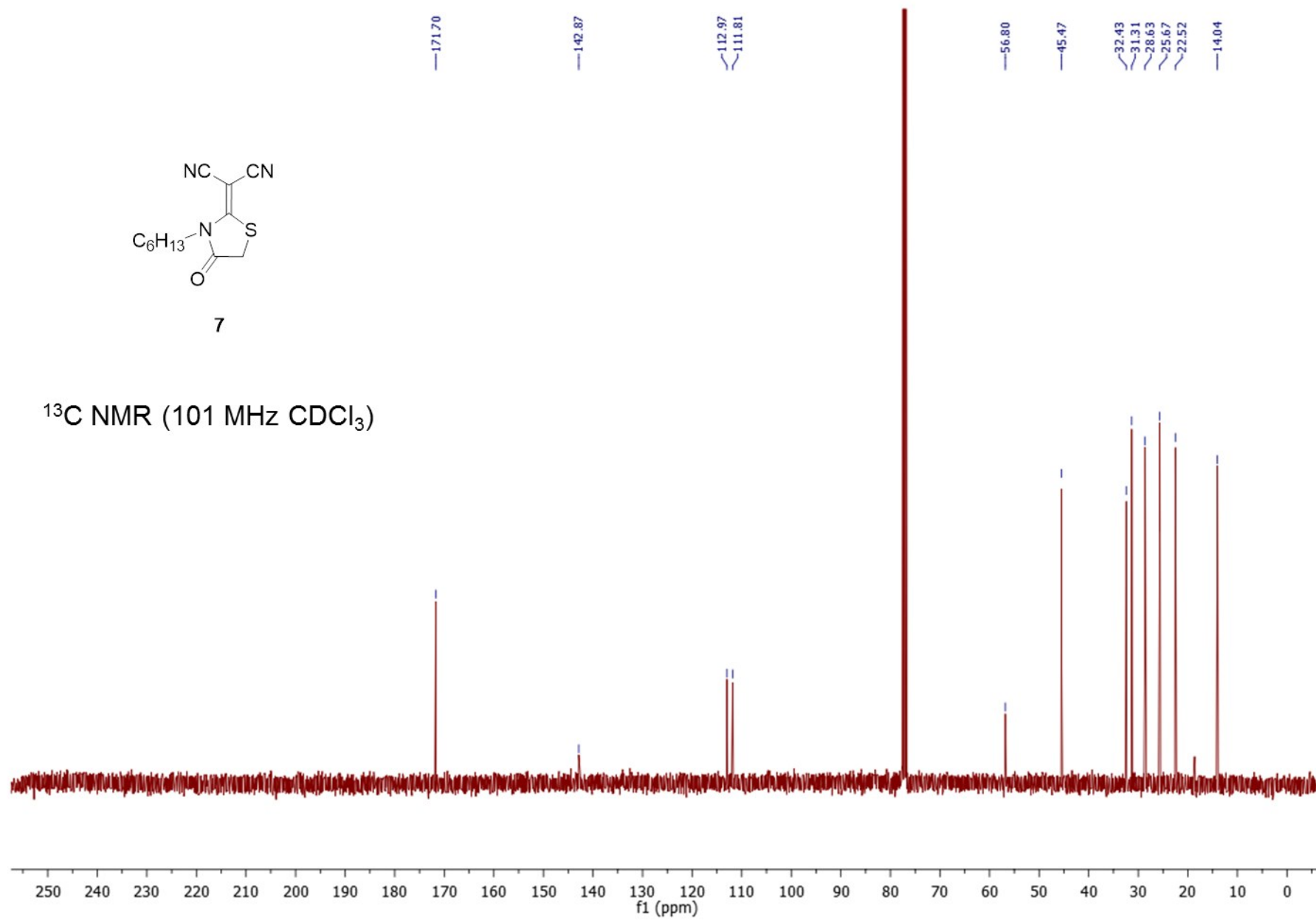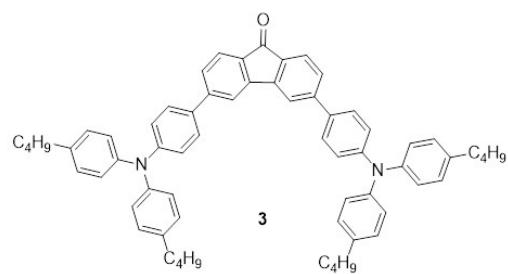
NMR Spectra

^{1}H NMR (400 MHz CDCl$_3$)

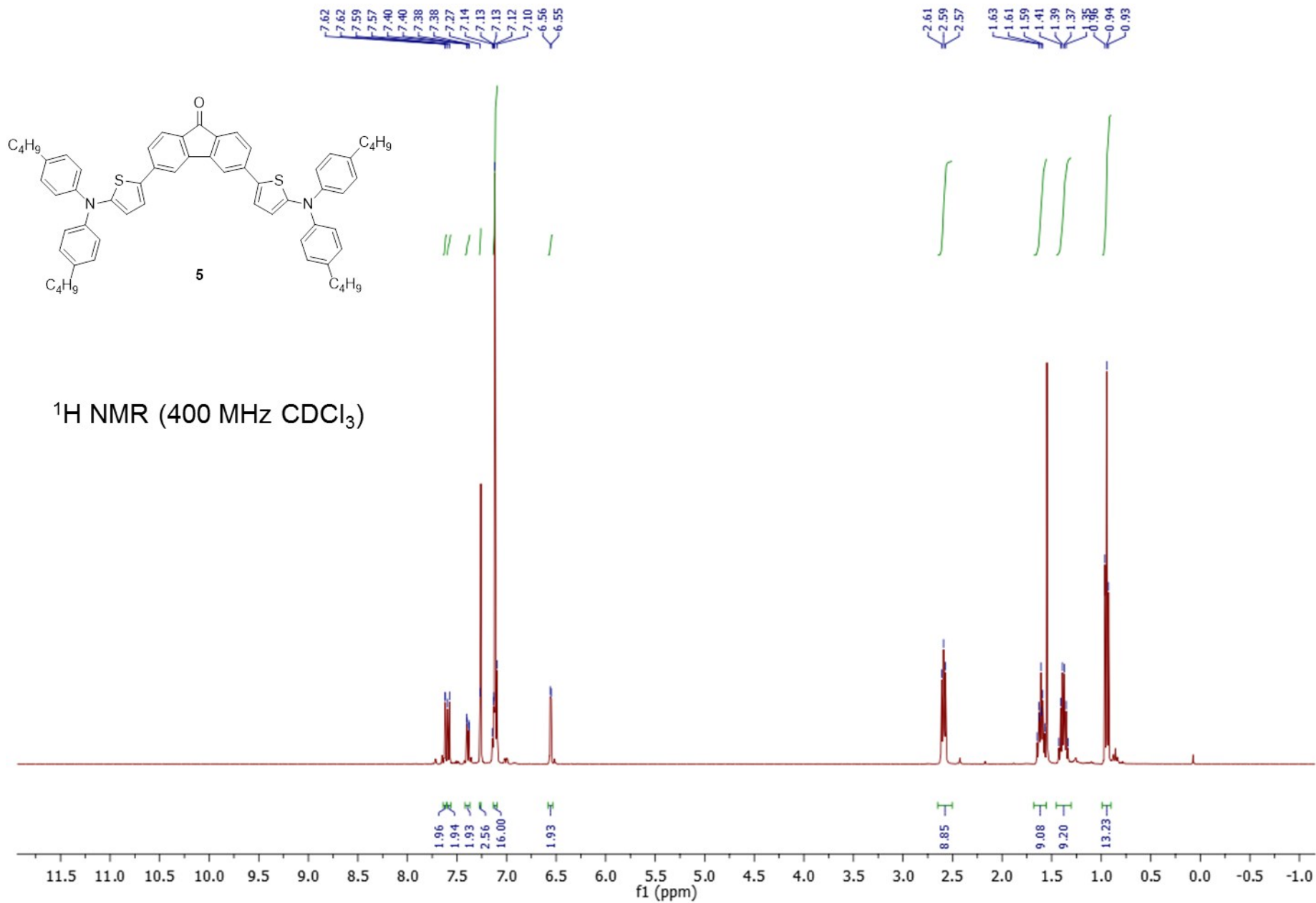^{13}C NMR (101 MHz CDCl$_3$)

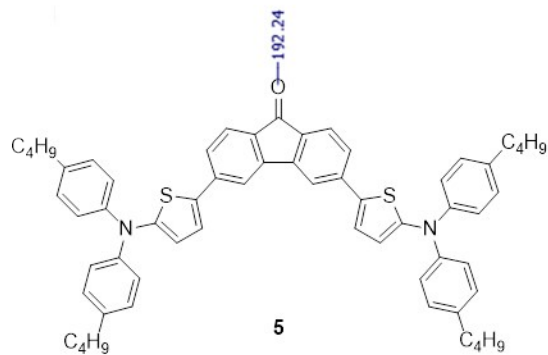171.70
142.87
112.97
111.81
56.80
45.47
32.43
31.31
28.63
25.67
22.52
14.04

7

^{1}H NMR (400 MHz CDCl$_3$)

13C NMR (101 MHz CDCl₃)

148.86
147.31
145.09
145.01
138.30
133.11
132.58
129.41
127.86
127.07
125.08
124.72
122.14
118.36

35.22
33.79

22.56

14.13

3

f1 (ppm)

