Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Tunable and Highly Efficient Light-Harvesting Antenna Systems Based on 1,7-Perylene-3,4,9,10-Tetracarboxylic Acid Derivatives

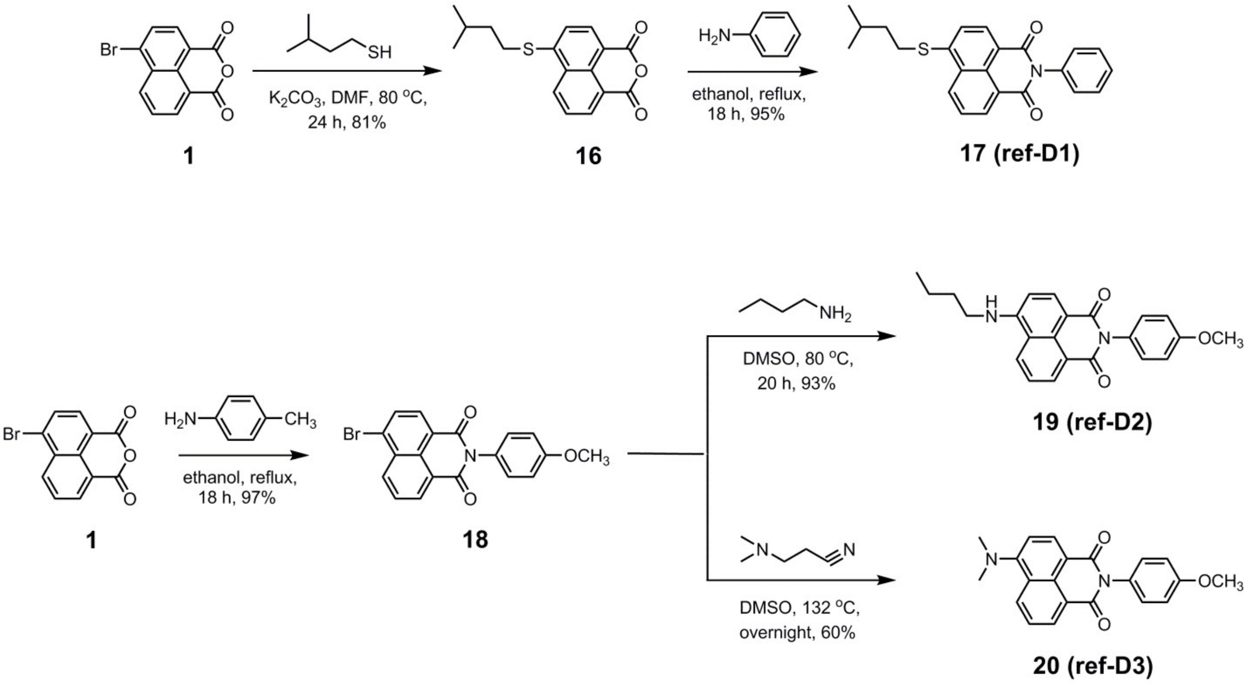
Rajeev K. Dubey,[†//] Damla Inan,[//] Sanchita Sengupta,[†//‡] Ernst J.R. Sudhölter,[†] Ferdinand C. Grozema[//]and Wolter F. Jager[†]*

[†]Laboratory of Organic Materials & Interfaces and [//]Laboratory of Optoelectronic Materials

Department of Chemical Engineering, Delft University of Technology, Julianalaan 136,
2628BL Delft, The Netherlands. BioSolar Cells, P.O. Box 98, 6700 AB Wageningen,
The Netherlands

The supporting information contains following items:

1. Syntheses and Chracterization of Model Donors:



Scheme S1. Synthesis of naphthalene monoimide derivatives used as model-donors in the spectroscopic and electrochemical studies (ref-D1, ref-D2, and ref-D3).

(i) **Synthesis of 4-(isopentylthio)naphthalene-1,8-dicarboxy Monoanhydride (16):** Synthesized from 4-bromo-1,8-naphthalic anhydride **1** (1.00 g, 3.61 mmol) and 3-methyl-1-butanethiol (1.35 mL, 10.83 mmol), K_2CO_3 (2.25 g, 16.25 mmol), and DMF (12 mL). The reaction mixture was stirred at 80 °C for 24 h. Afterwards, it was poured into the water (200 mL) to precipitate the crude product overnight. The precipitate was filtered off, washed with several portions of water to remove all the residual DMF and 3-methyl-1-butanethiol, and dried in vacuum oven. Subsequently, it was dissolved in chloroform and filtered to remove insoluble impurities. Chloroform was evaporated to afford the product **16** (0.88 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (t, J = 8.0 Hz, 2H), 8.44 (d, J = 7.6 Hz, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 3.18 (t, J = 7.6 Hz, 2H), 1.89–1.78 (m, 1H), 1.76−1.68 (m, 2H), 1.00 ppm (d, J = 6.8 Hz, 6H).

(ii) **Synthesis of *N*-phenyl-4-(isopentylthio)naphthalene-1,8-dicarboxy Monoimide (17):** Synthesized in a similar manner as compond **2** from 4-(isopentylthio)naphthalene-1,8-dicarboxy Monoanhydride **16** (0.50 g, 1.66 mmol), aniline (0.19 g, 1.99 mmol), and ethanol (15 mL). The crude product was purified by column chromatography (silica-60/$CHCl_3$) to afford the compound **17** (0.59 g, 95%). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.65 (d, J = 7.20 Hz, 1H), 8.61 (d, J = 8.4 Hz, 1H), 8.51 (d, J = 7.6 Hz, 1H), 7.77 (t, J = 8.4 Hz, 1H), 7.55 (m, 3H), 7.48 (d, J = 7.2 Hz, 1H), 7.31 (d, J = 6.8 Hz, 2H), 3.18 (t, J = 7.6 Hz, 2H), 1.82 (septet, 1H), 1.72 (q, J = 7.2 Hz, 2H), 1.00 (d, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, CDCl3): δ = 164.2, 146.1, 135.4, 131.9, 131.1, 130.4, 129.6, 129.3, 128.7, 128.6, 126.6, 123.2, 122.6, 119.0, 37.1, 30.3, 27.7, 22.2 ppm.

(iii) **Synthesis of *N*-(4′-Methoxyphenyl)-4-bromonaphthalene-1,8-dicarboxy Monoimide (18):** Synthesized in a similar manner as compond **2** from 4-bromo-1,8-naphthalic anhydride **1** (2.00 g, 7.22 mmol) and 4-methoxyaniline (1.07 g, 8.69 mmol) to afford compound **18** (2.68 g, 97%) as a white solid. ^1H NMR (400 MHz, DMSO-d6): δ = 8.60 (t, J = 8.8 Hz, 2H), 8.34 (d, J = 8.0 Hz, 1H), 8.26 (d, J = 8.0 Hz, 1H), 8.04 (t, J = 8.0 Hz, 1H), 7.29 (d, J = 8.8 Hz, 2H), 7.06 (d, J = 8.8 Hz, 2H), 3.83 ppm (s, 3H). ^{13}C NMR (100 MHz, DMSO-d6): δ = 163.8, 163.7, 159.4, 133.1, 132.0, 131.8, 131.4, 130.4, 129.5, 129.3, 129.2, 128.6, 123.9, 123.2, 114.6, 55.8 ppm.

(iv) **Synthesis of *N*-(4′-Methoxyphenyl)-4-(*n*-butylamino)naphthalene-1,8-dicarboxy Monoimide (19):** Synthesized as per the procedure followed for compound **4** from *N*-(4′-methoxyphenyl)-4-bromonaphthalene-1,8-dicarboxy Monoimide **18** (0.30 g, 0.79 mmol), *n*-butylamine (1.17 mL, 11.80 mmol), and DMSO (24 mL). The crude product was purified by column chromatography (silica-60/1:1 $CHCl_3$-EtOAc) to obtain compound **19** (0.27 g, 93%) as yellow solid. ^1H NMR (400 MHz, DMSO-d6): δ = 8.72 (d, J = 8.4 Hz, 1H), 8.40 (d, J = 7.6 Hz, 1H), 8.23 (d, J = 8.4 Hz, 1H), 7.75

(t, *J* = 5.2 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 1H), 3.80 (s, 3H), 3.36 (q, *J* = 6.4 Hz, 2H), 1.69 (m, 2H), 1.42 (m, 2H), 0.94 ppm (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d6): δ = 164.6, 163.8, 159.1, 151.2, 134.7, 131.2, 130.6, 129.5, 129.1, 124.6, 122.8, 120.7, 114.4, 108.3, 104.2, 55.8, 43.1, 30.4, 20.3, 14.2 ppm.

(v) **Synthesis of *N*-(4′-Methoxyphenyl)-4-(dimethylamino)naphthalene-1,8-dicarboxy Monoimide (20):** Synthesized as per the procedure followed for compound **5** from *N*-(4′-methoxyphenyl)-4-bromonaphthalene-1,8-dicarboxy monoimide **18** (0.30 g, 0.79 mmol), 3-(dimethylamino)propionitrile (0.35 mL, 3.14 mmol), and DMSO (25 mL). The crude product was purified by column chromatography (silica-60/$CHCl_3$) to obtain compound **20** (0.16 g, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.61 (d, *J* = 7.2 Hz, 1H), 8.50 (t, *J* = 8.4 Hz, 2H), 7.69 (t, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 2H), 3.87 (s, 3H), 3.13 ppm (s, 6H). ^{13}C NMR (100 MHz, CDCl3): δ = 164.9, 164.4, 159.4, 157.1, 132.9, 131.4, 131.3, 129.6, 128.3, 125.4, 124.9, 123.3, 115.1, 114.6, 113.3, 55.5, 44.8 ppm.

Figure S1. ^1H–^1H COSY spectrum of antenna D2A2 in $CDCl_3$.

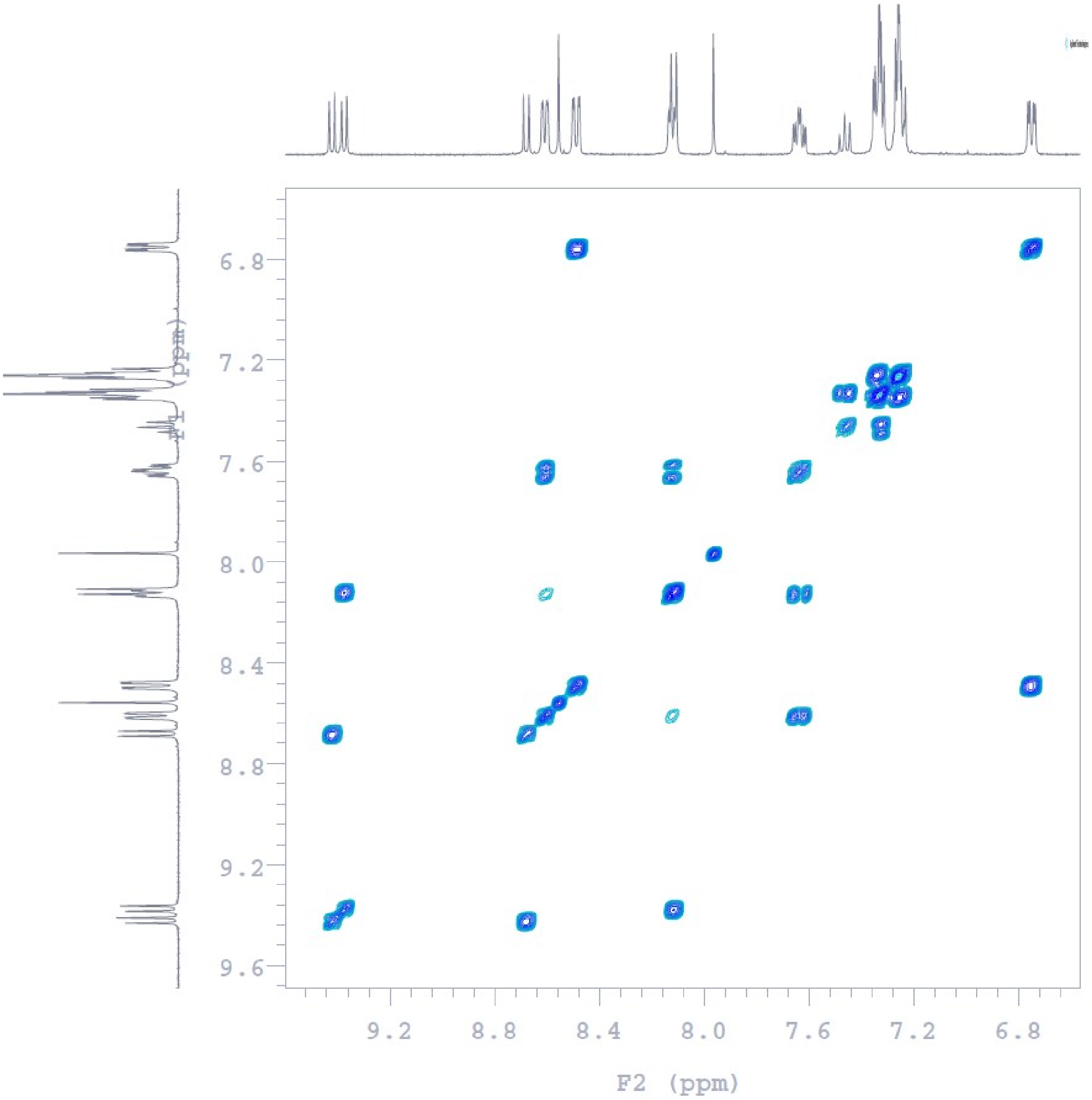
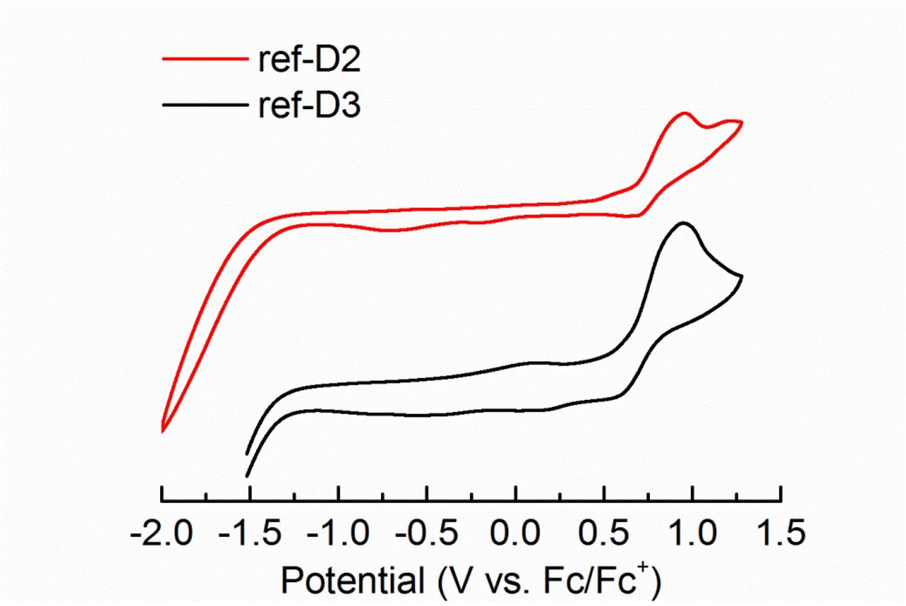
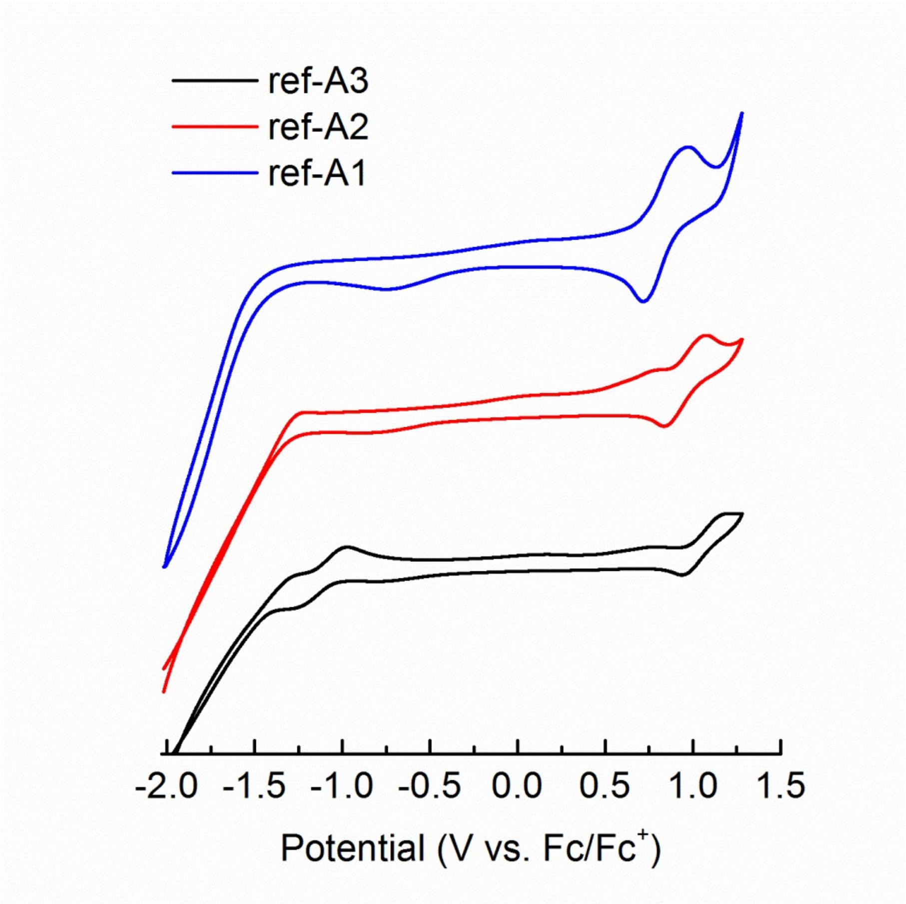


