Supporting Information

Oligo(quinoxalineethynylene)s: Synthesis, Properties, and Ag^+ -Mediated Complanation

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General methods. All reagents and chemicals were obtained from commercial sources and used without further purification unless otherwise noted. The solvents have been purified by standard procedures before use. Silica gel (10- 40 μ) was used for all column chromatography. The ^{1}H and ^{13}C NMR spectra were recorded on Varian Mercury spectrometers (300 MHz or 400 MHz) in the indicated solvents. Chemical shifts are expressed in parts per million (δ) using residual proton resonances of the deuterated solvents as the internal standards. Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using a platinum button working electrode of 2 mm diameter, a platinum wire counter electrode, and a SEC reference electrode on a computer-controlled CHI610D instrument. The solutions containing the samples were purged with Ar gas before the measurements were conducted and 0.1M tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte. A 0.5 M H_2SO_4 solution of quinine (10^{-5} M) was used as standard for the quantum yield (ϕ) estimation.

Synthesis and characterizations

Compound 2.[1] A mixture of 5,8-dibromoquinoxaline[2] (3.78 g, 14.2 mmol) and 9,10-Octadecanedione (4.02 g, 14.2 mmol) in ethanol (400 mL) was heated to reflux for 24 hours under an argon atmosphere. After cooled to room temperature, the solvent was removed with a rotavapor and the resulting residual was purified by flash column chromatography (petroleum ether/dichloromethane 6:1) to give compound **2** as a yellow solid (6.94 g, 95%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.81 (s, 2 H), 3.07 (t, J = 7.6 Hz, 4 H), 1.95-1.85 (m, 4 H), 150-1.29 (m, 20 H), 0.89 (t, J = 6.8 Hz, 6 H). MS (ESI): *m/z* 511.0 $[M + H]^+$. Anal. Calcd for $C_{24}H_{36}Br_2N_2$: C, 56.26; H, 7.08; N, 5.47. Found: C, 56.51; H, 7.02; N, 5.30.

Compound 3 and Compound 4. To a mixture of compound **2** (1.79 g, 3.49 mmol), $PdCl_2(PPh_3)_2$ (122 mg) and CuI (66 mg) in a flame-dried schlenk tube, THF (20 mL) and $^{i}Pr_2NH$ (10 mL) were added under argon atmophere. The tube was then cooled in an ice bath and 2-methylbut-3-yn-2-ol (0.31 mL, 3.17 mmol） was added by a syringe. The mixture was stirred at room temperature for 21 hours and then was filtered

through celite. After washing the solid with THF, the combined organic phase was concentrated and the resulting residual was purified by flash column chromatography (petroleum ether/THF 100:1 to 50:1 to 10:1 to 10:10) to give compound **3** (0.54 g, 30%) and compound **4** (0.43 g, 24%), respectively.

Compound 3: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.1 Hz, 1 H), 7.63 (d, *J* = 7.8 Hz, 1 H), 3.05 (t, *J* = 7.5 Hz, 4 H), 2.44 (brs, 1 H), 1.92-1.85 (m, 4 H), 1.72 (s, 6H), 1.49-1.29 (m, 20 H), 0.89 (t, *J* = 6.3 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 157.7, 141.8, 138.5, 132.2, 131.5, 124.4, 122.0, 78.9, 65.9, 34.9, 34.8, 31.9, 31.5, 29.6, 29.5, 29.3, 27.7, 27.4, 22.7, 14.1. MS (ESI): *m/z* 515.1 $[M + H]^+$, 537.2 $[M + Na]^+$. HRMS (ESI) *m/z* Calcd for $C_{29}H_{44}BrN_2O$ $[M + H]^+$: 515.2632, Found: 515.2651.

Compound 4: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 (s, 2 H), 3.00 (t, *J* = 7.5 Hz, 4 H), 2.71 (brs, 2 H), 1.94-1.89 (m, 4 H), 1.71 (s, 12 H), 1.46-1.28 (m, 20 H), 0.88 (t, *J* = 6.6 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2, 140.9, 131.6, 122.5, 101.4, 79.2, 65.8, 34.9, 31.9, 31.5, 31.1, 29.6, 29.5, 29.3, 27.2, 22.7, 14.1. MS (ESI): *m/z* 519.2 $[M + H]^+$, 541.2 $[M + Na]^+$. HRMS (ESI) *m/z* Calcd for $C_{34}H_{51}N_2O_2$ $[M + H]^+$: 519.3945, Found: 519.3935.

Compound 5. To a mixture of compound **3** (1.62 g, 3.13 mmol), $PdCl_2(PPh_3)_2$ (110 mg) and CuI (60 mg) in a flame-dried schlenk tube, THF (20 mL) and $^{i}Pr_2NH$ (10 mL) were added under argon. The tube was then cooled in an ice bath and triisopropylsilylacetylene (TIPSA) (0.84 mL, 3.76 mmol）was added by a syringe. The mixture was stirred at room temperature for 12.5 hours and then was filtered through celite. After washing the solid with THF, the combined organic phase was concentrated and the resulting residual was purified by flash column chromatography (CH_2Cl_2 → CH_2Cl_2 : MeOH = 100 : 1) to give a solid (1.13 g, 59%).

The above solid (0.61 g, 0.98 mmol) was dissolved in THF (30 mL) and water (0.3 mL). To this solution Bu_4NF in THF (1.00 mL, 1 M) was added at 0 ^{o}C. The resulting mixture was stirred at room temperature overnight. After removal of the solvent, the residue was subjected to flash column chromatography (CH_2Cl_2 : THF = 100 : 1) to afford compound 5 (565 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79

(d, *J* = 7.8 Hz, 1 H), 7.70 (d, *J* = 7.8 Hz, 1 H), 3.58 (s, 1 H), 3.04 (t, *J* = 7.5 Hz, 4 H), 2.44 (brs, 1 H), 1.96-1.82 (m, 4 H), 1.72 (s, 6 H), 1.47-1.23 (m, 20 H), 0.89 (t, *J* = 6.6 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8, 157.4, 141.2, 141.0, 132.8, 131.5, 123.2, 121.9, 84.2, 80.5, 79.2, 65.9, 35.1, 35.0, 31.9, 31.8, 31.5, 29.7, 29.6, 29.5 (d), 29.3, 27.9, 27.3, 22.8, 22.7, 14.1. MS (ESI): *m/z* 461.2 $[M + H]^+$, 483.2 $[M + Na]^+$. HRMS (ESI): *m/z* Calcd. for $[C_{31}H_{44}N_2O + H]^+$: 461.3526, Found: 461.3524.

Compound T1. This compound was prepared in 49% yield as a yellow solid starting from compound **3** and compound **5** according to a procedure similar to that described above for compound **3**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.5 Hz, 2 H), 7.73 (d, *J* = 7.8 Hz, 2 H), 3.09-3.03 (m, 8 H), 2.68 (brs, 2 H), 1.99-1.91 (m, 8 H), 1.74 (s, 12 H), 1.50-1.25 (m, 40 H), 0.91-0.84 (m, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 141.1, 141.0, 132.4, 131.8, 123.4, 122.7, 93.8, 79.5, 66.0, 35.1, 35.0, 31.9, 31.5, 29.7, 29.6, 29.3, 27.6, 27.4, 22.7, 14.1. MS (MALDI): *m/z* 895.7 $[M + H]^+$, 917.7 $[M + Na]^+$. HRMS (MALDI-TOF) *m/z* Calcd for $C_{60}H_{87}N_4O_2$ $[M + H]^+$: 895.6824, Found: 895.6816.

Compound 6. This compound was prepared in 97% yield as a yellow solid starting from compound **2** and TIPSA according to a procedure similar to that described above for compound **5**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (s, 2 H), 3.58 (s, 2 H), 3.05 (t, *J* = 7.7 Hz, 4 H), 1.90-1.87 (m, 4 H), 1.47-1.26 (m, 20 H), 0.88 (t, *J* = 6.8 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 141.2, 132.7, 122.6, 84.5, 80.4, 35.2, 31.9, 29.6, 29.5, 29.2, 28.0, 22.7, 14.1. MS (ESI): *m/z* 403.2 $[M + H]^+$. HRMS (ESI): *m/z* 403.3101. Calcd. for $[C_{28}H_{38}N_2 + H]^+$: 403.3108. Anal. Calcd for $C_{28}H_{38}N_2$: C, 83.53; H, 9.51; N, 6.96. Found: C, 83.95; H, 9.36; N, 6.45.

Compound T2. This compound was prepared in 50% yield as a yellow solid starting from compound **3** and compound **6** according to a procedure similar to that described above for compound **3**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04 (s, 2 H), 8.01 (d, *J* = 7.2 Hz, 2H), 7.80 (d, *J* = 7.5 Hz, 2 H), 3.12 (t, *J* = 6.0 Hz, 12 H), 2.03-1.93 (m, 12 H), 1.75 (s, 12 H), 1.52-1.25 (m, 60 H), 0.91-0.82 (m, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8, 157.5, 141.1, 141.0 (d), 132.5, 132.4, 131.8, 123.5, 123.4, 122.4, 94.8, 94.6, 79.5, 66.0, 35.1, 31.9 (d), 31.4, 29.6 (d), 29.5, 29.4, 29.3, 29.2, 27.7, 27.6,

22.6, 14.1. MS (MALDI-TOF): *m/z* 1155.8 $[M + H]^+$. MS (MALDI-TOF): *m/z* 1294.0 $[M + Na]^+$. HRMS (MALDI- TOF) *m/z* Calcd for $C_{86}H_{122}N_6O_2Na$ $[M + Na]^+$: 1293.9522, Found: 1293.9531.

