Supporting Information

Rhodium-catalyzed Highly Diastereoselective Intramolecular [4+2] Cycloaddition of 1,3-Disubstituted Allene-1,3-dienes

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General Information. NMR spectra were taken with an Agilent 400 MR DD2 or Varian 400-MR spectrometer (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR, and 376 MHz for ^{19}F NMR) in $CDCl_3$. NMR spectra were taken using TMS (^{1}H, δ = 0), residual $CHCl_3$ (7.26 ppm) in $CDCl_3$, and $CFCl_3$ (^{19}F CPD, δ = 0) as the internal standards, respectively. Chemical shifts were recorded in ppm and coupling constants were reported in Hz. Mass and HRMS spectra were carried out in EI or ESI mode. All reactions were carried out in oven-dried Schlenk tubes. $RhCl(PPh_3)_3$ (99%) was purchased from J & K and TCI, $AgSbF_6$ (99%) was purchased from Alfa Aesar and the petroleum ether (boiling range: 60-90 ^oC) was purchased from Adamas. Toluene was dried over sodium wire with benzophenone as the indicator and distilled freshly before use. Other reagents were used as received without further treatment. All the temperatures are referred to the oil baths used.

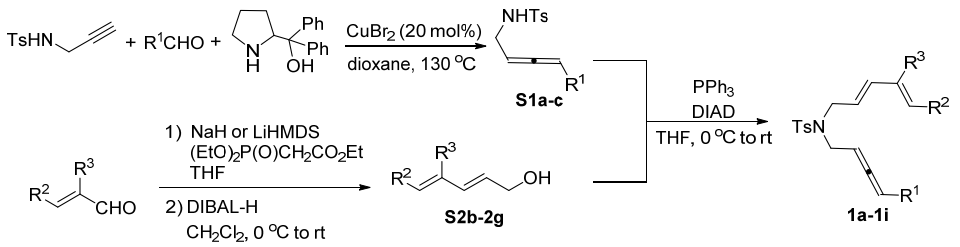
Experimental details and analytical data

1. General synthesis of starting materials

1.1 Synthesis of racemic allene-1,3-dienes containing NTs tether

The preparation of (2*E*,4*E*)-**1a-1i** was accomplished by the Mitsunobu reaction[1] of hexa-(2*E*,4*E*)-dienol **S2a**[2] and its analogues **S2b-g**[3] in 31-86% yields with allenyl amides **S1a-c**, which were prepared via the $CuBr_2$-catalyzed ATA reaction of propargyl tosylamide, commercially available aldehydes, and 2-(diphenylhydroxymethyl)pyrrolidine in 50-61% yields[4] (Scheme S1).

Scheme S1 Synthesis of racemic allene-dienes 1a-1i containing NTs tether



S1a R^1 = *n*-C_4H_9 (61%)
S1b R^1 = CH_3 (50%)
S1c R^1 = Cy (51%)

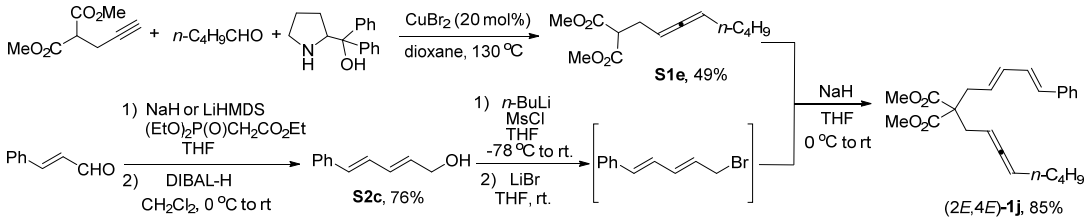
(2*E*,4*E*)-**S2b** R^2 = *n*-C_3H_7, R^3 = H (71%)
(2*E*,4*E*)-**S2c** R^2 = Ph, R^3 = H (76%)
(2*E*,4*E*)-**S2d** R^2 = *p*-ClC_6H_4, R^3 = H (86%)
(2*E*,4*E*)-**S2e** R^2 = *p*-FC_6H_4, R^3 = H (73%)
(2*E*,4*E*)-**S2f** R^2 = *o*-BrC_6H_4, R^3 = H (53%)
(*E*)-**S2g** R^2 = H, R^3 = CH_3 (31%)

(2*E*,4*E*)-**1a** R^1 = *n*-C_4H_9, R^2 = CH_3, R^3 = H (70%)
(2*E*,4*E*)-**1b** R^1 = CH_3, R^2 = CH_3, R^3 = H (63%)
(2*E*,4*E*)-**1c** R^1 = Cy, R^2 = CH_3, R^3 = H (71%)
(2*E*,4*E*)-**1d** R^1 = *n*-C_4H_9, R^2 = *n*-C_3H_7, R^3 = H (72%)
(2*E*,4*E*)-**1e** R^1 = CH_3, R^2 = Ph, R^3 = H (42%)
(2*E*,4*E*)-**1f** R^1 = CH_3, R^2 = *p*-FC_6H_4, R^3 = H (54%)
(2*E*,4*E*)-**1g** R^1 = Cy, R^2 = *p*-ClC_6H_4, R^3 = H (49%)
(2*E*,4*E*)-**1h** R^1 = *n*-C_4H_9, R^2 = *o*-BrC_6H_4, R^3 = H (79%)
(*E*)-**1i** R^1 = Cy, R^2 = H, R^3 = CH_3 (67%)

1. 2 Synthesis of racemic allene-1,3-dienes 1j containing malonate tether

Allene **S1e** containing a malonate unit was synthesized via the $CuBr_2$-catalyzed ATA reaction of dimethyl propargylmalonate, butyraldehyde, and 2-(diphenylhydroxymethyl)pyrrolidine. The preparation of (2*E*,4*E*)-**1j**[5] was accomplished in 85% yield by the alkylation of sodium salt of malonate derivative **S1e** with 1-bromo-(2*E*,4*E*)-diene, which was prepared via the reaction of **S2c** with methanesulfonyl chloride and LiBr (Scheme S2).

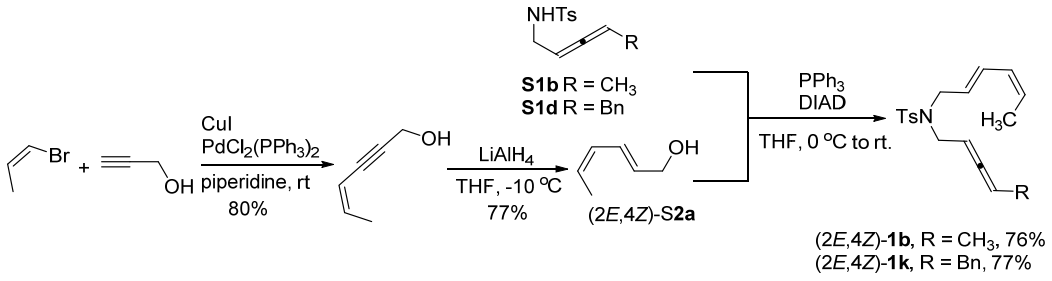
Scheme S2 Synthesis of racemic allene-dienes (2*E*,4*E*)-1j containing a malonate tether



1. 3 Synthesis of (2*E*,4*Z*)-1b and (2*E*,4*Z*)-1k

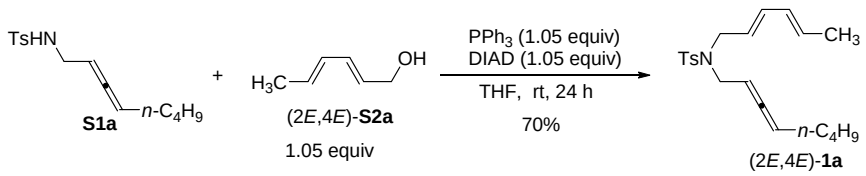
(2*E*,4*Z*)-hexa-2,4-dienol (2*E*,4*Z*)-**S2a**[6] [(2*E*,4*Z*):(2*Z*,4*Z*) > 99:1] was prepared via the Sonogashira reaction of (*Z*)-1-bromoprop-1-ene with propargyl alcohol giving (*Z*)-hexa-4-en-2-yn-1-ol in 80% yield (*Z*:*E* > 99:1), followed by stereoselective reduction with $LiAlH_4$ (THF, -10 °C) in 77% yield (Scheme S3). The reaction of (2*E*,4*Z*)-**S2a** with allene **S1b** or **S1d** afforded allene-diene (2*E*,4*Z*)-**1b** or (2*E*,4*Z*)-**1k**.

Scheme S3 Synthesis of (2*E*,4*Z*)-1b and (2*E*,4*Z*)-1k



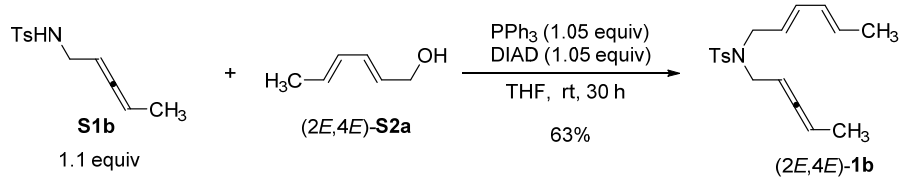
2. Synthesis of racemic allene-1,3-dienes

(1) Preparation of *N*-(2,3-octadienyl)-*N*-[(2*E*,4*E*)-hexadienyl] toluenesulfonamide (2*E*,4*E*)-1a. (hanyl-6-169)



To a dry round-bottom flask were added *N*-(2,3-octadienyl)toluenesulfonamide **S1a** (2.4102 g, 8.6 mmol), 10 mL of THF, PPh_3 (2.3865 g, 9.03 mmol, 1.05 equiv), and hexa-(2*E*,4*E*)-dienol **S2a** (0.8826 g, 9.03 mmol, 1.05 equiv), 20 mL of THF, diisopropylazodicarboxylate (DIAD) (1.8838 g, 9.03 mmol, 1.05 equiv), and 10 mL of THF sequentially. After being stirred for 24 h at rt, the reaction was complete as monitored by TLC. The resulting mixture was concentrated in vacuo and purified via chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford (2*E*,4*E*)-**1a** (2.1818 g, 70%) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2 H, ArH), 7.29 (d, *J* = 8.1 Hz, 2 H, ArH), 6.11-5.91 (m, 2 H, 2 × HC=), 5.70-5.59 (m, 1 H, HC=), 5.37-5.27 (m, 1 H, HC=), 5.13-5.04 (m, 1 H, HC=), 4.88-4.78 (m, 1 H, HC=), 3.86 (d, *J* = 6.9 Hz, 2 H, NCH_2), 3.80 (dd, J_1 = 6.9 Hz, J_2 = 2.1 Hz, 2 H, NCH_2), 2.42 (s, 3 H, CH_3), 2.04-1.89 (m, 2 H, CH_2), 1.73 (d, *J* = 6.8 Hz, 3 H, CH_3), 1.39-1.25 (m, 4 H, 2 × CH_2), 0.88 (t, *J* = 7.0 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.2, 143.0, 137.6, 134.5, 130.4, 130.2, 129.6, 127.1, 124.2, 92.4, 86.1, 48.2, 46.0, 31.2, 28.2, 22.1, 21.4, 18.0, 13.8; MS (ESI) *m/z*: 741 ($[2M+Na]^+$), 382 ($[M+Na]^+$), 360 ($[M+H]^+$); IR (neat): ν = 3021, 2957, 2926, 2856, 1962, 1660, 1598, 1494, 1439, 1342, 1304, 1259, 1156, 1092, 1051, 1018 cm^{-1}; HRMS calcd for $C_{21}H_{30}NO_2S$ ($[M+H]^+$): 360.1992, found: 360.1989.

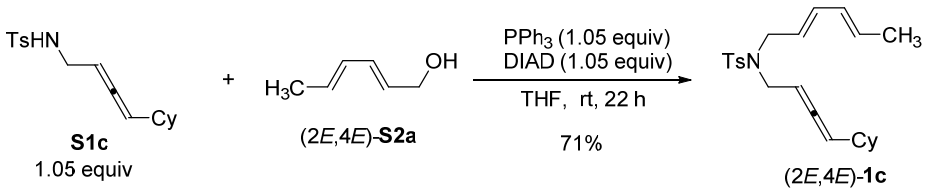
(2) Preparation of *N*-(2,3-pentadienyl)-*N*-[(2*E*,4*E*)-hexadienyl] toluenesulfonamide (2*E*,4*E*)-1b. (hanyl-7-040)



To a dry round-bottom flask were added *N*-(2,3-pentadienyl)toluenesulfonamide **S1b** (0.5238 g, 2.2 mmol, 1.1 equiv), PPh_3 (0.5570 g, 2.1 mmol, 1.05 equiv), 5 mL of

THF, hexa-(2*E*,4*E*)-dienol **S2a** (0.2090 g, 2 mmol), 3 mL of THF, DIAD (0.4443 g, 2.1 mmol, 1.05 equiv), and 2 mL of THF sequentially. After being stirred for 30 h at rt, the reaction was complete as monitored by TLC. The resulting mixture was concentrated in vacuo and purified via chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15/1) to afford (2*E*,4*E*)-**1b** (0.4254 g, 63%) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2 H, ArH), 7.28 (d, *J* = 8.0 Hz, 2 H, ArH), 6.11-5.89 (m, 2 H, 2 × HC=), 5.72-5.58 (m, 1 H, HC=), 5.38-5.25 (m, 1 H, HC=), 5.10-5.01 (m, 1 H, HC=), 4.86-4.74 (m, 1 H, HC=), 3.94-3.72 (m, 4 H, 2 × NCH_2), 2.42 (s, 3 H, CH_3), 1.73 (d, *J* = 6.6 Hz, 3 H, CH_3), 1.66-1.55 (m, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.0, 143.0, 137.6, 134.6, 130.4, 130.2, 129.6, 127.1, 124.2, 86.9, 85.6, 48.2, 45.9, 21.4, 18.0, 14.0; MS (ESI) *m/z*: 340 ($[M+Na]^+$); IR (neat): ν = 3021, 2921, 2856, 1966, 1660, 1598, 1494, 1440, 1408, 1341, 1221, 1156, 1092 cm^{-1}; HRMS calcd for $C_{18}H_{24}O_2NS$ ($[M+H]^+$): 318.1522, found: 318.1521.

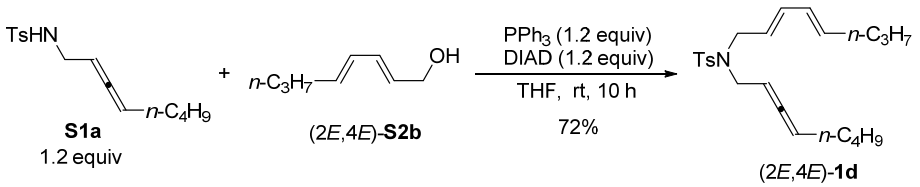
(3) Preparation of *N*-(4-cyclohexyl-2,3-butadienyl)-*N*-[(2*E*,4*E*)-hexadienyl] toluenesulfonamide (2*E*,4*E*)-1c. (hanyl-6-189)



To a dry round-bottom flask were added *N*-(4-cyclohexyl-2,3-butadienyl) toluenesulfonamide **S1c** (0.7878 g, 2.625 mmol, 1.05 equiv), 5 mL of THF, PPh_3 (0.7010 g, 2.625 mmol, 1.05 equiv), hexa-(2*E*,4*E*)-dienol **S2a** (0.2474 g, 2.5 mmol), 5 mL of THF, DIAD (0.5475 g, 2.625 mmol, 1.05 equiv), and 2 mL of THF sequentially. After being stirred for 22 h at rt, the reaction was complete as monitored by TLC. The resulting mixture was concentrated in vacuo and purified via chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford (2*E*,4*E*)-**1c** (0.6880 g, 71%) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2 H, ArH), 7.29 (d, *J* = 8.0 Hz, 2 H, ArH), 6.10-5.92 (m, 2 H, 2 × HC=), 5.70-5.59 (m, 1 H, HC=), 5.37-5.27 (m, 1 H, HC=), 5.12-5.05 (m, 1 H, HC=), 4.88 (qd, J_1 = 6.7 Hz, J_2 = 2.8 Hz,

1 H, HC=C), 3.86 (d, J = 6.8 Hz, 2 H, NCH_2), 3.80 (dd, J_1 = 7.0 Hz, J_2 = 2.2 Hz, 2 H, NCH_2), 2.42 (s, 3 H, CH_3), 1.98-1.87 (m, 1 H, CH of Cy), 1.77-1.60 (m, 8 H, CH_3 + five protons of Cy), 1.31-0.99 (m, five protons of Cy); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.9, 142.9, 137.5, 134.4, 130.3, 130.0, 129.4, 127.0, 124.1, 98.3, 87.0, 48.2, 46.1, 36.9, 32.8, 25.8, 25.7, 21.3, 17.9; MS (ESI) *m/z*: 402 ($[M+NH_3]^+$), 384 ($[M-H]^+$); IR (neat): ν = 3022, 2923, 2851, 1960, 1660, 1598, 1494, 1446, 1344, 1260, 1225, 1158, 1092, 1019 cm^{-1}; HRMS calcd for $C_{23}H_{32}NO_2S$ ($[M+H]^+$): 386.2148, found: 386.2145.

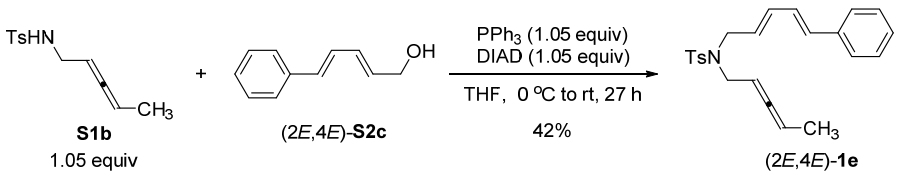
(4) Preparation of *N*-(2,3-octadienyl)-*N*-[(2*E*,4*E*)-octadienyl] toluenesulfonamide (2*E*,4*E*)-1d. (hanyl-7-064)



To a dry round-bottom flask were added *N*-(2,3-octadienyl)toluenesulfonamide **S1a** (0.8538 g, 3.0 mmol, 1.2 equiv), PPh_3 (0.7923 g, 3.0 mmol, 1.2 equiv), octa-(2*E*,4*E*)-dienol **S2b** (0.3201 g, 2.5 mmol), 7 mL of THF, DIAD (0.6327 g, 3.0 mmol, 1.2 equiv), and 3 mL of THF sequentially. After being stirred for 10 h at rt, the reaction was complete as monitored by TLC. The resulting mixture was concentrated in vacuo and purified via chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) to afford (2*E*,4*E*)-**1d** (0.7065 g, 72%) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.9 Hz, 2 H, ArH), 7.29 (d, J = 7.9 Hz, 2 H, ArH), 6.13-6.01 (m, 1 H, HC=), 6.00-5.88 (m, 1 H, HC=), 5.71-5.58 (m, 1 H, HC=), 5.40-5.28 (m, 1 H, HC=), 5.13-5.05 (m, 1 H, HC=), 4.90-4.78 (m, 1 H, HC=), 3.84 (dd, J_1 = 21.1 Hz, J_2 = 6.6 Hz, 4 H, 2 × NCH_2), 2.42 (s, 3 H, CH_3), 2.04 (q, J = 7.1 Hz, 2 H, CH_2), 2.00 -1.90 (m, 2 H, CH_2), 1.46-1.22 (m, 6 H, 3 × CH_2), 0.97-0.79 (m, 6 H, 2 × CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.2, 143.0, 137.6, 135.6, 134.6, 129.6, 129.2, 127.1, 124.4, 92.4, 86.1, 48.2, 46.1, 34.6, 31.2, 28.2, 22.3, 22.1, 21.4, 13.8, 13.6; MS (ESI) *m/z*: 410 ($[M+Na]^+$); IR (neat): ν = 3022, 2958, 2927, 2867, 1962, 1658, 1598, 1494,

1441, 1343, 1157, 1093, 1055, 1020 cm^{-1}; HRMS calcd for $C_{23}H_{34}O_2NS$ ($[M+H]^+$): 388.2305, found: 388.2304.

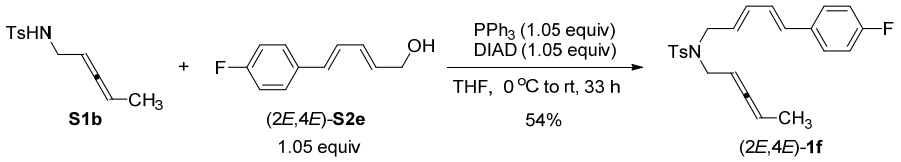
(5) Preparation of *N*-(2,3-pentadienyl)-*N*-[(2*E*,4*E*)-5-phenylhexadienyl]-toluenesulfonamide (2*E*,4*E*)-1e. (hanyl-7-140)



To a dry round-bottom flask placed in an ice bath were added PPh_3 (0.5515 g, 2.1 mmol, 1.05 equiv), *N*-(2,3-pentadienyl)toluenesulfonamide **S1b** (0.4818 g, 2.1 mmol, 1.05 equiv), 5-phenylhexa-(2*E*,4*E*)-dienol **S2c** (0.3220 g, 2.0 mmol), 8 mL of THF, DIAD (0.4367 g, 2.1 mmol, 1.05 equiv), and 2 mL of THF sequentially. The resulting mixture was allowed to warm up to room temperature naturally and stirred for 27 h at rt as monitored by TLC. Then the resulting mixture was concentrated in vacuo and purified via chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 40/1/1) to afford (2*E*,4*E*)-**1e** (0.3236 g, 42%) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.5 Hz, 2 H, ArH), 7.37 (d, J = 7.6 Hz, 2 H, ArH), 7.31 (t, J = 7.8 Hz, 4 H, ArH), 7.26-7.20 (m, 1 H, ArH), 6.69 (dd, J_1 = 15.6 Hz, J_2 = 10.5 Hz, 1 H, HC=), 6.48 (d, J = 15.9 Hz, 1 H, HC=), 6.26 (dd, J_1 = 15.1 Hz, J_2 = 10.7 Hz, 1 H, HC=), 5.60 (dt, J_1 = 15.1 Hz, J_2 = 6.8 Hz, 1 H, HC=), 5.14-5.04 (m, 1 H, HC=), 4.90-4.79 (m, 1 H, HC=), 4.01-3.90 (m, 2 H, NCH_2), 3.90-3.77 (m, 2 H, NCH_2), 2.42 (s, 3 H, CH_3), 1.63 (dd, J_1 = 7.2 Hz, J_2 = 3.1 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 143.2, 137.5, 136.9, 134.4, 132.9, 129.6, 128.6, 127.74, 127.71, 127.2, 126.3, 87.1, 85.7, 48.3, 46.2, 21.5, 14.1; MS (ESI) *m/z*: 781 ($[2M+Na]^+$), 402 ($[M+Na]^+$); IR (neat): ν = 3025, 2924, 2855, 2254, 1964, 1644, 1597, 1494, 1445, 1410, 1341, 1306, 1215, 1156, 1092, 1018 cm^{-1}; HRMS calcd for $C_{23}H_{25}NNaO_2S$ ($[M+Na]^+$): 402.1498, found: 402.1500.

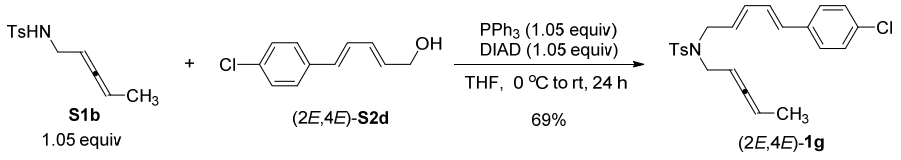
(6) Preparation of *N*-(2,3-pentadienyl)-*N*-[(2*E*,4*E*)-5-(4-fluorophenyl)-

2(*E*),4(*E*)-pentadienyl] toluenesulfonamide (2*E*,4*E*)-1f. (hanyl-7-153)



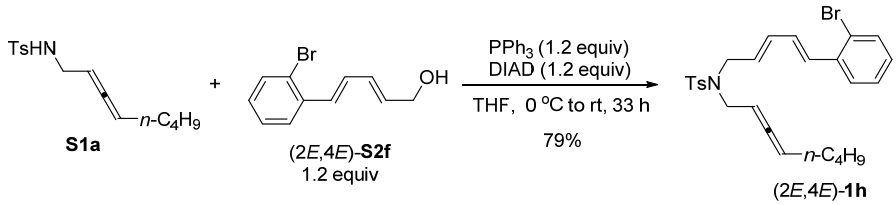
To a dry round-bottom flask placed in an ice bath were added PPh_3 (0.5532 g, 2.1 mmol, 1.05 equiv), *N*-(2,3-pentadienyl)toluenesulfonamide **S1b** (0.4748 g, 2.0 mmol), 5-(4-flurophenyl)-(2*E*,4*E*)-pentadienol (2*E*,4*E*)-**S2e** (0.3773 g, 2.1 mmol, 1.05 equiv), and 7 mL of THF, DIAD (0.4389 g, 2.1 mmol, 1.05 equiv), and 3 mL of THF sequentially. The resulting mixture was allowed to warm up to room temperature naturally and stirred for 33 h at rt as monitored by TLC. Then the resulting mixture was concentrated in vacuo and purified via chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) to afford (2*E*,4*E*)-**1f** (0.4302 g, 54%) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2 H, ArH), 7.38-7.27 (m, 4 H, ArH), 7.00 (t, *J* =8.6 Hz, 2 H, ArH), 6.61 (dd, J_1 = 15.5 Hz, J_2 = 10.3 Hz, 1 H, HC=), 6.44 (d, *J* = 15.6 Hz, 1 H, HC=), 6.25 (dd, J_1 = 15.2 Hz, J_2 = 10.4 Hz, 1 H, HC=), 5.61 (dt, J_1 = 15.1 Hz, J_2 = 6.9 Hz, 1 H, HC=), 5.14-5.04 (m, 1 H, HC=), 4.88-4.79 (m, 1 H, HC=), 4.01-3.89 (m, 2 H, NCH_2), 3.88-3.78 (m, 2 H, NCH_2), 2.42 (s, 3 H, CH_3), 1.63 (dd, J_1 = 7.2 Hz, J_2 = 3.2 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 162.2 (d, *J* = 247.9 Hz), 143.2, 137.4, 134.1, 133.1 (d, *J* = 3.1 Hz), 131.6, 129.6, 127.81 (d, *J* = 7.6 Hz), 127.80, 127.5, 127.1, 115.5 (d, *J* = 21.4 Hz), 87.0, 85.6, 48.2, 46.2, 21.4, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ -114.4; MS (ESI) *m/z*: 436 ($[M+K]^+$), 420 ($[M+Na]^+$); IR (neat): ν = 3034, 2988, 2924, 2857, 1966, 1599, 1507, 1442, 1344, 1305, 1230, 1159, 1120, 1094 cm^{-1}; HRMS calcd for $C_{23}H_{24}FNNaO_2S$ ($[M+Na]^+$): 420.1404, found: 420.1403.

