

Supporting Information

[3+2] Cycloaddition Reaction of in Situ Formed Azaoxyallyl Cations with Aldehydes: An Approach to Oxazolidin-4-ones

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1. General Information

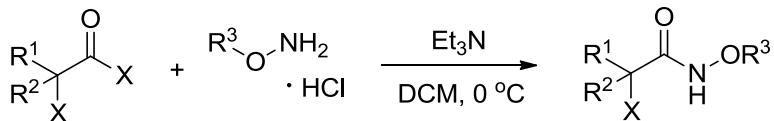
Reagents and Solvents: All solvents were purified and dried according to standard methods. PE refers to petroleum ether (b.p. 60 - 90 °C) and EA refers to ethyl acetate.

Chromatography: Flash column chromatography was carried out using commercially available 200-300 mesh under pressure and conducted by eluting with PE/EA, which are listed as volume/volume ratios.

Data Collection: Melting point (m.p.) was measured on a microscopic melting point apparatus. ^1H and ^{13}C NMR spectra were collected on BRUKER AV-300 (300 MHz) or BRUKER AV-500 (500 MHz) spectrometer using CDCl_3 or DMSO-d_6 as solvent. Chemical shifts of ^1H NMR were recorded in parts per million (ppm, δ) relative to tetramethylsilane ($\delta = 0.00$ ppm) with the solvent resonance as an internal standard (CDCl_3 , $\delta = 7.26$ ppm, DMSO-d_6 , $\delta = 2.50$ ppm). Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, m = multiplet), coupling constant (Hz), and integration. Chemical shifts of ^{13}C NMR were reported in ppm with the solvent as the internal standard (CDCl_3 , $\delta = 77.0$ ppm, DMSO-d_6 , $\delta = 39.5$ ppm). High Resolution Mass measurement was performed on Agilent QTOF 6520 mass spectrometer with electron spray ionization (ESI) as the ion source. Unless otherwise indicated, all other reagents and solvents were obtained from commercial suppliers and used without further purification.

2. General Procedures for the Preparation of α -Halohydroxamates

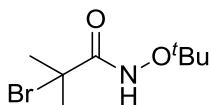
a) General Procedures¹



To a suspension of the O-benzyloxyamine hydrochloride and triethylamine in DCM (0.25 M) was added dropwise the alpha-haloacid halide at 0 °C. The reaction mixture was stirred at this temperature until complete consumption of starting material (detected by TLC). The mixture was warmed to room temperature and quenched with water. The organic phase was washed with water (x3), then washed with brine (x1), dried over sodium sulfate, filtered and evaporated. Purification *via* a flash column chromatography (PE/EA = 8/1) provided the α -halohydroxamates.

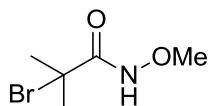
b) Characterization of the Products

2-bromo-N-(tert-butoxy)-2-methylpropanamide (2b)



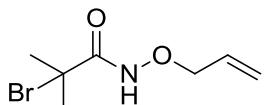
White solid, m. p. 93 – 94 °C. ¹H NMR (300 MHz, CDCl₃) δ 8.85 (s, 1H), 1.98 (s, 6H), 1.30 (s, 9H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 170.5, 82.8, 60.2, 32.6, 26.1 ppm. HRMS(ESI) *m/z* calcd for [C₈H₁₆BrNO₂+H]⁺ 238.0437, found 238.0431.

2-bromo-N-methoxy-2-methylpropanamide (2d)



Yellow solid, m. p. 56 – 58 °C. ¹H NMR (300 MHz, CDCl₃) δ 9.46 (s, 1H), 3.81 (s, 3H), 1.97 (s, 6H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 169.7, 64.2, 59.1, 32.2 ppm. HRMS(ESI) *m/z* calcd for [C₅H₁₀BrNO₂+H]⁺ 195.9968, found 195.9965.

N-(allyloxy)-2-bromo-2-methylpropanamide (2i)



Colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 9.41 (s, 1H), 6.00 (m, 1H), 5.53 – 5.21 (m, 2H), 4.43 (d, *J* = 6.5 Hz, 2H), 1.96 (s, 6H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 169.5, 131.7, 121.1, 77.1, 59.0, 32.2 ppm. HRMS(ESI) *m/z* calcd for [C₇H₁₂BrNO₂+Na]⁺ 222.0124, found 222.0123.

¹ Jeffrey, C. S.; Barnes, K. L.; Eickhoff, J. A.; Carson, C. R. *J. Am. Chem. Soc.* **2011**, *133*, 7688.

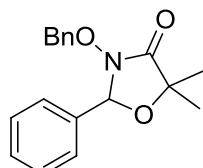
3. General Procedures for [3+2] Annulation Reaction

a) General Procedures

In a 10 mL test tube was sequentially added aldehydes **1** (0.25 mmol, 1.0 equiv), Na₂CO₃ (0.75 mmol, 3.0 equiv), α -halohydroxamates **2** (0.375 mmol, 1.5 equiv) and HFIP (1.0 mL). Then, the tube was sealed and stirred at room temperature. Once the aldehydes was complete consumption, the reaction mixture was diluted with ethyl acetate, filtered through celite and washed with ethyl acetate. The filtrate was concentrated under reduced pressure and the resulting residue was purified by flash column chromatography (PE/EA = 15/1) on silica gel to afford the pure product.

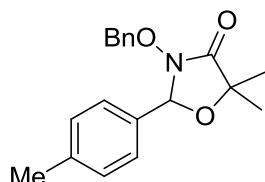
b) Characterization of the Products

3-(benzyloxy)-5,5-dimethyl-2-phenyloxazolidin-4-one (3aa)



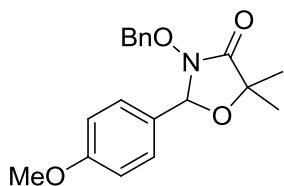
66.1 mg, 89% yield, Colorless oil; ¹H NMR (300 MHz, CDCl₃) δ 7.47 (m, 5H), 7.36 – 7.23 (m, 3H), 7.23 – 7.10 (m, 2H), 5.61 (s, 1H), 4.92 (d, *J* = 10.1 Hz, 1H), 4.41 (d, *J* = 10.1 Hz, 1H), 1.56 (s, 3H), 1.42 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 172.4, 135.7, 134.2, 130.3, 129.5, 128.9, 128.6, 128.3, 127.8, 87.6, 78.1, 78.1, 25.2, 22.6 ppm. HRMS(ESI) *m/z* calcd for [C₁₈H₁₉NO₃+H]⁺ 298.1438, found 298.1438.

*3-(benzyloxy)-5,5-dimethyl-2-(*p*-tolyl)oxazolidin-4-one (3ba)*



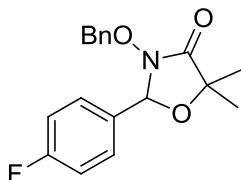
72.2mg, 93% yield, White solid, m. p. 62 – 64 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.42 – 7.26 (m, 5H), 7.26 – 7.13 (m, 4H), 5.57 (s, 1H), 4.92 (d, *J* = 10.1 Hz, 1H), 4.44 (d, *J* = 10.1 Hz, 1H), 2.39 (s, 3H), 1.55 (s, 3H), 1.41 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 172.3, 140.3, 134.3, 132.8, 129.5, 129.3, 128.8, 128.3, 127.7, 87.5, 78.0, 77.9, 25.2, 22.6, 21.3 ppm. HRMS(ESI) *m/z* calcd for [C₁₉H₂₁NO₃+H]⁺ 312.1594, found 312.1601.

3-(benzyloxy)-2-(4-methoxyphenyl)-5,5-dimethyloxazolidin-4-one (3ca)



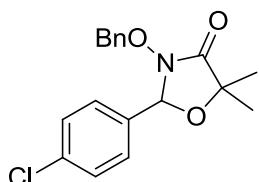
80.9 mg, 99% yield, White solid, m. p. 64 – 65 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.46 – 7.26 (m, 5H), 7.23 – 7.12 (m, 2H), 6.94 (d, J = 8.6 Hz, 2H), 5.57 (s, 1H), 4.91 (d, J = 10.1 Hz, 1H), 4.44 (d, J = 10.1 Hz, 1H), 1.55 (s, 3H), 1.40 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 172.3, 161.0, 134.3, 129.5, 129.1, 128.8, 128.3, 127.6, 113.9, 87.3, 78.0, 77.8, 55.2, 25.2, 22.4 ppm. HRMS(ESI) m/z calcd for $[\text{C}_{19}\text{H}_{21}\text{NO}_4+\text{H}]^+$ 328.1543, found 328.1545.

3-(benzyloxy)-2-(4-fluorophenyl)-5,5-dimethyloxazolidin-4-one (3da)



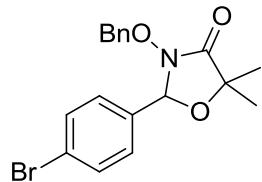
75.5 mg, 96% yield, White solid, m. p. 78 – 79 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.42 (dd, J = 8.5, 5.4 Hz, 2H), 7.30 (m, 3H), 7.18 (dd, J = 7.2, 1.7 Hz, 2H), 7.10 (t, J = 8.6 Hz, 2H), 5.57 (s, 1H), 4.94 (d, J = 10.3 Hz, 1H), 4.47 (d, J = 10.3 Hz, 1H), 1.55 (s, 3H), 1.42 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 172.5, 163.8 (d, J = 247.7 Hz), 134.2, 131.6 (d, J = 2.8 Hz), 129.7 (d, J = 8.6 Hz), 129.5, 129.0, 128.4, 115.6 (d, J = 21.7 Hz), 86.9, 78.1, 25.2, 22.5 ppm. HRMS(ESI) m/z calcd for $[\text{C}_{18}\text{H}_{18}\text{FNO}_3+\text{Na}]^+$ 338.1163, found 338.1166.

3-(benzyloxy)-2-(4-chlorophenyl)-5,5-dimethyloxazolidin-4-one (3ea)



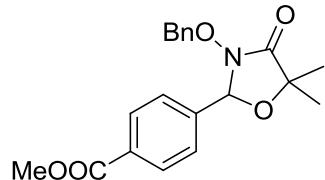
75.2 mg, 91% yield, White solid, m. p. 81 – 83 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.46 – 7.23 (m, 7H), 7.18 (dd, J = 7.5, 1.5 Hz, 2H), 5.55 (s, 1H), 4.94 (d, J = 10.3 Hz, 1H), 4.50 (d, J = 10.3 Hz, 1H), 1.55 (s, 3H), 1.41 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 172.6, 136.1, 134.3, 134.1, 129.5, 129.1, 129.0, 128.8, 128.4, 86.9, 78.1, 78.1, 25.2, 22.6 ppm. HRMS(ESI) m/z calcd for $[\text{C}_{18}\text{H}_{18}\text{ClNO}_3+\text{H}]^+$ 332.1048, found 332.1047.

3-(benzyloxy)-2-(4-bromophenyl)-5,5-dimethyloxazolidin-4-one (3fa)



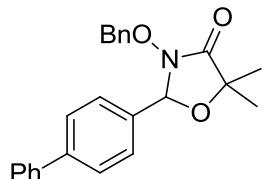
92.8 mg, 99% yield, White solid, m. p. 101 – 103 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.53 (d, $J = 8.3$ Hz, 2H), 7.38 – 7.23 (m, 5H), 7.17 (d, $J = 6.2$ Hz, 2H), 5.53 (s, 1H), 4.94 (d, $J = 10.4$ Hz, 1H), 4.51 (d, $J = 10.4$ Hz, 1H), 1.54 (s, 3H), 1.41 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 172.7, 134.9, 134.3, 131.9, 129.6, 129.4, 129.0, 128.5, 124.5, 87.1, 78.2, 78.2, 25.3, 22.6 ppm. HRMS(ESI) m/z calcd for $[\text{C}_{18}\text{H}_{18}\text{BrNO}_3+\text{H}]^+$ 378.0543, found 378.0541.

methyl 4-(3-(benzyloxy)-5,5-dimethyl-4-oxooxazolidin-2-yl)benzoate (3ga)



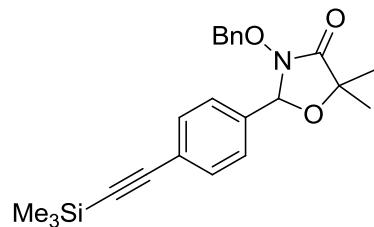
46.1 mg, 52% yield, White solid, m. p. 85 – 87 °C; ^1H NMR (300 MHz, CDCl_3) δ 8.10 (d, $J = 8.2$ Hz, 2H), 7.52 (d, $J = 8.2$ Hz, 2H), 7.41 – 7.23 (m, 3H), 7.23 – 7.06 (m, 2H), 5.64 (s, 1H), 4.94 (d, $J = 10.2$ Hz, 1H), 4.46 (d, $J = 10.2$ Hz, 1H), 3.95 (s, 3H), 1.57 (s, 3H), 1.44 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 172.6, 166.5, 140.6, 134.2, 131.9, 129.9, 129.6, 129.1, 128.5, 127.8, 87.0, 78.3, 78.2, 52.3, 25.3, 22.7 ppm. HRMS(ESI) m/z calcd for $[\text{C}_{20}\text{H}_{21}\text{NO}_5+\text{H}]^+$ 356.1492, found 356.1498.

2-([1,1'-biphenyl]-4-yl)-3-(benzyloxy)-5,5-dimethyloxazolidin-4-one (3ha)



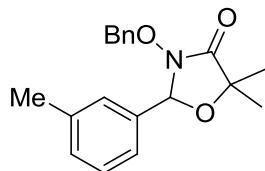
91.4 mg, 98% yield, White solid, m. p. 117 – 119 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.62 (t, $J = 8.3$ Hz, 4H), 7.55 – 7.40 (m, 4H), 7.37 (d, $J = 7.2$ Hz, 1H), 7.24 (m, 5H), 5.63 (s, 1H), 4.97 (d, $J = 10.3$ Hz, 1H), 4.52 (d, $J = 10.3$ Hz, 1H), 1.58 (s, 3H), 1.43 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 172.4, 143.1, 140.2, 134.6, 134.3, 129.5, 128.9, 128.8, 128.3, 128.2, 127.6, 127.3, 127.1, 87.4, 78.1, 78.0, 25.3, 22.6 ppm. HRMS(ESI) m/z calcd for $[\text{C}_{24}\text{H}_{23}\text{NO}_3+\text{H}]^+$ 374.1751, found 374.1756.

**3-(benzyloxy)-5,5-dimethyl-2-(4-((trimethylsilyl)ethynyl)phenyl)oxazolidin-4-one
(3ia)**



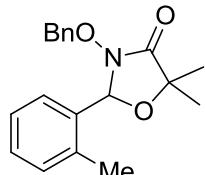
84.5 mg, 86% yield, White solid, m. p. 80 – 81 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.29 (m, 3H), 7.22 – 7.07 (m, 2H), 5.58 (s, 1H), 4.88 (d, *J* = 10.1 Hz, 1H), 4.41 (d, *J* = 10.1 Hz, 1H), 1.54 (s, 3H), 1.41 (s, 3H), 0.26 (s, 9H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 172.6, 135.9, 134.1, 132.2, 129.5, 129.0, 128.4, 127.6, 125.1, 104.2, 95.7, 87.2, 78.2, 78.1, 25.2, 22.5, -0.2 ppm. HRMS(ESI) *m/z* calcd for [C₂₃H₂₇NO₃Si+H]⁺ 394.1833, found 394.1842.

3-(benzyloxy)-5,5-dimethyl-2-(*m*-tolyl)oxazolidin-4-one (3ja)



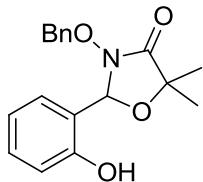
72.3 mg, 93% yield, White solid, m. p. 43 – 45 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.51 – 7.43 (m, 1H), 7.37 – 7.22 (m, 5H), 7.22 – 7.08 (m, 3H), 5.93 (s, 1H), 4.94 (d, *J* = 10.1 Hz, 1H), 4.45 (d, *J* = 10.1 Hz, 1H), 2.38 (s, 3H), 1.54 (s, 3H), 1.42 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 172.6, 137.5, 134.3, 133.1, 130.9, 129.8, 129.4, 128.9, 128.3, 127.9, 126.3, 84.9, 78.1, 78.0, 24.8, 22.5, 18.7 ppm. HRMS(ESI) *m/z* calcd for [C₁₉H₂₁NO₃+H]⁺ 312.1594, found 312.1590.

3-(benzyloxy)-5,5-dimethyl-2-(*o*-tolyl)oxazolidin-4-one (3ka)



70.8 mg, 91% yield, Colorless oil; ¹H NMR (300 MHz, CDCl₃) δ 7.28 (m, 7H), 7.17 (dd, *J* = 6.5, 2.8 Hz, 2H), 5.57 (s, 1H), 4.92 (d, *J* = 10.1 Hz, 1H), 4.43 (d, *J* = 10.1 Hz, 1H), 2.37 (s, 3H), 1.55 (s, 3H), 1.40 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 172.2, 138.2, 135.6, 134.2, 130.9, 129.4, 128.8, 128.4, 128.2, 124.8, 87.5, 78.0, 77.9, 25.1, 22.5, 21.2 ppm. HRMS(ESI) *m/z* calcd for [C₁₉H₂₁NO₃+H]⁺ 312.1594, found 312.1599.

3-(benzyloxy)-2-(2-hydroxyphenyl)-5,5-dimethyloxazolidin-4-one (3la)



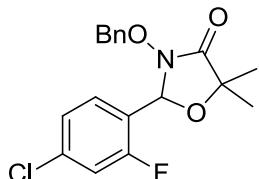
63.5 mg, 81% yield, White solid, m. p. 158 – 159 °C; ¹H NMR (300 MHz, DMSO-d₆) δ 9.97 (s, 1H), 7.49 – 7.11 (m, 7H), 6.99 – 6.79 (m, 2H), 6.29 (s, 1H), 4.95 (d, *J* = 10.0 Hz, 1H), 4.67 (d, *J* = 10.0 Hz, 1H), 1.41 (s, 3H), 1.34 (s, 3H) ppm. ¹³C NMR (75 MHz, DMSO-d₆) δ 170.4, 156.7, 134.5, 130.9, 129.2, 128.8, 128.7, 128.3, 121.7, 119.1, 115.7, 81.0, 77.1, 76.8, 24.8, 22.9 ppm. HRMS(ESI) *m/z* calcd for [C₁₈H₁₉NO₄+Na]⁺ 336.1206, found 336.1209.

3-(benzyloxy)-2-(3,4-dimethoxyphenyl)-5,5-dimethyloxazolidin-4-one (3ma)



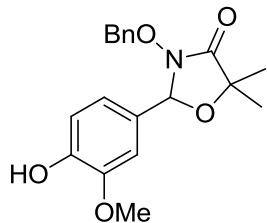
88.4 mg, 99% yield, White solid, m. p. 102 – 104 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.38 – 7.14 (m, 5H), 7.03 (dd, *J* = 8.2, 1.7 Hz, 1H), 6.91 (m, 2H), 5.56 (s, 1H), 4.93 (d, *J* = 10.2 Hz, 1H), 4.49 (d, *J* = 10.3 Hz, 1H), 3.91 (s, 3H), 3.87 (s, 3H), 1.56 (s, 3H), 1.42 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 172.3, 150.4, 149.0, 134.3, 129.4, 129.1, 128.8, 128.2, 127.9, 120.8, 110.6, 109.8, 87.5, 77.9, 77.8, 55.8, 55.6, 25.2, 22.4 ppm. HRMS(ESI) *m/z* calcd for [C₂₀H₂₃NO₅+H]⁺ 358.1649, found 358.1655.

3-(benzyloxy)-2-(4-chloro-2-fluorophenyl)-5,5-dimethyloxazolidin-4-one (3na)



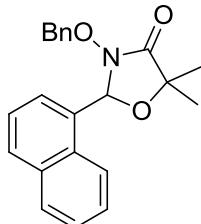
80.2 mg, 92% yield, Colorless oil; ¹H NMR (300 MHz, CDCl₃) δ 7.44 (dd, *J* = 8.7, 6.1 Hz, 1H), 7.35 – 7.17 (m, 5H), 7.11 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.00 (td, *J* = 8.4, 2.4 Hz, 1H), 6.14 (s, 1H), 5.00 (d, *J* = 10.5 Hz, 1H), 4.69 (d, *J* = 10.5 Hz, 1H), 1.52 (s, 3H), 1.42 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 172.2, 162.9 (d, *J* = 251.4 Hz), 135.3 (d, *J* = 10.5 Hz), 134.1, 130.7 (d, *J* = 9.3 Hz), 129.4, 129.1 (d, *J* = 3.6 Hz), 128.9, 128.3, 117.1 (d, *J* = 24.7 Hz), 114.7 (d, *J* = 21.3 Hz), 83.3, 78.2, 77.8, 24.9, 22.8 ppm. HRMS(ESI) *m/z* calcd for [C₁₈H₁₇ClFNO₃+H]⁺ 350.0954, found 350.0955.

3-(benzyloxy)-2-(4-hydroxy-3-methoxyphenyl)-5,5-dimethyloxazolidin-4-one (3oa)



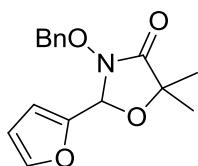
70.2 mg, 82% yield, White solid, m. p. 104 – 106 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.29 (m, 3H), 7.23 – 7.12 (m, 2H), 6.97 (d, $J = 0.7$ Hz, 2H), 6.90 (s, 1H), 6.04 (s, 1H), 5.54 (s, 1H), 4.94 (d, $J = 10.2$ Hz, 1H), 4.49 (d, $J = 10.2$ Hz, 1H), 3.87 (s, 3H), 1.56 (s, 3H), 1.42 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 172.5, 147.4, 146.8, 134.3, 129.5, 128.9, 128.3, 127.3, 121.6, 114.3, 109.4, 87.7, 78.1, 78.0, 55.8, 25.3, 22.5 ppm. HRMS(ESI) m/z calcd for $[\text{C}_{19}\text{H}_{21}\text{NO}_5+\text{Na}]^+$ 366.1312, found 366.1311.

3-(benzyloxy)-5,5-dimethyl-2-(naphthalen-1-yl)oxazolidin-4-one (3pa)



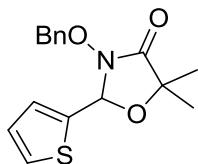
85.9 mg, 99% yield, Colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 8.31 – 8.10 (m, 1H), 7.90 (dd, $J = 11.5, 5.0$ Hz, 2H), 7.70 (d, $J = 6.6$ Hz, 1H), 7.61 – 7.41 (m, 3H), 7.32 – 7.06 (m, 3H), 6.95 (d, $J = 6.8$ Hz, 2H), 6.37 (s, 1H), 4.87 (d, $J = 10.1$ Hz, 1H), 4.34 (d, $J = 10.1$ Hz, 1H), 1.59 (s, 3H), 1.49 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 172.8, 134.0, 133.8, 131.3, 130.7, 130.5, 129.4, 128.8, 128.8, 128.2, 126.7, 126.5, 125.9, 125.0, 123.0, 85.8, 78.2, 78.0, 24.8, 22.7 ppm. HRMS(ESI) m/z calcd for $[\text{C}_{22}\text{H}_{21}\text{NO}_3+\text{Na}]^+$ 370.1414, found 370.1415.

3-(benzyloxy)-2-(furan-2-yl)-5,5-dimethyloxazolidin-4-one (3qa)



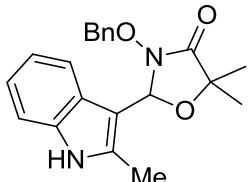
71.1 mg, 99% yield, White solid, m. p. 70 – 72 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.50 (s, 1H), 7.42 – 7.17 (m, 5H), 6.56 (d, $J = 2.9$ Hz, 1H), 6.42 (dd, $J = 3.2, 1.8$ Hz, 1H), 5.64 (s, 1H), 4.99 (d, $J = 10.3$ Hz, 1H), 4.58 (d, $J = 10.3$ Hz, 1H), 1.53 (s, 3H), 1.40 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 171.4, 148.4, 144.1, 134.2, 129.5, 129.0, 128.4, 112.3, 110.6, 80.9, 78.2, 78.0, 25.0, 23.6 ppm. HRMS(ESI) m/z calcd for $[\text{C}_{16}\text{H}_{17}\text{NO}_4+\text{H}]^+$ 288.1230, found 288.1230.

3-(benzyloxy)-5,5-dimethyl-2-(thiophen-2-yl)oxazolidin-4-one (3ra)



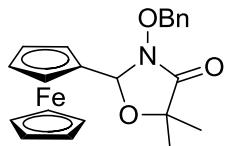
73.6 mg, 97% yield, White solid, m. p. 86 – 88 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.45 (d, $J = 4.9$ Hz, 1H), 7.40 – 7.15 (m, 6H), 7.03 (dd, $J = 4.9, 3.6$ Hz, 1H), 5.90 (s, 1H), 4.98 (d, $J = 10.0$ Hz, 1H), 4.53 (d, $J = 10.0$ Hz, 1H), 1.55 (s, 3H), 1.40 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 171.9, 140.2, 134.2, 129.5, 128.9, 128.6, 128.4, 128.1, 126.7, 83.7, 78.4, 78.2, 25.3, 22.7 ppm. HRMS(ESI) m/z calcd for $[\text{C}_{16}\text{H}_{17}\text{NO}_3\text{S}+\text{Na}]^+$ 326.0821, found 326.0828.

