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Supporting information

Palladium-Catalyzed Intermolecular Dearomatic Allenylaion of Hydrocycloalk[*b*]indoles with 2,3-Allenyl Carbonates

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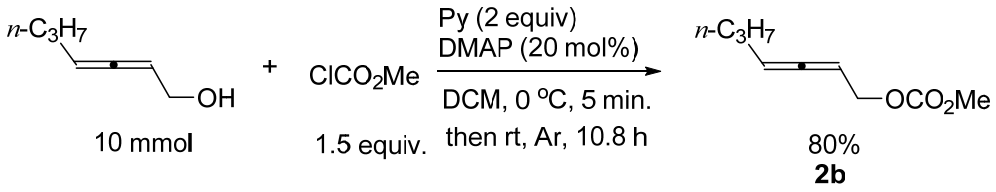
General Information. All reactions were carried out under the atmosphere of Ar in oven-dried Schlenk tubes. All of hydrocycloalk[*b*]indoles **1a-1i** were synthesized according to literature method.[1] 2,3-Dimethyl indole **1j** was purchased from Adamas Reagent. Terminal 2,3-butadienol was synthesized according to literature.[2] All of non-terminal alka-2,3-dienols were prepared as reported.[3] $Pd_2(dba)_3$ was synthesized according to the reported method.[4] $Pd(acac)_2$ was purchased from 9dingchem and stored in a glove box. DPEphos was purchased from Energy Chemical. BSA was purchased from Sigma-Aldrich and distilled before use. Et_3B was purchased from TCI. CH_2Cl_2 was dried over calcium hydride and distilled before use. Other reagents were used without further treatment. Petroleum ether (60 ^oC - 90 ^oC) was used for silica gel column chromatography. All the temperatures were referred to the oil baths used. Tetramethylsilane (TMS) was used as the internal standard for the ^1H NMR analysis; ^{13}C NMR experiments were measured in relative to the signal of $CDCl_3$ (77.00 ppm). Run-Duo Gao is responsible for compounds related to **Typical Procedure II**, and Yizhan Zhai is responsible for compounds related to **Typical Procedure I, III, IV,** and the preparation of **4jb**.

Synthesis of methyl carbonate of alka-2,3-dienols

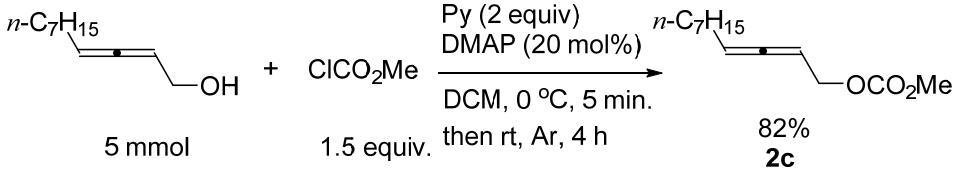
Compound **2a** was prepared according to literature.[5]

1. Synthesis of hepta-2,3-dienyl methyl carbonte (2b, zyz-2-34)



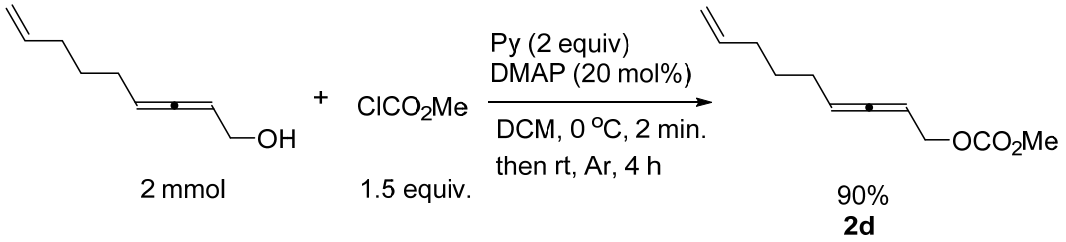
Typical Procedure I: hepta-2,3-dien-1-ol (1.1628 g, 10 mmol), DMAP (245.9 mg, 2 mmol), pyridine (1.6 mL, d = 0.9819 g/cm^3, 1.5710 g, 20 mmol), and DCM (30 mL) were added sequentially into a flask under argon at room temperature. Then methyl chloroformate (1.2 mL, d = 1.223 g/cm^3, 1.4676 g, 15 mmol) was added dropwise within 5 min at 0 ºC. The resulting mixture was allowed to stir at room temperature for 10.8 h as monitored by TLC. Upon completion, DCM (30 mL) and 1 M HCl (30 mL) were added and the organic phase was separated. The aqueous phase was extracted with DCM (30 mL × 2). The combined organic phase was washed with a saturated aqueous solution of $NaHCO_3$ (30 mL) and brine (30 mL) and dried over anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by silica gel column chromatography to afford **2b** (1.4074 g, 80%) (eluent: petroleum ether / ethyl acetate = 20/1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32-5.24 (m, 2 H, HC=C=CH), 4.64-4.55 (m, 2 H, OCH_2), 3.78 (s, 3 H, OCH_3), 2.05-1.97 (m, 2 H, CH_2), 1.44 (sext, *J* = 7.4 Hz, 2 H, CH_2), 0.93 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.7, 155.5, 92.8, 86.2, 66.2, 54.6, 30.2, 22.0, 13.4; MS (DART) *m/z* 188 $(M+NH_4)^+$, 171 $(M+H)^+$; IR (neat, cm^{-1}): 2959, 2933, 2873, 1965, 1746, 1444, 1368, 1247; HRMS (DART) Calcd for $C_9H_{15}O_3$ [$(M+H)^+$]: 171.1016, Found: 171.1015.

2. Synthesis of undeca-2,3-dienyl methyl carbonate (2c, zyz-2-111)



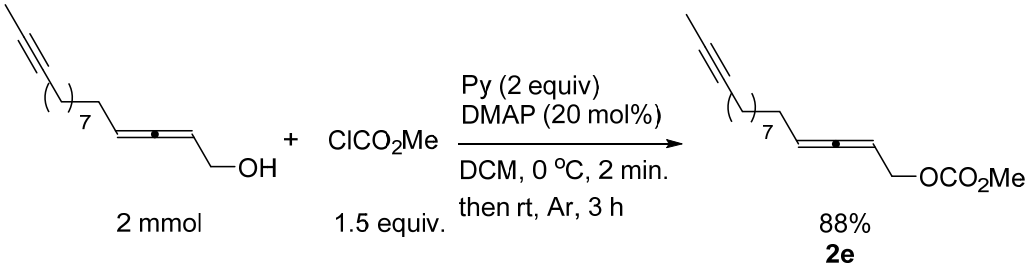
According to **Typical Procedure I**, the reaction of undeca-2,3-dienol (821.9 mg, 5 mmol), DMAP (121.1 mg, 1 mmol), pyridine (0.85 mL, d = 0.9819 g/cm^3, 834.6 mg, 10 mmol), DCM (20 mL), and methyl chloroformate (0.6 mL, d = 1.223 g/cm^3, 733.8 mg, 7.5 mmol) afforded **2c** (908.0 mg, 82%) (eluent: petroleum ether / ethyl acetate = 10/1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.33-5.22 (m, 2 H, HC=C=CH), 4.65-4.56 (m, 2 H, OCH_2), 3.79 (s, 3 H, OCH_3), 2.06-1.93 (m, 2 H, CH_2), 1.43-1.24 (m, 10 H, 5×CH_2), 0.88 (t, *J* = 6.4 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.7, 155.6, 93.1, 86.4, 66.4, 54.7, 31.8, 29.04, 28.95, 28.9, 28.2, 22.6, 14.0; MS (DART) *m/z* 244 $(M+NH_4)^+$, 227 $(M+H)^+$; IR (neat, cm^{-1}): 2956, 2925, 2855, 1966, 1748, 1444, 1367, 1251; HRMS (DART) Calcd for $C_{13}H_{23}O_3$ $(M+H)^+$: 227.1642, Found: 227.1640.

3. Synthesis of nona-2,3,8-trienyl methyl carbonate (2d, zyz-2-127)



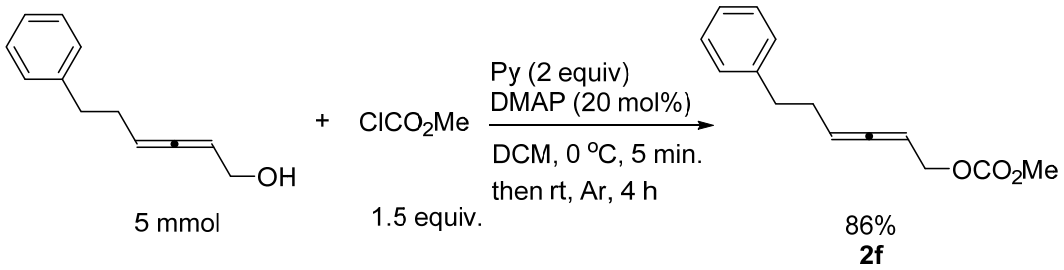
According to **Typical Procedure I**, the reaction of nona-2,3,8-trienol (278.9 mg, 2 mmol), DMAP (49.7 mg, 0.4 mmol), pyridine (0.32 mL, d = 0.9819 g/cm^3, 314.2 mg, 4 mmol), DCM (8 mL), and methyl chloroformate (0.23 mL, d = 1.223 g/cm^3, 281.3 mg, 3 mmol) afforded **2d** (354.6 mg, 90%) (eluent: petroleum ether / ethyl acetate = 10/1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87-5.72 (m, 1 H, =CH), 5.33-5.23 (m, 2 H, HC=C=CH), 5.05-4.92 (m, 2 H, =CH_2), 4.63-4.57 (m, 2 H, OCH_2), 3.78 (s, 3 H, OCH_3), 2.13-1.99 (m, 4 H, 2×CH_2), 1.51 (quint, *J* = 7.5 Hz, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.7, 155.5, 138.3, 114.7, 92.8, 86.5, 66.2, 54.7, 33.0, 28.0, 27.5; MS (DART) *m/z*: 214 $(M+NH_4)^+$; IR (neat, cm^{-1}): 3078, 2930, 2856, 1966, 1747, 1640, 1443,1368, 1251; HRMS (DART) Calcd for $C_{11}H_{17}O_3$ $(M+H)^+$: 197.1172, Found: 197.1172.

4. Synthesis of pentadeca-2,3-dien-13-ynyl methyl carbonate (2e, zyz-2-131)



According to **Typical Procedure I**, the reaction of pentadeca-2,3-dien-13-ynol (438.9 mg, 2 mmol), DMAP (47.1 mg, 0.4 mmol), pyridine (0.32 mL, d = 0.9819 g/cm^3, 314.2 mg, 4 mmol), DCM (8 mL), and methyl chloroformate (0.23 mL, d = 1.223 g/cm^3, 281.3 mg, 3 mmol) afforded **2e** (488.6 mg, 88%) (eluent: petroleum ether / ethyl acetate = 10/1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32-5.23 (m, 2 H, HC=C=CH), 4.63-4.57 (m, 2 H, OCH_2), 3.79 (s, 3 H, OCH_3), 2.15-2.08 (m, 2 H, CH_2), 2.06-1.98 (m, 2 H, CH_2), 1.79-1.76 (s, 3 H, CH_3), 1.51-1.24 (m, 12 H, 6×CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.6, 155.5, 93.0, 86.3, 79.3, 75.2, 66.3, 54.6, 29.2, 29.02, 28.97, 28.89, 28.83, 28.78, 28.1, 18.6, 3.4; MS (DART) *m/z* 296 $(M+NH_4)^+$, 279 $(M+H)^+$; IR (neat, cm^{-1}): 2925, 2854, 1965, 1748, 1443, 1367, 1252; HRMS (DART) Calcd for $C_{17}H_{27}O_3$ $(M+H)^+$: 279.1955, Found: 279.1953.

5. Synthesis of 6-phenylhexa-2,3-dienyl methyl carbonate (2f, zyz-2-112)

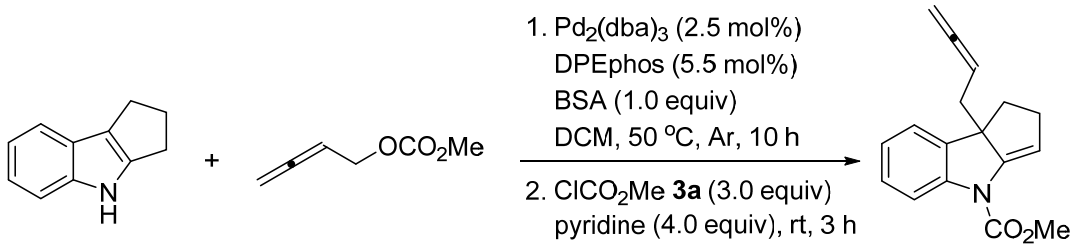


According to **Typical Procedure I**, the reaction of 6-phenylhexa-2,3-dienol (860.1 mg, 5 mmol), DMAP (120.1 mg, 1 mmol), pyridine (0.85 mL, d = 0.9819 g/cm^3, 834.6 mg, 10 mmol), DCM (20 mL), and methyl chloroformate (0.6 mL, d = 1.223 g/cm^3, 733.8 mg, 7.5 mmol) afforded **2f** (974.9 mg, 86%) (eluent: petroleum ether / ethyl acetate = 10/1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.24 (m, 2 H, Ar-H), 7.22-7.15 (m, 3 H, Ar-H), 5.36-5.24 (m, 2 H, HC=C=CH), 4.53 (dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 2 H, OCH_2), 3.78 (s, 3 H, OCH_3), 2.73 (t, J = 7.6 Hz, 2 H, CH_2), 2.39-2.29 (m, 2 H, CH_2); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 205.8, 155.5, 141.3, 128.4, 128.3, 125.9, 92.3, 86.9, 66.1, 54.7, 35.1, 29.8; MS (DART) *m/z* 250 $(M+NH_4)^+$; IR (neat, cm^{-1}): 3027, 2954, 2854, 1966, 1745, 1444, 1367, 1251; HRMS (DART) Calcd for $C_{14}H_{20}O_3N$ $(M+NH_4)^+$: 250.1438, Found: 250.1436.

Palladium-catalyzed reaction of hydrocycloalk[*b*]indoles with 2,3-allenyl carbonates

1. Methyl 8b-(2,3-butadienyl)-2,8b-dihydrocyclopenta[*b*]indole-4(*1H*)-yl carboxylate (4aaa, zyz-3-21)

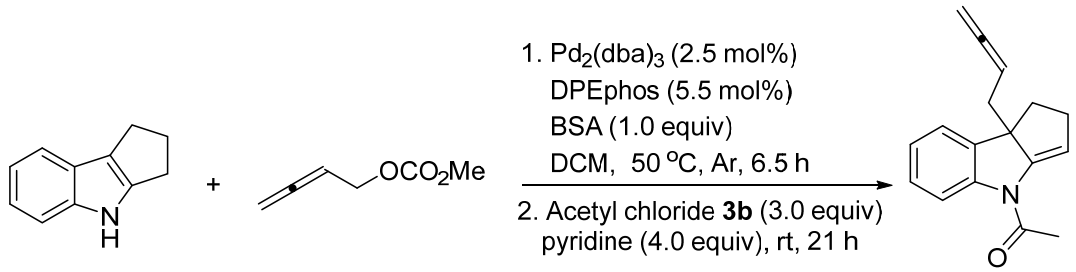


0.2 mmol **1a** | 1.3 equiv **2a** | 80% **4aaa**

Typical Procedure II: To an oven dried Schlenk tube equipped with a polytetrafluoroethylene plug were added $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol), DPEphos (5.9 mg, 0.011 mmol), and DCM (2.0 mL) sequentially under the atmosphere of Ar. The resulting mixture was stirred at room temperature for 30 min. Compound **1a** (31.3 mg, 0.2 mmol), BSA (40.6 mg, 0.2 mmol), **2a** (33.7 mg, 0.26 mmol), and DCM (2 mL) were then added sequentially. The Schlenk tube was then sealed by screwing the polytetrafluoroethylene plug tightly and stirred at 50 °C for 10 h. After the reaction was complete as monitored by TLC, the resulting mixture was cooled to room temperature. $ClCO_2Me$ (47 μL, d = 1.223 g/cm^3, 59.9 mg, 0.6 mmol) and pyridine (63 μL, d = 0.9819 g/cm^3, 61.9 mg, 0.8 mmol) were added and the resulting mixture was stirred at room temperature for 3 h as monitored by TLC. Then a saturated aqueous solution of $NaHCO_3$ (5 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 Na_2SO_4. After filtration and evaporation, the residue was purified by silica gel column chromatography to afford **4aaa** (42.5 mg, 80%) (eluent: petroleum ether / ethyl acetate = 80/1) as an oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (brs, 1 H, Ar-H), 7.20-7.13 (m, 1 H, Ar-H), 7.08 (d, *J* = 7.6 Hz, 1 H, Ar-H), 6.96 (t, *J* = 7.4 Hz, 1 H, Ar-H), 5.40 (brs, 1 H,

=CH), 4.92-4.80 (m, 1 H, =CH), 4.46 (dt, J_1 = 6.4 Hz, J_2 = 2.2 Hz, 2 H, =CH_2), 3.85 (s, 3 H, OCH_3), 2.81-2.70 (m, 1 H, one proton of CH_2), 2.46-2.35 (m, 1 H, one proton of CH_2), 2.25-2.13 (m, 2 H, CH_2), 2.11-2.03 (m, 1 H, one proton of CH_2), 1.99-1.89 (m, 1 H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.1, 152.9, 149.8, 144.3, 135.4, 127.7, 123.7, 123.2, 115.0, 106.8, 85.3, 73.9, 58.5, 52.9, 37.1, 35.0, 32.4; MS (ESI) *m/z* 290 $(M+Na)^+$, 268 $(M+H)^+$; IR (neat, cm^{-1}): 2952, 2932, 2849, 1953, 1718, 1668, 1605, 1475, 1458, 1439, 1367, 1302, 1265, 1222, 1095. HRMS (ESI) Calcd for $C_{17}H_{18}NO_2$ [$(M+H)^+$]: 268.1331, Found: 268.1330.

2. 4-Acetyl-8b-(2,3-butadienyl)-1,2,4,8b-tetrahydrocyclopenta[*b*]indole (4aab, grd-17-84)

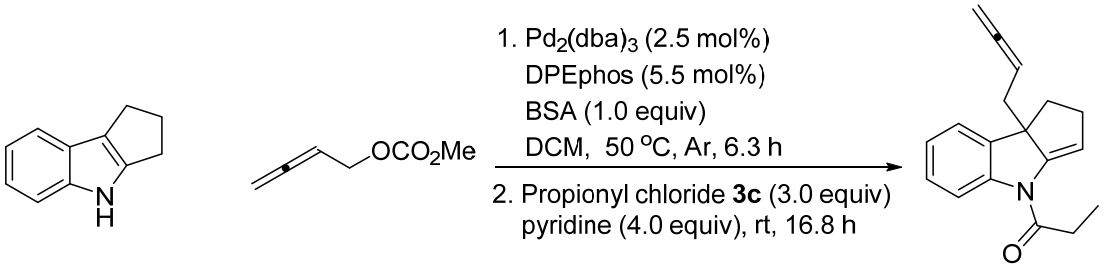


0.2 mmol **1a** | 1.3 equiv **2a** | 79% **4aab**

According to **Typical Procedure II**, the reaction of $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol), DPEphos (6.0 mg, 0.011 mmol), DCM (2 mL), **1a** (31.5 mg, 0.2 mmol), **2a** (33.4 mg, 0.26 mmol), BSA (40.7 mg, 0.2 mmol), DCM (2 mL), pyridine (65 μL, d = 0.9819 g/cm^3, 63.8 mg, 0.8 mmol), and **3b** (43 μL, d = 1.104 g/cm^3, 47.5 mg, 0.6 mmol) afforded **4aab** (39.4 mg, 79%) (eluent: petroleum ether / ethyl acetate = 60/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (brs, 1 H, Ar-H), 7.27-7.20 (m, 1 H, Ar-H), 7.16 (dd, J_1 = 7.4 Hz , J_2 = 1.0 Hz, 1 H, Ar-H), 7.07 (td, 1 H, J_1 = 7.4 Hz, J_2 = 1.1 Hz, Ar-H), 5.30 (brs, 1 H, =CH), 4.93-4.83 (m, 1 H, =CH), 4.56 (dt, J_1 = 6.8 Hz, J_2 = 2.3 Hz, 2 H, =CH_2), 2.90-2.79 (m, 1 H, one proton of CH_2), 2.55-2.47 (m, 1 H, one proton of CH_2), 2.43 (s, 3 H, CH_3), 2.32-2.26 (m, 1 H, one proton of CH_2), 2.25-2.19 (m, 2 H, CH_2), 2.09-1.99 (m, 1 H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) 209.9, 168.6, 151.3, 144.8, 135.9, 127.7, 124.0, 123.1, 117.1, 109.2, 85.2, 74.1, 59.1, 37.2, 35.0, 32.4, 24.6; IR (neat, cm^{-1}): 2931, 1953,

1675, 1602, 1455, 1376, 1350, 1284, 1205, 1106, 1014; HRMS (ESI) Calcd for $C_{17}H_{18}NO$ ($[M+H]^+$): 252.1383, Found: 252.1384.

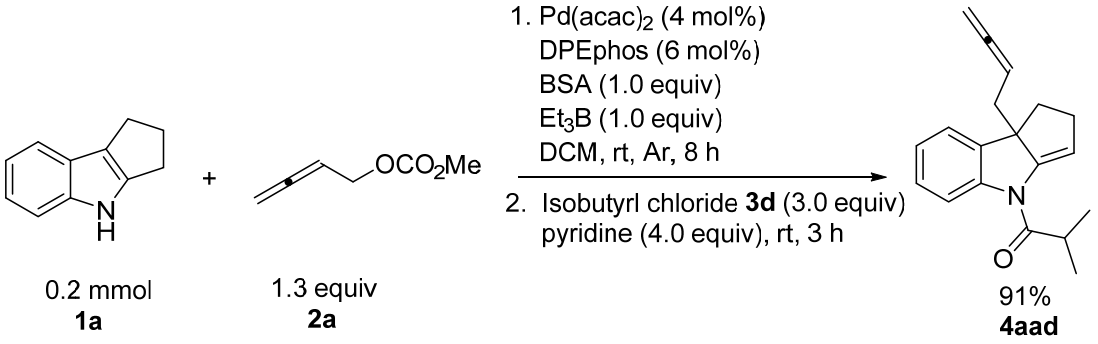
3. 8b-(2,3-Butadienyl)-4-propionyl-1,2,4,8b-tetrahydrocyclopenta[*b*]indole (4aac, grd-17-83-2)



0.2 mmol **1a** | 1.3 equiv **2a** | 86% **4aac**

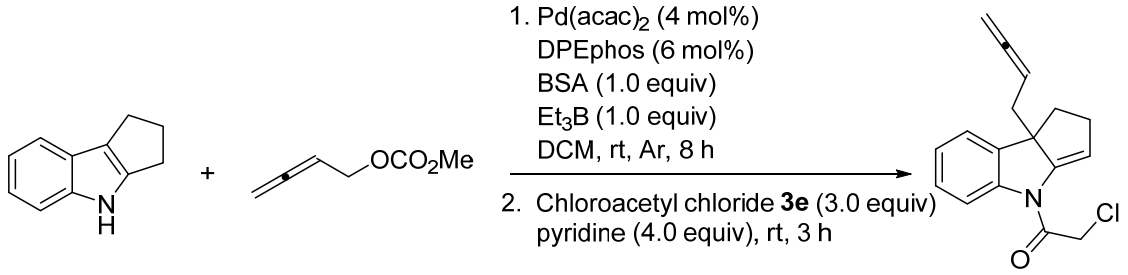
According to **Typical Procedure II**, the reaction of $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol), DPEphos (6.0 mg, 0.011 mmol), DCM (2 mL), **1a** (31.5 mg, 0.2 mmol), **2a** (33.4 mg, 0.26 mmol), BSA (40.7 mg, 0.2 mmol), DCM (2 mL), pyridine (65 μL, d = 0.9819 g/cm^3, 63.8 mg, 0.8 mmol), and **3c** (53 μL, d = 1.065 g/cm^3, 56.4 mg, 0.6 mmol) afforded **4aac** (45.7 mg, 86%) (eluent: petroleum ether/ethyl acetate = 40/1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.6 Hz, 1 H, Ar-H), 7.24 (t, *J* = 7.4 Hz, 1 H, Ar-H), 7.16 (d, *J* = 7.4 Hz, 1 H, Ar-H), 7.06 (t, *J* = 7.4 Hz, 1 H, Ar-H), 5.31 (d, *J* = 2.4 Hz, 1 H, =CH), 4.93-4.84 (m, 1 H, =CH), 4.60-4.50 (m, 2 H, =CH_2), 2.90-2.61 (m, 3 H, one proton of CH_2 and another CH_2), 2.56-2.44 (m, 1 H, one proton of CH_2), 2.33-2.18 (m, 3 H, CH_2 and another one proton of CH_2), 2.08-1.98 (m, 1 H, one proton of CH_2), 1.25 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9, 172.3, 150.9, 145.0, 135.9, 127.7, 123.9, 123.1, 117.1, 109.1, 85.2, 74.0, 59.2, 37.1, 34.8, 32.4, 29.5, 8.8; IR (neat, cm^{-1}): 2984, 2942, 2851, 1954, 1675, 1600, 1453, 1376, 1325, 1258, 1197, 1169, 1104, 1072, 1020; HRMS (ESI) Calcd. for $C_{18}H_{20}NO$ ($[M+H]^+$): 266.1539, Found: 266.1541.

4. 8b-(2,3-Butadienyl)-4-(2-methylpropionyl)-1,2,4,8b-tetrahydrocyclopenta[*b*]indole (4aad, zyz-2-158)



Typical Procedure III: To an oven dried Schlenk tube were added $Pd(acac)_2$ (2.4 mg, 0.008 mmol), DPEphos (5.9 mg, 0.012 mmol), and DCM (2 mL) sequentially under the atmosphere of Ar. The resulting mixture was stirred at room temperature 30 min. Compound **1a** (31.7 mg, 0.2 mmol), BSA (41.7 mg, 0.2 mmol)/DCM (1 mL), **2a** (33.7 mg, 0.26 mmol)/DCM (1 mL), and Et_3B (1M in THF, 0.2 mL, 0.2 mmol) were then added sequentially and the resulting mixture stirred at room temperature for 8 h. After the reaction was complete as monitored by TLC, pyridine (64 μL, d = 0.9819 g/cm³, 62.8 mg, 0.8 mmol) and **3d** (62 μL, d = 1.107 g/cm^3, 68.6 mg, 0.6 mmol) were added. The resulting mixture was stirred at room temperature for 3 h as monitored by TLC. A saturated aqueous solution of $NaHCO_3$ (15 mL) was added and the resulting mixture was extracted with DCM (15 mL×3). The combined organic layer was washed with brine (10 mL) and dried over anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by silica gel column chromatography to afford **4aad** (51.5 mg, 91%) (eluent: petroleum ether / ethyl acetate = 30/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.6 Hz, 1 H, Ar-H), 7.24 (t, *J* = 8.0 Hz, 1 H, Ar-H), 7.16 (d, *J* = 7.6 Hz, 1 H, Ar-H), 7.07 (t, *J* = 7.4 Hz, 1 H, Ar-H), 5.36 (brs, 1 H, =CH), 4.90 (quint, *J* = 7.3 Hz, 1 H, =CH), 4.59-4.51 (m, 2 H, $=CH_2$), 3.28 (sep, *J* = 6.7 Hz, 1 H, CH), 2.91-2.79 (m, 1 H, one proton of CH_2), 2.57-2.46 (m, 1 H, one proton of CH_2), 2.34-2.16 (m, 3 H, CH_2 and one proton of another CH_2), 2.09-1.99 (m, 1 H, one proton of CH_2), 1.28 (d, *J* = 6.8 Hz, 3 H, CH_3), 1.23 (d, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.0, 175.9, 150.8, 145.0, 136.3, 127.7, 124.0, 123.0, 117.5, 109.1, 85.3, 74.1, 59.2, 37.1, 34.8, 33.0, 32.2, 19.5, 19.2; MS (ESI) *m/z* 581 $(2M+Na)^+$, 302 $(M+Na)^+$, 280 $(M+H)^+$; IR (neat, cm^{-1}): 3070, 2966, 2933, 2852, 1954, 1672, 1602, 1472, 1456, 1389, 1362, 1259, 1193, 1108; HRMS (ESI) Calcd. for $C_{19}H_{22}NO$ ($[M+H]^+$): 280.1696, Found: 280.1693.

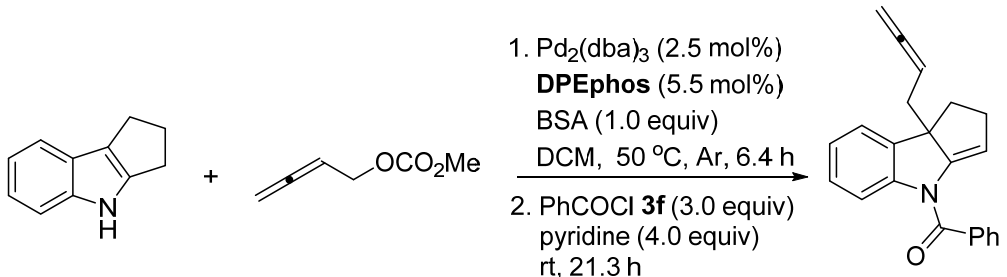
5. 8b-(2,3-Butadienyl)-4-chloroacetyl-1,2,4,8b-tetrahydrocyclopenta[*b*]indole (4aae, zyz-2-155C)



0.2 mmol **1a** | 1.3 equiv **2a** | 88% **4aae**

According to **Typical Procedure III**, the reaction of $Pd(acac)_2$ (4.6 mg, 0.008 mmol), DPEphos (5.9 mg, 0.012 mmol), DCM (2 mL), **1a** (30.9 mg, 0.2 mmol), BSA (40.7 mg, 0.2 mmol)/DCM (1 mL), **2a** (33.1 mg, 0.26 mmol)/DCM (1 mL), Et_3B (1M in THF, 0.2 mL, 0.2 mmol), pyridine (64 μL, d = 0.9819 g/cm^3, 62.8 mg, 0.8 mmol), and **3e** (48 μL, d = 1.419 g/cm^3, 68.1 mg, 0.6 mmol) afforded **4aae** (49.3 mg, 88%) (eluent: petroleum ether/ethyl acetate = 30/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.2 Hz, 1 H, Ar-H), 7.27 (t, *J* = 7.8 Hz, 1 H, Ar-H), 7.18 (d, *J* = 7.2 Hz, 1 H, Ar-H), 7.12 (t, *J* = 7.4 Hz, 1 H, Ar-H), 5.50 (brs, 1 H, =CH), 4.88 (quint, *J* = 7.2 Hz, 1 H, =CH), 4.57 (d, *J* = 6.4 Hz, 2 H, $=CH_2$), 4.45 (d, *J* = 13.6 Hz, 1 H, one proton of CH_2Cl), 4.41 (d, *J* = 13.2 Hz, 1 H, one proton of CH_2Cl), 2.94-2.80 (m, 1 H, one proton of CH_2), 2.60-2.48 (m, 1 H, one proton of CH_2), 2.31 (dd, J_1 = 12.0, J_2 = 6.0 Hz, 1 H, one proton of CH_2), 2.25-2.23 (m, 2 H, CH_2), 2.07 (dd, J_1 = 21.2 Hz, J_2 = 9.6 Hz, 1 H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9, 163.8, 150.0, 144.2, 136.2, 127.9, 124.9, 123.2, 117.4, 110.7, 85.0, 74.2, 59.2, 42.8, 37.2, 35.0, 32.4; MS (ESI) *m/z* 308 $(M(^{35}Cl)+Na)^+$, 288 $(M(^{37}Cl)+H)^+$, 286 $(M(^{35}Cl)+H)^+$, 288 $(M(^{37}Cl)+H)^+$; IR (neat, cm^{-1}): 2936, 2852, 1953, 1672, 1602, 1473, 1456, 1379, 1314, 1260, 1195, 1171, 1229, 1107, 1080, 1019; HRMS (ESI) Calcd for $C_{17}H_{17}{}^{35}ClNO$ ($[M+H]^+$): 286.0993, Found: 286.0993.

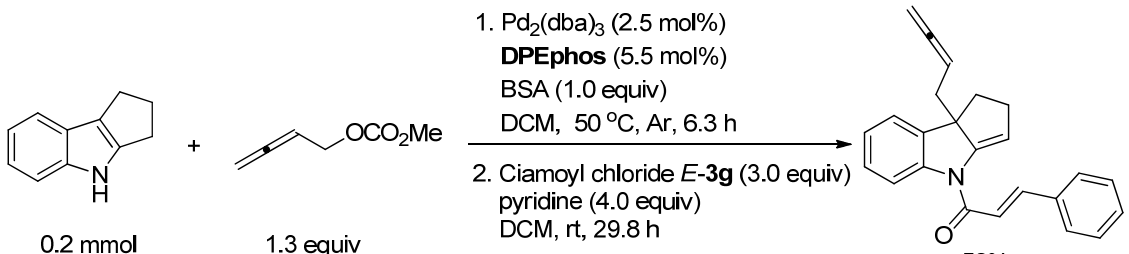
6. 4-Benzoyl-8b-(2,3-butadienyl)-1,2,4,8b-tetrahydrocyclopenta[*b*]indole (4aaf, grd-17-79-2)



0.2 mmol **1a** | 1.3 equiv **2a** | 63% **4aaf**

According to **Typical Procedure II**, the reaction of $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol), DPEphos (6.0 mg, 0.011 mmol), DCM (2 mL), **1a** (31.5 mg, 0.2 mmol), BSA (40.7 mg, 0.2 mmol), **2a** (33.4 mg, 0.26 mmol), DCM (2 mL), pyridine (65 μL, d = 0.9819 g/cm^3, 63.8 mg, 0.8 mmol), and **3f** (70 μL, d = 1.211 g/cm^3, 84.8 mg, 0.6 mmol) afforded **4aaf** (39.2 mg, 63%) (eluent: petroleum ether/ethyl acetate = 50/1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 4.8 Hz, 1 H, Ar-H), 7.71-7.64 (m, 2 H, Ar-H), 7.54-7.46 (m, 1 H, Ar-H), 7.46-7.39 (m, 2 H, Ar-H), 7.28-7.22 (m, 1 H, Ar-H), 7.22-7.18 (m, 1 H, Ar-H), 7.13-7.08 (m, 1 H, Ar-H), 5.06-4.95 (m, 1 H, =CH), 4.68-4.58 (m, 2 H, =CH_2), 4.45 (brs, 1 H, =CH), 2.72-2.60 (m, 1 H, one proton of CH_2), 2.38 (dt, J_1 = 8.0, J_2 = 2.4 Hz, 2 H, CH_2), 2.35-2.23 (m, 2 H, one proton of CH_2 and one proton of another CH_2), 2.06-1.96 (m, 1 H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.0, 168.6, 151.3, 145.2, 136.3, 136.0, 131.0, 128.25, 128.16, 127.7, 124.3, 123.4, 116.8, 109.8, 85.7, 74.3, 58.8, 37.5, 35.2, 32.2; IR (neat, cm^{-1}): 3062, 2931, 2851, 1953, 1659, 1600, 1454, 1362, 1306, 1174, 1106, 1053, 1024; HRMS (ESI) Calcd for $C_{22}H_{20}NO$ ([M+H]$^+$): 314.1539, Found: 314.1540.

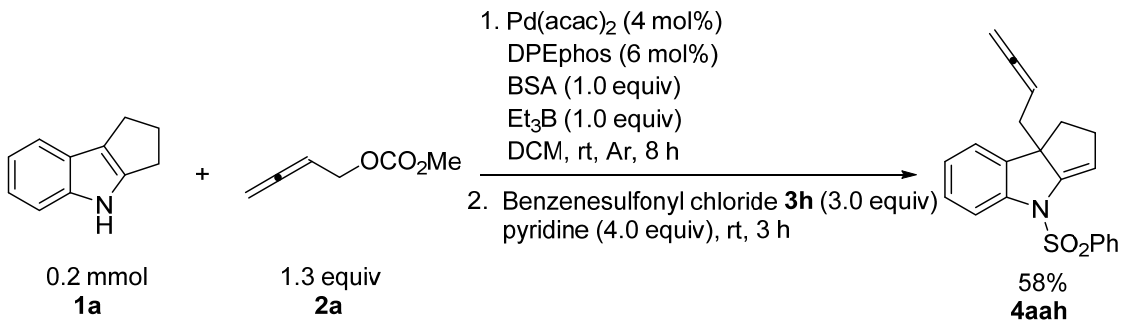
7. 8b-(2,3-Butadienyl)-4-cinnamoyl-1,2,4,8b-tetrahydrocyclopenta[*b*]indole (4aag, grd-17-83-3)



0.2 mmol **1a** | 1.3 equiv **2a** | 58% ***E*-4aag**

According to **Typical Procedure II**, the reaction of $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol), DPEphos (6.0 mg, 0.011 mmol), DCM (2 mL), **1a** (31.5 mg, 0.2 mmol), **2a** (33.4 mg, 0.26 mmol), BSA (40.7 mg, 0.2 mmol), DCM (2 mL), pyridine (65 μL, d = 0.9819 g/cm^3, 63.8 mg, 0.8 mmol), and *E*-**3g** (100 mg, 0.6 mmol) afforded *E*-**4aag** (39.6 mg, 58%) (eluent: petroleum ether/ethyl acetate = 50/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 7.6 Hz, 1 H, Ar-H), 7.83 (d, *J* = 15.6 Hz, 1 H, =CH), 7.62-7.56 (m, 2 H, Ar-H), 7.46-7.38 (m, 3 H, Ar-H), 7.32-7.22 (m, 2 H, Ar-H and =CH), 7.20 (d, *J* = 6.8 Hz, 1 H, =CH), 7.11 (t, *J* = 7.2 Hz, 1 H, Ar-H), 5.41 (d, *J* = 2.4 Hz, 1 H, =CH), 4.98-4.88 (m, 1 H, =CH), 4.62-4.50 (m, 2 H, =CH_2), 2.97-2.84 (m, 1 H, one proton of CH_2), 2.60-2.48 (m, 1 H, one proton of CH_2), 2.39-2.27 (m, 3 H, CH_2 and one pronton of another CH_2), 2.16-2.03 (m, 1 H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.0, 164.3, 151.2, 144.9, 143.2, 136.3, 134.9, 130.0, 128.9, 128.1, 127.9, 124.3, 123.2, 119.6, 117.3, 111.0, 85.2, 74.2, 58.8, 37.2, 35.3, 32.2; IR (neat, cm^{-1}): 3063, 2929, 1953, 1661, 1619, 1453, 1367, 1284, 1257, 1198, 1167, 1107, 1078; HRMS (ESI) Calcd for $C_{24}H_{22}NO$ ($[M+H]^+$): 340.1696, Found: 340.1700.

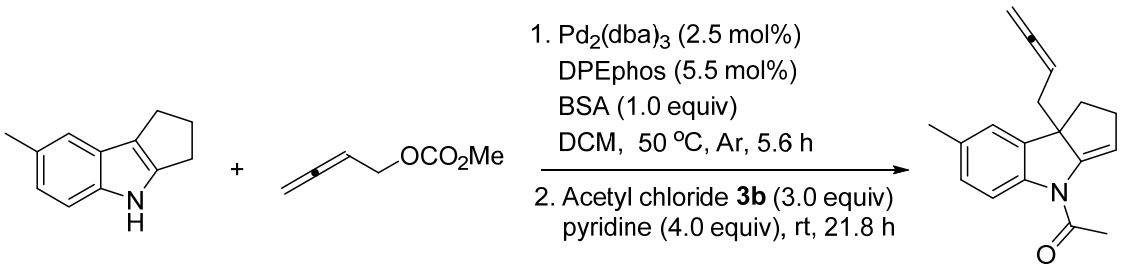
8. 8b-(2,3-Butadienyl)-4-(phenylsulfonyl)-1,2,4,8b-tetrahydrocyclopenta[*b*]indole (4aah, zyz-2-155B)



According to **Typical Procedure III**, the reaction of $Pd(acac)_2$ (2.4 mg, 0.008 mmol), DPEphos (6.0 mg, 0.012 mmol), DCM (2 mL), **1a** (30.7 mg, 0.2 mmol), BSA (40.9 mg, 0.2 mmol)/DCM (1 mL), **2a** (33.9 mg, 0.26 mmol)/DCM (1 mL), Et_3B (1M in THF, 0.2 mL, 0.2 mmol), pyridine (64 μL, d = 0.9819 g/cm^3, 62.8 mg, 0.8 mmol), and **3h** (77 μL, d = 1.384 g/cm^3, 106.6 mg, 0.6 mmol) afforded **4aah** (40.2 mg, 58%) (eluent: petroleum ether/ethyl acetate = 40/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 2 H, Ar-H), 7.68 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.55 (t, *J* = 7.4 Hz, 1 H, Ar-H), 7.44 (t, *J* = 7.6

Hz, 2 H, Ar-H), 7.25-7.20 (m, 1 H, Ar-H), 7.08 (d, J = 6.8 Hz, 1 H, Ar-H), 7.01 (t, J = 7.4 Hz, 1 H, Ar-H), 5.60 (d, J = 2.4 Hz, 1 H, =CH), 4.82 (quint, J = 7.3 Hz, 1 H, =CH), 4.56-4.47 (m, 2 H, $=CH_2$), 2.83-2.70 (m, 1 H, one proton of CH_2), 2.52-2.39 (m, 1 H, one proton of CH_2), 2.23 (dd, J_1 = 11.8 Hz, J_2 = 5.8 Hz, 1 H, one proton of CH_2), 2.02-1.84 (m, 2 H, one proton of CH_2 and one proton of another CH_2), 1.67-1.59 (m, 1 H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.1, 149.7, 144.0, 137.7, 135.6, 133.5, 128.9, 127.9, 127.1, 124.2, 123.8, 114.2, 107.8, 85.1, 74.0, 59.1, 37.0, 34.5, 32.3; MS (ESI) *m/z* 372 $(M+Na)^+$, 350 $(M+H)^+$; IR (neat, cm^{-1}): 3066, 2934, 2852, 1953, 1664, 1603, 1450, 1364, 1169, 1091, 1022; HRMS (ESI) Calcd for $C_{21}H_{20}NO_2S$ ($[M+H]^+$): 350.1209, Found: 350.1205.