Compound 7. This compound was prepared in 45% yield as a yellow solid starting from compound **2** and compound **5** according to a procedure similar to that described above for compound **3**. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.97-7.94 (m, 2 H), 7.87 (d, *J* = 8.1 Hz, 1 H), 7.76 (d, *J* = 8.1 Hz, 1 H), 3.13-3.05 (m, 8 H), 2.54 (brs, 1 H), 2.08-1.90 (m, 8 H), 1.80 (s, 6 H), 1.50-1.24 (m, 40 H), 0.91-0.82 (m, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 157.7, 157.4, 141.8, 141.1., 141.0, 138.6, 132.8, 132.3, 131.8, 131.6, 124.7, 123.4, 122.9, 122.7, 93.6, 65.9, 35.1, 35.0, 34.9, 31.9, 31.5, 29.6 (d), 29.3, 27.8, 27.6, 27.5, 27.4, 22.7, 14.1. MS (MALDI): *m/z* 891.5 $[M + H]^+$. HRMS (MALDI- TOF): *m/z*. Calcd. for $C_{55}H_{80}BrN_4O$: 913.5330, Found: 913.5315

Compound T3. This compound was prepared in 44% yield as a yellow solid starting from compound **6** and compound **7** according to a procedure similar to that described above for compound **3**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06-7.98 (m, 8 H), 7.78 (d, *J* = 7.5 Hz, 2 H), 3.13-3.04 (m, 20 H), 2.05-1.94 (m, 20 H), 1.74 (s, 12 H), 1.55-1.18 (m, 100 H), 0.89-0.83 (m, 30 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 141.1 (d), 132.4, 131.8, 123.5, 122.6, 95.0, 94.6, 79.4, 65.9, 35.1, 34.9, 31.9, 31.5, 29.6 (d), 29.3, 27.7, 27.6, 27.3, 22.7, 14.1. MS (MALDI-TOF): *m/z* 2024.5 $[M + H]^+$, 2046.5 $[M + Na]^+$. HRMS (MALDI-TOF) *m/z* Calcd for $C_{138}H_{195}N_{10}O_2$ $[M + H]^+$: 2024.5459, Found: 2024.5443.

Compound 8. Compound **T2** (0.14 g, 0.11 mmol) was dissolved in anhydrous toluene (14 mL) under argon. To this solution NaOH (680 mg, 17.0 mmol) was aded and the mixture was then heated to reflux for 5.5 hours. After cooled to room temperature, the reaction was quenched with water and followed by introduction of saturated NH_4Cl solution. The aqueous solution was extracted three times with dichloromethane (50 mL) and then dried over anhydrous sodium sulfate. After removal of the solvent with a rotavapor, the resulting residue was subjected to flash column chromatography (CH_2Cl_2) to give compound **8** as a yellow solid (53 mg, 42%). ^{1}H NMR ($CDCl_3$, 300 MHz): 8.04 (s, 2 H), 7.99 (d, *J* = 7.8 Hz, 2 H), 7.87 (d, *J*

= 7.5 Hz, 2 H), 3.63 (s, 2 H), 3.14-3.06 (m, 12 H), 2.06-1.86 (m, 12 H), 1.54-1.22 (m, 60 H), 0.92-0.82 (m, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$) 157.8, 157.5, 157.4, 141.3, 141.1, 140.9, 132.9, 132.3, 132.2, 124.1, 123.5, 121.9, 94.7, 94.4, 84.4, 80.7, 35.2, 35.1 (d), 31.9, 29.6, 29.5, 29.3, 28.0, 27.7, 27.6, 22.7, 14.1. MS (MALDI-TOF): *m/z* 1155.8 $[M + H]^+$. HRMS (MALDI-TOF): *m/z* Calcd. for $C_{80}H_{111}N_6$: 1155.8865, Found: 1155.8876.

Compound T4. This compound was prepared in 17% yield as a yellow solid starting from compound **7** and compound **8** according to a procedure similar to that described above for compound **3**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06-7.96 (m, 12 H), 7.78 (d, *J* = 7.8 Hz, 2 H), 3.17-3.04 (m, 28 H), 2.05-1.99 (m, 28 H), 1.74 (s, 12 H), 1.58-1.18 (m, 140 H), 0.90-0.83 (m, 42 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 157.2, 141.1, 132.5, 131.8, 123.5, 123.4, 122.6, 94.8, 79.4, 65.9, 35.1, 34.9, 31.9, 31.5, 29.6, 29.3, 27.8, 27.7, 27.3, 22.7, 14.1. MS (MALDI-TOF): *m/z* 2777.1 $[M + H]^+$, 2799.1 $[M + Na]^+$. HRMS (MALDI- TOF) *m/z* Calcd for $C_{190}H_{267}N_{14}O_2$ $[M + H]^+$: 2777.1216, Found: 2777.1200.

References:

(1) A. Tsami, T. W. Bünnagel, T. Farrell, M. Scharber, S. A. Choulis, C. J. Brabec, and U. Scherf, *J. Mater. Chem.*, 2007, **17**, 1353.

(2) F. Babudri, V. Fiandanese, G. Marchese and A. Punzi, *Tetrahedron Lett.*, 1995, **36**, 7305.

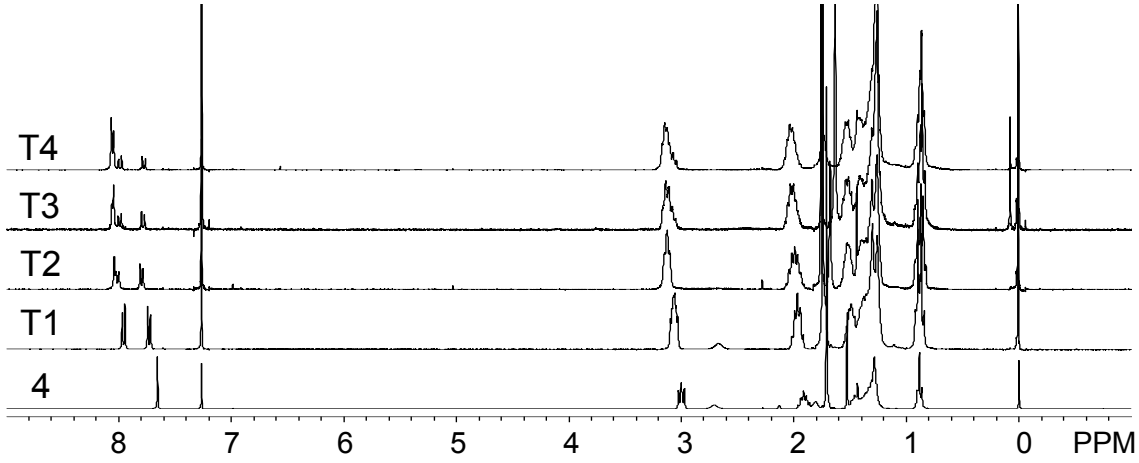

Figure S1. ^{1}H NMR of compounds **4** and **T1**-**T4** in $CDCl_3$ at 25 ^{o}C.

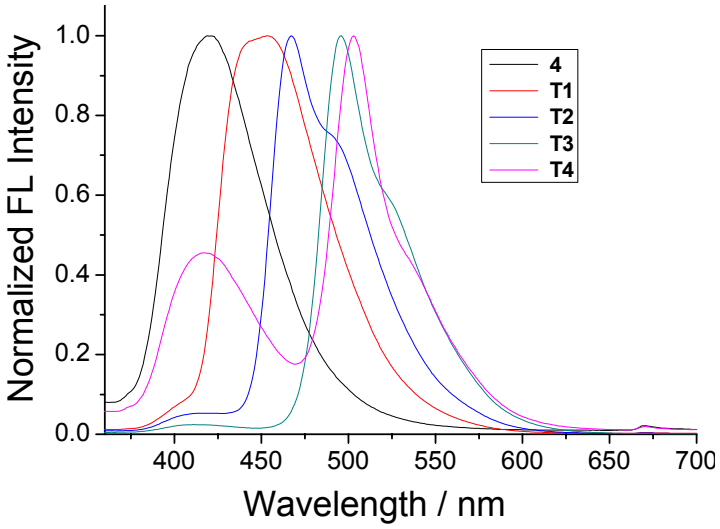

Figure S2. Normalized fluorescence spectra of compound **4** and oligomers **T1**-**T4** in THF at 25 ^{o}C (λ_{ex} = 330 nm). The emmision of **T4** around 420 nm is attributed to the transition of $S_2 \rightarrow S_0$.