3-(benzyloxy)-5,5-dimethyl-2-(2-methyl-1*H*-indol-3-yl)oxazolidin-4-one (3sa)



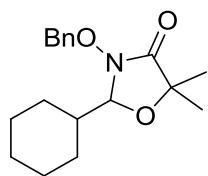
76.2 mg, 87% yield, White solid, m. p. 181 – 183 °C; ^1H NMR (300 MHz, CDCl_3) δ 8.65 (s, 1H), 7.76 – 7.61 (m, 1H), 7.32 – 7.07 (m, 6H), 7.02 (d, $J = 6.3$ Hz, 2H), 6.00 (s, 1H), 4.90 (d, $J = 10.4$ Hz, 1H), 4.40 (d, $J = 10.4$ Hz, 1H), 2.34 (s, 3H), 1.64 (s, 3H), 1.45 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 173.2, 136.9, 135.5, 134.6, 129.2, 128.6, 128.2, 126.4, 121.7, 120.2, 118.9, 110.8, 104.8, 82.6, 78.2, 77.6, 24.5, 22.0, 11.5 ppm. HRMS(ESI) m/z calcd for $[\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_3+\text{H}]^+$ 351.1073, found 351.1071.

3-(benzyloxy)-2-ferrocenyl-5,5-dimethyloxazolidin-4-one (3ta)



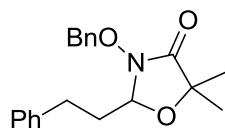
90.3 mg, 89% yield, Yellow solid, m. p. 119 – 121 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.30 (s, 5H), 5.53 (s, 1H), 4.87 (d, $J = 9.8$ Hz, 1H), 4.47 (d, $J = 9.8$ Hz, 1H), 4.34 (d, $J = 5.4$ Hz, 2H), 4.25 (s, 2H), 4.21 (s, 5H), 1.49 (s, 3H), 1.40 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 171.5, 134.2, 129.6, 128.8, 128.3, 85.3, 83.3, 78.3, 77.5, 69.1, 69.0, 68.9, 68.6, 65.5, 25.2, 22.8 ppm. HRMS(ESI) m/z calcd for $[\text{C}_{22}\text{H}_{21}\text{FeNO}_3+\text{Na}]^+$ 428.0920, found 428.0925.

3-(benzyloxy)-2-cyclohexyl-5,5-dimethyloxazolidin-4-one (3ua)



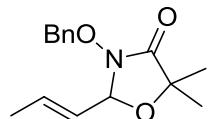
43.9 mg, 58% yield, Colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 7.62 – 7.27 (m, 5H), 5.16 (d, $J = 10.5$ Hz, 1H), 4.96 (d, $J = 10.5$ Hz, 1H), 4.54 (d, $J = 1.5$ Hz, 1H), 1.66 (m, 6H), 1.38 (s, 3H), 1.28 (s, 3H), 1.24 – 1.03 (m, 5H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 171.8, 134.5, 129.5, 129.0, 128.4, 89.3, 77.0, 77.0, 39.2, 27.2, 26.1, 25.5, 24.5, 24.4, 23.1 ppm. HRMS(ESI) m/z calcd for $[\text{C}_{18}\text{H}_{25}\text{NO}_3+\text{Na}]^+$ 326.1727, found 326.1733.

3-(benzyloxy)-5,5-dimethyl-2-phenethyloxazolidin-4-one (3va)



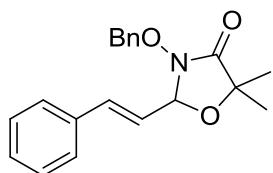
48.4 mg, 60% yield, Colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 7.40 – 6.97 (m, 10H), 5.06 (d, $J = 10.6$ Hz, 1H), 4.88 (d, $J = 10.6$ Hz, 1H), 4.64 (dd, $J = 6.2, 2.6$ Hz, 1H), 2.58 (m, 2H), 2.05 – 1.88 (m, 1H), 1.80 – 1.67 (m, 1H), 1.35 (s, 3H), 1.23 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 172.1, 140.9, 134.6, 129.6, 129.1, 128.6, 128.4, 128.3, 126.0, 114.9, 85.7, 77.8, 77.5, 34.7, 28.8, 25.1, 23.0 ppm. HRMS(ESI) m/z calcd for $[\text{C}_{20}\text{H}_{23}\text{NO}_3+\text{H}]^+$ 326.1751, found 351.1747.

(E)-3-(benzyloxy)-5,5-dimethyl-2-(prop-1-en-1-yl)oxazolidin-4-one (3wa)



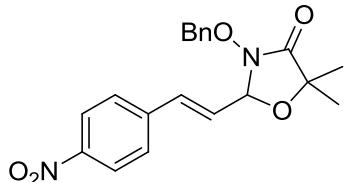
62.6 mg, 96% yield, Colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 7.46 – 7.30 (m, 5H), 5.91 (dq, $J = 13.2, 6.6$ Hz, 1H), 5.25 (m, 8.1, 1H), 5.00 (m, 3H), 1.74 (dd, $J = 6.6, 1.4$ Hz, 3H), 1.42 (s, 3H), 1.32 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 172.1, 135.5, 134.5, 129.7, 128.9, 128.3, 127.2, 87.5, 78.0, 77.2, 25.3, 22.8, 17.6 ppm. HRMS(ESI) m/z calcd for $[\text{C}_{15}\text{H}_{19}\text{NO}_3+\text{Na}]^+$ 284.1257, found 284.1263.

(E)-3-(benzyloxy)-5,5-dimethyl-2-styryloxazolidin-4-one (3xa)



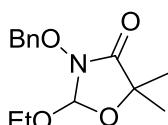
79.9 mg, 99% yield, White solid, m. p. 125 – 127 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.31 (m, 10H), 6.69 (d, $J = 15.8$ Hz, 1H), 5.88 (dd, $J = 15.8, 7.8$ Hz, 1H), 5.19 (d, $J = 7.7$ Hz, 1H), 5.08 (d, $J = 10.5$ Hz, 1H), 4.95 (d, $J = 10.5$ Hz, 1H), 1.47 (s, 3H), 1.37 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 172.3, 137.8, 134.9, 134.5, 129.8, 129.0, 128.8, 128.5, 128.4, 127.0, 124.3, 87.7, 78.3, 77.6, 25.4, 22.9 ppm. HRMS(ESI) m/z calcd for $[\text{C}_{20}\text{H}_{21}\text{NO}_3+\text{H}]^+$ 324.1594, found 324.1593.

(E)-3-(benzyloxy)-5,5-dimethyl-2-(4-nitrostyryl)oxazolidin-4-one (3ya)



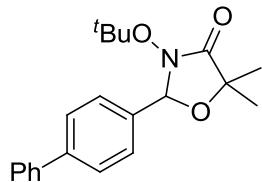
89.2 mg, 97% yield, Yellow solid, m. p. 102 – 103 °C; ^1H NMR (300 MHz, CDCl_3) δ 8.21 (d, $J = 8.7$ Hz, 2H), 7.47 (d, $J = 8.7$ Hz, 2H), 7.41 – 7.20 (m, 5H), 6.72 (d, $J = 15.9$ Hz, 1H), 5.95 (dd, $J = 15.9, 7.6$ Hz, 1H), 5.19 (d, $J = 7.5$ Hz, 1H), 5.09 (d, $J = 10.9$ Hz, 1H), 4.99 (d, $J = 10.9$ Hz, 1H), 1.49 (s, 3H), 1.40 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 172.0, 147.2, 140.8, 134.5, 134.1, 129.5, 128.7, 128.6, 128.0, 127.3, 123.5, 86.5, 77.8, 76.2, 25.0, 22.6 ppm. HRMS(ESI) m/z calcd for $[\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_5+\text{Na}]^+$ 391.1264, found 391.1270.

3-(benzyloxy)-2-ethoxy-5,5-dimethyloxazolidin-4-one (3za)



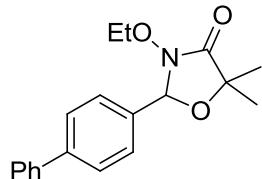
50.9 mg, 77% yield, Colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 7.57 – 7.31 (m, 5H), 5.51 (s, 1H), 5.08 (q, $J = 10.7$ Hz, 2H), 3.62 (m, 2H), 1.46 (s, 3H), 1.36 (s, 3H), 1.23 (t, $J = 7.1$ Hz, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 170.7, 134.7, 129.5, 129.0, 128.5, 103.4, 78.3, 77.7, 61.1, 25.3, 25.0, 15.0 ppm. HRMS(ESI) m/z calcd for $[\text{C}_{14}\text{H}_{19}\text{NO}_4+\text{Na}]^+$ 288.1206, found 288.1208.

2-([1,1'-biphenyl]-4-yl)-3-(tert-butoxy)-5,5-dimethyloxazolidin-4-one (3hb)



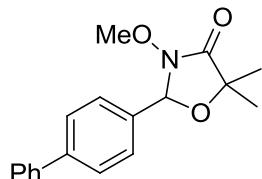
83.9 mg, 99% yield, White solid, m. p. 163 – 164 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.63 (m, 4H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.37 (d, *J* = 7.2 Hz, 1H), 5.88 (s, 1H), 1.52 (d, *J* = 20.7 Hz, 6H), 1.09 (s, 9H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 176.1, 142.8, 140.3, 135.4, 128.8, 128.6, 127.6, 127.1, 89.2, 84.0, 77.6, 27.5, 25.6, 23.7 ppm. HRMS(ESI) *m/z* calcd for [C₂₁H₂₅NO₃+Na]⁺ 362.1727, found 362.1731.

2-([1,1'-biphenyl]-4-yl)-3-ethoxy-5,5-dimethyloxazolidin-4-one (3hc)



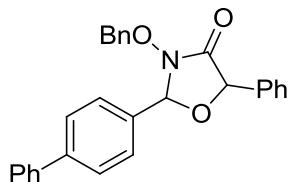
76.2 mg, 98% yield, White solid, m. p. 101 – 103 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.78 – 7.54 (m, 6H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.39 (d, *J* = 7.1 Hz, 1H), 5.83 (s, 1H), 3.97 – 3.76 (m, 1H), 3.66 – 3.45 (m, 1H), 1.60 (s, 3H), 1.47 (s, 3H), 1.09 (t, *J* = 7.0 Hz, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 173.4, 143.2, 140.3, 135.0, 128.9, 128.2, 127.7, 127.4, 127.1, 87.4, 78.2, 72.2, 25.4, 22.5, 13.5 ppm. HRMS(ESI) *m/z* calcd for [C₁₉H₂₁NO₃+Na]⁺ 334.1414, found 334.1420.

2-([1,1'-biphenyl]-4-yl)-3-methoxy-5,5-dimethyloxazolidin-4-one (3hd)



72.8 mg, 98% yield, White solid, m. p. 145 – 146 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.64 (m, *J* = 19.9, 6H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.37 (d, *J* = 7.2 Hz, 1H), 5.82 (s, 1H), 3.55 (s, 3H), 1.59 (s, 3H), 1.46 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 173.0, 143.2, 140.2, 134.8, 128.8, 128.1, 127.7, 127.3, 127.1, 86.9, 78.1, 64.1, 25.3, 22.4 ppm. HRMS(ESI) *m/z* calcd for [C₁₈H₁₉NO₃+Na]⁺ 320.1257, found 320.1262.

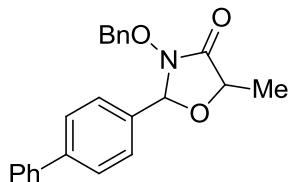
2-([1,1'-biphenyl]-4-yl)-3-(benzyloxy)-5-phenyloxazolidin-4-one (3he)



For the **major diastereomer**: 58.5 mg, 55% yield, White solid, m. p. 127 – 129 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.44 (m, 19H), 5.85 (s, 1H), 5.28 (s, 1H), 4.96 (d, *J* = 10.2 Hz, 1H), 4.56 (d, *J* = 10.2 Hz, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 169.6, 143.4, 140.3, 135.1, 134.4, 129.5, 128.9, 128.9, 128.9, 128.7, 128.6, 128.4, 127.8, 127.4, 127.2, 126.9, 89.4, 78.5, 77.7 ppm. HRMS(ESI) *m/z* calcd for [C₂₈H₂₃NO₃+Na]⁺ 444.1570, found 444.1573.

For the **minor diastereomer**: 16.7 mg, 16% yield, White solid, m. p. 142 – 143 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.64 (m, 4H), 7.56 – 7.16 (m, 15H), 5.76 (d, *J* = 1.6 Hz, 1H), 5.48 (s, 1H), 5.03 (d, *J* = 10.7 Hz, 1H), 4.73 (d, *J* = 10.7 Hz, 1H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 167.3, 143.3, 140.3, 135.5, 134.7, 134.4, 129.8, 129.2, 128.9, 128.7, 128.6, 128.0, 127.8, 127.5, 127.2, 126.3, 89.6, 78.1, 76.6 ppm. HRMS(ESI) *m/z* calcd for [C₂₈H₂₃NO₃+Na]⁺ 444.1570, found 444.1572.

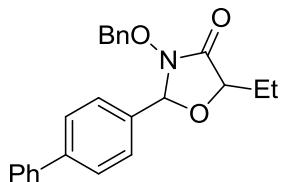
2-([1,1'-biphenyl]-4-yl)-3-(benzyloxy)-5-methyloxazolidin-4-one (3hf and 3hg)



For the **major diastereomer**: 45.7 mg, 51% yield (X = Br), 39.4 mg, 44% yield (X = Cl), White solid, m. p. 132 – 133 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.61 (t, *J* = 7.8 Hz, 4H), 7.55 – 7.39 (m, 4H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.30 – 7.06 (m, 5H), 5.64 (d, *J* = 1.2 Hz, 1H), 4.94 (d, *J* = 10.2 Hz, 1H), 4.49 (d, *J* = 10.2 Hz, 1H), 4.38 (m, 1H), 1.57 (d, *J* = 6.7 Hz, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 171.2, 143.3, 140.3, 134.5, 134.3, 129.5, 128.9, 128.9, 128.4, 128.4, 127.8, 127.4, 127.2, 89.4, 78.4, 72.8, 17.7 ppm. HRMS(ESI) *m/z* calcd for [C₂₃H₂₁NO₃+Na]⁺ 382.1414, found 382.1415.

For the **minor diastereomer**: 15.8 mg, 17% yield (X = Br), 10.9 mg, 12% yield (X = Cl), White solid, m. p. 102 – 104 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.83 – 7.07 (m, 14H), 5.66 (d, *J* = 1.4 Hz, 1H), 5.01 (d, *J* = 10.5 Hz, 1H), 4.65 (m, 2H), 1.48 (d, *J* = 6.9 Hz, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 170.2, 148.8, 143.1, 140.3, 134.9, 134.5, 129.6, 129.1, 128.9, 128.5, 127.9, 127.7, 127.5, 127.2, 127.1, 115.0, 88.8, 78.2, 72.1, 17.0 ppm. HRMS(ESI) *m/z* calcd for [C₂₃H₂₁NO₃+H]⁺ 360.1594, found 360.1593.

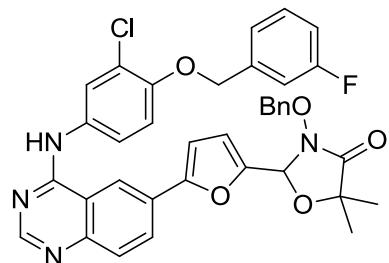
2-([1,1'-biphenyl]-4-yl)-3-(benzyloxy)-5-ethyloxazolidin-4-one (3hh)



For the **major diastereomer**: 46.1 mg, 49% yield, White solid, m. p. 97 – 99 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.41 (m, 14H), 5.66 (s, 1H), 4.91 (d, *J* = 10.2 Hz, 1H), 4.53 (d, *J* = 10.2 Hz, 1H), 4.30 (t, *J* = 4.4 Hz, 1H), 2.15 – 1.83 (m, 2H), 1.10 (t, *J* = 7.3 Hz, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 171.0, 143.2, 140.3, 134.5, 134.4, 129.5, 128.8, 128.8, 128.4, 128.3, 127.7, 127.3, 127.1, 89.3, 78.3, 77.2, 24.6, 8.8 ppm. HRMS(ESI) *m/z* calcd for [C₂₄H₂₃NO₃+H]⁺ 374.1751, found 374.1757.

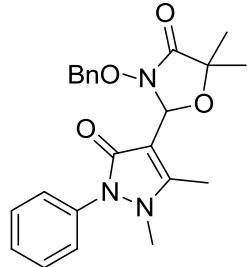
For the **minor diastereomer**: 11.2 mg, 12% yield, White solid, m. p. 97 – 99 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.93 – 6.98 (m, 14H), 5.65 (s, 1H), 5.00 (d, *J* = 10.6 Hz, 1H), 4.68 (d, *J* = 10.6 Hz, 1H), 4.49 (s, 1H), 1.86 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 169.4, 143.1, 140.3, 135.2, 134.5, 129.6, 129.1, 128.9, 128.5, 127.9, 127.7, 127.5, 127.2, 89.4, 78.3, 76.6, 24.8, 9.0 ppm. HRMS(ESI) *m/z* calcd for [C₂₄H₂₃NO₃+H]⁺ 374.1751, found 374.1758.

3-(benzyloxy)-2-(5-((4-((3-chloro-4-((3-fluorobenzyl)oxy)phenyl)amino)quinazolin-6-yl)furan-2-yl)-5,5-dimethyloxazolidin-4-one (5aa)



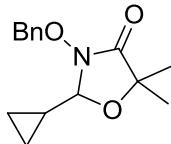
129.9 mg, 78% yield, Yellow solid, m. p. 190 – 191 °C; ¹H NMR (300 MHz, DMSO-d₆) δ 9.94 (s, 1H), 8.82 (s, 1H), 8.58 (s, 1H), 8.14 (d, *J* = 8.6 Hz, 1H), 8.01 (d, *J* = 2.1 Hz, 1H), 7.86 (d, *J* = 8.7 Hz, 1H), 7.72 (d, *J* = 6.8 Hz, 1H), 7.56 – 7.26 (m, 8H), 7.24 – 7.09 (m, 2H), 7.00 (d, *J* = 3.2 Hz, 1H), 6.12 (s, 1H), 5.27 (s, 2H), 5.02 (d, *J* = 10.4 Hz, 1H), 4.79 (d, *J* = 10.3 Hz, 1H), 1.52 (s, 3H), 1.39 (s, 3H) ppm. ¹³C NMR (75 MHz, DMSO-d₆) δ 170.2, 165.6, 157.7, 154.7, 153.9, 149.9, 149.3, 148.9, 139.6, 134.3, 132.9, 130.6, 130.5, 129.3, 128.9, 128.7, 128.5, 128.4, 127.5, 124.3, 123.3, 122.5, 121.1, 117.8, 115.3, 114.9, 114.8, 114.5, 114.4, 114.2, 113.9, 107.8, 79.9, 77.6, 77.3, 69.4, 25.1, 23.6 ppm. HRMS(ESI) *m/z* calcd for [C₃₇H₃₀ClFN₄O₅+H]⁺ 665.1962, found 665.1961.

3-(benzyloxy)-2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)-5,5-dimethyloxazolidin-4-one (5ca)



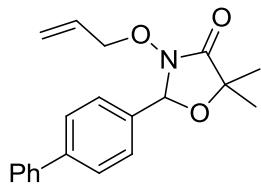
91.6 mg, 90% yield, Colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 7.58 – 7.14 (m, 10H), 5.86 (s, 1H), 5.13 (d, $J = 10.9$ Hz, 1H), 4.93 (d, $J = 10.9$ Hz, 1H), 3.08 (s, 3H), 2.17 (s, 3H), 1.53 (s, 3H), 1.34 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 171.8, 163.7, 154.2, 134.5, 133.9, 129.1, 128.9, 128.4, 128.0, 127.0, 124.7, 100.4, 79.8, 77.3, 77.2, 34.1, 23.9, 22.1, 10.5 ppm. HRMS(ESI) m/z calcd for $[\text{C}_{23}\text{H}_{25}\text{N}_3\text{O}_4+\text{H}]^+$ 408.1918, found 408.1917.

3-(benzyloxy)-2-cyclopropyl-5,5-dimethyloxazolidin-4-one (3Aa)



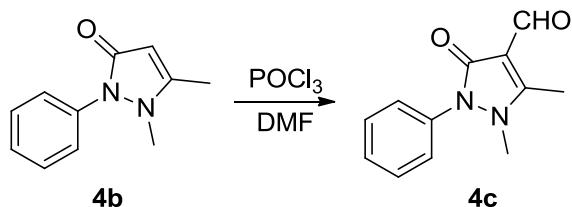
62.6 mg, 96% yield, White solid, m. p. 43 – 45 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.46 (dd, $J = 6.4, 2.9$ Hz, 2H), 7.37 (m, 3H), 5.16 (d, $J = 10.1$ Hz, 1H), 5.06 (d, $J = 10.1$ Hz, 1H), 4.09 (d, $J = 7.7$ Hz, 1H), 1.44 (s, 3H), 1.30 (s, 3H), 0.99 (m, 1H), 0.72 – 0.56 (m, 2H), 0.54 – 0.45 (m, 1H), 0.39 (m, 1H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 172.4, 134.4, 129.6, 128.9, 128.3, 90.5, 78.2, 77.2, 25.2, 22.6, 13.5, 1.4, 0.8 ppm. HRMS(ESI) m/z calcd for $[\text{C}_{15}\text{H}_{19}\text{NO}_3+\text{Na}]^+$ 284.1257, found 284.1262.

2-([1,1'-biphenyl]-4-yl)-3-(allyloxy)-5,5-dimethyloxazolidin-4-one (3hi)



78.3 mg, 97% yield, White solid, m. p. 88 – 90 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.63 (m, 6H), 7.41 (m, 3H), 5.96 – 5.68 (m, 2H), 5.16 (m, 2H), 4.24 (dd, $J = 11.5, 7.1$ Hz, 1H), 4.07 (dd, $J = 11.5, 6.0$ Hz, 1H), 1.58 (s, 3H), 1.46 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 173.0, 143.2, 140.2, 134.8, 131.7, 128.8, 128.3, 127.7, 127.3, 127.1, 120.8, 87.4, 78.1, 77.2, 25.3, 22.7. HRMS(ESI) m/z calcd for $[\text{C}_{20}\text{H}_{21}\text{NO}_3+\text{Na}]^+$ 346.1414, found 346.1415.

4. Preparation of 4-Formylantipyrine²



To a solution of DMF (0.76 mL, 9.9 mmol) in a 50 mL round-bottomed flask cooled to 0 °C was added POCl_3 (0.69 mL, 7.4 mmol). After 30 min, antipyrine (**4b**, 0.92 g, 4.9 mmol) was added to the mixture. The mixture was heated at 85 °C for 3 h and allowed to cool to rt. The mixture was poured into a mixture of ice, and the pH of the mixture was adjusted to ~11 with NaOH (2 N). The mixture was then extracted with DCM three times. The combined organic phases were washed with brine, dried over Na_2SO_4 , filtered, and concentrated in vacuo. The residue was recrystallized from PE and EA, affording the desired product as a white solid (0.72 g, 68%).

² Liu, L.; Norman, M. H.; Lee, M.; Xi, N.; Siegmund, A.; Boezio, A. A.; Booker, S.; Choquette, D.; D'Angelo, N. D.; Germain, J.; Yang, K.; Yang, Y.; Zhang, Y.; Bellon, S. F.; Whittington, D. A.; Harmange, J.-C.; Dominguez, C.; Kim, T.-S.; Dussault, I. *J. Med. Chem.* **2012**, *55*, 1868.

