# Supporting Information

## Phenoxysulfonyl azide: a new diazo-transfer reagent for the metal–free conversion of amines to azides

Sungduk Gwak,*† Ji Hye Lee,† You Jeong You, Hyeok-Jun Kwon* and Hogyu Han*

*Department of Chemistry, Korea University, Seoul 02841, Korea*

*Corresponding author: kkmmsd@korea.ac.kr; skiru@korea.ac.kr; hogyuhan@korea.ac.kr
†These authors contributed equally to this work.

Contents

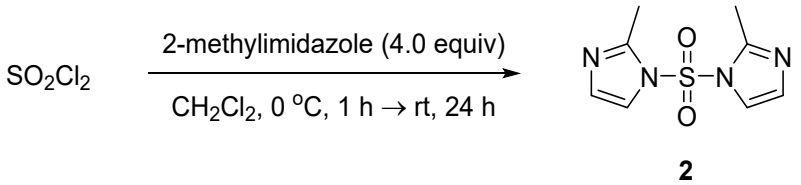
## I. Syntheses of 1, 2, 2′, 2′′, and 4

**General.** $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Bruker Ascend 500 NMR spectrometer. Chemical shifts ($\delta$) and coupling constants ($J$) are reported in parts per million (ppm) and hertz (Hz), respectively. $^{1}H$ NMR spectra are referenced to TMS (0.03% v/v tetramethylsilane in $CDCl_3$, DMSO-$d_6$) as an internal standard. $^{13}C$ NMR spectra are referenced to the solvent ($^{13}C$: $CDCl_3$, $\delta$ 77.00 ppm; DMSO-$d_6$, $\delta$ 39.50 ppm) as an internal standard. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-700 mass spectrometer using chemical ionization (CI), electron impact (EI), and fast atom bombardment (FAB) techniques. Differential scanning calorimetry (DSC) was performed on a TA Instruments Discovery DSC 250 Auto. Thin-layer chromatography (TLC) was performed on silica gel 60 $F_{254}$ precoated plates (0.25 mm thickness, Merck, Darmstadt). Flash chromatography was carried out on silica gel 60 (230−400 mesh, Merck). Reagent-grade chemicals were purchased from Sigma-Aldrich and TCI and used as received unless otherwise specified. Amino acids **3r**−**3w** were purchased from BACHEM.

**Safety note on azide compounds**

All azide-containing compounds were handled with extreme care due to their known toxicity and potential explosiveness. Reactions involving azides were conducted on a small scale in a well-ventilated fume hood with standard personal protective equipment (PPE). No accidents or unusual events occurred during the study.

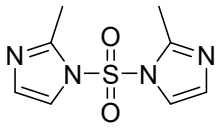
### 1.1. Procedure for the preparation of 2




**2**

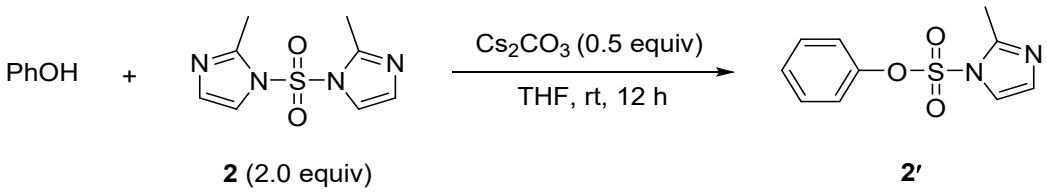
To a cooled (0 °C) solution of 2-methylimidazole (20.3 g, 247 mmol) in $CH_2Cl_2$ (300 mL) were slowly added a solution of sulfuryl chloride (5 mL, 61.9 mmol) in $CH_2Cl_2$ (40 mL). After stirring at 0 °C for 1 h and then room temperature for 24 h, the reaction mixture was filtered and the filtrate was extracted with $H_2O$ and brine. The organic layer was dried over $Na_2SO_4$ and concentrated *in vacuo*. The residue was recrystallized from *i*-PrOH (60 mL) to give **2** (11.2 g, 80%) as a white solid.

*1,1'-Sulfonylbis(2-methyl-1H-imidazole) (**2**)*[S1]



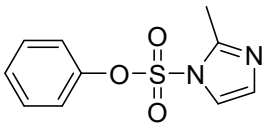
TLC (MeOH/$CH_2Cl_2$ = 1:20) $R_f$ = 0.30; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.38 (d, $J$ = 1.8 Hz, 2H), 6.96 (d, $J$ = 1.8 Hz, 2H), 2.53 (s, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 145.99, 128.47, 120.02, 14.94; HRMS (FAB+) for $C_8H_{11}N_4O_2S$ ($M$H$^+$), calcd 227.0603, found 227.0605.

### 1.2. Procedure for the preparation of 2′



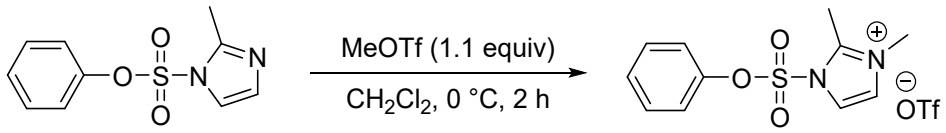

To a solution of **2** (6.79 g, 30.0 mmol) and phenol (1.41 g, 15.0 mmol) in THF (50 mL) was added cesium carbonate (2.44 g, 7.5 mmol). After stirring at room temperature for 12 h, the reaction mixture was concentrated *in vacuo*. The residue was dissolved in EtOAc (100 mL) and the organic layer was washed with saturated aqueous $NH_4Cl$ solution and brine. The organic layer was dried over $Na_2SO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography (EtOAc/*n*-hexane = 1:10) to give **2′** (3.5 g, 98%) as a colorless oil.

*1-Phenoxysulfonyl-2-methylimidazole (**2′**)*[S2]



TLC (EtOAc/*n*-hexane = 1:1) $R_f$ = 0.50; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.36 (m, 3H), 7.14 (d, $J$ = 1.8 Hz, 1H), 6.93 (m, 2H), 6.88 (d, $J$ = 1.8 Hz, 1H), 2.45 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 148.98, 146.78, 130.24, 128.52, 127.93, 121.53, 120.32, 14.84; HRMS (FAB+) for $C_{10}H_{11}N_2O_3S$ ($M$H$^+$), calcd 239.0490, found 239.0491.

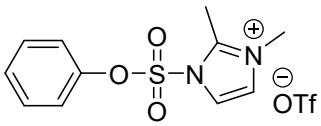
### 1.3. Procedure for the preparation of 2″




**2′** **2″**

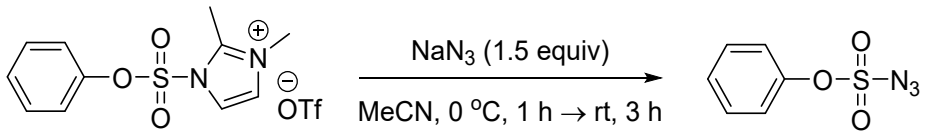
To a cooled (0 °C) solution of **2′** (2.38 g, 10.0 mmol) in $CH_2Cl_2$ (150 mL) was slowly added a solution of methyl trifluoromethanesulfonate (1.20 mL, 11.0 mmol) in $CH_2Cl_2$ (20 mL). After stirring at 0 °C for 2 h, the precipitate was collected by filtration to give **2″** (3.8 g, 94%) as a white solid.

*1-Phenoxysulfonyl-2,3-dimethylimidazol-3-ium triflate (**2″**)*[S2]




TLC (MeOH/$CH_2Cl_2$ = 1:5) $R_f$ = 0.20; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.57 (d, $J$ = 2.4 Hz, 1H), 7.46 (tm, $J$ = 8.1 Hz, 2H), 7.41 (tt, $J$ = 7.3, 1.1 Hz, 1H), 7.34 (d, $J$ = 2.4 Hz, 1H), 7.21 (dm, $J$ = 8.8 Hz, 2H), 3.99 (s, 3H), 2.85 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 149.04, 148.13, 131.00, 129.53, 124.09, 121.24, 120.55 (q, $J$ = 320.1 Hz), 120.41, 36.81, 11.59; HRMS (FAB+) for $C_{11}H_{13}N_2O_3S$ ($M^+$ − $TfO^-$), calcd 253.0647, found 253.0648.

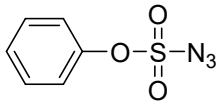
### 1.4. Procedure for the preparation of 1




**2″** **1**

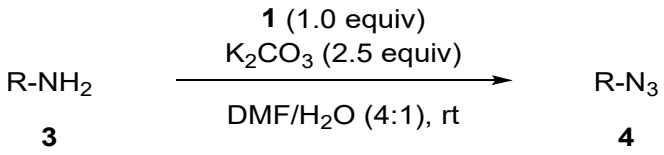
To a cooled (0 °C) solution of **2″** (3.62 g, 9.0 mmol) in MeCN (40 mL) were slowly added a solution of sodium azide (878 mg, 13.5 mmol) in $H_2O$ (10 mL). After stirring at 0 °C for 1 h and then room temperature for 3 h, the reaction mixture was diluted with $CH_2Cl_2$ (70 mL) and washed with brine. The organic layer was dried over $Na_2SO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography (EtOAc/*n*-hexane = 1:10) to give **1** (1.38 g, 77%) as a colorless oil.

*Phenoxysulfonyl azide (PSA, **1**)*[S3]



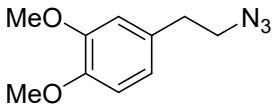
TLC (EtOAc/*n*-hexane = 1:5) $R_f$ = 0.50; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.47 (tm, $J$ = 8.0 Hz, 2H), 7.40 (tt, $J$ = 7.5, 1.2 Hz, 1H), 7.36 (dm, $J$ = 8.9 Hz, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 149.83, 130.27, 128.32, 121.55; HRMS (FAB+) for $C_6H_5N_3O_3S$ ($M^+$), calcd 199.0052, found 199.0055.

## 2. General procedure for the preparation of azides 4



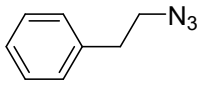

To a solution of primary amines (or anilines) **3** (1.0 mmol) in DMF/$H_2O$ (4:1, 10 mL) were added potassim carbonate (346 mg, 2.5 mmol) and **1** (1.0 mmol). After stirring at room temperature for 10 min–48 h, the reaction mixture was diluted with $Et_2O$ (60 mL) and washed with saturated aqueous $NaHCO_3$ solution and brine. The organic layer was dried over $Na_2SO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography to give azides **4**.

*3,4-Dimethoxyphenethylazide (**4a**)*[S4]



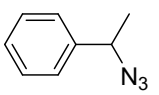

3,4-Dimethoxyphenethylamine (**3a**, 181 mg, 1.0 mmol) was treated according to the general procedure to give **4a** (205 mg, 99%) as a colorless oil. TLC (EtOAc/*n*-hexane = 1:10) $R_f$ = 0.25; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.82 (d, $J$ = 7.9 Hz, 1H), 6.76 (dd, $J$ = 8.1, 2.0 Hz, 1H), 6.74 (d, $J$ = 2.1 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.49 (t, $J$ = 7.3 Hz, 2H), 2.84 (t, $J$ = 7.3 Hz, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 149.01, 147.91, 130.55, 120.71, 111.97, 111.37, 55.90, 55.86, 52.63, 34.96; HRMS (FAB+) for $C_{10}H_{13}N_3O_2$ ($M^+$), calcd 207.1008, found 207.1004.

*2-Phenethylazide (**4b**)*[S5]



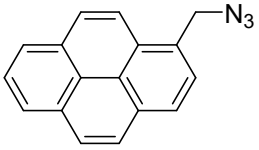

2-Phenethylamine (**3b**, 121 mg, 1.0 mmol) was treated according to the general procedure to give **4b** (143 mg, 97%) as a colorless oil. TLC (EtOAc/*n*-hexane = 1:10) $R_f$ = 0.55; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.32 (tm, $J$ = 7.3 Hz, 2H), 7.25 (tm, $J$ = 7.0 Hz, 1H), 7.23 (dm, $J$ = 7.3 Hz, 2H), 3.50 (t, $J$ = 7.3 Hz, 2H), 2.89 (t, $J$ = 7.3 Hz, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 137.95, 128.70, 128.58, 126.72, 52.39, 35.28; HRMS (EI+) for $C_8H_9N_3$ ($M^+$), calcd 147.0796, found 147.0794.

*DL-1-Phenylethylazide (**4c**)*[S6]



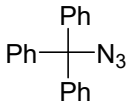
DL-1-Phenylethylamine (**3c**, 121 mg, 1.0 mmol) was treated according to the general procedure to give **4c** (141 mg, 96%) as a colorless oil. TLC (EtOAc/*n*-hexane = 1:10) $R_f$ = 0.55; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.38 (tm, $J$ = 7.2 Hz, 2H), 7.33 (dm, $J$ = 7.3 Hz, 2H), 7.32 (tt, $J$ = 7.0, 1.5 Hz, 1H), 4.62 (q, $J$ = 6.8 Hz, 1H), 1.53 (d, $J$ = 6.7 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 140.78, 128.71, 128.08, 126.32, 61.03, 21.53; HRMS (EI+) for $C_8H_9N_3$ ($M^+$), calcd 147.0796, found 147.0795.

*1-Pyrenemethylazide (**4d**)*[S7]



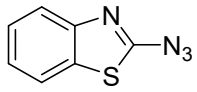
1-Pyrenemethylamine hydrochloride (**3d**, 268 mg, 1.0 mmol) was treated according to the general procedure to give **4d** (237 mg, 92%) as a yellow solid. TLC (EtOAc/*n*-hexane = 1:5) $R_f$ = 0.50; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.13 (d, $J$ = 8.8 Hz, 1H), 8.12 (d, $J$ = 7.3 Hz, 1H), 8.12 (d, $J$ = 7.0 Hz, 1H), 8.05 (d, $J$ = 9.8 Hz, 1H), 8.04 (d, $J$ = 8.2 Hz, 1H), 7.98 (d, $J$ = 8.8 Hz, 1H), 7.95 (t, $J$ = 7.9 Hz, 1H), 7.94 (d, $J$ = 8.5 Hz, 1H), 7.85 (d, $J$ = 7.6 Hz, 1H), 4.90 (s, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 131.57, 131.04, 130.54, 129.01, 128.17, 128.06, 127.69, 127.23, 127.16, 126.02, 125.46, 125.40, 124.81, 124.47, 124.43, 122.46, 52.90; HRMS (FAB+) for $C_{17}H_{11}N_3$ ($M^+$), calcd 257.0953, found 257.0950.

*Triphenylmethylazide (**4e**)*[S8]



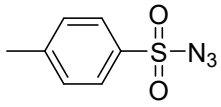
Triphenylmethylamine (**3e**, 259 mg, 1.0 mmol) was treated according to the general procedure to give **4e** (123 mg, 43%) as a yellow solid. TLC (EtOAc/*n*-hexane = 1:5) $R_f$ = 0.60; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.34 (tm, $J$ = 7.0 Hz, 6H), 7.30 (tm, $J$ = 6.6 Hz, 3H), 7.28 (dm, $J$ = 8.5 Hz, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 143.12, 128.46, 128.19, 127.69, 30.31; HRMS (FAB+) for $C_{19}H_{15}$ ($M^+ - N_3$), calcd 243.1168, found 243.1175.

*2-Azidobenzothiazole (**4f**)*[S9]



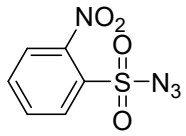
2-Aminobenzothiazole (**3f**, 150 mg, 1.0 mmol) was treated according to the general procedure to give **4f** (123 mg, 70%) as a white solid. TLC (*n*-hexane) $R_f$ = 0.15; $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 8.29 (dd, $J$ = 7.9, 0.9 Hz, 1H), 8.28 (dd, $J$ = 7.3, 0.6 Hz, 1H), 7.74 (dd, $J$ = 7.8, 1.1 Hz, 1H), 7.68 (dd, $J$ = 7.9, 1.1 Hz, 1H); $^{13}$C NMR (125 MHz, DMSO-$d_6$) $\delta$ 132.77, 128.15, 127.85, 126.31, 114.86.

*p-Toluenesulfonyl azide (**4g**)*[S10]



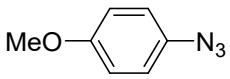
*p*-Toluenesulfonamide (**3g**, 171 mg, 1.0 mmol) was treated according to the general procedure to give **4g** (170 mg, 86%) as a colorless oil. TLC (EtOAc/*n*-hexane = 1:5) $R_f$ = 0.50; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.85 (dm, $J$ = 8.5 Hz, 2H), 7.41 (d, $J$ = 8.2 Hz, 2H), 2.49 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 146.17, 135.53, 130.26, 127.53, 21.74; HRMS (FAB+) for $C_7H_8N_3O_2S$ ($M$H$^+$), calcd 198.0337, found 198.0340.

*2-Nitrobenzenesulfonyl azide (**4h**)*[S11]



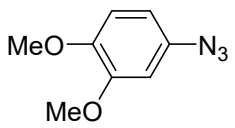
2-Nitrobenzenesulfonamide (**3h**, 202 mg, 1.0 mmol) was treated according to the general procedure to give **4h** (162 mg, 71%) as a white solid. TLC (EtOAc/*n*-hexane = 1:5) $R_f$ = 0.25; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.20 (dd, $J$ = 7.8, 1.4 Hz, 1H), 7.93 (dd, $J$ = 7.9, 1.5 Hz, 1H), 7.89 (td, $J$ = 7.6, 1.5 Hz, 1H), 7.84 (td, $J$ = 7.6, 1.6 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 147.68, 135.76, 133.09, 132.50, 131.65, 125.35; HRMS (EI+) for $C_6H_4N_4O_4S$ ($M^+$), calcd 227.9953, found 227.9956.

*1-Azido-4-methoxybenzene (**4i**)*[S12]



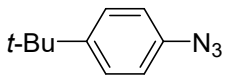
*p*-Anisidine (**3i**, 123 mg, 1.0 mmol) was treated according to the general procedure to give **4i** (128 mg, 86%) as a brown oil. TLC (*n*-hexane) $R_f$ = 0.25; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.95 (dm, $J$ = 9.0 Hz, 2H), 6.89 (dm, $J$ = 9.0 Hz, 2H), 3.79 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 156.99, 132.35, 119.98, 115.12, 55.56; HRMS (FAB+) for $C_7H_7N_3O$ ($M^+$), calcd 149.0589, found 149.0589.

