
Supporting Information for

NHC-Boryl Radical Catalysis for Cycloisomerization with C-C Triple Bond Reorganization

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General

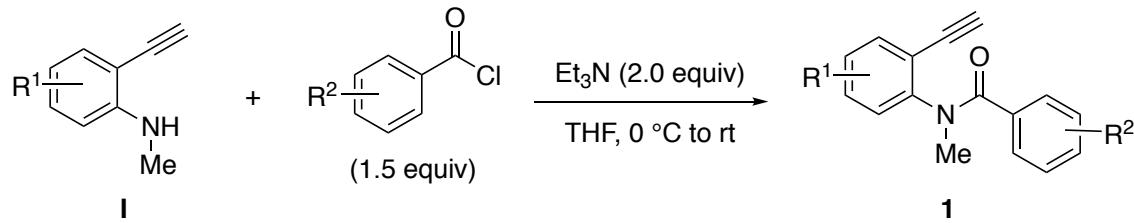
¹H NMR (400 MHz) spectra were recorded on a Bruker Avance 400 spectrometer in CDCl₃ [using CDCl₃ (for ¹H, δ = 7.26) as the internal standard]. ¹³C NMR (100 MHz) spectra on a Bruker Avance 400 spectrometer in CDCl₃ [using CDCl₃ (for ¹³C, δ = 77.0) as internal standard]. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = doublet of doublet of doublet, dt = doublet of triplet, m = multiplet, s br = single broad. High-resolution mass spectra were obtained with a Water XEVO G2 Q-Tof (Waters Corporation). X-ray crystallography analysis was performed on Bruker X8 APEX X-ray diffractionmeter. Melting points were uncorrected and were recorded on a Buchi B-54 melting point apparatus. Flash column chromatography was performed using Merck silica gel 60 with distilled solvents. Commercially available reagents were purchased from Energy Chemical, J & K Scientific, Adamas-beta and Sigma-Aldrich Co., Inc.

Starting material **1w**^[1], **1y**^[2], **1z**^[3] and NHC–boranes **2a**,^[4] **2b**,^[5] **2c**,^[6] **2d**^[7] were known compounds and were prepared according to the literature procedures.

Synthesis of *N*-(2-ethynylaryl)arylamides **1**

N-(2-ethynylaryl)arylamides **1** used in this work were prepared by the procedures shown below.

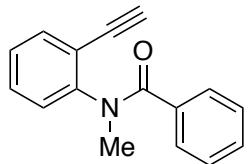
General procedure A



To a solution of **I** in THF was added Et₃N (2.0 equiv) and benzoyl chloride (1.5 equiv) at 0 °C. After 15 minutes, the reaction mixture was allowed to warm to rt and stirred for another 3 h. The reaction was then quenched with H₂O and extracted with

ethyl acetate (3 times). The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated. The crude residue was purified by flash column chromatography to give the product **1**.

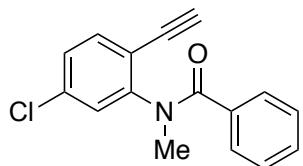
N-(2-Ethynylphenyl)-N-methylbenzamide (1a)



Following the general procedure A, **1a** was obtained in 80% yield (1.75 g, 7.4 mmol) from the reaction of 2-ethynyl-N-methylaniline^[8] (1.22 g, 9.3 mmol) and benzoyl chloride.

White solid, mp: 132-134 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.36 (1H, s), 3.45 (3H, s), 7.00 (1H, d, *J* = 7.6 Hz), 7.08-7.24 (5H, m), 7.30-7.40 (2H, d, *J* = 6.8 Hz), 7.44 (1H, d, *J* = 6.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 37.3, 79.9, 83.1, 121.0, 127.2, 127.5, 128.3, 128.9, 129.6, 129.7, 133.7, 135.9, 146.9, 171.1; ESIHRMS: Found: m/z 236.1075. Calcd for C₁₆H₁₄NO: (M+H)⁺ 236.1070.

N-(5-Chloro-2-ethynylphenyl)-N-methylbenzamide (1c)

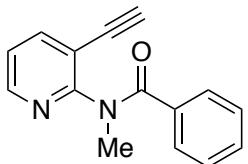


Following the general procedure A, **1c** was obtained in 74 % yield (360 mg, 1.3 mmol) from the reaction of 5-chloro-2-ethynylaniline^[9] (230 mg, 1.8 mmol) with benzoyl chloride.

White solid, mp: 137-138 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.39 (1H, s), 3.42 (3H, s), 7.06 (1H, s), 7.10-7.30 (4H, m), 7.30-7.40 (3H, m); ¹³C NMR (100 MHz, CDCl₃) δ 37.4, 79.0, 83.9, 119.7, 127.7, 127.8, 128.2, 129.1, 130.0, 134.5, 135.1, 135.5, 147.9, 170.9; ESIHRMS: Found: m/z 270.0682. Calcd for C₁₆H₁₃NOCl: (M+H)⁺

270.0680.

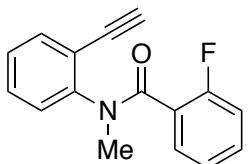
N-(3-Ethynylpyridin-2-yl)-N-methylbenzamide (1d)



Following the general procedure A, **1d** was obtained in 90 % yield (177 mg, 0.75 mmol) from the reaction of 3-ethynyl-N-methylpyridin-2-amine^[10] (103 mg, 0.78 mmol) and benzoyl chloride.

White solid, mp: 83-84 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.37 (1H, s), 3.51 (3H, s), 7.11 (1H, dd, *J* = 4.8, 7.6 Hz), 7.13-7.19 (2H, m), 7.22-7.28 (1H, m), 7.35-7.40 (2H, m), 7.68 (1H, dd, *J* = 2.0, 7.6 Hz), 8.40 (1H, dd, *J* = 1.6, 4.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 35.9, 78.1, 84.6, 117.0, 121.9, 127.5, 128.6, 129.9, 136.0, 142.1, 148.8, 158.5, 171.0; ESIHRMS: Found: m/z 237.1026. Calcd for C₁₅H₁₃N₂O: (M+H)⁺ 237.1022.

N-(2-Ethynylphenyl)-2-fluoro-N-methylbenzamide (1e)

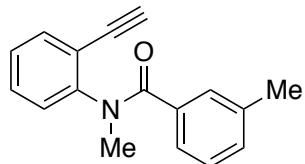


Following the general procedure A, **1e** was obtained in 93% yield (590 mg, 2.3 mmol) from the reaction of 2-ethynyl-N-methylaniline (306 mg, 2.3 mmol) and 2-fluorobenzoyl chloride.

White solid, mp: 109-110 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.38 (1H, s), 3.46 (3H, s), 6.79-6.86 (1H, m), 6.94 (1H, ddd, *J* = 0.8, 7.2, 7.2, Hz), 7.10-7.23 (4H, m), 7.34 (1H, ddd, *J* = 1.2, 7.6, 7.6 Hz), 7.38 (1H, dd, *J* = 1.2, 7.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 36.5, 79.7, 82.9, 115.2 (d, *J* = 22 Hz), 121.1, 123.5 (d, *J* = 3.4 Hz), 124.9 (d, *J* = 16.8 Hz), 127.7, 128.4 (d, *J* = 1.5 Hz), 128.8 (d, *J* = 3.4 Hz), 129.5, 130.9 (d,

$J = 8.0$ Hz), 133.4 145.2, 158.2 (d, $J = 247.0$ Hz), 166.7; ^{19}F NMR (376 MHz, CDCl_3) δ -113.0 (m); ESIHRMS: Found: m/z 254.0978. Calcd for $\text{C}_{16}\text{H}_{13}\text{NOF}$: $(\text{M}+\text{H})^+$ 254.0976.

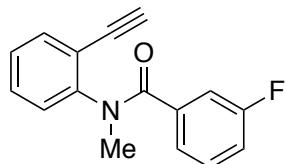
***N*-(2-Ethynylphenyl)-*N*,3-dimethylbenzamide (**1f**)**



Following the general procedure A, **1f** was obtained in 96% yield (710.5 mg, 3.3 mmol) from reaction of 2-ethynyl-*N*-methylaniline (449 mg, 3.4 mmol) and 3-methylbenzoyl chloride.

White solid, mp: 103-104 °C; ^1H NMR (400 MHz, CDCl_3) δ 2.21 (3H, s), 3.36 (1H, s), 3.44 (3H, s), 6.90-7.10 (4H, m), 7.10-7.26 (3H, m), 7.40-7.48 (1H, d, $J = 6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 21.2, 37.3, 80.0, 83.0, 121.0, 125.2, 127.2, 127.3, 128.9, 129.0, 129.7, 130.3, 133.7, 135.9, 137.3, 147.0, 171.3; ESIHRMS: Found: m/z 250.1226. Calcd for $\text{C}_{17}\text{H}_{16}\text{NO}$: $(\text{M}+\text{H})^+$ 250.1226.

***N*-(2-Ethynylphenyl)-3-fluoro-*N*-methylbenzamide (**1g**)**

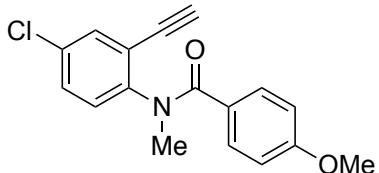


Following the general procedure A, **1g** was obtained in 52% yield (418 mg, 1.6 mmol) from the reaction of 2-ethynyl-*N*-methylaniline (778 mg, 6.7 mmol) and 3-fluorobenzoyl chloride.

White solid, mp: 111-112 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.37 (1H, s), 3.45 (3H, s), 3.86-3.94 (1H, m), 6.88-6.92 (1H, m), 7.03 (1H, d, $J = 7.6$ Hz), 7.06-7.12 (3H, m), 7.14-7.26 (2H, m), 7.45 (1H, d, $J = 6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 37.3, 79.7, 83.2, 115.4 (d, $J = 22.9$ Hz), 116.6 (d, $J = 21.0$ Hz), 121.0, 123.9, 127.5, 128.7,

129.2 (d, $J = 7.5$ Hz), 129.9, 133.8, 138.0 (d, $J = 7.0$ Hz), 146.4, 161.8 (d, $J = 245.7$ Hz), 169.6; ^{19}F NMR (376 MHz, CDCl_3) δ -112.9; ESIHRMS: Found: m/z 276.0790. Calcd for $\text{C}_{16}\text{H}_{12}\text{NONaF}$: ($\text{M}+\text{Na}$) $^+$ 276.0795.

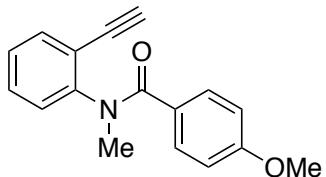
N-(4-Chloro-2-ethynylphenyl)-4-methoxy-N-methylbenzamide (1h)



Following the general procedure A, **1h** was obtained in 96% yield (1.2 g, 3.9 mmol) from the reaction of 5-chloro-2-ethynylaniline^[9] (465 mg, 2.8 mmol) and 4-methoxybenzoyl chloride.

White solid, mp: 114-116 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.39 (1H, s), 3.40 (3H, s), 3.74 (3H, s), 6.68 (2H, d, $J = 8.4$ Hz), 6.93 (1H, d, $J = 8.4$ Hz), 7.17 (1H, dd, $J = 2.4, 8.4$ Hz), 7.30 (2H, d, $J = 8.4$ Hz), 7.43 (1H, d, $J = 2.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 37.7, 55.2, 78.8, 84.2, 113.1, 122.4, 130.0, 130.1, 130.4, 132.6, 133.5, 146.0, 146.1, 160.7, 170.7; ESIHRMS: Found: m/z 300.0790. Calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_2\text{Cl}$: ($\text{M}+\text{H}$) $^+$ 300.0786.

N-(2-Ethynylphenyl)-4-methoxy-N-methylbenzamide (1i)

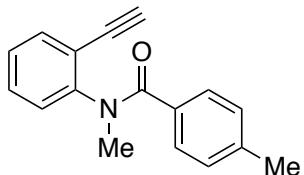


Following the general procedure A, **1i** was obtained in 64% yield (550 mg, 2.1 mmol) from the reaction of 2-ethynyl-N-methylaniline (430 mg, 3.3 mmol) and 4-methoxybenzoyl chloride.

White solid, mp: 94-95 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.34 (1H, s), 3.43 (3H, s), 3.72 (3H, s), 6.64 (2H, d, $J = 8.4$ Hz), 7.00 (1H, d, $J = 7.6$ Hz), 7.12-7.24 (2H, m), 7.30 (2H, d, $J = 8.4$ Hz), 7.45 (1H, dd, $J = 1.2, 7.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3)

δ 37.7, 55.2, 78.8, 84.2, 113.1, 122.4, 127.8, 130.0, 130.4, 132.6, 133.5, 146.0, 160.7, 170.7; ESIHRMS: Found: m/z 266.1175. Calcd for C₁₇H₁₆NO₂: (M+H)⁺ 266.1176.

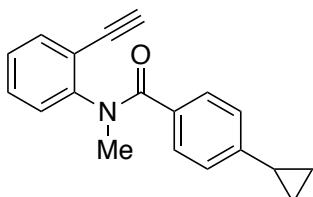
N-(2-Ethynylphenyl)-N,4-dimethylbenzamide (1j)



Following the general procedure A, **1j** was obtained in 47% yield (530 mg, 2.1 mmol) from the reaction of 2-ethynyl-N-methylaniline (594 mg, 4.5 mmol) and 4-methylbenzoyl chloride.

White solid, mp: 113-114 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.23 (3H, s), 3.35 (1H, s), 3.44 (3H, s), 6.93 (2H, d, *J* = 6.8 Hz), 7.00 (1H, d, *J* = 6.4 Hz), 7.10-7.32 (4H, m), 7.44 (1H, d, *J* = 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 21.3, 37.4, 79.9, 83.0, 120.9, 127.0, 128.2, 128.4, 128.8, 129.7, 133.0, 133.7, 139.7, 147.1, 171.1; ESIHRMS: Found: m/z 250.1227. Calcd for C₁₇H₁₆NO: (M+H)⁺ 250.1226.

4-Cyclopropyl-N-(2-ethynylphenyl)-N-methylbenzamide (1k)

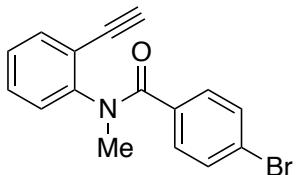


Following the general procedure A, **1k** was obtained in 44% yield (740 mg, 2.7 mmol) from the reaction of 2-ethynyl-N-methylaniline (804 mg, 6.1 mmol) and 4-cyclopropylbenzoyl chloride,^[11] which was prepared from 4-cyclopropylbenzoic acid^[12] and (COCl)₂.

White solid, mp: 91-92 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.50-0.65 (2H, m), 0.85-0.95 (2H, m), 1.70-1.84 (1H, m), 3.34 (1H, s), 3.44 (3H, s), 6.82 (2H, d, *J* = 7.2 Hz), 7.00 (1H, d, *J* = 6.8 Hz), 7.10-7.28 (4H, m), 7.45 (1H, d, *J* = 7.2 Hz); ¹³C NMR

(100 MHz, CDCl₃) δ 9.7, 15.3, 37.5, 80.0, 83.0, 120.9, 124.6, 127.1, 128.5, 128.8, 129.8, 132.8, 133.8, 146.1, 147.2, 171.0; ESIHRMS: Found: m/z 276.1382. Calcd for C₁₉H₁₈NO: (M+H)⁺ 276.1383.

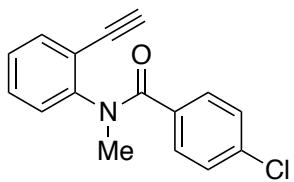
4-Bromo-N-(2-ethynylphenyl)-N-methylbenzamide (1m)



Following the general procedure A, **1m** was obtained in 66% yield (1.20 g, 3.9 mmol) from the reaction of 2-ethynyl-N-methylaniline (1.48 g, 7.4 mmol) and 4-bromobenzoyl chloride.

White solid, mp: 88-90 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.36 (1H, s), 3.44 (3H, s), 7.02 (1H, d, *J* = 7.6 Hz), 7.14-7.32 (6H, m), 7.42-7.48 (1H, d, *J* = 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 37.4, 79.7, 83.2, 121.0, 124.0, 127.5, 128.7, 130.0, 130.8, 133.9, 134.8, 146.5, 170.0; ESIHRMS: Found: m/z 314.0179. Calcd for C₁₆H₁₃NO⁷⁹Br: (M+H)⁺ 314.0175.

4-Chloro-N-(2-ethynylphenyl)-N-methylbenzamide (1n)

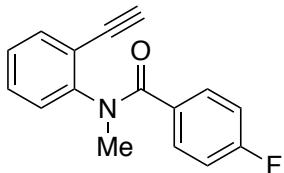


Following the general procedure A, **1n** was obtained in 80% yield (465 mg, 1.7 mmol) from the reaction of 2-ethynyl-N-methylaniline (505 mg, 3.8 mmol) and 4-chlorobenzoyl chloride.

White solid, mp: 61-63 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.36 (1H, s), 3.44 (3H, s), 7.02 (1H, d, *J* = 7.6 Hz), 7.12 (2H, d, *J* = 8.4 Hz), 7.15-7.26 (2H, m), 7.28 (2H, d, *J* = 8.4 Hz), 7.45 (1H, d, *J* = 6.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 37.5, 79.7, 83.2, 121.0, 127.5, 127.9, 128.7, 129.8, 130.0, 133.9, 134.3, 135.6, 146.5, 170.0;

ESIHRMS: Found: m/z 270.0681. Calcd for C₁₆H₁₃NOCl: (M+H)⁺ 270.0680.

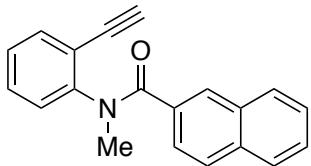
N-(2-Ethynylphenyl)-4-fluoro-N-methylbenzamide (1o)



Following the general procedure A, **1o** was obtained in 66% yield (410 mg, 1.6 mmol) from the reaction of 2-ethynyl-N-methylaniline (324 mg, 2.5 mmol) and 4-fluorobenzoyl chloride.

White solid, mp: 74-76 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.36 (1H, s), 3.45 (3H, s), 6.83 (2H, dd, *J* = 8.4, 8.4 Hz), 7.01 (1H, d, *J* = 7.6 Hz), 7.14-7.26 (2H, m), 7.35 (2H, dd, *J* = 6.0, 7.2 Hz), 7.45 (1H, d, *J* = 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 37.5, 79.8, 83.2, 114.7 (d, *J* = 21.7 Hz), 121.0, 127.4, 128.8, 129.9, 130.6 (d, *J* = 8.6 Hz), 132.0 (d, *J* = 3.3 Hz), 133.9, 146.8, 163.2 (d, *J* = 248.6 Hz), 170.0; ¹⁹F NMR (376 MHz, CDCl₃) δ -110.1; ESIHRMS: Found: m/z 276.0790. Calcd for C₁₆H₁₂NONaF: (M+Na)⁺ 276.0795.

N-(2-Ethynylphenyl)-N-methyl-2-naphthamide (1p)

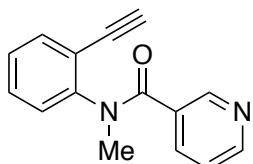


Following the general procedure A, **1p** was obtained in 90 % yield (1.9 g, 6.9 mmol) from the reaction of 2-ethynyl-N-methylaniline (1.01 g, 7.7 mmol) and 2-naphthoyl chloride (1.59 g, 8.4 mmol).

White solid, mp: 97-99 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.41 (1H, s), 3.51 (3H, s), 7.02-7.18 (3H, m), 7.36-7.50 (4H, m), 7.60 (1H, d, *J* = 8.4 Hz), 7.71 (2H, d, *J* = 7.6 Hz), 7.89 (1H, s); ¹³C NMR (100 MHz, CDCl₃) δ 37.6, 80.0, 83.2, 121.0, 125.2, 126.2, 127.0, 127.2, 127.5, 128.6, 128.8, 128.9, 129.8, 132.2, 133.3, 133.5, 133.8,

146.9, 171.0; ESIHRMS: Found: m/z 286.1229. Calcd for C₂₀H₁₆NO: (M+H)⁺ 286.1226.

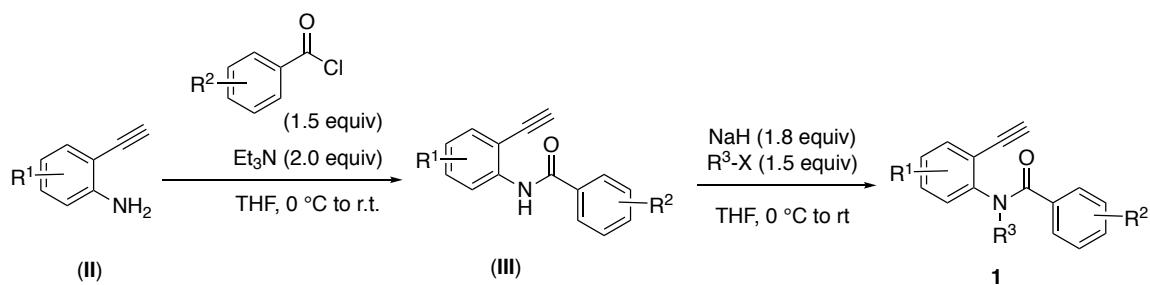
N-(2-Ethynylphenyl)-N-methylnicotinamide (**1q**)



Following the general procedure A, **1q** was obtained in 48 % yield (352 mg, 1.5 mmol) from the reaction of 2-ethynyl-N-methylaniline (411 mg, 3.1 mmol) and picolinoyl chloride.^[13]

White solid, mp: 92-94 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.35 (1H, s), 3.47 (3H, s), 7.08-7.14 (2H, m), 7.16-7.22 (1H, m), 7.24-7.30 (1H, m), 7.42 (1H, d, *J* = 7.6 Hz), 7.67 (1H, ddd, *J* = 2.0, 2.0, 8.0 Hz), 8.43 (1H, dd, *J* = 1.6, 4.8 Hz), 8.54 (1H, d, *J* = 1.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 37.5, 79.6, 83.4, 121.3, 122.6, 127.9, 128.8, 130.2, 131.9, 134.0, 135.8, 146.1, 149.2, 150.4, 168.7; ESIHRMS: Found: m/z 237.1022. Calcd for C₁₅H₁₃N₂O: (M+H)⁺ 237.1022.

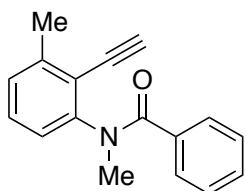
General procedure B



To a solution of **II** in THF was added Et₃N (2.0 equiv.) and benzoyl chloride (1.5 equiv.) at 0 °C. After 15 minutes, the reaction mixture was allowed to warm to rt and stirred for another 3 h. The reaction was then quenched with H₂O and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated to give **III**. The crude residue was used for the next step directly without further purification.

To a solution of **III** in THF (0.25 M) was added NaH (1.8 equiv.) portion wise at 0 °C. After 15 minutes, alkyl halide (1.5 equiv.) was added dropwise. The reaction mixture was stirred at 0 °C for 15 minutes, then allowed to warm to rt and stirred until TLC indicating reaction complete. The reaction was then quenched with H₂O and extracted with ethyl acetate (3 times). The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated. The crude residue was purified by flash column chromatography to give the corresponding product **1**.

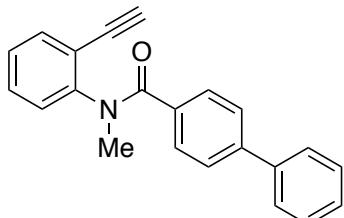
N-(2-Ethynyl-3-methylphenyl)-N-methylbenzamide (1b)



Following the general procedure **B**, **1b** was obtained in 76 % yield (586 mg, 2.4 mmol) from the reaction of 2-ethynyl-3-methylaniline^[14] 401 mg, 3.1 mmol), benzoyl chloride and iodomethane.

White solid, mp: 94-97 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.40 (3H, s), 3.44 (3H, s), 3.58 (1H, s), 6.78-6.86 (1H, m), 7.00-7.08 (2H, m), 7.10-7.24 (3H, m), 7.34 (2H, d, J = 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 20.8, 37.4, 78.7, 87.1, 121.0, 126.2, 127.5, 128.2, 128.3, 128.9, 129.5, 136.1, 142.7, 147.2, 171.1; ESIHRMS: Found: m/z 250.1232. Calcd for C₁₇H₁₆NO: (M+H)⁺ 250.1226.

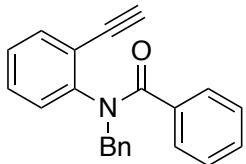
N-(2-Ethynylphenyl)-N-methyl-[1,1'-biphenyl]-4-carboxamide (1l)



Following the general procedure **B**, **1l** was obtained in 57 % yield (829 mg, 2.8 mmol) from the reaction of 2-ethynylaniline^[15] (568 mg, 4.8 mmol), [1,1'-biphenyl]-4-carbonyl chloride and iodomethane.

White solid, mp: 100-101 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.38 (1H, s), 3.48 (3H, s), 7.05 (1H, d, J = 7.2 Hz), 7.13-7.24 (2H, m), 7.28-7.35 (1H, m), 7.35-7.54 (9H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 37.5, 79.9, 83.1, 121.0, 126.2, 127.0, 127.3, 127.6, 128.7, 128.9, 129.9, 133.8, 134.7, 140.1, 142.2, 146.9, 170.8; ESIHRMS: Found: m/z 312.1381. Calcd for $\text{C}_{22}\text{H}_{18}\text{NO}$: ($\text{M}+\text{H}$) $^+$ 312.1383.

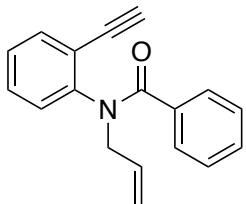
***N*-Benzyl-*N*-(2-ethynylphenyl)benzamide (1r)**



Following the general procedure **B**, **1r** was obtained in 64 % yield (780 mg, 2.5 mmol) from the reaction of *N*-(2-ethynylphenyl)benzamide^[16] (866 mg, 3.9 mmol) and benzylbromide (0.6 ml, 5.0 mmol).

White solid, mp: 78-79 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.36 (1H, s), 4.58 (1H, d, J = 14.4 Hz), 5.74 (1H, d, J = 14.4 Hz), 6.64 (1H, d, J = 8.0 Hz), 6.95-7.33 (10H, m), 7.34-7.42 (3H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 52.5, 80.2, 83.3, 121.4, 127.2, 127.4, 127.5, 128.2, 128.3, 129.2, 129.5, 130.4, 133.7, 136.1, 137.1, 144.8, 170.8; ESIHRMS: Found: m/z 312.1381. Calcd for $\text{C}_{22}\text{H}_{18}\text{NO}$: ($\text{M}+\text{H}$) $^+$ 312.1383.

***N*-Allyl-*N*-(2-ethynylphenyl)benzamide (1t)**

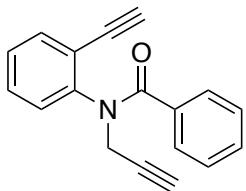


Following the general procedure **B**, **1t** was obtained in 60 % yield (630 mg, 2.4 mmol) from the reaction of *N*-(2-ethynylphenyl)benzamide (890 mg, 4.0 mmol) and 3-bromoprop-1-ene (0.5 ml, 6.0 mmol).

White solid, mp: 119-121 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.36 (1H, s), 4.22 (1H, dd, J = 7.2, 14.4 Hz), 4.89 (1H, dd, J = 5.2, 14.4 Hz), 5.11-5.14 (2H, m), 5.95-6.04

(1H, m), 6.99 (1H, d, J = 7.6 Hz), 6.96-7.24 (5H, m), 7.35 (2H, d, J = 7.2 Hz), 7.41 (1H, d, J = 7.6 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 52.3, 80.3, 83.2, 118.3, 121.6, 127.2, 127.5, 128.3, 129.4, 129.6, 130.0, 132.9, 133.7, 136.1, 145.0, 170.6; ESIHRMS: Found: m/z 284.1047. Calcd for $\text{C}_{18}\text{H}_{15}\text{NONa}$: ($\text{M}+\text{Na}$) $^+$ 284.1046.

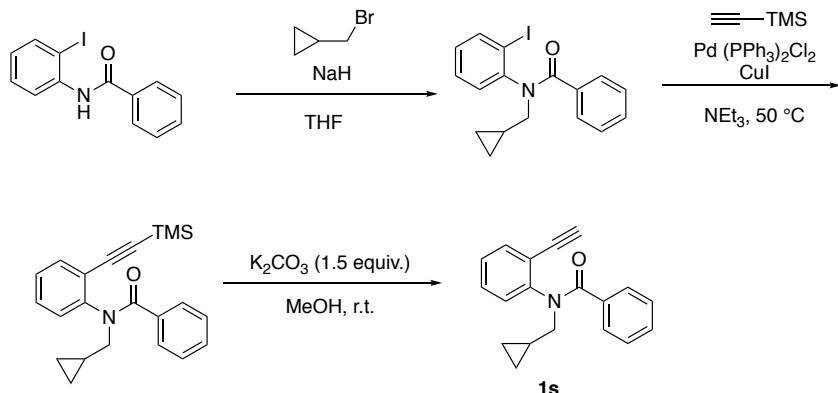
N-(2-Ethynylphenyl)-*N*-(prop-2-yn-1-yl)benzamide (**1u**)



Following the general procedure **B**, **1u** was obtained in 86 % yield (730 mg, 2.8 mmol) from the reaction of *N*-(2-ethynylphenyl)benzamide (720 mg, 3.3 mmol) and 3-bromoprop-1-yne (0.5 ml, 6.0 mmol).

White solid, mp: 120-121 °C; ^1H NMR (400 MHz, CDCl_3) δ 2.21 (1H, s), 3.40 (1H, s), 4.30 (1H, d, J = 17.2 Hz), 5.20 (1H, d, J = 17.2 Hz), 7.03-7.25 (6H, m), 7.37 (2H, d, J = 6.8 Hz), 7.46 (1H, d, J = 6.0 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 38.3, 72.3, 78.8, 79.8, 83.6, 121.2, 127.7, 127.8, 128.4, 129.5, 130.0, 130.5, 133.7, 135.2, 144.2, 170.5; ESIHRMS: Found: m/z 282.0889. Calcd for $\text{C}_{18}\text{H}_{13}\text{NONa}$: ($\text{M}+\text{Na}$) $^+$ 282.0889.

N-(Cyclopropylmethyl)-*N*-(2-ethynylphenyl)benzamide (**1s**)



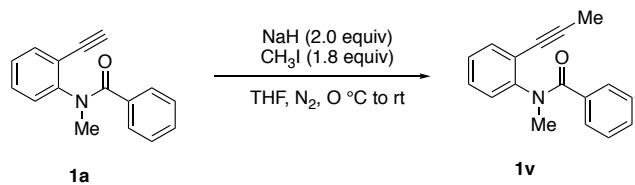
To a solution of *N*-(2-iodophenyl)benzamide^[19] (1.46 g, 4.5 mmol) in THF (0.25 M) was added NaH (486 mg, 20 mmol) at 0 °C portionwise. The reaction mixture was stirred for 0.5 h at 0 °C before (bromomethyl)-cyclopropane (0.7 ml) was added.

After 15 minutes the reaction mixture was allowed to warm to room temperature and stirred until TLC indicating reaction complete. The reaction was then quenched with H₂O and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated. The crude residue was used directly for the next step without further purification.

To a solution of crude residue (692 mg, 1.8 mmol) in Et₃N (0.5 M) was added PdCl₂(PPh₃)₂ (25 mg, 0.036 mmol), CuI (14 mg, 7.2 mmol) and ethynyltrimethylsilane (0.33 mL). The reaction mixture was stirred at room temperature for 12 h. Then it was diluted with water and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine and dried over Na₂SO₄. The resulting mixture was filtered, and the filtrate was concentrated in *vacuo* to give the crude product. It was used for the next step directly without further purification. To a solution of crude product in MeOH (0.5 M) was added K₂CO₃ (500 mg). After being stirred at room temperature for 2 h, the reaction mixture was poured into water and then extracted with CH₂Cl₂ (30 mL x 3). The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel to afford the corresponding product **1s** (780 mg, 1.2 mmol) in 67 % yield.^[18]

White solid, mp: 44-45 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.04-0.07 (1H, m), 0.17-0.18 (1H, m), 0.39-0.43 (2H, m), 1.00-1.15 (1H, m), 3.32 (1H, s), 3.53 (1H, dd, *J* = 7.2, 13.6 Hz), 4.14 (1H, dd, *J* = 7.2, 13.6 Hz), 7.08-7.24 (6H, m), 7.34 (2H, d, *J* = 7.6 Hz), 7.40 (1H, d, *J* = 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 3.18, 4.26, 9.59, 53.7, 80.4, 82.9, 121.8, 127.2, 127.5, 128.3, 129.3, 130.4, 133.6, 136.5, 145.5, 170.8; ESIHRMS: Found: m/z 276.1386. Calcd for C₁₉H₁₈NO: (M+H)⁺ 276.1383.

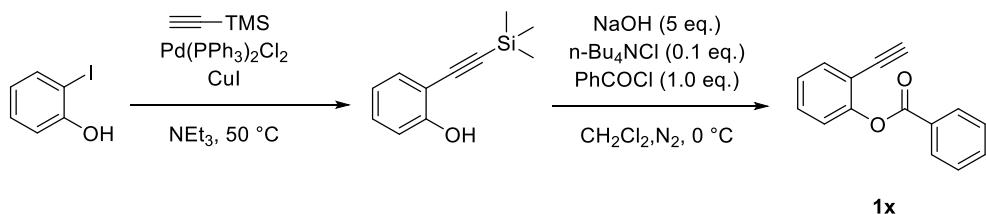
***N*-methyl-*N*-(2-(prop-1-yn-1-yl)phenyl)benzamide (**1v**)**



To a stirred solution of **1a** (223 mg, 0.95 mmol) in THF (0.2 M) was added NaH (80 mg, 2.0 mmol) portionwise at 0 °C. After stirred for 0.5 hour, CH₃I was added. The reaction mixture was allowed to warm to room temperature and stirred for 72 hours. Then it was quenched with water and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine and dried over Na₂SO₄. The resulting mixture was filtered, and the filtrate was concentrated in *vacuo* to give the crude product. The residue was purified by column chromatography on silica gel to afford the corresponding product **1v** (189 mg, 0.76 mmol) in 80 % yield.

¹H NMR (400 MHz, CDCl₃) δ 2.11 (3H, s), 3.43 (3H, s), 6.90-7.00 (1H, m), 7.04-7.16 (4H, m), 7.28-7.40 (3H, m); ¹³C NMR (100 MHz, CDCl₃) δ 4.57, 37.3, 76.1, 92.0, 122.7, 127.1, 127.5, 128.2, 128.4, 128.6, 129.5, 133.0, 136.1, 146.2, 171.1; ESIHRMS: Found: m/z 250.1232. Calcd for C₁₇H₁₆NO: (M+H)⁺ 250.1226.

2-Ethynylphenyl benzoate (**1x**)



To a solution of 2-iodophenol (2.21 g, 10.1 mmol) in Et₃N (0.5 M) was added PdCl₂(PPh₃)₂ (144 mg, 0.205 mmol), CuI (70.3 mg, 0.369 mmol) and ethynyltrimethylsilane (1.7 ml, 12.0 mmol). The reaction mixture was stirred at 50 °C for 12 h. Then it was diluted with water and extracted with ethyl acetate (3 times). The combined organic layer was washed with brine and dried over Na₂SO₄. The resulting mixture was filtered, and the filtrate was concentrated in *vacuo*. The residue was purified by column chromatography on silica gel to afford the corresponding product 2-((trimethylsilyl)ethynyl)phenol (927 mg, 4.87 mmol) in 49 % yield.^[18]

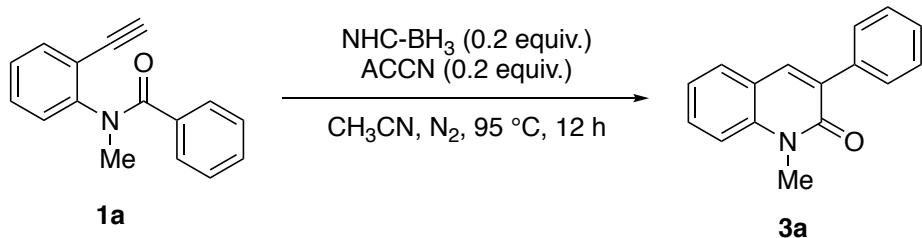
2-((Trimethylsilyl)ethynyl)phenol (927 mg, 4.87 mmol) was dissolved in 10% aqueous sodium hydroxide (780 mg, 19.5 mmol) solution in a flask. A solution of tetrabutylammonium chloride (133 mg, 0.479 mmol) in CH₂Cl₂ (1 M) and benzoyl

chloride (0.57 ml, 4.91 mmol) in CH₂Cl₂ (1 M) were prepared. After cooling all solution at 0 °C, they were mixed at once. The reaction mixture was kept under vigorous magnetic stirring at 0 °C for 15 min and then poured over 50 mL of ice water. The organic layer was washed with brine. After drying on Na₂SO₄, the solvent was evaporated. The residue was purified by column chromatography on silica gel to afford the corresponding product 2-ethynylphenyl benzoate (332 mg, 1.49 mmol) in 31% yield.

White solid; mp: 56-57 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.16 (1H, s), 7.23-7.28 (2H, m), 7.40-7.45 (1H, m), 7.50-7.55 (2H, m), 7.57-7.61 (1H, m), 7.62-7.68 (1H, m), 8.23-8.27 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 78.5, 82.2, 116.4, 122.5, 125.9, 128.6, 129.3, 130.0, 130.3, 133.6, 152.3, 164.6; ESIHRMS: Found: m/z 223.0761. Calcd for C₁₅H₁₁O₂: (M+H)⁺ 223.0754.

3. NHC-boryl radical-catalyzed cycloisomerization of *N*-(2-ethynylaryl)arylamides

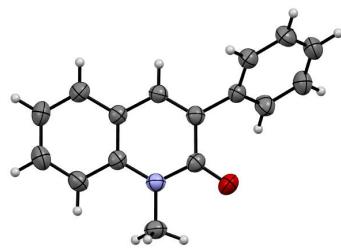
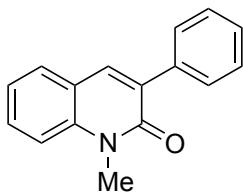
Typical procedure:



To an N₂ flushed, oven-dried glass tube with a magnetic stir bar, *N*-(2-ethynylphenyl)-*N*-methylbenzamide (**1a**) (88.5 mg, 0.3761 mmol), NHC-BH₃ (8.4 mg, 0.2 equiv) and ACCN (18.9 mg, 0.2 equiv) were added. The reaction mixture was stirred at 95 °C for 12 hours. After cooling to room temperature, the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 6 : 1) to afford **3a** (77.2 mg, 0.3281 mmol) in 87% yield. Recrystallization from ethyl acetate/ petroleum

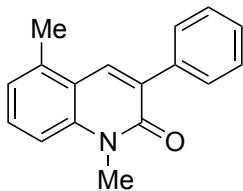
ether gave a colorless crystal.

1-Methyl-3-phenylquinolin-2(1*H*)-one (3a)



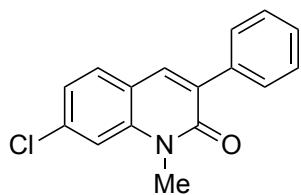
CCDC: 1887424; ^1H NMR (400 MHz, CDCl_3) δ 3.76 (3H, s), 7.21 (1H, t, $J = 7.6$ Hz), 7.34 (2H, m), 7.42 (2H, dd, $J = 7.2, 7.2$ Hz), 7.50-7.60 (2H, m), 7.71 (2H, d, $J = 7.6$ Hz), 7.76 (1H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 29.9, 114.0, 120.7, 122.2, 128.0, 128.1, 128.8, 128.9, 130.2, 132.5, 136.8, 139.6, 161.5. The spectral data for this compound are in agreement with those reported in the literature.^[20]

1,5-Dimethyl-3-phenylquinolin-2(1*H*)-one (3b)



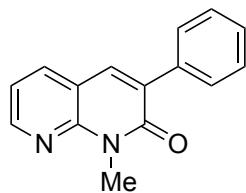
According to the typical procedure, the reaction of **1b** (61.1 mg, 0.2451 mmol), NHC- BH_3 (5.3 mg, 0.2 equiv.) and ACCN (12.1 mg, 0.2 equiv.) under nitrogen at 95 °C for 12 hours after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 6 : 1) afforded 55.6 mg (91%) **3b** as a white solid; mp: 87-89 °C; ^1H NMR (400 MHz, CDCl_3) δ 2.61 (3H, s), 3.80 (3H, s), 7.09 (1H, d, $J = 8.0$ Hz), 7.26 (1H, d, $J = 8.0$ Hz), 7.35-7.41 (1H, m), 7.42-7.49 (3H, m), 7.72 (2H, d, $J = 8.0$ Hz), 8.01 (1H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 19.1, 30.2, 112.4, 119.4, 123.8, 128.0, 128.1, 129.0, 130.1, 131.8, 133.3, 136.2, 137.2, 140.0, 161.3; ESIHRMS: Found: m/z 250.1231. Calcd for $\text{C}_{17}\text{H}_{16}\text{NO}$: ($\text{M}+\text{H}$)⁺ 250.1226.

7-Chloro-1-methyl-3-phenylquinolin-2(1*H*)-one (3c)



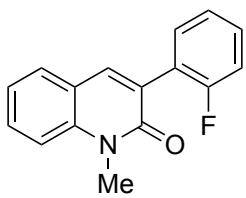
According to the typical procedure, the reaction of **1c** (109.2 mg, 0.4048 mmol), NHC-BH₃ (9.2 mg, 0.2 equiv.) and ACCN (19.4 mg, 0.2 equiv.) under nitrogen at 95 °C for 12 hours after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) afforded 92.6 mg (85%) **3c**; ¹H NMR (400 MHz, CDCl₃) δ 3.74 (3H, s), 7.20 (1H, dd, *J* = 2.0, 8.4 Hz), 7.34-7.46 (4H, m), 7.52 (1H, d, *J* = 8.0 Hz), 7.66-7.72 (2H, m), 7.74 (1H, s); ¹³C NMR (100 MHz, CDCl₃) δ 30.0, 114.0, 119.1, 122.5, 128.1, 128.2, 128.8, 129.8, 132.4, 135.9, 136.2, 136.3, 140.2, 161.2. The spectral data for this compound are in agreement with those reported in the literature.^[22]

1-Methyl-3-phenyl-1,8-naphthyridin-2(1H)-one (3d)



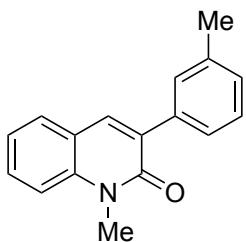
According to the typical procedure, the reaction of **1d** (64.4 mg, 0.2523 mmol), NHC-BH₃ (5.5 mg, 0.2 equiv.) and ACCN (12.6 mg, 0.2 equiv.) under nitrogen at 95 °C for 12 hours after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 3 : 1) afforded 52.4 mg (81%) **3d** as a white solid; mp: 174-176 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.92 (3H, s), 7.19 (1H, dd, *J* = 4.8, 7.6 Hz), 7.36-7.48 (3H, m), 7.68-7.73 (2H, m), 7.75 (1H, s), 7.90 (1H, dd, *J* = 2.0, 8.0 Hz), 8.61 (1H, dd, *J* = 1.6, 4.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 28.8, 115.9, 118.1, 128.2, 128.4, 129.0, 133.8, 134.6, 136.1, 136.2, 149.4, 149.6, 162.3; ESIHRMS: Found: m/z 237.1028. Calcd for C₁₅H₁₃N₂O: (M+H)⁺ 237.1022.

3-(2-Fluorophenyl)-1-methylquinolin-2(1H)-one (3e)



According to the typical procedure, the reaction of **1e** (104.9 mg, 0.4142 mmol), NHC-BH₃ (45.4 mg, 1.0 equiv.) and ACCN (20.4 mg, 0.2 equiv.) was stirred under nitrogen at 95 °C for 12 hours. A second portion of ACCN (20.5 mg, 0.2 equiv) was added and stirred for another 12 hours. After flash column chromatography on silica gel (petroleum ether : ethyl acetate = 6 : 1), 37.6 mg (36%) of **3e** was obtained as a white solid, mp: 128-130 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.79 (3H, s), 7.15 (1H, ddd, *J* = 1.2, 8.4, 9.2 Hz), 7.20 (1H, ddd, *J* = 1.2, 7.6, 7.6 Hz), 7.25 (1H, ddd, *J* = 1.2, 7.6, 7.6 Hz), 7.31-7.40 (2H, m), 7.52 (1H, ddd, *J* = 2.0, 5.6, 7.6 Hz), 7.55-7.61 (2H, m), 7.80 (1H, s); ¹³C NMR (100 MHz, CDCl₃) δ 30.0, 114.1, 115.7 (d, *J* = 22.3 Hz), 120.3, 122.2, 123.8 (d, *J* = 3.5 Hz), 124.5 (d, *J* = 14.6 Hz), 127.7, 129.0, 129.8 (d, *J* = 8.2 Hz), 130.7, 131.6 (d, *J* = 3.1 Hz), 138.9, 139.9, 160.2 (d, *J* = 246.6 Hz), 160.9; ¹⁹F NMR (376 MHz, CDCl₃) δ -114.3 (m); ESIHRMS: Found: m/z 276.0804. Calcd for C₁₆H₁₂NOFNa: (M+Na)⁺ 276.0795.

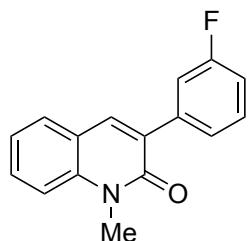
1-Methyl-3-(*m*-tolyl)quinolin-2(1*H*)-one (3f**)**



According to the typical procedure, the reaction of **1f** (105.9 mg, 0.4248 mmol), NHC-BH₃ (18.6 mg, 0.4 equiv.) and ACCN (20.8 mg, 0.2 equiv.) under nitrogen at 95 °C for 12 hours after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 6 : 1) afforded 78.5 mg (74%) **3f** as a white solid; mp: 149-150 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.41 (3H, s), 3.79 (3H, s), 7.18 (1H, d, *J* = 7.6 Hz), 7.21-7.27 (1H, m), 7.32 (1H, t, *J* = 7.8 Hz), 7.35-7.39 (1H, d, *J* = 8.4 Hz), 7.49 (1H, d, *J* = 7.6 Hz), 7.52-7.62 (3H, m), 7.78 (1H, s); ¹³C NMR (100 MHz, CDCl₃) δ 21.4,

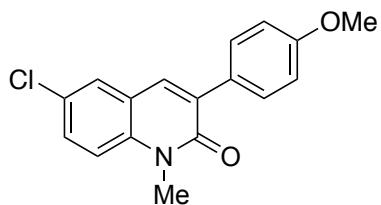
29.8, 113.9, 120.6, 122.0, 125.9, 128.0, 128.68, 128.74, 129.5, 130.1, 132.4, 136.6, 136.7, 137.5, 139.4, 161.4; ESIHRMS: Found: m/z 250.1227. Calcd for C₁₇H₁₆NO: (M+H)⁺ 250.1226.

3-(3-Fluorophenyl)-1-methylquinolin-2(1*H*)-one (3g)



According to the typical procedure, the reaction of **1g** (131.9 mg, 0.5208 mmol), NHC-BH₃ (11.5 mg, 0.2 equiv.) and ACCN (25.1 mg, 0.2 equiv.) under nitrogen at 95 °C for 12 hours after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 6 : 1) afforded 104.2 mg (79 %) **3g** as a white solid, mp: 136-137 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.80 (3H, s), 7.04-7.10 (1H, m), 7.24-7.29 (1H, m), 7.35-7.43 (2H, m), 7.46-7.51 (2H, m), 7.56-7.64 (2H, m), 7.82 (1H, s); ¹³C NMR (100 MHz, CDCl₃) δ 30.0, 114.0, 114.9 (d, *J* = 20.9 Hz), 116.0 (d, *J* = 22.6 Hz), 120.5, 122.3, 124.5 (d, *J* = 2.9 Hz), 129.0, 129.5 (d, *J* = 8.5 Hz), 130.6, 131.2 (d, *J* = 2.1 Hz), 137.2, 138.8 (d, *J* = 8.2 Hz), 139.7, 161.2, 162.6 (d, *J* = 243.6 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -113.6 (m); ESIHRMS: Found: m/z 254.0978. Calcd for C₁₆H₁₃NOF: (M+H)⁺ 254.0976.

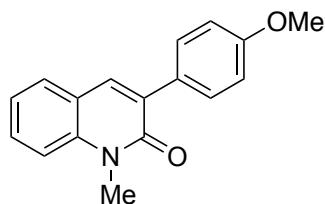
6-Chloro-3-(4-methoxyphenyl)-1-methylquinolin-2(1*H*)-one (3h)



According to the typical procedure, the reaction of **1h** (81.1 mg, 0.2706 mmol), NHC-BH₃ (11.8 mg, 0.4 equiv.) and ACCN (13.1 mg, 0.2 equiv.) under nitrogen at 95 °C for 12 hours after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 6 : 1) afforded 74.7 mg (89%) **3h** as a white solid, mp: 87-89 °C; ¹H

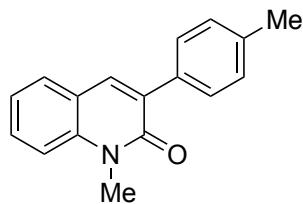
NMR (400 MHz, CDCl₃) δ 2.61 (3H, s), 3.81 (3H, s), 7.07-7.11 (1H, m), 7.25 (1H, d, *J* = 8.4 Hz), 7.36-7.42 (1H, m), 7.43-7.48 (3H, m), 7.70-7.76 (2H, m), 8.01 (1H, d, *J* = 0.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 19.1, 30.2, 112.3, 119.4, 123.8, 128.0, 128.1, 129.0, 130.1, 131.8, 133.2, 136.2, 137.3, 140.0, 161.2; ESIHRMS: Found: m/z 300.0790. Calcd for C₁₇H₁₅NO₂Cl: (M+H)⁺ 300.0786.

3-(4-Methoxyphenyl)-1-methylquinolin-2(1*H*)-one (3i)



According to the typical procedure, the reaction of **1i** (114.7 mg, 0.4323 mmol), NHC-BH₃ (9.8 mg, 0.2 equiv.) and ACCN (21.3 mg, 0.2 equiv.) under nitrogen at 95 °C for 12 hours after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 6 : 1) afforded 103.8 mg (91%) **3i**; ¹H NMR (400 MHz, CDCl₃) δ 3.77 (3H, s), 3.84 (3H, s), 6.93-6.98 (2H, m), 7.22 (1H, ddd, *J* = 0.8, 7.6, 7.6 Hz), 7.33 (1H, d, *J* = 8.4 Hz), 7.53 (1H, ddd, *J* = 1.6, 7.2, 8.4 Hz), 7.57 (1H, dd, *J* = 1.6, 7.6 Hz), 7.66-7.70 (2H, m), 7.74 (1H, s); ¹³C NMR (100 MHz, CDCl₃) δ 29.9, 55.3, 113.5, 113.8, 120.8, 122.0, 128.6, 129.2, 129.9, 130.1, 131.9, 135.7, 139.3, 159.5, 161.6. The spectral data for this compound are in agreement with those reported in the literature.^[20]

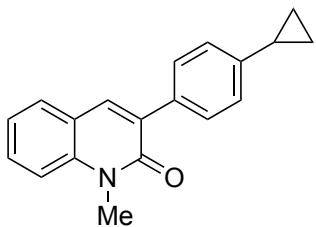
1-Methyl-3-(*p*-tolyl)quinolin-2(1*H*)-one (3j)



According to the typical procedure, the reaction of **1j** (110.4 mg, 0.4428 mmol), NHC-BH₃ (19.4 mg, 0.4 equiv.) and ACCN (21.7 mg, 0.2 equiv.) under nitrogen at 95 °C for 12 hours after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 6 : 1) afforded 107.1 mg (97%) **3j**; ¹H NMR (400 MHz, CDCl₃) δ 2.39

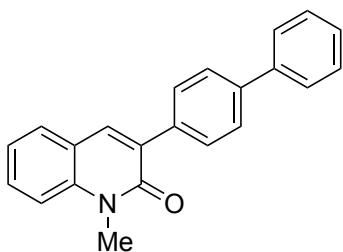
(3H, s), 3.78 (3H, s), 7.20-7.26 (3H, m), 7.35 (1H, d, $J = 8.4$ Hz), 7.54 (1H, ddd, $J = 1.2, 7.2, 8.4$ Hz), 7.57-7.64 (3H, m), 7.77 (1H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 21.2, 29.9, 113.9, 120.7, 122.1, 128.67, 127.74, 128.8, 130.0, 132.3, 133.8, 136.2, 137.8, 139.4, 161.5; The spectral data for this compound are in agreement with those reported in the literature.^[22]

3-(4-Cyclopropylphenyl)-1-methylquinolin-2(1*H*)-one (**3k**)



According to the typical procedure, the reaction of **1k** (122.0 mg, 0.4431 mmol), NHC- BH_3 (19.8 mg, 0.4 equiv.) and ACCN (21.2 mg, 0.2 equiv.) under nitrogen at 95 °C for 12 hours after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 6 : 1) afforded 106.0 mg (87%) **3k** as a white solid, mp: 96-97 °C. ^1H NMR (400 MHz, CDCl_3) δ 0.71-0.75 (2H, m), 0.94-1.01 (2H, m), 1.87-1.97 (1H, m), 3.76 (3H, s), 7.12 (2H, d, $J = 8.4$ Hz), 7.21 (1H, ddd, $J = 0.8, 7.2, 7.2$ Hz), 7.33 (2H, d, $J = 8.8$ Hz), 7.52 (1H, ddd, $J = 1.2, 7.6, 8.4$ Hz), 7.56 (1H, dd, $J = 1.2, 7.6$ Hz), 7.59-7.63 (2H, m), 7.74 (1H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 9.3, 15.2, 29.8, 113.8, 120.7, 122.0, 125.3, 128.6, 128.7, 130.0, 132.2, 133.8, 136.1, 139.4, 144.0, 161.5; ESIHRMS: Found: m/z 276.1386. Calcd for $\text{C}_{19}\text{H}_{18}\text{NO}$: ($\text{M}+\text{H}$)⁺ 276.1383.

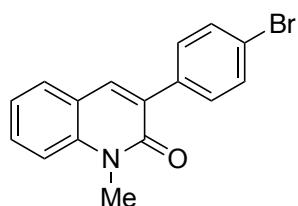
3-([1,1'-Biphenyl]-4-yl)-1-methylquinolin-2(1*H*)-one (**3l**)



According to the typical procedure, the reaction of **1l** (83.3 mg, 0.2675 mmol), NHC- BH_3 (29.0 mg, 1.0 equiv.) and ACCN (13.5 mg, 0.2 equiv.) was stirred under

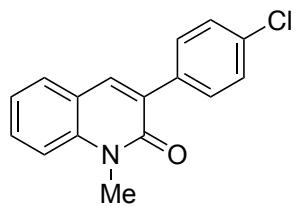
nitrogen at 95 °C for 12 hours, ACCN was added (13.5 mg, 0.2 equiv.) and stirred for another 12 hours. After flash column chromatography on silica gel (petroleum ether : ethyl acetate = 6 : 1) afforded 59.1 mg (71%) **3l**; ¹H NMR (400 MHz, CDCl₃) δ 3.79 (3H, s), 7.23 (1H, ddd, *J* = 1.2, 7.6, 7.6 Hz), 7.32-7.38 (2H, m), 7.41-7.48 (2H, m), 7.55 (1H, ddd, *J* = 1.6, 7.2, 8.8 Hz), 7.59 (1H, dd, *J* = 1.2, 7.6 Hz), 7.62-7.68 (4H, m), 7.78-7.82 (2H, m), 7.83 (1H, s); ¹³C NMR (100 MHz, CDCl₃) δ 29.9, 113.9, 120.6, 122.1, 126.8, 127.0, 127.3, 128.7, 128.8, 129.3, 130.2, 131.9, 135.7, 136.6, 139.5, 140.73, 140.74, 161.4; ESIHRMS: Found: m/z 334.1205. Calcd for C₂₂H₁₇NNaO: (M+Na)⁺ 334.1202.

3-(4-Bromophenyl)-1-methylquinolin-2(1*H*)-one (3m**)**



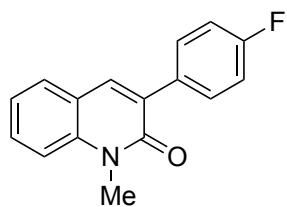
According to the typical procedure, the reaction of **1m** (114.9 mg, 0.3657 mmol), NHC-BH₃ (24.1 mg, 0.6 equiv.) and ACCN (18.0 mg, 0.2 equiv.) was stirred under nitrogen at 95 °C for 12 hours after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 6 : 1) afforded 79.8 mg (70%) **3m**; ¹H NMR (400 MHz, CDCl₃) δ 3.78 (3H, s), 7.24-7.29 (1H, m), 7.38 (1H, d, *J* = 8.4 Hz), 7.53-7.59 (3H, m), 7.60-7.61 (2H, m), 7.62-7.64 (1H, m), 7.79 (1H, s); ¹³C NMR (100 MHz, CDCl₃) δ 30.0, 114.0, 120.6, 122.2, 122.3, 128.9, 130.6, 131.2, 131.3, 135.6, 136.8, 139.7, 161.2; ESIHRMS: Found: m/z 314.0179. Calcd for C₁₆H₁₃⁷⁹BrNO: (M+H)⁺ 314.0181. The spectral data for this compound are in agreement with those reported in the literature.^[20]

3-(4-Chlorophenyl)-1-methylquinolin-2(1*H*)-one (3n**)**



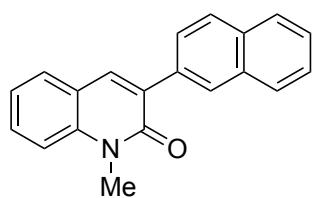
According to the typical procedure, the reaction of **1n** (113.3 mg, 0.4200 mmol), NHC-BH₃ (19.1 mg, 0.4 equiv.) and ACCN (20.8 mg, 0.2 equiv.) was stirred under nitrogen at 95 °C for 12 hours after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 6 : 1) afforded 92.7 mg (82%) **3n**; ¹H NMR (400 MHz, CDCl₃) δ 3.77 (3H, s), 7.22-7.27 (1H, m), 7.34-7.41 (3H, m), 7.54-7.61 (2H, m), 7.63-7.68 (2H, m), 7.77 (1H, s); ¹³C NMR (100 MHz, CDCl₃) δ 29.9, 114.0, 120.5, 122.3, 128.2, 128.9, 130.2, 130.5, 131.1, 133.9, 135.1, 136.8, 139.6, 161.2; The spectral data for this compound are in agreement with those reported in the literature.^[22]

3-(4-Fluorophenyl)-1-methylquinolin-2(1*H*)-one (3o**)**



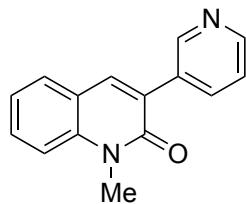
According to the typical procedure, the reaction of **1o** (134.7 mg, 0.5318 mmol), NHC-BH₃ (11.4 mg, 0.2 equiv.) and ACCN (26.3 mg, 0.2 equiv.) was stirred under nitrogen at 95 °C for 12 hours after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 6 : 1) afforded 108.7 mg (81 %) **3o**; ¹H NMR (400 MHz, CDCl₃) δ 3.80 (3H, s), 7.08-7.15 (2H, m), 7.26 (1H, m), 7.38 (1H, d, *J* = 8.8 Hz), 7.55-7.64 (2H, m), 7.67-7.73 (2H, m), 7.78 (1H, s); ¹³C NMR (100 MHz, CDCl₃) δ 29.9, 114.0, 115.0 (d, *J* = 21.3 Hz), 120.6, 122.3, 128.8, 130.4, 130.7 (d, *J* = 8 Hz), 131.4, 132.7 (d, *J* = 3.2 Hz), 136.6, 139.5, 161.4, 162.6 (d, *J* = 242.9 Hz); The spectral data for this compound are in agreement with those reported in the literature.^[24]

1-Methyl-3-(naphthalen-2-yl)quinolin-2(1*H*)-one (3p**)**



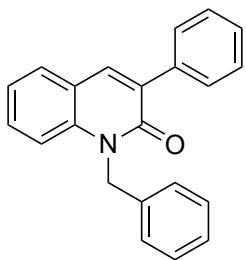
According to the typical procedure, the reaction of **1p** (77.7 mg, 0.2723 mmol), NHC-BH₃ (29.4 mg, 1.0 equiv.) and ACCN (13.3 mg, 0.2 equiv.) was stirred under nitrogen at 95 °C for 12 hours, ACCN was added (13.6 mg, 0.2 equiv) and stirred for another 12 hours. After flash column chromatography on silica gel (petroleum ether : ethyl acetate = 6 : 1) afforded 48.4 mg (62%) **3p** as a white solid, mp: 65-66 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.81 (3H, s), 7.25 (1H, ddd, *J* = 0.8, 8.0, 8.0 Hz), 7.37 (1H, d, *J* = 8.8 Hz), 7.45-7.51 (2H, m), 7.57 (1H, ddd, *J* = 1.6, 7.2, 7.6 Hz), 7.62 (1H, dd, *J* = 1.2, 7.6 Hz), 7.81-7.91 (5H, m), 8.22 (1H, s); ¹³C NMR (100 MHz, CDCl₃) δ 29.9, 114.0, 120.7, 122.2, 125.9, 126.1, 126.8, 127.46, 127.51, 128.0, 128.3, 128.8, 130.3, 132.2, 133.0, 133.2, 134.3, 137.1, 139.5, 161.6; ESIHRMS: Found: m/z 308.1046. Calcd for C₂₀H₁₅NONa: (M+Na)⁺ 308.1046.

1-Methyl-3-(pyridin-3-yl)quinolin-2(1*H*)-one (3q)



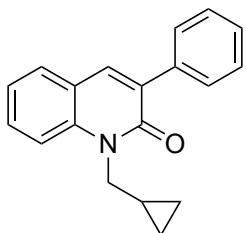
According to the typical procedure, the reaction of **1q** (46.9 mg, 0.1976 mmol), NHC-BH₃ (21.6 mg, 1.0 equiv.) and ACCN (9.5 mg, 0.2 equiv.) was stirred under nitrogen at 95 °C for 12 hours, ACCN was added (10.0 mg, 0.2 equiv) and stirred for another 12 hours. After flash column chromatography on silica gel (petroleum ether : ethyl acetate = 3 : 1) afforded 37.1 mg (79%) **3q** as a white solid, mp: 156-158 °C. ¹H NMR (400 MHz, CDCl₃) δ 3.81 (3H, s), 7.25-7.32 (1H, m), 7.36 (1H, dd, *J* = 5.2, 8.0 Hz), 7.40 (1H, d, *J* = 8.4 Hz), 7.58-7.68 (2H, m), 7.86 (1H, s), 8.16 (1H, dd, *J* = 2.0, 8.0 Hz), 8.61 (1H, dd, *J* = 1.2, 4.8 Hz), 8.87 (1H, d, *J* = 2.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 30.0, 114., 120.4, 122.4, 122.8, 129.1, 130.9, 132.6, 136.6, 137.2, 139.8, 149.0, 149.2, 161.2; ESIHRMS: Found: m/z 259.0847. Calcd for C₁₅H₁₂N₂ONa: (M+Na)⁺ 259.0842.

