

Supporting Information

Tf₂NH-Catalyzed formal [3+2] cycloaddition of oxadiazolones with ynamides: a simple access to aminoimidazoles

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1. General information

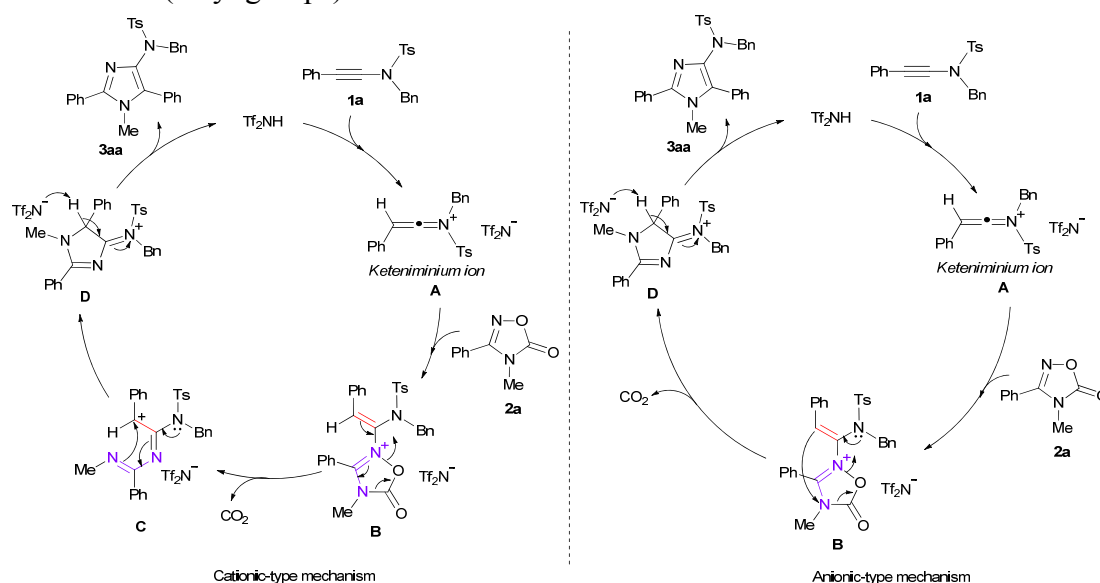
Unless otherwise noted, all reactions were carried out under inert atmosphere using standard Schlenk techniques or in an argon-filled glove-box. All chemicals were purchased from commercial sources and were used directly without further purification. Solvents were treated prior to use according to the standard methods. Column chromatography was conducted on silica gel (300–400 mesh) using a forced flow of eluent at 0.3–0.5 bar pressure. NMR Spectra were recorded at room temperature in CDCl₃ or *d*⁶-DMSO on 400 MHz spectrometers. The chemical shifts for ¹H NMR were recorded in ppm downfield from tetramethylsilane (TMS) with CDCl₃ (7.26 ppm) or *d*⁶-DMSO (2.50 ppm) as the internal standard. The chemical shifts for ¹³C NMR were recorded in ppm downfield using the central peak of CDCl₃ (77.16 ppm) or *d*⁶-DMSO (39.52 ppm) as the internal standard. Coupling constants (J) are reported in hertz and refer to apparent peak multiplications. The abbreviations *s*, *d*, *t*, *q* and *m* stand for singlet, doublet, triplet, quartet and multiplet in that order. HRMS data was obtained with Micromass HPLC-Q-TOF mass spectrometer (ESI) or Agilent 6540 Accurate-MS spectrometer (Q-TOF).

2. Mechanism discussions

The carbon atom adjacent to phenyl group in intermediate **B** has both “cationic” and “anionic” characters. Two mechanisms based on its different characters are proposed in the below scheme (left, cationic carbon; right, anionic carbon). From the anionic-type mechanism, we can see that the enamine motif in intermediate **B** attacks the nitrogen atom (–NMe) with the release of CO₂ to form cyclic iminium ion **D**. However, we think it is not feasible for this process. Because the nitrogen atom is generally regarded as the nucleophile, not electrophile.

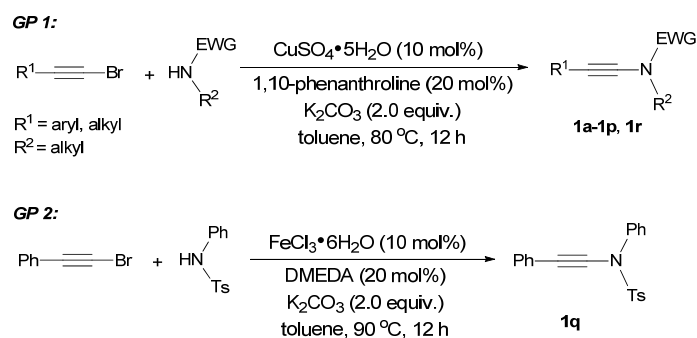
Besides, the substrate scope supports the cationic-type mechanism. The annulations of alkyl-derived ynamides with oxadiazolone **2a** afforded the desired imidazoles in low yields, while the aryl-substituted substrates gave good results. Because the benzylic cation in intermediate **C** (aryl groups) is more stable than alkyl

carbocation (alkyl groups).



3. Synthesis and characterization data of ynamides

N-Alkyl substituted ynamides **1a-1p**, and **1r** were synthesized by copper-catalyzed cross-couplings of amides with the corresponding alkynyl bromides.¹⁻⁴ *N*-Phenyl substituted ynamide **1q** was synthesized by iron-catalyzed cross-coupling of phenylbenzenesulfonamide with (bromoethynyl)benzene.⁴



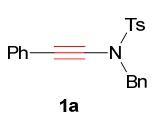
General procedure 1 (GP 1): In a 50 mL flame-dried Schlenk tube, *N*-alkyl substituted amides (5.0 mmol), CuSO₄·5H₂O (10 mol%), 1,10-phenanthroline (20 mol%), K₂CO₃ (2.0 equiv.) and toluene (20 mL) were added in sequence under argon atmosphere. Then alkynyl bromides (6.0 mmol) was introduced and the resulting mixture was stirred at 80 °C for 12 h. After that, the crude mixture was filtered through a short pad of celite and washed with ethyl acetate. Removal of the solvent and purification by silica gel column chromatography yielded the *N*-alkyl substituted

ynamides (eluent: petroleum ether/ethyl acetate 5/1).

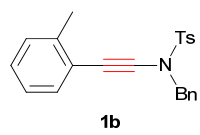
General procedure 2 (GP 2): In a 50 mL flame-dried Schlenk tube, 4-methyl-*N*-phenylbenzenesulfonamide (5.0 mmol), FeCl₃•6H₂O (10 mol%), K₂CO₃ (2.0 equiv.) and toluene (20 mL) were added in sequence under argon atmosphere. Then *N,N'*-dimethylethanediamine (DMEDA, 20 mol%) and (bromoethynyl)benzene (6.0 mmol) were introduced. The resulting mixture was stirred at 90 °C for 12 h. After that, the crude mixture was filtered through a short pad of celite and washed with ethyl acetate. Removal of the solvent and purification by silica gel column chromatography yielded the *N*-phenyl ynamide **1q** (eluent: petroleum ether/ethyl acetate 5/1).

Characterization data of ynamides:

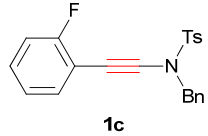
N-Benzyl-4-methyl-*N*-(phenylethynyl)benzenesulfonamide (**1a**)


Known compound;¹ 7.8 g (in 25 mmol scale); 96% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.36–7.28 (m, 7H), 7.26–7.19 (m, 5H), 4.58 (s, 2H), 2.44 (s, 3H).

N-Benzyl-4-methyl-*N*-(*o*-tolylethynyl)benzenesulfonamide (**1b**)

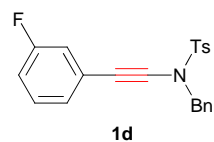

Known compound;⁸ 790.0 mg (in 3.0 mmol scale); 70% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.38–7.26 (m, 7H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.14–7.02 (m, 3H), 4.59 (s, 2H), 2.42 (s, 3H), 2.16 (s, 3H).

N-Benzyl-*N*-((2-fluorophenyl)ethynyl)-4-methylbenzenesulfonamide (**1c**)


White solid; 1.12 g (in 3.4 mmol scale); 87% yield; mp 72–73 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.37–7.27 (m, 7H), 7.26–7.17 (m, 2H), 7.05–6.96 (m, 2H), 4.59 (s, 2H), 2.43 (s, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 162.4 (d, *J* = 250.6 Hz), 144.8, 134.7, 134.4, 133.0 (d, *J* = 1.4 Hz), 129.8, 1129.3 (d, *J* = 7.8 Hz), 129.1, 128.6, 128.5, 127.9, 123.9 (d, *J* = 3.7 Hz), 115.4 (d, *J* = 20.7 Hz), 111.6 (d, *J* = 15.7 Hz), 87.5, 65.3, 55.9,

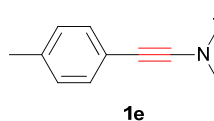
21.8. ^{19}F NMR (376 MHz, CDCl_3) δ -110.27. HRMS (ESI) calcd. for $\text{C}_{22}\text{H}_{19}\text{FNO}_2\text{S}$ $[\text{M} + \text{H}]^+$ 380.1115, found 380.1121.

***N*-Benzyl-*N*-((3-fluorophenyl)ethynyl)-4-methylbenzenesulfonamide (1d)**



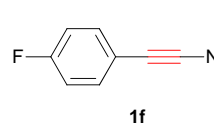
Yellow solid; 0.98 g (in 3.0 mmol scale); 86% yield; mp 69–70 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, J = 8.3 Hz, 2H), 7.37–7.29 (m, 7H), 7.23–7.16 (m, 1H), 7.01–6.86 (m, 3H), 4.58 (s, 2H), 2.45 (s, 3H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 162.4 (d, J = 246.2 Hz), 145.0, 134.7, 134.3, 129.93, 129.9 (d, J = 9.2 Hz), 129.0, 128.7, 128.6, 127.8, 126.9 (d, J = 3.1 Hz), 124.8 (d, J = 9.6 Hz), 117.8 (d, J = 22.8 Hz), 115.0 (d, J = 21.2 Hz), 83.7, 70.7 (d, J = 3.5 Hz), 55.7, 21.8. ^{19}F NMR (376 MHz, CDCl_3) δ -113.16. HRMS (ESI) calcd. for $\text{C}_{22}\text{H}_{19}\text{FNO}_2\text{S}$ $[\text{M} + \text{H}]^+$ 380.1115, found 380.1119.

***N*-Benzyl-4-methyl-*N*-(*p*-tolylethynyl)benzenesulfonamide (1e)**



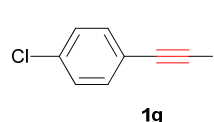
Known compound;² 680 mg (in 2.5 mmol scale); 73% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.78 (d, J = 8.1 Hz, 2H), 7.39–7.25 (m, 7H), 7.13 (d, J = 7.9 Hz, 2H), 7.04 (d, J = 7.9 Hz, 2H), 4.56 (s, 2H), 2.43 (s, 3H), 2.30 (s, 3H).

***N*-Benzyl-*N*-((4-fluorophenyl)ethynyl)-4-methylbenzenesulfonamide (1f)**



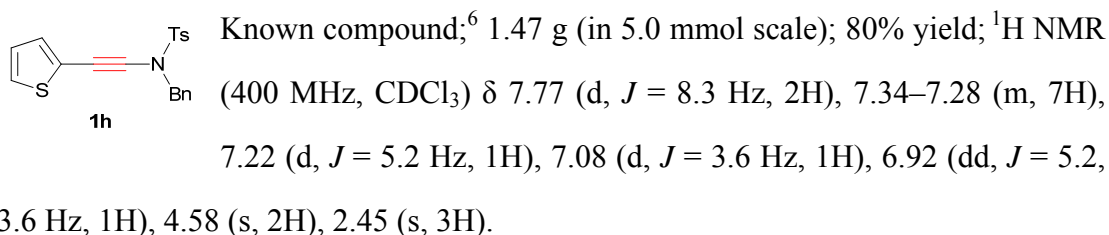
Known compound;⁵ 510.0 mg (in 2.5 mmol scale); 54% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.78 (d, J = 8.2 Hz, 2H), 7.37–7.27 (m, 7H), 7.19 (dd, J = 8.5, 5.4 Hz, 2H), 6.92 (t, J = 8.6 Hz, 2H), 4.56 (s, 2H), 2.43 (s, 3H).

***N*-Benzyl-*N*-((4-chlorophenyl)ethynyl)-4-methylbenzenesulfonamide (1g)**

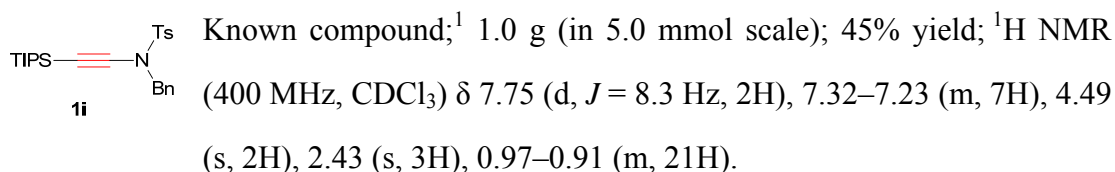


Known compound;⁶ 1.38 g (in 4.0 mmol scale); 88% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.78 (d, J = 8.3 Hz, 2H), 7.35–7.27 (m, 7H), 7.20 (d, J = 8.5 Hz, 2H), 7.13 (d, J = 8.6 Hz, 2H), 4.57 (s, 2H), 2.43 (s, 3H).

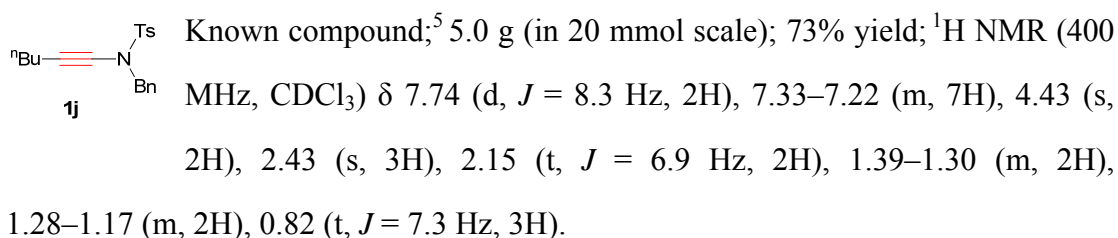
***N*-Benzyl-4-methyl-*N*-(thiophen-2-ylethynyl)benzenesulfonamide (1h)**



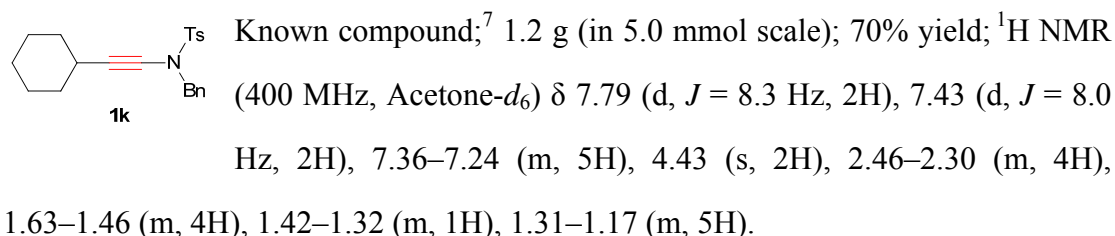
***N*-Benzyl-4-methyl-*N*-((triisopropylsilyl)ethynyl)benzenesulfonamide (1i)**



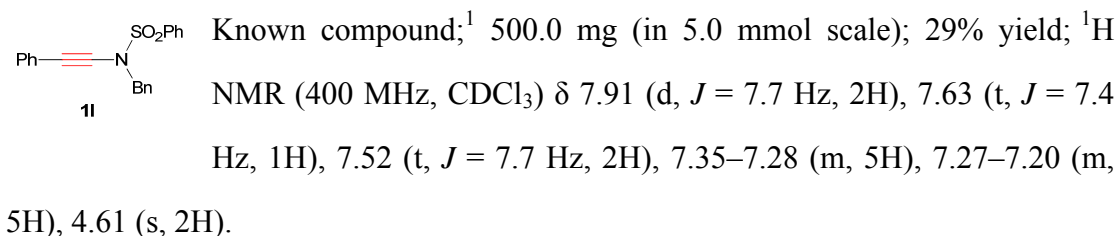
***N*-Benzyl-*N*-(hex-1-ynyl)-4-methylbenzenesulfonamide (1j)**



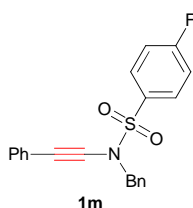
***N*-Benzyl-*N*-(cyclohexylethynyl)-4-methylbenzenesulfonamide (1k)**



***N*-Benzyl-*N*-(phenylethynyl)benzenesulfonamide (1l)**

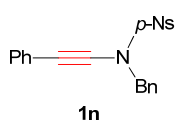


***N*-Benzyl-4-fluoro-*N*-(phenylethynyl)benzenesulfonamide (1m)**



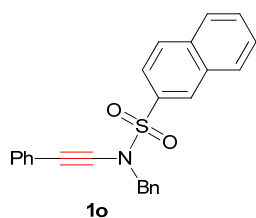
Known compound;⁵ 380.0 mg (in 5.0 mmol scale); 21% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.91–7.85 (m, 2H), 7.33–7.31 (m, 4H), 7.28–7.24 (m, 6H), 7.20–7.14 (m, 2H), 4.62 (s, 2H).

***N*-Benzyl-4-nitro-*N*-(phenylethynyl)benzenesulfonamide (1n)**



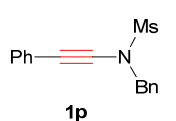
Known compound;¹ 574.0 mg (in 2.5 mmol scale); 58% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, *J* = 8.6 Hz, 2H), 7.98 (d, *J* = 8.5 Hz, 2H), 7.39–7.22 (m, 10H), 4.68 (s, 2H).

***N*-Benzyl-*N*-(phenylethynyl)naphthalene-2-sulfonamide (1o)**



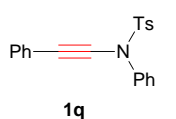
Yellow solid; 570.0 mg (in 2.5 mmol scale); 80% yield; mp 109–110°C; ¹H NMR (400 MHz, CDCl₃) δ 8.44 (s, 1H), 7.97–7.86 (m, 4H), 7.68–7.57 (m, 2H), 7.36–7.30 (m, 2H), 7.28–7.19 (m, 8H), 4.64 (s, 2H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 135.3, 134.6, 134.4, 132.1, 131.3, 129.5, 129.4, 129.0, 128.6, 128.5, 128.3, 128.1, 127.9, 127.78, 122.77, 122.7, 82.7, 71.5, 56.0. HRMS (ESI) calcd. for C₂₅H₂₀NO₂S [M + H]⁺ 398.1209, found 398.1215.

***N*-Benzyl-*N*-(phenylethynyl)methanesulfonamide (1p)**



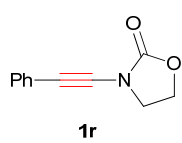
Known compound;⁴ 785.6 mg (in 4.0 mmol scale); 69% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.51–7.46 (m, 2H), 7.43–7.32 (m, 5H), 7.31–7.25 (m, 3H), 4.71 (s, 2H), 2.93 (s, 3H).

4-Methyl-*N*-phenyl-*N*-(phenylethynyl)benzenesulfonamide (1q)



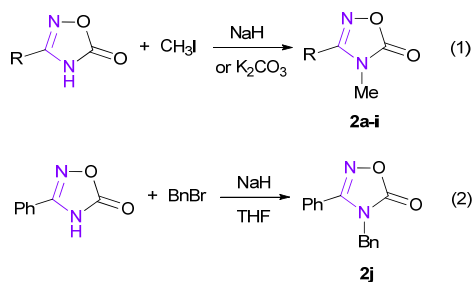
Known compound;¹ 500.0 mg (in 5 mmol scale); 29% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.43–7.25 (m, 12H), 2.44 (s, 3H).

3-(Phenylethynyl)oxazolidin-2-one (**1r**)



Known compound;⁴ 200.0 mg (in 2.5 mmol scale); 43% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.48–7.40 (m, 2H), 7.35–7.27 (m, 3H), 4.53–4.43 (m, 2H), 4.04–3.95 (m, 2H).

4. Synthesis and characterization data of oxadiazolones



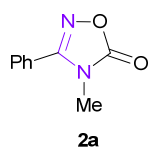
Various free N-H oxadiazolones, which were prepared according to the known method,⁹ reacted with CH₃I or BnBr to yield *N*-substituted oxadiazolones **2a–j**.

General procedure 1 (GP 1): To a solution of NaH (8.0 mmol) in THF (40.0 mL) at 0 °C was added free N-H oxadiazolones (4.0 mmol) and stirred for 40 min. The resulting mixture was then treated with CH₃I or BnBr (8.0 mmol, 2.0 equiv) and stirred at room temperature for 12 h. The reaction was quenched with water, and extracted with ethyl acetate. The combined organic layers were dried with anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification by silica gel column chromatography afforded *N*-substituted oxadiazolones.

General procedure 2 (GP 2): In a 100 mL flask, free N-H oxadiazolones (4.0 mmol), K₂CO₃ (8.0 mmol, 2.0 equiv) and acetone (40 mL) were added in sequence. Then CH₃I (8.0 mmol, 2.0 equiv) was introduced and the resulting mixture was stirred at 50 °C for 2 h. The reaction was quenched with water, and extracted with ethyl acetate. The combined organic layers were dried with anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Direct crystallization in DCM/pentane afforded *N*-substituted oxadiazolones.

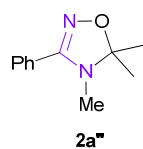
Characterization data of *N*-substituted oxadiazolones:

4-Methyl-3-phenyl-1,2,4-oxadiazol-5(4*H*)-one (2a)



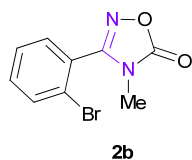
By following GP 1, the product was obtained as a white solid; 280 mg (in 5 mmol scale); 32% yield; mp 113–114 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.69 – 7.52 (m, 5H), 3.33 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 159.9, 158.9, 132.3, 129.5, 128.2, 123.3, 29.9. **HRMS (ESI)** calcd. for $\text{C}_9\text{H}_9\text{N}_2\text{O}_2$ $[\text{M} + \text{H}]^+$ 177.0659, found 177.0658.

4,5,5-Trimethyl-3-phenyl-4,5-dihydro-1,2,4-oxadiazole (2a'')



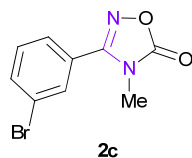
By following GP 1, the product was obtained as colorless oil; 300 mg (in 2.8 mmol scale); 56% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.73 – 7.68 (m, 2H), 7.52 – 7.40 (m, 3H), 3.06 (s, 3H), 1.60 (s, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 163.7, 131.3, 128.8, 128.6, 128.2, 106.4, 43.6, 28.9. **HRMS (ESI)** calcd. for $\text{C}_{11}\text{H}_{15}\text{N}_2\text{O}$ $[\text{M} + \text{H}]^+$ 191.1179, found 191.1182.

3-(2-Bromophenyl)-4-methyl-1,2,4-oxadiazol-5(4*H*)-one (2b)



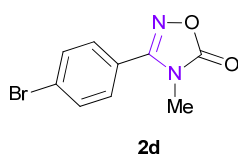
By following GP 1, the product was obtained as colorless oil; 113 mg (in 0.8 mmol scale); 56% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.81 – 7.72 (m, 1H), 7.57 – 7.45 (m, 3H), 3.14 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 159.3, 158.6, 133.7, 133.6, 132.1, 128.3, 125.0, 123.0, 29.1. **HRMS (ESI)** calcd. for $\text{C}_9\text{H}_8\text{BrN}_2\text{O}_2$ $[\text{M} + \text{H}]^+$ 254.9764, found 254.9760.

3-(3-Bromophenyl)-4-methyl-1,2,4-oxadiazol-5(4*H*)-one (2c)



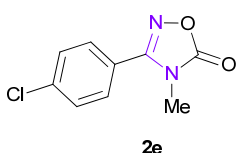
By following GP 1, the product was obtained as a white solid; 485.8 mg (in 3.2 mmol scale); 60% yield; mp 102–103 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.82 – 7.73 (m, 2H), 7.57 (d, $J = 7.8$ Hz, 1H), 7.47 (t, $J = 7.8$ Hz, 1H), 3.34 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 159.6, 157.6, 135.4, 131.1, 131.0, 126.8, 125.2, 123.5, 29.9. **HRMS (ESI)** calcd. for $\text{C}_9\text{H}_8\text{BrN}_2\text{O}_2$ $[\text{M} + \text{H}]^+$ 254.9764, found 254.9761.

3-(4-Bromophenyl)-4-methyl-1,2,4-oxadiazol-5(4H)-one (2d)



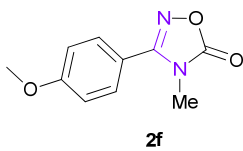
By following GP 1, the product was obtained as a white solid; 575 mg (in 8.3 mmol scale); 27% yield; mp 126–127 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, $J = 8.5$ Hz, 2H), 7.47 (d, $J = 8.5$ Hz, 2H), 3.29 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.7, 158.1, 132.9, 129.7, 127.2, 122.2, 29.9. HRMS (ESI) calcd. for $\text{C}_9\text{H}_8\text{BrN}_2\text{O}_2$ $[\text{M} + \text{H}]^+$ 254.9764, found 254.9761.

3-(4-Chlorophenyl)-4-methyl-1,2,4-oxadiazol-5(4H)-one (2e)



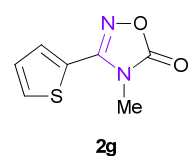
By following GP 1, the product was obtained as a white solid; 560 mg (in 7.1 mmol scale); 38% yield; mp 116–117 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.67 – 7.49 (m, 4H), 3.33 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.6, 158.0, 138.7, 129.9, 129.5, 121.7, 29.8. HRMS (ESI) calcd. for $\text{C}_9\text{H}_8\text{ClN}_2\text{O}_2$ $[\text{M} + \text{H}]^+$ 211.0269, found 211.0268.

3-(4-Methoxyphenyl)-4-methyl-1,2,4-oxadiazol-5(4H)-one (2f)



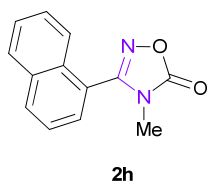
By following GP 1, the product was obtained as a white solid; 151.1 mg (in 1.7 mmol scale); 50% yield; mp 89–90 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.40 (d, $J = 8.7$ Hz, 2H), 6.92 (d, $J = 8.7$ Hz, 2H), 3.83 (s, 3H), 2.73 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.6, 157.1, 130.1, 123.7, 113.9, 55.4, 30.8. HRMS (ESI) calcd. for $\text{C}_{10}\text{H}_{11}\text{N}_2\text{O}_3$ $[\text{M} + \text{H}]^+$ 207.0764, found 207.0762.

4-Methyl-3-(thiophen-2-yl)-1,2,4-oxadiazol-5(4H)-one (2g)



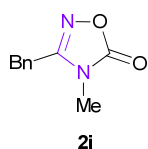
By following GP 1, the product was obtained as a white solid; 710 mg (in 7.1 mmol scale); 55% yield; mp 140–141 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, $J = 5.1$ Hz, 1H), 7.60 (d, $J = 3.8$ Hz, 1H), 7.30 – 7.18 (m, 1H), 3.47 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.5, 154.1, 130.9, 130.3, 128.4, 123.3, 30.0. HRMS (ESI) calcd. for $\text{C}_7\text{H}_7\text{N}_2\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$ 183.0223, found 183.0224.

4-Methyl-3-(naphthalen-1-yl)-1,2,4-oxadiazol-5(4H)-one (2h)



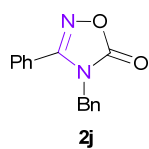
By following GP 1, the product was obtained as colorless oil; 343 mg (in 4.7 mmol scale); 32% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.11 (d, $J = 7.9$ Hz, 1H), 8.03 – 7.93 (m, 1H), 7.80 – 7.73 (m, 1H), 7.70 – 7.57 (m, 4H), 3.06 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 159.7, 158.7, 133.6, 132.7, 130.7, 129.10, 129.06, 128.4, 127.3, 125.2, 123.9, 120.3, 29.3. **HRMS (ESI)** calcd. for $\text{C}_{13}\text{H}_{11}\text{N}_2\text{O}_2$ $[\text{M} + \text{H}]^+$ 227.0815, found 227.0819.

3-Benzyl-4-methyl-1,2,4-oxadiazol-5(4H)-one (2i)



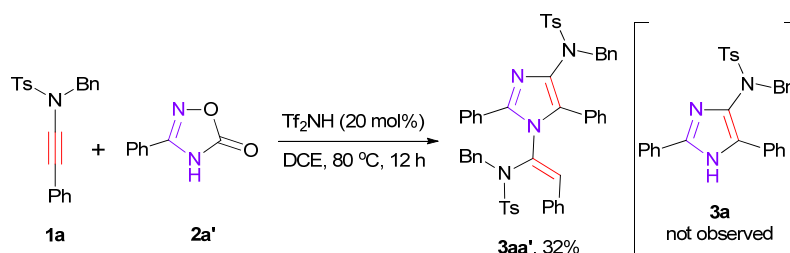
By following GP 2, the product was obtained as a white solid; 400 mg (in 2.5 mmol scale); 83% yield; mp 107–108 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.43 – 7.31 (m, 3H), 7.29 – 7.23 (m, 2H), 3.94 (s, 2H), 3.00 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 159.7, 158.1, 131.7, 129.5, 128.6, 128.3, 31.3, 28.4. **HRMS (ESI)** calcd. for $\text{C}_{10}\text{H}_{11}\text{N}_2\text{O}_2$ $[\text{M} + \text{H}]^+$ 191.0815, found 191.0810.

4-Benzyl-3-phenyl-1,2,4-oxadiazol-5(4H)-one (2j)



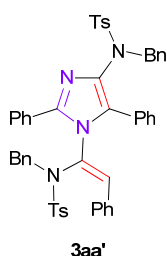
By following GP 1, the product was obtained as a white solid; 200 mg (in 1.5 mmol scale); 53% yield; mp 81–82 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.58 (t, $J = 7.3$ Hz, 1H), 7.51 – 7.41 (m, 4H), 7.33 – 7.27 (m, 3H), 7.13 – 7.06 (m, 2H), 4.83 (s, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 159.9, 159.1, 134.6, 132.2, 129.4, 129.2, 128.60, 128.57, 127.3, 123.3, 46.6. **HRMS (ESI)** calcd. for $\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_2$ $[\text{M} + \text{H}]^+$ 253.0972, found 253.0968.

5. Tf₂NH-catalyzed formal cycloaddition of *N*-H oxadiazolone **2a'** with **1a**



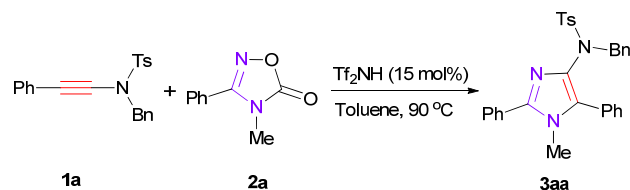
In a 10 mL flame-dried Schlenk flask, **1a** (0.20 mmol), **2a'** (0.20 mmol) and DCE (1.5 mL) were added in sequence. Then a solution of Tf₂NH (20 mol%) in DCE (0.5 mL) was added dropwise to the system. The resulting mixture was stirred at 80 °C for 12 h. The reaction was quenched by Et₃N solution (10 vol.% in pentane) and extracted with ethyl acetate. The solvent was evaporated and the crude product was purified by silica gel column chromatography to obtain **3aa'** as the main product.

(*Z*)-*N*-Benzyl-*N*-(1-(4-(*N*-benzyl-4-methylphenylsulfonamido)-2,5-diphenyl-1*H*-imidazol-1-yl)-2-phenylvinyl)-4-methylbenzenesulfonamide (**3aa'**)



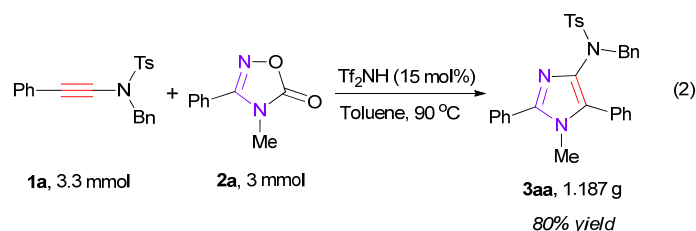
White solid; 27 mg; 32% yield; mp 241–242 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.81 – 7.71 (m, 3H), 7.52 – 7.47 (m, 2H), 7.42 – 7.34 (m, 7H), 7.33 – 7.29 (m, 4H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.97 – 6.90 (m, 4H), 6.89 – 6.80 (m, 3H), 6.78 – 6.69 (m, 3H), 6.60 (t, *J* = 7.7 Hz, 2H), 5.76 – 5.69 (m, 2H), 4.80 (d, *J* = 13.4 Hz, 1H), 4.26 (d, *J* = 13.4 Hz, 1H), 4.13 (d, *J* = 6.2 Hz, 1H), 3.76 (d, *J* = 13.6 Hz, 1H), 3.57 (d, *J* = 13.6 Hz, 1H), 2.46 (s, 3H), 2.27 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 143.8, 143.1, 137.1, 136.3, 135.5, 135.3, 132.92, 132.85, 131.7, 131.6, 130.3, 130.2, 129.94, 129.90, 129.6, 129.3, 129.21, 129.16, 129.1, 128.93, 128.86, 128.85, 128.8, 128.6, 128.5, 128.2, 128.0, 127.9, 127.5, 127.4, 127.34, 127.26, 127.2, 56.6, 54.8, 21.8, 21.6. HRMS (ESI) calcd. for C₅₁H₄₅N₄O₄S₂ [M + H]⁺ 841.2877, found 841.2875.

6. Tf₂NH-catalyzed formal cycloaddition of *N*-substituted oxadiazolones with ynamides



Representative procedure: In a 10 mL flame-dried Schlenk flask, **1a** (0.24 mmol, 1.2 equiv), **2a** (0.20 mmol) and toluene (1.5 mL) were added in sequence. Then a solution of Tf₂NH (15 mol%, 8.4 mg) in toluene (0.5 mL) was added dropwise to the system. The resulting mixture was stirred at 90 °C for 12 h. The reaction was quenched by Et₃N solution (10 vol.% in pentane) and extracted with ethyl acetate. The solvent was evaporated and the crude product was purified by silica gel column chromatography to give the desired product **3aa** (eluent: petroleum ether/ethyl acetate 10/1).

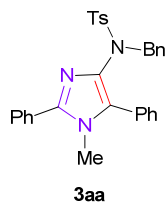
7. Gram-scale experiment



In a 50 mL flame-dried Schlenk flask, **1a** (3.3 mmol, 1.1 equiv), **2a** (3.0 mmol) and toluene (30 mL) were added in sequence. Then Tf₂NH (15 mol%, 126.5 mg) was introduced. The resulting mixture was stirred 90 °C for 12 h. The reaction was quenched by Et₃N solution (10 vol.% in pentane) and extracted with ethyl acetate. The combined organic phase was dried with anhydrous sodium sulfate. Removal of the solvent and purification by silica gel column chromatography afforded the desired aminoimidazole **3aa** in 80% yield (1.187 g).

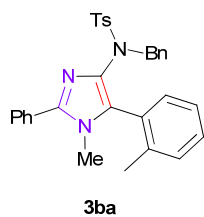
8. Characterization data of aminoimidazoles

N-Benzyl-4-methyl-*N*-(1-methyl-2,5-diphenyl-1*H*-imidazol-4-yl)benzenesulfonamide (**3aa**)



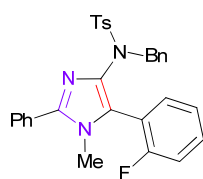
White solid; 79.8 mg; 81% yield; mp 163–164 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.96 (d, $J = 8.2$ Hz, 2H), 7.57 (d, $J = 8.3$ Hz, 2H), 7.49 – 7.30 (m, 8H), 7.23 – 7.17 (m, 2H), 7.07 (t, $J = 7.3$ Hz, 1H), 6.95 (t, $J = 7.6$ Hz, 2H), 6.88 (d, $J = 7.3$ Hz, 2H), 4.49 (s, 2H), 3.43 (s, 3H), 2.47 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 145.8, 143.6, 136.5, 135.5, 134.0, 133.4, 130.6, 130.3, 129.5, 129.03, 129.00, 128.97, 128.95, 128.7, 128.4, 128.3, 127.9, 127.2, 54.6, 34.1, 21.8. **HRMS (ESI)** calcd. for $\text{C}_{30}\text{H}_{28}\text{N}_3\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$ 494.1897, found 494.1904.

N-Benzyl-4-methyl-*N*-(1-methyl-2-phenyl-5-*o*-tolyl-1*H*-imidazol-4-yl)benzenesulfonamide (**3ba**)



White solid; 71.3 mg; 70% yield; mp 220–221 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.91 (d, $J = 8.2$ Hz, 2H), 7.58 (d, $J = 6.9$ Hz, 2H), 7.49 – 7.39 (m, 3H), 7.37 – 7.28 (m, 3H), 7.23 – 7.19 (m, 2H), 7.16 (t, $J = 7.4$ Hz, 1H), 7.10 (d, $J = 7.5$ Hz, 1H), 7.05 (t, $J = 7.6$ Hz, 2H), 6.98 (d, $J = 7.3$ Hz, 2H), 4.68 (d, $J = 13.8$ Hz, 1H), 4.37 (d, $J = 13.9$ Hz, 1H), 3.28 (s, 3H), 2.46 (s, 3H), 1.56 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 145.4, 143.5, 138.9, 136.6, 136.2, 134.0, 132.7, 132.7, 130.7, 129.7, 129.4, 129.2, 129.0, 128.9, 128.7, 128.1, 128.0, 127.4, 125.8, 54.5, 32.9, 21.8, 19.1. **HRMS (ESI)** calcd. for $\text{C}_{31}\text{H}_{30}\text{N}_3\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$ 508.2053, found 508.2055.

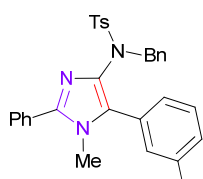
***N*-Benzyl-*N*-(5-(2-fluorophenyl)-1-methyl-2-phenyl-1*H*-imidazol-4-yl)-4-methylbenzenesulfonamide (3ca)**



3ca

White solid; 89.7 mg; 88% yield; mp 161–162 °C; $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 7.81 (d, $J = 8.0$ Hz, 2H), 7.67 (d, $J = 7.1$ Hz, 2H), 7.59 – 7.39 (m, 6H), 7.36 – 7.12 (m, 4H), 7.07 (t, $J = 7.4$ Hz, 2H), 6.93 (d, $J = 7.4$ Hz, 2H), 4.47 (s, 2H), 3.41 (s, 3H), 2.44 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, $\text{DMSO-}d_6$) δ 159.7 (d, $J = 247.5$ Hz), 145.0, 143.5, 135.6 (d, $J = 23.4$ Hz), 134.5, 132.6, 131.4 (d, $J = 8.2$ Hz), 129.8, 129.5, 128.9, 128.6, 128.3, 128.2, 127.9, 127.3, 126.7, 124.3 (d, $J = 3.1$ Hz), 116.1 (d, $J = 15.3$ Hz), 115.5 (d, $J = 21.4$ Hz), 53.8, 33.14 (d, $J = 4.2$ Hz), 21.1. $^{19}\text{F NMR}$ (376 MHz, $\text{DMSO-}d_6$) δ -111.93. **HRMS (ESI)** calcd. for $\text{C}_{30}\text{H}_{27}\text{FN}_3\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$ 512.1803, found 512.1808.

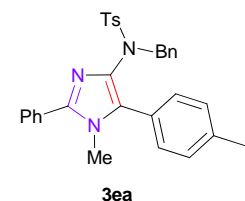
***N*-Benzyl-*N*-(5-(3-fluorophenyl)-1-methyl-2-phenyl-1*H*-imidazol-4-yl)-4-methylbenzenesulfonamide (3da)**



3da

White solid; 79 mg; 77% yield; mp 156–157 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.95 (d, $J = 8.2$ Hz, 2H), 7.56 (d, $J = 7.7$ Hz, 2H), 7.50 – 7.41 (m, 3H), 7.38 (d, $J = 8.2$ Hz, 2H), 7.35 – 7.28 (m, 1H), 7.10 (d, $J = 7.4$ Hz, 2H), 7.08 – 6.96 (m, 3H), 6.90 (d, $J = 7.2$ Hz, 2H), 6.71 (d, $J = 9.7$ Hz, 1H), 4.48 (s, 2H), 3.43 (s, 3H), 2.47 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 162.4 (d, $J = 245.8$ Hz), 146.3, 143.7, 136.5, 135.5, 134.3, 132.20, 132.18, 130.4, 129.9 (d, $J = 8.5$ Hz), 129.5, 129.2, 129.2, 129.0, 128.9, 128.8, 127.9, 127.5, 126.2 (d, $J = 2.9$ Hz), 116.9 (d, $J = 22.1$ Hz), 115.3 (d, $J = 20.9$ Hz), 54.6, 34.1, 21.8. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -113.18. **HRMS (ESI)** calcd. for $\text{C}_{30}\text{H}_{27}\text{FN}_3\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$ 512.1803, found 512.1810.

***N*-Benzyl-4-methyl-*N*-(1-methyl-2-phenyl-5-*p*-tolyl-1*H*-imidazol-4-yl)benzenesulfonamide (3ea)**

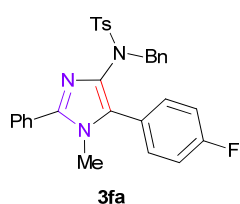


3ea

Colorless oil; 78 mg; 77% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.95 (d, $J = 8.2$ Hz, 2H), 7.55 (d, $J = 6.9$ Hz, 2H), 7.47 – 7.39 (m, 3H), 7.36 (d, $J = 8.1$ Hz, 2H), 7.14 (d, $J = 7.9$ Hz, 2H), 7.11 –

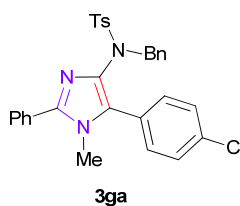
7.03 (m, 3H), 6.97 (t, $J = 7.6$ Hz, 2H), 6.91 (d, $J = 7.3$ Hz, 2H), 4.49 (s, 2H), 3.41 (s, 3H), 2.46 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 145.6, 143.5, 138.1, 136.6, 135.7, 133.8, 133.4, 130.7, 130.2, 129.4, 129.1, 129.0, 128.91, 128.87, 128.7, 127.8, 127.2, 125.5, 54.6, 33.9, 21.8, 21.5. **HRMS (ESI)** calcd. for $\text{C}_{31}\text{H}_{30}\text{N}_3\text{O}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 508.2053, found 508.2054.

***N*-Benzyl-*N*-(5-(4-fluorophenyl)-1-methyl-2-phenyl-1*H*-imidazol-4-yl)-4-methylbenzenesulfonamide (3fa)**



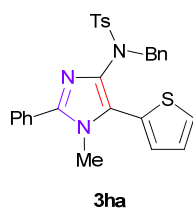
White solid; 82.0 mg; 80% yield; mp 173–174 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, $J = 8.2$ Hz, 2H), 7.56 (dd, $J = 8.0, 1.4$ Hz, 2H), 7.51 – 7.39 (m, 3H), 7.38 (d, $J = 8.1$ Hz, 2H), 7.18 – 7.05 (m, 3H), 7.06 – 6.95 (m, 4H), 6.90 (d, $J = 7.3$ Hz, 2H), 4.47 (s, 2H), 3.40 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.9 (d, $J = 248.2$ Hz), 145.9, 143.7, 136.4, 135.6, 134.1, 132.5, 132.2 (d, $J = 8.2$ Hz), 130.5, 129.5, 129.13, 129.06, 129.0, 128.9, 128.8, 127.9, 127.4, 124.4 (d, $J = 3.3$ Hz), 115.3 (d, $J = 21.6$ Hz), 54.6, 34.0, 21.8. ^{19}F NMR (376 MHz, CDCl_3) δ -113.23. **HRMS (ESI)** calcd. for $\text{C}_{30}\text{H}_{27}\text{FN}_3\text{O}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 512.1803, found 512.1809.

***N*-Benzyl-*N*-(5-(4-chlorophenyl)-1-methyl-2-phenyl-1*H*-imidazol-4-yl)-4-methylbenzenesulfonamide (3ga)**



White solid; 92 mg; 87% yield; mp 134–135 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, $J = 8.2$ Hz, 2H), 7.55 (d, $J = 9.3$ Hz, 2H), 7.49 – 7.41 (m, 3H), 7.38 (d, $J = 8.1$ Hz, 2H), 7.30 (d, $J = 8.4$ Hz, 2H), 7.15 – 7.07 (m, 3H), 6.99 (t, $J = 7.6$ Hz, 2H), 6.90 (d, $J = 7.2$ Hz, 2H), 4.47 (s, 2H), 3.41 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 146.2, 143.7, 136.4, 135.5, 134.4, 134.2, 132.3, 131.5, 130.3, 129.5, 129.2, 129.1, 129.0, 128.9, 128.8, 128.6, 127.9, 127.4, 126.8, 54.6, 34.0, 21.8. **HRMS (ESI)** calcd. for $\text{C}_{30}\text{H}_{27}\text{ClN}_3\text{O}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 528.1507, found 528.1508.

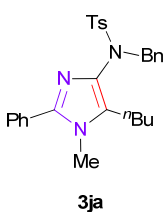
***N*-Benzyl-4-methyl-*N*-(1-methyl-2-phenyl-5-(thiophen-2-yl)-1*H*-imidazol-4-yl)benzenesulfonamide (3ha)**



White solid; 90.3 mg; 90% yield; mp 145–146 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.93 (d, $J = 8.2$ Hz, 2H), 7.57 – 7.49 (m, 2H), 7.50 – 7.34 (m, 6H), 7.21 – 7.15 (m, 1H), 7.14 – 6.96 (m, 6H), 4.54 (s, 2H), 3.53 (s, 3H), 2.46 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ

146.3, 143.7, 136.4, 135.7, 135.3, 130.3, 129.9, 129.5, 129.1, 129.0, 128.9, 128.7, 128.4, 128.0, 127.7, 127.3, 127.2, 126.9, 54.5, 34.2, 21.8. **HRMS (ESI)** calcd. for $\text{C}_{28}\text{H}_{26}\text{N}_3\text{O}_2\text{S}_2$ $[\text{M} + \text{H}]^+$ 500.1461, found 500.1466.

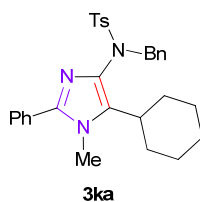
***N*-Benzyl-*N*-(5-butyl-1-methyl-2-phenyl-1*H*-imidazol-4-yl)-4-methylbenzenesulfonamide (3ja)**



Yellow oil; 40.0 mg; 42% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.81 (d, $J = 8.0$ Hz, 2H), 7.46 – 7.37 (m, 5H), 7.36 – 7.29 (m, 5H), 7.25 – 7.22 (m, 2H), 4.61 (s, 2H), 3.48 (s, 3H), 2.44 (s, 5H), 1.20 – 1.13 (m, 2H), 0.92 – 0.83 (m, 2H), 0.80 (t, $J = 7.3$ Hz, 3H). $^{13}\text{C NMR}$ (100

MHz, CDCl_3) δ 144.6, 143.4, 136.9, 136.4, 132.8, 132.7, 130.8, 129.4, 129.4, 128.9, 128.7, 128.61, 128.56, 128.2, 127.6, 54.1, 32.4, 30.8, 23.2, 23.0, 21.7, 13.9. **HRMS (ESI)** calcd. for $\text{C}_{28}\text{H}_{32}\text{N}_3\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$ 474.2210, found 474.2211.

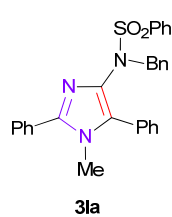
***N*-Benzyl-*N*-(5-cyclohexyl-1-methyl-2-phenyl-1*H*-imidazol-4-yl)-4-methylbenzenesulfonamide (3ka)**



Yellow oil; 48.9 mg; 49% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.87 (d, $J = 8.2$ Hz, 2H), 7.44 – 7.37 (m, 5H), 7.33 (d, $J = 8.1$ Hz, 2H), 7.29 – 7.18 (m, 5H), 3.54 (s, 3H), 2.63 (t, $J = 10.8$ Hz, 1H), 2.44 (s, 3H), 1.77 – 1.56 (m, 4H), 1.35 – 1.04 (m, 6H). $^{13}\text{C NMR}$ (100 MHz,

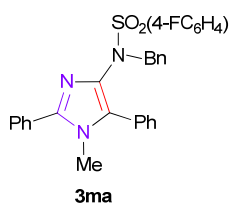
CDCl_3) δ 145.0, 143.4, 136.5, 135.8, 132.5, 130.9, 129.7, 129.4, 129.3, 128.74, 128.68, 128.6, 128.2, 127.64, 127.59, 54.5, 35.2, 33.2, 30.4, 27.0, 26.0, 21.7. **HRMS (ESI)** calcd. for $\text{C}_{30}\text{H}_{34}\text{N}_3\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$ 500.2366, found 500.2367.

N-Benzyl-*N*-(1-methyl-2,5-diphenyl-1*H*-imidazol-4-yl)benzenesulfonamide (**3la**)



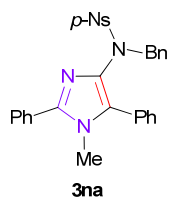
White solid; 83.3 mg; 77% yield; mp 147–148 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.09 (d, $J = 7.2$ Hz, 2H), 7.67 – 7.53 (m, 5H), 7.50 – 7.39 (m, 3H), 7.38 – 7.29 (m, 3H), 7.22 – 7.15 (m, 2H), 7.08 (t, $J = 7.3$ Hz, 1H), 6.96 (t, $J = 7.6$ Hz, 2H), 6.89 (d, $J = 7.3$ Hz, 2H), 4.51 (s, 2H), 3.44 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 145.8, 139.6, 135.5, 133.8, 133.4, 132.9, 130.6, 130.3, 129.1, 129.0, 128.9, 128.8, 128.7, 128.4, 128.34, 128.29, 127.9, 127.3, 54.7, 34.1. **HRMS (ESI)** calcd. for $\text{C}_{29}\text{H}_{26}\text{N}_3\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$ 480.1740, found 480.1743.

N-Benzyl-4-fluoro-*N*-(1-methyl-2,5-diphenyl-1*H*-imidazol-4-yl)benzenesulfonamide (**3ma**)



White solid; 81.8 mg; 82% yield; mp 181–182 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.14 – 8.03 (m, 2H), 7.56 (d, $J = 6.7$ Hz, 2H), 7.50 – 7.40 (m, 3H), 7.37 – 7.30 (m, 3H), 7.27 – 7.21 (m, 2H), 7.17 (d, $J = 7.2$ Hz, 2H), 7.09 (t, $J = 7.3$ Hz, 1H), 6.97 (t, $J = 7.6$ Hz, 2H), 6.89 (d, $J = 7.4$ Hz, 2H), 4.50 (s, 2H), 3.43 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 165.4 (d, $J = 254.2$ Hz), 145.9, 135.7 (d, $J = 3.2$ Hz), 135.3, 133.8, 133.5, 131.6 (d, $J = 9.2$ Hz), 130.5, 130.3, 129.10, 129.08, 129.0, 128.8, 128.4, 128.33, 128.29, 128.0, 127.4, 116.0 (d, $J = 22.5$ Hz), 54.8, 34.1. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -105.76. **HRMS (ESI)** calcd. for $\text{C}_{29}\text{H}_{25}\text{FN}_3\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$ 498.1646, found 498.1645.

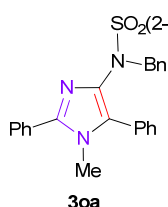
N-benzyl-*N*-(1-methyl-2,5-diphenyl-1*H*-imidazol-4-yl)-4-nitrobenzenesulfonamide (**3na**)



Yellow solid; 75.4 mg; 72% yield; mp 171–172 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.40 (d, $J = 8.8$ Hz, 2H), 8.26 (d, $J = 8.8$ Hz, 2H), 7.55 (d, $J = 7.5$ Hz, 2H), 7.51 – 7.41 (m, 3H), 7.40 – 7.30 (m, 3H), 7.11 (t, $J = 7.5$ Hz, 3H), 6.99 (t, $J = 7.6$ Hz, 2H), 6.91 (d, $J = 7.3$ Hz, 2H), 4.53 (s, 2H), 3.44 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 150.2, 146.1, 145.5, 134.7, 133.5, 133.2, 130.21, 130.18, 130.1, 129.3, 129.2, 128.88, 128.87, 128.6, 128.4, 128.1, 128.0,

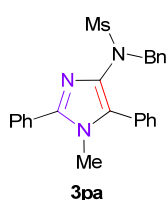
127.7, 124.0, 55.1, 34.1. **HRMS (ESI)** calcd. for $C_{29}H_{25}N_4O_4S$ $[M + H]^+$ 525.1591, found 525.1606.

***N*-Benzyl-*N*-(1-methyl-2,5-diphenyl-1*H*-imidazol-4-yl)naphthalene-2-sulfonamide (3oa)**



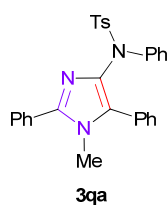
White solid; 90.8 mg; 86% yield; mp 141–142 °C; **1H NMR** (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.10 (d, $J = 10.4$ Hz, 1H), 8.06 – 7.91 (m, 3H), 7.67–7.59 (m, 2H), 7.53 (d, $J = 7.4$ Hz, 2H), 7.45 – 7.29 (m, 6H), 7.21 (d, $J = 7.8$ Hz, 2H), 7.07 (t, $J = 7.2$ Hz, 1H), 6.96 (t, $J = 7.6$ Hz, 2H), 6.90 (d, $J = 7.2$ Hz, 2H), 4.57 (s, 2H), 3.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.9, 136.5, 135.5, 135.3, 133.9, 133.5, 132.4, 130.5, 130.31, 130.27, 129.4, 129.1, 129.0, 128.9, 128.70, 128.68, 128.4, 128.3, 128.3, 128.1, 127.9, 127.30, 127.26, 124.4, 54.8, 34.1. **HRMS (ESI)** calcd. for $C_{33}H_{28}N_3O_2S$ $[M + H]^+$ 530.1897, found 530.1895.