9. 4-Acetyl-8b-(2,3-butadienyl)-7-methyl-1,2,4,8b-tetrahydrocyclopenta[*b*]indole (4bab, grd-17-102)

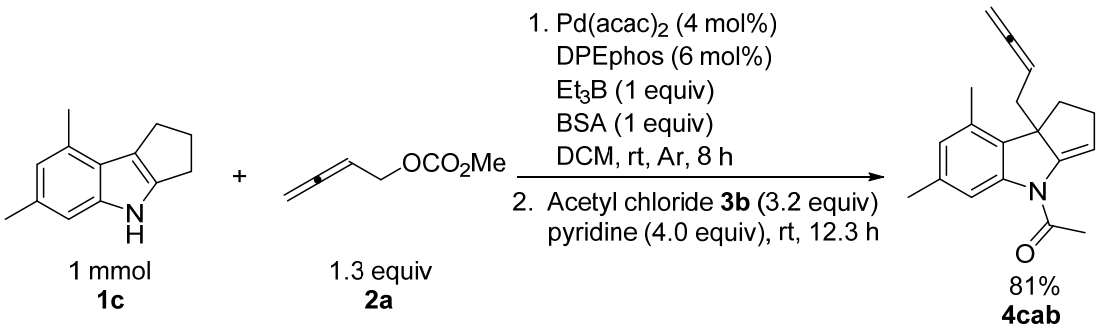


0.2 mmol **1b** | 1.3 equiv **2a** | 83% **4bab**

According to **Typical Procedure II**, the reaction of $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol), DPEphos (6.0 mg, 0.011 mmol), DCM (2 mL), **1b** (34.3 mg, 0.2 mmol), **2a** (37.1 mg, 2.9 mmol), BSA (40.7 mg, 0.2 mmol), DCM (2 mL), pyridine (65 μL, d = 0.9819 g/cm^3, 63.8 mg, 0.8 mmol), and **3b** (43 μL, d = 1.104 g/cm^3, 47.5 mg, 0.6 mmol) afforded **4bab** (43.8 mg, 83%) (eluent: petroleum ether/ ethyl acetate = 50:1) as an oil: ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (brs, 1 H, Ar-H), 7.03 (d, J = 6.8 Hz, 1 H, Ar-H), 6.97 (s, 1 H, Ar-H), 5.35-5.22 (m, 1 H, =CH), 4.95-4.83 (m, 1 H, =CH), 4.62-4.53 (m, 2 H, $=CH_2$), 2.89-2.78 (m, 1 H, one proton of CH_2), 2.54-2.46 (m, 1 H, one proton of CH_2), 2.41 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 2.30-2.19 (m, 3 H, one proton of CH_2 and another CH_2), 2.08-1.97 (m, 1 H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9, 168.3, 151.6, 142.5, 136.0, 133.6, 128.1, 123.8, 116.8, 109.0, 85.3, 74.1, 59.0, 37.2, 34.9, 32.4, 24.5, 21.1; IR

(neat, cm^{-1}): 2929, 2852, 1954, 1673, 1473, 1372, 1346, 1303, 1195, 1013; HRMS (ESI) Calcd for $C_{18}H_{20}NO$ ($[M+H]^+$): 266.1539, Found: 266.1541.

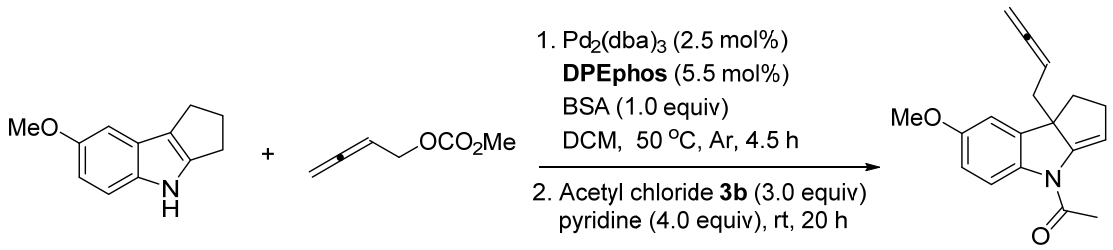
10.4-Acetyl-8b-(2,3-butadienyl)-6,8-dimethyl-1,2,4,8b-tetrahydrocyclopenta[*b*]indole (4cab, zyz-2-168)



Typical Procedure IV: To a 50 mL oven dried pear-shaped Schlenk flask were added $Pd(acac)_2$ (12.3mg, 0.04 mmol), DPEphos (32.7 mg, 0.06 mmol), and DCM (10 mL) under the atmosphere of Ar. The resulting mixture was stirred at room temperature for 30 min. Then compound **1c** (185.9 mg, 1.0 mmol), BSA (203.9 mg, 1.0 mmol)/DCM (5 mL), **2a** (167.7 mg, 1.3 mmol)/DCM (5 mL), and Et_3B (1 M in THF, 1.0 mL, 1.0 mmol) were added sequentially. The resulting mixture was stirred at room temperature for 8 h as monitored by TLC. Then **3b** (0.23 mL, d = 1.104 g/cm^3, 253.9 mg, 3.2 mmol) and pyridine (0.32 mL, d = 0.9819 g/cm^3, 314.2 mg, 4.0 mmol) were added. The resulting mixture was stirred at room temperature for 12.5 h as monitored by TLC. A saturated aqueous solution of $NaHCO_3$ (20 mL) was added to quench the reaction. The organic layer was separated and the aqueous layer was extracted with DCM (20 mL × 2). The combined organic layer was washed with brine (20 mL) and dried over anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by silica gel column chromatography to afford **4cab** (227.3 mg, 81%) (eluent: petroleum ether/ethyl acetate = 60/1) as an oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (brs, 1 H, Ar-H), 6.70 (s, 1 H, Ar-H), 5.26 (brs, 1 H, =CH), 4.83-4.71 (m, 1 H, =CH), 4.58-4.45 (m, 2 H, $=CH_2$), 2.89-2.76 (m, 1 H, one proton of CH_2), 2.53-2.43 (m, 1 H, one proton of CH_2), 2.40 (s, 3 H, CH_3), 2.40 (s, 3 H, CH_3), 2.38-2.32 (m, 1 H, one proton of CH_2), 2.31 (s, 3 H, CH_3), 2.28-2.14 (m, 6 H, CH_3, CH_2 and one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 168.3, 151.4, 144.9, 137.5, 132.6, 130.5, 126.6, 115.2, 108.9, 85.2, 73.8, 58.6, 36.3, 36.0, 32.5, 24.5,

21.5, 17.9; MS (EI, 70 eV) *m/z* (%) 279 (M^+, 8.08), 184 (100); IR (neat, cm^{-1}): 2928, 2853, 1954, 1673, 1594, 1411, 1372, 1351, 1303, 1266, 1252, 1232, 1094, 1070, 1032; HRMS (ESI) Calcd for $C_{19}H_{22}NO$ ($[M+H]^+$): 280.1696, Found: 280.1692.

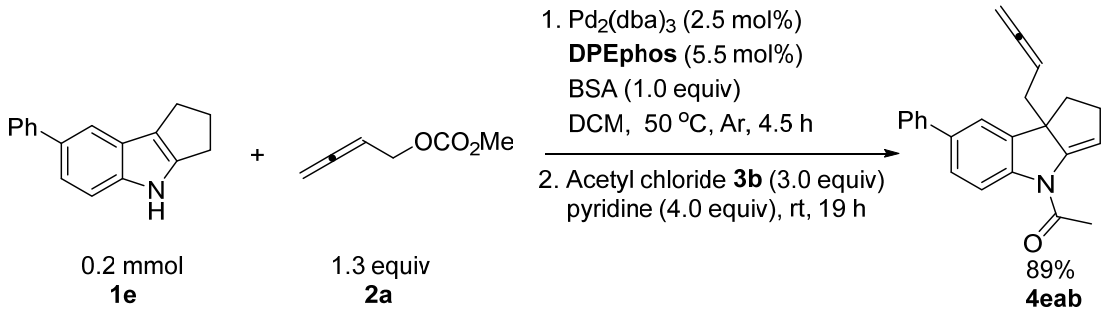
11. 4-Acetyl-8b-(2,3-butadienyl)-7-methoxy-1,2,4,8b-tetrahydrocyclopenta[*b*]indole (4dab, grd-17-94)



0.2 mmol **1d** | 1.3 equiv **2a** | 88% **4dab**

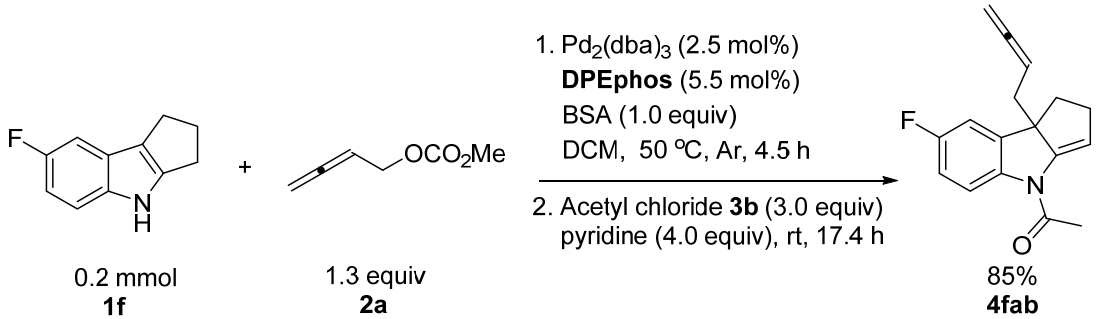
According to **Typical Procedure II**, the reaction of $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol), DPEphos (6.0 mg, 0.011 mmol), DCM (2 mL), **1d** (37.5 mg, 0.2 mmol), **2a** (33.4 mg, 0.26 mmol), BSA (40.7 mg, 0.2 mmol), DCM (2 mL), pyridine (65 μL, d = 0.9819 g/cm^3, 63.8 mg, 0.8 mmol), and **3b** (43 μL, d = 1.104 g/cm^3, 47.5 mg, 0.6 mmol) afforded **4dab** (49.5 mg, 88%) (eluent: petroleum ether/ethyl acetate = 40/1) as an oil: ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 6.0 Hz, 1 H, Ar-H), 6.77-6.71 (m, 2 H, Ar-H), 5.27 (brs, 1 H, =CH), 4.94-4.85 (m, 1 H, =CH), 4.58 (dt, J_1 = 6.8 Hz, J_2 = 2.2 Hz, 2 H, $=CH_2$), 3.79 (s, 3 H, OCH_3), 2.89-2.78 (m, 1 H, one proton of CH_2), 2.56-2.46 (m, 1 H, one proton of CH_2), 2.40 (s, 3 H, CH_3), 2.30-2.19 (m, 3 H, CH_2 and one proton of another CH_2), 2.09-1.98 (m, 1 H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.0, 168.0, 156.4, 151.5, 138.5, 137.4, 117.8, 111.7, 109.7, 109.0, 85.2, 74.1, 59.1, 55.5, 37.1, 34.8, 32.3, 24.4; IR (neat, cm^{-1}): 2934, 2846, 1956, 1664, 1610, 1475, 1449, 1379, 1344, 1293; HRMS (ESI) Calcd for $C_{18}H_{20}NO_2$ ($[M+H]^+$): 282.1489, Found: 282.1487.

12. 4-Acetyl-8b-(2,3-butadienyl)-7-phenyl-1,2,4,8b-tetrahydrocyclopenta[*b*]indole (4eab, grd-17-97)



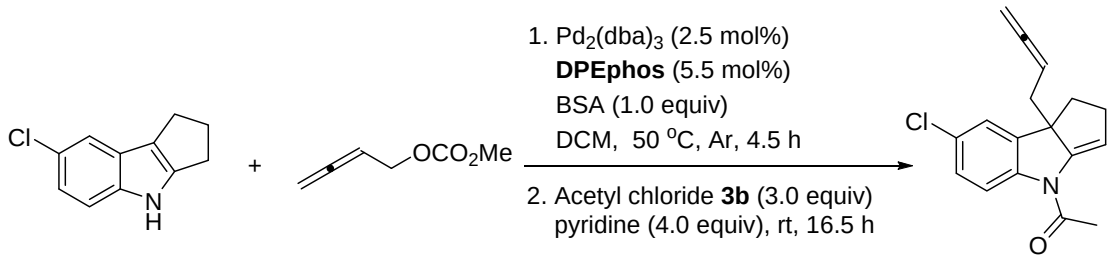
According to **Typical Procedure II**, the reaction of $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol), DPEphos (6.0 mg, 0.011 mmol), DCM (2 mL), **1e** (46.7 mg, 0.2 mmol), **2a** (33.4 mg, 0.26 mmol), BSA (40.7 mg, 0.2 mmol), DCM (2 mL), pyridine (65 μL, d = 0.9819 g/cm^3, 63.8 mg, 0.8 mmol), and **3b** (43 μL, d = 1.104 g/cm^3, 47.5 mg, 0.6 mmol) afforded **4eab** (58.2 mg, 89%) (eluent: petroleum ether/ethyl acetate = 40/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (brs, 1 H, Ar-H), 7.57 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.48 (dd, J_1 = 8.4, J_2 =1.6 Hz, 1 H, Ar-H), 7.44-7.37 (m, 3 H, Ar-H), 7.31 (t, *J* = 7.4 Hz, 1 H, Ar-H), 5.31 (brs, 1 H, =CH), 4.94 (quint, *J* = 7.3 Hz, 1 H, =CH), 4.61-4.49 (m, 2 H, =CH_2), 2.92-2.80 (m, 1 H, one proton of CH_2), 2.57-2.48 (m, 1 H, one proton of CH_2), 2.44 (s, 3 H, CH_3), 2.36-2.22 (m, 3 H, CH_2 and one proton of another CH_2), 2.14-2.03 (m, 1 H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.0, 168.5, 151.4, 144.2, 140.8, 137.1, 136.5, 128.7, 127.0, 126.8, 126.5, 121.8, 117.2, 109.2, 85.2, 74.2, 59.2, 37.2, 34.9, 32.4, 24.6; IR (neat, cm^{-1}): 3031, 2930, 1953, 1675, 1601, 1466, 1371, 1344, 1300, 1204, 1124, 1011; HRMS (ESI) Calcd for $C_{23}H_{22}NO$ ($[M+H]^+$): 328.1696, Found: 328.1696.

13. 4-Acetyl-8b-(2,3-butadienyl)-7-fluoro-1,2,4,8b-tetrahydrocyclopenta[*b*]indole (4fab, grd-18-6)



According to **Typical Procedure II**, the reaction of $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol), DPEphos (6.0 mg, 0.011 mmol), DCM (2 mL), **1f** (35.1 mg, 0.2 mmol), **2a** (33.3 mg, 0.26 mmol), BSA (40.7 mg, 0.2 mmol), DCM (2 mL), pyridine (65 μL, d = 0.9819 g/cm^3, 63.8 mg, 0.8 mmol), and **3b** (49 μL, d = 1.104 g/cm^3, 54.1 mg, 0.7 mmol) afforded **4fab** (45.7 mg, 85%) (eluent: petroleum ether/ethyl acetate = 50/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (brs, 1 H, Ar-H), 6.92 (td, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1 H, Ar-H), 6.87 (dd, J_1 = 8.0, J_2 = 2.8 Hz, 1 H, Ar-H), 5.31 (brs, 1 H, =CH), 4.93-4.84 (m, 1 H, =CH), 4.58 (dt, J_1 = 6.6, J_2 = 2.3 Hz, 2 H, =CH_2), 2.90-2.79 (m, 1 H, one proton of CH_2), 2.57-2.47 (m, 1 H, one proton of CH_2), 2.42 (s, 3 H, CH_3), 2.30-2.18 (m, 3 H, CH_2 and one proton of another CH_2), 2.09-1.98 (m, 1 H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.0, 168.3, 159.5 (d, J = 242.1 Hz), 151.1, 140.81 (d, J = 2.4 Hz), 137.86 (d, J = 7.6 Hz), 118.08 (d, J = 7.2 Hz), 113.8 (d, J = 22.6 Hz), 110.7 (d, J = 23.8 Hz), 109.5, 84.8, 74.3, 59.1, 37.0, 34.8, 32.2, 24.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.1 (s); IR (neat, cm^{-1}): 2934, 2852, 1954, 1675, 1599, 1465, 1374, 1345, 1305, 1256, 1013; HRMS (ESI) Calcd for $C_{17}H_{17}FNO$ ($[M+H]^+$): 270.1289, Found: 270.1291.

14. 4-Acetyl-8b-(2,3-butadienyl)-7-chloro-1,2,4,8b-tetrahydrocyclopenta[*b*]indole (4gab, grd-18-7)

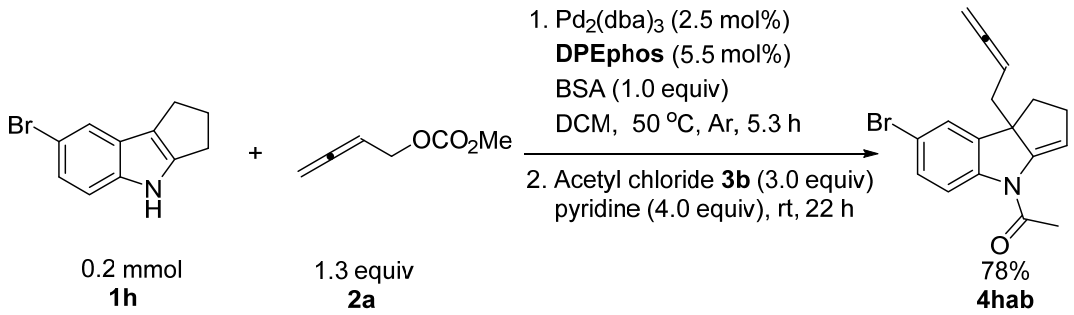


0.2 mmol **1g** | 1.3 equiv **2a** | 85% **4gab**

According to **Typical Procedure II**, the reaction of $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol), DPEphos (6.0 mg, 0.011 mmol), DCM (2 mL), **1g** (38.4 mg, 0.2 mmol), **2a** (33.4 mg, 0.26 mmol), BSA (40.7 mg, 0.2 mmol), DCM (2 mL), pyridine (65 μL, d = 0.9819 g/cm^3, 63.8 mg, 0.8 mmol), and **3b** (43 μL, d = 1.104 g/cm^3, 47.5 mg, 0.6 mmol) afforded **4gad** (49.0 mg, 85%) (eluent: petroleum ether/ethyl acetate = 50/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.2 Hz, 1 H, Ar-H), 7.20 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1 H, Ar-H), 7.13 (d, J = 1.2 Hz, 1 H, Ar-H), 5.31 (brs, 1 H, =CH), 4.88 (quint, 1 H, =CH),

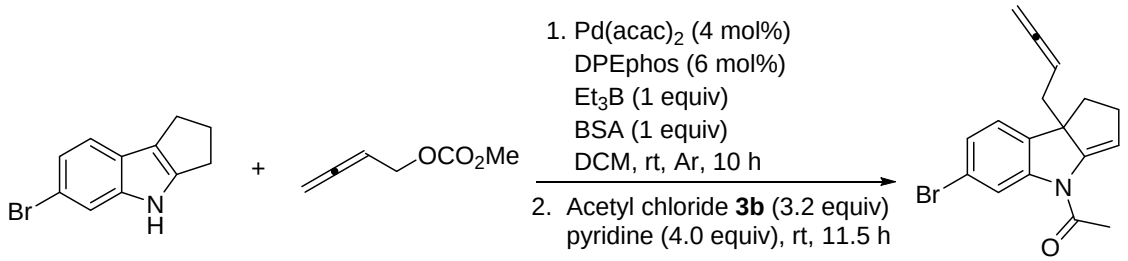
4.62-4.53 (m, 2 H, =CH_2), 2.90-2.78 (m, 1 H, one proton of CH_2), 2.57-2.47 (m, 1 H, one proton of CH_2), 2.42 (s, 3 H, CH_3), 2.32-2.15 (m, 3 H, CH_2 and one proton of another CH_2), 2.03 (dd, 1 H, J_1 = 20.6 Hz, J_2 = 9.8 Hz, one proton of CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.1, 168.5, 150.8, 143.3, 137.6, 129.1, 127.5, 123.5, 118.1, 109.6, 84.7, 74.3, 59.1, 36.9, 34.8, 32.3, 24.5; IR (neat, cm^{-1}): 2986, 2957, 2934, 2847, 1953, 1679, 1459, 1373, 1341, 1301, 1261, 1169, 1070; HRMS (ESI) Calcd for $C_{17}H_{17}{}^{35}ClNO$ ([M+H]$^+$): 286.0993, Found: 286.0995.

15. 4-Acetyl-7-bromo-8b-(2,3-butadienyl)-1,2,4,8b-tetrahydrocyclopenta[*b*]indole (4hab, grd-17-101)



According to **Typical Procedure II**, the reaction of $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol), DPEphos (6.0 mg, 0.011 mmol), DCM (2 mL), **1h** (47.3 mg, 0.2 mmol), **2a** (37.1 mg, 0.26 mmol), BSA (40.7 mg, 0.2 mmol), DCM (2 mL), pyridine (65 μL, d = 0.9819 g/cm^3, 63.8 mg, 0.8 mmol), and **3b** (43 μL, d = 1.104 g/cm^3, 47.5 mg, 0.6 mmol) afforded **4had** (51.3 mg, 78%) (eluent: petroleum ether/ethyl acetate = 50/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 1 H, Ar-H), 7.35 (dd, J_1 = 8.6 Hz, J_2 = 1.8 Hz, 1 H, Ar-H), 7.28 (d, J = 2.0 Hz, 1 H, Ar-H), 5.31 (brs, 1 H, =CH), 4.93-4.83 (m, 1 H, =CH), 4.59 (dt, J_1 = 6.4 Hz, J_2 = 2.0 Hz, 2 H, =CH_2), 2.89-2.79 (m, 1 H, one proton of CH_2), 2.57-2.48 (m, 1 H, one proton of CH_2), 2.42 (s, 3 H, CH_3), 2.31-2.16 (m, 3 H, CH_2 and one proton of another CH_2), 2.08-1.98 (m, 1 H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.1, 168.5, 150.7, 143.8, 138.0, 130.5, 126.4, 118.6, 116.8, 109.6, 84.7, 74.4, 59.2, 37.0, 34.8, 32.3, 24.6; IR (neat, cm^{-1}): 2932, 2852, 1953, 1678, 1456, 1370, 1342, 1302, 1257, 1174, 1012; HRMS (ESI) Calcd for $C_{17}H_{17}{}^{79}BrNO$ ([M+H]$^+$): 330.0488, Found: 330.0489.

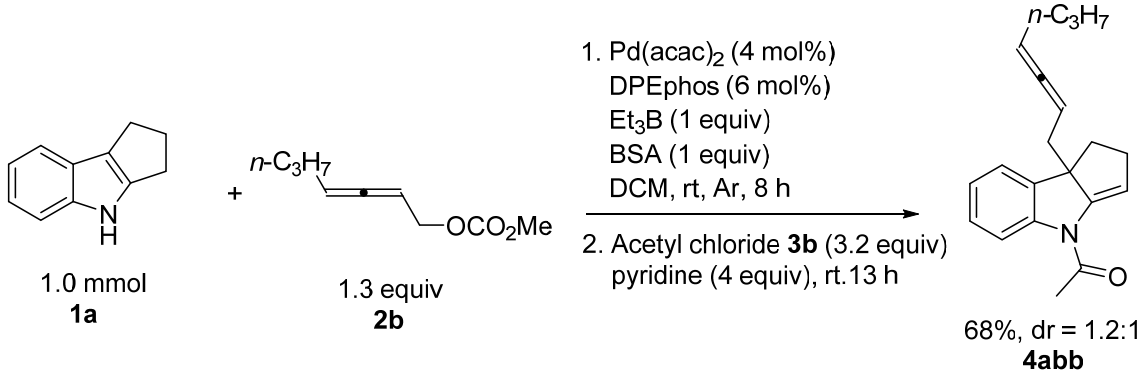
16. 4-Acetyl-6-bromo-8b-(2,3-butadienyl)-1,2,4,8b-tetrahydrocyclopenta[*b*]indole (4iab, zyz-2-166)



1.0 mmol **1i** | 1.3 equiv **2a** | 80% **4iab**

According to **Typical Procedure IV**, the reaction of $Pd(acac)_2$ (12.2 mg, 0.04 mmol), DPEphos (32.9 mg, 0.06 mmol), DCM (10 mL), **1i** (236.7 mg, 1.0 mmol), BSA (205.1 mg, 1.0 mmol)/DCM (5 mL), **2a** (167.9 mg, 1.3 mmol)/DCM (5 mL), Et_3B (1 M in THF, 1.0 mL, 1.0 mmol), **3b** (0.23 mL, d = 1.104 g/cm^3, 253.9 mg, 3.2 mmol), and pyridine (0.32 mL, d = 0.9819 g/cm^3, 314.2 mg, 4.0 mmol) afforded **4iab** (265.1 mg, 80%) (eluent: petroleum ether/ethyl acetate = 60/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (brs, 1 H, Ar-H), 7.22 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1 H, Ar-H), 7.02 (d, J = 8.0 Hz, 1 H, Ar-H), 5.31 (d, J = 1.6 Hz, 1 H, =CH), 4.91-4.81 (m, 1 H, =CH), 4.61-4.52 (m, 2 H, =CH_2), 2.90-2.79 (m, 1 H, one proton of CH_2), 2.57-2.47 (m, 1 H, one proton of CH_2), 2.42 (s, 3 H, CH_3), 2.32-2.14 (m, 3 H, CH_2 and one proton of another CH_2), 2.06-1.97 (m, 1 H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9, 168.5, 150.8, 145.7, 134.8, 126.8, 124.2, 121.0, 120.2, 109.5, 84.8, 74.2, 58.8, 36.9, 34.9, 32.3, 24.5; MS (EI, 70eV) *m/z* (%) 331 ((M(^{81}Br))$^+$, 4.98), 329 ((M(^{79}Br)$^+$, 5.25), 234 (100); IR (neat, cm^{-1}): 2933, 2851, 1953, 1678, 1596, 1574, 1408, 1373, 1302, 1254, 1203, 1172, 1117, 1089, 1058, 1031, 1014; HRMS (ESI) Calcd for $C_{17}H_{17}{}^{79}BrNO$ ([M+H]$^+$): 330.0488, Found: 330.0482.

17. 4-Acetyl-8b-(2,3-heptadienyl)- 1,2,4,8b-tetrahydrocyclopenta[*b*]indole (4abb, zyz-2-105)



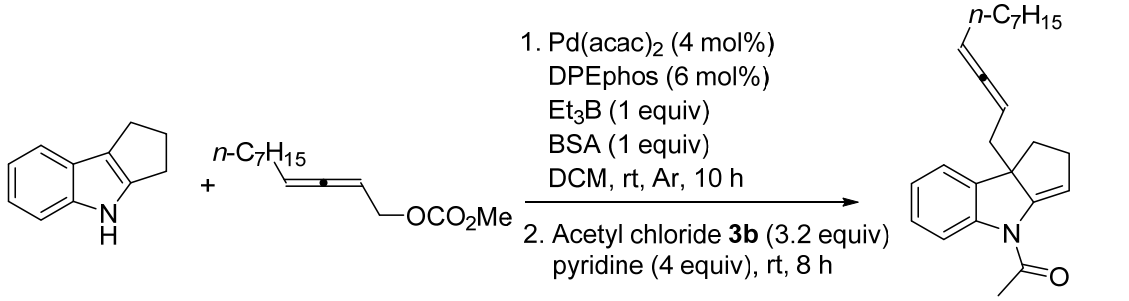
1.0 mmol
1a

1.3 equiv
2b

68%, dr = 1.2:1
4abb

According to **Typical Procedure IV**, the reaction of $Pd(acac)_2$ (12.3 mg, 0.04 mmol), DPEphos (32.7 mg, 0.06 mmol), DCM (10 mL), **1a** (157.9 mg, 1.0 mmol), BSA (215.0 mg, 1.0 mmol)/DCM (5 mL), **2b** (221.9 mg, 1.3 mmol)/DCM (5 mL)/DCM(5 mL), Et_3B (1 M in THF, 1.0 mL, 1.0 mmol), pyridine (0.32 mL, d = 0.9819 g/cm^3, 314.2 mg, 4.0 mmol), and **3b** (0.23 mL, d = 1.104 g/cm^3, 253.9 mg, 3.2 mmol) afforded **4abb** (198.3 mg, 68%, dr =1.2:1) (eluent: petroleum ether/ethyl acetate = 60/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (brs, 1 H, Ar-H), 7.25-7.20 (m, 1 H, Ar-H), 7.19-7.13 (m, 1 H, Ar-H), 7.10-7.03 (m, 1 H, Ar-H), 5.28 (brs, 1 H, =CH), 5.00-4.77 (m, 2 H, CH=C=CH), 2.90-2.78 (m, 1 H, one proton of CH_2), 2.54-2.45 (m, 1 H, one proton of CH_2), 2.44-2.40 (m, 3 H, CH_3), 2.34-2.26 (m, 1 H, one proton of CH_2), 2.25-2.10 (m, 2 H, CH_2), 2.09-1.98 (m, 1 H, one proton of CH_2), 1.91-1.77 (m, 2 H, CH_2), 1.37-1.27 (m, 2 H, CH_2), 0.90-0.83 (m, 3 H, CH_3); MS (EI, 70 eV) *m/z* (%): 293 (M^+, 6.49), 156 (100); IR (neat, cm^{-1}): 2956, 2930, 2853, 1960, 1677, 1602, 1472, 1456, 1375, 1350, 1304, 1282, 1206, 1174, 1108, 1068, 1012; Anal. calcd for $C_{20}H_{23}NO$ (%): C 81.87, H 7.90, N 4.77, Found: C 81.63, H 8.06, N 4.77.

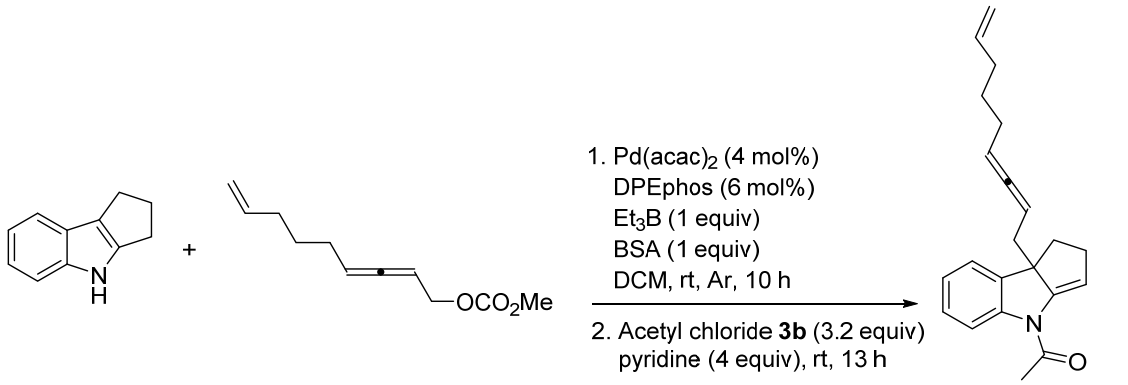
18. 4-Acetyl-8b-(2,3-undecadienyl)-1,2,4,8b-tetrahydrocyclopenta[*b*]indole (4acb, zyz-2-113)



1.0 mmol **1a** | 1.3 equiv **2c** | 60%, dr = 1.4:1 **4acb**

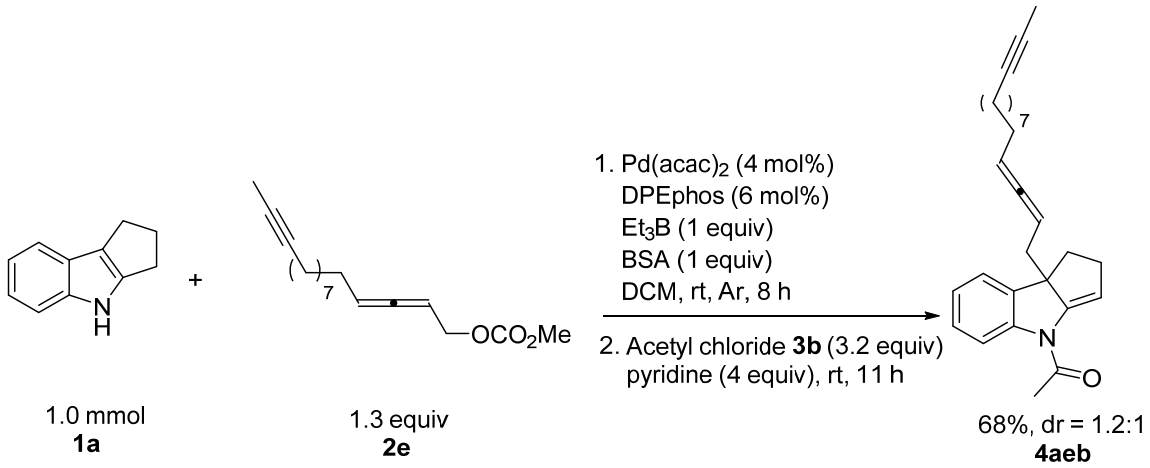
According to **Typical Procedure IV**, the reaction of $Pd(acac)_2$ (12.3 mg, 0.04 mmol), DPEphos (32.7 mg, 0.06 mmol), DCM (10 mL), **1a** (157.9 mg, 1.0 mmol), BSA (214.7 mg, 1.0 mmol)/DCM (5 mL), **2c** (294.7 mg, 1.3 mmol)/DCM (5 mL), Et_3B (1 M in THF, 1.0 mL, 1.0 mmol), pyridine (0.32 mL, d = 0.9819 g/cm^3, 314.2 mg, 4.0 mmol), and **3b** (0.23 mL, d = 1.104 g/cm^3, 253.9 mg, 3.2 mmol) afforded **4acb** (210.7 mg, 60%, dr = 1.4:1) (eluent: petroleum ether/ethyl acetate = 60/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (brs, 1 H, Ar-H), 7.22 (t, *J* = 7.8 Hz, 1 H, Ar-H), 7.19-7.12 (m, 1 H, Ar-H), 7.06 (t, *J* = 7.6 Hz, 1 H, Ar-H), 5.29 (brs, 1 H, =CH), 5.01-4.78 (m, 2 H, CH=C=CH), 2.90-2.79 (m, 1 H, one proton of CH_2), 2.55-2.45 (m, 1 H, one proton of CH_2), 2.45-2.40 (m, 3 H, CH_3), 2.35-2.26 (m, 1 H, one proton of CH_2), 2.24-2.13 (m, 2 H, one proton of CH_2 and another CH_2), 2.09-1.98 (m, 1 H, one proton of CH_2), 1.93-1.76 (m, 2 H, CH_2), 1.36-1.20 (m, 10 H, 5×CH_2), 0.88 (t, *J* = 6.6 Hz, 3 H, CH_3); MS (EI, 70 eV) *m/z* (%): 349 (M^+, 8.35), 156 (100); IR (neat, cm^{-1}): 2954, 2924, 2852, 1960, 1679, 1602, 1456, 1375, 1350, 1282, 1206, 1174, 1108, 1012; HRMS (ESI) Calced for $C_{24}H_{32}NO$ $(M+H)^+$: 350.2478, Found: 350.2474.

19. 4-Acetyl-8b-(2,3,8-nonatrienyl)-1,2,4,8b-tetrahydrocyclopenta[*b*]indole (4adb, zyz-2-128)



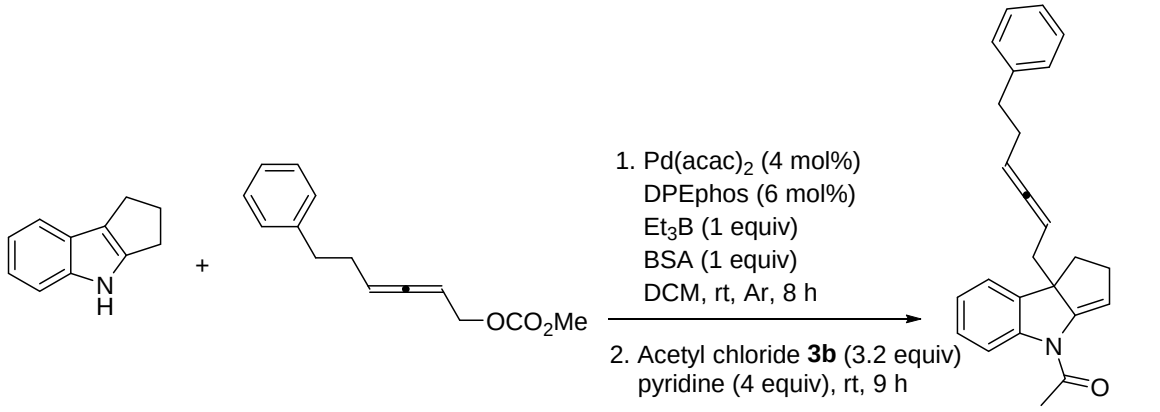
According to **Typical Procedure IV**, the reaction of $Pd(acac)_2$ (12.4 mg, 0.04 mmol), DPEphos (32.9 mg, 0.06 mmol), DCM (10 mL), **1a** (157.7 mg, 1.0 mmol), BSA (214.3 mg, 1.0 mmol)/DCM (5 mL), **2d** (255.9 mg, 1.3 mmol)/DCM (5 mL), Et_3B (1 M in THF, 1.0 mL, 1.0 mmol), pyridine (0.32 mL, d = 0.9819 g/cm^3, 314.2 mg, 4.0 mmol), and **3b** (0.23 mL, d = 1.104 g/cm^3, 253.9 mg, 3.2 mmol) afforded **4adb** (152.3 mg, 48%, dr = 1.1:1) (eluent: petroleum ether/ethyl acetate = 60/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (brs, 1 H, Ar-H), 7.26-7.19 (m, 1 H, Ar-H), 7.19-7.13 (m, 1 H, Ar-H), 7.10-7.03 (m, 1 H, Ar-H), 5.85-5.71 (m, 1 H, =CH), 5.29 (brs, 1 H, =CH), 5.04-4.80 (m, 4 H, CH=C=CH and $=CH_2$), 2.90-2.79 (m, 1 H, one proton of CH_2), 2.55-2.46 (m, 1 H, one proton of CH_2), 2.42 (s, 3 H, CH_3), 2.36-2.26 (m, 1 H, one proton of CH_2), 2.26-2.12 (m, 2 H, CH_2), 2.08-1.98 (m, 3 H, CH_2 and one proton of another CH_2), 1.95-1.83 (m, 2 H, CH_2), 1.40 (quint, J = 7.6 Hz, 2 H, CH_2); MS (EI, 70 eV) *m/z* (%): 319 (M^+, 3.87), 156 (100); IR (neat, cm^{-1}): 3073, 2929, 2851, 1960, 1677, 1602, 1456, 1376, 1303, 1282, 1206, 1174, 1108, 1012; Anal. calcd for $C_{22}H_{25}NO$ (%): C 82.72, H 7.89, N 4.38, Found: C 82.50, H 8.12, N 4.35.

20. 4-Acetyl-8b-(2,3-pentadecadien-13-ynyl)-1,2,4,8b-tetrahydrocyclopenta [*b*]indole (4aeb, zyz-2-137)



According to **Typical Procedure IV**, the reaction of $Pd(acac)_2$ (12.3 mg, 0.04 mmol), DPEphos (32.8 mg, 0.06 mmol), DCM (10 mL), **1a** (157.9 mg, 1.0 mmol), BSA (214.9 mg, 1.0 mmol)/DCM (5 mL), **2e** (360.7 mg, 1.3 mmol)/DCM (5 mL), Et_3B (1 M in THF, 1.0 mL, 1.0 mmol), pyridine (0.32 mL, d = 0.9819 g/cm^3, 314.2 mg, 4.0 mmol), and **3b** (0.23 mL, d = 1.104 g/cm^3, 253.9 mg, 3.2 mmol) afforded **4aeb** (268.1 mg, 68%, dr = 1.2:1) (eluent: petroleum ether/ethyl acetate = 60/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (brs, 1 H, Ar-H), 7.22 (t, *J* = 7.8 Hz, 1 H, Ar-H), 7.18-7.13 (m, 1 H, Ar-H), 7.06 (t, *J* = 7.4 Hz, 1 H, Ar-H), 5.28 (brs, 1 H, =CH), 5.01-4.78 (m, 2 H, HC=C=CH), 2.90-2.78 (m, 1 H, one proton of CH_2), 2.55-2.45 (m, 1 H, one proton of CH_2), 2.42 (s, 3 H, CH_3), 2.35-2.00 (m, 6 H, 3×CH_2), 1.92-1.80 (m, 2 H, CH_2), 1.77 (s, 3 H, CH_3), 1.52-1.40 (m, 2 H, CH_2), 1.39-1.21 (m, 10 H, 5×CH_2); MS (EI, 70 eV) *m/z* (%): 401 (M^+, 11.99), 156 (100); IR (neat, cm^{-1}): 2925, 2852, 1960, 1679, 1602, 1472, 1456, 1376, 1350, 1304, 1282, 1206, 1174, 1108, 1012; Anal. calcd for $C_{28}H_{35}NO$ (%): C 83.74, H 8.78, N 3.49, Found: C 83.68, H 8.78, N 3.47.

