Electronic Supplementary Material (ESI) for Chemical Communications

$FeCl_3$-Catalyzed Cyclization of α-Sulfonamido-Allenes with Aldehydes-The Substituent Effect

Jiajia Cheng, Xinjun Tang, Yihua Yu, and Shengming Ma*

Supporting Information

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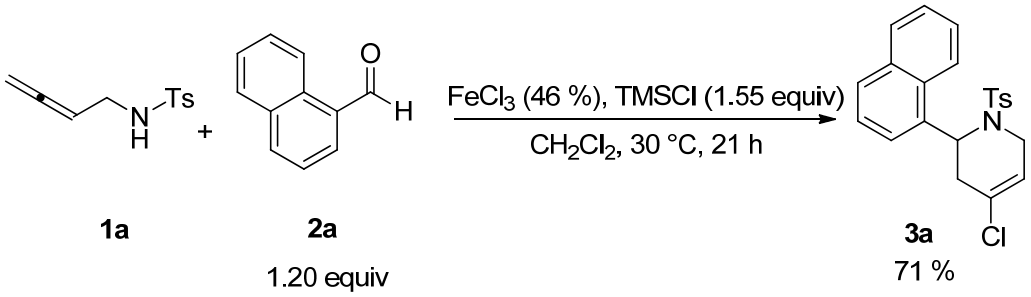
(1) 4-Chloro-2-(1-naphthyl)-1-tosyl-1,2,3,6-tetrahydropyridine 3a (cjj-6-30)



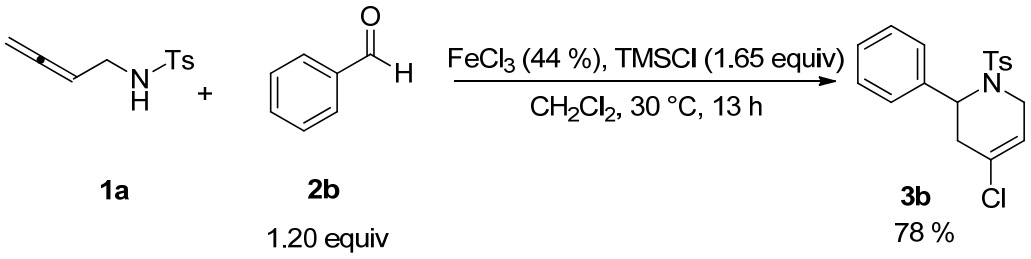
1a **2a** 1.20 equiv **3a** 71 %

Typical Procedure. To a Schlenk tube were added $FeCl_3$ (14.9 mg, 0.092 mmol)/CH_2Cl_2 (0.5 mL), *N*-(buta-2,3-dienyl)-4-tolylsulfonamide **1a** (45.7 mg, 0.20 mmol)/CH_2Cl_2 (0.5 mL), 1-naphthaldehyde **2a** (37.1 mg, 0.24 mmol)/CH_2Cl_2 (0.5 mL), and TMSCl (33.2 mg, 0.31 mmol)/CH_2Cl_2 (0.5 mL) sequentially. Then the mixture was stirred at 30 ^oC for 21 h. After the reaction was complete as monitored by TLC (petroleum ether : ethyl acetate = 5 : 1), the resulting mixture was diluted with CH_2Cl_2 (5 mL) and diethyl ether (10 mL). Then anhydrous $MgSO_4$ was added and the resulting mixture was then filtered through a short column of silica gel to remove the inorganic salts (eluent: 6× (5 mL of CH_2Cl_2 + 10 mL Et_2O)). After evaporation, the mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate/CH_2Cl_2 = 30/1/1) to afford 58.1 mg (71 %) of **3a**: white solid; m.p. 121-123 ^oC (CH_2Cl_2/petroleum ether); ^1H NMR (300 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.86-7.70 (m, 4 H, Ar-H), 7.61 (t, *J* = 7.7 Hz, 1 H, Ar-H), 7.51 (t, *J* = 7.4 Hz, 1 H, Ar-H), 7.38-7.32 (m, 2 H), 7.24 (d, *J* = 8.1 Hz, 2 H, Ar-H), 6.14 (d, *J* = 7.2 Hz, 1 H, CH), 5.73-5.71 (m, 1 H, CH=), 4.04 (dd, *J* = 18.6, 4.2 Hz, 1 H, one proton of CH_2), 3.22 (d, *J* = 18.6 Hz, 1 H, one proton of CH_2), 2.92-2.78 (m, 1 H, one proton of CH_2), 2.68-2.57 (m, 1 H, one proton of CH_2), 2.41 (s, 3 H, CH_3 of Ts); ^{13}C

NMR (75 MHz, $CDCl_3$) δ 143.9, 136.6, 134.0, 133.1, 131.4, 129.8, 129.6, 129.4, 128.7, 127.6, 126.8, 126.0, 124.6, 124.2, 124.1, 121.0, 51.0, 41.5, 34.1, 21.5; MS (EI) *m/z* (%) 399 ($M^+(^{37}Cl)$, 2.80), 397 ($M^+(^{35}Cl)$, 8.49), 91(100); IR (neat) 1662, 1597, 1511, 1494, 1440, 1339, 1245, 1156, 1091, 1053, 1034, 1019 cm^{-1}; Anal Calcd for $C_{22}H_{20}NO_2SCl$: C, 66.40; H, 5.07; N, 3.52. Found: C, 66.35; H, 5.38; N, 3.43. The structure of this compound was further conformed by the NOESY, HSQC and H-H COSY experiments.

The following compounds were prepared according to this procedure.

(2) 4-Chloro-2-phenyl-1-tosyl-1,2,3,6-tetrahydropyridine 3b (cjj-6-41)

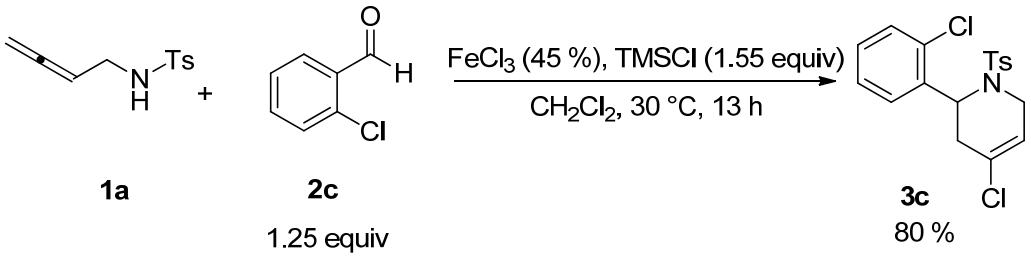


1a **2b** 1.20 equiv **3b** 78 %

The reaction of $FeCl_3$ (14.3 mg, 0.088 mmol), *N*-(buta-2,3-dienyl)-4-tolylsulfonamide **1a** (45.1 mg, 0.20 mmol), benzaldehyde **2b** (25.6 mg, 0.24 mmol), and TMSCl (35.9 mg, 0.33 mmol) in CH_2Cl_2 (2 mL) afforded 54.8 mg (78 %) of **3b** (eluent: petroleum ether/ethyl acetate/CH_2Cl_2 = 30/1/1): white solid; m.p. 117-119 ^oC (CH_2Cl_2/petroleum ether); ^1H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 2 H, Ar-H), 7.34-7.24 (m, 7 H, Ar-H), 5.72-5.67 (m, 1 H, CH=), 5.34 (t, *J* = 3.9 Hz, 1 H, ArCHNTs), 4.19 (dd, *J* = 18.5, 4.7 Hz, 1 H, one proton of CH_2), 3.42-3.30 (m, 1 H, one proton of CH_2), 2.66-2.57 (m, 2 H, CH_2), 2.43 (s, 3 H, CH_3 of Ts); ^{13}C NMR (75

MHz, $CDCl_3$) δ 143.6, 137.8, 137.3, 129.7, 129.0, 128.6, 127.9, 127.1, 127.0, 120.8, 53.8, 41.3, 33.6, 21.5; MS (EI) *m/z* (%) 349 (M^+(^{37}Cl), 1.52), 347 (M^+(^{35}Cl), 4.02), 91(100); IR (neat) 1662, 1595, 1493, 1448, 1400, 1344, 1321, 1304, 1252, 1206, 1159, 1118, 1094, 1063, 1044, 1016, 1003 cm^{-1}; Anal Calcd for $C_{18}H_{18}NO_2SCl$: C, 62.15; H, 5.22; N, 4.03. Found: C, 62.06; H, 5.28; N, 3.89.

(3) 4-Chloro-2-(2-chlorophenyl)-1-tosyl-1,2,3,6-tetrahydropyridine 3c (cjj-6-42)

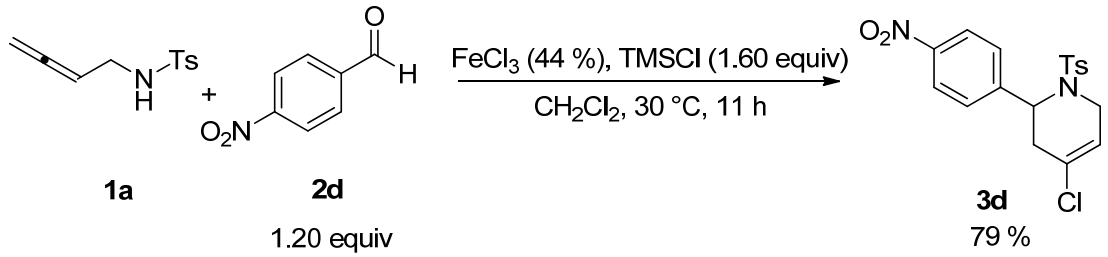


1a **2c** 1.25 equiv **3c** 80 %

The reaction of $FeCl_3$ (14.5 mg, 0.089 mmol), *N*-(buta-2,3-dienyl)-4-tolylsulfonamide **1a** (45.2 mg, 0.20 mmol), 2-chlorobenzaldehyde **2c** (35.1 mg, 0.25 mmol), and TMSCl (33.2 mg, 0.31 mmol) in CH_2Cl_2 (2 mL) afforded 62.1 mg (80 %) of **3c** (eluent: petroleum ether/ethyl acetate/CH_2Cl_2 = 30/1/1): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.1 Hz, 2 H, Ar-H), 7.36 (dd, *J* = 7.8, 0.9 Hz, 1 H, Ar-H), 7.24-7.01 (m, 5 H, Ar-H), 5.87-5.83 (m, 1 H, CH=), 5.79 (d, *J* = 6.9 Hz, 1 H, ArCHNTs), 4.23-4.11 (m, 1 H, one proton of CH_2), 3.65-3.55 (m, 1 H, one proton of CH_2), 3.05-2.85 (m, 1 H, one proton of CH_2), 2.52-2.41 (m, 1 H, one proton of CH_2), 2.39 (s, 3 H, CH_3 of Ts); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 136.8, 136.2, 133.7, 130.2, 129.5, 129.2, 129.1, 127.5, 127.4, 126.8, 120.6, 51.6, 42.4, 35.6, 21.5; MS (EI) *m/z* (%) 383 (M^+(^{35}Cl^{37}Cl), 1.30), 381 (M^+(^{35}Cl^{35}Cl), 2.47), 91(100); IR (neat) 3066, 2923, 2855, 1666, 1597, 1494, 1474, 1443, 1346, 1305, 1289, 1163, 1092, 1075, 1040,

1018 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{17}NO_2S^{35}Cl^{35}Cl$ (M^+): 381.0357. Found: 381.0360.

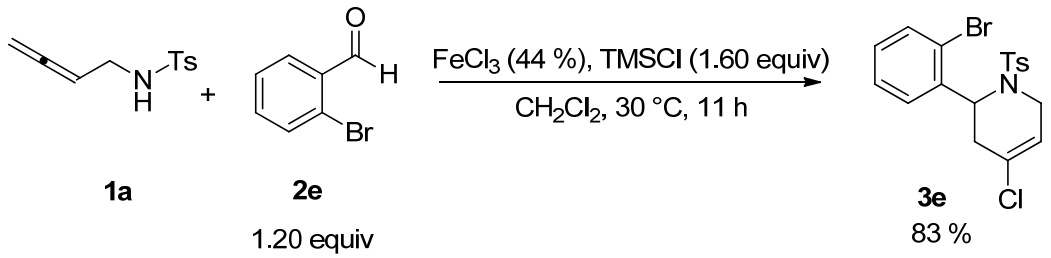
(4) 4-Chloro-2-(4-nitrophenyl)-1-tosyl-1,2,3,6-tetrahydropyridine 3d (cjj-6-34)



1a **2d** 1.20 equiv **3d** 79 %

The reaction of $FeCl_3$ (14.3 mg, 0.088 mmol), *N*-(buta-2,3-dienyl)-4-tolylsulfonamide **1a** (45.2 mg, 0.20 mmol), 4-nitrobenzaldehyde **2d** (36.4 mg, 0.24 mmol), and TMSCl (35.1 mg, 0.32 mmol) in CH_2Cl_2 (2 mL) afforded 62.7 mg (79 %) of **3d** (eluent: petroleum ether/ethyl acetate/CH_2Cl_2 = 20/1/1): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.7 Hz, 2 H, Ar-H), 7.71 (d, *J* = 8.1 Hz, 2 H, Ar-H), 7.51 (d, *J* = 8.7 Hz, 2 H, Ar-H), 7.32 (d, *J* = 8.4 Hz, 2 H, Ar-H), 5.76-5.70 (m, 1 H, CH=), 5.42 (d, *J* = 4.8 Hz, 1 H, ArCHNTs), 4.29-4.17 (m, 1 H, one proton of CH_2), 3.43-3.31 (m, 1 H, one proton of CH_2), 2.78-2.56 (m, 2 H, CH_2), 2.45 (s, 3 H, CH_3 of Ts); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.5, 145.2, 144.1, 136.8, 130.0, 128.3, 128.2, 126.9, 123.9, 120.8, 53.3, 41.4, 33.4, 21.5; MS (EI) *m/z* (%) 394 (M^+(^{37}Cl), 0.63), 392 (M^+(^{35}Cl), 1.56), 91(100); IR (neat) 1664, 1596, 1515, 1491, 1444, 1348, 1294, 1248, 1207, 1179, 1155, 1097, 1068, 1045, 1017 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{17}N_2O_4S^{35}Cl$ (M^+): 392.0598. Found: 392.0593.

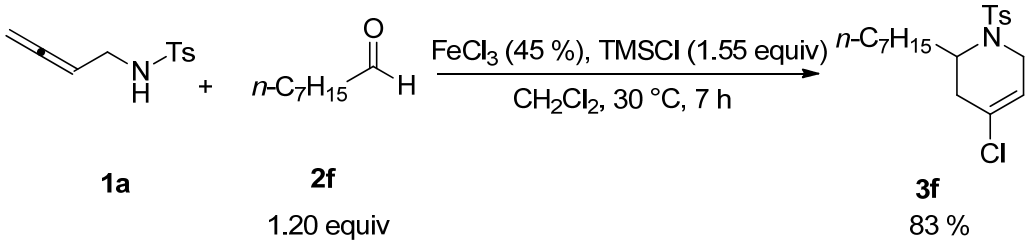
(5) 2-(2-Bromophenyl)-4-chloro-1-tosyl-1,2,3,6-tetrahydropyridine 3e (cjj-6-36)



1a **2e** 1.20 equiv **3e** 83 %

The reaction of $FeCl_3$ (14.2 mg, 0.088 mmol), *N*-(buta-2,3-dienyl)-4-tolylsulfonamide **1a** (45.3 mg, 0.20 mmol), 2-bromobenzaldehyde **2e** (45.1 mg, 0.24 mmol), and TMSCl (35.0 mg, 0.32 mmol) in CH_2Cl_2 (2 mL) afforded 72.2 mg (83 %) of **3e** (eluent: petroleum ether/ethyl acetate/CH_2Cl_2 = 30/1/1): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.58-7.52 (m, 1 H, Ar-H), 7.18 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.14-7.05 (m, 3 H, Ar-H), 5.90-5.83 (m, 1 H, CH=), 5.74 (d, *J* = 6.3 Hz, 1 H, ArCHNTs), 4.24-4.15 (m, 1 H, one proton of CH_2), 3.77-3.64 (m, 1 H, one proton of CH_2), 3.05-2.90 (m, 1 H, one proton of CH_2), 2.50 (d, *J* = 17.7 Hz, 1 H, one proton of CH_2), 2.38 (s, 3 H, CH_3 of Ts); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 138.6, 136.0, 133.5, 129.4, 129.3, 128.8, 127.6, 127.4, 127.3, 123.8, 120.4, 54.1, 42.8, 36.0, 21.4; MS (EI) *m/z* (%) 429 (M^+($^{37}Cl^{81}Br$), 0.70), 427 (M^+($^{35}Cl^{81}Br$ + $^{37}Cl^{79}Br$), 2.13), 425 (M^+($^{35}Cl^{79}Br$), 1.60), 91(100); IR (neat) 3065, 2923, 1675, 1596, 1494, 1469, 1440, 1344, 1305, 1291, 1277, 1261, 1163, 1121, 1055, 1026 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{17}NO_2S^{35}Cl^{79}Br$ (M^+): 424.9852. Found: 424.9855.

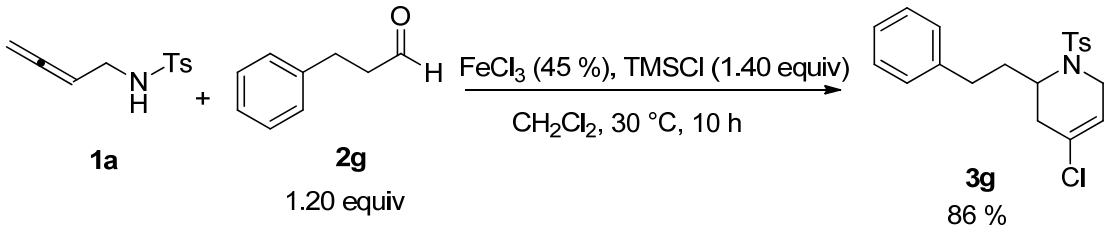
(6) 4-Chloro-2-heptyl-1-tosyl-1,2,3,6-tetrahydropyridine 3f (cjj-6-49)



1a **2f** 1.20 equiv **3f** 83 %

The reaction of $FeCl_3$ (14.6 mg, 0.090 mmol), *N*-(buta-2,3-dienyl)-4-tolylsulfonamide **1a** (45.2 mg, 0.20 mmol), octanal **2f** (31.3 mg, 0.24 mmol), and TMSCl (33.7 mg, 0.31 mmol) in CH_2Cl_2 (2 mL) afforded 62.1 mg (83 %) of **3f** (eluent: petroleum ether/ethyl acetate/CH_2Cl_2 = 30/1/1): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.27 (d, *J* = 8.1 Hz, 2 H, Ar-H), 5.72-5.68 (m, 1 H, CH=), 4.30-4.17 (m, 1 H, one proton of CH_2), 4.09 (q, *J* = 6.9 Hz, 1 H, CH), 3.67-3.54 (m, 1 H, one proton of CH_2), 2.50-2.35 (m, 4 H, CH_3 of Ts + one proton of CH_2), 1.97 (d, *J* = 17.4 Hz, 1 H, one proton of CH_2), 1.58-1.05 (m, 12 H, C_6H_{12}), 0.88 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4, 137.5, 129.6, 129.1, 126.9, 119.4, 51.6, 40.8, 35.6, 31.7, 31.1, 29.11, 29.06, 26.1, 22.6, 21.4, 14.0; MS (EI) *m/z* (%) 369 (M^+(^{35}Cl), 0.15), 272 (M^+-C_7H_{15} (^{37}Cl), 17.62), 270 (M^+-C_7H_{15} (^{35}Cl), 45.31), 91(100); IR (neat) 3065, 2927, 2856, 1735, 1686, 1596, 1494, 1459, 1378, 1351, 1306, 1162, 1120, 1092, 1067, 1018 cm^{-1}; Anal Calcd for $C_{19}H_{28}NO_2SCl$: C, 61.69; H, 7.63; N, 3.79. Found: C, 61.41; H, 7.41; N, 3.78.

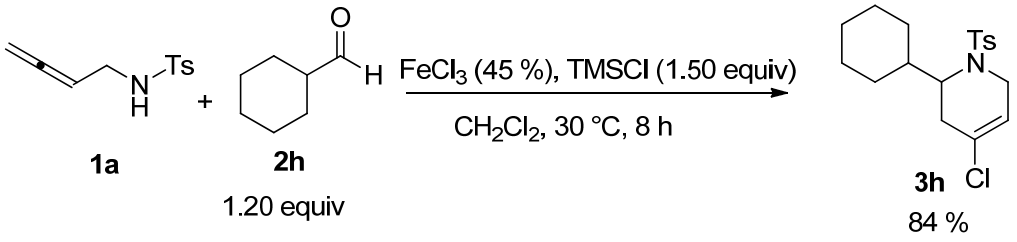
(7) 4-Chloro-2-phenethyl-1-tosyl-1,2,3,6-tetrahydropyridine 3g (cjj-6-45)



1a **2g** 1.20 equiv **3g** 86 %

The reaction of $FeCl_3$ (14.4 mg, 0.089 mmol), *N*-(buta-2,3-dienyl)-4-tolylsulfonamide **1a** (45.7 mg, 0.20 mmol), hydrocinnamaldehyde **2g** (32.8 mg, 0.24 mmol), and TMSCl (30.9 mg, 0.28 mmol) in CH_2Cl_2 (2 mL) afforded 66.1 mg (86 %) of **3g** (eluent: petroleum ether/ethyl acetate/CH_2Cl_2 = 30/1/1): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.32-7.24 (m, 4 H, Ar-H), 7.24-7.10 (m, 3 H, Ar-H), 5.73-5.68 (m, 1 H, CH=), 4.28 (dt, *J* = 18.6, 3.6 Hz, 1 H, one proton of CH_2), 4.17 (q, *J* = 7.1 Hz, 1 H, CH), 3.72-3.59 (m, 1 H, one proton of CH_2), 2.64 (t, *J* = 8.0 Hz, 2 H, CH_2), 2.48-2.34 (m, 4 H, CH_3 of Ts + one proton of CH_2), 1.99 (d, *J* = 17.4 Hz, 1 H, one proton of CH_2), 1.88-1.62 (m, 2 H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 141.0, 137.2, 129.7, 128.9, 128.4, 128.3, 126.8, 126.0, 119.4, 51.3, 40.8, 35.5, 33.1, 32.3, 21.4; MS (EI) *m/z* (%) 375 (M^+(^{35}Cl), 0.28), 272 (M^+(^{37}Cl)-C_8H_9, 7.71), 270 (M^+(^{35}Cl)-C_8H_9, 22.78), 91(100); IR (neat) 1665, 1597, 1495, 1454, 1380, 1332, 1305, 1290, 1245, 1156, 1097, 1048, 1017 cm^{-1}; Anal Calcd for $C_{20}H_{22}NO_2SCl$: C, 63.90; H, 5.90; N, 3.73. Found: C, 63.83; H, 5.96; N, 3.81.

(8) 4-Chloro-2-cyclohexyl-1-tosyl-1,2,3,6-tetrahydropyridine 3h (cjj-12-50)

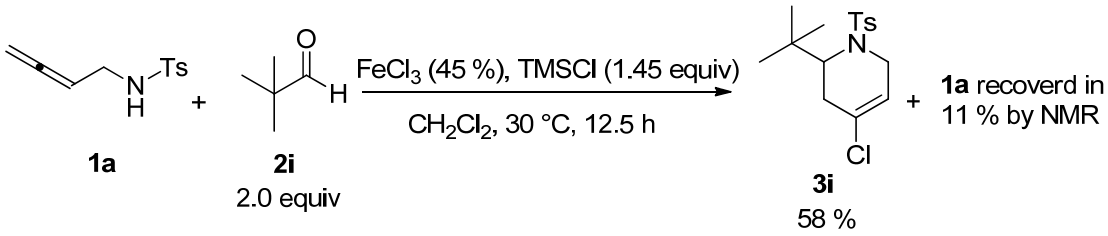


1a **2h** 1.20 equiv **3h** 84 %

The reaction of $FeCl_3$ (14.6 mg, 0.090 mmol), *N*-(buta-2,3-dienyl)-4-tolylsulfonamide **1a** (44.7 mg, 0.20 mmol), cyclohexylcarboxaldehyde **2h** (33.7 mg, 0.30 mmol),

and TMSCl (32.6 mg, 0.30 mmol) in CH_2Cl_2 (2 mL) afforded 59.5 mg (84 %) of **3h** (eluent: petroleum ether/ethyl acetate/CH_2Cl_2 = 30/1/1): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.27 (d, *J* = 8.4 Hz, 2 H, Ar-H), 5.69-5.66 (m, 1 H, CH=), 4.27-4.17 (m, 1 H, one proton of CH_2), 3.80-3.70 (m, 1 H, CH), 3.68-3.56 (m, 1 H, one proton of CH_2), 2.42 (s, 3 H, CH_3 of Ts), 2.27-2.05 (m, 2 H, CH_2), 1.87-1.60 (m, 5 H, 5 protons in *c*-hexyl group), 1.50-1.35 (m, 1 H, one proton in *c*-hexyl group), 1.35-0.83 (m, 5 H, 5 protons in *c*-hexyl group); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.3, 137.8, 129.6, 128.9, 126.7, 119.6, 56.7, 41.4, 37.1, 32.0, 30.7, 29.9, 26.1, 25.9, 25.8, 21.5; MS (EI) *m/z* (%) 272 (M^+(^{37}Cl)-C_6H_{11}, 37.23), 270 (M^+(^{35}Cl)-C_6H_{11}, 100); IR (neat) 2962, 2853, 1669, 1597, 1495, 1449, 1412, 1349, 1259, 1163, 1013 cm^{-1}; Anal Calcd for $C_{18}H_{24}NO_2SCl$: C, 61.09; H, 6.84; N, 3.96. Found: C, 61.15; H, 6.84; N, 3.98.

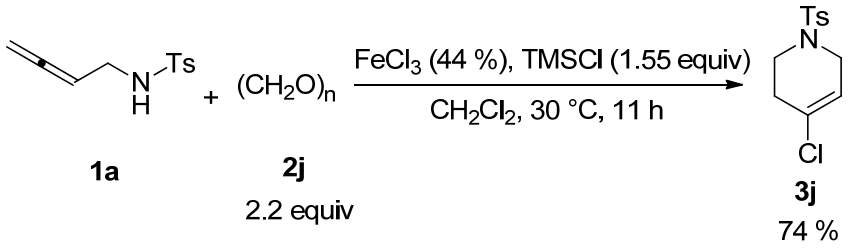
(9) 2-(*tert*-Butyl)-4-chloro-1-tosyl-1,2,3,6-tetrahydropyridine 3i (cjj-6-48)



The reaction of $FeCl_3$ (14.5 mg, 0.089 mmol), *N*-(buta-2,3-dienyl)-4-tolylsulfonamide **1a** (45.3 mg, 0.20 mmol), pivaldehyde **2i** (34.1 mg, 0.40 mmol), and TMSCl (31.0 mg, 0.29 mmol) in CH_2Cl_2 (2 mL) afforded 38.7 mg (58 %) of **3i** (eluent: petroleum ether/ethyl acetate/CH_2Cl_2 = 30/1/1): white solid; m.p. 132-134 ^{o}C (CH_2Cl_2/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.4 Hz, 2 H,

Ar-H), 7.27 (d, J = 7.8 Hz, 2 H, Ar-H), 5.65-5.60 (m, 1 H, CH=), 4.30-4.25 (m, 1 H, one proton of CH_2), 3.91-3.75 (m, 3 H, one proton of CH_2 + CH), 2.42 (s, 3 H, CH_3 of Ts), 2.17-2.08 (m, 2 H, CH_2), 0.99 (s, 9 H, C_3H_9); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.3, 137.3, 129.8, 129.7, 126.7, 119.2, 58.8, 43.1, 36.3, 30.5, 27.7, 21.5; MS (EI) *m/z* (%) 314 (M^+(^{37}Cl)-CH_3, 0.50), 312 (M^+(^{35}Cl)-CH_3, 1.22), 270 (100); IR (neat) 2963, 1682, 1595, 1493, 1470, 1399, 1384, 1370, 1358, 1326, 1290, 1259, 1223, 1205, 1185, 1153, 1097, 1075, 1056, 1009 cm^{-1}; Anal Calcd for $C_{16}H_{22}NO_2SCl$: C, 58.61; H, 6.76; N, 4.27. Found: C, 58.64; H, 6.72; N, 4.05.

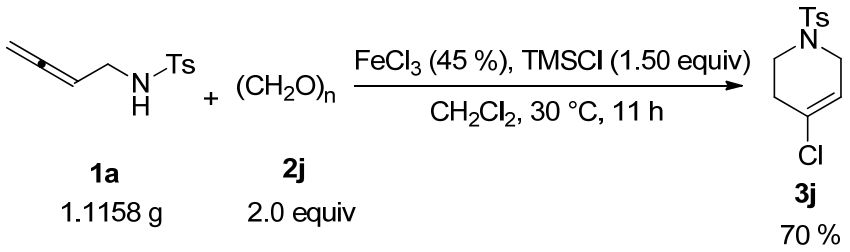
(10) 4-Chloro-1-tosyl-1,2,3,6-tetrahydropyridine 3j (cjj-10-172, cjj-10-186)



1a **2j** 2.2 equiv **3j** 74 %

The reaction of $FeCl_3$ (14.1 mg, 0.087 mmol), *N*-(buta-2,3-dienyl)-4-tolylsulfonamide **1a** (44.7 mg, 0.20 mmol), paraformaldehyde **2j** (12.9 mg, 0.43 mmol), and TMSCl (33.2 mg, 0.31 mmol) in CH_2Cl_2 (2 mL) afforded 40.3 mg (74 %) of **3j** (eluent: petroleum ether/ethyl acetate/CH_2Cl_2 = 8/1/1): white solid; m.p. 145-146 °C (CH_2Cl_2/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, J = 8.7 Hz, 2 H, Ar-H), 7.33 (d, J = 8.1 Hz, 2 H, Ar-H), 5.76-5.71 (m, 1 H, CH=), 3.68-3.60 (m, 2 H, CH_2), 3.27 (t, J = 5.9 Hz, 2 H, CH_2), 2.50-2.38 (m, 5 H, CH_3 of Ts + CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9, 133.1, 129.9, 129.7, 127.5, 119.8, 45.2, 43.2, 32.5, 21.5; MS (EI) *m/z* (%) 273 (M^+(^{37}Cl), 0.57), 271 (M^+(^{35}Cl), 1.35), 91(100); IR (neat) 3064,

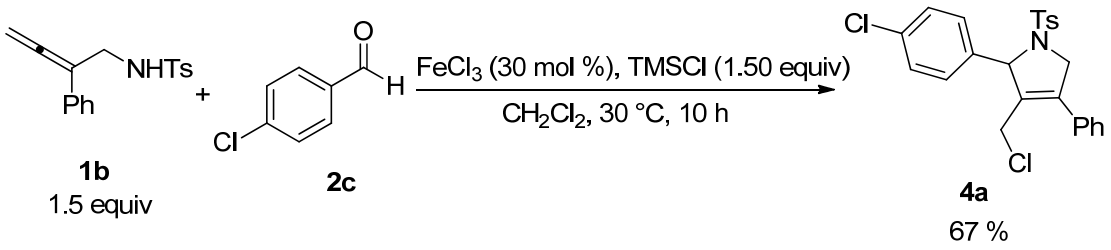
2923, 2857, 1666, 1597, 1494, 1462, 1429, 1400, 1340, 1306, 1239, 1165, 1100, 1052, 1018 cm^{-1}. Anal Calcd for $C_{12}H_{14}NO_2SCl$: C, 53.03; H, 5.19; N, 5.15. Found: C, 53.25; H, 5.24; N, 4.82.