(7) Preparation of *N*-(2,3-pentadienyl)-*N*-[((2*E*,4*E*)-5-(4-chlorophenyl)-pentadienyl] toluenesulfonamide (2*E*,4*E*)-1g. (hanyl-7-137)



To a dry round-bottom flask placed in an ice bath were added 5-(4-chlorophenyl)-(2*E*,4*E*)-pentadienol **S2d** (0.3808 g, 2.0 mmol), PPh_3 (0.5542 g, 2.1 mmol, 1.05 equiv), *N*-(2,3-pentadienyl)toluenesulfonamide **S1b** (0.4912 g, 2.1 mmol, 1.05 equiv), 8 mL of THF, DIAD (0.4391 g, 2.1 mmol, 1.05 equiv), and 2 mL of THF sequentially. The resulting mixture was allowed to warm up to room temperature naturally and stirred for 24 h at rt as monitored by TLC. Then the resulting mixture was concentrated in vacuo and purified via chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 40/1) to afford (2*E*,4*E*)-**1g** (0.5603 g, 69%) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.9 Hz, 2 H, ArH), 7.35-7.23 (m, 6 H, ArH), 6.66 (dd, J_1 = 15.7 Hz, J_2 = 10.4 Hz, 1 H, HC=), 6.43 (d, J = 15.7 Hz, 1 H, HC=), 6.25 (dd, J_1 = 15.0 Hz, J_2 = 10.6 Hz, 1 H, HC=), 5.70-5.59 (m, 1 H, HC=), 5.14-5.04 (m, 1 H, HC=), 4.88-4.79 (m, 1 H, HC=), 4.00-3.89 (m, 2 H, NCH_2), 3.89-3.77 (m, 2 H, NCH_2), 2.42 (s, 3 H, CH_3), 1.62 (dd, J_1 = 7.1 Hz, J_2 = 2.9 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 143.2, 137.4, 135.4, 133.9, 133.2, 131.5, 129.6, 128.7, 128.4, 128.3, 127.5, 127.1, 87.1, 85.6, 48.2, 46.3, 21.5, 14.0; MS (ESI) *m/z*: 438 $[M^+(^{37}Cl)+Na]^+$, 436 ($[M^+(^{35}Cl)+Na]^+$); IR (neat): ν = 3030, 2924, 2855, 1965, 1595, 1490, 1442, 1406, 1340, 1214, 1156, 1120, 1090, 1012 cm^{-1}; HRMS calcd for $C_{23}H_{25}{}^{35}ClNO_2S$ ($[M(^{35}Cl)+H]^+$): 414.1289, found: 414.1274.

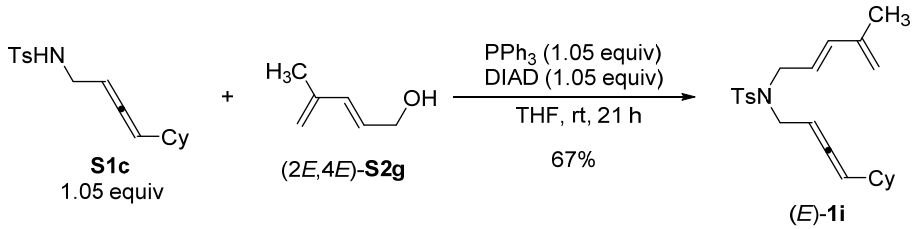
(8) Preparation of *N*-(2,3-pentadienyl)-*N*-[(2*E*,4*E*)-5-(2-bromophenyl)-pentadienyl] toluenesulfonamide (2*E*,4*E*)-1h. (hanyl-7-163)



To a dry round-bottom flask placed in an ice bath were added PPh_3 (0.6314 g, 2.4 mmol, 1.2 equiv), *N*-(2,3-octadienyl)toluenesulfonamide **S1a** (0.5567 g, 2.0 mmol), 4 mL of THF, 5-(2-bromophenyl)-(2*E*,4*E*)-pentadienol **S2f** (0.5705 g, 2.4 mmol, 1.2 equiv), 4 mL of THF, DIAD (0.5016 g, 2.4 mmol, 1.2 equiv), and 2 mL of THF sequentially. The resulting mixture was allowed to warm up to room temperature

naturally and stirred for 33 h at rt as monitored by TLC. The mixture was concentrated in vacuo and purified via chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford (2*E*,4*E*)-**1h** (0.7925 g, 79%) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.4 Hz, 2 H, ArH), 7.58-7.48 (m, 2 H, ArH), 7.34-7.23 (m, 3 H, ArH), 7.08 (td, J_1 = 7.7 Hz, J_2 = 1.5 Hz, 1 H, ArH), 6.84 (d, J = 15.6 Hz, 1 H, HC=), 6.64 (dd, J_1 = 15.5 Hz, J_2 = 10.5 Hz, 1 H, HC=), 6.32 (dd, J_1 = 15.2 Hz, J_2 = 10.6 Hz, 1 H, HC=), 5.67 (dt, J_1 = 15.4 Hz, J_2 = 6.6 Hz, 1 H, HC=), 5.17-5.09 (m, 1 H, HC=), 4.92-4.83 (m, 1 H, HC=), 3.95 (d, J = 6.7 Hz, 2 H, NCH_2), 3.85 (dd, J_1 = 7.0 Hz, J_2 = 2.0 Hz, 2 H, NCH_2), 2.42 (s, 3 H, CH_3), 2.02-1.94 (m, 2 H, CH_2), 1.42-1.25 (m, 4 H, 2 × CH_2), 0.87 (t, J = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.3, 143.2, 137.4, 136.5, 134.0, 133.0, 131.2, 130.3, 129.6, 129.1, 128.8, 127.4, 127.1, 126.4, 123.8, 92.6, 86.1, 48.2, 46.5, 31.2, 28.2, 22.1, 21.5, 13.8; MS (ESI) *m/z*: 524 ([M(^{81}Br)+Na]$^+$), 522 ([M$^+$(^{79}Br)+Na]$^+$); IR (neat): ν = 3031, 2956, 2927, 2858, 1962, 1914, 1642, 1598, 1559, 1494, 1465, 1437, 1338, 1304, 1214, 1184, 1159, 1093, 1042, 1021 cm^{-1}; HRMS calcd for $C_{26}H_{30}{}^{79}BrNNaO_2S$ ([M(^{79}Br)+Na]$^+$): 522.1073, found: 522.1070.

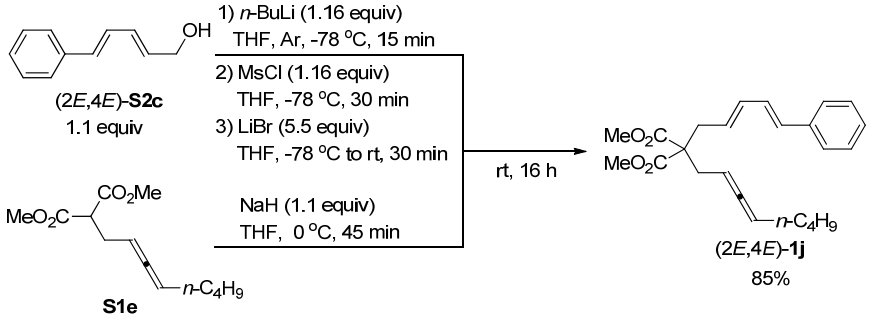
(9) Preparation of *N*-(4-cyclohexyl-2,3-butadienyl)-*N*-[*E*-4-methyl-2,4-pentadienyl] toluenesulfonamide (*E*)-1i. (hanyl-7-075)



To a dry round-bottom flask were added *N*-(4-cyclohexyl-2,3-butadienyl) toluenesulfonamide **S1c** (0.6386 g, 2.1 mmol, 1.05 equiv), PPh_3 (0.5550 g, 2.1 mmol, 1.05 equiv), 5 mL of THF, 4-methyl-(2*E*,4*E*)-pentadienol **S2g** (0.1964 g, 2.0 mmol), 2 mL of THF, DIAD (0.4521 g, 2.1 mmol, 1.05 equiv), and 3 mL of THF sequentially. After being stirred for 21 h at rt as monitored by TLC, the resulting mixture was concentrated in vacuo and purified via chromatography on silica gel (eluent:

petroleum ether/ethyl acetate = 20/1) to afford (*E*)-**1i** (0.5155 g, 67%) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2 H, ArH), 7.29 (d, *J* = 7.9 Hz, 2 H, ArH), 6.18 (d, *J* = 15.7 Hz, 1 H, HC=), 5.41 (dt, J_1 = 15.7 Hz, J_2 = 6.6 Hz, 1 H, HC=), 5.15-5.05 (m, 1 H, HC=), 4.96 (s, 1 H, one proton of H_2C=), 4.93-4.84 (m, 2 H, one proton of H_2C= + HC=), 3.91 (d, *J* = 6.6 Hz, 2 H, NCH_2), 3.82 (dd, J_1 = 7.0 Hz, J_2 = 1.9 Hz, 2 H, NCH_2), 2.42 (s, 3 H, CH_3), 1.99-1.87 (m, 1 H, CH), 1.78-1.55 (m, 8 H, CH_3 + five protons of Cy), 1.31-0.96 (m, 5 H, five protons of Cy); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.1, 143.1, 141.0, 137.6, 136.7, 129.5, 127.1, 123.6, 116.9, 98.4, 87.1, 48.3, 46.4, 37.0, 32.9, 25.9, 25.8, 21.4, 18.3; MS (ESI) *m/z*: 386 ($[M+H]^+$); IR (neat): ν = 3082, 3031, 2924, 2851, 1960, 1604, 1494, 1446, 1345, 1236, 1158, 1094, 1019 cm^{-1}; HRMS calcd for $C_{23}H_{32}NO_2S$ ($[M+H]^+$): 386.2148, found: 386.2147.

(10) Preparation of Dimethyl 2-(2,3-octadienyl)-2-(5-phenyl-(2*E*,4*E*)-penta-dienyl) malonate (2*E*,4*E*)-1j. (hanyl-9-153, hanyl-9-154)

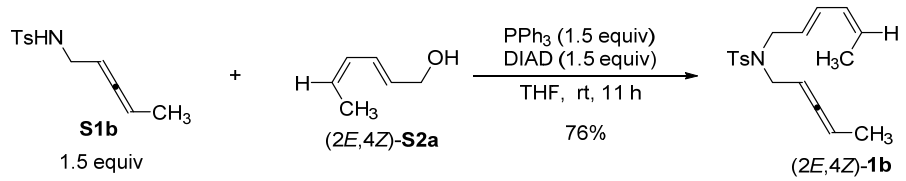


To a flame-dried Schlenk tube were 5-phenylpenta-(2*E*,4*E*)-dienol **S2c** (0.3543 g, 2.2 mmol, 1.1 equiv) and anhydrous THF (5 mL) under Ar. The Schlenk tube was then placed into a dry ice/ethanol bath (-78 °C). *n*-BuLi (2.5 M in hexane, 0.93 mL, 2.31 mmol, 1.16 equiv) was added dropwise over 1 minute and the resulting solution was stirred for 15 minutes at this temperature. MsCl (0.18 mL, d = 1.48 g/mL, 0.2664 g, 2.31 mmol, 1.16 equiv) was then added and the resulting mixture was stirred for 30 minutes followed by the addition of LiBr (0.9745 g, 11 mmol, 5.5 equiv) at -78 °C. The resulting mixture was removed from the dry ice/ethanol bath and then allowed to warm up to room temperature for 30 minutes, and the solution was used directly in the next step.

To a separate flame-dried Schlenk tube was added NaH (60% dispersion in mineral

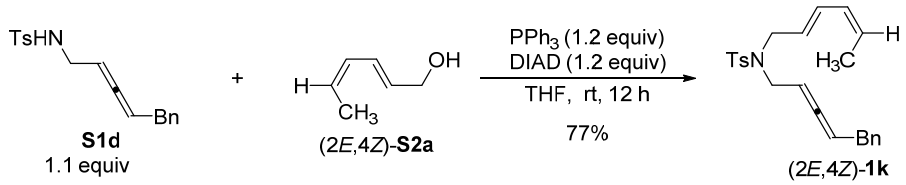
oil, 0.0886 g, 2.2 mmol, 1.1 equiv). The tube was placed into an ice bath (0 ^{o}C). To the Schlenk tube was added THF (3 mL) followed by the dropwise addition of dimethyl 2-(2,3-octadienyl)malonate **S1e** (0.4820 g, 2.0 mmol) over 2 minutes at 0 ^{o}C and the resulting mixture was then stirred for 45 minutes at this temperature. The solution containing the (2*E*,4*E*)-dienyl bromide prepared above was then transferred via a syringe to the Schlenk tube containing the malonate and the resulting mixture was allowed to warm up to room temperature naturally and was stirred for 16 h as monitored by TLC. A saturated aqueous solution of NH_4Cl (5 mL) and water (5 mL) were then added sequentially and mixture was poured into a separatory funnel and extracted with Et_2O (20 mL × 3). The organic layer was combined, washed with brine (20 mL), dried with anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified via flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) to afford (2*E*,4*E*)-**1j** (0.6532 g, 85%) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.34 (m, 2 H, ArH), 7.29 (t, J = 7.6 Hz, 2 H, ArH), 7.20 (tt, J_1 = 7.2 Hz, J_2 = 2.9 Hz, 1 H, ArH), 6.72 (dd, J_1 = 15.4 Hz, J_2 = 10.2 Hz, 1 H, HC=), 6.45 (d, J = 15.6 Hz, 1 H, HC=), 6.25 (dd, J_1 = 15.0 Hz, J_2 = 10.6 Hz, 1 H, HC=), 5.68-5.58 (m, 1 H, HC=), 5.13-5.05 (m, 1 H, HC=), 4.95-4.87 (m, 1 H, HC=), 3.72 (s, 6 H, 2 × CH_3), 2.78 (d, J = 7.6 Hz, 2 H, NCH_2), 2.61 (dd, J_1 = 7.6 Hz, J_2 = 2.4 Hz, 2 H, NCH_2), 1.98 (qd, J_1 = 6.8 Hz, J_2 = 2.8 Hz, 2 H, CH_2), 1.41-1.30 (m, 4 H, 2 × CH_2), 0.89 (t, J = 7.0 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.8, 171.0, 137.1, 134.6, 131.5, 128.54, 128.50, 127.9, 127.4, 126.2, 91.0, 84.5, 58.1, 52.40, 52.36, 35.9, 32.7, 31.3, 28.4, 22.1, 13.8; MS (ESI) *m/z*: 405 ($[M+Na]^+$), 383 ($[M+H]^+$); IR (neat): ν = 3024, 2954, 2928, 2856, 1961, 1732, 1596, 1493, 1436, 1278, 1229, 1198, 1072, 1028 cm^{-1}; HRMS calcd for $C_{24}H_{31}O_4$ ($[M+H]^+$): 383.2217, found: 383.2213.

(11) Preparation of *N*-(2,3-pentadienyl)-*N*-[(2*E*,4*Z*)-hexadienyl] toluenesulfonamide (2*E*,4*Z*)-1b. (hanyl-10-102)



To a dry round-bottom flask were added PPh_3 (0.2943 g, 1.1 mmol, 1.5 equiv), 2 mL of THF, *N*-(2,3-pentadienyl) toluenesulfonamide **S1b** (0.2588 g, 1.1 mmol, 1.5 equiv), 1 mL of THF, hexa-(2*E*,4*Z*)-dienol **S2a** (0.0708 g, 0.72 mmol), 2 mL of THF, DIAD (0.2274 g, 1.1 mmol, 1.5 equiv), and 1 mL of THF sequentially. After being stirred for 11 h at rt as monitored by TLC, the resulting mixture was concentrated in vacuo and purified via chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford (2*E*,4*Z*)-**1b** (0.1743 g, 76%) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 2 H, ArH), 7.29 (d, *J* = 8.1 Hz, 2 H, ArH), 6.39 (dd, J_1 = 14.8 Hz, J_2 = 11.2 Hz, 1 H, HC=), 5.92 (td, J_1 = 4.0 Hz, J_2 = 0.9 Hz, 1 H, HC=), 5.54-5.38 (m, 2 H, 2 × HC=), 5.13-5.04 (m, 1 H, HC=), 4.88-4.79 (m, 1 H, HC=), 3.91 (d, *J* = 6.7 Hz, 2 H, NCH_2), 3.88-3.76 (m, 2 H, NCH_2), 2.42 (s, 3 H, CH_3), 1.70 (dd, J_1 = 7.2 Hz, J_2 = 1.4 Hz, 3 H, CH_3), 1.62 (dd, J_1 = 7.1 Hz, J_2 = 3.1 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 143.1, 137.6, 129.6, 129.3, 128.2, 127.1, 127.0, 126.5, 86.9, 85.7, 48.3, 45.9, 21.4, 14.0, 13.3; MS (ESI) *m/z*: 340 ($[M+Na]^+$); IR (neat): ν = 3022, 2977, 2922, 2857, 1964, 1597, 1493, 1440, 1409, 1341, 1156, 1121, 1092, 1016 cm^{-1}; HRMS calcd for $C_{18}H_{24}NO_2S$ ($[M+H]^+$): 318.1522, found: 318.1521.

(12) Preparation of *N*-(5-phenyl-2,3-pentadienyl)-*N*-[(2*E*,4*Z*)-hexadienyl] toluenesulfonamide (2*E*,4*Z*)-1k. (hanyl-10-030)

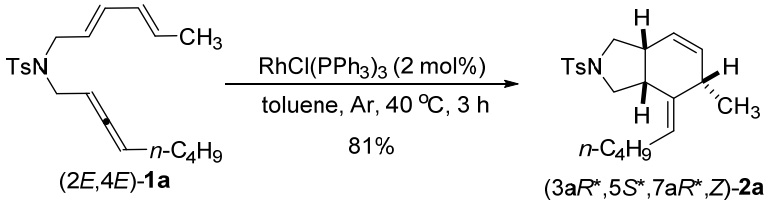


To a dry round-bottom flask were added PPh_3 (0.6361 g, 2.4 mmol, 1.2 equiv), *N*-(5-phenyl-2,3-pentadienyl) toluenesulfonamide **S1d** (0.6825 g, 2.2 mmol, 1.1 equiv), 6 mL of THF, hexa-(2*E*,4*Z*)-dienol **S2a** (0.1802 g, 2.0 mmol), 2 mL of THF,

DIAD (0.4989 g, 2.4 mmol, 1.2 equiv), and 2 mL of THF sequentially. After being stirred for 12 h at rt as monitored by TLC, the resulting mixture was concentrated in vacuo and purified via chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford (2*E*,4*Z*)-**1k** (0.5597 g, 77%) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.9 Hz, 2 H, ArH), 7.31-7.24 (m, 4 H, ArH), 7.23-7.13 (m, 3 H, ArH), 6.35 (dd, J_1 = 14.9 Hz, J_2 = 11.2 Hz, 1 H, HC=), 5.91 (t, *J* = 11.0 Hz, 1 H, HC=), 5.53-5.35 (m, 2 H, 2 × HC=), 5.28 (q, *J* = 6.8 Hz, 1 H, HC=), 4.97-4.89 (m, 1 H, HC=), 3.89-3.76 (m, 4 H, 2 × NCH_2), 3.30 (d, *J* = 7.0 Hz, 2 H, CH_2), 2.41 (s, 3 H, CH_3), 1.66 (d, *J* = 7.0 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.5, 191.8, 143.1, 139.5, 137.5, 129.6, 129.2, 128.33, 128.31, 128.1, 127.1, 126.5, 126.2, 91.9, 86.9, 48.3, 45.9, 35.1, 21.4, 13.3; MS (ESI) *m/z*: 416 ([M+Na]$^+$); IR (neat): ν = 3024, 2916, 2854, 1963, 1598, 1494, 1452, 1439, 1410, 1344, 1305, 1156, 1092, 1028 cm^{-1}; HRMS calcd for $C_{24}H_{28}NO_2S$ ([M+H]$^+$): 394.1835, found: 394.1833.

3. Rhodium-catalyzed Highly Diastereoselective Intramolecular [4+2] Cycloaddition of Allene-1,3-dienes 1

(1) Preparation of 5-methyl-2-((4-methylphenyl)sulfonyl)-4-pentylidene-2,3,3a,4, 5,7a-hexahydro-1*H*-isoindole (3a*R,5*S**,7a*R**,*Z*)-2a.** (hanyl-6-193)

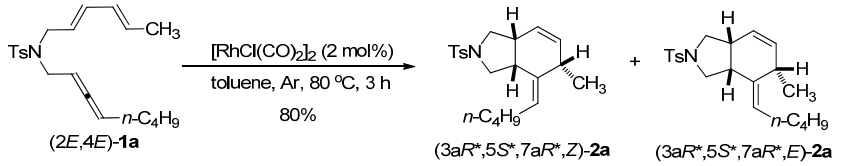


(2*E*,4*E*)-**1a** (3a*R**,5*S**,7a*R**,*Z*)-**2a**

Typical Procedure I: To a flame-dried Schlenk tube were added $RhCl(PPh_3)_3$ (18.6 mg, 0.02 mmol), (2*E*,4*E*)-**1a** (360.5 mg, 1 mmol), and toluene (5 mL) sequentially under Ar atmosphere. The Schlenk tube was then placed in an oil bath pre-heated at 40 °C. After being stirred for 3 h, the reaction was complete as monitored by TLC. The crude reaction mixture was filtrated through a pad of silica gel and eluted with diethyl ether (50 mL). After concentration in vacuo, the residue was purified via chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford (3a*R**,5*S**,7a*R**,*Z*)-**2a** (292.4 mg, 81%) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.71 (d, J = 8.3 Hz, 2 H, ArH), 7.32 (d, J = 7.9 Hz, 2 H, ArH), 5.43-5.35 (m, 2 H, 2 × HC=), 5.11 (d, J = 9.9 Hz, 1 H, HC=), 3.49 (dd, J_1 = 10.2 Hz, J_2 = 6.4 Hz, 1 H, one proton of NCH_2), 3.36 (t, J = 8.4 Hz, 1 H, one proton of NCH_2), 3.29 (d, J = 10.4 Hz, 1 H, one proton of NCH_2), 3.20-3.12 (m, 1 H, CH), 3.10-3.03 (m, 1 H, one proton of NCH_2), 2.78-2.68 (m, 1 H, CH), 2.64-2.56 (m, 1 H, CH), 2.44 (s, 3 H, CH_3), 2.00-1.91 (m, 2 H, CH_2), 1.31-1.22 (m, 4 H, 2 × CH_2), 1.07 (d, J = 7.6 Hz, 3 H, CH_3), 0.88 (t, J = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 135.6, 133.8, 133.1, 129.4, 129.3, 127.5, 125.7, 54.5, 50.6, 39.2, 38.1, 35.2, 32.1, 26.7, 24.9, 22.2, 21.5, 13.9; MS (EI) *m/z* (%): 359 (M^+, 3.45), 42 (100); IR (neat): ν = 3018, 2955, 2917, 2893, 2862, 1658, 1596, 1449, 1330, 1295, 1237, 1162, 1129, 1087, 1050, 1029 cm^{-1}; HRMS calcd for $C_{21}H_{29}NO_2S$ (M^+): 359.1919, found: 359.1917.

(2) Preparation of 5-methyl-2-((4-methylphenyl)sulfonyl)-4-pentylidene-2,3,3a,4,5,7a-hexahydro-1*H*-isoindole (3a*R,5*S**,7a*R**,*E*)-2a.** (hanyl-9-114)



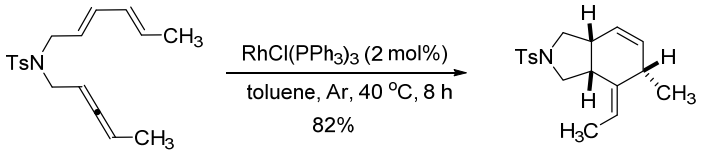
To a flame-dried Schlenk tube were added $[RhCl(CO)_2]_2$ (0.8 mg, 0.002 mmol), (2*E*,4*E*)-**1a** (35.1 mg, 0.1 mmol), and toluene (1 mL) sequentially under Ar atmosphere. The Schlenk tube was then placed in an oil bath pre-heated at 80 °C. After being stirred for 3 h, the reaction was complete as monitored by TLC. The crude reaction mixture was filtrated through a pad of silica gel and eluted with ether (20 mL). After concentration in vacuo, the residue was purified via chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford a mixture of (3a*R**,5*S**,7a*R**,*Z*)-**2a** and (3a*R**,5*S**,7a*R**,*E*)-**2a** (28.1 mg, *Z*:*E* = 50:50, 80%) as liquid.

(3a*R**,5*S**,7a*R**,*E*)-**2a** (12.3 mg, 34%) was prepared by preparative HPLC: liquid, HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 98/2, 5.0 mL/min, λ = 214 nm, t_R(*Z*-**2a**) = 43.09 min, t_R(*E*-**2a**) = 47.28 and 50.11 min; ^{1}H NMR (500 MHz,

$CDCl_3$) δ 7.70 (d, J = 7.8 Hz, 2 H, Ar-H), 7.31 (d, J = 7.8 Hz, 2 H, Ar-H), 5.38 (dt, J_1 = 9.9 Hz, J_2 = 2.9 Hz, 1 H, HC=), 5.24 (t, J = 7.4 Hz, 1 H, HC=), 5.12 (d, J = 9.7 Hz, 1 H, HC=), 3.42 (dd, J_1 = 9.8 Hz, J_2 = 6.2 Hz, 1 H, one proton of NCH_2), 3.34-3.26 (m, 2 H, NCH_2), 3.19 (t, J = 10.3 Hz, 1 H, one proton of NCH_2), 3.00-2.92 (m, 1 H, CH), 2.82-2.74 (m, 1 H, CH), 2.67-2.60 (m, 1 H, CH), 2.44 (s, 3 H, CH_3), 2.07-1.93 (m, 2 H, CH_2), 1.35-1.27 (m, 4 H, 2 × CH_2), 1.06 (d, J = 7.3 Hz, 3 H, CH_3), 0.88 (t, J = 7.0 Hz, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.2, 135.1, 134.1, 132.8, 129.5, 127.6, 125.9, 54.4, 50.8, 46.5, 39.8, 31.8, 30.2, 27.2, 22.4, 22.0, 21.5, 14.0; MS (EI) *m*/*z* (%): 359 (M^+, 2.22), 198 (100); IR (neat): ν = 3017, 2956, 2924, 2855, 1598, 1456, 1346, 1304, 1213, 1161, 1117, 1092, 1052 cm^{-1}; HRMS calcd for $C_{21}H_{29}NO_2S$ (M^+): 359.1919, found: 359.1925.