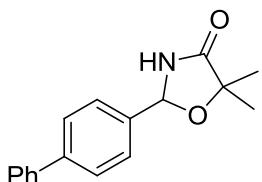
5. General Procedure for N–O Bond Cleavage Reaction

a) General Procedure³

To a solution of Oxazolidin-4-one **3ha** (74.6 mg, 0.2 mmol, 1 eq) in acetonitrile/water (9:1, 2 mL), Mo(CO)₆ (63.4 mg, 0.24 mmol, 1.2 eq) was added. The reaction was stirred at 120 °C under argon for 12 h. After cooling to room temperature, the mixture was filtered through celite and washed with ethyl acetate. Then, filtrate was concentrated under rotary evaporation, and the resulting residue was purified by silica gel chromatography (PE/EA = 5/1) to afford **4ha** as a white solid (47.2 mg, 88%).

b) Characterization of the Products

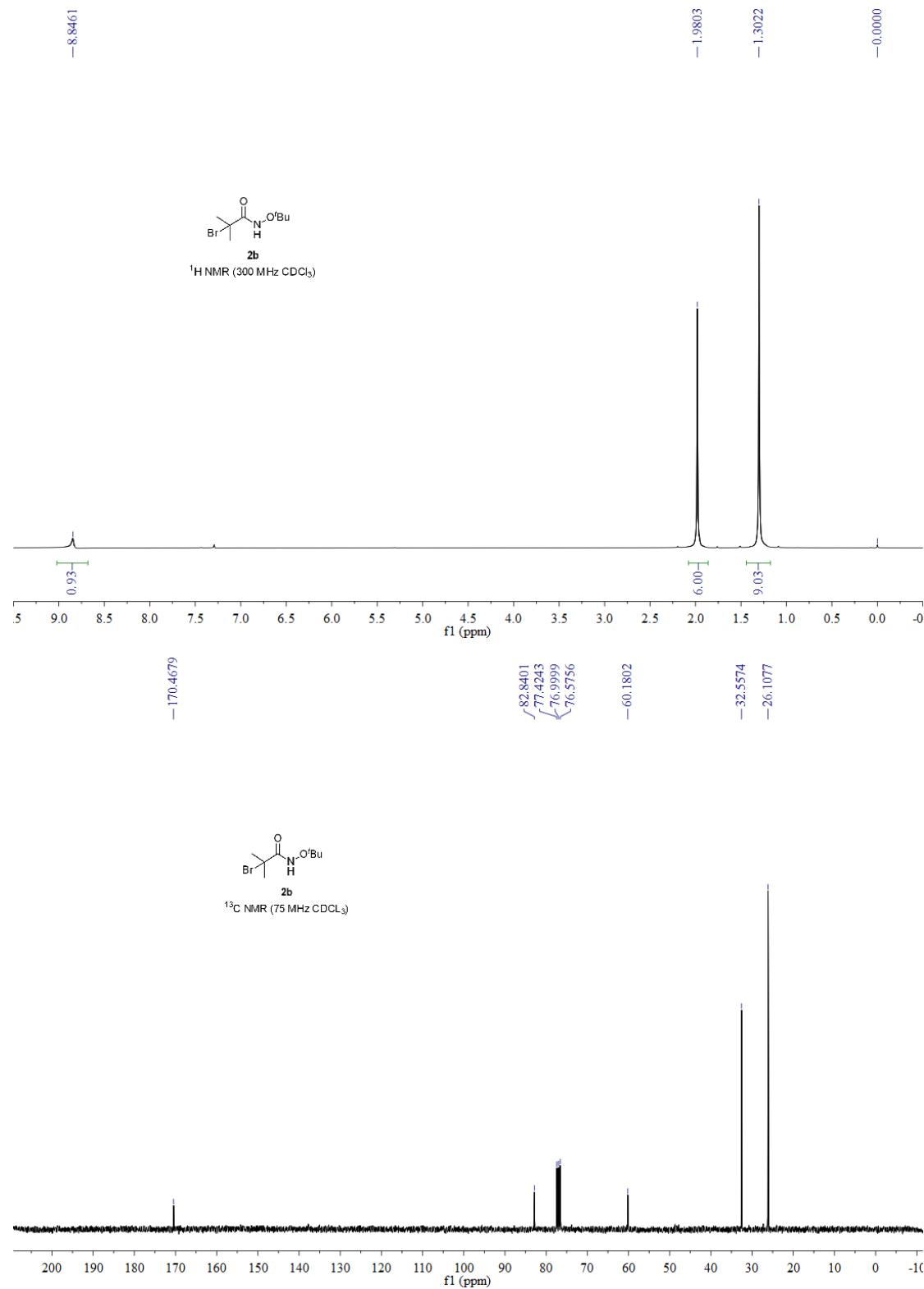
2-([1,1'-biphenyl]-4-yl)-5,5-dimethyloxazolidin-4-one (6ha)

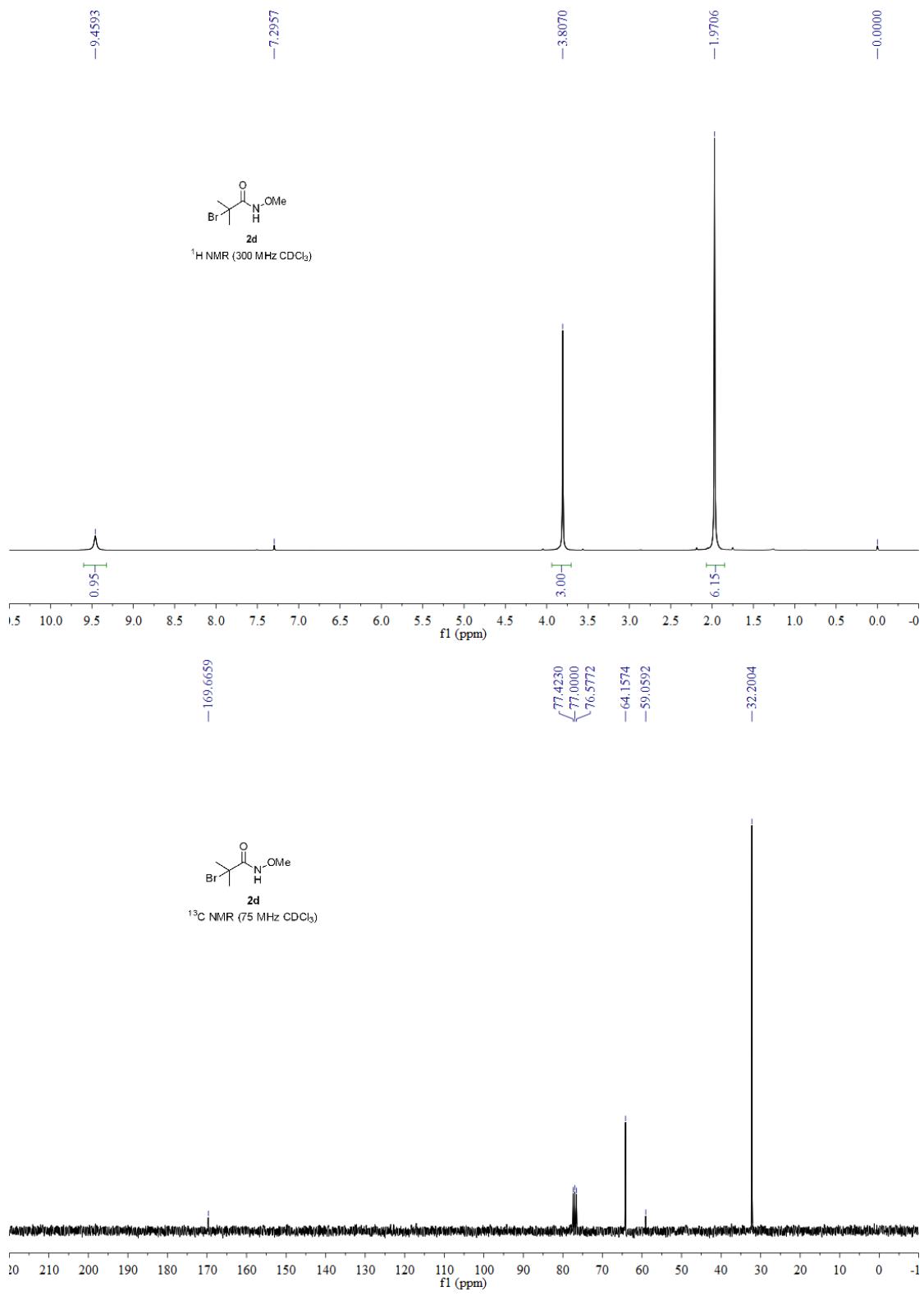


47.2 mg, 88% yield, White solid, m. p. 215 – 216 °C; ¹H NMR (300 MHz, DMSO-d₆) δ 9.11 (s, 1H), 7.87 – 7.61 (m, 4H), 7.61 – 7.25 (m, 5H), 6.06 (s, 1H), 1.34 (d, *J* = 4.9 Hz, 6H) ppm. ¹³C NMR (75 MHz, DMSO-d₆) δ 175.9, 141.1, 139.6, 138.6, 129.0, 127.7, 127.4, 126.8, 126.8, 83.8, 78.5, 25.0, 22.9 ppm. HRMS(ESI) *m/z* calcd for [C₁₇H₁₇NO₂+H]⁺ 268.1332, found 268.1336.

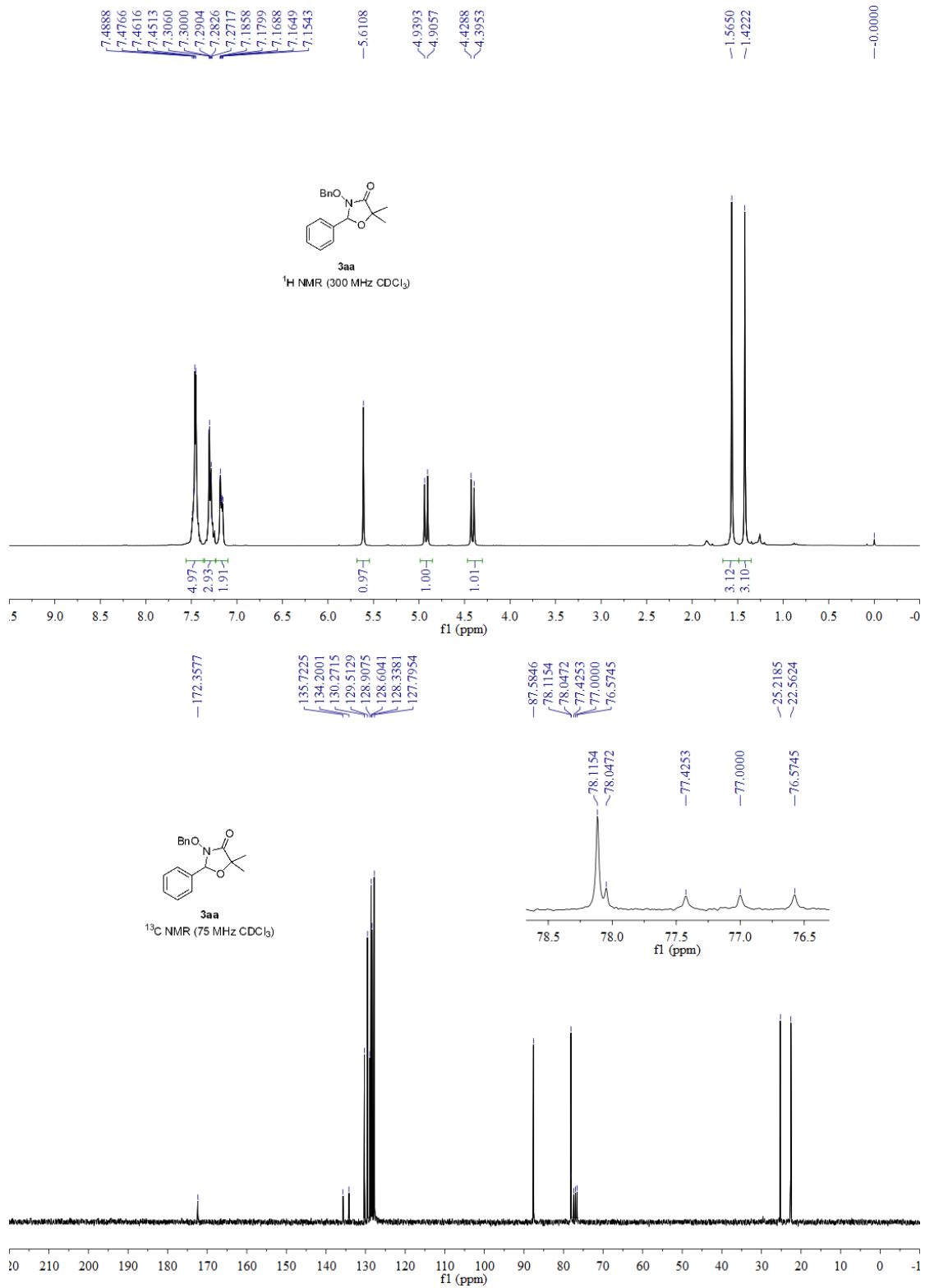
³ DiPoto, M. C.; Hughes, R. P.; Wu, J. *J. Am. Chem. Soc.* **2015**, *137*, 14861.

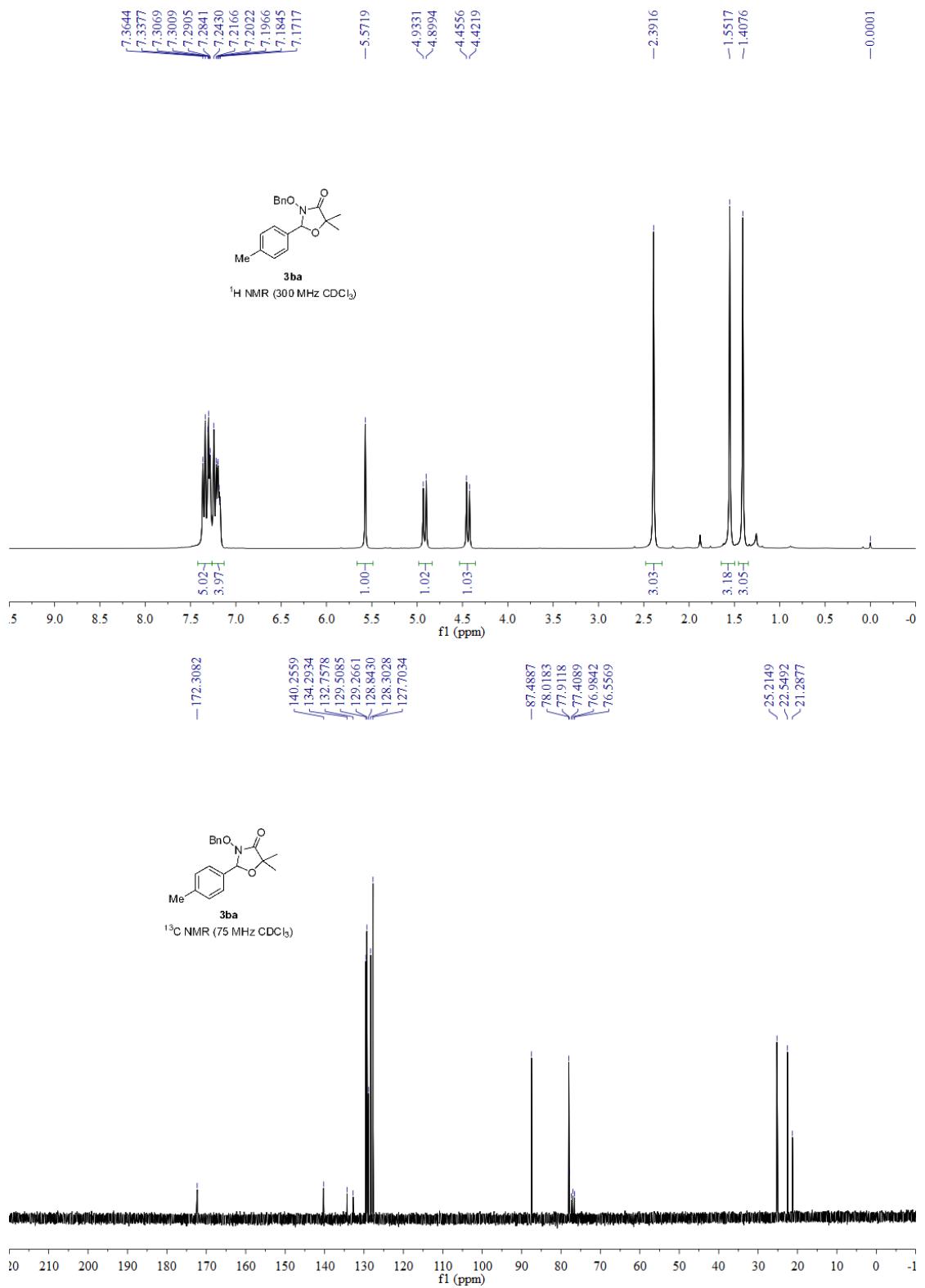
6. Copies of ^1H NMR and ^{13}C NMR Spectra of the Titled Compounds

