

Electronic Supplementary Information for

Water-soluble copolymeric materials: the switchable NIR two-photon fluorescence imaging agents for living cancer cells

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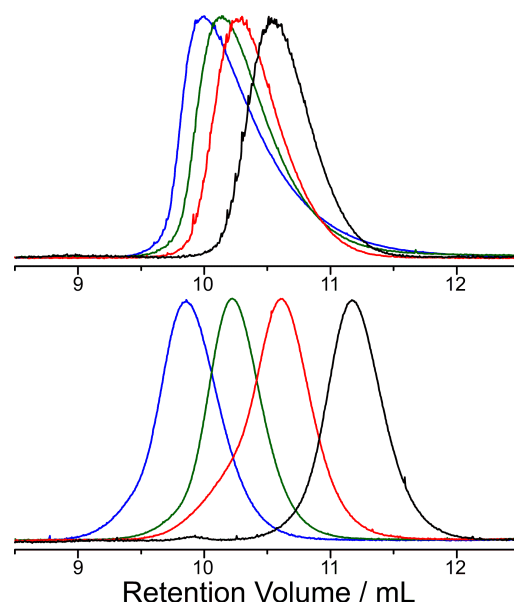


Figure S1. Normalized GPC curves of PNB-Boc-NH_n (bottom) and PNB-P3_n (top) homopolymers, the degree of polymerization is 25 (black), 50 (red), 75 (green) and 100 (blue), respectively.

Table S1. GPC data for PNB-Boc-NH_n and PNB-P3_n homopolymers.

Polymer ^a	[M]/[C]	M _n /kDa	M _w /kDa	PDI
PNB-Boc-NH ₂₅	25	8.0	9.0	1.13
PNB-Boc-NH ₅₀	50	18.6	23.7	1.27
PNB-Boc-NH ₇₅	75	24.8	27.9	1.13
PNB-Boc-NH ₁₀₀	100	35.1	39.1	1.11
PNB-P3 ₂₅	25	14.8	17.0	1.15
PNB-P3 ₅₀	50	33.2	38.9	1.17
PNB-P3 ₇₅	75	58.5	71.0	1.21
PNB-P3 ₁₀₀	100	77.8	103	1.32

^aDetermined by GPC using a LS detector in THF at 298 K.

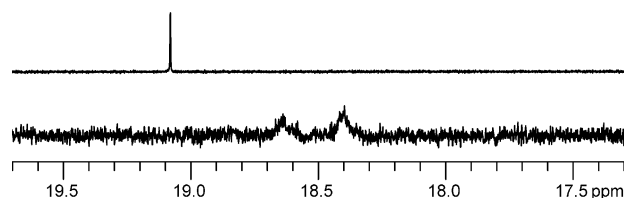


Figure S2. Carbene ¹H NMR signals for Grubbs' third-generation initiator (top), and during the polymerizations of NB-P3 monomer (bottom) in CDCl₃.

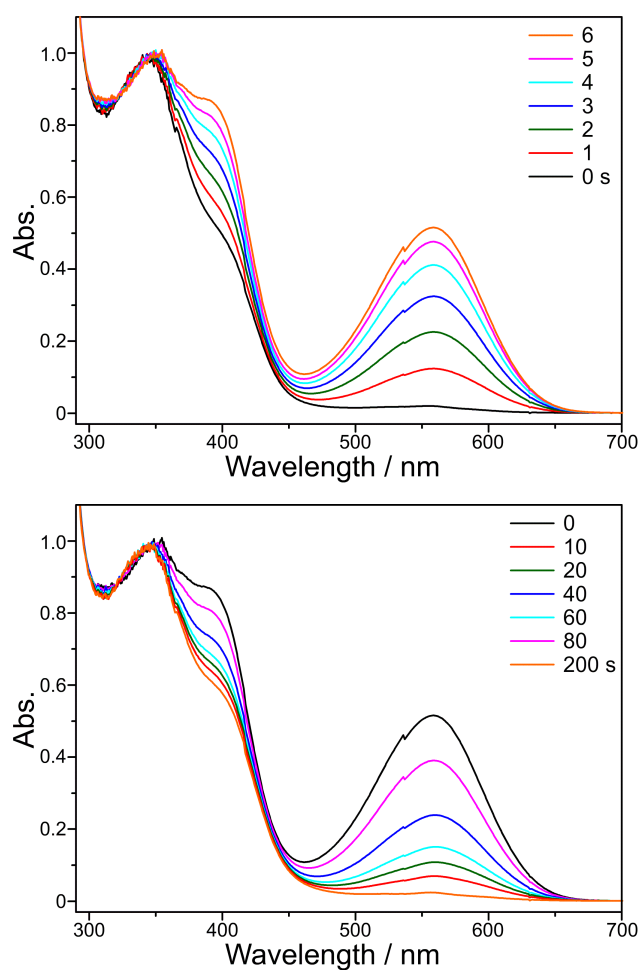


Figure S3. UV-Vis absorption spectra for PNB-SP₂₀-co-(NH₂·HCl)₂₀-co-P3₆₀ copolymer upon UV @ 365 nm (top) and visible-light @ 530 nm (bottom) irradiation with the concentration of 0.082 mg·mL⁻¹ in 10 mM PBS buffer.

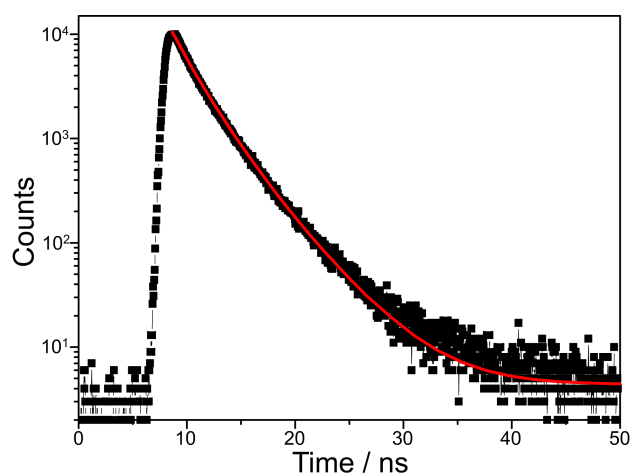


Figure S4. The decay profile of fluorescence @ 638 nm for PNB-SP_{20-co}-(NH₂·HCl)_{20-co}-P3₆₀ copolymer with the concentration of 0.082 mg·mL⁻¹ in 10 mM PBS buffer, it gives the lifetime of 2.87 ns.

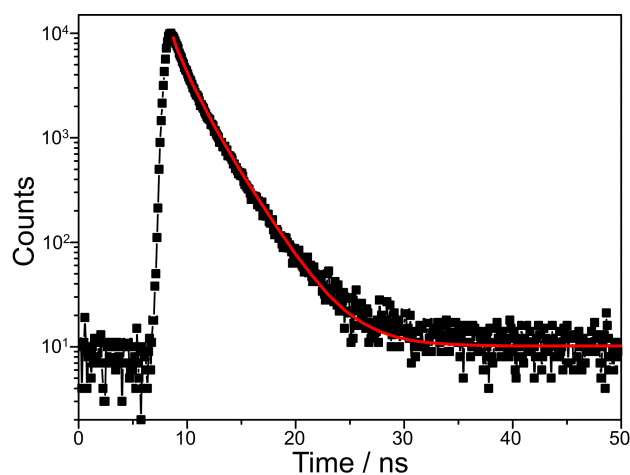


Figure S5. The decay profile of fluorescence @ 636 nm for PNB-SP_{20-co}-(Boc-NH)_{20-co}-P3₆₀ copolymer with the concentration of 0.087 mg·mL⁻¹ in 10 mM PBS buffer, it gives the lifetime of 1.73 ns.

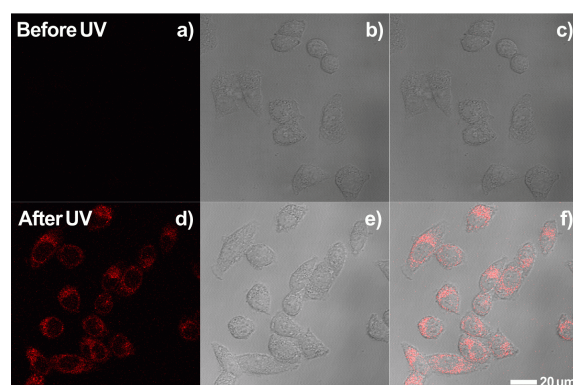


Figure S6. Single-photon fluorescence imaging of Bel-7402 cells incubated with 0.025 mg/mL PNB-SP_{20-co}-(NH₂·HCl)_{20-co}-P3₆₀ copolymer before (a-c) and after (d-f) 365-nm UV irradiation: dark field (a,d), bright field (b,e) and merged images (c,f).

