Electronic Supplementary Information (ESI)

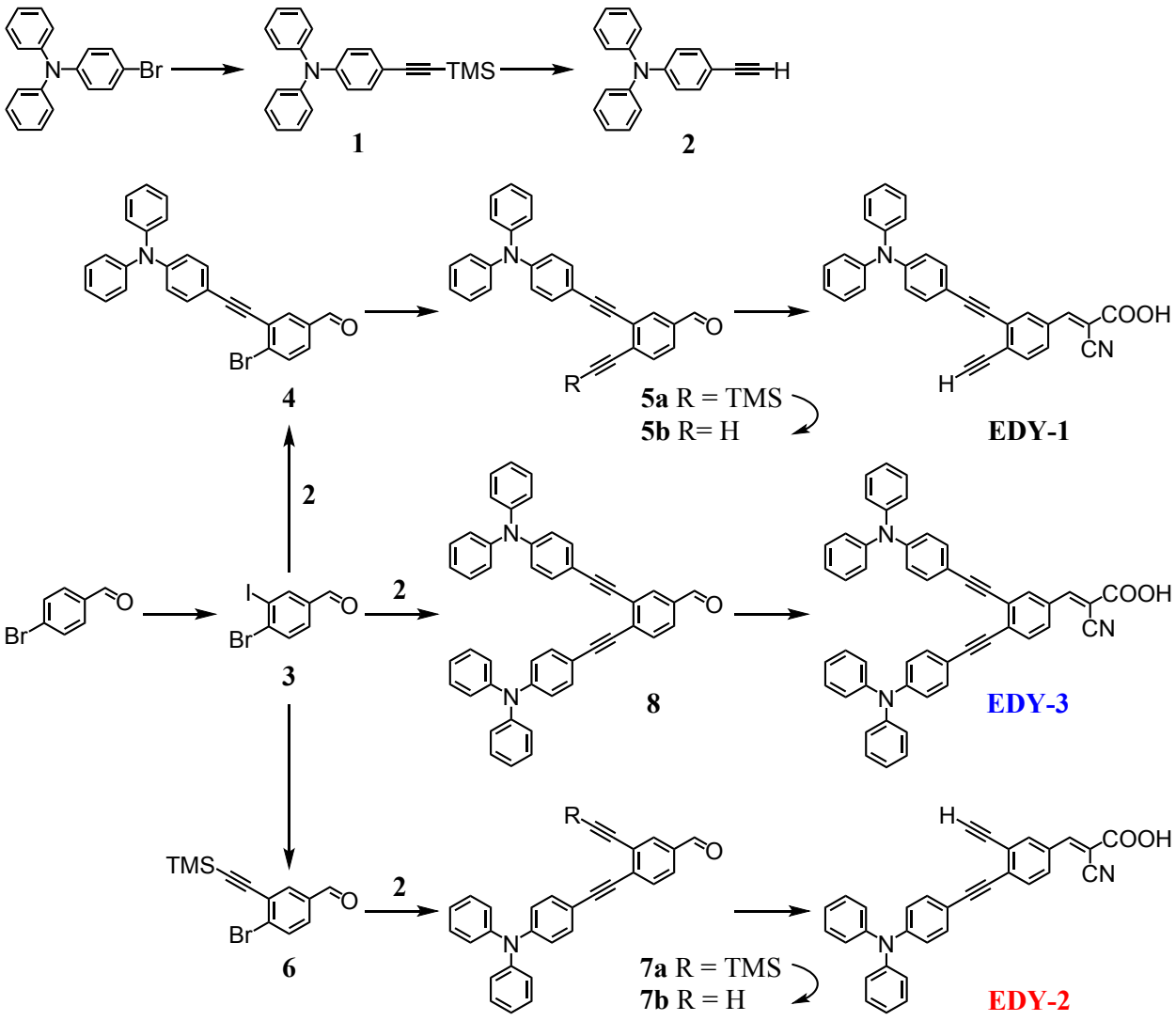
Enediyne as π linker in D-π-A dyes for dye-sensitized solar cells

Youfu Wang,[a] Luhua Dong,[a] Zhiwei Zheng,[b] Xing Li,[b] Rulin Xiong,[a] Jianli Hua*[b] and Aiguo Hu*[a]

[a]Shanghai Key Laboratory of Advanced Polymeric Materials, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai, 200237, China.
E-mail: hagmhsn@ecust.edu.cn

[b]Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, Shanghai 200237, China.
E-mail: jlhua@ecust.edu.cn

The synthetic protocol of related compounds is shown in **Figure S1**. The details of synthetic process of **EDY-2** are shown in the manuscript. The Sonogashira coupling reactions between aryl halide and alkyne and subsequent Knoevenagel condensation between arylaldehyde and cyanoacetic acid are similar to the processes described in the manuscript. The related NMR and mass spectra of these compounds are shown here.



Scheme S1. Synthetic protocols of three enediyne-based donor-π-acceptor type dyes with different donor positions and numbers.

N,N-dipheyl-4-((trimethylsily)ethynyl)aniline (1): The synthesis of **1** was following to the literature procedure.[1] Yield 86%. ^{1}H-NMR (DMSO-D_6, 400 MHz, ppm): 7.36-7.26 (m, 6H); 7.10 (t, *J* =7.4 Hz, 2H); 7.04 (d, *J* = 7.7 Hz, 4H); 6.82 (d, *J* = 8.6 Hz, 2H); 0.20 (s, 9H). ^{13}C-NMR (DMSO-D_6, 100 MHz, ppm): 147.82; 146.36; 132.78; 129.74; 125.04; 124.10; 120.90; 114.55; 105.60; 92.79; 0.01. HR-MS (ESI): m/z calcd. for $C_{23}H_{24}NSi$ $(M+H)^+$: 342.1600; found: 342.1669.

4-ethynyl-N,N-diphenylaniline (2): The synthesis of **2** was following to the literature procedure.[1] Yield 90%. ^{1}H-NMR (DMSO-D_6, 400 Hz, ppm): 7.33 (dd, *J* = 9.9, 5.1 Hz, 6H); 7.10 (t, *J* = 7.2 Hz, 2H); 7.05 (d, *J* = 7.2 Hz, 4H); 6.86 (d, *J* = 8.5 Hz, 2H); 4.05 (s, 1H). ^{13}C-NMR (DMSO-D_6, 100 MHz, ppm): 147.80; 146.44; 132.87; 129.74; 124.93; 124.01; 121.24; 114.25; 83.65; 79.65. HR-MS (ESI): m/z calcd. for $C_{20}H_{15}N$ $(M)^+$: 269.1204; found: 269.1205.

4-bromo-3-((4-(diphenylamino)phenyl)ethynyl)benzaldehyde (4): Yield 94.6%. ^{1}H-NMR (DMSO-D_6, 400 Hz, ppm): 9.99 (s, 1H); 8.10 (s, 1H); 7.96 (d, *J* = 8.1 Hz, 1H); 7.77 (d, *J* = 8.2 Hz, 1H); 7.45 (s, 2H); 7.36 (t, *J* = 7.1 Hz, 4H); 7.12 (m, 6H); 6.92 (d, *J* = 7.9 Hz, 2H). ^{13}C-NMR (DMSO-D_6, 100 MHz, ppm): 191.90; 148.39; 146.25; 135.40; 134.01; 133.49; 132.79; 130.91; 129.82; 129.28; 125.57; 125.25; 124.33; 120.83; 113.40; 95.55; 86.17. HR-MS (ESI): m/z calcd. for $C_{27}H_{18}BrNO$ $(M)^+$: 451.0572, found: 451.0565.

3-((4-(diphenylamino)phenyl)ethynyl)-4-((trimethylsilyl)ethynyl)benzaldehyde (5a): Yield 65%. ^{1}H-NMR (DMSO-D_6, 400 Hz, ppm): 10.00 (s, 1H); 8.06 (s, 1H); 7.83 (d, *J* = 8.0 Hz, 1H); 7.72 (d, *J* = 8.0 Hz, 1H); 7.42 (d, *J* = 8.4 Hz, 2H); 7.37 (t, *J* = 7.7 Hz, 4H); 7.16-7.09 (m, 6H); 6.91 (d, *J* = 8.4 Hz, 2H); 0.24 (s, 9H). ^{13}C-NMR (DMSO-D_6, 100 MHz, ppm): 192.11; 148.30; 146.28; 135.71; 132.89; 132.74; 129.87; 129.25; 127.95; 126.25; 125.33; 124.39; 120.74; 113.72; 102.78;

95.17; 86.21; 54.96; -0.24. HR-MS (ESI): m/z calcd. for $C_{32}H_{27}NOSi$ $(M)^+$: 469.1862, found: 469.1858.