*1-Azido-3,4-dimethoxybenzene (**4j**)*[S13]



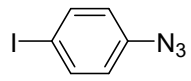
3,4-Dimethoxyaniline (**3j**, 153 mg, 1.0 mmol) was treated according to the general procedure to give **4j** (152 mg, 85%) as a brown solid. TLC (EtOAc/*n*-hexane = 1:5) $R_f$ = 0.40; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.84 (d, $J$ = 8.5 Hz, 1H), 6.60 (dd, $J$ = 8.5, 2.6 Hz, 1H), 6.53 (d, $J$ = 2.6 Hz, 1H), 3.86 (s, 3H), 3.86 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 150.02, 146.56, 132.77, 112.16, 110.44, 103.26, 56.19, 55.92.

*1-Azido-4-(tert-butyl)benzene (**4k**)*[S14]



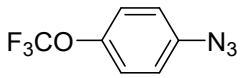
4-*tert*-Butylaniline (**3k**, 149 mg, 1.0 mmol) was treated according to the general procedure to give **4k** (133 mg, 76%) as a yellow oil. TLC (*n*-hexane) $R_f$ = 0.60; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.37 (dm, $J$ = 8.9 Hz, 2H), 6.96 (dm, $J$ = 8.8 Hz, 2H), 1.31 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 148.02, 137.09, 126.66, 118.61, 34.40, 31.31; HRMS (EI+) for $C_{10}H_{13}N_3$ ($M^+$), calcd 175.1109, found 175.1108.

*1-Azido-4-iodobenzene (**4l**)*[S15]



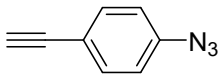
4-Iodoaniline (**3l**, 219 mg, 1.0 mmol) was treated according to the general procedure to give **4l** (154 mg, 63%) as a yellow oil. TLC (*n*-hexane) $R_f$ = 0.60; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.64 (dm, $J$ = 8.5 Hz, 2H), 6.78 (dm, $J$ = 8.5 Hz, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 139.98, 138.69, 121.02, 88.18.

*1-Azido-4-(trifluoromethoxy)benzene (**4m**)*[S16]



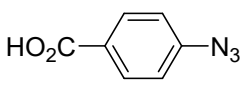
4-(Trifluoromethoxy)aniline (**3m**, 177 mg, 1.0 mmol) was treated according to the general procedure to give **4m** (108 mg, 53%) as a yellow oil. TLC (*n*-hexane) $R_f$ = 0.60; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.21 (dm, $J$ = 9.2 Hz, 2H), 7.03 (dm, $J$ = 9.2 Hz, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 146.02, 138.83, 122.63, 120.44 (q, $J$ = 257.4 Hz), 120.16.

*1-Azido-4-ethynylbenzene (**4n**)*[S17]



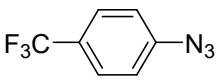
4-Ethynylaniline (**3n**, 117 mg, 1.0 mmol) was treated according to the general procedure to give **4n** (92 mg, 64%) as a yellow oil. TLC (*n*-hexane) $R_f$ = 0.40; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.47 (dm, $J$ = 8.9 Hz, 2H), 6.97 (dm, $J$ = 8.9 Hz, 2H), 3.07 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 140.57, 133.62, 119.00, 118.62, 82.91, 77.45; HRMS (EI+) for $C_8H_5N_3$ ($M^+$), calcd 143.0483, found 143.0485.

*4-Azidobenzoic acid (**4o**)*[S18]



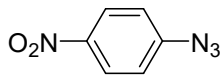
4-Aminobenzoic acid (**3o**, 137 mg, 1.0 mmol) was treated according to the general procedure to give **4o** (142 mg, 87%) as a yellow solid. TLC (EtOAc/*n*-hexane = 1:1) $R_f$ = 0.20; $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 12.87 (brs, 1H), 7.96 (d, $J$ = 8.2 Hz, 2H), 7.22 (d, $J$ = 8.2 Hz, 2H); $^{13}$C NMR (125 MHz, DMSO-$d_6$) $\delta$ 166.74, 143.84, 131.24, 127.68, 119.11.

*1-Azido-4-(trifluoromethyl)benzene (**4p**)*[S19]



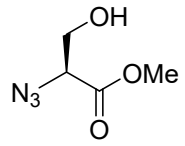
4-(Trifluoromethyl)aniline (**3p**, 161 mg, 1.0 mmol) was treated according to the general procedure to give **4p** (30 mg, 16%) as a yellow oil. TLC (*n*-hexane) $R_f$ = 0.50; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.60 (dm, $J$ = 8.8 Hz, 2H), 7.11 (dm, $J$ = 9.0 Hz, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 143.75, 127.34 (q, $J$ = 33.2 Hz), 127.00 (q, $J$ = 3.6 Hz), 123.91 (q, $J$ = 271.6 Hz), 119.20.

*1-Azido-4-nitrobenzene (**4q**)*[S20]



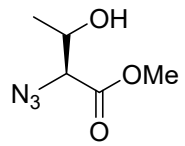
4-Nitroaniline (**3q**, 138 mg, 1.0 mmol) was treated according to the general procedure to give **4q** (72 mg, 44%) as a brown solid. TLC (EtOAc/*n*-hexane = 1:1) $R_f$ = 0.60; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.25 (dm, $J$ = 9.2 Hz, 2H), 7.15 (dm, $J$ = 9.2 Hz, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 146.86, 144.61, 125.62, 119.38; HRMS (FAB+) for $C_6H_5N_4O_2$ ($M$H$^+$), calcd 165.0413, found 165.0416.

*$N_3$-Ser-OMe (**4r**)*[S21]



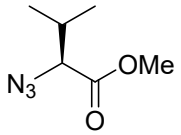
H-Ser-OMe·HCl **3r** (156 mg, 1.0 mmol) was treated according to the general procedure to give **4r** (144 mg, 99%) as a colorless oil. TLC (EtOAc/*n*-hexane = 1:3) $R_f$ = 0.30; $^1$H NMR (500 MHz, CDCl3) $\delta$ 4.10 (t, $J$ = 4.7 Hz, 1H), 3.93 (dd, $J$ = 4.7, 1.5 Hz, 2H), 3.84 (s, 3H), 2.33 (brs, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 169.21, 63.41, 62.74, 52.86; HRMS (CI+) for $C_4H_8N_3O_3$ ($M$H$^+$), calcd 146.0566, found 146.0570.

*$N_3$-Thr-OMe (**4s**)*[S22]



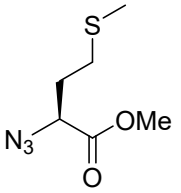
H-Thr-OMe·HCl **3s** (170 mg, 1.0 mmol) was treated according to the general procedure to give **4s** (159 mg, 100%) as a colorless oil. TLC (EtOAc/*n*-hexane = 1:3) $R_f$ = 0.30; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 4.25 (m, 1H), 3.85 (s, 3H), 3.83 (d, $J$ = 3.9 Hz, 1H), 2.28 (brs, 1H), 1.32 (d, $J$ = 6.4 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 169.49, 68.29, 67.25, 52.76, 19.84.

*$N_3$-Val-OMe (**4t**)*[S23]



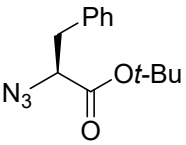
H-Val-OMe·HCl **3t** (168 mg, 1.0 mmol) was treated according to the general procedure to give **4t** (154 mg, 98%) as a colorless oil. TLC (EtOAc/*n*-hexane = 1:3) $R_f$ = 0.30; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 3.80 (s, 3H), 3.67 (d, $J$ = 6.1 Hz, 1H), 2.20 (m, 1H), 1.01 (d, $J$ = 7.0 Hz, 3H), 0.99 (d, $J$ = 6.7 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 170.57, 68.18, 52.32, 30.91, 19.29, 17.96.

*$N_3$-Met-OMe (**4u**)*



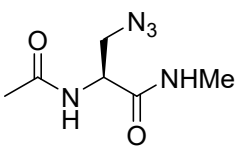
H-Met-OMe·HCl **3u** (200 mg, 1.0 mmol) was treated according to the general procedure to give **4u** (125 mg, 66%) as a colorless oil. TLC (EtOAc/*n*-hexane = 1:5) $R_f$ = 0.40; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 4.14 (dd, $J$ = 8.9, 4.9 Hz, 1H), 3.81 (s, 3H), 2.66−2.56 (m, 2H), 2.15−2.08 (m, 1H), 2.11 (s, 3H), 2.04−1.96 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 170.62, 60.48, 52.59, 30.52, 30.05, 15.26; HRMS (CI+) for $C_6H_{12}N_3O_2S$ ($M$H$^+$), calcd 190.0650, found 190.0650.

*$N_3$-Phe-OtBu (**4v**)*



H-Phe-O*t*Bu·HCl **3v** (258 mg, 1.0 mmol) was treated according to the general procedure to give **4v** (223 mg, 90%) as a colorless oil. TLC (EtOAc/*n*-hexane = 1:5) $R_f$ = 0.60; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.32 (tt, $J$ = 7.2, 1.6 Hz, 2H), 7.26 (tt, $J$ = 6.9, 1.7 Hz, 1H), 7.24 (dm, $J$ = 8.2 Hz, 2H), 3.91 (dd, $J$ = 8.5, 5.8 Hz, 1H), 3.13 (dd, $J$ = 13.9, 6.0 Hz, 1H), 2.99 (dd, $J$ = 14.0, 8.5 Hz, 1H), 1.45 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 168.99, 136.17, 129.25, 128.56, 127.11, 83.00, 63.61, 37.56, 27.94; HRMS (FAB+) for $C_{13}H_{18}N_3O_2$ ($M$H$^+$), calcd 248.1399, found 248.1402.

*Ac-Ala($N_3$)-NHMe (**4w**)*[S24]



Ac-DAP-NHMe·TFA **3w** (273 mg, 1.0 mmol) was treated according to the general procedure to give **4w** (163 mg, 88%) as a white solid. TLC (MeOH/$CH_2Cl_2$ = 1:20) $R_f$ = 0.25; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.45 (brs, 1H), 6.44 (brs, 1H), 4.56 (td, $J$ = 7.0, 5.0 Hz, 1H), 3.77 (dd, $J$ = 12.2, 4.9 Hz, 1H), 3.51 (dd, $J$ = 12.2, 6.4 Hz, 1H), 2.85 (d, $J$ = 4.9 Hz, 3H), 2.06 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 170.46, 169.62, 52.22, 51.73, 26.47, 23.16; HRMS (FAB+) for $C_6H_{12}N_5O_2$ ($M$H$^+$), calcd 186.0991, found 186.0996.

## II. Dfferential scanning calorimetry (DSC) of 1

PSA **1** is an arylsulfonyl azide bearing the explosophoric $SO_2$–$N_3$ functional group and exists as a liquid at ambient temperature. To assess its thermal stability and decomposition behavior, differential scanning calorimetry (DSC) was performed on **1** (3.237 mg) under an argon atmosphere. The measurements were carried out over a temperature range of 30 to 350 °C at a heating rate of 10 °C/min. The DSC thermogram showed the initiation of an exothermic event at approximately 145 °C, which rapidly progressed to a maximum exothermic peak ($T_{peak}$) at 193.4 °C. The initial decomposition temperature ($T_{init}$) and onset temperature ($T_{onset}$) were determined to be 145 °C and 165.1 °C, respectively. The enthalpy of decomposition ($\Delta H_D$) was measured to be −1273.2 J $g^{-1}$, corresponding to a molar enthalpy of −253.4 kJ $mol^{-1}$, based on the calculated molecular weight (199.0055 g $mol^{-1}$).

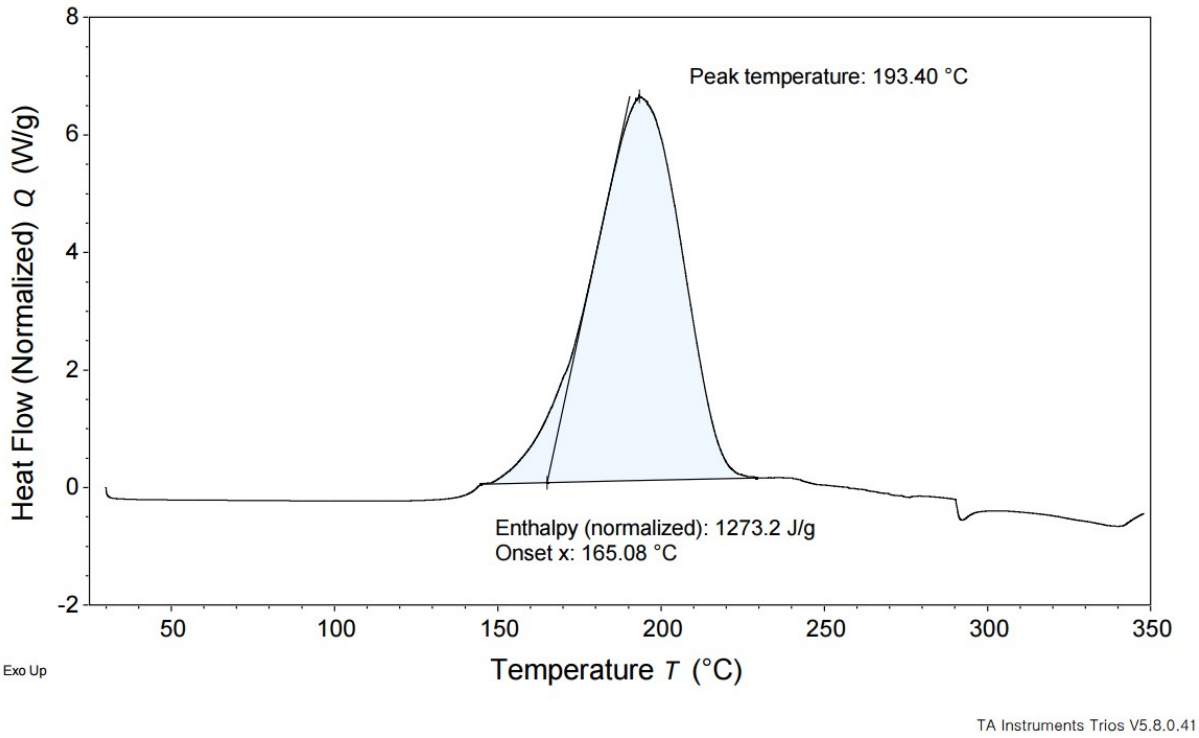
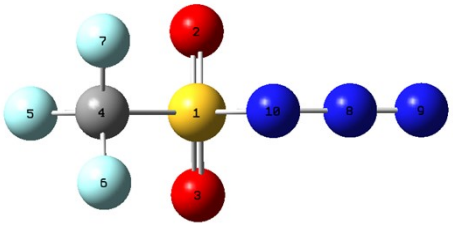


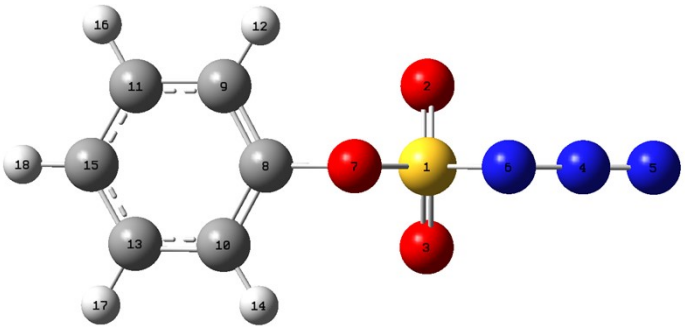

**Figure S1.** DSC thermogram of **1**.

## III. Geometry-optimized structures and Cartesian coordinates of $TfN_3$, 1, and $FSO_2N_3$

(a)




(b)




(c)

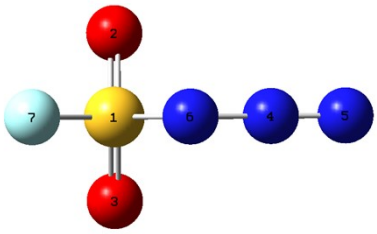



**Figure S2.** Geometry-optimized structures of $TfN_3$, **1**, and $FSO_2N_3$. The Cartesian coordinates are given in Tables S1−S3.