1-Benzyl-3-phenylquinolin-2(1*H*)-one (3r)



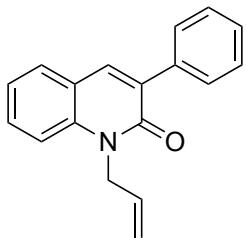
According to the typical procedure, the reaction of **1r** (112.5 mg, 0.3613 mmol), NHC-BH₃ (16.1 mg, 0.4 equiv.) and ACCN (17.7 mg, 0.2 equiv.) was stirred under nitrogen at 95 °C for 12 hours. After flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) afforded 72.7 mg (65%) **3r**; ¹H NMR (400 MHz, CDCl₃) δ 5.62 (2H, s), 7.16-7.21 (1H, m), 7.21-7.25 (1H, m), 7.25-7.32 (5H, m), 7.35-7.47 (4H, m), 7.60 (1H, dd, *J* = 1.6, 7.6 Hz), 7.75-7.80 (2H, m), 7.86 (1H, s); ¹³C NMR (100 MHz, CDCl₃) δ 46.5, 114.8, 121.0, 122.2, 126.7, 127.2, 128.1, 128.1, 128.7, 128.9, 129.0, 130.2, 132.3, 136.5, 136.6, 137.3, 139.1, 161.6; The spectral data for this compound are in agreement with those reported in the literature.^[20]

1-(Cyclopropylmethyl)-3-phenylquinolin-2(1H)-one (3s)



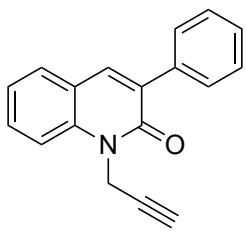
According to the typical procedure, the reaction of **1s** (98.9 mg, 0.3592 mmol), NHC-BH₃ (15.6 mg, 0.4 equiv.) and ACCN (17.9 mg, 0.2 equiv.) was stirred under nitrogen at 95 °C for 12 hours after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) afforded 75.7 mg (77%) **3s**; ¹H NMR (400 MHz, CDCl₃) δ 0.48-0.53 (2H, m), 0.56-0.64 (2H, m), 1.26-1.38 (1H, m), 4.33 (2H, d, *J* = 6.8 Hz), 7.20-7.26 (1H, m), 7.33-7.39 (1H, m), 7.40-7.46 (2H, m), 7.50 (1H, d, *J* = 8.4 Hz), 7.56 (1H, ddd, *J* = 1.6, 6.8, 7.2 Hz), 7.61 (1H, dd, *J* = 1.2, 7.6 Hz), 7.69-7.74 (2H, m), 7.80 (1H, s); ¹³C NMR (100 MHz, CDCl₃) δ 4.1, 9.8, 46.5, 114.3, 121.0, 122.0, 128.0, 128.1, 128.96, 129.02, 130.1, 132.5, 136.9, 139.1, 161.5. The spectral data for this compound are in agreement with those reported in the literature.^[20]

1-Allyl-3-phenylquinolin-2(1*H*)-one (3t**)**



According to the typical procedure, the reaction of **1t** (95.2 mg, 0.3643 mmol), NHC-BH₃ (40.2 mg, 1.0 equiv.) and ACCN (18.0 mg, 0.2 equiv.) was stirred under nitrogen at 95 °C for 12 hours, ACCN was added (18.4 mg, 0.2 equiv.) and stirred for another 12 hours. After flash column chromatography on silica gel (petroleum ether : ethyl acetate = 3 : 1) afforded 30.0 mg (32%) **3t**; ¹H NMR (400 MHz, CDCl₃) δ 5.02-5.04 (2H, m), 5.16-5.20 (1H, m), 5.23-5.25 (1H, m), 5.95-6.07 (1H, m), 7.20-7.27 (1H, m), 7.32-7.40 (2H, m), 7.40-7.47 (2H, m), 7.53 (1H, ddd, *J* = 1.6, 7.2, 7.6 Hz), 7.62 (1H, dd, *J* = 1.2, 7.6 Hz), 7.71-7.77 (2H, m), 7.84 (1H, s); ¹³C NMR (100 MHz, CDCl₃) δ 45.2, 114.5, 117.2, 120.9, 122.2, 128.07, 128.10, 128.9, 129.0, 130.2, 131.8, 132.3, 136.6, 137.1, 138.9, 161.1; ESIHRMS: Found: m/z 284.1047. Calcd for C₁₈H₁₅NONa: (M+Na)⁺ 284.1046.

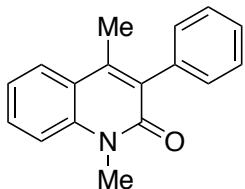
3-Phenyl-1-(prop-2-yn-1-yl)quinolin-2(1*H*)-one (3u**)**



According to the typical procedure, the reaction of **1u** (81.4 mg, 0.3139 mmol), NHC-BH₃ (34.6 mg, 1.0 equiv.) and ACCN (16.0 mg, 0.2 equiv.) was stirred under nitrogen at 95 °C for 12 hours, ACCN was added (16.3 mg, 0.2 equiv.) and stirred for another 12 hours. After flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) afforded 16.3 mg (21%) **3u**; ¹H NMR (400 MHz, CDCl₃) δ 2.26 (1H, t, *J* = 2.4 Hz), 5.18 (2H, d, *J* = 2.4 Hz), 7.24-7.31 (1H, m), 7.35-7.40 (1H, m), 7.40-7.47 (2H, m), 7.53 (1H, d, *J* = 8.4 Hz), 7.58-7.65 (2H, m), 7.69-7.74 (2H, m),

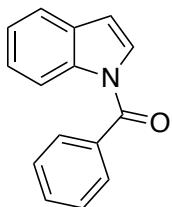
7.82 (1H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 32.1, 72.3, 78.1, 114.4, 120.9, 122.6, 128.1, 128.2, 128.9, 129.0, 130.4, 132.2, 136.3, 137.4, 138.2, 160.6; ESIHRMS: Found: m/z 282.0889. Calcd for $\text{C}_{18}\text{H}_{13}\text{NONa}$: ($\text{M}+\text{Na}$) $^+$ 282.0889.

1,4-Dimethyl-3-phenylquinolin-2(1*H*)-one (3v)



According to the typical procedure, the reaction of **1v** (72.1 mg, 0.2892 mmol), NHC- BH_3 (31.2 mg, 1.0 equiv.) and ACCN (28.0 mg, 0.4 equiv.) was stirred under nitrogen at 120 °C for 12 hours. After flash column chromatography on silica gel (petroleum ether : ethyl acetate = 6 : 1) afforded 8.6 mg (12%) **3v** along with 55.5 mg (77%) **1v**. ^1H NMR (400 MHz, CDCl_3) δ 2.33 (1H, s), 3.78 (3H, s), 7.25-7.32 (3H, m), 7.37 (1H, tt, J = 1.6, 6.8 Hz), 7.40-7.48 (3H, m), 7.60 (1H, ddd, J = 1.6, 7.2, 8.4 Hz), 7.82 (1H, dd, J = 1.2, 8.0 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 16.9, 29.8, 114.2, 121.5, 122.0, 125.6, 127.4, 128.2, 130.0, 130.1, 132.5, 136.8, 139.1, 142.3, 161.7. The spectral data for this compound are in agreement with those reported in the literature.^[20]

(1*H*-indol-1-yl)(phenyl)methanone (3w')

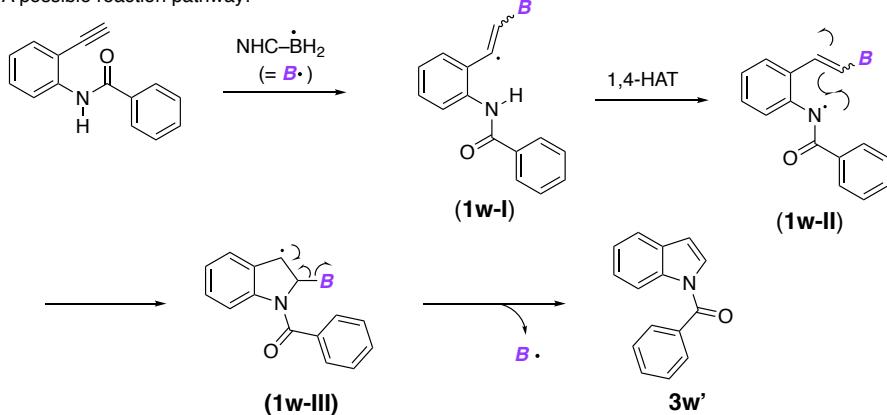


According to the typical procedure, the reaction of **1w** (54.0 mg, 0.244 mmol), NHC- BH_3 (5.9 mg, 0.2 equiv.) and ACCN (11.1 mg, 0.2 equiv.) was stirred under nitrogen at 95 °C for 12 hours. After flash column chromatography on silica gel (petroleum ether : ethyl acetate = 6 : 1) afforded 4.3 mg (8%) **3w'**. ^1H NMR (400 MHz, CDCl_3) δ 6.63 (1H, dd, J = 0.8, 4.0 Hz), 7.30-7.36 (2H, m), 7.38-7.43 (1H, m),

7.50-7.56 (2H, m), 7.59-7.65 (2H, m), 7.73-7.77 (2H, m), 8.43 (1H, dd, $J = 0.8, 8.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 108.5, 116.4, 120.8, 124.9, 127.6, 128.5, 129.1, 130.7, 131.8, 134.5, 136.0, 168.7. The spectral data for this compound are in agreement with those reported in the literature^[23].

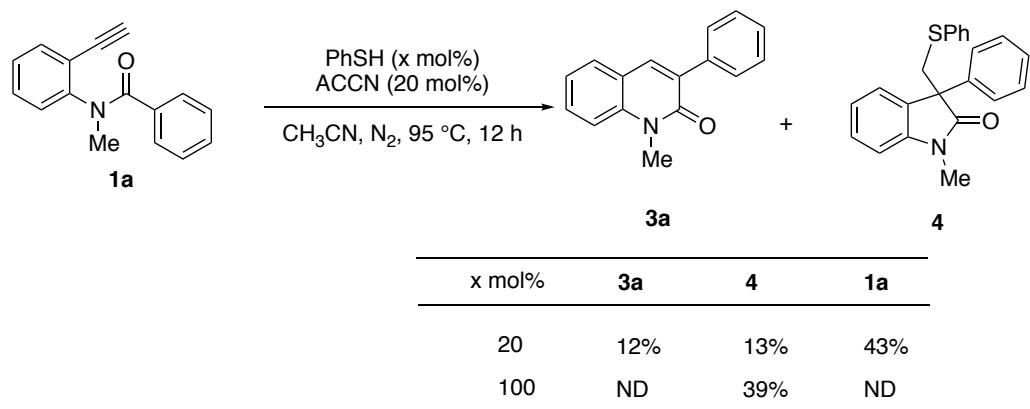
We assumed that the formation of **3w'** may also proceed through an NHC-boryl radical catalyzed pathway, albeit with low efficiency. The NHC-boryl radical first undergoes addition to the alkyne moiety to generate a highly reactive vinyl radical intermediate **1w-I**. After that, a 1,4-hydrogen atom shift^[25] may occur to give amidyl radical **1w-II**. It should be noted that the direct hydrogen atom abstraction by NHC-boryl radical is quite difficult, because the BDE of the amide N-H bond is 98 kcal/mol^[26] and the BDE of B-H bond in NHC-BH₃ is about 80 kcal/mol. This means that the reverse reaction (hydrogen atom transfer from NHC-BH₃ to amidyl radical) is much more favored. However, the HAT from amide N-H to a vinyl radical is feasible, since the resulted alkenyl C-H bond has even higher BDE (>100 kcal/mol). The subsequent 5-endo cyclization and β -fragmentation affords product **3w'** with the regeneration of NHC-boryl radical. Although this would be a nicely organized catalytic process, the catalytic cycle could be interrupted by some other side reactions. For example, the reduction of amidyl radical **1w-II** by NHC-BH₃, and also some unknown polymerization reaction might also exist. As a consequence, a complex mixture was resulted, and **3w'** was obtained in a very low yield.

A possible reaction pathway:



Supplementary Figure 1.

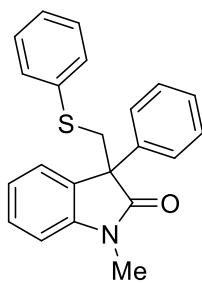
4. Thiyl radical catalyzed and mediated reactions



To an N_2 flushed, oven-dried glass tube with a magnetic stir bar, *N*-(2-ethynylphenyl)-*N*-methylbenzamide (**1a**) (76.5 mg, 0.325 mmol), benzenethiol (6.6 μL , 0.2 equiv), ACCN (16.5 mg, 0.2 equiv) and CH_3CN (3.0 mL) were added. The reaction mixture was stirred at 95 °C for 12 hours. After cooling to room temperature, the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) to afford **4** (14.6 mg, 0.0423 mmol) in 13 % yield, **3a** (9.18 mg, 0.039 mmol) in 12 % yield and **1a** (32.9 mg, 0.140 mmol) in 43 % yield.

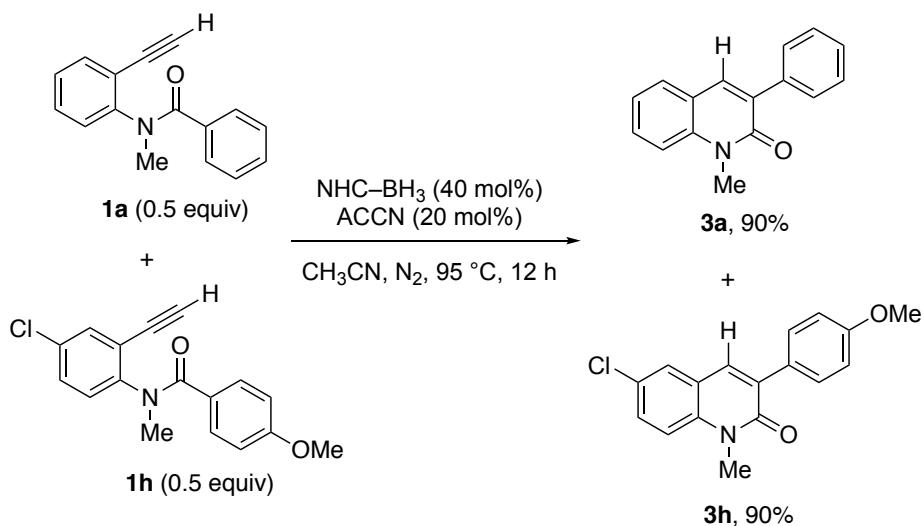
To an N_2 flushed, oven-dried glass tube with a magnetic stir bar, *N*-(2-ethynylphenyl)-*N*-methylbenzamide (**1a**) (71.9 mg, 0.306 mmol), benzenethiol (31 μL , 1.0 equiv), ACCN (15.0 mg, 0.2 equiv) and CH_3CN (3.0 mL) were added. The reaction mixture was stirred at 95 °C for 12 hours. After cooling to room temperature, the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) to afford **4** (41.2 mg, 0.119 mmol) in 39 % yield.

1-Methyl-3-phenyl-3-((phenylthio)methyl)indolin-2-one (4)



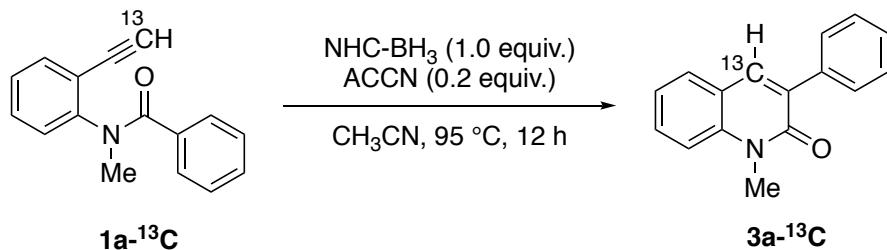
¹H NMR (400 MHz, CDCl₃) δ 3.22 (3H, s), 3.84 (1H, d, *J* = 12.4 Hz), 3.88 (1H, d, *J* = 12.4 Hz), 6.92 (1H, d, *J* = 7.6 Hz), 7.04 (1H, ddd, *J* = 1.2, 7.6, 7.6 Hz), 7.10-7.22 (5H, m), 7.24-7.32 (4H, m), 7.35 (1H, ddd, *J* = 1.2, 7.6, 7.6 Hz), 7.38-7.43 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 26.5, 43.2, 56.8, 108.3, 122.5, 125.6, 126.6, 127.0, 127.7, 128.6, 128.7, 128.8, 130.1, 130.8, 136.1, 138.7, 144.2, 177.0. The spectral data for this compound are in agreement with those reported in the literature. [28]

5. Mechanistic studies



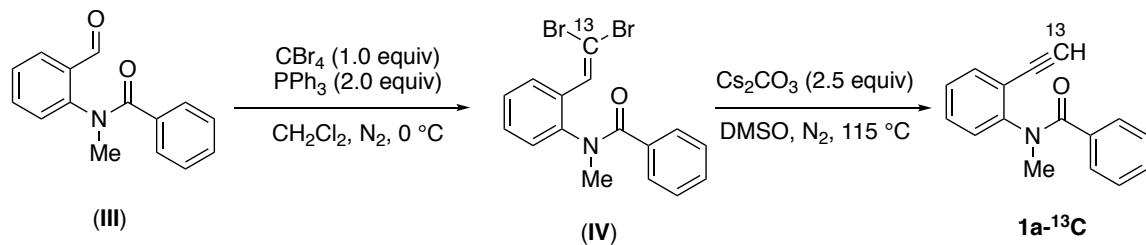
To an N₂ flushed, oven-dried glass tube with a magnetic stir bar, N-(2-ethynylphenyl)-N-methylbenzamide **1a** (50.9 mg, 0.216 mmol), N-(4-chloro-2-ethynylphenyl)-4-methoxy-N-methylbenzamide **1h** (64.7 mg, 0.216 mmol), NHC-BH₃ (18.0 mg, 0.164 mmol), ACCN (19.4 mg, 0.086 mmol) and CH₃CN (2.0 ml) were added. The reaction mixture was stirred at 95 °C for 12 hours. After cooling to room temperature, the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 6 : 1) to afford **3a** (45.8 mg, 0.195 mmol) in 90%

yield and **3h** (58.0 mg, 0.194 mmol) in 90 % yield.



To an N_2 flushed, oven-dried glass tube with a magnetic stir bar, *N*-(2-(2,2-dibromovinyl-2- ^{13}C)phenyl)-*N*-methylbenzamide (**1a- ^{13}C**) (25.0 mg, 0.1058 mmol), NHC-BH₃ (11.8 mg, 1.0 equiv), ACCN (5.3 mg, 0.2 equiv) and CH₃CN (2.0 ml) were added. The reaction mixture was stirred at 95 °C for 12 hours. After cooling to room temperature, the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) to afford **3a- ^{13}C** (20.2 mg, 0.086 mmol) in 81% as white solid; ¹H NMR (400 MHz, CDCl₃) δ 3.80 (3H, s), 7.22-7.28 (1H, dd, *J* = 7.2, 7.2 Hz), 7.34-7.40 (2H, m), 7.40-7.46 (2H, m), 7.53-7.64 (2H, m), 7.79 (1H, d, *J* = 160 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 29.9, 114.0 (d, *J* = 2.0 Hz), 120.7 (d, *J* = 53.0 Hz), 122.1 (d, *J* = 5.0 Hz), 128.0, 128.1, 128.8 (d, *J* = 2.0 Hz), 128.9 (d, *J* = 3.0 Hz), 130.2, 132.5 (d, *J* = 53 Hz), 136.8 (intense, s), 139.6, 161.5; ESIHRMS: Found: m/z 259.0928. Calcd for C₁₅ $^{13}\text{CH}_{13}\text{NONa}$: (M+Na)⁺ 259.0923.

Synthesis of *N*-(2-(ethynyl- ^{13}C)phenyl)-*N*-methylbenzamide (**1a- ^{13}C**):

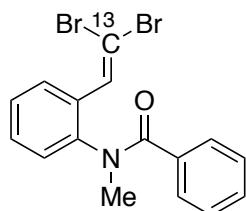


To a stirred solution of $^{13}\text{CBr}_4$ (198.7 mg, 0.597 mmol) in CH₂Cl₂ (1M) at 0 °C was added a solution of Ph₃P (329 mg, 1.25 mmol) in CH₂Cl₂ (2 M) dropwise over 10 min. The resulting brown-colored solution was stirred at 0 °C for 30 min. After that, a solution of *N*-(2-formylphenyl)-*N*-methylbenzamide (**III**)^[27] (47.4 mg,

0.6160 mmol) and Et₃N (0.33 mL, 4.0 equiv.) in CH₂Cl₂ (1M) was added to the reaction system slowly over 10 min. The reaction was allowed to warm to room temperature and stirred for 2 hours, then quenched with water (10 mL) and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated. The crude residue was purified by flash column chromatography (petroleum ether : ethyl acetate = 6 : 1) to give the **IV** (54.0 mg, 0.137 mmol) in 23 % yield.^[28]

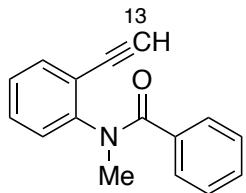
To a solution of **IV** (58.5 mg, 0.148 mmol) in DMSO (1M) was added Cs₂CO₃ (122.8 mg, 2.5 equiv.). The reaction mixture was stirred at 115 °C for 12 hours. After cooling to room temperature, the reaction was quenched with water (10 ml), and then extracted with ethyl acetate. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated. The crude residue was purified by flash column chromatography to give the *N*-(2-(ethynyl-¹³C)phenyl)-*N*-methylbenzamide (16 mg, 0.0608 mmol) in 46 % yield.^[29]

***N*-(2-(2,2-Dibromovinyl-2-¹³C)phenyl)-*N*-methylbenzamide**



White solid; ¹H NMR (400 MHz, CDCl₃) δ 3.41 (3H, s), 7.10-7.20 (3H, m), 7.20-7.32 (6H, m), 7.55 (1H, dd, *J* = 7.2, 0.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 18.4, 38.1, 93.7 (intense s), 110.4, 127.3, 127.7, 128.3 (d, *J* = 9.6 Hz), 129.6, 130.0 (d, *J* = 5.1 Hz), 132.6, 133.0, 133.5, 135.5, 170.8; ESIHRMS: Found: m/z 416.9300. Calcd for C₁₅¹³CH₁₂⁷⁹Br₂NONa: (M+Na)⁺ 416.9290.

***N*-(2-(Ethynyl-¹³C)phenyl)-*N*-methylbenzamide**



White solid; ^1H NMR (400 MHz, CDCl_3) δ 3.58 (1H, d, $J = 252.8$ Hz), 3.46 (3H, s), 7.00 (1H, d, $J = 7.2$ Hz), 7.06-7.25 (5H, m), 7.34 (2H, d, $J = 7.2$ Hz), 7.44 (1H, d, $J = 7.6$ Hz); ^{13}C NMR (400 MHz, CDCl_3) δ 37.4, 80.5, 83.1 (intense s), 121.0 (d, $J = 12.0$ Hz), 127.2, 127.6, 128.3, 128.9, 129.6, 129.7, 133.7 (d, $J = 3.0$ Hz), 135.9, 146.9, 171.1; ESIHRMS: Found: m/z 259.0930. Calcd for $\text{C}_{15}^{13}\text{CH}_{13}\text{NONa}$: ($\text{M}+\text{Na}$) $^+$ 259.0923.

6. Computational studies

All the calculations were employed at (U)B3LYP level of theory^{[31][32]} at 298 K with an empirical dispersion term (Grimme-D3(0))^[33] as implemented in Gaussian 16 software packages.^[34] Geometry optimizations were carried out with the 6-31+G(d) basis set in MeCN solvent (using SMD solvation model^[35]). Vibrational frequency analysis was calculated at the same level of theory to verify whether each optimized structure is an energy minimum or a transition state and to evaluate its zero-point vibrational energy. For each transition state, the intrinsic reaction coordinate (IRC) analysis was conducted to ensure that it connects the right reactant and product.^[36] To obtain more accurate energies, single-point energy calculations were performed on all optimized structures applying the 6-311+G(d,p) basis set at the same (U)B3LYP-D3 level of theory.^[37] Standard state concentrations of 1.0 mol/L were used for all the species. All discussed energies are Gibbs free energies in solution phase (ΔG_{sol} 298 K) unless specified.s

Supplementary Table 1. Thermal correction of Gibbs free energy (TCG, hartree) and total Gibbs free energy (G, hartree) in CH₃CN solvent for all species involved in this study

Compounds	TCG	G	Compounds	TCG	G
1a	0.20123	-747.4971366	IV	0.345942	-1078.408107
NHC-BH₂•	0.116779	-330.8686518	TS-5	0.342607	-1078.389558
TS-1	0.336597	-1078.350024	V	0.345516	-1078.392024
I	0.339987	-1078.384489	TS-6	0.346983	-1078.38891
TS-2	0.343702	-1078.359681	VI	0.35037	-1078.434768
II	0.347852	-1078.382481	TS-7	0.349691	-1078.421494
TS-3	0.346722	-1078.363251	3a	0.208824	-747.5692107
III	0.343994	-1078.381541	TS-8	0.345147	-1078.373935
TS-4	0.345203	-1078.378172	TS-9	0.344749	-1078.380216

Cartesian coordinates for all optimized geometries				H	2.68069800	0.85692100	-0.89084400
1a				H	2.68114600	0.85612700	0.89106500
C 1.27853900 -2.07887500 -1.74797800				C	-2.47771400	0.25343600	-0.00013700
C 0.76278200 -0.78626400 -1.62908300				H	-2.68063200	0.85703500	-0.89080500
C 1.14578200 0.03390900 -0.56472900				H	-3.12883500	-0.62264000	-0.00083700
C 2.07389300 -0.43845800 0.39217400				H	-2.68121200	0.85601200	0.89110400
C 2.59825700 -1.73796800 0.25117500				B	0.00000100	2.16434300	0.00012400
C 2.19993200 -2.55306700 -0.80800300				H	-1.04262200	2.75908000	0.00030300
C 0.96724800 -2.70874600 -2.57693700				H	1.04262400	2.75907900	0.00026500
H 0.05354500 -0.40408700 -2.35781200				TS-1			
H 3.30880400 -2.10245700 0.98735800				C	0.50901900	-3.21489900	1.30161800
H 2.60817200 -3.55588300 -0.89892500				C	0.65541600	-1.91187700	1.78248400
C 2.44998700 0.37547000 1.50534000				C	0.52849500	-0.81517000	0.92807100
C 2.76199100 1.06633100 2.45251600				C	0.21038900	-1.00975700	-0.44448100
H 3.03760600 1.67632000 3.28903400				C	0.10130100	-2.34132900	-0.92103900
N 0.61832000 1.36050200 -0.45509600				C	0.24397100	-3.42404500	-0.06076700
C -0.72719100 1.61961700 -0.39070100				H	0.61739600	-4.05841600	1.97791600
O -1.17760200 2.74210600 -0.65870900				H	0.88822500	-1.73256700	2.82902200
C -1.64331600 0.51874700 0.06141400				H	-0.11752800	-2.50196900	-1.97240800
C -2.84003300 0.31463400 -0.64073500				H	0.14345600	-4.43467100	-0.44843500
C -1.36853700 -0.25084700 1.20191300				C	0.00505200	0.08324300	-1.31805400
C -3.73935600 -0.66997000 -0.22498600				C	-0.36412800	1.01096300	-2.03766500
H -3.05584900 0.92159700 -1.51573300				H	-0.23614100	1.81741000	-2.73294300
C -2.27897600 -1.22115300 1.62817500				N	0.68690300	0.50537800	1.46091400
H -0.45426300 -0.08343900 1.76298200				C	1.62745100	1.39344400	1.01275400
C -3.46082800 -1.43935600 0.91108200				O	1.54963700	2.60037300	1.28737500
H -4.65729200 -0.83429700 -0.78375100				C	2.79335000	0.87197100	0.22120000
H -2.06435600 -1.80592100 2.51910800				C	3.54343300	-0.23448200	0.64652700
H -4.16357200 -2.20144100 1.23867200				C	3.18564400	1.57262500	-0.92884300
C 1.50655200 2.47609500 -0.81422300				C	4.66734400	-0.64076400	-0.07865000
H 1.28271900 3.34299400 -0.18874100				H	3.25788400	-0.77160800	1.54554800
H 2.54086200 2.17110200 -0.65233500				C	4.29809500	1.15517100	-1.66223200
H 1.37207500 2.75082700 -1.86768100				H	2.60827300	2.43501300	-1.24928200
				C	5.04134800	0.04654300	-1.23857000
NHC-BH₂•				H	5.24857400	-1.49380500	0.26251200
C 0.68220000 -1.51073800 0.00002600				H	4.58555900	1.69402100	-2.56166200
C -0.68220100 -1.51073800 0.00007300				H	5.91020600	-0.27627400	-1.80690400
H 1.38716400 -2.32900200 0.00008000				C	-0.35609400	1.02646400	2.35563200
H -1.38716500 -2.32900200 0.00017500				H	-1.01239900	1.71912200	1.82005500
C 0.00000000 0.65631800 0.00002500				H	-0.94550100	0.18946000	2.72920700
N 1.09442500 -0.19378300 0.00001300				H	0.10367900	1.55551300	3.19486100
N -1.09442500 -0.19378300 0.00002600				C	-3.60368800	-1.01197300	0.56529800
C 2.47771400 0.25343500 -0.00011200				C	-3.66272400	0.16098400	1.25800800
H 3.12883500 -0.62264100 -0.00065700							

H	-3.70656700	-2.03482200	0.89550000	H	5.80019200	-0.35440500	1.90131700
H	-3.82748500	0.35510300	2.30715400	C	-0.41952900	-0.52007200	-2.51609500
C	-3.26003000	0.67064600	-0.91160000	H	-1.27834700	-0.94914200	-1.98874600
N	-3.34677300	-0.69365500	-0.75426300	H	-0.72757700	0.40635300	-3.00323700
N	-3.44593200	1.18149900	0.35341900	H	-0.07472300	-1.23140700	-3.26931100
C	-3.23963100	-1.65605000	-1.84104500	C	-4.08971900	0.83298700	-0.32729600
H	-3.20068300	-2.65979800	-1.41501700	C	-4.10540000	-0.31606800	-1.05666600
H	-4.10533500	-1.57523800	-2.50703800	H	-4.49994200	1.81151700	-0.52731300
H	-2.32801200	-1.47005700	-2.41228300	H	-4.52923900	-0.54185800	-2.02359500
C	-3.42494200	2.60103400	0.67548500	C	-2.98027100	-0.73596400	0.84903000
H	-4.22910400	3.12069100	0.14500600	N	-3.39057800	0.55594400	0.83473000
H	-3.56506500	2.71696300	1.75149600	N	-3.41672800	-1.26548900	-0.32023200
H	-2.46523200	3.03816100	0.38495200	C	-3.19614900	1.51586600	1.92092000
B	-2.90171500	1.42774300	-2.18013800	H	-3.13299700	2.51824100	1.49383000
H	-2.84399500	2.62483600	-2.14967500	H	-4.03798200	1.46557200	2.61822700
H	-2.92254300	0.85220900	-3.23116300	H	-2.26966900	1.28930100	2.44590200
				C	-3.20344600	-2.64737000	-0.75402300
I				H	-3.77678400	-3.33133800	-0.12344400
C	0.86796400	3.47314300	-1.08369600	H	-3.53937000	-2.73519500	-1.78836800
C	0.92702100	2.19964400	-1.66626200	H	-2.14321300	-2.89701600	-0.69369700
C	0.64739100	1.05545100	-0.92900700	B	-2.08725400	-1.45529600	1.97765100
C	0.26108600	1.15190600	0.46045500	H	-2.12992800	-2.66421900	1.82174900
C	0.23337500	2.47277100	1.03471700	H	-2.53362600	-1.17878200	3.08581800
C	0.52434800	3.59434800	0.27818500				
H	1.09850300	4.35412300	-1.67603000	TS-2			
H	1.20490000	2.08859800	-2.71176300	C	0.20804300	2.51324000	1.42894700
H	-0.03776500	2.57019900	2.08208900	C	-0.30397800	1.54023200	0.56523500
H	0.48415200	4.57775200	0.74099700	C	0.06464800	0.18033900	0.72634300
C	-0.05068300	0.04883600	1.21717300	C	0.90399000	-0.16918100	1.80024900
C	-0.52371200	-0.95312000	1.90268000	C	1.41751300	0.80528200	2.65778800
H	0.18307400	-1.53371100	2.51433600	C	1.07213800	2.14735600	2.46795100
N	0.67335000	-0.22131400	-1.58074300	H	-0.07014200	3.55483800	1.30349300
C	1.45057100	-1.26565900	-1.15400000	H	1.16025500	-1.21489700	1.94014400
O	1.21294500	-2.43380400	-1.49670300	H	2.08205500	0.51787100	3.46856400
C	2.64709600	-0.95846600	-0.29871500	H	1.46175400	2.91399500	3.13269200
C	3.54317300	0.07242400	-0.61796300	C	-0.51654400	-0.79327500	-0.15615000
C	2.90696800	-1.78329500	0.80557600	C	-0.11958900	-1.77265900	-0.95338300
C	4.67952800	0.28287700	0.16875300	N	-1.16314800	1.89763800	-0.50797200
H	3.35980200	0.70253000	-1.48240100	C	-0.95741500	3.20074300	-1.15333100
C	4.03292700	-1.56128200	1.60083600	H	-1.50116900	3.99219300	-0.62406600
H	2.21568400	-2.58648500	1.04314300	H	0.10909800	3.43657900	-1.15512900
C	4.92146800	-0.52599400	1.28444400	H	-1.31719100	3.14911000	-2.18014800
H	5.37345300	1.07876500	-0.08990500	C	-2.14860800	1.06784200	-1.00825300
H	4.21775900	-2.19424300	2.46520000	O	-2.74506000	1.34741500	-2.05399500

C	-2.54475800	-0.17195100	-0.22321700	H	-0.88988200	-2.61066700	0.75600800
C	-3.19868900	-1.21189100	-0.96597700	C	3.61985000	0.51090200	1.34213900
C	-2.94600900	-0.01755600	1.15143700	C	4.32915300	-0.02650200	0.31307500
C	-3.97226100	-2.16702100	-0.32692600	H	3.80639800	1.37332400	1.96440000
H	-3.03372900	-1.26610500	-2.03719300	H	5.25973800	0.27331700	-0.14453900
C	-3.73527900	-0.97422700	1.77343700	C	2.49499400	-1.30221200	0.61298500
H	-2.59041500	0.83729600	1.71848900	N	2.50494200	-0.29020800	1.51740200
C	-4.23234800	-2.07521600	1.05393500	N	3.62709400	-1.14009800	-0.11665600
H	-4.40344100	-2.98111100	-0.90550700	C	1.47932200	-0.04543100	2.52888400
H	-3.98749400	-0.85539900	2.82491500	H	0.68334300	0.58086600	2.11855700
H	-4.84805500	-2.82221900	1.54797700	H	1.05853700	-0.99683400	2.85606400
H	-0.91100900	-2.34152600	-1.45509300	H	1.94408900	0.46004000	3.37784200
H	1.44132800	-2.25227300	-2.59154200	C	4.05818200	-2.00015500	-1.21787000
H	1.65405100	-3.31851500	-0.92775200	H	3.31443200	-1.99062300	-2.01749300
C	2.51544500	-1.15800200	-0.87375600	H	5.00502000	-1.61462200	-1.59879600
N	2.67329000	0.11047400	-1.32724400	H	4.19789400	-3.02350300	-0.86356900
C	4.20734600	-0.16185700	0.22871300	B	1.37018000	-2.44898500	0.46260700
C	3.70802600	0.74088300	-0.65999400	H	1.66274100	-3.16537600	-0.48542300
H	5.00958500	-0.08605400	0.94709100	H	1.44156200	-3.14282100	1.48045700
H	3.98751500	1.76189400	-0.87201400	N	-1.29273700	1.92184100	0.52673200
N	3.46214600	-1.31914800	0.08190900	C	-1.38121000	3.24234000	1.15854200
C	1.86493000	0.72408400	-2.37981900	H	-0.38637200	3.55646300	1.48537400
H	2.00536400	0.18112600	-3.31808800	H	-1.78564400	3.98502600	0.46114200
H	0.81013100	0.70051400	-2.10236200	H	-2.03996900	3.17176700	2.02225000
H	2.18755000	1.75852600	-2.50380000	C	-2.26353200	0.99065300	0.81211700
C	3.66978700	-2.53598800	0.86618400	O	-3.18009900	1.22632100	1.60230400
H	2.72339000	-2.86581500	1.29733500	C	-2.18716600	-0.38125700	0.06571800
H	4.07724800	-3.32794000	0.23278200	C	-2.95262200	-1.39074200	0.88534900
H	4.37476000	-2.30978900	1.66738200	C	-2.80993100	-0.18687300	-1.30770500
B	1.39893900	-2.20628100	-1.36390700	C	-4.01601900	-2.09726300	0.39781600
				C	-3.88328500	-0.91716700	-1.74477900
II				H	-2.34642900	0.54779200	-1.96039000
C	0.43965100	2.73749000	-1.00852400	C	-4.50353400	-1.89195500	-0.92136900
C	-0.25881000	1.67645700	-0.41372100	H	-4.50910500	-2.82633500	1.03812100
C	0.07743900	0.34068400	-0.72663200	H	-4.26429700	-0.74938800	-2.75045400
C	1.08430700	0.10863100	-1.67289700	H	-5.34900600	-2.46524200	-1.29044100
C	1.78895000	1.16026300	-2.26201600	H	-2.61536800	-1.54191000	1.90656600
C	1.46526700	2.47667400	-1.92246100				
H	0.18904300	3.76577600	-0.77384500	TS-3			
H	1.30690300	-0.91719100	-1.94690200	C	-0.52500800	2.56293000	1.02348800
H	2.57586500	0.95255800	-2.98242900	C	0.17530500	1.51390000	0.40900800
H	1.99874700	3.30904700	-2.37445200	C	-0.07406900	0.17469400	0.79273500
C	-0.68538900	-0.74907100	-0.08690100	C	-1.01514500	-0.05575900	1.80627600
C	-0.15285700	-1.91177300	0.35127400	C	-1.72396700	0.98344900	2.41097800

C	-1.47258500	2.29867100	2.01558900	III			
H	-0.33553100	3.59139100	0.73847800	C	1.10005900	2.19374600	1.60860900
H	-1.18803500	-1.08223500	2.11466700	C	0.26441800	1.67769900	0.60709900
H	-2.45792100	0.76671400	3.18276700	C	-0.13188100	0.32218300	0.64130100
H	-2.00453400	3.12652100	2.47743700	C	0.30575300	-0.46548700	1.71658200
C	0.67363000	-0.96425800	0.19750600	C	1.14308000	0.04157600	2.71157400
C	0.06661900	-2.07675600	-0.28315800	C	1.54453000	1.37860800	2.65087400
H	0.76145300	-2.85922900	-0.60211600	H	1.40241700	3.23538800	1.58111100
C	-3.51576200	0.63991500	-1.34106600	H	-0.00022300	-1.50833300	1.74719500
C	-4.24592300	0.15415800	-0.30080800	H	1.48378300	-0.60214400	3.51835500
H	-3.64563600	1.51777000	-1.95608500	H	2.19659200	1.79472400	3.41461400
H	-5.14167600	0.52306900	0.17553300	C	-0.97042900	-0.31386300	-0.43126300
C	-2.51973600	-1.25571800	-0.63563100	C	-0.41184900	-0.63512400	-1.62533400
N	-2.46792100	-0.24288100	-1.53704400	N	-0.15804600	2.53866600	-0.45106400
N	-3.62209900	-1.01037900	0.11513800	C	0.67753100	3.68465400	-0.86427700
C	-1.43756000	-0.07659400	-2.55925000	H	0.53247900	4.53646700	-0.19148300
H	-0.57731700	0.45564700	-2.14807000	H	1.72821300	3.38914000	-0.86052500
H	-1.11934800	-1.05752800	-2.91489500	H	0.38720900	3.97156400	-1.87601900
H	-1.86006600	0.49368400	-3.38892900	C	-1.35306700	2.34607200	-1.03003200
C	-4.10131000	-1.84408800	1.21656600	O	-1.88101100	2.95002800	-1.94112700
H	-3.31236200	-1.97536500	1.95873300	C	-2.38160300	-0.63253700	-0.06579500
H	-4.95295600	-1.34187100	1.67792600	C	-3.07394100	-1.70848800	-0.65747400
H	-4.41409500	-2.82132400	0.84140200	C	-3.06652100	0.13022000	0.90188600
B	-1.48102200	-2.48140700	-0.51525800	C	-4.40050900	-1.98894000	-0.32048800
H	-1.86842100	-3.24547800	0.35985500	H	-2.56537300	-2.34385200	-1.37734900
H	-1.54313200	-3.09720900	-1.58316900	C	-4.39256700	-0.14935700	1.24222800
N	1.10863200	1.80957800	-0.62428400	H	-2.55808800	0.96074600	1.38406700
C	1.03811500	3.11320200	-1.31393700	C	-5.07041700	-1.20976900	0.63045200
H	0.00066100	3.32616900	-1.58503600	H	-4.90711600	-2.82796900	-0.79235600
H	1.42275200	3.91307400	-0.67280200	H	-4.89647200	0.46393200	1.98603500
H	1.64397900	3.05601600	-2.21759800	H	-6.10096300	-1.43180900	0.89681400
C	2.06752400	0.92919200	-0.99691500	H	-1.10172200	-1.07189100	-2.35355700
O	2.89445100	1.06911300	-1.87356400	H	1.41541300	0.72011200	-2.26913700
C	2.17282300	-0.78241200	0.20685700	H	1.31410600	-1.06275100	-3.14113600
C	3.01599000	-1.62379800	-0.60492000	C	2.16028100	-1.06997100	-1.00306800
C	2.79864200	-0.22159500	1.38399200	N	3.24767000	-0.48257500	-0.44414100
C	4.37242800	-1.73954900	-0.36102900	C	3.14586100	-2.49936900	0.43734500
C	4.16333700	-0.33736900	1.60675800	C	3.86638900	-1.34562500	0.44544800
H	2.18572800	0.33484800	2.08756300	H	3.27483400	-3.42502000	0.97792300
C	4.97238200	-1.08523100	0.73392300	H	4.75197100	-1.06145700	0.99363600
H	4.98406100	-2.34740300	-1.02477900	N	2.10937700	-2.31355500	-0.46108600
H	4.60323400	0.13416800	2.48313100	C	3.72700800	0.86669600	-0.74085800
H	6.03970200	-1.18042700	0.91537200	H	2.95748000	1.59611800	-0.48940300
H	2.58429600	-2.11298200	-1.47301300	H	4.61544600	1.05368700	-0.13558700

H	3.98208100	0.95151700	-1.79943100	C	0.28138400	-0.85653600	1.23234400
C	1.08432100	-3.31560700	-0.74156800	O	0.38258600	-1.93813800	1.77144400
H	0.21124000	-3.15083600	-0.10491600	C	3.05841100	-1.51299800	-0.45126500
H	0.78566300	-3.24884100	-1.78874100	C	3.24130500	0.86168700	-0.08125500
H	1.50285600	-4.30468700	-0.54504600	C	4.41005200	-1.66779000	-0.14071700
B	1.12891400	-0.45513800	-2.08629000	C	4.59620700	0.70789300	0.23385300
				H	2.80315300	1.85460700	-0.05017800
TS-4				C	5.19105200	-0.55626900	0.20244900
C	-0.85165100	2.61483200	1.17229000	H	4.85221400	-2.66159600	-0.15345000
C	-0.28250900	1.38772800	0.81190500	H	5.18469500	1.58226500	0.50303600
C	0.35280500	1.22554600	-0.43560600	H	6.24318600	-0.67743000	0.44862200
C	0.38799500	2.31392800	-1.31172700	H	2.46448100	-2.39247200	-0.68248800
C	-0.17533900	3.54722500	-0.96298700	C	2.44733200	-0.24259000	-0.44263400
C	-0.78996700	3.69265000	0.28282200				
H	-1.34288300	2.73831600	2.13125500	IV			
H	0.87039800	2.18760600	-2.27766900	C	1.21144900	0.87893200	2.32505300
H	-0.13404400	4.38154400	-1.65833800	C	0.42212400	0.14623900	1.44329100
H	-1.23362600	4.64306000	0.56856500	C	-0.34861700	0.76084200	0.44479300
C	0.99264600	-0.08651400	-0.79553700	C	-0.36404300	2.14276800	0.33384100
C	0.39874800	-0.88069600	-1.76628300	C	0.41555000	2.90617800	1.22094800
H	1.02433700	-1.69752800	-2.13432000	C	1.19767600	2.27774400	2.19611500
C	-3.70310100	-0.62179900	0.52683800	H	1.81350100	0.39099600	3.08557100
C	-3.22692300	-1.88774100	0.68002600	H	-0.96625700	2.62518200	-0.43186700
H	-4.43933400	-0.06418600	1.08566900	H	0.41891100	3.99004200	1.14004000
H	-3.46108500	-2.65636700	1.40096700	H	1.80418000	2.87758700	2.87023500
C	-2.16433500	-0.96723800	-1.08351100	C	-1.06508600	-0.31100200	-0.36098200
N	-3.03724600	-0.07299400	-0.55759900	C	-0.47699400	-0.52101400	-1.74893200
N	-2.28675500	-2.08049300	-0.31653800	H	-1.06061400	-1.25177300	-2.31496200
C	-3.30065500	1.26637100	-1.08331500	C	3.76570500	-0.92331000	-0.06971300
H	-3.84182200	1.83150200	-0.32313900	C	3.97280900	0.41964000	-0.12476100
H	-2.36082400	1.76770800	-1.30681100	H	4.29484600	-1.70812500	0.44961700
H	-3.90718600	1.19996800	-1.99098300	H	4.71666200	1.04611400	0.34395400
C	-1.53666200	-3.31602200	-0.52972500	C	2.16377200	-0.03955300	-1.39154900
H	-0.46913000	-3.12836800	-0.40464900	N	2.65424200	-1.18536600	-0.85184400
H	-1.86510000	-4.04999400	0.20732600	N	2.98160600	0.94506800	-0.93730400
H	-1.72839200	-3.69449700	-1.53691400	C	2.17750500	-2.53627800	-1.13975900
B	-1.12464100	-0.78907800	-2.30924900	H	2.21153100	-3.12940500	-0.22399900
H	-1.33556800	-1.70652700	-3.09967200	H	1.15262900	-2.49095200	-1.50408000
H	-1.36253500	0.27253100	-2.86752400	H	2.81574700	-2.99762000	-1.89983100
N	-0.33698000	0.26099900	1.66519800	C	2.90248400	2.36005300	-1.30248700
C	-1.02483100	0.31364700	2.96261700	H	1.87786600	2.71315900	-1.20313400
H	-0.53045400	1.03269100	3.62405500	H	3.54724300	2.92326400	-0.62577000
H	-2.06993300	0.60347100	2.82136900	H	3.24210800	2.49965800	-2.33258100
H	-0.98294900	-0.68026800	3.40903800	B	0.87166500	0.09592500	-2.36403100

H	0.74157200	1.28885900	-2.62742300	H	2.19751900	1.43362000	-1.16530500
H	1.14299300	-0.49477000	-3.40888900	H	3.10208000	1.91289500	0.29189900
N	0.24721600	-1.24594900	1.39133300	C	3.02782700	-3.29262300	0.94733100
C	0.91564900	-2.17979500	2.27803900	H	1.99665900	-3.52678300	0.67634000
H	2.00165800	-2.08971200	2.16770100	H	3.68339100	-4.10072000	0.61903700
H	0.64395200	-1.97841200	3.32061500	H	3.10286000	-3.17849800	2.03133800
H	0.60434700	-3.19071100	2.01124200	B	1.40930700	-0.54343800	1.10054700
C	-0.67728200	-1.59793700	0.43465300	H	1.21681100	-1.40488800	1.95421300
O	-1.07917200	-2.73971400	0.22313400	H	1.53698700	0.53348600	1.66658000
C	-3.22069900	0.49723800	-1.45780200	N	-0.85860900	1.83027900	1.58996800
C	-3.34818600	-0.38940200	0.78167200	C	-0.72310600	2.72130400	2.72728500
C	-4.59427000	0.76614800	-1.42991700	H	0.33295600	2.96187600	2.89317400
C	-4.71983400	-0.12523600	0.81239500	H	-1.27834400	3.64905700	2.55020300
H	-2.87186800	-0.83197000	1.65368000	H	-1.12536000	2.22008100	3.60893500
C	-5.35009300	0.45379000	-0.29587300	C	-1.37791600	0.55658700	1.66297300
H	-5.07075700	1.21945300	-2.29616400	O	-1.85576900	0.03804200	2.67169500
H	-5.29585700	-0.37241400	1.70118900	C	-2.31465100	-2.32848900	-0.19318700
H	-6.41777800	0.65849700	-0.27410200	C	-3.58429800	-0.30616600	-0.56908700
H	-2.64055800	0.74506700	-2.34293300	C	-3.41190400	-3.09421700	-0.60323900
C	-2.58169500	-0.08608000	-0.35541000	C	-4.68060200	-1.06765600	-0.98204300
				H	-3.64779400	0.77986200	-0.55722200
TS-5				C	-4.59710600	-2.46587700	-1.00046200
C	0.01757700	3.35959200	-0.18897800	H	-3.33986700	-4.17934000	-0.61298800
C	-0.44446000	2.15124300	0.29511800	H	-5.59765800	-0.57177300	-1.29156500
C	-0.64505700	1.00670900	-0.55577500	H	-5.44904100	-3.05948200	-1.32330700
C	-0.58349200	1.20737000	-1.96889000	H	-1.39220500	-2.81687100	0.11210800
C	-0.12476500	2.42768600	-2.45440100	C	-2.39149800	-0.93014500	-0.17094900
C	0.20918900	3.48895700	-1.58442200				
H	0.18863400	4.20126600	0.47670100	V			
H	-0.84398900	0.39430600	-2.64120400	C	-1.06829500	2.14362900	-1.59686500
H	-0.02979000	2.57070000	-3.52868000	C	-0.28252200	1.59017800	-0.61163100
H	0.57542500	4.42819300	-1.98968000	C	0.29151700	0.23906600	-0.72579100
C	-1.22653700	-0.09804900	0.28672500	C	0.31102600	-0.32216800	-2.07569300
C	0.18774600	-0.54325200	0.04787200	C	-0.47337100	0.24937800	-3.05583400
H	0.25649500	-1.14513900	-0.86024900	C	-1.21476100	1.43936900	-2.81950400
C	4.62880900	-0.65684500	-0.94409900	H	-1.51587400	3.12547400	-1.46765800
C	4.58707500	-1.94415400	-0.50205000	H	0.86586700	-1.23975100	-2.25432200
H	5.33732400	-0.14281000	-1.57617700	H	-0.52466300	-0.21644000	-4.03798200
H	5.25236800	-2.77771100	-0.66971600	H	-1.83679100	1.85537700	-3.60694700
C	2.78980900	-0.87724700	0.33860100	C	1.34361400	0.13779400	0.40857400
N	3.51795800	-0.02052600	-0.41842100	C	0.11150100	-0.73145000	0.50024400
N	3.44984600	-2.05983100	0.28033600	H	0.34336200	-1.73853300	0.14854100
C	3.16182200	1.37765500	-0.65815200	C	-4.12877300	-1.99078700	-0.31173700
H	3.93301700	1.82778700	-1.28495100	C	-4.55807700	-0.73010200	-0.03334900

H	-4.597999900	-2.80356500	-0.84556800	H	-0.50704200	-4.42386800	0.40640900
H	-5.47922600	-0.22066700	-0.27351000	H	1.14435500	-3.86291000	2.19058000
C	-2.50278700	-0.96066700	0.86518800	C	-1.27001400	0.42609800	-0.23140200
N	-2.86994600	-2.11422300	0.25110900	C	-0.34614400	-0.05815400	-1.30454900
N	-3.54826600	-0.11464000	0.68799800	H	-0.91068000	-0.54293700	-2.10245000
C	-2.04331300	-3.31468100	0.14158800	C	4.21026200	-0.41998900	-0.38835300
H	-2.69813100	-4.18666900	0.08737700	C	4.24653500	0.88503900	-0.00511300
H	-1.42472100	-3.26520800	-0.75891700	H	4.90269000	-1.23229500	-0.22550300
H	-1.40299600	-3.39412700	1.02075200	H	4.98045800	1.44278000	0.55691700
C	-3.61984800	1.26009200	1.18467400	C	2.33436100	0.56897300	-1.15718400
H	-2.80129700	1.84613100	0.76616400	N	3.03402500	-0.59229100	-1.09732200
H	-4.57292100	1.68635700	0.86769800	N	3.08702700	1.47404600	-0.48158900
H	-3.55929100	1.27073900	2.27487700	C	2.60439200	-1.87281800	-1.65373300
B	-1.09310200	-0.65182000	1.59335800	H	3.47819700	-2.39288000	-2.05321700
H	-1.16767900	0.42800800	2.14540700	H	2.13771100	-2.48117300	-0.87537800
H	-0.90172100	-1.52664300	2.43756600	H	1.88825600	-1.69509500	-2.45571400
N	0.20125000	2.19671500	0.54167100	C	2.75911100	2.88874900	-0.30351500
C	-0.21643500	3.50812100	1.00549900	H	1.72622000	2.99282600	0.02753600
H	0.06334200	4.27738700	0.27622400	H	3.42800700	3.30084300	0.45371200
H	-1.30087400	3.53013200	1.14974000	H	2.89527000	3.42827100	-1.24461700
H	0.28112900	3.71242100	1.95458500	B	0.92717200	0.80671100	-1.90426300
C	1.20297800	1.45527500	1.14184000	H	0.66972800	1.99891400	-1.88227600
O	1.85980800	1.82525500	2.11590700	H	1.09449400	0.46171300	-3.07141800
C	3.08327400	-1.66874900	0.71756600	N	0.49817100	0.63002700	1.34426600
C	3.68169500	0.34774600	-0.47215600	C	1.31043700	1.21863100	2.39777500
C	4.37750200	-2.16553600	0.52534500	H	0.98162600	0.86882900	3.38429000
C	4.97417200	-0.14496700	-0.66493900	H	2.35801600	0.94561500	2.24981200
H	3.40866600	1.32588800	-0.86282100	H	1.20629800	2.30272500	2.35178100
C	5.32653400	-1.40620600	-0.16693700	C	-0.59199600	1.28393400	0.79423500
H	4.64355800	-3.14359200	0.91957500	O	-0.93229700	2.42974200	1.10854700
H	5.70517500	0.45158600	-1.20576700	C	-3.42897800	0.22913100	-1.51383700
H	6.33198100	-1.79184700	-0.31752800	C	-3.50558200	0.50178300	0.88740400
H	2.35144300	-2.26126900	1.26079500	C	-4.82488100	0.16499200	-1.54815600
C	2.72027500	-0.40852100	0.22095700	C	-4.89842900	0.44308200	0.85177100
				H	-2.99873300	0.62399000	1.84107900
TS-6				C	-5.56816900	0.27169100	-0.36765200
C	1.05781600	-1.72986400	1.83417900	H	-5.33188100	0.03860400	-2.50207300
C	0.51507200	-0.73320100	1.04176600	H	-5.46381400	0.52441300	1.77730600
C	-0.29921900	-1.03465400	-0.12470500	H	-6.65393200	0.22278800	-0.39551000
C	-0.73116600	-2.40314400	-0.26317000	H	-2.87157300	0.15966700	-2.44326300
C	-0.21225000	-3.38812700	0.56006100	C	-2.74138400	0.39845500	-0.29568600
C	0.72273600	-3.07454000	1.57334800				
H	1.68665000	-1.47567300	2.68269700	VI			
H	-1.40742800	-2.65553100	-1.07616100	C	-2.66334600	1.83871400	1.29361700

C	-1.48636400	1.23749300	0.81611700	H	5.54033800	0.38922800	1.79901900
C	-0.95935800	1.61026500	-0.43584900	H	6.52166100	0.60296200	-0.48761000
C	-1.63229300	2.57893000	-1.18894800	H	2.57231300	0.69747100	-2.16178400
C	-2.81130300	3.17082700	-0.72716200	C	2.61446600	0.49427300	0.00509000
C	-3.32431200	2.79646800	0.51895400				
H	-3.06685200	1.57045500	2.26369300	TS-7			
H	-1.22602100	2.85804400	-2.15909800	C	-3.03582800	-1.36773100	1.17380800
H	-3.32039900	3.91786000	-1.33107500	C	-1.70125700	-1.06566400	0.83675900
H	-4.23598700	3.25150100	0.89819200	C	-1.13317900	-1.63384000	-0.33104700
C	1.16967400	0.49921200	0.16203700	C	-1.91369300	-2.50172500	-1.12176100
C	0.27152600	0.92563700	-0.94176500	C	-3.22956600	-2.79665800	-0.78424500
H	0.79061400	1.59853300	-1.62984200	C	-3.78929700	-2.22084700	0.36731000
C	-2.73684600	-2.59778800	-0.16685900	H	-3.49088800	-0.94820900	2.06296300
C	-1.58604200	-3.25671100	0.13848300	H	-1.46511100	-2.92875500	-2.01587100
H	-3.76385200	-2.79098700	0.10453800	H	-3.81872600	-3.46509800	-1.40672300
H	-1.40714000	-4.14416800	0.72682000	H	-4.81731900	-2.44082300	0.64409300
C	-1.03779900	-1.49279200	-1.15472500	C	0.23292700	-1.31752400	-0.66107700
N	-2.38248700	-1.52297100	-0.96338000	H	0.66865300	-1.87465100	-1.48465100
N	-0.55626700	-2.56619900	-0.47363800	C	1.07798900	-0.71924500	0.28407900
C	-3.35908700	-0.56981300	-1.49085500	N	-0.91477100	-0.21268800	1.61588600
H	-4.23875600	-1.12363800	-1.82786100	C	0.47637800	-0.06232700	1.43907800
H	-3.64675400	0.14138700	-0.71339600	O	1.11181500	0.64131600	2.25188300
H	-2.91990800	-0.03281400	-2.32921200	C	-1.53140600	0.46074200	2.75962400
C	0.84142000	-3.00148500	-0.45098400	H	-2.44511400	0.97031800	2.44437800
H	1.49548500	-2.15569700	-0.24742100	H	-1.77411100	-0.25942500	3.55134800
H	0.95439600	-3.74175400	0.34235400	H	-0.82749900	1.19243100	3.14845900
H	1.10747100	-3.44897800	-1.41267700	C	2.53894600	-0.67263000	0.07133200
B	-0.16669100	-0.40208600	-1.94836100	C	3.46066100	-0.57550500	1.14070700
H	0.84974400	-0.92891800	-2.35535400	C	3.08009600	-0.77637000	-1.23218800
H	-0.81482100	0.06229100	-2.86891900	C	4.83877600	-0.58097000	0.91548000
N	-0.81469500	0.23978800	1.55557400	H	3.09039100	-0.50166600	2.15516500
C	-1.49748700	-0.39277600	2.68230000	C	4.45844600	-0.77550800	-1.45511700
H	-1.50424300	0.25857200	3.56605600	H	2.41845500	-0.83777700	-2.08865400
H	-2.52723400	-0.62339100	2.39949900	C	5.35250300	-0.67592600	-0.38347900
H	-0.97730600	-1.31558000	2.93284200	H	5.51577100	-0.51334600	1.76459800
C	0.53893600	-0.04885100	1.36784400	H	4.83276500	-0.84698200	-2.47416900
O	1.12462800	-0.78574000	2.18687900	H	6.42603000	-0.67410700	-0.55633300
C	3.20248800	0.63581000	-1.28244400	C	-0.82318600	1.50251800	-1.35321600
C	3.50878000	0.40305700	1.10837800	C	-0.92588600	3.07283700	0.26677100
C	4.58493300	0.66736800	-1.45460500	H	-0.54251800	3.79625700	0.97066000
C	4.88956800	0.44873300	0.92937500	C	-2.19974600	2.65598100	0.01533700
H	3.10783700	0.31002900	2.10915000	H	-3.14024600	2.95145000	0.45537300
C	5.44337800	0.57438700	-0.35189600	N	-0.09299600	2.36314600	-0.57191700
H	4.99439600	0.76386500	-2.45766900	N	-2.12682700	1.69484400	-0.96807500

TS-8							
C	-3.28446600	1.03884300	-1.56996800	C	-1.18540600	0.94664800	2.21100000
H	-3.15911300	-0.04316300	-1.54532300	C	-0.37670700	0.89270100	1.06394300
H	-4.17078600	1.31270800	-0.99583200	C	0.27325100	-0.31627000	0.72064200
H	-3.40382300	1.36892600	-2.60658300	C	0.13618600	-1.41545900	1.57985500
C	1.35427600	2.55613000	-0.60015800	C	-0.65573300	-1.35859600	2.72770600
H	1.76352700	2.34832300	0.39148400	C	-1.32610300	-0.17132500	3.03502800
H	1.79820100	1.87326600	-1.32073800	H	-1.70875000	1.86214800	2.46586800
B	-0.30448600	0.45407500	-2.34443500	H	0.66207800	-2.33304100	1.32852800
H	0.81648700	0.53984300	-2.74582000	H	-0.75278400	-2.23083600	3.36910800
H	-1.10302700	-0.19376500	-2.95315800	H	-1.96217300	-0.10903300	3.91444600
				C	1.12151100	-0.38752700	-0.50137200
3a				C	0.54323300	-0.22853700	-1.73747900
C	3.62305200	0.41376500	0.01611300	H	1.26571000	-0.09197900	-2.54971900
C	2.21785200	0.28503800	0.01771300	C	-3.95420600	-0.43997300	0.04676600
C	1.64325300	-1.00702700	-0.10691600	C	-3.51775800	-1.71884300	0.19952400
C	2.48286100	-2.13534700	-0.22799400	H	-4.77962800	0.09168500	0.49581700
C	3.86315200	-1.99974500	-0.22446300	H	-3.88731900	-2.53130300	0.80692400
C	4.42576500	-0.71678800	-0.10243700	C	-2.13797100	-0.69936500	-1.26392600
H	4.09315700	1.38503200	0.10633100	N	-3.09811900	0.16915900	-0.85640000
H	2.02109300	-3.11529000	-0.32376700	N	-2.40475100	-1.85747600	-0.60965900
H	4.50303300	-2.87295200	-0.31584700	C	-3.21620800	1.57777100	-1.22709900
H	5.50614900	-0.59697300	-0.10023200	H	-2.62560400	1.76664500	-2.12167400
C	0.21781200	-1.12368300	-0.11777700	H	-4.26677600	1.80393600	-1.42534900
H	-0.20968200	-2.11681900	-0.23610700	H	-2.85457800	2.20715300	-0.40924400
C	-0.60228800	-0.03921400	-0.00603000	C	-1.64833000	-3.09803100	-0.76339600
N	1.37815000	1.39106400	0.13782600	H	-0.58257200	-2.87434600	-0.80365300
C	-0.01947300	1.30547900	0.14117400	H	-1.85280600	-3.73553900	0.09830600
O	-0.71342900	2.32635300	0.27705100	H	-1.95026400	-3.61141200	-1.68099700
C	1.98058300	2.72152800	0.28659400	B	-0.94363700	-0.48022100	-2.32354600
H	2.60309200	2.75466600	1.18606200	H	-0.86347700	-1.51965200	-2.98068500
H	2.59287200	2.95727000	-0.58920200	H	-1.24783900	0.41347000	-3.09883800
H	1.18011400	3.45186000	0.37445200	N	-0.16025200	2.08950100	0.31644800
C	-2.07906300	-0.19425400	-0.00660100	C	-0.23546400	3.38942500	1.01553100
C	-2.67531100	-1.23004300	0.73651200	H	-1.27550300	3.71438500	1.12931400
C	-2.91042800	0.64578400	-0.77116900	H	0.22940700	3.30166400	2.00046900
C	-4.05887800	-1.42792200	0.71013700	H	0.30531500	4.12844100	0.42314800
H	-2.05179000	-1.87568600	1.34998800	C	0.07224400	2.08046000	-1.01887000
C	-4.29232500	0.44465600	-0.80087900	O	0.31584500	3.03823600	-1.73042300
H	-2.46969000	1.45146400	-1.34835600	C	2.58846700	-0.43737300	-0.29986600
C	-4.87363300	-0.59156200	-0.05996900	C	3.45531500	-0.94196300	-1.29555000
H	-4.49869700	-2.23072600	1.29711800	C	3.17498200	0.02220300	0.90021400
H	-4.91668600	1.09859800	-1.40522300	C	4.83840700	-0.96184600	-1.10976700
H	-5.95016900	-0.74271600	-0.08045700	C	4.55926500	-0.00016800	1.08715700

H	2.53945800	0.41429900	1.68933700
C	5.40198400	-0.48968700	0.08287000
H	5.47842000	-1.36153900	-1.89334900
H	4.97997400	0.37005600	2.01952600
H	6.47911000	-0.51153700	0.22933100
H	3.03812400	-1.34221300	-2.21569800
TS-9			
C	2.45420500	-3.10905400	0.05872700
C	1.91875500	-1.89606800	-0.36499600
C	1.25027300	-1.01023400	0.50398800
C	1.10705900	-1.37240500	1.84097600
C	1.64015000	-2.59233800	2.29252200
C	2.30932700	-3.44752800	1.41255700
H	2.95904100	-3.77395300	-0.63542900
H	0.56655600	-0.74096900	2.53454100
H	1.52160600	-2.87116900	3.33635700
H	2.71630200	-4.38895000	1.77312300
C	0.82427300	0.18898000	-0.30515100
C	-0.47635200	0.91804400	-0.17208700
H	-0.76080100	1.36160600	-1.12862300
C	-4.34434600	-1.44599900	-0.21359800
C	-4.78345200	-0.25975800	-0.71717900
H	-4.75124700	-2.44372100	-0.28116400
H	-5.65097100	-0.01461300	-1.31141100
C	-2.87711800	0.14494700	0.41654300
N	-3.17464700	-1.17720900	0.47742000
N	-3.86982600	0.70267100	-0.32154500
C	-2.36333000	-2.18629800	1.15753400
H	-2.84240300	-3.15765300	1.02554600
H	-1.36086500	-2.21007100	0.72658200
H	-2.29246100	-1.95437000	2.22239700
C	-3.96677800	2.12427800	-0.65286000
H	-3.03540900	2.46328700	-1.11043400
H	-4.78792400	2.25620100	-1.35915300
H	-4.16270000	2.70838200	0.24970200
B	-1.57348200	0.89230100	1.01176500
H	-1.90226700	2.03802000	1.30537700
H	-1.20606300	0.30577100	2.00881600
N	1.91869300	-1.38534300	-1.67075400
C	2.45362400	-2.08977400	-2.82207900
H	3.51644000	-2.30463000	-2.66949600
H	1.91670500	-3.03269000	-2.97851200
H	2.33392000	-1.45357300	-3.70018100

