Electronic Supplementary Information

for

Synthesis, Structures, and Solid-State Photoresponsive Color Change Behavior of Boronium Complexes Bearing a Pyridine-Imine, Diimine, or Pyridine-Ketone Bidentate Ligand

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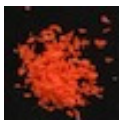
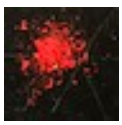
Table S1. Photographs showing colors of the solids of **2–4** before and after UV irradiation.

Compound	Before irradiation	After irradiation
2a	 pale yellow	 vivid yellow
2b	 pale yellow	 pale orange
2c	 pale yellow	 yellow
2d	 colorless	 pale yellow
2e	 pale yellow	 pale orange
3a	 pale yellow	– [a]
3b	 colorless	– [a]
4a	 red	– [a]
4b	 red	– [a]

[a] No color change upon UV irradiation.

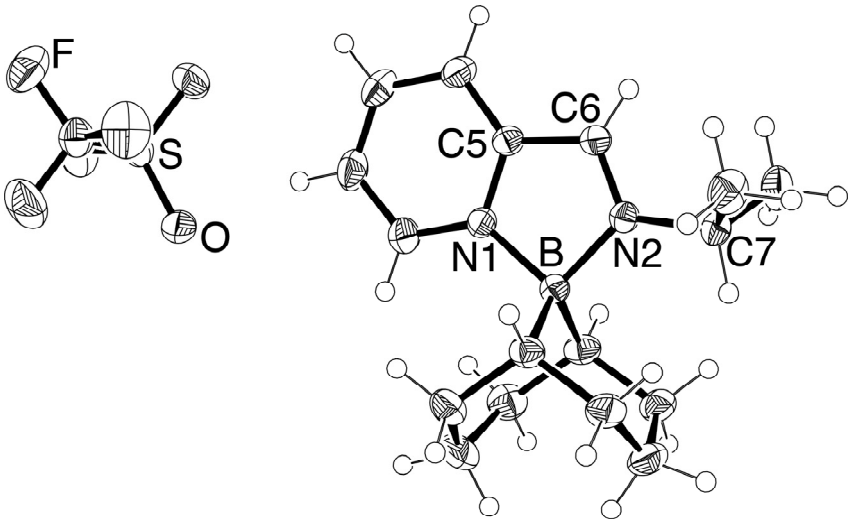


Figure S1. ORTEP drawing of **2b** (50% probability). Selected bond lengths: B–N1 = 1.606(2) Å; B–N2 = 1.5956(16) Å; B–C = 1.6233(18) Å, 1.6153(17) Å; N1–C5 = 1.3576(16) Å; C5–C6 = 1.445(2) Å; C6–N2 = 1.2863(19) Å, N2–C7 = 1.495(2) Å. Selected bond angles: N1–B–N2 = 95.20(10) °; C–B–C = 107.14(10) °; N1–B–C = 112.82(9) °, 113.37(12) °; N2–B–C = 113.69(11) °, 114.52(8) °; B–N2–C6 = 112.77(12) °; N2–C6–C5 = 112.10(11) °; C6–C5–N1 = 108.63(13) °; C5–N1–B = 111.29(11) °.

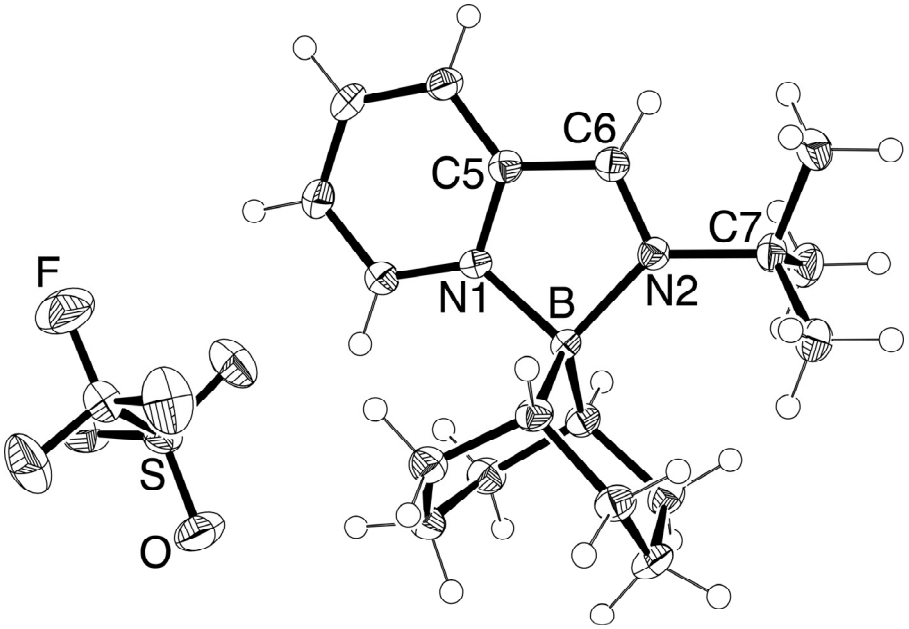


Figure S2. ORTEP drawing of **2c** (50% probability). Selected bond lengths: B–N1 = 1.637(2) Å; B–N2 = 1.675(2) Å; B–C = 1.636(2) Å, 1.613(3) Å; N1–C5 = 1.351(2) Å; C5–C6 = 1.440(3) Å; C6–N2 = 1.287(2) Å, N2–C7 = 1.540(2) Å. Selected bond angles: N1–B–N2 = 94.25(12) °; C–B–C = 106.36(14) °; N1–B–C = 109.17(12) °, 112.46(16) °; N2–B–C = 115.80(16) °, 118.27(12) °; B–N2–C6 = 110.12(14) °; N2–C6–C5 = 114.26(16) °; C6–C5–N1 = 109.74(15) °; C5–N1–B = 111.17(15) °.

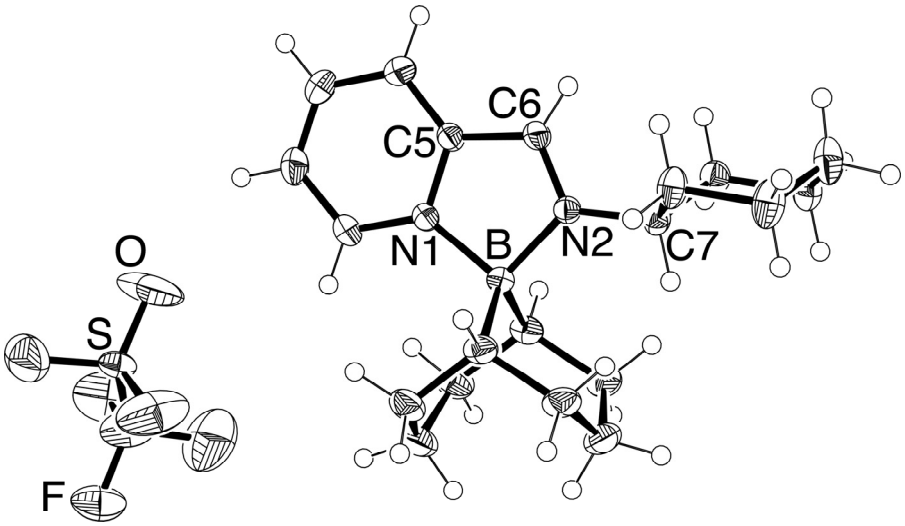


Figure S3. ORTEP drawing of **2d** (50% probability). Selected bond lengths: B–N1 = 1.610(5) Å; B–N2 = 1.604(5) Å; B–C = 1.618(4) Å, 1.622(5) Å; N1–C5 = 1.356(4) Å; C5–C6 = 1.446(6) Å; C6–N2 = 1.282(4) Å, N2–C7 = 1.488(5) Å. Selected bond angles: N1–B–N2 = 95.2(2) °; C–B–C = 107.3(3) °; N1–B–C = 113.8(3) °, 112.7(3) °; N2–B–C = 114.8(3) °, 113.0(3) °; B–N2–C6 = 112.6(3) °; N2–C6–C5 = 112.2(3) °; C6–C5–N1 = 108.9(3) °; C5–N1–B = 111.0(3) °.

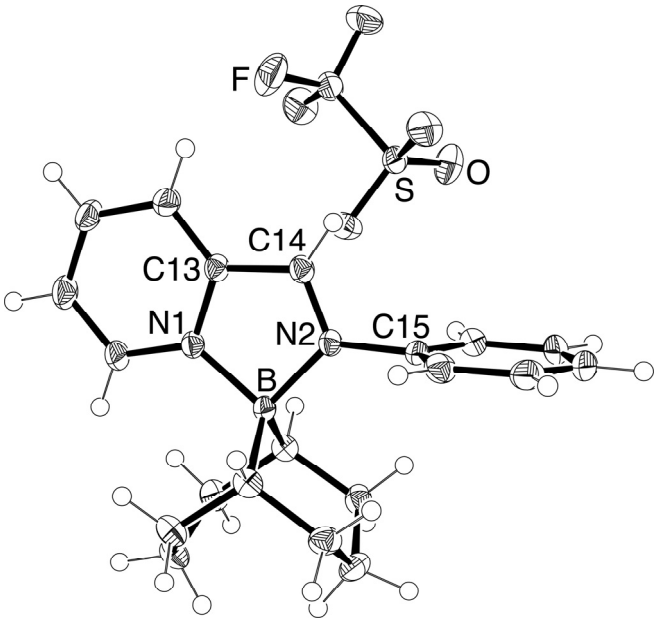


Figure S4. ORTEP drawing of **2e** (50% probability). Selected bond lengths: B–N1 = 1.607(2) Å; B–N2 = 1.6098(19) Å; B–C = 1.617(2) Å, 1.624(2) Å; N1–C13 = 1.3576(16) Å; C13–C14 = 1.448(2) Å; C14–N2 = 1.2877(17) Å, N2–C15 = 1.459(2) Å. Selected bond angles: N1–B–N2 = 94.37(9) °; C–B–C = 106.86(10) °; N1–B–C = 114.99(11) °, 111.62(14) °; N2–B–C = 114.39(14) °, 114.53(10) °; B–N2–C14 = 113.28(13) °; N2–C14–C13 = 111.63(12) °; C14–C13–N1 = 108.71(12) °; C13–N1–B = 111.99(12) °. Selected dihedral angles: C14–N2–C15–C = 85.96(14) °, 90.35(14) °.

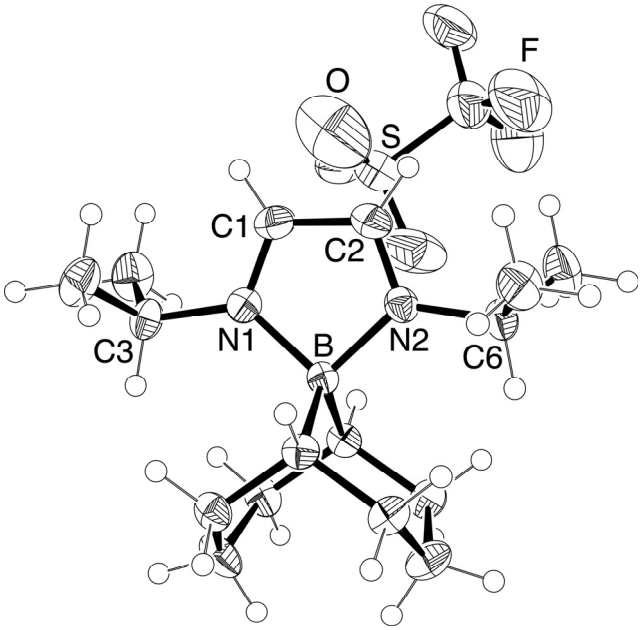


Figure S5. ORTEP drawing of **3a** (50% probability). Selected bond lengths: B–N1 = 1.590(3) Å; B–N2 = 1.589(3) Å; B–C = 1.631(3) Å, 1.627(3) Å; N1–C1 = 1.285(4) Å; N2–C2 = 1.280(4) Å; C1–C2 = 1.449(4) Å; N1–C3 = 1.502(3) Å, N2–C6 = 1.491(3) Å. Selected bond angles: N1–B–N2 = 95.54(17) °; C–B–C = 106.68(18) °; N1–B–C = 113.74(18) °, 113.52(18) °; N2–B–C = 114.07(18) °, 113.29(18) °; B–N2–C2 = 112.1(2) °; N2–C2–C1 = 110.0(3) °; C2–C1–N1 = 111.3(3) °; C1–N1–B = 111.0(2) °.

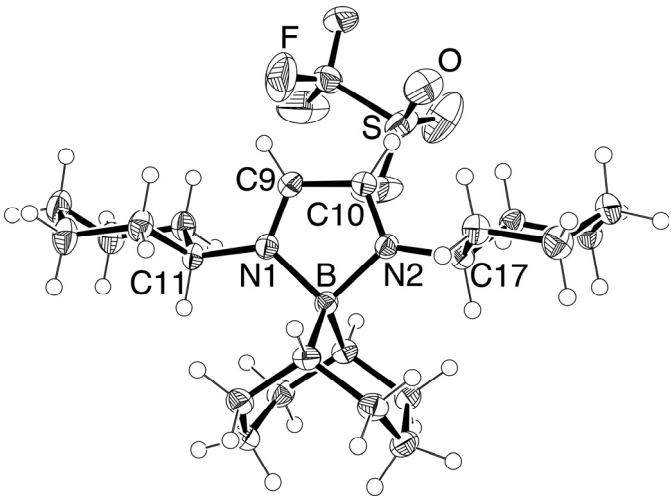


Figure S6. ORTEP drawing of **3b** (50% probability). Selected bond lengths: B–N1 = 1.594(3) Å; B–N2 = 1.596(3) Å; B–C = 1.626(3) Å, 1.634(4) Å; N1–C9 = 1.288(3) Å; N2–C10 = 1.281(3) Å; C9–C10 = 1.444(3) Å; N1–C11 = 1.493(3) Å, N2–C17 = 1.485(3) Å. Selected bond angles: N1–B–N2 = 95.52(16) °; C–B–C = 106.42(18) °; N1–B–C = 114.00(17) °, 113.18(19) °; N2–B–C = 114.03(19) °, 113.75(16) °; B–N2–C10 = 111.63(18) °; N2–C10–C9 = 110.6(2) °; C10–C9–N1 = 111.2(2) °; C9–N1–B = 111.00(18) °.

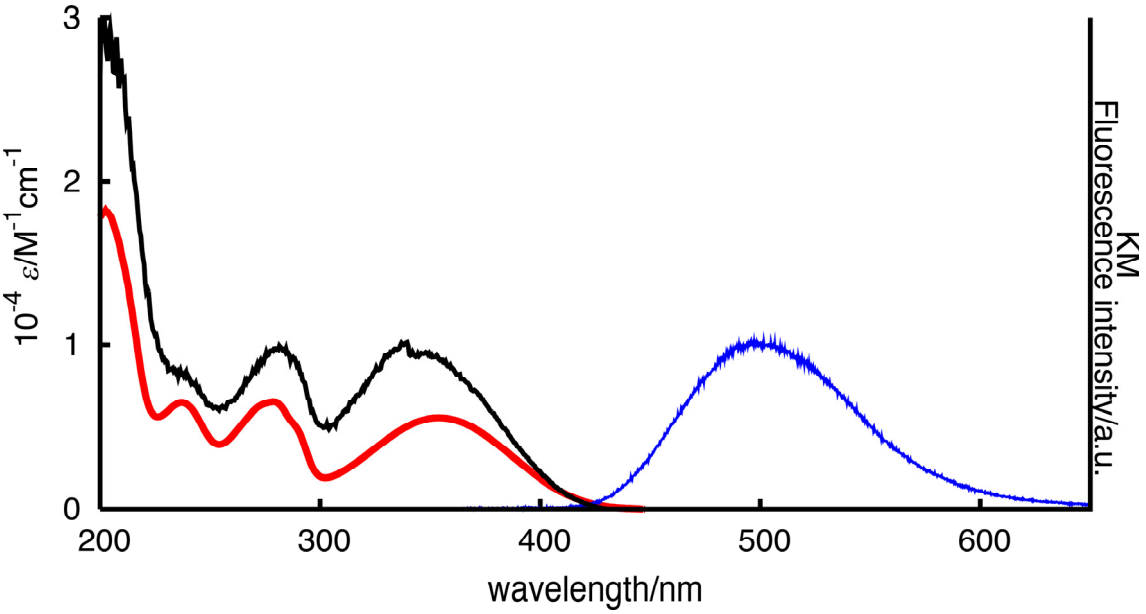


Figure S7. UV-Vis absorption (red line) and fluorescence (blue line) spectra of **2a** in MeCN and diffuse reflectance spectrum (black line) of **2a** in the solid state.

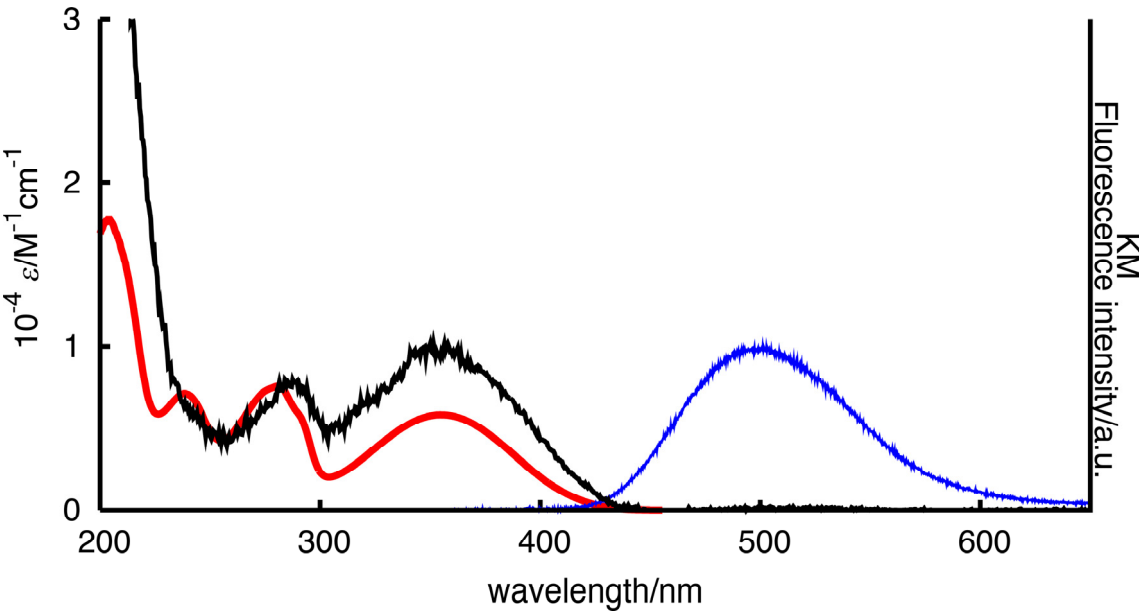


Figure S8. UV-Vis absorption (red line) and fluorescence (blue line) spectra of **2b** in MeCN and diffuse reflectance spectrum (black line) of **2b** in the solid state.