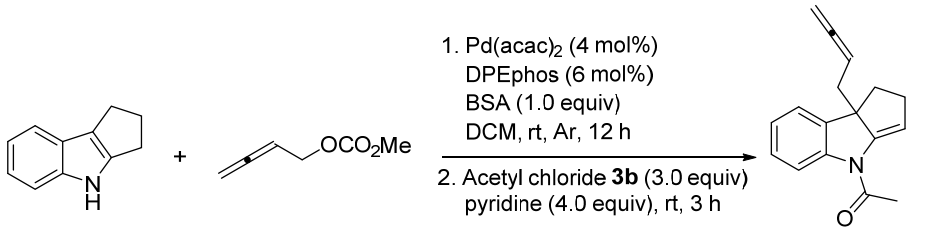
21. 4-Acetyl-8b-(6-phenyl-2,3-hexadienyl)-1,2,4,8b-tetrahydrocyclopenta[*b*]indole (4afb, zyz-2-139)



1.0 mmol **1a** | 1.3 equiv **2f** | 78%, dr = 1.4:1 **4afb**

According to **Typical Procedure IV**, the reaction of $Pd(acac)_2$ (12.3 mg, 0.04 mmol), DPEphos (32.8 mg, 0.06 mmol), DCM (10 mL), **1a** (157.9 mg, 1.0 mmol), BSA (202.9 mg, 1.0 mmol)/DCM (5 mL), **2f** (302.5 mg, 1.3 mmol)/DCM (5 mL), Et_3B (1 M in THF, 1.0 mL, 1.0 mmol), **3b** (0.23 mL, d = 1.104 g/cm^3, 253.9 mg, 3.2 mmol), and pyridine (0.32 mL, d = 0.9819 g/cm^3, 314.2 mg, 4.0 mmol) afforded **4afb** (277.7 mg, 78%, dr = 1.4:1) (eluent: petroleum ether/ethyl acetate = 60/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (brs, 1 H, Ar-H), 7.29-7.10 (m, 7 H, Ar-H), 7.04 (t, *J* = 7.4 Hz, 1 H, Ar-H), 5.26 (brs, 1 H, =CH), 5.12-4.77 (m, 2 H, HC=C=CH), 2.87-2.74 (m, 1 H, one proton of CH_2), 2.64-2.52 (m, 2 H, CH_2), 2.51-2.43 (m, 1 H, one proton of CH_2), 2.40 (s, 3 H, CH_3), 2.29-1.95 (m, 6 H, 3×CH_2); MS (EI, 70 eV) *m/z* (%): 355 (M^+, 9.14), 156 (100); IR (neat, cm^{-1}): 3062, 3025, 2930, 2851, 1960, 1676, 1602, 1473, 1376, 1282, 1205, 1174, 1107, 1078, 1012; Anal. calcd for $C_{25}H_{25}NO$ (%): C 84.47, H 7.09, N 3.94, Found: C 84.51, H 7.15, N 3.71.

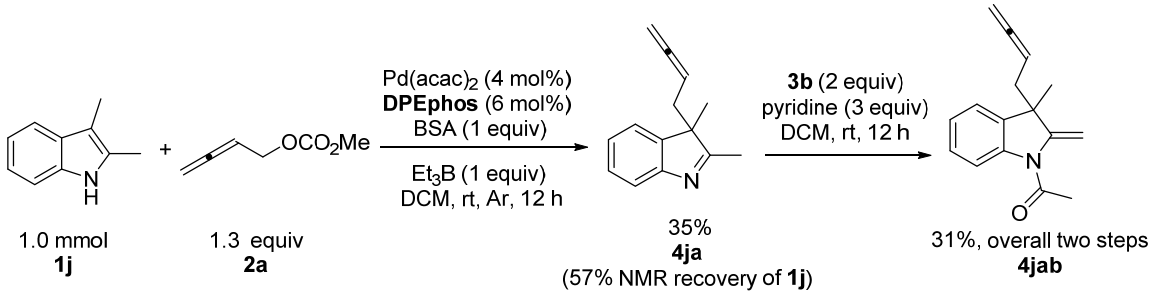
22. Gram scale of 4-acetyl-8b-(2,3-butadienyl)-1,2,4,8b-tetrahydrocyclopenta [*b*]indole(4aab, zyz-3-12)



5 mmol **1a** | 1.3 equiv **2a** | 1.0410 g (83%) **4aab**

According to **Typical Procedure IV**, the reaction of $Pd(acac)_2$ (61.0 mg, 0.2 mmol), DPEphos (161.3 mg, 0.3 mmol), DCM (50 mL), **1a** (786.7 mg, 5.0 mmol), BSA (1.0179 g, 1.0 mmol)/DCM (25 mL), **2a** (833.9 mg, 6.5 mmol)/DCM (25 mL), Et_3B (1 M in THF, 5.0 mL, 5.0 mmol), pyridine (1.6 mL, d = 0.9819 g/cm^3, 1.5710 g, 20 mmol) and **3b** (1.1 mL, d = 1.104 g/cm^3, 1.2144 g, 15 mmol) afforded **4aab** (1.0410 g, 83%) (eluent: petroleum ether/ethyl acetate = 60/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (brs, 1 H, Ar-H), 7.24 (t, *J* = 7.8 Hz, 1 H, Ar-H), 7.16 (d, J_1 = 7.2 Hz, 1 H, Ar-H), 7.07 (t, 1 H, J_1 = 7.4 Hz, Ar-H), 5.30 (brs, 1 H, =CH), 4.89 (quint, *J* = 7.6 Hz, 1 H, =CH), 4.59-4.52 (m, 2 H, =CH_2), 2.90-2.79 (m, 1 H, one proton of CH_2), 2.55-2.46 (m, 1 H, one proton of CH_2), 2.43 (s, 3 H, CH_3), 2.32-2.19 (m, 3 H, CH_2 and one proton of another CH_2), 2.10-1.98 (m, 1 H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9, 168.6, 151.3, 144.8, 135.9, 127.7, 124.0, 123.1, 117.1, 109.2, 85.2, 74.1, 59.1, 37.1, 34.9, 32.3, 24.6.

23. 3-(Buta-2,3-dienyl)-2,3-dimethyl-*3H*-indole (4ja, zyz-2-189) and 1-acetyl-3-(buta-2,3-dienyl)-3-methyl-2-methylene indoline (4jab, zyz-2-190)



To a oven dried Schlenk tube were added $Pd(acac)_2$ (12.2 mg, 0.04 mmol), DPEphos (32.4 mg, 0.06 mmol), and DCM (10 mL) under the atmosphere of Ar. The resulting mixture was stirred at room temperature for 30 min. Compound **1j** (146.7 mg, 1.0 mmol), **2a** (167.7 mg, 1.3 mmol)/DCM (5 mL), BSA (205.1 mg, 1.0 mmol)/DCM (5 mL), and Et_3B (1 M in THF, 1.0 mL, 1.0 mmol) were added sequentially. The resulting mixture was stirred at room temperature for 12 h as monitored by TLC. A saturated aqueous solution of $NaHCO_3$ (20 mL) was added to quench the reaction. The organic layer was separated and the aqueous layer was extracted with DCM (20 mL × 2). The combined organic layer was washed with brine (20 mL) and dried over anhydrous Na_2SO_4, After filtration and evaporation, the residue was purified by silica gel column chromatography to afford **4ja** (69.3 mg, 35%) (eluent: petroleum ether/ethyl acetate = 10/1 (600 mL) to

1/1 (400 mL)) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 1 H, and Ar-H), 7.34-7.25 (m, 2 H, Ar-H), 7.19 (t, *J* = 7.2 Hz, 1 H, Ar-H), 4.61-4.38 (m, 3 H, =CH and $=CH_2$), 2.62-2.54 (m, 1 H, one proton of CH_2), 2.44-2.36 (m, 1 H, one proton of CH_2), 2.27 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 186.4, 154.2, 142.9, 127.7, 125.0, 121.7, 119.8, 84.2, 74.6, 57.6, 36.1, 21.7, 15.8; MS (ESI) *m/z* 198 $(M+H)^+$; IR (neat, cm^{-1}): 3049, 2962, 2928, 2867, 1954, 1578, 1451, 1427, 1376, 1309, 1254, 1206, 1185, 1093, 1014; HRMS (ESI) Calcd for $C_{14}H_{16}N$ $(M+H)^+$: 198.1277, Found: 198.1275.

Compound **4ja** (69.3 mg, 0.35 mmol) was dissolved in DCM (10 mL). Pyridine (85 μL, d = 0.9817 g/cm^3, 83.4 mg, 1.05 mmol) and **3b** (50 μL, d = 1.104 g/cm^3, 55.2 mg, 0.7 mmol) were added sequentially and the resulting mixture was stirred at room temperature for 12 h as monitored by TLC. A saturated aqueous solution of $NaHCO_3$ (10 mL) was added to quench the reaction. The organic layer was separated and the aqueous layer was extracted with DCM (10 mL × 2). The combined organic layer was washed with brine (10 mL) and dried over anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by silica gel column chromatography to afford **4jab** (74.2 mg, 31%, overall two steps) (eluent: petroleum ether/ethyl acetate = 20/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.23 (t, *J* = 7.8 Hz, 1 H, Ar-H), 7.16 (d, *J* = 7.2 Hz, 1 H, Ar-H), 7.10 (t, *J* = 7.2 Hz, 1 H, Ar-H), 5.15 (s, 1 H, one proton of $=CH_2$), 4.84-4.71 (m, 2 H, one proton of $=CH_2$ and =CH), 4.58-4.43 (m, 2 H, $=CH_2$), 2.50 (s, 3 H, CH_3), 2.41-2.27 (m, 2 H, CH_2), 1.44 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9, 169.6, 154.5, 141.8, 136.3, 127.7, 124.2, 122.3, 116.5, 95.8, 84.7, 74.0, 48.0, 42.2, 25.9, 25.7; MS (ESI) *m/z* 262 $(M+Na)^+$, 240 $(M+H)^+$; IR (neat, cm^{-1}): 3051, 2965, 2932, 1954, 1669, 1599, 1477, 1462, 1367, 1341, 1321, 1283, 1226, 1206, 1176, 1108, 1072, 1051, 1031, 1013; HRMS (ESI) Calcd for $C_{16}H_{18}NO$ $([M+H]^+)$: 240.1383, Found: 240.1382.

References:

1. S. Gore, S. Baskaran, and B. König, *Org. Lett*, **2012**, *14*, 4568.
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.
3. X. Huang, T. Cao, Y. Han, X. Jiang, W. Lin, J. Zhang, and S. Ma, *Chem. Commun*. **2015**, *51*, 6956
4. M. V. Vita, P. Caramenti, and J. Waser, *Org. Lett,* **2015**, *17*. 5832.
5. H. Wang, B. Beiring, D. Yu, K. D. Collins, and F. Glorius, *Angew. Chem. Int. Ed*. **2013**, *52*, 12430.

zyz-2-34H.fid
Mar 5 2017
SOLVENT: CDCl3
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F1 = 400.031616 MHz
F2 = 100.596855 MHz

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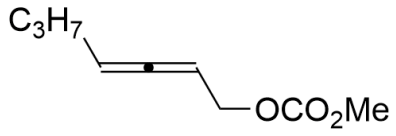
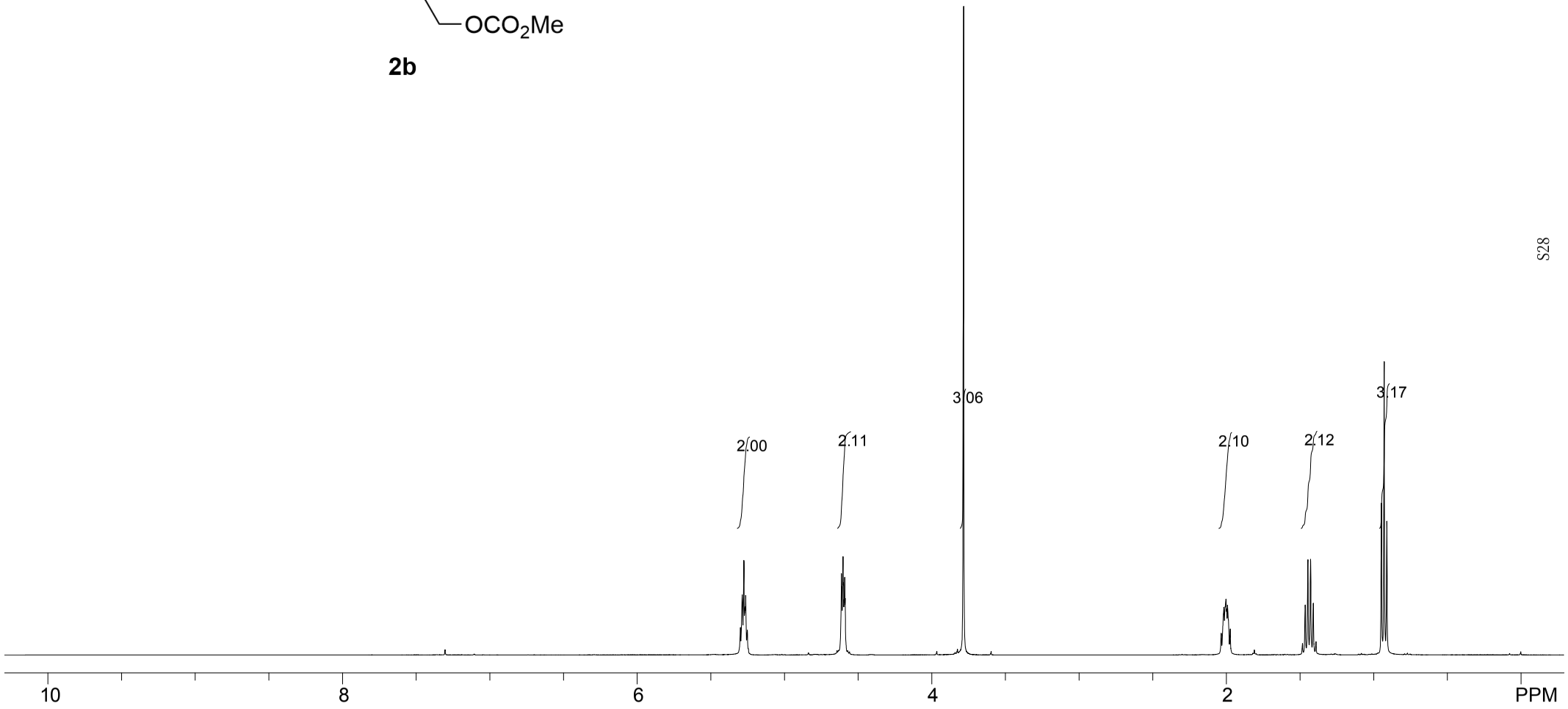
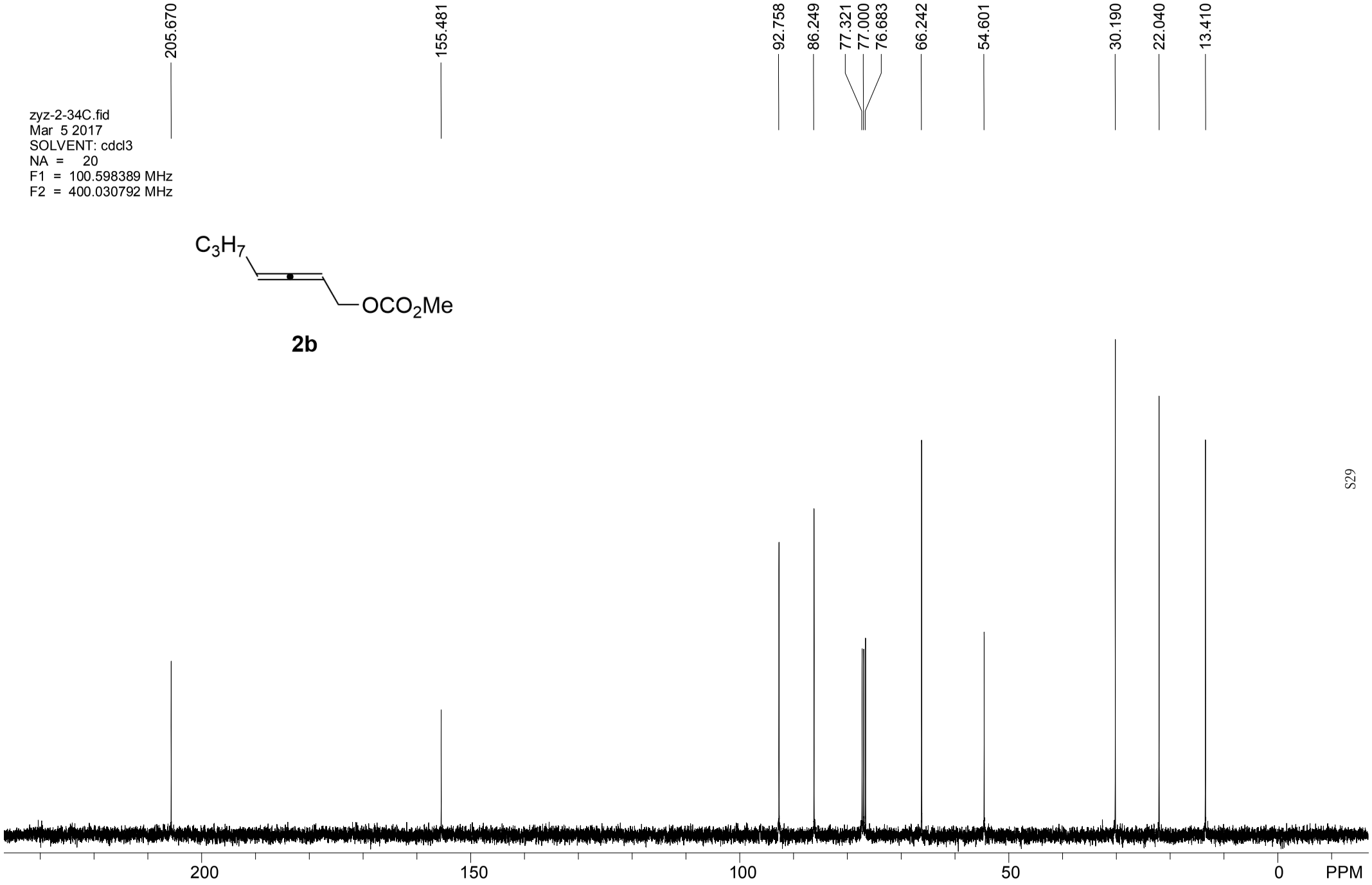
4.614 4.611 4.603 4.600 4.595 4.591 4.588
3.784
2.035 2.017 2.003 1.992 1.973
1.483 1.464 1.446 1.428 1.409 1.391
0.946 0.928 0.910
-0.000



2b

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77.000
76.683
66.242
54.601
30.190
22.040
13.410
zyz-2-34C.fid
Mar 5 2017
SOLVENT: cdcl3
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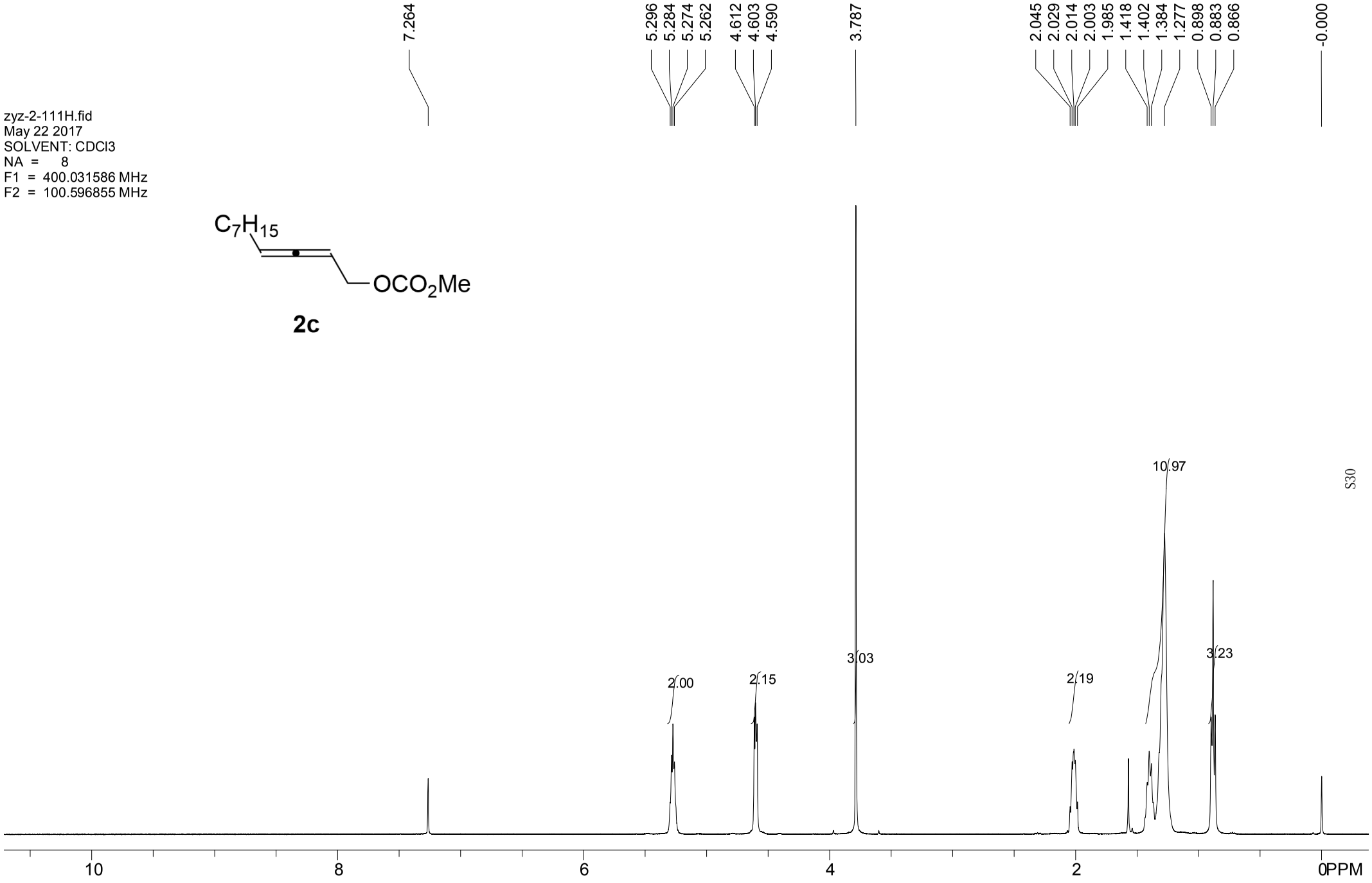
F2 = 400.030792 MHz
C3H7
OCO2Me
2b
200
150
100
50
0
PPM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5.296
5.284
5.274
5.262
4.612
4.603
4.590
3.787
2.045
2.029
2.014
2.003
1.985
1.418
1.402
1.384
1.277
0.898
0.883
0.866
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zyz-2-111H.fid
May 22 2017
SOLVENT: CDCl3
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F2 = 100.596855 MHz
C7H15
OCO2Me
2c
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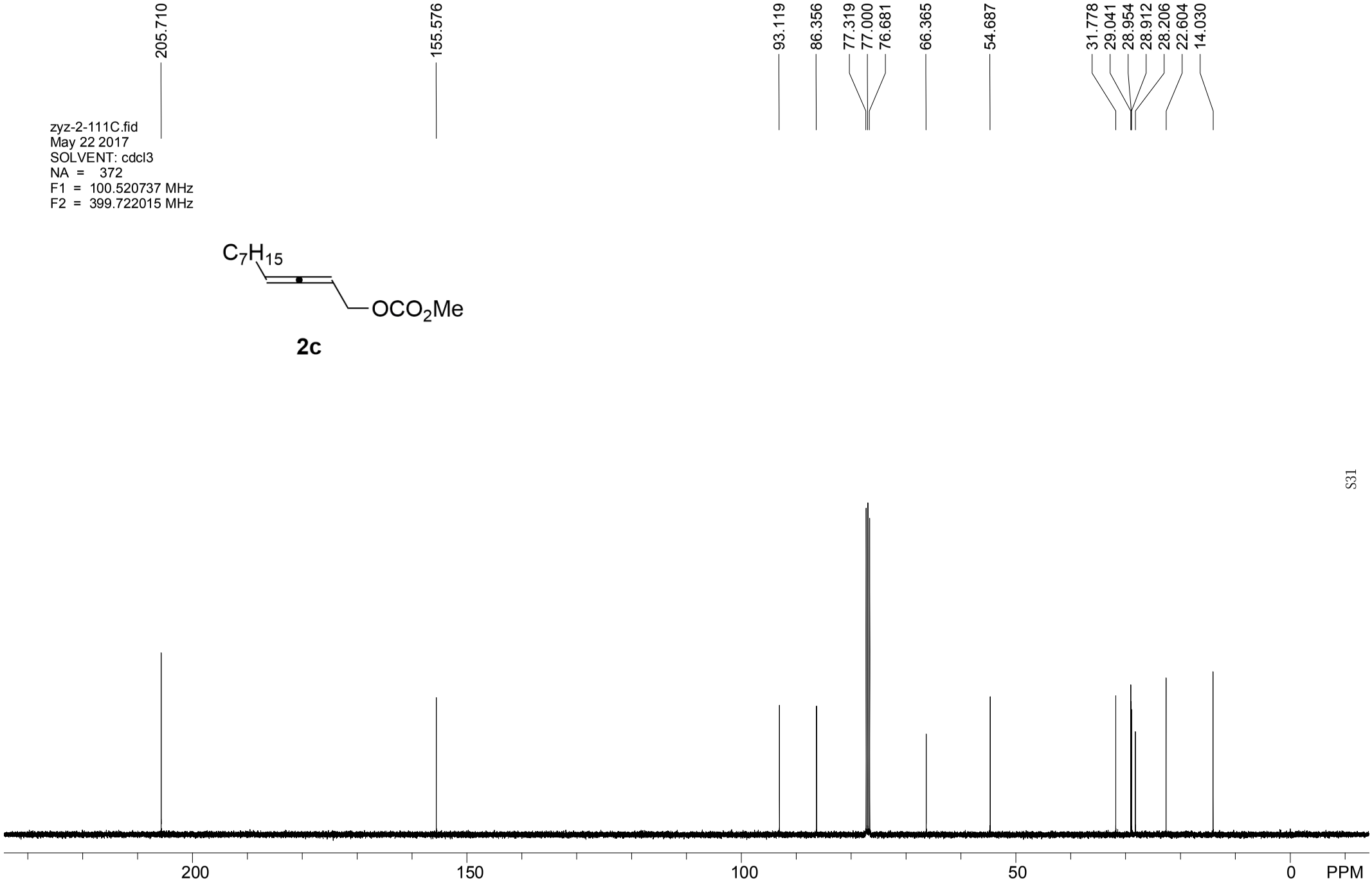
2.15
3.03
2.19
10.97
3.23
S30
10
8
6
4
2
0PPM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86.356
77.319
77.000
76.681
66.365
54.687
31.778
29.041
28.954
28.912
28.206
22.604
14.030
zyz-2-111C.fid
May 22 2017
SOLVENT: cdcl3
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OCO2Me
2c
200
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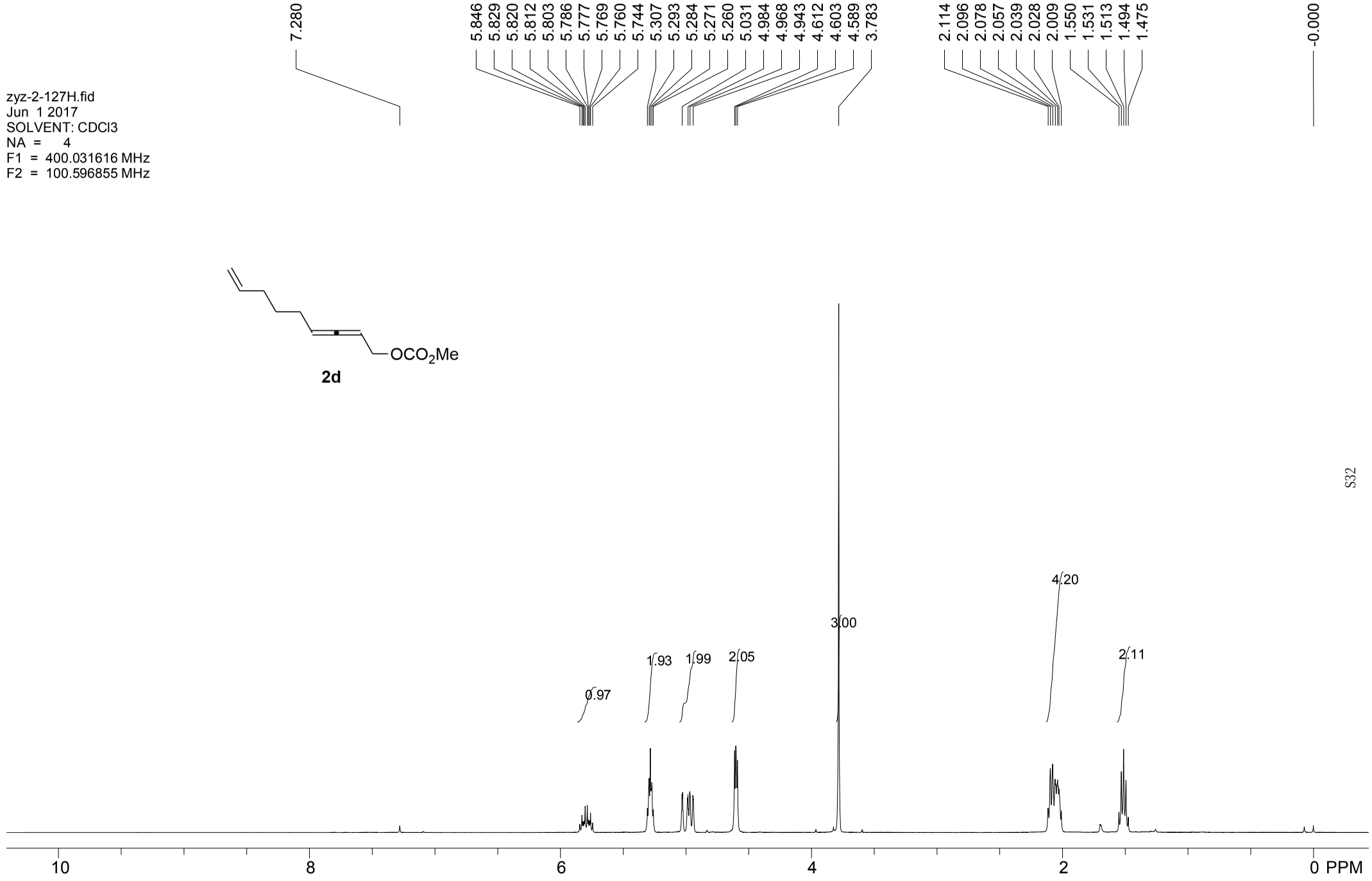
100
50
0
PPM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5.820
5.812
5.803
5.786
5.777
5.769
5.760
5.744
5.307
5.293
5.284
5.271
5.260
5.031
4.984
4.968
4.943
4.612
4.603
4.589
3.783
2.114
2.096
2.078
2.057
2.039
2.028
2.009
1.550
1.531
1.513
1.494
1.475
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zyz-2-127H.fid
Jun 1 2017
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F2 = 100.596855 MHz
OCO2Me
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3.00
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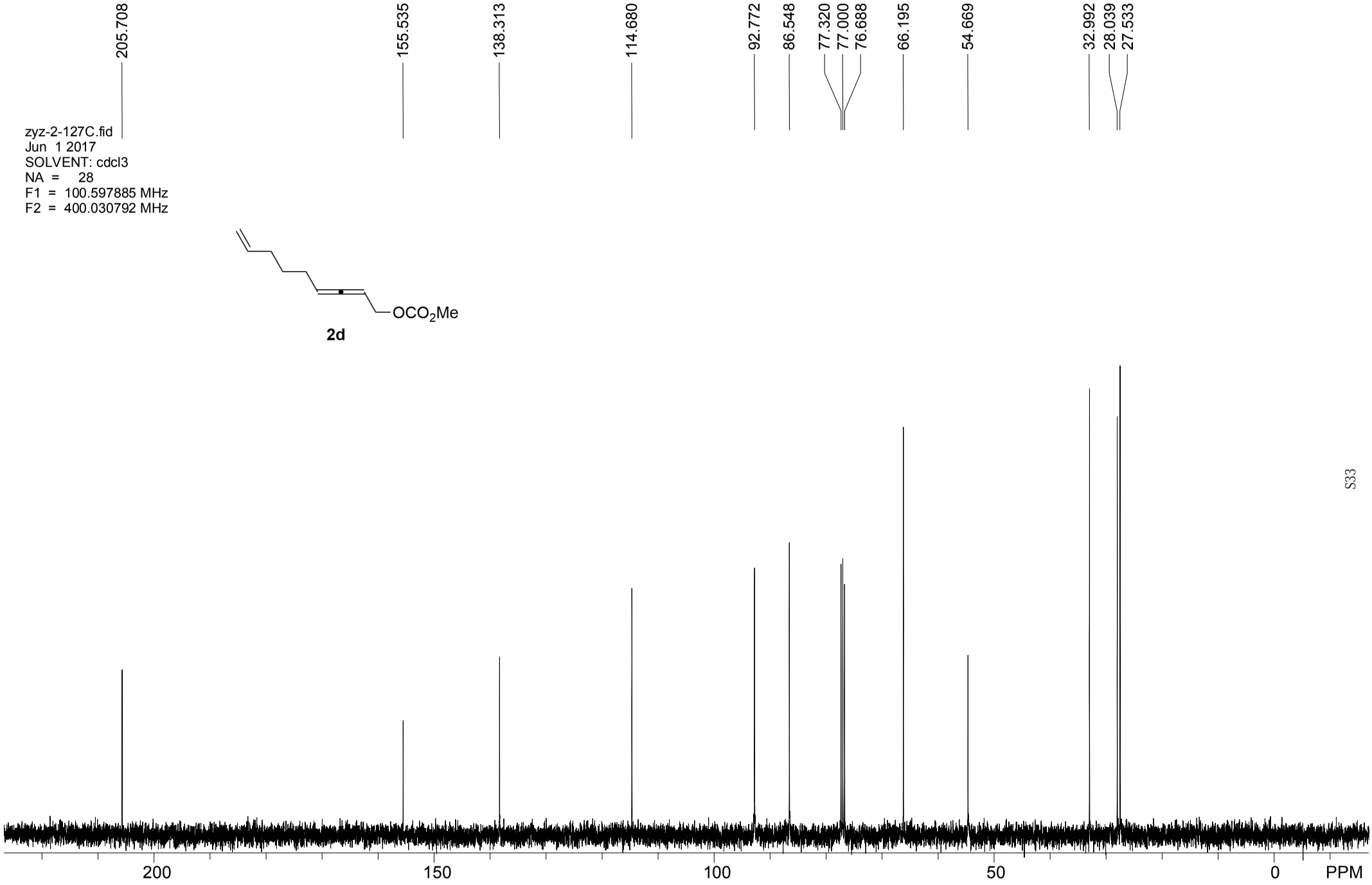
2.11
10
8
6
4
2
0 PPM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77.000
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54.669
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28.039
27.533
zyz-2-127C.fid
Jun 1 2017
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2d
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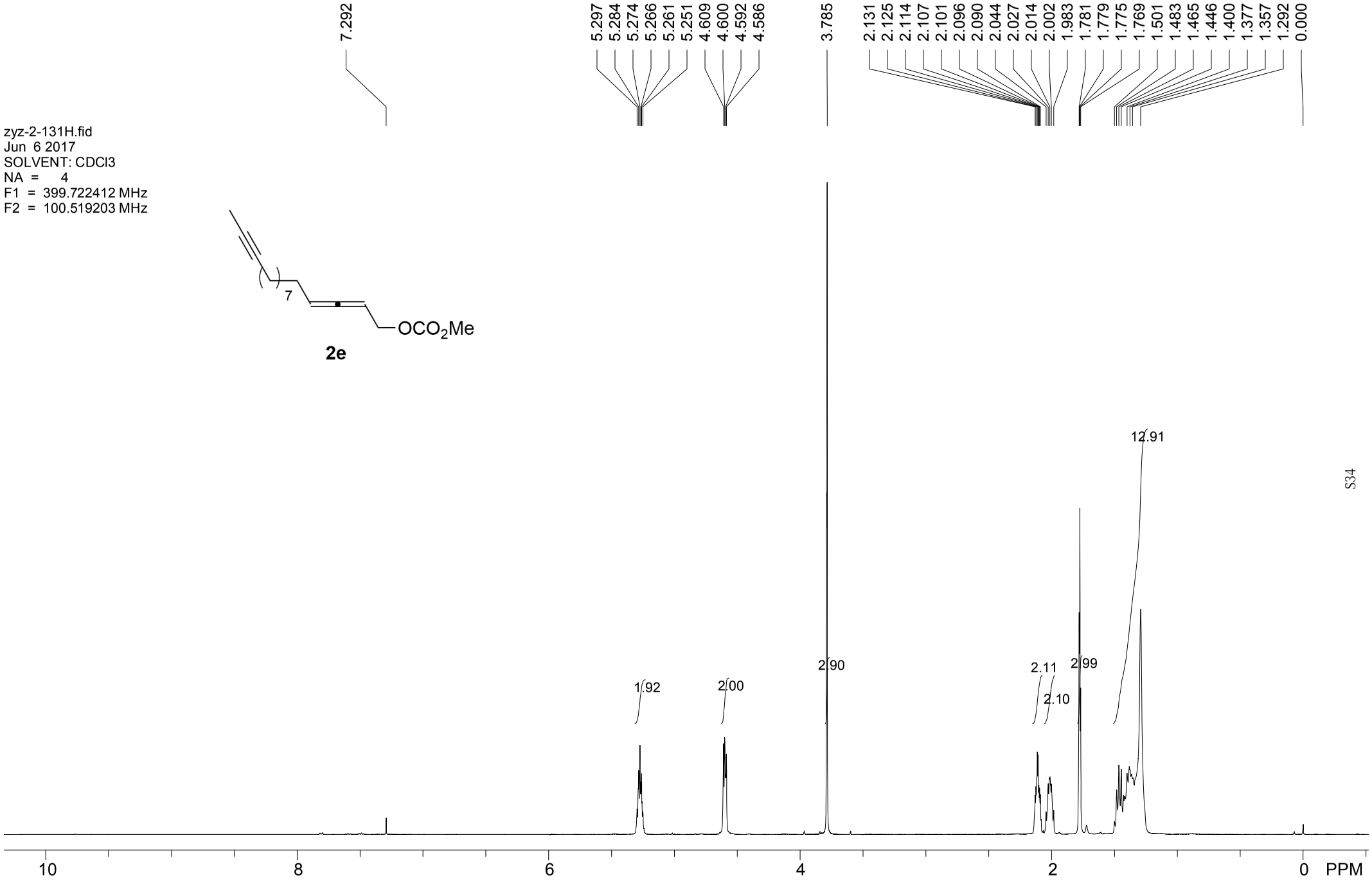
150
100
50
0
PPM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5.274
5.266
5.261
5.251
4.609
4.600
4.592
4.586
3.785
2.131
2.125
2.114
2.107
2.101
2.096
2.090
2.044
2.027
2.014
2.002
1.983
1.781
1.779
1.775
1.769
1.501
1.483
1.465
1.446
1.400
1.377
1.357
1.292
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zyz-2-131H.fid
Jun 6 2017
SOLVENT: CDCl3
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F2 = 100.519203 MHz
7
OCO2Me
2e
1.92
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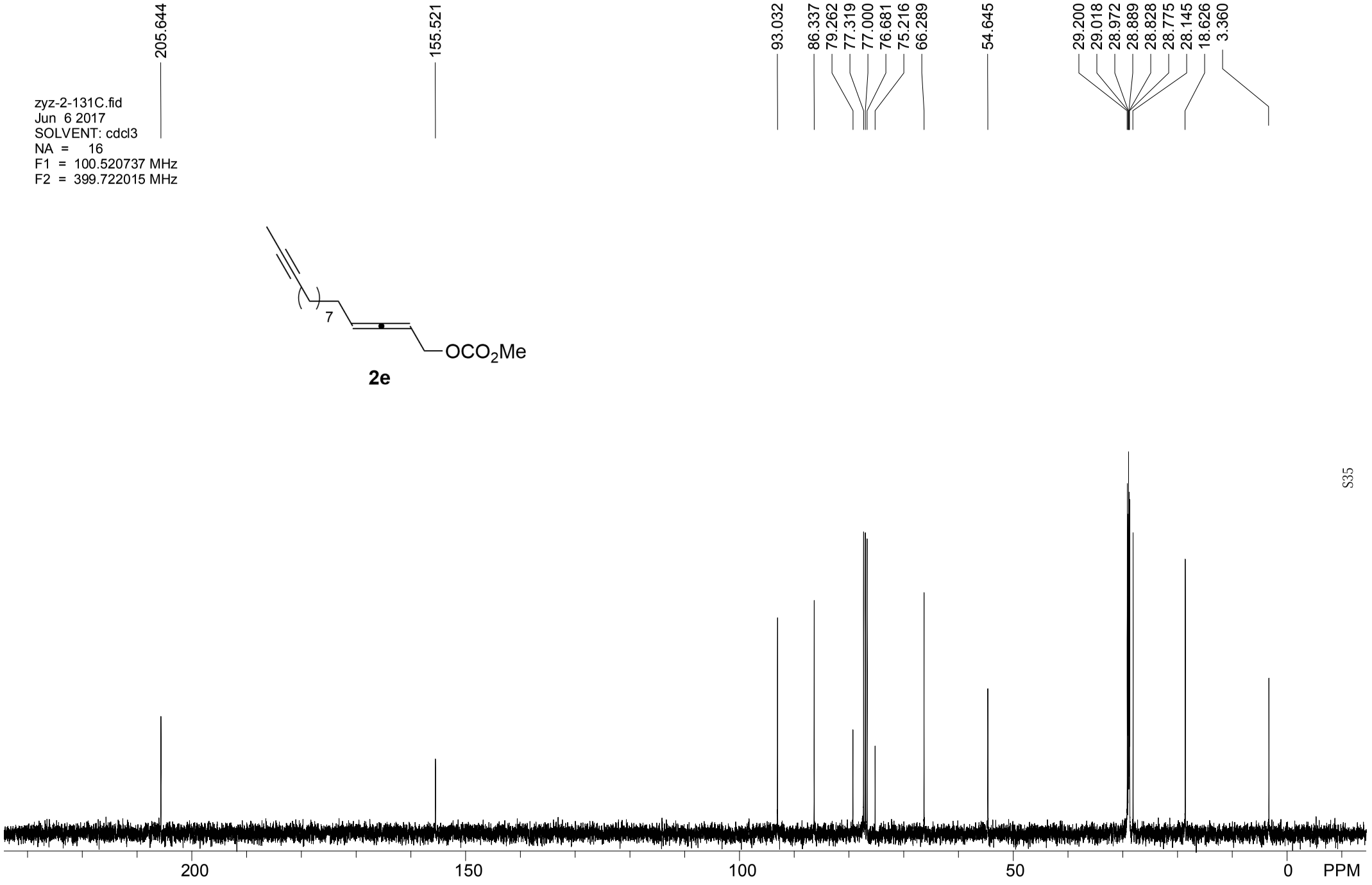
2.90
2.11
2.10
2.99
12.91
S34
10
8
6
4
2
0
PPM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66.289
54.645
29.200
29.018
28.972
28.889
28.828
28.775
28.145
18.626
3.360
zyz-2-131C.fid
Jun 6 2017
SOLVENT: cdcl3
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F2 = 399.722015 MHz
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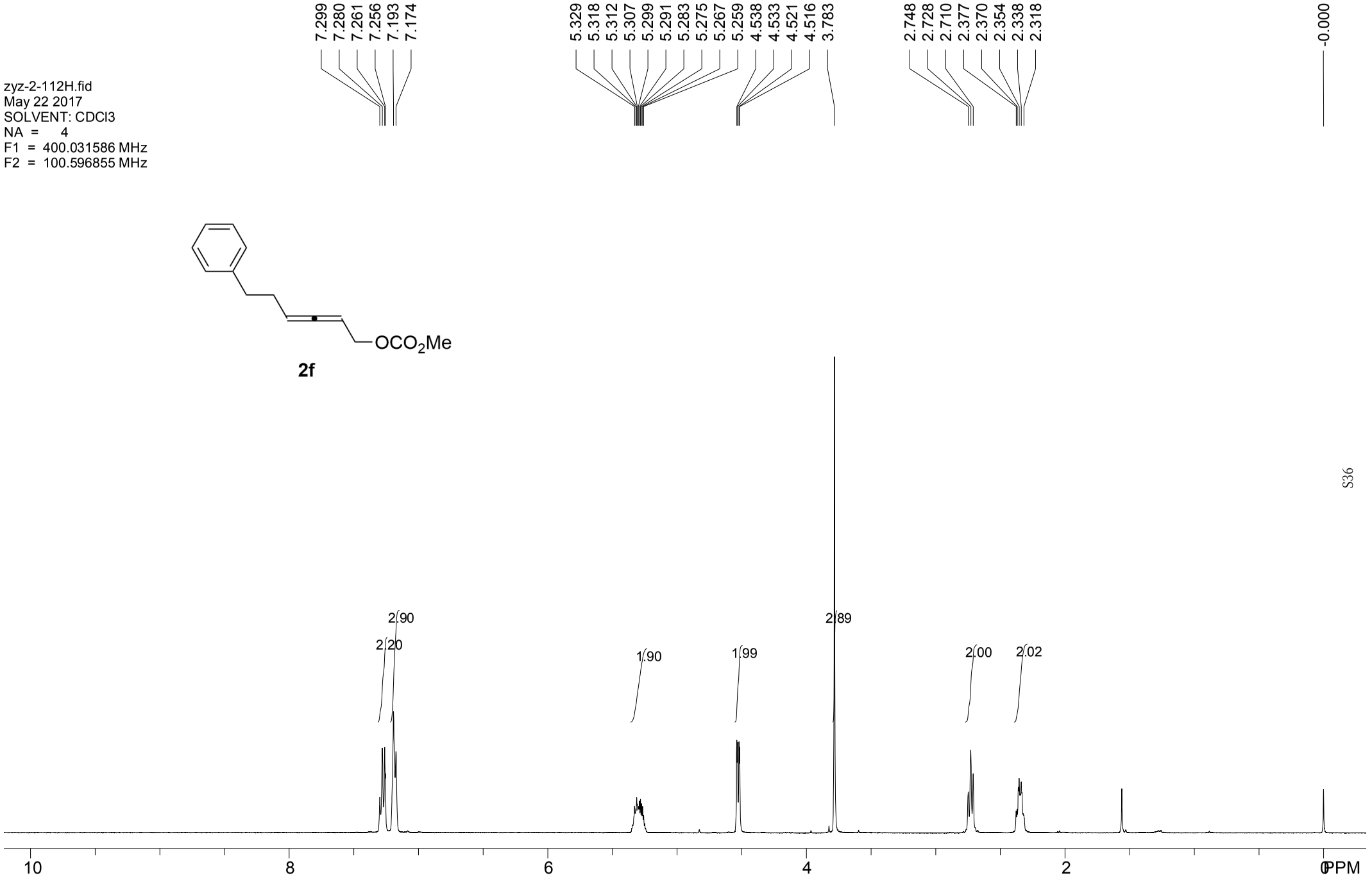
OCO2Me
2e
200
150
100
50
0
PPM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5.307
5.299
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5.283
5.275
5.267
5.259
4.538
4.533
4.521
4.516
3.783
2.748
2.728
2.710
2.377
2.370
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zyz-2-112H.fid
May 22 2017
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F1 = 400.031586 MHz
F2 = 100.596855 MHz
OCO2Me
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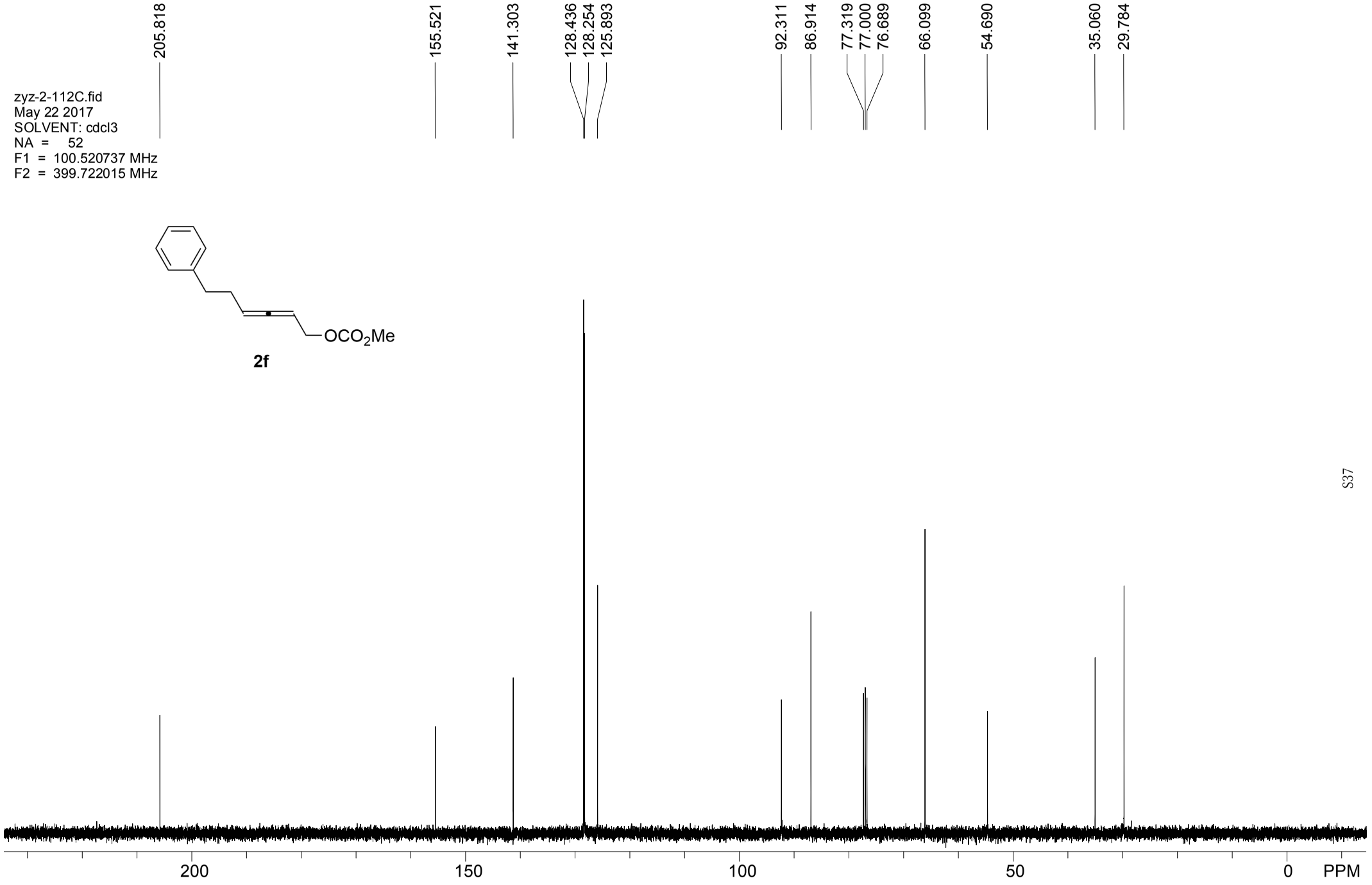
10
8
6
4
2
0
PPM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77.000
76.689
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54.690
35.060
29.784
zyz-2-112C.fid
May 22 2017
SOLVENT: cdcl3
NA = 52
F1 = 100.520737 MHz
F2 = 399.722015 MHz
OCO2Me
2f
200
150
100
50
0
PPM

