

Brønsted Acid-Promoted Hydroamination of Unsaturated Hydrazones via an Ionic Pathway: Access to Biologically Important 5-Arylpyrazolines

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Supporting Information

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General information. All commercially available reagents were used without further purification. Column chromatography was performed on silica gel (200-300 mesh). ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a 400 MHz spectrometer. Chemical shifts (δ) were reported in ppm, and coupling constants (J) were given in Hertz (Hz). Data were reported as s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet. High-resolution mass spectra (HRMS) were recorded on an AB SCIEX Triple TOF 5600+ mass spectrometer. Melting points were uncorrected. Alkenyl hydrazone substrates **1a–1ac** were prepared according to the reported methods.¹⁻⁴

General procedure for the hydroamination reaction (Scheme 2). To a reaction tube equipped with a magnetic stir bar were added alkenyl hydrazone **1** (0.20 mmol), conc. H₂SO₄ (11 μ L, 0.20 mmol), and CH₃CN (2.0 mL). The reaction mixture was stirred at 50 °C under nitrogen atmosphere for 12 h, cooled to room temperature, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) to give product **2**.

Mechanistic studies

The experiment of the addition of radical scavenger BHT (Scheme 3a). To a reaction tube equipped with a magnetic stir bar were added alkenyl hydrazone **1a** (78.1 mg, 0.20 mmol), conc. H₂SO₄ (11 μ L, 0.20 mmol), BHT (121.2 mg, 0.60 mmol), and CH₃CN (2.0 mL). The reaction mixture was stirred at 50 °C under nitrogen atmosphere for 12 h, cooled to room temperature, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) to give product **2a** (71.5 mg, 92%) as a white solid. The addition of a radical scavenger did not inhibit the reaction, still generating product **2a** in 92% yield, which indicated a radical pathway might not be involved in the reaction process.

Procedure for the preparation of intermediates Z-3 and E-3 from 1a (Scheme 3b).

To a reaction tube equipped with a magnetic stir bar were added alkenyl hydrazone **1a** (781.2 mg, 2.0 mmol), conc. H₂SO₄ (110 μL, 2.0 mmol), and CH₃CN (20.0 mL). The reaction mixture was stirred at 50 °C under nitrogen atmosphere for a much shorter reaction time (0.5 h). Thin-layer chromatography (TLC) analysis indicated that substrate **1a** was completely consumed, and pyrazoline **2a** was not observed. The crude reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1 ~ 10:1) to afford intermediate product Z-3 (228.6 mg, 29%, white solid) and E-3 (443.2 mg, 57%, white solid).

Procedure for the preparation of pyrazoline product 2a from intermediate Z-3 (Scheme 3c).

To a reaction tube equipped with a magnetic stir bar were added Z-3 (78.1 mg, 0.20 mmol), conc. H₂SO₄ (11 μL, 0.20 mmol), and CH₃CN (2.0 mL). The reaction mixture was stirred at 50 °C under nitrogen atmosphere for 12 h, cooled to room temperature, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) to give product **2a** (70.1 mg, 90%) as a white solid.

Procedure for the preparation of pyrazoline product 2a from intermediate E-3 (Scheme 3c).

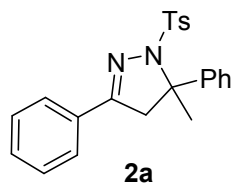
To a reaction tube equipped with a magnetic stir bar were added E-3 (78.1 mg, 0.20 mmol), H₂SO₄ (11 μL, 0.20 mmol), and CH₃CN (2.0 mL). The reaction mixture was stirred at 50 °C under nitrogen atmosphere for 12 h, cooled to room temperature, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) to provide product **2a** (65.3 mg, 84%) as a white solid.

The investigation of the formation of pyrazoline product 2a from the intermediate *Z*-3 or *E*-3 in the absence of H₂SO₄ (Scheme 3d).

To a reaction tube equipped with a magnetic stir bar were added *Z*-3 or *E*-3 (78.1 mg, 0.20 mmol) and CH₃CN (2.0 mL). The reaction mixture was stirred at 50 °C under nitrogen atmosphere for 12 h and cooled to room temperature. Thin-layer chromatography (TLC) analysis indicated that the intermediate *Z*-3 or *E*-3 kept intact, and the formation of product 2a was not observed. The results suggest that the Brønsted acid plays an important role in the formation of the pyrazoline product from the intermediate.

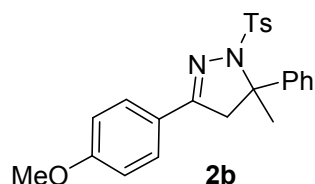
Characterization data

5-methyl-3,5-diphenyl-1-tosyl-4,5-dihydro-1*H*-pyrazole (2a)



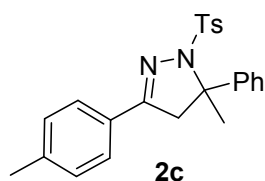
White solid (73.7 mg, 94%); mp 81–83 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.75 – 7.66 (m, 2H) 7.58 (d, *J* = 8.2 Hz, 2H), 7.45 – 7.38 (m, 3H), 7.36 – 7.30 (m, 2H), 7.27 – 7.19 (m, 3H), 7.14 (d, *J* = 8.1 Hz, 2H), 3.50 (d, *J* = 17.2 Hz, 1H), 3.37 (d, *J* = 17.2 Hz, 1H), 2.37 (s, 3H), 2.03 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 152.5, 143.4, 143.0, 136.9, 131.1, 130.1, 129.0, 128.6, 128.2, 127.60, 127.55, 126.5, 125.8, 71.8, 52.8, 25.2, 21.5; HRMS (ESI-TOF) *m/z*: [M+H]⁺ calcd for C₂₃H₂₃N₂O₂S 391.1475, found 391.1478.

3-(4-methoxyphenyl)-5-methyl-5-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrazole (2b)



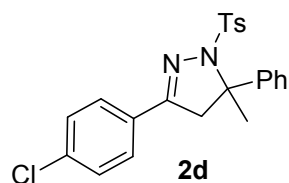
White solid (71.1 mg, 85%); mp 109–110 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, $J = 8.8$ Hz, 2H), 7.57 (d, $J = 8.2$ Hz, 2H), 7.33 (dd, $J = 7.6, 2.1$ Hz, 2H), 7.25 – 7.18 (m, 3H), 7.13 (d, $J = 8.2$ Hz, 2H), 6.92 (d, $J = 8.8$ Hz, 2H), 3.84 (s, 3H), 3.46 (d, $J = 17.1$ Hz, 1H), 3.34 (d, $J = 17.1$ Hz, 1H), 2.36 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.1, 152.3, 143.5, 142.9, 136.9, 128.9, 128.2, 128.1, 127.6, 127.5, 125.8, 123.8, 114.0, 71.6, 55.4, 53.0, 25.2, 21.5; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{25}\text{N}_2\text{O}_3\text{S}$ 421.1580, found 421.1582.

5-methyl-5-phenyl-3-(*p*-tolyl)-1-tosyl-4,5-dihydro-1*H*-pyrazole (2c)



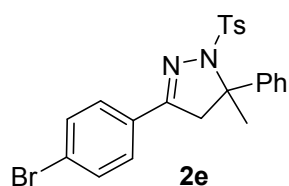
White solid (70.1 mg, 87%); mp 146–147 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, $J = 8.2$ Hz, 2H), 7.57 (d, $J = 8.3$ Hz, 2H), 7.32 (dd, $J = 7.7, 1.8$ Hz, 2H), 7.25 – 7.18 (m, 5H), 7.12 (d, $J = 8.1$ Hz, 2H), 3.48 (d, $J = 17.2$ Hz, 1H), 3.35 (d, $J = 17.2$ Hz, 1H), 2.39 (s, 3H), 2.36 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.6, 143.4, 143.0, 140.4, 136.9, 129.3, 128.9, 128.3, 128.2, 127.6, 127.5, 126.5, 125.8, 71.6, 52.9, 25.3, 21.48, 21.45; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{25}\text{N}_2\text{O}_2\text{S}$ 405.1631, found 405.1634.

3-(4-chlorophenyl)-5-methyl-5-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrazole (2d)



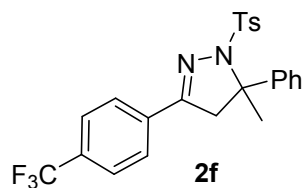
White solid (71.1 mg, 84%); mp 130–132 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.62 (d, $J = 8.6$ Hz, 2H), 7.56 (d, $J = 8.3$ Hz, 2H), 7.37 (d, $J = 8.6$ Hz, 2H), 7.32 (dd, $J = 7.6$, 2.0 Hz, 3H), 7.27 – 7.19 (m, 2H), 7.15 (d, $J = 8.1$ Hz, 2H), 3.46 (d, $J = 17.2$ Hz, 1H), 3.34 (d, $J = 17.2$ Hz, 1H), 2.37 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.3, 143.3, 143.2, 136.8, 136.0, 129.6, 129.0, 128.8, 128.3, 127.7, 127.64, 127.58, 125.7, 72.1, 52.7, 25.3, 21.5; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{22}\text{ClN}_2\text{O}_2\text{S}$ 425.1085, found 425.1083.

3-(4-bromophenyl)-5-methyl-5-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2e)



White solid (89.5 mg, 95%); mp 133–135 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.59 – 7.50 (m, 6H), 7.31 (dd, $J = 7.6$, 1.9 Hz, 2H), 7.28 – 7.20 (m, 3H), 7.14 (d, $J = 8.1$ Hz, 2H), 3.46 (d, $J = 17.2$ Hz, 1H), 3.34 (d, $J = 17.2$ Hz, 1H), 2.37 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.4, 143.3, 143.2, 136.8, 131.8, 130.1, 129.0, 128.3, 127.9, 127.7, 127.6, 125.7, 124.4, 72.1, 52.7, 25.3, 21.5; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{22}\text{BrN}_2\text{O}_2\text{S}$ 469.0580, found 469.0580.

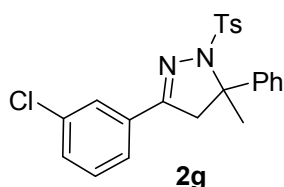
5-methyl-5-phenyl-1-tosyl-3-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrazole (2f)



White solid (77.2 mg, 84%); mp 133–134 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, $J = 8.2$ Hz, 2H), 7.63 (d, $J = 8.3$ Hz, 2H), 7.55 (d, $J = 8.3$ Hz, 2H), 7.31 (dd, $J = 7.7$, 1.8 Hz, 2H), 7.26 – 7.18 (m, 3H), 7.14 (d, $J = 8.1$ Hz, 2H), 3.49 (d, $J = 17.3$ Hz, 1H), 3.38 (d, $J = 17.3$ Hz, 1H), 2.36 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.0, 143.3, 143.1, 136.7, 134.4, 131.4 (q, $J = 33.0$ Hz), 129.0, 128.3, 127.7, 127.5,

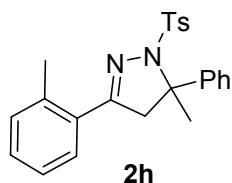
126.6, 125.6, 125.4 (q, $J = 4.0$ Hz), 123.7 (q, $J = 270.0$ Hz), 72.3, 52.5, 25.2, 21.4; HRMS (ESI-TOF) m/z : $[M+H]^+$ calcd for $C_{24}H_{22}F_3N_2O_2S$ 459.1349, found 459.1348.

3-(3-chlorophenyl)-5-methyl-5-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2g)



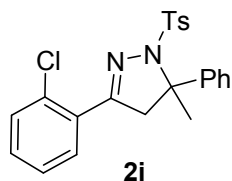
Yellow oil (84.0 mg, 99%); 1H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.55 (t, $J = 9.2$ Hz, 3H), 7.39 – 7.31 (m, 3H), 7.31 (d, $J = 2.0$ Hz, 1H), 7.28 – 7.20 (m, 3H), 7.16 (d, $J = 8.1$ Hz, 2H), 3.47 (d, $J = 17.3$ Hz, 1H), 3.34 (d, $J = 17.3$ Hz, 1H), 2.38 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 143.2, 136.8, 134.7, 132.9, 130.0, 129.9, 129.1, 128.3, 127.7, 127.6, 126.4, 125.7, 124.6, 72.1, 52.7, 25.3, 21.5; HRMS (ESI-TOF) m/z : $[M+H]^+$ calcd for $C_{23}H_{22}ClN_2O_2S$ 425.1085, found 425.1087.

5-methyl-5-phenyl-3-(*o*-tolyl)-1-tosyl-4,5-dihydro-1H-pyrazole (2h)



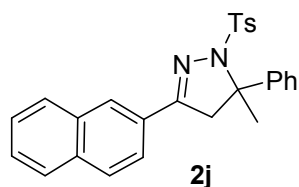
Yellow oil (59.2 mg, 73%); 1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, $J = 8.1$ Hz, 2H), 7.36 (dd, $J = 6.5, 2.8$ Hz, 2H), 7.29 – 7.21 (m, 6H), 7.19 (dd, $J = 8.1, 4.3$ Hz, 1H), 7.14 (d, $J = 8.2$ Hz, 2H), 3.54 (d, $J = 17.0$ Hz, 1H), 3.40 (d, $J = 17.0$ Hz, 1H), 2.65 (s, 3H), 2.37 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 143.6, 143.2, 138.1, 136.6, 131.8, 129.8, 129.3, 128.9, 128.5, 128.3, 127.9, 127.5, 125.8, 70.8, 55.1, 25.0, 23.6, 21.5; HRMS (ESI-TOF) m/z : $[M+H]^+$ calcd for $C_{24}H_{25}N_2O_2S$ 405.1631, found 405.1633.

3-(2-chlorophenyl)-5-methyl-5-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2i)



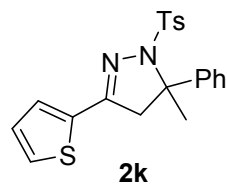
White solid (71.8 mg, 85%); mp 116–118 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.77 – 7.68 (m, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.43 – 7.33 (m, 3H), 7.33 – 7.27 (m, 2H), 7.25 (q, *J* = 3.7 Hz, 3H), 7.15 (d, *J* = 8.1 Hz, 2H), 3.66 (d, *J* = 17.6 Hz, 1H), 3.54 (d, *J* = 17.6 Hz, 1H), 2.37 (s, 3H), 2.01 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 152.3, 143.2, 143.2, 136.8, 132.6, 130.7, 130.6, 130.4, 130.3, 128.9, 128.2, 127.7, 127.6, 126.8, 125.7, 72.5, 55.5, 24.8, 21.5; HRMS (ESI-TOF) *m/z*: [M+H]⁺ calcd for C₂₃H₂₂ClN₂O₂S 425.1085, found 425.1085.

5-methyl-3-(naphthalen-2-yl)-5-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2j)



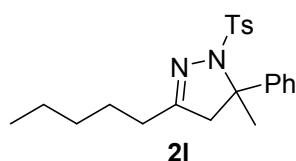
White solid (77.5 mg, 88%); mp 169–170 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.08 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.92 – 7.83 (m, 3H), 7.83 – 7.78 (m, 1H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.56 – 7.46 (m, 2H), 7.35 (dd, *J* = 7.7, 1.9 Hz, 2H), 7.29 – 7.19 (m, 3H), 7.15 (d, *J* = 8.1 Hz, 2H), 3.64 (d, *J* = 17.1 Hz, 1H), 3.51 (d, *J* = 17.1 Hz, 1H), 2.36 (s, 3H), 2.07 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 152.6, 143.4, 143.1, 136.9, 134.0, 132.9, 129.0, 128.8, 128.4, 128.31, 128.29, 127.8, 127.64, 127.62, 127.2, 126.71, 126.69, 125.8, 123.5, 72.0, 52.8, 25.4, 21.5; HRMS (ESI-TOF) *m/z*: [M+H]⁺ calcd for C₂₇H₂₅N₂O₂S 441.1631, found 441.1632.

5-methyl-5-phenyl-3-(thiophen-2-yl)-1-tosyl-4,5-dihydro-1H-pyrazole (2k)



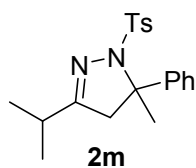
White solid (63.9 mg, 81%); mp 162–163 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, $J = 8.1$ Hz, 2H), 7.41 (d, $J = 5.0$ Hz, 1H), 7.32 (d, $J = 6.4$ Hz, 2H), 7.28 – 7.18 (m, 3H), 7.13 (d, $J = 7.8$ Hz, 3H), 7.07 – 7.00 (m, 1H), 3.48 (d, $J = 17.0$ Hz, 1H), 3.36 (d, $J = 17.0$ Hz, 1H), 2.36 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.4, 143.1, 143.0, 136.7, 134.7, 128.9, 128.6, 128.2, 128.1, 127.6, 127.4, 125.8, 72.0, 53.4, 25.2, 21.5; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{21}\text{N}_2\text{O}_2\text{S}_2$ 397.1039, found 397.1040.

5-methyl-3-pentyl-5-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2l)



Yellow oil (75.6 mg, 98%); ^1H NMR (400 MHz, CDCl_3) δ 7.54 (d, $J = 8.3$ Hz, 2H), 7.34 – 7.27 (m, 2H), 7.25 – 7.19 (m, 3H), 7.14 (d, $J = 8.1$ Hz, 2H), 3.04 (d, $J = 17.6$ Hz, 1H), 2.91 (d, $J = 17.6$ Hz, 1H), 2.38 (s, 3H), 2.34 (t, $J = 7.7$ Hz, 2H), 1.88 (s, 3H), 1.61 – 1.49 (m, 2H), 1.38 – 1.23 (m, 4H), 0.88 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.5, 143.7, 142.8, 137.1, 128.8, 128.1, 127.5, 127.3, 125.6, 70.8, 55.2, 31.3, 30.0, 25.8, 24.9, 22.3, 21.4, 13.9; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{29}\text{N}_2\text{O}_2\text{S}$ 385.1944, found 385.1947.

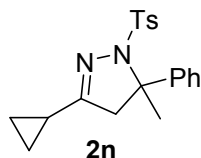
3-isopropyl-5-methyl-5-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2m)



White solid (63.6 mg, 89%); mp 121–123 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.53 (d, $J = 8.3$ Hz, 2H), 7.32 – 7.26 (m, 2H), 7.25 – 7.18 (m, 3H), 7.13 (d, $J = 8.1$ Hz, 2H), 3.04 (d, $J = 17.5$ Hz, 1H), 2.92 (d, $J = 17.5$ Hz, 1H), 2.75 – 2.62 (m, 1H), 2.37 (s, 3H), 1.86 (s, 3H), 1.15 (d, $J = 6.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.9, 143.6,

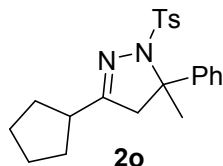
142.7, 136.9, 128.7, 128.0, 127.5, 127.2, 125.5, 70.9, 52.9, 29.7, 24.6, 21.4, 19.8, 19.7;
HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₂₀H₂₅N₂O₂S 357.1631, found 357.1633.

3-cyclopropyl-5-methyl-5-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2n)



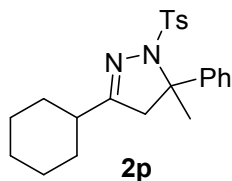
White solid (45.7 mg, 65%); mp 100–101 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.25 – 7.20 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 2.88 (d, *J* = 17.2 Hz, 1H), 2.75 (d, *J* = 17.2 Hz, 1H), 2.38 (s, 3H), 1.90 (s, 3H), 1.86 – 1.76 (m, 1H), 0.96 – 0.82 (m, 2H), 0.80 – 0.66 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 159.0, 143.5, 142.8, 136.9, 128.9, 128.1, 127.6, 127.4, 125.6, 70.7, 52.7, 24.8, 21.5, 11.5, 6.5, 6.3; HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₂₀H₂₃N₂O₂S 355.1475, found 355.1472.

3-cyclopentyl-5-methyl-5-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2o)



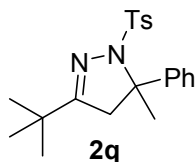
White solid (71.1 mg, 90%); mp 48–49 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 7.13 (d, *J* = 8.0 Hz, 2H), 3.05 (d, *J* = 17.4 Hz, 1H), 2.91 (d, *J* = 17.4 Hz, 1H), 2.87 – 2.78 (m, 1H), 2.38 (s, 3H), 1.87 – 1.81 (m, 5H), 1.74 – 1.52 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 160.4, 143.7, 142.8, 137.0, 128.8, 128.1, 127.6, 127.3, 125.6, 70.9, 53.7, 40.4, 30.2, 30.1, 25.3, 24.7, 21.5; HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₂₂H₂₇N₂O₂S 383.1788, found 383.1789.

3-cyclohexyl-5-methyl-5-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2p)



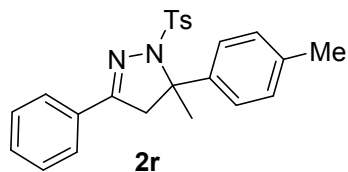
White solid (77.5 mg, 98%); mp 97–98 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, J = 8.3 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.24 – 7.16 (m, 3H), 7.12 (d, J = 8.0 Hz, 2H), 3.04 (d, J = 17.5 Hz, 1H), 2.91 (d, J = 17.5 Hz, 1H), 2.44 – 2.39 (m, 1H), 2.37 (s, 3H), 1.87 (s, 3H), 1.86 – 1.64 (m, 5H), 1.41 – 1.17 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.1, 143.6, 142.7, 137.0, 128.8, 128.1, 127.5, 127.3, 125.6, 70.6, 53.4, 39.2, 30.1, 30.0, 25.8, 25.63, 25.61, 24.8, 21.5; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{29}\text{N}_2\text{O}_2\text{S}$ 397.1944, found 397.1946.

3-(*tert*-butyl)-5-methyl-5-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2q)



White solid (63.7 mg, 86%); mp 83–85 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, J = 8.3 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.24 – 7.20 (m, 3H), 7.14 (d, J = 8.0 Hz, 2H), 3.07 (d, J = 17.3 Hz, 1H), 2.94 (d, J = 17.3 Hz, 1H), 2.38 (s, 3H), 1.84 (s, 3H), 1.18 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.1, 143.7, 142.8, 137.0, 128.7, 128.1, 127.7, 127.3, 125.6, 71.5, 52.1, 34.1, 27.8, 24.5, 21.5; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{27}\text{N}_2\text{O}_2\text{S}$ 371.1788, found 371.1785.

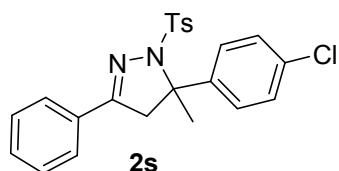
5-methyl-3-phenyl-5-(*p*-tolyl)-1-tosyl-4,5-dihydro-1H-pyrazole (2r)



White solid (78.8 mg, 97%); mp 137–138 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.75 – 7.67 (m, 2H), 7.57 (d, J = 8.3 Hz, 2H), 7.45 – 7.37 (m, 3H), 7.21 (d, J = 8.2 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 3.49 (d, J = 17.2 Hz, 1H), 3.36 (d, J

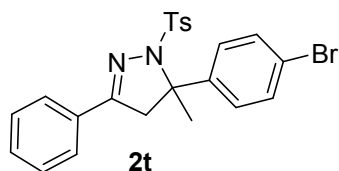
= 17.2 Hz, 1H), 2.37 (s, 3H), 2.33 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.5, 142.9, 140.4, 137.3, 136.9, 131.1, 130.1, 128.82, 128.79, 128.6, 127.5, 126.5, 125.7, 71.7, 52.7, 25.3, 21.5, 21.0; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{25}\text{N}_2\text{O}_2\text{S}$ 405.1631, found 405.1630.

5-(4-chlorophenyl)-5-methyl-3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2s)



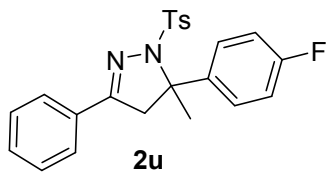
White solid (83.5 mg, 98%); mp 70–71 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.75 – 7.63 (m, 2H), 7.58 (d, J = 8.3 Hz, 2H), 7.45 – 7.38 (m, 3H), 7.28 – 7.21 (m, 2H), 7.20 – 7.12 (m, 4H), 3.45 (d, J = 17.2 Hz, 1H), 3.37 (d, J = 17.2 Hz, 1H), 2.38 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.5, 143.3, 141.9, 136.7, 133.6, 130.9, 130.3, 129.0, 128.7, 128.3, 127.5, 127.2, 126.5, 71.3, 52.6, 25.2, 21.5; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{22}\text{ClN}_2\text{O}_2\text{S}$ 425.1085, found 425.1083.

5-(4-bromophenyl)-5-methyl-3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2t)



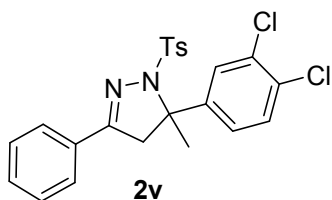
White solid (89.6 mg, 95%); mp 67–69 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.74 – 7.67 (m, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.45 – 7.38 (m, 3H), 7.34 – 7.27 (m, 2H), 7.21 – 7.13 (m, 4H), 3.45 (d, J = 17.2 Hz, 1H), 3.37 (d, J = 17.2 Hz, 1H), 2.39 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.6, 143.3, 142.3, 136.6, 131.2, 130.8, 130.3, 129.0, 128.6, 127.5, 127.4, 126.5, 121.7, 71.3, 52.5, 25.1, 21.5; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{22}\text{BrN}_2\text{O}_2\text{S}$ 469.0580, found 469.0578.

5-(4-fluorophenyl)-5-methyl-3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2u)



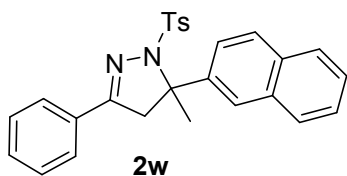
White solid (80.2 mg, 98%); mp 130–131 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.74 – 7.66 (m, 2H), 7.58 (d, $J = 8.3$ Hz, 2H), 7.45 – 7.37 (m, 3H), 7.33 – 7.26 (m, 2H), 7.16 (d, $J = 8.1$ Hz, 2H), 6.95 – 6.82 (m, 2H), 3.47 (d, $J = 17.2$ Hz, 1H), 3.37 (d, $J = 17.2$ Hz, 1H), 2.37 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.1 (d, $J = 245.0$ Hz), 152.5, 143.3, 139.3 (d, $J = 3.0$ Hz), 136.8, 131.1, 130.2, 129.0, 128.6, 127.6 (d, $J = 8.0$ Hz), 127.5, 126.5, 115.0 (d, $J = 21.0$ Hz), 71.3, 52.7, 25.5, 21.5; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{22}\text{FN}_2\text{O}_2\text{S}$ 409.1381, found 409.1382.

5-(3,4-dichlorophenyl)-5-methyl-3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2v)



White solid (77.7 mg, 85%); mp 152–153 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.74 – 7.65 (m, 2H), 7.60 (d, $J = 8.1$ Hz, 2H), 7.47 – 7.38 (m, 3H), 7.33 – 7.27 (m, 2H), 7.24 – 7.15 (m, 3H), 3.44 (d, $J = 17.3$ Hz, 1H), 3.38 (d, $J = 17.3$ Hz, 1H), 2.39 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.5, 143.7, 143.5, 136.4, 132.4, 131.9, 130.7, 130.4, 130.1, 129.2, 128.7, 128.0, 127.4, 126.6, 125.3, 70.8, 52.2, 25.1, 21.6; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{21}\text{Cl}_2\text{N}_2\text{O}_2\text{S}$ 459.0695, found 459.0695.

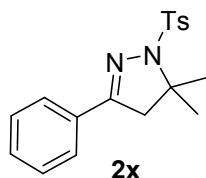
5-methyl-5-(naphthalen-2-yl)-3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2w)



White solid (80.4 mg, 91%); mp 174–176 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.82 – 7.70 (m, 5H), 7.63 (d, $J = 8.7$ Hz, 1H), 7.55 – 7.46 (m, 4H), 7.46 – 7.41 (m, 3H), 7.36 (dd, $J = 8.7, 2.0$ Hz, 1H), 6.95 (d, $J = 8.1$ Hz, 2H), 3.60 (d, $J = 17.3$ Hz, 1H), 3.44 (d,

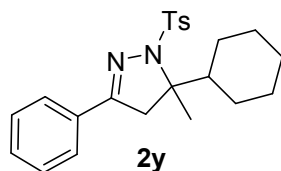
$J = 17.3$ Hz, 1H), 2.29 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.6, 143.0, 140.2, 136.7, 132.7, 132.6, 131.1, 130.1, 128.8, 128.6, 128.3, 128.0, 127.4, 127.3, 126.5, 126.2, 126.1, 124.6, 123.9, 71.8, 52.6, 25.4, 21.4; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{25}\text{N}_2\text{O}_2\text{S}$ 441.1631, found 441.1630.

5,5-dimethyl-3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2x)



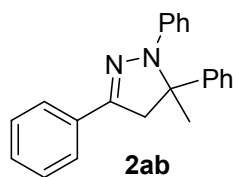
White solid (39.1 mg, 60%); mp 53-55 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 8.3$ Hz, 2H), 7.68 – 7.61 (m, 2H), 7.43 – 7.34 (m, 3H), 7.27 (d, $J = 10.3$ Hz, 2H), 3.04 (s, 2H), 2.40 (s, 3H), 1.56 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.4, 143.4, 137.3, 131.4, 130.0, 129.2, 128.5, 128.1, 126.4, 69.1, 49.2, 27.1, 21.5; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_2\text{S}$ 329.1318, found 329.1315.

5-cyclohexyl-5-methyl-3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (2y)



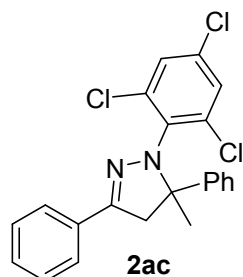
White solid (55.4 mg, 72%); mp 57–58 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 8.3$ Hz, 2H), 7.70 – 7.62 (m, 2H), 7.44 – 7.33 (m, 3H), 7.28 (d, $J = 8.2$ Hz, 2H), 3.22 (d, $J = 17.0$ Hz, 1H), 2.66 (d, $J = 17.0$ Hz, 1H), 2.39 (s, 3H), 2.36 – 2.18 (m, 1H), 1.92 – 1.77 (m, 3H), 1.77 – 1.66 (m, 2H), 1.42 (s, 3H), 1.26 – 1.30 (m, 1H), 1.30 – 1.24 (m, 1H), 1.15 – 1.04 (m, 1H), 0.94 – 0.82 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.7, 143.2, 137.6, 131.4, 129.8, 129.2, 128.4, 127.8, 126.3, 75.9, 45.2, 42.4, 28.4, 27.6, 26.3, 26.3, 25.8, 24.3, 21.5; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{29}\text{N}_2\text{O}_2\text{S}$ 397.1944, found 397.1943.

5-methyl-1,3,5-triphenyl-4,5-dihydro-1H-pyrazole (2ab)



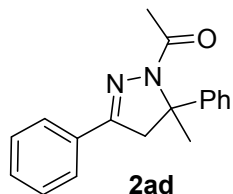
Yellow solid (39.5 mg, 63%); mp 166–167 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.76 – 7.69 (m, 2H), 7.57 – 7.49 (m, 2H), 7.43 – 7.37 (m, 4H), 7.36 – 7.29 (m, 2H), 7.14 – 7.09 (m, 2H), 7.06 – 6.99 (m, 2H), 6.82 – 6.74 (m, 1H), 3.44 (d, $J = 16.8$ Hz, 1H), 3.43 (d, $J = 16.8$ Hz, 1H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.9, 145.2, 143.6, 133.0, 129.0, 128.6, 128.5, 128.4, 127.2, 125.6, 125.5, 119.4, 115.3, 69.9, 53.5, 22.2; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{20}\text{N}_2$ 312.1626, found 312.1628.

5-methyl-3,5-diphenyl-1-(2,4,6-trichlorophenyl)-4,5-dihydro-1H-pyrazole (2ac)



Yellow solid (76.8 mg, 92%); mp 127–128 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.75 – 7.67 (m, 2H), 7.48 – 7.43 (m, 2H), 7.42 – 7.35 (m, 3H), 7.33 – 7.21 (m, 5H), 3.63 (d, $J = 16.7$ Hz, 1H), 3.49 (d, $J = 16.7$ Hz, 1H), 1.77 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.5, 145.4, 138.2, 137.0, 132.8, 132.3, 128.8, 128.6, 128.0, 127.1, 125.92, 125.85, 70.9, 51.4, 24.0; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{18}\text{Cl}_3\text{N}_2$ 415.0530, found 415.0533.

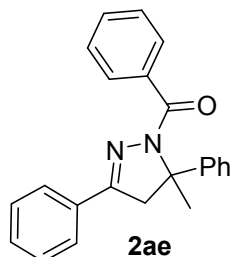
1-(5-methyl-3,5-diphenyl-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (2ad)



White solid (34.1 mg, 61%); mp 146–147 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.74 – 7.68 (m, 2H), 7.46 – 7.39 (m, 3H), 7.37 – 7.28 (m, 4H), 7.28 – 7.21 (m, 1H), 3.46 (d, $J = 17.6$ Hz, 1H), 3.40 (d, $J = 17.6$ Hz, 1H), 2.42 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100

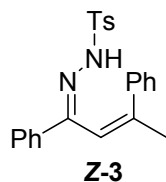
MHz, CDCl₃) δ 168.8, 151.5, 144.9, 131.5, 130.1, 128.7, 128.6, 127.0, 126.4, 124.4, 67.5, 52.3, 24.5, 23.2; HRMS (ESI-TOF) m/z : [M+H]⁺ calcd for C₁₈H₁₉N₂O 279.1492, found 279.1492.