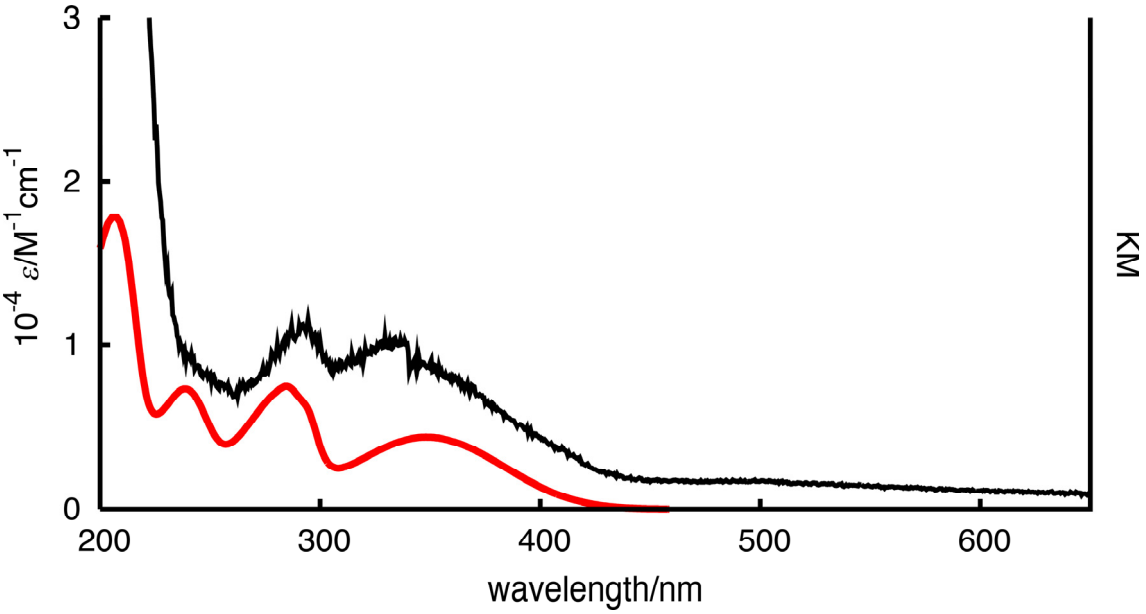


Figure S9. UV-Vis absorption spectrum (red line) of **2c** in MeCN and diffuse reflectance spectrum (black line) of **2c** in the solid state.

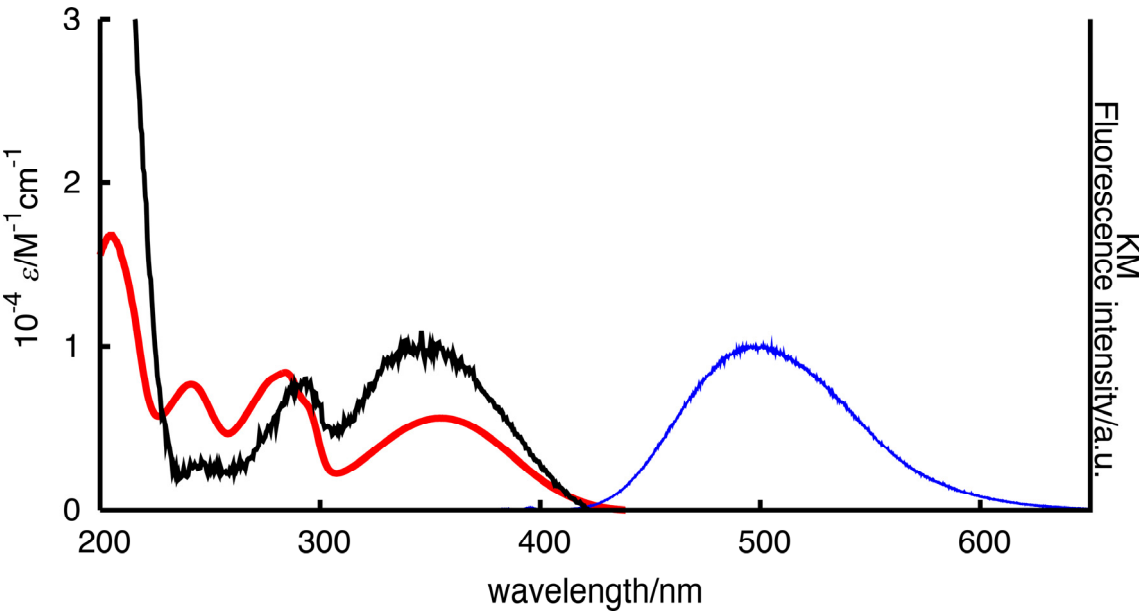


Figure S10. UV-Vis absorption (red line) and fluorescence (blue line) spectra of **2d** in MeCN and diffuse reflectance spectrum (black line) of **2d** in the solid state.

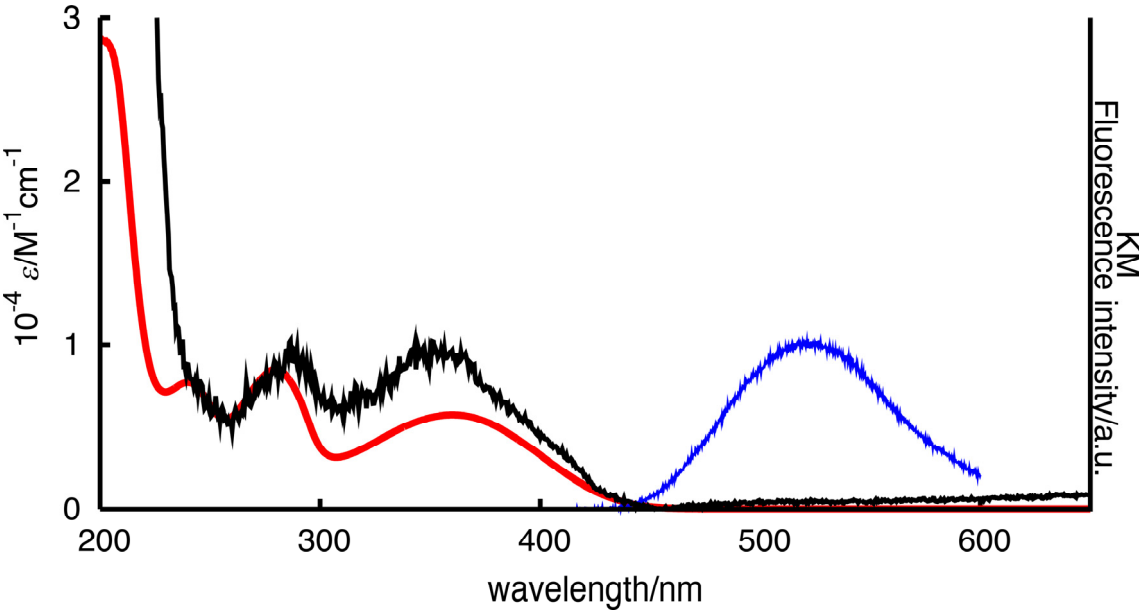


Figure S11. UV-Vis absorption (red line) and fluorescence (blue line) spectra of **2e** in MeCN and diffuse reflectance spectrum (black line) of **2e** in the solid state.

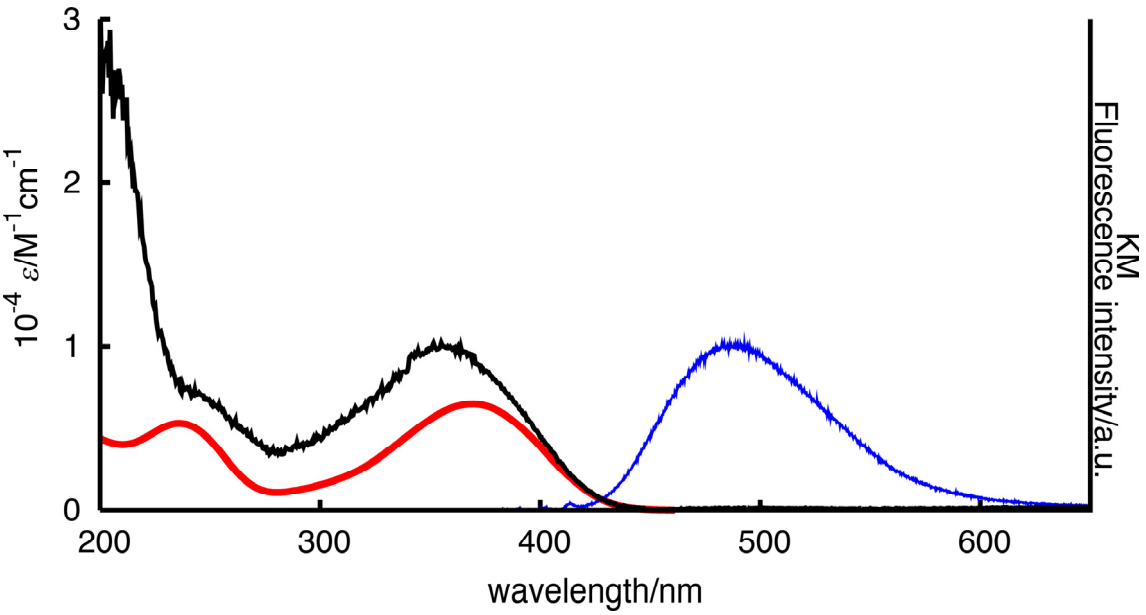


Figure S12. UV-Vis absorption (red line) and fluorescence (blue line) spectra of **3a** in MeCN and diffuse reflectance spectrum (black line) of **3a** in the solid state.

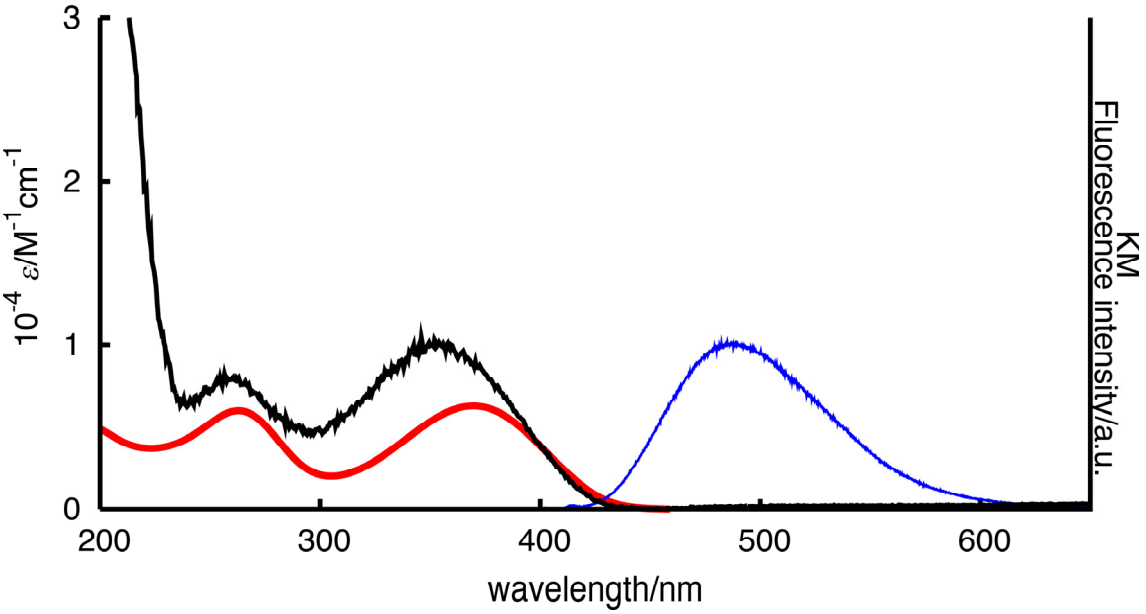


Figure S13. UV-Vis absorption (red line) and fluorescence (blue line) spectra of **3b** in MeCN and diffuse reflectance spectrum (black line) of **3b** in the solid state.

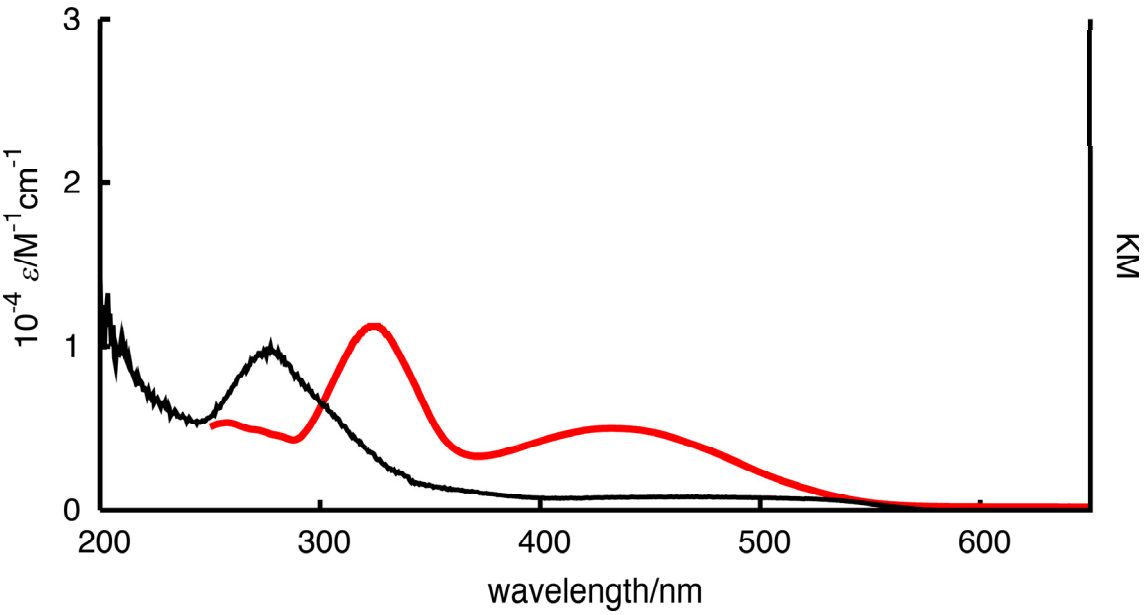


Figure S14. UV-Vis absorption spectrum (red line) of **4a** in MeCN and diffuse reflectance spectrum (black line) of **4a** in the solid state.

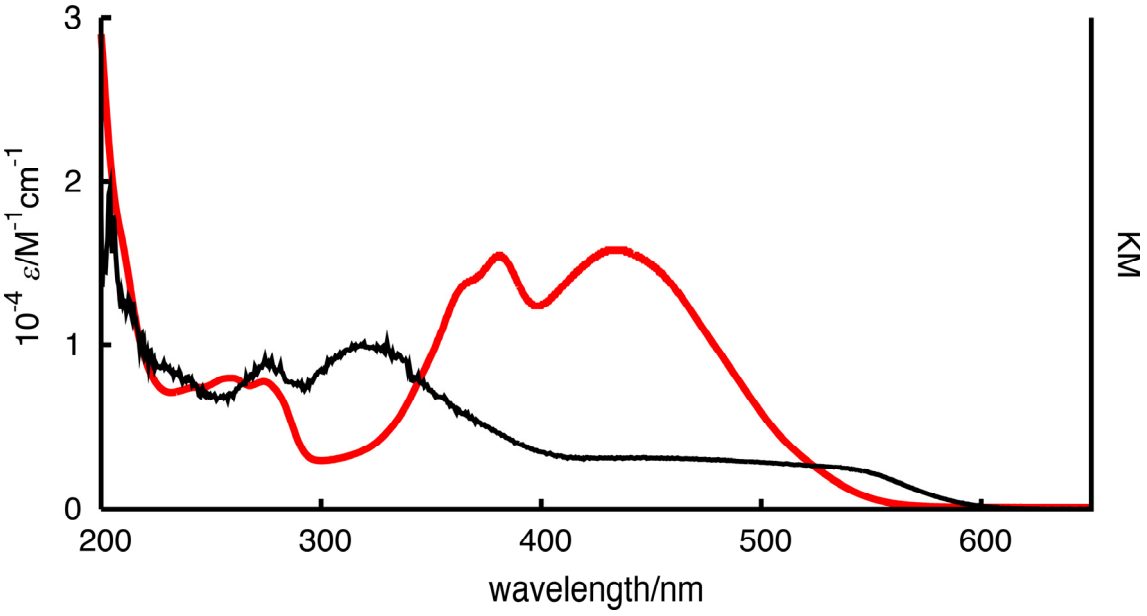
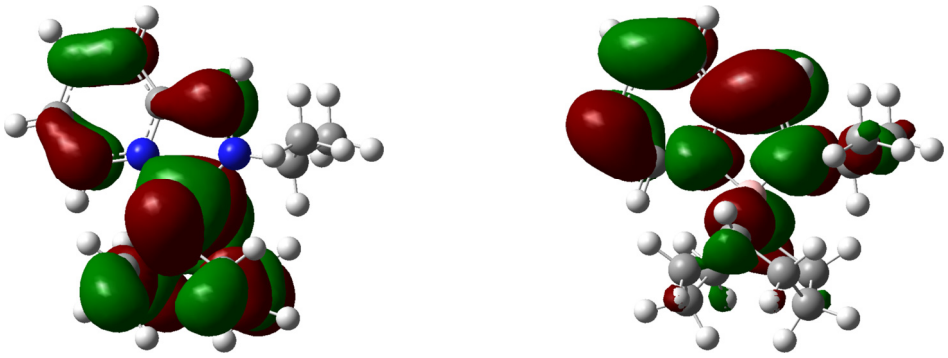


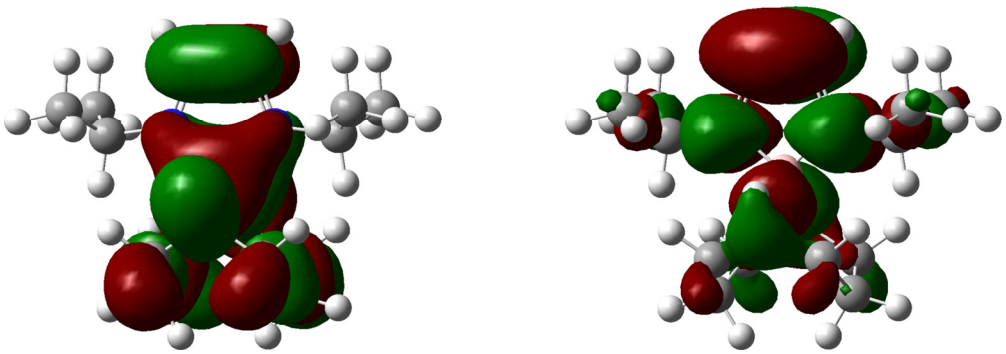
Figure S15. UV-Vis absorption spectrum (red line) of **4b** in MeCN and diffuse reflectance spectrum (black line) of **4b** in the solid state.