Figure S2. Cyclic voltammograms of the model compounds and antenna systems.





Note: No redox activity was observed for ref-D1 in the measured potential window. ref-D2 and ref-D3 did not exhibit any reduction peak. For ref-A2, a very small irreversible reduction peak was obtained at ca. -1.30 V. No reduction peak was observed for ref-A1.

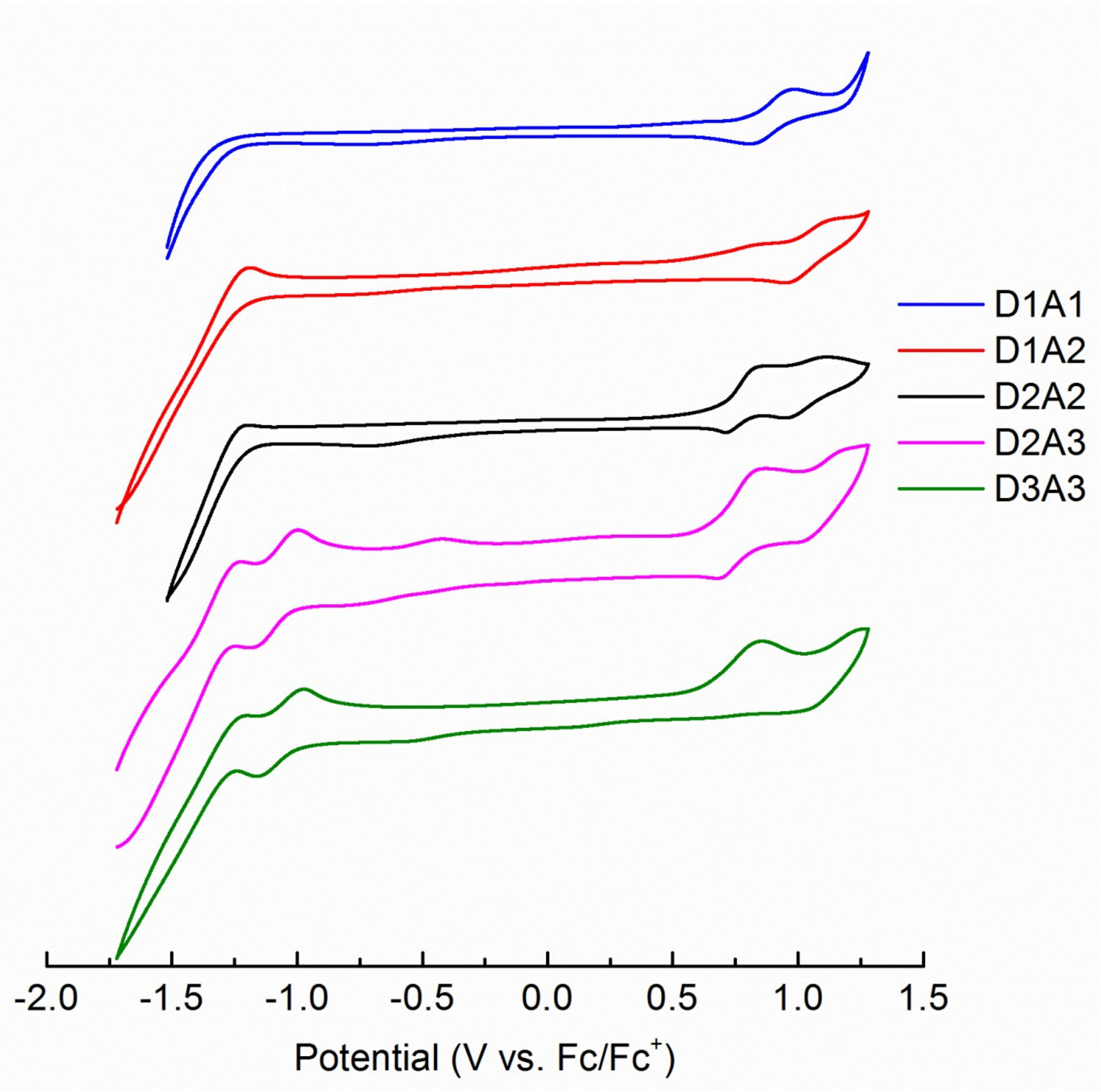


Table S1. First redox potentials of model donors and acceptors (V vs. Fc/Fc$^+$) obtained by cyclic voltammetry in CH_2Cl_2.

Compound	$E_{1/2\ \mathrm{ox}}$	$E_{1/2\ \mathrm{red}}$
ref-D1	–	–
ref-D2	+0.83	–
ref-D3	+0.75	–
ref-A1	+0.84	–
ref-A2	+0.95	−1.38
ref-A3	+1.05	−1.11

Figure S3. Fluorescence decay curves of antenna systems and respective reference compounds in toluene after excitation at 400 nm.

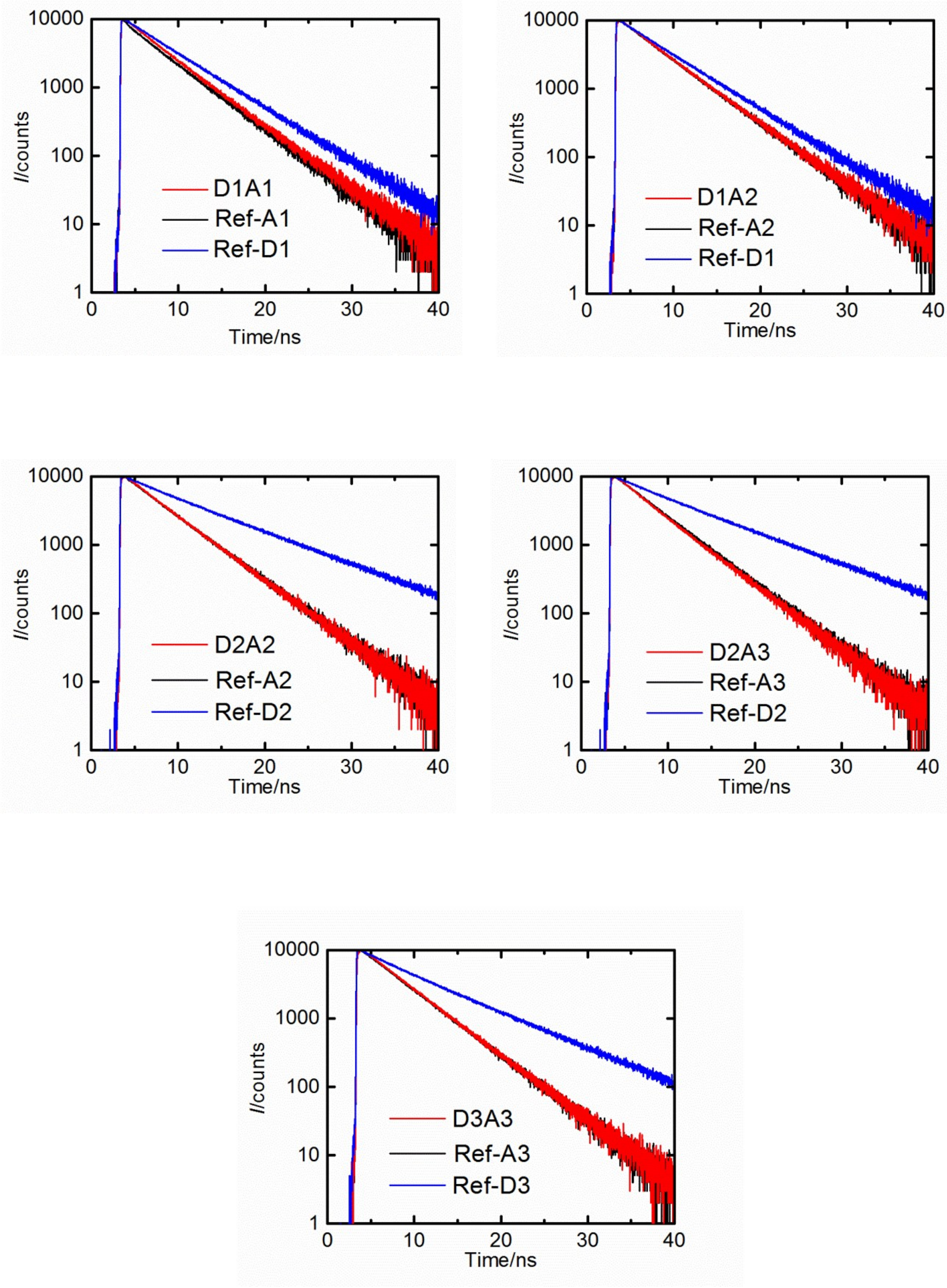


Figure S4. Comparison of absorption and emission spectra of antenna systems in toluene.

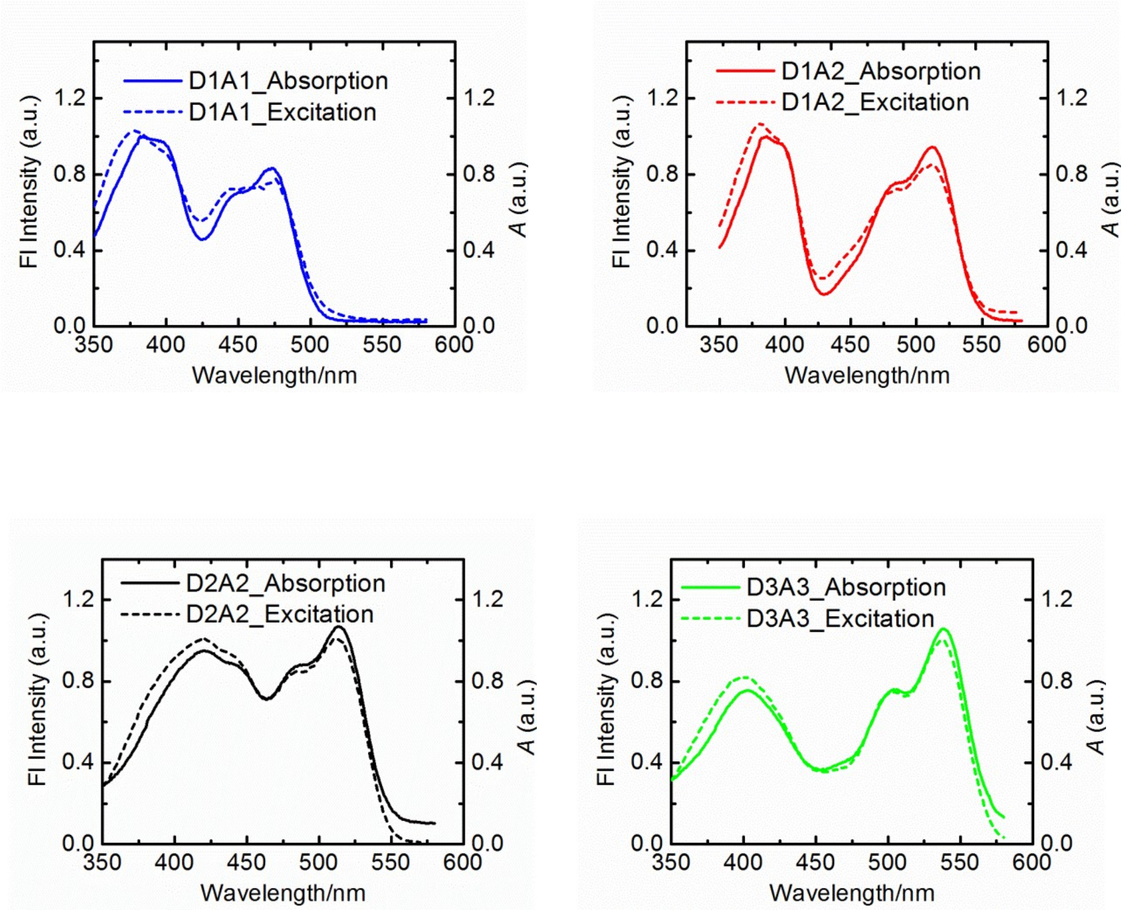
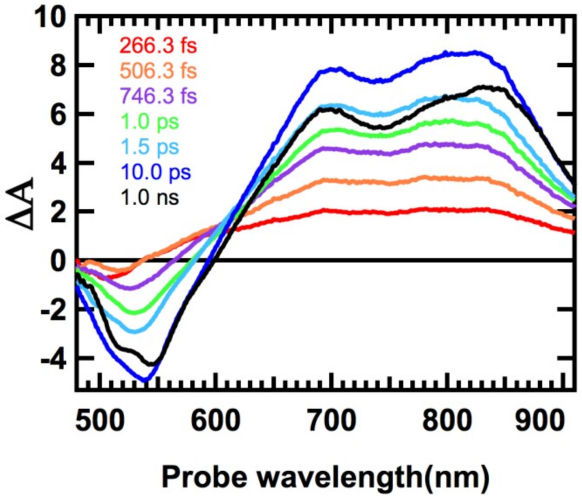