***N*-Benzyl-*N*-(1-methyl-2,5-diphenyl-1*H*-imidazol-4-yl)methanesulfonamide (3pa)**



Yellow solid; 61.5 mg; 74% yield; mp 145–146 °C; **1H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, $J = 7.0$ Hz, 2H), 7.53 – 7.41 (m, 3H), 7.33 – 7.23 (m, 3H), 7.16 – 7.06 (m, 3H), 7.05 – 6.92 (m, 4H), 4.68 (s, 2H), 3.42 (s, 3H), 3.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.1, 135.5, 134.0, 132.8, 130.4, 130.1, 129.14, 129.08, 129.06, 128.8, 128.29, 128.25, 128.1, 127.9, 127.4, 55.18, 38.5, 33.9. **HRMS (ESI)** calcd. for $C_{24}H_{24}N_3O_2S$ $[M + H]^+$ 418.1584, found 418.1581.

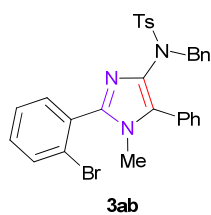
4-Methyl-*N*-(1-methyl-2,5-diphenyl-1*H*-imidazol-4-yl)-*N*-phenylbenzenesulfonamide (3qa)



White solid; 70 mg; 73% yield; mp 197–198 °C; **1H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, $J = 8.3$ Hz, 2H), 7.66 (d, $J = 8.3$ Hz, 2H), 7.61 (d, $J = 8.3$ Hz, 2H), 7.55 – 7.38 (m, 6H), 7.27 – 7.18 (m, 4H), 7.17 – 7.06 (m, 3H), 3.57 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ

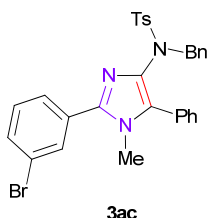
145.8, 143.4, 141.0, 136.7, 136.2, 132.0, 130.8, 130.2, 129.2, 129.13, 129.09, 129.0, 128.8, 128.73, 128.65, 128.5, 128.3, 127.2, 34.3, 21.8. **HRMS (ESI)** calcd. for $C_{29}H_{26}N_3O_2S$ $[M + H]^+$ 480.1740, found 480.1744.

***N*-Benzyl-*N*-(2-(2-bromophenyl)-1-methyl-5-phenyl-1*H*-imidazol-4-yl)-4-methylbenzenesulfonamide (3ab)**



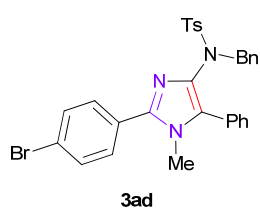
Yellow oil; 93.7 mg; 82% yield; 1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, $J = 8.1$ Hz, 2H), 7.66 (d, $J = 8.1$ Hz, 1H), 7.43 (d, $J = 3.9$ Hz, 2H), 7.35 – 7.29 (m, 6H), 7.13 (t, $J = 7.2$ Hz, 1H), 7.08 (d, $J = 6.3$ Hz, 2H), 7.03 (t, $J = 7.5$ Hz, 2H), 6.97 (d, $J = 7.3$ Hz, 2H), 4.48 (s, 2H), 3.20 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 143.6, 136.1, 135.4, 133.1, 132.9, 132.7, 132.4, 131.3, 130.4, 129.8, 129.5, 128.8, 128.3, 128.22, 128.17, 128.0, 127.7, 127.4, 124.9, 54.3, 32.7, 21.7. **HRMS (ESI)** calcd. for $C_{30}H_{27}BrN_3O_2S$ $[M + H]^+$ 572.1002, found 572.1016.

***N*-Benzyl-*N*-(2-(3-bromophenyl)-1-methyl-5-phenyl-1*H*-imidazol-4-yl)-4-methylbenzenesulfonamide (3ac)**



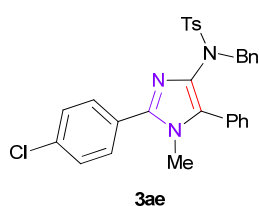
White solid; 93.3 mg; 82% yield; mp 165–166 °C; 1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, $J = 8.2$ Hz, 2H), 7.71 (s, 1H), 7.53 (d, $J = 8.1$ Hz, 1H), 7.48 (d, $J = 7.8$ Hz, 1H), 7.40 (d, $J = 8.1$ Hz, 2H), 7.37 – 7.29 (m, 4H), 7.18 (d, $J = 7.7$ Hz, 2H), 7.07 (t, $J = 7.3$ Hz, 1H), 6.95 (t, $J = 7.6$ Hz, 2H), 6.86 (d, $J = 7.3$ Hz, 2H), 4.49 (s, 2H), 3.43 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 143.8, 136.4, 135.4, 134.2, 133.9, 132.5, 132.2, 131.9, 130.3, 130.1, 129.5, 129.0, 128.9, 128.5, 128.3, 128.1, 127.9, 127.3, 127.1, 122.9, 54.8, 34.1, 21.8. **HRMS (ESI)** calcd. for $C_{30}H_{27}BrN_3O_2S$ $[M + H]^+$ 572.1002, found 572.1000.

***N*-Benzyl-*N*-(2-(4-bromophenyl)-1-methyl-5-phenyl-1*H*-imidazol-4-yl)-4-methylbenzenesulfonamide (3ad)**



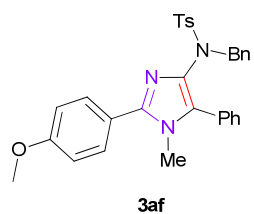
White solid; 95.2 mg; 83% yield; mp 180–181 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.93 (d, $J = 8.2$ Hz, 2H), 7.59 (d, $J = 8.4$ Hz, 2H), 7.44 (d, $J = 8.4$ Hz, 2H), 7.39 – 7.30 (m, 5H), 7.17 (d, $J = 6.1$ Hz, 2H), 7.07 (t, $J = 7.3$ Hz, 1H), 6.95 (t, $J = 7.6$ Hz, 2H), 6.87 (d, $J = 7.4$ Hz, 2H), 4.47 (s, 2H), 3.42 (s, 3H), 2.47 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 144.7, 143.7, 136.5, 135.5, 134.2, 133.8, 132.0, 130.4, 130.3, 129.5, 129.0, 128.9, 128.5, 128.3, 128.2, 127.9, 127.3, 123.3, 54.7, 34.1, 21.8. **HRMS (ESI)** calcd. for $\text{C}_{30}\text{H}_{27}\text{BrN}_3\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$ 572.1002, found 572.1007.

***N*-Benzyl-*N*-(2-(4-chlorophenyl)-1-methyl-5-phenyl-1*H*-imidazol-4-yl)-4-methylbenzenesulfonamide (3ae)**



White solid; 99.3 mg; 94% yield; mp 183–184 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.93 (d, $J = 8.2$ Hz, 2H), 7.51 (d, $J = 8.5$ Hz, 2H), 7.43 (d, $J = 8.5$ Hz, 2H), 7.39 – 7.29 (m, 5H), 7.18 (d, $J = 7.3$ Hz, 2H), 7.07 (t, $J = 7.3$ Hz, 1H), 6.95 (t, $J = 7.6$ Hz, 2H), 6.87 (d, $J = 7.3$ Hz, 2H), 4.47 (s, 2H), 3.41 (s, 3H), 2.47 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 144.7, 143.7, 136.5, 135.5, 135.1, 134.2, 133.8, 130.3, 130.2, 129.5, 129.03, 129.00, 128.9, 128.4, 128.3, 128.2, 127.9, 127.3, 54.7, 34.1, 21.8. **HRMS (ESI)** calcd. for $\text{C}_{30}\text{H}_{27}\text{ClN}_3\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$ 528.1507, found 528.1503.

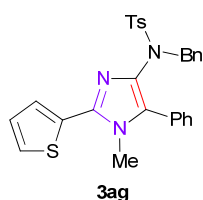
***N*-Benzyl-*N*-(2-(4-methoxyphenyl)-1-methyl-5-phenyl-1*H*-imidazol-4-yl)-4-methylbenzenesulfonamide (3af)**



Yellow oil; 77.4 mg; 74% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.95 (d, $J = 8.2$ Hz, 2H), 7.49 (d, $J = 8.7$ Hz, 2H), 7.40 – 7.29 (m, 5H), 7.22 – 7.17 (m, 2H), 7.06 (t, $J = 7.3$ Hz, 1H), 7.00 – 6.92 (m, 4H), 6.88 (d, $J = 7.3$ Hz, 2H), 4.48 (s, 2H), 3.86 (s, 3H), 3.40 (s, 3H), 2.47 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 160.2, 145.8, 143.6, 136.6, 135.6, 133.7, 133.1, 130.4, 130.3, 129.5, 129.02, 128.96, 128.6, 128.2, 128.2, 127.8,

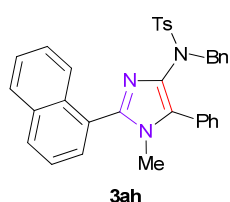
127.2, 123.1, 114.2, 55.5, 54.6, 34.0, 21.8. **HRMS (ESI)** calcd. for $C_{31}H_{30}N_3O_3S$ [$M + H$]⁺ 524.2002, found 524.2006.

***N*-Benzyl-4-methyl-*N*-(1-methyl-5-phenyl-2-(thiophen-2-yl)-1*H*-imidazol-4-yl)benzenesulfonamide (3ag)**



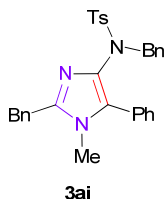
White solid; 68.2 mg; 69% yield; mp 134–135 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.41 – 7.35 (m, 3H), 7.35 – 7.29 (m, 3H), 7.28 – 7.25 (m, 1H), 7.18 – 7.02 (m, 4H), 6.94 (t, *J* = 7.6 Hz, 2H), 6.87 (d, *J* = 7.3 Hz, 2H), 4.45 (s, 2H), 3.51 (s, 3H), 2.48 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 143.6, 140.0, 136.4, 135.5, 134.2, 133.5, 133.0, 130.3, 129.4, 129.2, 129.1, 128.4, 128.3, 128.1, 127.9, 127.6, 127.3, 127.0, 126.5, 54.7, 33.8, 21.8. **HRMS (ESI)** calcd. for $C_{28}H_{26}N_3O_2S_2$ [$M + H$]⁺ 500.1461, found 500.1466.

***N*-Benzyl-4-methyl-*N*-(1-methyl-2-(naphthalen-1-yl)-5-phenyl-1*H*-imidazol-4-yl)benzenesulfonamide (3ah)**



White solid; 90.8 mg; 84% yield; mp 120–121 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.00 – 7.87 (m, 4H), 7.63 – 7.51 (m, 5H), 7.40 – 7.33 (m, 3H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.23 – 7.14 (m, 3H), 7.07 (t, *J* = 7.5 Hz, 2H), 6.99 (d, *J* = 7.4 Hz, 2H), 4.54 (s, 2H), 3.16 (s, 3H), 2.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 144.5, 143.6, 136.3, 135.6, 133.8, 133.6, 132.8, 132.7, 130.4, 130.0, 129.6, 129.5, 129.0, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 127.9, 127.4, 127.0, 126.4, 125.5, 125.2, 54.5, 33.1, 21.7. **HRMS (ESI)** calcd. for $C_{34}H_{30}N_3O_2S$ [$M + H$]⁺ 544.2053, found 544.2060.

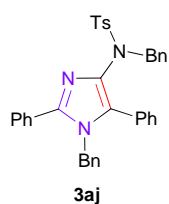
***N*-Benzyl-*N*-(2-benzyl-1-methyl-5-phenyl-1*H*-imidazol-4-yl)-4-methylbenzenesulfonamide (3ai)**



Yellow solid; 78.0 mg; 77% yield; mp 110–111 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 7.8 Hz, 2H), 7.33 – 7.23 (m, 8H), 7.11 (d, *J* = 7.5 Hz, 3H), 7.06 – 7.00 (m, 2H), 6.97 (t, *J* = 8.4 Hz, 4H), 4.51 (s,

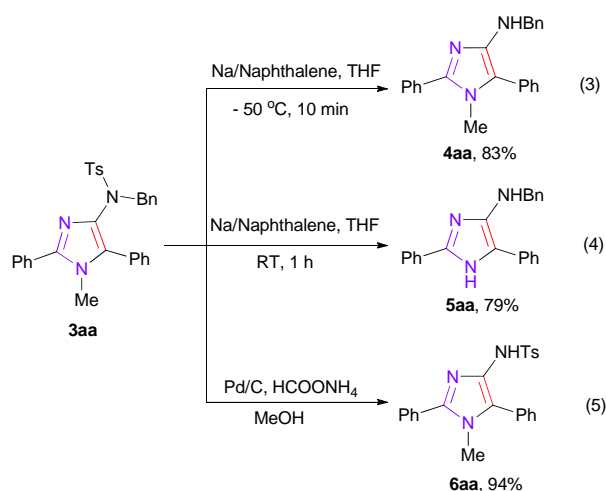
2H), 4.05 (s, 2H), 3.11 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.2, 143.4, 137.0, 136.3, 135.6, 132.3, 132.1, 130.3, 129.4, 129.3, 128.72, 128.69, 128.5, 128.3, 128.10, 128.05, 127.9, 127.3, 126.7, 54.1, 33.9, 31.5, 21.7. HRMS (ESI) calcd. for $\text{C}_{31}\text{H}_{30}\text{N}_3\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$ 508.2053, found 508.2052.

***N*-Benzyl-*N*-(1-benzyl-2,5-diphenyl-1*H*-imidazol-4-yl)-4-methylbenzenesulfonamide (3aj)**



White solid; 90.4 mg; 79% yield; mp 161–162 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 8.2$ Hz, 2H), 7.43 – 7.38 (m, 2H), 7.38 – 7.29 (m, 6H), 7.20 – 7.12 (m, 6H), 7.08 (t, $J = 7.5$ Hz, 2H), 6.98 (d, $J = 7.1$ Hz, 2H), 6.86 (d, $J = 7.1$ Hz, 2H), 6.63 – 6.56 (m, 2H), 4.98 (s, 2H), 4.54 (s, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 145.8, 143.6, 137.6, 136.4, 135.6, 134.2, 133.2, 130.7, 130.6, 129.8, 129.5, 129.0, 128.92, 128.91, 128.7, 128.6, 128.4, 128.0, 128.00, 127.95, 127.5, 127.4, 125.7, 54.4, 48.6, 21.8. HRMS (ESI) calcd. for $\text{C}_{36}\text{H}_{32}\text{N}_3\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$ 570.2210, found 570.2217.

9. Further transformations



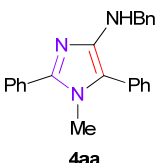
Procedure for Eq 3: A flame-dried Schlenk tube (10 mL) was charged with an excess of sodium (1.0 mmol, 5.0 equiv), naphthalene (1.0 mmol, 5.0 equiv), and THF (2 mL). The reaction mixture was stirred at room temperature for 2 h and then was cooled to -50 °C. The imidazole **3aa** (0.2 mmol) was quickly transferred to the cooled tube and the resulting mixture was stirred at this temperature for 10 min. The reaction was then slowly quenched with water and extracted with DCM. The combined organic phase was dried with anhydrous sodium sulfate. The solvent was evaporated and the crude product was purified by silica gel column chromatography to give the detosylated product **4aa** (eluent: petroleum ether/ethyl acetate 4/1).

Procedure for Eq 4: A flame-dried Schlenk tube (10 mL) was charged with an excess of sodium (1.0 mmol, 5.0 equiv), naphthalene (1.0 mmol, 5.0 equiv), and THF (2 mL). The reaction mixture was stirred at room temperature for 2 h. The imidazole **3aa** (0.2 mmol) was then quickly added and the resulting mixture was stirred at room temperature for 1 h. The reaction was then slowly quenched with water and extracted with DCM. The combined organic phase was dried with anhydrous sodium sulfate. The solvent was evaporated and the crude product was purified by silica gel column chromatography to give the unprotected imidazole **5aa** (eluent: petroleum ether/ethyl acetate 4/1).

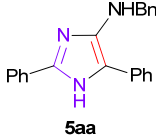
Procedure for Eq 5: In a 35 mL sealed tube, **3aa** (0.1 mmol, 49.3 mg), HCOONH₄ (1.0 mmol, 10 equiv), 5% Pd/C (98.6 mg), and MeOH (10 mL) were added in

sequence. The resulting mixture was stirred at 90 °C until the substrate was completely consumed (detected by TLC). The reaction mixture was filtered through a short pad of celite, and solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography to give the debenzylated product **6aa** (eluent: petroleum ether/ethyl acetate 1/1).

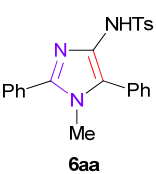
***N*-Benzyl-1-methyl-2,5-diphenyl-1*H*-imidazol-4-amine (4aa)**

 Yellow oil; 56.6 mg; 83% yield; ¹H NMR (400 MHz, *d*⁶-DMSO) δ 7.67 (d, *J* = 7.6 Hz, 2H), 7.50 – 7.43 (m, 6H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.30 – 7.22 (m, 3H), 7.16 (t, *J* = 7.3 Hz, 1H), 5.22 (t, *J* = 6.5 Hz, 1H), 4.38 (d, *J* = 6.5 Hz, 2H), 3.54 (s, 3H). ¹³C NMR (100 MHz, *d*⁶-DMSO) δ 145.3, 143.5, 142.0, 130.8, 130.5, 128.7, 128.4, 128.3, 127.9, 127.9, 127.5, 126.2, 126.0, 113.7, 47.3, 34.0. HRMS (ESI) calcd. for C₂₃H₂₂N₃ [M + H]⁺ 340.1808, found 340.1803.

***N*-Benzyl-2,5-diphenyl-1*H*-imidazol-4-amine (5aa)**

 White solid; 51.3 mg; 79% yield; mp 107–108 °C; ¹H NMR (400 MHz, *d*⁶-DMSO) δ 11.96 (s, 1H), 7.99 (d, *J* = 7.0 Hz, 2H), 7.68 (d, *J* = 7.2 Hz, 2H), 7.45 – 7.36 (m, 6H), 7.29 (t, *J* = 7.4 Hz, 3H), 7.21 – 7.08 (m, 2H), 5.51 (d, *J* = 5.9 Hz, 1H), 4.52 (s, 2H). ¹³C NMR (100 MHz, *d*⁶-DMSO) δ 146.0, 142.1, 141.4, 131.5, 130.6, 128.6, 128.5, 128.0, 127.6, 127.5, 126.2, 124.8, 124.2, 124.1, 110.8, 47.4. HRMS (ESI) calcd. for C₂₂H₂₀N₃ [M + H]⁺ 326.1652, found 326.1652.

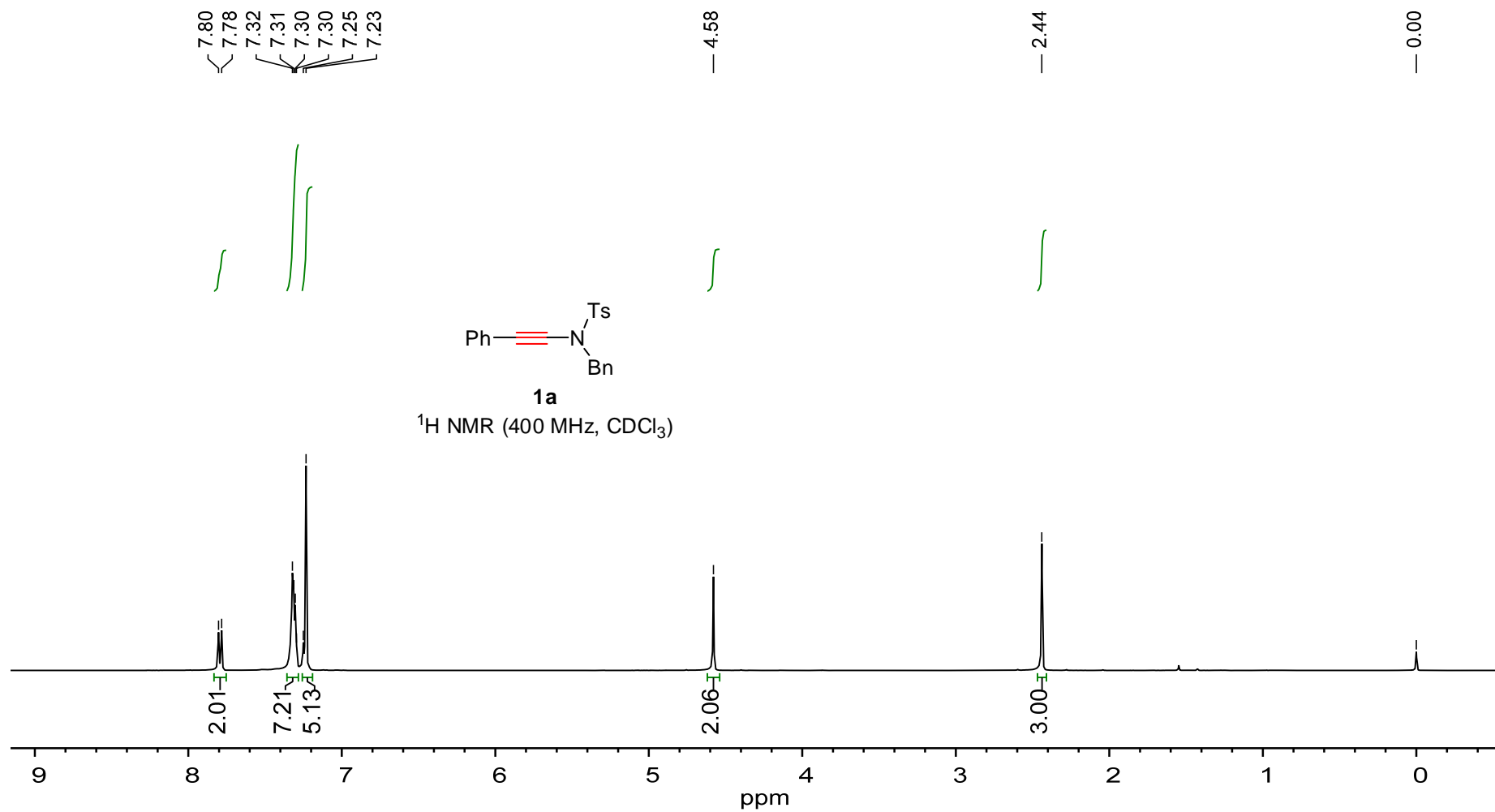
4-Methyl-*N*-(1-methyl-2,5-diphenyl-1*H*-imidazol-4-yl)benzenesulfonamide (6aa)

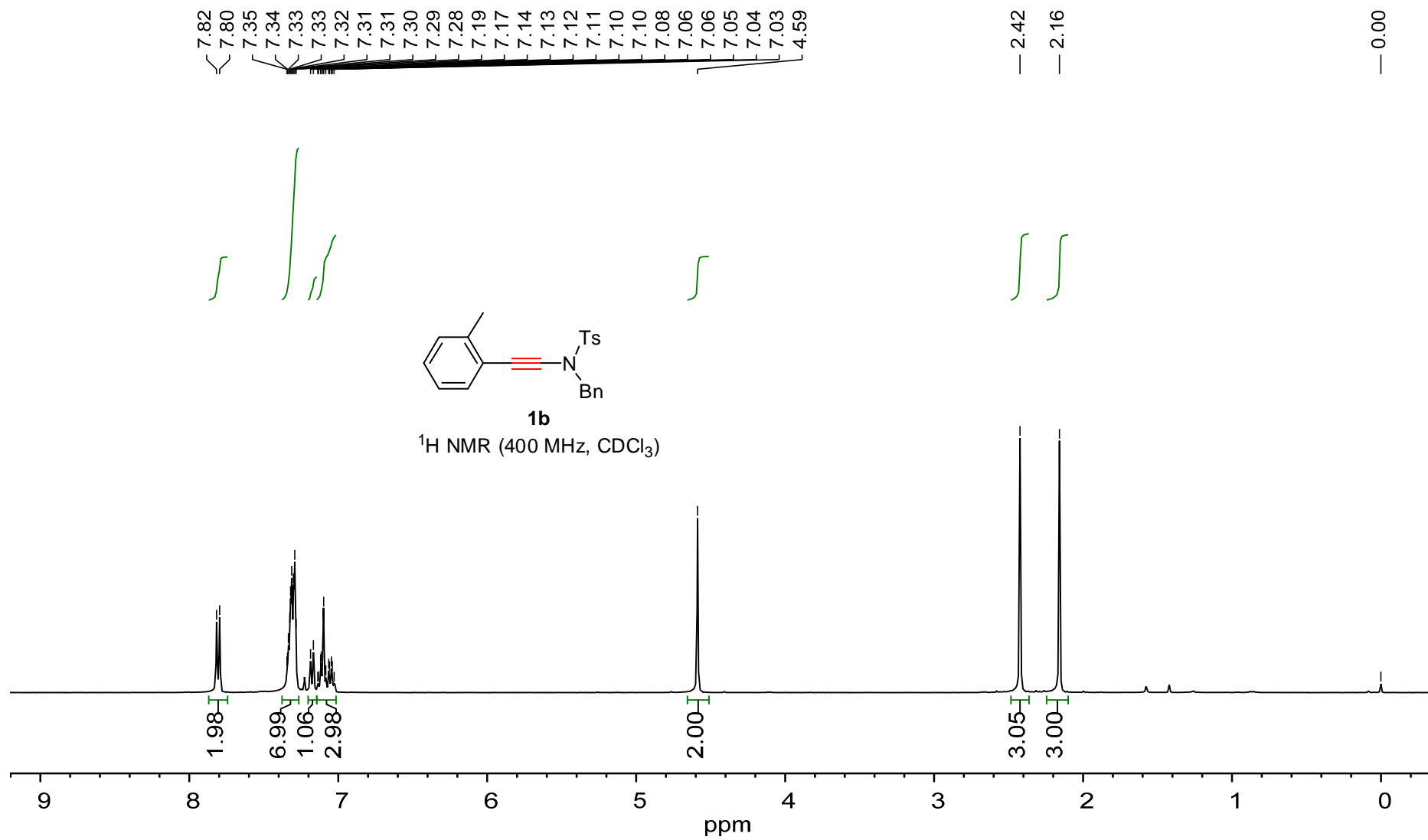
 White solid; 37.7 mg; 94% yield; mp 154–155 °C; ¹H NMR (400 MHz, *d*⁶-DMSO) δ 9.53 (s, 1H), 7.69 – 7.58 (m, 4H), 7.56 – 7.36 (m, 8H), 7.27 (d, *J* = 7.9 Hz, 2H), 3.54 (s, 3H), 2.36 (s, 3H). ¹³C NMR (100 MHz, *d*⁶-DMSO) δ 144.5, 142.2, 139.1, 131.1, 130.2, 130.0, 129.7, 129.0, 128.7, 128.6, 128.5, 128.4, 127.9, 127.0, 34.0, 21.0. HRMS (ESI) calcd. for C₂₃H₂₂N₃O₂S [M + H]⁺ 404.1427, found 404.1426.

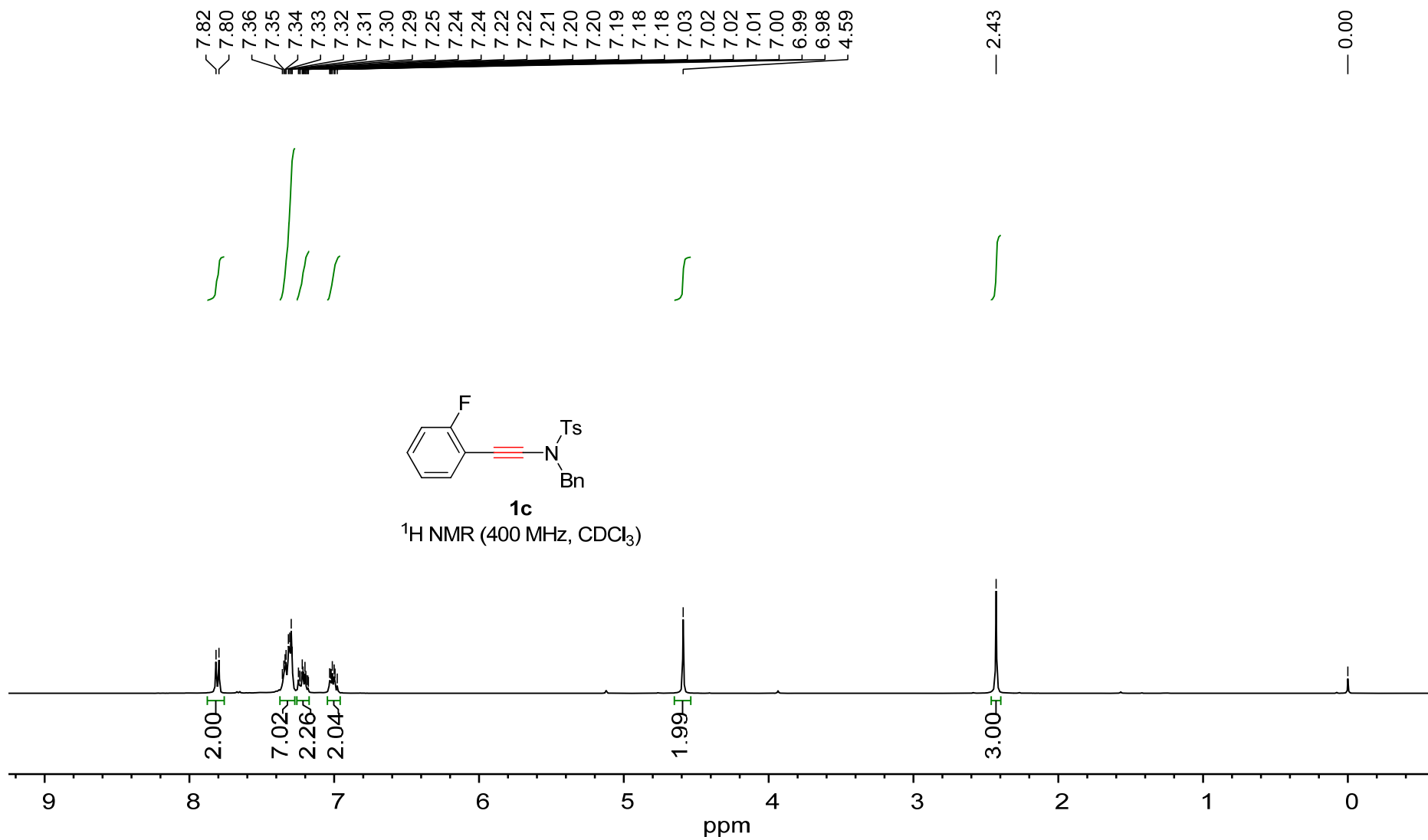
10. References

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11. NMR spectroscopy of ynamides







— 163.66
— 161.17

— 144.83
— 134.67
— 134.37
— 132.99
— 132.97
— 129.84
— 129.38
— 129.31
— 129.05
— 128.63
— 128.47
— 127.90
— 123.93
— 123.89
— 115.53
— 115.32
— 111.63
— 111.47

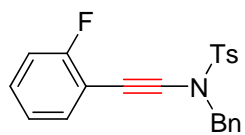
— 87.54

— 77.48
— 77.16
— 76.84

— 65.25

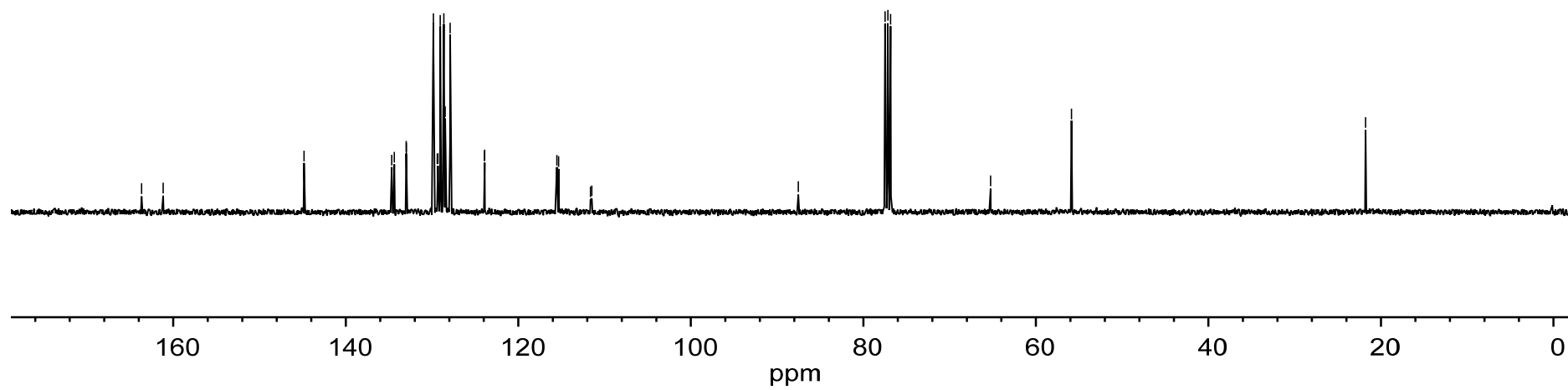
— 55.86

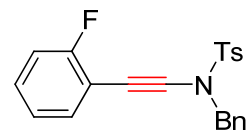
— 21.79



1c

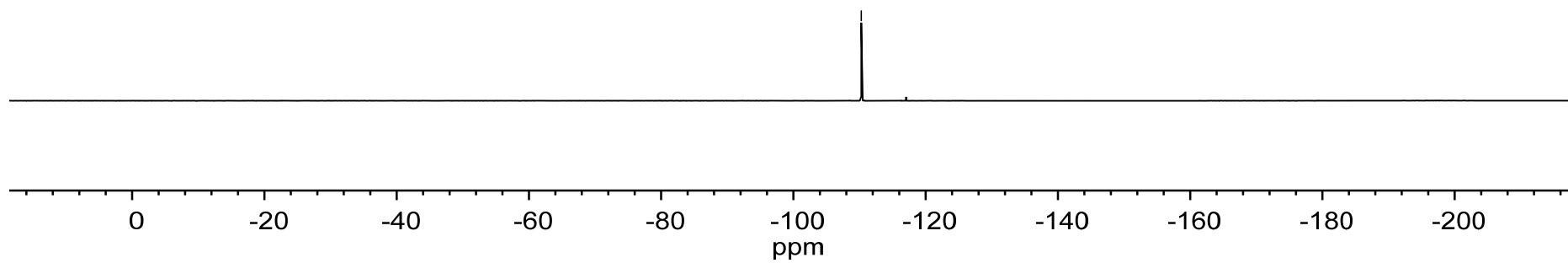
^{13}C NMR (100 MHz, CDCl_3)

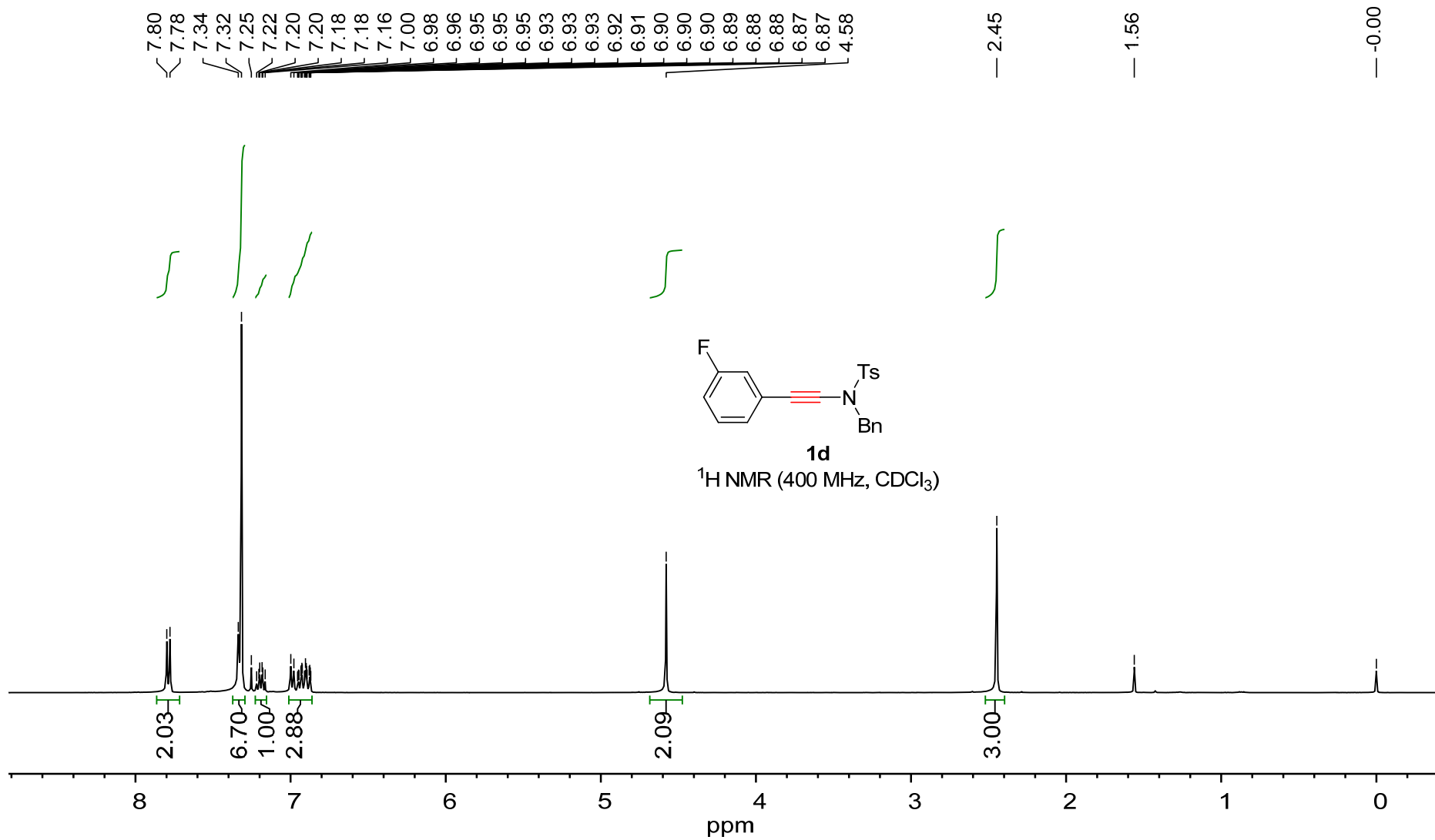




1c
¹⁹F NMR (376 MHz, CDCl₃)

— -110.27





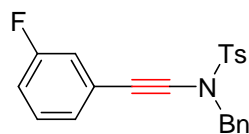
163.61
161.16

144.95
134.67
134.34
129.93
129.92
129.82
129.01
128.69
128.56
127.84
126.89
126.86
124.85
124.75
117.89
117.66
115.07
114.86

83.72
77.48
77.16
76.84
70.73
70.69

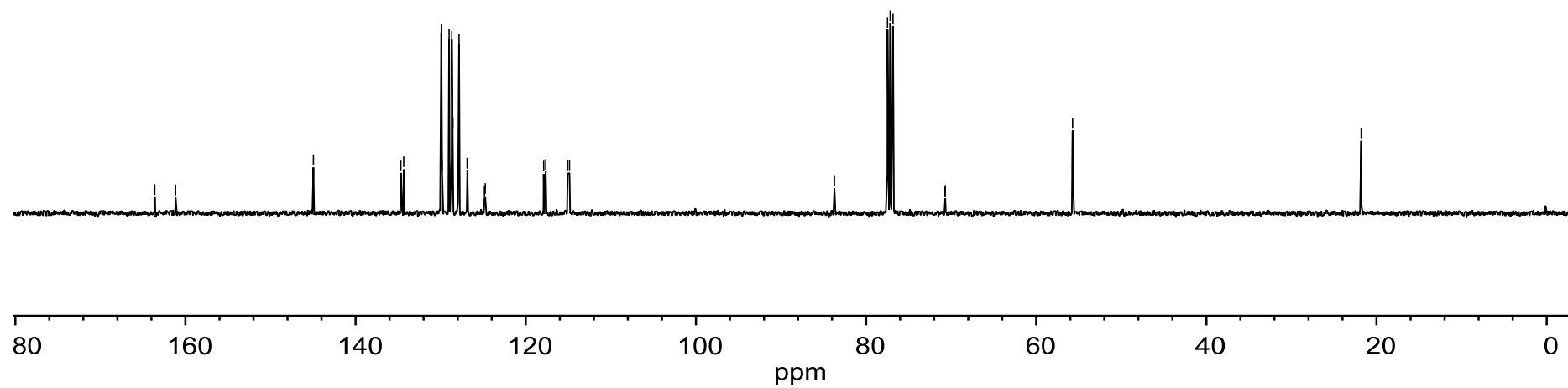
55.73

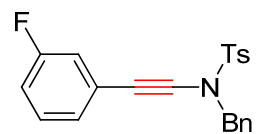
21.81



1d

¹³C NMR (100 MHz, CDCl₃)

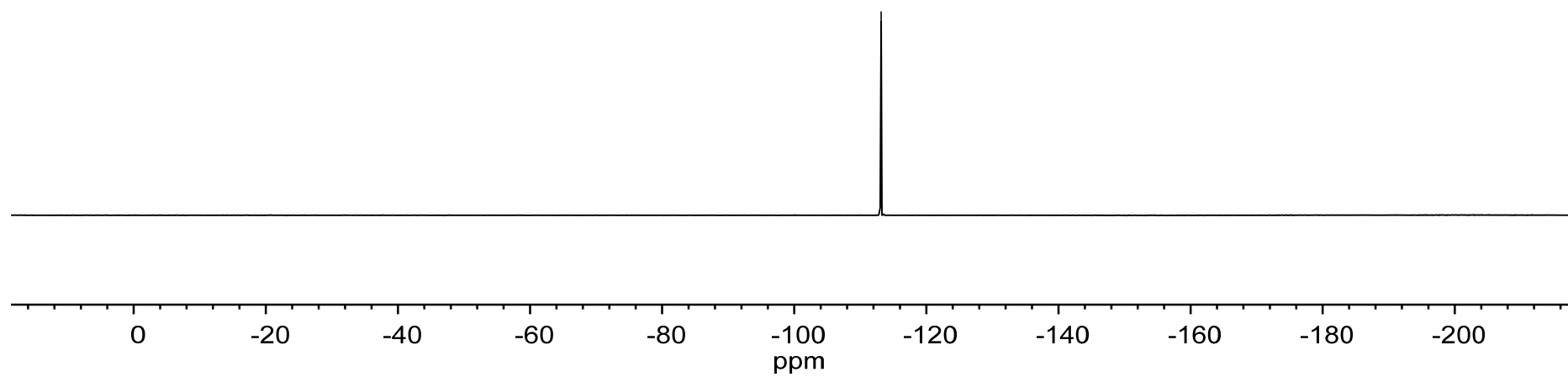


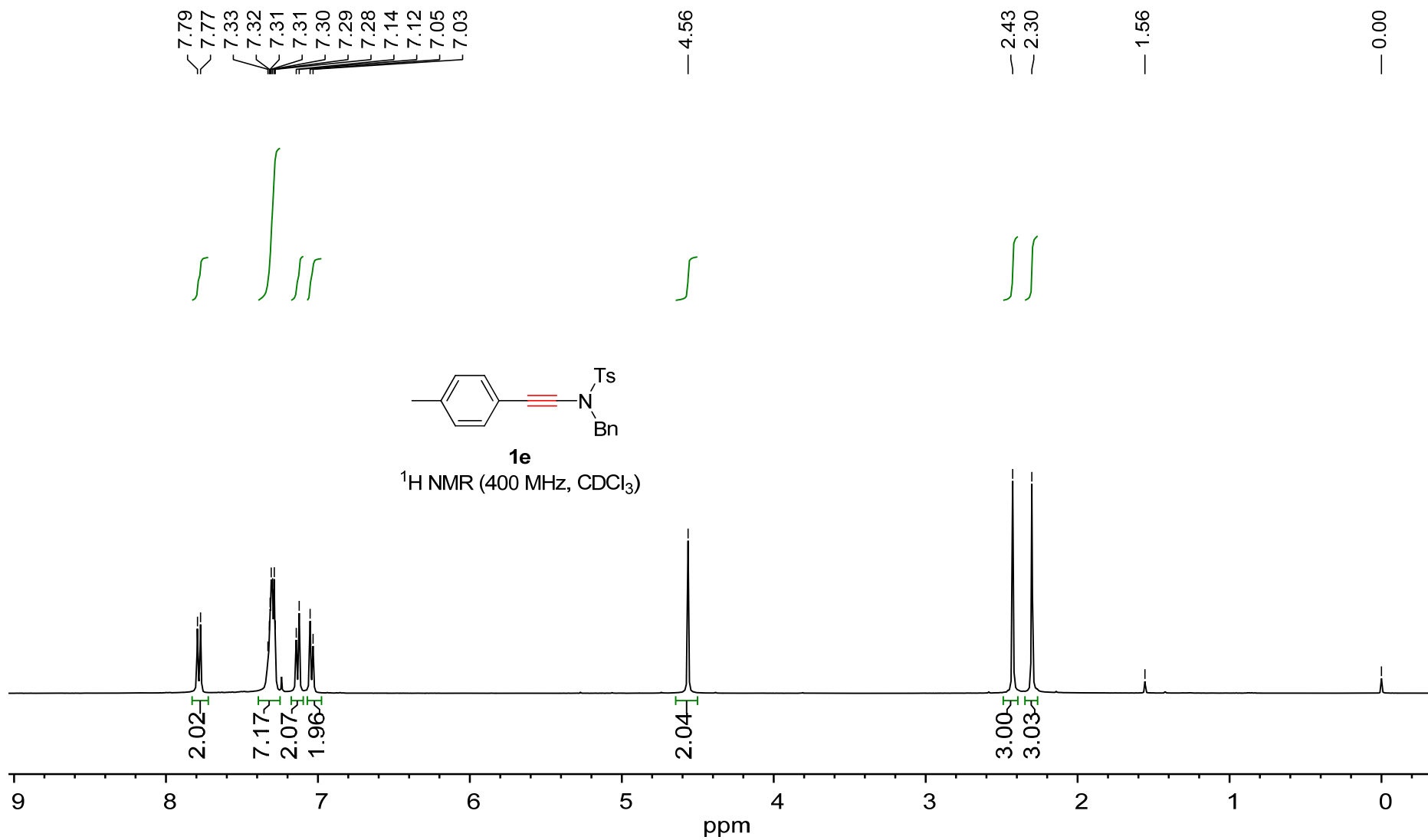


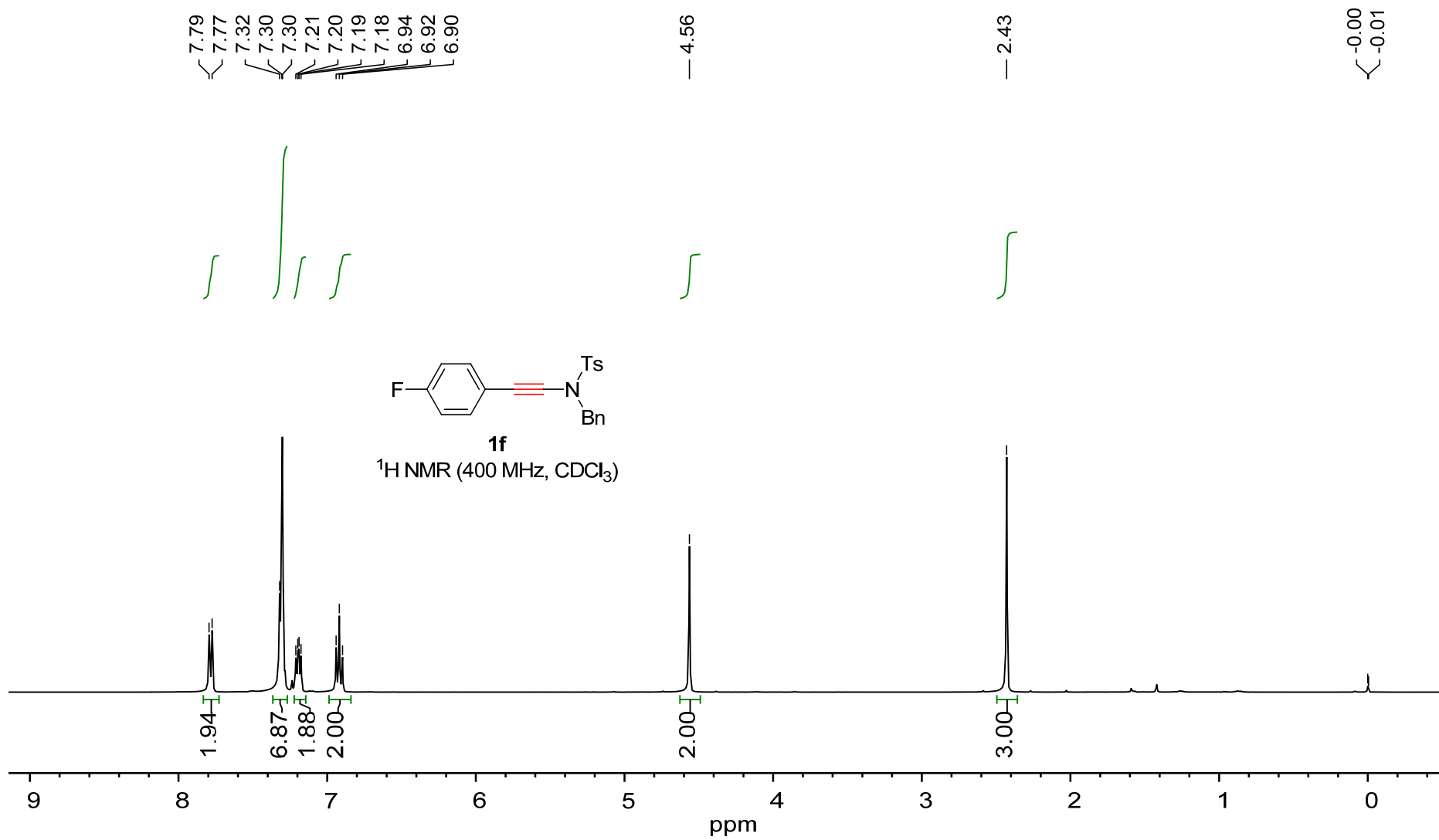
1d

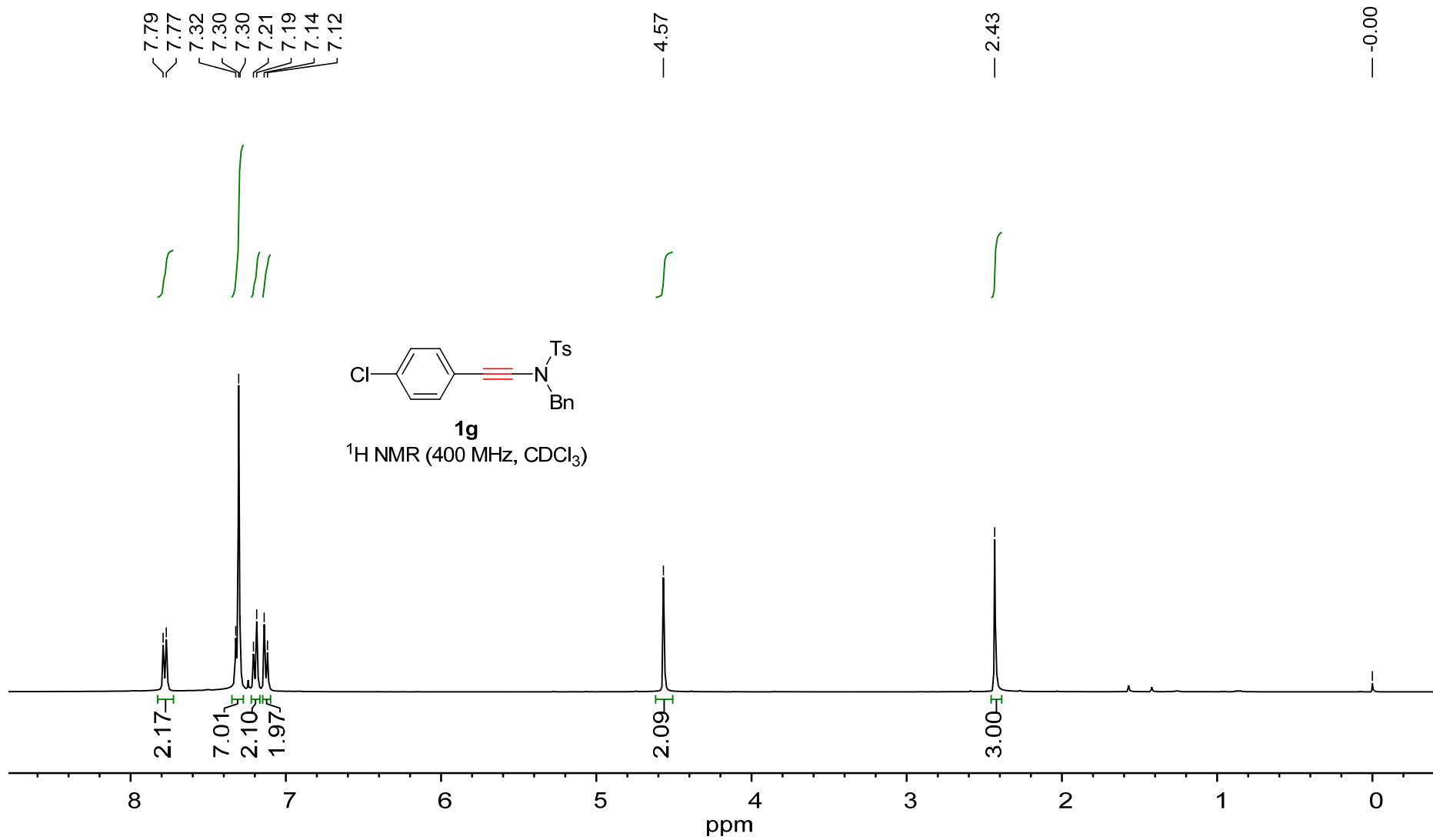
^{19}F NMR (376 MHz, CDCl_3)