3-((4-(diphenylamino)phenyl)ethynyl)-4-ethynylbenzaldehyde (5b): Yield 92%. ^{1}H-NMR (DMSO-D_6, 400 Hz, ppm): 10.01 (s, 1H); 8.07 (s, 1H); 7.85 (d, *J* = 8.0 Hz, 1H); 7.76 (d, *J* = 8.0 Hz, 1H); 7.44 (d, *J* = 8.6 Hz, 2H); 7.36 (t, *J* = 7.8 Hz, 4H); 7.16-7.09 (m, 6H); 6.92 (d, *J* = 8.6 Hz, 2H); 4.82 (s, 1H). ^{13}C-NMR (DMSO-D_6, 100 MHz, ppm): 192.09; 148.27; 146.28; 135.79; 133.17; 132.81; 132.68; 129.82; 129.02; 127.95; 126.34; 125.23; 124.30; 120.89; 113.75; 95.04; 88.49; 86.06; 81.47. HR-MS (ESI): m/z calcd. for $C_{29}H_{19}NO$ $(M)^+$: 397.1467, found: 397.1460.

2-cyano-3-(3-((4-(diphenylamino)phenyl)ethynyl)-4-ethynylphenyl)acrylic acid (EDY-1): Yield 55%. ^{1}H-NMR (DMSO-D_6, 400 Hz, ppm): 8.02 (s, 2H); 7.89 (d, *J* = 8.3 Hz, 1H); 7.68 (d, *J* = 8.2 Hz, 1H); 7.42 (d, *J* = 8.3 Hz, 2H); 7.35 (t, *J* = 7.6 Hz, 4H); 7.13 (t, J = 7.4 Hz, 2H); 7.10 (d, *J* = 7.8 Hz, 4H); 6.91 (d, *J* = 8.2 Hz, 2H); 4.69 (s, 1H). ^{13}C-NMR (DMSO-D_6, 100 MHz, ppm): 163.05; 148.56; 146.70; 133.93; 133.28; 133.13; 132.40; 130.18; 129.05; 126.47; 126.18; 125.55; 125.42; 124.63; 121.37; 118.77; 114.33; 94.43; 87.09; 86.37; 81.69. HR-MS (ESI): m/z calcd. for $C_{32}H_{20}N_2O_2$ $(M)^+$: 464. 1525, found: 464.1597.

3,4-bis((4-(diphenylamino)phenyl)ethynyl)benzaldehyde (8): Yield 53%. ^{1}H-NMR (DMSO-D_6, 400 Hz, ppm): 9.99 (s, 1H); 8.06 (s, 1H); 7.85 (d, *J* = 8.0 Hz, 1H); 7.74 (d, *J* = 8.0 Hz, 1H); 7.42 (d, *J* = 7.7 Hz, 4H); 7.32 (d, *J* = 2.5 Hz, 8H); 7.16-7.10 (m, 4H); 7.10-7.03 (m, 8H); 6.88 (d, *J* = 8.3 Hz, 4H). ^{13}C-NMR ($CDCl_3$, 100 MHz, ppm): 191.07; 148.81; 148.54; 147.17; 147.07; 134.97; 133.35; 133.02; 132.83; 132.18; 131.78; 129.60; 129.57; 127.78; 126.88; 125.40; 125.29; 124.02; 123.89; 122.10; 121.88; 115.45; 115.11; 98.50; 95.50; 87.71; 86.79. HR-MS (ESI): m/z calcd. for $C_{47}H_{32}N_2O$ $(M)^+$: 640.2515, found: 640.2613.

3-(3,4-bis((4-(diphenylamino)phenyl)ethynyl)phenyl)-2-cyanoacrylic acid (EDY-3): Yield 64%. ^{1}H-NMR (DMSO-D_6, 400 Hz, ppm): 8.04 (s, 1H); 8.01 (s, 1H); 7.88 (d, J = 8.0 Hz, 1H); 7.65 (d, J = 8.0 Hz, 1H); 7.39 (d, J = 7.5, 4H); 7.30 (m, 8H); 7.11 (m, 4H); 7.04 (m, 8H); 6.87 (t, J = 6.2 Hz, 4H). ^{13}C-NMR (DMSO-D6, 100 MHz, ppm): 163.64; 148.24; 148.10; 146.31; 146.24; 132.83; 132.77; 132.67; 132.63; 132.29; 131.91; 129.90; 129.79; 129.77; 128.73; 127.06; 125.44; 125.30; 125.23; 125.13; 124.32; 124.22; 121.02; 120.82; 114.00; 113.85; 96.62; 94.62; 87.46; 86.74; 67.03. HR-MS (ESI): m/z calcd. for $C_{50}H_{33}N_3O_2$ $(M)^+$: 707.2573, found: 707.3050.

Reference:

1. Lee, D. H.; Lee, M. J.; Song, H. M.; Song, B. J.; Seo, K. D.; Pastore, M.; Anselmi, C.; Fantacci, S.; De Angelis, F.; Nazeeruddin, M. K., Organic Dyes Incorporating Low-Band-Gap Chromophores Based on Π-Extended Benzothiadiazole for Dye-Sensitized Solar Cells. *Dyes and Pigments* **2011**, *91*, 192-198.

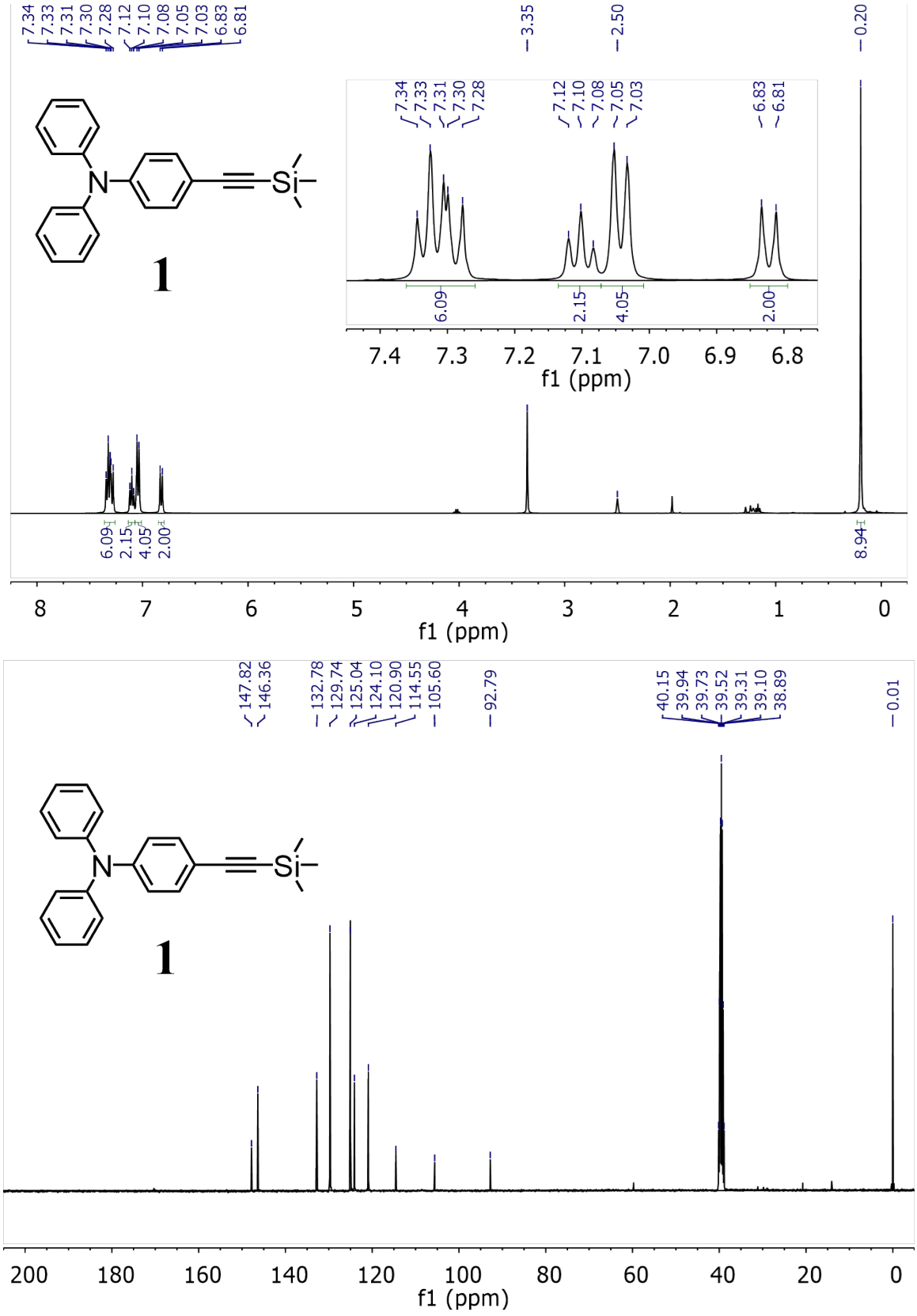


Figure S1. ^{1}H- and ^{13}C-NMR spectra of compound **1**.