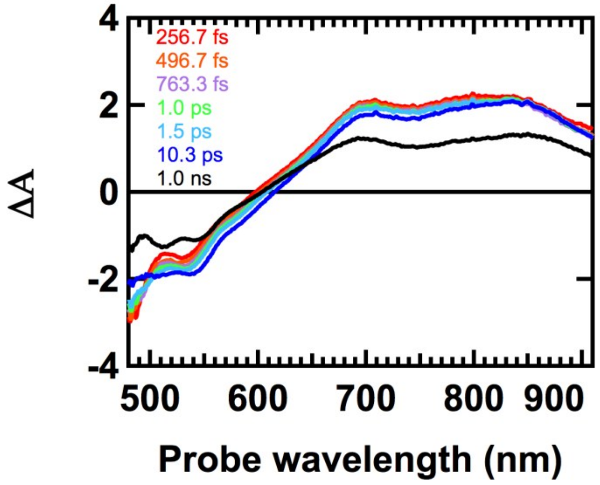
Figure S5. Transient absorption spectra of of antenna systems in toluene and their decay kinetics at 820 nm.

(i) Antenna D1A1

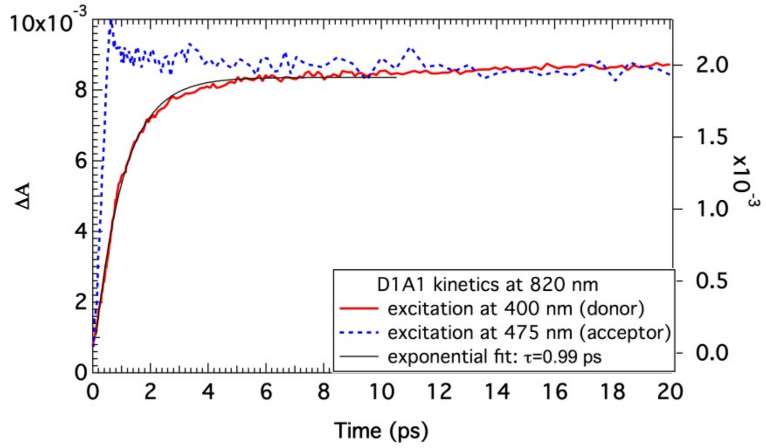
Excitation at 400 nm (Donor)



Excitation at 475 nm (Acceptor)

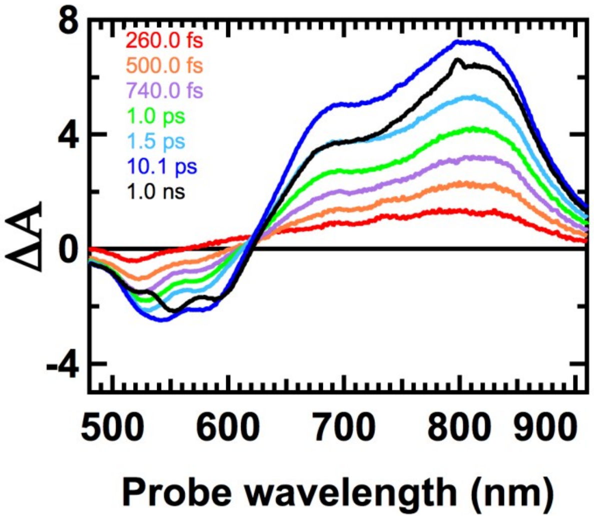


Kinetics at 820 nm

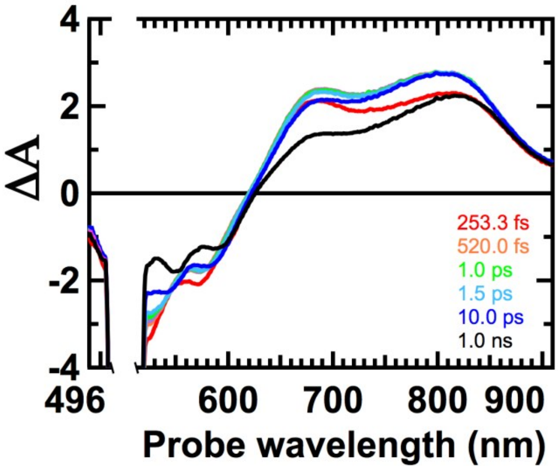


(ii) Antenna D2A2

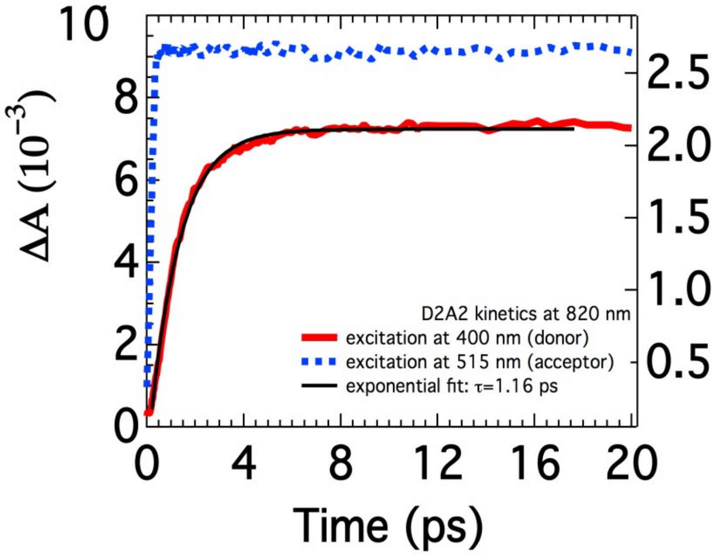
Excitation at 400 nm (Donor)



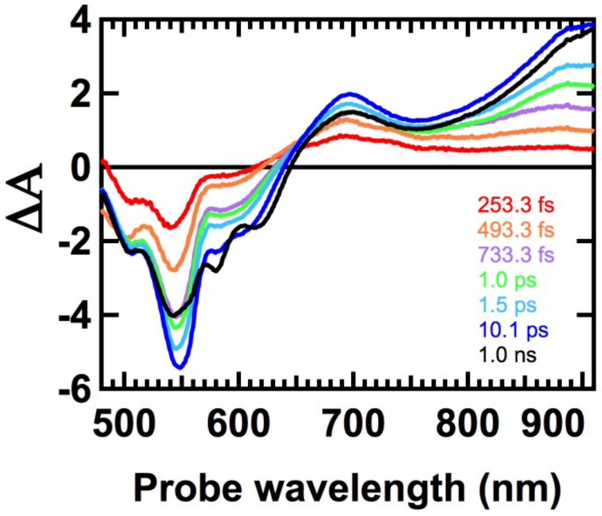
Excitation at 515 nm (Acceptor)

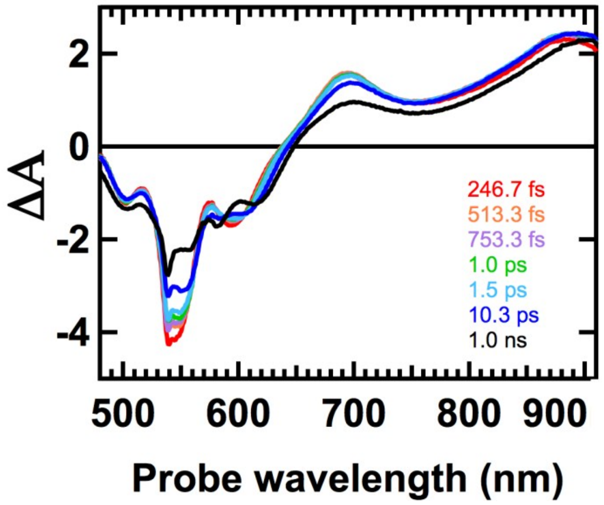


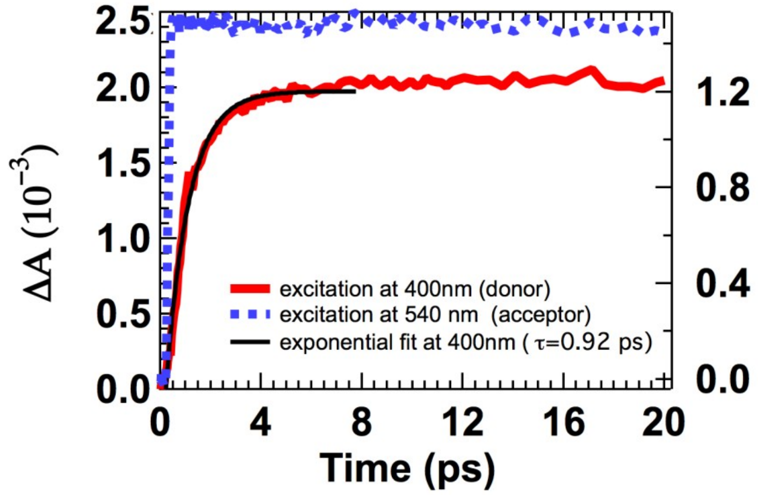
Kinetics at 820 nm



(iii) Antenna D2A3

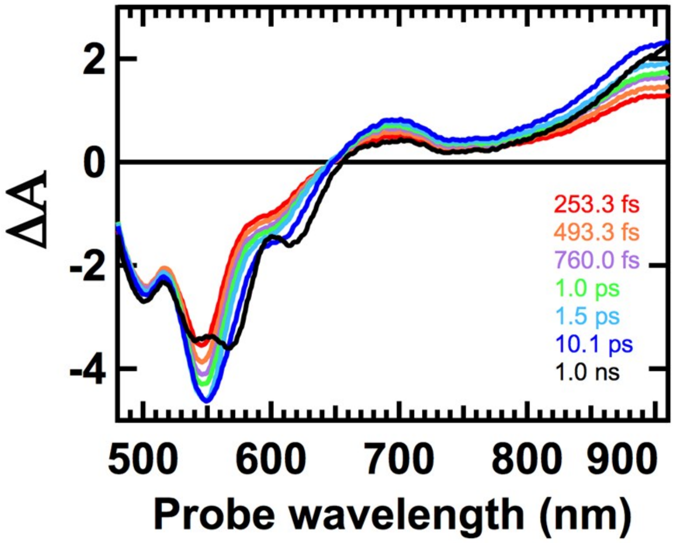

Excitation at 400 nm (Donor)


Excitation at 540 nm (Acceptor)

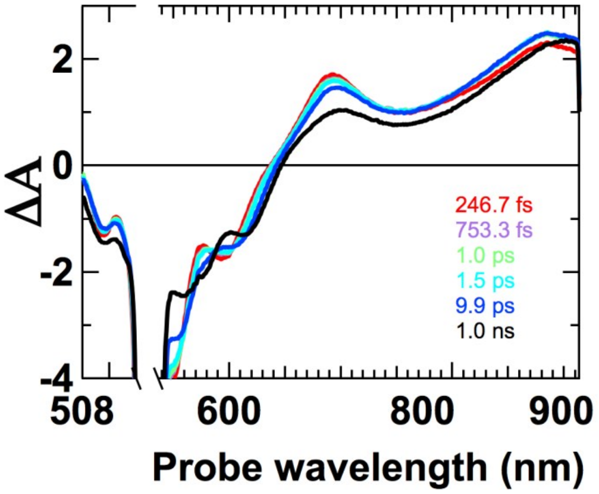

Kinetics at 820 nm

(iv) Antenna D3A3

Excitation at 400 nm (Donor)



Excitation at 540 nm (Acceptor)



Kinetics at 820 nm

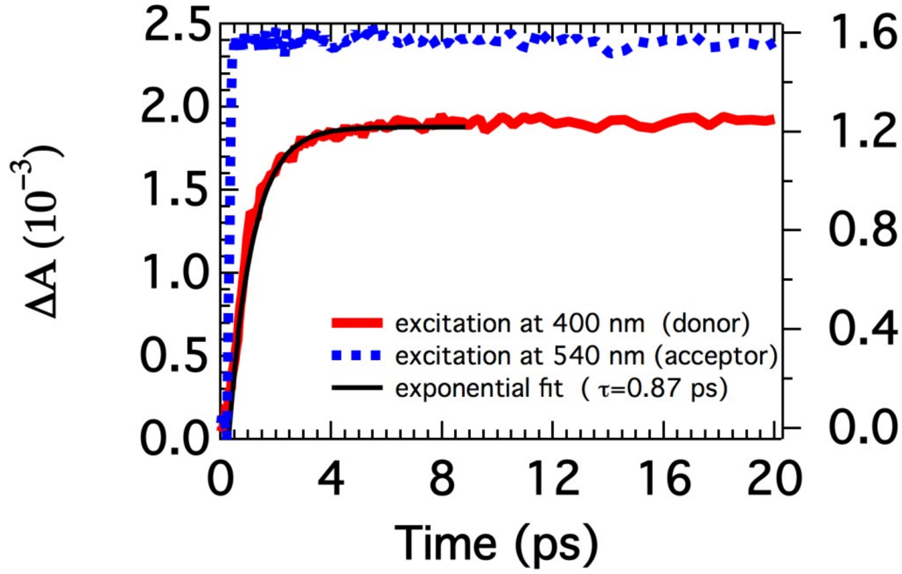


Figure S6. ^{1}H and ^{13}C NMR spectra of *N*-(4-Hydroxyphenyl)-4-bromo-1,8-naphthalimide (**2**) in DMSO-d6.

