

Supporting information

Palladium-Catalyzed Intermolecular Allenylation Reactions of 2,3-Disubstituted Indoles and Allenyl Carbonate

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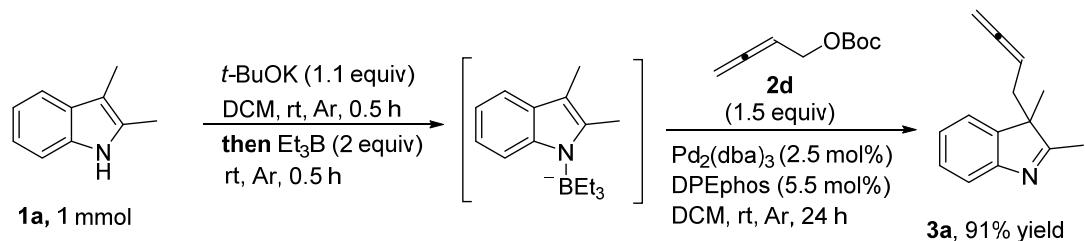
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General Information. All reactions were carried out under the atmosphere of Ar in oven-dried Schlenk tubes. 2,3-Disubstituted indoles **1a-1m**,^{1a} **1n**,^{1b} **1p**,^{1a} and **1o**^{1b}, terminal 2,3-dienol derivatives **2a-2d**,^{2,3} and Pd₂(dba)₃⁴ were prepared according to the reported method. Pd(acac)₂ was purchased from 9dingchem. DPEphos was purchased from J&K Chemicals. BSA was purchased from Sigma-Aldrich and distilled before use. Et₃B and *t*-BuOK were purchased from TCI and stored in a glove box. CH₂Cl₂ was dried over calcium hydride and distilled before use. Other reagents were used without further treatment. Petroleum ether (60 °C-90 °C) was used for chromatography. Tetramethylsilane (TMS) was used as the internal standard for the ¹H NMR analysis. ¹³C NMR experiments were measured in relative to the signal of CDCl₃ (77.00 ppm). ¹⁹F NMR experiments were measured in relative to the signal of CFCl₃ (0 ppm) in CDCl₃.

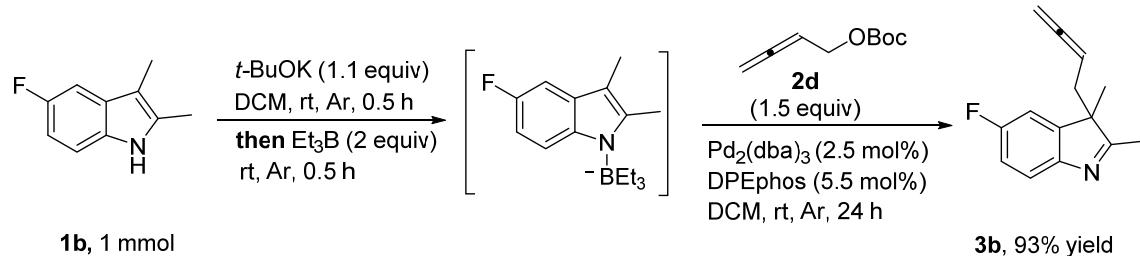
Palladium-catalyzed intermolecular allenylation reactions of 2,3-disubstituted indoles and allenyl carbonates

1. 3-(Buta-2,3-dienyl)-2,3-dimethyl-3*H*-indole (3a, zyz-3-183)



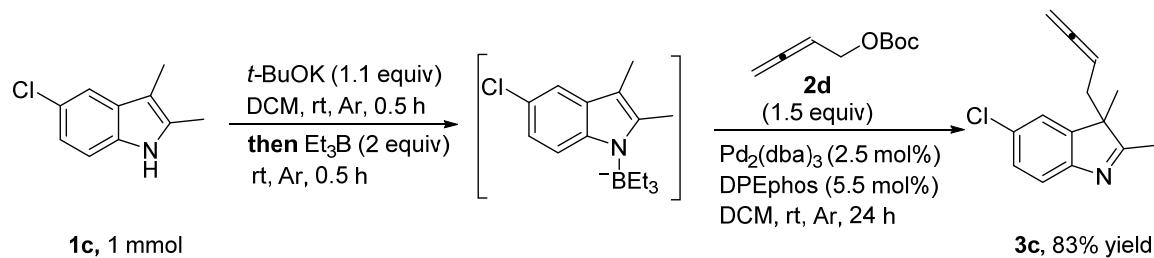
Typical Procedure I: To an oven dried Schlenk tube **A** were added compound **1a** (145.6 mg, 1.0 mmol), *t*-BuOK (123.9 mg, 1.1 mmol), and DCM (2.0 mL) sequentially under the atmosphere of Ar. The resulting mixture was stirred at room temperature for 30 min. A solution of Et₃B (1 M in THF, 2.0 mL, 2.0 mmol) was then added dropwise within 2 minutes. The resulting mixture was stirred for another 30 minutes. To another oven dried Schlenk tube **B** were added Pd₂(dba)₃ (22.9 mg, 0.025 mmol), DPEphos (29.6 mg, 0.055 mmol), and DCM (2.0 mL) sequentially under the atmosphere of Ar and was stirred for 30 minutes. The resulting mixture was transferred into the Schlenk tube **A** via a syringe and the Schlenk tube **B** was washed with 0.5 mL of DCM. Compound **2d** (256.1 mg, 1.5 mmol) and DCM (0.5 mL) were added into Schlenk tube **A** sequentially. The resulting mixture was stirred at room temperature in Schlenk tube **A** for 24 h. After the reaction was complete as monitored by TLC, a saturated aqueous solution of NH₄Cl (20 mL) was added and the resulting mixture was extracted with DCM (3×20 mL). The combined organic layer was washed with brine (20 mL) and dried over anhydrous Na₂SO₄. After evaporation, the residue was purified by silica gel column chromatography to afford **3a**⁵ (179.8 mg, 91%) (eluent: petroleum ether/ethyl acetate = 10/1) as an oil: ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, *J* = 7.6 Hz, 1 H, Ar-H), 7.32-7.23 (m, 2 H, Ar-H), 7.17 (t, *J* = 7.4 Hz, 1 H, Ar-H), 4.58-4.39 (m, 3 H, HC=C=CH₂), 2.61-2.53 (m, 1 H, one proton of CH₂), 2.43-2.34 (m, 1 H, one proton of CH₂), 2.25 (s, 3 H, CH₃), 1.29 (s, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 209.1, 186.1, 154.1, 142.8, 127.5, 124.8, 121.5, 119.6, 84.0, 74.4, 57.4, 35.9, 21.5, 15.6.

2. 3-(Buta-2,3-dienyl)-5-fluoro-2,3-dimethyl-3*H*-indole (**3b**, zyz-3-188)



Following **Typical Procedure I**, the reaction of **1b** (163.7 mg, 1.0 mmol), *t*-BuOK (123.9 mg, 1.1 mmol), DCM (2 mL), Et₃B (1 M in THF, 2.0 mL, 2.0 mmol), Pd₂(dba)₃ (22.9 mg, 0.025 mmol), DPEphos (29.5 mg, 0.055 mmol), DCM (2 mL + 0.5 mL), and **2d** (255.9 mg, 1.5 mmol)/DCM (0.5 mL) afforded **3b** (200.5 mg, 93%) (eluent: petroleum ether/ethyl acetate = 10/1) as an oil: ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.31 (m, 1 H, Ar-H), 6.94-6.84 (m, 2 H, Ar-H), 4.51-4.31 (m, 3 H, HC=C=CH₂) 2.50-2.38 (m, 1 H, one proton of CH₂), 2.35-2.24 (m, 1 H, one proton of CH₂), 2.15 (s, 3 H, CH₃), 1.20 (s, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 209.2, 185.9 (*J* = 2.9 Hz), 160.8 (*J* = 242.3 Hz), 150.2 (*J* = 2.2 Hz), 144.9 (*J* = 8.1 Hz), 120.2 (*J* = 8.8 Hz), 114.1 (*J* = 23.3 Hz), 109.3 (*J* = 24.1 Hz), 83.7, 74.5, 58.0 (*J* = 2.2 Hz), 35.7, 21.4, 15.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -118.1; MS (ESI) *m/z* 216 (M+H)⁺; IR (neat, cm⁻¹): 2965, 2929, 1954, 1581, 1460, 1377, 1330, 1286, 1249, 1168, 1102, 1050; HRMS (ESI) Calcd for C₁₄H₁₅FN (M+H)⁺: 216.1183, Found: 216.1180.

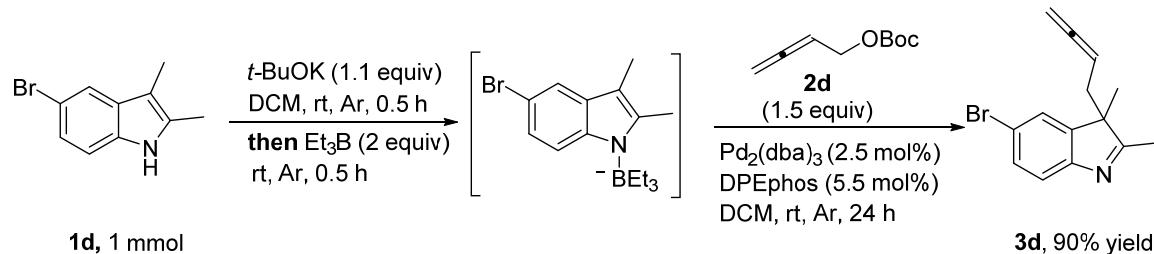
3. 3-(Buta-2,3-dienyl)-5-chloro-2,3-dimethyl-3*H*-indole (**3c**, zyz-3-194)



According to **Typical Procedure I**, the reaction of **1c** (179.0 mg, 1.0 mmol), *t*-BuOK (123.8 mg, 1.1 mmol), DCM (2 mL), Et₃B (1 M in THF, 2.0 mL, 2.0 mmol), Pd₂(dba)₃ (22.9 mg, 0.025 mmol), DPEphos (29.4 mg, 0.055 mmol), DCM (2 mL + 0.5 mL), and **2d** (255.0 mg, 1.5 mmol)/DCM (0.5 mL) afforded **3c** (190.5 mg, 83%) (eluent: petroleum

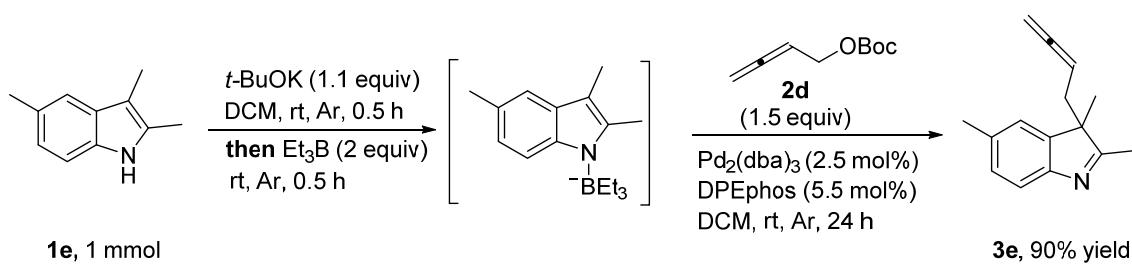
ether/ethyl acetate = 10/1) as an oil: ^1H NMR (400 MHz, CDCl_3) δ 7.34 (d, J = 8.0 Hz, 1 H, Ar-H), 7.21-7.12 (m, 2 H, Ar-H), 4.53-4.31 (m, 3 H, $\text{HC}=\text{C}=\text{CH}_2$), 2.50-2.41 (m, 1 H, one proton of CH_2), 2.33-2.25 (m, 1 H, one proton of CH_2), 2.16 (s, 3 H, CH_3), 1.21 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 209.3, 186.7, 152.7, 144.7, 130.7, 127.8, 122.2, 120.5, 83.7, 74.7, 58.0, 35.7, 21.4, 15.7; MS (ESI) m/z 234 ($\text{M}^{(37)\text{Cl}}+\text{H}$) $^+$, 232 ($\text{M}^{(35)\text{Cl}}+\text{H}$) $^+$; IR (neat, cm^{-1}): 2965, 2928, 1954, 1576, 1449, 1376, 1298, 1241, 1183, 1132, 1078, 1053; HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{15}^{35}\text{ClN}$ ($\text{M}+\text{H}$) $^+$: 232.0888, Found: 232.0882.

4. 5-Bromo-3-(buta-2,3-dienyl)-2,3-dimethyl-3*H*-indole (3d, zyz-3-196)



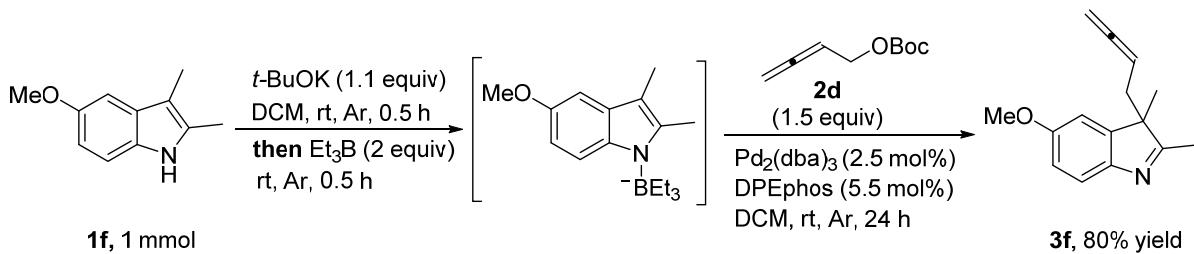
According to **Typical Procedure I**, the reaction of **1d** (223.6 mg, 1.0 mmol), *t*-BuOK (123.6 mg, 1.1 mmol), DCM (2 mL), Et_3B (1 M in THF, 2.0 mL, 2.0 mmol), $\text{Pd}_2(\text{dba})_3$ (22.8 mg, 0.025 mmol), DPEphos (29.6 mg, 0.055 mmol), DCM (2 mL + 0.5 mL), and **2d** (255.9 mg, 1.5 mmol)/DCM (0.5 mL) afforded **3d** (249.1 mg, 90%) (eluent: petroleum ether/ethyl acetate = 10/1) as an oil: ^1H NMR (400 MHz, CDCl_3) δ 7.47-7.34 (m, 3 H, Ar-H), 4.61-4.41 (m, 3 H, $\text{HC}=\text{C}=\text{CH}_2$), 2.58-2.50 (m, 1 H, one proton of CH_2), 2.42-2.33 (m, 1 H, one proton of CH_2), 2.24 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 209.3, 186.8, 153.2, 145.2, 130.7, 125.1, 121.1, 118.6, 83.7, 74.8, 58.1, 35.8, 21.4, 15.8; MS (ESI) m/z 278 ($\text{M}^{(81)\text{Br}}+\text{H}$) $^+$, 276 ($\text{M}^{(79)\text{Br}}+\text{H}$) $^+$; IR (neat, cm^{-1}): 2964, 2928, 1954, 1575, 1446, 1376, 1298, 1242, 1206, 1183, 1111, 1066; HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{15}^{79}\text{BrN}$ ($\text{M}+\text{H}$) $^+$ 276.0382, Found: 276.0374.

5. 3-(Buta-2,3-dienyl)-2,3,5-trimethyl-3*H*-indole (3e, zyz-4-4)



According to **Typical Procedure I**, the reaction of **1e** (159.6 mg, 1.0 mmol), *t*-BuOK (123.9 mg, 1.1 mmol), DCM (2 mL), Et₃B (1 M in THF, 2.0 mL, 2.0 mmol), Pd₂(dba)₃ (22.8 mg, 0.025 mmol), DPEphos (29.6 mg, 0.055 mmol), DCM (2 mL + 0.5 mL), and **2d** (255.7 mg, 1.5 mmol)/DCM (0.5 mL) afforded **3e** (190.2 mg, 90%) (eluent: petroleum ether/ethyl acetate = 10/1) as an oil: ¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, *J* = 7.6 Hz, 1 H, Ar-H), 7.10 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.07 (s, 1 H, Ar-H), 4.60-4.40 (m, 3 H, HC=C=CH₂), 2.59-2.51 (m, 1 H, one proton of CH₂), 2.41-2.33 (m, 4 H, one proton of CH₂ and CH₃), 2.24 (s, 3 H, CH₃), 1.29 (s, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 209.2, 185.3, 152.1, 143.1, 134.6, 128.2, 122.4, 119.2, 84.3, 74.4, 57.3, 36.0, 21.7, 21.3, 15.7; MS (ESI) *m/z* 212 (M+H)⁺; IR (neat, cm⁻¹): 2962, 2925, 2865, 1954, 1690, 1579, 1454, 1428, 1376, 1322, 1300, 1255, 1208, 1121, 1093, 1038, 1000; HRMS (ESI) Calcd for C₁₅H₁₈N (M+H)⁺: 212.1434, Found: 212.1428.

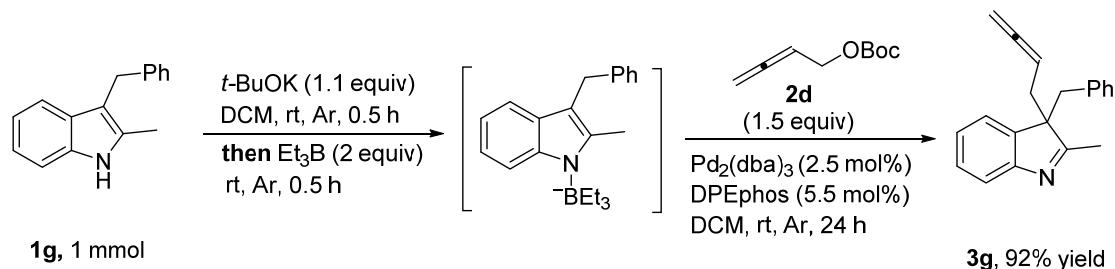
6. 3-(Buta-2,3-dienyl)-5-methoxy-2,3-dimethyl-3*H*-indole (**3f**, zyz-3-192)



According to **Typical Procedure I**, the reaction of **1f** (175.7 mg, 1.0 mmol), *t*-BuOK (123.9 mg, 1.1 mmol), DCM (2 mL), Et₃B (1 M in THF, 2.0 mL, 2.0 mmol), Pd₂(dba)₃ (22.8 mg, 0.025 mmol), DPEphos (29.6 mg, 0.055 mmol), DCM (2 mL + 0.5 mL), and **2d** (255.7 mg, 1.5 mmol)/DCM (0.5 mL) afforded **3f** (181.7 mg, 80%) (eluent: petroleum ether/ethyl acetate = 10/1) as an oil: ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, *J* = 8.8 Hz, 1 H, Ar-H), 6.86-6.79 (m, 2 H, Ar-H), 4.62-4.40 (m, 3 H, HC=C=CH₂), 3.80 (s, 3 H, OMe),

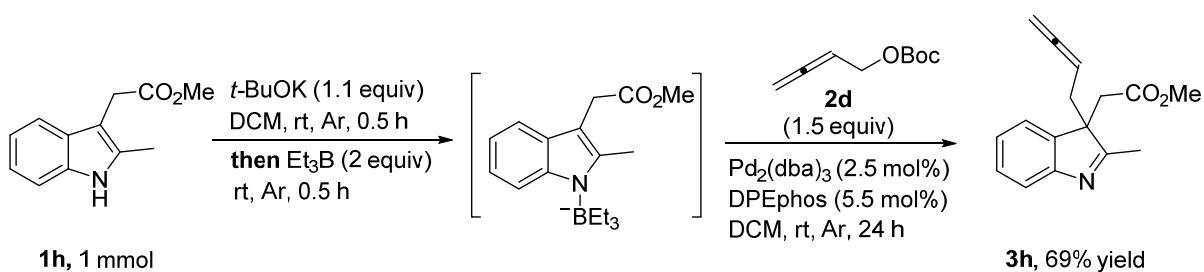
2.60-2.49 (m, 1 H, one proton of CH₂), 2.43-2.32 (m, 1 H, one proton of CH₂), 2.22 (s, 3 H, CH₃), 1.29 (s, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 209.1, 183.9, 157.6, 147.8, 144.4, 119.7, 112.0, 108.3, 84.0, 74.4, 57.5, 55.4, 35.9, 21.6, 15.5; MS (ESI) *m/z* 228 (M+H)⁺; IR (neat, cm⁻¹): 2960, 2930, 2835, 1954, 1583, 1520, 1468, 1431, 1377, 1337, 1289, 1257, 1197, 1172, 1112, 1056, 1028; HRMS (ESI) Calcd for C₁₅H₁₈NO (M+H)⁺: 228.1383, Found: 228.1378.

7. 3-Benzyl-3-(buta-2,3-dienyl)-2-methyl-3*H*-indole (3g, zyz-4-56)



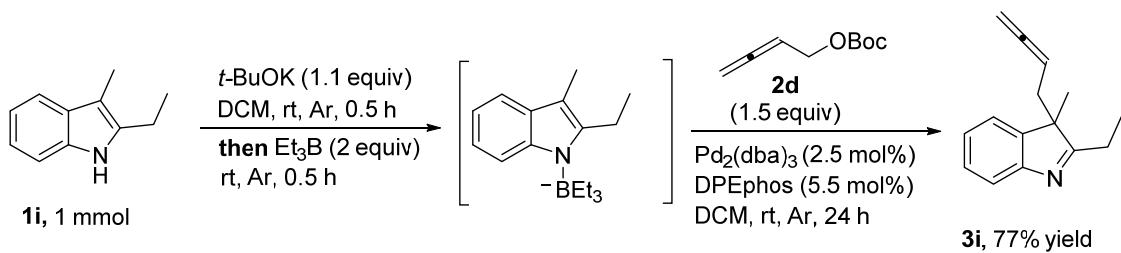
According to **Typical Procedure I**, the reaction of **1g** (221.4 mg, 1.0 mmol), *t*-BuOK (124.9 mg, 1.1 mmol), DCM (2 mL), Et₃B (1 M in THF, 2.0 mL, 2.0 mmol), Pd₂(dba)₃ (23.0 mg, 0.025 mmol), DPEphos (29.8 mg, 0.055 mmol), DCM (2 mL + 0.5 mL), and **2d** (256.2 mg, 1.5 mmol)/DCM (0.5 mL) afforded **3g** (251.7 mg, 92%) (eluent: petroleum ether/ethyl acetate = 10/1) as an oil: ¹H NMR (400 MHz, CDCl₃) δ 7.39 (d, *J* = 7.6 Hz, 1 H, Ar-H), 7.26 (t, *J* = 7.0 Hz, 1 H, Ar-H), 7.14 (t, *J* = 7.4 Hz, 1 H, Ar-H), 7.11-7.01 (m, 4 H, Ar-H), 6.78-6.73 (m, 2 H, Ar-H), 4.58-4.43 (m, 2 H, =CH₂), 4.39-4.29 (m, 1 H, =CH), 3.22 (d, *J* = 13.2 Hz, 1 H, one proton of CH₂), 2.89 (d, *J* = 13.6 Hz, 1 H, one proton of CH₂), 2.76-2.68 (m, 1 H, one proton of CH₂), 2.61-2.52 (m, 1 H, one proton of CH₂), 2.32 (s, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 209.3, 184.5, 155.0, 140.3, 135.5, 129.3, 127.8, 127.7, 126.6, 124.5, 122.8, 119.7, 83.8, 74.6, 62.8, 41.8, 35.2, 16.7; MS (EI, 70 eV) *m/z* (%) 273 (M⁺, 87.33), 182 (100); IR (neat, cm⁻¹): 3061, 3029, 2914, 2847, 1954, 1577, 1495, 1467, 1454, 1376, 1321, 1258, 1239, 1208, 1184, 1109, 1080, 1031, 1015; HRMS (ESI) Calcd for C₂₀H₂₀N (M+H)⁺: 274.1590, Found: 274.1589.

8. 3-(Buta-2,3-dienyl)-3-(2-methoxy-2-oxoethyl)-2-methyl-3*H*-indole (3h, zyz-4-88)



According to **Typical Procedure I**, the reaction of **1h** (203.9 mg, 1.0 mmol), *t*-BuOK (123.9 mg, 1.1 mmol), DCM (2 mL), Et₃B (1 M in THF, 2.0 mL, 2.0 mmol), Pd₂(dba)₃ (22.8 mg, 0.025 mmol), DPEphos (29.5 mg, 0.055 mmol), DCM (2 mL + 0.5 mL), and **2d** (255.9 mg, 1.5 mmol)/DCM (0.5 mL) afforded **3h** (191.0 mg, 69%, purity 92%) (eluent: petroleum ether/ethyl acetate = 5/1) as an oil: ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, *J* = 4.0 Hz, 1 H, Ar-H), 7.35-7.29 (m, 2 H, Ar-H), 7.20 (t, *J* = 7.4 Hz, 1 H, Ar-H), 4.63-4.47 (m, 2 H, =CH₂), 4.42 (quint, *J* = 7.2 Hz, 1 H, =CH), 3.40 (s, 3 H, Me), 2.96 (d, *J* = 14.4 Hz, 1 H, one proton of CH₂), 2.75 (d, *J* = 14.8 Hz, 1 H, one proton of CH₂), 2.73-2.64 (m, 1 H, one proton of CH₂), 2.45-2.32 (m, 4 H, CH₃ and one proton of CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 209.5, 184.3, 169.4, 154.2, 139.4, 128.3, 125.2, 122.2, 119.9, 83.1, 74.8, 59.0, 51.5, 39.6, 35.4, 16.1; MS (EI, 70 eV) *m/z* (%) 255 (M⁺, 4.94), 196 (100); IR (neat, cm⁻¹): 3060, 2952, 2876, 1955, 1735, 1581, 1458, 1435, 1355, 1278, 1235, 1208, 1193, 1165, 1108, 1045, 1016; HRMS (ESI) Calcd for C₁₆H₁₈NO₂ (M+H)⁺: 256.1332, Found: 256.1335.

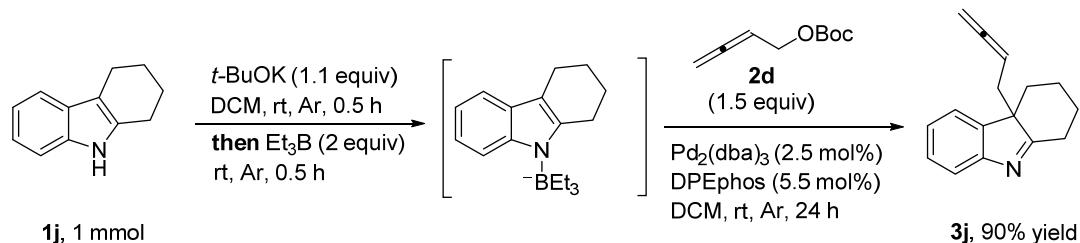
9. 3-(Buta-2,3-dienyl)-2-ethyl-3-methyl-3*H*-indole (**3i**, zyz-4-108)



According to **Typical Procedure I**, the reaction of **1i** (159.9 mg, 1.0 mmol), *t*-BuOK (123.5 mg, 1.1 mmol), DCM (2 mL), Et₃B (1 M in THF, 2.0 mL, 2.0 mmol), Pd₂(dba)₃ (22.9 mg, 0.025 mmol), DPEphos (29.5 mg, 0.055 mmol), DCM (2 mL + 0.5 mL), and **2d** (255.1 mg, 1.5 mmol)/DCM (0.5 mL) afforded **3i** (163.2 mg, 77%) (eluent: petroleum

ether/ethyl acetate = 20/1) as an oil: ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, J = 8.0 Hz, 1 H, Ar-H), 7.31 (t, J = 7.6 Hz, 1 H, Ar-H), 7.26 (d, J = 7.2 Hz, 1 H, Ar-H), 7.18 (t, J = 7.4 Hz, 1 H, Ar-H), 4.58-4.36 (m, 3 H, $\text{CH}=\text{C}=\text{CH}_2$), 2.62-2.51 (m, 3 H, CH_2 and one proton of CH_2), 2.45-2.36 (m, 1 H, one proton of CH_2), 1.38 (t, J = 7.4 Hz, 3 H, CH_3), 1.31 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 209.2, 190.3, 154.4, 143.1, 127.7, 124.9, 121.5, 119.9, 84.3, 74.4, 57.7, 36.4, 22.3, 21.9, 10.2; MS (EI, 70 eV) m/z (%) 211 (M^+ , 6.98), 43 (100); IR (neat, cm^{-1}): 3060, 2969, 2930, 2868, 1955, 1685, 1611, 1574, 1535, 1469, 1452, 1375, 1338, 1318, 1270, 1204, 1074; HRMS (ESI) Calcd for $\text{C}_{15}\text{H}_{18}\text{N}$ ($\text{M}+\text{H})^+$: 212.1434, Found: 212.1439.

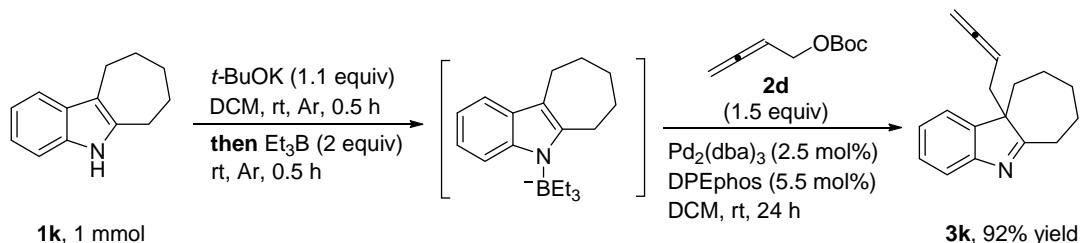
10. 4a-(Buta-2,3-dienyl)-2,3,4,4a-tetrahydro-1*H*-carbazole (**3j**, zyz-3-186B)



According to **Typical Procedure I**, the reaction of **1j** (171.5 mg, 1.0 mmol), *t*-BuOK (123.1 mg, 1.1 mmol), DCM (2 mL), Et_3B (1 M in THF, 2.0 mL, 2.0 mmol), $\text{Pd}_2(\text{dba})_3$ (22.9 mg, 0.025 mmol), DPEphos (29.6 mg, 0.055 mmol), DCM (2 mL + 0.5 mL), and **2d** (254.7 mg, 1.5 mmol)/DCM (0.5 mL) afforded **3j** (200.2 mg, 90%) (eluent: petroleum ether/ethyl acetate = 10/1) as an oil: ^1H NMR (400 MHz, CDCl_3) δ 7.58 (d, J = 7.6 Hz, 1 H, Ar-H), 7.33-7.24 (m, 2 H, Ar-H), 7.15 (t, J = 7.4 Hz, 1 H, Ar-H), 4.58-4.38 (m, 3 H, $\text{HC}=\text{C}=\text{CH}_2$), 2.87 (d, J = 12.8 Hz, 1 H, one proton of CH_2), 2.60-2.46 (m, 3 H, CH_2 and one proton of another CH_2), 2.34 (d, J = 13.2 Hz, 1 H, one proton of CH_2), 2.15 (d, J = 12.8 Hz, 1 H, one proton of CH_2), 1.86-1.70 (m, 1 H, one proton of CH_2), 1.63 (d, J = 13.6 Hz, 1 H, one proton of CH_2), 1.46-1.33 (m, 1 H, one proton of CH_2), 1.14 (td, J_1 = 13.5 Hz, J_2 = 3.7 Hz, 1 H, one proton of CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ 209.1, 188.3, 154.7, 143.9, 127.4, 124.4, 121.5, 119.8, 83.6, 74.2, 57.5, 36.5, 32.4, 29.7, 28.5, 20.7; MS (ESI) m/z 224 ($\text{M}+\text{H})^+$; 3054, 2932, 2857, 1953, 1613, 1581, 1447, 1344, 1310,

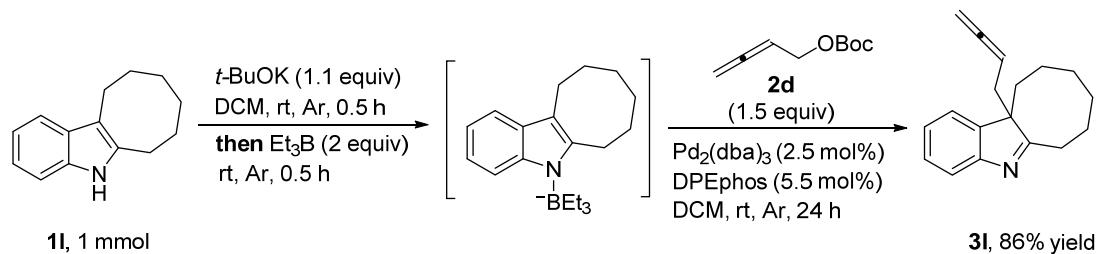
1251, 1200, 1137, 1093, 1055, 1013; HRMS (ESI) Calcd for C₁₆H₁₈N (M+H)⁺ 224.1434, Found: 224.1429.

11. 10a-(Buta-2,3-dienyl)-6,7,8,9,10,10a-hexahydrocyclohepta[b]indole (3k, zyz-4-2)



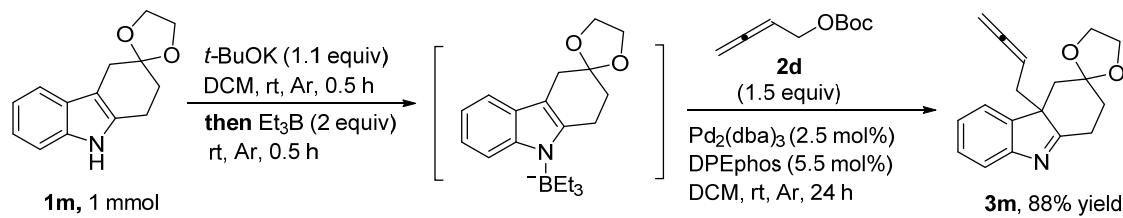
According to **Typical Procedure I**, the reaction of **1k** (185.6 mg, 1.0 mmol), *t*-BuOK (123.7 mg, 1.1 mmol), DCM (2 mL), Et₃B (1 M in THF, 2.0 mL, 2.0 mmol), Pd₂(dba)₃ (22.8 mg, 0.025 mmol), DPEphos (29.5 mg, 0.055 mmol), DCM (2 mL + 0.5 mL), and **2d** (255.0 mg, 1.5 mmol)/DCM (0.5 mL) afforded **3k** (218.4 mg, 92%) (eluent: petroleum ether/ethyl acetate = 10/1) as an oil: ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.32-7.27 (td, *J*₁ = 7.6 Hz, *J*₂ = 1.3 Hz, 1 H, Ar-H), 7.25-7.21 (m, 1 H, Ar-H), 7.17 (td, *J*₁ = 7.4 Hz, *J*₂ = 0.8 Hz, 1 H, Ar-H), 4.58-4.45 (m, 3 H, HC=C=CH₂), 2.98-2.87 (m, 1 H, one proton of CH₂), 2.67-2.50 (m, 2 H, CH₂), 2.47-2.39 (m, 1 H, one proton of CH₂), 2.12-1.99 (m, 2 H, CH₂), 1.85-1.69 (m, 2 H, CH₂), 1.66-1.54 (m, 2 H, CH₂), 1.54-1.41 (m, 1 H, one proton of CH₂), 0.83-0.66 (m, 1 H, one proton of CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 209.4, 190.3, 154.9, 143.3, 127.7, 124.8, 121.6, 119.6, 84.0, 74.3, 62.1, 36.4, 34.8, 31.4, 30.3, 28.3, 24.5; MS (ESI) *m/z* 238 (M+H)⁺; IR (neat, cm⁻¹): 3047, 2923, 2851, 1953, 1692, 1609, 1571, 1451, 1346, 1302, 1261, 1208, 1192, 1171, 1108, 1077, 1102; HRMS (ESI) Calcd for C₁₇H₂₀N (M+H)⁺: 238.1590, Found: 238.1583.