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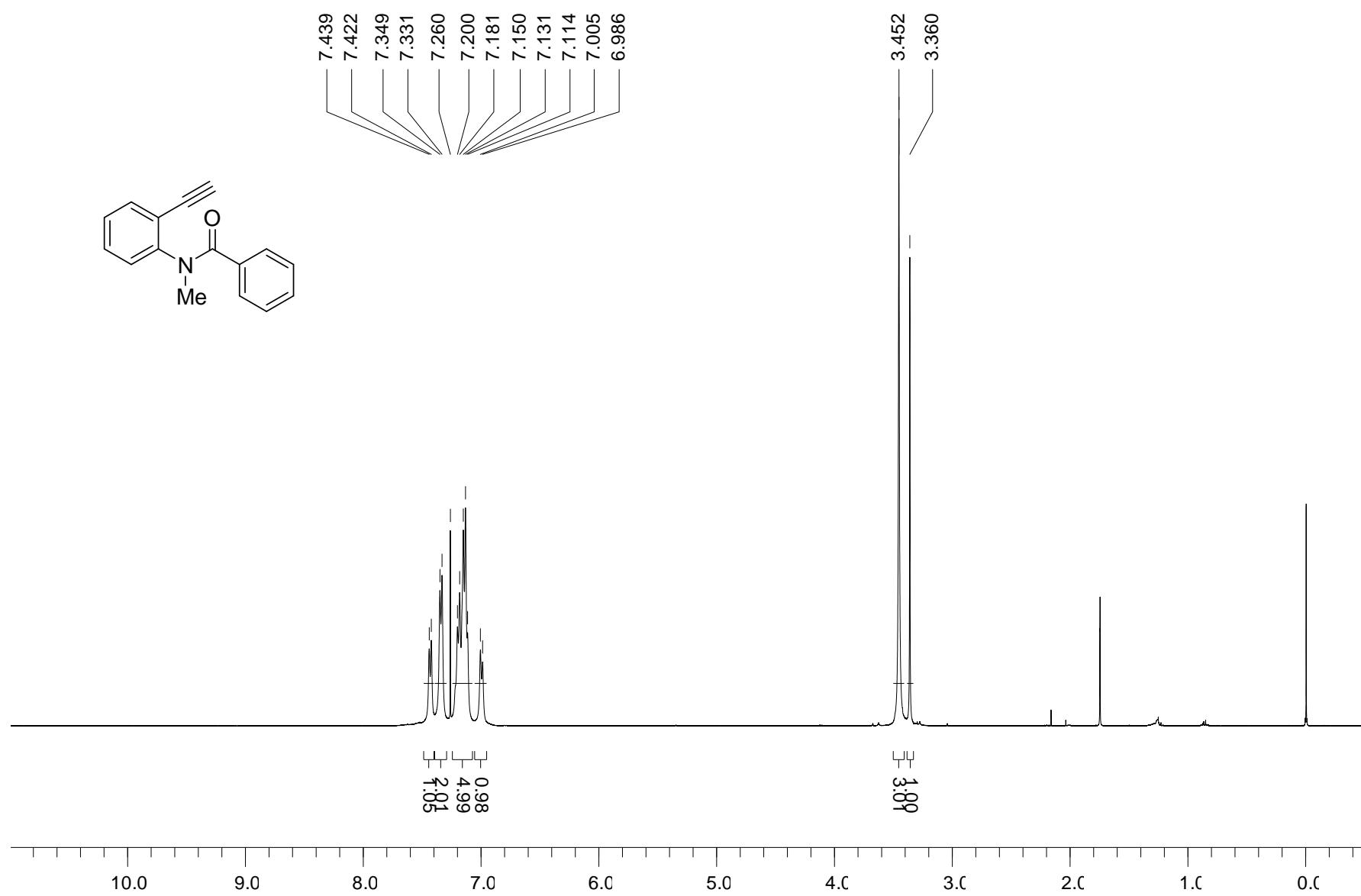
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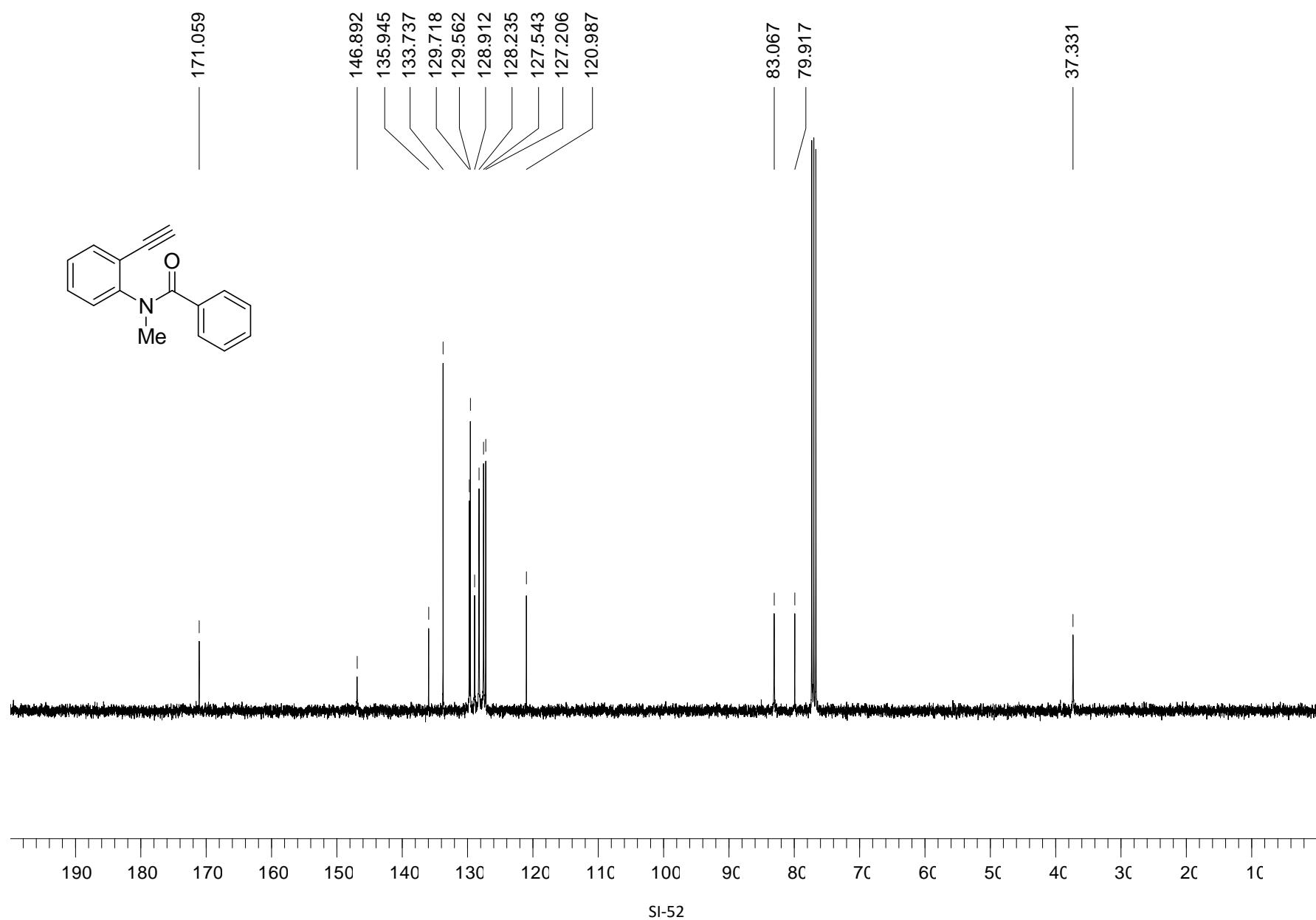
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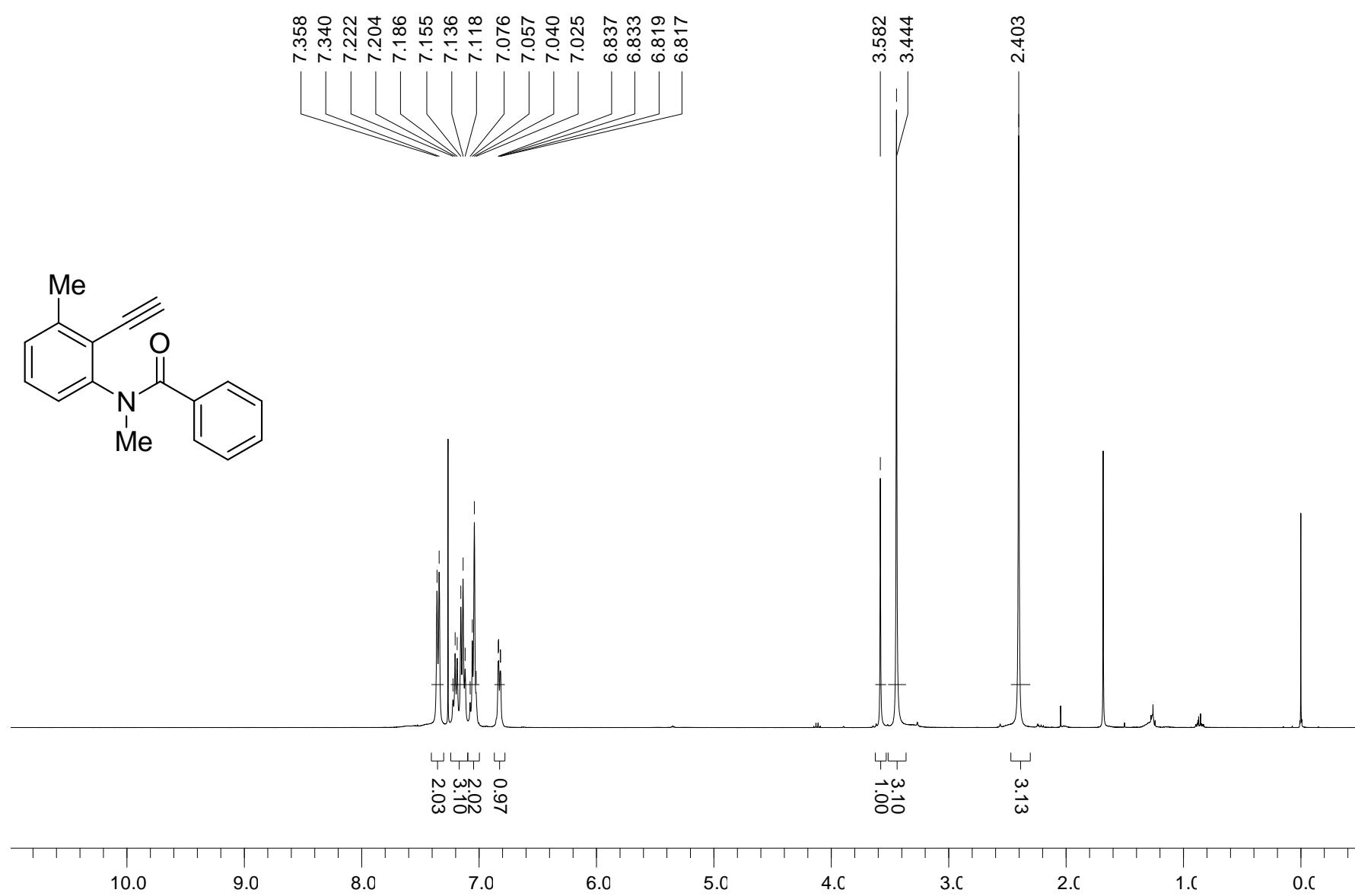
¹H NMR (400 MHz, CDCl₃) spectrum of **1a**



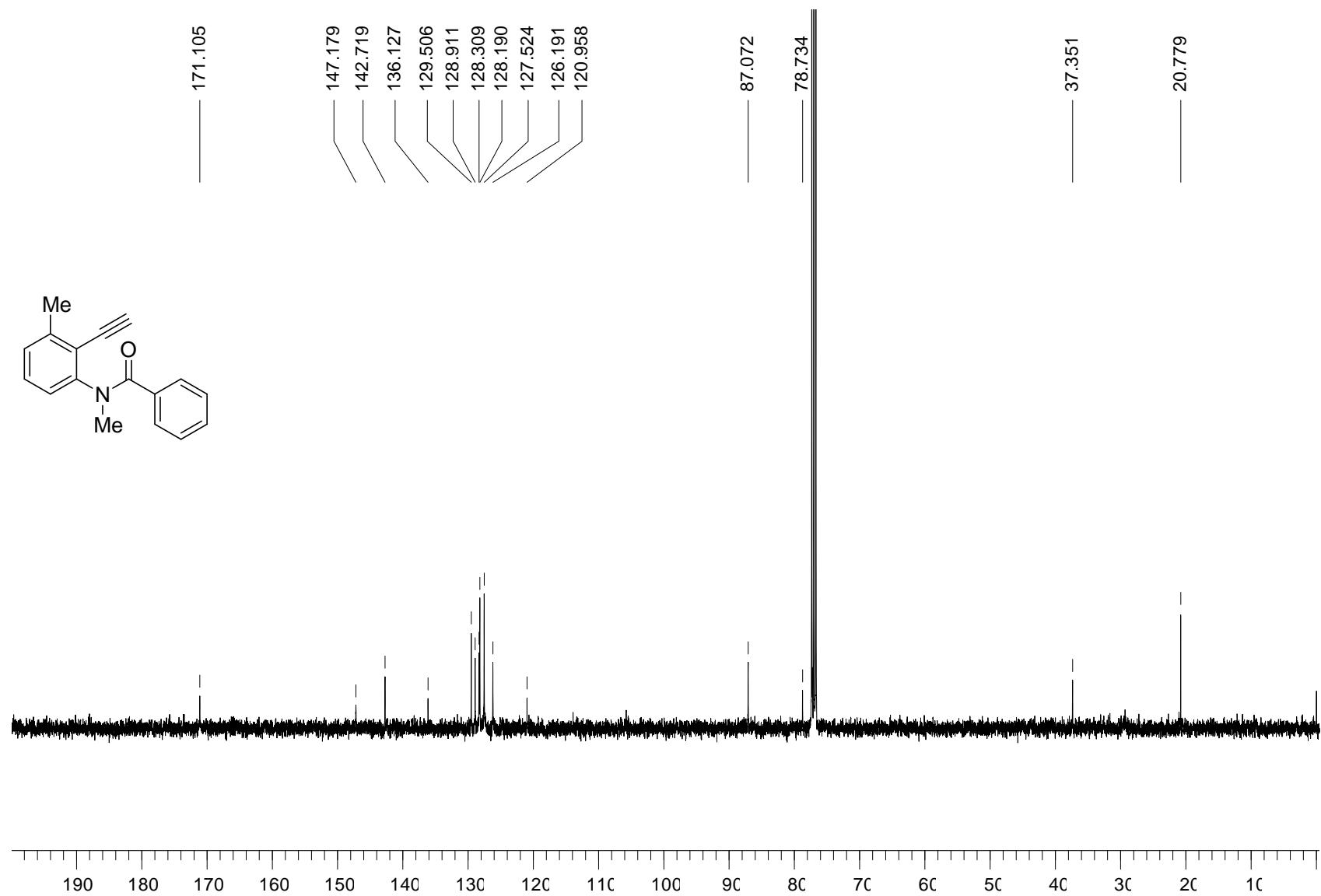
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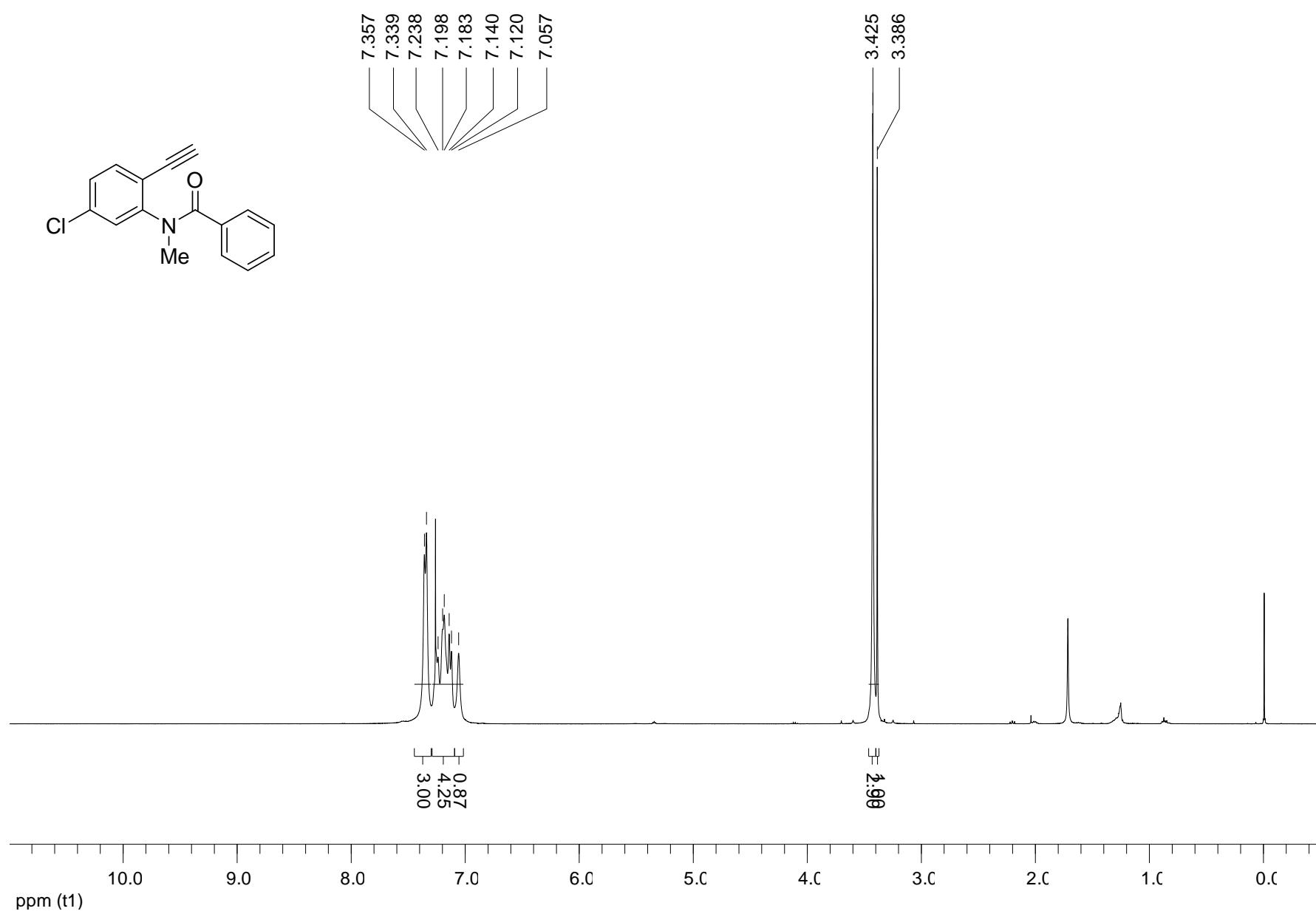
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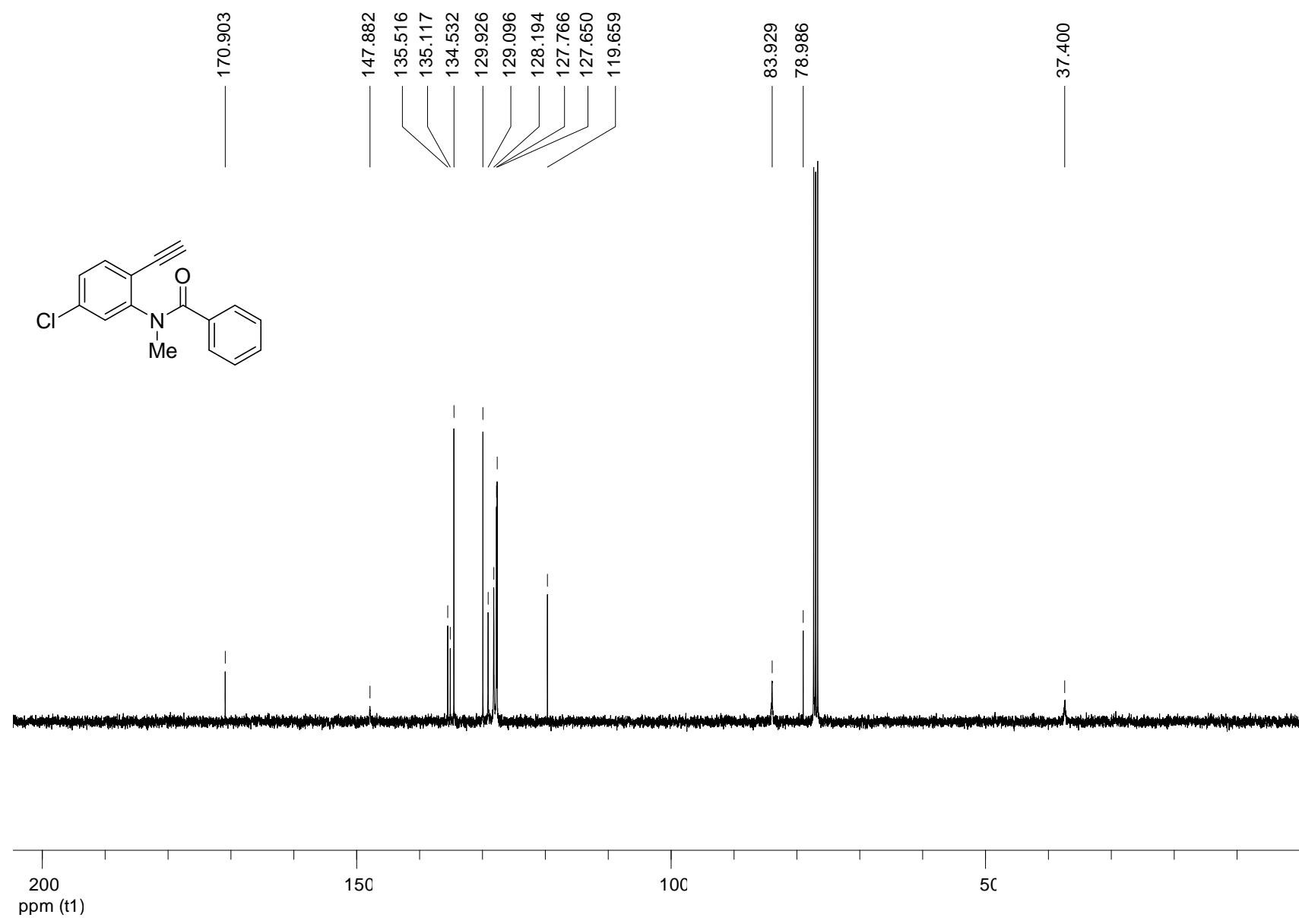
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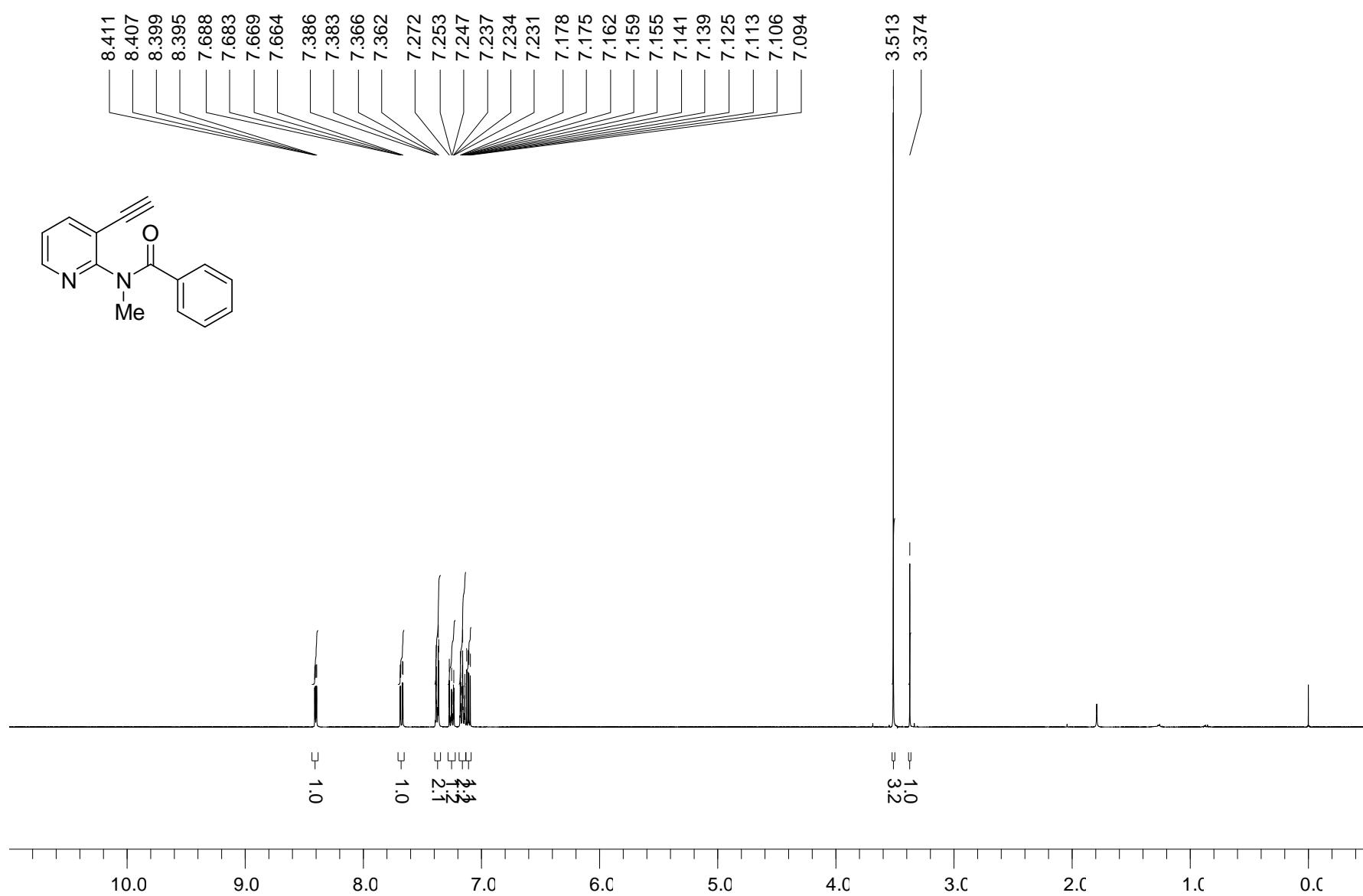
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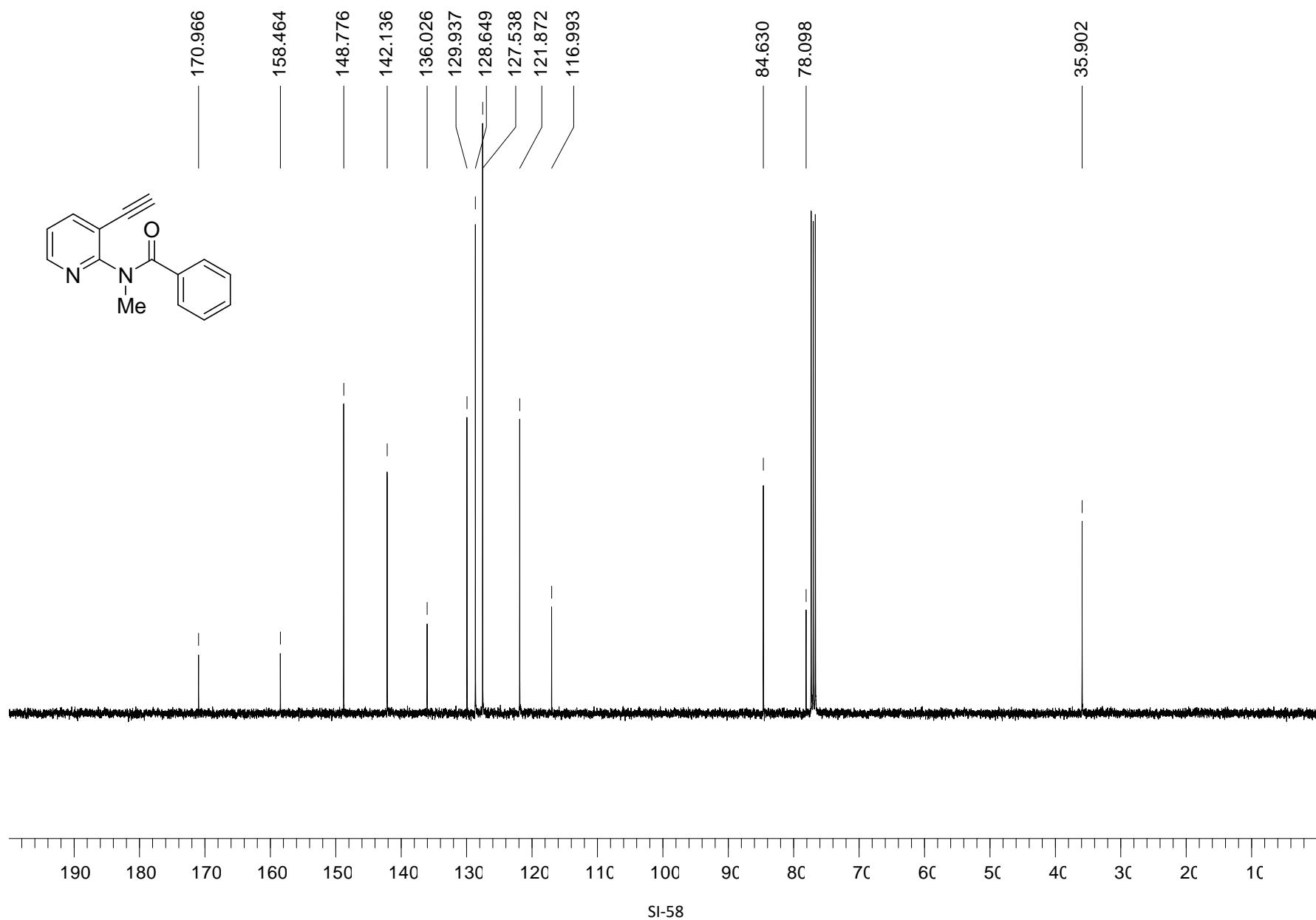
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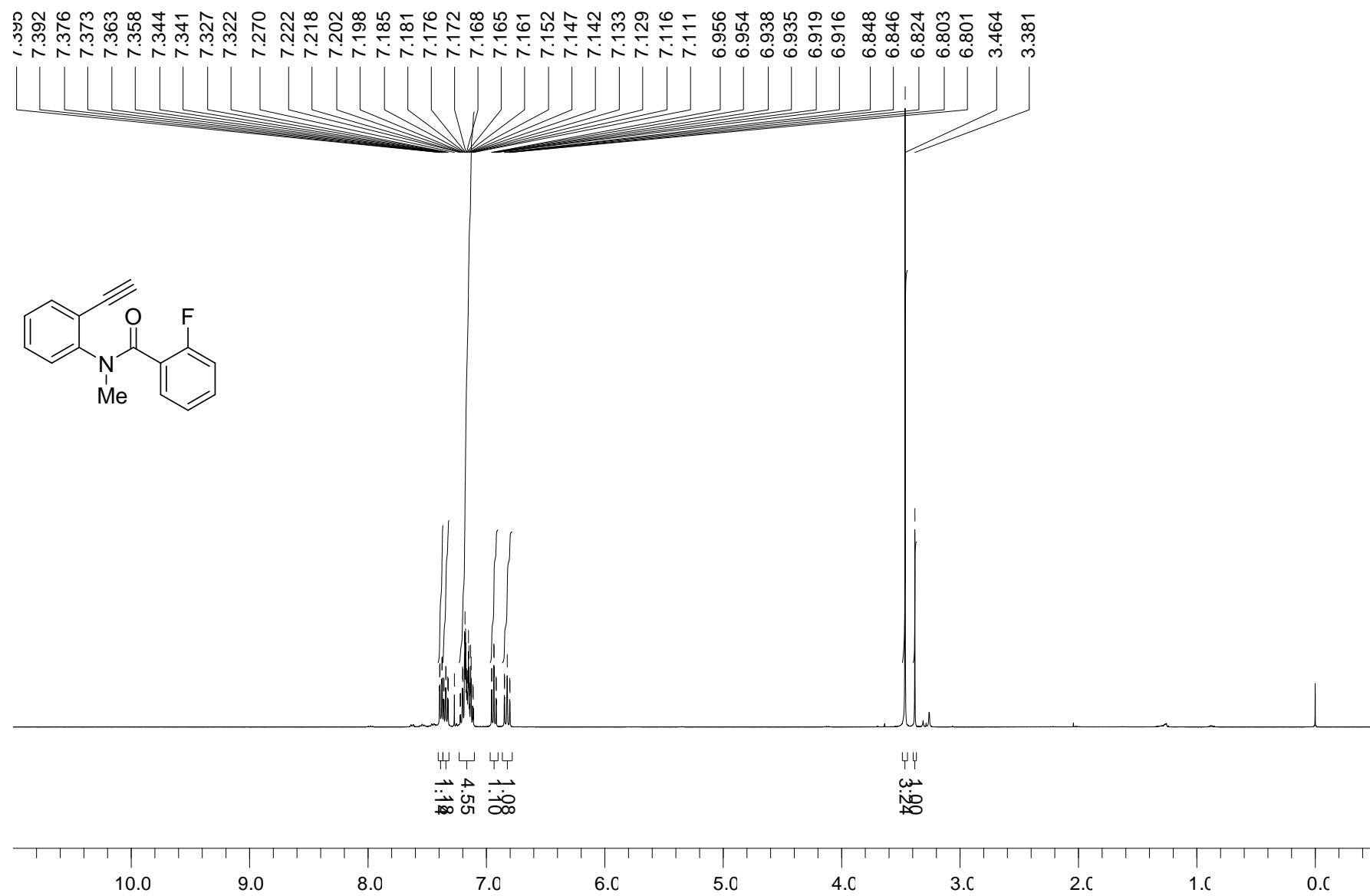
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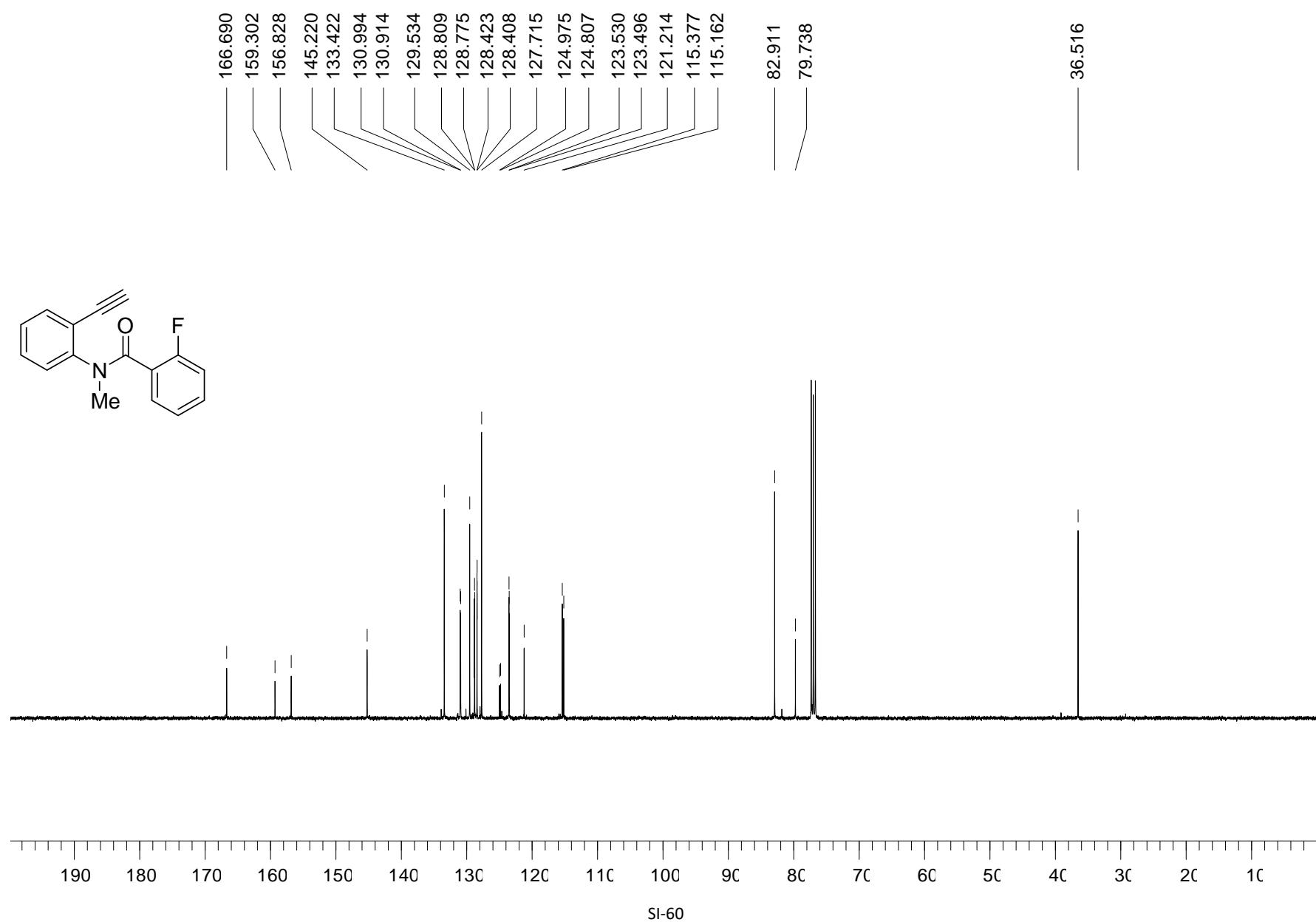
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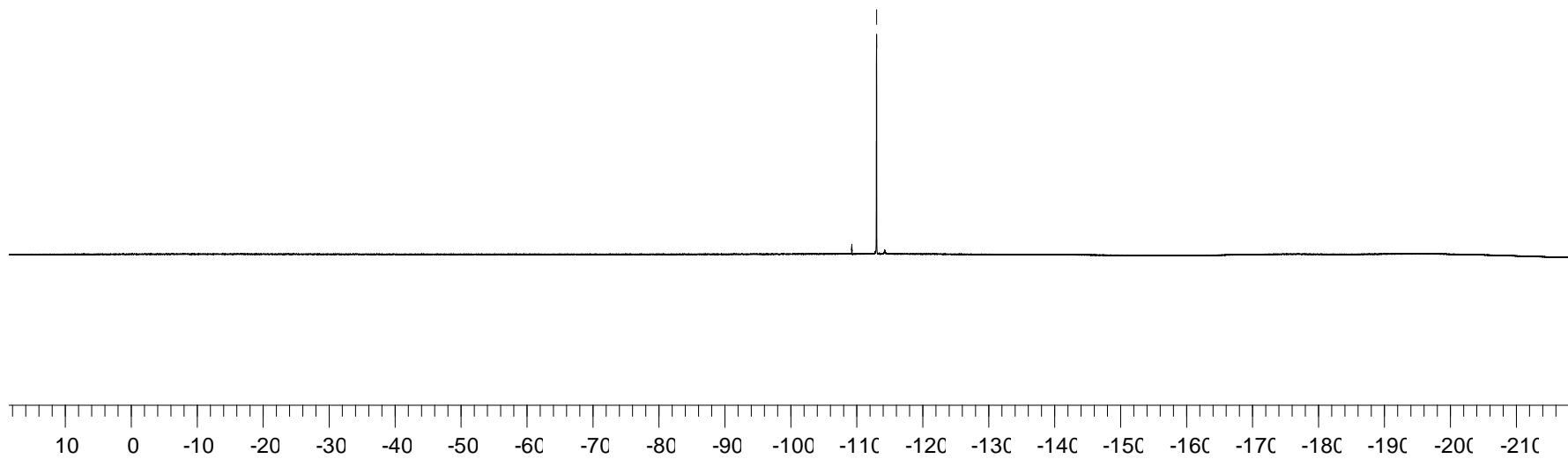
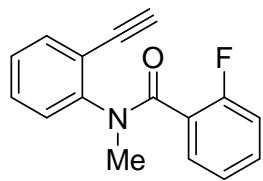
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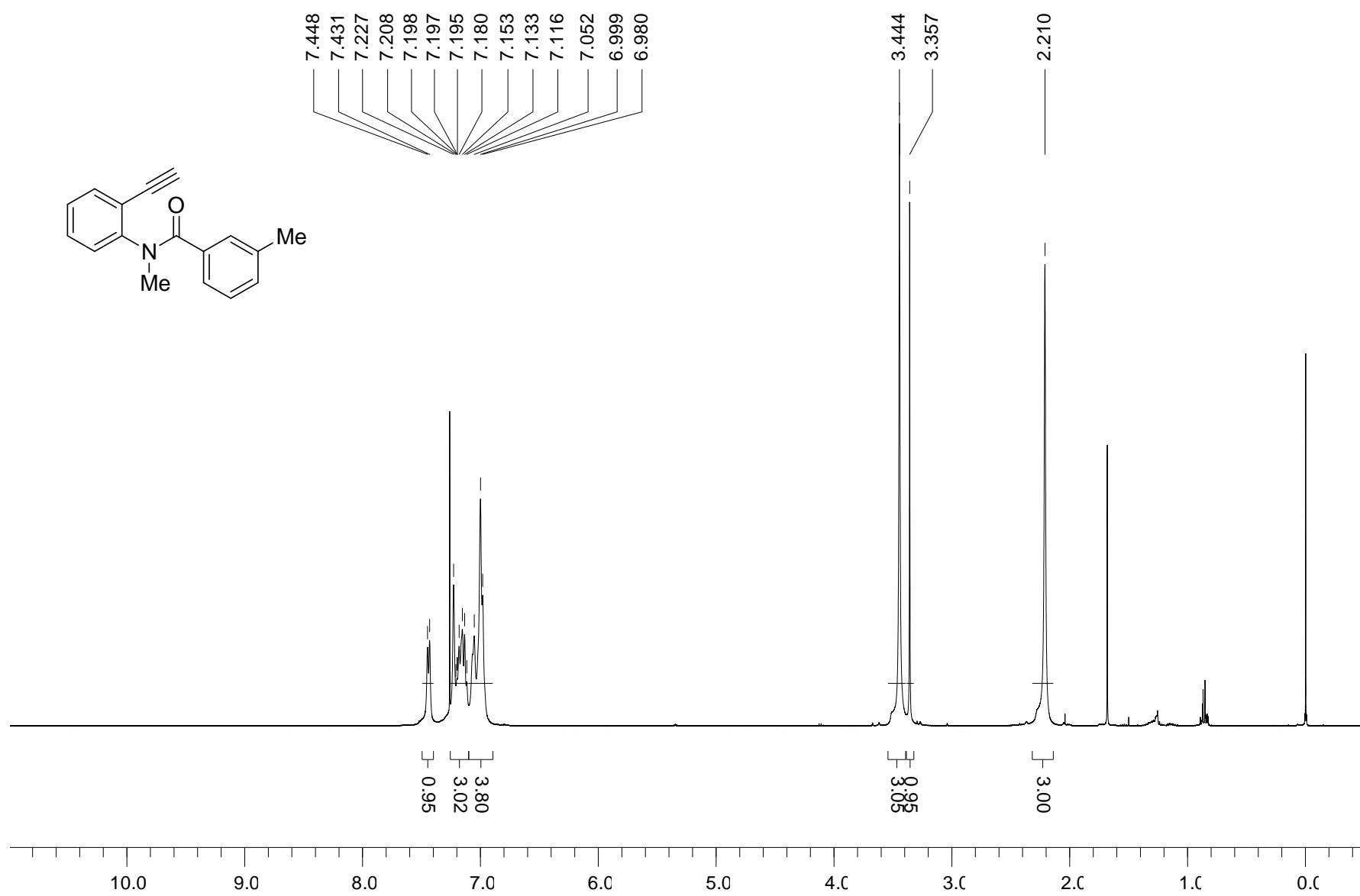
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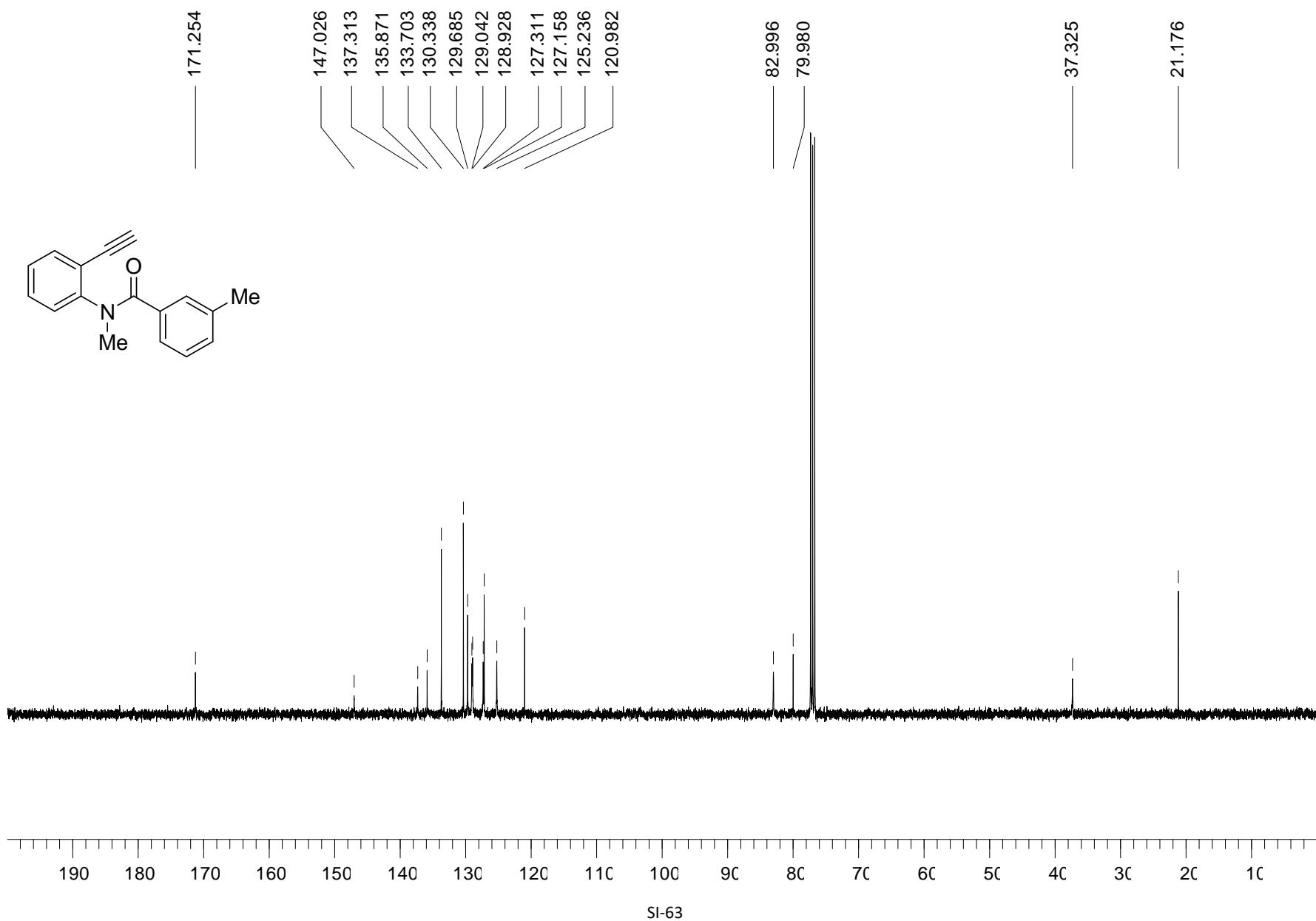
¹⁹F NMR (376 MHz, CDCl₃) spectrum of **1e**



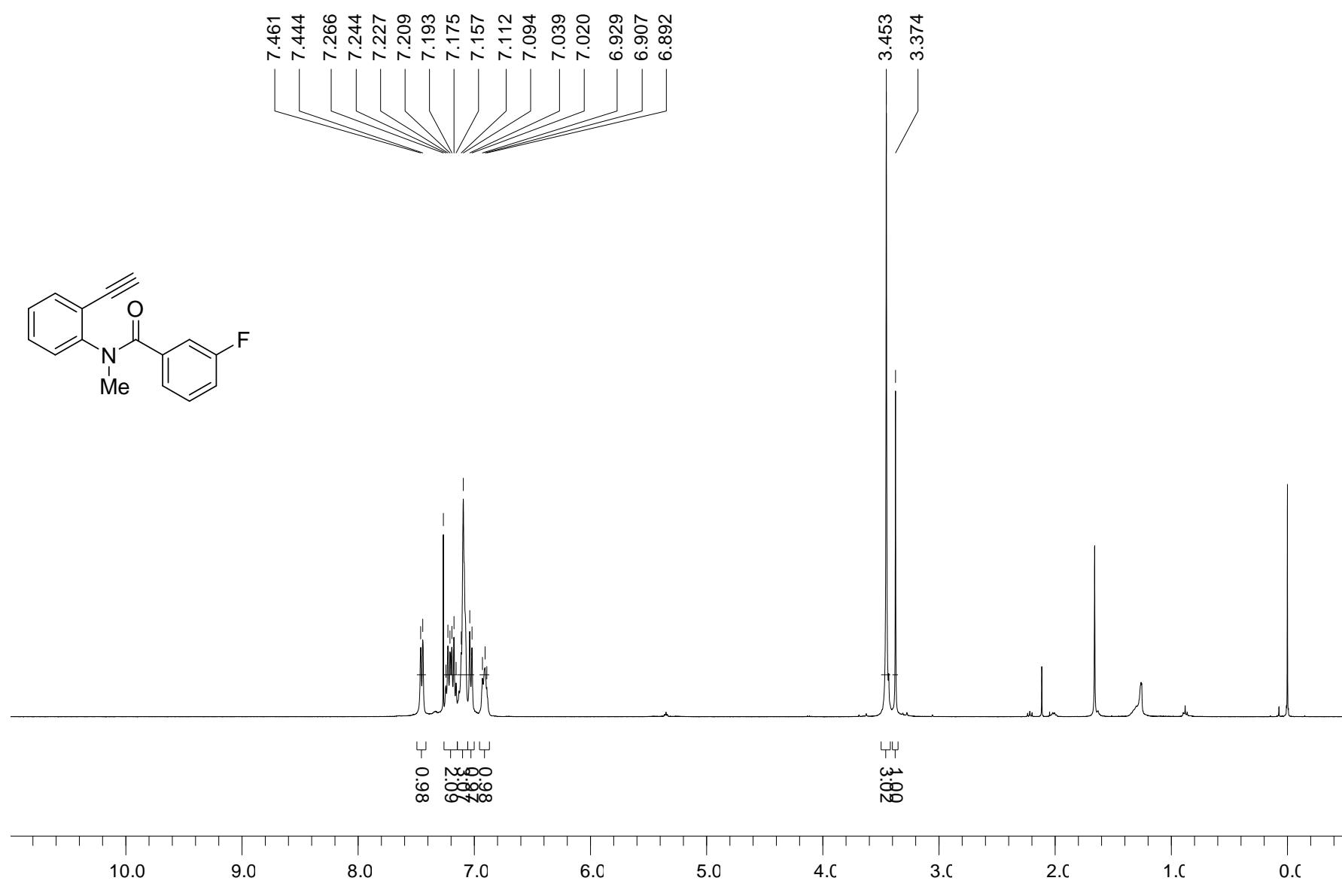
^1H NMR (400 MHz, CDCl_3) spectrum of **1f**



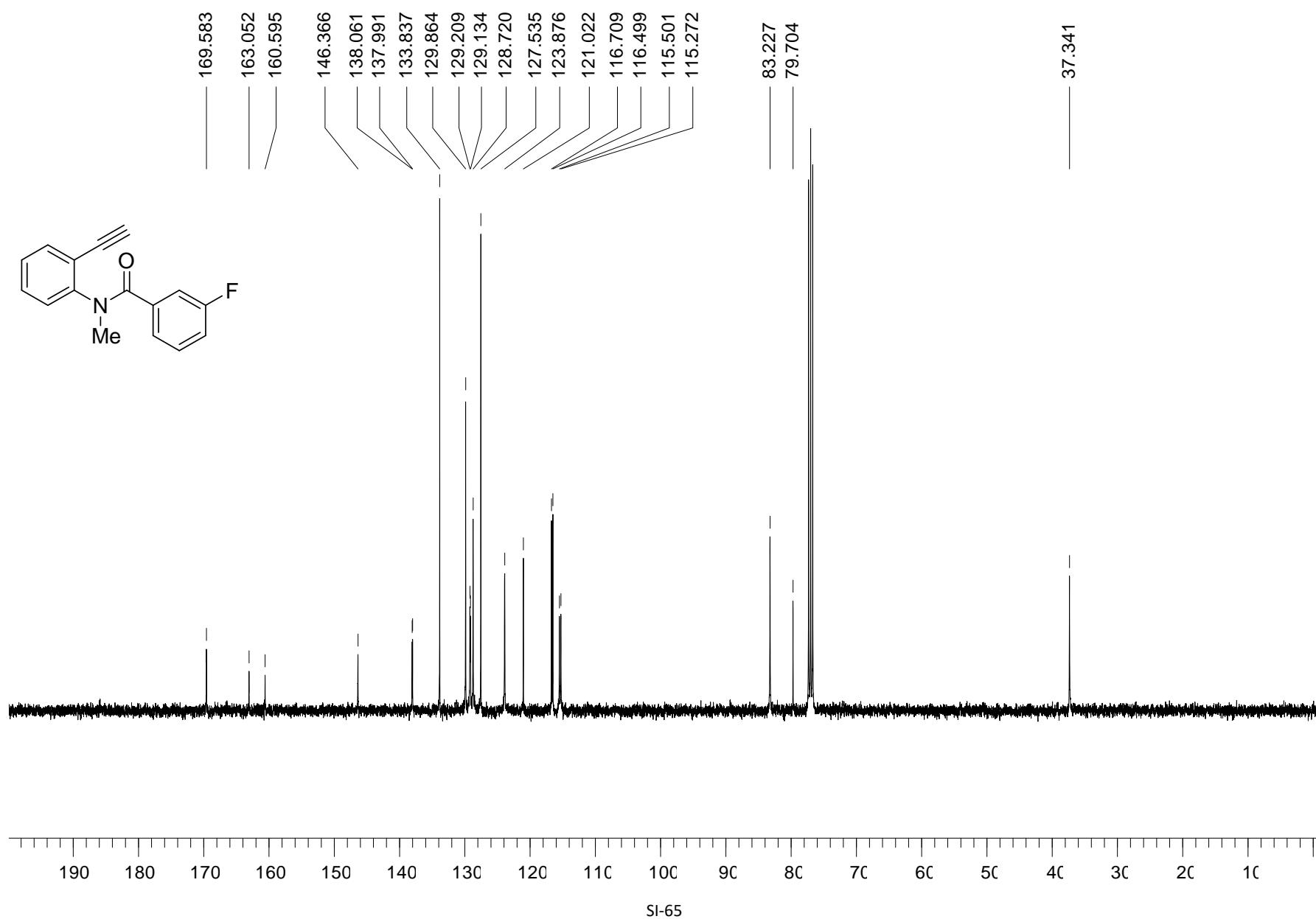
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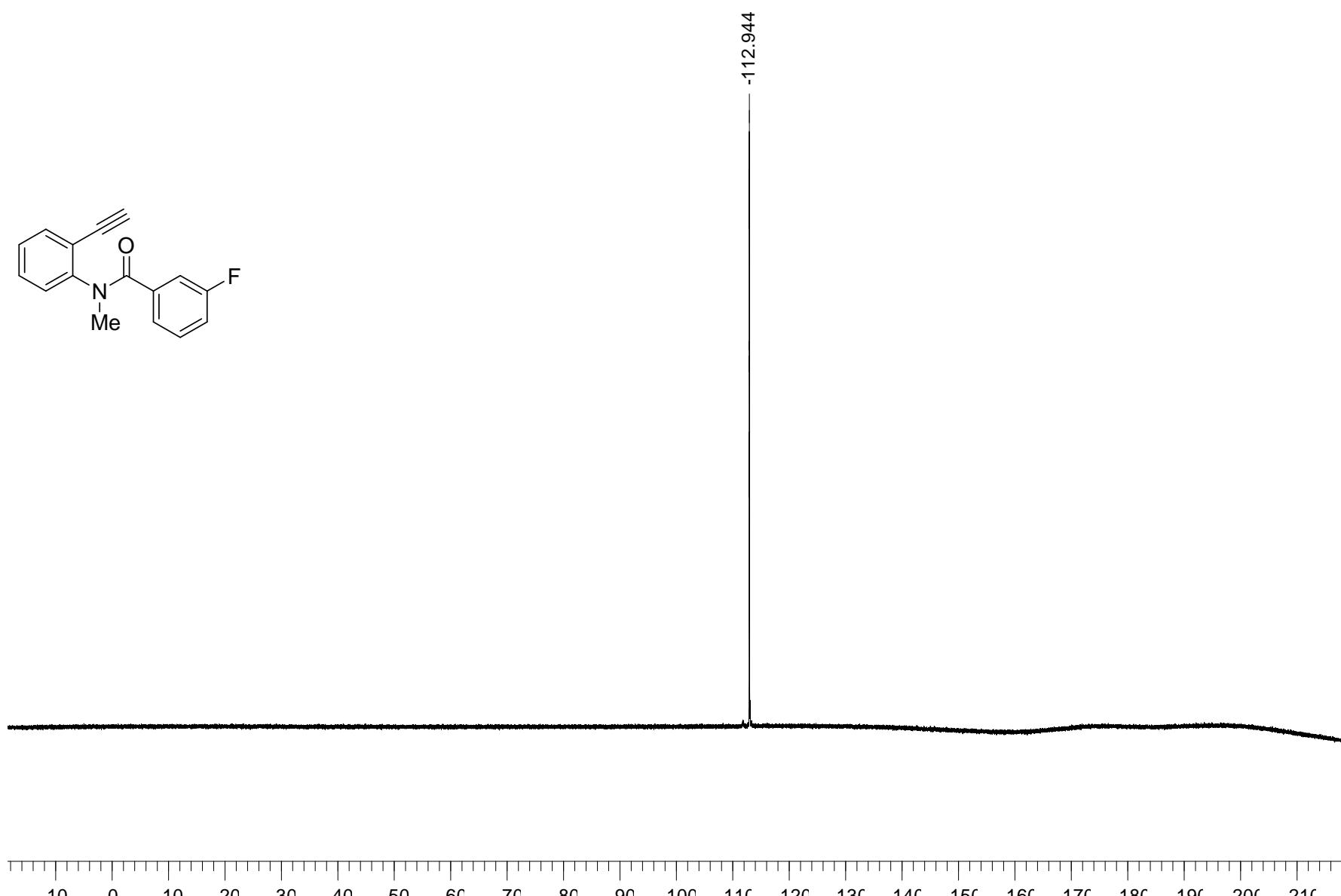
¹H NMR (400 MHz, CDCl₃) spectrum of **1g**