The following compounds were prepared according to **Typical Procedure I**.

(3) Preparation of 5-methyl-2-((4-methylphenyl)sulfonyl)-4-ethylidene-2,3,3a,4,5,7a-hexahydro-1*H*-isoindole (3a*R,5*S**,7a*R**,*Z*)-2b.** (hanyl-7-049)

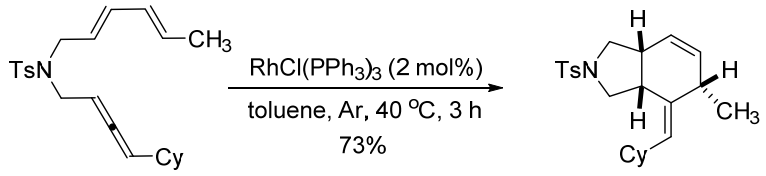


(2*E*,4*E*)-**1b** (3a*R**,5*S**,7a*R**,*Z*)-**2b**

The reaction of $RhCl(PPh_3)_3$ (18.9 mg, 0.02 mmol) and (2*E*,4*E*)-**1b** (317.8 mg, 1.0 mmol) in 5 mL of toluene at 40 °C for 8 h afforded (3a*R**,5*S**,7a*R**,*Z*)-**2b** (260.8 mg, 82%) (eluent: petroleum ether/ethyl acetate = 15/1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.2 Hz, 2 H, ArH), 7.32 (t, J = 8.1 Hz, 2 H, ArH), 5.46 (q, J = 6.8 Hz, 1 H, HC=), 5.40 (dt, J_1 = 10.0 Hz, J_2 = 3.0 Hz, 1 H, HC=), 5.13 (d, J = 10.1 Hz, 1 H, HC=), 3.49 (dd, J_1 = 10.2 Hz, J_2 = 6.5 Hz, 1 H, one proton of NCH_2), 3.39 (dd, J_1 = 9.2 Hz, J_2 = 8.4 Hz, 1 H, one proton of NCH_2), 3.29 (dd, J_1 = 10.2 Hz, J_2 = 1.4 Hz, 1 H, one proton of NCH_2), 3.26-3.17 (m, 1 H, CH), 3.08-3.00 (m, 1 H, one proton of NCH_2), 2.78-2.68 (m, 1 H, CH), 2.66-2.59 (m, 1 H, CH), 2.44 (s, 3 H, CH_3), 1.59 (dd, J_1 = 6.8 Hz, J_2 = 0.8 Hz, 3 H, CH_3), 1.06 (d, J = 9.5 Hz, 3 H, CH_3); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 143.3, 136.4, 133.7, 133.0, 129.4, 127.5, 125.7, 122.8, 54.5, 50.2, 38.9, 37.7, 35.1, 24.7, 21.5, 12.6; MS (EI) *m/z* (%): 317 (M^+, 2.69), 42 (100); IR (neat): ν = 3019, 2953, 2914, 2880, 2856, 1596, 1492, 1448, 1399, 1374, 1335, 1296, 1193, 1158, 1108, 1088, 1041, 1015 cm^{-1}; HRMS calcd for $C_{18}H_{23}NO_2S$ (M^+): 317.1450, found: 317.1451.

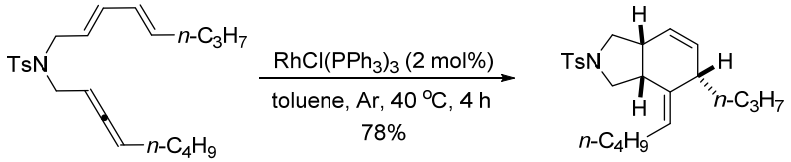
(4) Preparation of 5-methyl-2-((4-methylphenyl)sulfonyl)-4-cyclohexylmethylene-2,3,3a,4,5,7a-hexahydro-1*H*-isoindole (3a*R,5*S**,7a*R**,*Z*)-2c.** (hanyl-6-194)



(2*E*,4*E*)-**1c** (3a*R**,5*S**,7a*R**,*Z*)-**2c**

The reaction of $RhCl(PPh_3)_3$ (18.6 mg, 0.02 mmol) and (2*E*,4*E*)-**1c** (383.7 mg, 1.0 mmol) in 5 mL of toluene at 40 °C for 3 h afforded (3a*R**,5*S**,7a*R**,*Z*)-**2c** (279.5 mg, 73%) (eluent: petroleum ether/ethyl acetate = 20/1) as a white solid: m.p. 130-133 °C (dichloromethane/petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.3 Hz, 2 H, ArH), 7.32 (d, J = 8.1 Hz, 2 H, ArH), 5.38 (dt, J_1 = 10.0 Hz, J_2 = 3.0 Hz, 1 H, HC=), 5.22 (d, J = 9.3 Hz, 1 H, HC=), 5.09 (d, J = 10.2 Hz, 1 H, HC=), 3.51 (dd, J_1 = 10.3 Hz, J_2 = 6.6 Hz, 1 H, one proton of NCH_2), 3.36 (t, J = 8.2 Hz, 1 H, one proton of NCH_2), 3.28 (d, J = 10.2 Hz, 1 H, one proton of NCH_2), 3.20-3.11 (m, 1 H, CH), 3.11-3.03 (m, 1 H, one proton of NCH_2), 2.74-2.65 (m, 1 H, CH), 2.64-2.57 (m, 1 H, CH), 2.44 (s, 3 H, CH_3), 2.16-2.03 (m, 1 H, CH of Cy), 1.76-1.60 (m, 3 H, CH_2 + one proton of CH_2), 1.51 (d, J = 12.5 Hz, 2 H, CH_2), 1.33-0.95 (m, 8 H, CH_3 + 2 × CH_2 + one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 135.6, 133.8, 133.7, 133.0, 129.5, 127.5, 125.7, 54.6, 50.9, 39.3, 38.4, 36.0, 35.1, 33.9, 33.4, 25.9, 25.84, 25.81, 25.0, 21.5; MS (EI) *m/z* (%) 385 (M^+, 2.16), 42 (100); IR (neat): ν = 2920, 2849, 1444, 1343, 1326, 1307, 1290, 1235, 1155, 1088, 1040 cm^{-1}; Anal Calcd for $C_{23}H_{31}NO_2S$: C 71.65, H 8.10, N 3.63; found: C 71.65, H 8.21, N 3.44.

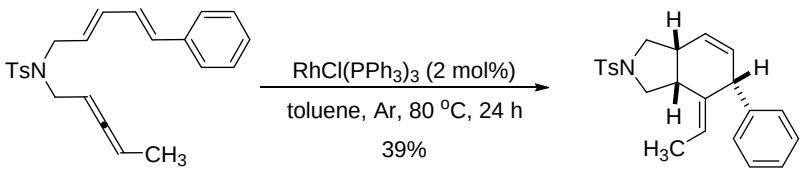
(5) Preparation of 5-*n*-propyl-2-((4-methylphenyl)sulfonyl)-4-pentylidene-2,3,3a,4,5,7a-hexahydro-1*H*-isoindole (3a*R,5*S**,7a*R**,*Z*)-2d.** (hanyl-7-070)



(2*E*,4*E*)-**1d** (3a*R**,5*S**,7a*R**,*Z*)-**2d**

The reaction of $RhCl(PPh_3)_3$ (18.5 mg, 0.02 mmol) and (2*E*,4*E*)-**1d** (391.1 mg, 1.0 mmol) in 5 mL of toluene at 40 °C for 4 h afforded (3a*R**,5*S**,7a*R**,*Z*)-**2d** (303.2 mg, 78%) (eluent: petroleum ether/ethyl acetate = 20/1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2 H, ArH), 7.31 (d, *J* = 8.0 Hz, 2 H, ArH), 5.50 (ddd, J_1 = 10.1 Hz, J_2 = 3.6 Hz, J_3 = 2.6 Hz, 1 H, HC=), 5.32 (t, *J* = 7.5 Hz, 1 H, HC=), 5.16 (d, *J* = 10.1 Hz, 1 H, HC=), 3.49 (dd, J_1 = 10.0 Hz, J_2 = 6.6 Hz, 1 H, one proton of NCH_2), 3.34 (t, *J* = 8.9 Hz, 1 H, one proton of NCH_2), 3.26-3.14 (m, 2 H, one proton of NCH_2 + CH), 3.04 (t, *J* = 9.8 Hz, 1 H, one proton of NCH_2), 2.68-2.60 (m, 1 H, CH), 2.58-2.50 (m, 1 H, CH), 2.44 (s, 3 H, CH_3), 1.97 (q, *J* = 6.9 Hz, 2 H, CH_2), 1.36-1.18 (m, 8 H, 4 × CH_2), 0.93-0.81 (m, 6 H, 2 × CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 134.2, 133.6, 131.7, 129.6, 129.4, 127.6, 126.0, 54.5, 50.4, 41.0, 40.8, 39.6, 37.8, 32.1, 26.8, 22.2, 21.5, 20.9, 14.0, 13.9; MS (EI) *m/z* (%): 387 (M^+, 1.16), 42 (100); IR (neat): ν = 2956, 2925, 2866, 1596, 1462, 1331, 1228, 1160, 1129, 1087, 1045, 1028, 1002 cm^{-1}; HRMS calcd for $C_{23}H_{33}NO_2S$ (M^+): 387.2232, found: 387.2235.

(6) Preparation of 5-phenyl-2-((4-methylphenyl)sulfonyl)-4-ethylidene-2,3,3a,4,5,7a-hexahydro-1*H*-isoindole (3a*R,5*R**,7a*R**,*Z*)-2e.** (hanyl-7-146)

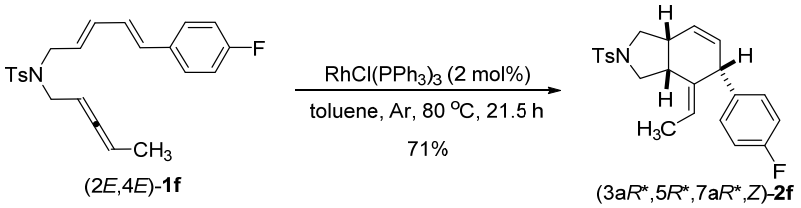


(2*E*,4*E*)-**1e** (3a*R**,5*R**,7a*R**,*Z*)-**2e**

The reaction of $RhCl(PPh_3)_3$ (9.3 mg, 0.01 mmol) and (2*E*,4*E*)-**1e** (188.2 mg, 0.5 mmol) in 2.5 mL of toluene at 80 °C for 24 h afforded (3a*R**,5*R**,7a*R**,*Z*)-**2e** (73.0

mg, 39%) (eluent: petroleum ether/ethyl acetate = 30/1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2 H, ArH), 7.32-7.18 (m, 5 H, ArH), 7.13-7.08 (m, 2 H, ArH), 5.81 (ddd, J_1 = 10.1 Hz, J_2 = 4.3 Hz, J_3 = 2.4 Hz, 1 H, HC=), 5.64 (q, *J* = 6.9 Hz, 1 H, HC=), 5.50 (dt, J_1 = 10.1 Hz, J_2 = 1.8 Hz, 1 H, HC=), 3.93 (s, 1 H, CH), 3.56 (dd, J_1 = 10.1 Hz, J_2 = 7.0 Hz, 1 H, one proton of NCH_2), 3.39-3.30 (m, 1 H, CH), 3.21 (dd, J_1 = 10.2 Hz, J_2 = 2.5 Hz, 1 H, one proton of NCH_2), 3.12 (t, *J* = 9.2 Hz, 1 H, one proton of NCH_2), 2.86-2.77 (m, 1 H, CH), 2.71 (t, *J* = 10.2 Hz, 1 H, one proton of NCH_2), 2.46 (s, 3 H, CH_3), 1.65 (d, *J* = 6.7 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 143.2, 134.8, 133.3, 129.8, 129.5, 128.5, 128.2, 127.6, 127.2, 126.2, 124.6, 54.0, 49.4, 45.7, 39.4, 37.7, 21.5, 13.0; MS (ESI) *m/z*: 402 ($[M+Na]^+$), 380 ($[M+H]^+$); IR (neat): ν = 3024, 2957, 2922, 2891, 1597, 1492, 1478, 1448, 1342, 1304, 1289, 1222, 1197, 1160, 1124, 1091, 1042, 1017 cm^{-1}; HRMS calcd for $C_{23}H_{26}NO_2S$ ($[M+H]^+$): 380.1679, found: 380.1680.

(7) Preparation of 5-(4-fluorophenyl)-2-((4-methylphenyl)sulfonyl)-4-ethylidene-2,3,3a,4,5,7a-hexahydro-1*H*-isoindole (3a*R,5*R**,7a*R**,*Z*)-2f.** (hanyl-7-170)

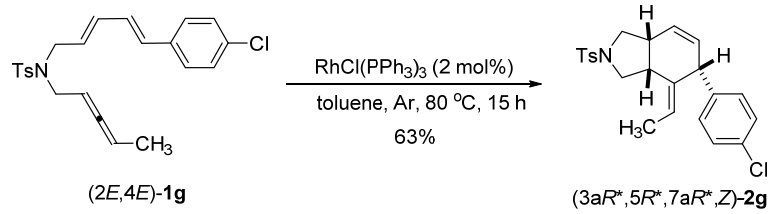


(2*E*,4*E*)-**1f** (3a*R**,5*R**,7a*R**,*Z*)-**2f**

The reaction of $RhCl(PPh_3)_3$ (9.3 mg, 0.01 mmol) and (2*E*,4*E*)-**1f** (194.8 mg, 0.5 mmol) in 2.5 mL of toluene at 80 °C for 21.5 h afforded (3a*R**,5*R**,7a*R**,*Z*)-**2f** (138.5 mg, 71%) (eluent: petroleum ether/ethyl acetate = 10/1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.1 Hz, 2 H, ArH), 7.29 (d, *J* = 8.1 Hz, 2 H, ArH), 7.05 (dd, J_1 = 8.3 Hz, J_2 = 5.5 Hz, 2 H, ArH), 5.87 (t, *J* = 8.6 Hz, 2 H, ArH), 5.81 (ddd, J_1 = 10.0 Hz, J_2 = 4.2 Hz, J_3 = 2.2 Hz, 1 H, HC=), 5.62 (q, *J* = 6.8 Hz, 1 H, HC=), 5.56 (d, *J* = 10.1 Hz, 1 H, HC=), 3.90 (s, 1 H, CH), 3.55 (dd, J_1 = 10.0 Hz, J_2 = 7.1 Hz, 1 H, one proton of NCH_2), 3.41-3.30 (m, 1 H, CH), 3.19-3.05 (m, 2 H, NCH_2), 2.88-2.79 (m, 1 H, CH), 2.57 (t, *J* = 10.1 Hz, 1 H, one proton of NCH_2), 2.46 (s, 3 H,

CH_3), 1.65 (d, J = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3 (d, J = 244.1 Hz), 143.4, 139.3 (d, J = 3.1 Hz), 135.0, 133.1, 129.6, 129.5, 128.9, 128.7 (d, J = 7.6 Hz), 127.7, 124.6, 114.9 (d, J = 21.4 Hz), 54.0, 49.5, 45.1, 39.3, 37.5, 21.5, 13.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.5; MS (ESI) *m/z*: 398 ($[M+H]^+$); IR (neat): ν = 3411, 3025, 2957, 2924, 2892, 1599, 1505, 1478, 1451, 1345, 1305, 1290, 1222, 1162, 1123, 1091, 1042, 1016 cm^{-1}; HRMS calcd for $C_{23}H_{25}NO_2SF$ ($[M+H]^+$): 398.1585, found: 398.1588.

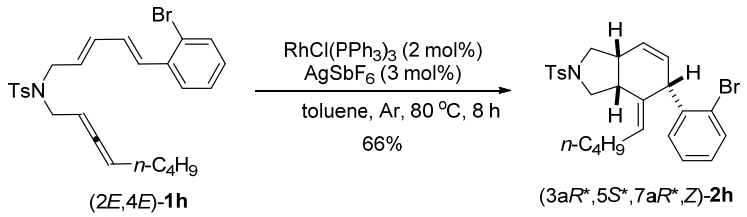
(8) Preparation of 5-(4-chlorophenyl)-2-((4-methylphenyl)sulfonyl)-4-ethylidene-2,3,3a,4,5,7a-hexahydro-1*H*-isoindole (3a*R,5*R**,7a*R**,*Z*)-2g.** (hanyl-7-167)



(2*E*,4*E*)-**1g** (3a*R**,5*R**,7a*R**,*Z*)-**2g**

The reaction of $RhCl(PPh_3)_3$ (9.3 mg, 0.01 mmol) and (2*E*,4*E*)-**1g** (206.6 mg, 0.5 mmol) in 2.5 mL of toluene at 80 °C for 15 h afforded (3a*R**,5*R**,7a*R**,*Z*)-**2g** (129.6 mg, 63%) (eluent: petroleum ether/ethyl acetate = 15/1) as a liquid: ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.1 Hz, 2 H, ArH), 7.30 (d, J = 8.1 Hz, 2 H, ArH), 7.14 (d, J = 8.5 Hz, 2 H, ArH), 7.02 (d, J = 8.3 Hz, 2 H, ArH), 5.79 (ddd, J_1 = 10.0 Hz, J_2 = 4.2 Hz, J_3 = 2.2 Hz, 1 H, HC=), 5.63 (q, J = 6.8 Hz, 1 H, HC=), 5.57 (d, J = 10.1 Hz, 1 H, HC=), 3.89 (s, 1 H, CH), 3.57 (dd, J_1 = 9.8 Hz, J_2 = 7.2 Hz, 1 H, one proton of NCH_2), 3.37 (q, J = 8.9 Hz, 1 H, CH), 3.17-3.07 (m, 2 H, NCH_2), 2.90-2.80 (m, 1 H, CH), 2.54 (t, J = 10.0 Hz, 1 H, one proton of NCH_2), 2.48 (s, 3 H, CH_3), 1.65 (d, J = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 142.2, 134.7, 133.0, 131.9, 129.5, 129.14, 129.07, 128.6, 128.2, 127.6, 124.8, 54.0, 49.5, 45.2, 39.2, 37.4, 21.6, 13.0; MS (ESI) *m/z*: 416 ($[M^+(^{37}Cl)+H]^+$), 414 ($[M^+(^{35}Cl)+H]^+$); IR (neat): ν = 3026, 2974, 2934, 2907, 2883, 2859, 1598, 1487, 1470, 1449, 1403, 1377, 1341, 1330, 1290, 1224, 1196, 1182, 1166, 1128, 1108, 1091, 1052, 1013 cm^{-1}; HRMS calcd for $C_{23}H_{25}{}^{35}ClNO_2S$ ($[M^+(^{35}Cl)+H]^+$): 414.1289, found: 414.1290.

(9) Preparation of 5-(2-bromophenyl)-2-((4-methylphenyl)sulfonyl)-4-pentylidene-2,3,3a,4,5,7a-hexahydro-1*H*-isoindole (3a*R,5*S**,7a*R**,*Z*)-2h.** (hanyl-7-189)

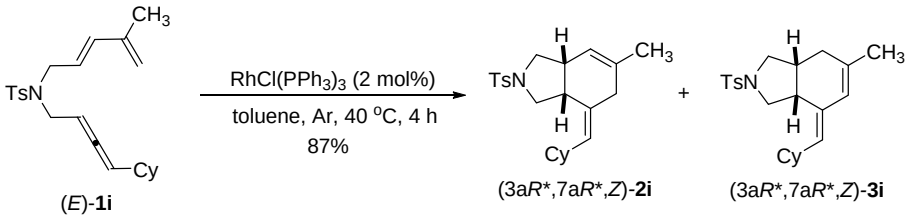


(2*E*,4*E*)-**1h** (3a*R**,5*S**,7a*R**,*Z*)-**2h**

Typical Procedure II: To a flame-dried Schlenk tube were added $AgSbF_6$ (5.0 mg, 0.015 mmol) and $RhCl(PPh_3)_3$ (9.3 mg, 0.01 mmol) inside a glove box. Under Ar atmosphere, to the Schlenk tube was added 1.5 mL of toluene outside the glove box. Then the resulting mixture was stirred at room temperature for 10 min. To the tube were added (2*E*,4*E*)-**1h** (250.9 mg, 0.5 mmol) and toluene (1 mL) sequentially. The tube was then placed in an oil bath pre-heated at 80 °C. After being stirred for 8 h, the reaction was complete as monitored by TLC. The crude reaction mixture was filtrated through a short pad of silica gel and eluted with diethyl ether (20 mL). After concentration in vacuo, the residue was purified via chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford (3a*R**,5*S**,7a*R**,*Z*)-**2h** (164.6 mg, 66%) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.1 Hz, 2 H, ArH), 7.53 (dd, J_1 = 7.9 Hz, J_2 = 1.1 Hz, 1 H, ArH), 7.28 (d, J = 8.1 Hz, 2 H, ArH), 7.22 (td, J_1 = 7.5 Hz, J_2 = 1.1 Hz, 1 H, ArH), 7.09-7.00 (m, 2 H, ArH), 5.61 (dt, J_1 = 10.1 Hz, J_2 = 2.8 Hz, 1 H, HC=), 5.43-5.34 (m, 2 H, 2 × HC=), 4.48 (s, 1 H, CH), 3.51-3.44 (m, 2 H, NCH_2), 3.43-3.36 (m, 1 H, one proton of NCH_2), 3.30-3.21 (m, 1 H, CH), 3.06 (t, J = 9.8 Hz, 1 H, one proton of NCH_2), 2.74 (brs, 1 H, CH), 2.42 (s, 3 H, CH_3), 2.03-1.84 (m, 2 H, CH_2), 1.27-1.17 (m, 4 H, 2 × CH_2), 0.84 (t, J = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 143.4, 133.5, 132.9, 132.6, 132.2, 130.8, 130.2, 129.5, 128.2, 127.8, 127.6, 127.5, 124.5, 65.7, 54.4, 50.3, 44.6, 38.4, 38.1, 31.6, 27.5, 22.2, 21.4, 15.2, 13.8; MS (ESI) *m/z*: 502 ($[M^+(^{81}Br)+H]^+$), 500 ($[M^+(^{79}Br)+H]^+$); IR (neat): ν = 3652, 3556, 3030, 2956, 2254, 1922, 1810, 1596, 1465, 1345, 1160, 1092, 1020 cm^{-1}; HRMS calcd for $C_{26}H_{31}O_2N^{79}BrS$ ($[M^+(^{79}Br)+H]^+$): 500.1264, found:

500.1245.

(10) Preparation of 6-methyl-2-((4-methylphenyl)sulfonyl)-4-cyclohexylmethylene-2,3,3a,4,5,7a-hexahydro-1*H*-isoindole (3a*R,7a*R**,*Z*)-2i.** (hanyl-7-084)

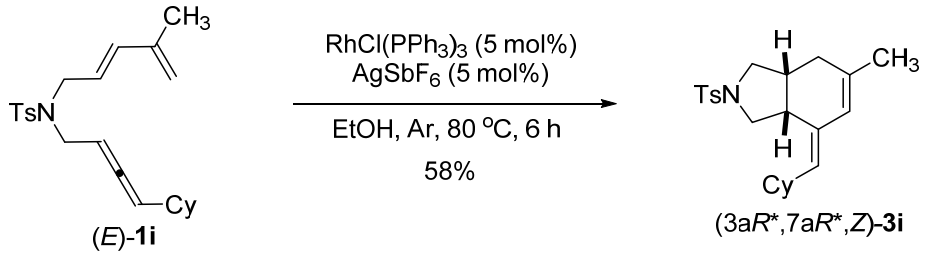


Following **Typical Procedure I**, the reaction of $RhCl(PPh_3)_3$ (18.9 mg, 0.02 mmol) and (2*E*)-**1i** (367.3 mg, 1.0 mmol) in 5 mL of toluene at 40 °C for 4 h afforded the mixture of (3a*R**,7a*R**,*Z*)-**2i** and (3a*R**,7a*R**,*Z*)-**3i**. The ratio of **2i**/**3i** (15/1) was determined by ^{1}H NMR analysis of the crude product, which was separated by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford a mixture of (3a*R**,7a*R**,*Z*)-**2i** and (3a*R**,7a*R**,*Z*)-**3i** (319.2 mg, **2i/3i =** 27/1, 87%) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.1 Hz, 2 H, ArH), 7.31 (d, J = 8.1 Hz, 2 H, ArH), 5.13 (d, J = 8.0 Hz, 1 H, HC=), 4.75 (s, 1 H, HC=), 3.47 (dd, J_1 = 10.4 Hz, J_2 = 6.2 Hz, 1 H, one proton of NCH_2), 3.33 (t, J = 8.8 Hz, 1 H, one proton of NCH_2), 3.29-3.15 (m, 2 H, one proton of NCH_2 + CH), 3.00 (t, J = 9.8 Hz, 1 H, one proton of NCH_2), 2.67-2.56 (m, 2 H, CH + one proton of $=CCH_2$), 2.42 (s, 3 H, CH_3), 2.29 (d, J = 18.3 Hz, 1 H, one proton of $=CCH_2$), 2.20-2.05 (m, 1 H, CH of Cy), 1.74-1.58 (m, 3 H, CH_2 + one proton of CH_2), 1.53-1.45 (m, 2 H, CH_2), 1.38 (s, 3 H, CH_3), 1.28-0.95 (m, 5 H, 2 × CH_2 + one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ143.1, 134.6, 133.9, 133.0, 129.4, 129.1, 127.4, 121.5, 54.1, 49.4, 40.6, 38.4, 36.1, 35.2, 33.8, 33.6, 25.9, 25.8, 23.0, 21.4; MS (ESI) *m/z*: 386 ($[M+H]^+$); IR (neat): ν = 2921, 2848, 1921, 1597, 1445, 1343, 1220, 1160, 1091, 1065, 1031 cm^{-1}; HRMS calcd for $C_{23}H_{32}O_2NS$ ($[M+H]^+$): 386.2148, found: 386.2147.