The reaction of $FeCl_3$ (0.3651 g, 2.25 mmol), *N*-(buta-2,3-dienyl)-4-tolyl-sulfonamide **1a** (1.1158 g, 5.00 mmol), paraformaldehyde **2j** (0.3012 g, 10.0 mmol), and TMSCl (0.8148 g, 7.50 mmol) in CH_2Cl_2 (50 mL) was stirred at 30 ^oC for 11 h. After the reaction was complete as monitored by TLC (eluent: petroleum ether : ethyl acetate = 5 : 1), the mixture was evaporated and then purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate/CH_2Cl_2 = 50/1/1) to afford 0.9501 g (70 %) of **3j** (eluent: petroleum ether/ethyl acetate/CH_2Cl_2 = 50/1/1). ^1H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.33 (d, *J* = 7.8 Hz, 2 H, Ar-H), 5.76-5.71 (m, 1 H, CH=), 3.66-3.61 (m, 2 H, CH_2), 3.27 (t, *J* = 5.7 Hz, 2 H, CH_2), 2.50-2.40 (m, 5 H, CH_3 of Ts + CH_2).

Synthesis of 2,5-dihydro-1*H*-pyrrole derivatives

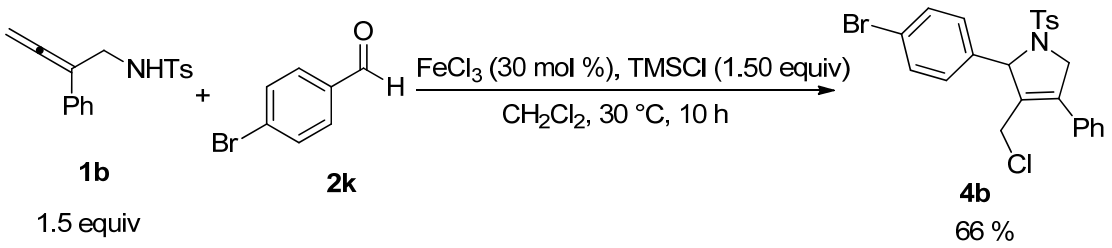
(1) 3-(Chloromethyl)-2-(4-chlorophenyl)-4-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrole 4a (cjj-9-139)



The reaction of $FeCl_3$ (19.4 mg, 0.12 mmol), 4-chlorobenzaldehyde **2c** (56.2 mg, 0.40 mmol), *N*-(2-phenylbuta-2,3-dienyl)-4-tolylsulfonamide **1b** (179.7 mg, 0.60 mmol), and TMSCl (65.4 mg, 0.60 mmol) in CH_2Cl_2 (4 mL) afforded 122.8 mg (67 %) of **4a** (eluent: petroleum ether/ethyl acetate/CH_2Cl_2 = 30/1/1): white solid; m.p. 137-139 ^oC (CH_2Cl_2/petroleum ether); ^1H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.1 Hz, 2 H, Ar-H), 7.45-7.33 (m, 3 H, Ar-H), 7.31-7.18 (m, 8 H, Ar-H), 5.80-5.75 (m, 1 H, ArCHNTs), 4.74-4.57 (m, 2 H, CH_2), 4.15 (d, *J* = 11.7 Hz, 1 H, one proton of CH_2), 3.50 (d, *J* = 12.0 Hz, 1 H, one proton of CH_2), 2.40 (s, 3 H, CH_3 of Ts); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 137.9, 136.4, 135.0, 134.1, 132.1, 131.9, 129.6, 129.1, 129.0, 128.9, 128.8, 127.6, 127.2, 70.7, 57.7, 37.8, 21.5; MS (EI) *m/z* (%) 461 (M^+($^{37}Cl^{37}Cl$), 2.04), 459 (M^+($^{35}Cl^{37}Cl$), 8.82), 457 (M^+($^{35}Cl^{35}Cl$), 11.57), 91(100); IR (neat) 3061, 2923, 2862, 1597, 1491, 1446, 1411, 1347, 1305, 1275, 1261, 1218, 1164, 1093, 1015 cm^{-1}; Anal Calcd for $C_{24}H_{21}NO_2SCl_2$: C, 62.88; H, 4.62; N, 3.06. Found: C, 62.83; H, 4.77; N, 2.81.

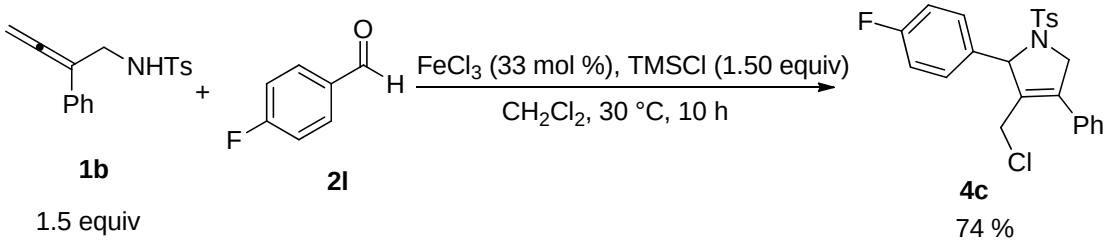
(2) 2-(4-Bromophenyl)-3-(chloromethyl)-4-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrole 4b

(cjj-9-127)



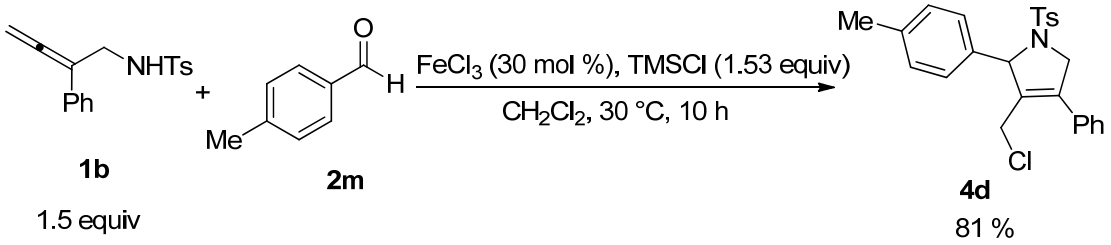
The reaction of $FeCl_3$ (19.2 mg, 0. 12 mmol), 4-bromobenzaldehyde **2k** (73.3 mg, 0.40 mmol), *N*-(2-phenylbuta-2,3-dienyl)-4-tolylsulfonamide **1b** (179.9 mg, 0.60 mmol), and TMSCl (64.7 mg, 0.60 mmol) in CH_2Cl_2 (4 mL) afforded 131.7 mg (66 %) of **4b** (eluent: petroleum ether/ethyl acetate/CH_2Cl_2 = 30/1/1): white solid; m.p. 144-145 ^{o}C (CH_2Cl_2/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, J = 8.4 Hz, 2 H, Ar-H), 7.47-7.34 (m, 5 H, Ar-H), 7.31-7.14 (m, 6 H, Ar-H), 5.80-5.73 (m, 1 H, CH), 4.73-4.57 (m, 2 H, CH_2), 4.15 (d, J = 11.7 Hz, 1 H, one proton of CH_2), 3.51 (d, J = 12.0 Hz, 1 H, one proton of CH_2), 2.41 (s, 3 H, CH_3 of Ts); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 138.4, 136.5, 135.0, 132.1, 131.9, 131.8, 129.6, 129.3, 129.1, 129.0, 127.7, 127.3, 122.3, 70.8, 57.7, 37.8, 21.5; MS (EI) *m/z* (%) 505 (M^+($^{39}Cl^{81}Br$), 0.49), 503 (M^+($^{35}Cl^{81}Br$ + $^{37}Cl^{79}Br$), 1.56), 501 (M^+($^{35}Cl^{79}Br$), 1.08), 91(100); IR (neat) 1597, 1487, 1446, 1407, 1346, 1305, 1275, 1261, 1217, 1163, 1099, 1070, 1011 cm^{-1}; Anal Calcd for $C_{24}H_{21}NO_2SClBr$: C, 57.32; H, 4.21; N, 2.79. Found: C, 57.51; H, 4.26; N, 2.78.

(3) 3-(Chloromethyl)-2-(4-fluorophenyl)-4-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrole 4c (cjj-9-130)



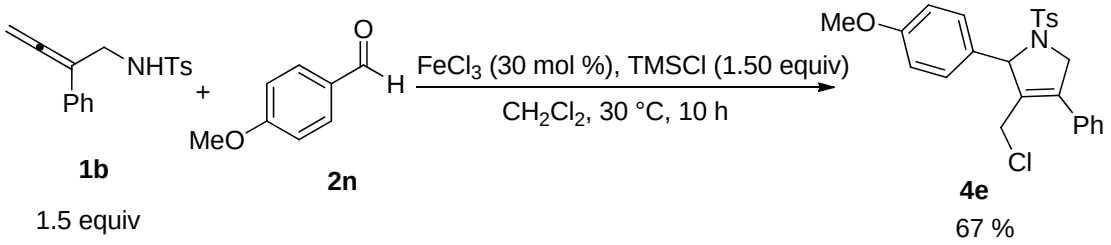
The reaction of $FeCl_3$ (21.1 mg, 0. 13 mmol), 4-fluorobenzaldehyde **2l** (49.0 mg, 0.39 mmol), *N*-(2-phenylbuta-2,3-dienyl)-4-tolylsulfonamide **1b** (179.7 mg, 0.60 mmol), and TMSCl (65.7 mg, 0.60 mmol) in CH_2Cl_2 (4 mL) afforded 129.6 mg (74 %) of **4c** (eluent: petroleum ether/ethyl acetate/CH_2Cl_2 = 40/1/1): white solid; m.p. 134-136 ^oC (CH_2Cl_2/petroleum ether); ^1H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.44-7.34 (m, 3 H, Ar-H), 7.33-7.18 (m, 6 H, Ar-H), 7.00 (t, *J* = 8.7 Hz, 2 H, Ar-H), 5.81-5.75 (m, 1 H, CH), 4.72-4.55 (m, 2 H, CH_2), 4.15 (d, *J* = 11.7 Hz, 1 H, one proton of CH_2), 3.51 (d, *J* = 11.7 Hz, 1 H, one proton of CH_2), 2.39 (s, 3 H, CH_3 of Ts); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, *J* = 245.8 Hz), 143.4, 136.2, 135.1 (d, *J* = 3.0 Hz), 135.0, 132.2, 131.9, 129.5, 129.3 (d, *J* = 8.3 Hz), 128.9, 128.8, 127.5, 127.1, 115.4 (d, *J* = 21.3 Hz), 70.6, 57.5, 37.7, 21.3; ^{19}F NMR (282 MHz, $CDCl_3$) -112.8; MS (EI) *m/z* (%) 443 ($M^+(^{37}Cl)$, 0.67), 441 ($M^+(^{35}Cl)$, 1.67), 91(100); IR (neat) 3061, 2922, 2864, 1604, 1508, 1446, 1422, 1347, 1305, 1261, 1221, 1184, 1164, 1096, 1064, 1016 cm^{-1}; Anal Calcd for $C_{24}H_{21}NO_2SClF$: C, 65.22; H, 4.79; N, 3.17. Found: C, 64.96; H, 4.93; N, 2.90.

(4) 3-(Chloromethyl)-4-phenyl-2-(4-methylphenyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole 4d (cjj-9-145)



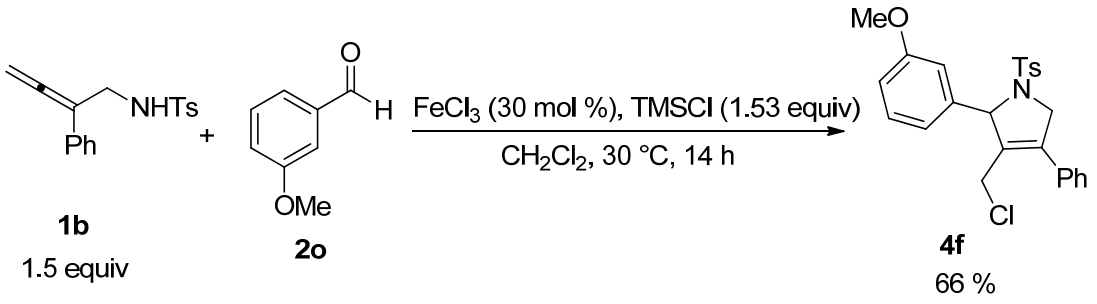
The reaction of $FeCl_3$ (19.5 mg, 0. 12 mmol), 4-methylbenzaldehyde **2m** (48.1 mg, 0.40 mmol), *N*-(2-phenylbuta-2,3-dienyl)-4-tolylsulfonamide **1b** (179.5 mg, 0.60 mmol), and TMSCl (66.3 mg, 0.61 mmol) in CH_2Cl_2 (4 mL) afforded 142.3 mg (81 %) of **4d** (eluent: petroleum ether/ethyl acetate/CH_2Cl_2 = 30/1/1): white solid; m.p. 144-146 ^oC (CH_2Cl_2/petroleum ether); ^1H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.1 Hz, 2 H, Ar-H), 7.44-7.33 (m, 3 H, Ar-H), 7.31-7.23 (m, 2 H, Ar-H), 7.20 (d, *J* = 8.1 Hz, 4 H, Ar-H), 7.11 (d, *J* = 8.1 Hz, 2 H, Ar-H), 5.81-5.75 (m, 1 H, ArCHNTs), 4.72-4.50 (m, 2 H, CH_2), 4.13 (d, *J* = 11.4 Hz, 1 H, one proton of CH_2), 3.53 (d, *J* = 11.7 Hz, 1 H, one proton of CH_2), 2.39 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 137.9, 136.2, 135.9, 135.2, 132.7, 132.2, 129.4, 129.3, 128.82, 128.81, 127.6, 127.5, 127.2, 71.2, 57.6, 37.9, 21.4, 21.1; MS (EI) *m/z* (%) 439 (M^+(^{37}Cl), 1.33), 437 (M^+(^{35}Cl), 2.96), 91(100); IR (neat) 3025, 2922, 2862, 1598, 1512, 1495, 1446, 1346, 1305, 1274, 1260, 1181, 1163, 1098, 1064, 1018 cm^{-1}; Anal Calcd for $C_{25}H_{24}NO_2SCl$: C, 68.56; H, 5.52; N, 3.20. Found: C, 68.86; H, 5.82; N, 3.04.

(5) 3-(Chloromethyl)-2-(4-methoxyphenyl)-4-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrole 4e (cjj-9-178)



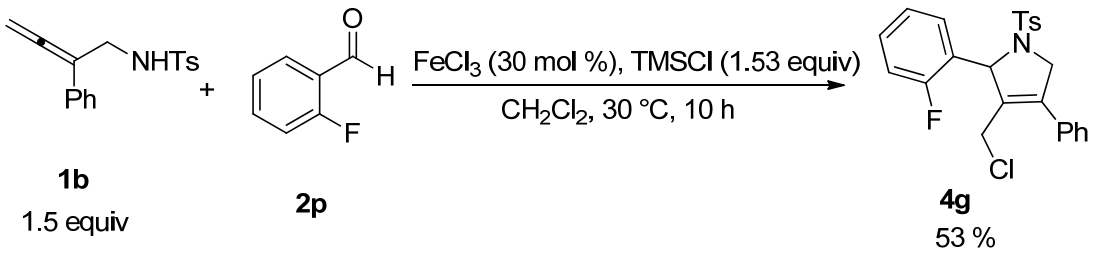
The reaction of $FeCl_3$ (19.5 mg, 0.12 mmol), 4-methoxybenzaldehyde **2n** (54.5 mg, 0.40 mmol), *N*-(2-phenylbuta-2,3-dienyl)-4-tolylsulfonamide **1b** (179.3 mg, 0.60 mmol), and TMSCl (65.2 mg, 0.60 mmol) in CH_2Cl_2 (4 mL) afforded 122.6 mg (67 %) of **4e** (eluent: petroleum ether/ethyl acetate/CH_2Cl_2 = 20/1/1): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.1 Hz, 2 H, Ar-H), 7.45-7.33 (m, 3 H, Ar-H), 7.29-7.17 (m, 6 H, Ar-H), 6.83 (d, *J* = 8.7 Hz, 2 H, Ar-H), 5.80-5.70 (m, 1 H, ArCHNTs), 4.69-4.53 (m, 2 H, CH_2), 4.14 (d, *J* = 11.4 Hz, 1 H, one proton of CH_2), 3.81 (s, 3 H, CH_3 of OMe), 3.54 (d, *J* = 11.7 Hz, 1 H, one proton of CH_2), 2.38 (s, 3 H, CH_3 of Ts); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 143.3, 135.8, 135.3, 132.8, 132.3, 131.3, 129.5, 128.91, 128.90, 127.7, 127.3, 114.0, 71.0, 57.5, 55.3, 38.0, 21.5; MS (EI) *m/z* (%) 455 (M^+(^{37}Cl), 2.03), 453 (M^+(^{35}Cl), 4.84), 91(100); IR (neat) 3022, 2922, 2863, 2821, 1596, 1491, 1457, 1447, 1377, 1342, 1309, 1276, 1261, 1245, 1188, 1162, 1100, 1071, 1045 cm^{-1}; HRMS (EI) calcd for $C_{25}H_{24}NO_3S^{35}Cl$ (M^+) 453.1165. Found 453.1161.

(6) 3-(Chloromethyl)-2-(3-methoxyphenyl)-4-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrole 4f (txj-1-21)



The reaction of $FeCl_3$ (19.2 mg, 0.12 mmol), 3-methoxybenzaldehyde **2o** (54.5 mg, 0.40 mmol), *N*-(2-phenylbuta-2,3-dienyl)-4-tolylsulfonamide **1b** (175.1 mg, 0.58 mmol), and TMSCl (66.3 mg, 0.61 mmol) in CH_2Cl_2 (4 mL) afforded 119.8 mg (66 %) of **4f** (eluent: petroleum ether/ethyl acetate/CH_2Cl_2 = 10/1/1): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.1 Hz, 2 H, Ar-H), 7.45-7.33 (m, 3 H, Ar-H), 7.30-7.17 (m, 5 H, Ar-H), 6.92 (d, *J* = 7.5 Hz, 1 H, Ar-H), 6.83 (d, *J* = 8.1 Hz, 1 H, Ar-H), 6.78 (s, 1 H, Ar-H), 5.83-5.76 (m, 1 H, ArCHNTs), 4.72-4.57 (m, 2 H, CH_2), 4.15 (d, *J* = 11.7 Hz, 1 H, one proton of CH_2), 3.76 (s, 3 H, CH_3 of OMe), 3.54 (d, *J* = 11.7 Hz, 1 H, one proton of CH_2), 2.39 (s, 3 H, CH_3 of Ts); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 143.5, 140.9, 136.2, 135.3, 132.8, 132.3, 129.9, 129.6, 129.1, 129.0, 127.8, 127.4, 120.1, 113.7, 113.3, 71.5, 57.9, 55.3, 38.0, 21.6; MS (EI) *m/z* (%) 455 (M^+(^{37}Cl), 1.84), 453 (M^+(^{35}Cl), 5.38), 91(100); IR (neat) 3057, 3030, 2955, 2924, 2854, 1599, 1489, 1455, 1346, 1279, 1257, 1218, 1164, 1101, 1047 cm^{-1}; HRMS (EI) calcd for $C_{25}H_{24}NO_3S^{35}Cl$ (M^+): 453.1165. Found: 453.1161.

(7) 3-(Chloromethyl)-2-(2-fluorophenyl)-4-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrole 4g (cjj-9-169)



1b
1.5 equiv

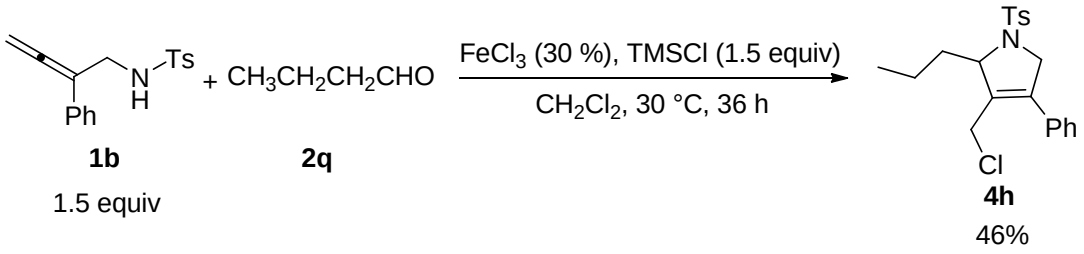
2p

4g
53 %

The reaction of $FeCl_3$ (19.5 mg, 0.12 mmol), 2-fluorobenzaldehyde **2p** (49.6 mg, 0.40 mmol), *N*-(2-phenylbuta-2,3-dienyl)-4-tolylsulfonamide **1b** (179.3 mg, 0.60 mmol), and TMSCl (66.3 mg, 0.61 mmol) in CH_2Cl_2 (4 mL) afforded 93.5 mg (53 %) of **4g** (eluent: petroleum ether/ethyl acetate/CH_2Cl_2 = 30/1/1): white solid; m.p. 125-127 ^oC (CH_2Cl_2/petroleum ether); ^1H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.44-7.32 (m, 4 H, Ar-H), 7.32-7.17 (m, 5 H, Ar-H), 7.12 (t, *J* = 7.5 Hz, 1 H, Ar-H), 6.95 (t, *J* = 9.5 Hz, 1 H, Ar-H), 6.10-6.00 (m, 1 H, ArCHNTs), 4.67-4.55 (m, 2 H, CH_2), 4.13 (d, *J* = 11.4 Hz, 1 H, one proton of CH_2), 3.58 (d, *J* = 11.4 Hz, 1 H, one proton of CH_2), 2.38 (s, 3 H, CH_3 of Ts); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8 (d, *J* = 247.7 Hz), 143.4, 136.9, 134.8, 132.0, 130.9, 130.1 (d, *J* = 3.4 Hz), 130.0 (d, *J* = 8.3 Hz), 129.5, 128.9, 128.8, 127.5, 127.1, 126.0 (d, *J* = 11.8 Hz), 124.4 (d, *J* = 3.4 Hz), 115.7 (d, *J* = 21.6 Hz), 66.2, 57.6, 37.6, 21.4; ^{19}F NMR (282 MHz, $CDCl_3$) -118.2; MS (EI) *m/z* (%) 443 ($M^+(^{37}Cl)$, 0.79), 441 ($M^+(^{35}Cl)$, 2.06), 91(100); IR (neat) 3061, 2922, 2863, 1615, 1598, 1491, 1457, 1446, 1349, 1306, 1267, 1220, 1165, 1096, 1033, 1017 cm^{-1}; Anal Calcd for $C_{24}H_{21}NO_2SClF$: C, 65.22; H, 4.79; N, 3.17. Found: C, 65.32; H, 4.92; N, 3.00.

(8) 3-(Chloromethyl)-4-phenyl-2-propyl-1-tosyl-2,5-dihydro-1*H*-pyrrole 4h

(tangxj-4-81)



1b
1.5 equiv

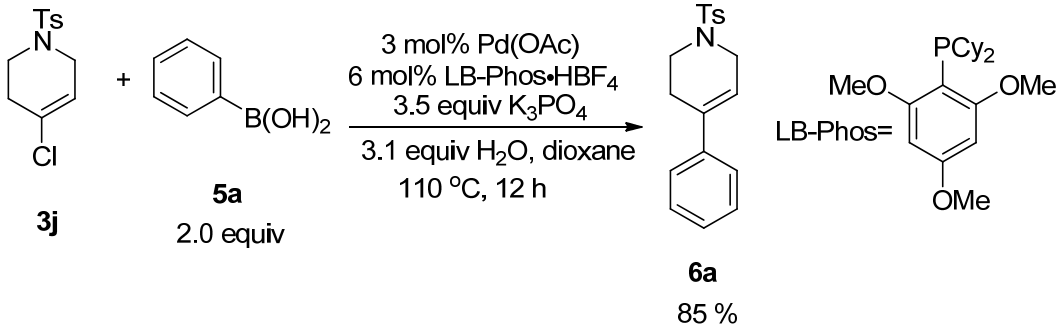
2q

4h
46%

The reaction of $FeCl_3$ (19.4 mg, 0.12 mmol), *n*-C_3H_7CHO **2q** (29.0 mg, 0.40 mmol), *N*-(2-phenylbuta-2,3-dienyl)-4-tolylsulfonamide **1b** (180.0 mg, 0.60 mmol), and TMSCl (65.4 mg, 0.6 mmol) in CH_2Cl_2 (4 mL) afforded 72.3 mg (46 %) of **4h** (eluent: petroleum ether/ethyl acetate/CH_2Cl_2 = 30/1/1): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.39-7.27 (m, 5 H, Ar-H), 7.13-7.08 (m, 2 H, Ar-H), 4.91-4.86 (m, 1 H, CHNTs), 4.42 (s, 2 H, CH_2NTs), 4.15 (d, *J* = 12.0 Hz, 1 H, one proton of CH_2), 3.93 (d, *J* = 12.0 Hz, 1 H, one proton of CH_2), 2.41 (s, 3 H, CH_3 of Ts), 2.06-1.95 (m, 1 H, one proton of CH_2), 1.76-1.65 (m, 1 H, one proton of CH_2), 1.60-1.45 (m, 1 H, one proton of CH_2), 1.42-1.28 (m, 1 H, one proton of CH_2), 0.96 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 136.8, 134.4, 132.4, 131.8, 129.7, 128.8, 128.7, 127.5, 127.4, 68.2, 58.0, 38.1, 35.3, 21.5, 16.9, 14.0; MS (ESI) *m/z* (%) 486 (M+Py+NH_4^+, ^{35}Cl), 392 (M+H^+, ^{37}Cl), 390 (M+H^+, ^{35}Cl); IR (neat) 2956, 2866, 1660, 1596, 1495, 1453, 1340, 1267, 1217, 1158, 1095, 1031 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{24}{}^{35}ClNO_2S$ (M^+): 389.1216. Found: 389.1226.

Synthetic application via coupling of the C-Cl bond

(1) Synthesis of 4-phenyl-1-tosyl-1,2,3,6-tetrahydropyridine 6a (cjj-12-40)

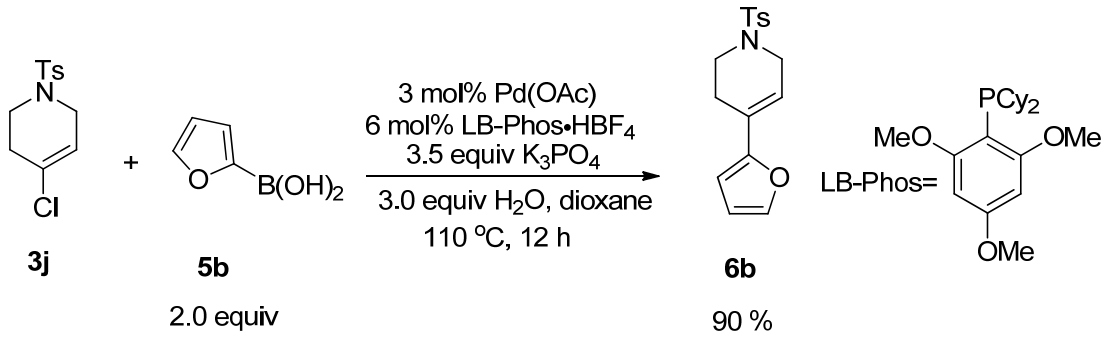


Typical Procedure. To a rubber-capped Schlenk vessel was added K_3PO_4 (152.0 mg, 0.70 mmol). This equipment was dried with flame under vacuum and backfilled with Ar for three times. Then $Pd(OAc)_2$ (1.4 mg, 0.006 mmol), LB-Phos • HBF_4 (5.6 mg, 0.012 mmol), phenyl boronic acid (48.8 mg, 0.40 mmol), and 0.5 mL of dioxane were added sequentially to the Schlenk vessel. Then **3j** (54.5 mg, 0.20 mmol), 0.5 mL of dioxane, and water (11.2 mg, 0.62 mmol) were added sequentially. The resulting mixture was stirred at 110 ^oC for 12 h. After the reaction was complete as monitored by TLC (petroleum ether : ethyl acetate = 5 : 1), the reaction mixture was evaporated and purified via flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate/CH_2Cl_2 = 10/1/1) to afford 53.4 mg (85 %) of **6a**: white solid; m.p. 213-215 ^oC (CH_2Cl_2/petroleum ether); ^1H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, J = 8.4 Hz, 2 H, Ar-H), 7.38-7.20 (m, 7 H, Ar-H), 5.60-5.58 (m, 1 H, CH=), 3.80-3.72 (m, 2 H, CH_2), 3.31 (t, J = 5.7 Hz, 2 H, CH_2), 2.66-2.52 (m, 2 H, CH_2), 2.43 (s, 3 H, CH_3 of Ts); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 140.0, 135.3, 133.0, 129.6, 128.4, 127.7, 127.5, 124.9, 118.9, 45.2, 43.0, 27.5, 21.5; MS (EI) *m/z* (%) 313 (M^+, 7.25), 131 (100); IR (neat) 2960, 2926, 2859, 1595, 1497, 1446, 1342, 1259, 1165, 1103, 1063, 1020 cm^{-1};

Anal Calcd for $C_{18}H_{19}NO_2S$: C, 68.98; H, 6.11; N, 4.47. Found: C, 68.95; H, 6.25; N, 4.41.

The following compounds were prepared according to this procedure.