12. 11a-(Buta-2,3-dienyl)-7,8,9,10,11,11a-hexahydrocycloocta[b]indole (3l, zyz-4-14)



According to **Typical Procedure I**, the reaction of **1l** (199.9 mg, 1.0 mmol), *t*-BuOK (124.1 mg, 1.1 mmol), DCM (2 mL), Et₃B (1 M in THF, 2.0 mL, 2.0 mmol), Pd₂(dba)₃ (22.8 mg, 0.025 mmol), DPEphos (29.6 mg, 0.055 mmol), DCM (2 mL + 0.5 mL), and **2d** (255.7 mg, 1.5 mmol)/DCM (0.5 mL) afforded **3l** (216.8 mg, 86%) (eluent: petroleum ether/ethyl acetate = 10/1) as an oil: ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, *J* = 7.6 Hz, 1 H, Ar-H), 7.34-7.28 (m, 1 H, Ar-H), 7.24-7.15 (m, 2 H, Ar-H), 4.56-4.36 (m, 3 H, HC=CH₂), 2.88-2.78 (m, 1 H, one proton of CH₂), 2.67-2.58 (m, 1 H, one proton of CH₂), 2.54-2.45 (m, 1 H, one proton of CH₂), 2.36-2.28 (m, 1 H, one proton of CH₂), 2.27-2.20 (m, 1 H, one proton of CH₂), 2.20-2.12 (m, 1 H, one proton of CH₂), 2.11-2.00 (m, 1 H, one proton of CH₂), 1.98-1.86 (m, 1 H, one proton of CH₂), 1.68-1.57 (m, 1 H, one proton of CH₂), 1.52-1.30 (m, 1 H, one proton of CH₂), 1.39-1.25 (m, 2 H, CH₂), 1.08-0.95 (m, 1 H, one proton of CH₂), 0.95-0.83 (m, 1 H, one proton of CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 209.2, 191.8, 155.0, 141.0, 127.5, 124.6, 121.6, 119.7, 83.7, 74.1, 61.6, 37.2, 31.5, 30.2, 29.7, 25.6, 25.0, 23.5; MS (EI, 70 eV) *m/z* (%) 251 (M⁺, 100); IR (neat, cm⁻¹): 3057, 2923, 2853, 1954, 1566, 1455, 1444, 1355, 1341, 1311, 1269, 1236, 1209, 1171, 1134, 1114, 1090, 1014; HRMS (ESI) Calcd for C₁₈H₂₂N (M+H)⁺: 252.1747, Found: 252.1738.

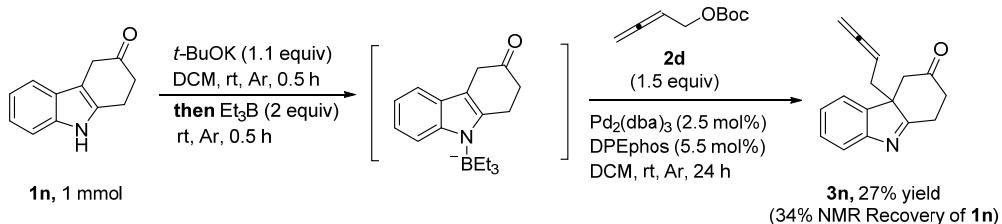
13. 4a-(Buta-2,3-dienyl)-1,2,4,4a-tetrahydrospiro[carbazole-3,2'-[1,3]dioxolane] (**3m**, zyz-4-82)



According to **Typical Procedure I**, the reaction of **1m** (229.9 mg, 1.0 mmol), *t*-BuOK (123.9 mg, 1.1 mmol), DCM (2 mL), Et₃B (1 M in THF, 2.0 mL, 2.0 mmol), Pd₂(dba)₃ (22.9 mg, 0.025 mmol), DPEphos (29.4 mg, 0.055 mmol), DCM (2 mL + 0.5 mL), and **2d** (255.9 mg, 1.5 mmol)/DCM (0.5 mL) afforded **3m** (257.3 mg, 88%, purity 97%) (eluent: petroleum ether/ethyl acetate = 6/1) as an oil: ¹H NMR (400 MHz, CDCl₃) δ 7.58

(d, $J = 7.6$ Hz, 1 H, Ar-H), 7.31 (t, $J = 7.4$ Hz, 1 H, Ar-H), 7.26 (d, $J = 7.2$ Hz, 1 H, Ar-H), 7.17 (d, $J = 7.2$ Hz, 1 H, Ar-H), 4.58-4.40 (m, 3 H, HC=C=CH₂), 4.14-4.02 (m, 2 H, OCH₂), 3.97-3.87 (m, 2 H, OCH₂), 3.00-2.80 (m, 3 H, CH₂ and one proton of CH₂), 2.73-2.64 (m, 1 H, one proton of CH₂), 2.41 (dd, $J_1 = 13.8$ Hz, $J_2 = 3.0$ Hz, 1 H, one proton of CH₂), 2.19-2.10 (m, 1 H, one proton of CH₂), 1.79 (td, $J_1 = 13.7$, $J_2 = 5.5$ Hz, 1 H, one proton of CH₂), 1.53 (d, $J = 14.0$ Hz, 1 H, one proton of CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 209.5, 187.3, 154.6, 143.8, 127.8, 124.9, 121.7, 120.1, 107.9, 84.0, 74.1, 64.8, 64.0, 57.4, 42.2, 36.4, 33.5, 26.2; MS (EI, 70 eV) *m/z* (%) 281 (M⁺, 44.48), 195 (100); IR (neat, cm⁻¹): 2957, 2882, 1954, 1614, 1586, 1435, 1341, 1304, 1264, 1226, 1207, 1180, 1147, 1102, 1067, 1034, 1013; HRMS (ESI) Calcd for C₁₈H₂₀NO₂ (M+H)⁺: 282.1489, Found: 282.1493.

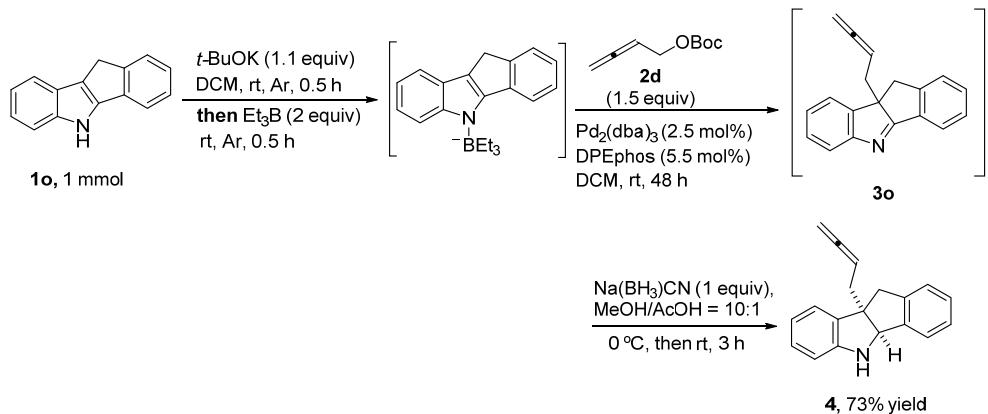
14. 4a-(Buta-2,3-dienyl)-1,2,4,4a-tetrahydro-3*H*-carbazol-3-one (**3n**, zyz-4-96)



According to **Typical Procedure I**, the reaction of **1n** (185.9 mg, 1.0 mmol), *t*-BuOK (124.6 mg, 1.1 mmol), DCM (2 mL), Et₃B (1 M in THF, 2.0 mL, 2.0 mmol), Pd₂(dba)₃ (22.9 mg, 0.025 mmol), DPEphos (29.8 mg, 0.055 mmol), DCM (2 mL + 0.5 mL), and **2d** (255.9 mg, 1.5 mmol)/DCM (0.5 mL) afforded **3n** (81.8 mg, 27%, purity 79%) (eluent: petroleum ether/ethyl acetate = 5/1 (900 mL) to 3/1 (1200 mL)) as an oil: 7.63 (d, $J = 7.6$ Hz, 1 H, Ar-H), 7.42-7.37 (m, 1 H, Ar-H), 7.29-7.23 (m, 2 H, Ar-H), 4.64-4.49 (m, 2 H, =CH₂), 4.48-4.37 (m, 1 H, =CH), 3.26-3.16 (m, 1 H, one proton of CH₂), 3.14-3.03 (m, 1 H, one proton of CH₂), 2.94 (dd, $J_1 = 14.4$ Hz, $J_2 = 2.4$ Hz, 1 H, one proton of CH₂), 2.80-2.72 (m, 1 H, one proton of CH₂), 2.68-2.57 (m, 2 H, CH₂), 2.48-2.41 (m, 1 H, one proton of CH₂), 2.34 (d, $J = 14.4$ Hz, 1 H, one proton of CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 209.6, 206.9, 183.4, 154.7, 141.6, 128.7, 125.8, 121.8, 120.7, 82.9, 75.2, 58.7, 49.5, 39.4, 34.6, 27.0; MS (ESI) *m/z* 238 (M+H)⁺; IR (neat, cm⁻¹): 3381, 2959, 2913,

1954, 1712, 1613, 1589, 1455, 1431, 1349, 1263, 1216, 1196, 1150, 1100, 1059, 1013; HRMS (ESI) Calcd for C₁₆H₁₆NO (M+H)⁺: 238.1226, Found: 238.1228.

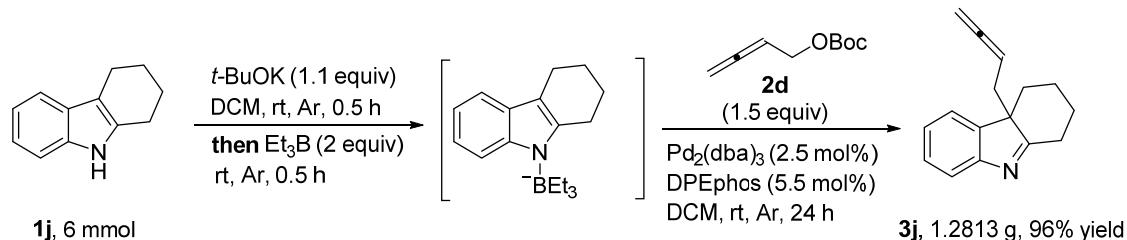
15. *cis*-9b-(Buta-2,3-dienyl)-4b,5,9b,10-tetrahydroindeno[1,2-b]indole (4, zyz-4-146, zyz-4-148)



To an oven dried Schlenk tube **A** were added compound **1o** (205.7 mg, 1.0 mmol), *t*-BuOK (124.7 mg, 1.1 mmol), and DCM (2.0 mL) sequentially under the atmosphere of Ar. The resulting mixture was stirred at room temperature for 30 min. A solution of Et₃B (1 M in THF, 2.0 mL, 2.0 mmol) was then added dropwise within 3 minutes, the resulting mixture was stirred for another 30 minutes. To another oven dried Schlenk tube **B** were added compound Pd₂(dba)₃ (22.8 mg, 0.025 mmol), DPEphos (29.5 mg, 0.055 mmol), and DCM (2.0 mL) sequentially under the atmosphere of Ar and the resulting mixture was stirred for 30 minutes and transferred into the Schlenk tube **A** via a syringe and the Schlenk tube **B** was washed with 0.5 mL of DCM. Compound **2d** (256.2 mg, 1.5 mmol) and DCM (0.5 mL) were added into Schlenk tube **A** sequentially. The resulting mixture was stirred at room temperature for 48 h as monitored by TLC. A saturated aqueous solution of NH₄Cl (20 mL) was added and the resulting mixture was extracted with DCM (3×20 mL). The combined organic layer was washed with brine (20 mL) and dried over anhydrous Na₂SO₄. After evaporation, the residue was dissolved in MeOH (20 mL) and AcOH (2 mL) and cooled to 0 °C. Na(BH₃)CN (63.7 mg, 1.0 mmol) was added sequentially. The resulting mixture was stirred at room temperature for 3 h as monitored by TLC, quenched with a saturated aqueous solution of Na₂CO₃, and extracted with ethyl acetate (3×20 mL). The combined organic layer was washed with brine (20 mL) and

dried over anhydrous Na_2SO_4 . After evaporation, the residue was purified by silica gel column chromatography to afford **4** (209.5 mg, 73%, purity 90%) (eluent: petroleum ether/diethyl ether = 30/1) as an oil: ^1H NMR (400 MHz, CDCl_3) δ 7.29 (d, J = 6.8 Hz, 1 H, Ar-H), 7.23-7.12 (m, 4 H, Ar-H), 7.01 (t, J = 7.8 Hz, 1 H, Ar-H), 6.74 (t, J = 7.2 Hz, 1 H, Ar-H), 6.60 (d, J = 7.6 Hz, 1 H, Ar-H), 5.06 (quint, J = 7.2 Hz, 1 H, =CH), 4.96 (s, 1 H, CH), 4.68-4.57 (m, 2 H, =CH₂), 4.25 (brs, 1 H, NH), 3.32 (s, 2 H, CH_2), 2.65-2.43 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ 209.9, 149.7, 144.0, 142.0, 135.2, 128.1, 127.9, 127.0, 124.9, 123.9, 123.7, 119.2, 110.5, 86.0, 74.2, 71.6, 57.5, 44.4, 38.9; MS (EI, 70 eV) m/z (%) 259 (M^+ , 41.89), 205 (100); IR (neat, cm^{-1}): 3378, 3045, 3023, 2983, 2900, 2843, 1952, 1650, 1605, 1481, 1462, 1436, 1392, 1315, 1297, 1256, 1237, 1199, 1179, 1151, 1099, 1020; HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{18}\text{N}$ ($\text{M}+\text{H}$)⁺: 260.1434, Found: 260.1444.

16. Gram scale of **4a-(buta-2,3-dienyl)-2,3,4a-tetrahydro-1*H*-carbazole (3j, zyz-4-104)**

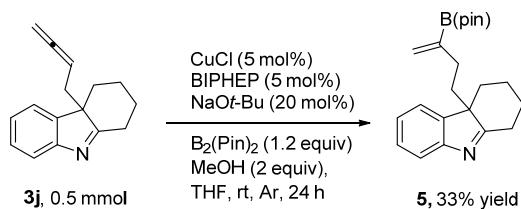


According to **Typical Procedure I**, the reaction of **1j** (1.0279 g, 6.0 mmol), *t*-BuOK (742.1 mg, 6.6 mmol), DCM (12 mL), Et_3B (1 M in THF, 12.0 mL, 12.0 mmol), Pd₂(dba)₃ (138.5 mg, 0.15 mmol), DPEphos (177.1 mg, 0.33 mmol), DCM (12 mL+3 mL), and **2d** (1.5330 g, 9.0 mmol)/DCM (3 mL) afforded **3j** (1.2813 g, 96%) (eluent: petroleum ether/ethyl acetate = 10/1) as an oil: ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, J = 8.0 Hz, 1 H, Ar-H), 7.35-7.26 (m, 2 H, Ar-H), 7.17 (t, J = 7.4 Hz, 1 H, Ar-H), 4.59-4.40 (m, 3 H, HC=C=CH₂), 2.94-2.83 (m, 1 H, one proton of CH_2), 2.61-2.51 (m, 3 H, CH_2 and one proton of CH_2), 2.40-2.33 (m, 1 H, one proton of CH_2), 2.23-2.13 (m, 1 H, one proton of CH_2), 1.87-1.72 (m, 1 H, one proton of CH_2), 1.71-1.63 (m, 1 H, one proton of CH_2), 1.49-1.35 (m, 1 H, one proton of CH_2), 1.16 (td, J_1 = 13.5 Hz, J_2 = 4.3 Hz, 1 H, one

proton of CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 209.2, 188.5, 154.8, 144.1, 127.5, 124.5, 121.6, 119.9, 83.7, 74.4, 57.7, 36.7, 32.6, 29.9, 28.6, 20.9.

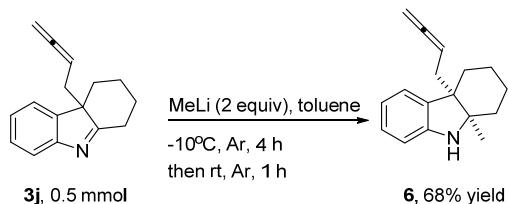
Synthetic applications

17. 4a-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl)-2,3,4,4a-tetrahydro-1*H*-carbazole⁶ (**5**, zyz-4-125)



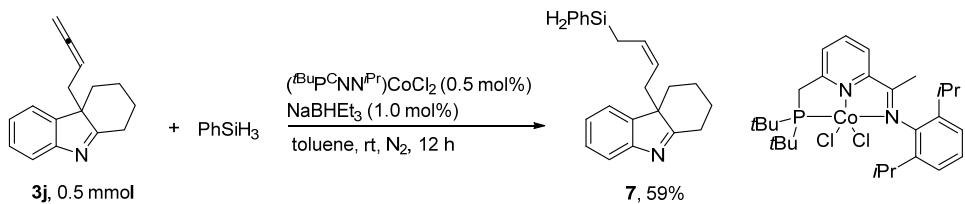
To an oven-dried Schlenk tube were added sequentially bis(pinacolato)diboron (152.9 mg, 0.6 mmol), BIPHEP (13.2 mg, 0.025 mmol), CuCl (2.7 mg, 0.025 mmol), NaO-*t*-Bu (9.5 mg, 0.1 mmol), **3j** (111.9 g, 0.5 mmol), MeOH (40μL, d = 0.7915 g/cm³, 32.0 mg, 1.0 mmol), and THF (2 mL) under argon. The resulting mixture was stirred at room temperature for 24 h as monitored by TLC. Upon completion, the resulting mixture was filtered through a short column of silica gel eluted with Et₂O (10 mL×3) and concentrated. The residue was purified by chromatography on silica gel to afford **5** (64.1 mg, 33%, purity 90%) (eluent: petroleum ether/ ethyl acetate = 5/1) as an oil: ¹H NMR (400 MHz, CDCl₃) δ 7.59 (d, *J* = 7.2 Hz, 1 H, Ar-H), 7.35-7.27 (m, 2 H, Ar-H), 7.19 (t, *J* = 7.4 Hz, 1 H, Ar-H), 5.64 (d, *J* = 3.6 Hz, 1 H, one proton of =CH₂), 5.41 (s, 1 H, one proton of =CH₂), 2.94-2.81 (m, 1 H, one proton of CH₂), 2.76-2.60 (m, 1 H, one proton of CH₂), 2.40-2.27 (m, 1 H, one proton of CH₂), 2.26-2.10 (m, 2 H, CH₂), 1.98-1.76 (m, 2 H, one proton of CH₂), 1.72-1.60 (m, 1 H, one proton of CH₂), 1.57-1.37 (m, 3 H, CH₂ and one proton of CH₂), 1.25 (s, 12 H, 4×CH₃), 1.20-1.06 (m, 1 H, one proton of CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 189.7, 155.1, 144.9, 129.2, 127.3, 124.6, 121.6, 120.0, 83.3, 58.2, 38.3, 33.5, 29.8, 29.0, 24.8, 24.7, 21.2; MS (EI, 70 eV) *m/z* (%) 351 (M⁺, 95.41), 171 (100); IR (neat, cm⁻¹): 3059, 2976, 2931, 2859, 1718, 1615, 1581, 1466, 1454, 1441, 1422, 1389, 1368, 1309, 1259, 1204, 1165, 1139, 1110, 1056, 1012; HRMS (ESI) Calcd for C₂₂H₃₁BNO₂ (M+H)⁺: 351.2479, Found: 351.2479.

18. *cis*-4a-(Buta-2,3-dien-1-yl)-9a-methyl-2,3,4,4a,9,9a-hexahydro-1*H*-carbazole⁷ (6, zyz-4-117)



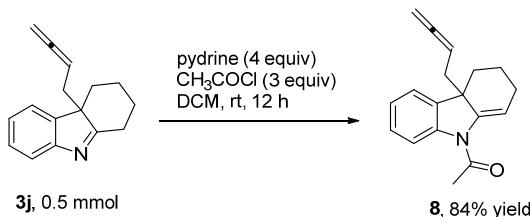
To an oven-dried Schlenk tube were added sequentially **3j** (111.9 mg, 0.5 mmol) and toluene (1.5 mL) under argon. The resulting mixture was cooled at -10 °C. MeLi (1.6 M in Et₂O, 0.63 mL, 1 mmol) was added dropwise within 3 minutes. The resulting mixture was stirred at -10 °C for 4 h and room temperature for 1 h. Upon completion, the mixture was hydrolyzed with a 1:1 mixture of toluene:water (6 mL). The organic layer was separated. The aqueous phase was extracted with ethyl acetate (5 mL×3). The combined organic layer was washed with brine (10 mL) and dried over anhydrous Na₂SO₄. The solvent was evaporated and the residue was purified by column chromatography affording **6** (85.5 mg, 68%, purity 95%) (eluent: petroleum ether/ ethyl acetate = 20/1) as an oil: ¹H NMR (400 MHz, CDCl₃) δ 7.07-6.98 (m, 2 H, Ar-H), 6.74 (t, *J* = 7.4 Hz, 1 H, Ar-H), 6.62 (d, *J* = 7.6 Hz, 1 H, Ar-H), 4.92-4.82 (m, 1 H, =CH), 4.60-4.44 (m, 2 H, =CH₂), 3.41 (brs, 1 H, NH), 2.38-2.26 (m, 1 H, one proton of CH₂), 2.24-2.15 (m, 1 H, one proton of CH₂), 2.03-1.93 (m, 1 H, one proton of CH₂), 1.58-1.43 (m, 4 H, 2×CH₂), 1.43-1.18 (m, 6 H, CH₃, CH₂ and one proton of CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 209.6, 149.2, 134.2, 127.2, 123.8, 118.2, 110.5, 86.3, 73.3, 66.3, 49.8, 38.7, 36.3, 29.7, 22.8, 22.3, 19.9; MS (EI, 70 eV) *m/z* (%) 239 (M⁺, 14.32), 186 (100); IR (neat, cm⁻¹): 3348, 3049, 2986, 2926, 2852, 1953, 1606, 1479, 1460, 1441, 1377, 1340, 1322, 1248, 1201, 1161, 1128, 1105, 1062, 1033, 1018; HRMS (ESI) Calcd for C₁₇H₂₂N (M+H)⁺: 240.1747, Found: 240.1753.

19. (*Z*)-4a-(4-(phenylsilyl)but-2-en-1-yl)-2,3,4,4a-tetrahydro-1*H*-carbazole⁸ (7, zyz-4-118)



In a glove box, (*t*BuP(*C*NN*i*Pr)*CoCl*₂ (1.4 mg, 0.0025 mmol), **3j** (111.7 mg, 0.5 mmol), toluene (0.5 mL), PhSiH₃ (62 μ L, d = 0.88 g/mL, 54.6 mg, 0.5 mmol), and NaBHET₃ (1.0 M in THF, 5 μ L, 0.005 mmol) were sequentially added to a 10 mL flame-dried Schlenk tube equipped with a magnetic stir bar at room temperature. After 12 h, the solvent was then removed in vacuo. The residue was purified by chromatography on silica gel to afford **7** (97.6 mg, 59%) (eluent: petroleum ether/ethyl acetate = 6/1) as an oil: ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, *J* = 7.6 Hz, 1 H, Ar-H), 7.52 (d, *J* = 6.8 Hz, 1 H, Ar-H), 7.42-7.27 (m, 4 H, Ar-H), 7.24 (d, *J* = 6.8 Hz, 1 H, Ar-H), 7.14 (t, *J* = 7.4 Hz, 1 H, Ar-H), 5.39-5.29 (m, 1 H, =CH), 4.66-4.57 (m, 1 H, =CH), 4.23 (s, 2 H, SiH₂), 2.82 (d, *J* = 12.8 Hz, 1 H, one proton of CH₂), 2.49-2.37 (m, 3 H, CH₂ and one proton of CH₂), 2.31 (d, *J* = 13.2 Hz, 1 H, one proton of CH₂), 2.13 (d, *J* = 12.8 Hz, 1 H, one proton of CH₂), 1.81-1.62 (m, 4 H, 2 \times CH₂), 1.44-1.32 (m, 1 H, one proton of CH₂), 1.11 (td, *J*₁ = 13.4 Hz, *J*₂ = 4.3 Hz, 1 H, one proton of CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 189.0, 154.8, 144.7, 135.1, 131.7, 129.7, 127.9, 127.5, 126.8, 124.6, 122.3, 121.7, 119.9, 57.3, 37.0, 30.3, 29.9, 28.8, 21.2, 12.2; MS (EI, 70 eV) *m/z* (%) 331 (M⁺, 44.48), 107 (100); IR (neat, cm⁻¹): 3047, 3016, 2931, 2859, 2132, 1612, 1580, 1466, 1454, 1428, 1413, 1392, 1336, 1310, 1207, 1188, 1150, 1116, 1094, 1052, 1014; HRMS (ESI) Calcd for C₂₂H₂₆NSi (M+H)⁺: 332.1829, Found: 332.1845.

20. 1-(4a-(Buta-2,3-dien-1-yl)-2,3,4,4a-tetrahydro-9*H*-carbazol-9-yl)ethan-1-one⁵ (**8**, zyz-4-113)



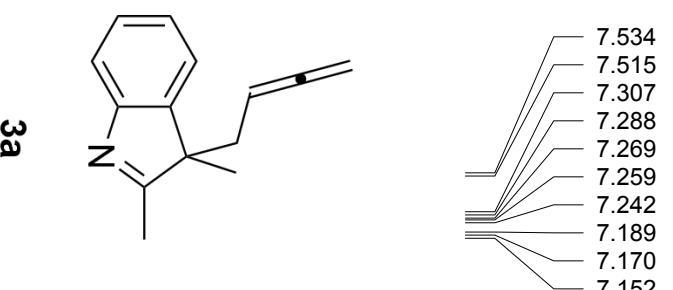
To a schlenk tube were added sequentially **3j** (112.3 mg, 0.5 mmol), DCM (4 mL), CH₃COCl (0.11 mL, d = 1.104 g/cm³, 121.4 mg, 1.5 mmol), and pyridine (0.16 mL, d =

0.9819 g/cm³, 157.1 mg, 2.0 mmol) equipped with a magnetic stir bar. The mixture was stirred at room temperature for 12 h as monitored by TLC. Upon completion, a saturated aqueous solution of NaHCO₃ (10 mL) was added and the resulting mixture was extracted with DCM (3×10 mL). The combined organic layer was washed with brine (10 mL) and dried over anhydrous Na₂SO₄. After filtration and evaporation, the residue was purified via silica gel column chromatography to afford **8** (111.5 mg, 84%) (eluent: petroleum ether/ethyl acetate = 10/1) as an oil: ¹H NMR (400 MHz, CDCl₃) δ 8.04 (brs, 1 H, Ar-H), 7.21 (t, *J* = 8.2 Hz, 1 H, Ar-H), 7.14-7.01 (m, 2 H, Ar-H), 5.47 (brs, 1 H, =CH), 4.76 (quint, *J* = 7.4 Hz, 1 H, =CH), 4.56-4.47 (m, 2 H, CH₂), 2.39 (s, 3 H, CH₃), 2.39-2.15 (m, 5 H, one proton of CH₂ and 2×CH₂), 1.97-1.75 (m, 2 H, one proton of CH₂ and one proton of another CH₂), 1.51 (td, *J*₁ = 13.3 Hz, *J*₂ = 4.1 Hz, 1 H, one proton of CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 209.6, 168.3, 145.8, 141.8, 136.9, 127.4, 123.8, 122.3, 116.9, 112.4, 84.5, 73.9, 45.1, 37.9, 28.6, 24.1, 23.4, 17.3; MS (EI, 70 eV) *m/z* (%) 265 (M⁺, 23.58), 222 (100); IR (neat, cm⁻¹): 2937, 2837, 1952, 1663, 1600, 1473, 1460, 1433, 1376, 1339, 1308, 1274, 1224, 1196, 1175, 1122, 1100, 1015; HRMS (ESI) Calcd for C₁₈H₂₀NO (M+H)⁺: 266.1539, Found: 266.1546.

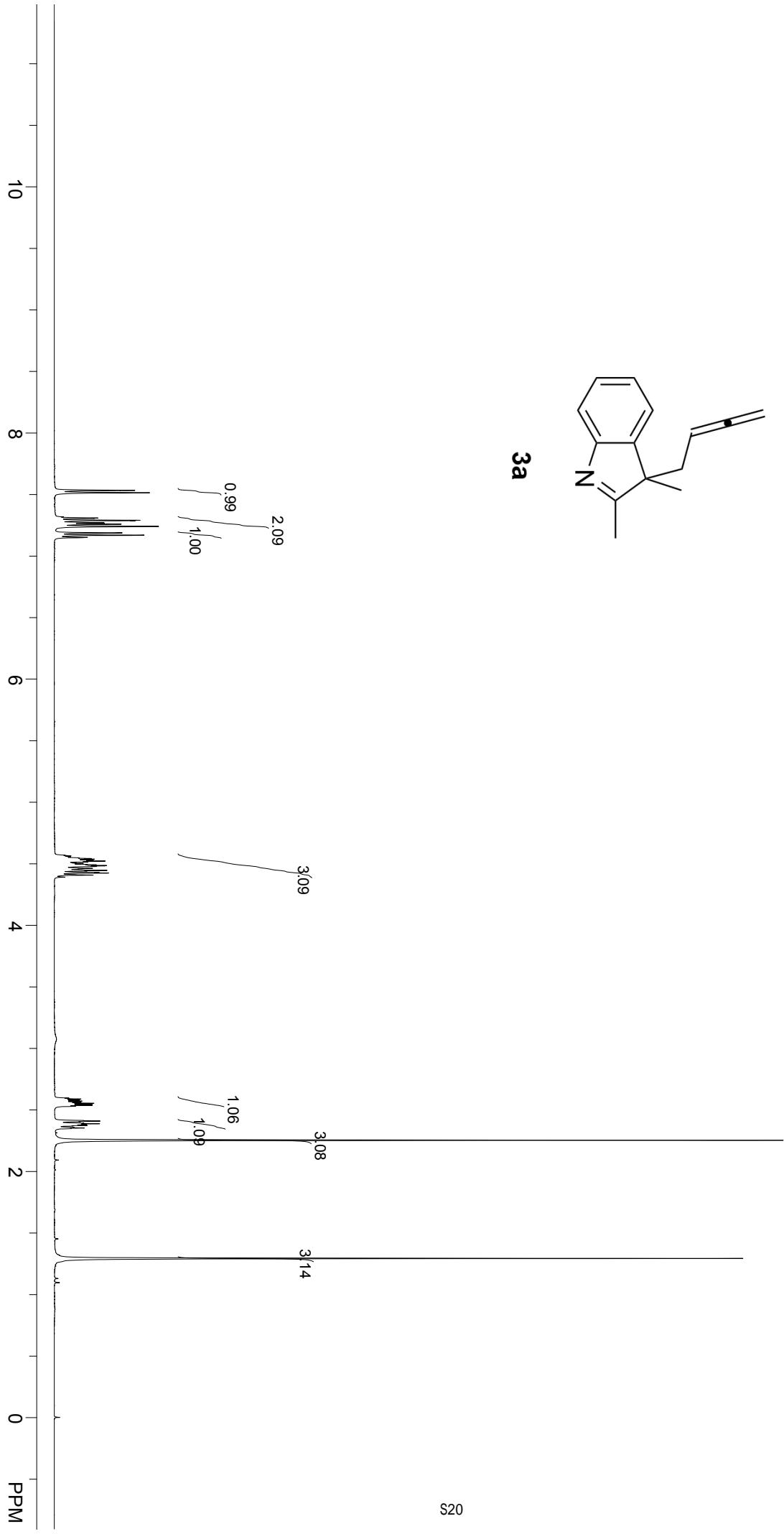
References:

