

Supporting Information

Asymmetric synthesis of 4-aryl-1,2,5-thiadiazolidin-3-one 1,1-dioxides by Pd-catalyzed hydrogenation of cyclic ketimines

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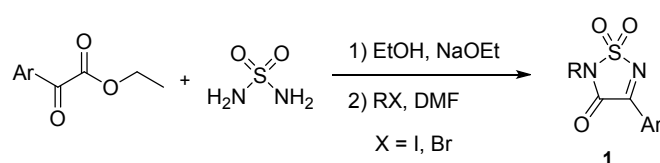
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1. General

All reactions were carried out under an atmosphere of nitrogen using the standard Schlenk techniques, unless otherwise noted. Commercially available reagents were used without further purification. Solvents were treated prior to use according to the standard methods. ^1H NMR, ^{13}C NMR ^{31}P NMR and ^{19}F NMR spectra were recorded at room temperature in CDCl_3 on 400 MHz instrument with tetramethylsilane (TMS) as internal standard. Optical rotations were measured with JASCO P-1010 polarimeter. Flash column chromatography was performed on silica gel (200-300 mesh). All reactions were monitored by TLC analysis.

2. General Procedure for Synthesis of Cyclic Ketimines **1**

Cyclic ketimines **1** can be conveniently synthesized according to the known literature procedures.¹ Among them, **1a**, **1d** and **1g-h** are the known compounds.



Following a known literature procedure,¹ to a solution of sulfamide (1.920 g, 20 mmol) in ethanol (30 mL) was slowly added sodium ethoxide (1.360 g, 20 mmol) in ethanol (5 mL). The suspension was stirred at room temperature for 15 min and then ethyl arylglyoxylate (20 mmol) in ethanol (15 mL) was added. After stirring for 15 min, the mixture was refluxed overnight and concentrated on rotary evaporator. The residue was suspended in diethyl ether for 0.5 h and the resulting white solid was filtered, which was used for the next reaction without further purification. To a suspension of the above white solid (5.0 mmol) in dimethylformamide (10 mL) was added alkyl halide (7.5 mmol), and the mixture was stirred at room temperature for 24 h. Water was added to the mixture and it was extracted with ethyl acetate. The organic extracts were washed with water, brine, dried over anhydrous sodium sulfate, filtered, and concentrated on a rotary evaporator. The residue was subjected to column chromatography on silica gel with hexanes/ethyl acetate (100:1) to give the product **1**.

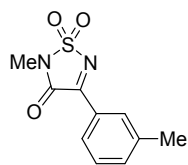
2-ethyl-4-phenyl-1,2,5-thiadiazol-3(2H)-one 1,1-dioxide (1b): unknown compound, white solid,

m.p. = 133-134 °C, yield: 7%, R_f = 0.60 (petroleum ether/ethyl acetate 10:1). ^1H NMR (400 MHz, CDCl_3) δ 8.57 (d, J = 7.7 Hz, 2H), 7.74 (t, J = 7.5 Hz, 1H), 7.57 (t, J = 7.8 Hz, 2H), 3.87 (q, J = 7.3 Hz, 2H), 1.46 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.6, 156.1, 136.4, 132.3, 129.5, 127.1, 37.6, 13.2. HRMS Calculated for $\text{C}_{10}\text{H}_{11}\text{N}_2\text{O}_3\text{S}$ ($\text{M}+\text{H}$)⁺ 239.0485, found: 239.0483.

2-benzyl-4-phenyl-1,2,5-thiadiazol-3(2H)-one 1,1-dioxide (1c): unknown compound, white

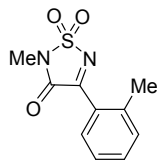
solid, m.p. = 134-135 °C, yield: 18%, R_f = 0.46 (petroleum ether/ethyl acetate 10:1). ^1H NMR (400 MHz, CDCl_3) δ 8.57 (d, J = 7.4 Hz, 2H), 7.74 (t, J = 7.5 Hz, 1H), 7.56 (t, J = 7.9 Hz, 2H), 7.52-7.45 (m, 2H), 7.43-7.31 (m, 3H), 4.91 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.6, 156.4, 136.6, 133.2, 132.4, 129.6, 129.2, 129.1, 129.0, 127.0, 45.8. HRMS Calculated for $\text{C}_{15}\text{H}_{16}\text{N}_3\text{O}_3\text{S}$ ($\text{M}+\text{NH}_4$)⁺ 318.0907, found: 318.0909.

2-methyl-4-(*m*-tolyl)-1,2,5-thiadiazol-3(2*H*)-one 1,1-dioxide (1e): New compound, white solid, m.p. = 119-120 °C, yield: 26%, R_f = 0.48 (petroleum ether/ethyl acetate 10:1).



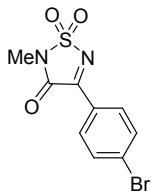
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.40 (d, J = 7.9 Hz, 1H), 8.35 (s, 1H), 7.55 (d, J = 7.6 Hz, 1H), 7.45 (t, J = 7.7 Hz, 1H), 3.32 (s, 3H), 2.45 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 165.0, 156.3, 139.6, 137.5, 132.5, 129.8, 129.5, 126.9, 26.4, 21.5. HRMS Calculated for $\text{C}_{10}\text{H}_{11}\text{N}_2\text{O}_3\text{S}$ ($\text{M}+\text{H}$) $^+$ 239.0485, found: 239.0481.

2-methyl-4-(*o*-tolyl)-1,2,5-thiadiazol-3(2*H*)-one 1,1-dioxide (1f): New compound, yellow solid,



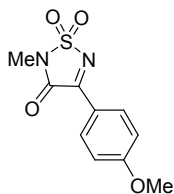
m.p. = 123-124 °C, yield: 22%, R_f = 0.28 (petroleum ether/ethyl acetate 10:1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.36 (d, J = 7.9 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.44-7.35 (m, 2H), 3.33 (s, 3H), 2.67 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.1, 156.6, 143.0, 134.9, 134.3, 132.7, 126.5, 125.2, 26.5, 22.7. HRMS Calculated for $\text{C}_{10}\text{H}_{11}\text{N}_2\text{O}_3\text{S}$ ($\text{M}+\text{H}$) $^+$ 239.0485, found: 239.0486.

4-(4-bromophenyl)-2-methyl-1,2,5-thiadiazol-3(2*H*)-one 1,1-dioxide (1i): New compound, yellowish solid, m.p. = 202-203 °C, yield: 37%, R_f = 0.51 (petroleum ether/ethyl acetate 10:1).



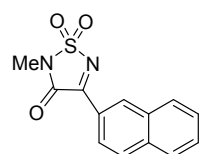
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.45 (d, J = 8.6 Hz, 2H), 7.73 (d, J = 8.6 Hz, 2H), 3.33 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 164.1, 156.0, 133.5, 133.1, 132.9, 125.8, 26.5. HRMS Calculated for $\text{C}_9\text{H}_8\text{BrN}_2\text{O}_3\text{S}$ [$\text{M}+\text{H}$] $^+$ 302.9434, found: 302.9433.

4-(4-methoxyphenyl)-2-methyl-1,2,5-thiadiazol-3(2*H*)-one 1,1-dioxide (1j): New compound, greenish yellow solid, m.p. = 169-170 °C, yield: 16%, R_f = 0.33 (petroleum ether/ethyl acetate 10:1).



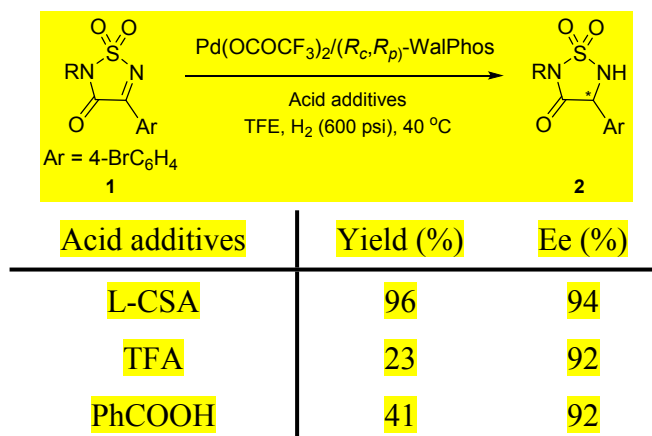
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.62 (d, J = 9.1 Hz, 2H), 7.03 (d, J = 9.1 Hz, 2H), 3.94 (s, 3H), 3.30 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.9, 163.3, 156.9, 135.3, 119.6, 115.3, 56.1, 26.3. HRMS Calculated for $\text{C}_{10}\text{H}_{11}\text{N}_2\text{O}_4\text{S}$ [$\text{M}+\text{H}$] $^+$ 255.0434, found: 255.0435.

2-methyl-4-(naphthalen-2-yl)-1,2,5-thiadiazol-3(2*H*)-one 1,1-dioxide (1k): New compound, yellow solid, m.p. = 209-210 °C, yield: 21%, R_f = 0.42 (petroleum ether/ethyl acetate 10:1).

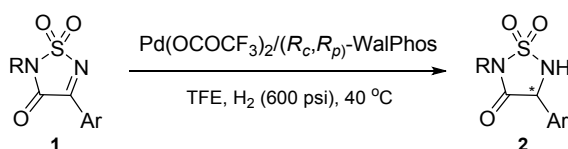


$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.44 (s, 1H), 8.37-8.28 (m, 1H), 8.04 (d, J = 8.2 Hz, 1H), 7.96 (d, J = 8.8 Hz, 1H), 7.91 (d, J = 8.2 Hz, 1H), 7.71 (t, J = 7.4 Hz, 1H), 7.62 (t, J = 7.4 Hz, 1H), 3.36 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 164.4, 156.5, 137.2, 137.1, 132.7, 130.9, 130.9, 129.7, 128.3, 127.8, 125.3, 124.4, 26.5. HRMS Calculated for $\text{C}_{13}\text{H}_{11}\text{N}_2\text{O}_3\text{S}$ ($\text{M}+\text{H}$) $^+$ 275.0485, found: 275.0485.

3. Screen of Optimizations for the Acid Additives



4. General Procedure for Asymmetric Hydrogenation

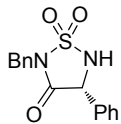


Pd(OCOCF₃)₂ (1.3 mg, 0.004 mmol) and (*R_c*,*R_p*)-Walphos (4.5 mg, 0.0048 mmol) were placed in a dried Schlenk tube under nitrogen atmosphere, and degassed anhydrous acetone was added. The mixture was stirred at room temperature for 1 h, then, the solvent was removed under vacuum to give the catalyst. In a glove box, to **1** (0.20 mmol) was added the above catalyst with 3.0 mL TFE. The hydrogenation was performed at 40 °C under hydrogen gas (600 psi) in a stainless steel autoclave for 12 h. After carefully releasing the hydrogen, the autoclave was opened and the reaction mixture was evaporated in *vacuo*. Flash chromatography on silica gel using dichloromethane/methanol 100:1 as the eluent gave the products **2**.

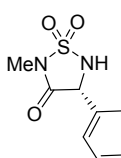
(*R*)-2-methyl-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (2a): known compound,² yellow solid, m.p. = 69-70 °C, >99% yield, 98% ee, [α]_D²⁰ = -3.7 (*c* 0.90, CHCl₃), R_f = 0.48 (petroleum ether/ethyl acetate 3:1). ¹H NMR (400 MHz, CDCl₃) δ 7.47-7.33 (m, 5H), 5.78 (s, 1H), 5.16 (s, 1H), 3.08 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.6, 133.5, 129.6, 129.3, 127.3, 64.1, 25.8. HPLC (AD-H column, *i*PrOH/hexane 15/85, 0.7 mL/min, 220 nm, 30 °C): t₁ = 11.9 min, t₂ = 13.4 min (major). HRMS Calculated for C₉H₁₁N₂O₃S (M+H)⁺ 227.0485, found: 227.0486.

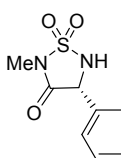
(*R*)-2-ethyl-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (2b): known compound,² yellow solid, m.p. = 94-95 °C, 98% yield, 96% ee, [α]_D²⁰ = +2.2 (*c* 0.94, CHCl₃), R_f = 0.40 (petroleum ether/ethyl acetate 3:1). ¹H NMR (400 MHz, CDCl₃) δ 7.57-7.35 (m, 5H), 5.34 (s, 1H), 5.20 (s, 1H), 3.71 (q, *J* = 7.3 Hz, 2H), 1.37 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.3, 133.6, 129.8, 129.5, 127.4, 63.9, 36.9, 13.6. HPLC (IC column, *i*PrOH/hexane 10/90, 0.7 mL/min, 220 nm, 30 °C): t₁ = 11.5 min, t₂ = 12.6 min (major). HRMS Calculated for C₁₀H₁₃N₂O₃S (M+H)⁺ 241.0641, found: 241.0643.

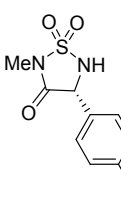
(*R*)-2-benzyl-4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (2c): New compound, white solid, m.p. = 82-83 °C, 94% yield, 94% ee, [α]_D²⁰ = +19.4 (*c* 1.14, CHCl₃), R_f = 0.48 (petroleum ether/ethyl acetate 3:1). ¹H NMR (400 MHz, CDCl₃) δ 7.53-7.28 (m, 10H), 5.27 (s, 1H), 5.16 (s,

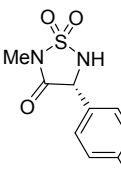

 1H), 4.74 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 166.6, 134.0, 133.4, 129.7, 129.4, 129.0, 129.0, 128.8, 127.3, 63.7, 45.1. HPLC (AD-H column, ⁱPrOH/hexane 15/85, 0.7 mL/min, 220 nm, 30 °C): t₁ = 18.5 min, t₂ = 19.6 min (major). HRMS Calculated for C₁₅H₁₅N₂O₃S (M+H)⁺ 303.0798, found: 303.0796.

(R)-2-methyl-4-(p-tolyl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (2d): New compound, yellow solid, m.p. = 103-104 °C, >99% yield, 97% ee, [α]²⁰_D = +3.5 (c 0.95, CHCl₃), R_f = 0.52 (petroleum ether/ethyl acetate 3:1). ¹H NMR (400 MHz, CDCl₃) δ 7.32 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 5.27 (s, 1H), 5.18 (s, 1H), 3.15 (s, 3H), 2.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.7, 139.9, 130.4, 130.2, 127.3, 64.2, 25.9, 21.4. HPLC (AD-H column, ⁱPrOH/hexane 15/85, 0.7 mL/min, 220 nm, 30 °C): t₁ = 12.7 min, t₂ = 14.5 min (major). HRMS Calculated for C₁₀H₁₃N₂O₃S (M+H)⁺ 241.0641, found: 241.0642.

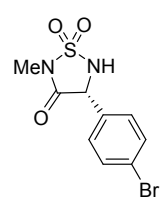

(R)-2-methyl-4-(m-tolyl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (2e): New compound, yellow solid, m.p. = 81-82 °C, 98% yield, 98% ee, [α]²⁰_D = -2.4 (c 0.95, CHCl₃), R_f = 0.61 (dichloromethane). ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.27 (m, 1H), 7.26-7.18 (m, 3H), 5.38 (s, 1H), 5.17 (s, 1H), 3.16 (s, 3H), 2.37 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.6, 139.5, 133.3, 130.6, 129.4, 128.0, 124.5, 64.4, 25.9, 21.6. HPLC (AD-H column, ⁱPrOH/hexane 15/85, 0.7 mL/min, 220 nm, 30 °C): t₁ = 12.1 min, t₂ = 13.8 min (major). HRMS Calculated for C₁₀H₁₃N₂O₃S (M+H)⁺ 241.0641, found: 241.0641.


(R)-2-methyl-4-(o-tolyl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (2f): New compound, yellow solid, m.p. = 145-146 °C, 99% yield, 80% ee, [α]²⁰_D = +28.6 (c 0.94, CHCl₃), R_f = 0.60 (dichloromethane). ¹H NMR (400 MHz, CDCl₃) δ 7.35-7.21 (m, 4H), 5.48 (s, 1H), 4.97 (s, 1H), 3.20 (s, 3H), 2.45 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.0, 137.5, 131.8, 131.6, 130.1, 127.4, 127.3, 61.9, 26.0, 19.6. HPLC (AS-H column, ⁱPrOH/hexane 30/70, 0.7 mL/min, 220 nm, 30 °C): t₁ = 13.1 min (major), t₂ = 16.6 min. HRMS Calculated for C₁₀H₁₃N₂O₃S (M+H)⁺ 241.0641, found: 241.0643.


(R)-4-(4-fluorophenyl)-2-methyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (2g): New compound, yellow solid, m.p. = 108-109 °C, 99% yield, 97% ee, [α]²⁰_D = -7.9 (c 0.96, CHCl₃), R_f = 0.20 (dichloromethane). ¹H NMR (400 MHz, CDCl₃) δ 7.51-7.43 (m, 2H), 7.16-7.06 (m, 2H), 5.42 (s, 1H), 5.26 (s, 1H), 3.16 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.2, 163.5 (d, J_{FC} = 249.4 Hz), 129.3 (d, J_{FC} = 8.5 Hz), 129.1 (d, J_{FC} = 3.3 Hz), 116.5 (d, J_{FC} = 22.0 Hz), 63.5, 26.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -111.5. HPLC (AD-H column, ⁱPrOH/hexane 15/85, 0.7 mL/min, 220 nm, 30 °C): t₁ = 11.8 min, t₂ = 13.3 min (major). HRMS Calculated for C₉H₁₀FN₂O₃S (M+H)⁺ 245.0391, found: 245.0391.

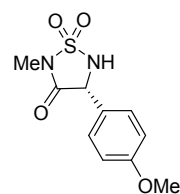

(R)-4-(4-chlorophenyl)-2-methyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (2h): New compound, yellow solid, m.p. = 100-101 °C, 99% yield, 96% ee, [α]²⁰_D = -5.9 (c 0.97, CHCl₃), R_f = 0.26 (dichloromethane). ¹H NMR (400 MHz, CDCl₃) δ 7.46-7.33 (m, 4H), 5.66 (s, 1H), 5.23 (s, 1H), 3.14 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.0, 135.8, 131.8, 129.6, 128.6, 63.4, 26.0. HPLC (AD-H column, ⁱPrOH/hexane 10/90, 0.7 mL/min, 220 nm, 30 °C): t₁ = 18.0 min, t₂ = 19.8 min (major). HRMS Calculated for C₉H₁₀ClN₂O₃S (M+H)⁺ 261.0095, found: 261.0095.

(R)-4-(4-bromophenyl)-2-methyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (2i): New compound,

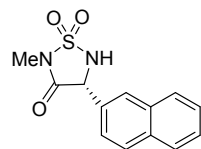


yellow solid, m.p. = 95-96 °C, 96% yield, 94% ee, $[\alpha]_D^{20} = -5.7$ (*c* 1.21, CHCl₃), $R_f = 0.21$ (DCM). ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 5.46 (s, 1H), 5.23 (s, 1H), 3.15 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.0, 132.5, 132.3, 128.9, 124.0, 63.4, 26.0. HPLC (AD-H column, ⁱPrOH/hexane 10/90, 0.7 mL/min, 220 nm, 30 °C): *t*₁ = 19.8 min, *t*₂ = 21.4 min (major). HRMS Calculated for C₉H₁₀BrN₂O₃S (M+H)⁺ 304.9590, found: 304.9591.

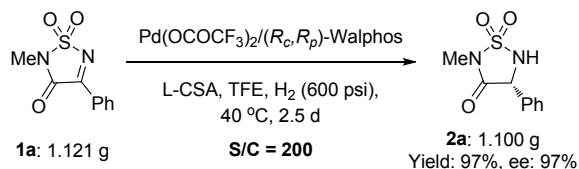
(R)-4-(4-methoxyphenyl)-2-methyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide (2j): New compound, yellow solid, m.p. = 111-112 °C, 98% yield, 97% ee, $[\alpha]_D^{20} = +8.1$ (*c* 0.80, CHCl₃), $R_f = 0.50$ (dichloromethane). ¹H NMR (400 MHz, CDCl₃) δ 7.36 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 5.20 (s, 1H), 5.08 (s, 1H), 3.81 (s, 3H), 3.18 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.9, 160.8, 128.9, 125.3, 114.9, 64.0, 55.6, 25.9. HPLC (AD-H column, ⁱPrOH/hexane 15/85, 0.7 mL/min, 220 nm, 30 °C): *t*₁ = 17.1 min, *t*₂ = 18.6 min (major). HRMS Calculated for C₁₀H₁₃N₂O₄S (M+H)⁺ 257.0591, found: 257.0594.



(R)-2-methyl-4-(naphthalen-2-yl)-1,2,5-thiadiazolidin-3-one 1,1-dioxide (2k): New compound, yellow solid, m.p. = 153-154 °C, 95% yield, 93% ee, $[\alpha]_D^{20} = +2.0$ (*c* 1.04, CHCl₃), $R_f = 0.42$ (dichloromethane). ¹H NMR (400 MHz, CDCl₃) δ 7.90 (s, 1H), 7.88-7.80 (m, 3H), 7.56-7.44 (m, 3H), 5.51 (s, 1H), 5.35 (s, 1H), 3.16 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.4, 133.7, 133.2, 130.6, 129.6, 128.4, 128.0, 127.3, 127.1, 124.0, 64.5, 26.0. HPLC (OJ-H column, ⁱPrOH/hexane 30/70, 0.7 mL/min, 220 nm, 30 °C): *t*₁ = 37.6 min (major), *t*₂ = 46.2 min. HRMS Calculated for C₁₃H₁₃N₂O₃S (M+H)⁺ 277.0641, found: 277.0641.

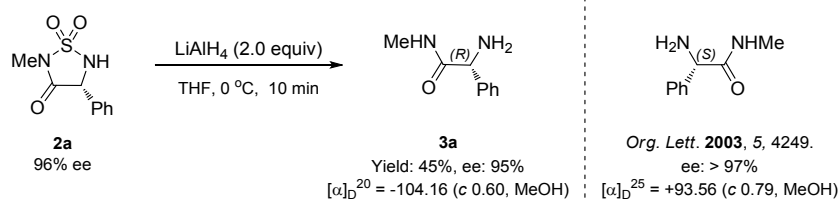


5. Gram Scale Experiment



Pd(OCOCF₃)₂ (8.3 mg, 0.025 mmol) and (*R_c*,*R_p*)-Walphos (28 mg, 0.030 mmol) were placed in a dried Schlenk tube under nitrogen atmosphere, and degassed anhydrous acetone was added. The mixture was stirred at room temperature for 1 h, then, the solvent was removed under vacuum to give the catalyst. In a glove box, to the mixture of **1a** (1.121 g, 5.0 mmol) and L-CSA (0.116 g, 0.5 mmol) was added the above catalyst with 25 mL TFE. The hydrogenation was performed at 40 °C under hydrogen (600 psi) in a stainless steel autoclave for 2.5 d. After carefully releasing the hydrogen, the autoclave was opened and the reaction mixture was evaporated in *vacuo*. Flash chromatography on silica gel using dichloromethane/methanol 100:1 as the eluent gave the product **2a** with 97% yield and 97% ee.

6. Determination of the Absolute Configuration of **2a**



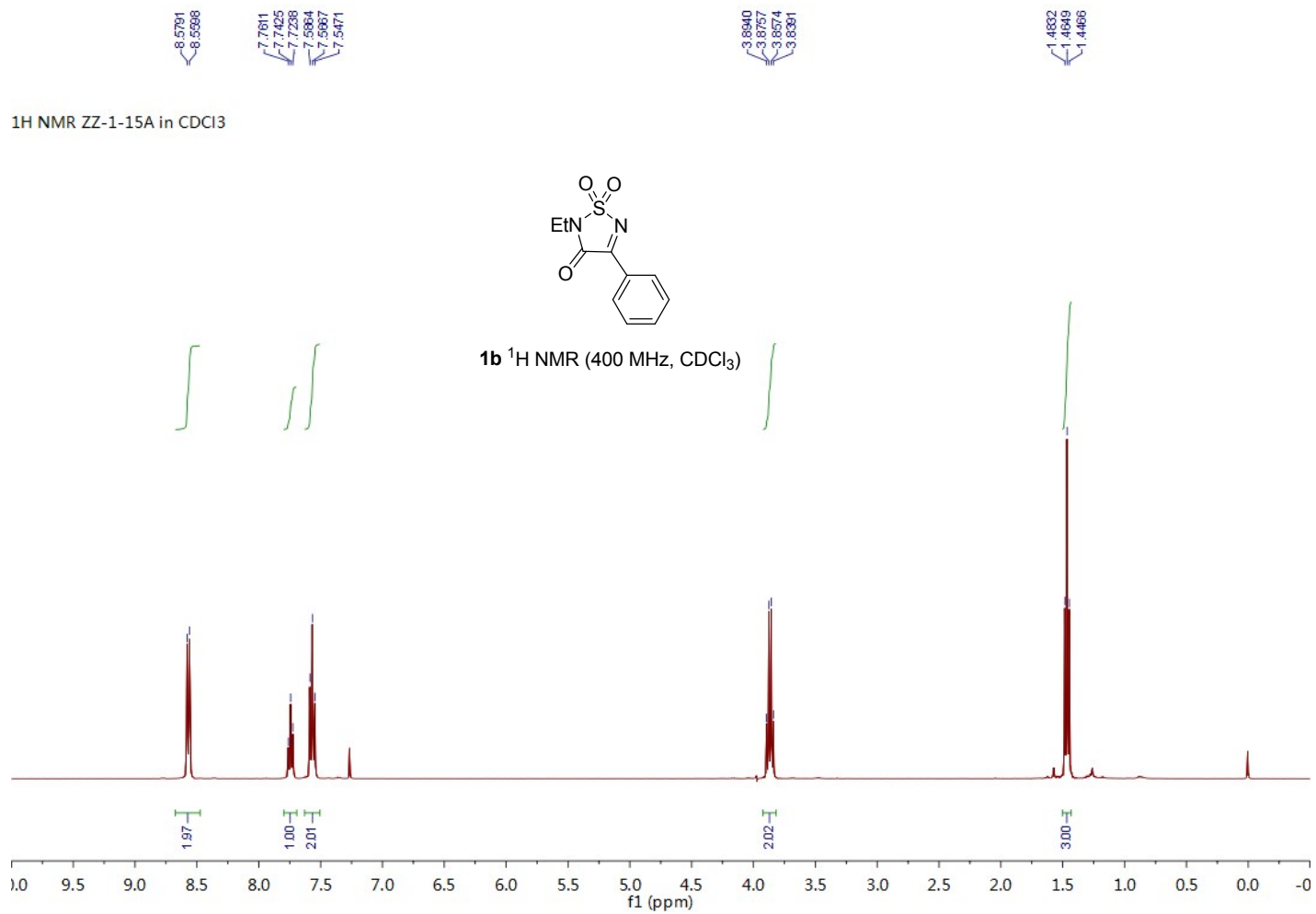
To a suspension of LiAlH₄ (30 mg, 0.8 mmol, 2.0 equiv) in THF (2 mL), a solution of **2a** (93 mg, 0.4 mmol, 1.0 equiv) in THF (4 mL) was added dropwise at 0 °C. After stirring for 10 min, the mixture was cooled, quenched with ice water and 10% sodium hydroxide was then added. The aqueous layer was extracted with ethyl acetate, washed with brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford compound **3a**.