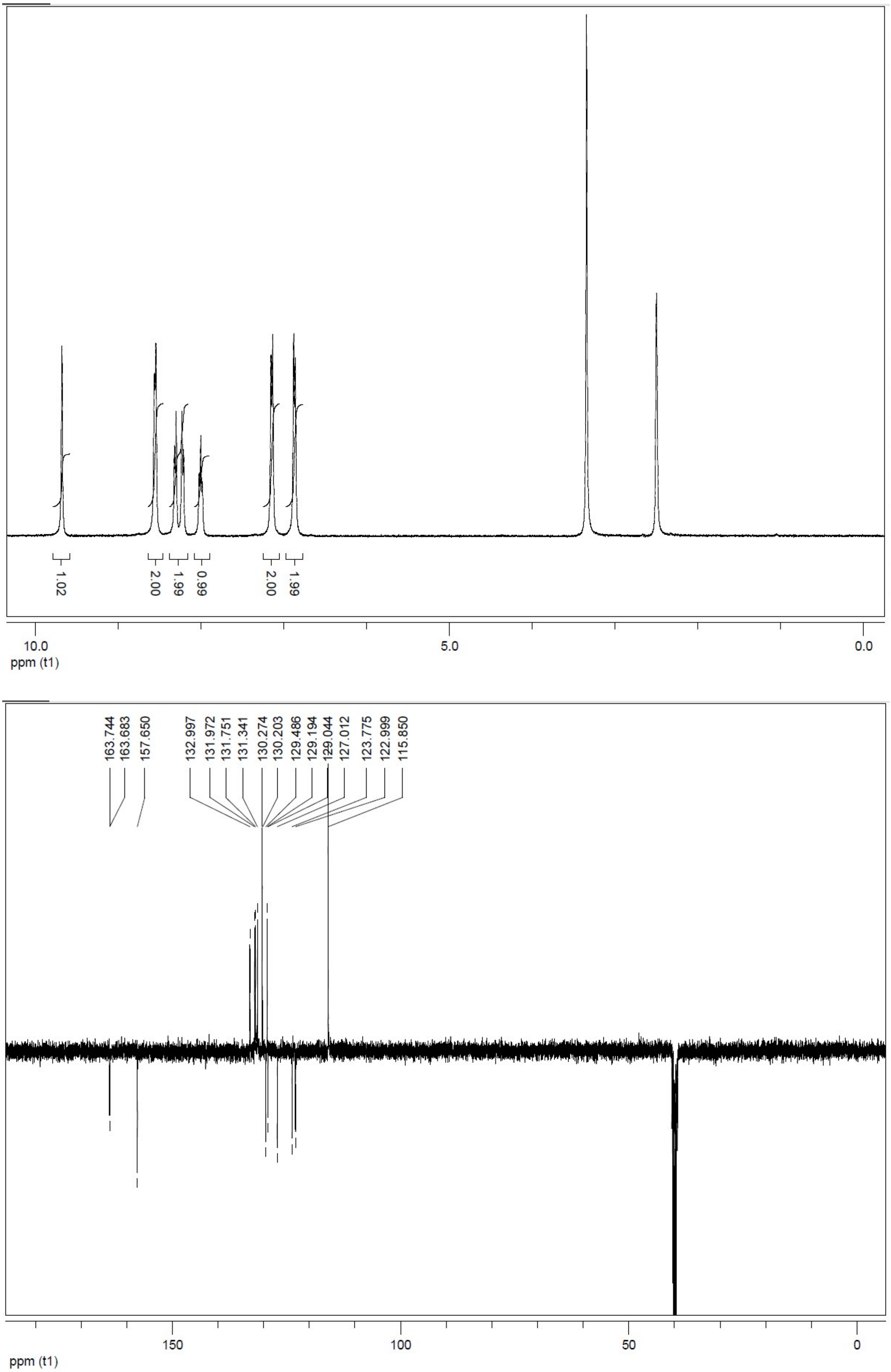


Figure S7. ^{1}H and ^{13}C NMR spectra of *N*-(4′-Hydroxyphenyl)-4-(isopentylthio)naphthalene-1,8-dicarboxy Monoimide **(3)** in DMSO-d6.

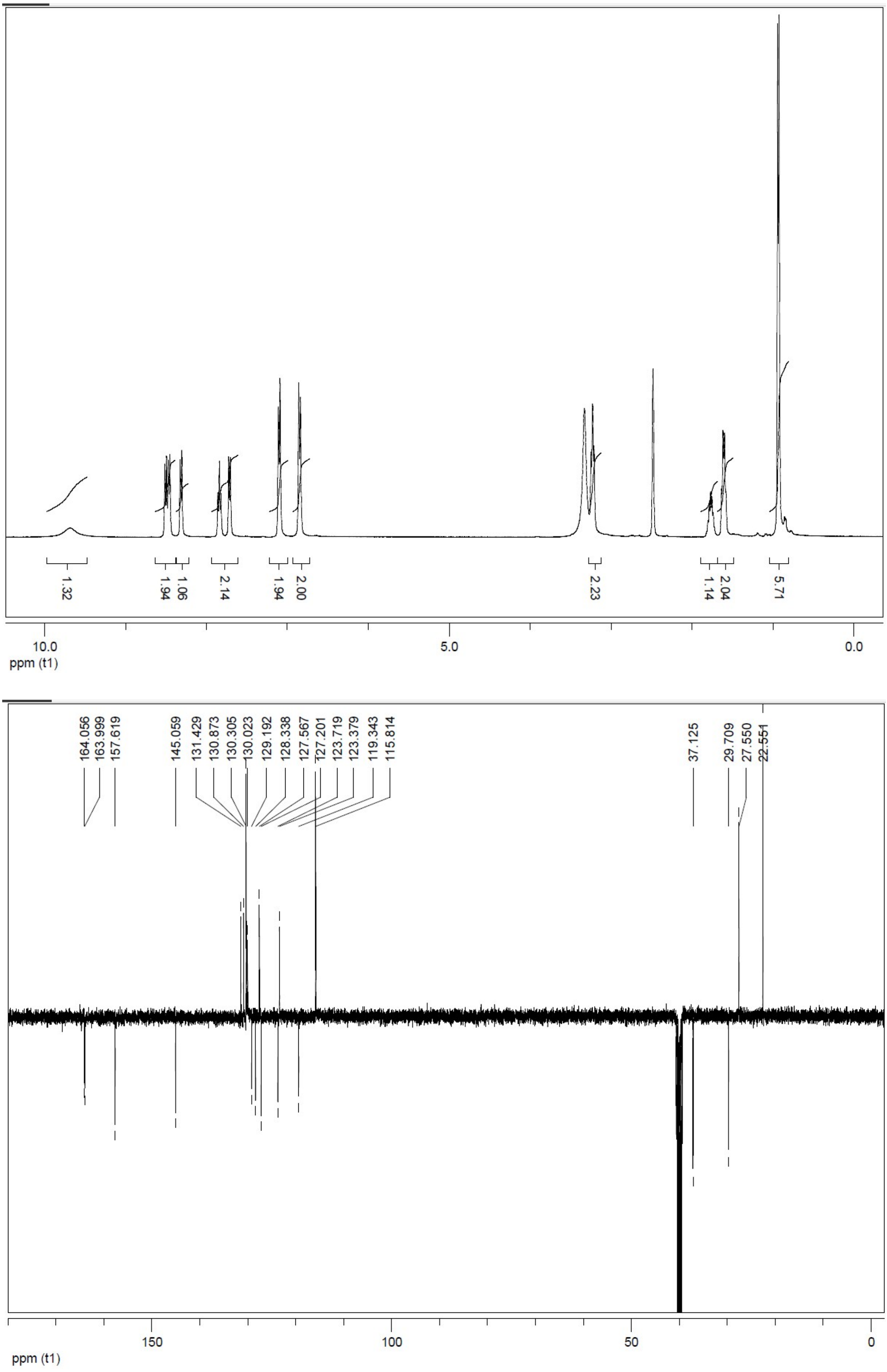


Figure S8. ^{1}H and ^{13}C NMR spectra of *N*-(4′-Hydroxyphenyl)-4-(*n*-butylamino)naphthalene-1,8-dicarboxy Monoimide (**4**) in DMSO-d6.

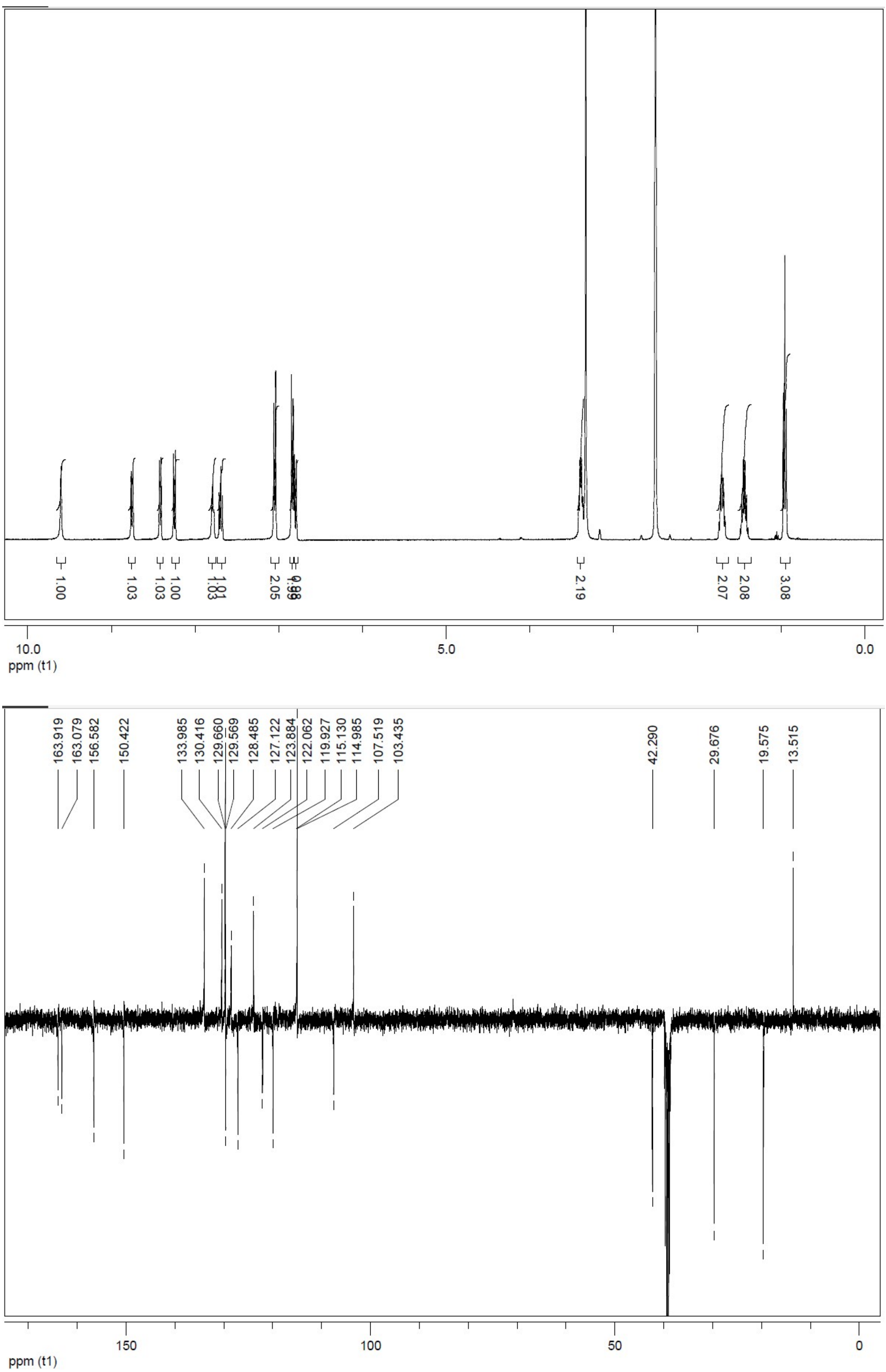


Figure S9. ^{1}H and ^{13}C NMR spectra of *N*-(4′-Hydroxyphenyl)-4-(dimethylamino)naphthalene-1,8-dicarboxy Monoimide (**5**) in DMSO-d6.

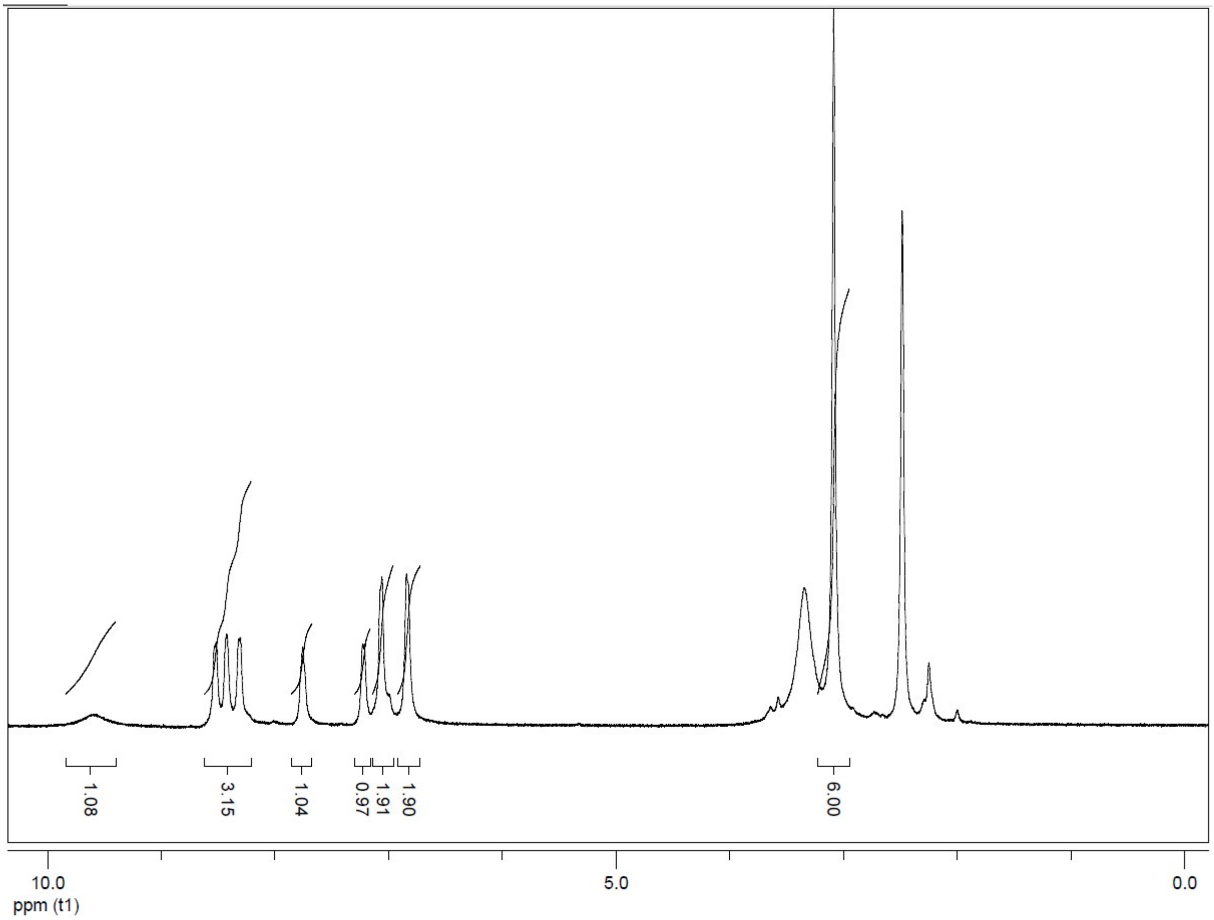


Figure S10. ^{1}H NMR spectrum of antenna system **D1A2** (**7**) in $CDCl_3$.