zyz-3-21H.fid
Jan 2 2018
SOLVENT: CDCl3
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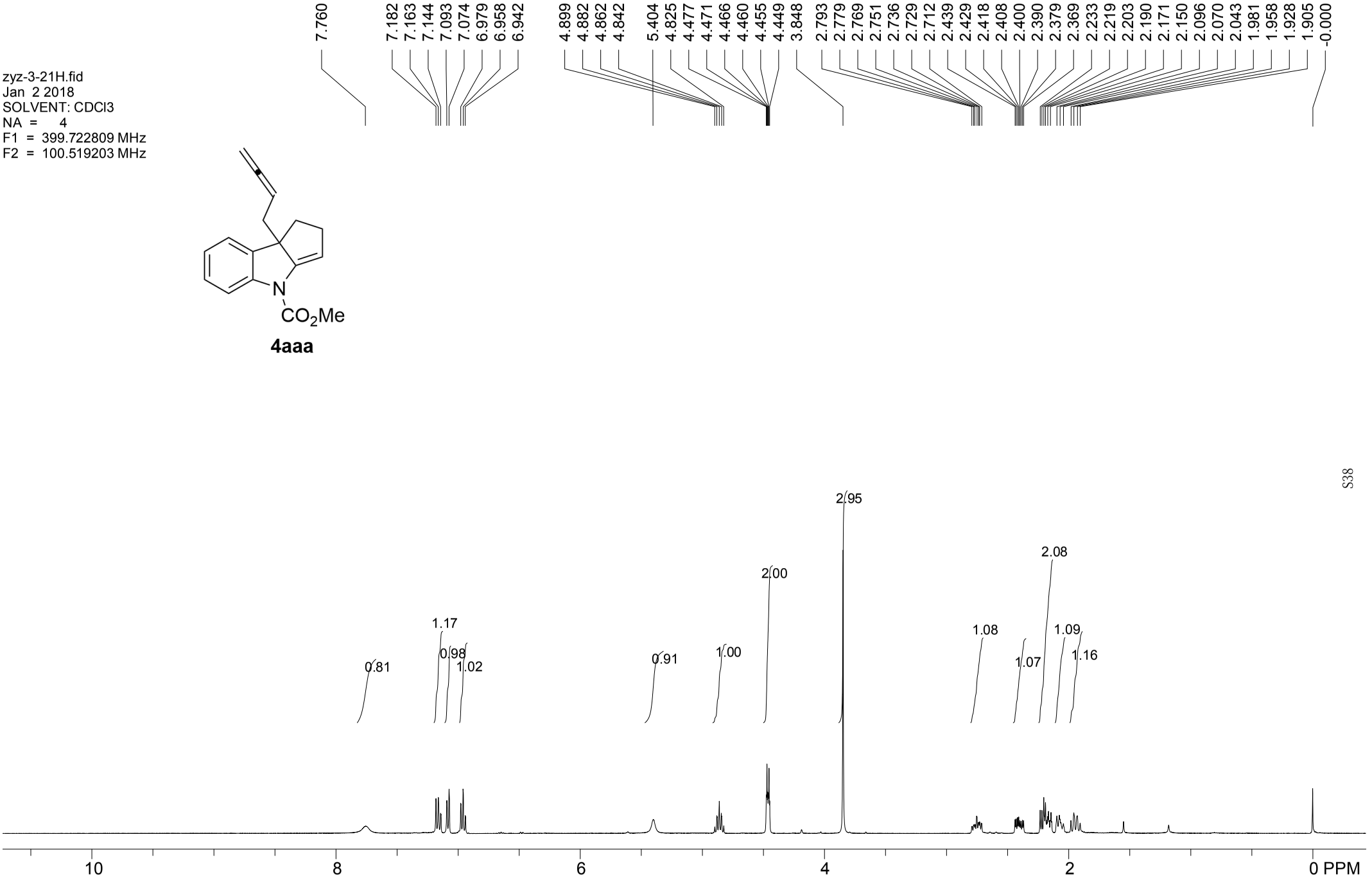
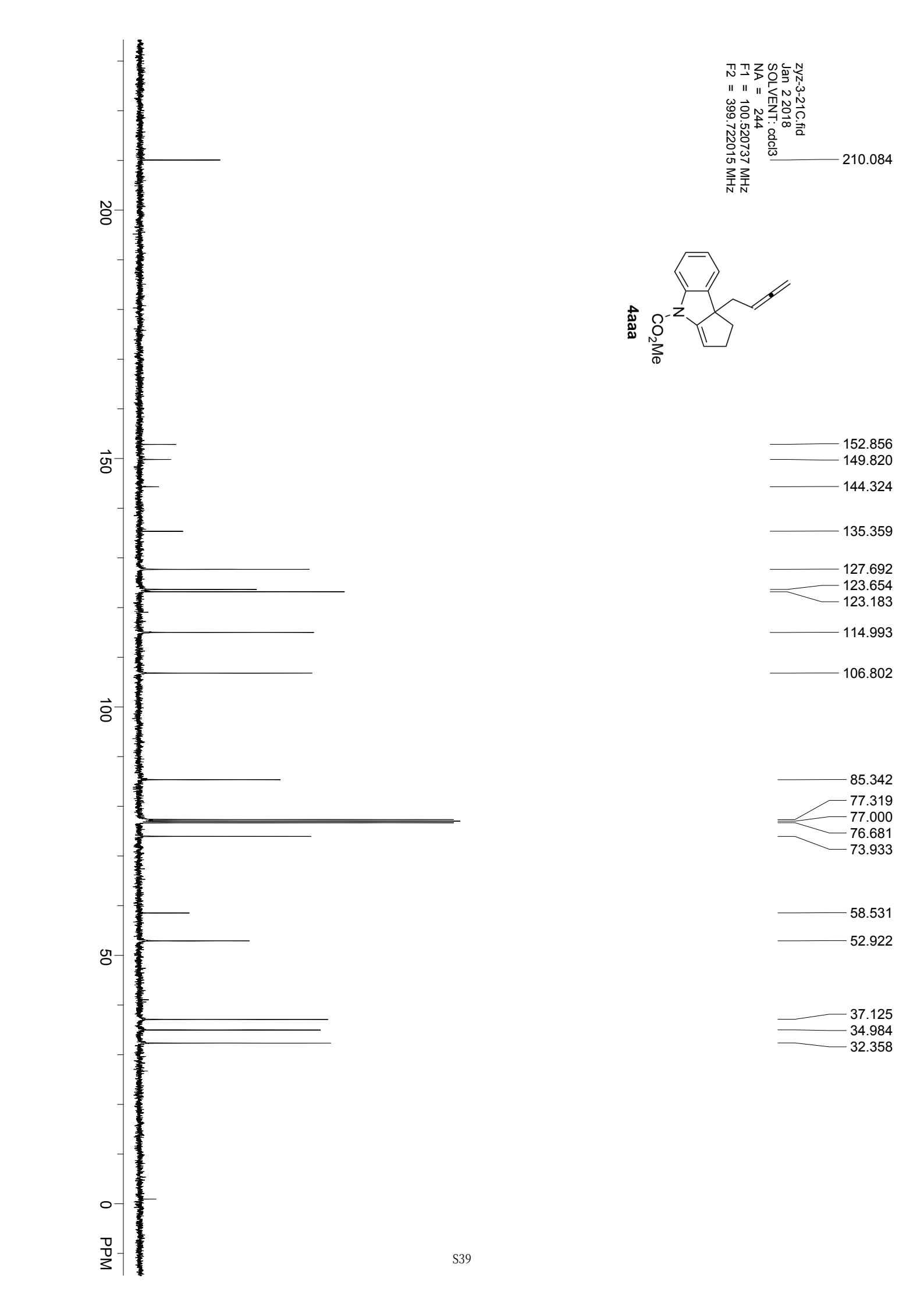
F2 = 100.519203 MHz

4aaa




zyz-3-21C.fid
Jan 2 2018
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CO2Me
4aaa
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149.820
144.324
135.359
127.692
123.654
123.183
114.993
106.802
85.342
77.319
77.000
76.681
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58.531
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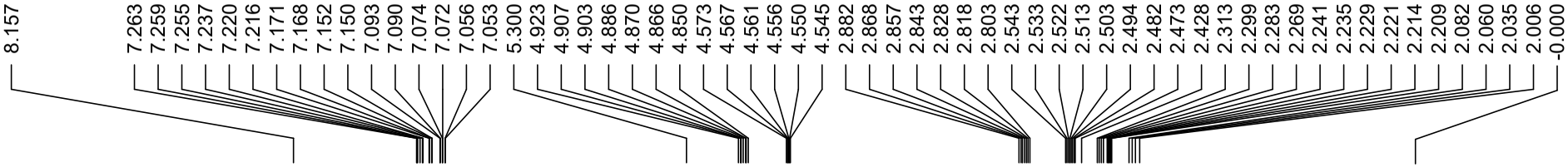
32.358
200
150
100
50
0
PPM



grd-17-84-H.fid
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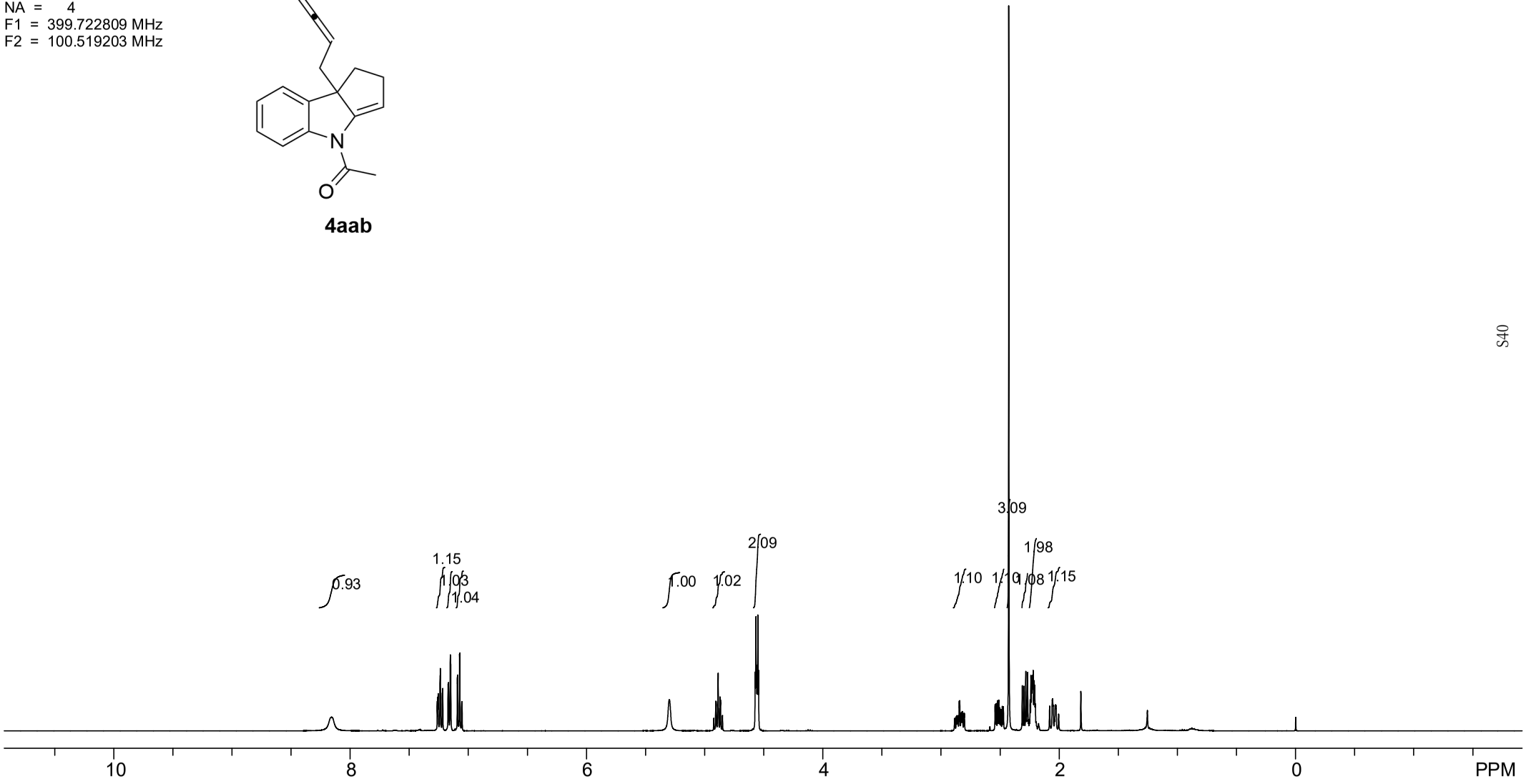
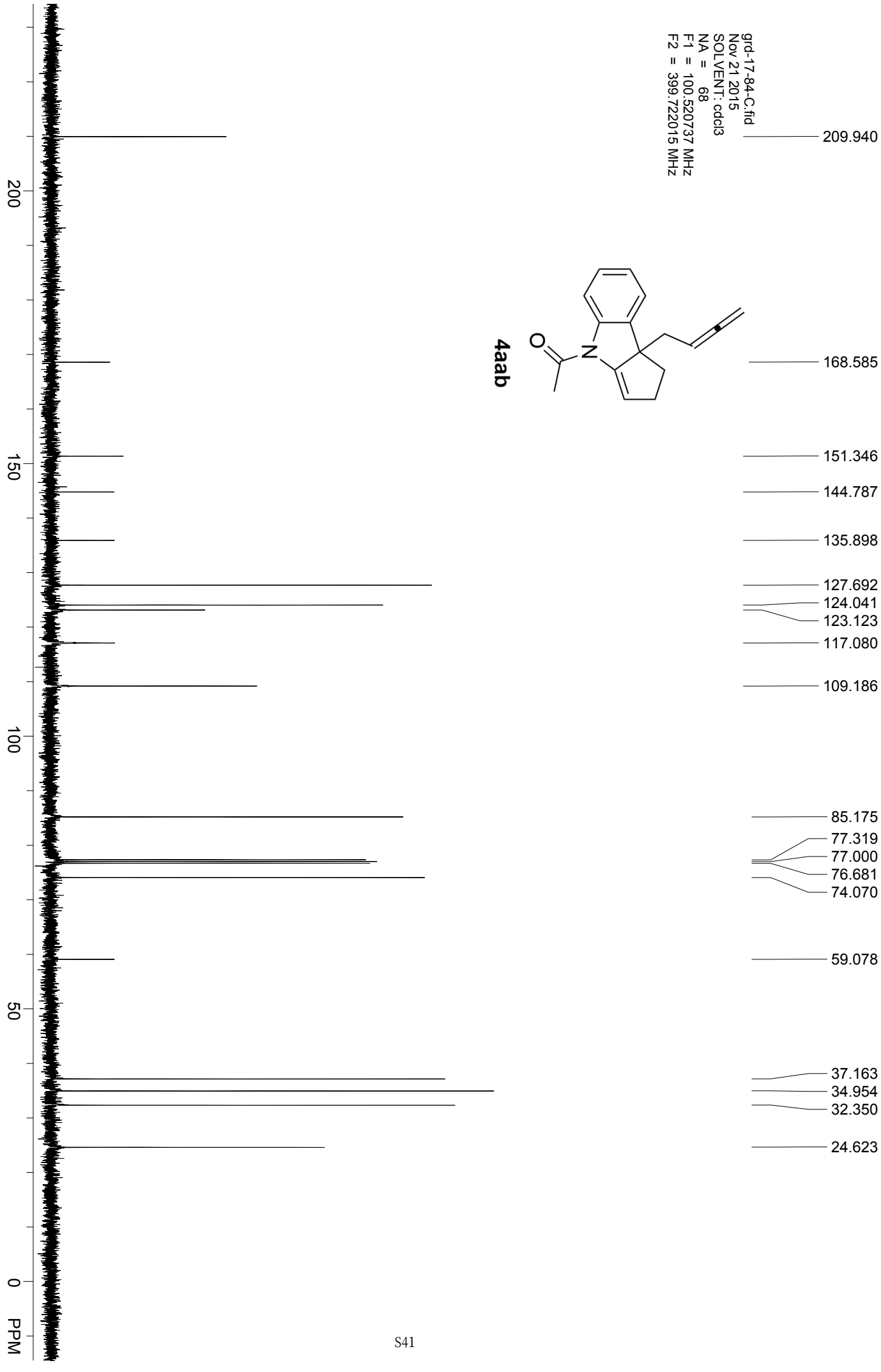
4aab




grd-17-84-C.fid
Nov 21 2015
SOLVENT: cdcl3
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F2 = 399.722015 MHz
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N
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144.787
135.898
127.692
124.041
123.123
117.080
109.186
85.175
77.319
77.000
76.681
74.070
59.078
37.163
34.954
32.350
24.623
200
150
100
50
0
PPM

grd-17-83-2-H.fid
Nov 19 2015
SOLVENT: CDCl3
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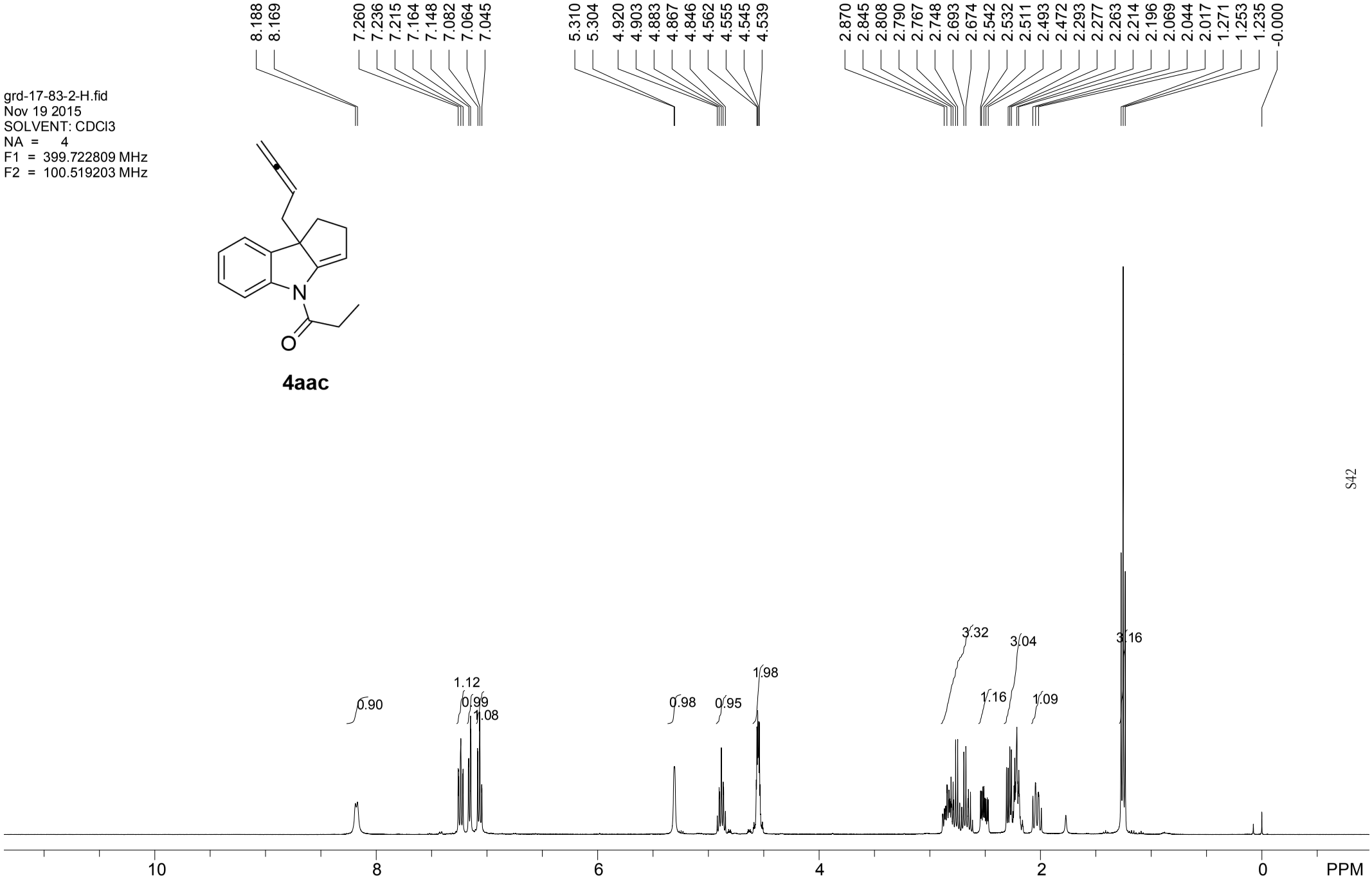
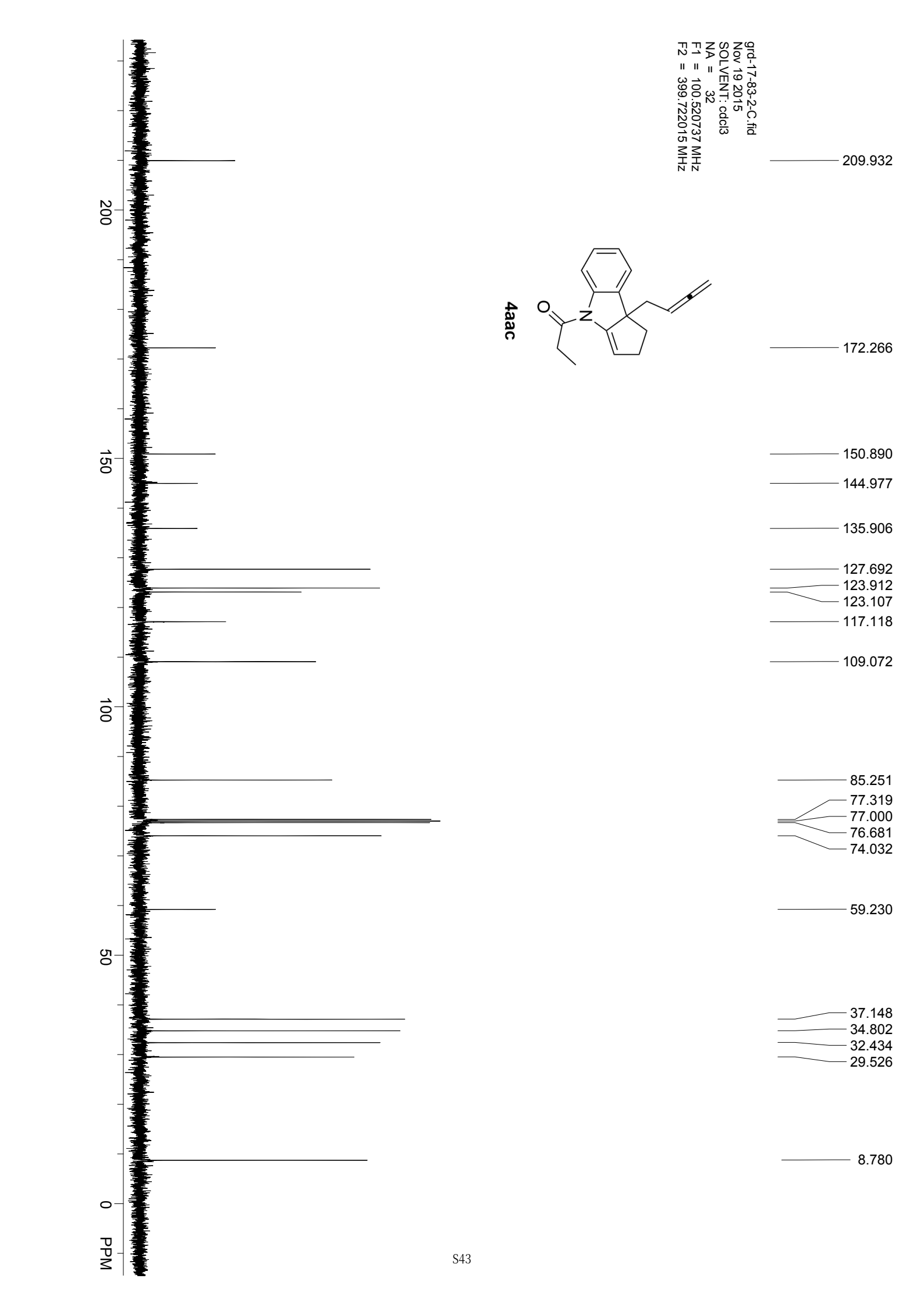
F1 = 399.722809 MHz
F2 = 100.519203 MHz

4aac




grd-17-83-2-C.fid
Nov 19 2015
SOLVENT: cdcl3
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N
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144.977
135.906
127.692
123.912
123.107
117.118
109.072
85.251
77.319
77.000
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50
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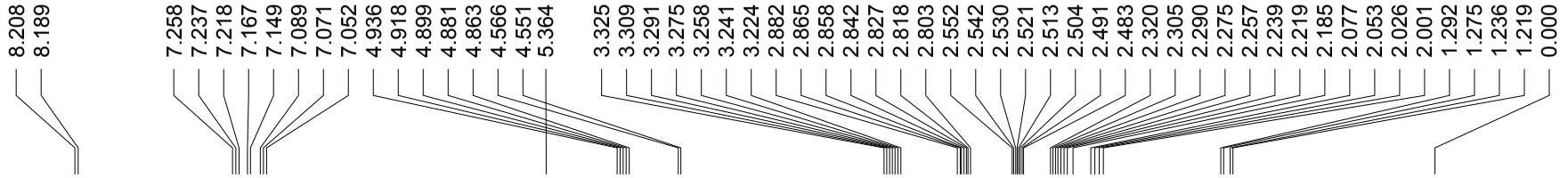
PPM



zyz-2-158H.fid
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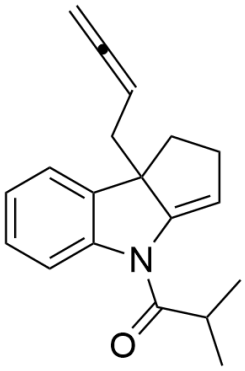
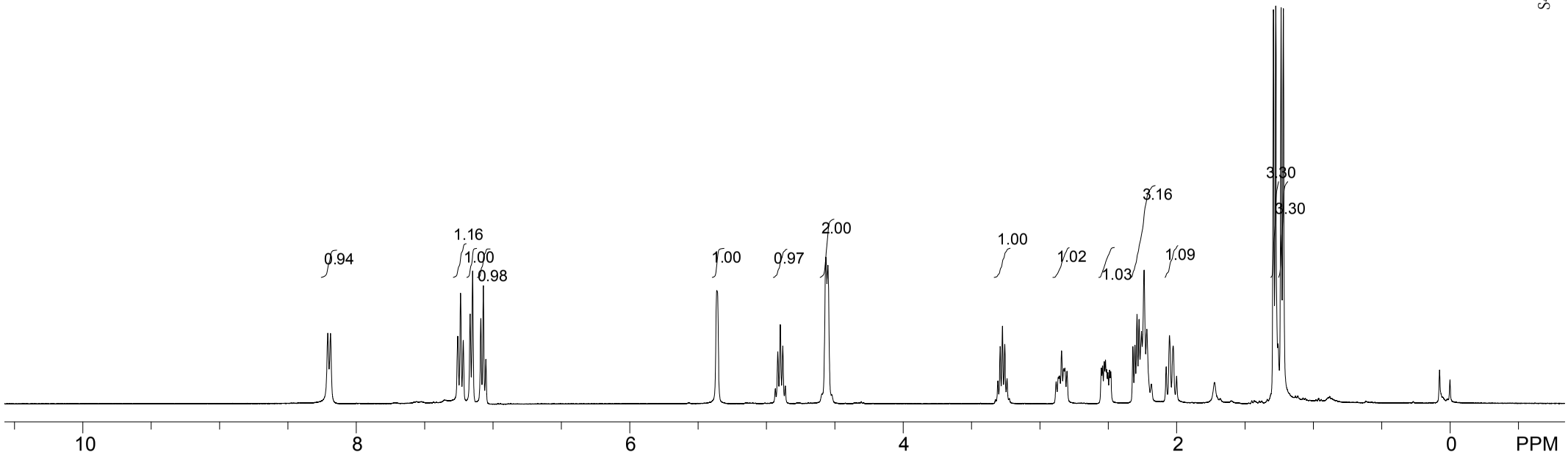
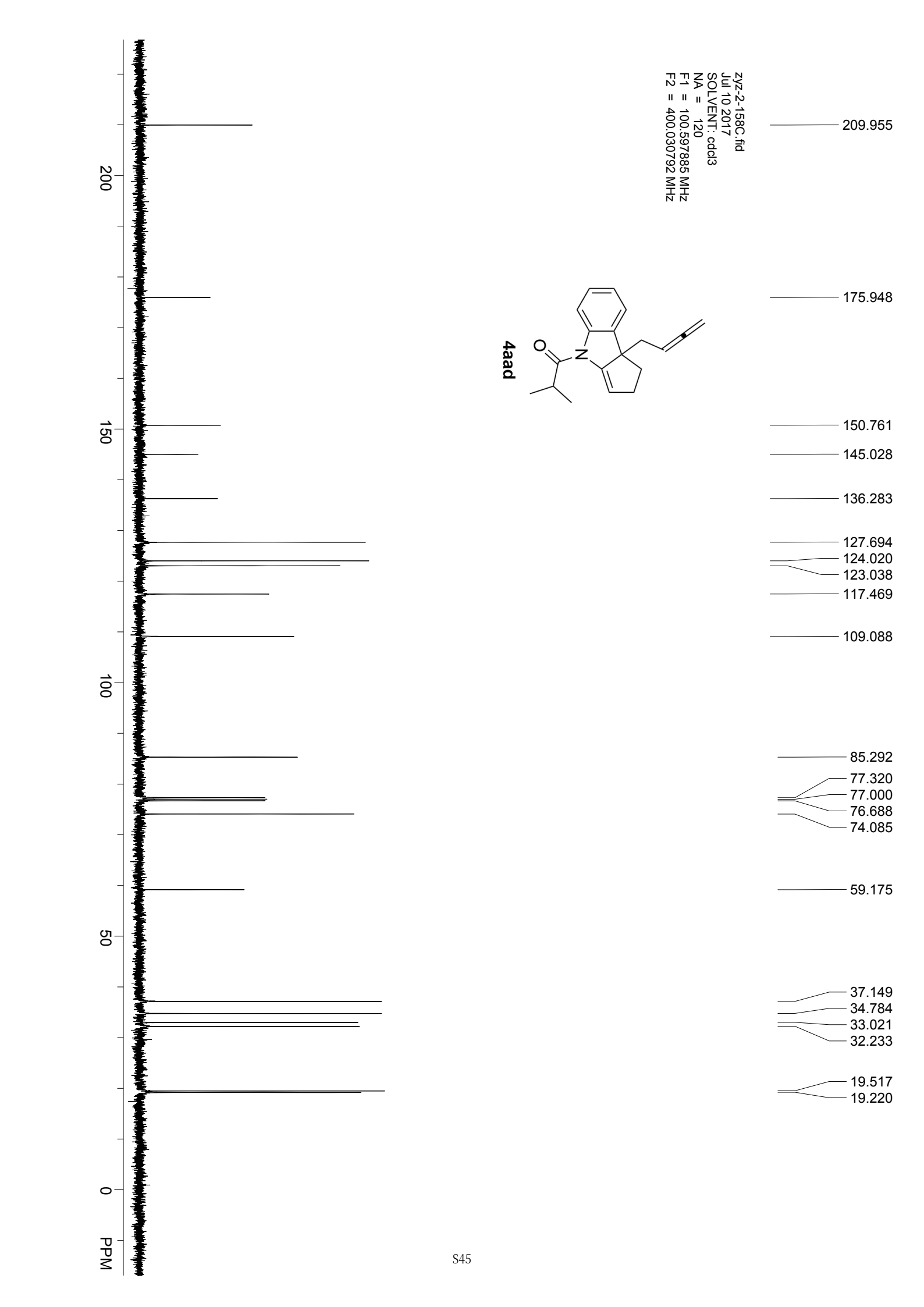