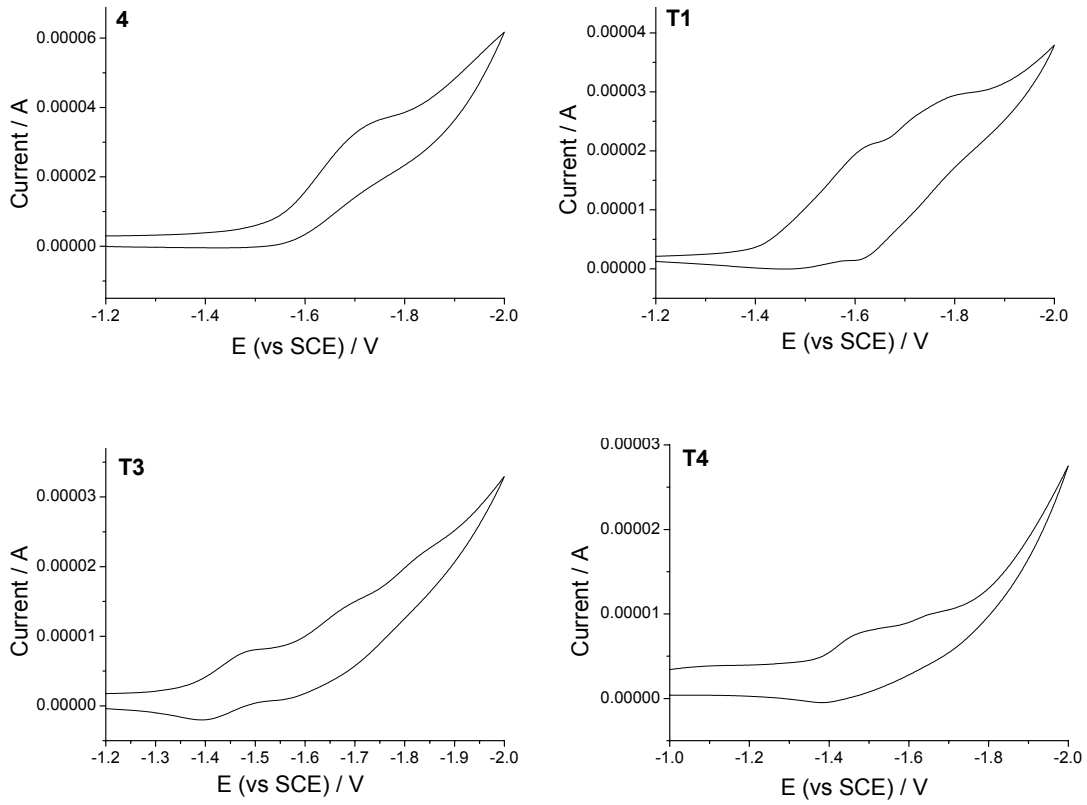

Figure S3. Cyclic voltammograms for the reduction of compounds **4** (4.2 mM), **T1** (1.1 mM), **T3** (0.9 mM), and **T4** (1.2 mM) in dichloromethane. Scan rate = 50 mV s^{-1}.

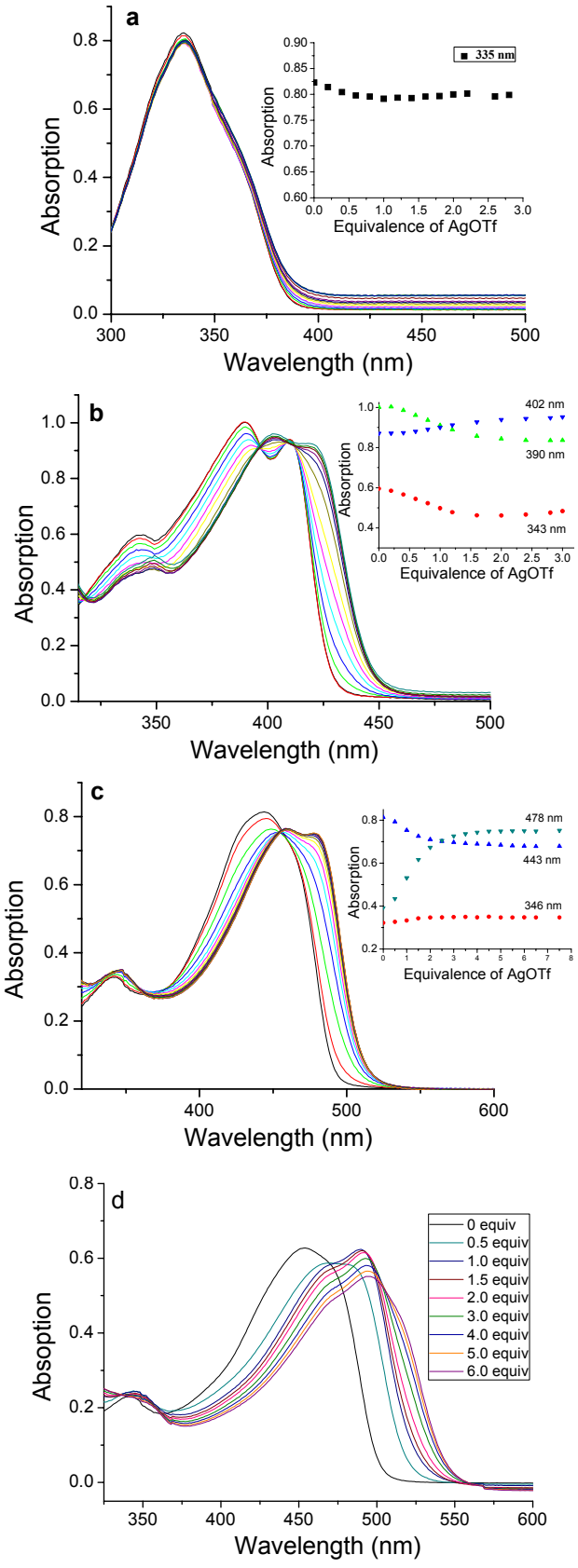

Figure S4. UV-vis spectra changes of (a) **4**, (b) **T1**, (c) **T3** and (d) **T4** upon addition of AgOTf in THF at 25 ^{o}C. The concentration of quinoxaline unit is 50 μM for **4** and **T1**-**T3**, 150 μM for **T4**. Inset: titration curves.

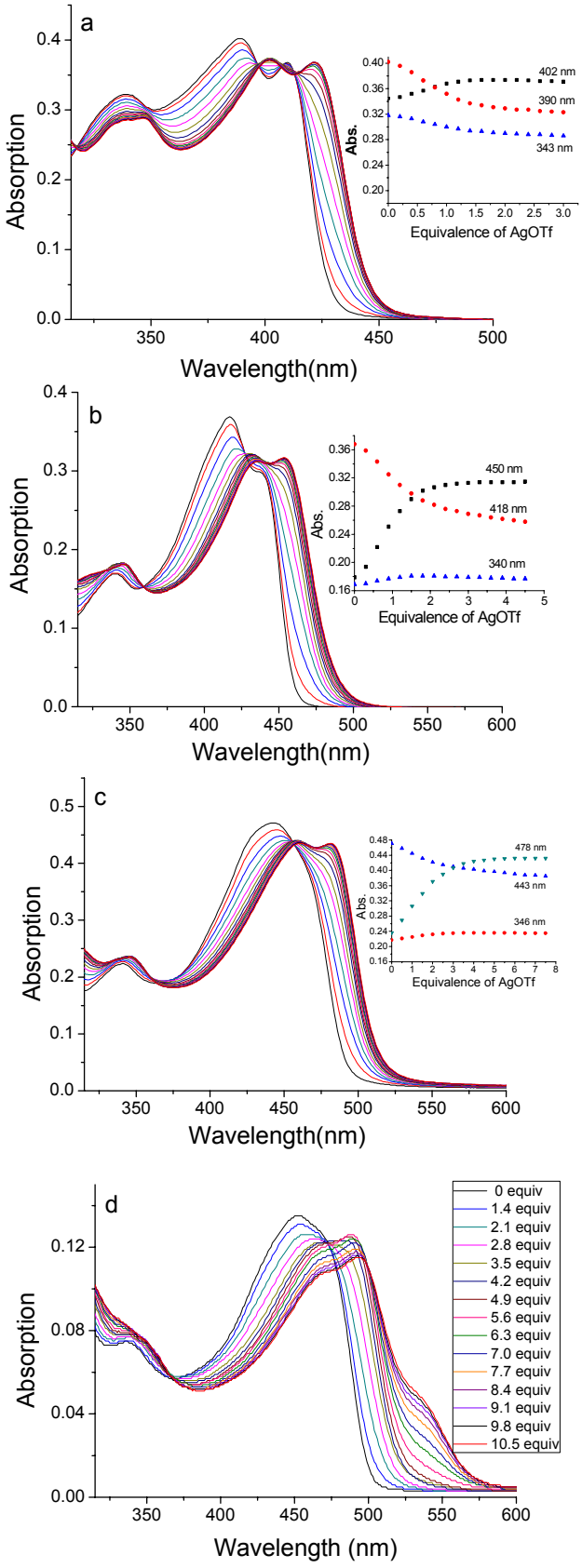

Figure S5. UV-vis spectra changes of (a) **T1**, (b) **T2**, (c) **T3** and (d) **T4** upon addition of AgOTf in THF at 25 ^{o}C. The concentration of quinoxaline unit is 30 μM. Inset: titration curves.