2b



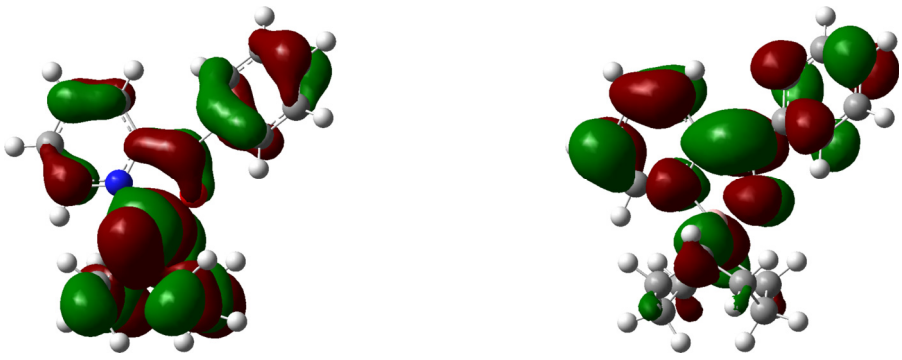
HOMO LUMO

3a



HOMO LUMO

4a



HOMO LUMO

Figure S16. Molecular orbital diagrams of the cations of **2b**, **3a** and **4a** calculated at the B3LYP/6-31+G(d) level of theory.

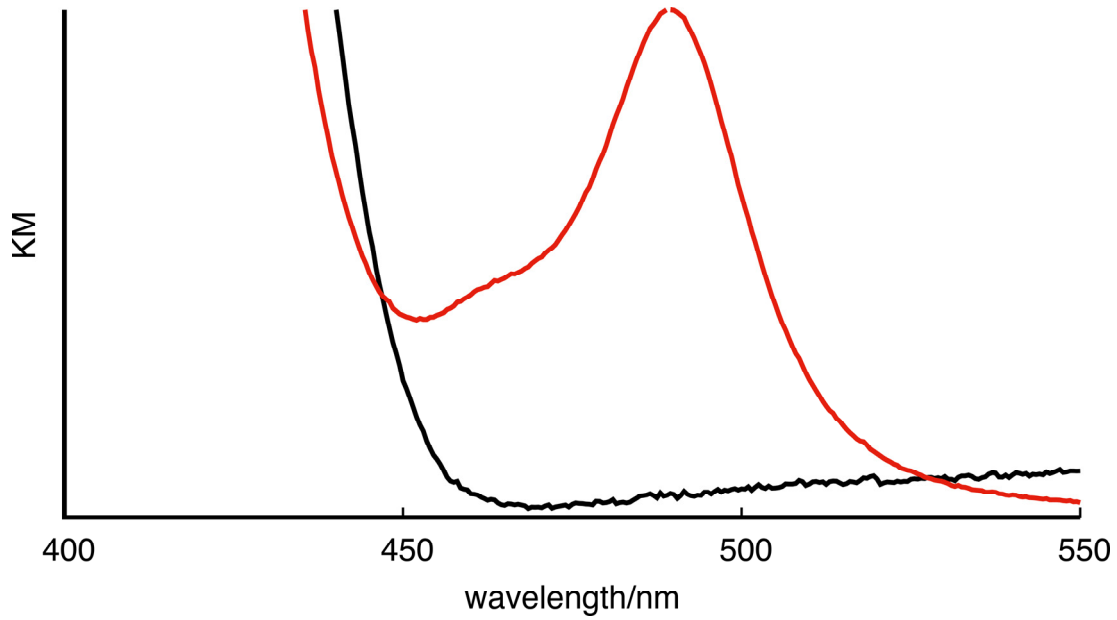


Figure S17. Diffuse reflectance spectra of **2b** in the solid state before (black line) and after (red line) UV irradiation.

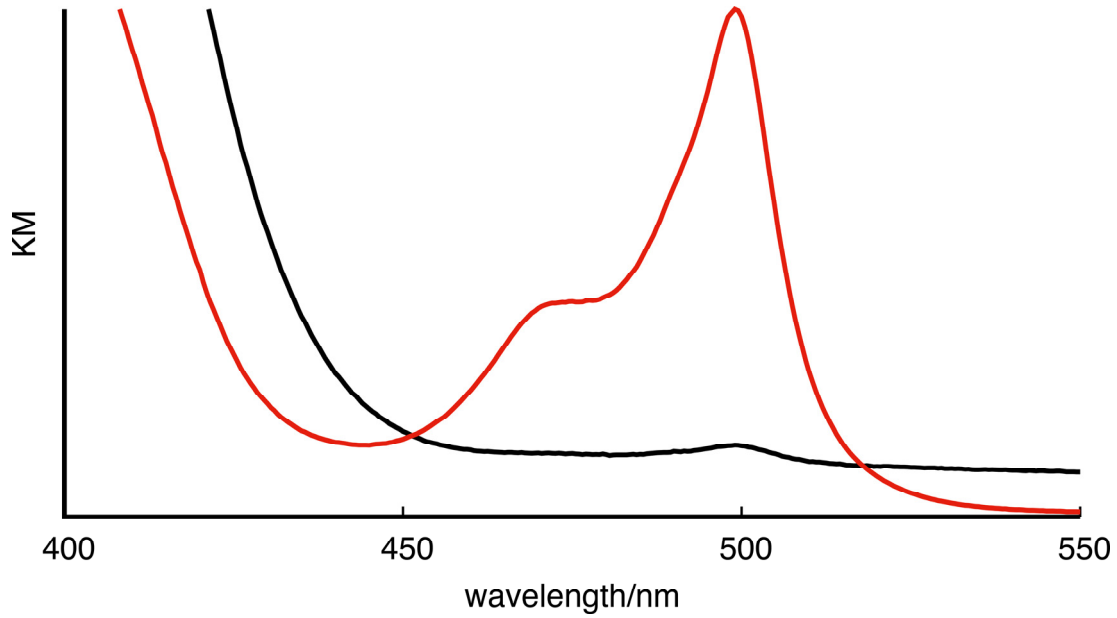


Figure S18. Diffuse reflectance spectra of **2c** in the solid state before (black line) and after (red line) UV irradiation.

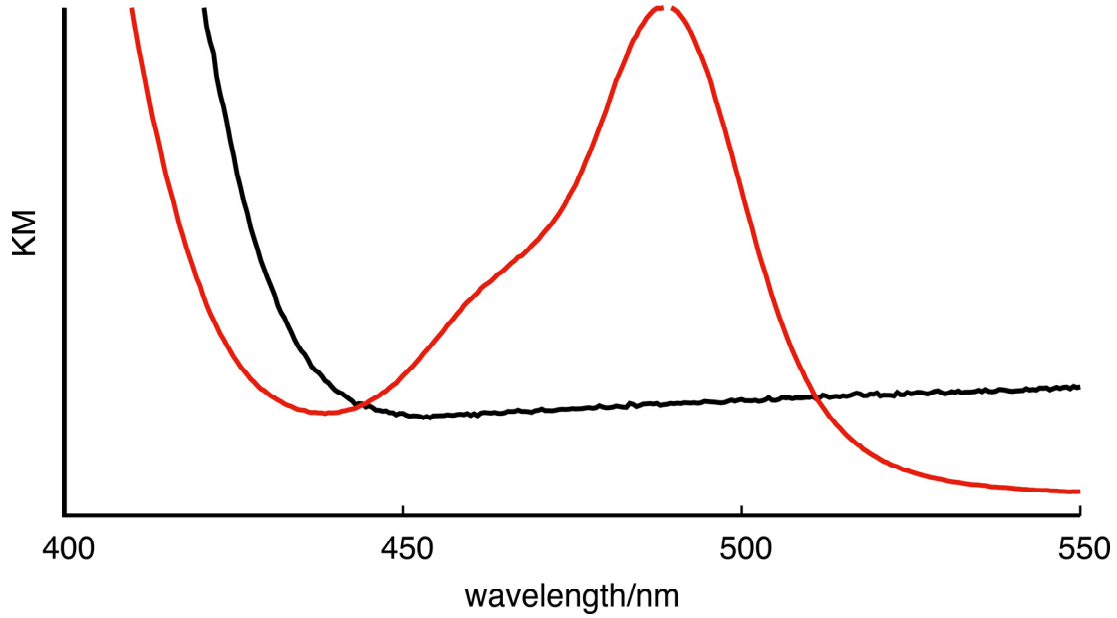


Figure S19. Diffuse reflectance spectra of **2d** in the solid state before (black line) and after (red line) UV irradiation.

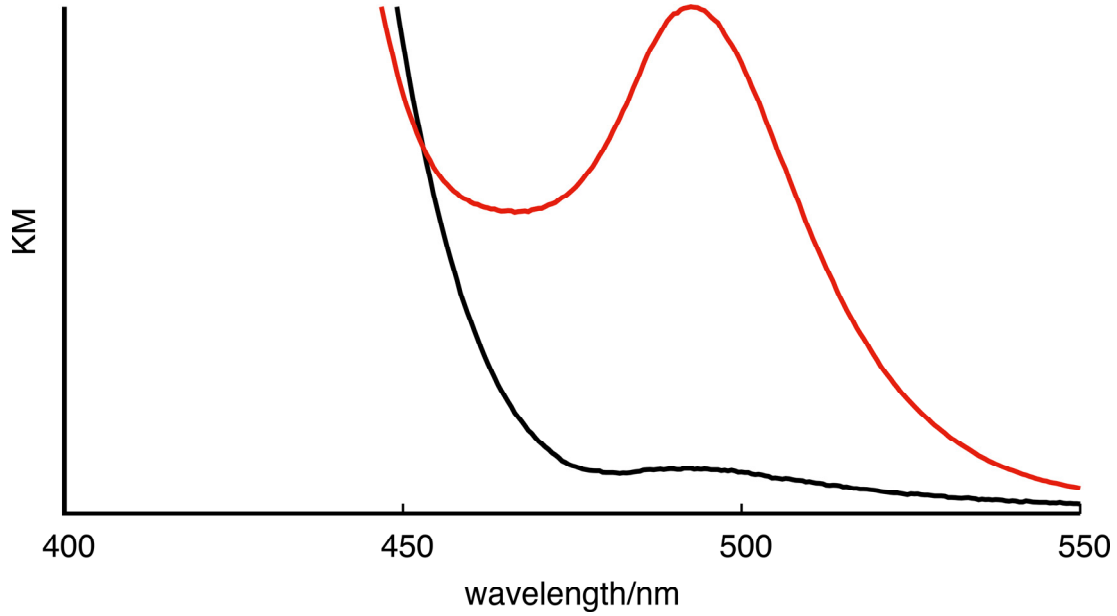


Figure S20. Diffuse reflectance spectra of **2e** in the solid state before (black line) and after (red line) UV irradiation.

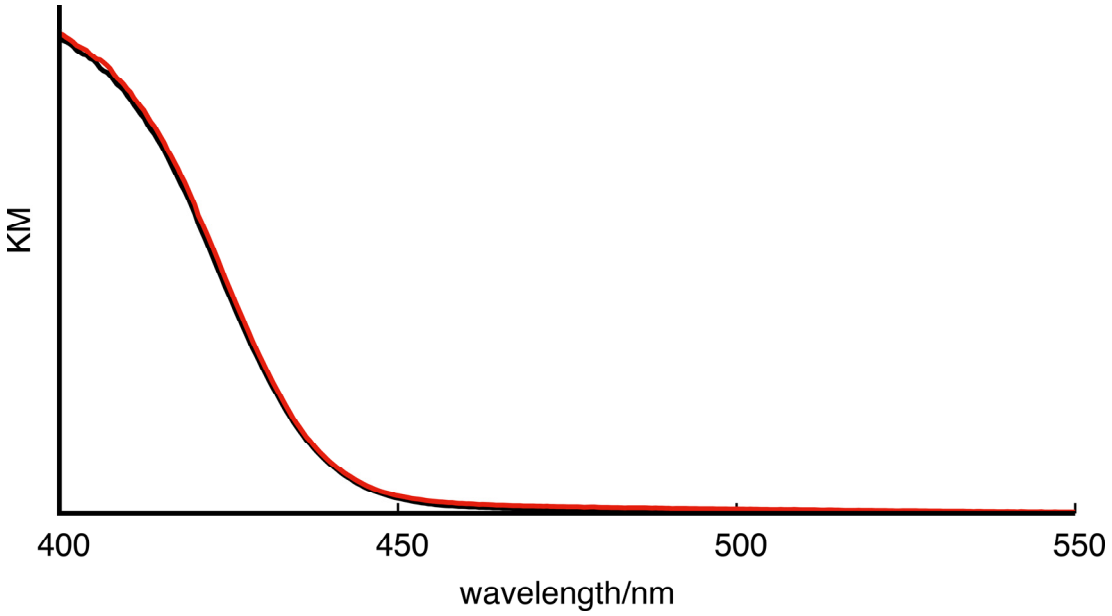


Figure S21. Diffuse reflectance spectra of **3a** in the solid state before (black line) and after (red line) UV irradiation.

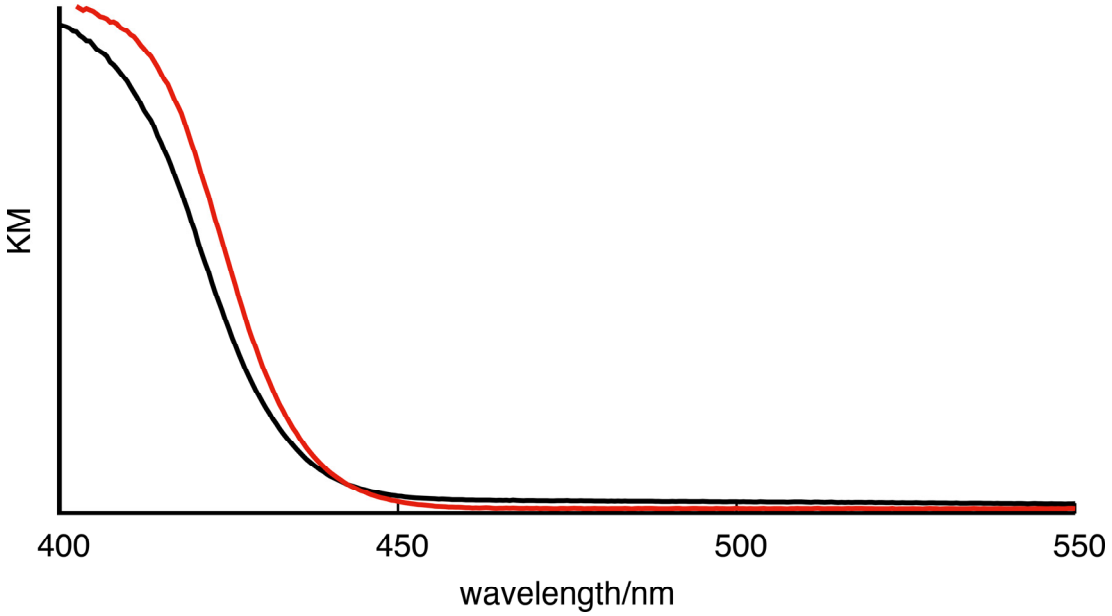


Figure S22. Diffuse reflectance spectra of **3b** in the solid state before (black line) and after (red line) UV irradiation.