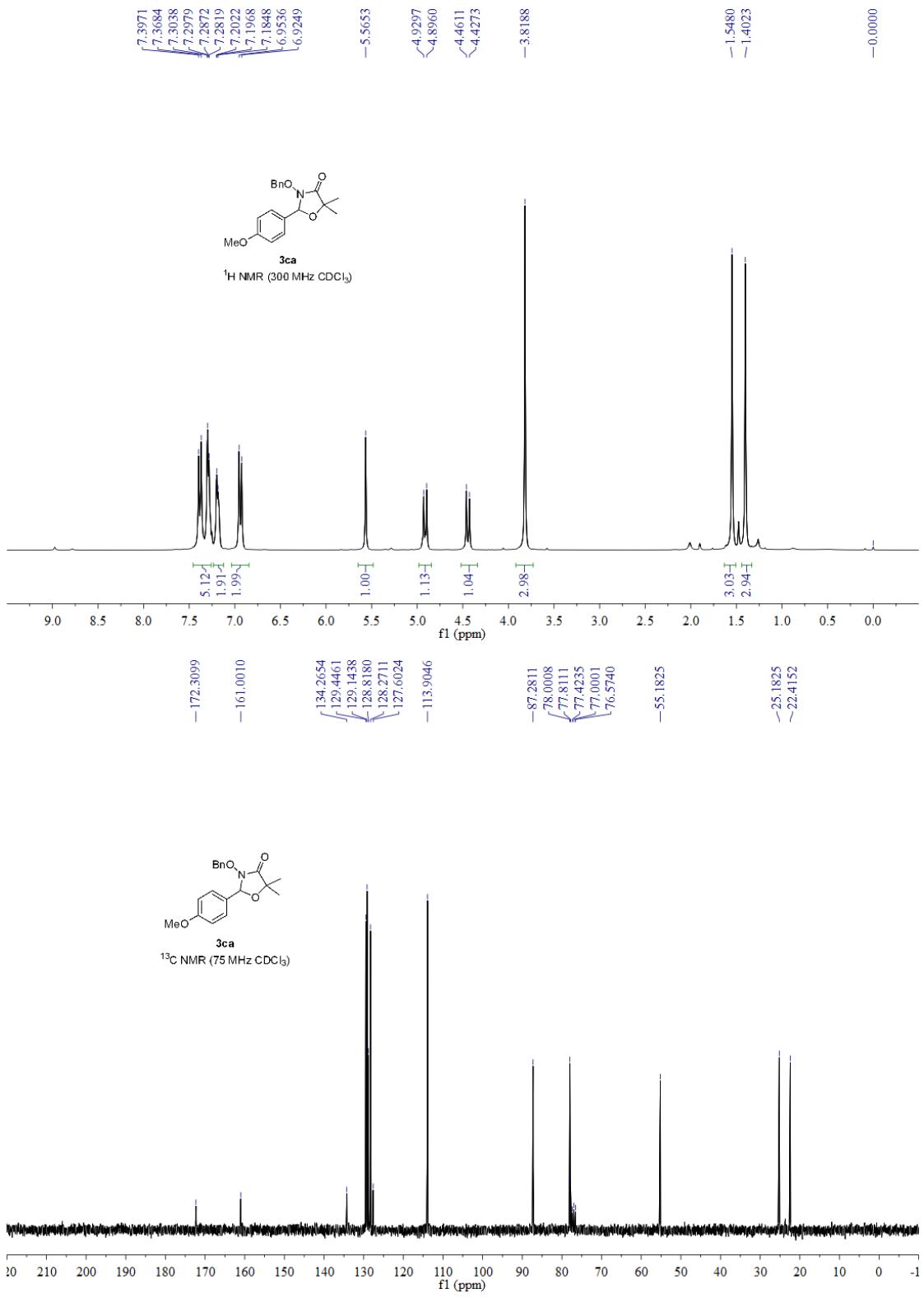


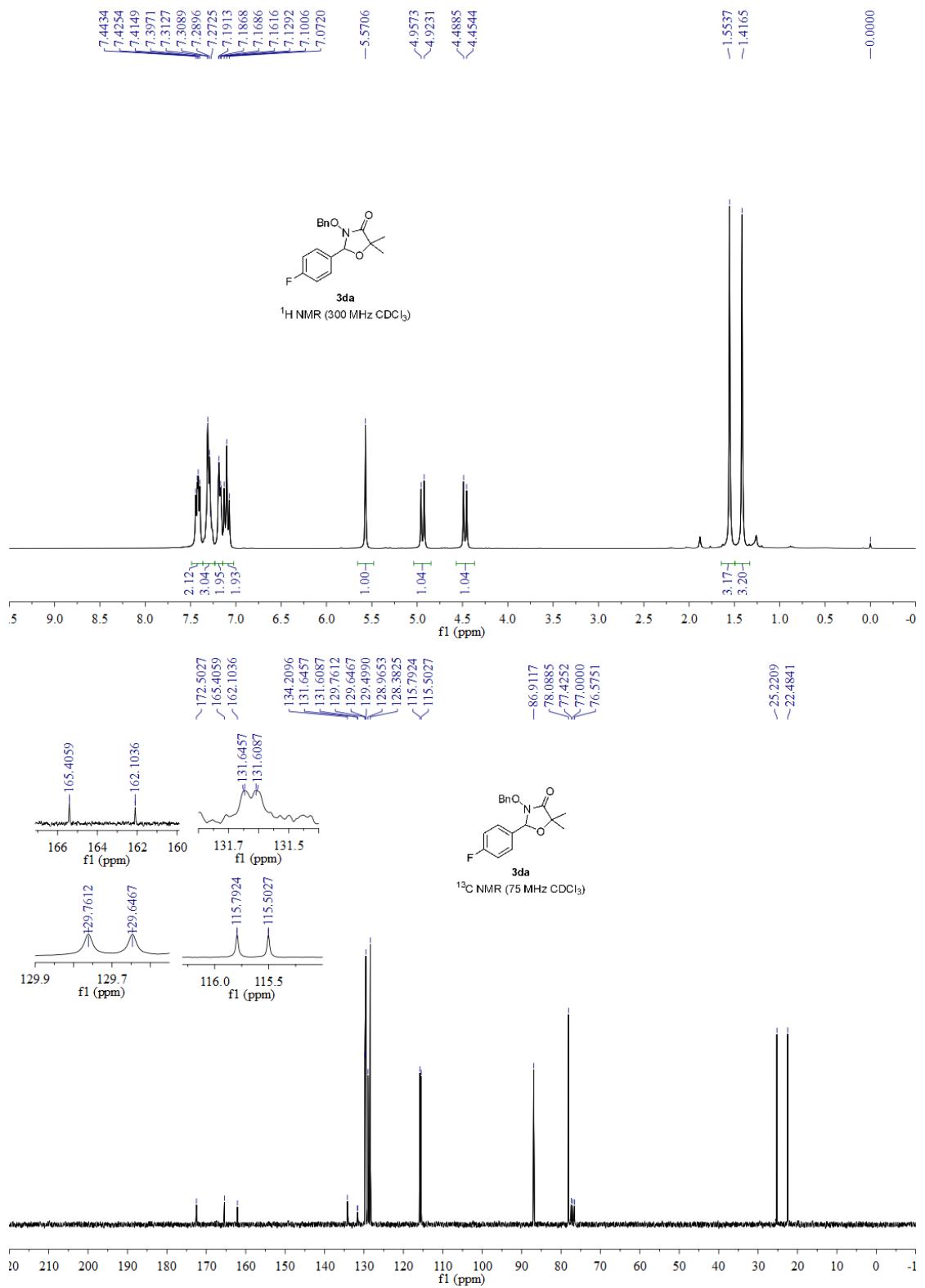


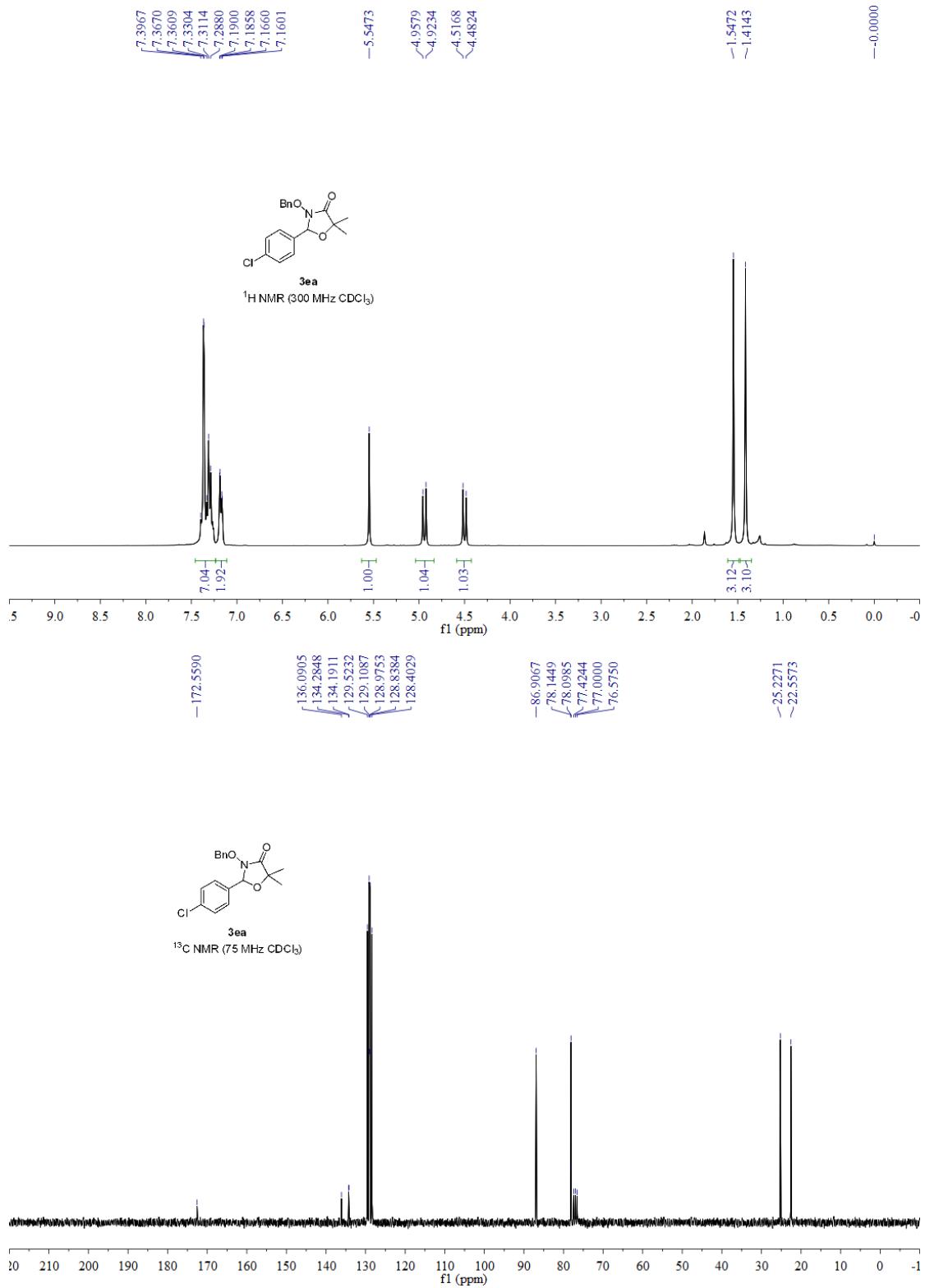


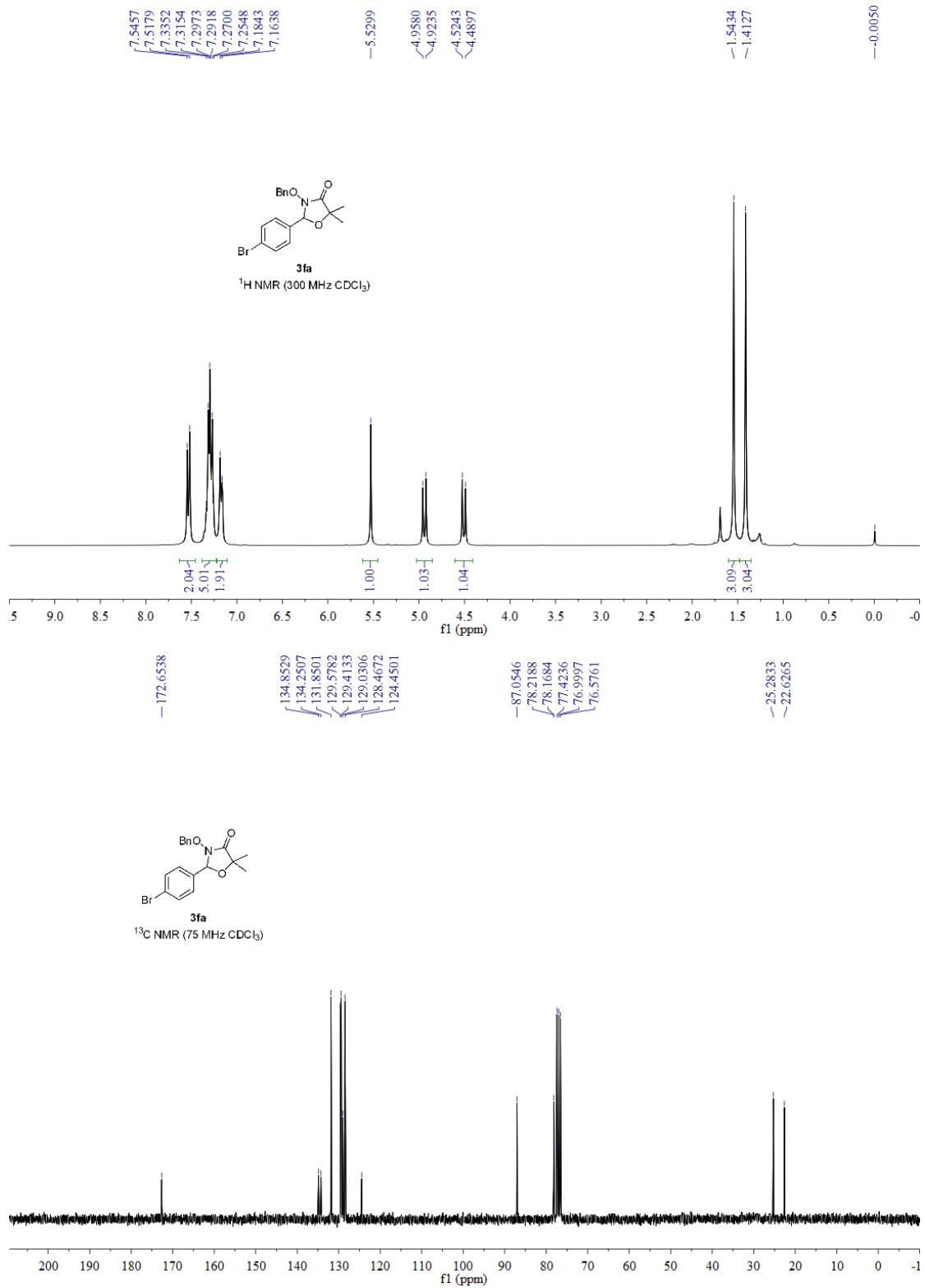


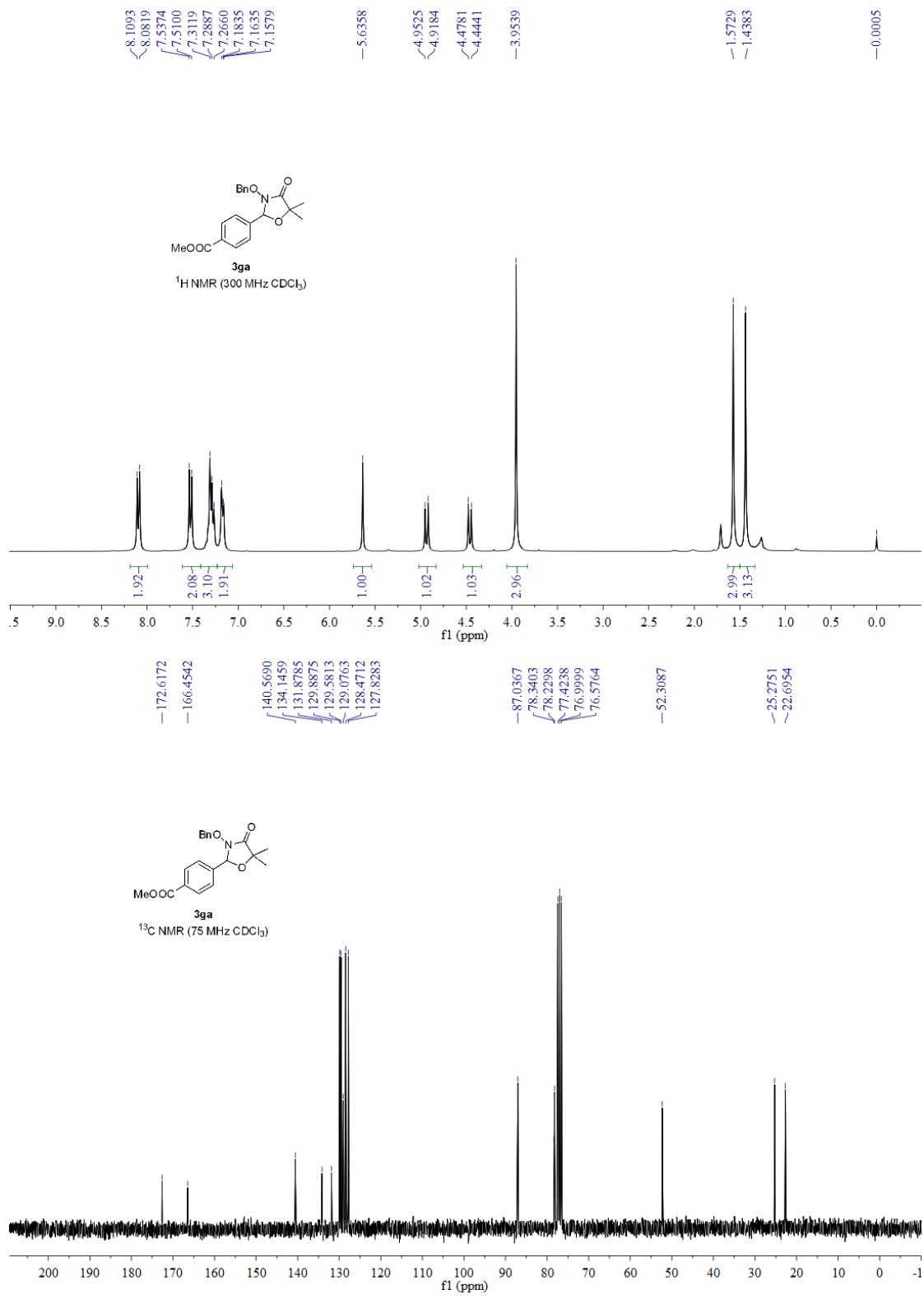


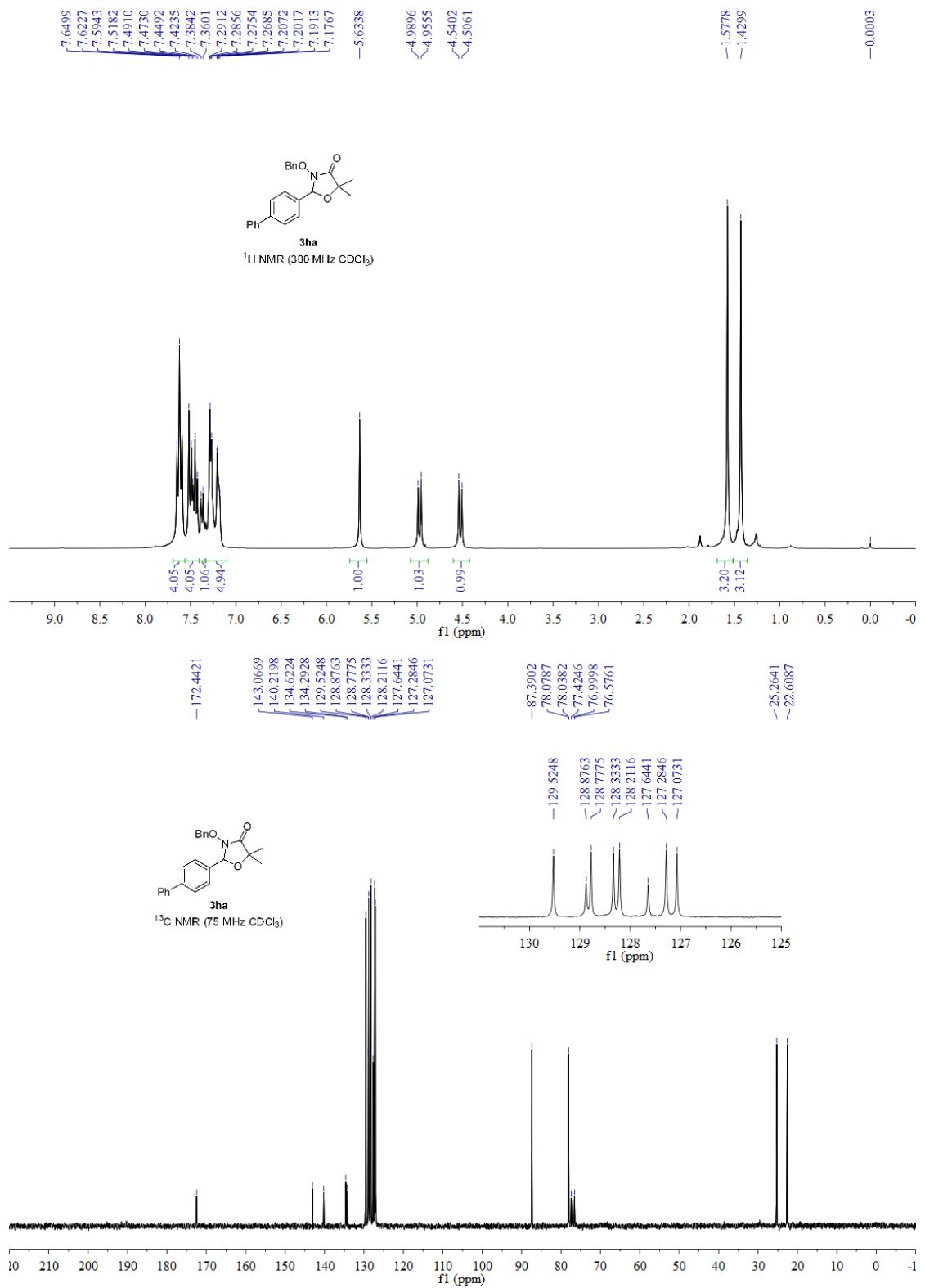


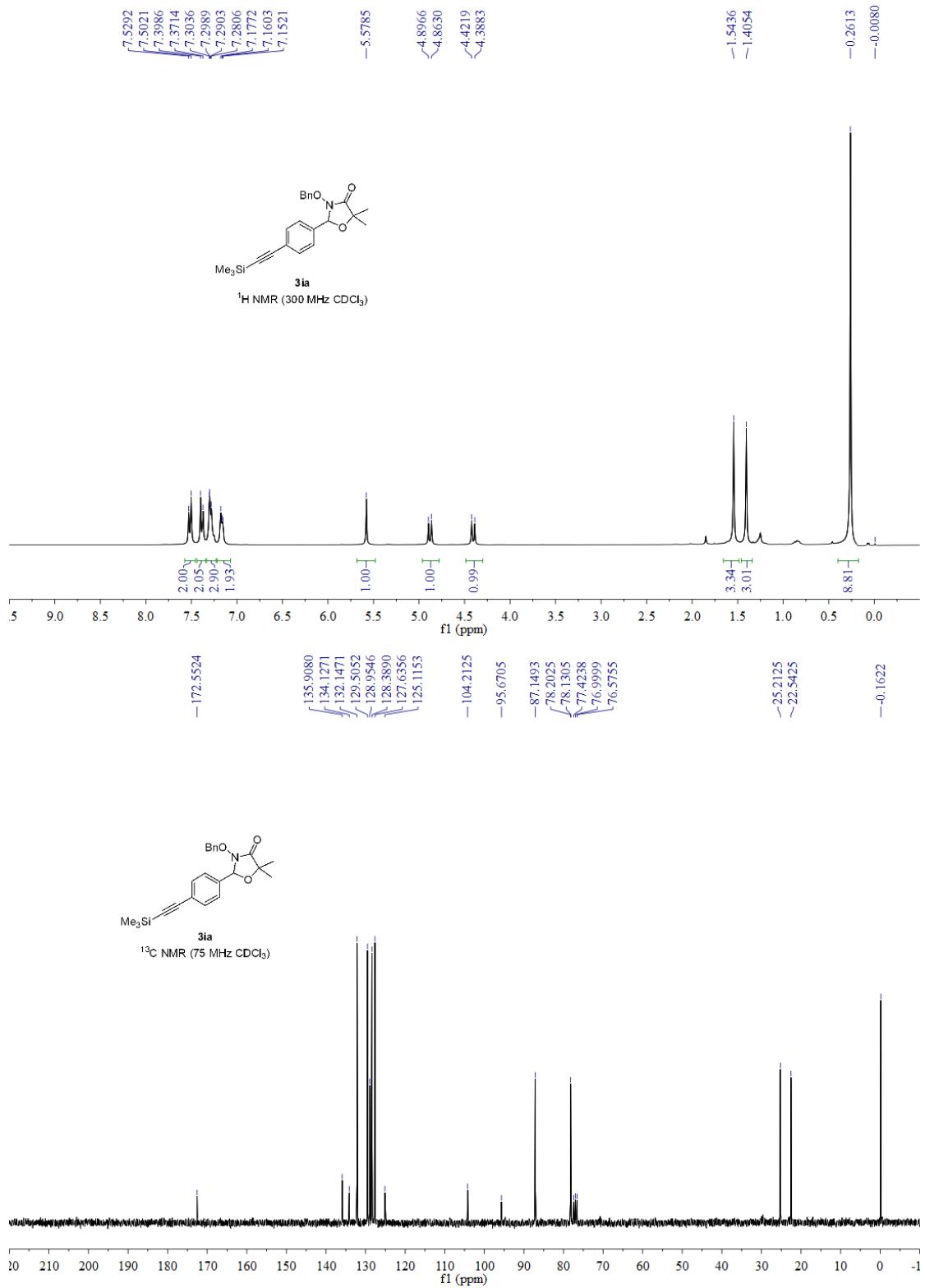


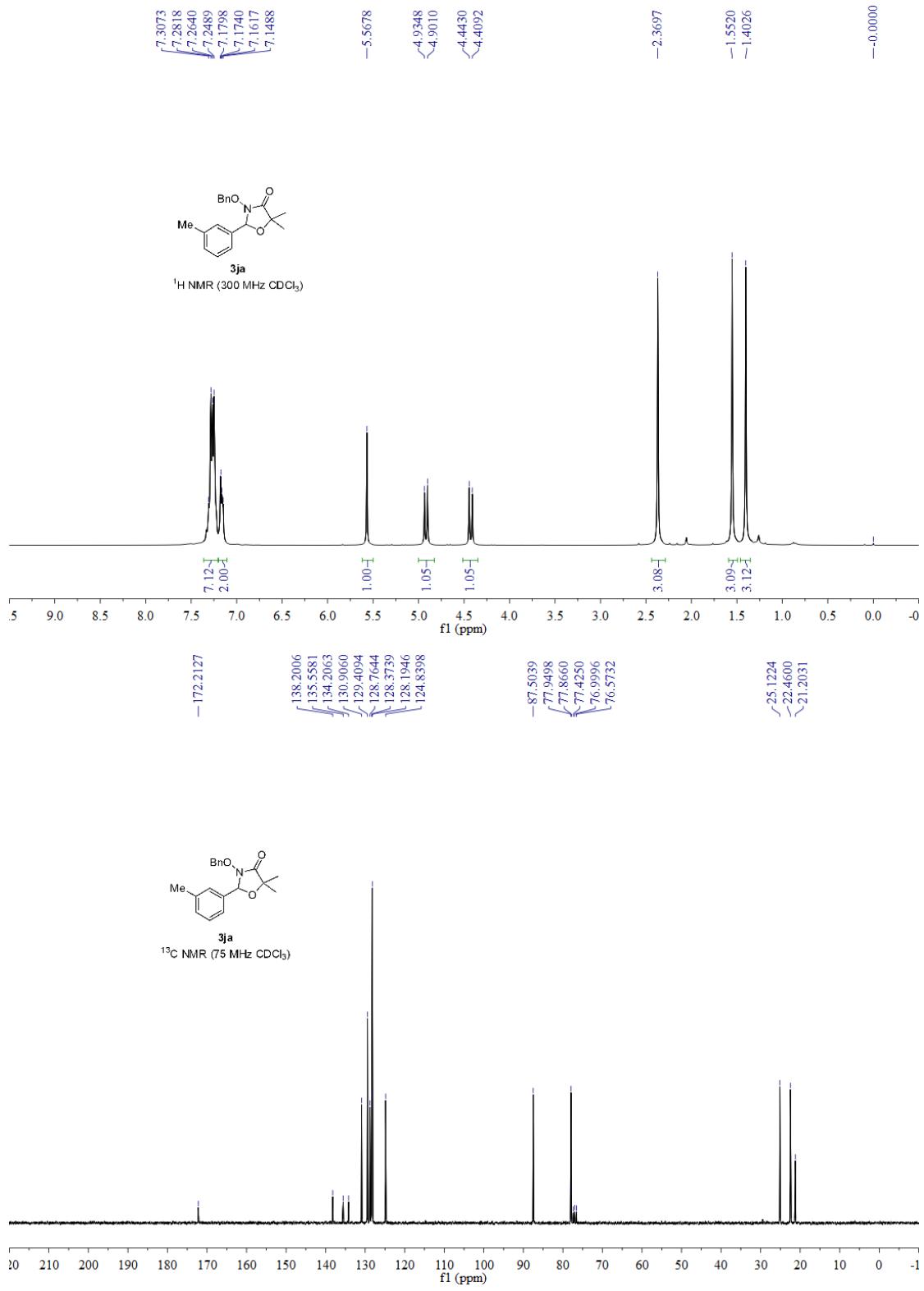


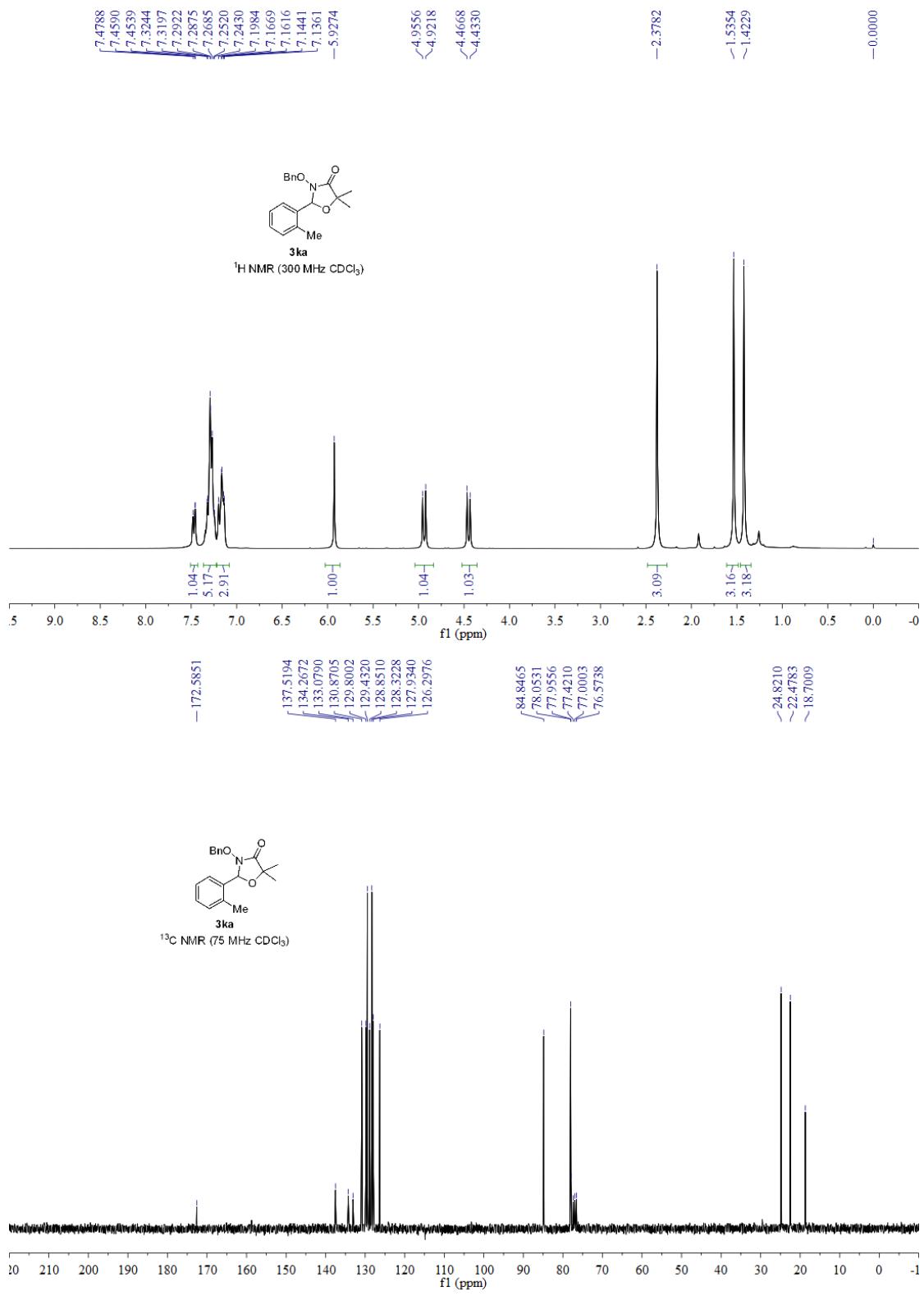


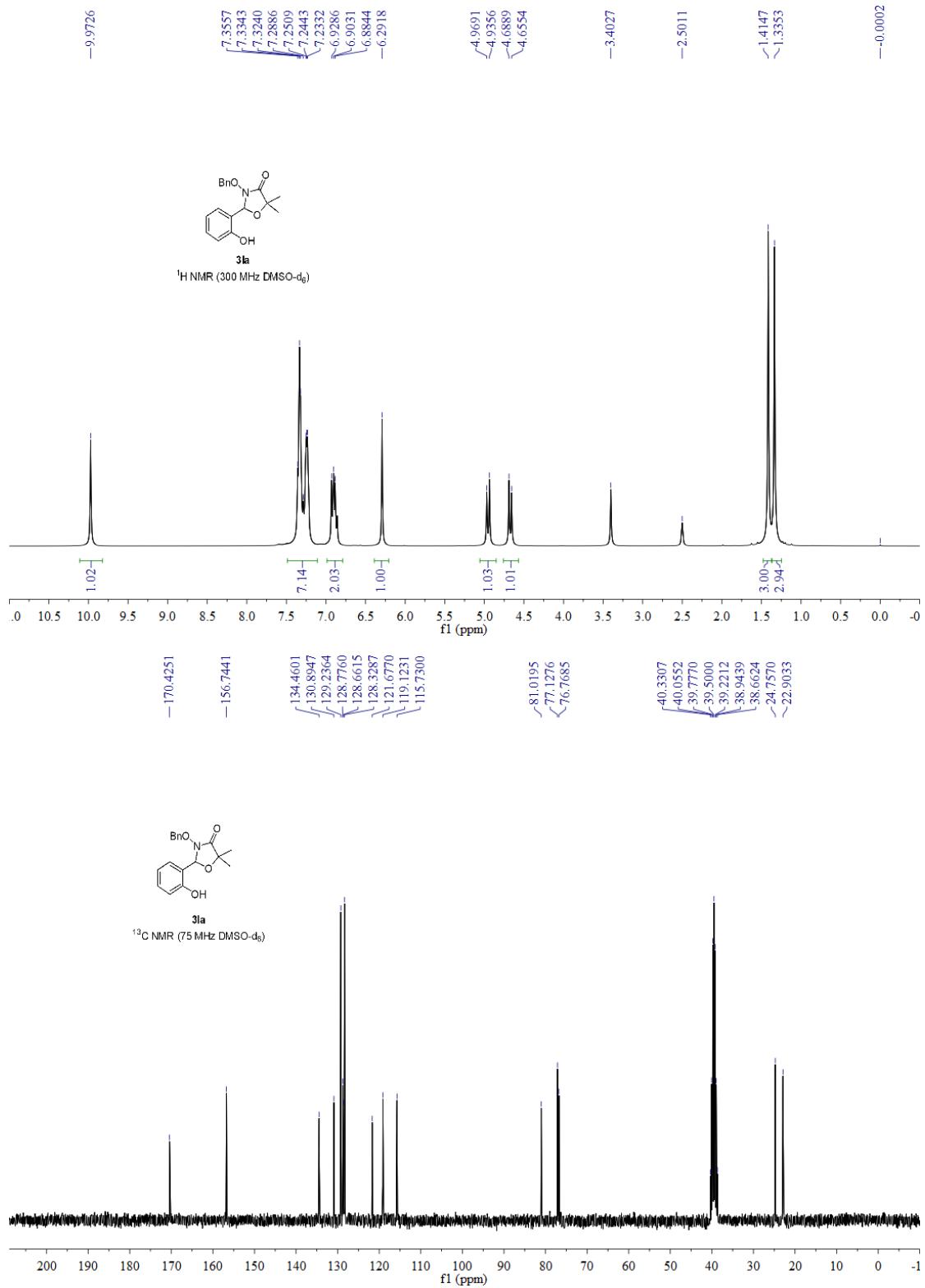