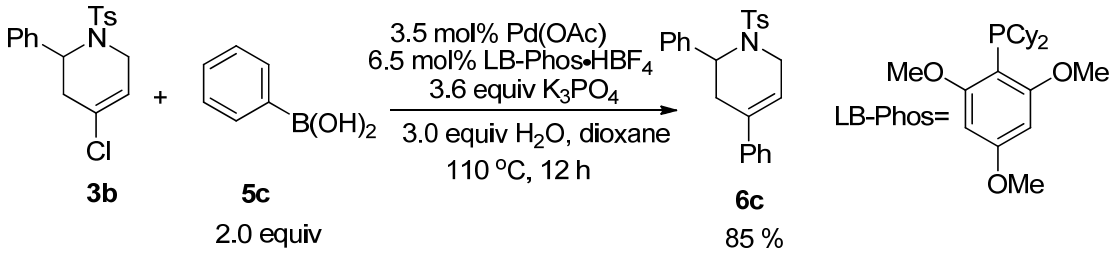
(2) 4-(2-Furanyl)-1-tosyl-1,2,3,6-tetrahydropyridine 6b (cjj-9-135)



The reaction of K_3PO_4 (152.1 mg, 0.70 mmol), $Pd(OAc)_2$ (1.4 mg, 0.006 mmol), LB-Phos • HBF_4 (5.5 mg, 0.012 mmol), 2-furanyl boronic acid (44.8 mg, 0.40 mmol), **3j** (53.7 mg, 0.20 mmol), and water (10.7 mg, 0.59 mmol) in dioxane (1 mL) afforded 54.0 mg (90 %) of **6b** (eluent: petroleum ether/ethyl acetate/CH_2Cl_2 = 8/1/1): white solid; m.p. 194-195 °C (CH_2Cl_2/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.33 (d, *J* = 6.9 Hz, 3 H, Ar-H + Furan-H), 6.39-6.32 (m, 1 H, CH), 6.22-6.17 (m, 1 H, CH), 6.14-6.07 (m, 1 H, CH), 3.80-3.74 (m, 2 H, CH_2), 3.28 (t, *J* = 5.9 Hz, 2 H, CH_2), 2.55-2.46 (m, 2 H, CH_2), 2.43 (s, 3 H, CH_3 of Ts); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 143.6, 141.8, 133.2, 129.7, 127.7, 125.6, 116.2, 111.0, 105.2, 44.7, 42.4, 25.2, 21.5; MS (EI) *m/z* (%) 303 (M^+, 8.79), 148 (100); IR (neat) 2974, 2922, 1597, 1489, 1458, 1400, 1339, 1310, 1291, 1276, 1261, 1240, 1162,

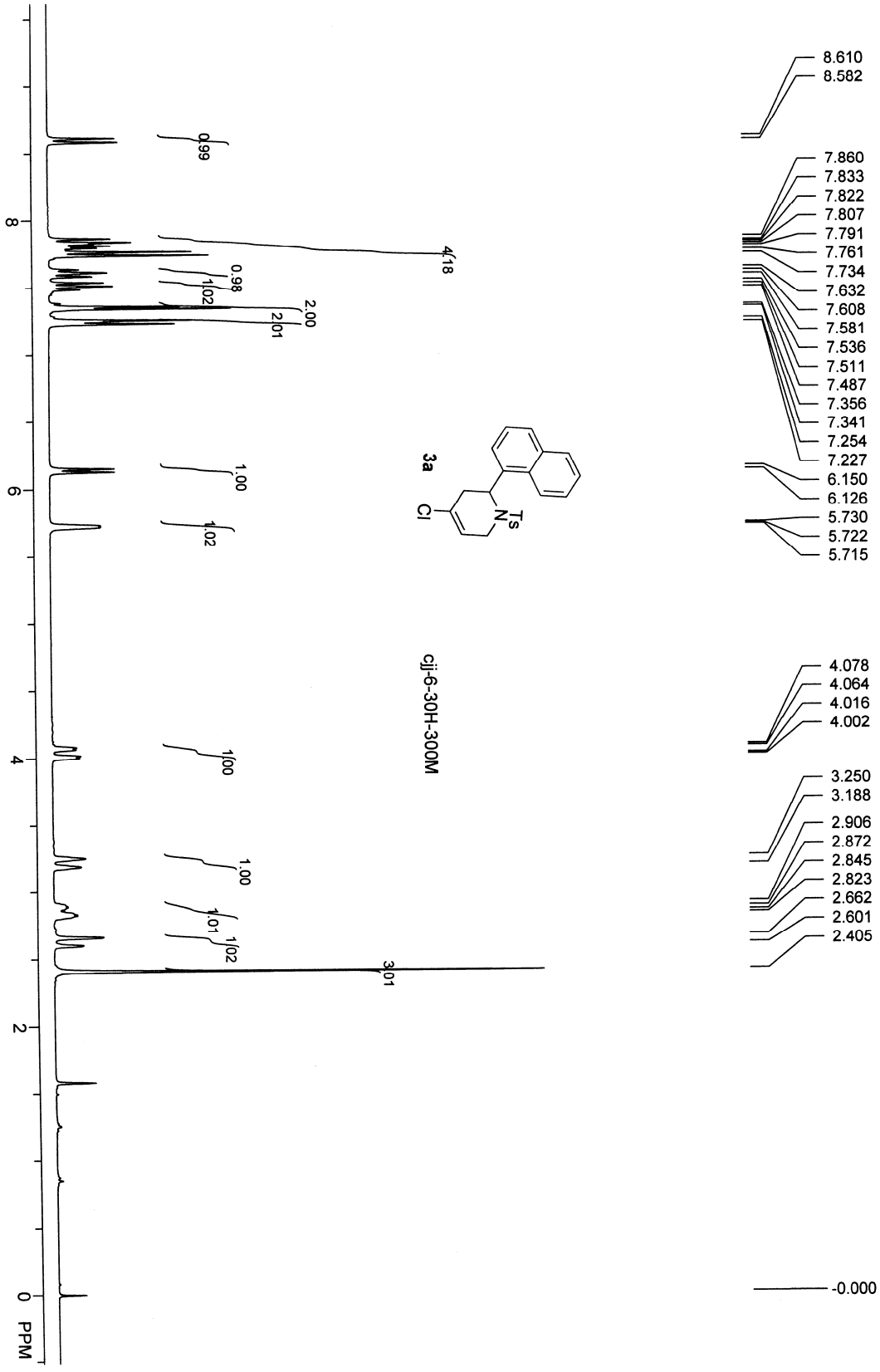
1122, 1101, 1063, 1005 cm^{-1}; Anal Calcd for $C_{16}H_{17}NO_3S$: C, 63.34; H, 5.65; N, 4.62. Found: C, 63.10; H, 5.73; N, 4.51.

(3) 2,4-Diphenyl-1-tosyl-1,2,3,6-tetrahydropyridine 6c (cjj-8-191)



The reaction of K_3PO_4 (153.2 mg, 0.71 mmol), $Pd(OAc)_2$ (1.5 mg, 0.007 mmol), LB-Phos •HBF_4 (5.7 mg, 0.013 mmol), phenyl boronic acid (48.2 mg, 0.39 mmol), **3b** (71.2 mg, 0.20 mmol), and water (11.3 mg, 0.63 mmol) in dioxane (1 mL) afforded 67.8 mg (85 %) of **6c** (eluent: petroleum ether/ethyl acetate/CH_2Cl_2 = 20/1/1): oil ; ^1H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.37-7.15 (m, 12 H, Ar-H), 5.94-5.87 (m, 1 H, CH=), 5.46 (d, *J* = 6.0 Hz, 1 H, ArCHNTs), 4.38-4.27 (m, 1 H, one proton of $TsNCH_2$), 3.61-3.48 (m, 1 H, one proton of $TsNCH_2$), 2.87-2.60 (m, 2 H, CH_2), 2.37 (s, 3 H, CH_3 of Ts); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 140.2, 138.9, 137.5, 134.2, 129.5, 128.42, 128.36, 127.54, 127.49, 127.2, 127.0, 124.9, 120.0, 53.1, 41.3, 28.4, 21.4; MS (EI) *m/z* (%) 389 (M^+, 7.58), 94 (100); IR (neat) 3059, 3030, 2922, 2849, 1684, 1597, 1578, 1495, 1448, 1370, 1342, 1305, 1290, 1262, 1161, 1097, 1070, 1031, 1018 cm^{-1}; HRMS (EI) calcd for $C_{24}H_{23}NO_2S$ (M^+) 389.1450. Found 389.1448.