(5-methyl-3,5-diphenyl-4,5-dihydro-1*H*-pyrazol-1-yl)(phenyl)methanone (2ae)



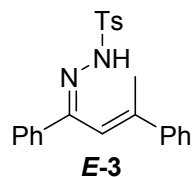
White solid (49.0 mg, 70%); mp 100–101 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.97 – 7.89 (m, 2H), 7.68 – 7.62 (m, 2H), 7.50 – 7.43 (m, 2H), 7.43 – 7.36 (m, 6H), 7.36 – 7.31 (m, 2H), 7.28 – 7.22 (m, 1H), 3.50 (d, J = 17.6 Hz, 1H), 3.43 (d, J = 17.6 Hz, 1H), 2.19 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.3, 152.3, 144.7, 135.5, 131.5, 130.6, 130.2, 130.0, 128.69, 128.65, 127.5, 127.1, 126.6, 124.4, 68.8, 51.7, 24.4; HRMS (ESI-TOF) m/z : [M+H]⁺ calcd for C₂₃H₂₁N₂O 341.1648, found 341.1646.

***N'*-((1*E*,2*Z*)-1,3-diphenylbut-2-en-1-ylidene)-4-methylbenzenesulfonohydrazide (Z-3)**



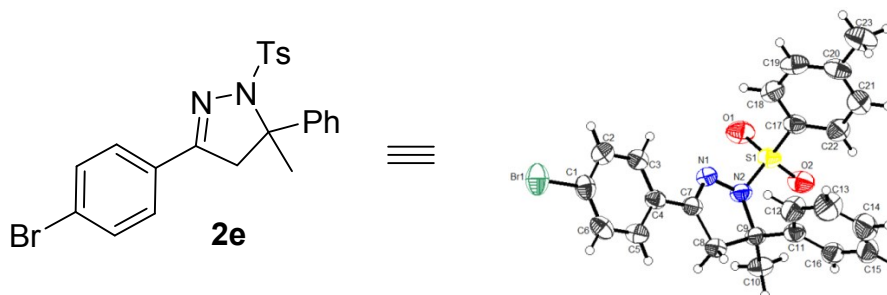
White solid (228.6 mg, 29%); mp 157–159 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.86 (s, 1H), 7.68 – 7.62 (m, 2H), 7.58 (d, J = 8.2 Hz, 2H), 7.32 – 7.24 (m, 3H), 7.21 (d, J = 8.2 Hz, 2H), 7.14 – 7.07 (m, 1H), 7.00 (d, J = 4.3 Hz, 4H), 5.92 (s, 1H), 2.41 (s, 3H), 2.33 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 151.1, 147.1, 143.6, 138.8, 135.9, 135.4, 129.5, 129.3, 128.7, 128.4, 128.2, 127.7, 126.9, 126.2, 116.7, 24.8, 21.6; HRMS (ESI-TOF) m/z : [M +H]⁺ calcd for C₂₃H₂₃N₂O₂S 391.1475, found 391.1475.

***N'*-((1*E*,2*E*)-1,3-diphenylbut-2-en-1-ylidene)-4-methylbenzenesulfonohydrazide⁵
(**E-3**)**



White solid (443.2 mg, 57%); mp 99–101 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.00 (s, 1H), 7.92 (d, *J* = 7.9 Hz, 2H), 7.72 – 7.66 (m, 2H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.45 – 7.38 (m, 3H), 7.38 – 7.30 (m, 5H), 6.23 (s, 1H), 2.42 (s, 3H), 1.88 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 151.8, 146.2, 144.0, 139.6, 135.7, 135.6, 129.8, 129.5, 128.7, 128.6, 128.4, 127.9, 126.8, 125.8, 115.8, 21.5, 18.1; HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₃H₂₃N₂O₂S 391.1475, found 391.1478.

X-ray structure of 2e (CCDC 2018227)



Crystal data and structure refinement for 2e

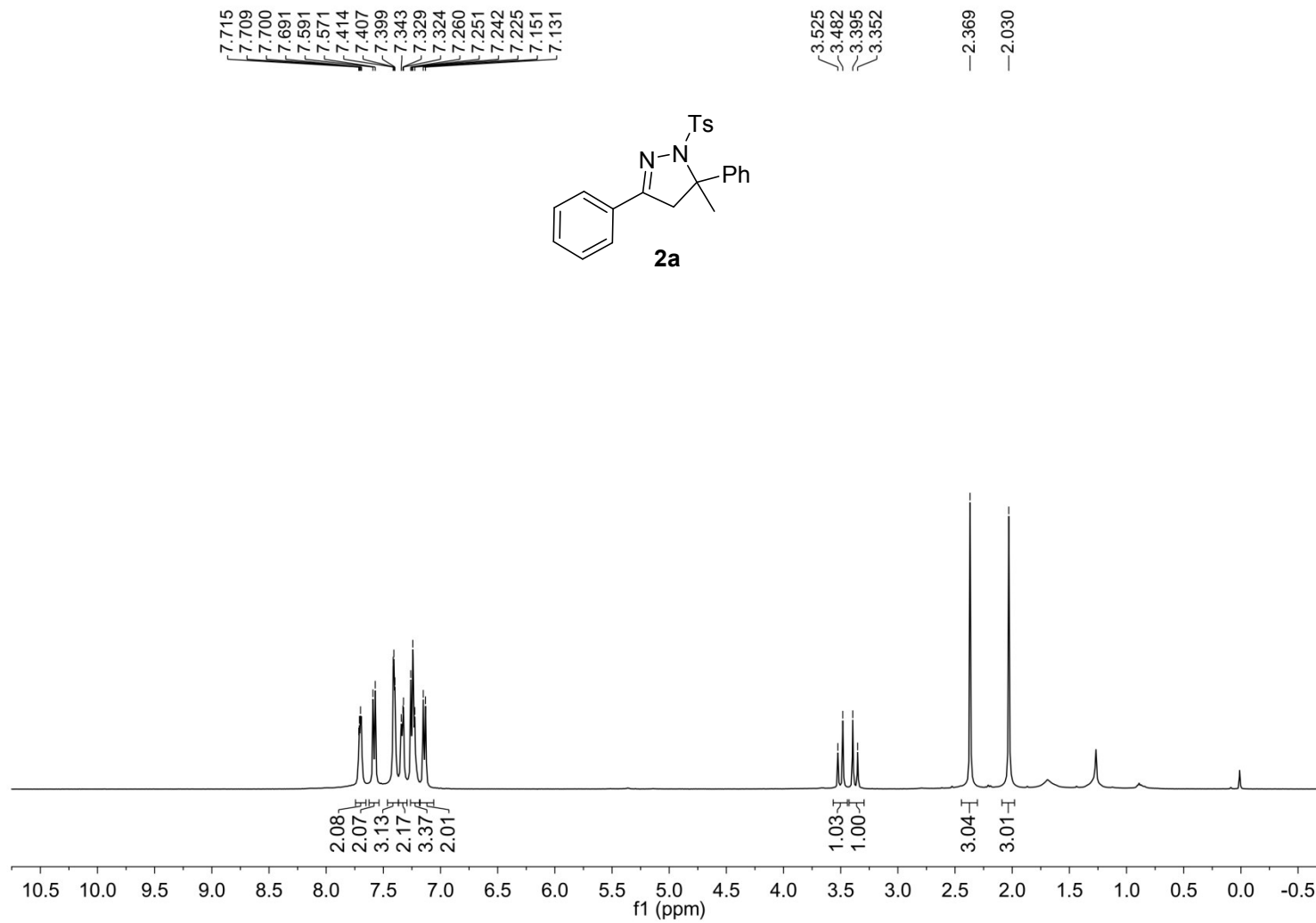
Identification code	2e
Empirical formula	C ₂₃ H ₂₁ BrN ₂ O ₂ S
Formula weight	469.39
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic

Space group	P2 ₁ /n	
Unit cell dimensions	a = 12.3545(4) Å	α = 90°.
	b = 11.9990(4) Å	β = 94.0510(10)°.
	c = 14.3274(6) Å	γ = 90°.
Volume	2118.61(13) Å ³	
Z	4	
Density (calculated)	1.472 Mg/m ³	
Absorption coefficient	2.061 mm ⁻¹	
F(000)	960	
Crystal size	0.320 x 0.250 x 0.220 mm ³	
Theta range for data collection	2.104 to 27.567°.	
Index ranges	-13<=h<=16, -14<=k<=15, -18<=l<=18	
Reflections collected	32627	
Independent reflections	4888 [R(int) = 0.0397]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.4795	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4888 / 0 / 264	
Goodness-of-fit on F ²	1.016	
Final R indices [I>2sigma(I)]	R1 = 0.0430, wR2 = 0.1048	
R indices (all data)	R1 = 0.0672, wR2 = 0.1167	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.675 and -0.744 e.Å ⁻³	

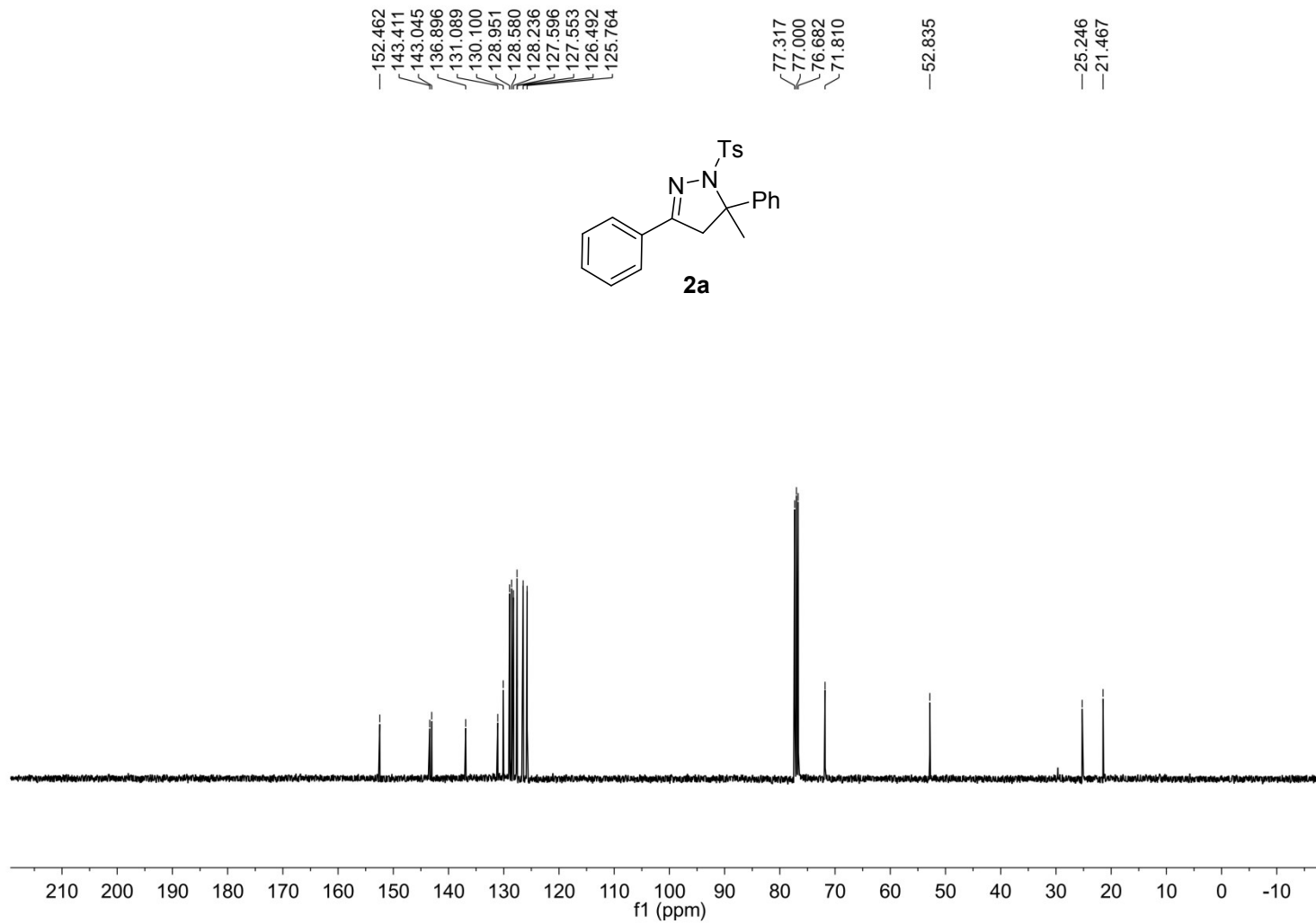
References

- (1) Tripathi, C. B.; Mukherjee, S. *Org. Lett.* **2014**, *16*, 3368.
- (2) Imai, T.; Nishida, S. *Synthesis* **1993**, *1993*, 395.
- (3) Rajam, S.; Jadhav, A. V.; Li, Q.; Sarkar, S. K.; Singh, P. N. D.; Rohr, A.; Pace, T.

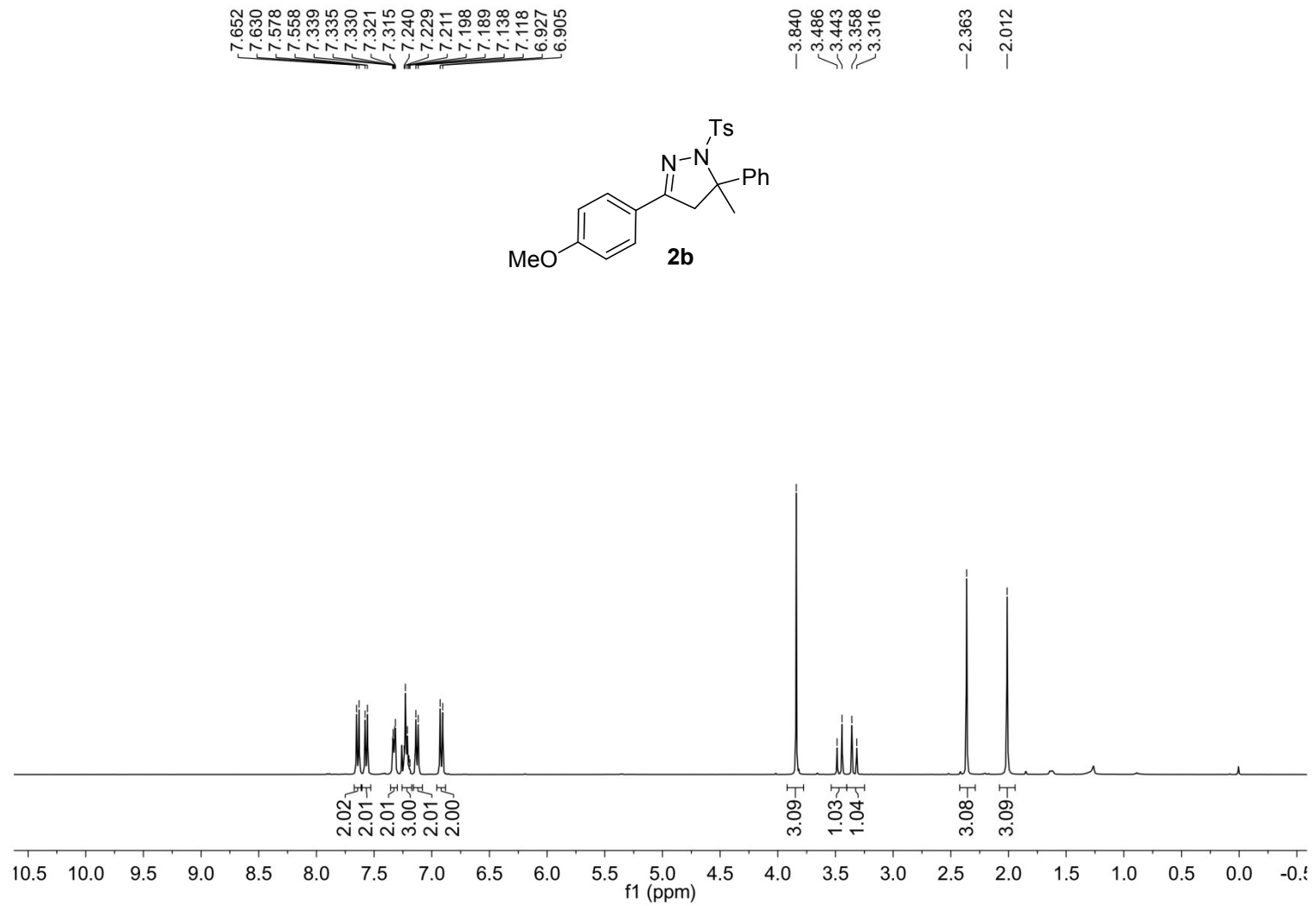
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- (4) Hu, X.-Q.; Qi, X.; Chen, J.-R.; Zhao, Q.-Q.; Wei, Q.; Lan, Y.; Xiao, W.-J. *Nat. Chem.* **2016**, *7*, 11188.
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S20



S21



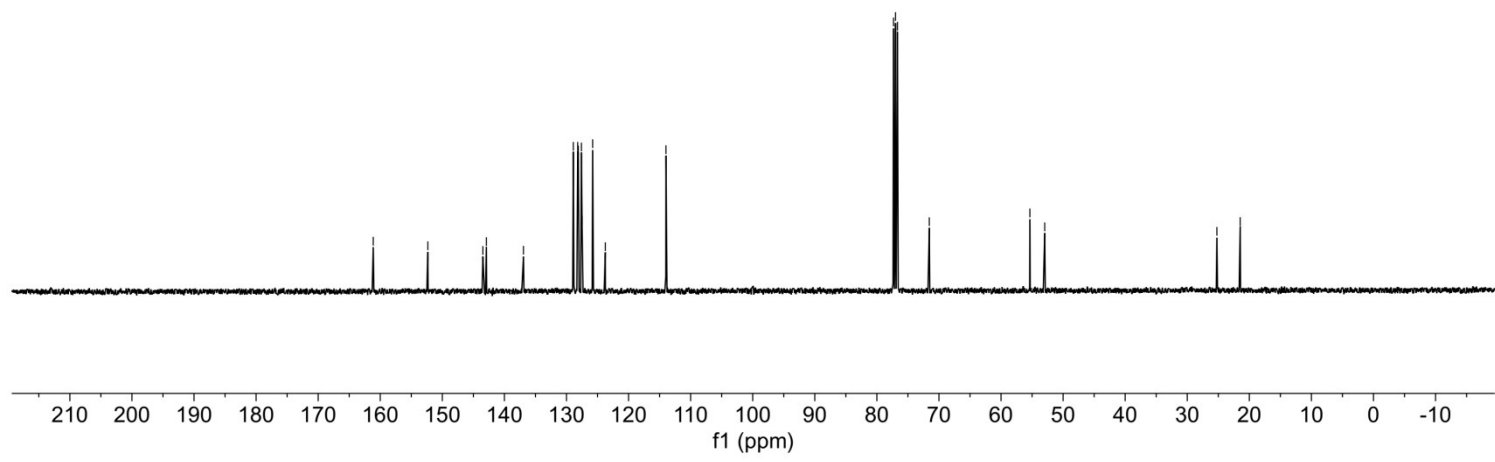
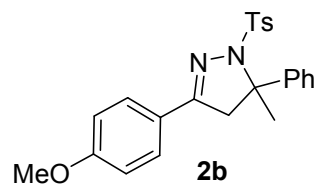
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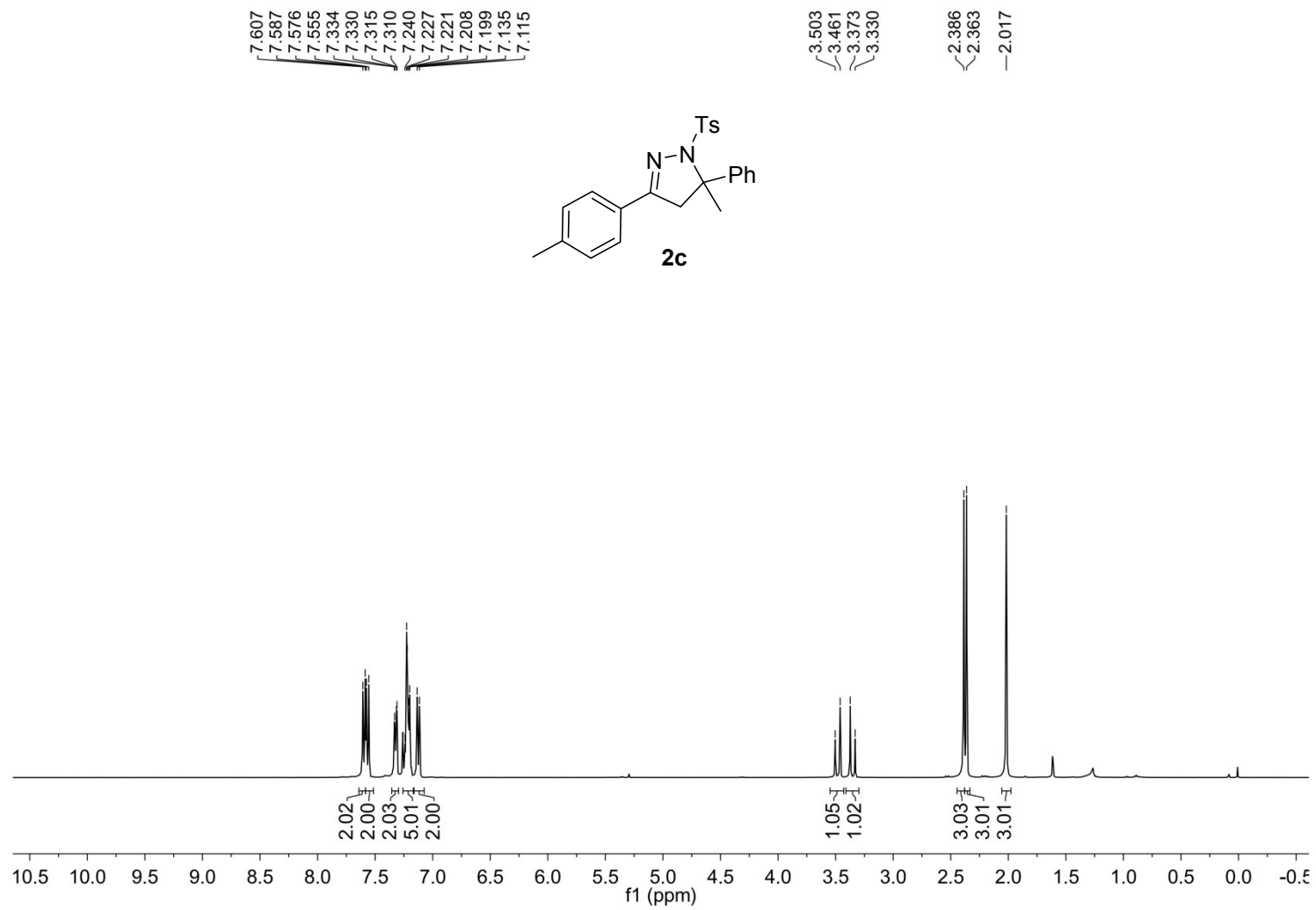
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— 152.338
143.465
142.905
136.929
128.888
128.194
128.094
127.593
127.489
125.785
123.750
113.973

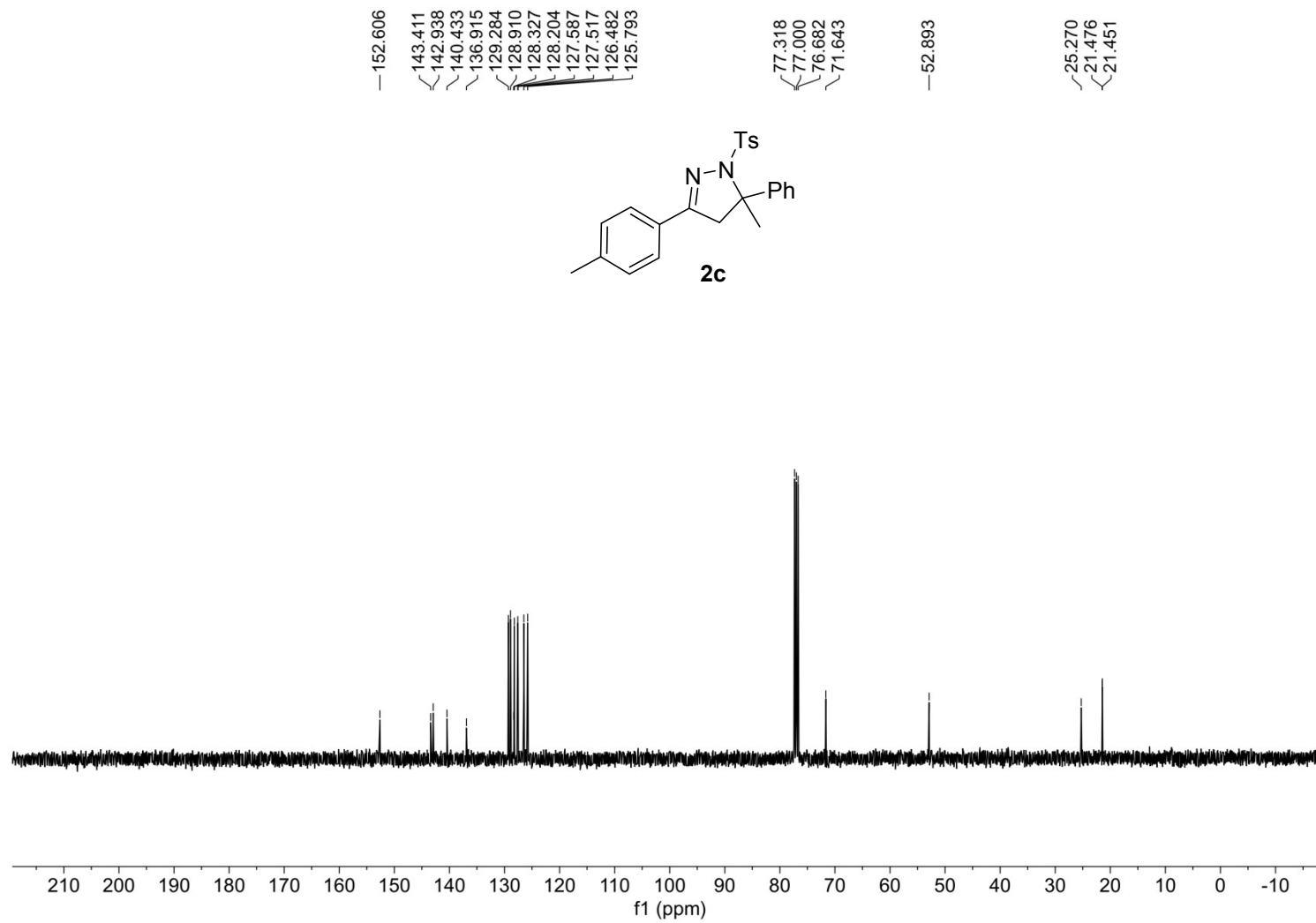
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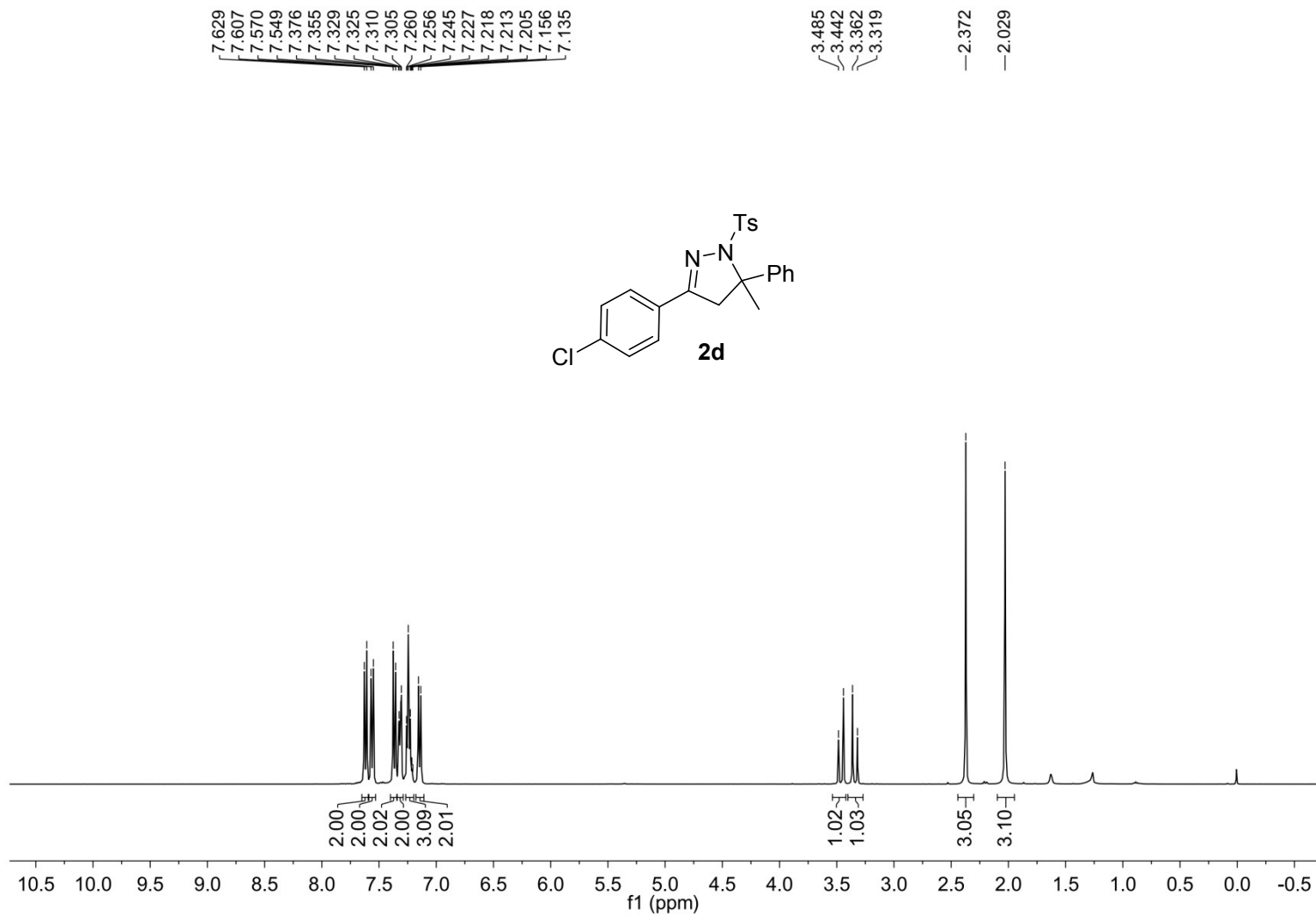
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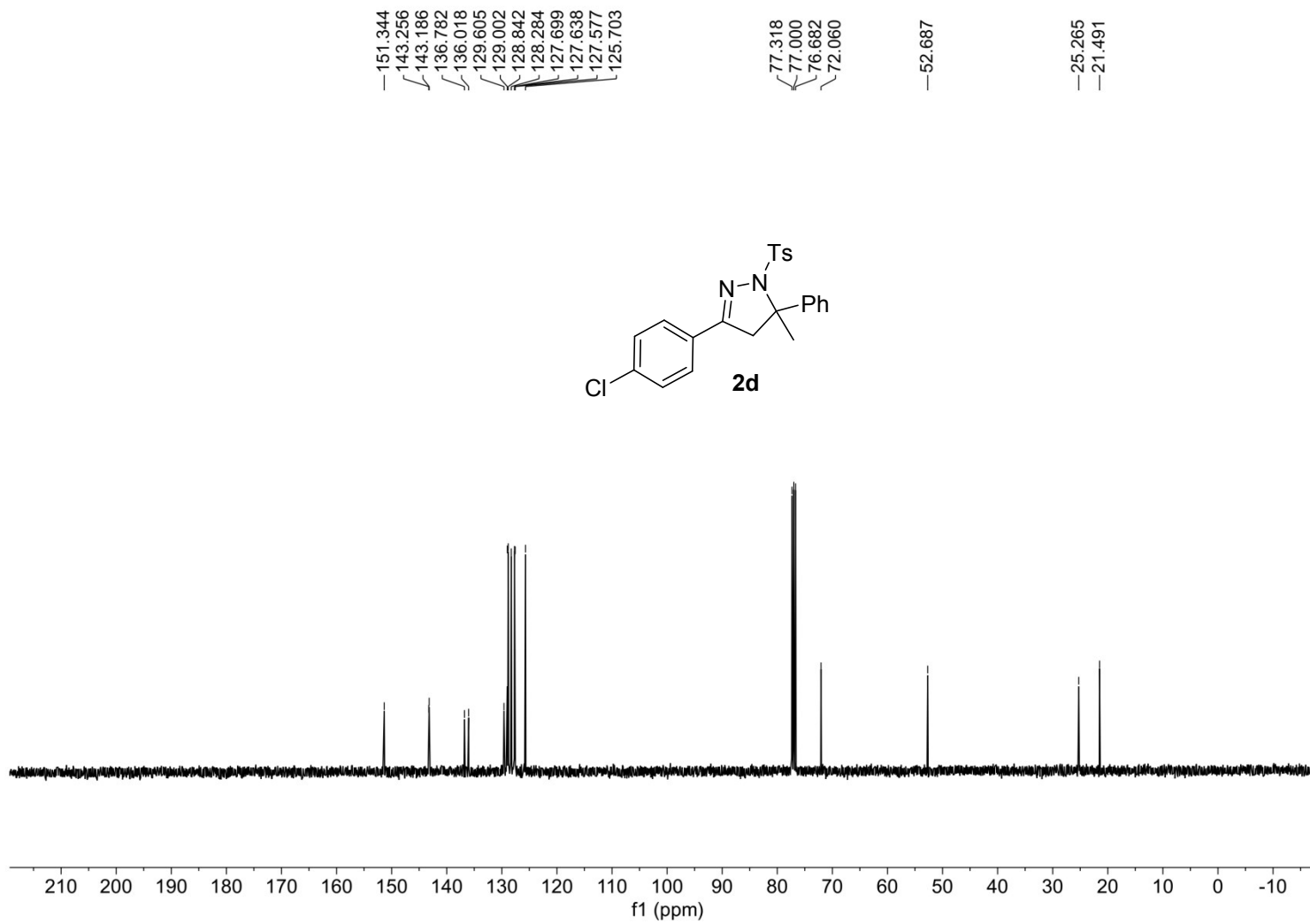