(R)-2-Amino-N-methyl-2-phenylacetamide: 30 mg, 45% yield, 95% ee, [α]²⁰_D = -104.16 (c 0.60, MeOH), [lit.³: [α]²⁵_D = +93.56 (c 0.79, MeOH) for the (S)-enantiomer], known compound,³ yellow oil, R_f = 0.20 (dichloromethane/methanol 15/1). ¹H NMR (400 MHz, CDCl₃) δ 7.43-7.27 (m, 5H), 7.21 (brs, 1H), 4.58 (s, 1H), 2.78 (d, J = 4.9 Hz, 3H), 2.65 (brs, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 173.5, 140.7, 129.0, 128.2, 127.1, 59.7, 26.2. HPLC (AS-H column, *i*PrOH/hexane 30/70, 0.7 mL/min, 220 nm, 30 °C): t₁ = 16.3 min (major), t₂ = 23.3 min.

7. References

- [1]. Nishimura, T.; Ebe, Y.; Fujimoto, H.; Hayashi, T. *Chem. Commun.* **2013**, 49, 5504.
- [2]. Unterhalt, B.; Hanewacker, G.-A. *Arch. Pharm. (Weinheim)* **1988**, 321, 749.
- [3]. Reichard, G. A.; Stengone, C.; Paliwal, S.; Mergelsberg, I.; Majmundar, S.; Wang, C.; Tiberi, R.; McPhail, A. T.; Piwinski, J. J.; Shih, N.-Y. *Org. Lett.* **2003**, 5, 4249.

8. Copy of NMR and HPLC for the Compounds



164.80

156.13

136.42

132.30

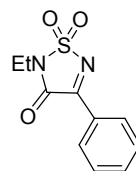
129.53

127.05

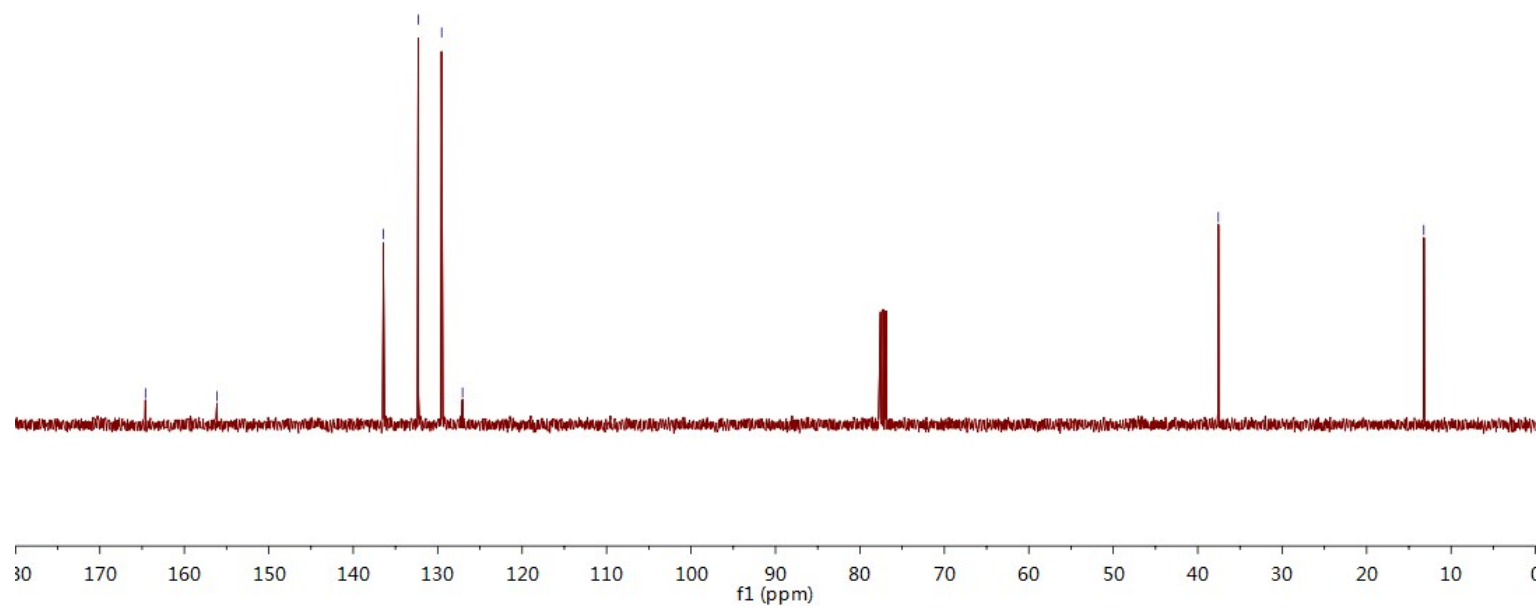
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13.23

¹³C NMR ZZ-1-15A in CDCl₃



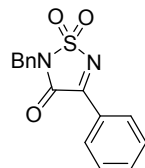
1b ¹³C NMR (100 MHz, CDCl₃)



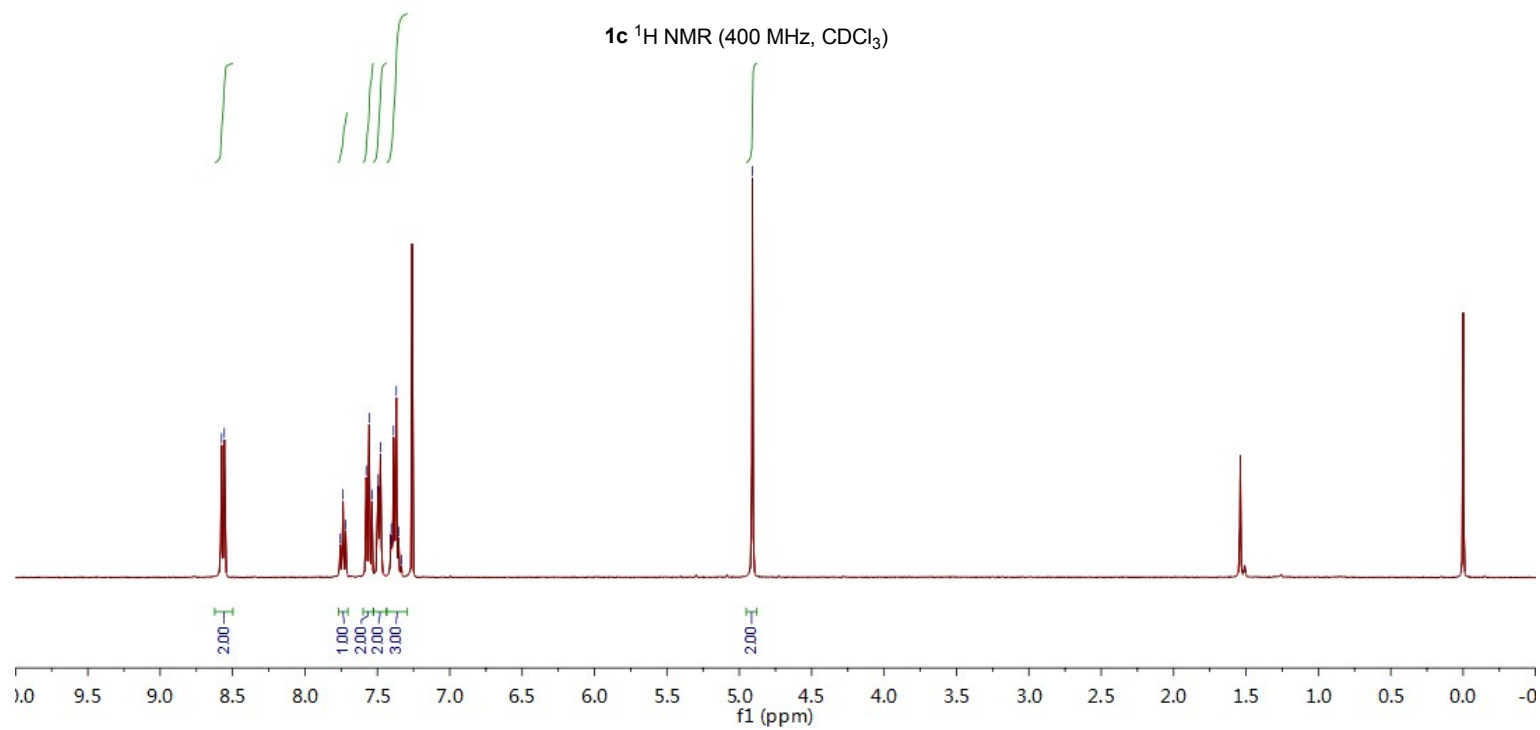
8.5756
8.5572
7.7561
7.7374
7.7187
7.6786
7.5967
7.5372
7.4983
7.4942
7.4785
7.4101
7.4003
7.3884
7.3693
7.3533
7.3343

4.9090

¹H NMR ZZ-1-16B in CDCl₃



1c ¹H NMR (400 MHz, CDCl₃)

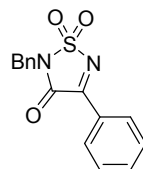


164.55
156.36
136.55
133.19
132.36
129.55
129.20
129.11
129.02
126.98

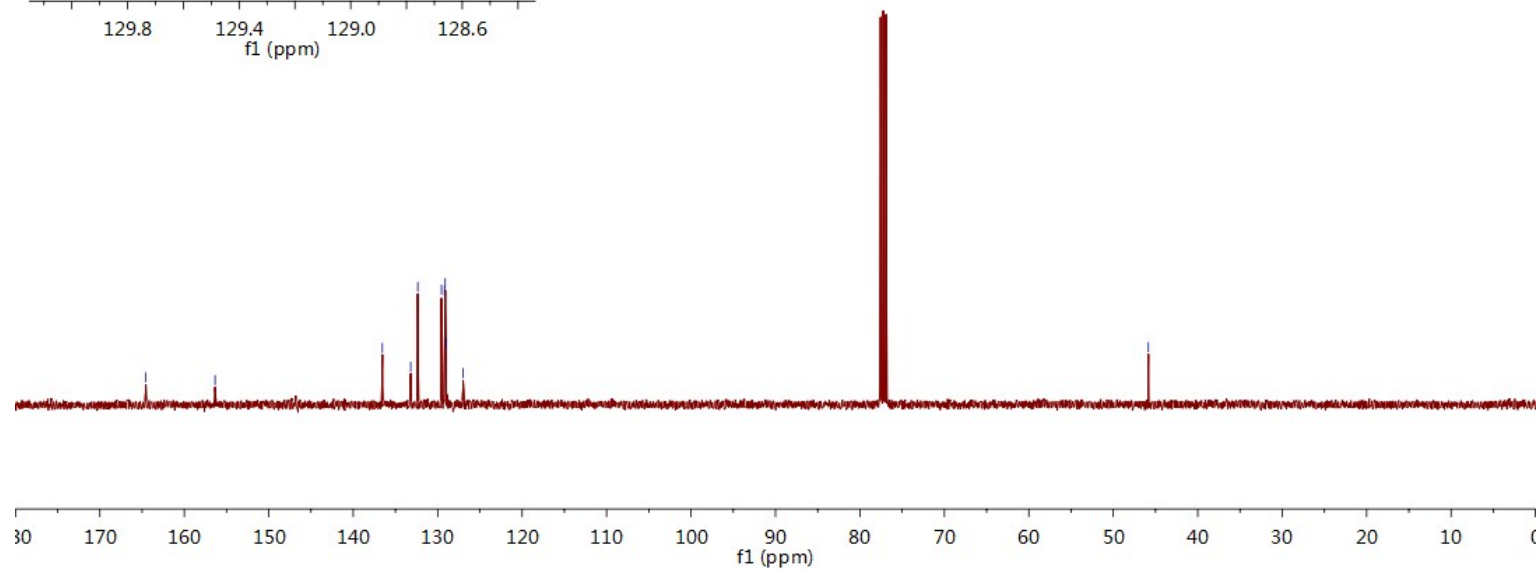
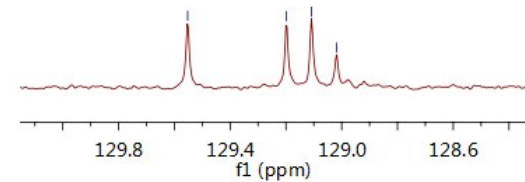
45.84

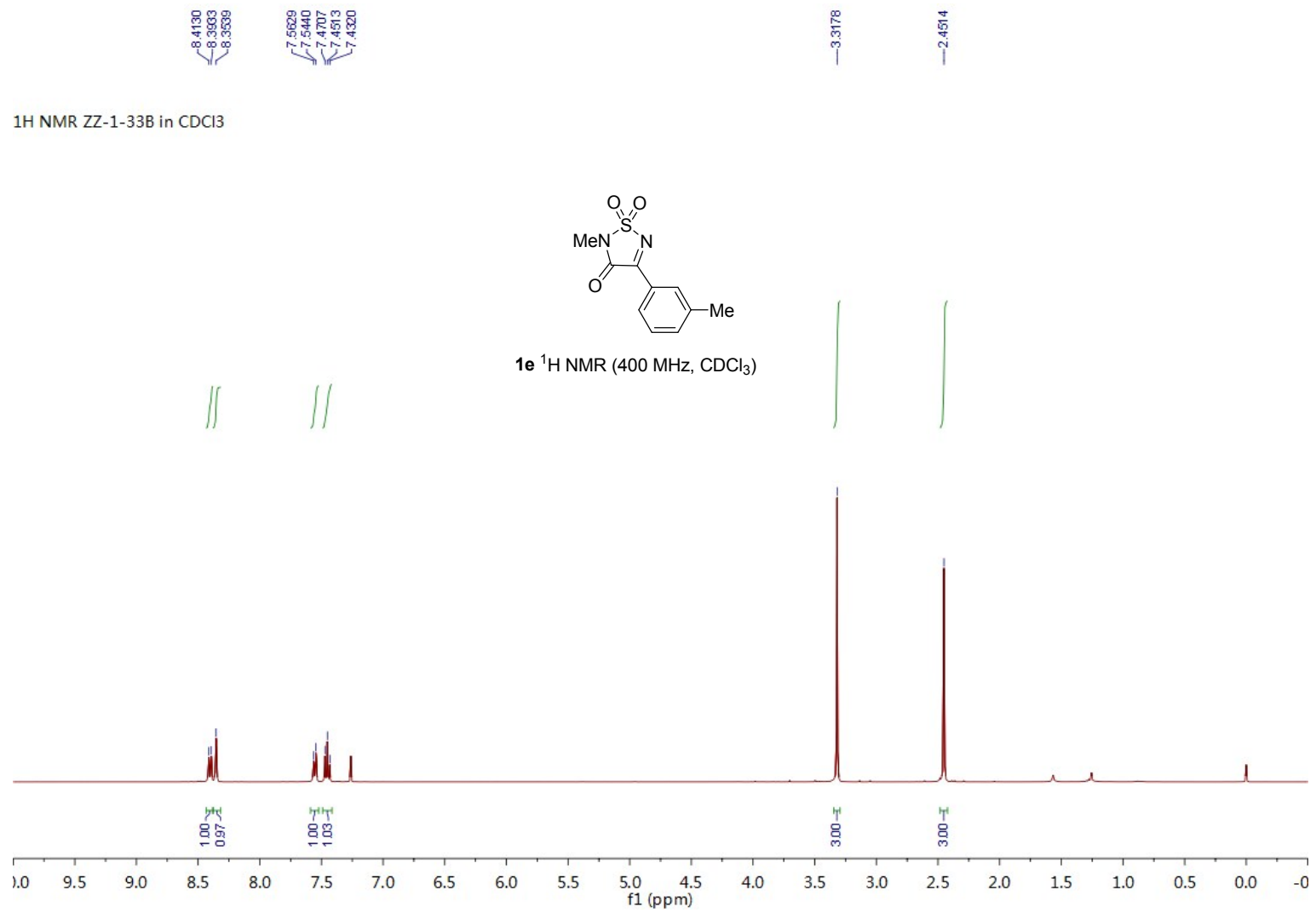
¹³C NMR ZZ-1-16B in CDCl₃

129.55
129.20
129.11
129.02



1c ¹³C NMR (100 MHz, CDCl₃)





164.97

156.30

139.61

137.54

132.51

129.82

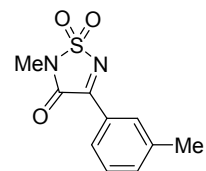
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126.92

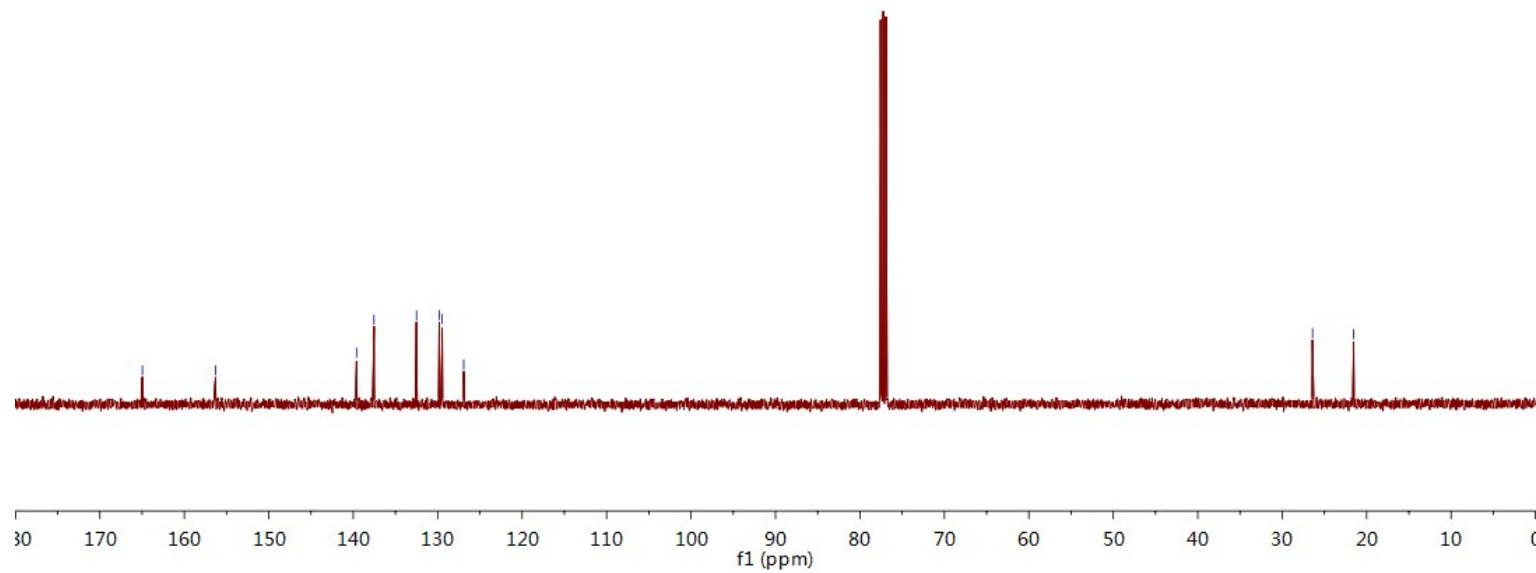
26.40

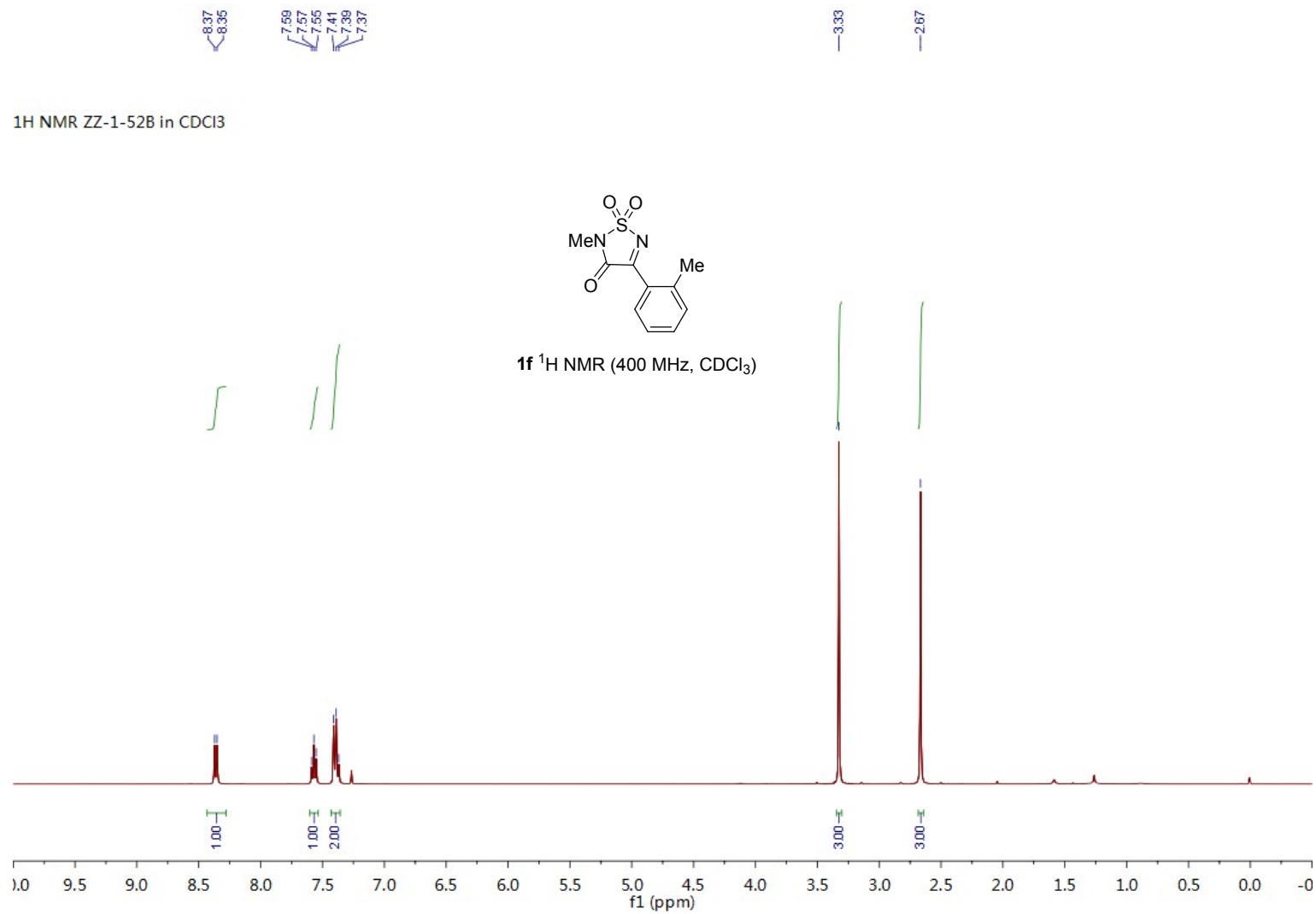
21.54

^{13}C NMR ZZ-1-33B in CDCl_3



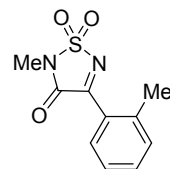
1e ^{13}C NMR (100 MHz, CDCl_3)