^{1}H NMR, ^{13}C NMR, and ^{19}F NMR Spectra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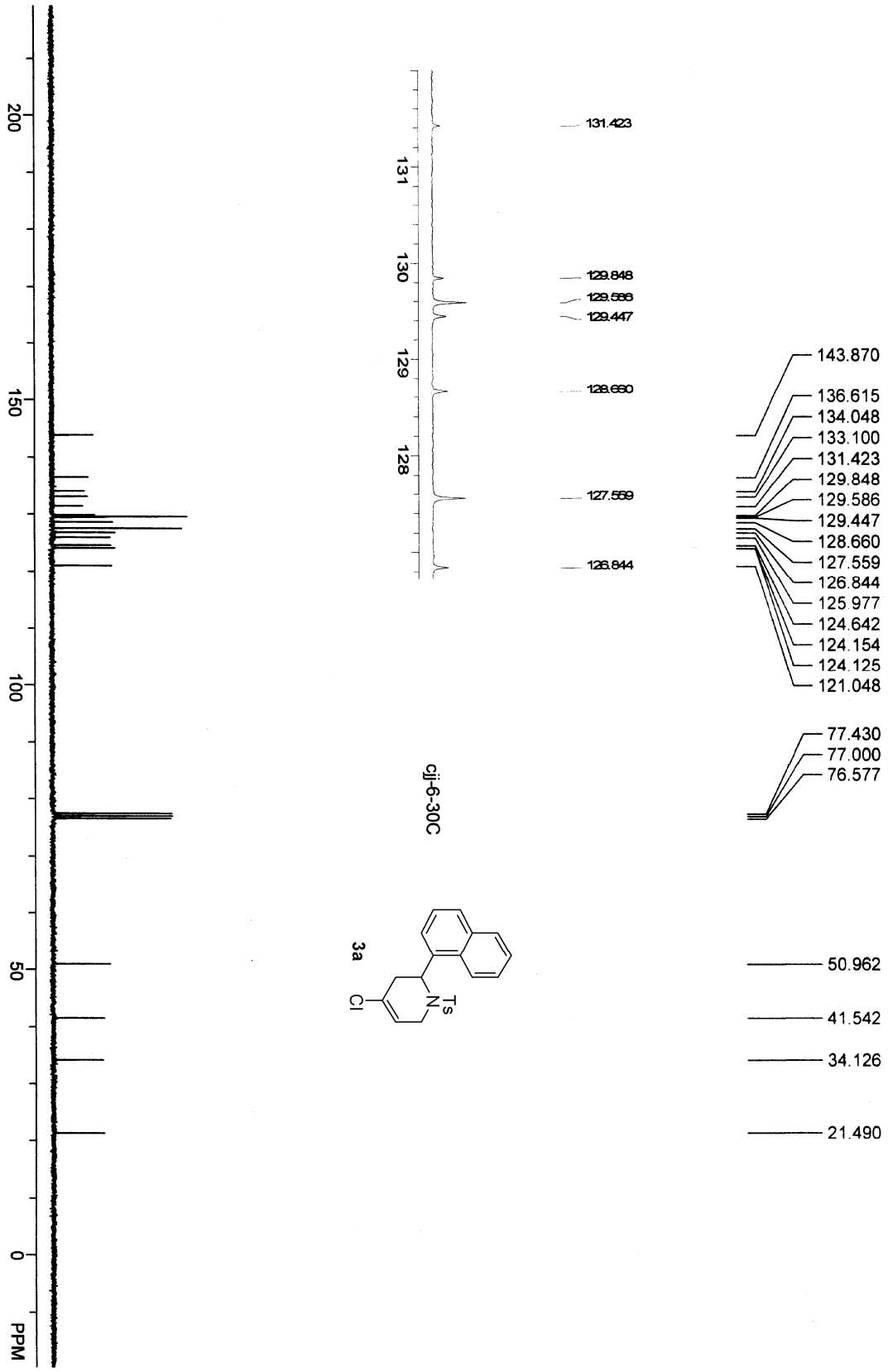
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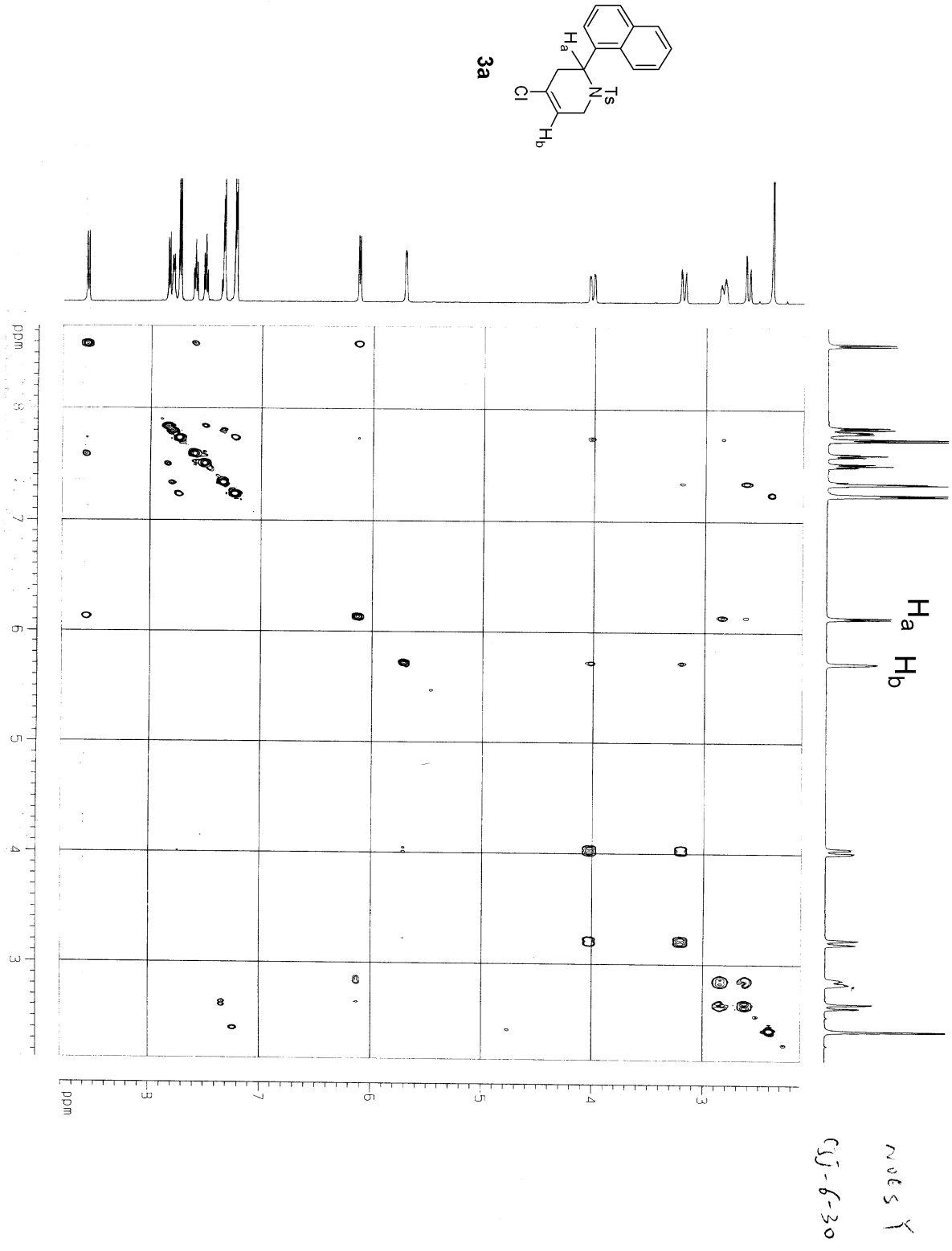
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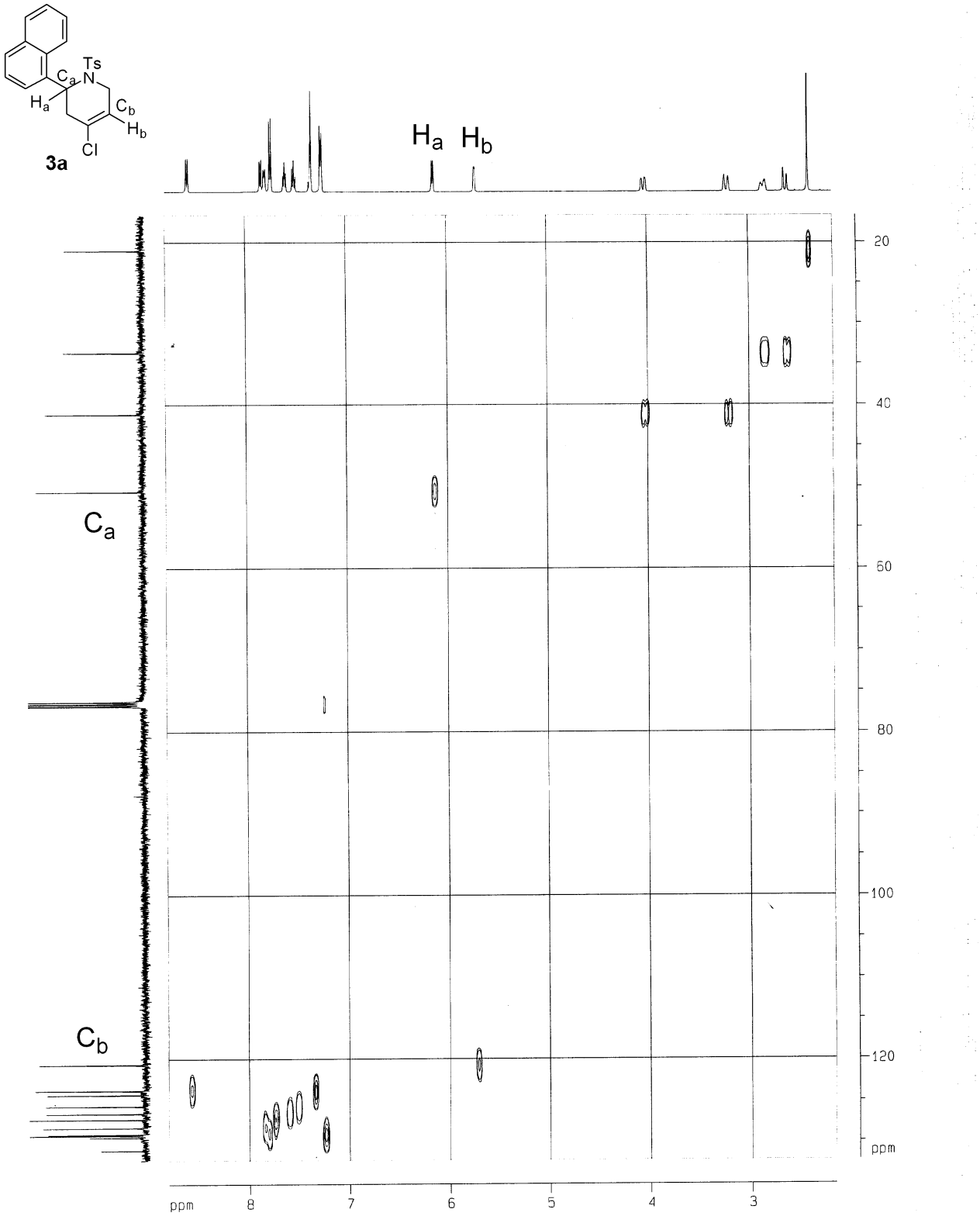
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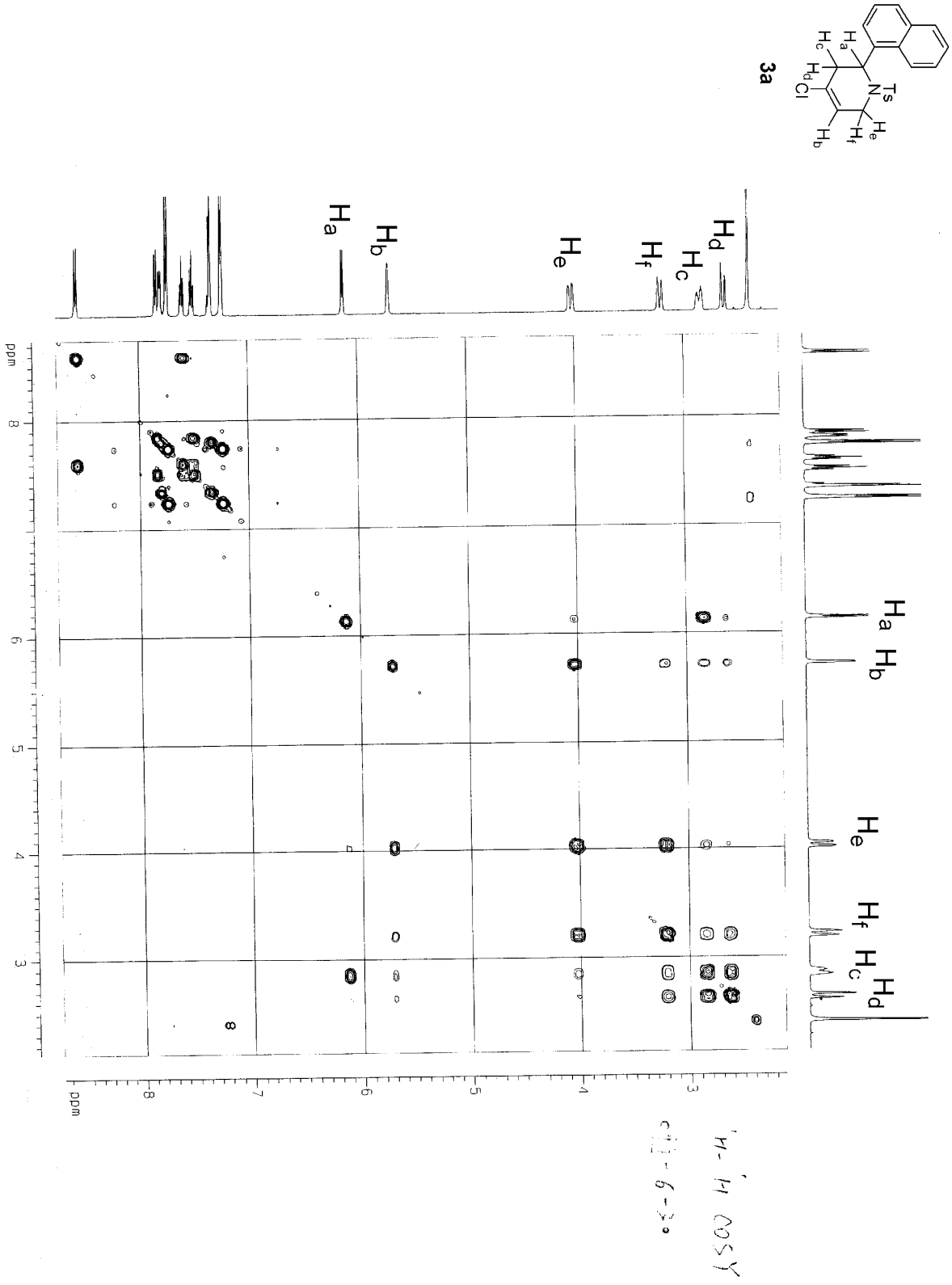
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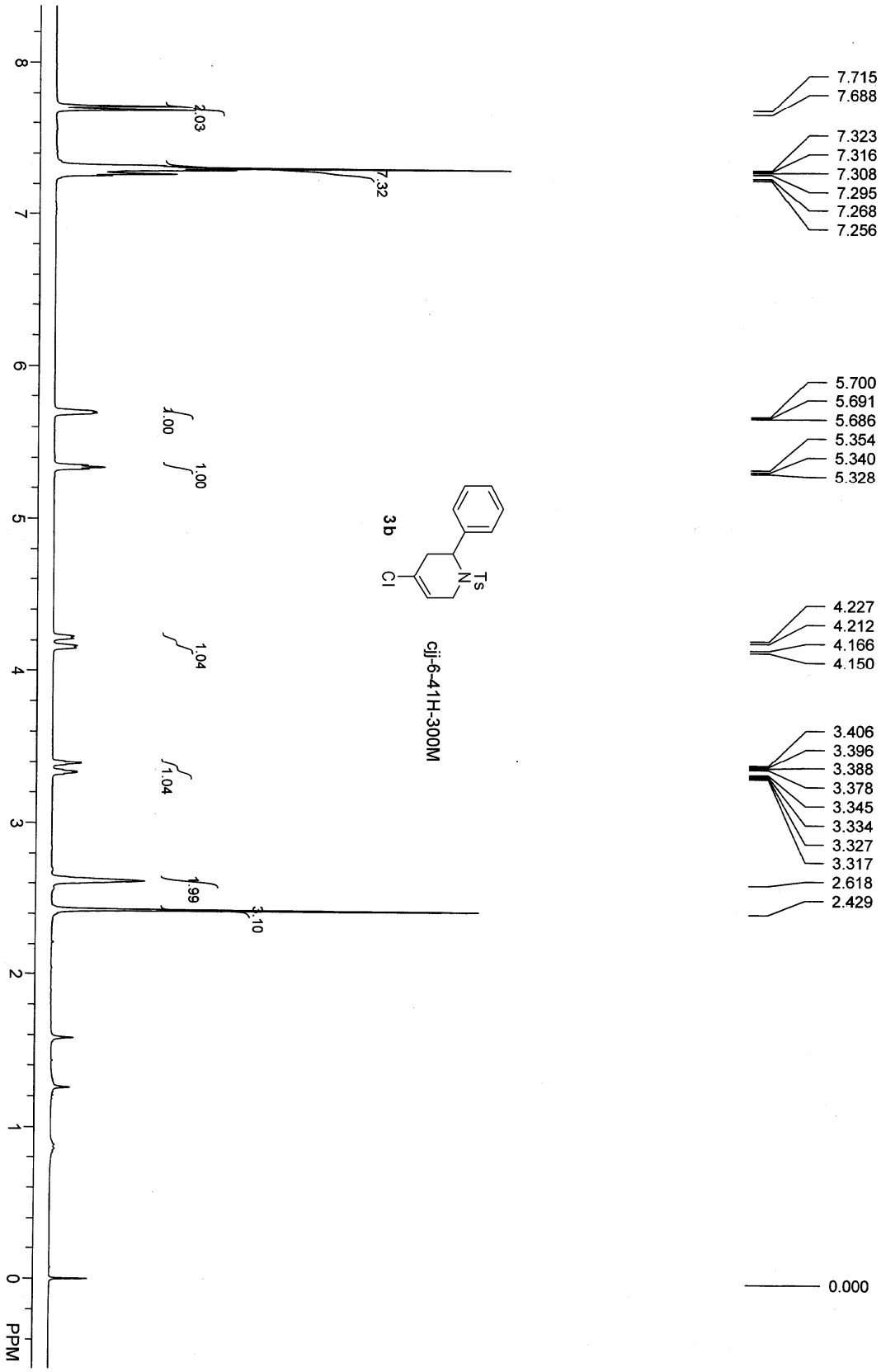
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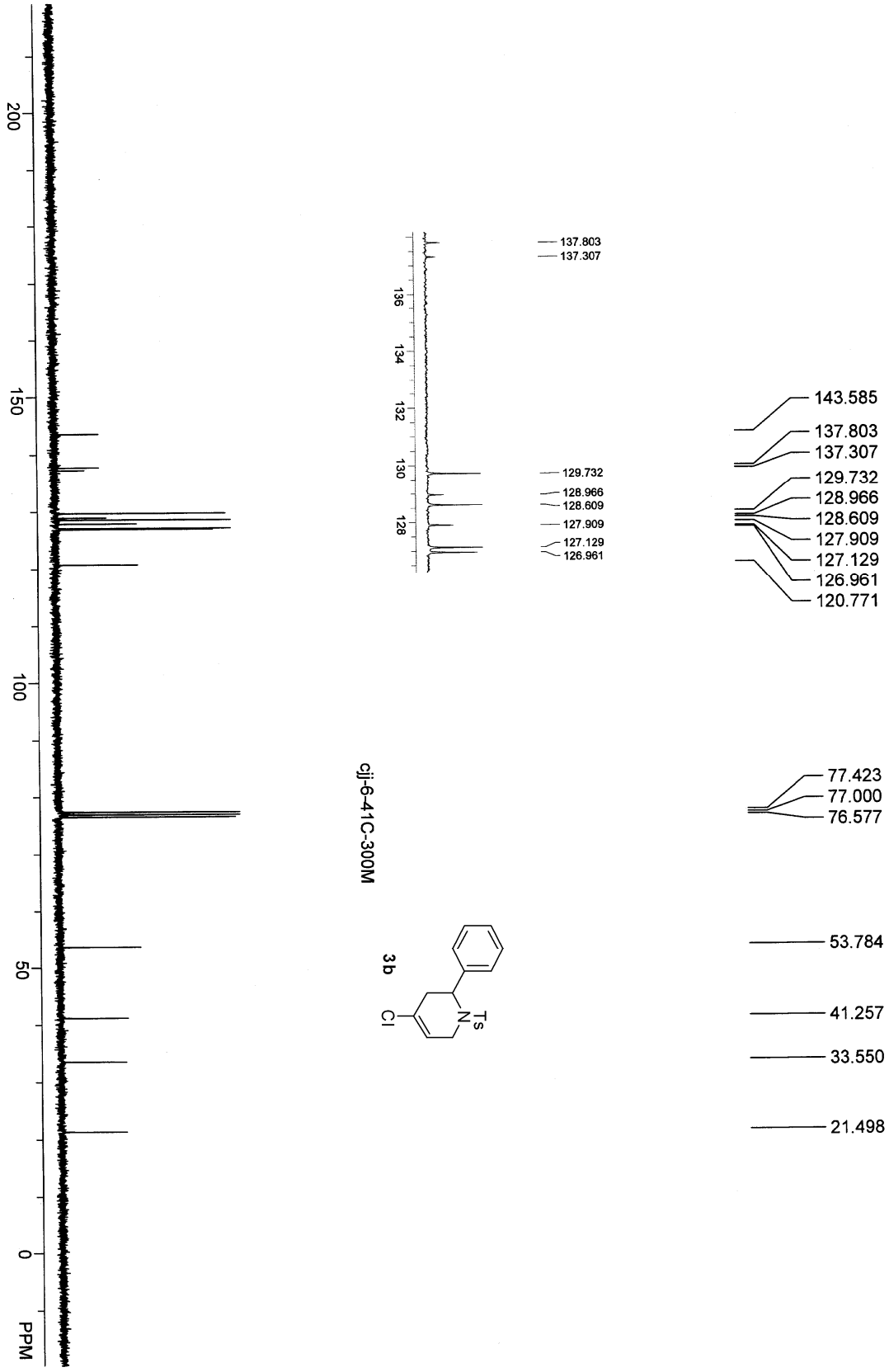
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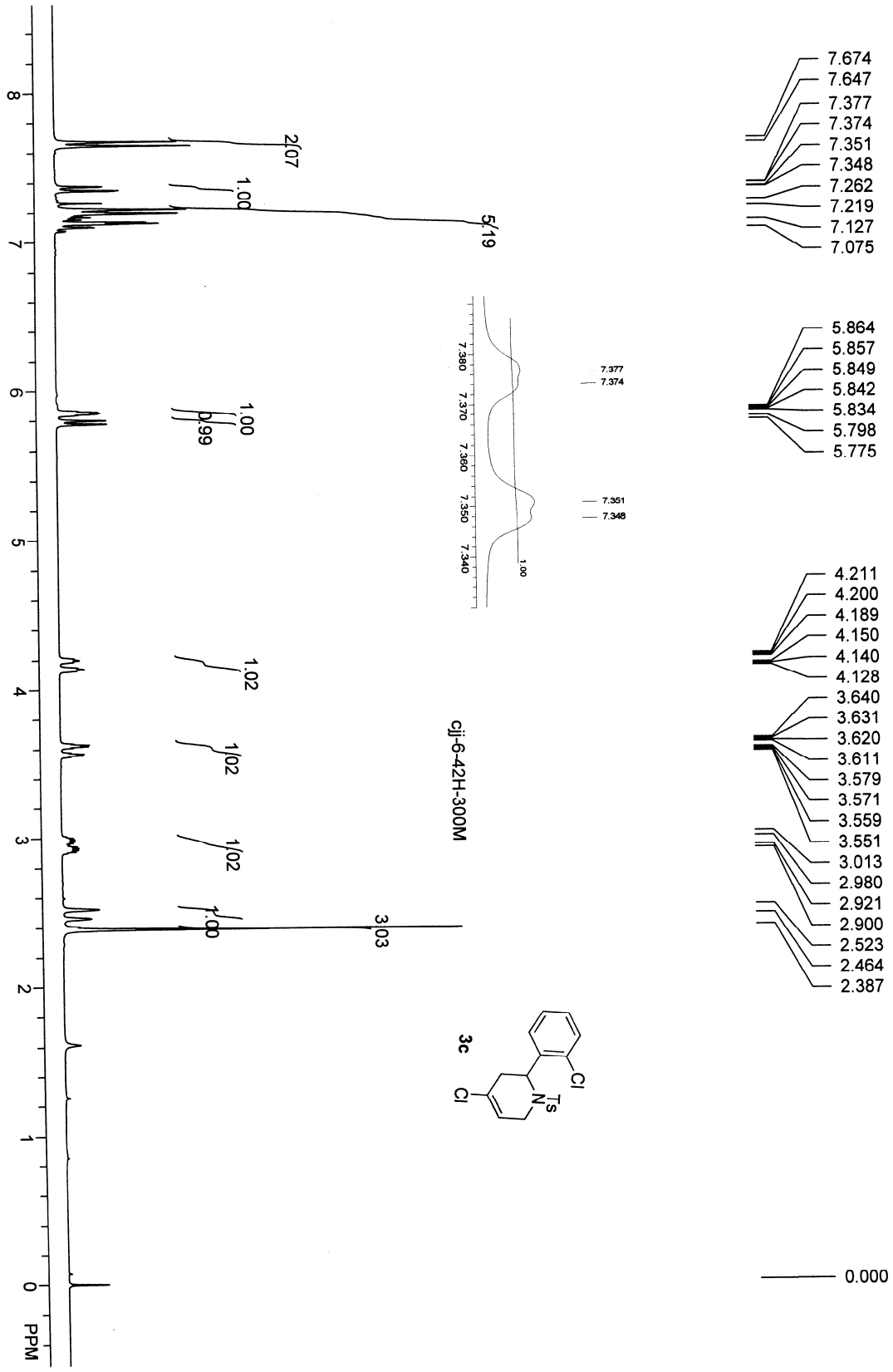
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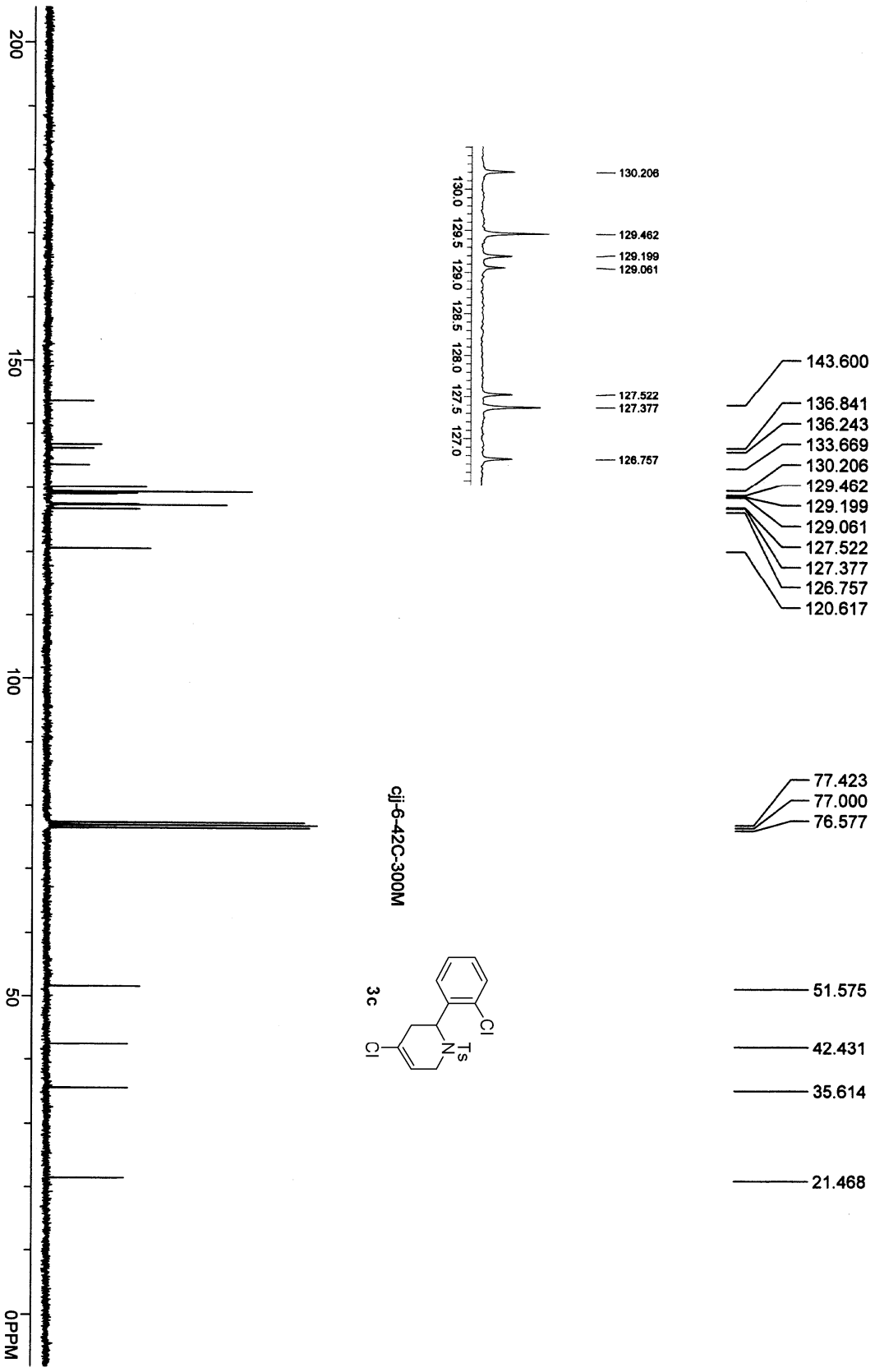
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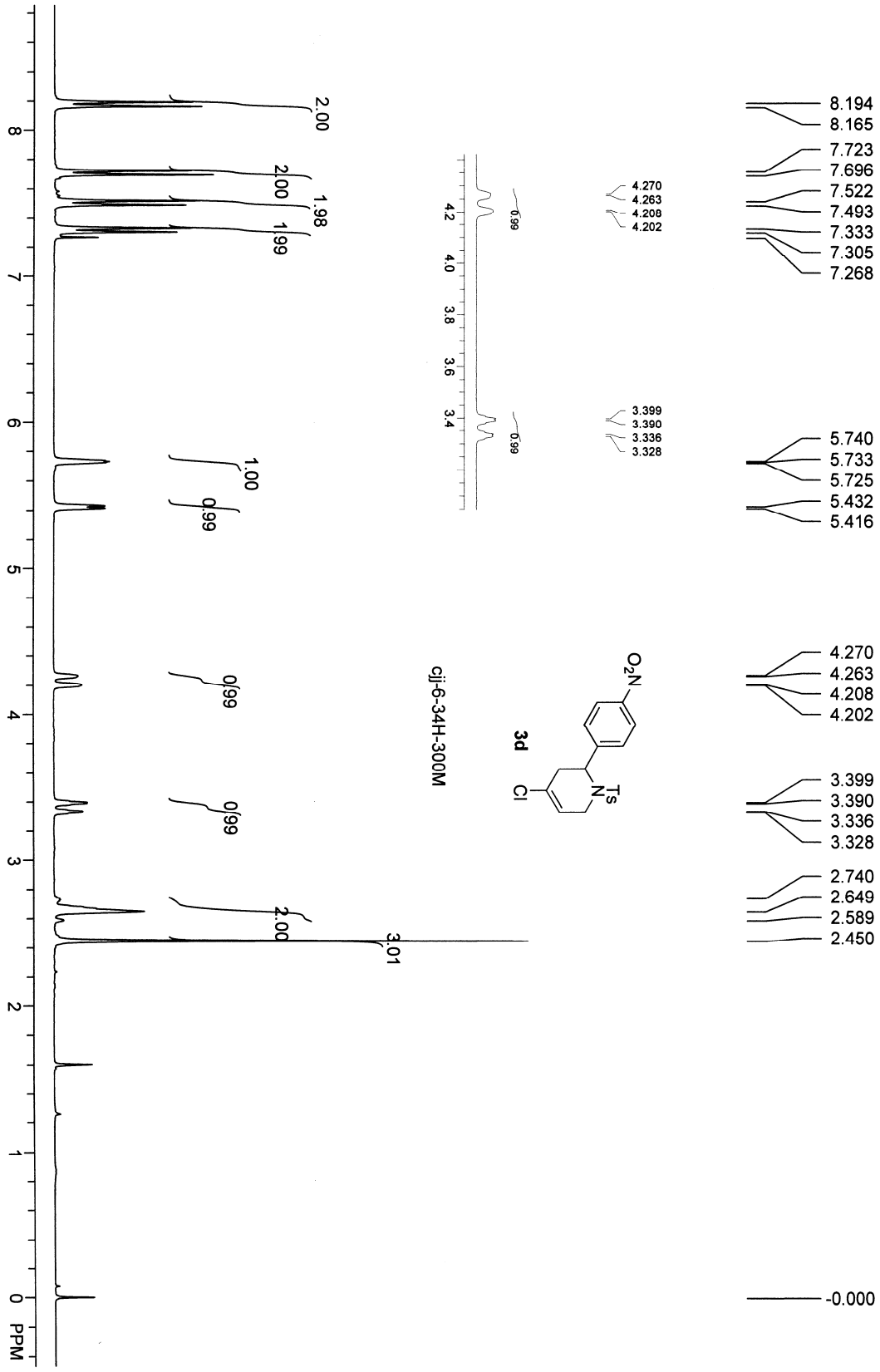
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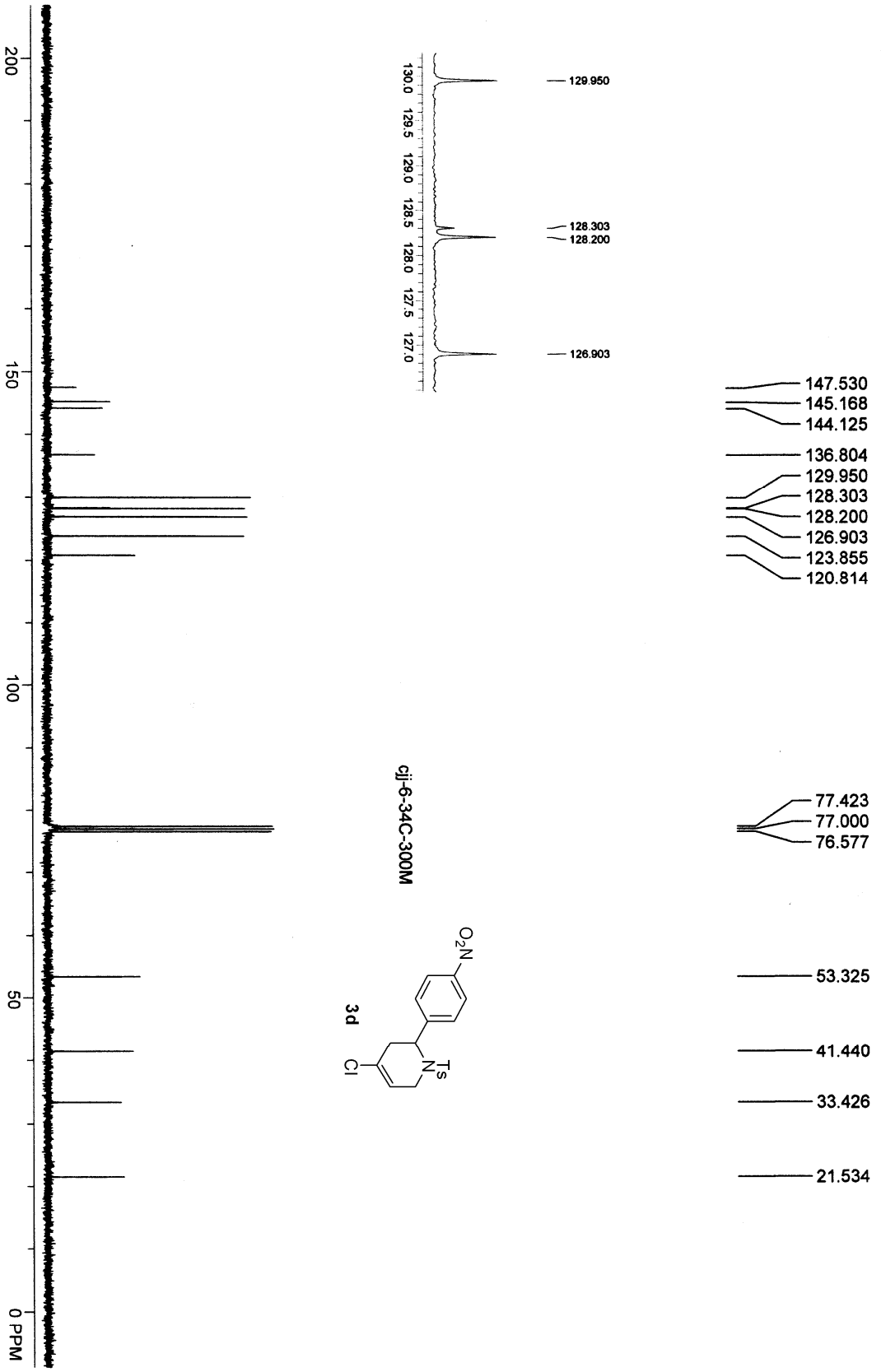
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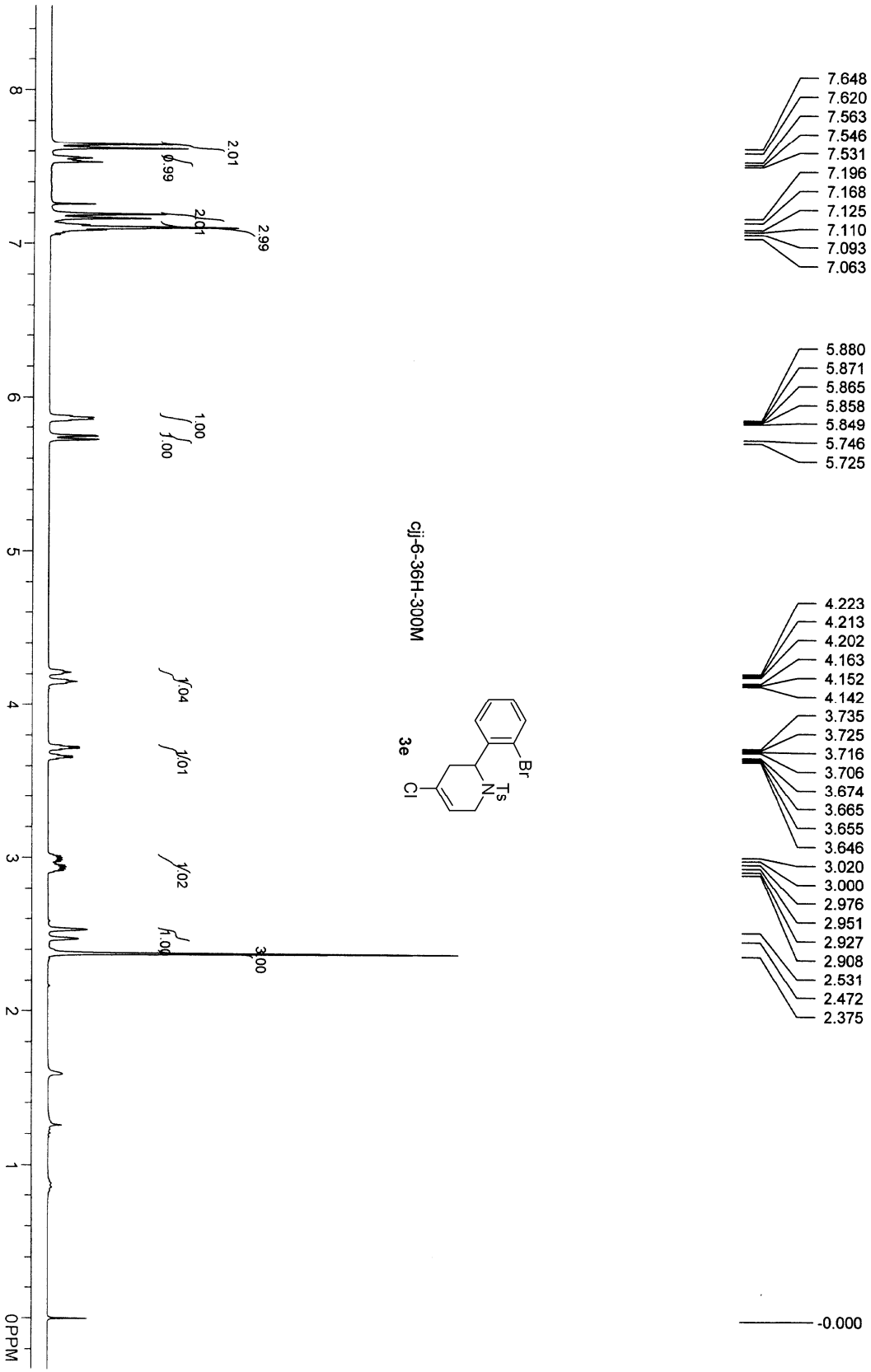
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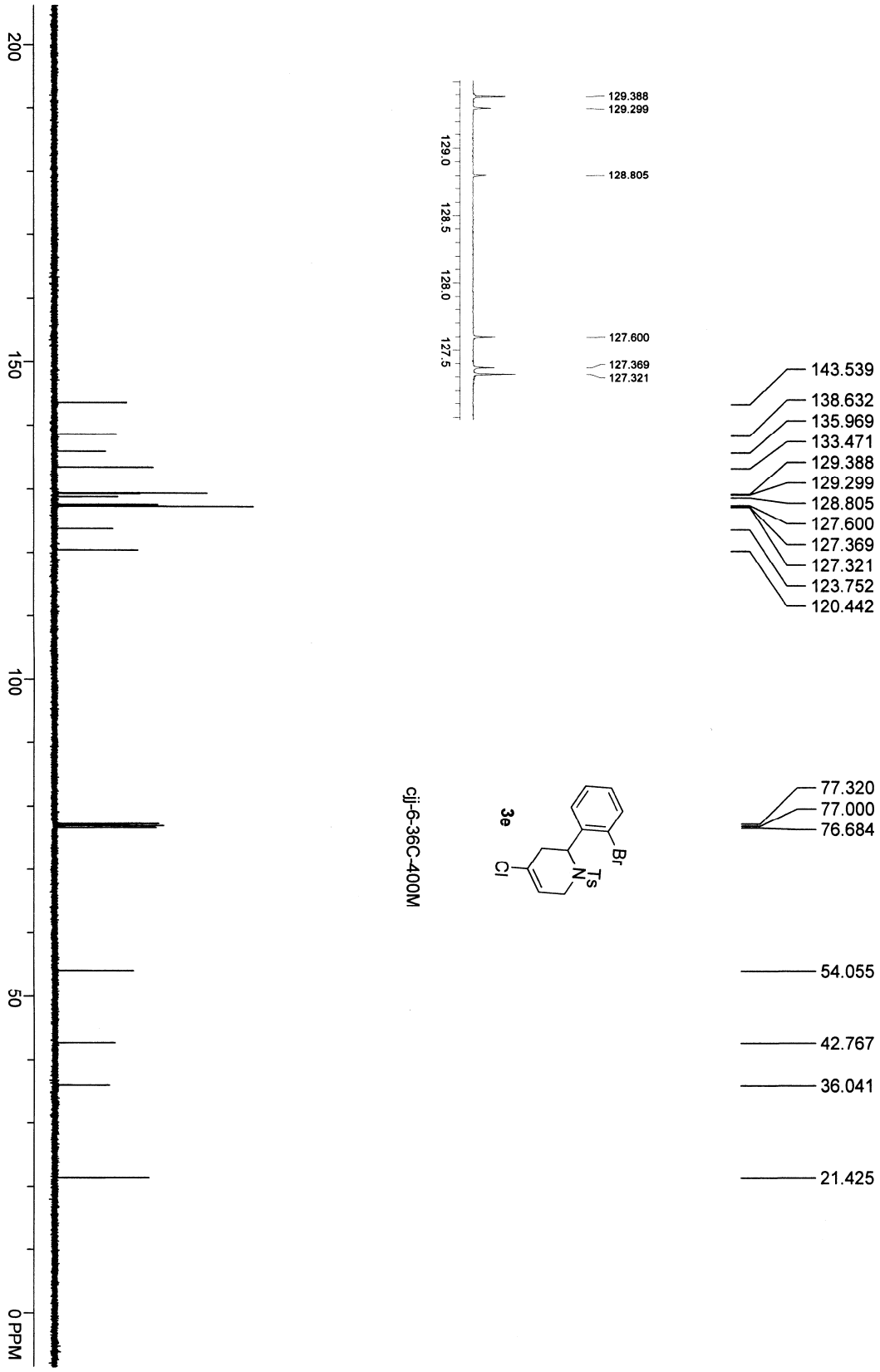
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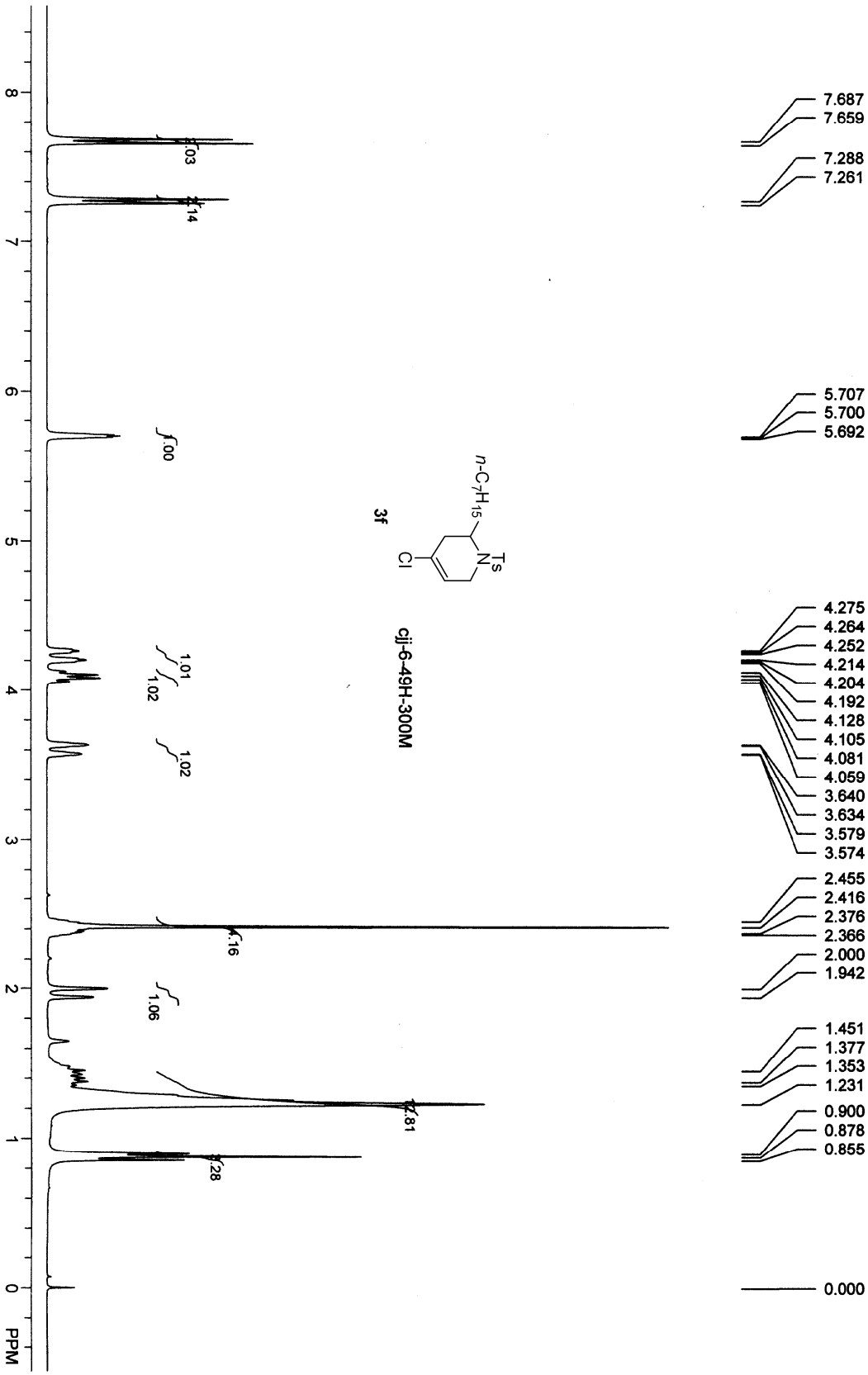
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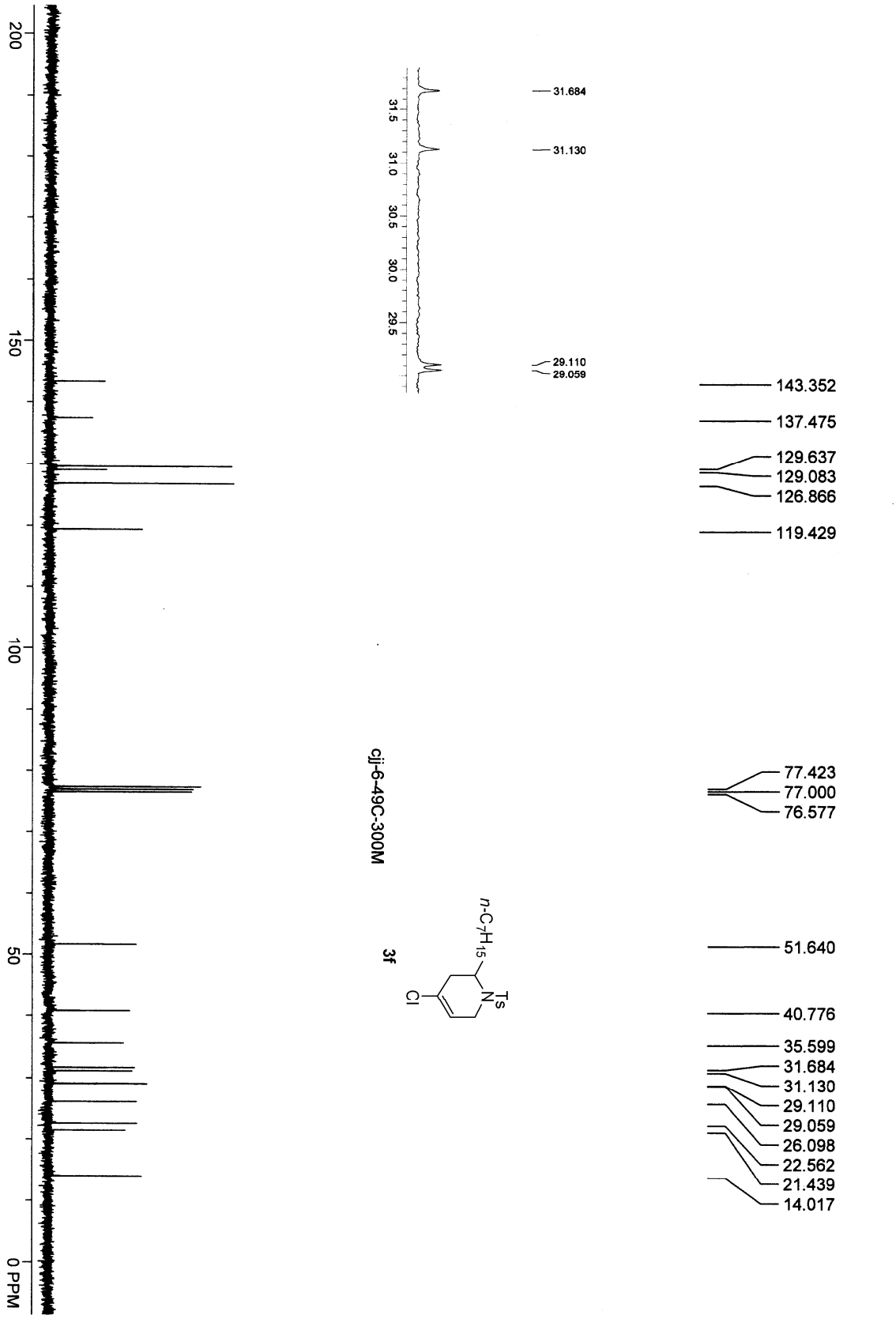
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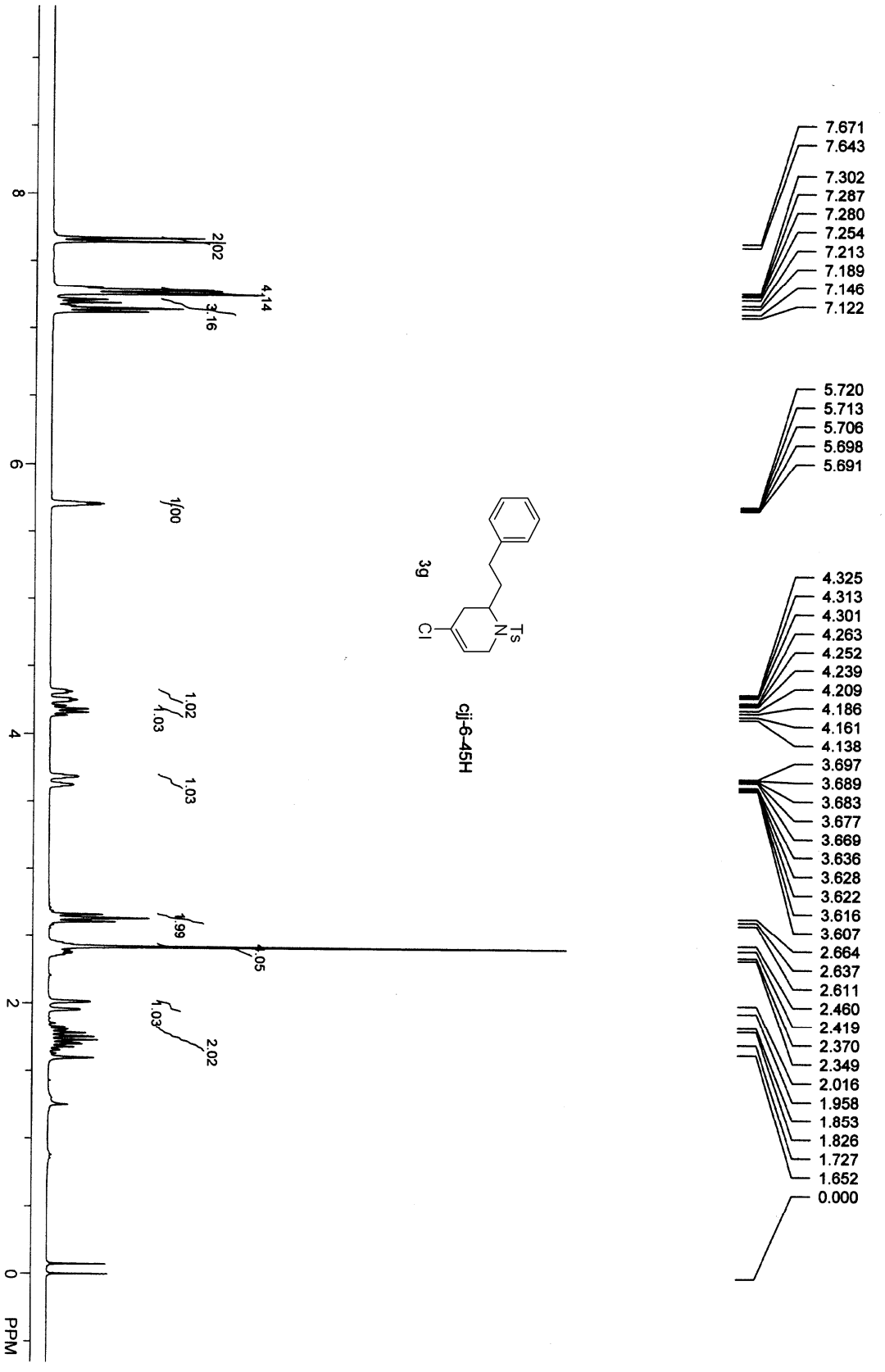
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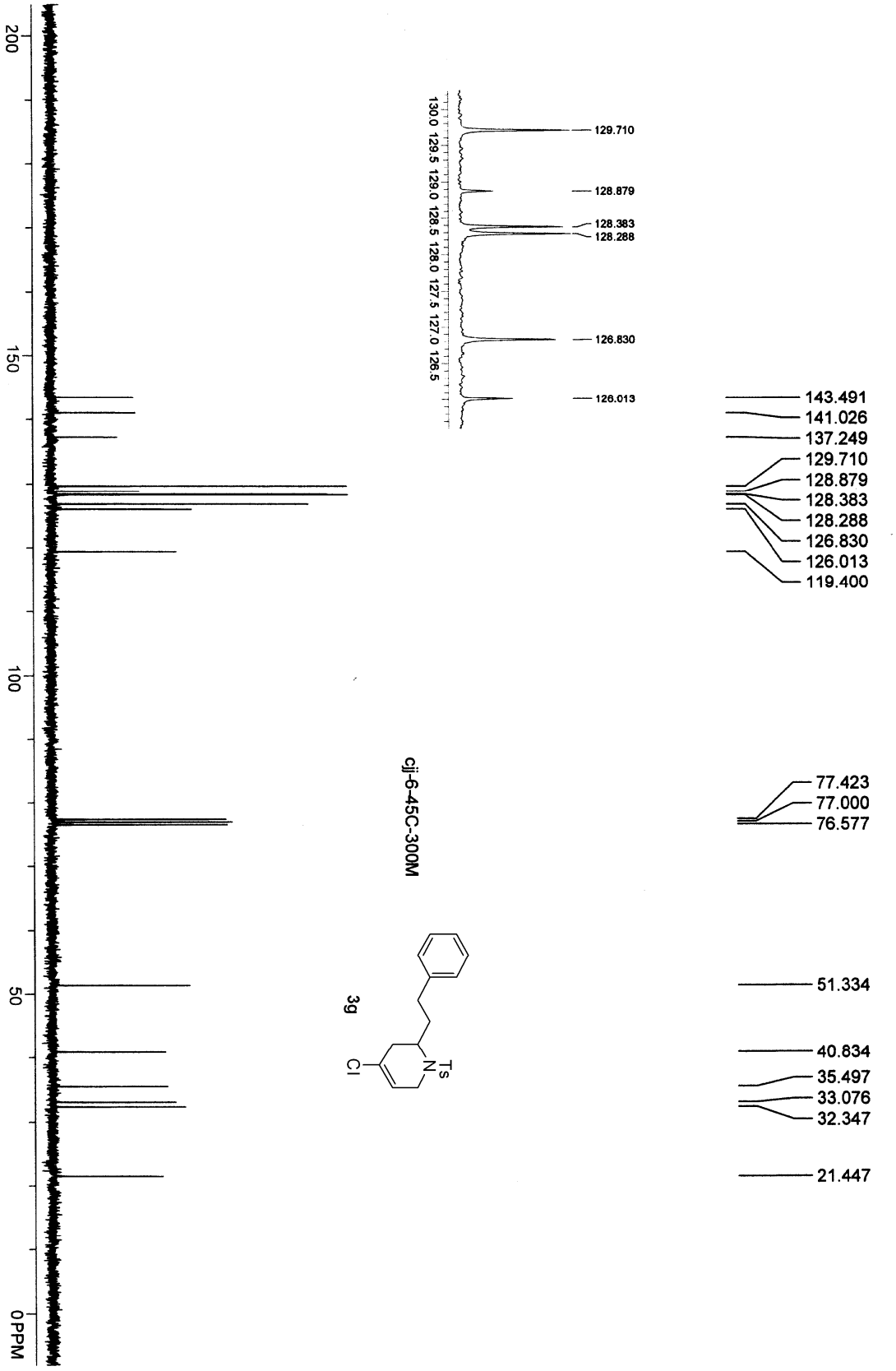
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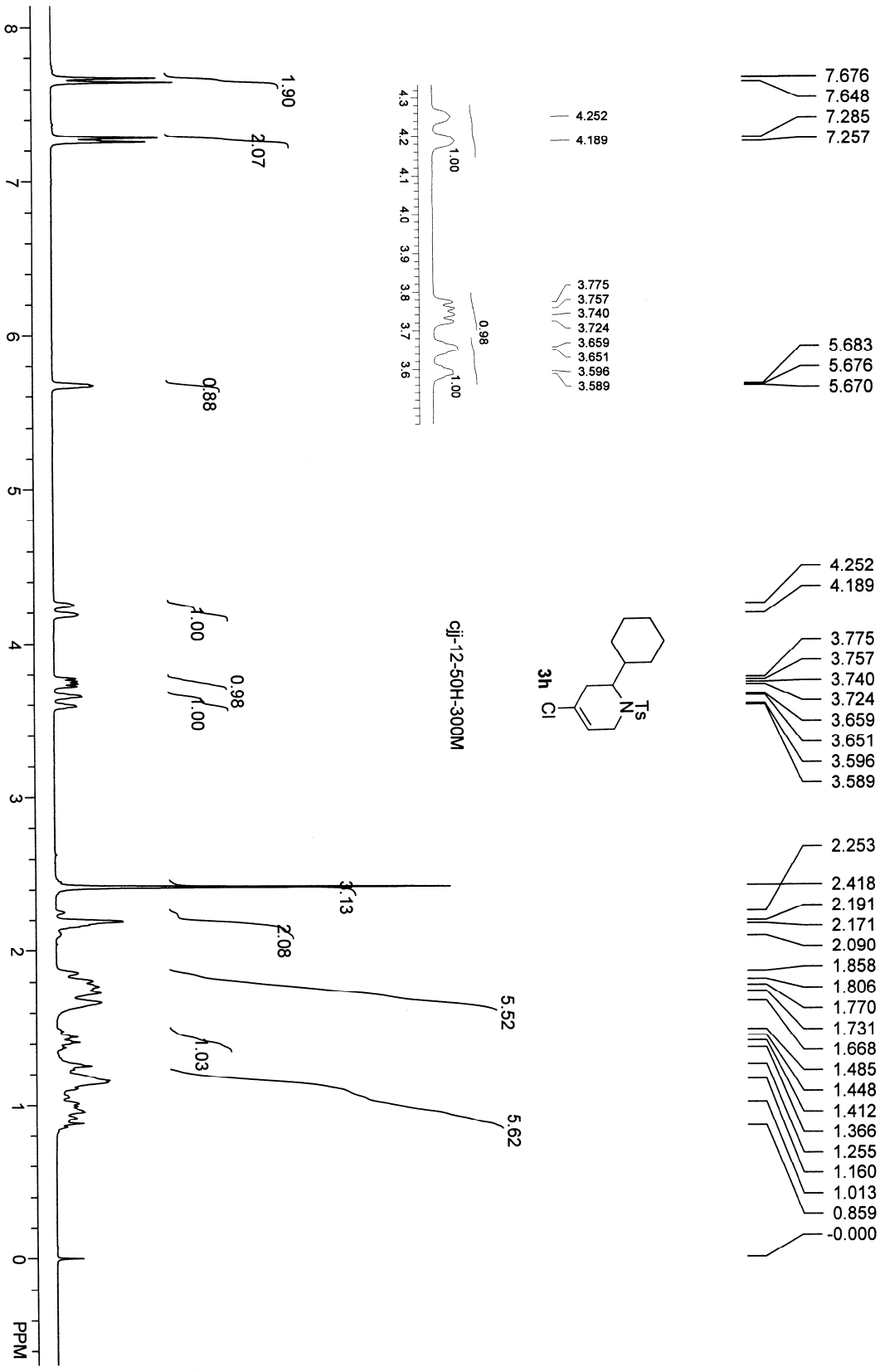