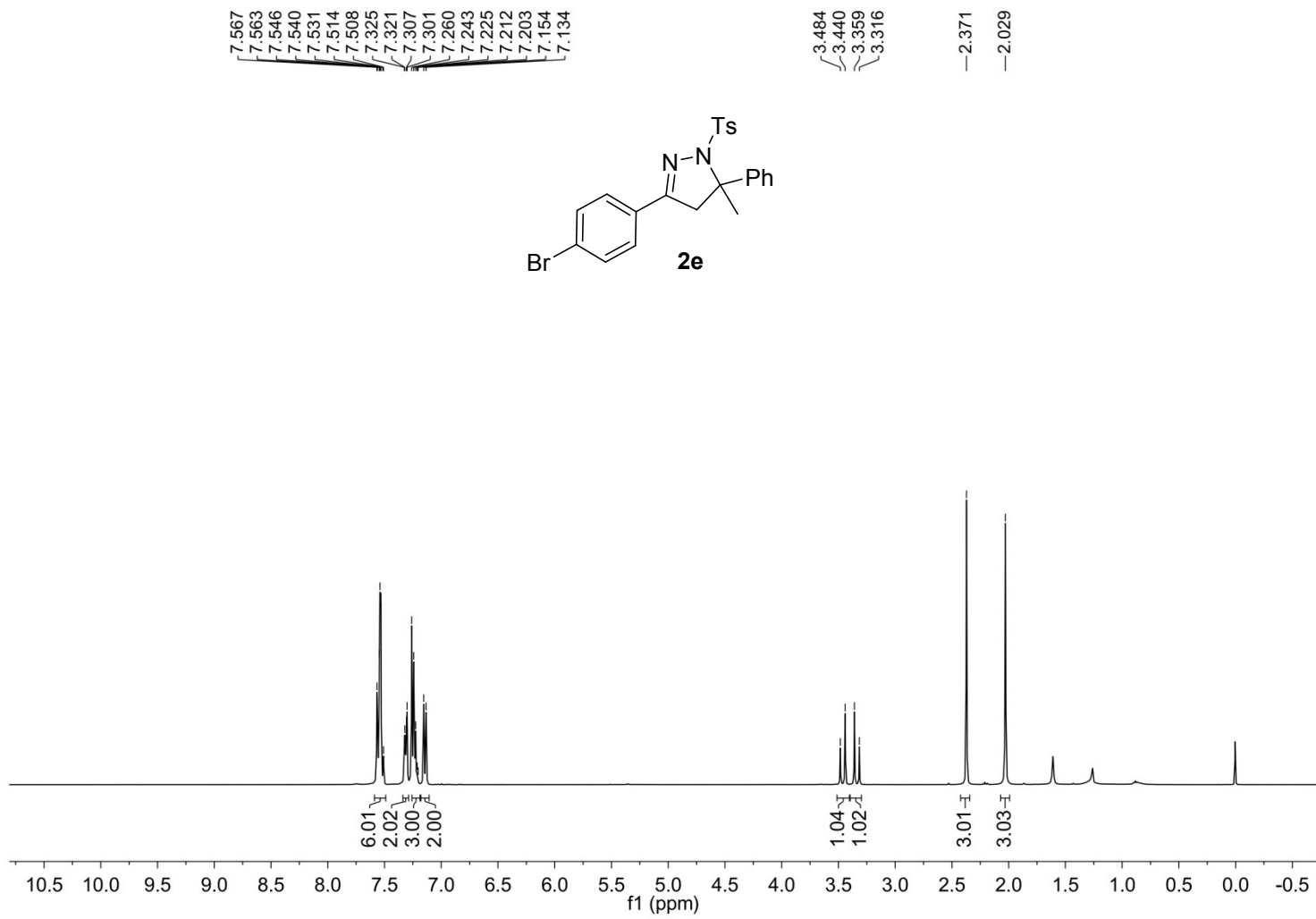


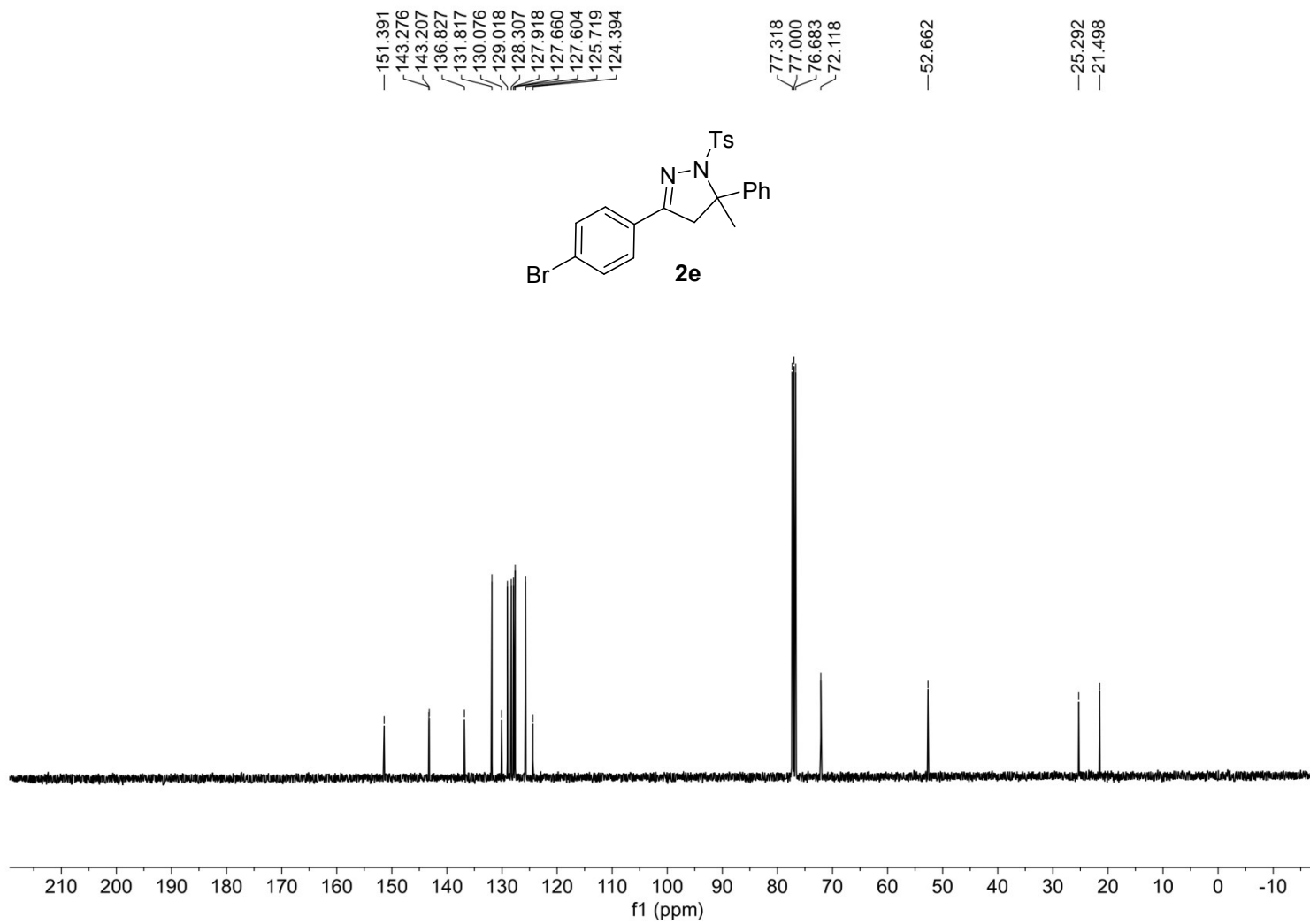
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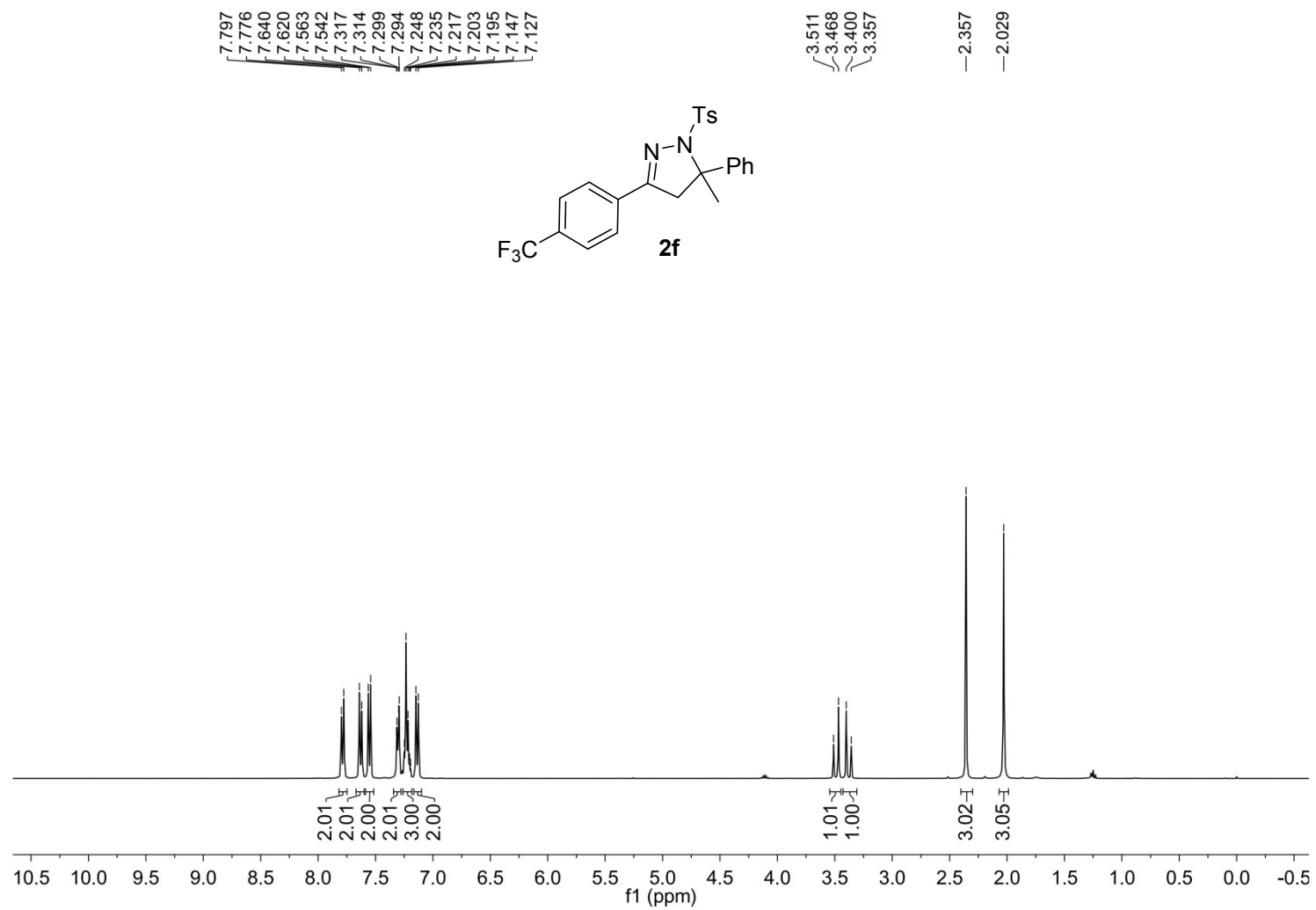


S27

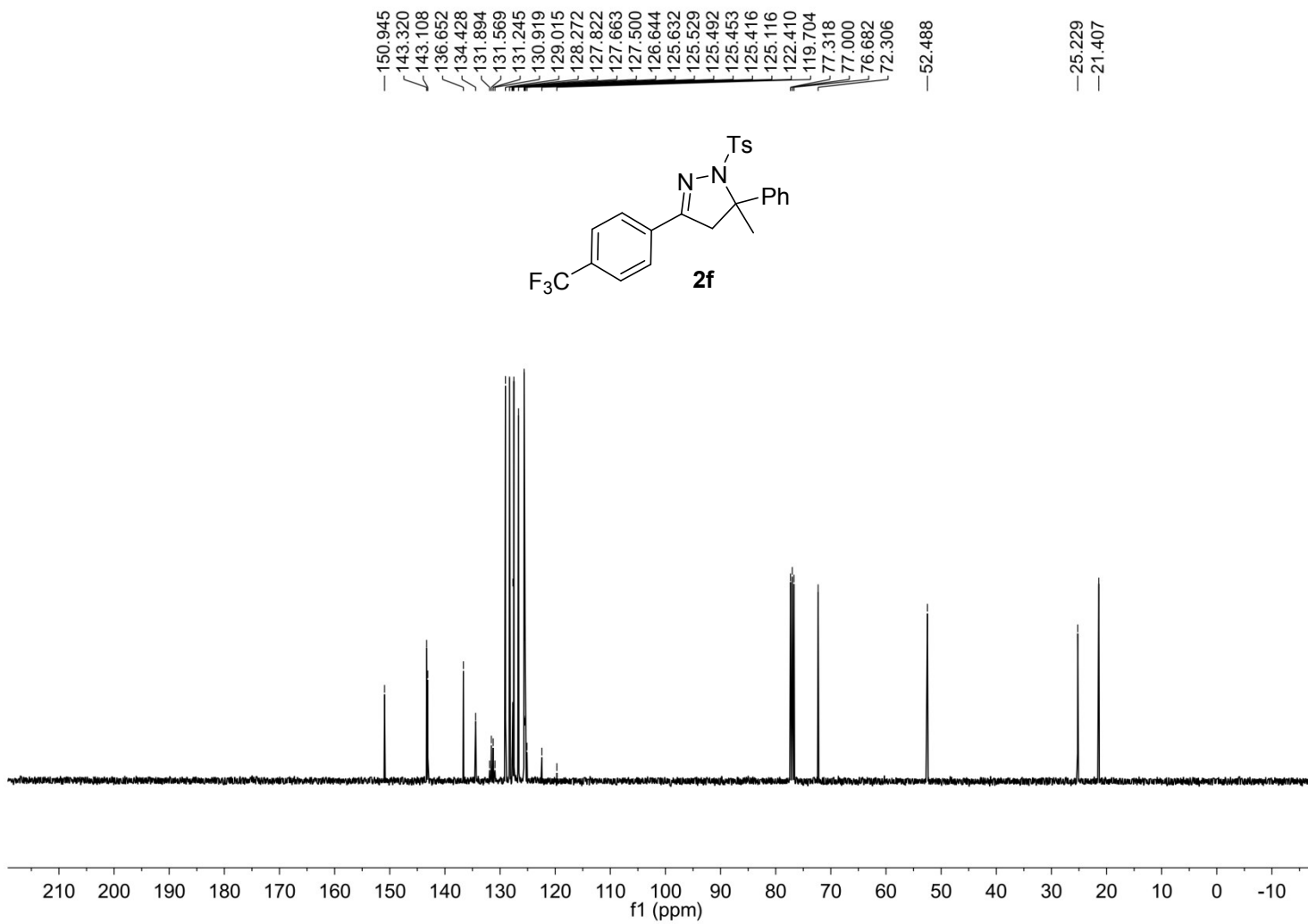




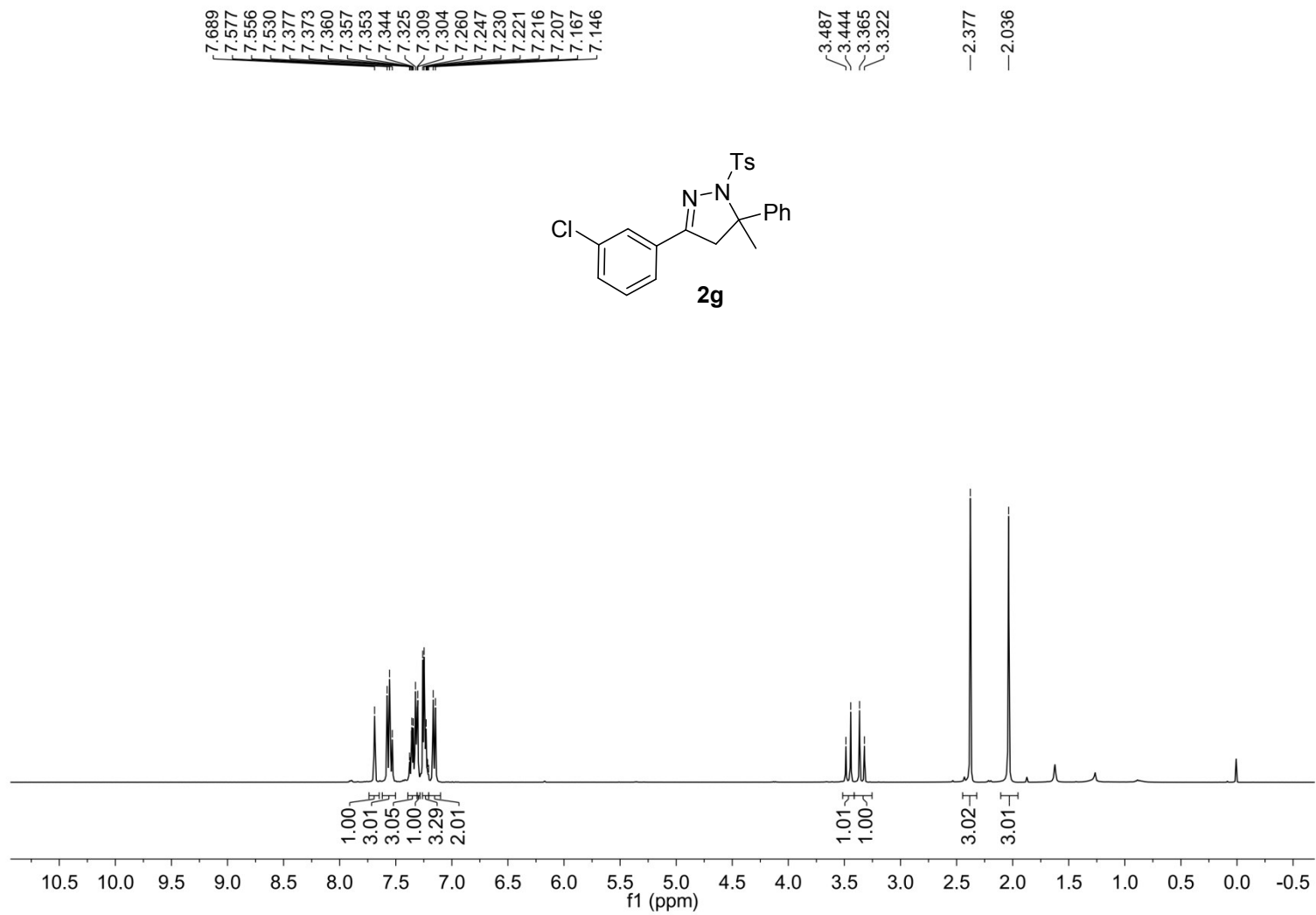
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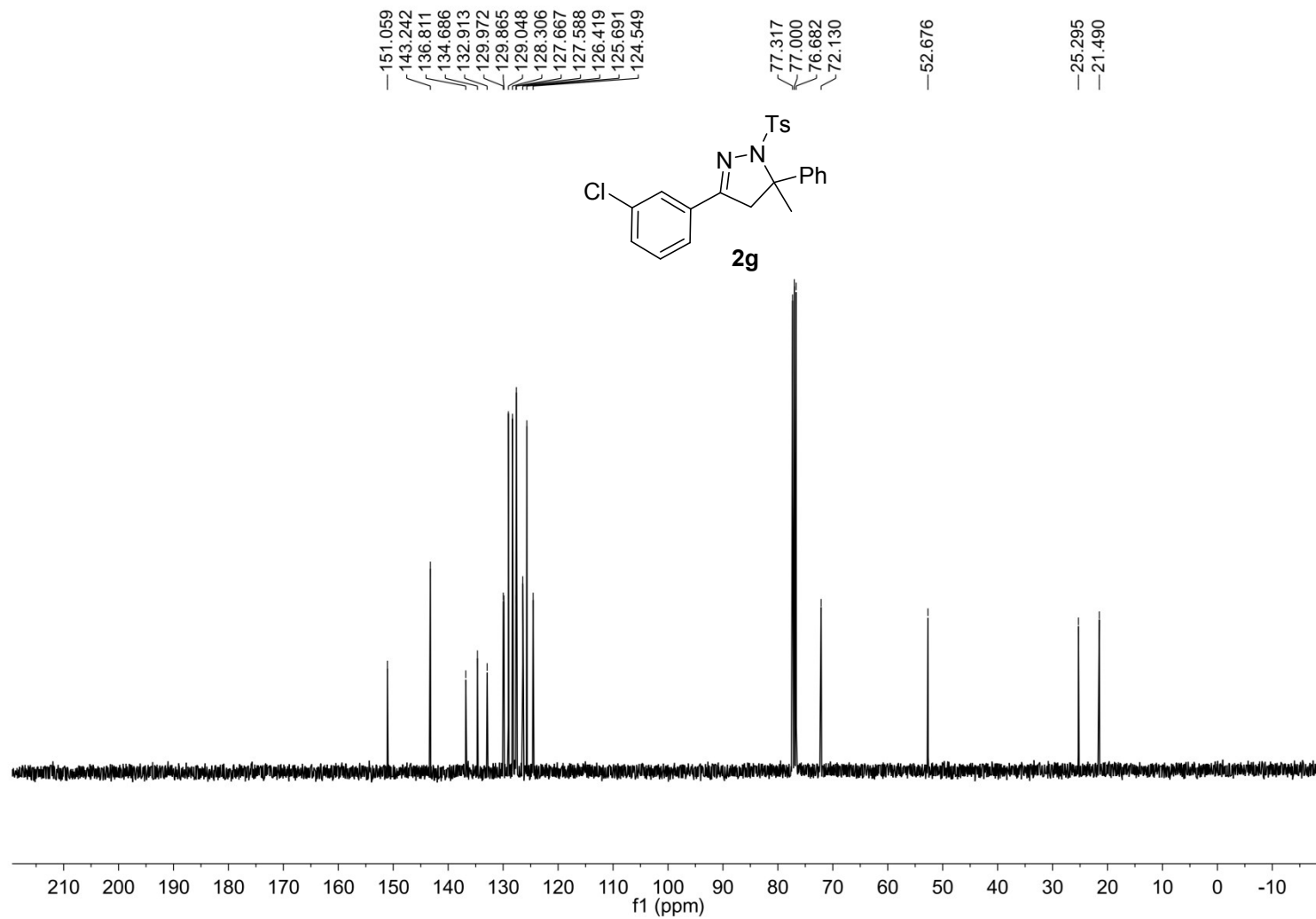


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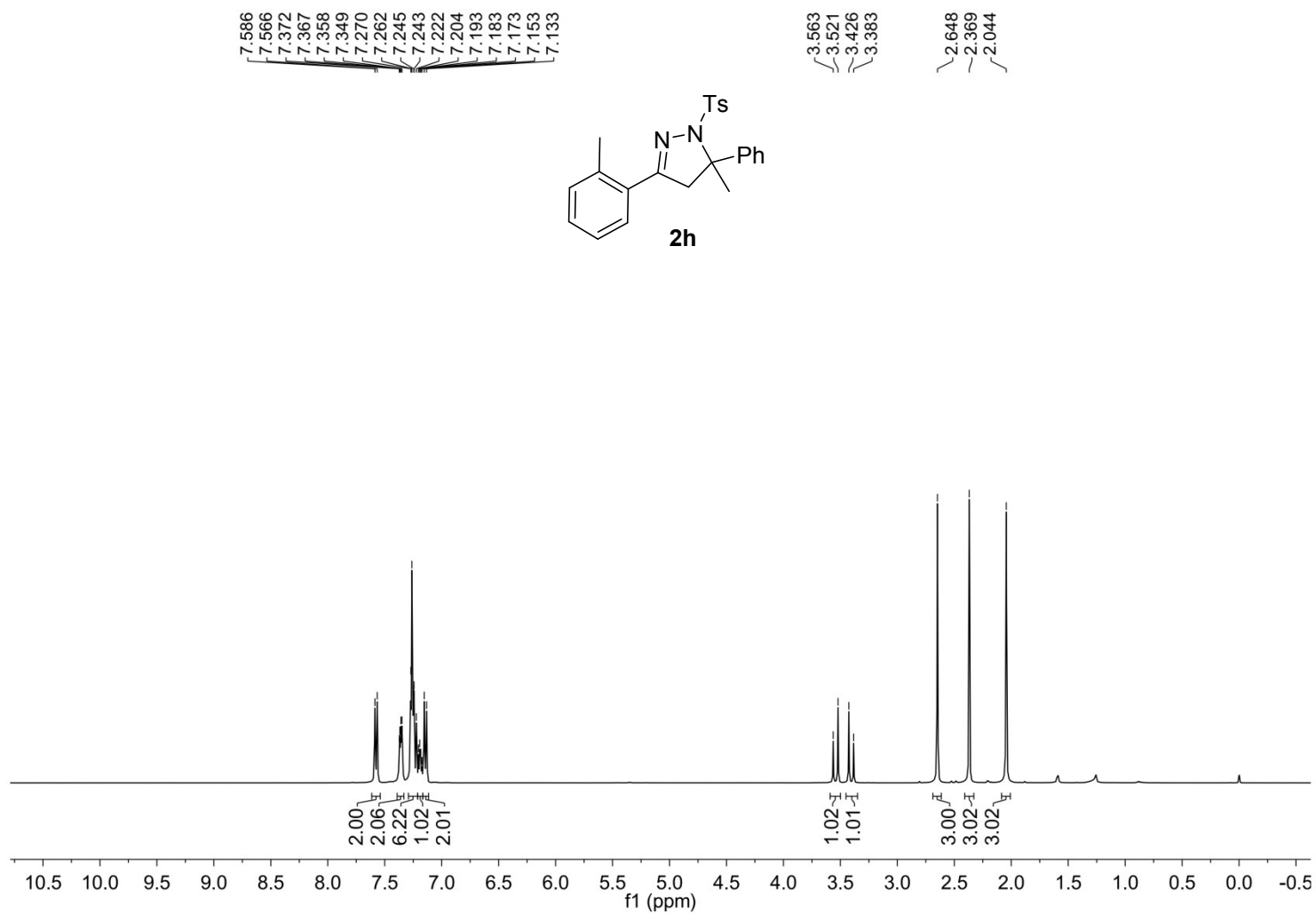


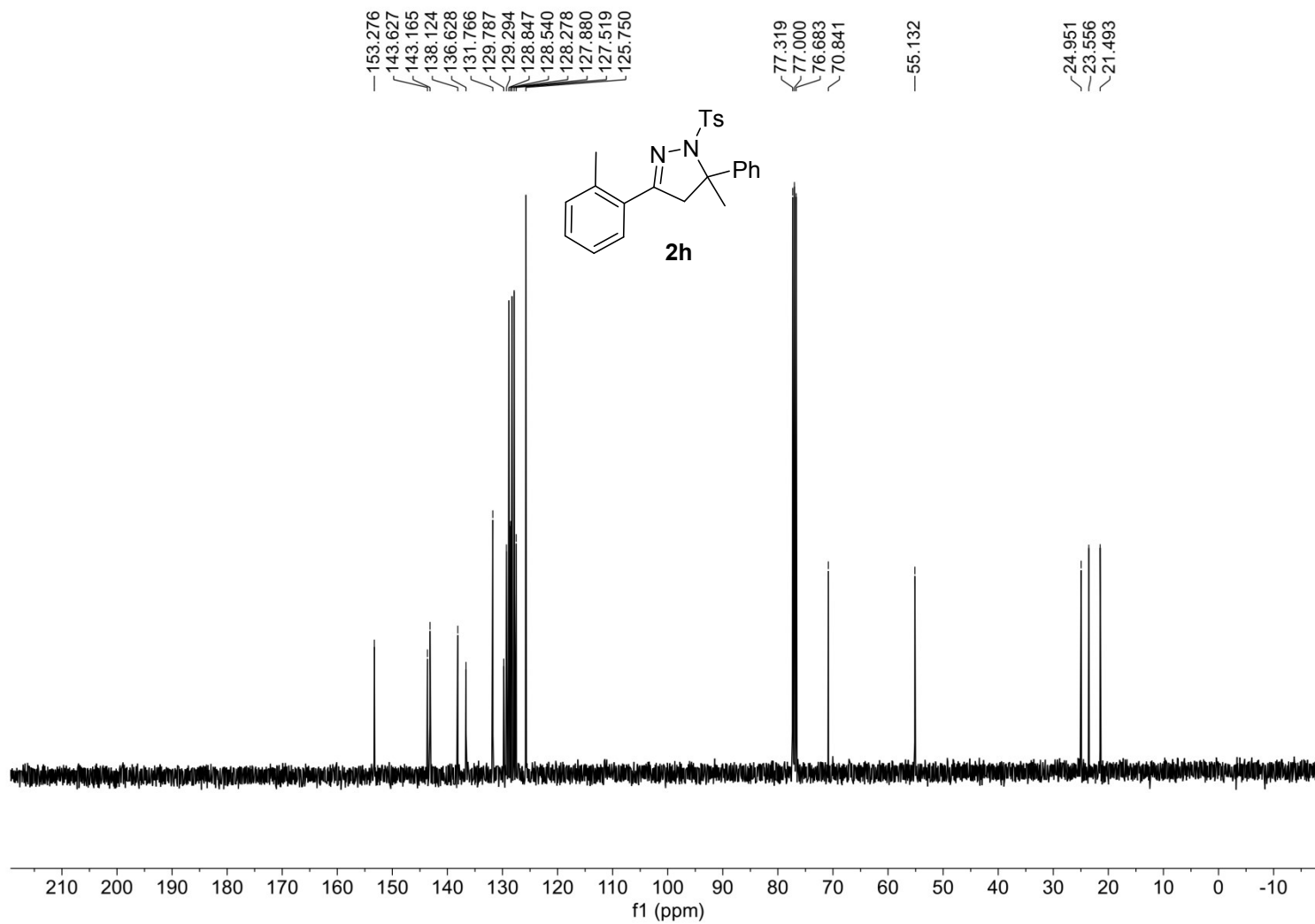
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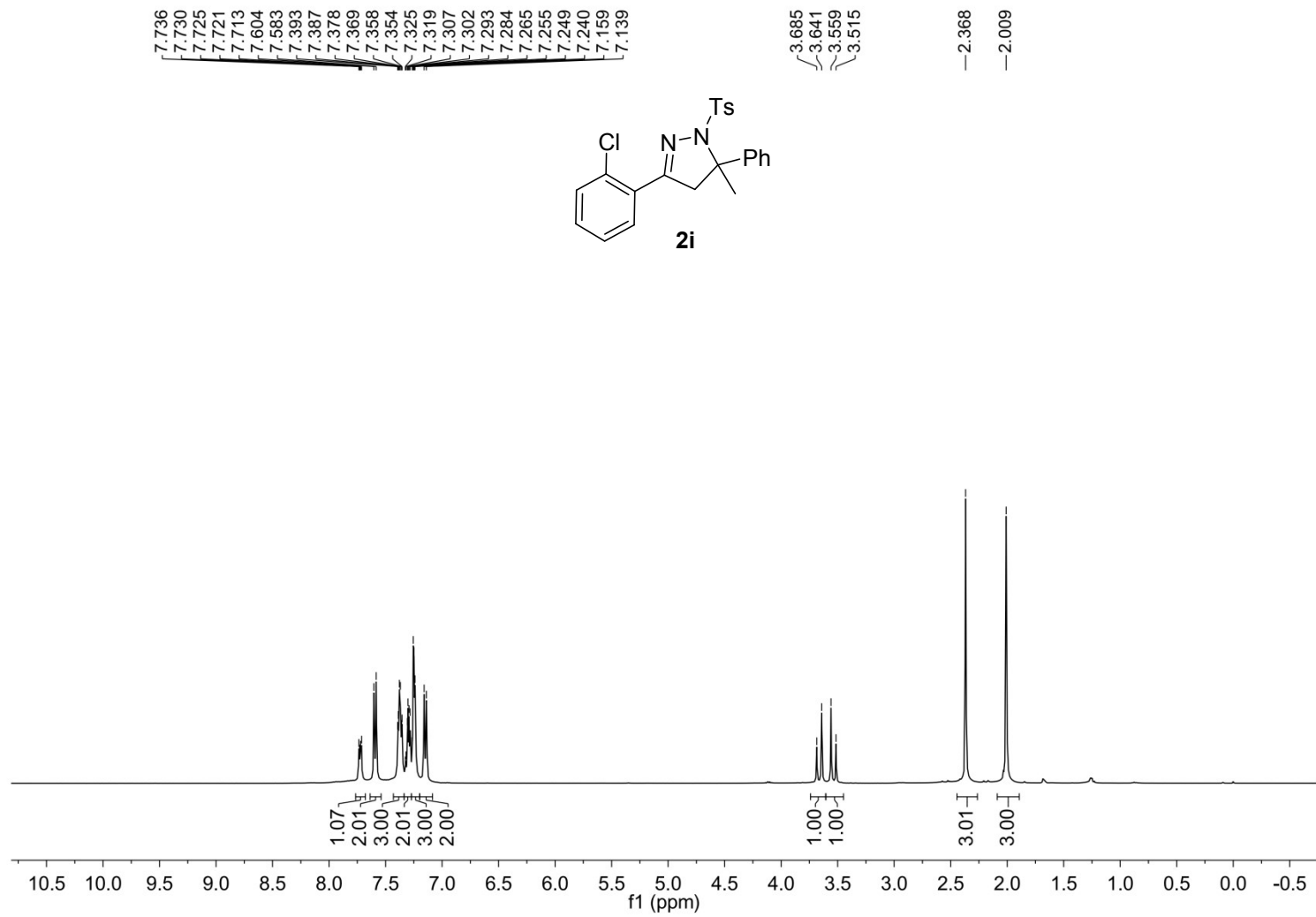