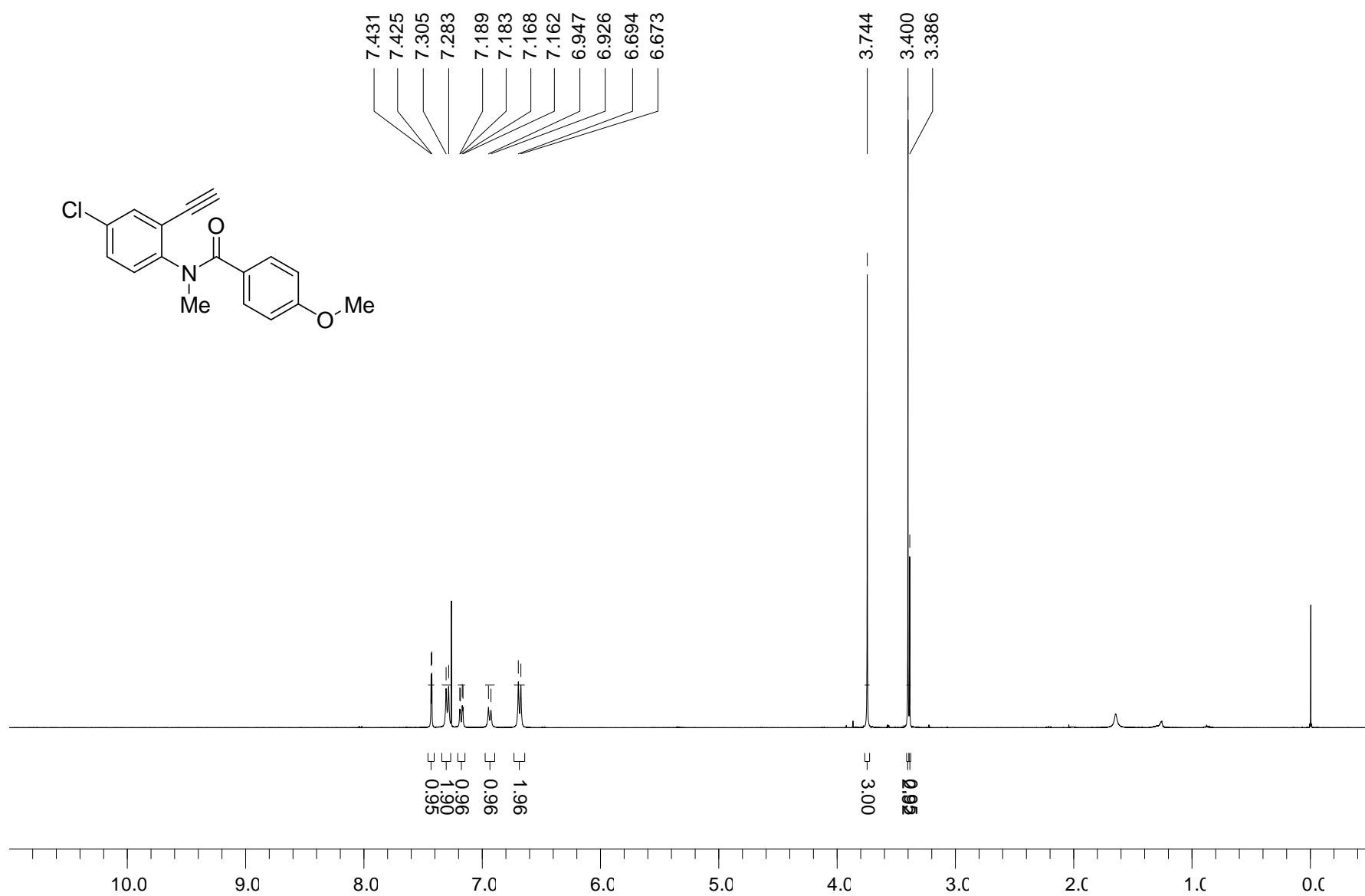
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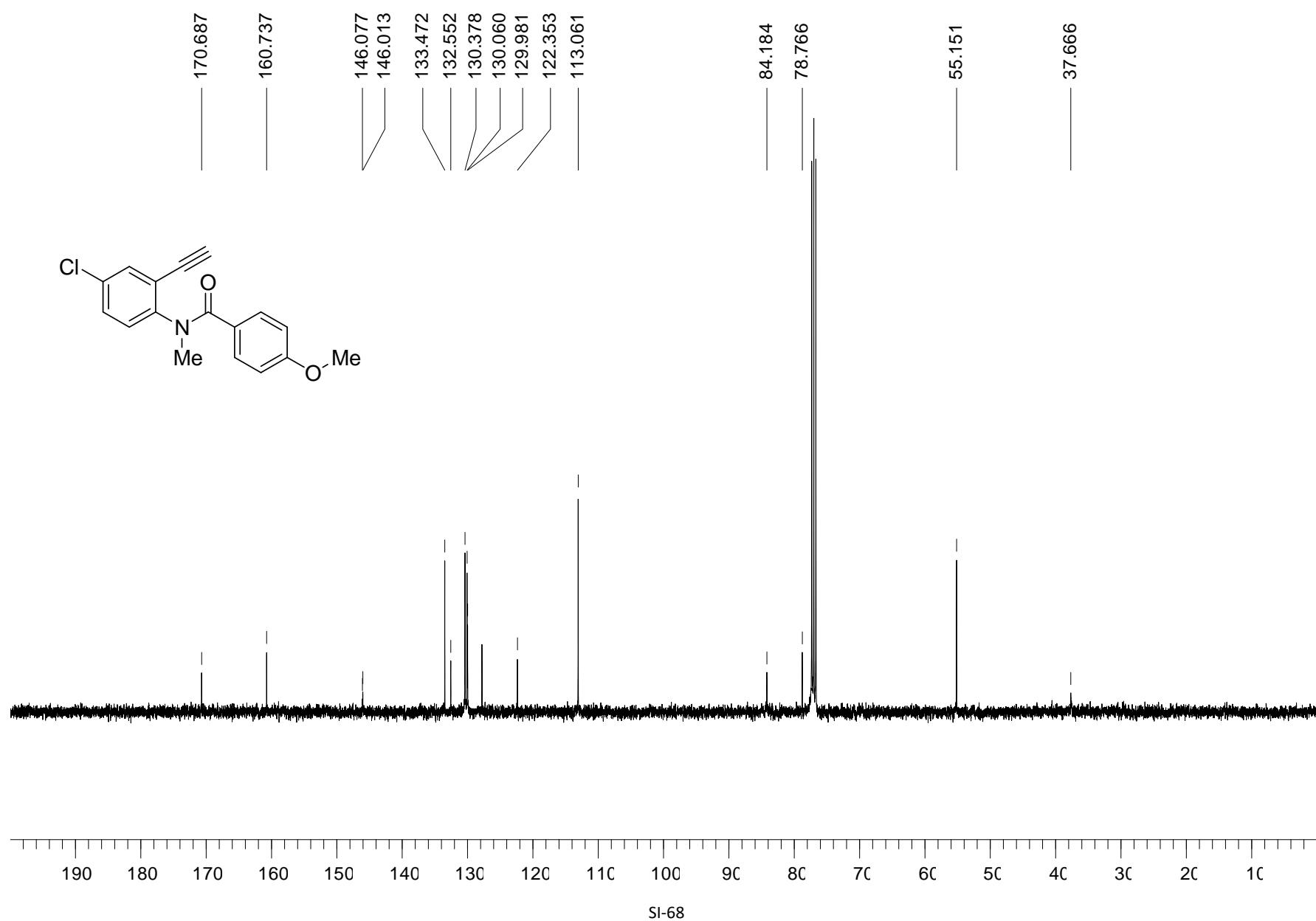
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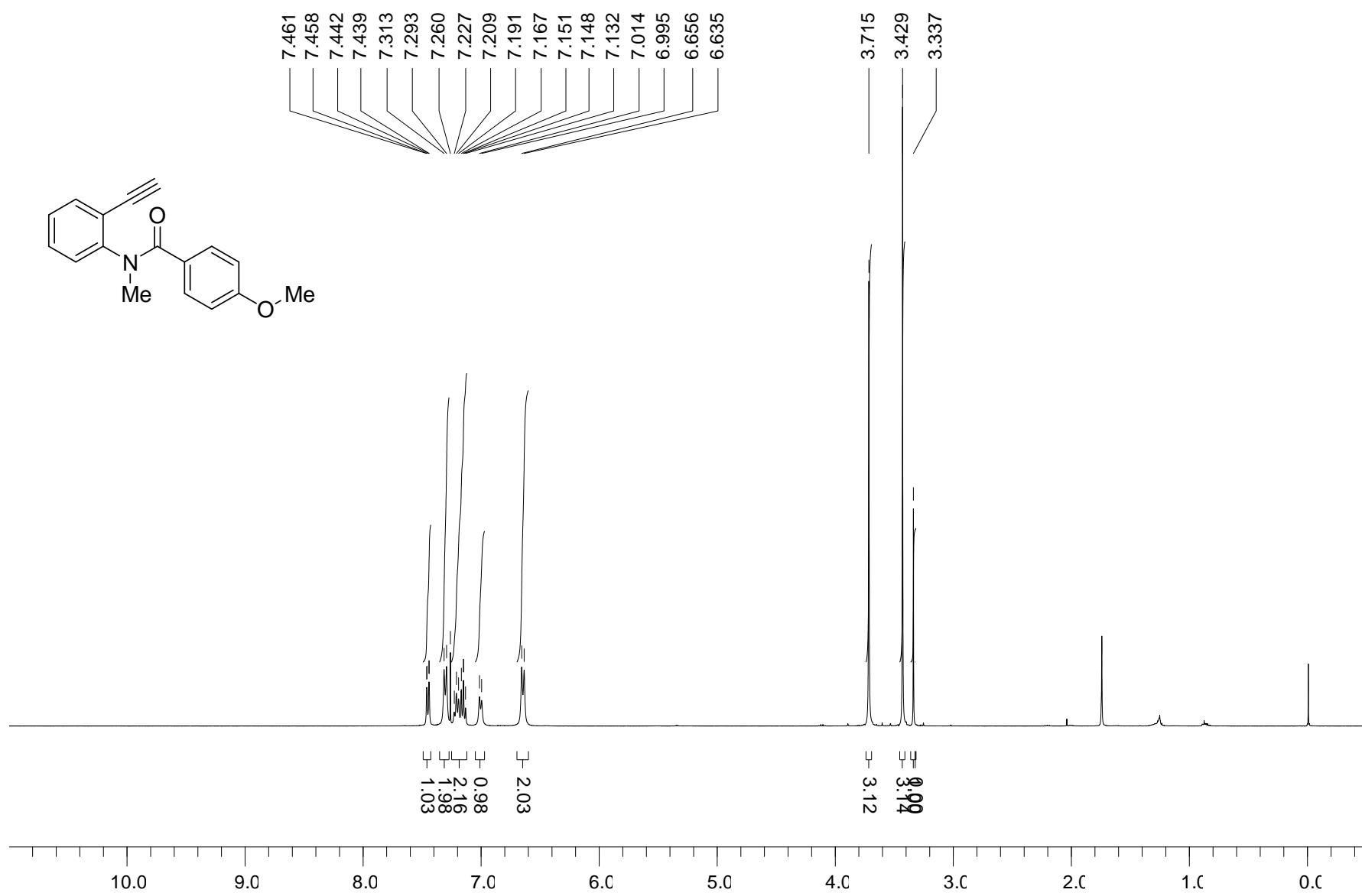
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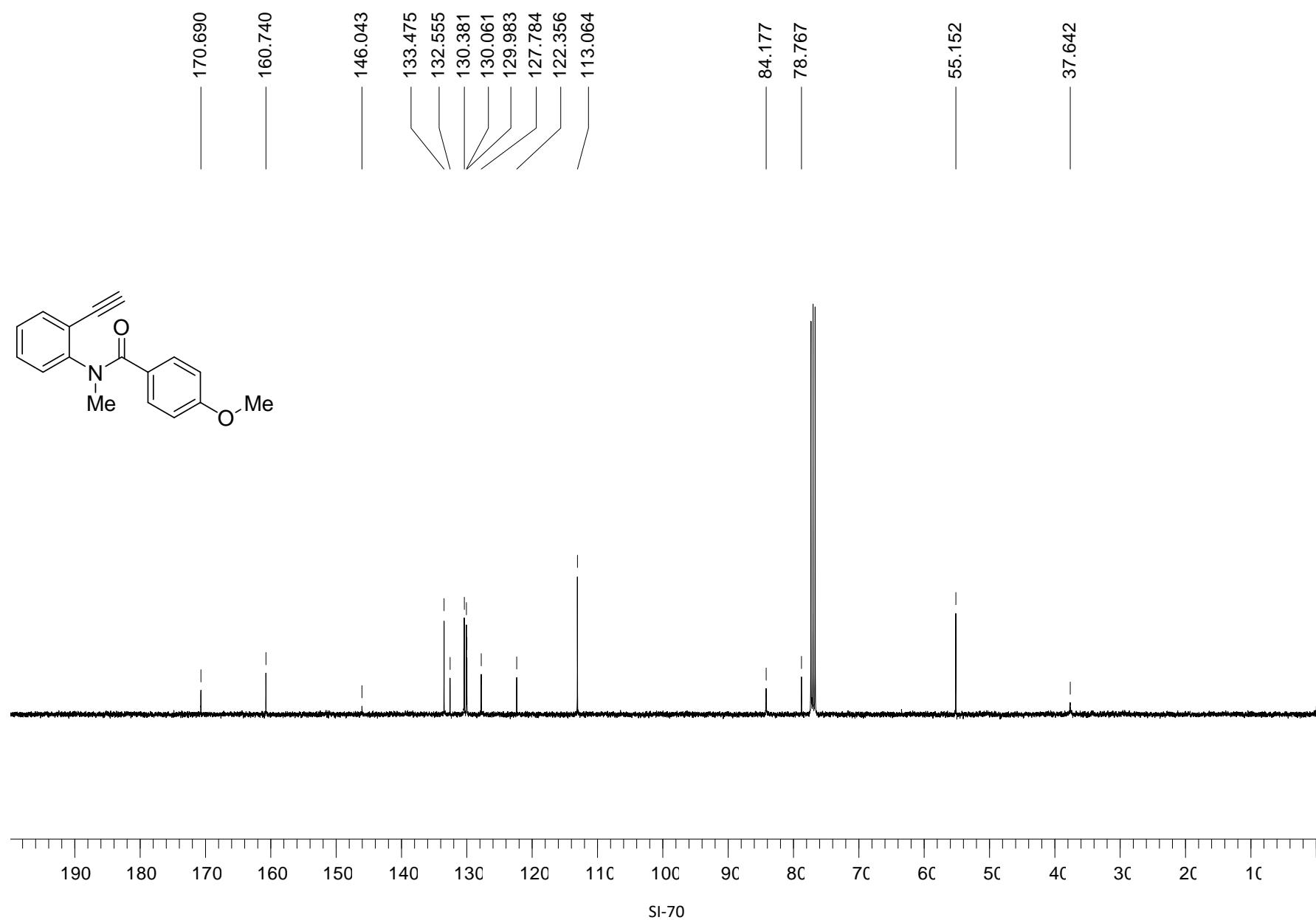
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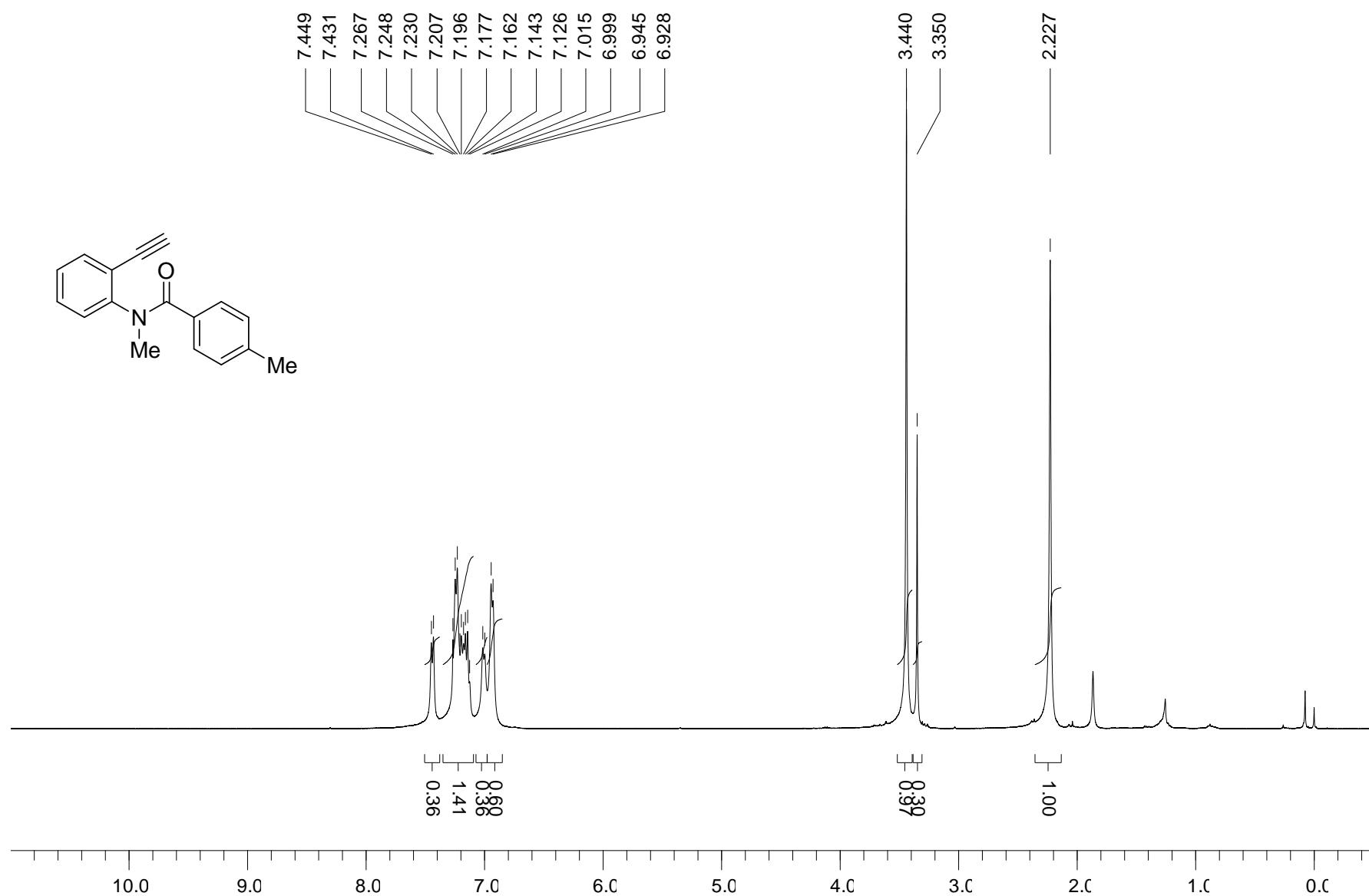
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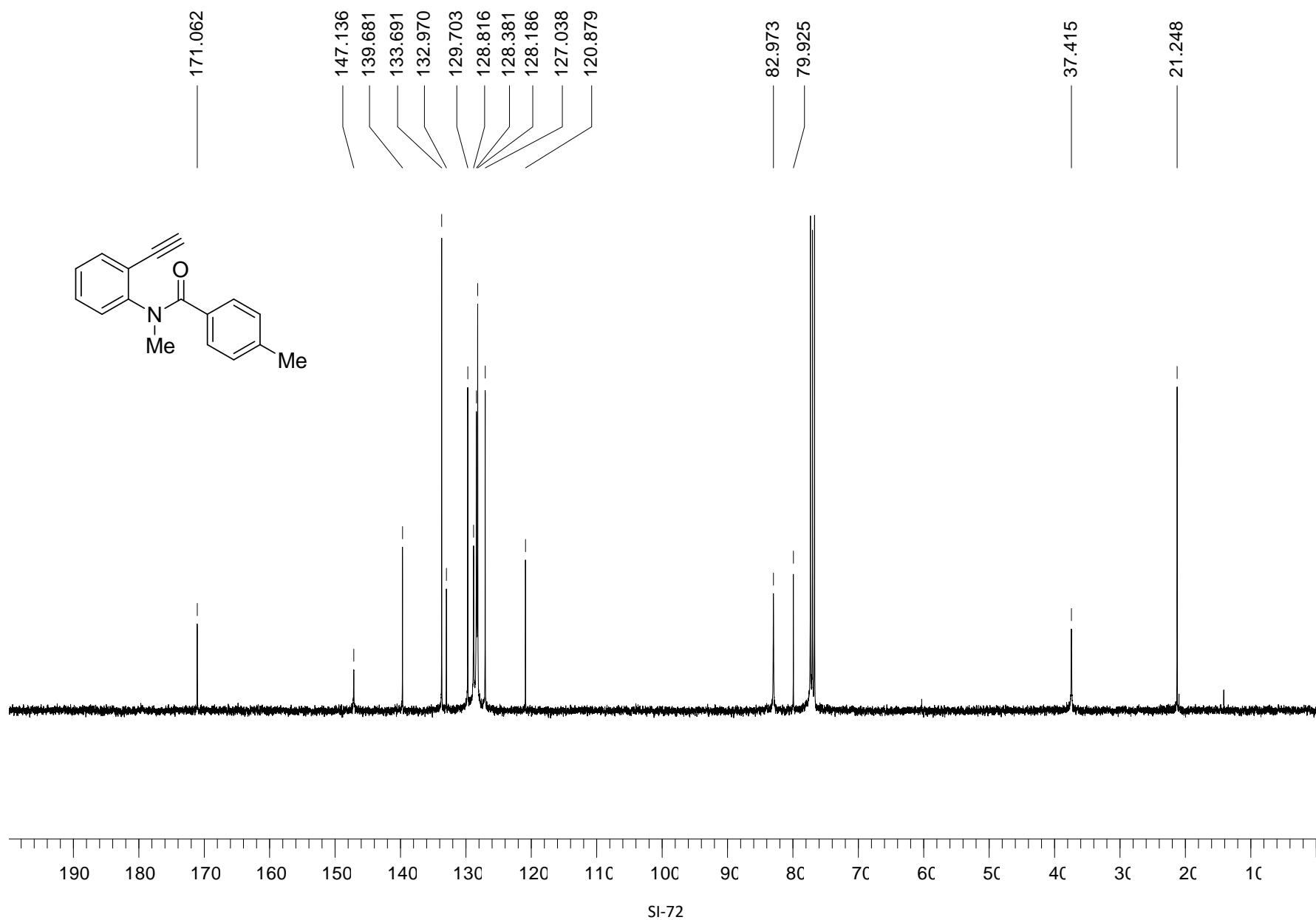
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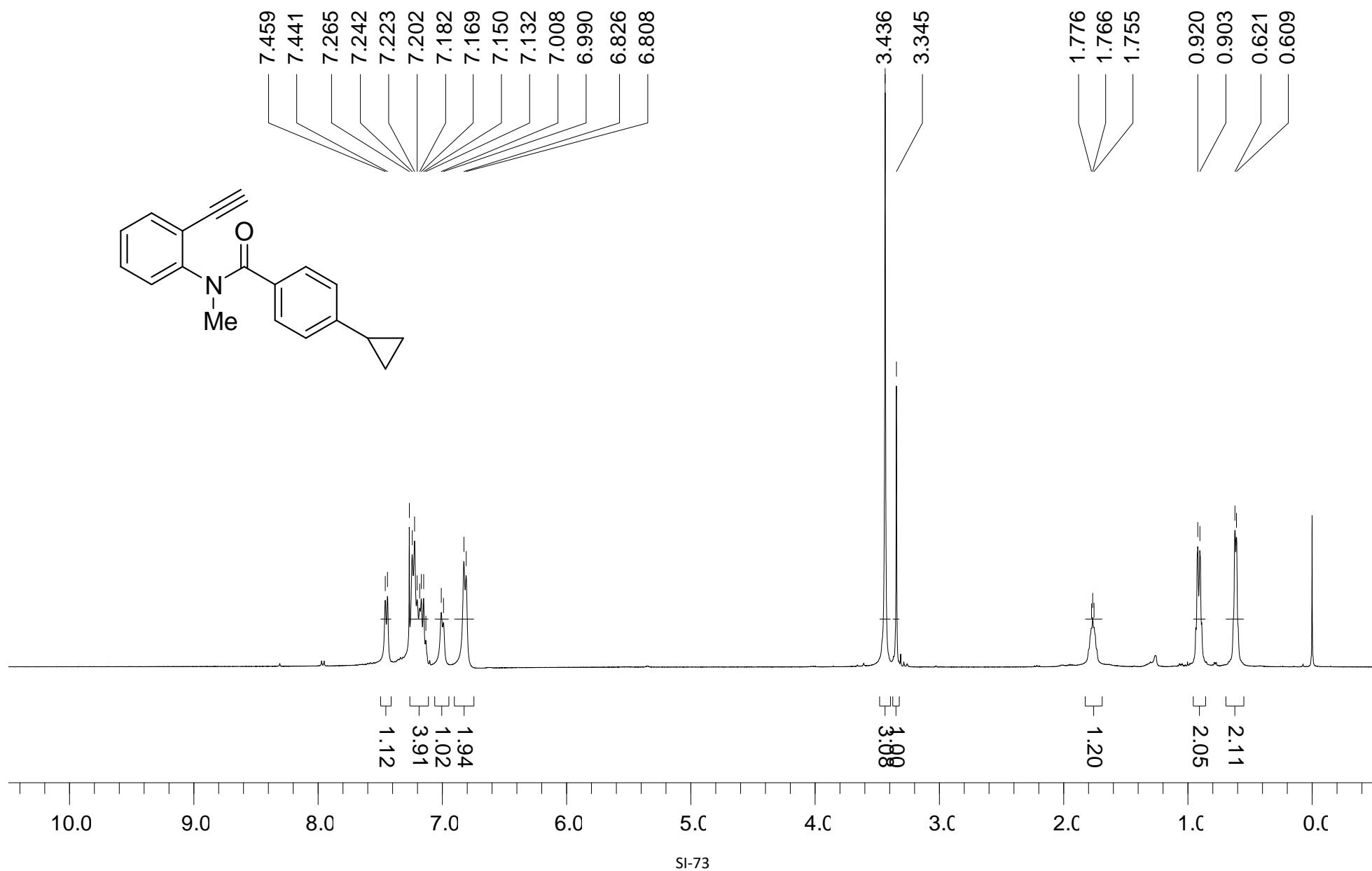
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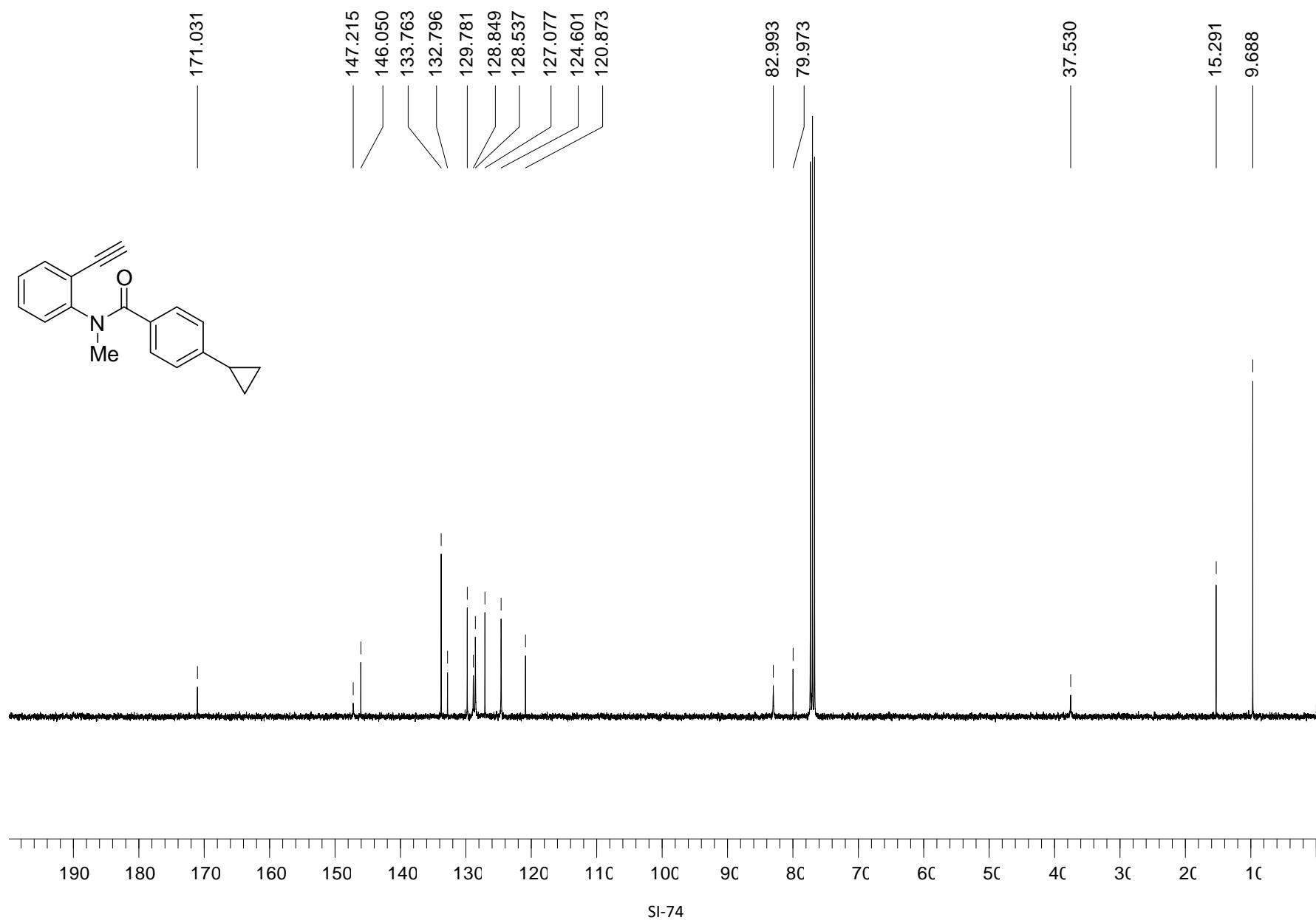
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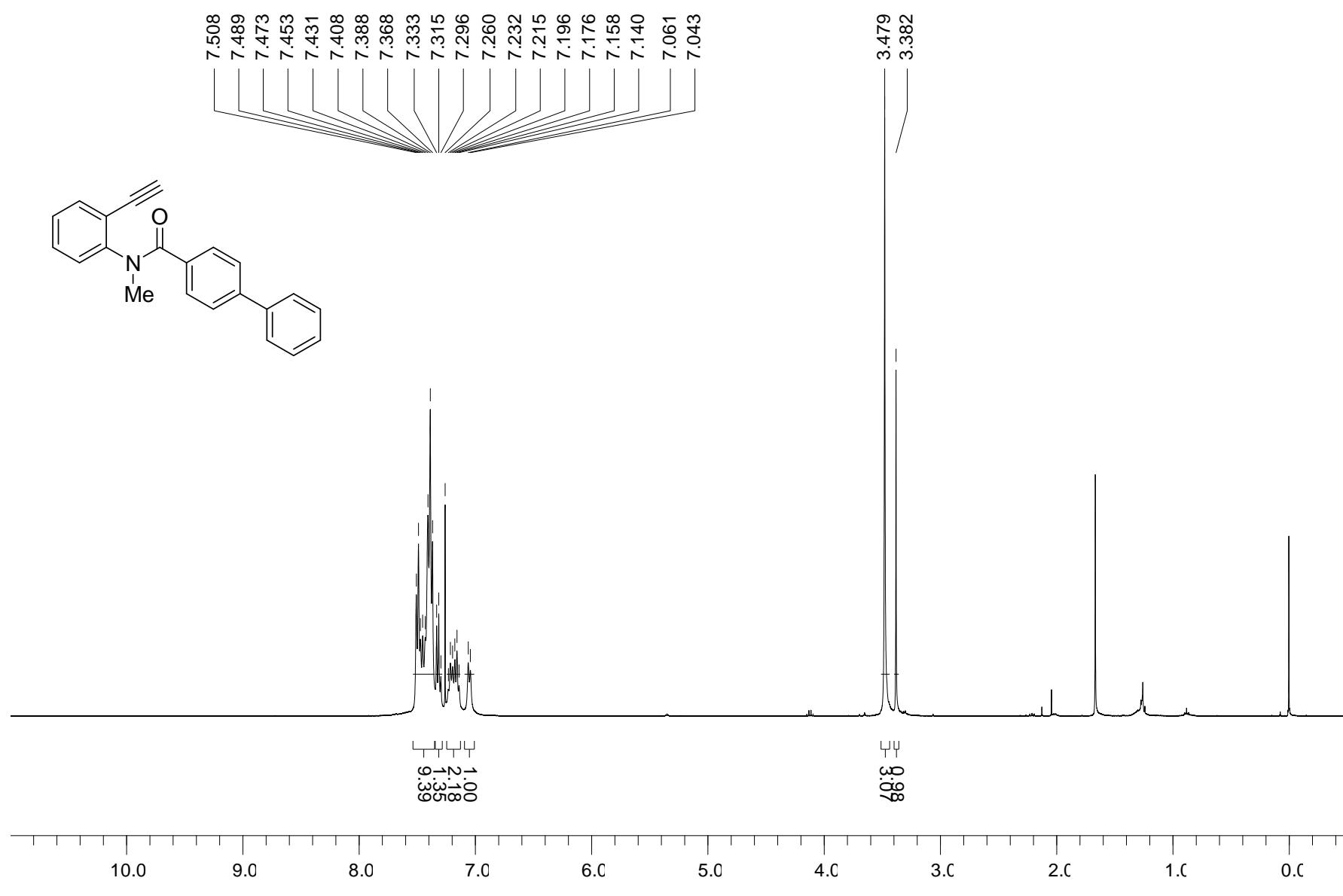
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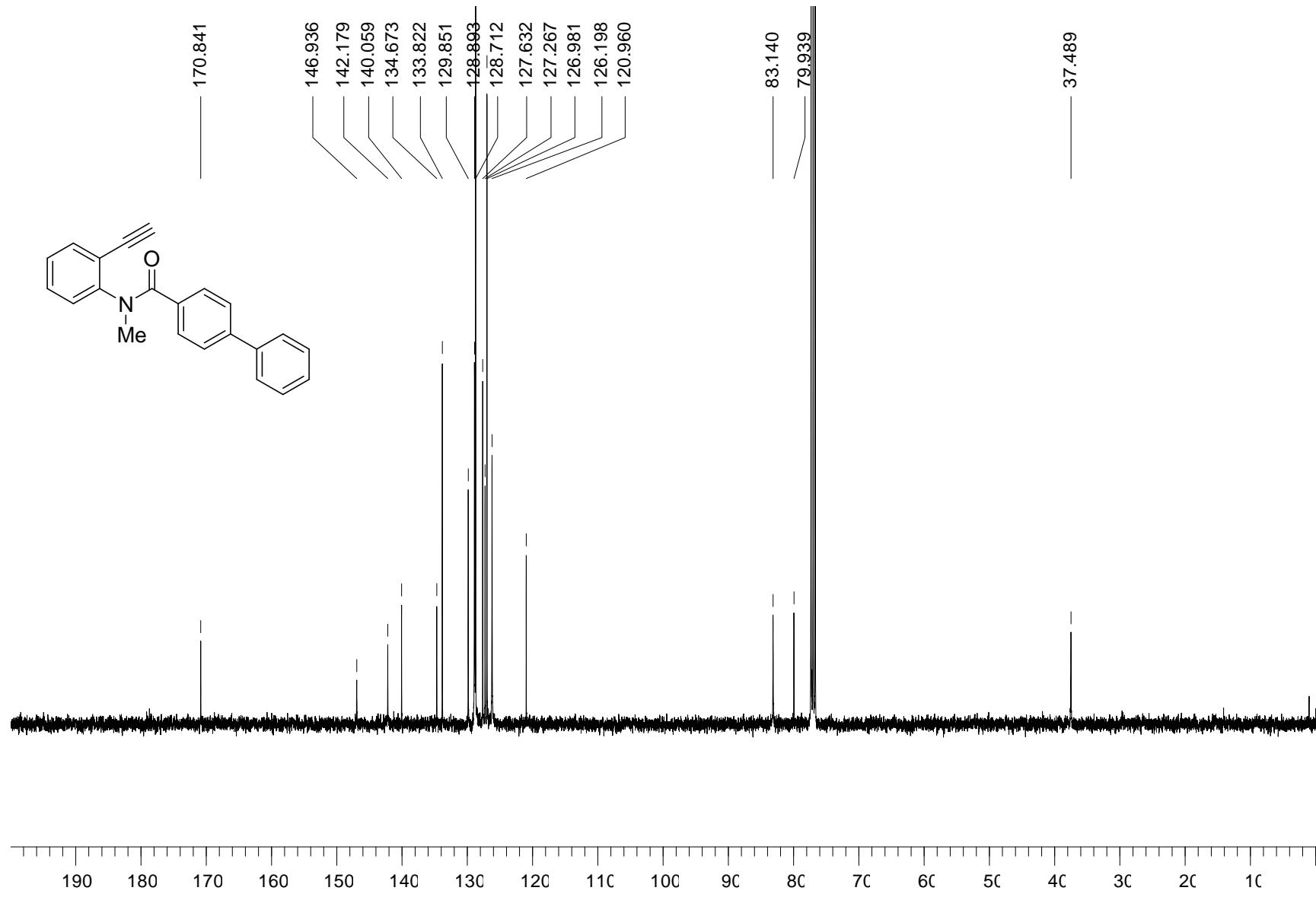
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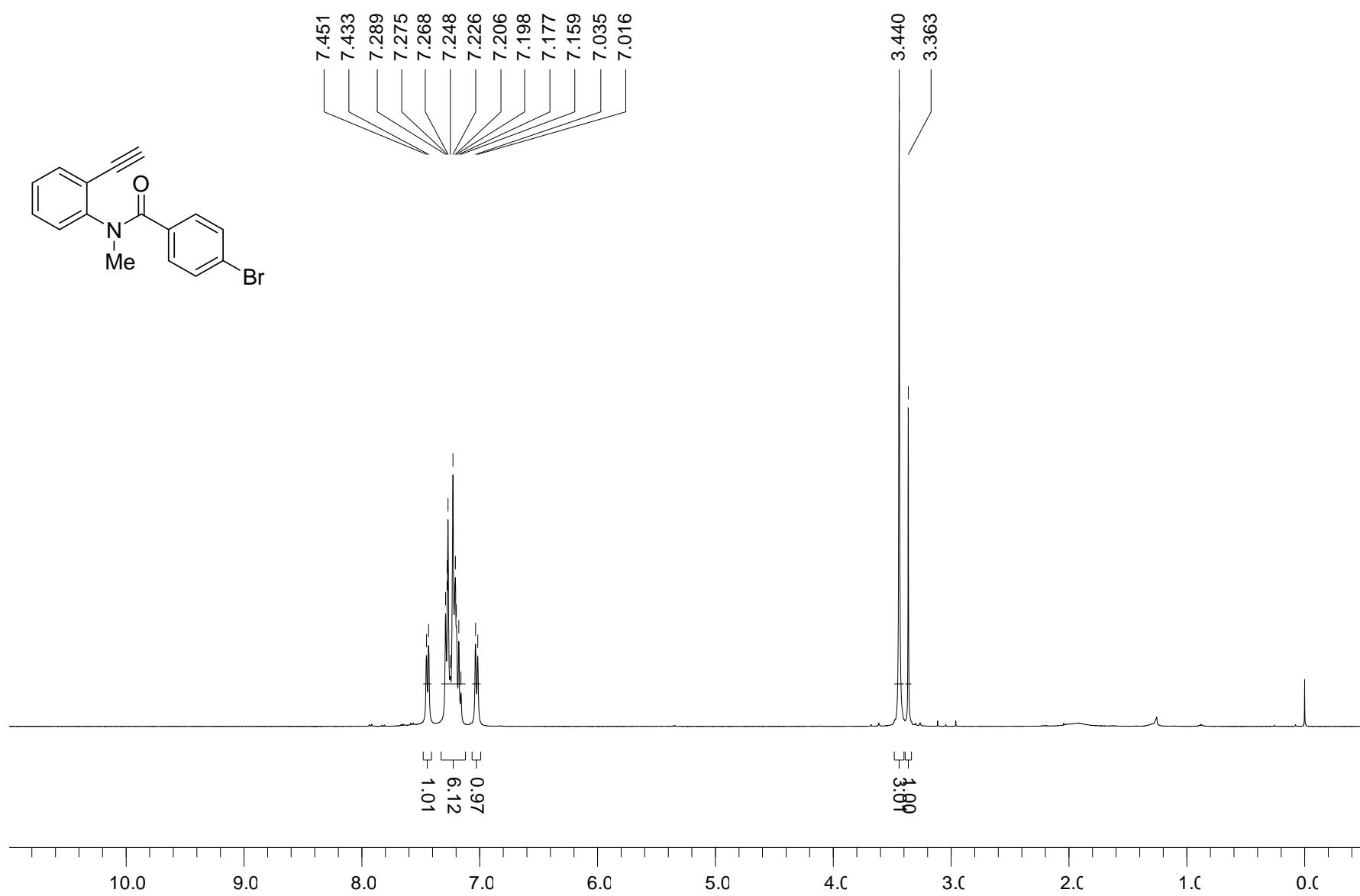
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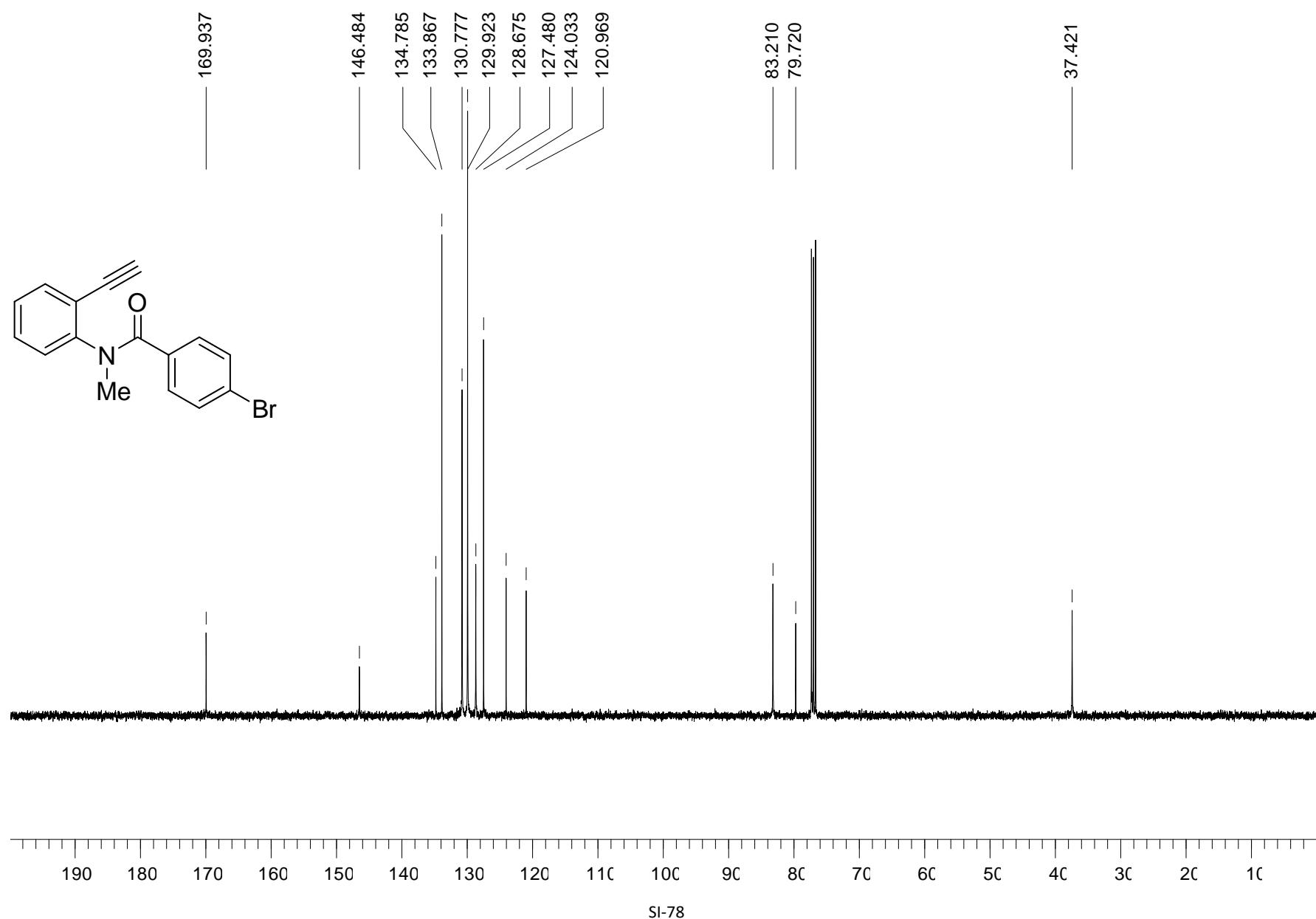
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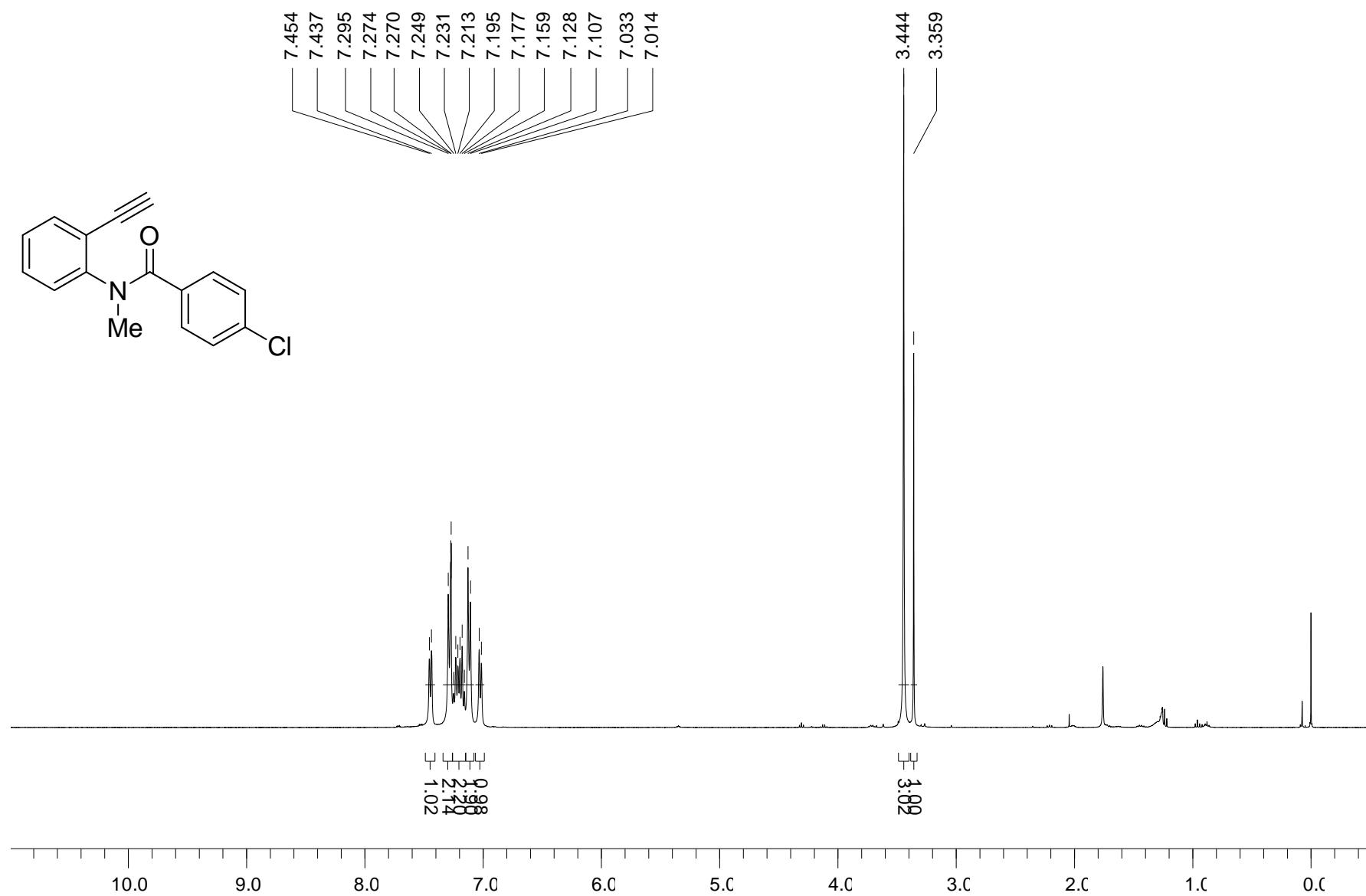
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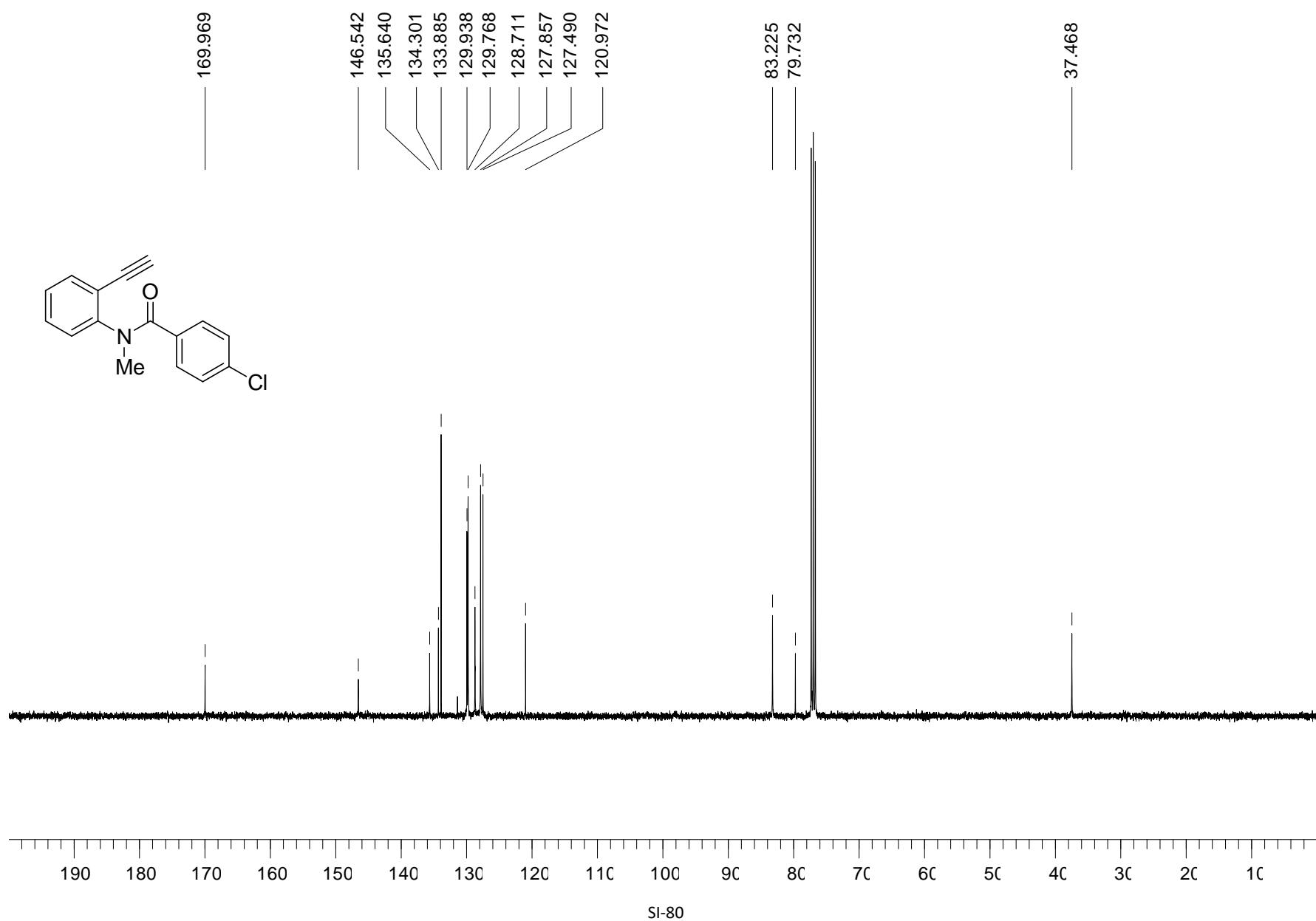
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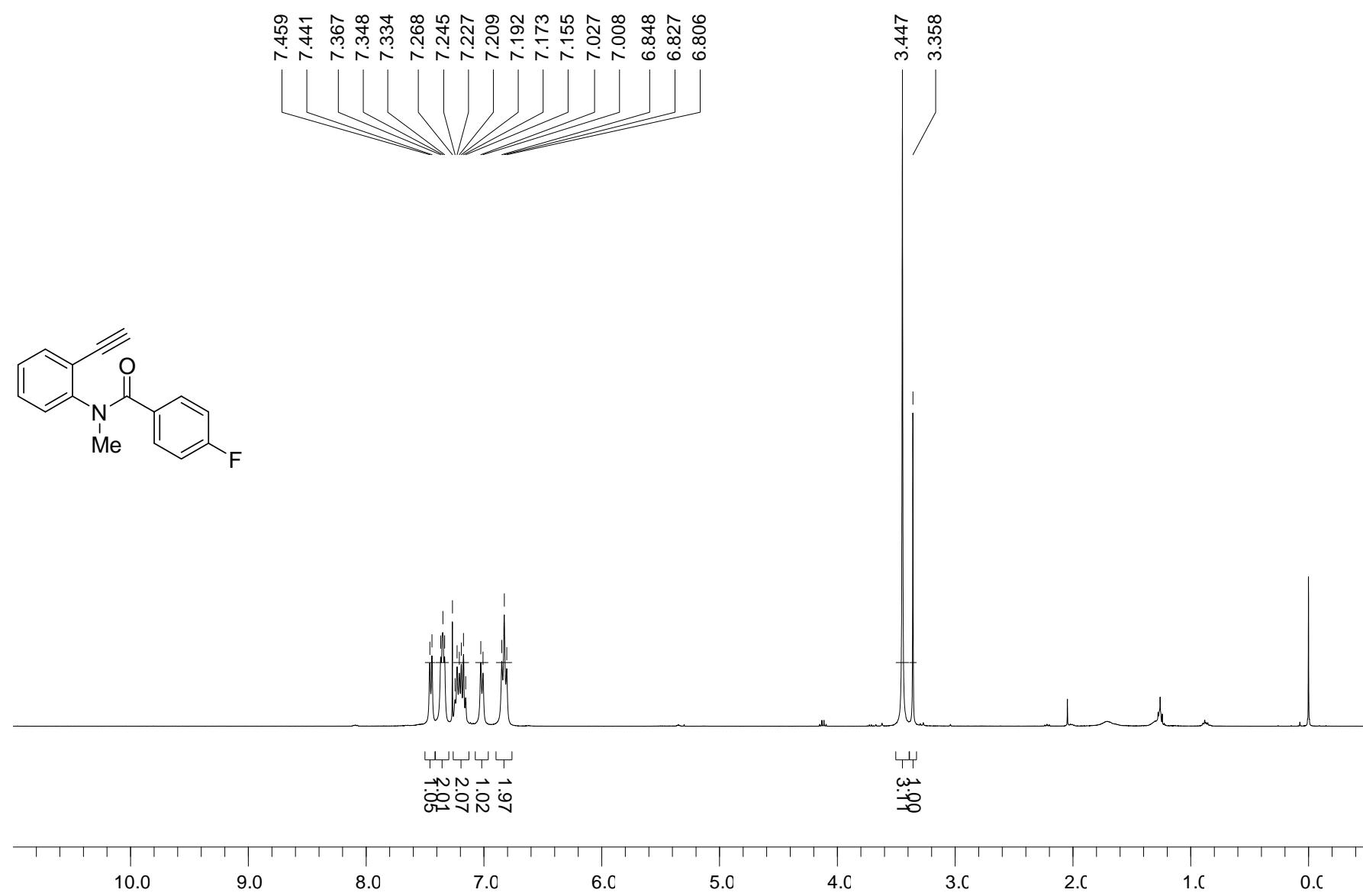
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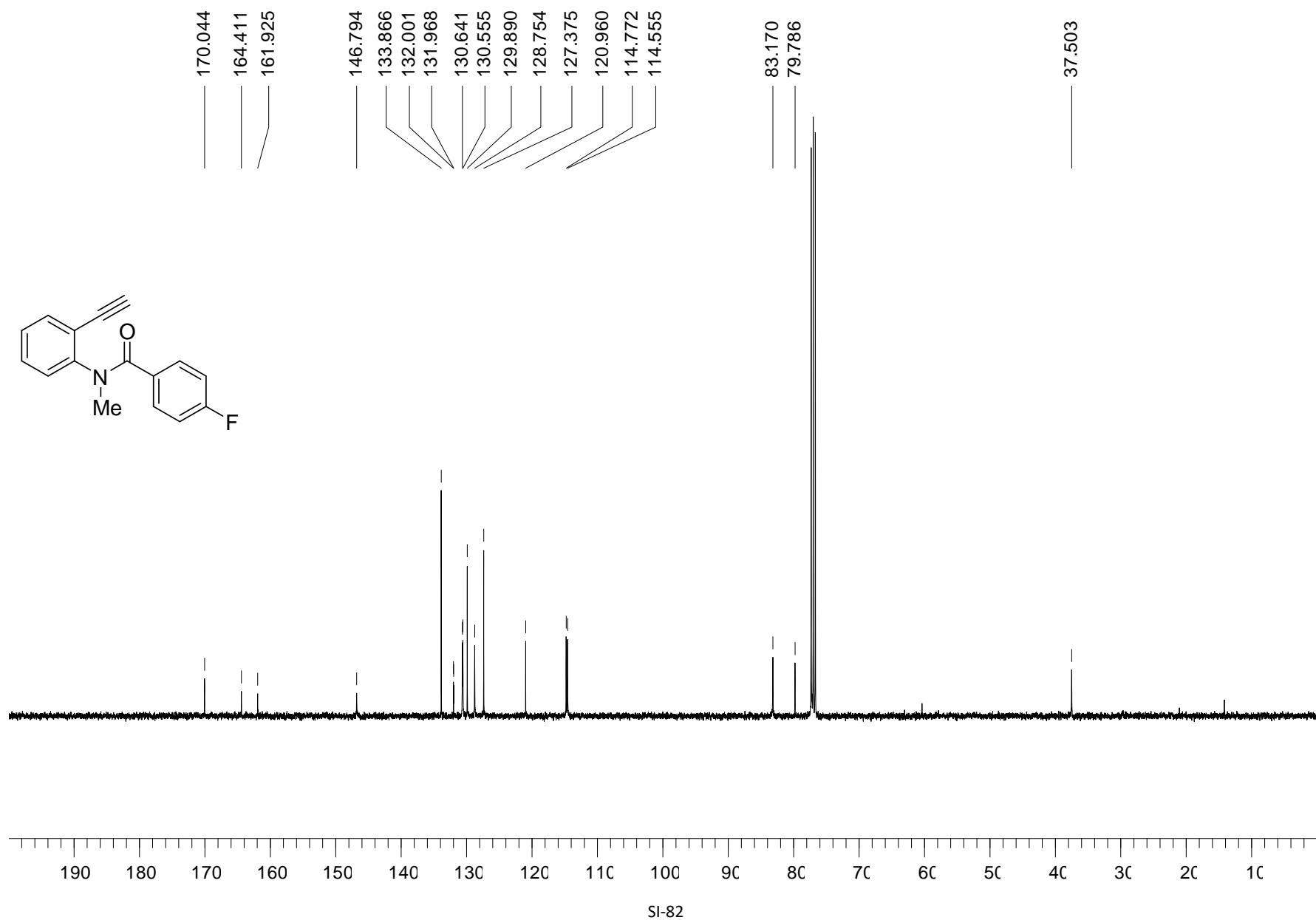
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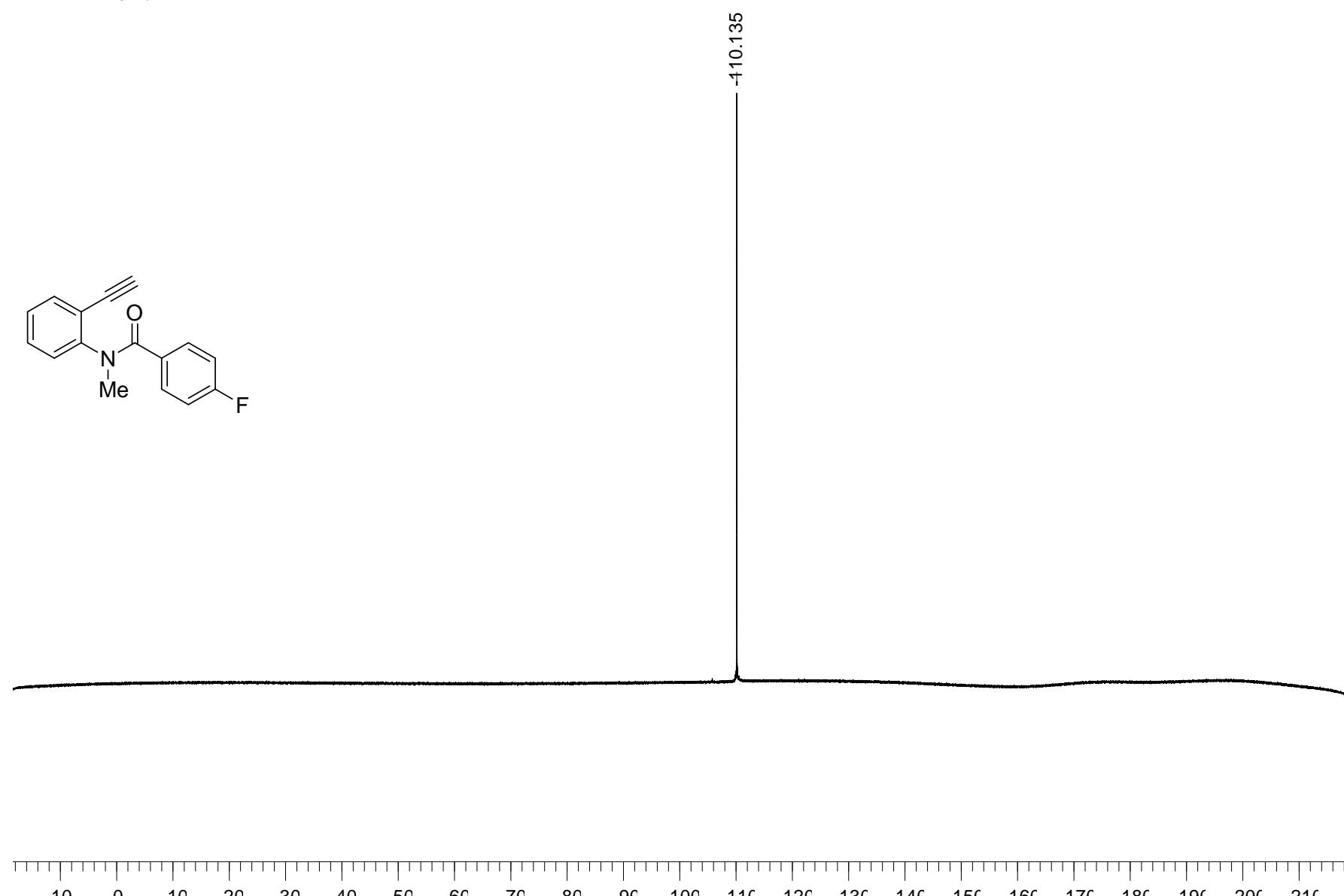
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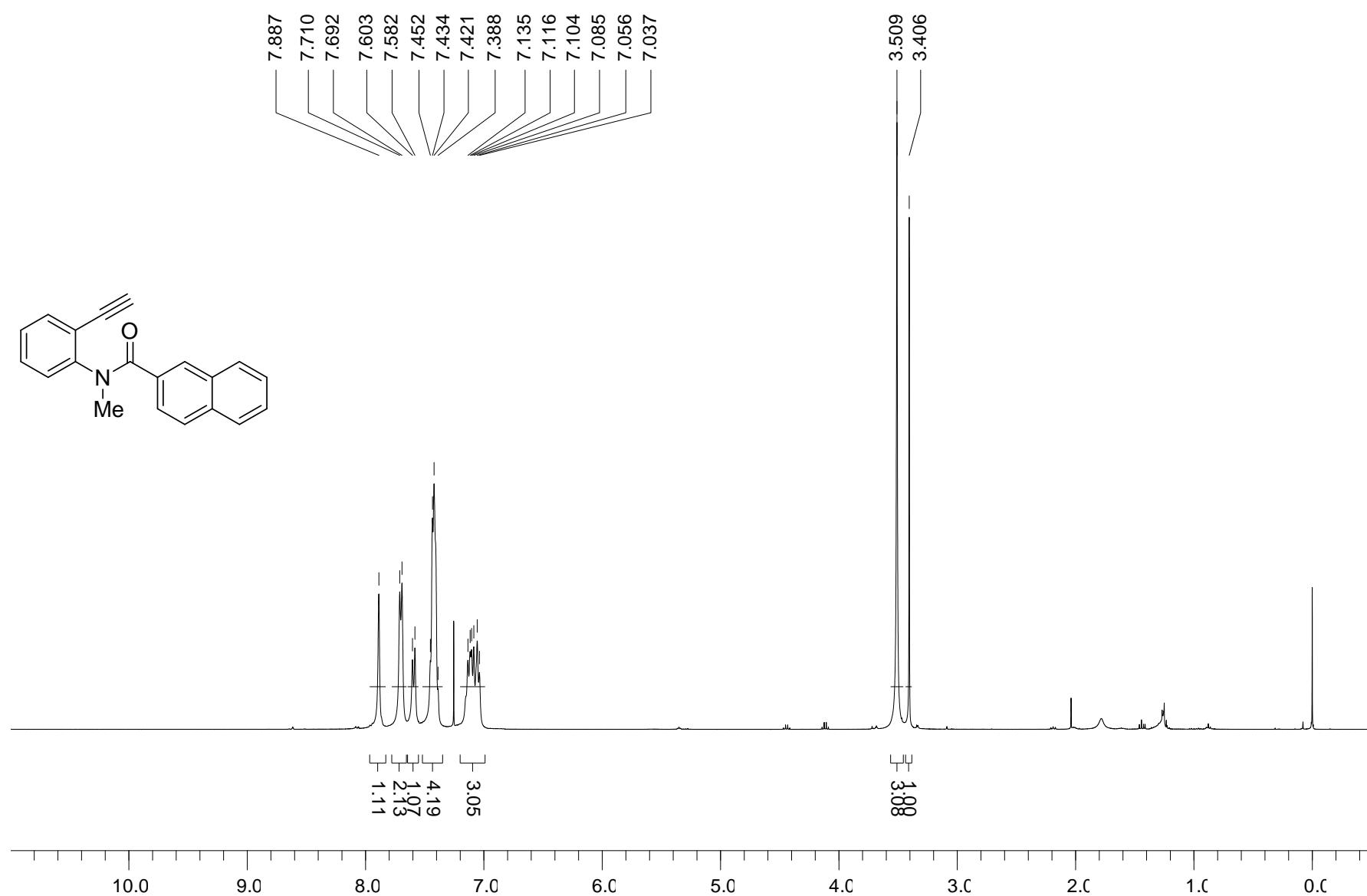
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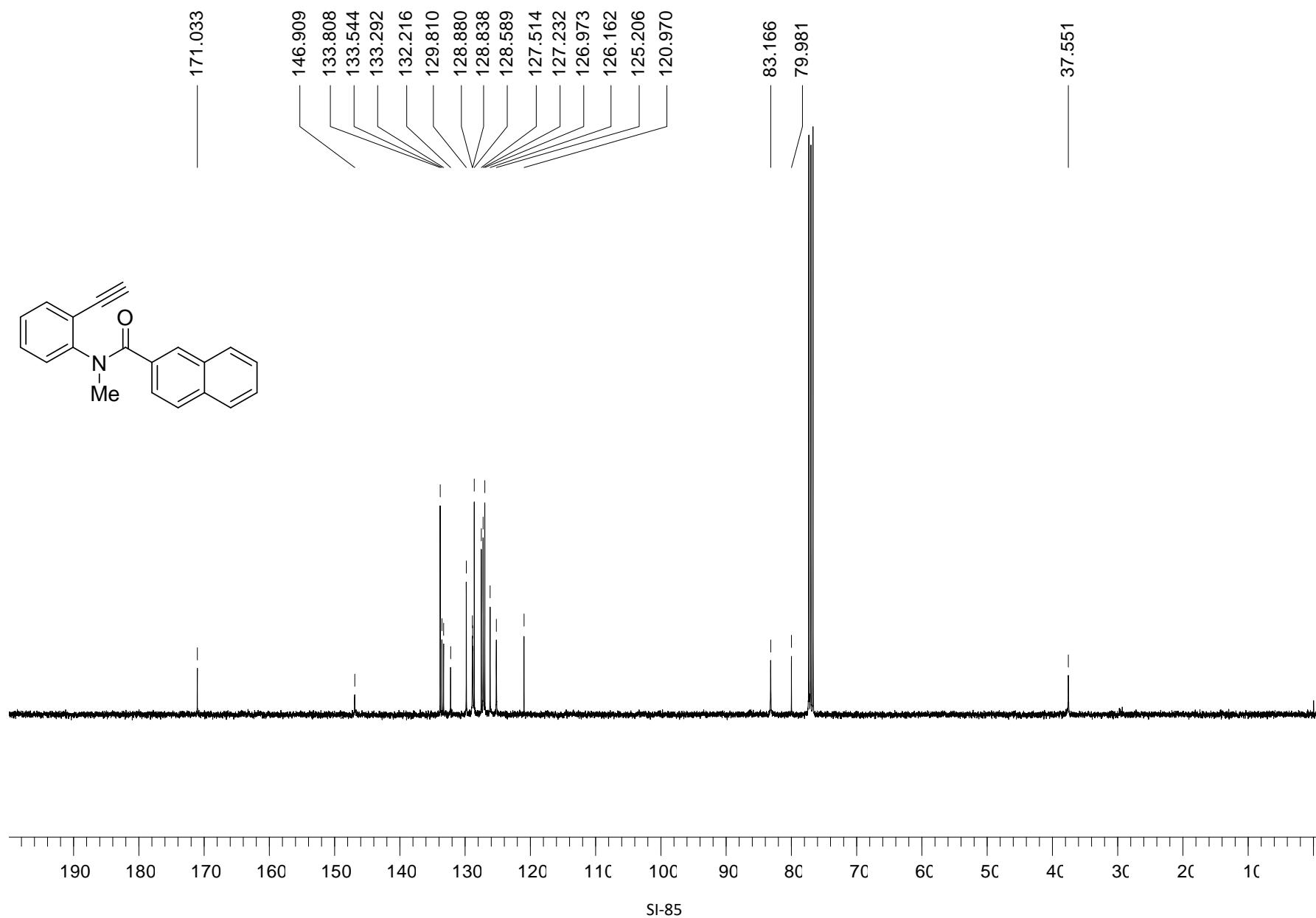
¹⁹F NMR (376 MHz, CDCl₃) spectrum of **1o**