^{1}H NMR (400 MHz CDCl$_3$)
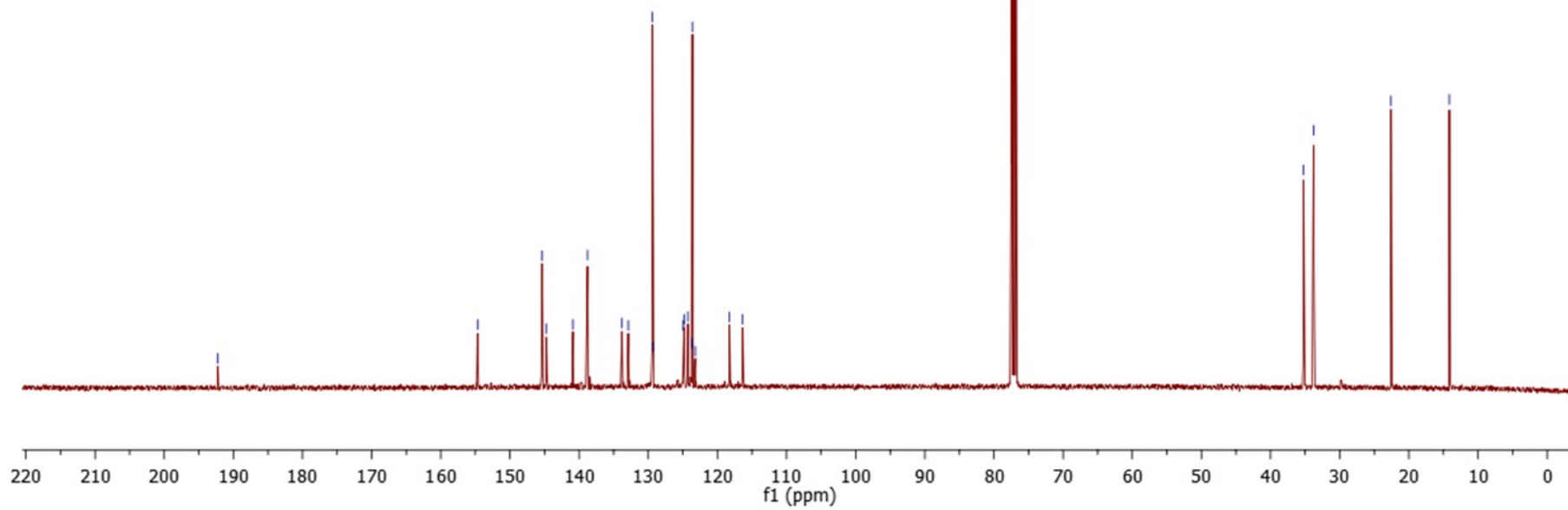
^{13}C NMR (101 MHz CDCl$_3$)

Peak labels: 192.24, 154.68, 145.34, 144.72, 140.89, 138.78, 133.80, 132.89, 129.39, 129.32, 124.94, 124.82, 124.26, 123.69, 123.61, 123.21, 118.25, 116.35, 35.22, 33.78, 22.58, 14.13

Structure label: 5

RFTA-1

^{1}H NMR (400 MHz CDCl$_3$)

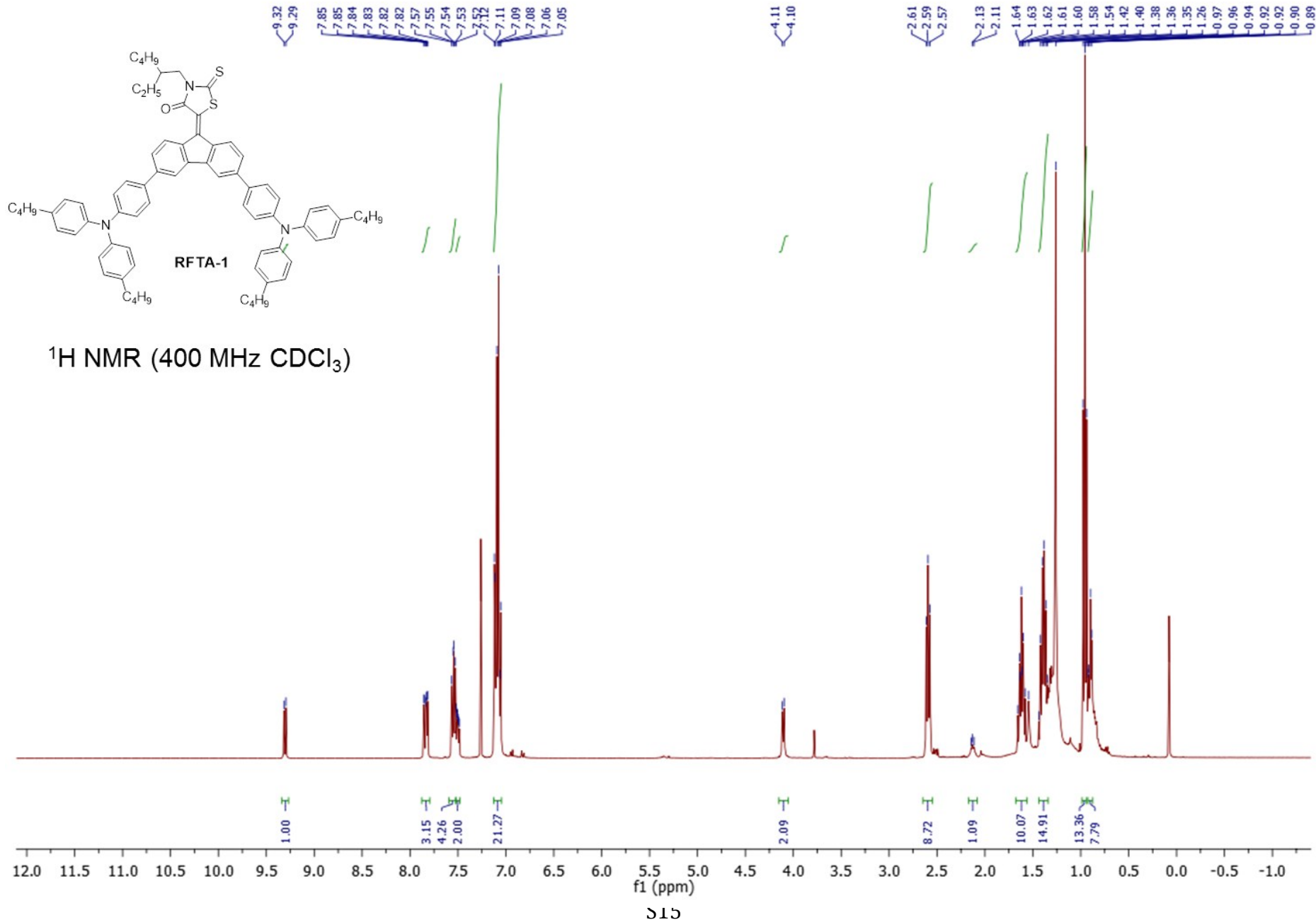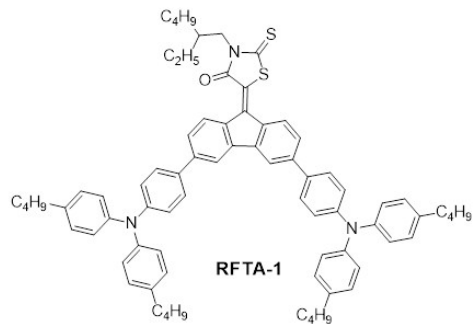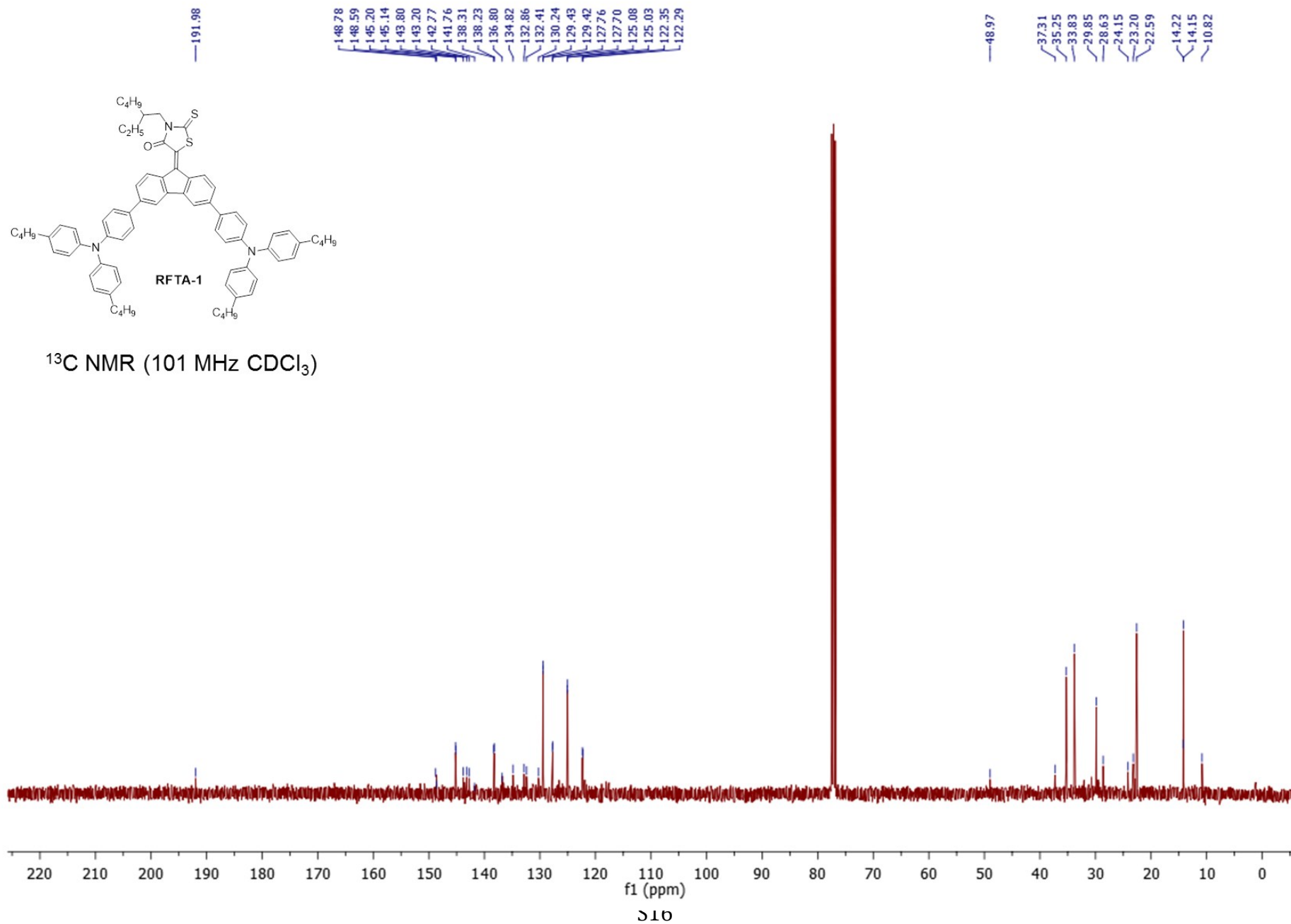^{13}C NMR (101 MHz CDCl$_3$)