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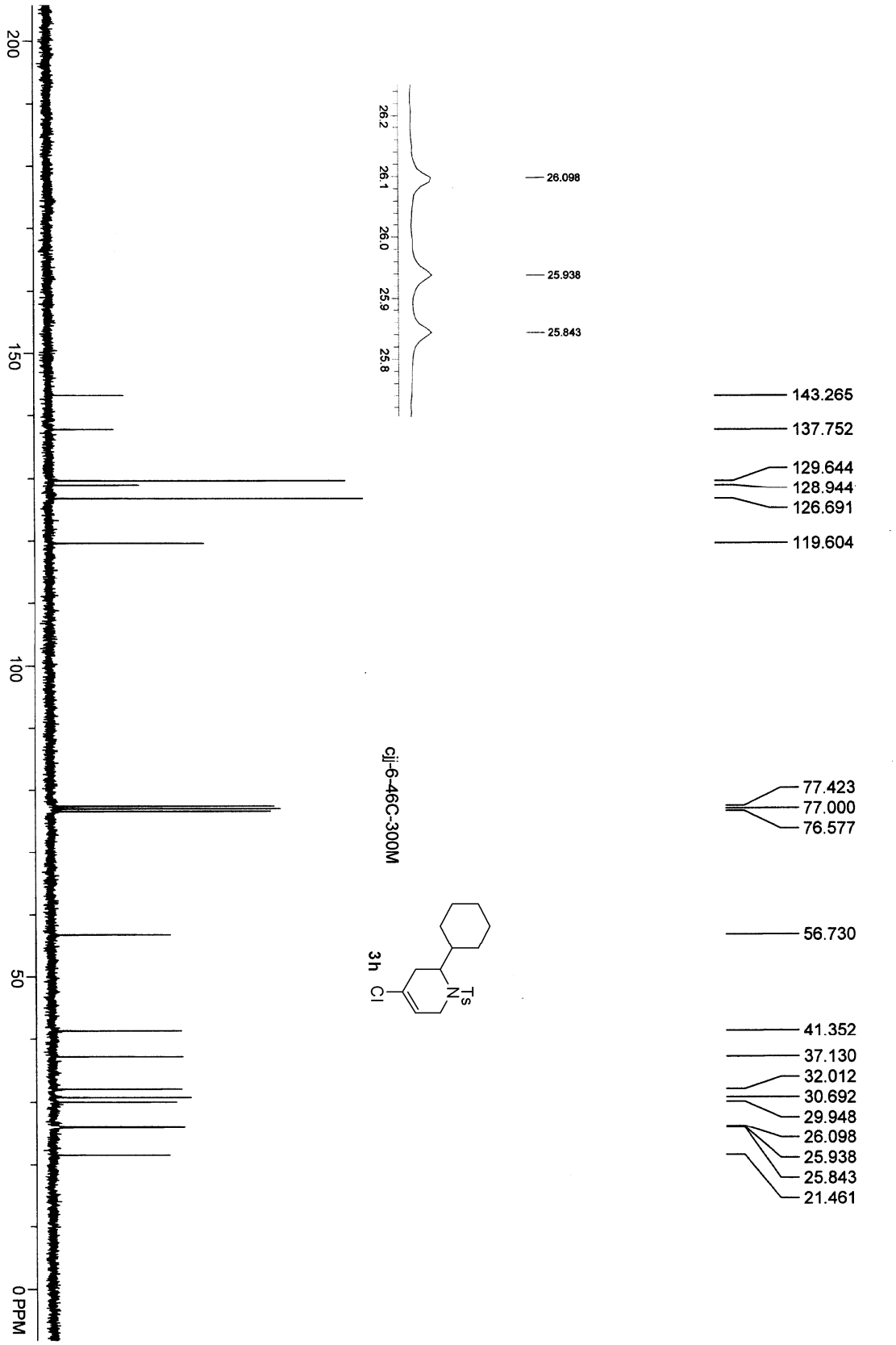
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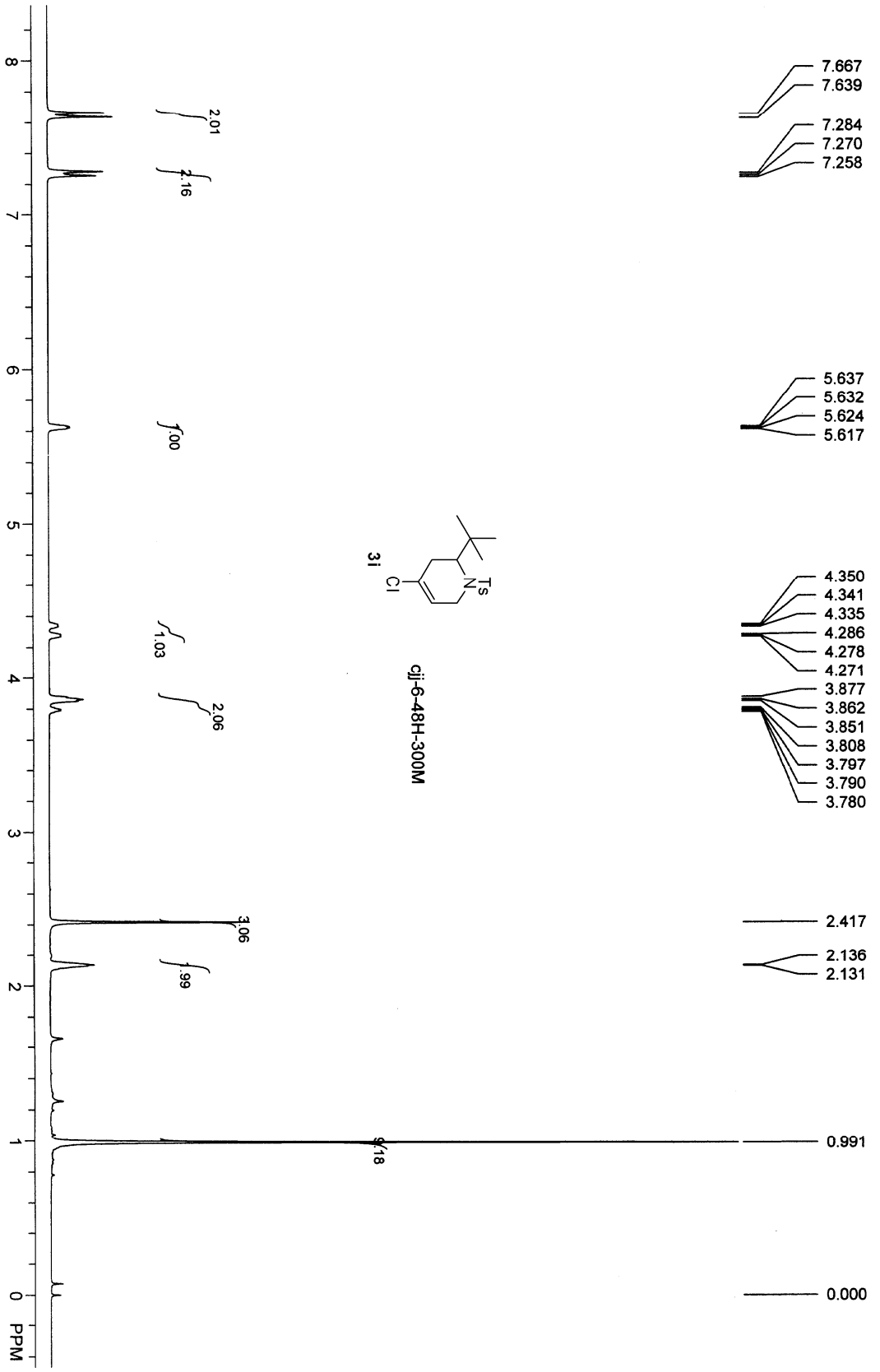
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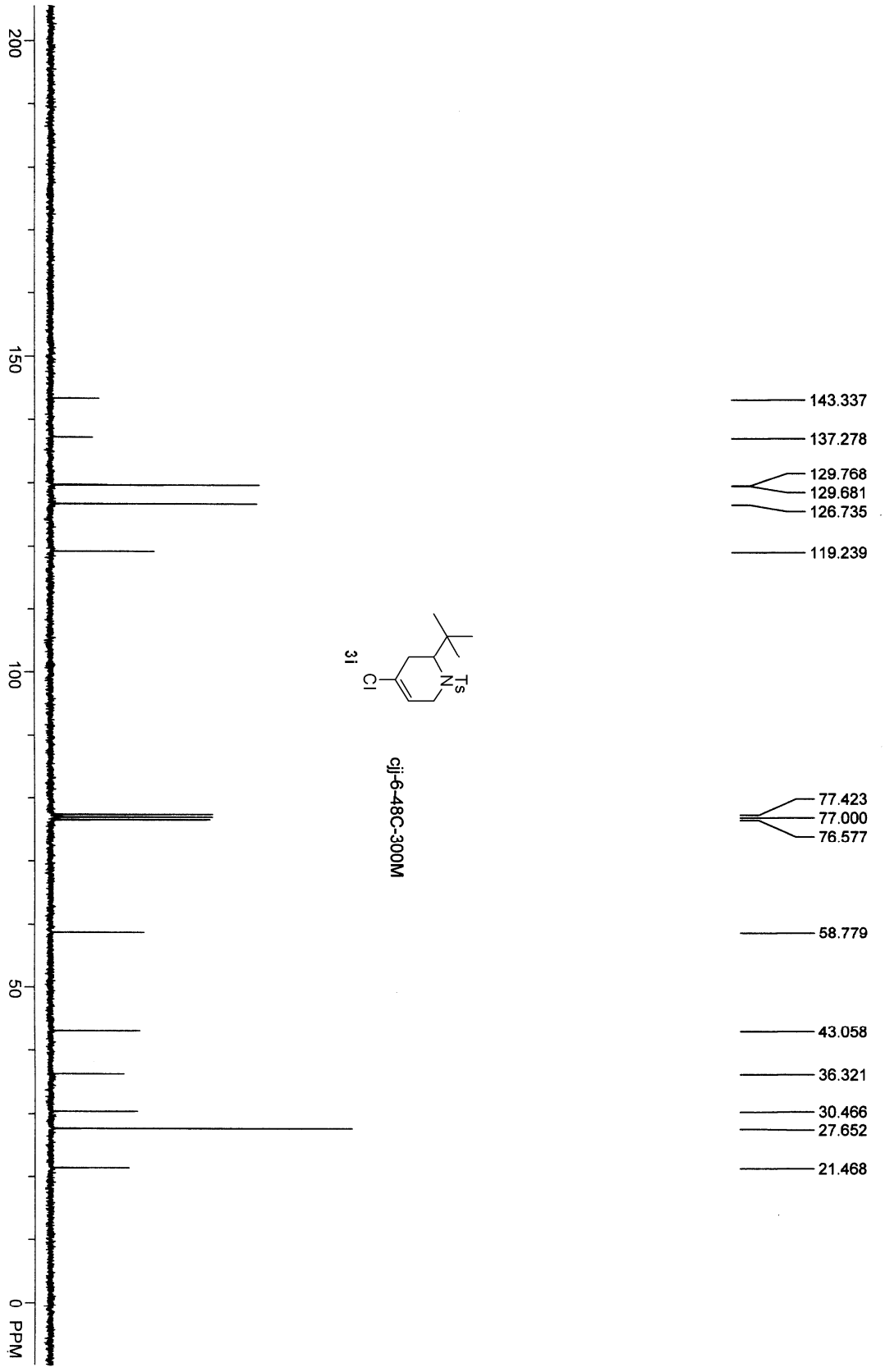
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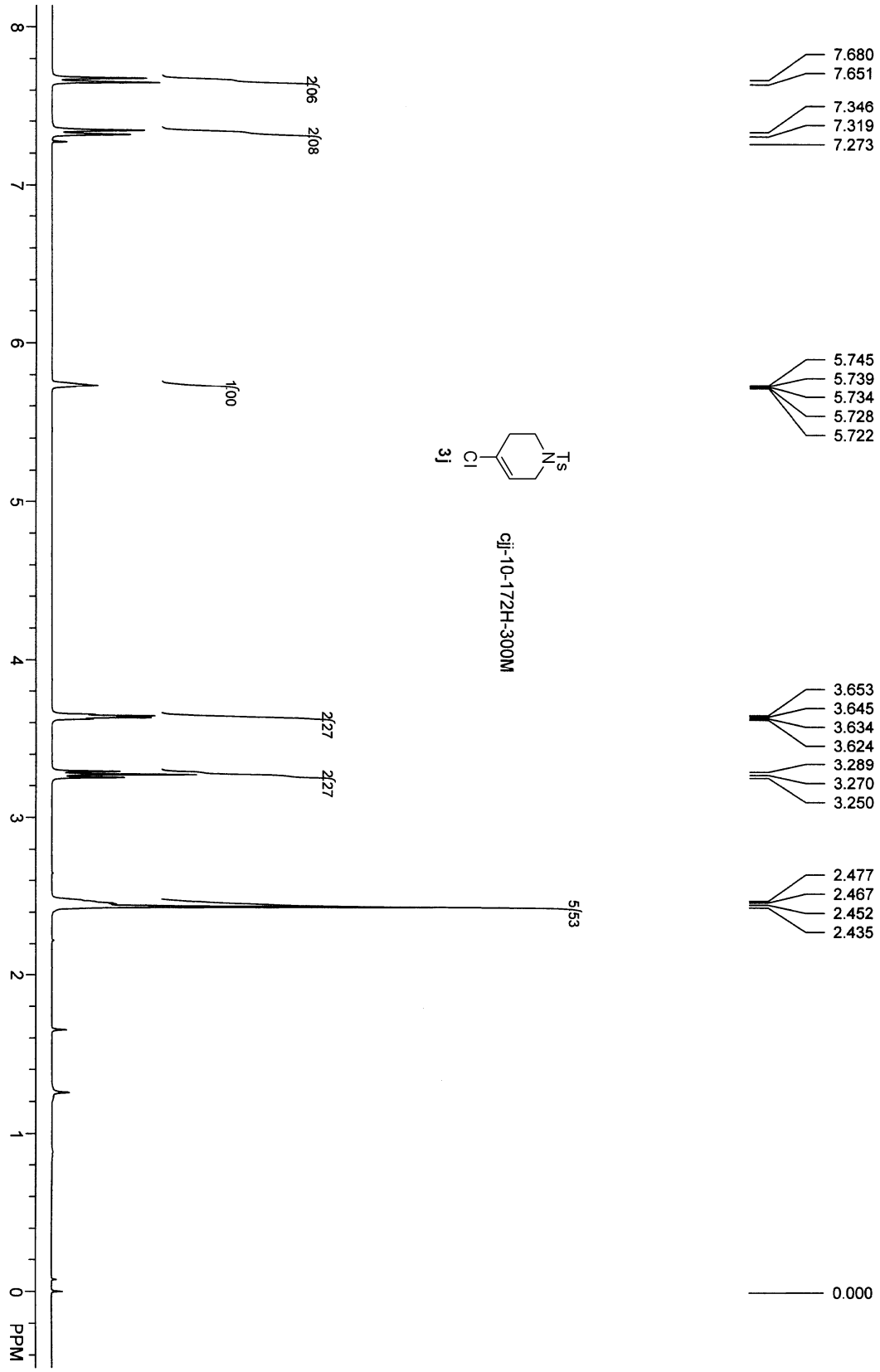
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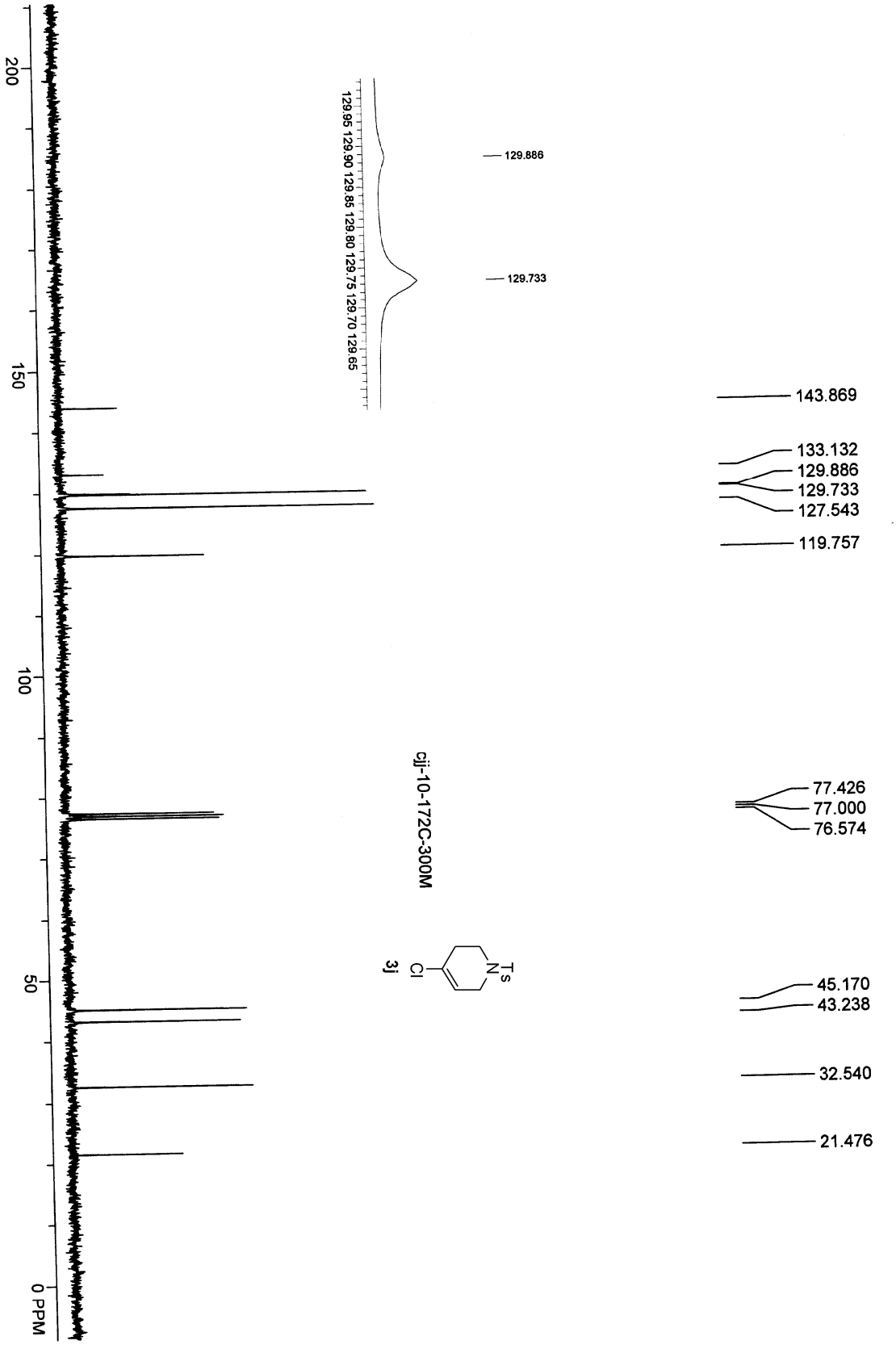
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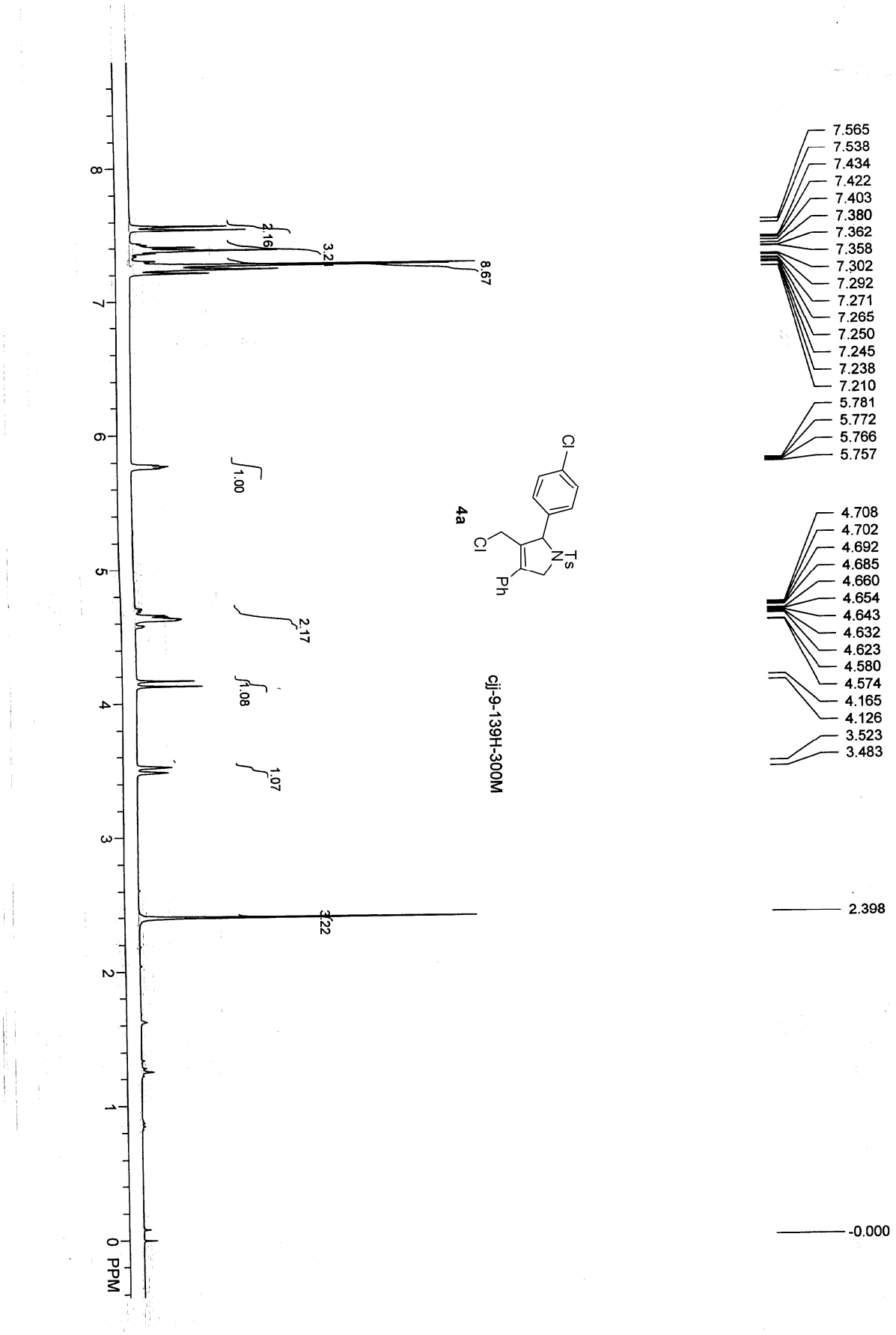
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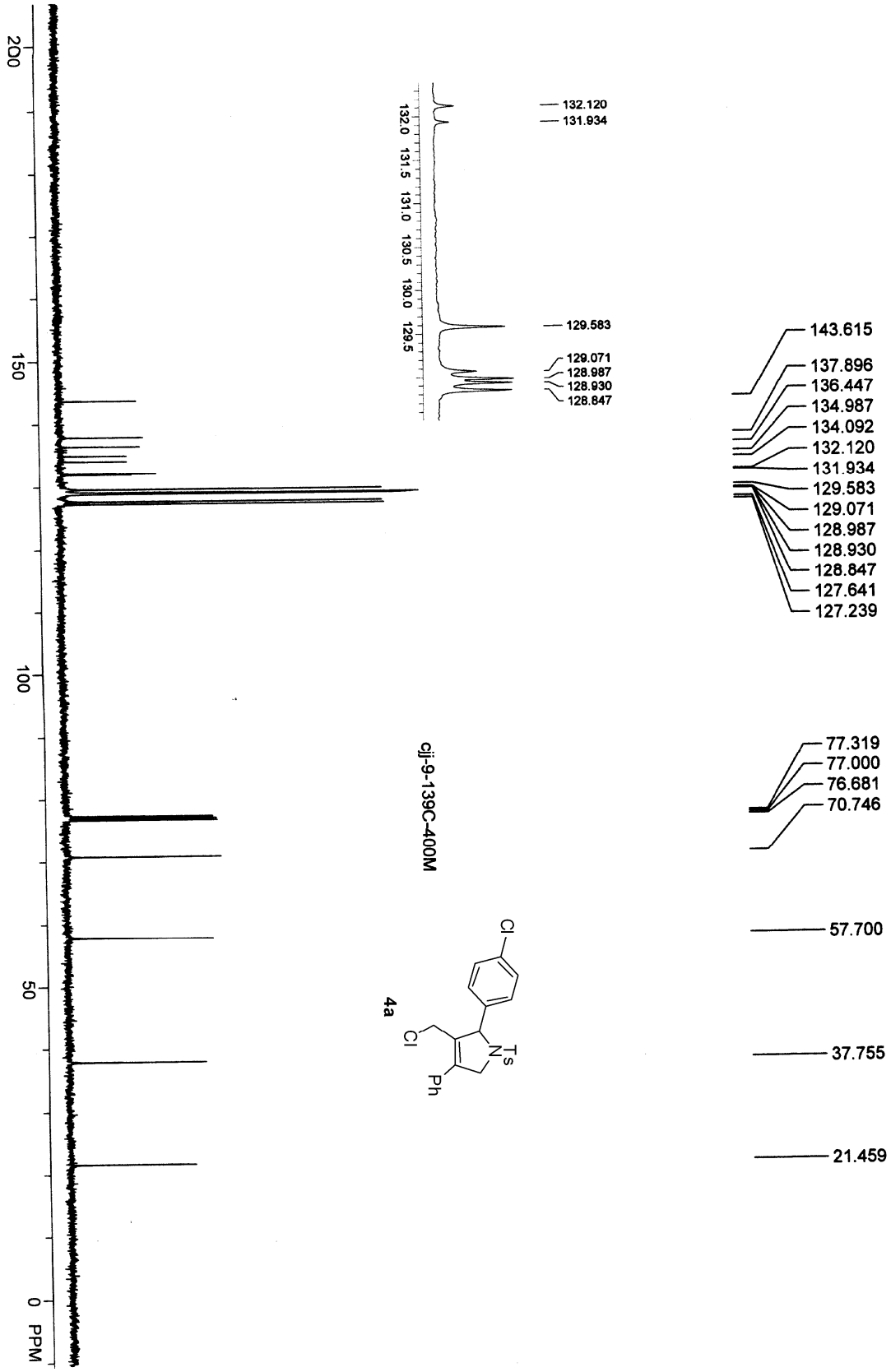
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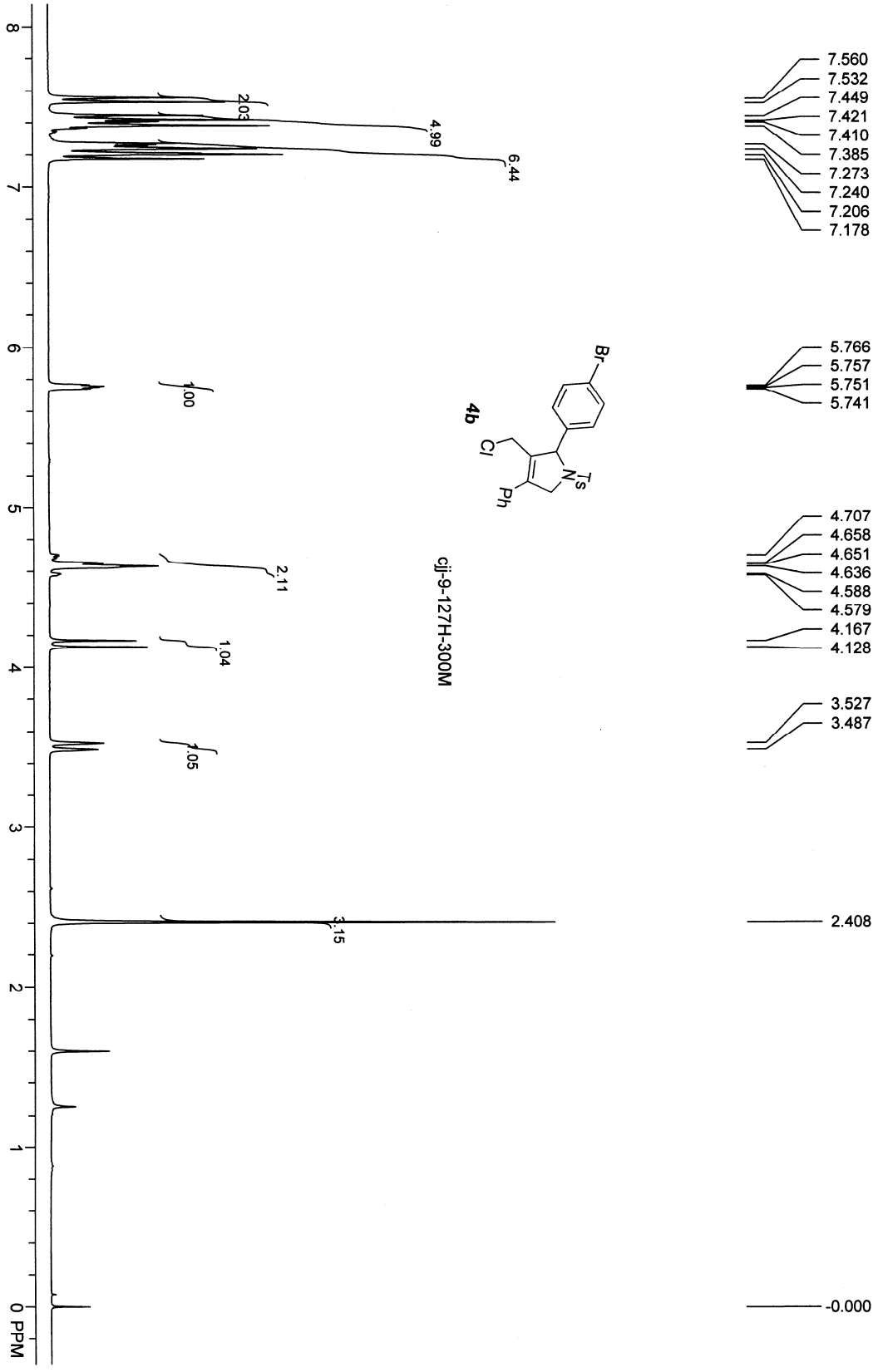
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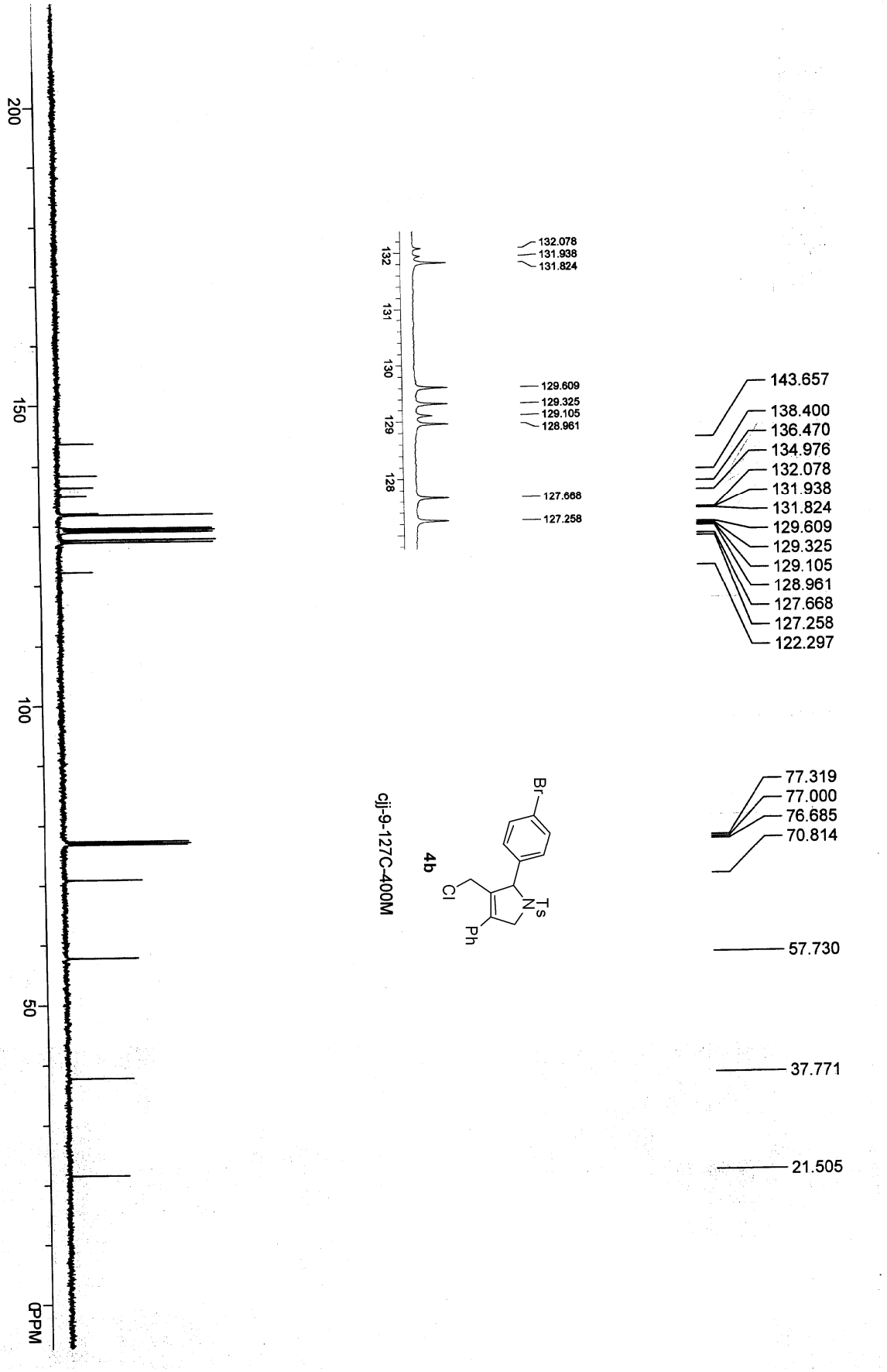
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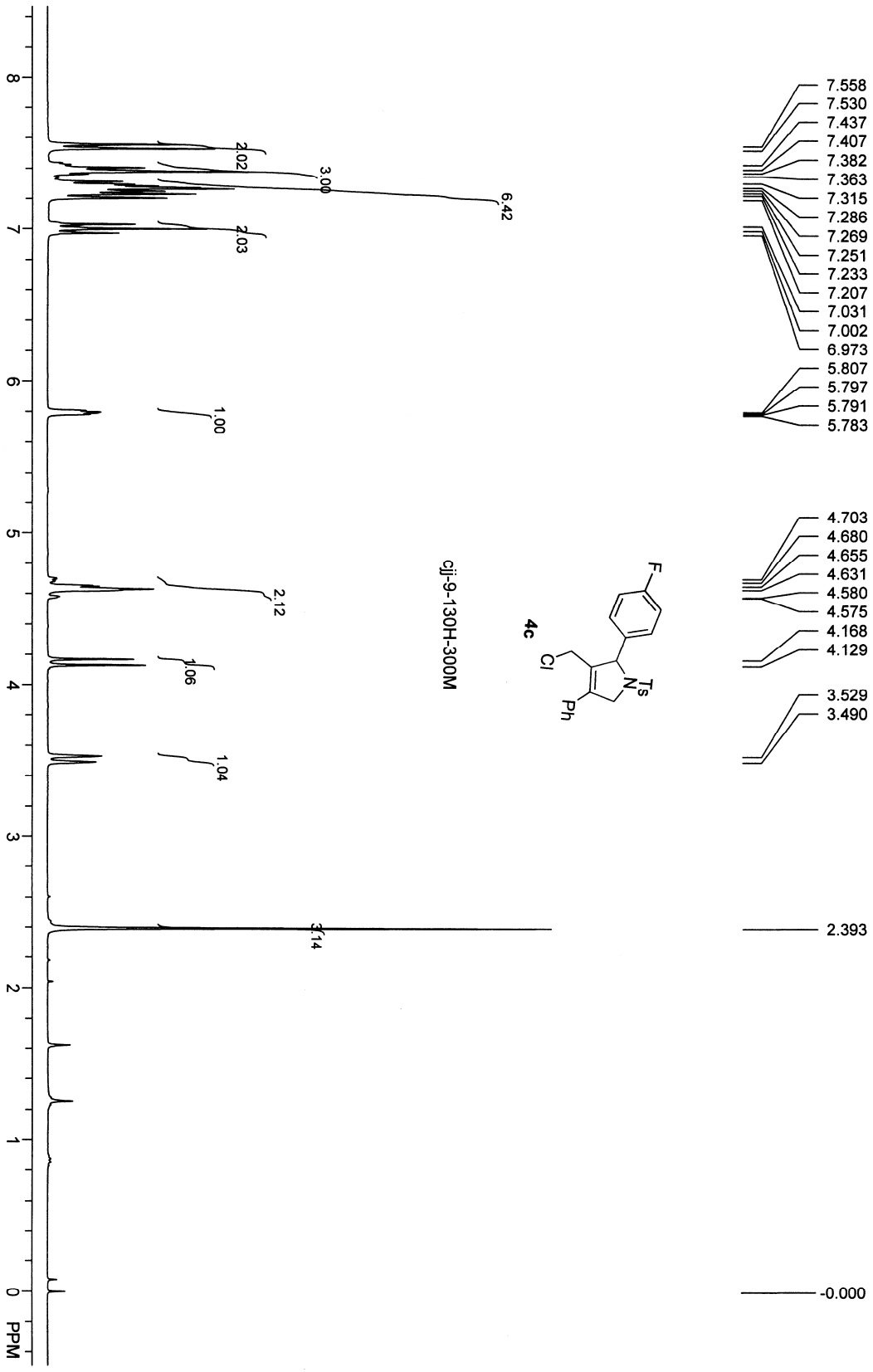
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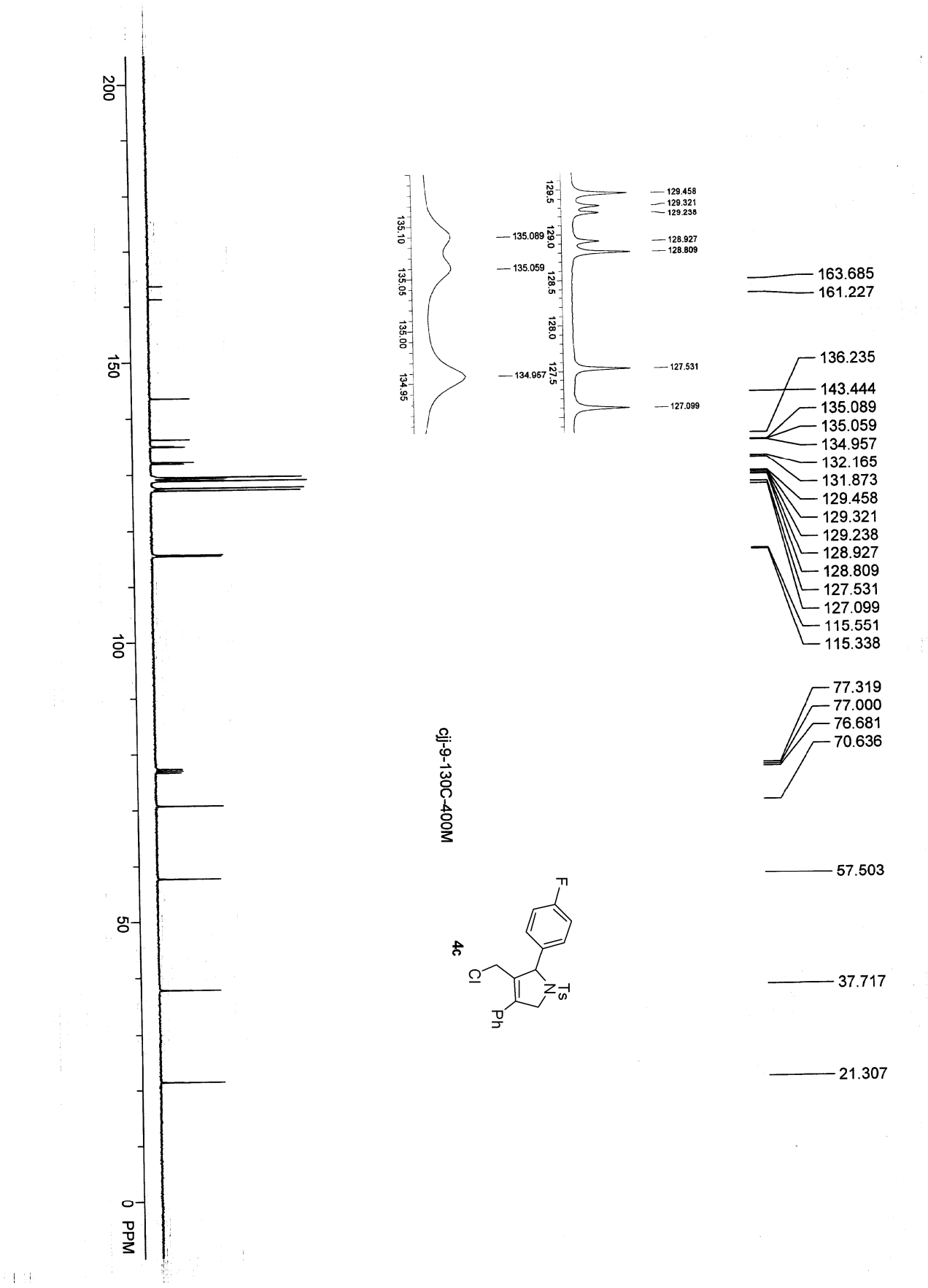
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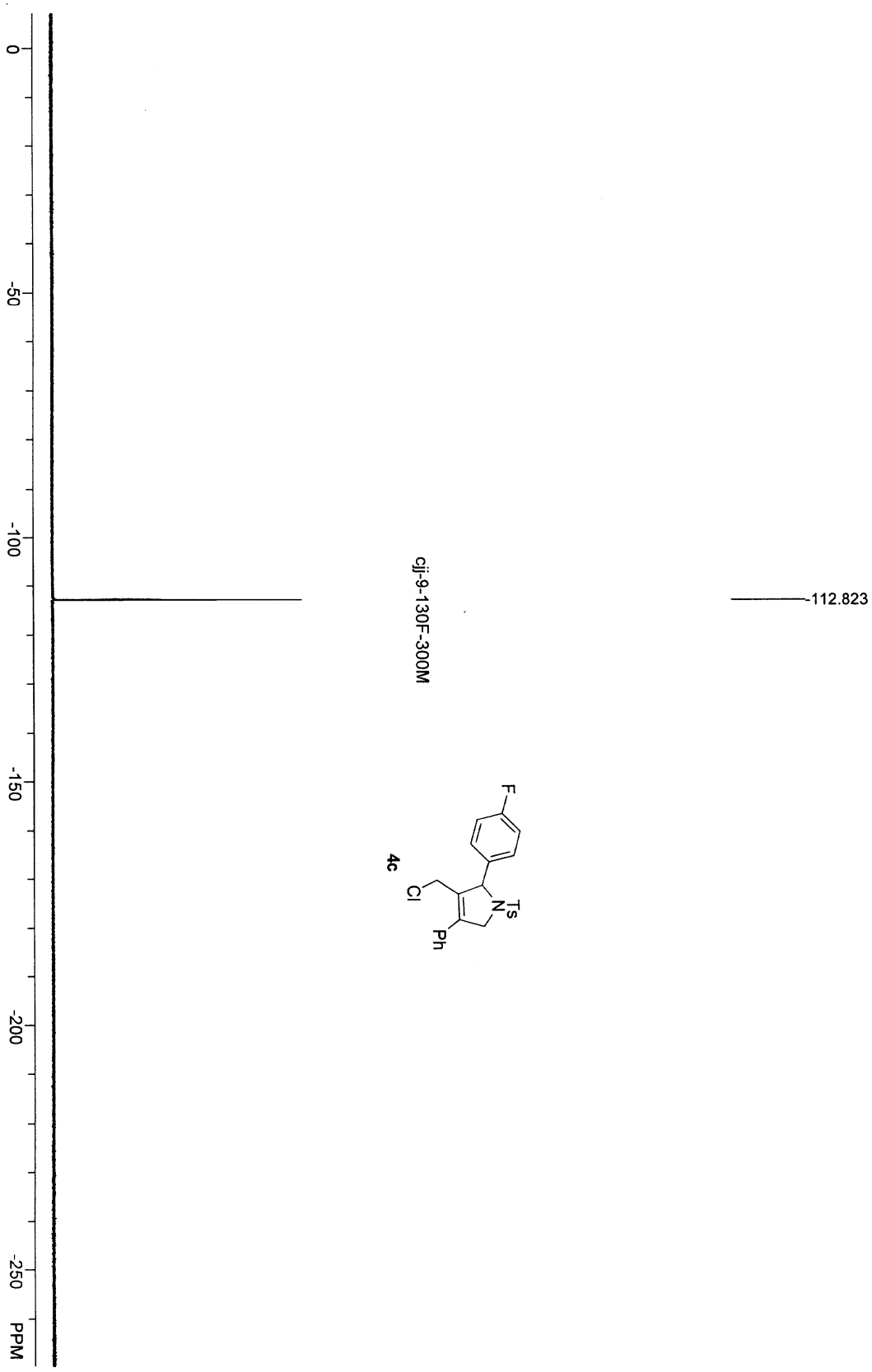
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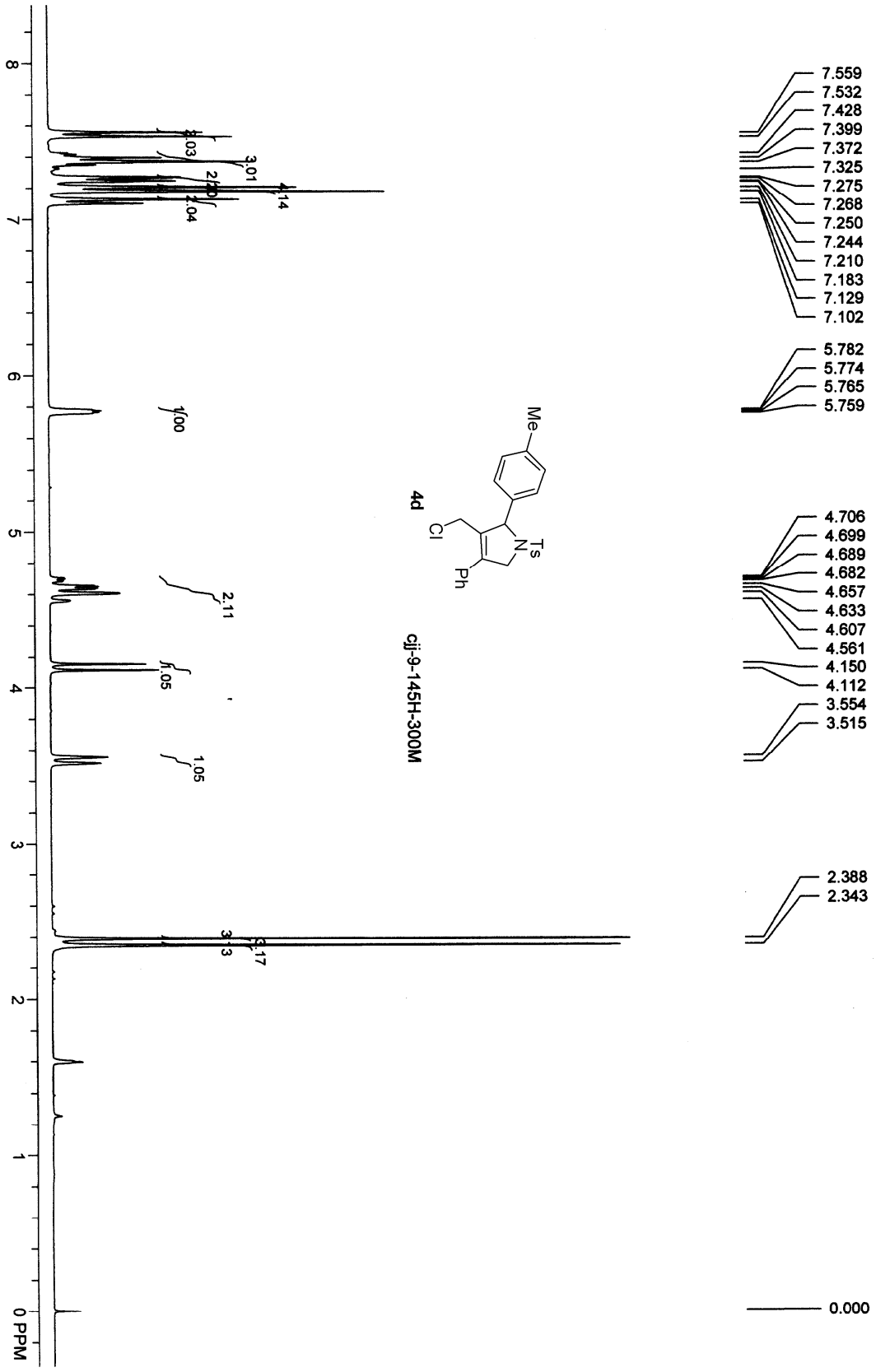
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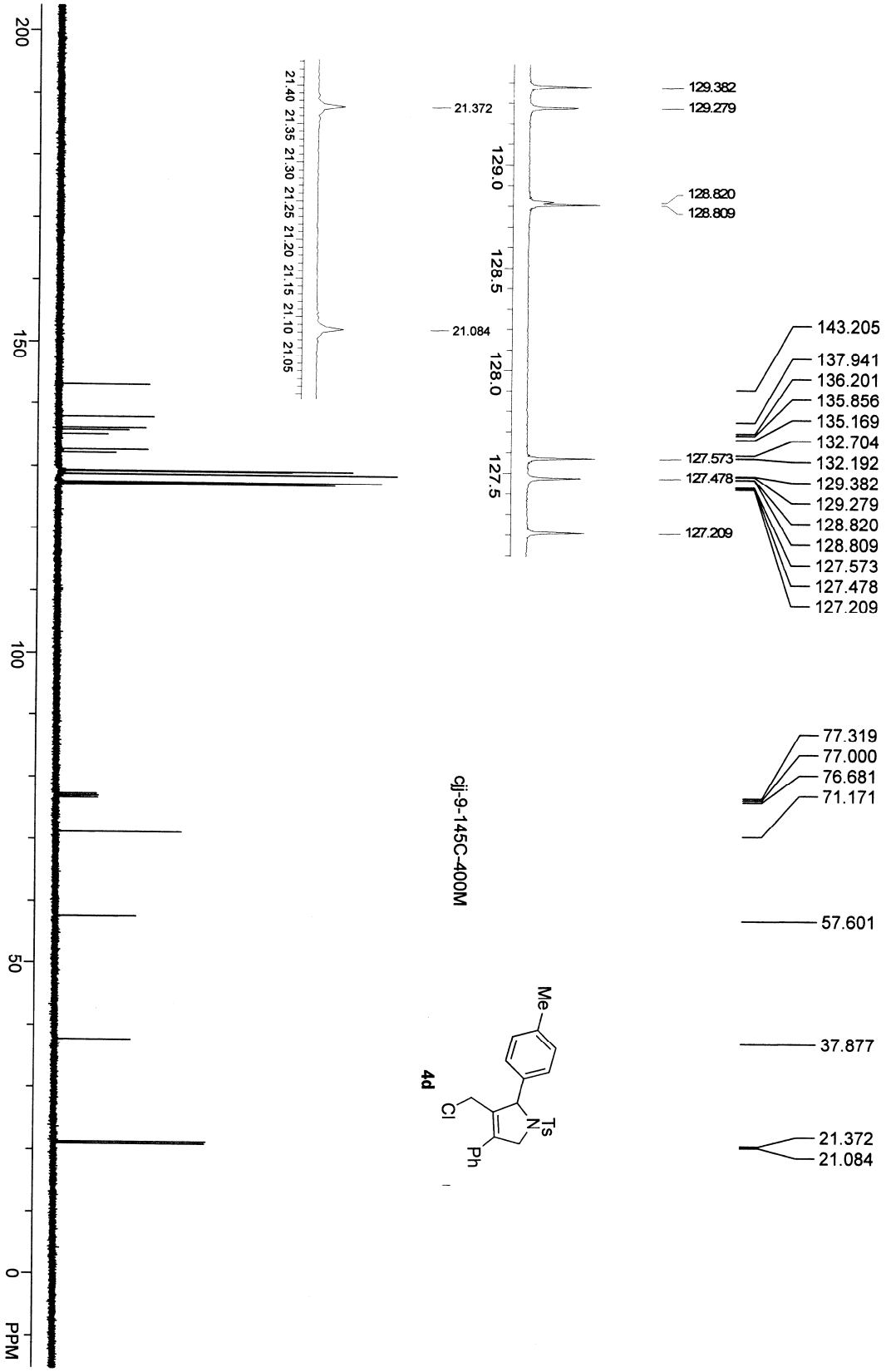
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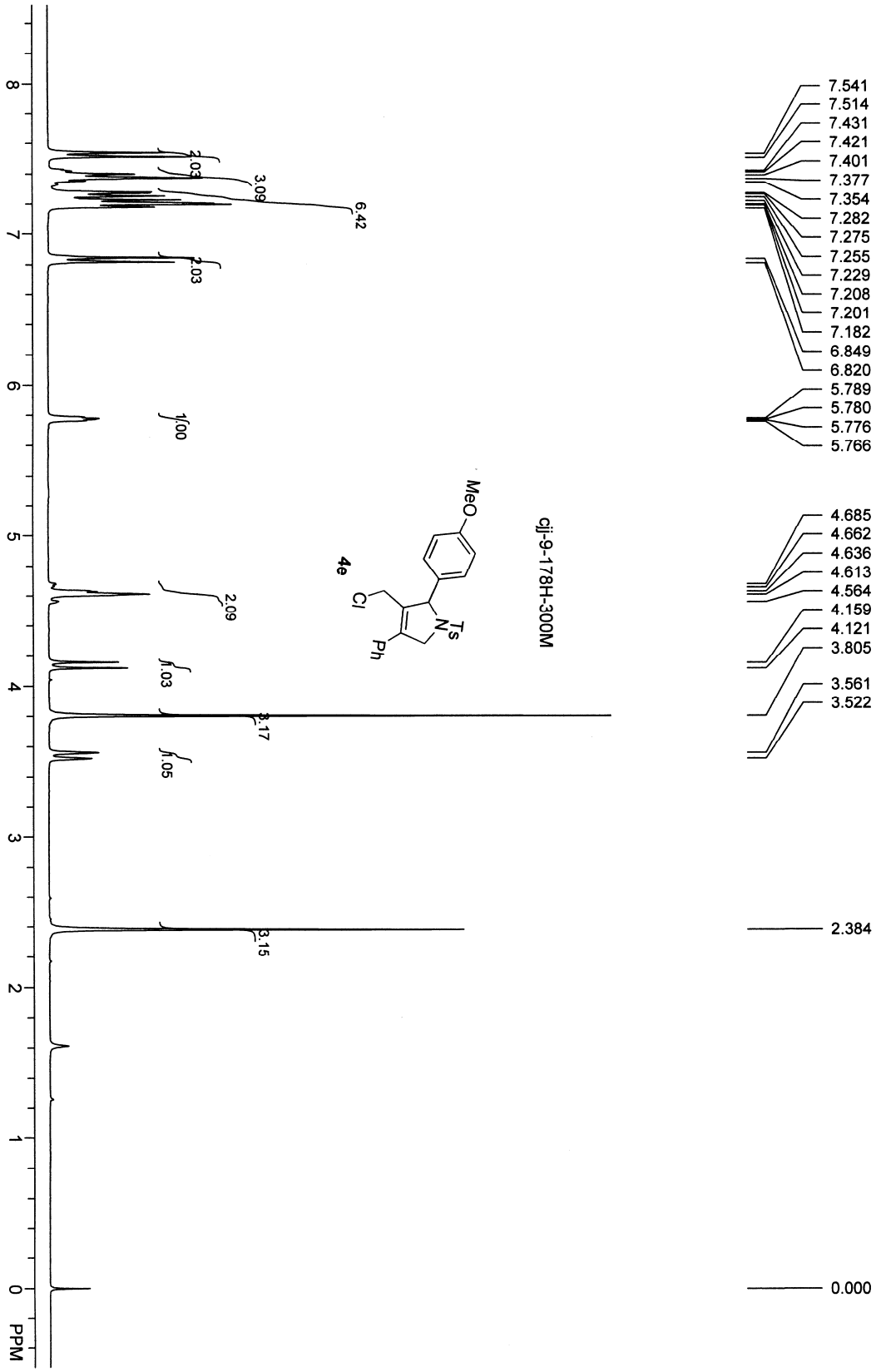
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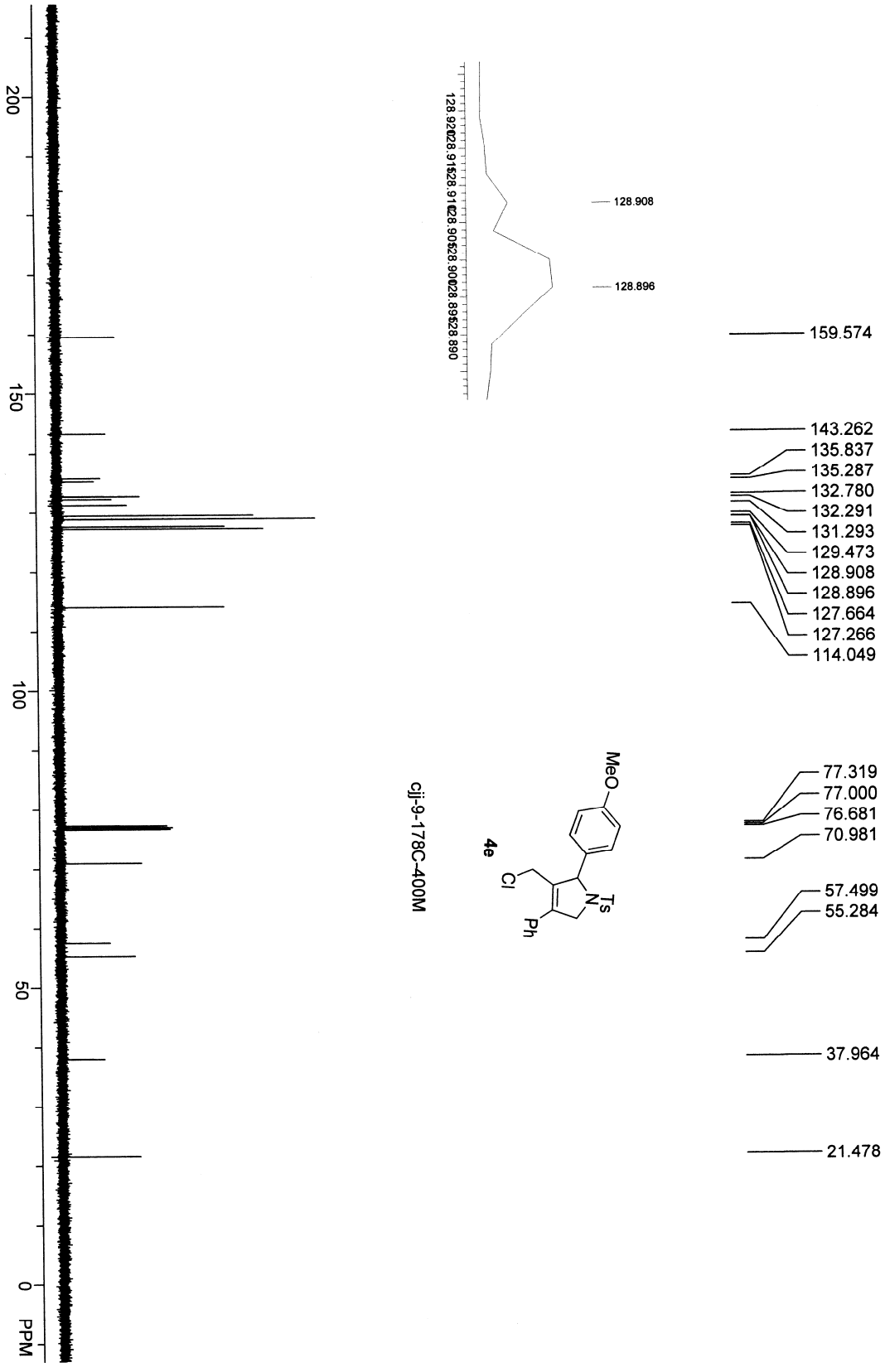
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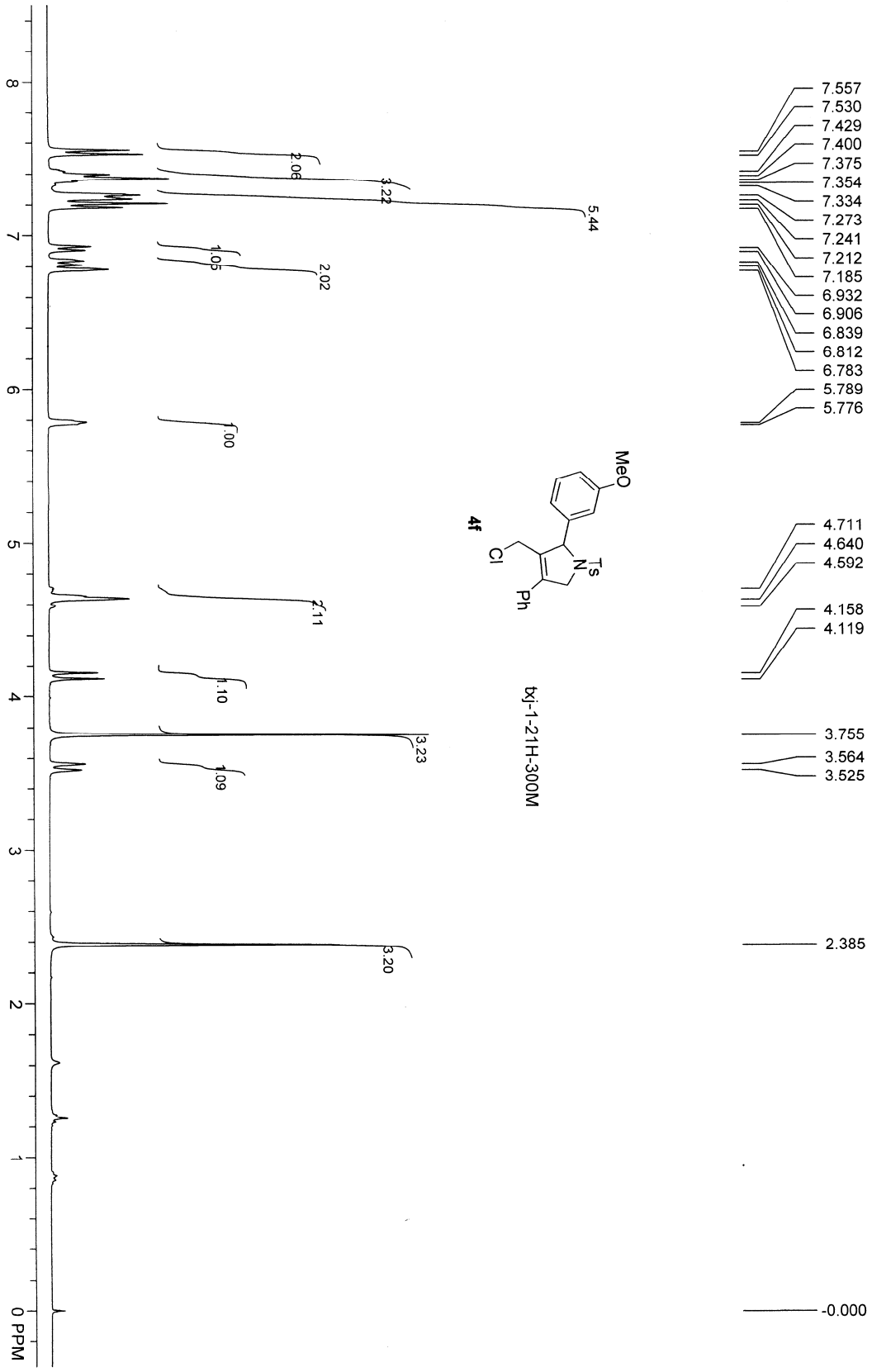