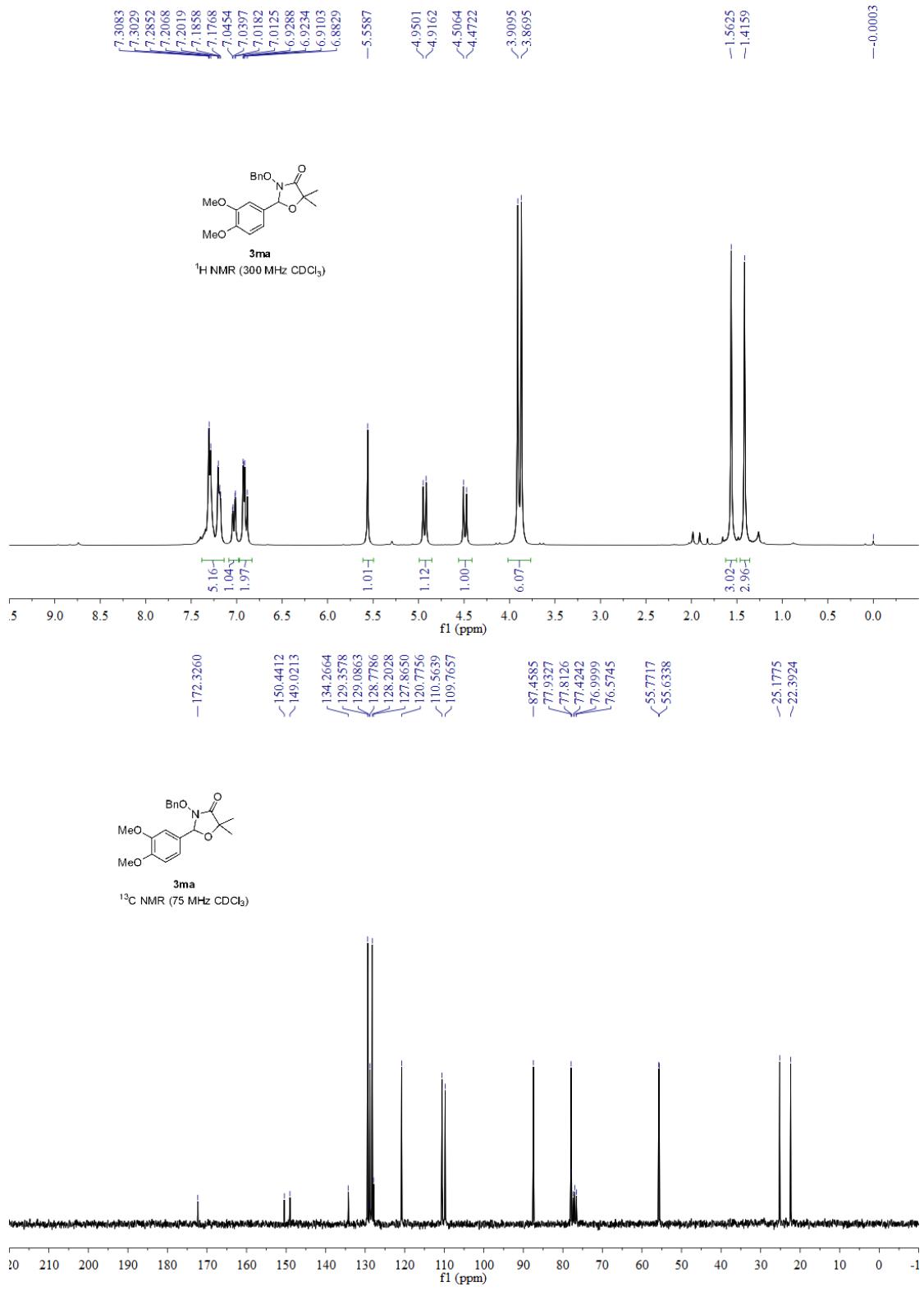


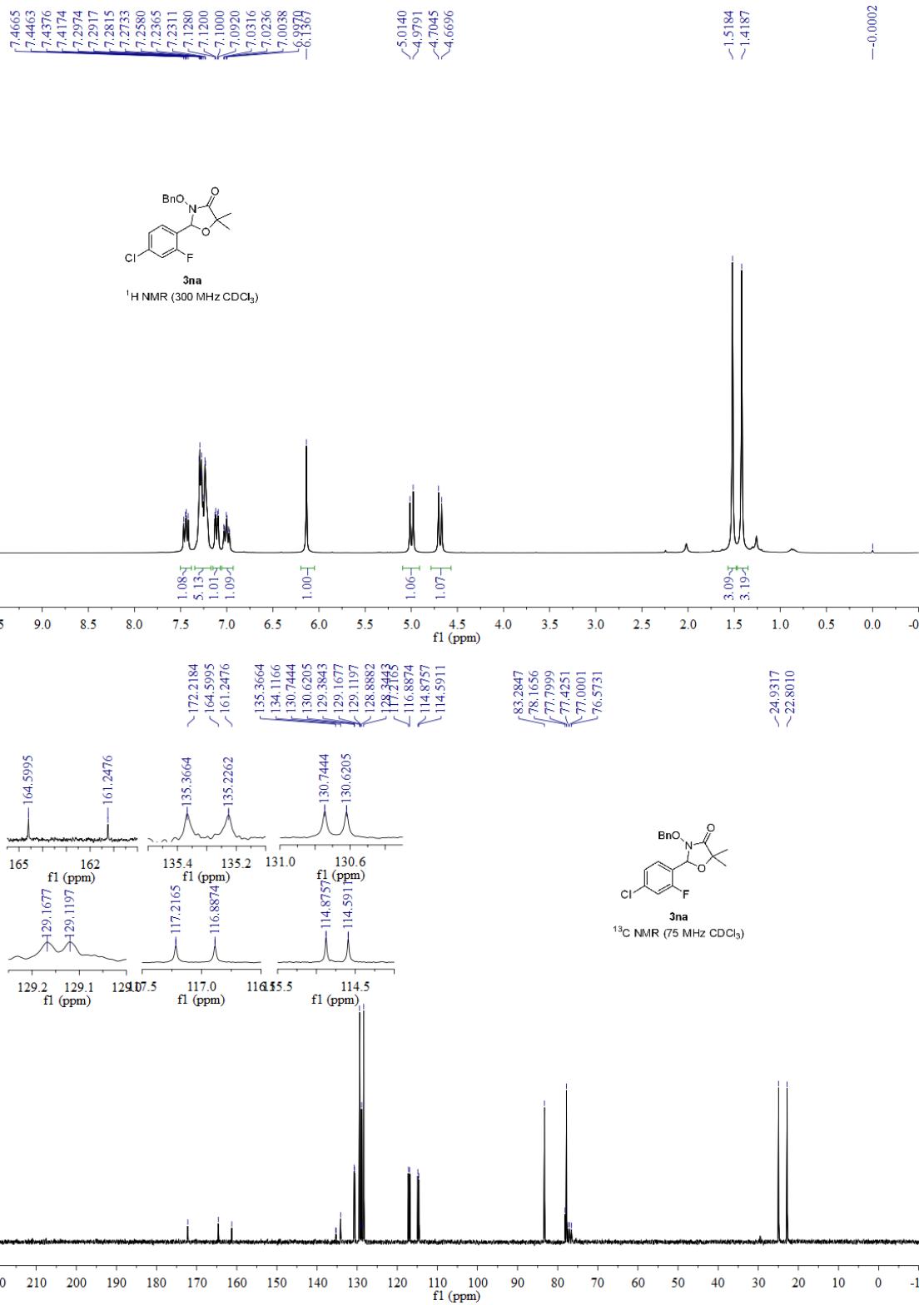


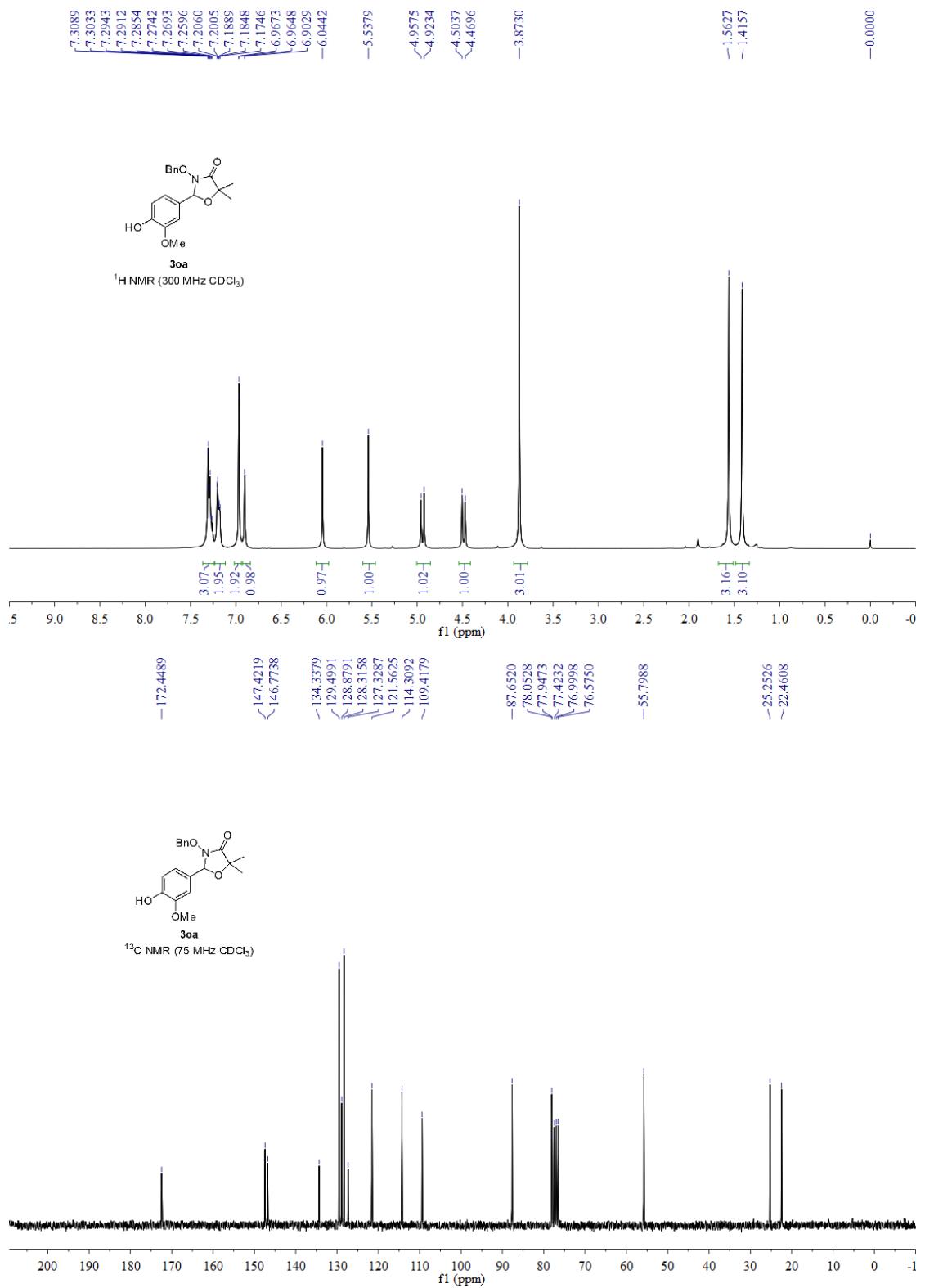


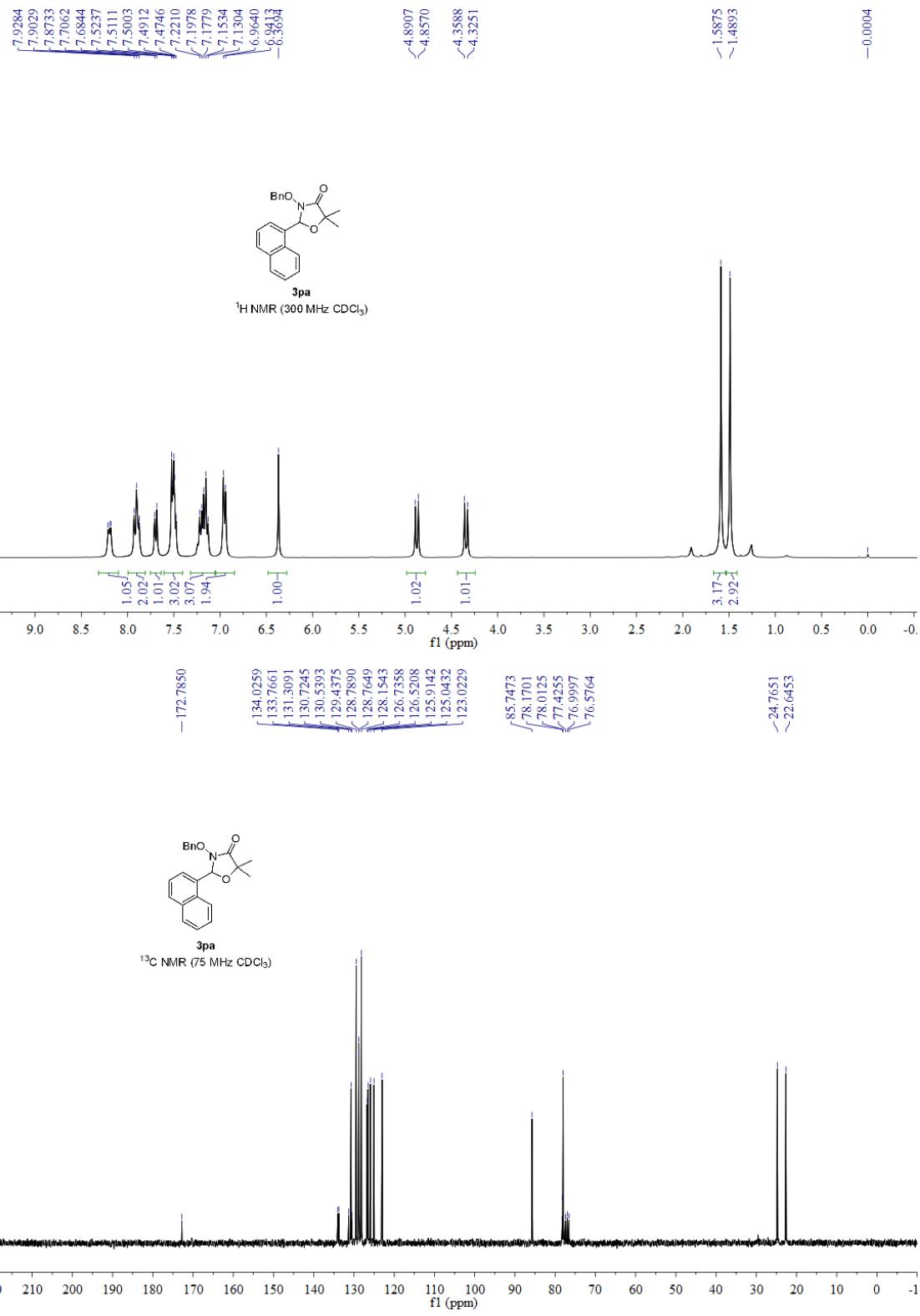


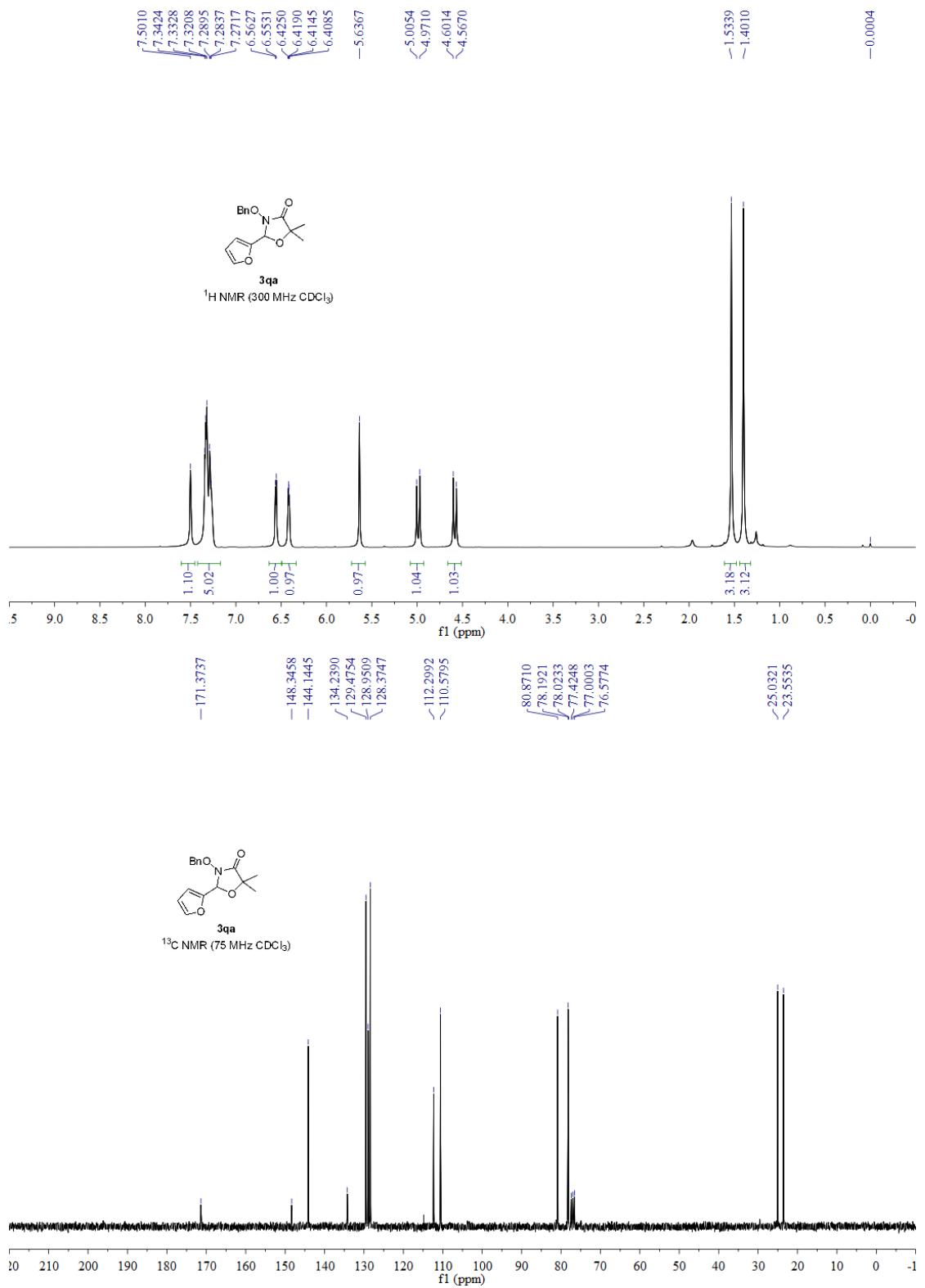


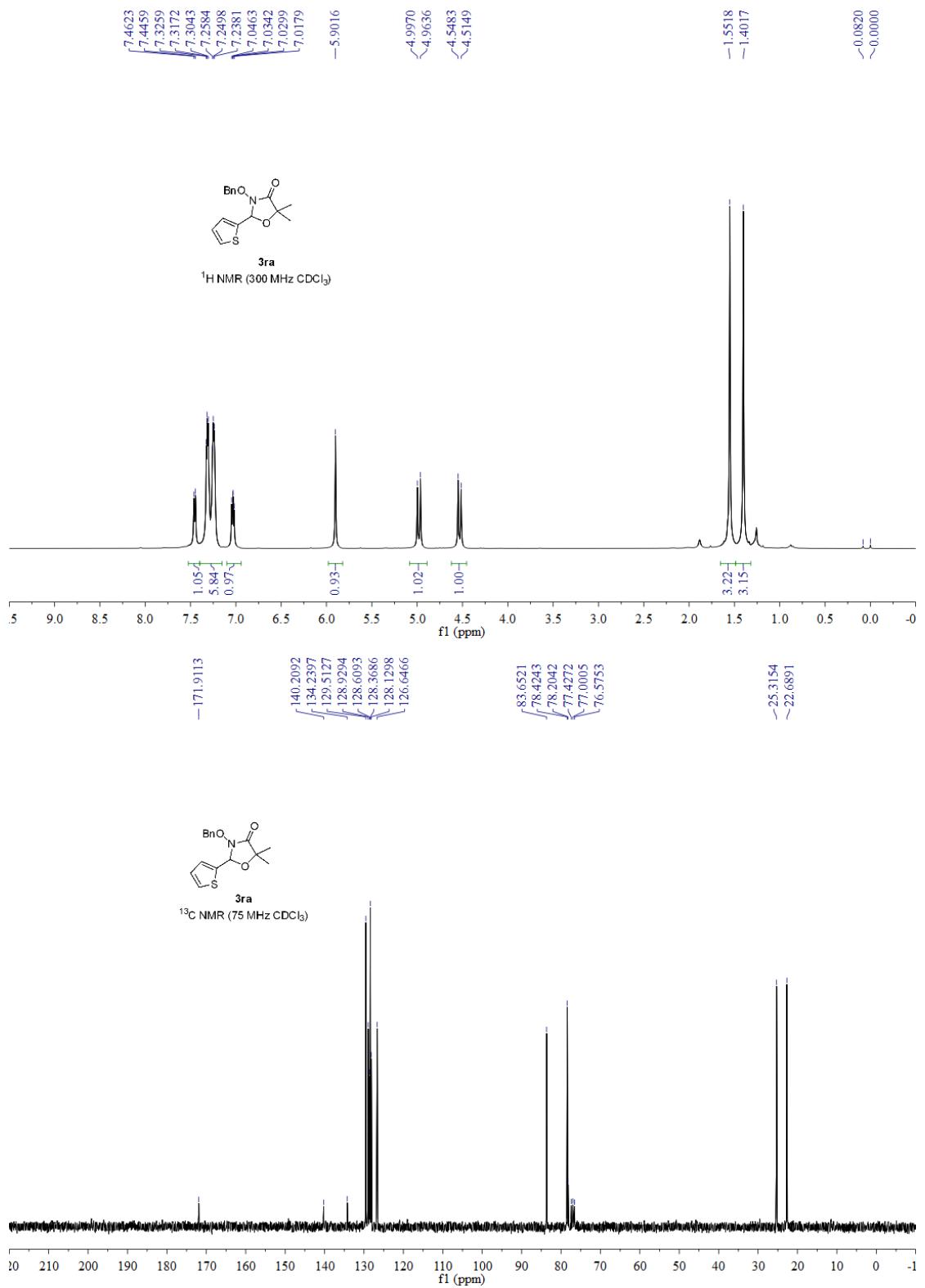


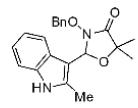




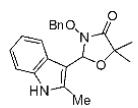
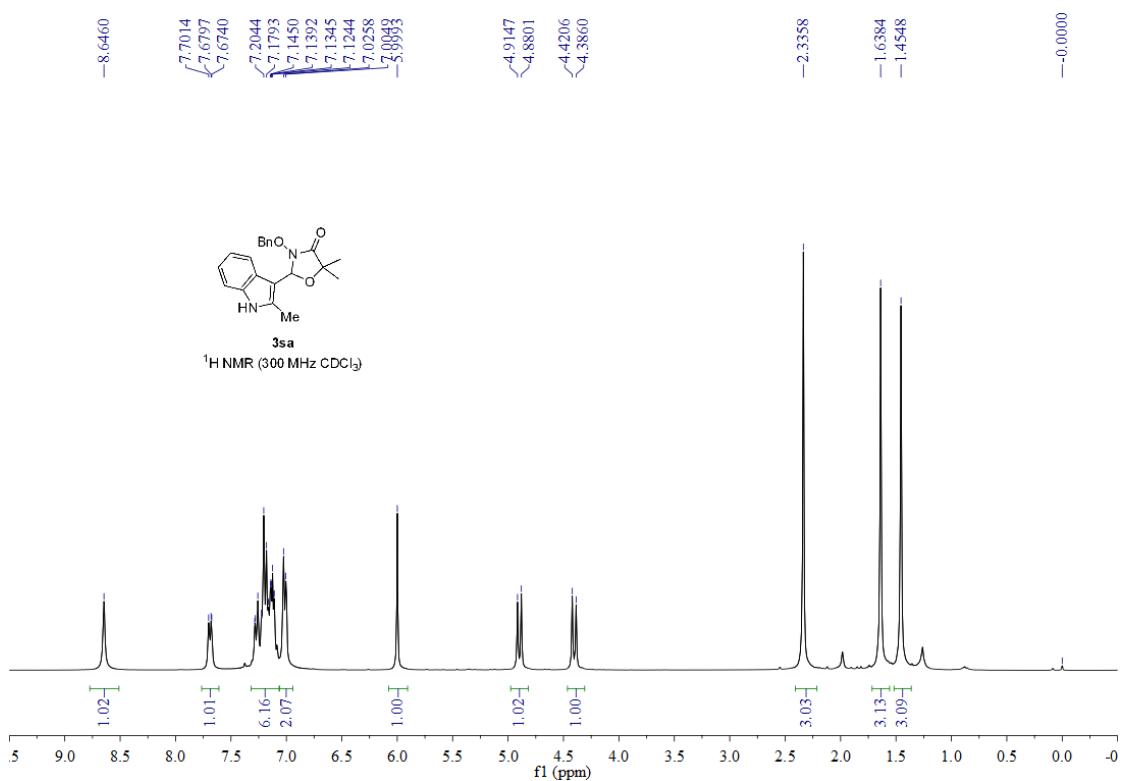