^{1}H NMR (400 MHz CDCl$_3$)

^{13}C NMR (101 MHz CDCl$_3$)

164.91
164.46
149.08
148.98
145.31
145.04
144.97
144.17
144.13
143.16
142.40
138.51
138.42
135.72
134.25
131.78
131.38
129.47
129.45
127.67
127.56
126.29
125.89
125.31
125.24
121.98
121.80
117.92
117.26
114.79
113.48
112.46

45.38
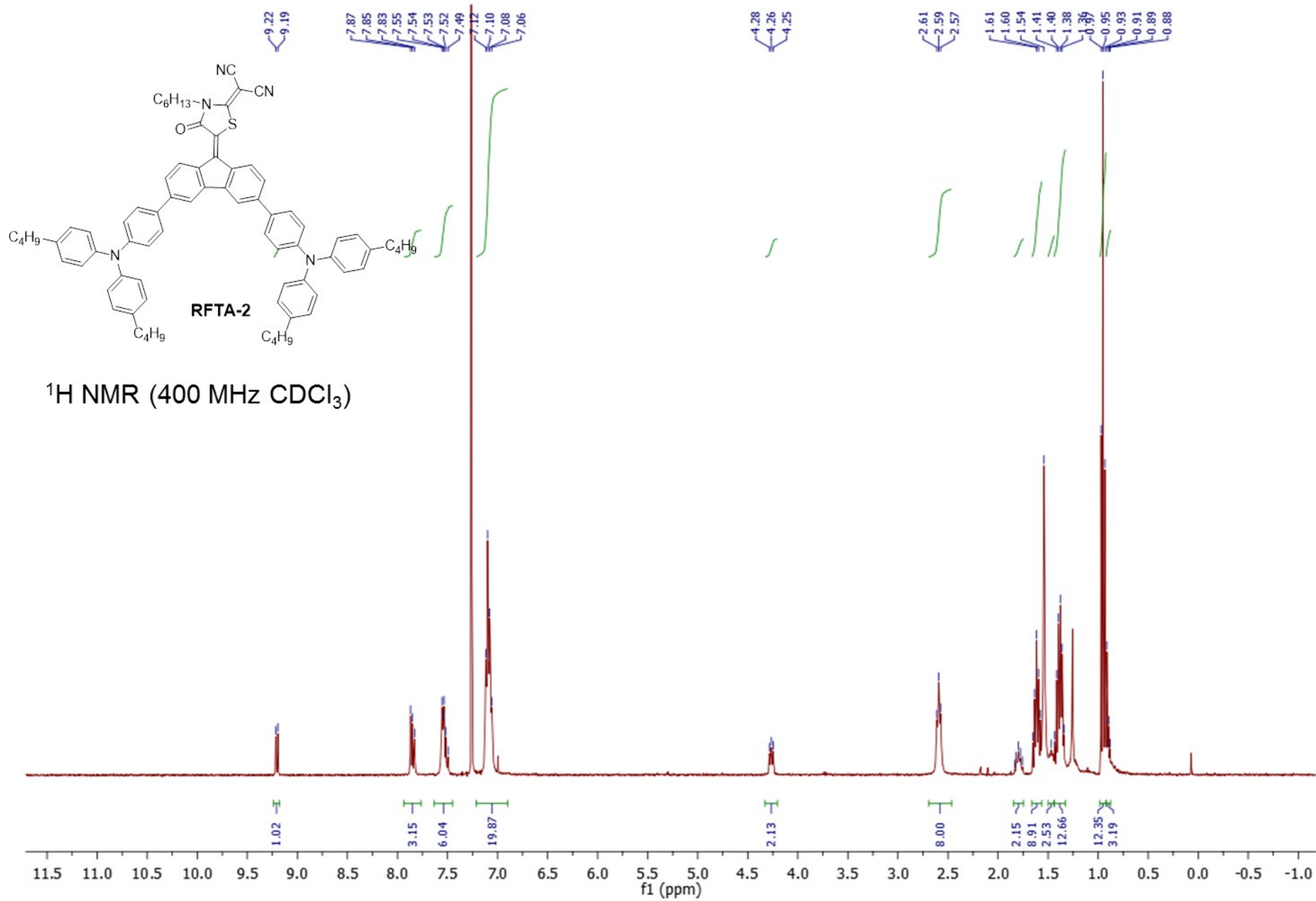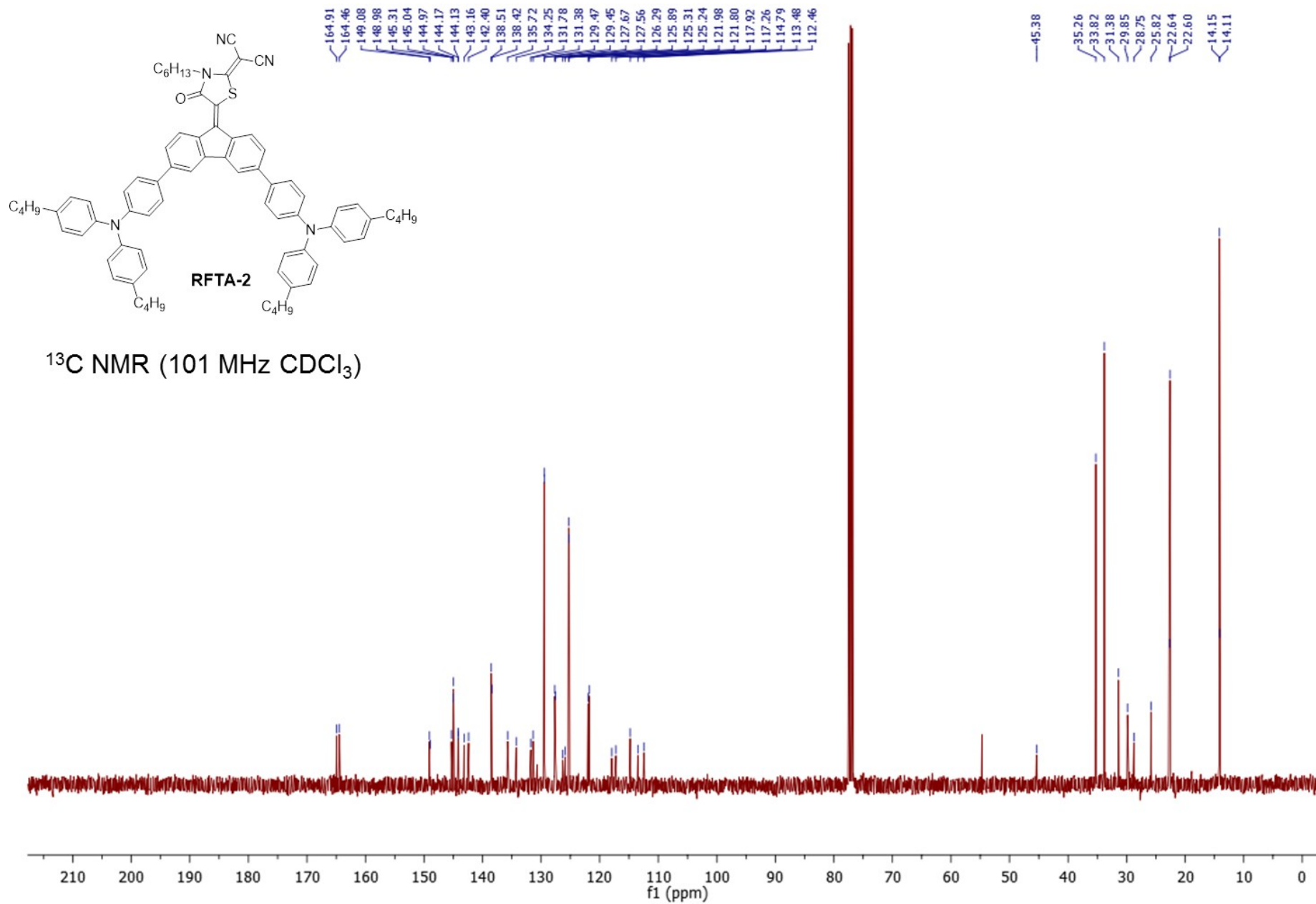
35.26
33.82
31.38
29.85
28.75
25.82
22.64
22.60