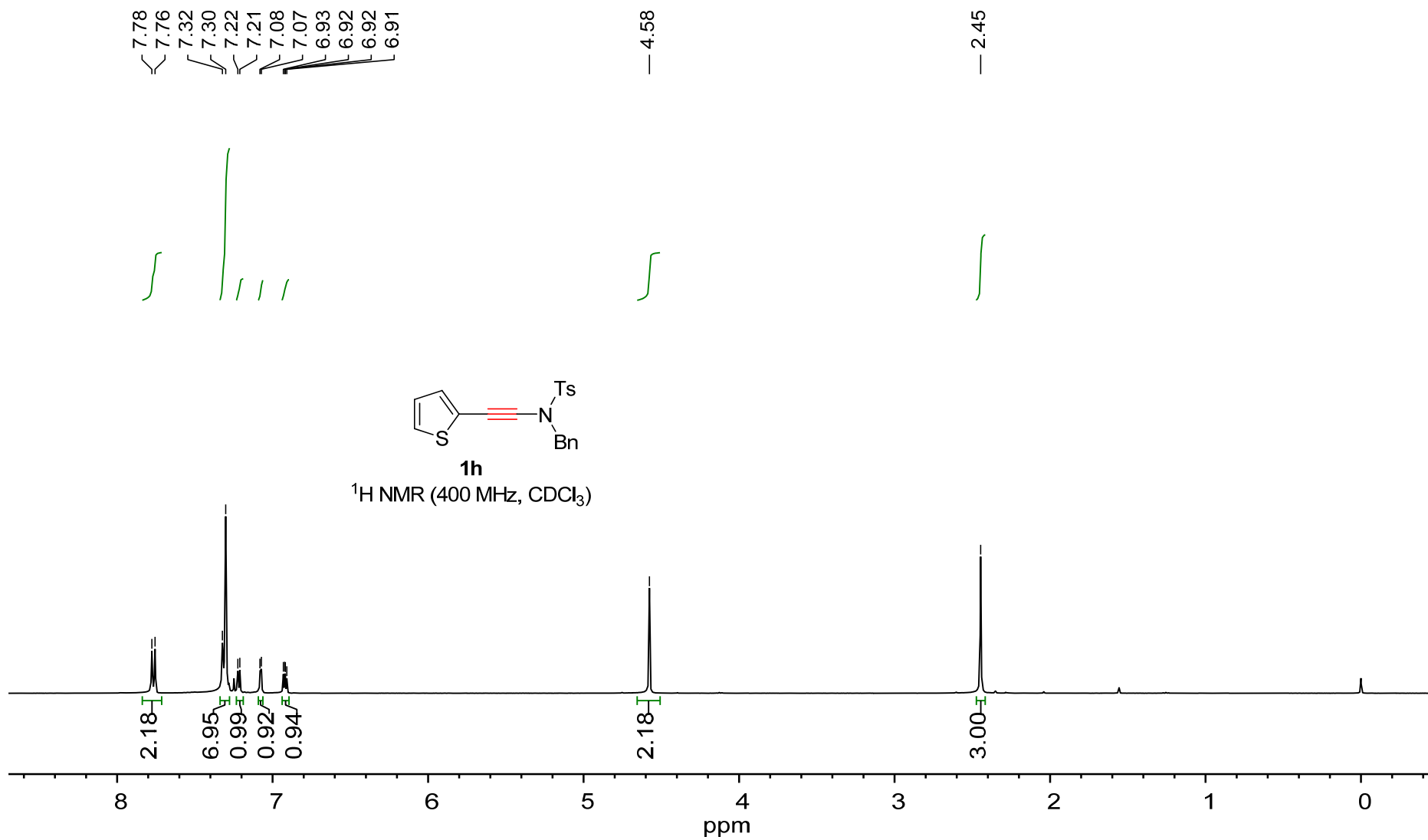
— -113.16

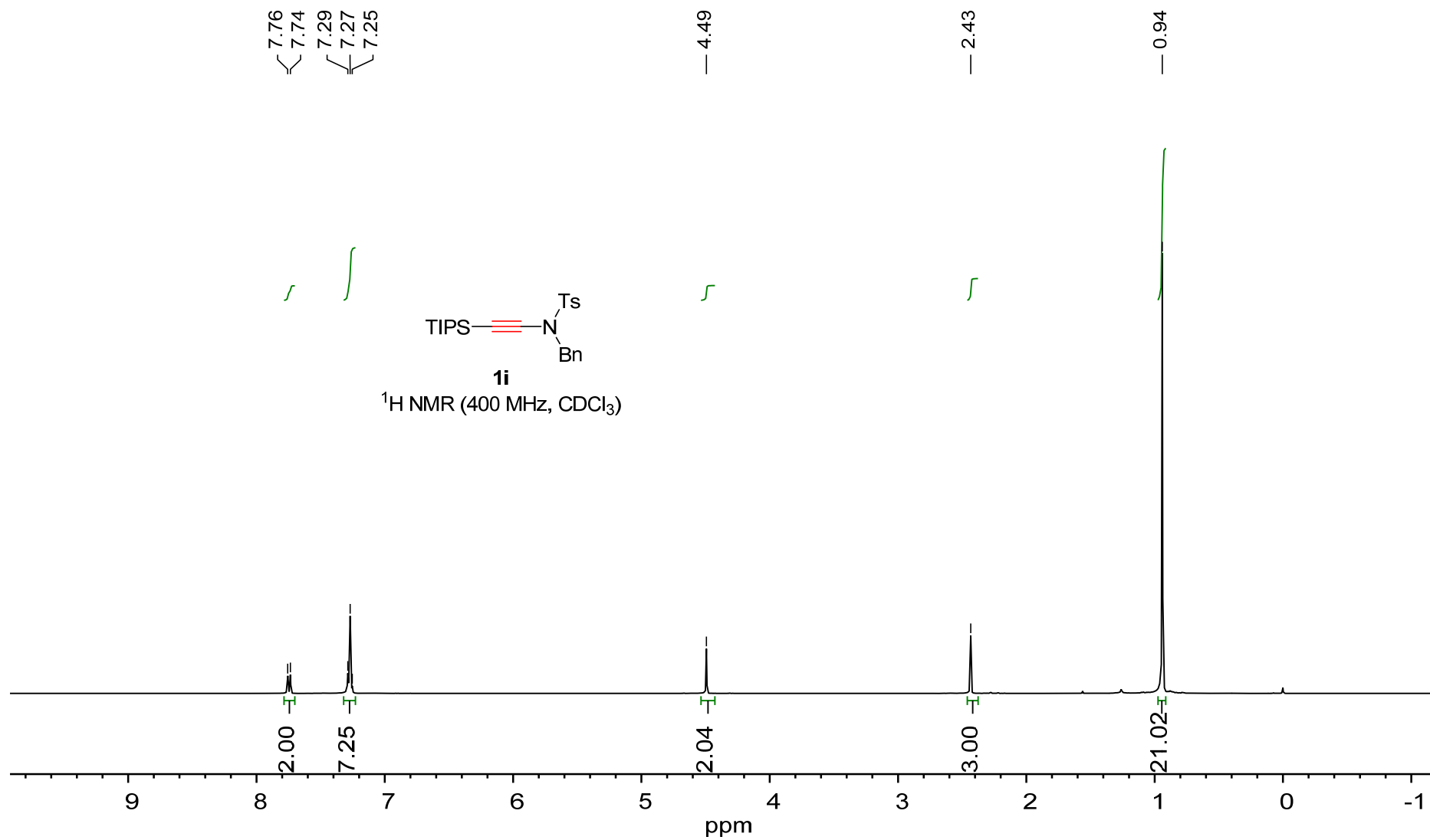


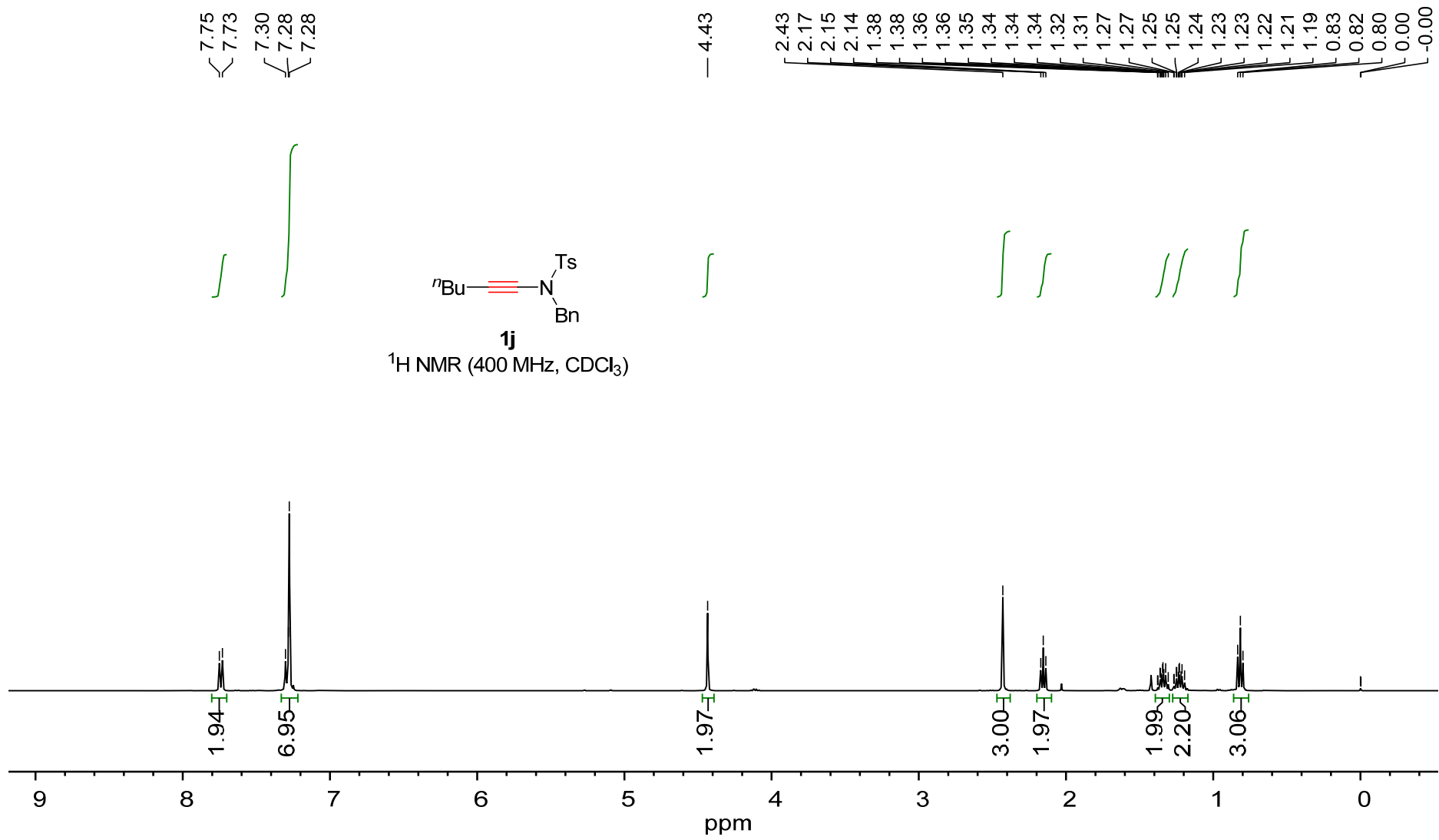


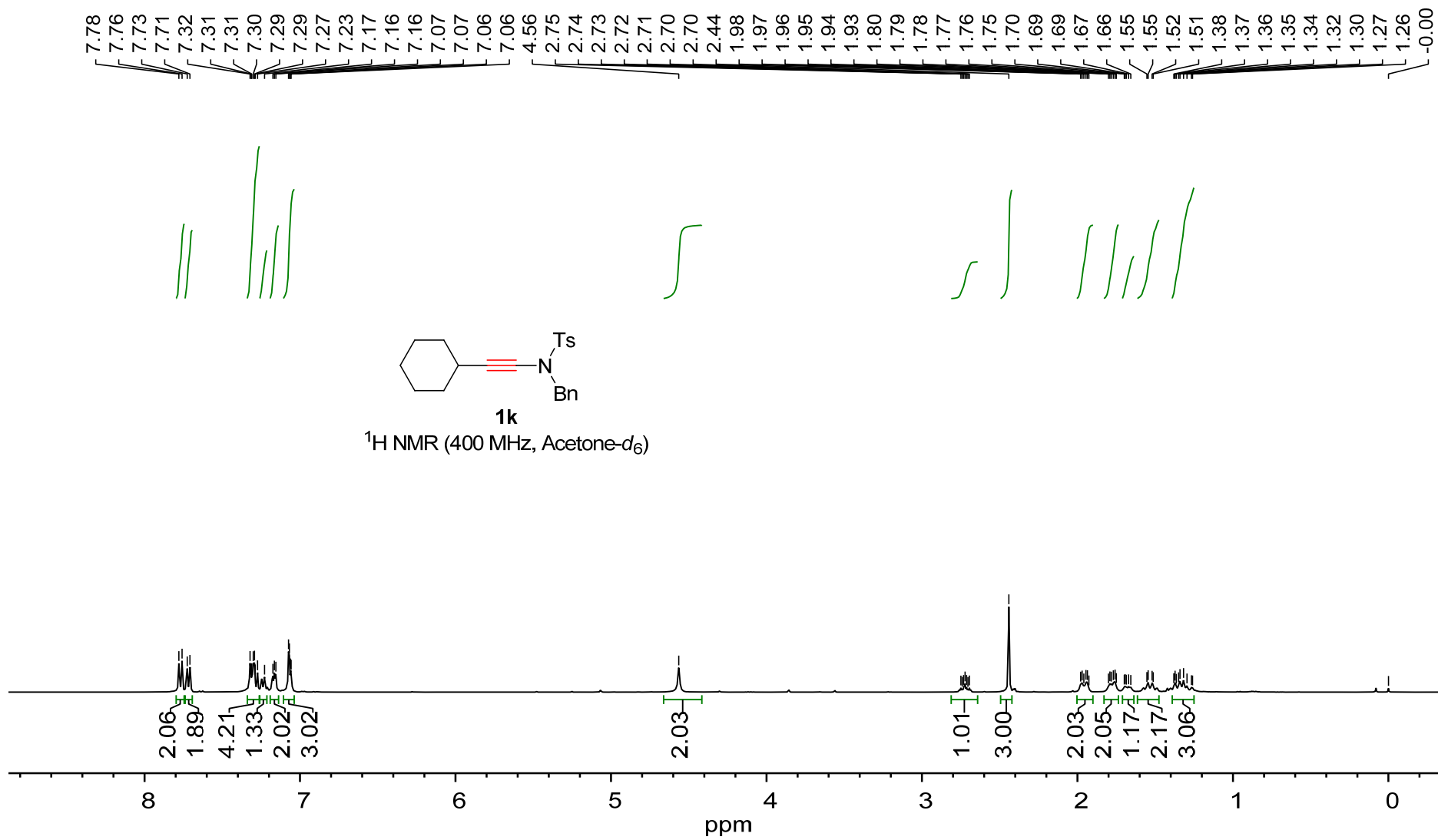


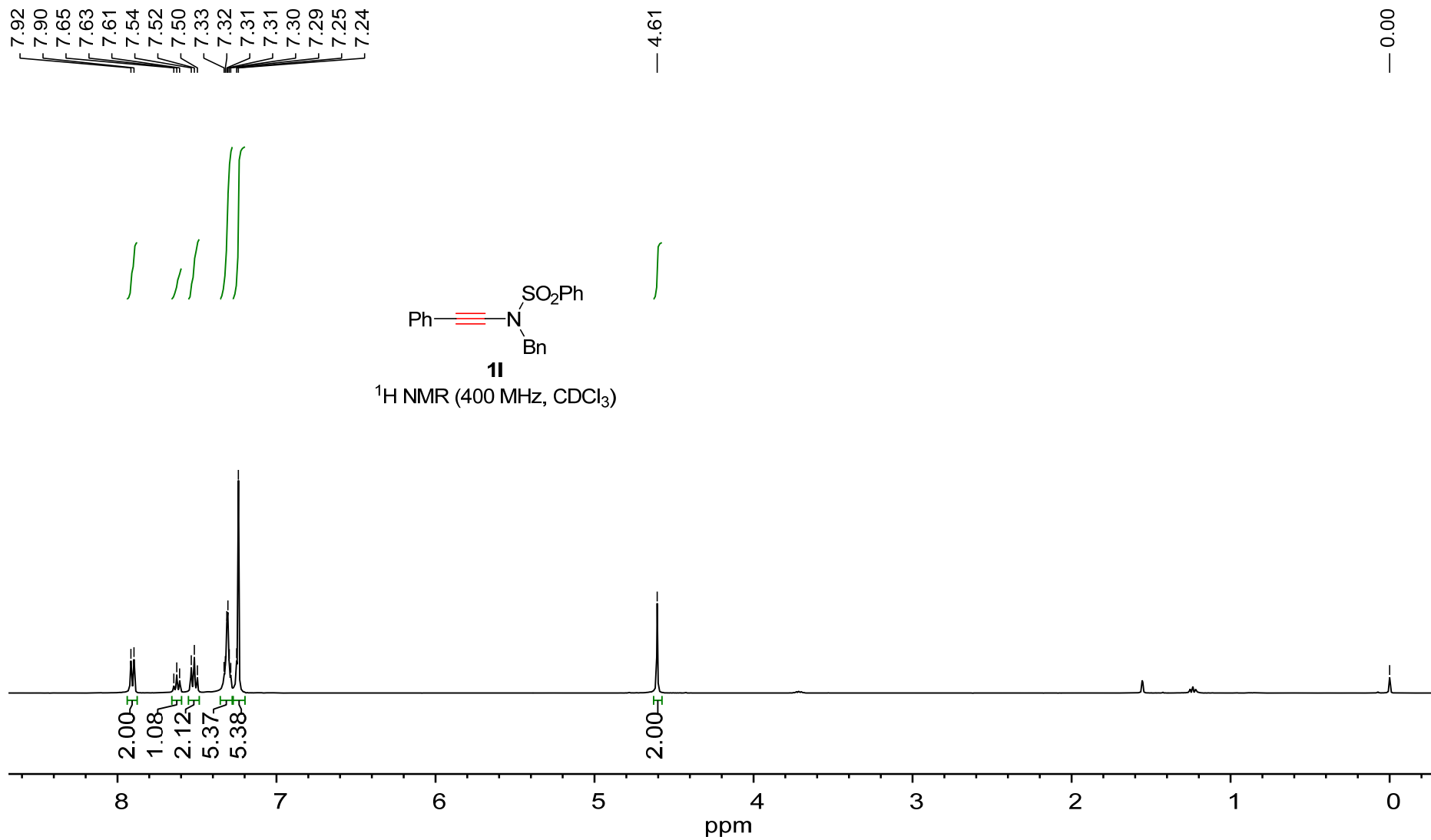


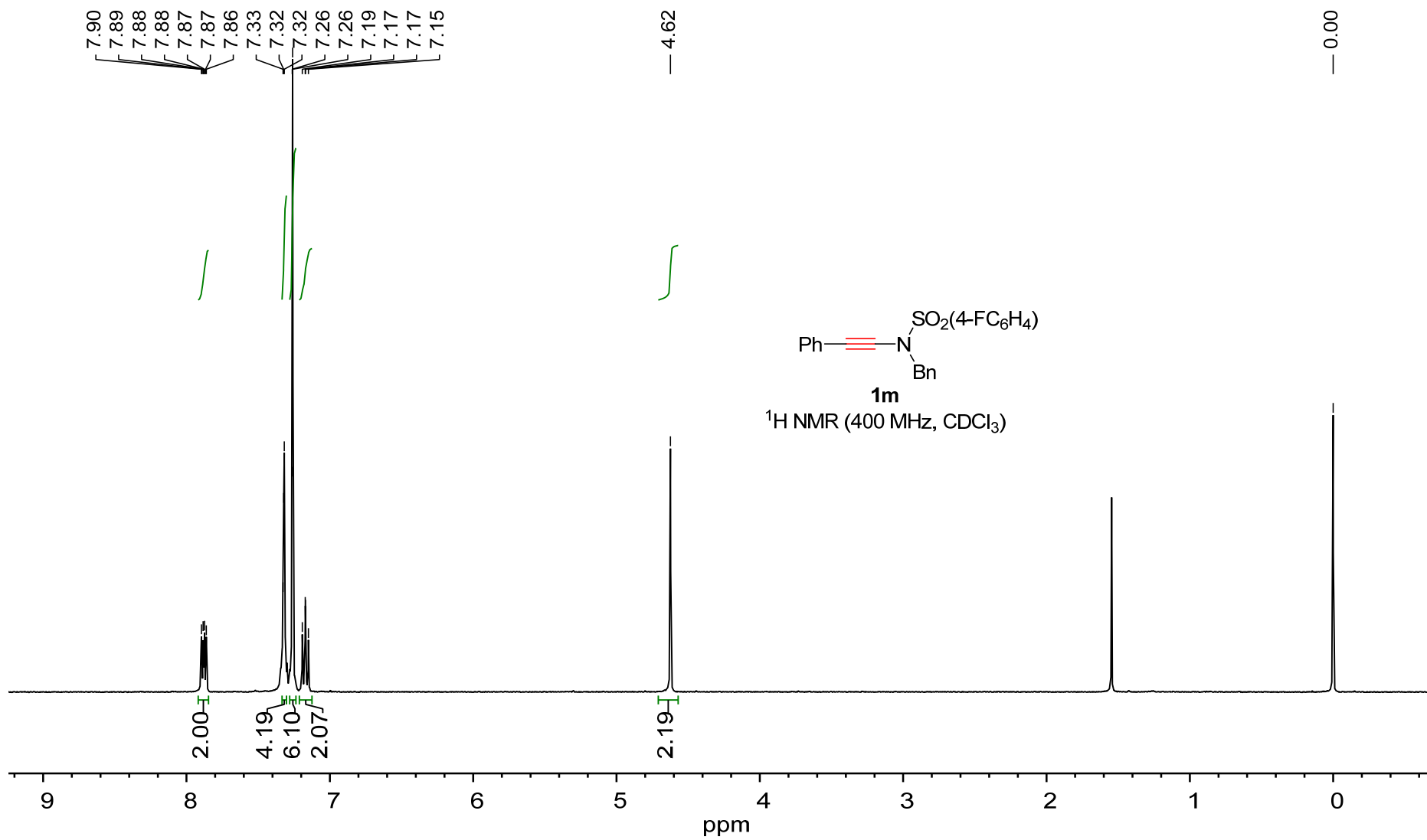


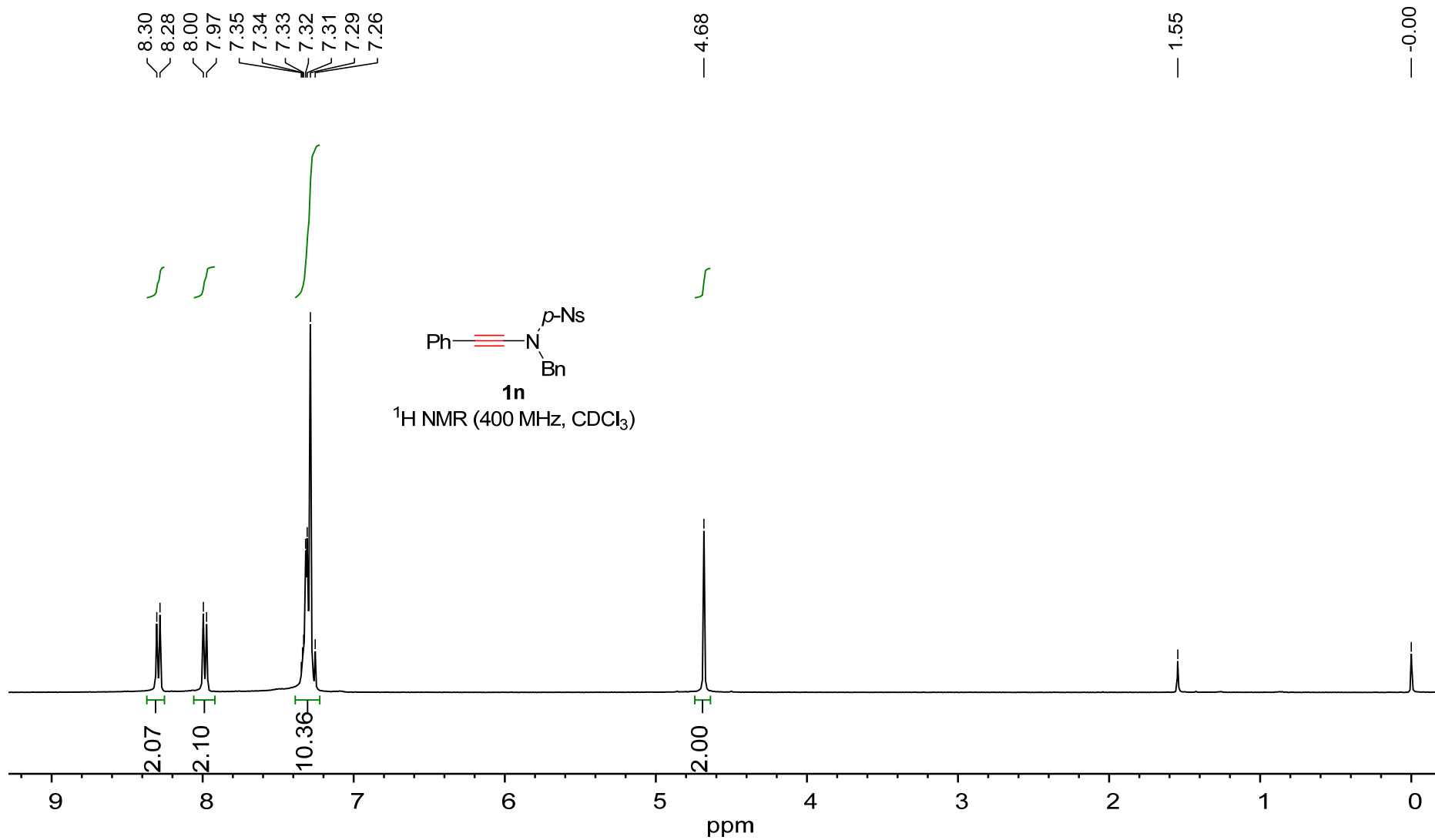


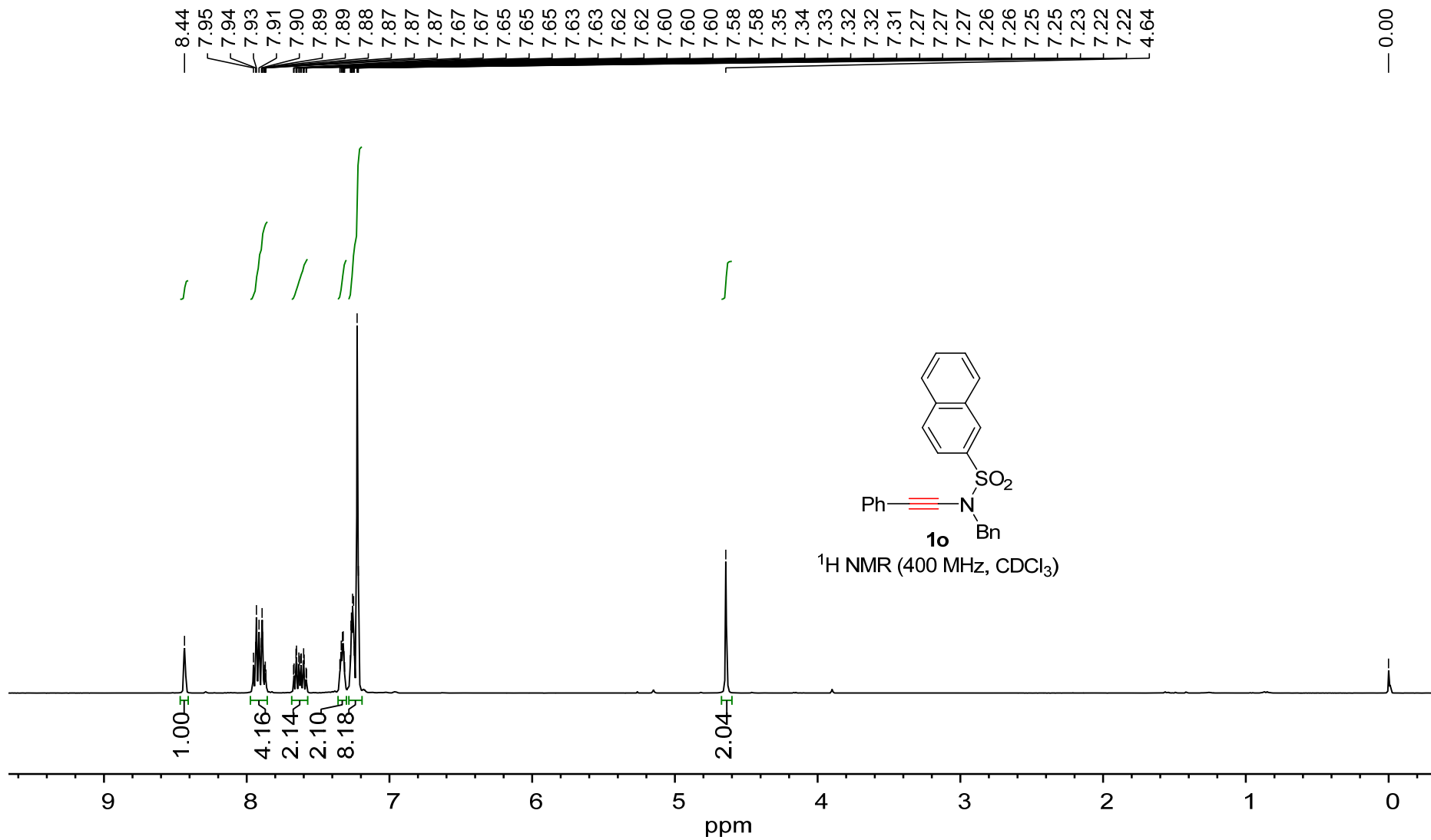


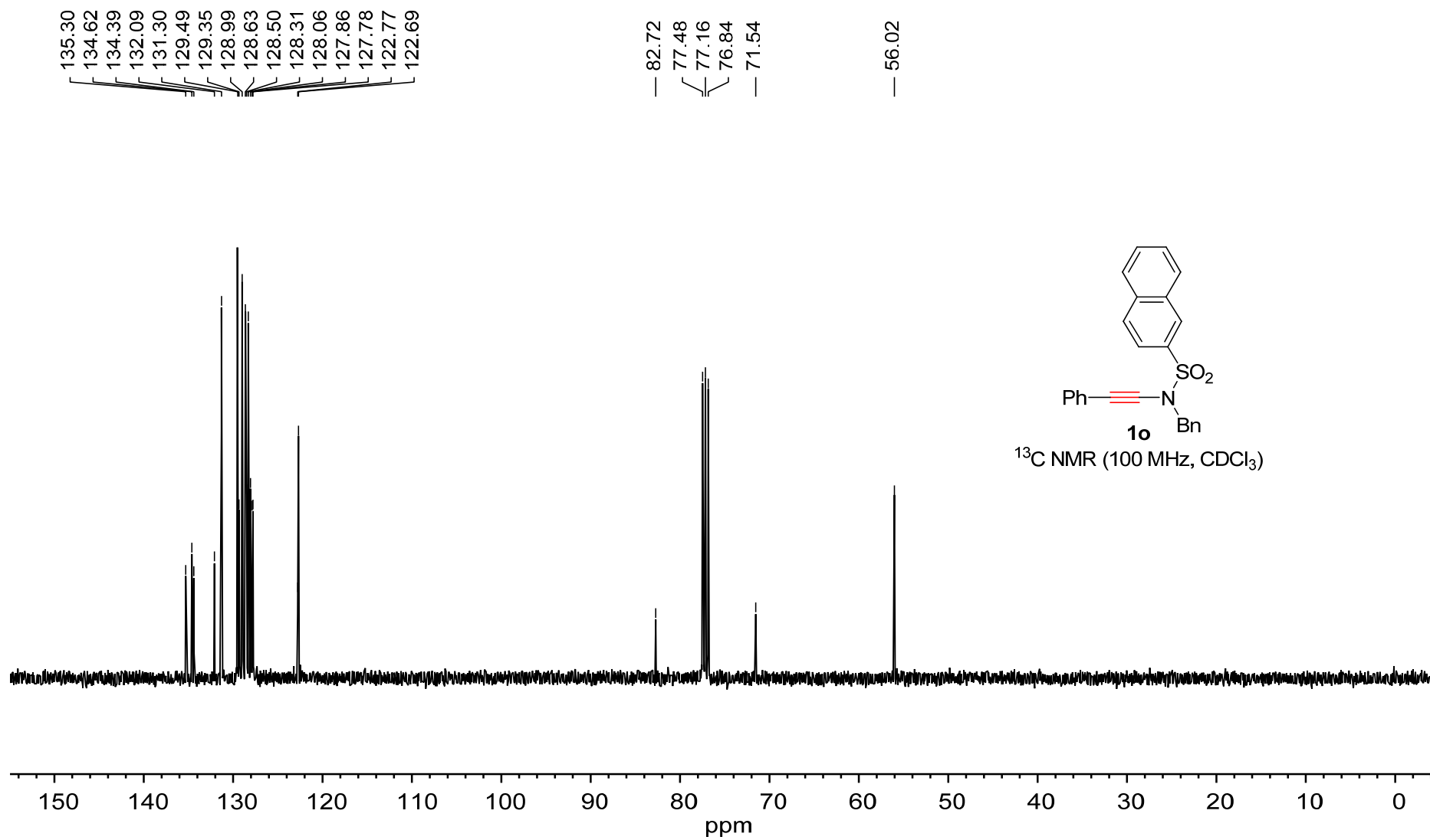


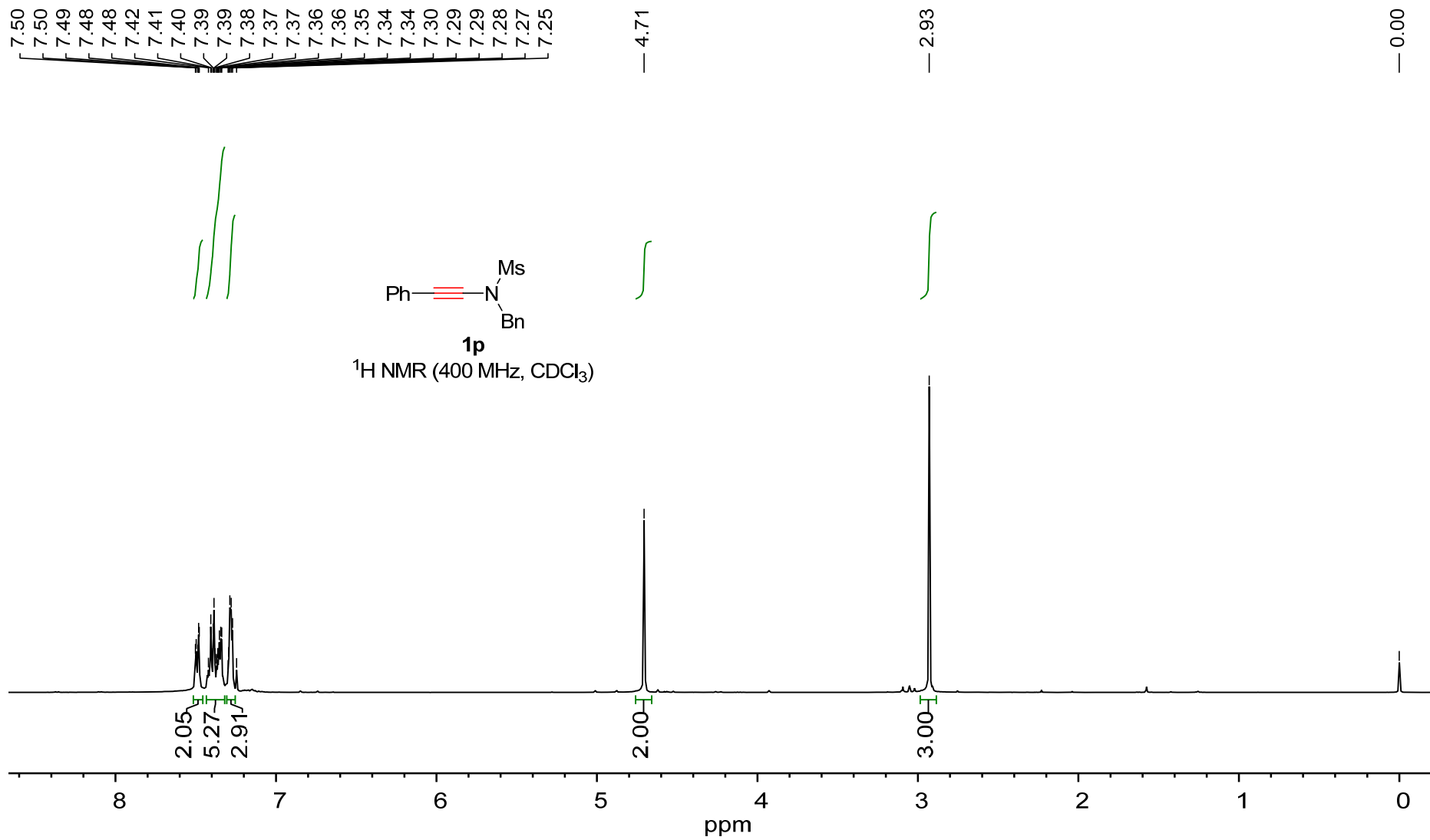




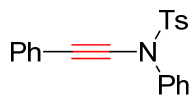




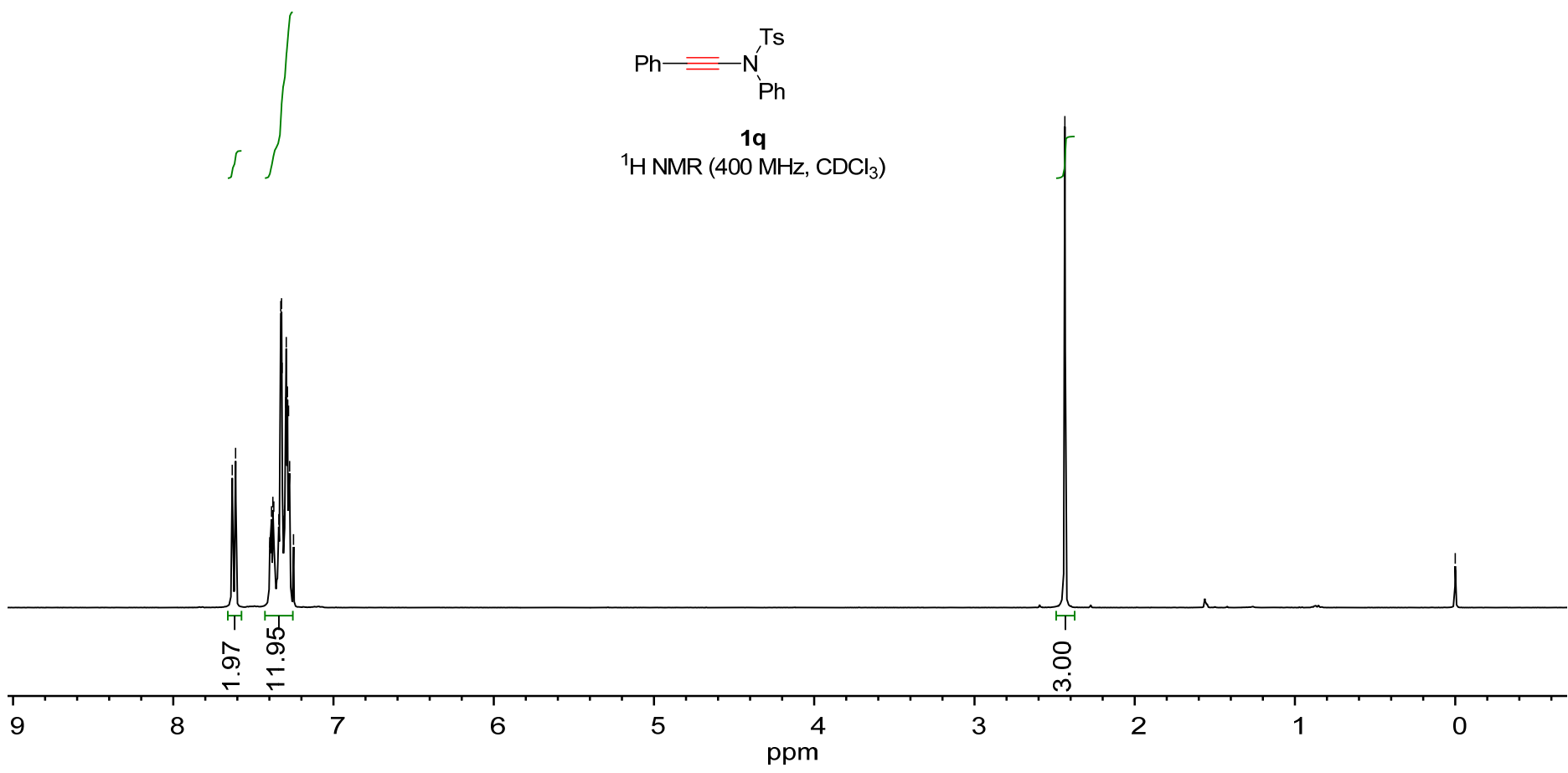




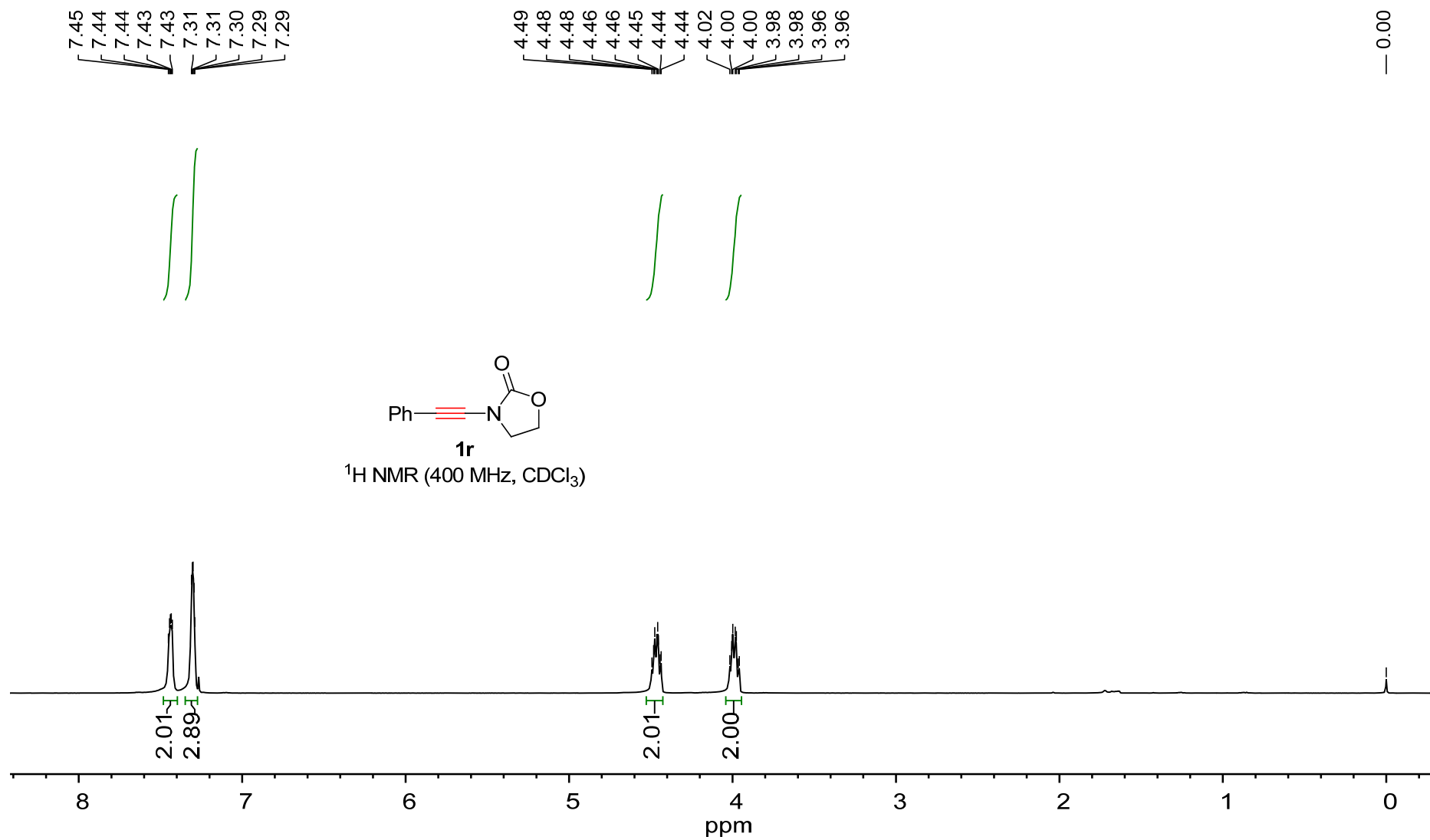
7.63
7.61
7.40
7.39
7.39
7.38
7.37
7.34
7.33
7.32
7.32
7.32
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7.30
7.30
7.29
7.29
7.28
7.27
7.25



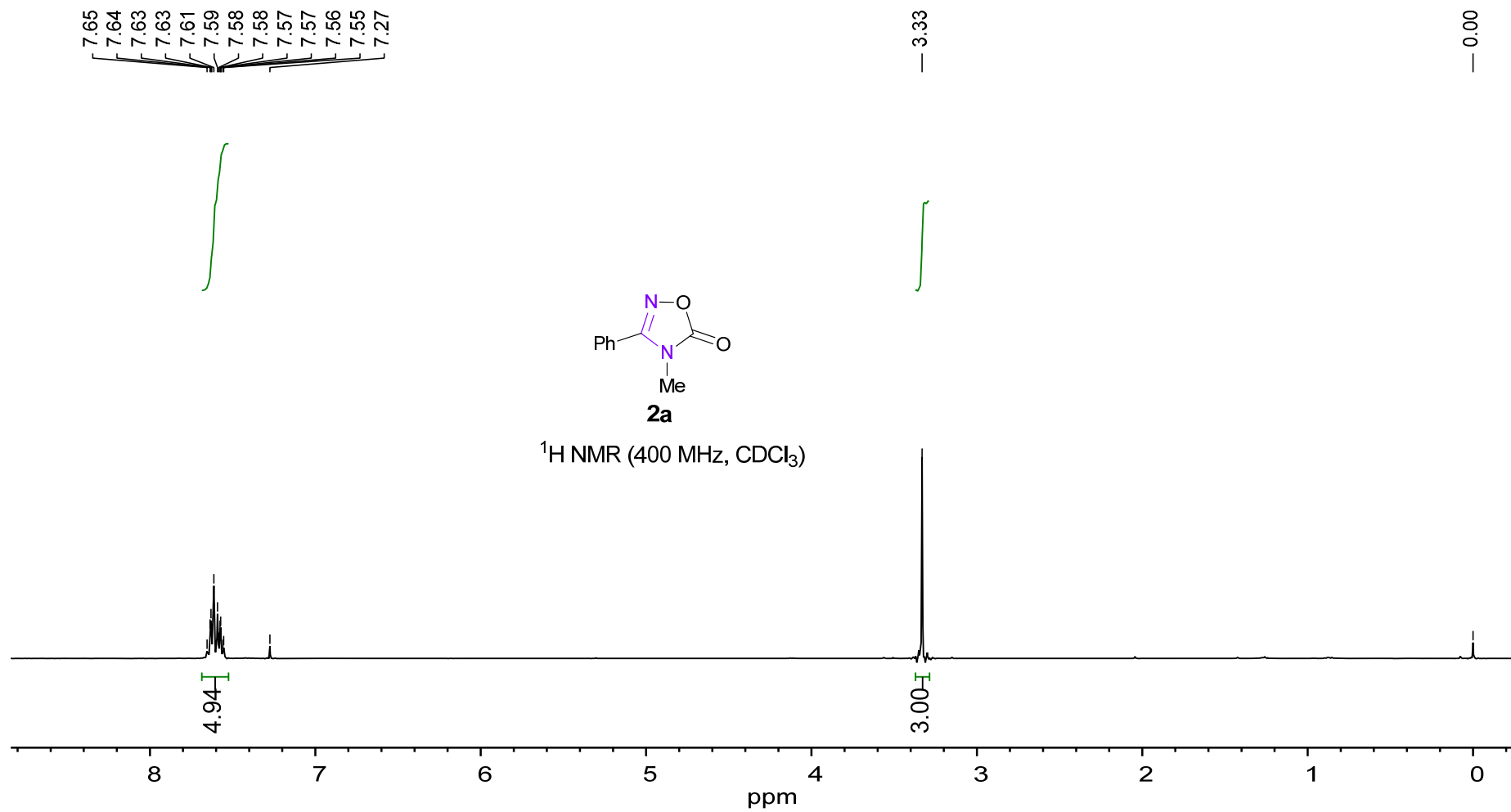
1q
¹H NMR (400 MHz, CDCl₃)



0.00
-0.00



12. NMR spectroscopy of oxadiazolones

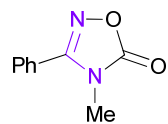


159.88
158.86

132.28
129.51
128.24
123.33

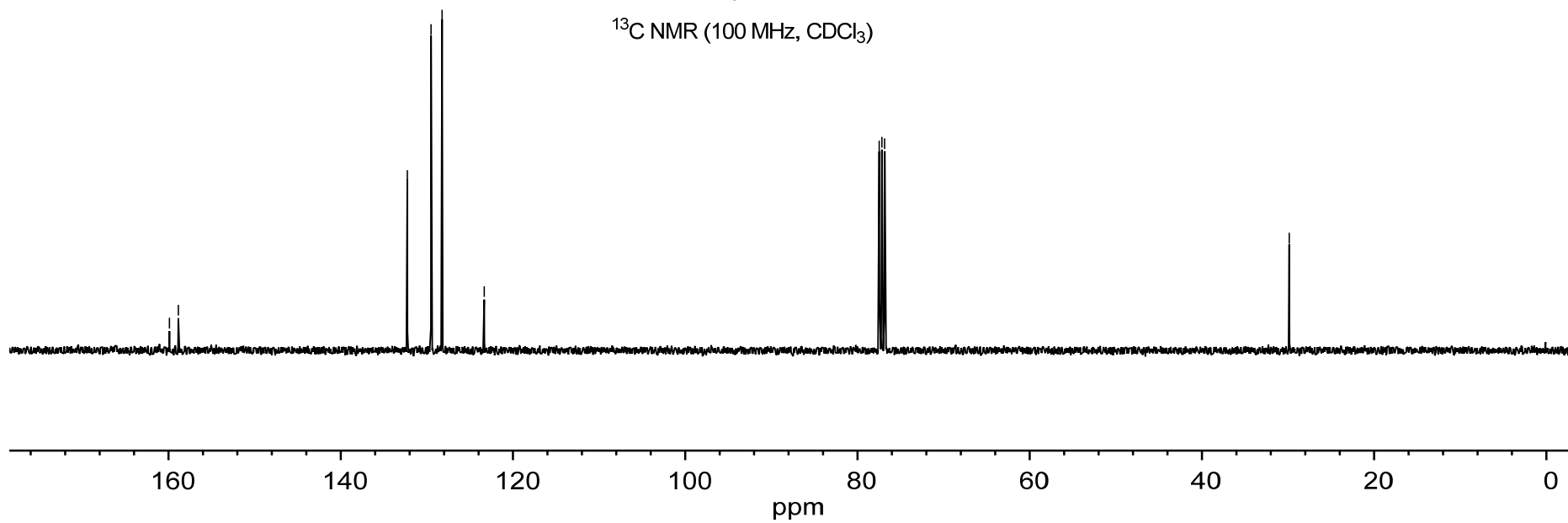
77.48
77.16
76.84

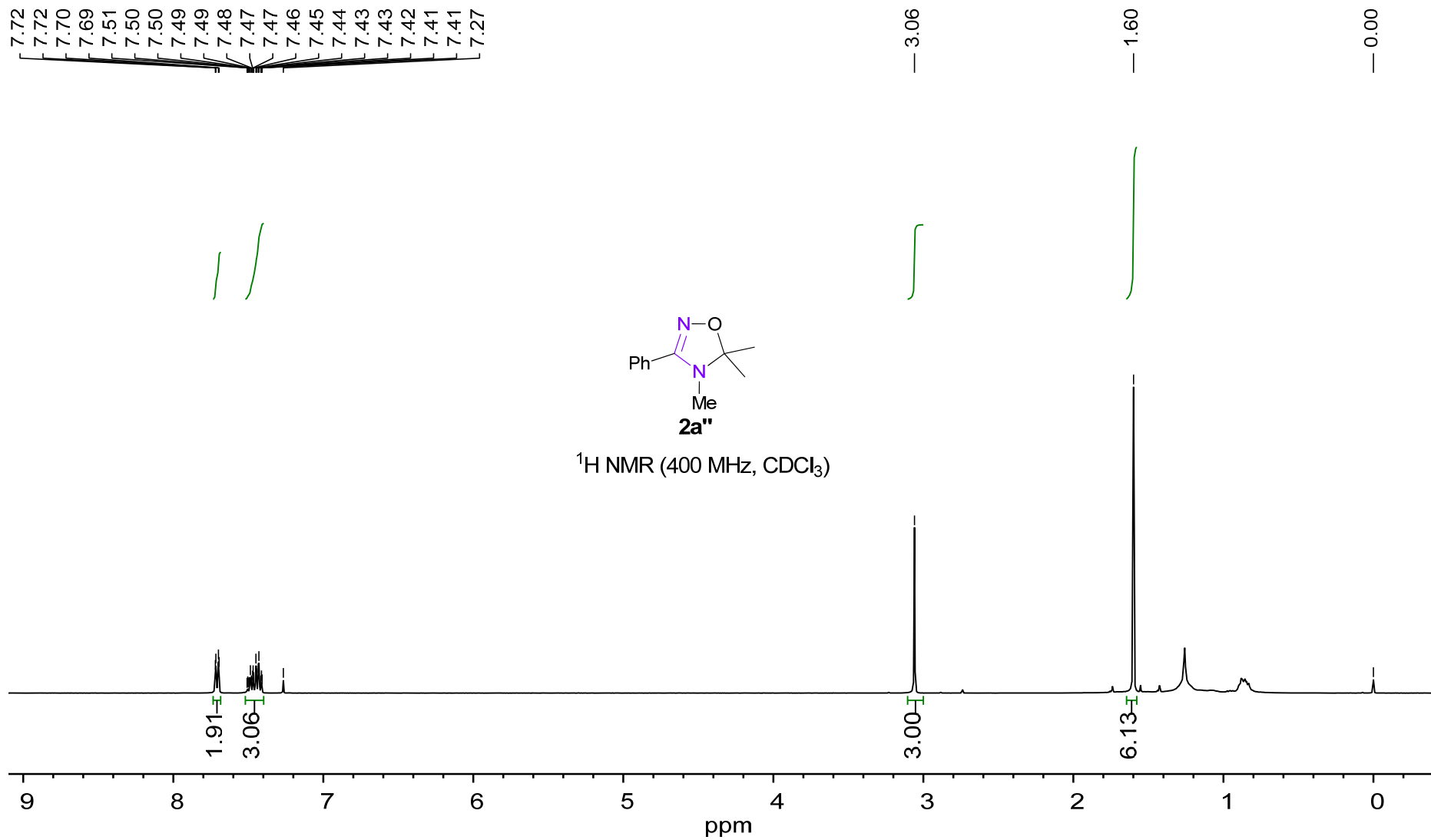
29.86

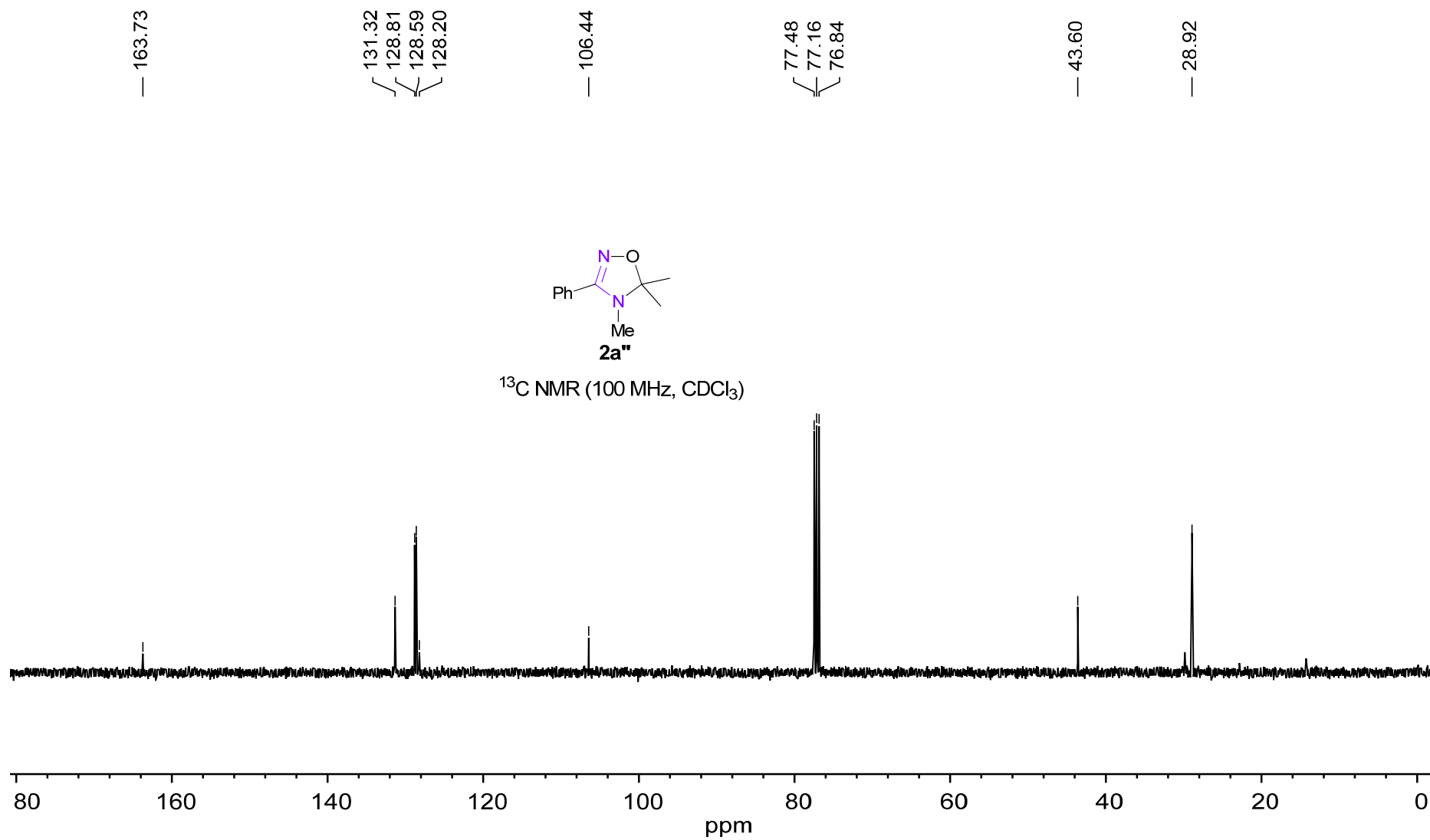


2a

¹³C NMR (100 MHz, CDCl₃)