The following signals are discernible for (3a*R**,7a*R**,*Z*)-**3i:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.4 Hz, 2 H, ArH), 7.35 (d, J = 8.0 Hz, 2 H, ArH), 5.69 (s, 1 H, HC=), 3.52 (t, J = 7.4 Hz, 1 H, one proton of NCH_2), 3.40 (dd, J_1 = 10.0 Hz, J_2 = 5.2

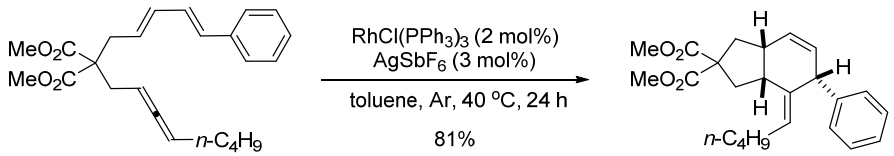
Hz, 1 H, one proton of NCH_2), 2.44 (s, 3 H, CH_3).

(11) **Preparation of 6-methyl-2-((4-methylphenyl)sulfonyl)-4-(cyclohexylmethylene)-2,3,3a,4,7,7a-hexahydro-1*H*-isoindole (3a*R**,7a*R**,*Z*)-3i. (hanyl-11-168)**



To a flame-dried Schlenk tube were added $RhCl(PPh_3)_3$ (4.7 mg, 0.005 mmol) and $AgSbF_6$ (1.8 mg, 0.005 mmol) inside a glove box. Under Ar atmosphere, to the Schlenk tube was added 0.5 mL of EtOH outside the glove box. Then the resulting mixture was stirred at room temperature for 10 min. To the tube were added (*E*)-**1i** (38.1 mg, 0.1 mmol) and EtOH (0.5 mL) sequentially. The tube was then placed in an oil bath pre-heated at 80 ^oC. After being stirred for 6 h, the reaction was complete as monitored by TLC. The crude reaction mixture was filtrated through a pad of kieselguhr and eluted with ethyl acetate (20 mL). After concentration in vacuo, the residue was purified via chromatography on silica gel afforded (3a*R**,7a*R**,*Z*)-**3i** (22.1 mg, 58%) (eluent: petroleum ether/ethyl acetate = 30/1) as a liquid: ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.0 Hz, 2 H, ArH), 7.35 (t, J = 7.6 Hz, 2 H, ArH), 5.69 (s, 1 H, HC=), 5.11 (d, J = 10.0 Hz, 1 H, HC=), 3.57-3.47 (m, 1 H, one proton of NCH_2), 3.40 (dd, J_1 = 10.0 Hz, J_2 = 5.2 Hz, 1 H, one proton of NCH_2), 3.22 (d, J = 10.0 Hz, 1 H, one proton of NCH_2), 2.92-2.79 (m, 2 H, CH + one proton of NCH_2), 2.45 (s, 3 H, CH_3), 2.26-2.17 (m, 1 H, CH), 2.09-1.98 (m, 1 H, CH), 1.85-1.65 (m, 4 H, 2 × CH_2), 1.60 (s, 3 H, CH_3), 1.56-1.47 (m, 2 H, two protons of Cy), 1.43-0.96 (m, 6 H, 3 × CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 135.1, 134.2, 132.6, 129.7, 129.6, 127.4, 124.6, 54.1, 50.2, 37.5, 36.9, 35.9, 33.7, 33.2, 30.9, 25.9, 25.87, 25.81, 23.4, 21.5; MS (EI) *m/z* (%): 385 (M^+, 20.85), 230 (100); IR (neat): ν = 2918, 2851, 1727, 1596, 1470, 1442, 1345, 1286, 1219, 1179, 1156, 1089, 1046, 1009 cm^{-1}; HRMS calcd for $C_{23}H_{32}NO_2S$ ($[M+H]^+$): 386.2148, found: 386.2140.

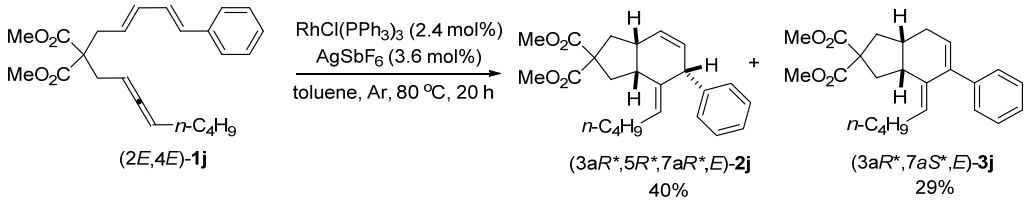
(12) **Preparation of dimethyl 5-phenyl-4-pentylidene-1,3,3a,4,5,7a-hexahydro-2*H*-indene-2,2-dicarboxylate (3a*R**,5*R**,7a*R**,*E*)-2j.** (hanyl-9-160)



(2*E*,4*E*)-**1j** (3a*R**,5*R**,7a*R**,*E*)-**2j**

Following **Typical Procedure II**, the reaction of $RhCl(PPh_3)_3$ (9.2 mg, 0.01 mmol), $AgSbF_6$ (5.1 mg, 0.015 mmol), and (2*E*,4*E*)-**1j** (191.2 mg, 0.5 mmol) in 2.5 mL of toluene at 40 °C for 24 h afforded (3a*R**,5*R**,7a*R**,*E*)-**2j** (155.6 mg, 81%) (eluent: petroleum ether/ethyl acetate = 30/1) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 7.4 Hz, 2 H, ArH), 7.27 (t, J = 7.5 Hz, 2 H, ArH), 7.17 (t, J = 7.2 Hz, 1 H, ArH), 5.93 (ddd, J_1 = 10.0 Hz, J_2 = 4.0 Hz, J_3 = 2.2 Hz, 1 H, HC=), 5.75 (d, J = 10.1 Hz, 1 H, HC=), 5.56 (t, J = 7.4 Hz, 1 H, HC=), 3.99 (s, 1 H, CH), 3.70 (s, 3 H, OCH_3), 3.64 (s, 3 H, OCH_3), 3.24 (dt, J_1 = 15.0 Hz, J_2 = 12.3 Hz, 1 H, CH), 2.83-2.74 (m, 1 H, CH), 2.55 (dd, J_1 = 13.7 Hz, J_2 = 8.4 Hz, 1 H, one proton of CH_2), 2.30 (dd, J_1 = 13.6 Hz, J_2 = 3.5 Hz, 1 H, one proton of CH_2), 2.15-1.99 (m, 3 H, one proton of CH_2 + CH_2), 1.94 (t, J = 13.0 Hz, 1 H, one proton of CH_2), 1.42-1.24 (m, 4 H, 2 × CH_2), 0.90 (t, J = 7.0 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 172.3, 144.5, 136.8, 131.1, 129.2, 128.0, 127.97, 127.3, 125.9, 59.6, 52.7, 52.5, 46.1, 40.3, 40.2, 38.9, 37.8, 32.1, 27.0, 22.2, 14.0; MS (ESI) *m/z*: 405 ($[M+Na]^+$), 383 ($[M+H]^+$); IR (neat): ν = 3023, 2953, 2928, 2858, 1732, 1599, 1492, 1434, 1378, 1340, 1247, 1199, 1158, 1109, 1065, 1031 cm^{-1}; HRMS calcd for $C_{24}H_{31}O_4$ ($[M+H]^+$): 383.2217, found: 383.2220.

(13) **Preparation of Dimethyl 4-pentylidene-5-phenyl-1,3,3a,4,7,7a-hexahydro-2*H*-indene-2,2-dicarboxylate (3a*R**,5*R**,7a*R**,*E*)-2j and Dimethyl 4-pentylidene-5-phenyl-1,3,3a,4,7,7a-hexahydro-2H-indene-2,2-dicarboxylate (3a*R**,7a*S**,*E*)-3j.** (hanyl-8-021)



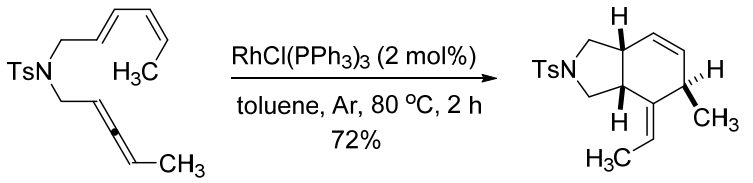
Following **Typical Procedure II**, the reaction of $RhCl(PPh_3)_3$ (9.4 mg, 0.01 mmol), $AgSbF_6$ (5.4 mg, 0.015 mmol), and (2*E*,4*E*)-**1j** (162.1 mg, 0.42 mmol) in 2.5 mL of toluene at 80 °C for 20 h afforded (3a*R**,7a*S**,*E*)-**3j** (38% NMR yield), (3a*R**,5*R**,7a*R**,*E*)-**2j** (47% NMR yield) and an unidentified product. The crude product was purified via chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) to afford (3a*R**,7a*S**,*E*)-**3j** (46.8 mg, 29%) and (3a*R**,5*R**,7a*R**,*E*)-**2j** (65.2 mg, 40%).

(3a*R**,7a*S**,*E*)-**3j:** solid, m.p. 80-81 °C (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.23 (m, 3 H, Ar-H), 7.21-7.16 (m, 2 H, Ar-H), 5.56 (dd, J_1 = 4.8 Hz, J_2 = 3.2 Hz, 1 H, HC=), 5.25 (t, J = 7.4 Hz, 1 H, HC=), 3.77 (s, 3 H, CH_3), 3.73 (s, 3 H, CH_3), 3.23-3.13 (m, 1 H, CH), 2.62 (dd, J_1 = 13.5 Hz, J_2 = 6.8 Hz, 1 H, CH), 2.44-2.21 (m, 4 H, 2 × CH_2), 2.20-2.10 (m, 2 H, CH_2), 2.09-1.94 (m, 2 H, CH_2), 1.34-1.22 (m, 4 H, 2 × CH_2), 0.87 (t, J = 7.0 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 173.1, 142.2, 140.0, 134.5, 130.8, 129.2, 127.7, 126.4, 125.5, 58.5, 52.8, 52.7, 40.1, 39.9, 38.3, 36.2, 31.8, 27.8, 27.5, 22.5, 14.0; MS (EI) *m*/*z* (%): 382 (M^+, 8.67), 145 (100); IR (neat): ν = 3656, 3470, 3024, 2953, 2857, 2256, 1949, 1732, 1603, 1491, 1436, 1247, 1196, 1178, 1152, 1127, 1067, 1023 cm^{-1}; Anal Calcd for $C_{24}H_{30}O_4$: C 75.36, H 7.91; found: C 75.23, H 7.99.

(3a*R**,5*R**,7a*R**,*E*)-**2j**: liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.23 (m, 2 H, Ar-H), 7.22-7.16 (m, 2 H, Ar-H), 7.09 (t, J = 7.2 Hz, 1 H, Ar-H), 5.85 (ddd, J_1 = 10.0 Hz, J_2 = 4.2 Hz, J_3 = 2.3 Hz, 1 H, HC=), 5.68 (dt, J_1 = 10.1 Hz, J_2 = 2.0 Hz, 1 H, HC=), 5.48 (t, J = 7.2 Hz, 1 H, HC=), 3.91 (s, 1 H, CH), 3.62 (s, 3 H, OCH_3), 3.56 (s, 3 H, OCH_3), 3.17 (dt, J_1 = 12.4 Hz, J_2 = 7.6 Hz, 1 H, CH), 2.75-2.67 (m, 1 H, CH), 2.47 (dd, J_1 = 13.8 Hz, J_2 = 8.4 Hz, 1 H, one proton of CH_2), 2.22 (dd, J_1 = 13.7 Hz, J_2 = 3.6 Hz, 1 H, one proton of CH_2), 2.07-1.93 (m, 3 H, CH_2 + one proton of CH_2), 1.86 (t, J = 13.0 Hz, 1 H, one proton of CH_2), 1.33-1.19 (m, 4 H, 2 × CH_2), 0.82 (t, J =

7.2 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 172.3, 144.4, 136.8, 131.0, 129.2, 128.0, 127.9, 127.3, 125.9, 59.6, 52.6, 52.4, 46.1, 40.3, 40.2, 38.9, 37.8, 32.1, 27.0, 22.2, 13.9.

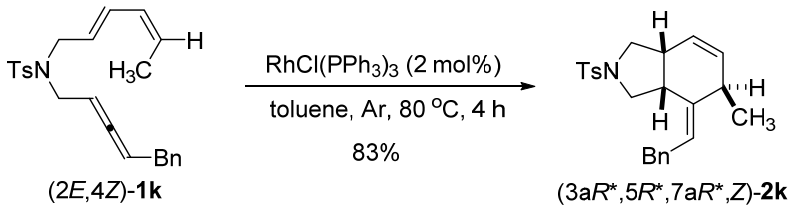
(14) **Preparation of 5-methyl-2-((4-methylphenyl)sulfonyl)-4-ethylidene-2,3,3a,4,5,7a-hexahydro-1*H*-isoindole (3a*R**,5*R**,7a*R**,*Z*)-2b.** (hanyl-10-105)



(2*E*,4*Z*)-**1b** (3a*R**,5*R**,7a*R**,*Z*)-**2b**

Following **Typical Procedure I**, the reaction of $RhCl(PPh_3)_3$ (9.3 mg, 0.01 mmol) and (2*E*,4*Z*)-**1b** (159.3 mg, 0.5 mmol) in 2.5 mL of toluene at 80 °C for 2 h afforded (3a*R**,5*R**,7a*R**,*Z*)-**2b** (115.5 mg, 72%) (eluent: petroleum ether/ethyl acetate = 20/1) as a solid: m.p. 86-87 °C (dichloromethane/hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.1 Hz, 2 H, ArH), 7.32 (d, J = 8.1 Hz, 2 H, ArH), 5.38-5.28 (m, 2 H, 2 × HC=), 5.16 (d, J = 9.8 Hz, 1 H, HC=), 3.44 (dd, J_1 = 10.0 Hz, J_2 = 6.6 Hz, 1 H, one proton of NCH_2), 3.40-3.27 (m, 2 H, one proton of NCH_2 + CH), 3.23 (d, J = 10.1 Hz, 1 H, one proton of NCH_2), 3.05 (t, J = 8.9 Hz, 1 H, one proton of NCH_2), 2.77-2.66 (m, 2 H, 2 × CH), 2.43 (s, 3 H, CH_3), 1.59 (dd, J_1 = 6.6 Hz, J_2 = 1.8 Hz, 3 H, CH_3), 1.06 (d, J = 7.0 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 136.0, 133.8, 133.7, 129.3, 127.3, 126.3, 118.4, 53.4, 49.4, 39.8, 38.1, 30.9, 21.3, 18.2, 12.6; MS (ESI) *m/z*: 318 ($[M+H]^+$); IR (neat): ν = 3068, 2967, 2912, 2872, 2806, 1595, 1469, 1401, 1335, 1302, 1227, 1204, 1162, 1091, 1047 cm^{-1}; Anal Calcd for $C_{18}H_{23}NO_2S$: C 68.11, H 7.30, N 4.41; found: C 68.24, H 7.37, N 4.37.

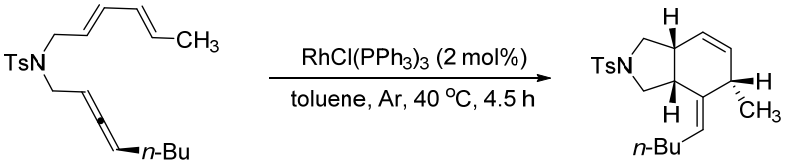
(15) **Preparation of 5-methyl-4-(2-phenylethylidene)-2-((4-methylphenyl)-sulfonyl)-2,3,3a,4,5,7a-hexahydro-1H-isoindole (3a*R**,5*R**,7a*R**,*Z*)-2k.** (hanyl-10-034)



(2*E*,4*Z*)-**1k** (3a*R**,5*R**,7a*R**,*Z*)-**2k**

Following **Typical Procedure I**, the reaction of $RhCl(PPh_3)_3$ (9.2 mg, 0.01 mmol) and (2*E*,4*Z*)-**1k** (196.7 mg, 0.5 mmol) in 2.5 mL of toluene at 80 °C for 4 h afforded (3a*R**,5*R**,7a*R**,*Z*)-**2k** (162.0 mg, 83%) (eluent: petroleum ether/ethyl acetate = 20/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 2 H, ArH), 7.28 (t, *J* = 8.7 Hz, 4 H, ArH), 7.19 (t, *J* = 7.4 Hz, 1 H, ArH), 7.09 (d, *J* = 7.5 Hz, 2 H, ArH), 5.48 (t, *J* = 7.6 Hz, 1 H, HC=), 5.36 (d, *J* = 9.8 Hz, 1 H, HC=), 5.20 (d, *J* = 9.8 Hz, 1 H, HC=), 3.47-3.32 (m, 5 H, CH_2 of Bn + two protons of NCH_2 + CH), 3.27 (d, *J* = 10.1 Hz, 1 H, one proton of NCH_2), 3.19-3.10 (m, 1 H, one proton of NCH_2), 2.86-2.77 (m, 1 H, CH), 2.76-2.69 (m, 1 H, CH), 2.42 (s, 3 H, CH_3), 1.10 (d, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 140.7, 136.9, 133.95, 133.91, 129.5, 128.5, 128.1, 127.5, 126.5, 126.0, 123.1, 53.5, 49.8, 40.4, 38.8, 33.3, 31.2, 21.5, 18.4; MS (ESI) *m/z*: 394 ($[M+H]^+$); IR (neat): ν = 3060, 3022, 2960, 2891, 2875, 1598, 1493, 1452, 1397, 1342, 1304, 1289, 1220, 1159, 1108, 1090, 1043 cm^{-1}; HRMS calcd for $C_{24}H_{28}NO_2S$ ($[M+H]^+$): 394.1835, found: 394.1832.

4. Rhodium-catalyzed Intramolecular [4+2] Cycloaddition of Optically Active Allene-1,3-dienes (R_a,2*E*,4*E*)-1a



(R_a,2*E*,4*E*)-**1a**
92% ee

(3a*R*,5*S*,7a*R*,*Z*)-**2a**
76% yield, 75% ee

To a flame-dried Schlenk tube were added $RhCl(PPh_3)_3$ (3.9 mg, 0.02 mmol), (R_a,2*E*,4*E*)-**1a** (72.4 mg, 0.2 mmol, 92% ee) and toluene (2 mL) sequentially under Ar atmosphere. The Schlenk tube was then placed in an oil bath pre-heated at 40 °C. After being stirred for 4.5 h, the reaction was complete as monitored by TLC. The crude reaction mixture was filtrated through a pad of silica gel and eluted with ether

(20 mL). After concentration in vacuo, the residue was purified via chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford (3a*R*,5*S*,7a*R*,*Z*)-**2a** (55.3 mg, 76%) as a liquid: 75% ee (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 214 nm, t_R(major) = 8.68 min, t_R(minor) = 11.29 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2 H, ArH), 7.32 (d, *J* = 8.0 Hz, 2 H, ArH), 5.44-5.35 (m, 2 H, 2 × HC=), 5.11 (d, *J* = 10.4 Hz, 1 H, HC=), 3.49 (dd, J_1 = 10.4 Hz, J_2 = 6.4 Hz, 1 H, one proton of NCH_2), 3.36 (t, *J* = 8.4 Hz, 1 H, one proton of NCH_2), 3.29 (d, *J* = 10.0 Hz, 1 H, one proton of NCH_2), 3.21-3.12 (m, 1 H, CH), 3.11-3.03 (m, 1 H, one proton of NCH_2), 2.78-2.68 (m, 1 H, CH), 2.65-2.57 (m, 1 H, CH), 2.44 (s, 3 H, CH_3), 2.02-1.91 (m, 2 H, CH_2), 1.33-1.22 (m, 4 H, 2 × CH_2), 1.07 (d, *J* = 7.6 Hz, 3 H, CH_3), 0.88 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 135.5, 133.7, 132.9, 129.4, 129.1, 127.4, 125.6, 54.4, 50.5, 39.1, 38.0, 35.1, 32.0, 26.6, 24.8, 22.1, 21.4, 13.8; MS (ESI) *m/z*: 360 ($[M+H]^+$); IR (neat): ν = 2956, 2923, 2894, 2859, 1597, 1492, 1451, 1332, 1300, 1232, 1160, 1131, 1088, 1051, 1028 cm^{-1}; HRMS calcd for $C_{21}H_{30}NO_2S$ ($[M+H]^+$): 360.1992, found: 360.1994.

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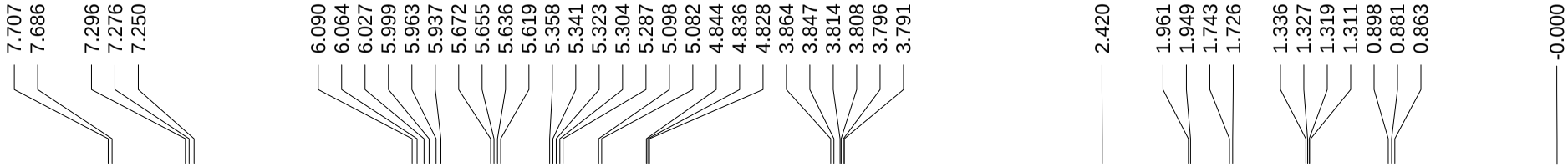

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Dec 18 2015
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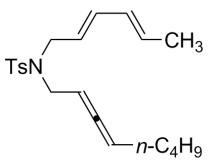
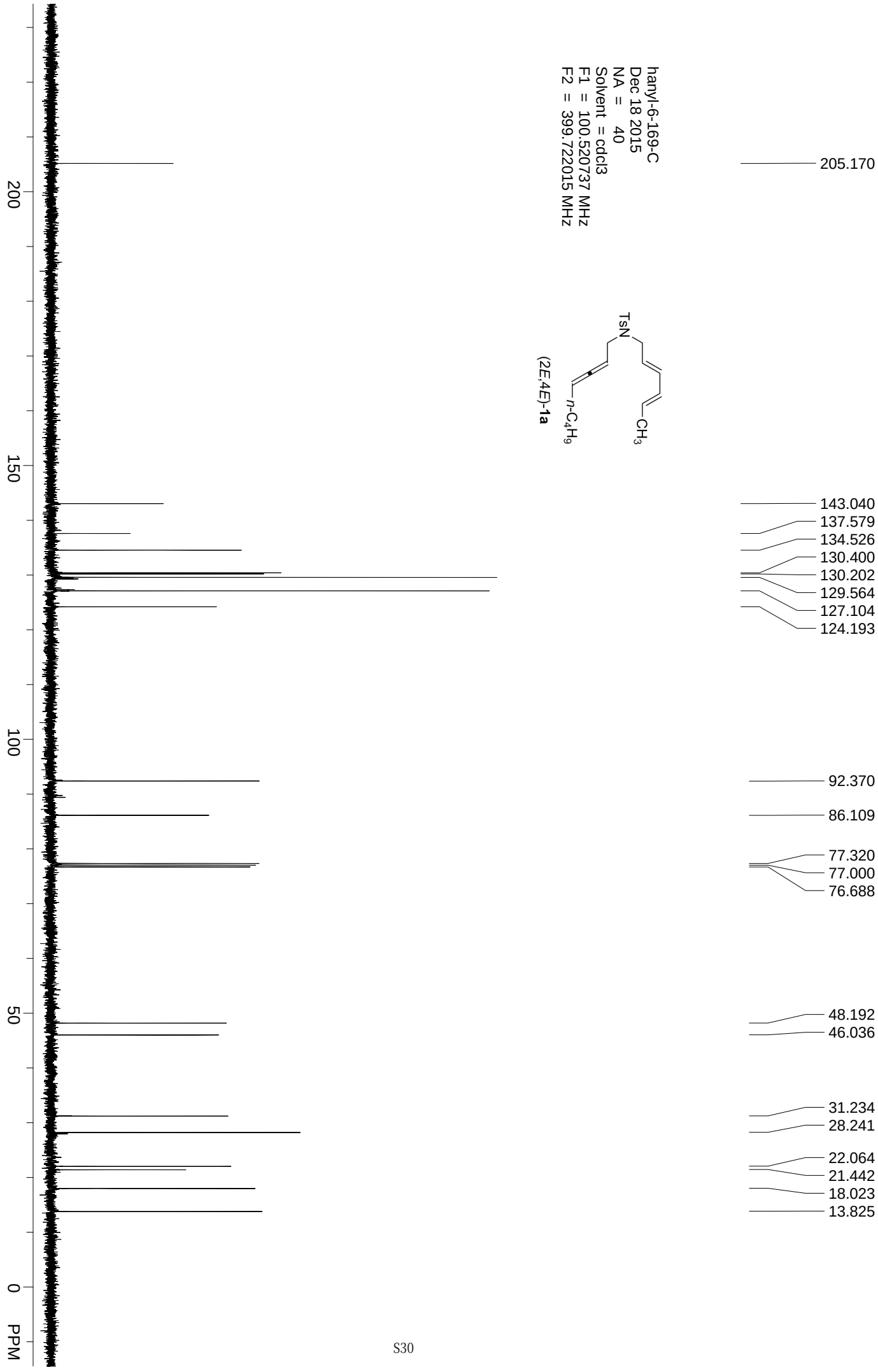
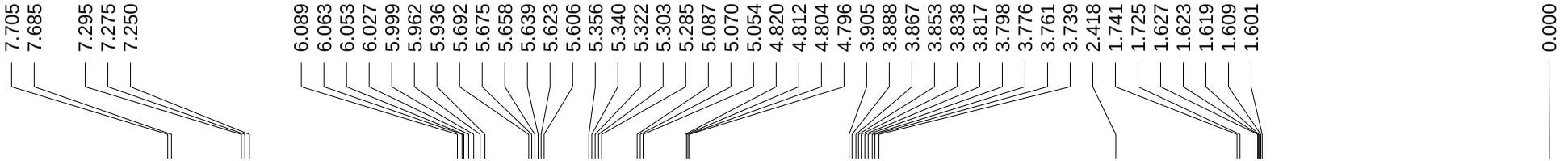
Solvent = CDCl3
F1 = 399.725433 MHz
F2 = 100.519203 MHz