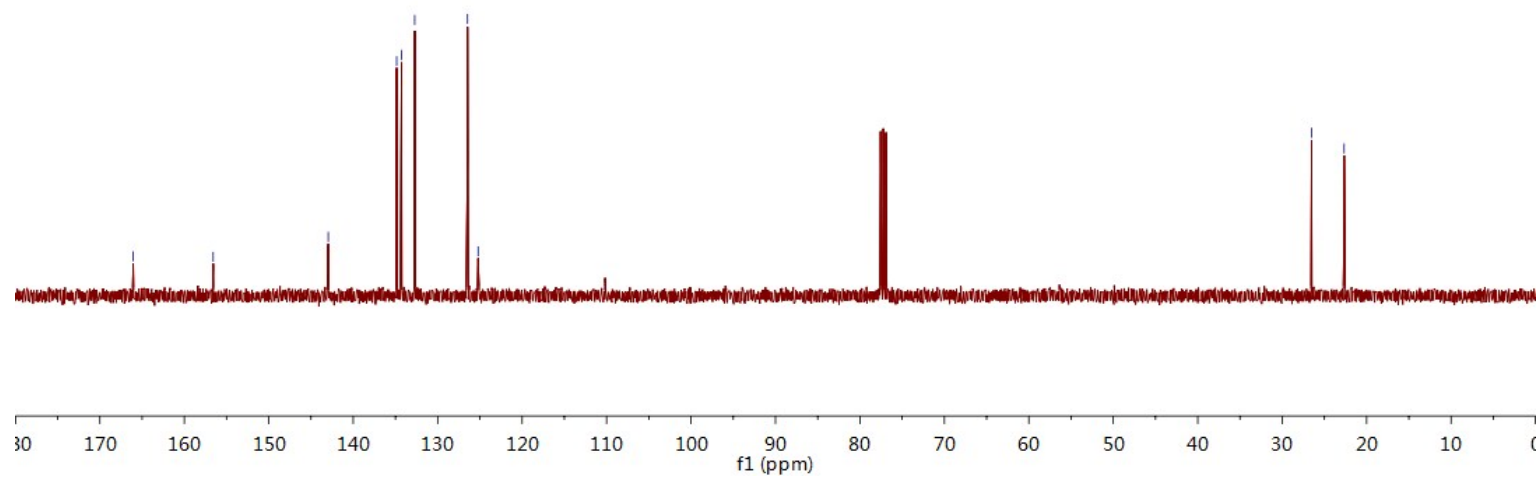


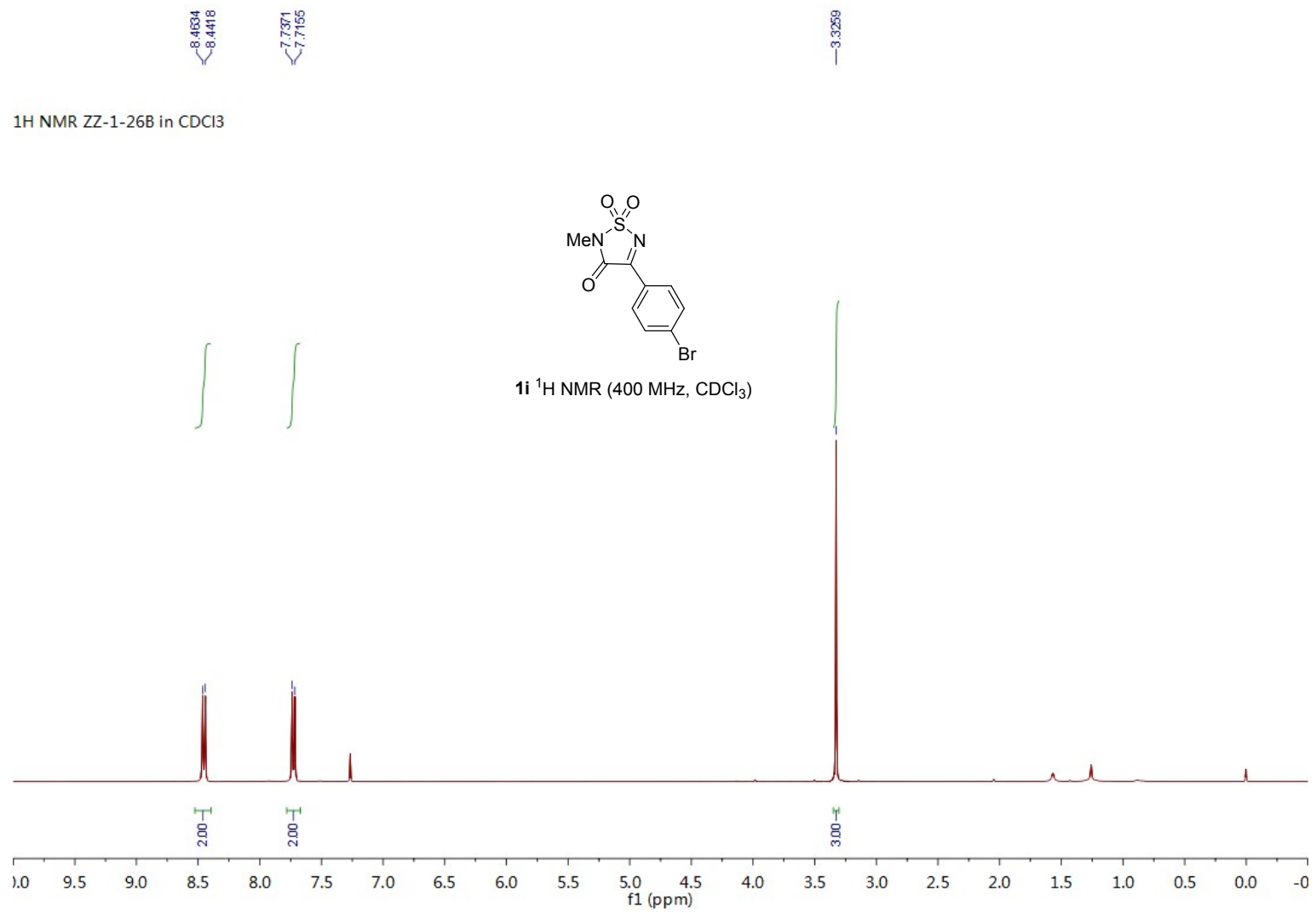


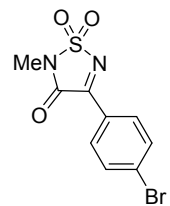
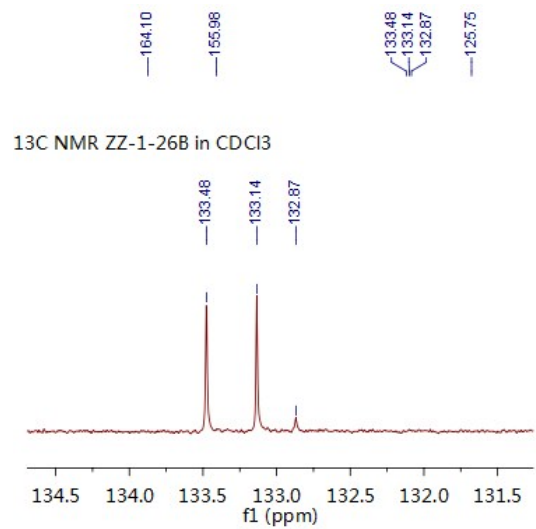
^{13}C NMR ZZ-1-52B in CDCl_3



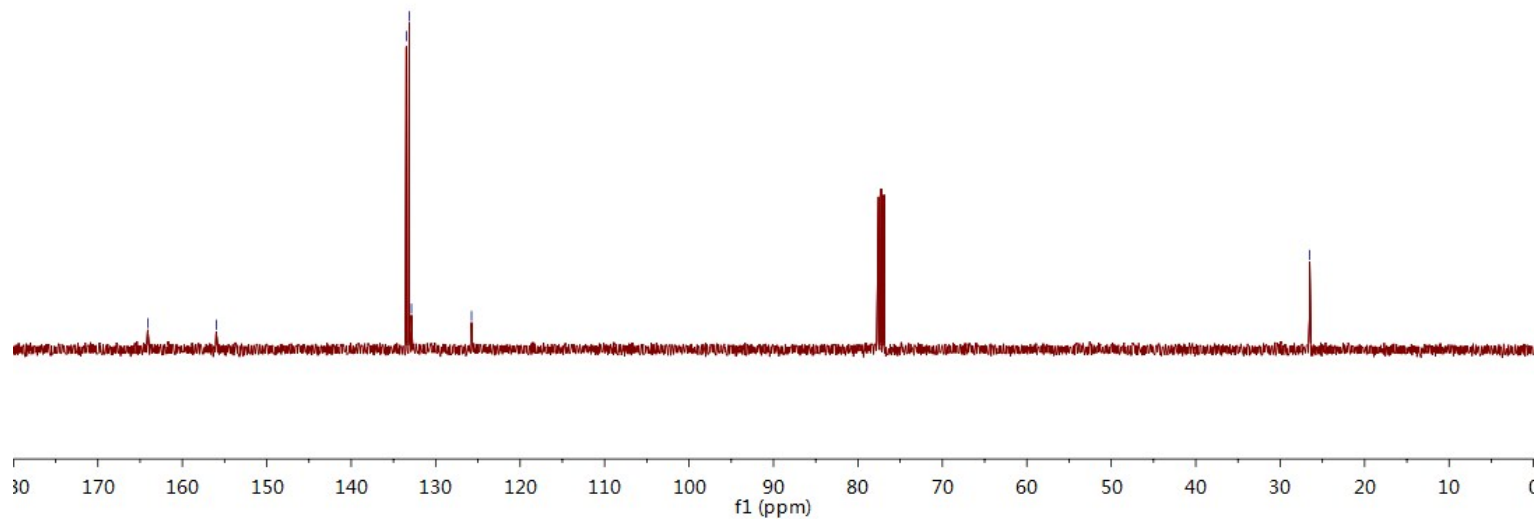
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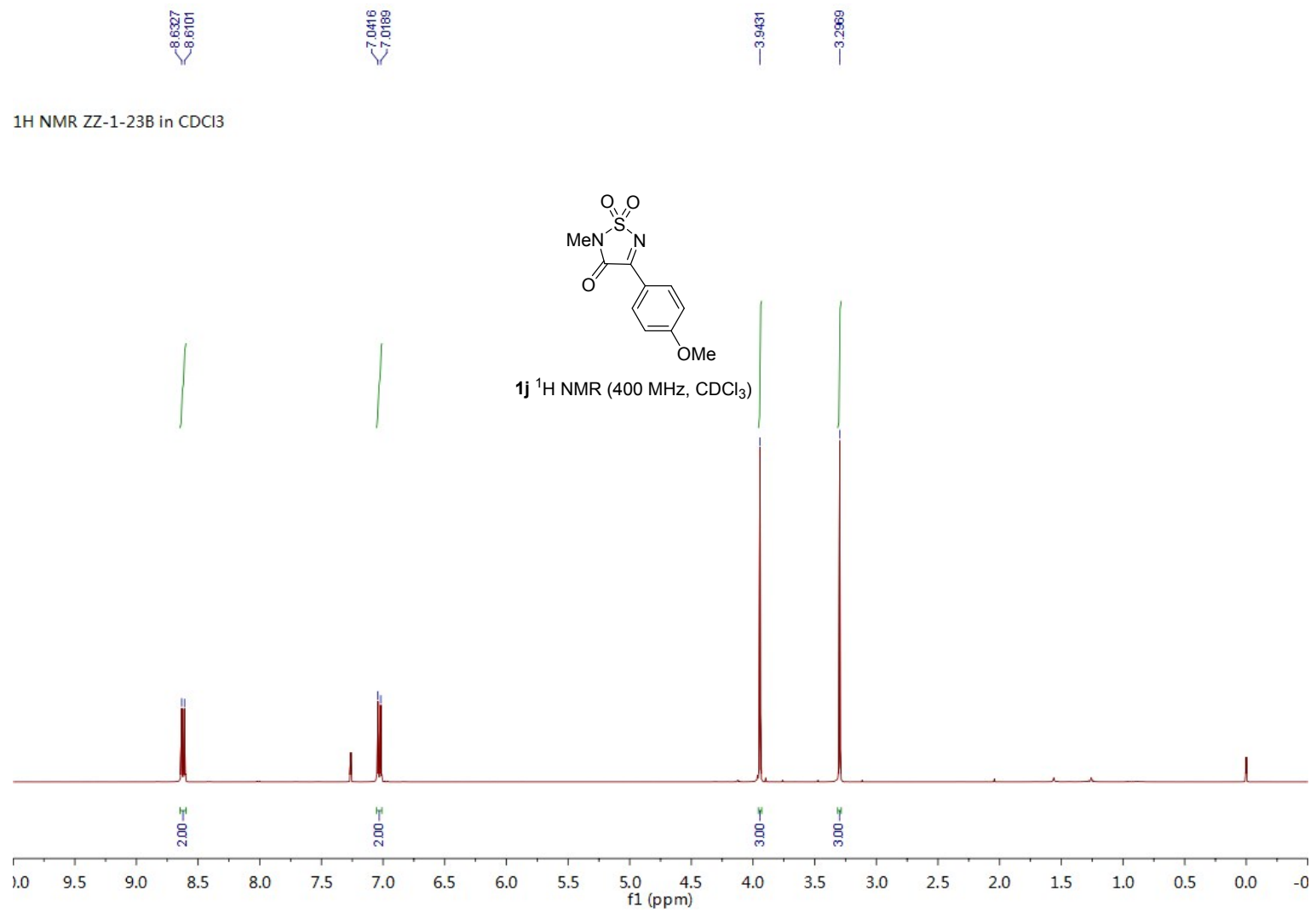






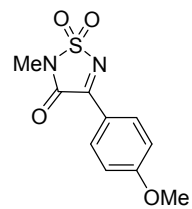
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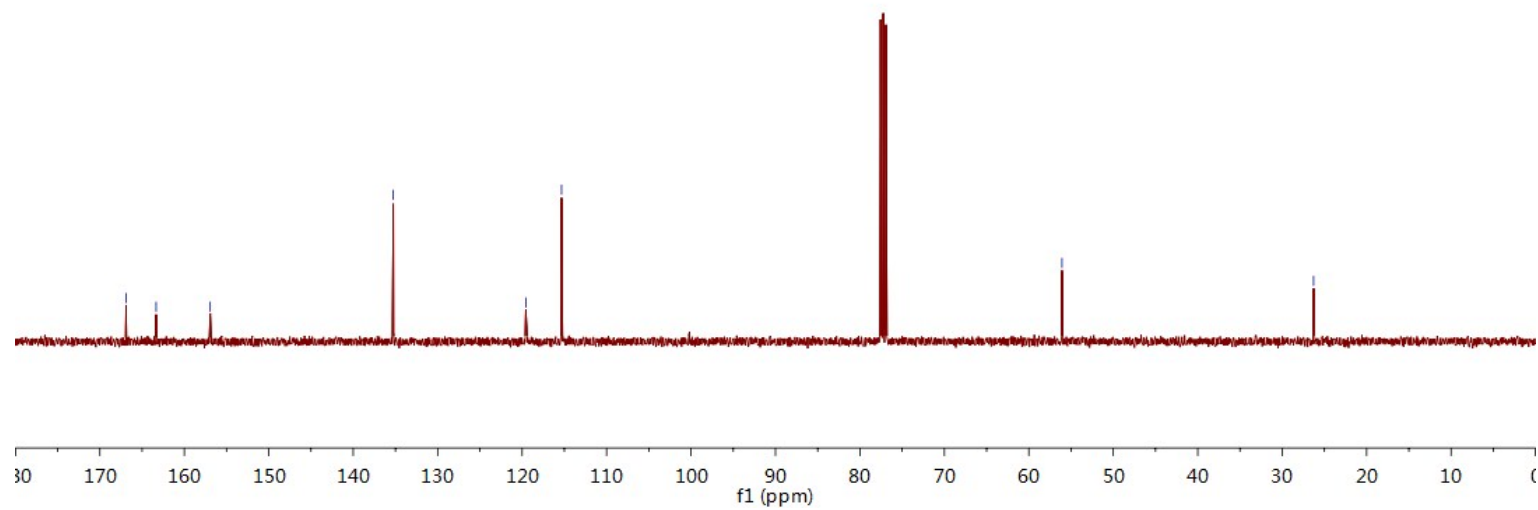


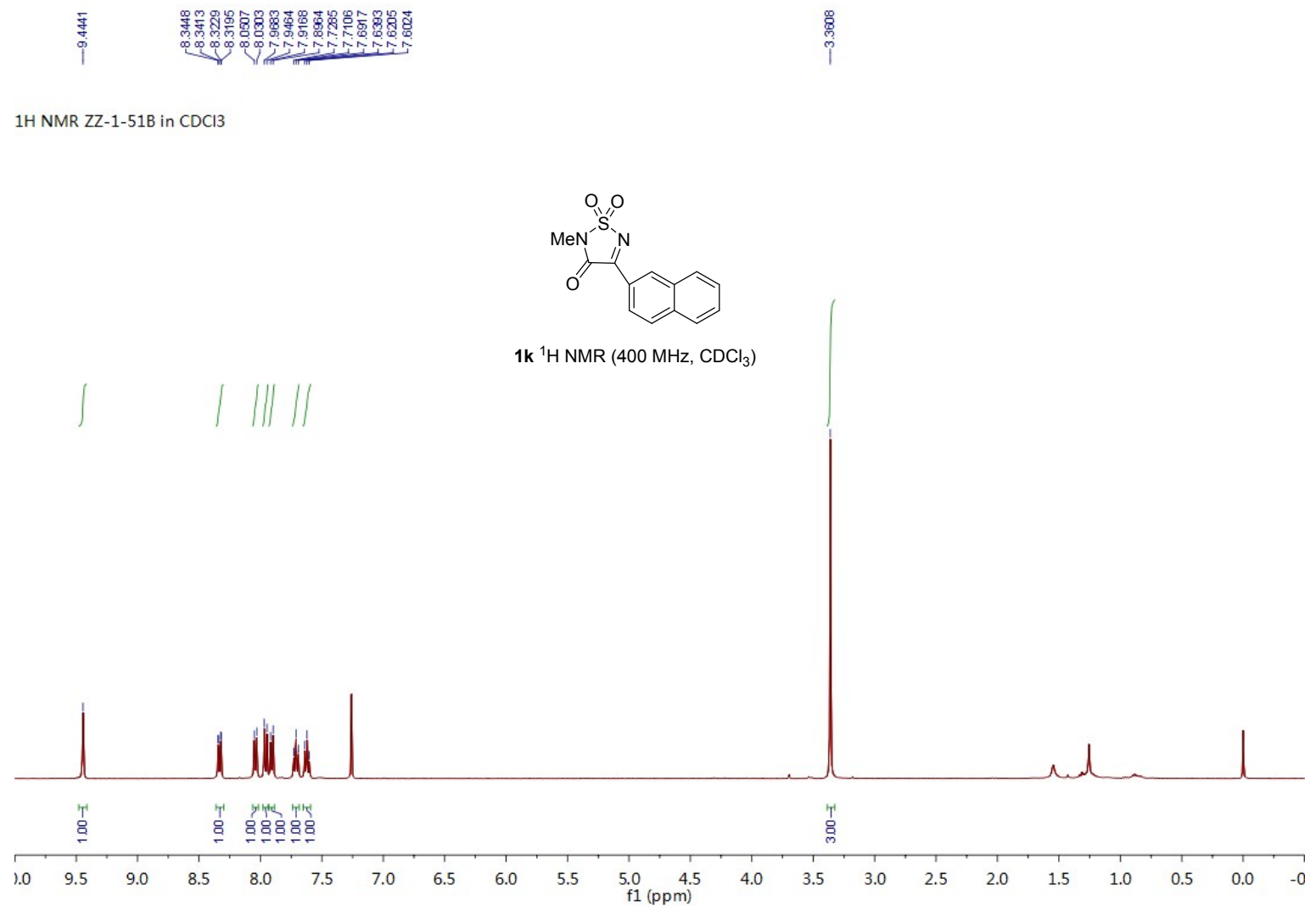


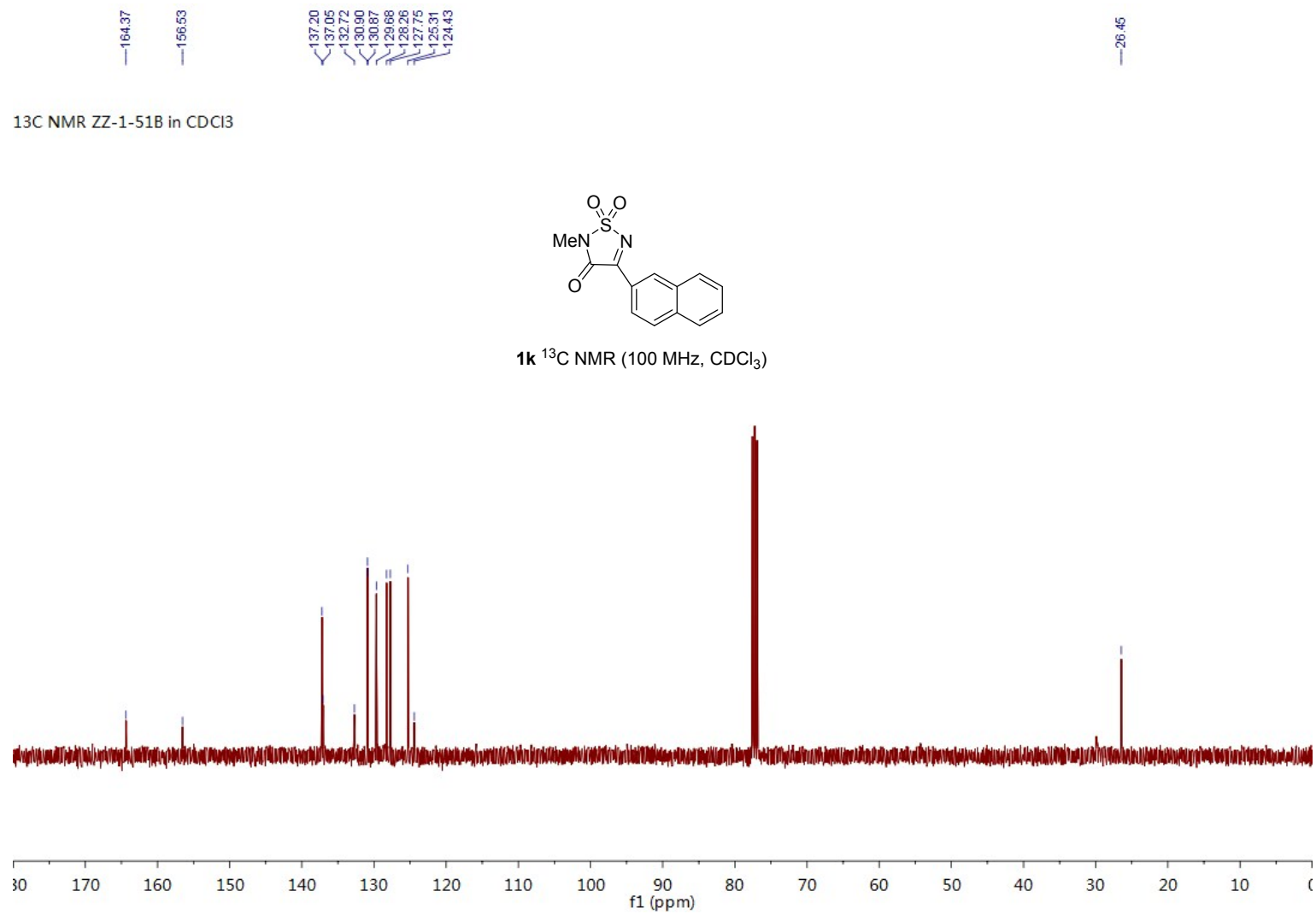
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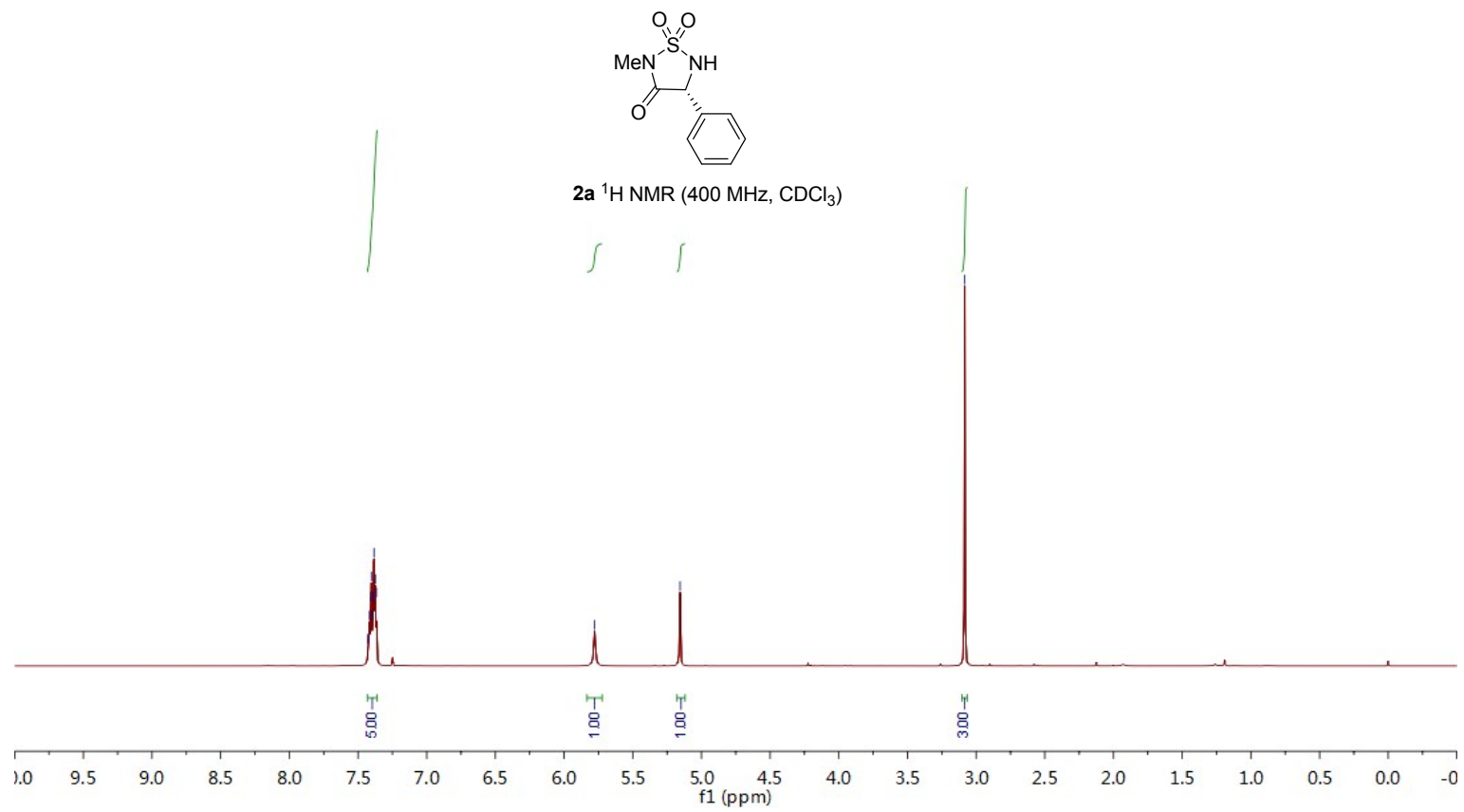
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¹H NMR ZZ-1-17 in CDCl₃



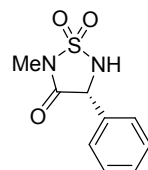
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133.45
129.63
129.31
127.28