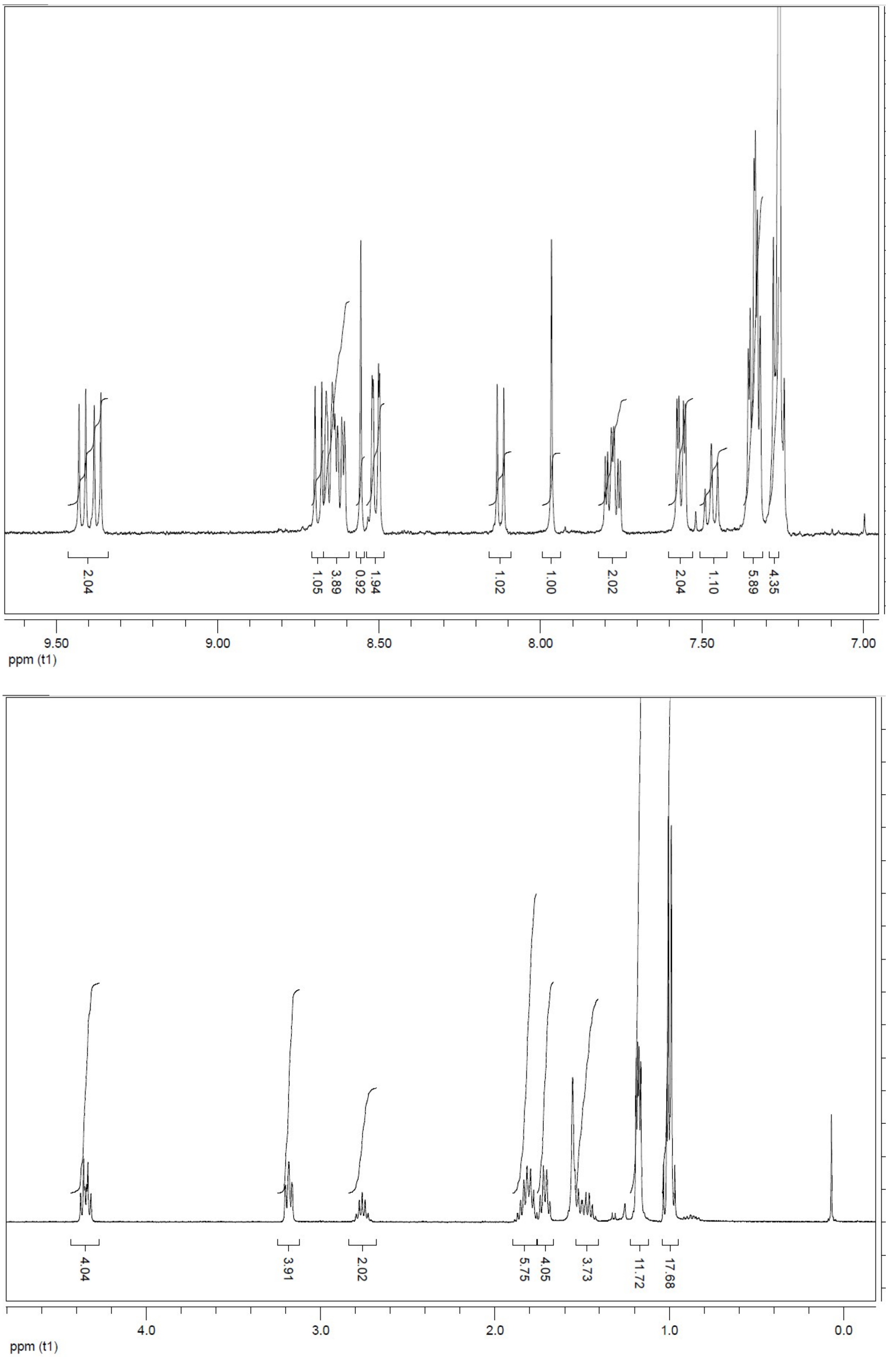


Figure S11. ^{13}C NMR spectrum of antenna system **D1A2** (**7**) in CDCl$_3$.

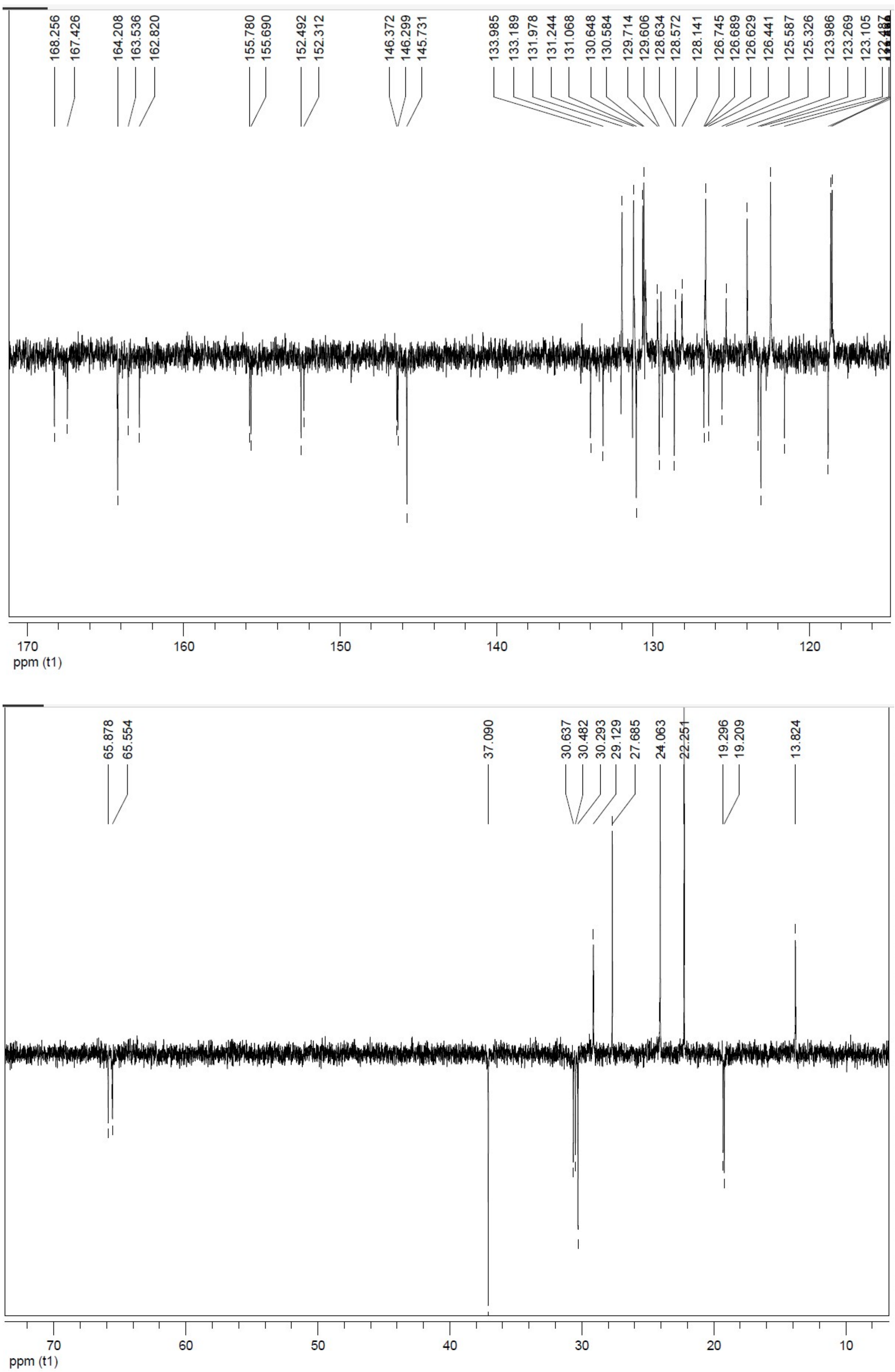


Figure S12. ^{1}H NMR spectrum of antenna system D2A2 **(8)** in $CDCl_3$.

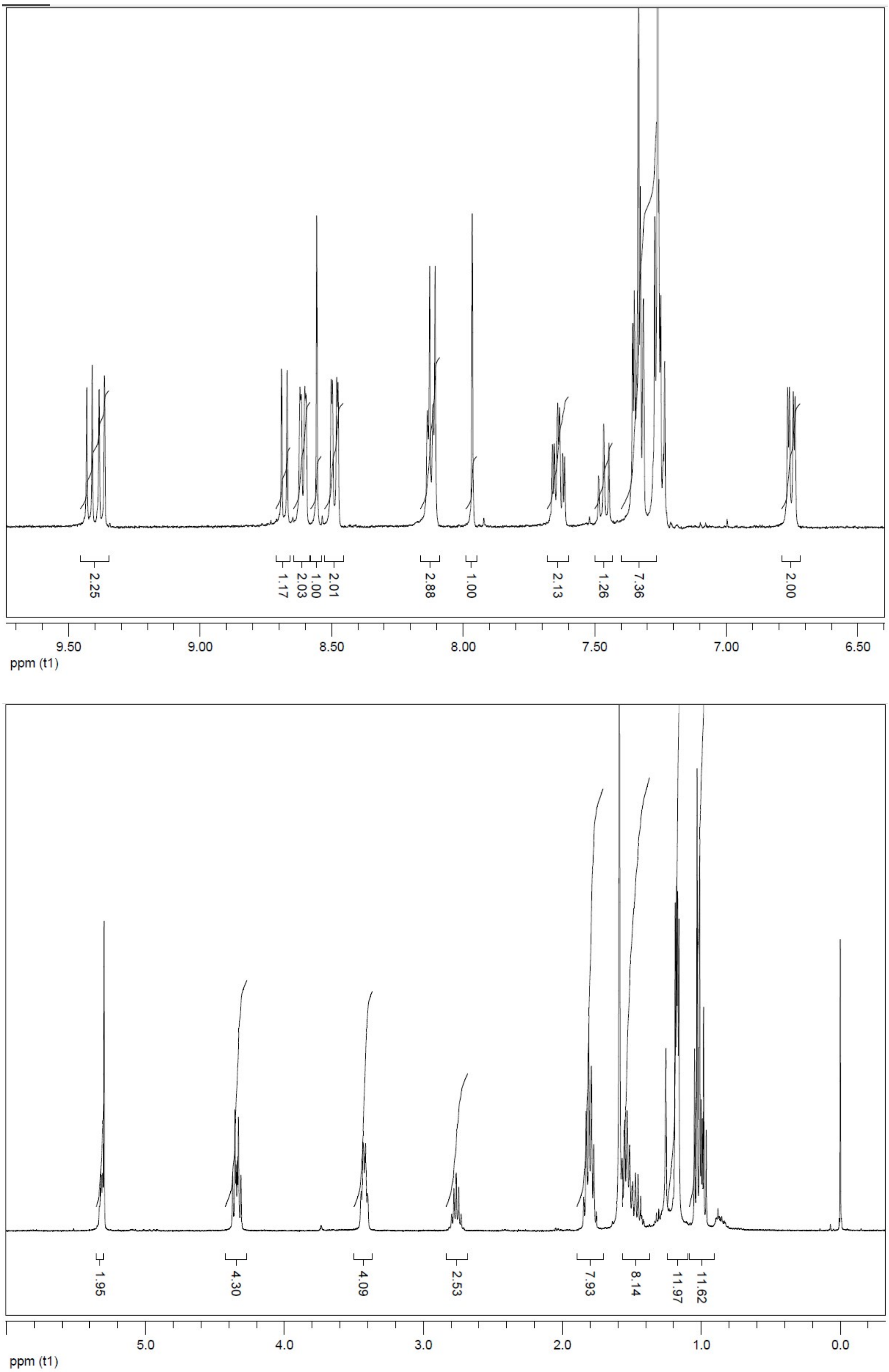


Figure S13. ^{13}C NMR spectrum of antenna system D2A2 **(8)** in $CDCl_3$.