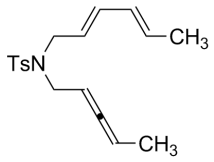


(2*E*,4*E*)-**1a**

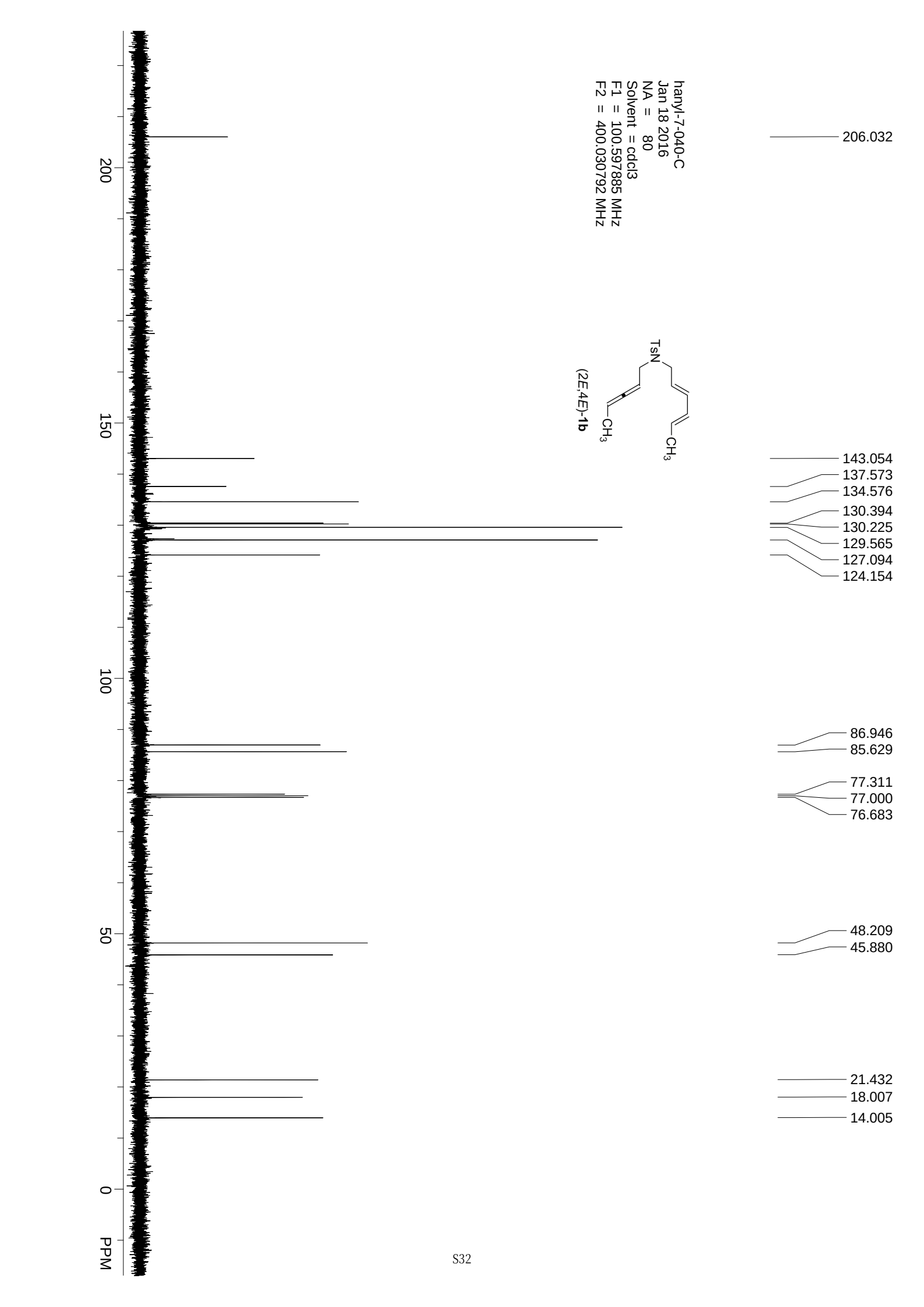

hanyl-6-169-C
Dec 18 2015
NA = 40
Solvent = cdcl3
F1 = 100.520737 MHz
F2 = 399.722015 MHz
TsN
n-C4H9
CH3
(2E,4E)-1a
205.170
143.040
137.579
134.526
130.400
130.202
129.564
127.104
124.193
92.370
86.109
77.320
77.000
76.688
48.192
46.036
31.234
28.241
22.064
21.442
18.023
13.825
200
150
100
50
0
PPM

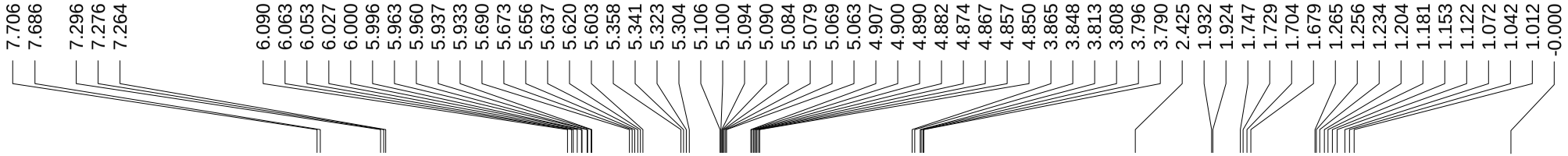


hanyl-7-040-H
Jan 18 2016
NA = 4
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz

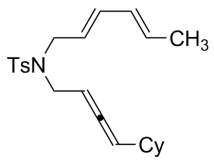


(2*E*,4*E*)-**1b**

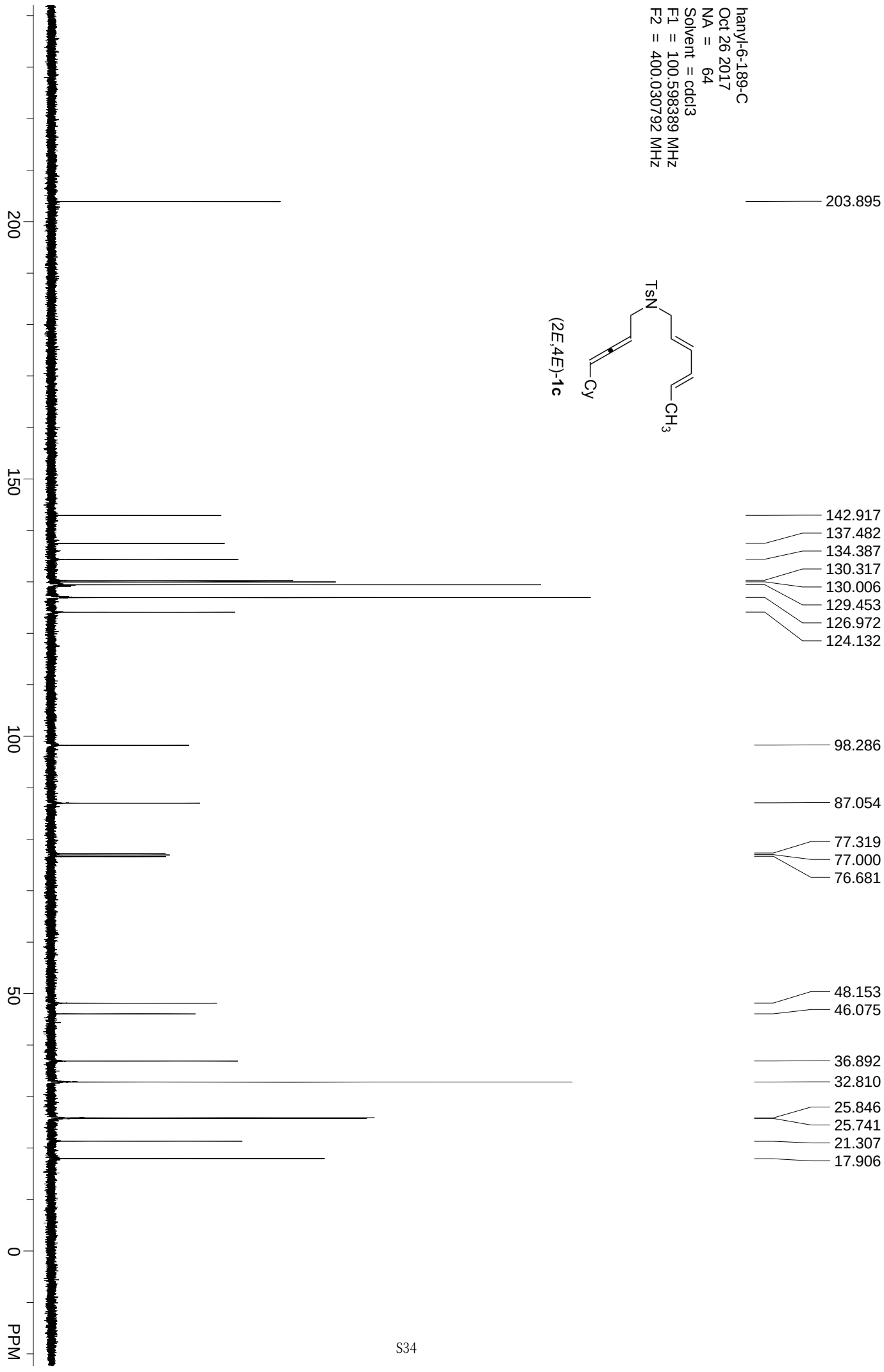

hanyl-7-040-C
Jan 18 2016
NA = 80
Solvent = cdcl3
F1 = 100.597885 MHz
F2 = 400.030792 MHz
TsN
CH3
CH3
(2E,4E)-1b
206.032
143.054
137.573
134.576
130.394
130.225
129.565
127.094
124.154
86.946
85.629
77.311
77.000
76.683
48.209
45.880
21.432
18.007
14.005
200
150
100
50
0
PPM

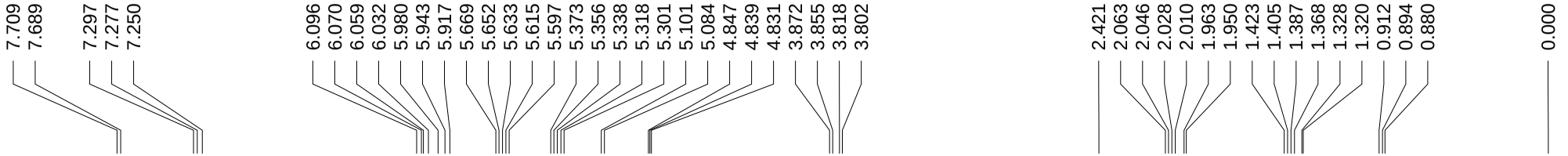


hanyl-6-189-H
Mar 14 2017
NA = 12
Solvent = CDCl3
F1 = 399.722412 MHz
F2 = 100.519203 MHz

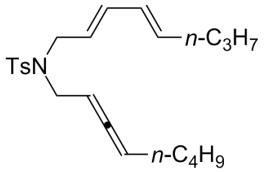


(2*E*,4*E*)-**1c**

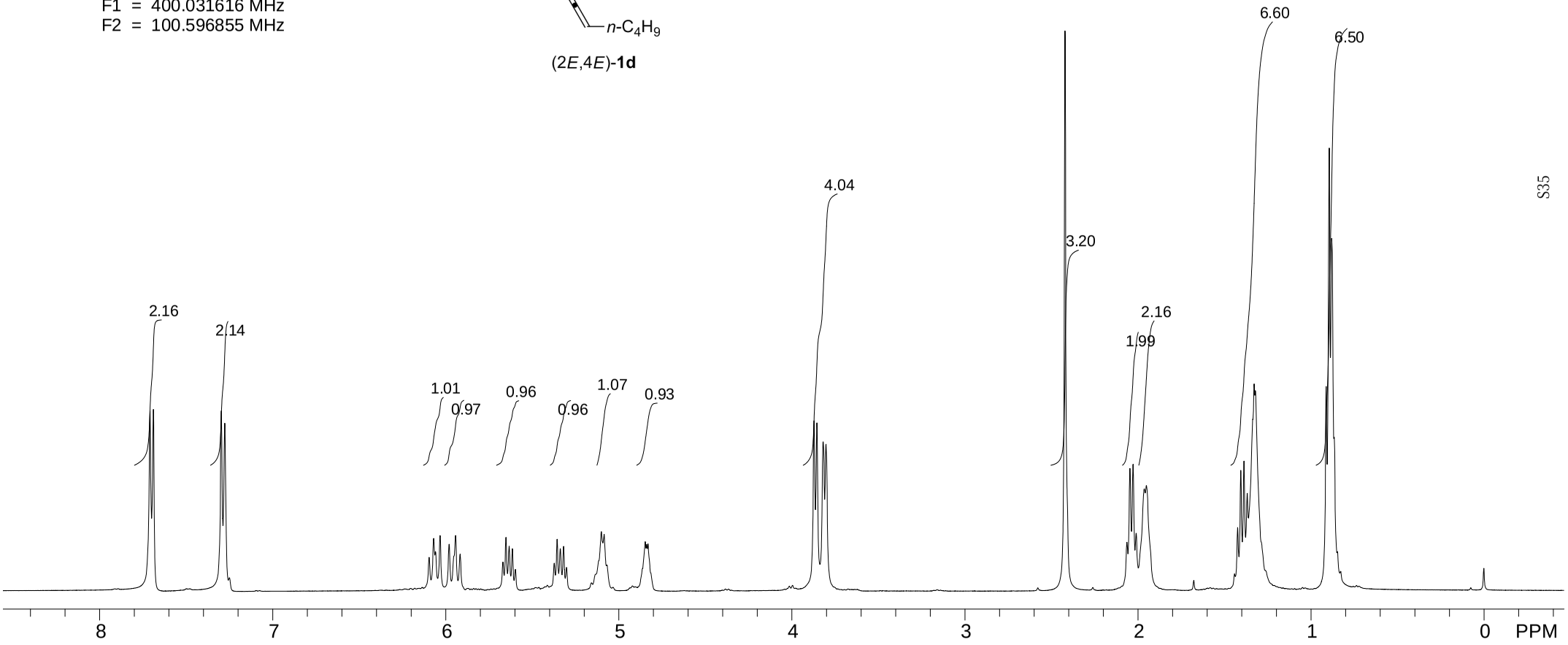

hanyl-6-189-C
Oct 26 2017
NA = 64
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
(2E,4E)-1c
TsN
Cy
CH3
203.895
142.917
137.482
134.387
130.317
130.006
129.453
126.972
124.132
98.286
87.054
77.319
77.000
76.681
48.153
46.075
36.892
32.810
25.846
25.741
21.307
17.906
200
150
100
50
0
PPM

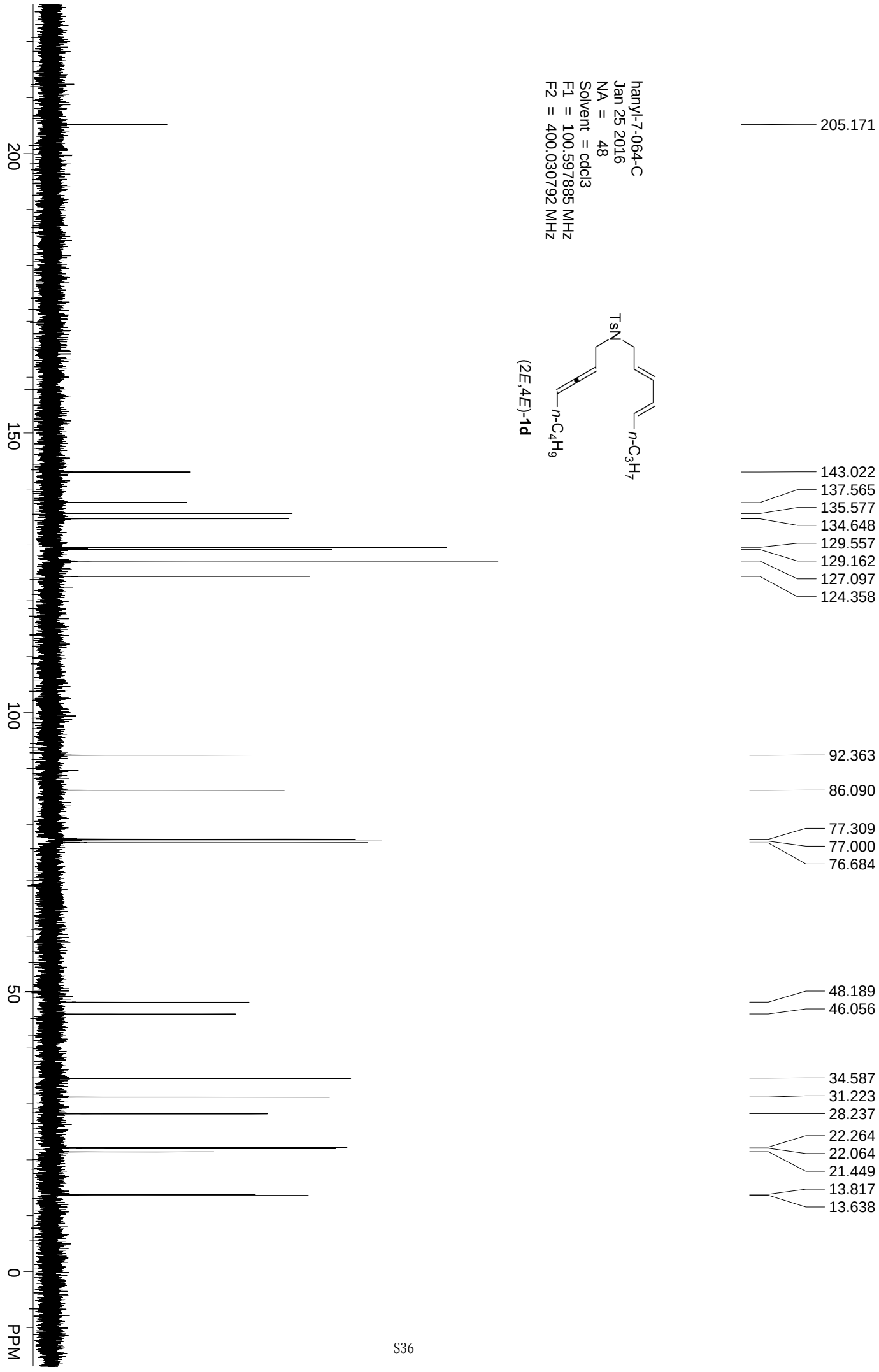


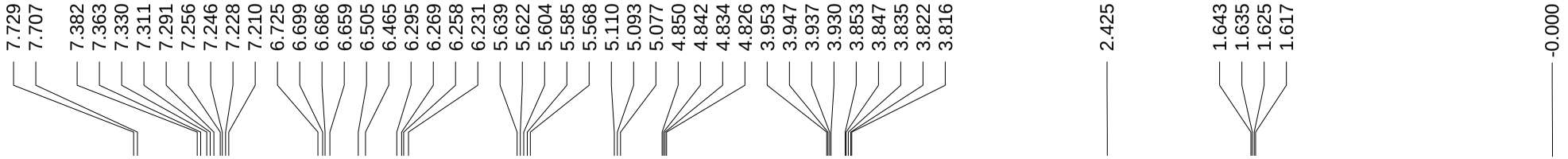
hanyl-7-064-H
Jan 25 2016
NA = 4
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz



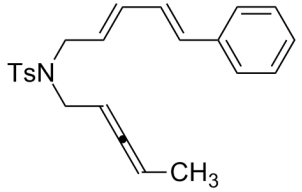
(2*E*,4*E*)-**1d**



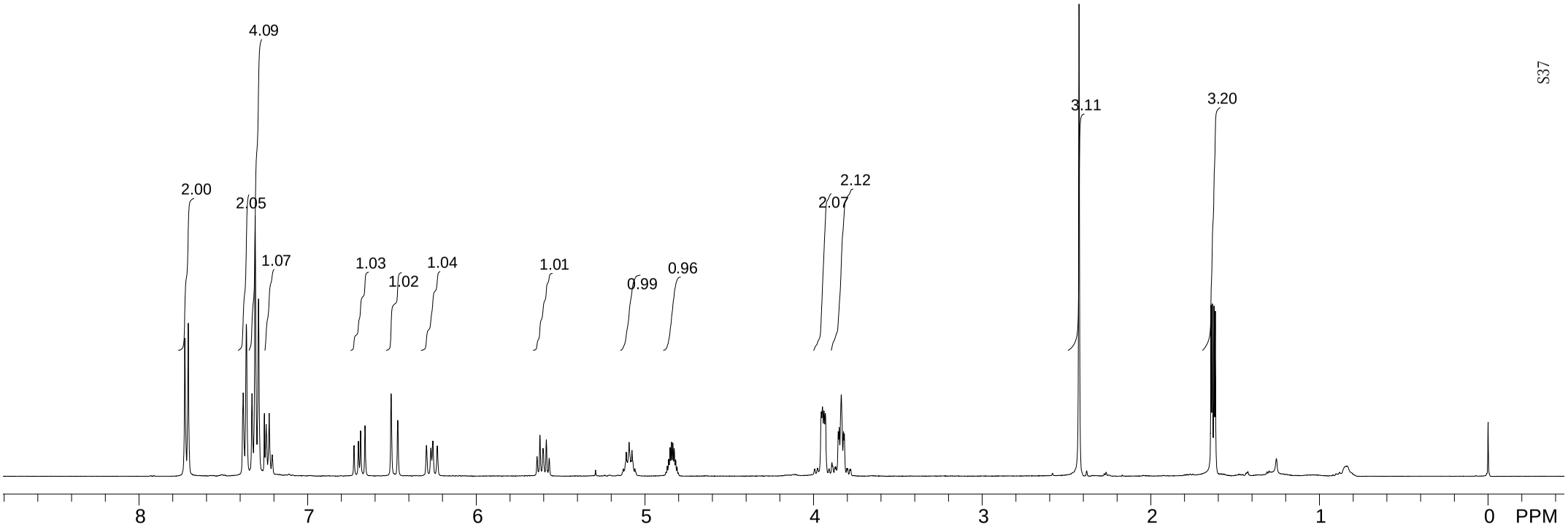

hanyl-7-064-C
Jan 25 2016
NA = 48
Solvent = cdcl3
F1 = 100.597885 MHz
F2 = 400.030792 MHz
TsN
n-C4H9
n-C3H7
(2E,4E)-1d
205.171
143.022
137.565
135.577
134.648
129.557
129.162
127.097
124.358
92.363
86.090
77.309
77.000
76.684
48.189
46.056
34.587
31.223
28.237
22.264
22.064
21.449
13.817
13.638
200
150
100
50
0
PPM