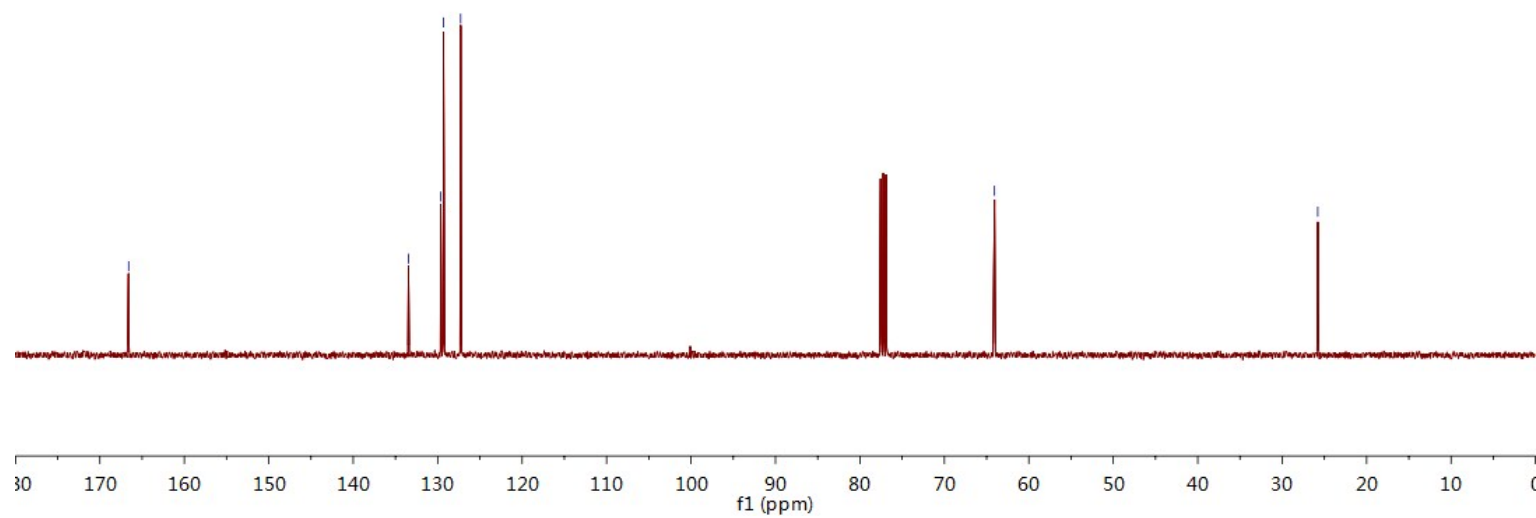
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25.78

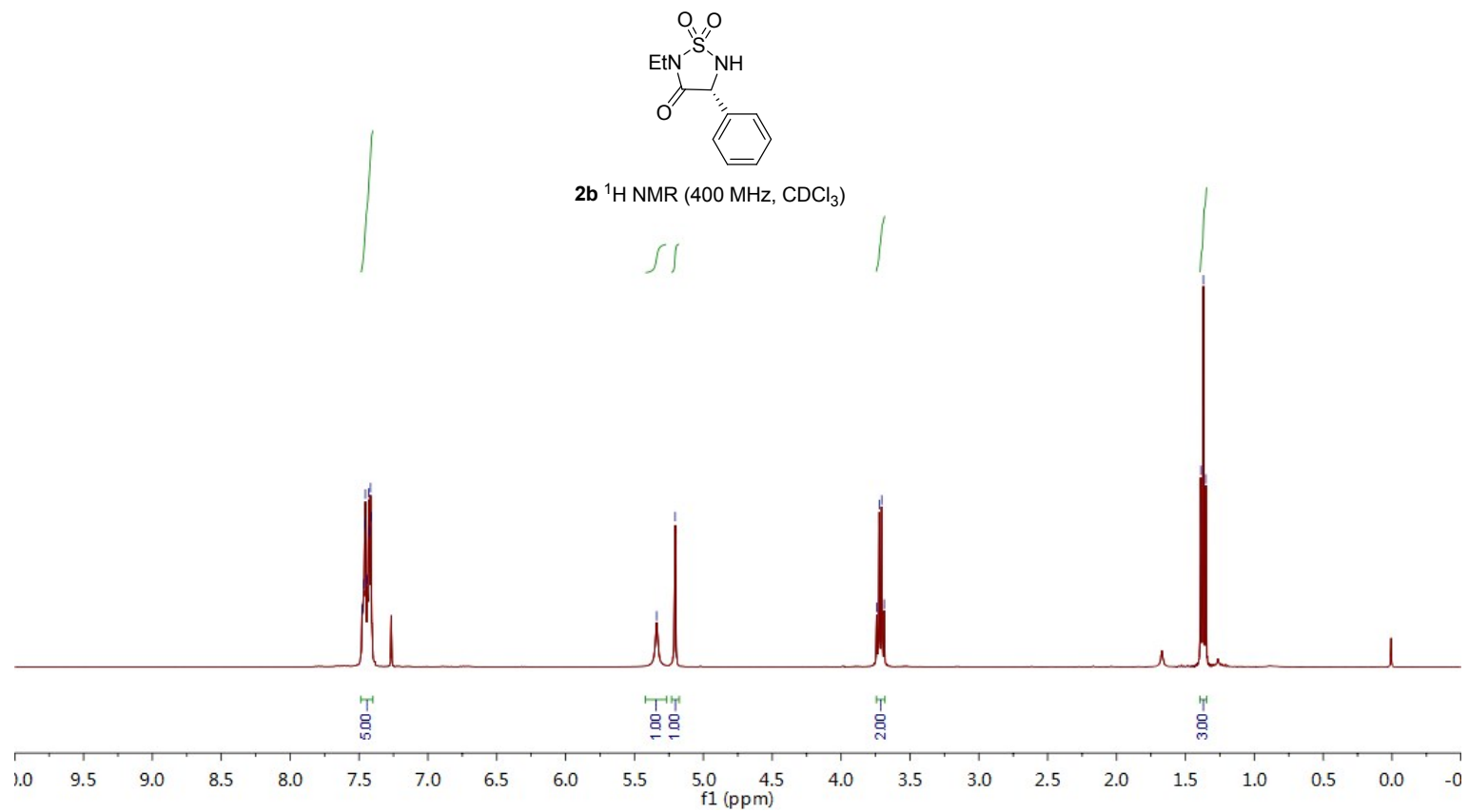
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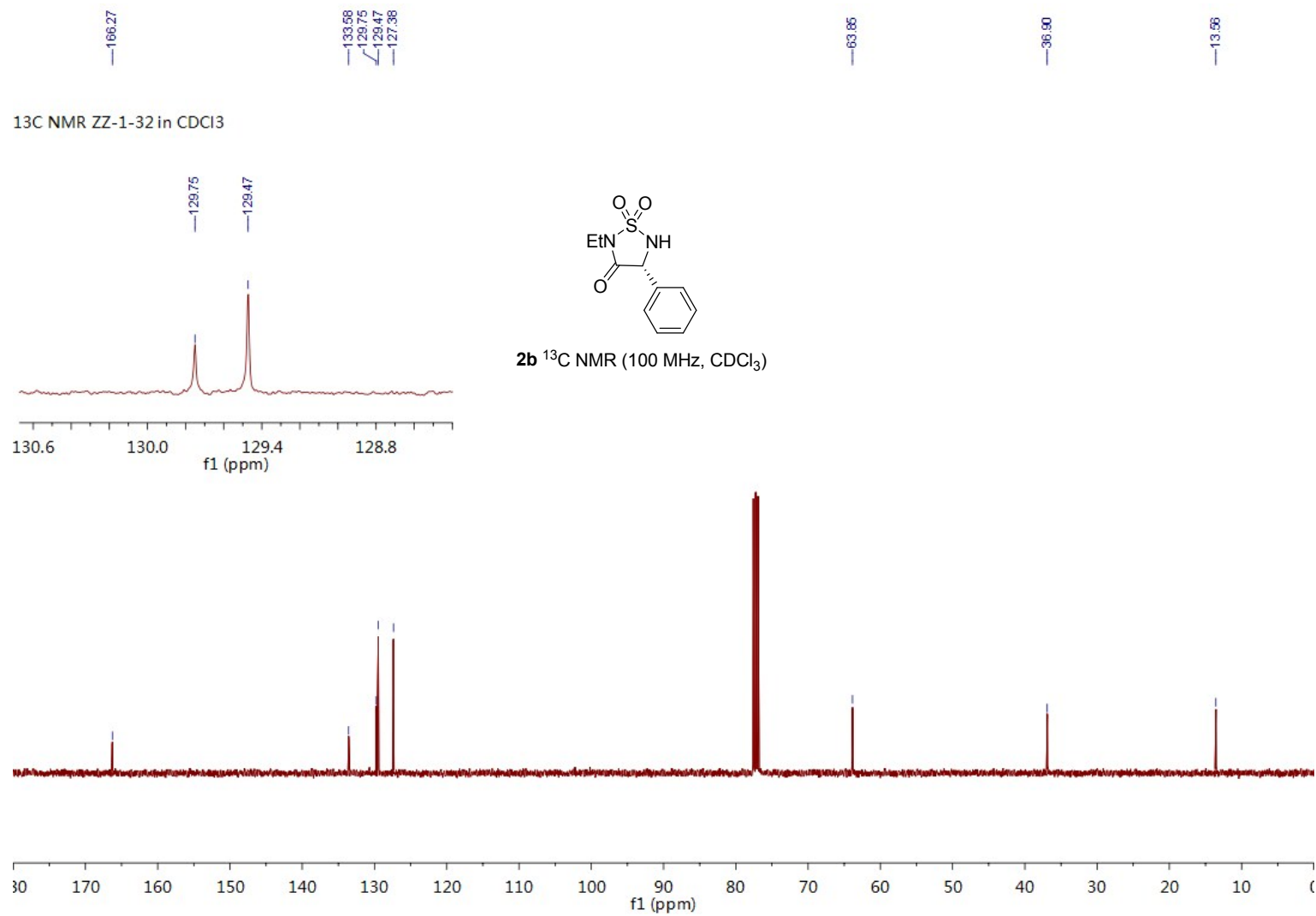


2a ¹³C NMR (100 MHz, CDCl₃)