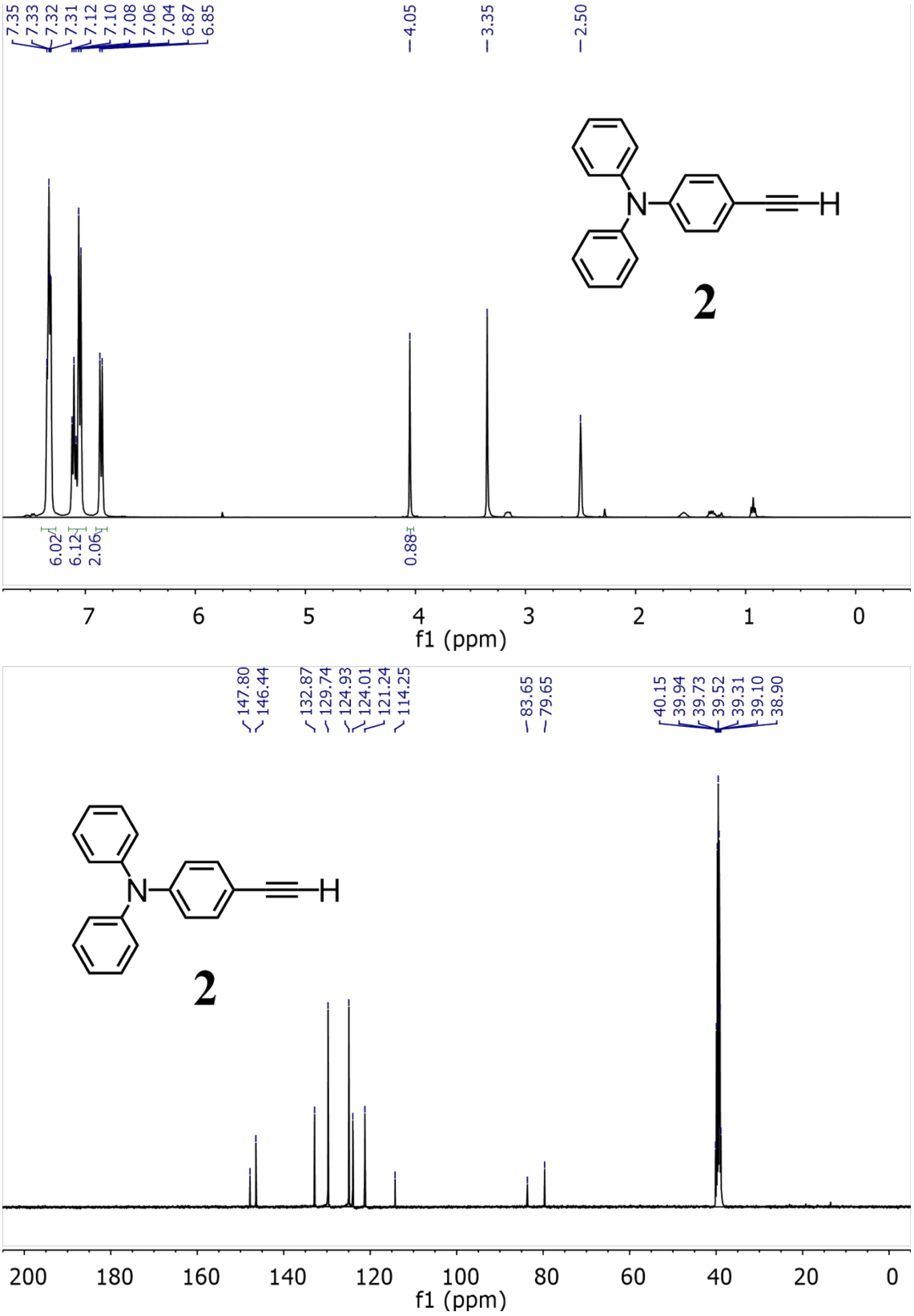


Figure S2. ^{1}H- and ^{13}C-NMR spectra of compound **2**.

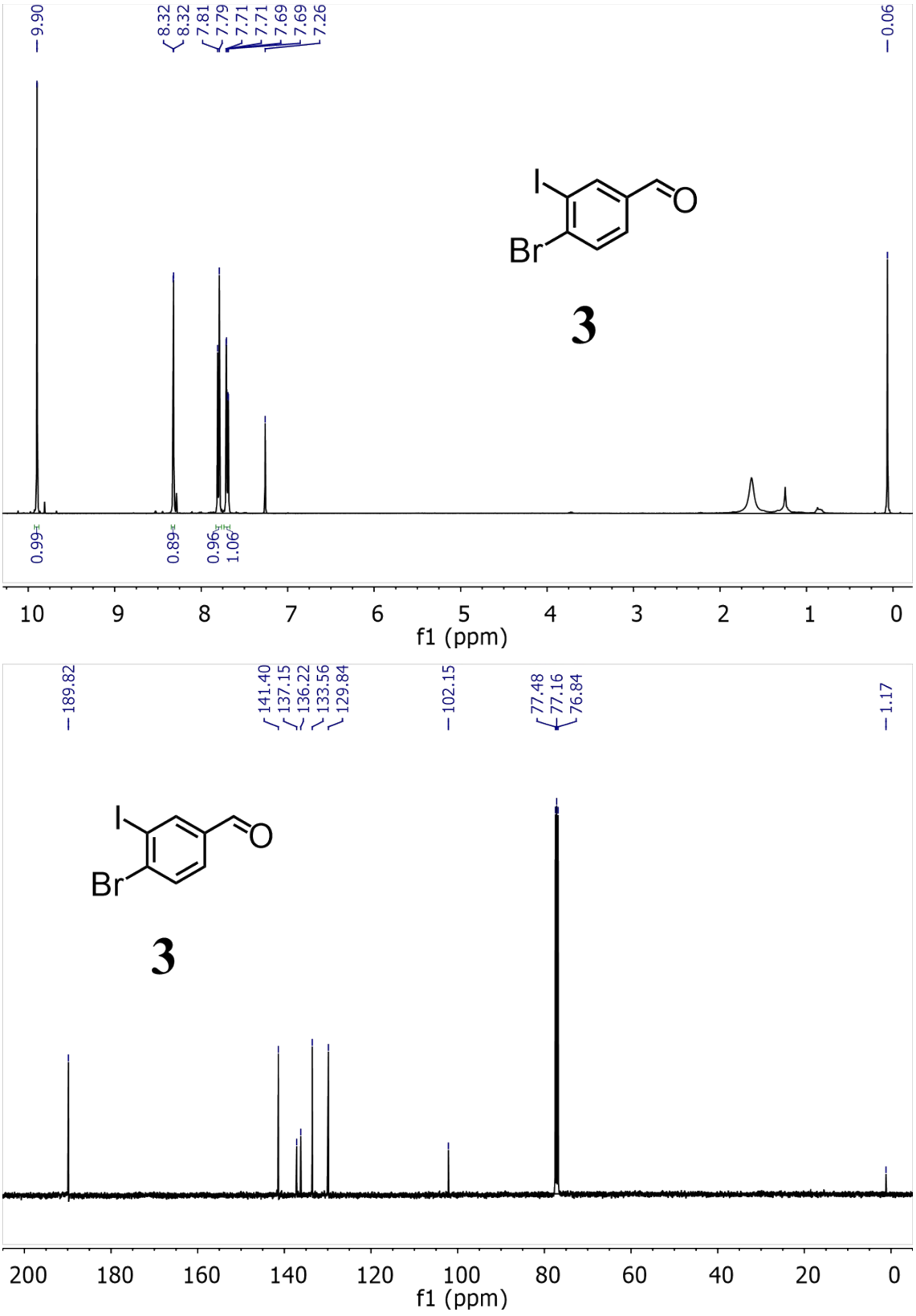


Figure S3. ^{1}H- and ^{13}C-NMR spectra of compound **3**.