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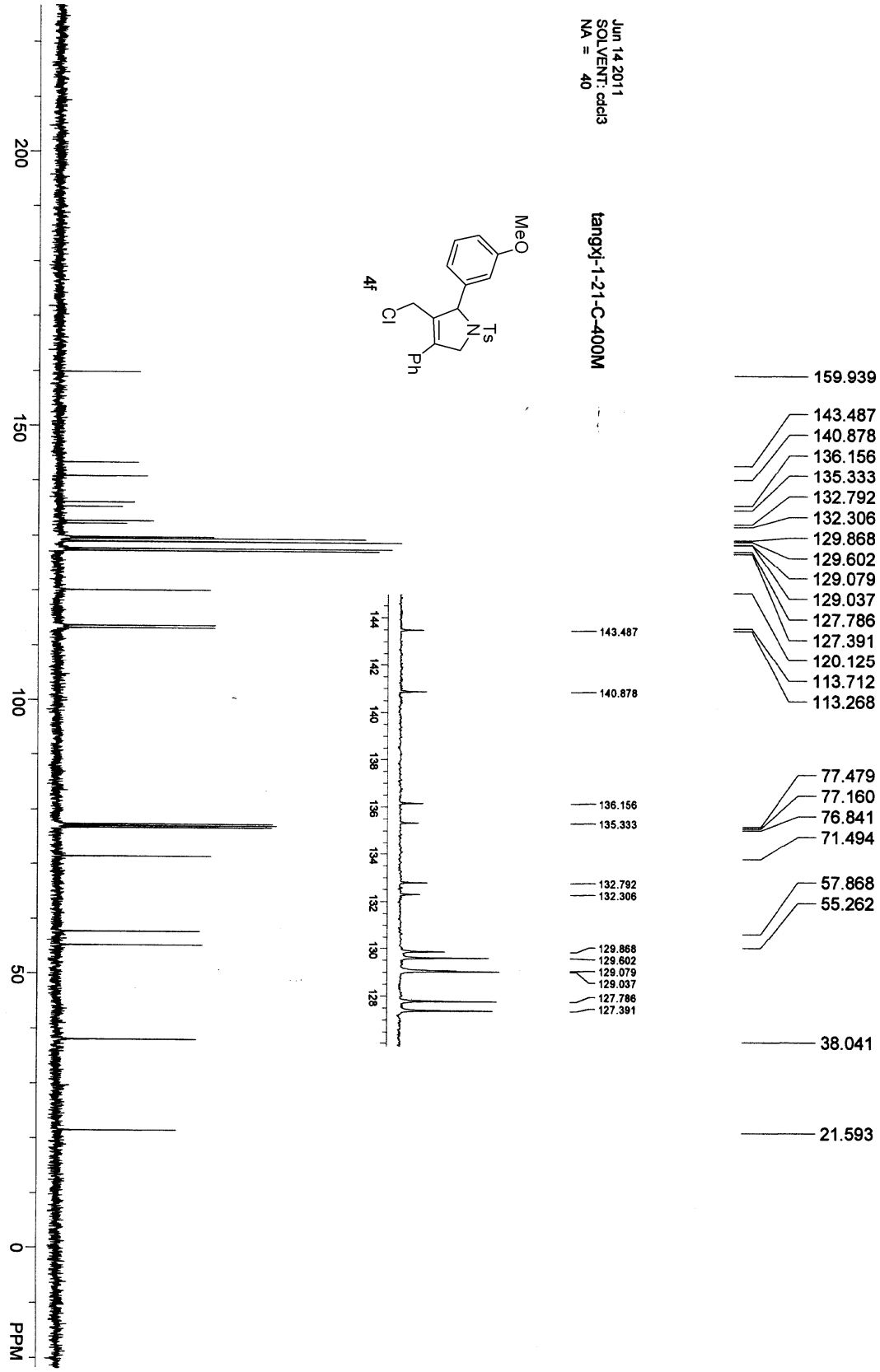
Jun 14 2011
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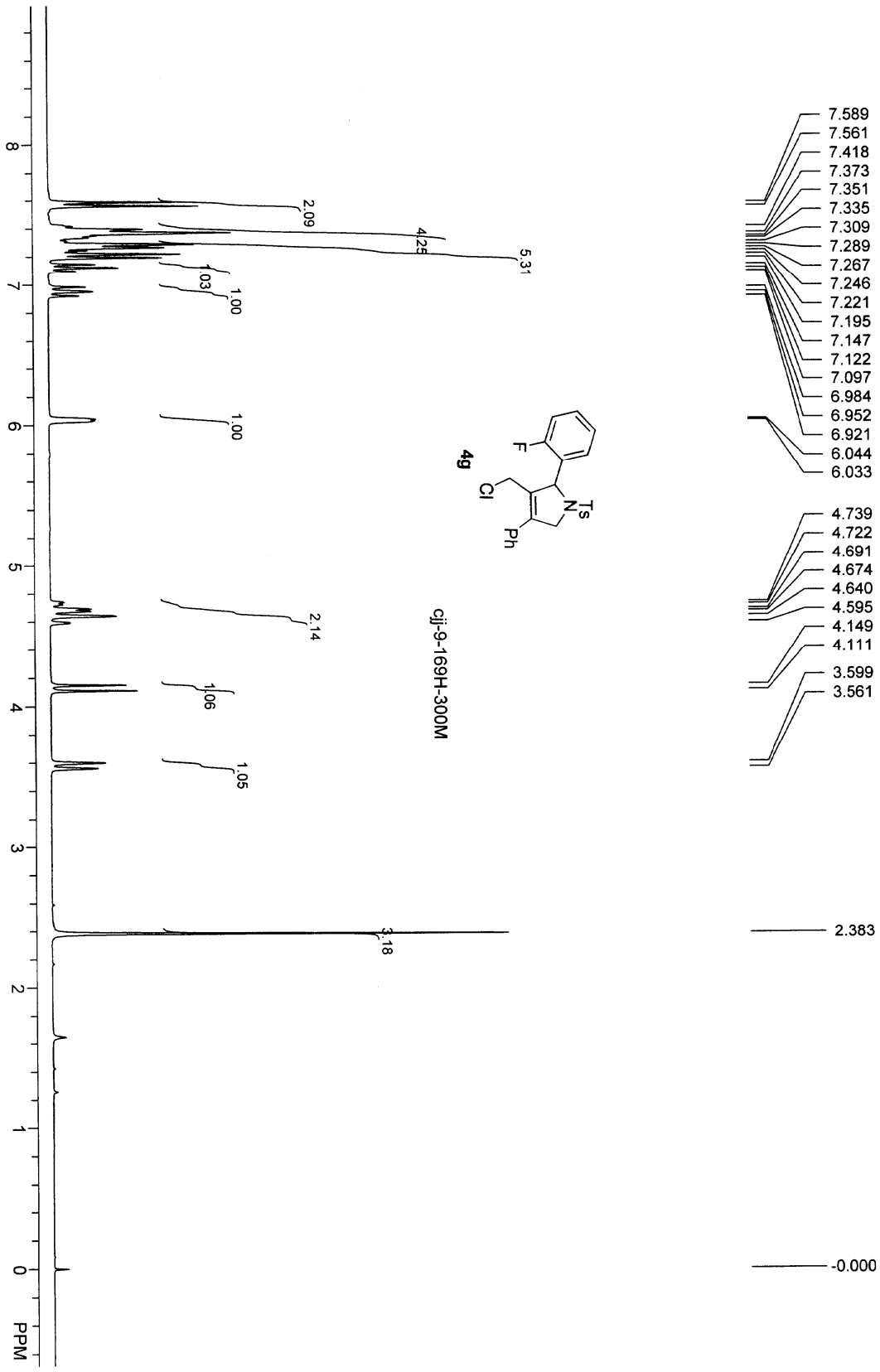
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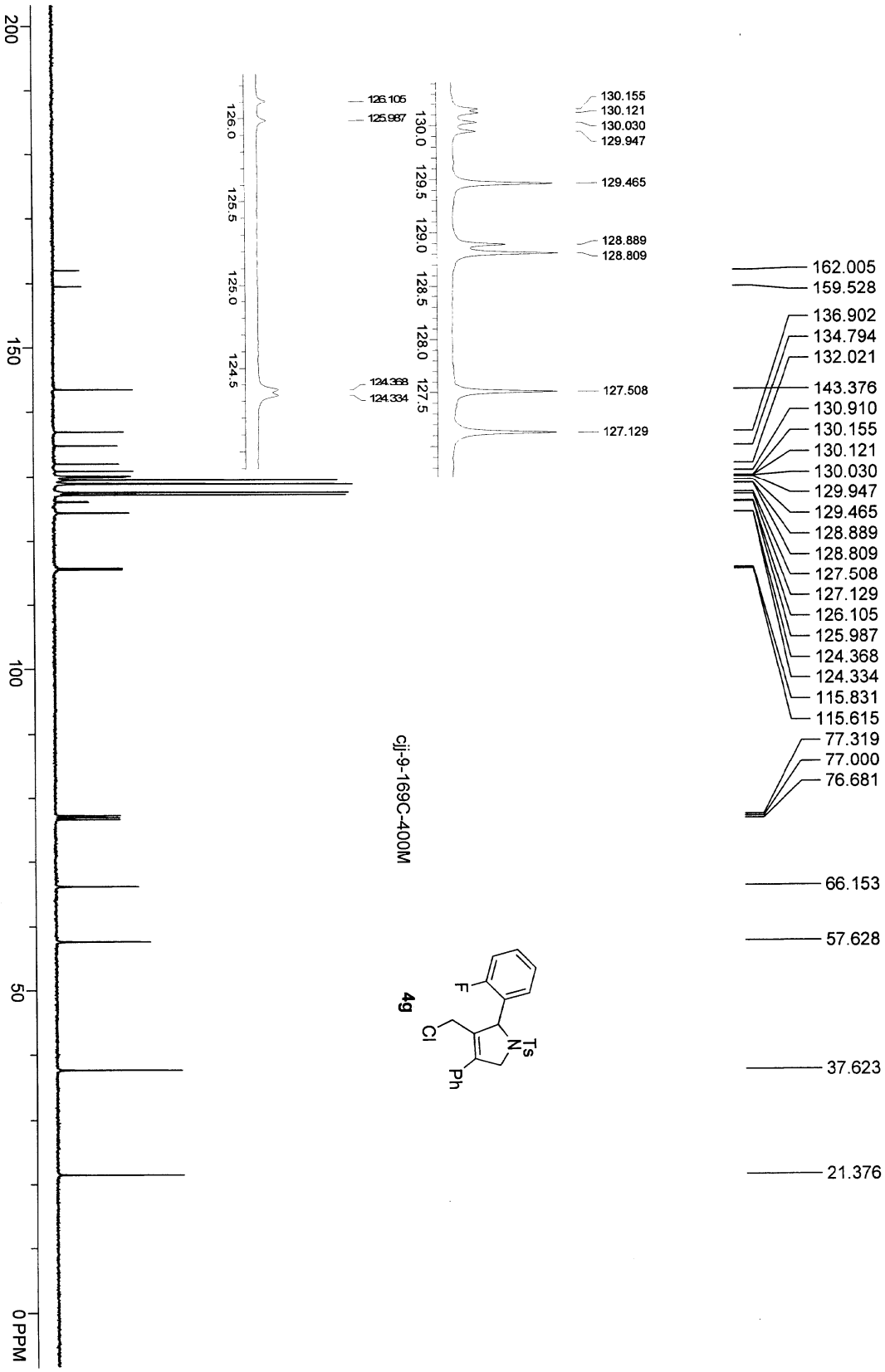
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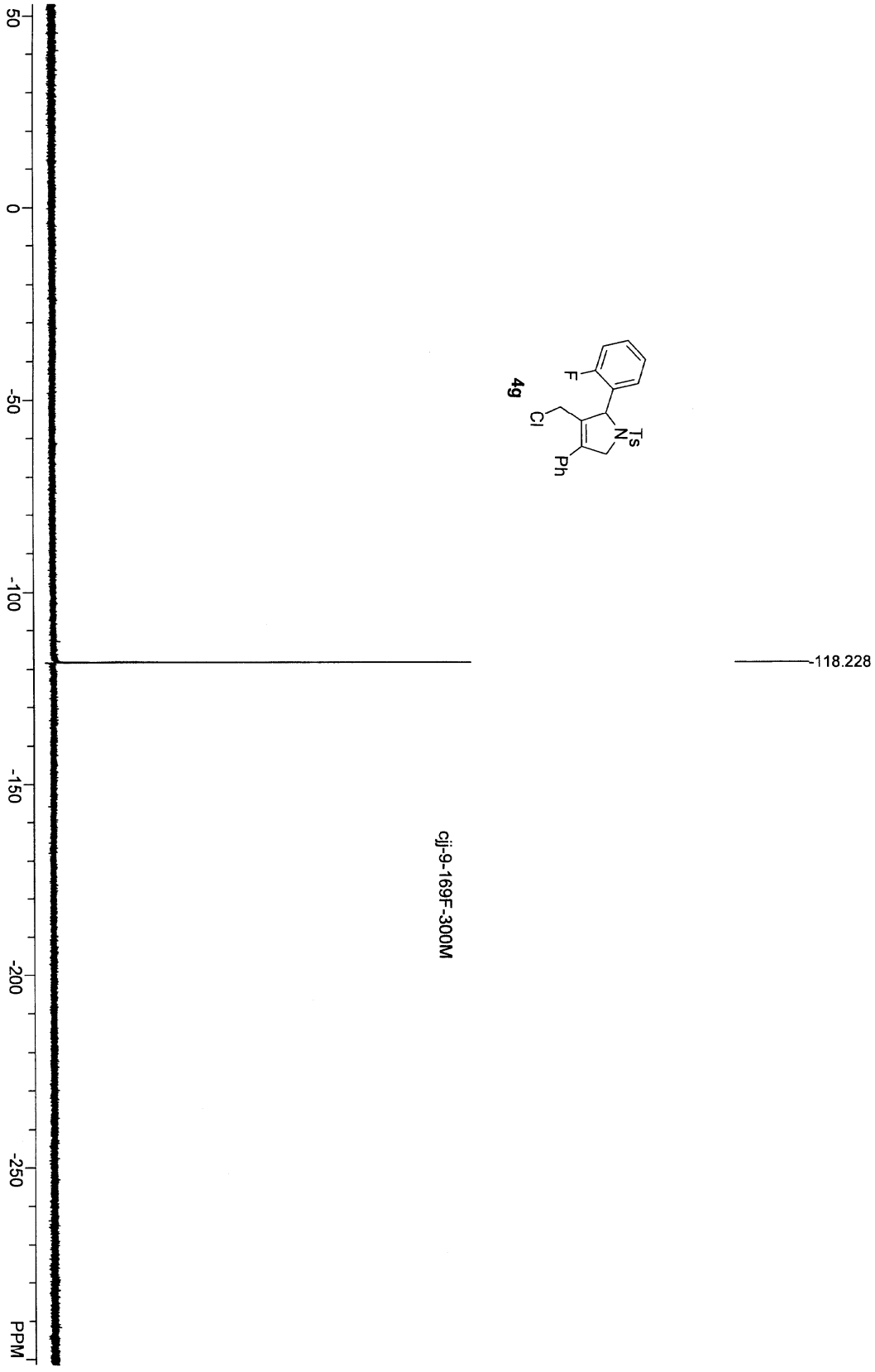
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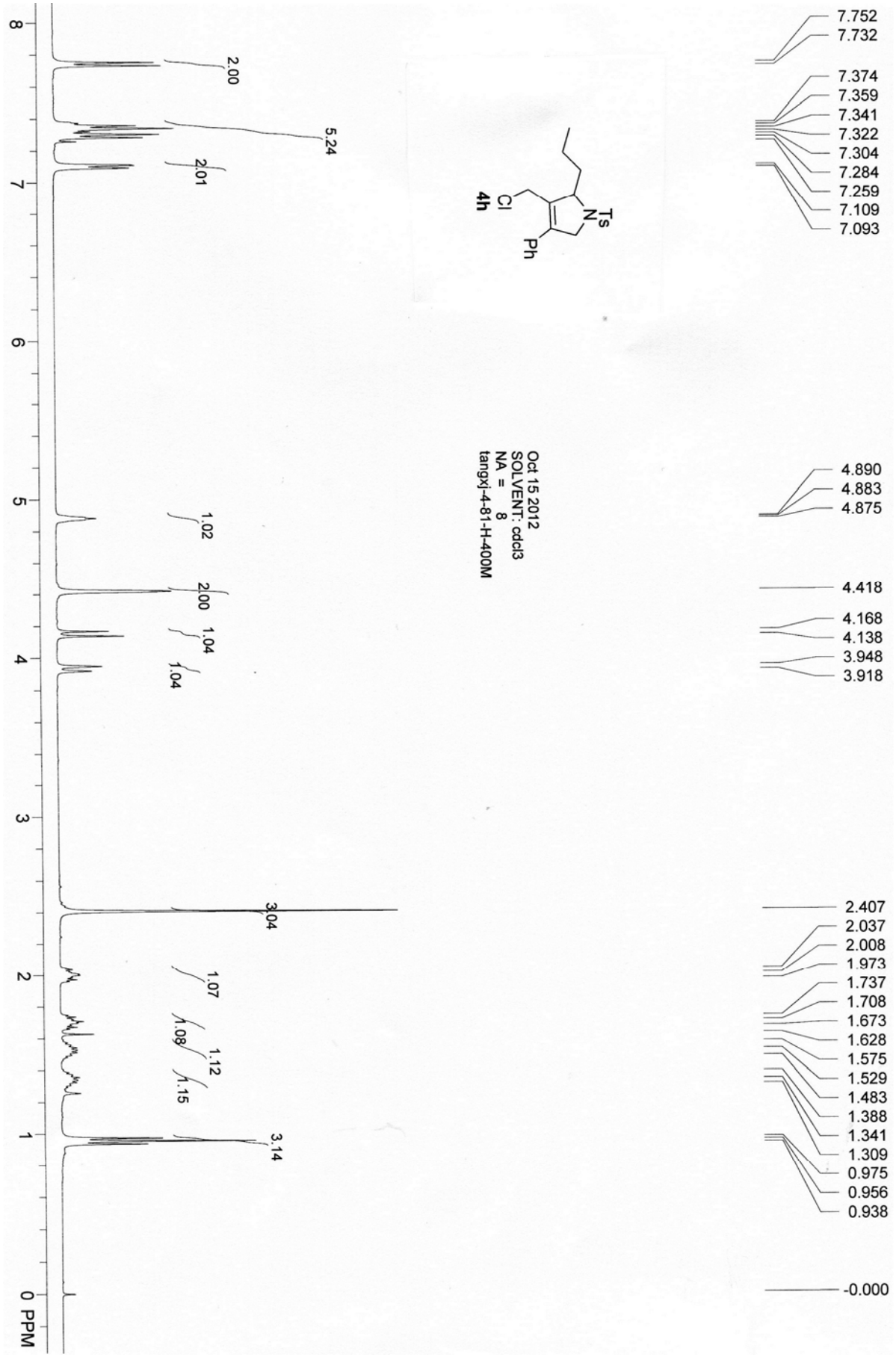
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Oct 15 2012
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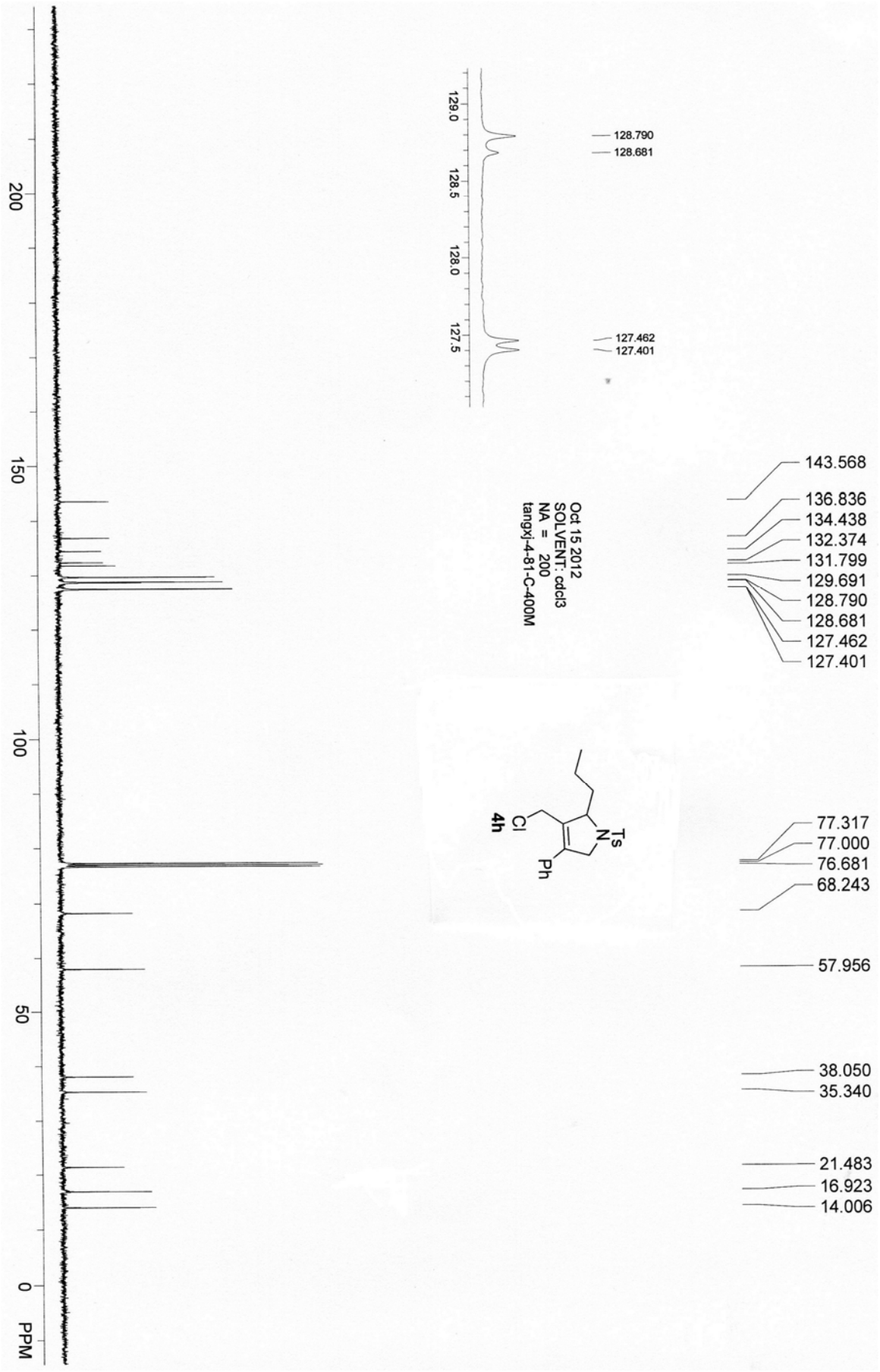
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Oct 15 2012
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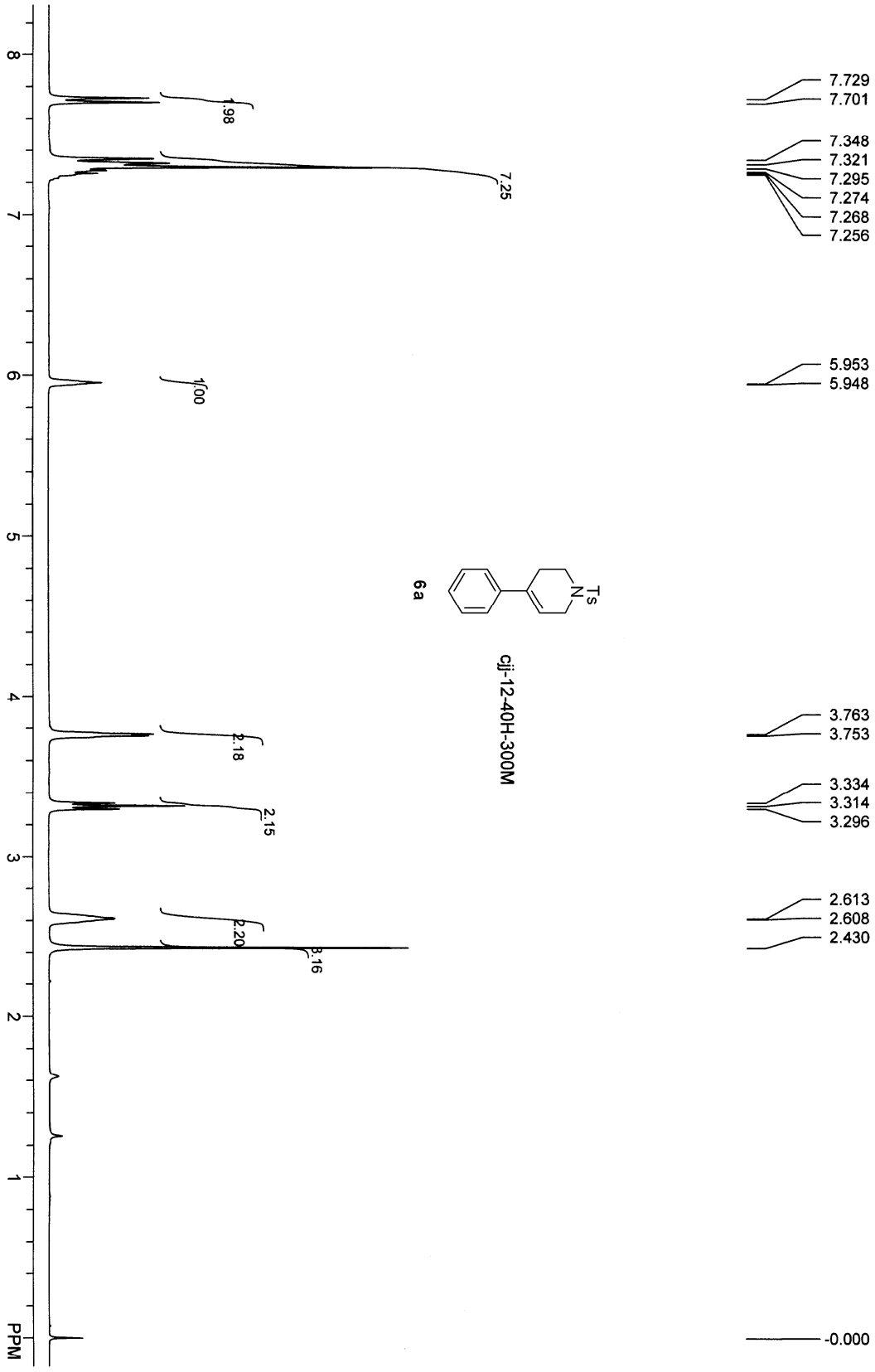
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7.348
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7.274
7.268
7.256
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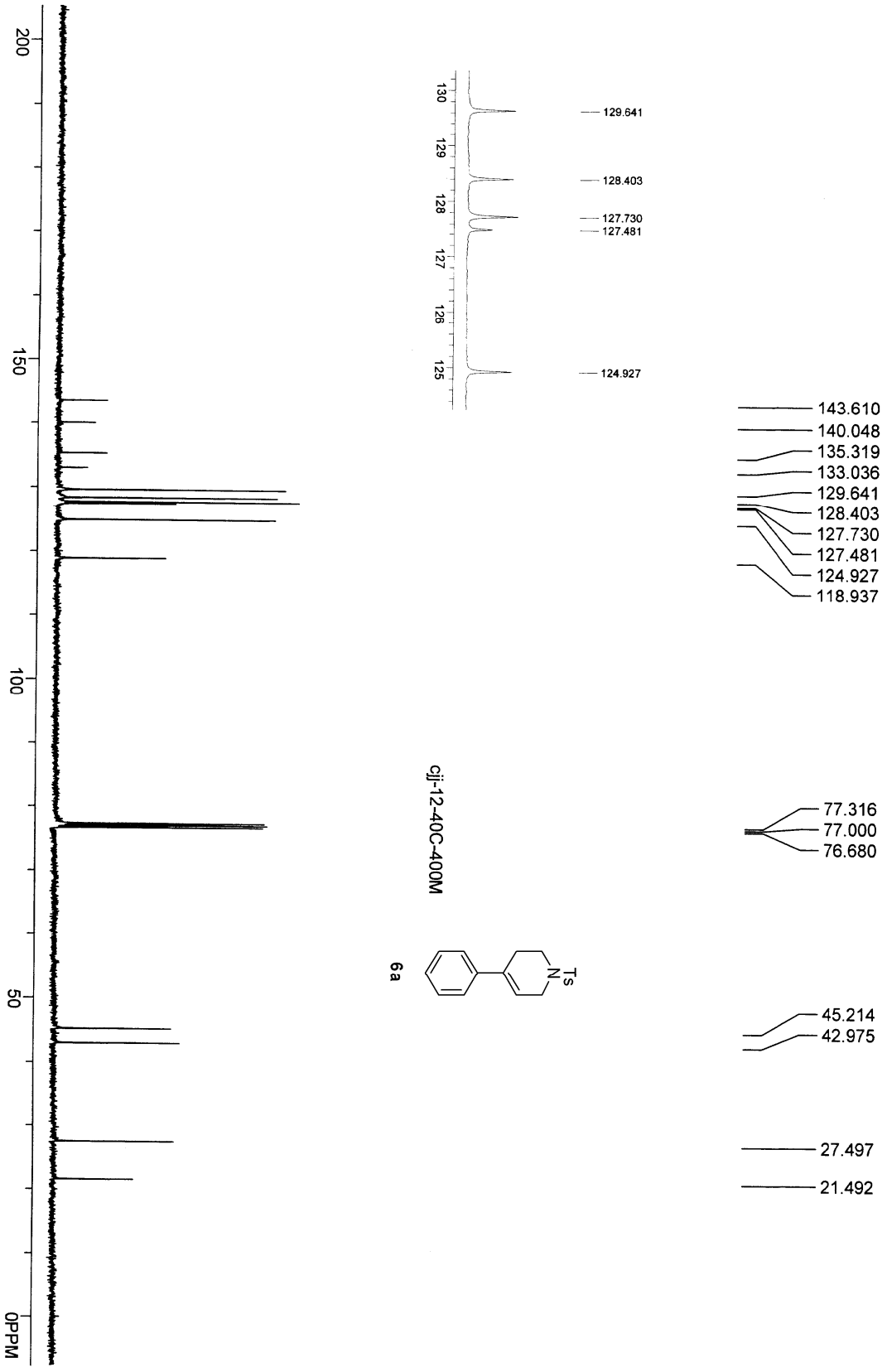
5.948
3.763
3.753
3.334
3.314
3.296
2.613
2.608
2.430
-0.000
1.98
7.25
1.00
2.18
2.15
2.20
3.16
6a
Ts
N
cjj-12-40H-300M
PPM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100
50
0PPM
130
129
128
127
126
125
129.641
128.403
127.730
127.481
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143.610
140.048
135.319
133.036
129.641
128.403
127.730
127.481
124.927
118.937
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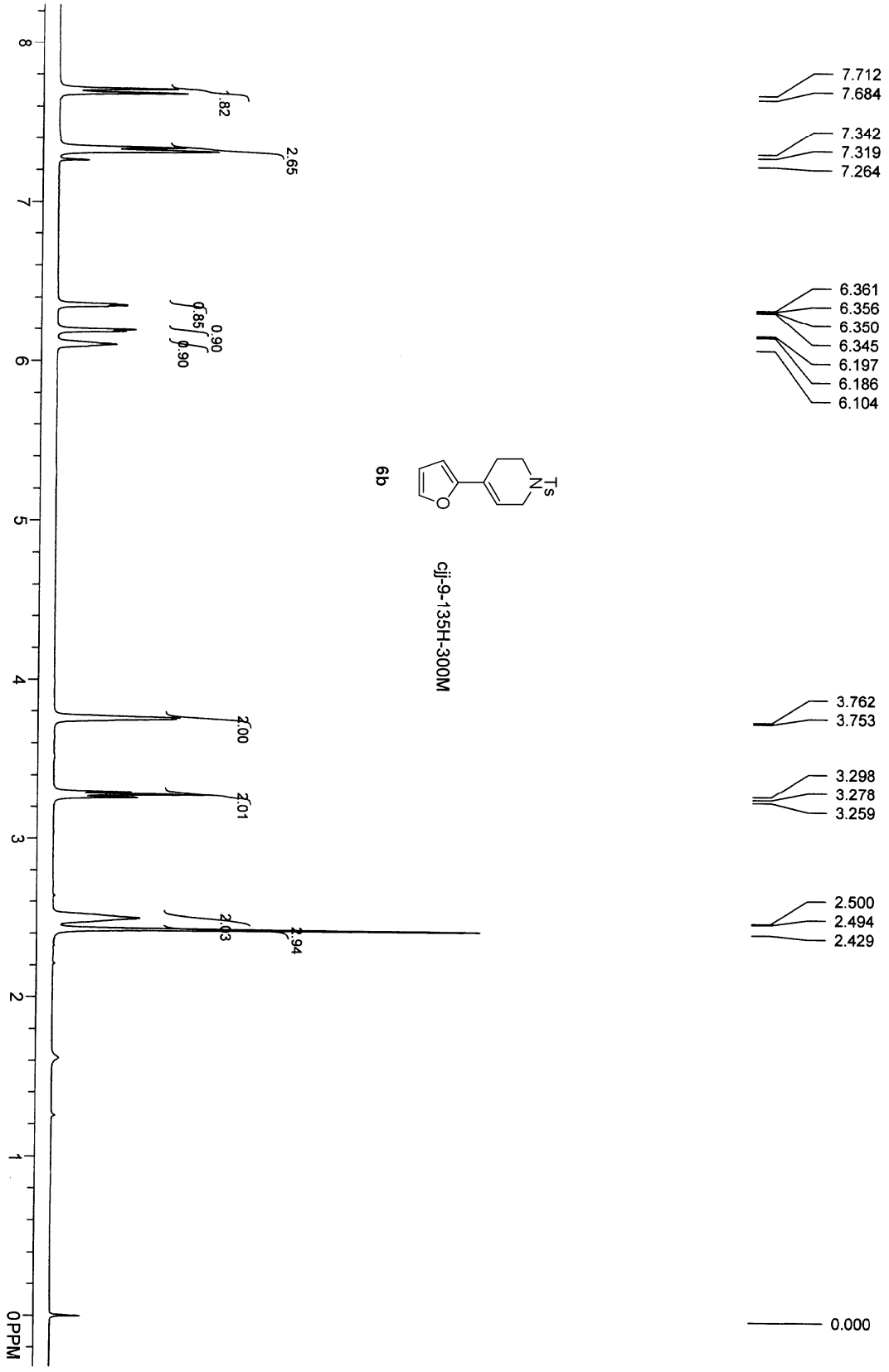
76.680
45.214
42.975
27.497
21.492
cjj-12-40C-400M
6a
Ts