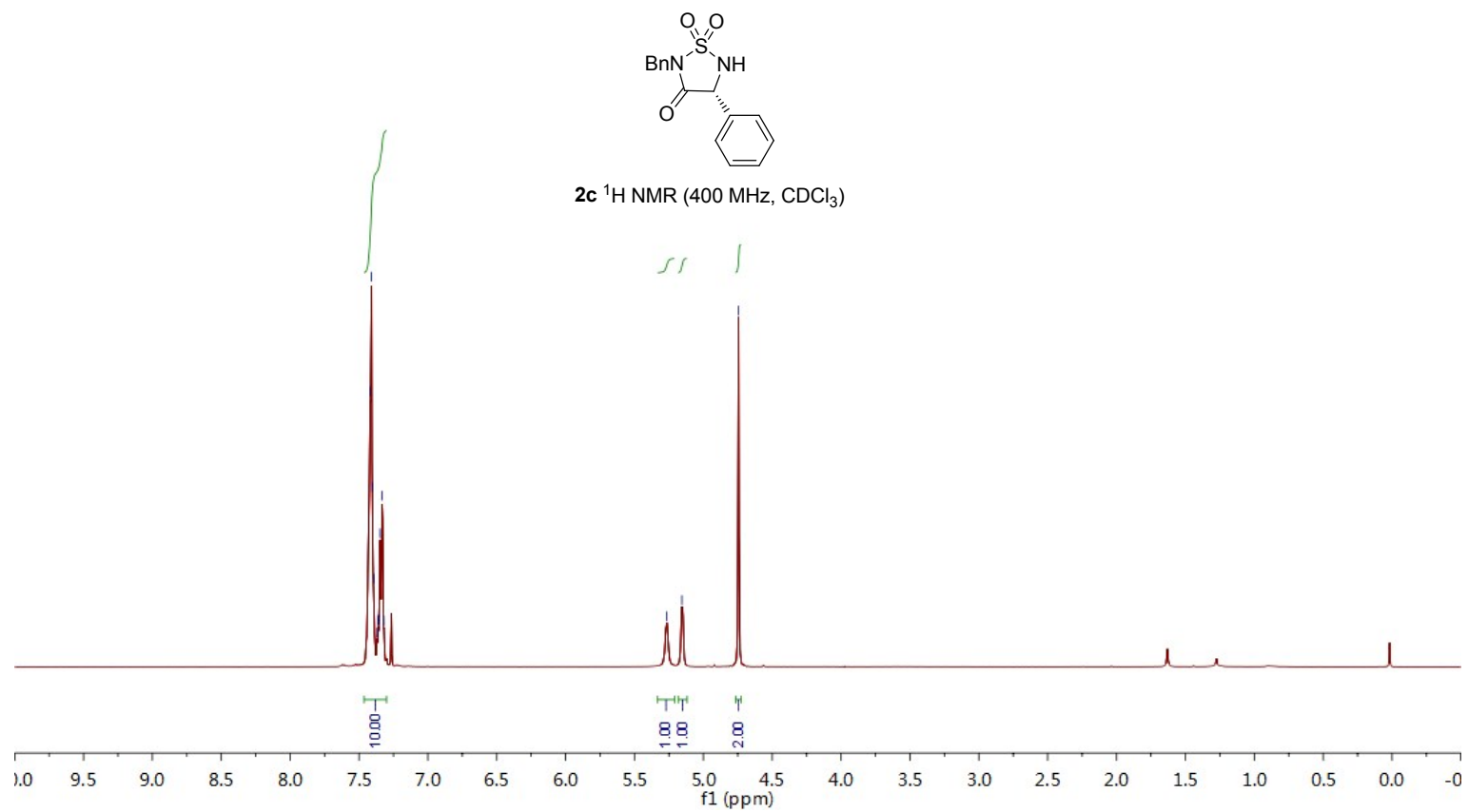


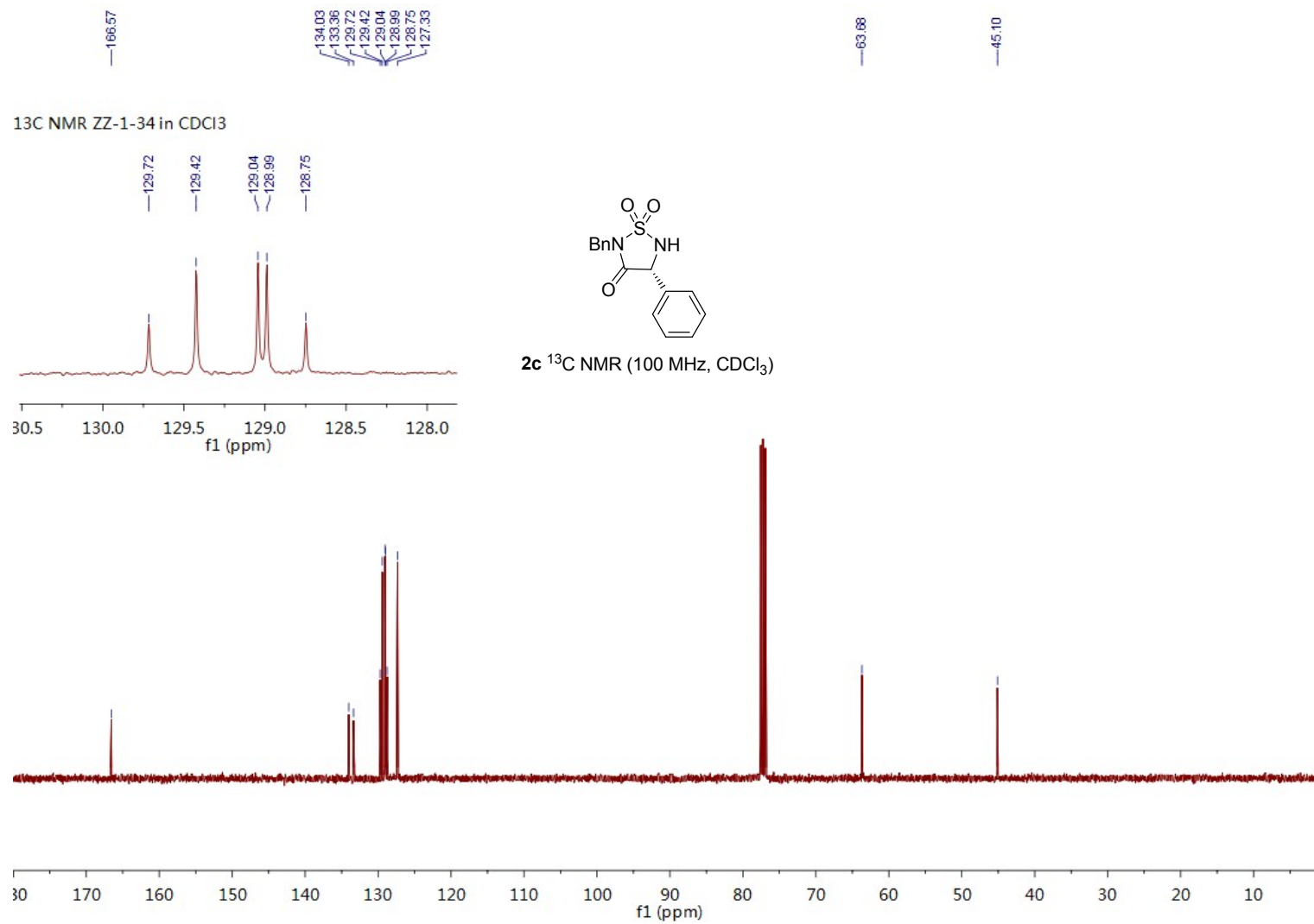
¹H NMR ZZ-1-32 in CDCl₃



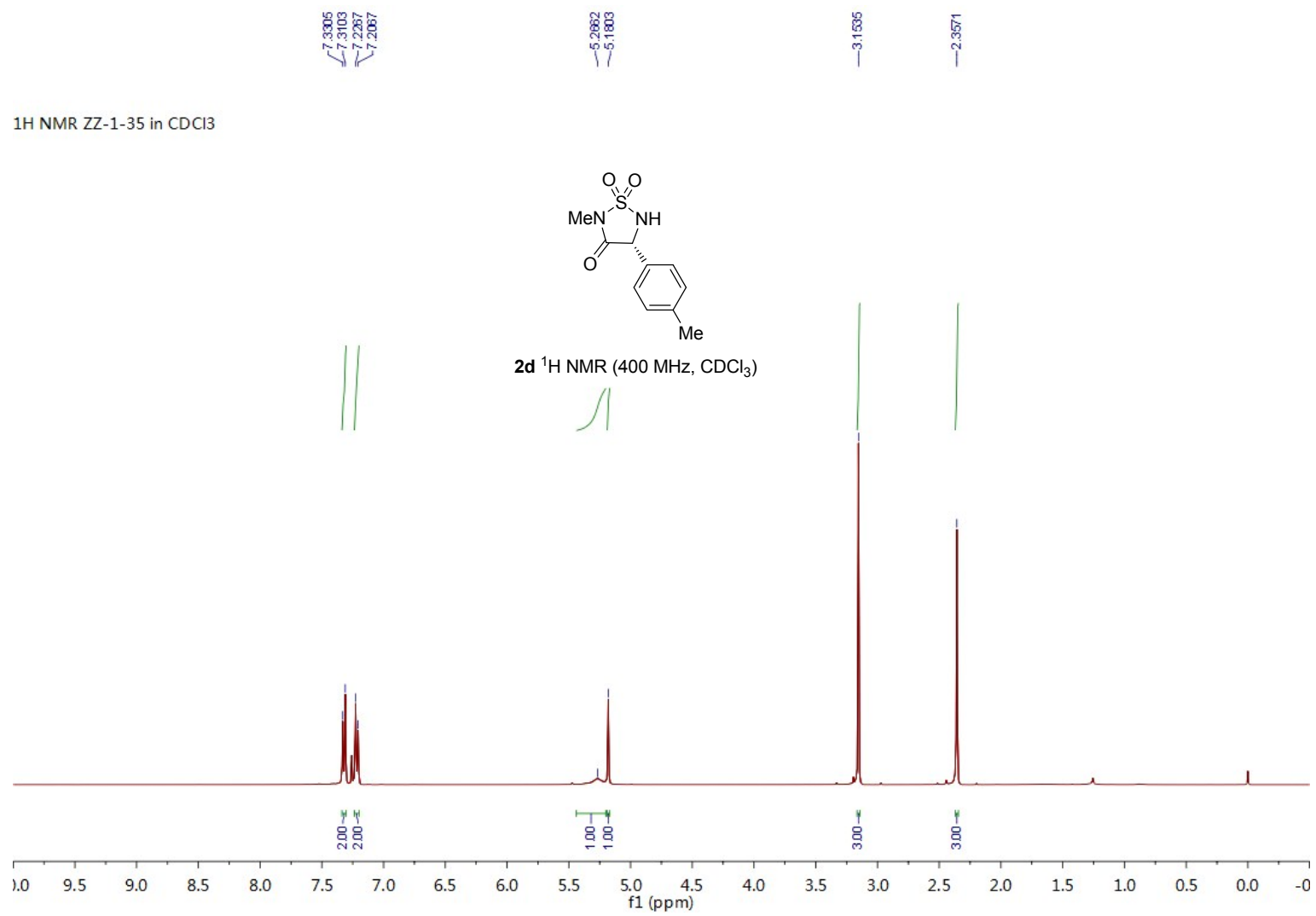


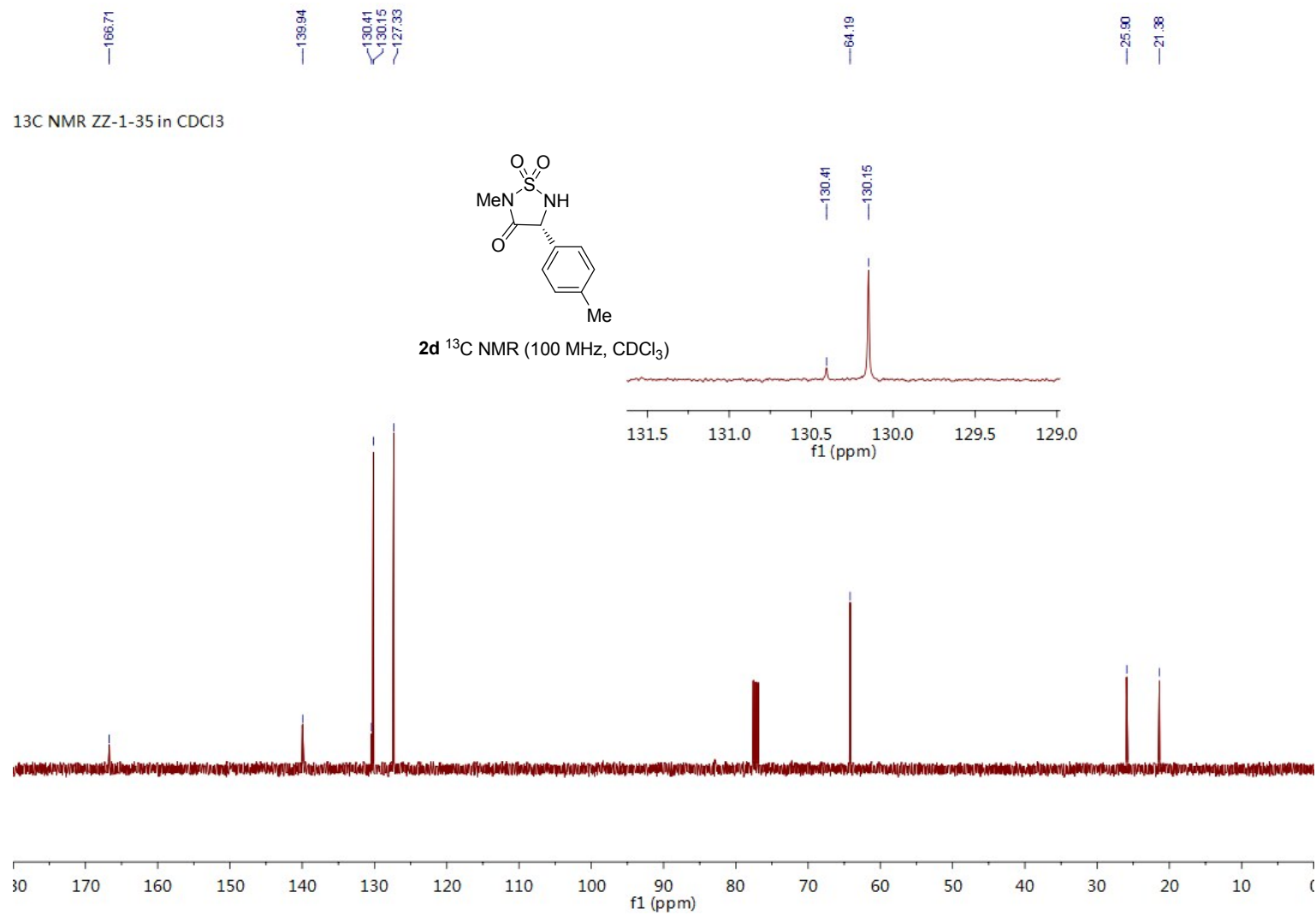
¹H NMR ZZ-1-34 in CDCl₃



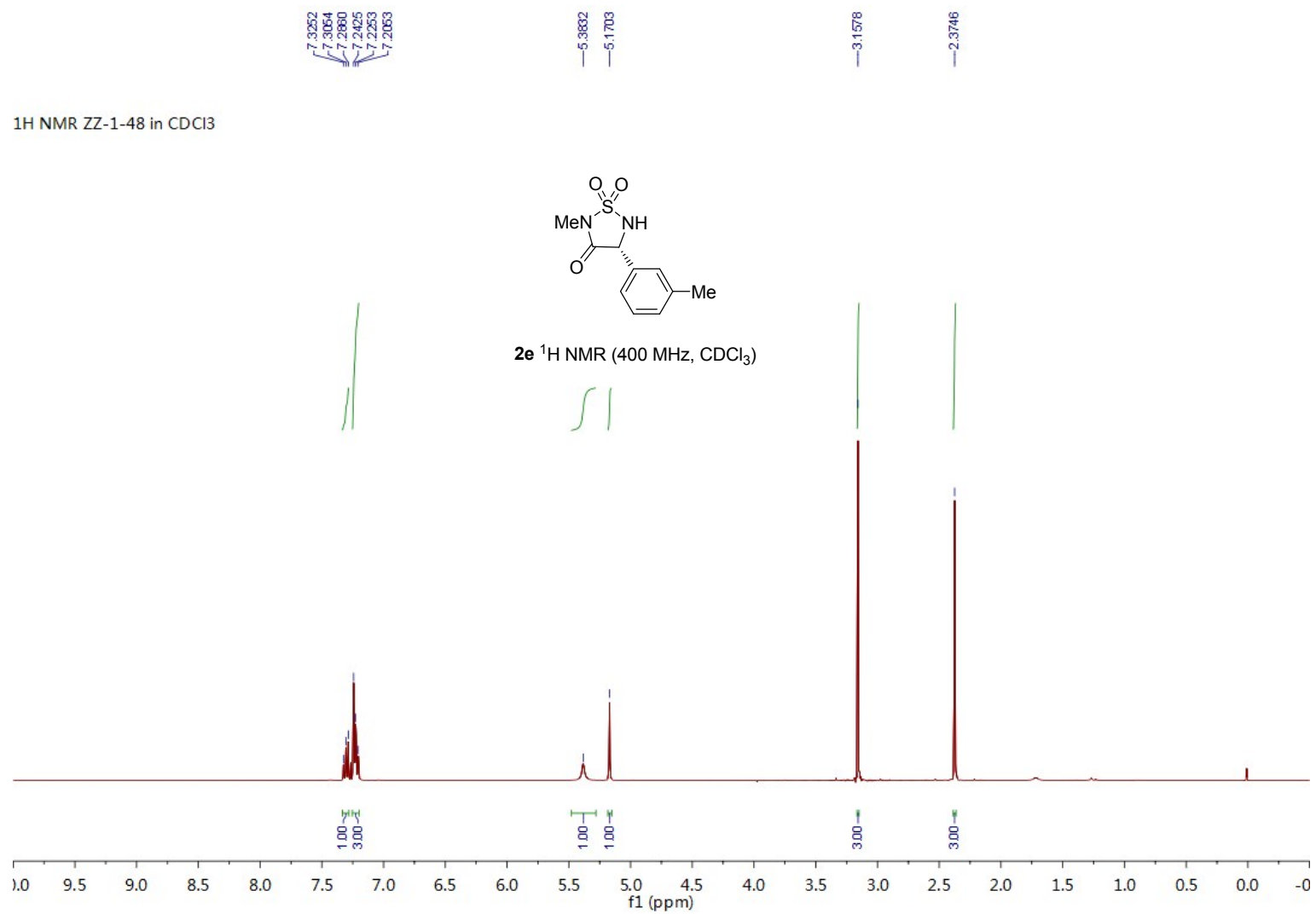


¹H NMR ZZ-1-35 in CDCl₃





¹H NMR ZZ-1-48 in CDCl₃



166.60

139.45

133.32

130.62

129.37

128.01

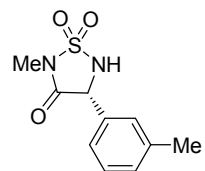
124.51

64.35

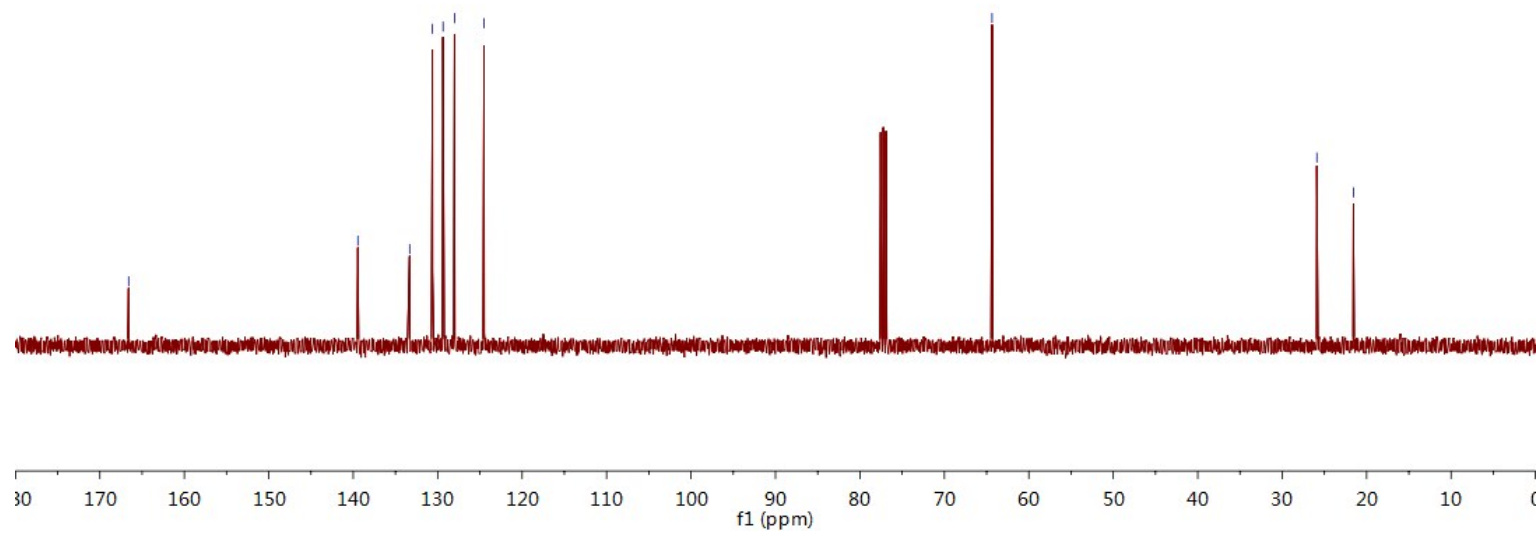
25.90

21.57

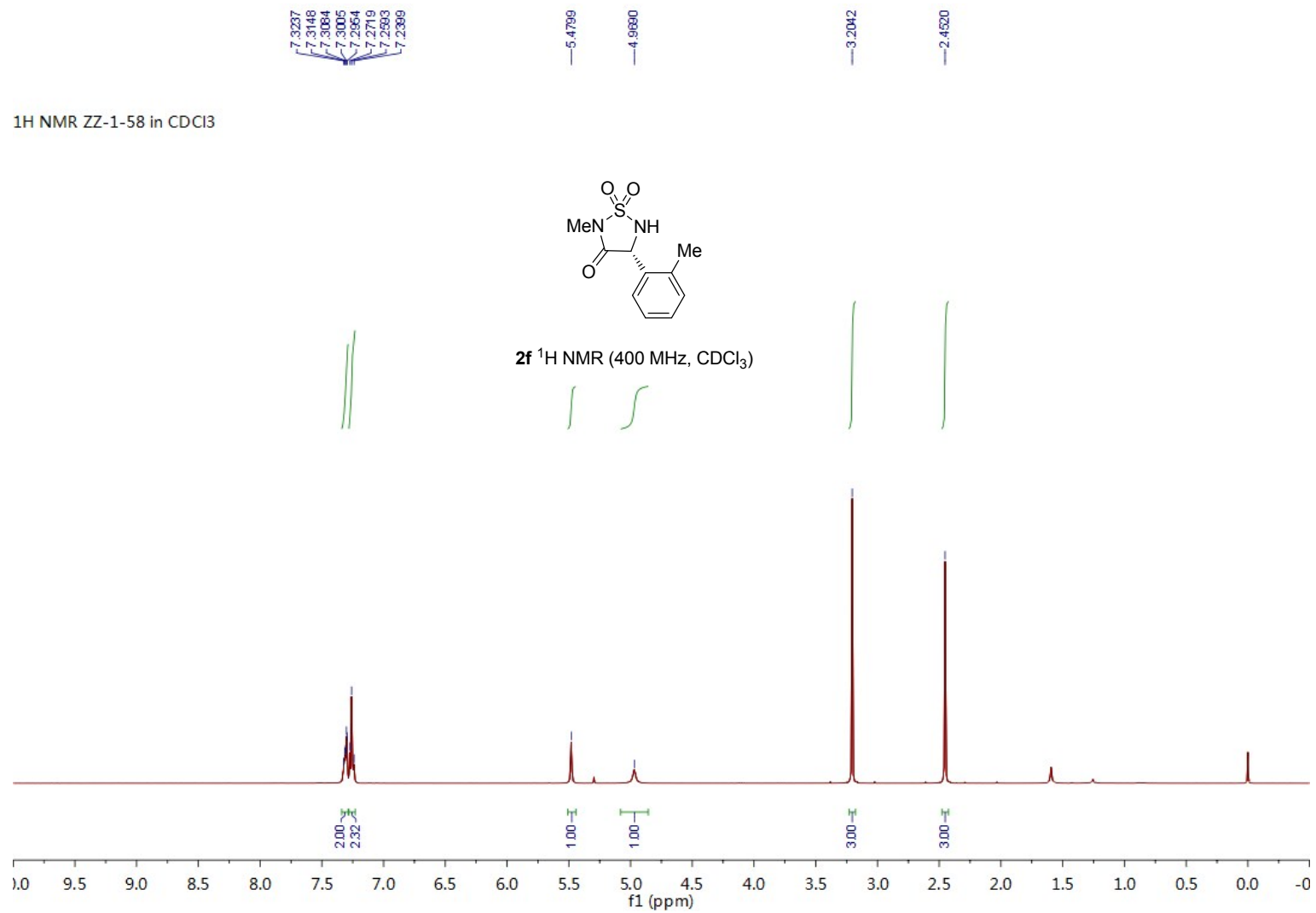
¹³C NMR ZZ-1-48 in CDCl₃



2e ¹³C NMR (100 MHz, CDCl₃)



¹H NMR ZZ-1-58 in CDCl₃



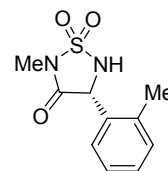
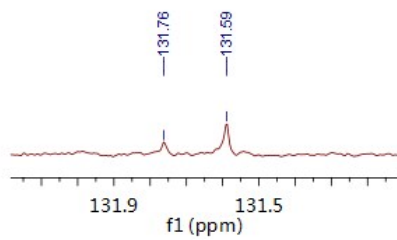
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131.59
130.09
127.88
127.33

61.93

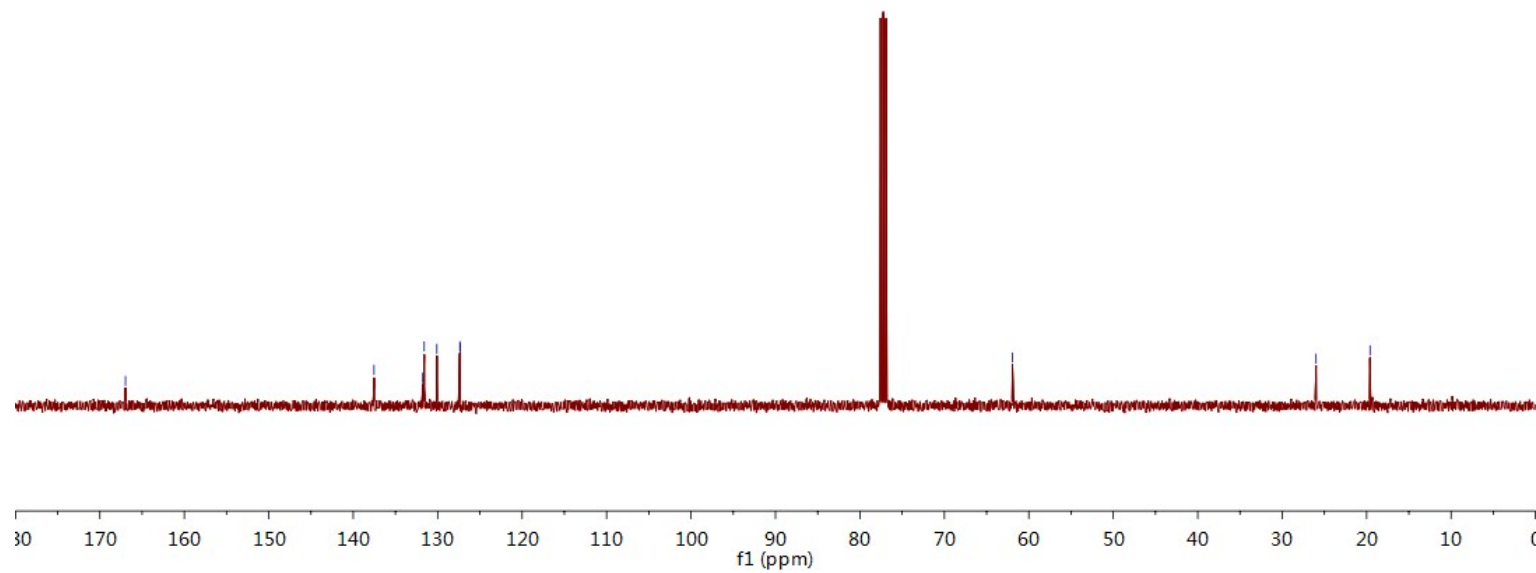
25.99

19.80

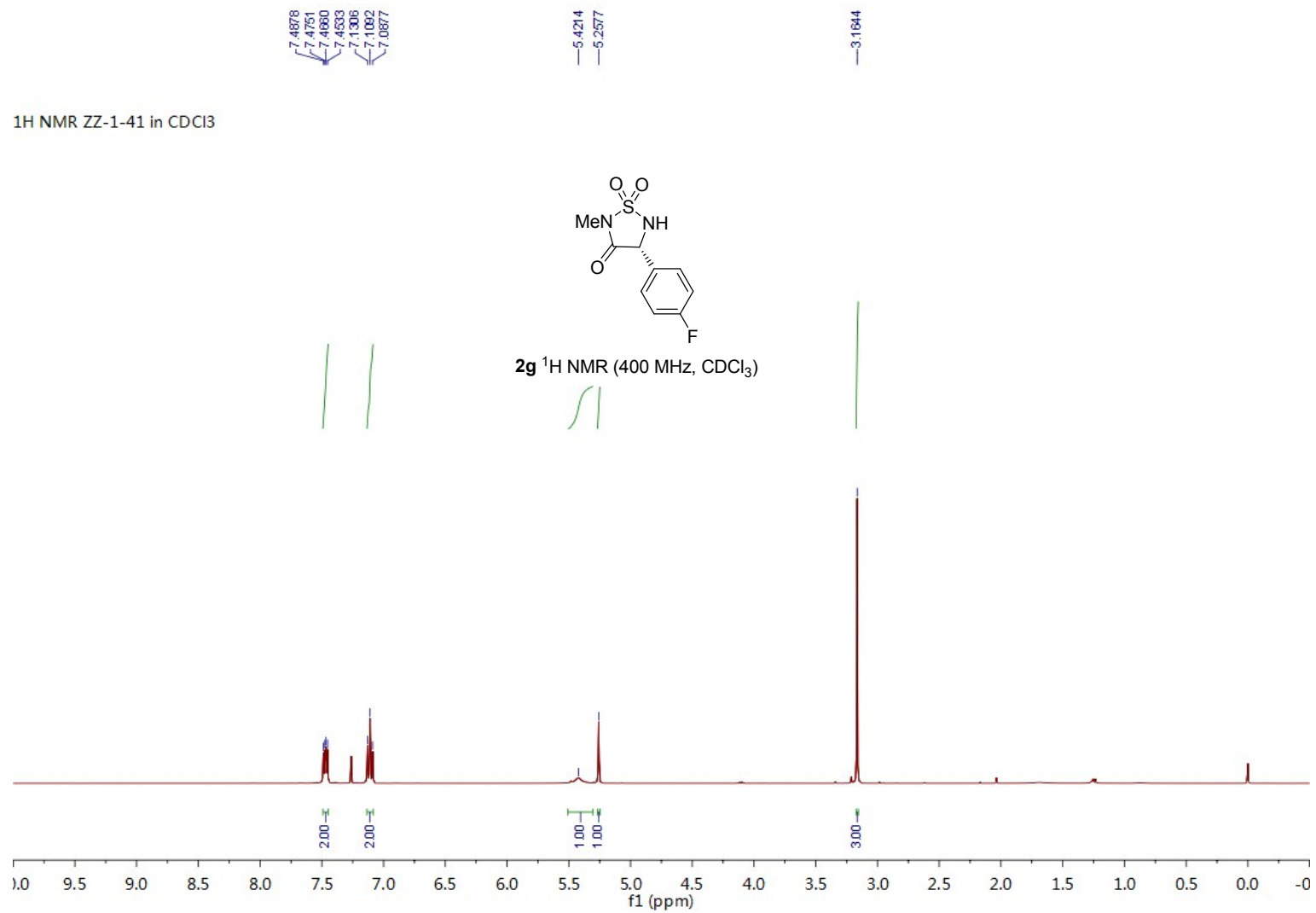
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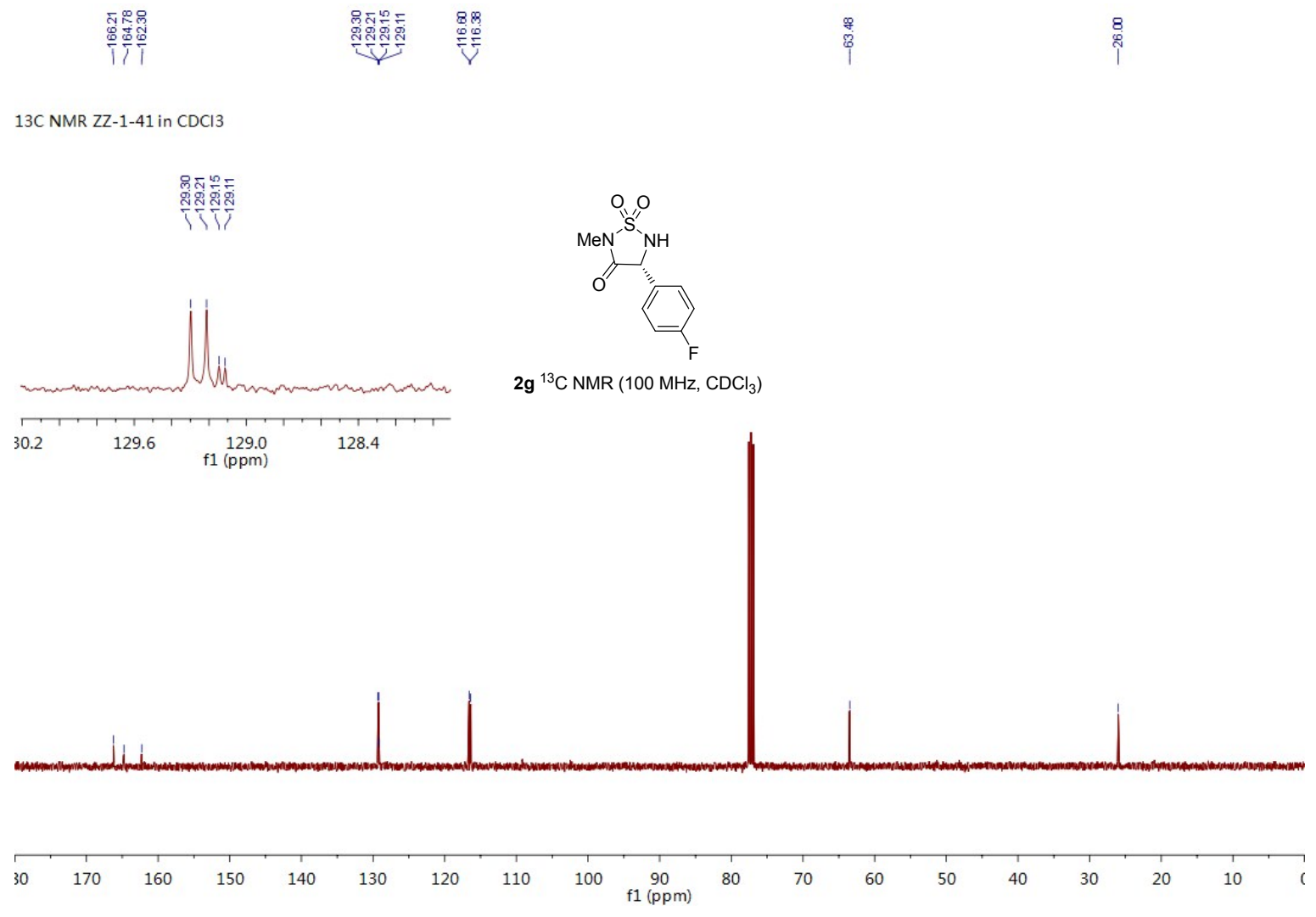


2f ^{13}C NMR (100 MHz, CDCl_3)