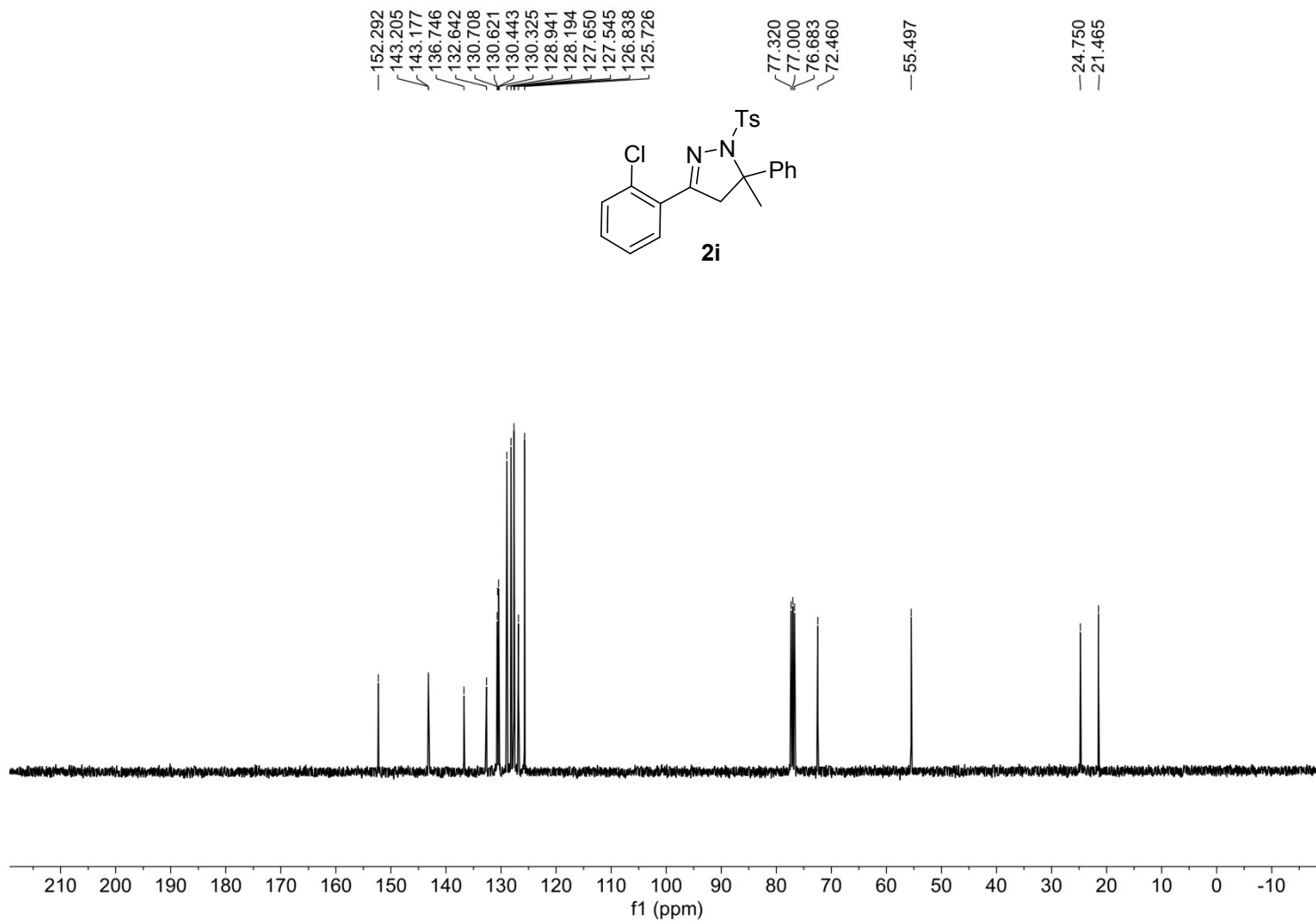
S33



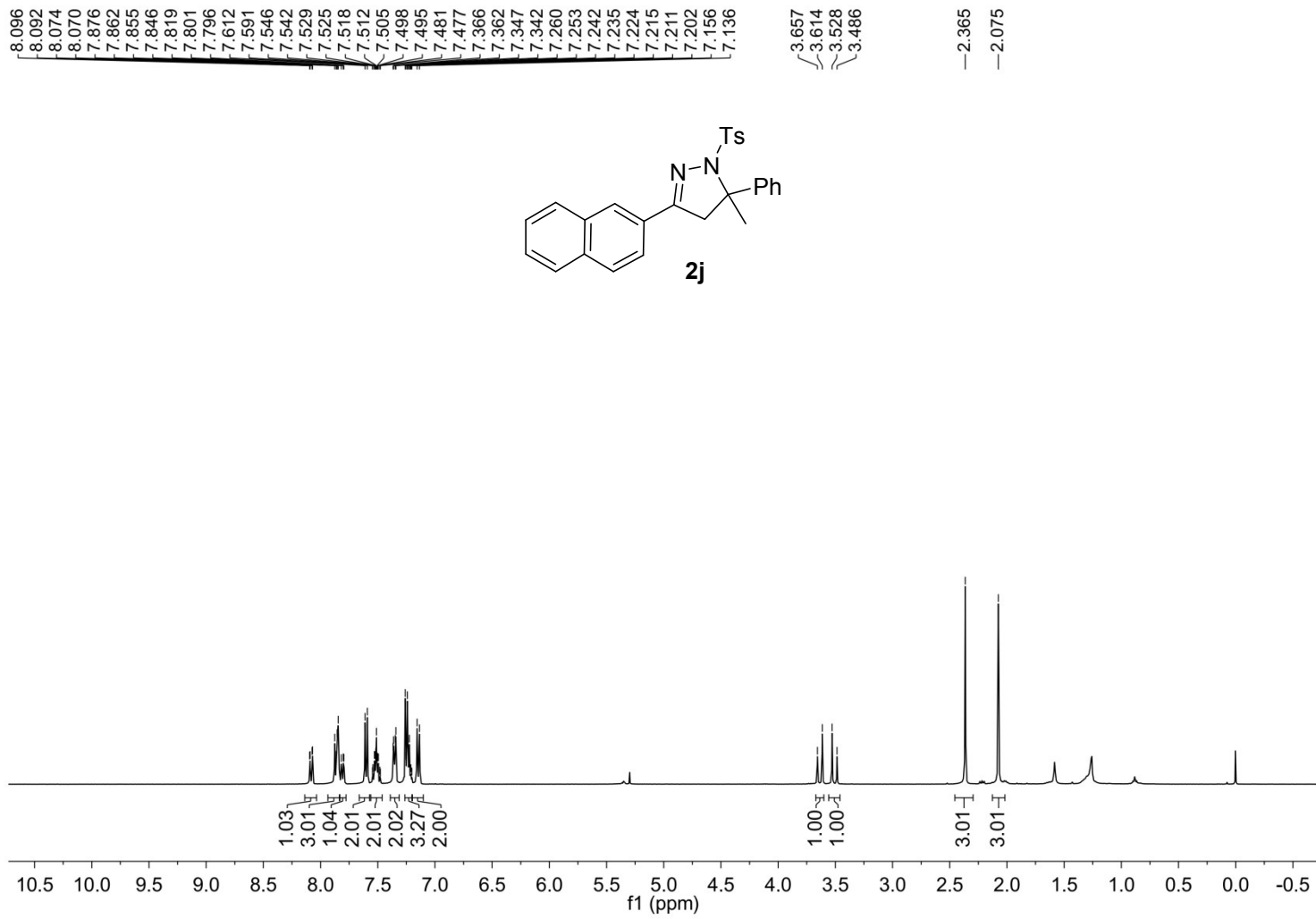


S35





S37

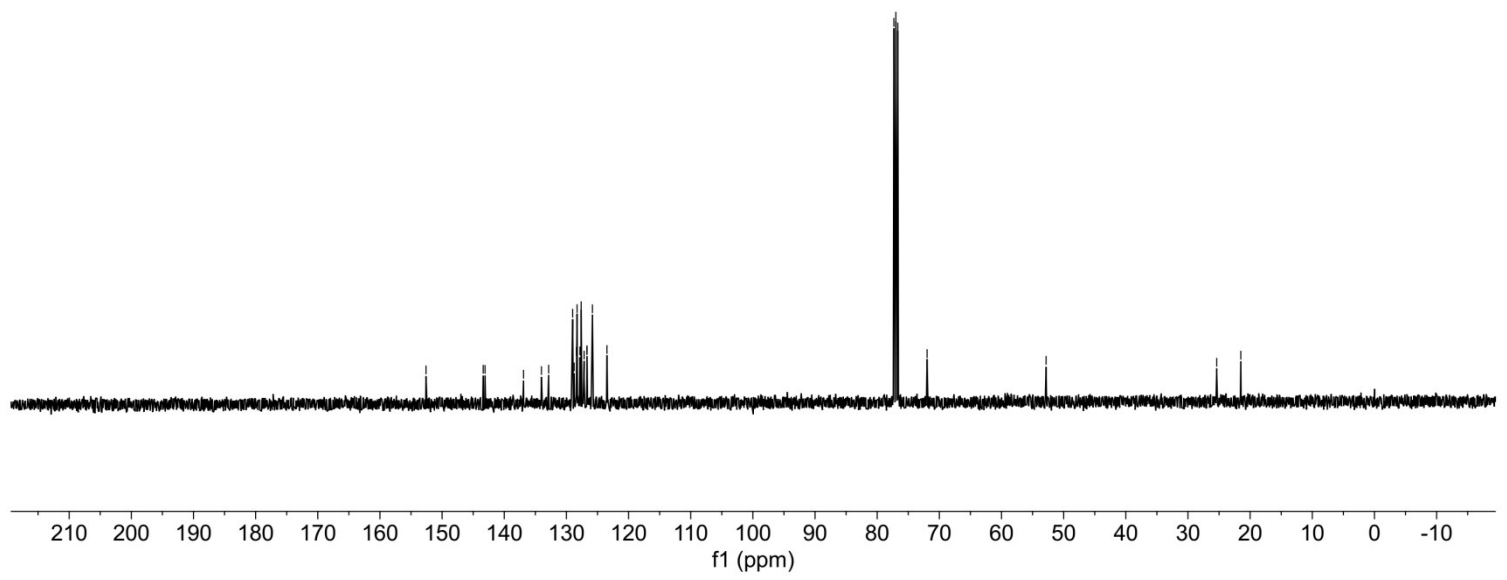
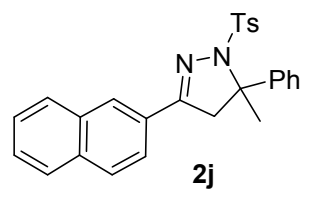


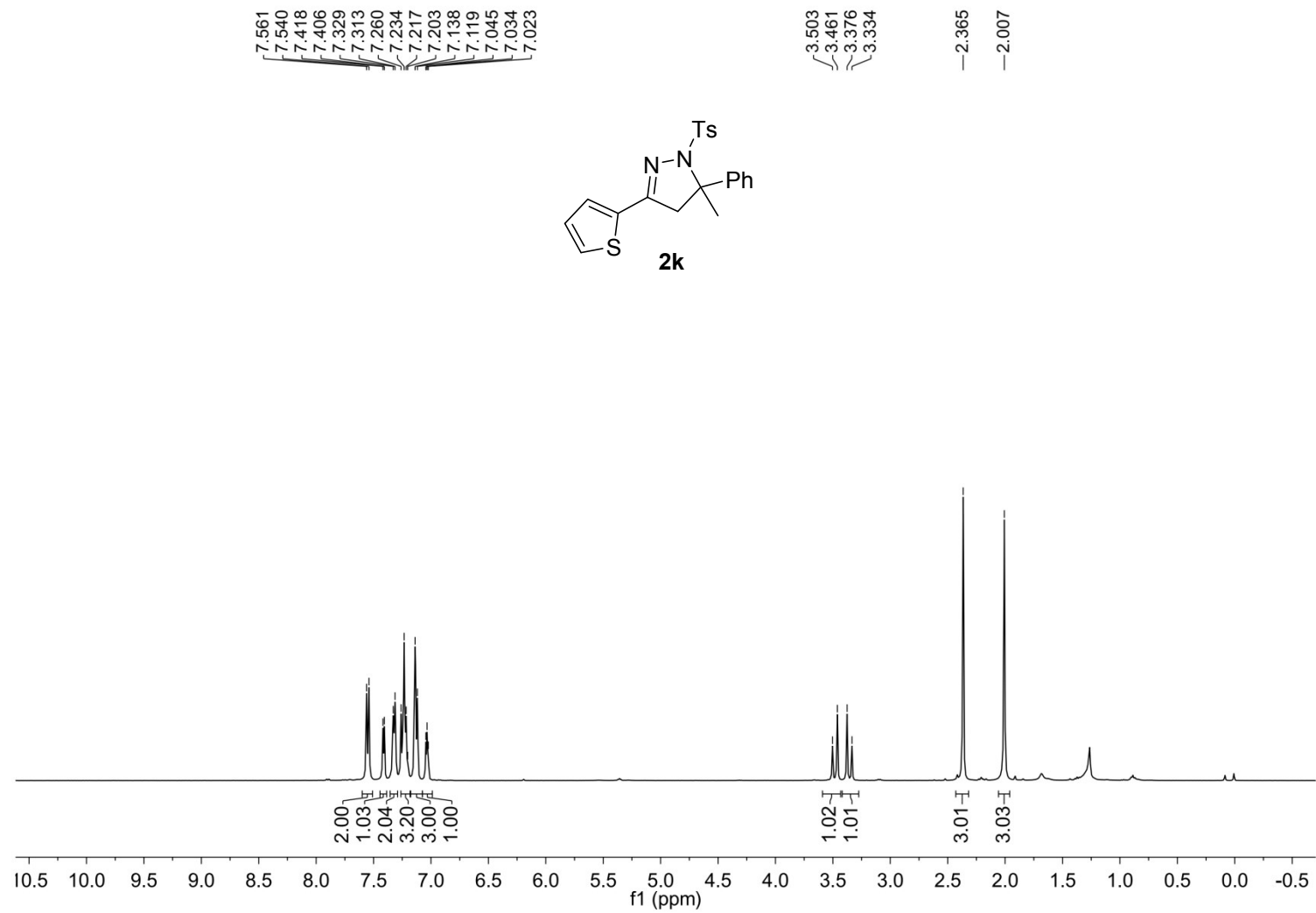
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127.611
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123.477

77.318
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76.682
71.974

52.832

25.375
21.504





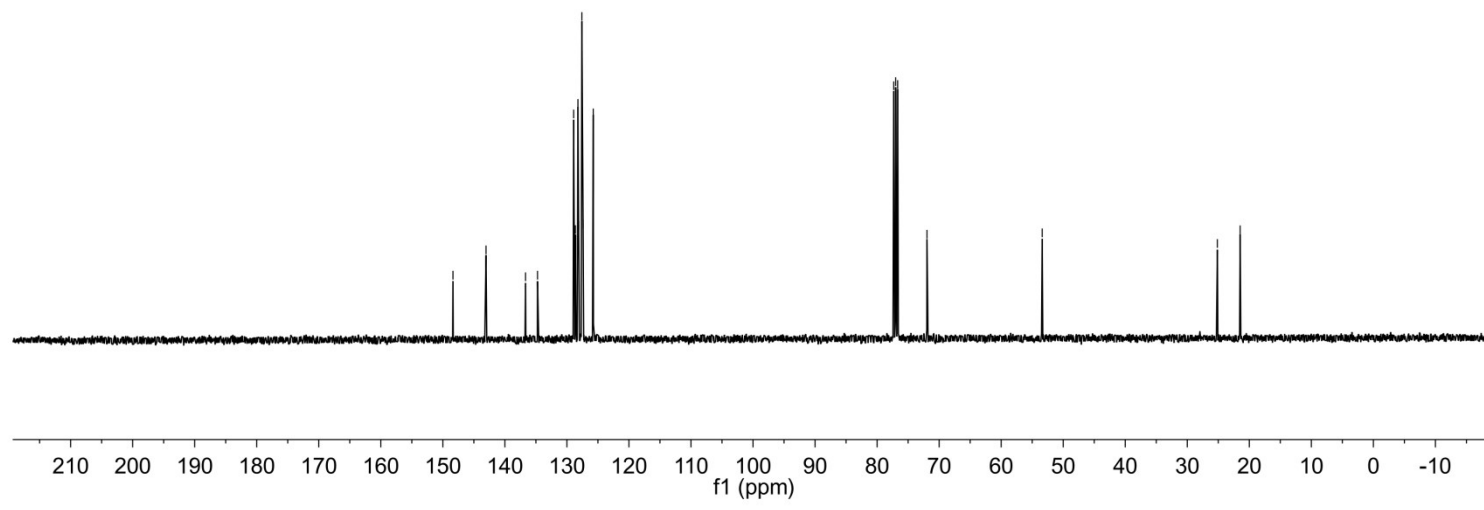
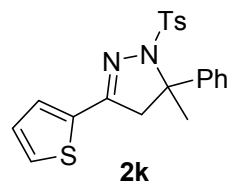
S40

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125.756

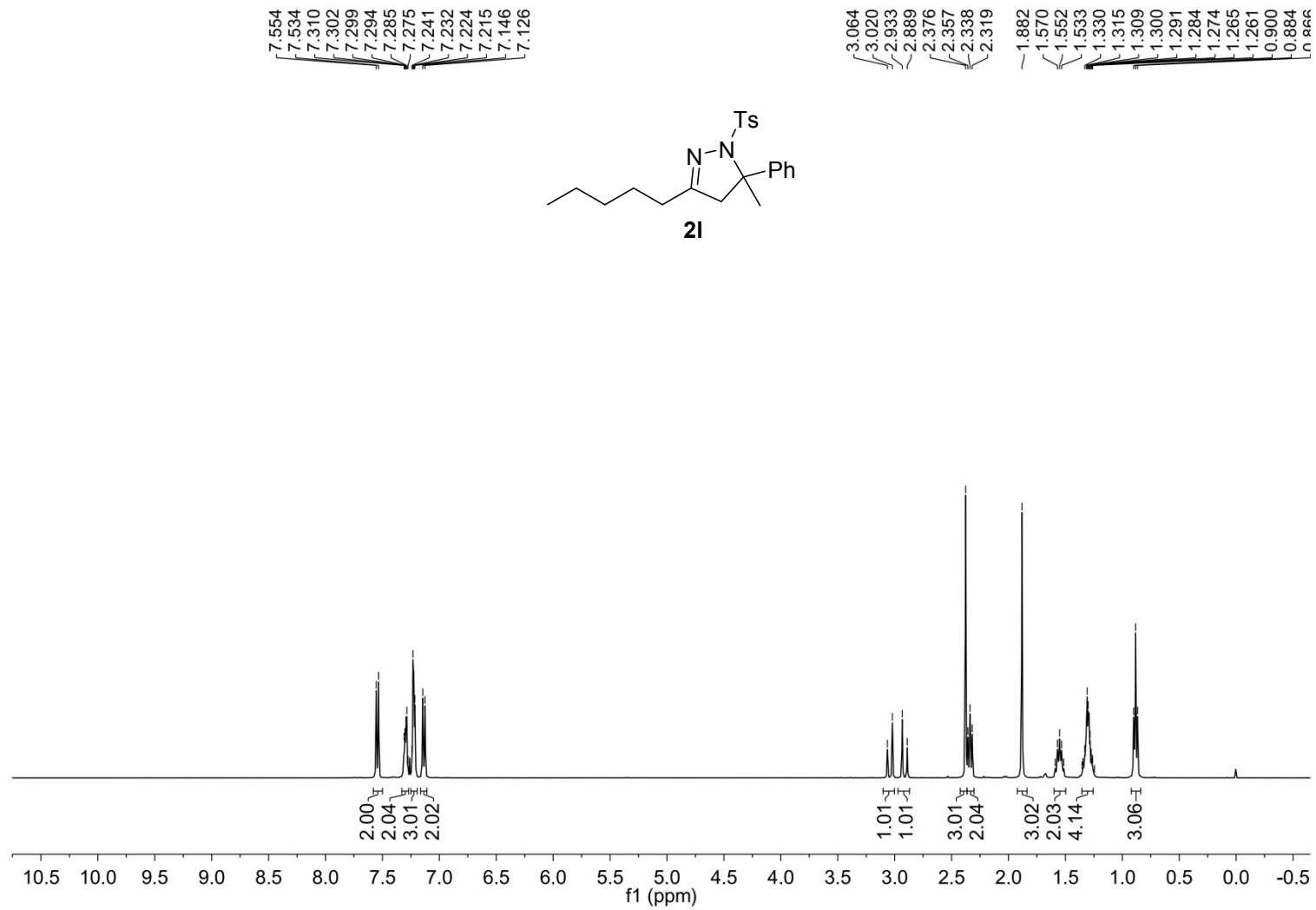
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71.958

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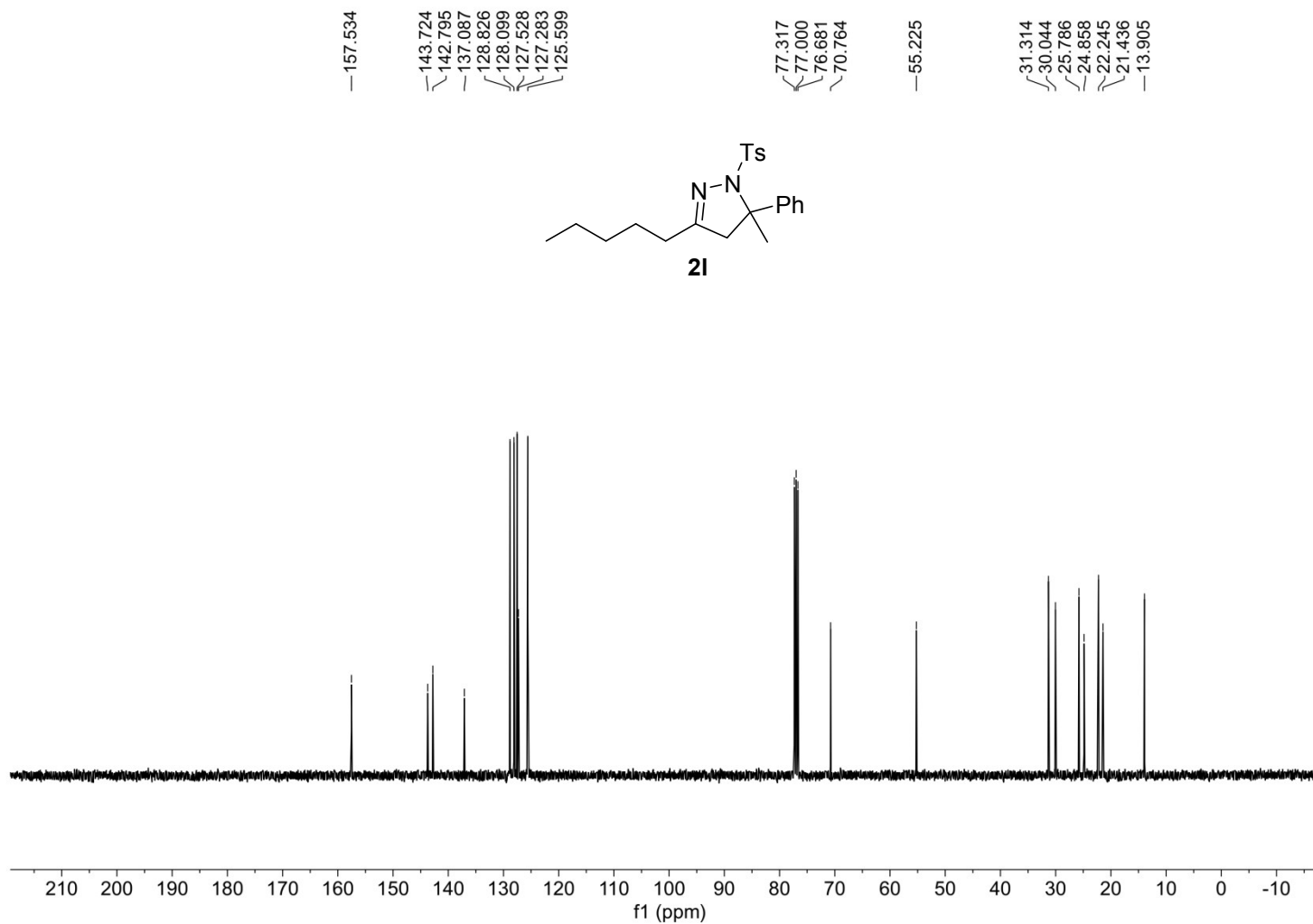
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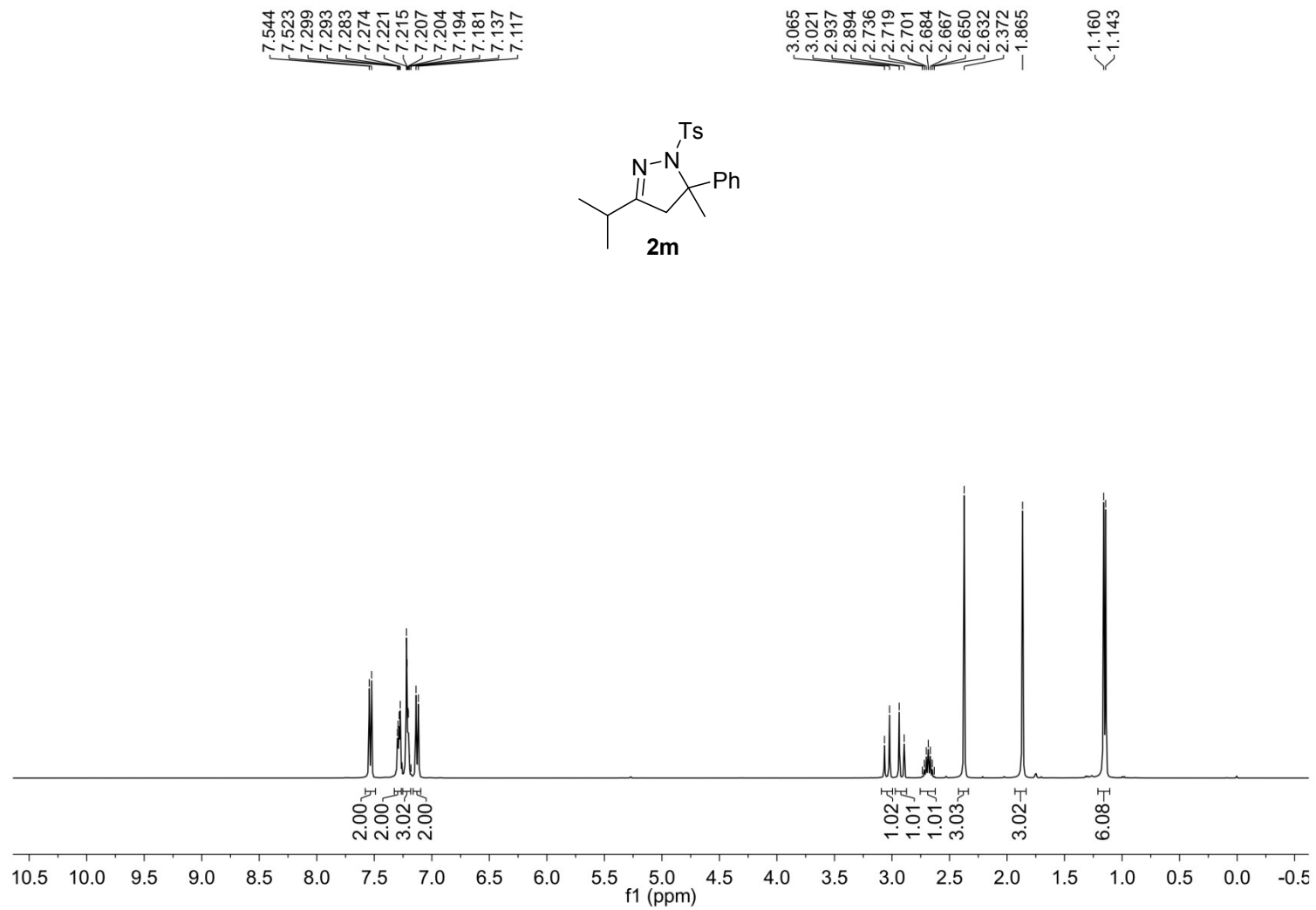
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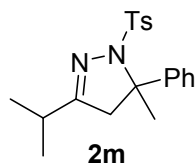
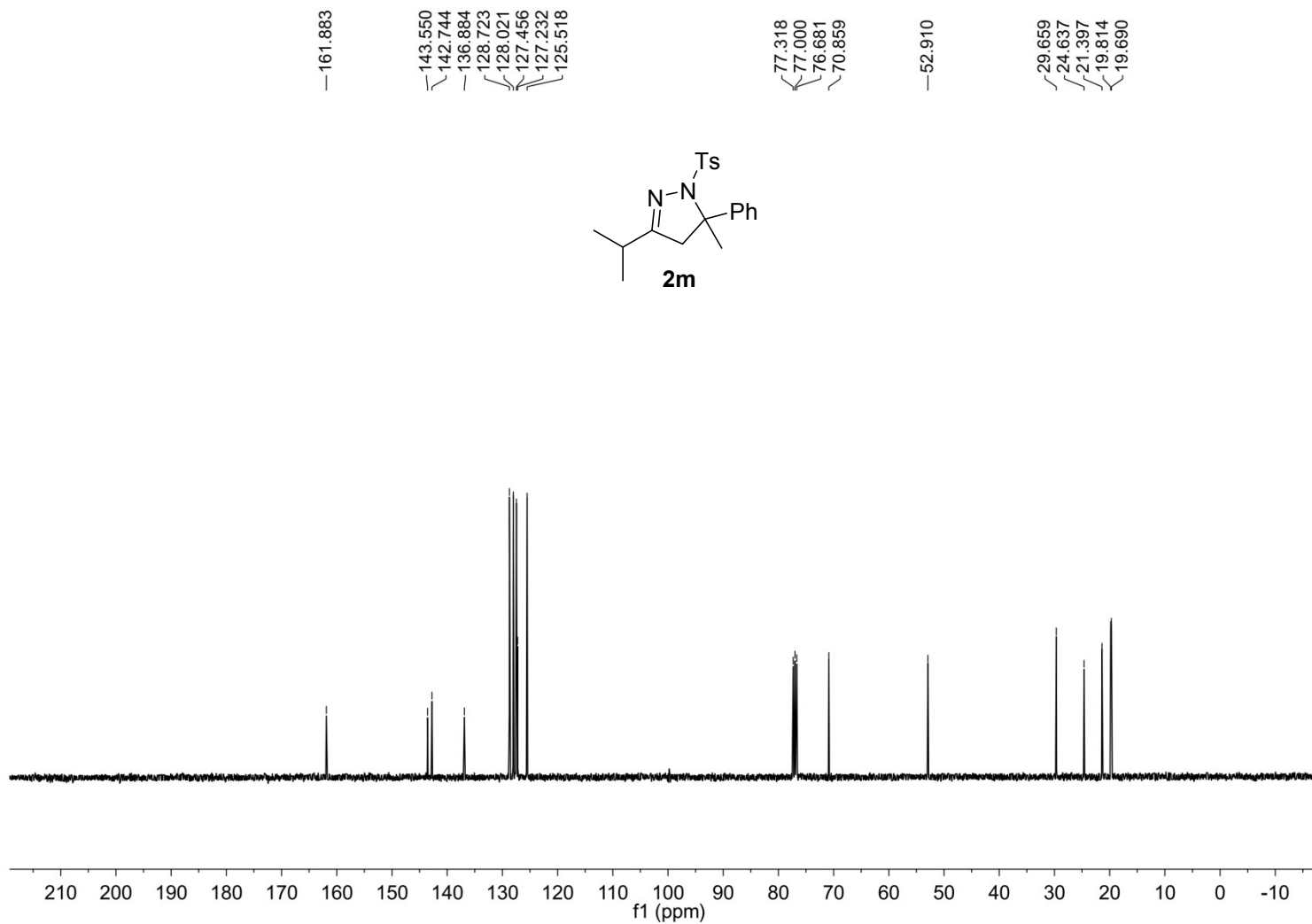
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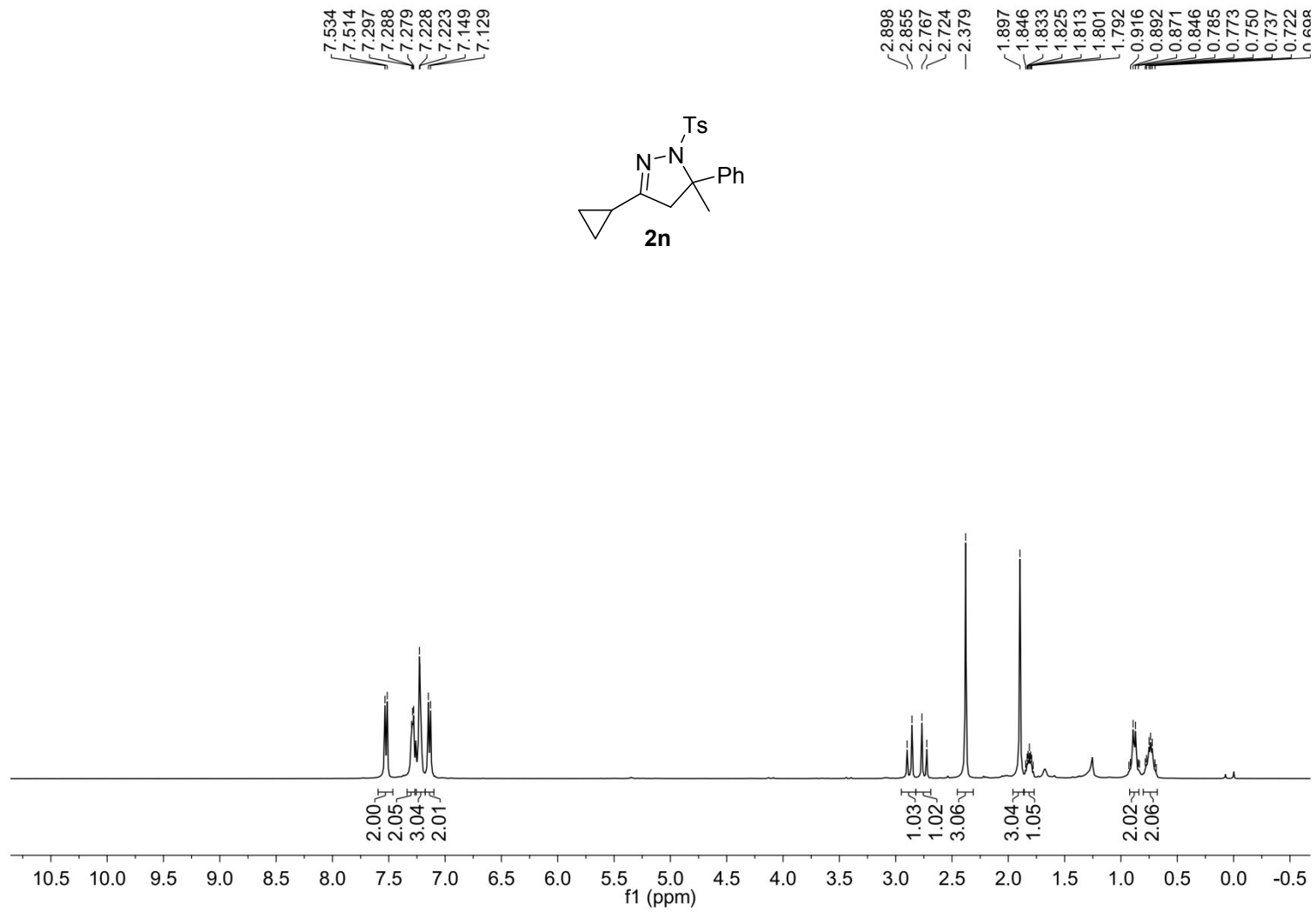
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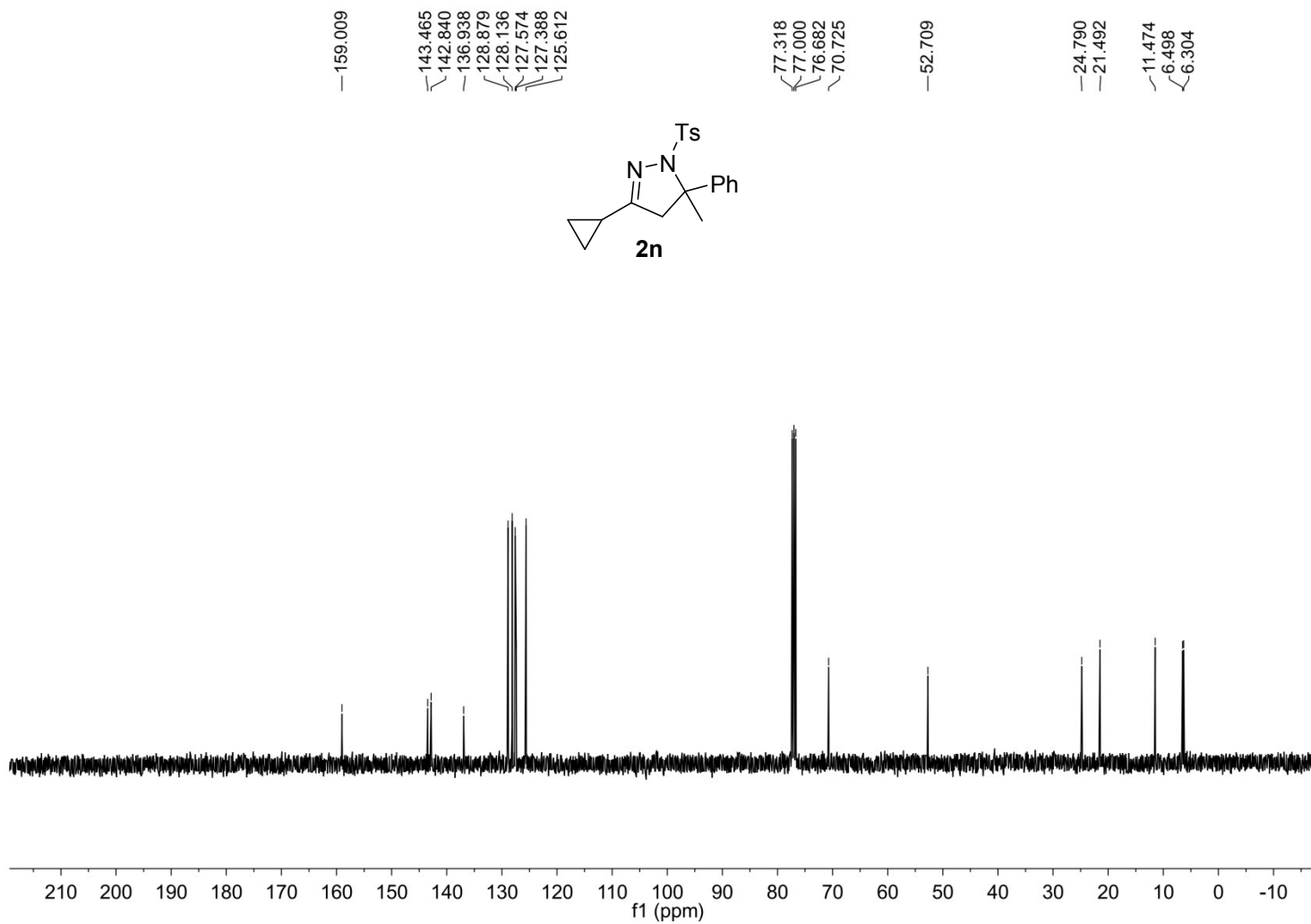