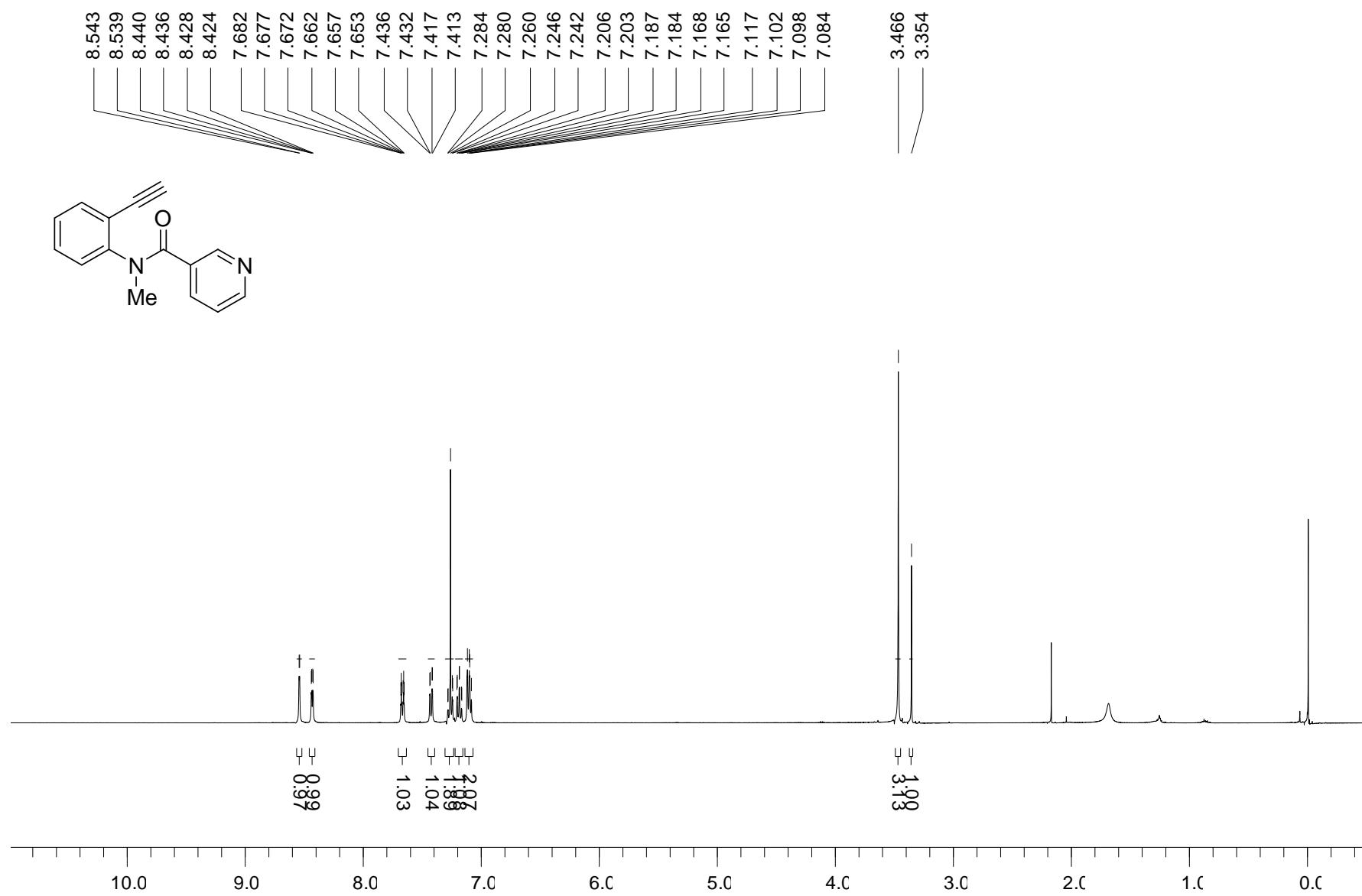
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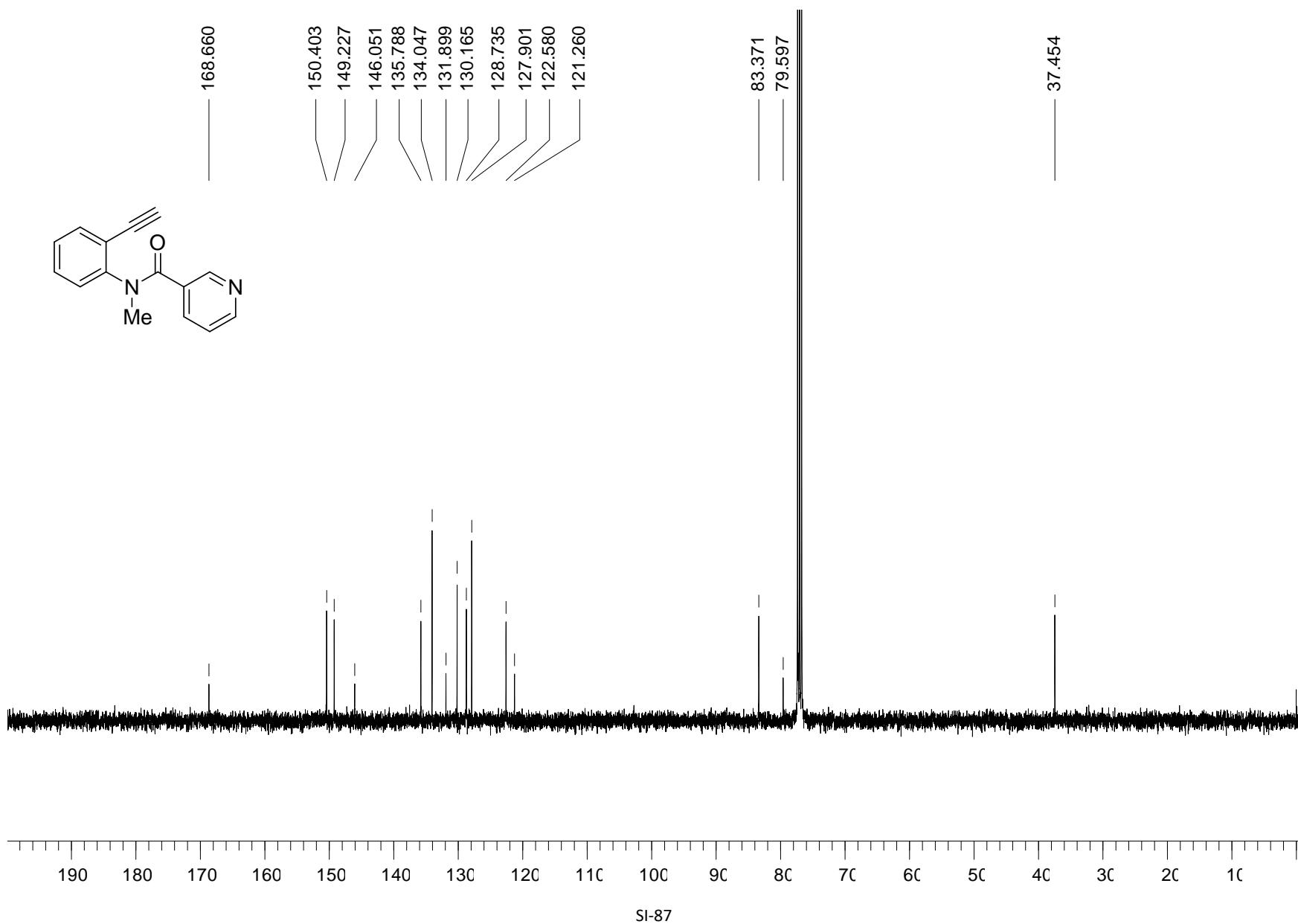
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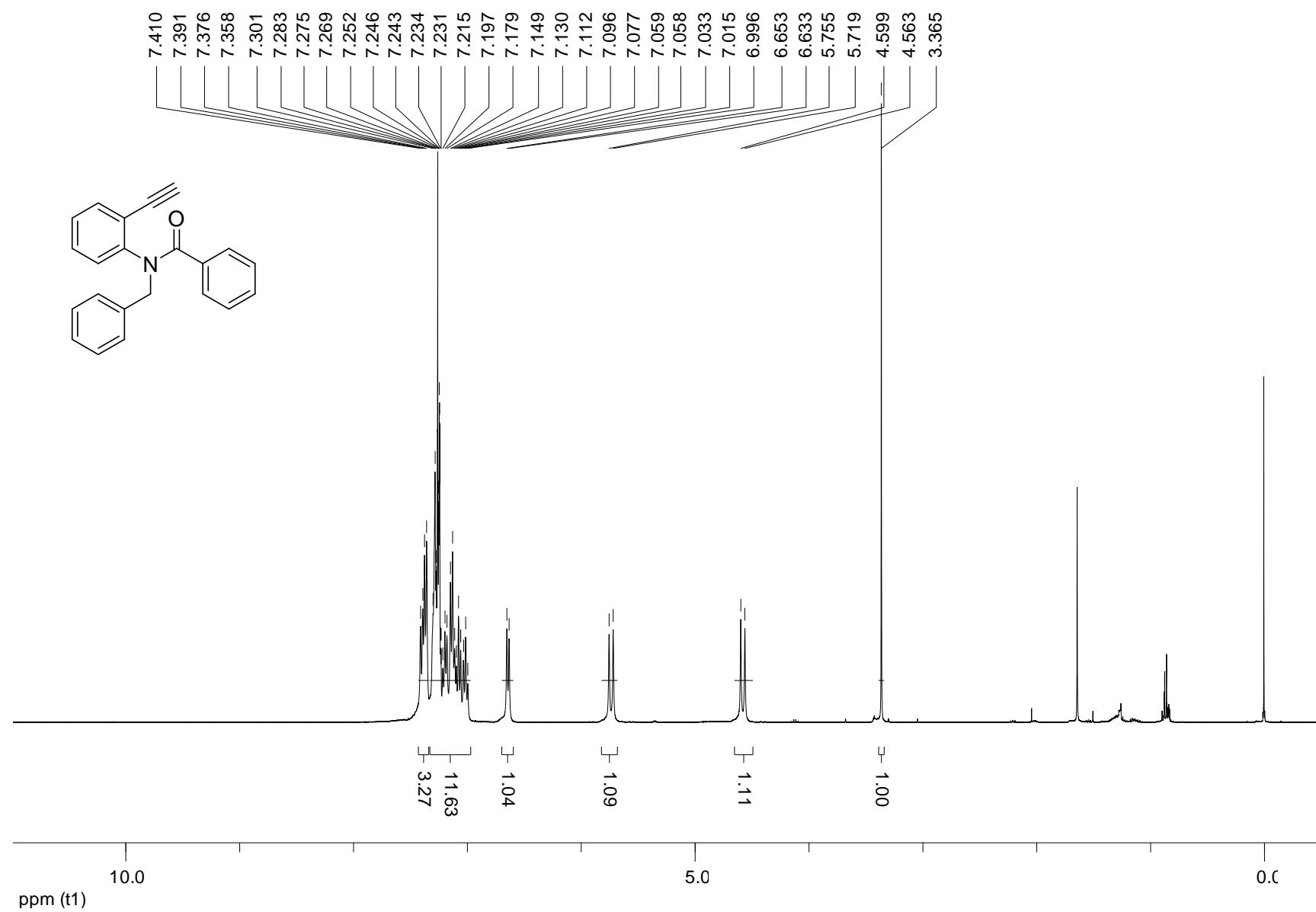
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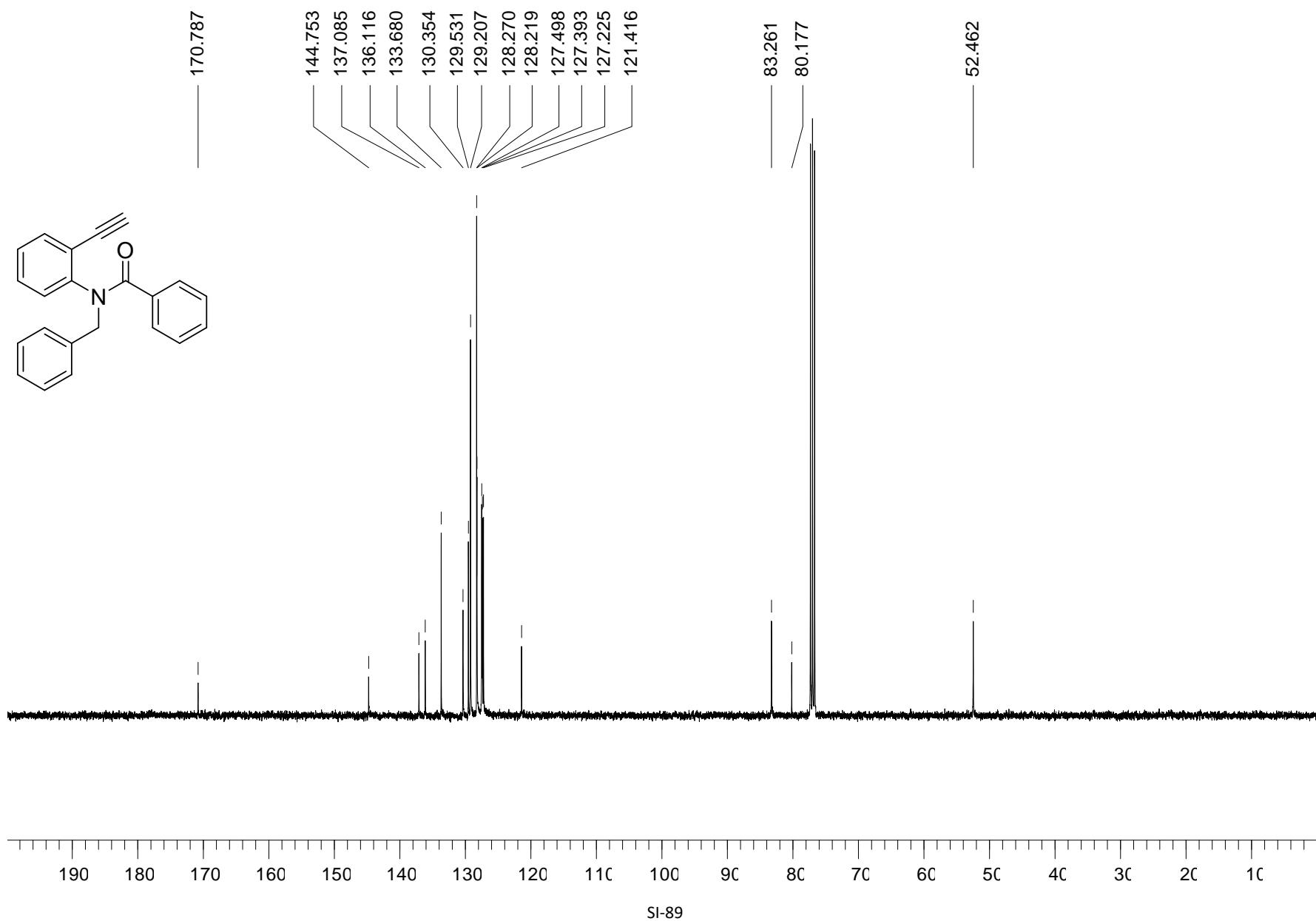
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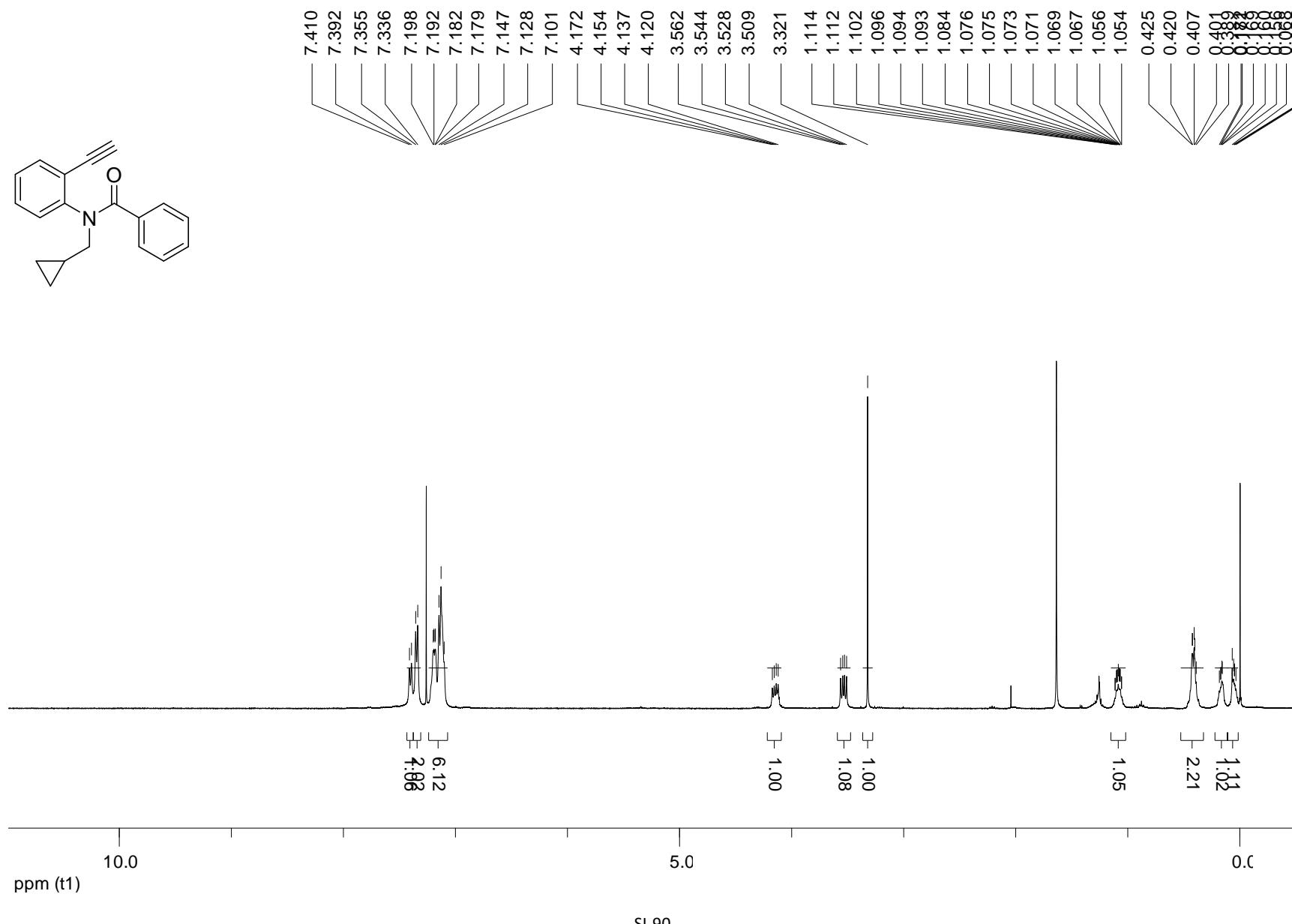
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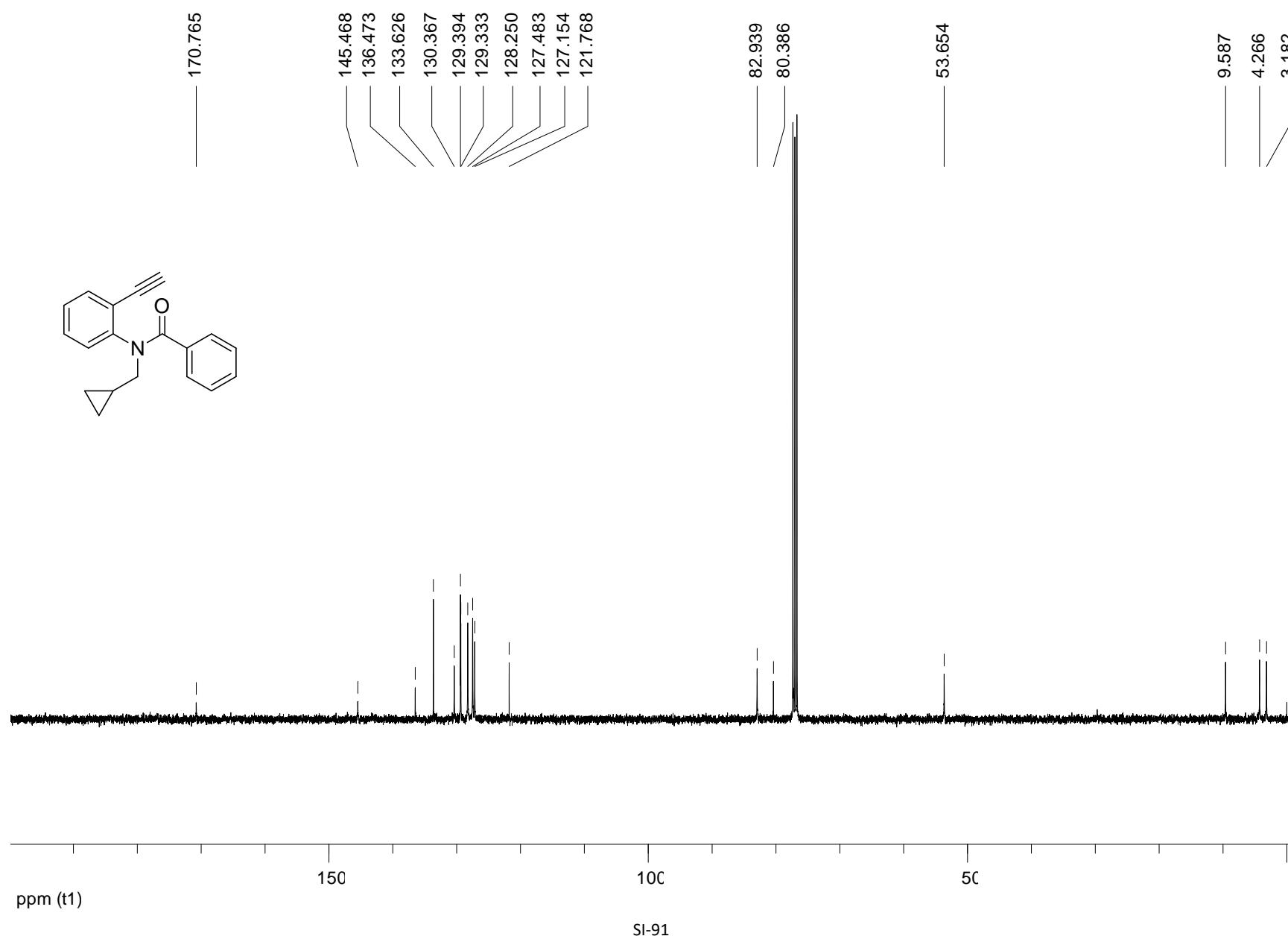
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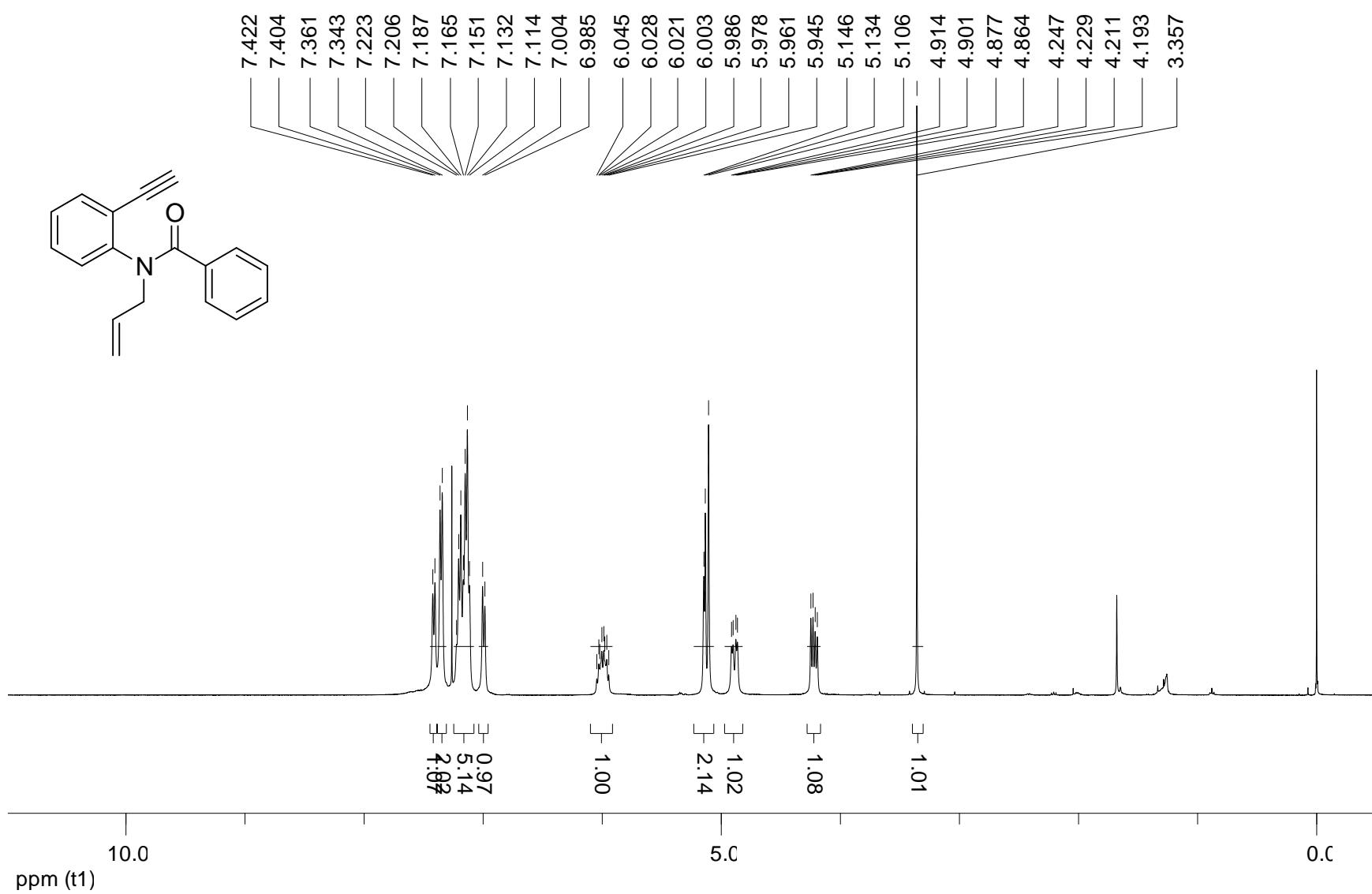
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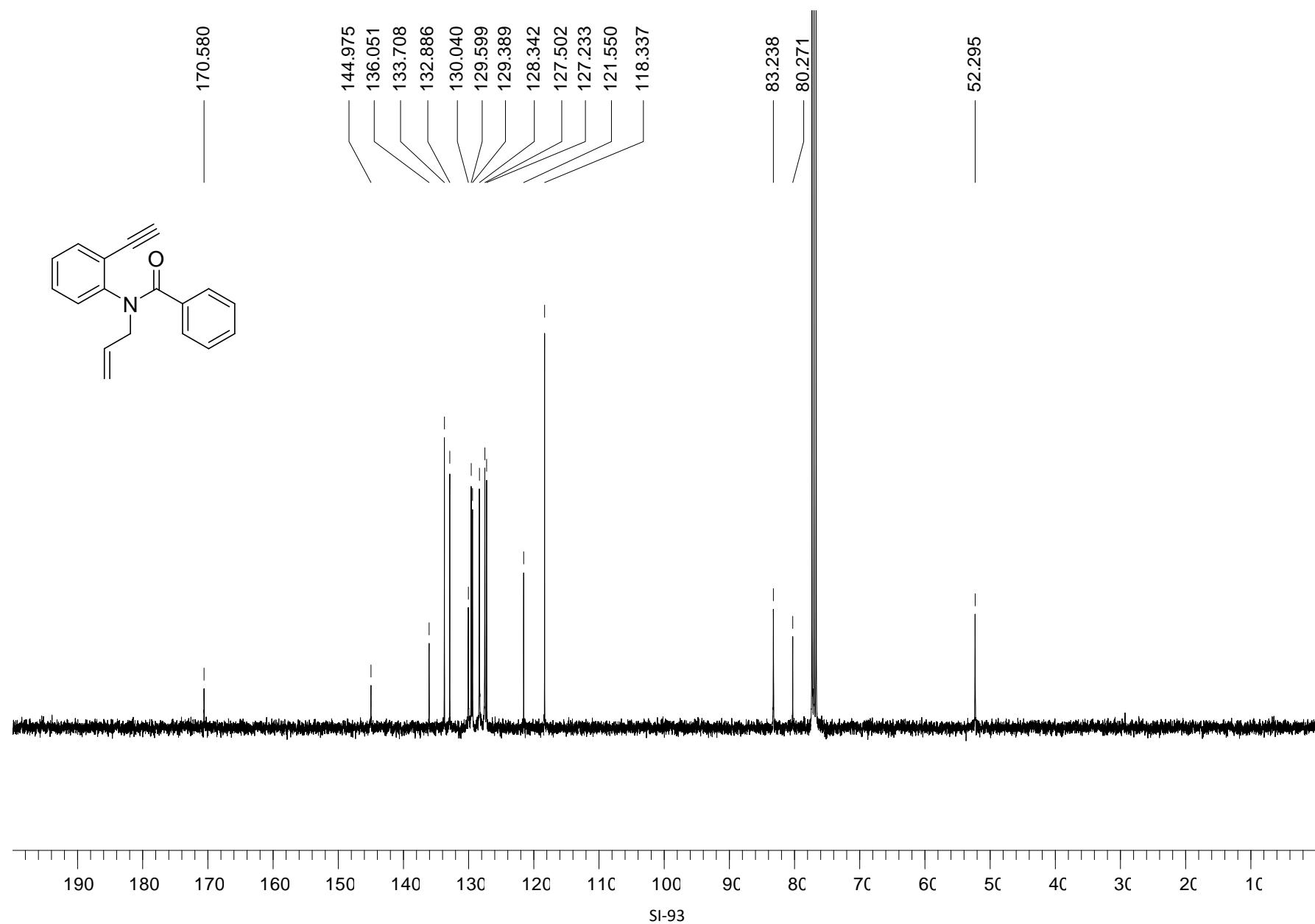
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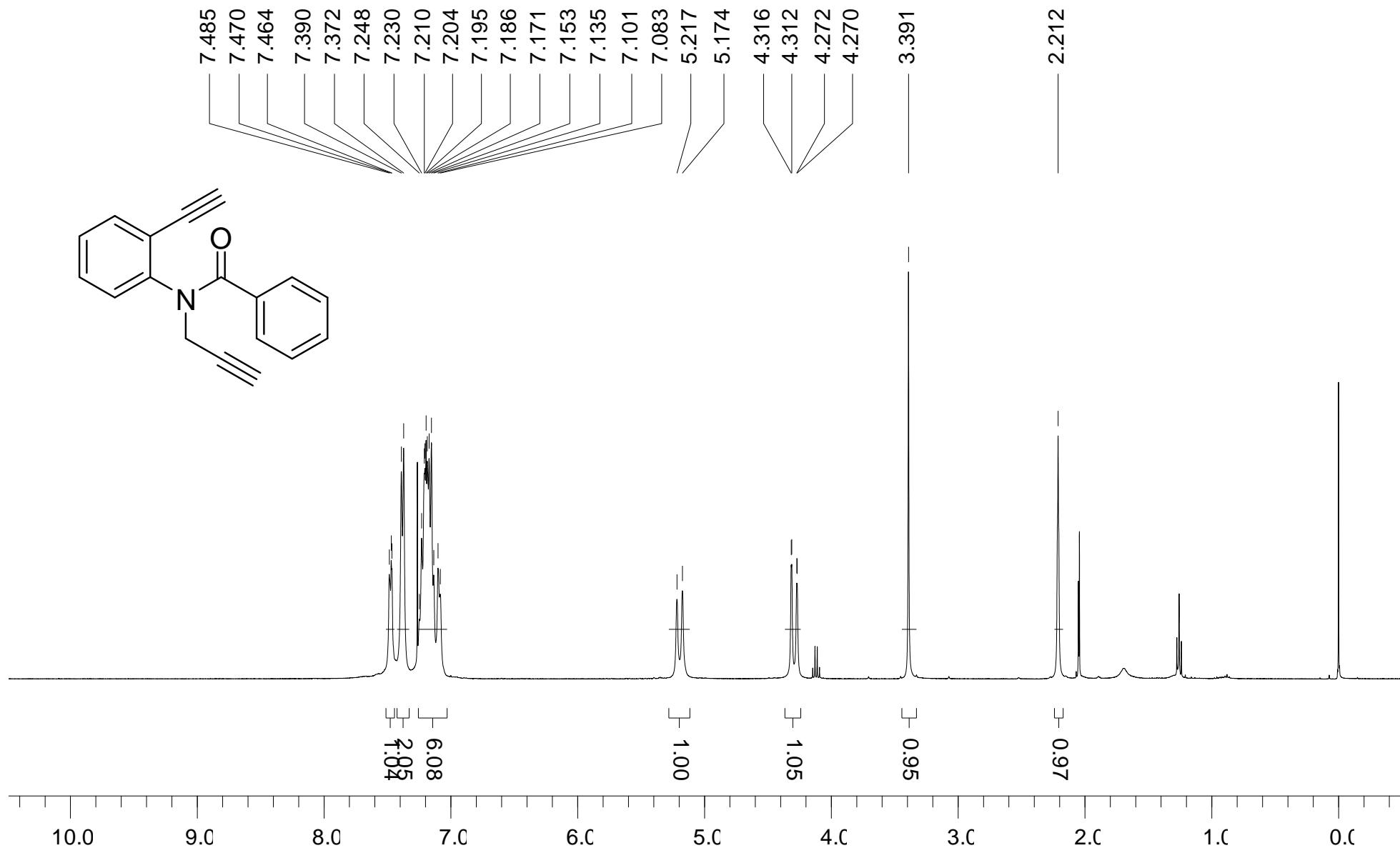
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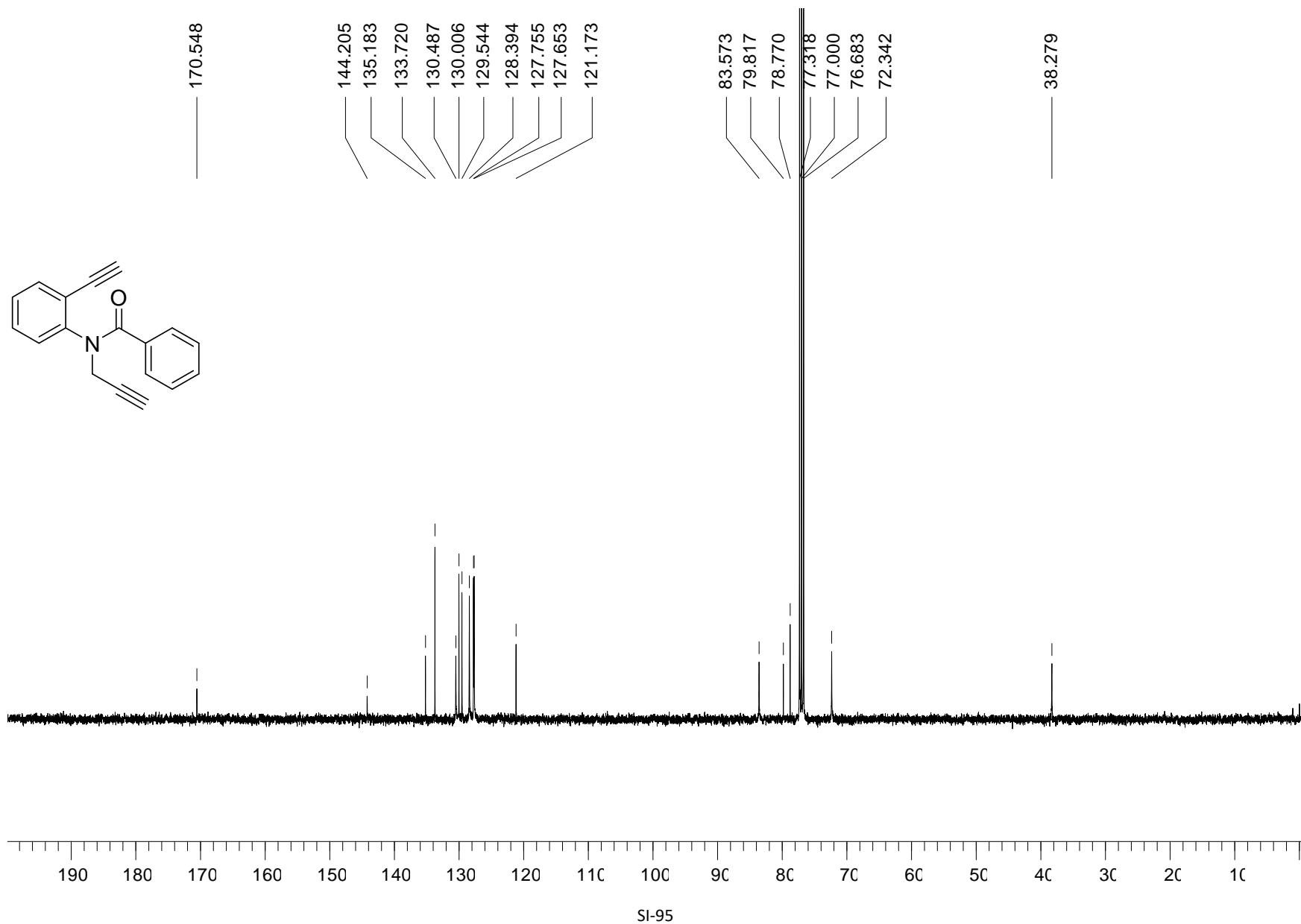
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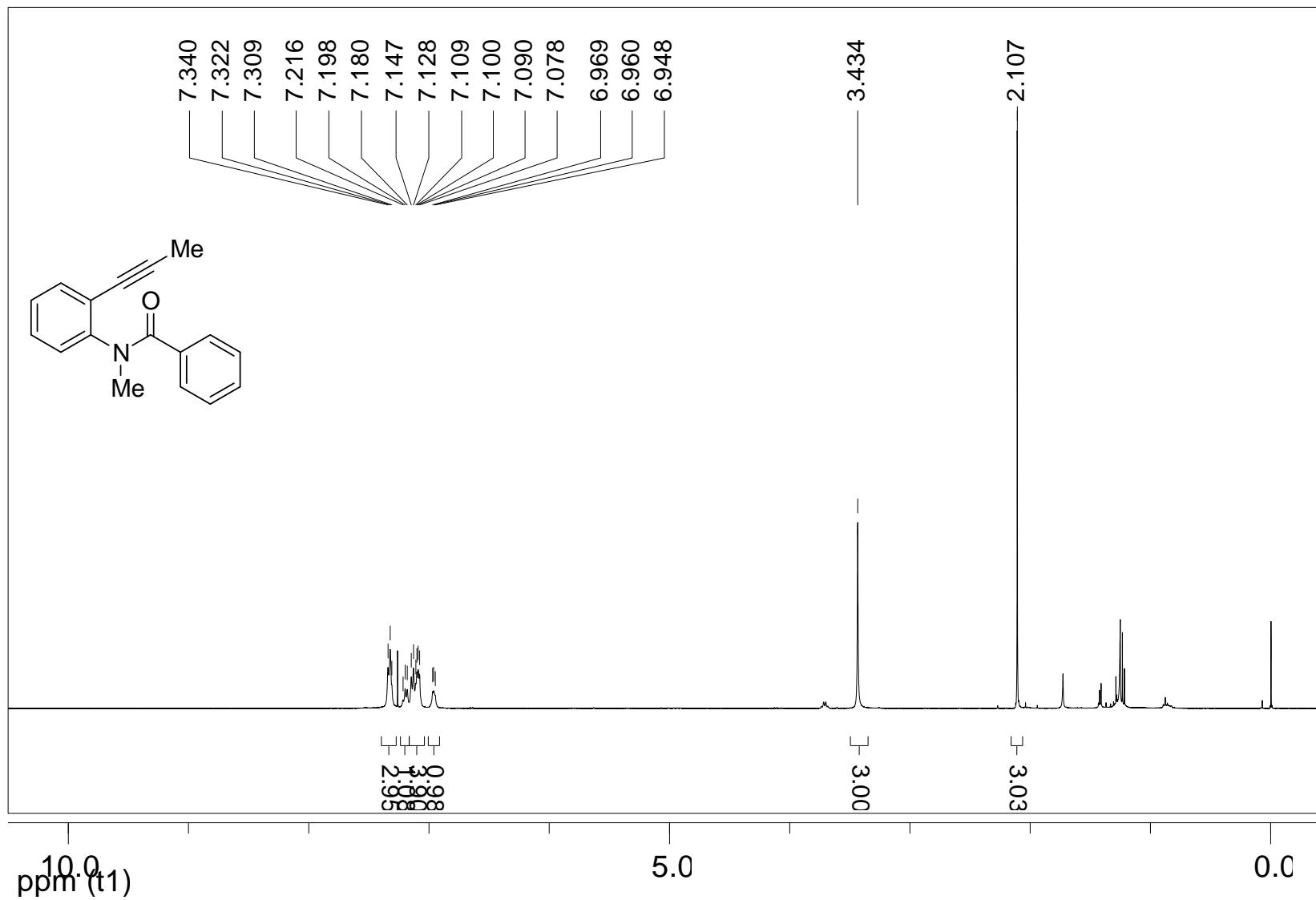
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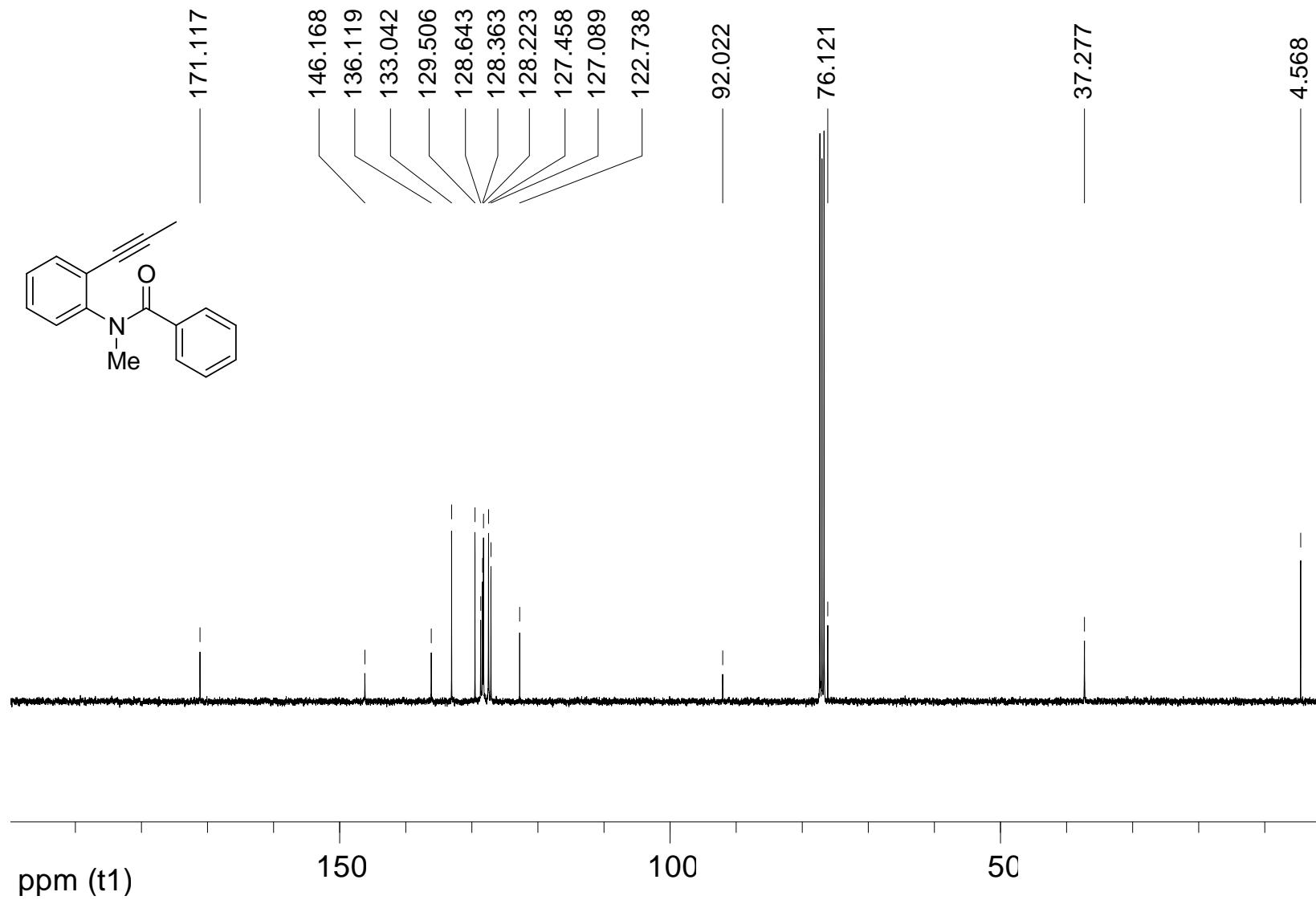
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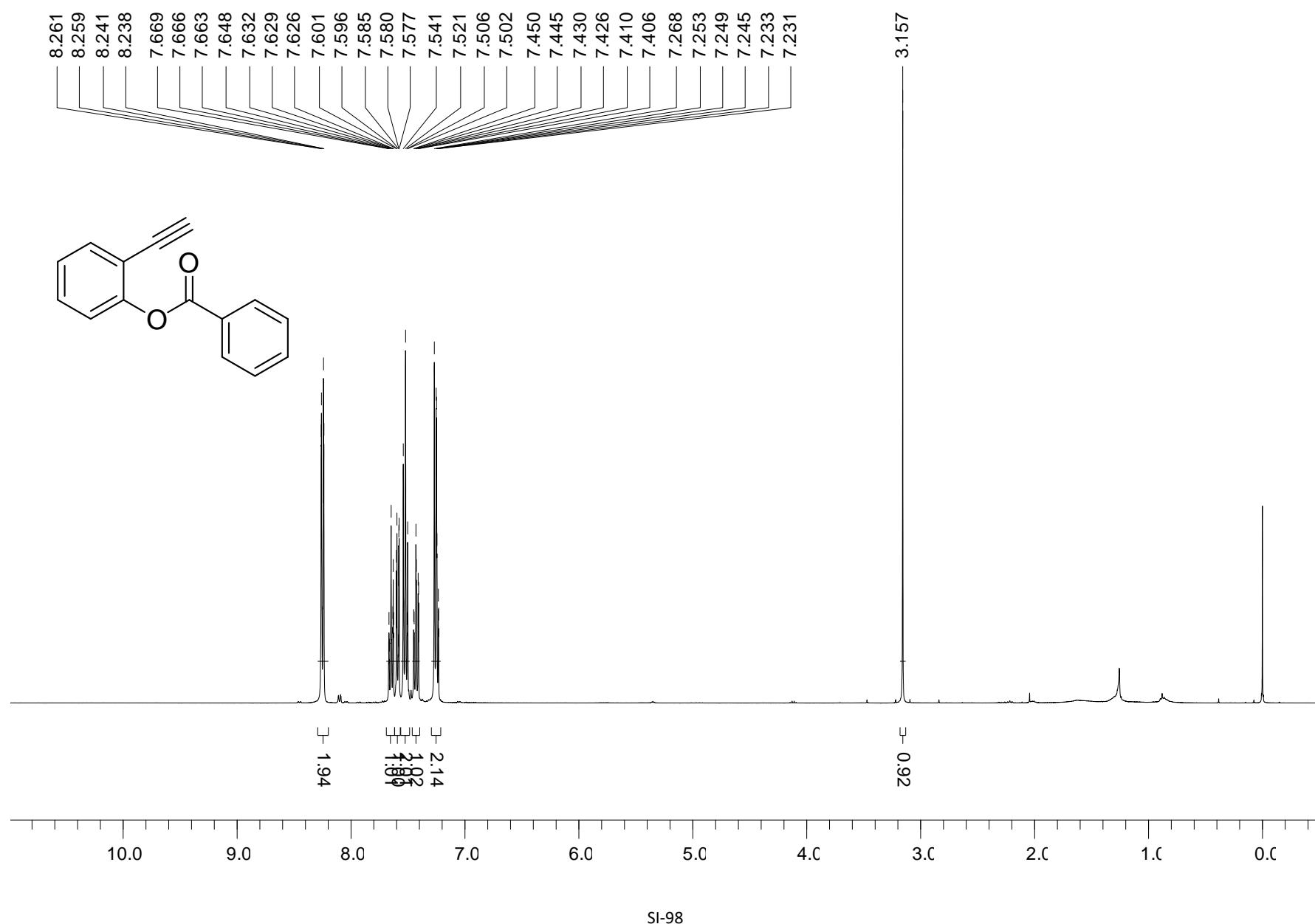
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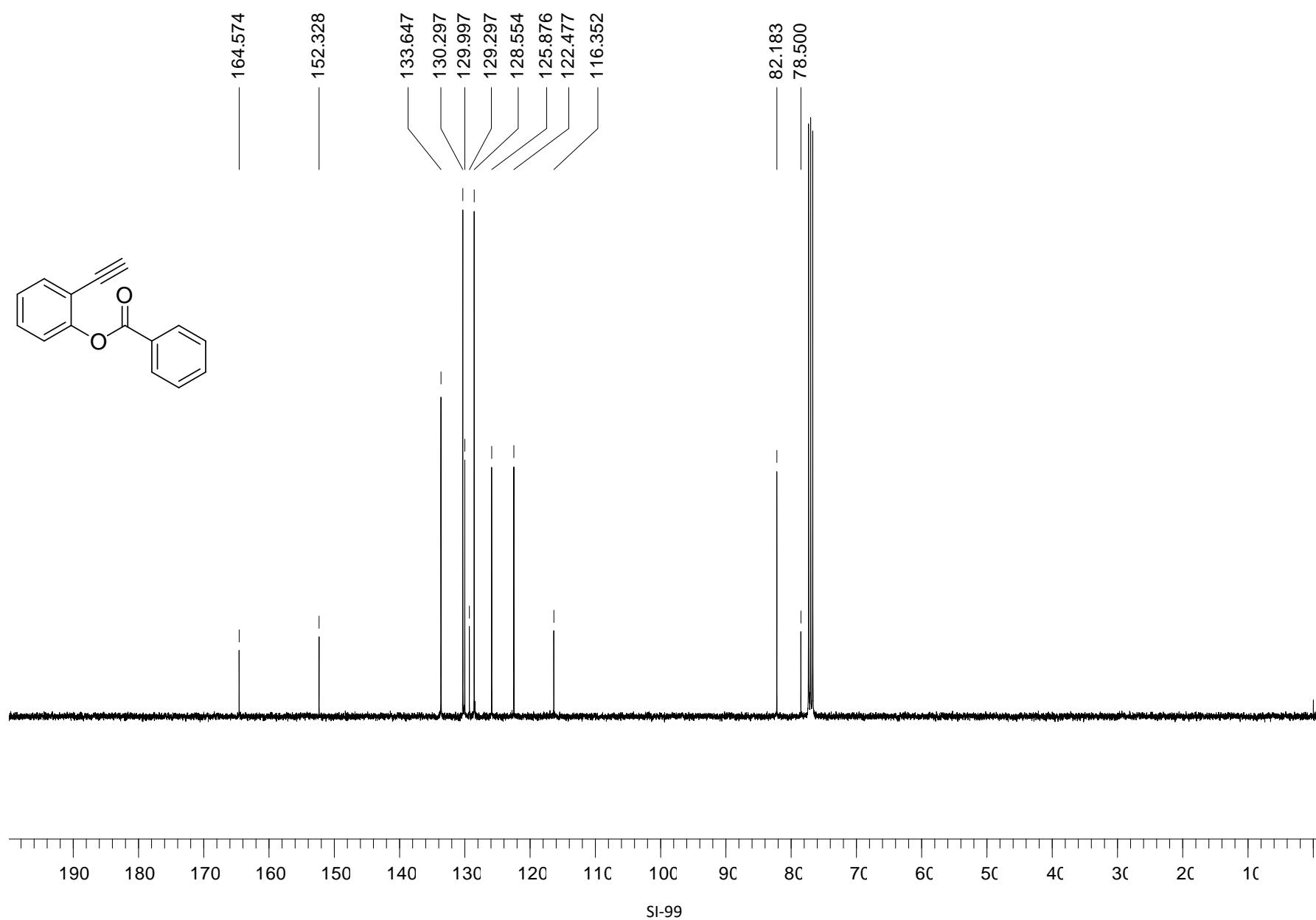
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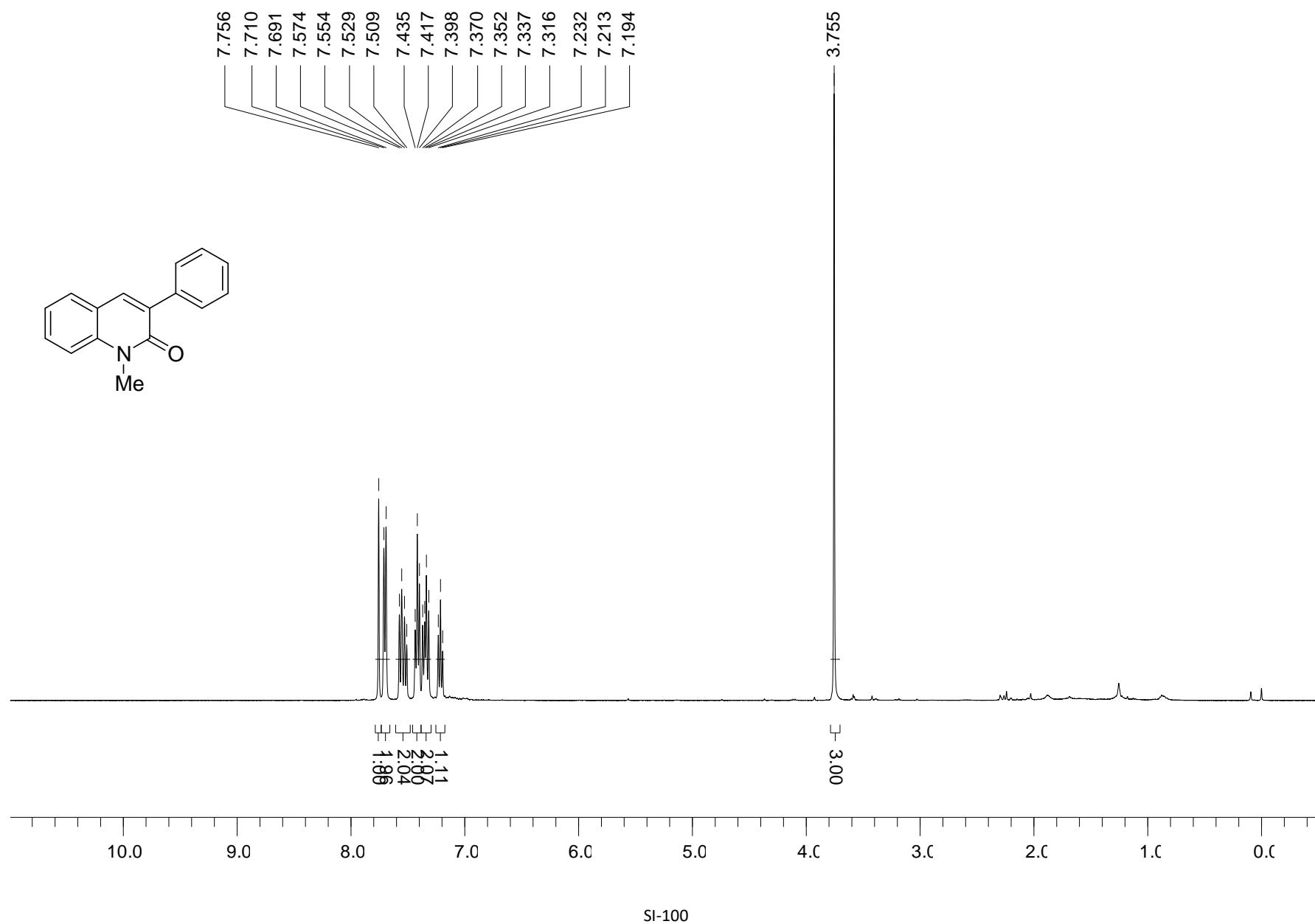
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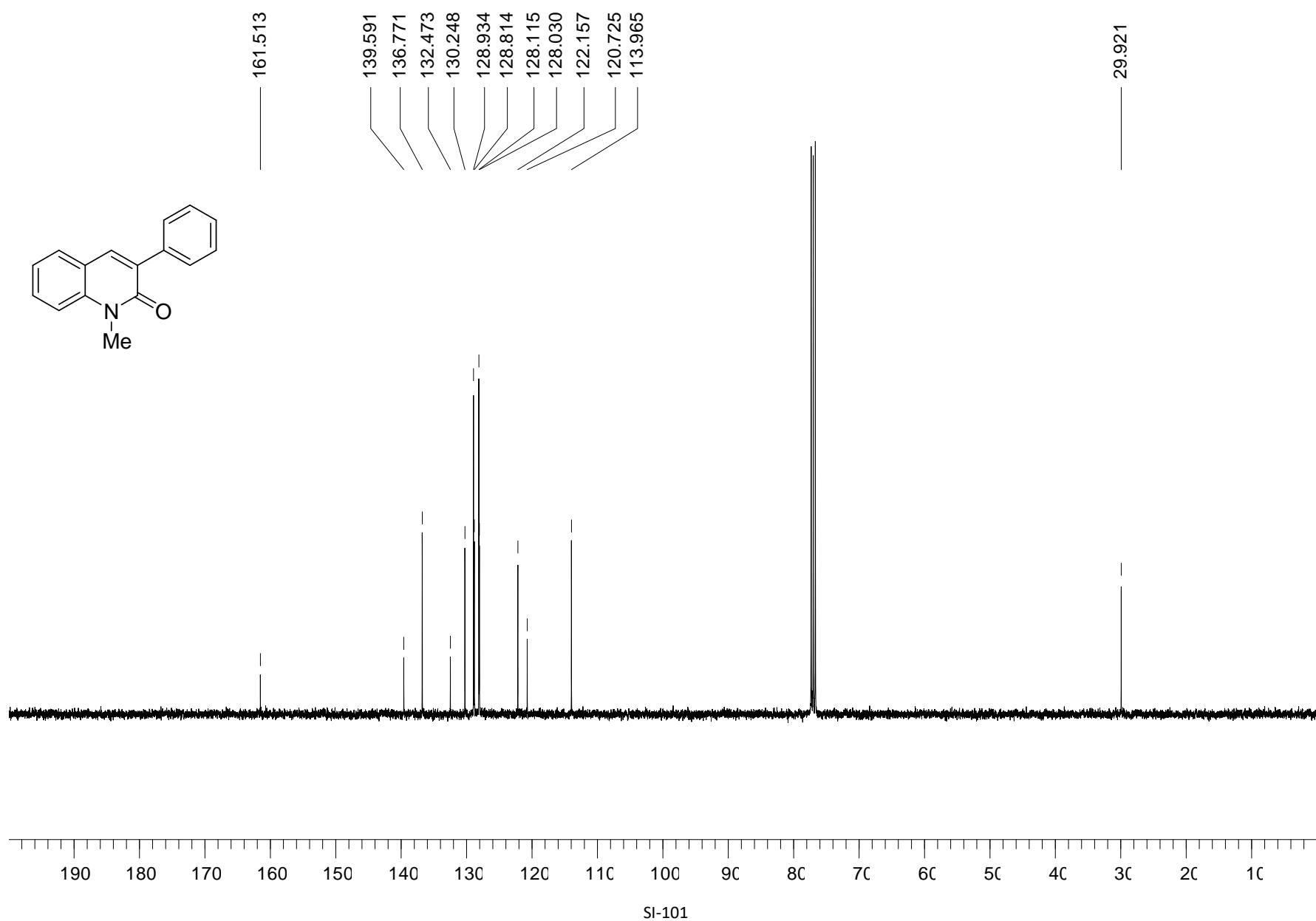
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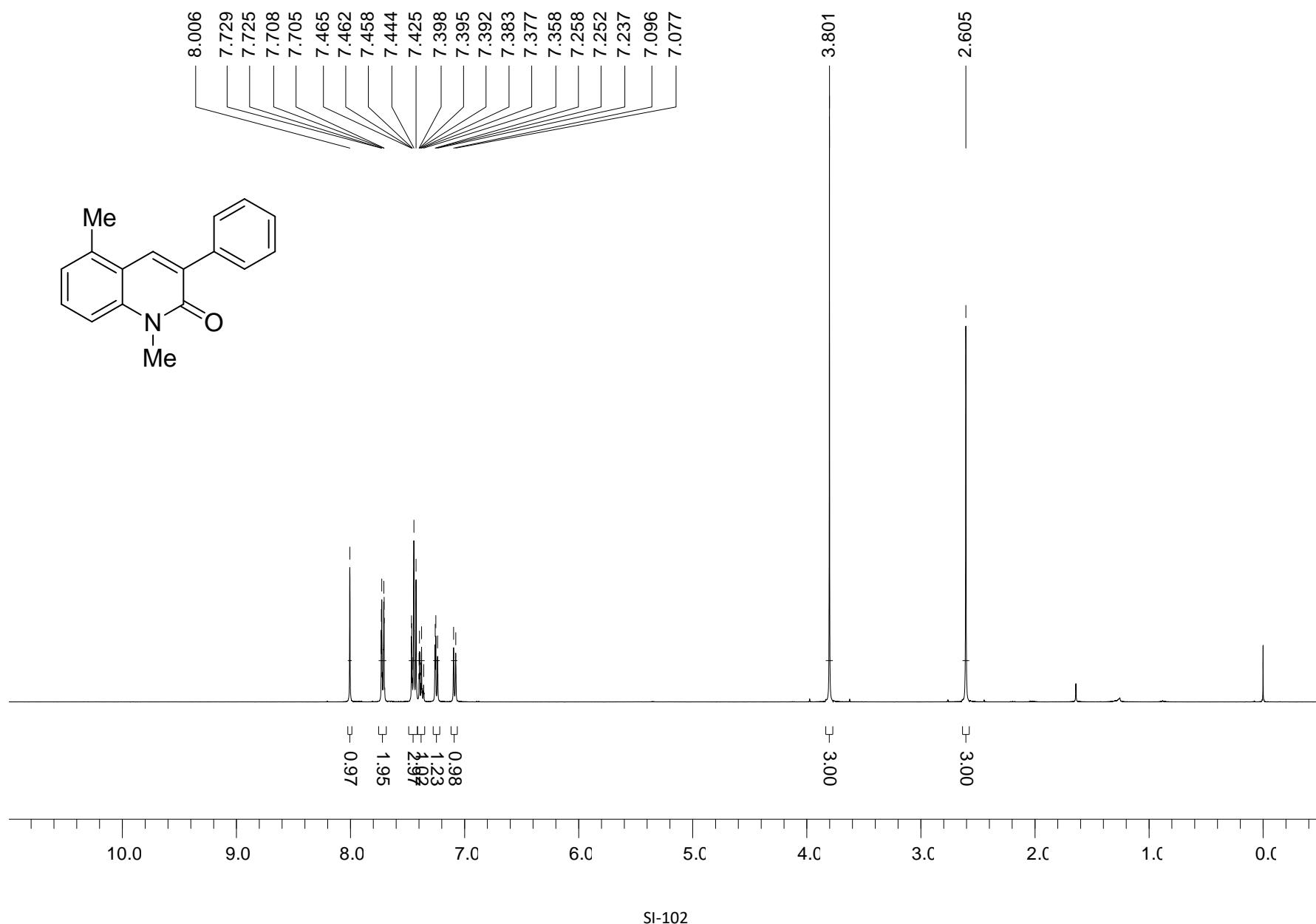
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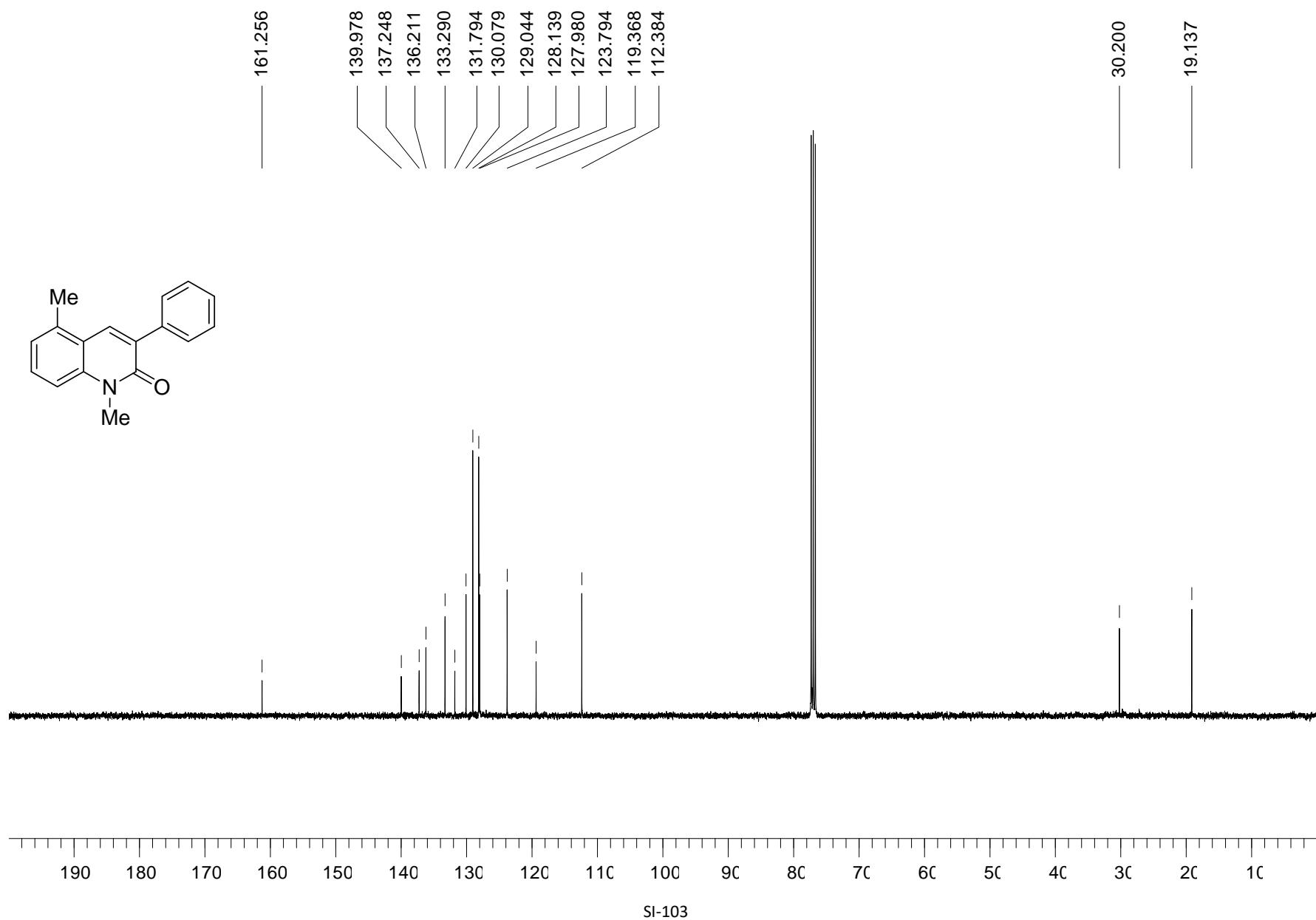
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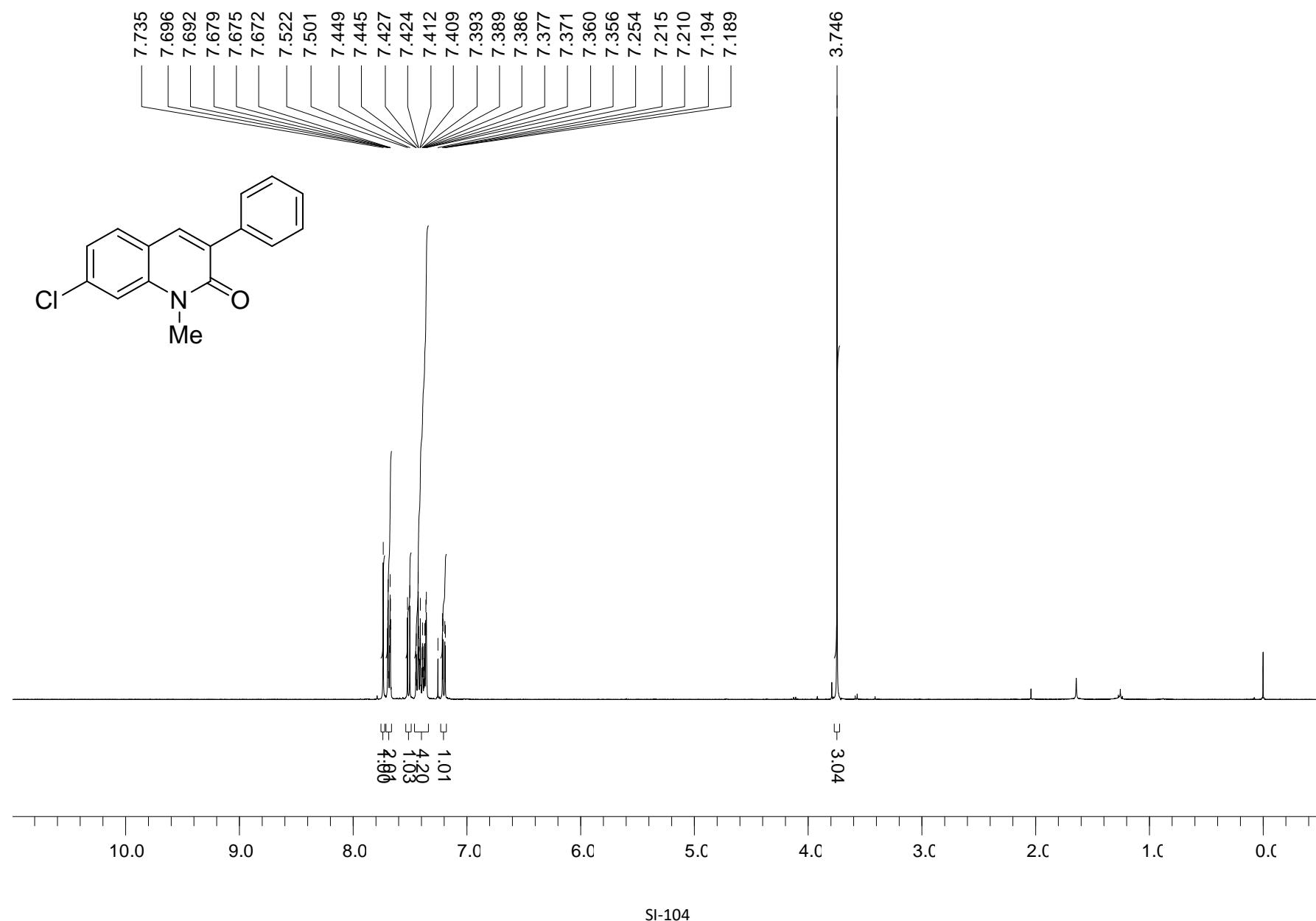
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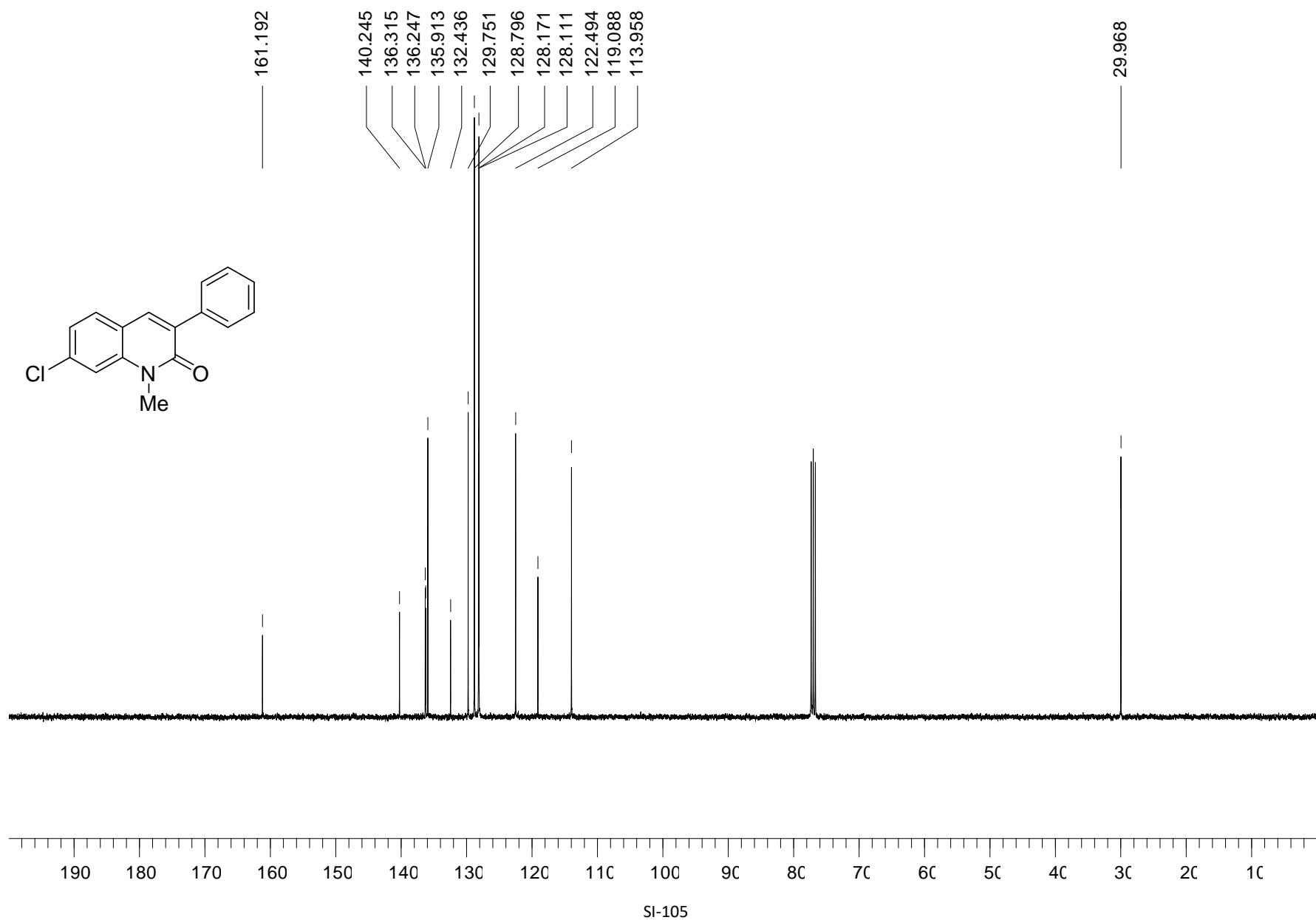
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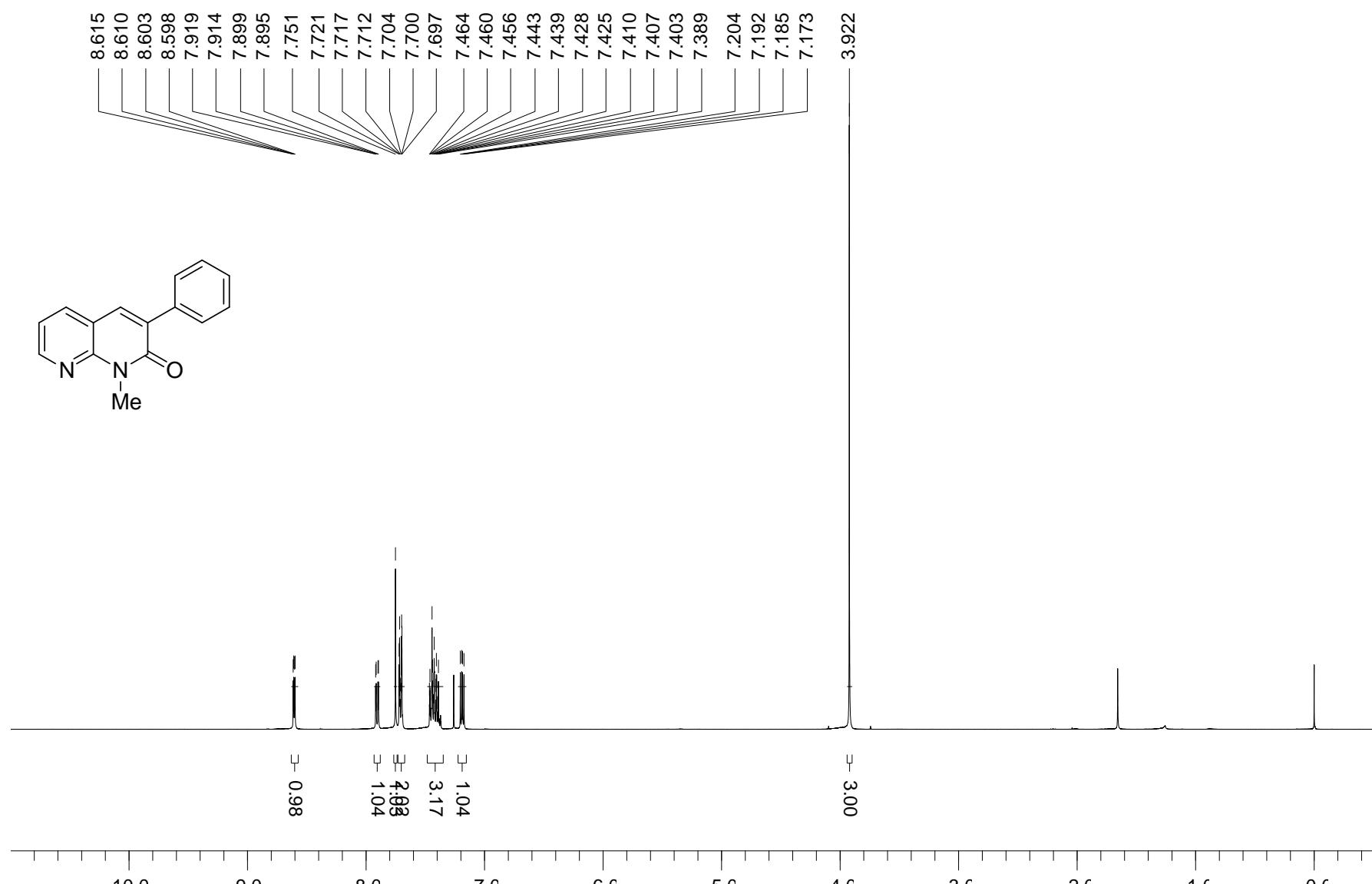
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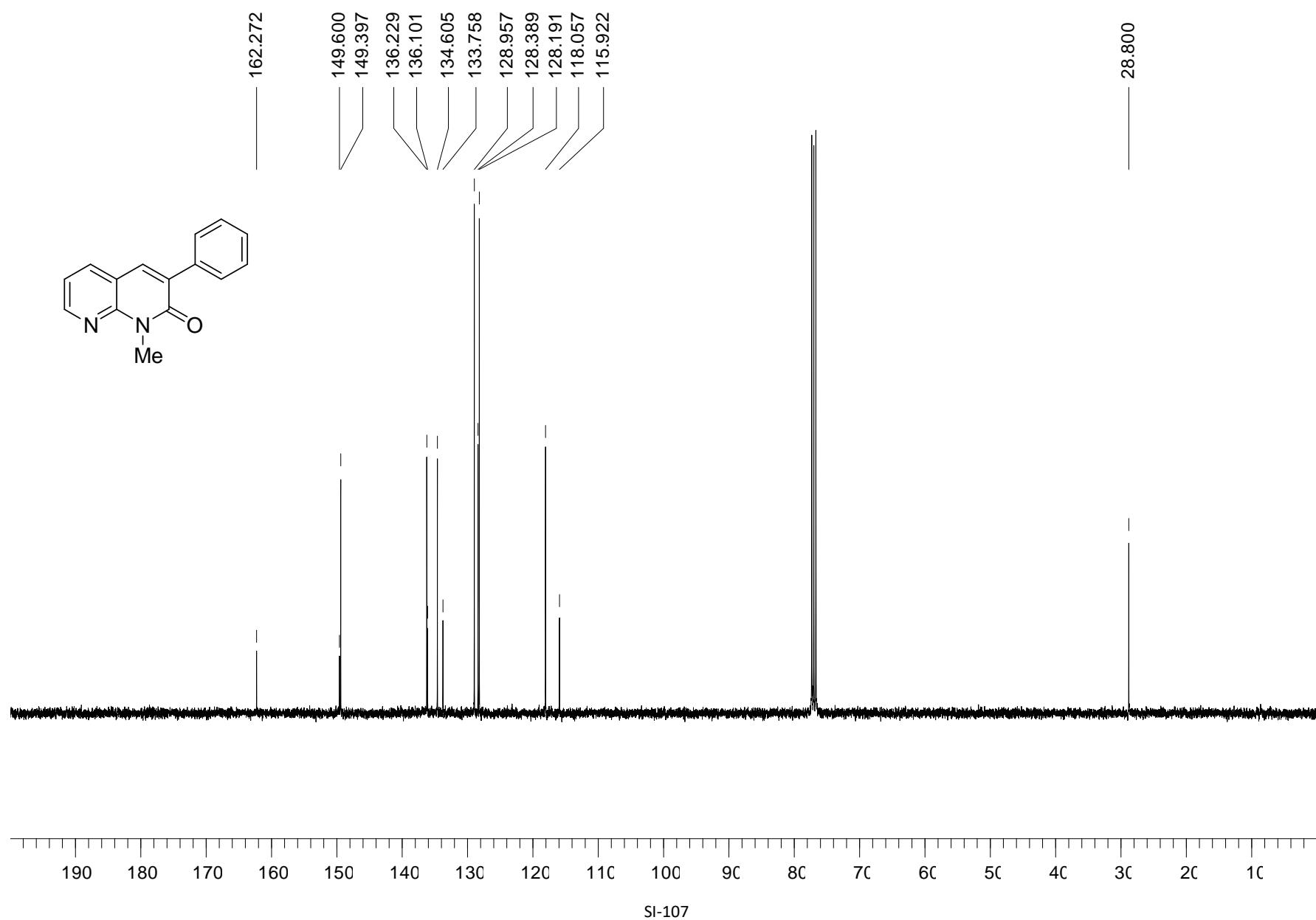
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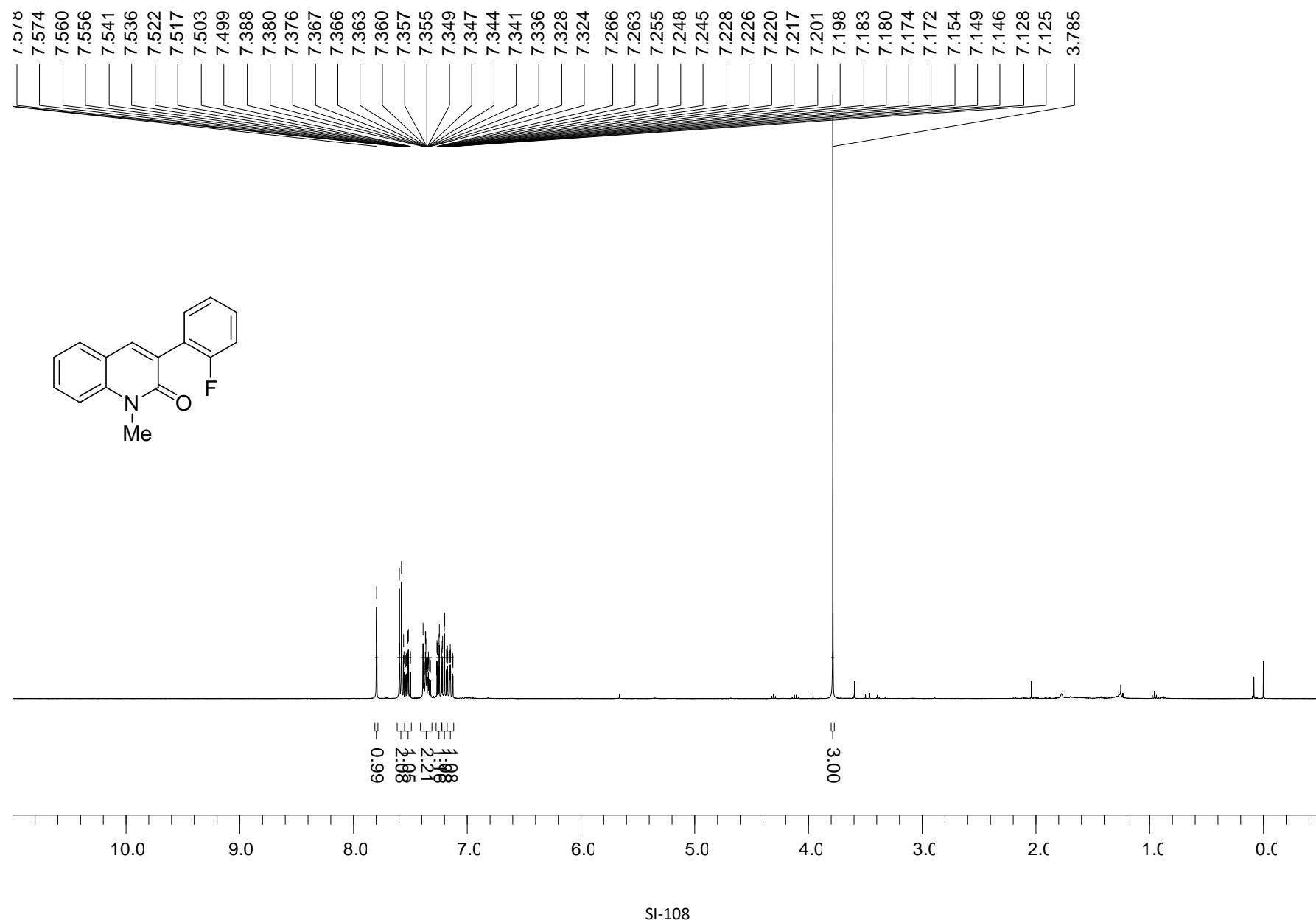
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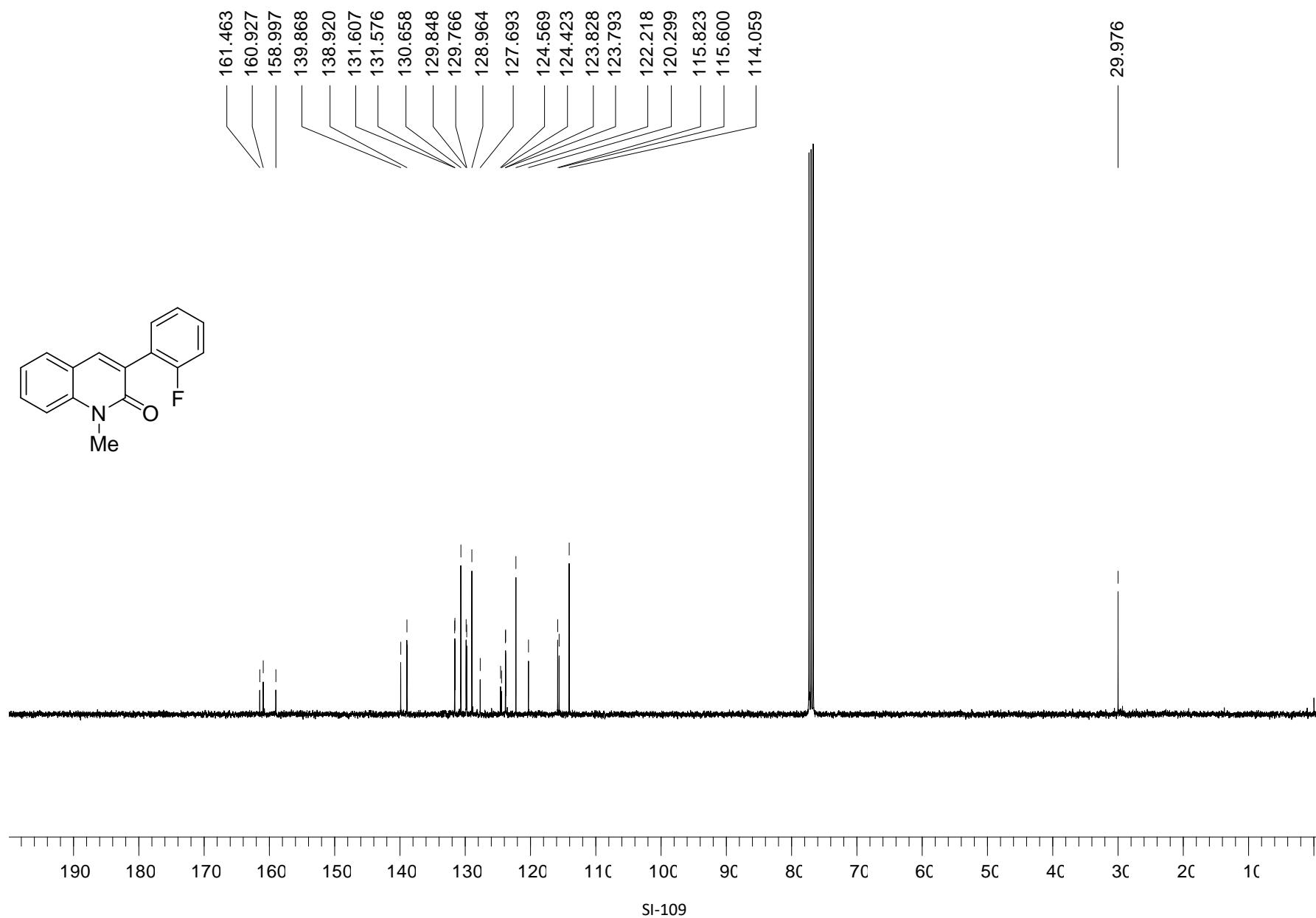
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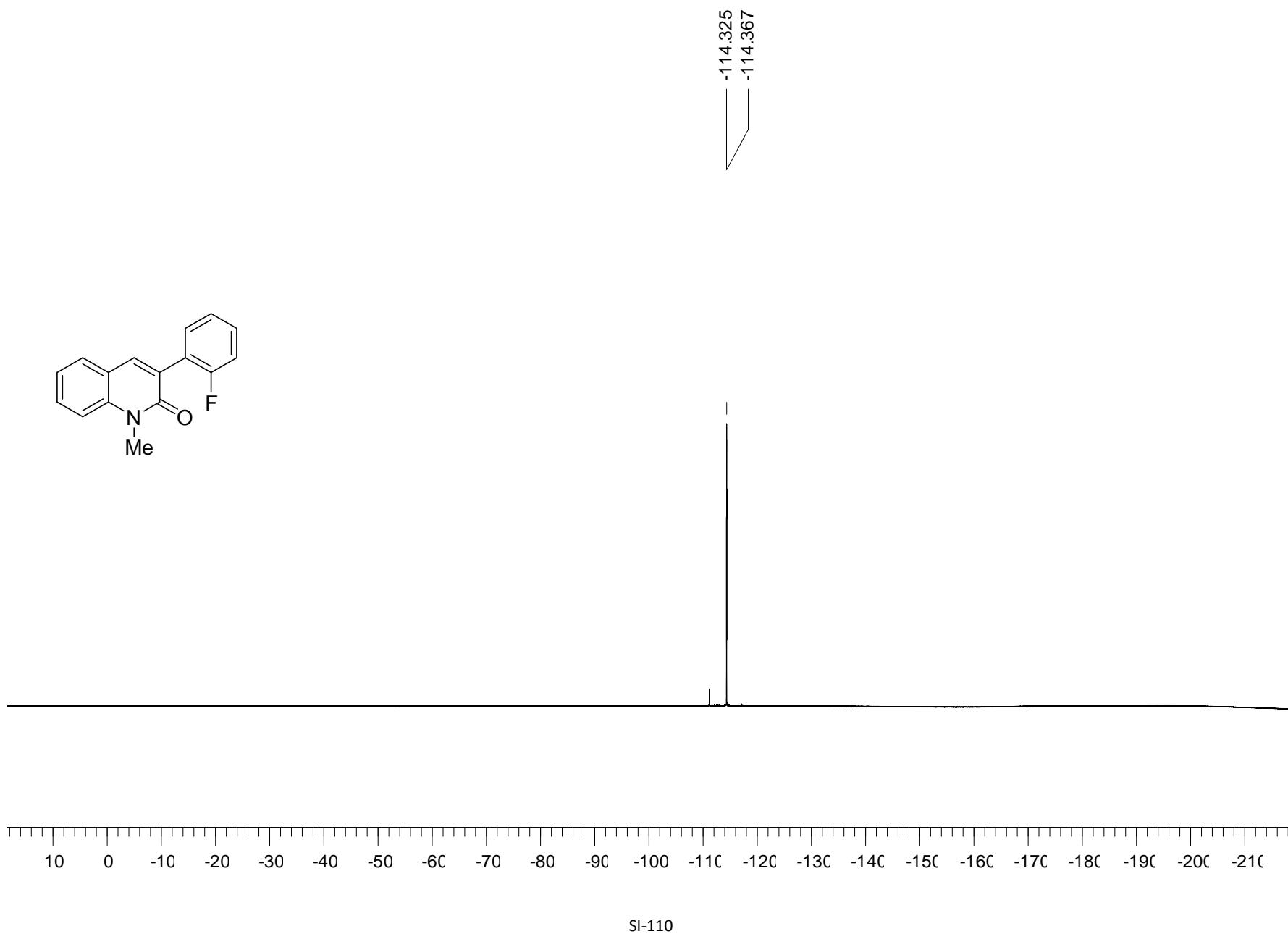
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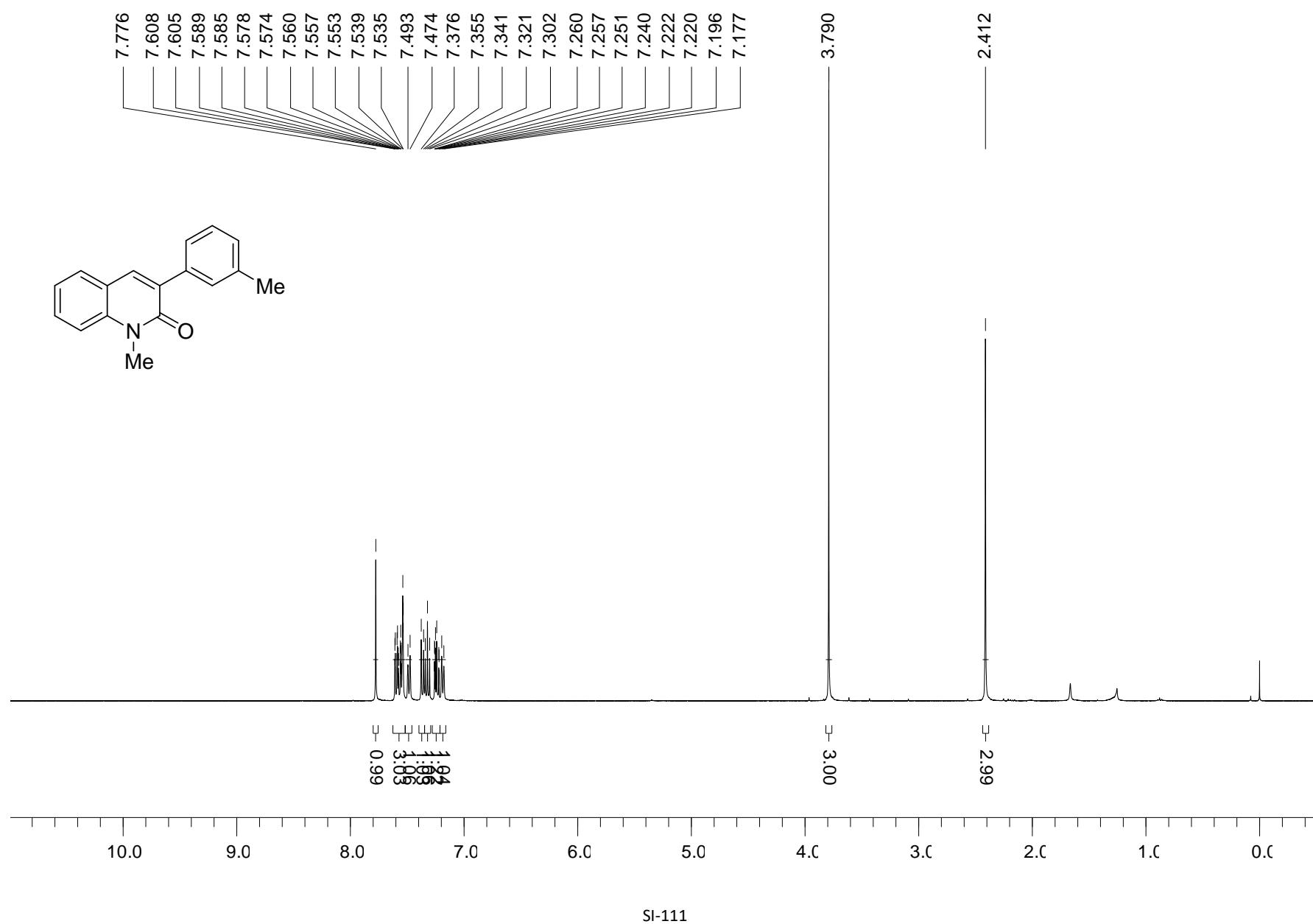
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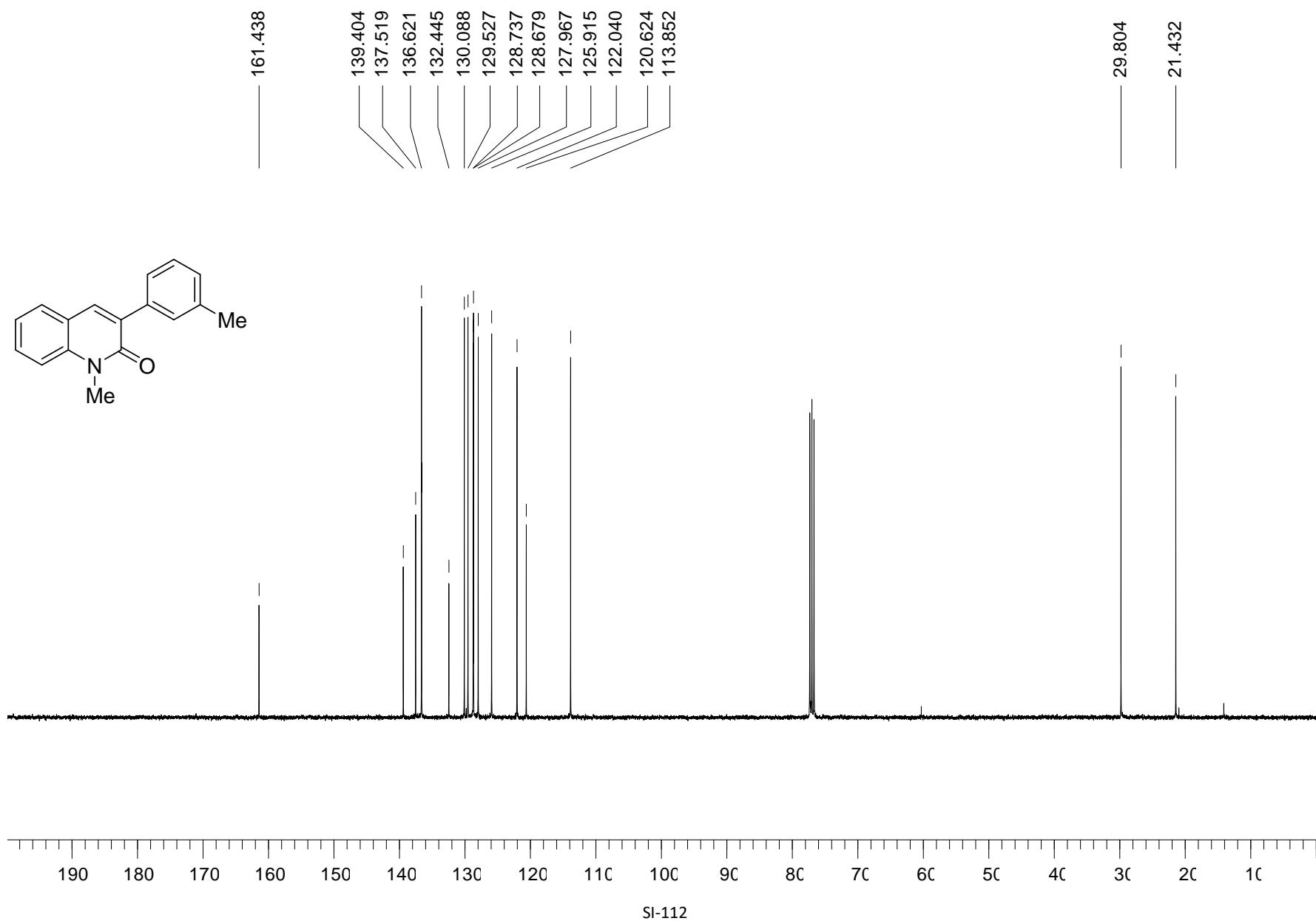
¹⁹F NMR (376 MHz, CDCl₃) spectrum of **3e**