**Table S1.** Trifluoromethanesulfonyl azide ($TfN_3$)

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 16 | 0 | 0.194582 | 0.602658 | 0.000035 |
| 2 | 8 | 0 | 0.305555 | 1.287589 | 1.247789 |
| 3 | 8 | 0 | 0.304492 | 1.289257 | -1.246888 |
| 4 | 6 | 0 | -1.423400 | -0.347034 | 0.000042 |
| 5 | 9 | 0 | -2.393856 | 0.557687 | 0.000990 |
| 6 | 9 | 0 | -1.517032 | -1.101061 | -1.083655 |
| 7 | 9 | 0 | -1.516217 | -1.102448 | 1.082844 |
| 8 | 7 | 0 | 2.386890 | -0.592843 | -0.000289 |
| 9 | 7 | 0 | 3.505091 | -0.522456 | 0.000208 |
| 10 | 7 | 0 | 1.163825 | -0.793658 | -0.001293 |

**Table S2.** Phenoxysulfonyl azide (PSA, **1**)

Standard orientation:

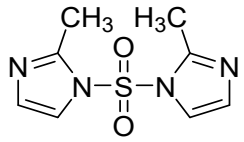
| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 16 | 0 | -1.149863 | 0.000656 | -0.285069 |
| 2 | 8 | 0 | -1.141439 | -1.234429 | -1.000008 |
| 3 | 8 | 0 | -1.139388 | 1.235120 | -1.001023 |
| 4 | 7 | 0 | -3.536409 | -0.000291 | 0.374327 |
| 5 | 7 | 0 | -4.611052 | -0.002131 | 0.053683 |
| 6 | 7 | 0 | -2.398098 | 0.002167 | 0.862573 |
| 7 | 8 | 0 | -0.038204 | 0.000297 | 0.852532 |
| 8 | 6 | 0 | 1.317182 | -0.000039 | 0.446138 |
| 9 | 6 | 0 | 1.963881 | -1.214189 | 0.291351 |
| 10 | 6 | 0 | 1.964568 | 1.213770 | 0.291540 |
| 11 | 6 | 0 | 3.315483 | -1.205415 | -0.032027 |
| 12 | 1 | 0 | 1.415981 | -2.138254 | 0.421360 |
| 13 | 6 | 0 | 3.316163 | 1.204279 | -0.031837 |
| 14 | 1 | 0 | 1.417187 | 2.138124 | 0.421675 |
| 15 | 6 | 0 | 3.990918 | -0.000747 | -0.193537 |
| 16 | 1 | 0 | 3.840216 | -2.145167 | -0.156725 |
| 17 | 1 | 0 | 3.841430 | 2.143752 | -0.156392 |
| 18 | 1 | 0 | 5.044971 | -0.001024 | -0.444669 |

**Table S3.** Fluorosulfuryl azide ($FSO_2N_3$)

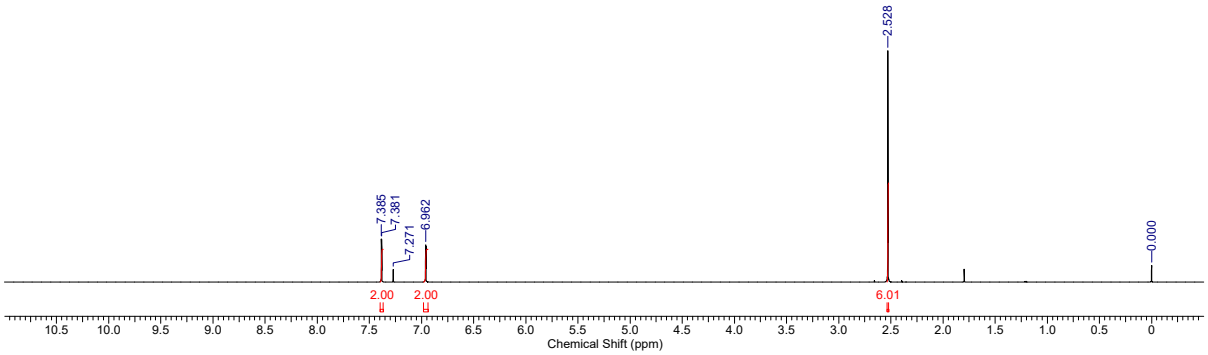
Standard orientation:

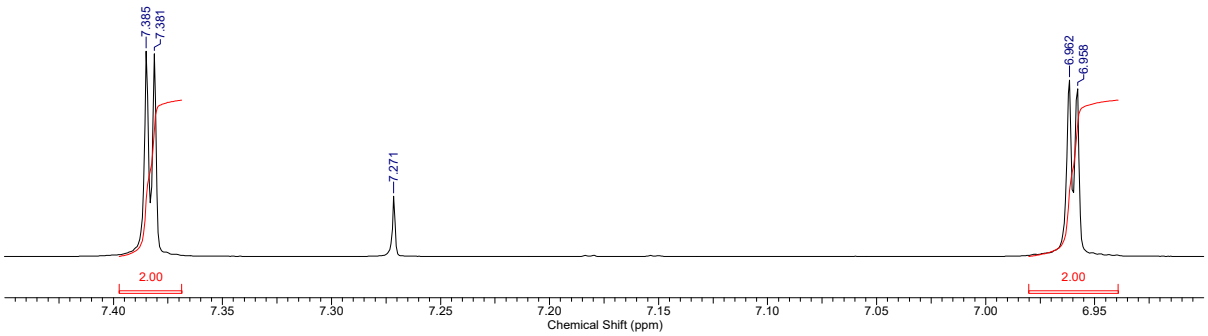
| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 16 | 0 | -0.643778 | -0.155844 | 0.000505 |
| 2 | 8 | 0 | -0.775841 | -0.829151 | -1.239790 |
| 3 | 8 | 0 | -0.781921 | -0.819768 | 1.245160 |
| 4 | 7 | 0 | 1.799652 | 0.236610 | 0.000708 |
| 5 | 7 | 0 | 2.837084 | -0.184434 | -0.000141 |
| 6 | 7 | 0 | 0.713964 | 0.840881 | 0.000194 |
| 7 | 9 | 0 | -1.632484 | 1.048162 | -0.006263 |

## IV. $^{1}H$ and $^{13}C$ NMR spectra of 1, 2, 2′, 2″, and 4




**2**



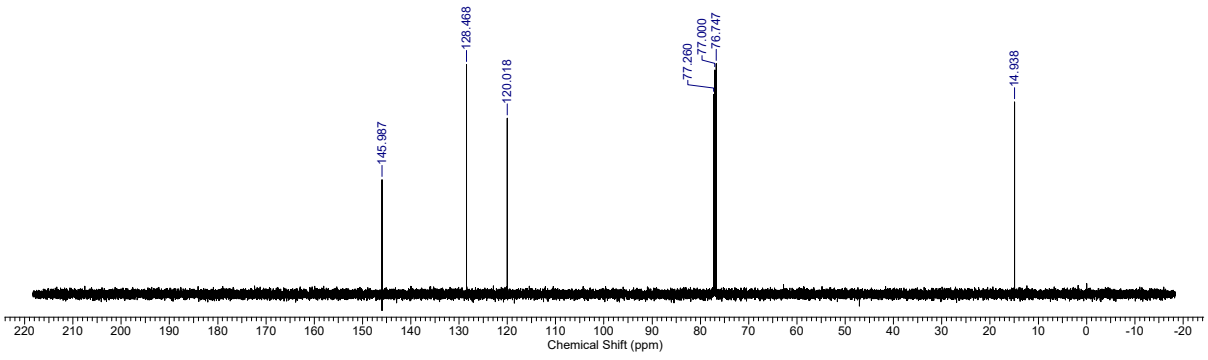




**Figure S3.** $^{1}H$ (top, middle) and $^{13}C$ (bottom) NMR spectra of **2** in $CDCl_3$ at 500 and 125 MHz, respectively.

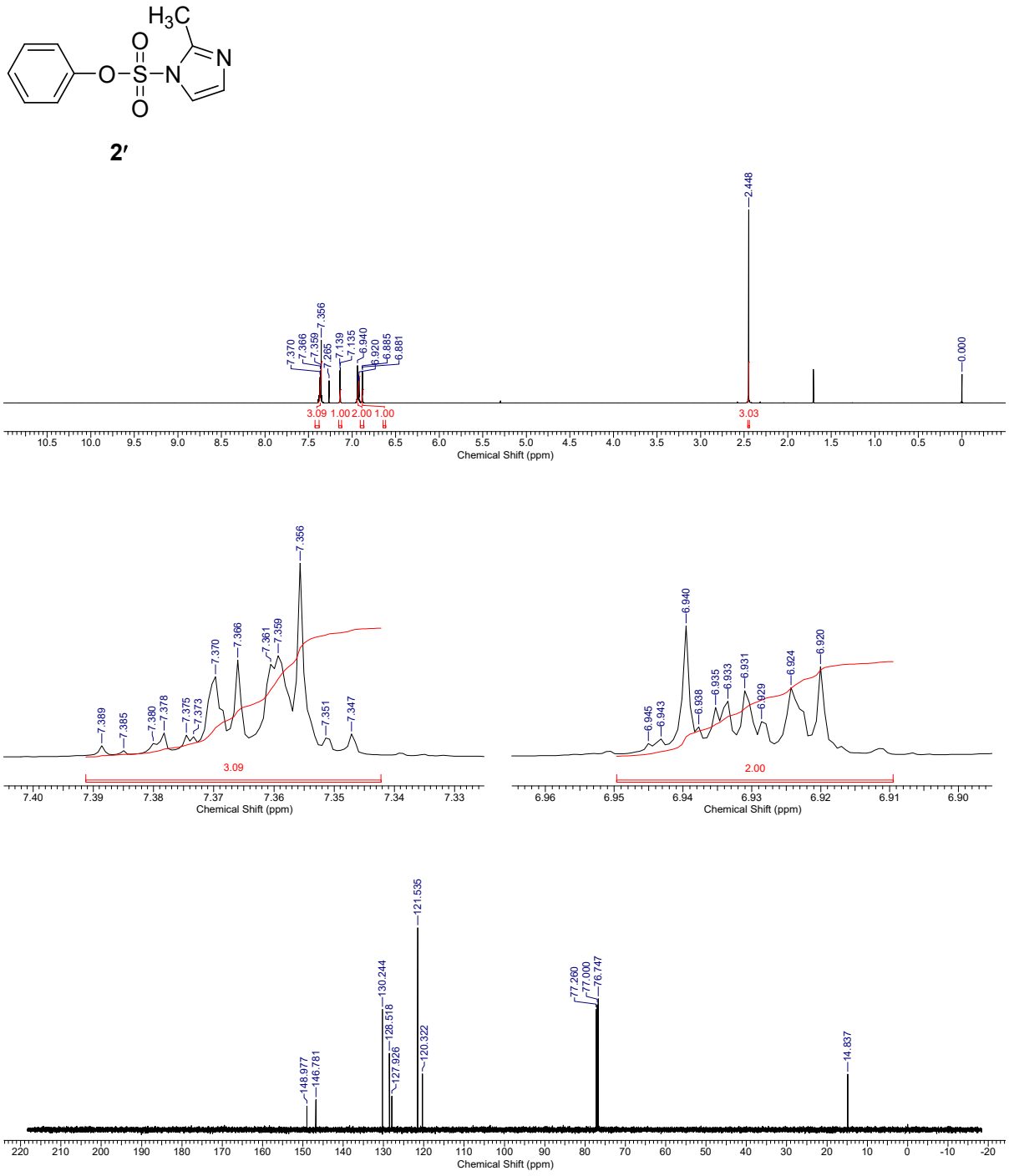



**Figure S4.** $^{1}H$ (top, middle) and $^{13}C$ (bottom) NMR spectra of **2′** in $CDCl_3$ at 500 and 125 MHz, respectively.

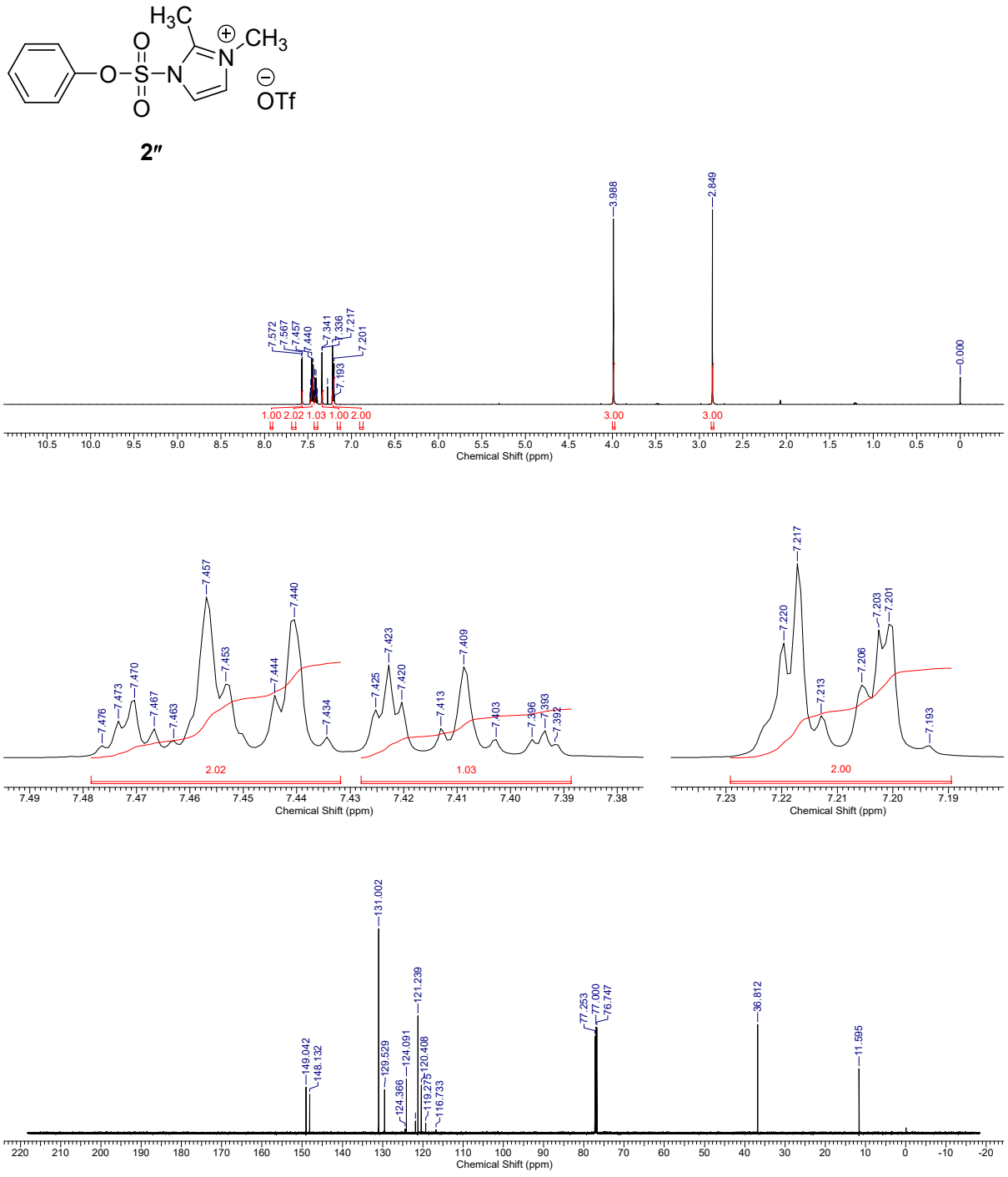



**Figure S5.** $^{1}H$ (top, middle) and $^{13}C$ (bottom) NMR spectra of **2″** in $CDCl_3$ at 500 and 125 MHz, respectively.

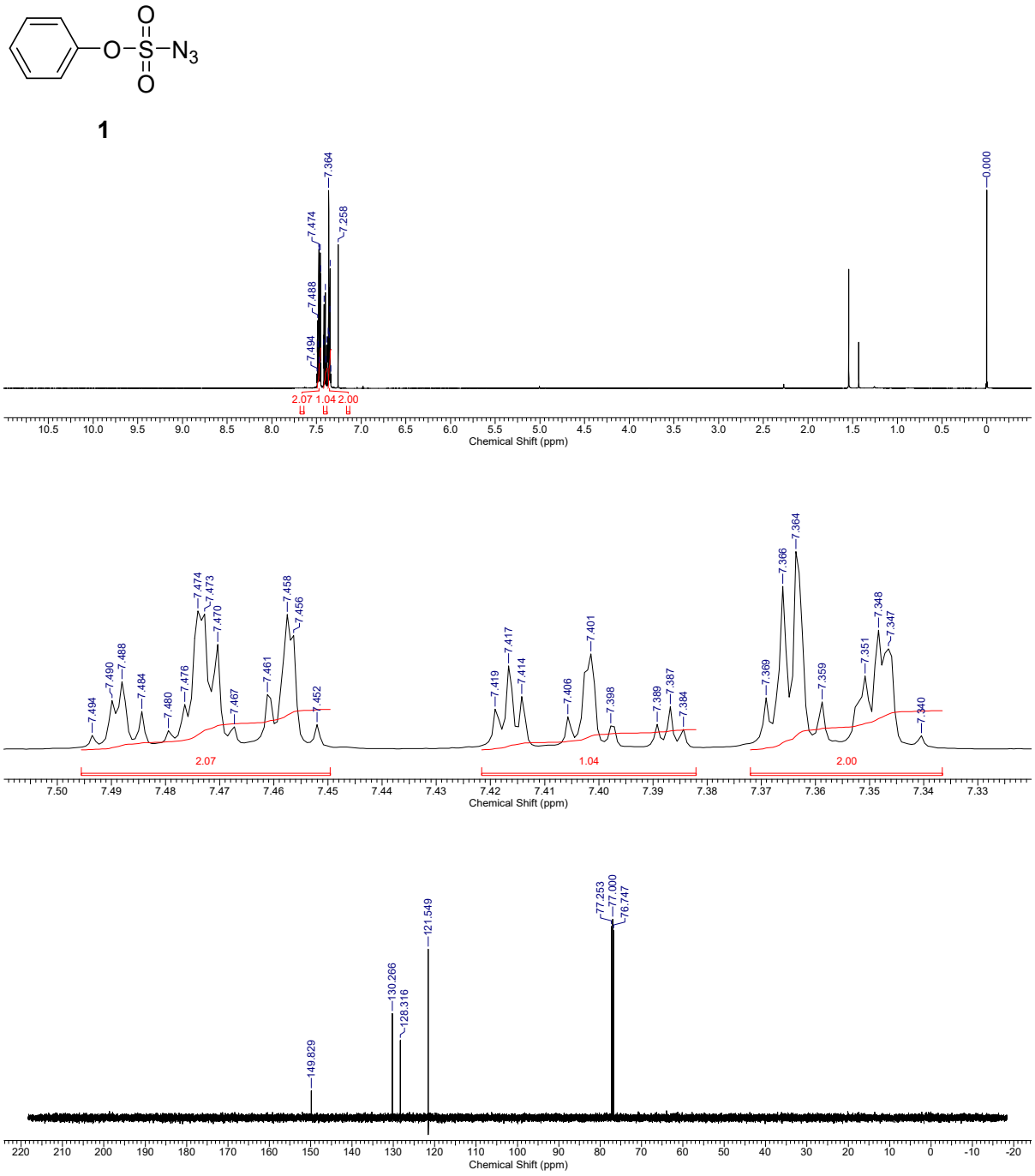



**Figure S6.** $^{1}H$ (top, middle) and $^{13}C$ (bottom) NMR spectra of **1** in $CDCl_3$ at 500 and 125 MHz, respectively.