14.15
14.11

RFTA-3

^{1}H NMR (400 MHz CDCl$_3$)

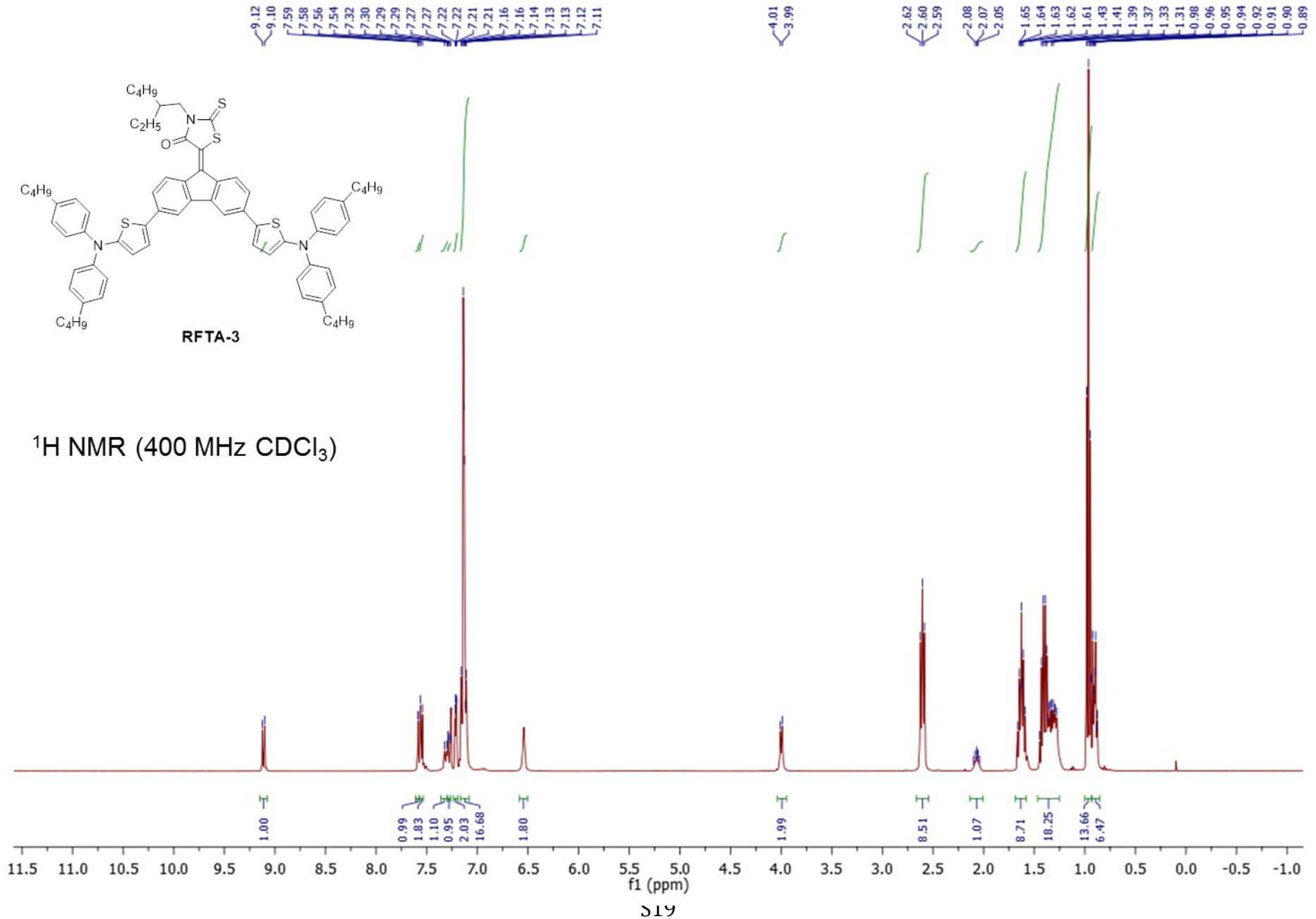^{13}C NMR (101 MHz CDCl$_3$)
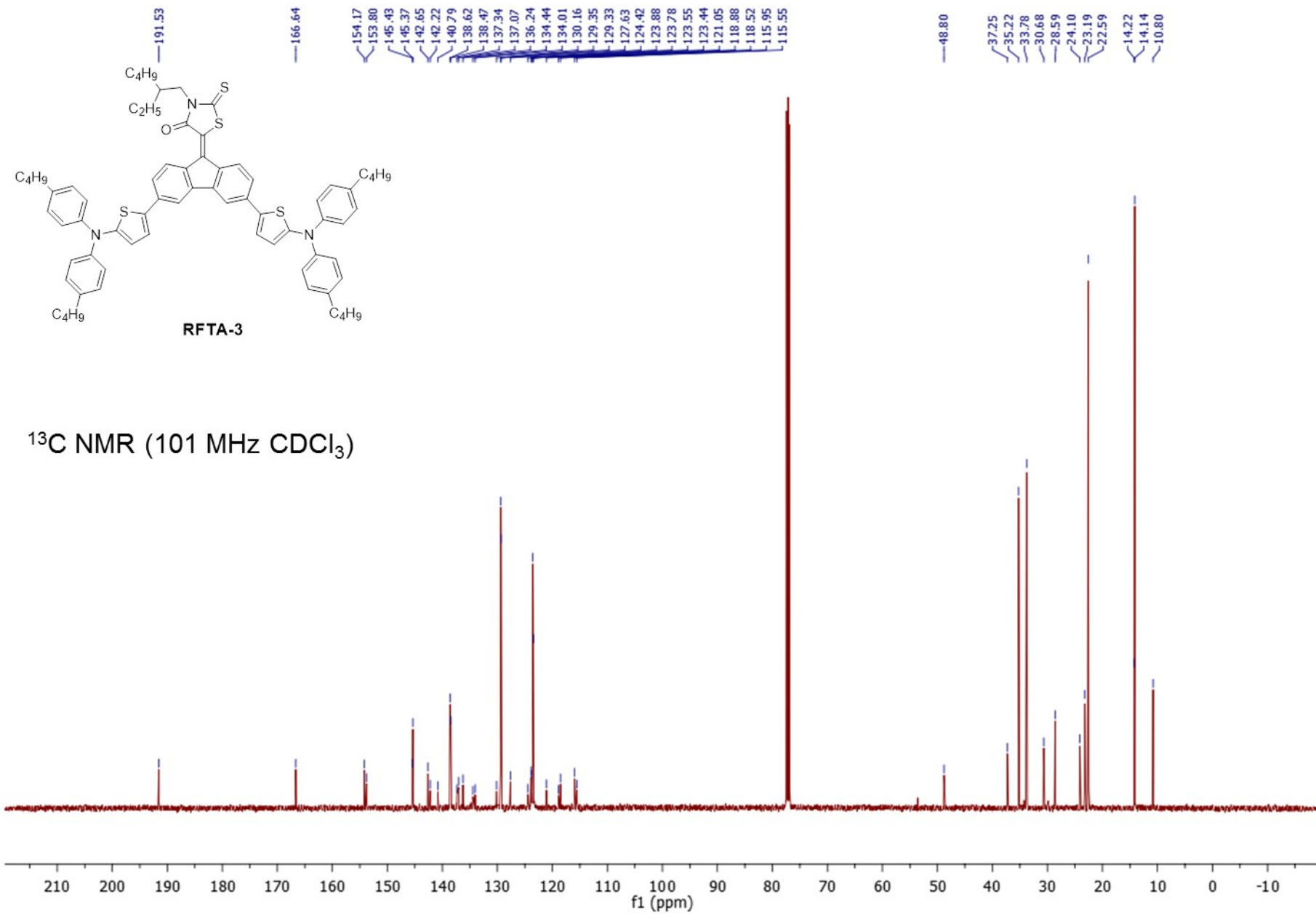
RFTA-4

^{1}H NMR (400 MHz CDCl$_3$)