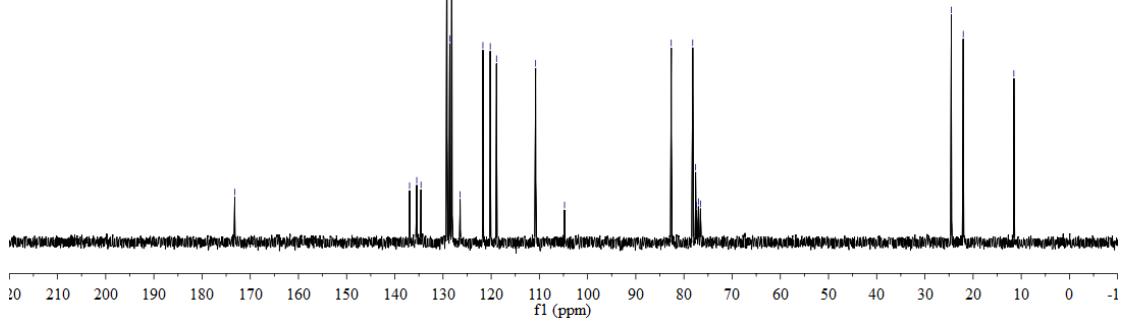


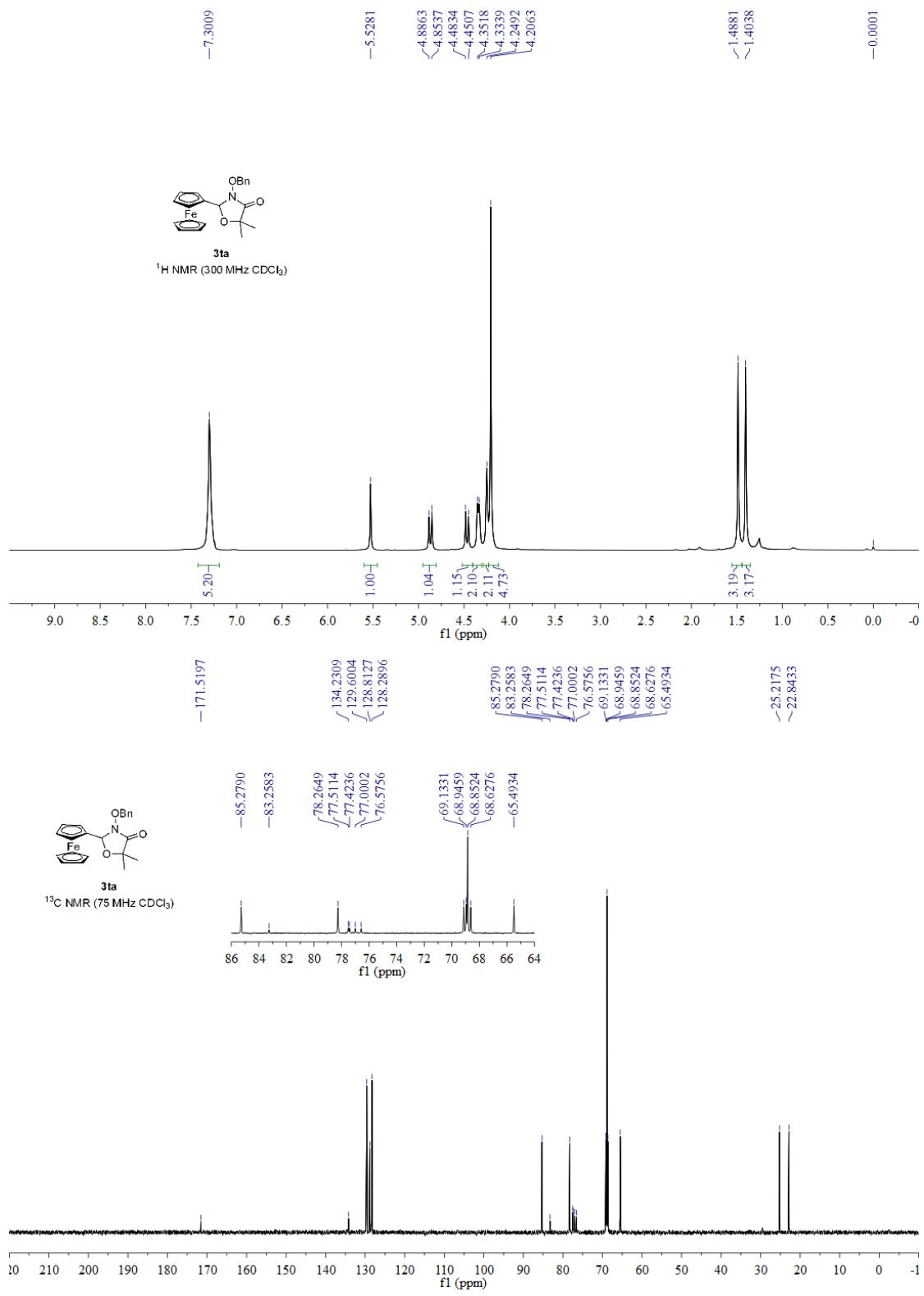


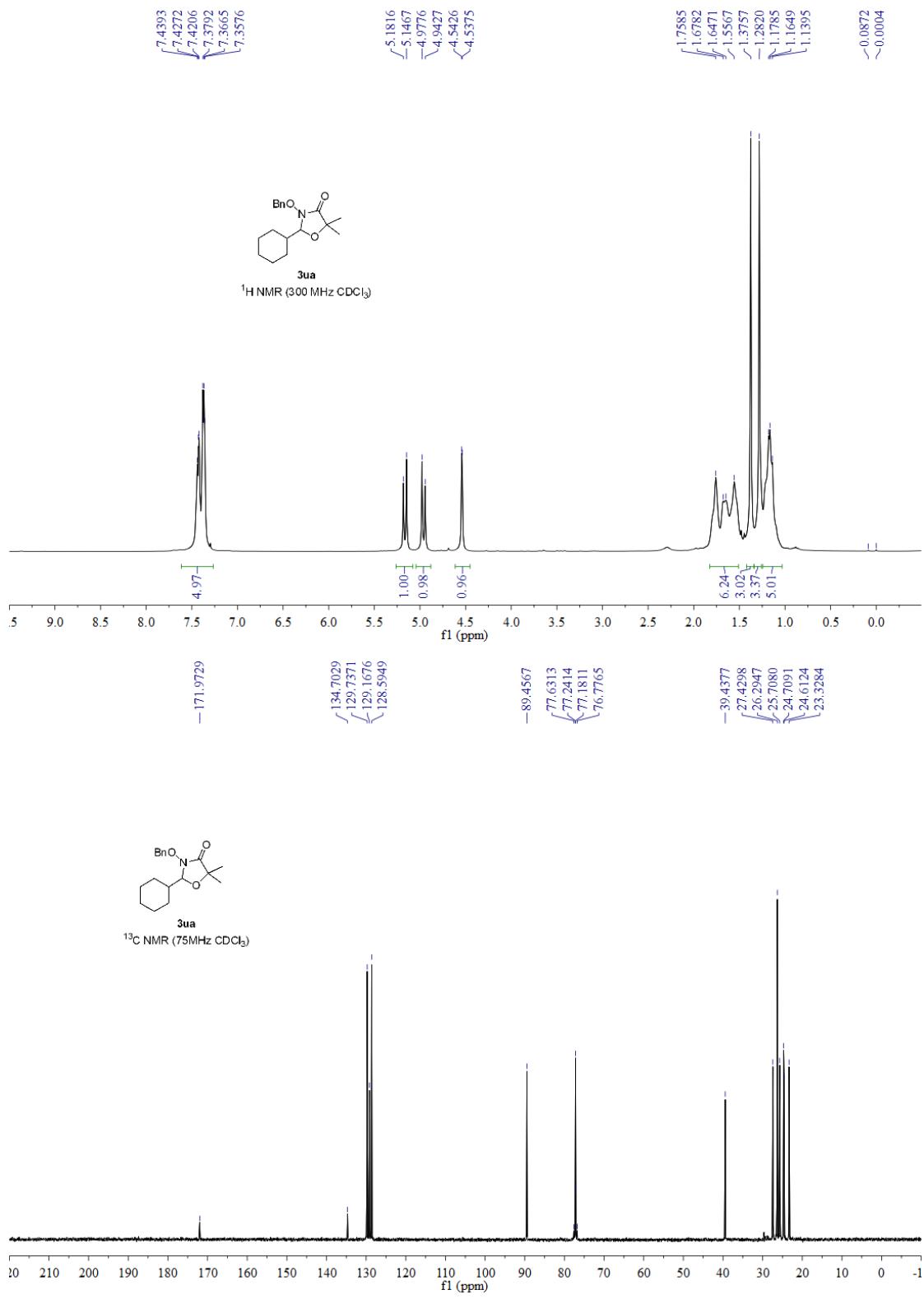
¹H NMR (300 MHz CDCl₃)

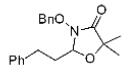


3sa

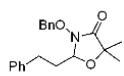
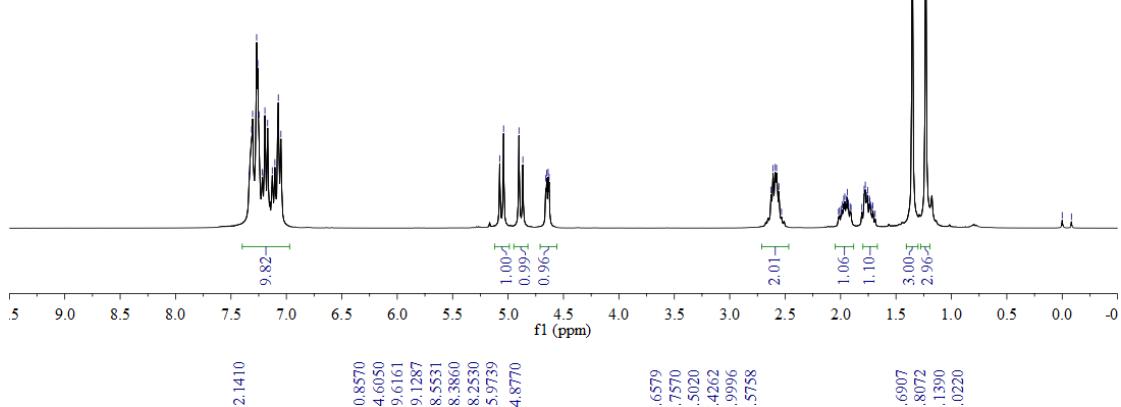




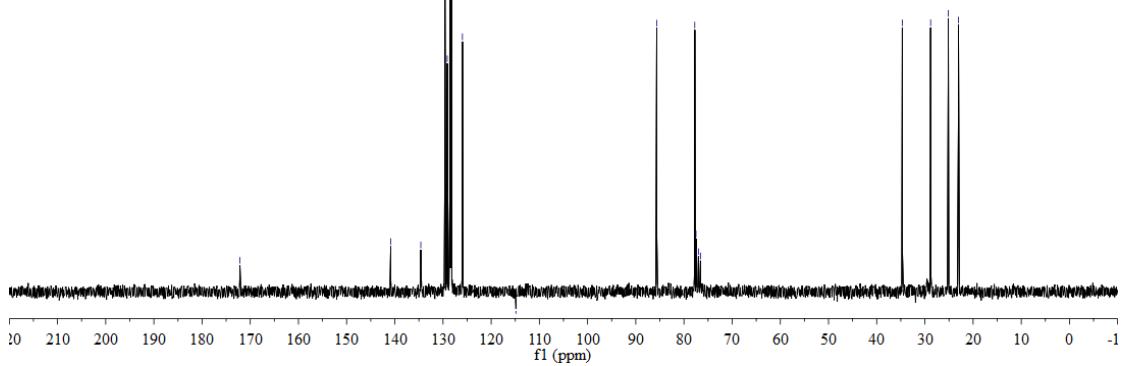


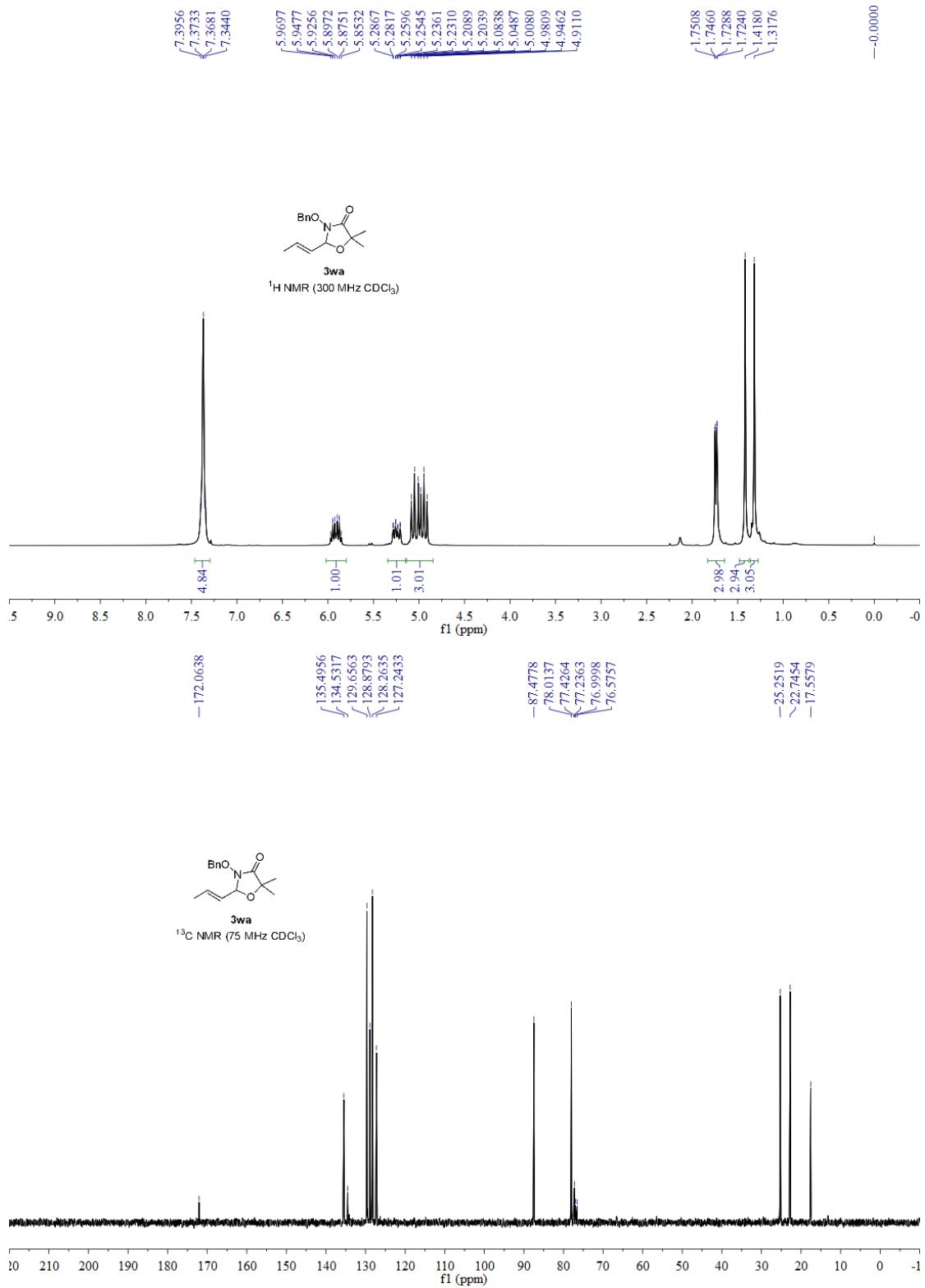


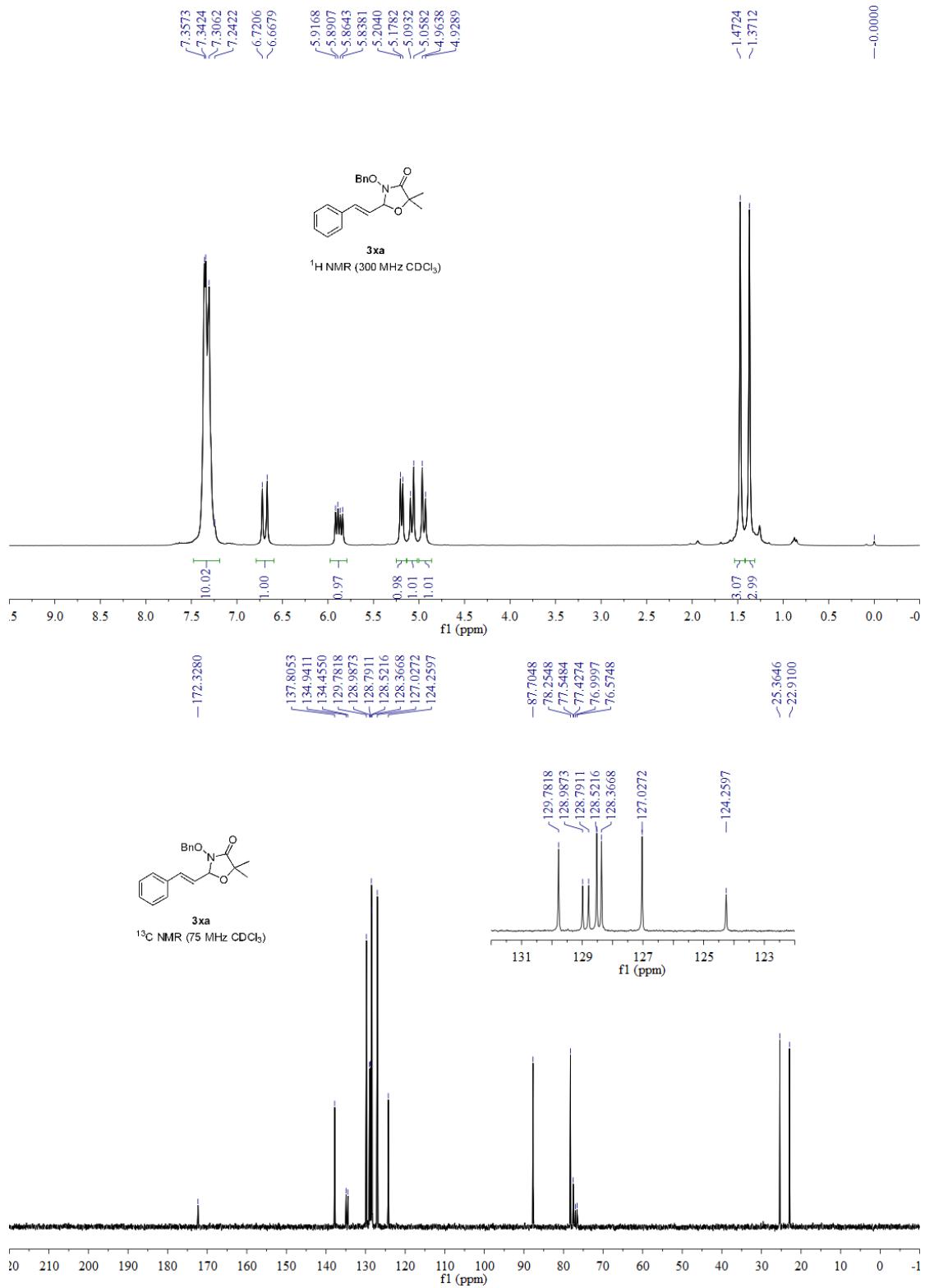
¹H NMR (300 MHz CDCl₃)

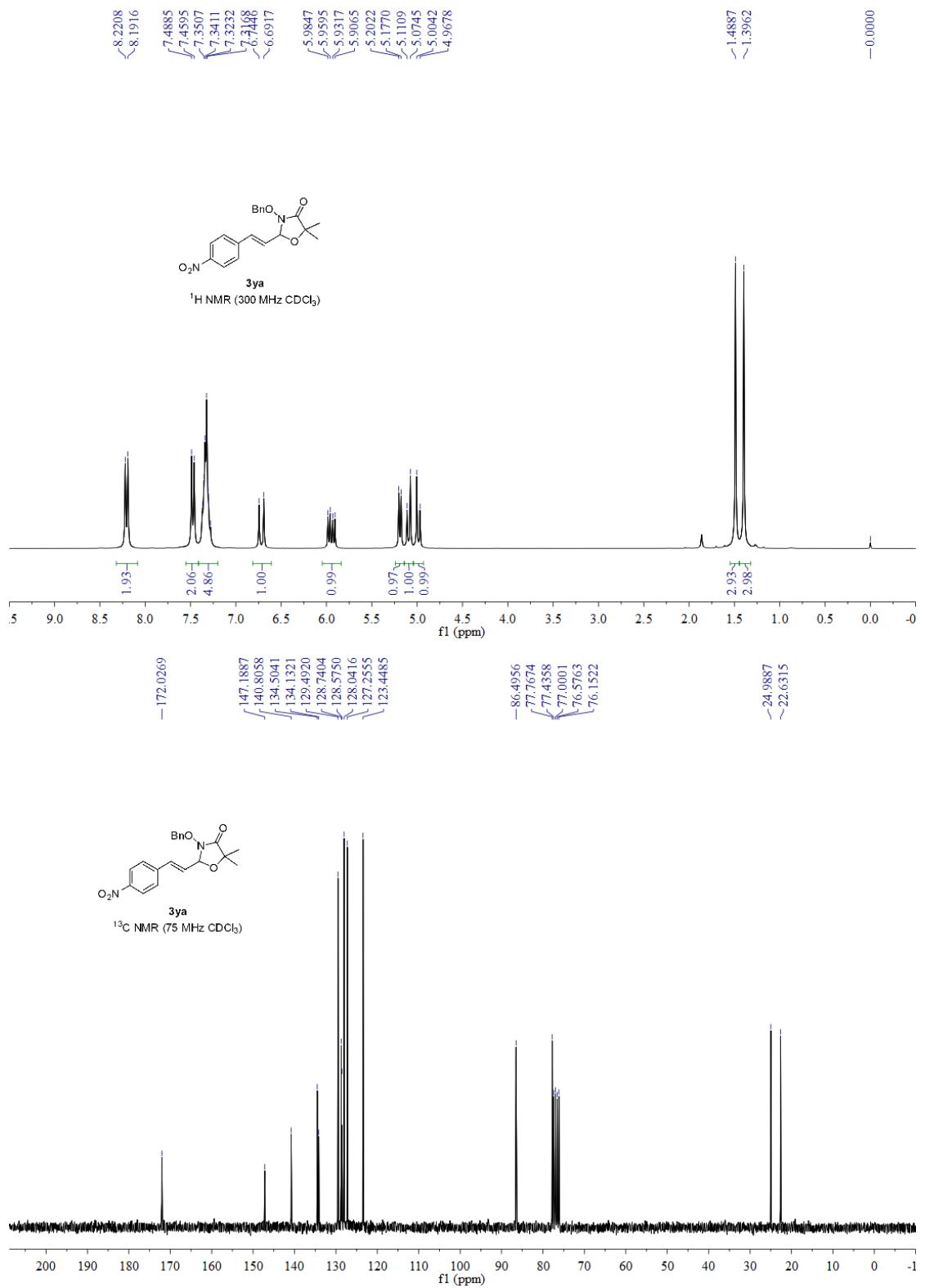


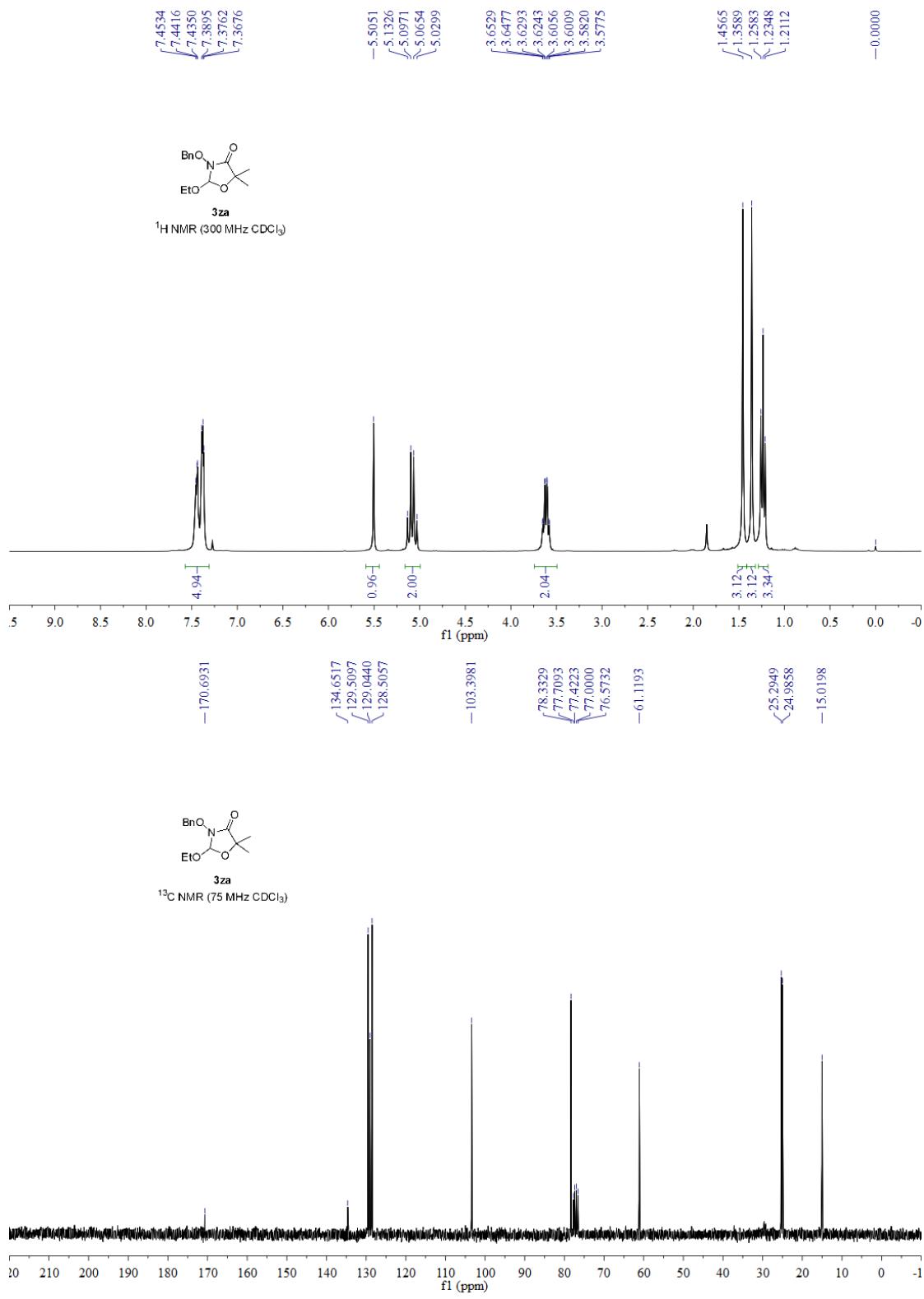
¹³C NMR (75 MHz CDCl₃)