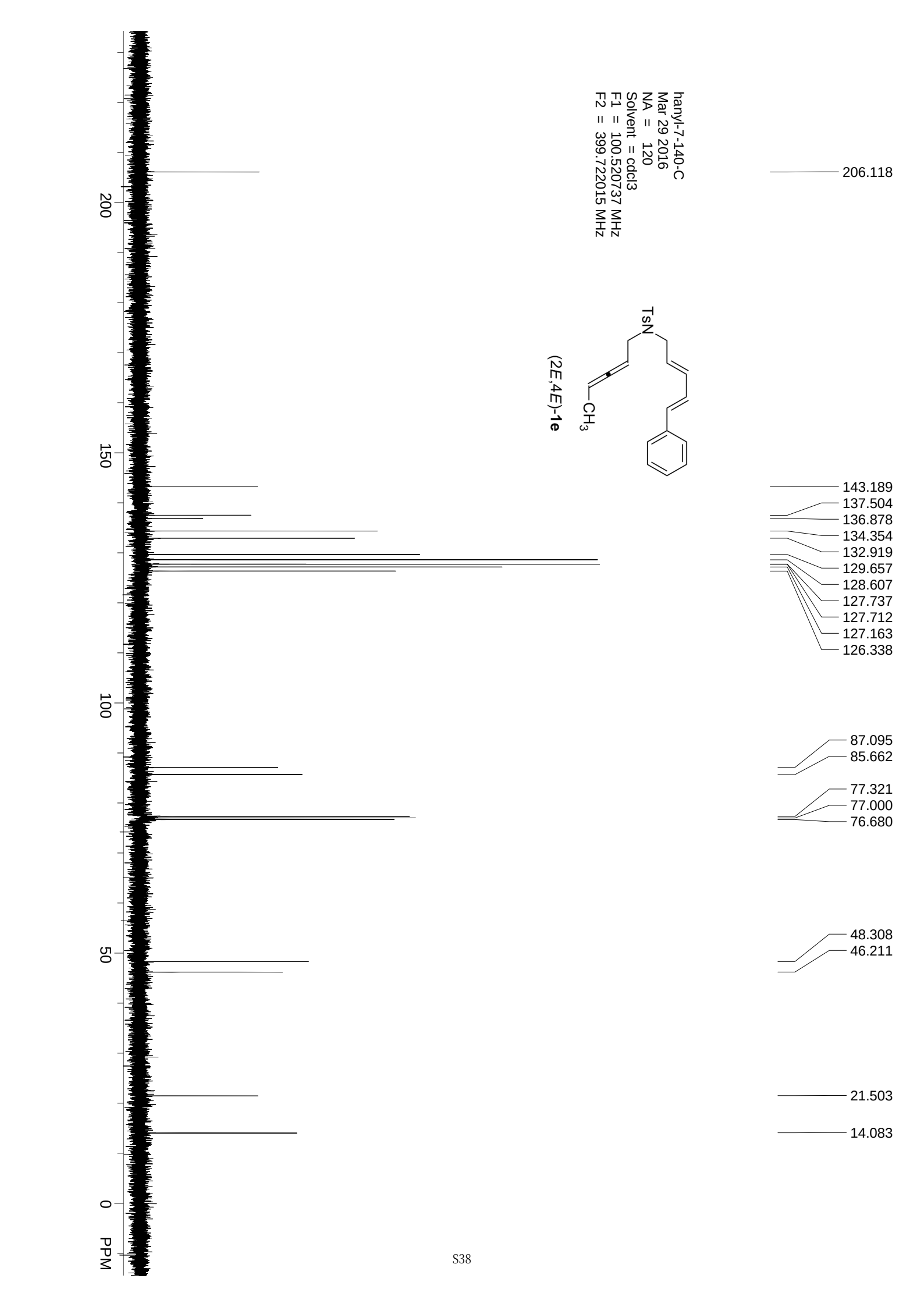


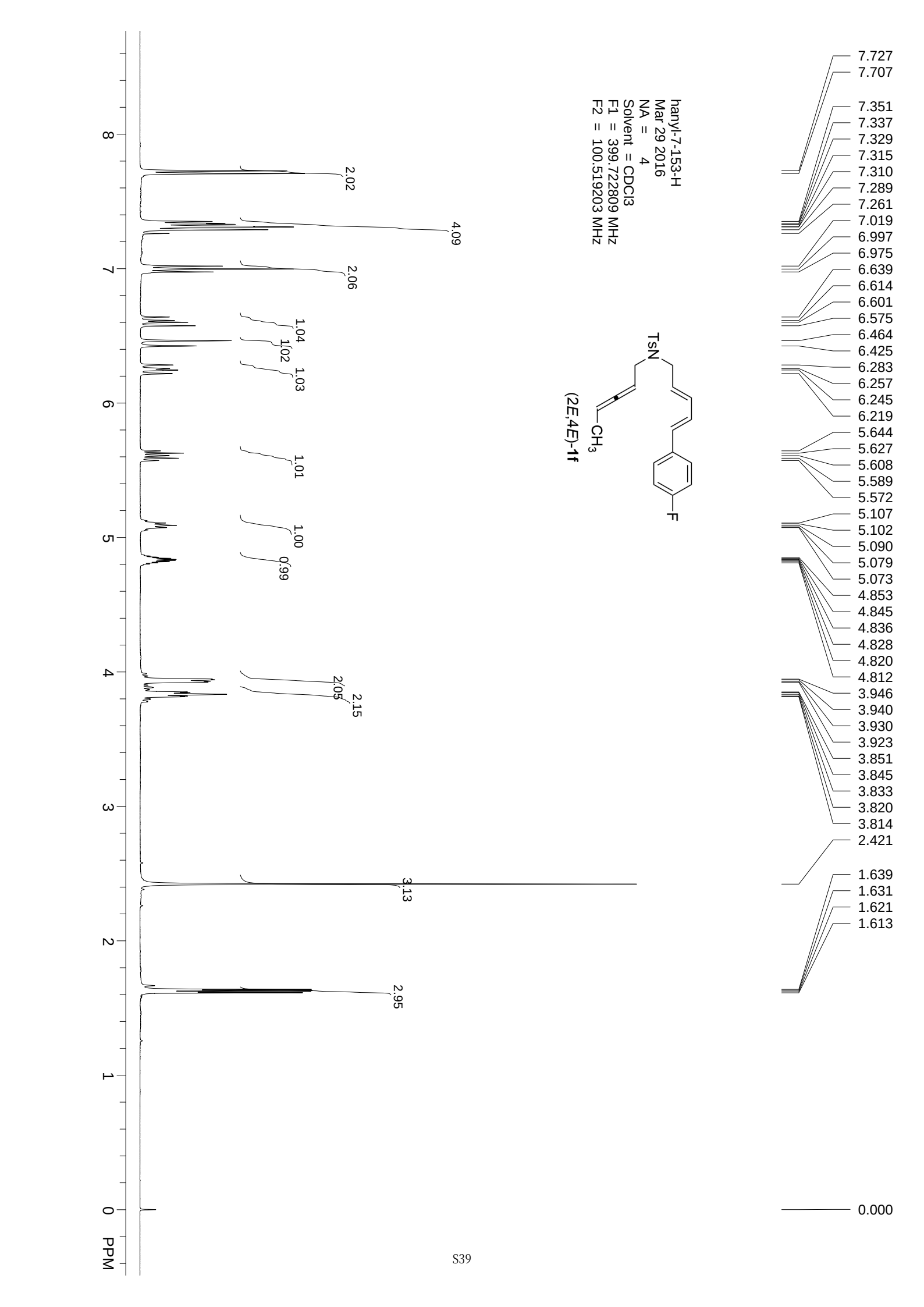
hanyl-7-140-H
Mar 29 2016
NA = 8
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz

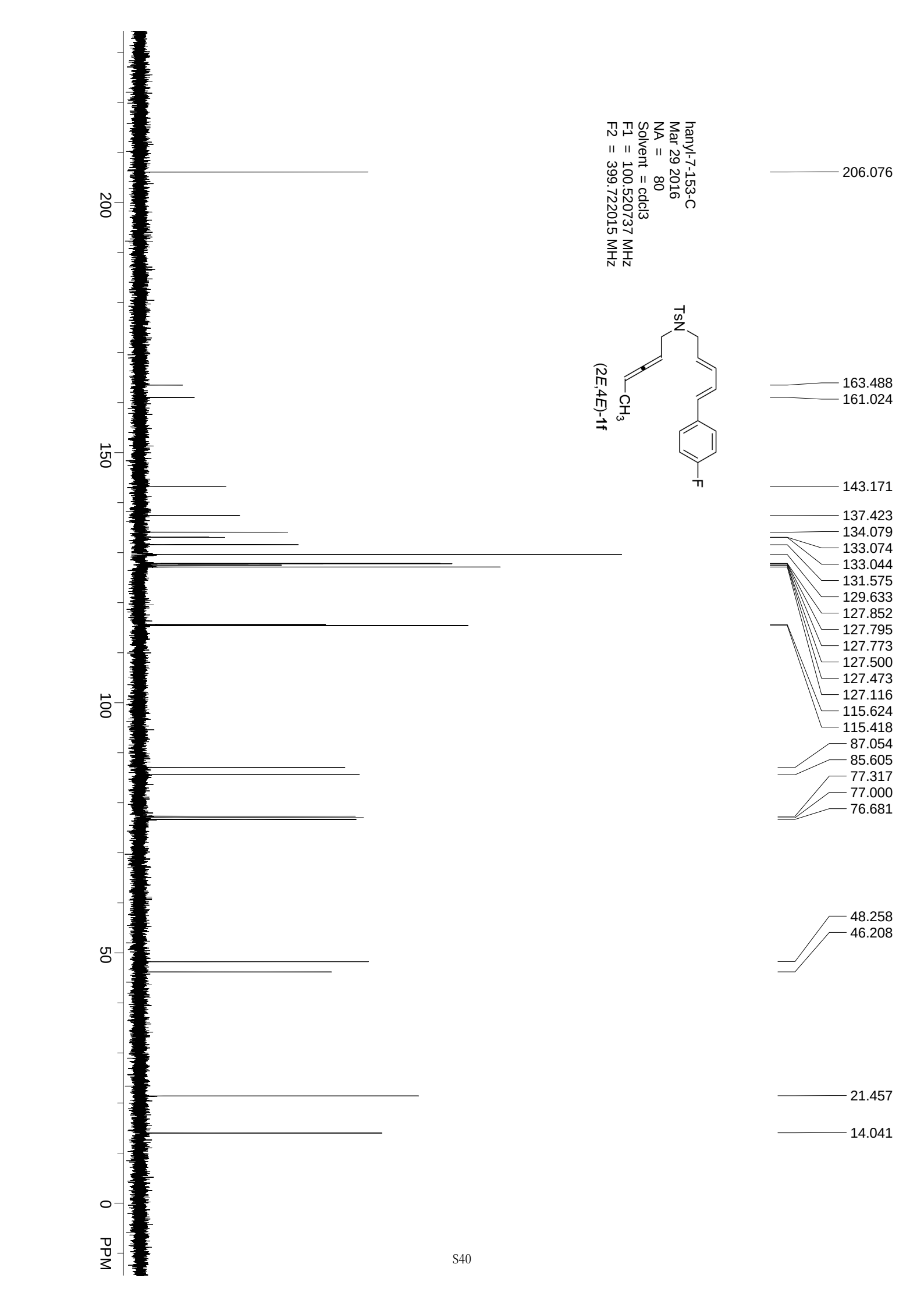


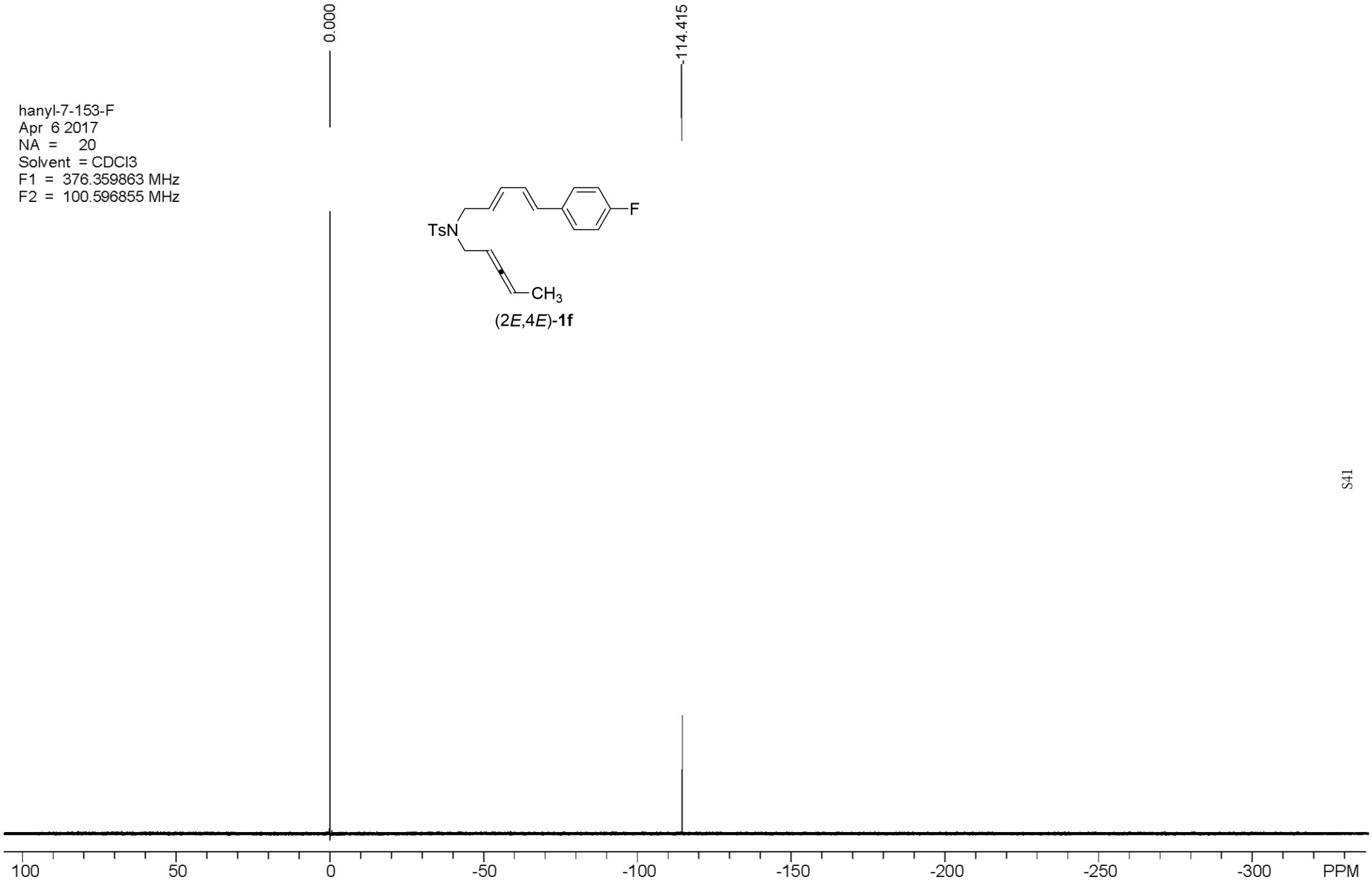
(2*E*,4*E*)-**1e**



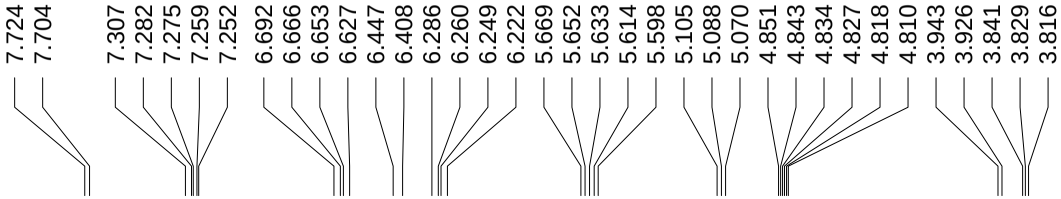

hanyl-7-140-C
Mar 29 2016
NA = 120
Solvent = cdcl3
F1 = 100.520737 MHz
F2 = 399.722015 MHz
TsN
CH3
(2E,4E)-1e
206.118
143.189
137.504
136.878
134.354
132.919
129.657
128.607
127.737
127.712
127.163
126.338
87.095
85.662
77.321
77.000
76.680
48.308
46.211
21.503
14.083
200
150
100
50
0
PPM


hanyl-7-153-H
Mar 29 2016
NA = 4
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz
TsN
CH3
F
(2E,4E)-1f
7.727
7.707
7.351
7.337
7.329
7.315
7.310
7.289
7.261
7.019
6.997
6.975
6.639
6.614
6.601
6.575
6.464
6.425
6.283
6.257
6.245
6.219
5.644
5.627
5.608
5.589
5.572
5.107
5.102
5.090
5.079
5.073
4.853
4.845
4.836
4.828
4.820
4.812
3.946
3.940
3.930
3.923
3.851
3.845
3.833
3.820
3.814
2.421
1.639
1.631
1.621
1.613
0.000
2.02
4.09
2.06
1.04
1.02
1.03
1.01
1.00
0.99
2.05
2.15
3.13
2.95
8
7
6
5
4
3
2
1
0
PPM

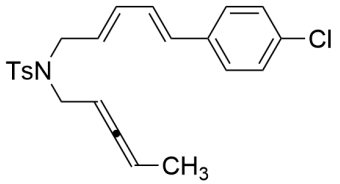

hanyl-7-153-C
Mar 29 2016
NA = 80
Solvent = cdcl3
F1 = 100.520737 MHz
F2 = 399.722015 MHz
TsN
CH3
F
(2E,4E)-1f
206.076
163.488
161.024
143.171
137.423
134.079
133.074
133.044
131.575
129.633
127.852
127.795
127.773
127.500
127.473
127.116
115.624
115.418
87.054
85.605
77.317
77.000
76.681
48.258
46.208
21.457
14.041
200
150
100
50
0
PPM


0.000
-114.415
hanyl-7-153-F
Apr 6 2017
NA = 20
Solvent = CDCl3
F1 = 376.359863 MHz
F2 = 100.596855 MHz
TsN
F
CH3
100
50
0
-50
-100
-150
-200
-250
-300
PPM

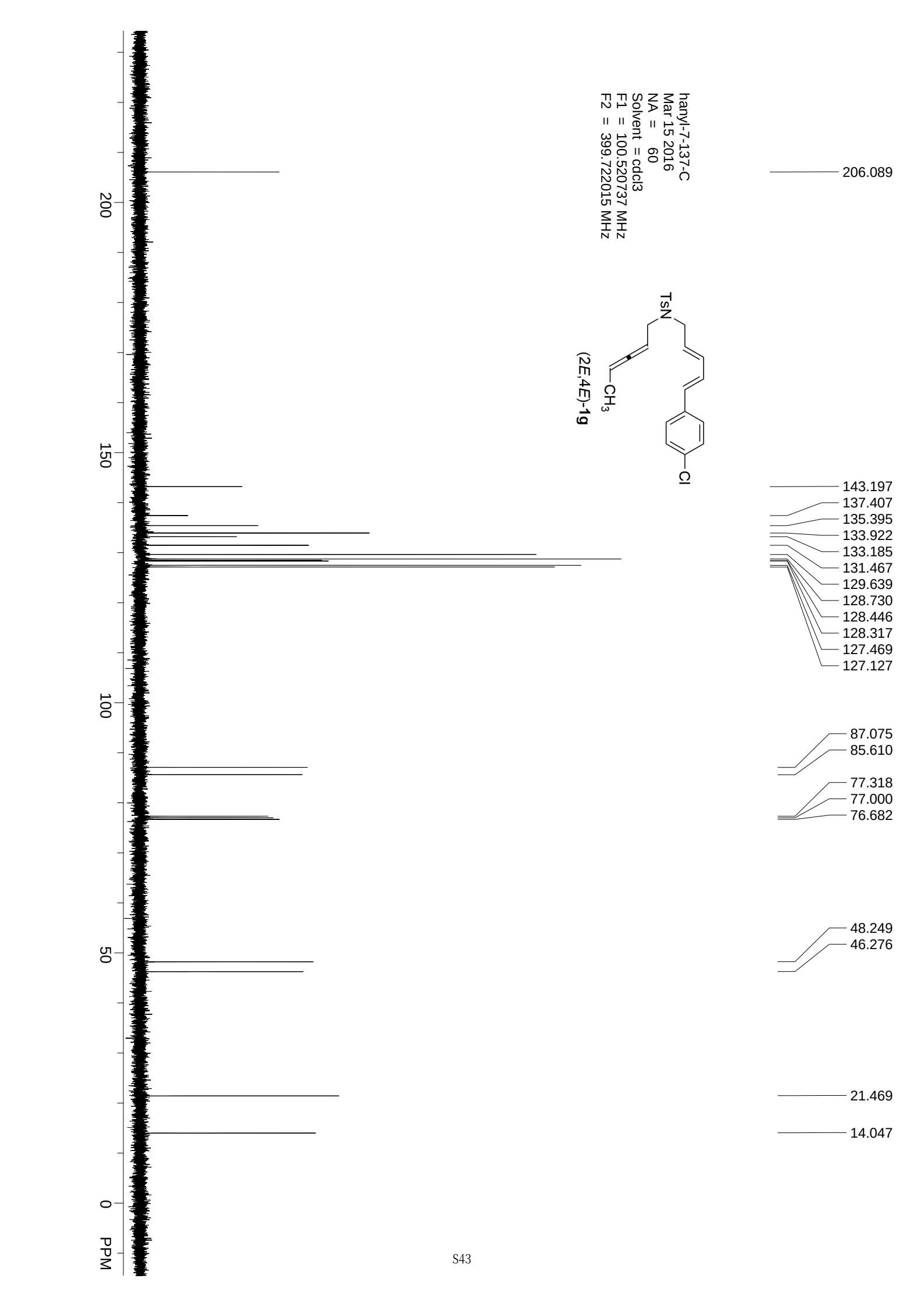
(2*E*,4*E*)-**1f**

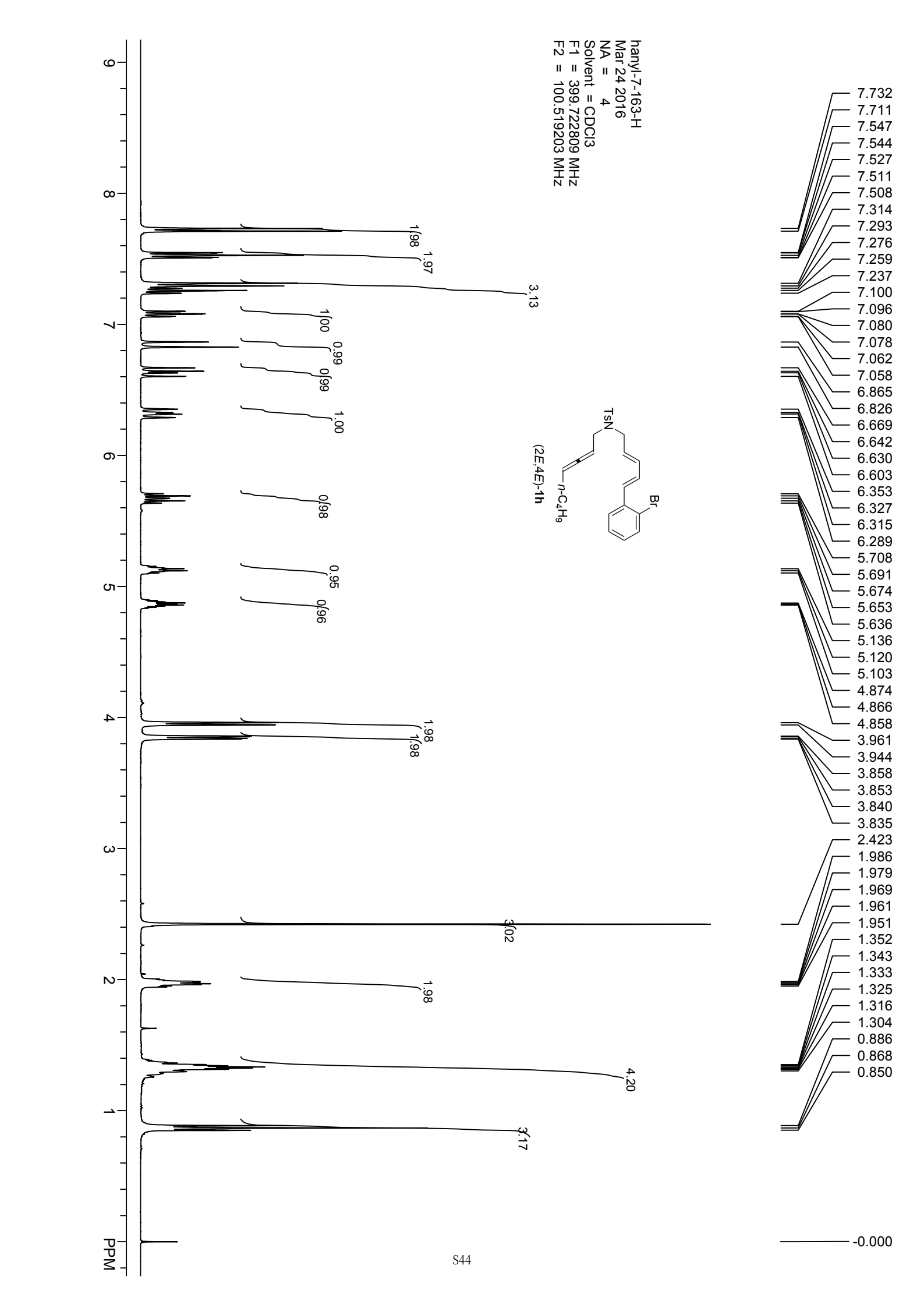


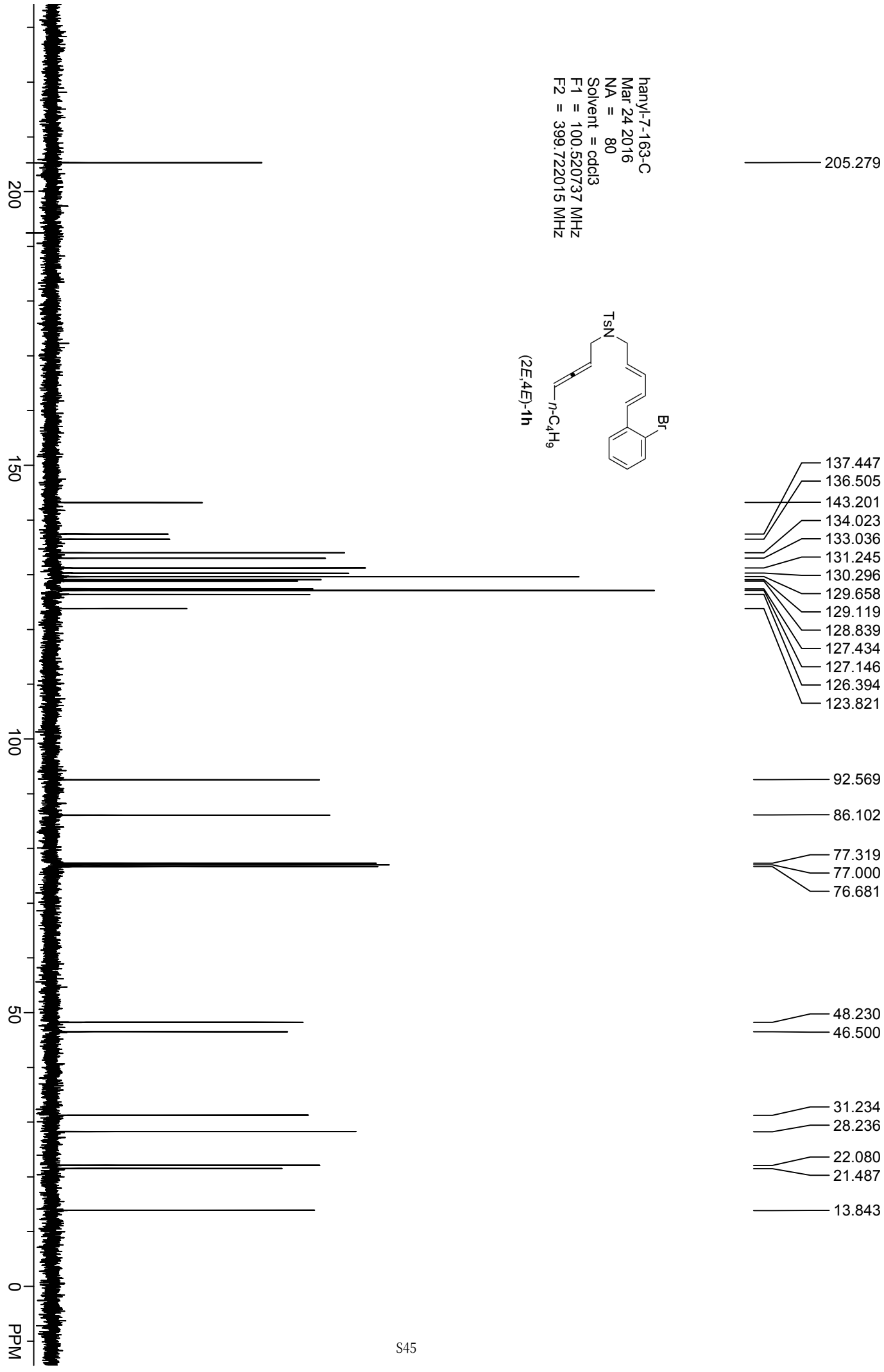
hanyl-7-137-H
Mar 15 2016
NA = 8
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz

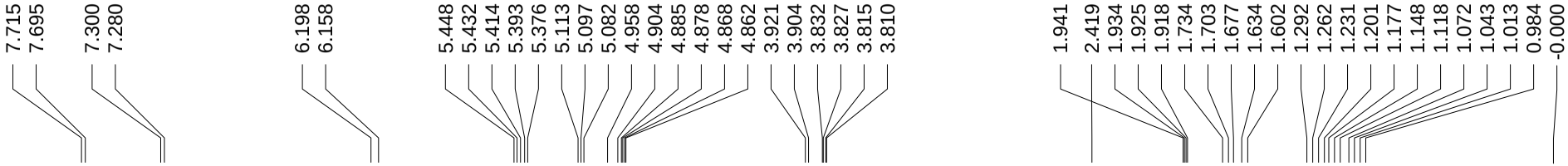


(2*E*,4*E*)-**1g**

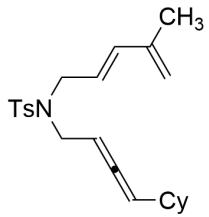

hanyl-7-137-C
Mar 15 2016
NA = 60
Solvent = cdcl3
F1 = 100.520737 MHz
F2 = 399.722015 MHz
TsN
CH3
Cl
(2E,4E)-1g
206.089
143.197
137.407
135.395
133.922
133.185
131.467
129.639
128.730
128.446
128.317
127.469
127.127
87.075
85.610
77.318
77.000
76.682
48.249
46.276
21.469
14.047
200
150
100
50
0
PPM


hanyl-7-163-H
Mar 24 2016
NA = 4
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz
TsN
Br
n-C4H9
(2E,4E)-1h
7.732
7.711
7.547
7.544
7.527
7.511
7.508
7.314
7.293
7.276
7.259
7.237
7.100
7.096
7.080
7.078
7.062
7.058
6.865
6.826
6.669
6.642
6.630
6.603
6.353
6.327
6.315
6.289
5.708
5.691
5.674
5.653
5.636
5.136
5.120
5.103
4.874
4.866
4.858
3.961
3.944
3.858
3.853
3.840
3.835
2.423
1.986
1.979
1.969
1.961
1.951
1.352
1.343
1.333
1.325
1.316
1.304
0.886
0.868
0.850
-0.000
1.98
1.97
3.13
1.00
0.99
0.99
1.00
0.98
0.95
0.96
1.98
1.98
3.02
1.98
4.20
3.17
PPM

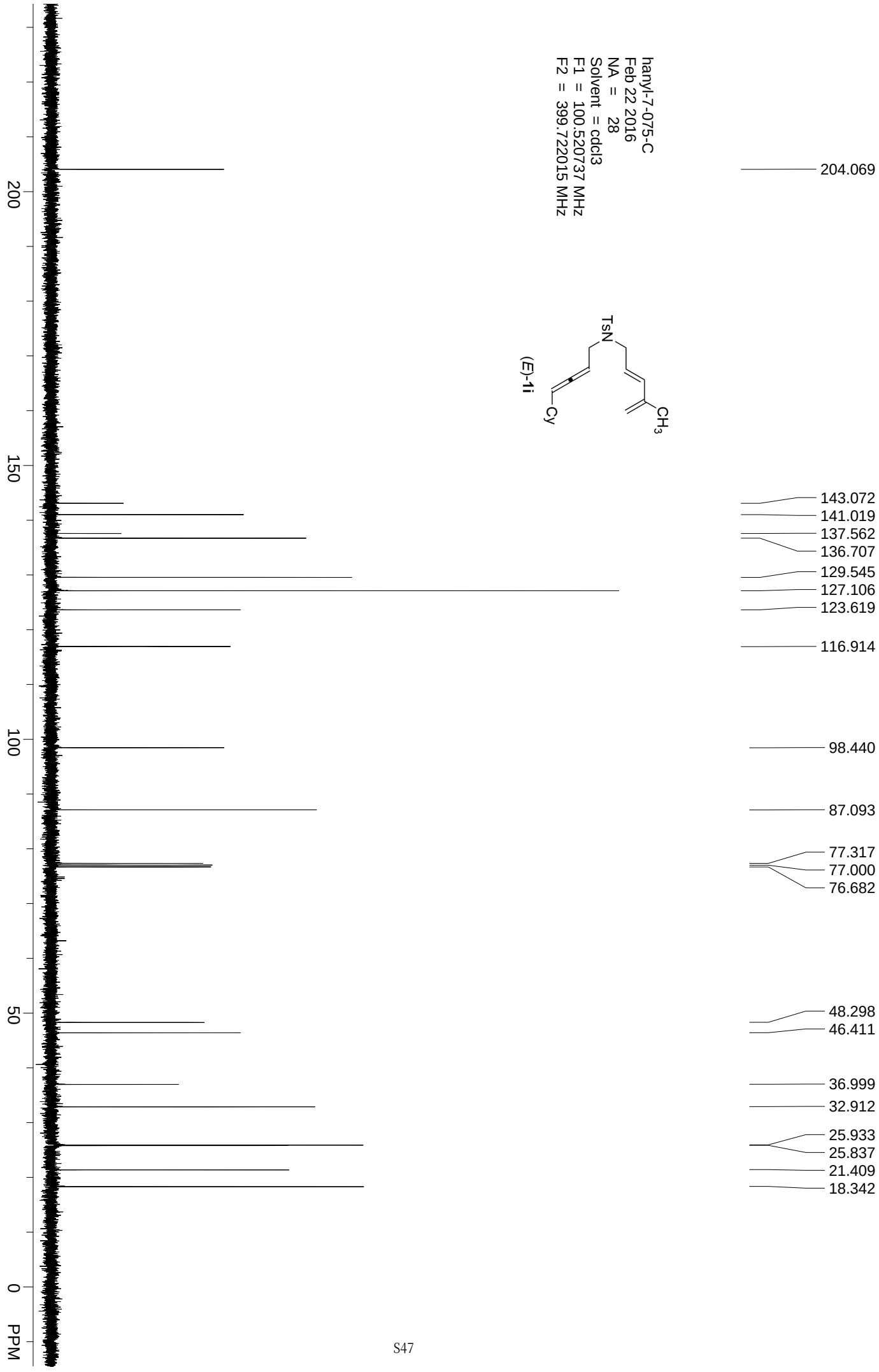

hanyl-7-163-C
Mar 24 2016
NA = 80
Solvent = cdcl3
F1 = 100.520737 MHz
F2 = 399.722015 MHz
TsN
Br
n-C4H9
(2E,4E)-1h
205.279
137.447
136.505
143.201
134.023
133.036
131.245
130.296
129.658
129.119
128.839
127.434
127.146
126.394
123.821
92.569
86.102
77.319
77.000
76.681
48.230
46.500
31.234
28.236
22.080
21.487
13.843
200
150
100
50
0
PPM

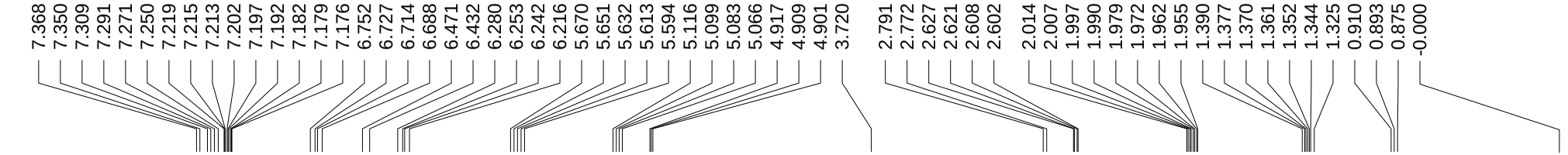


hanyl-7-075-H
Feb 26 2016
NA = 8
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz

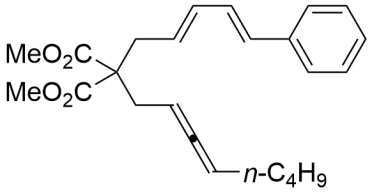


(*E*)-**1i**

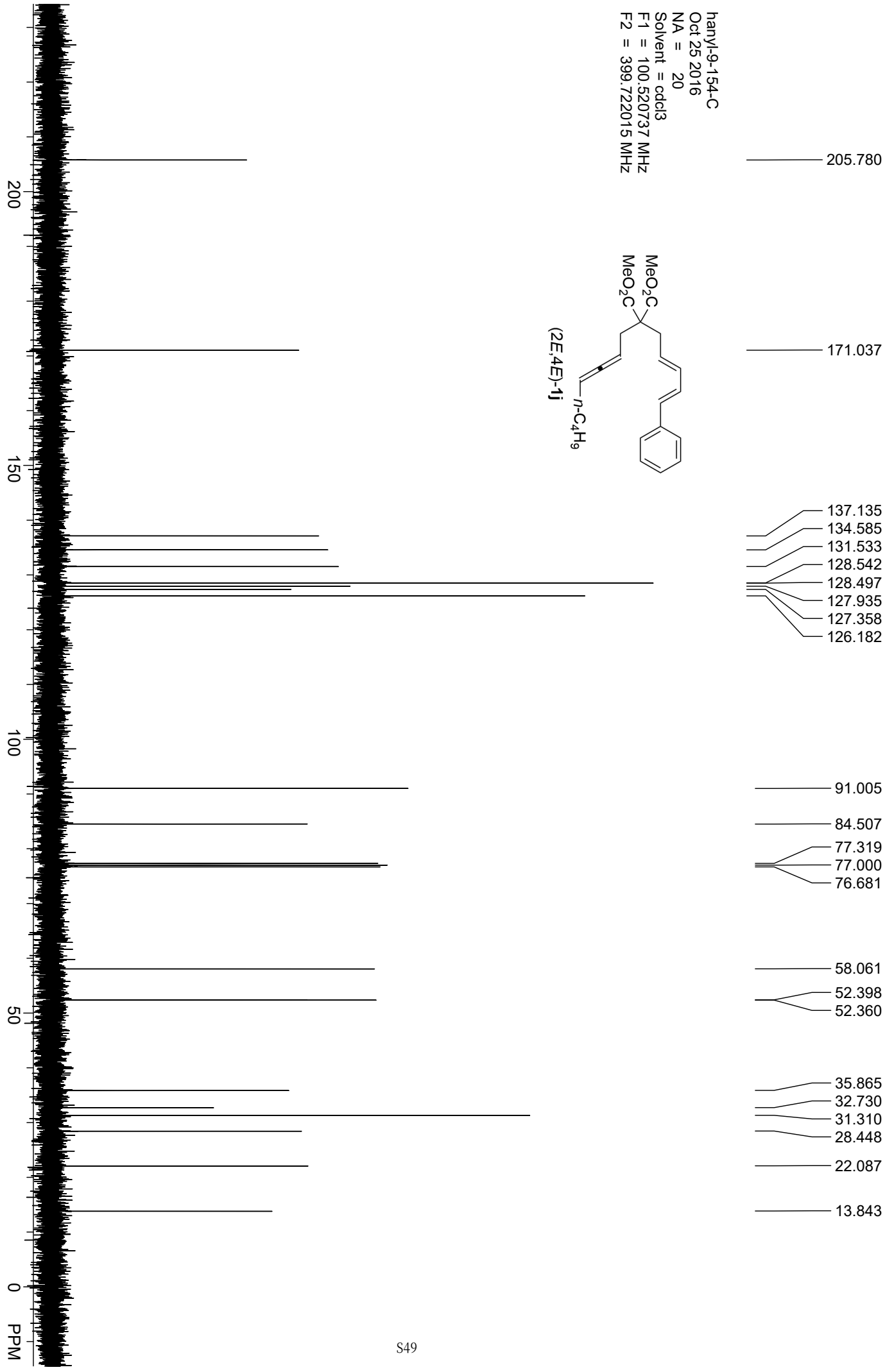

hanyl-7-075-C
Feb 22 2016
NA = 28
Solvent = cdcl3
F1 = 100.520737 MHz
F2 = 399.722015 MHz
(E)-1i
TsN
Cy
CH3
204.069
143.072
141.019
137.562
136.707
129.545
127.106
123.619
116.914
98.440
87.093
77.317
77.000
76.682
48.298
46.411
36.999
32.912
25.933
25.837
21.409
18.342
200
150
100
50
0
PPM

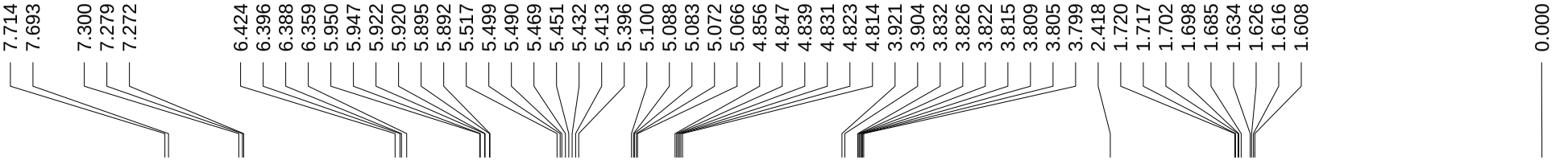


hanyl-9-154-H
Oct 25 2016
NA = 4
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz

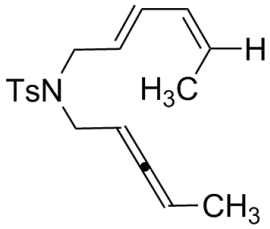


(2*E*,4*E*)-**1j**

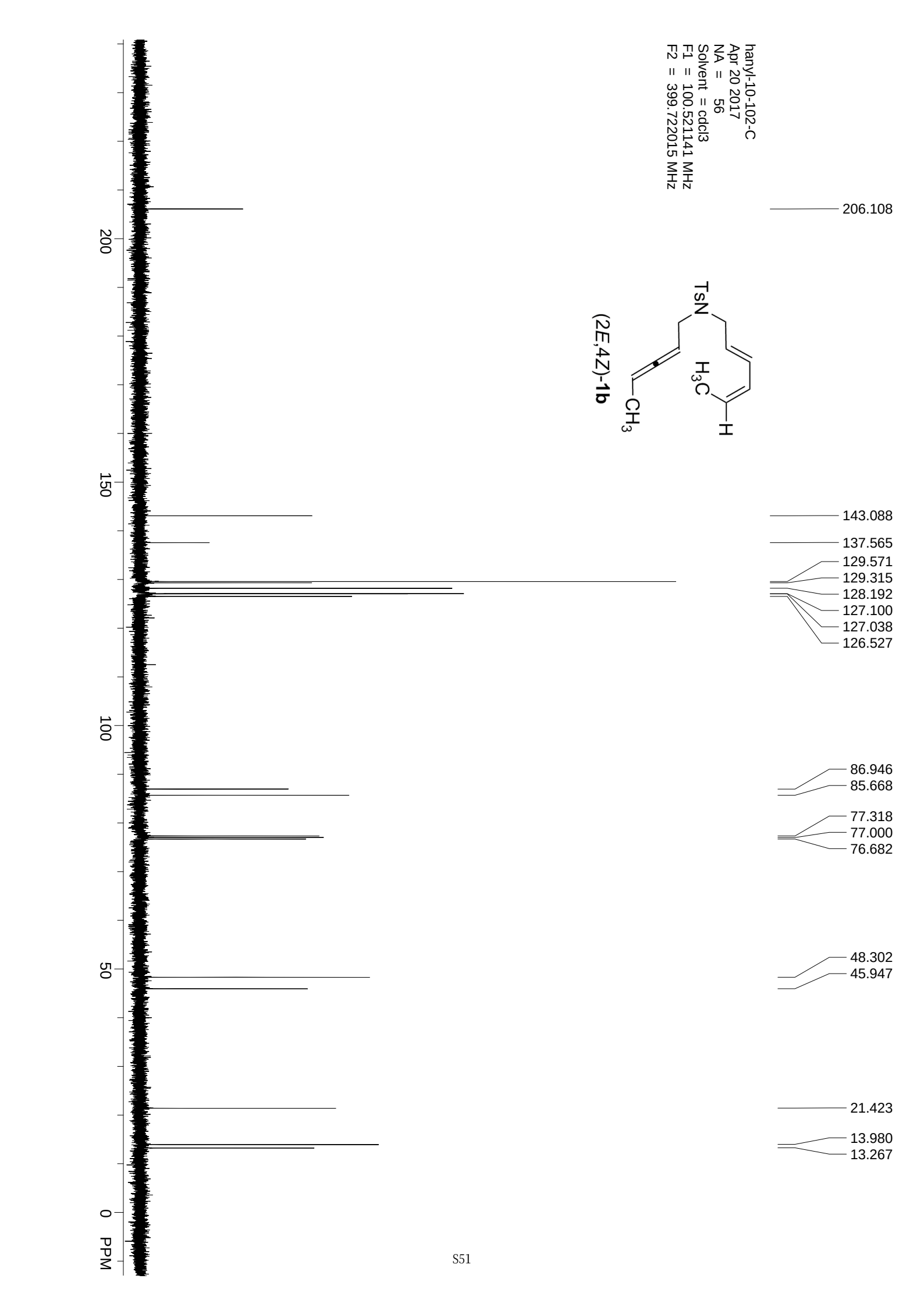

hanyl-9-154-C
Oct 25 2016
NA = 20
Solvent = cdcl3
F1 = 100.520737 MHz
F2 = 399.722015 MHz
MeO2C
MeO2C
n-C4H9
(2E,4E)-1j
205.780
171.037
137.135
134.585
131.533
128.542
128.497
127.935
127.358
126.182
91.005
84.507
77.319
77.000
76.681
58.061
52.398
52.360
35.865
32.730
31.310
28.448
22.087
13.843
200
150
100
50
0
PPM

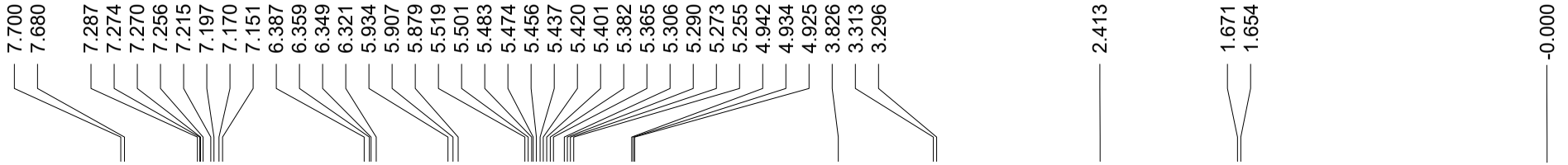


hanyl-10-102-H
Apr 20 2017
NA = 4
Solvent = CDCl3
F1 = 399.723633 MHz
F2 = 100.519203 MHz

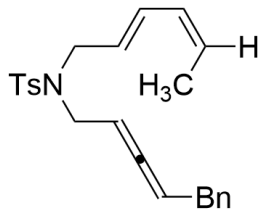


(2*E*,4*Z*)-**1b**

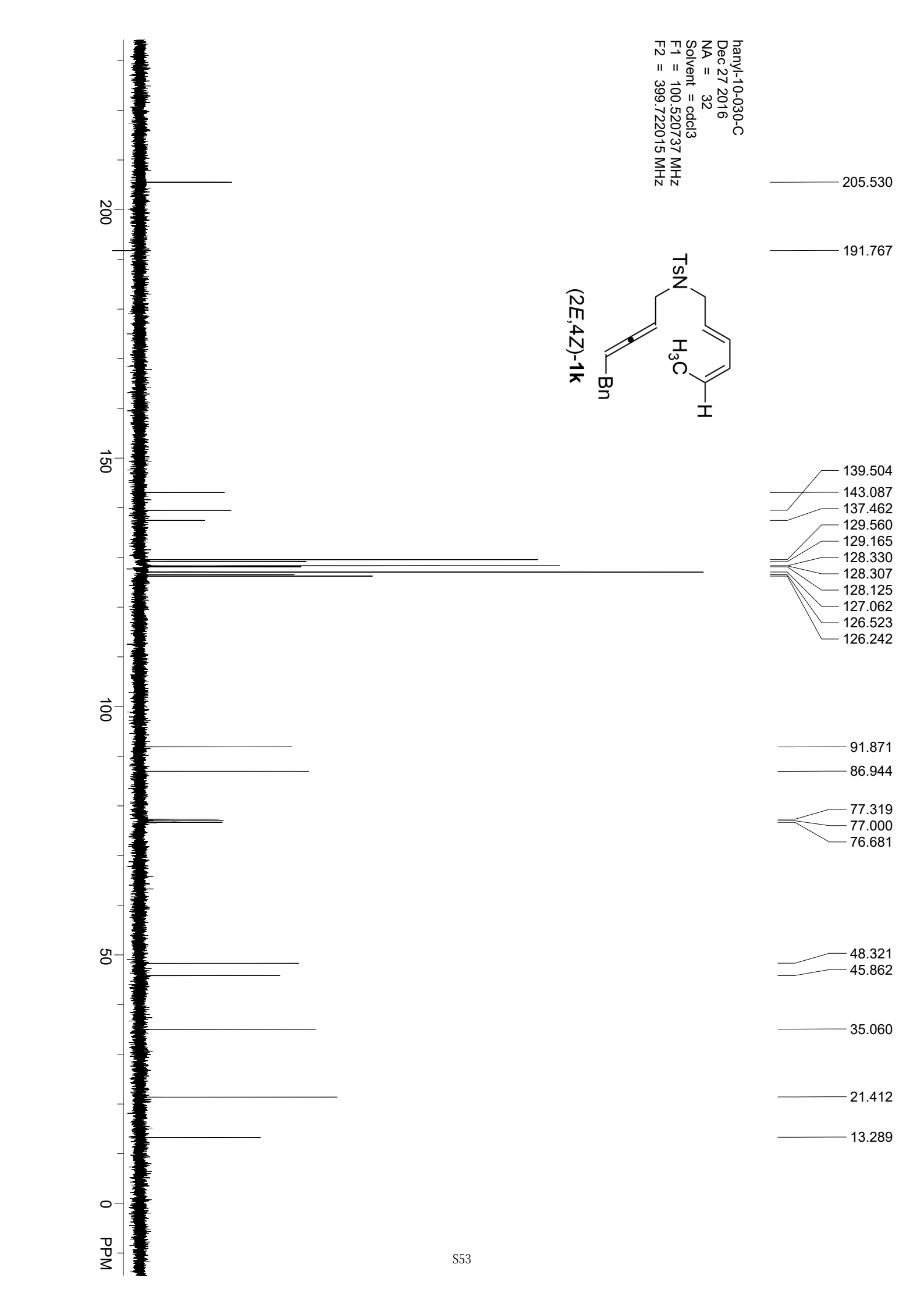

hanyl-10-102-C
Apr 20 2017
NA = 56
Solvent = cdcl3
F1 = 100.521141 MHz
F2 = 399.722015 MHz
TsN
H3C
H
CH3
(2E,4Z)-1b
206.108
143.088
137.565
129.571
129.315
128.192
127.100
127.038
126.527
86.946
85.668
77.318
77.000
76.682
48.302
45.947
21.423
13.980
13.267
200
150
100
50
0
PPM

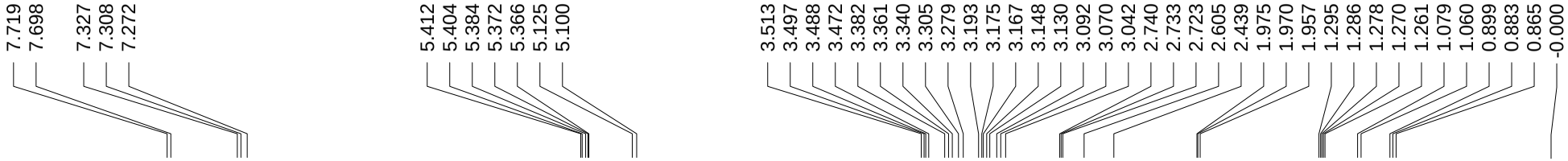


hanyl-10-030-H
Dec 27 2016
NA = 4
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz

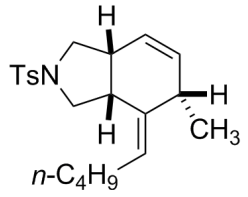


(2*E*,4*Z*)-**1k**

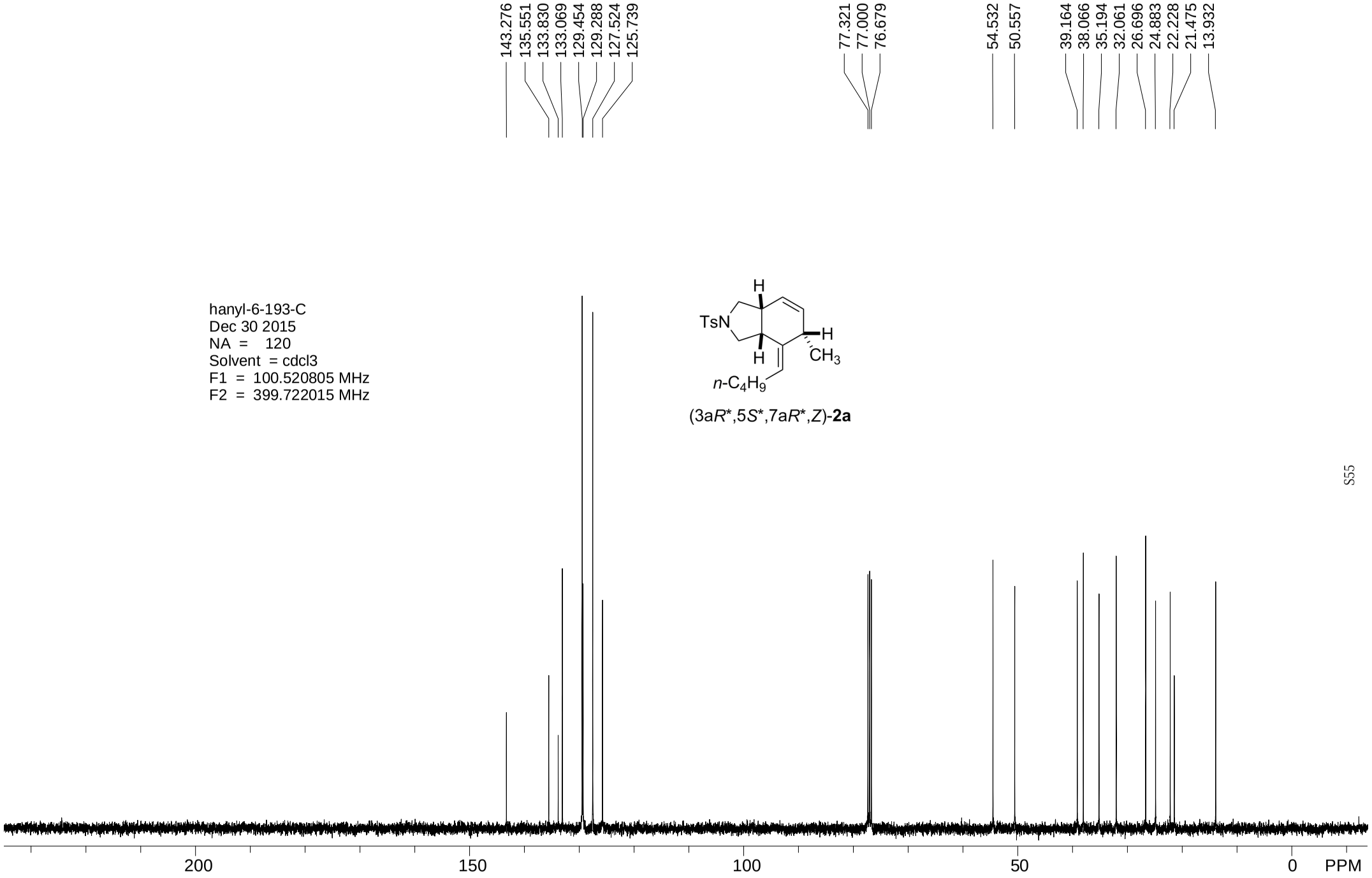

hanyl-10-030-C
Dec 27 2016
NA = 32
Solvent = cdcl3
F1 = 100.520737 MHz
F2 = 399.722015 MHz
TsN
H3C
Bn
H
(2E,4Z)-1k
205.530
191.767
139.504
143.087
137.462
129.560
129.165
128.330
128.307
128.125
127.062
126.523
126.242
91.871
86.944
77.319
77.000
76.681
48.321
45.862
35.060
21.412
13.289
200
150
100
50
0
PPM