S44

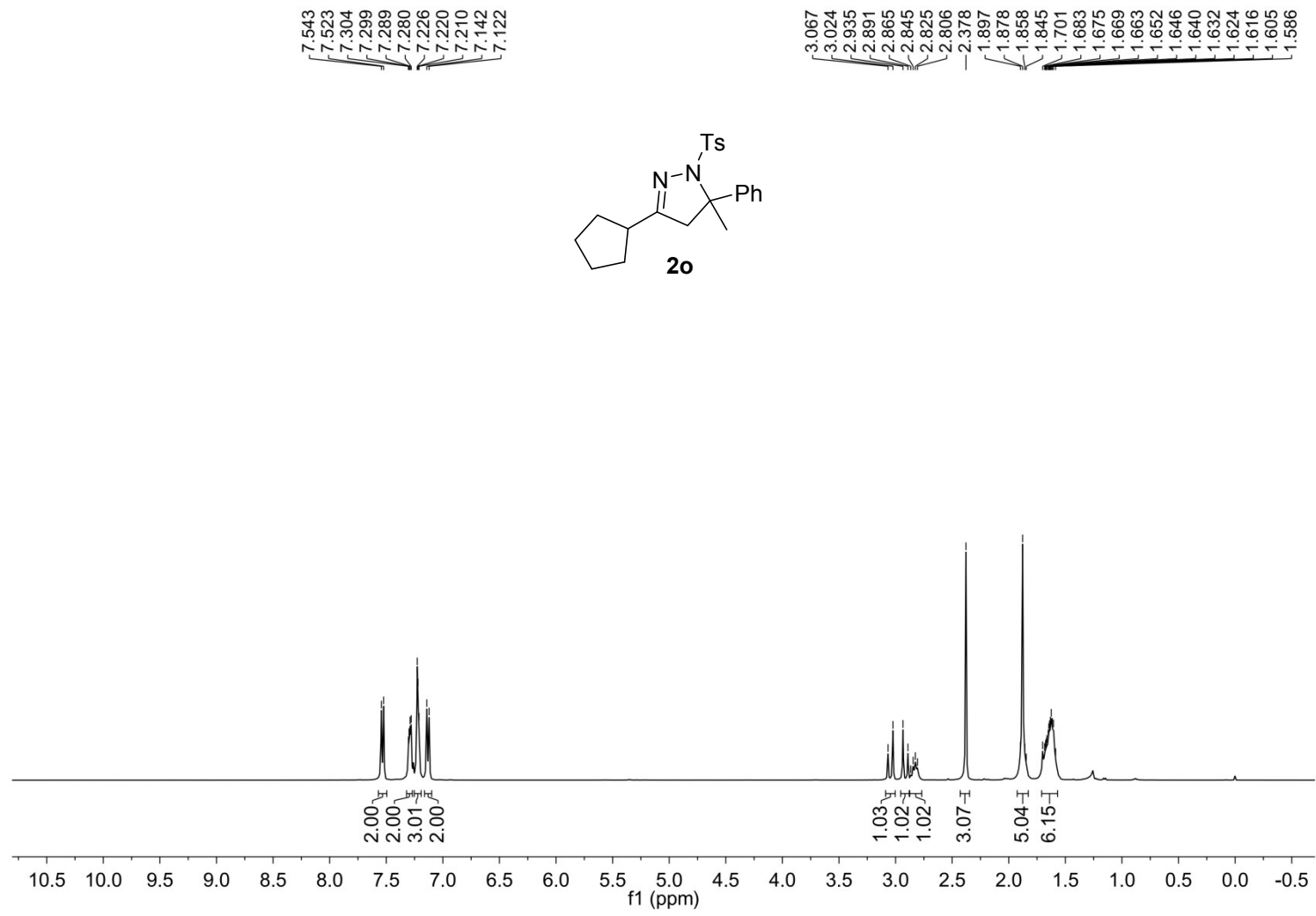


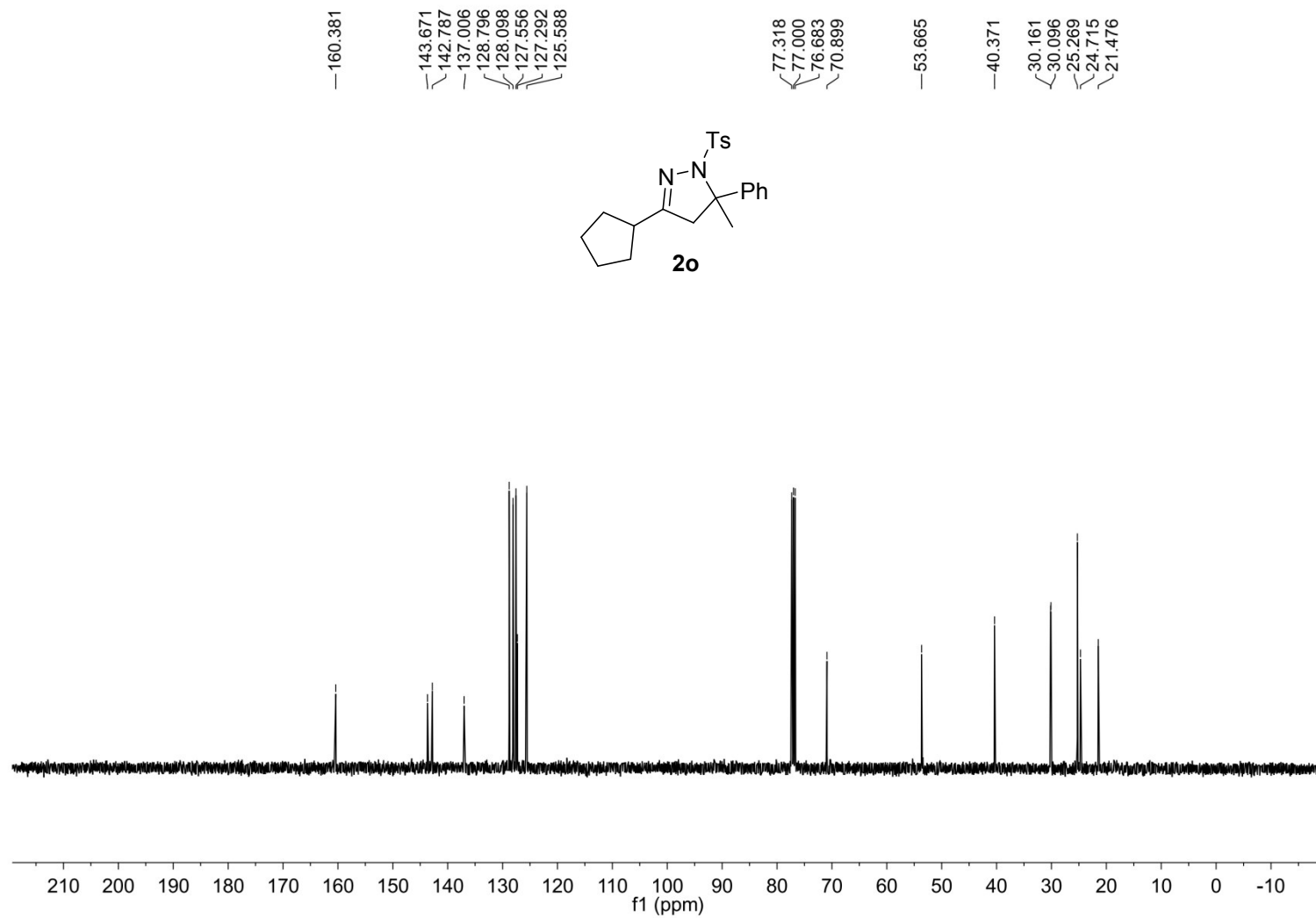
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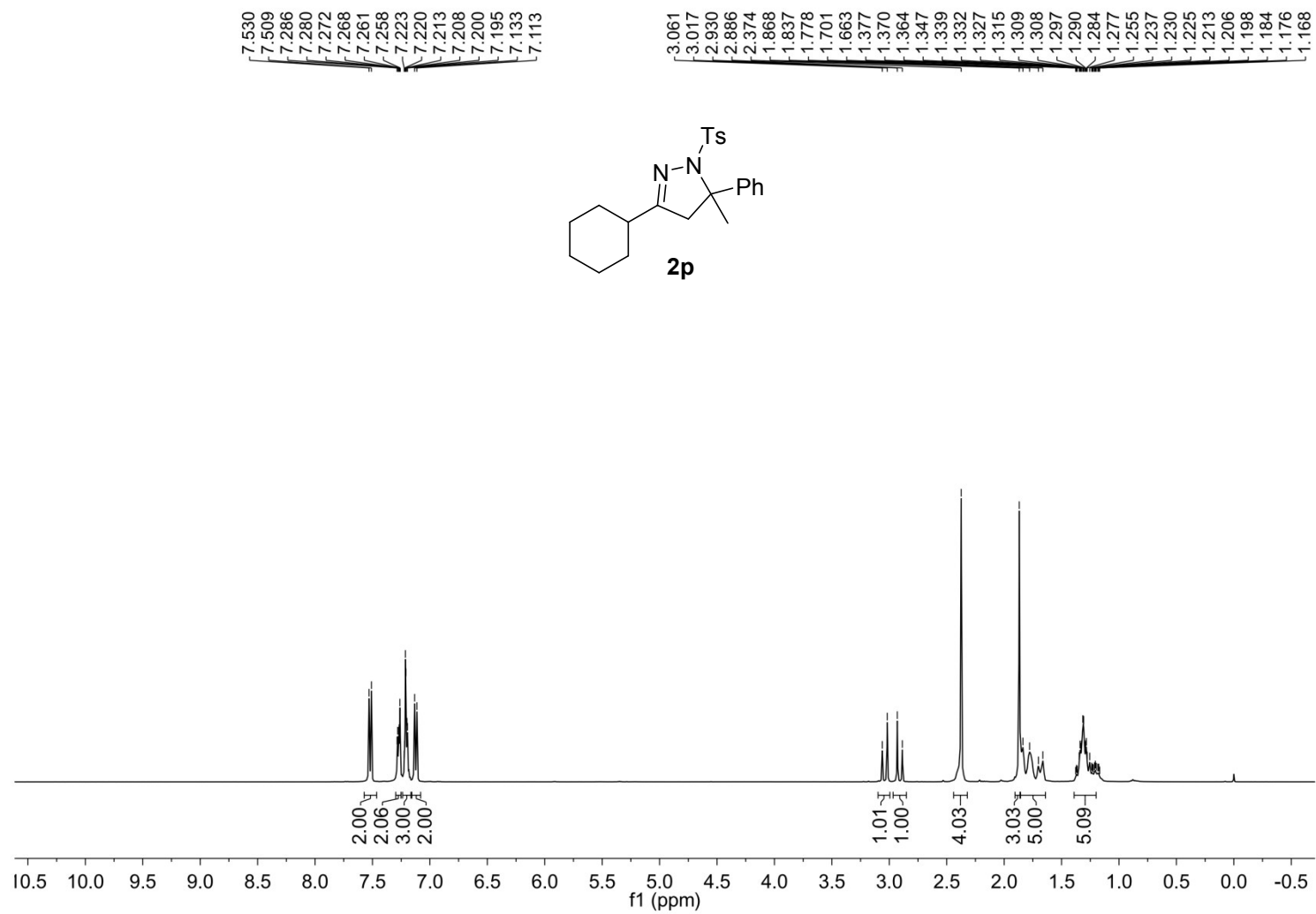


S47

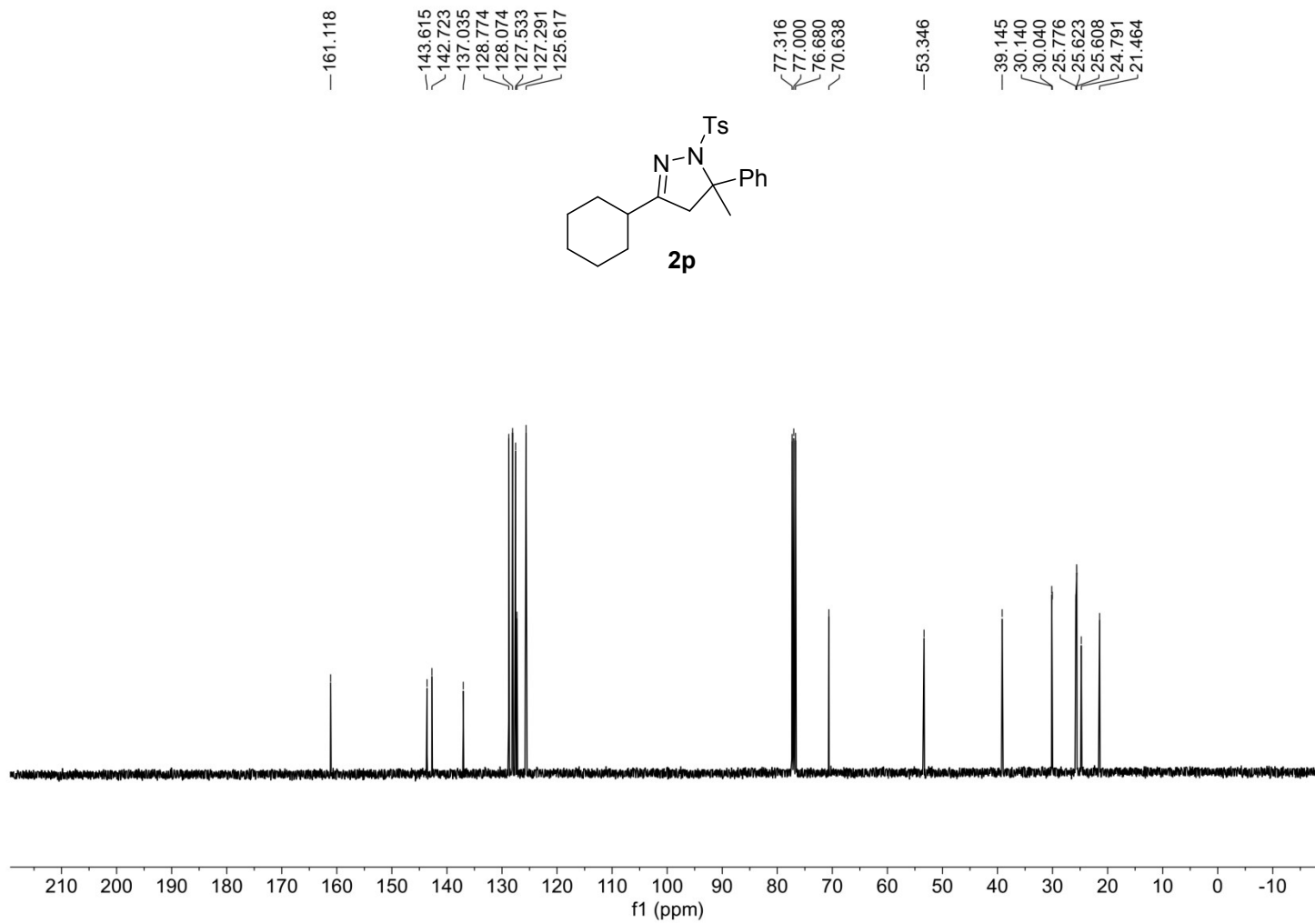




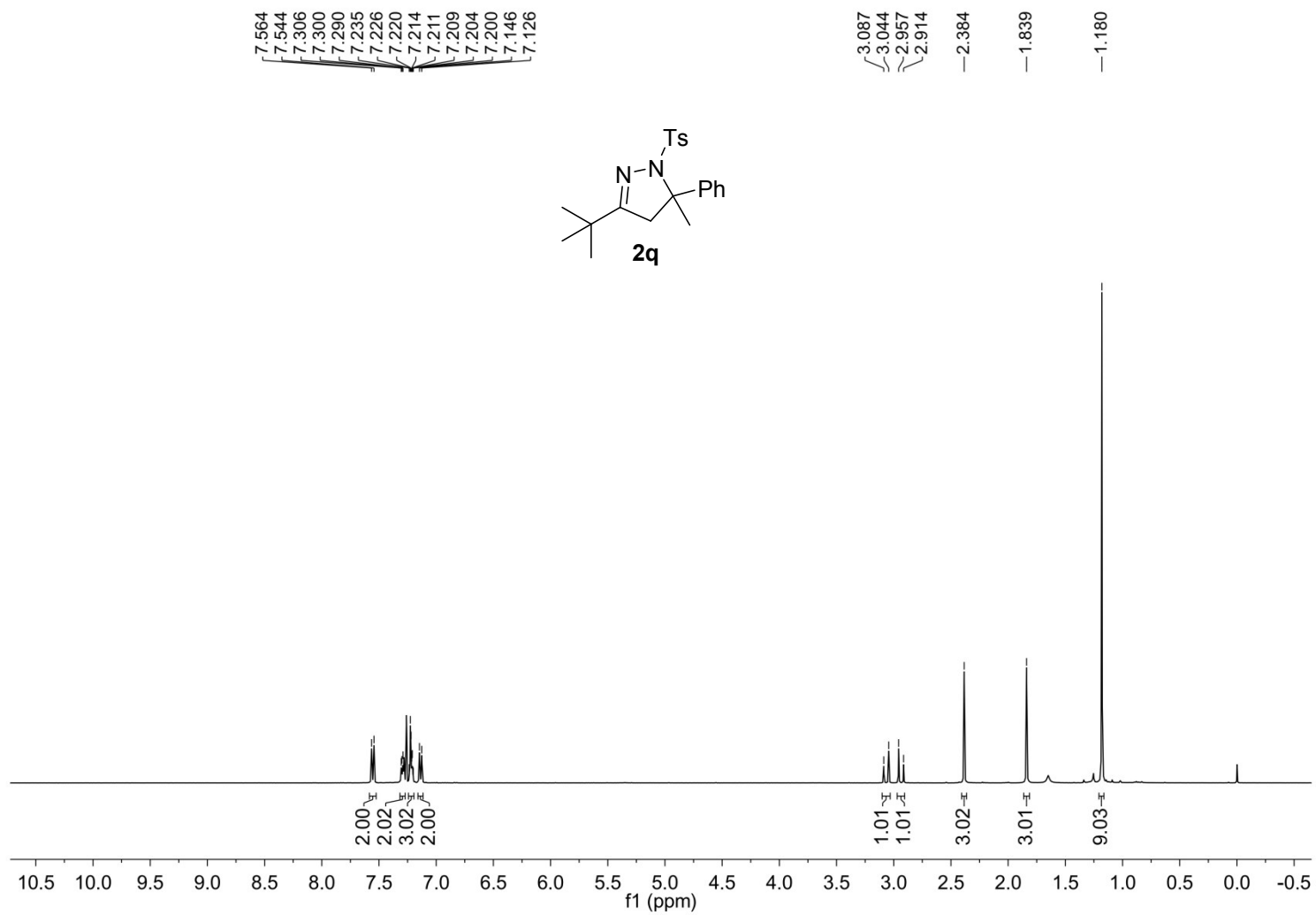
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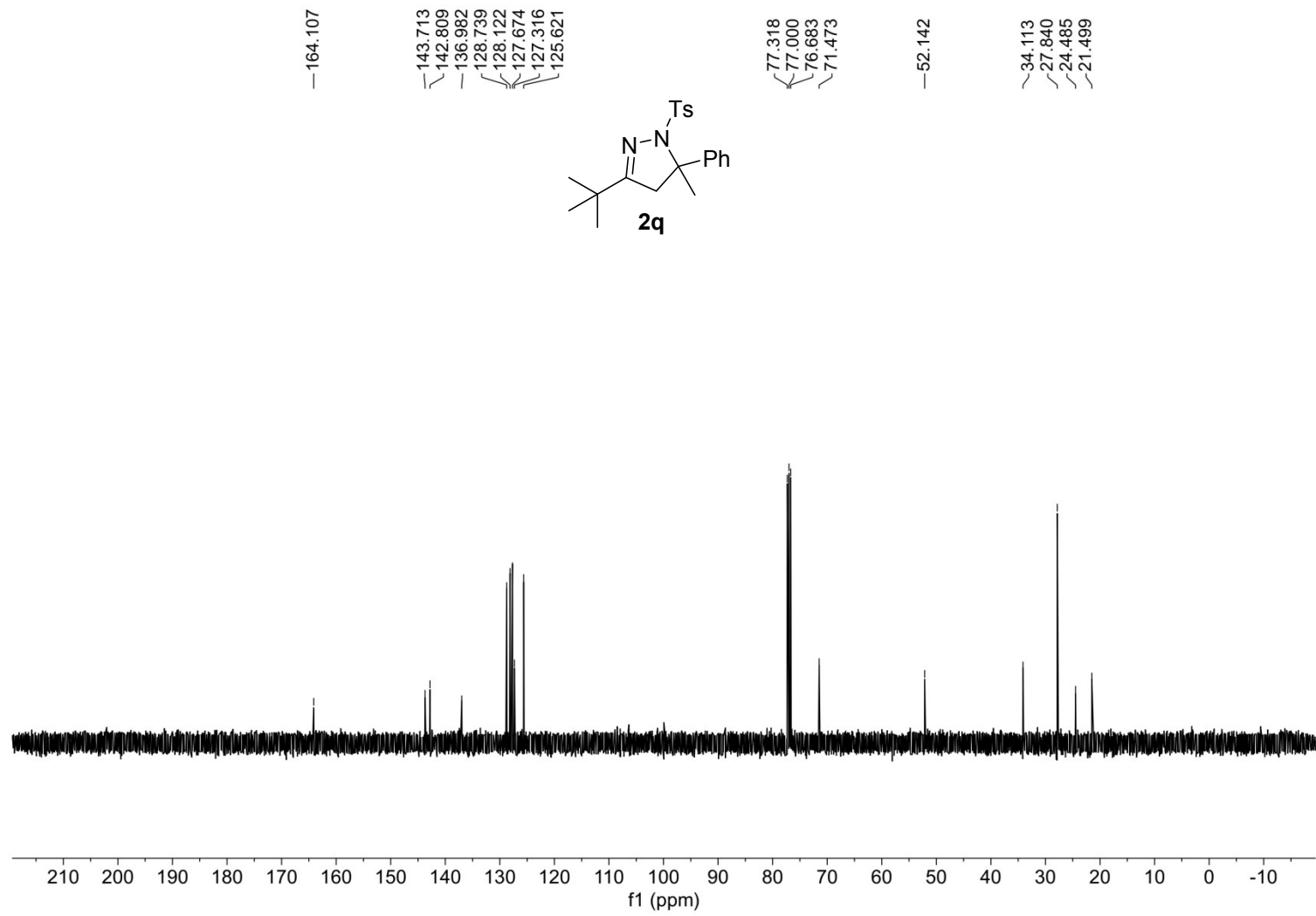


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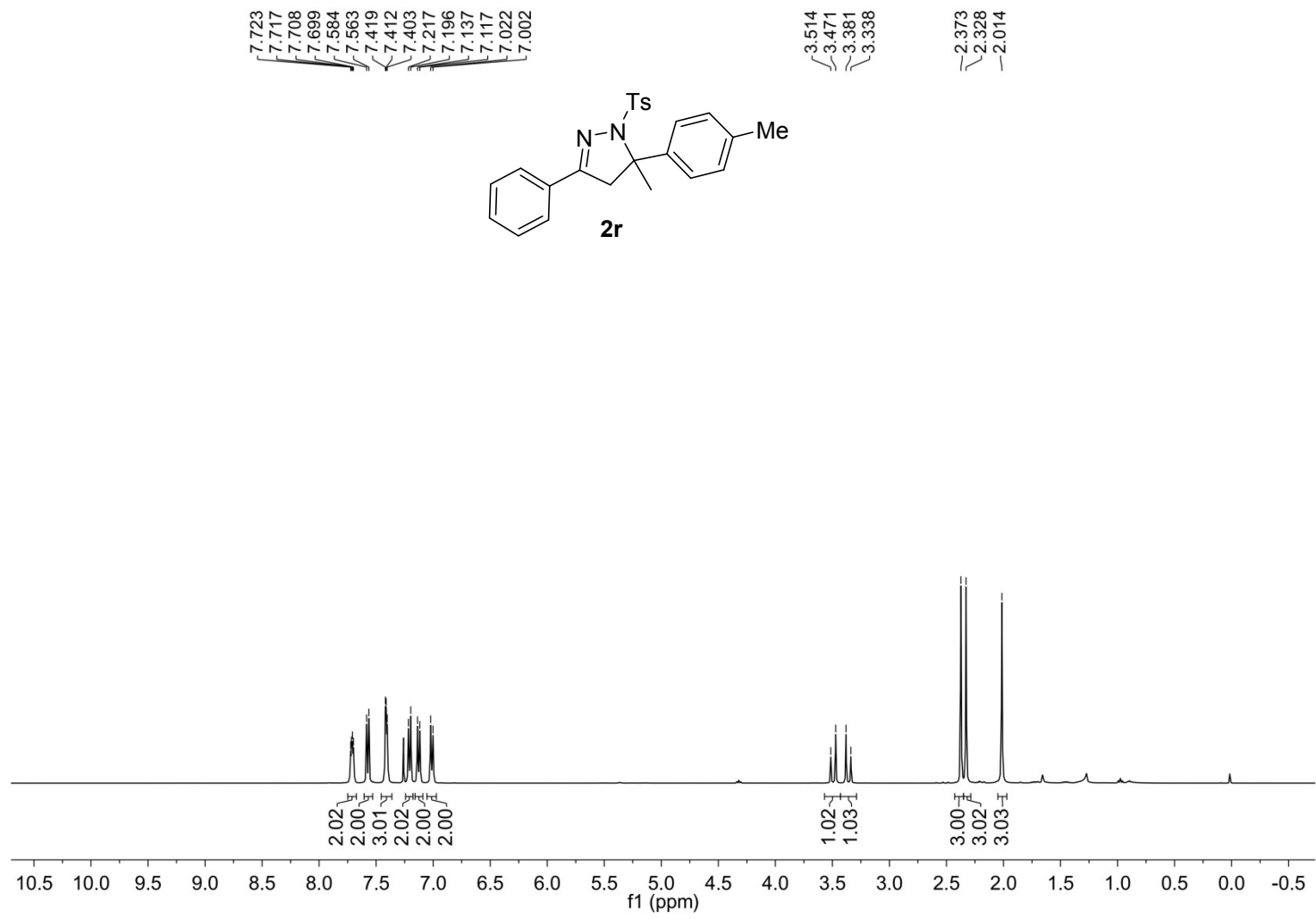