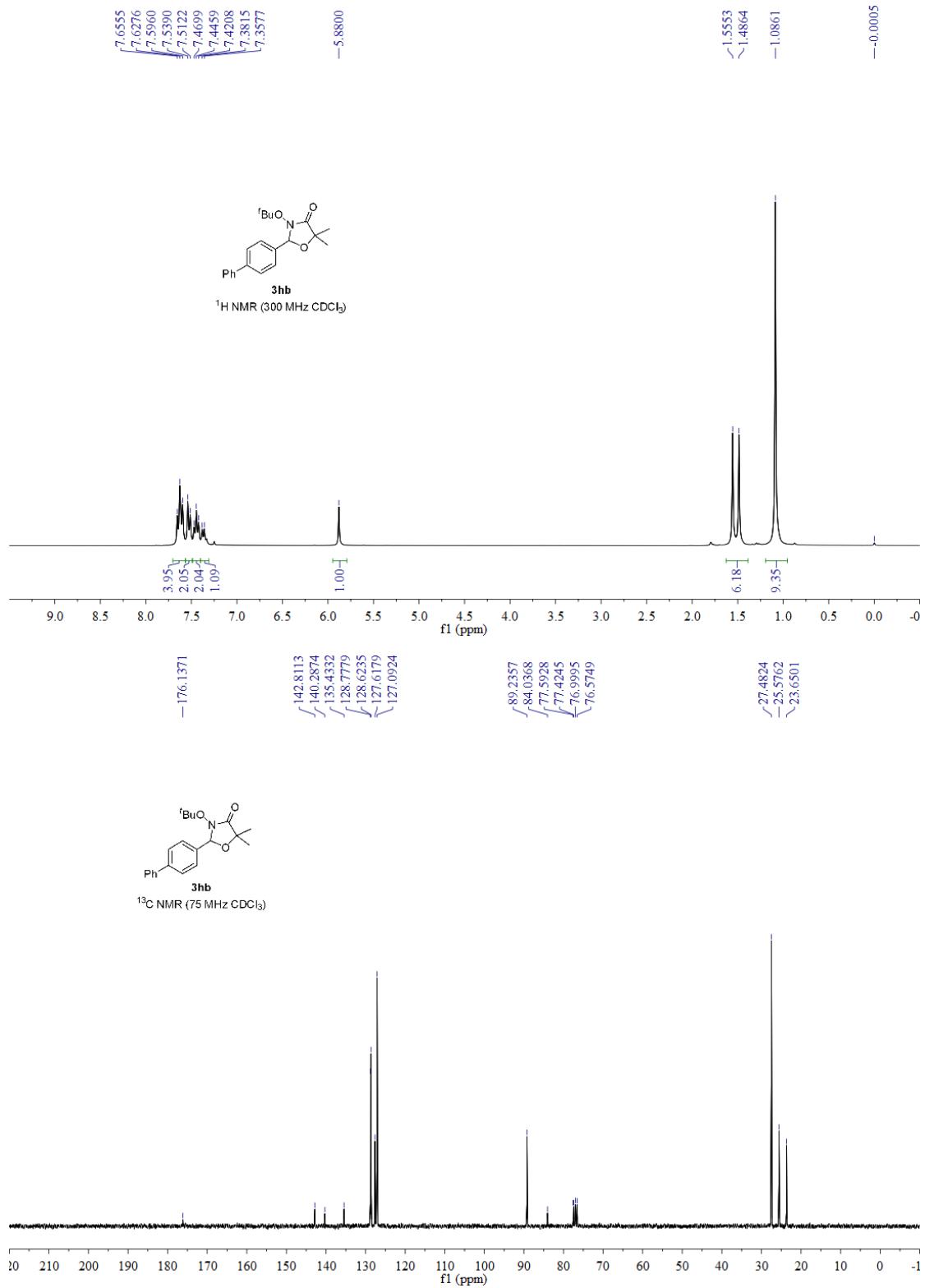


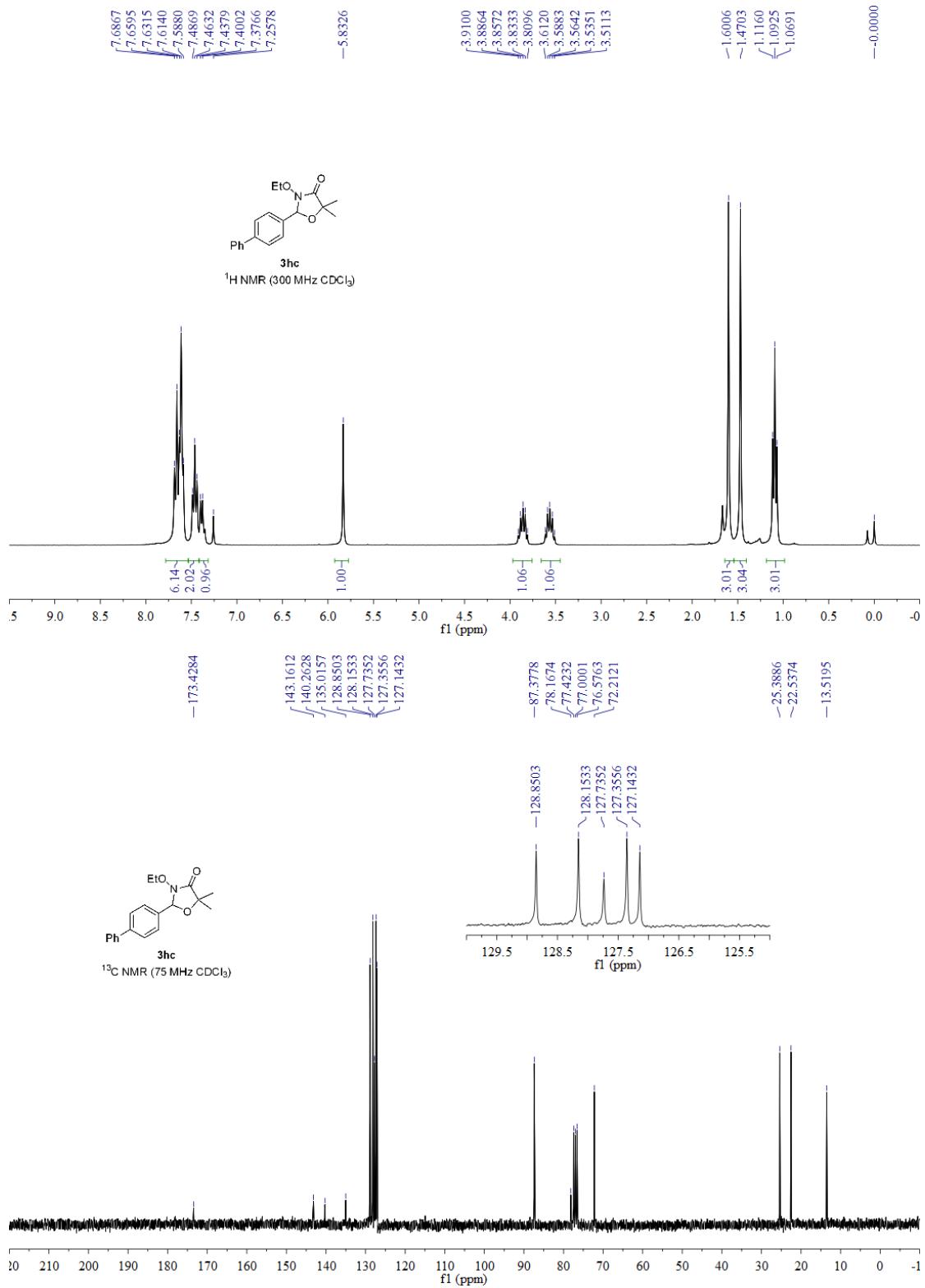


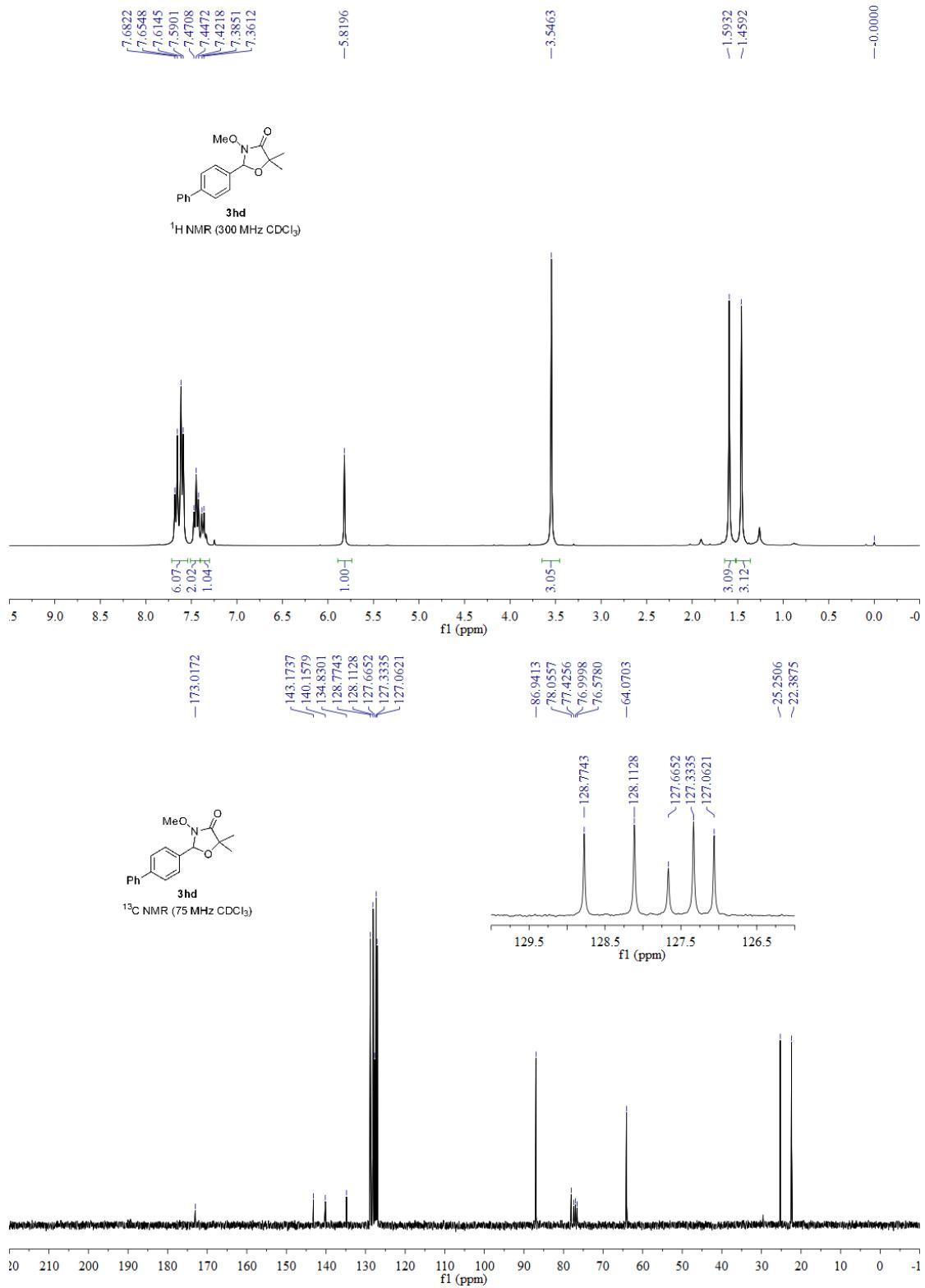


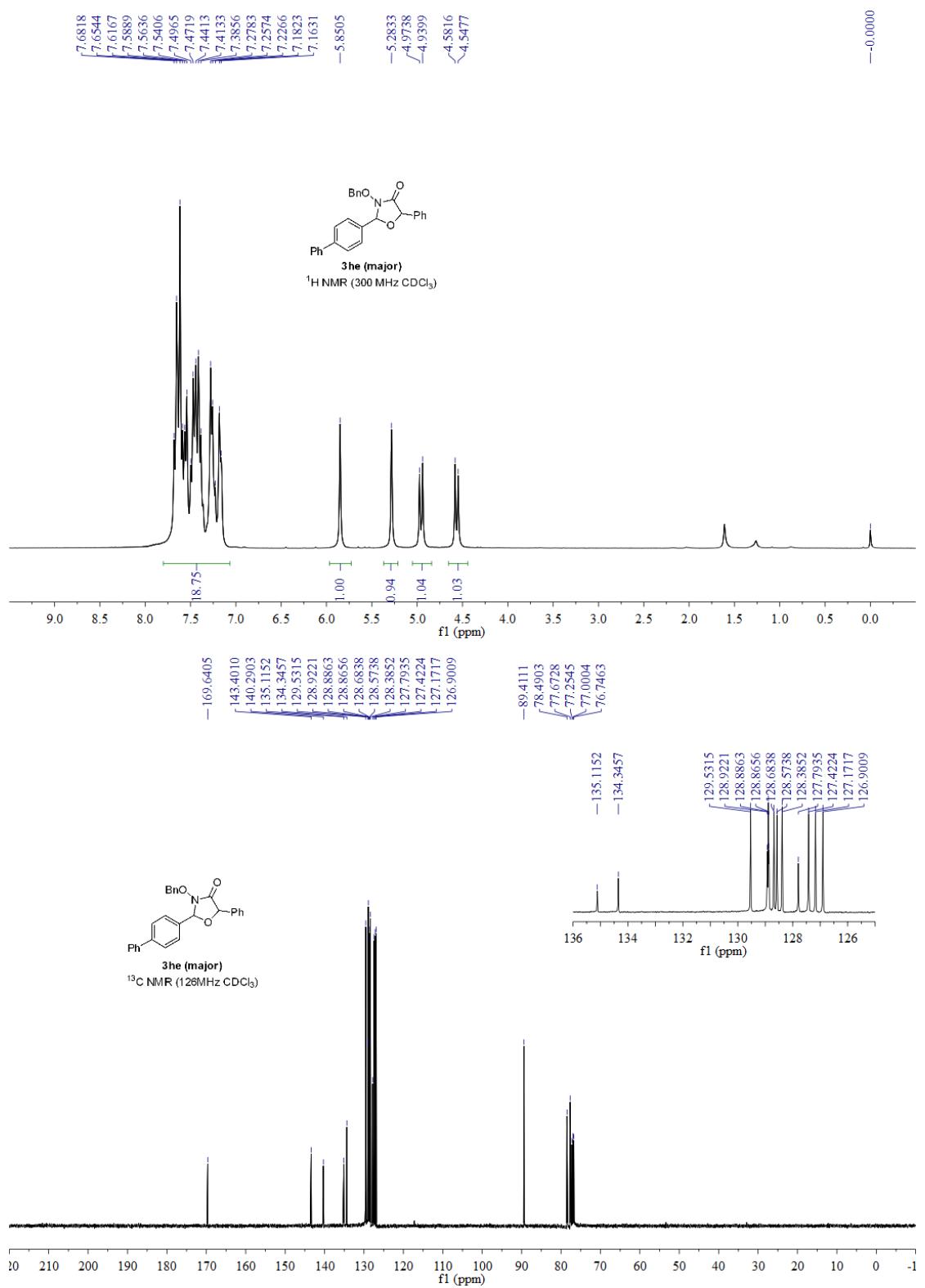


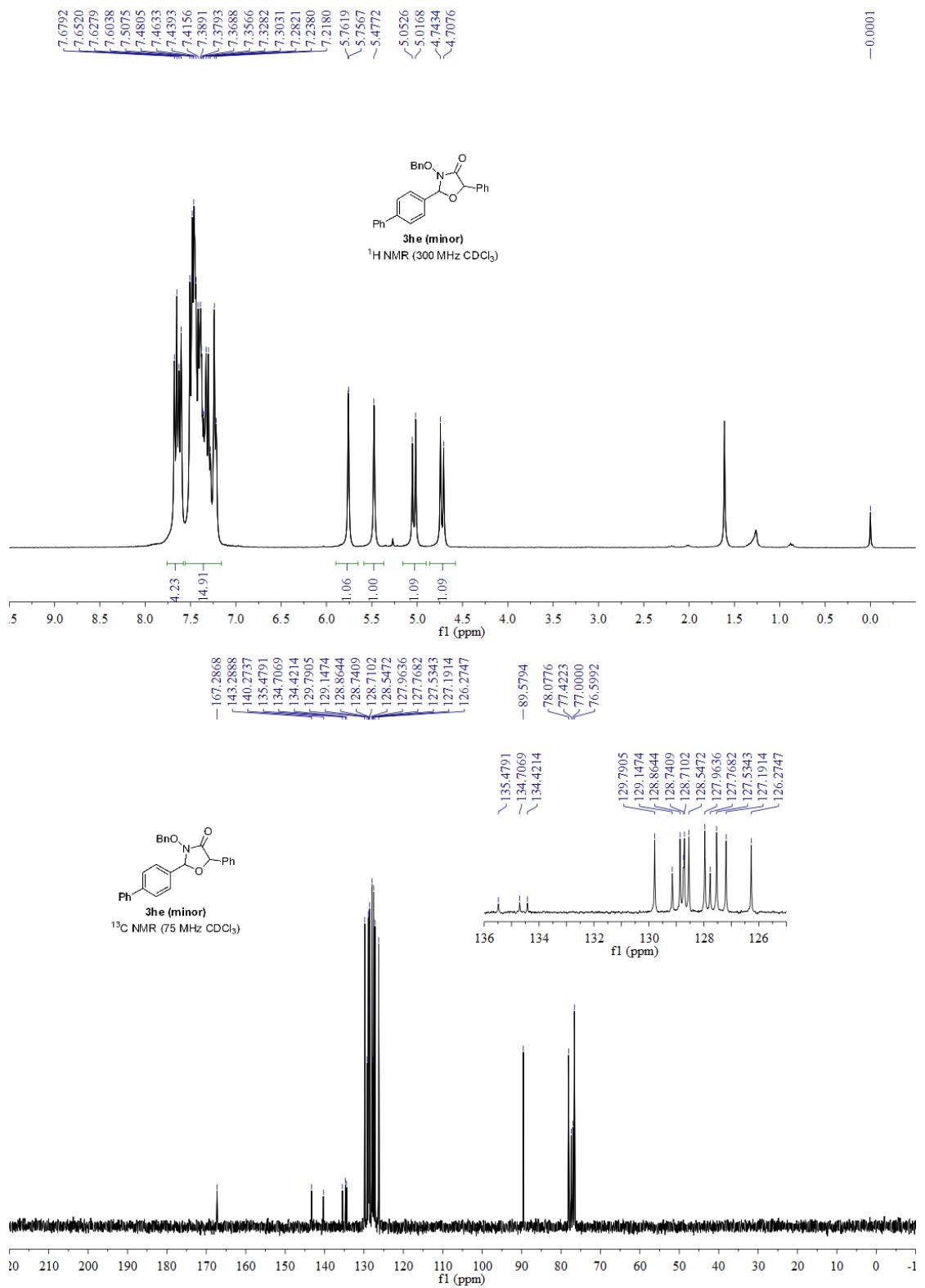


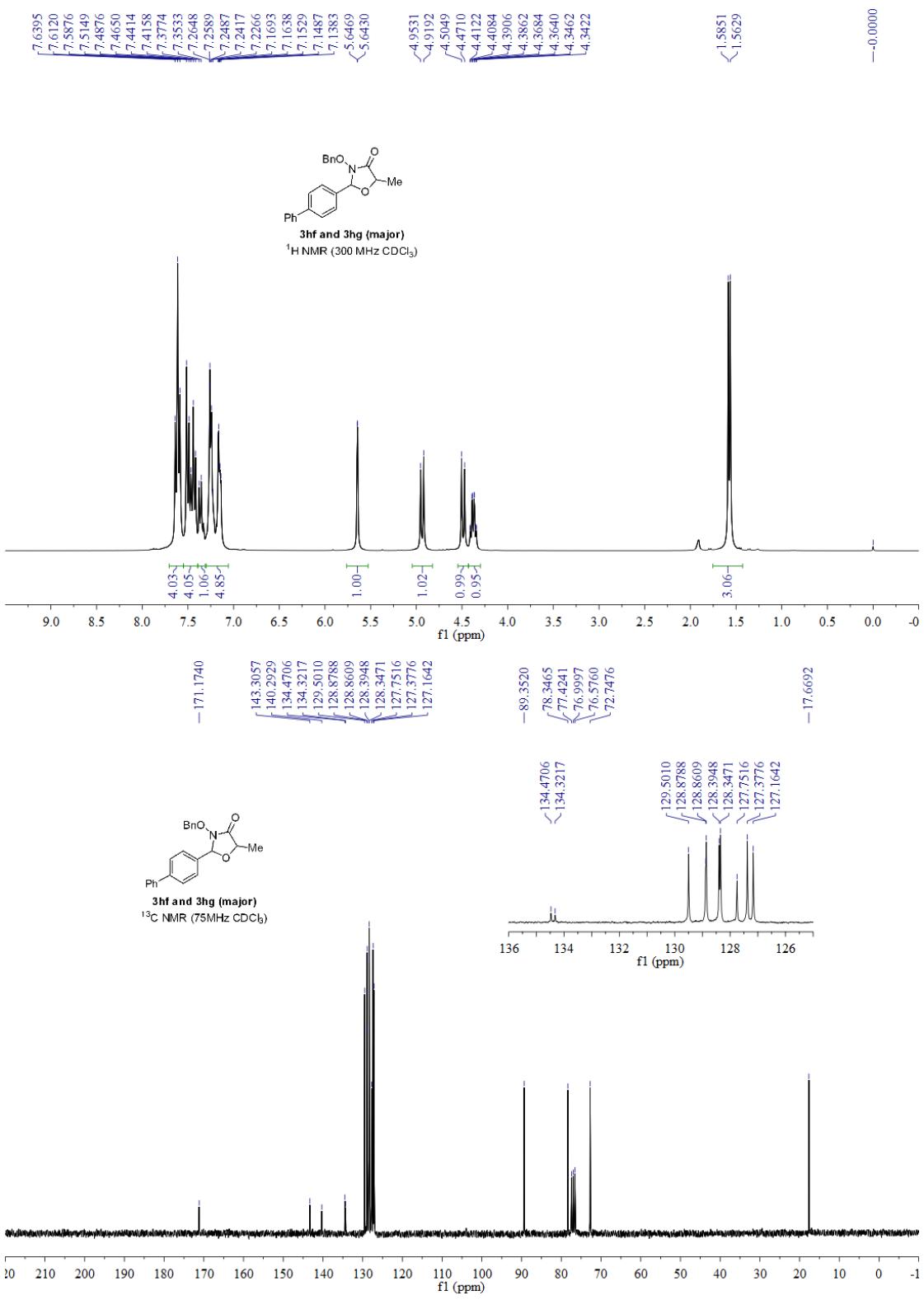


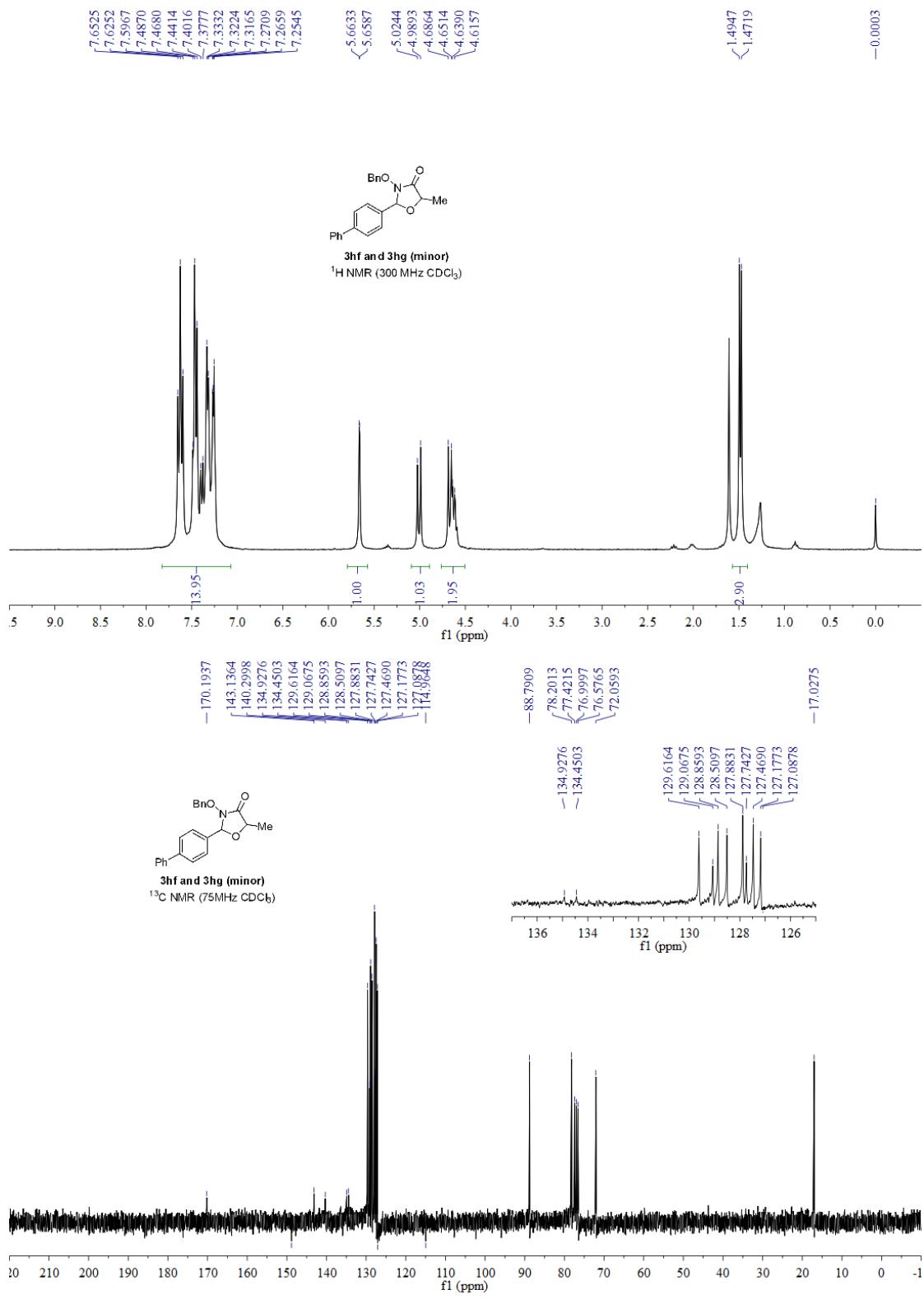


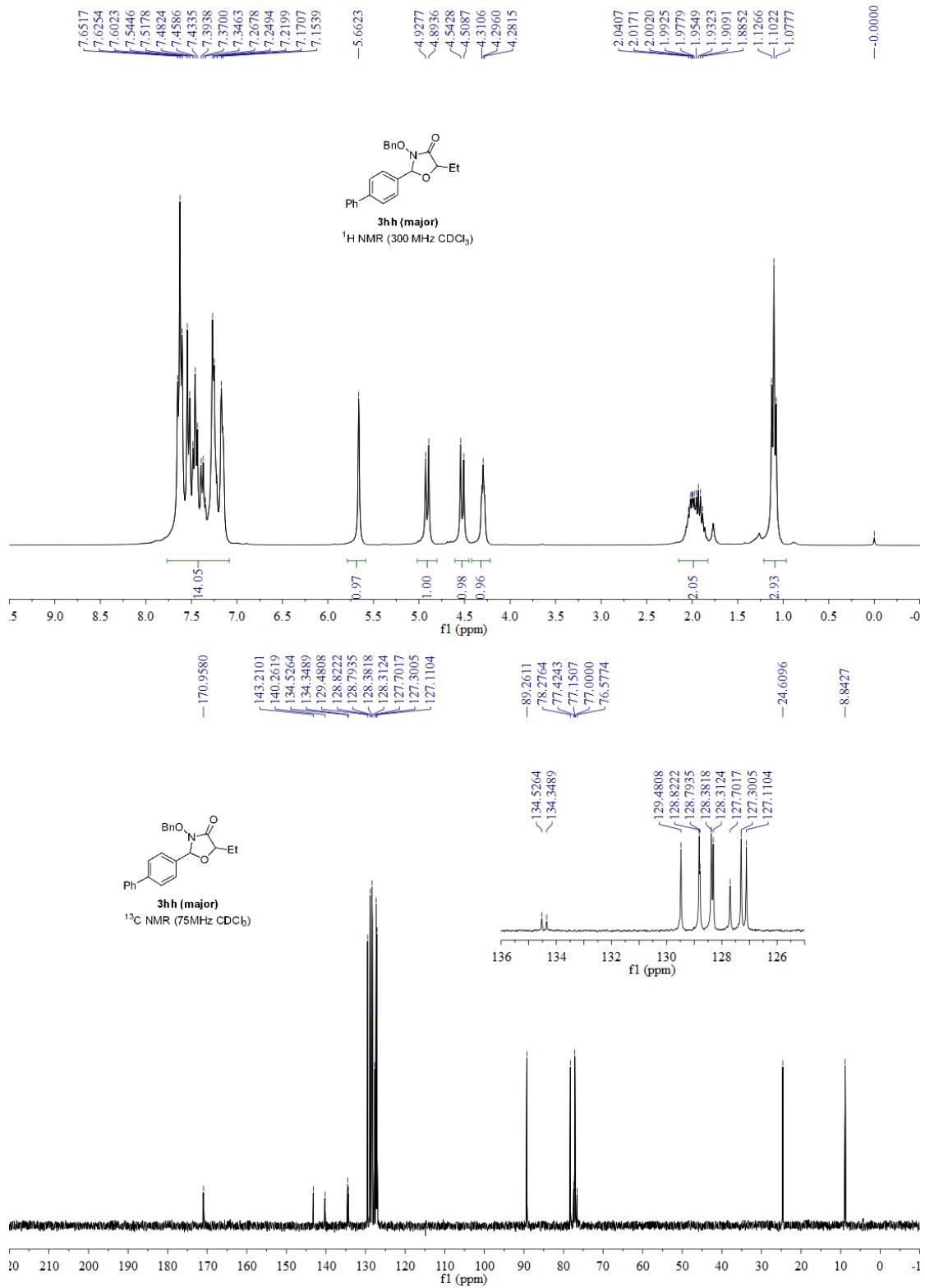