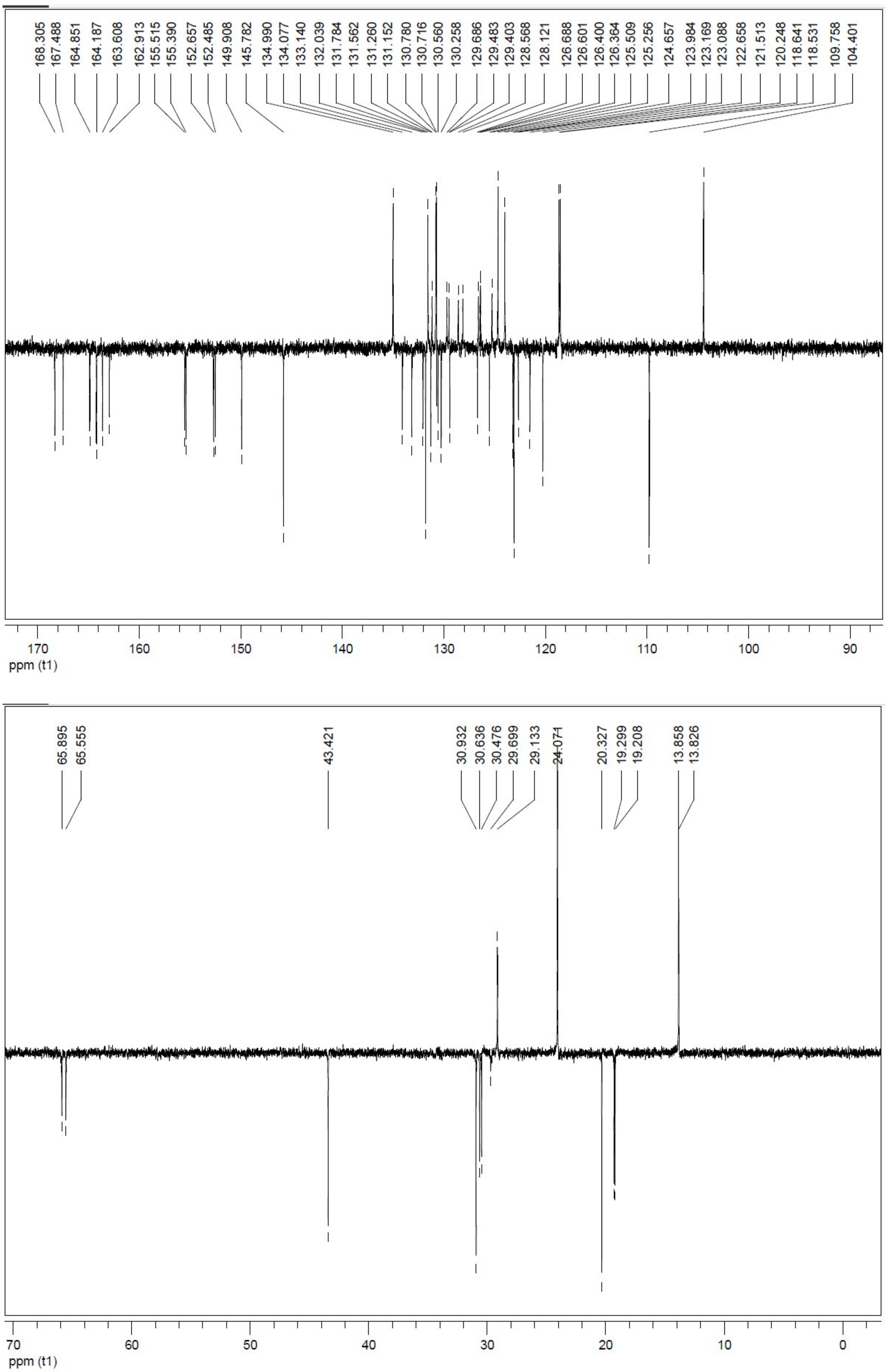


Figure S14. ^{1}H NMR spectrum of antenna system **D2A3 (10)** in $CDCl_3$.

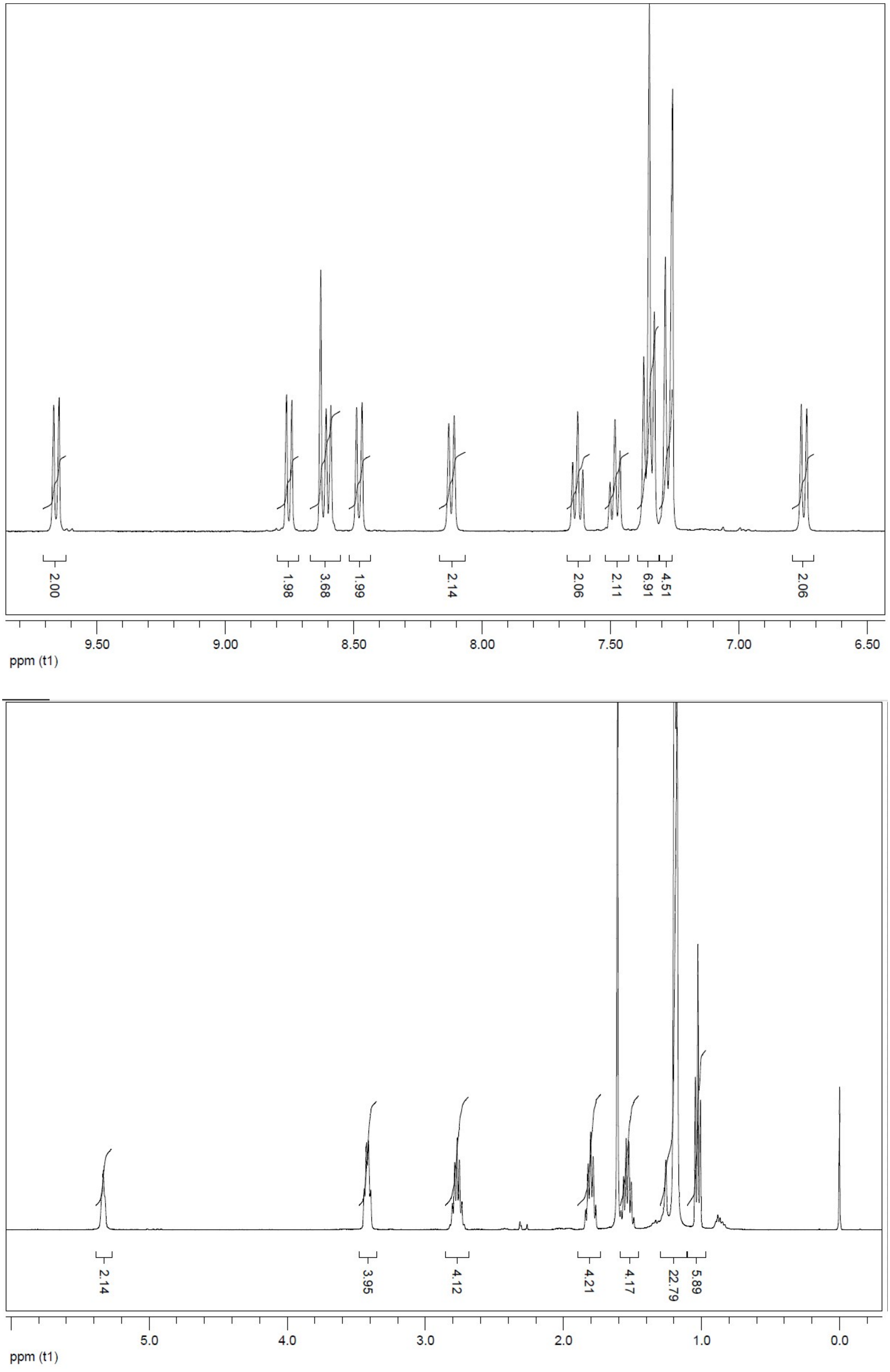


Figure S15. ^{13}C NMR spectrum of antenna system **D2A3 (10)** in $CDCl_3$.

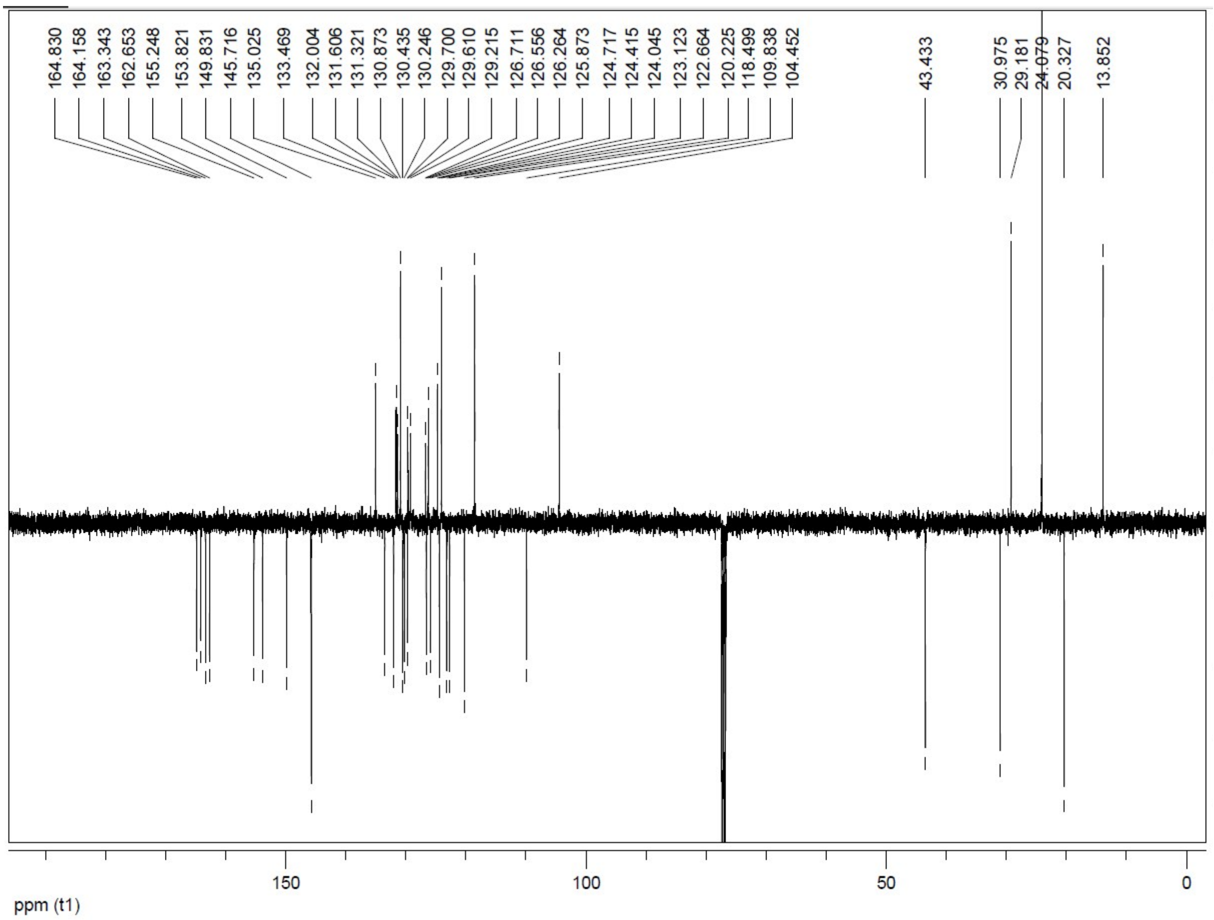


Figure S16. ^{1}H NMR spectrum of antenna system **D3A3 (11)** in CDCl$_3$.

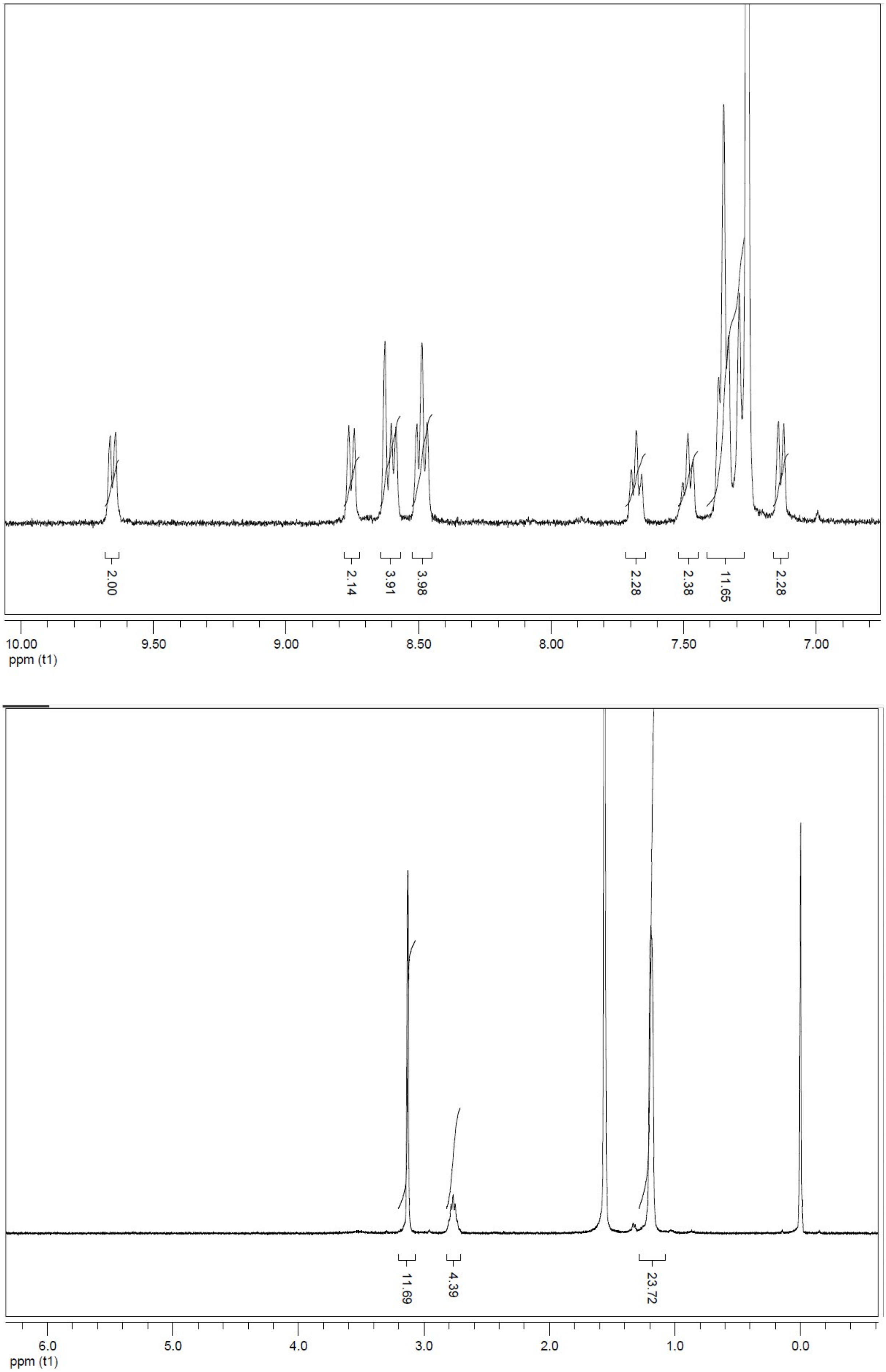


Figure S17. ^{13}C NMR spectrum of antenna system **D3A3 (11)** in $CDCl_3$.