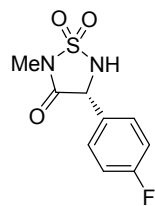


¹H NMR ZZ-1-41 in CDCl₃

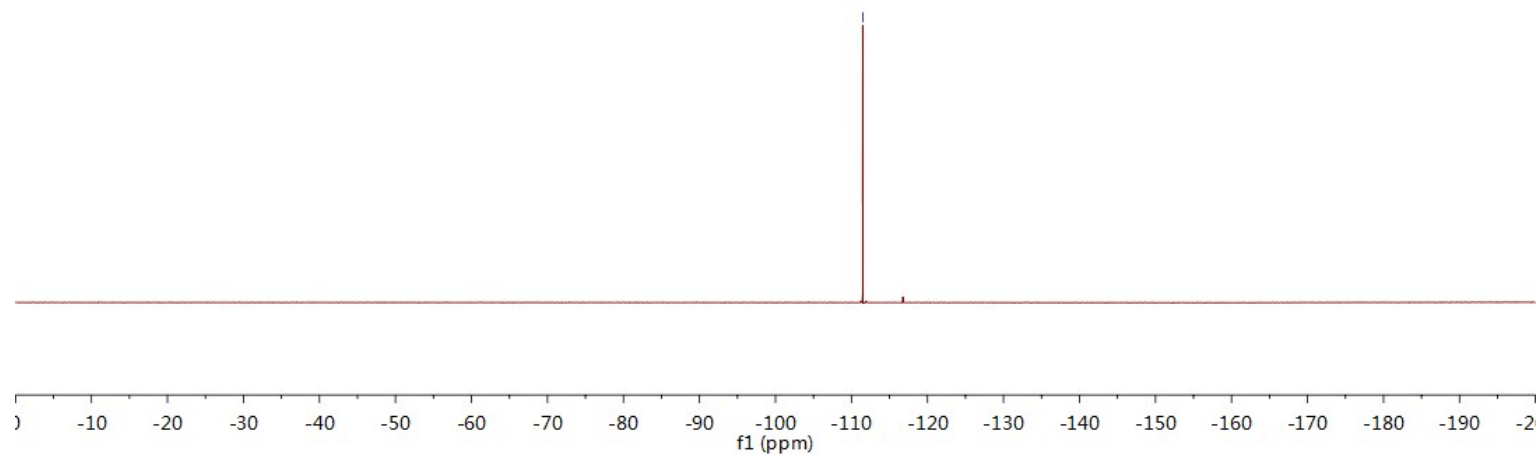




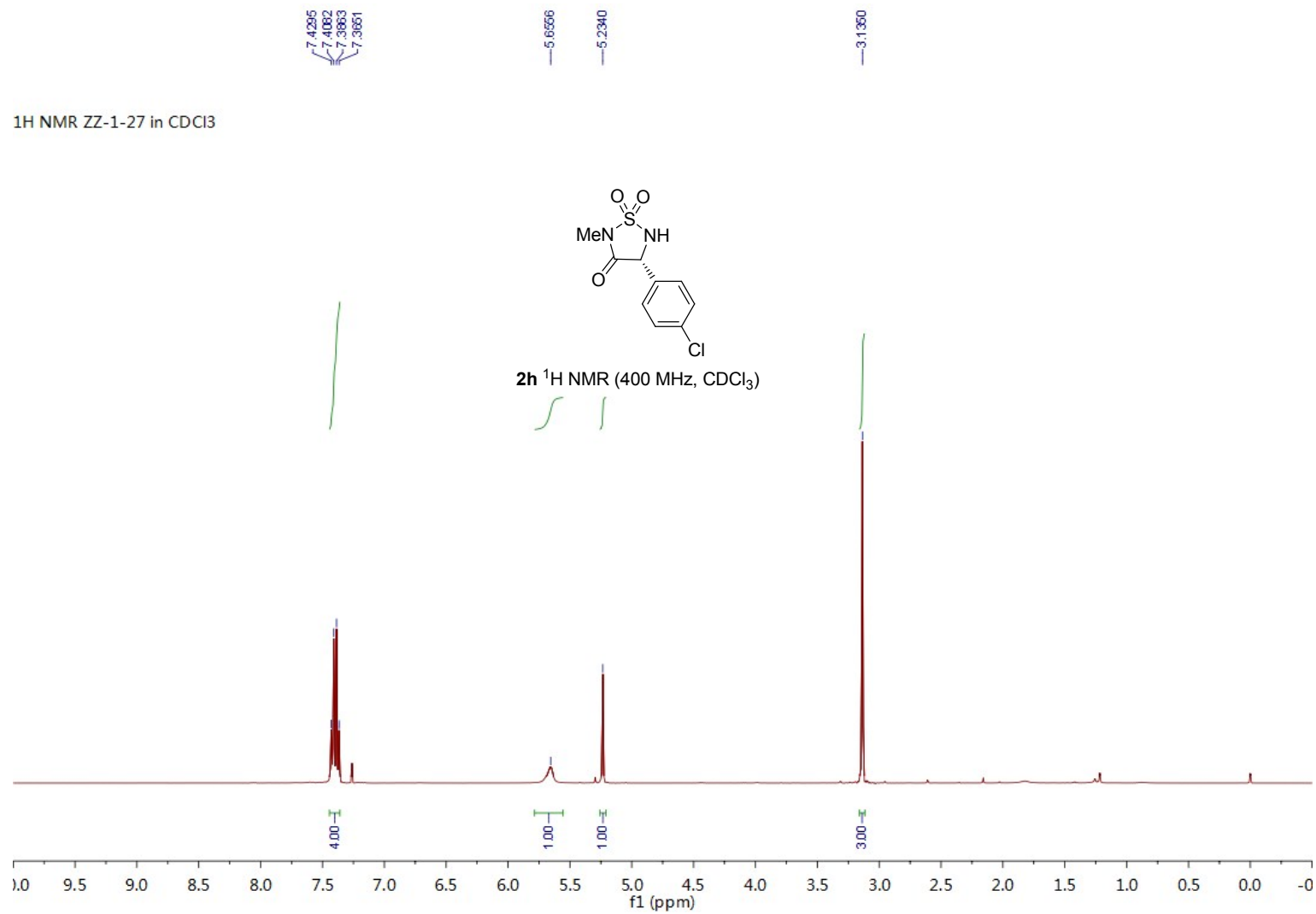
¹⁹F NMR ZZ-1-41 in CDCl₃

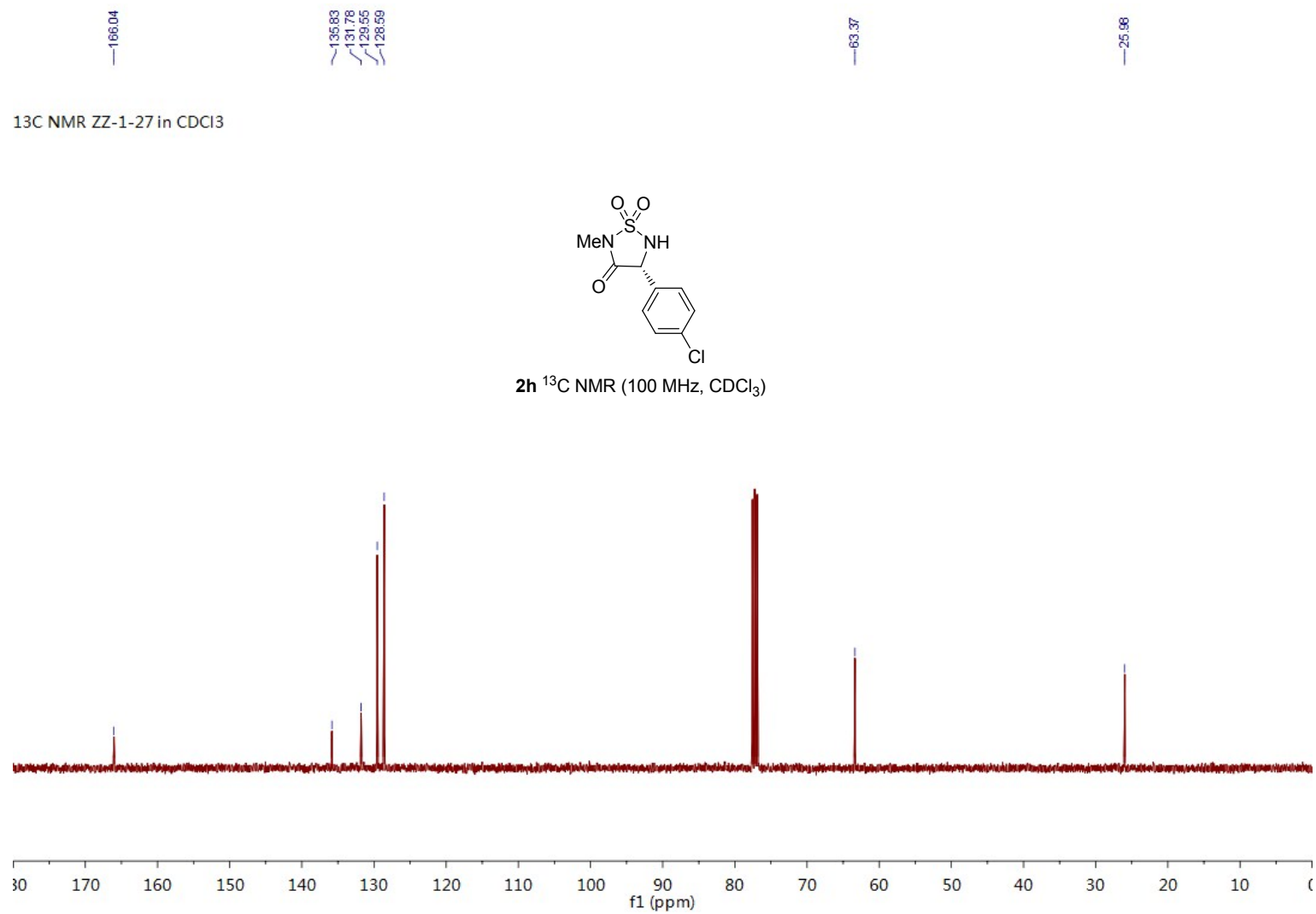


2g ¹⁹F NMR (376 MHz, CDCl₃)

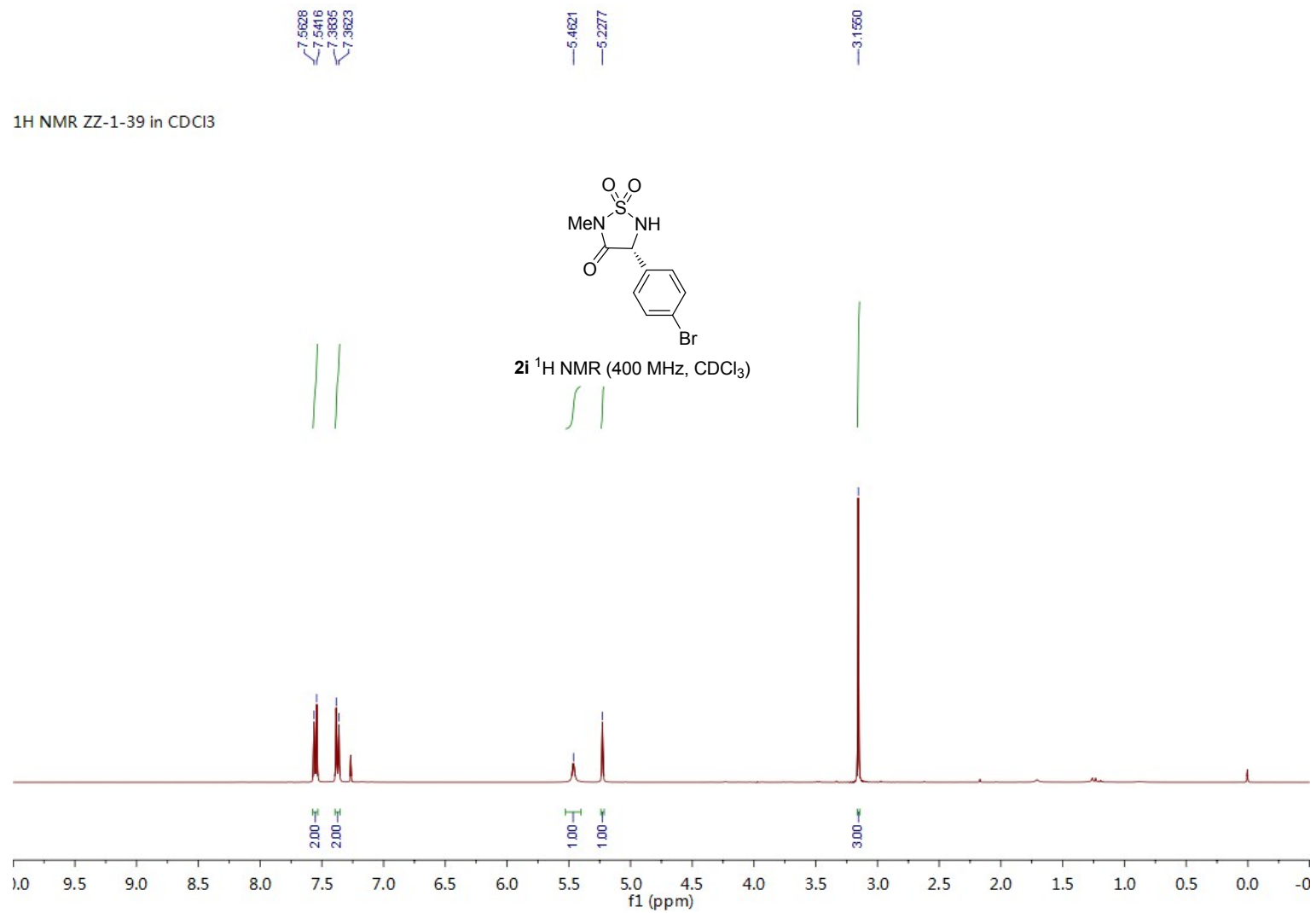


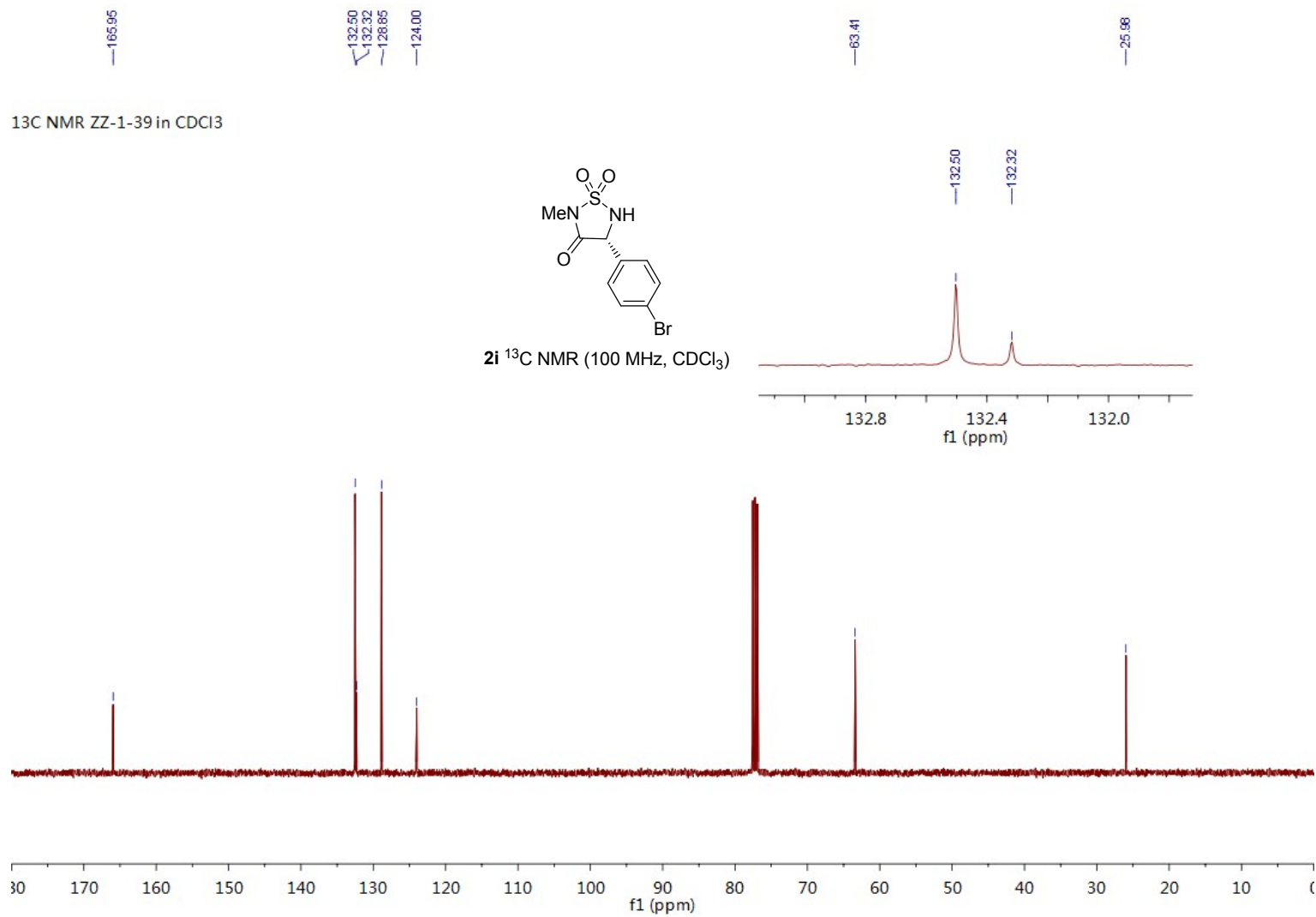
¹H NMR ZZ-1-27 in CDCl₃



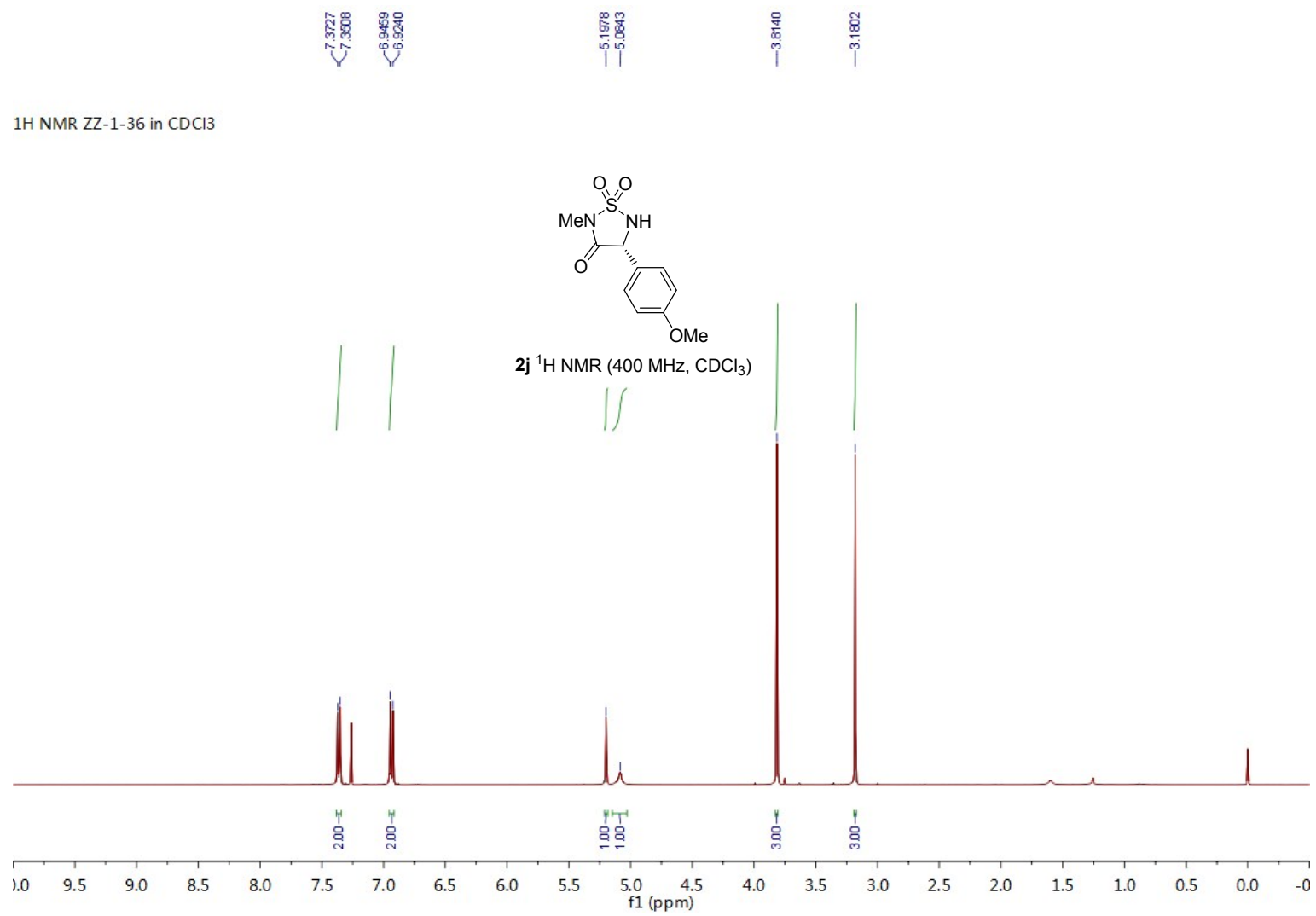


¹H NMR ZZ-1-39 in CDCl₃





¹H NMR ZZ-1-36 in CDCl₃



166.86
160.75

128.86
125.31

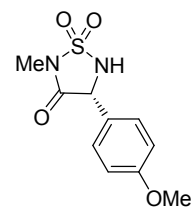
114.80

64.00

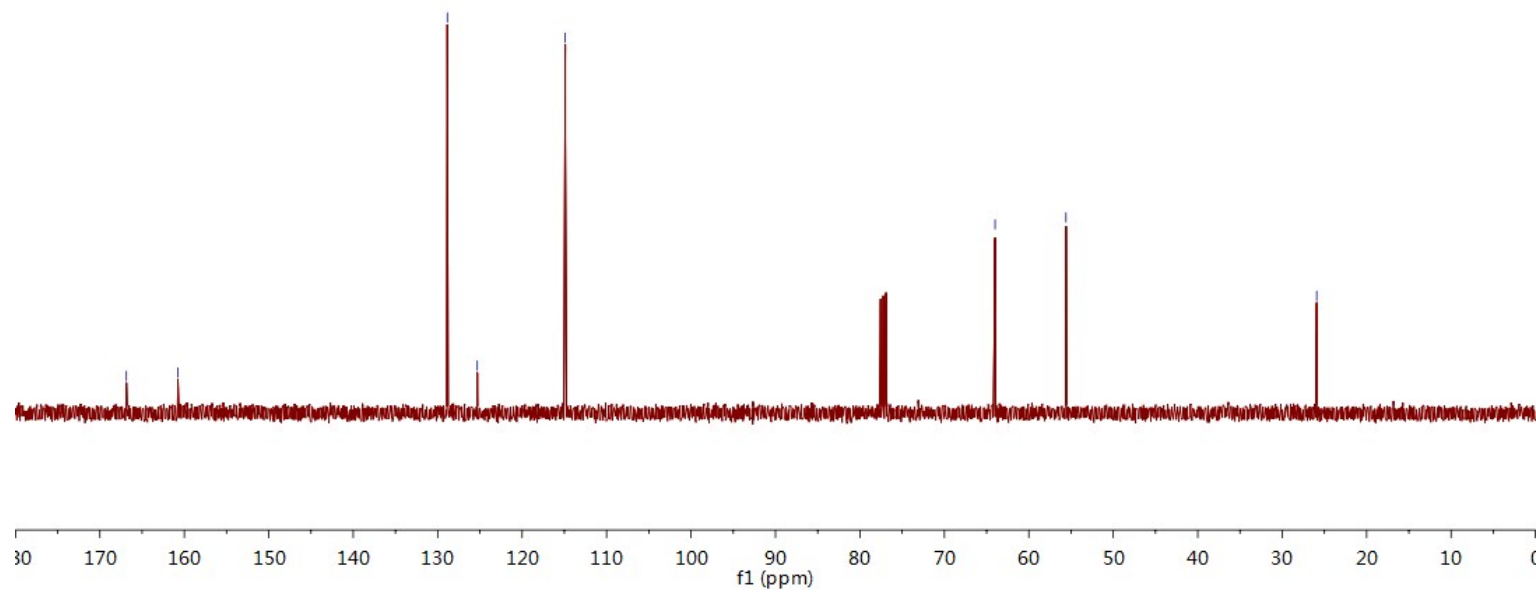
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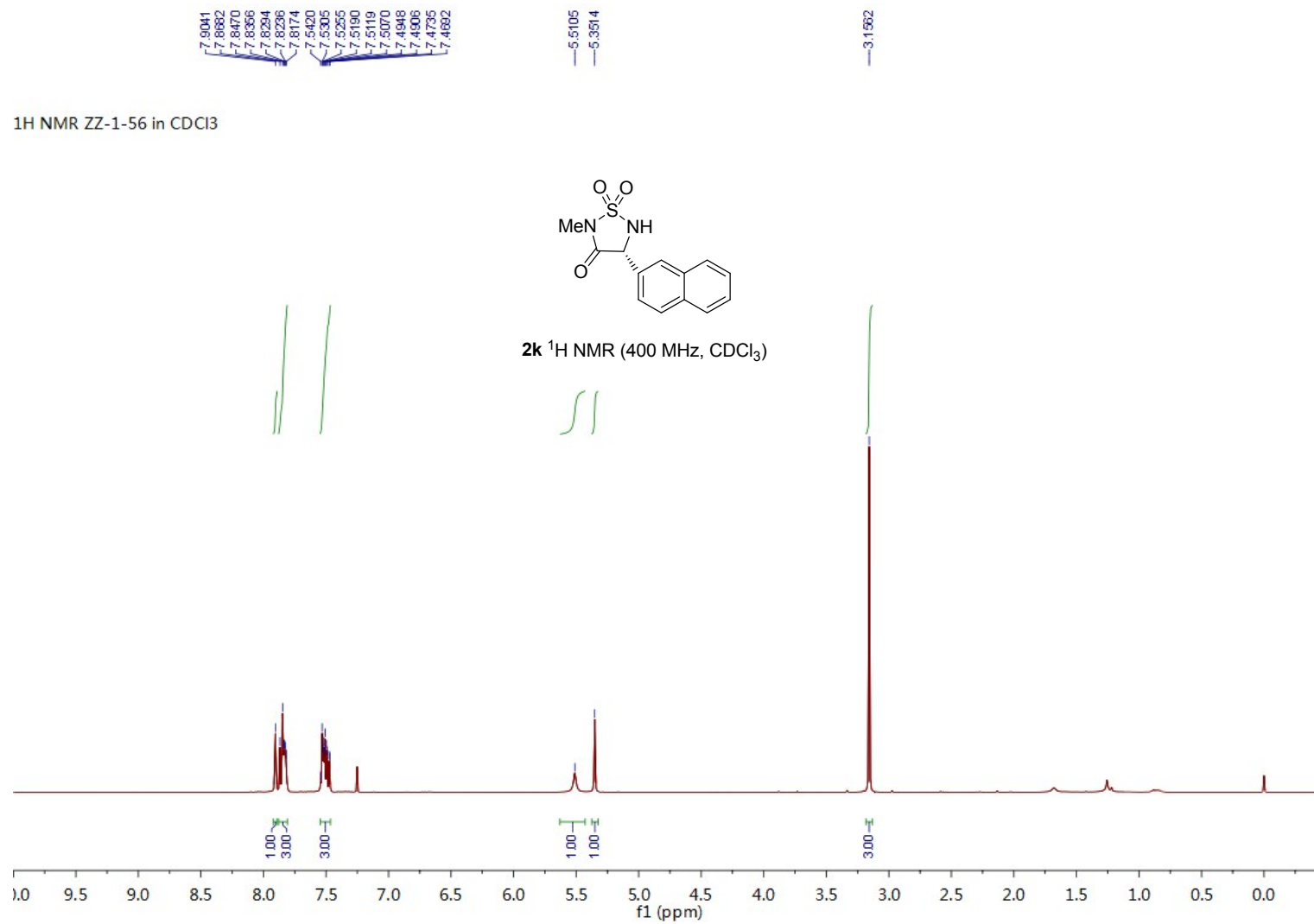
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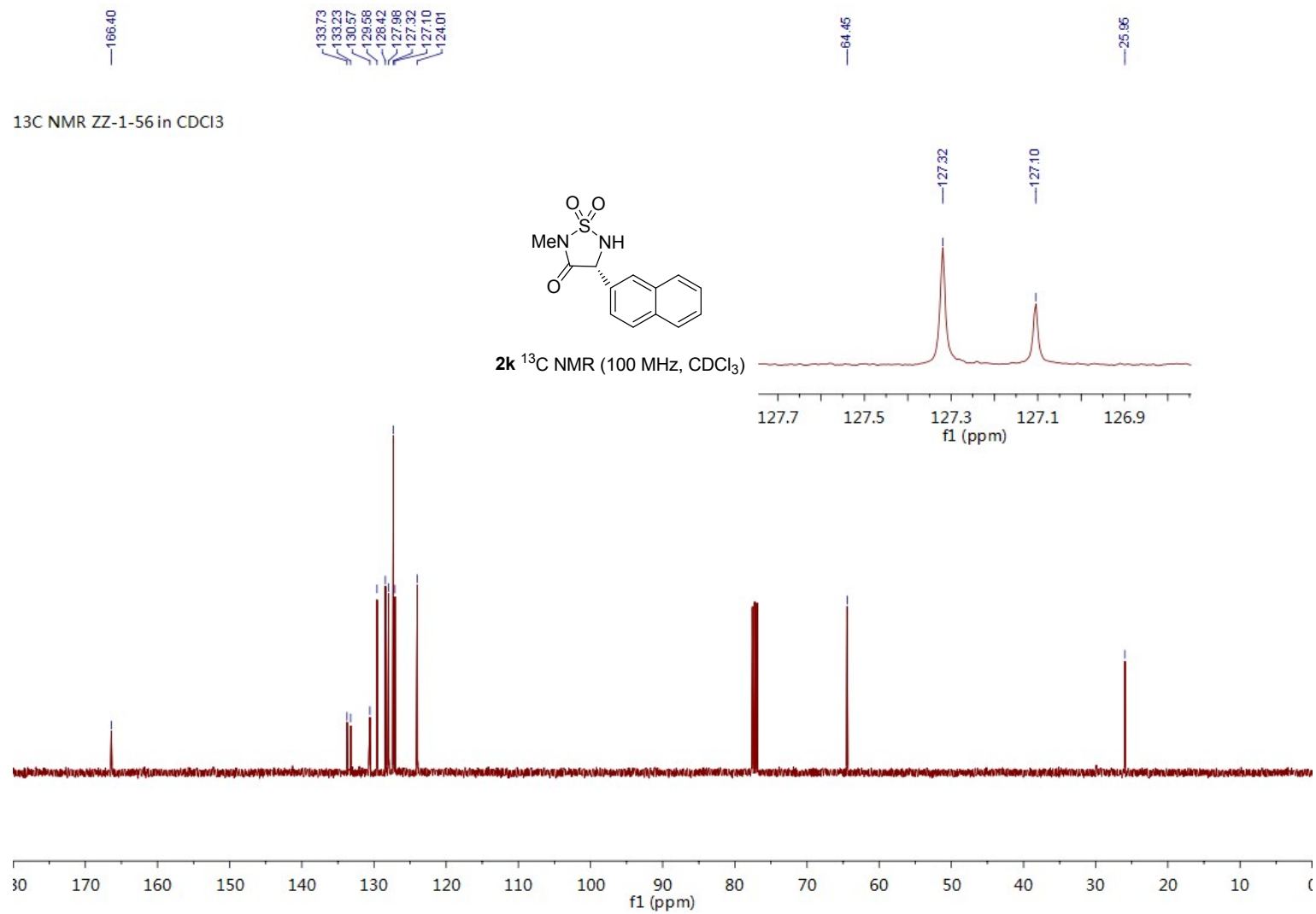
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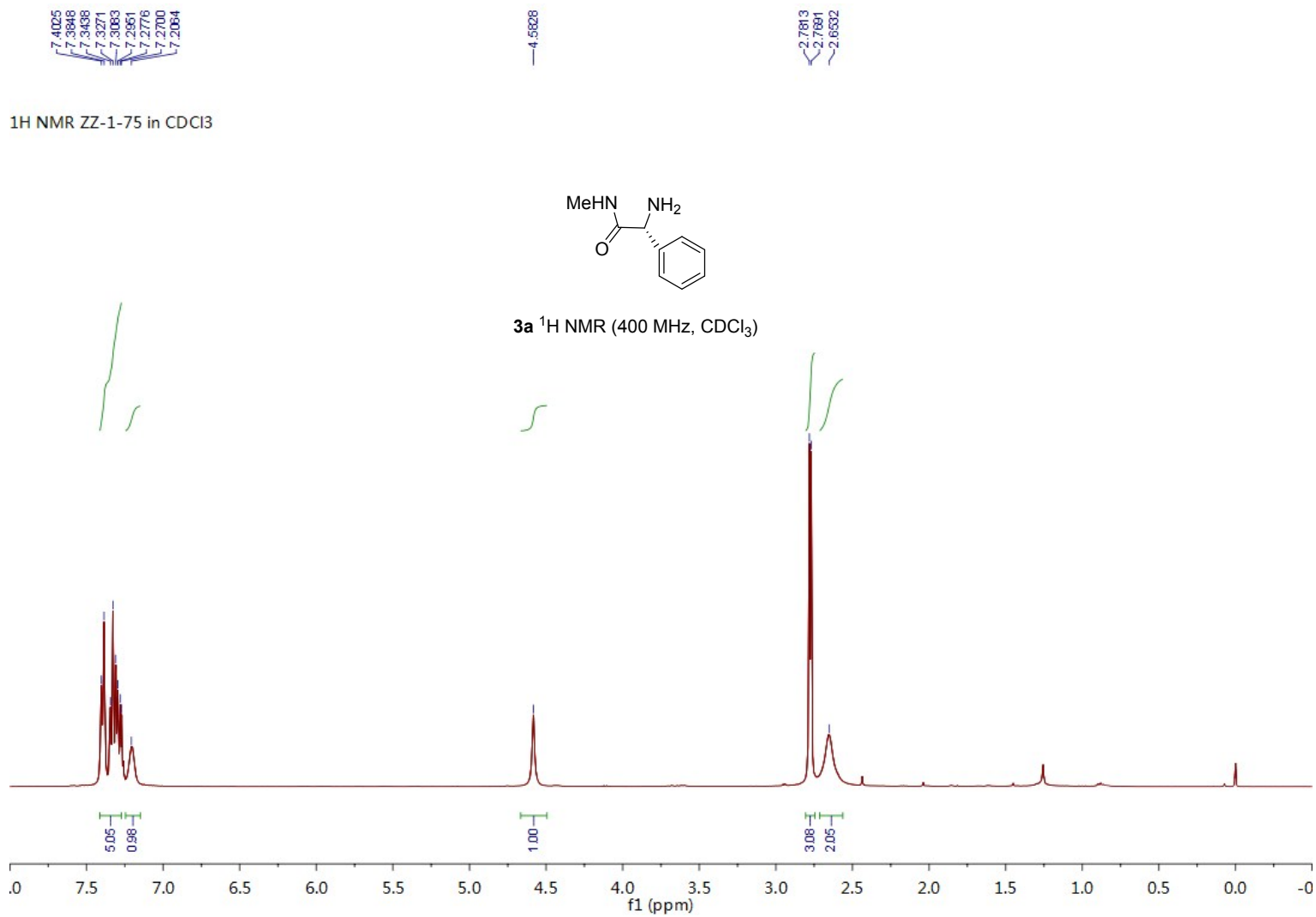