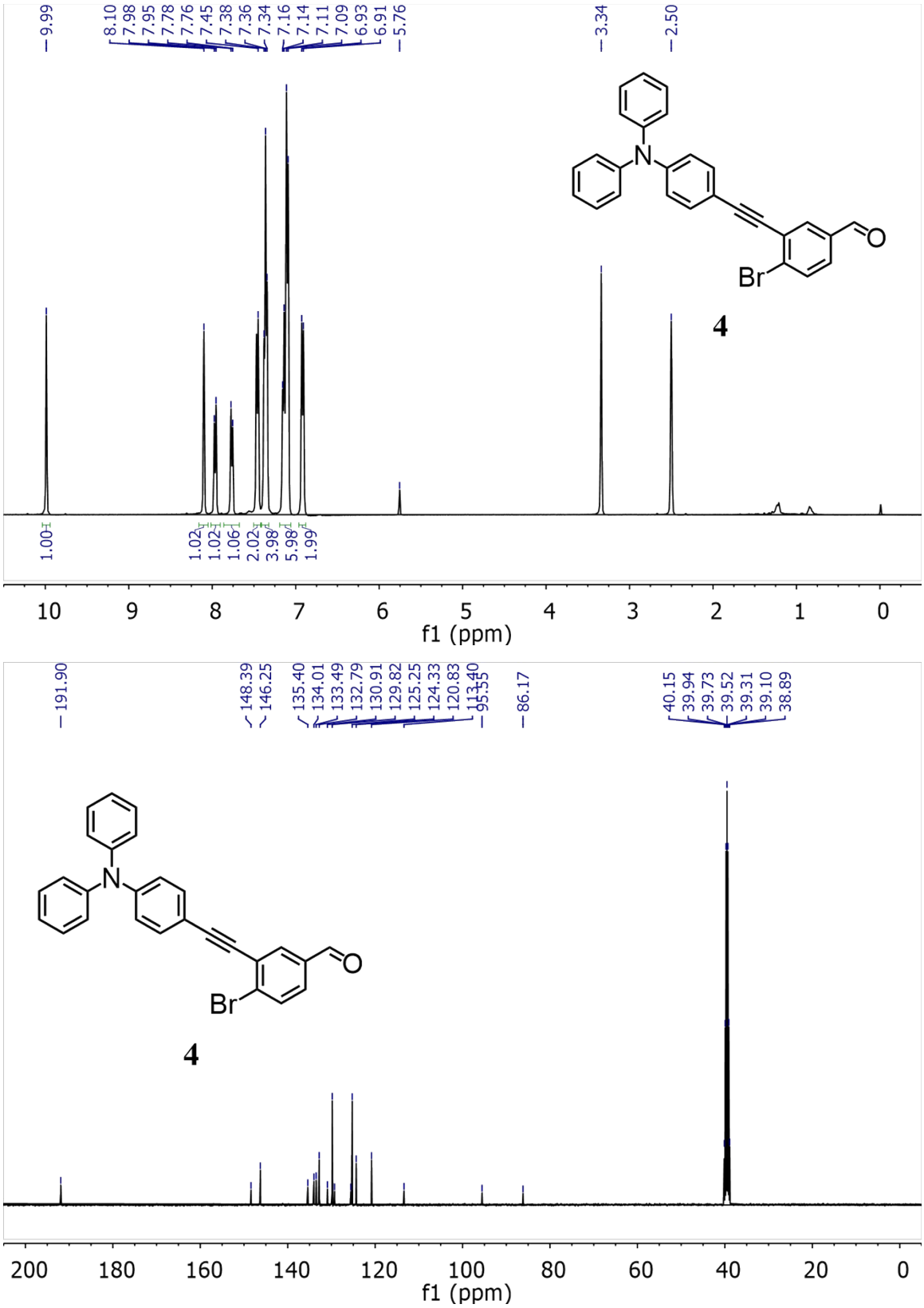


Figure S4. ^{1}H- and ^{13}C-NMR spectra of compound **4**.

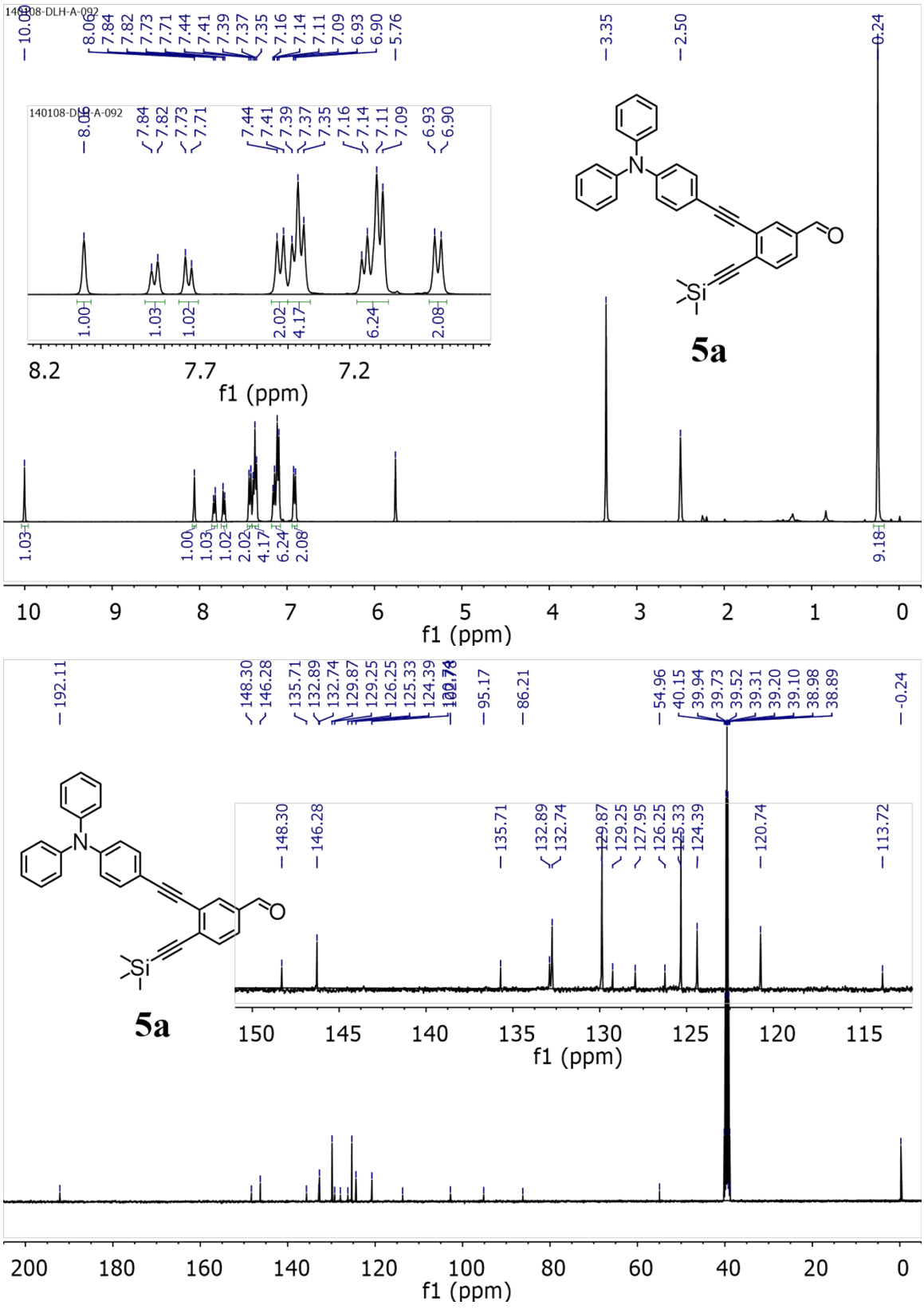


Figure S5. ^{1}H- and ^{13}C-NMR spectra of compound **5a**.