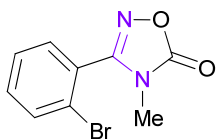






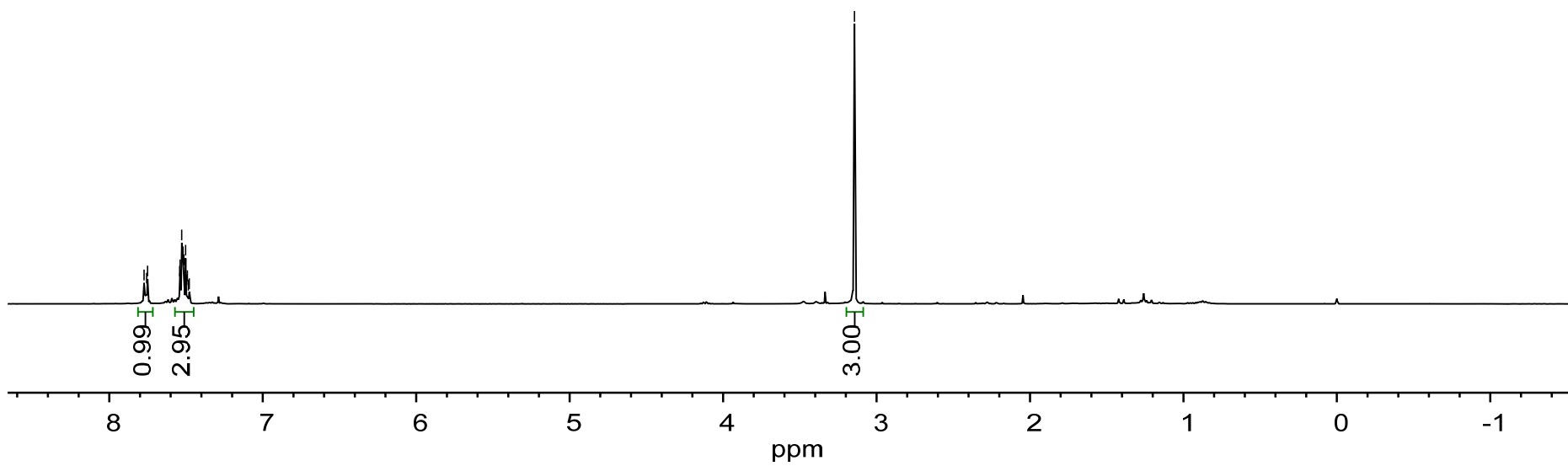
7.77
7.76
7.75
7.54
7.54
7.54
7.53
7.52
7.51
7.50
7.49
7.49
7.49
7.48

3.14



2b

¹H NMR (400 MHz, CDCl₃)

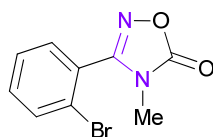


159.28
158.61

133.68
133.57
132.06
128.25
124.96
122.97

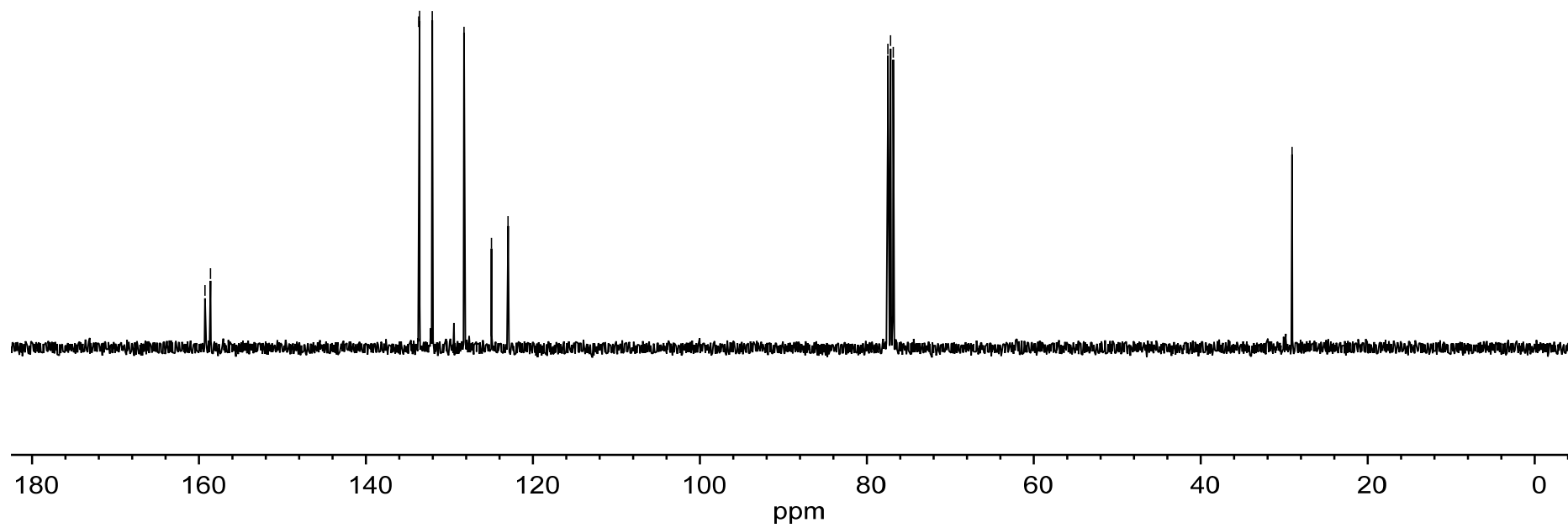
77.48
77.16
76.84

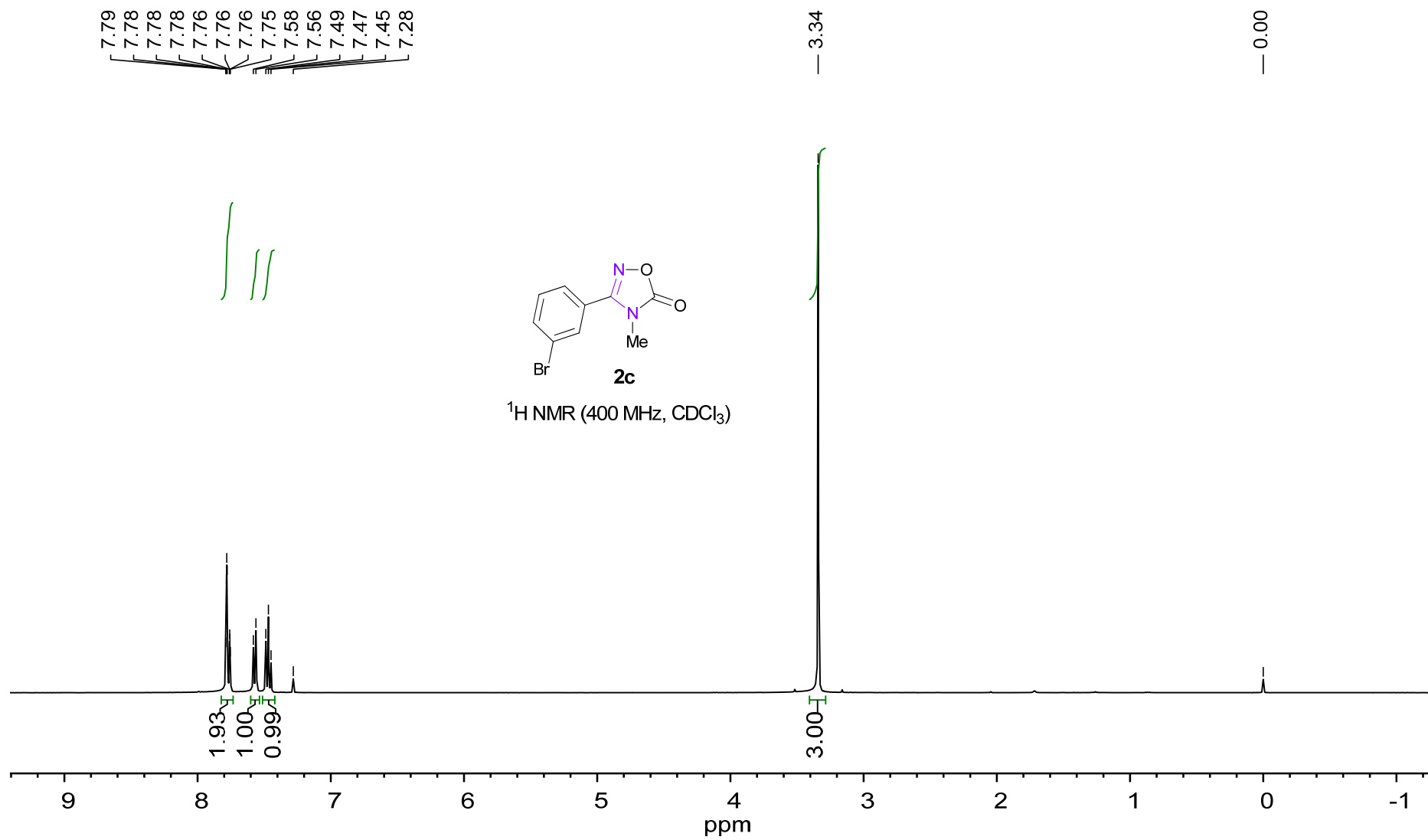
29.05



2b

¹³C NMR (100 MHz, CDCl₃)



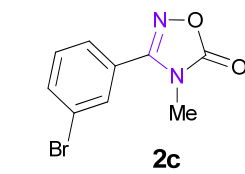


159.59
157.61

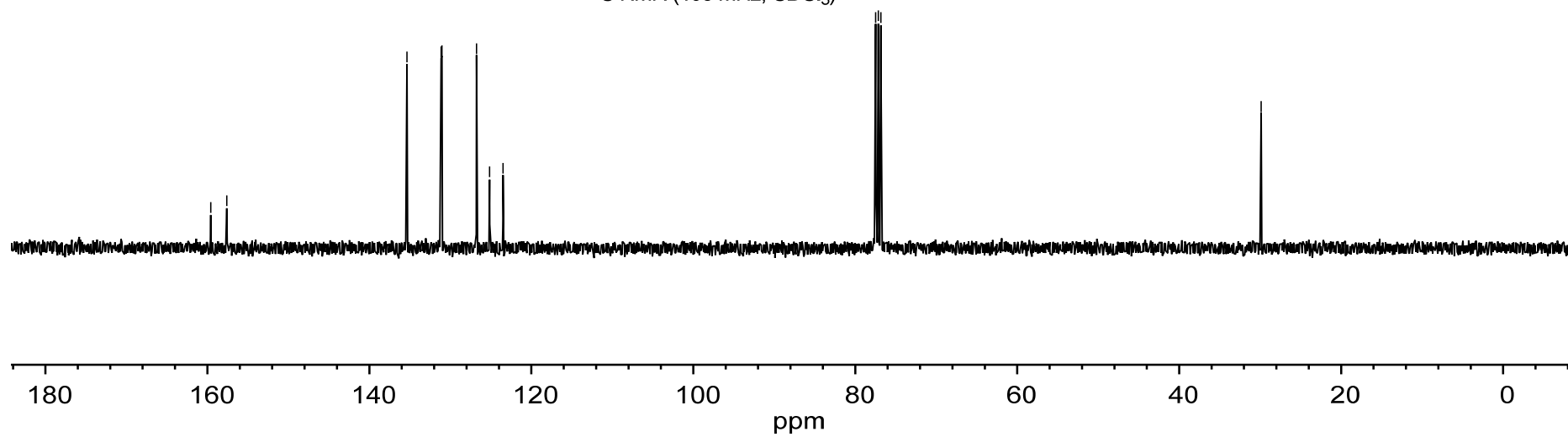
135.35
131.14
131.03
126.76
125.16
123.49

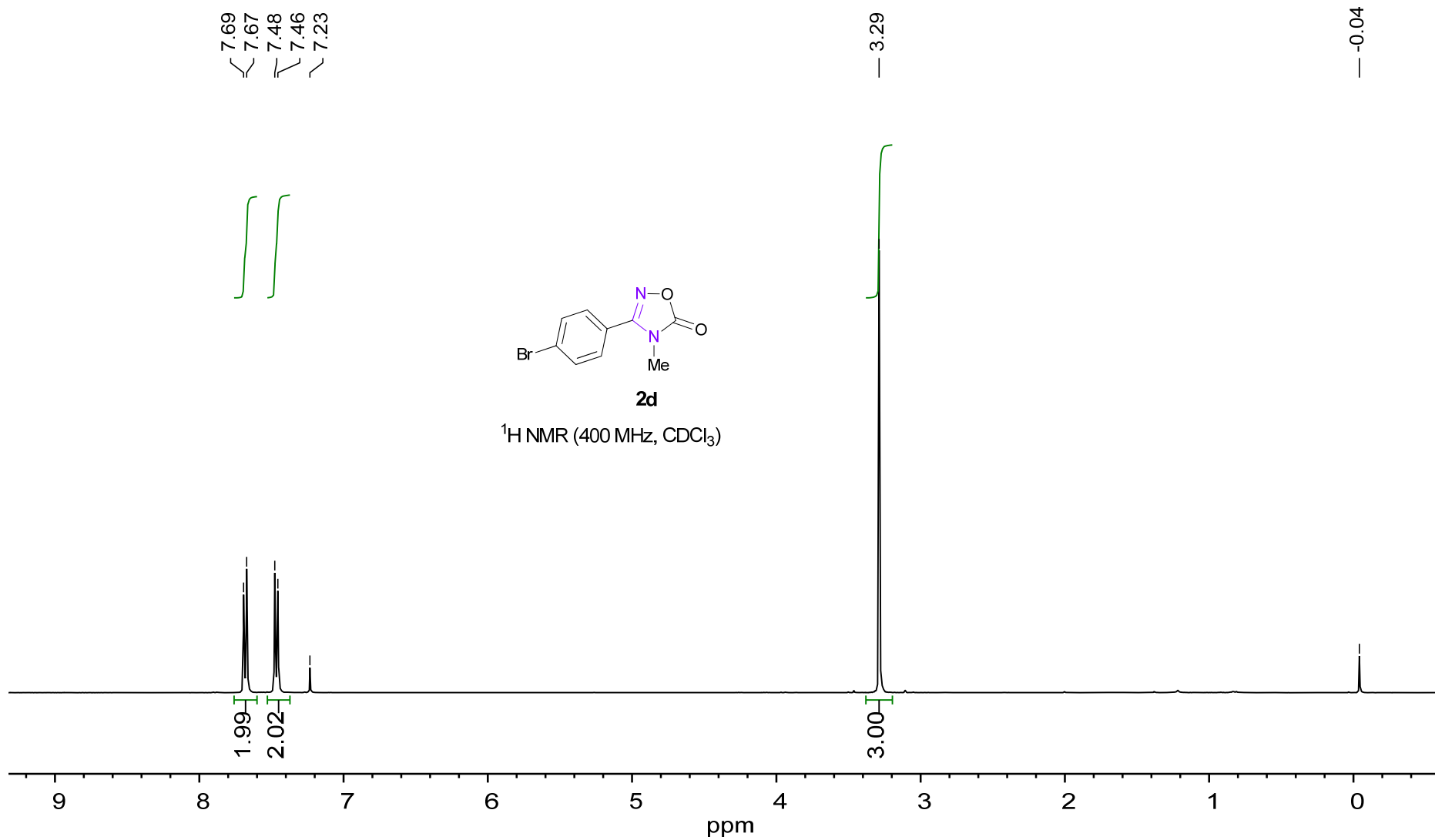
77.48
77.16
76.84

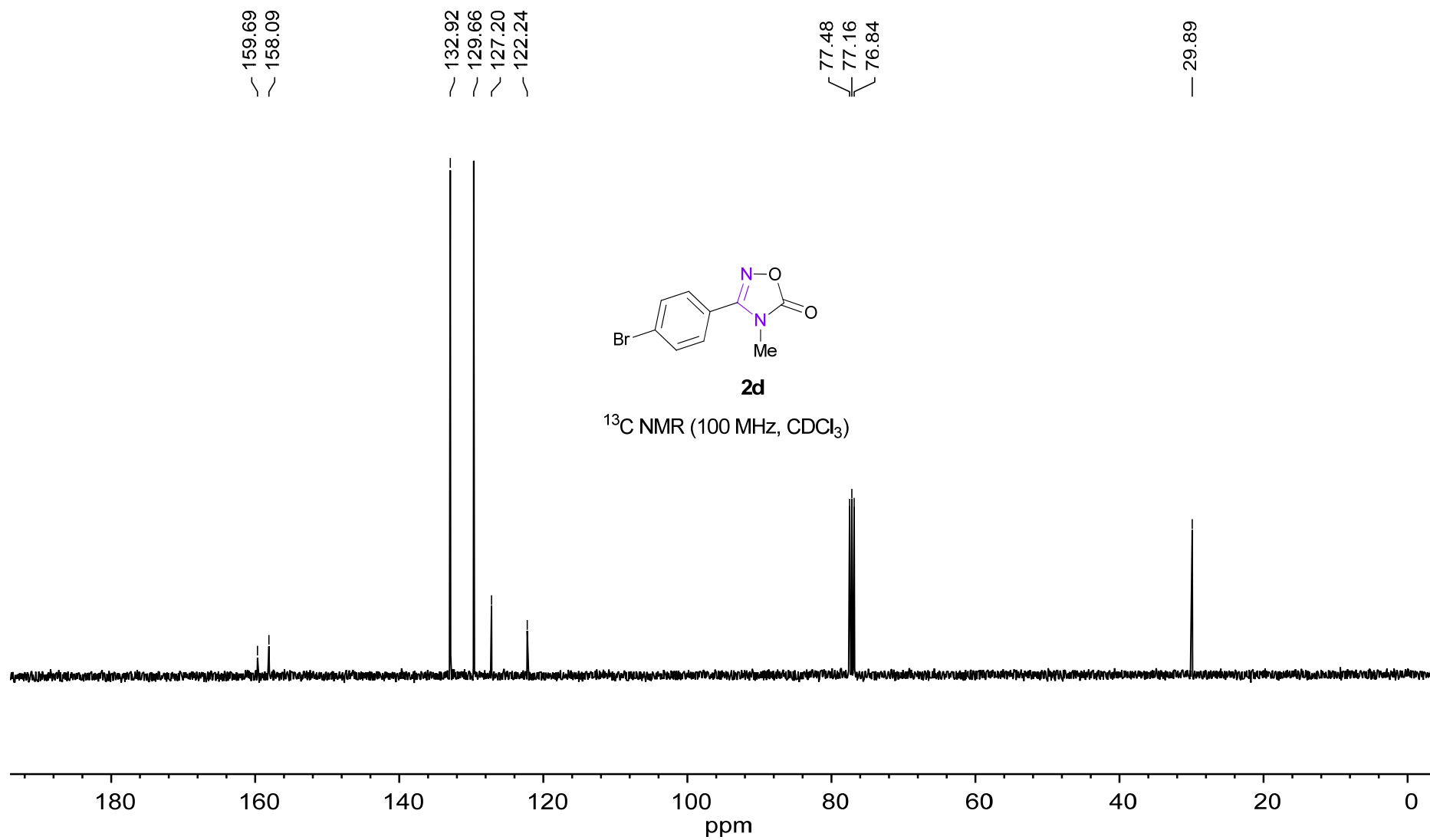
29.89

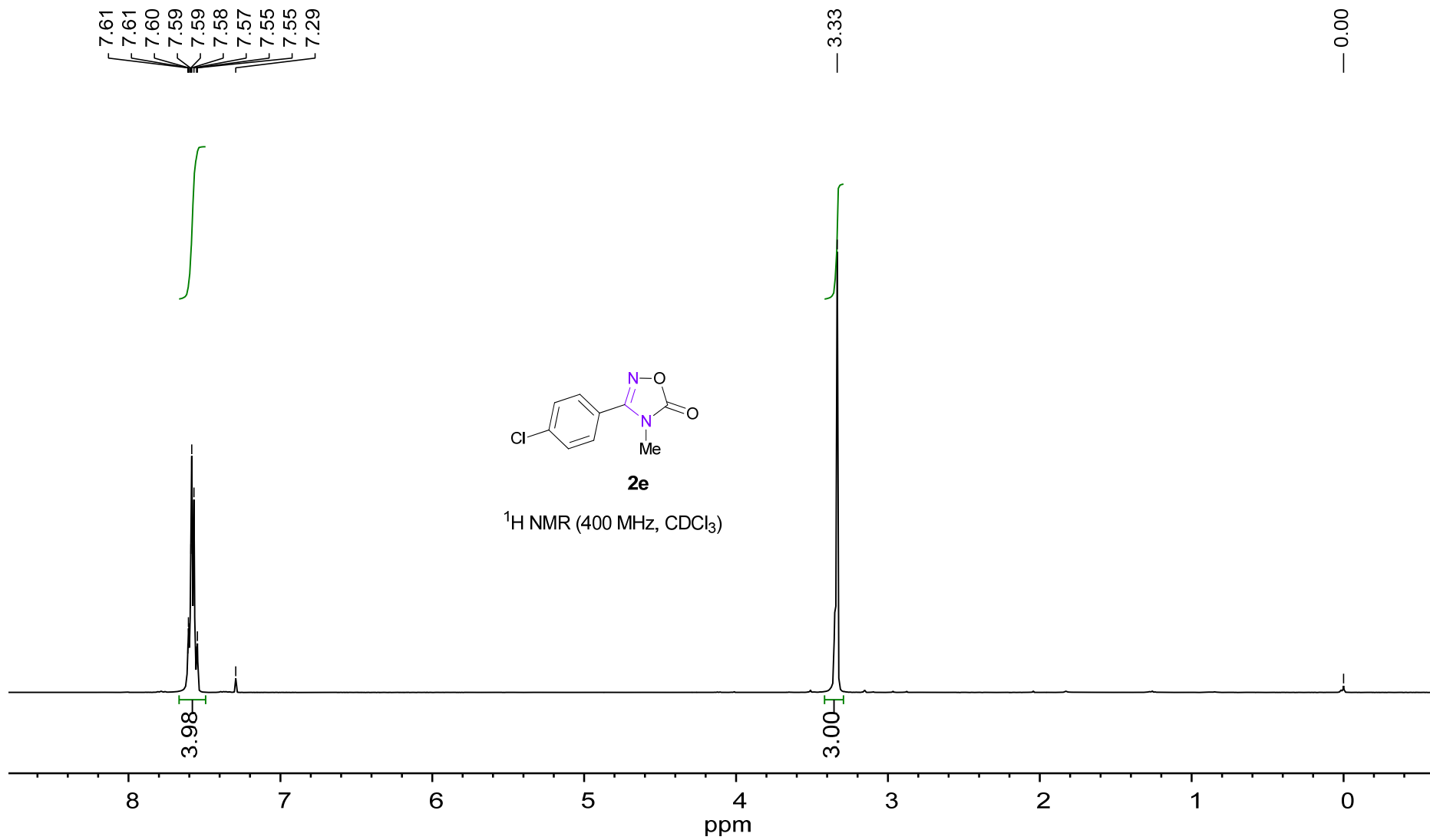


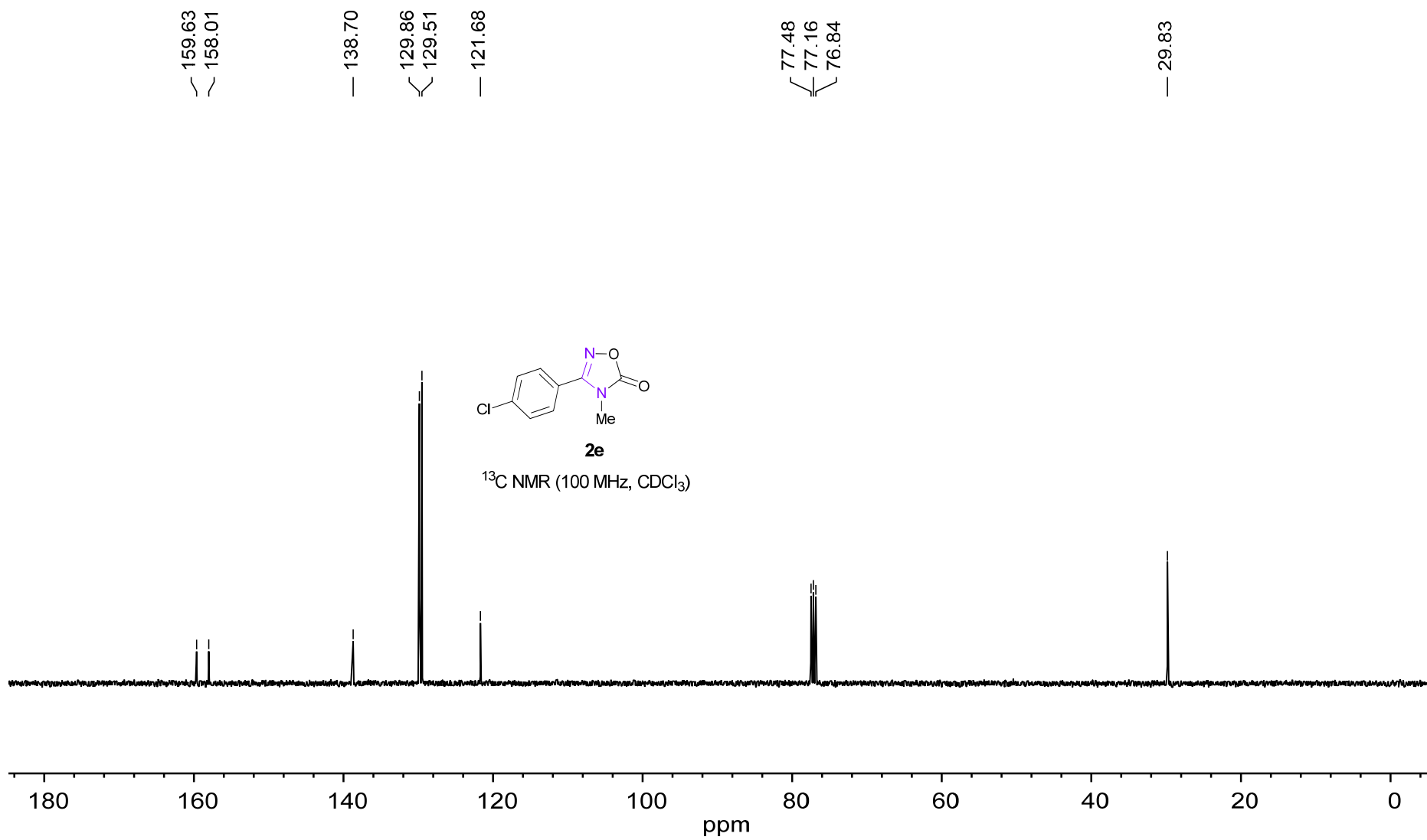
¹³C NMR (100 MHz, CDCl₃)

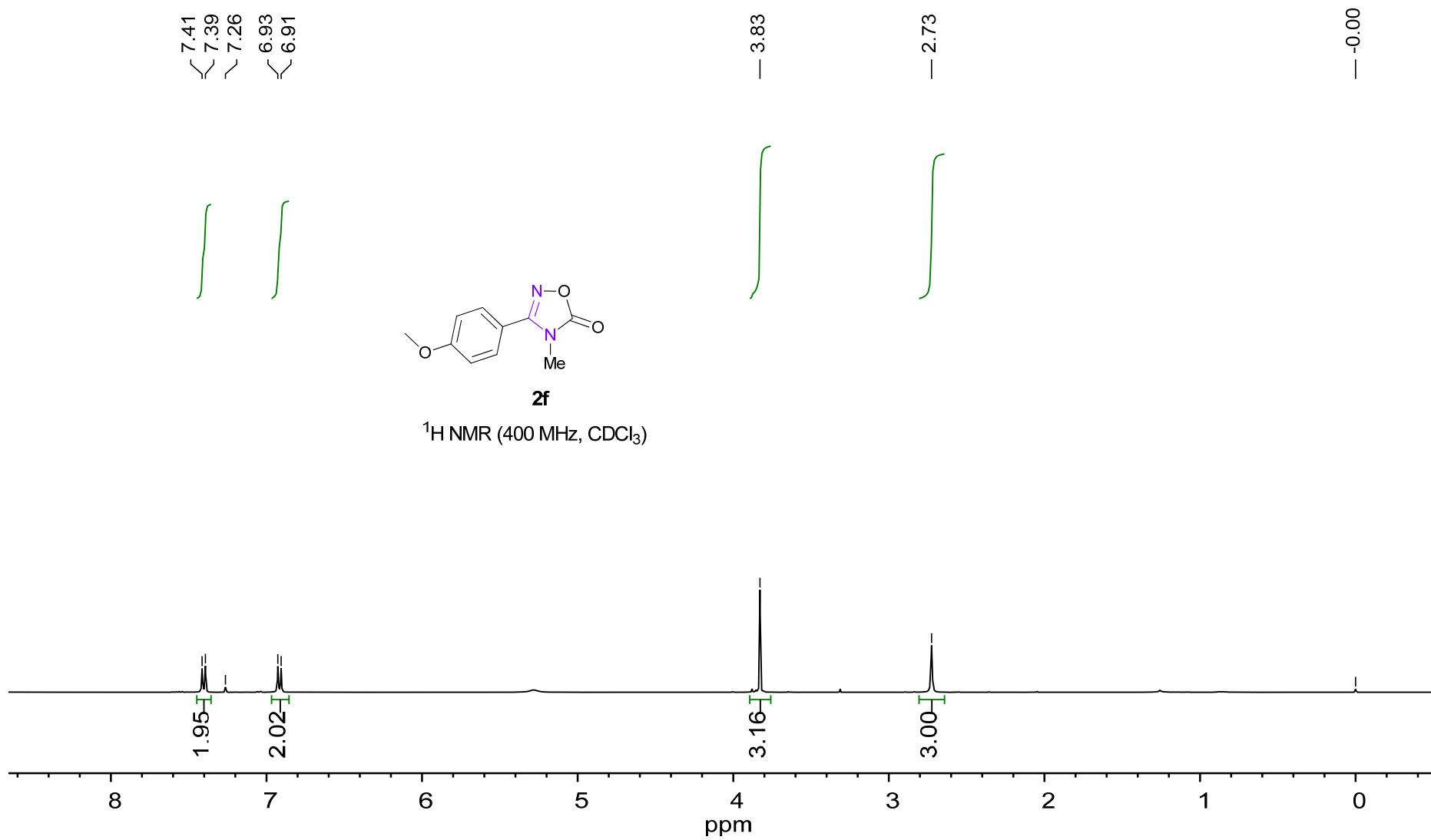












— 160.60
— 157.11

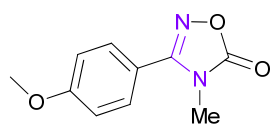
— 130.06
— 123.65

— 113.86

77.48
77.16
76.84

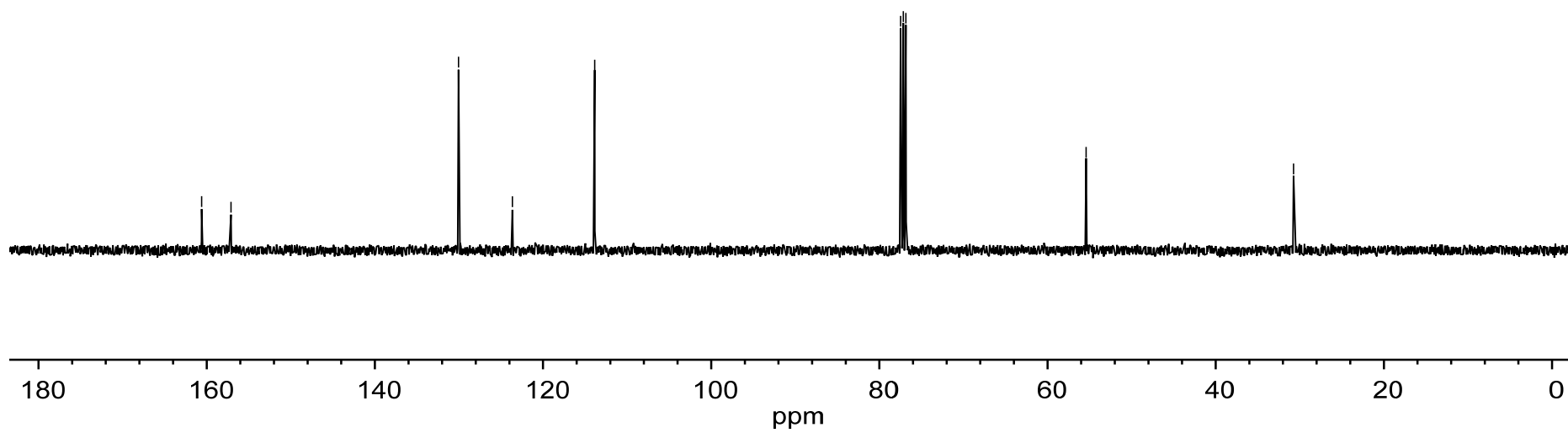
— 55.41

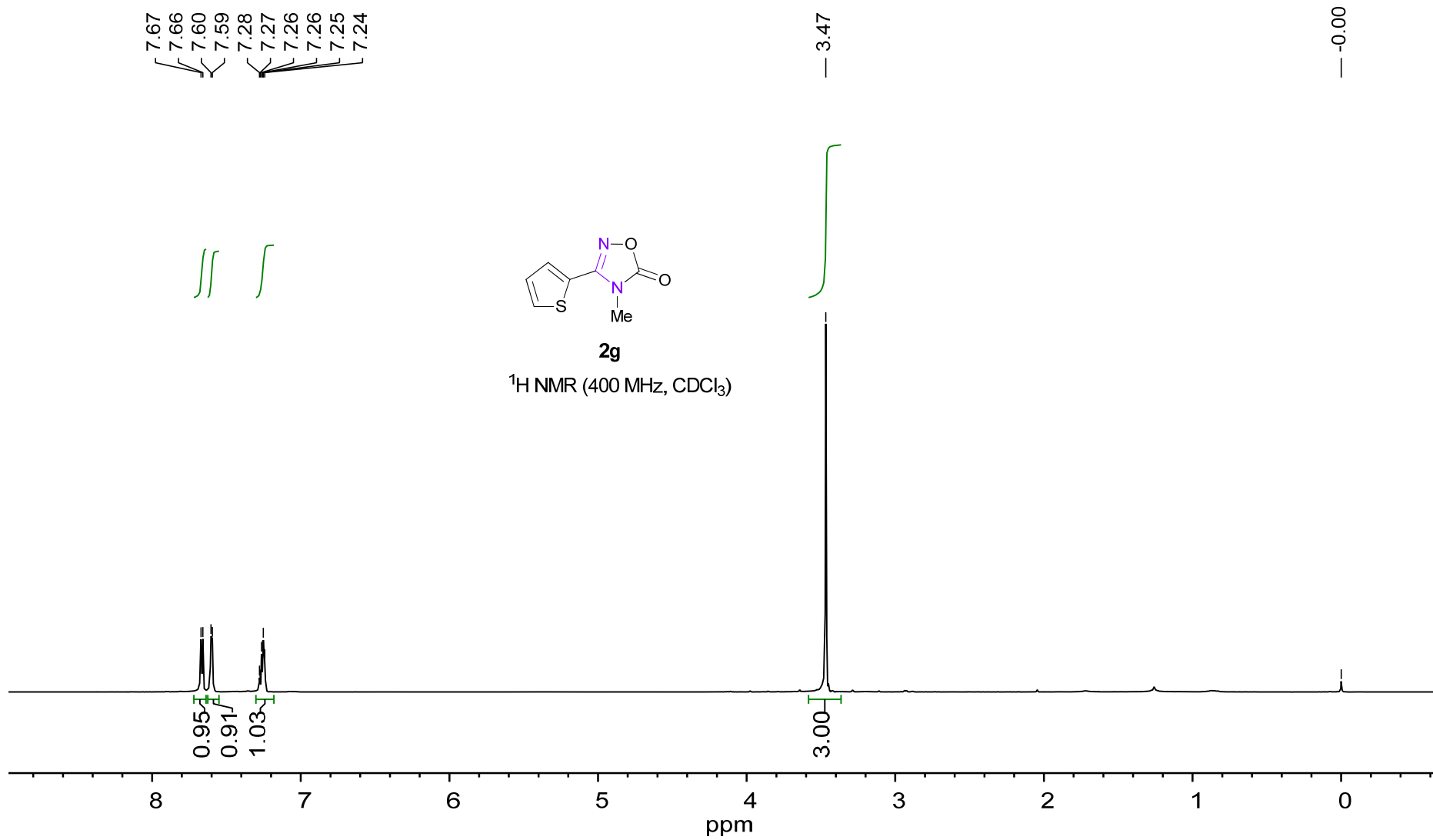
— 30.75



2f

¹³C NMR (100 MHz, CDCl₃)



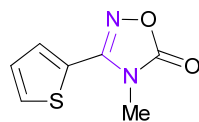


— 159.53
— 154.11

130.85
130.25
128.40
123.29

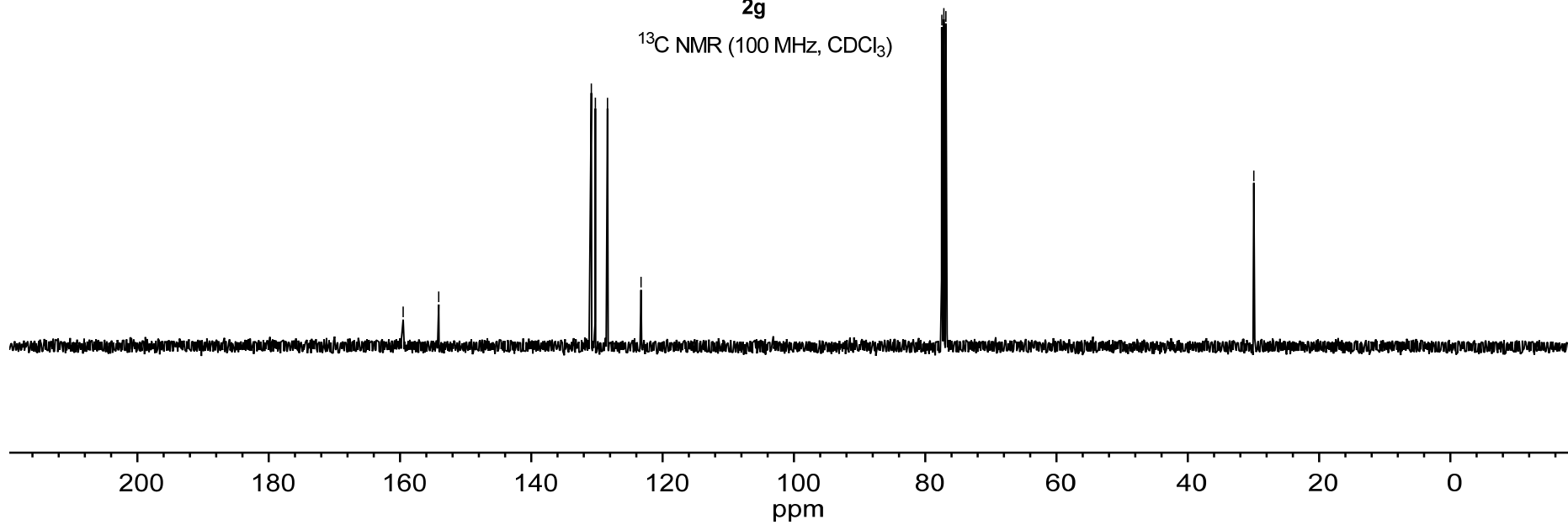
77.48
77.16
76.84

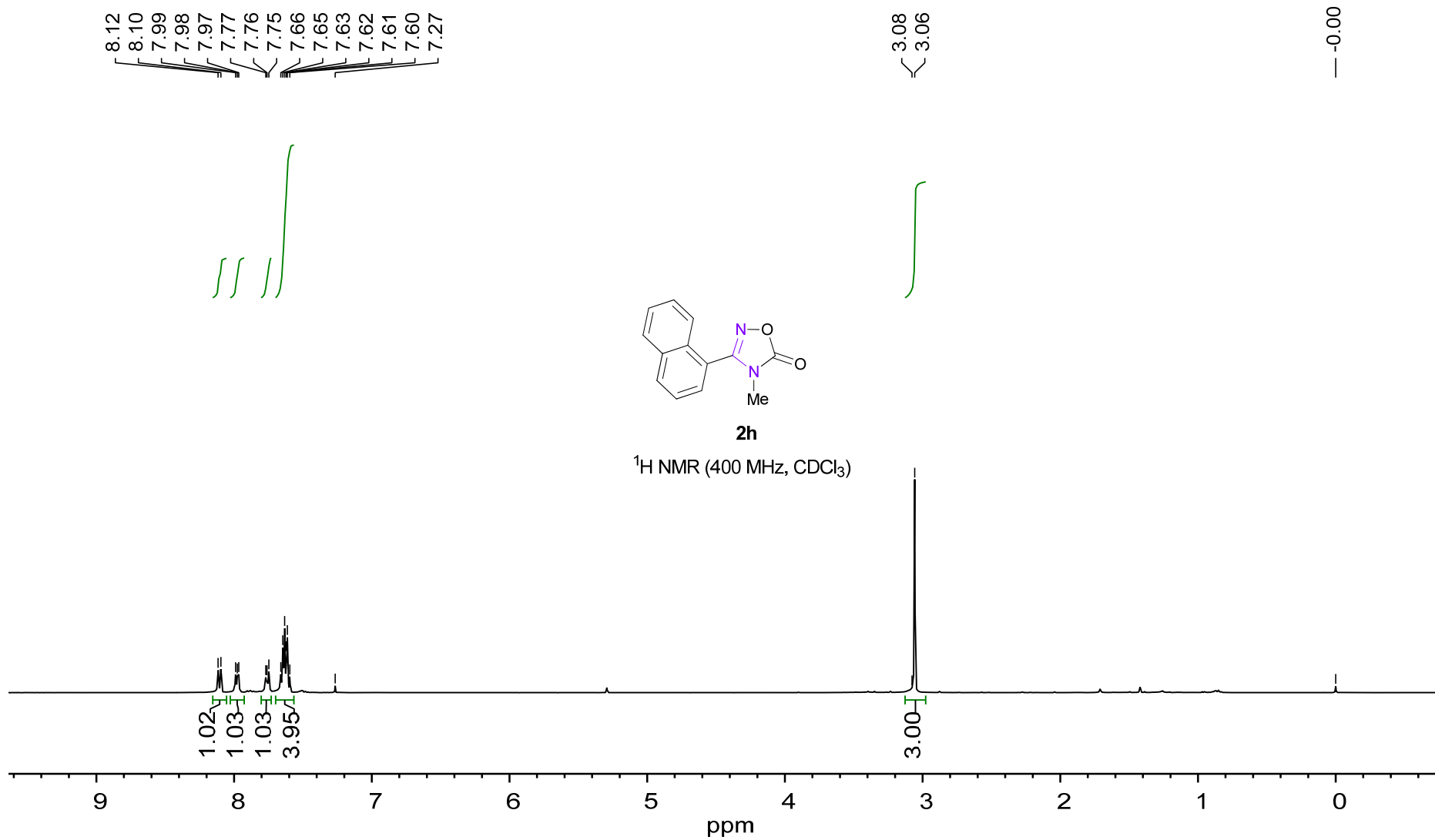
— 29.95



2g

¹³C NMR (100 MHz, CDCl₃)