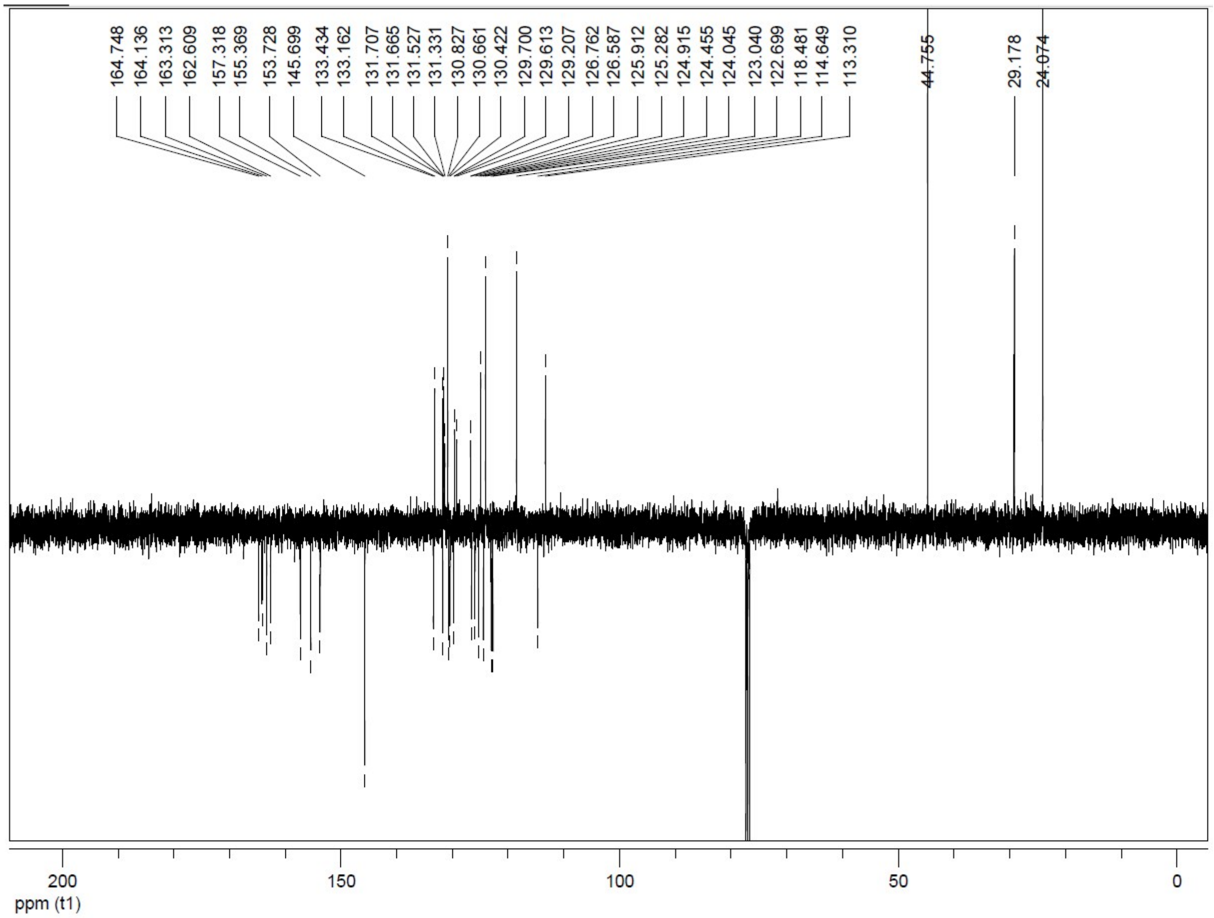
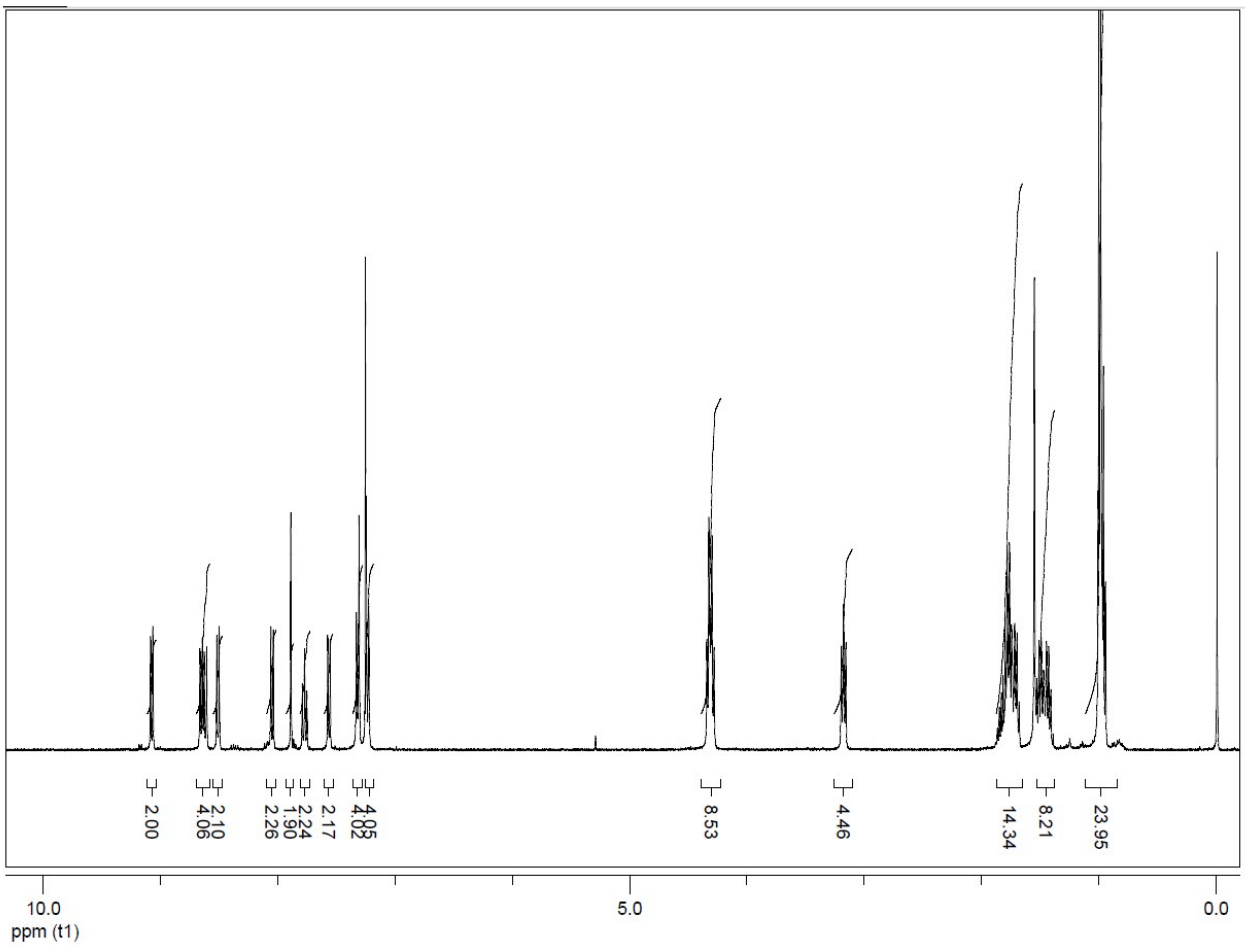


Figure S18. ^{1}H and ^{13}C NMR spectra of antenna system **D1A1 (14)** in $CDCl_3$.



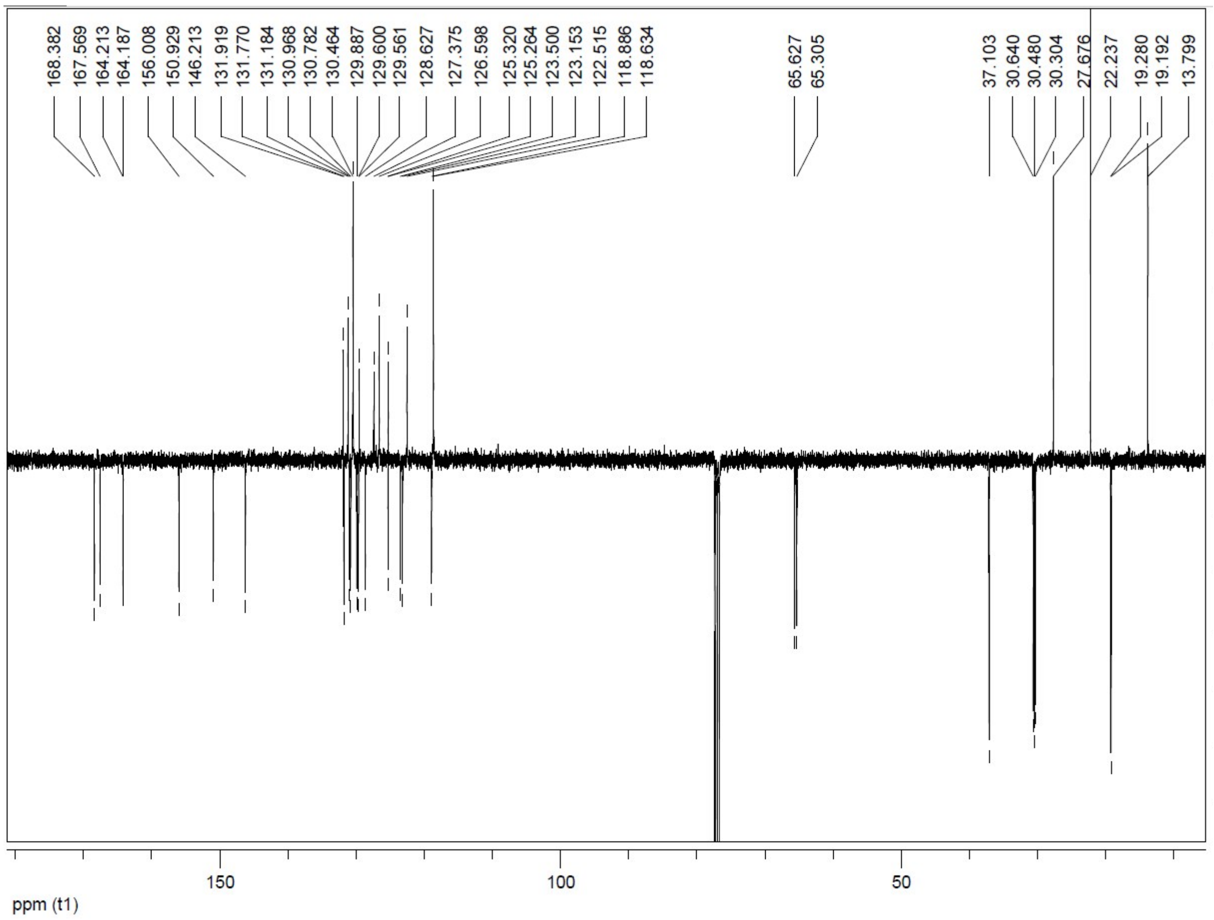


Figure S19. ^{1}H NMR spectrum of 4-(isopentylthio)naphthalene-1,8-dicarboxy Monoanhydride **(16)** in CDCl$_3$.

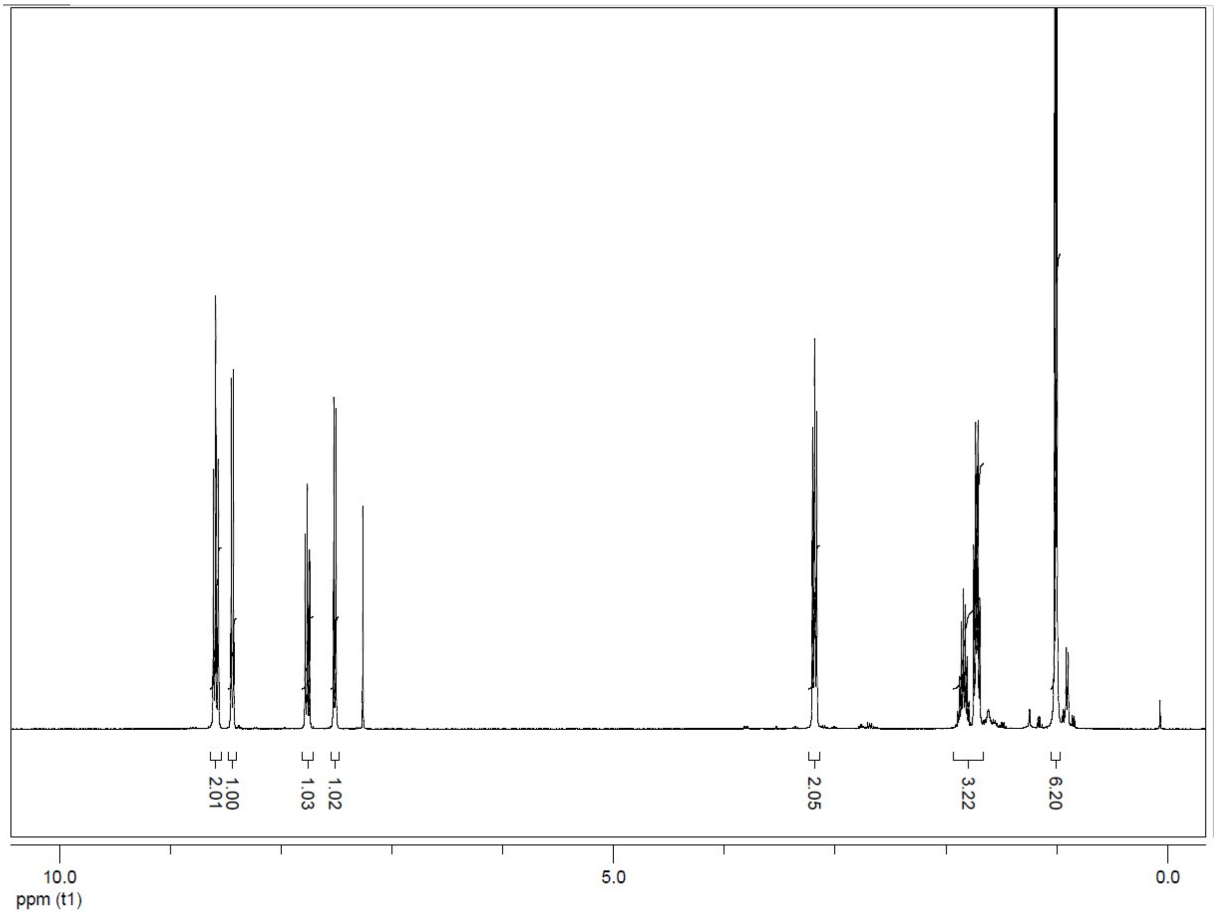
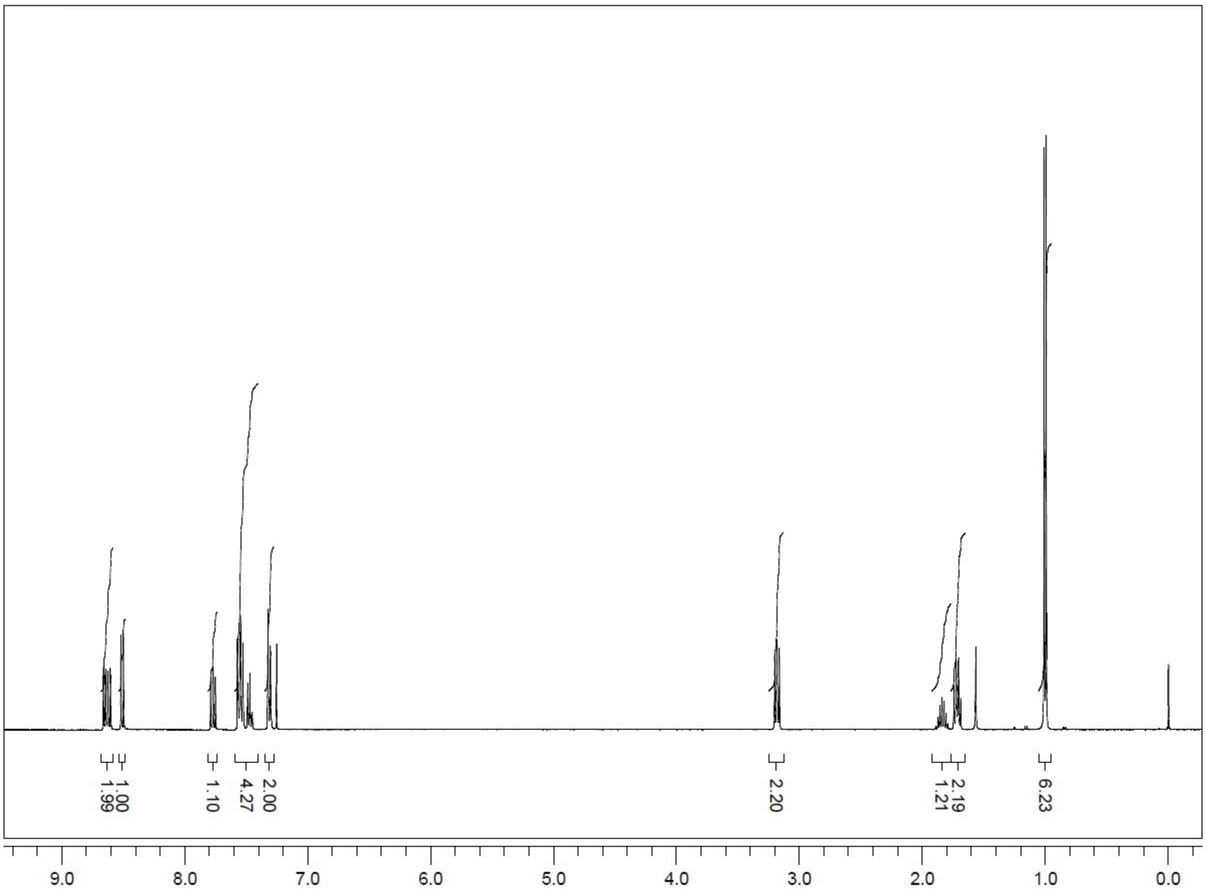