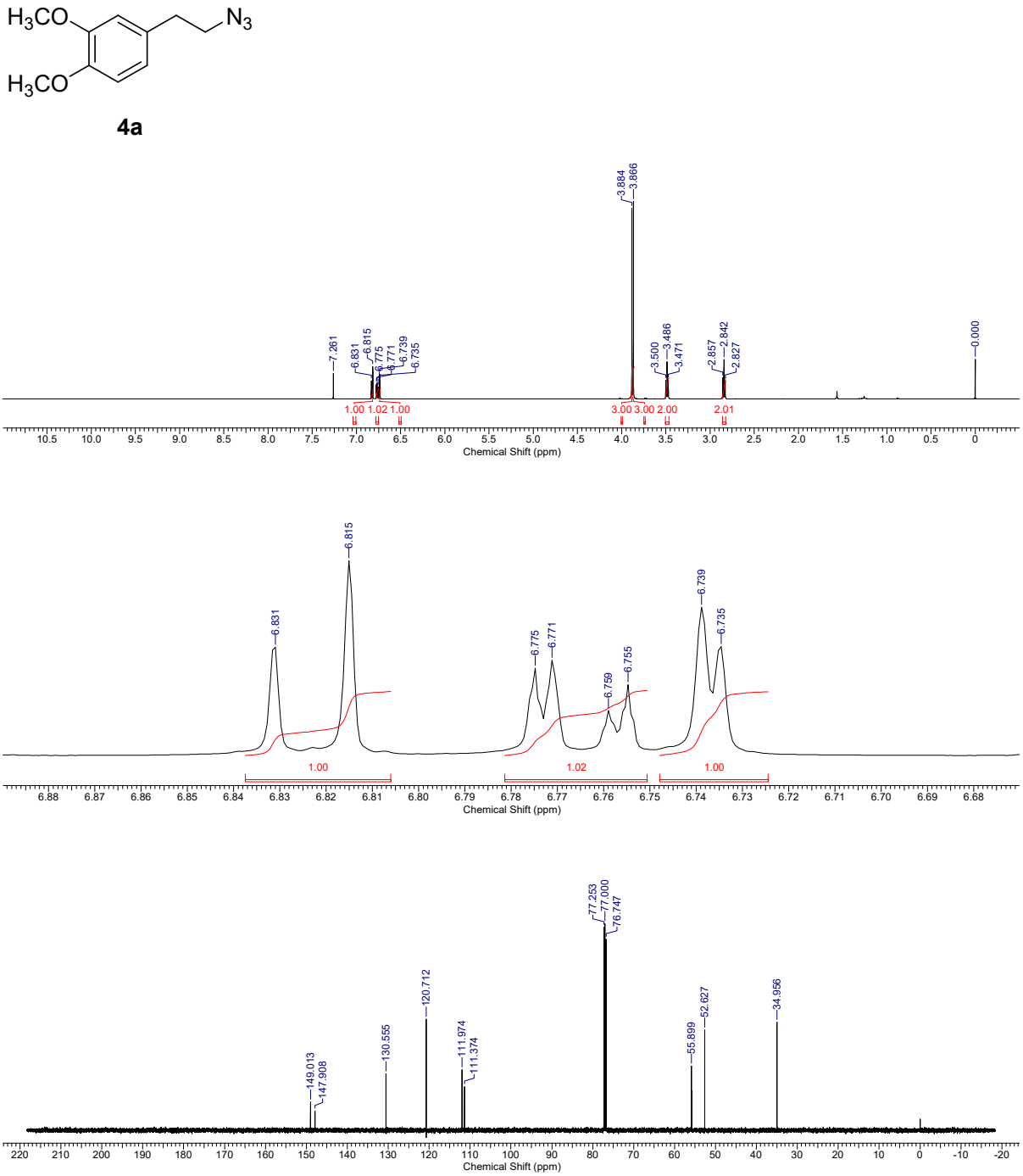



**Figure S7.** $^{1}H$ (top, middle) and $^{13}C$ (bottom) NMR spectra of **4a** in $CDCl_3$ at 500 and 125 MHz, respectively.

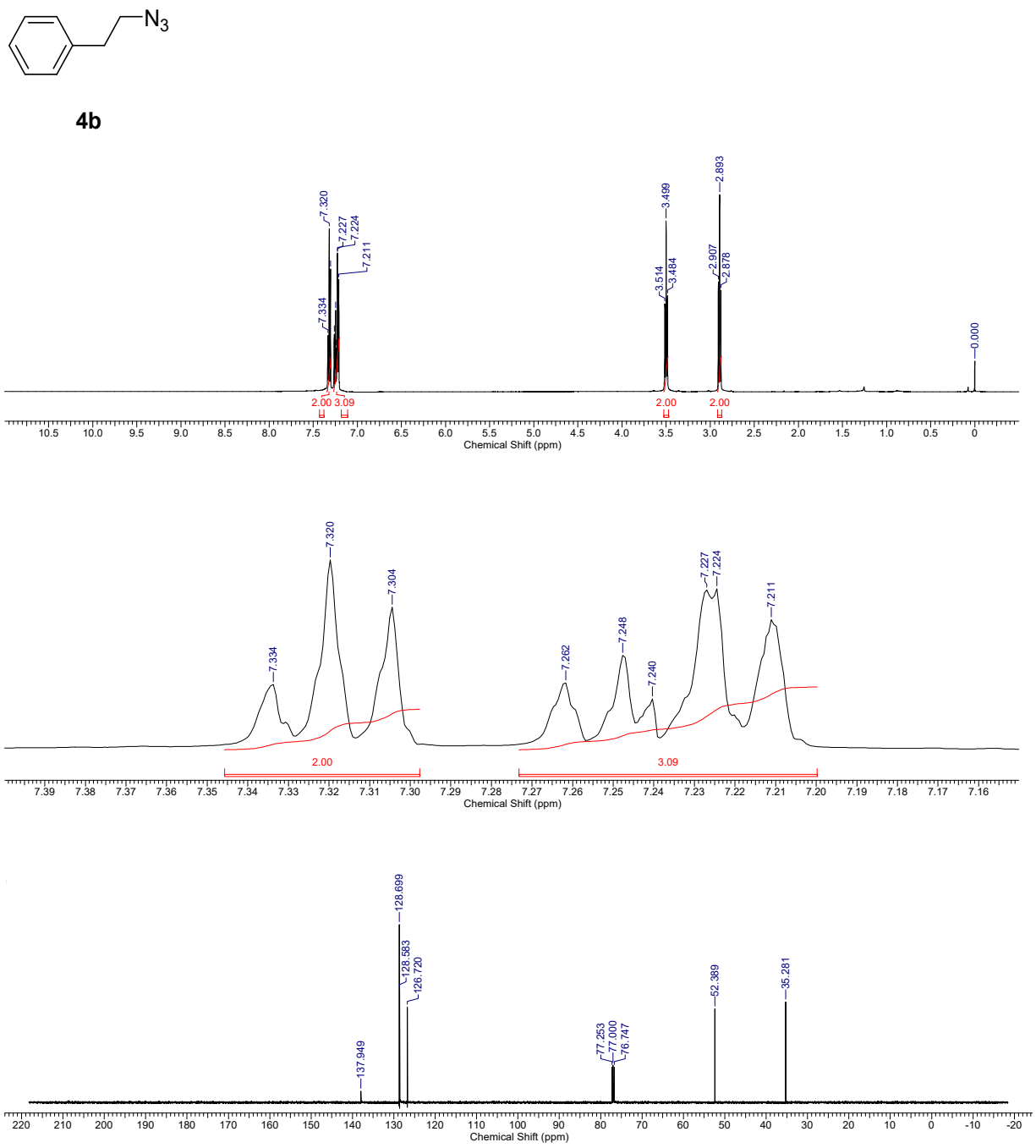



**Figure S8.** $^{1}H$ (top, middle) and $^{13}C$ (bottom) NMR spectra of **4b** in $CDCl_3$ at 500 and 125 MHz, respectively.

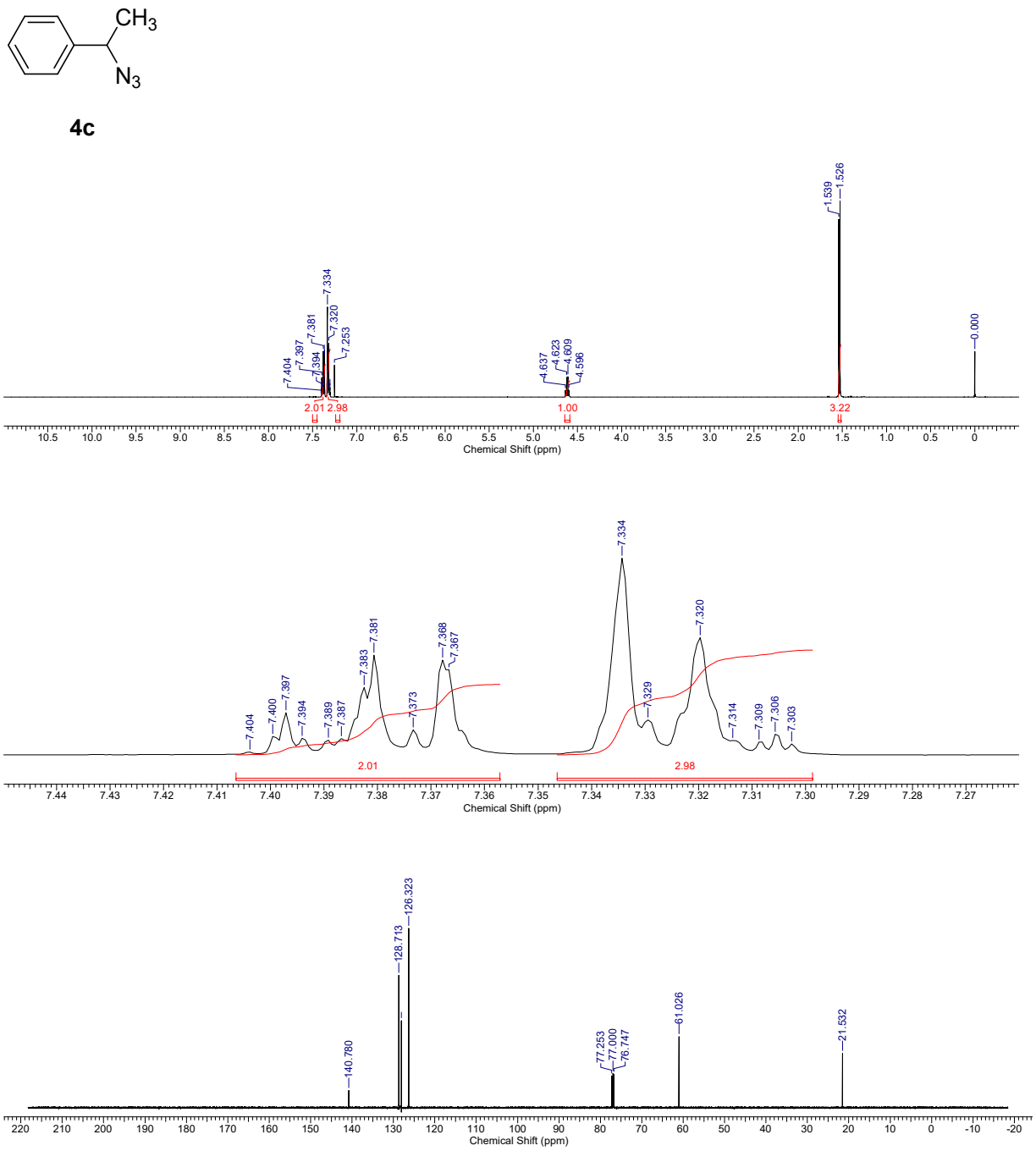



**Figure S9.** $^{1}H$ (top, middle) and $^{13}C$ (bottom) NMR spectra of **4c** in $CDCl_3$ at 500 and 125 MHz, respectively.

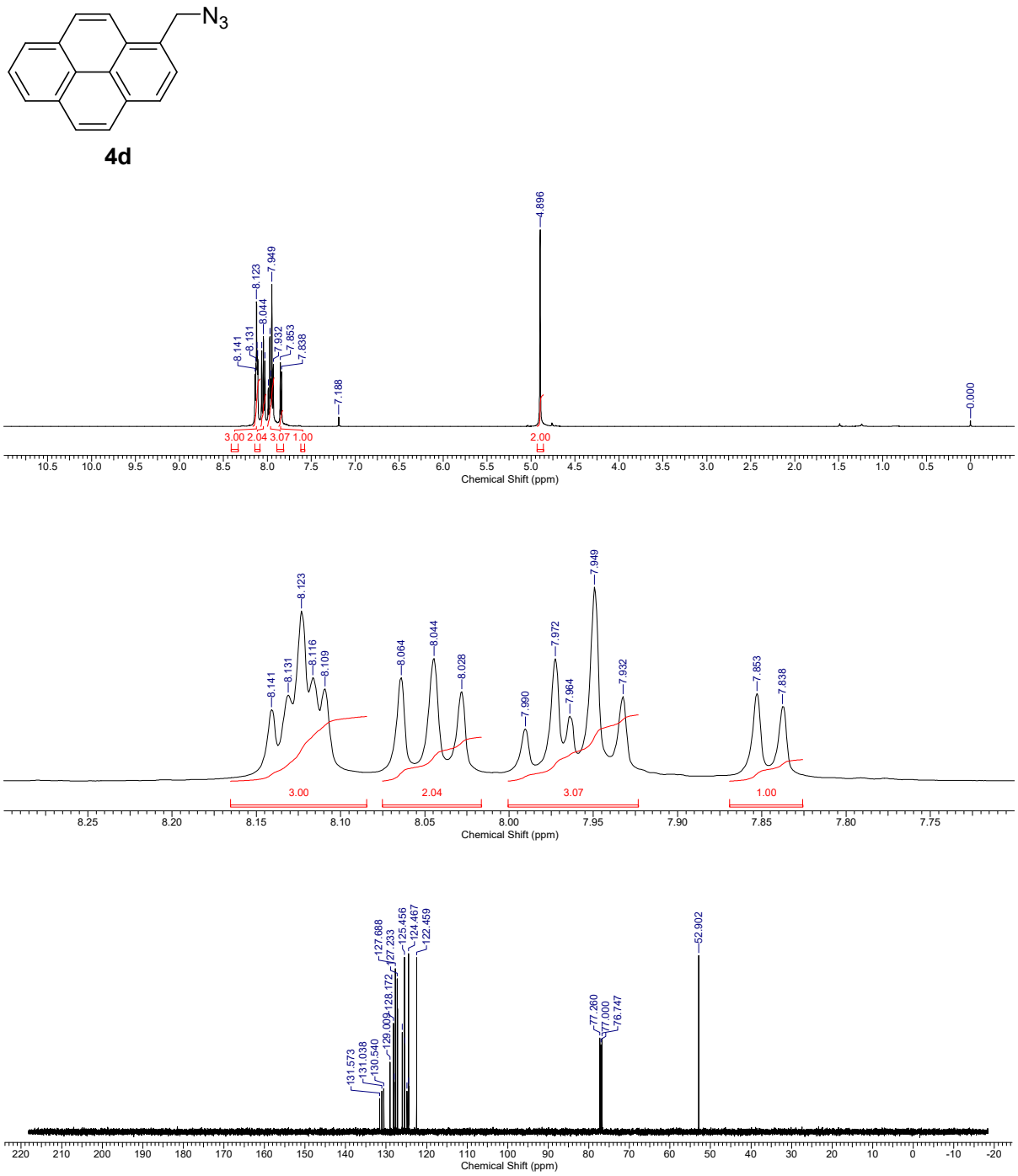



**Figure S10.** $^{1}H$ (top, middle) and $^{13}C$ (bottom) NMR spectra of **4d** in $CDCl_3$ at 500 and 125 MHz, respectively.

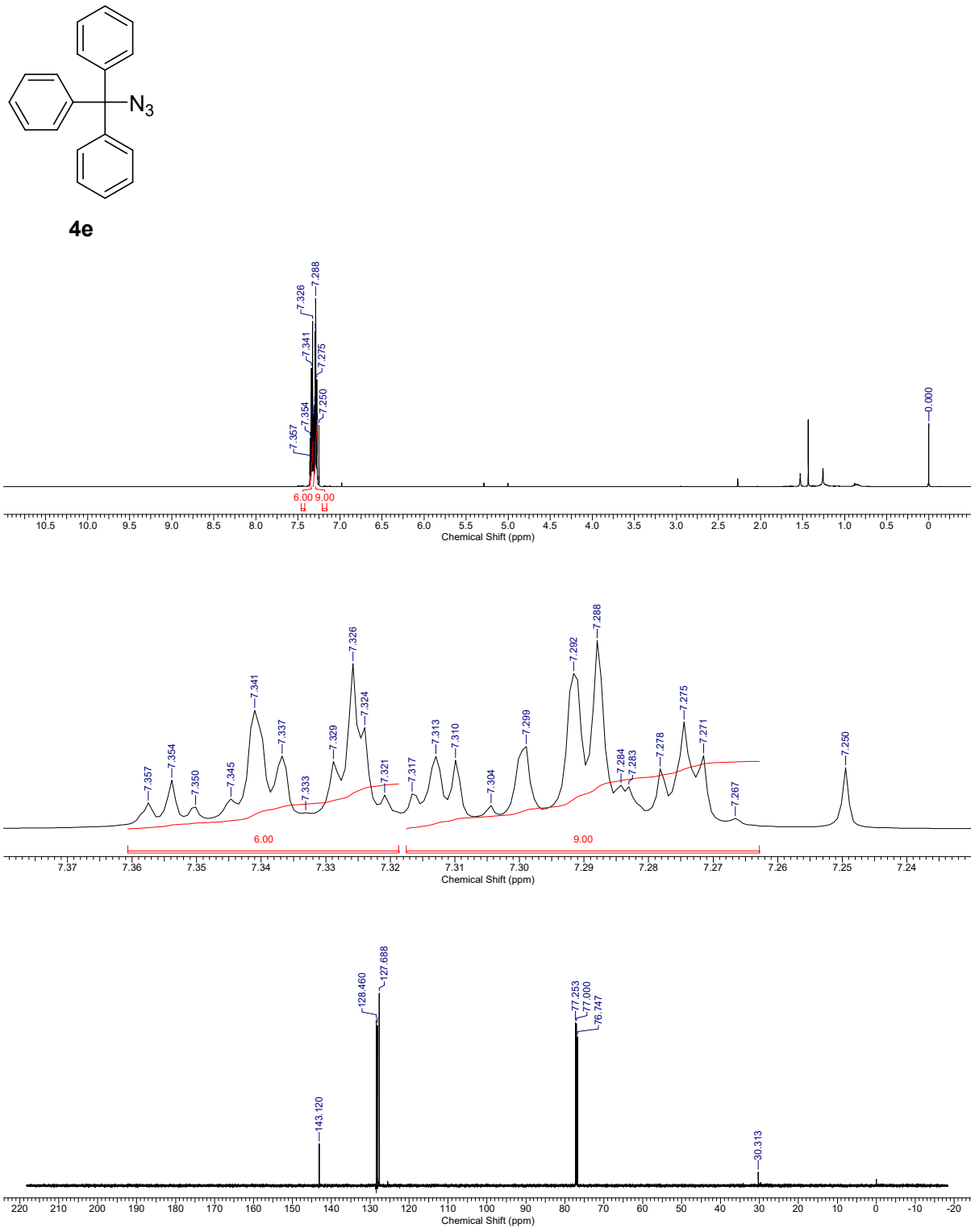



**Figure S11.** $^{1}H$ (top, middle) and $^{13}C$ (bottom) NMR spectra of **4e** in $CDCl_3$ at 500 and 125 MHz, respectively.