4aad




zyz-2-158C.fid
Jul 10 2017
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4aad
O
N
209.955
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150.761
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136.283
127.694
124.020
123.038
117.469
109.088
85.292
77.320
77.000
76.688
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200
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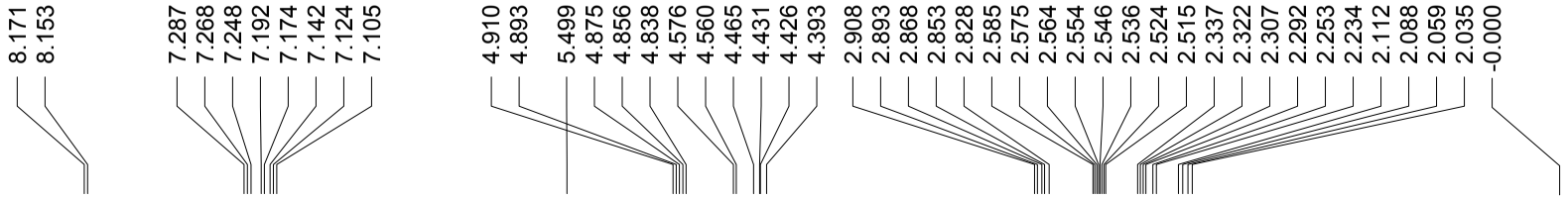
50
0
PPM



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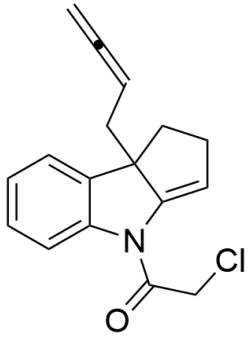
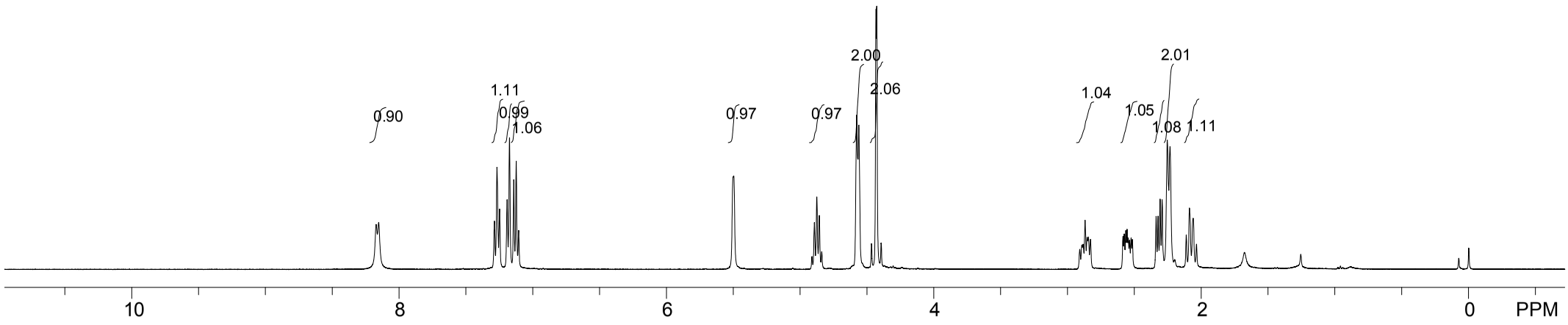
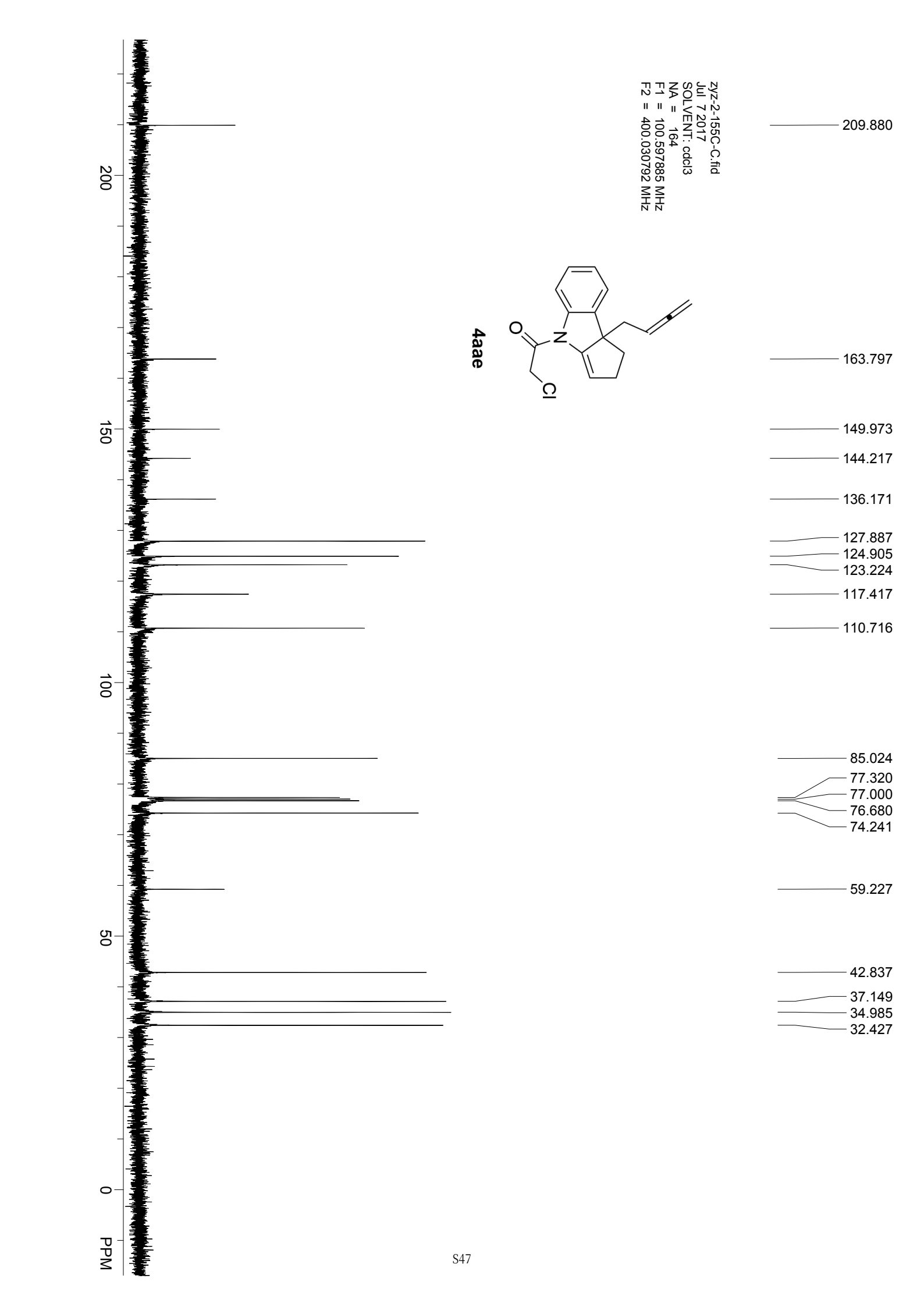
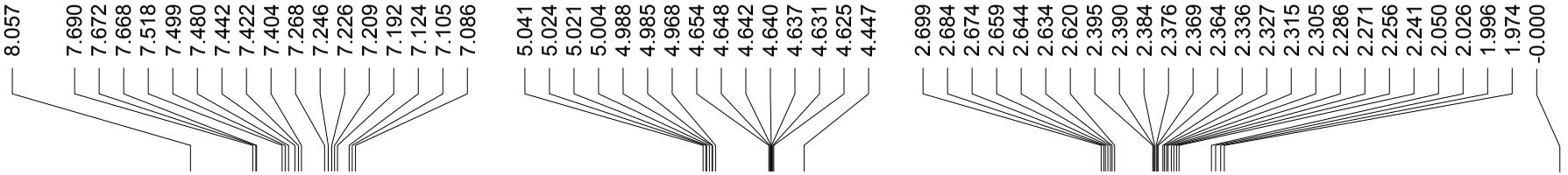
F2 = 100.596855 MHz



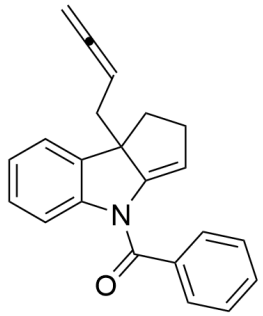
4aae



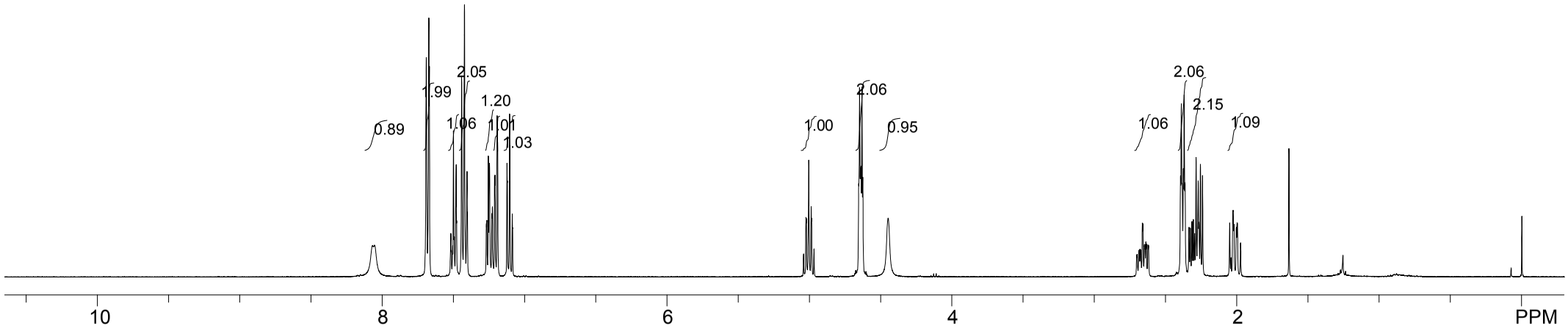

zyz-2-155C-C.fid
Jul 7 2017
SOLVENT: cdcl3
NA = 164
F1 = 100.597885 MHz
F2 = 400.030792 MHz
4aae
O
N
Cl
209.880
163.797
149.973
144.217
136.171
127.887
124.905
123.224
117.417
110.716
85.024
77.320
77.000
76.680
74.241
59.227
42.837
37.149
34.985
32.427
200
150
100
50
0
PPM

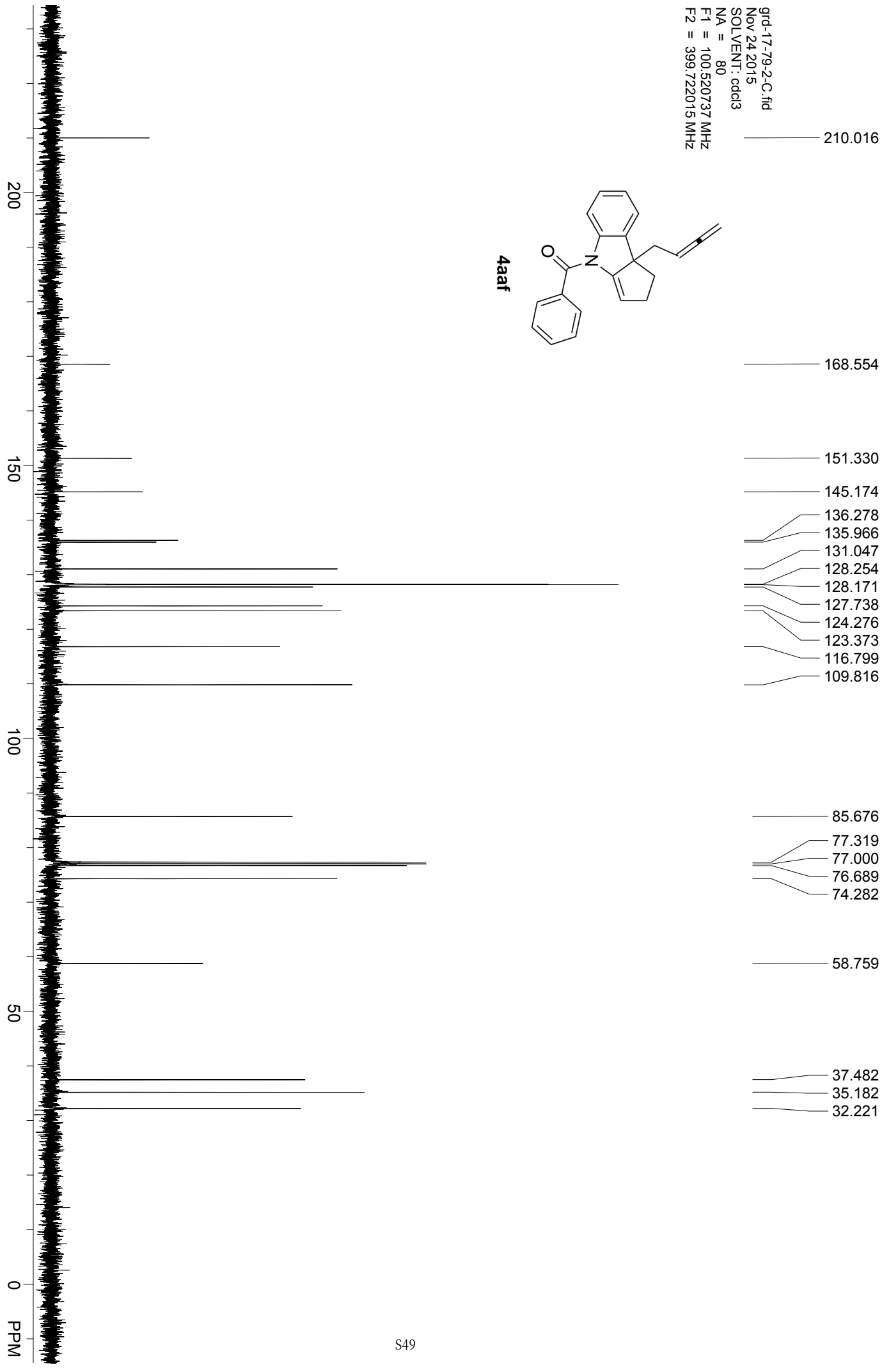


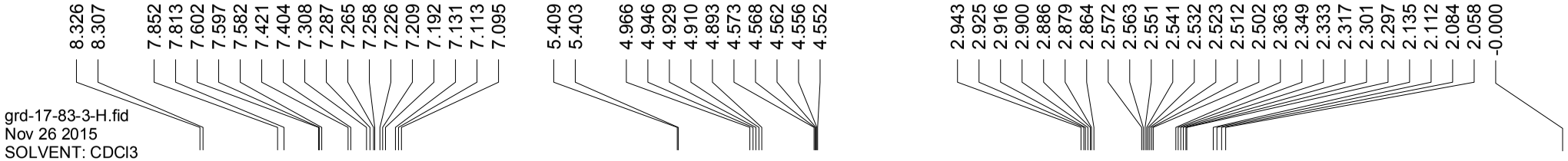
grd-17-79-2-H.fid
Nov 24 2015
SOLVENT: CDCl3
NA = 4
F1 = 399.722809 MHz
F2 = 100.519203 MHz



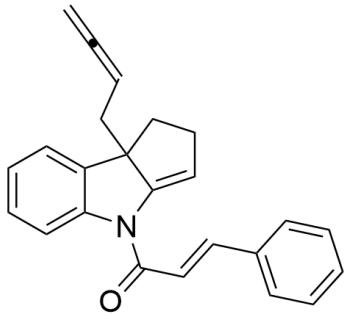
4aaf



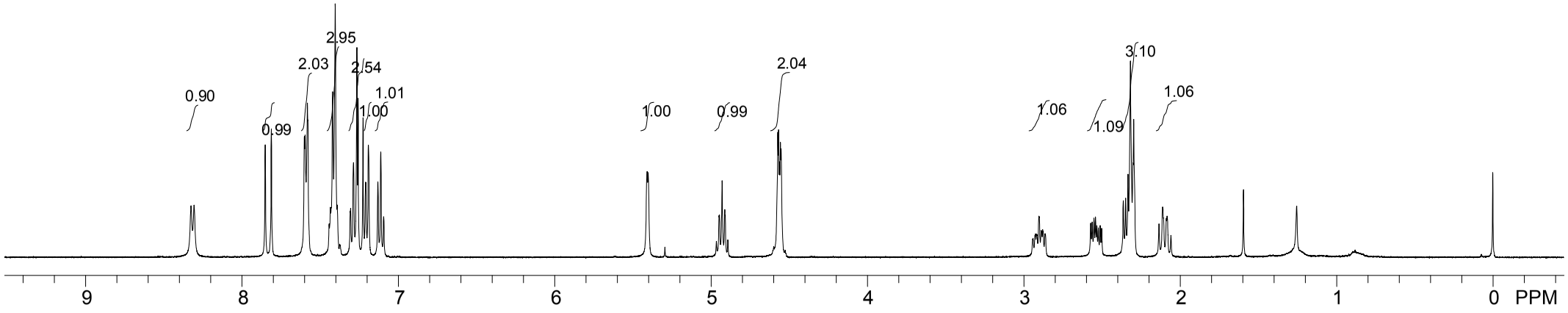

grd-17-79-2-C.fid
Nov 24 2015
SOLVENT: cdcl3
NA = 80
F1 = 100.520737 MHz
F2 = 399.722015 MHz
4aaf
210.016
168.554
151.330
145.174
136.278
135.966
131.047
128.254
128.171
127.738
124.276
123.373
116.799
109.816
85.676
77.319
77.000
76.689
74.282
58.759
37.482
35.182
32.221
200
150
100
50
0
PPM

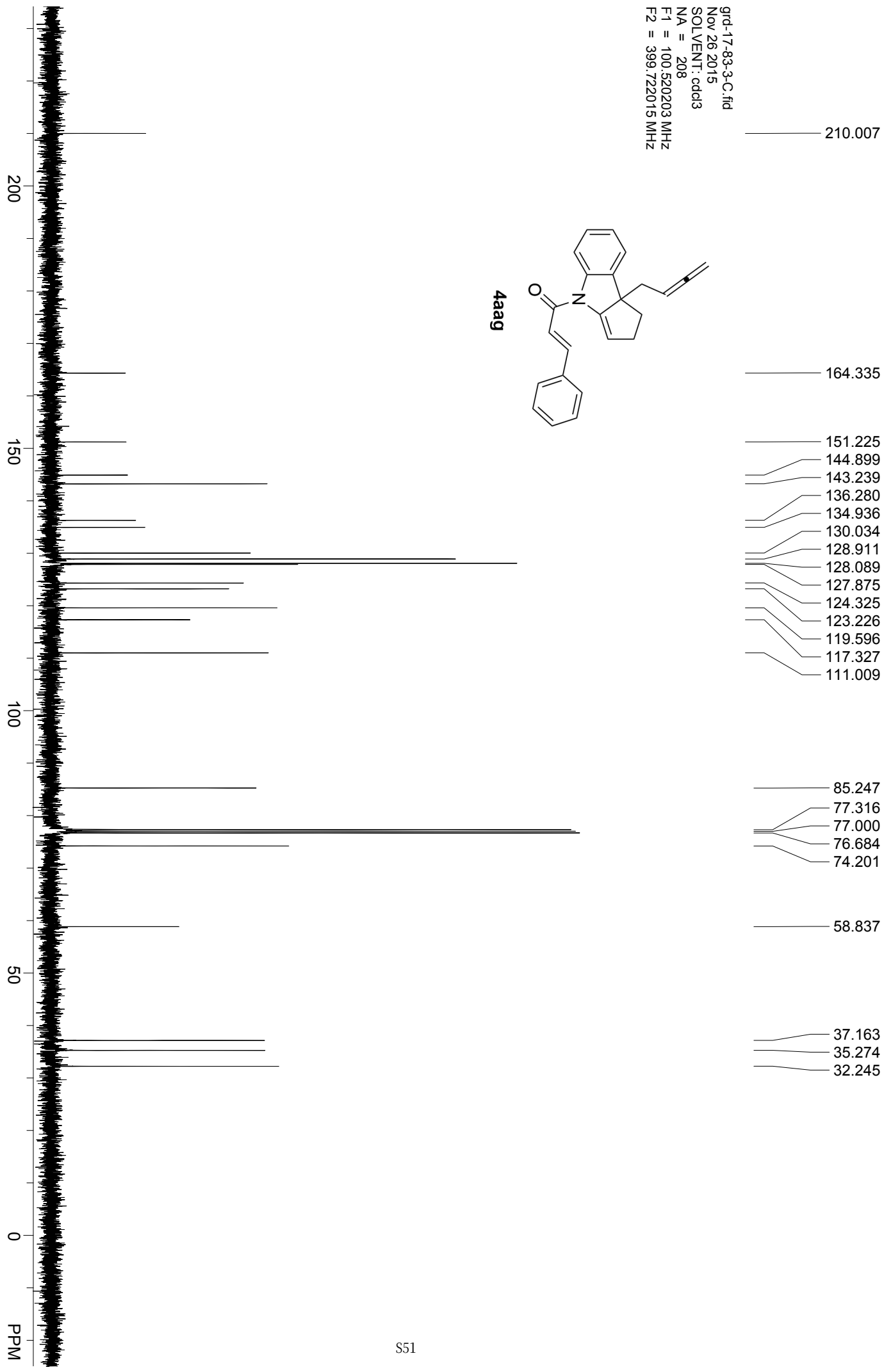


grd-17-83-3-H.fid
Nov 26 2015
SOLVENT: CDCl3
NA = 4
F1 = 399.722809 MHz
F2 = 100.519203 MHz



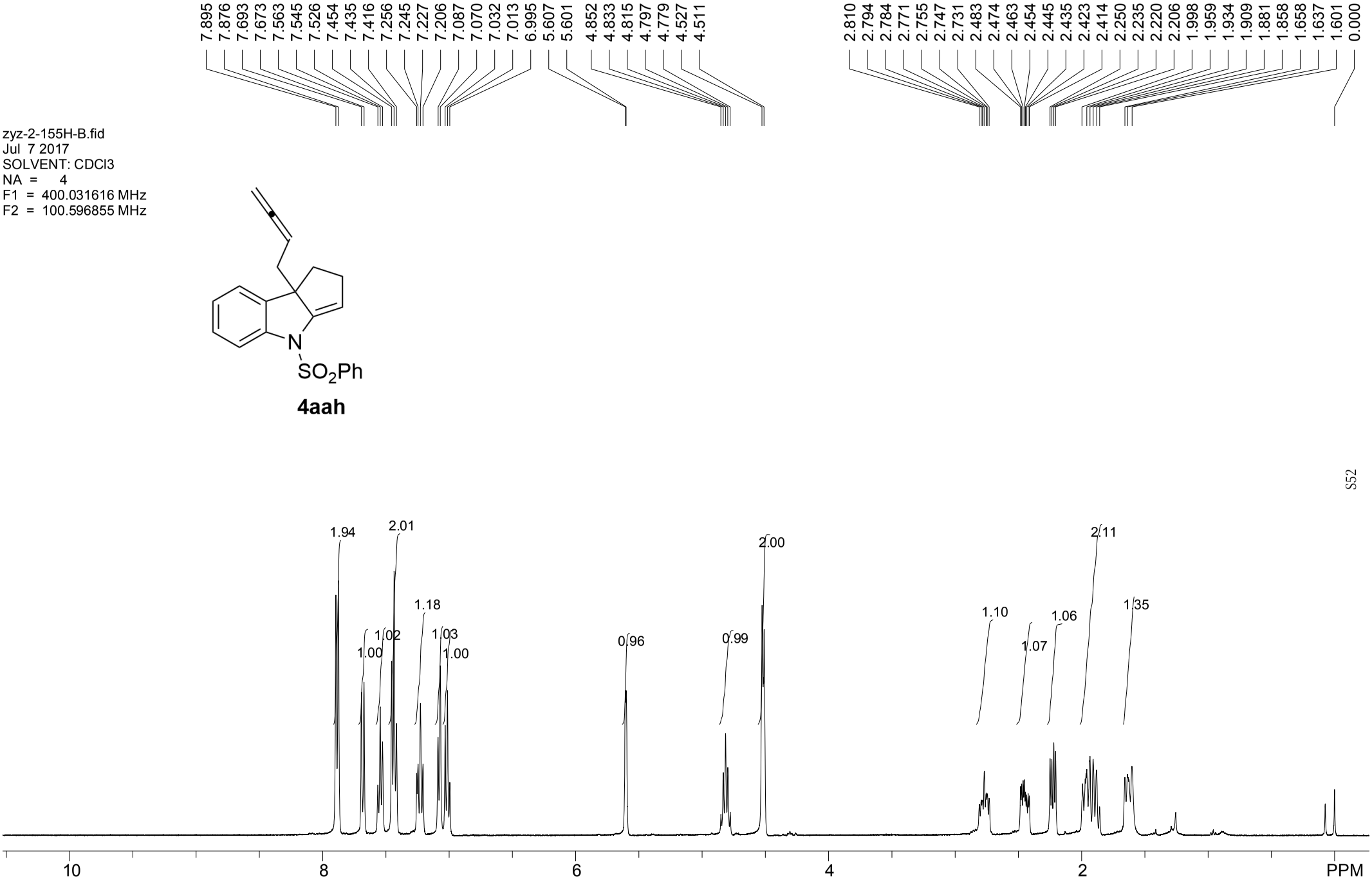
4aag

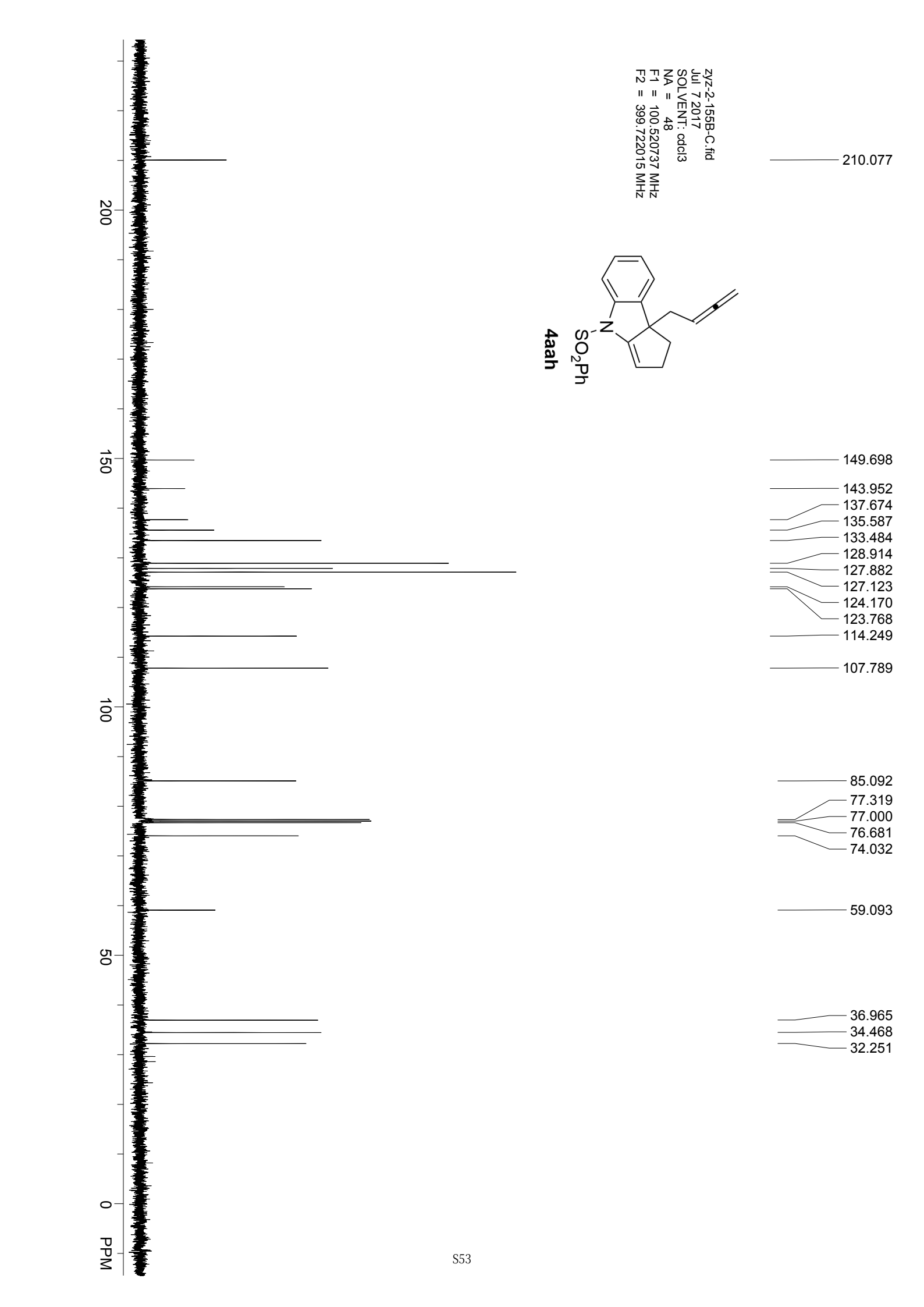


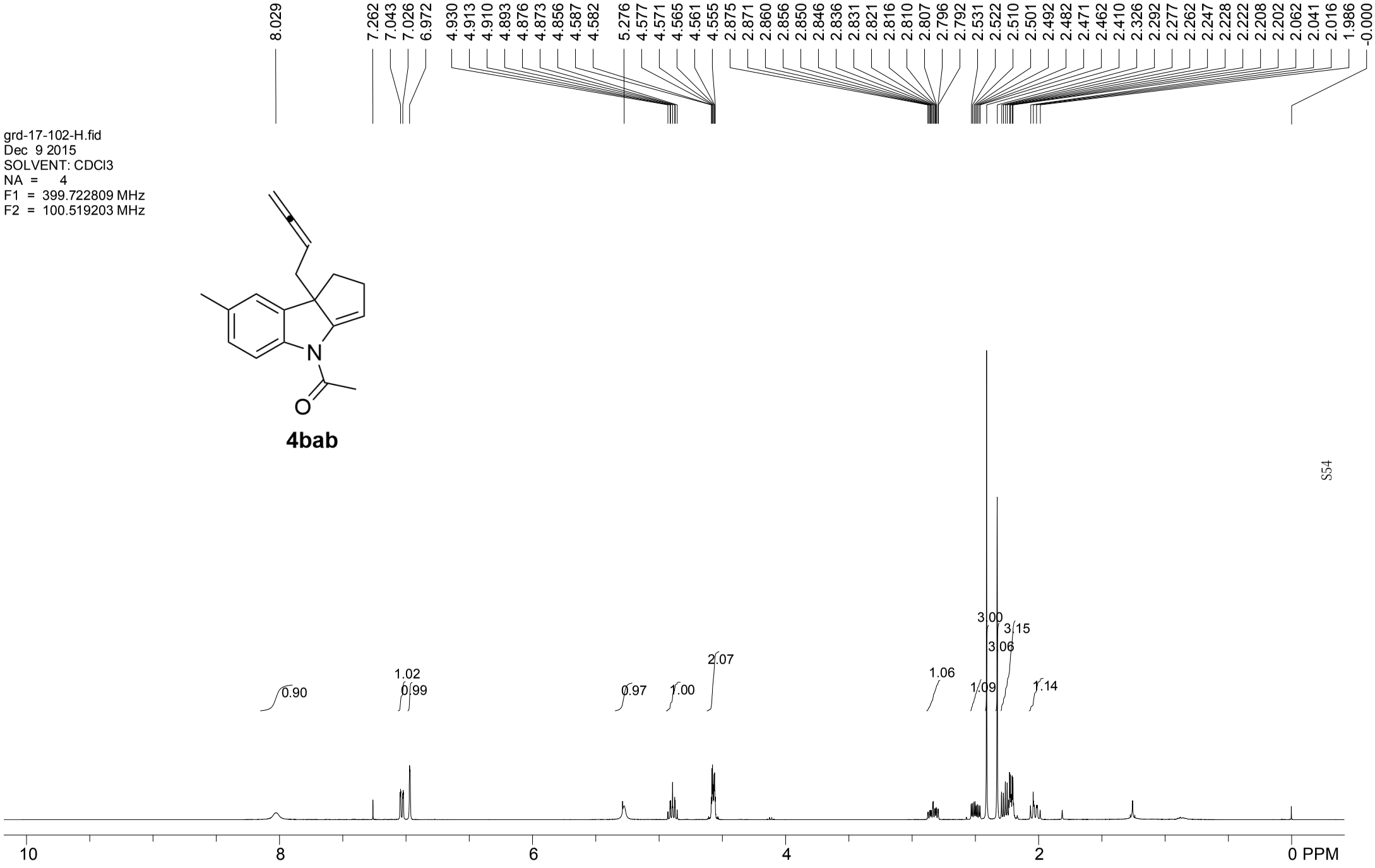

grd-17-83-3-C.fid
Nov 26 2015
SOLVENT: cdcl3
NA = 208
F1 = 100.520203 MHz
F2 = 399.722015 MHz
4aag
210.007
164.335
151.225
144.899
143.239
136.280
134.936
130.034
128.911
128.089
127.875
124.325
123.226
119.596
117.327
111.009
85.247
77.316
77.000
76.684
74.201
58.837
37.163
35.274
32.245
200
150
100
50
0
PPM

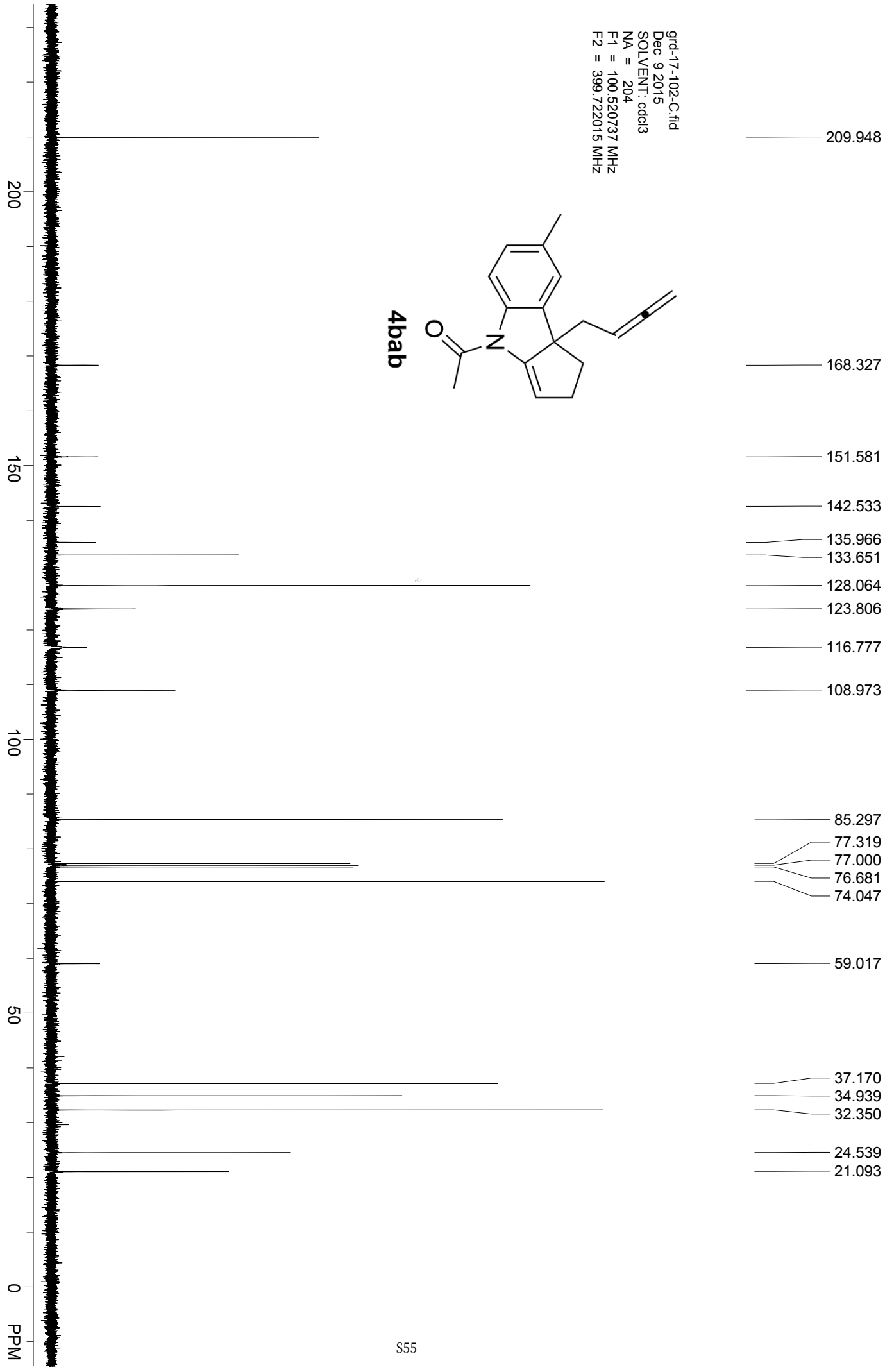
zyz-2-155H-B.fid
Jul 7 2017
SOLVENT: CDCl3
NA = 4
F1 = 400.031616 MHz
F2 = 100.596855 MHz

4aah



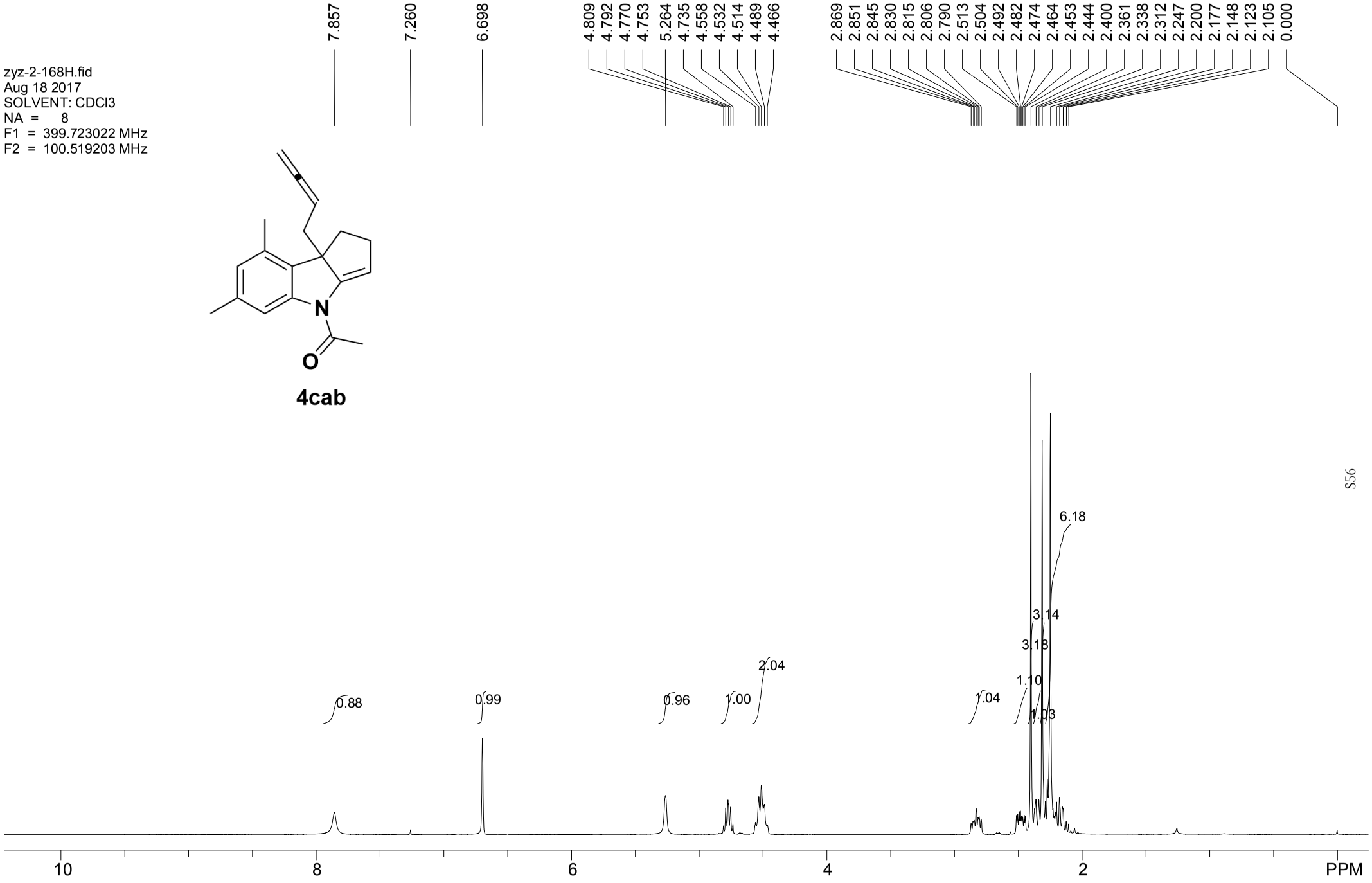

zyz-2-155B-C.fid
Jul 7 2017
SOLVENT: cdcl3
NA = 48
F1 = 100.520737 MHz
F2 = 399.722015 MHz
4aah
N
SO2Ph
210.077
149.698
143.952
137.674
135.587
133.484
128.914
127.882
127.123
124.170
123.768
114.249
107.789
85.092
77.319
77.000
76.681
74.032
59.093
36.965
34.468
32.251
200
150
100
50
0
PPM