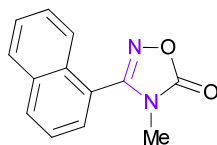


159.68
158.71

133.59
132.68
130.72
129.10
129.06
128.38
127.29
125.22
123.93
120.29

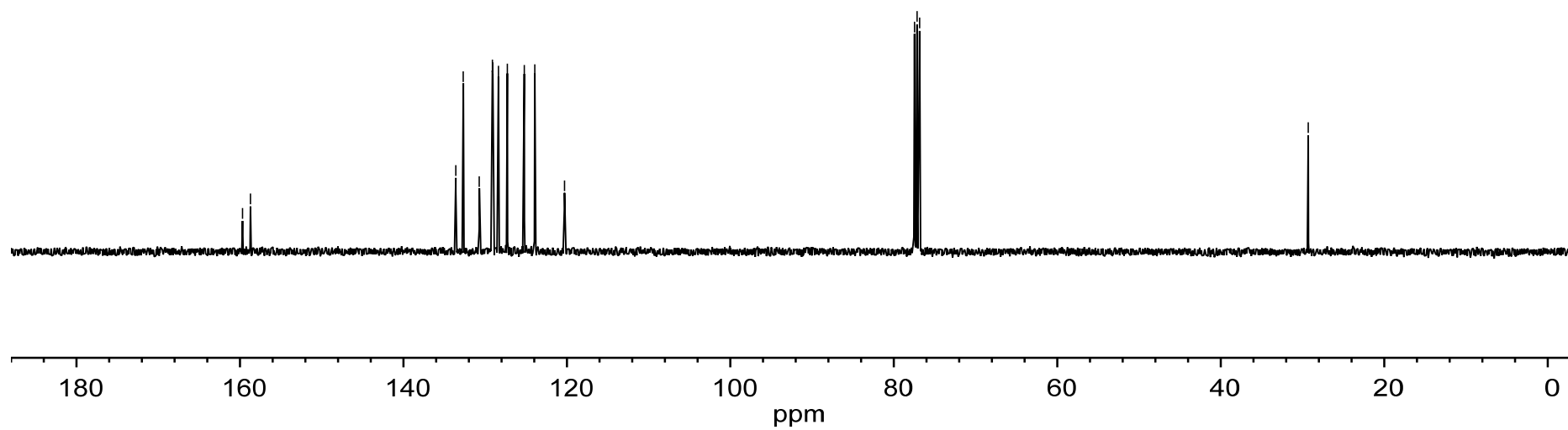
77.48
77.16
76.84

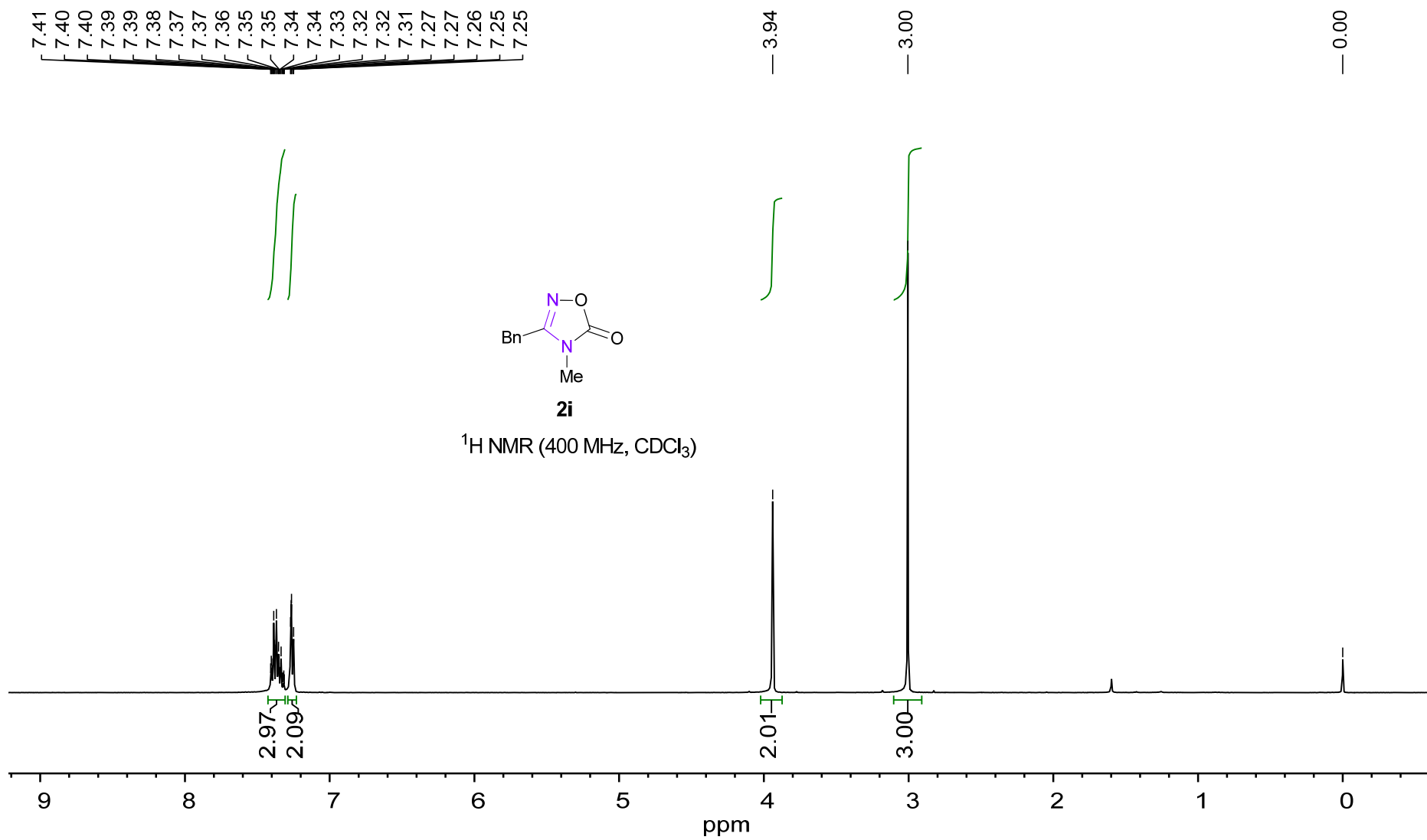
29.30

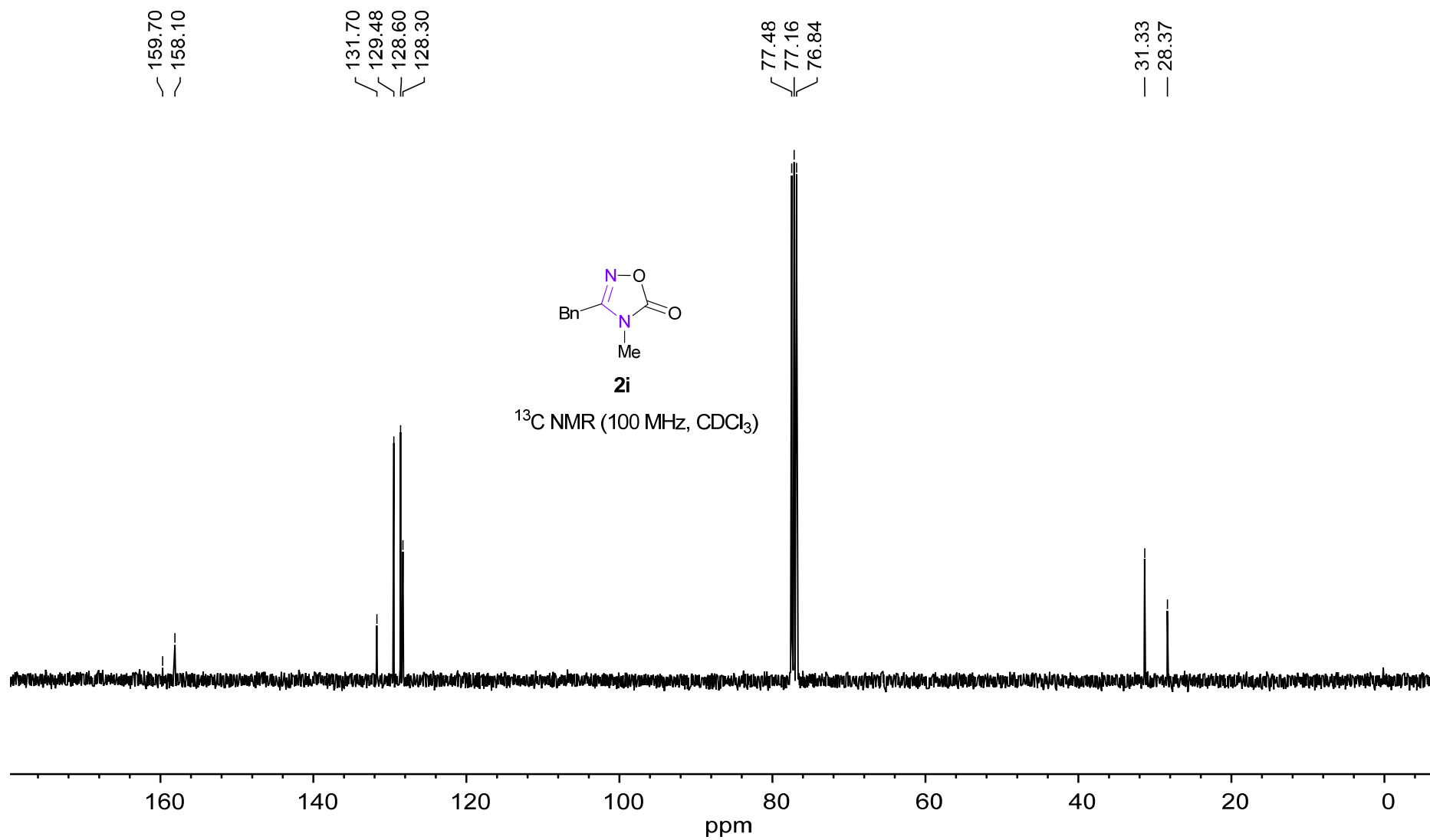


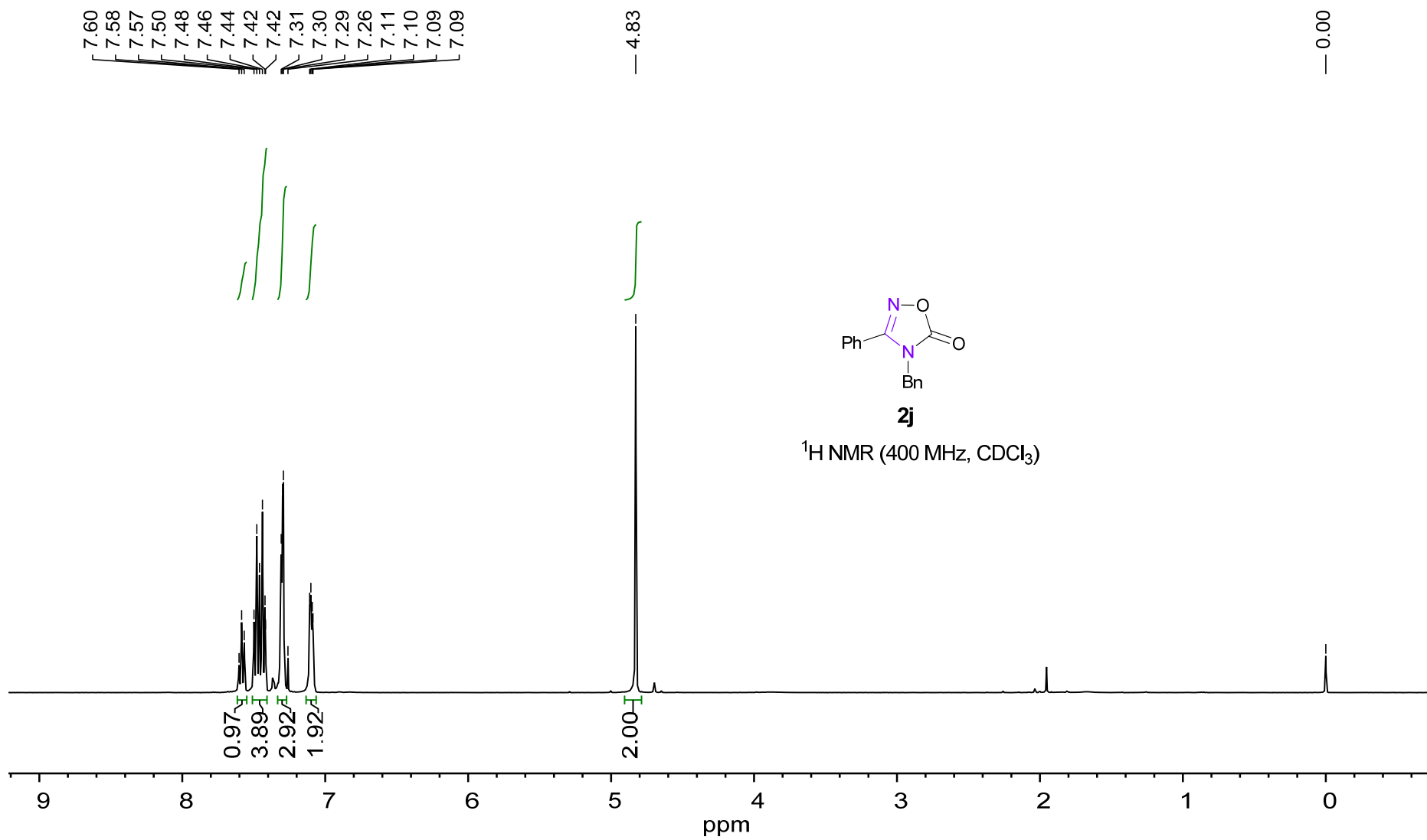
2h

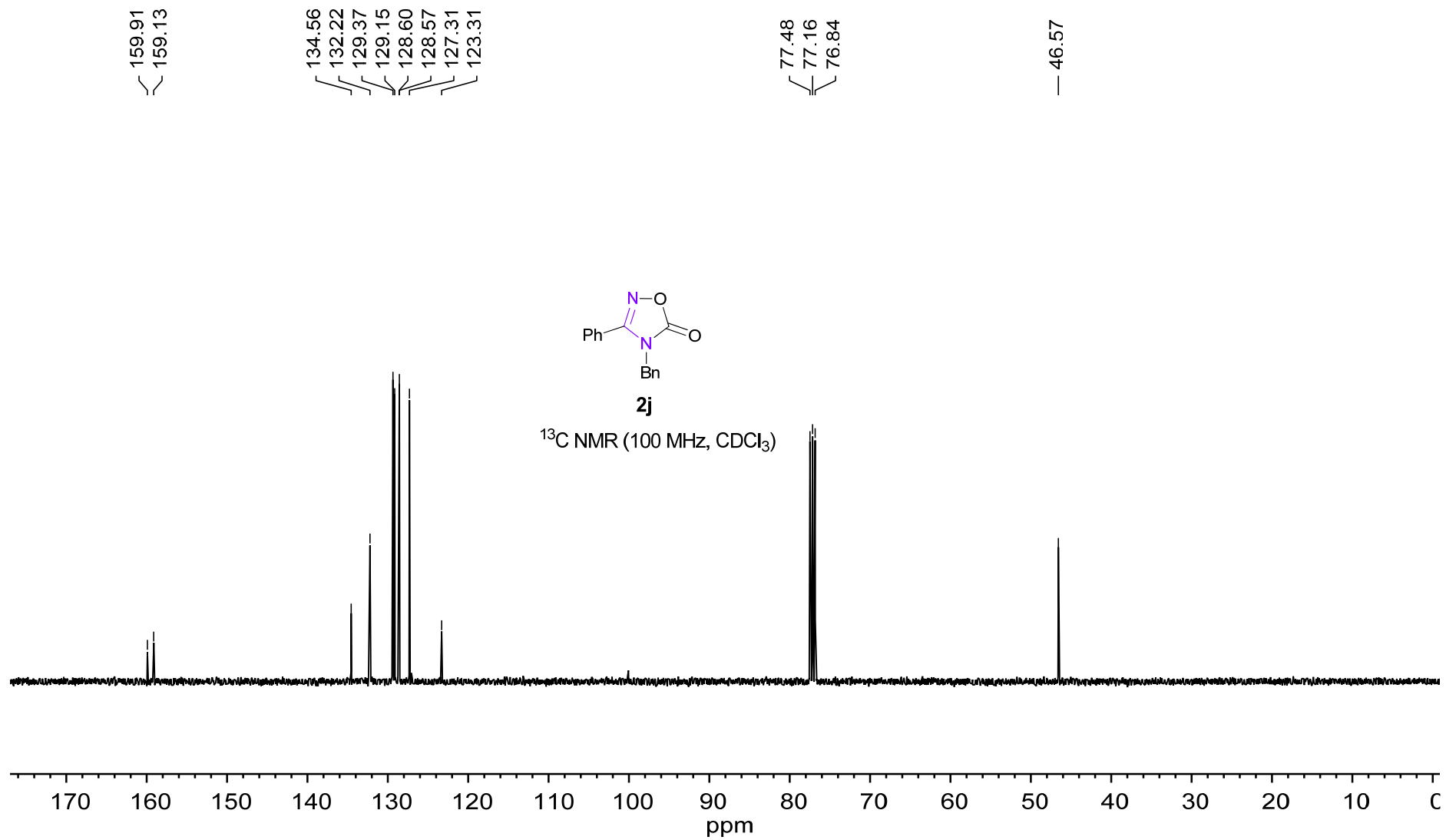
^{13}C NMR (100 MHz, CDCl_3)



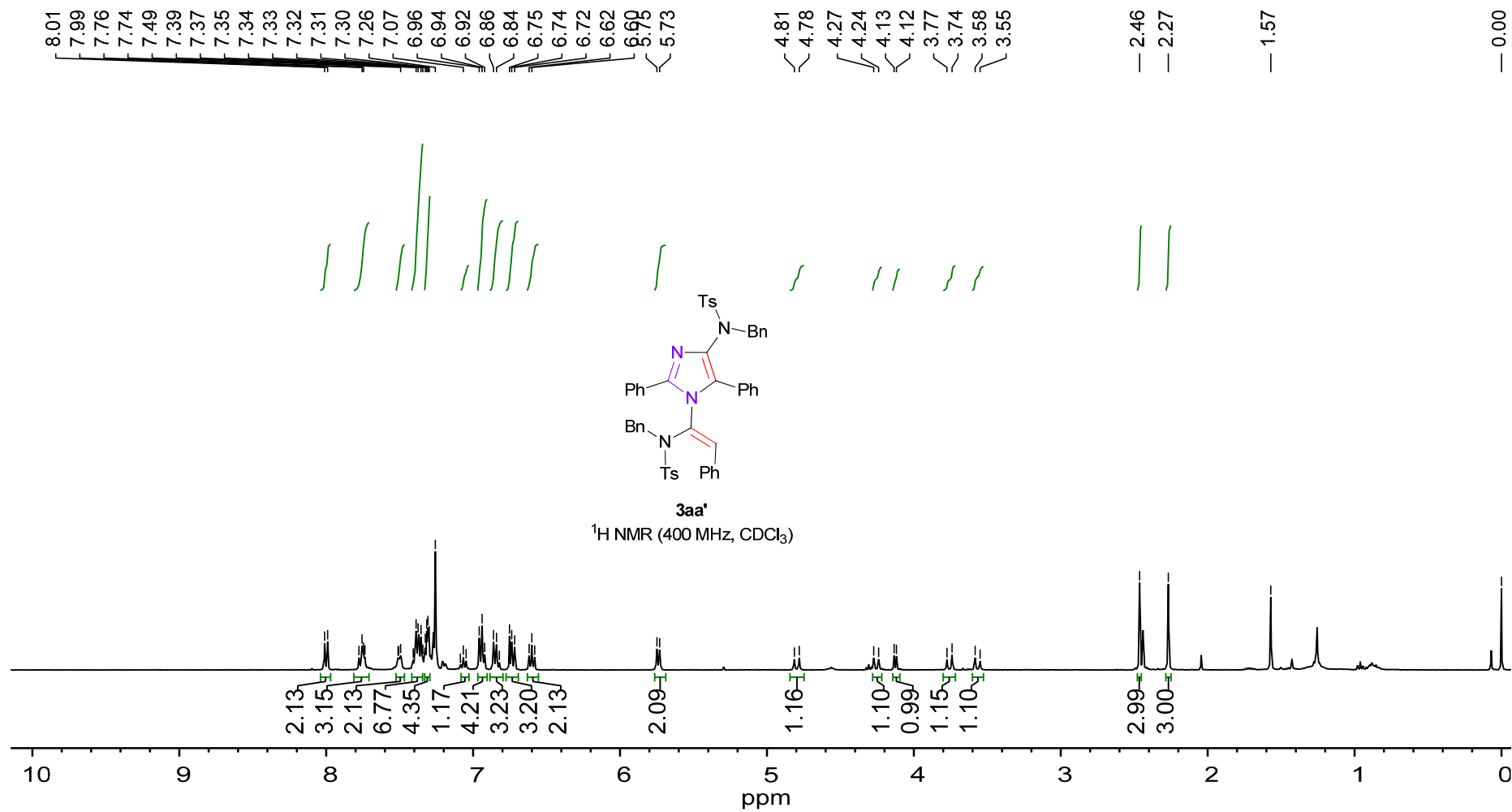


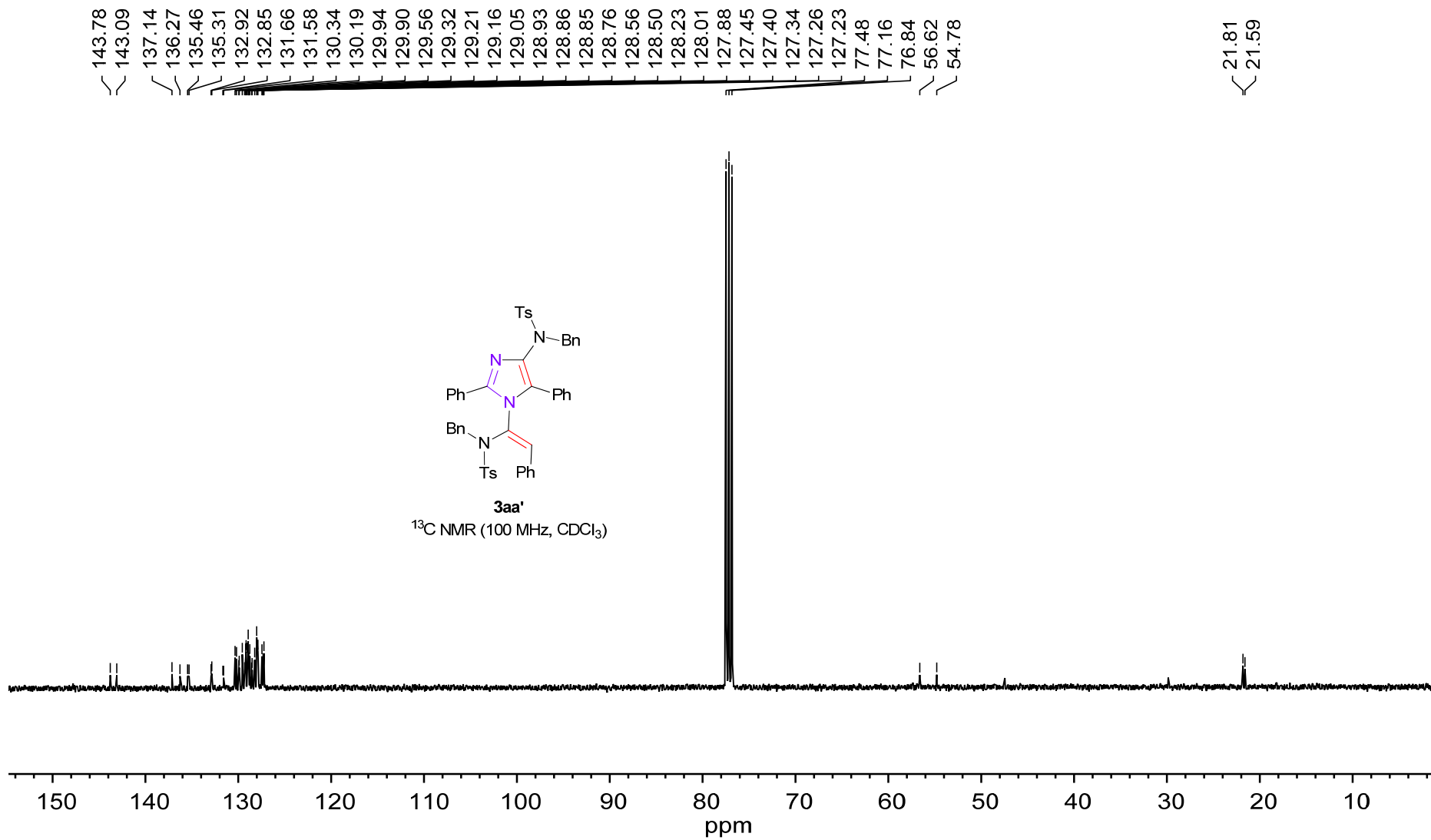




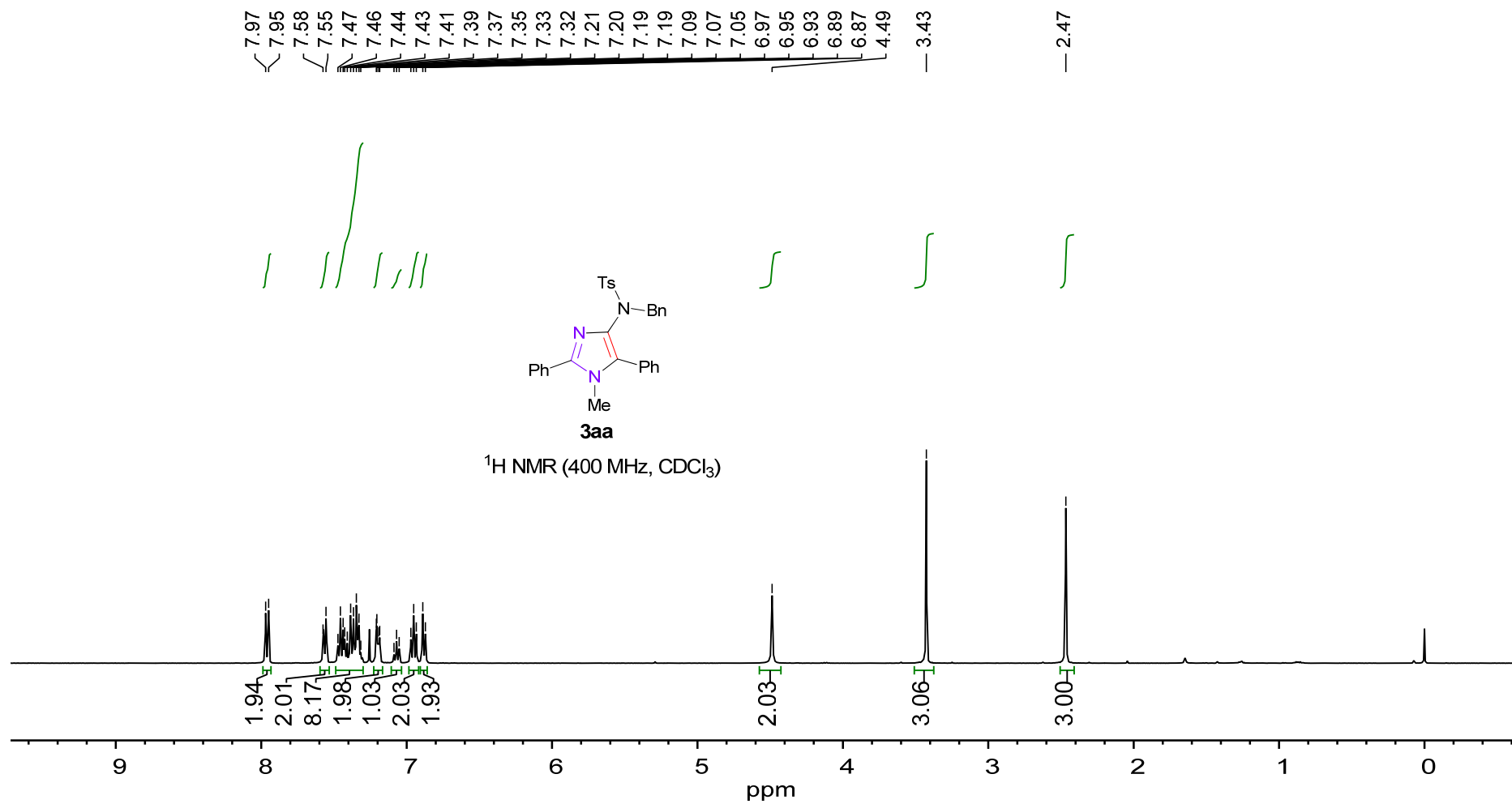


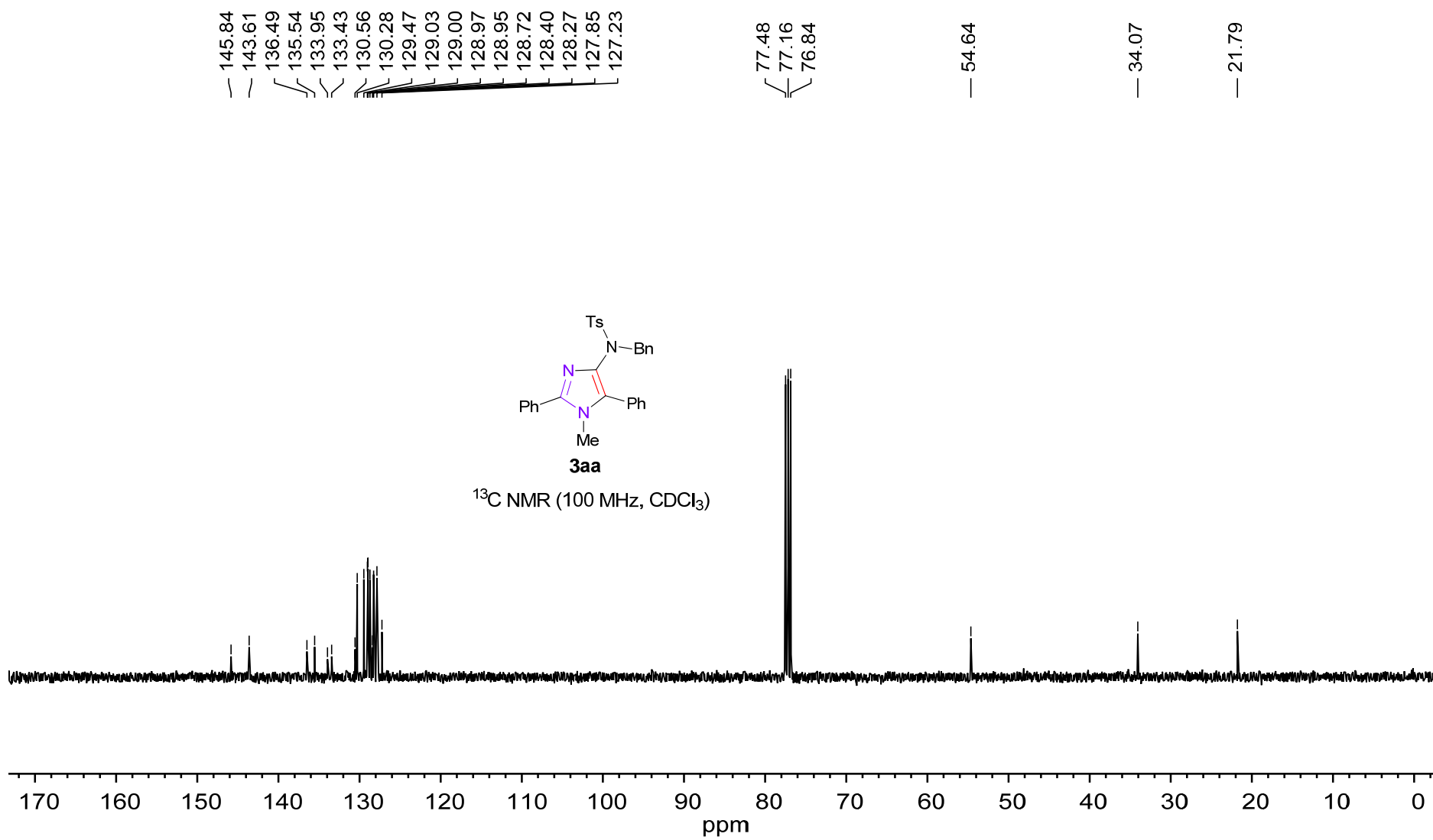
13. NMR spectroscopy of product 3aa'

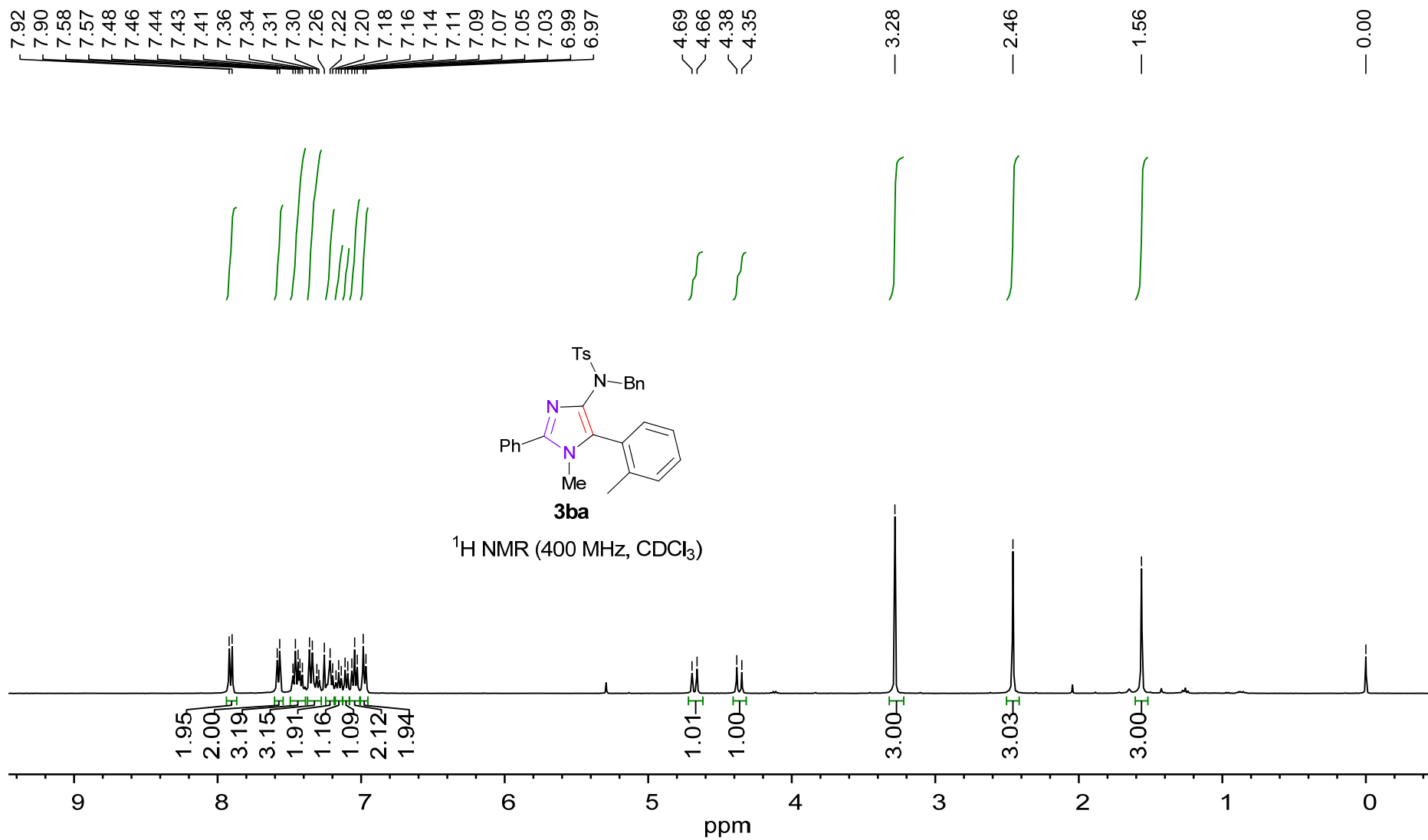


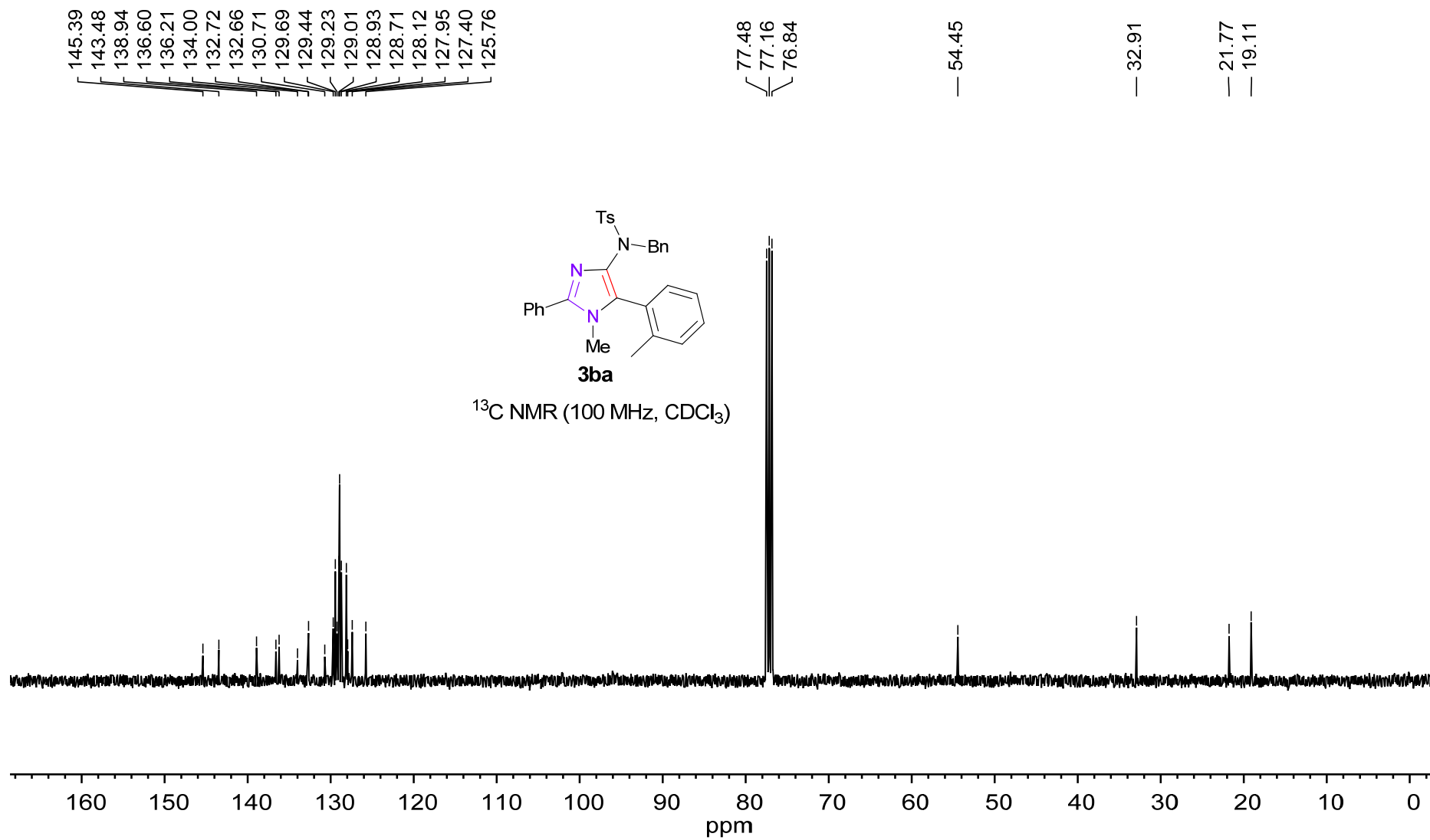


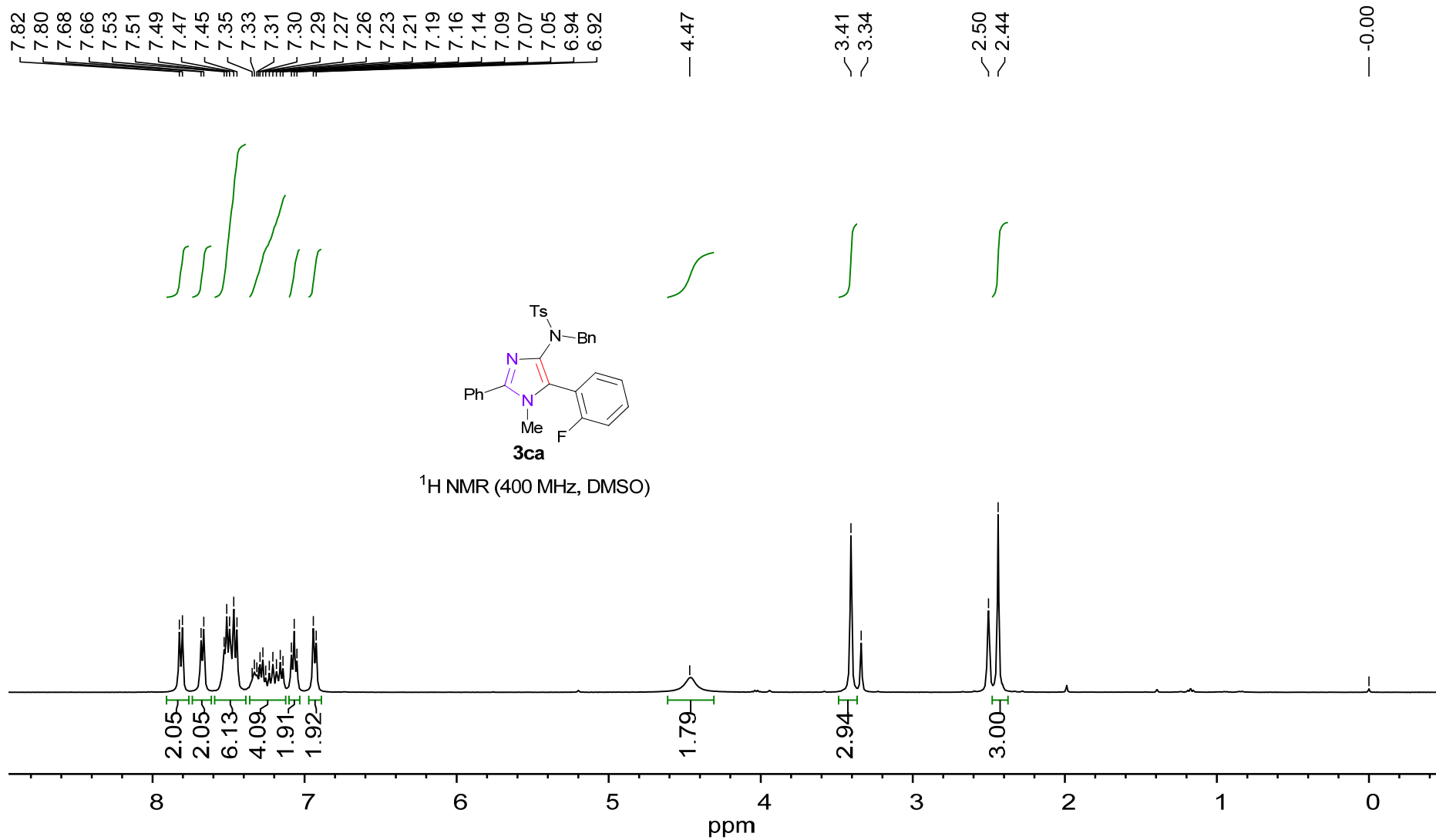
14. NMR spectroscopy of aminoimidazoles

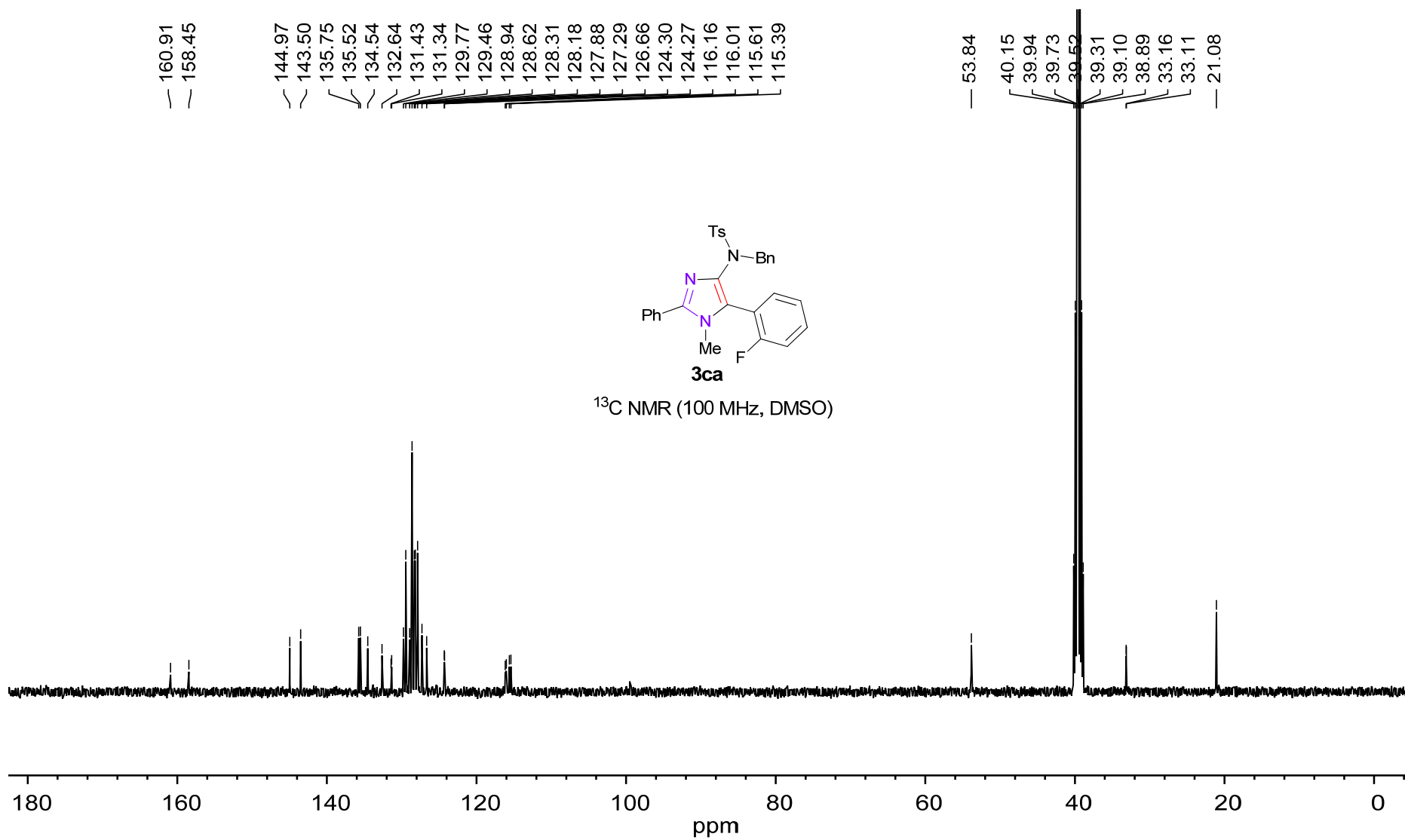


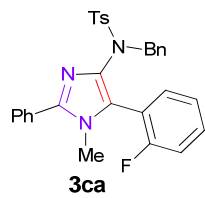






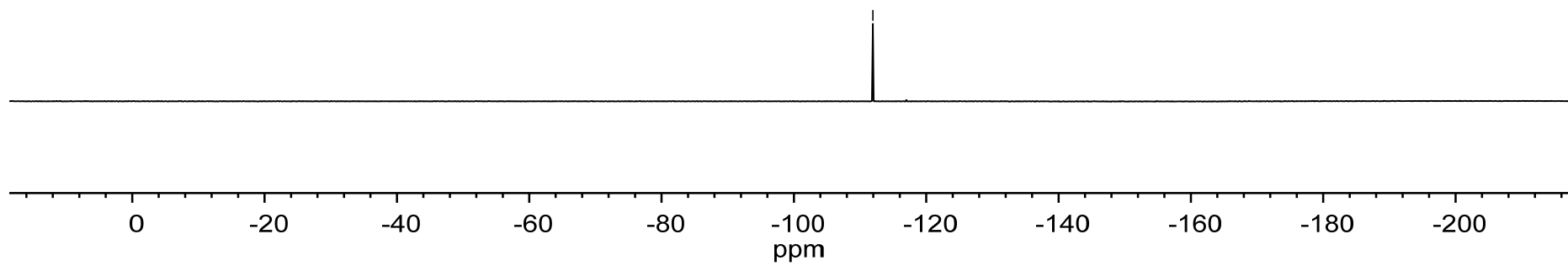


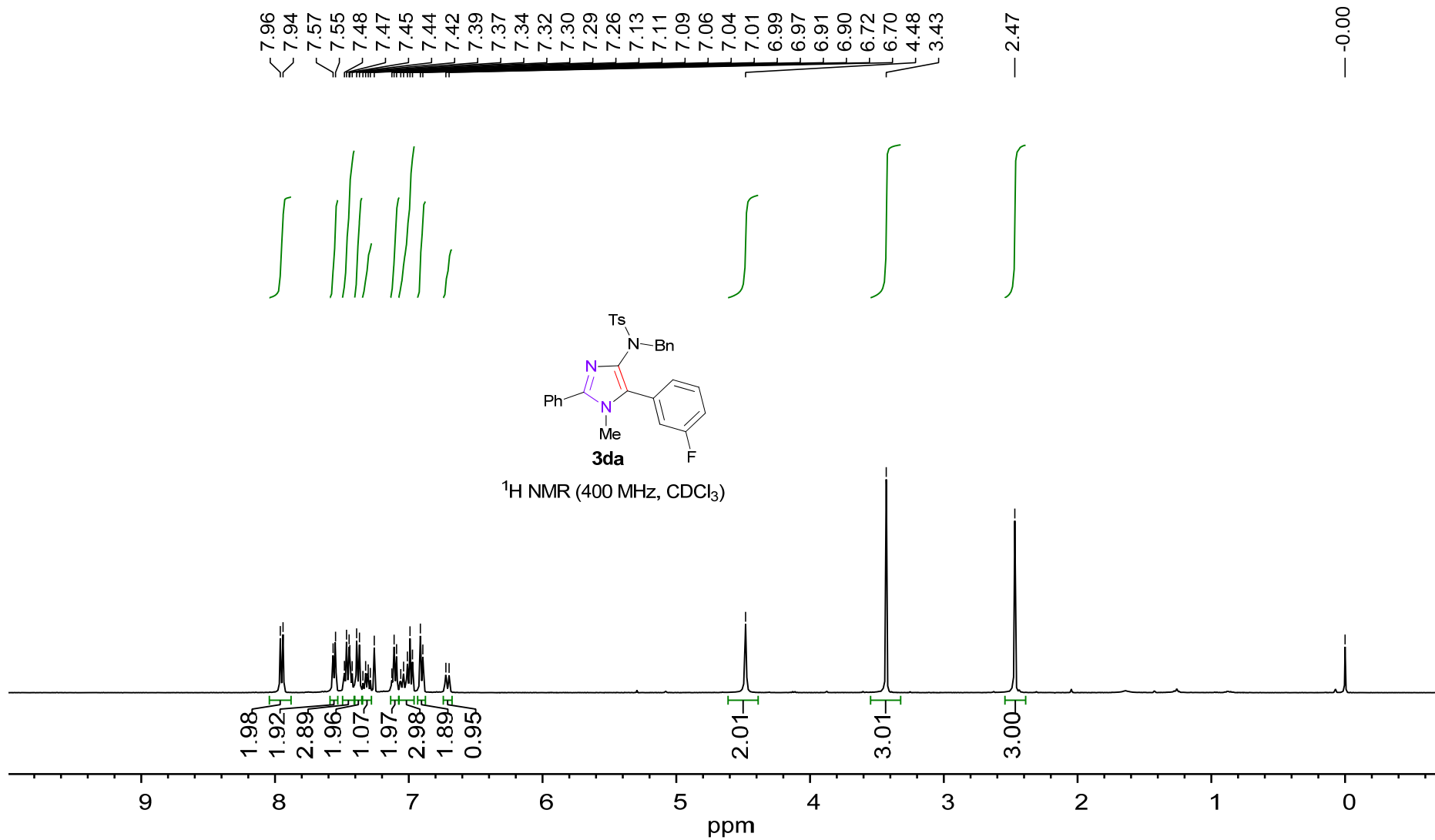


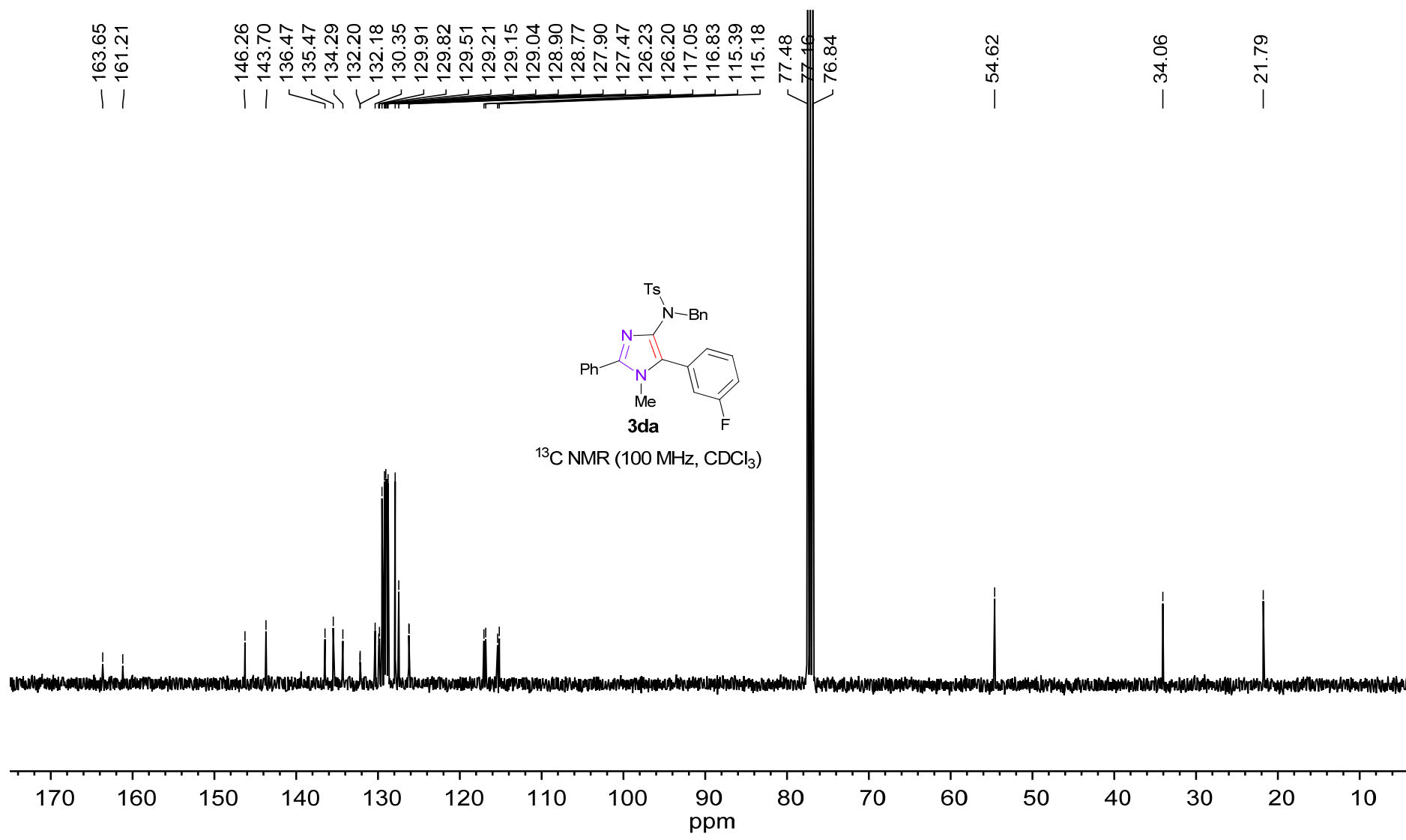


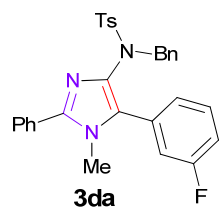
¹⁹F NMR (376 MHz, DMSO)