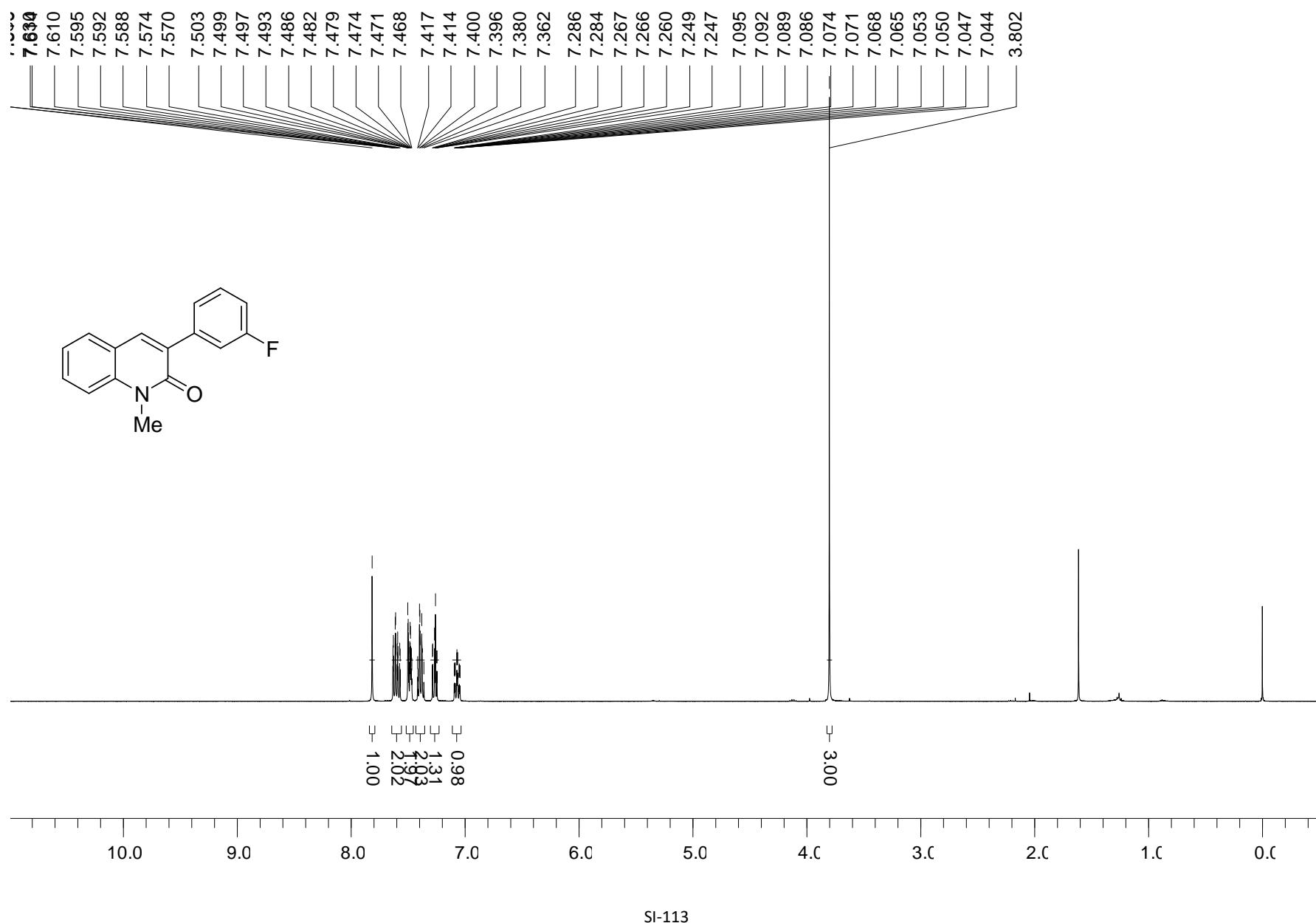
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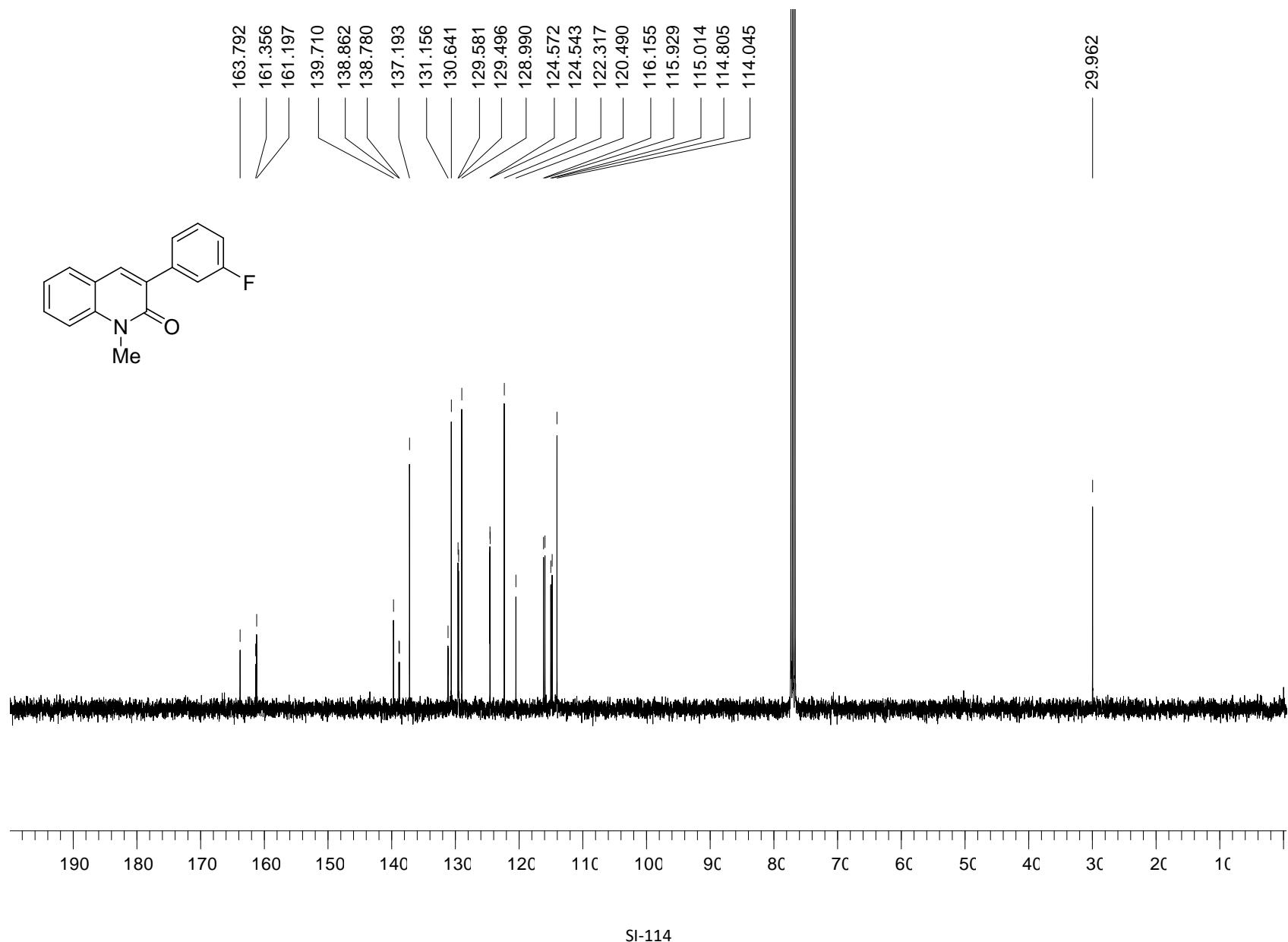
¹³C NMR (100 MHz, CDCl₃) spectrum of **3f**



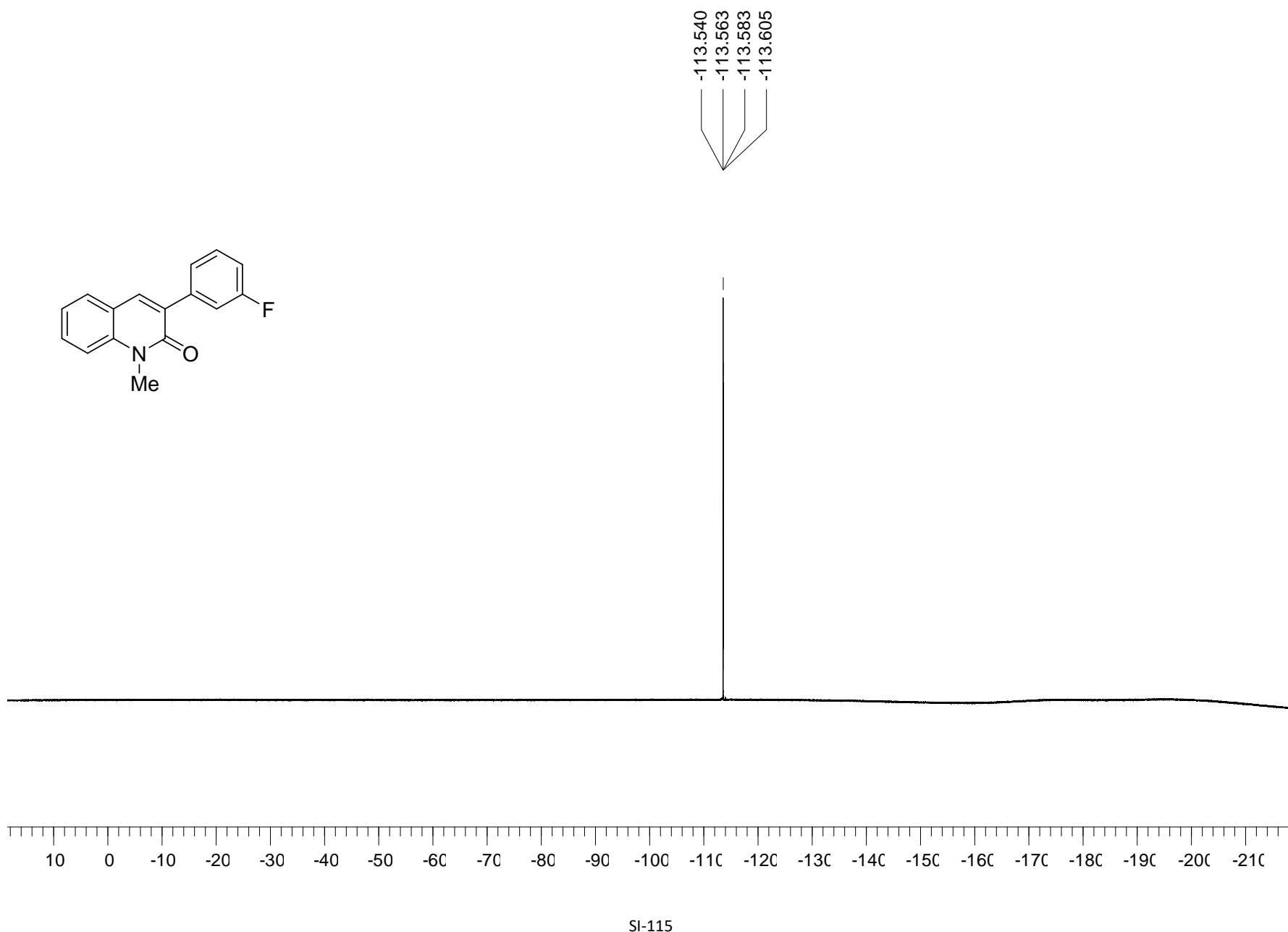
¹H NMR (400 MHz, CDCl₃) spectrum of **3g**



¹³C NMR (100 MHz, CDCl₃) spectrum of **3g**

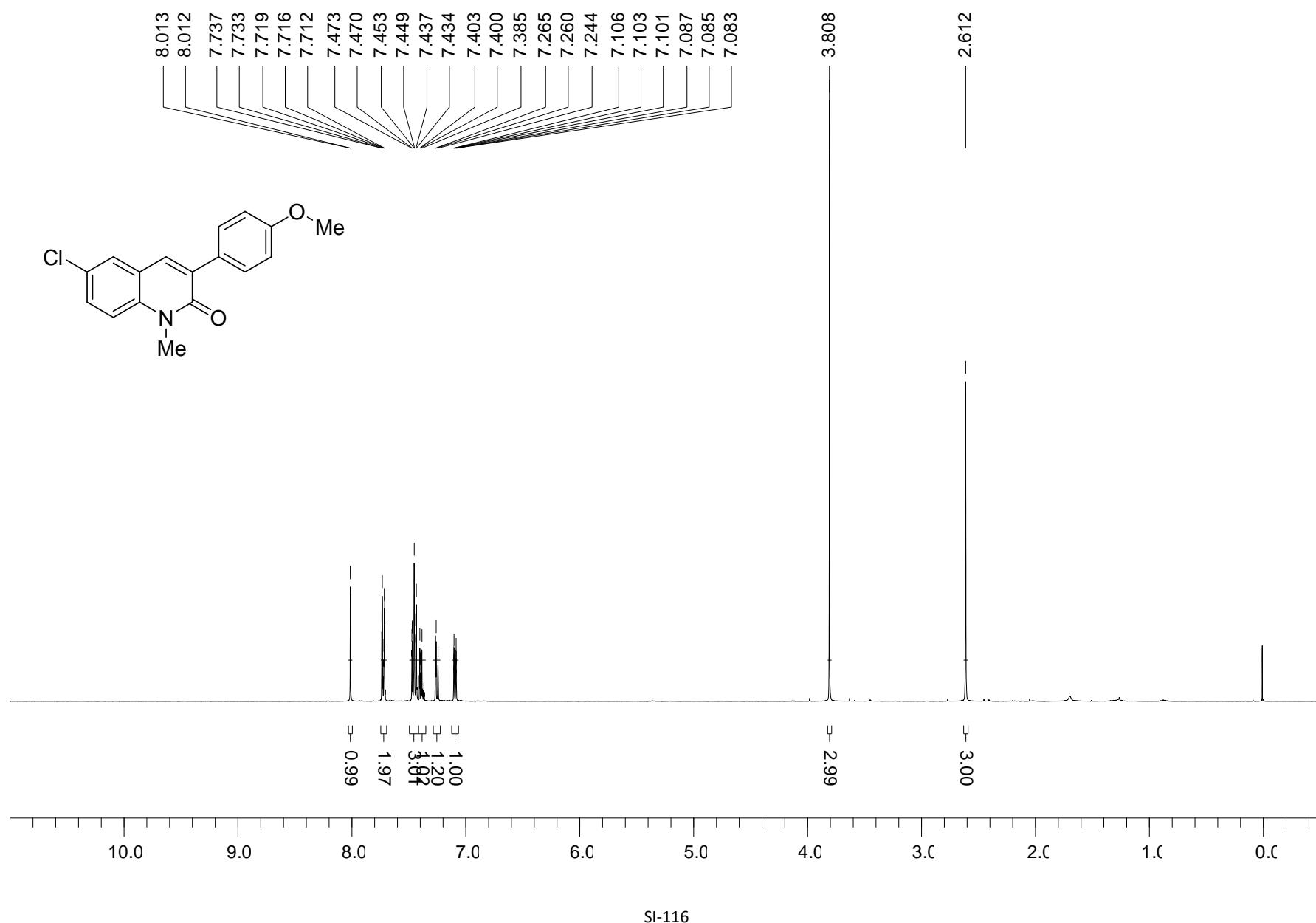


¹⁹F NMR (376 MHz, CDCl₃) spectrum of **3g**

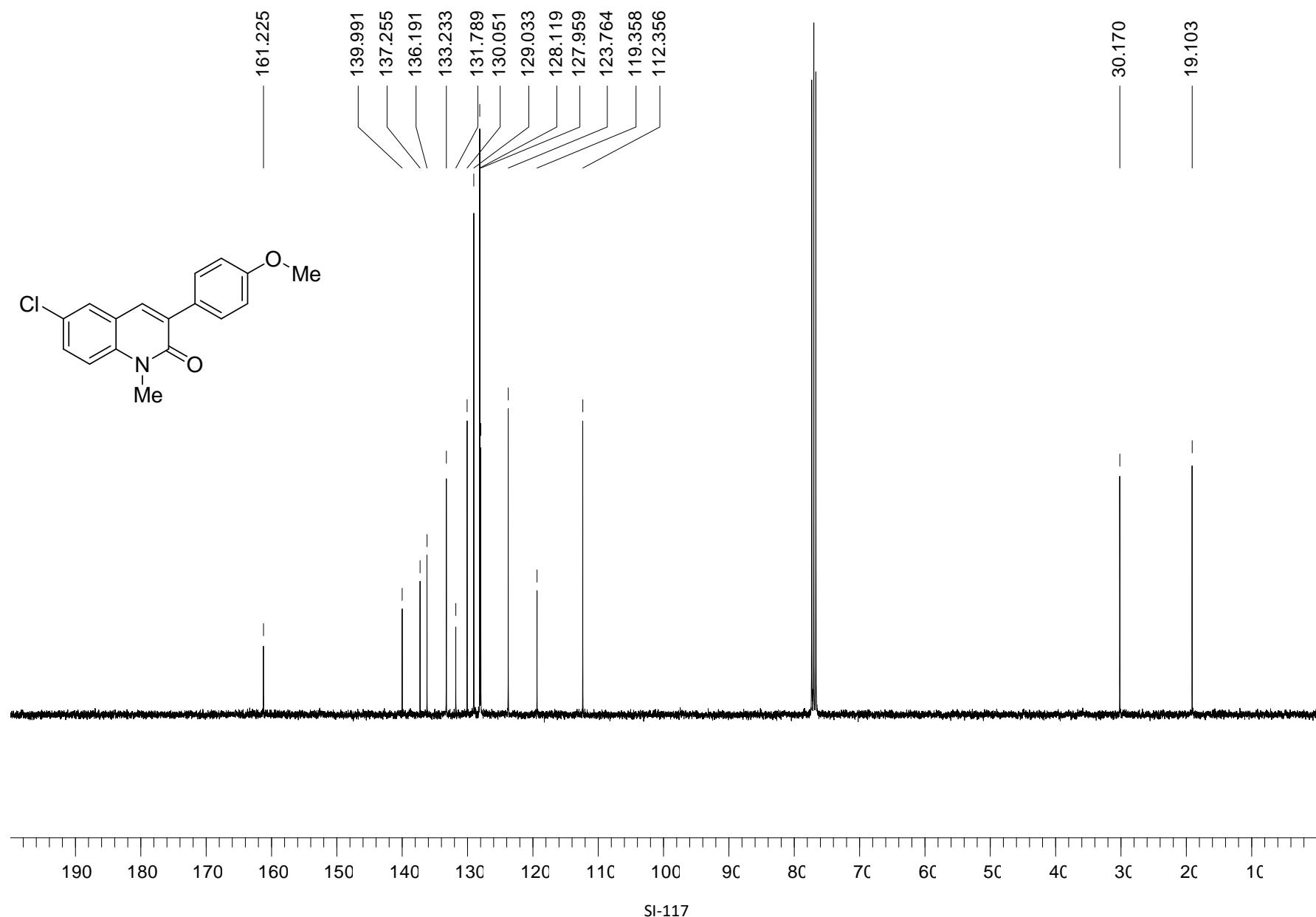


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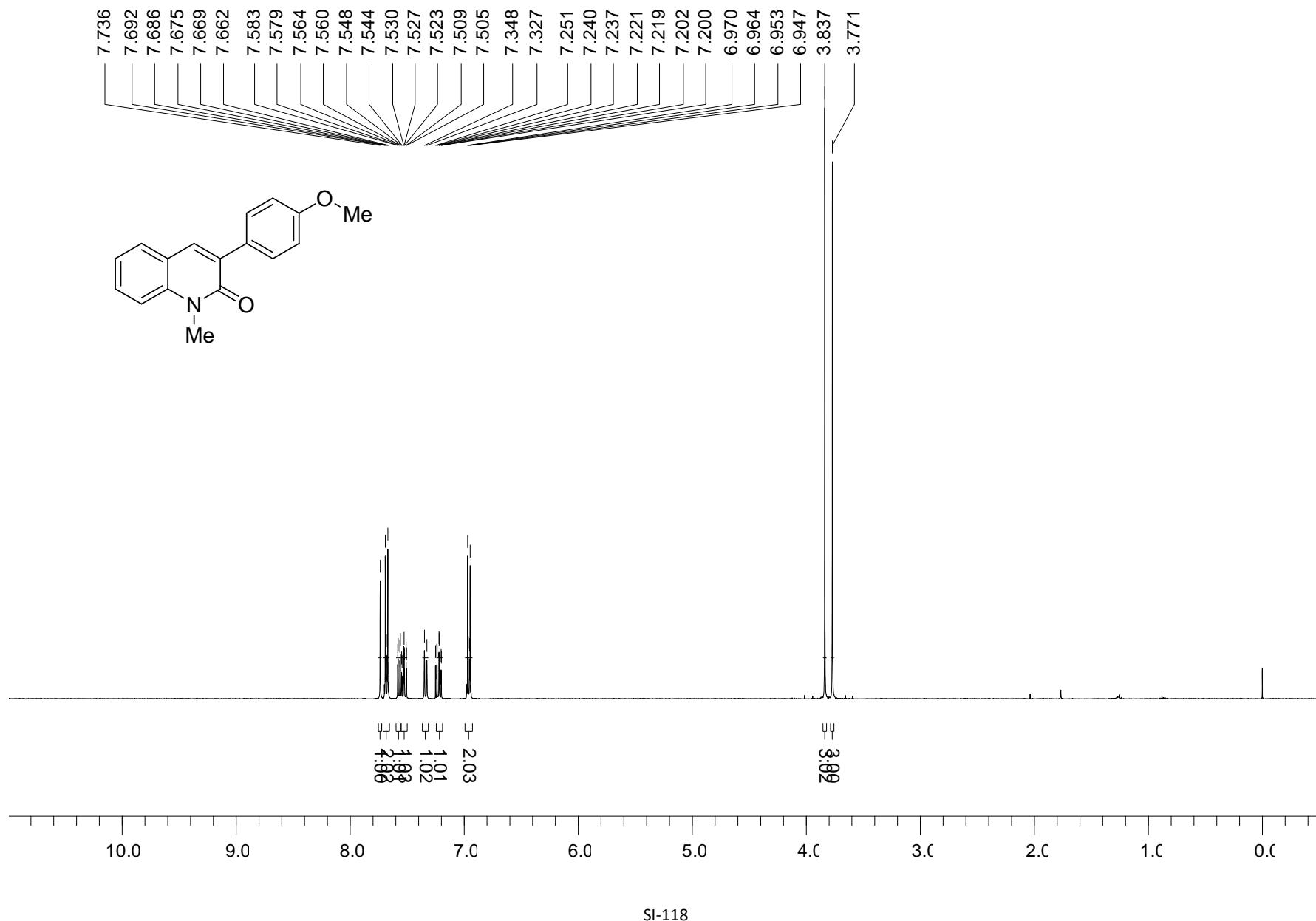
¹H NMR (400 MHz, CDCl₃) spectrum of **3h**



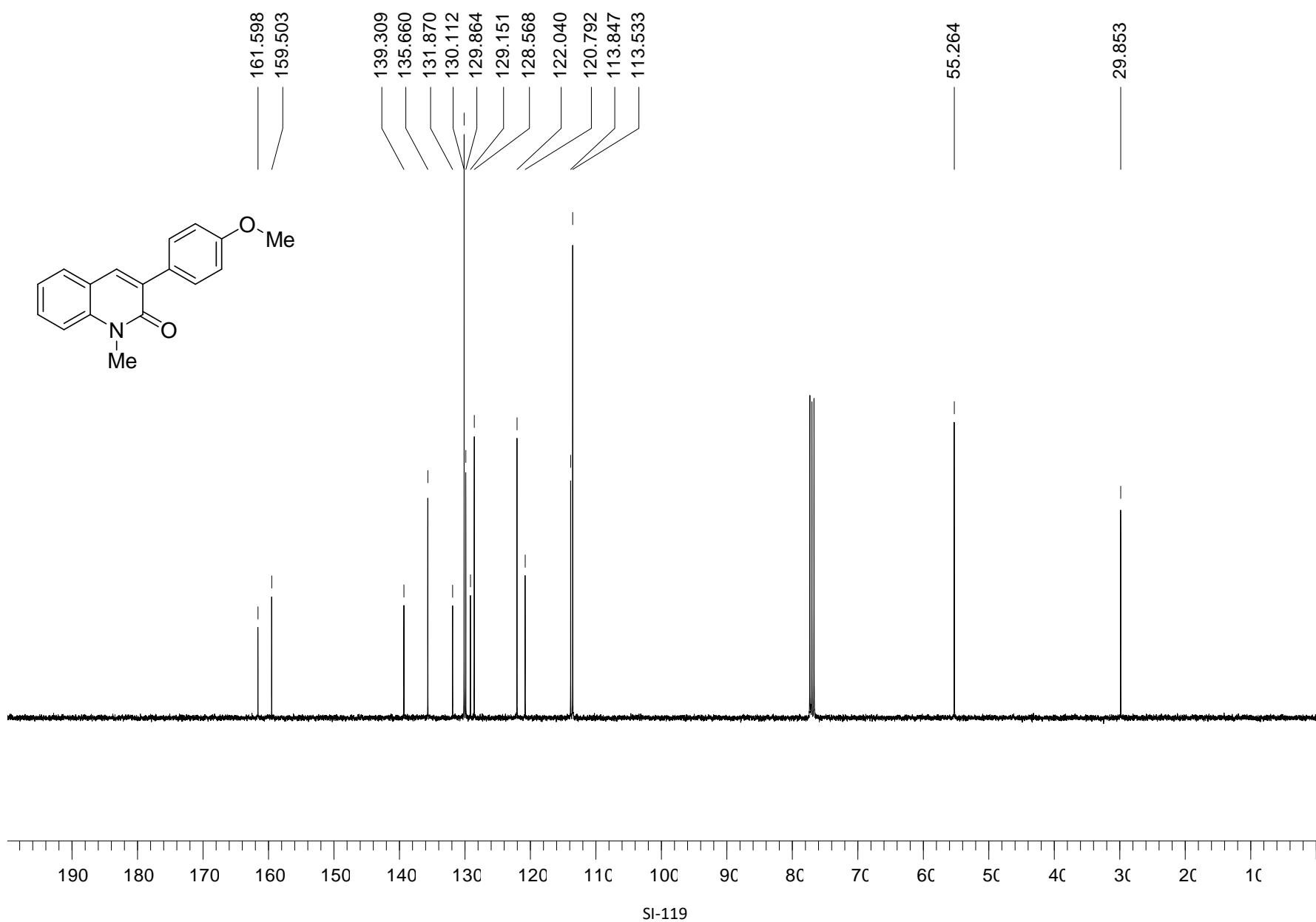
¹³C NMR (100 MHz, CDCl₃) spectrum of **3h**



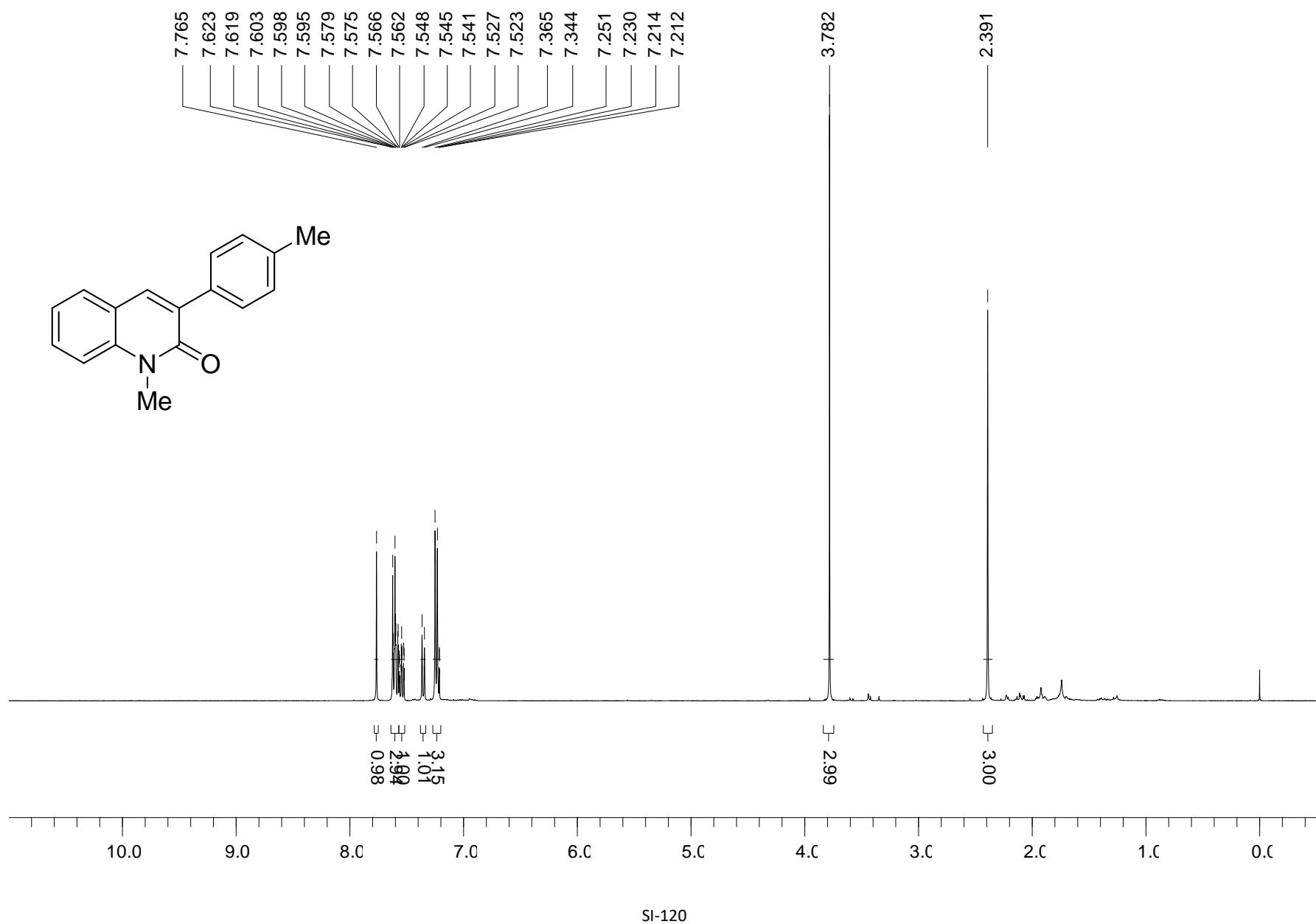
¹H NMR (400 MHz, CDCl₃) spectrum of **3i**