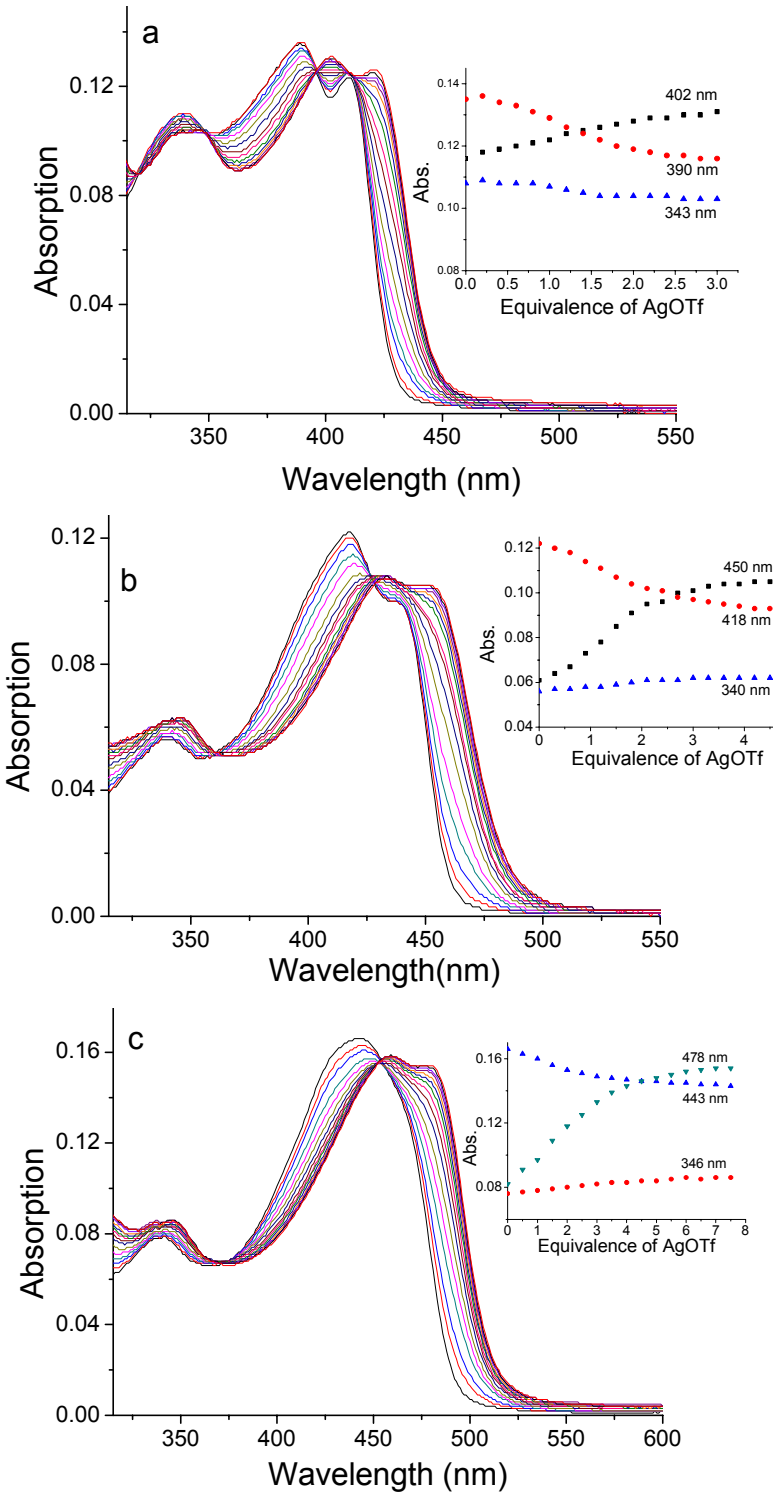

Figure S6. UV-vis spectra changes of (a) **T1**, (b) **T2**, and (c) **T3** upon addition of AgOTf in THF at 25 ^{o}C. The concentration of quinoxaline unit is 10 μM. Inset: titration curves. The UV-vis titration of **T4** with AgOTf doesn't show here because the absorbance is too small to get well-resolved spectra at this concentration.

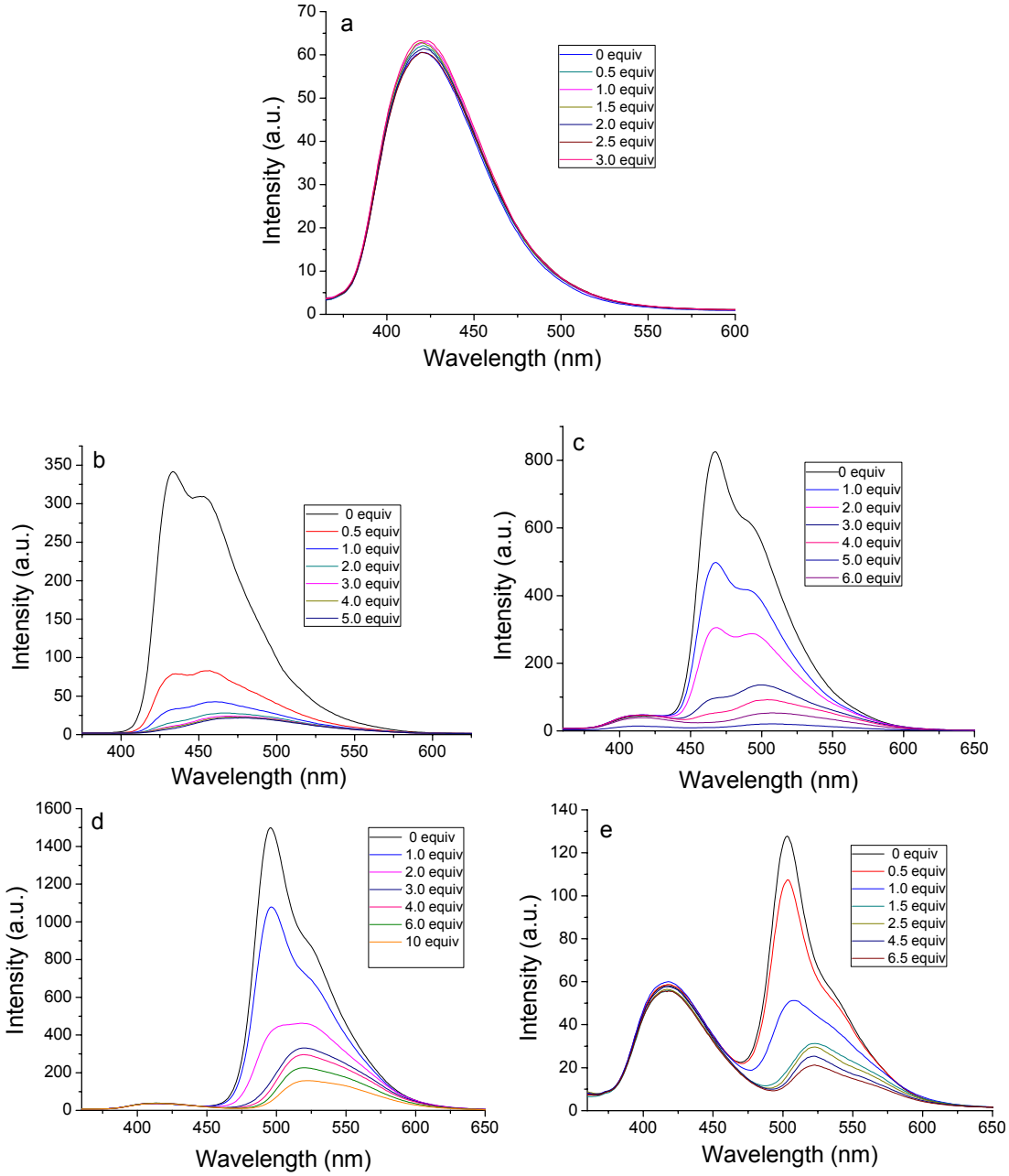

Figure S7. Fluorescence spectra changes of (a) **4**, (b) **T1**, (c) **T2**, (d) **T3**, and (e) **T4** upon addition of AgOTf in THF at 25 ^{o}C (λ_{ex} = 330 nm).