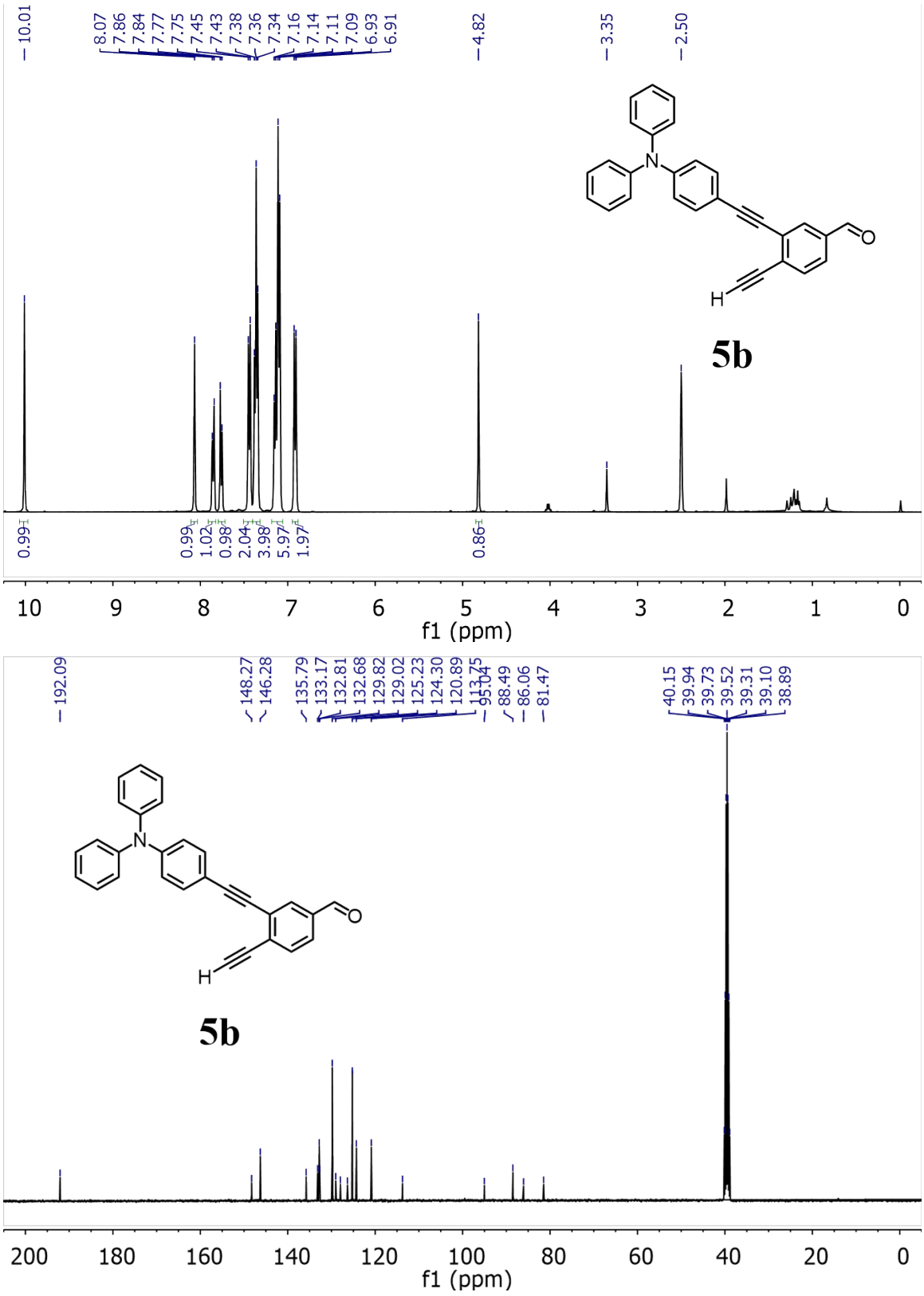


Figure S6. ^{1}H- and ^{13}C-NMR spectra of compound **5b**.

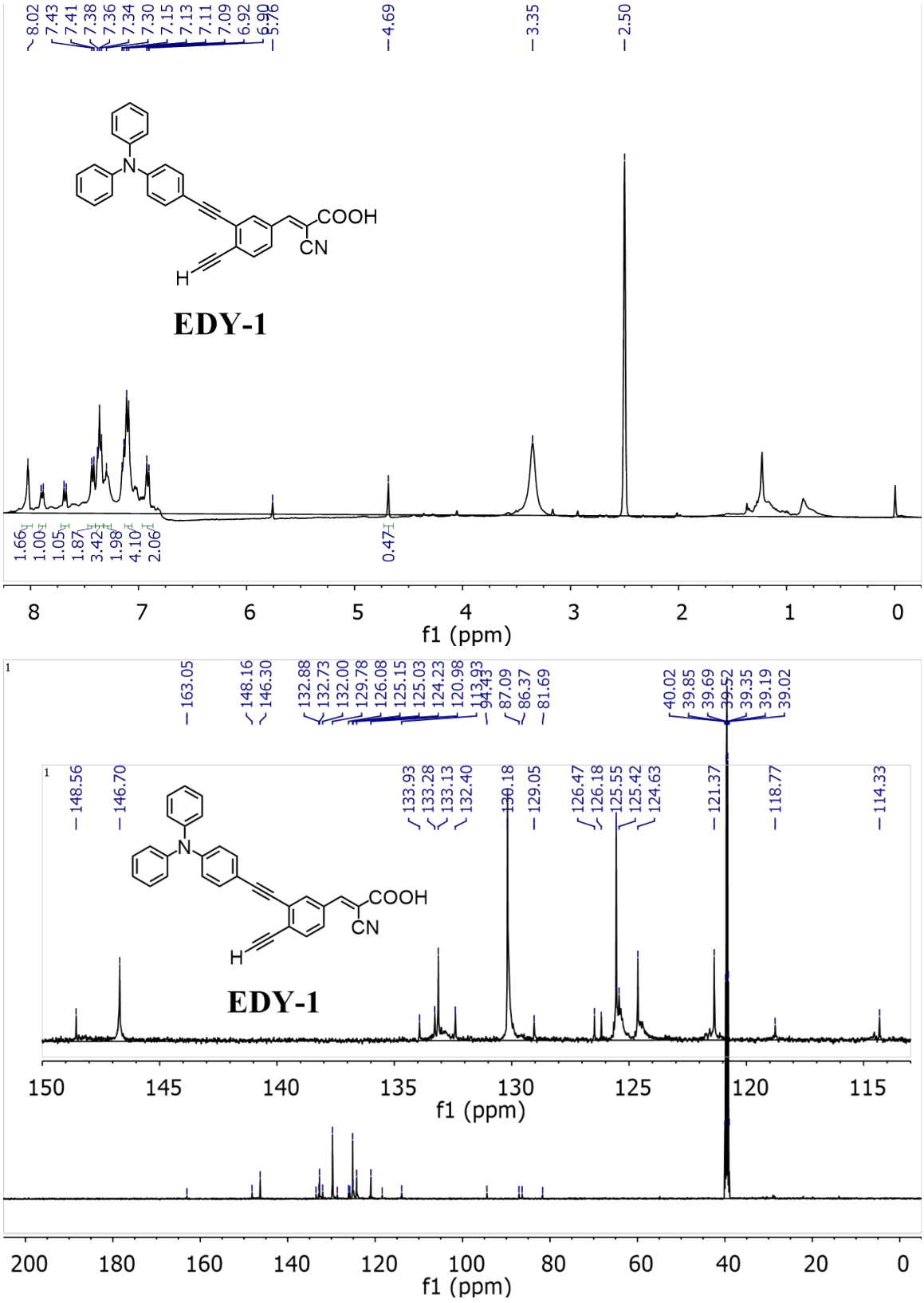


Figure S7. ^{1}H- and ^{13}C-NMR spectra of compound **EDY-1**.