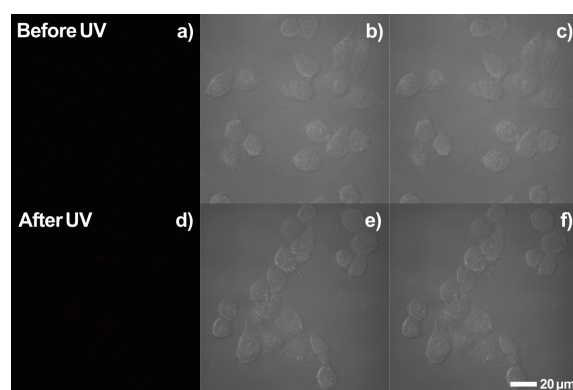


Figure S7. Single-photon fluorescence imaging of Bel-7402 cells incubated with 0.025 mg/mL PNB-SP_{20-co}-(NH₂·HCl)_{20-co}-P3₆₀ copolymer @ 4 °C before (a-c) and after (d-f) 365-nm UV irradiation: dark field (a,d), bright field (b,e) and merged images (c,f).

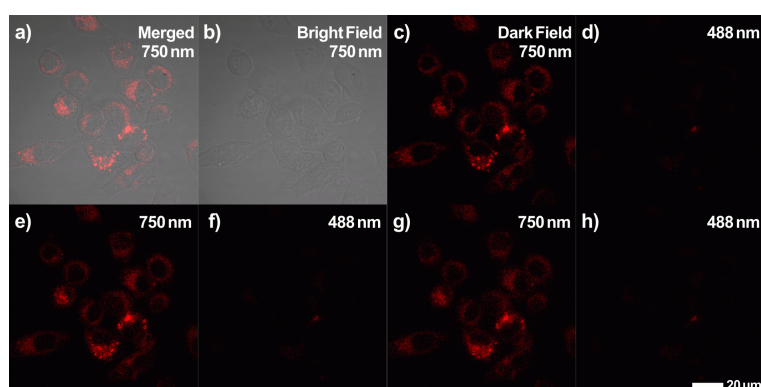


Figure S8 The switching of fluorescence imaging with alternating NIR two-photon (a-c,e,g) and visible single-photon (d,f,h) excitations for Bel-7402 cells.

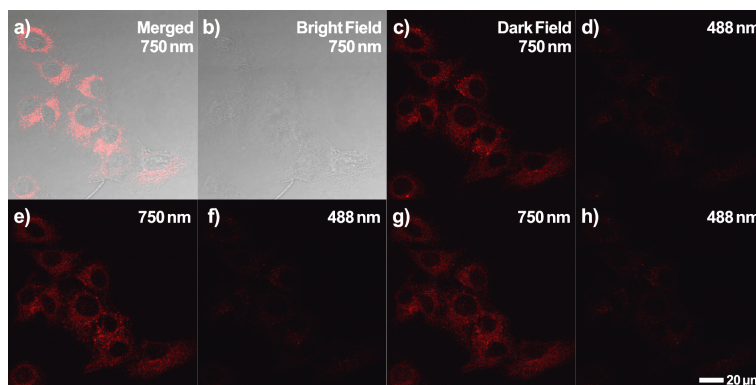


Figure S9 The switching of fluorescence imaging with alternating NIR two-photon (a-c,e,g) and visible single-photon (d,f,h) excitations for HepG2 cells.

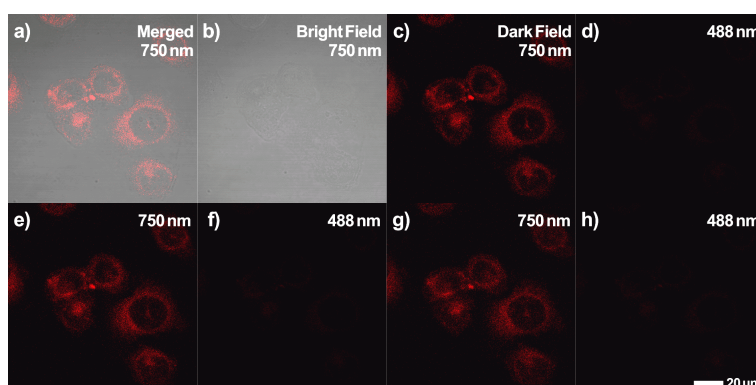


Figure S10 The switching of fluorescence imaging with alternating NIR two-photon (a-c,e,g) and visible single-photon (d,f,h) excitations for MCF-7 cells.

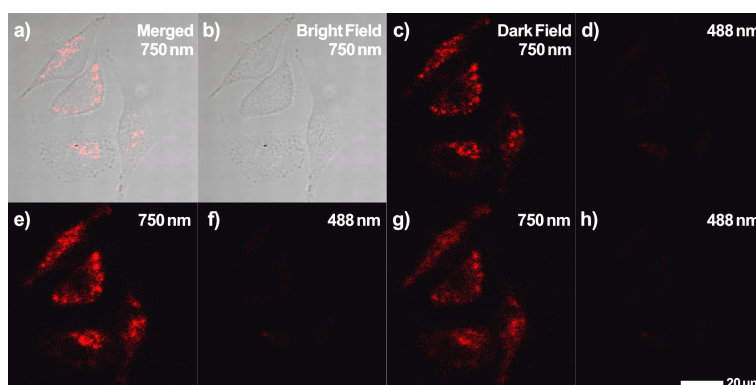


Figure S11 The switching of fluorescence imaging with alternating NIR two-photon (a-c,e,g) and visible single-photon (d,f,h) excitations for A549 cells.

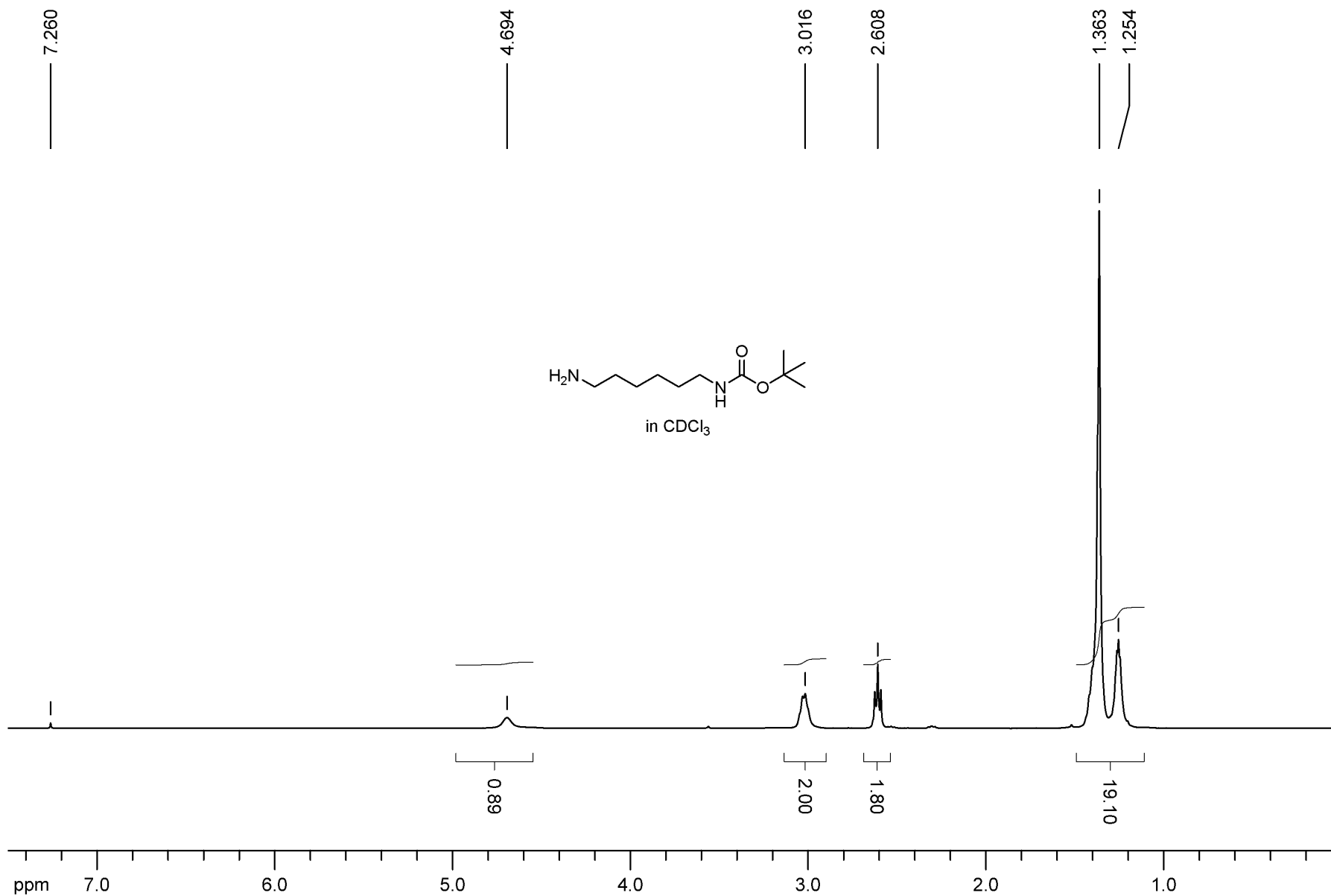


Figure S12. ^1H NMR spectrum for *N*-(*tert*-butoxycarbonyl)hexyl diamine in CDCl_3 .