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2. (a) H. Luo and Ma, S. *Eur. J. Org. Chem.* **2013**, 3041. (b) H. Luo, D. Ma, and S. Ma, *Org. Synth.* **2017**, *94*, 153.
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4. M. V. Vita, P. Caramenti, and J. Waser, *Org. Lett.*, **2015**, *17*. 5832.
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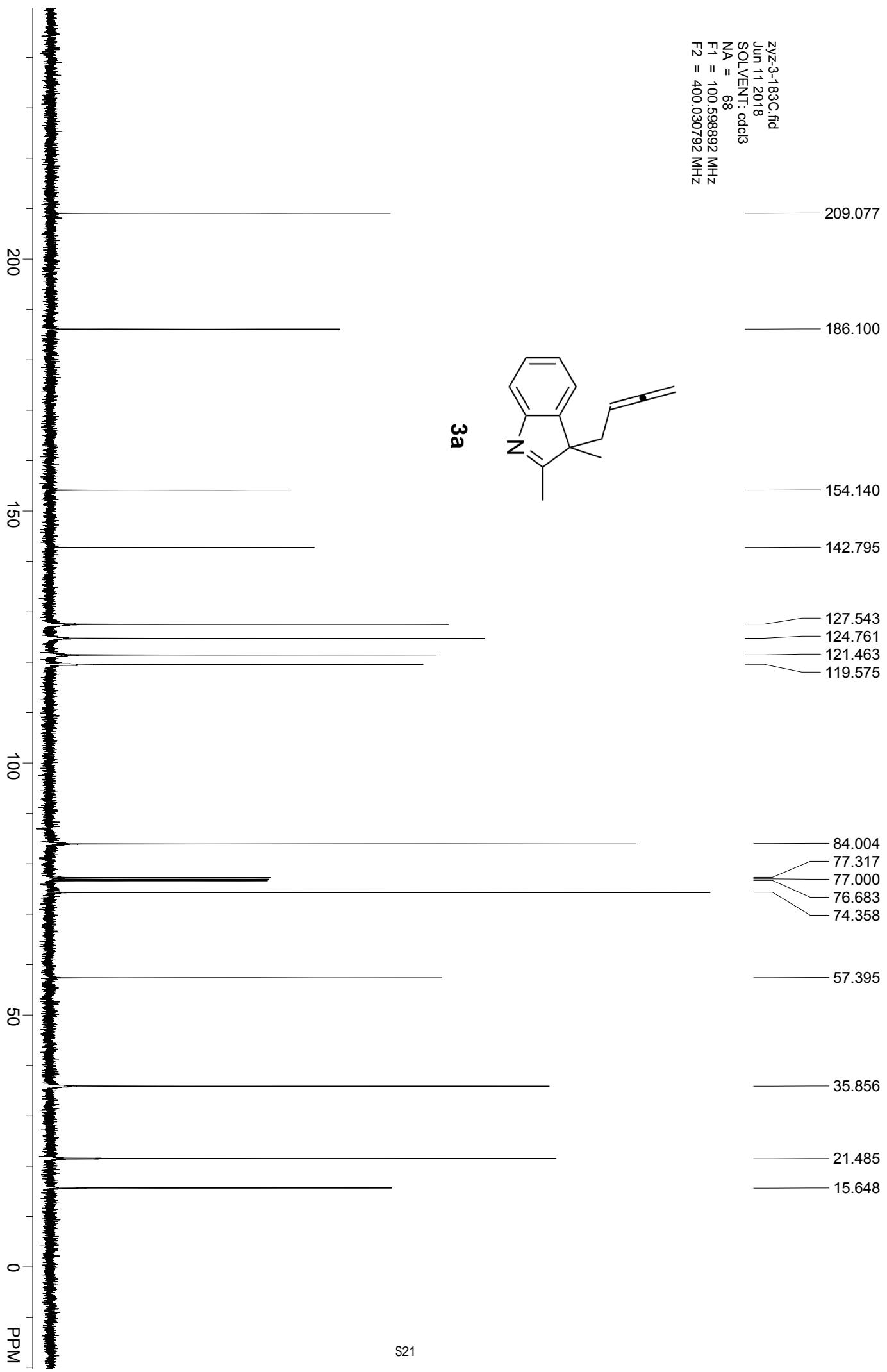
zyz-3-183H.fid
Jun 11 2018
SOLVENT: CDCl₃
NA = 4
F1 = 400.031616 MHz
F2 = 100.596855 MHz

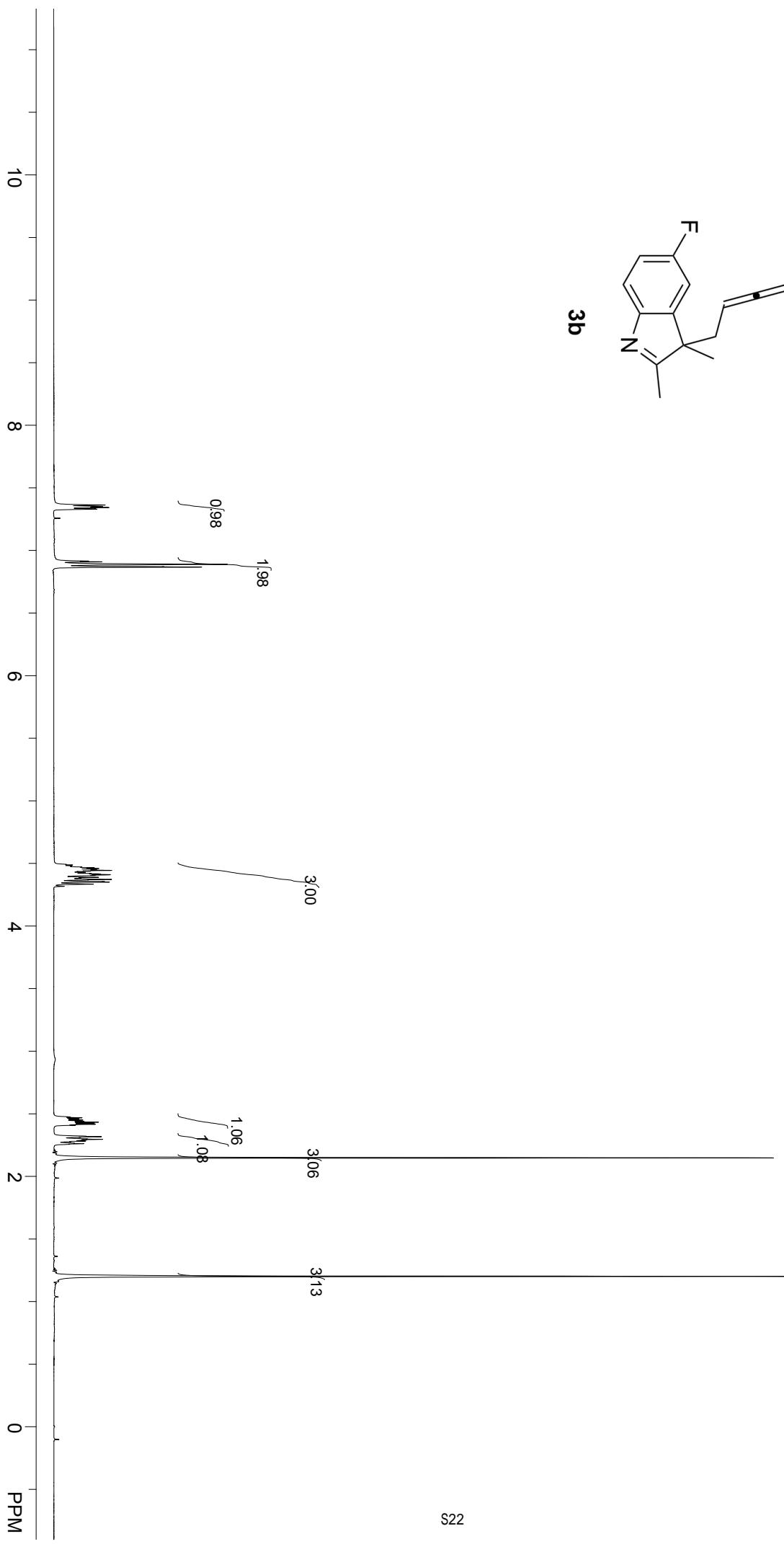
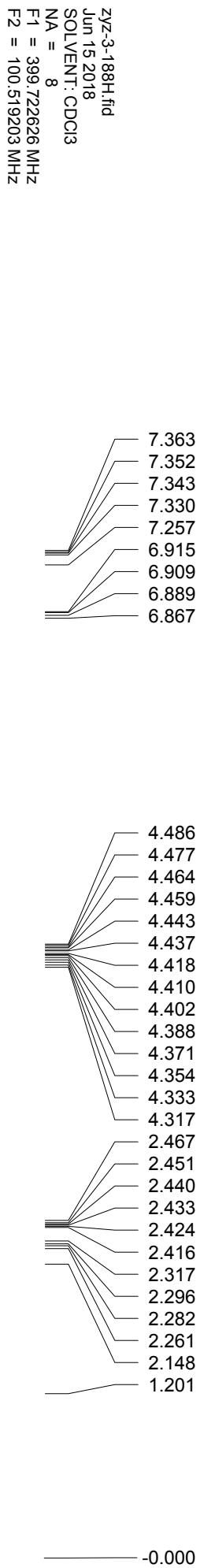


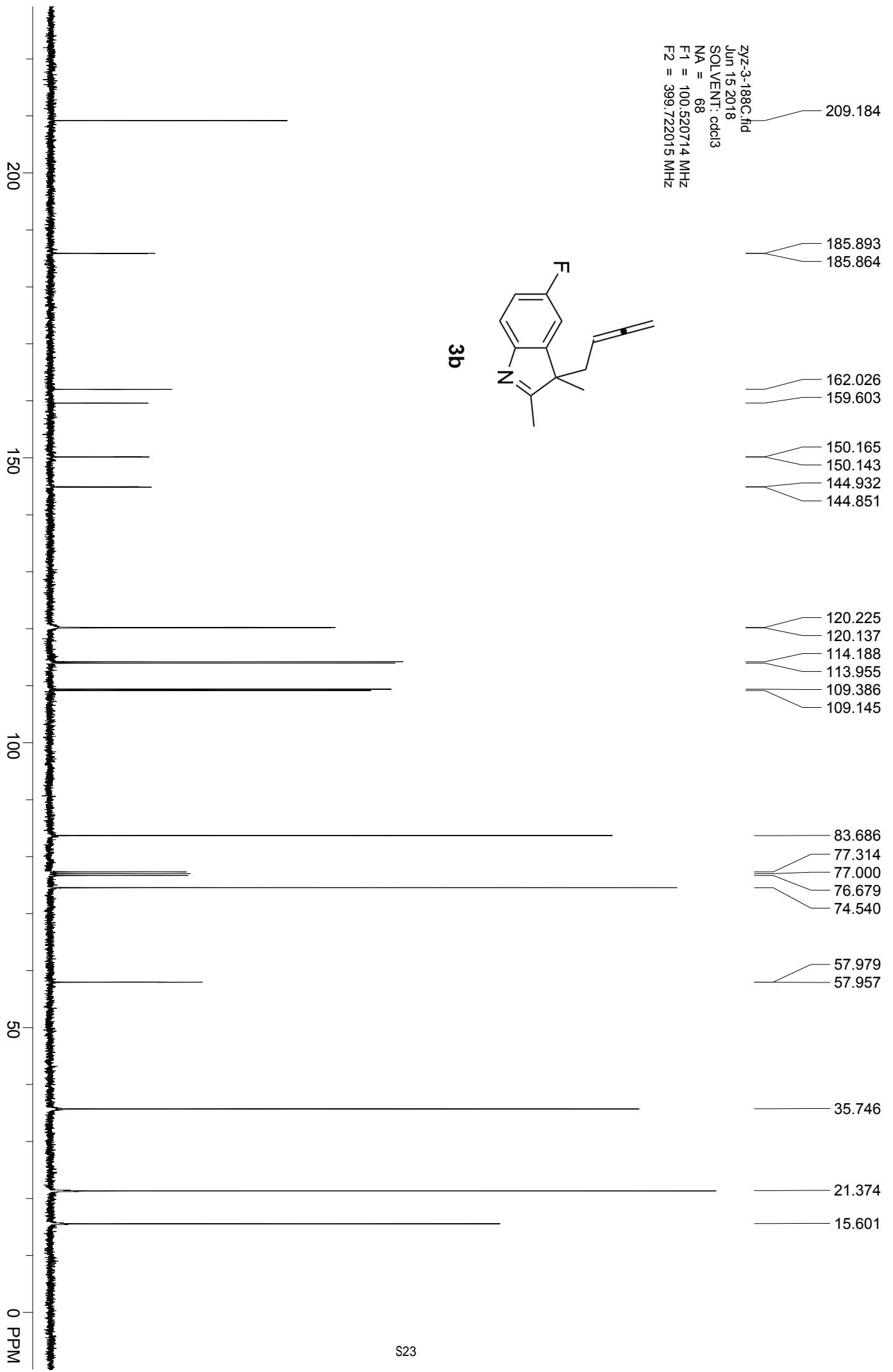
7.534
7.515
7.307
7.288
7.269
7.259
7.242
7.189
7.170
7.152
4.565
4.558
4.543
4.522
4.516
4.491
4.484
4.463
4.447
4.442
4.425
4.409
4.392
2.589
2.580
2.562
2.554
2.546
2.537
2.530
2.409
2.387
2.374
2.353
2.253
1.292



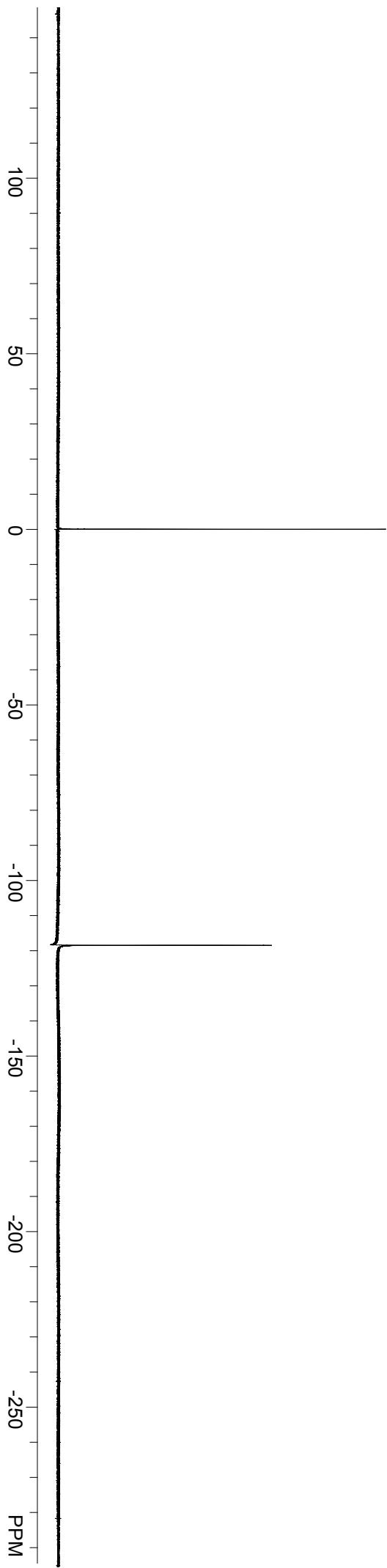
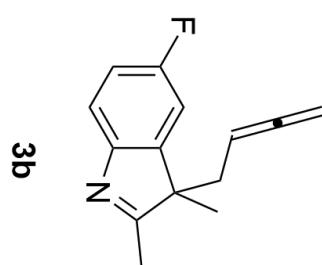
zyz-3-183C.fid
Jun 11 2018
SOLVENT: *cdcl*3
NA = 68
F1 = 100.598892 MHz
F2 = 400.030792 MHz



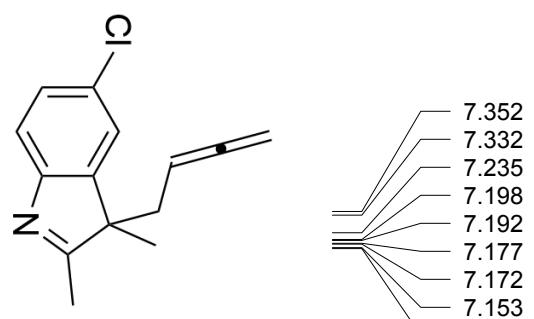




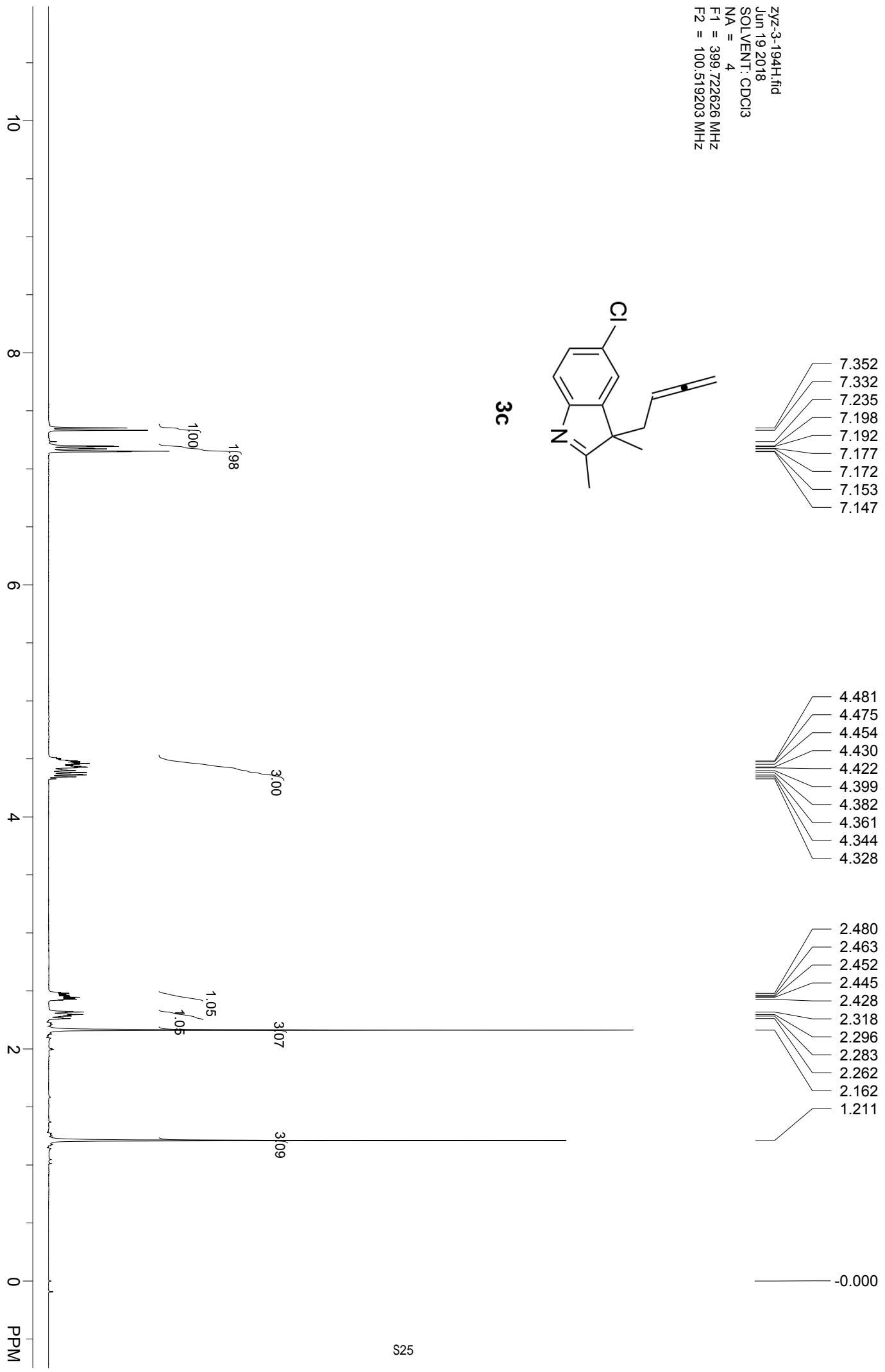
ZYZ-3-188F.fid
Jun 15 2018
SOLVENT: CDCl₃
NA = 4
F1 = 376.085358 MHz
F2 = 100.519203 MHz



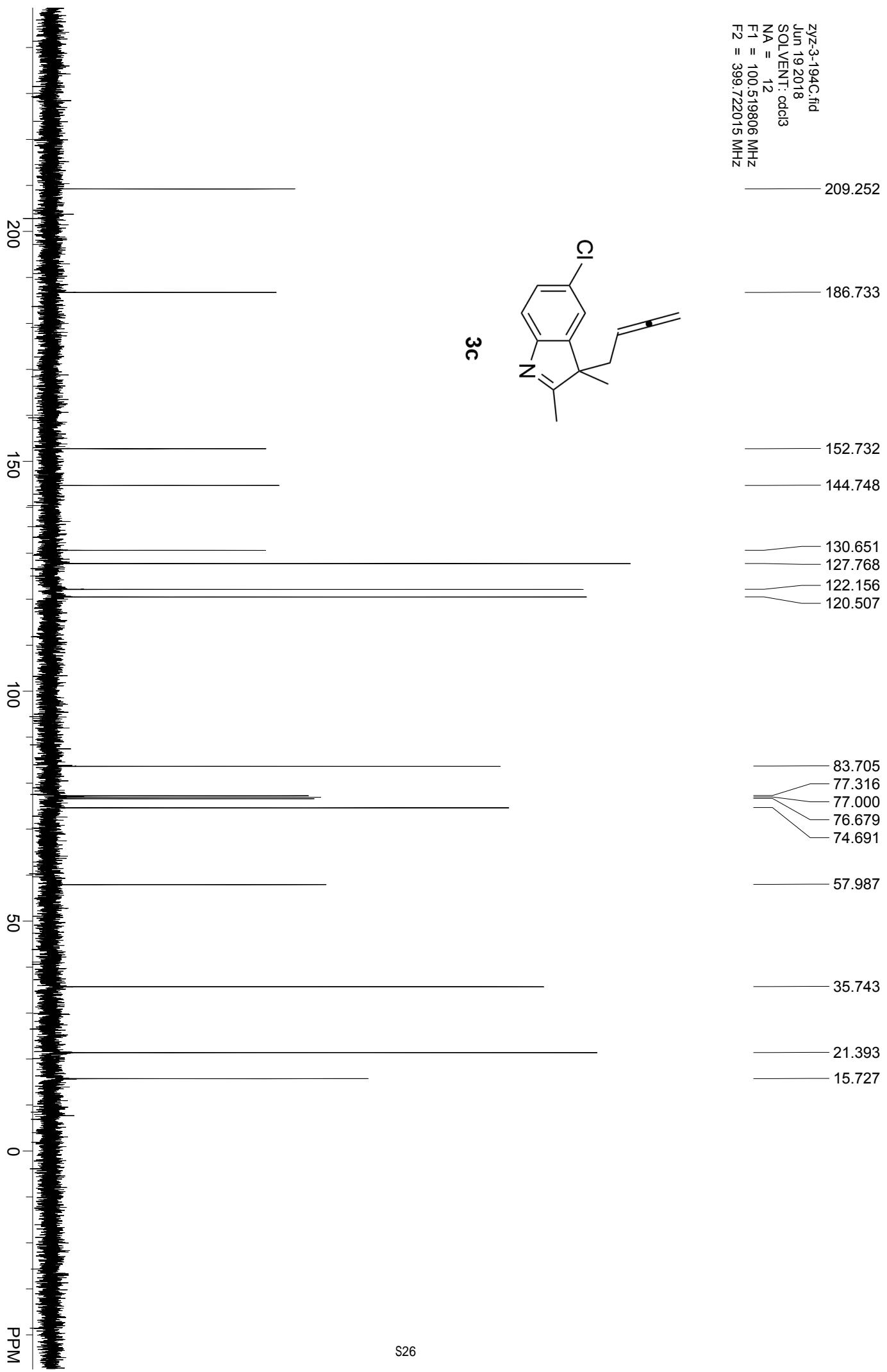
zyz-3-194H.fid
Jun 19 2018
SOLVENT: CDCl₃
NA = 4
F1 = 399.722626 MHz
F2 = 100.519203 MHz



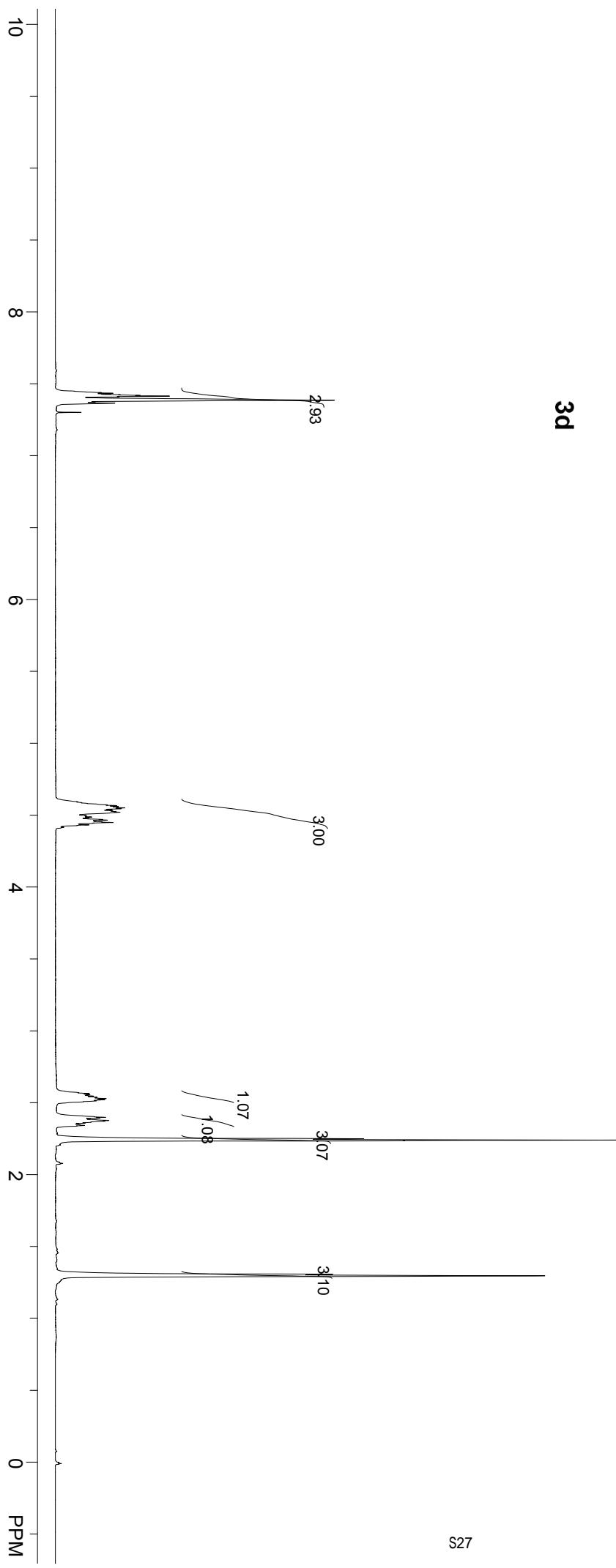
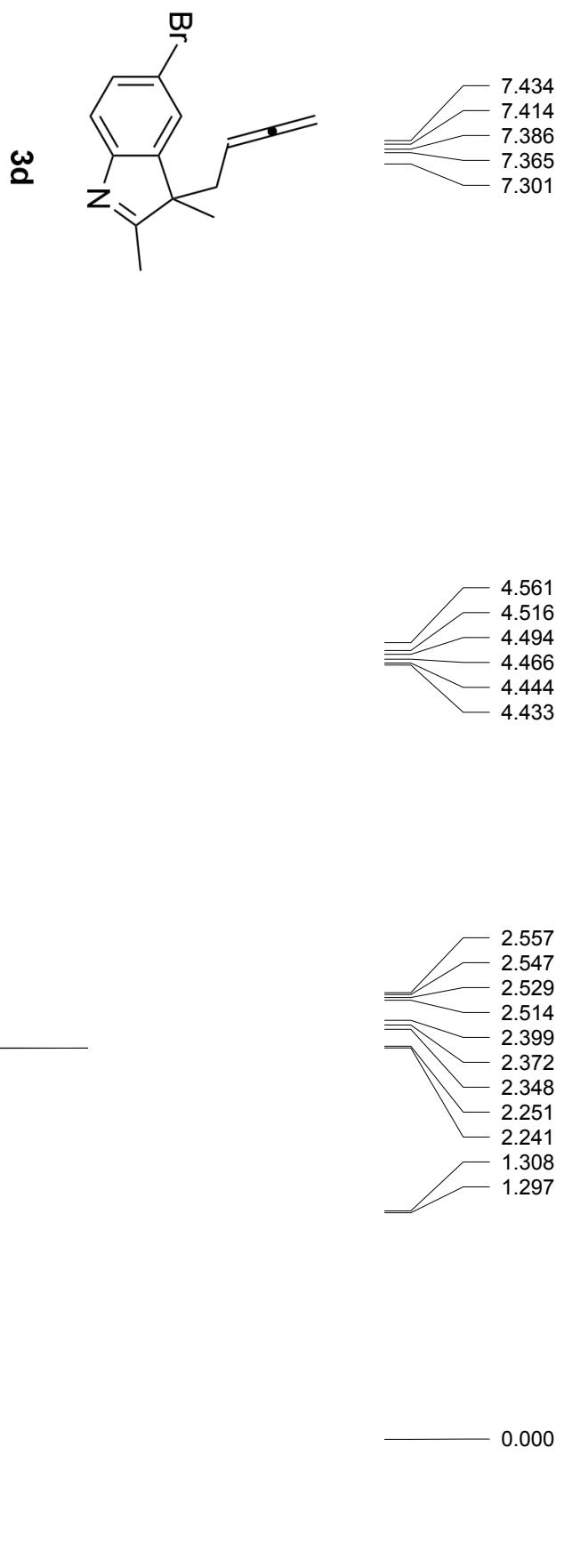
3c



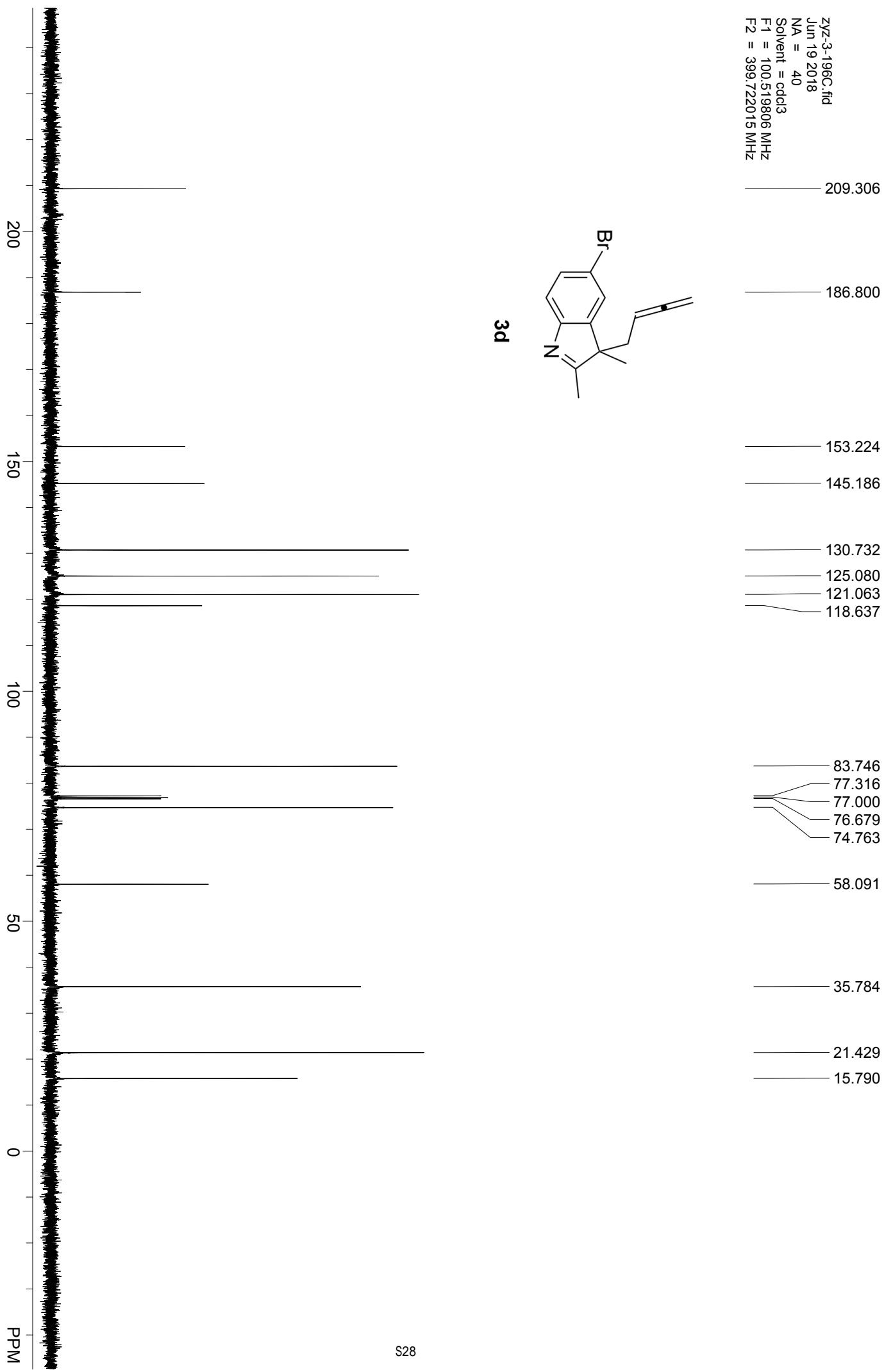
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Jun 19 2018
SOLVENT: cdcl3
NA = 12
F1 = 100.519806 MHz
F2 = 399.722015 MHz