S21

RFTA-4

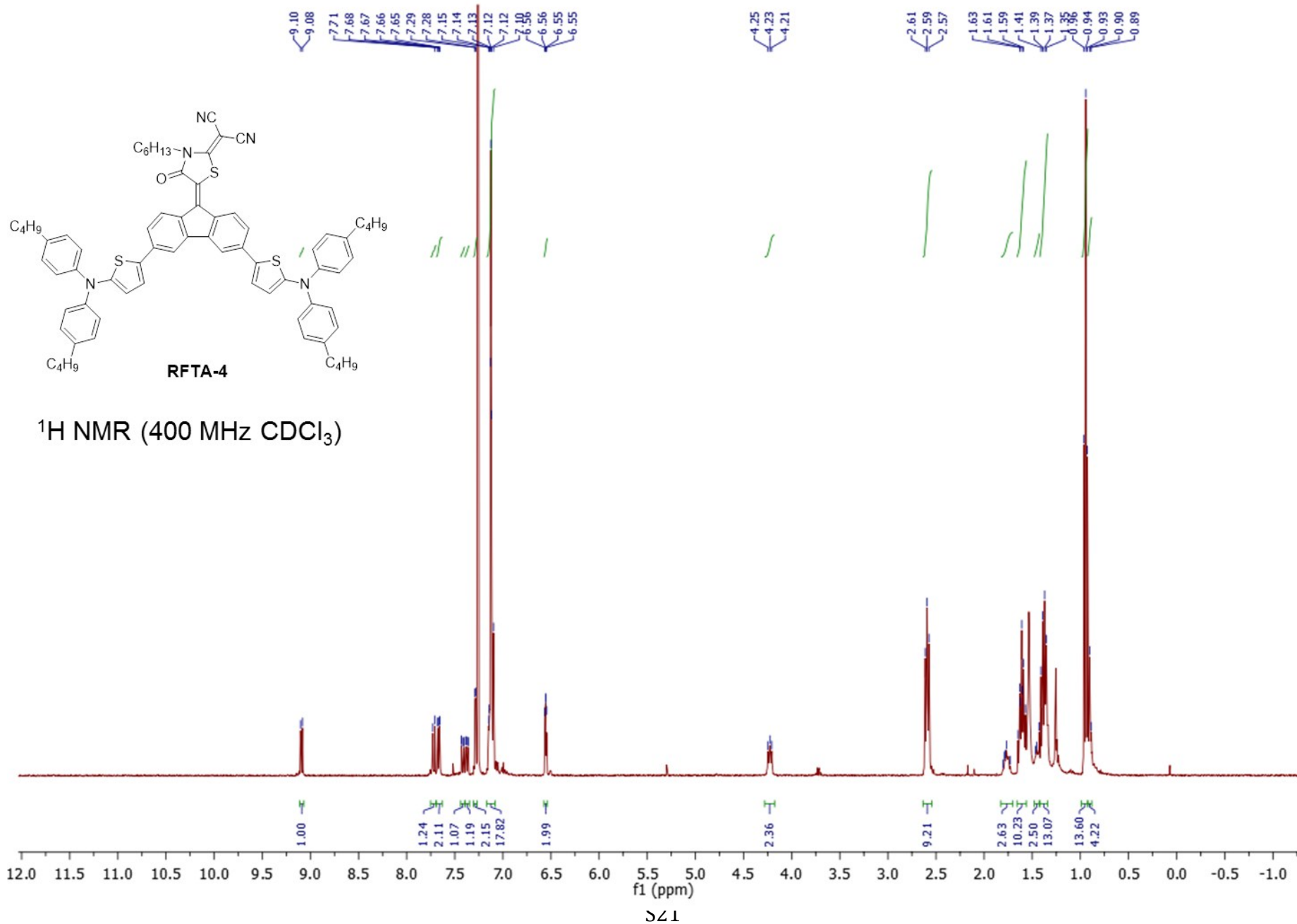^{13}C NMR (101 MHz CDCl$_3$)

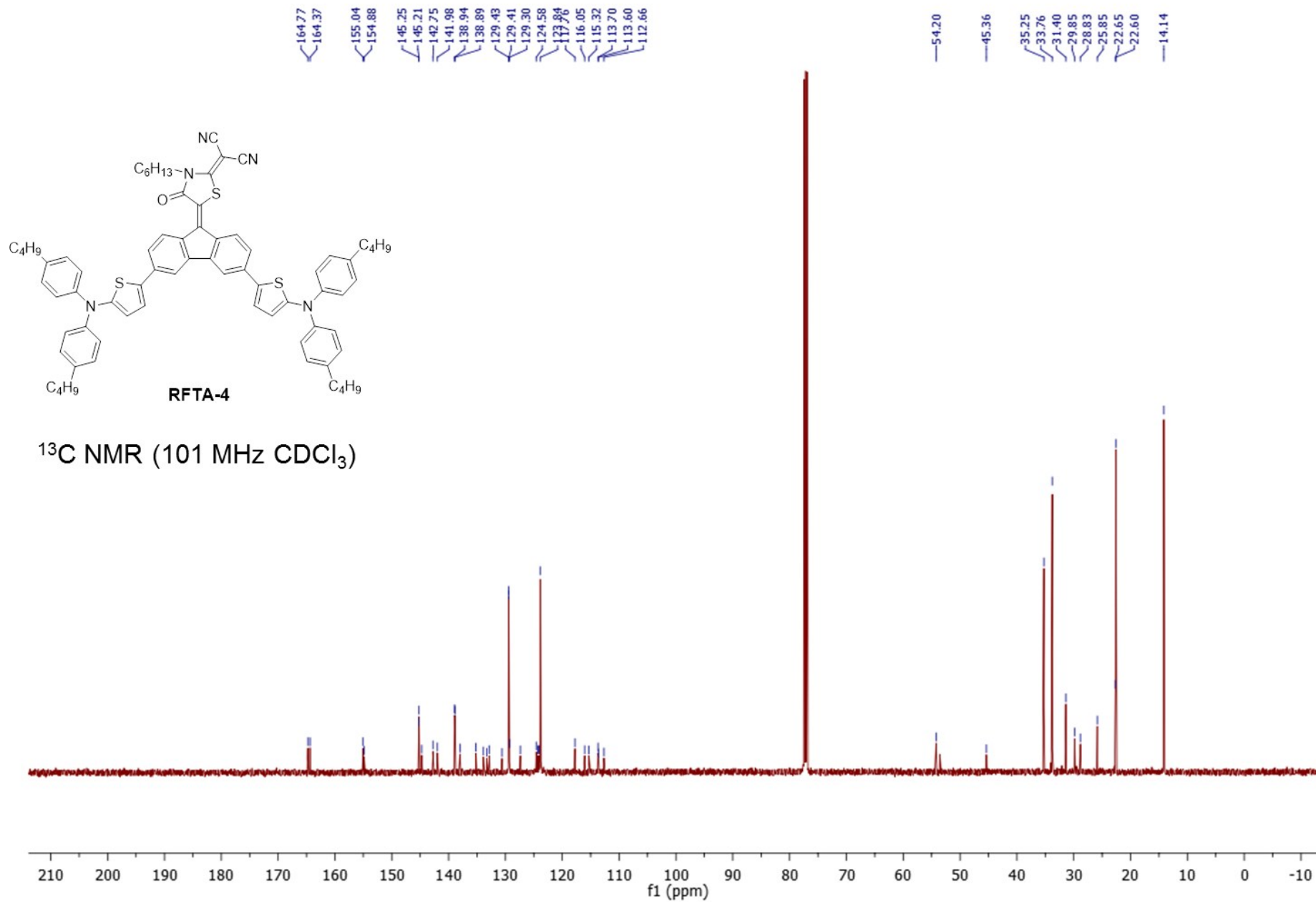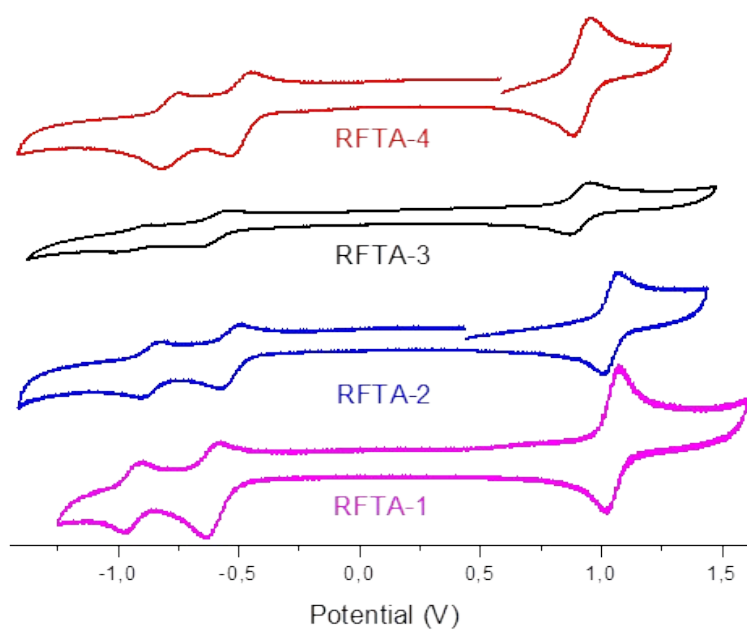**Cyclic voltammetry plots**

Figure S1. Cyclic voltammograms of **RFTA-1−4** dyes.