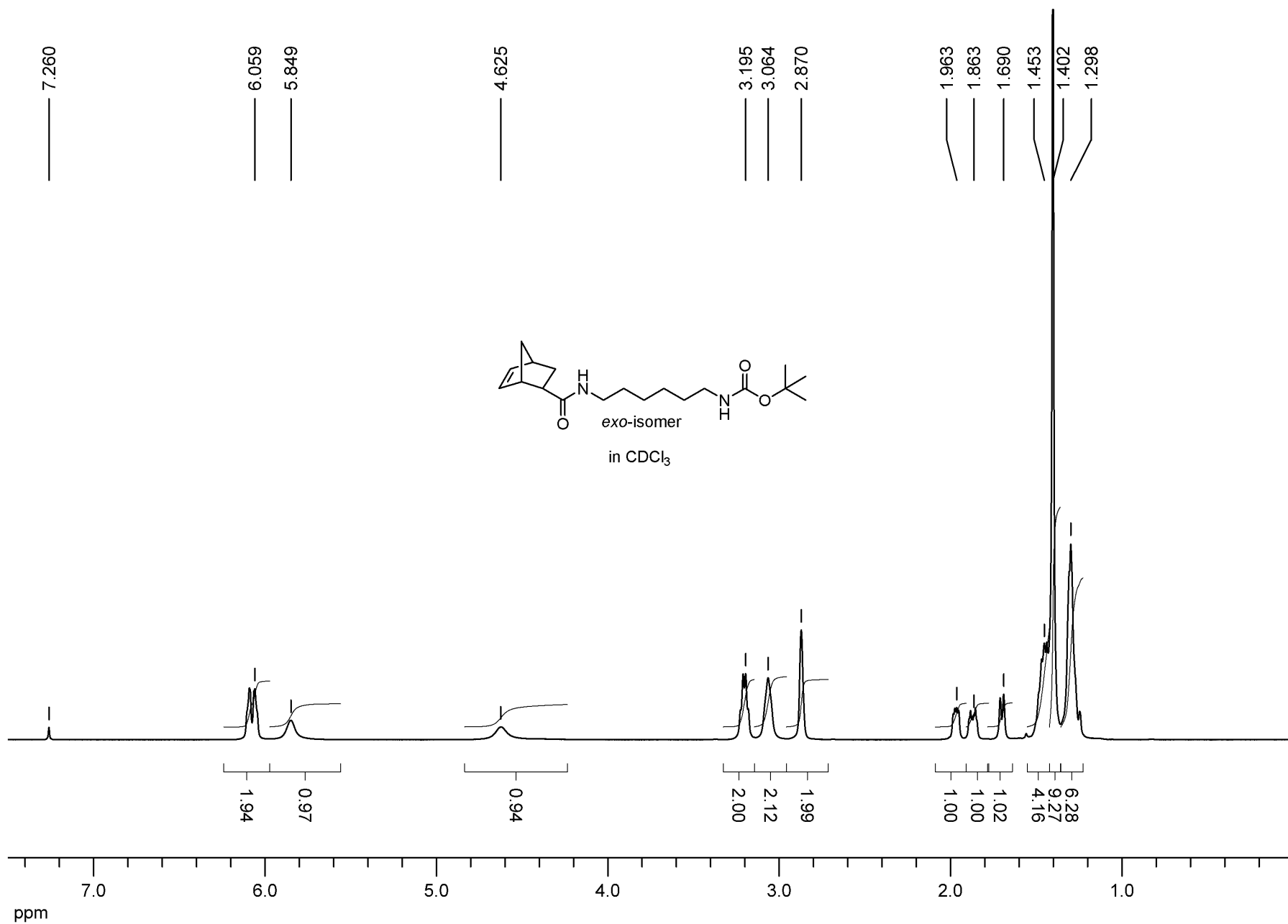


Figure S13. ^1H NMR spectrum for NB-Boc-NH monomer in CDCl_3 .

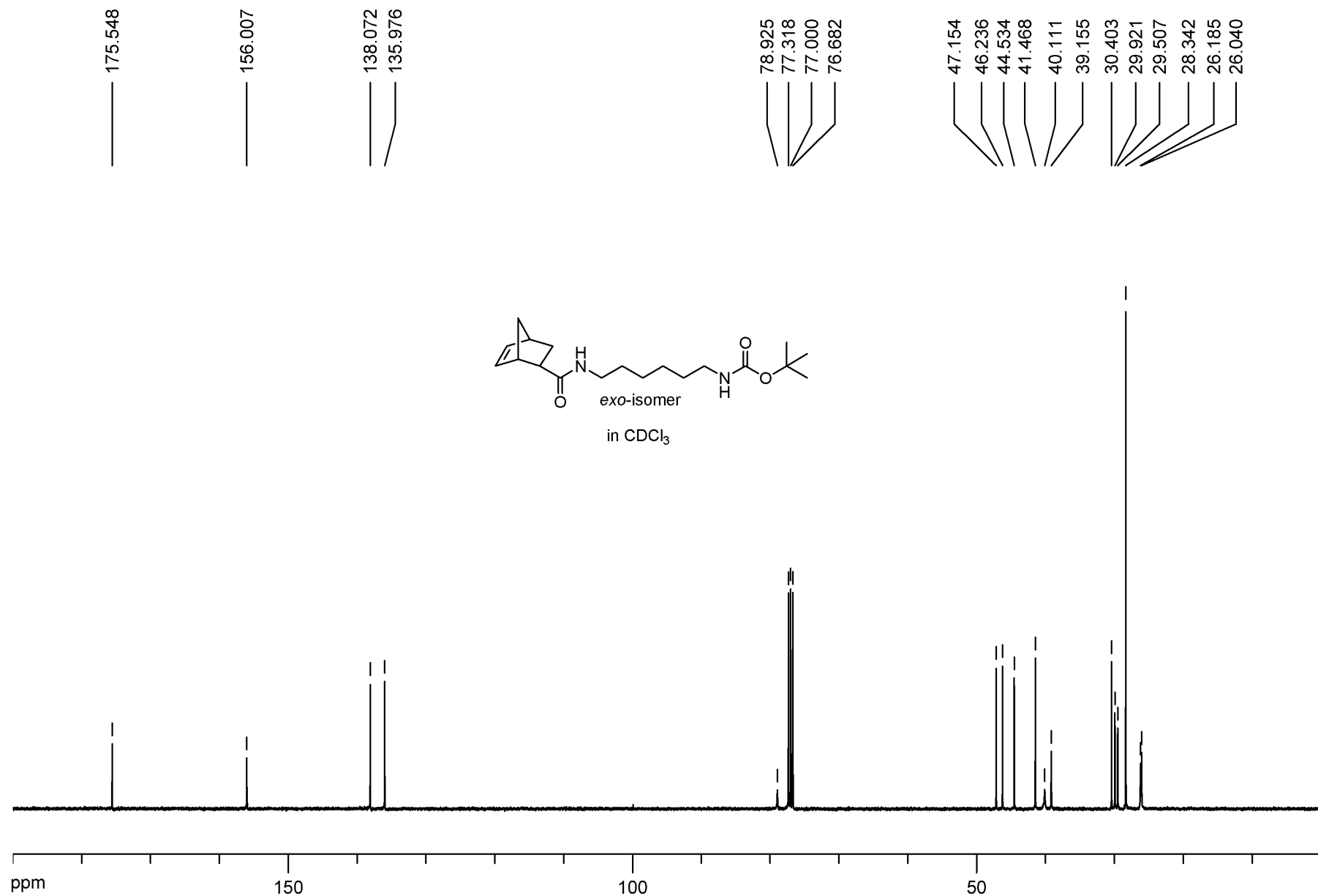


Figure S14. ¹³C{¹H} NMR spectrum for NB-Boc-NH monomer in CDCl₃.

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name 13010366_20130111_000003.d
Sample 20130111-3
Comment ESI Positive

Acquisition Date 1/11/2013 11:46:06 AM
Instrument Bruker Apex IV FTMS
Operator Peking University