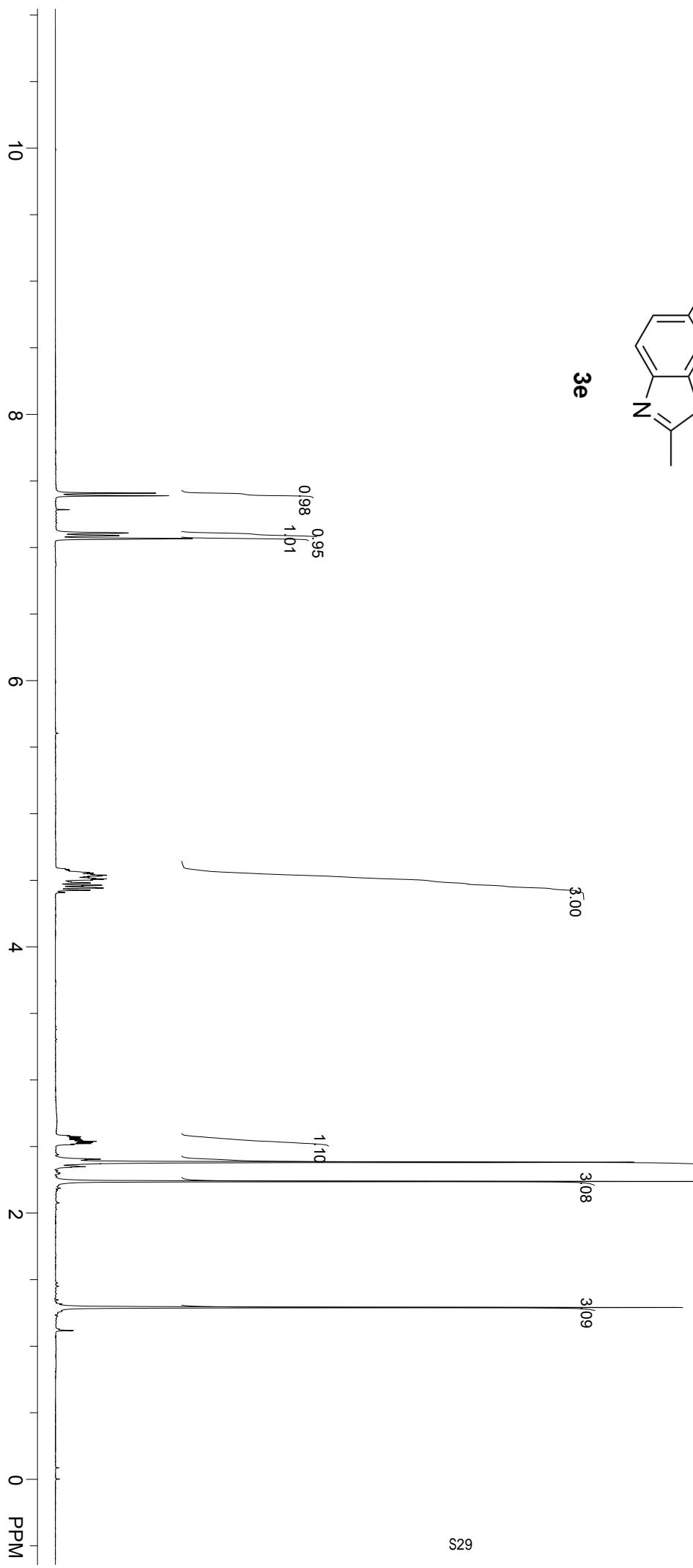
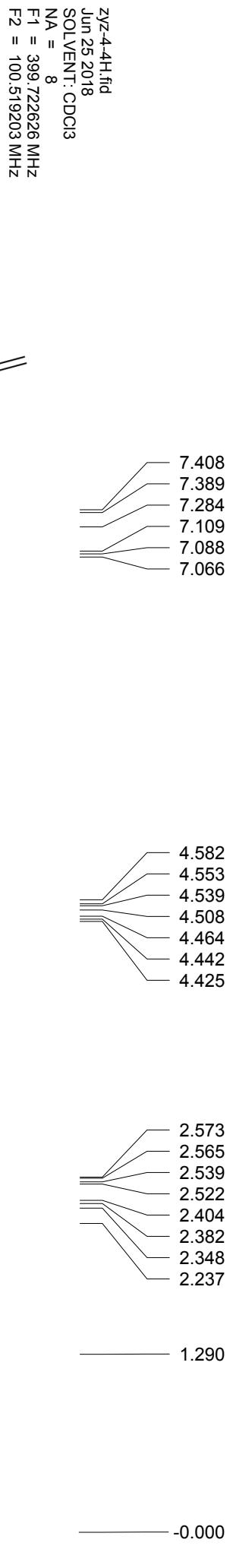


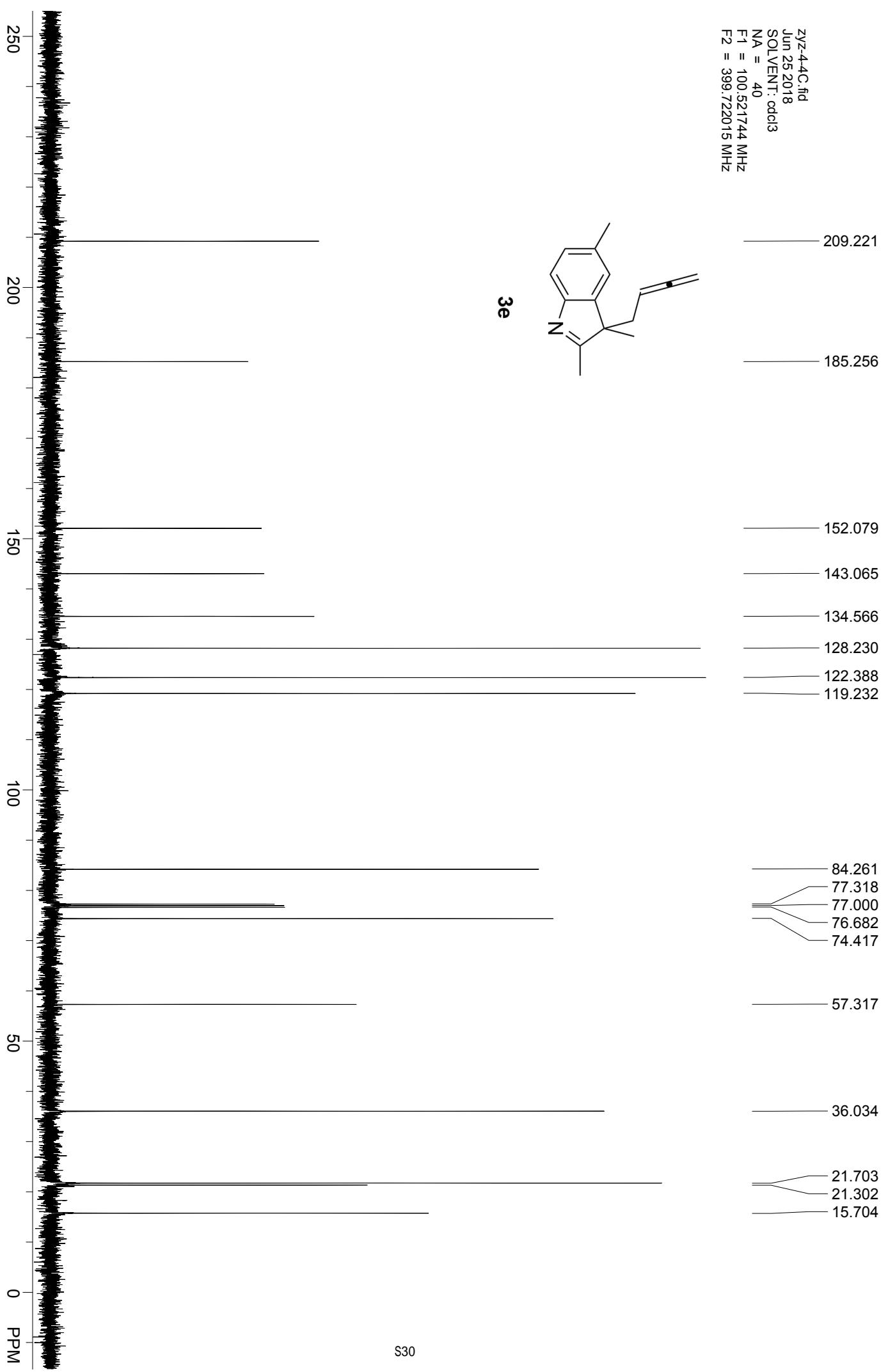
zyz-3-196H.fid
Jun 19 2018
SOLVENT: CDCl₃
NA = 8
F1 = 399.722626 MHz
F2 = 100.519203 MHz



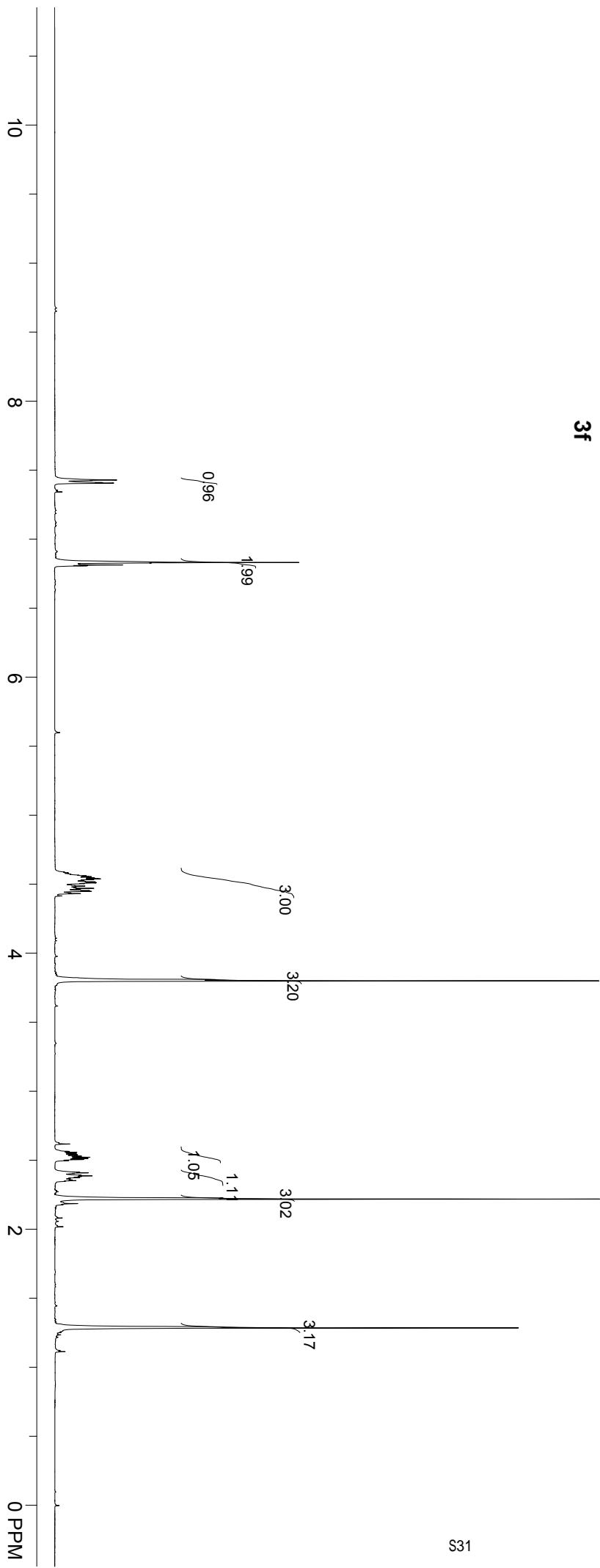
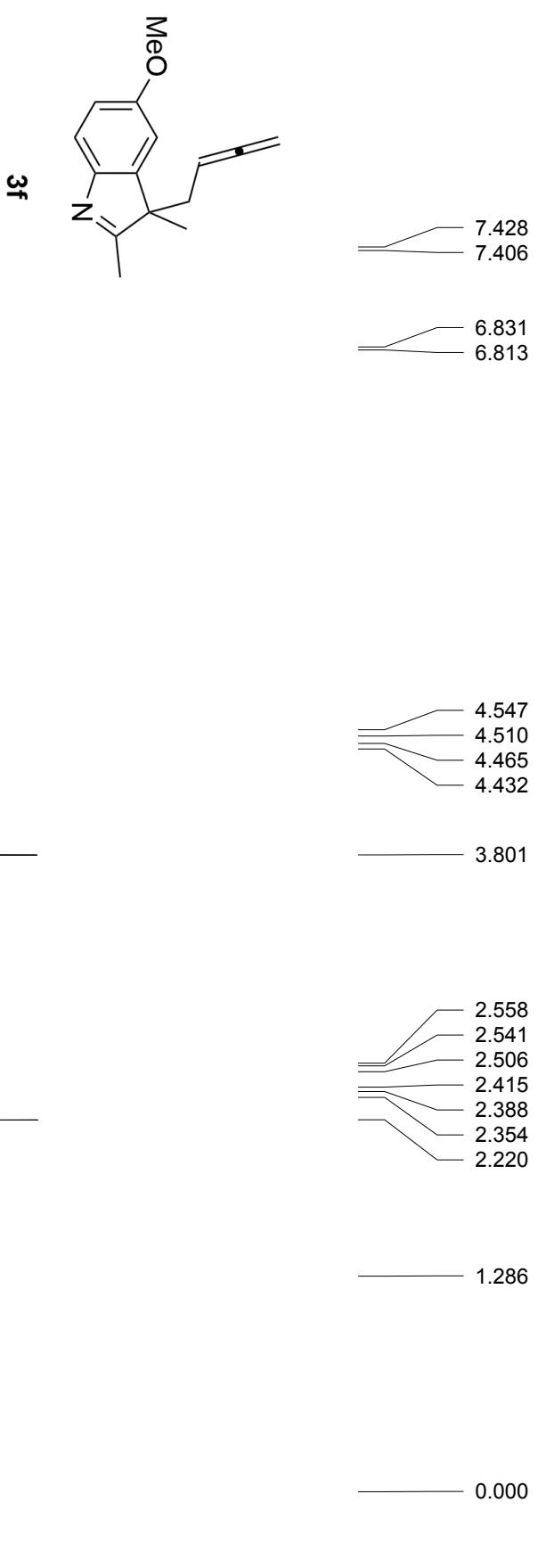
zyz-3-196C.fid
Jun 19 2018
NA = 40
Solvent = cdcl₃
F1 = 100.51906 MHz
F2 = 399.722015 MHz



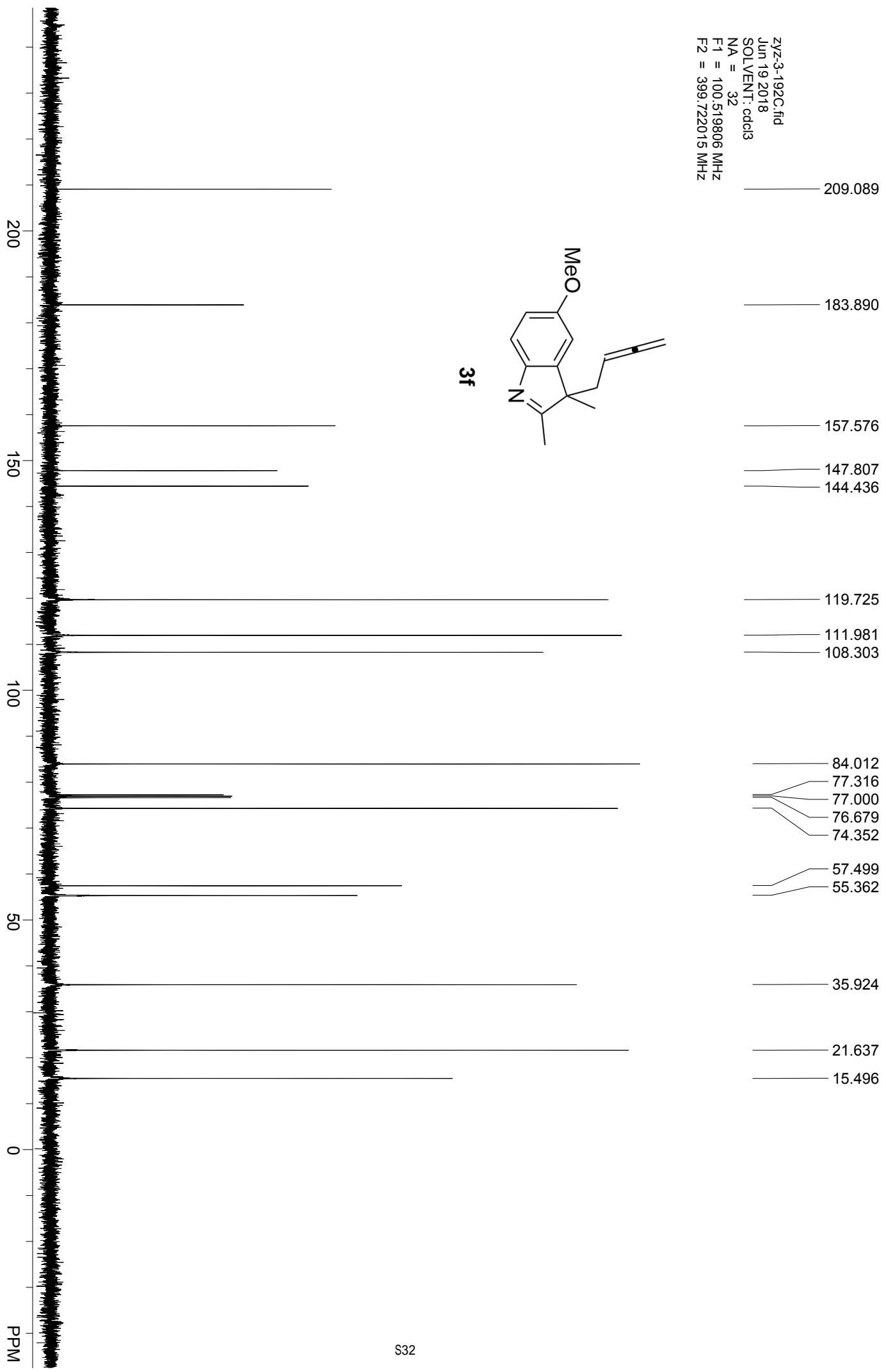


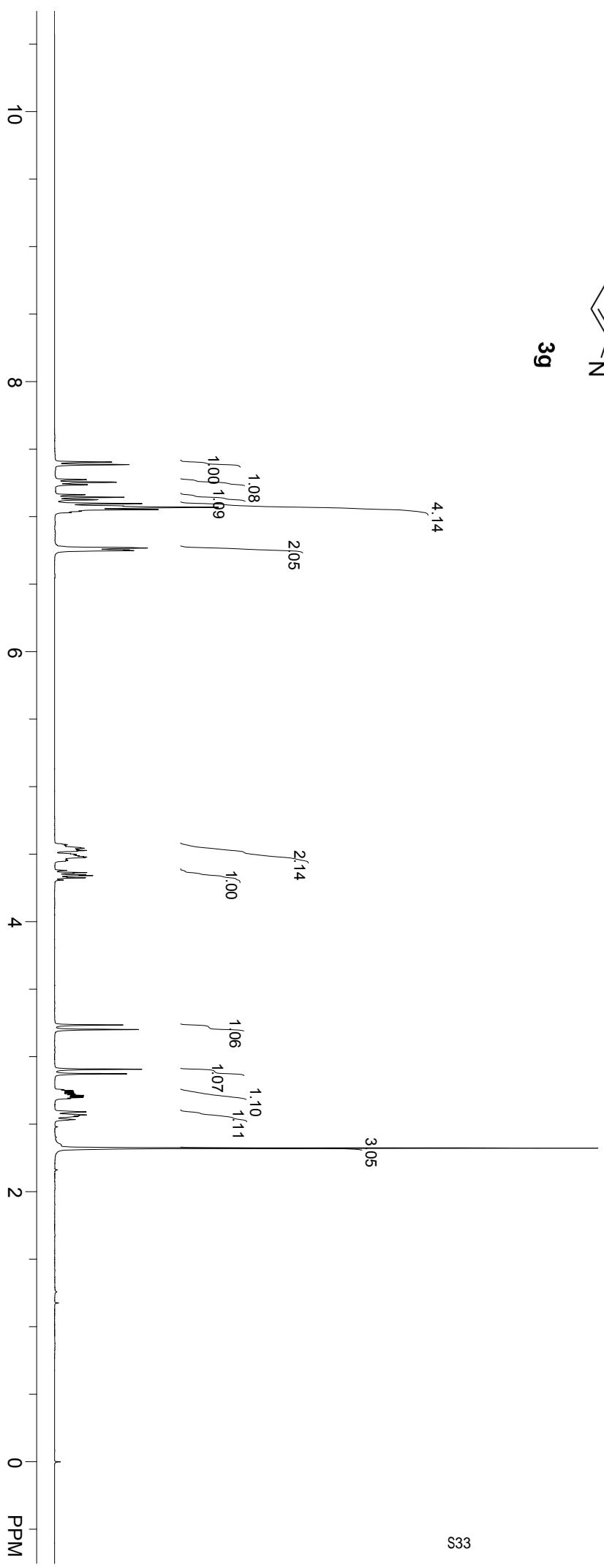
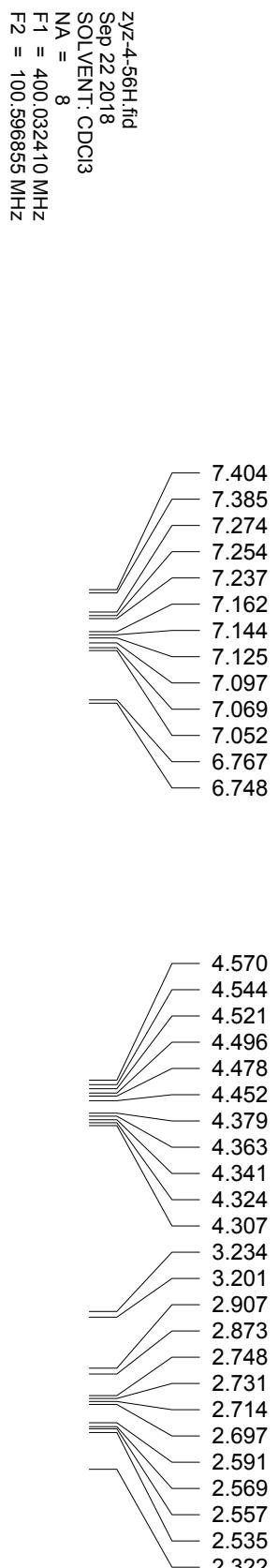


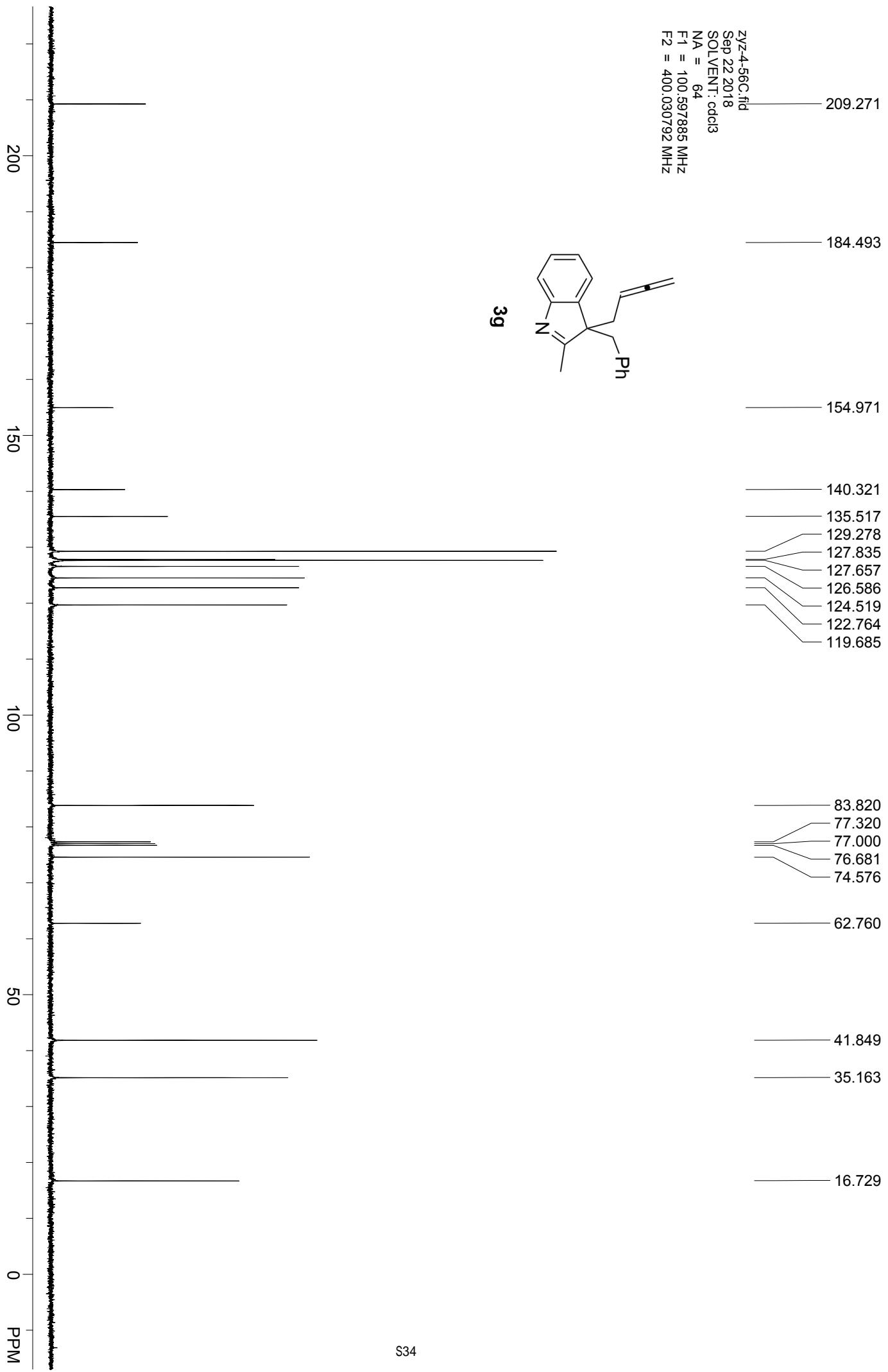
zyz-3-192H.fid
Jun 19 2018
SOLVENT: CDCl₃
NA = 12
F₁ = 399.722626 MHz
F₂ = 100.519203 MHz



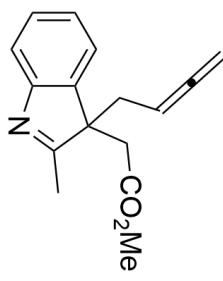
zyz-3-192C.fid
Jun 19 2018
SOLVENT: cdcl₃
NA = 32
F1 = 100.519806 MHz
F2 = 399.722015 MHz



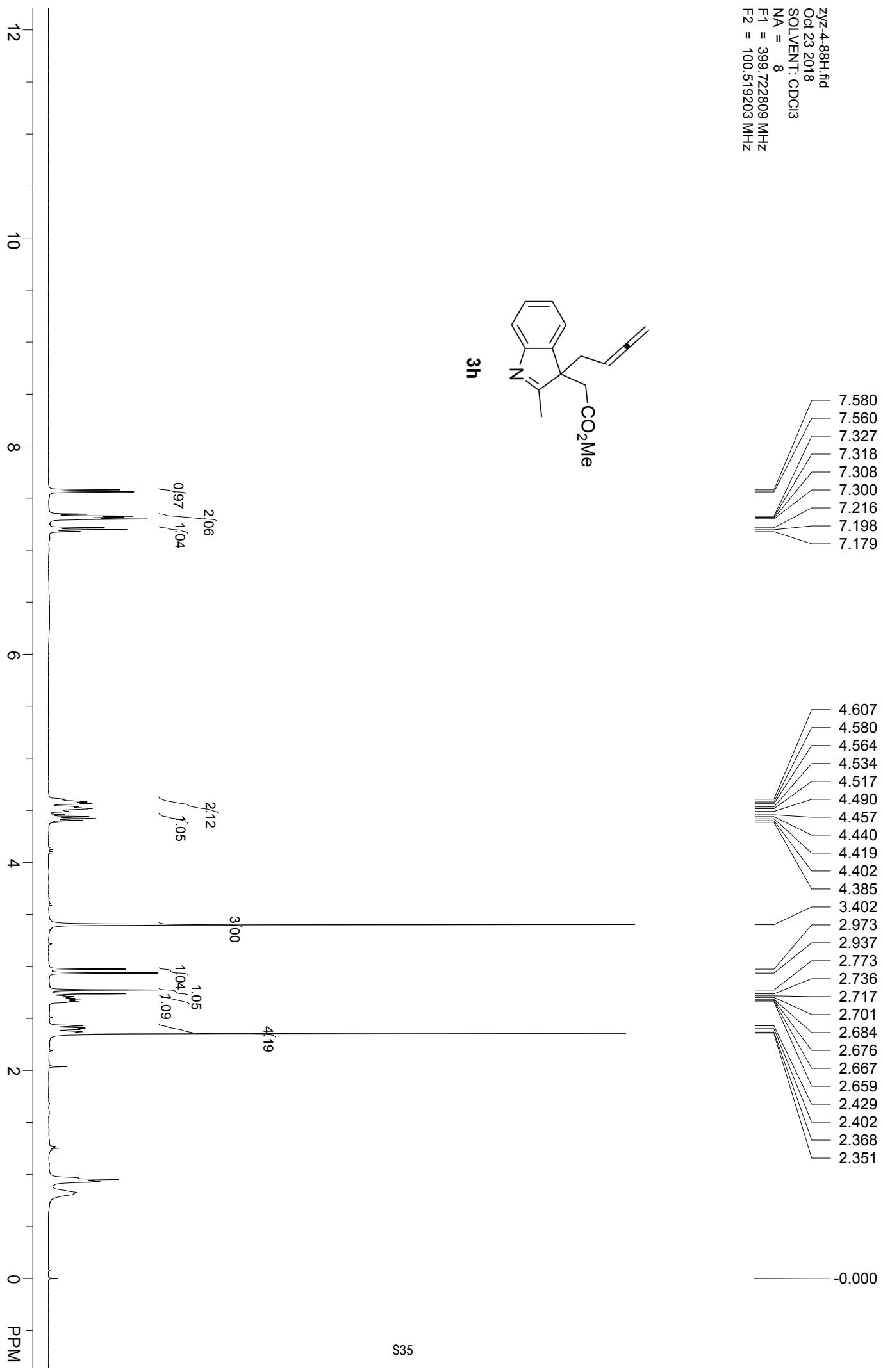




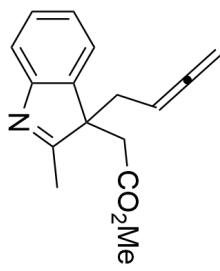
ZVZ-4-88H.fid
Oct 23 2018
SOLVENT: CDCl₃
NA = 8
F1 = 399.722809 MHz
F2 = 100.519203 MHz



三

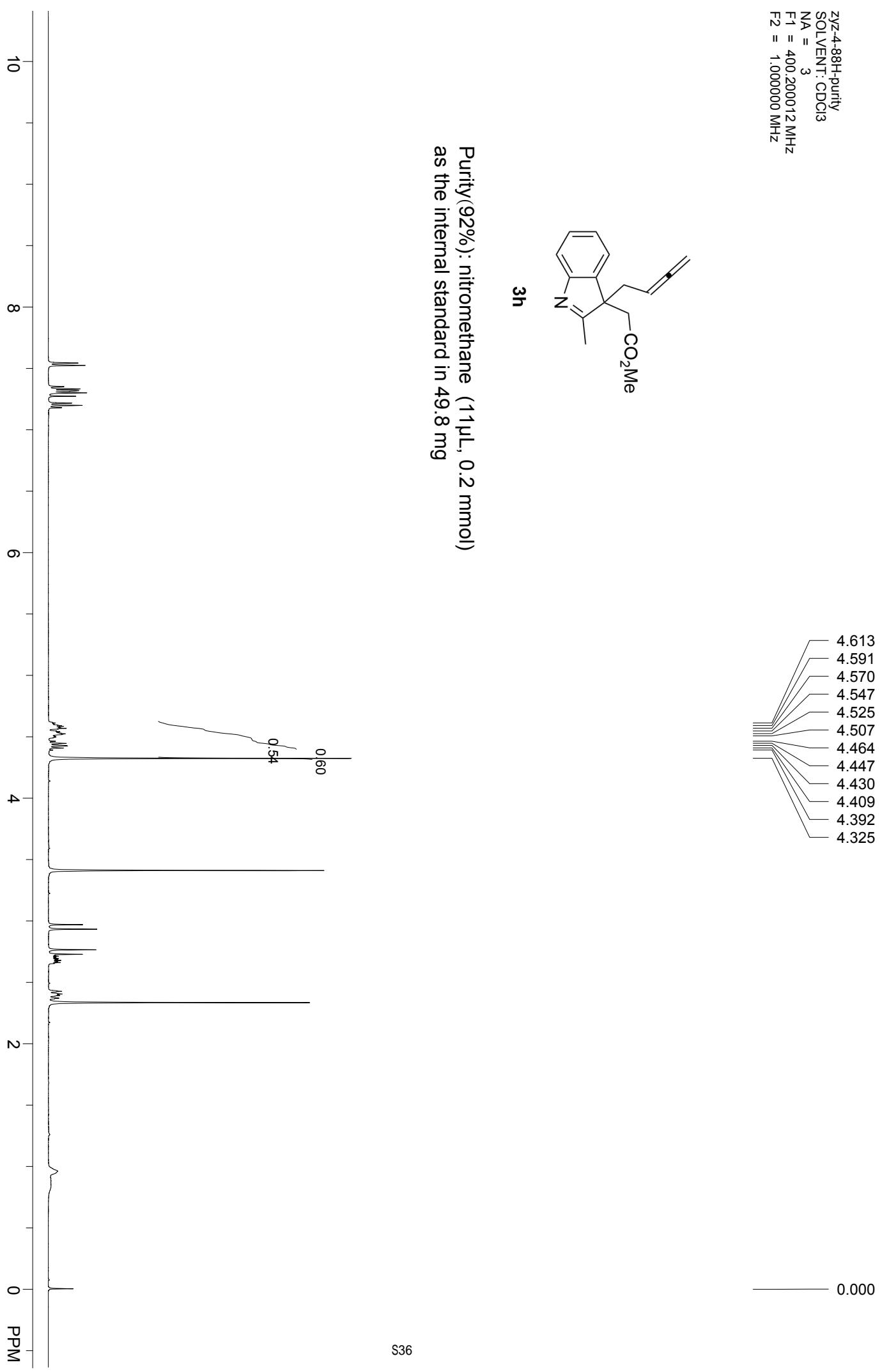


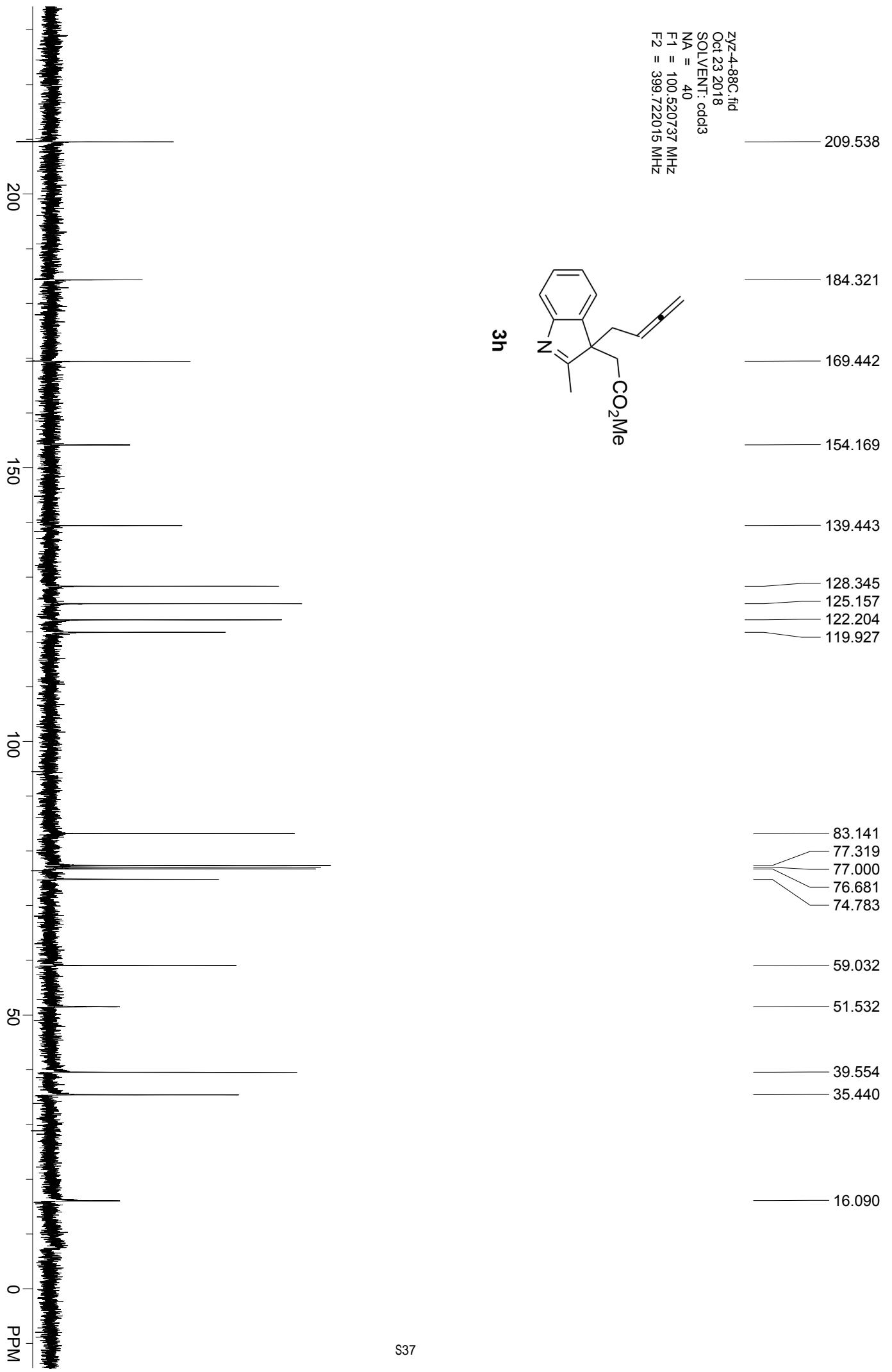
ZYZZ-4-88H-purity
SOLVENT: CDCl₃
NA = 3
F1 = 400.200012 MHz
F2 = 1.000000 MHz