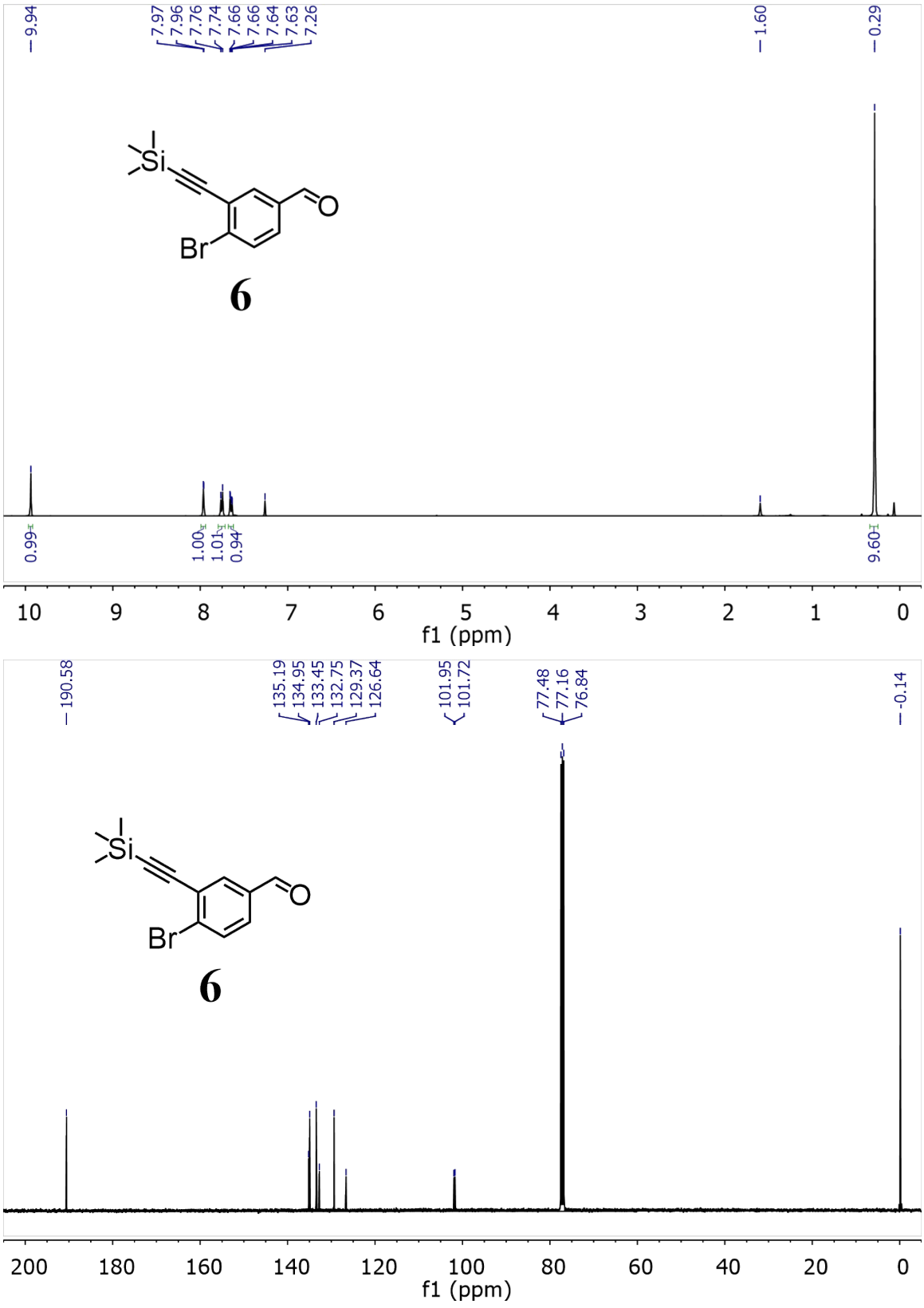


Figure S8. ^{1}H- and ^{13}C-NMR spectra of compound **6**.

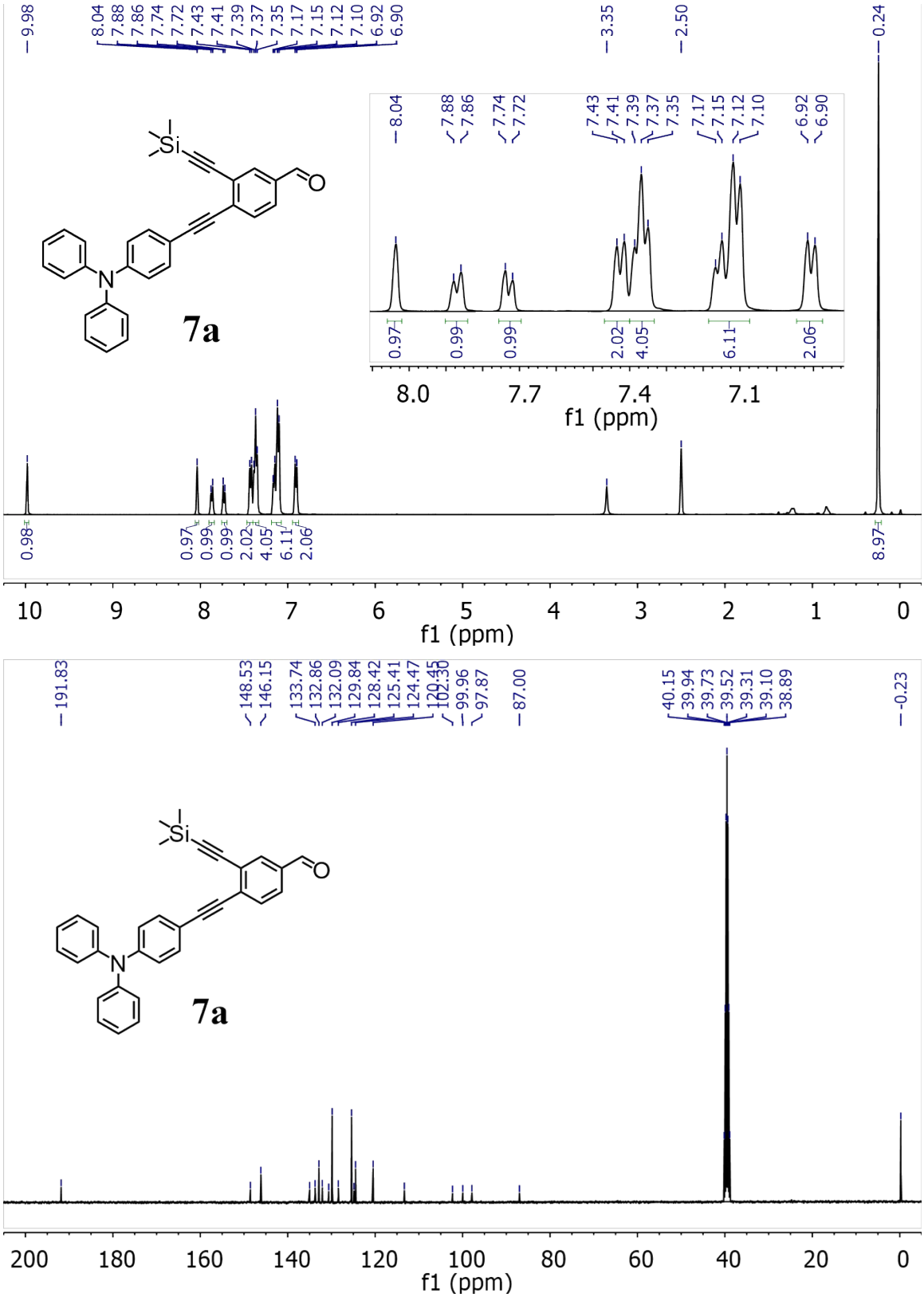


Figure S9. ^{1}H- and ^{13}C-NMR spectra of compound **7a**.

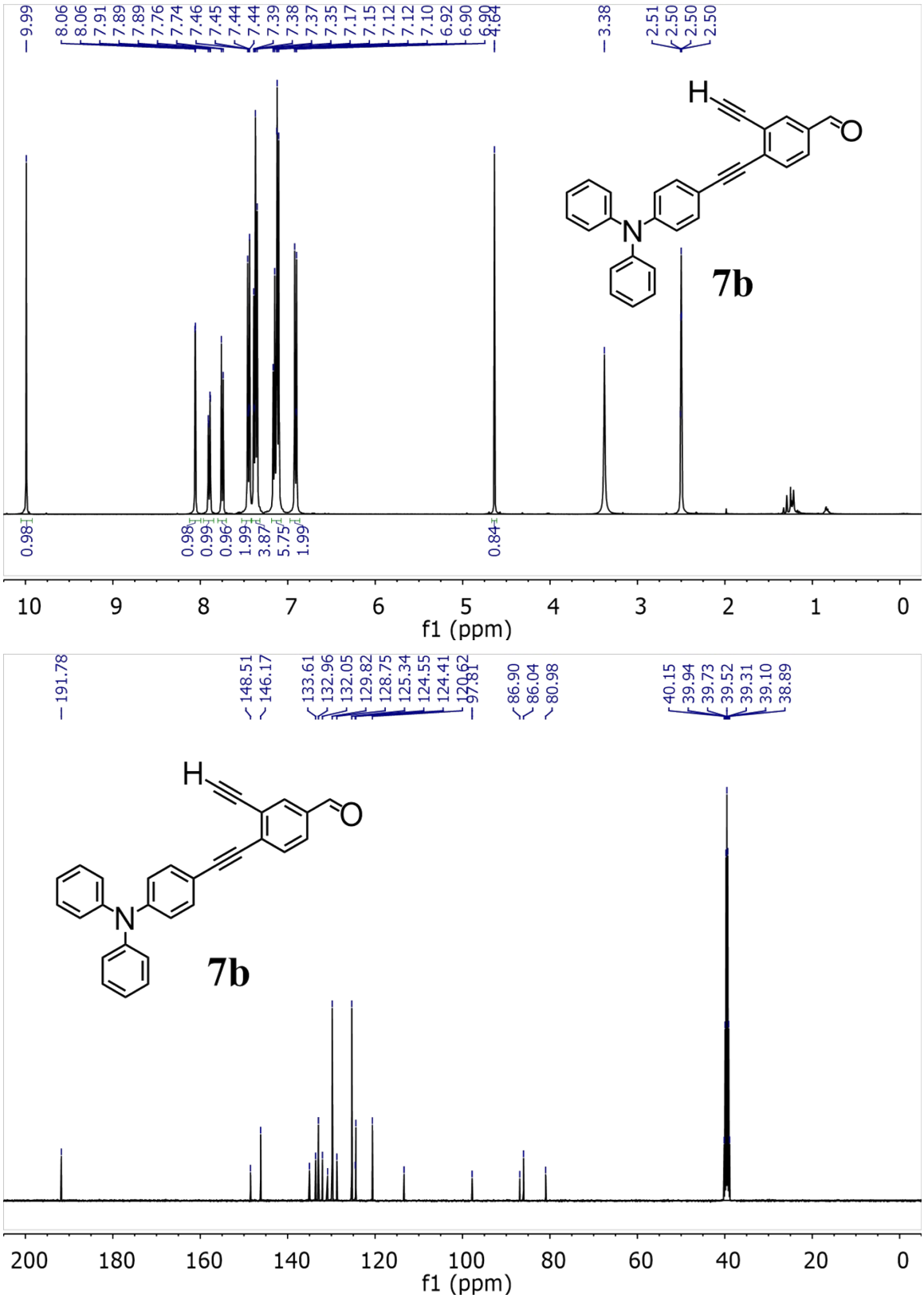


Figure S10. ^{1}H- and ^{13}C-NMR spectra of compound **7b**.