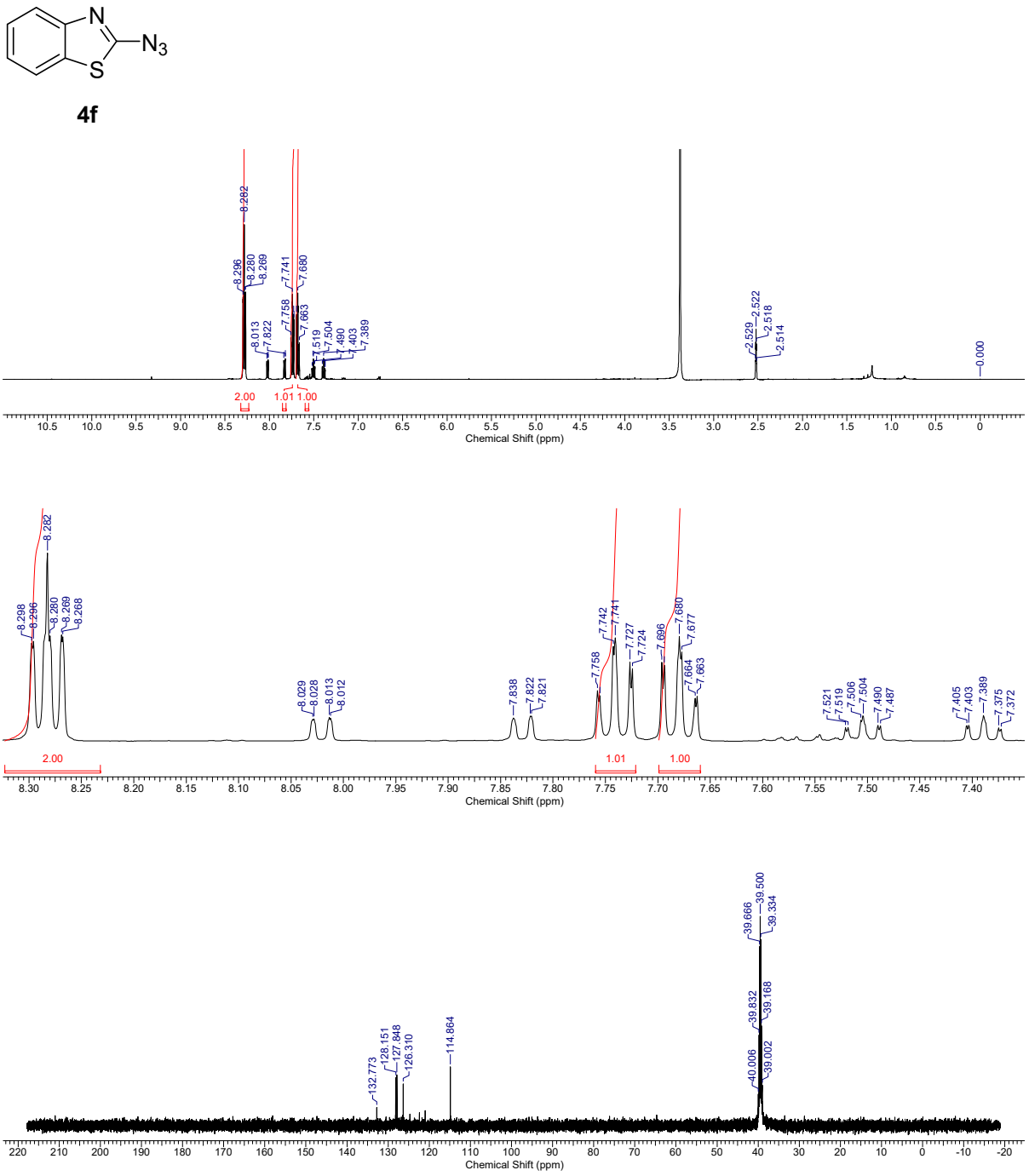



**Figure S12.** $^{1}$H (top, middle) and $^{13}$C (bottom) NMR spectra of **4f** in DMSO-$d_6$ at 500 and 125 MHz, respectively.

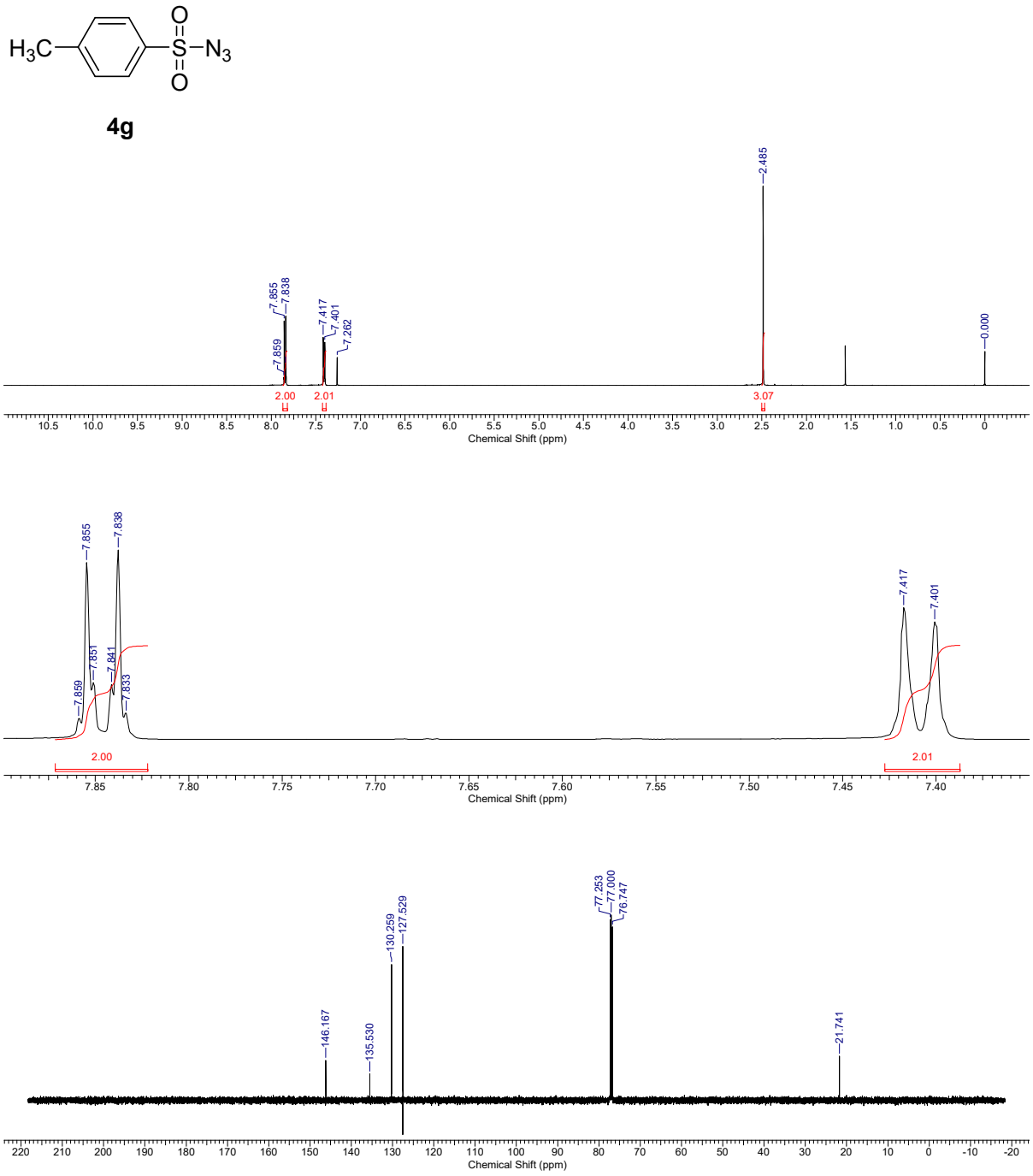



**Figure S13.** $^{1}H$ (top, middle) and $^{13}C$ (bottom) NMR spectra of **4g** in $CDCl_3$ at 500 and 125 MHz, respectively.

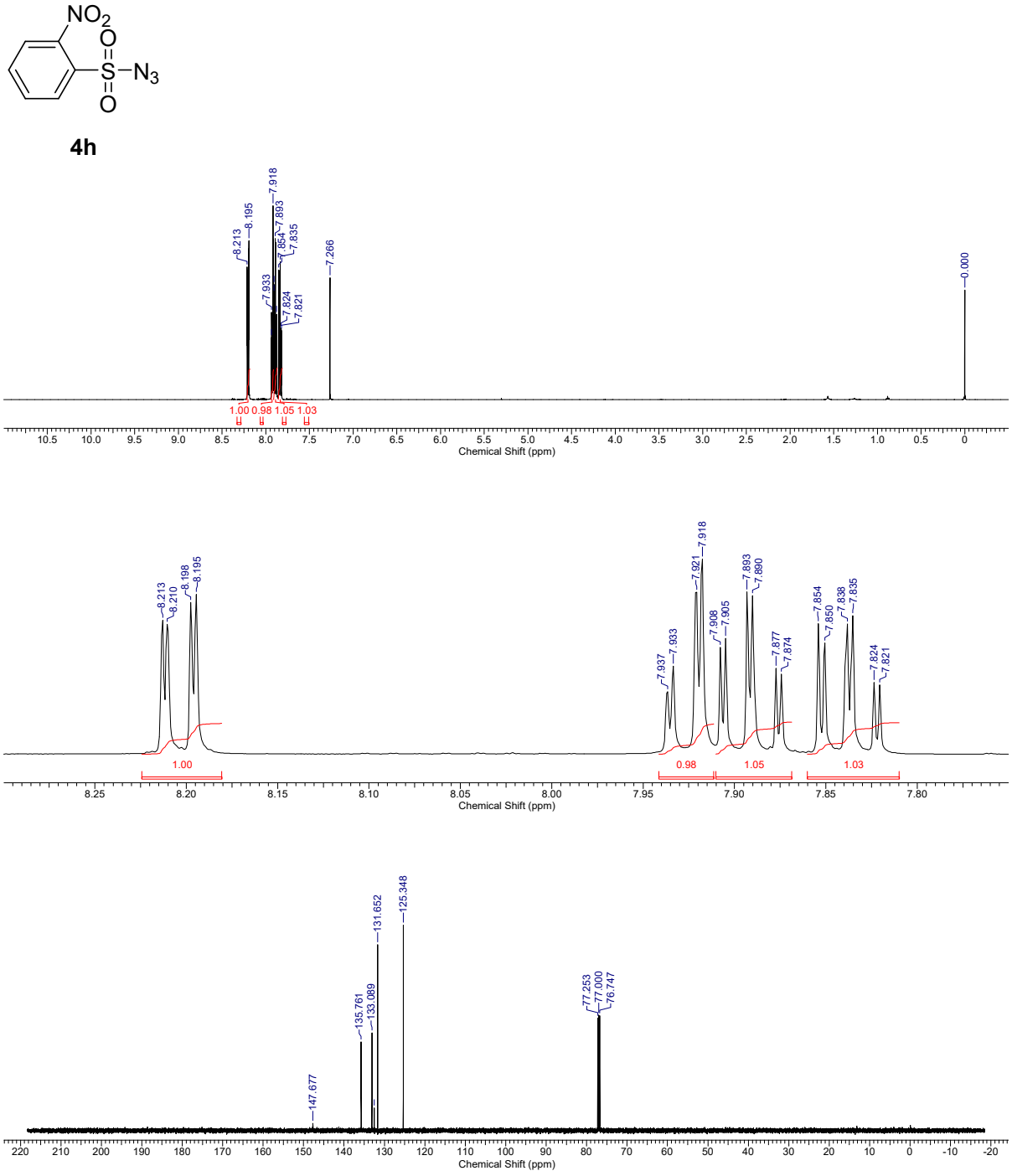



**Figure S14.** $^{1}H$ (top, middle) and $^{13}C$ (bottom) NMR spectra of **4h** in $CDCl_3$ at 500 and 125 MHz, respectively.

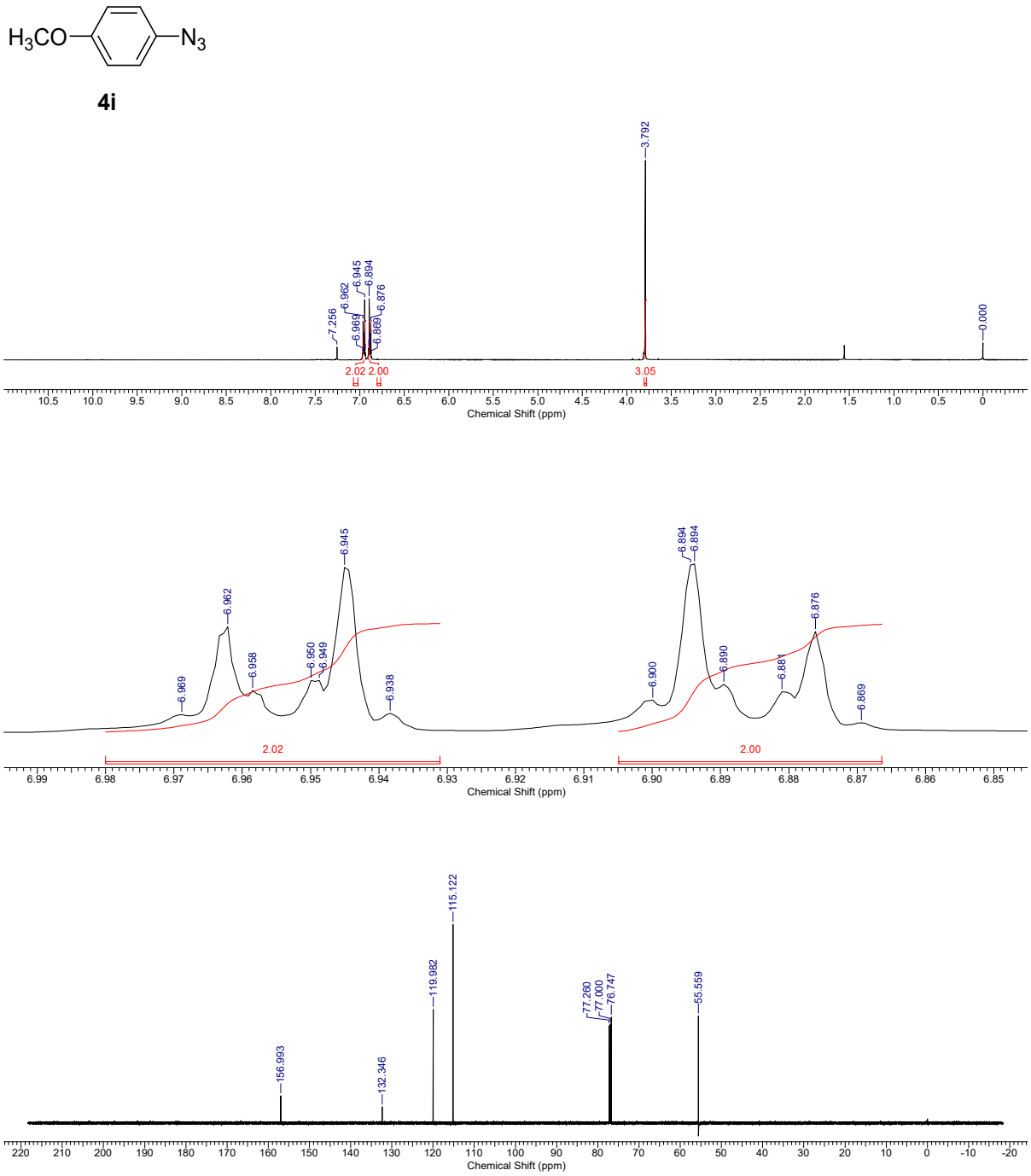



**Figure S15.** $^{1}H$ (top, middle) and $^{13}C$ (bottom) NMR spectra of **4i** in $CDCl_3$ at 500 and 125 MHz, respectively.