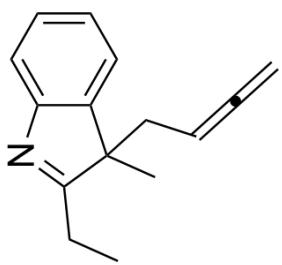
3h

Purity(92%): nitromethane (11μL, 0.2 mmol)
as the internal standard in 49.8 mg

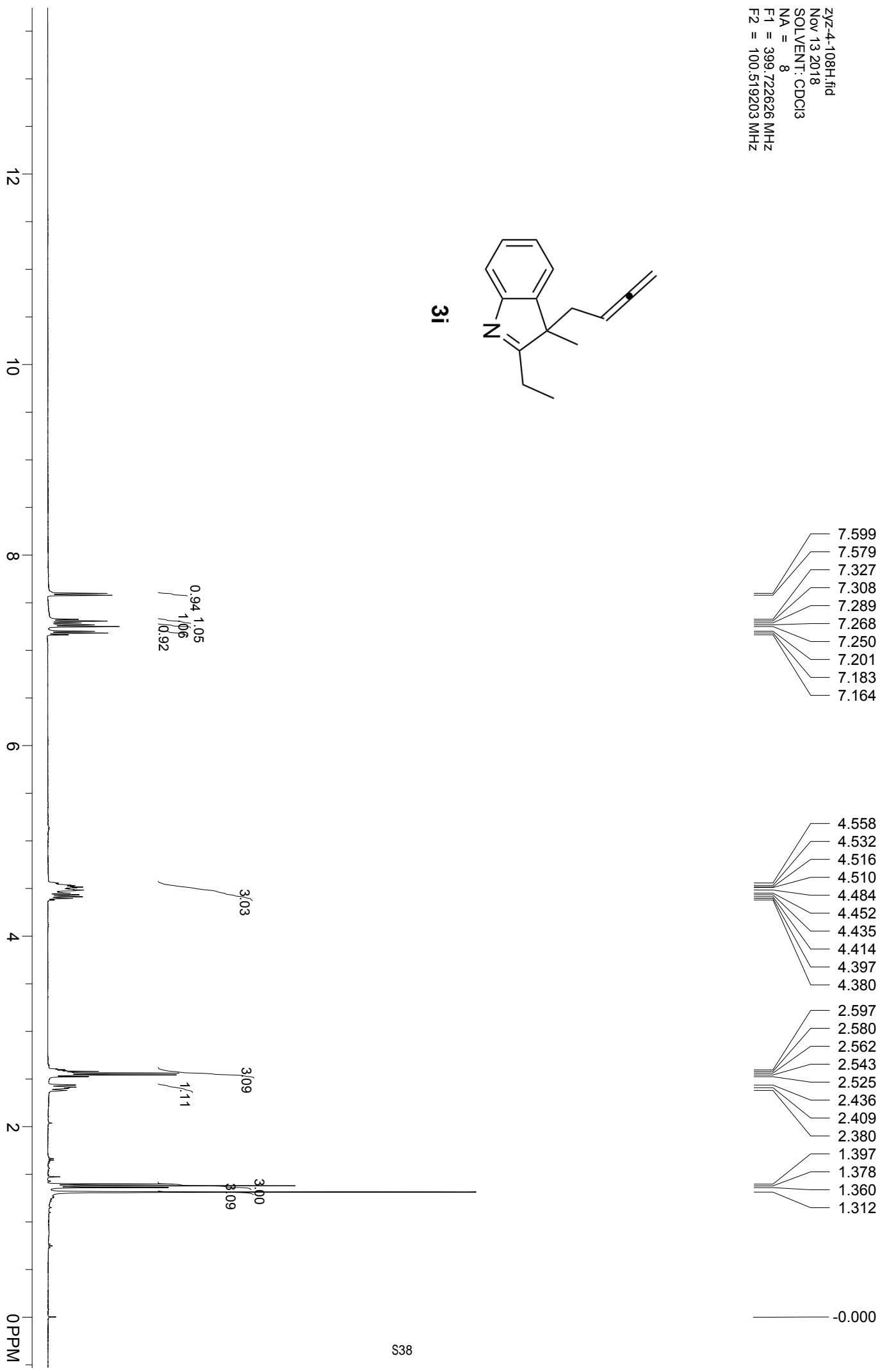


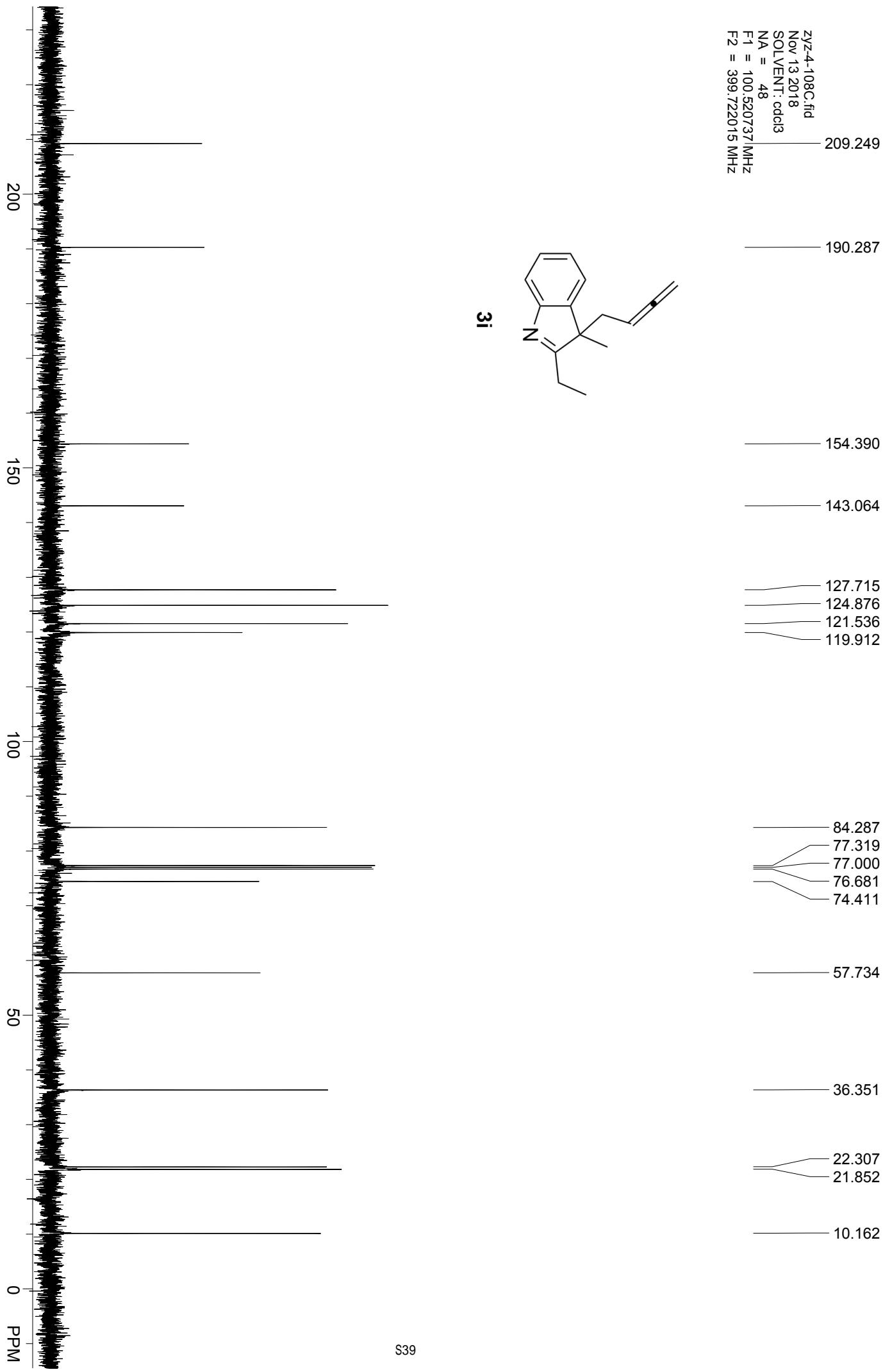


zyz-4-108H.fid
Nov 13 2018
SOLVENT: CDCl₃
NA = 8
F1 = 399.722626 MHz
F2 = 100.519203 MHz

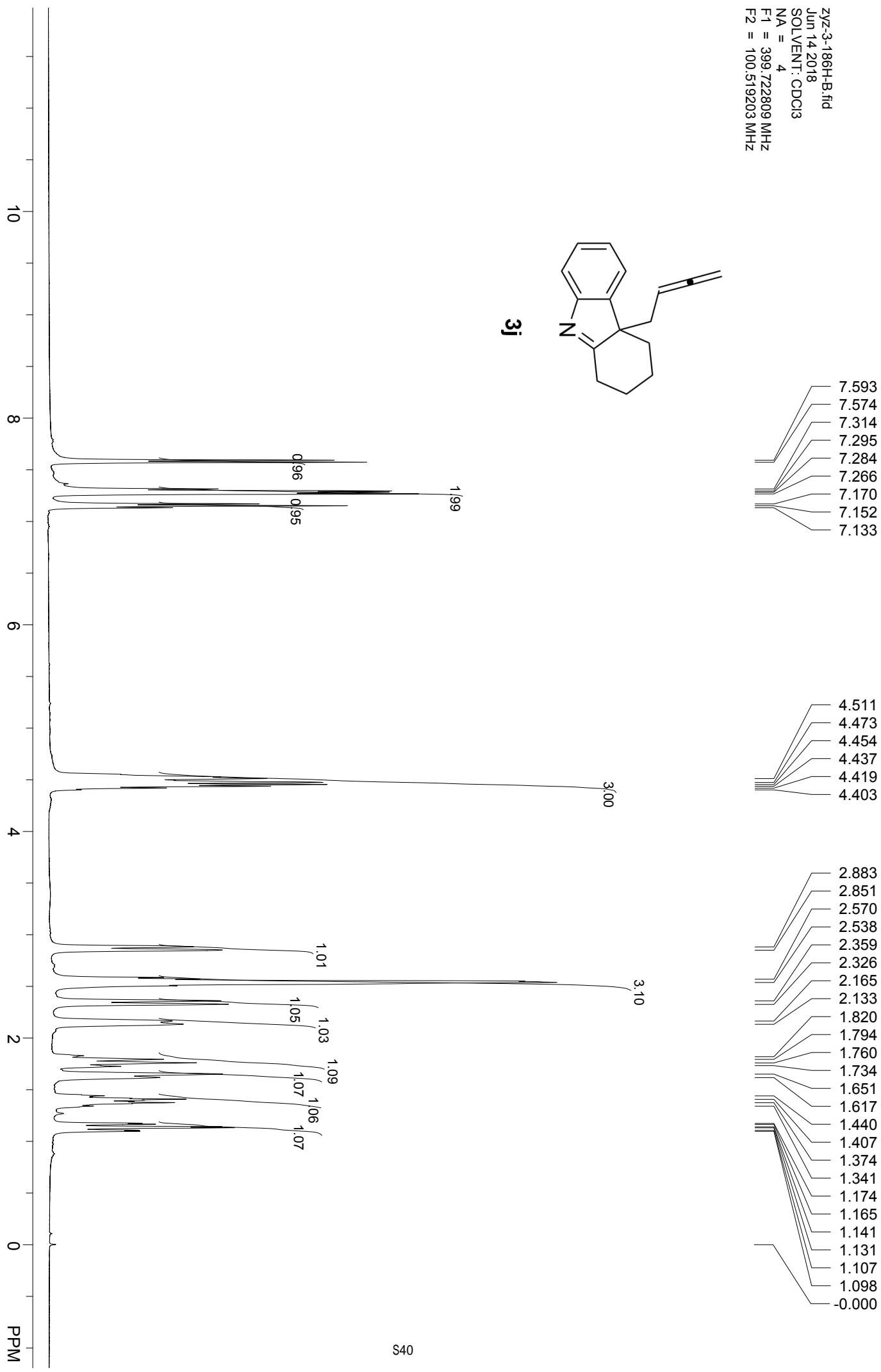


3i

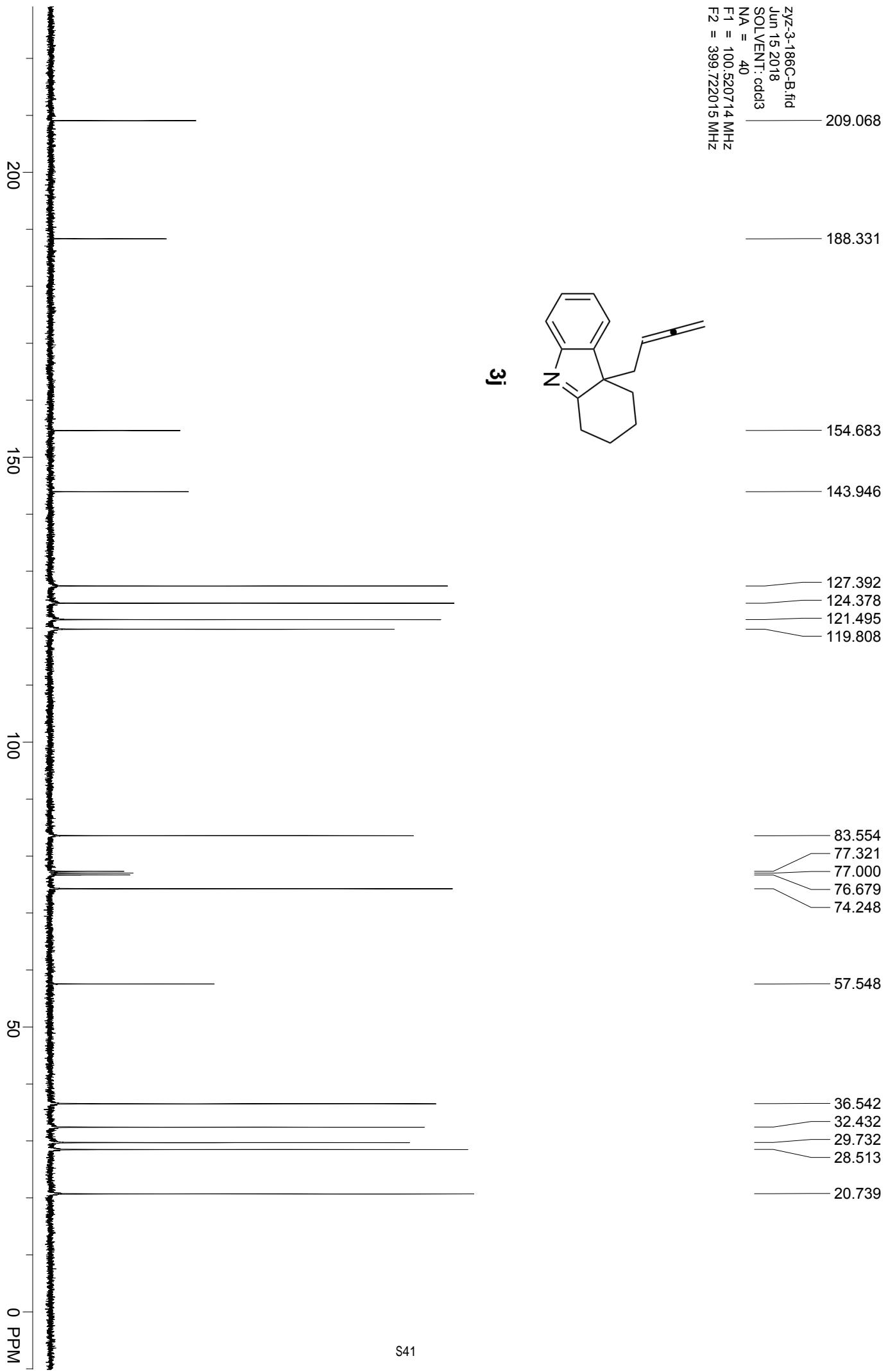




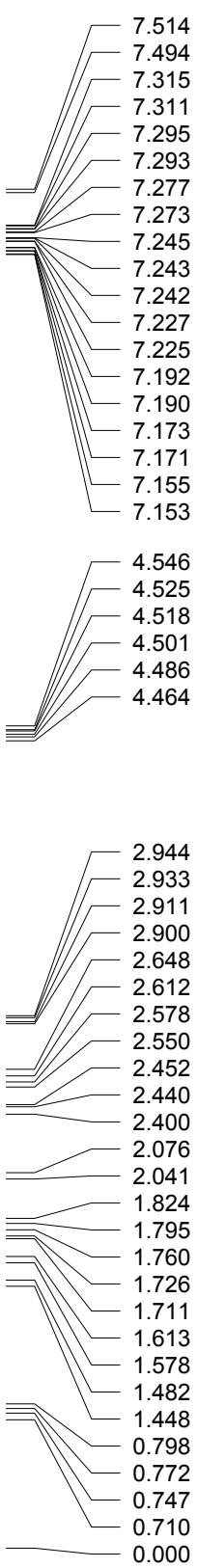
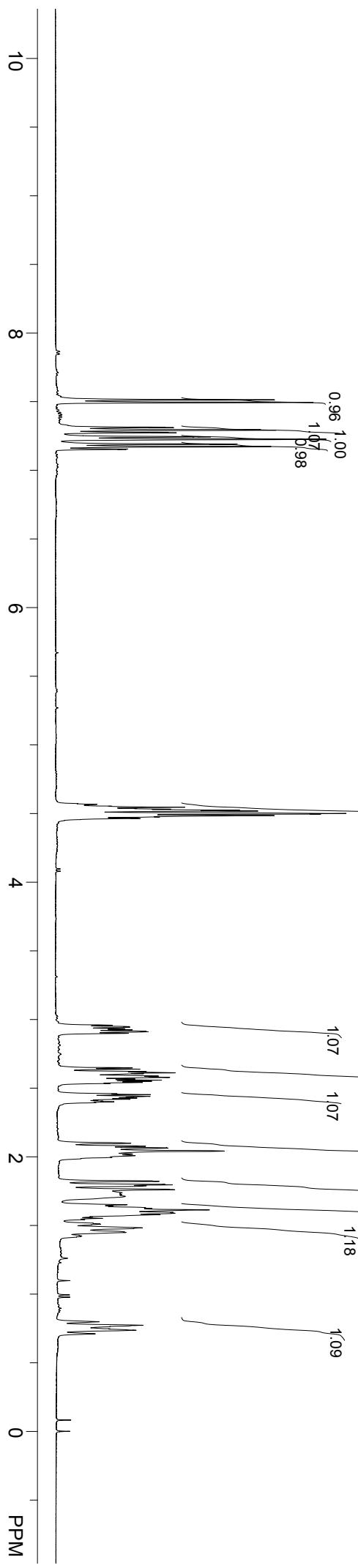
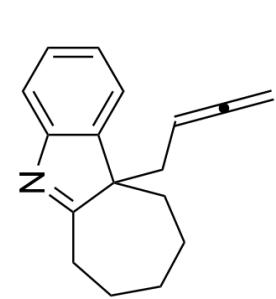
ZYZZ-3-186H-B.fid
Jun 14 2018
SOLVENT: CDCl₃
NA = 4
F1 = 399.722809 MHz
F2 = 100.519203 MHz



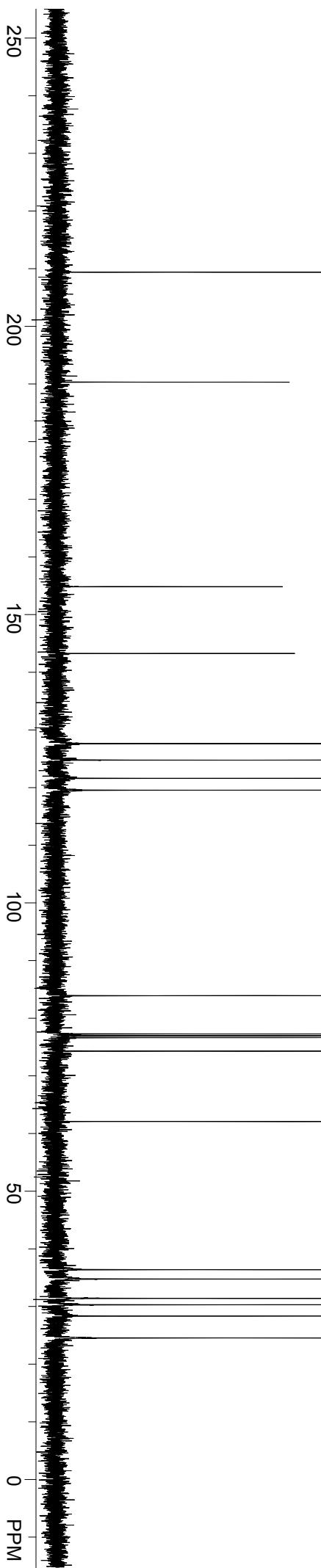
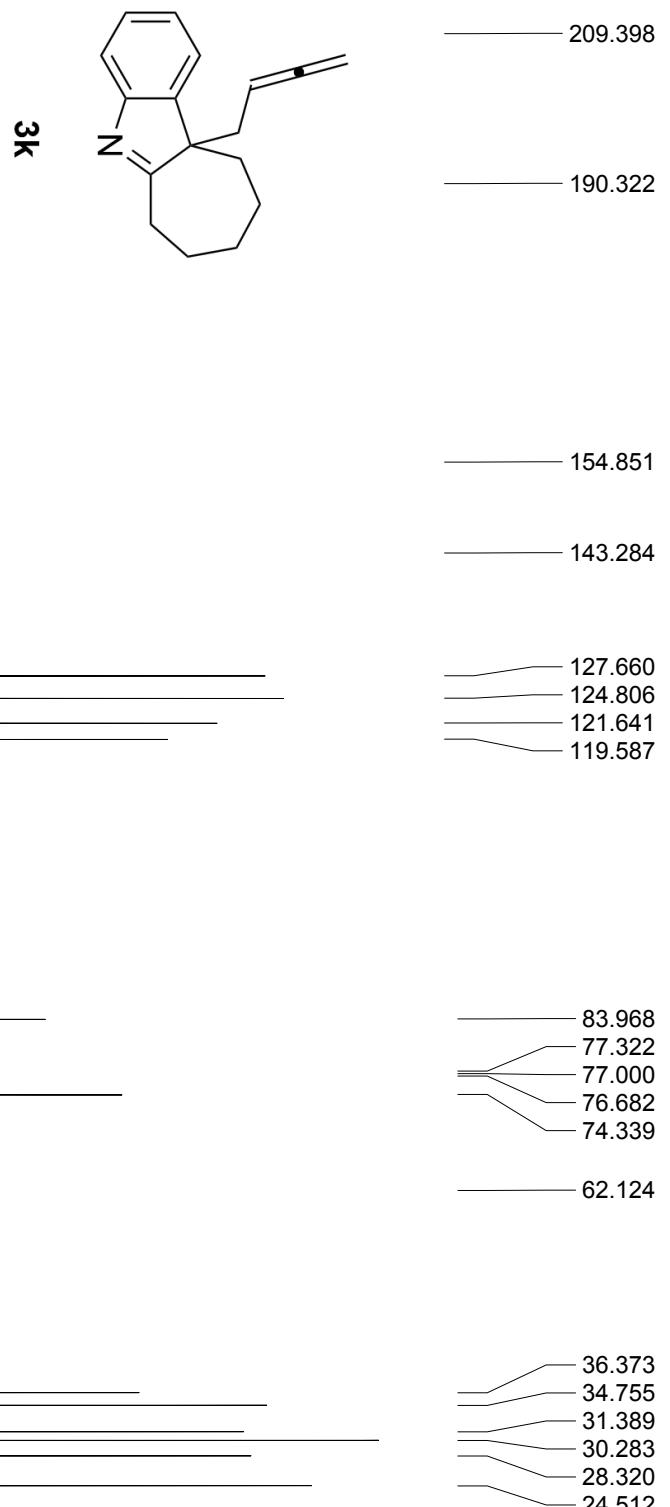
zyz-3-186C-B.fid
Jun 15 2018
SOLVENT: odd3
NA = 40
F1 = 100.520714 MHz
F2 = 399.722015 MHz



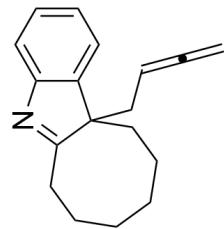
ZVZ-4-2H fid
Jun 23 2018
SOLVENT: CDCl₃
NA = 4
F1 = 399.722626 MHz
F2 = 100.519203 MHz



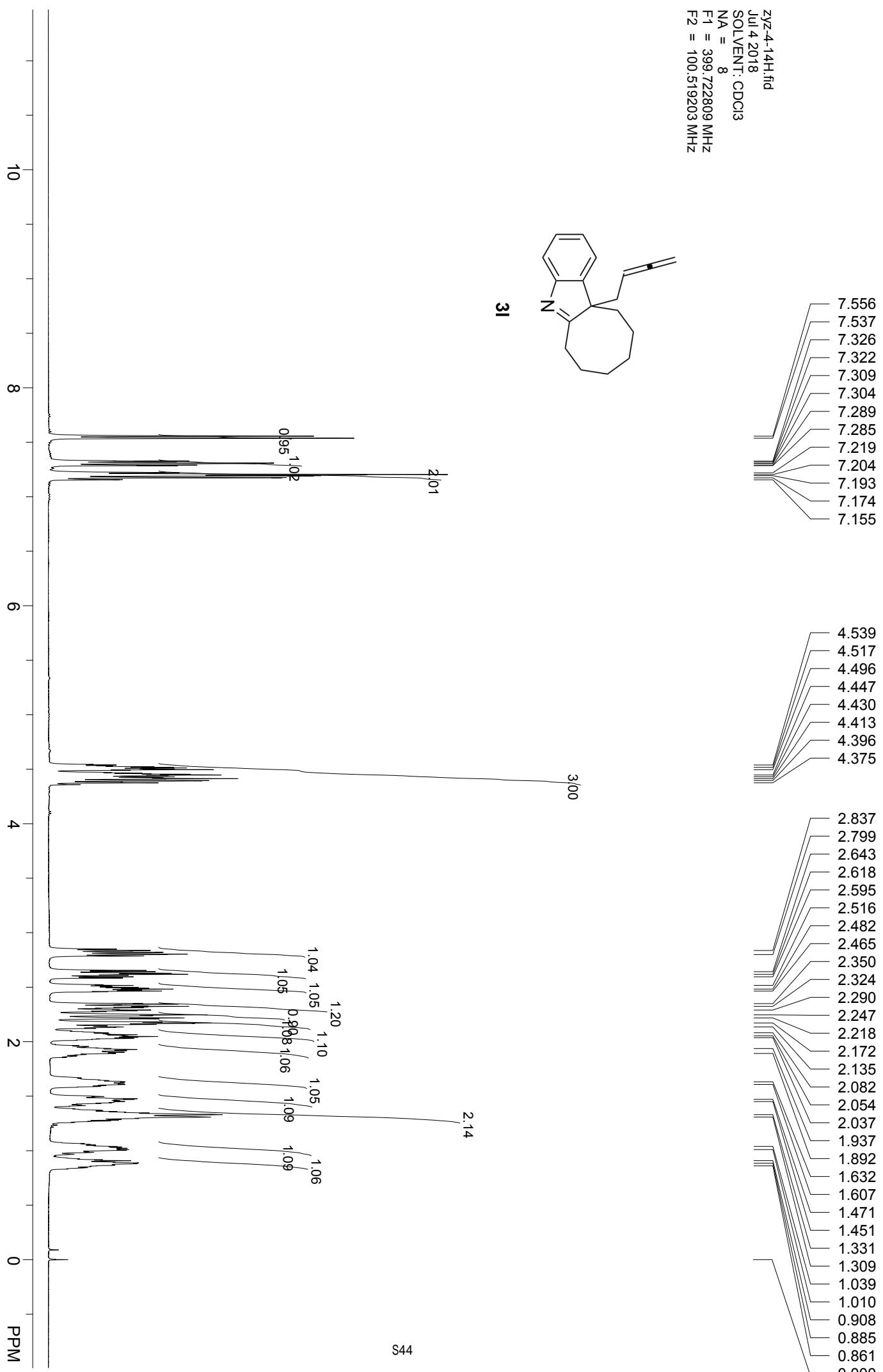
zyz4-2C.fid
Jun 23 2018
SOLVENT: cdcl₃
NA = 40
F1 = 100.521744 MHz
F2 = 399.722015 MHz



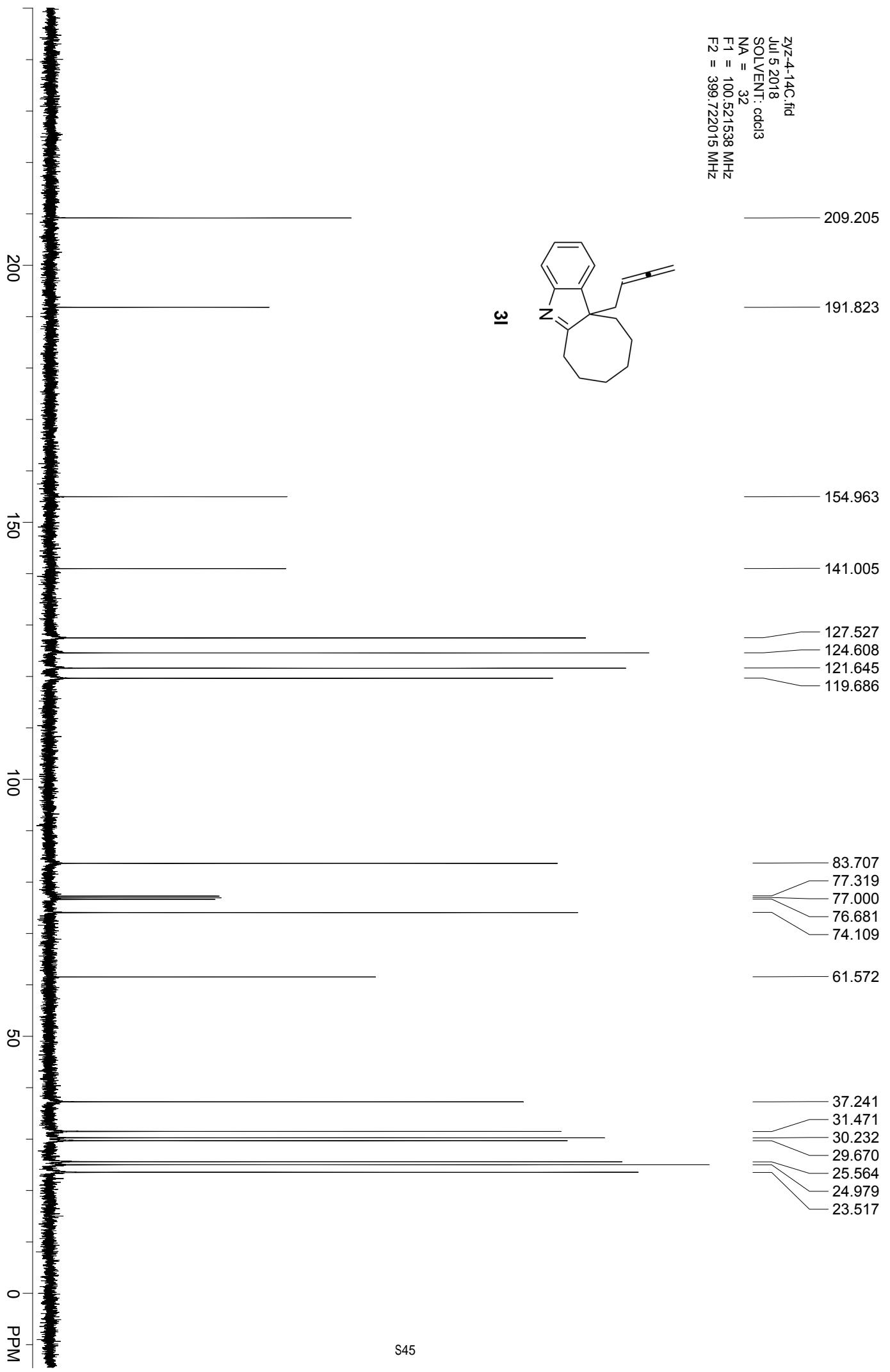
ZYK-4-14H.fid
Jul 4 2018
SOLVENT: CDCl₃
NA = 8
F1 = 399.722809 MHz
F2 = 100.519203 MHz