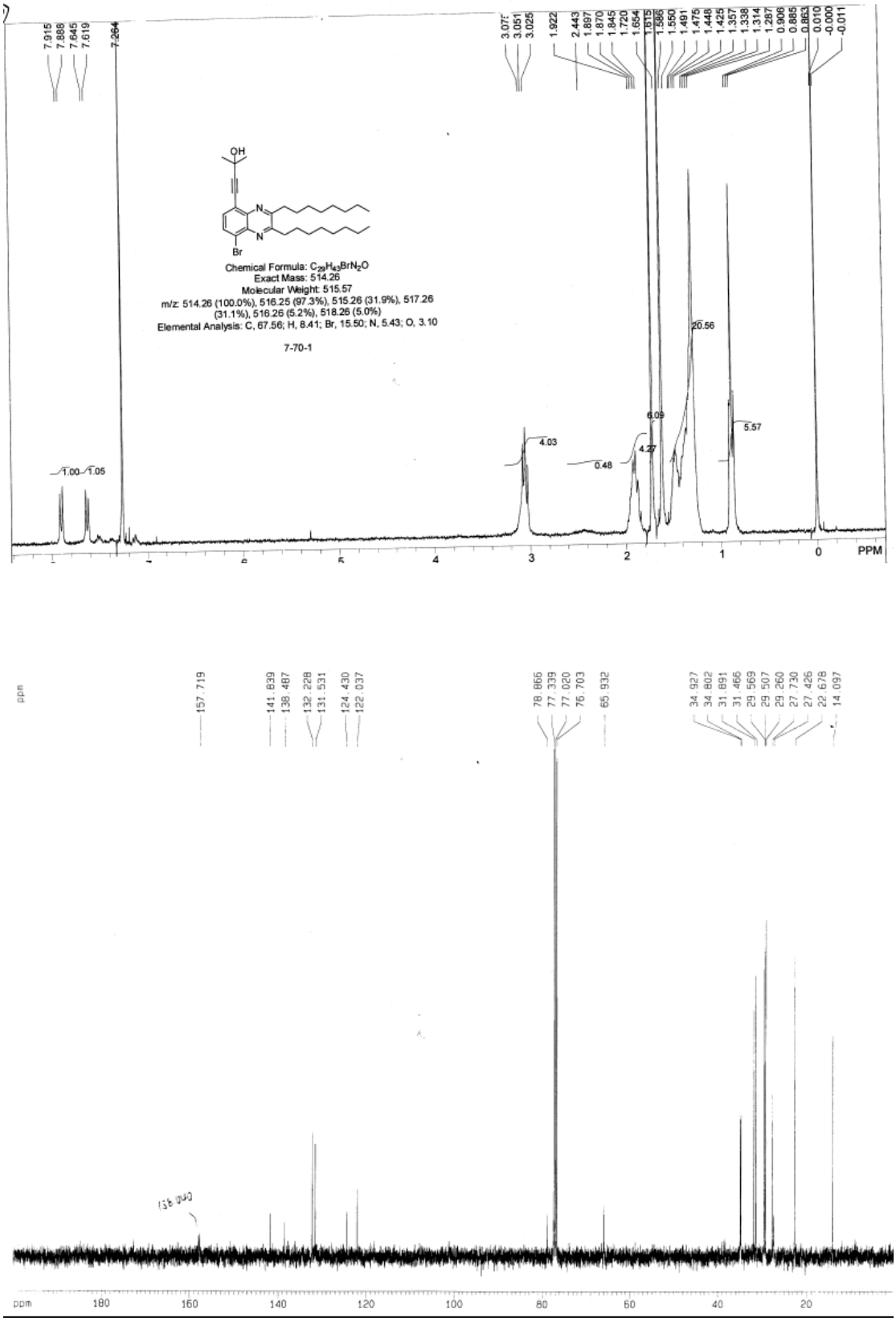

Figure S8. ^{1}H NMR and ^{13}C NMR spectra of compound **3** in $CDCl_3$.

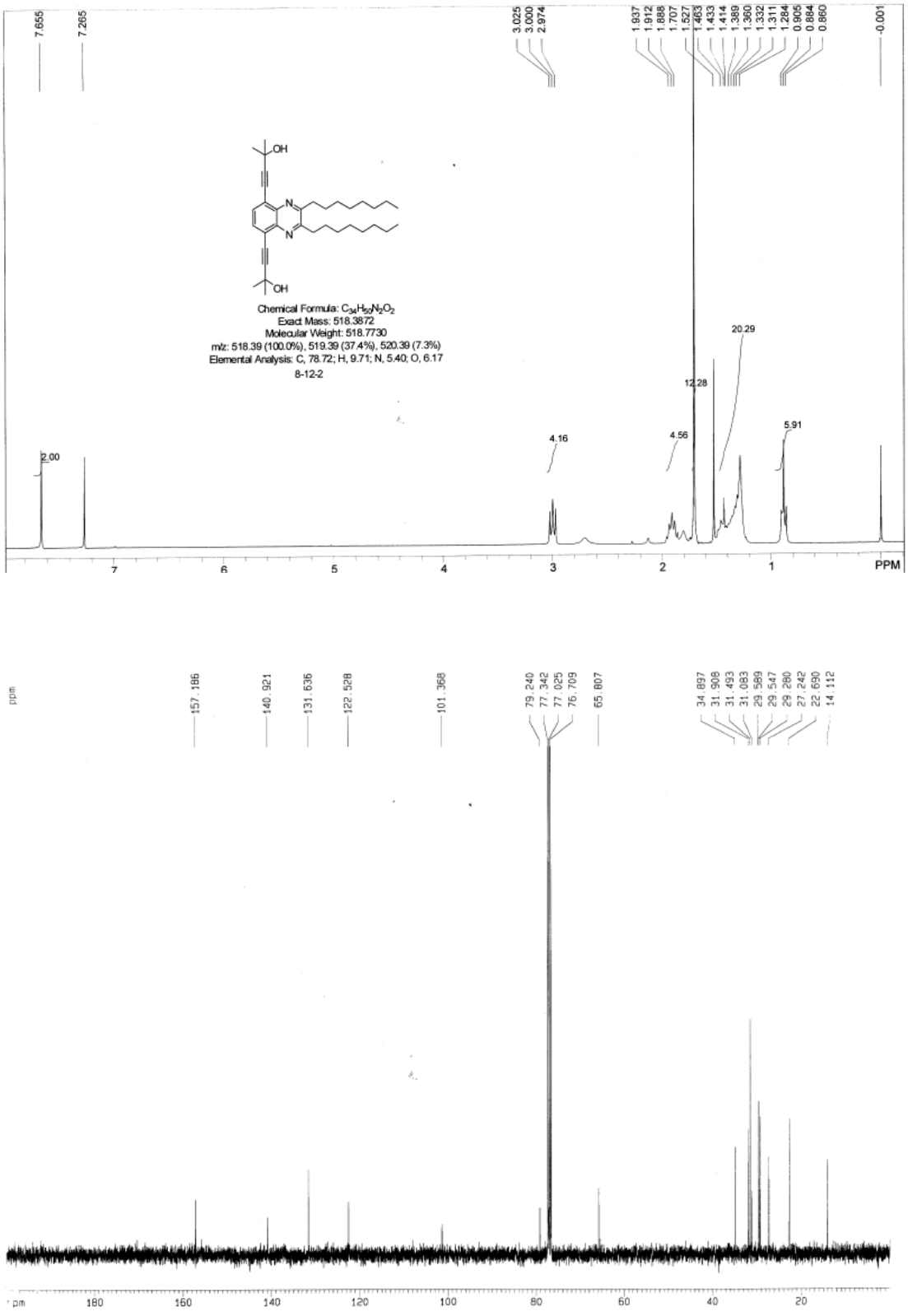

Figure S9. ^{1}H NMR and ^{13}C NMR spectra of compound **4** in $CDCl_3$.

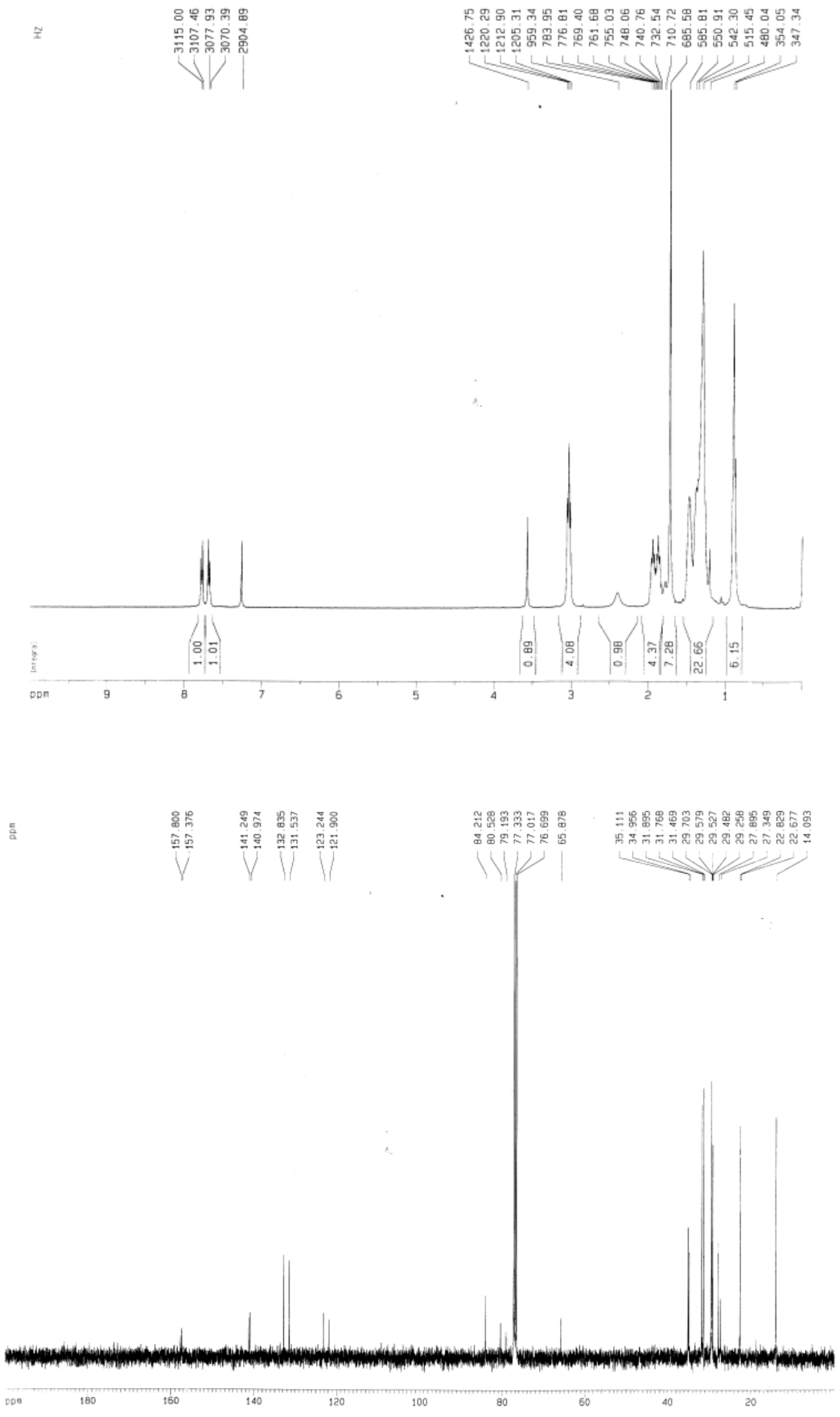

Figure S10. ^{1}H NMR and ^{13}C NMR spectra of compound **5** in $CDCl_3$.