N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6.350
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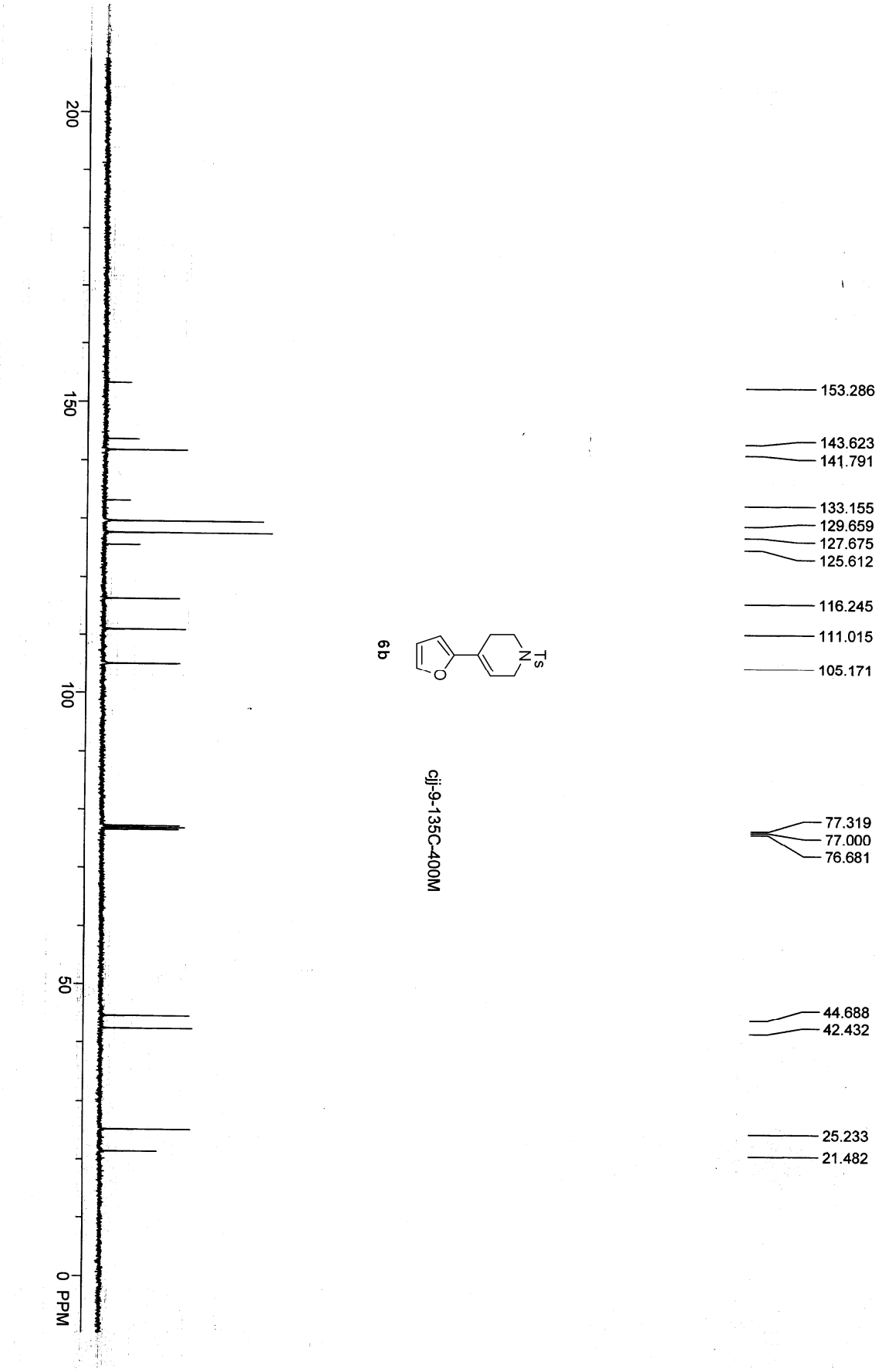
6.197
6.186
6.104
3.762
3.753
3.298
3.278
3.259
2.500
2.494
2.429
0.000
1.82
2.65
0.90
0.85
0.90
2.00
2.01
2.03
2.94
6b
cjj-9-135H-300M
Ts
N
O
8
7
6
5
4
3
2
1
0 PPM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50
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6b
Ts
N
O
cjj-9-135C-400M
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133.155
129.659
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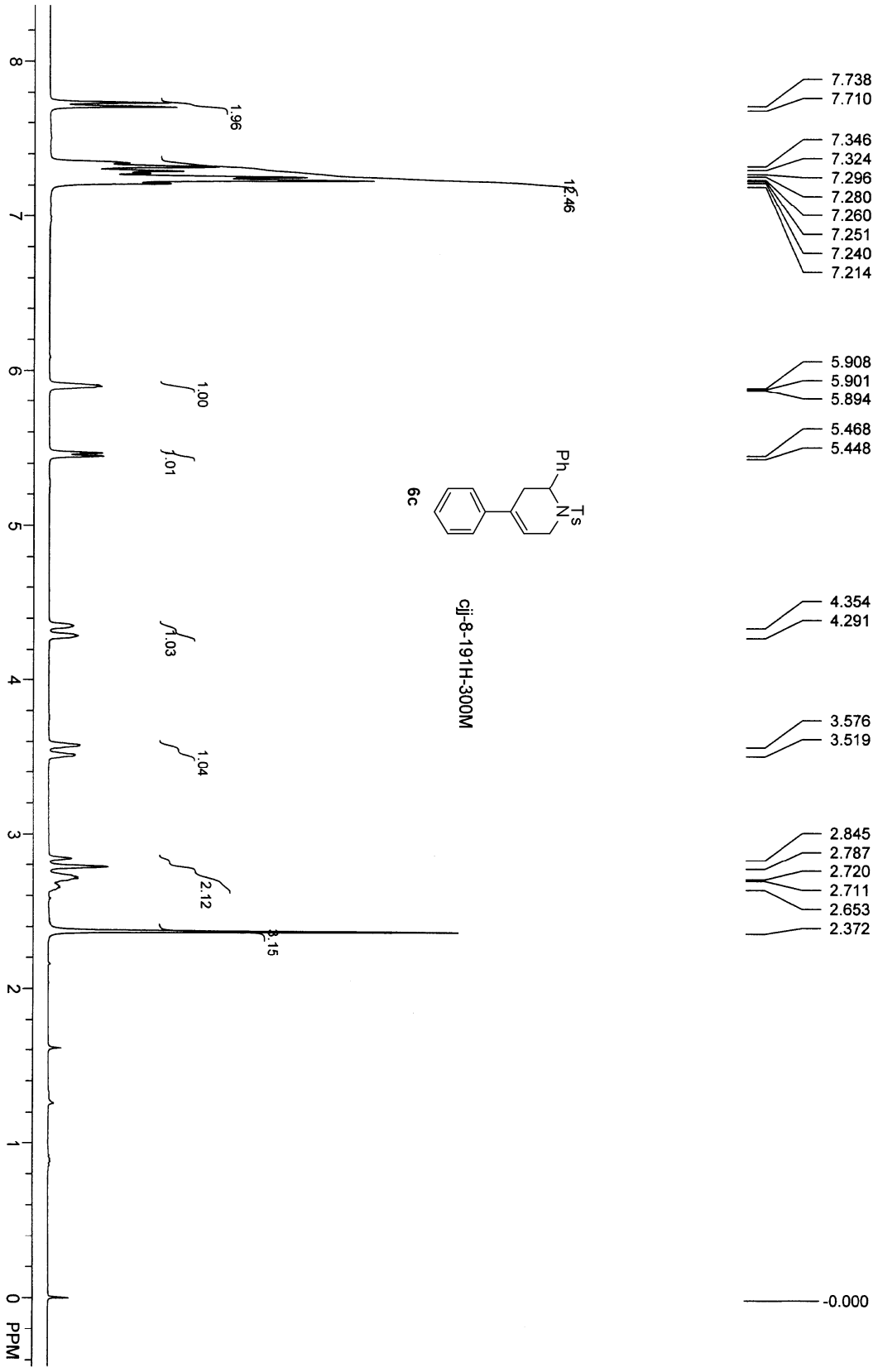
116.245
111.015
105.171
77.319
77.000
76.681
44.688
42.432
25.233
21.482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7.346
7.324
7.296
7.280
7.260
7.251
7.240
7.214
5.908
5.901
5.894
5.468
5.448
4.354
4.291
3.576
3.519
2.845
2.787
2.720
2.711
2.653
2.372
-0.000
1.96
12.46
1.00
1.01
1.03
1.04
2.12
3.15
Ph
Ts
N
6c
cji-8-191H-300M
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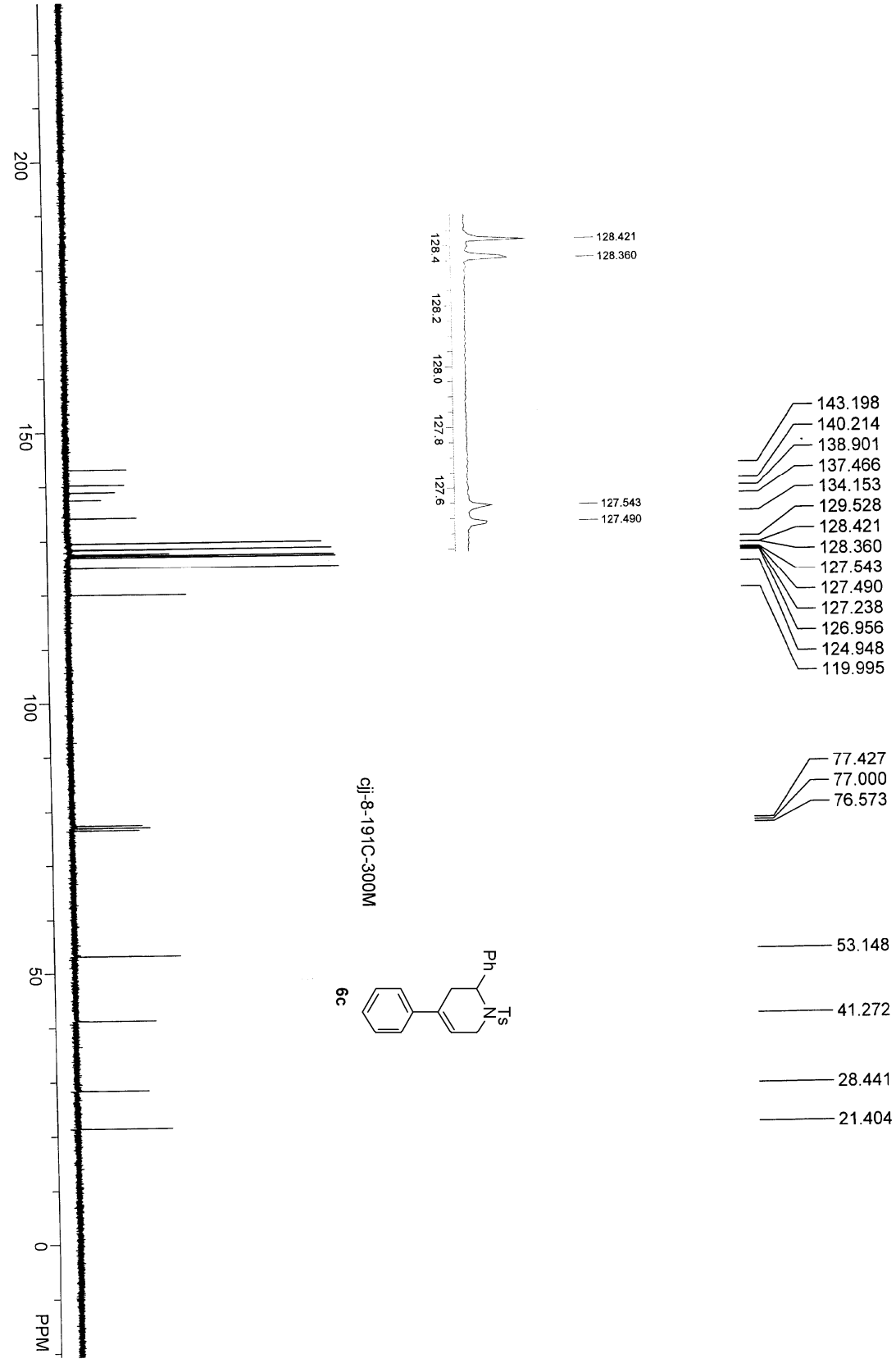
1
2
3
4
5
6
7
8
PPM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150
100
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0
PPM
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128.2
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128.360
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127.490
143.198
140.214
138.901
137.466
134.153
129.528
128.421
128.360
127.543
127.490
127.238
126.956
124.948
119.995
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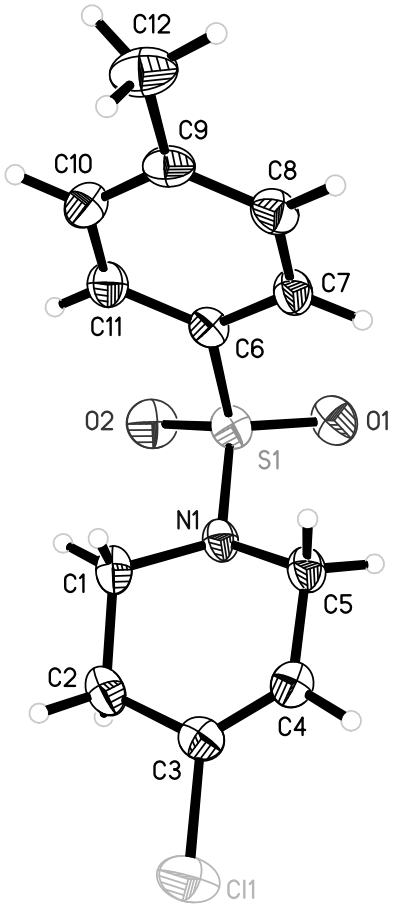
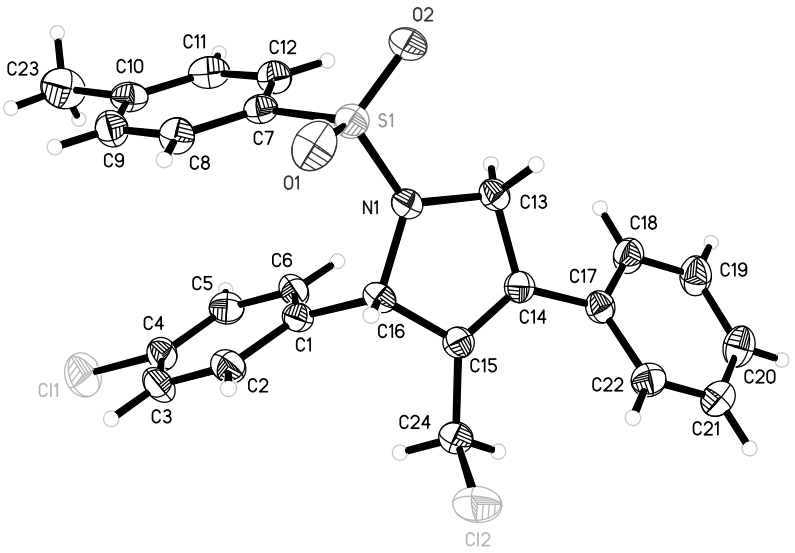
6c
Ph
Ts
N