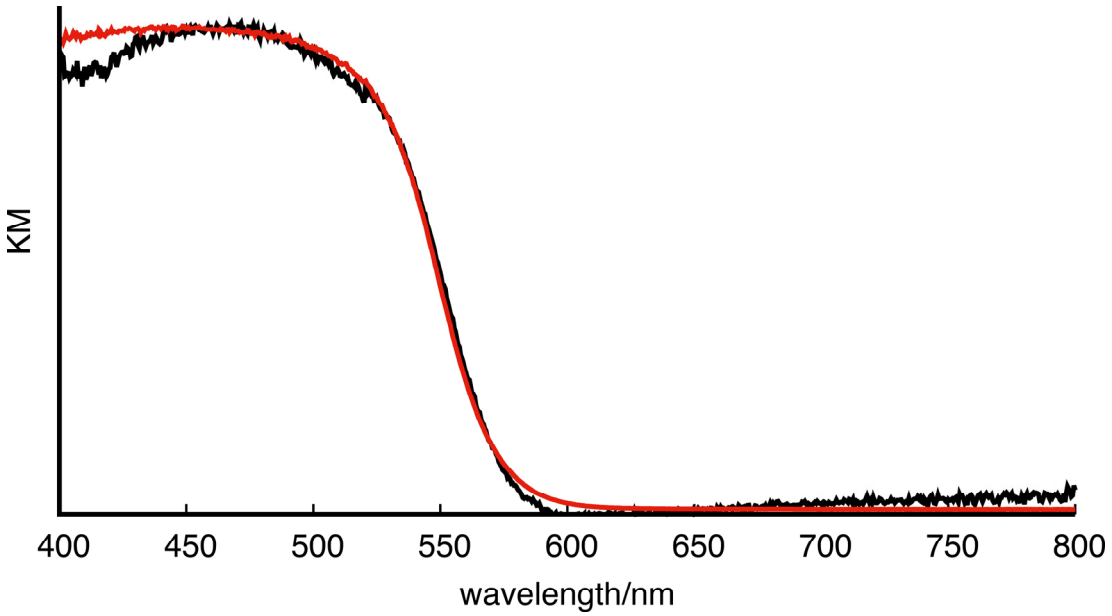


Figure S23. Diffuse reflectance spectra of **4a** in the solid state before (black line) and after (red line) UV irradiation.

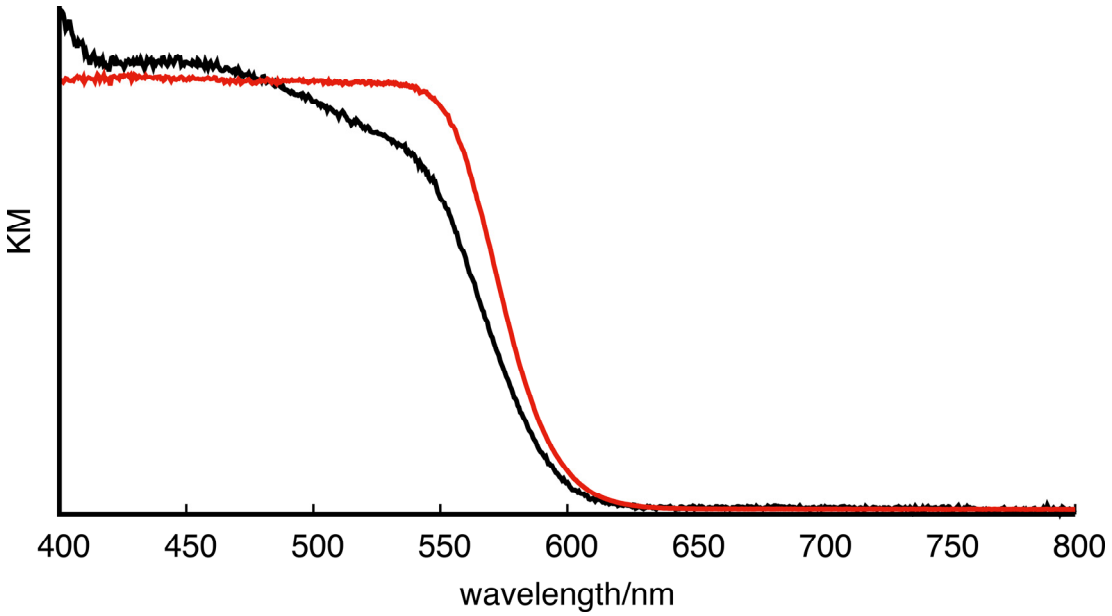


Figure S24. Diffuse reflectance spectra of **4b** in the solid state before (black line) and after (red line) UV irradiation.

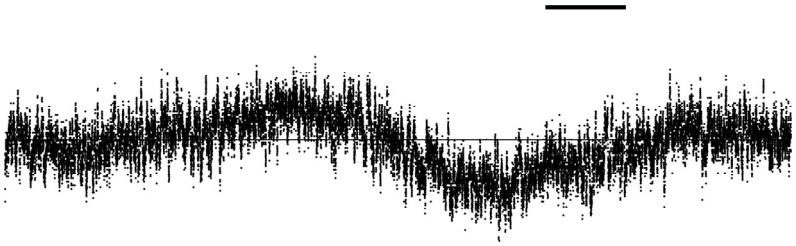


Figure S25. ESR spectrum of compound **2b** in the solid state after UV irradiation. A horizontal bar indicates 1 mT. g = 2.0038.

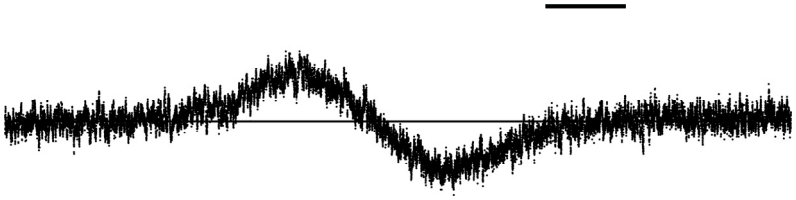


Figure S26. ESR spectrum of compound **2c** in the solid state after UV irradiation. A horizontal bar indicates 1 mT. g = 2.0037.

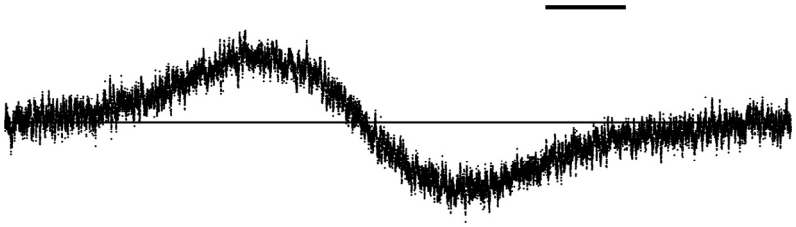


Figure S27. ESR spectrum of compound **2d** in the solid state after UV irradiation. A horizontal bar indicates 1 mT. g = 2.0036.

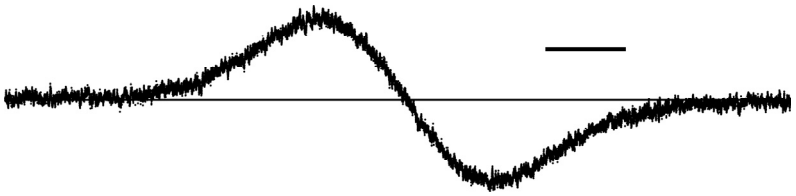


Figure S28. ESR spectrum of compound **2e** in the solid state after UV irradiation. A horizontal bar indicates 1 mT. g = 2.0036.

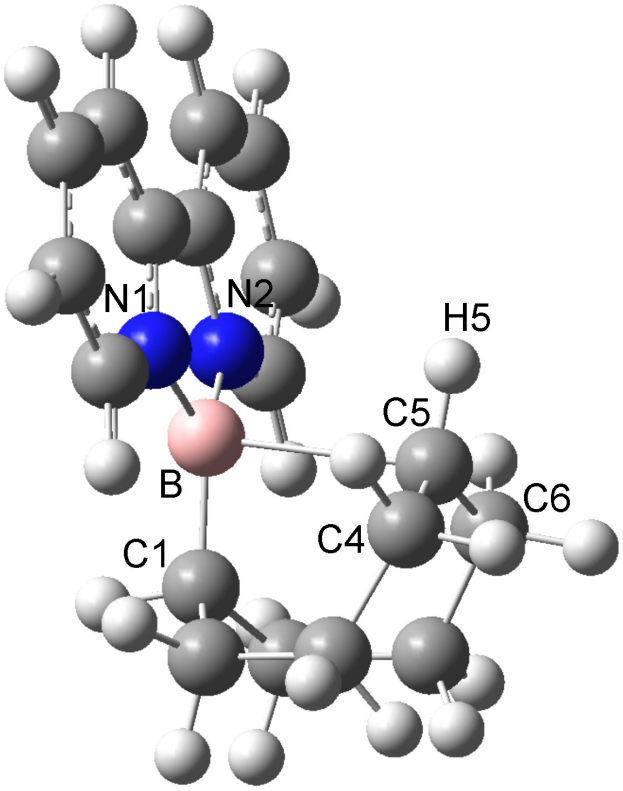


Figure S29. Optimized geometry of **1"** as a triplet species. Selected bond lengths: B–N = 1.50 Å, 1.50 Å; B–C1 = 1.59 Å; B–C5 = 2.57 Å; C5–C = 1.50 Å, 1.50 Å. Selected bond angles: N1–B–N2 = 101.2 °; N–B–C1 = 128.1 °, 128.0 °; C1–B–C5 = 85.4 °; N–B–C5 = 101.5 °, 101.7 °; C4–C5–C6 = 125.6 °; H5–C5–C = 114.7 °, 114.7 °; B–C5–H5 = 94.0 °.

Experimental section

General information. Solvents were purified by reported methods before use.[1] All reactions were carried out under an argon atmosphere unless otherwise noted. ^{1}H NMR (300 MHz), ^{13}C NMR (76 MHz), ^{11}B NMR (96 MHz), and ^{19}F NMR (283 MHz) spectra were measured with a JEOL JNM-ECX300 spectrometer. Tetramethylsilane was used as an internal standard for the ^{1}H and ^{13}C NMR spectra. Boron trifluoride diethyl etherate was used as an external standard for the ^{11}B NMR spectra. Fluorobenzene was used as an external standard for the ^{19}F NMR spectra, using the chemical shift of−113 ppm referenced to the chemical shift of trichlorofluoromethane at 0 ppm. High-resolution mass spectra were measured with a JEOL MStation JMS-700V spectrometer. Absorption spectra in the solution and diffuse reflectance spectra in the solid state were measured with a JASCO V-570 spectrometer. Fluorescence spectra were measured with a Shimadzu RF-5300PC spectrometer. The absolute values of the fluorescence quantum yields were measured by a Hamamatsu Photonics C11347 Quantaurus-QY absolute PL quantum yield spectrometer. Elemental Analyses were carried out with an Elementar Vario Micro Cube elemental analyzer. Powder samples for diffuse reflectance spectroscopy, except in the photoirradiation experiments, were diluted one thousand-fold with barium sulfate. For UV-light irradiation experiments, a UVP UVGL-25 compact UV lamp and an Analytik Jena UVL-28 EL series handheld UV lamp were used. Electron spin resonance spectra were measured with a JEOL JES-X310 spectrometer. *N*-(2-Pyridylmethylidene)methanamine (**6a**),[2] *N*-(2-pyridylmethylidene)-2-propanamine (**6b**),[3] 2-methyl-*N*-(2-pyridylmethylidene)-2-propanamine (**6c**),[3] *N*-(2-pyridylmethylidene)cyclohexanamine (**6d**),[3] *N*-(2-pyridylmethylidene)aniline (**6e**),[2] *N*,*N*′-diisopropylethane-1,2-diimine (**7a**),[4] *N*,*N*′-dicyclohexylethane-1,2-diimine (**7b**),[5] and 2-(4-methoxybenzoyl)pyridine (**8b**)[6] were prepared according to the literature.

Synthesis of (1,5-cyclooctanediyl)[*N*-(2-pyridylmethylidene)-2-propanamine-*N*,*N*′]-boronium(III) trifluoromethanesulfonate (2b). A method similar to that for the synthesis of **2a** with *N*-(2-pyridylmethylidene)-2-propanamine (**6b**) (0.600 g, 4.05 mmol) gave compound **2b** (0.519 g, 31%). **2b**: pale yellow solid, mp 214.8–215.2 °C (dec). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 9.73 (s, 1H), 9.34 (d, 1H, J = 6.2 Hz), 8.65 (t, 1H, J = 7.6 Hz), 8.53 (d, 1H, J = 7.6 Hz), 8.13 (t, 1H, J = 6.5 Hz), 4.83 (sept, 1H, J = 6.5 Hz), 2.24–1.65 (m, 12H), 1.51 (d, 6H, J = 6.5 Hz), 0.79 (s, 2H). ^{13}C{^{1}H} NMR (DMSO-d_6, 76 MHz): δ 160.9, 145.73, 145.69, 143.0, 128.1, 127.7, 120.7 (q, J = 322 Hz, *C*F$_3$), 54.5, 30.6, 29.3, 23.2 (br s, *C*B), 23.0, 22.4, 21.6. ^{11}B NMR (DMSO-d_6, 96 MHz): δ 9.5 (line width $h_{1/2}$ = 771 Hz). ^{19}F NMR (DMSO-d_6, 283 MHz): δ −76.2 (s). HRMS (FAB) *m/z*: [M − CF_3SO_3]$^{+}$ Calcd for $C_{17}H_{26}BN_2$ 269.2189; Found 269.2209.

Synthesis of (1,5-cyclooctanediyl)[2-methyl-*N*-(2-pyridylmethylidene)-2-propanamine-*N*,*N*′] boronium(III) trifluoromethanesulfonate (2c). A method similar to that for the synthesis of **2a** with 2-methyl-*N*-(2-pyridylmethylidene)-2-propanamine (**6c**) (0.55 mL, 3.1 mmol) gave compound **2c** (0.500 g, 37%). **2c**: pale yellow solid, mp 109.6–111.0 °C (dec). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 9.59 (s, 1H), 9.29 (d, 1H, J = 5.8 Hz), 8.71–8.58 (m, 2H), 8.20–8.10 (m, 1H), 2.43–1.20 (m, 21H), 0.73 (s, 2H). ^{13}C{^{1}H} NMR (DMSO-d_6, 76 MHz): δ 163.1, 146.4, 144.7, 143.2, 128.4, 128.2, 120.7 (q, J = 322 Hz, *C*F$_3$), 67.5, 31.3, 31.2, 30.6, 23.3 (br s, *C*B), 21.8, 21.0. ^{11}B NMR (DMSO-d_6, 96 MHz): δ 15.1 (line width $h_{1/2}$ = 656 Hz). ^{19}F NMR (DMSO-d_6, 283 MHz): δ −76.2 (s). HRMS (FAB) *m/z*: [M − CF_3SO_3]$^+$ Calcd for $C_{18}H_{28}BN_2$ 283.2346; Found 283.2346.

Synthesis of (1,5-cyclooctanediyl)[*N*-(2-pyridylmethylidene)cyclohexanamine-*N*,*N*′]-boronium(III) trifluoromethanesulfonate (2d). A method similar to that for the synthesis of **2a** with *N*-(2-pyridylmethylidene)cyclohexanamine (**6d**) (0.40 mL, 2.2 mmol) gave compound **2d** (0.558 g, 55%). **2d**: pale yellow solid, mp 238.4–240.0 °C (dec). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 9.72 (s, 1H), 9.35 (d, 1H, J = 6.2 Hz), 8.65 (t, 1H, J = 7.6 Hz), 8.53 (d, 1H, J = 7.6 Hz), 8.13 (t, 1H, J = 7.2 Hz), 4.40–4.26 (m, 1H), 2.23–1.63 (m, 19H), 1.48–1.20 (m, 3H), 0.79 (s, 2H). ^{13}C{^{1}H} NMR (DMSO-d_6, 76 MHz): δ 161.1, 145.8, 145.7, 143.1, 128.1, 127.7, 120.7 (q, J = 322 Hz, *C*F$_3$), 62.1, 33.4, 30.8, 29.3, 25.2, 24.5, 23.3 (br s, *C*B), 22.5, 21.6. ^{11}B NMR (DMSO-d_6, 96 MHz): δ 9.6 (line width $h_{1/2}$ = 656 Hz). ^{19}F NMR (DMSO-d_6, 283 MHz): δ −76.2 (s). HRMS (FAB) *m/z*: [M − CF_3SO_3]$^+$ Calcd for $C_{20}H_{30}BN_2$ 309.2502; Found 309.2493.

Synthesis of (1,5-cyclooctanediyl)[*N*-(2-pyridylmethylidene)aniline-*N*,*N*′]boronium(III) trifluoromethanesulfonate (2e). A method similar to that for the synthesis of **2a** with *N*-(2-pyridylmethylidene)aniline (**6e**) (1.0 g, 5.5 mmol) gave compound **2e** (0.695 g, 28%). **2e**: yellow solid, mp 196.0–197.1 °C (dec). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 9.53 (s, 1H), 9.38 (d, 1H, J = 5.8 Hz), 8.78–8.66 (m, 2H), 8.25 (t, 1H, J = 6.5 Hz), 7.68–7.50 (m, 5H), 2.30–0.80 (m, 14H). ^{13}C{^{1}H} NMR (DMSO-d_6, 76 MHz): δ 164.7, 146.1, 145.2, 143.7, 143.3, 129.7, 129.2, 128.8, 128.6, 124.7, 120.7 (q, J = 322 Hz, *C*F$_3$), 30.8, 28.9, 23.1 (br s, *C*B), 22.8, 21.3. ^{11}B NMR (DMSO-d_6, 96 MHz): δ 10.9 (line width $h_{1/2}$ = 1054 Hz). ^{19}F NMR (DMSO-d_6, 283 MHz): δ −76.2 (s). HRMS (FAB) *m/z*: [M − CF_3SO_3]$^+$ Calcd for $C_{20}H_{24}BN_2$ 303.2033; Found 303.2020.

Synthesis of (1,5-cyclooctanediyl)[*N*,*N*′-diisopropylethane-1,2-diimine-*N*,*N*′]boronium(III) trifluoromethanesulfonate (3a). A method similar to that for the synthesis of **2a** with *N*,*N*′-diisopropylethane-1,2-diimine (**7a**) (0.40 g, 2.9 mmol) gave compound **3a** (0.293 g, 25%). **3a**: yellow solid, mp 125.0–125.8 °C (dec). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 9.22 (s, 2H), 4.68 (sept, 2H, J = 6.5 Hz), 2.08–1.67 (m, 12H), 1.43 (d, 12H, J = 6.5 Hz), 1.00 (s, 2H). ^{13}C{^{1}H} NMR (DMSO-d_6, 76

MHz): δ 159.9, 120.7 (q, J = 323 Hz, CF$_3$), 54.9, 31.0, 26.6 (br s, CB), 22.7, 22.3. ^{11}B NMR (DMSO-d_6, 96 MHz): δ 8.7 (line width $h_{1/2}$ = 711 Hz). ^{19}F NMR (DMSO-d_6, 283 MHz): δ −76.3 (s). HRMS (FAB) *m/z*: [M − CF_3SO_3]$^+$ Calcd for $C_{16}H_{30}BN_2$ 261.2502; Found 261.2497. Anal. Calcd for $C_{17}H_{30}BF_3N_2O_3S$: C, 49.76; H, 7.37; N, 6.83. Found: C, 49.92; H, 7.32; N, 6.74.