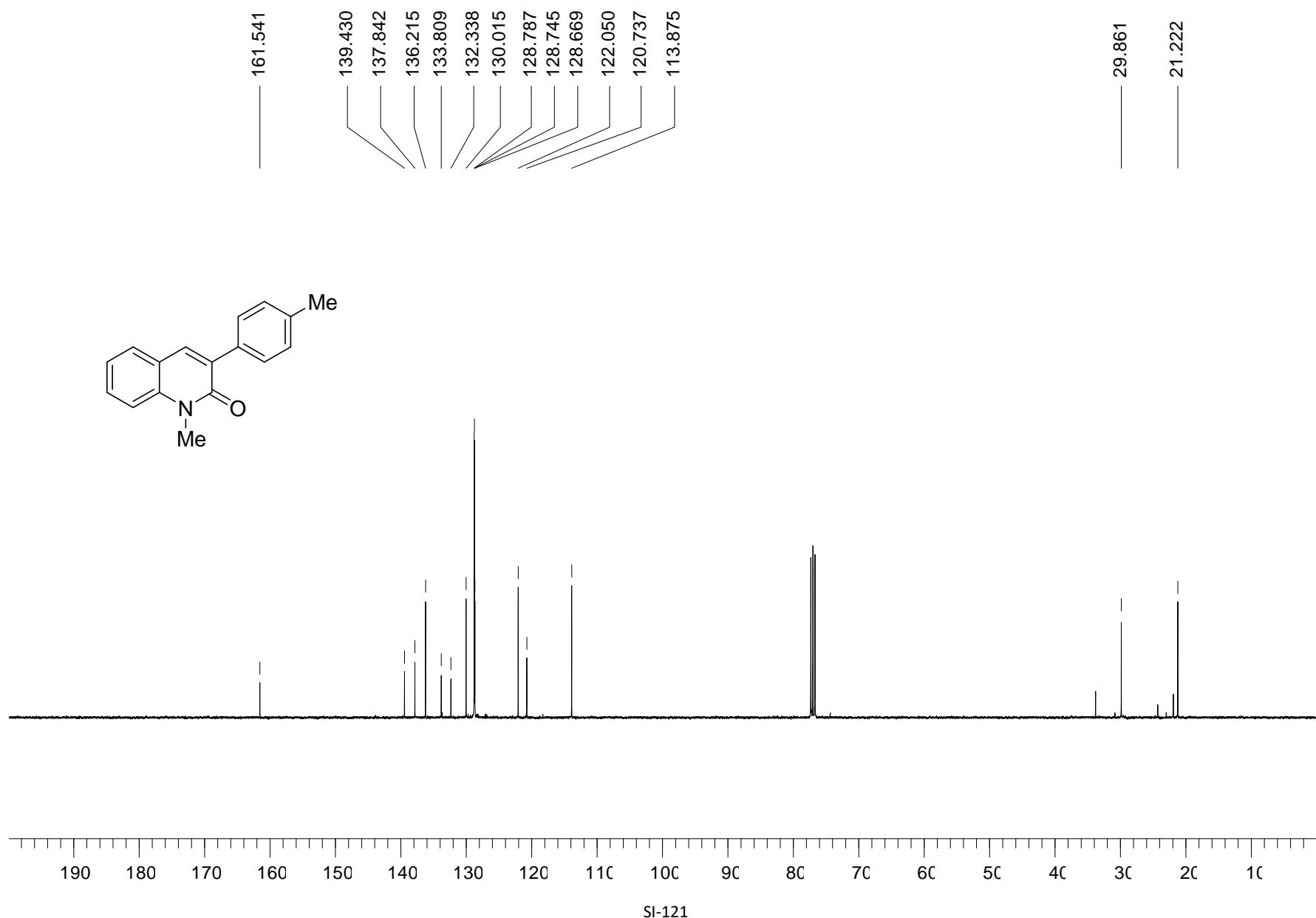
¹³C NMR (100 MHz, CDCl₃) spectrum of **3i**



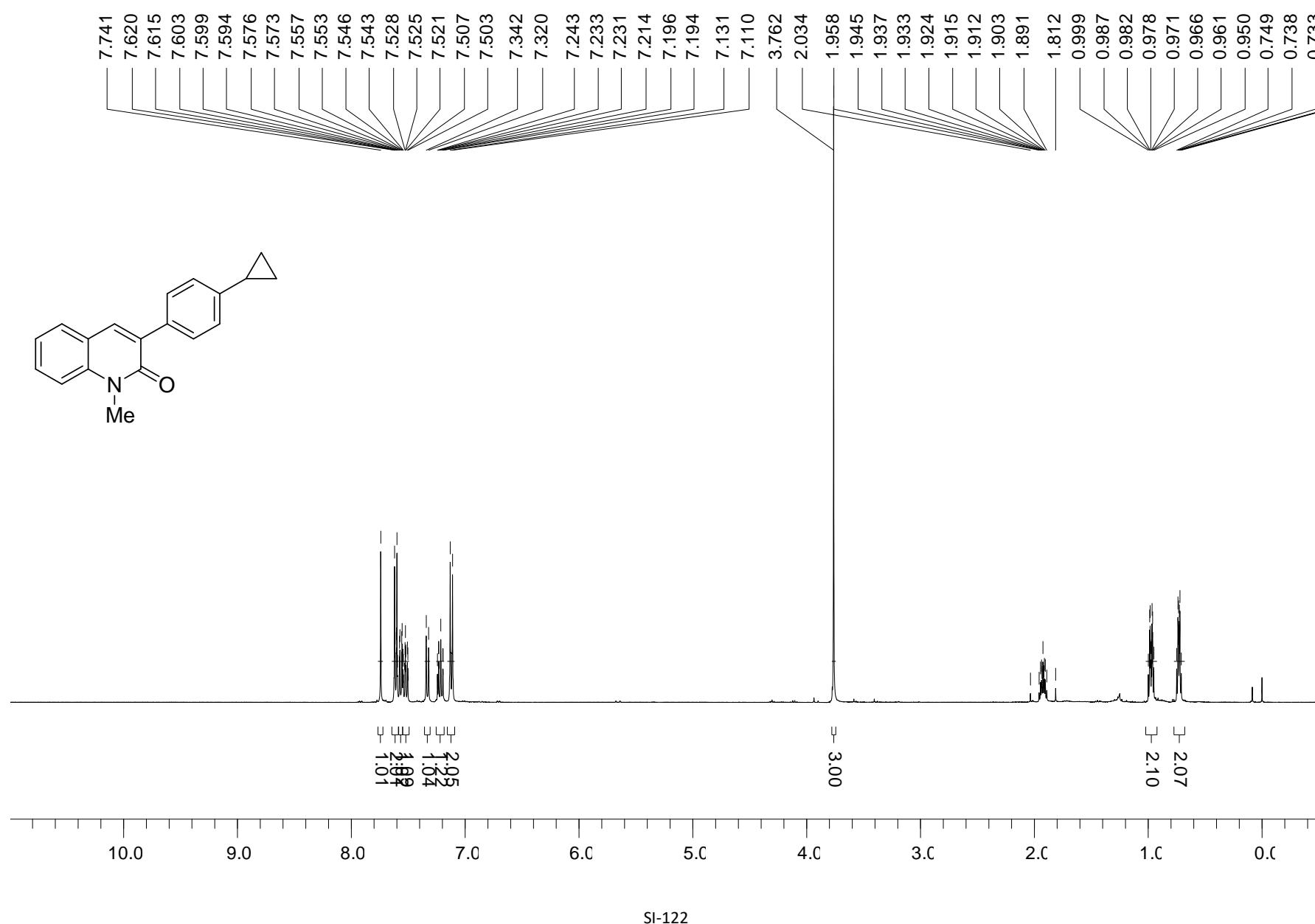
¹H NMR (400 MHz, CDCl₃) spectrum of **3j**



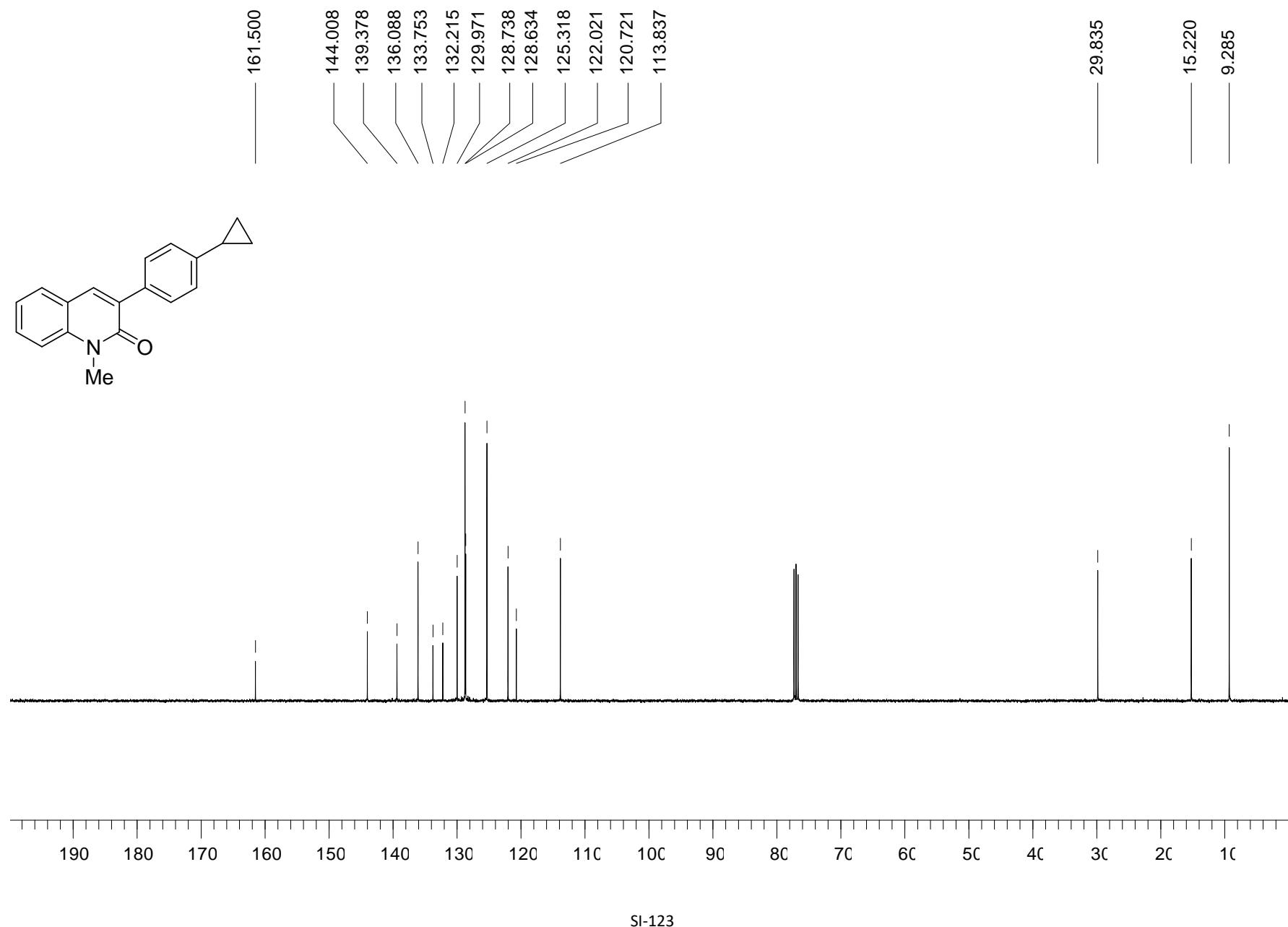
¹³C NMR (100 MHz, CDCl₃) spectrum of **3j**



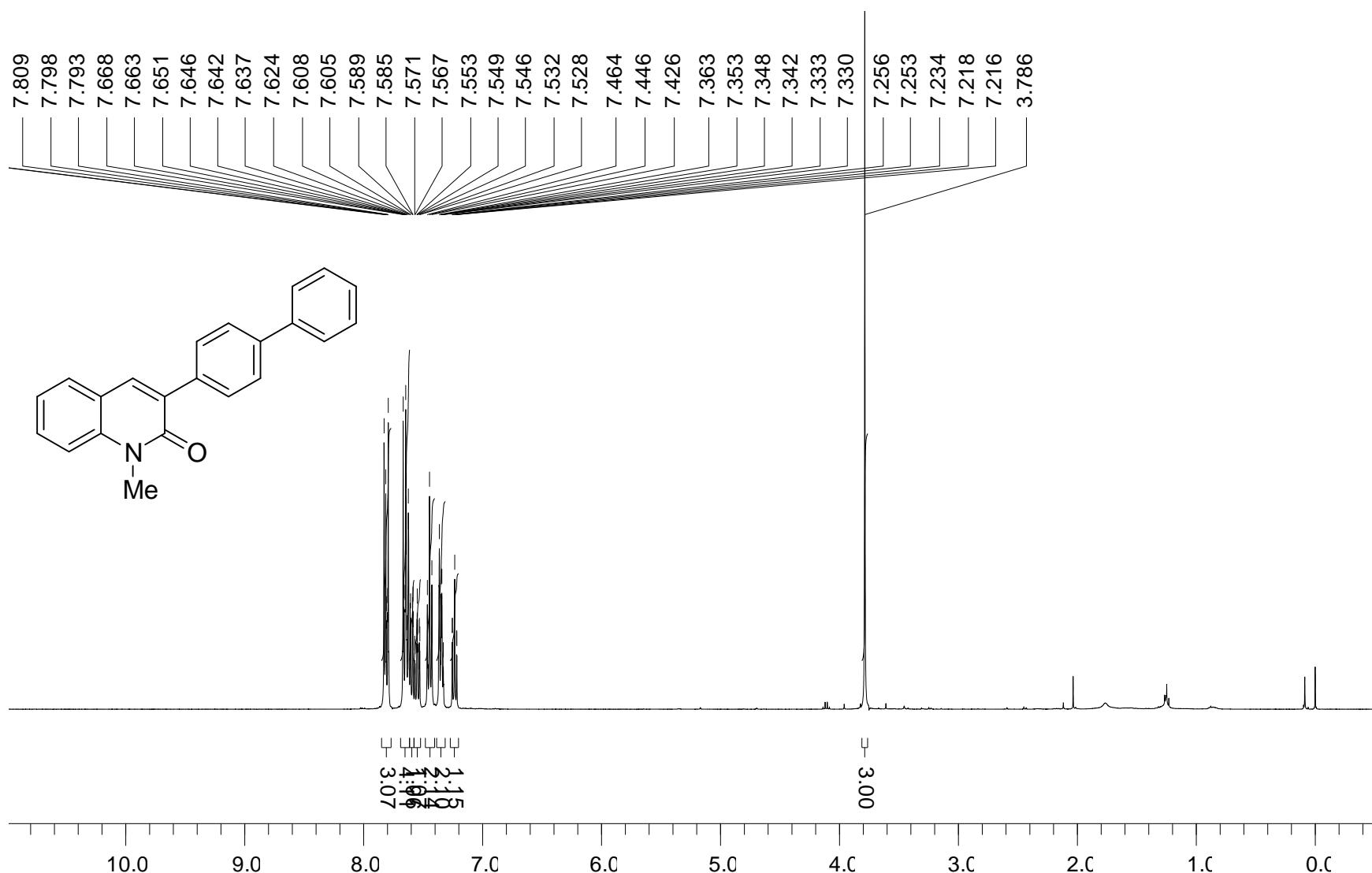
¹H NMR (400 MHz, CDCl₃) spectrum of **3k**



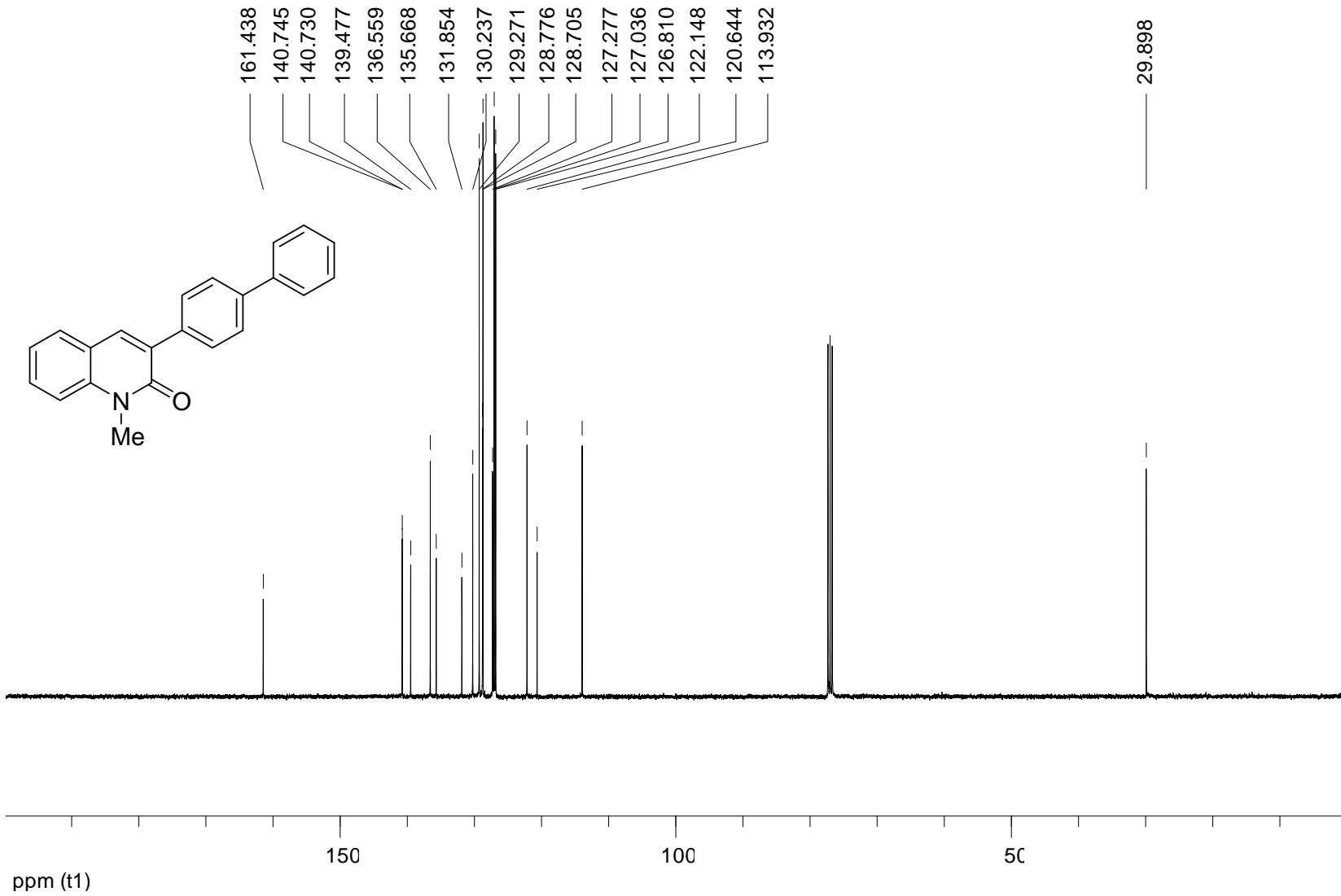
¹³C NMR (100 MHz, CDCl₃) spectrum of **3k**



¹H NMR (400 MHz, CDCl₃) spectrum of **3l**

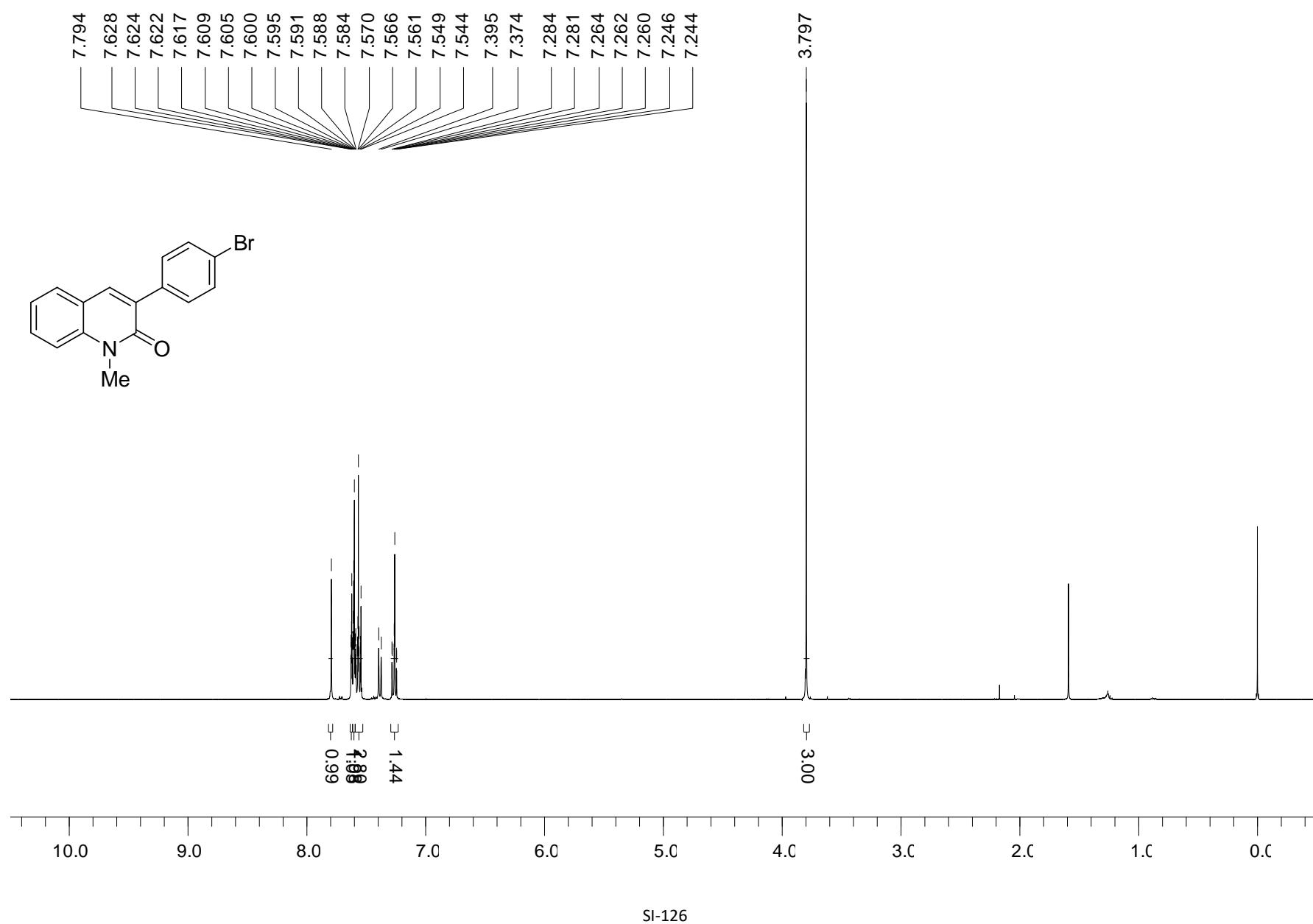


¹³C NMR (100 MHz, CDCl₃) spectrum of **3I**

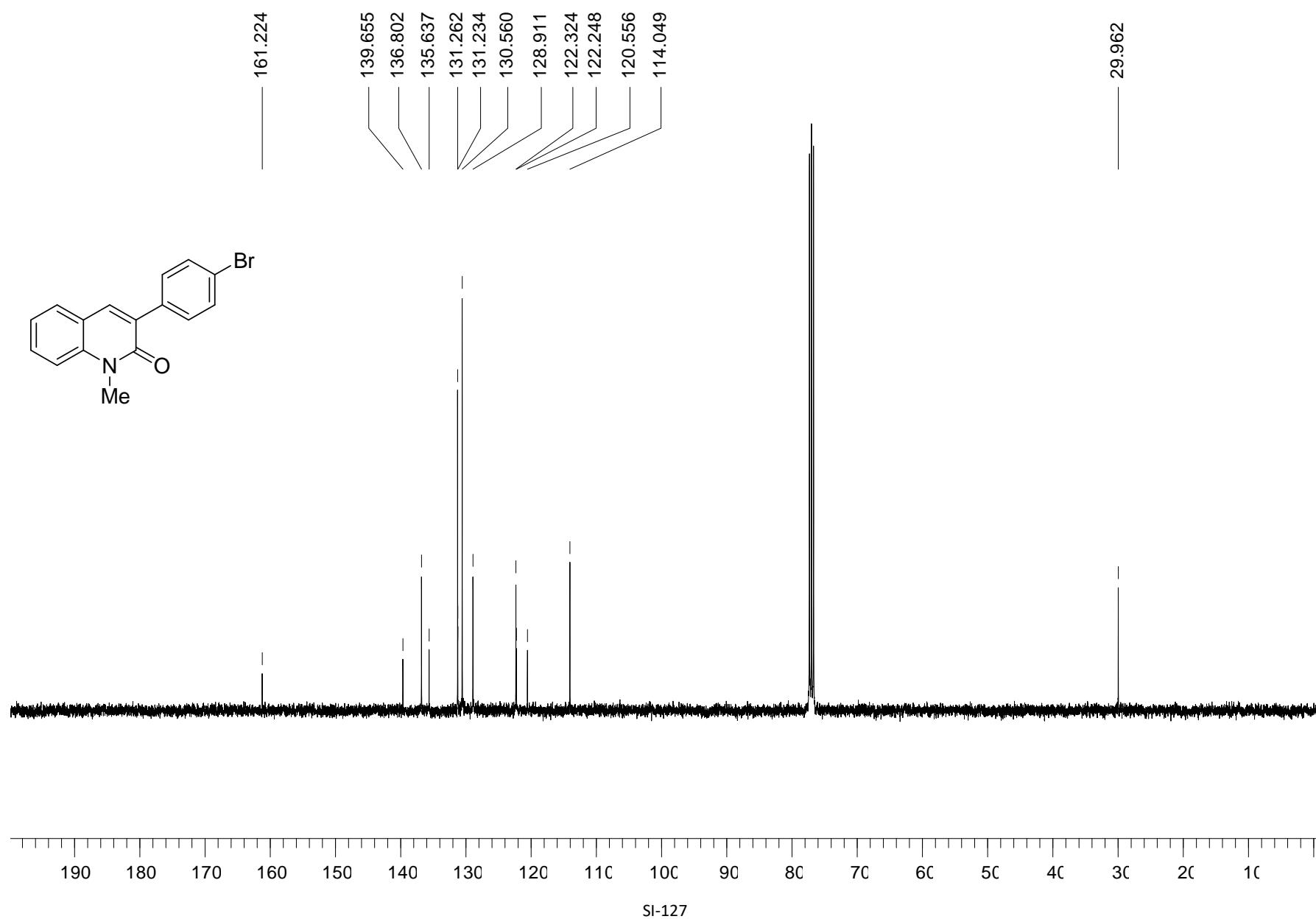


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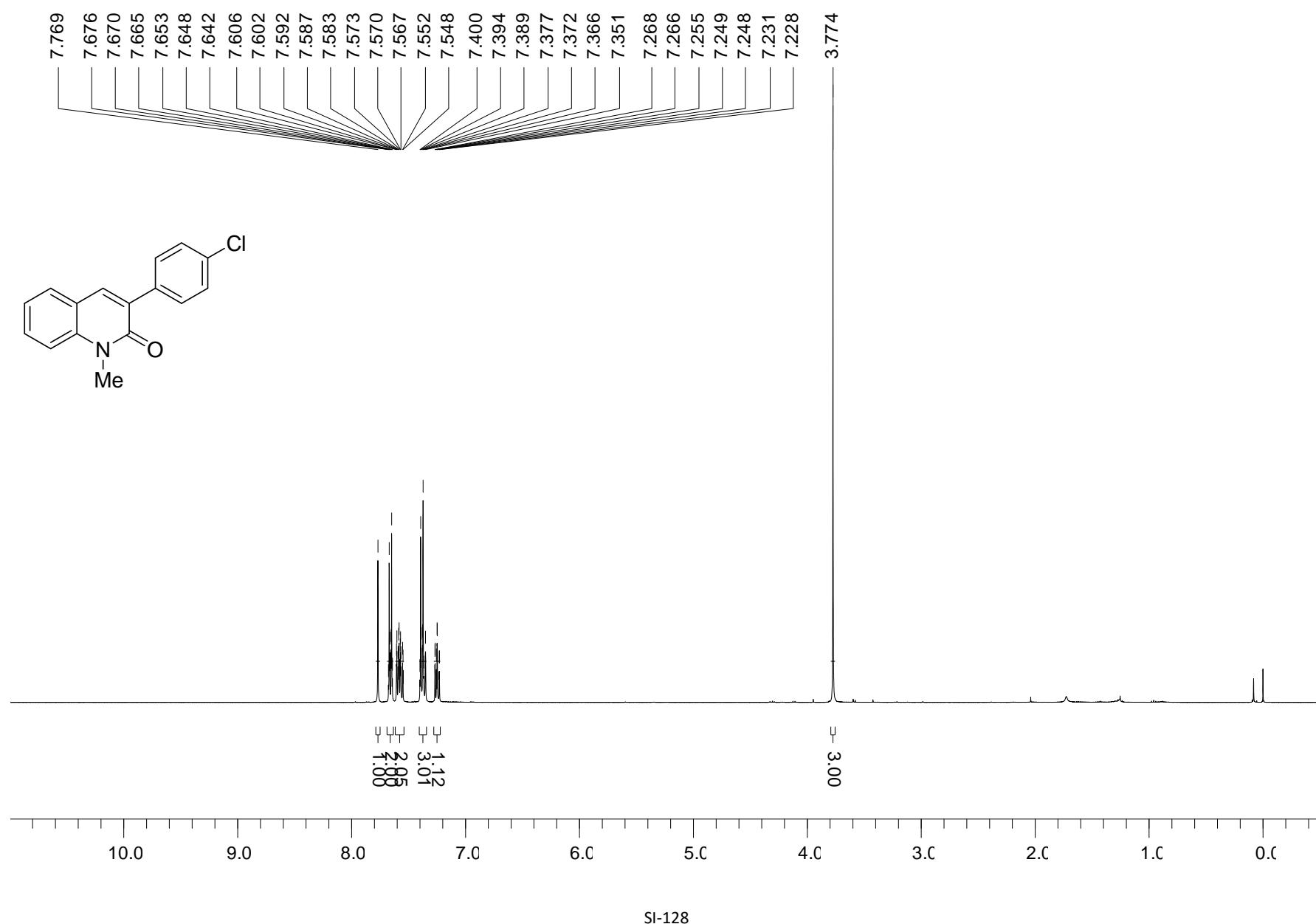
^1H NMR (400 MHz, CDCl_3) spectrum of **3m**



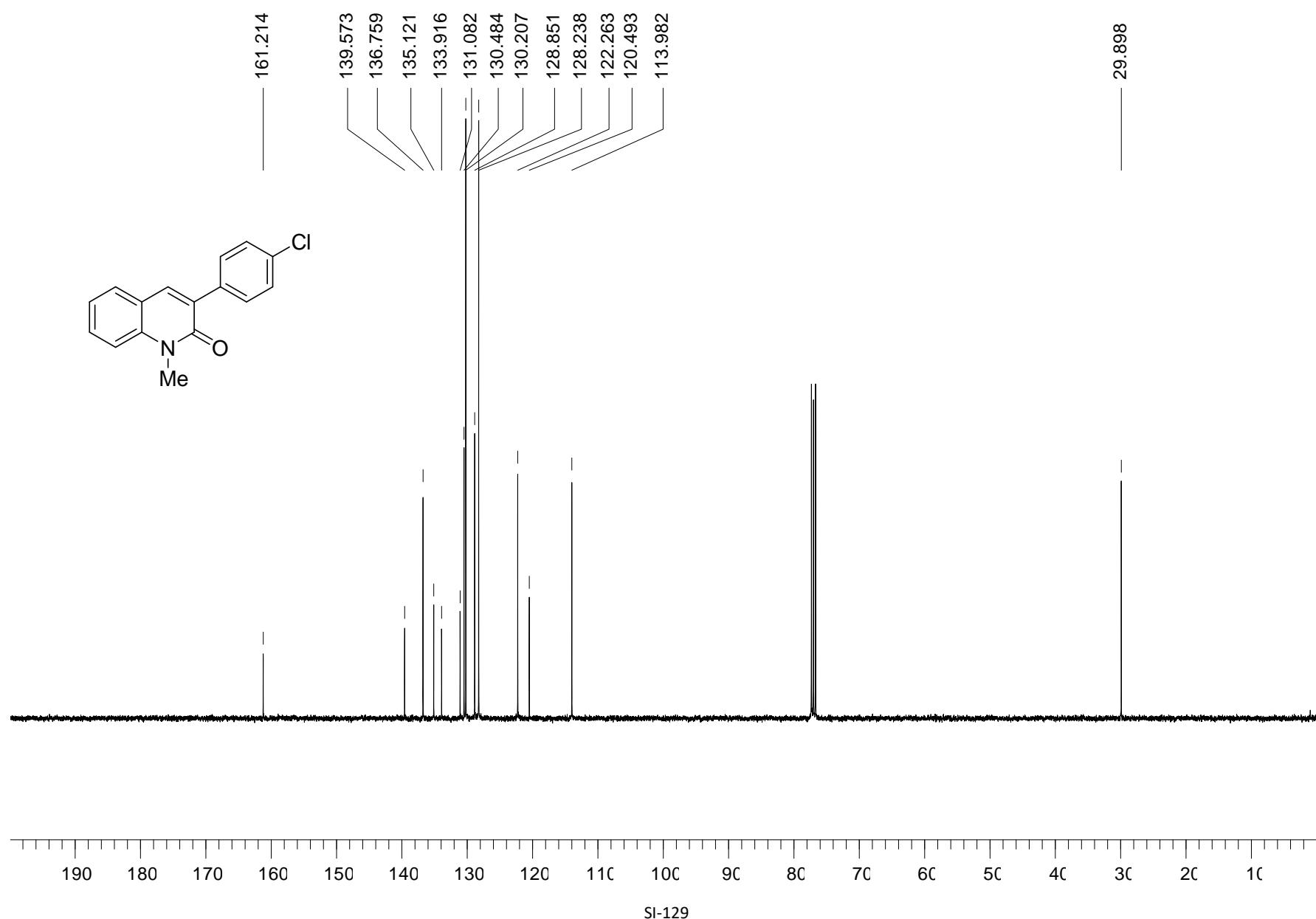
¹³C NMR (100 MHz, CDCl₃) spectrum of **3m**



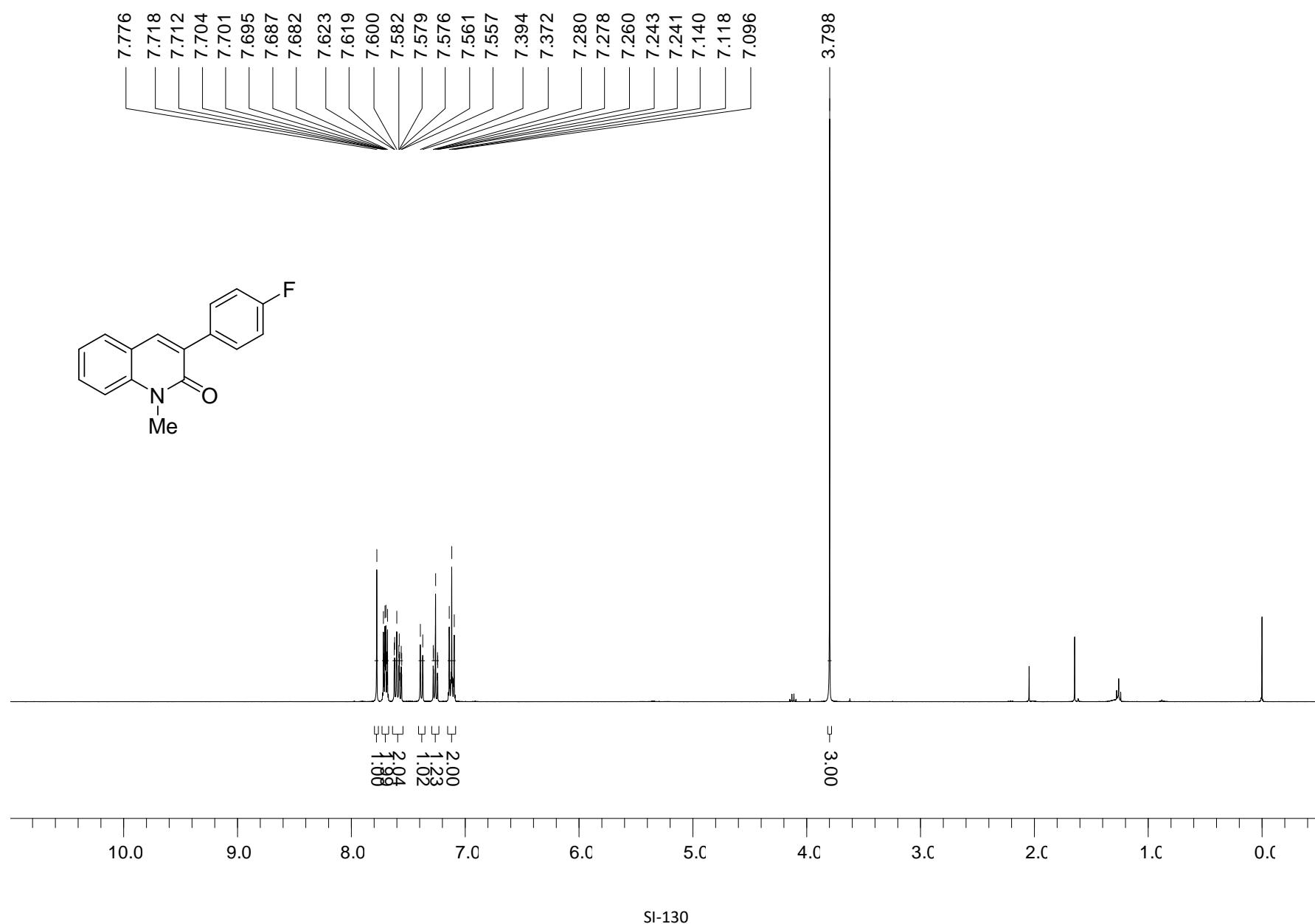
¹H NMR (400 MHz, CDCl₃) spectrum of **3n**



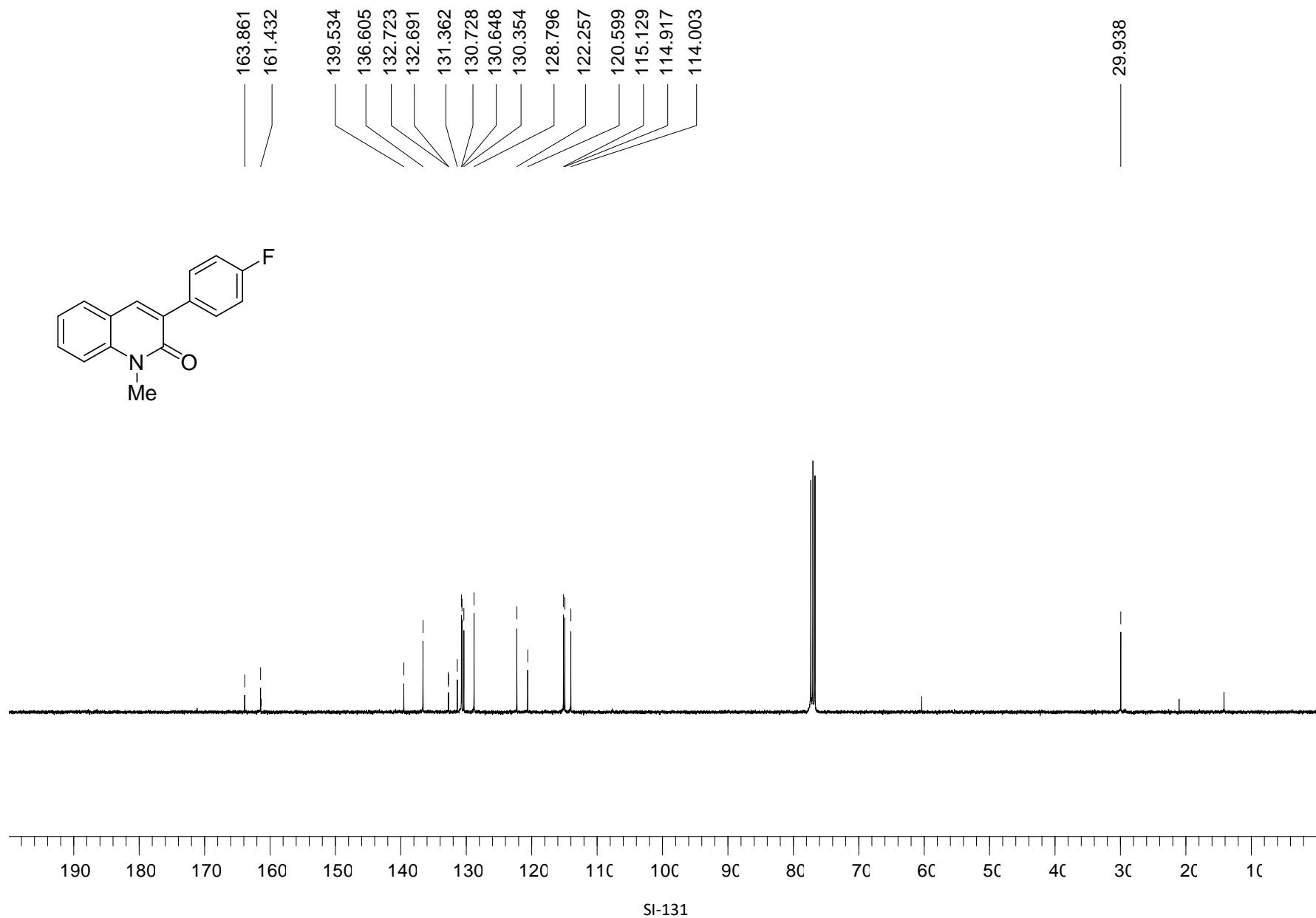
¹³C NMR (100 MHz, CDCl₃) spectrum of **3n**



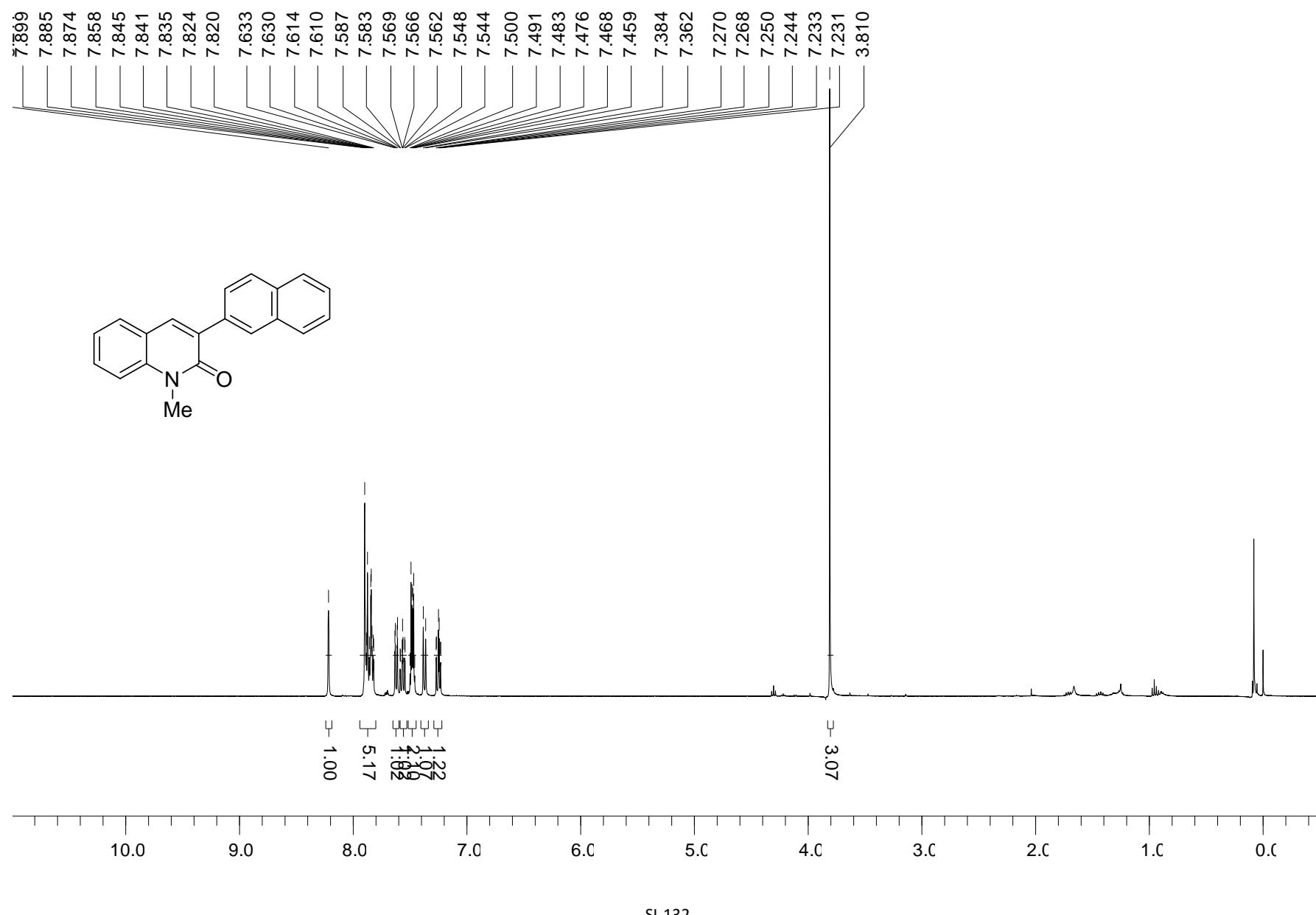
¹H NMR (400 MHz, CDCl₃) spectrum of **3o**



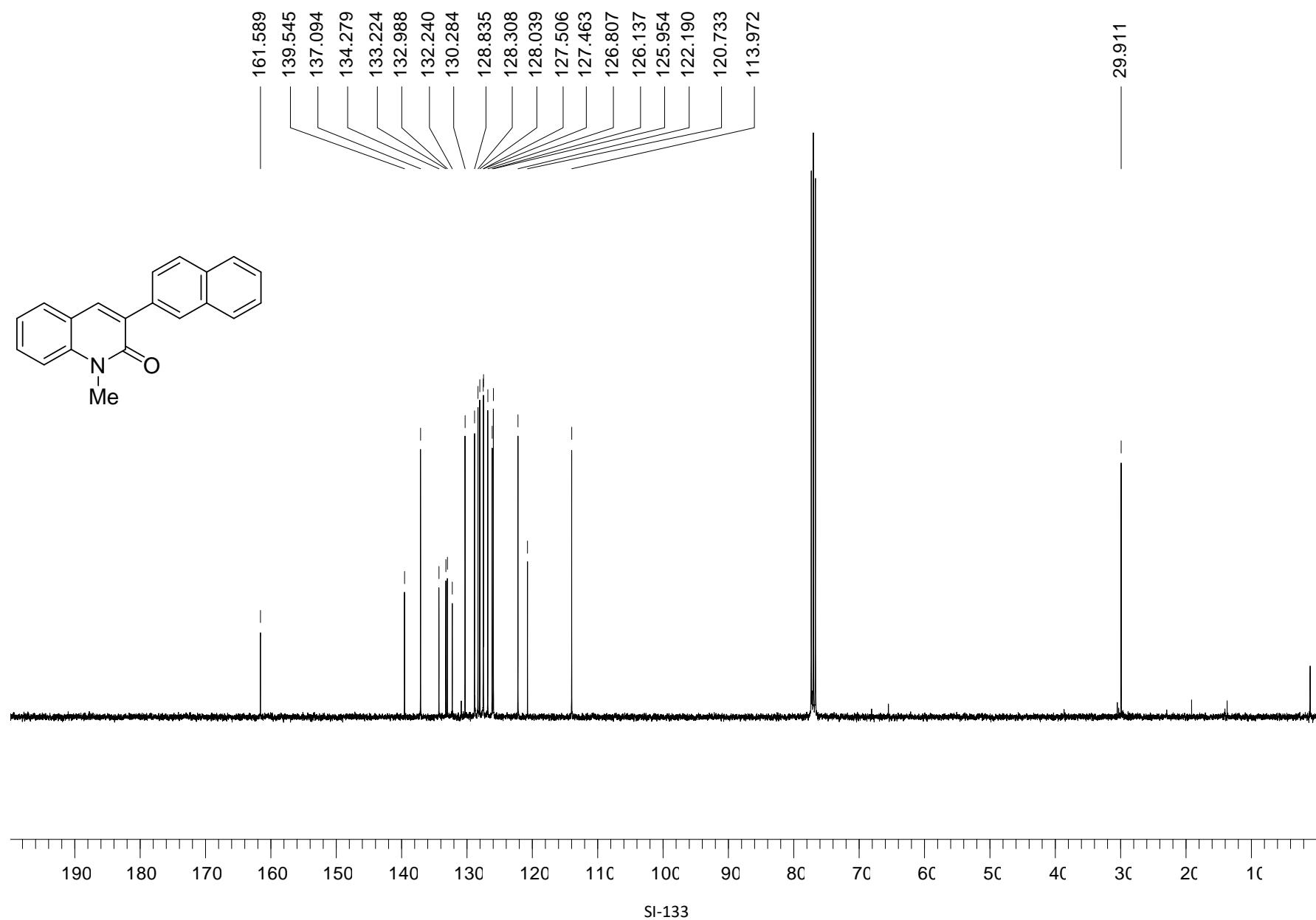
¹³C NMR (100 MHz, CDCl₃) spectrum of **3o**



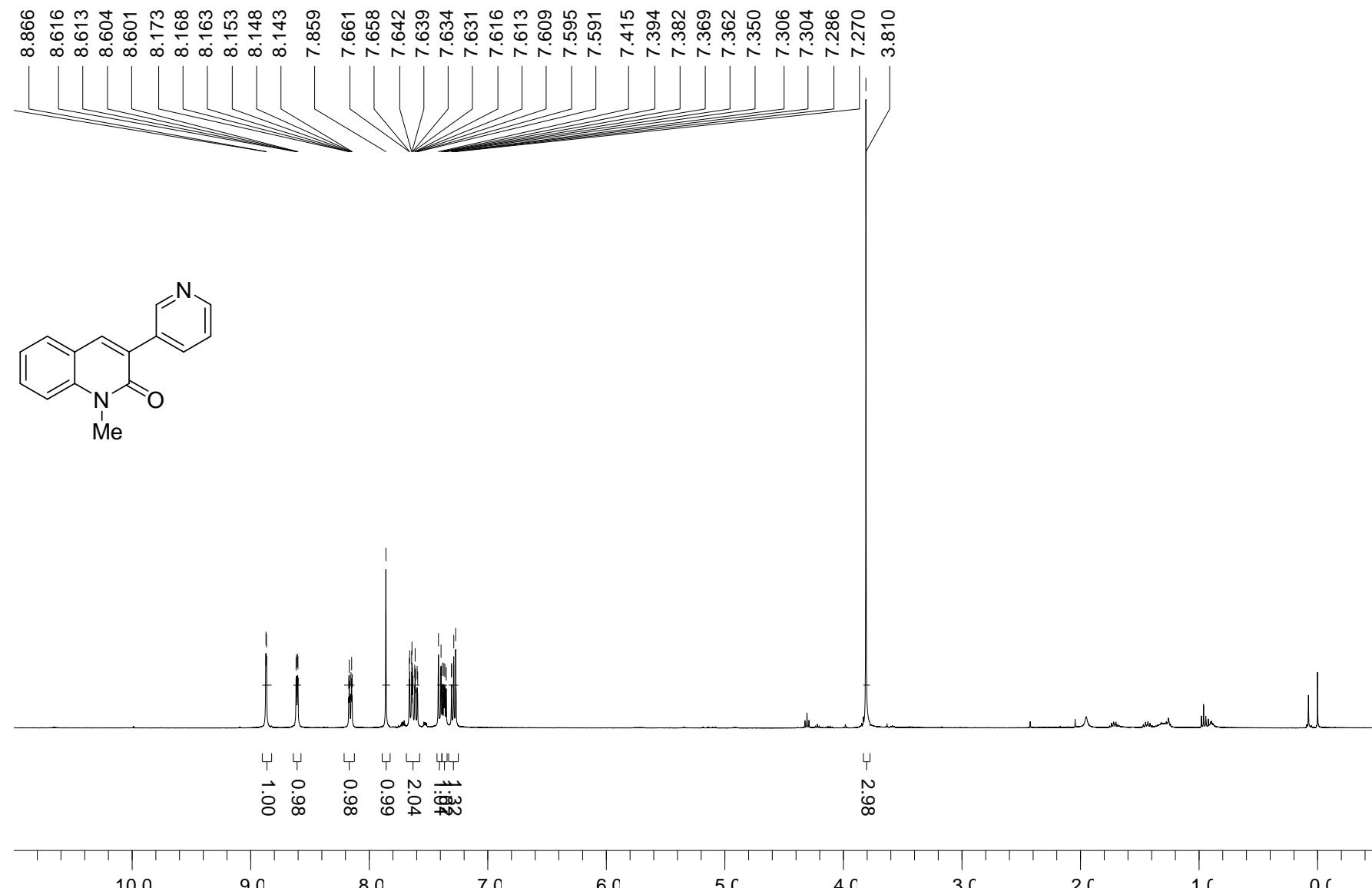
¹H NMR (400 MHz, CDCl₃) spectrum of **3p**



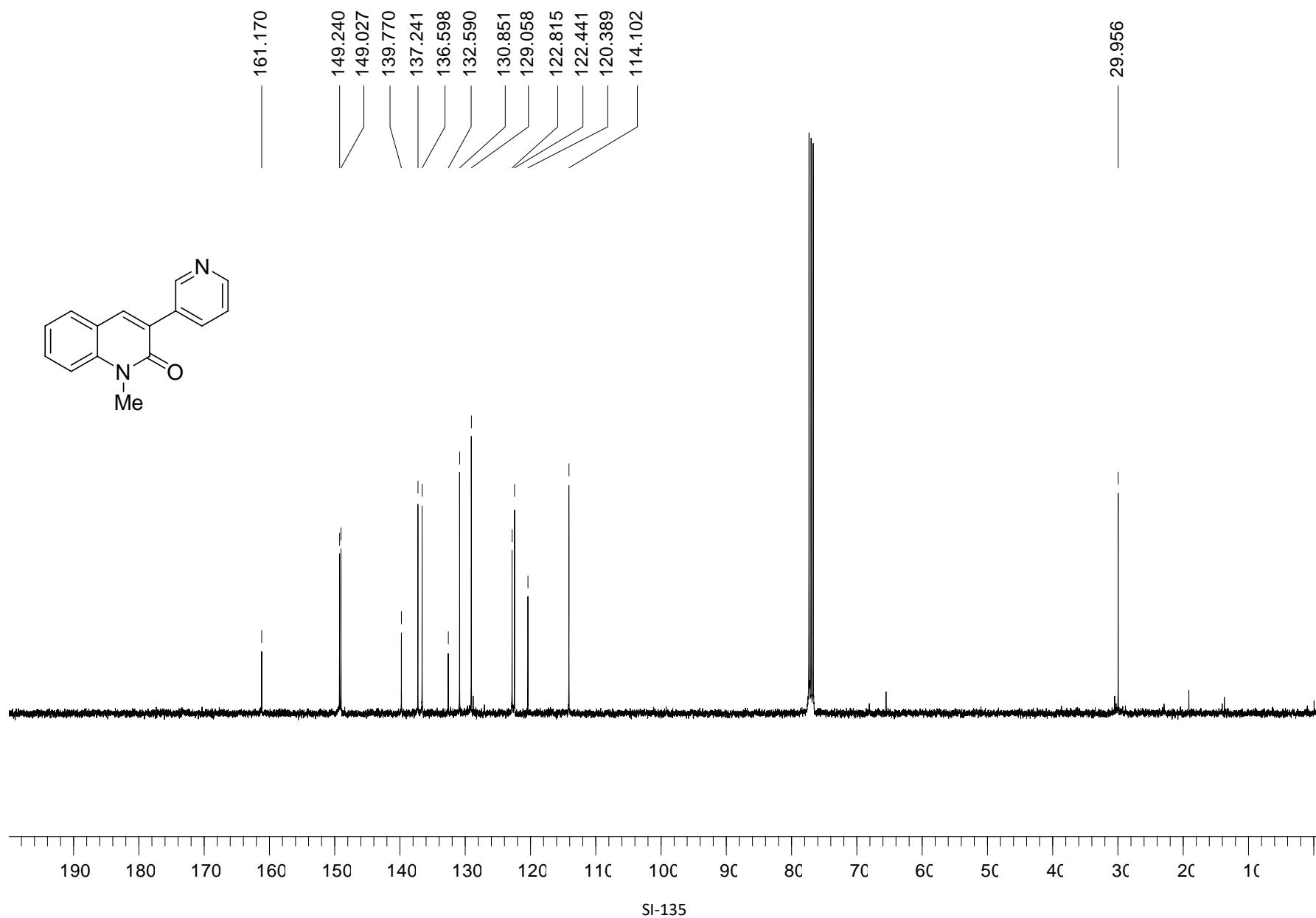
¹³C NMR (100 MHz, CDCl₃) spectrum of **3p**



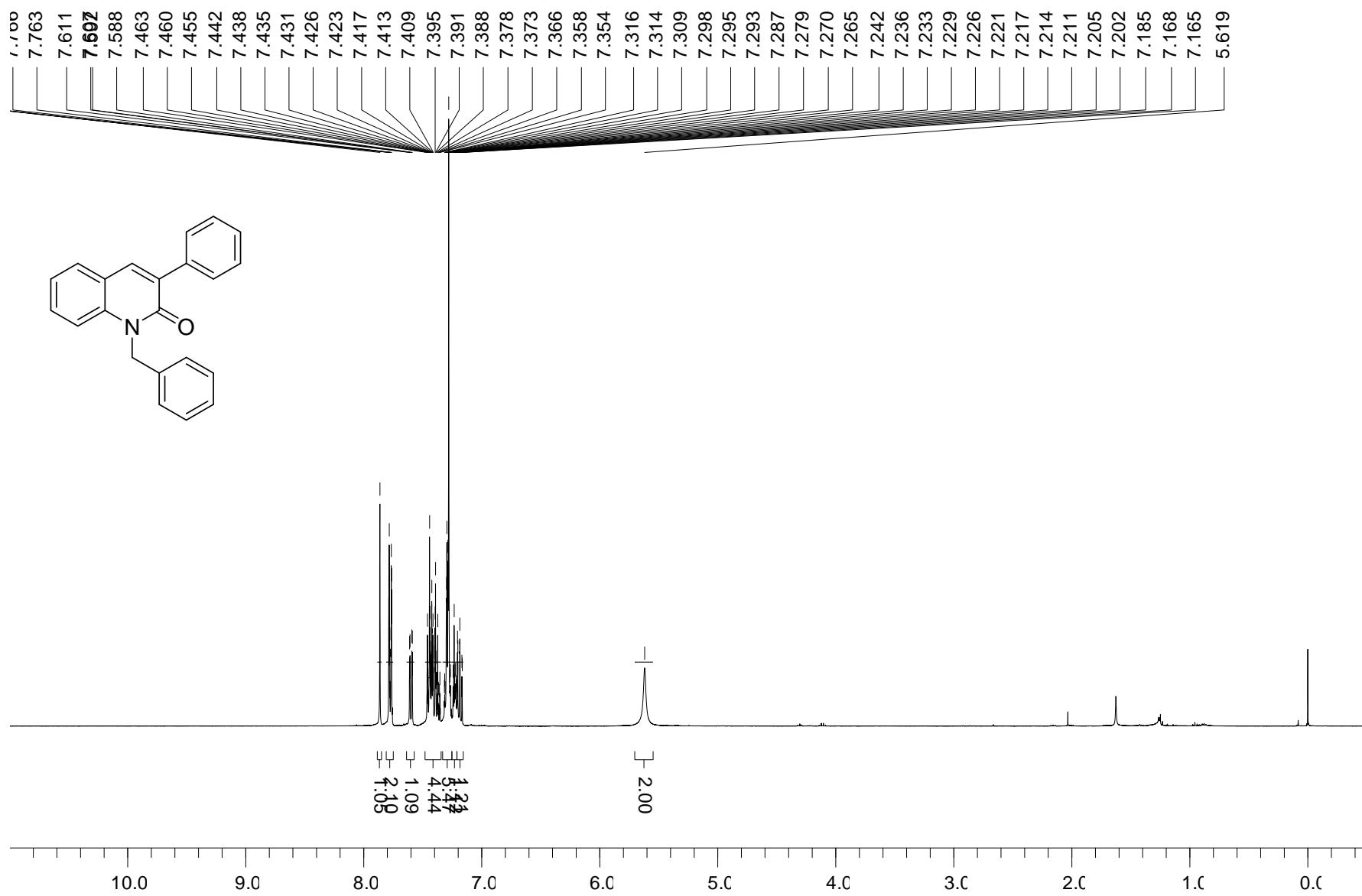
¹H NMR (400 MHz, CDCl₃) spectrum of **3q**



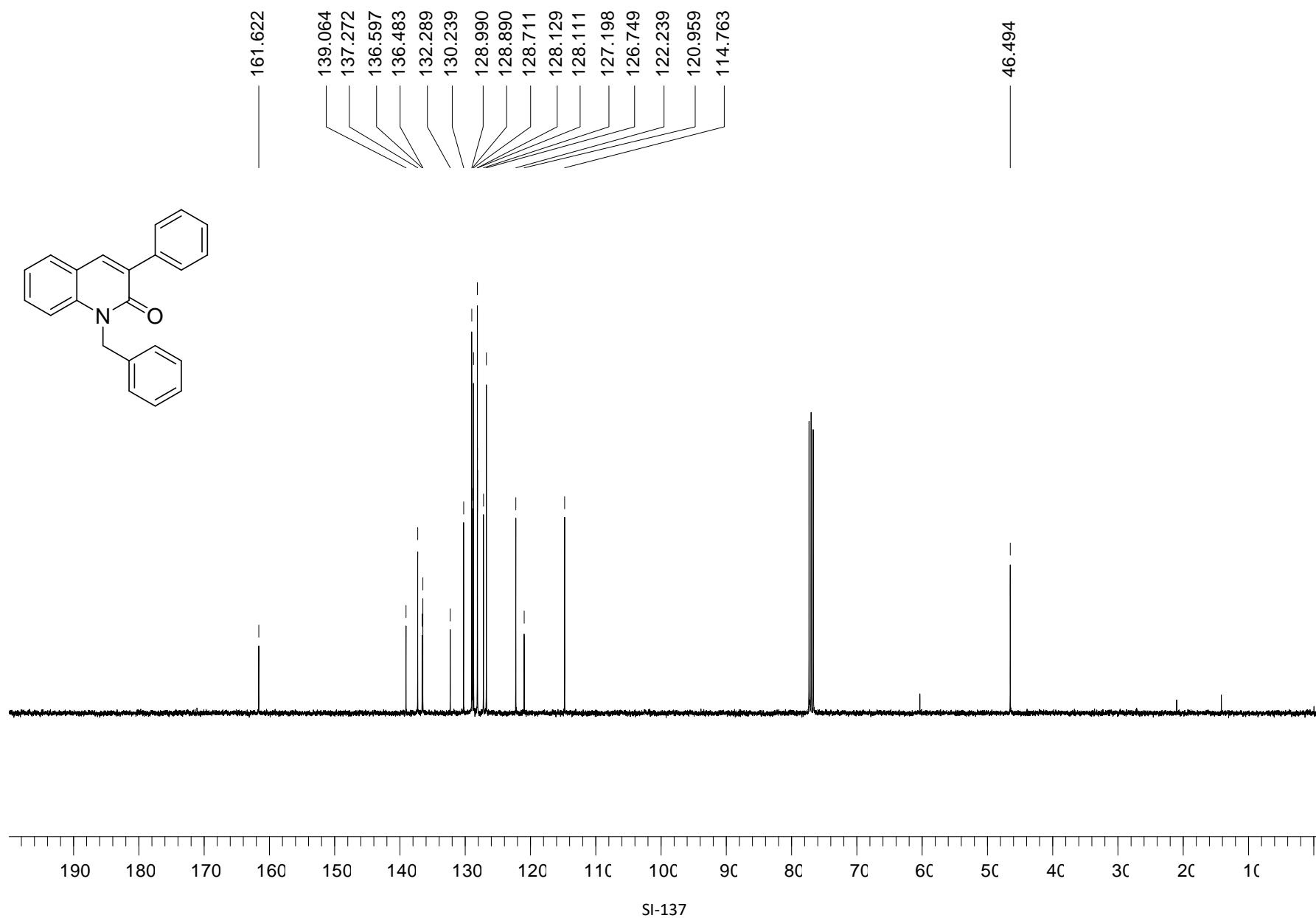
¹³C NMR (100 MHz, CDCl₃) spectrum of **3q**