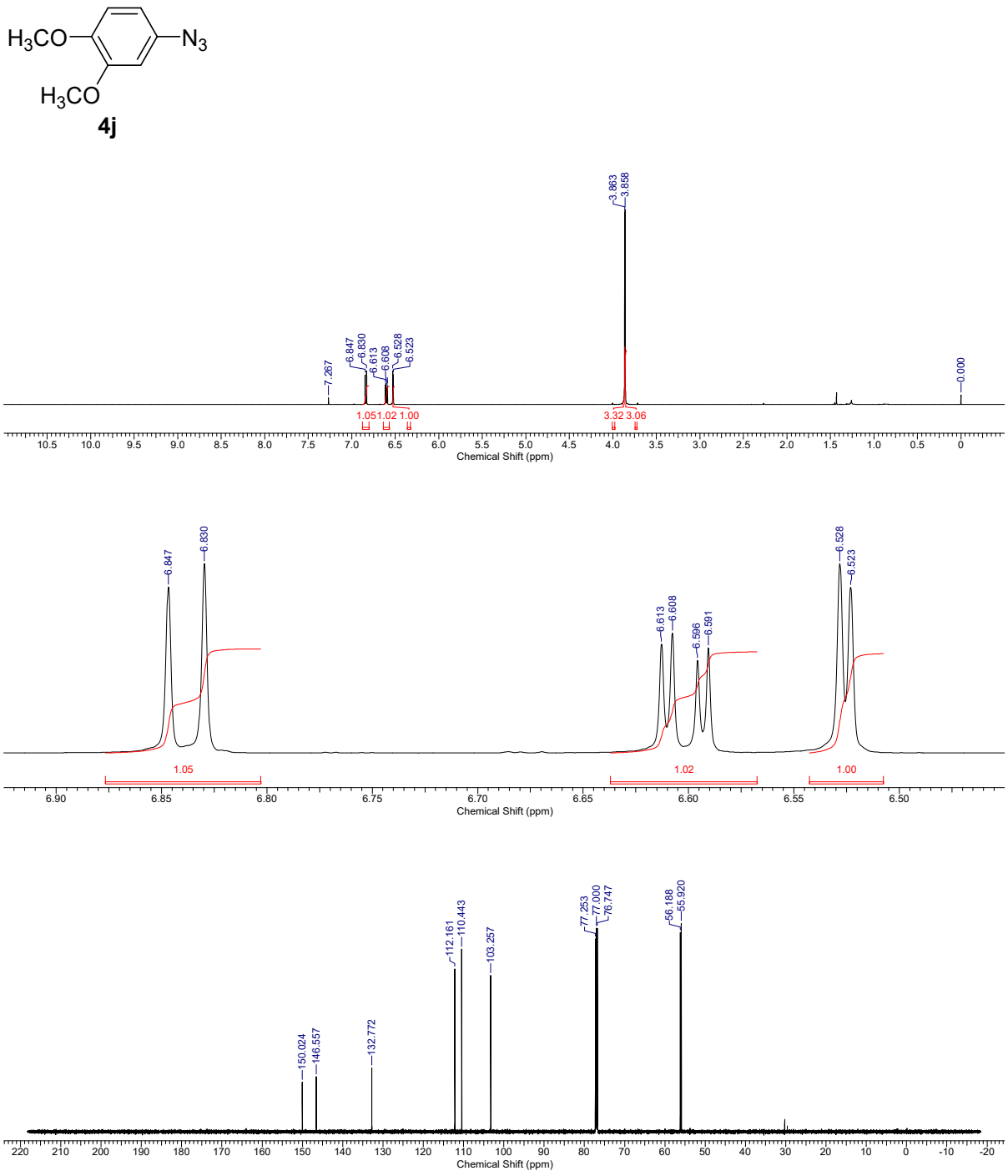



**Figure S16.** $^{1}H$ (top, middle) and $^{13}C$ (bottom) NMR spectra of **4j** in $CDCl_3$ at 500 and 125 MHz, respectively.

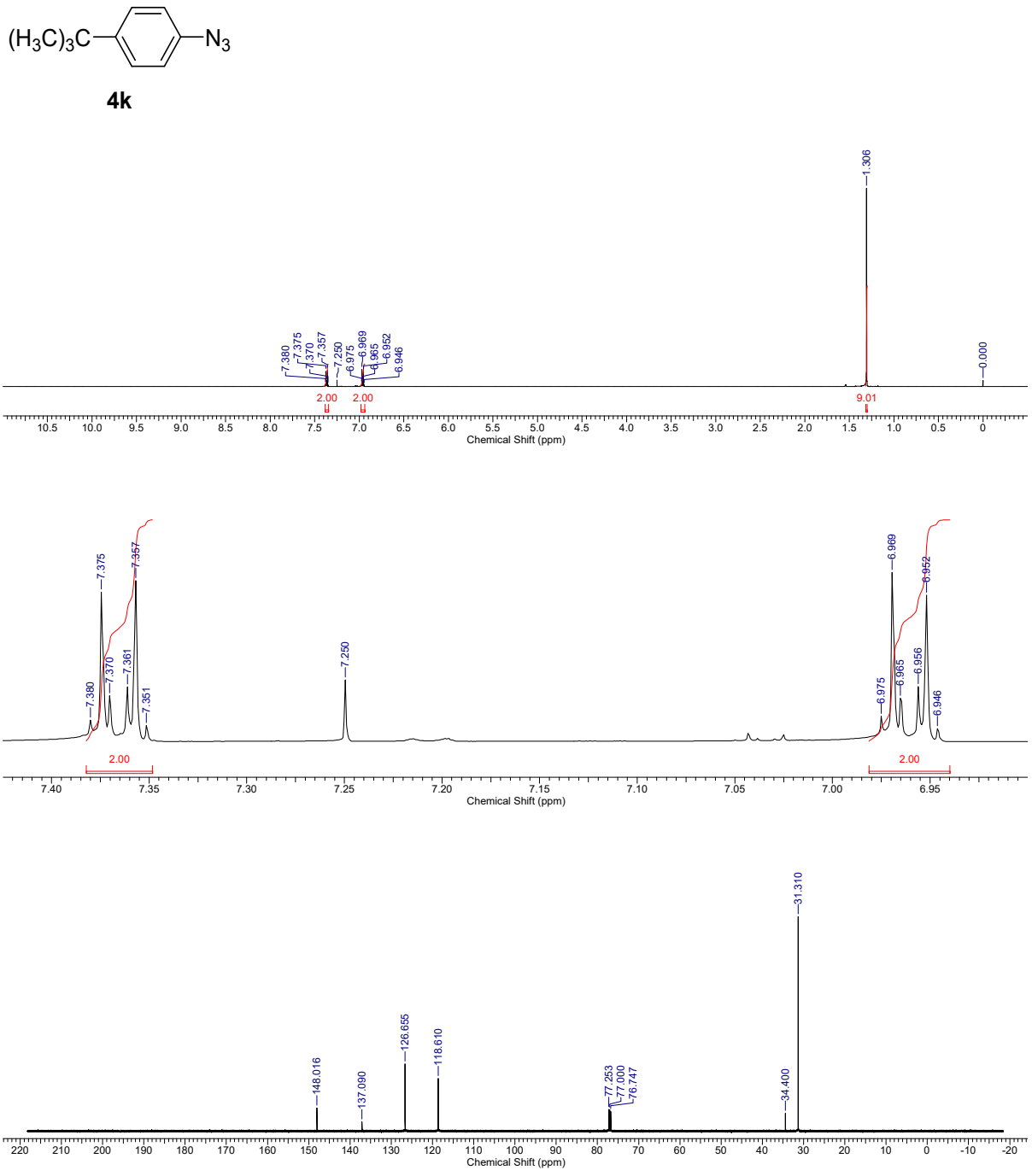



**Figure S17.** $^{1}H$ (top, middle) and $^{13}C$ (bottom) NMR spectra of **4k** in $CDCl_3$ at 500 and 125 MHz, respectively.

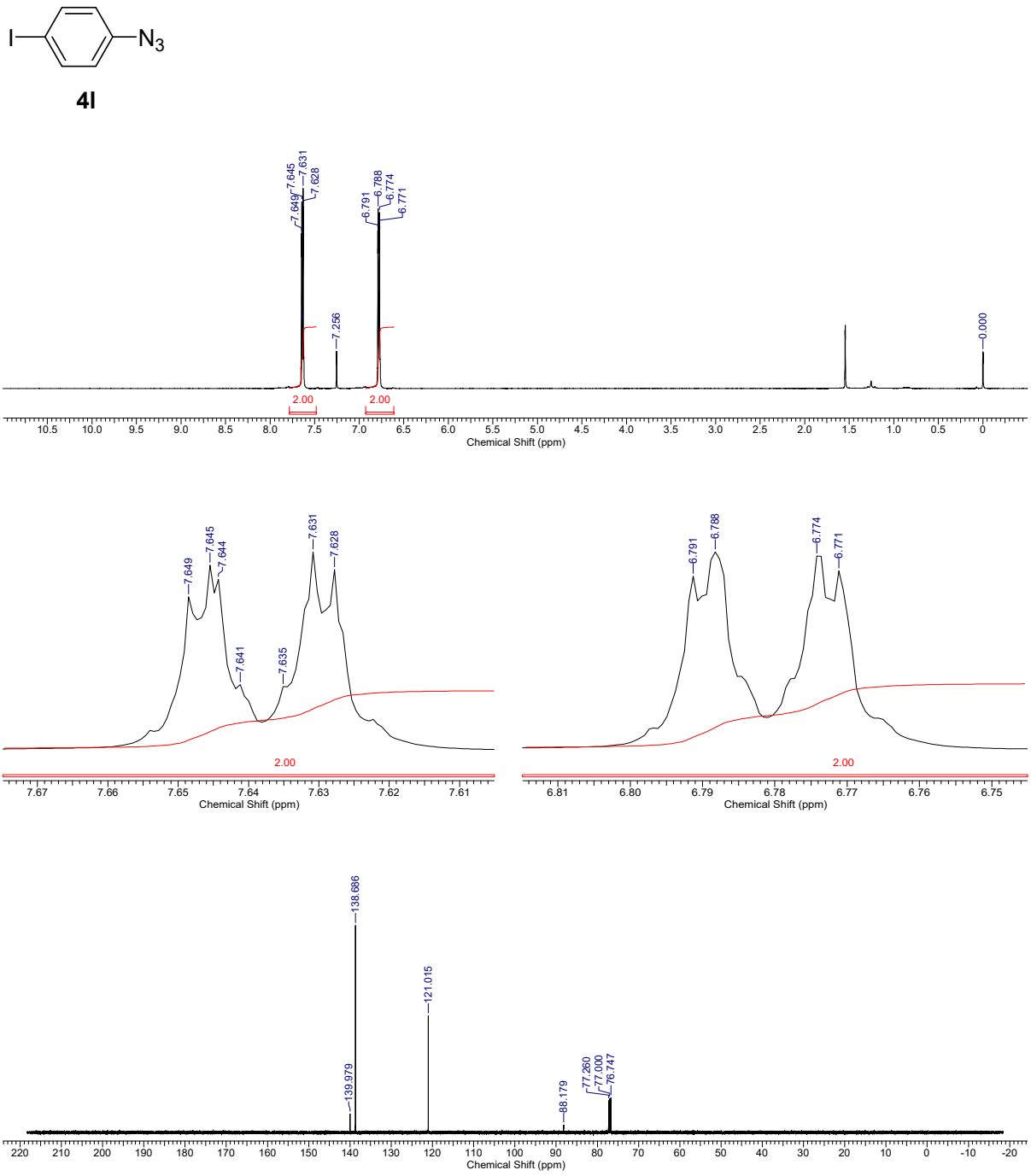



**Figure S18.** $^{1}H$ (top, middle) and $^{13}C$ (bottom) NMR spectra of **4l** in $CDCl_3$ at 500 and 125 MHz, respectively.

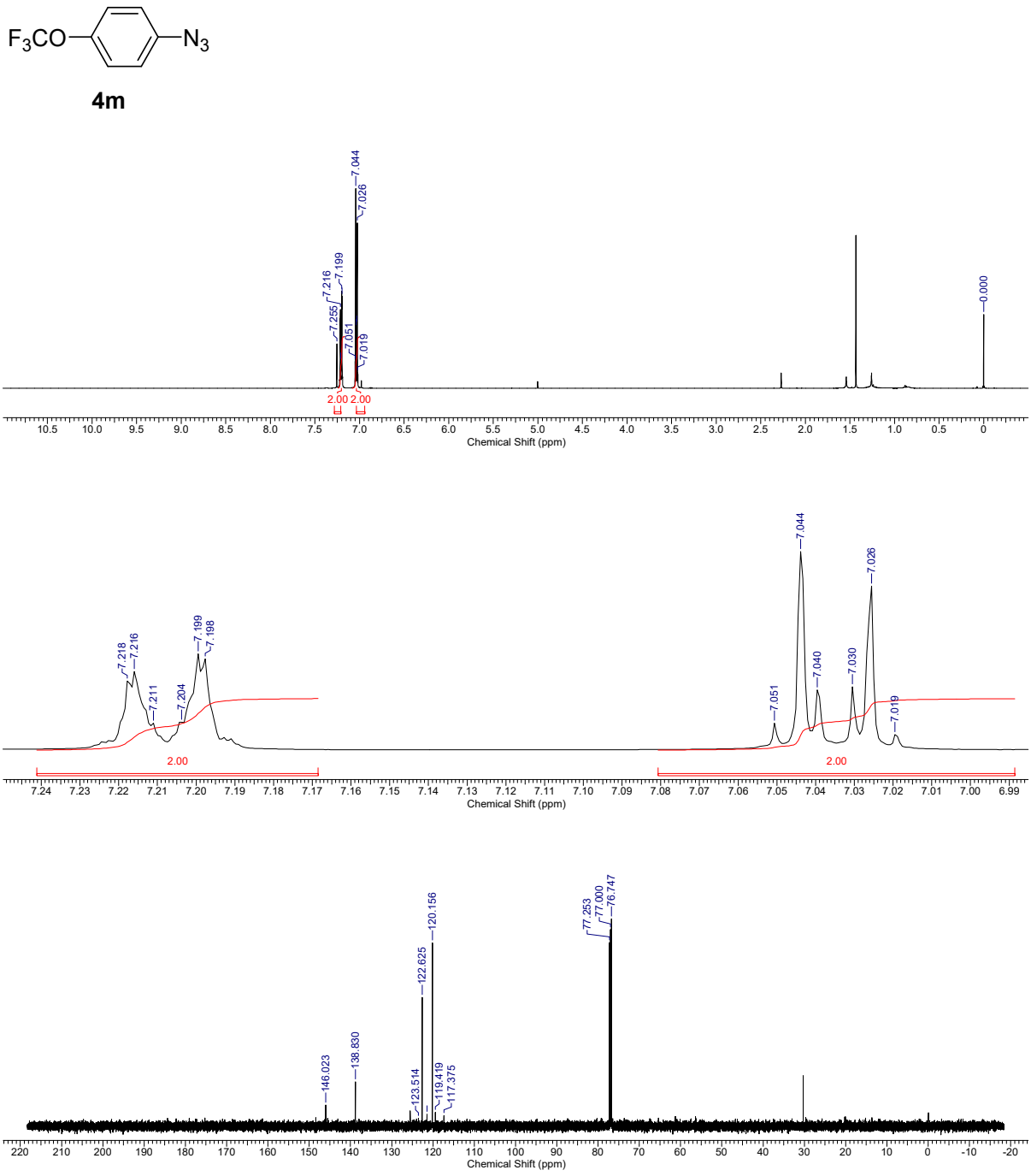



**Figure S19.** $^{1}H$ (top, middle) and $^{13}C$ (bottom) NMR spectra of **4m** in $CDCl_3$ at 500 and 125 MHz, respectively.

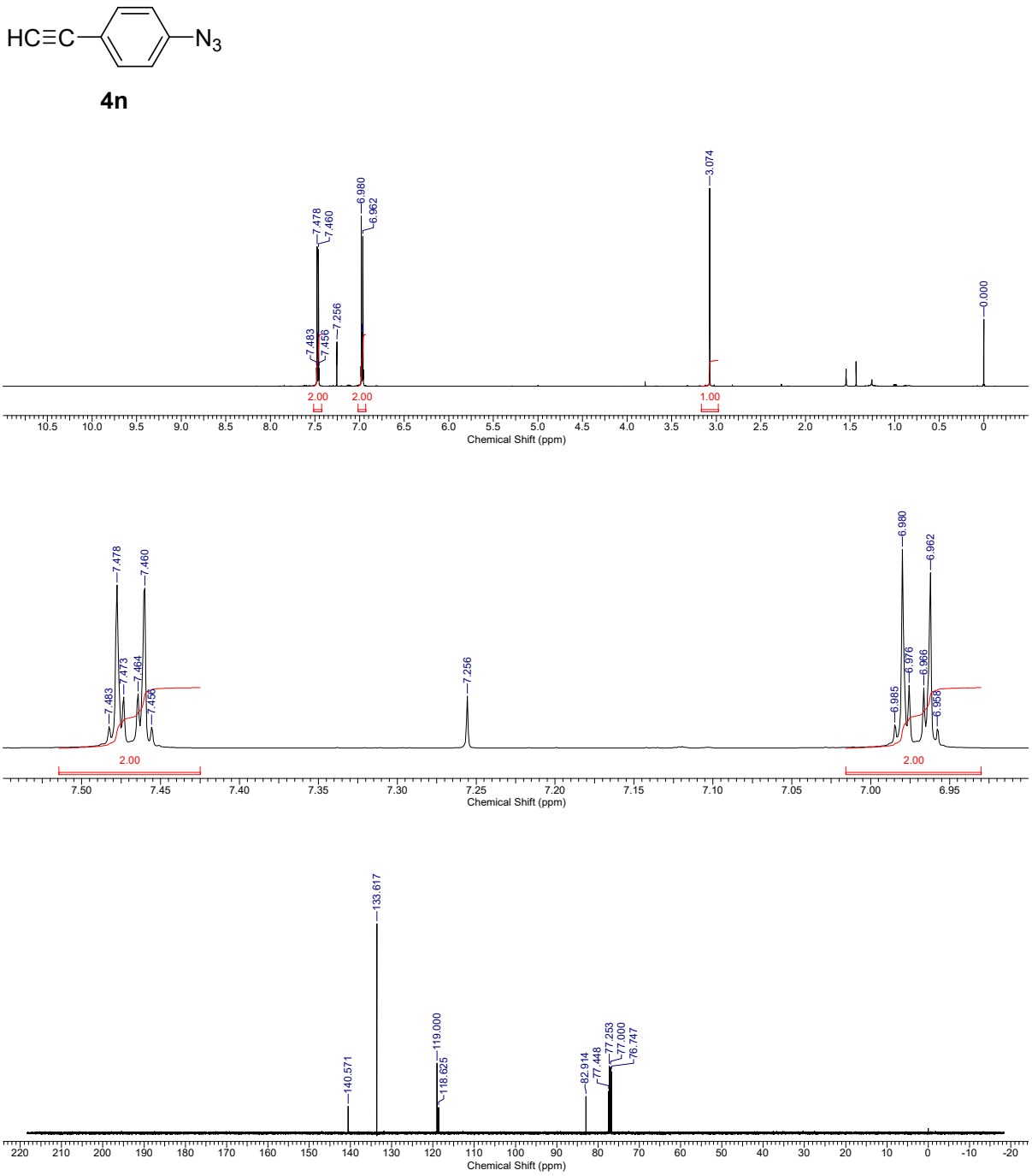



**Figure S20.** $^{1}H$ (top, middle) and $^{13}C$ (bottom) NMR spectra of **4n** in $CDCl_3$ at 500 and 125 MHz, respectively.