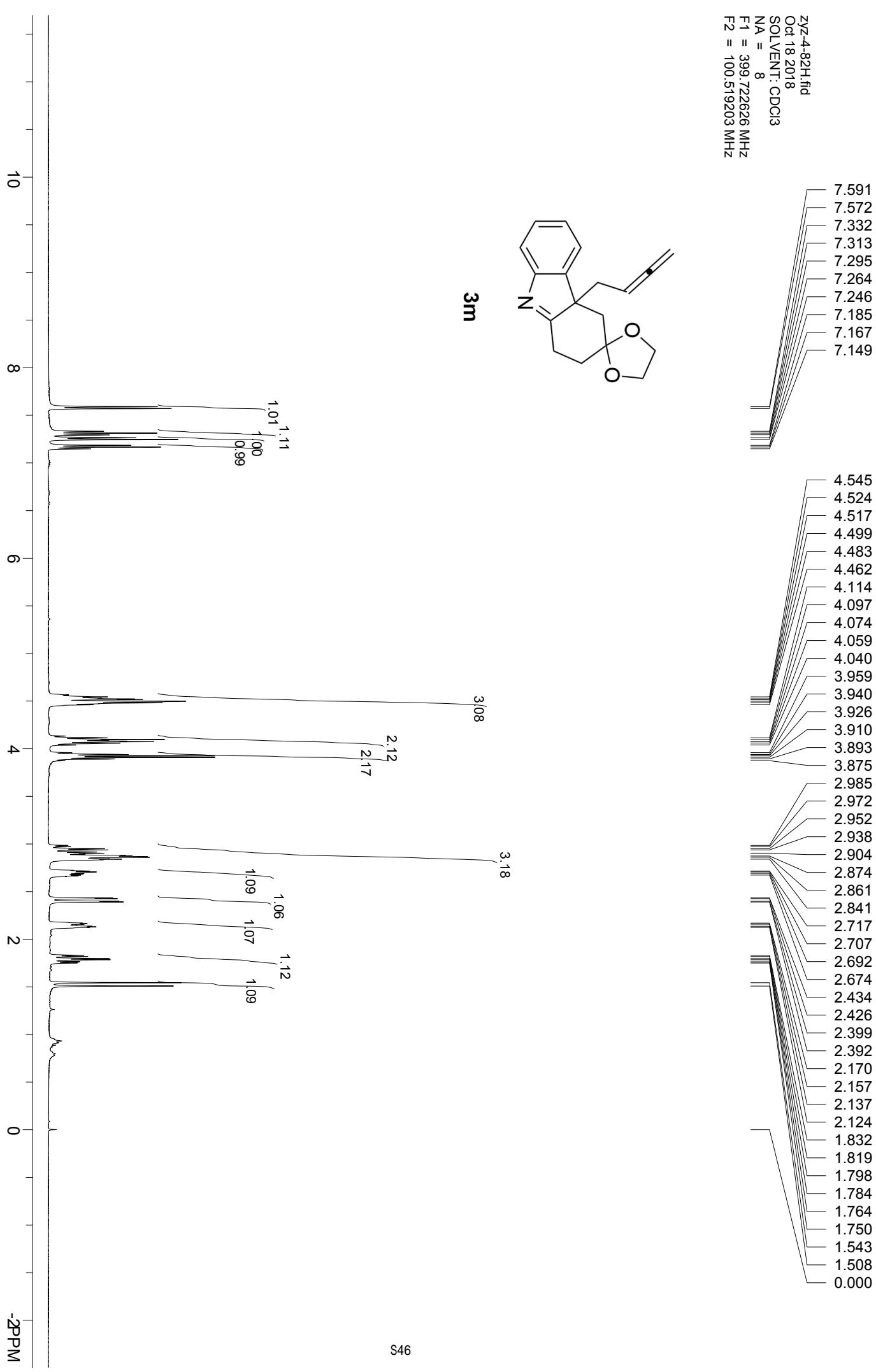
3



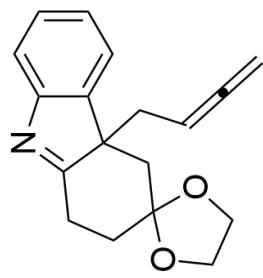
ZY2-4-14C.fid
Jul 5 2018
SOLVENT: cdcl₃
NA = 32
F1 = 100.521538 MHz
F2 = 399.722015 MHz



ZYZZ-4-82H.fid
Oct 18 2018
SOLVENT: CDCl₃
NA = 8
F1 = 399.722026 MHz
F2 = 100.519203 MHz

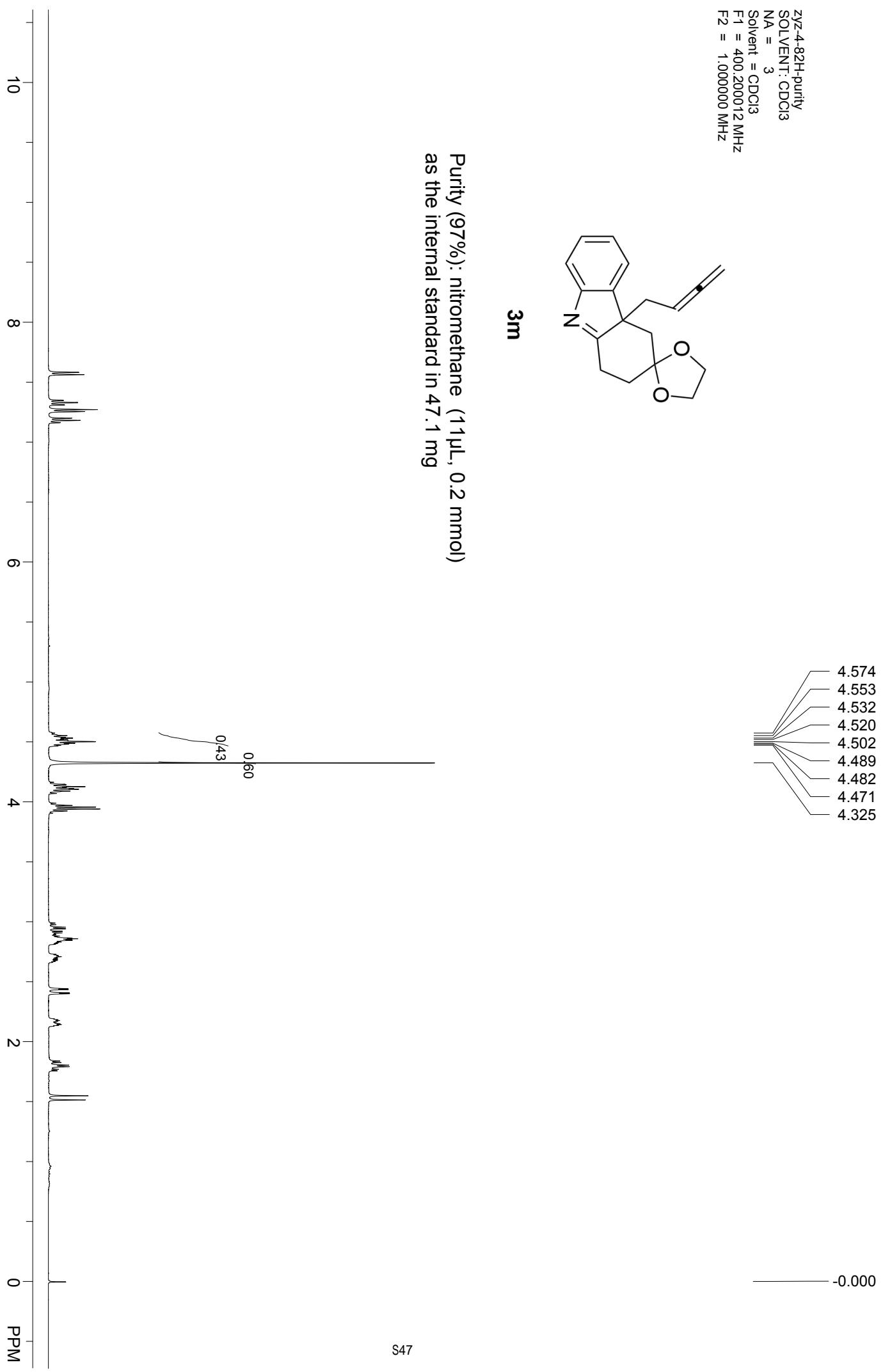


ZVZ-4-82H-purity
SOLVENT: CDCl₃
NA = 3
Solvent = CDCl₃
F1 = 400.200012 MHz
F2 = 1.000000 MHz

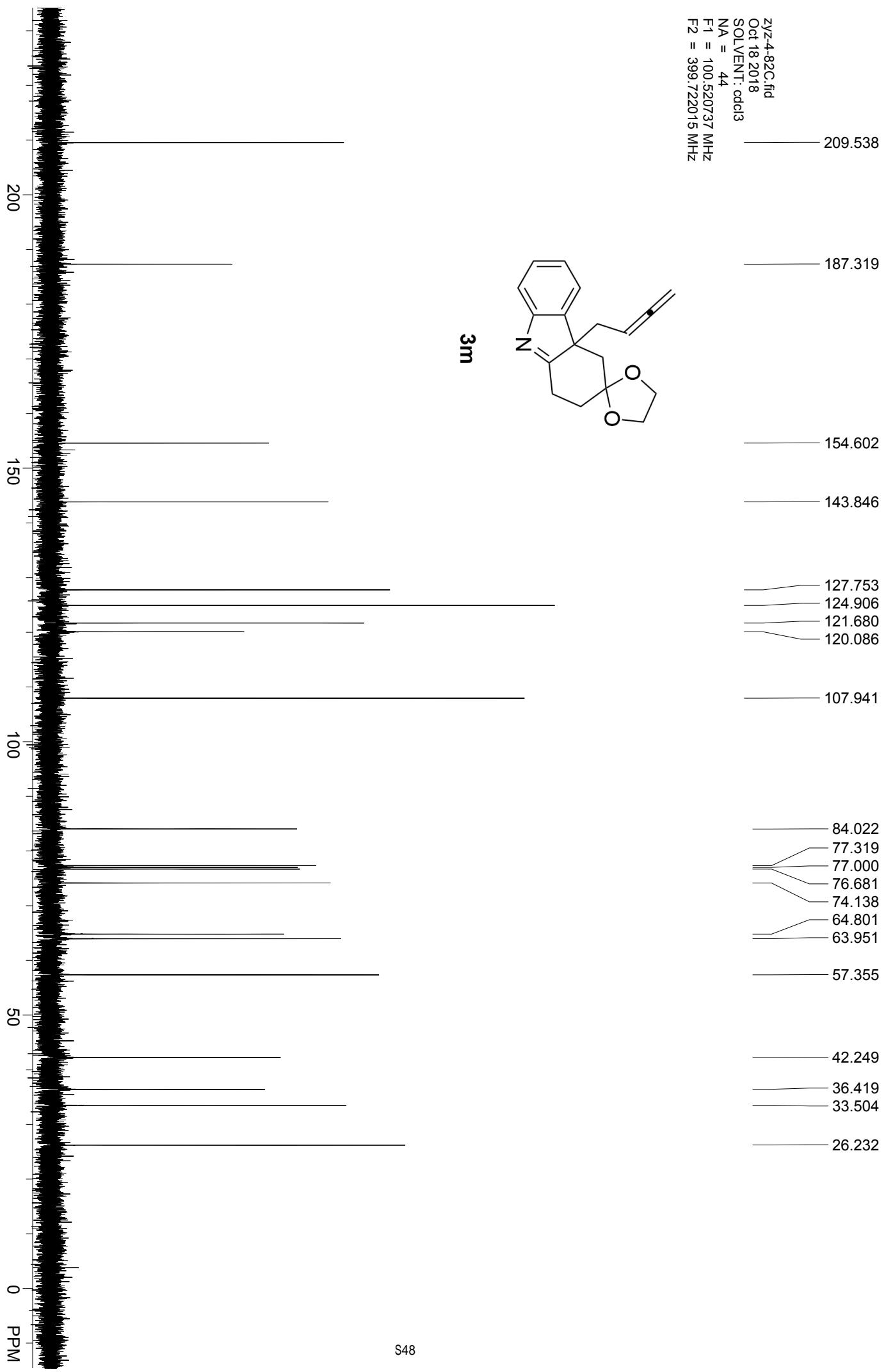


3m

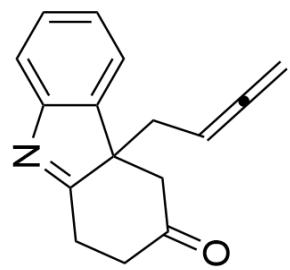
Purity (97%): nitromethane (11 μL, 0.2 mmol)
as the internal standard in 47.1 mg



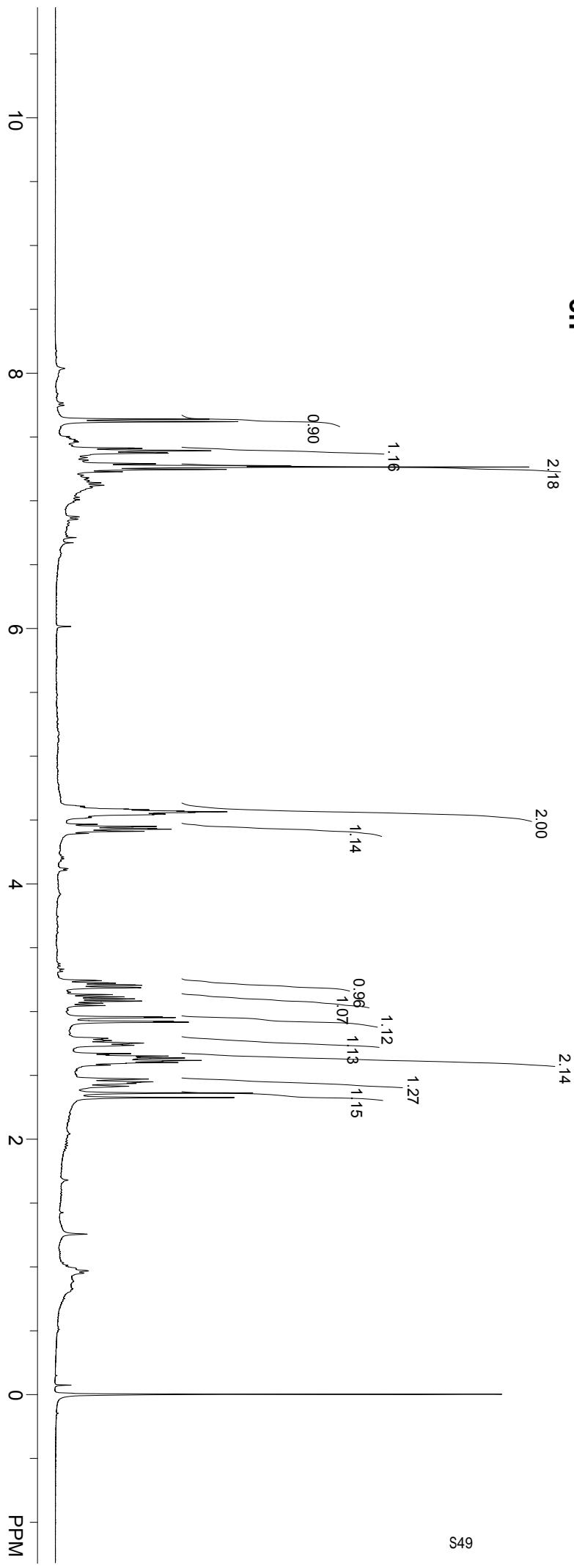
ZYZZ-4-82C.fid
Oct 18 2018
SOLVENT: cdcl₃
NA = 44
F1 = 100.520737 MHz
F2 = 399.722015 MHz



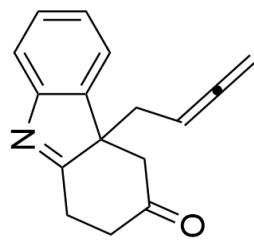
ZYZZ-4-96H-5
SOLVENT: CDCl₃
NA = 16
F1 = 400.100006 MHz
F2 = 1.000000 MHz



3n

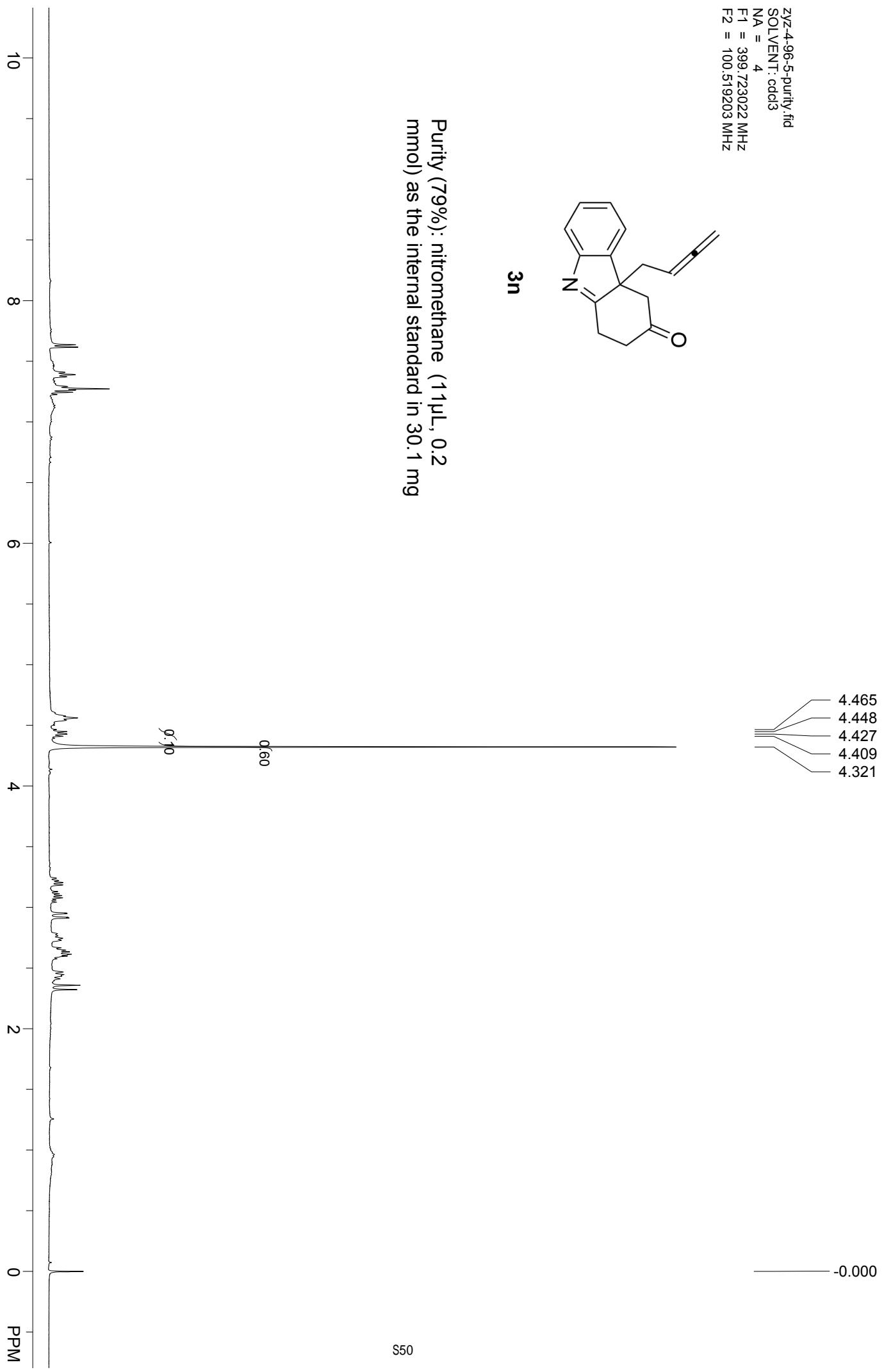


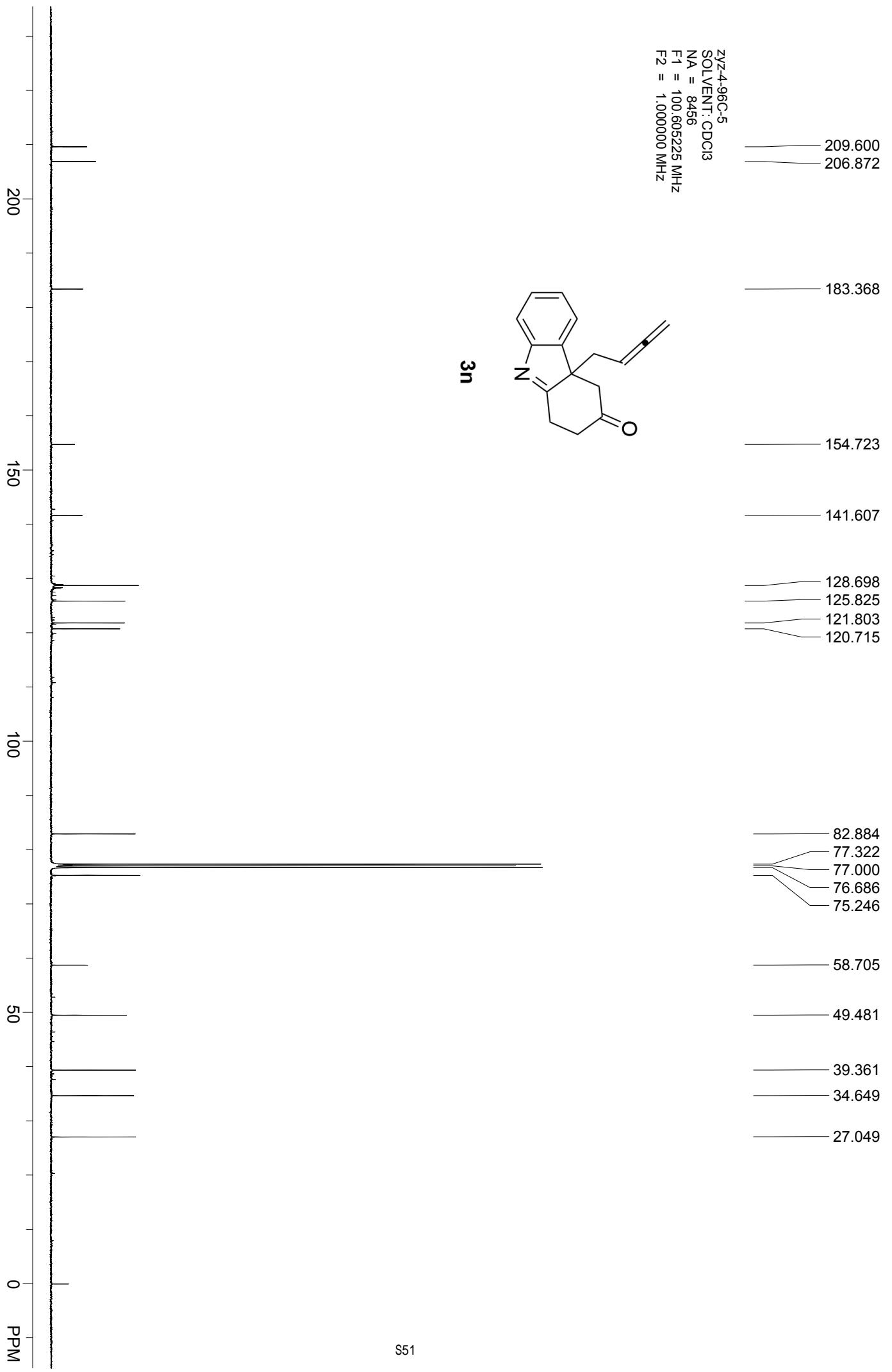
ZYZ-4-96-5-purity.fid
SOLVENT: cdcl₃
NA = 4
F1 = 399.723022 MHz
F2 = 100.519203 MHz



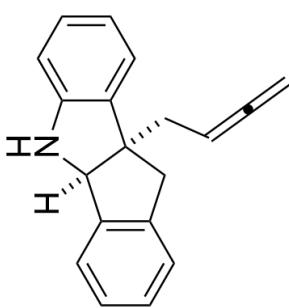
3n

Purity (79%): nitromethane (11 μ L, 0.2 mmol) as the internal standard in 30.1 mg

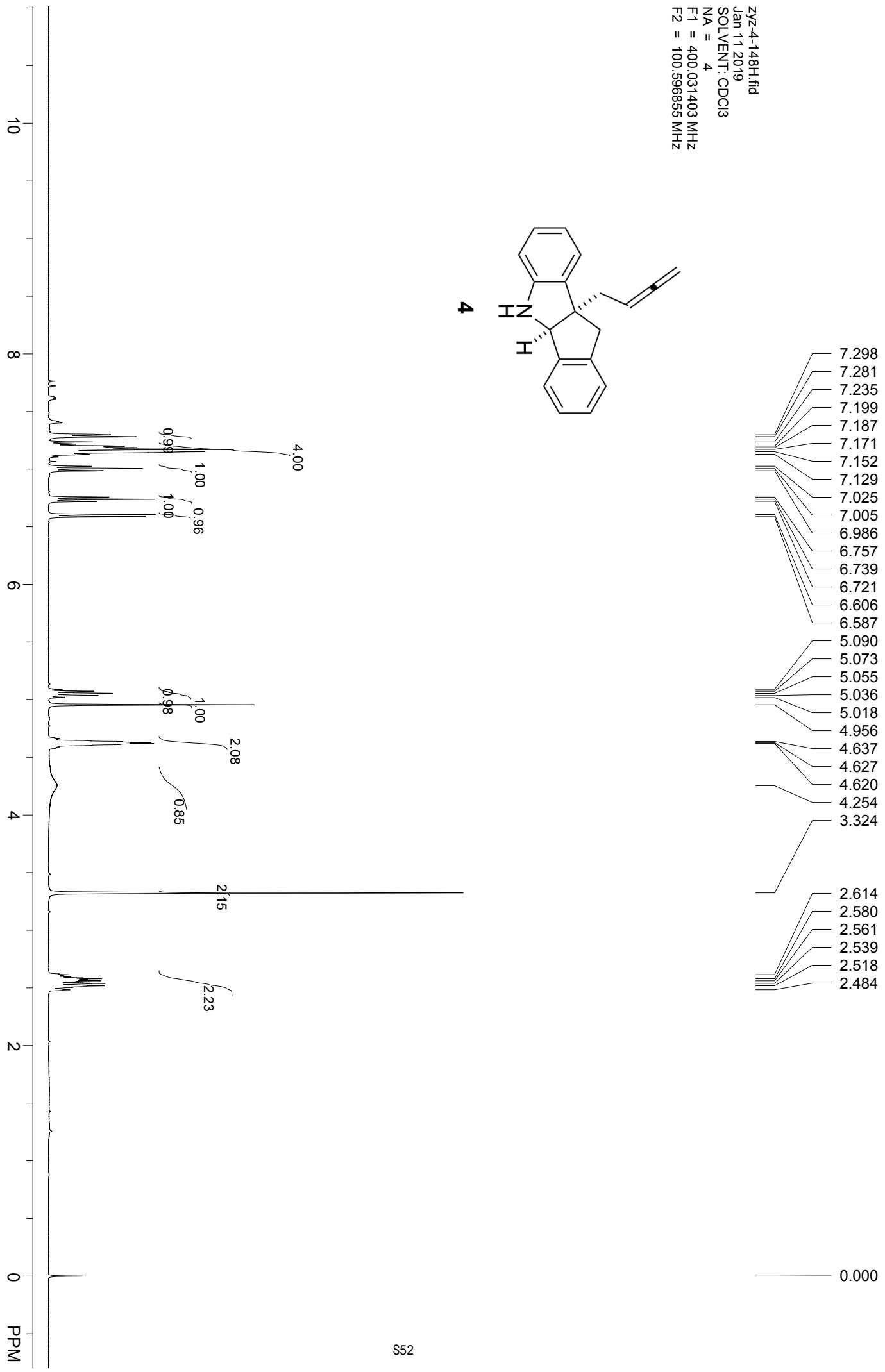




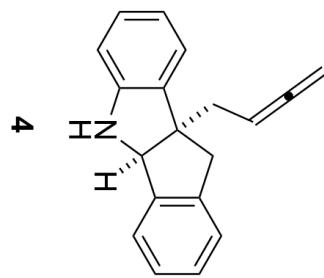
zyz-4-148H.fid
Jan 11 2019
SOLVENT: CDCl₃
NA = 4
F1 = 400.031403 MHz
F2 = 100.596855 MHz



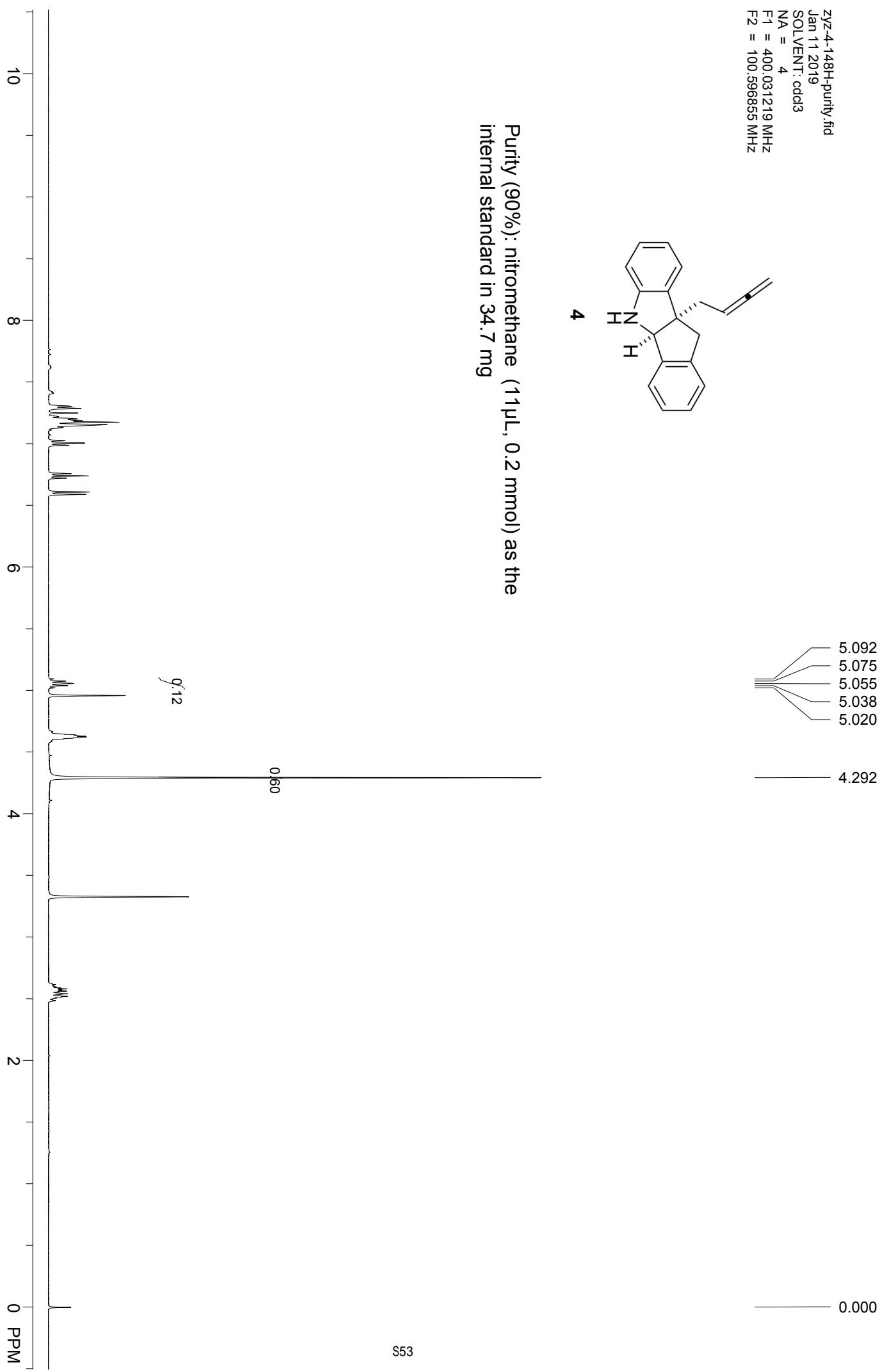
4



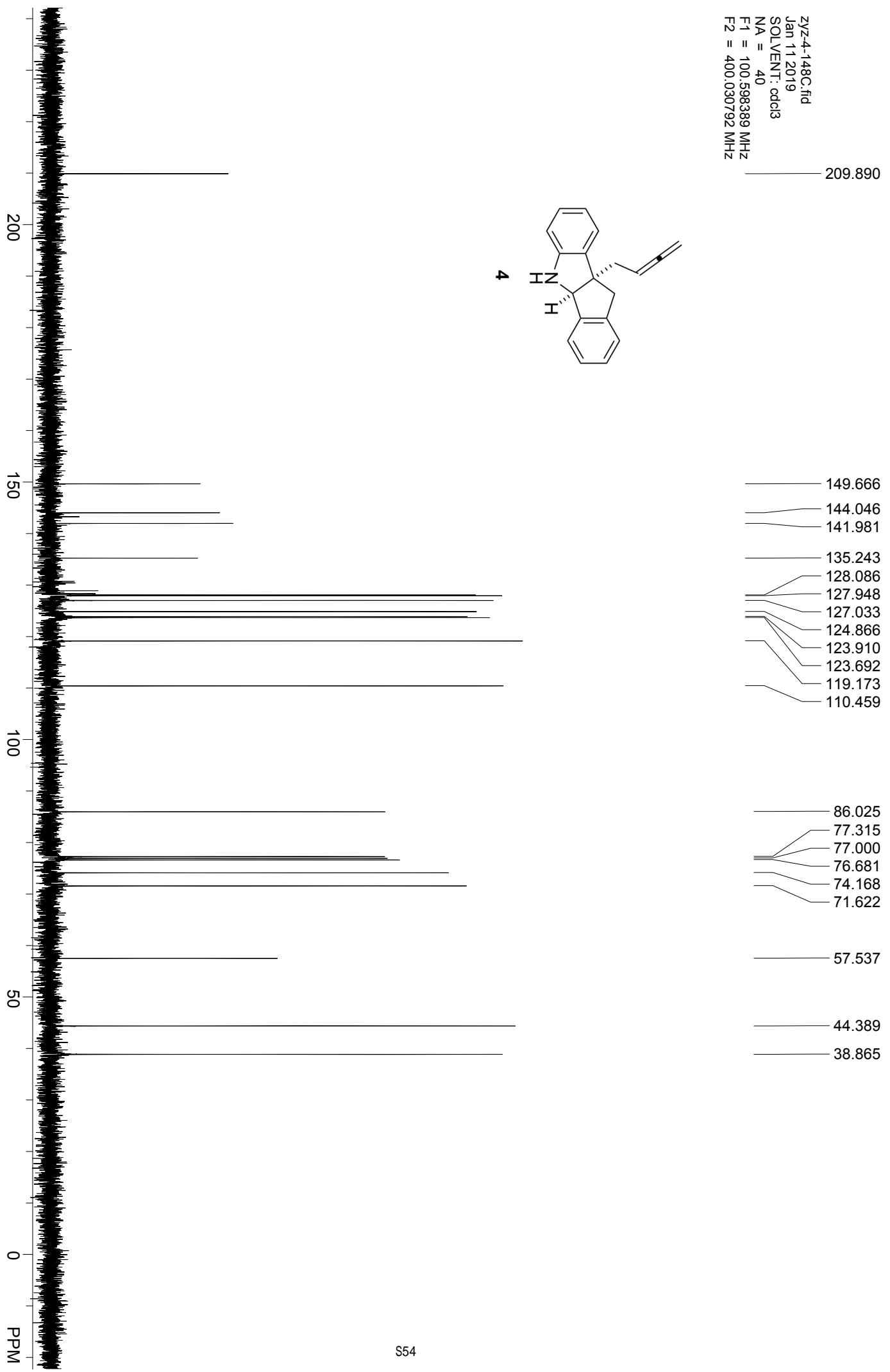
ZVZ-4-148H-purity.fid
Jan 11 2019
SOLVENT: odd3
NA = 4
F1 = 400.031219 MHz
F2 = 100.596955 MHz