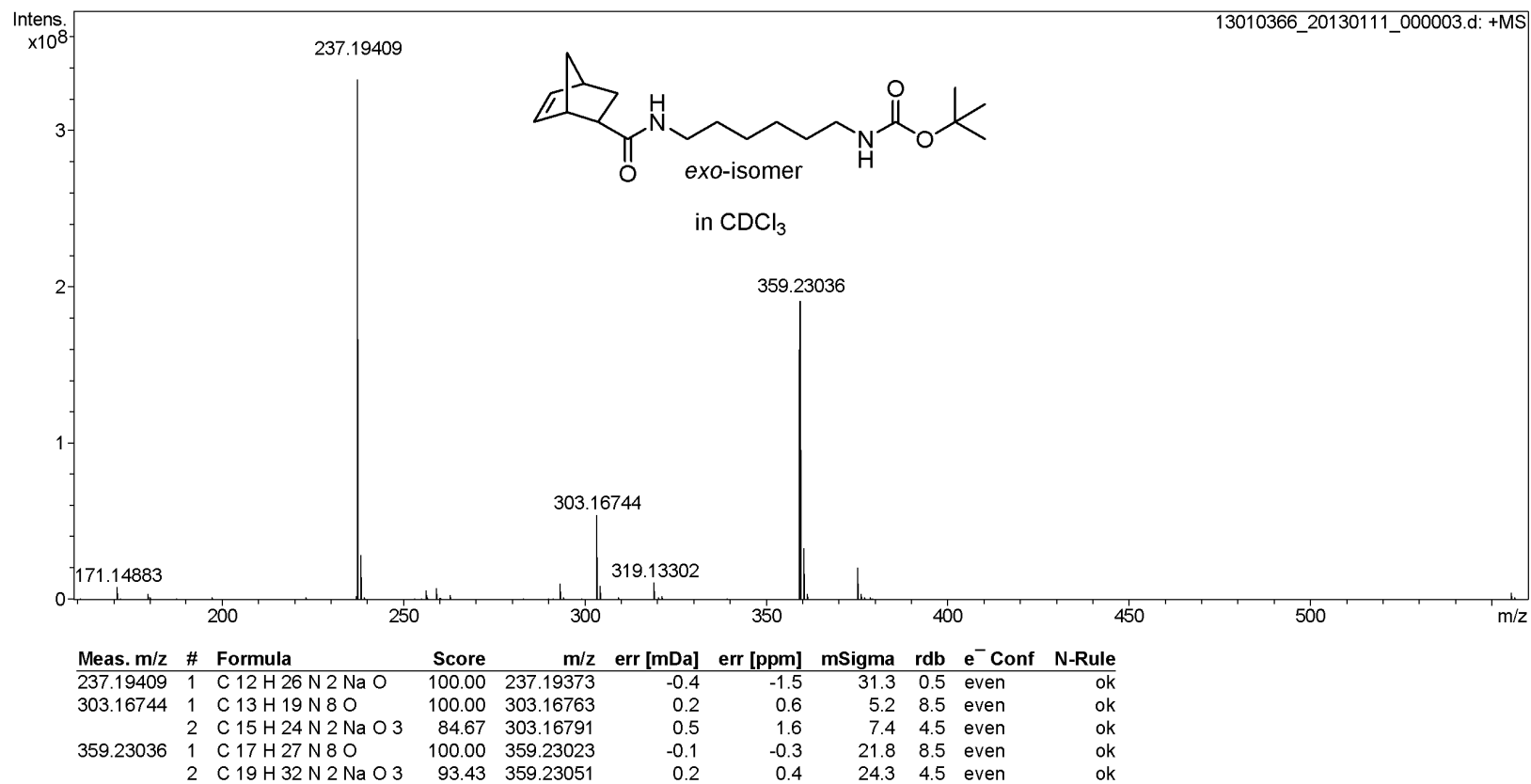


Figure S15. ESI-MS spectrum for NB-Boc-NH monomer.

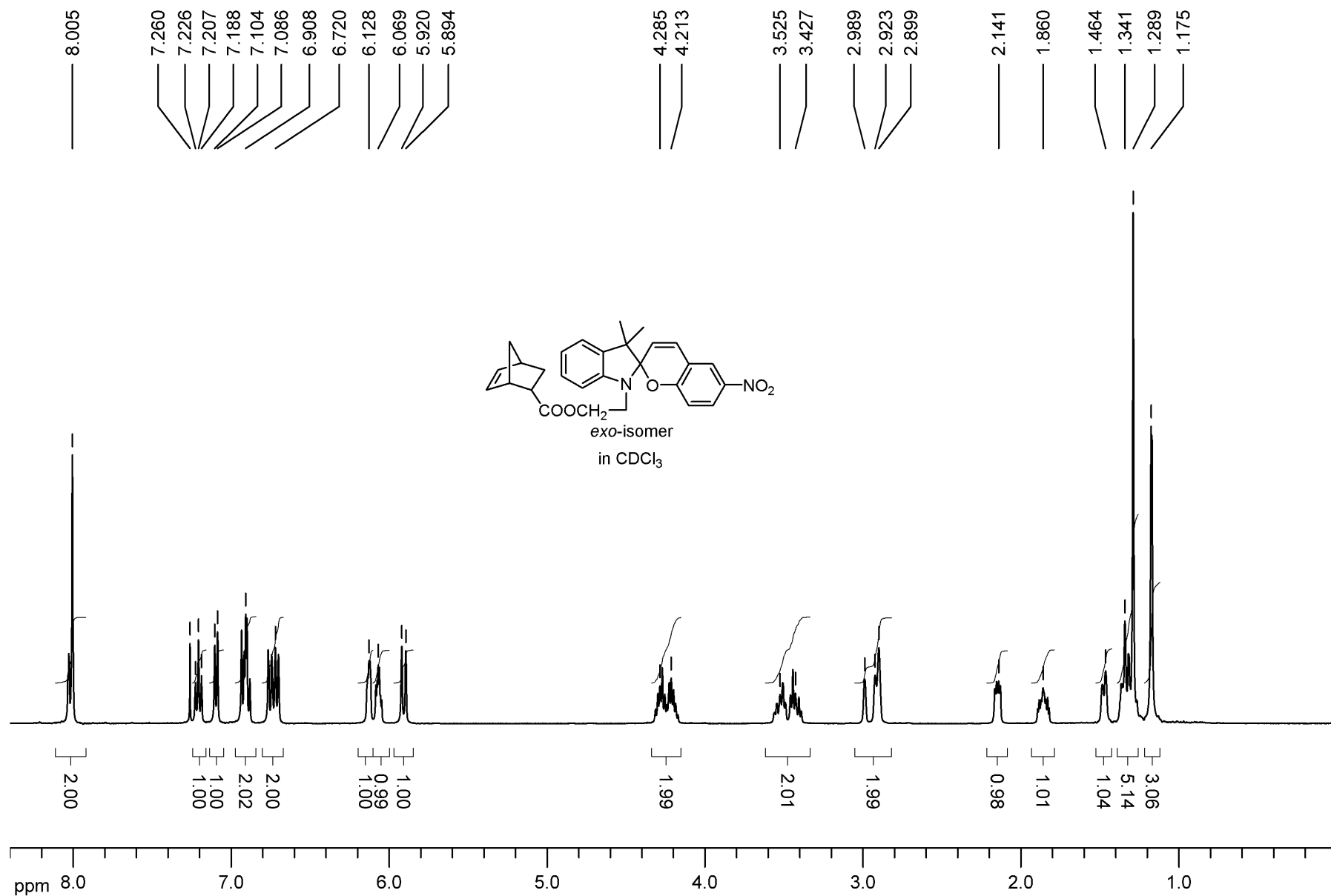


Figure S16. ^1H NMR spectrum for NB-SP monomer in CDCl_3 .

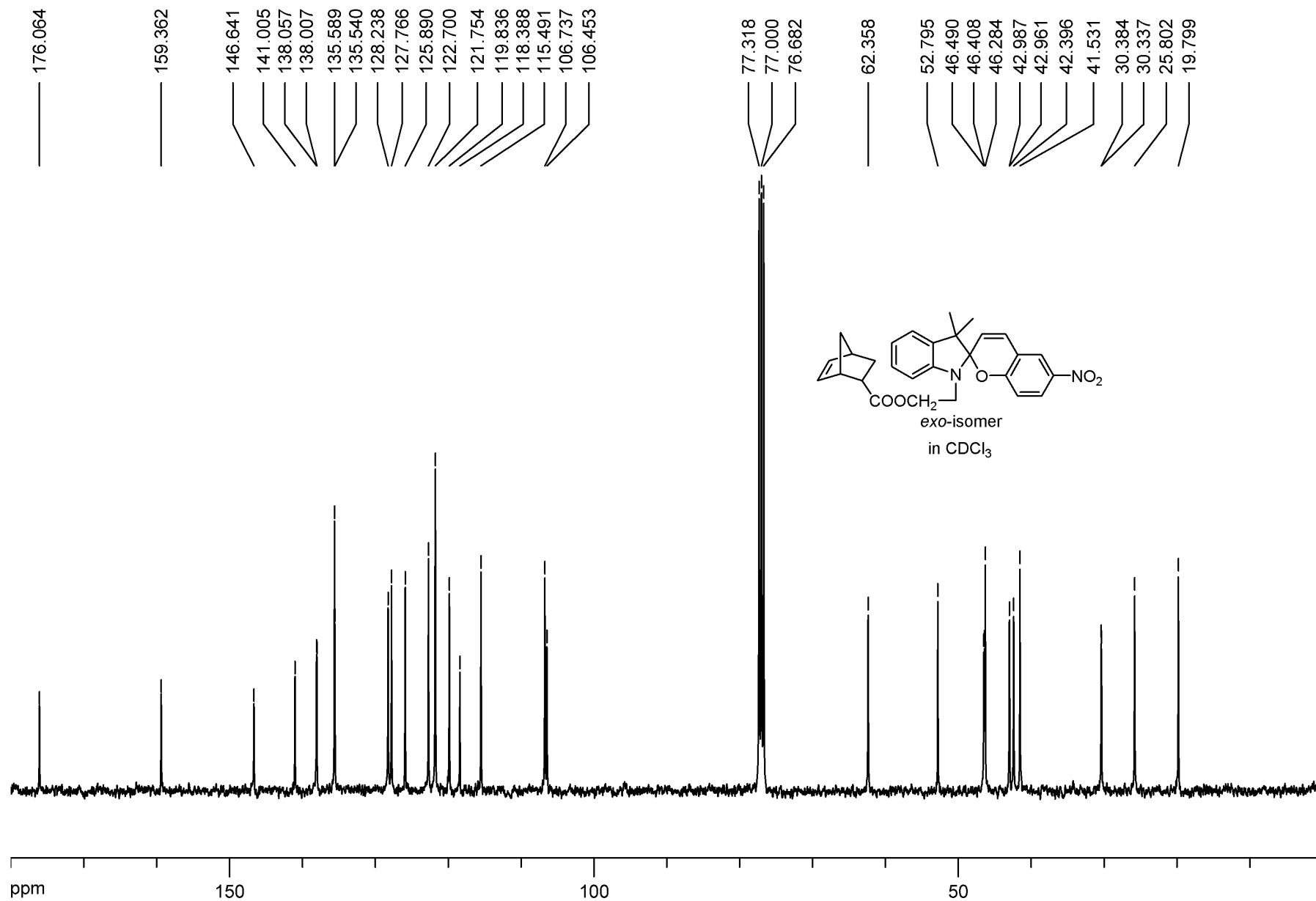


Figure S17. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for NB-SP monomer in CDCl_3 .