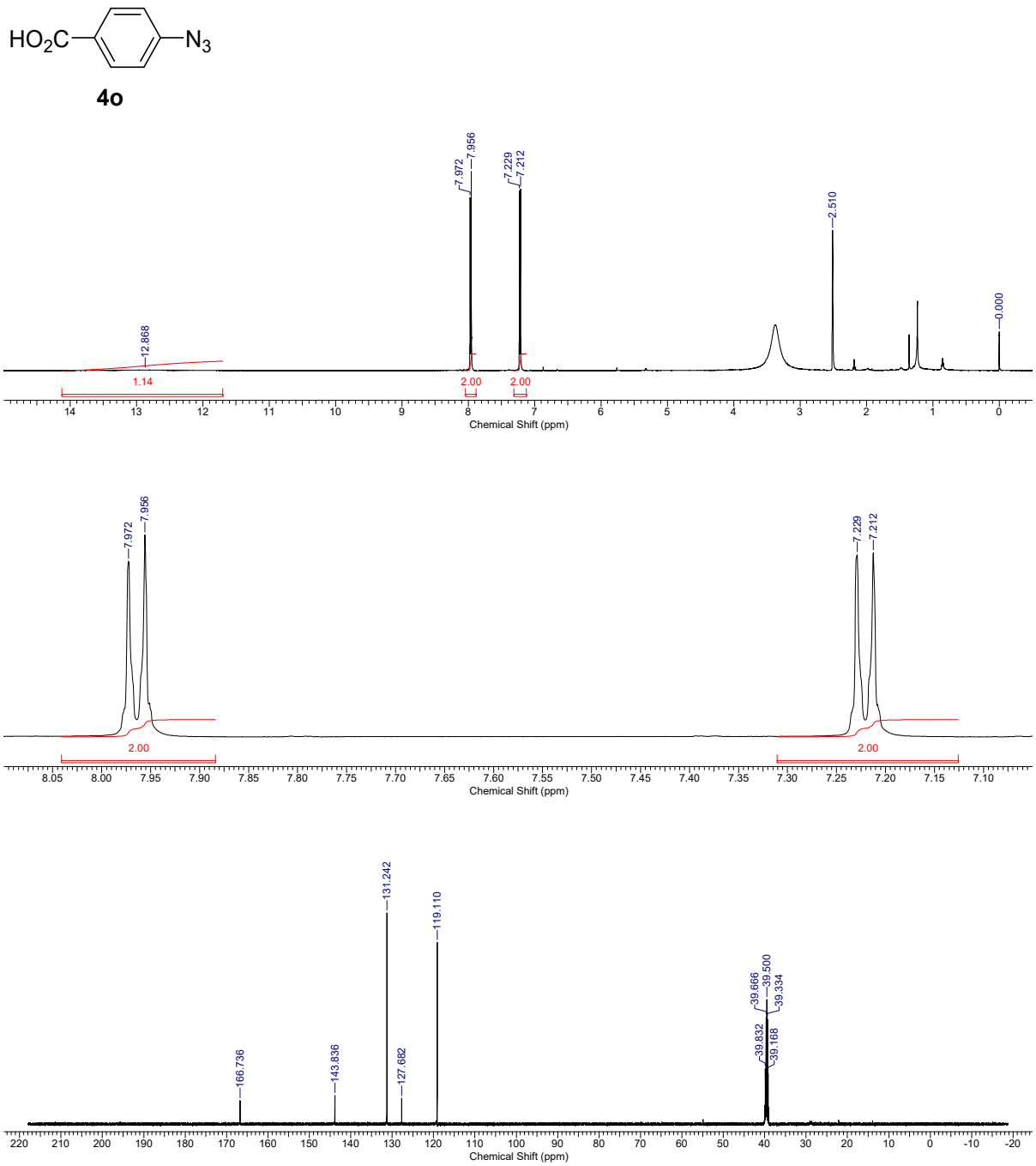



**Figure S21.** $^{1}$H (top, middle) and $^{13}$C (bottom) NMR spectra of **4o** in DMSO-$d_6$ at 500 and 125 MHz, respectively.

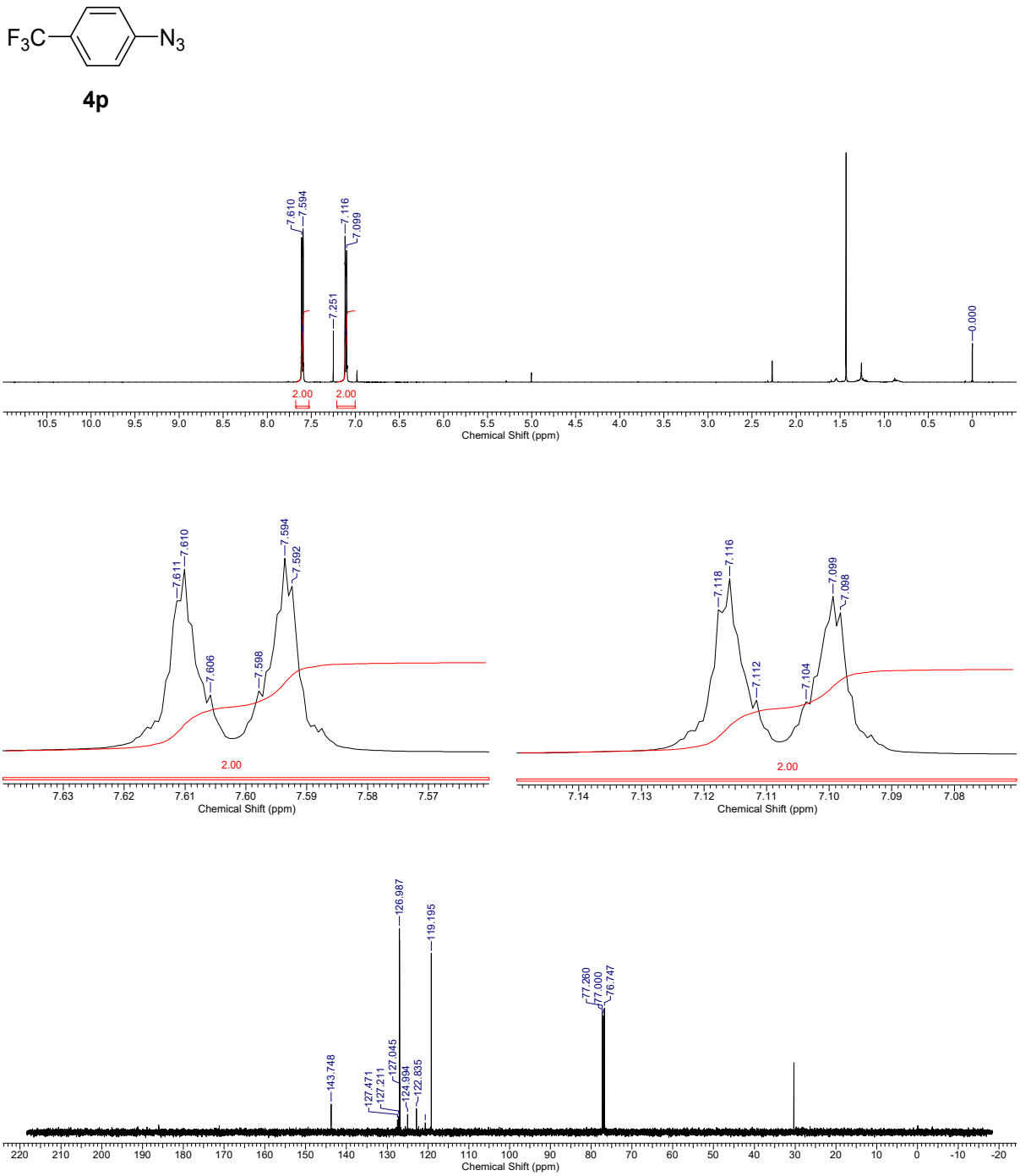



**Figure S22.** $^{1}H$ (top, middle) and $^{13}C$ (bottom) NMR spectra of **4p** in $CDCl_3$ at 500 and 125 MHz, respectively.

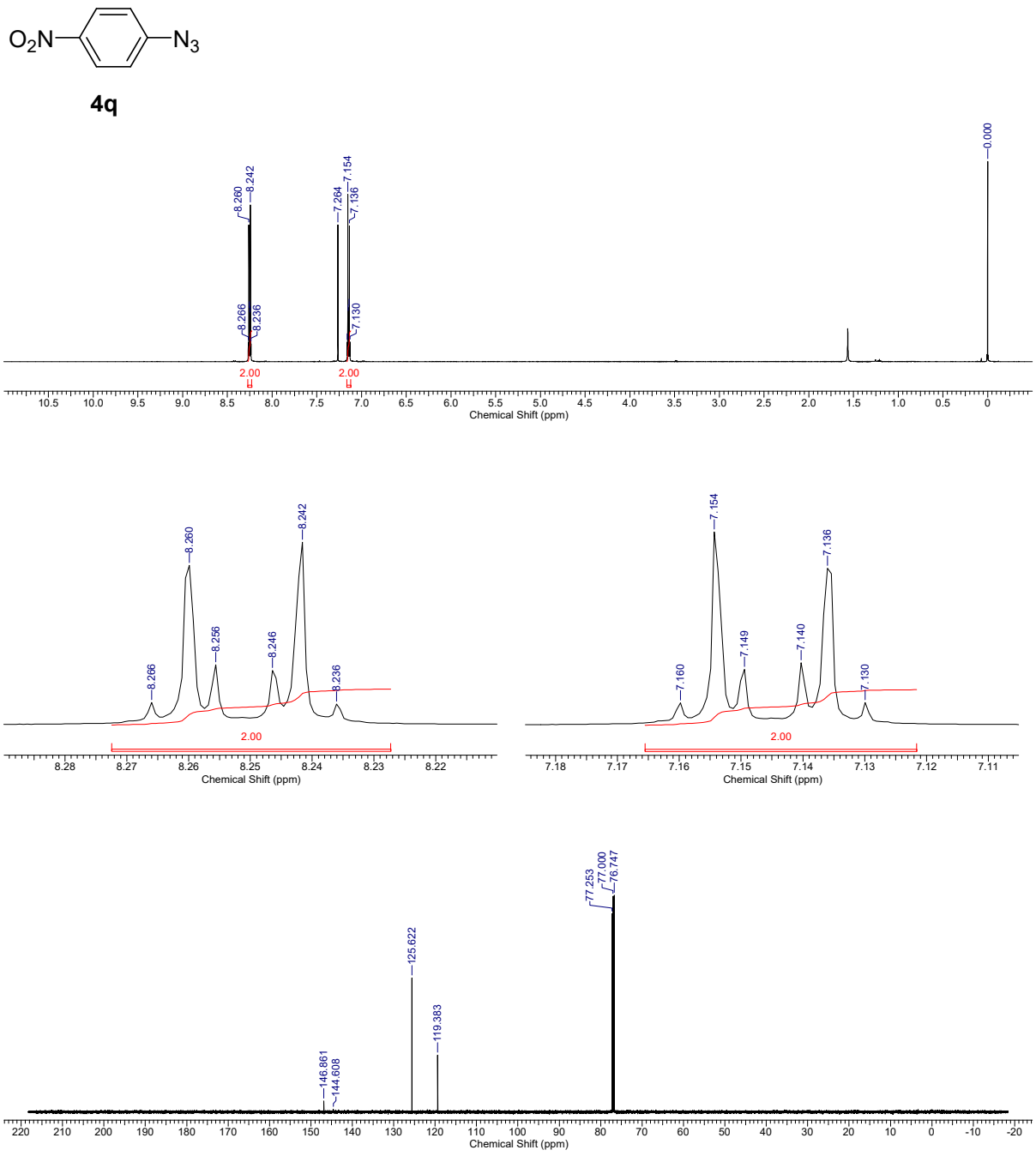



**Figure S23.** $^{1}H$ (top, middle) and $^{13}C$ (bottom) NMR spectra of **4q** in $CDCl_3$ at 500 and 125 MHz, respectively.

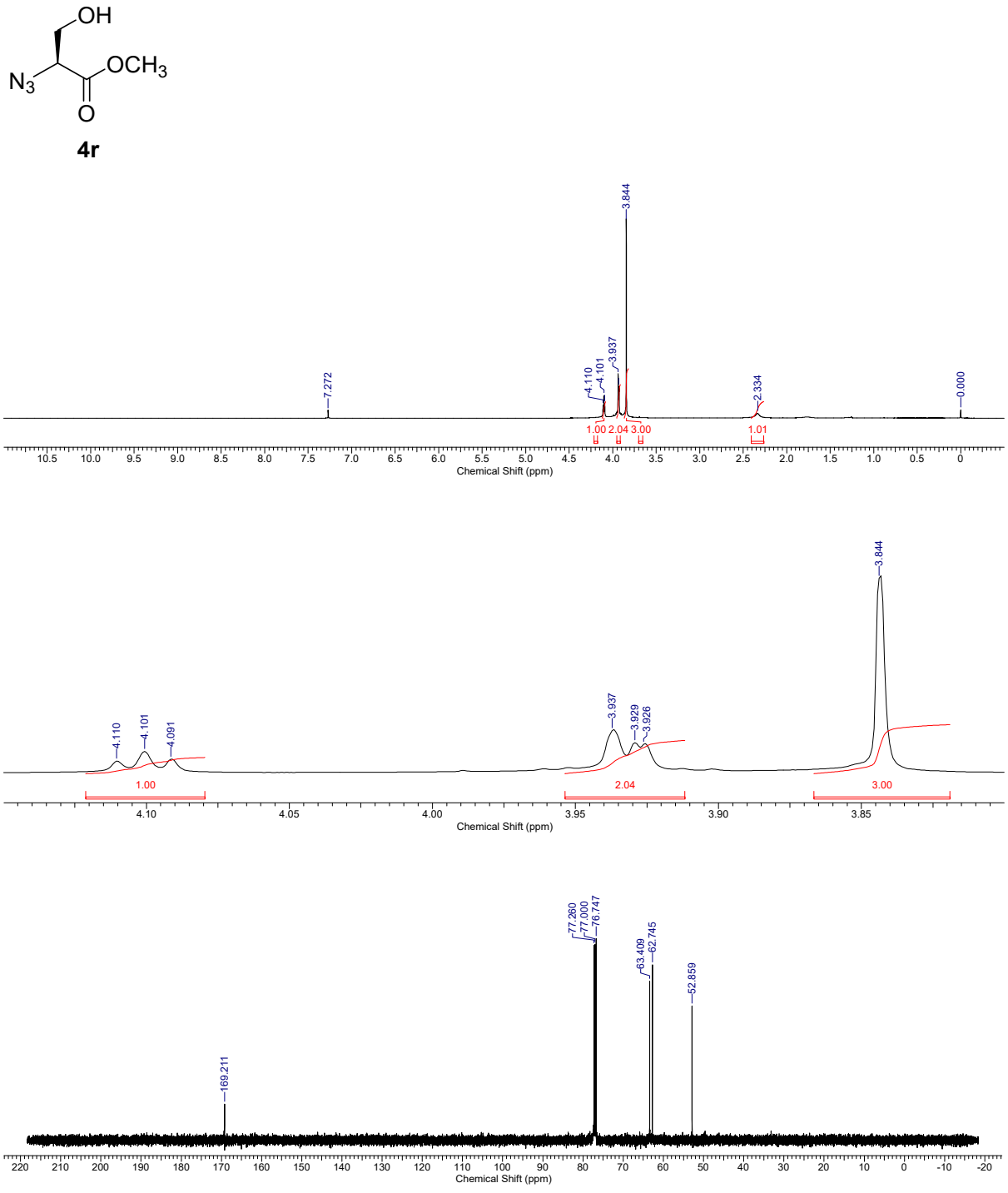



**Figure S24.** $^{1}H$ (top, middle) and $^{13}C$ (bottom) NMR spectra of **4r** in $CDCl_3$ at 500 and 125 MHz, respectively.