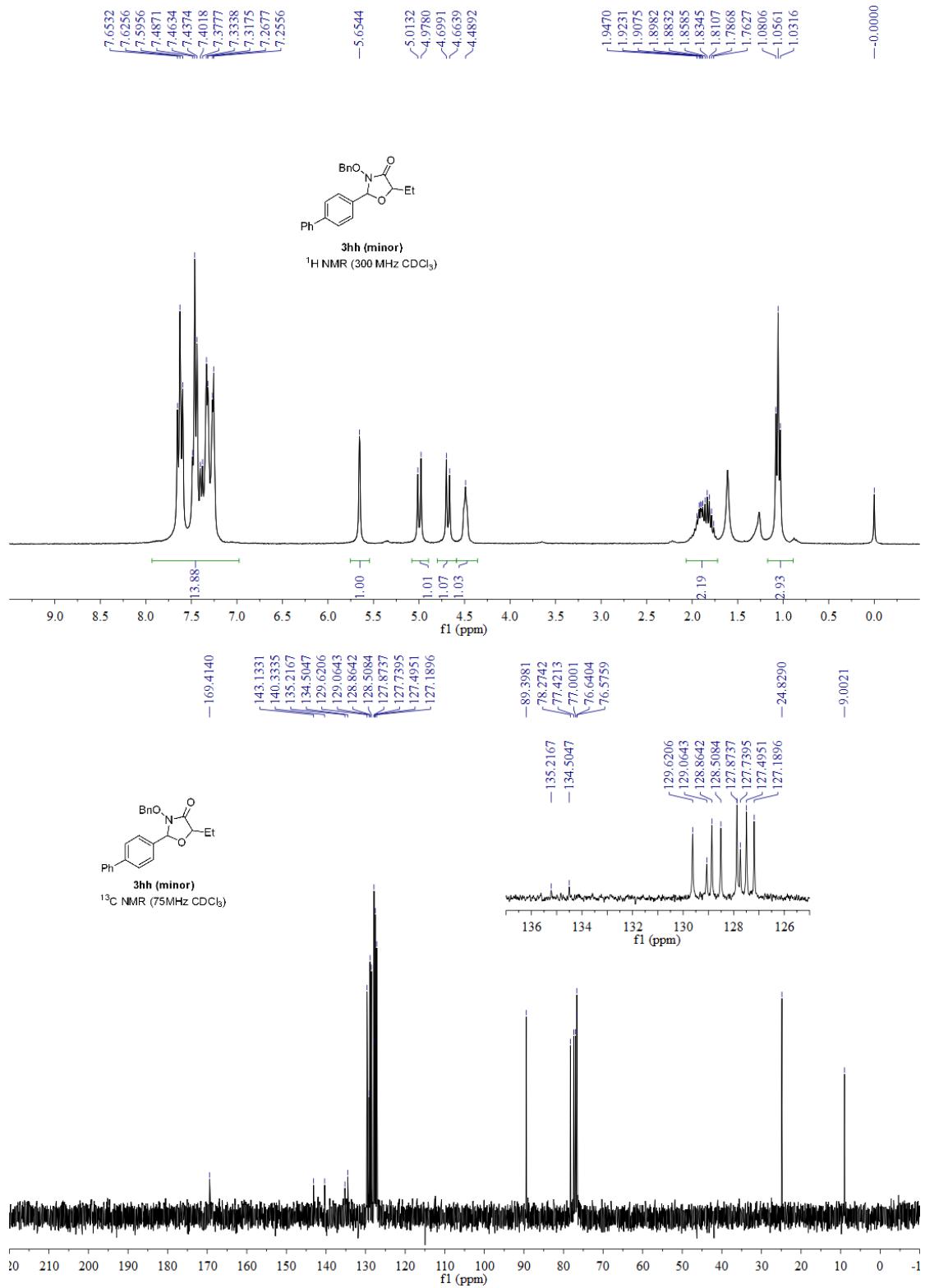


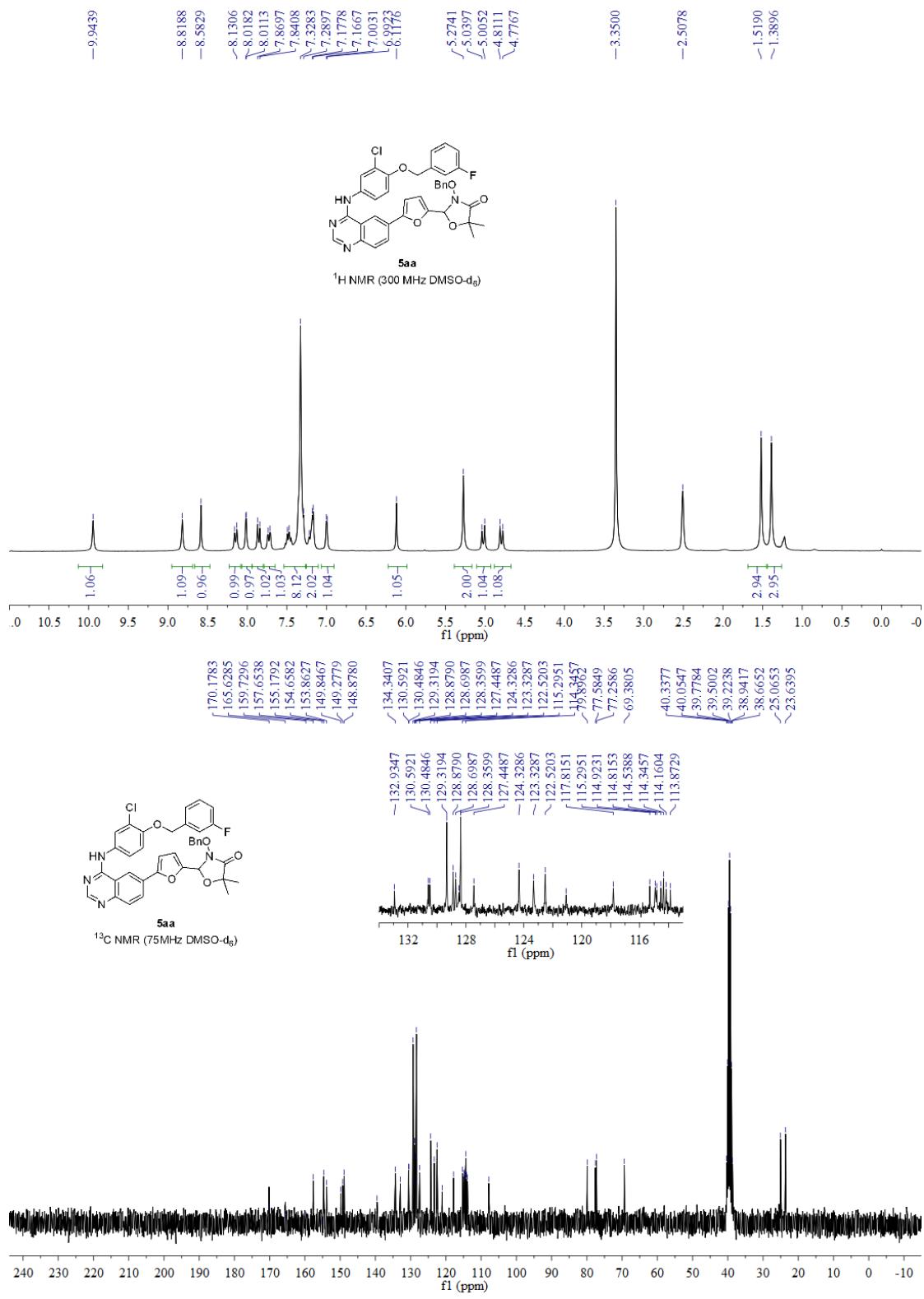


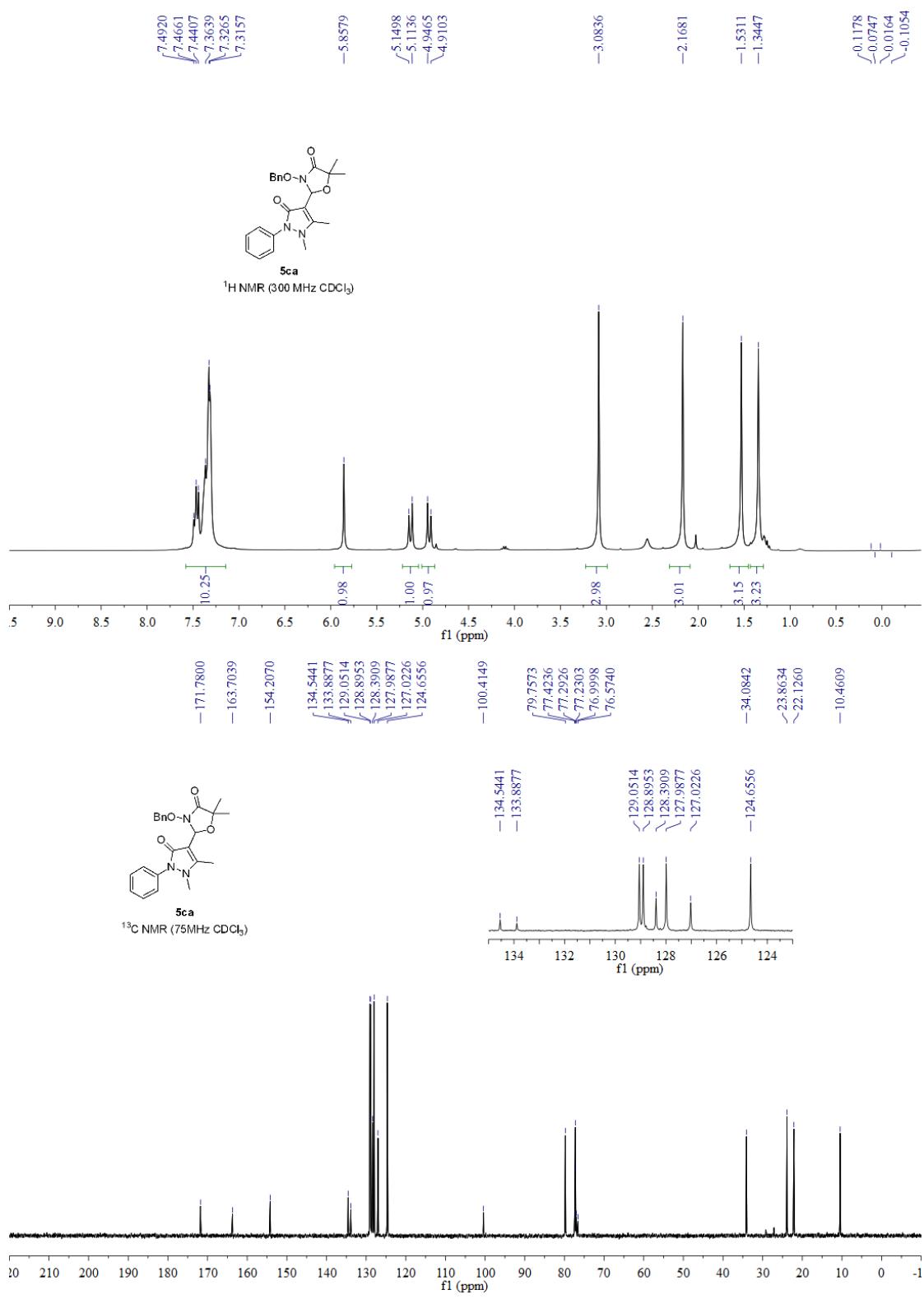


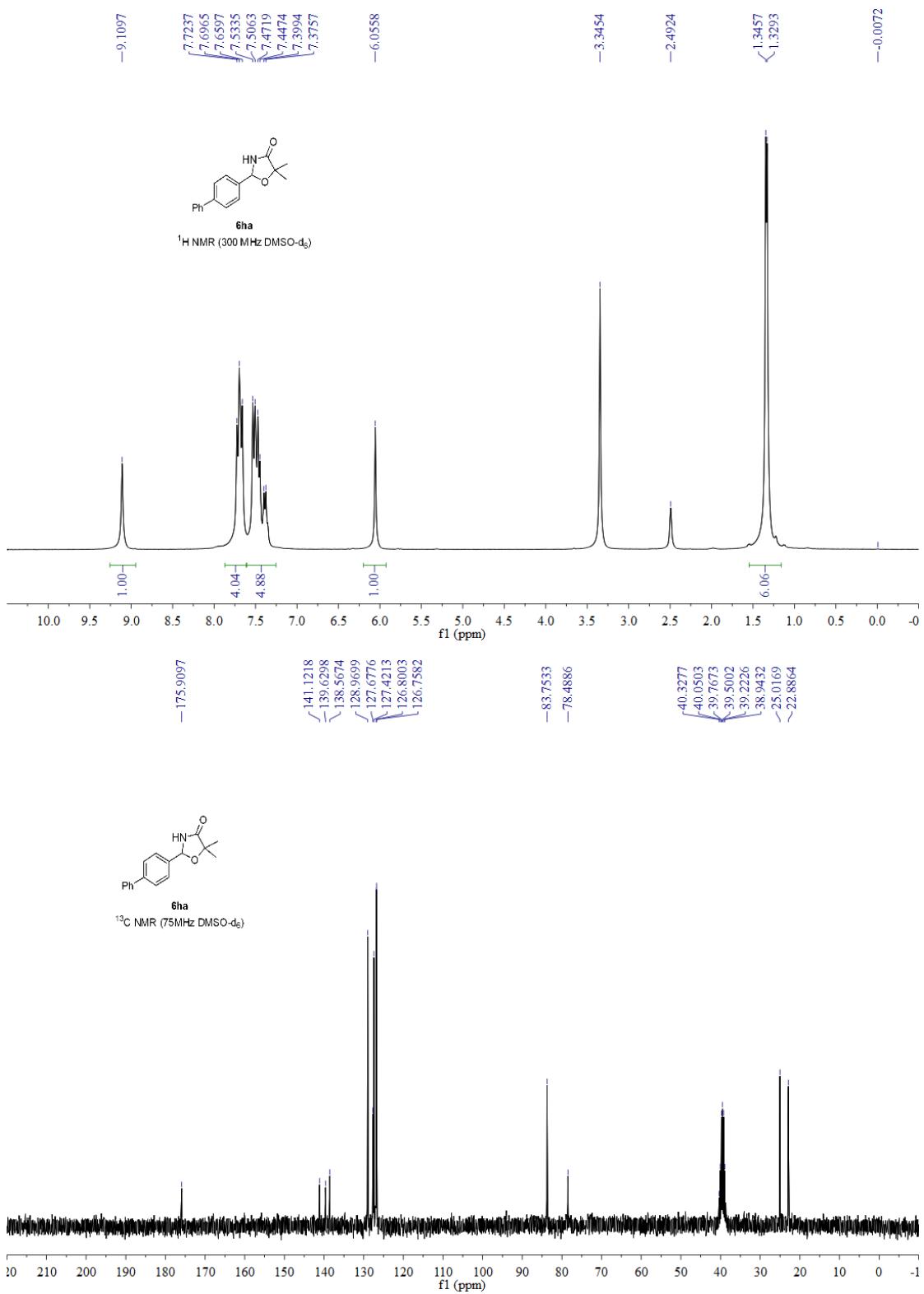


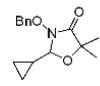
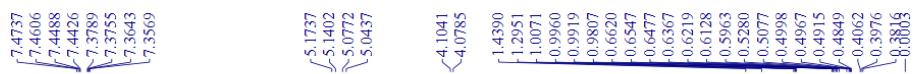




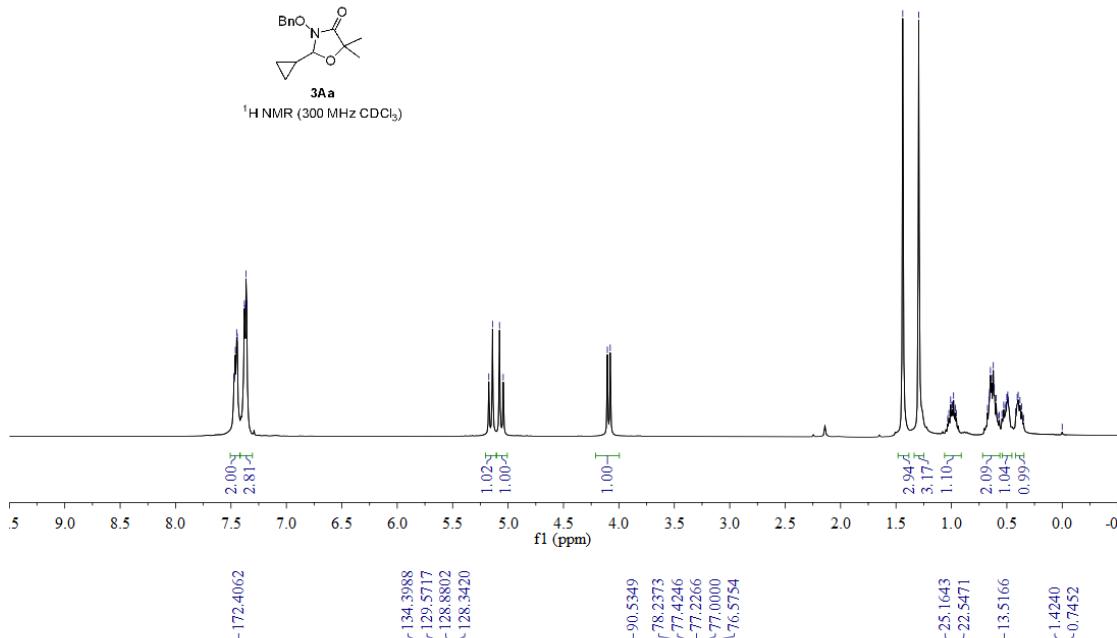








¹H NMR (300 MHz CDCl₃)



3Aa