— -111.93



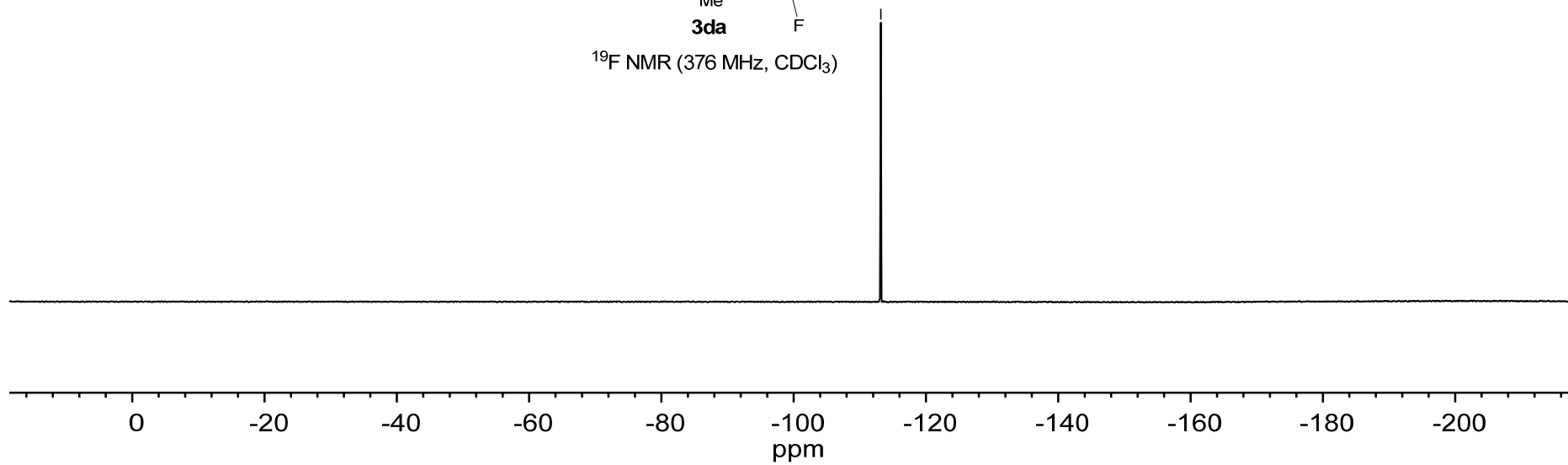


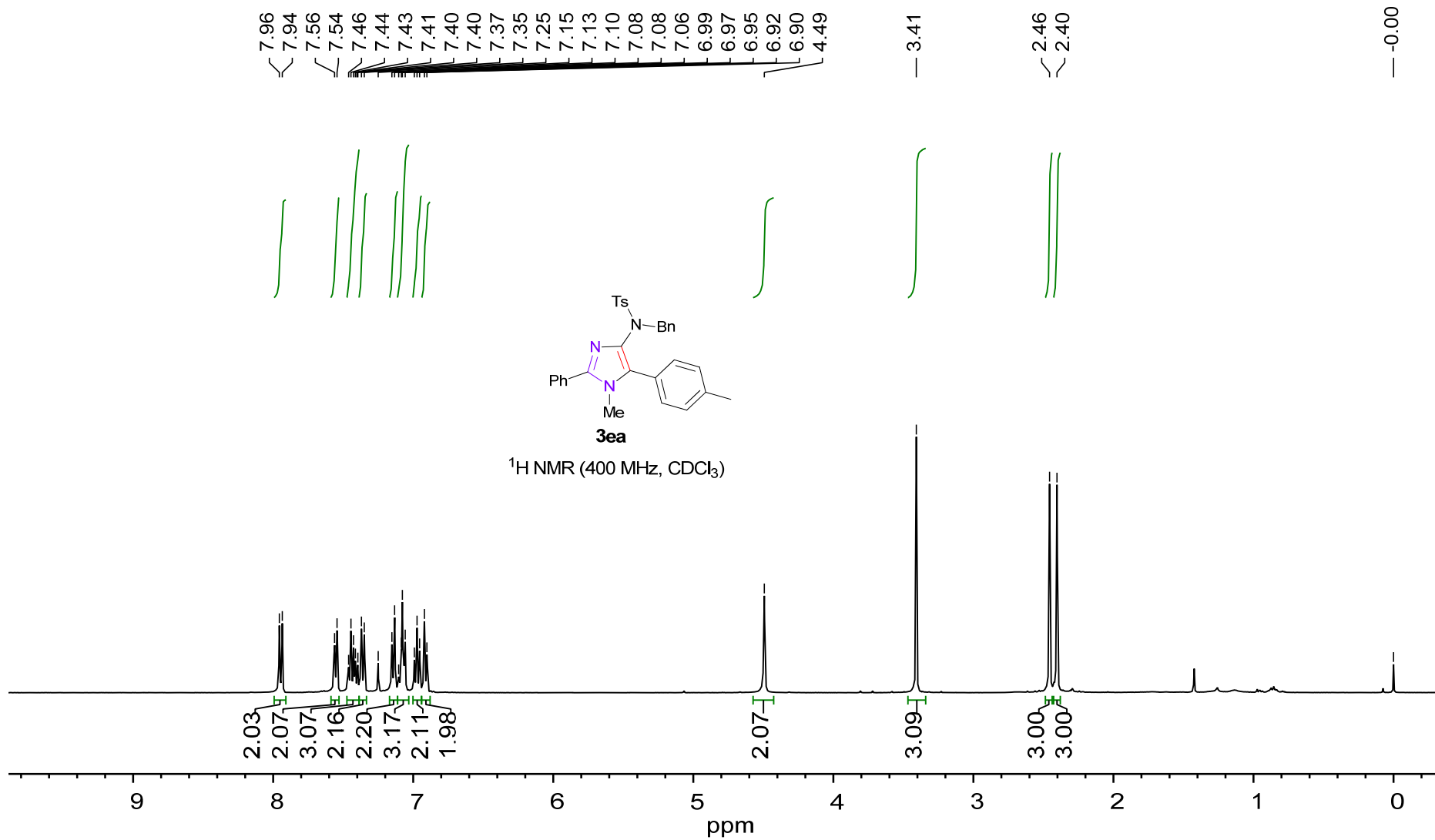


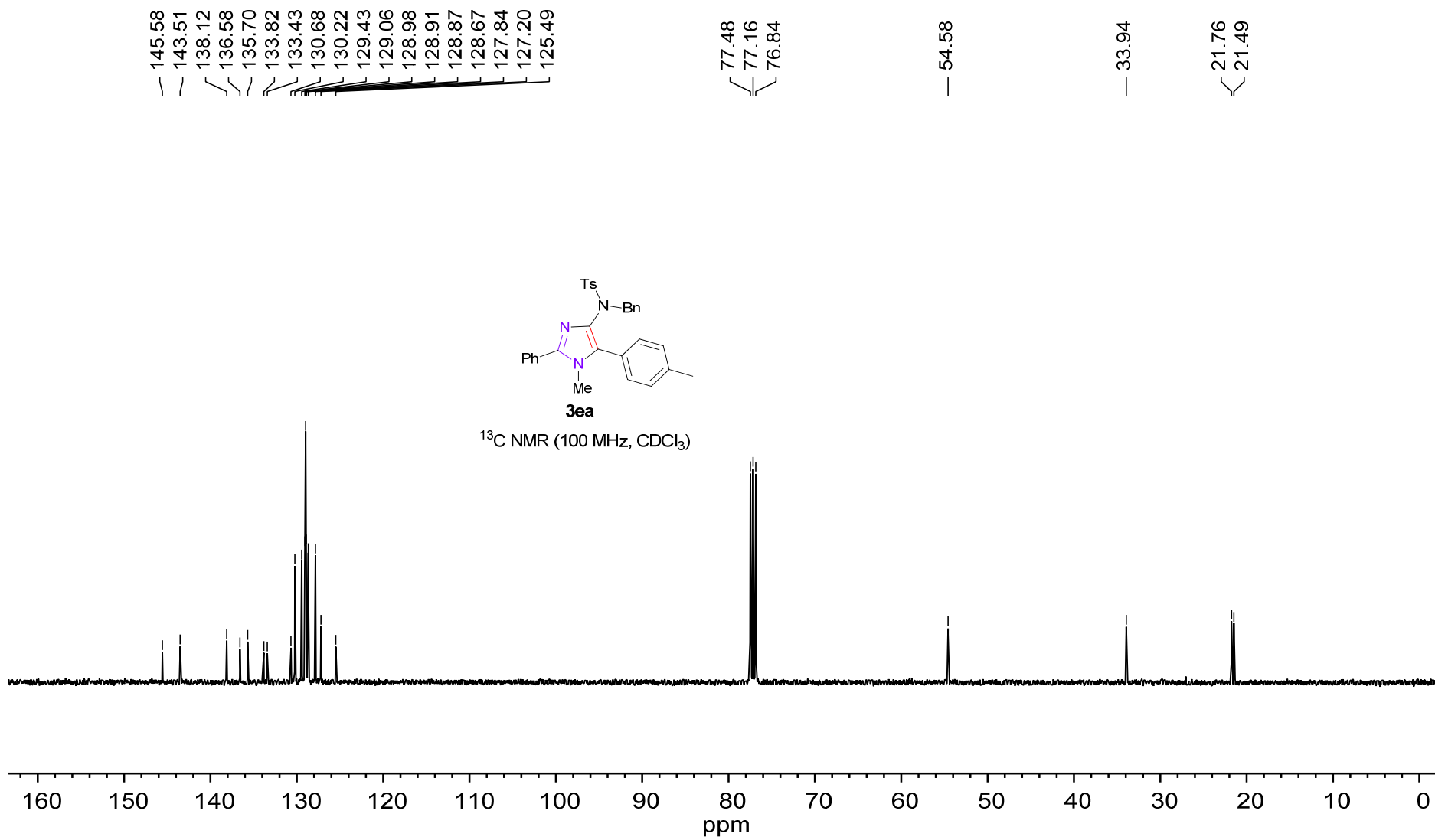


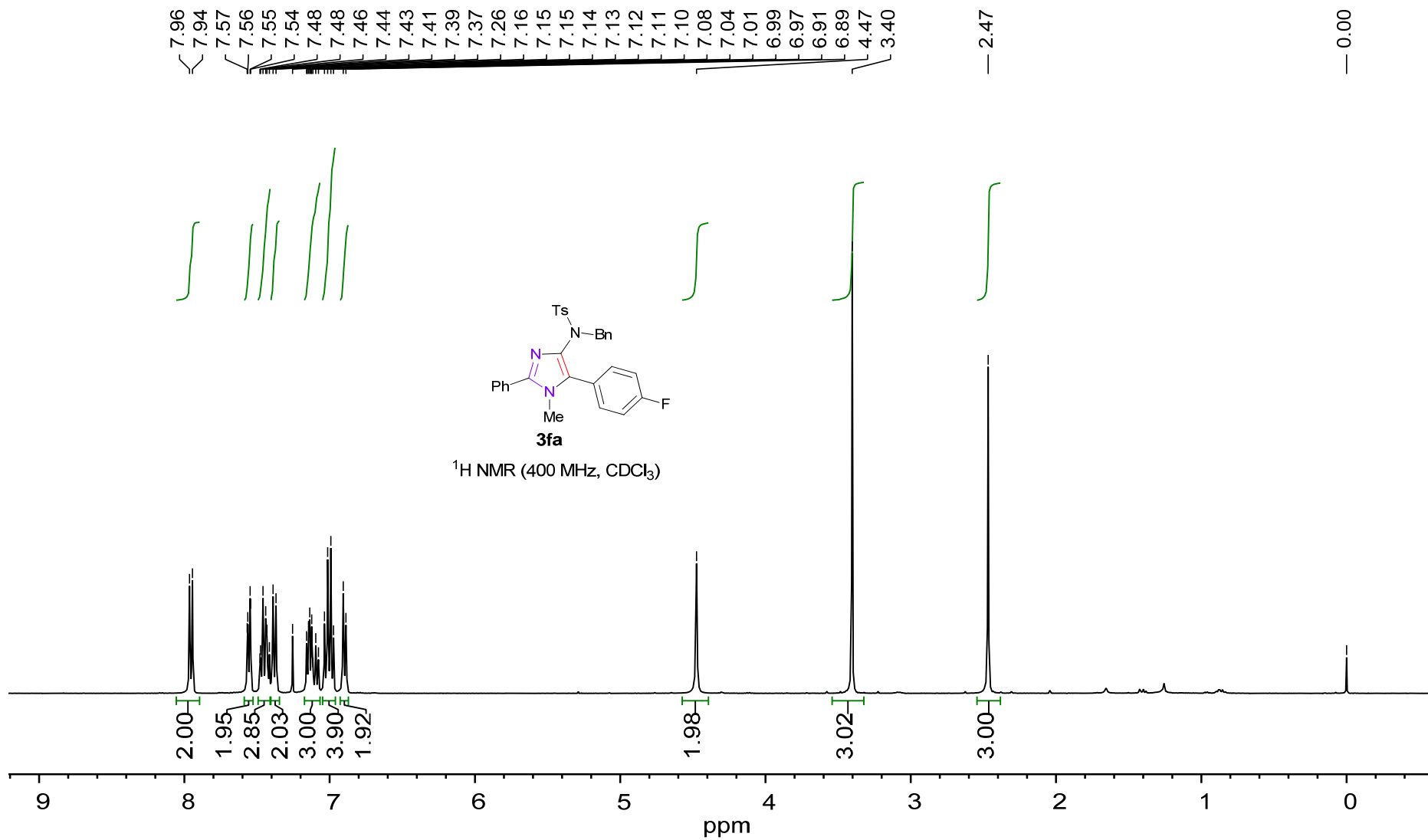
¹⁹F NMR (376 MHz, CDCl₃)

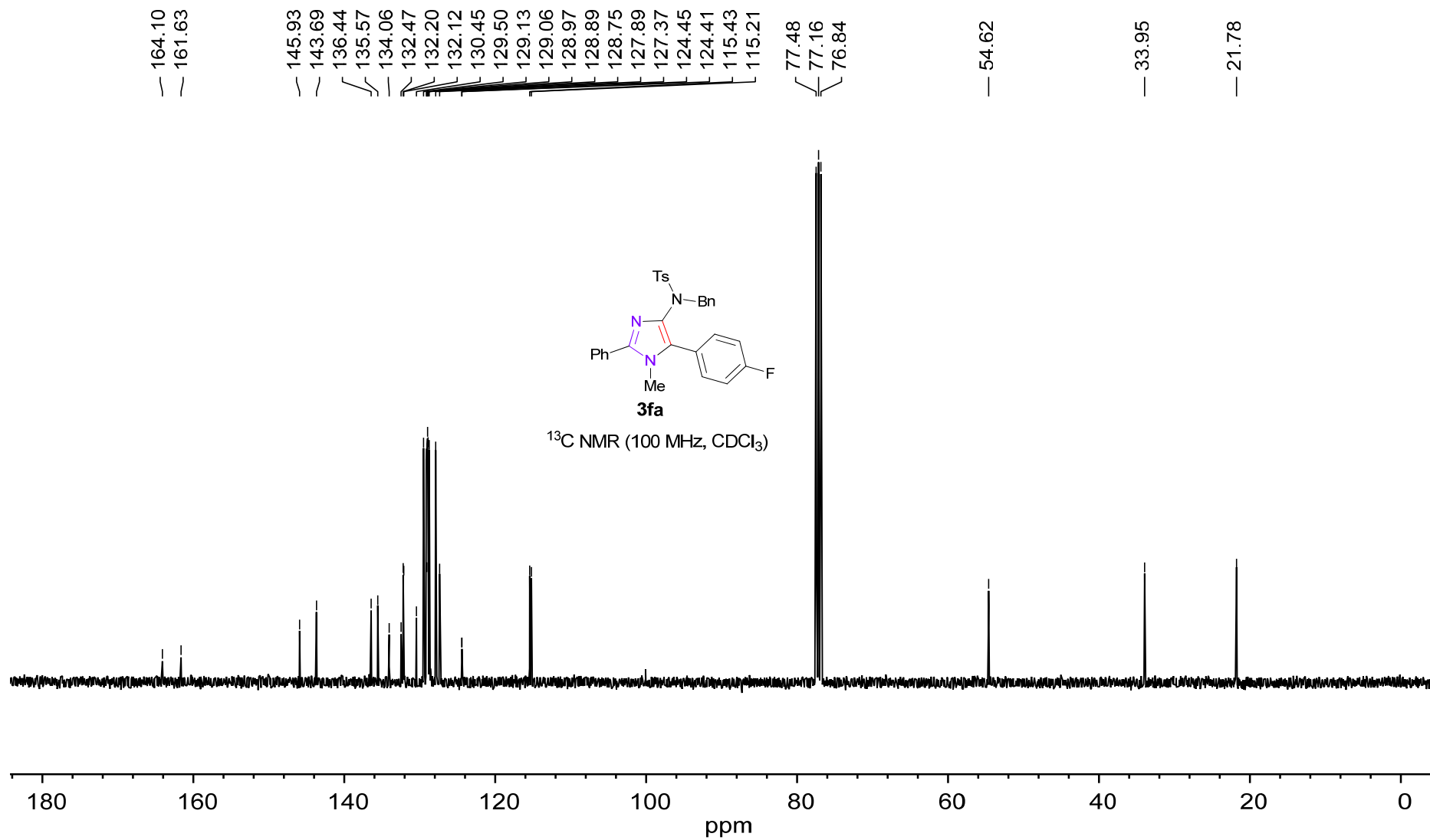
— -113.18

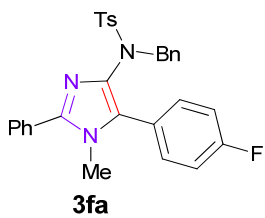






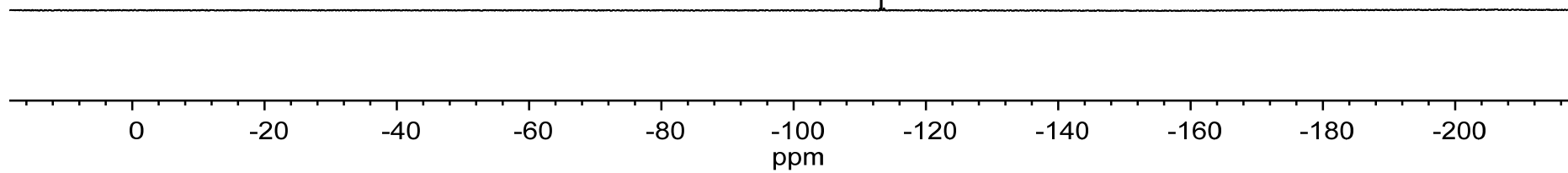


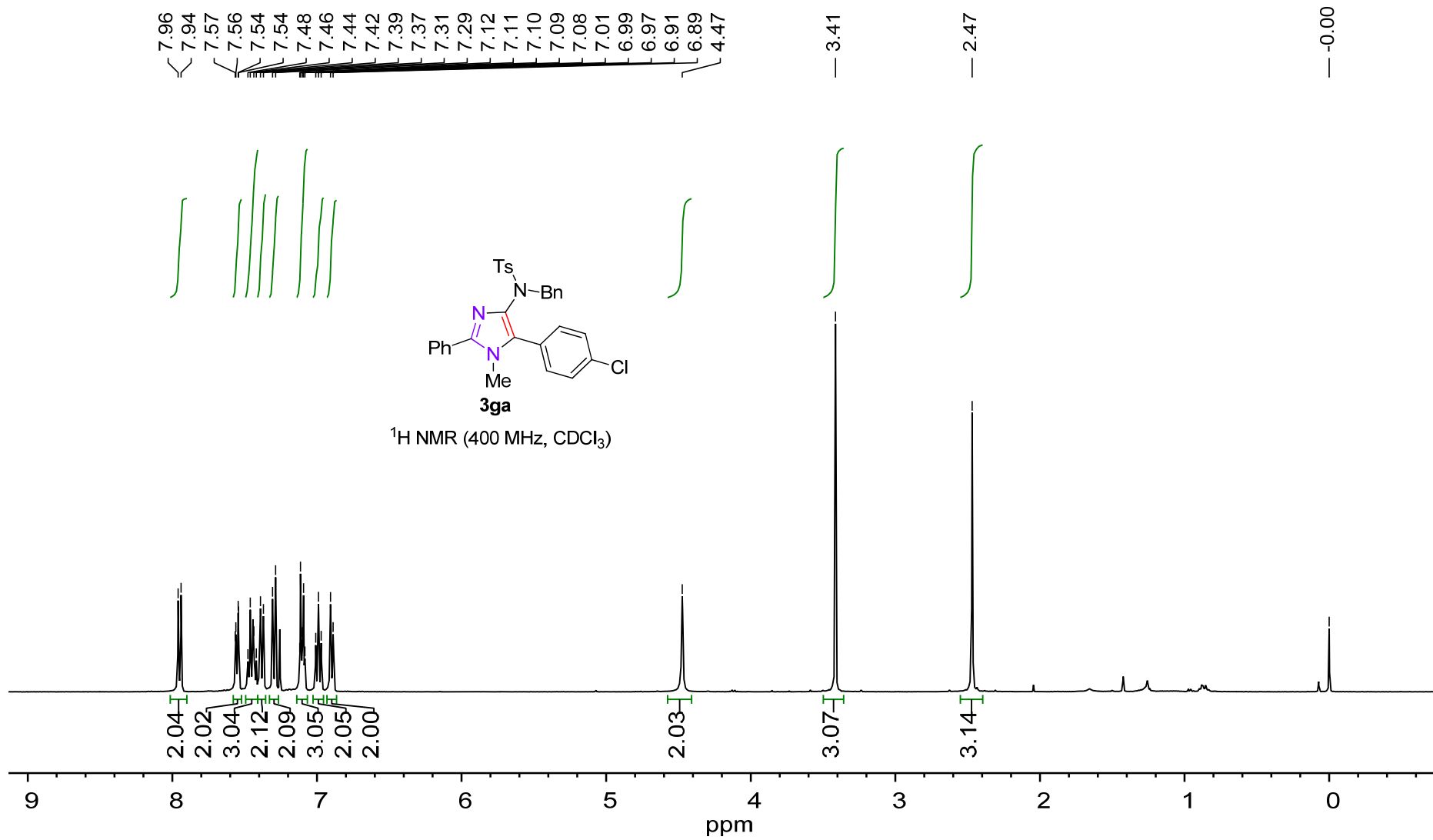


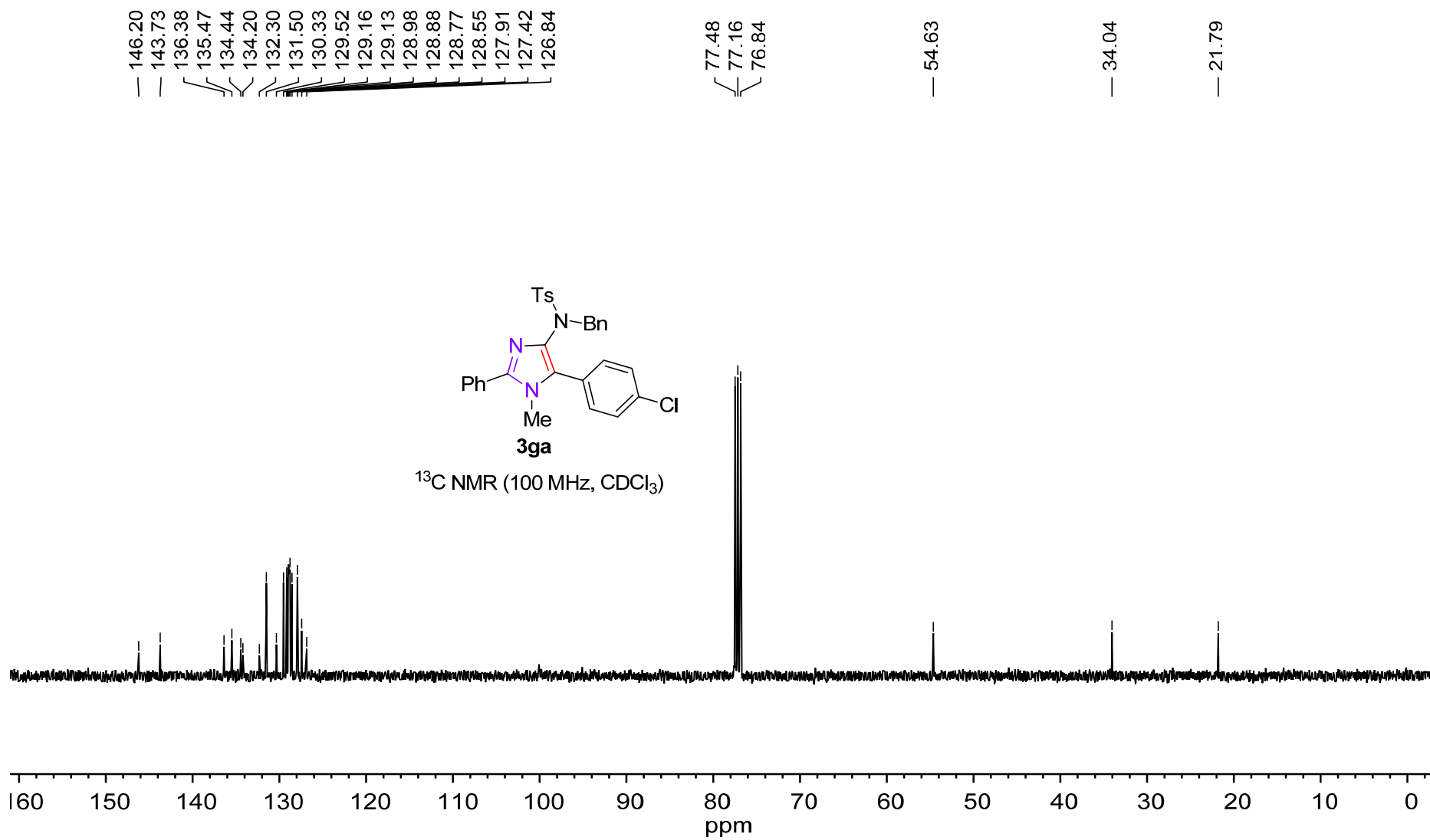


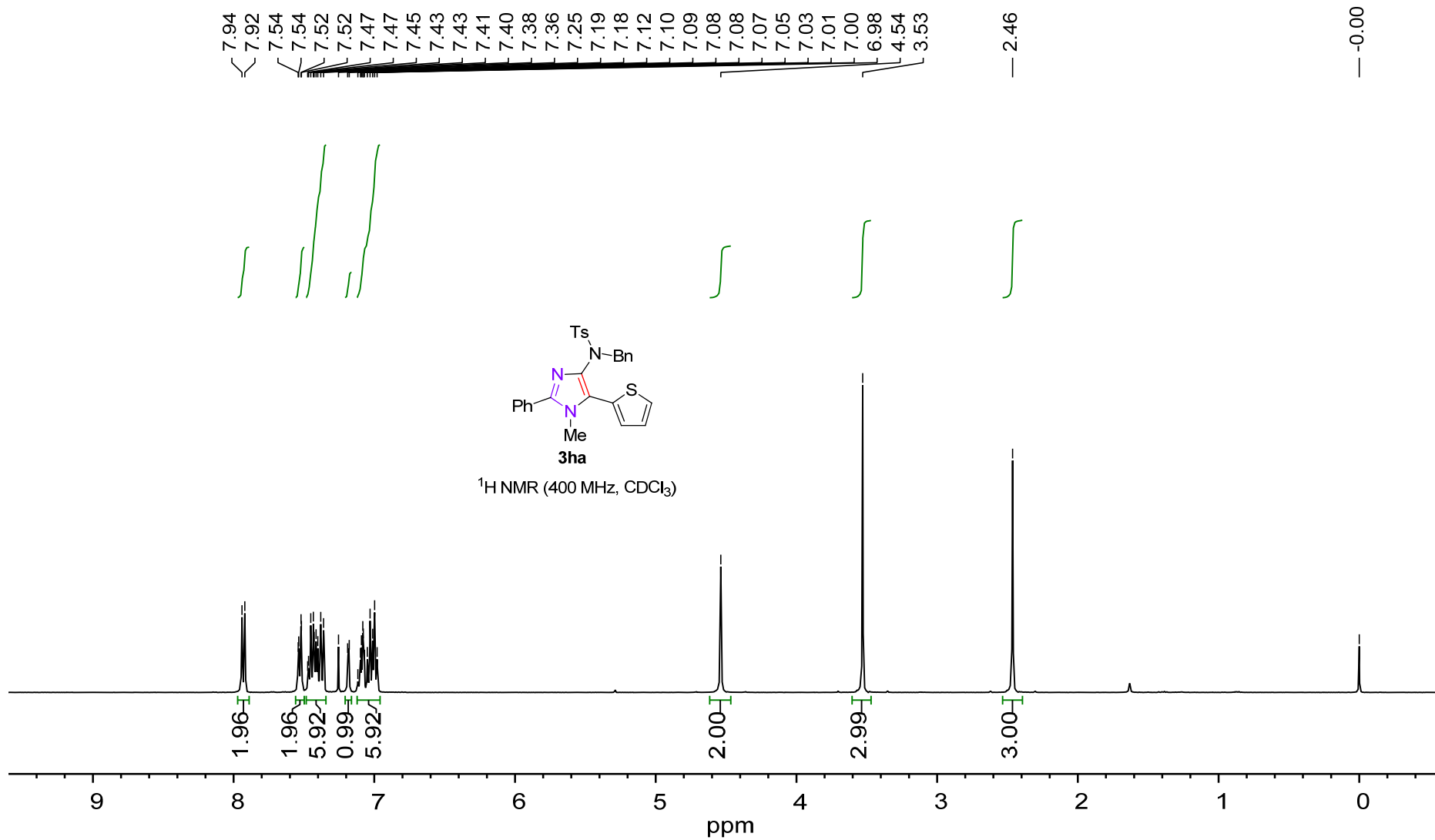
¹⁹F NMR (376 MHz, CDCl₃)

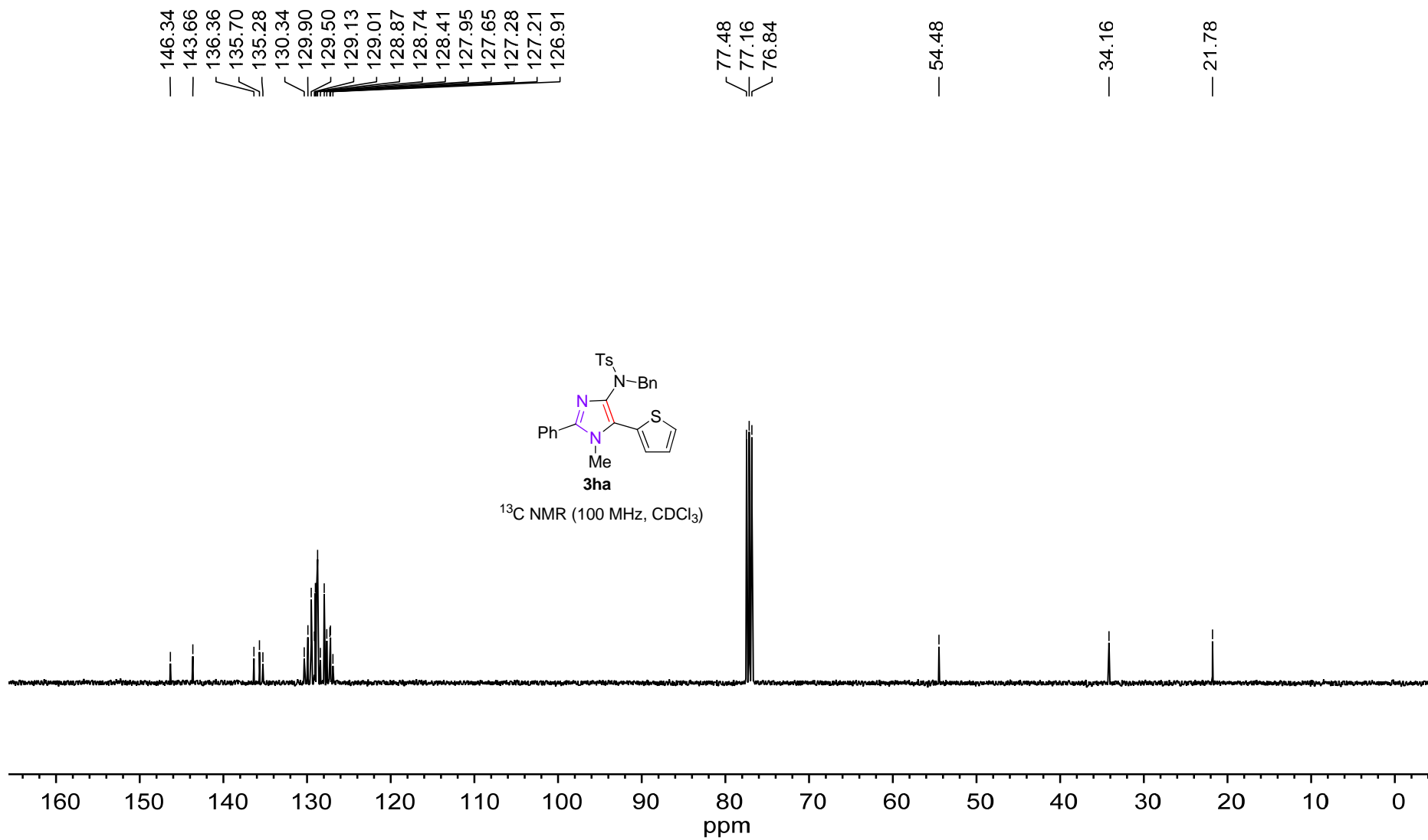
— -113.23

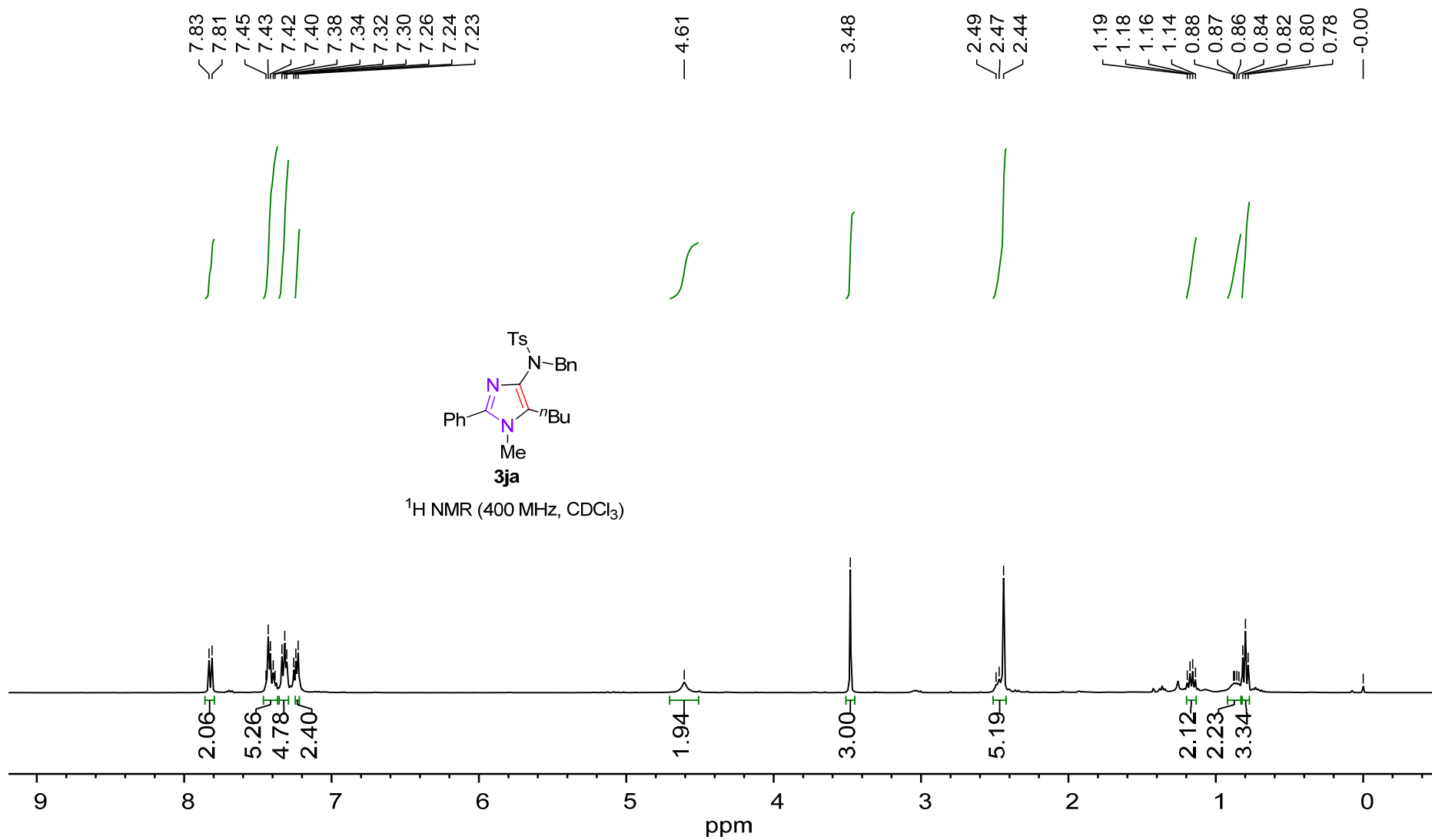












144.64
143.41
136.90
136.41
132.84
132.74
130.79
129.42
129.38
128.93
128.67
128.61
128.56
128.24
127.58

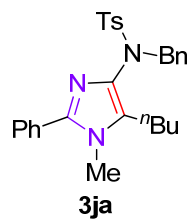
77.48
77.16
76.84

54.07

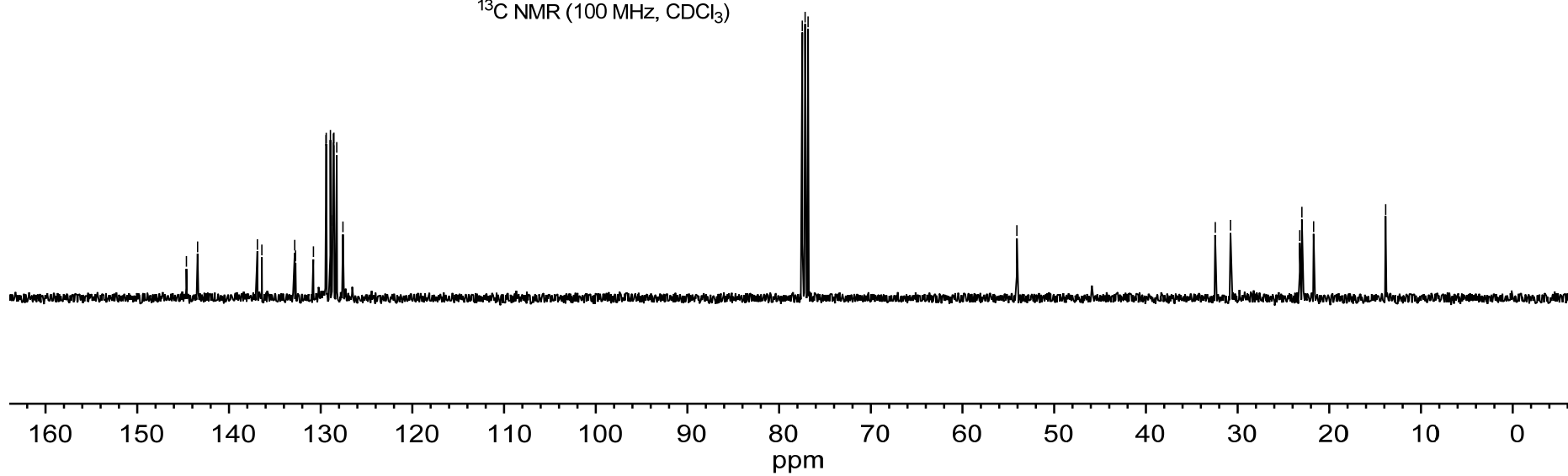
32.44
30.77

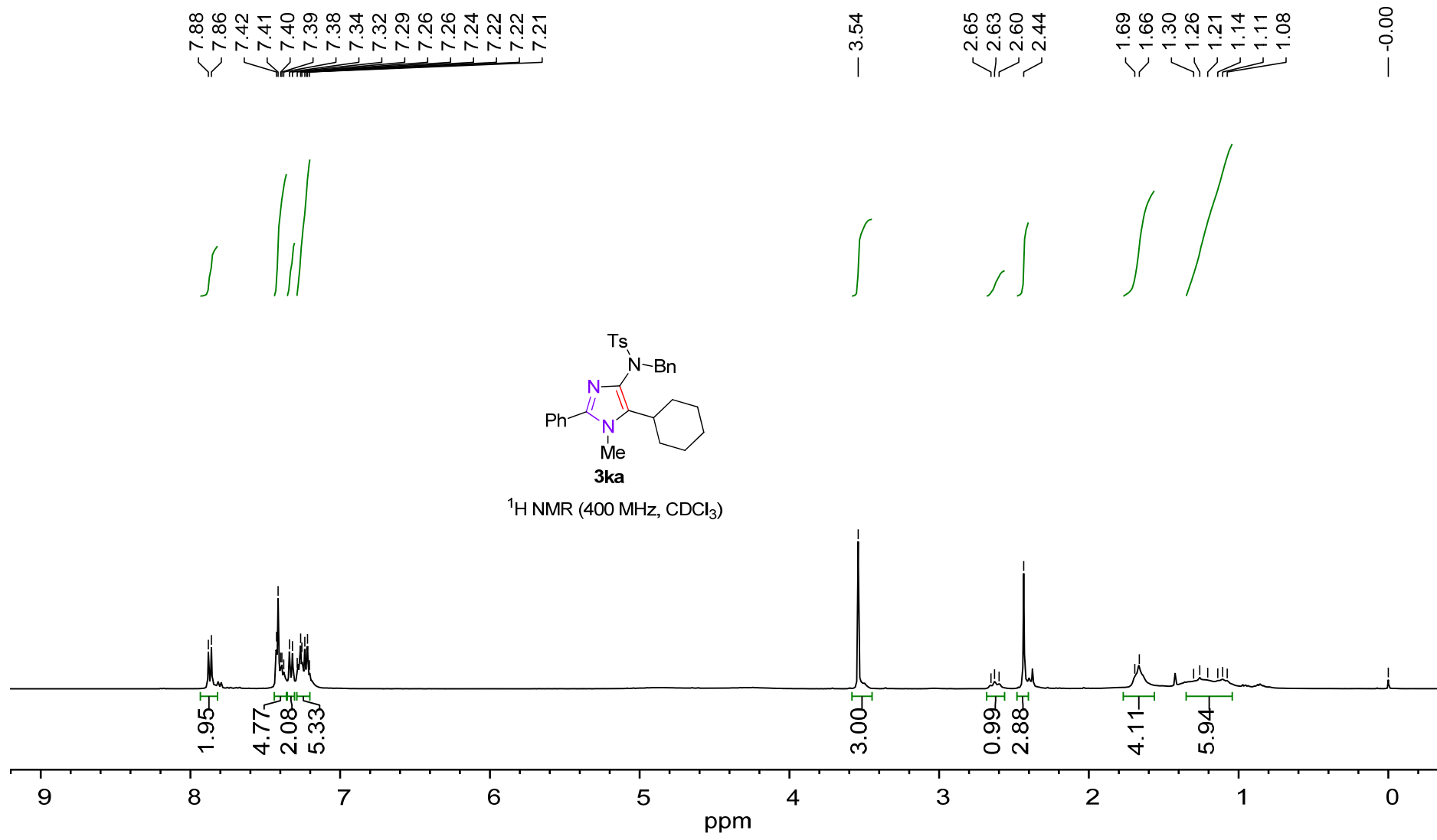
23.22
22.99
21.71

13.86



¹³C NMR (100 MHz, CDCl₃)



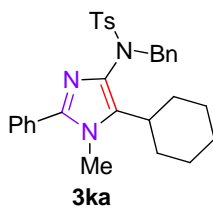


145.02
143.35
136.52
135.78
132.46
130.85
129.73
129.38
129.34
129.27
128.74
128.68
128.56
128.21
127.64
127.59

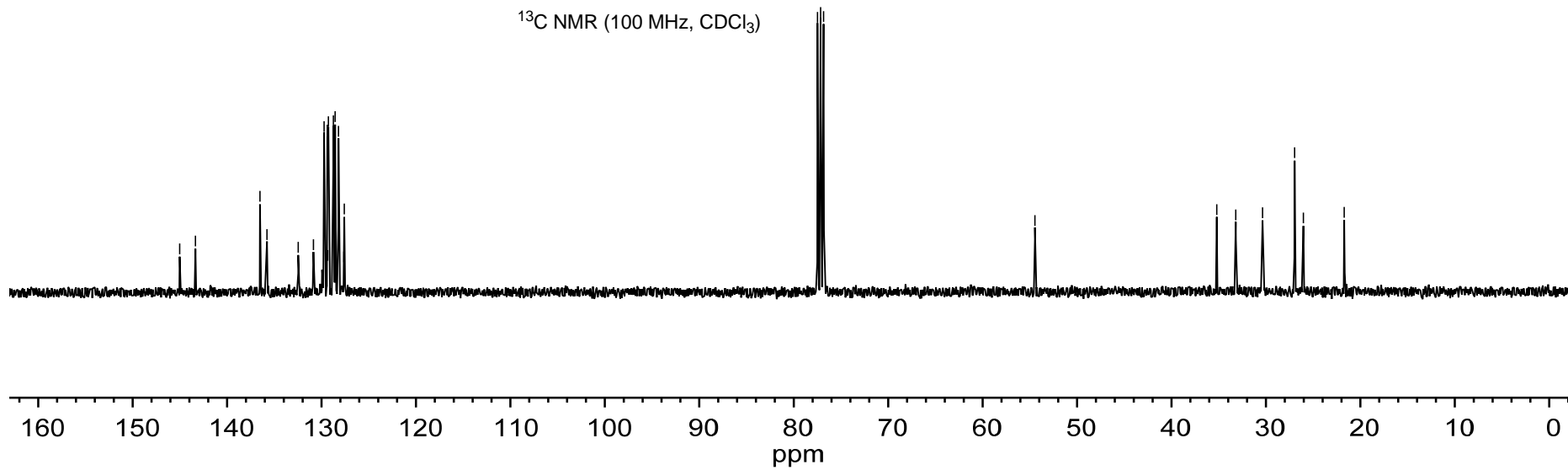
77.48
77.16
76.84

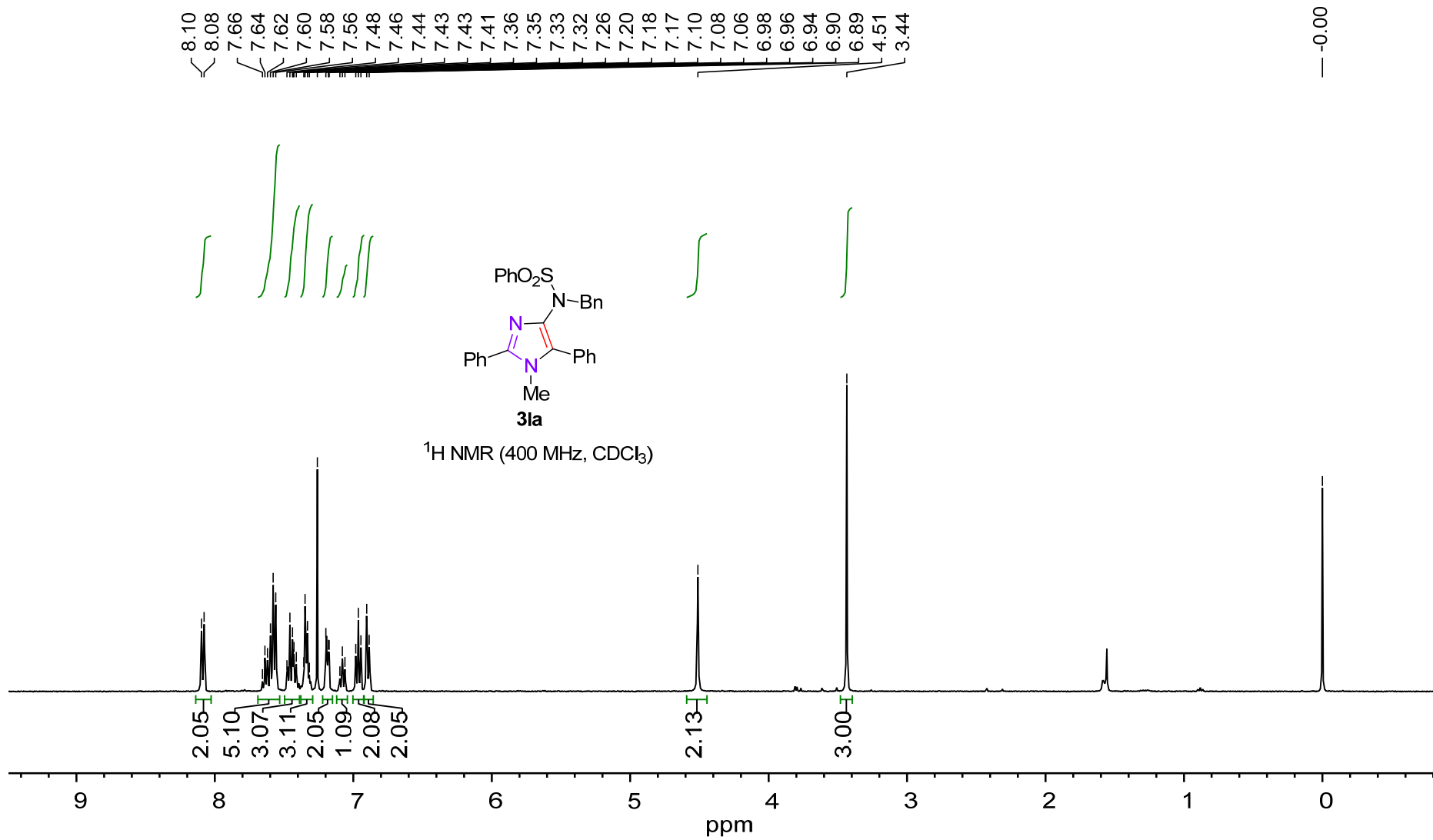
54.46

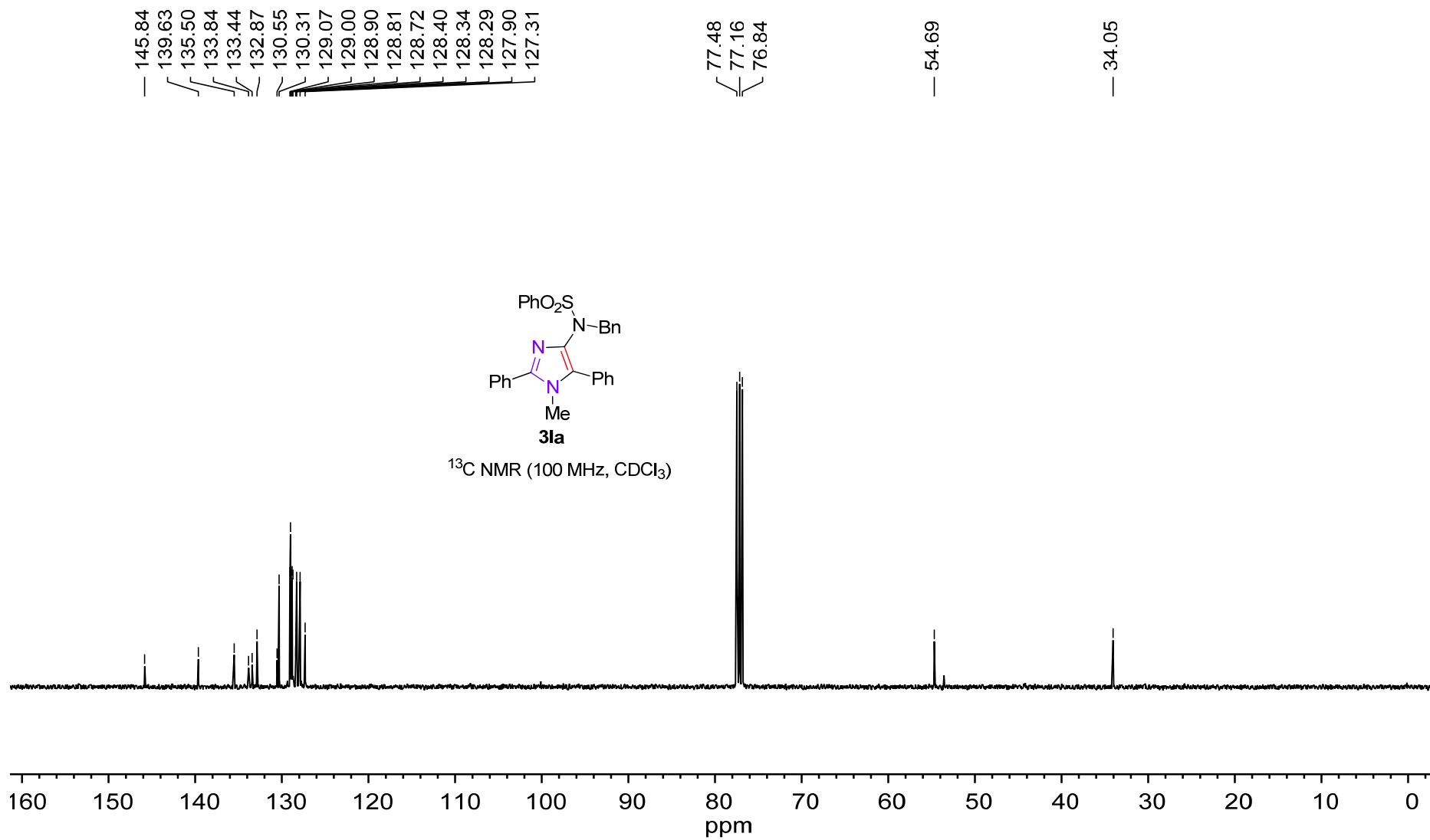
35.21
33.19
30.35
26.97
26.04
21.71

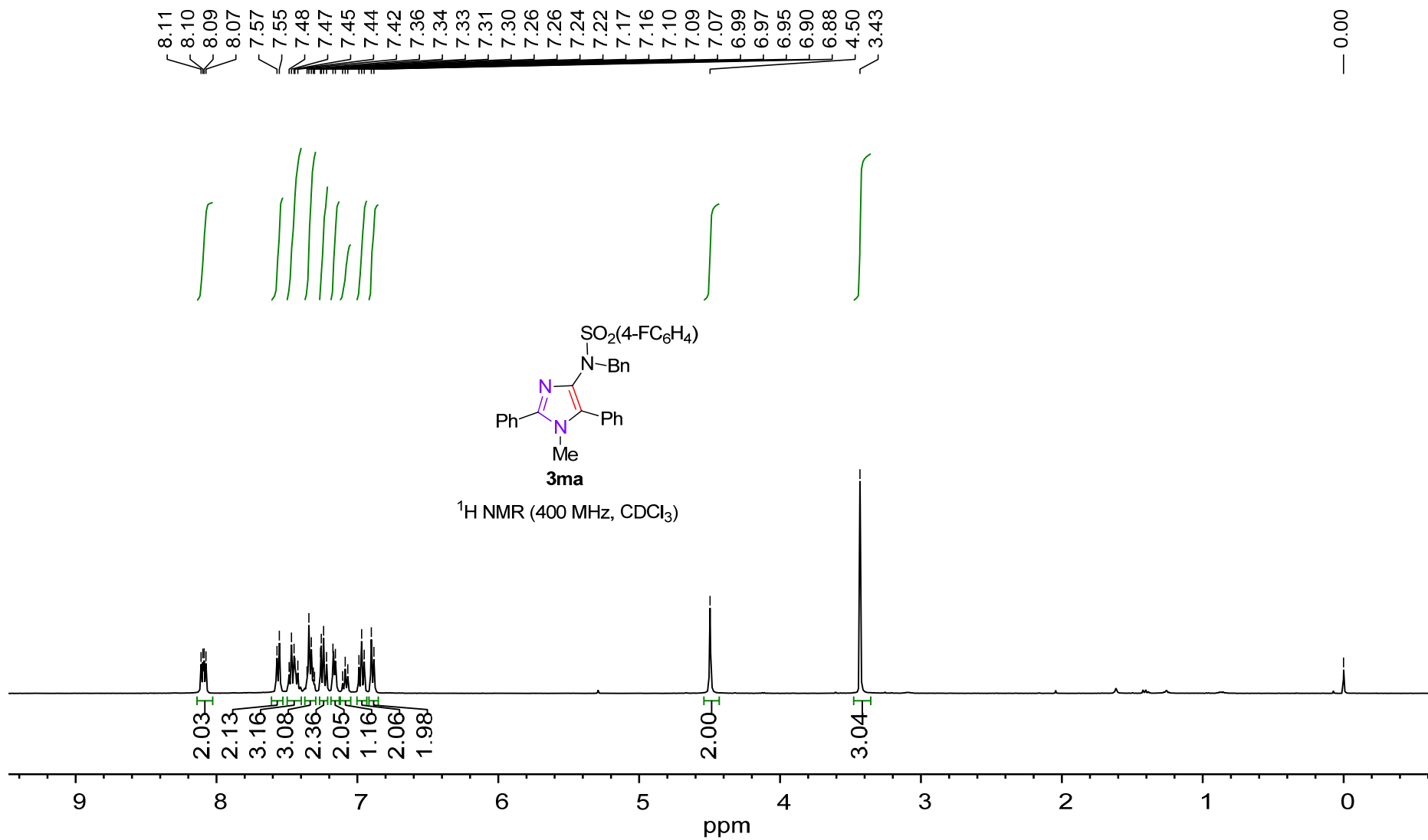


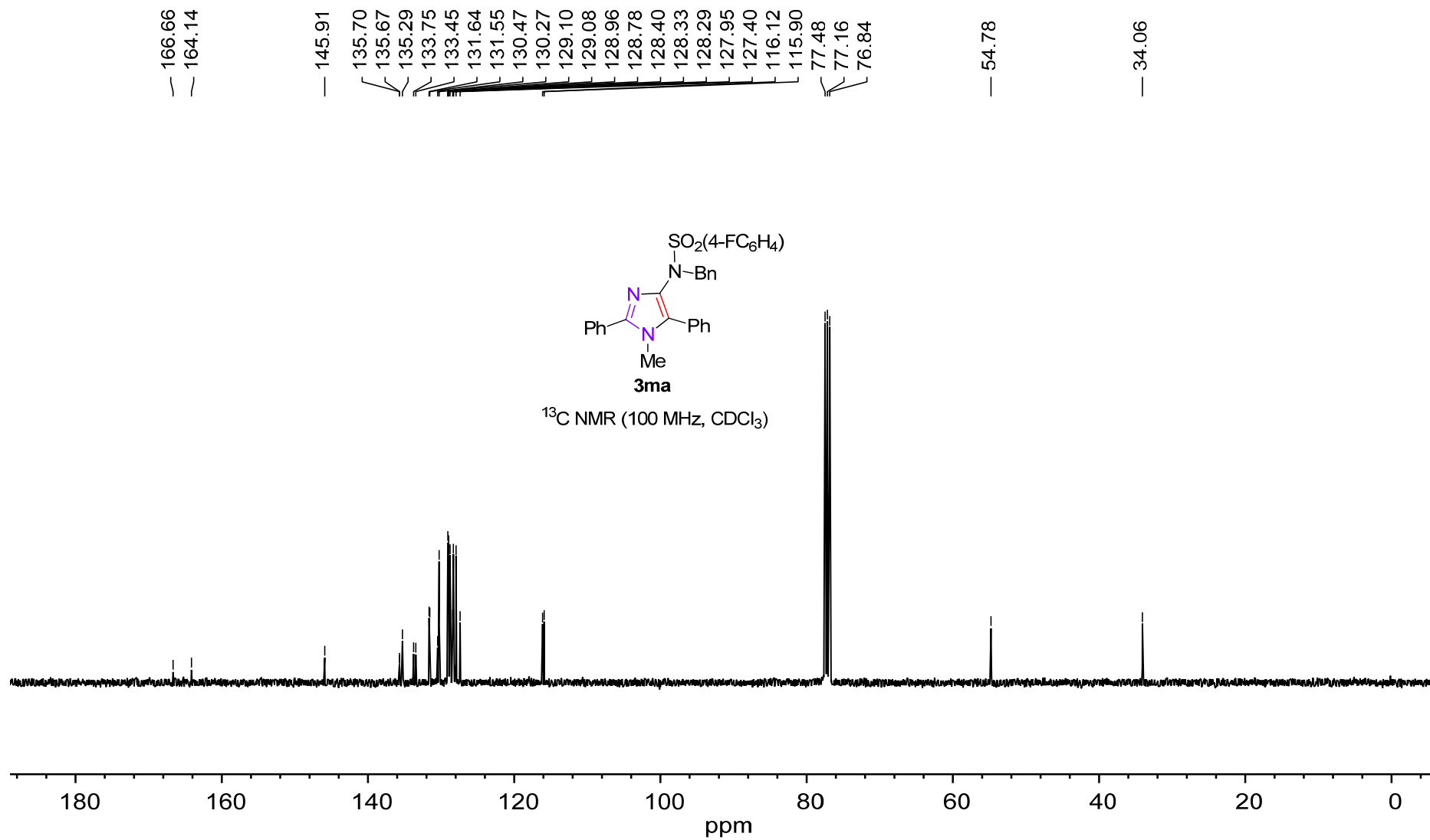
¹³C NMR (100 MHz, CDCl₃)