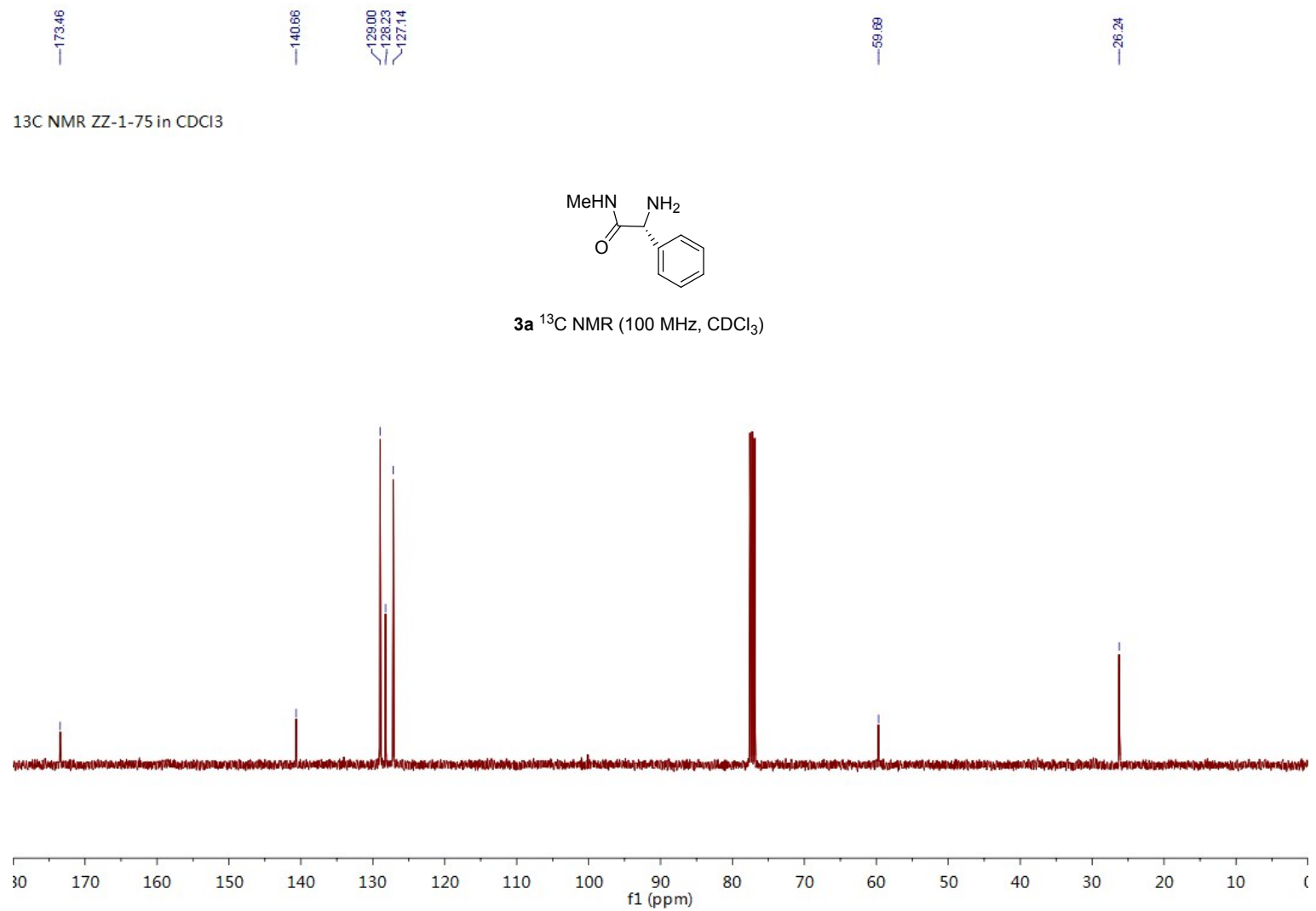
2j ¹³C NMR (100 MHz, CDCl₃)





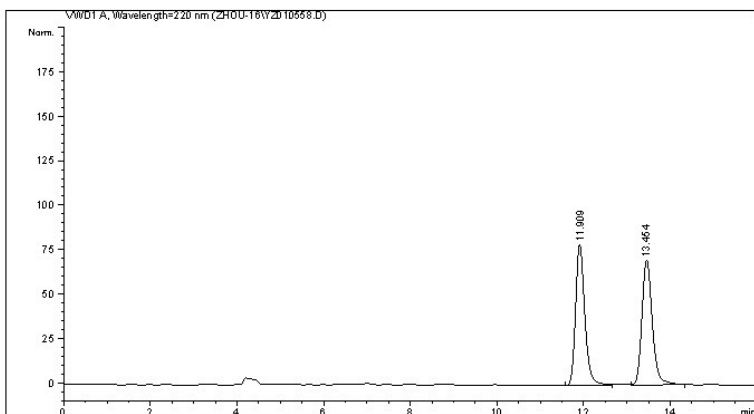






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 Acq. Method : C:\HPCHEM\1\METHODS\DEF.LC.M
 Last changed : 5/11/2016 4:44:11 AM by
 (modified after loading)
 Analysis Method : C:\CHEM32\1\METHODS\DEF.LC.M
 Last changed : 5/10/2016 8:44:27 PM
 (modified after loading)
 Sample Info : AD-H, H/i-PrOH = 85/15, 0.7 mL/min, 30 oC, 220 nm



=====
 Area Percent Report
 =====
 Sorted By : Signal
 Multiplier: : 1.0000
 Dilution: : 1.0000
 Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

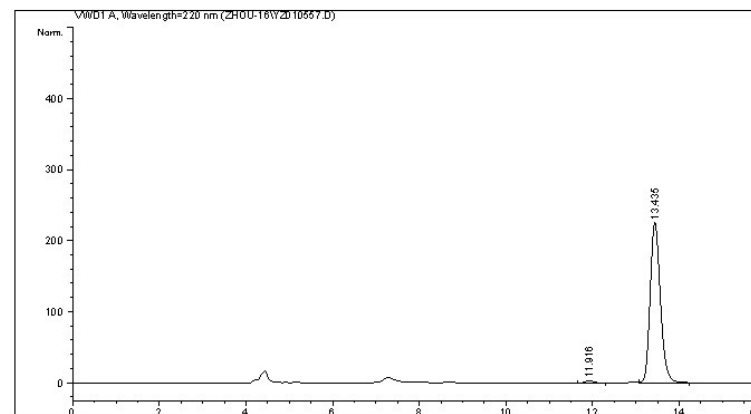
Peak #	RetTime [min]	Type	Width [min]	Area [mAU]	Height [%]	Area %
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2	13.454	VB	0.2541	1171.80359	70.30521	49.9536

Totals : 2345.78418 149.54134

*** End of Report ***

Data File C:\CHEM32\1\DATA\ZHOU-16\YZ010557.D
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 Sample Info : AD-H, H/i-PrOH = 85/15, 0.7 mL/min, 30 oC, 220 nm



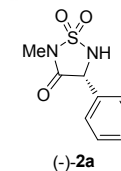
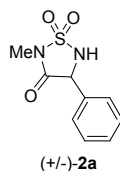
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 =====
 Sorted By : Signal
 Multiplier: : 1.0000
 Dilution: : 1.0000
 Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU]	Height [%]	Area %
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Totals : 3735.18252 228.40317

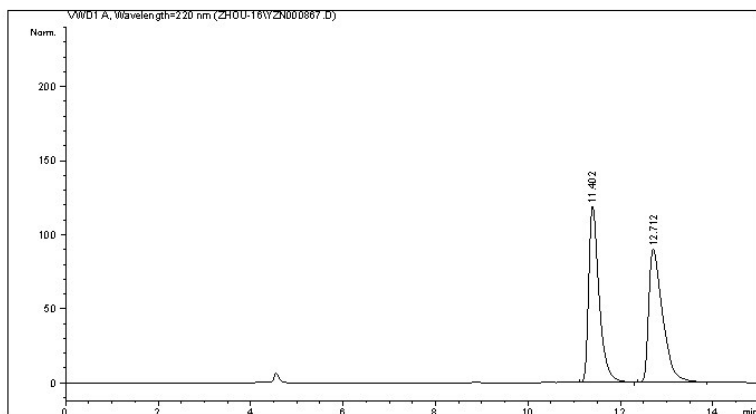
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Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
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 Area Percent Report
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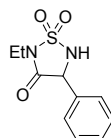
Sorted By      :      Simal
Multiplier:    :      1.0000
Dilution:      :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
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Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.402	BB	0.2356	1867.08289	118.89330	49.8396
2	12.712	BB	0.3109	1879.10205	89.86385	50.1604

Totals : 3746.18494 208.75715

=====
 *** End of Report ***

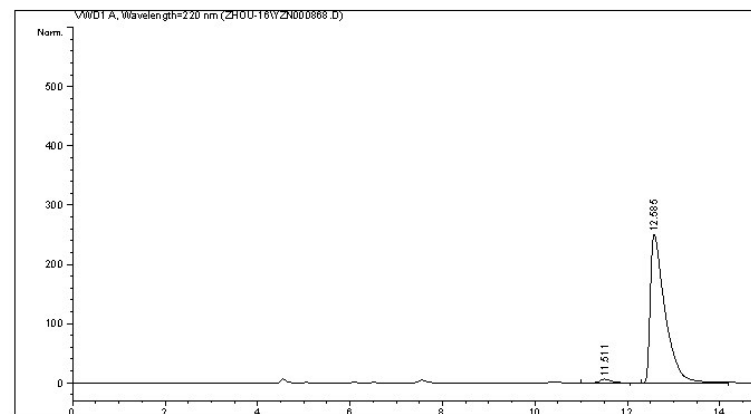


(+/-)-2b

Data File C:\CHEM32\1\DATA\ZHOU-16\YZN000868.D
 Sample Name: ZZ-1-32B

```

=====
Acq. Operator   :
Acq. Instrument : Instrument 1           Location : Vial 1
Injection Date  : 4/2/2016 8:29:15 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 4/2/2016 8:27:22 PM
                 (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 5/9/2016 3:32:47 PM
                 (modified after loading)
Sample Info     : IC, H/i-PrOH = 90/10, 0.7mL/min, 30oC, 220 nm
=====
  
```



=====
 Area Percent Report
 =====

```

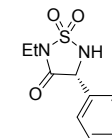
Sorted By      :      Simal
Multiplier:    :      1.0000
Dilution:      :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.511	BB	0.2619	105.95583	6.11288	1.8813
2	12.585	BB	0.3199	5526.11133	250.58168	98.1187

Totals : 5632.06715 256.69456

=====
 *** End of Report ***

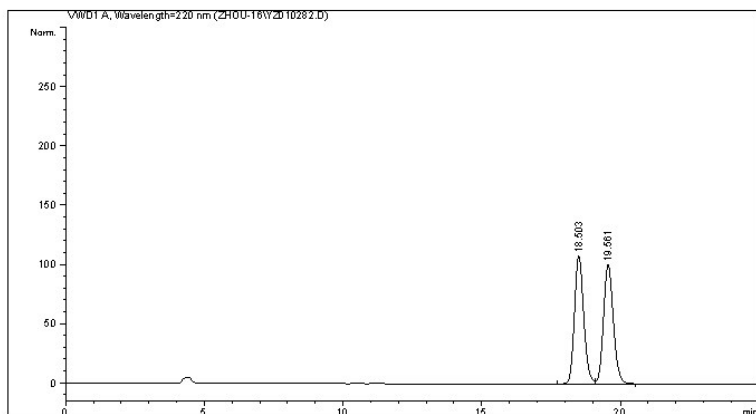


(+)-2b

Data File C:\CHEM32\1\DATA\ZHOU-16\YZ010282.D
 Sample Name: ZZ-1-34A(+)

```

=====
Acq. Operator   : j
Acq. Instrument : Instrument 1          Location : Vial 1
Injection Date  : 4/7/2016 5:27:11 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC.M
Last changed    : 4/7/2016 4:59:17 AM by j
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 5/9/2016 3:35:31 PM
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 85/15, 0.7 mL/min, 30 oC, 220 nm
=====
  
```



```

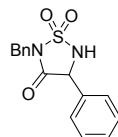
=====
                          Area Percent Report
=====
Sorted By      :      Simal
Multiplier:    :      1.0000
Dilution:      :      1.0000
Sample Amount: :      1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU]	Height [%]	Area %
1	18.503	BV	0.3616	2527.86548	108.13077	50.2307
2	19.561	VB	0.3822	2504.64673	100.58949	49.7693

Totals : 5032.51221 208.72026

*** End of Report ***

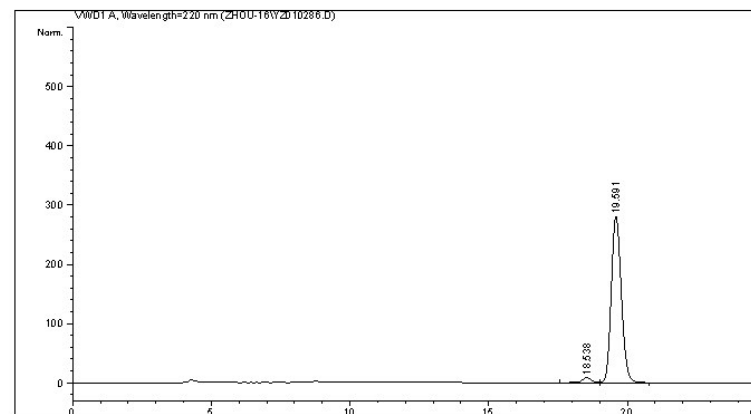


(+/-)-2c

Data File C:\CHEM32\1\DATA\ZHOU-16\YZ010286.D
 Sample Name: ZZ-1-34B

```

=====
Acq. Operator   : j
Acq. Instrument : Instrument 1          Location : Vial 1
Injection Date  : 4/7/2016 8:09:29 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC.M
Last changed    : 4/7/2016 7:43:26 AM by j
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 5/9/2016 3:36:55 PM
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 85/15, 0.7 mL/min, 30 oC, 220 nm
=====
  
```



```

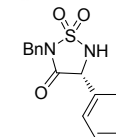
=====
                          Area Percent Report
=====
Sorted By      :      Simal
Multiplier:    :      1.0000
Dilution:      :      1.0000
Sample Amount: :      1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU]	Height [%]	Area %
1	18.538	VV	0.3747	209.61920	8.46764	2.8646
2	19.591	VB	0.3943	7107.86621	280.80362	97.1354

Totals : 7317.48541 289.27126

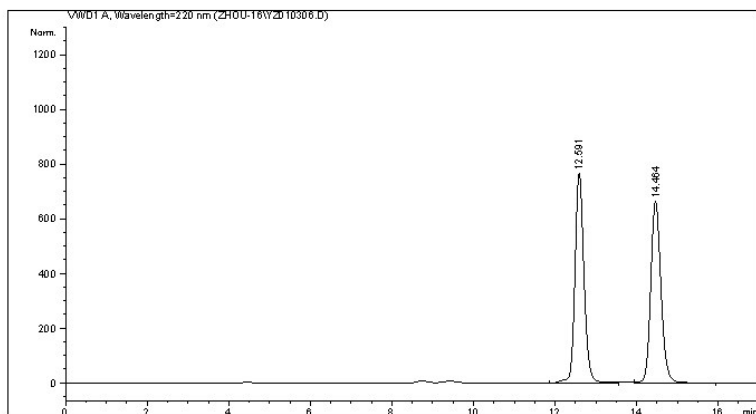
*** End of Report ***



(+)-2c

Data File C:\CHEM32\1\DATA\ZHOU-16\YZ010306.D
 Sample Name: ZZ-1-35A(+)

=====
 Acq. Operator : j
 Acq. Instrument : Instrument 1 Location : Vial 1
 Injection Date : 4/9/2016 5:29:51 AM
 Acq. Method : C:\HPCHEM\1\METHODS\DEF LC.M
 Last changed : 4/9/2016 5:10:22 AM by j
 (modified after loading)
 Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
 Last changed : 5/9/2016 3:39:59 PM
 (modified after loading)
 Sample Info : AD-H, H/i-PrOH = 85/15, 0.7 mL/min, 30 oC, 220 nm



=====
 Area Percent Report
 =====
 Sorted By : Signal
 Multiplier: : 1.0000
 Dilution: : 1.0000
 Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

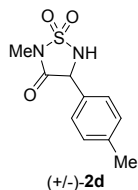
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height %	Area %
1	12.591	BB	0.2346	1.17910e4	767.19946	50.3791
2	14.464	VB	0.2679	1.16136e4	664.82758	49.6209

Totals : 2.34046e4 1432.02704

*** End of Report ***

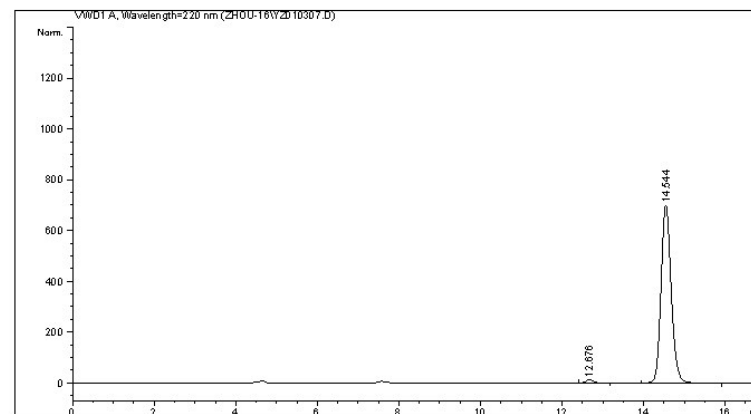
Instrument 1 5/9/2016 3:40:06 PM

Page 1 of 1



Data File C:\CHEM32\1\DATA\ZHOU-16\YZ010307.D
 Sample Name: ZZ-1-35B

=====
 Acq. Operator : j
 Acq. Instrument : Instrument 1 Location : Vial 1
 Injection Date : 4/9/2016 5:59:39 AM
 Acq. Method : C:\HPCHEM\1\METHODS\DEF LC.M
 Last changed : 4/9/2016 5:10:22 AM by j
 (modified after loading)
 Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
 Last changed : 5/9/2016 3:41:00 PM
 (modified after loading)
 Sample Info : AD-H, H/i-PrOH = 85/15, 0.7 mL/min, 30 oC, 220 nm



=====
 Area Percent Report
 =====
 Sorted By : Signal
 Multiplier: : 1.0000
 Dilution: : 1.0000
 Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

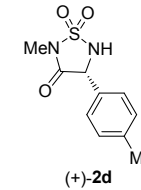
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height %	Area %
1	12.676	VB	0.2339	203.76875	13.31237	1.6438
2	14.544	BB	0.2668	1.21924e4	701.49585	98.3562

Totals : 1.23961e4 714.80822

*** End of Report ***

Instrument 1 5/9/2016 3:41:10 PM

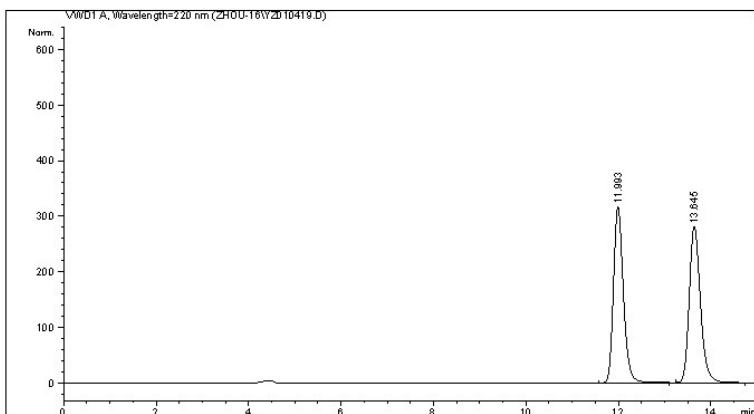
Page 1 of 1



Data File C:\CHEM32\1\DATA\ZHOU-16\YZ010419.D
 Sample Name: ZZ-1-48A(+)

```

=====
Acq. Operator   :
Acq. Instrument : Instrument 1           Location : Vial 1
Injection Date  : 4/21/2016 6:40:08 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC.M
Last changed    : 4/21/2016 6:32:59 AM by
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 5/9/2016 3:57:04 PM
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 85/15, 0.7 mL/min, 30 oC, 220 nm
=====
  
```

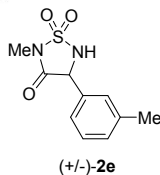


```

=====
                          Area Percent Report
=====
Sorted By      :          Signal
Multiplier:    :          1.0000
Dilution:      :          1.0000
Sample Amount: :          1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs
  
```

```

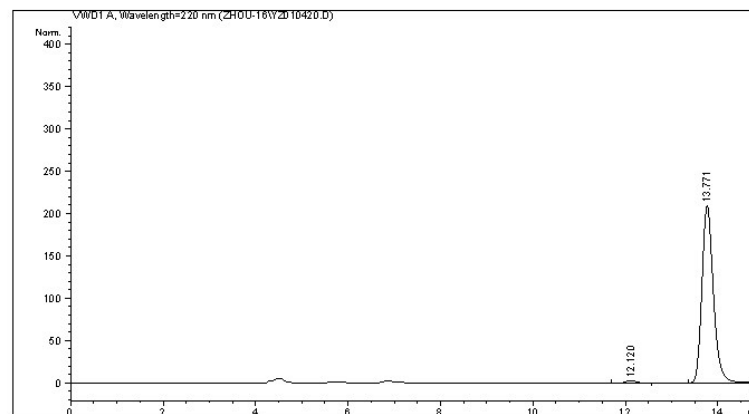
Signal 1: VWD1 A, Wavelength=220 nm
Peak # RetTime Type Width Area Height Area
     [min] [min] [min] mAU %s [mAU] %
-----|-----|-----|-----|-----|-----|
1 11.993 BB 0.2294 4732.86768 317.16467 50.0463
2 13.645 BB 0.2572 4724.11279 281.16769 49.9537
Totals :                9456.98047 598.33237
  
```



Data File C:\CHEM32\1\DATA\ZHOU-16\YZ010420.D
 Sample Name: ZZ-1-48B

```

=====
Acq. Operator   :
Acq. Instrument : Instrument 1           Location : Vial 1
Injection Date  : 4/21/2016 7:01:05 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC.M
Last changed    : 4/21/2016 6:32:59 AM by
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 5/9/2016 3:58:08 PM
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 85/15, 0.7 mL/min, 30 oC, 220 nm
=====
  
```

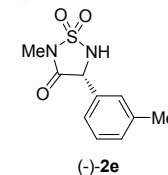