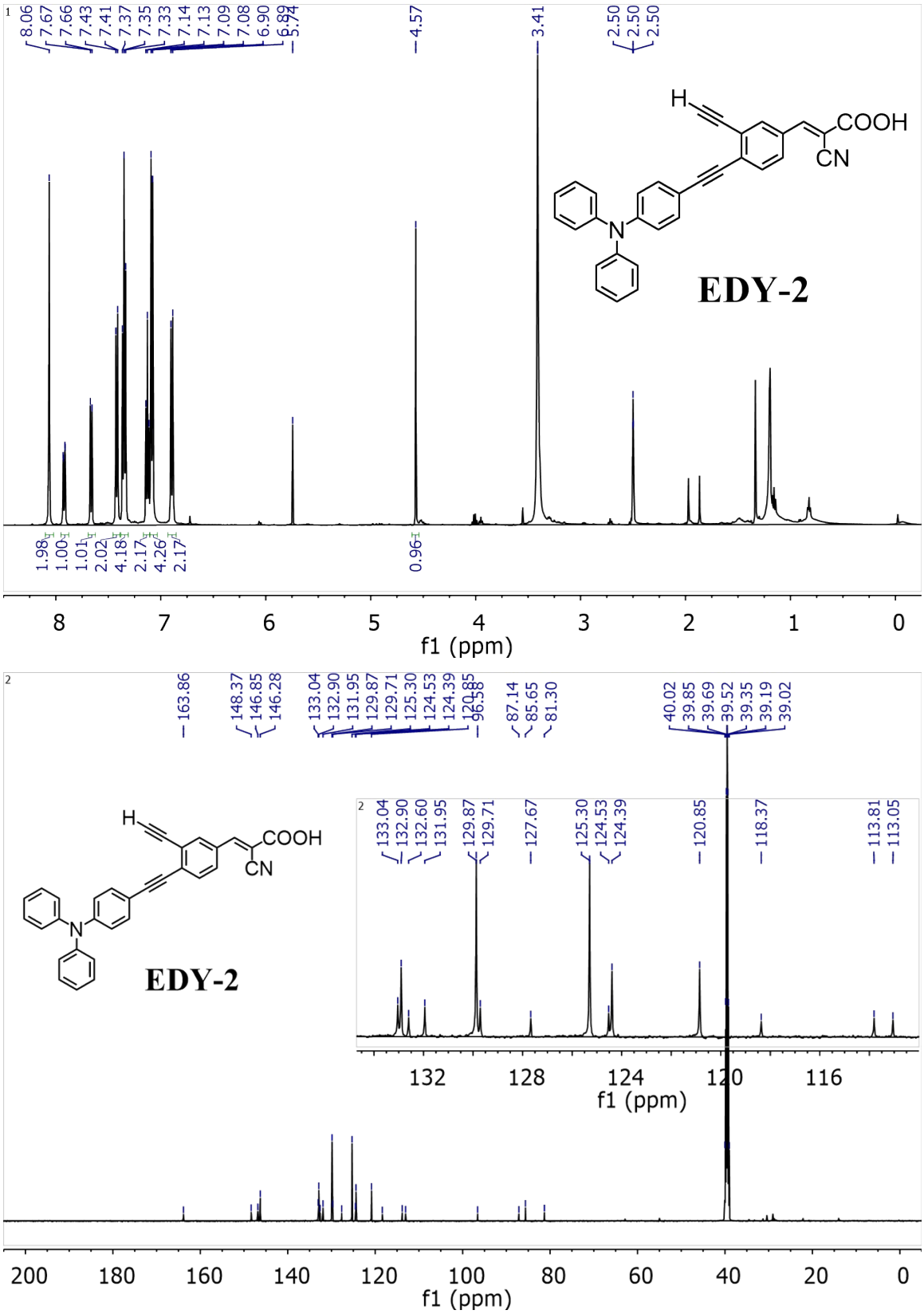


Figure S11. ^{1}H- and ^{13}C-NMR spectra of compound **EDY-2**.

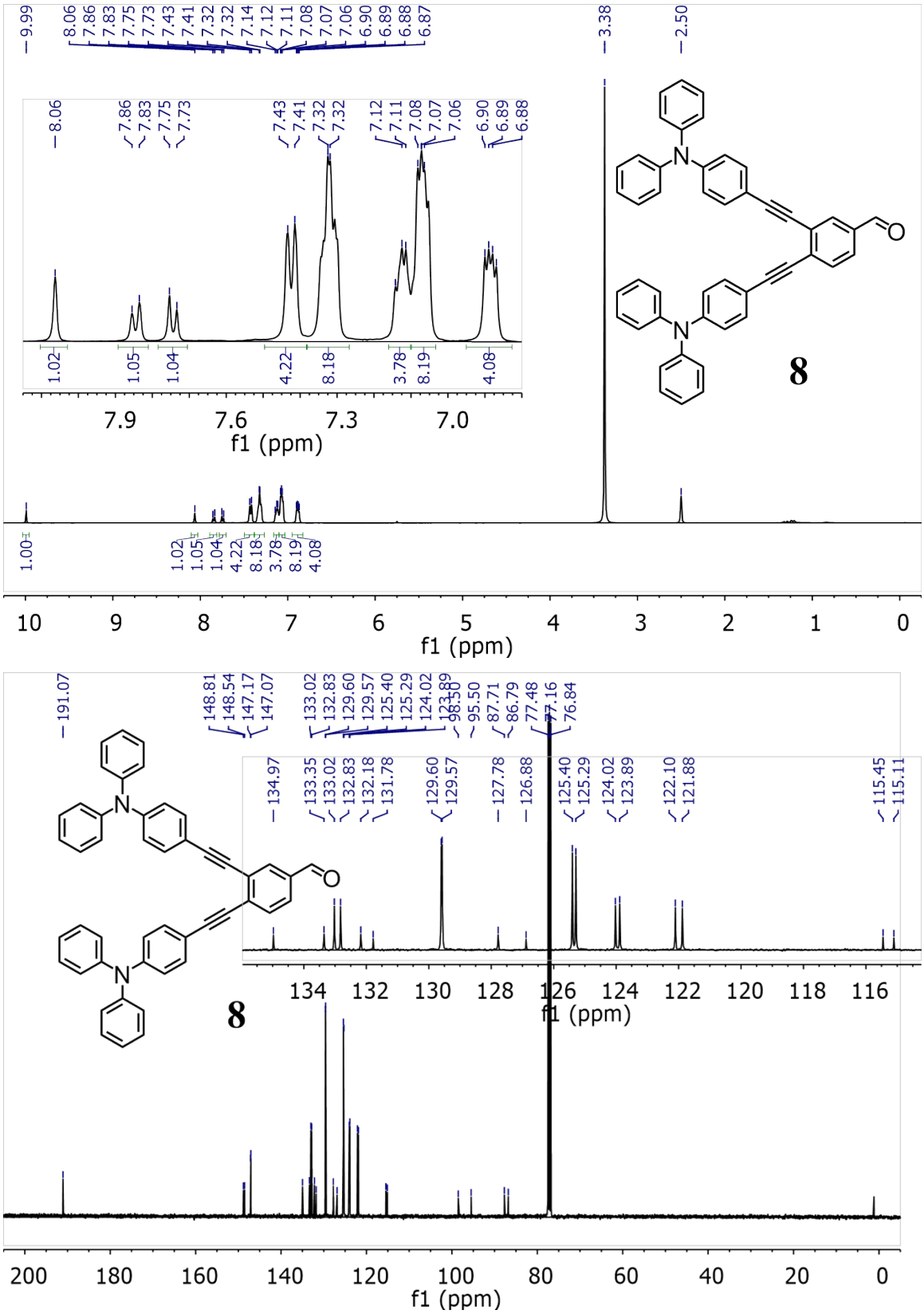


Figure S12. ^{1}H- and ^{13}C-NMR spectra of compound **8**.