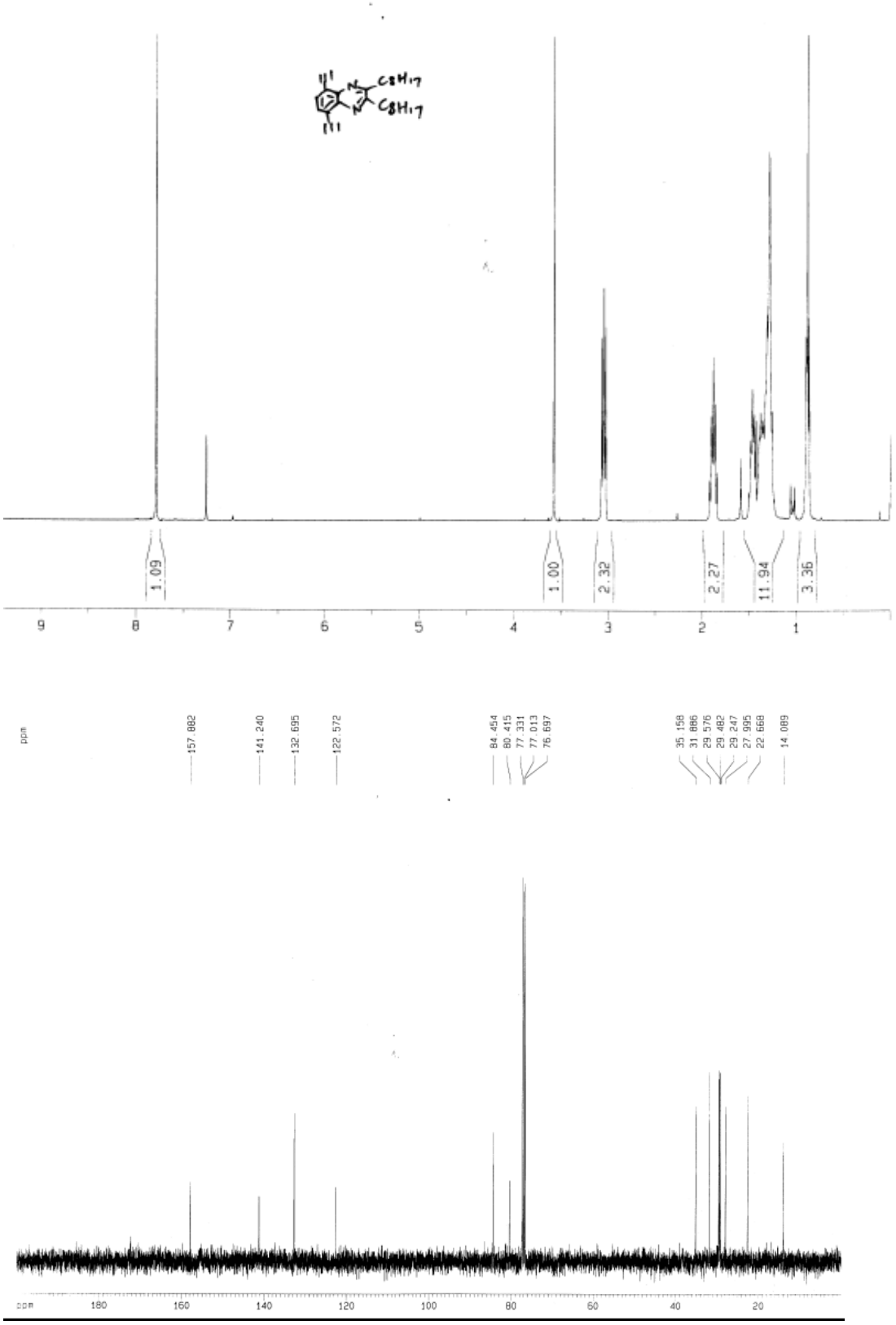

Figure S11. ^{1}H NMR and ^{13}C NMR spectra of compound **6** in $CDCl_3$.

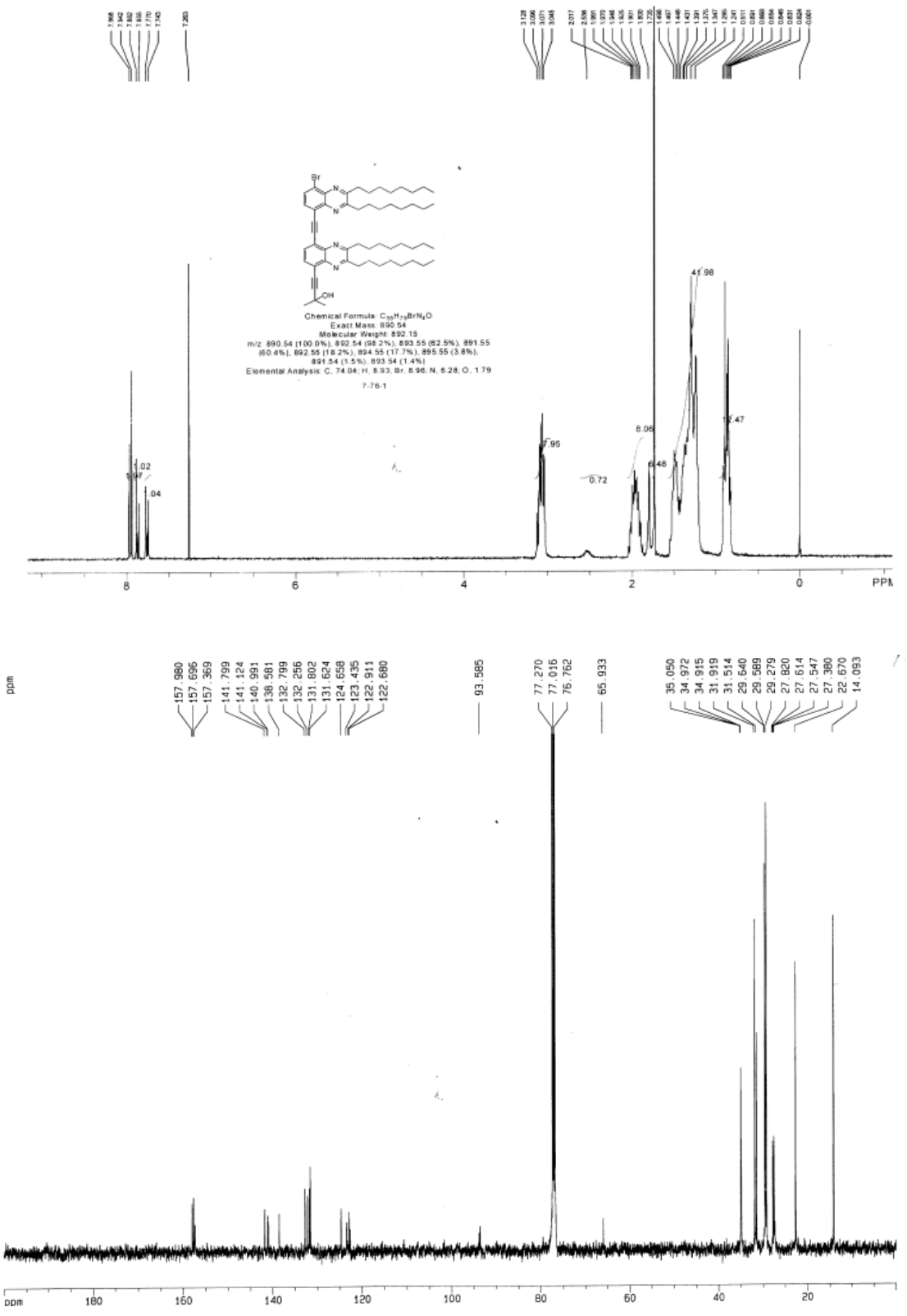

Figure S12. ^{1}H NMR and ^{13}C NMR spectra of compound **7** in $CDCl_3$.