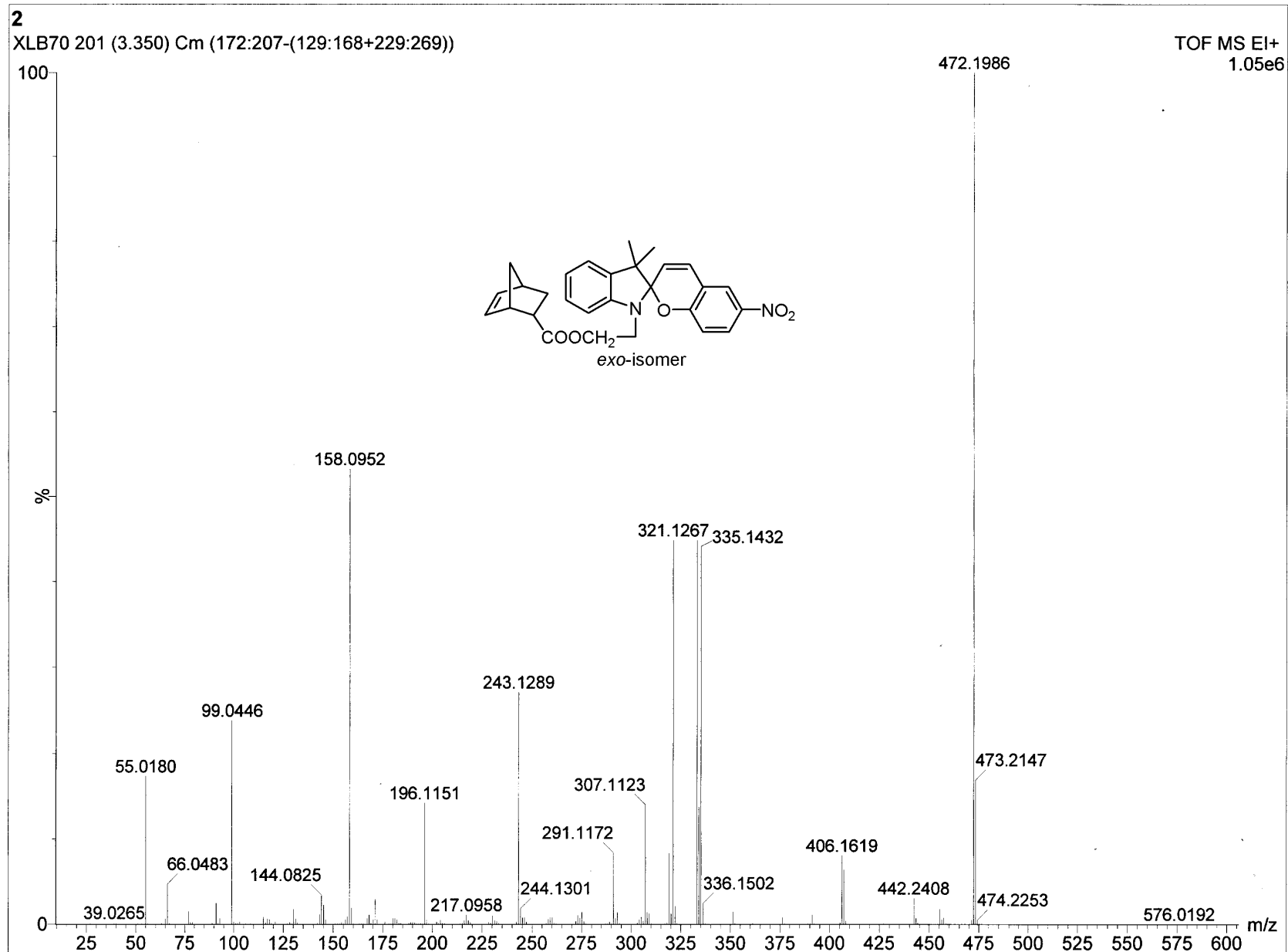


Figure S18. EI-MS spectrum for NB-SP monomer.

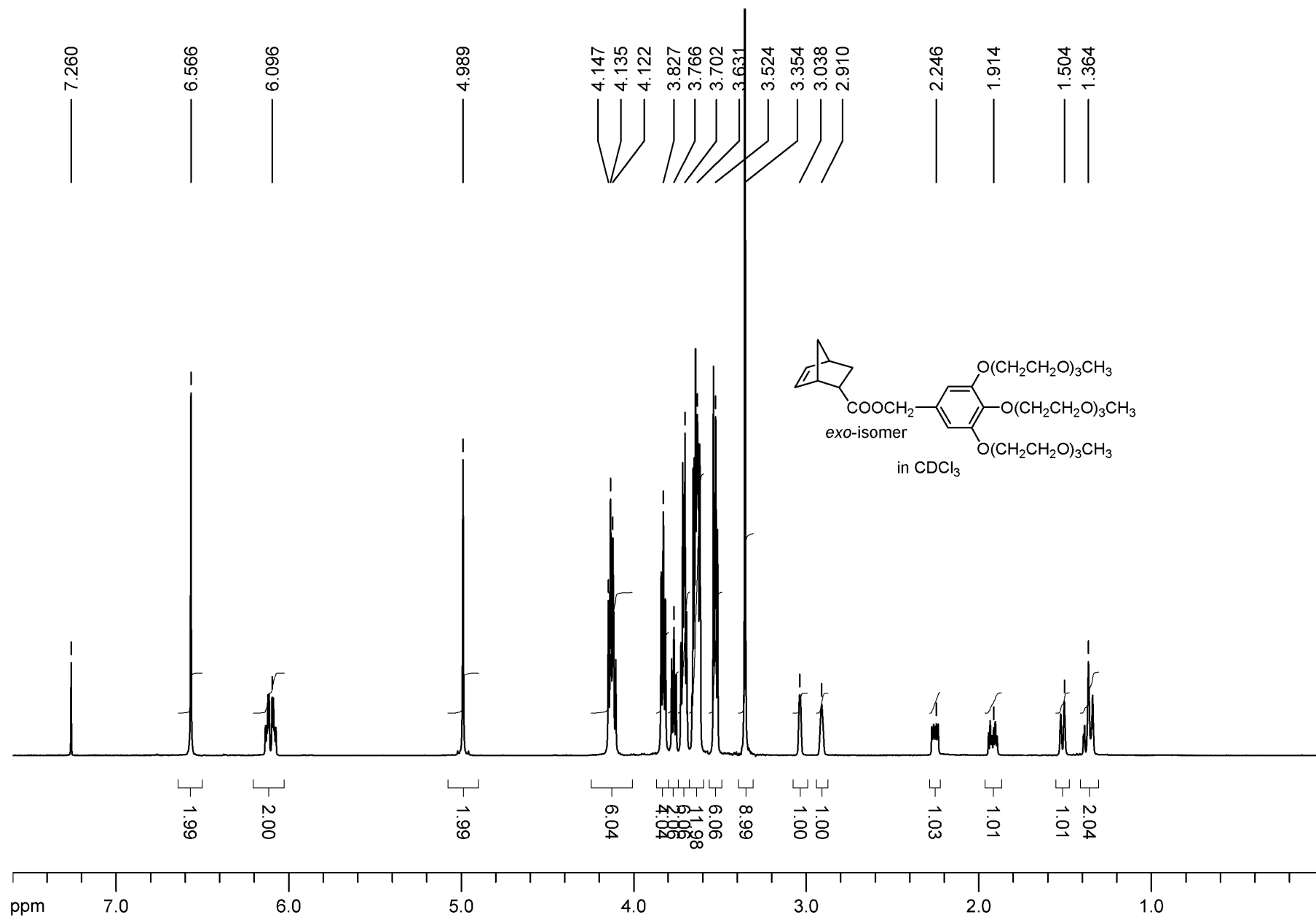


Figure S19. ^1H NMR spectrum for NB-P3 monomer in CDCl_3 .