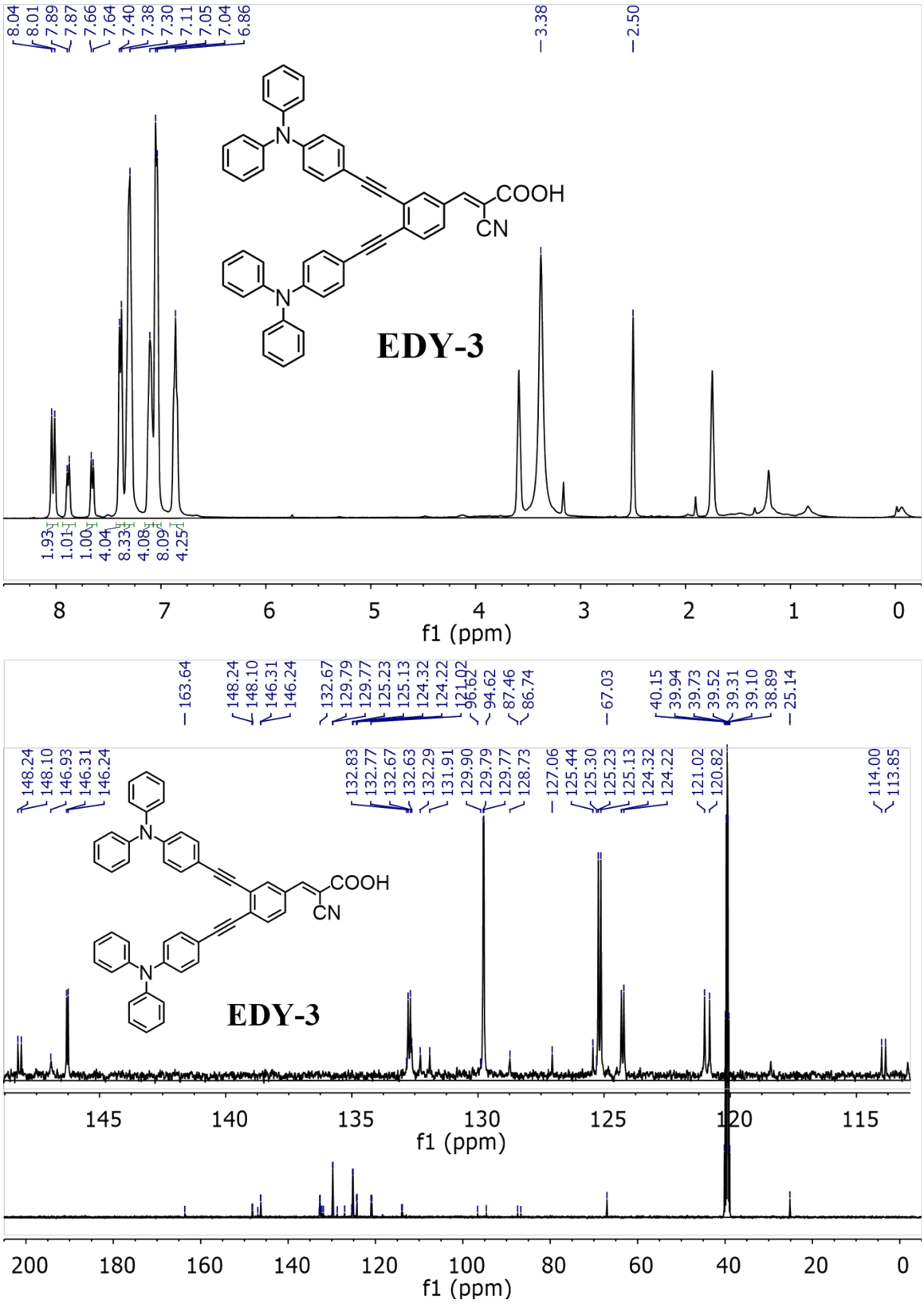


Figure S13. ^{1}H- and ^{13}C-NMR spectra of compound **EDY-3**.

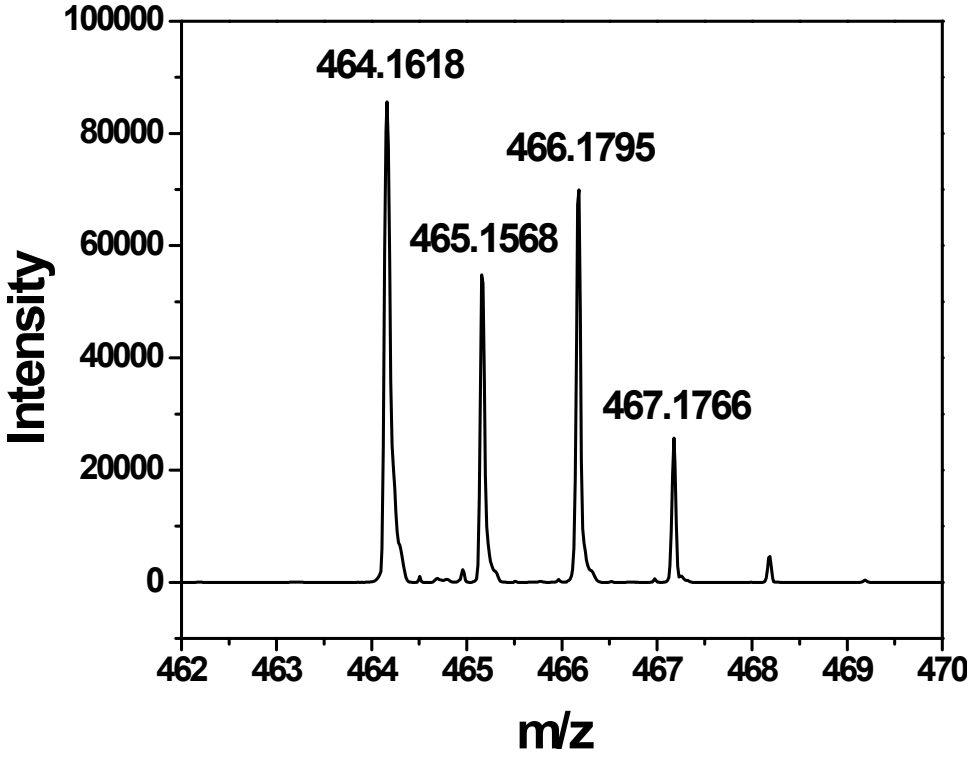


Figure S14. MALDI-TOF Mass spectrum of compound **EDY-1**.

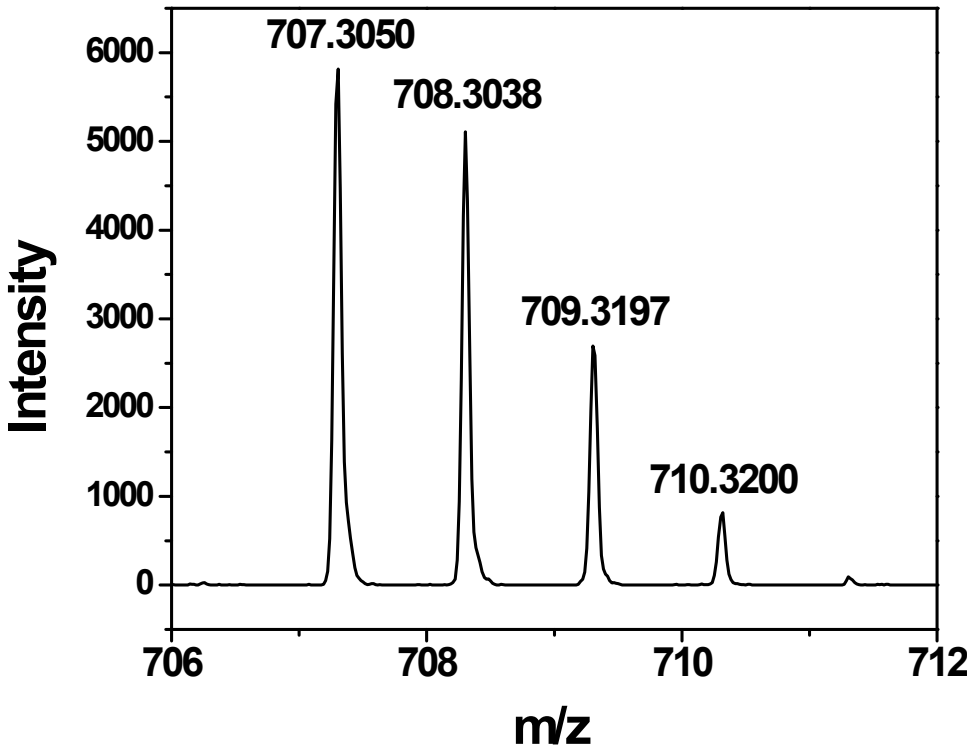


Figure S15. MALDI-TOF Mass spectrum of compound **EDY-3**.