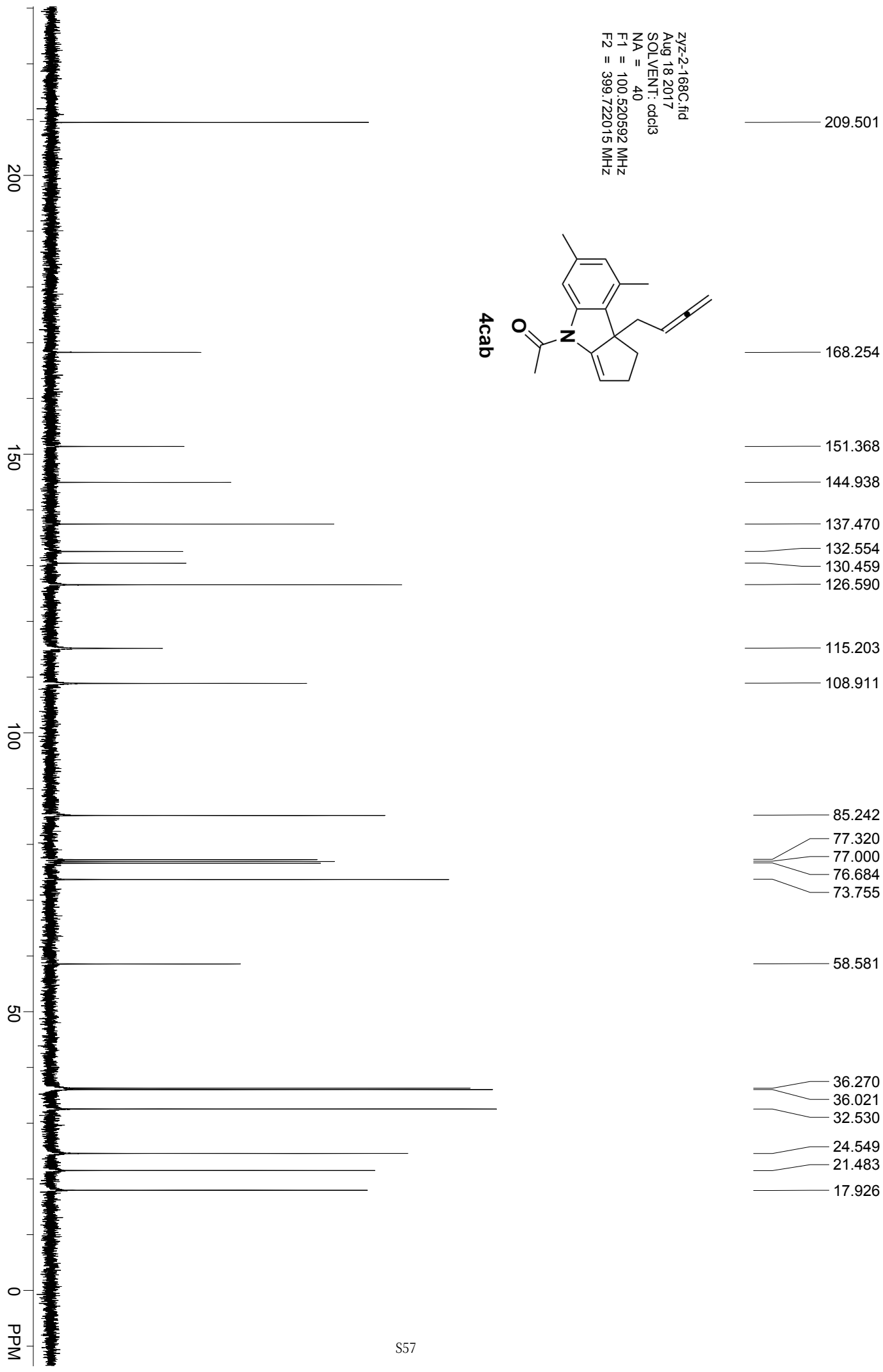

8.029
7.262
7.043
7.026
6.972
4.930
4.913
4.910
4.893
4.876
4.873
4.856
4.587
4.582
5.276
4.577
4.571
4.565
4.561
4.555
2.875
2.871
2.860
2.856
2.850
2.846
2.836
2.831
2.821
2.816
2.810
2.807
2.796
2.792
2.531
2.522
2.510
2.501
2.492
2.482
2.471
2.462
2.410
2.326
2.292
2.277
2.262
2.247
2.228
2.222
2.208
2.202
2.062
2.041
2.016
1.986
-0.000
grd-17-102-H.fid
Dec 9 2015
SOLVENT: CDCl3
NA = 4
F1 = 399.722809 MHz
F2 = 100.519203 MHz
N
O
4bab
S54
0.90
1.02
0.99
0.97
1.00
2.07
1.06
3.00
1.09
3.15
3.06
1.14
10
8
6
4
2
0 PPM


grd-17-102-C.fid
Dec 9 2015
SOLVENT: cdcl3
NA = 204
F1 = 100.520737 MHz
F2 = 399.722015 MHz
4bab
O
N
209.948
168.327
151.581
142.533
135.966
133.651
128.064
123.806
116.777
108.973
85.297
77.319
77.000
76.681
74.047
59.017
37.170
34.939
32.350
24.539
21.093
200
150
100
50
0
PPM

zyz-2-168H.fid
Aug 18 2017
SOLVENT: CDCl3
NA = 8
F1 = 399.723022 MHz
F2 = 100.519203 MHz

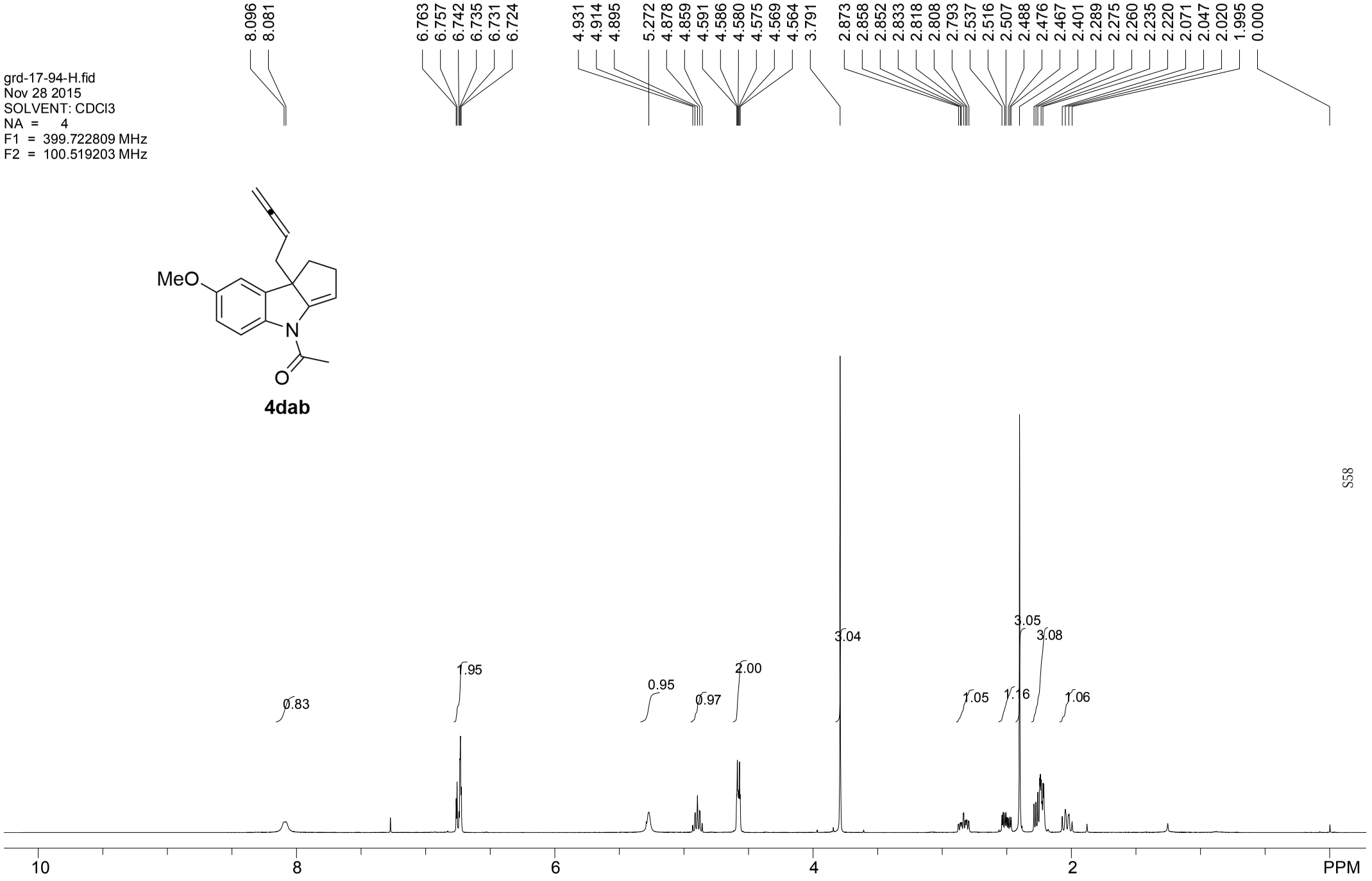
4cab

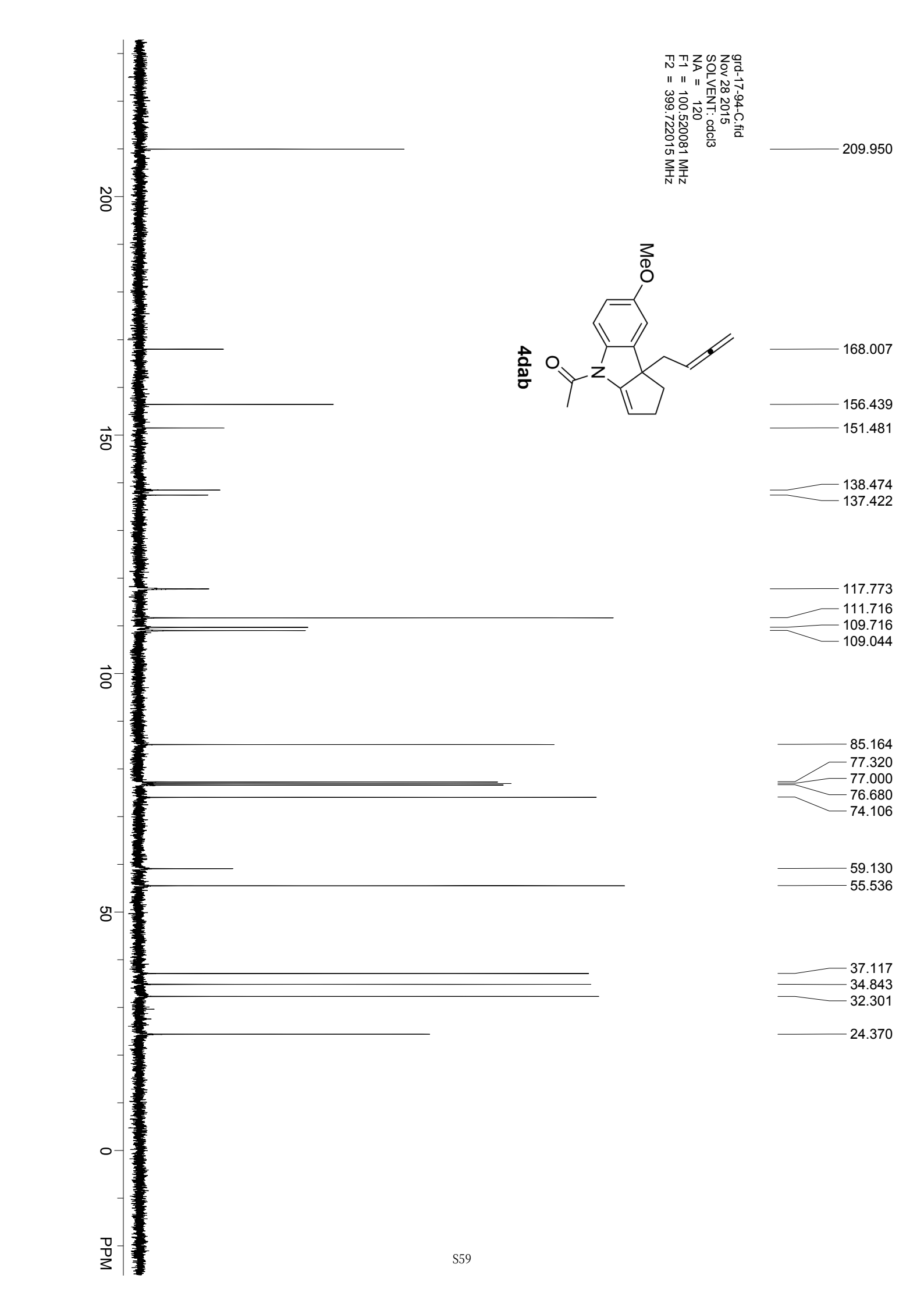


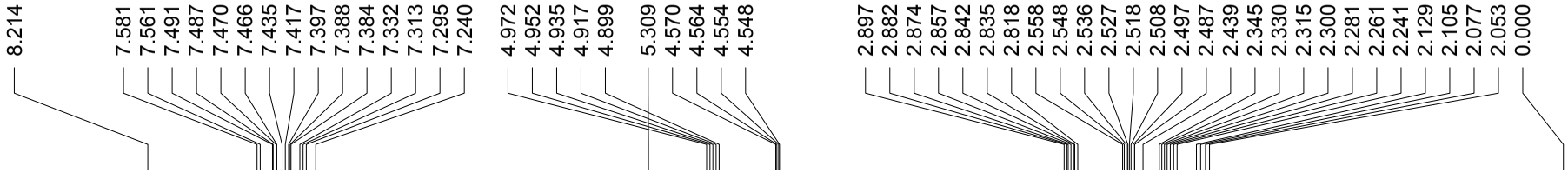

zyz-2-168C.fid
Aug 18 2017
SOLVENT: cdcl3
NA = 40
F1 = 100.520592 MHz
F2 = 399.722015 MHz
4cab
O
N
209.501
168.254
151.368
144.938
137.470
132.554
130.459
126.590
115.203
108.911
85.242
77.320
77.000
76.684
73.755
58.581
36.270
36.021
32.530
24.549
21.483
17.926
200
150
100
50
0
PPM

grd-17-94-H.fid
Nov 28 2015
SOLVENT: CDCl3
NA = 4
F1 = 399.722809 MHz
F2 = 100.519203 MHz

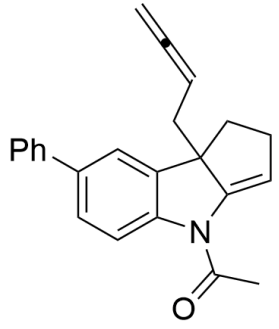
4dab



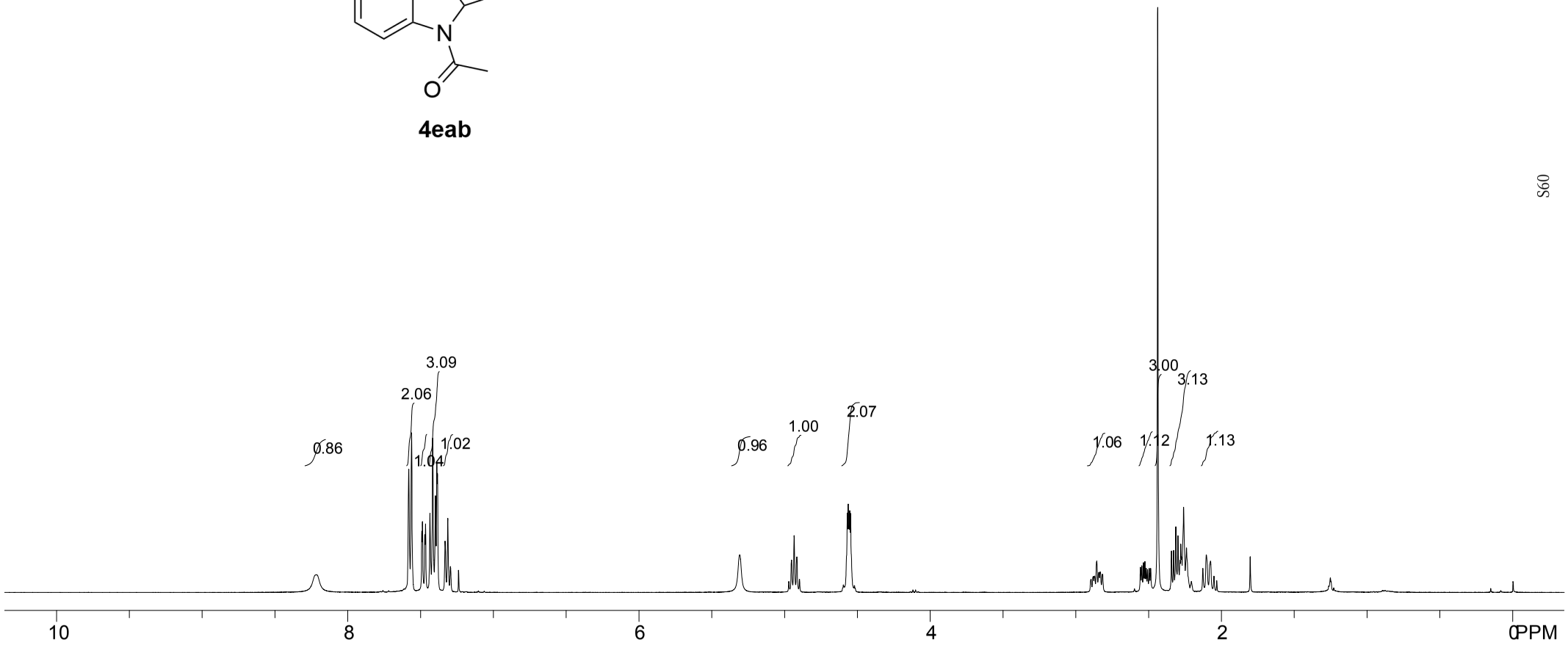

grd-17-94-C.fid
Nov 28 2015
SOLVENT: cdcl3
NA = 120
F1 = 100.520081 MHz
F2 = 399.722015 MHz
MeO
O
N
4dab
209.950
168.007
156.439
151.481
138.474
137.422
117.773
111.716
109.716
109.044
85.164
77.320
77.000
76.680
74.106
59.130
55.536
37.117
34.843
32.301
24.370
200
150
100
50
0
PPM

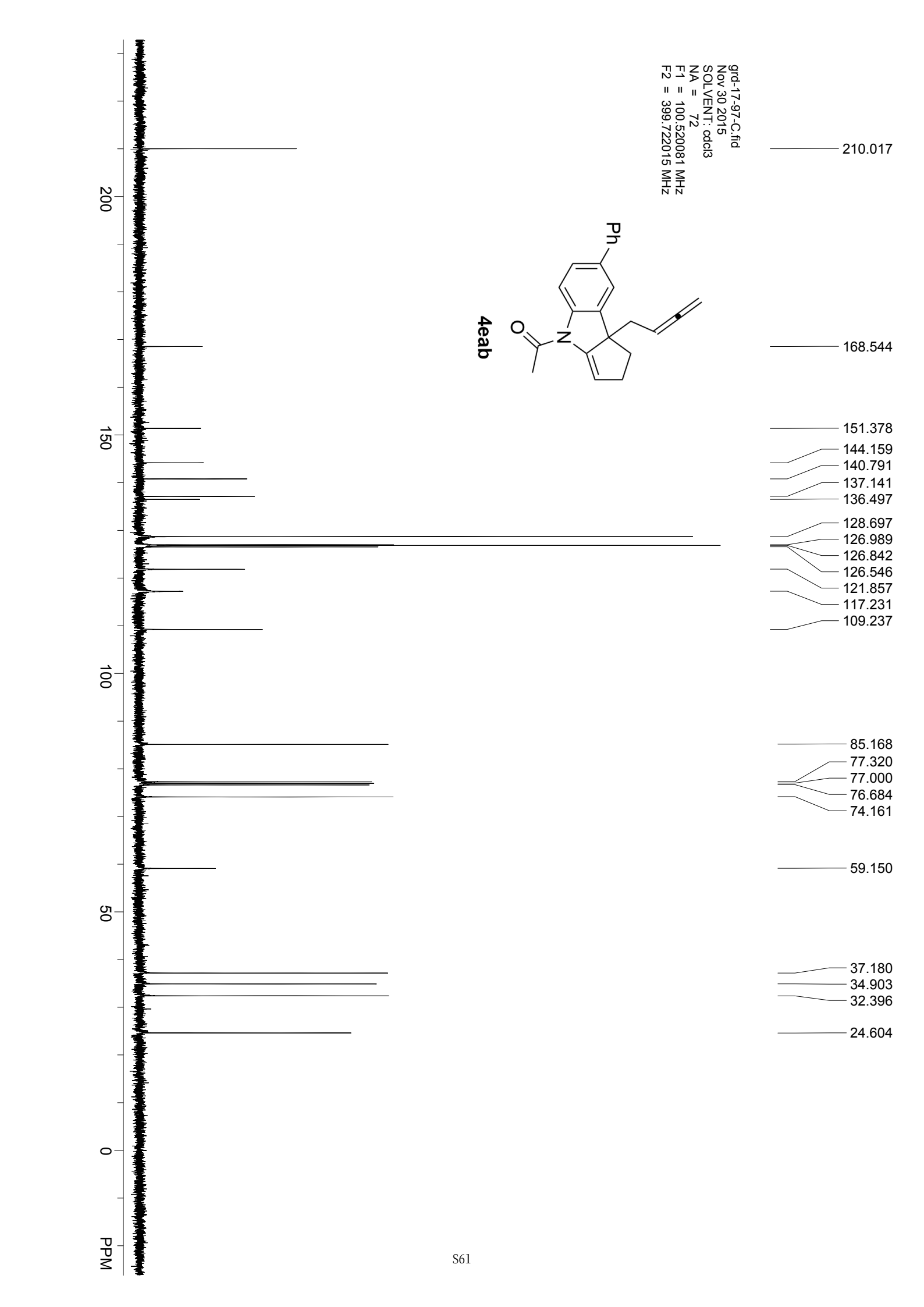


grd-17-97-H.fid
Nov 30 2015
SOLVENT: CDCl3
NA = 4
F1 = 399.722809 MHz
F2 = 100.519203 MHz

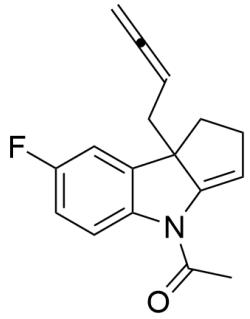


4eab

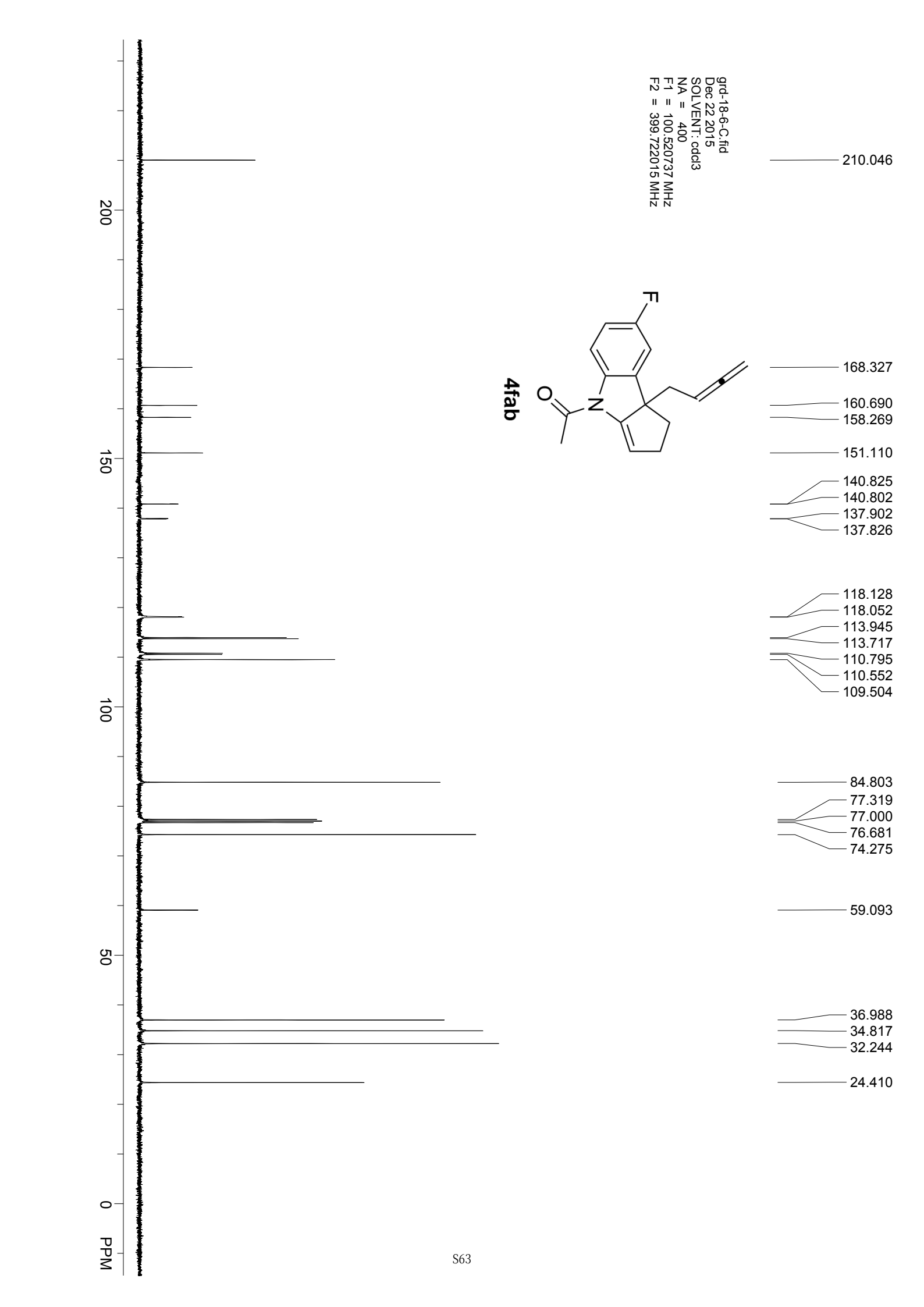



grd-17-97-C.fid
Nov 30 2015
SOLVENT: cdcl3
NA = 72
F1 = 100.520081 MHz
F2 = 399.722015 MHz
4eab
Ph
N
O
210.017
168.544
151.378
144.159
140.791
137.141
136.497
128.697
126.989
126.842
126.546
121.857
117.231
109.237
85.168
77.320
77.000
76.684
74.161
59.150
37.180
34.903
32.396
24.604
200
150
100
50
0
PPM

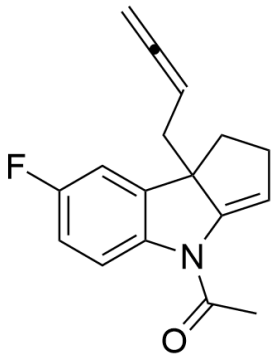
grd-18-6-H.fid
Dec 22 2015
SOLVENT: CDCl3
NA = 4
F1 = 399.723419 MHz
F2 = 100.519203 MHz



4fab

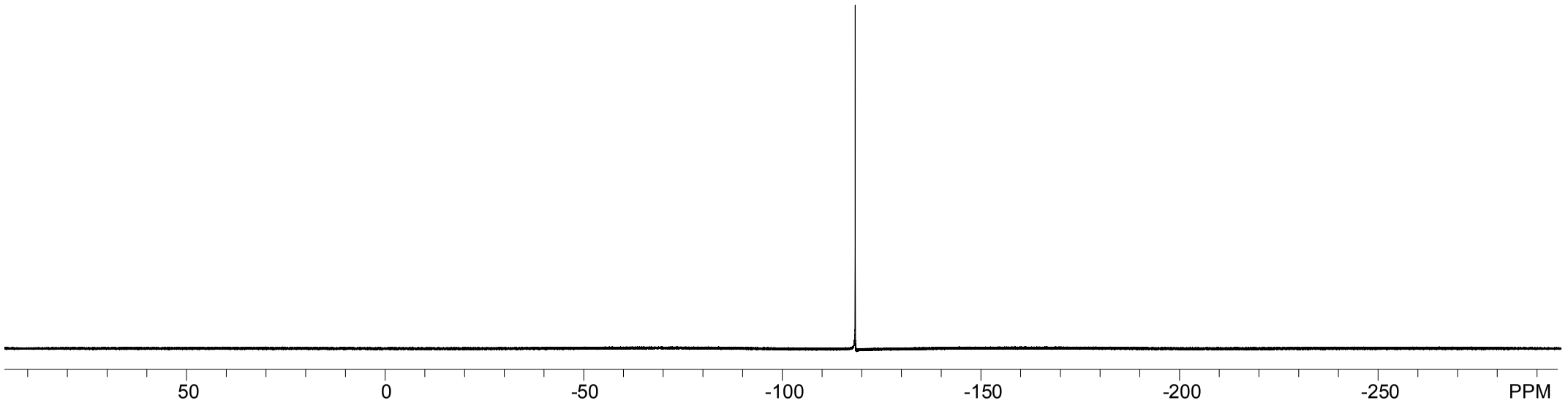

grd-18-6-C.fid
Dec 22 2015
SOLVENT: cdcl3
NA = 400
F1 = 100.520737 MHz
F2 = 399.722015 MHz
4fab
F
O
N
210.046
168.327
160.690
158.269
151.110
140.825
140.802
137.902
137.826
118.128
118.052
113.945
113.717
110.795
110.552
109.504
84.803
77.319
77.000
76.681
74.275
59.093
36.988
34.817
32.244
24.410
200
150
100
50
0
PPM

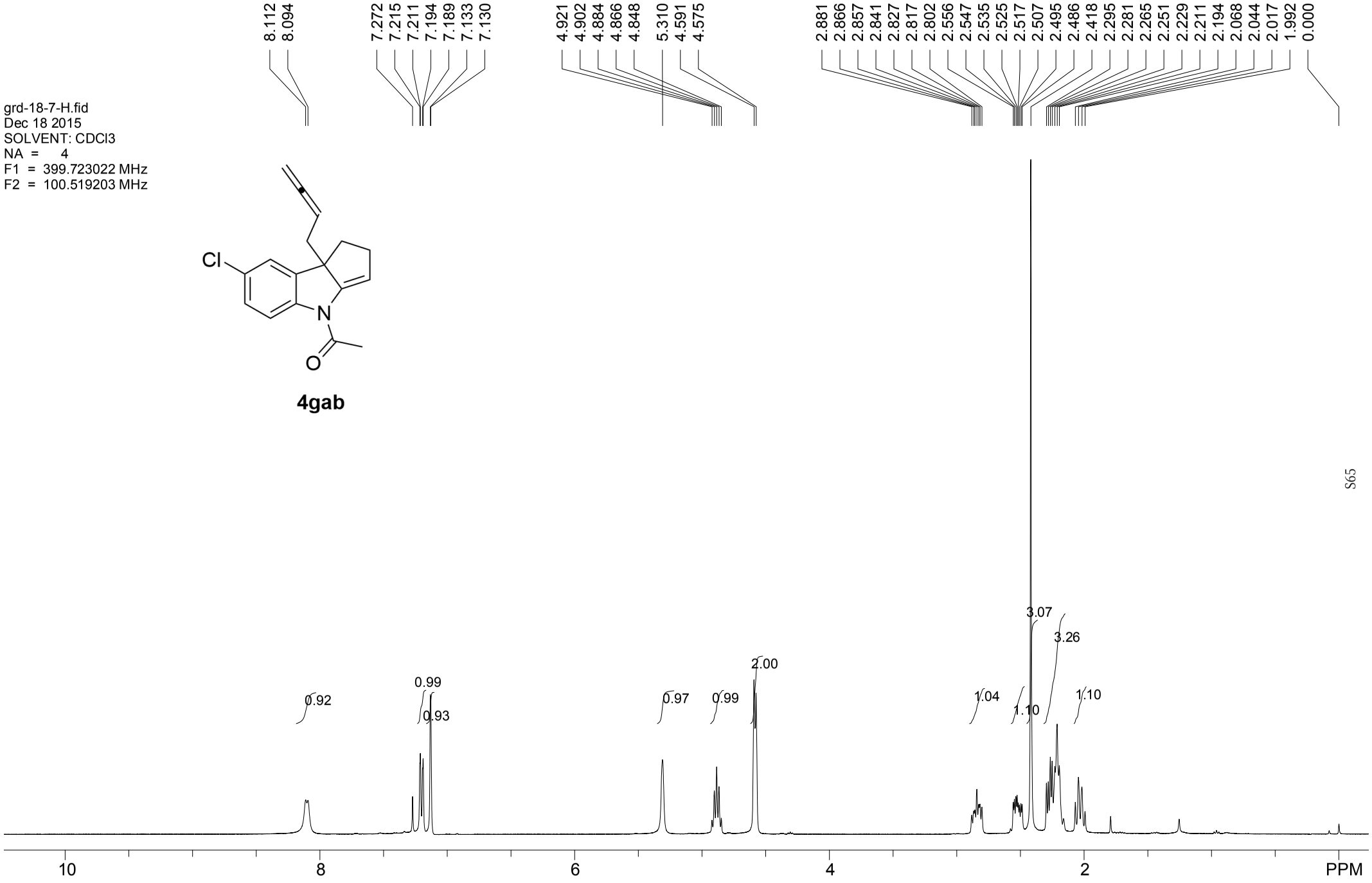
grd-18-6-F.fid
Dec 22 2015
SOLVENT: CDCl3
NA = 4
F1 = 376.075134 MHz
F2 = 100.519203 MHz

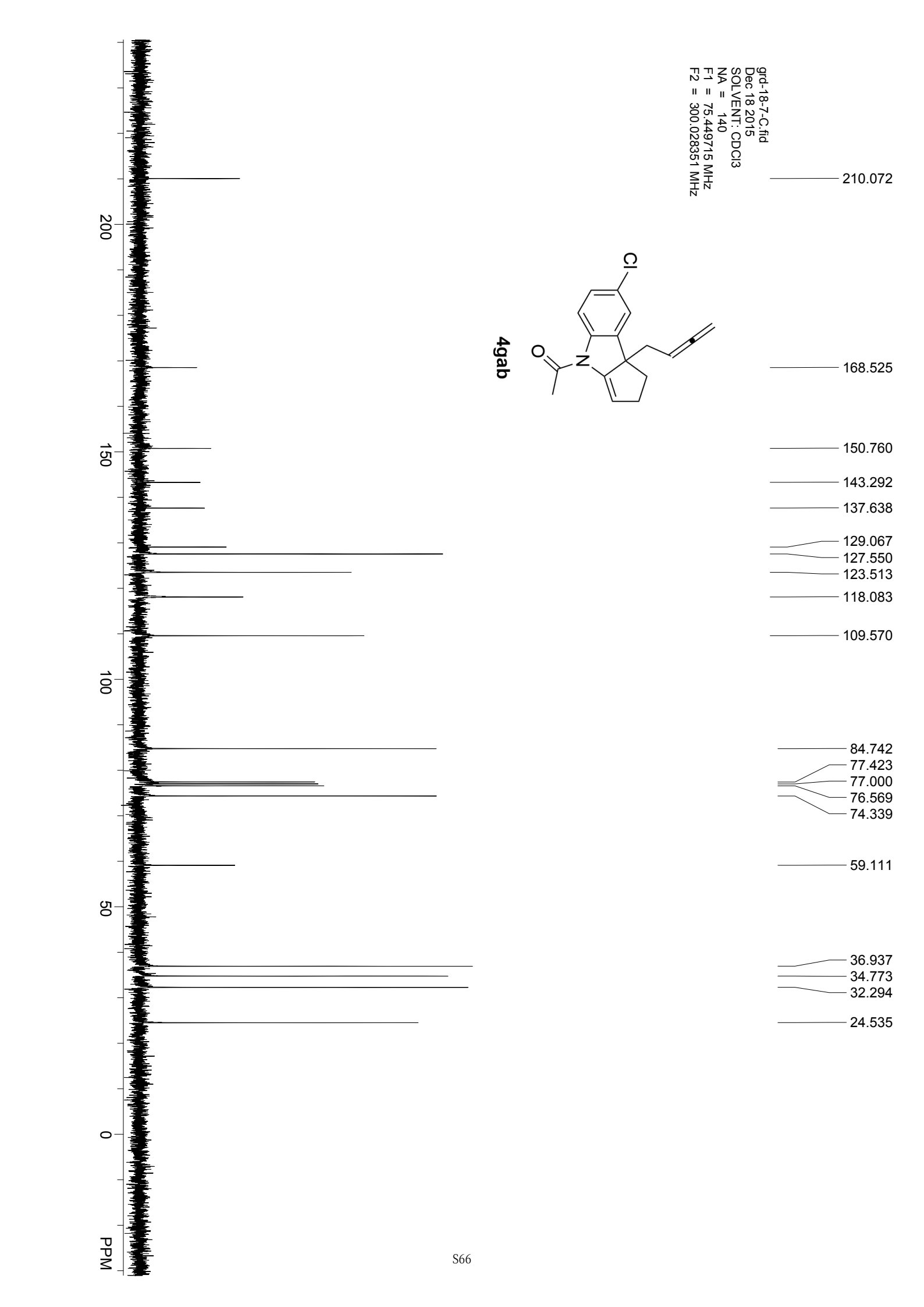


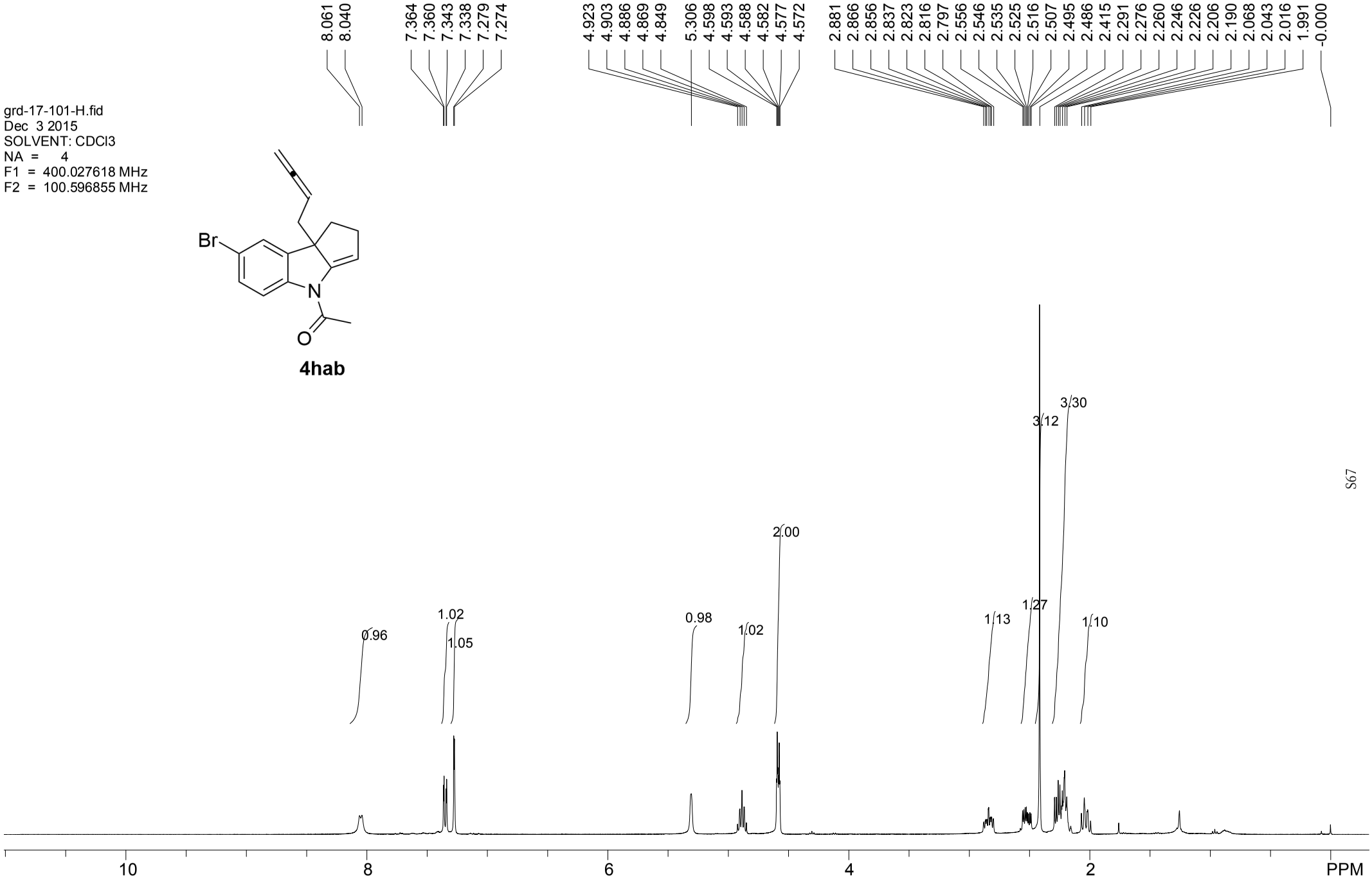
4fab

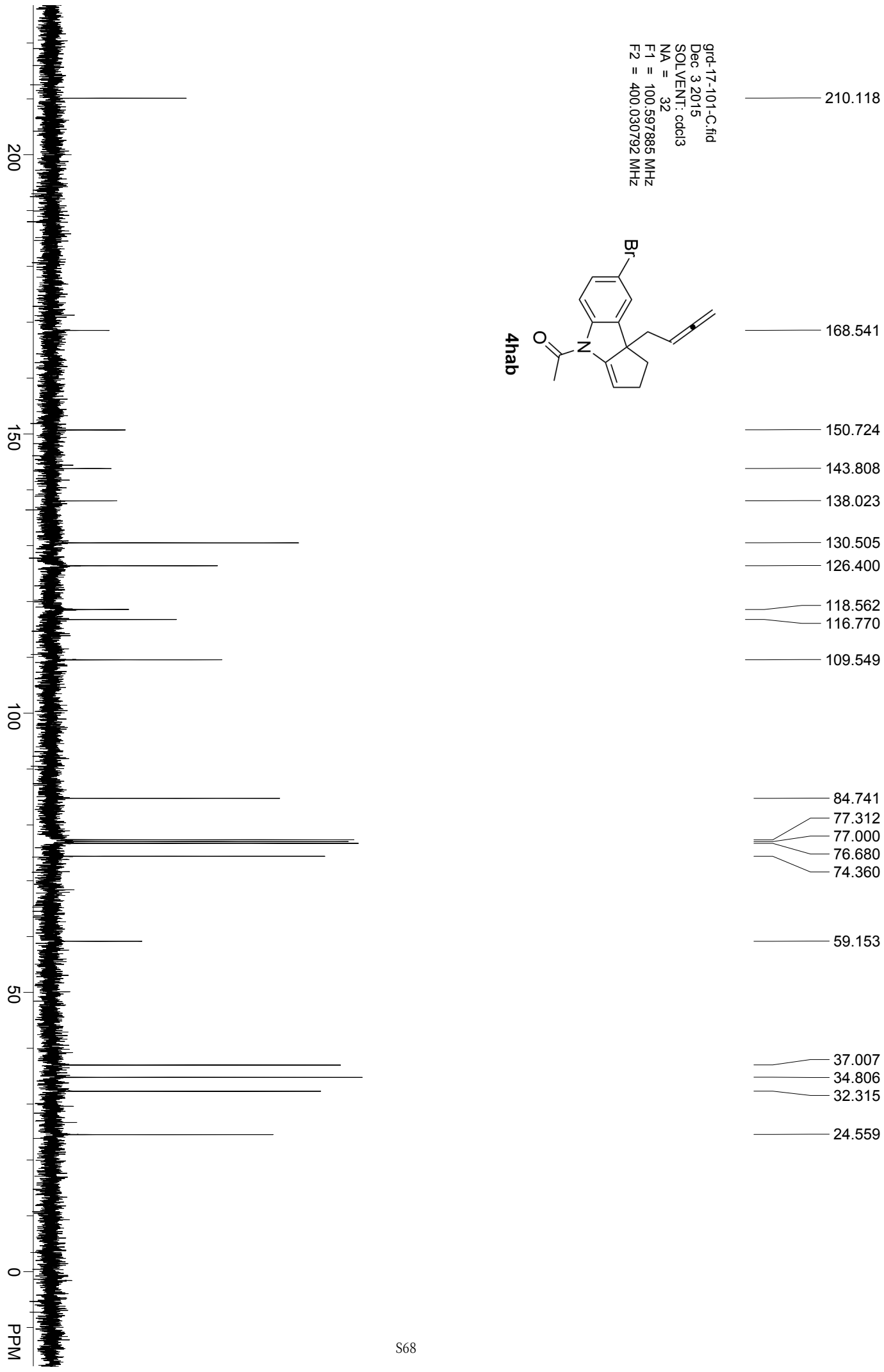
-118.101

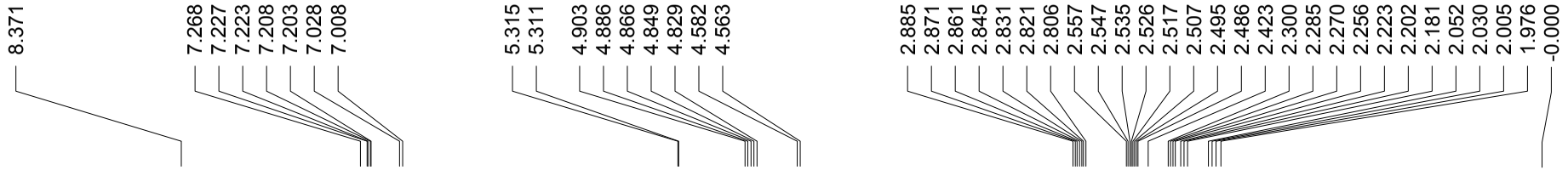



8.112
8.094
7.272
7.215
7.211
7.194
7.189
7.133
7.130
4.921
4.902
4.884
4.866
4.848
5.310
4.591
4.575
2.881
2.866
2.857
2.841
2.827
2.817
2.802
2.556
2.547
2.535
2.525
2.517
2.507
2.495
2.486
2.418
2.295
2.281
2.265
2.251
2.229
2.211
2.194
2.068
2.044
2.017
1.992
0.000
grd-18-7-H.fid
Dec 18 2015
SOLVENT: CDCl3
NA = 4
F1 = 399.723022 MHz
F2 = 100.519203 MHz
Cl
N
O
4gab
0.92
0.99
0.93
0.97
0.99
2.00
1.04
1.10
3.07
3.26
1.10
10
8
6
4
2
PPM