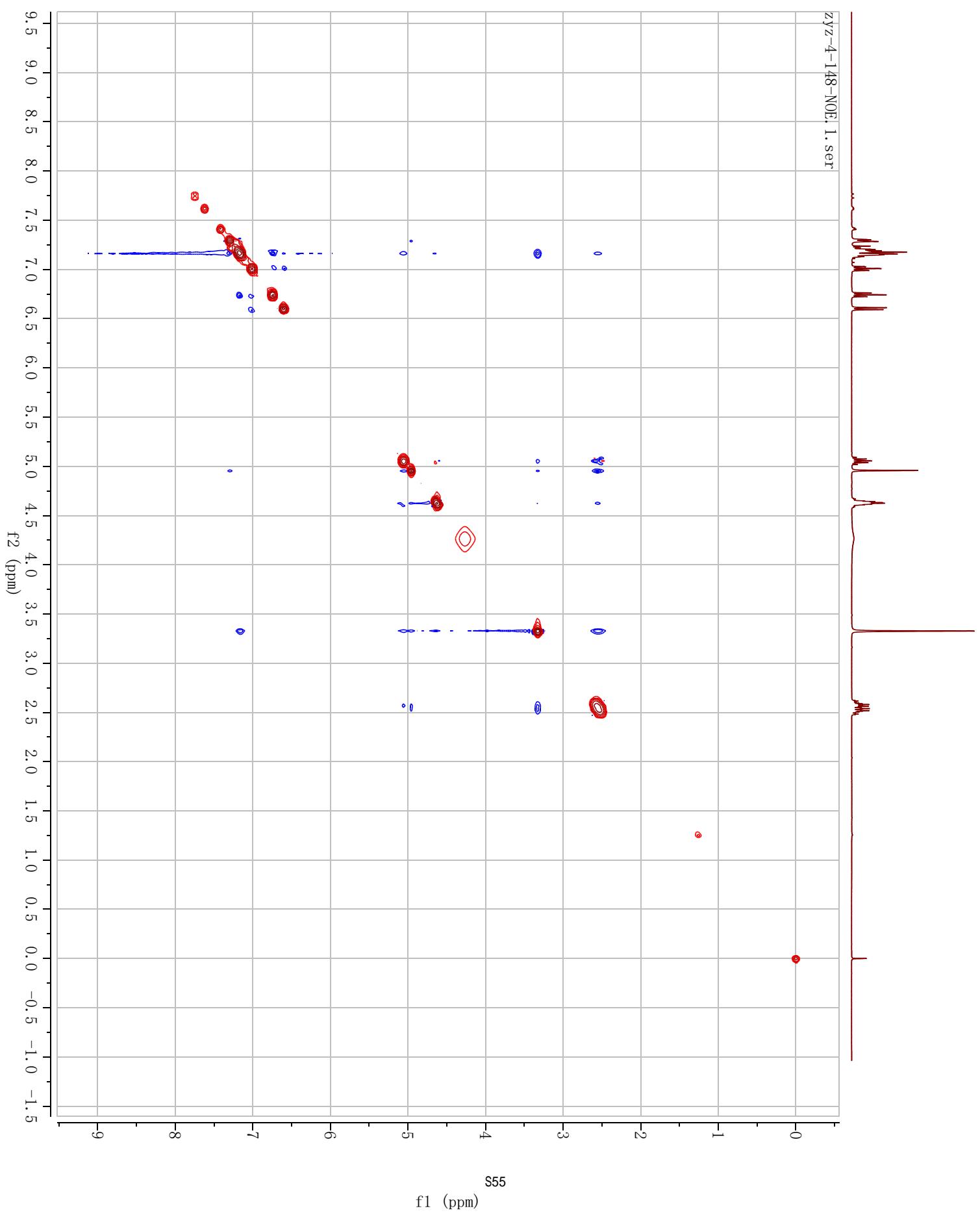
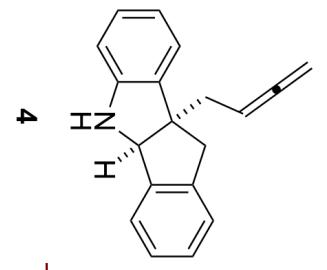


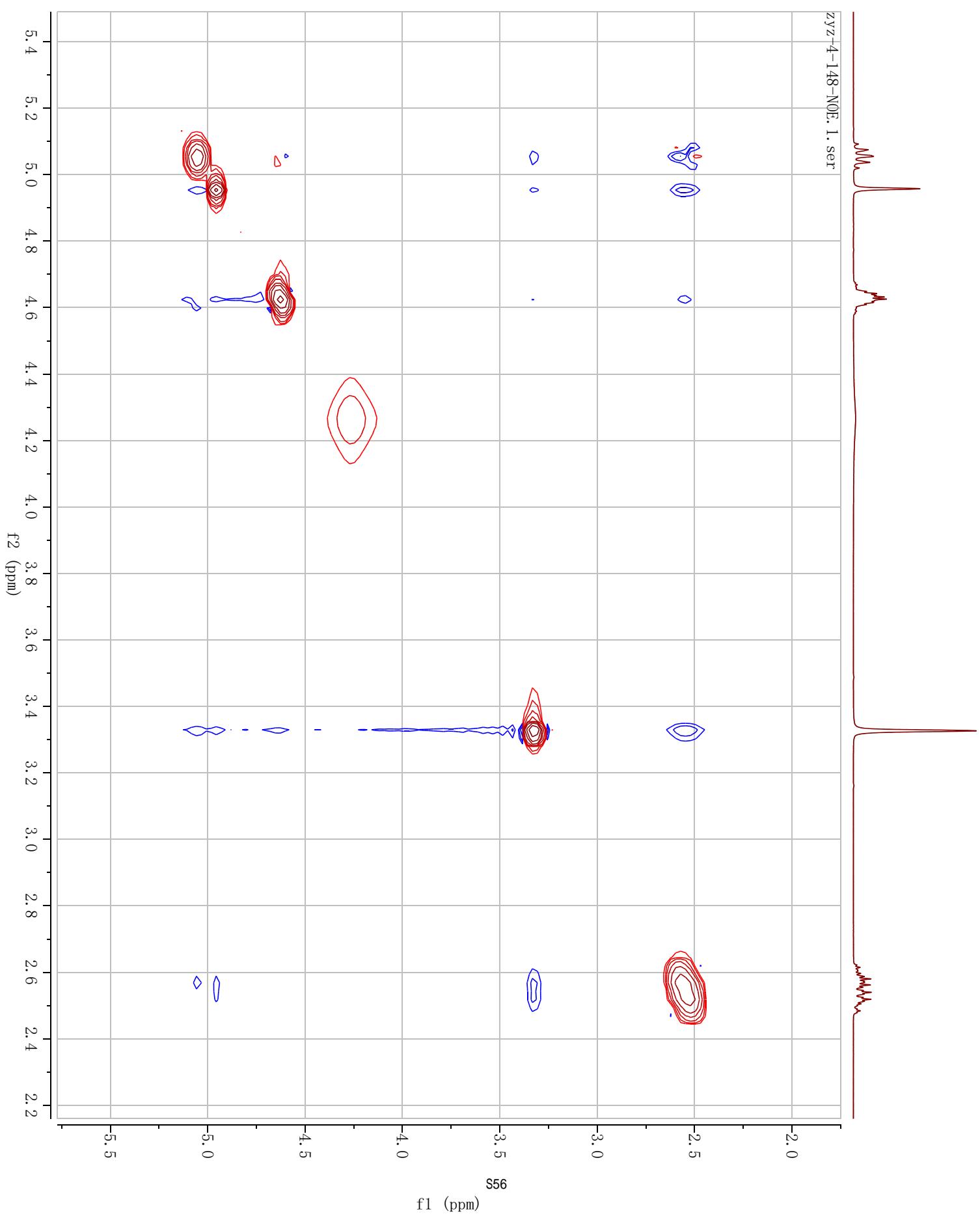
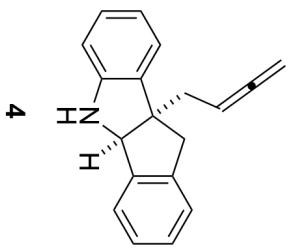
Purity (90%): nitromethane (11 μ L, 0.2 mmol) as the internal standard in 34.7 mg



zyz4-148C.fid
Jan 11 2019
SOLVENT: cdcl₃
NA = 40
F1 = 100.598389 MHz
F2 = 400.030792 MHz

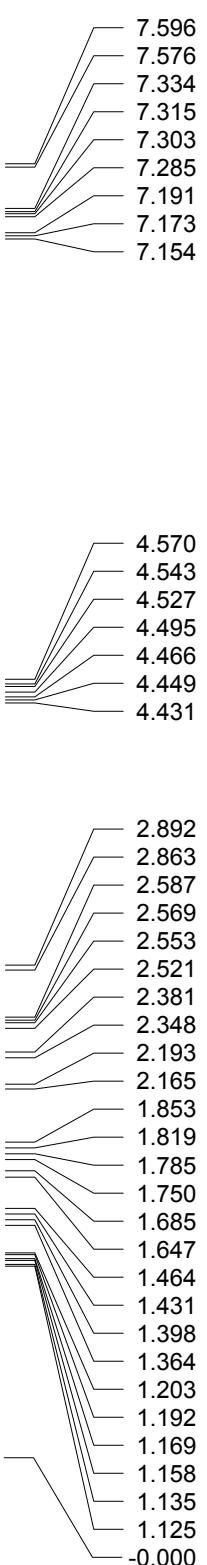
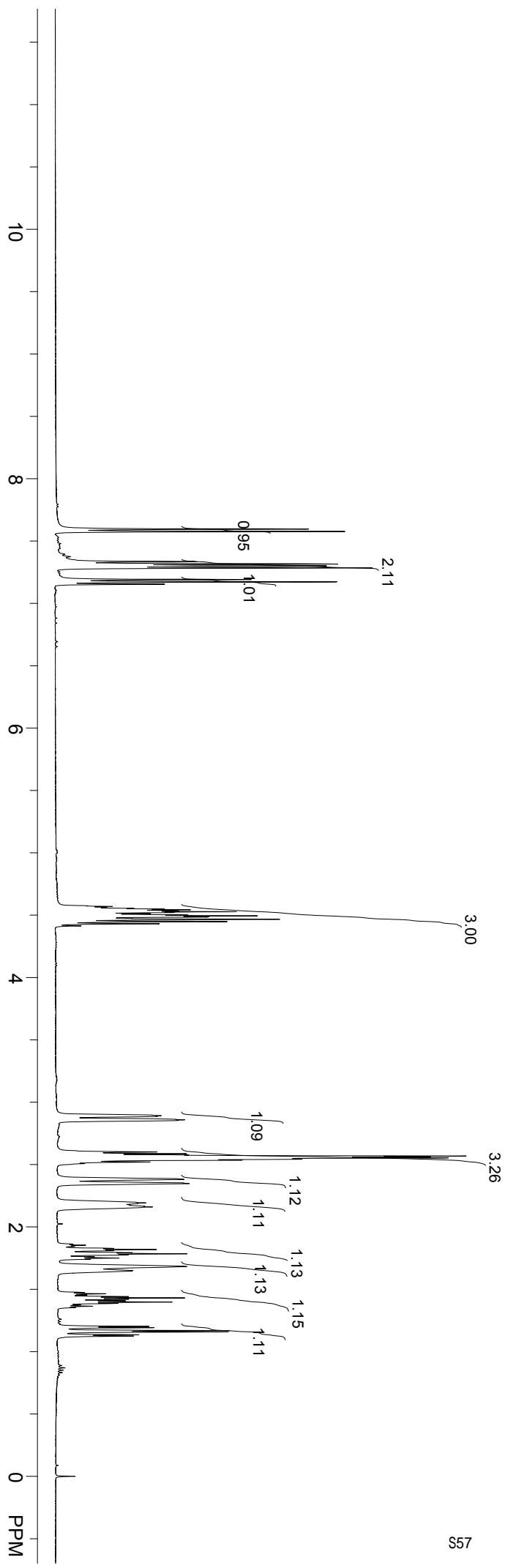
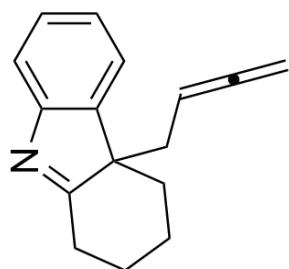




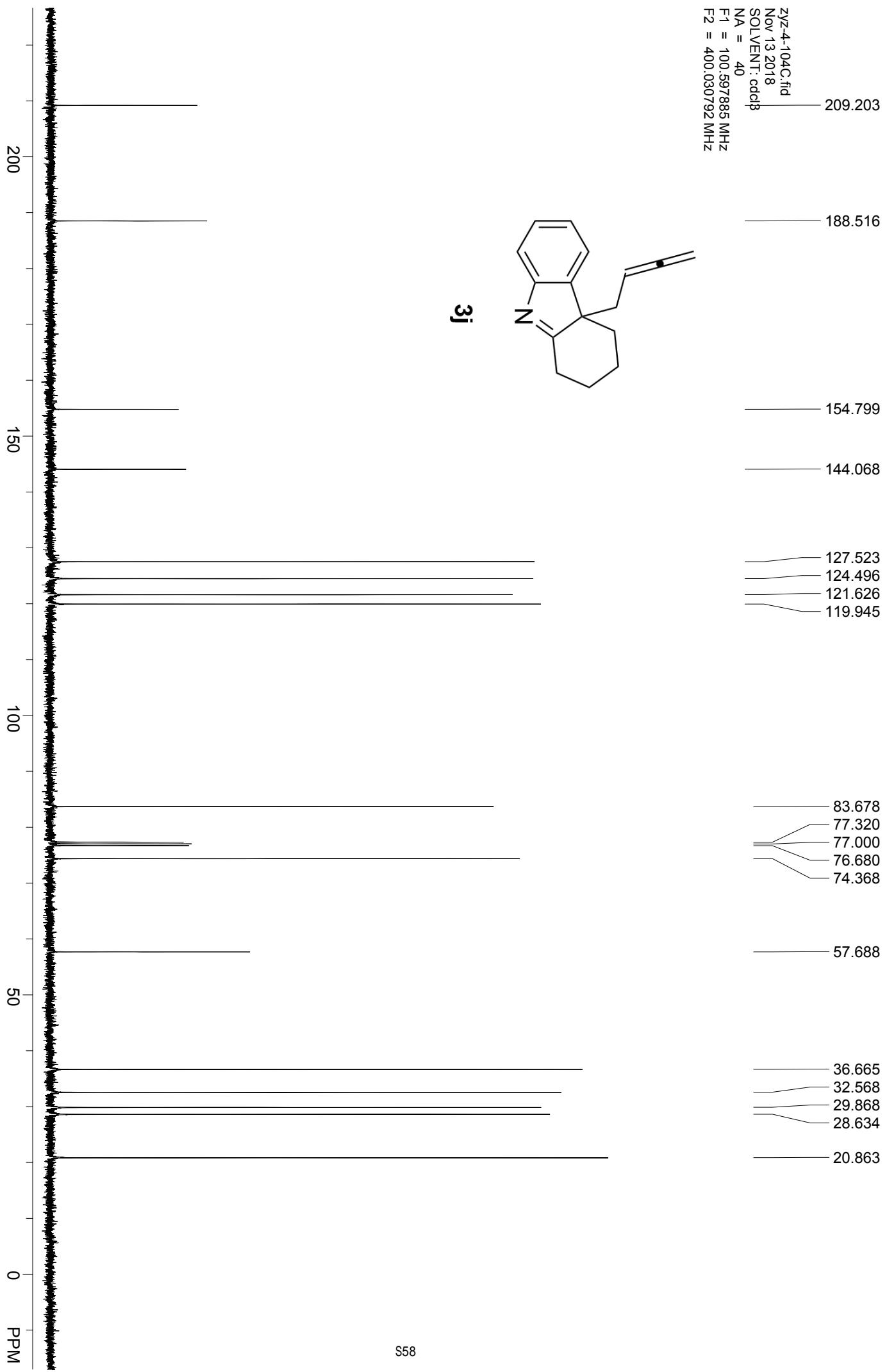
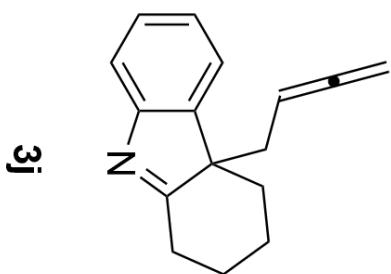


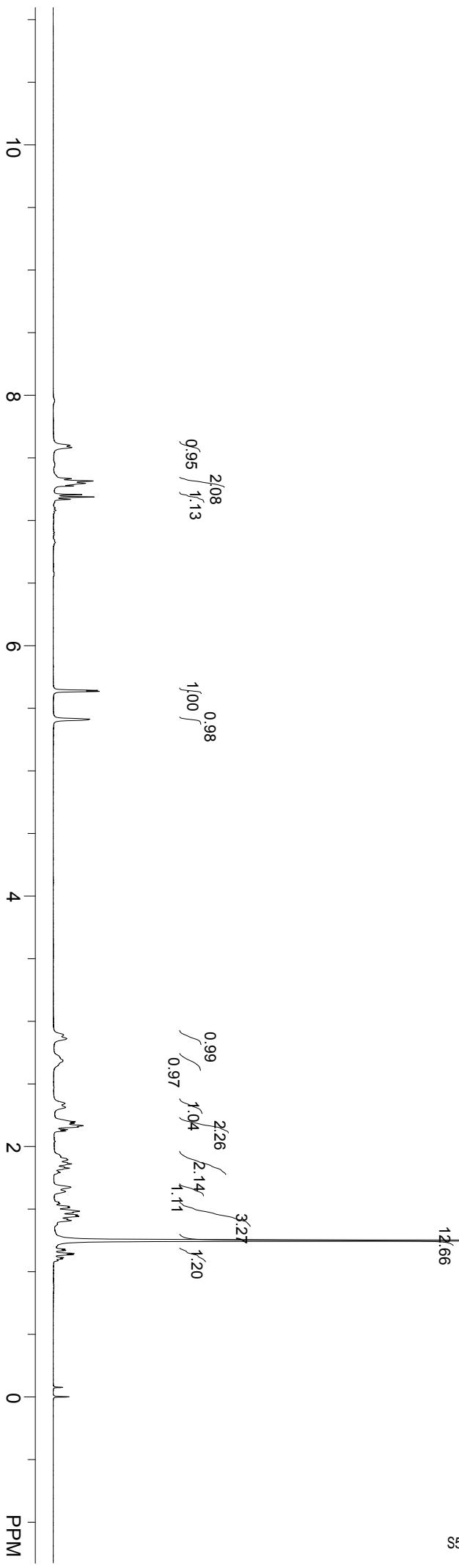
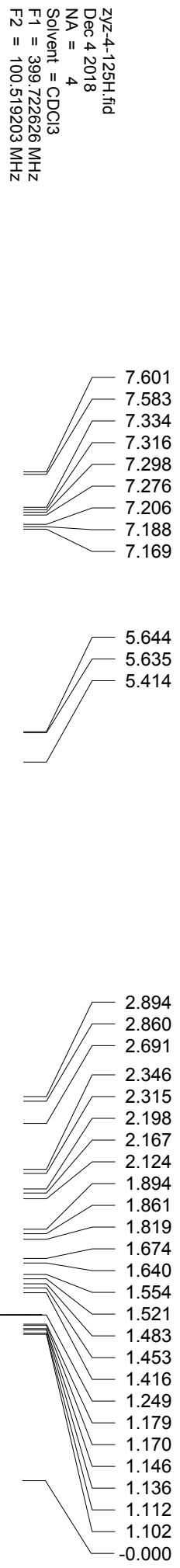
ZYX-4-104H.fid
Nov 13 2018
SOLVENT: CDCl₃
NA = 8
F1 = 400.031799 MHz
F2 = 100.596855 MHz

3j

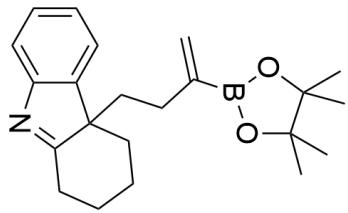


ZYZZ-4-104C.fid
Nov 13 2018
SOLVENT: CDCl_3
NA = 40
F1 = 100.597885 MHz
F2 = 400.030792 MHz



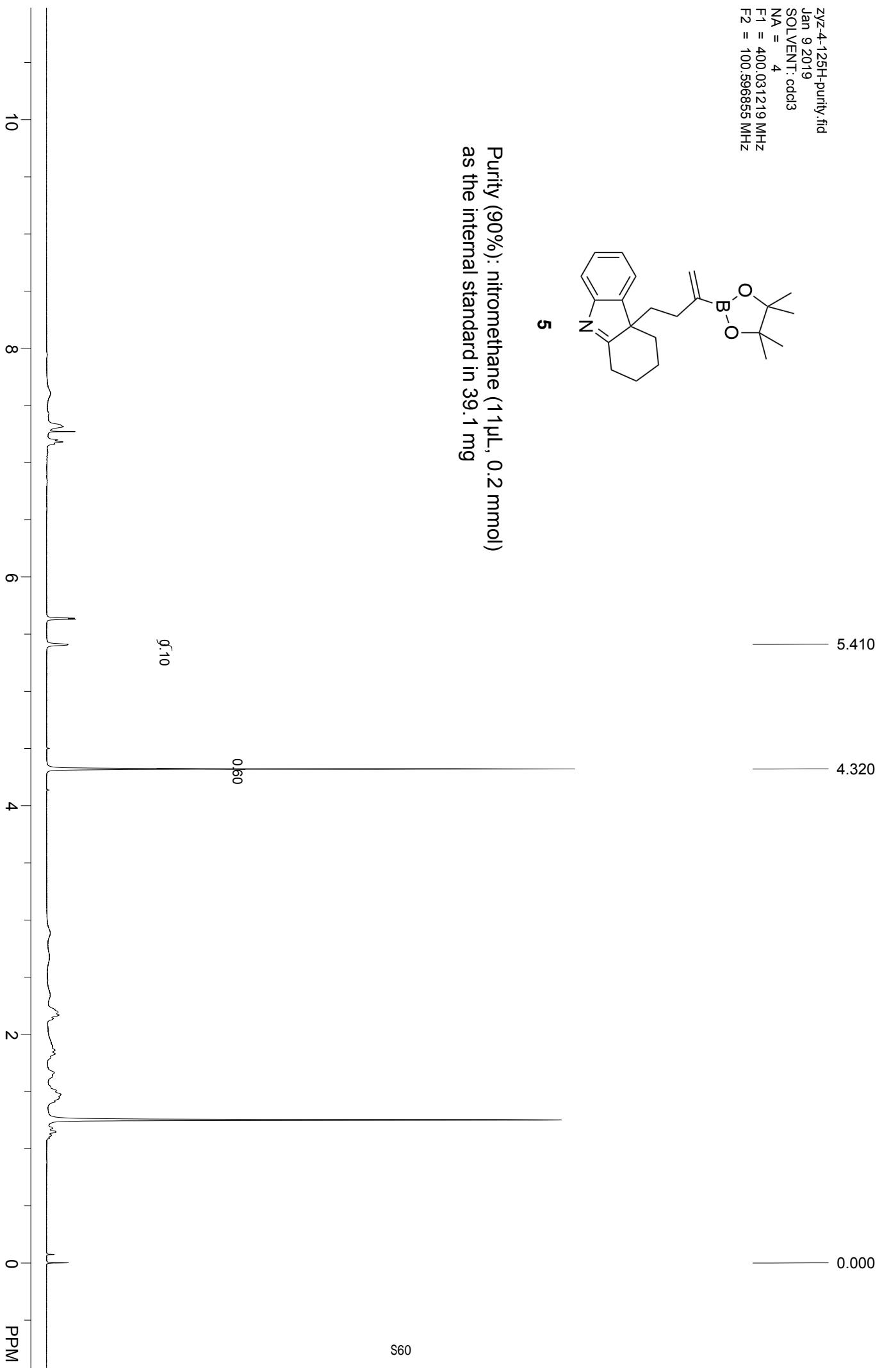


zyz-4-125H-purity.fid
Jan 9 2019
SOLVENT: cdd3
NA = 4
F1 = 400.031219 MHz
F2 = 100.596855 MHz

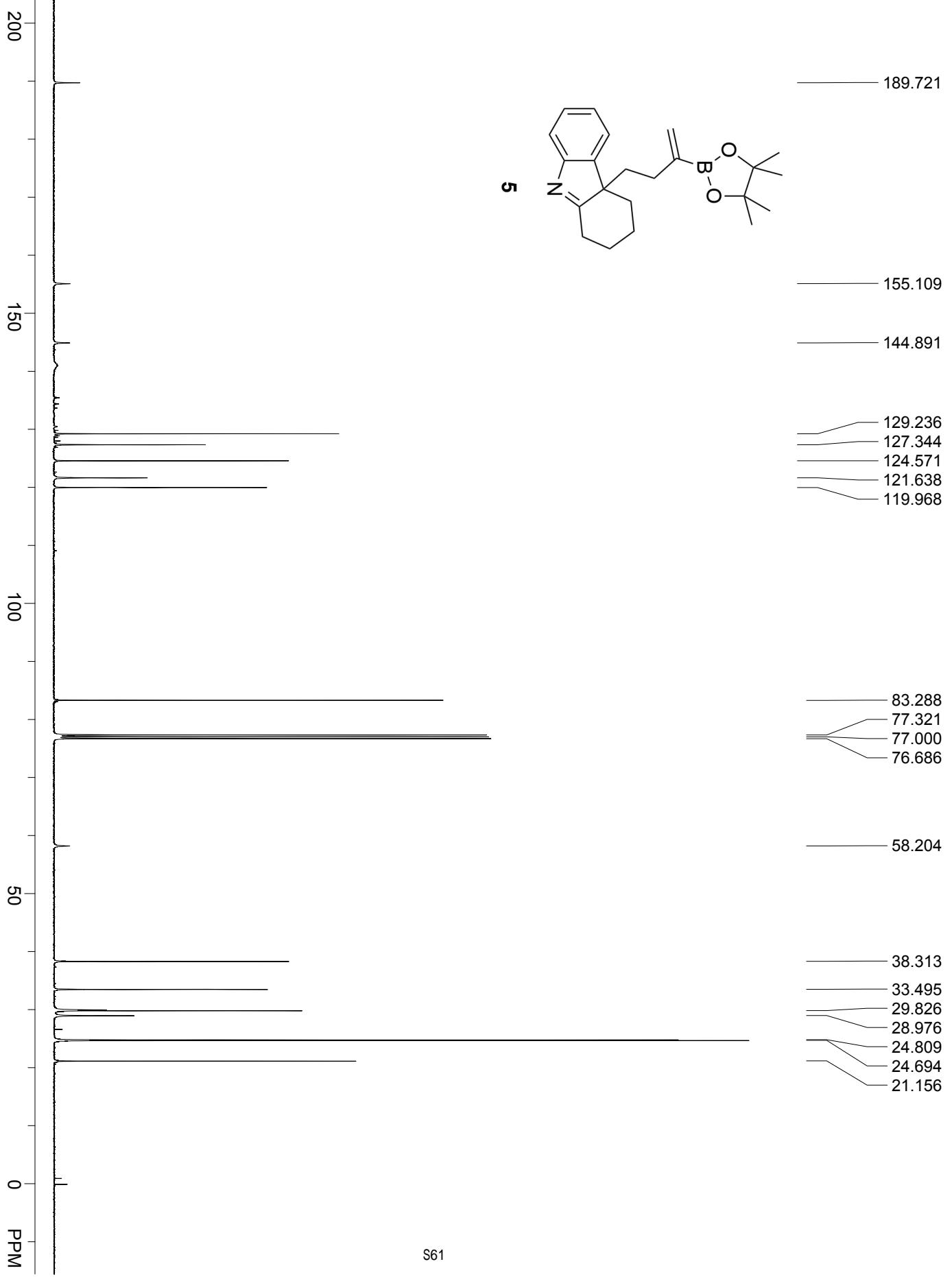


5

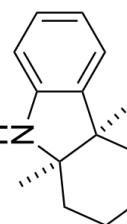
Purity (90%): nitromethane (11 μ L, 0.2 mmol)
as the internal standard in 39.1 mg



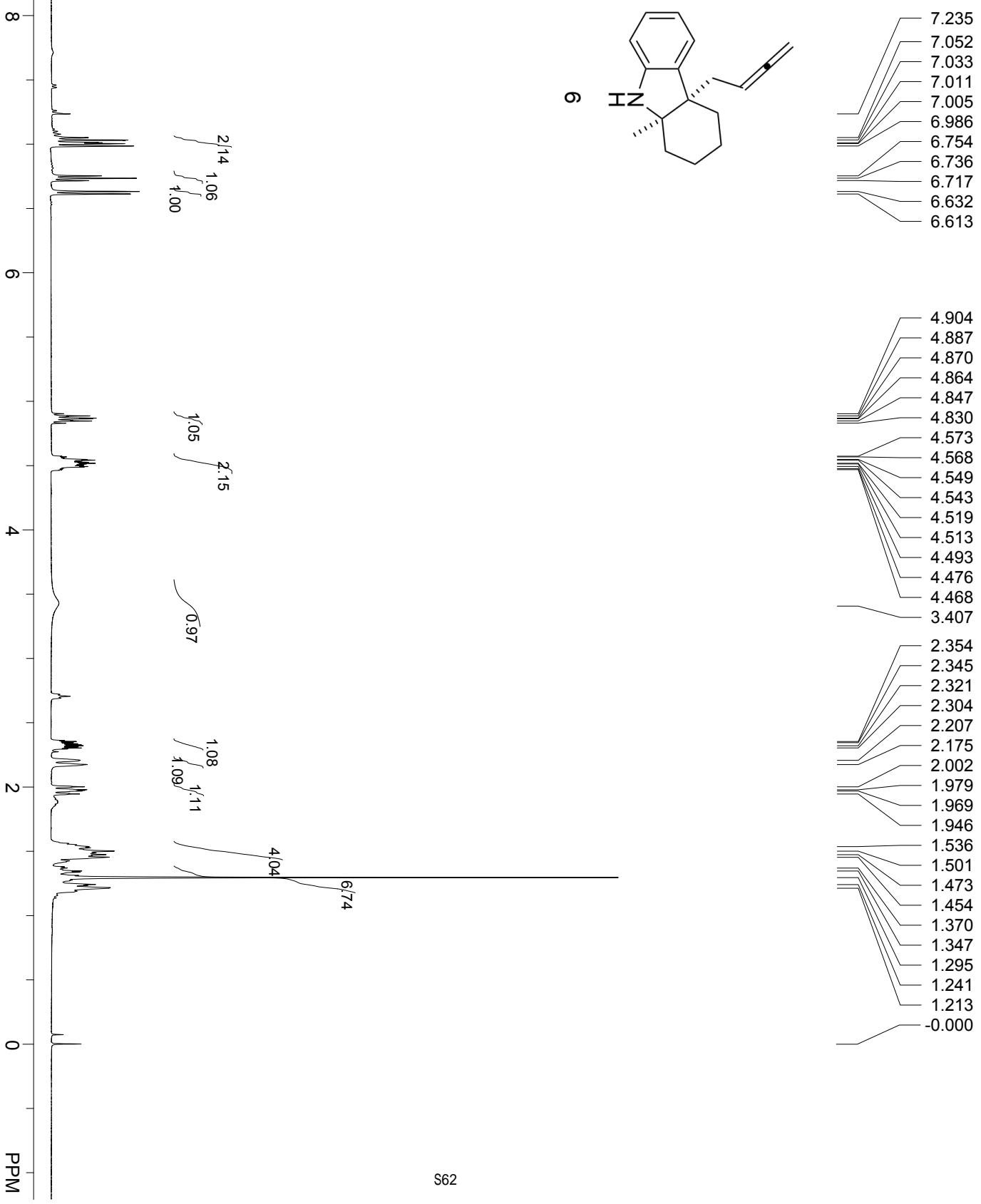
ZYZ-4-125C
SOLVENT: CDCl₃
NA = 12917
F1 = 100.630371 MHz
F2 = 1.000000 MHz



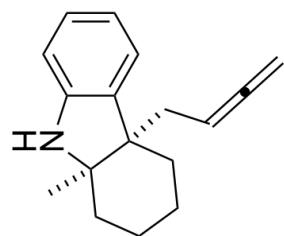
ZYX-4-117H_f1d
Nov 20 2018
SOLVENT: CDCl₃
NA = 8
F1 = 399.72226 MHz
F2 = 100.519203 MHz