S51





S53

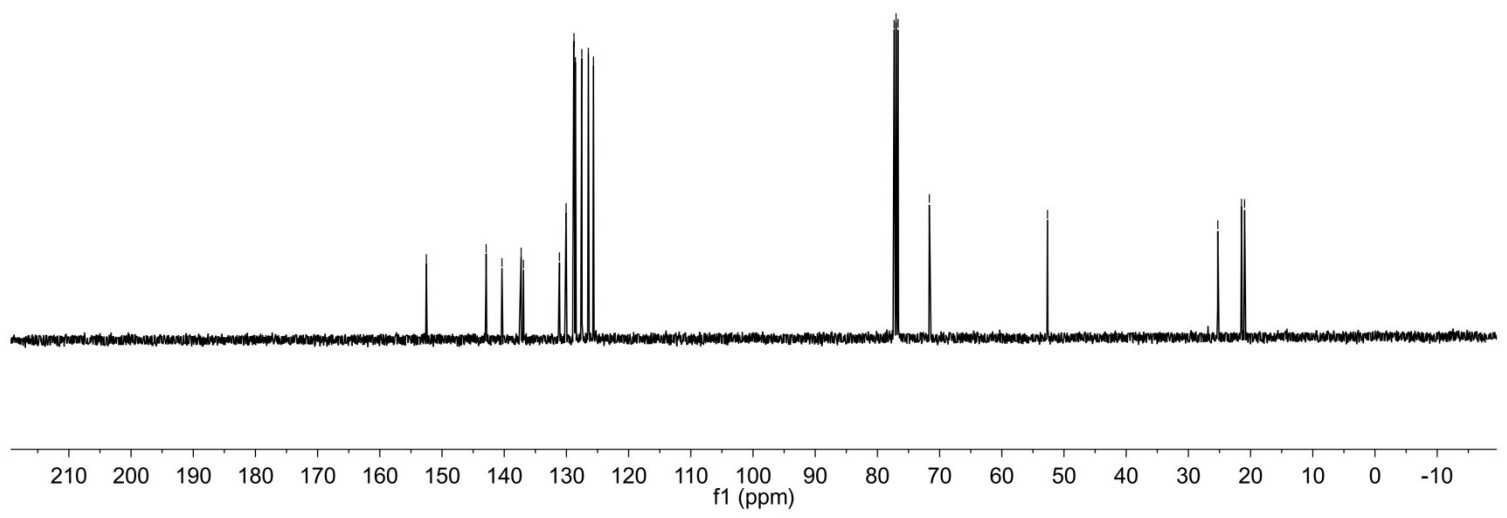
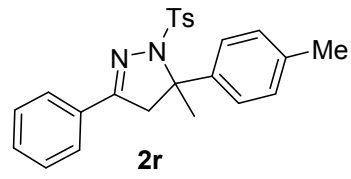


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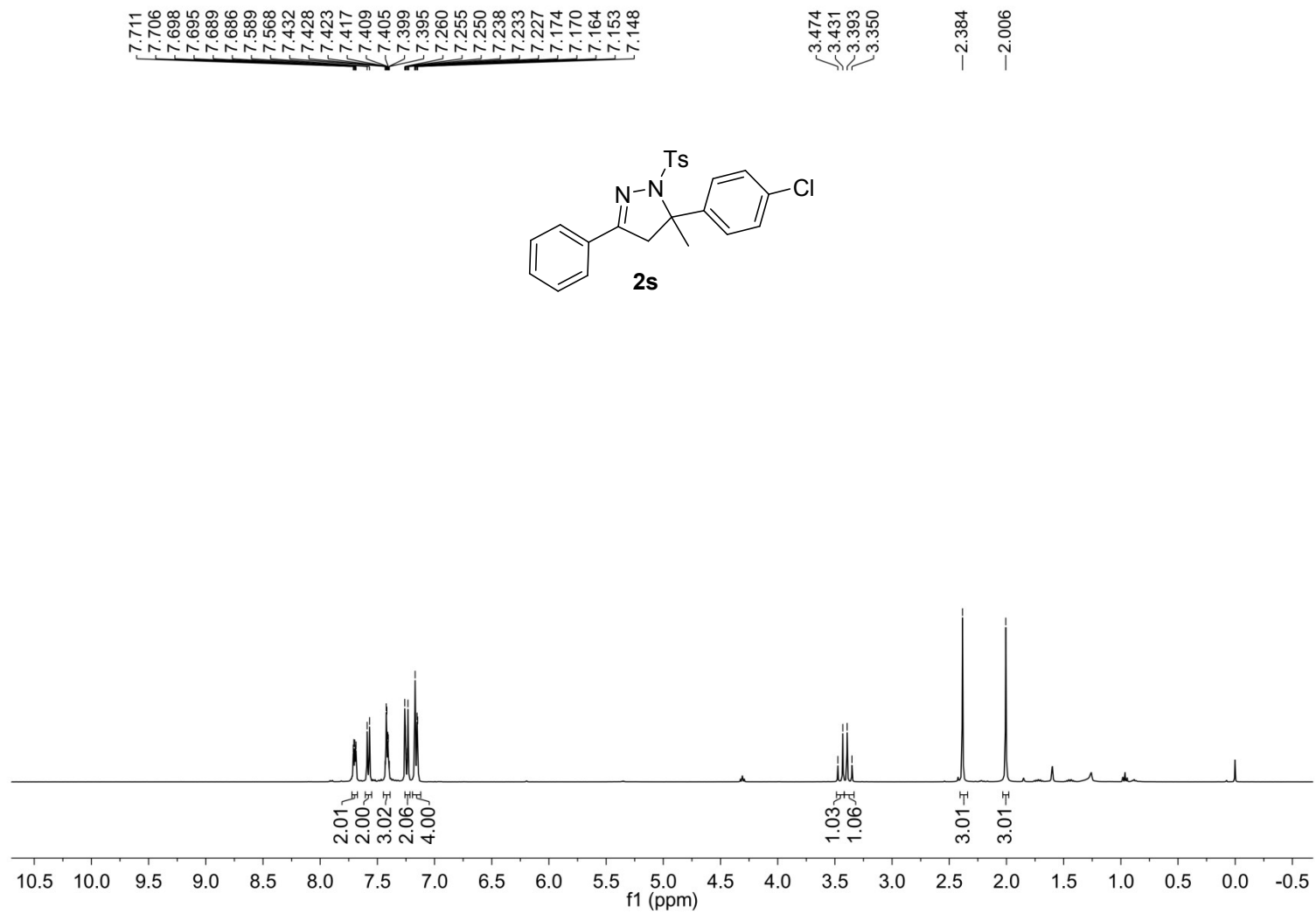
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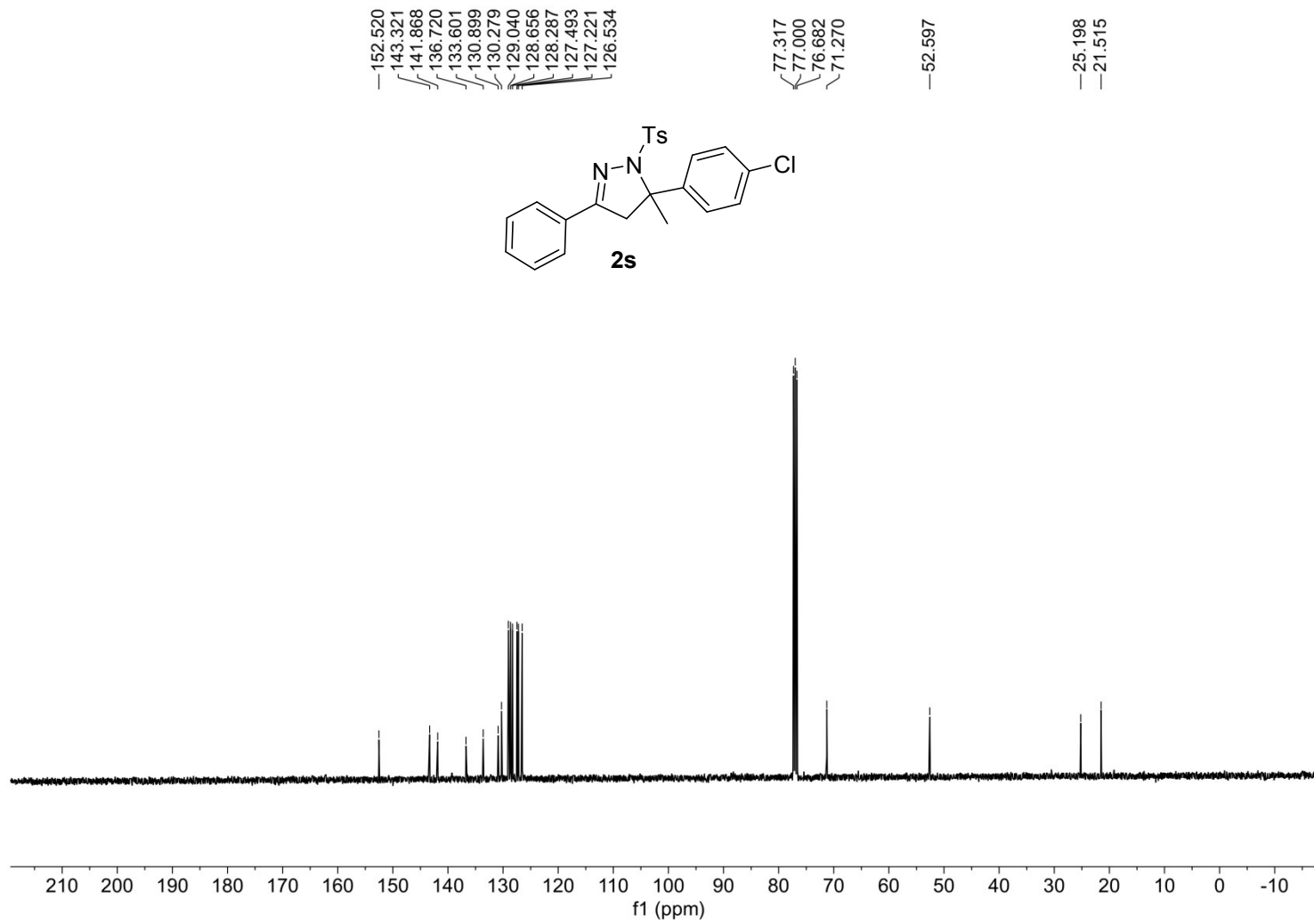
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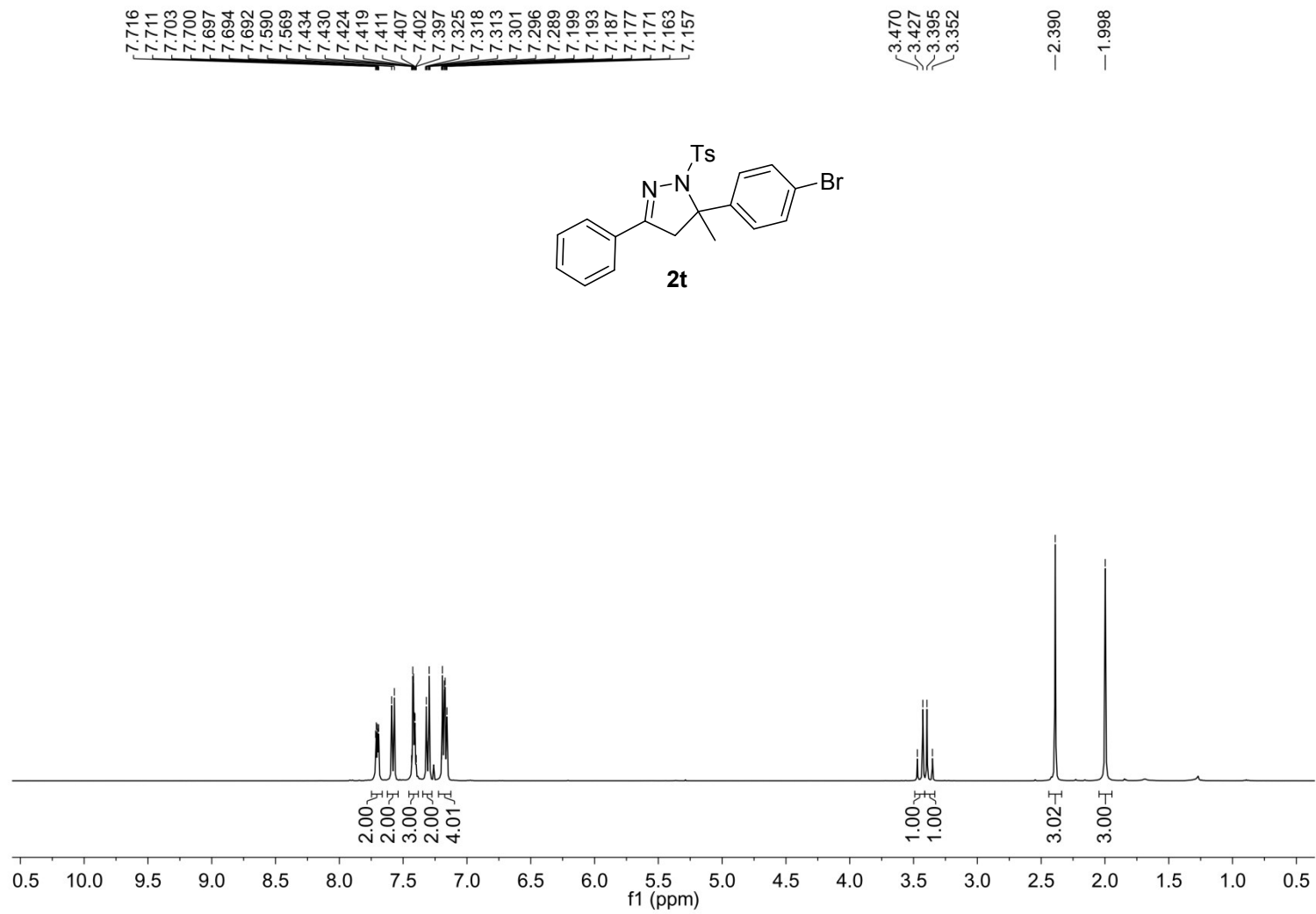
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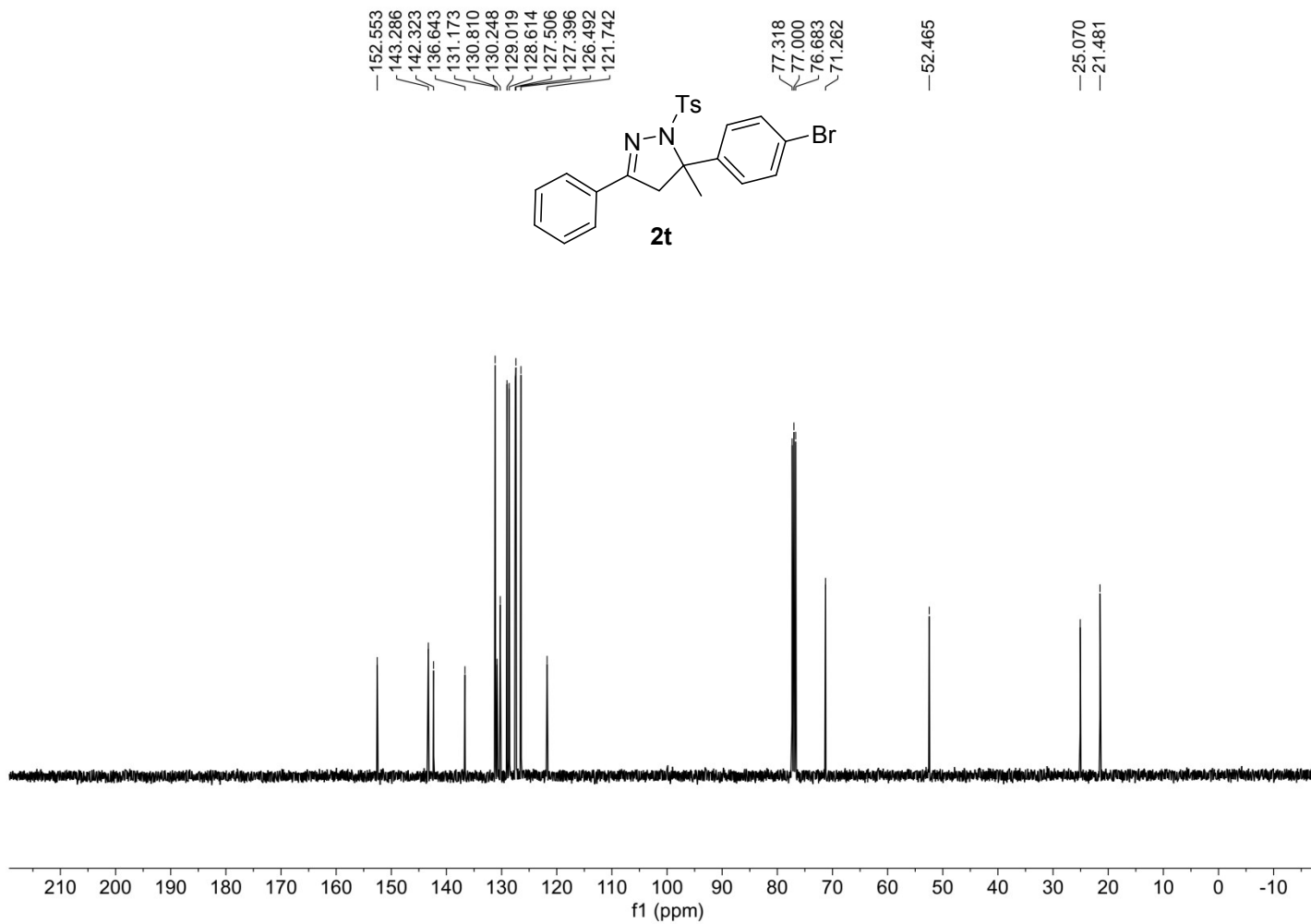
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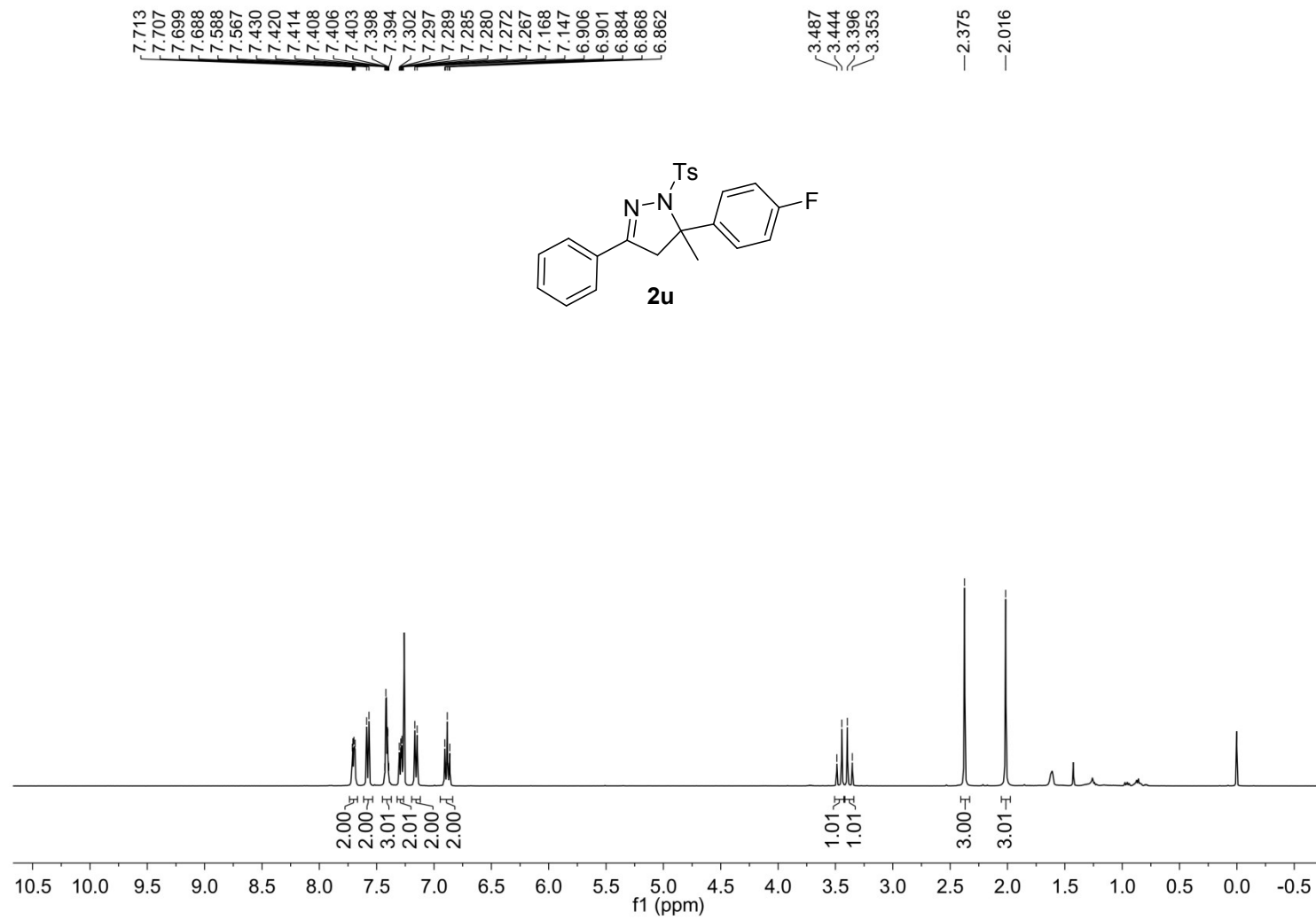
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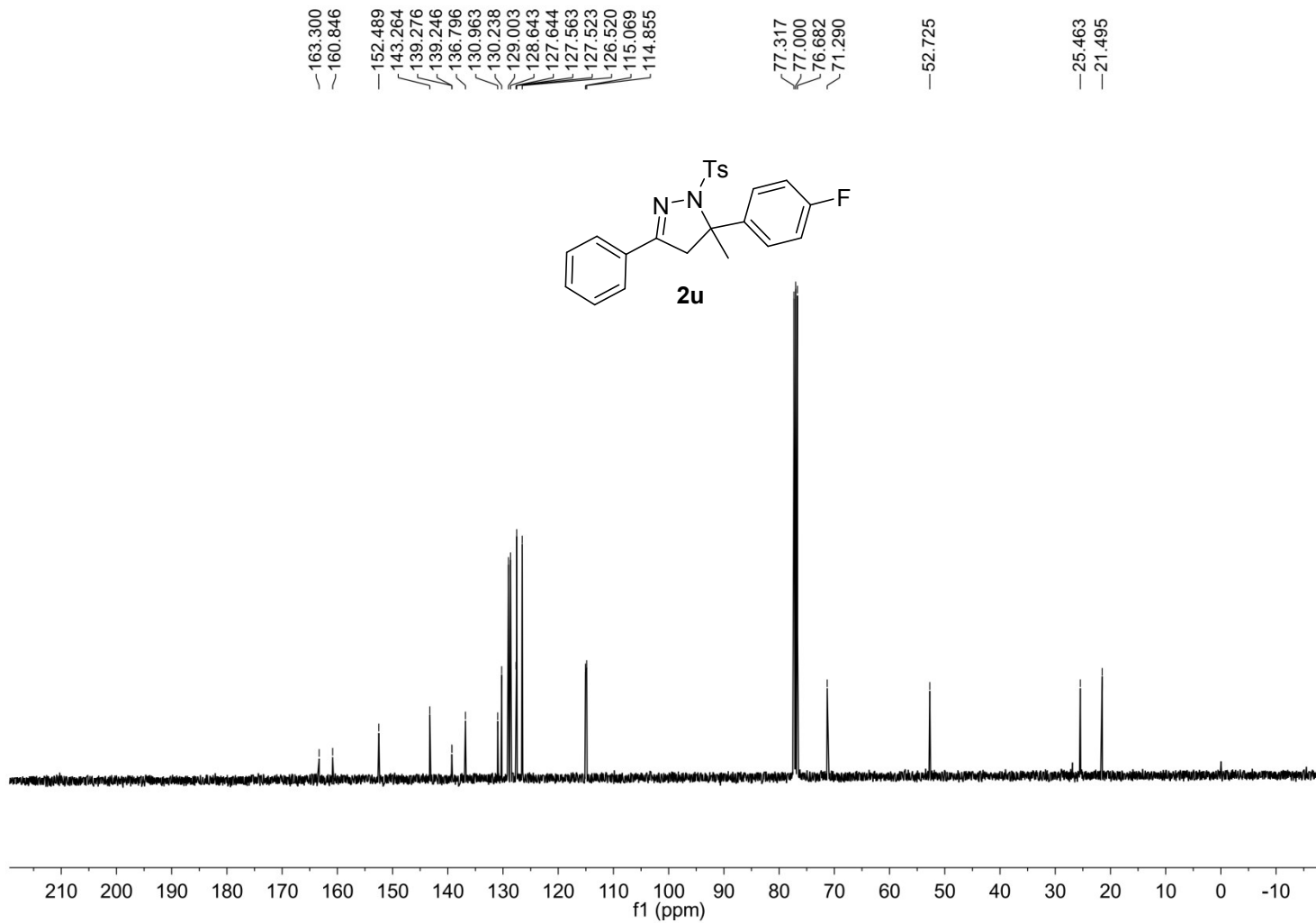
S58