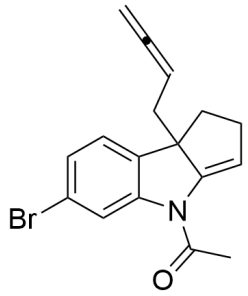

grd-18-7-C.fid
Dec 18 2015
SOLVENT: CDCl3
NA = 140
F1 = 75.449715 MHz
F2 = 300.028351 MHz
4gab
Cl
O
N
210.072
168.525
150.760
143.292
137.638
129.067
127.550
123.513
118.083
109.570
84.742
77.423
77.000
76.569
74.339
59.111
36.937
34.773
32.294
24.535
200
150
100
50
0
PPM


8.061
8.040
7.364
7.360
7.343
7.338
7.279
7.274
4.923
4.903
4.886
4.869
4.849
5.306
4.598
4.593
4.588
4.582
4.577
4.572
2.881
2.866
2.856
2.837
2.823
2.816
2.797
2.556
2.546
2.535
2.525
2.516
2.507
2.495
2.486
2.415
2.291
2.276
2.260
2.246
2.226
2.206
2.190
2.068
2.043
2.016
1.991
-0.000
grd-17-101-H.fid
Dec 3 2015
SOLVENT: CDCl3
NA = 4
F1 = 400.027618 MHz
F2 = 100.596855 MHz
Br
N
O
4hab
0.96
1.02
1.05
0.98
1.02
2.00
1.13
1.27
3.12
3.30
1.10
10
8
6
4
2
PPM

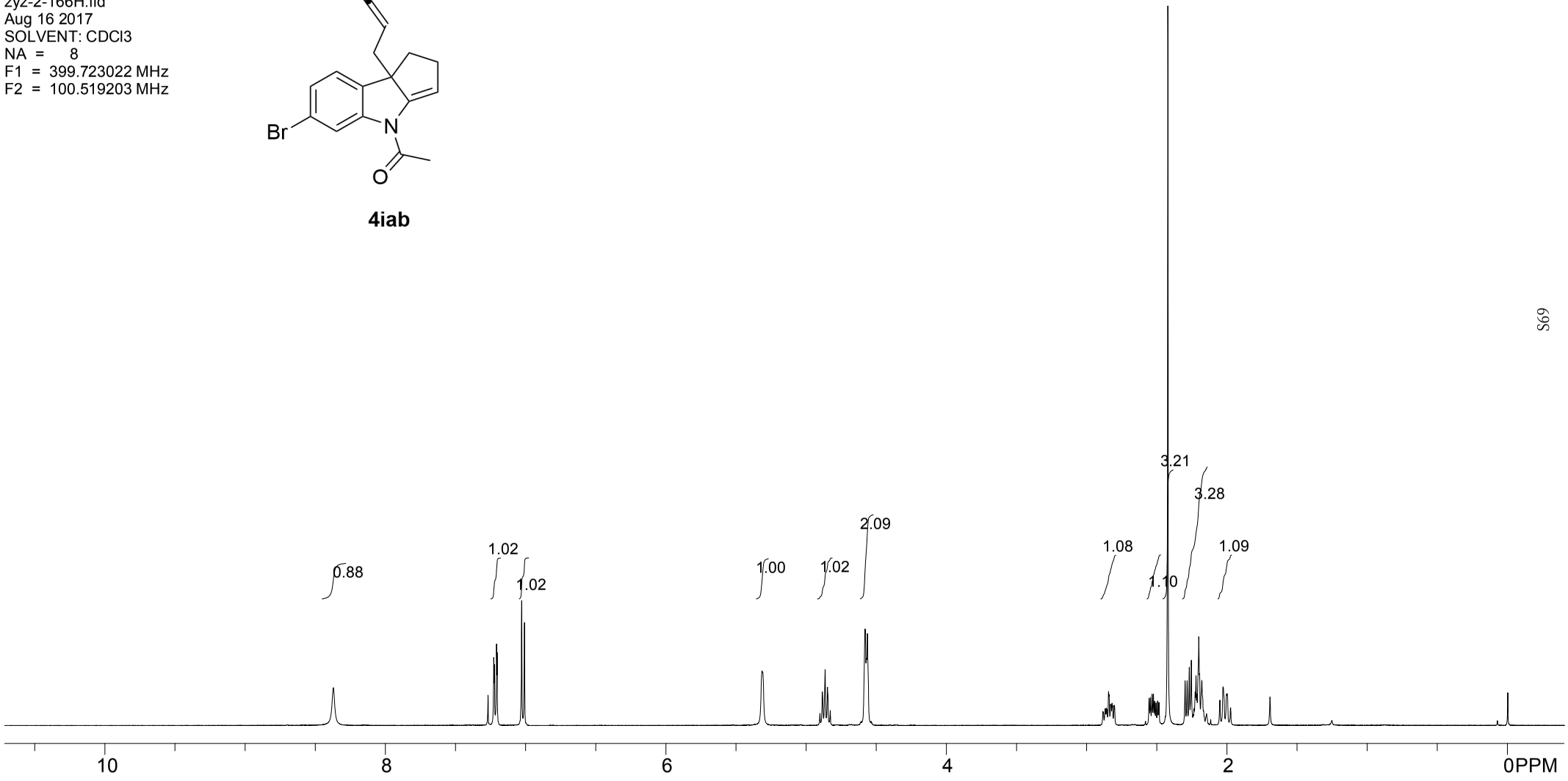

grd-17-101-C.fid
Dec 3 2015
SOLVENT: cdcl3
NA = 32
F1 = 100.597885 MHz
F2 = 400.030792 MHz
Br
O
N
4hab
210.118
168.541
150.724
143.808
138.023
130.505
126.400
118.562
116.770
109.549
84.741
77.312
77.000
76.680
74.360
59.153
37.007
34.806
32.315
24.559
200
150
100
50
0
PPM

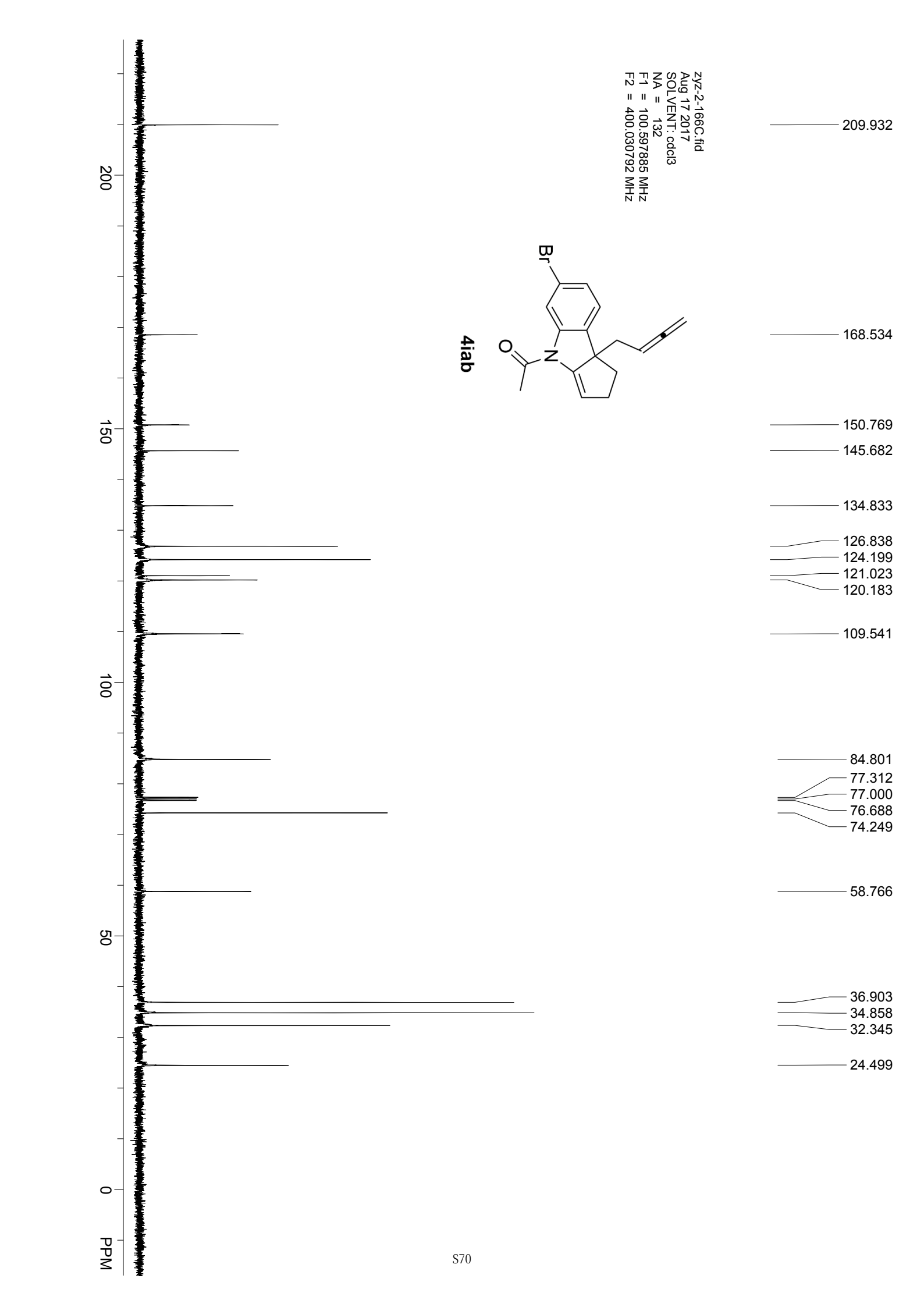


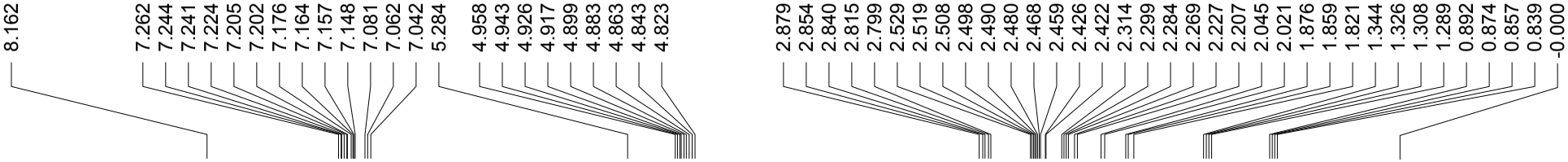
zyz-2-166H.fid
Aug 16 2017
SOLVENT: CDCl3
NA = 8
F1 = 399.723022 MHz
F2 = 100.519203 MHz



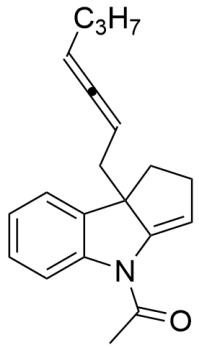
4iab



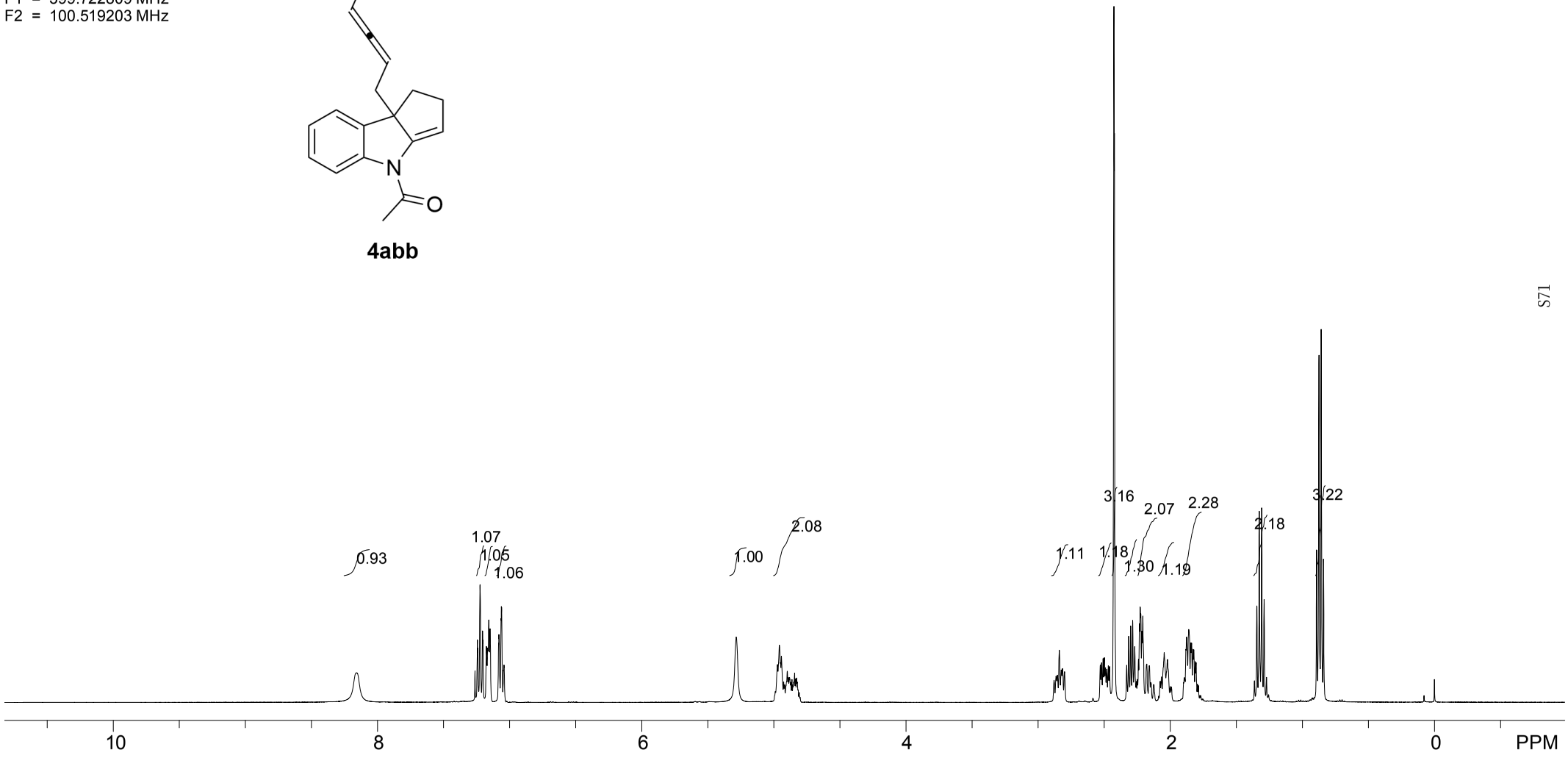

zyz-2-166C.fid
Aug 17 2017
SOLVENT: cdcl3
NA = 132
F1 = 100.597885 MHz
F2 = 400.030792 MHz
4iab
Br
O
N
209.932
168.534
150.769
145.682
134.833
126.838
124.199
121.023
120.183
109.541
84.801
77.312
77.000
76.688
74.249
58.766
36.903
34.858
32.345
24.499
200
150
100
50
0
PPM

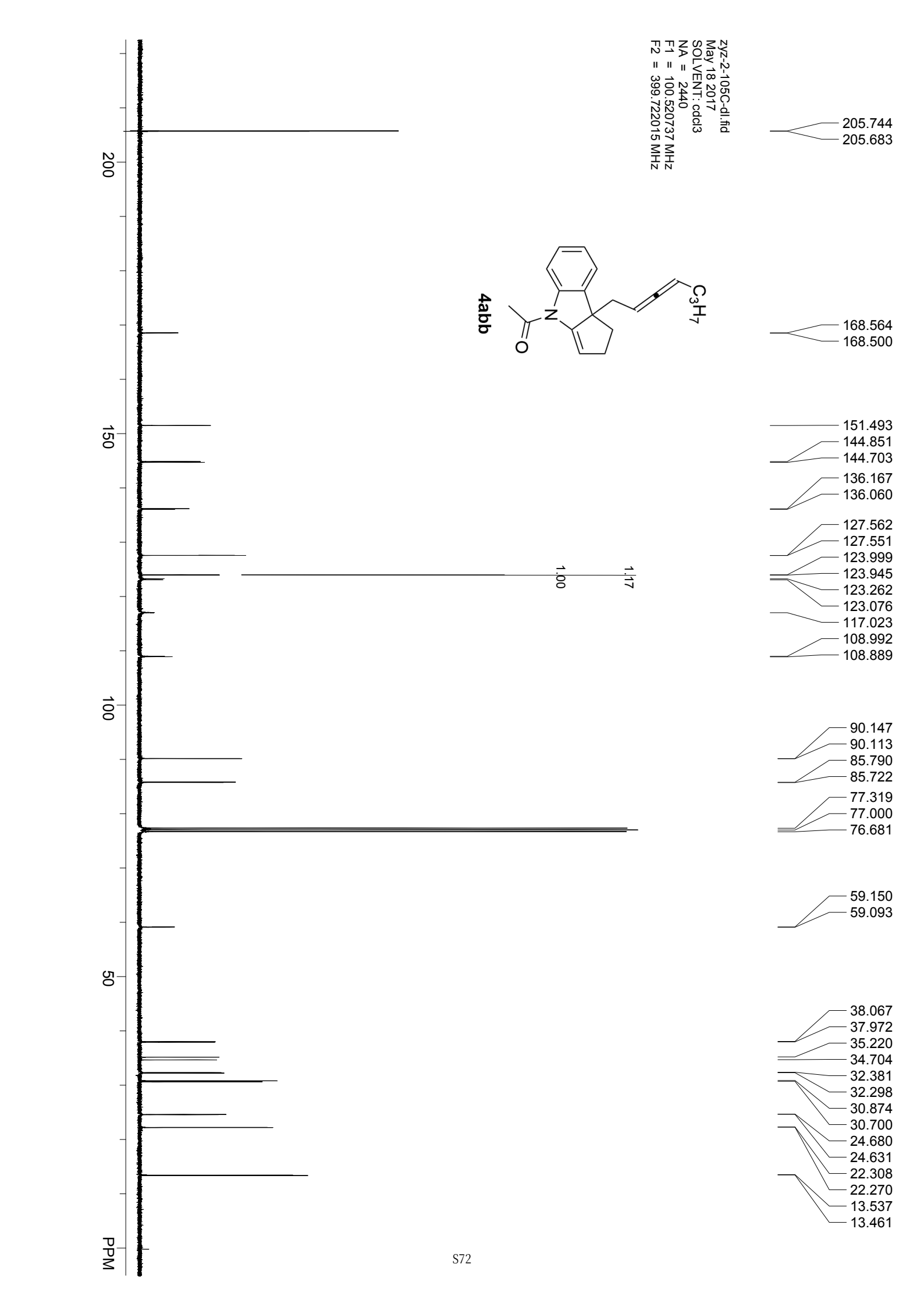


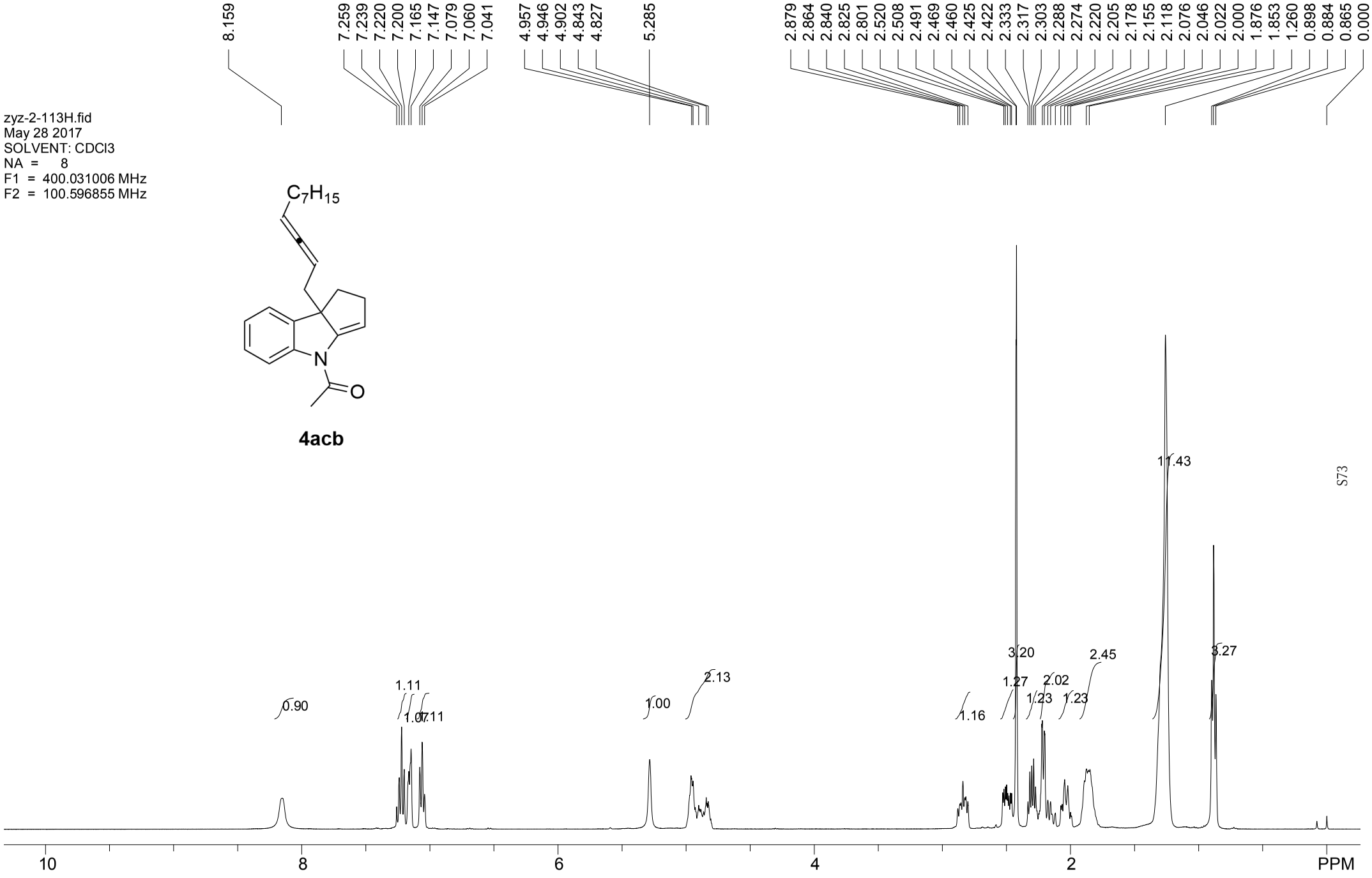
zyz-2-105H.fid
May 16 2017
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz
F2 = 100.519203 MHz

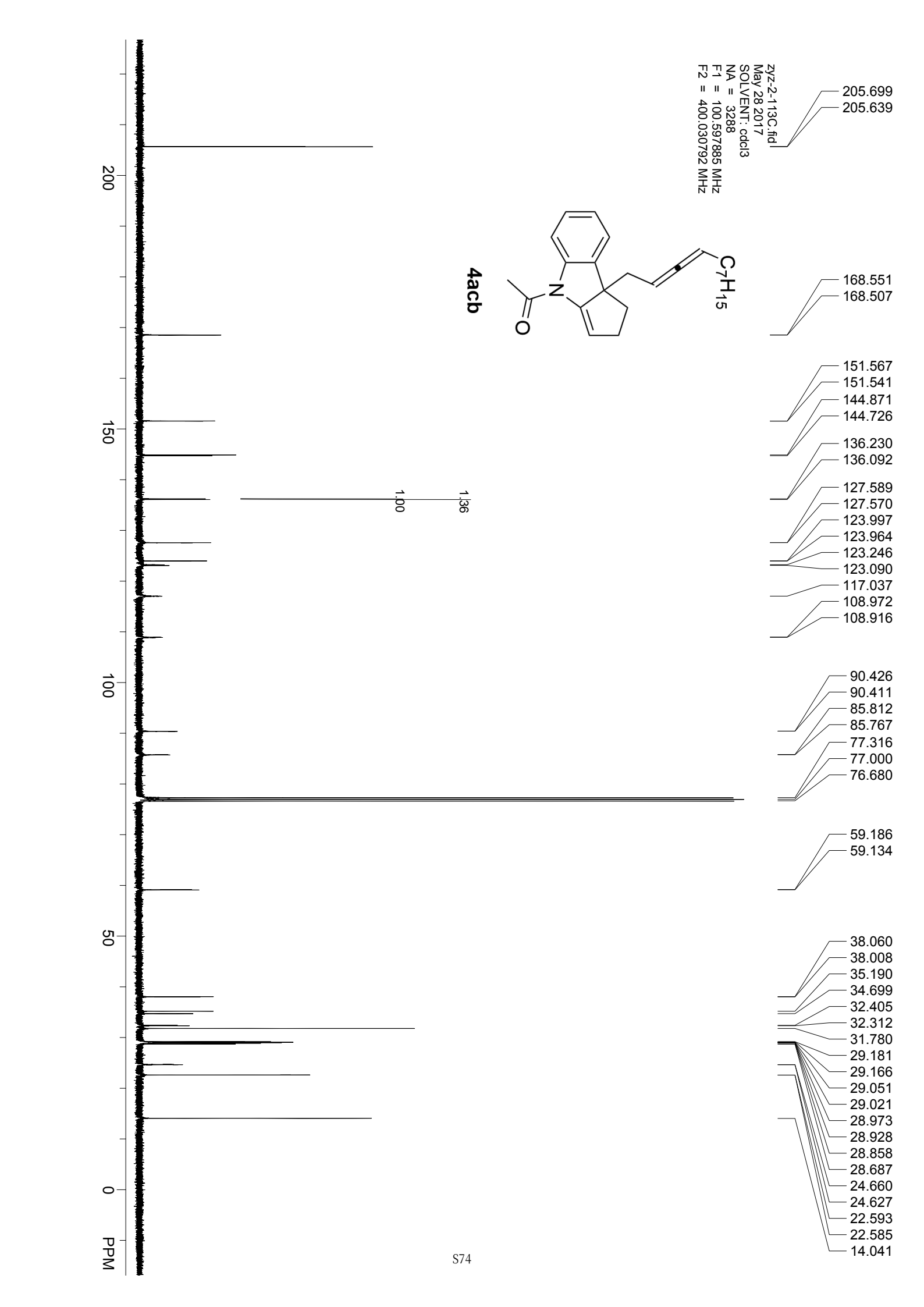


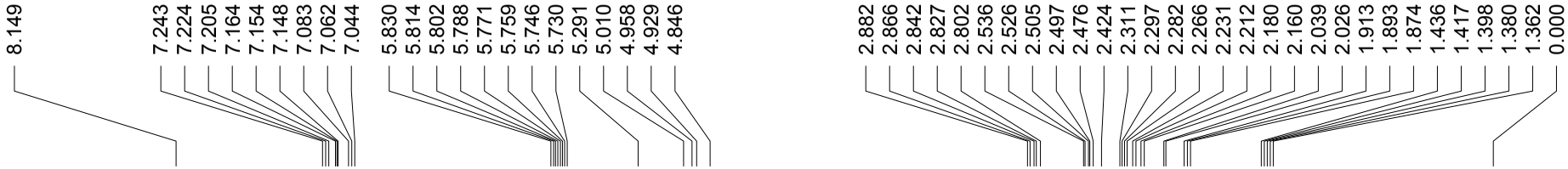
4abb



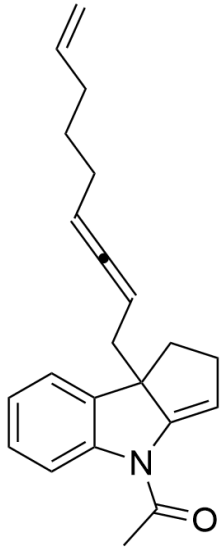

zyz-2-105C-dl.fid
May 18 2017
SOLVENT: cdcl3
NA = 2440
F1 = 100.520737 MHz
F2 = 399.722015 MHz
4abb
C3H7
N
O
205.744
205.683
168.564
168.500
151.493
144.851
144.703
136.167
136.060
127.562
127.551
123.999
123.945
123.262
123.076
117.023
108.992
108.889
90.147
90.113
85.790
85.722
77.319
77.000
76.681
59.150
59.093
38.067
37.972
35.220
34.704
32.381
32.298
30.874
30.700
24.680
24.631
22.308
22.270
13.537
13.461
1.00
1.17
200
150
100
50
PPM


8.159
7.259
7.239
7.220
7.200
7.165
7.147
7.079
7.060
7.041
4.957
4.946
4.902
4.843
4.827
5.285
2.879
2.864
2.840
2.825
2.801
2.520
2.508
2.491
2.469
2.460
2.425
2.422
2.333
2.317
2.303
2.288
2.274
2.220
2.205
2.178
2.155
2.118
2.076
2.046
2.022
2.000
1.876
1.853
1.260
0.898
0.884
0.865
0.000
zyz-2-113H.fid
May 28 2017
SOLVENT: CDCl3
NA = 8
F1 = 400.031006 MHz
F2 = 100.596855 MHz
C7H15
N
O
4acb
0.90
1.11
1.07
1.11
1.00
2.13
1.16
3.20
1.27
2.02
1.23
1.23
2.45
11.43
3.27
S73
10
8
6
4
2
PPM

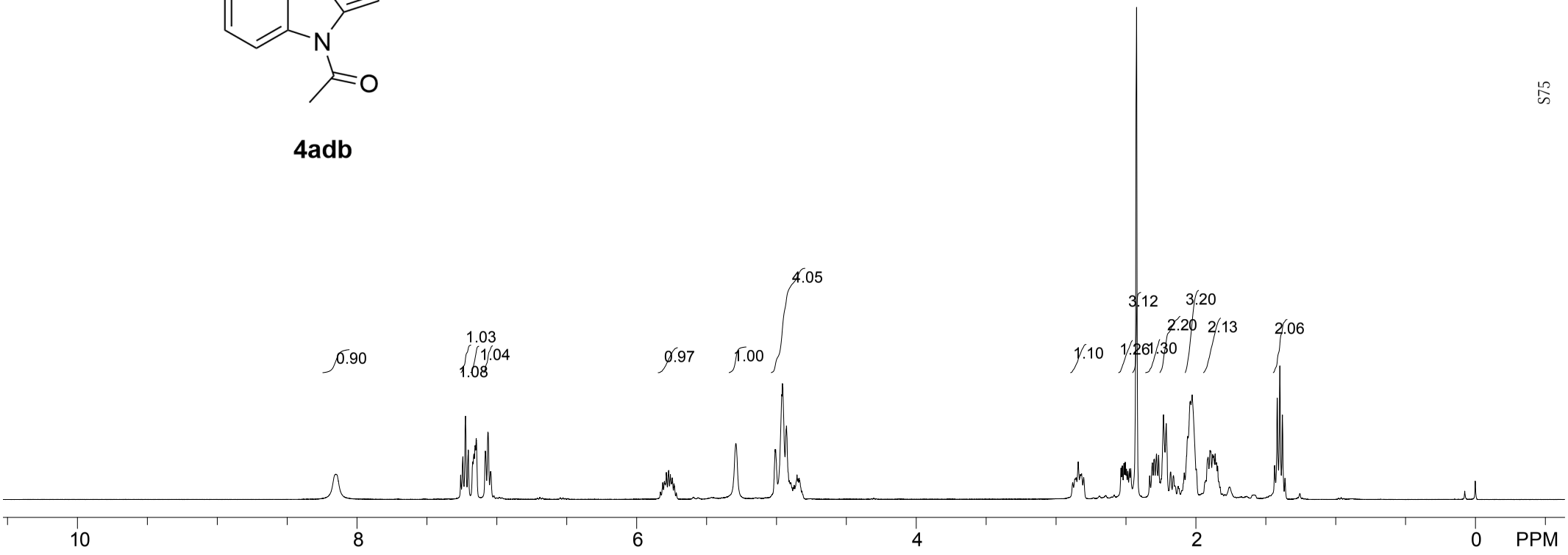

zyz-2-113C.fid
May 28 2017
SOLVENT: cdcl3
NA = 3288
F1 = 100.597885 MHz
F2 = 400.030792 MHz
4acb
C7H15
N
O
205.699
205.639
168.551
168.507
151.567
151.541
144.871
144.726
136.230
136.092
127.589
127.570
123.997
123.964
123.246
123.090
117.037
108.972
108.916
90.426
90.411
85.812
85.767
77.316
77.000
76.680
59.186
59.134
38.060
38.008
35.190
34.699
32.405
32.312
31.780
29.181
29.166
29.051
29.021
28.973
28.928
28.858
28.687
24.660
24.627
22.593
22.585
14.041
1.36
1.00
200
150
100
50
0
PPM

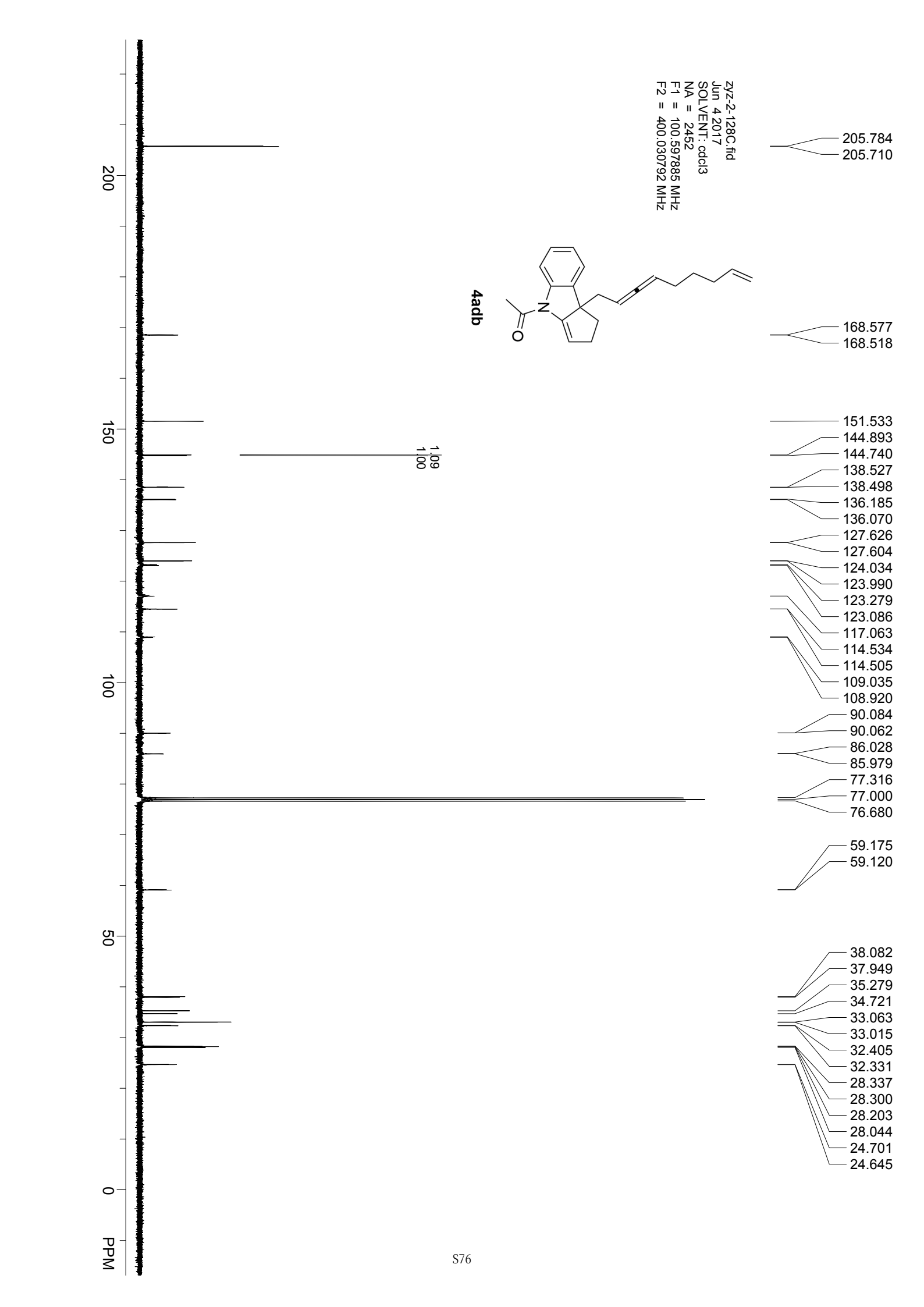


zyz-2-128H.fid
Jun 4 2017
SOLVENT: CDCl3
NA = 8
F1 = 400.031616 MHz
F2 = 100.596855 MHz