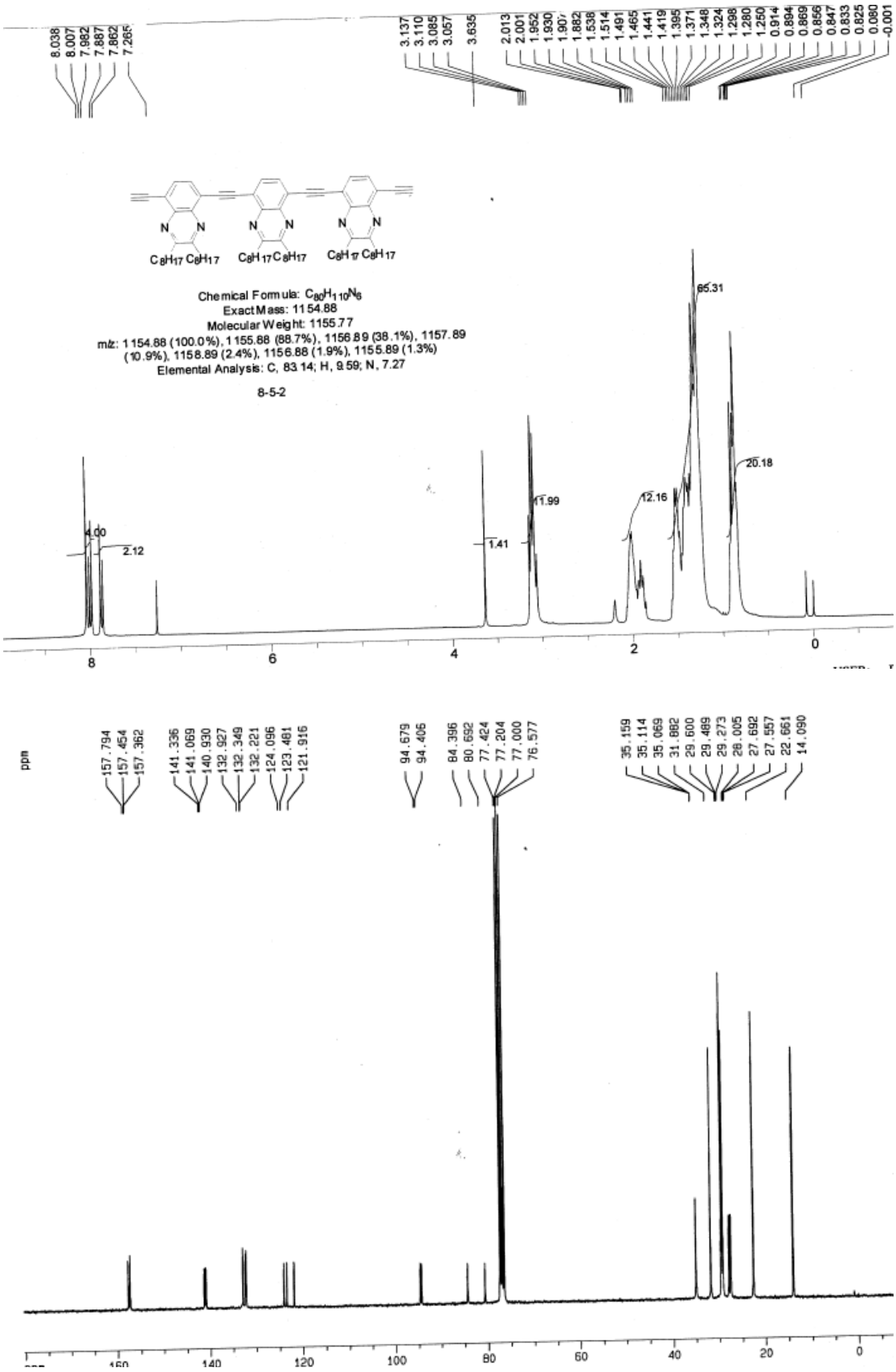

Figure S13. ^{1}H NMR and ^{13}C NMR spectra of compound **8** in $CDCl_3$.

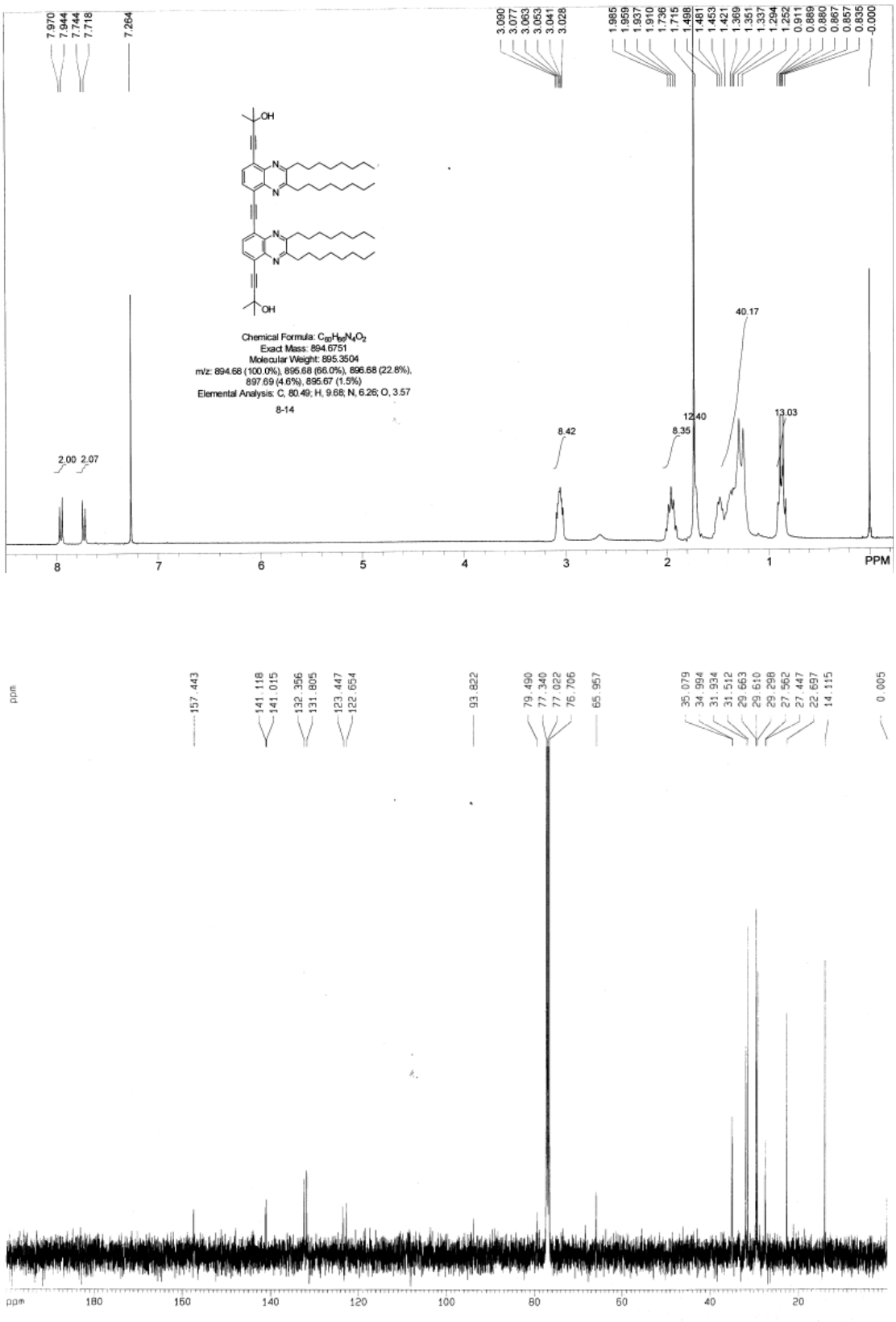

Figure S14. ^{1}H NMR and ^{13}C NMR spectra of compound **T1** in $CDCl_3$.