6

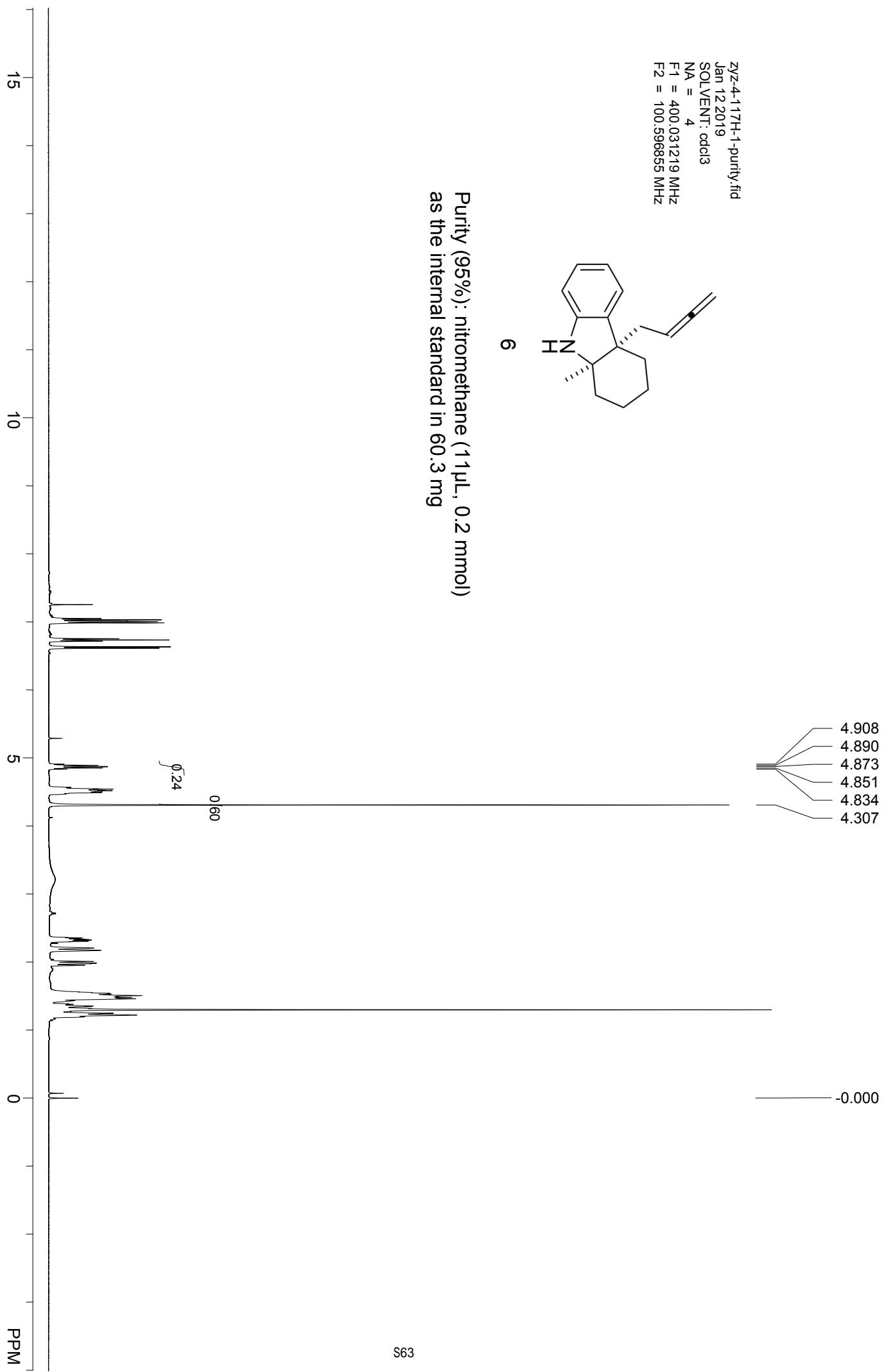


zyz-4-117H-1-purity.fid
Jan 12 2019
SOLVENT: cdd13
NA = 4
F1 = 400.031219 MHz
F2 = 100.596855 MHz

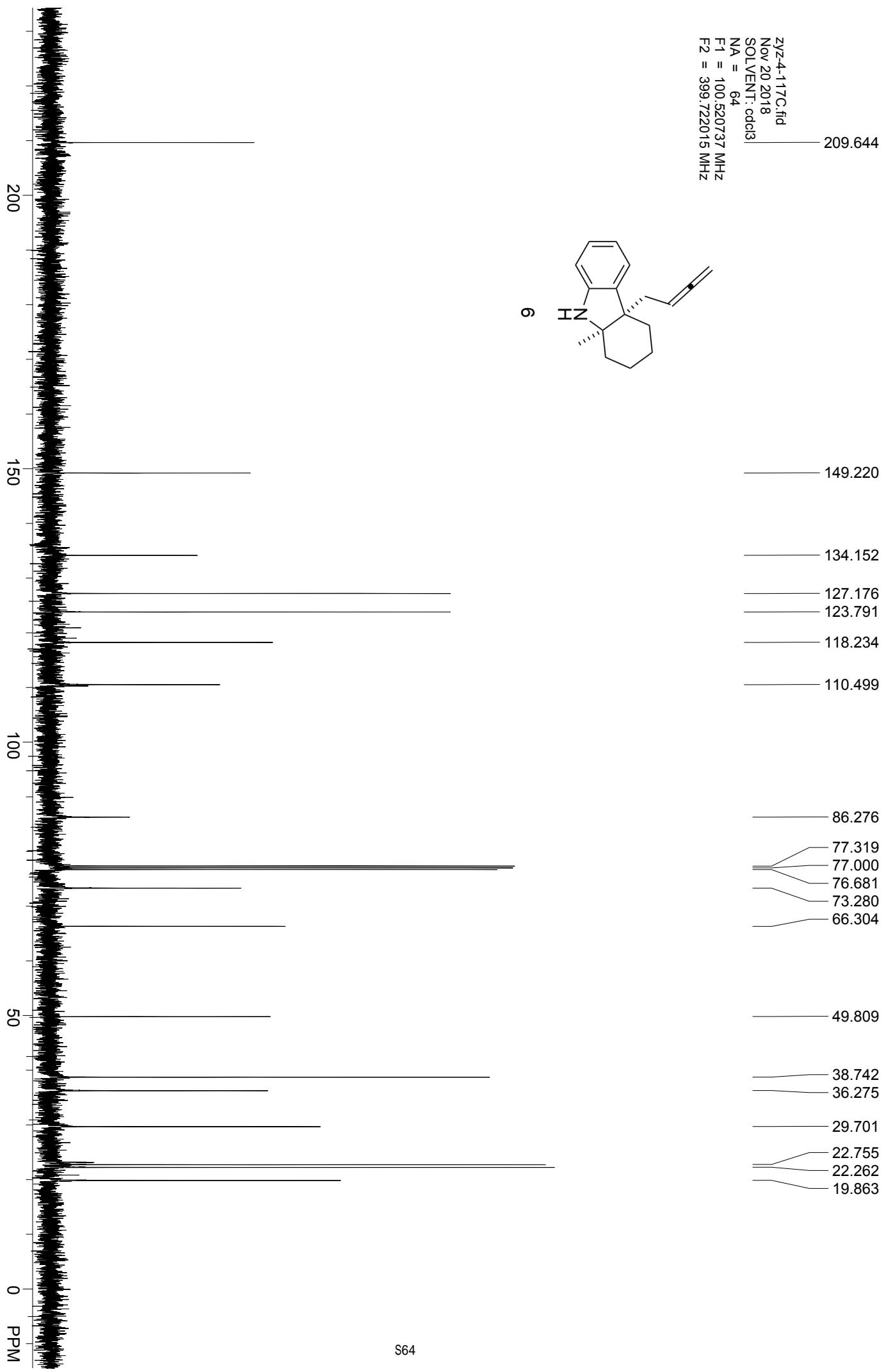


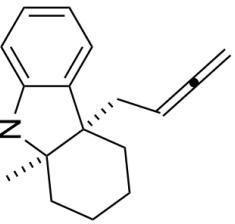
6

Purity (95%): nitromethane (11 μ L, 0.2 mmol)
as the internal standard in 60.3 mg



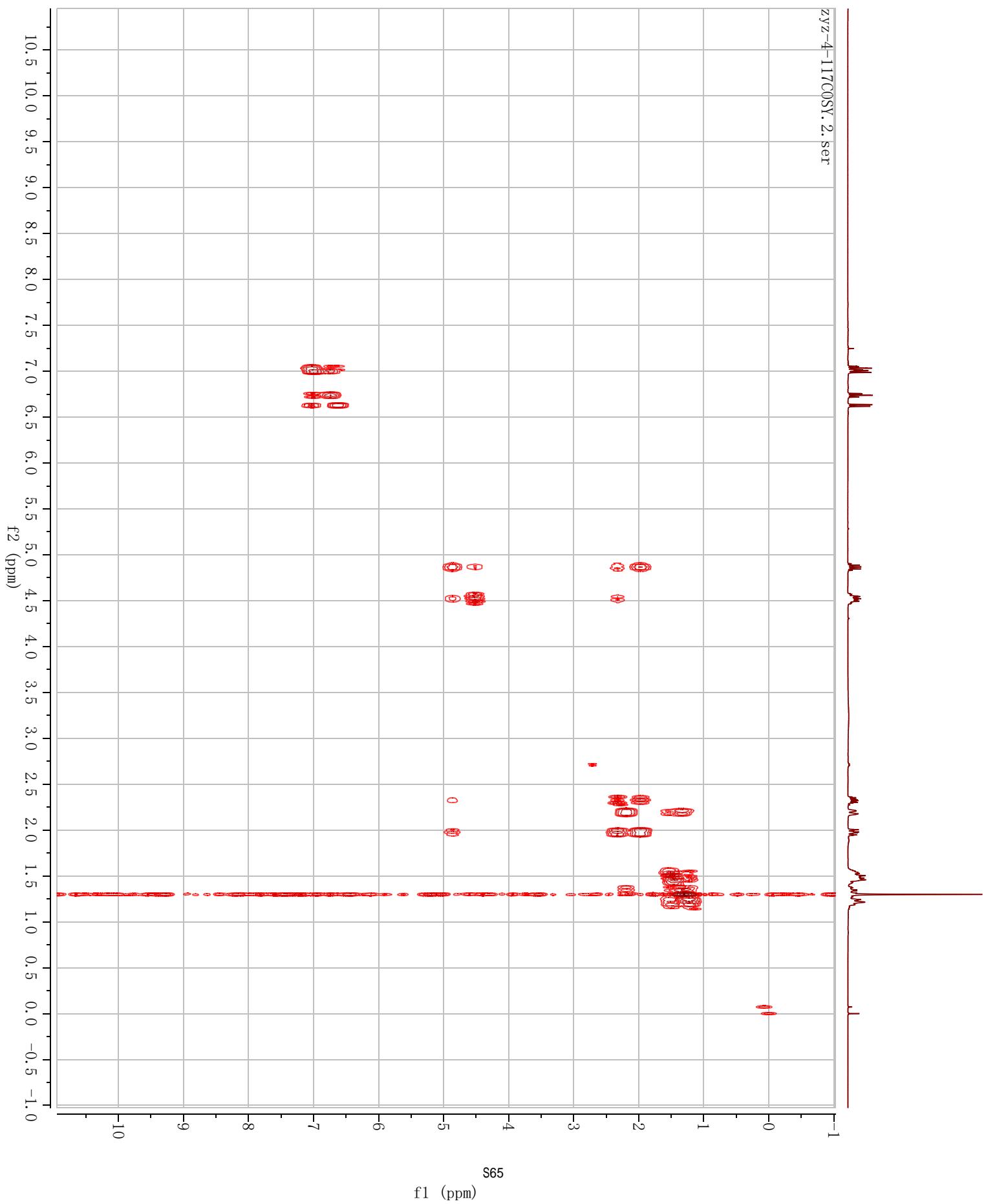
ZYZZ4-117C.fid
Nov 20 2018
SOLVENT: cdcl3
NA = 64
F1 = 100.520737 MHz
F2 = 399.722015 MHz

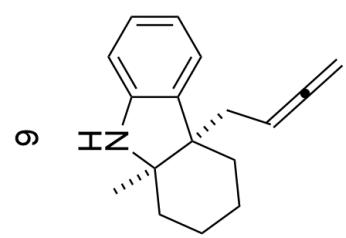




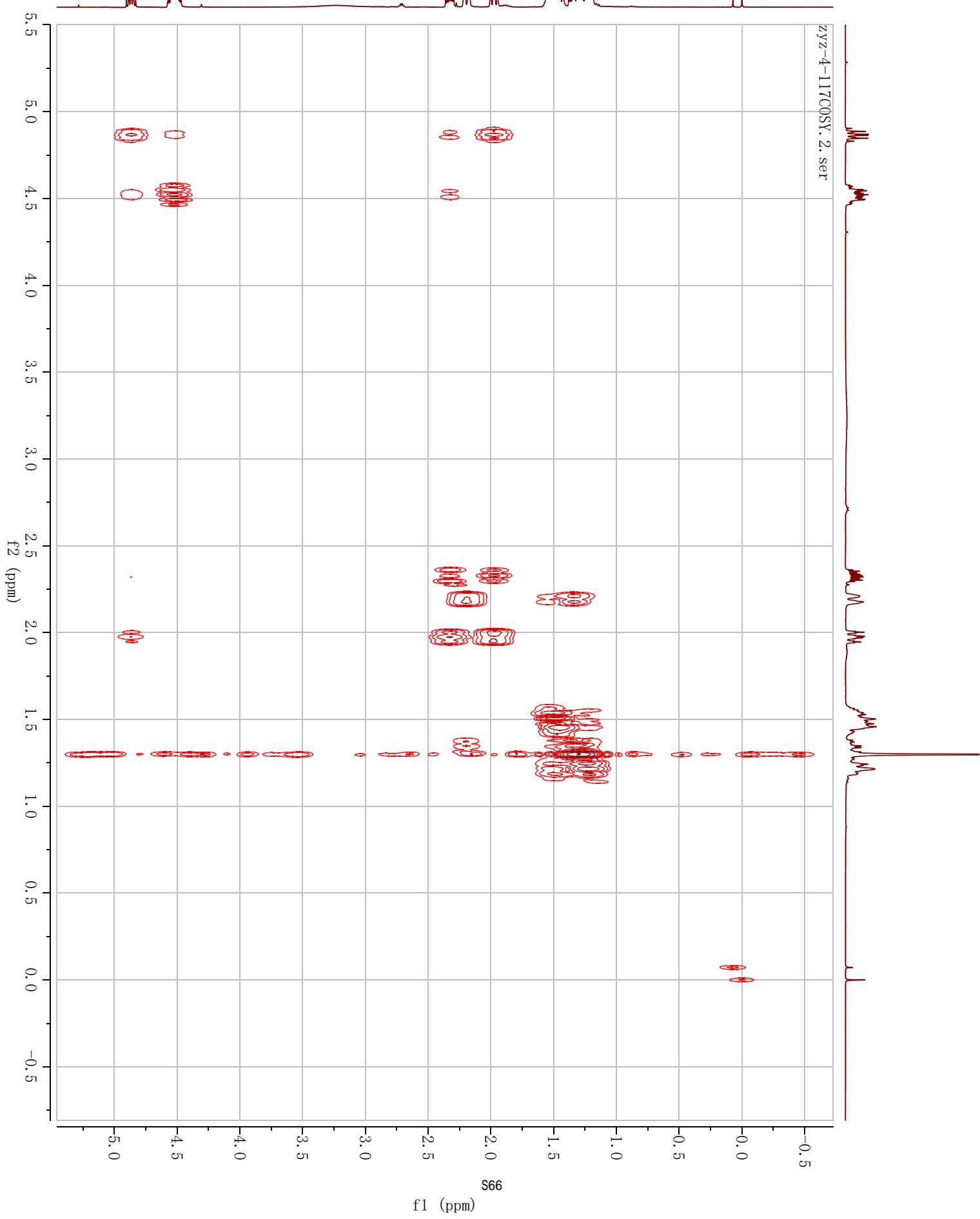
6

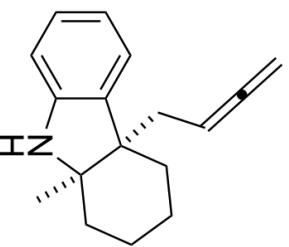
zyz-4-117COSY.2.ser





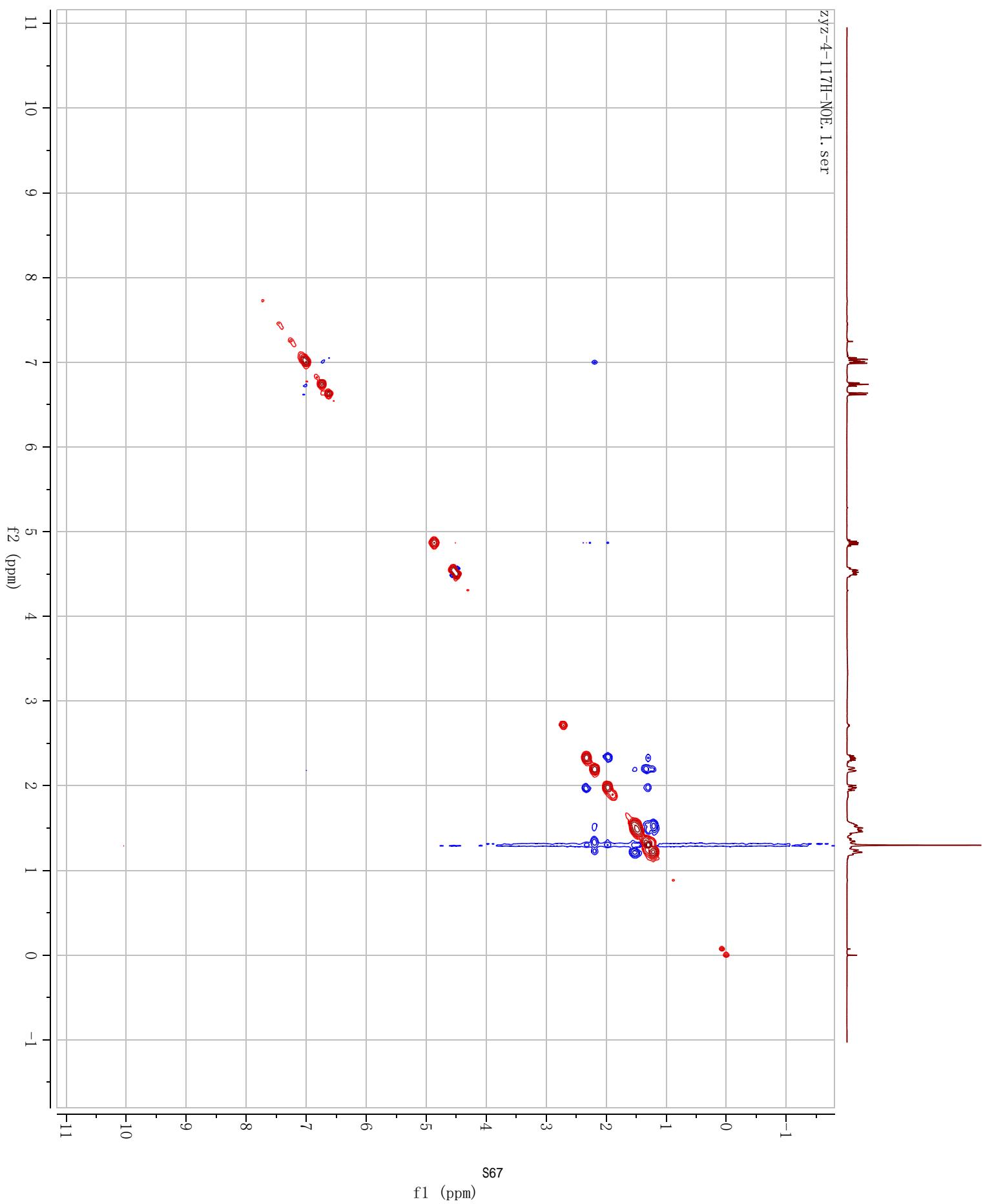
zyz-4-117COSY.2.ser

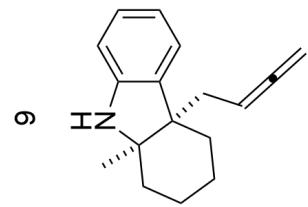




6

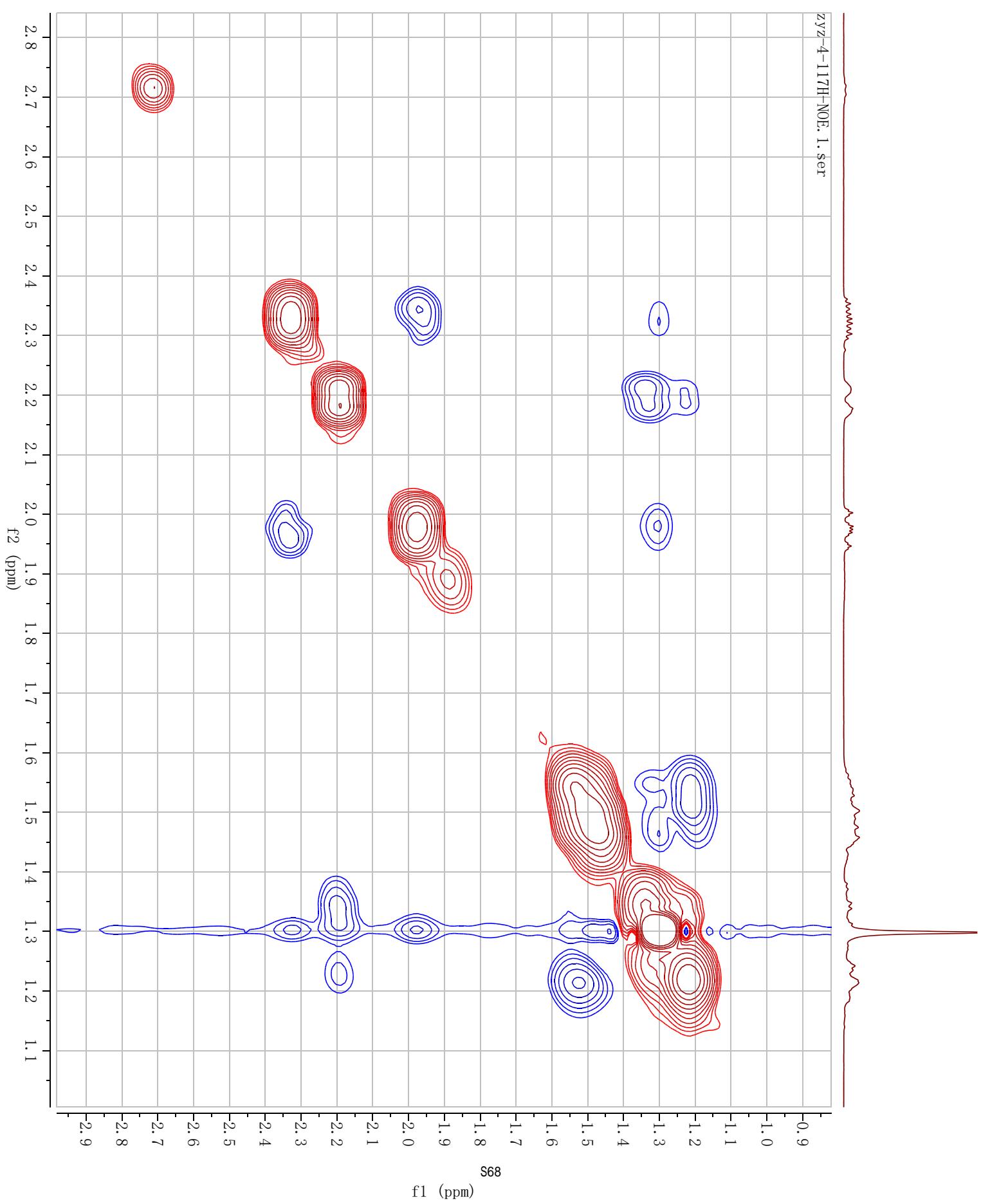
zyz-4-117H-NOE.1.ser





6

zyz-4-117H-NOE.1.ser

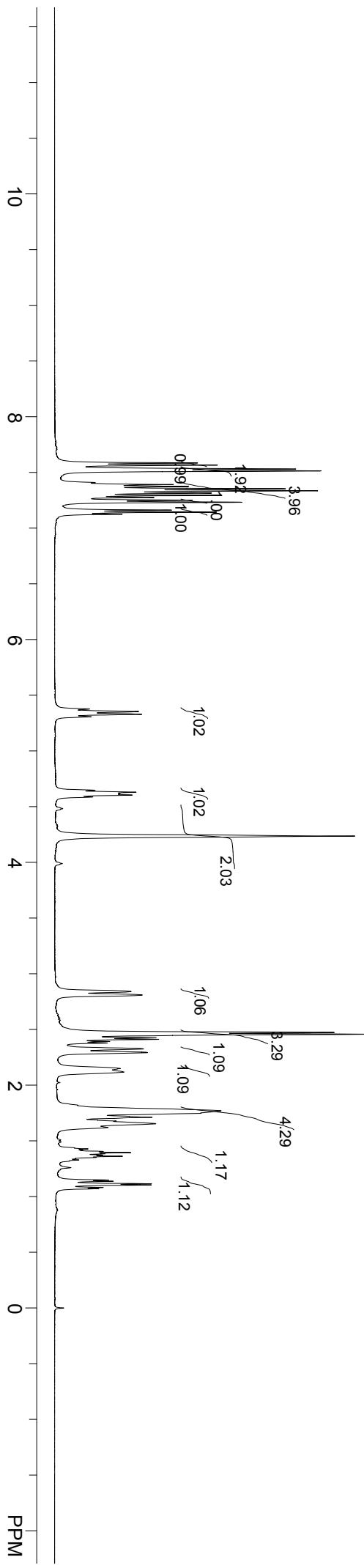


ZYX-4-118H.fid
 Nov 20 2018
 SOLVENT: CDCl₃
 NA = 8
 Solvent = CDCl₃
 F1 = 400.031403 MHz
 F2 = 100.596855 MHz

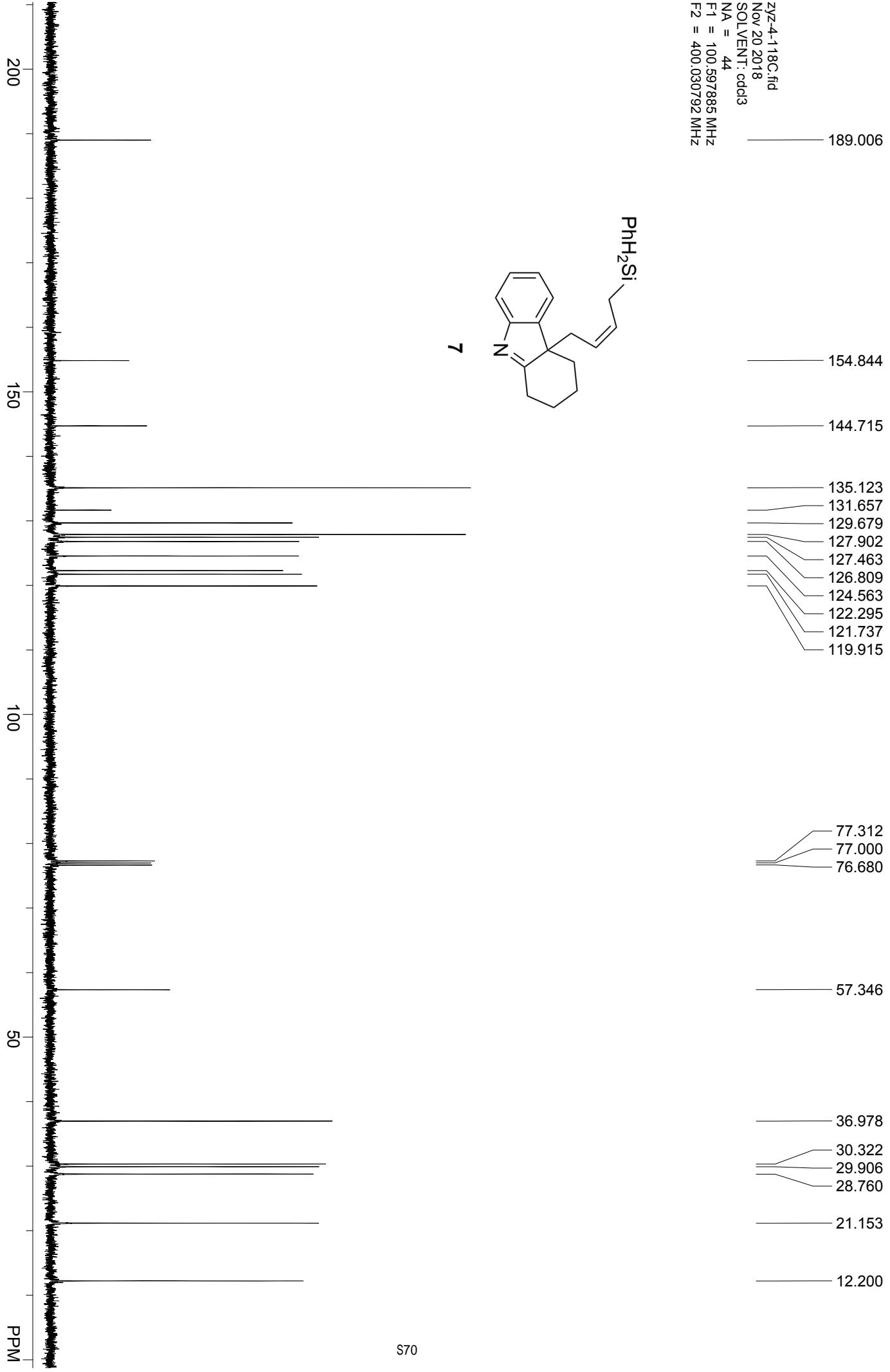
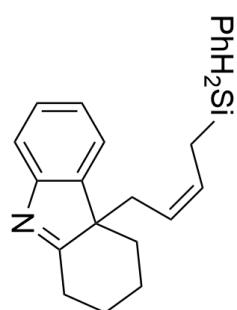
PhH₂Si

7

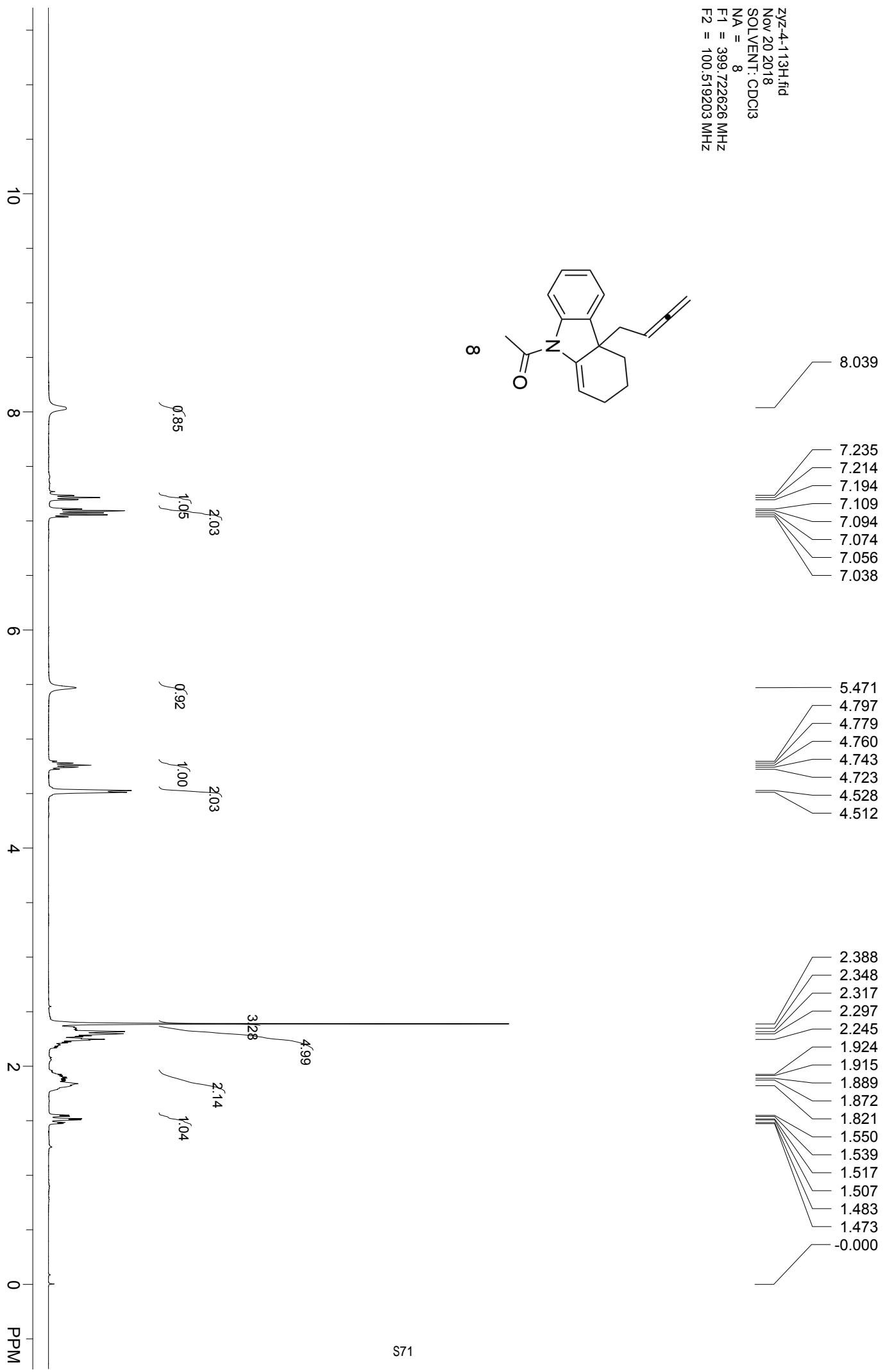
7.584
 7.565
 7.530
 7.513
 7.391
 7.373
 7.353
 7.335
 7.314
 7.294
 7.274
 7.250
 7.233
 7.162
 7.143
 7.125
 5.375
 5.353
 5.328
 5.306
 4.646
 4.629
 4.603
 4.586
 4.489
 4.481
 4.473
 4.234
 3.995
 3.987
 2.839
 2.807
 2.472
 2.456
 2.424
 2.410
 2.391
 2.377
 2.324
 2.291
 2.149
 2.117
 1.769
 1.719
 1.653
 1.394
 1.361
 1.328
 1.148
 1.137
 1.114
 1.104
 1.081
 1.070
 -0.000



ZYZZ-4-118C.fid
Nov 20 2018
SOLVENT: odc3
NA = 44
F1 = 100.597885 MHz
F2 = 400.030792 MHz



zyz-4-113H.fid
Nov 20 2018
SOLVENT: CDCl₃
NA = 8
F1 = 399.722626 MHz
F2 = 100.519203 MHz



ZYZZ-4-1 ^{13}C fid
Nov 20 2018
SOLVENT: cdcl_3
NA = 40
F1 = 100.520737 MHz
F2 = 399.722015 MHz