Synthesis of (1,5-cyclooctanediyl)[*N*,*N*′-dicyclohexylethane-1,2-diimine-*N*,*N*′]boronium(III) trifluoromethanesulfonate (3b). A method similar to that for the synthesis of **2a** with *N*,*N*′-dicyclohexylethane-1,2-diimine (**7b**) (0.382 g, 1.73 mmol) gave compound **3b** (0.142 g, 17%). **3b**: pale yellow solid, mp 136.9–137.3 °C (dec). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 9.18 (s, 2H), 4.25–4.09 (m, 2H), 2.14–1.56 (m, 26H), 1.40–1.18 (m, 6H), 1.01 (s, 2H). ^{13}C{^{1}H} NMR (DMSO-d_6, 76 MHz): δ 160.1, 120.7 (q, J = 322 Hz, CF$_3$), 62.6, 33.0, 31.2, 26.7 (br s, CB), 25.2, 24.3, 22.4. ^{11}B NMR (DMSO-d_6, 96 MHz): δ 8.9 (line width $h_{1/2}$ = 675 Hz). ^{19}F NMR (DMSO-d_6, 283 MHz): δ −76.2 (s). HRMS (FAB) *m/z*: [M − CF_3SO_3]$^+$ Calcd for $C_{22}H_{38}BN_2$ 341.3128; Found 341.3109. Anal. Calcd for $C_{23}H_{38}BF_3N_2O_3S$: C, 56.33; H, 7.81; N, 5.71. Found: C, 56.56; H, 7.46; N, 5.65.

Synthesis of (2-benzoylpyridine-*N*,*O*)(1,5-cyclooctanediyl)boronium(III) trifluoromethanesulfonate (4a). A method similar to that for the synthesis of **2a** with 2-benzoylpyridine (**8a**)(0.608 g, 3.32 mmol) and recrystallization from minimum amount of acetonitrile at −18 °C gave compound **4a** (0.567 g, 38%). **4a**: orange crystals. ^{1}H NMR (CD_3CN, 300 MHz): δ 9.42 (d, 1H, J = 5.8 Hz), 9.16 (dt, 1H, J = 7.9, 1.0 Hz), 8.72 (td, 1H, J = 7.9, 1.0 Hz), 8.51–8.49 (m, 2H), 8.31 (ddd, 1H, J = 7.9, 5.8, 1.0 Hz), 8.12–8.06 (m, 1H), 7.89–7.82 (m, 2H), 2.27–1.80 (m, 12H, The observed integral value was not accurate due to peak overlapping with those of water and residual protons of the deuterated solvent), 0.99 (s, 2H). A ^{13}C NMR spectrum of this compound cannot be measured because of its high moisture sensitivity. ^{11}B NMR (CD_3CN, 96 MHz): δ 16.6 (line width $h_{1/2}$ = 326 Hz). HRMS (FAB) *m/z*: [M − CF_3SO_3]$^+$ Calcd for $C_{20}H_{23}BNO$ 304.1873; Found 304.1898.

Synthesis of (1,5-cyclooctanediyl)[2-(4-methoxybenzoyl)pyridine-*N*,*O*]boronium(III) trifluoromethanesulfonate (4b). A method similar to that for the synthesis of **4a** with 2-(4-methoxybenzoyl)pyridine (**8b**)(0.671 g, 3.15 mmol) gave compound **4b** (0.163 g, 11%). **4b**: red solid. ^{1}H NMR (CD_3CN, 300 MHz): δ 9.37 (d, 1H, J = 5.8 Hz), 9.15 (d, 1H, J = 8.6 Hz), 8.72–8.64 (m, 1H), 8.62–8.55 (m, 2H), 8.29–8.21 (m, 1H), 7.36–7.29 (m, 2H), 4.06 (s, 3H), 2.29–1.76 (m, 12H, The observed integral value was not accurate due to peak overlapping with those of water and residual protons of the deuterated solvent), 0.90 (s, 2H). A ^{13}C NMR spectrum of this compound cannot be measured because of its high moisture sensitivity. ^{11}B NMR (CD_3CN, 96 MHz): δ 16.4 (line width $h_{1/2}$ = 258 Hz). HRMS (FAB) *m/z*: [M − CF_3SO_3]$^+$ Calcd for $C_{21}H_{25}BNO_2$ 334.1978; Found 334.1958.

Theoretical calculations

Geometry (Cartesian coordinates) of the cation of **2b**

7	2.166707	6.868989	2.276923
7	4.378237	7.719449	2.479200
6	0.859646	6.537325	2.209084
1	0.141940	7.301423	2.459946
6	0.450194	5.262753	1.831324
1	-0.611817	5.045131	1.791938
6	1.399517	4.286987	1.510117
1	1.089390	3.289738	1.214268
6	2.749639	4.618992	1.577065
1	3.527546	3.900703	1.338701
6	3.092244	5.913691	1.962640
6	4.406046	6.479503	2.101306
1	5.321824	5.929675	1.910676
6	5.678900	8.445963	2.666693
1	5.407287	9.448387	2.979885
6	6.503799	7.791927	3.783372
1	7.390020	8.404631	3.976659
1	6.850218	6.789833	3.505847
1	5.932652	7.718526	4.714227
6	6.439060	8.538964	1.336720
1	7.323949	9.168058	1.475845
1	5.822591	8.989529	0.552473
1	6.783459	7.557852	0.990236
6	2.539480	8.750945	4.211238
1	2.796854	7.966324	4.938840
6	1.015957	9.007647	4.331640
1	0.813986	9.441859	5.320800
1	0.492079	8.043485	4.347800
6	0.401825	9.940526	3.256077
1	-0.687311	9.800706	3.241256
1	0.546363	10.978011	3.567924
6	0.952002	9.772864	1.816120
1	0.710488	10.681304	1.246740
1	0.414138	8.973651	1.290459

6	2.475601	9.513974	1.702132
1	2.687638	9.270478	0.649987
6	3.304870	10.772008	2.065410
1	2.928726	11.617674	1.472485
1	4.337765	10.632317	1.724730
6	3.288567	11.179067	3.559218
1	2.384238	11.760023	3.758828
1	4.118265	11.872156	3.748846
6	3.368389	10.010191	4.571553
1	3.031550	10.377603	5.551209
1	4.413943	9.719632	4.729185
5	2.889193	8.256826	2.680761

Geometry (Cartesian coordinates) of the cation of **3a**

7	2.255379	1.972954	10.013709
7	2.292446	4.320565	10.235756
6	2.624244	2.323134	11.220843
1	2.876487	1.617974	12.003969
6	2.646406	3.738944	11.354825
1	2.917531	4.276528	12.255751
6	2.175385	0.510667	9.689904
1	1.856194	0.455046	8.654983
6	3.559594	-0.143175	9.808841
1	3.494686	-1.178653	9.459974
1	4.303974	0.375108	9.196121
1	3.916021	-0.166030	10.844693
6	1.116710	-0.176763	10.564108
1	0.999580	-1.213016	10.231528
1	1.407612	-0.200377	11.620211
1	0.143626	0.317744	10.482232
6	2.257473	5.819339	10.192361
1	1.943035	6.077540	9.187132
6	1.217211	6.361976	11.182848
1	1.132146	7.445261	11.050945
1	0.230002	5.921001	11.012237
1	1.505457	6.178254	12.223861

6	3.660220	6.397603	10.428103
1	3.627081	7.481660	10.280249
1	4.014244	6.214846	11.448769
1	4.390658	5.981878	9.726828
6	0.406120	3.327895	8.531068
1	-0.294518	3.260409	9.375262
6	0.134497	2.131455	7.592791
1	-0.860510	2.274123	7.147347
1	0.043145	1.217302	8.189122
6	1.152199	1.926449	6.444275
1	1.043141	0.908971	6.048354
1	0.886318	2.584171	5.612876
6	2.635303	2.164216	6.819247
1	3.201158	2.328297	5.890951
1	3.069416	1.256527	7.251905
6	2.913434	3.359704	7.757207
1	3.969263	3.313161	8.059100
6	2.678622	4.719072	7.062064
1	3.138800	5.514371	7.658211
1	3.243558	4.715180	6.118862
6	1.205488	5.070136	6.740822
1	0.922613	4.588903	5.801178
1	1.130436	6.146759	6.542856
6	0.176715	4.686357	7.832242
1	-0.820238	4.660768	7.369388
1	0.111218	5.475601	8.588803
5	1.968071	3.244845	9.139410

Geometry (Cartesian coordinates) of the cation of **4a**

6	-0.078059	-0.943181	-0.264551
6	-0.187885	-3.642267	0.220251
6	-0.078019	-2.729356	1.262500
1	-0.220369	-4.702437	0.447967
1	-0.032273	-3.041753	2.295840
6	-0.227258	-1.813070	-1.346139
1	-0.325239	-1.427092	-2.352671

7	-0.034685	-1.403360	1.025499
6	-1.274907	-0.071496	3.052639
1	-2.211960	-0.168221	2.482130
6	1.347681	-0.074125	2.972939
1	2.246176	-0.169572	2.343348
6	1.369561	-1.222459	4.008313
1	2.230934	-1.081711	4.676819
1	1.576804	-2.167731	3.484867
6	0.093677	-1.370209	4.870829
1	0.127500	-0.644944	5.687380
1	0.105321	-2.352932	5.359685
6	-1.239040	-1.208006	4.100870
1	-2.047480	-1.045619	4.828001
1	-1.499963	-2.155043	3.605964
6	-1.239903	1.354830	3.659210
1	-2.068855	1.456577	4.374162
1	-1.445359	2.074572	2.855774
6	0.078993	1.745984	4.362644
1	0.102757	1.310752	5.365615
1	0.086479	2.831962	4.518593
6	1.357325	1.347008	3.590850
1	2.221807	1.436635	4.264089
1	1.528045	2.069565	2.782308
5	0.007318	-0.196138	2.047835
6	-0.278341	-3.182407	-1.097956
1	-0.394951	-3.882816	-1.918938
6	-0.020114	0.517681	-0.211218
8	-0.009318	0.913504	1.005998
6	0.000778	1.477779	-1.296015
6	0.532250	1.165578	-2.567505
6	-0.488664	2.780993	-1.047942
6	0.556964	2.132614	-3.567206
1	0.982583	0.197603	-2.758348
6	-0.476327	3.733369	-2.059497
1	-0.891187	3.022797	-0.069810
6	0.043837	3.411332	-3.319677

1	0.986032	1.895707	-4.536009
1	-0.869451	4.727492	-1.869902
1	0.057555	4.160052	-4.106545

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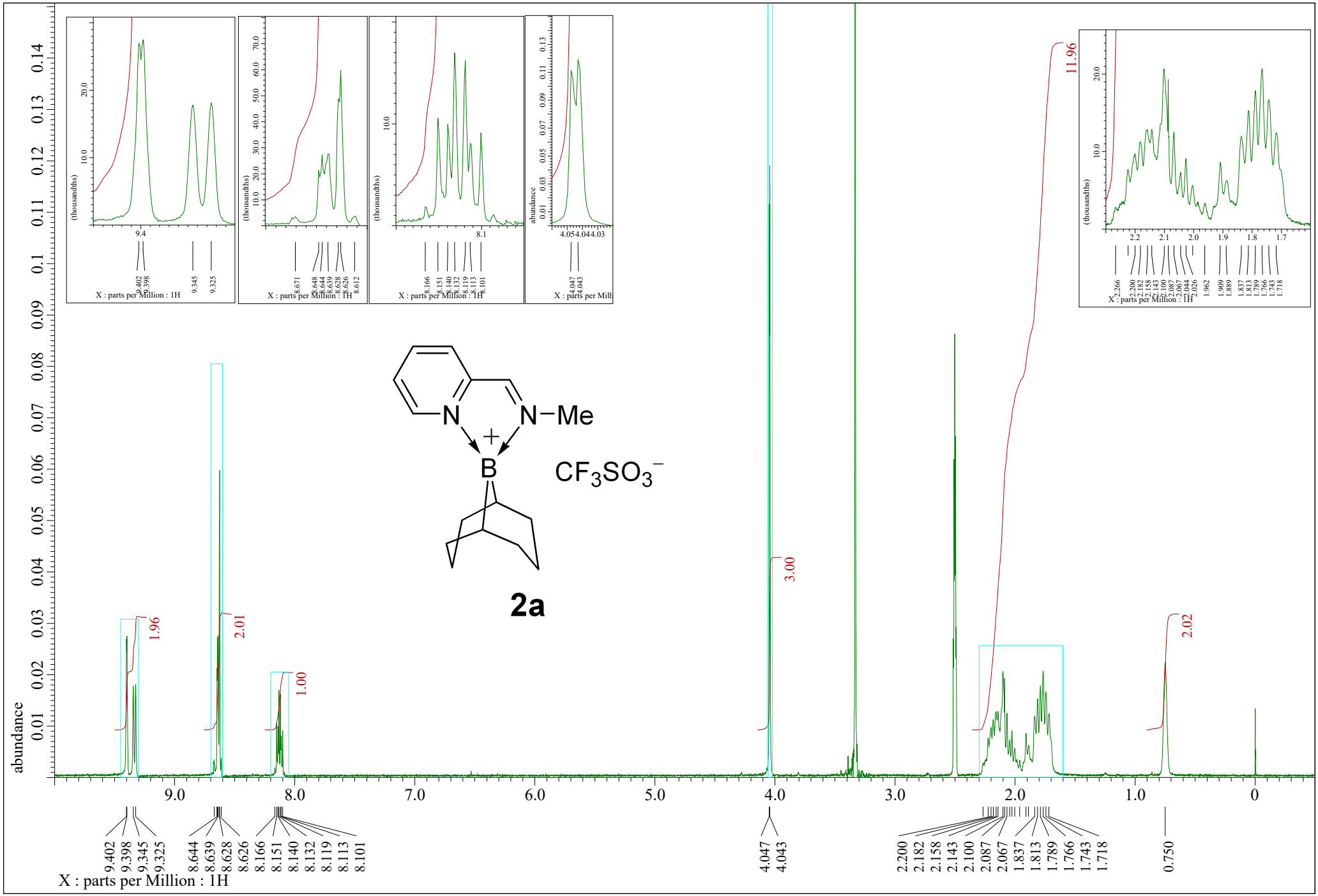
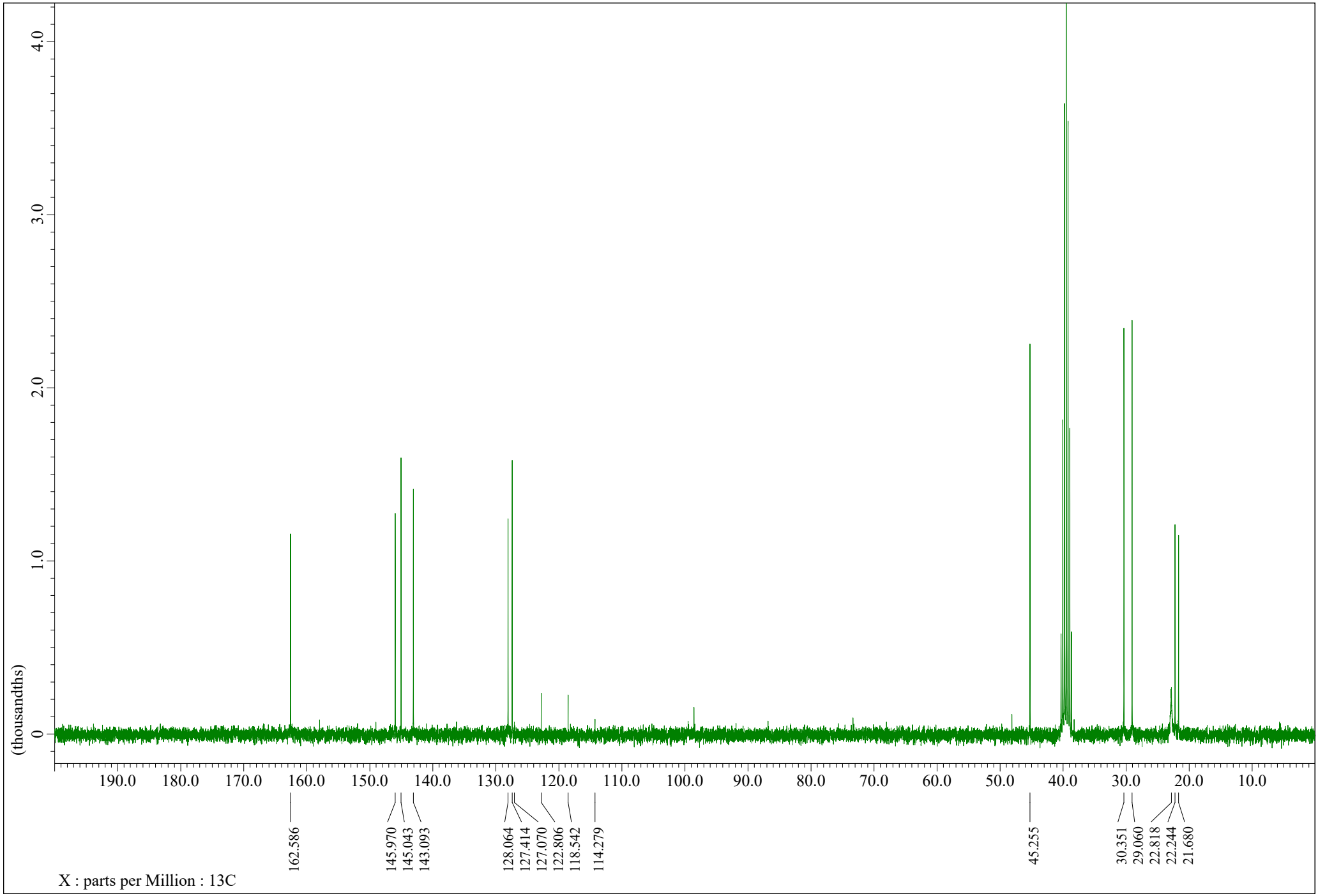


[1]H NMR spectrum of compound **2a** (300 MHz, DMSO-d_6).