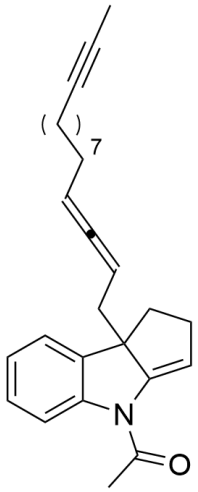
4adb



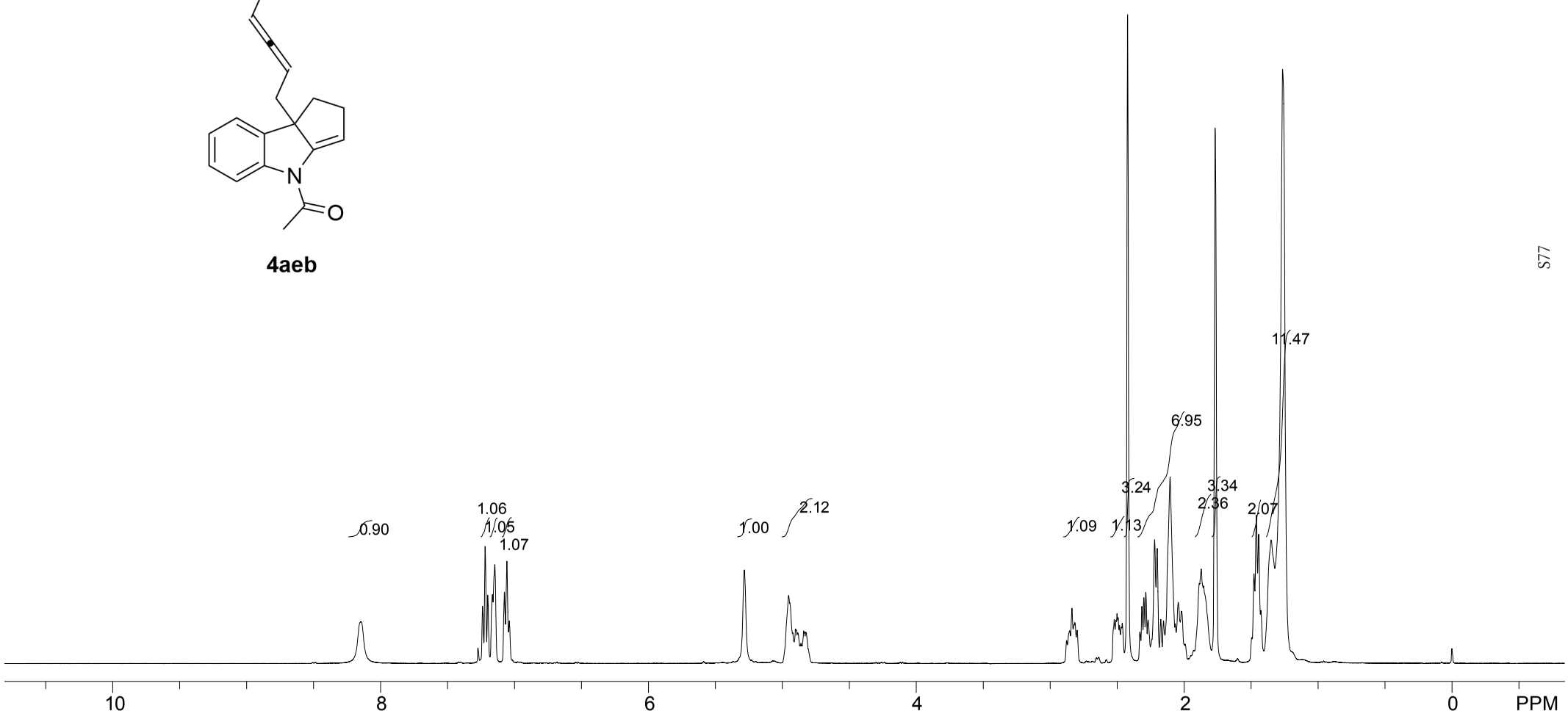

zyz-2-128C.fid
Jun 4 2017
SOLVENT: cdcl3
NA = 2452
F1 = 100.597885 MHz
F2 = 400.030792 MHz
4adb
205.784
205.710
168.577
168.518
151.533
144.893
144.740
138.527
138.498
136.185
136.070
127.626
127.604
124.034
123.990
123.279
123.086
117.063
114.534
114.505
109.035
108.920
90.084
90.062
86.028
85.979
77.316
77.000
76.680
59.175
59.120
38.082
37.949
35.279
34.721
33.063
33.015
32.405
32.331
28.337
28.300
28.203
28.044
24.701
24.645
1.09
1.00
200
150
100
50
0
PPM

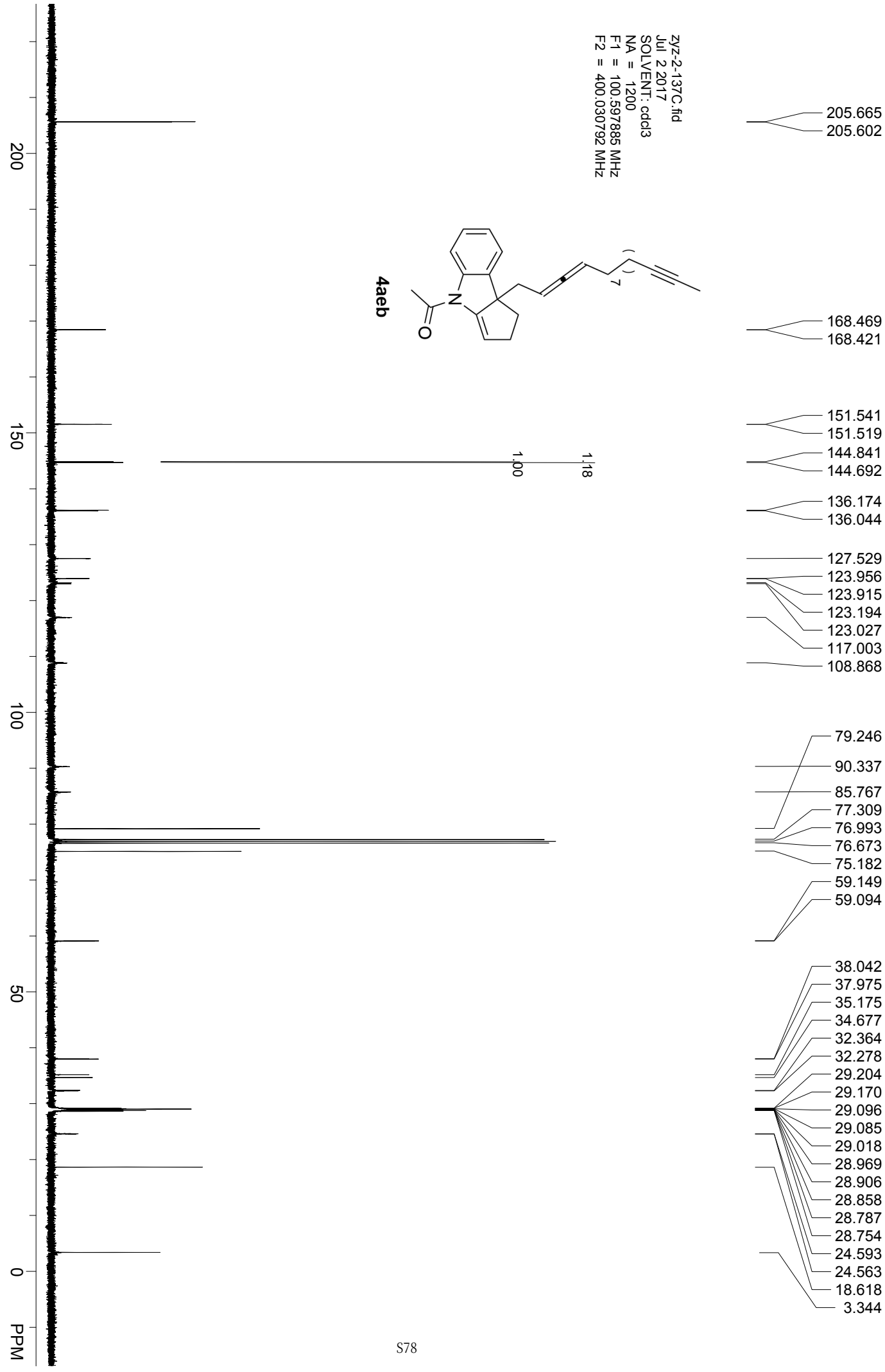
zyz-2-137H.fid
Jun 12 2017
SOLVENT: CDCl3
NA = 4
F1 = 399.722412 MHz
F2 = 100.519203 MHz

8.147
7.239 7.220 7.200 7.163 7.148 7.075 7.057 7.038
4.954 4.902 4.835 5.284
2.877 2.856 2.838 2.820 2.798 2.522 2.501 2.468 2.422 2.330 2.315 2.300 2.286 2.220 2.201 2.105 2.043 2.018 1.871 1.768 1.477 1.460 1.443 1.350 1.264 0.000



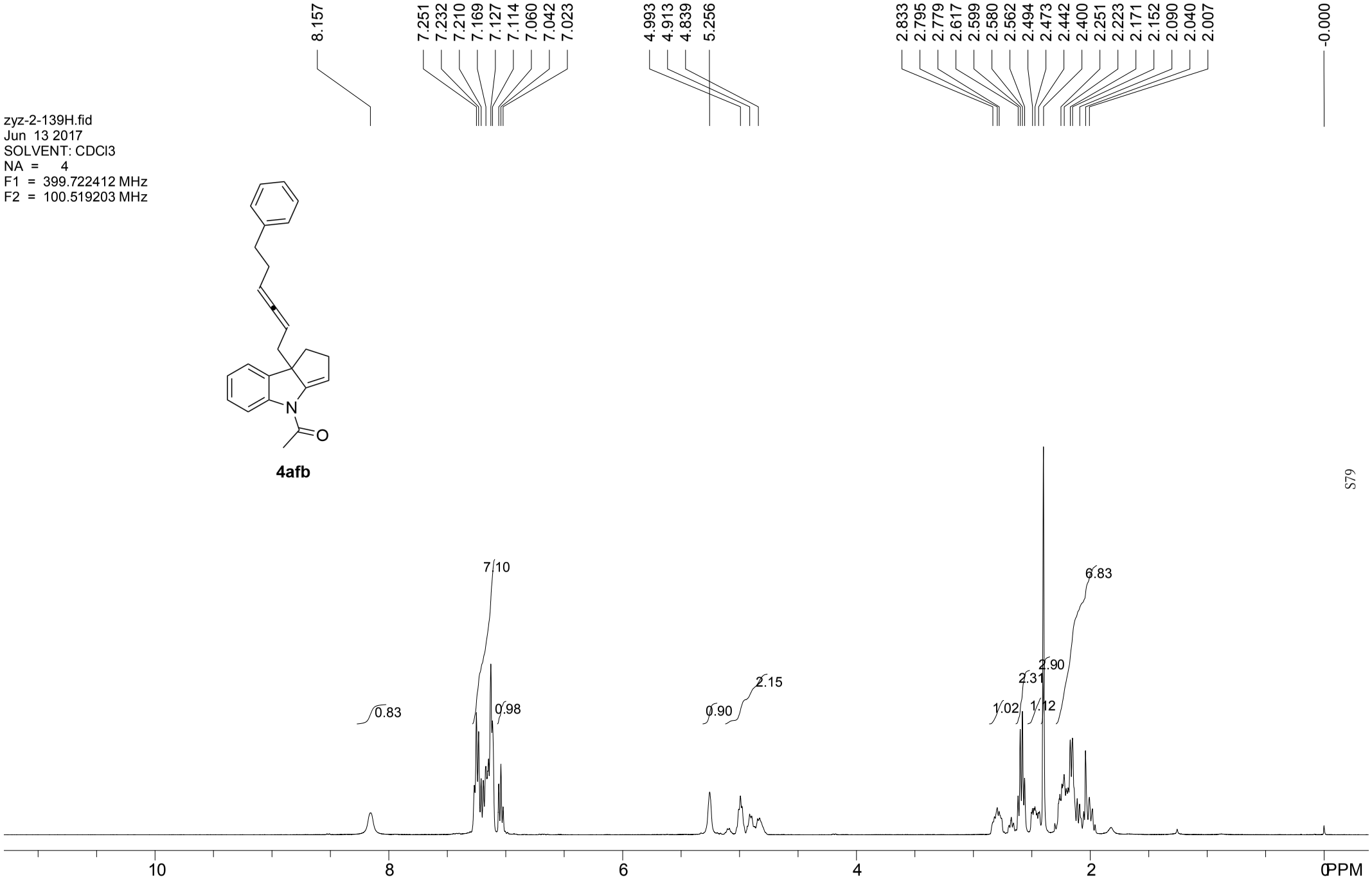
4aeb

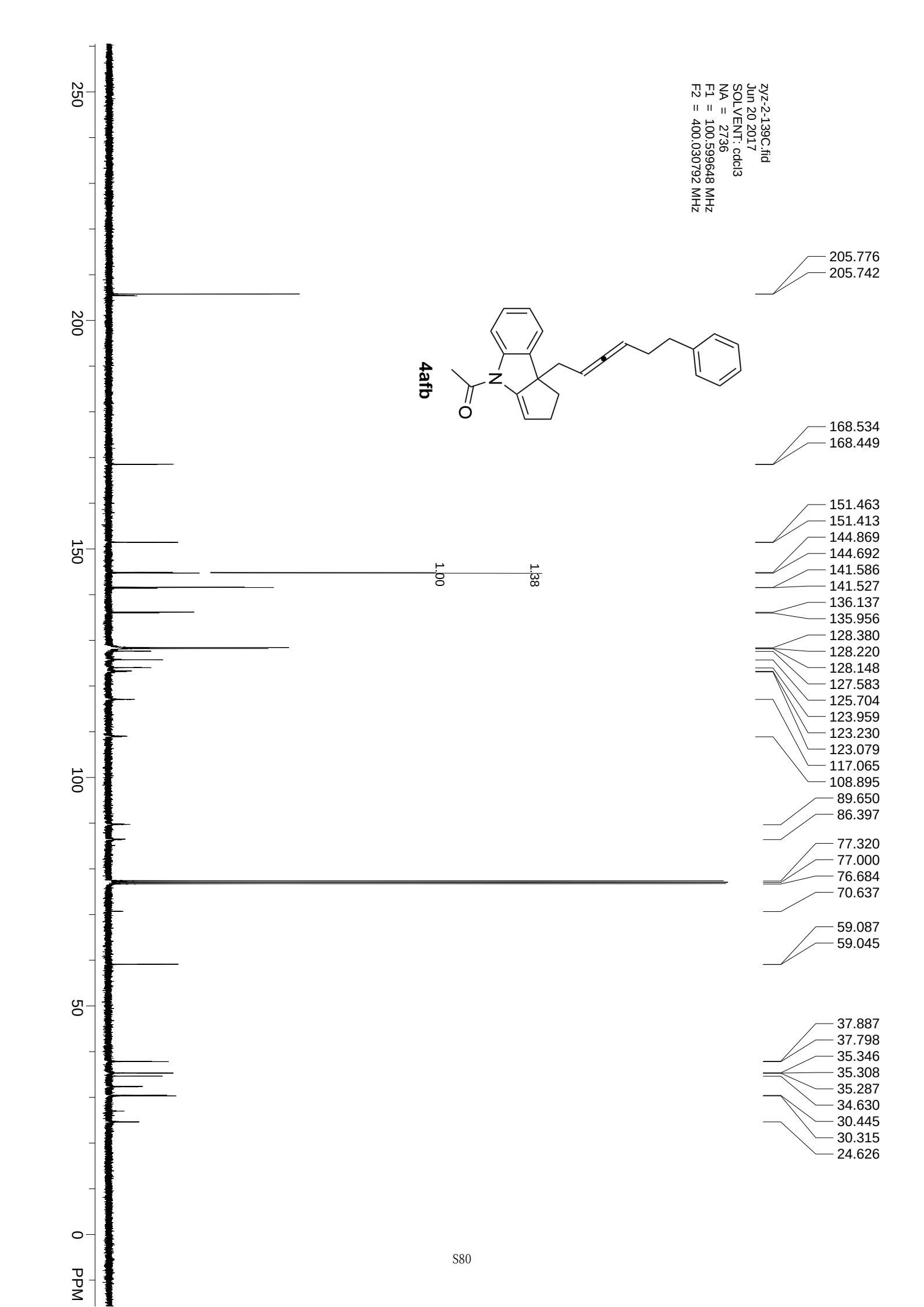


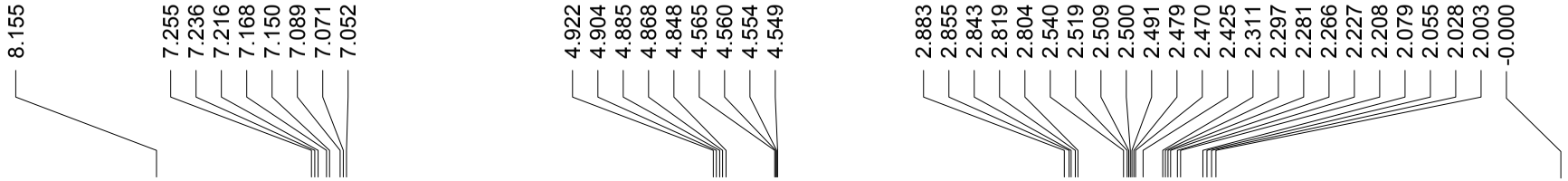

zyz-2-137C.fid
Jul 2 2017
SOLVENT: cdcl3
NA = 1200
F1 = 100.597885 MHz
F2 = 400.030792 MHz
4aeb
205.665
205.602
168.469
168.421
151.541
151.519
144.841
144.692
136.174
136.044
127.529
123.956
123.915
123.194
123.027
117.003
108.868
79.246
90.337
85.767
77.309
76.993
76.673
75.182
59.149
59.094
38.042
37.975
35.175
34.677
32.364
32.278
29.204
29.170
29.096
29.085
29.018
28.969
28.906
28.858
28.787
28.754
24.593
24.563
18.618
3.344
1.00
1.18
200
150
100
50
0
PPM

zyz-2-139H.fid
Jun 13 2017
SOLVENT: CDCl3
NA = 4
F1 = 399.722412 MHz
F2 = 100.519203 MHz

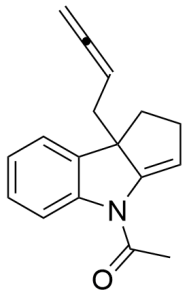
4afb



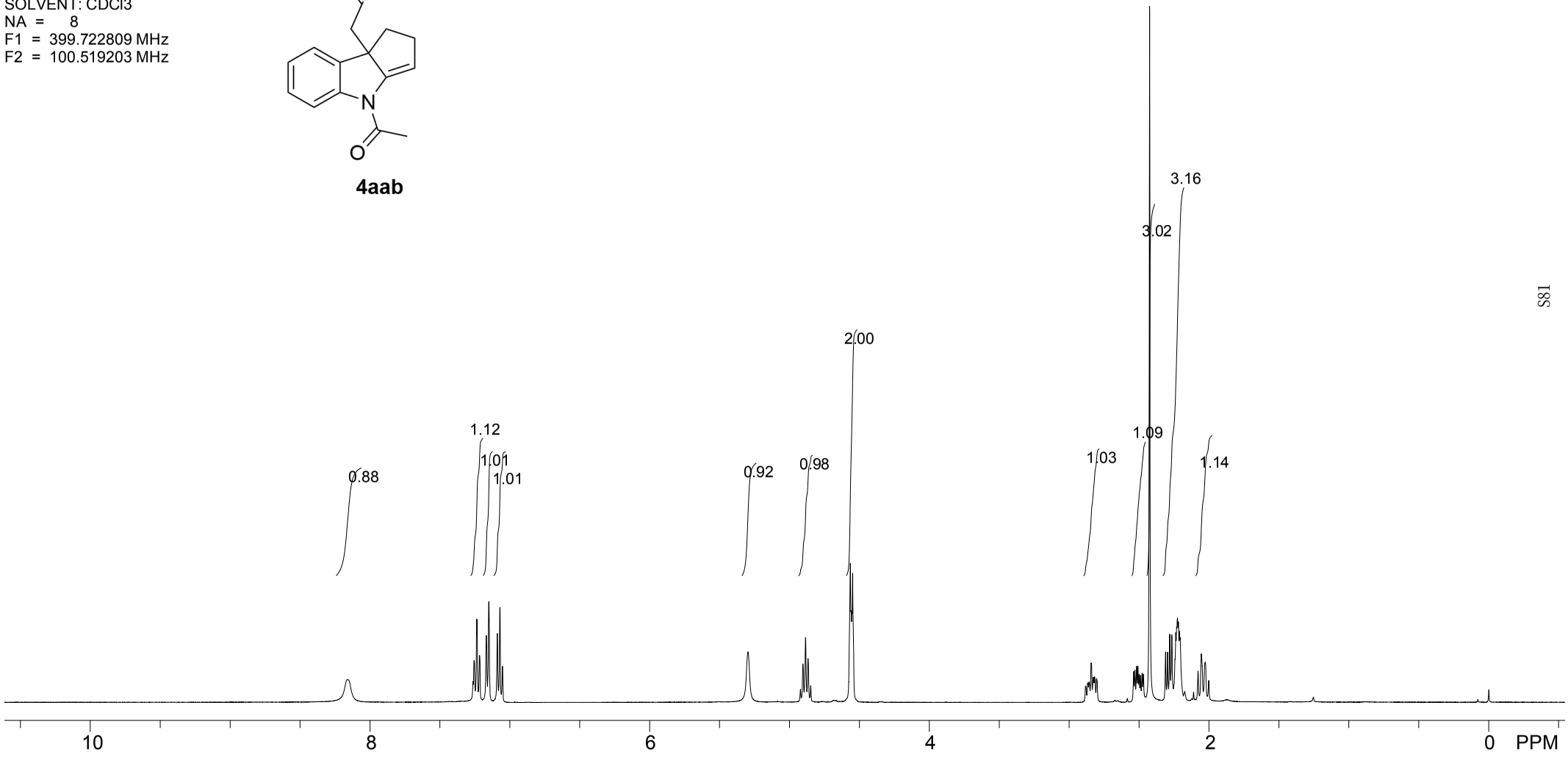

zyz-2-139C.fid
Jun 20 2017
SOLVENT: cdcl3
NA = 2736
F1 = 100.599648 MHz
F2 = 400.030792 MHz
4afib
205.776
205.742
168.534
168.449
151.463
151.413
144.869
144.692
141.586
141.527
136.137
135.956
128.380
128.220
128.148
127.583
125.704
123.959
123.230
123.079
117.065
108.895
89.650
86.397
77.320
77.000
76.684
70.637
59.087
59.045
37.887
37.798
35.346
35.308
35.287
34.630
30.445
30.315
24.626
1.00
1.38
250
200
150
100
50
0
PPM

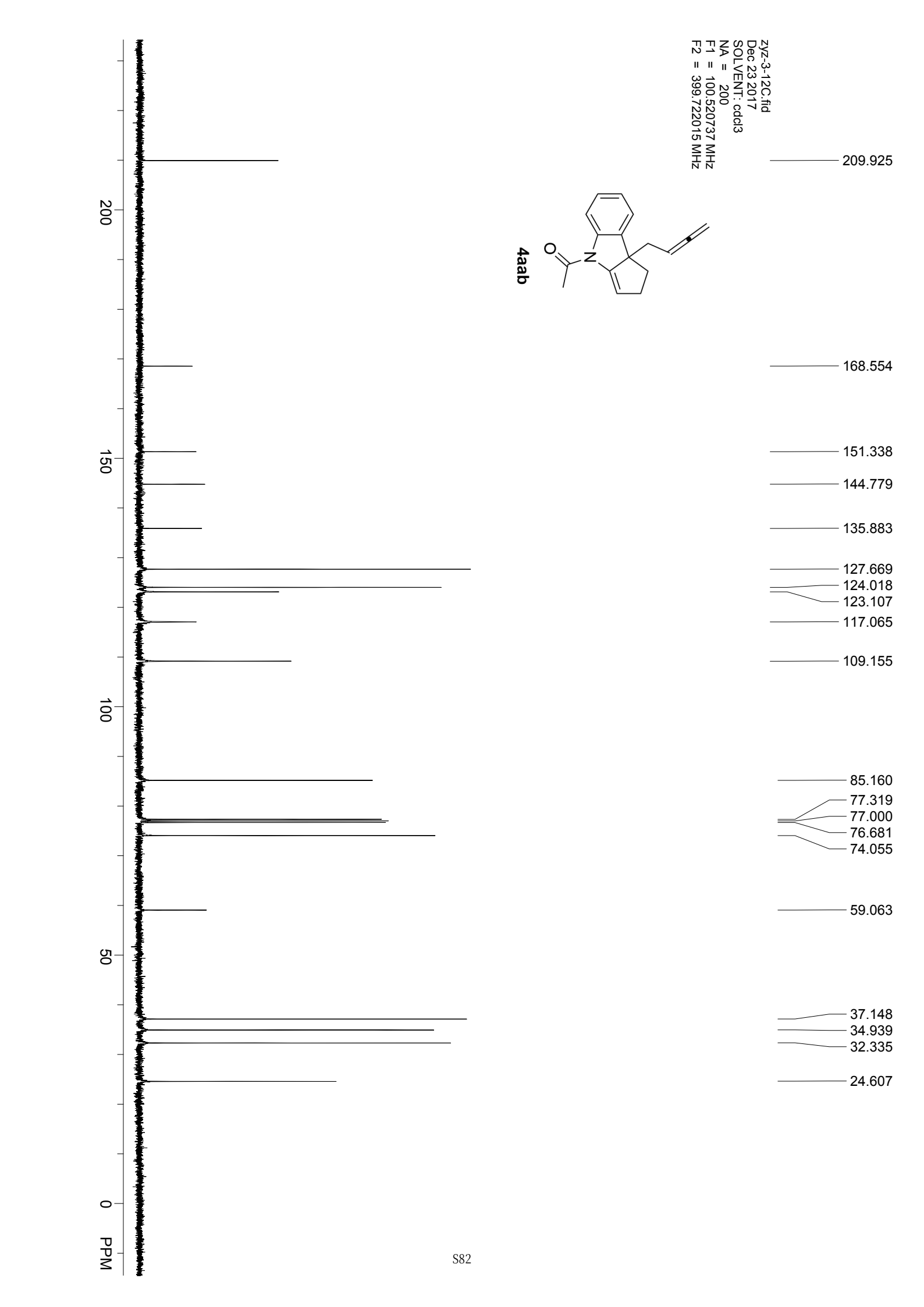


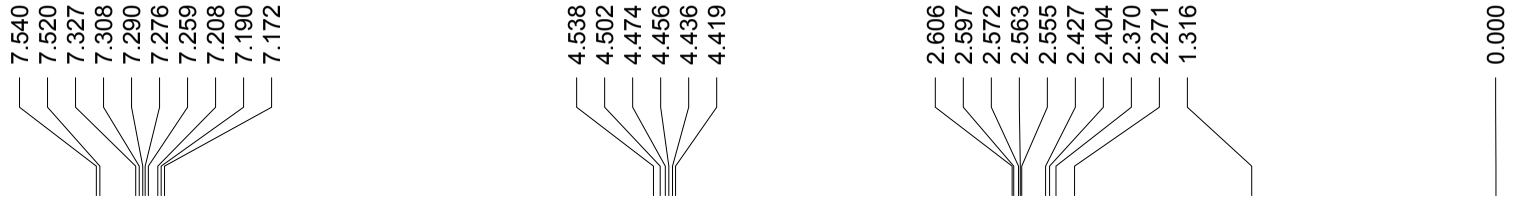
zyz-3-12H.fid
Dec 26 2017
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz
F2 = 100.519203 MHz



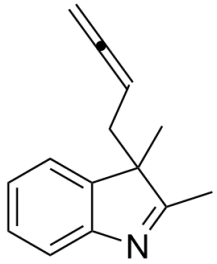
4aab



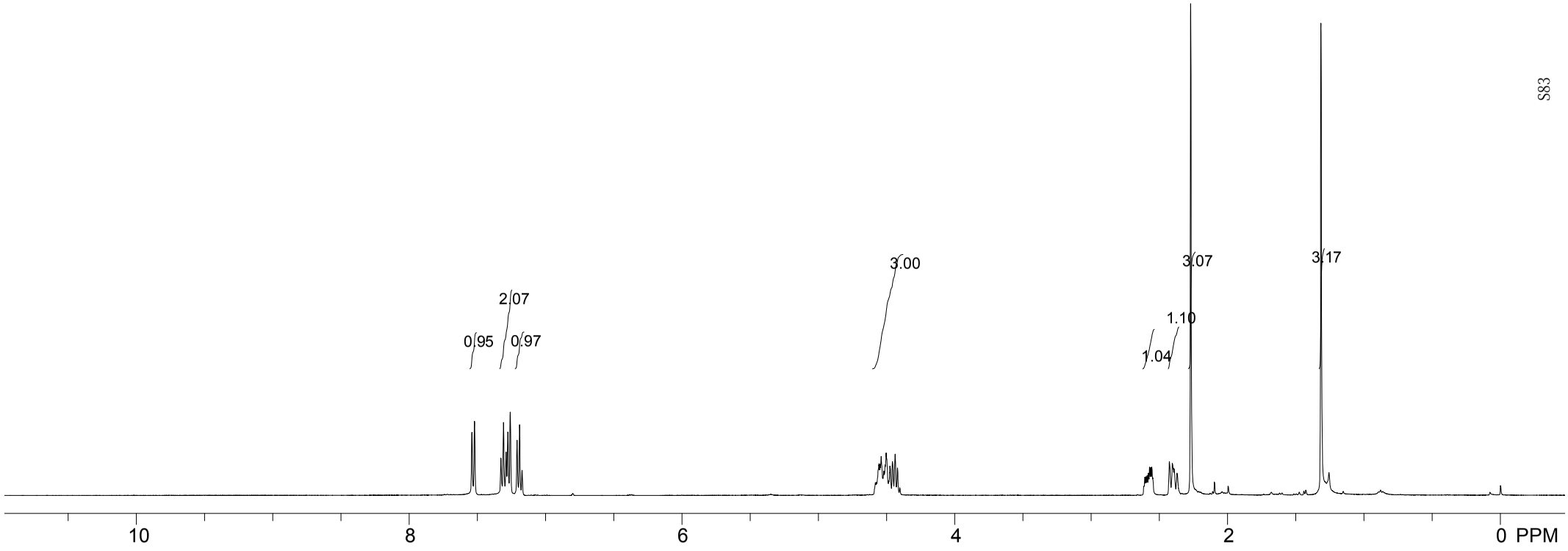

zyz-3-12C.fid
Dec 23 2017
SOLVENT: cdcl3
NA = 200
F1 = 100.520737 MHz
F2 = 399.722015 MHz
4aab
O
N
209.925
168.554
151.338
144.779
135.883
127.669
124.018
123.107
117.065
109.155
85.160
77.319
77.000
76.681
74.055
59.063
37.148
34.939
32.335
24.607
200
150
100
50
0
PPM

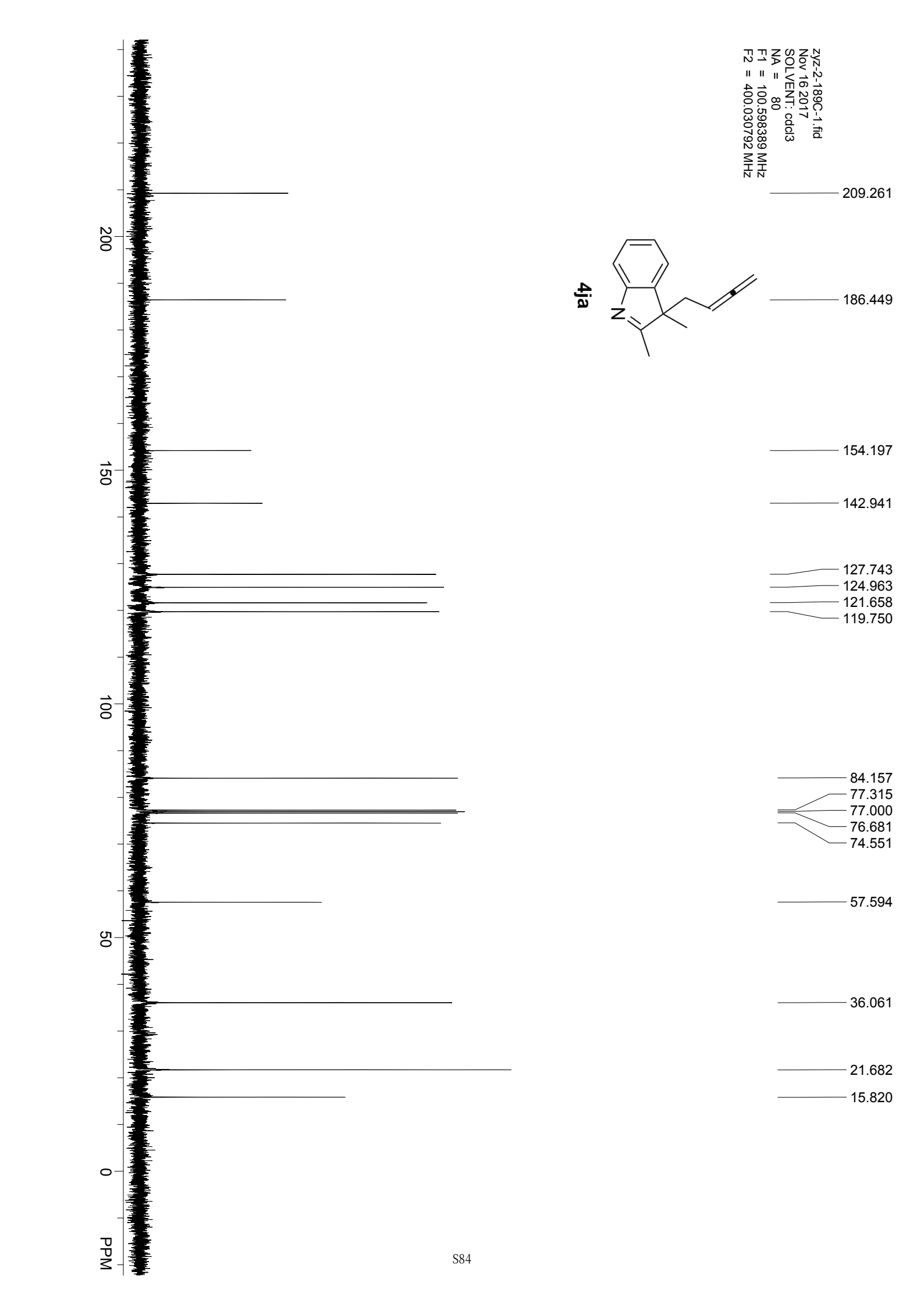


zyz-2-189H.fid
Nov 16 2017
SOLVENT: CDCl3
NA = 12
F1 = 400.031616 MHz
F2 = 100.596855 MHz



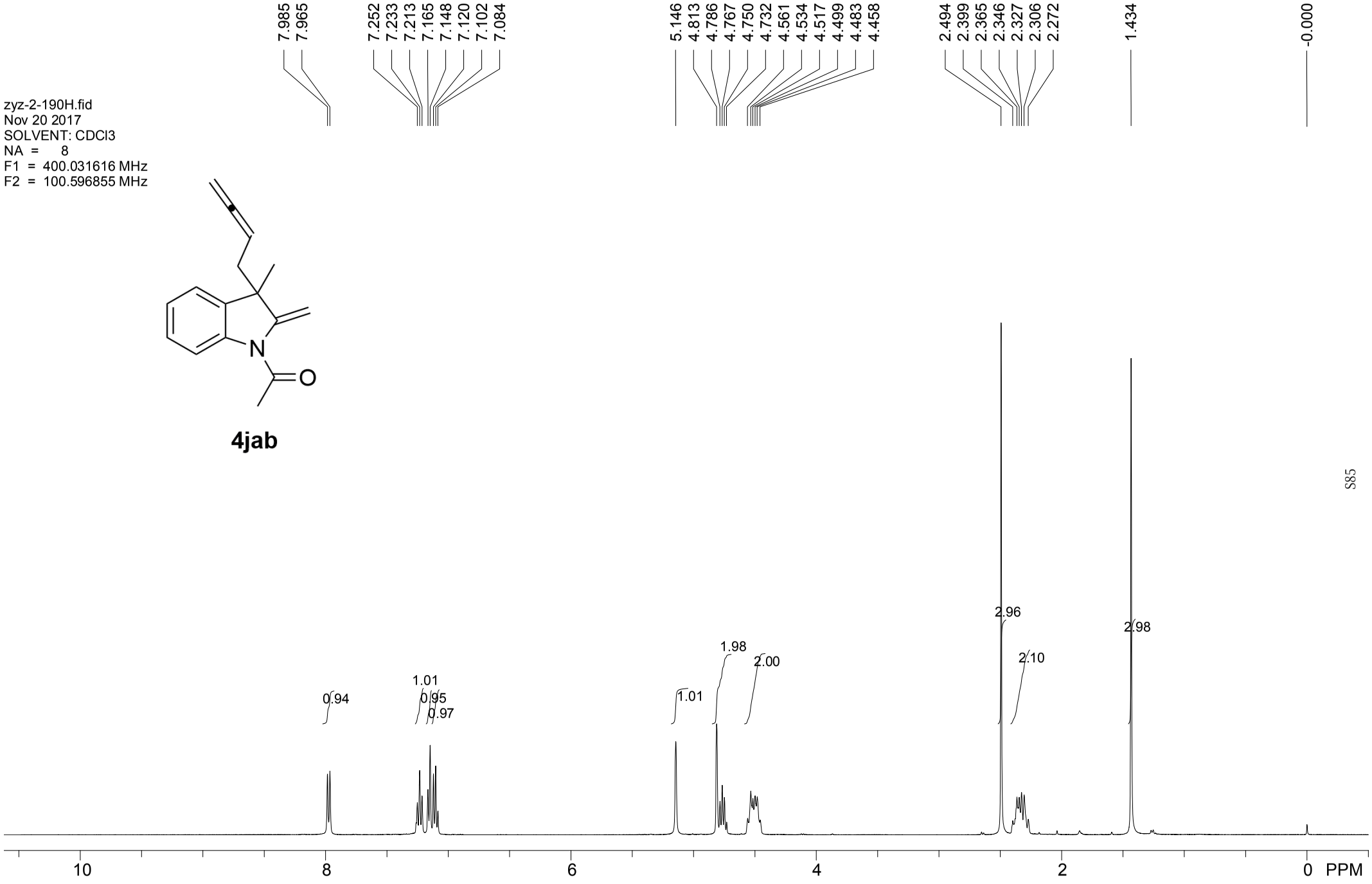
4ja

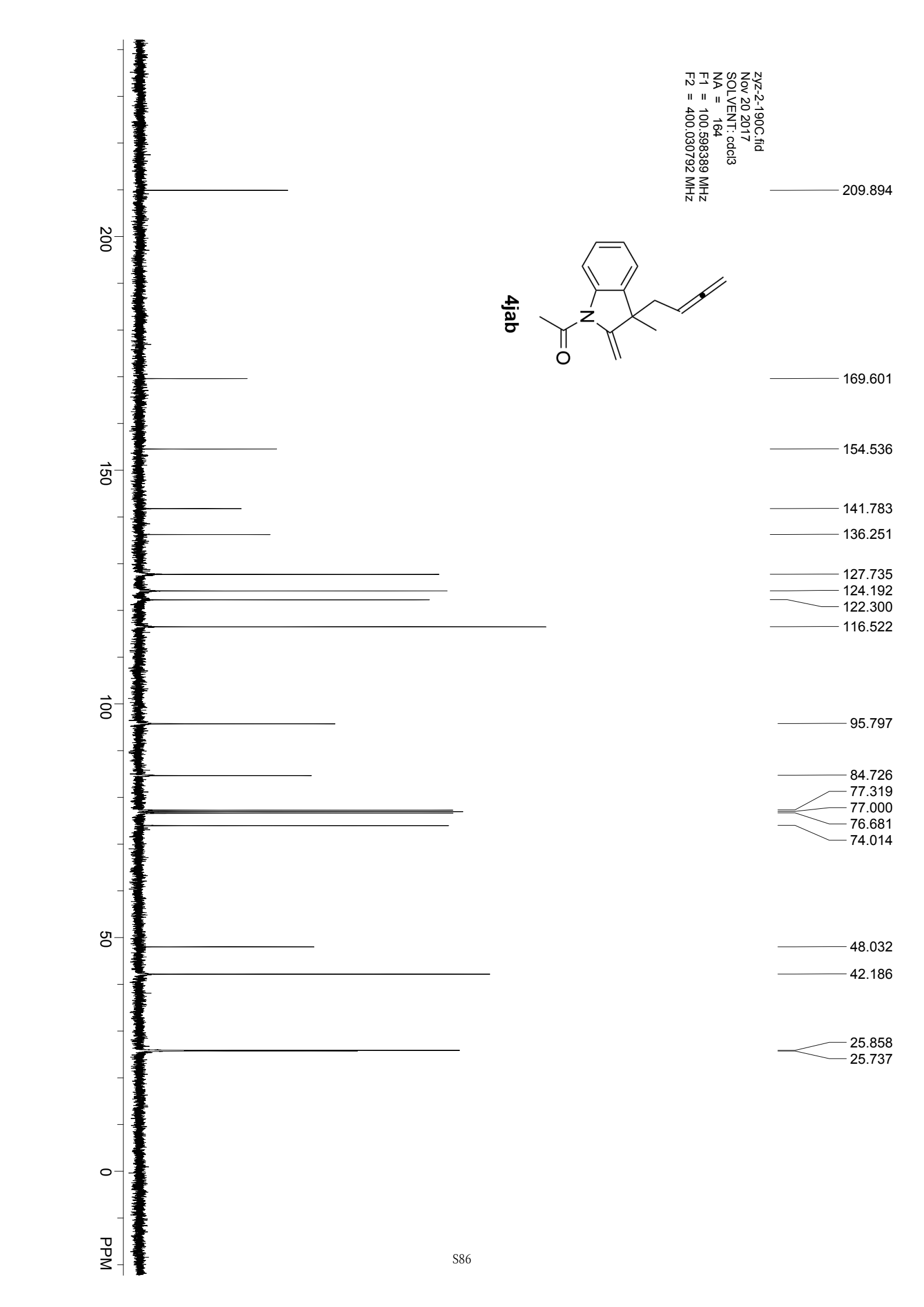



zyz-2-189C-1.fid
Nov 16 2017
SOLVENT: cdcl3
NA = 80
F1 = 100.598389 MHz
F2 = 400.030792 MHz
4ja
N
209.261
186.449
154.197
142.941
127.743
124.963
121.658
119.750
84.157
77.315
77.000
76.681
74.551
57.594
36.061
21.682
15.820
200
150
100
50
0
PPM

zyz-2-190H.fid
Nov 20 2017
SOLVENT: CDCl3
NA = 8
F1 = 400.031616 MHz
F2 = 100.596855 MHz

4jab




zyz-2-190C.fid
Nov 20 2017
SOLVENT: cdcl3
NA = 164
F1 = 100.598389 MHz
F2 = 400.030792 MHz
4jab
N
O
209.894
169.601
154.536
141.783
136.251
127.735
124.192
122.300
116.522
95.797
84.726
77.319
77.000
76.681
74.014
48.032
42.186
25.858
25.737
200
150
100
50
0
PPM