Figure S20. ^{1}H NMR spectrum of *N*-(phenyl)-4-(isopentylthio)naphthalene-1,8-dicarboxy Monoimide **(17)** in $CDCl_3$.



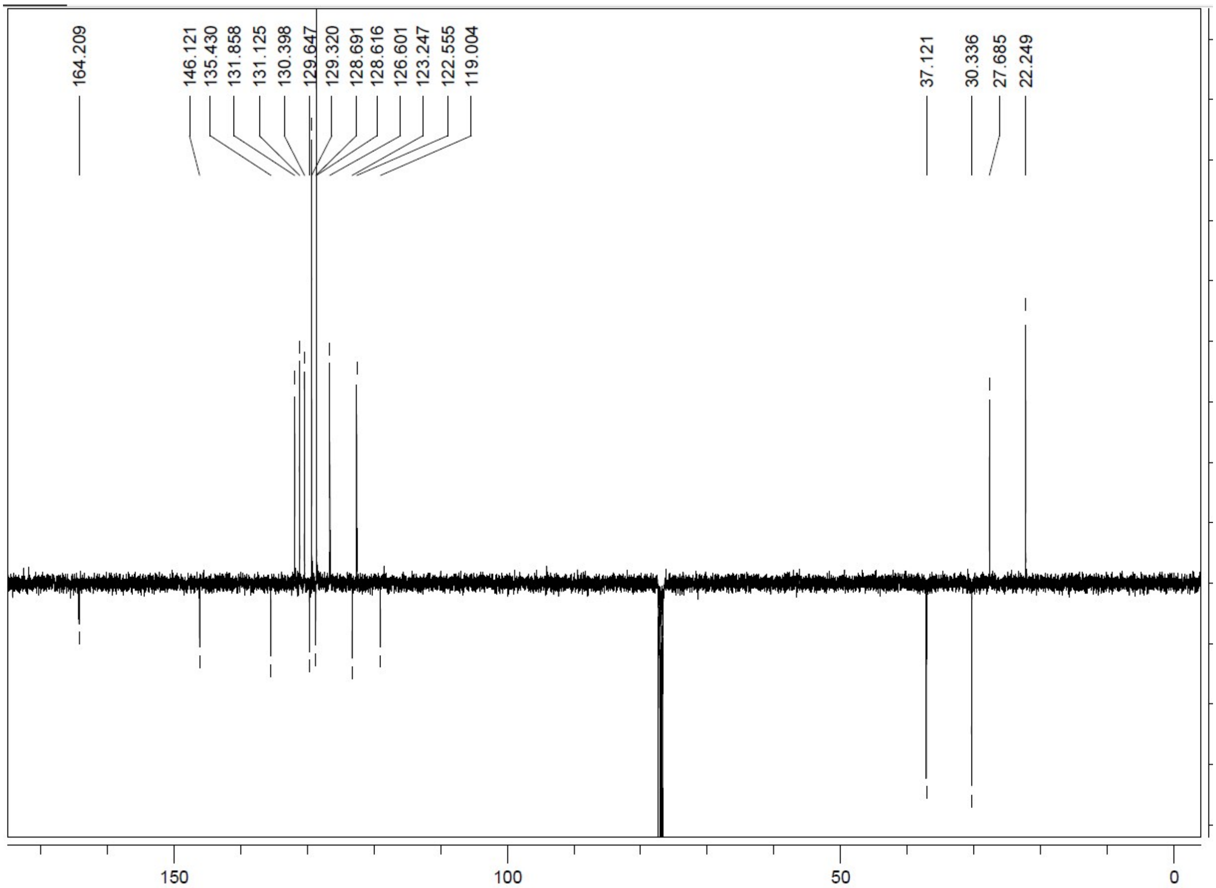


Figure S21. ^{1}H and ^{13}C NMR spectra of *N*-(4′-methoxyphenyl)-4-bromonaphthalene-1,8-dicarboxy monoimide (**18**) in DMSO-d6.

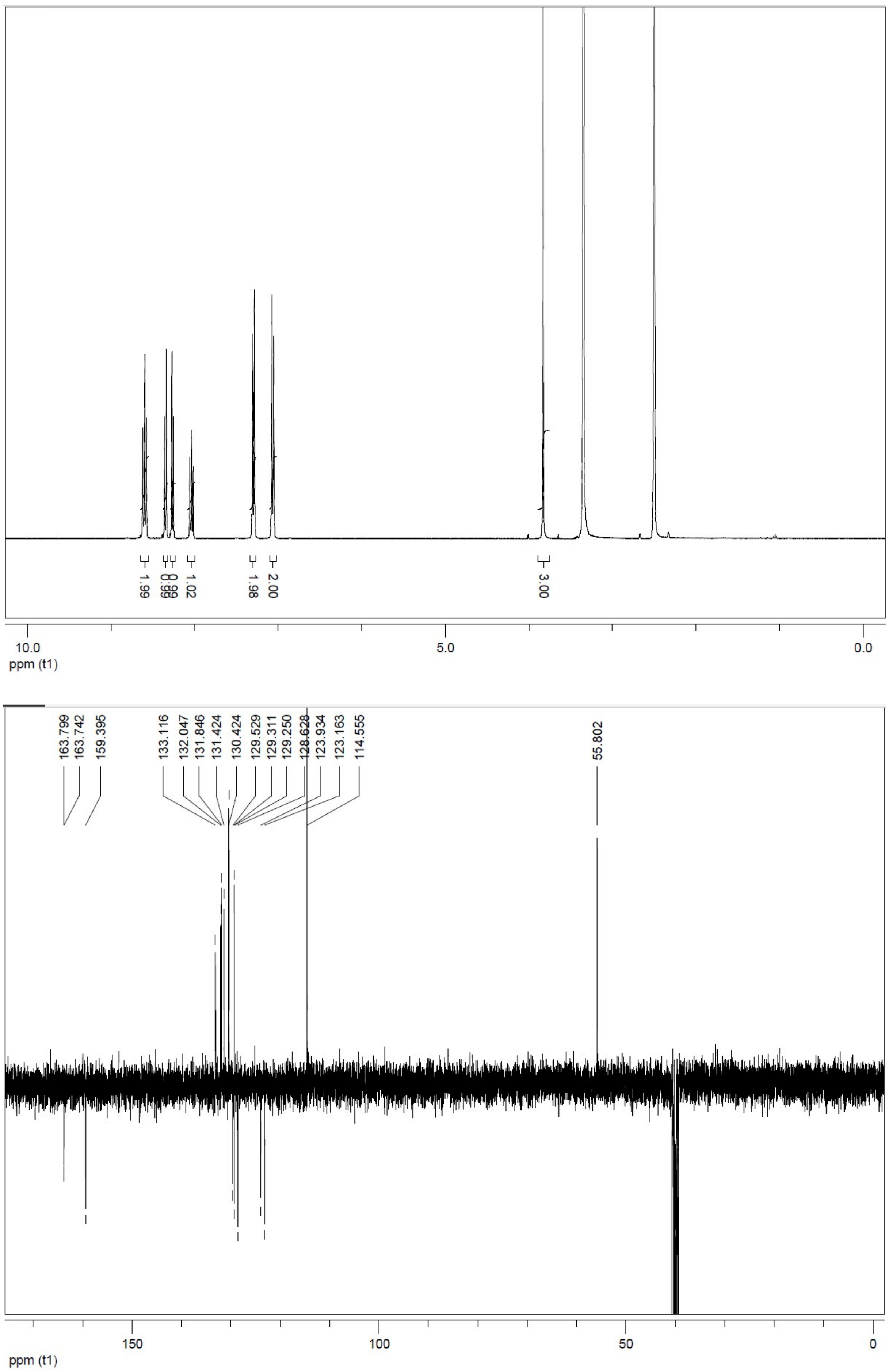


Figure S22. ^1H and ^{13}C NMR spectra of *N*-(4′-Methoxyphenyl)-4-(*n*-butylamino)naphthalene-1,8-dicarboxy Monoimide **(19)** in DMSO-d6.

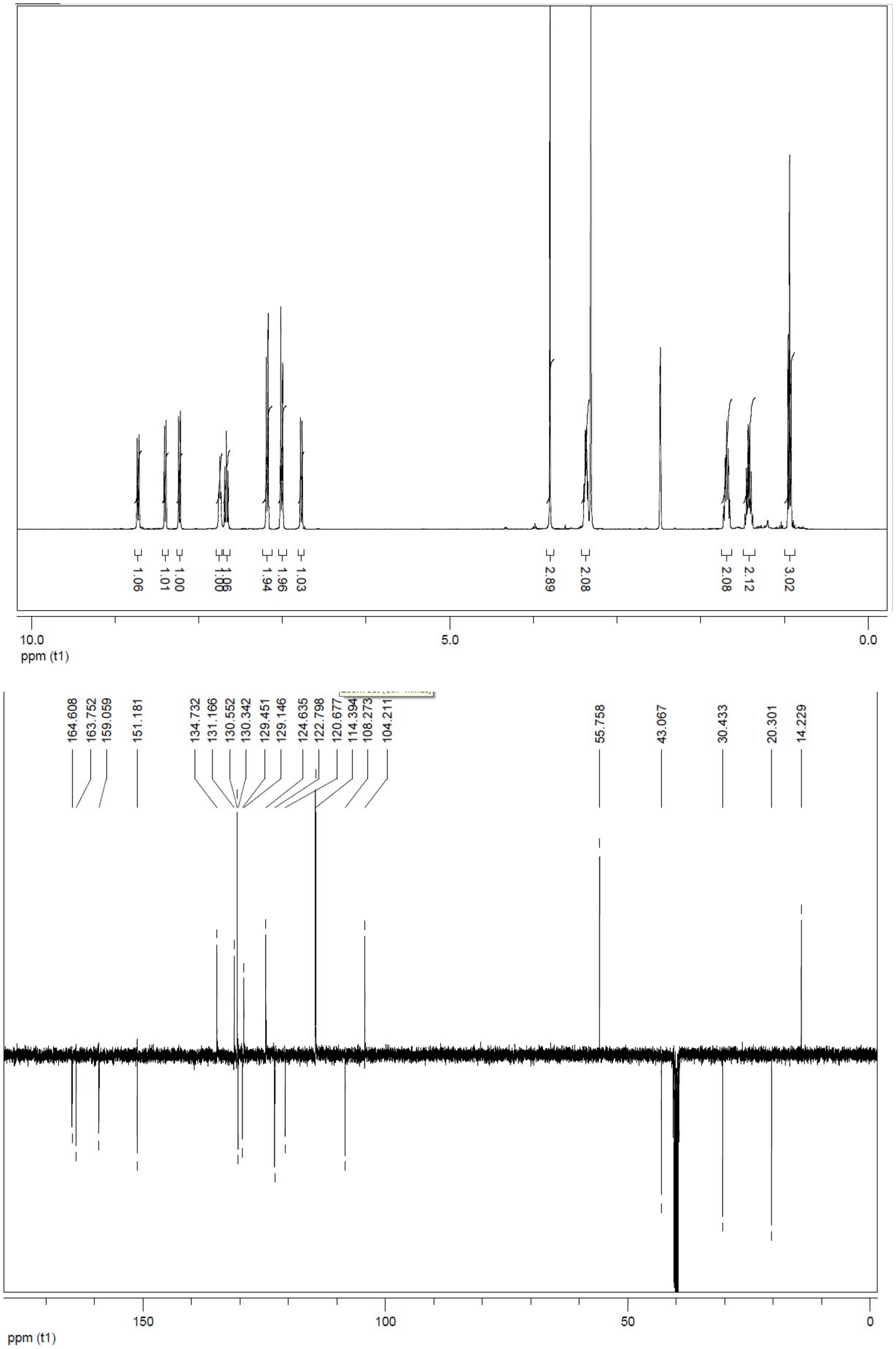


Figure S23. ^{1}H and ^{13}C NMR spectra of *N*-(4′-Methoxyphenyl)-4-(dimethylamino)naphthalene-1,8-dicarboxy Monoimide **(20)** in $CDCl_3$.