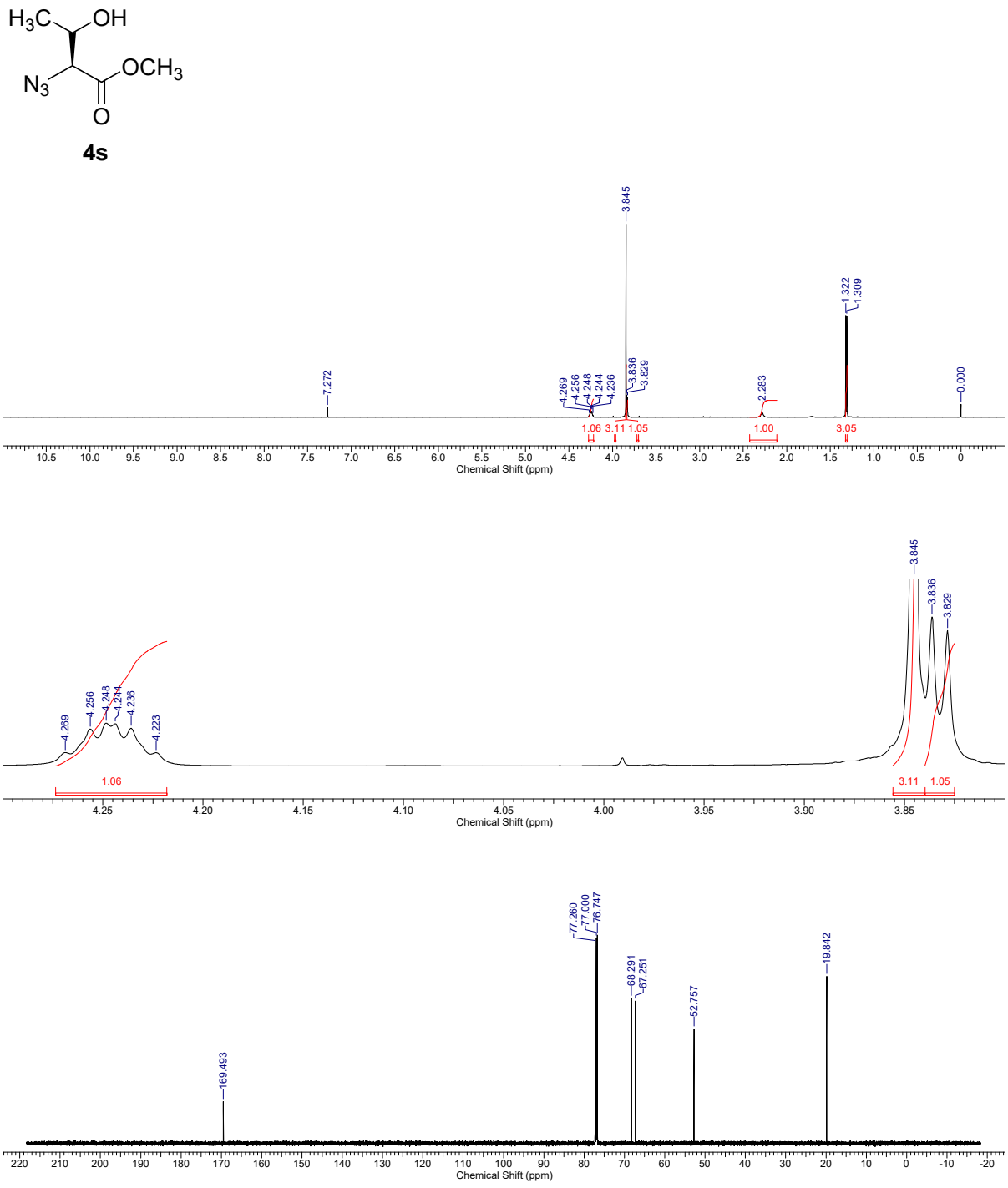



**Figure S25.** $^{1}H$ (top, middle) and $^{13}C$ (bottom) NMR spectra of **4s** in $CDCl_3$ at 500 and 125 MHz, respectively.

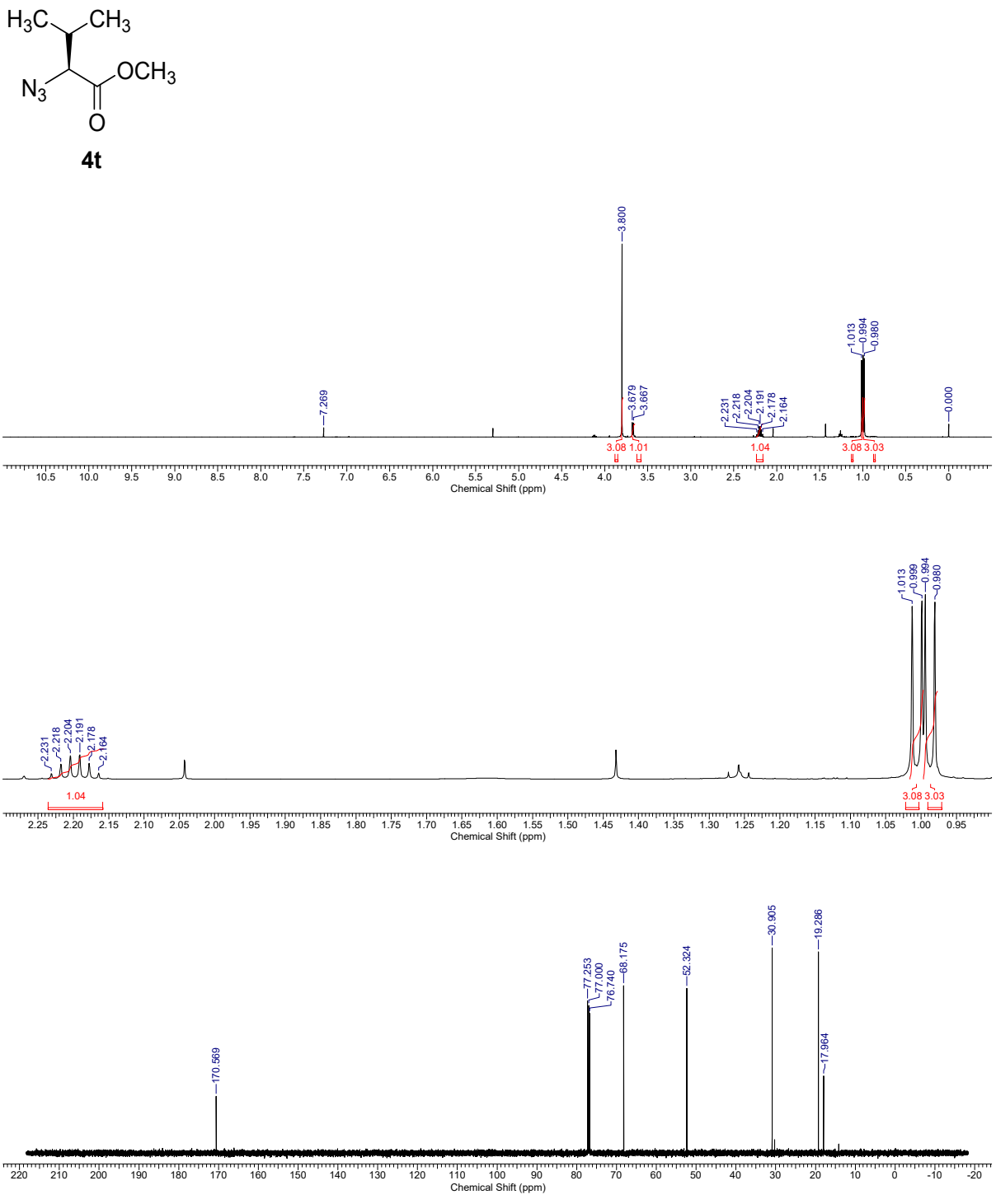



**Figure S26.** $^{1}H$ (top, middle) and $^{13}C$ (bottom) NMR spectra of **4t** in $CDCl_3$ at 500 and 125 MHz, respectively.

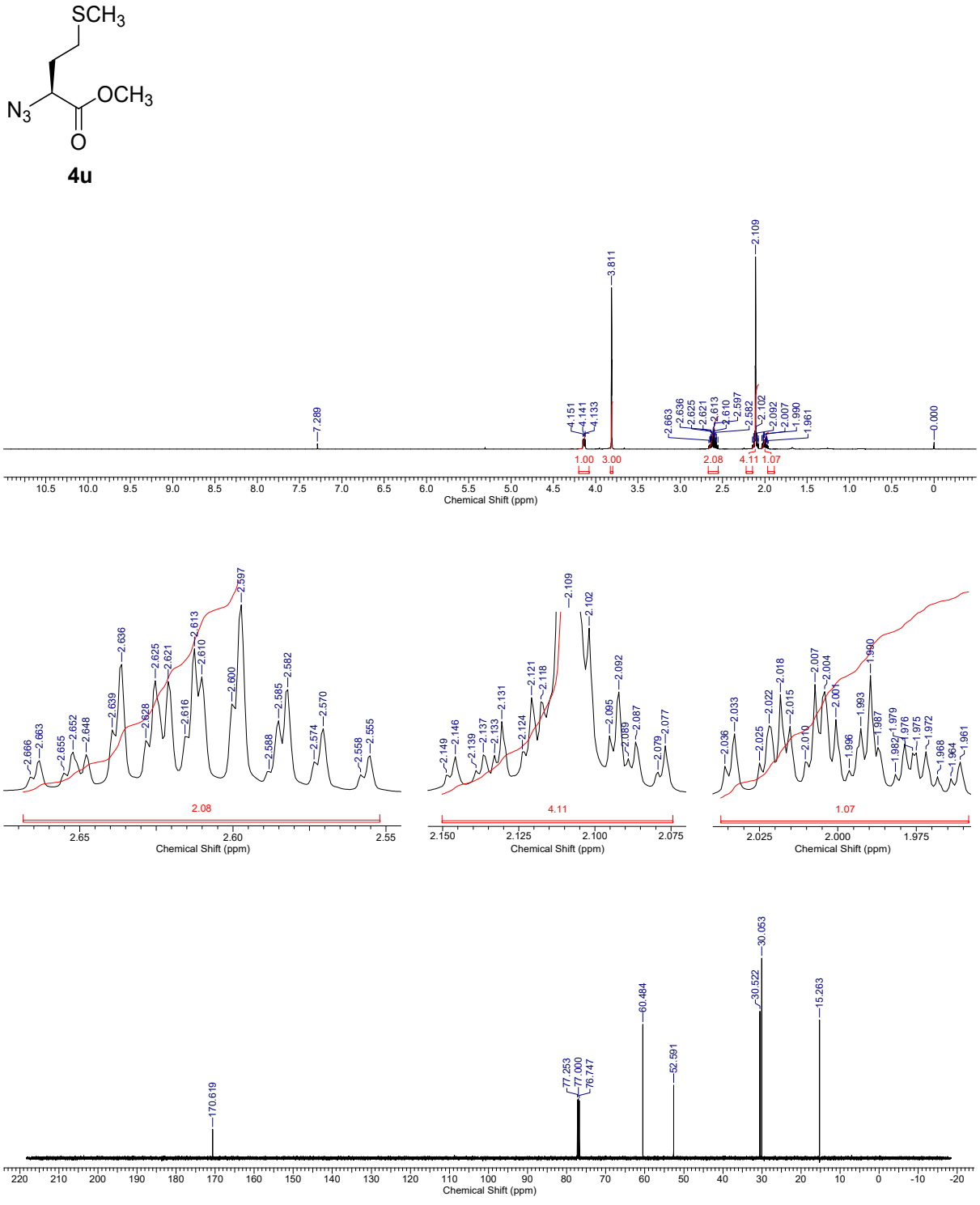



**Figure S27.** $^{1}H$ (top, middle) and $^{13}C$ (bottom) NMR spectra of **4u** in $CDCl_3$ at 500 and 125 MHz, respectively.

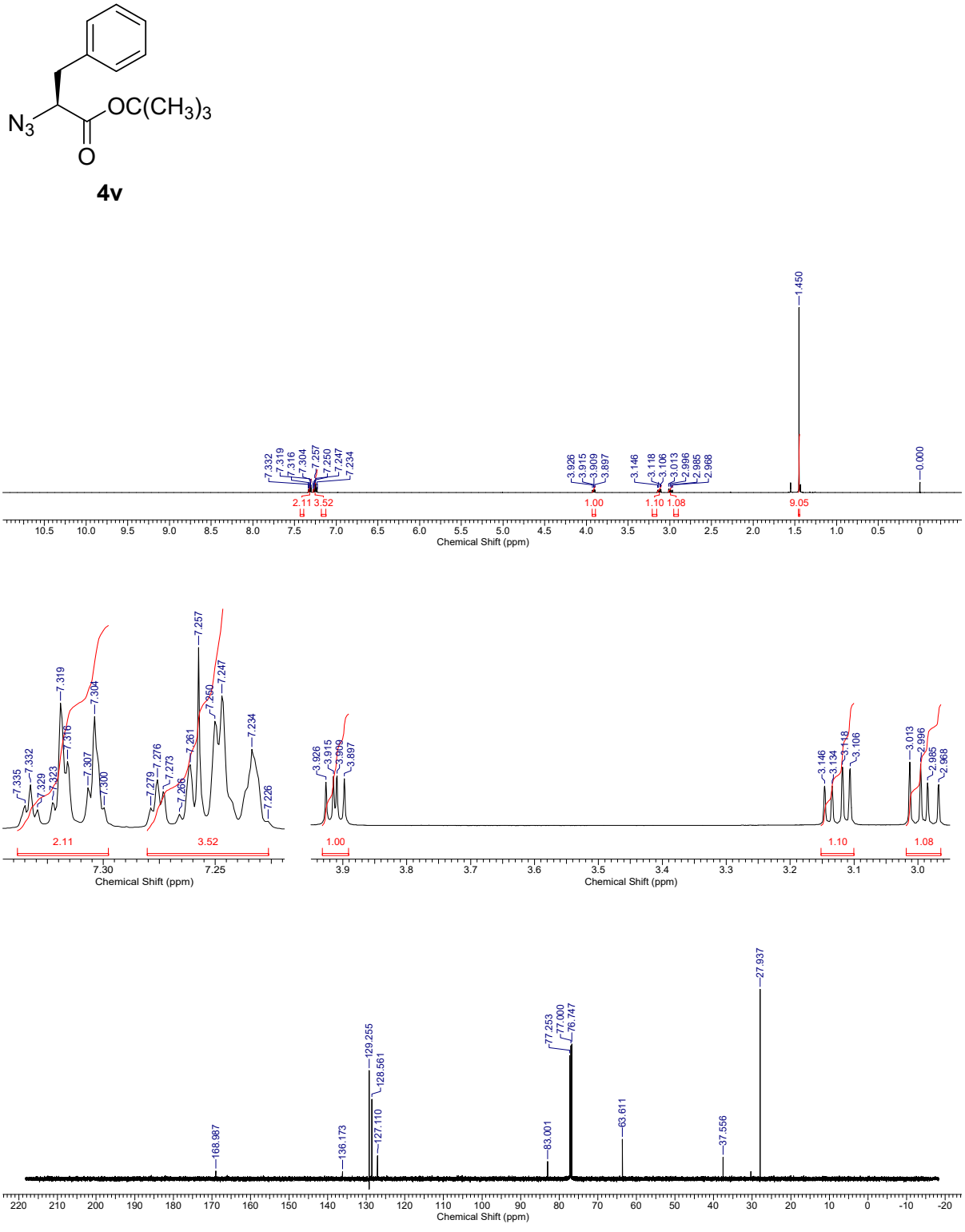



**Figure S28.** $^{1}H$ (top, middle) and $^{13}C$ (bottom) NMR spectra of **4v** in $CDCl_3$ at 500 and 125 MHz, respectively.

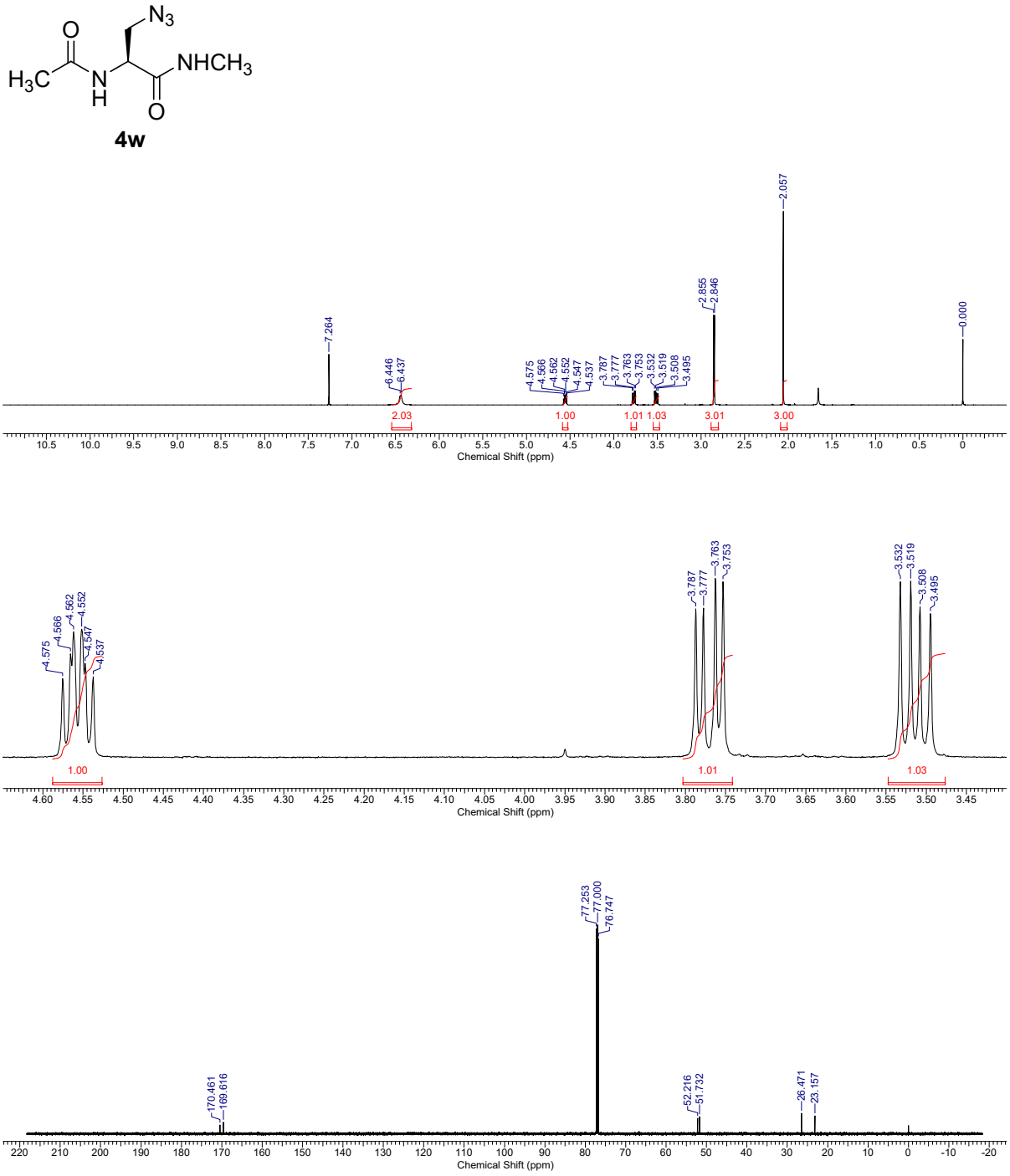



**Figure S29.** $^{1}H$ (top, middle) and $^{13}C$ (bottom) NMR spectra of **4w** in $CDCl_3$ at 500 and 125 MHz, respectively.

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