```

=====
                          Area Percent Report
=====
Sorted By      :          Signal
Multiplier:    :          1.0000
Dilution:      :          1.0000
Sample Amount: :          1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs
  
```

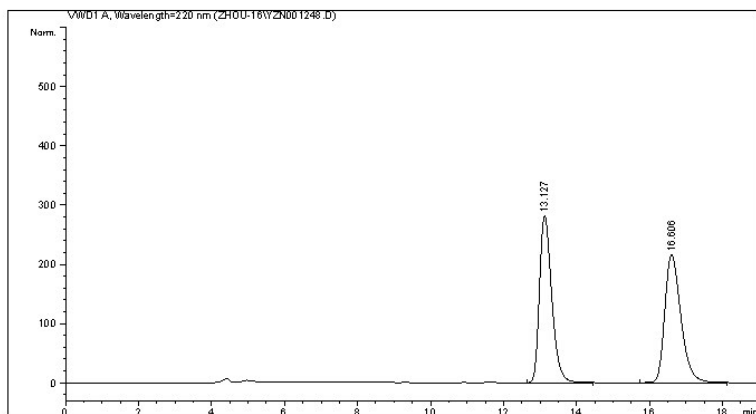
```

Signal 1: VWD1 A, Wavelength=220 nm
Peak # RetTime Type Width Area Height Area
     [min] [min] [min] mAU %s [mAU] %
-----|-----|-----|-----|-----|-----|
1 12.120 BB 0.2283 44.19563 2.95682 1.2137
2 13.771 BB 0.2629 3597.23608 209.49031 98.7863
Totals :                3641.43171 212.44713
  
```



Data File C:\CHEM32\1\DATA\ZHOU-16\YZN001248.D
 Sample Name: ZZ-1-58A(+)

=====
 Acq. Operator :
 Acq. Instrument : Instrument 1 Location : Vial 1
 Injection Date : 5/3/2016 2:57:22 PM
 Acq. Method : C:\CHEM32\1\METHODS\DEF_LC.M
 Last changed : 5/3/2016 2:48:20 PM
 (modified after loading)
 Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
 Last changed : 5/9/2016 3:59:26 PM
 (modified after loading)
 Sample Info : AS-H, Hex/i-PrOH = 70/30, 0.7 mL/min, 30oC, 220 nm



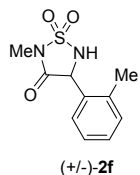
=====
 Area Percent Report
 =====
 Sorted By : Signal
 Multiplier: : 1.0000
 Dilution: : 1.0000
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU *s]	Height [mAU]	Area %
1	13.127	BB	0.3599	6583.14404	281.85156	49.8542
2	16.606	BB	0.4712	6621.63623	215.98576	50.1458

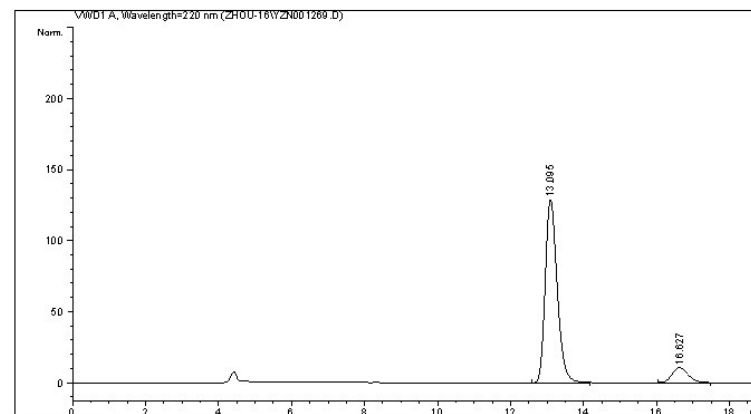
Totals : 1.32048e4 497.83733

=====
 *** End of Report ***



Data File C:\CHEM32\1\DATA\ZHOU-16\YZN001269.D
 Sample Name: ZZ-1-59

=====
 Acq. Operator :
 Acq. Instrument : Instrument 1 Location : Vial 1
 Injection Date : 5/5/2016 3:44:16 PM
 Acq. Method : C:\CHEM32\1\METHODS\DEF_LC.M
 Last changed : 5/5/2016 3:00:42 PM
 (modified after loading)
 Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
 Last changed : 5/9/2016 4:01:56 PM
 (modified after loading)
 Sample Info : AS-H, Hex/i-PrOH = 70/30, 0.7 mL/min, 30oC, 220 nm



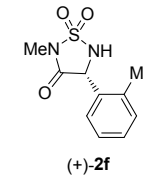
=====
 Area Percent Report
 =====
 Sorted By : Signal
 Multiplier: : 1.0000
 Dilution: : 1.0000
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU *s]	Height [mAU]	Area %
1	13.095	BB	0.3507	2939.56470	128.81834	90.1447
2	16.627	BB	0.4701	321.37704	10.55816	9.8553

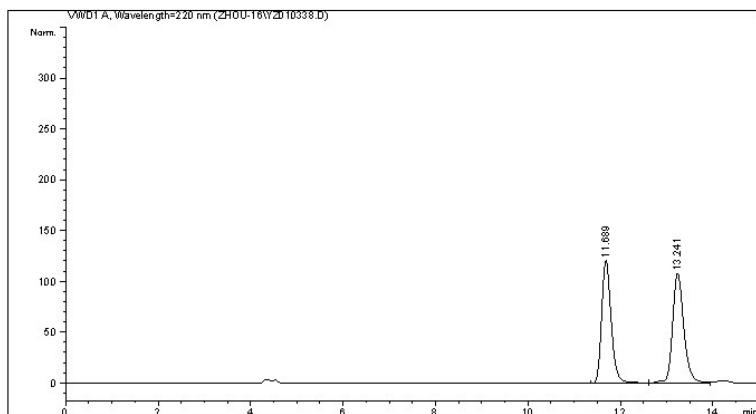
Totals : 3260.94174 139.37651

=====
 *** End of Report ***



Data File C:\CHEM32\1\DATA\ZHOU-16\YZ010338.D
 Sample Name: ZZ-1-41A(+)

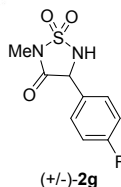
=====
 Acq. Operator :
 Acq. Instrument : Instrument 1 Location : Vial 1
 Injection Date : 4/13/2016 5:56:08 AM
 Acq. Method : C:\HPCHEM\1\METHODS\DEF LC.M
 Last changed : 4/13/2016 5:33:04 AM by
 (modified after loading)
 Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
 Last changed : 5/9/2016 3:54:47 PM
 (modified after loading)
 Sample Info : AD-H, H/i-PrOH = 85/15, 0.7 mL/min, 30 oC, 220 nm



=====
 Area Percent Report
 =====
 Sorted By : Sigmal
 Multiplier: : 1.0000
 Dilution: : 1.0000
 Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
 Use Multiplier & Dilution Factor with ISTDs

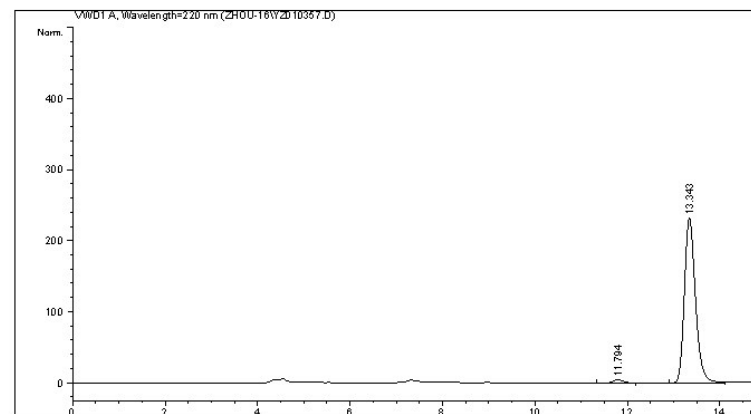
Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	11.689	BV	0.2215	1753.58655	120.96341	48.5493	
2	13.241	VB	0.2595	1858.38196	108.51495	51.4507	
Totals :				3611.96851		229.47836	



Data File C:\CHEM32\1\DATA\ZHOU-16\YZ010357.D
 Sample Name: ZZ-1-45

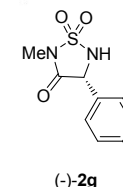
=====
 Acq. Operator :
 Acq. Instrument : Instrument 1 Location : Vial 1
 Injection Date : 4/16/2016 8:58:05 AM
 Acq. Method : C:\HPCHEM\1\METHODS\DEF LC.M
 Last changed : 4/16/2016 8:47:36 AM by
 (modified after loading)
 Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
 Last changed : 5/9/2016 3:56:08 PM
 (modified after loading)
 Sample Info : AD-H, H/i-PrOH = 85/15, 0.7 mL/min, 30 oC, 220 nm



=====
 Area Percent Report
 =====
 Sorted By : Sigmal
 Multiplier: : 1.0000
 Dilution: : 1.0000
 Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

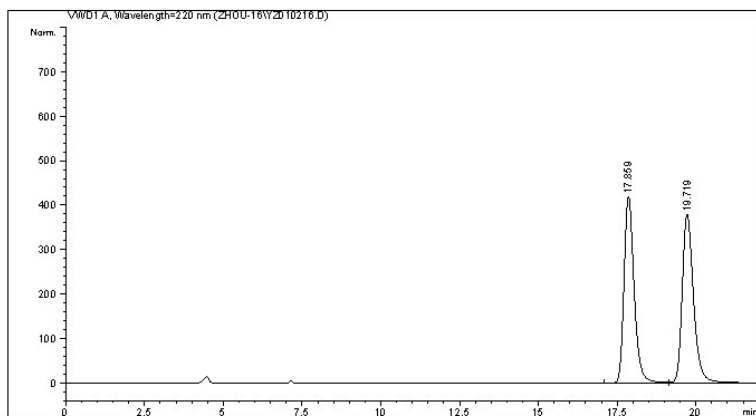
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	11.794	BB	0.2198	63.38647	4.38014	1.6105	
2	13.343	VB	0.2541	3872.34497	232.44867	98.3895	
Totals :				3935.73145		236.82881	



Data File C:\CHEM32\1\DATA\ZHOU-16\YZ010216.D
 Sample Name: ZZ-1-27(+)

```

=====
Acq. Operator   : j
Acq. Instrument : Instrument 1          Location : Vial 1
Injection Date  : 3/31/2016 11:23:10 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF.LC.M
Last changed    : 3/31/2016 11:16:13 AM by j
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF.LC.M
Last changed    : 5/9/2016 3:03:03 PM
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH =90/10, 0.7 mL/min, 30 oC, 220 nm
=====
  
```



Area Percent Report

```

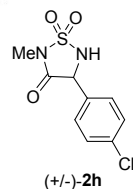
=====
Sorted By      :      Signal
Multiplier:    :      1.0000
Dilution:      :      1.0000
Sample Amount: :      1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs
=====
  
```

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [MAU]	Height [%s]	Area %
1	17.859	BV	0.3422	9393.56641	420.48749	49.6179
2	19.719	VB	0.3848	9538.24805	379.71072	50.3821

Totals : 1.89318e4 800.19821

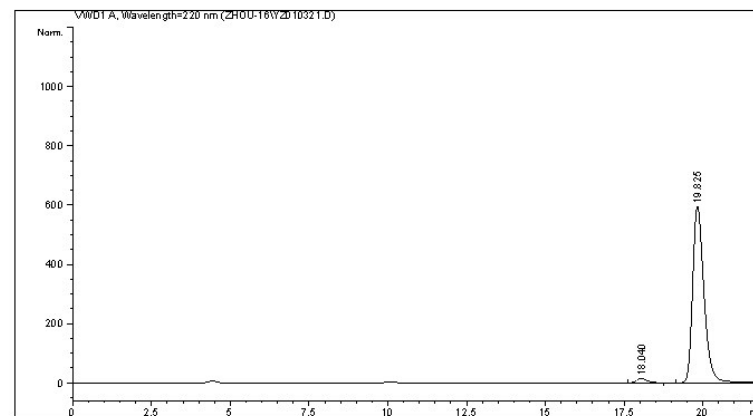
*** End of Report ***



Data File C:\CHEM32\1\DATA\ZHOU-16\YZ010321.D
 Sample Name: ZZ-1-38

```

=====
Acq. Operator   :
Acq. Instrument : Instrument 1          Location : Vial 1
Injection Date  : 4/10/2016 11:56:20 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF.LC.M
Last changed    : 4/10/2016 11:31:46 AM by
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF.LC.M
Last changed    : 5/9/2016 3:05:36 PM
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 90/10, 0.7 mL/min, 30 oC, 220 nm
=====
  
```



Area Percent Report

```

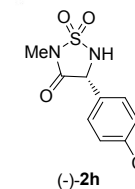
=====
Sorted By      :      Signal
Multiplier:    :      1.0000
Dilution:      :      1.0000
Sample Amount: :      1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs
=====
  
```

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [MAU]	Height [%s]	Area %
1	18.040	BE	0.3507	335.21701	14.68941	2.2012
2	19.825	BE	0.3816	1.48934e4	596.35004	97.7988

Totals : 1.52286e4 611.03945

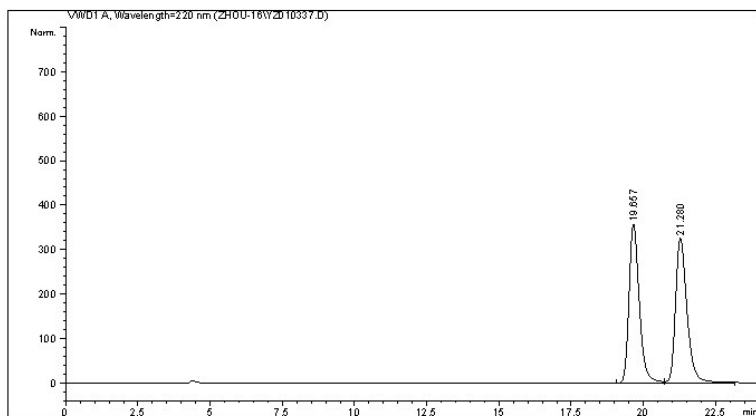
*** End of Report ***



Data File C:\CHEM32\1\DATA\ZHOU-16\YZ010337.D
 Sample Name: ZZ-1-39(+)

```

=====
Acq. Operator   :
Acq. Instrument : Instrument 1           Location : Vial 1
Injection Date  : 4/13/2016 4:49:31 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 4/13/2016 4:38:35 AM by
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 5/9/2016 3:51:26 PM
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 90/10, 0.7 mL/min, 30 oC, 220 nm
  
```



Area Percent Report

```

=====
Sorted By      :          Sigma
Multiplier:    :          1.0000
Dilution:      :          1.0000
Sample Amount: :          1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU]	Height [%s]	Area %
1	19.657	BV	0.3784	8827.71484	357.42062	49.6512
2	21.280	WB	0.4202	8951.73926	325.16458	50.3488

Totals : 1.77795e4 682.58521

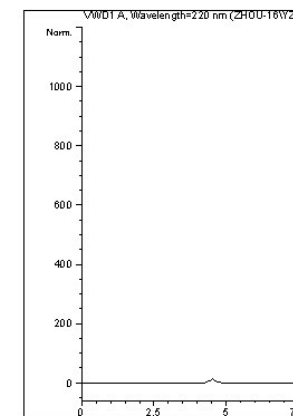
*** End of Report ***



Data File C:\CHEM32\1\DATA\ZHOU-16\YZ010337.D
 Sample Name: ZZ-1-40

```

=====
Acq. Operator   :
Acq. Instrument : Instrument 1           Location : Vial 1
Injection Date  : 4/13/2016 2:12:00 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 4/13/2016 1:26:30 AM by
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 5/9/2016 3:52:20 PM
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 90/10, 0.7 mL/min, 30 oC, 220 nm
  
```



Area Percent Report

```

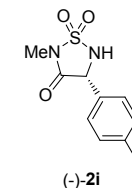
=====
Sorted By      :          Sigma
Multiplier:    :          1.0000
Dilution:      :          1.0000
Sample Amount: :          1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU]	Height [%s]	Area %
1	19.838	VV	0.4066	504.597	325.16458	50.3488
2	21.380	WB	0.4285	1.71497	325.16458	50.3488

Totals : 1.76543e4

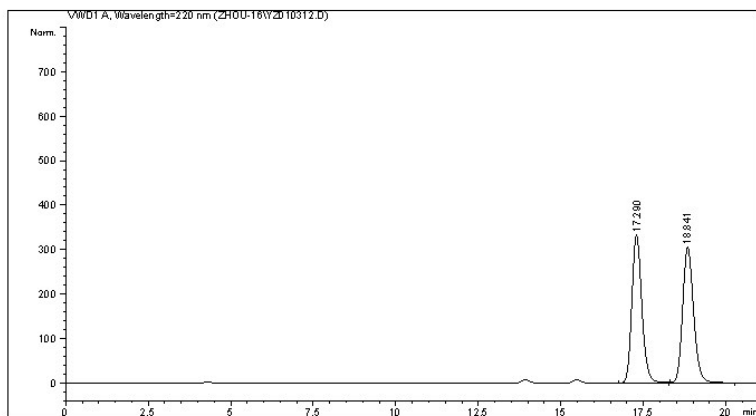
*** End of Report ***



Data File C:\CHEM32\1\DATA\ZHOU-16\YZ010312.D
 Sample Name: ZZ-1-36A(+)

```

=====
Acq. Operator   :
Acq. Instrument : Instrument 1          Location : Vial 1
Injection Date  : 4/9/2016 10:13:50 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 4/9/2016 9:24:32 AM by
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 5/9/2016 3:45:20 PM
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 85/15, 0.7 mL/min, 30 oC, 220 nm
  
```



Area Percent Report

```

=====
Sorted By      :      Signal
Multiplier:    :      1.0000
Dilution:      :      1.0000
Sample Amount: :      1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height %s	Area %
1	17.290	BB	0.3251	7039.30420	333.15082	49.8774
2	18.841	BB	0.3564	7073.91309	305.12646	50.1226
Totals :				1.41132e4	638.27728	

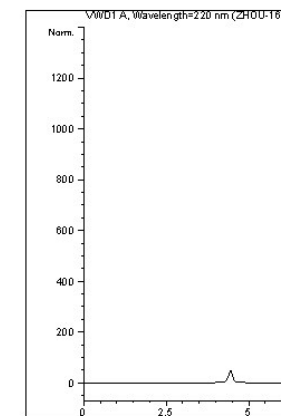
*** End of Report ***



Data File C:\CHEM32\1\DATA\ZHOU-16\YZ010317.D
 Sample Name: ZZ-1-57

```

=====
Acq. Operator   :
Acq. Instrument : Instrument 1          Location : Vial 1
Injection Date  : 5/1/2016 5:28:30 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 5/1/2016 5:06:30 AM by
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 5/9/2016 3:47:32 PM
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 85/15, 0.7 mL/min, 30 oC, 220 nm
  
```



Area Percent Report

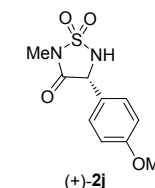
```

=====
Sorted By      :      Signal
Multiplier:    :      1.0000
Dilution:      :      1.0000
Sample Amount: :      1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: VWD1 A, Wavelength=220 nm

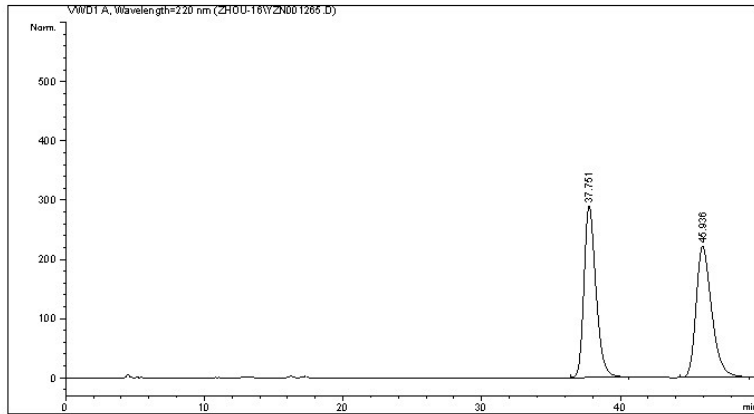
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height %s	Area %
1	17.080	BB	0.3453	251.5082	305.12646	251.5082
2	18.572	BB	0.3516	1.47810		
Totals :				1.50328		

*** End of Report ***



Data File C:\CHEM32\1\DATA\ZHOU-16\YZN001265.D
 Sample Name: ZZ-1-56A(+)

=====
 Acq. Operator :
 Acq. Instrument : Instrument 1 Location : Vial 1
 Injection Date : 5/4/2016 6:49:36 PM
 Acq. Method : C:\CHEM32\1\METHODS\DEF_LC.M
 Last changed : 5/4/2016 5:51:32 PM
 (modified after loading)
 Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
 Last changed : 5/9/2016 4:03:07 PM
 (modified after loading)
 Sample Info : 0J-H, Hex/i-PrOH = 70/30, 0.7 mL/min, 30oC, 220 nm



=====
 Area Percent Report
 =====

Sorted By : Signal
 Multiplier: : 1.0000
 Dilution: : 1.0000
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU]	Height [%]	Area %
1	37.751	BB	0.9156	1.73535e4	289.18442	50.1100
2	45.936	BB	1.1919	1.72773e4	221.28200	49.8900
Totals :				3.46308e4	510.46642	

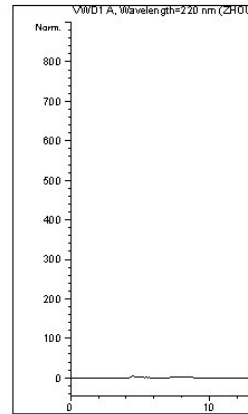
=====
 *** End of Report ***



(+/-)-2k

Data File C:\CHEM32\1\DATA\ZHOU-16
 Sample Name: ZZ-1-56B

=====
 Acq. Operator :
 Acq. Instrument : Instrument 1
 Injection Date : 5/4/2016 7:4
 Acq. Method : C:\CHEM32\1
 Last changed : 5/4/2016 7:4
 (modified af
 Analysis Method : C:\CHEM32\1
 Last changed : 5/9/2016 4:0
 (modified af
 Sample Info : 0J-H, Hex/i-

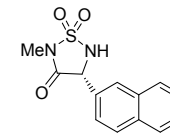


=====
 Area
 =====

Sorted By : S
 Multiplier: :
 Dilution:
 Use Multiplier & Dilution Factor

Signal 1: VWD1 A, Wavelength=2

Peak #	RetTime [min]	Type	Width [min]	Area [mAU]	Height [%]	Area %
1	37.551	BB	0.9139	2.67		
2	46.177	BB	1.1755	1006		
Totals :				2.77		



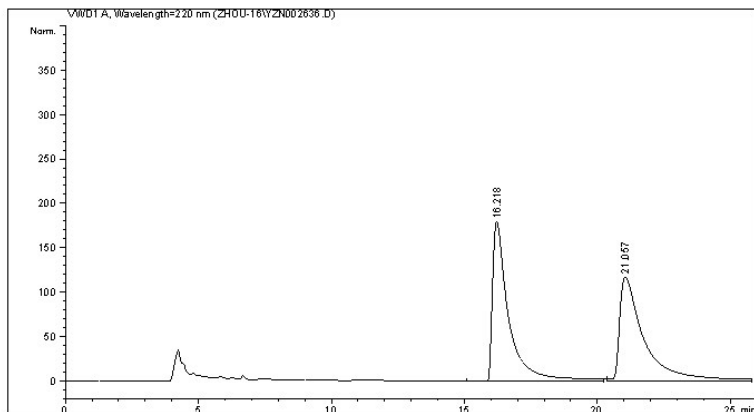
(+)-2k

=====

Data File C:\CHEM32\1\DATA\ZHOU-16\YZN002636.D
 Sample Name: ZZ-1-74(+)

```

=====
Acq. Operator   : 0
Acq. Instrument : Instrument 1          Location : Vial 1
Injection Date  : 10/20/2016 9:02:27 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF.LC.M
Last changed    : 10/20/2016 8:51:51 PM by 0
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF.LC.M
Last changed    : 10/23/2016 9:01:32 PM by 0
                  (modified after loading)
Sample Info     : AS-H, Hexane/i-PrOH = 70/30, 0.7 mL/min, 30oC, 220 nm
  
```



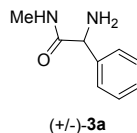
Area Percent Report

```

=====
Sorted By      : Signal
Multiplier:    : 1.0000
Dilution:      : 1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.218	BB	0.6108	7678.07275	180.14059	50.3050
2	21.057	BBA	0.9095	7584.95752	117.62991	49.6950
Totals :				1.52630e4	297.77051	

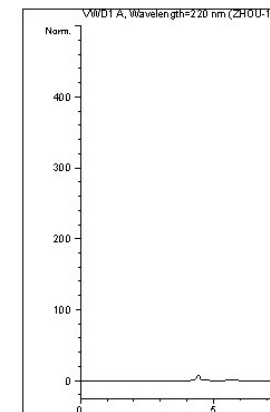


*** End of Report ***

Data File C:\CHEM32\1\DATA\ZHOU-16\YZN002636.D
 Sample Name: ZZ-1-75

```

=====
Acq. Operator   : 0
Acq. Instrument : Instrument 1          Location : Vial 1
Injection Date  : 10/23/2016 9:03:32 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF.LC.M
Last changed    : 10/23/2016 9:03:32 PM by 0
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF.LC.M
Last changed    : 10/23/2016 9:03:32 PM by 0
                  (modified after loading)
Sample Info     : AS, Hexane/i-PrOH = 70/30, 0.7 mL/min, 30oC, 220 nm
  
```



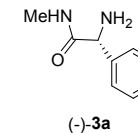
Area Percent Report

```

=====
Sorted By      : Signal
Multiplier:    : 1.0000
Dilution:      : 1.0000
Use Multiplier & Dilution Factor with ISTDs
  
```

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.321	BV	0.6321	1.622	1.622	1.622
2	23.266	VB	1.4371	450.1	450.1	450.1
Totals :				1.667		



*** End of Report ***