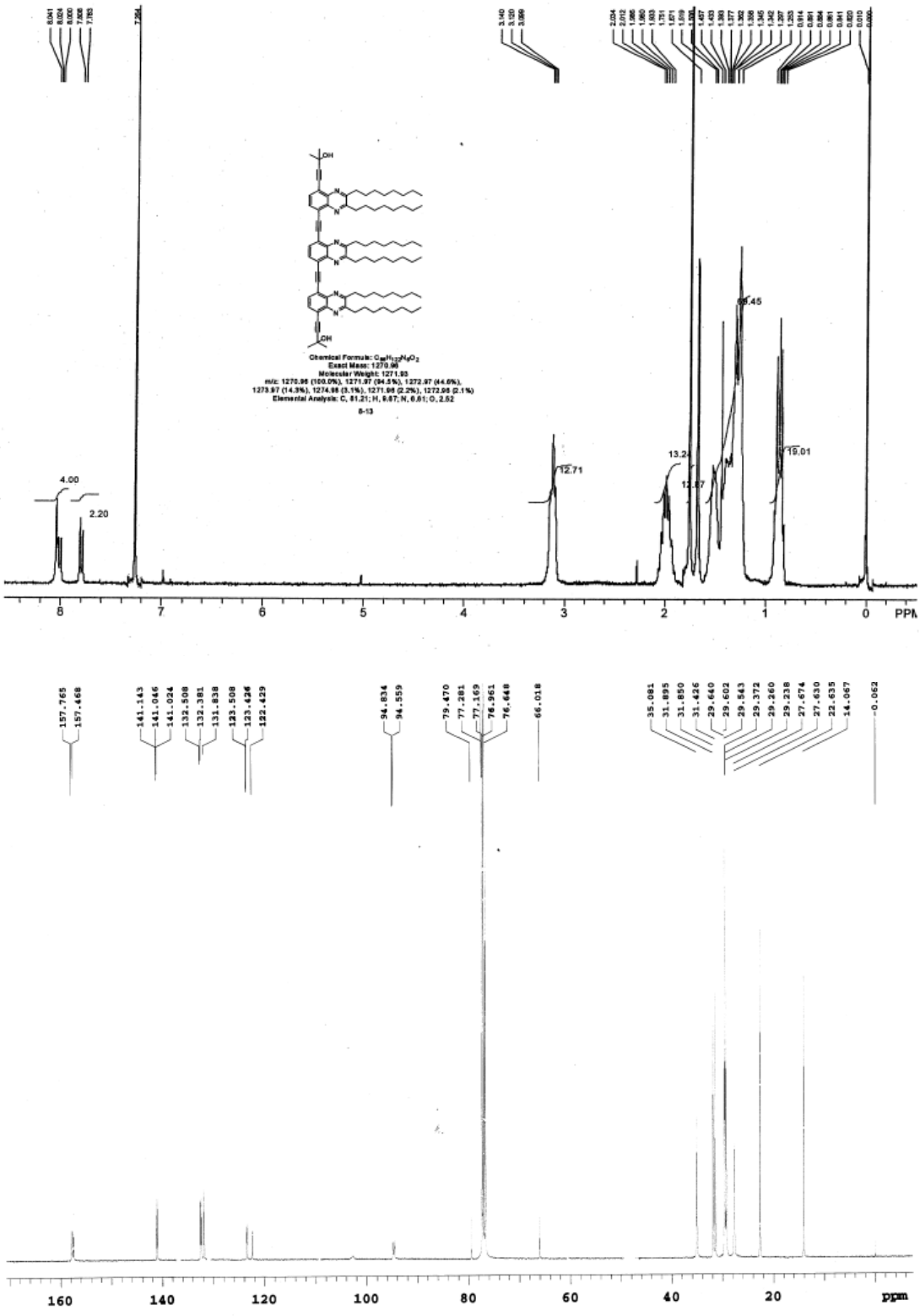

Figure S15. ^{1}H NMR and ^{13}C NMR spectra of compound **T2** in $CDCl_3$.

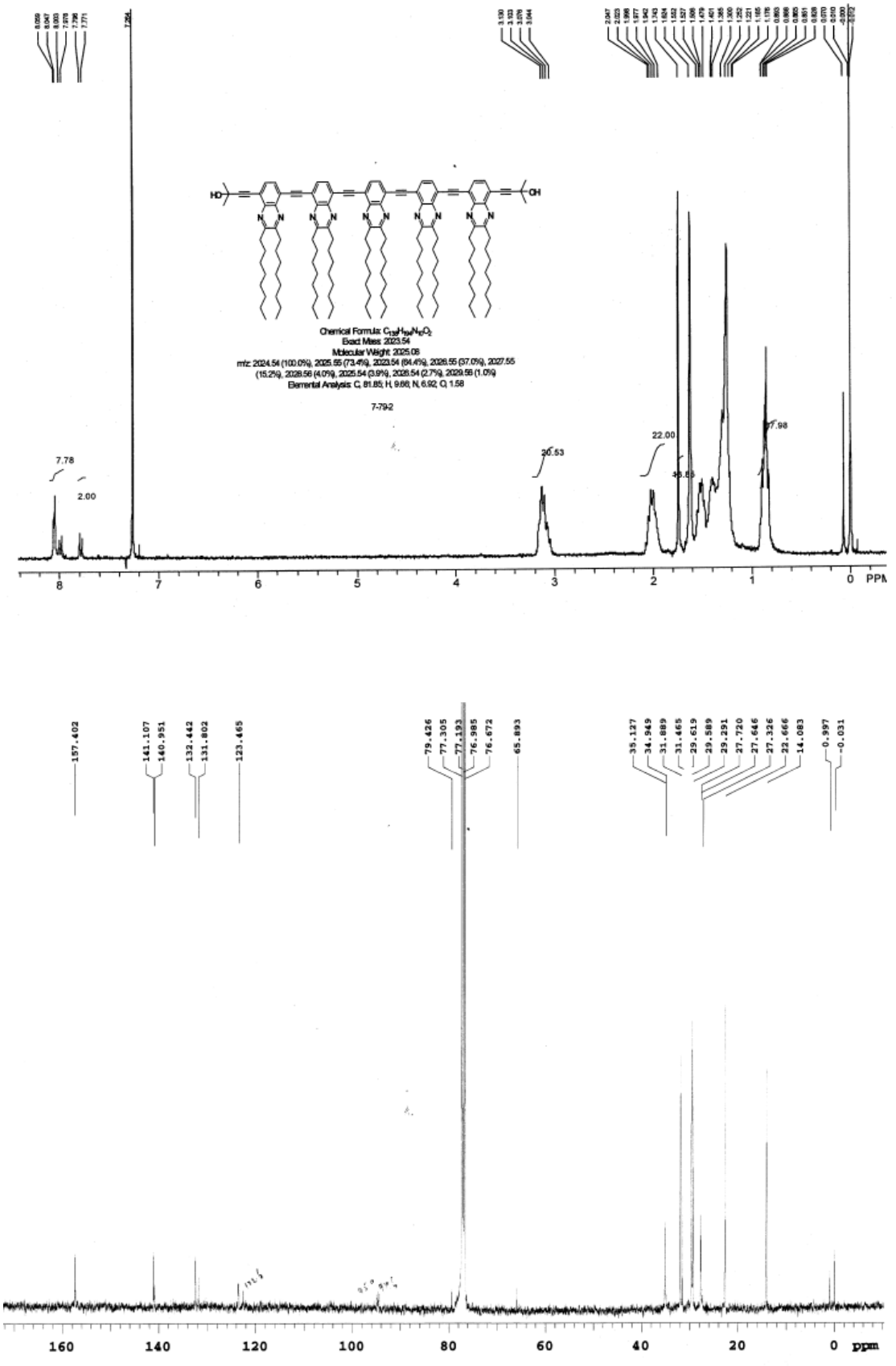

Figure S16. ^{1}H NMR and ^{13}C NMR spectra of compound **T3** in $CDCl_3$.

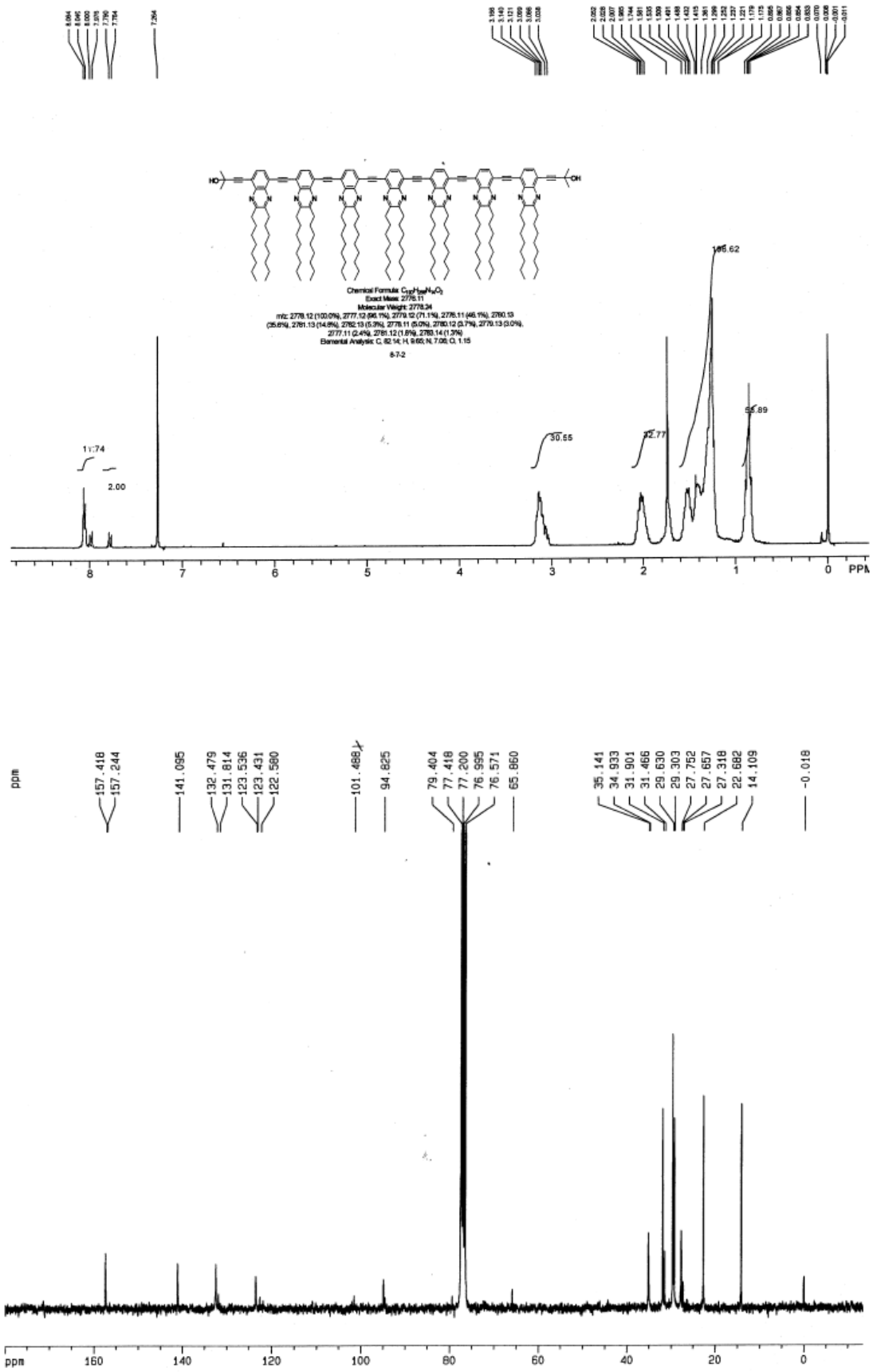

Figure S17. ^{1}H NMR and ^{13}C NMR spectra of compound **T4** in $CDCl_3$.