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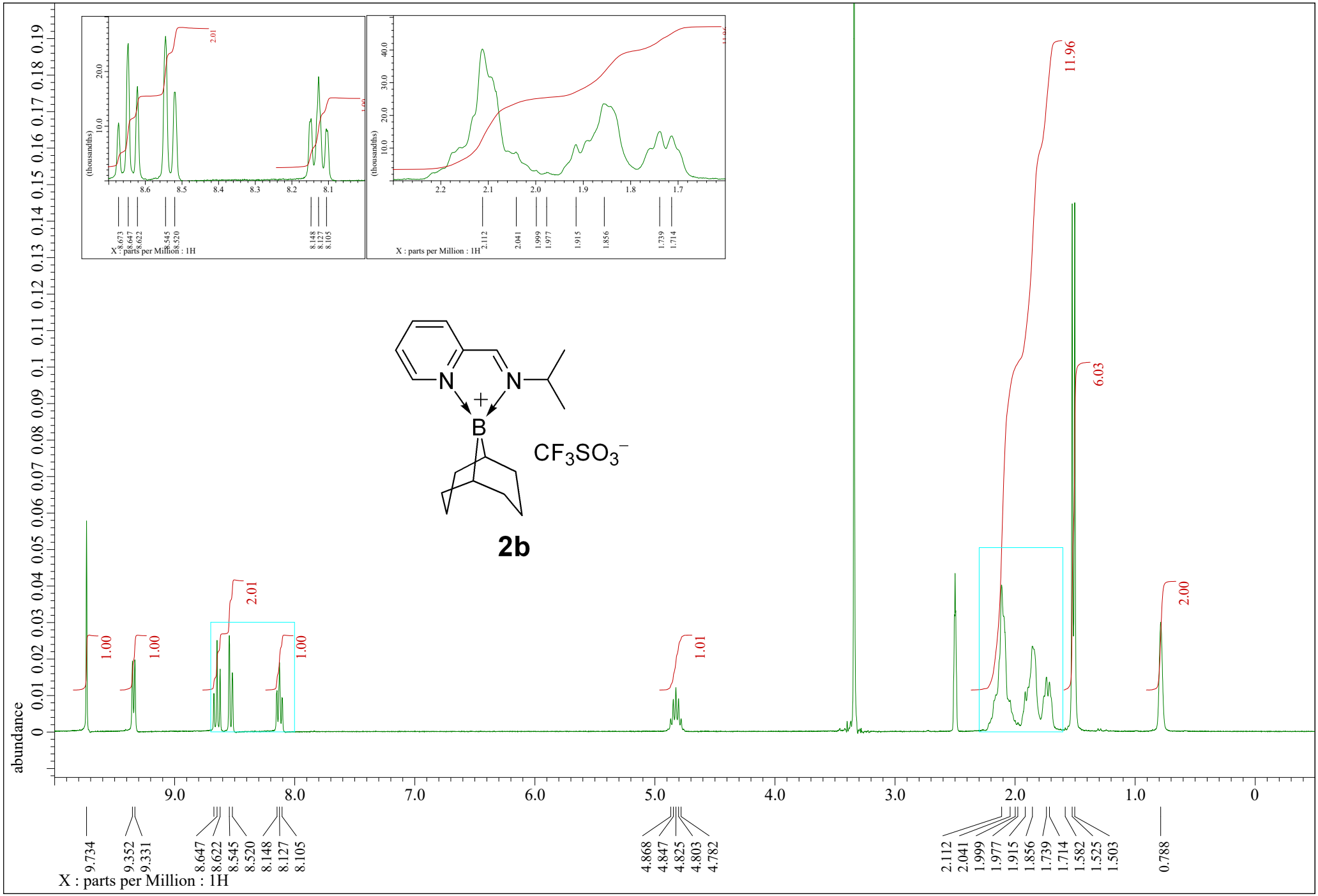

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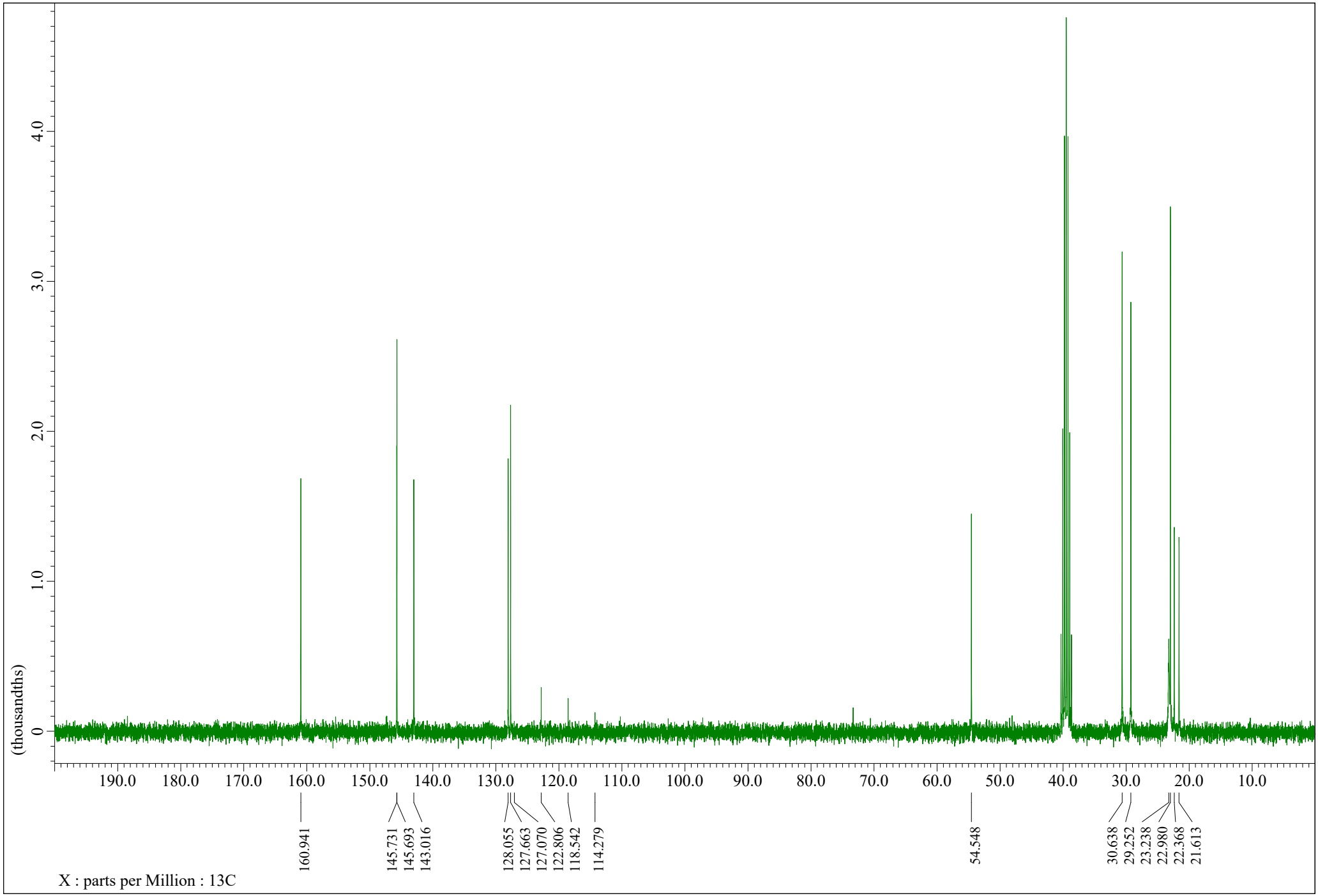
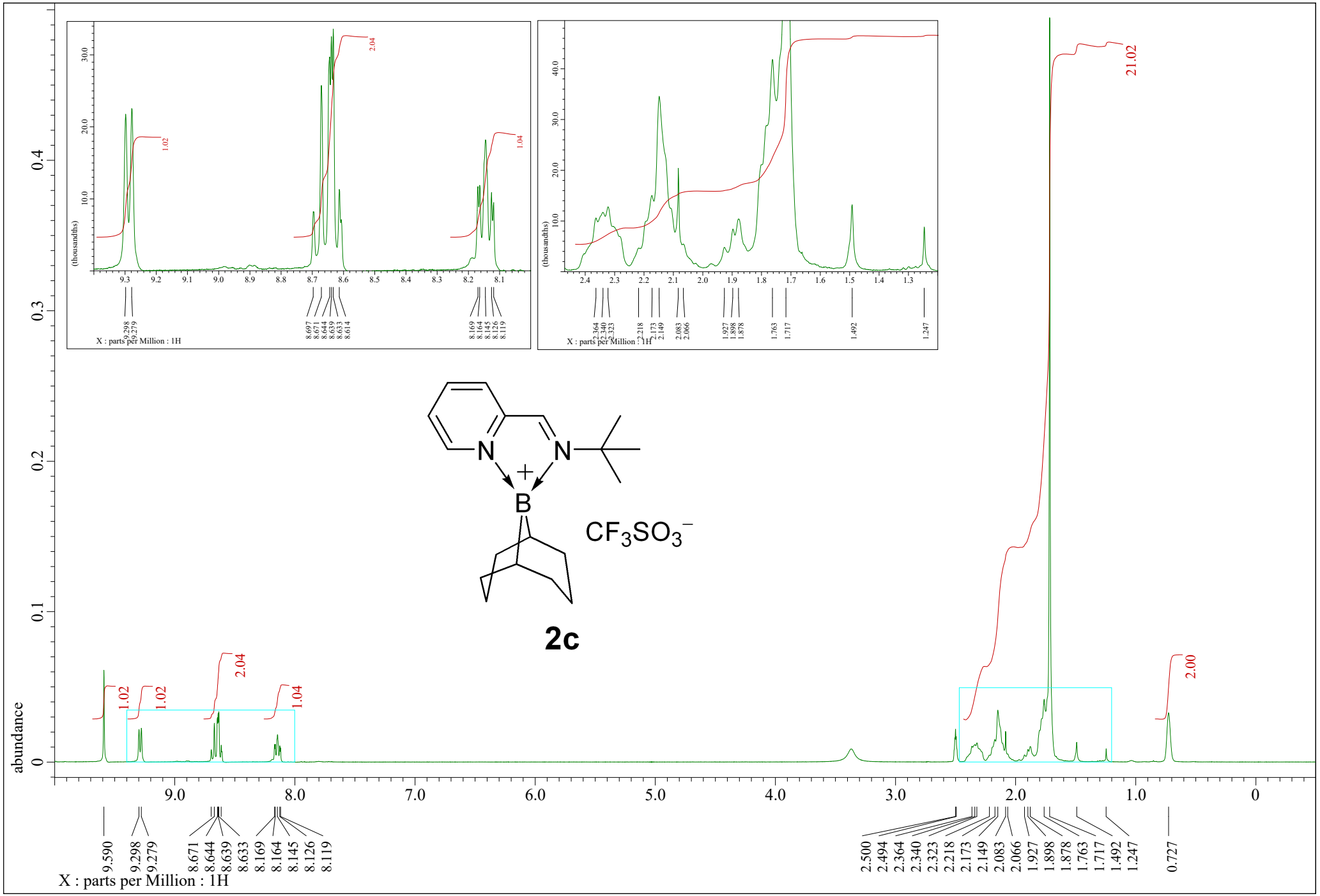
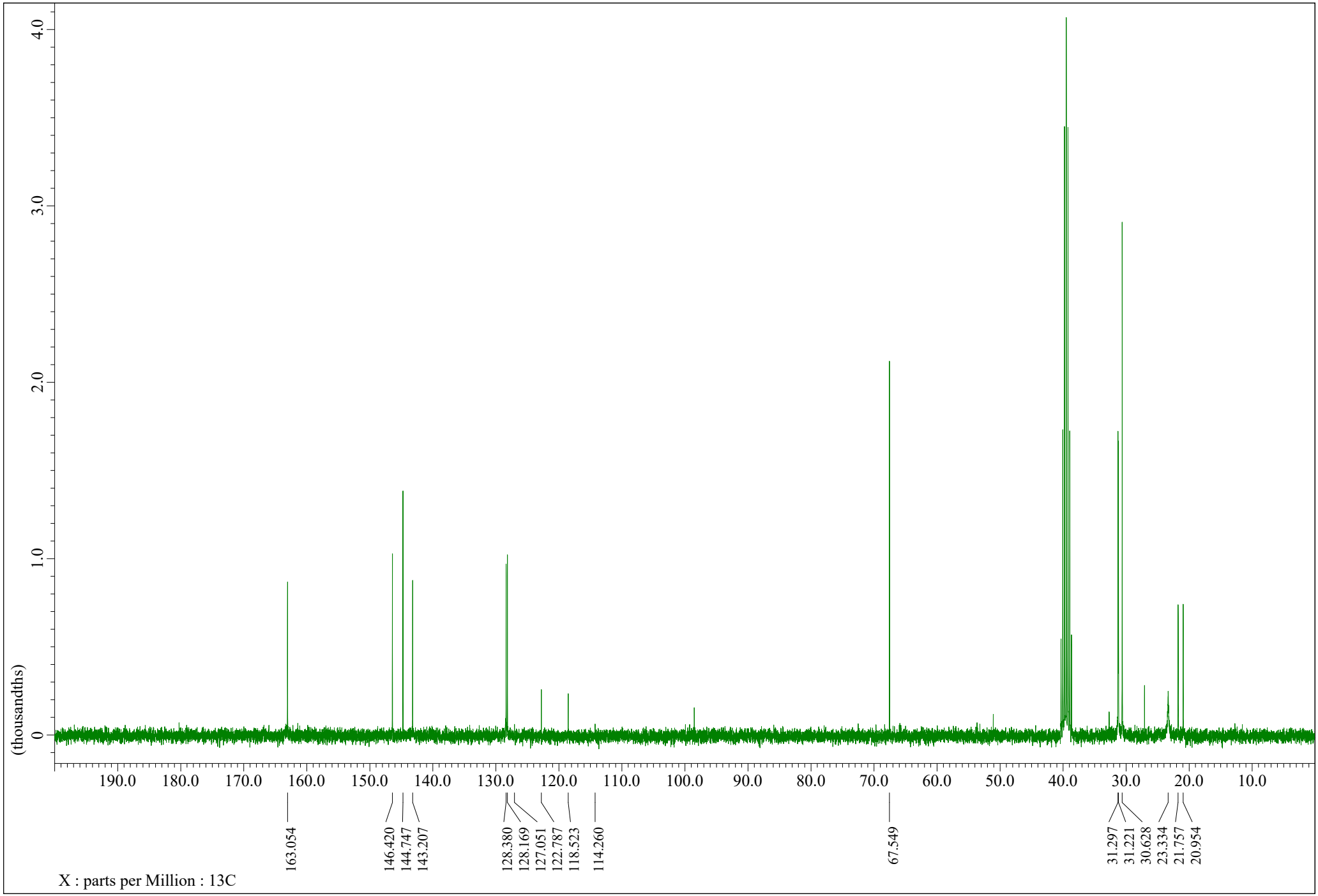


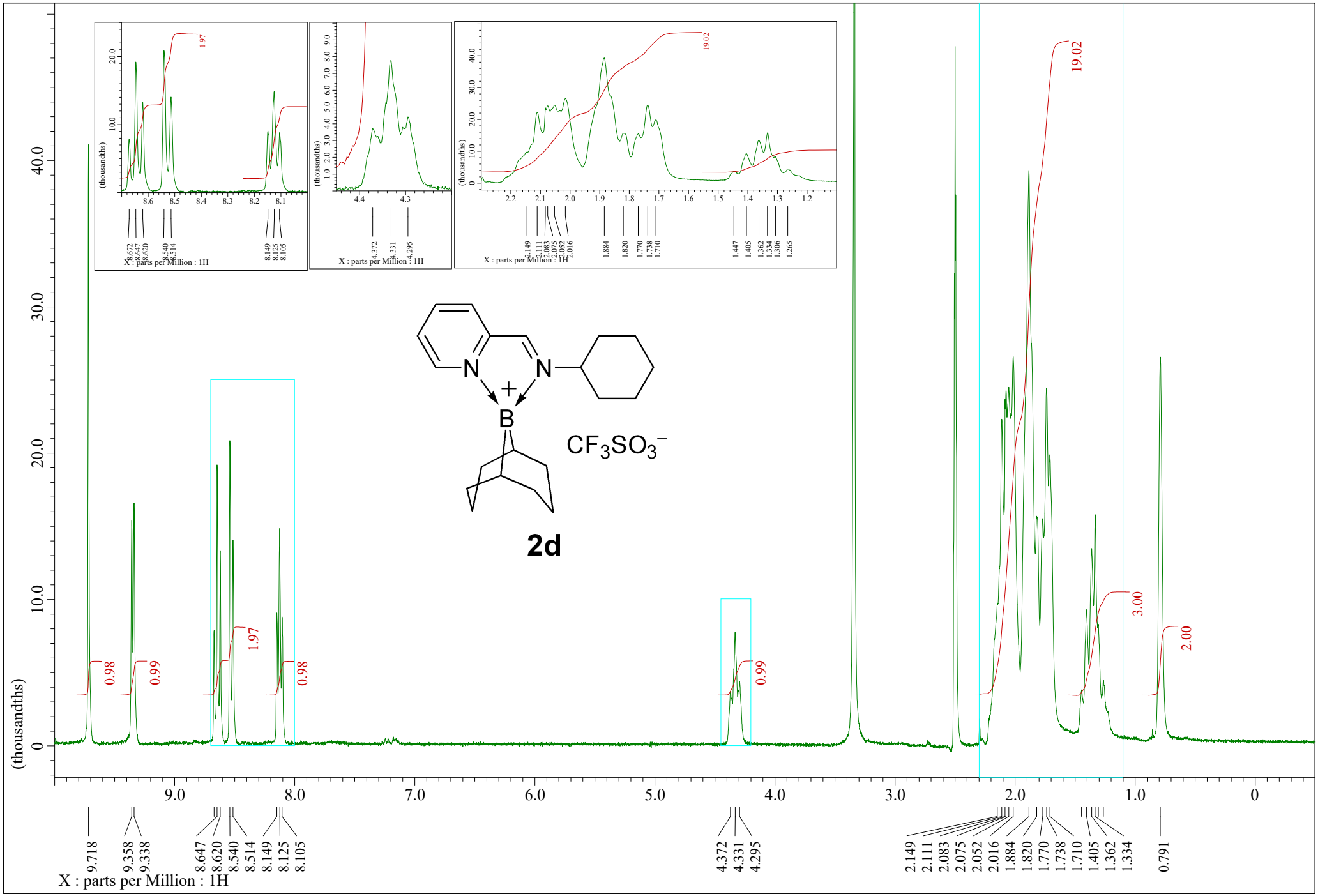
^{13}C NMR spectrum of compound **2b** (76 MHz, DMSO-d_6).