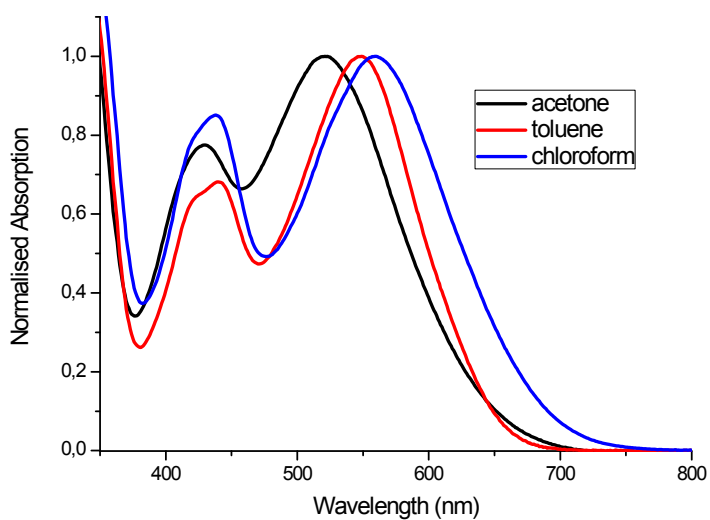**Photoluminescence & solvatochromic experiments**

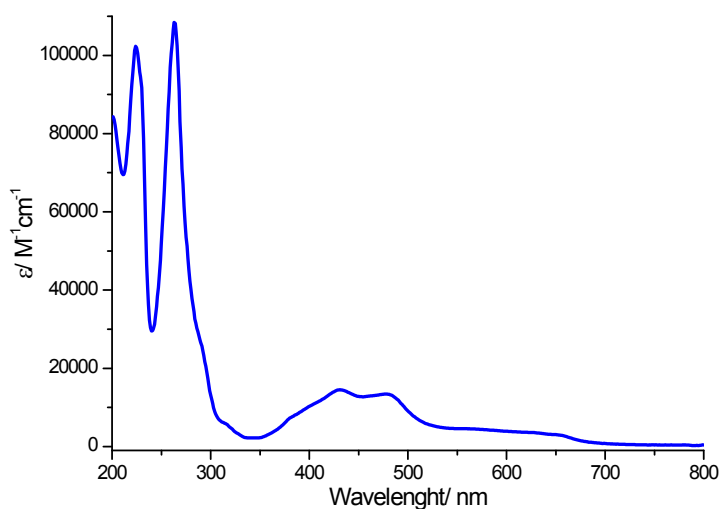**Figure S2.** Absorption spectra of **RFTA2** in different solvents evidences significant solvatochromism over the lower energy band.

Figure S3. Molar absorption spectrum of $[Os^{II}(phen)_3](PF_6)_2$ in acetonitrile solution.

Corrected emission spectra were collected using a Fluorolog-3 HORIBA spectrofluorometer. The emission quantum yields for all the dyes under study were determined, at 25 ± 2 ºC from N_2-purged solutions in distilled dry dichloromethane with optical densities ≤ 0.1, by comparison with the corresponding emission spectrum of $[Os(phen)_3]^{2+}$ standard (Φ_{em} = 0.021 in acetonitrile).[4] Same excitation wavelength and identical emission wavelength ranges were used for all the samples. The optical density of each solution was checked before and after collection of the corresponding emission spectrum. In these conditions, the unknown Φ_{em} values were calculated as follows:

$$\Phi_{em} = \Phi_{Ref} \frac{I}{I_{Ref}} \frac{A_{Ref}}{A} \frac{n^2}{n_{Ref}^2}$$

where Φ_{em} is the emission quantum yield, I is the integrated emission intensity, A is the absorbance at the excitation wavelength, and n is the refractive index of the solvent. The subscript *Ref* refers to the reference standard of known quantum yield.

The energy of the 0-0 transition (E_{0-0}) of each dye was determined by converting to wavenumbers the wavelengths of the absorption and emission maxima, and taking half the difference between the peaks, which was added to the wavenumber of the emission peak and then converted to eV units. This allowed the calculation of the excited state redox potentials of the RFTA compounds by using the following equations:

$E_{Ox}* = E_{Ox} - E_{0-0}$

$E_{Red}* = E_{Red} + E_{0-0}$

where $E_{Ox}*$ and $E_{Red}*$ are the excited state oxidation and reduction potentials, respectively; E_{Ox} and E_{Red} are the ground state oxidation and reduction

potentials, respectively, determined from cyclic voltametry measurements (Table 2 of the manuscript), and E_{0-0} is the energy of the 0-0 transition between the lowest vibrational levels of the ground and excited states.
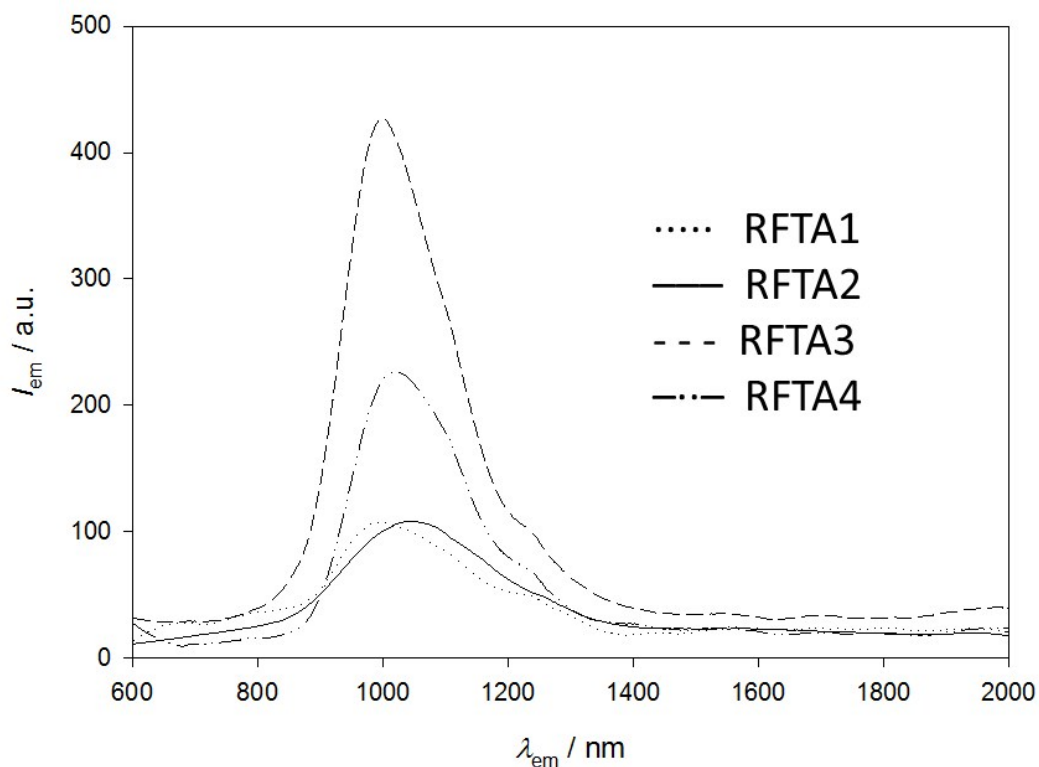

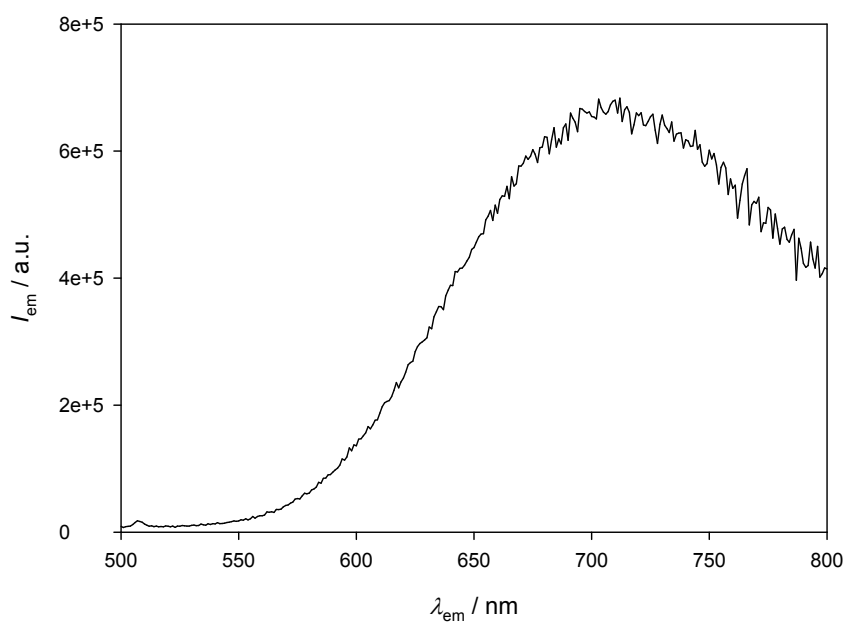**Figure S4.** Emission spectra for dyes **RFTA1−4** recorded in DCM solution (λ_{exc} = 580 nm).