Crystal data for **3j**. $C_{12}H_{14}ClNO_2S$, MW = 271.75, monoclinic, space group P2(1)/c, final R indices [$I > 2\ (I)$], $R_1 = 0.0401$, $wR_2 = 0.1023$, R indices (all data) $R_1 = 0.0439$, $wR_2 = 0.1062$, $a = 7.7348(5)$ Å, $b = 8.2950(5)$ Å, $c = 20.1342(13)$ Å, $\alpha = 90^{o}$., $\beta = 98.598(1)^{o}$., $\gamma = 90^{o}$, V = 1277.3(14) $Å^3$, T = 293 K, Z = 4, reflections collected/unique: 7493/2511 ($R_{int} = 0.0285$), number of observations [$I > 2(I)$] 2253, parameters: 156. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC 880541).



Crystal data for **4a**. $C_{24}H_{21}Cl_2NO_2S$, MW = 458.38, monoclinic, space group P2(1)/n, final R indices [$I > 2\ (I)$], $R_1 = 0.0536$, $wR_2 = 0.1300$, R indices (all data) $R_1 = 0.0759$, $wR_2 = 0.1405$, $a = 17.918(2)$ Å, $b = 5.8464(8)$ Å, $c = 21.295(3)$ Å, $\alpha = 90^o$, $\beta = 99.577(4)^o$, $\gamma = 90^o$, $V = 2199.7(5)$ Å^3, $T = 296$ K, $Z = 4$, reflections collected/unique: 24225/3857 ($R_{int} = 0.0603$), number of observations [$I > 2\ (I)$] 2849, parameters:271. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC 880542).