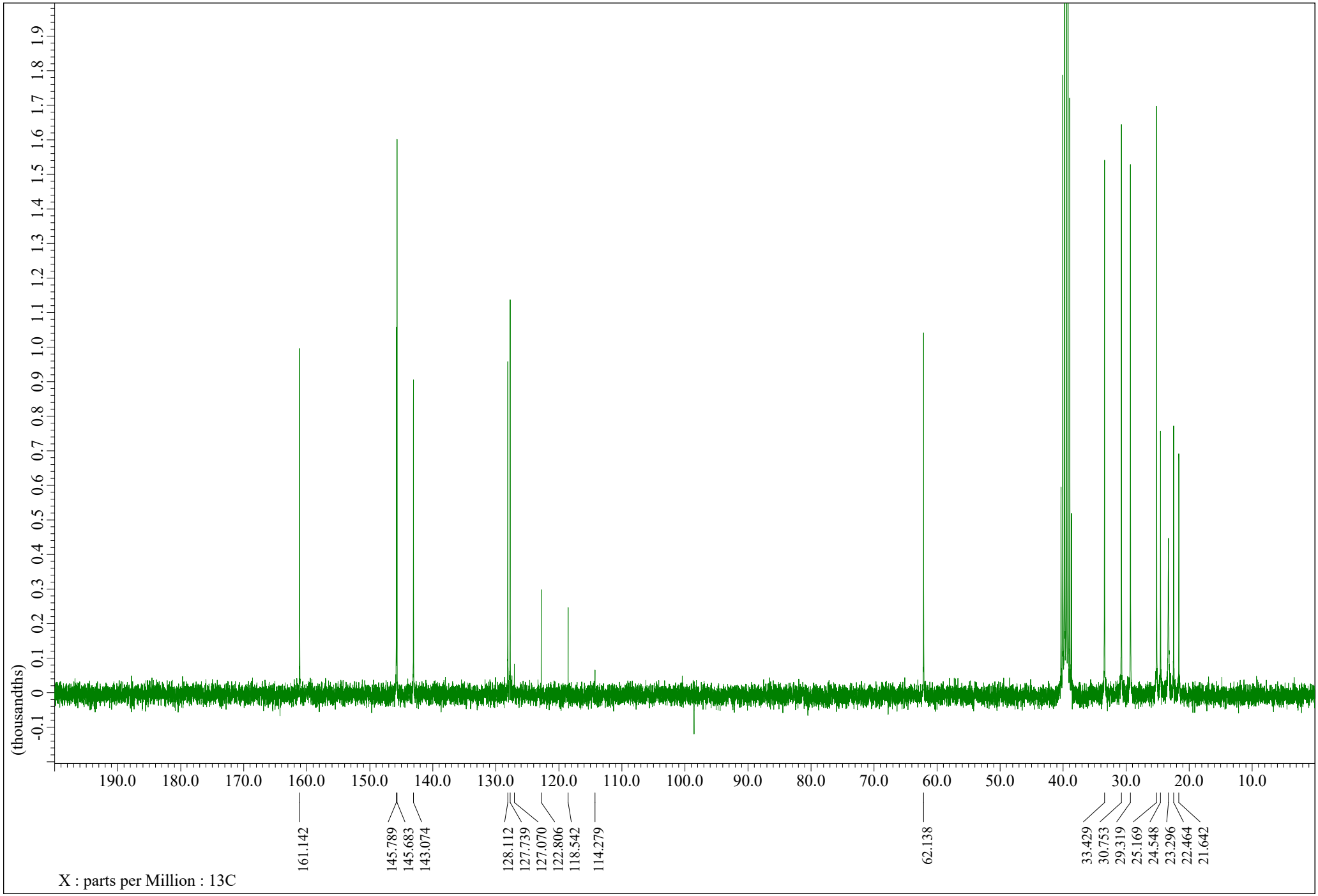
[1]H NMR spectrum of compound **2c** (300 MHz, DMSO-d_6).



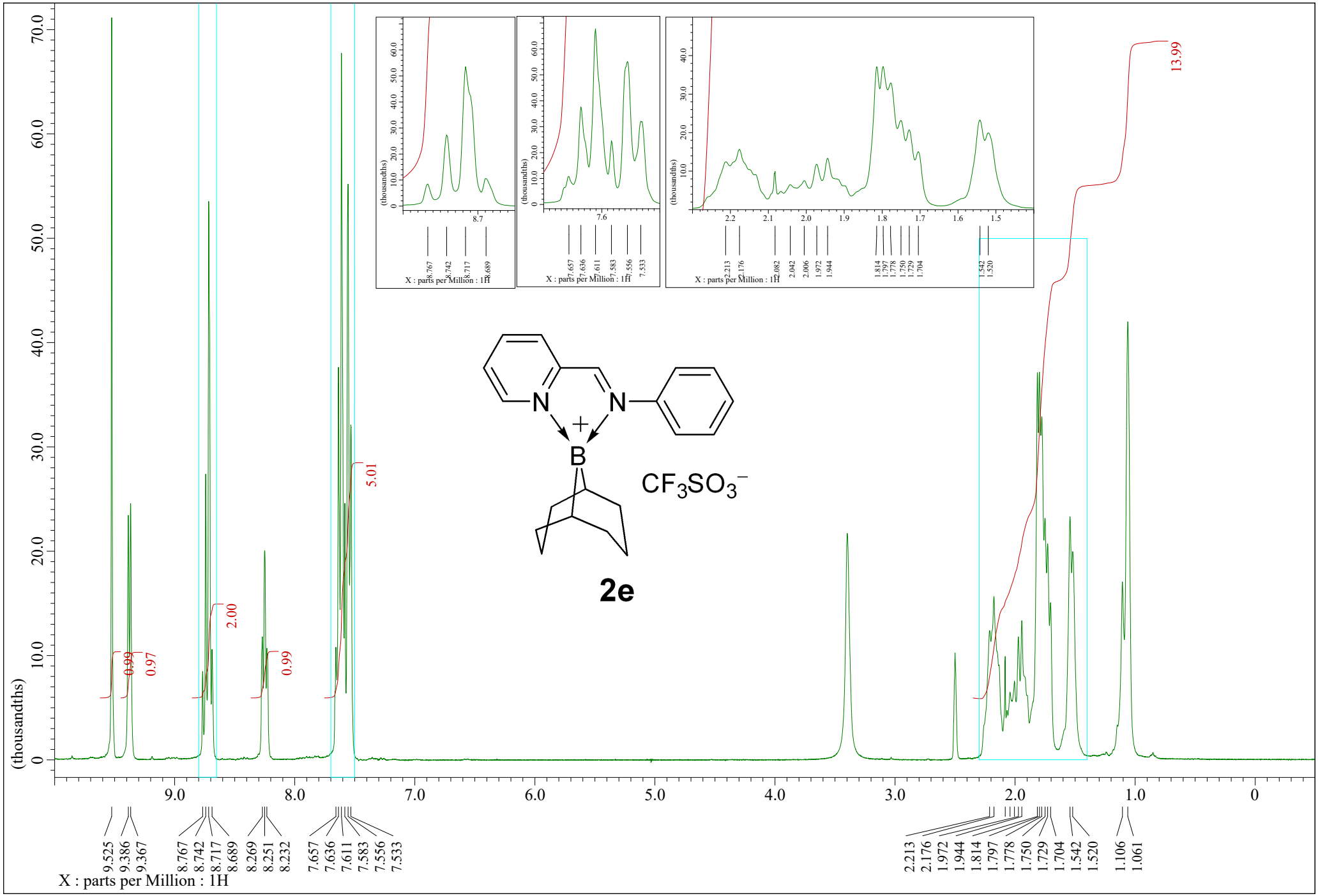
^{13}C NMR spectrum of compound **2c** (76 MHz, DMSO-d_6).



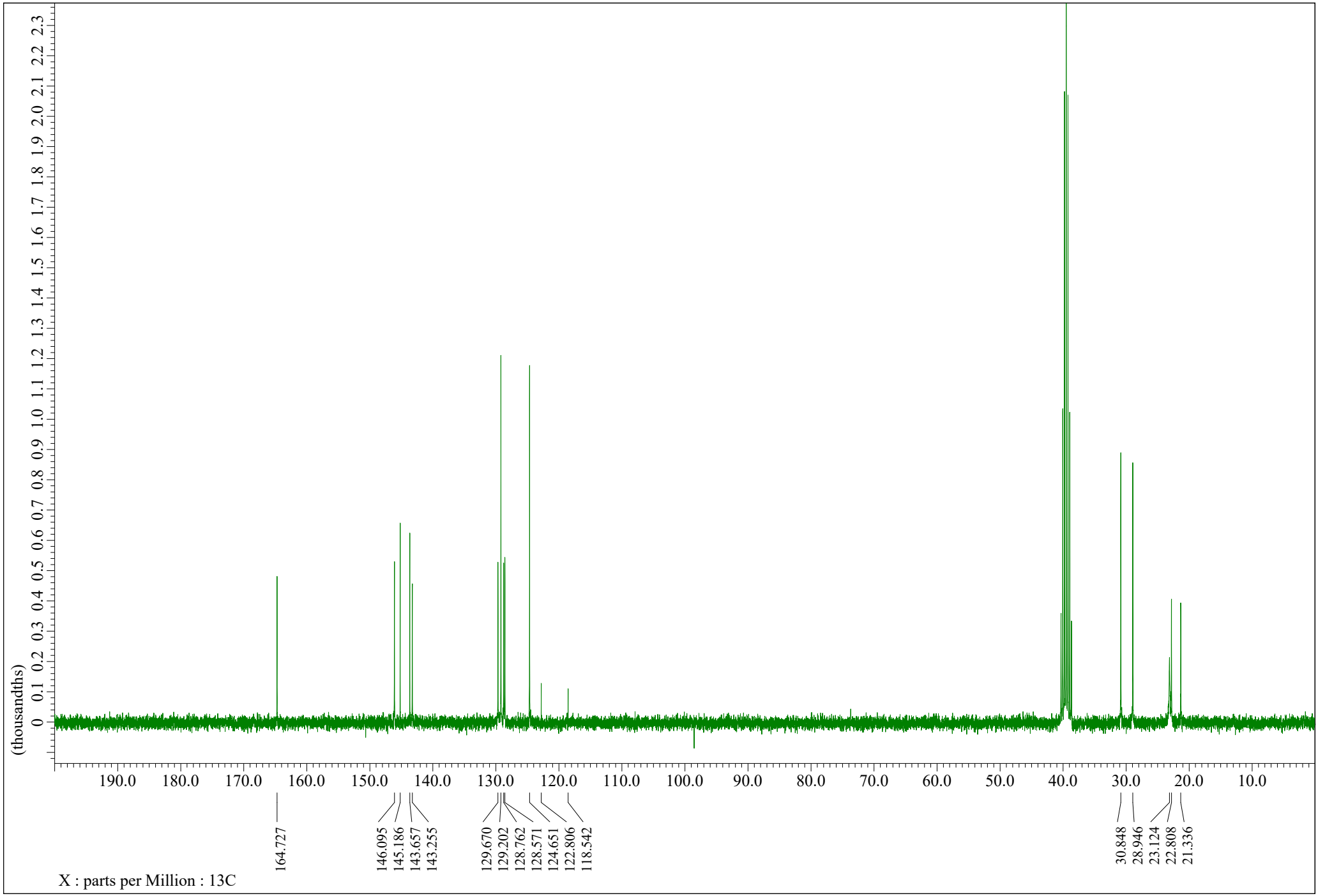
[1]H NMR spectrum of compound **2d** (300 MHz, DMSO-d_6).



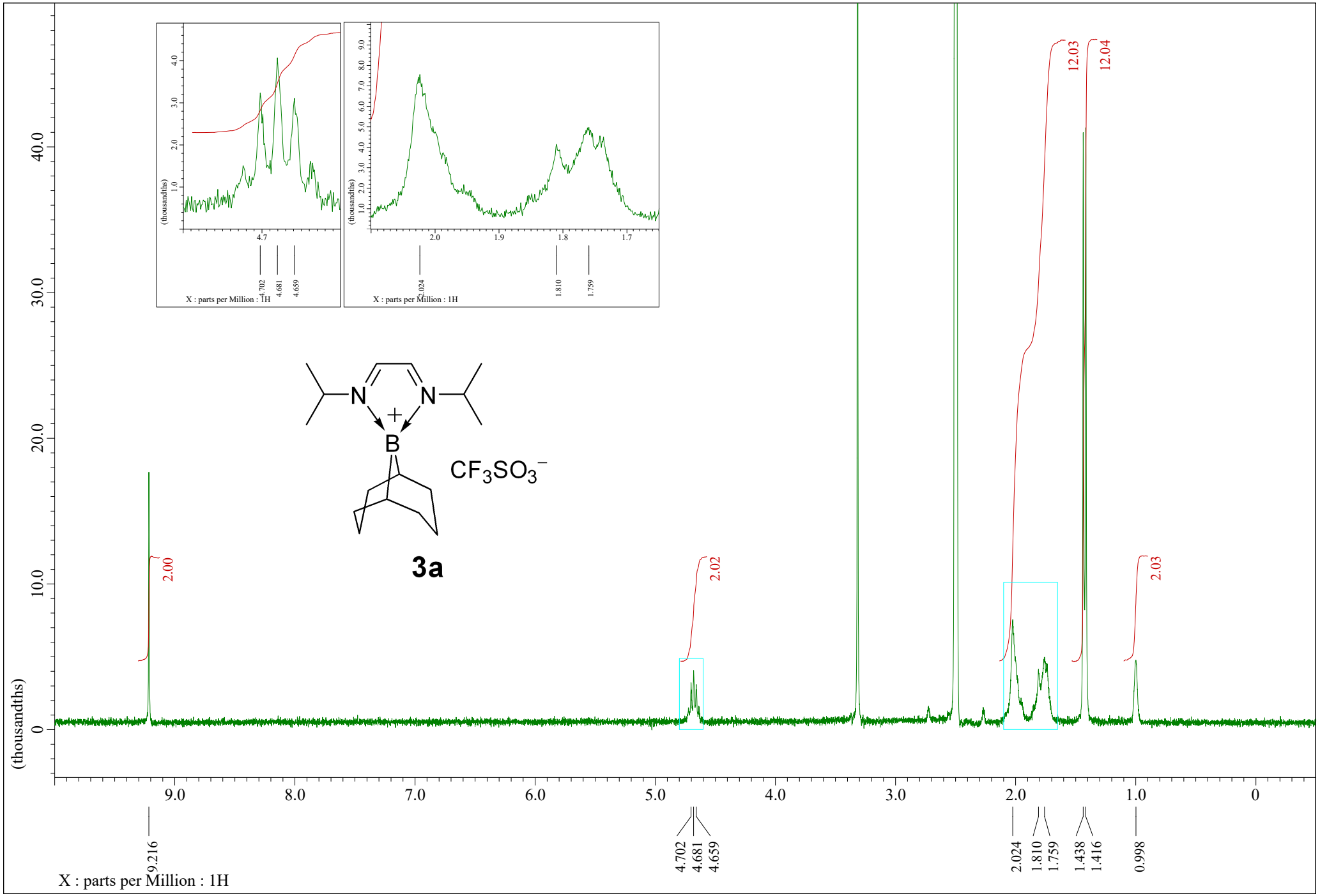
^{13}C NMR spectrum of compound **2d** (76 MHz, DMSO-d_6).