Figure S5. Emission spectrum for compound **3** recorded in DCM solution in the visible range (λ_{exc} = 440 nm).
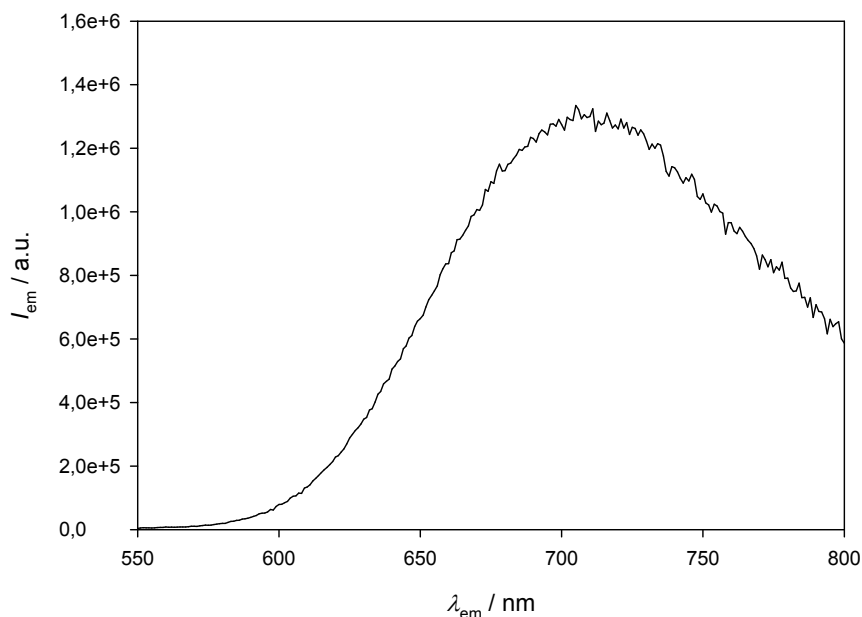
Figure S6. Emission spectrum for compound **5** recorded in DCM solution solution in the visible range (λ_{exc} = 510 nm).

Theoretical calculations

Theoretical calculations were performed for the rhodanine-based D-A-D dyes under the density functional theory (DFT) framework using the Gaussian 09 (version D01) suite of programs.[6] The well-established hybrid exchange-correlation B3LYP functional[7] was used in combination with the correlation consistent Dunning's cc-pVDZ basis set.[8] Fully relaxed minimum-energy structures were obtained at the B3LYP/cc-pVDZ level (Figure S2). Solvent effects were included in the optimization according to the self-consistent reaction field (SCRF) procedure through the polarizable continuum model (PCM) using dichloromethane as a solvent.[9] Frontier molecular orbitals were calculated at the B3LYP/cc-pVDZ+PCM level (Figure S3). The molecular orbital topologies were depicted by means of the Chemcraft 1.6 software[10] using isovalue contours of ±0.03 a.u. Time-dependent DFT (TD-DFT) calculations[10,11] were carried out for the D–A–D systems at the B3LYP/6-31G** level in dichloromethane. The 30 lowest-lying singlet excited states (S_n) were computed. TDDFT simulations of the UV–vis spectra were generated by convoluting each electronic transition with a Gaussian function of full-width-at-half-maximum FWHM = 0.20 eV (Figures S4 and S5).
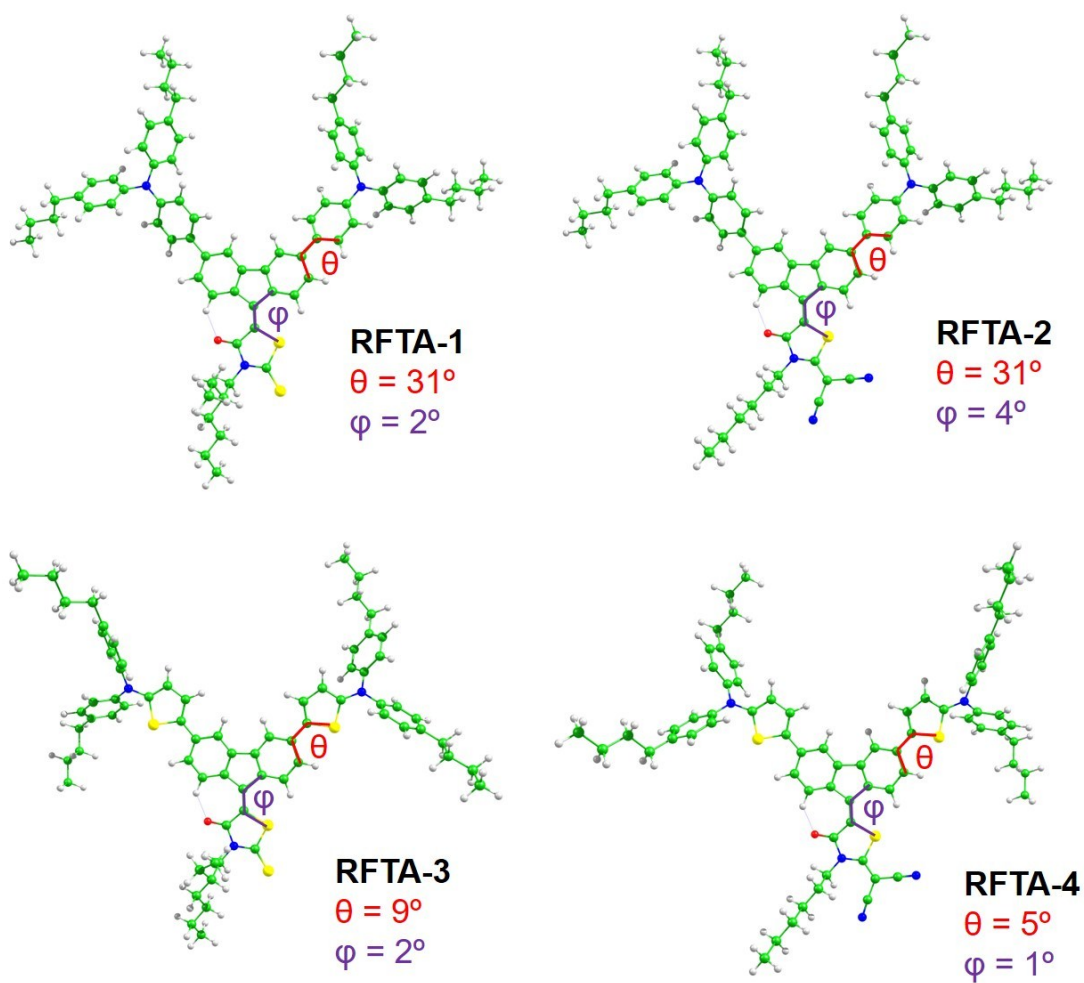
Figure S7. Minimum-energy optimized structures calculated for the RFTA D–A–D dyes at the B3LYP/cc-pVDZ level of theory in dichloromethane. Characteristic dihedral angles are indicated.
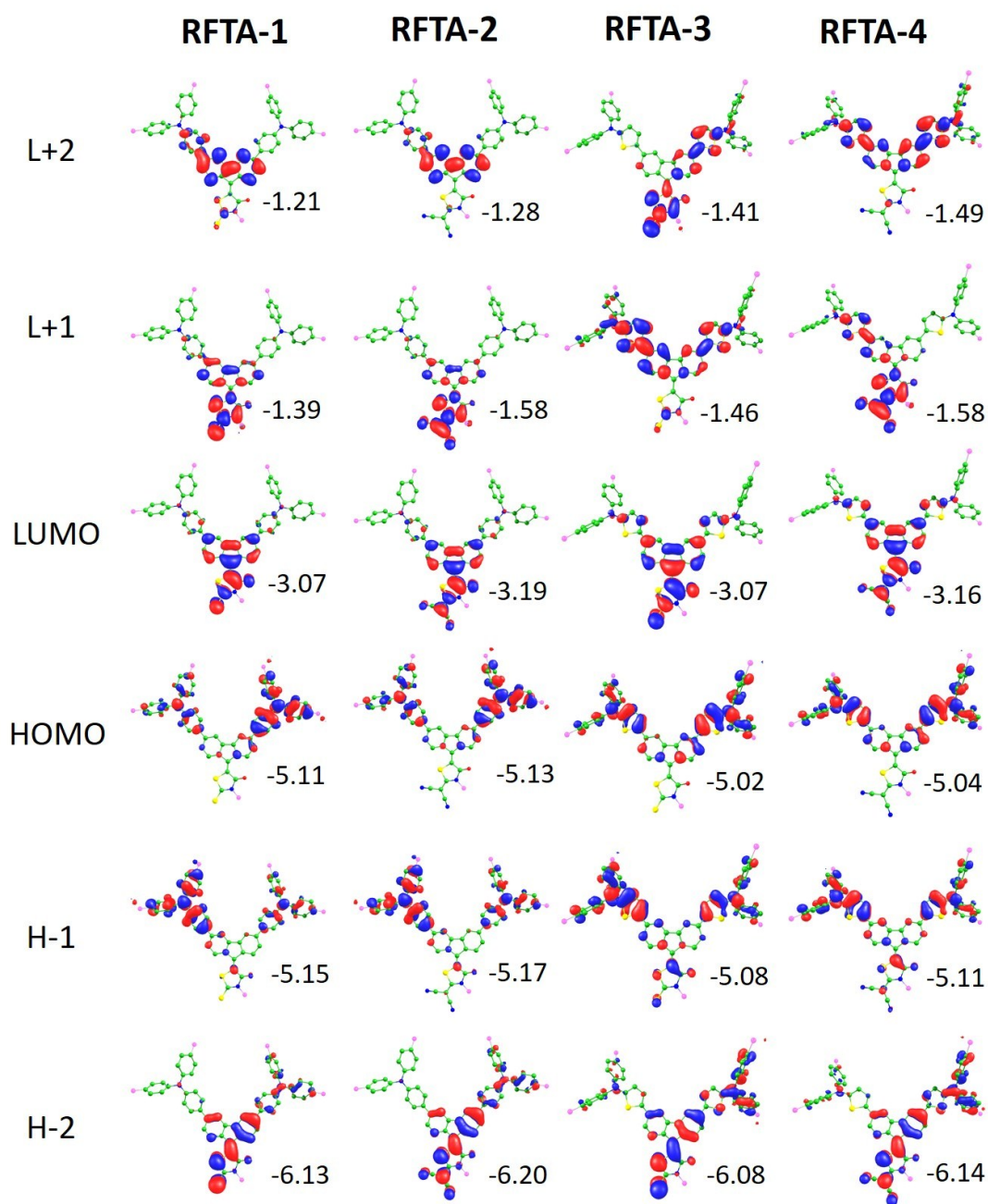
Figure S8. Isovalue contours (±0.025 a.u.) computed for the frontier molecular orbitals of rhodanine-based dyes **RFTA-1−4** at the B3LYP/cc-pVDZ level in dichloromethane. Orbital energies are indicated in eV. Alkyl chains and hydrogen atoms are omitted for better viewing.