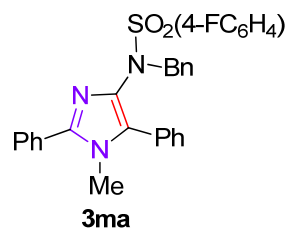






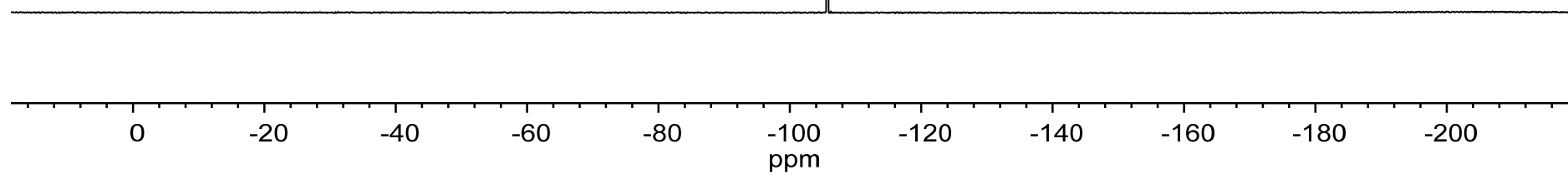


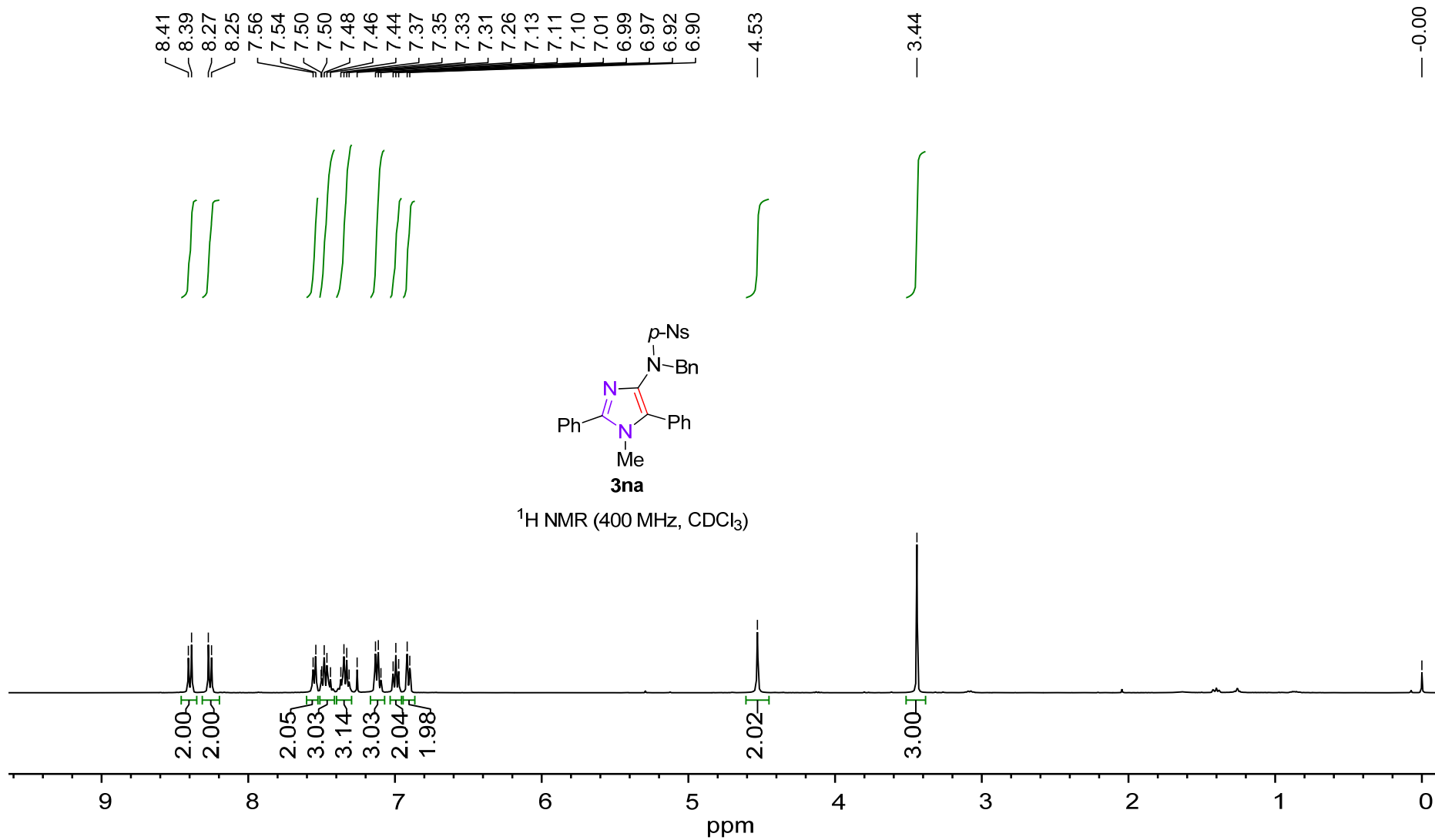


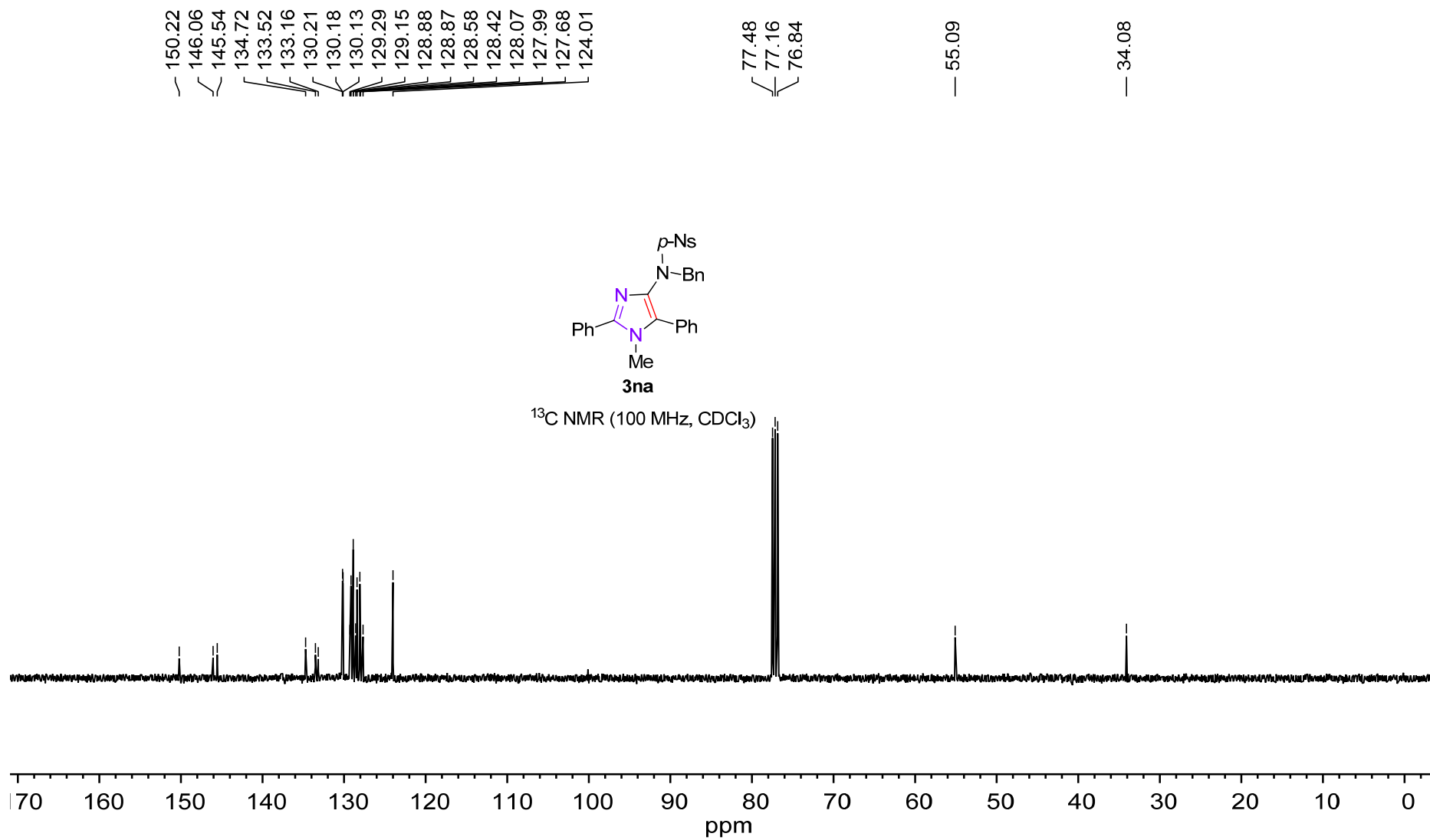


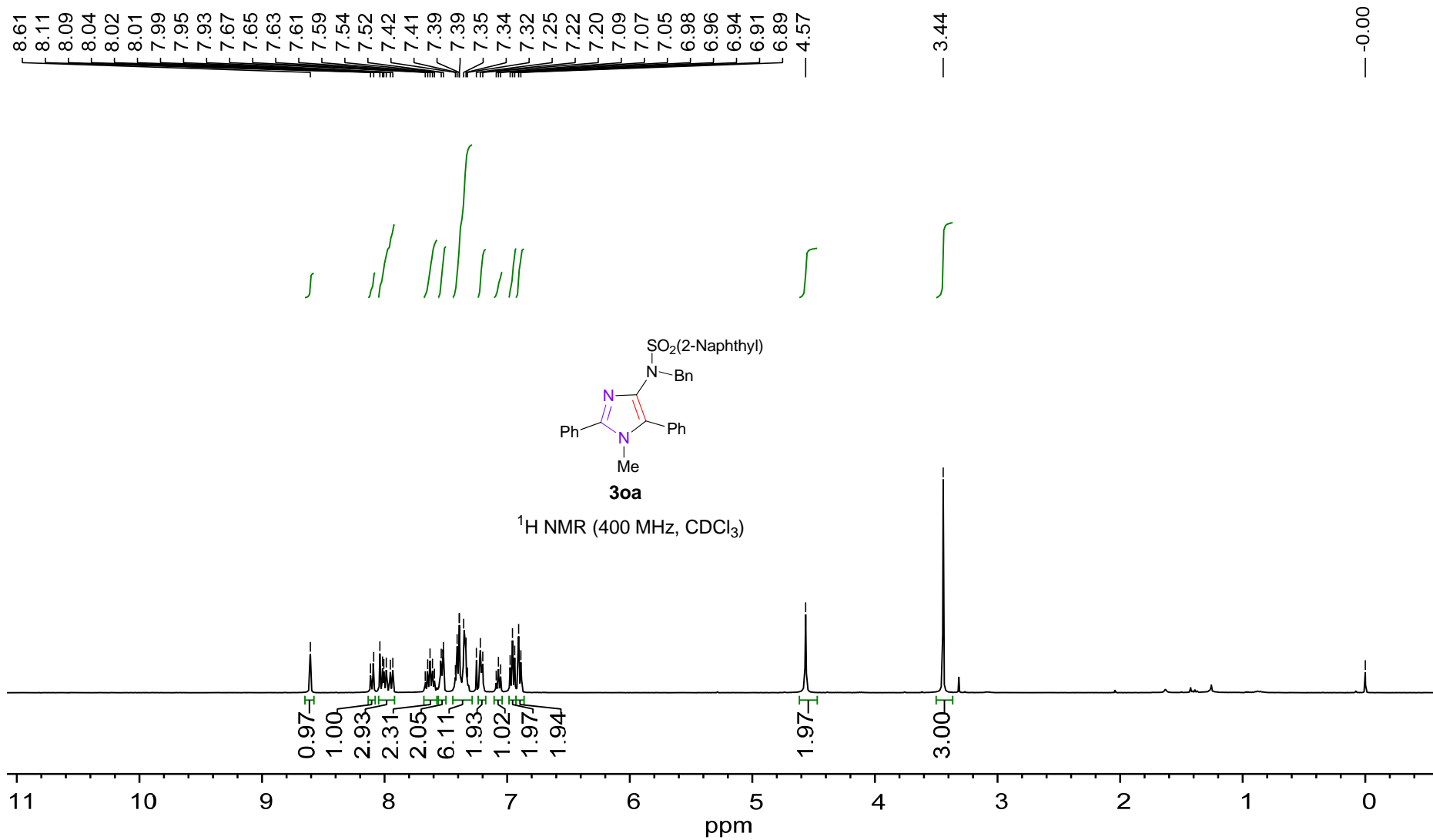
¹⁹F NMR (376 MHz, CDCl₃)

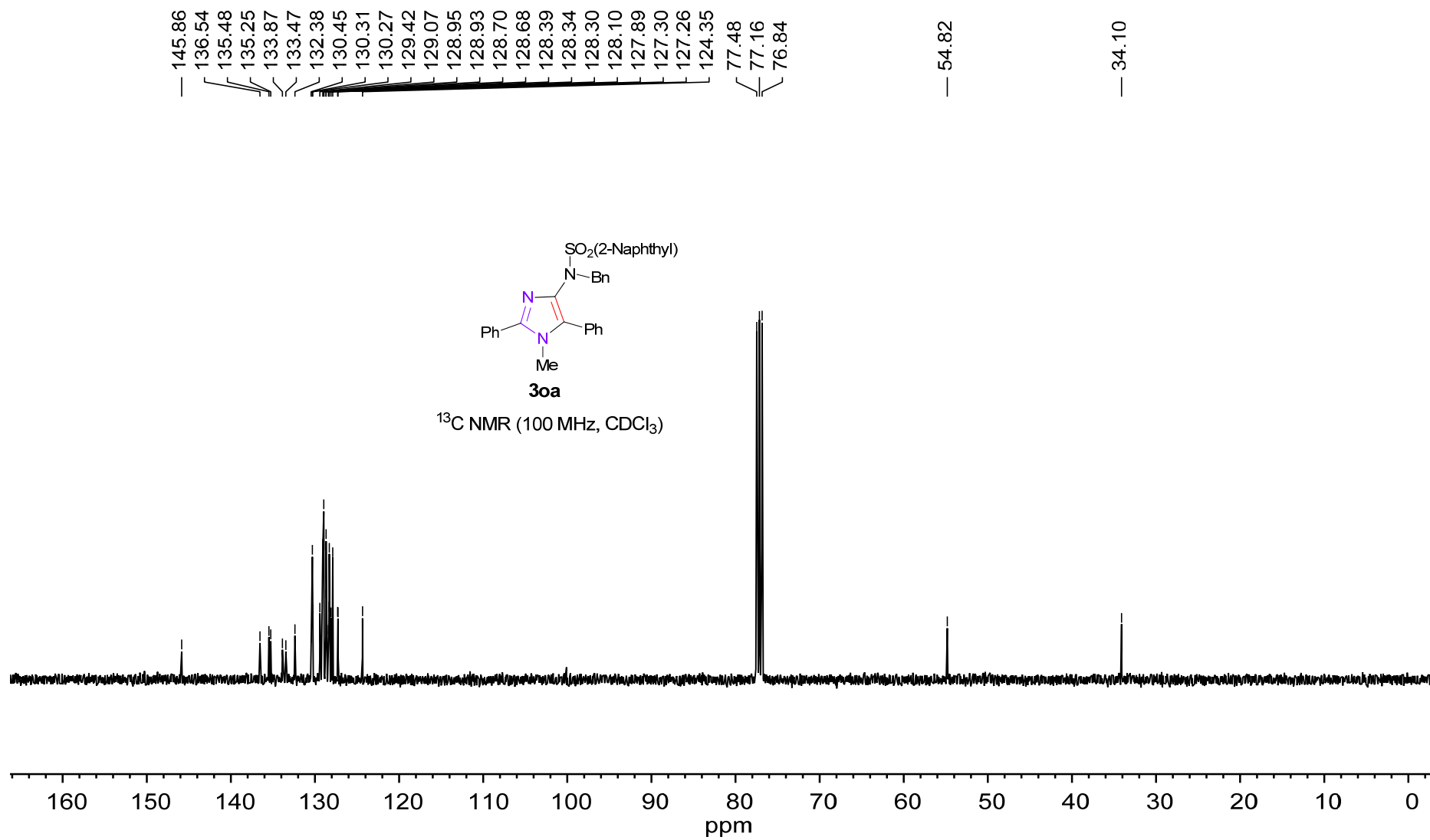
— -105.76

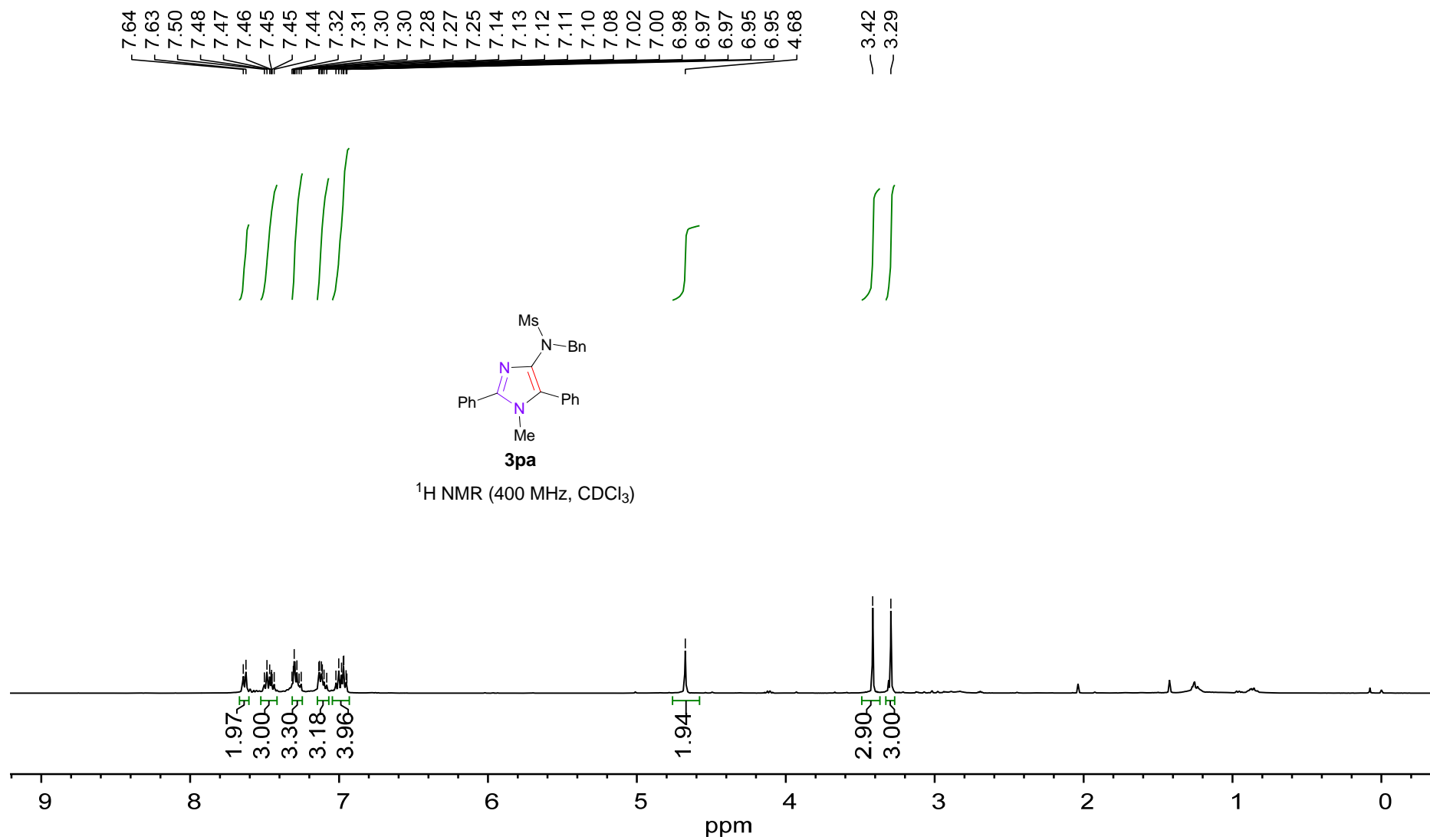










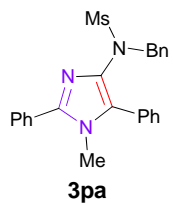


146.09
135.50
134.00
132.79
130.39
130.12
129.14
129.08
129.06
128.77
128.29
128.25
128.08
127.94
127.40

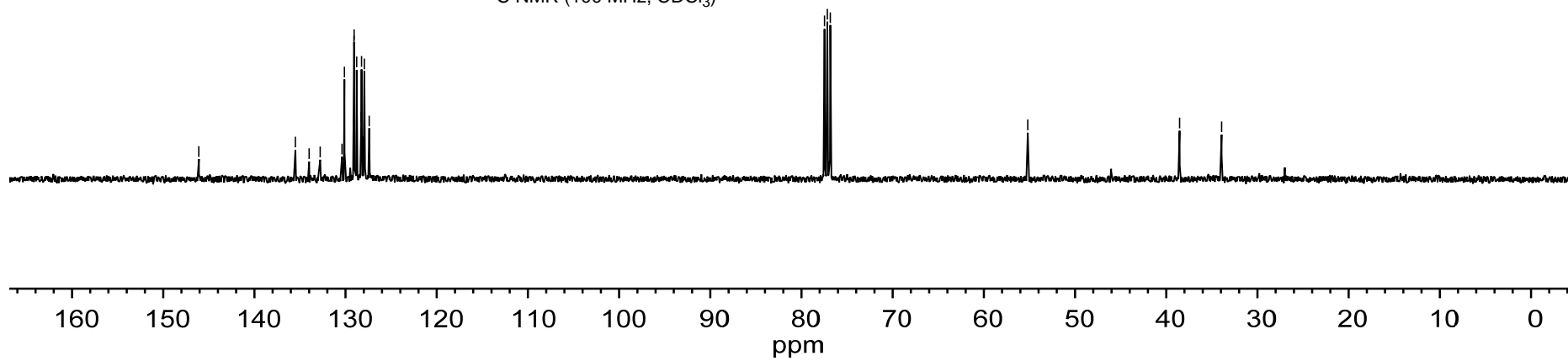
77.48
77.16
76.84

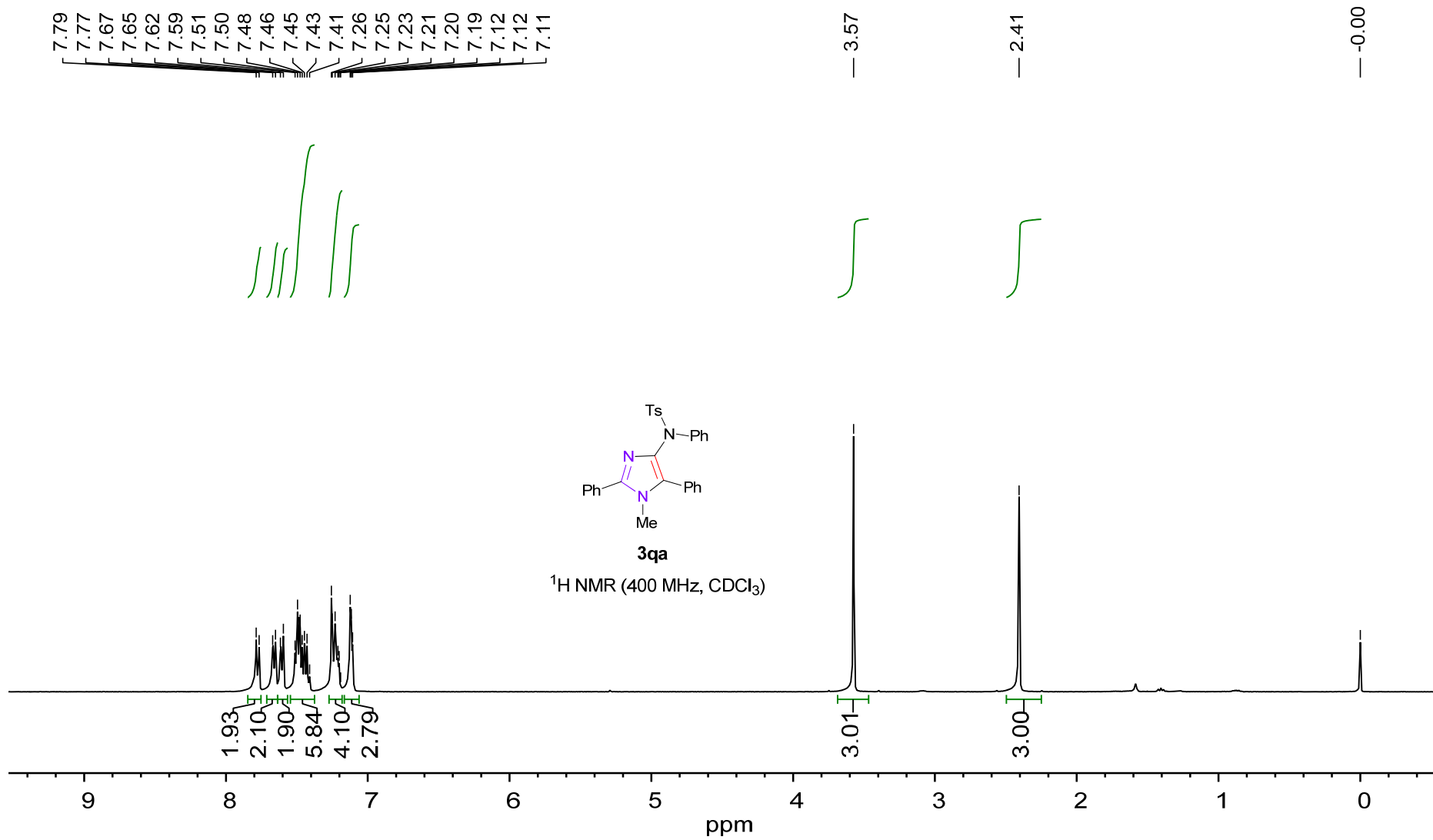
55.18

38.53
33.93



¹³C NMR (100 MHz, CDCl₃)



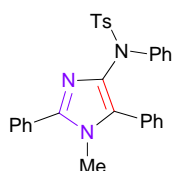


145.78
143.41
141.00
136.69
136.15
132.04
130.75
130.16
129.15
129.13
129.09
128.96
128.75
128.73
128.65
128.52
128.27
127.20

77.48
77.16
76.84

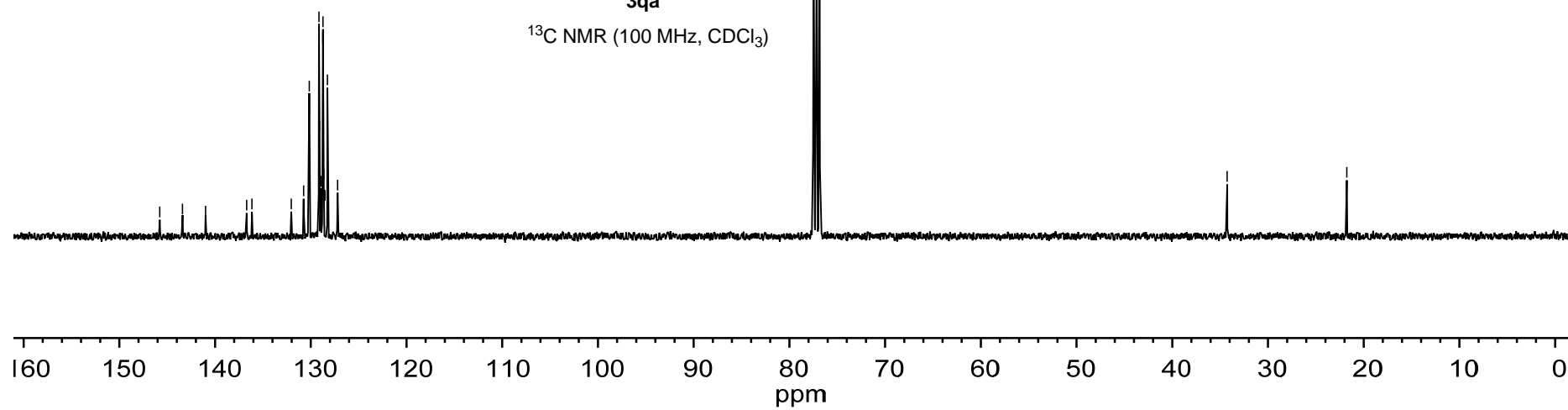
— 34.27

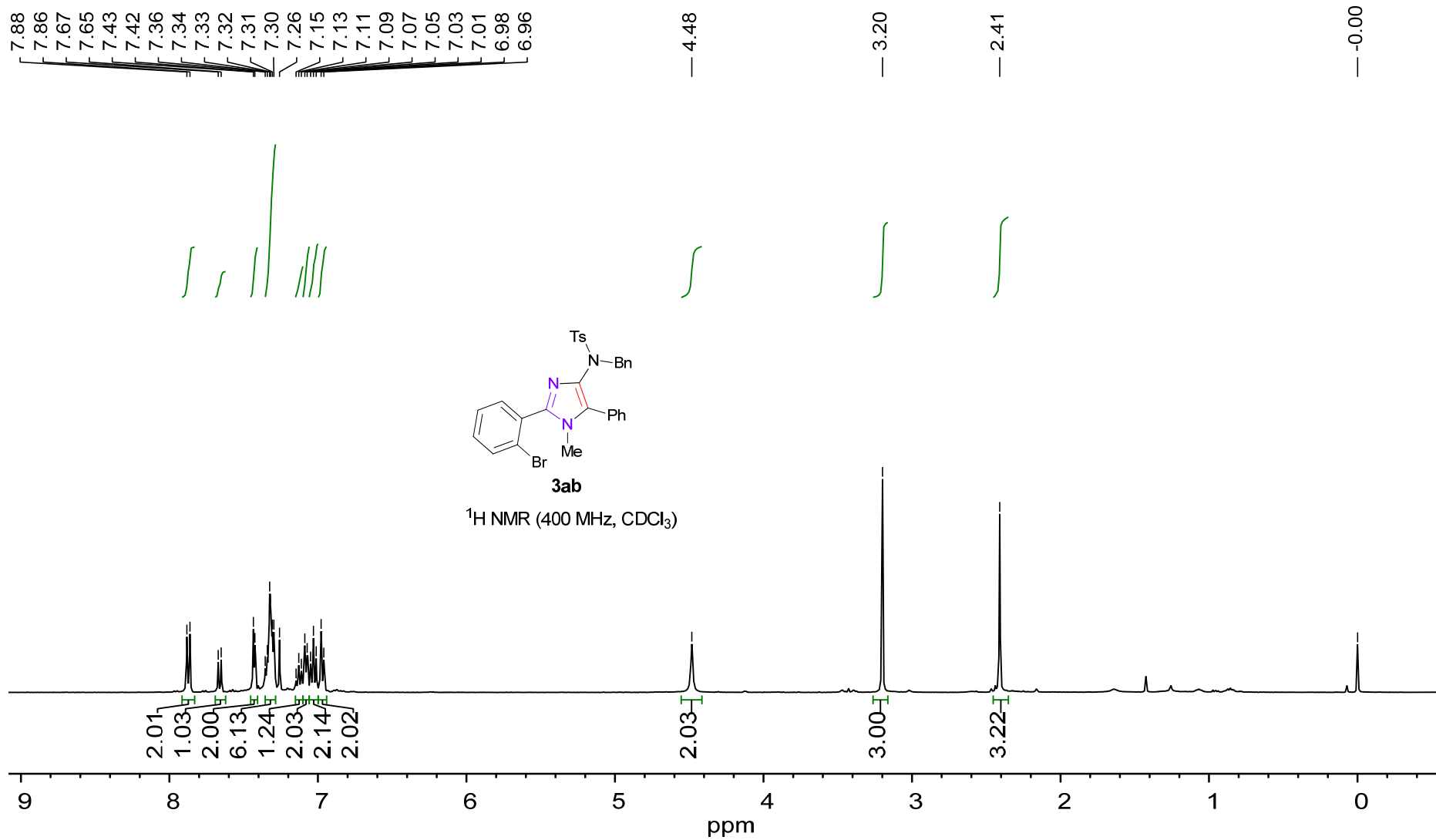
— 21.77

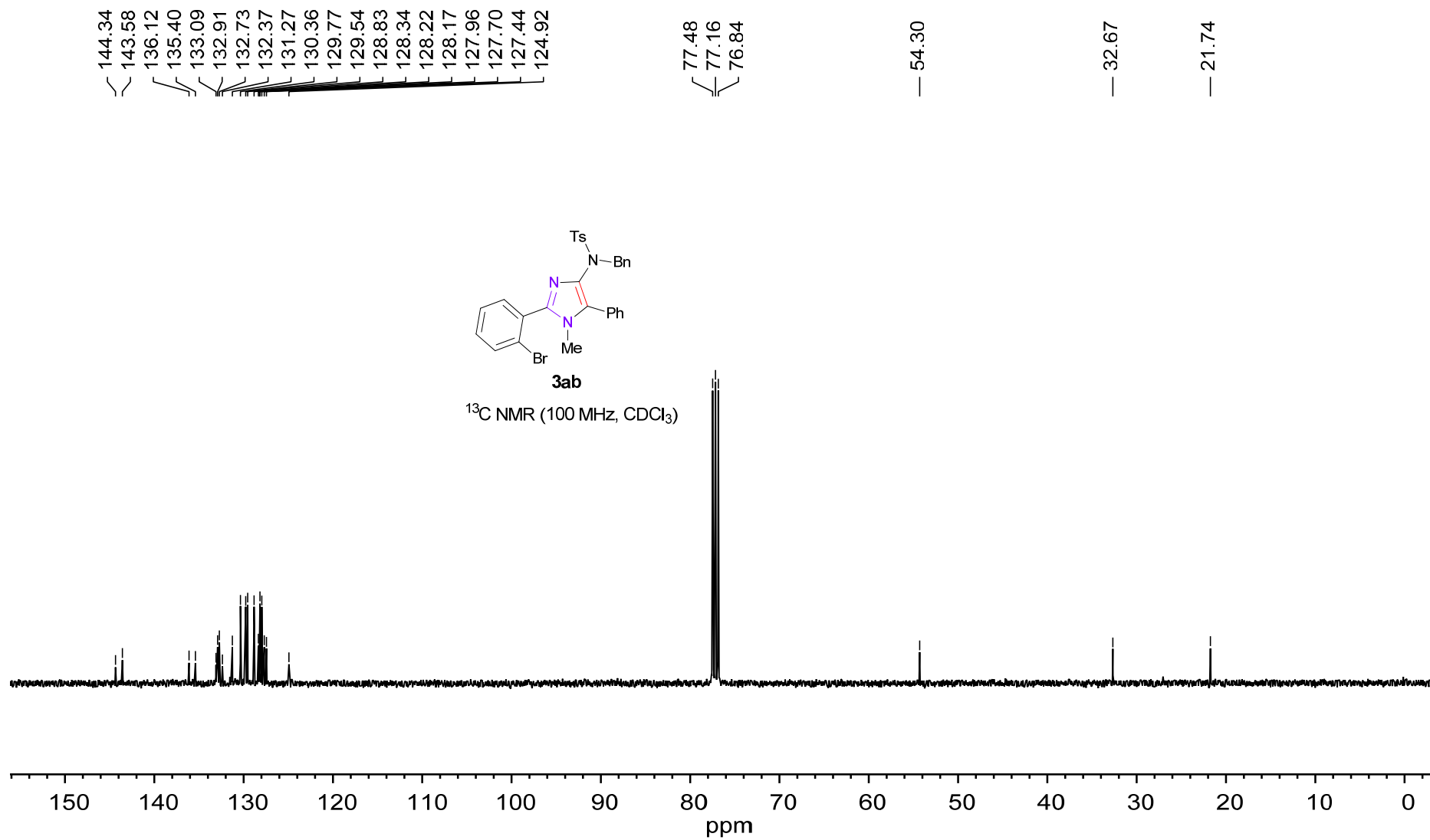


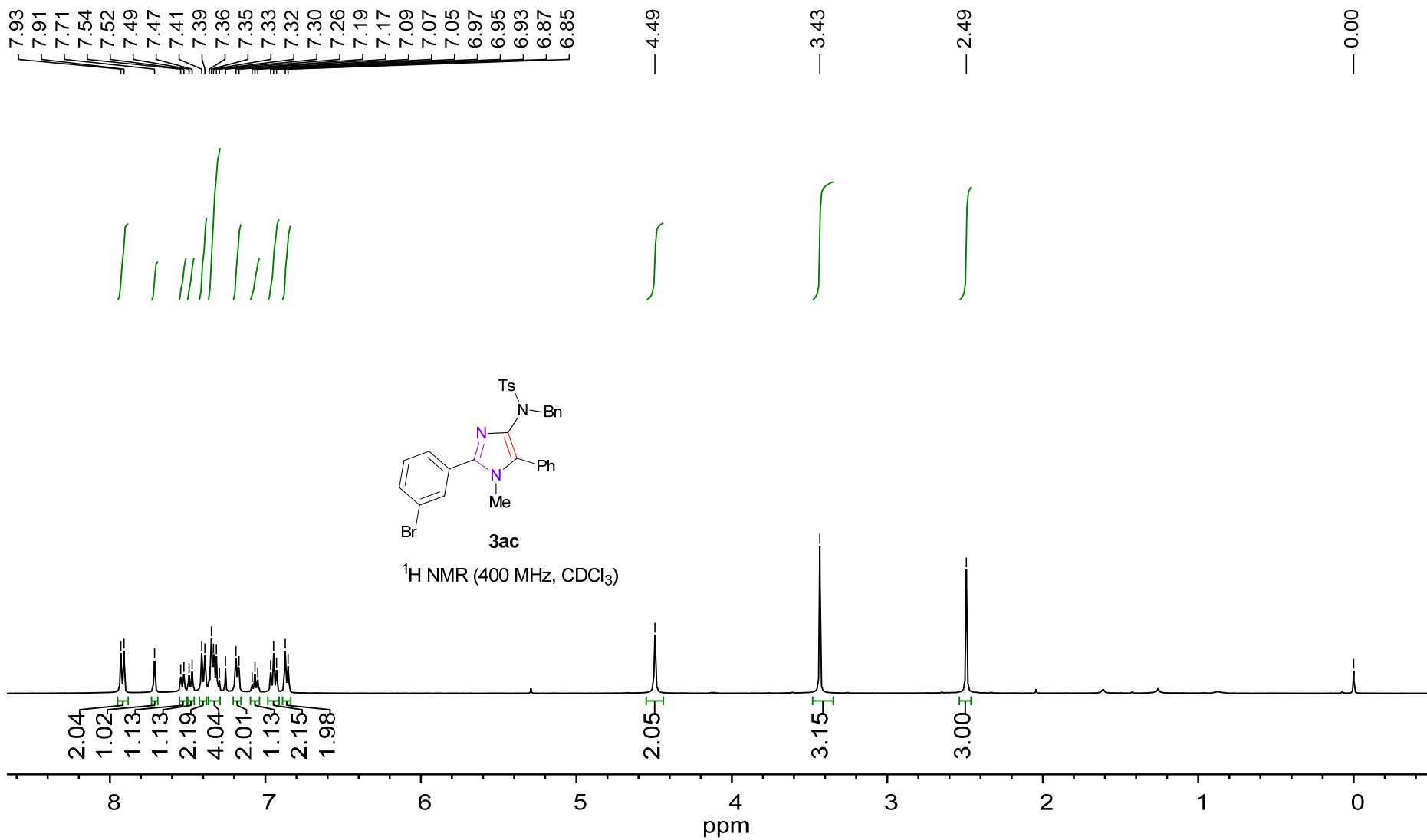
3qa

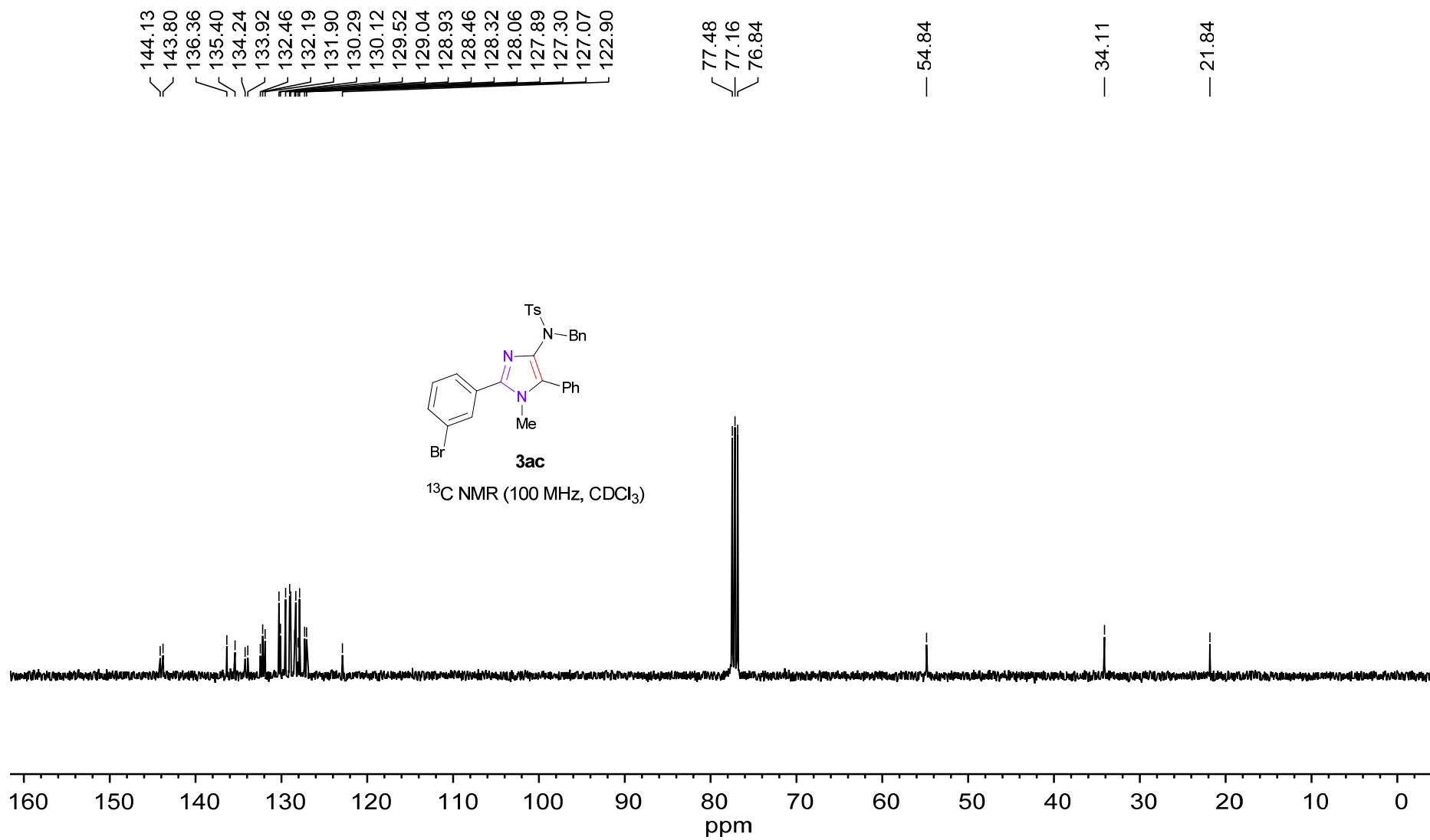
¹³C NMR (100 MHz, CDCl₃)