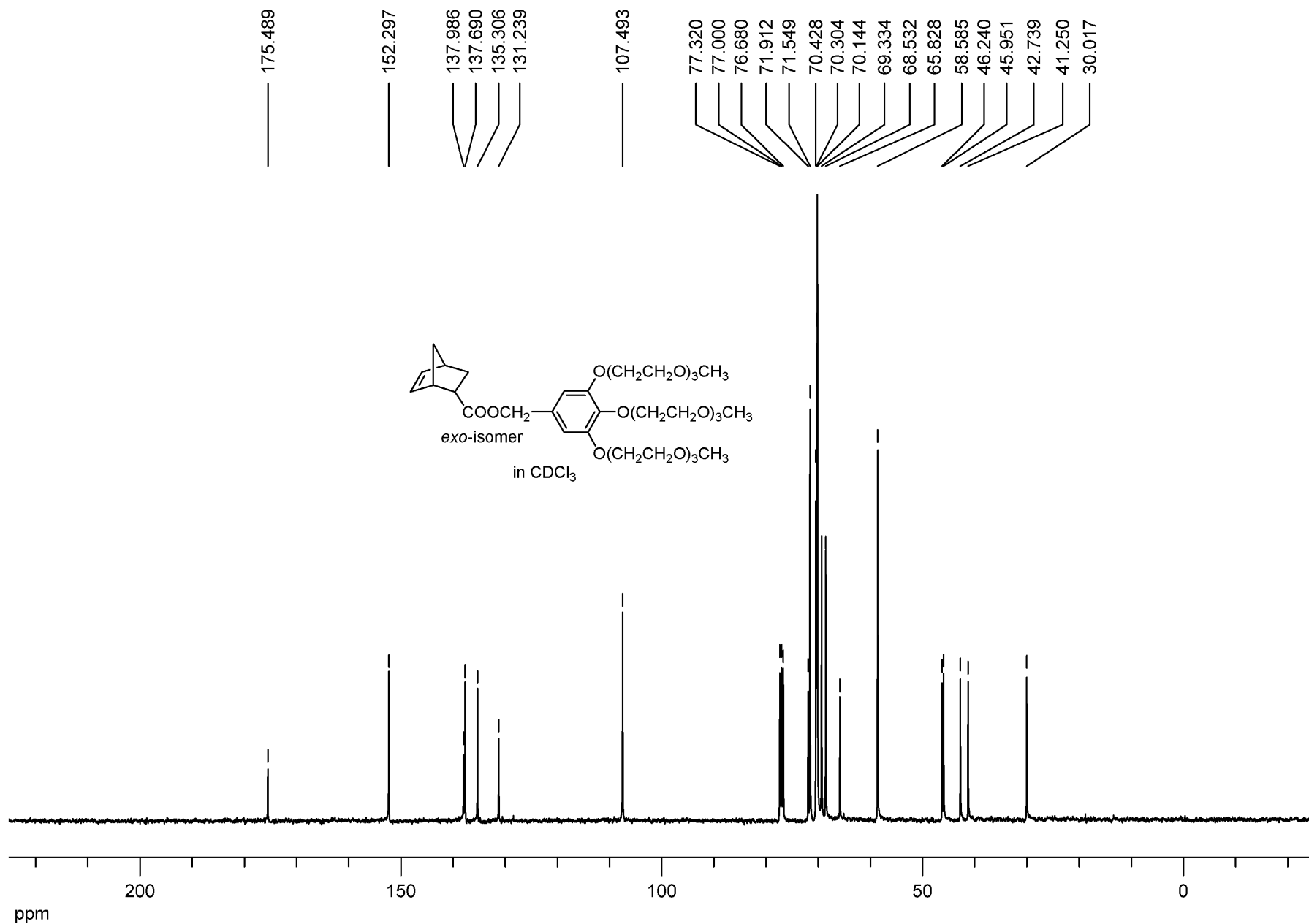


Figure S20. ¹³C{¹H} NMR spectrum for NB-P3 monomer in CDCl₃.

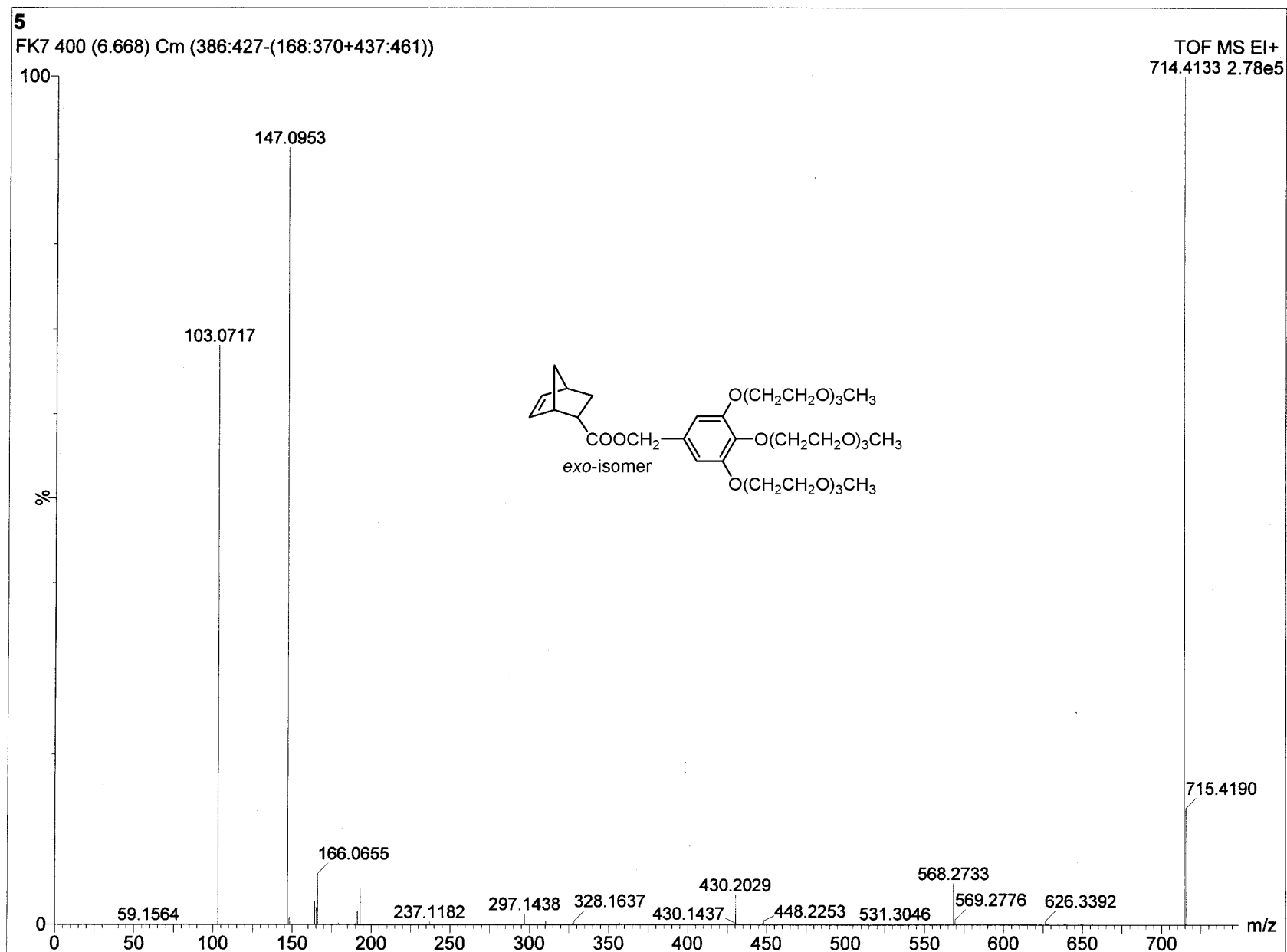


Figure S21. EI-MS spectrum for NB-P3 monomer.