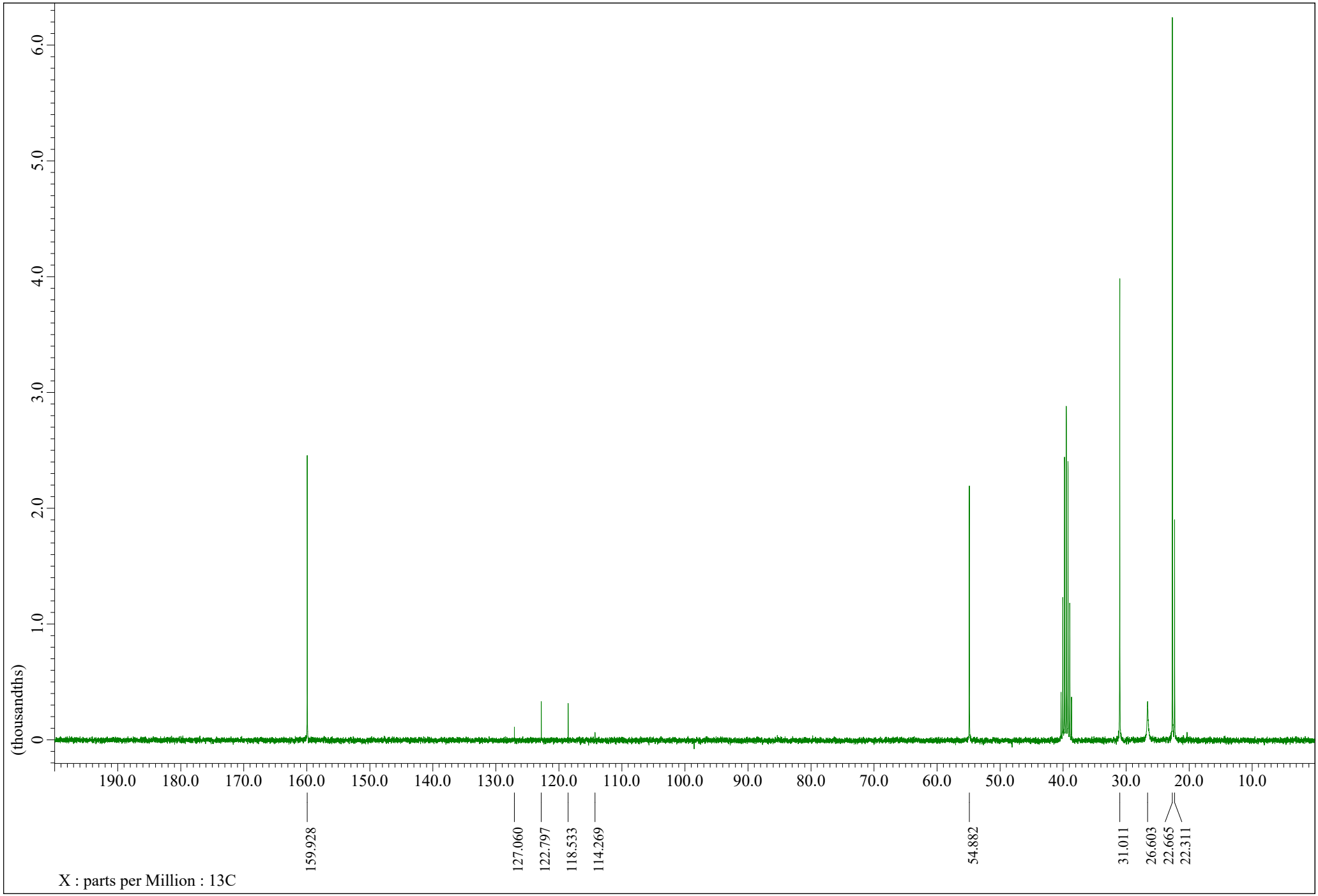
[1]H NMR spectrum of compound **2e** (300 MHz, DMSO-d_6).



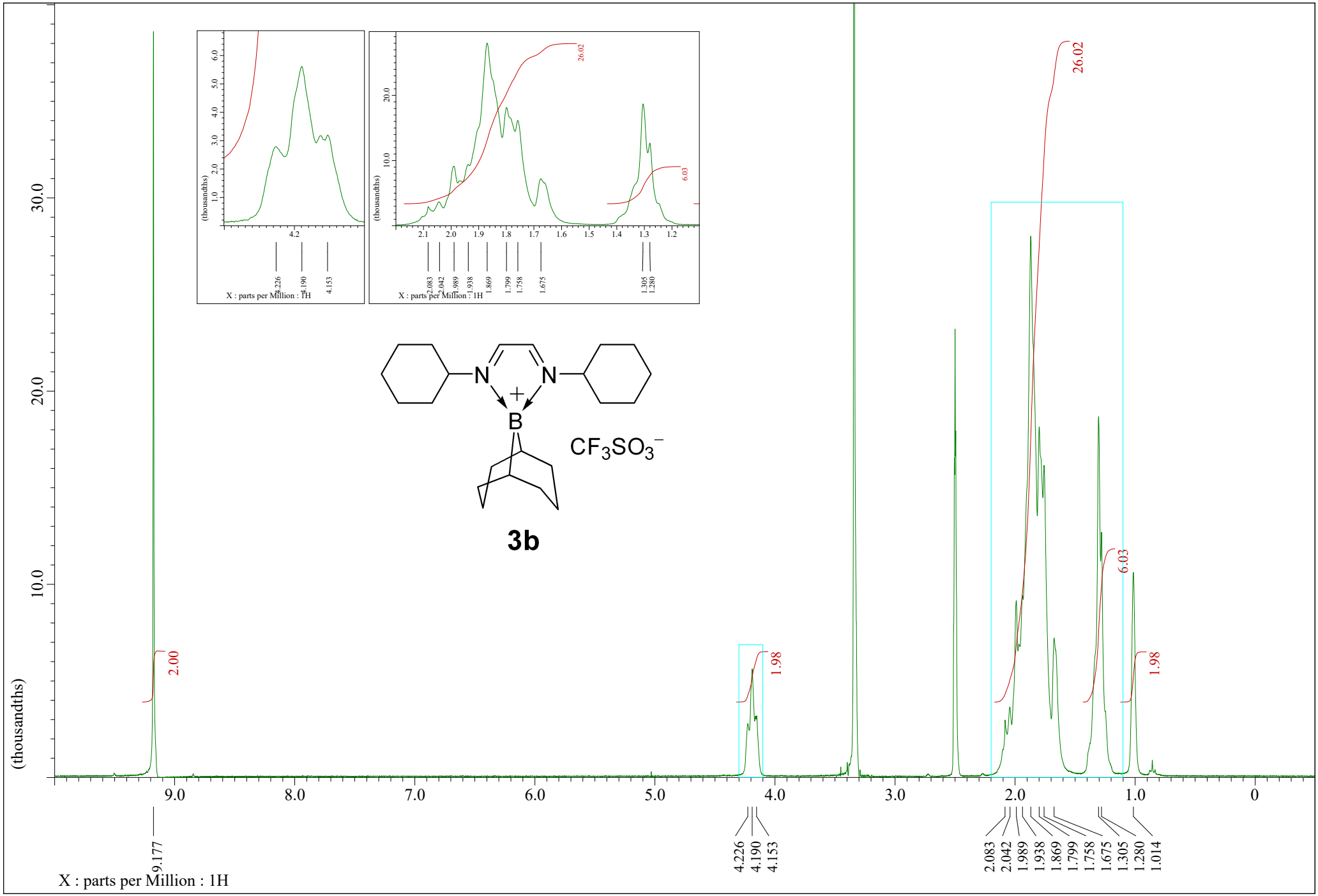
^{13}C NMR spectrum of compound **2e** (76 MHz, DMSO-d_6).



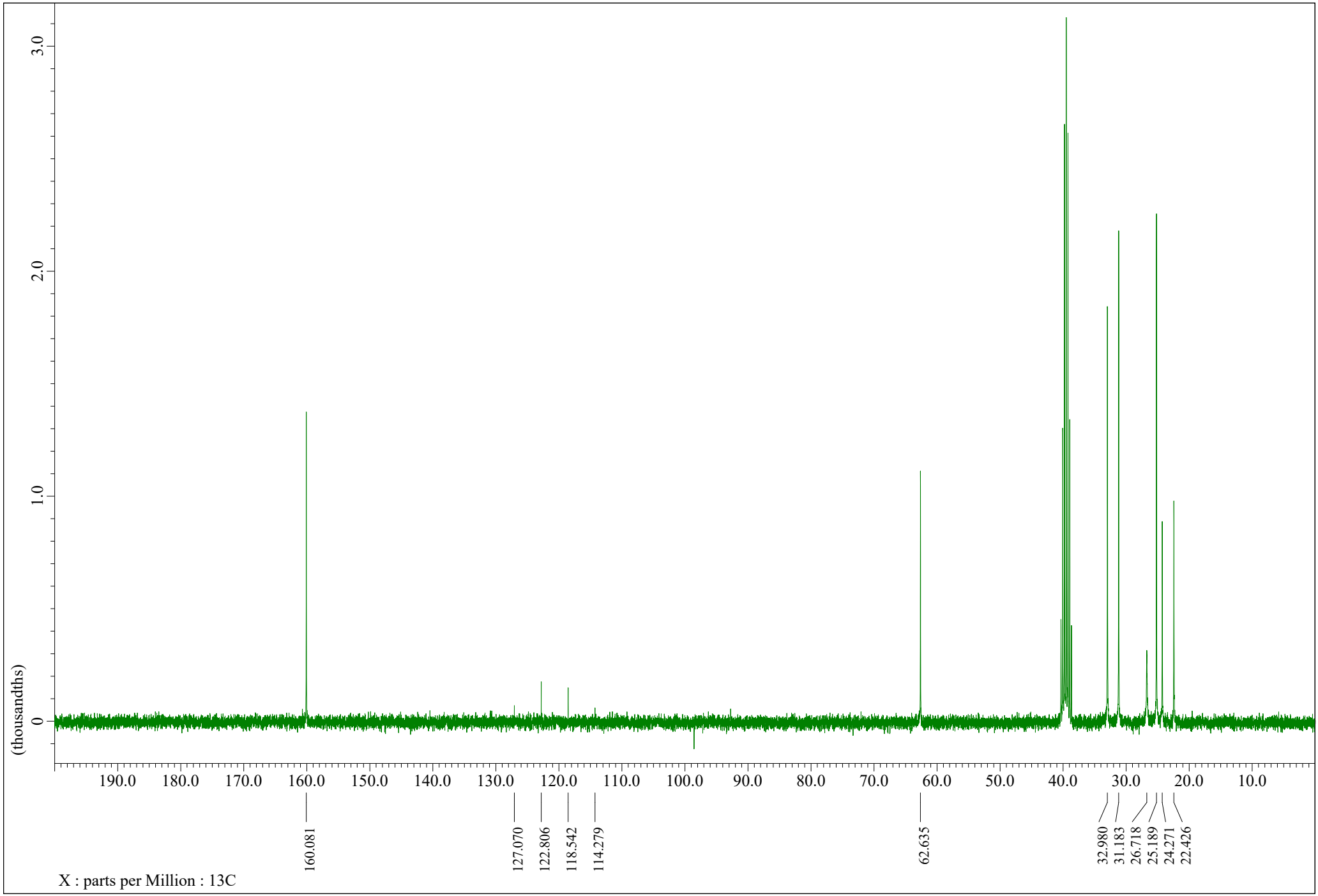
^{1}H NMR spectrum of compound **3a** (300 MHz, DMSO-d_6).



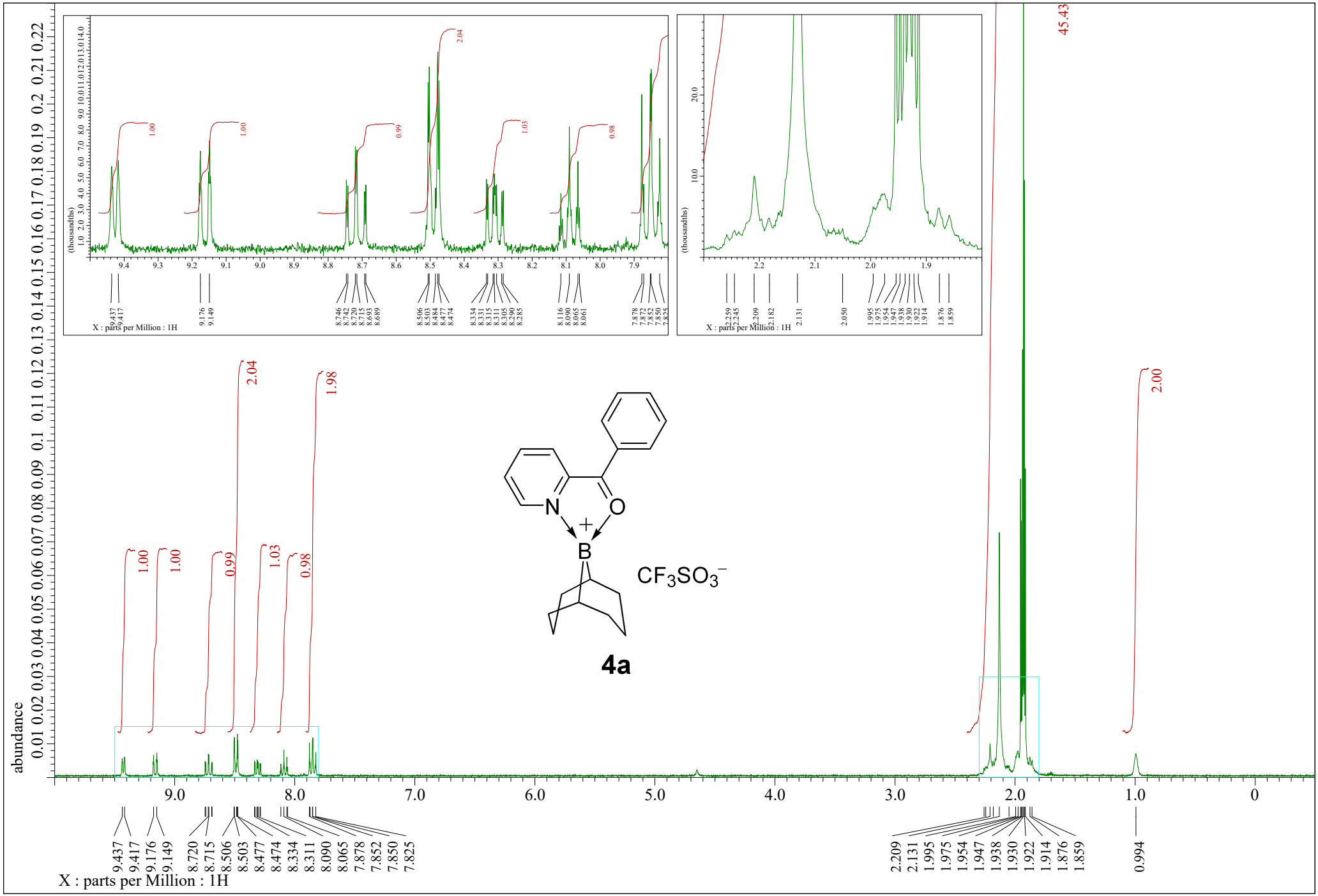
^{13}C NMR spectrum of compound **3a** (76 MHz, DMSO-d_6).



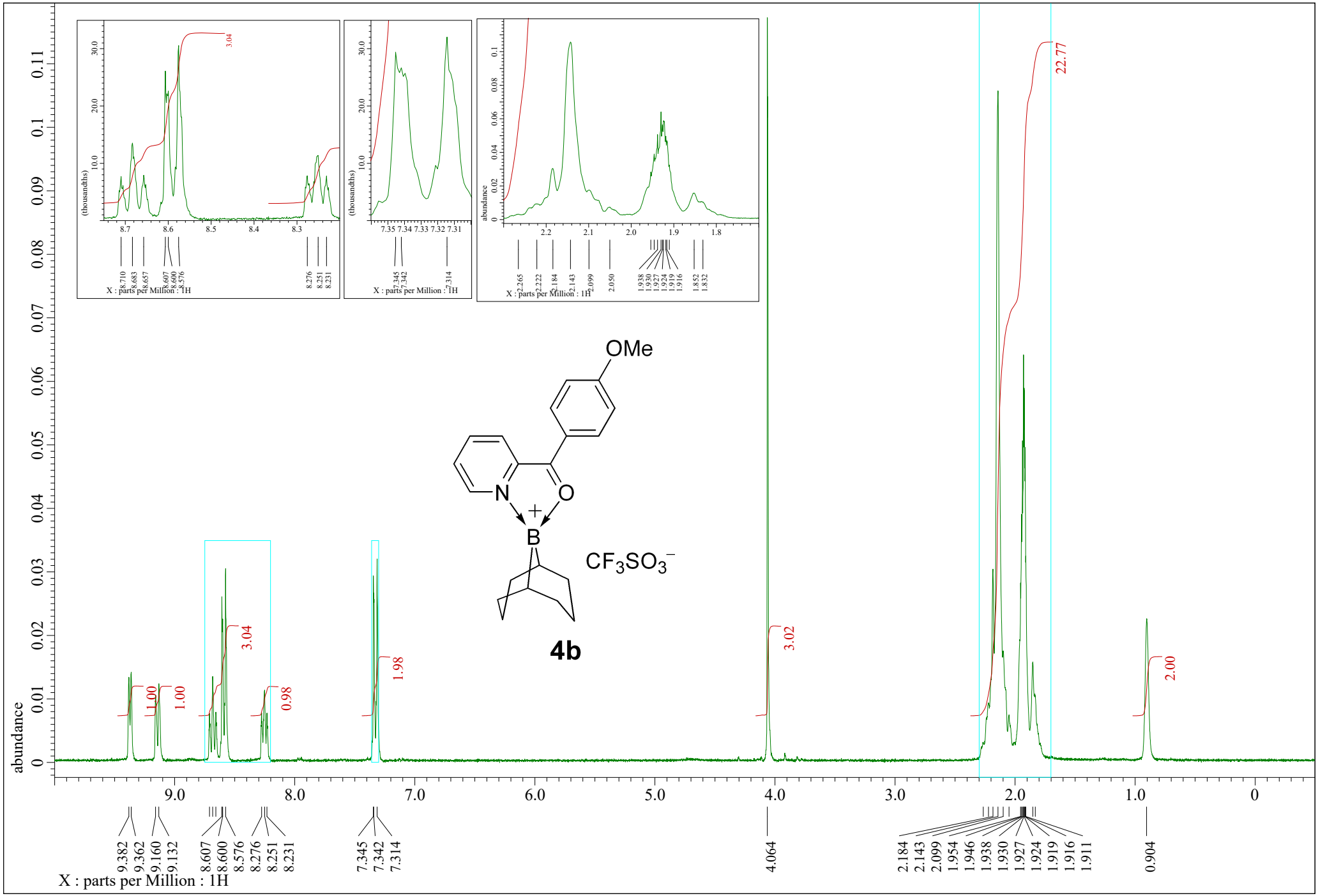
^{1}H NMR spectrum of compound **3b** (300 MHz, DMSO-d_6).



^{13}C NMR spectrum of compound **3b** (76 MHz, DMSO-d_6).



^{1}H NMR spectrum of compound **4a** (300 MHz, CD_3CN).



^{1}H NMR spectrum of compound **4b** (300 MHz, CD_3CN).