Table S1. Lowest-energy singlet excited states calculated for the RFTA dyes at the TD-B3LYP/cc-pVDZ level in CH_2Cl_2. Vertical excitation energies (E), oscillator strengths (f), dominant monoexcitations with contributions (in percentage) greater than 30%, and nature of the excited state are summarized. H and L denote HOMO and LUMO, respectively.

State	E (eV)	E (nm)	f	Description	%	Nature[a]
			RFTA-1			
S1	1.717	722	0.2831	H → L	96	D → A
S2	1.834	676	0.5013	H-1 → L	98	D → A
S5	2.788	445	0.8594	H-2 → L	91	A → A
S6	3.174	391	0.2193	H-5 → L	85	F → A
S7	3.423	362	0.3851	H-1 → L+1	30	D → A
			RFTA-2			
S1	1.626	762	0.3050	H → L	97	D → A
S2	1.748	709	0.5281	H-1 → L	99	D → A
S4	2.721	456	0.9378	H-2 → L	89	A → A
S5	3.101	400	0.2244	H-4 → L	83	F → A
S10	3.398	365	0.2345	H → L+2	40	D → F
			RFTA-3			
S1	1.617	767	0.5601	H → L	98	D → A
S2	1.804	687	0.6579	H-1 → L	99	D → A
S5	2.748	451	0.6527	H-2 → L	88	A → A
S6	3.077	403	0.5026	H-5 → L	62	F → A
S7	3.135	395	0.4463	H-1 → L+1	41	D → A
			RFTA-4			
S1	1.555	797	0.5992	H → L	99	D → A
S2	1.750	708	0.7042	H-1 → L	100	D → A
S4	2.692	461	0.6979	H-2 → L	90	A → A
S5	3.026	410	0.4353	H-4 → L	60	F → A
S6	3.096	401	0.2986	H → L+1	36	D → A
S7	3.135	395	0.2749	H → L+2	72	D → F

[a]Labels A, D, and F refer to acceptor, donor, and fluorene-core moieties, respectively
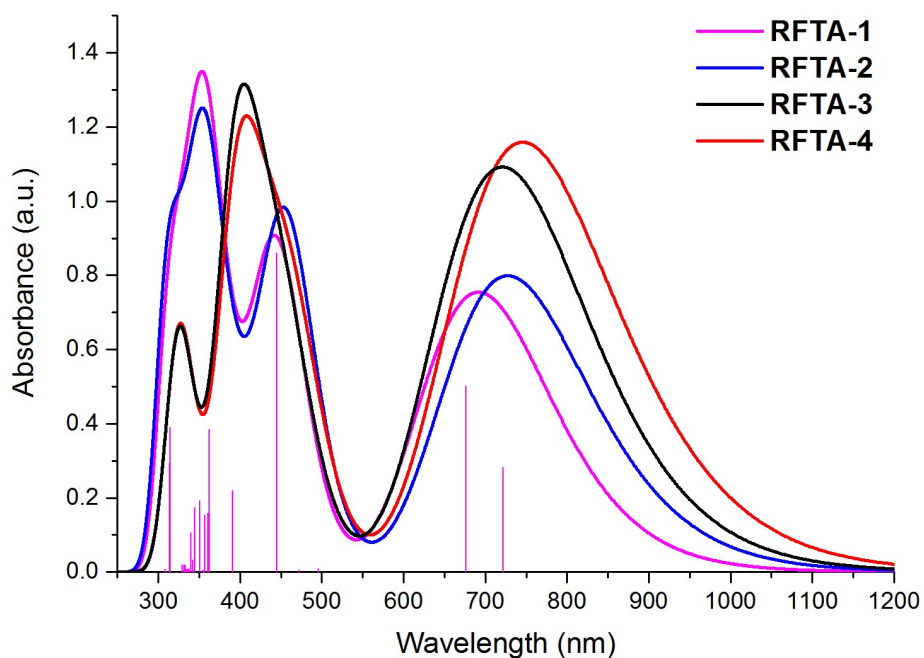
Figure S9. TD-DFT simulations of the absorption spectra calculated at the B3LYP/cc-pVDZ level of theory in dichloromethane. Electronic excitations are displayed as vertical lines in the case of **RFTA-1**.
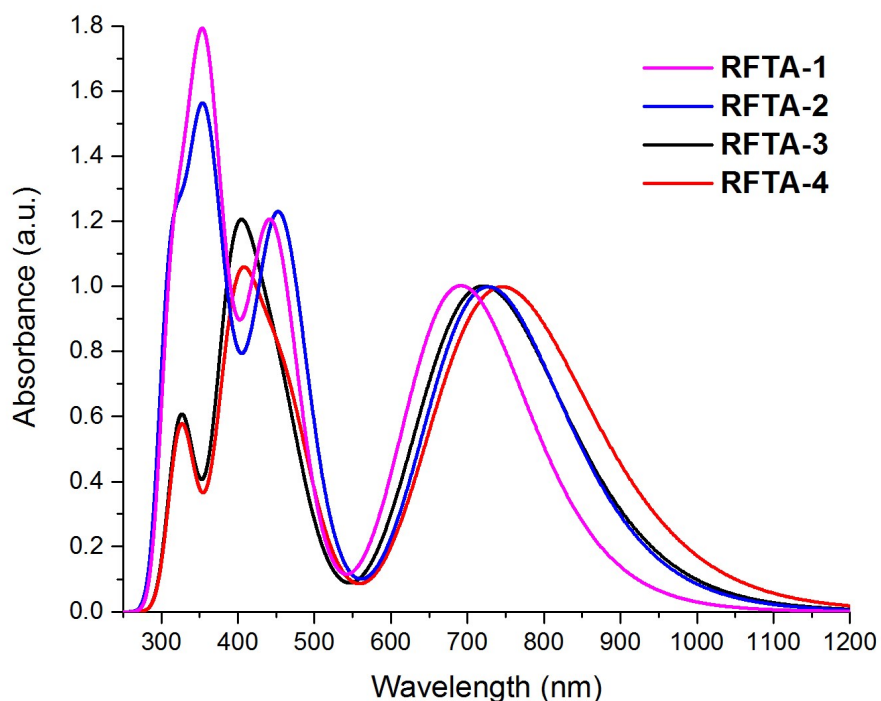

Figure S10. Normalized TD-DFT simulations of the absorption spectra calculated at the B3LYP/cc-pVDZ level of theory in dichloromethane taking into account the maximum value of the lowest-energy charge-transfer peak.

References

(1)   Y. Song, W. Xu and D. Zhu, *Tetrahedron Lett.*, 2010, **51**, 4894–4897.

(2)   V. Maurel, L. Skorka, N. Onofrio, E. Szewczyk, D. Djurado, L. Dubois, J.-M. Mouesca and I. Kulszewicz-Bajer, *J. Phys. Chem. B*, 2014, **118**, 7657–7667.

(3)   K. C. Moss, K. N. Bourdakos, V. Bhalla, K. T. Kamtekar, M. R. Bryce, M. A. Fox, H. L. Vaughan, F. B. Dias and A. P. Monkman, *J. Org. Chem.*, 2010, **75**, 6771–6781.

(4)   E. M. Kober, J. V. Caspar, R. S. Lumpkin and T. J. Meyer, *J. Phys. Chem.*, 1986, **90**, 3722–3734.

(5)   M. Montalti, A. Credi, L. Prodi and M. T. Gandolfi, Handbook of Photochemistry, 3rd ed.; CRC Press: Boca Raton, FL, 2006; Chapter 10, pp 561–581.

(6)   M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, 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, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Farkas; J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, GAUSSIAN 09 (Revision D.01), Gaussian Inc., Wallingford, CT, 2009.

(7)   A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.

(8)   J. T. H. Dunning, *J. Chem. Phys.*, 1989, **90**, 1007–1023.

(9)   G. Scalmani and M. J. Frisch, *J. Chem. Phys.*, 2010, **132**, 114110.

(10)   G. A. Zhurko, ChemCraft 1.8. http://www.chemcraftprog.com.

(11)   (a) C. Jamorski, M. E. Casida and D. R. Salahub, *J. Chem. Phys.*, 1996, **104**, 5134–5147; (b) M. E. Casida, C. Jamorski, K. C. Casida and D. R. Salahub, *J. Chem. Phys.*, 1998, **108**, 4439–4449.

(12)   M. Petersilka, U. J. Gossmann and E. K. U. Gross, *Phys. Rev. Lett.*, 1996, **76**, 1212–1215.