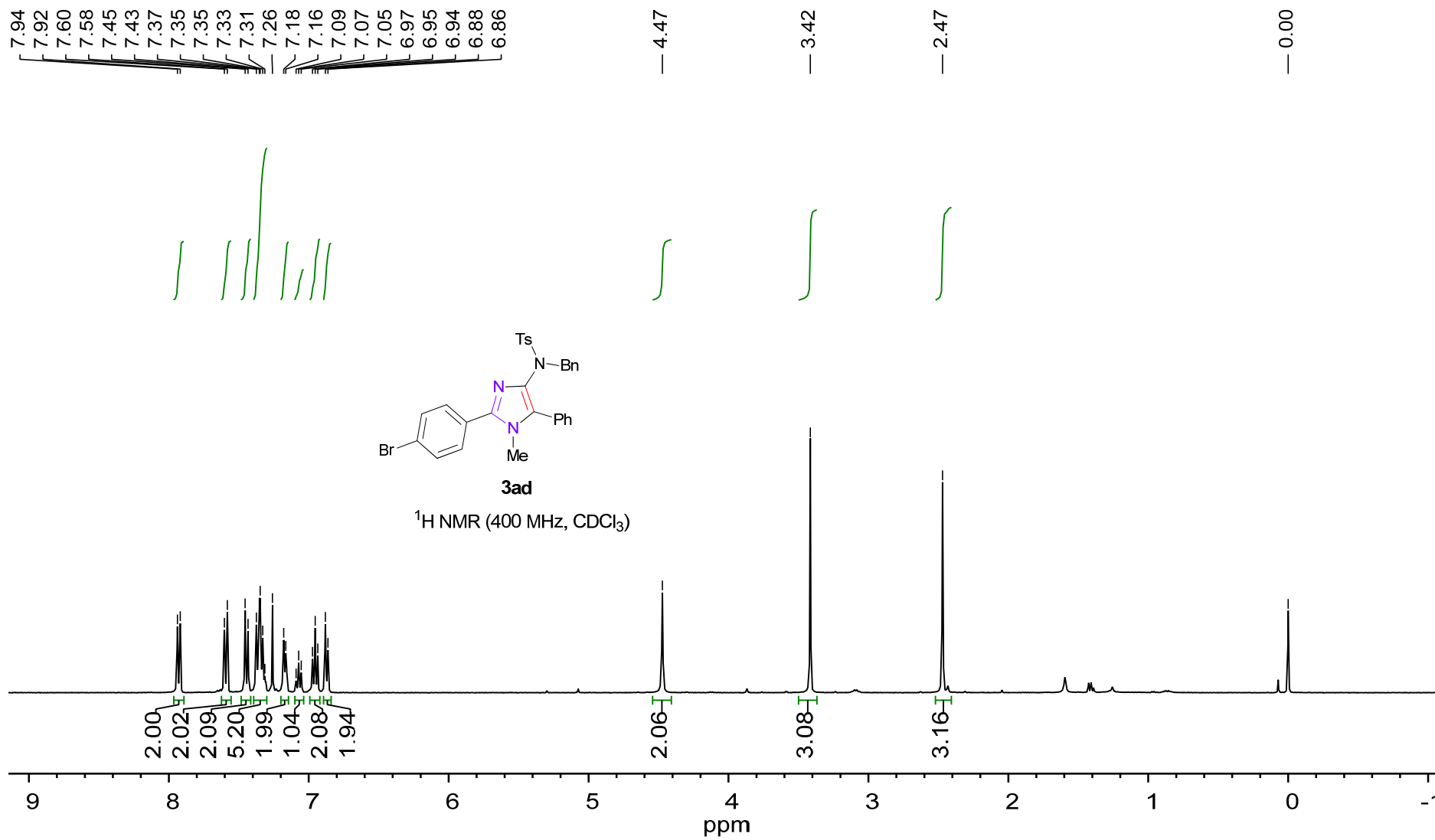


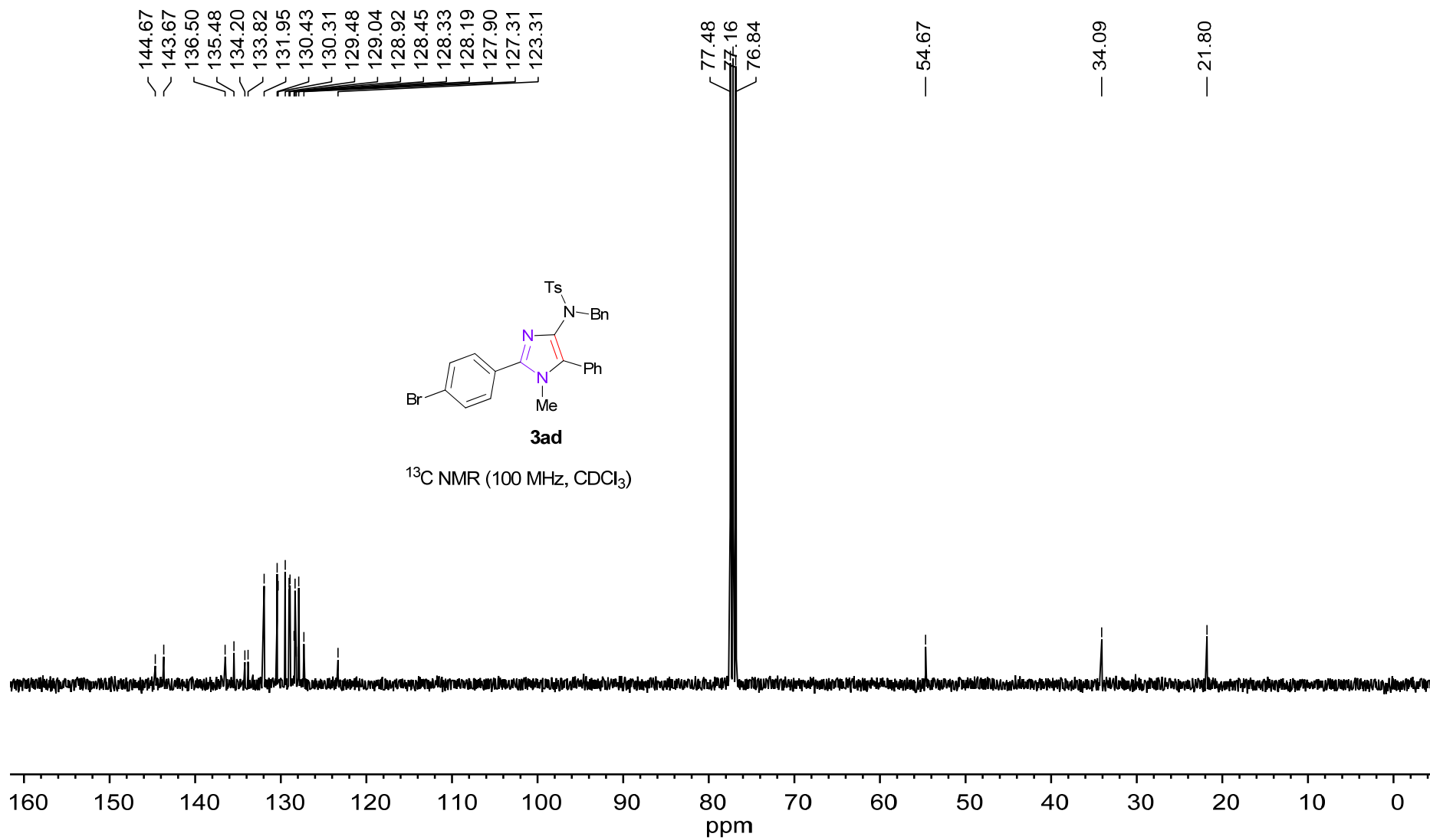


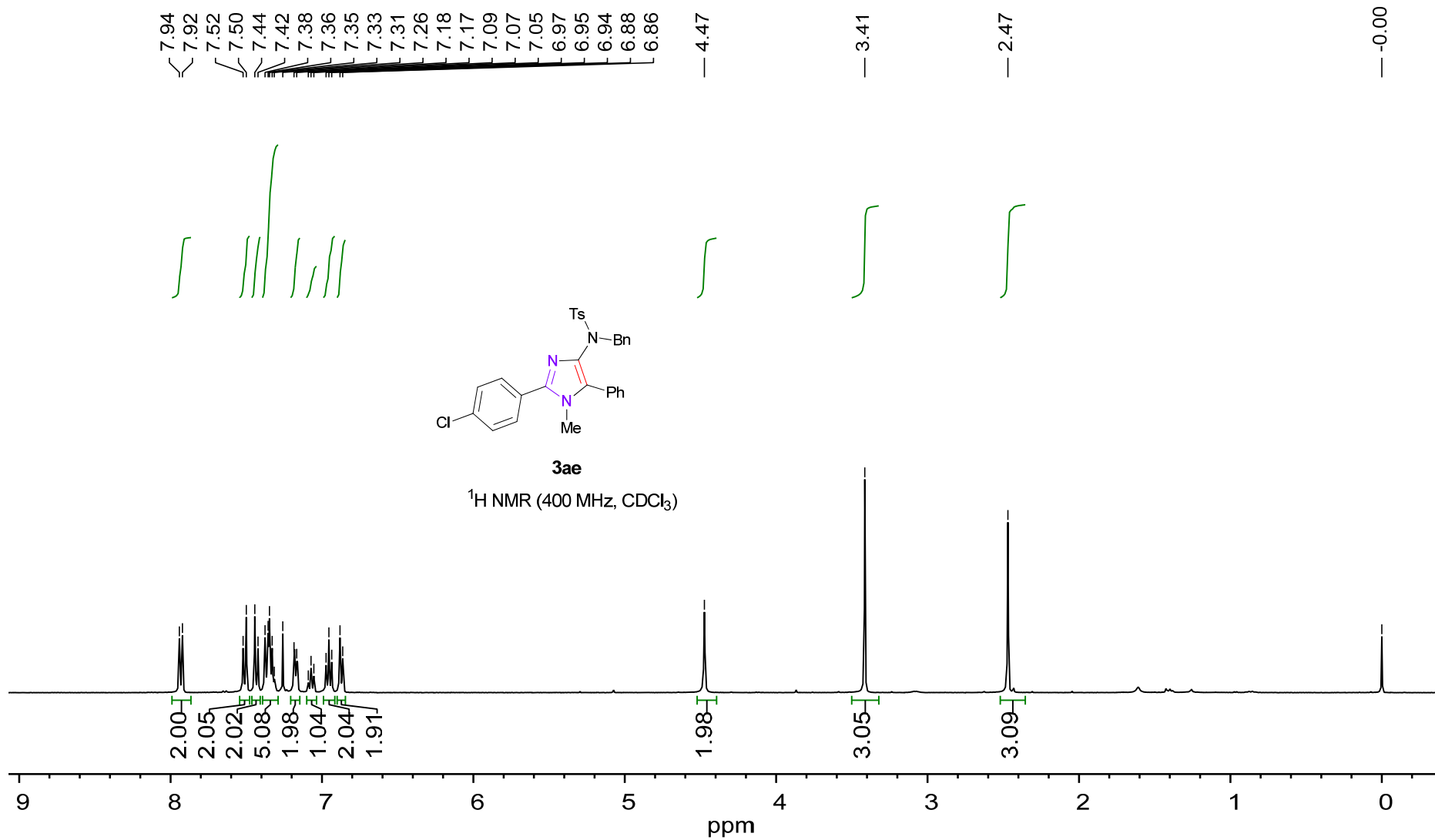


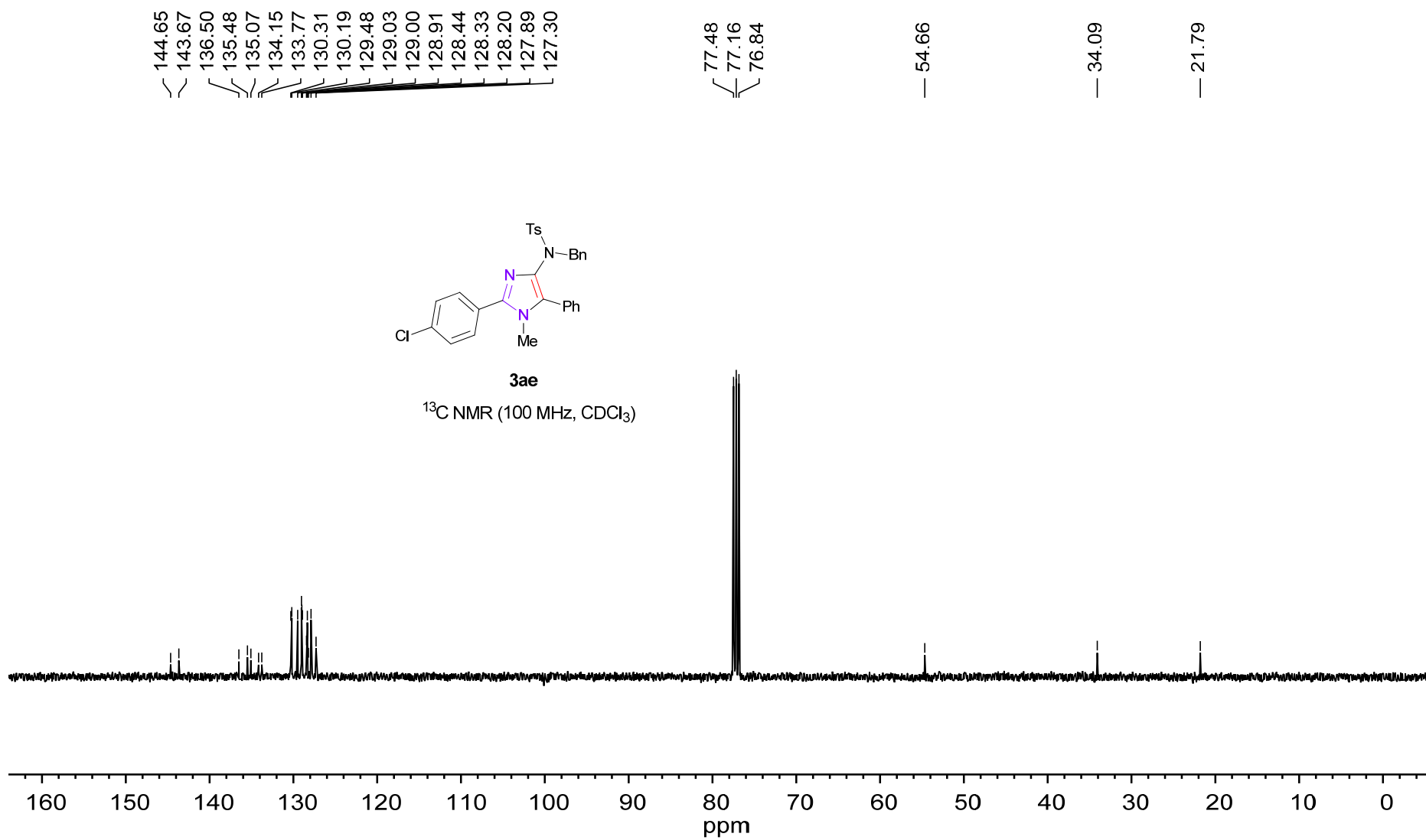


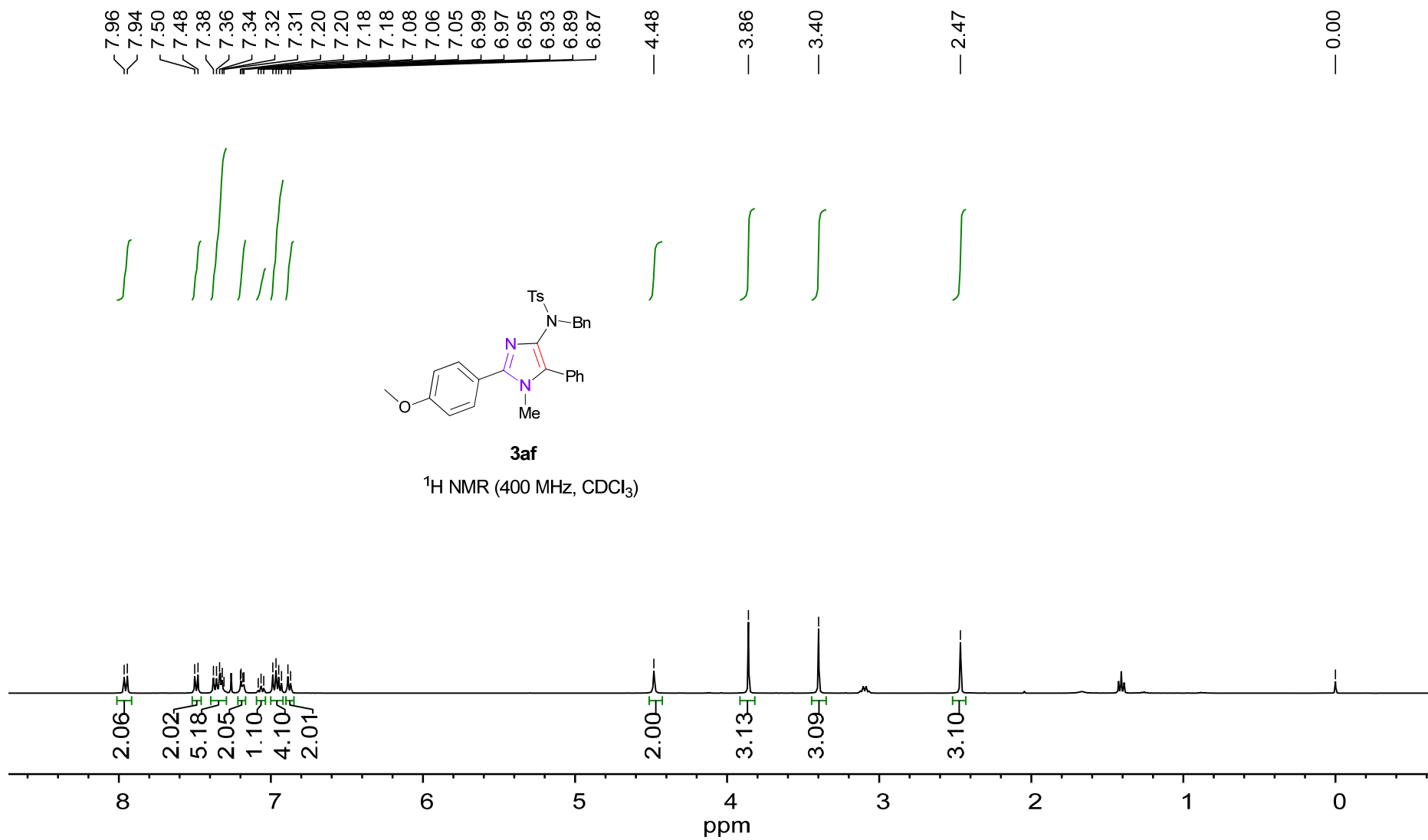


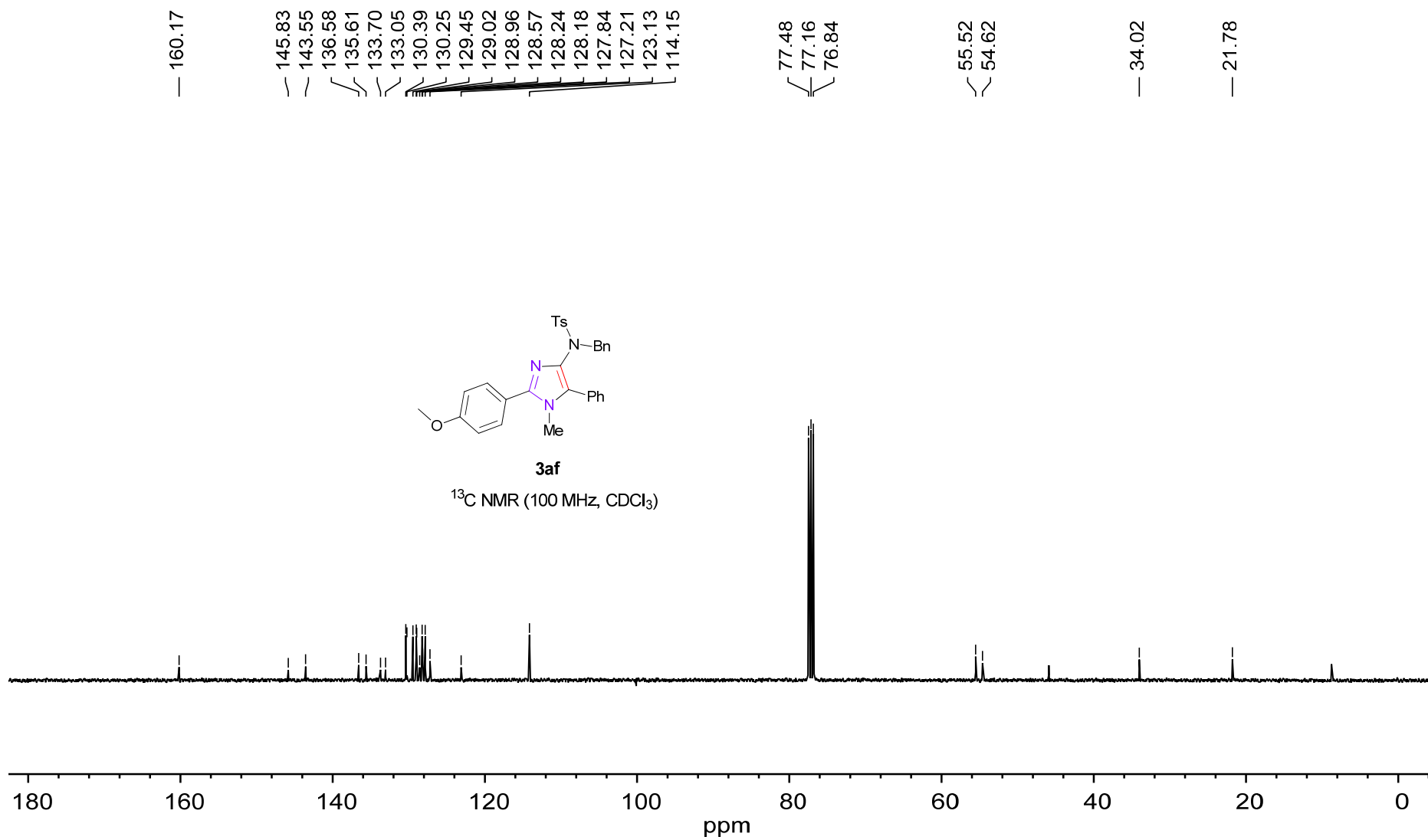


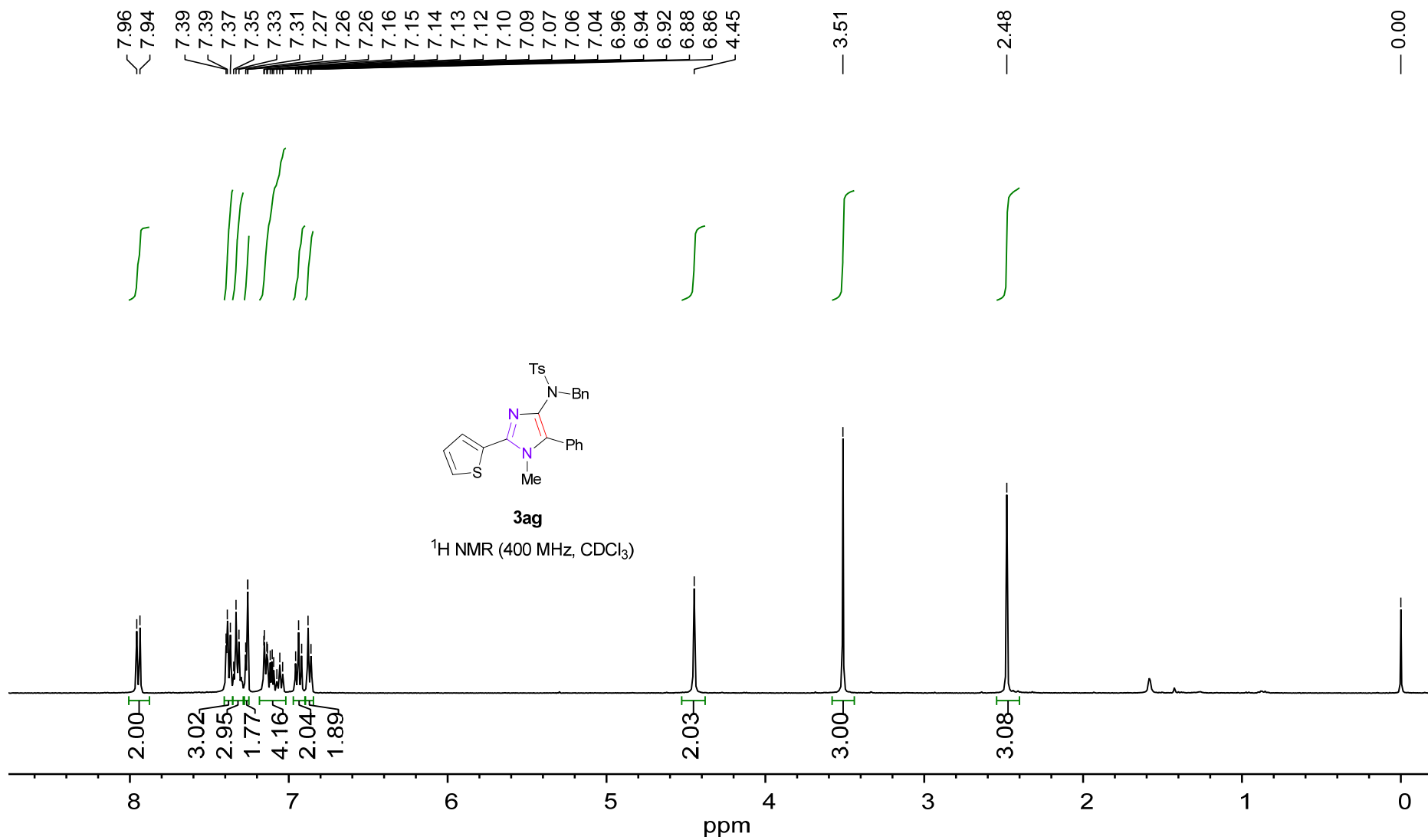


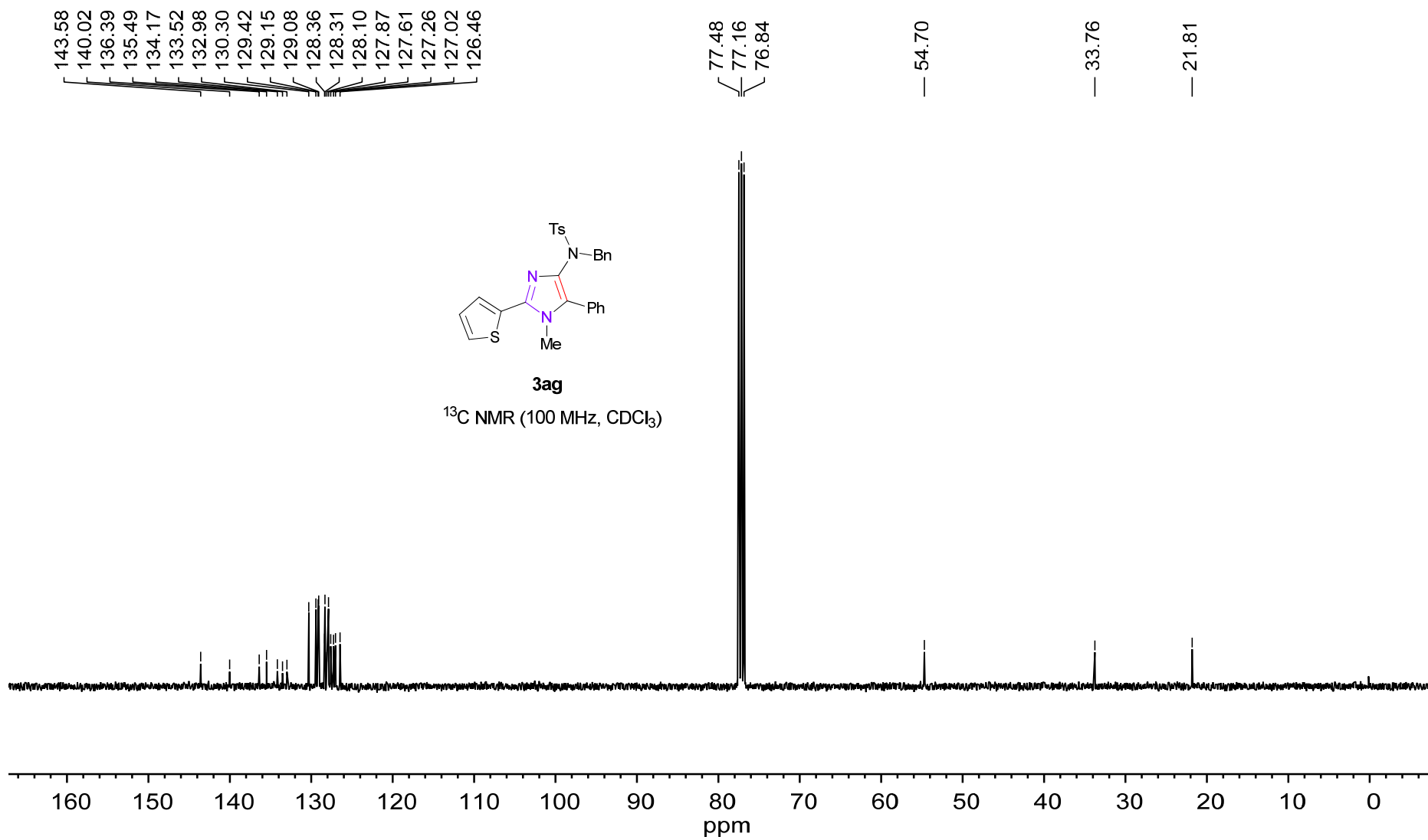


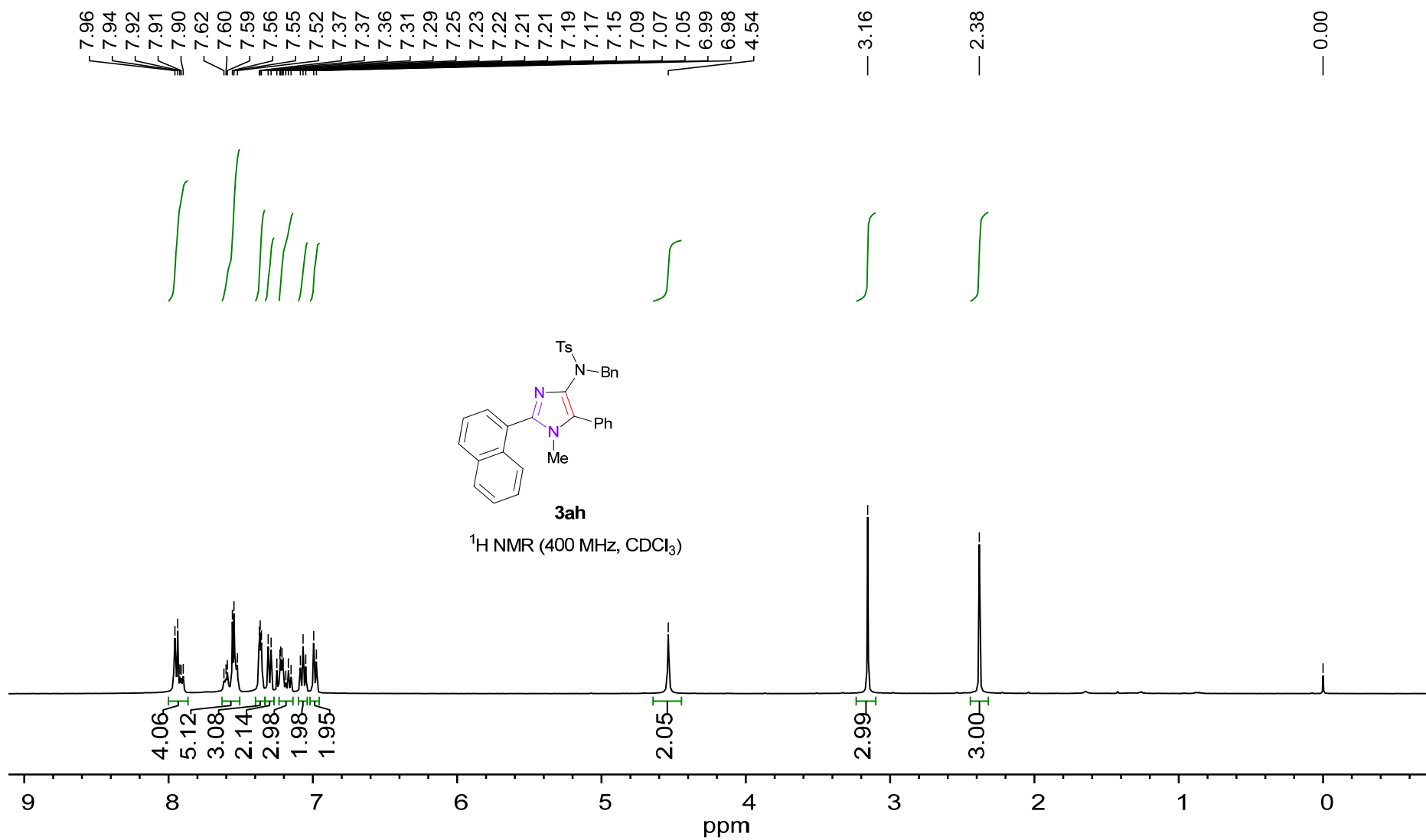


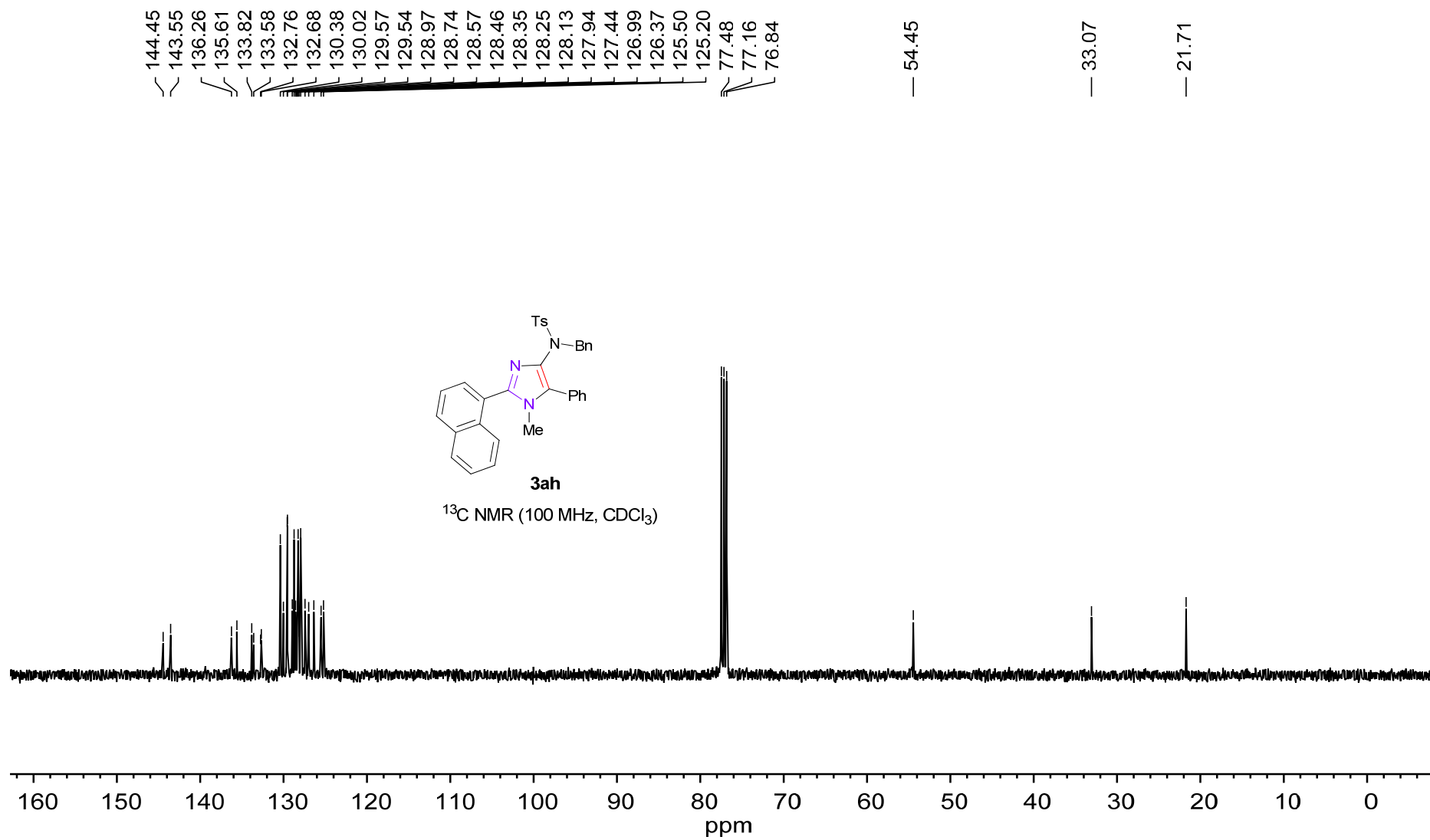


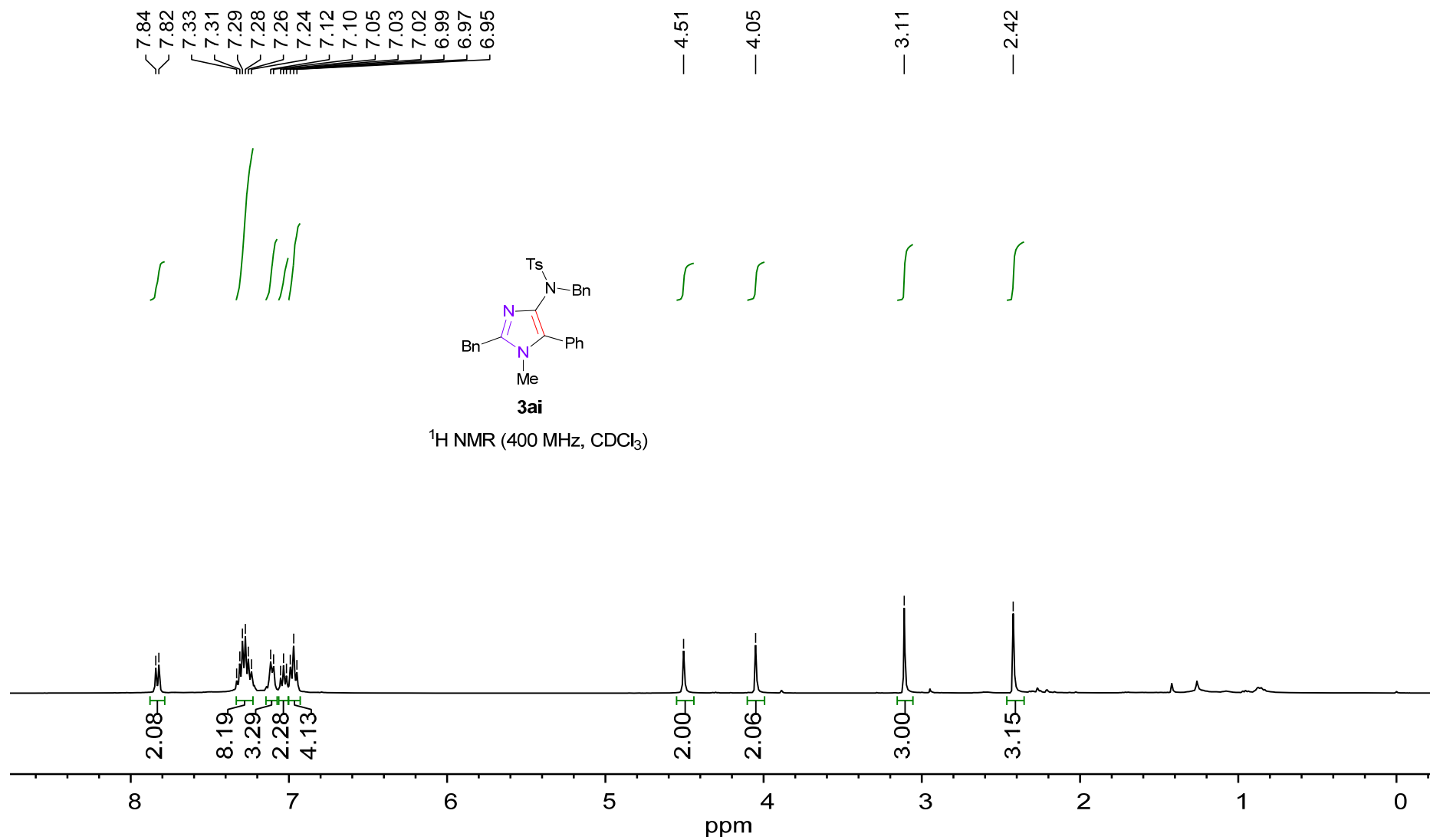












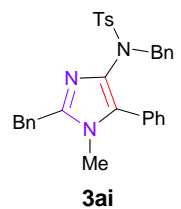
144.16
143.38
137.04
136.33
135.64
132.30
132.09
130.29
129.42
129.34
128.72
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128.45
128.26
128.10
128.05
127.88
127.34
126.72

77.48
77.16
76.84

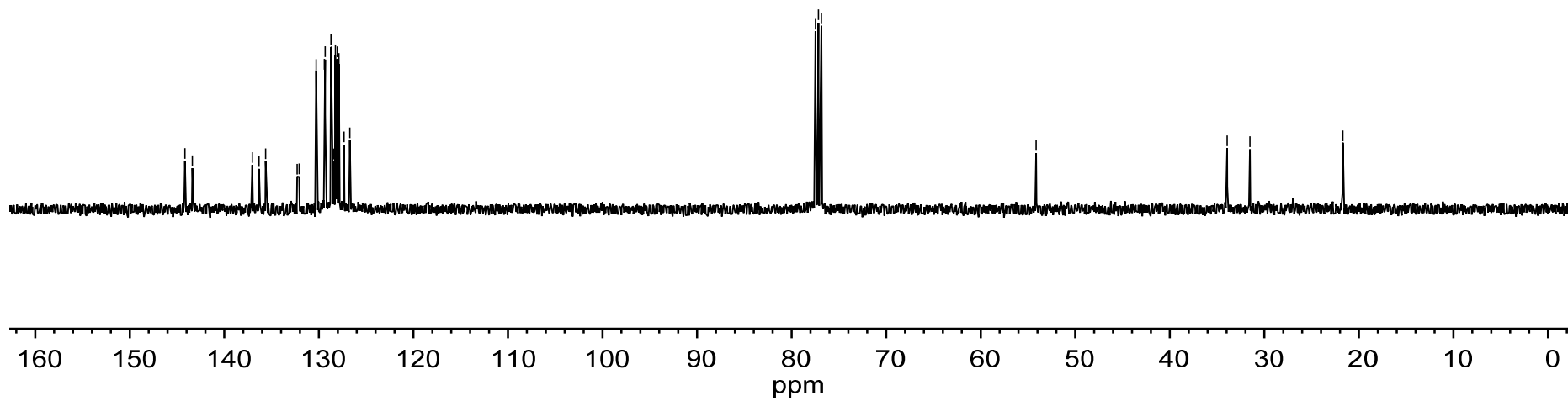
— 54.14

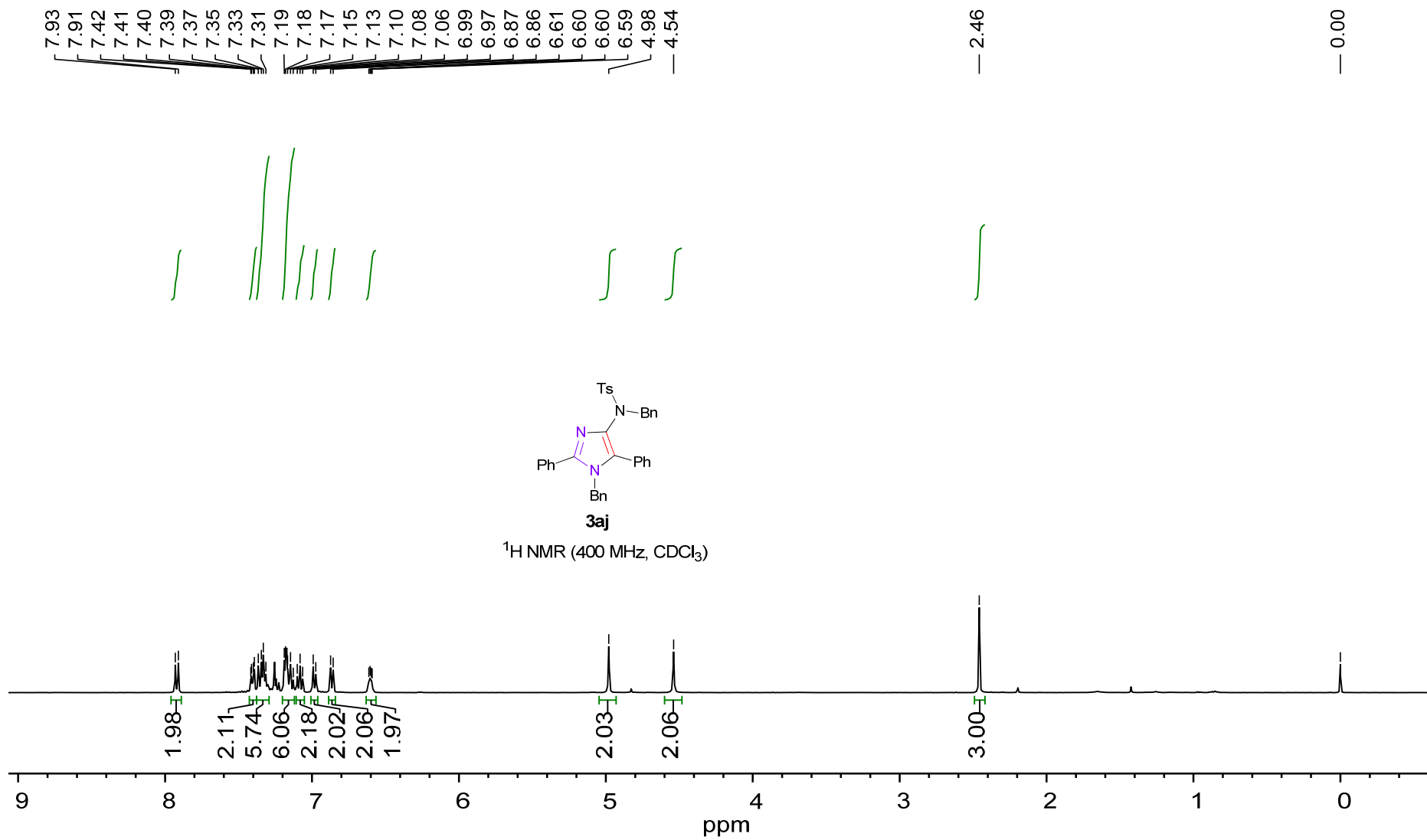
— 33.93
— 31.52

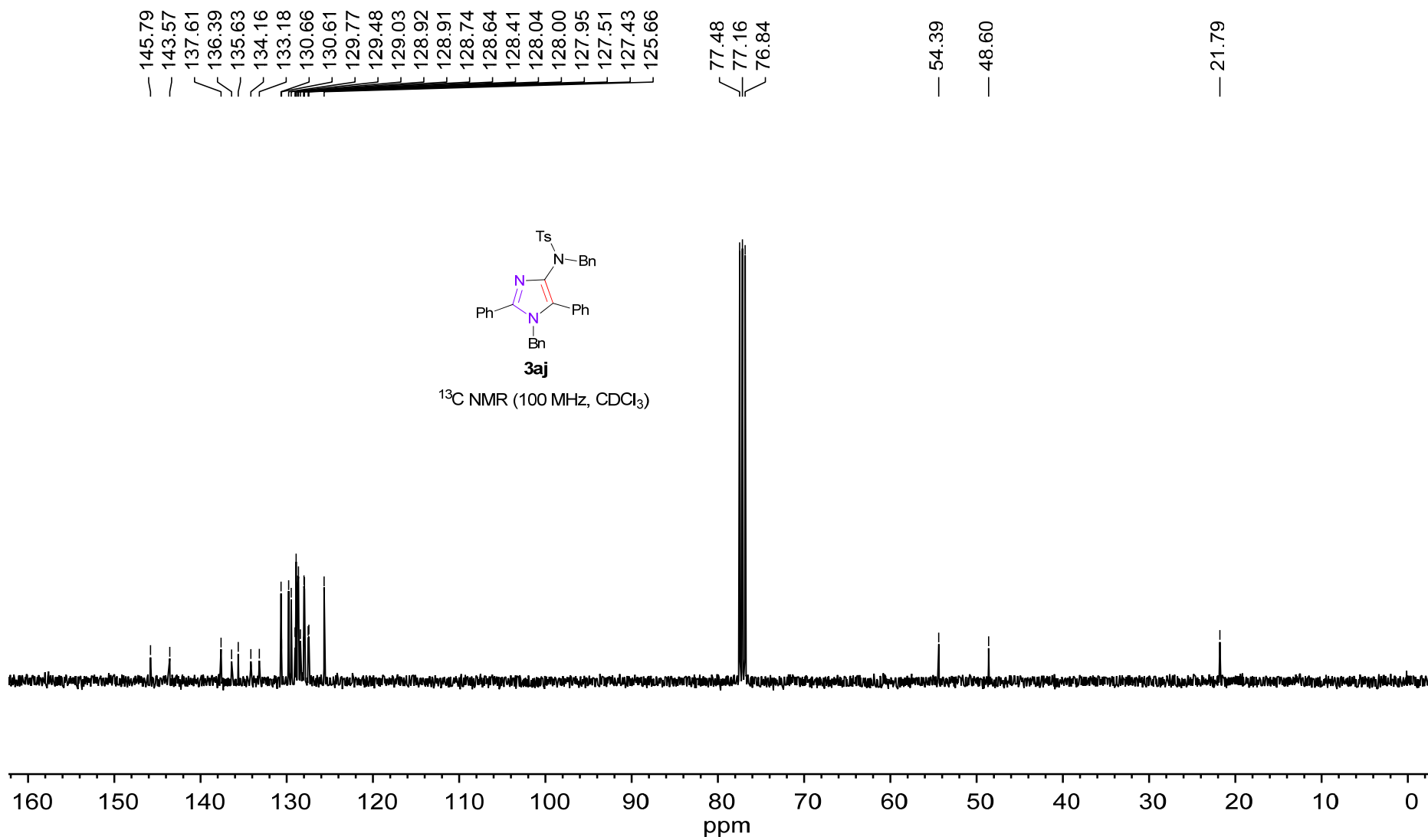
— 21.69



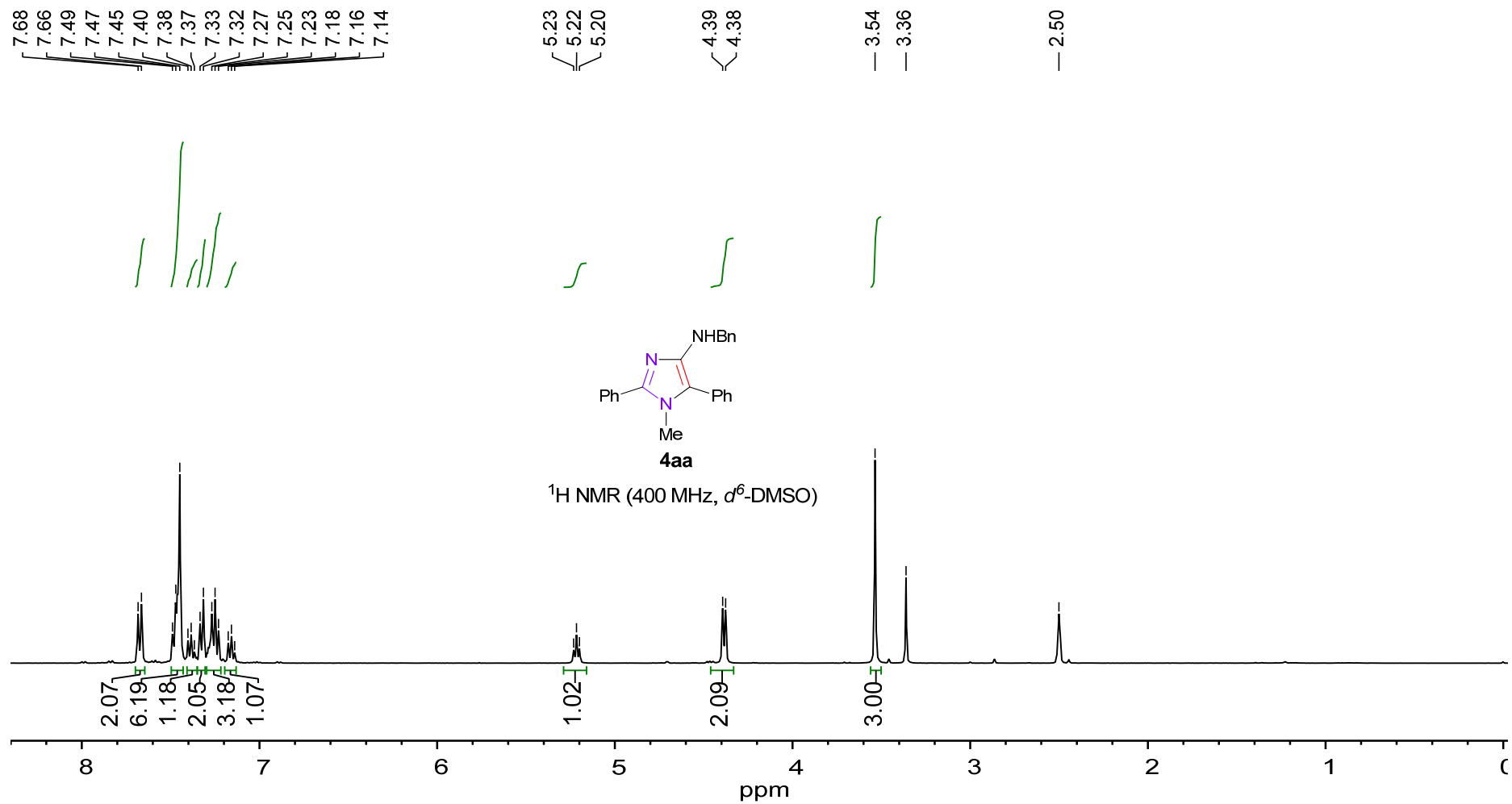
¹³C NMR (100 MHz, CDCl₃)

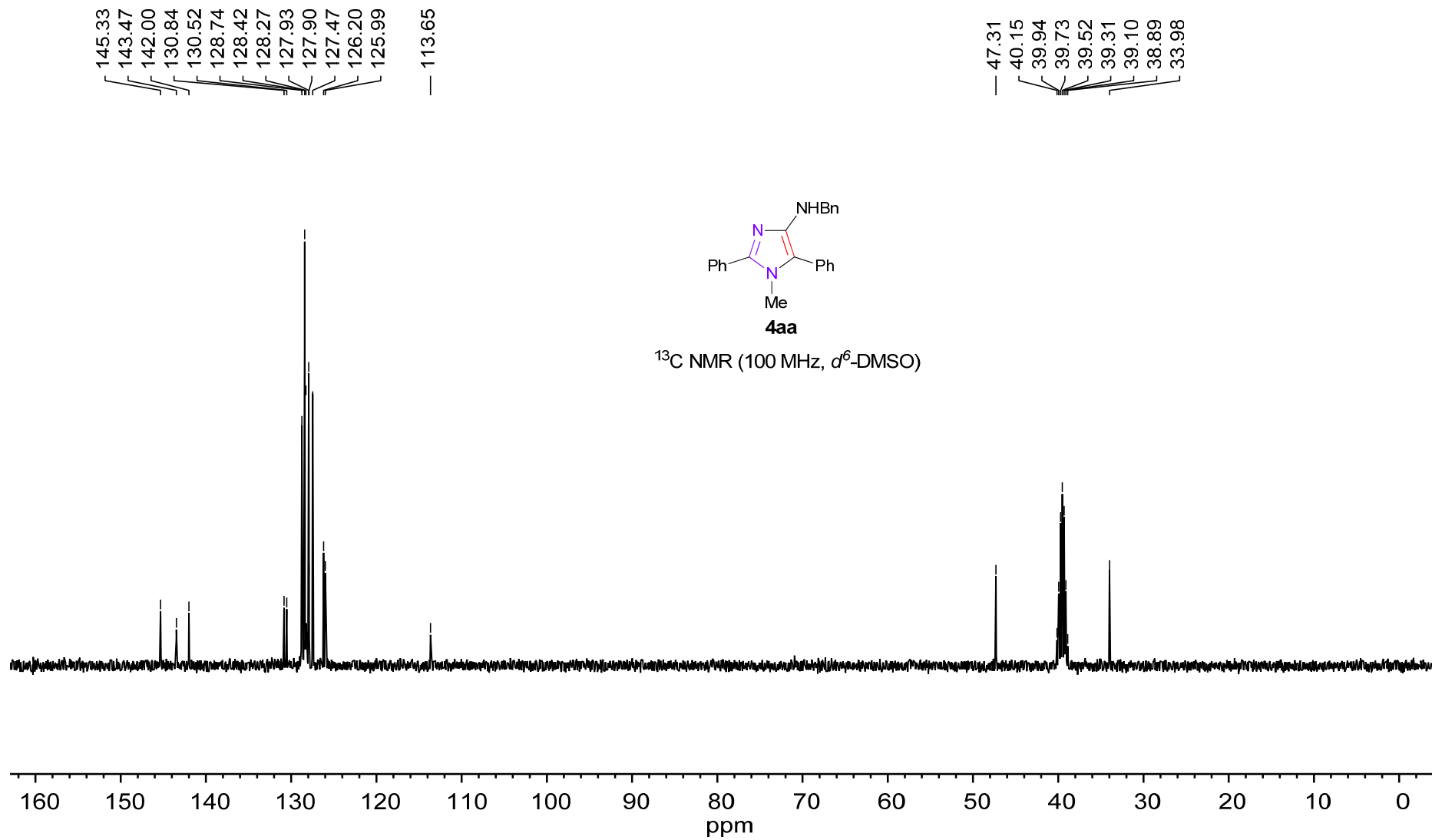


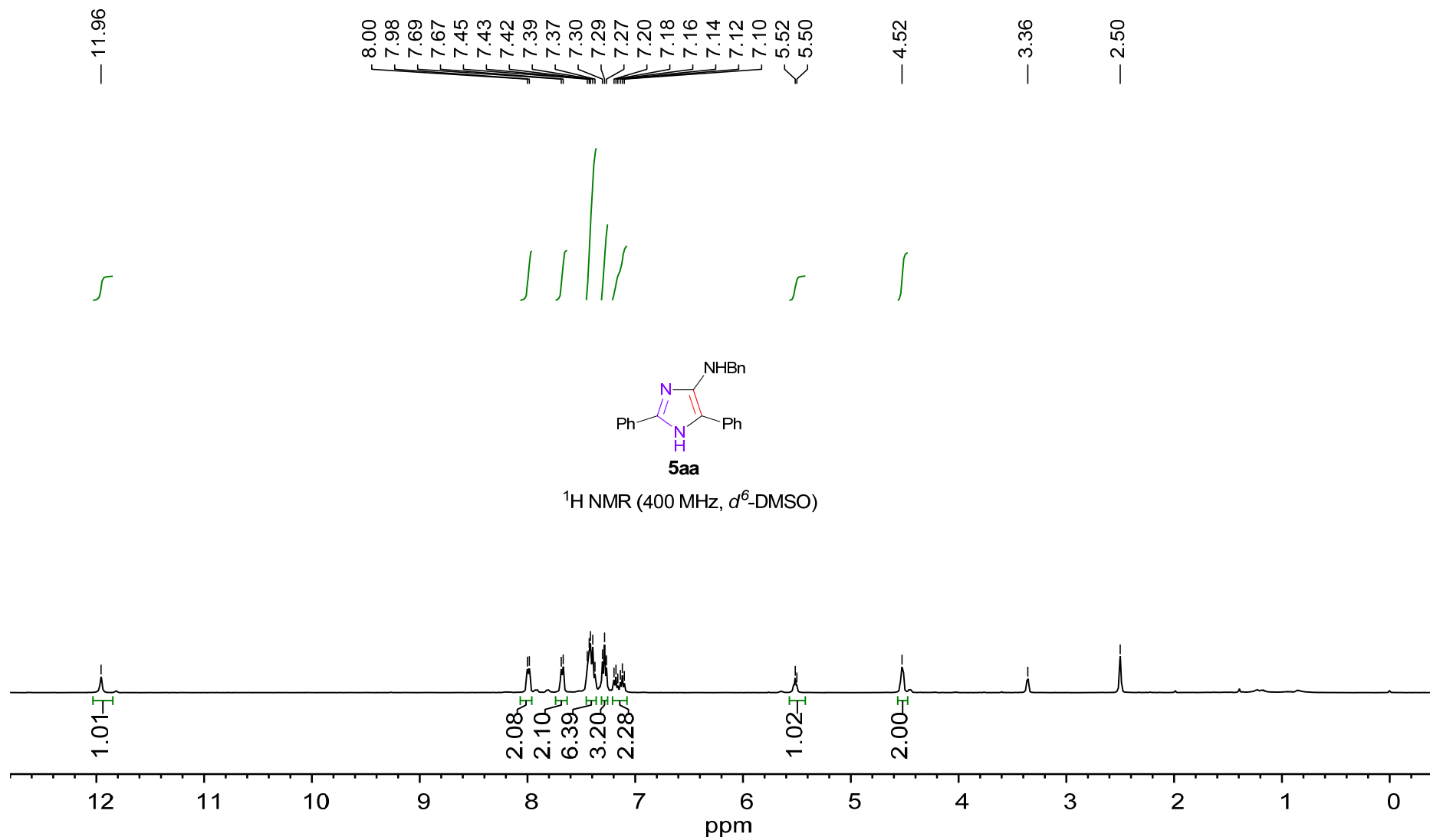




15. NMR spectroscopy of products 4aa-6aa

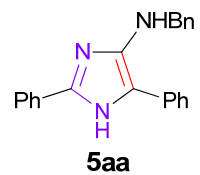






146.00
142.07
141.44
131.46
130.55
128.57
128.50
127.95
127.63
127.45
126.22
124.75
124.17
124.06
110.81

47.41
39.94
39.73
39.52
39.31
39.10



^{13}C NMR (100 MHz, d^6 -DMSO)