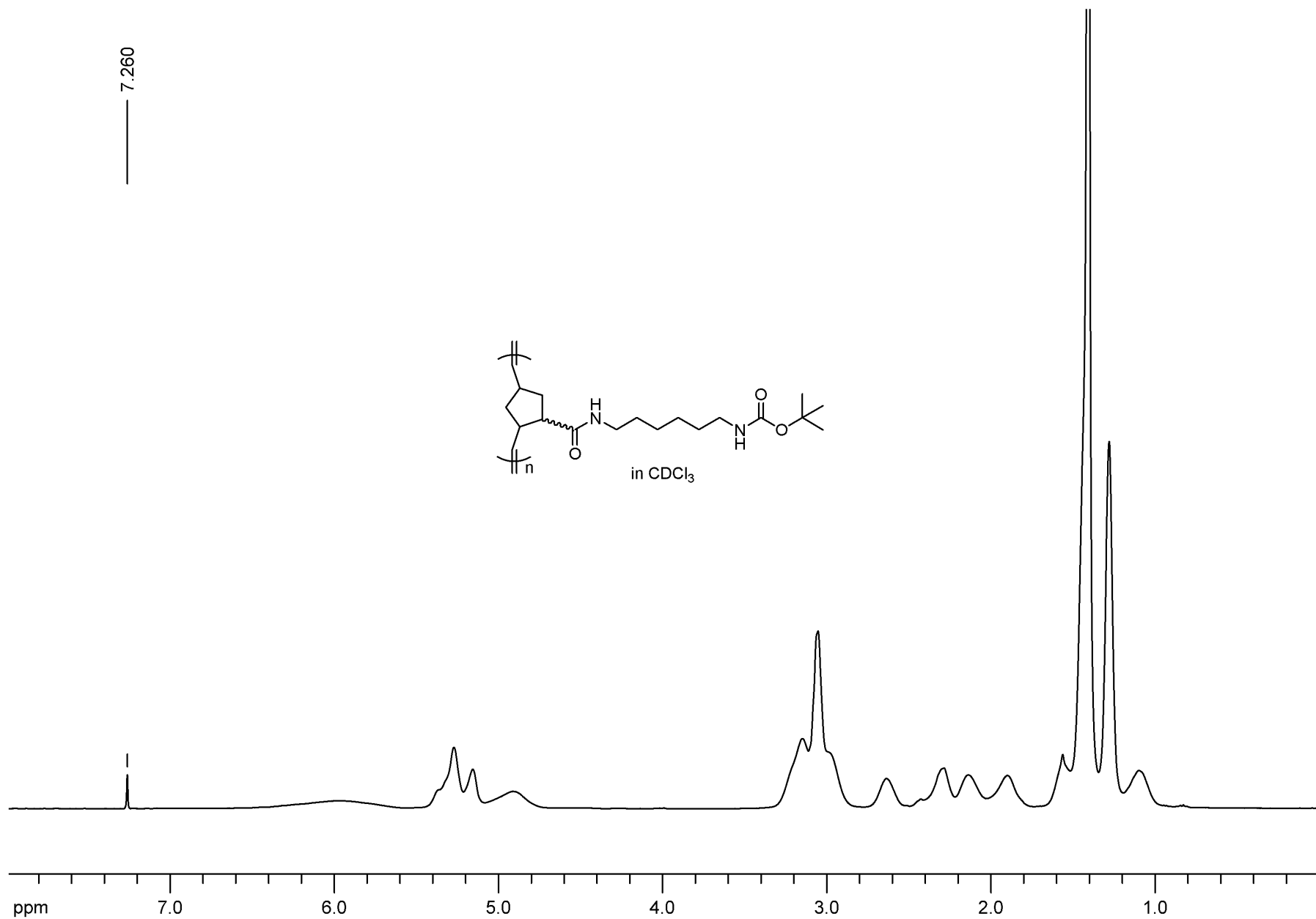


Figure S22. ^1H NMR spectrum for PNB-Boc-NH polymer in CDCl_3 .

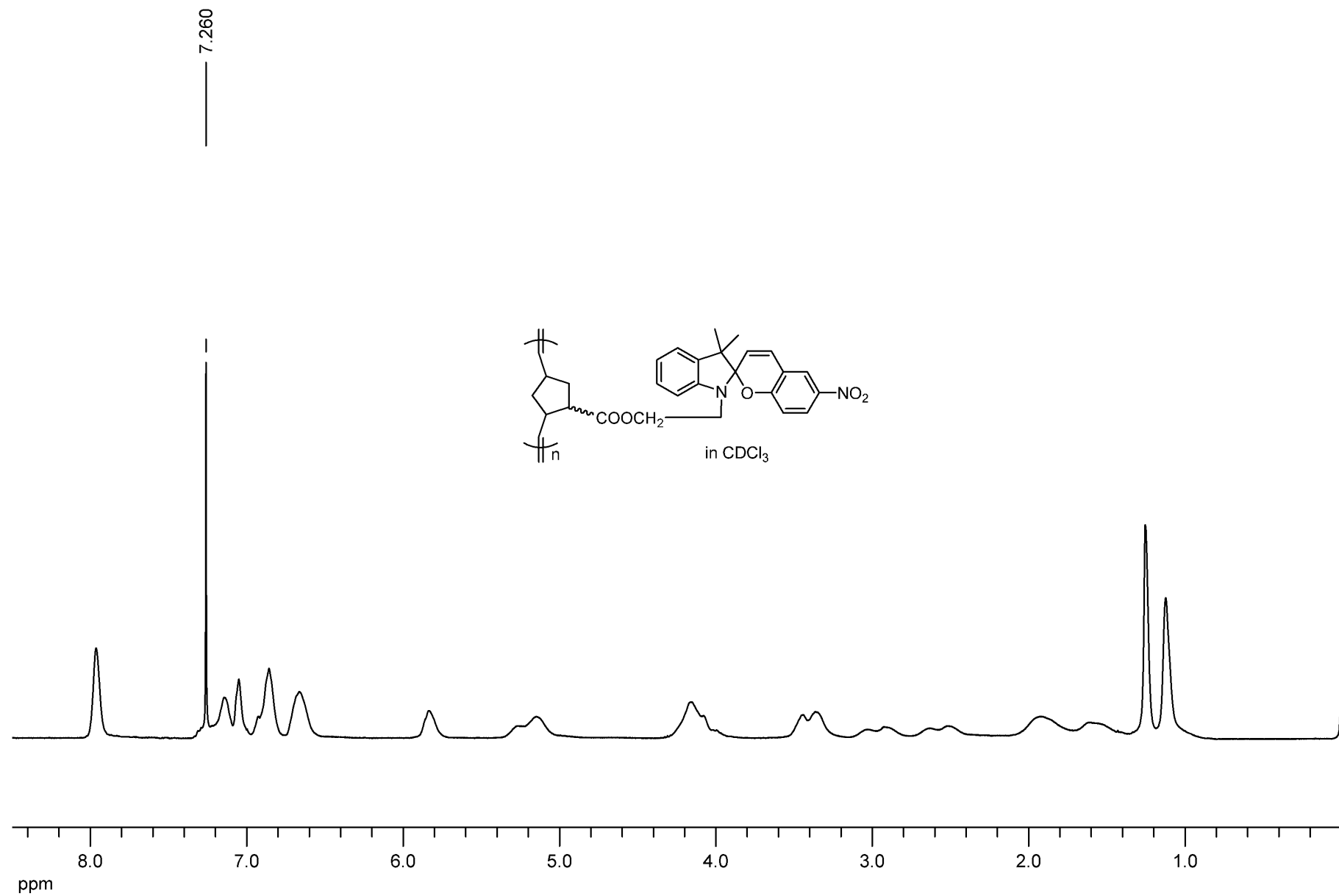
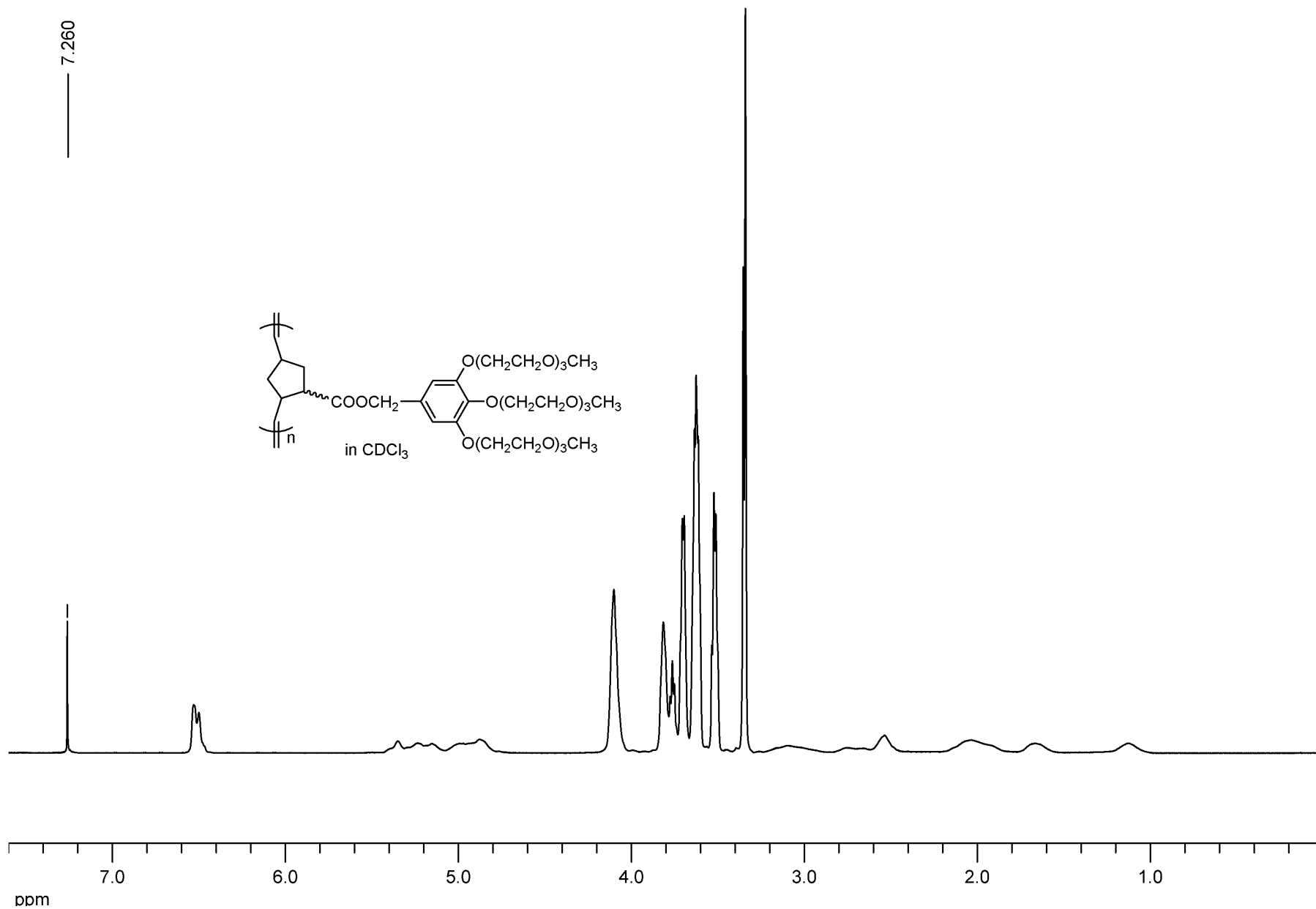


Figure S23. ^1H NMR spectrum for PNB-SP polymer in CDCl_3 .