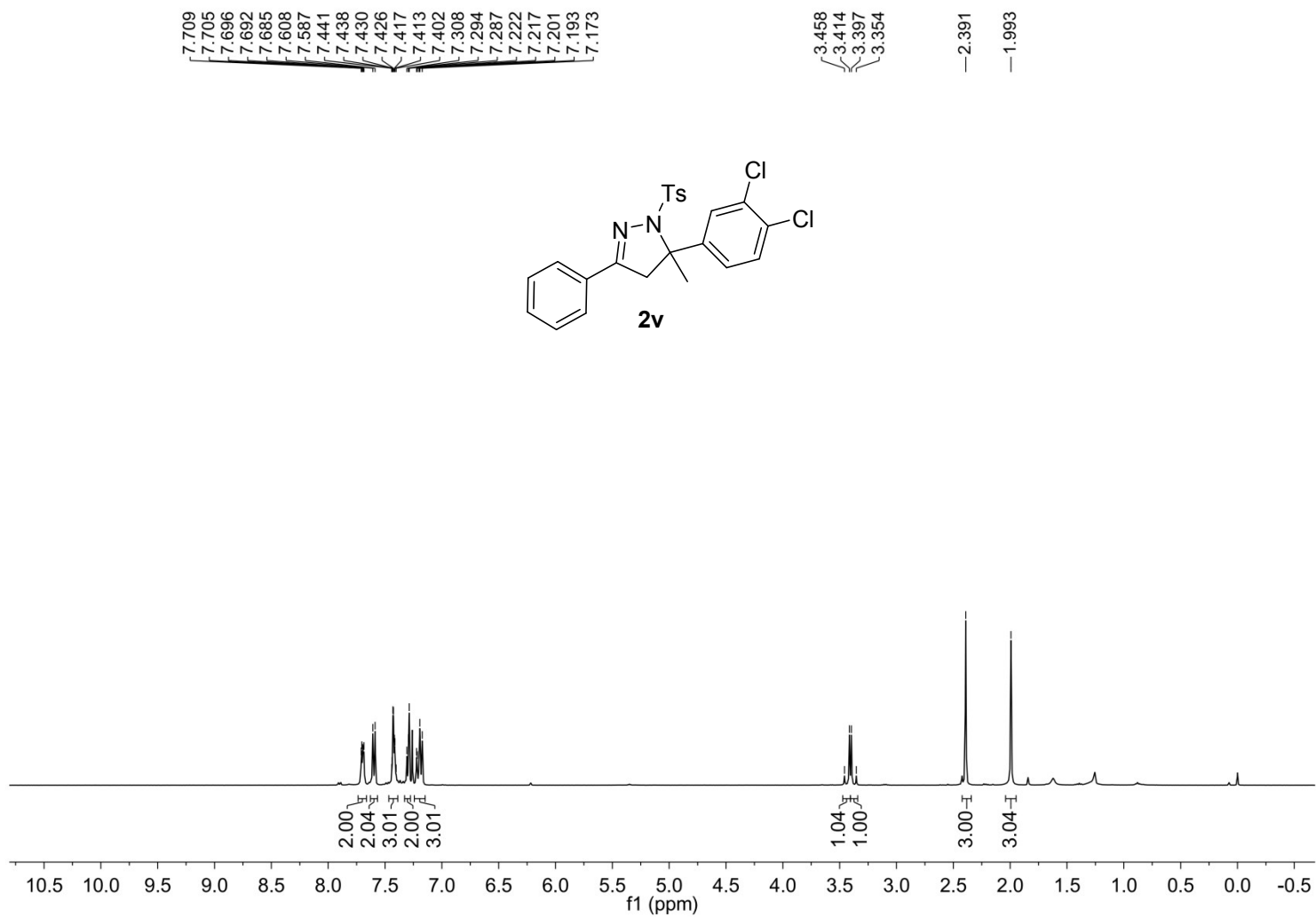
S59

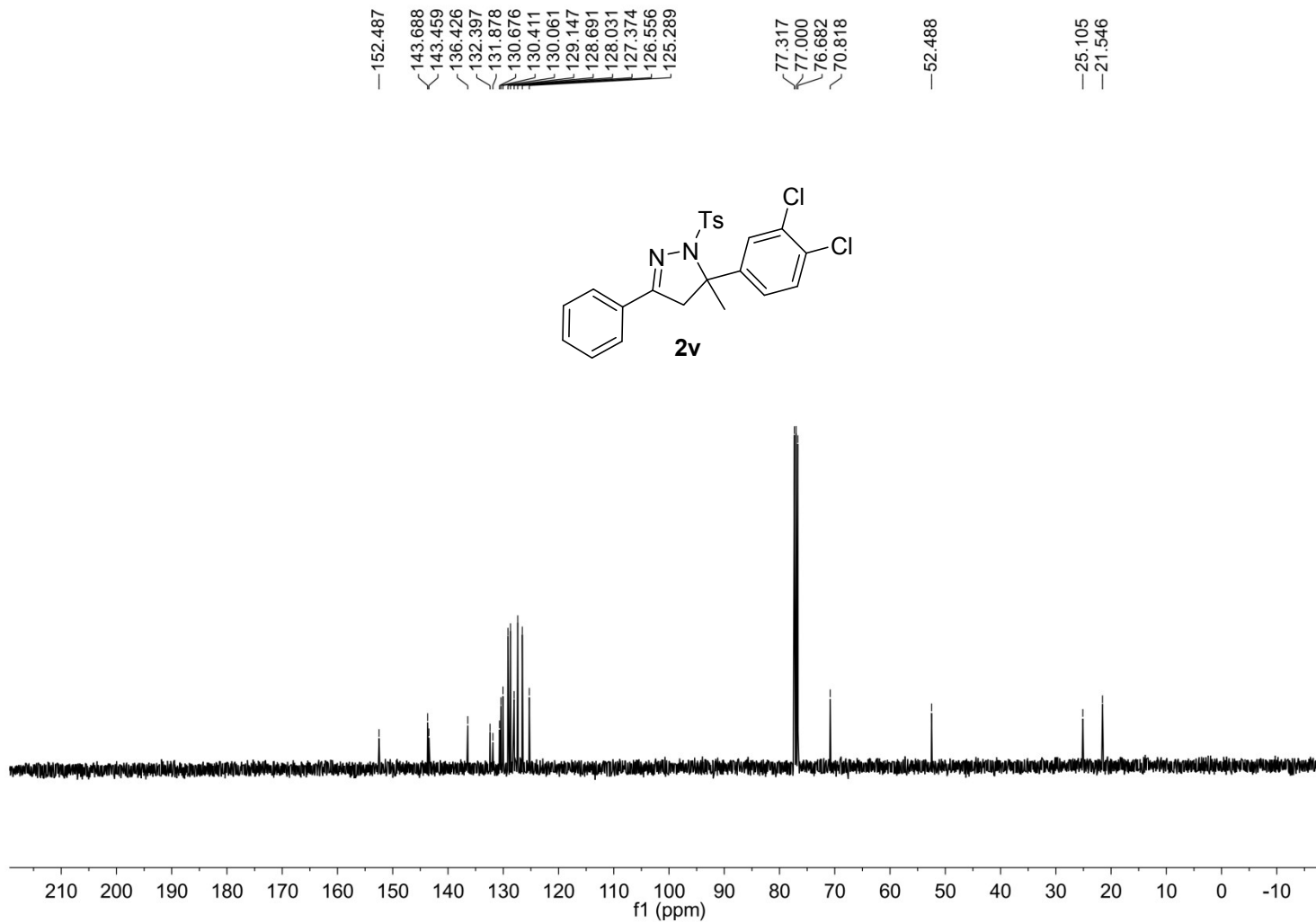


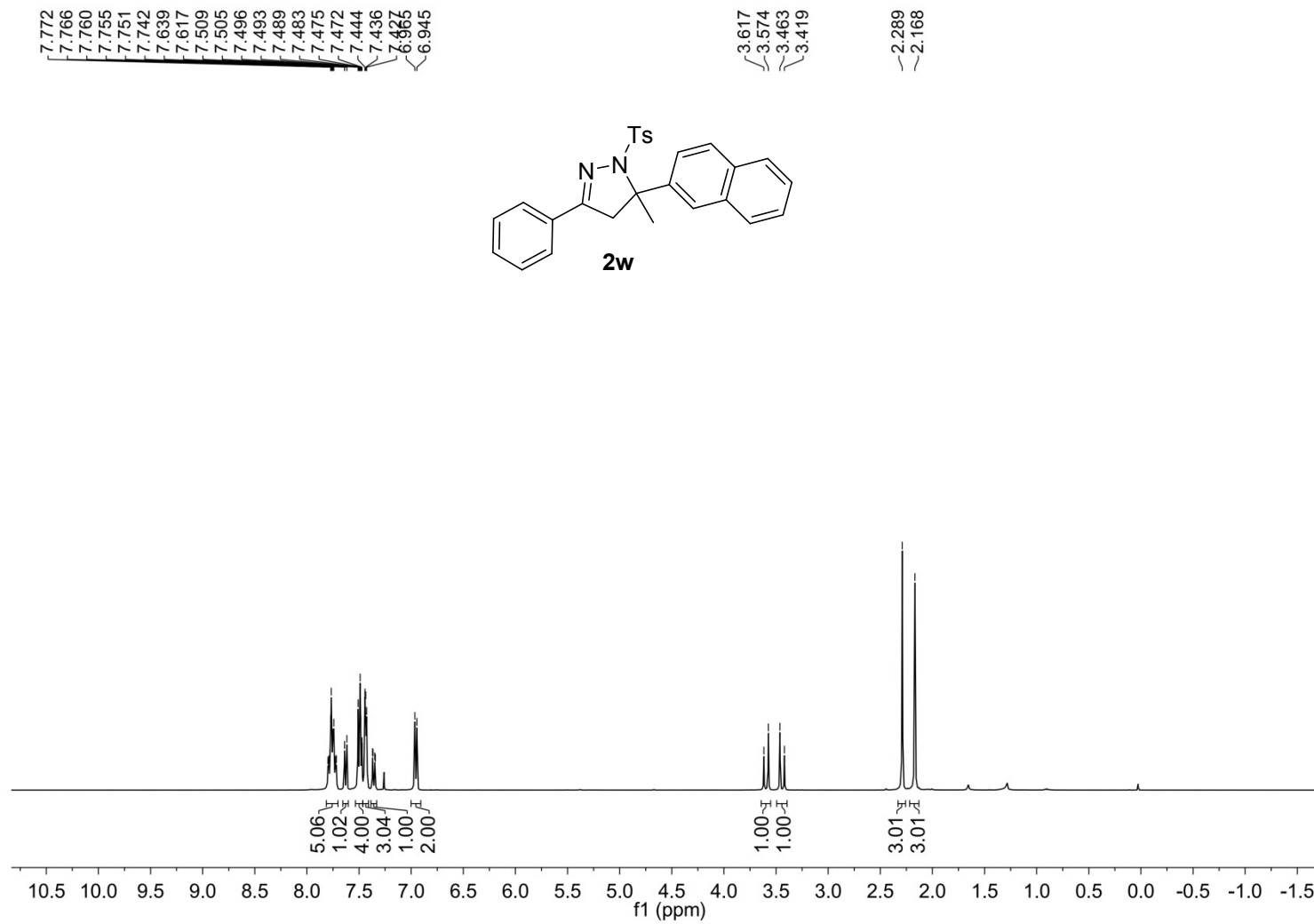
S60



S61







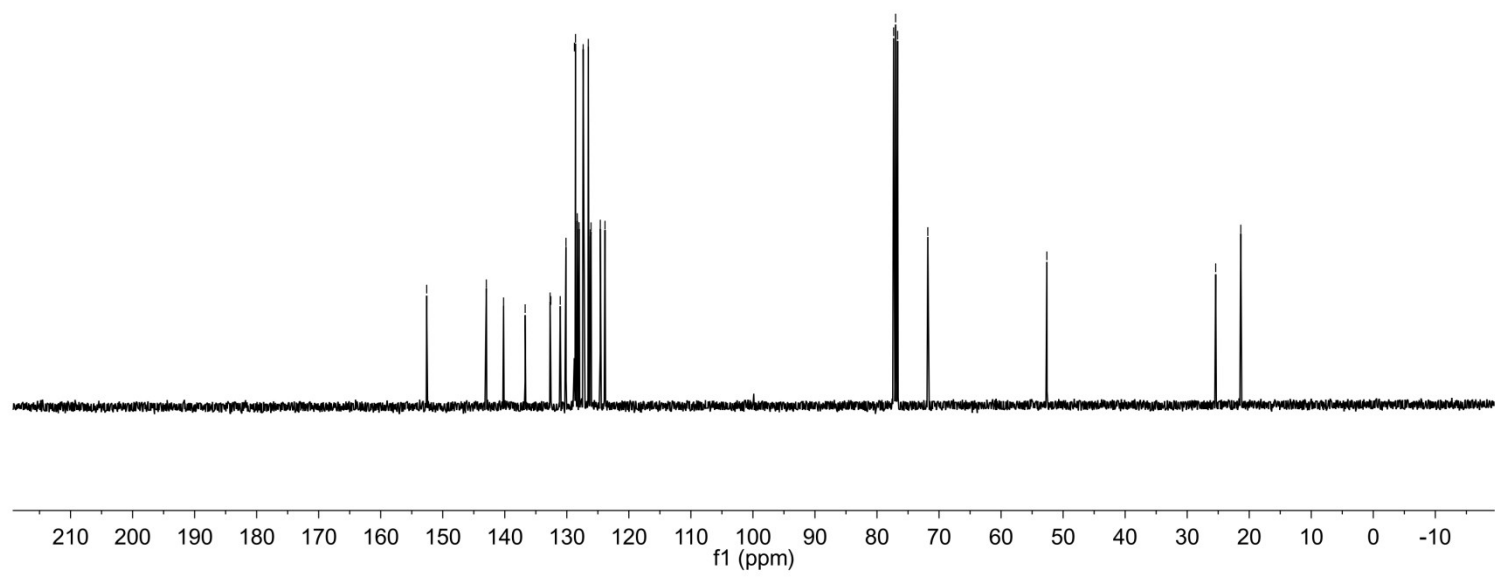
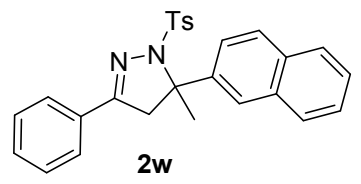
S64

152.587
142.971
140.195
136.715
132.684
132.582
131.065
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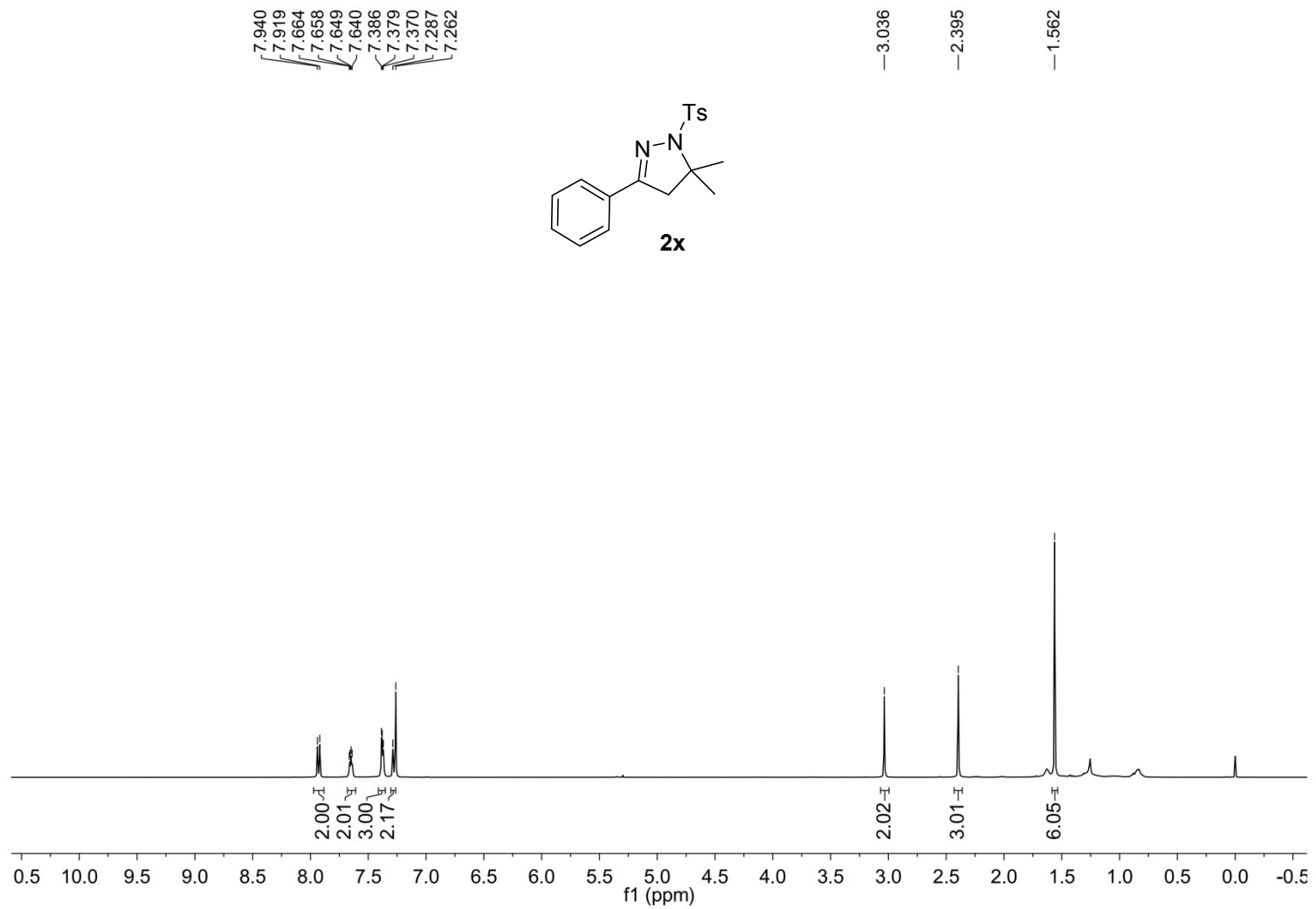
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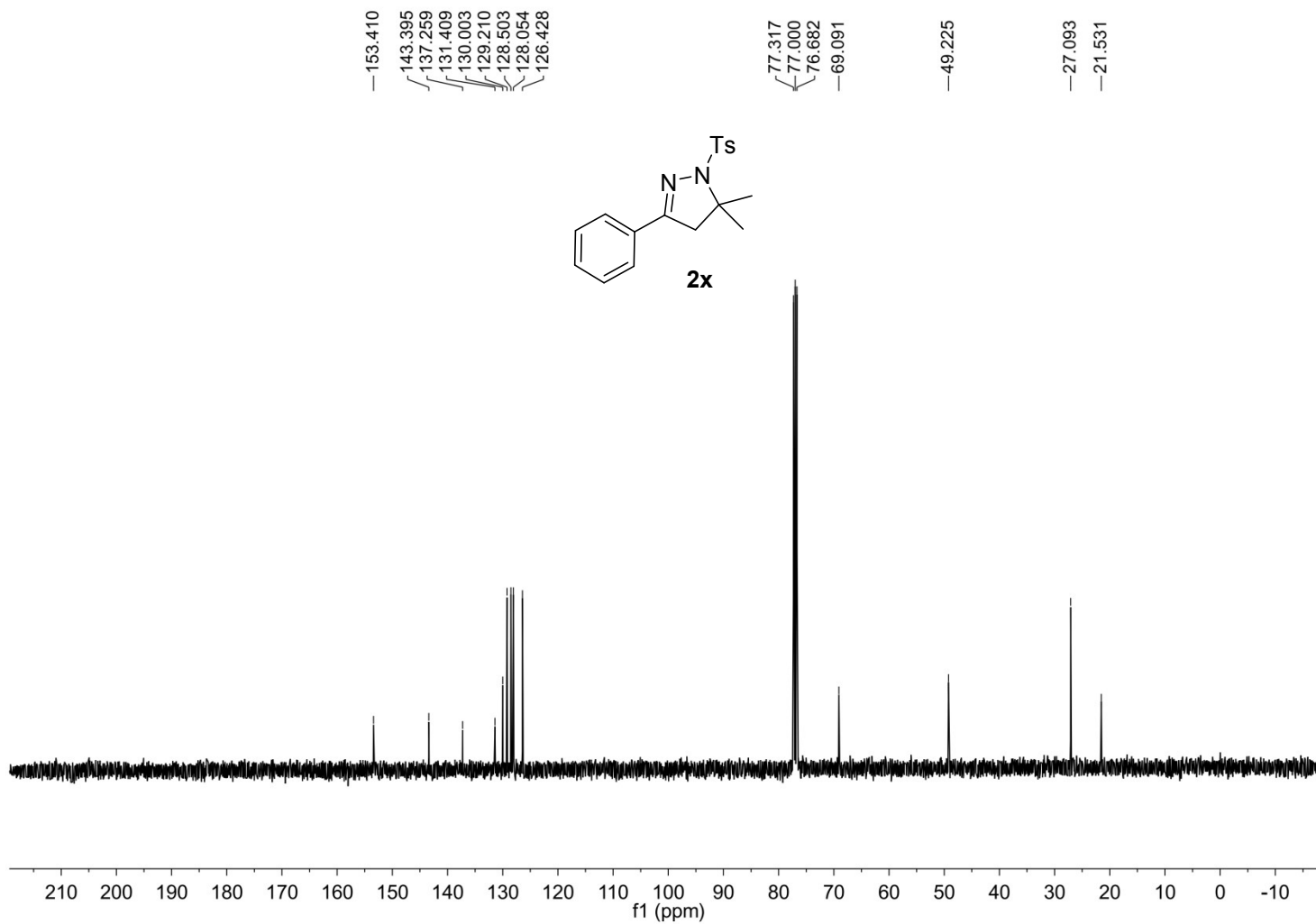
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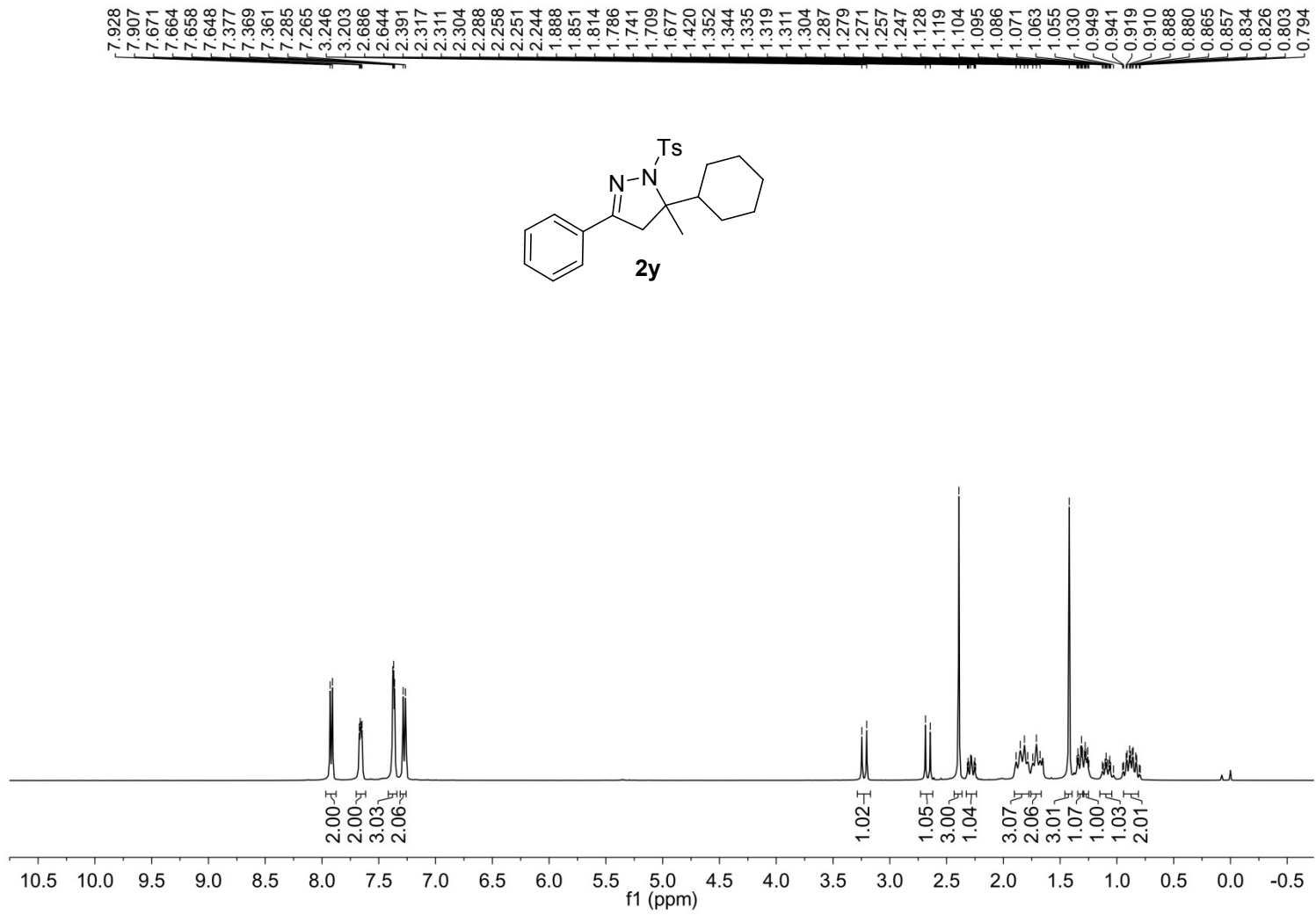


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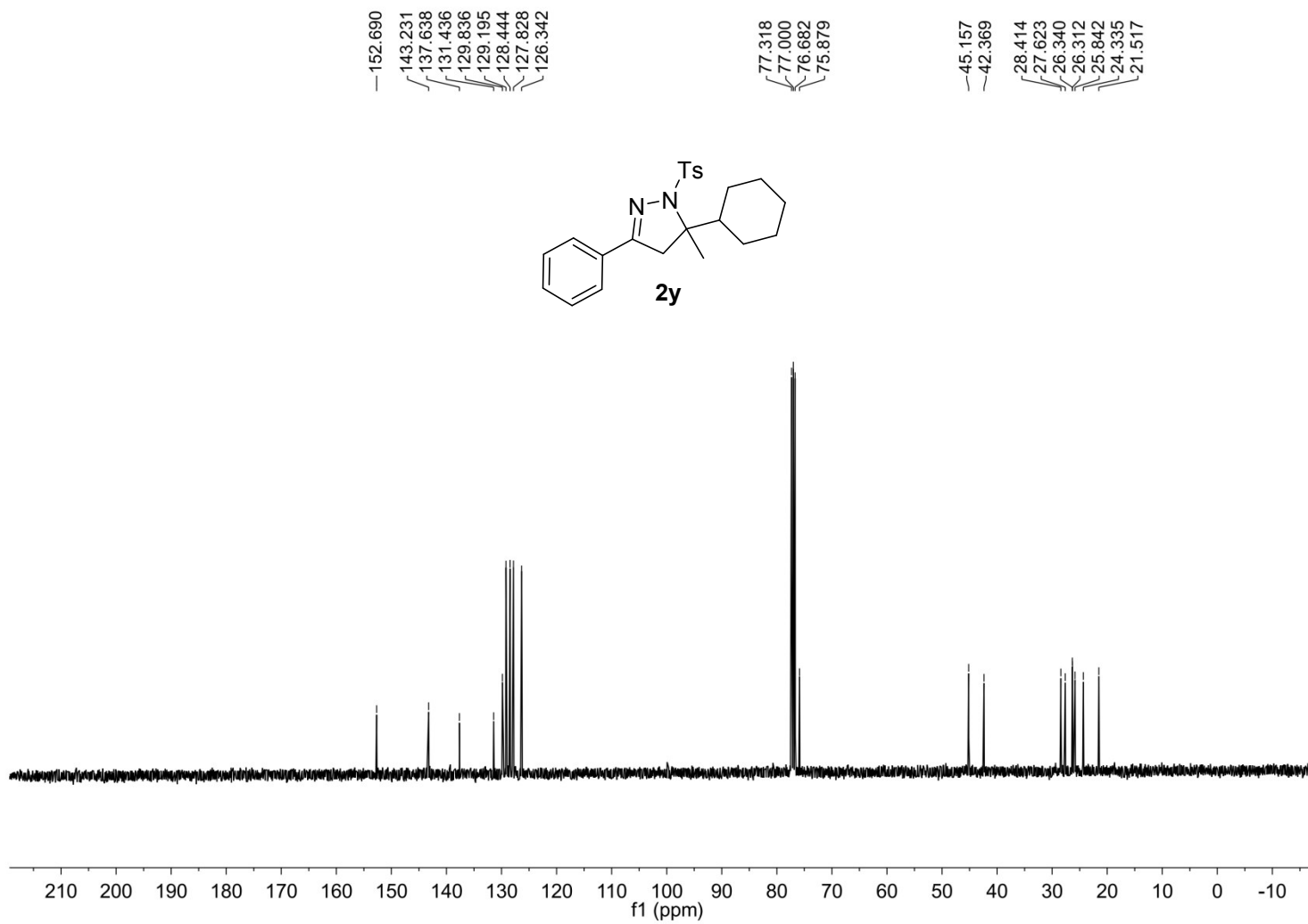


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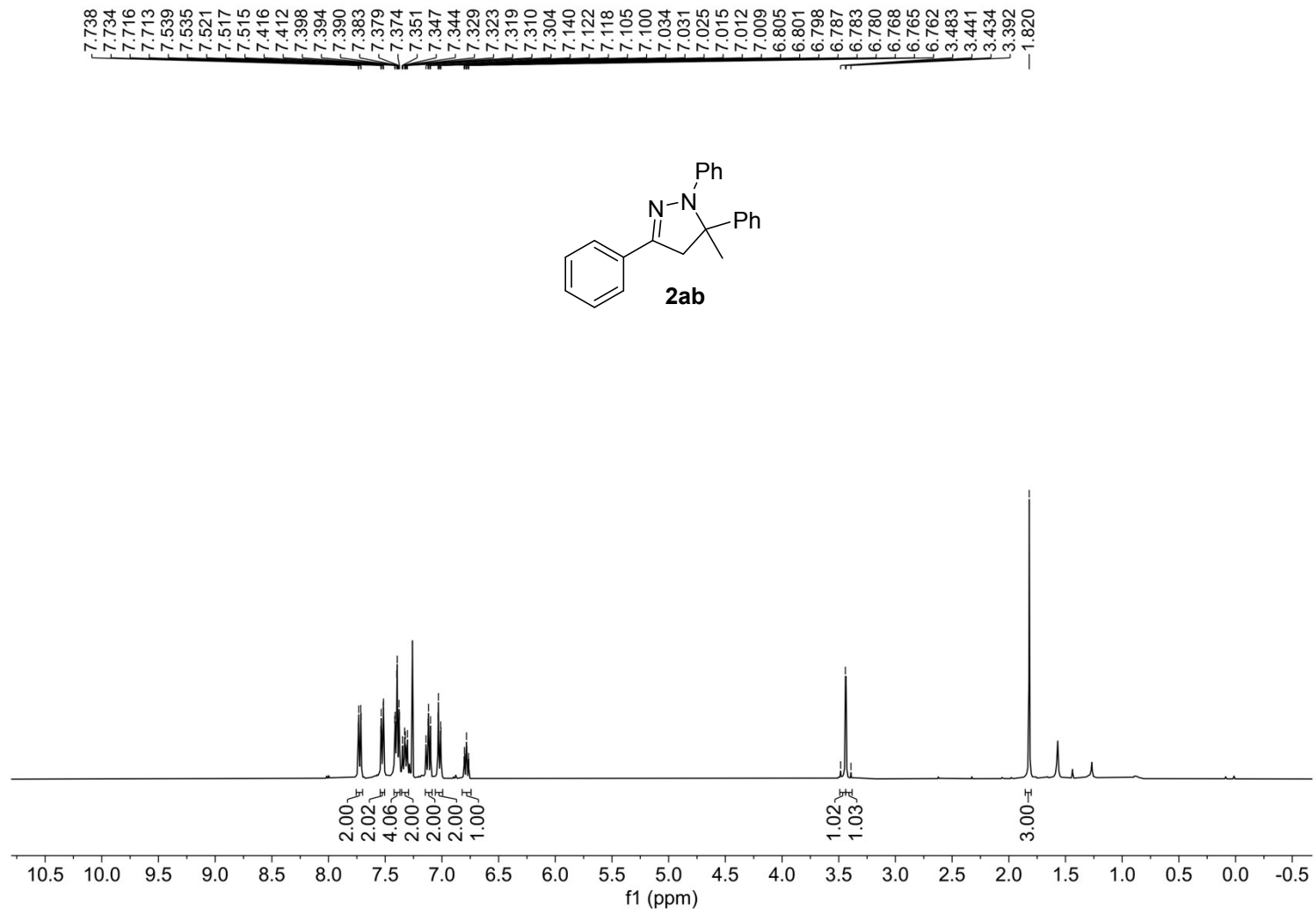