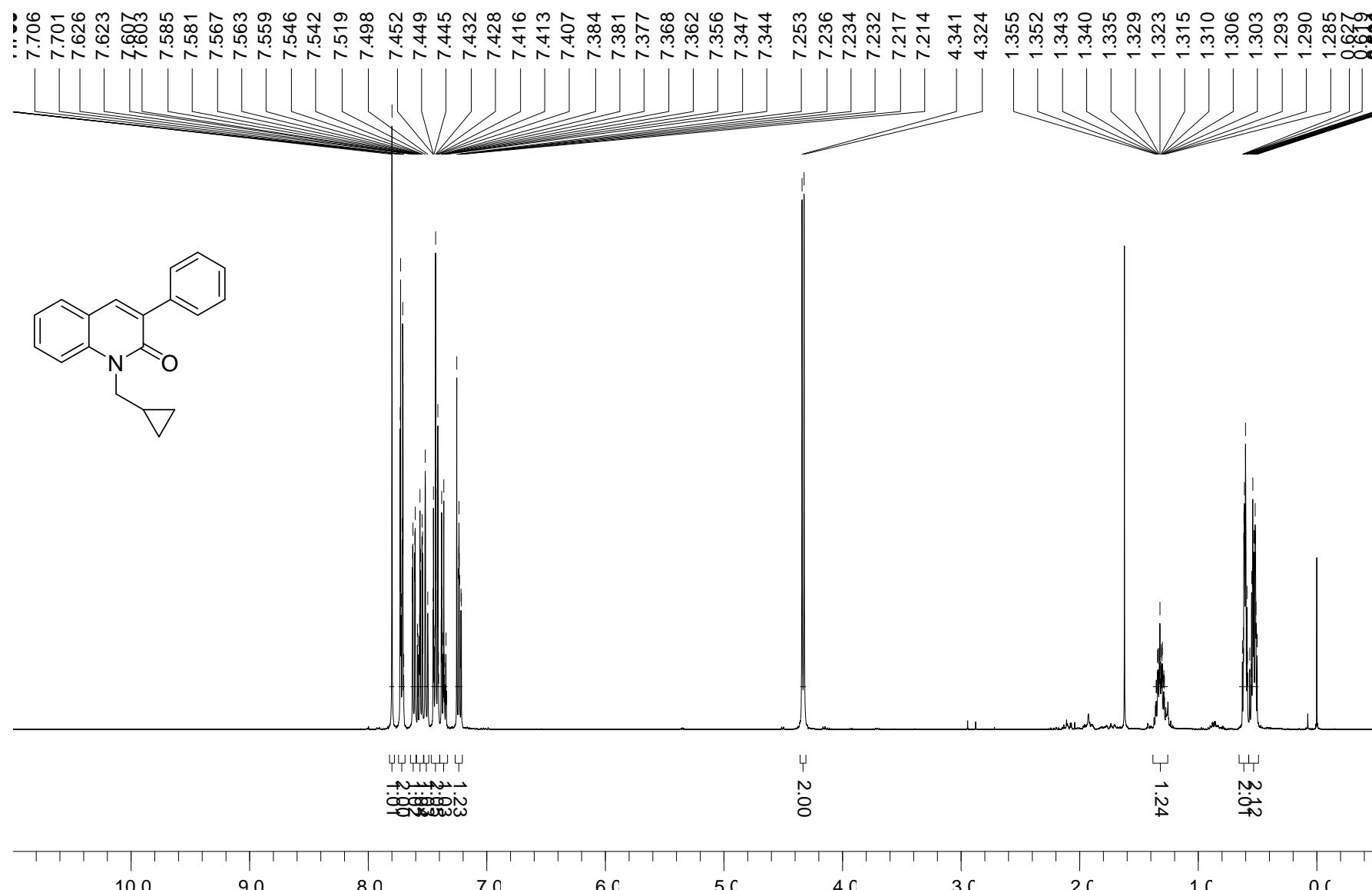
¹H NMR (400 MHz, CDCl₃) spectrum of **3r**



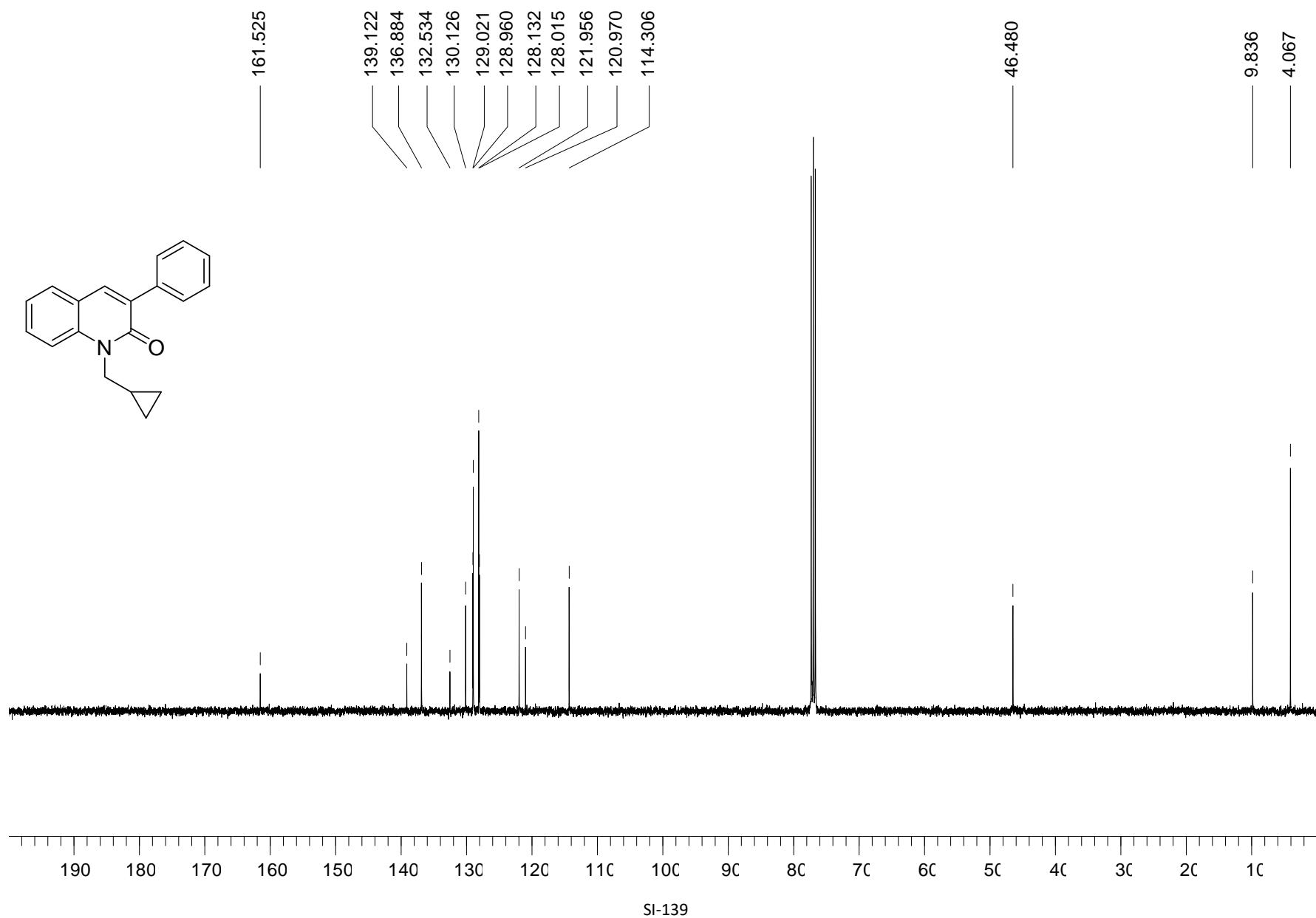
¹³C NMR (100 MHz, CDCl₃) spectrum of **3r**



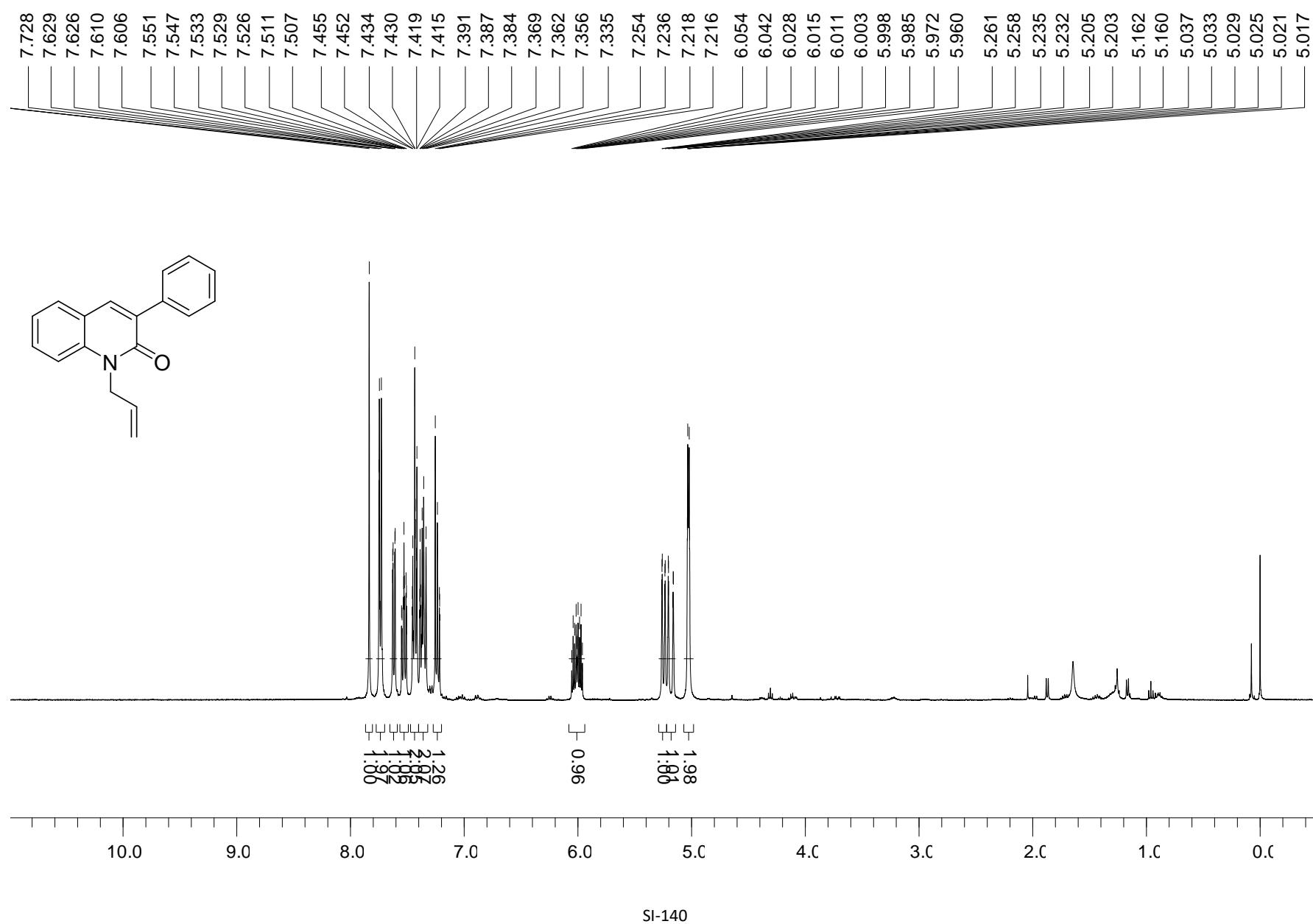
¹H NMR (400 MHz, CDCl₃) spectrum of **3s**



¹³C NMR (100 MHz, CDCl₃) spectrum of **3s**

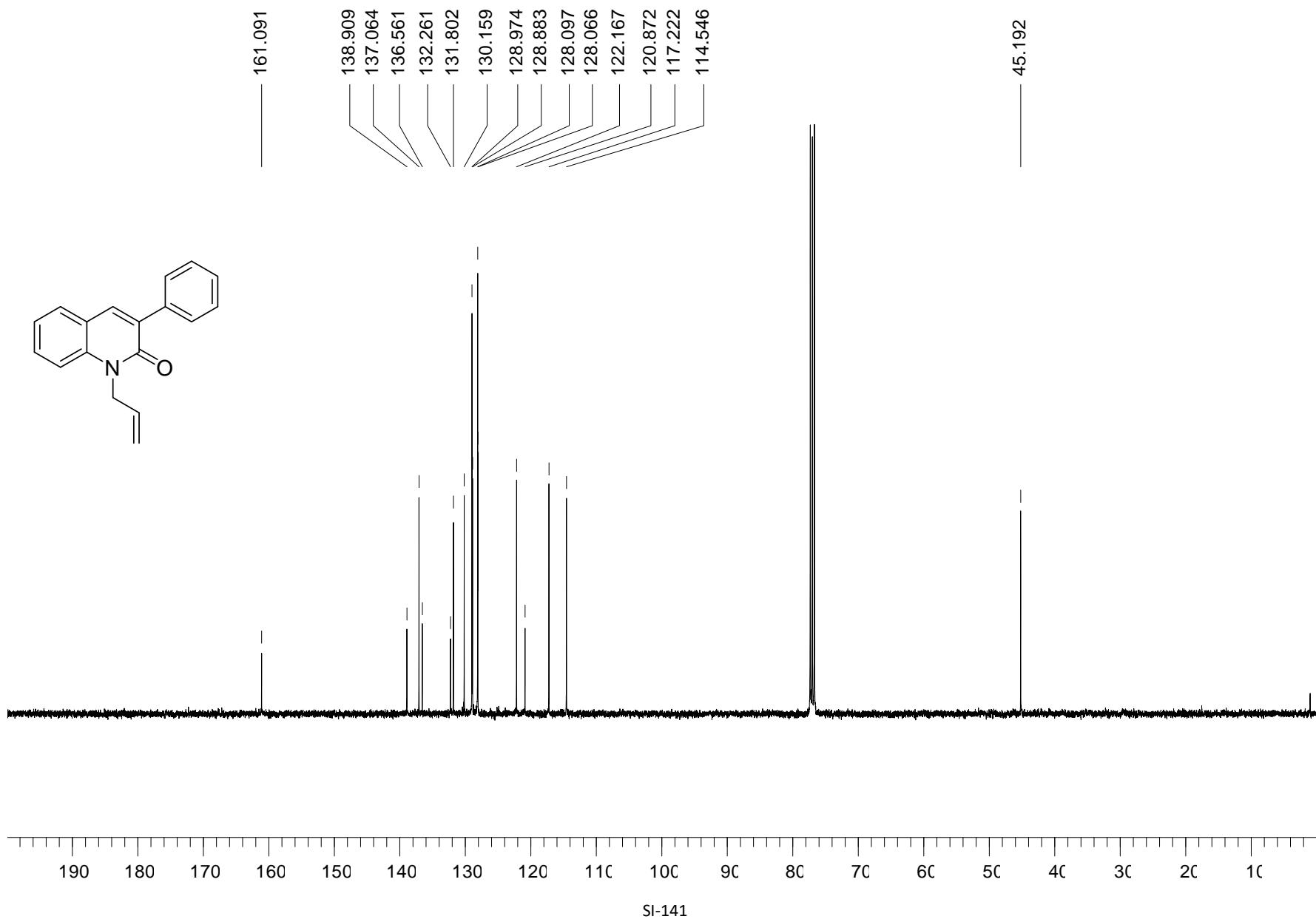


¹H NMR (400 MHz, CDCl₃) spectrum of **3t**

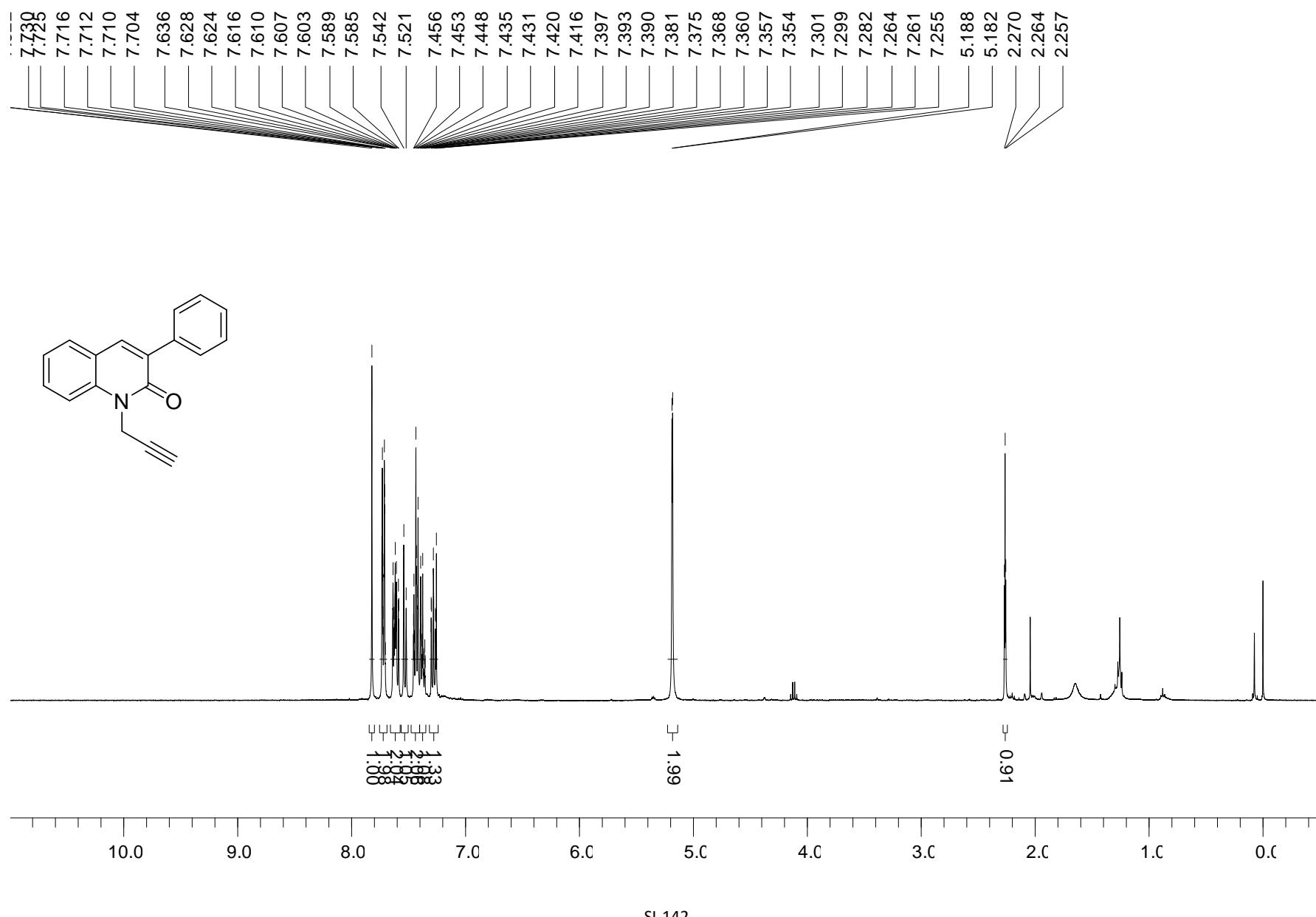


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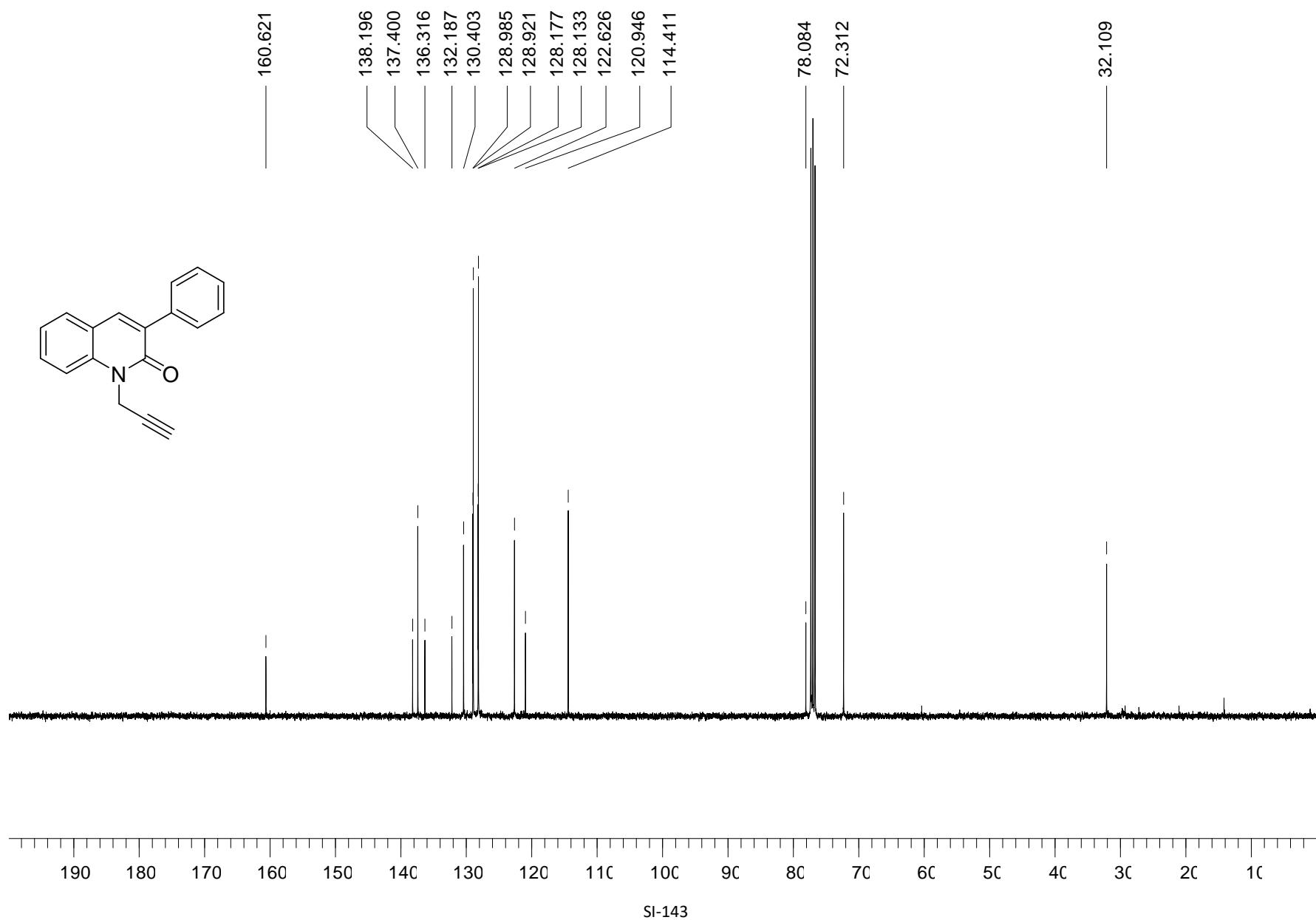
¹³C NMR (100 MHz, CDCl₃) spectrum of **3t**



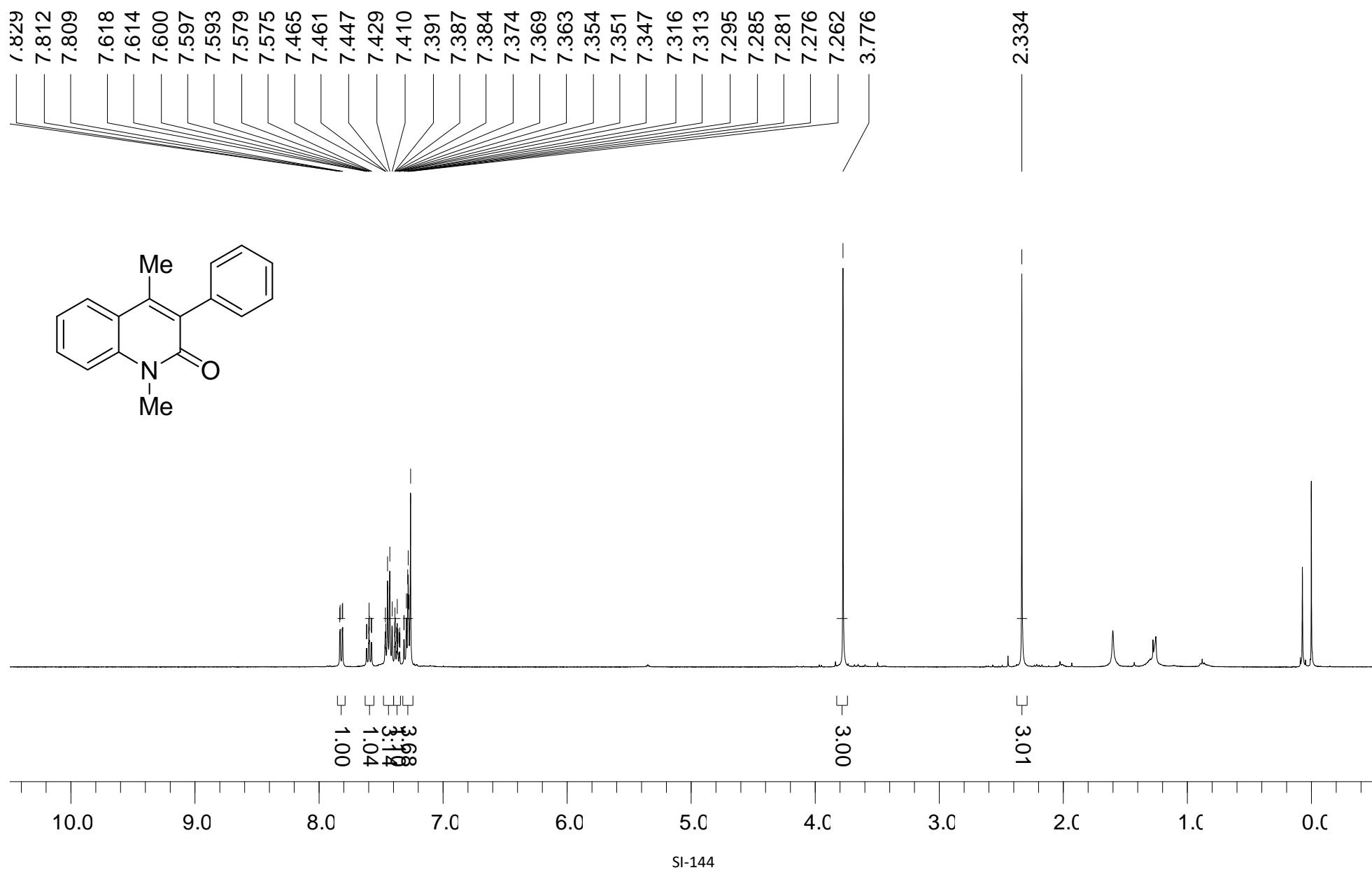
¹H NMR (400 MHz, CDCl₃) spectrum of **3u**



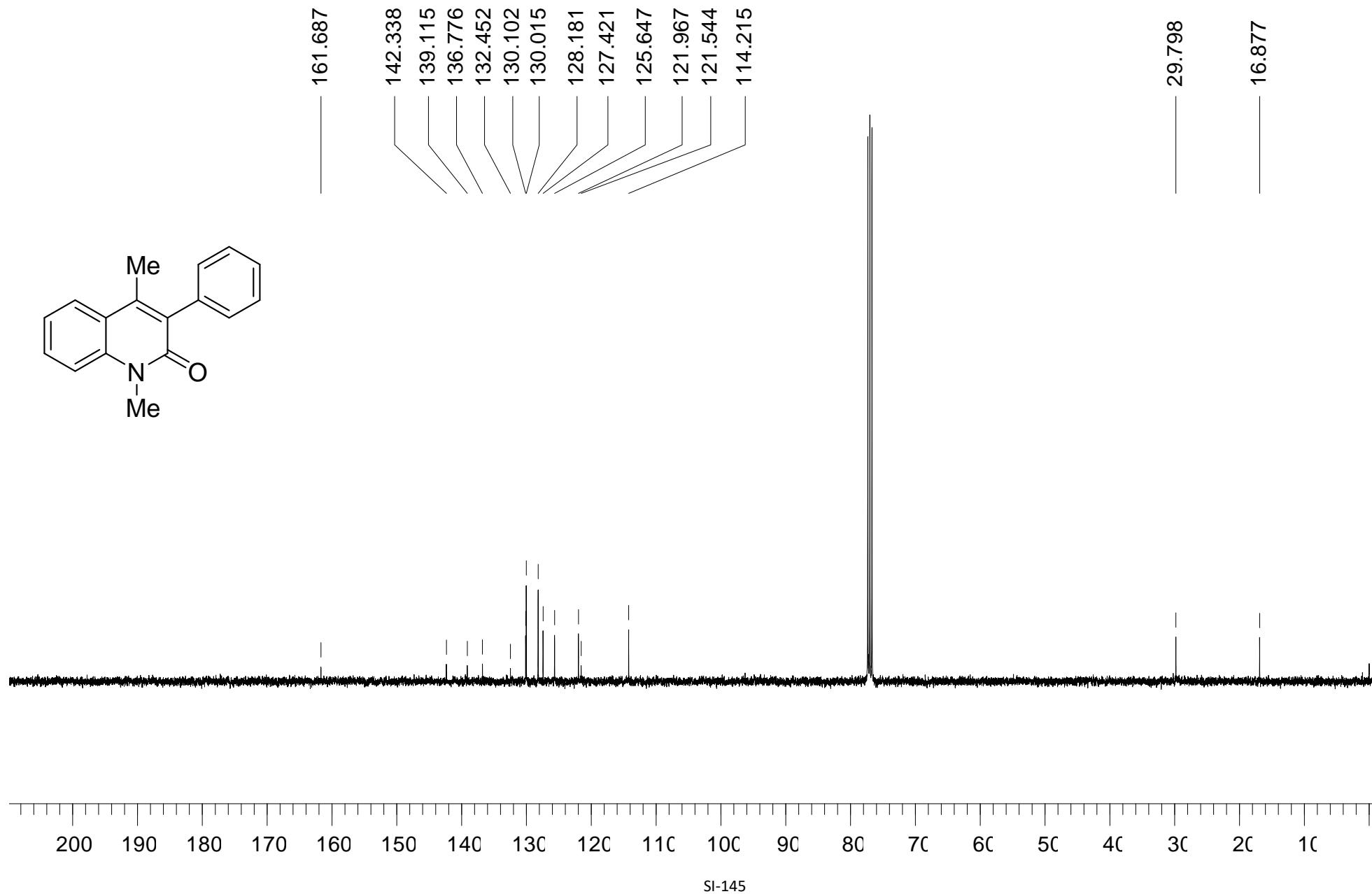
¹³C NMR (100 MHz, CDCl₃) spectrum of **3u**



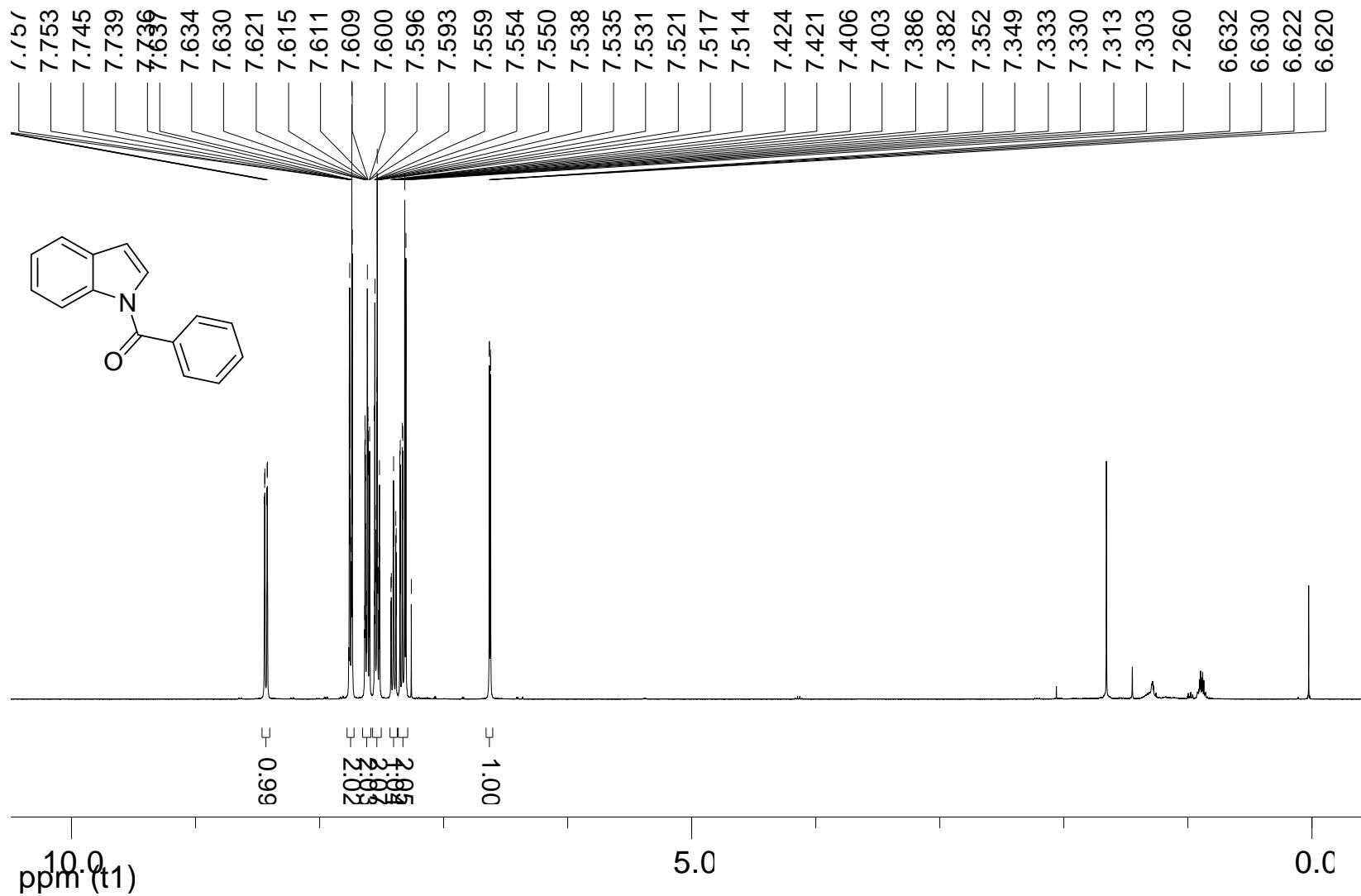
¹H NMR (400 MHz, CDCl₃) spectrum of **3v**



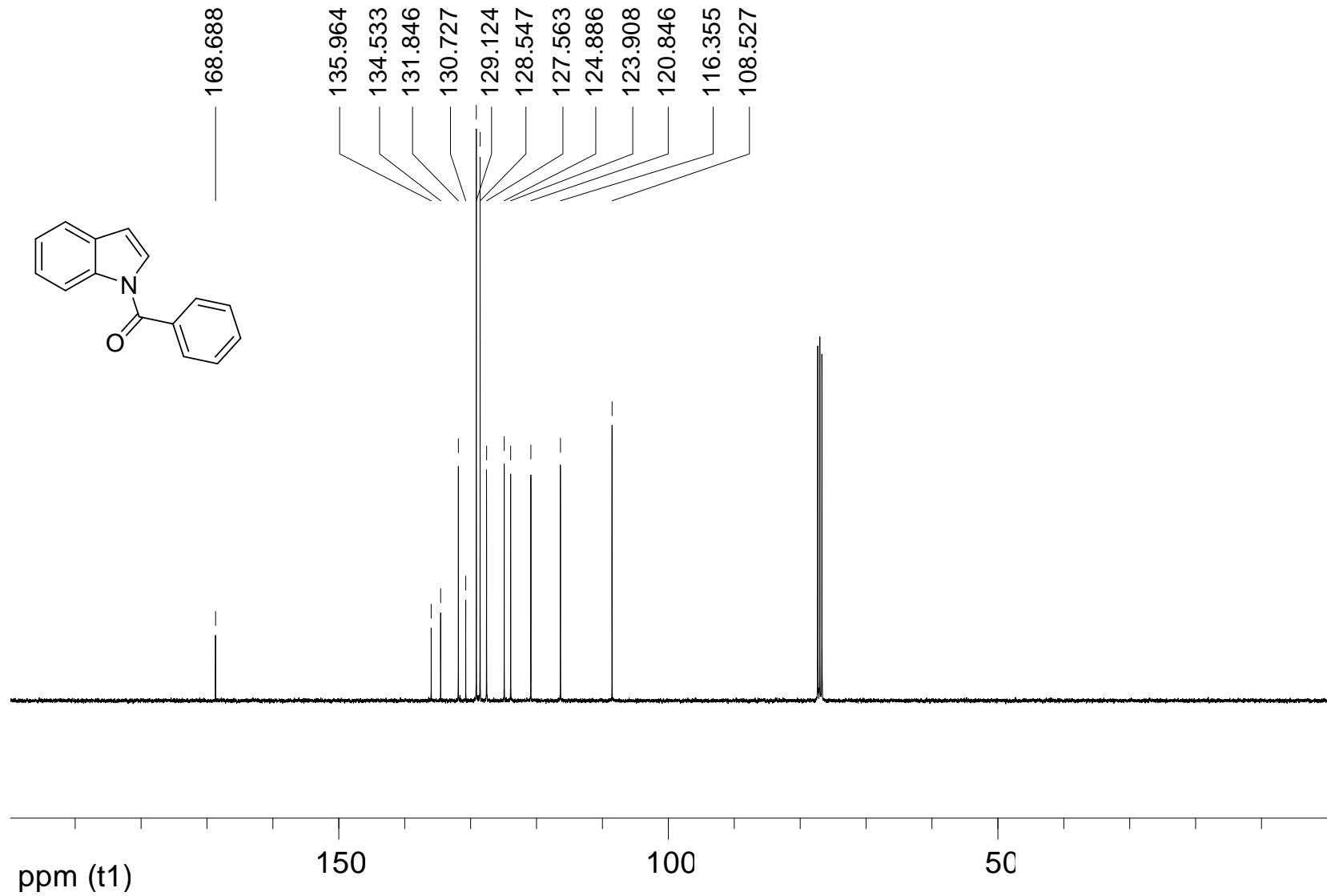
¹³C NMR (100 MHz, CDCl₃) spectrum of **3v**



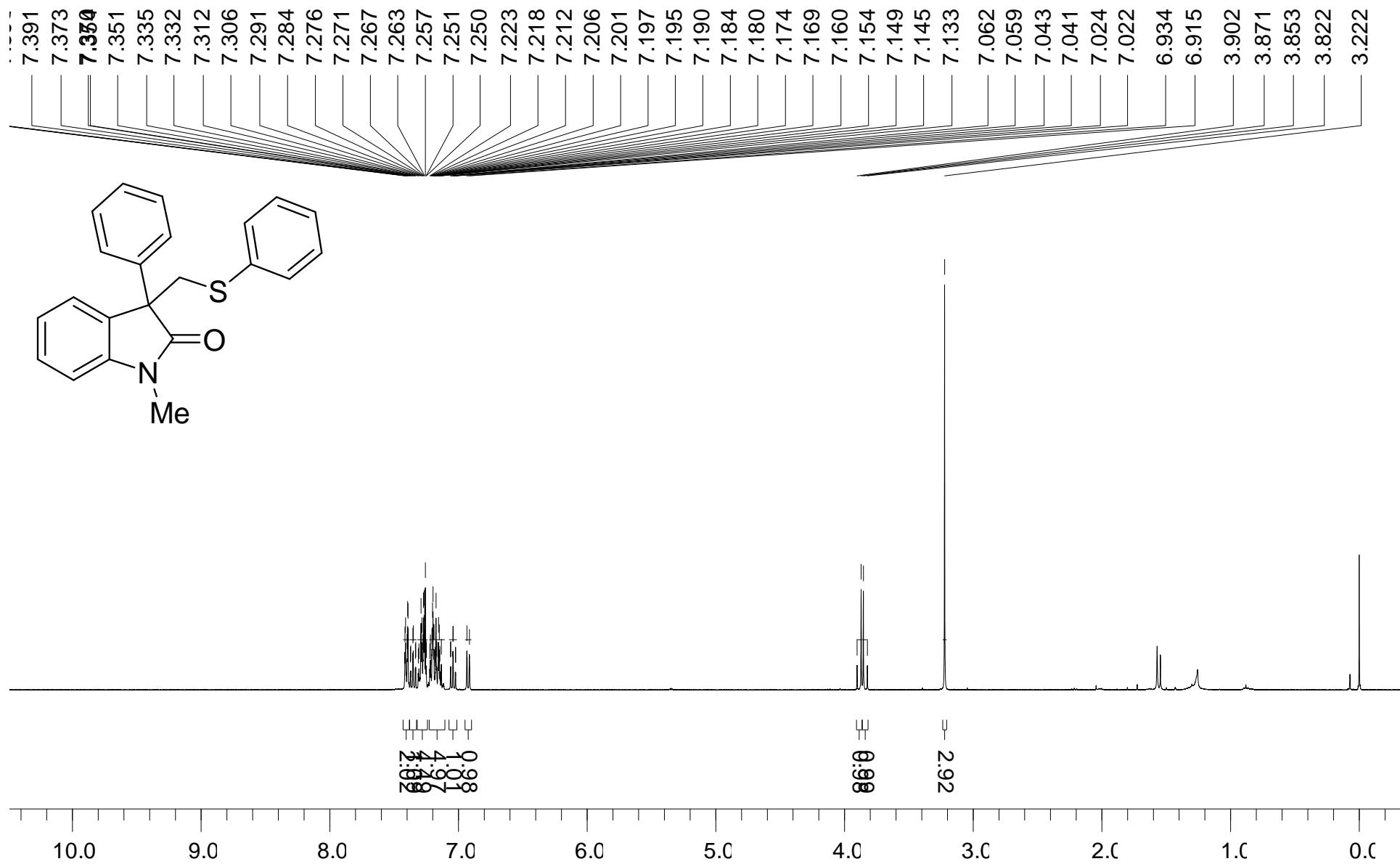
¹H NMR (400 MHz, CDCl₃) spectrum of **3w'**



¹³C NMR (100 MHz, CDCl₃) spectrum of **3w'**

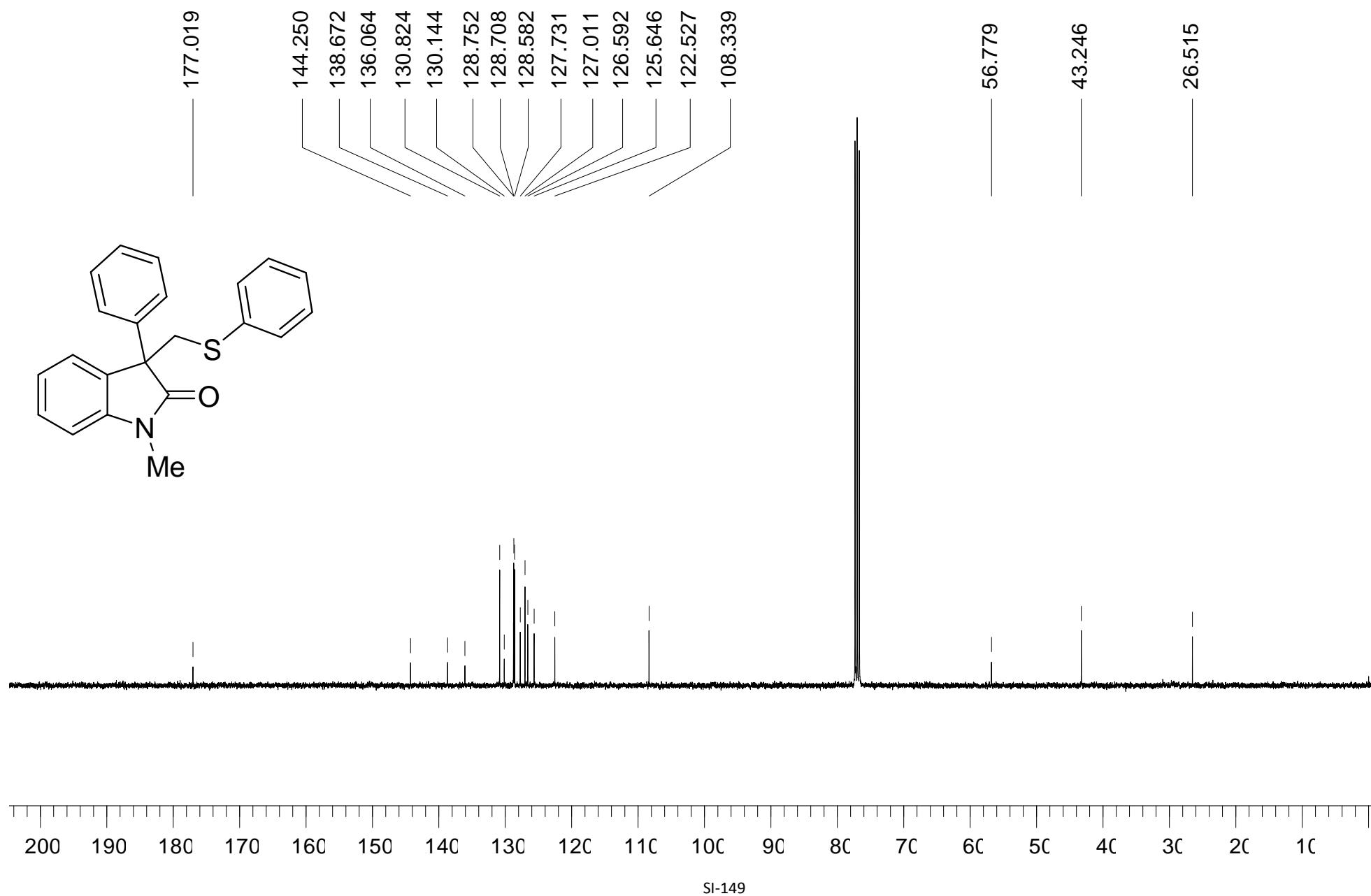


¹H NMR (400 MHz, CDCl₃) spectrum of **4**

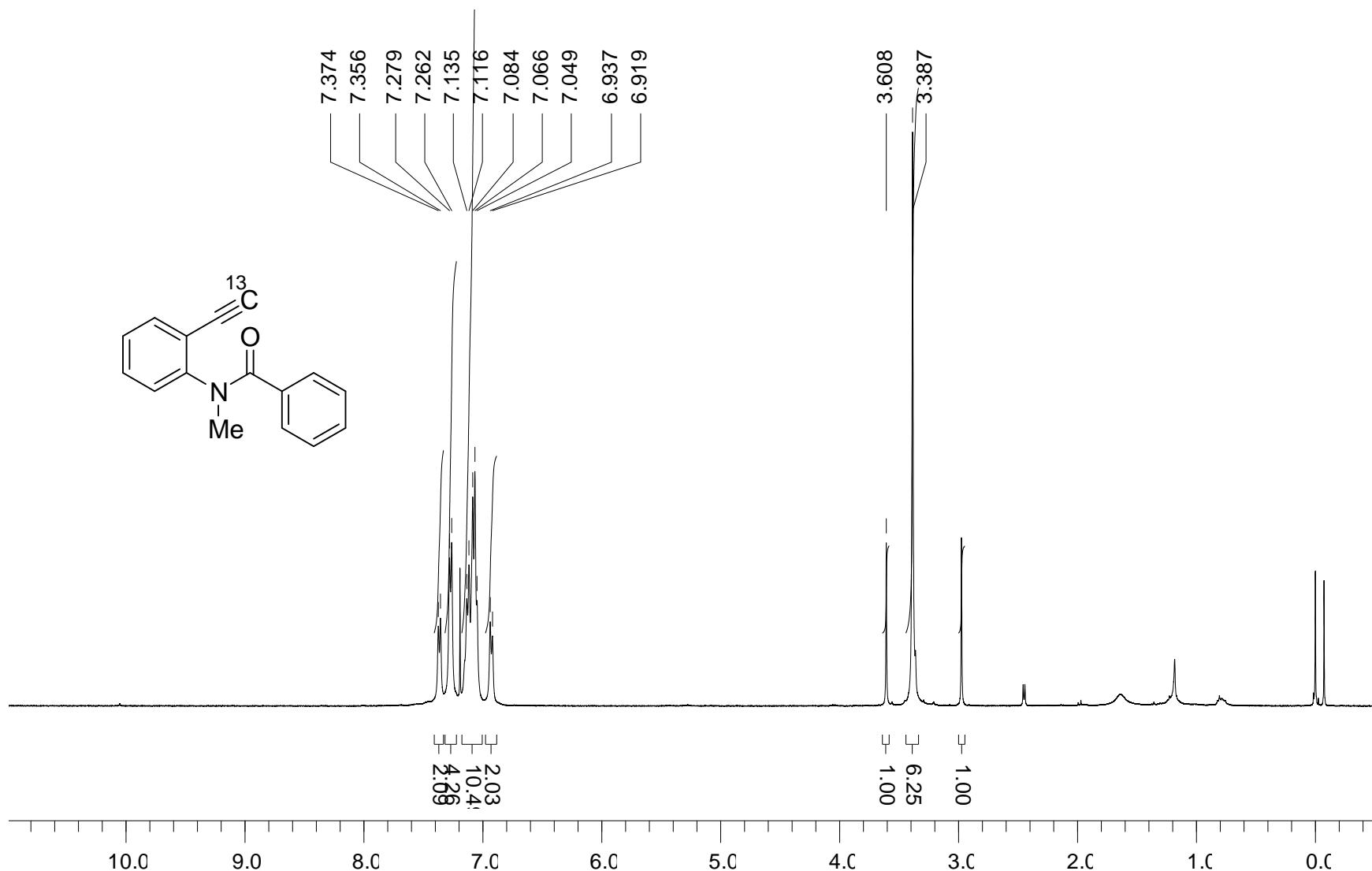


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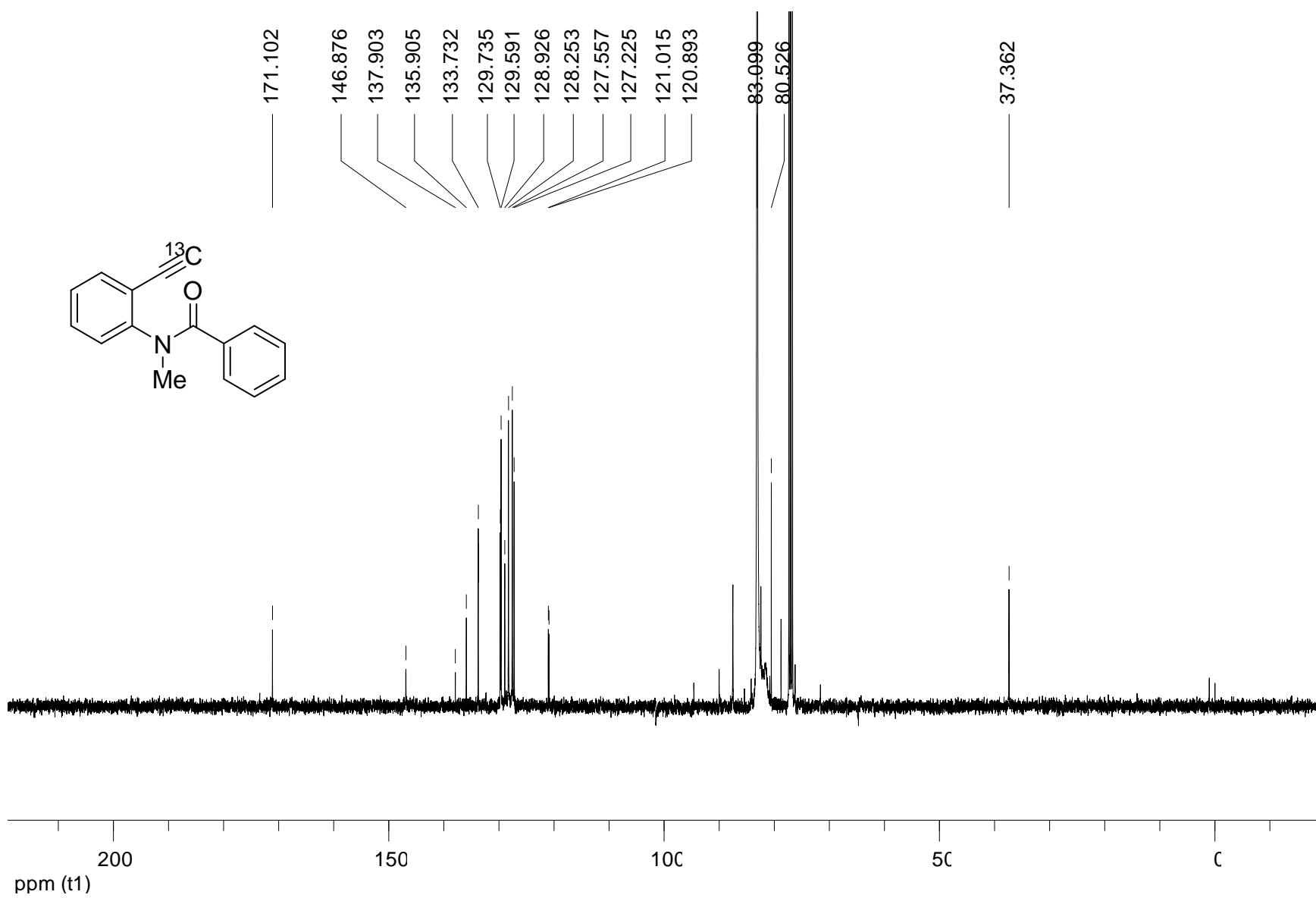
¹³C NMR (100 MHz, CDCl₃) spectrum of **4**



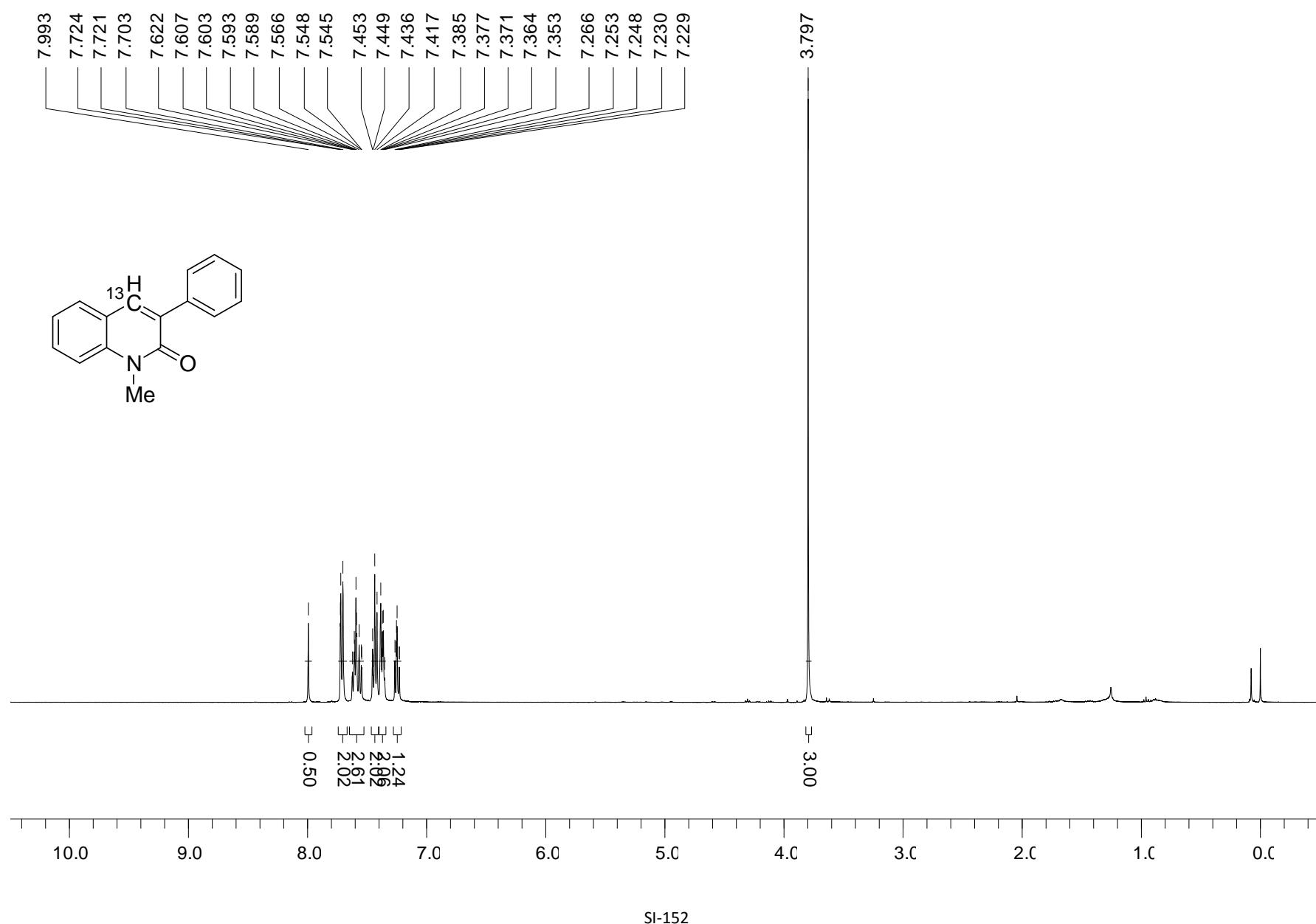
^1H NMR (400 MHz, CDCl_3) spectrum of **1a**- ^{13}C



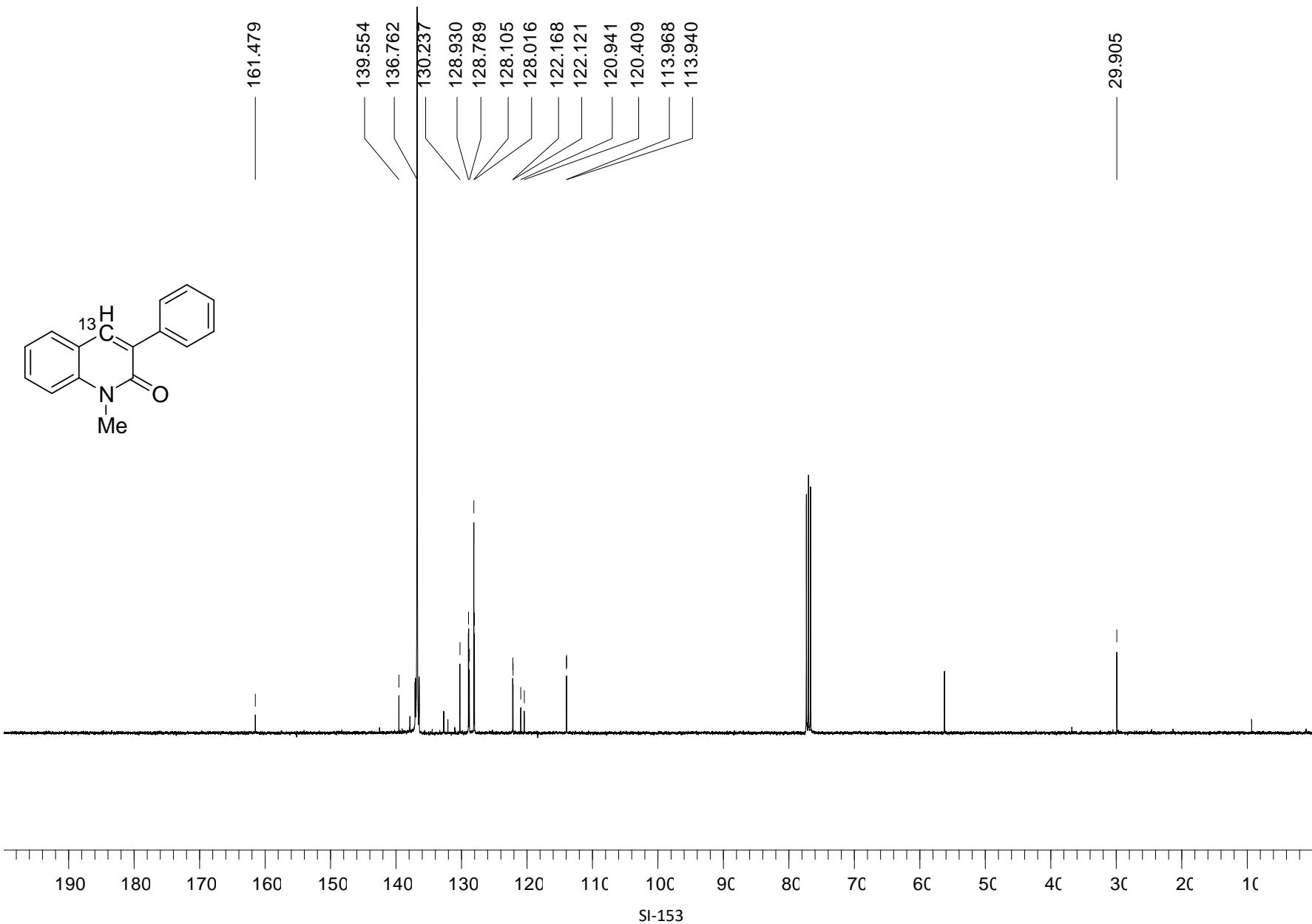
^{13}C NMR (100 MHz, CDCl_3) spectrum of **1a**- ^{13}C



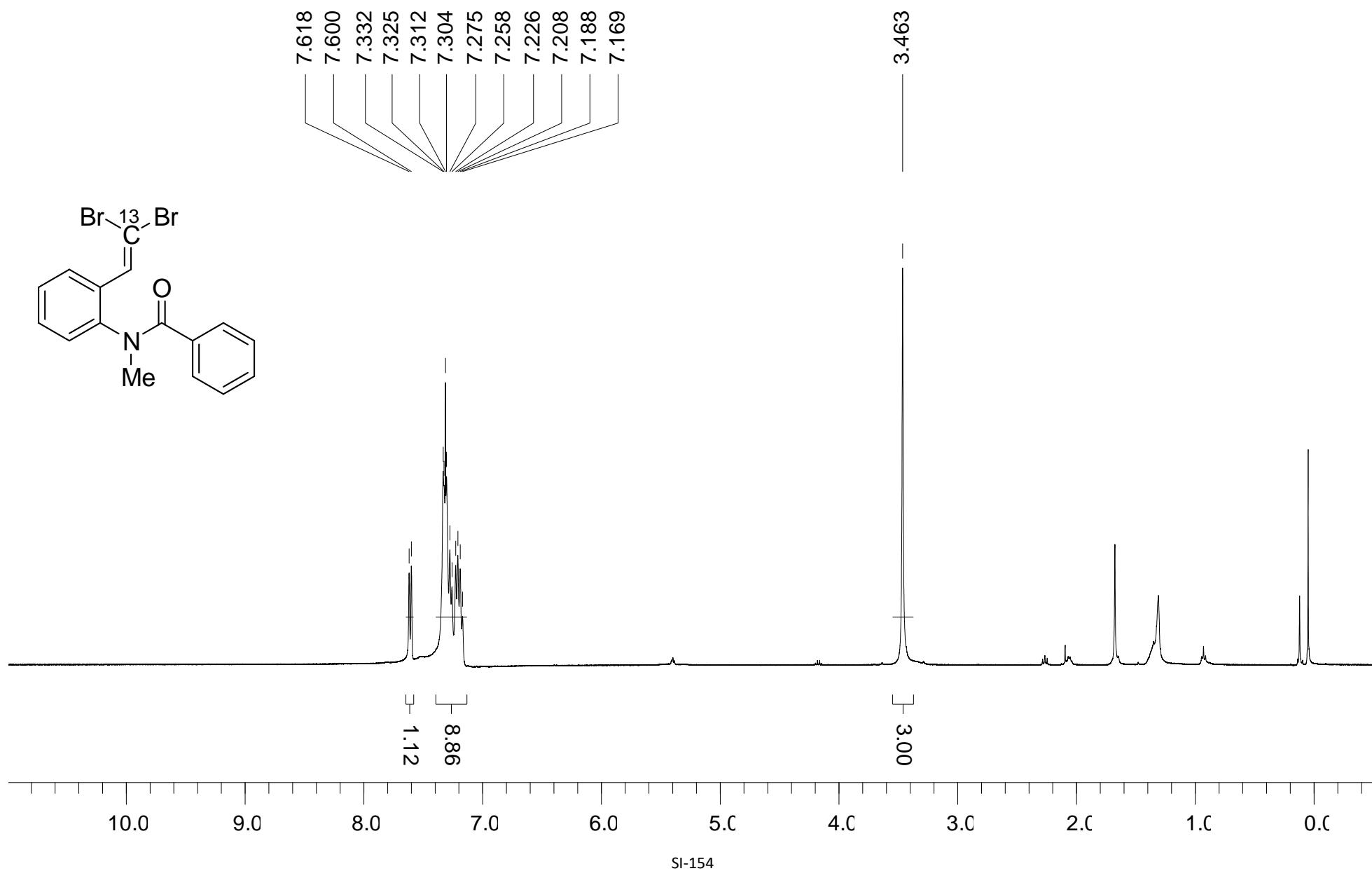
¹H NMR (400 MHz, CDCl₃) spectrum of **3a**-¹³C



^{13}C NMR (100 MHz, CDCl_3) spectrum of **3a-}^{13}\text{C}**



^1H NMR (400 MHz, CDCl_3) spectrum of IV



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