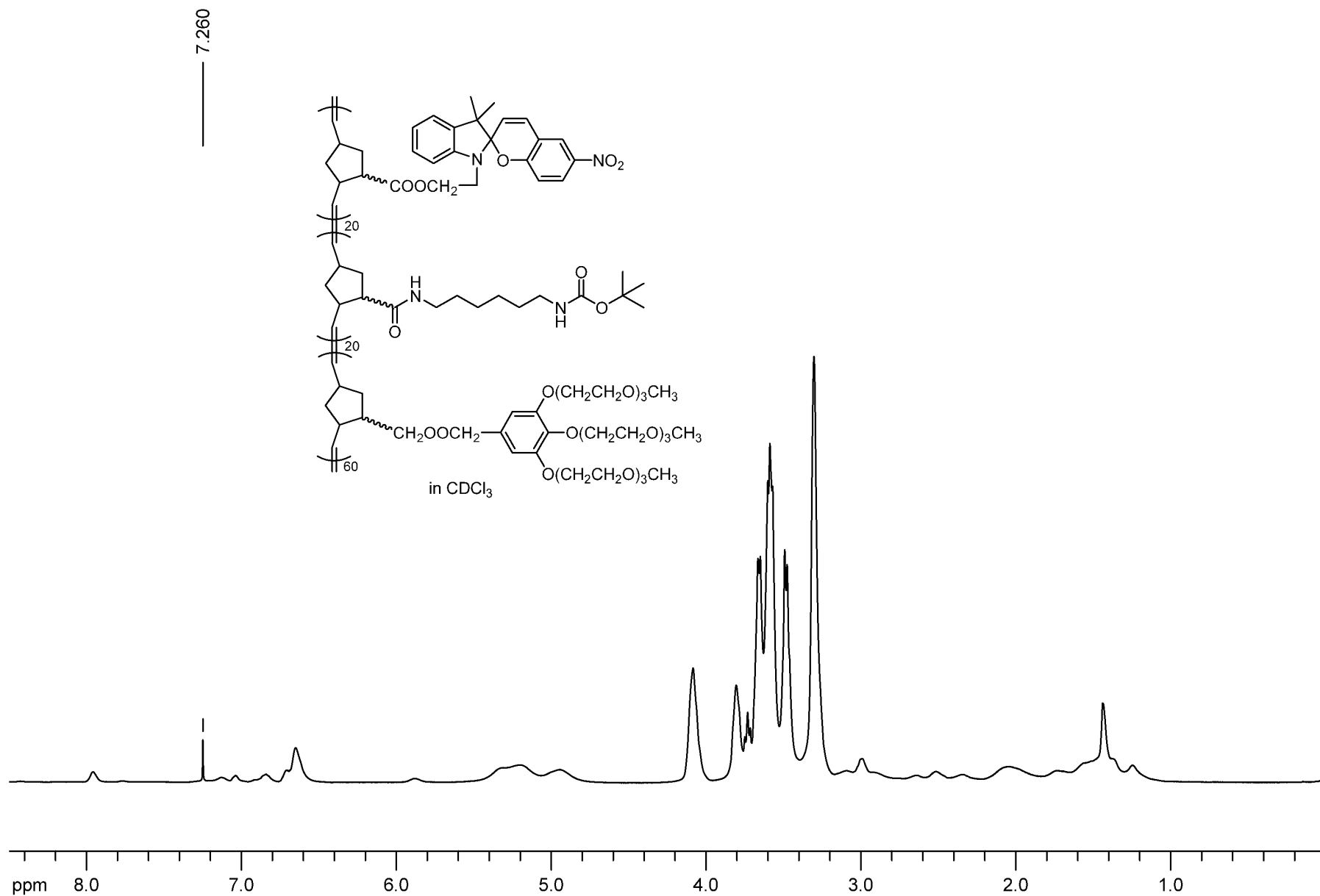


Figure S25. ^1H NMR spectrum for PNB-SP₂₀-co-(Boc-NH)₂₀-co-P3₆₀ copolymer in CDCl_3 .

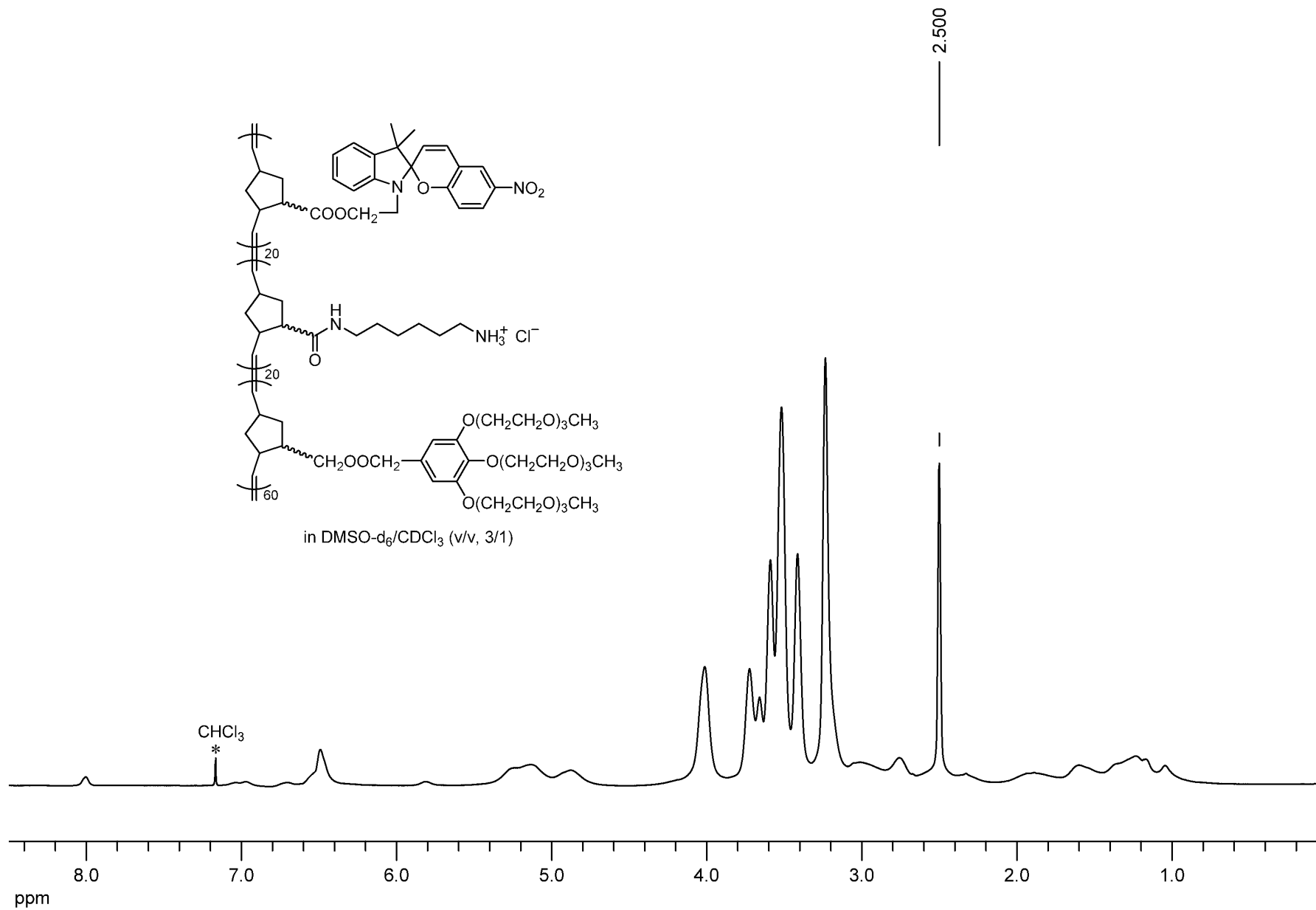


Figure S26. ¹H NMR spectrum for PNB-SP₂₀-co-(NH₂·HCl)₂₀-co-P₃₆₀ copolymer in DMSO-*d*₆/CDCl₃ (v/v, 3/1).