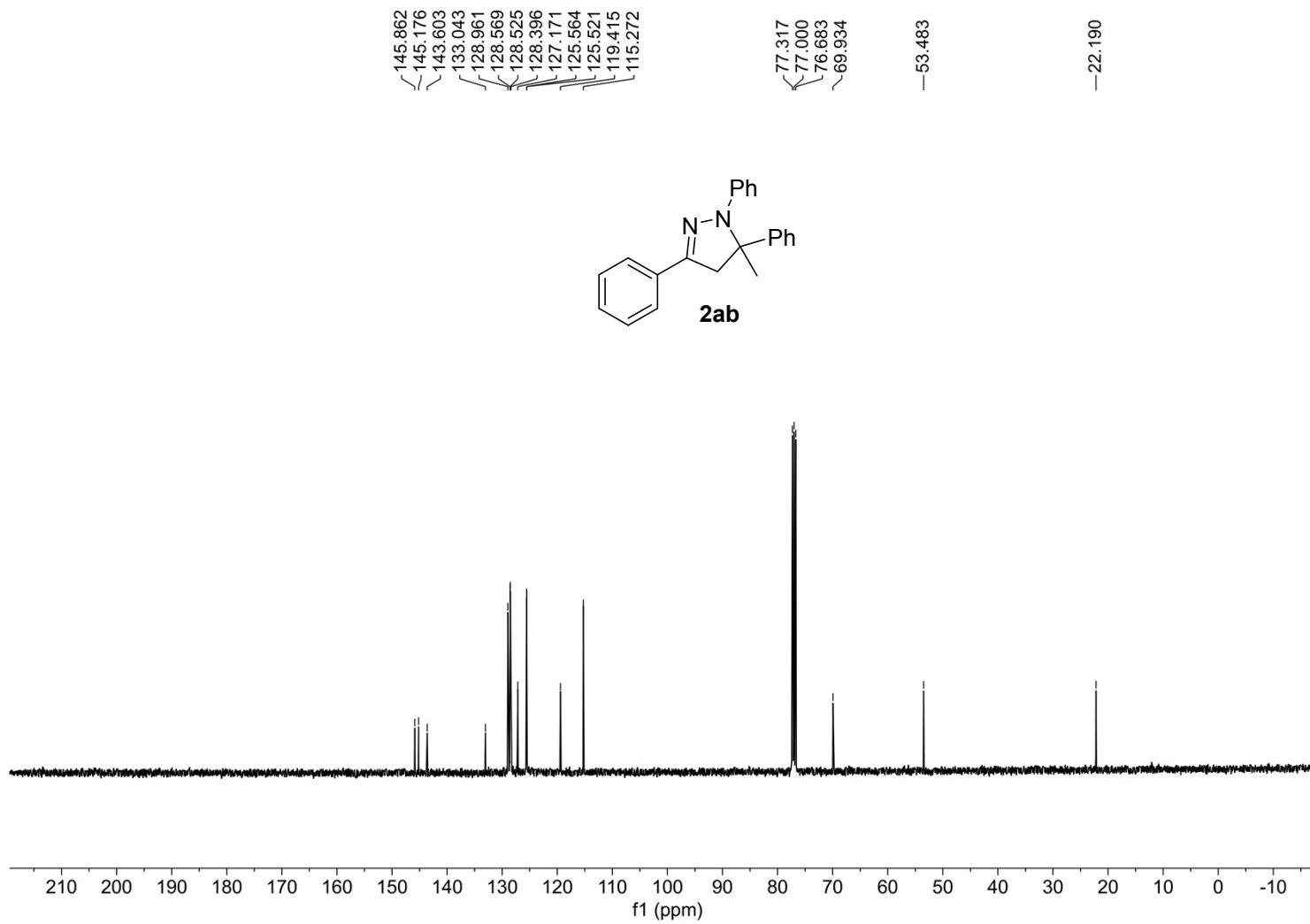
S68



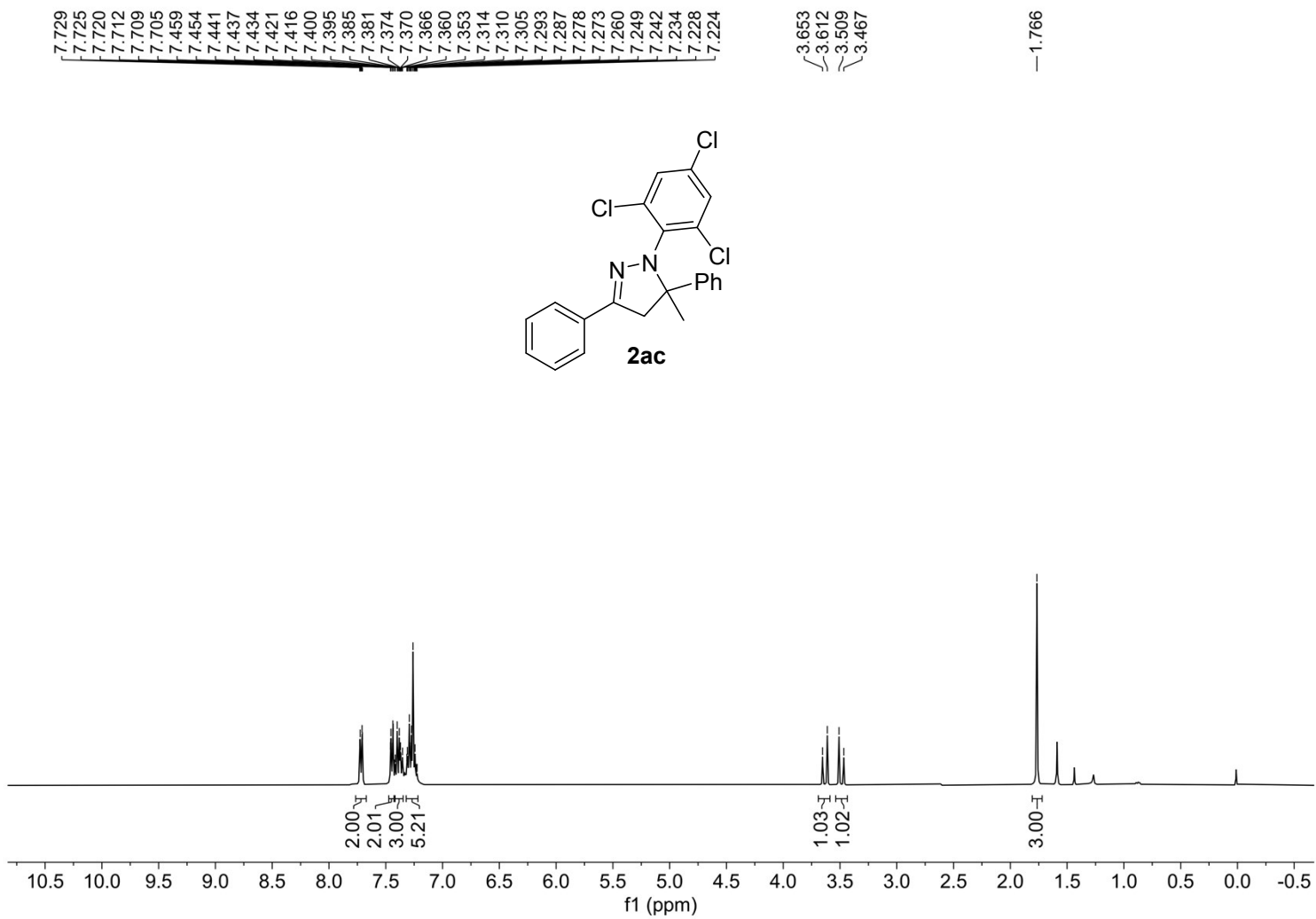
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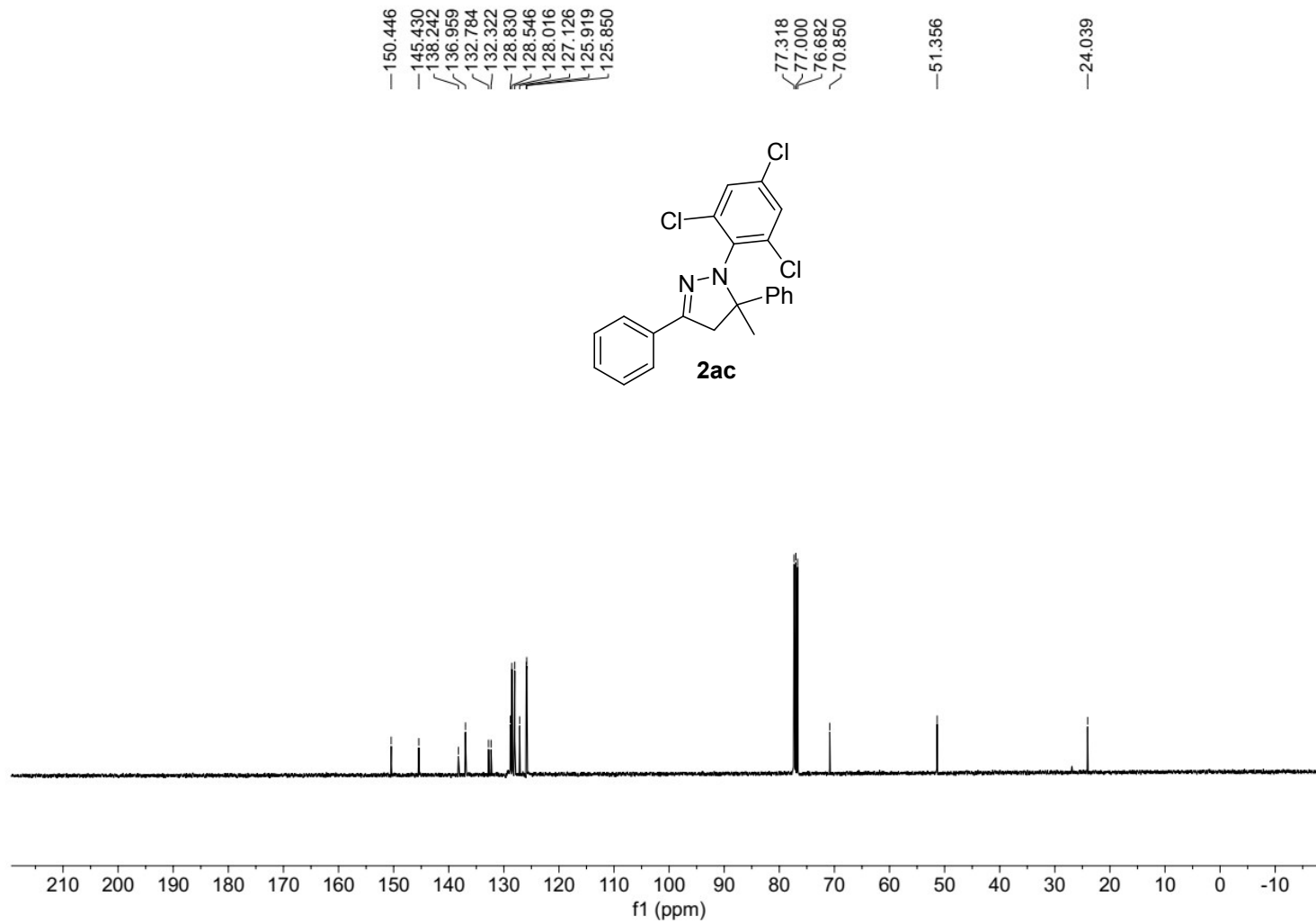
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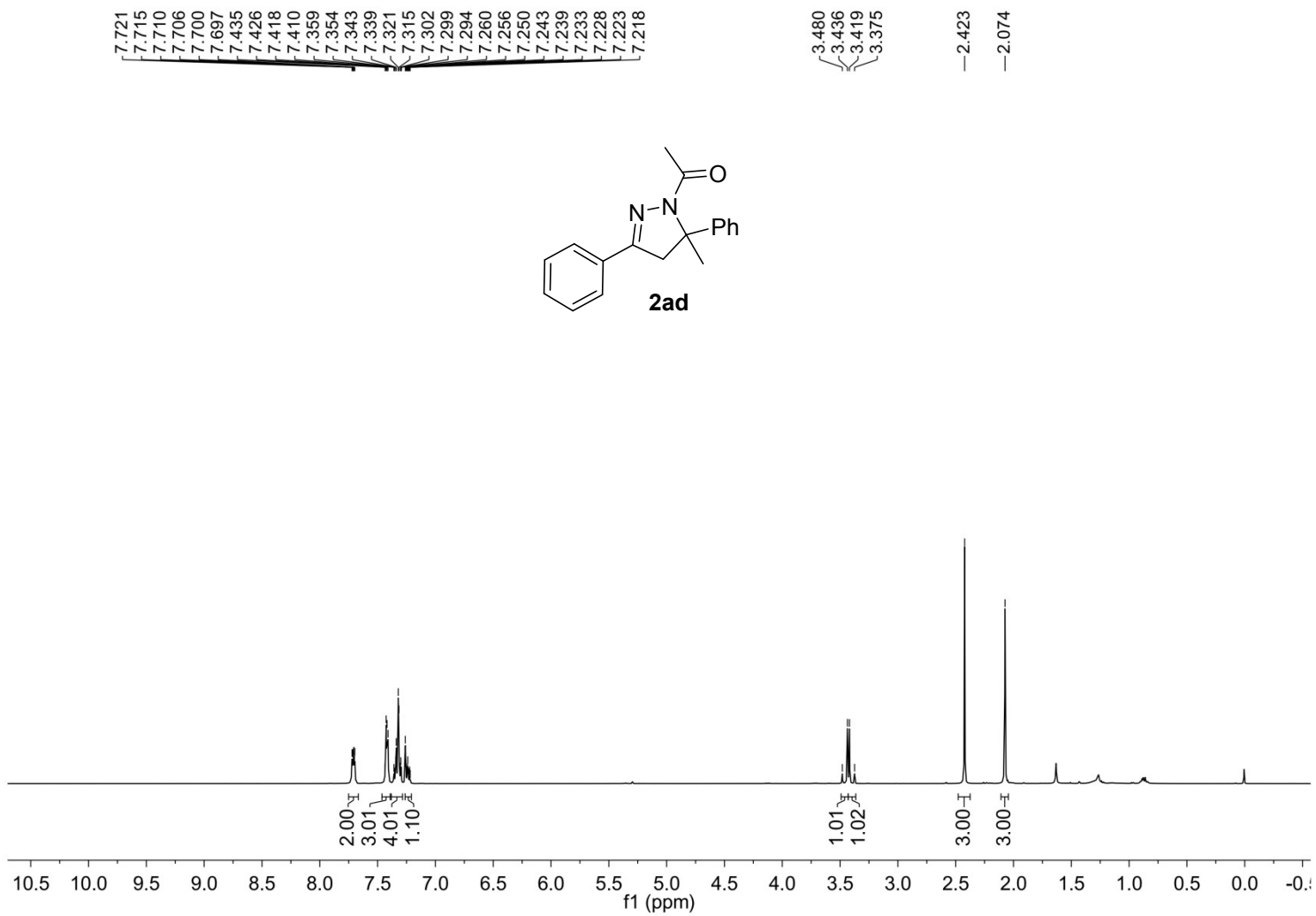


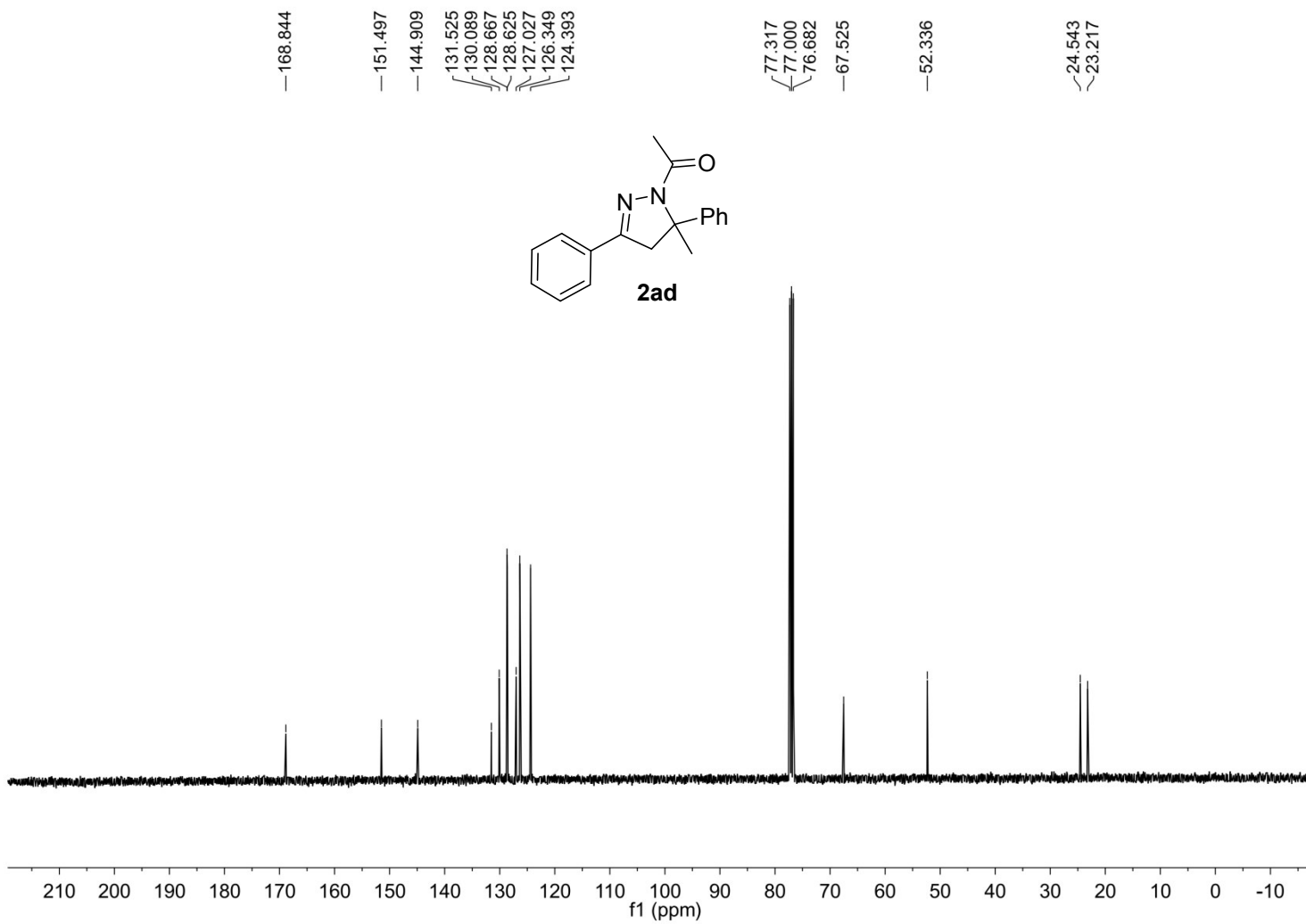
S71



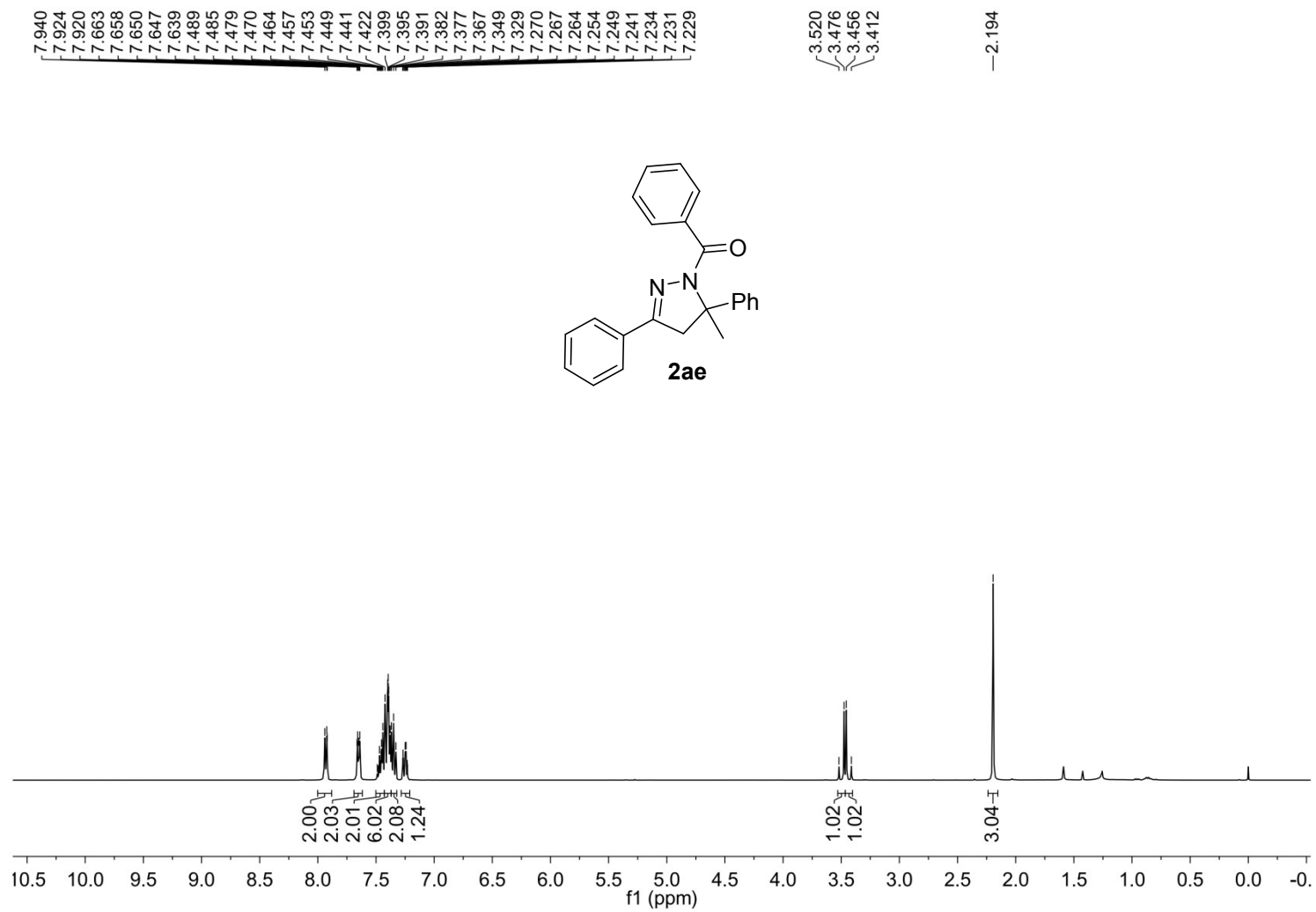
S72

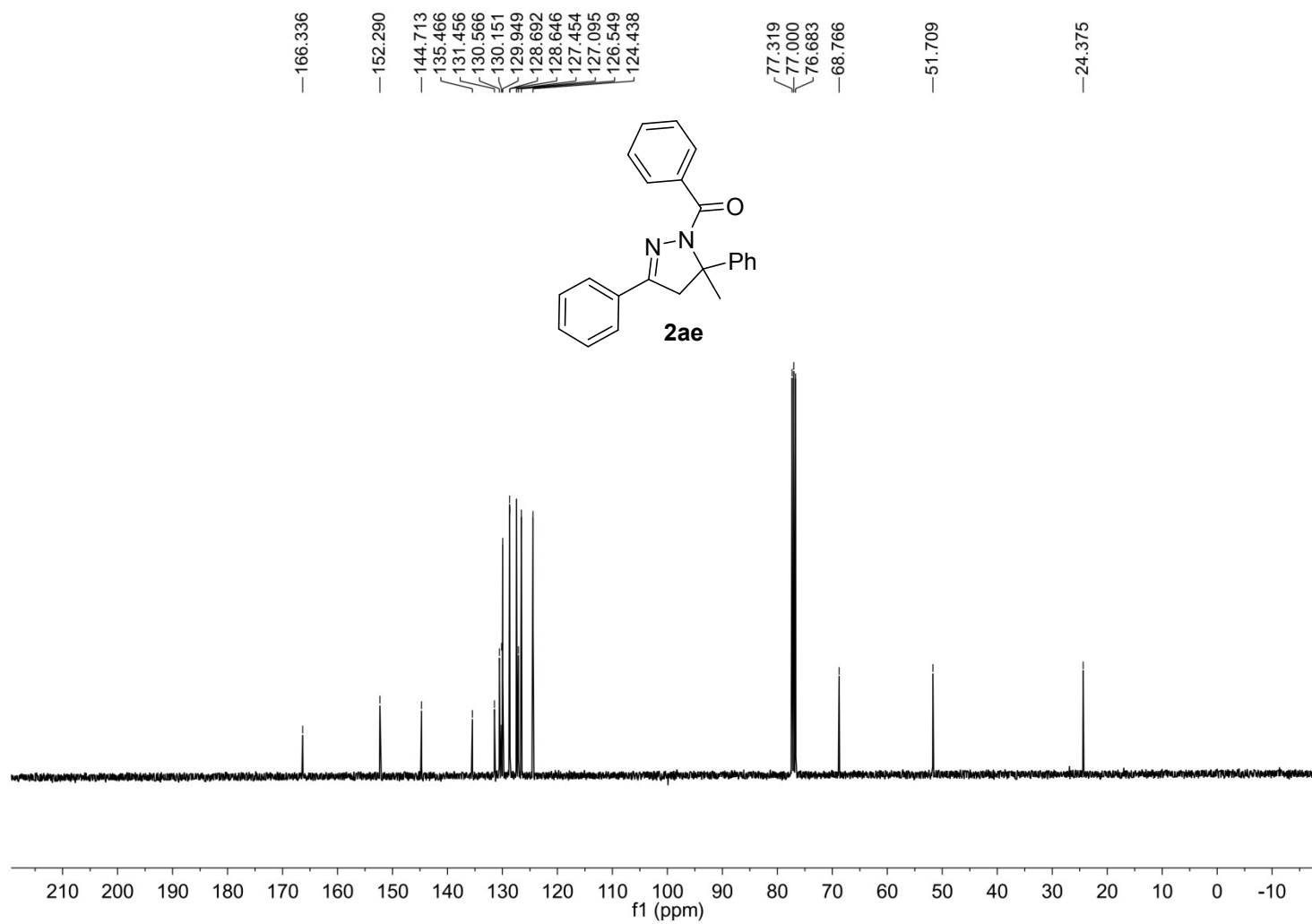




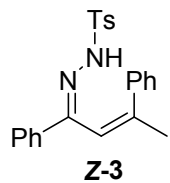
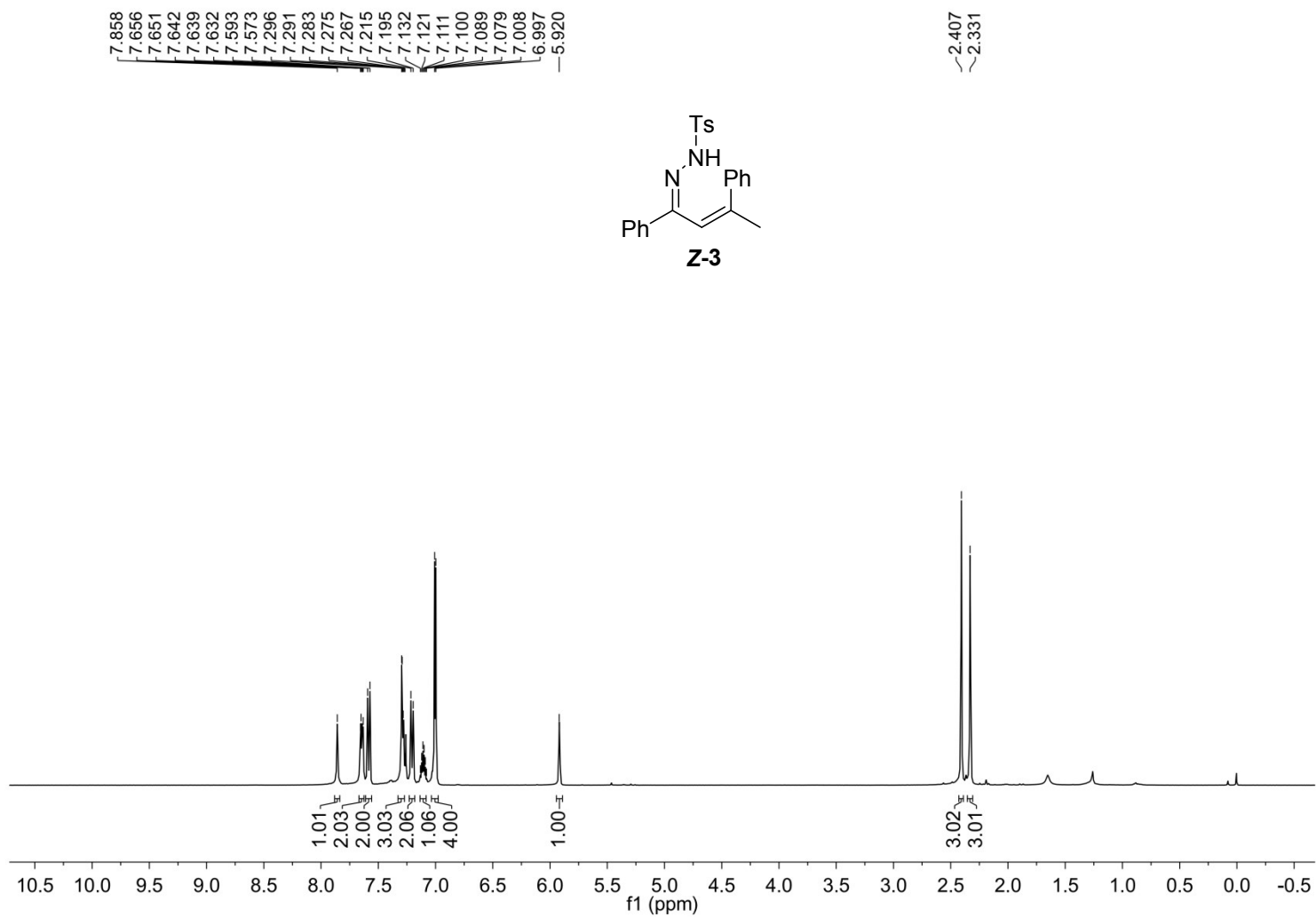


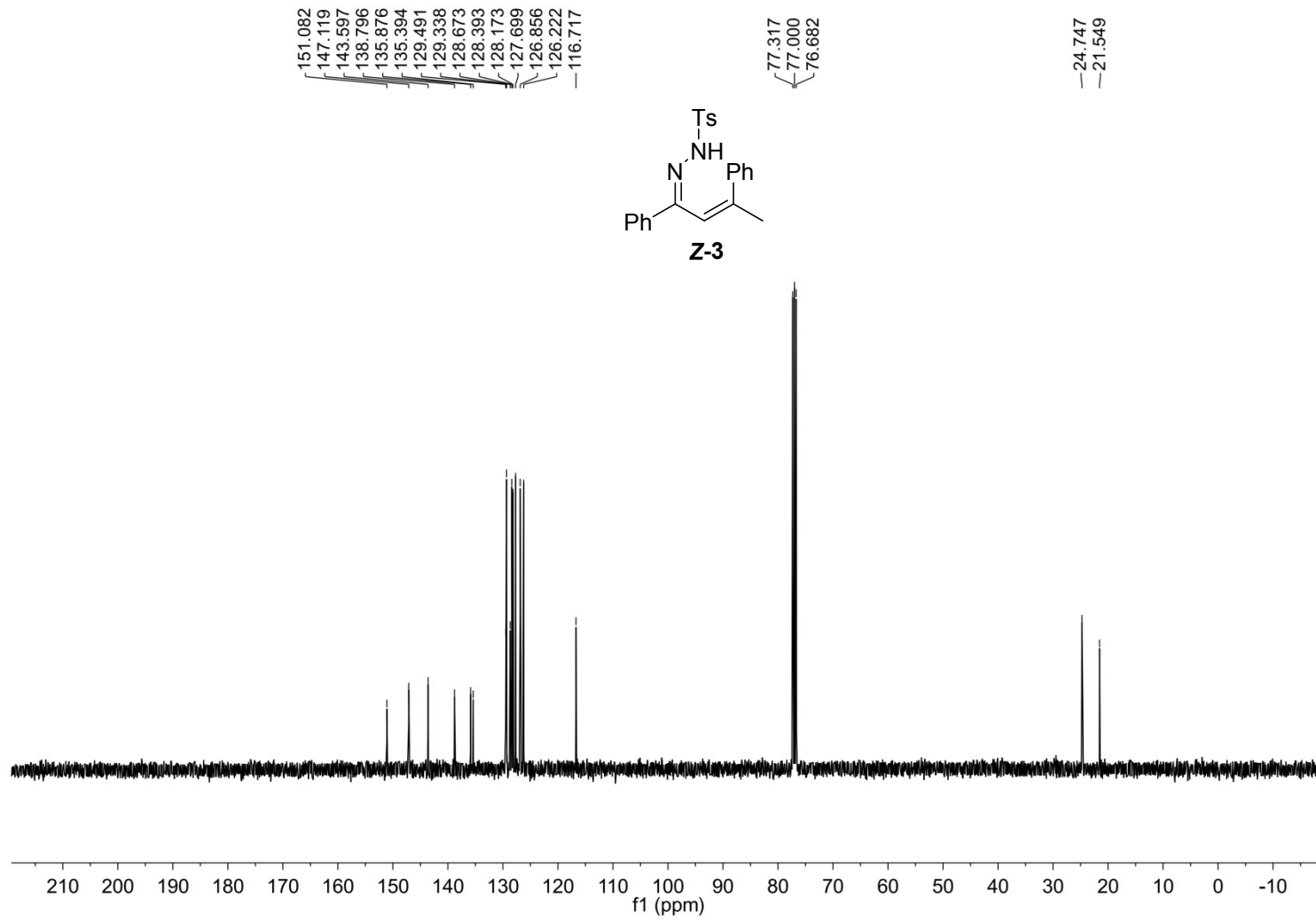
S75



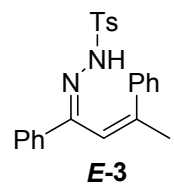
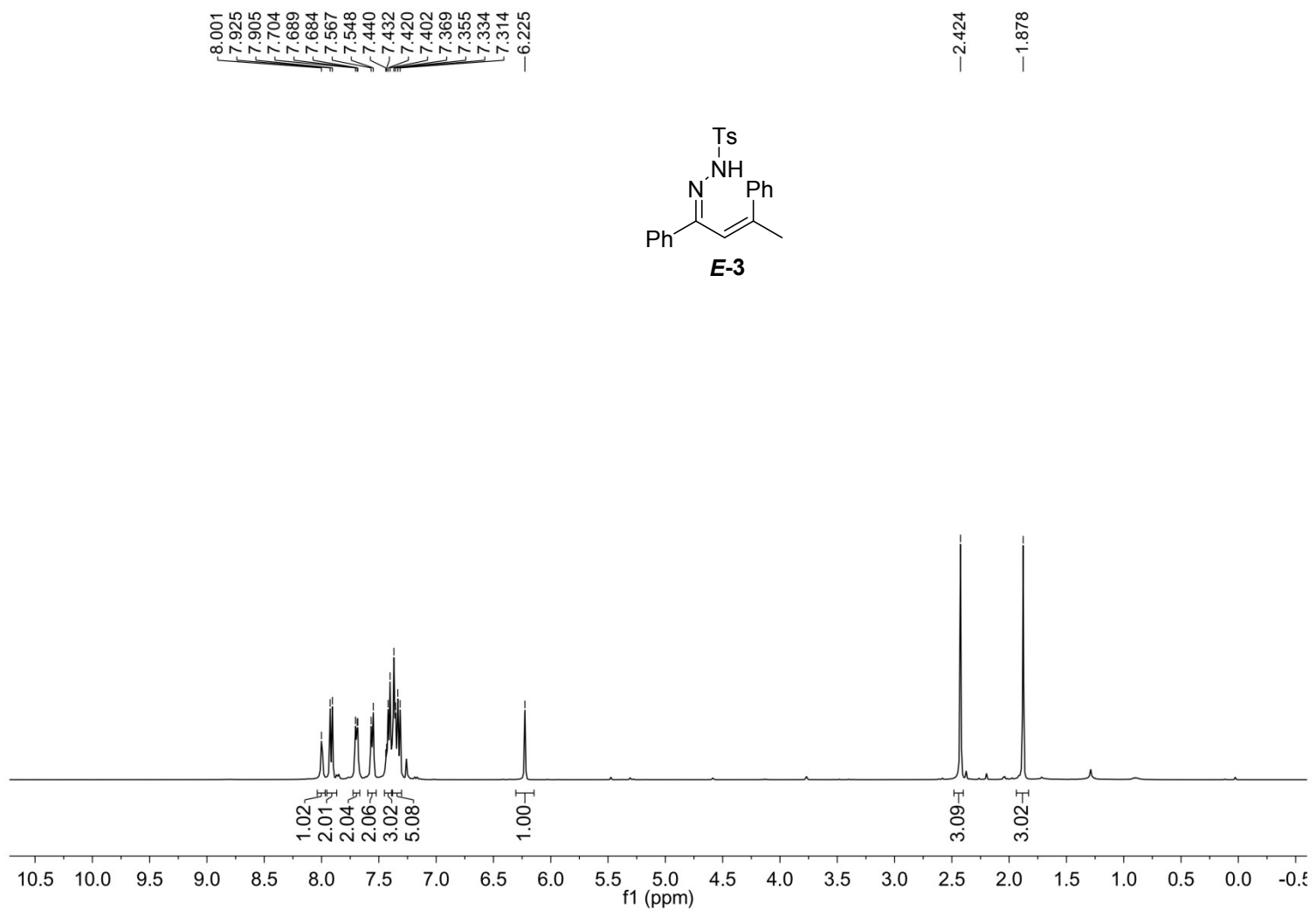


S77

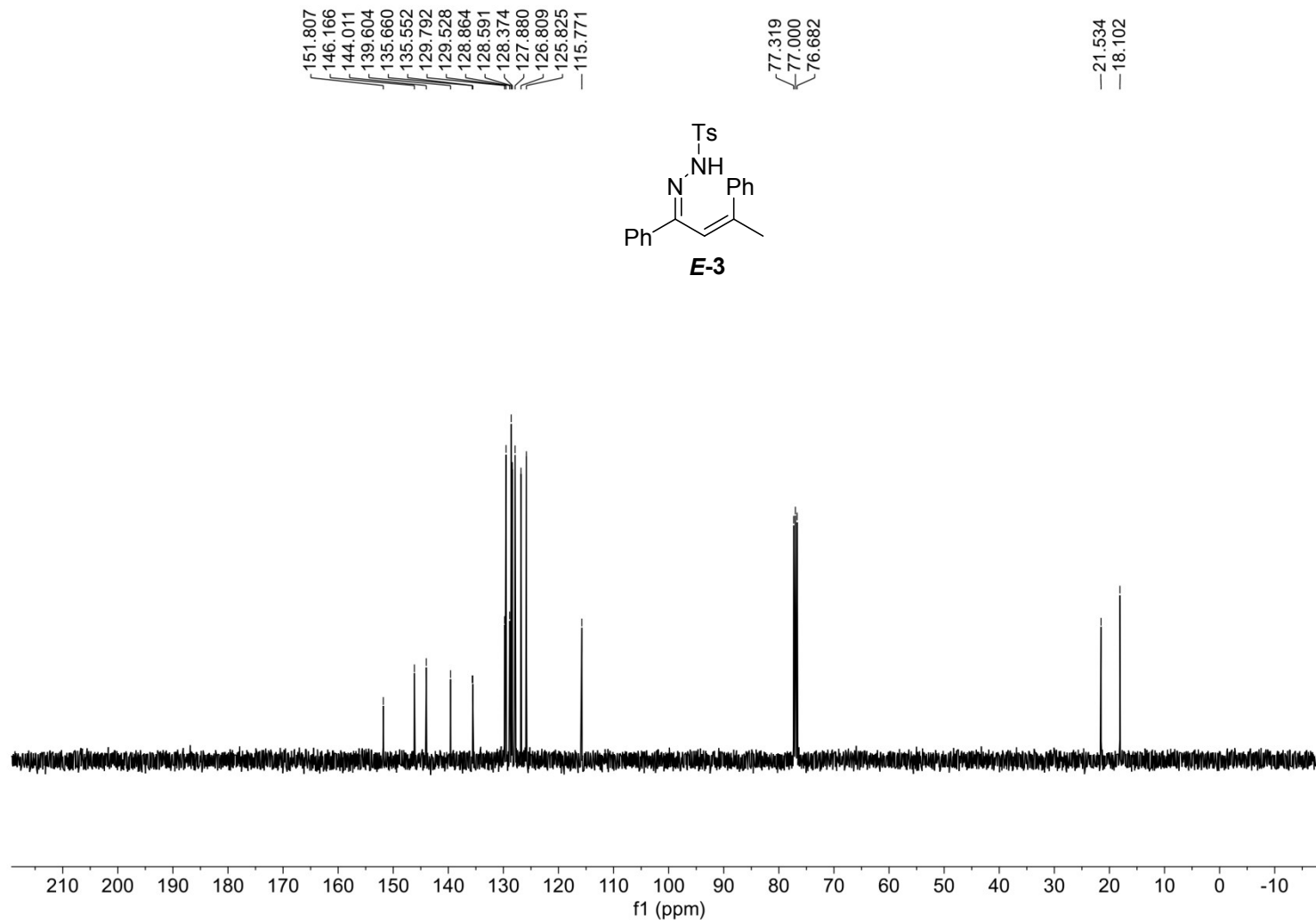




S79



S80



S81