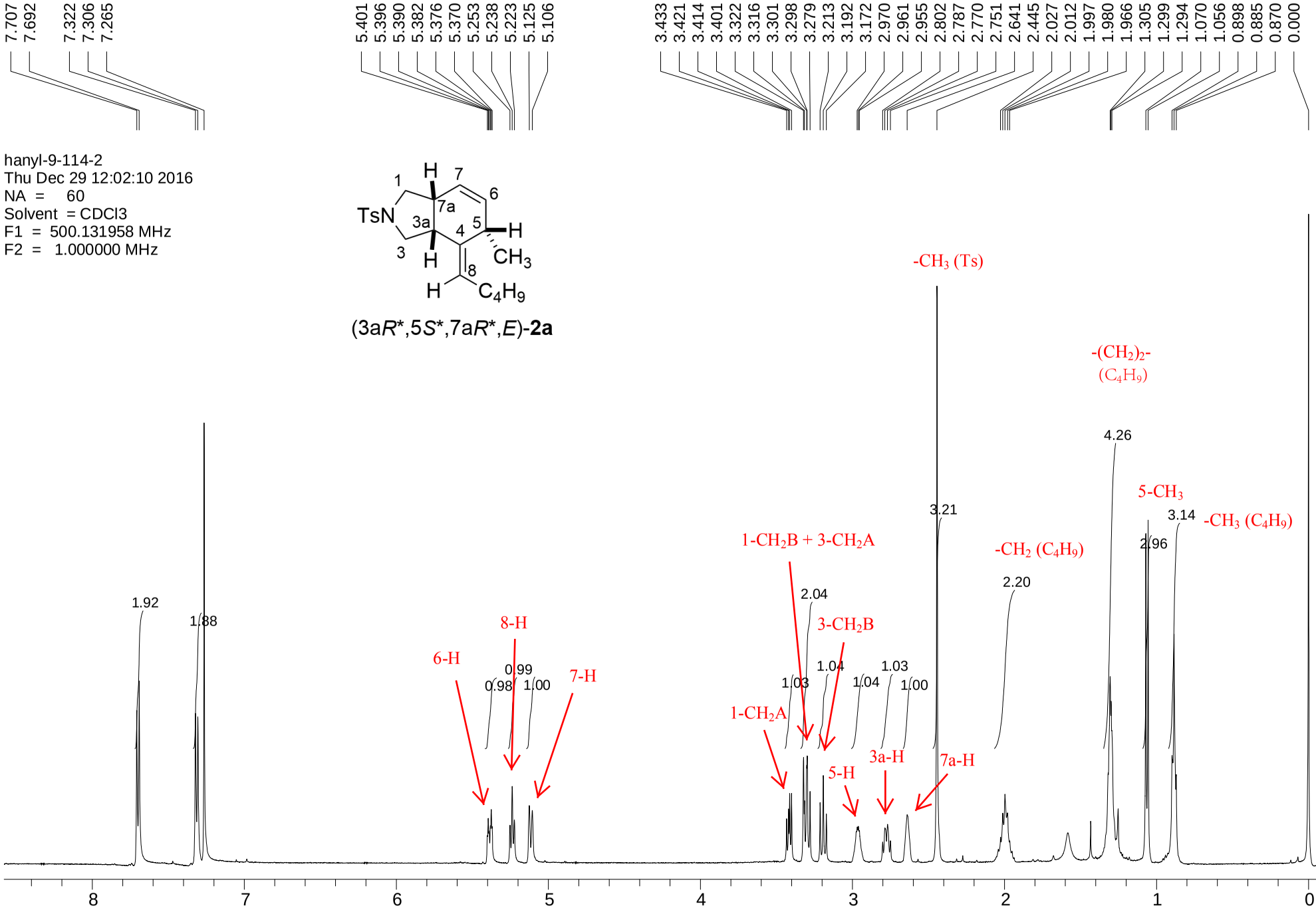


hanyl-6-193-H
Dec 30 2015
NA = 8
Solvent = CDCl3
F1 = 399.722626 MHz
F2 = 100.519203 MHz

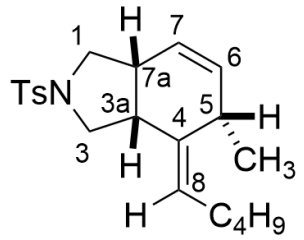


(3a*R**,5*S**,7a*R**,*Z*)-**2a**

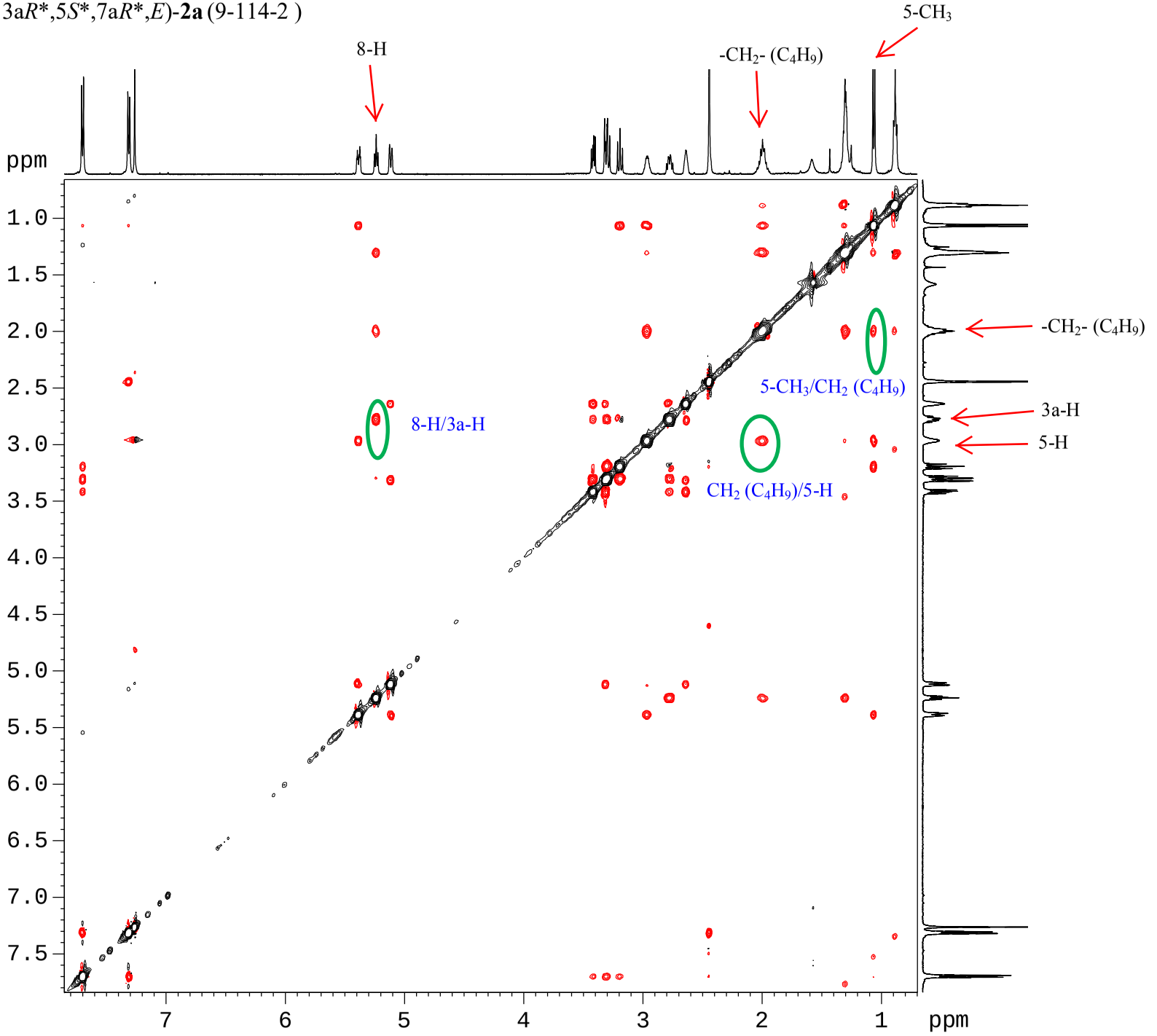

143.276
135.551
133.830
133.069
129.454
129.288
127.524
125.739
77.321
77.000
76.679
54.532
50.557
39.164
38.066
35.194
32.061
26.696
24.883
22.228
21.475
13.932
hanyl-6-193-C
Dec 30 2015
NA = 120
Solvent = cdcl3
F1 = 100.520805 MHz
F2 = 399.722015 MHz
TsN
H
H
H
CH3
n-C4H9
(3aR*,5S*,7aR*,Z)-2a
S55
200
150
100
50
0
PPM

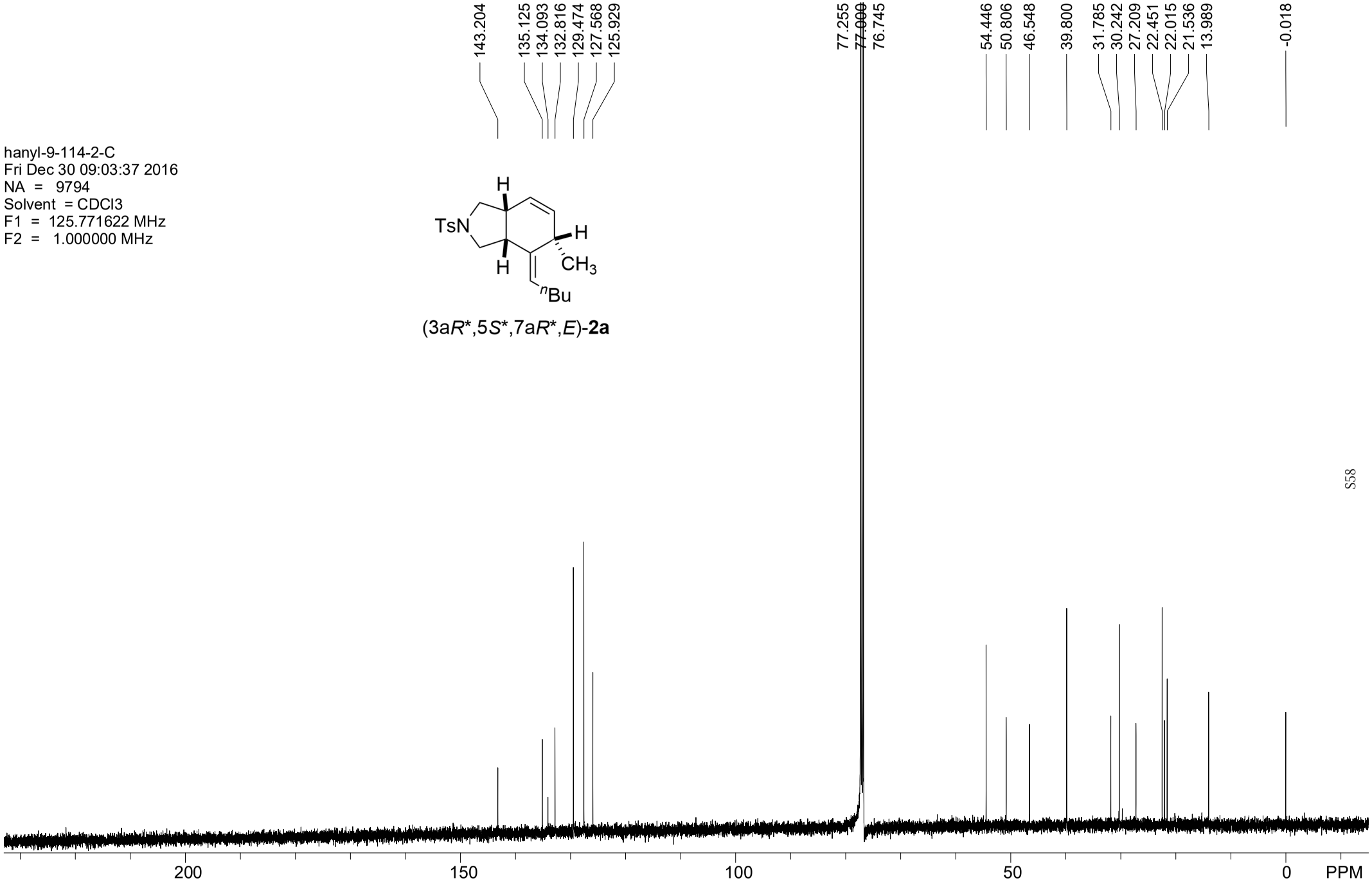

7.707
7.692
7.322
7.306
7.265
5.401
5.396
5.390
5.382
5.376
5.370
5.253
5.238
5.223
5.125
5.106
3.433
3.421
3.414
3.401
3.322
3.316
3.301
3.298
3.279
3.213
3.192
3.172
2.970
2.961
2.955
2.802
2.787
2.770
2.751
2.641
2.445
2.027
2.012
1.997
1.980
1.966
1.305
1.299
1.294
1.070
1.056
0.898
0.885
0.870
0.000
hanyl-9-114-2
Thu Dec 29 12:02:10 2016
NA = 60
Solvent = CDCl3
F1 = 500.131958 MHz
F2 = 1.000000 MHz
TsN
H
CH3
C4H9
(3aR*,5S*,7aR*,E)-2a
-CH3 (Ts)
-(CH2)2-
(C4H9)
4.26
5-CH3
3.14
-CH3 (C4H9)
2.96
3.21
1-CH2B + 3-CH2A
-CH2 (C4H9)
2.20
2.04
3-CH2B
8-H
6-H
7-H
1-CH2A
5-H
3a-H
7a-H
1.92
1.88
0.99
0.98
1.00
1.03
1.04
1.04
1.03
1.00
S56
8
7
6
5
4
3
2
1
0
PPM

the NOESY NMR spectrum of （3a*R**,5*S**,7a*R**,*E*)-**2a** (9-114-2)

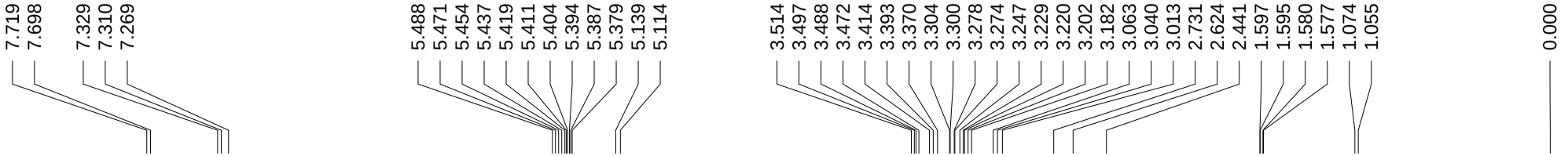


(3a*R**,5*S**,7a*R**,*E*)-**2a**

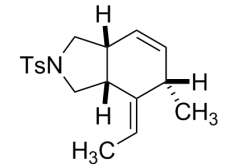




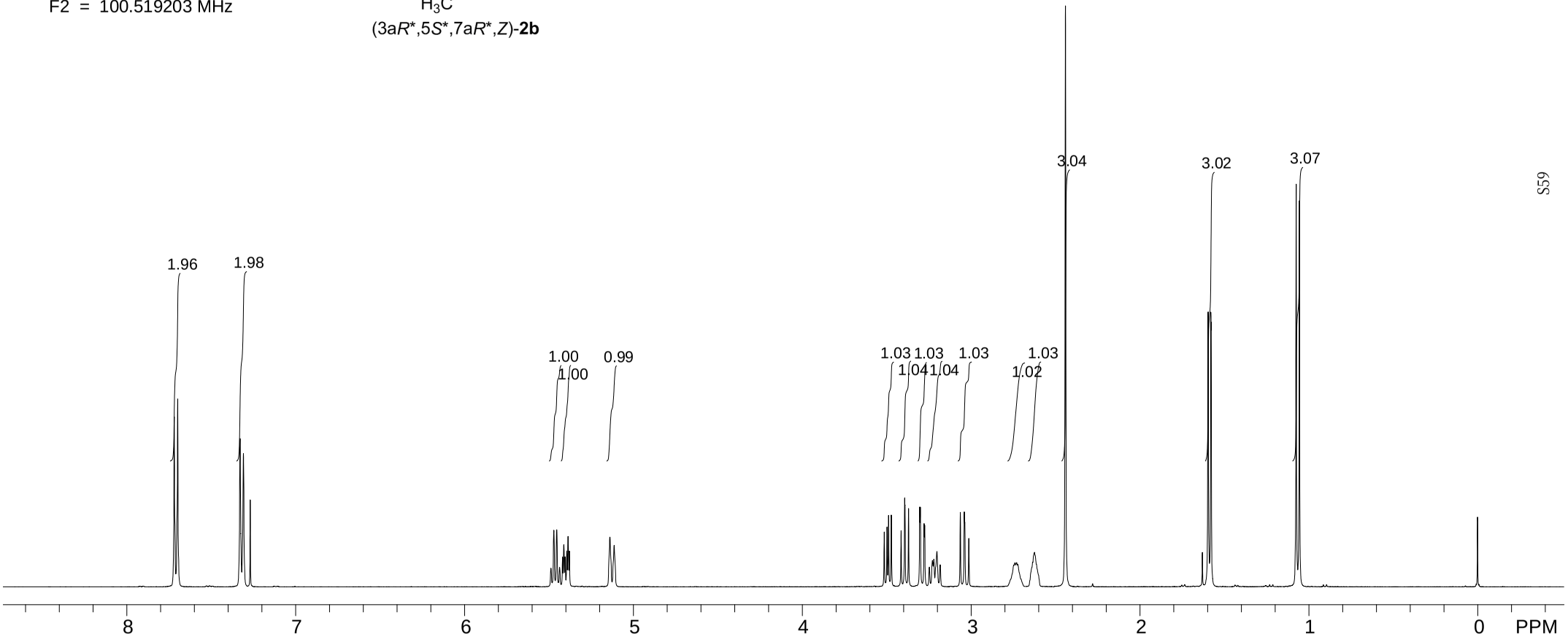
(3a*R**,5*S**,7a*R**,*E*)-**2a**



hanyl-7-049-H
Jan 20 2016
NA = 4
Solvent = CDCl3
F1 = 399.722229 MHz
F2 = 100.519203 MHz

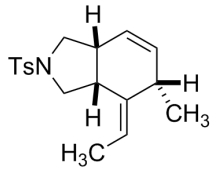


(3a*R**,5*S**,7a*R**,*Z*)-**2b**



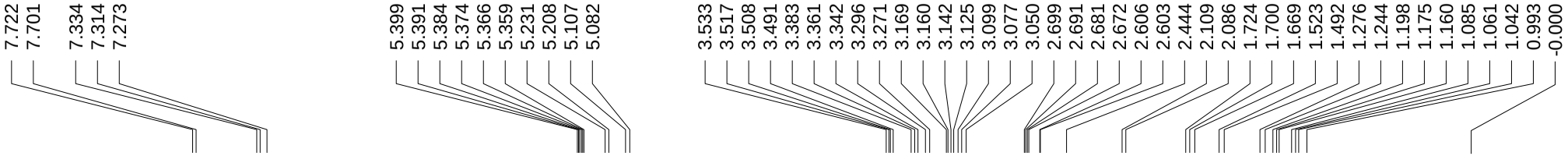
143.273
136.455
133.732
133.039
129.443
127.500
125.738
122.838
77.318
77.000
76.682
54.483
50.244
38.928
37.667
35.103
24.738
21.477
12.595

hanyl-7-049-C
Jan 20 2016
NA = 60
Solvent = cdcl3
F1 = 100.520737 MHz
F2 = 399.722015 MHz

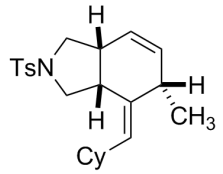


(3a*R**,5*S**,7a*R**,*Z*)-**2b**

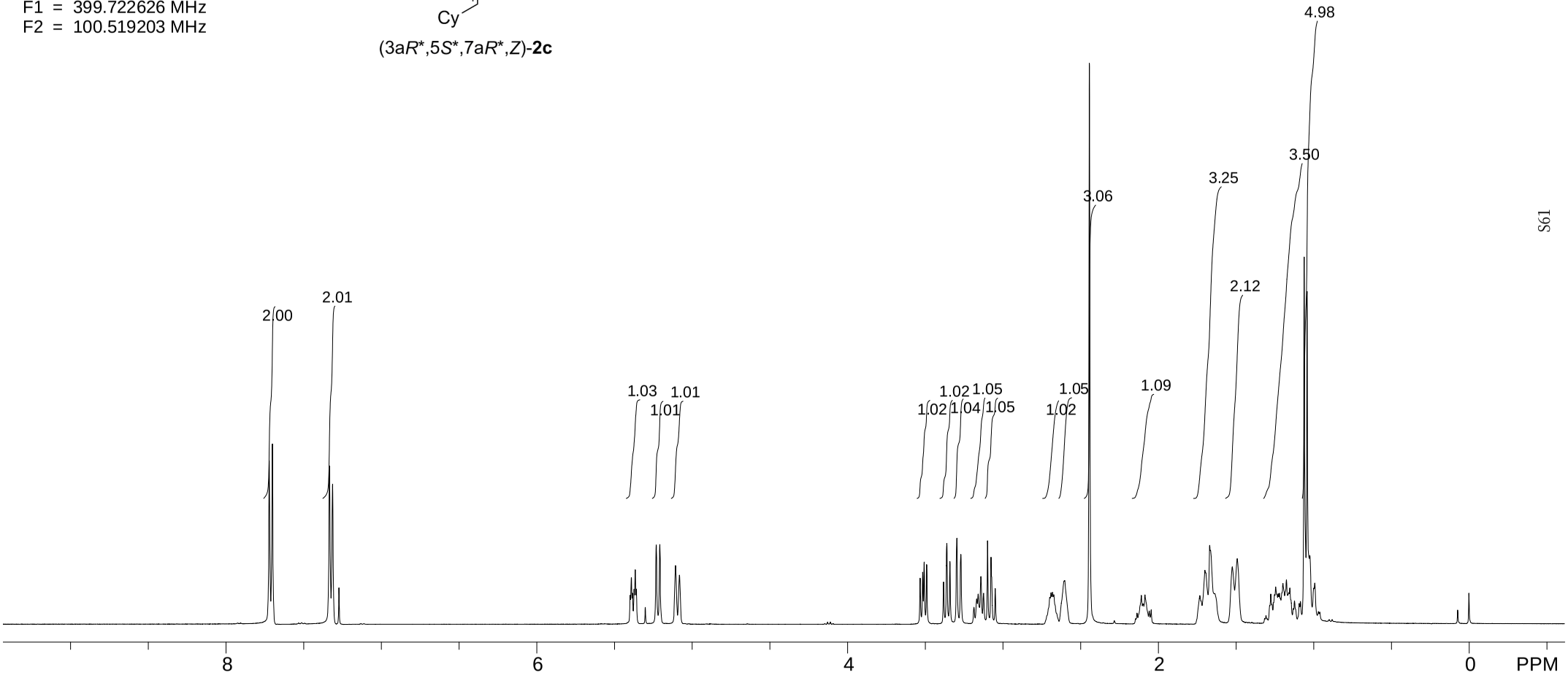
200 150 100 50 0 PPM



hanyl-6-194-H
Dec 30 2015
NA = 4
Solvent = CDCl3
F1 = 399.722626 MHz
F2 = 100.519203 MHz

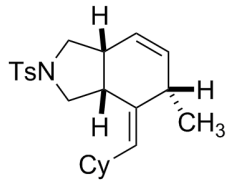


(3a*R**,5*S**,7a*R**,*Z*)-**2c**



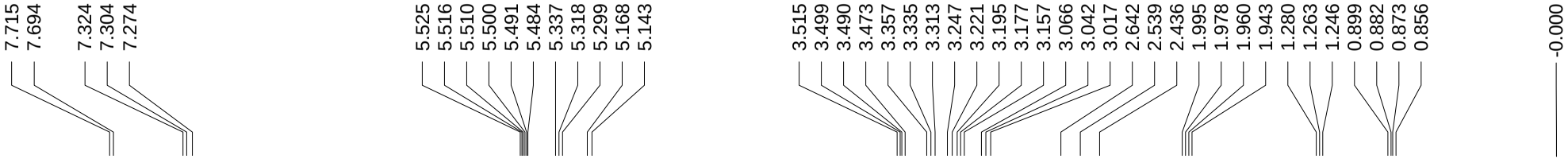
143.249
135.554
133.823
133.692
133.048
129.462
127.523
125.707
77.318
77.000
76.682
54.554
50.911
39.279
38.402
36.054
35.089
33.902
33.380
25.900
25.838
25.814
24.991
21.493

hanyl-6-194-C
Dec 30 2015
NA = 96
Solvent = cdcl3
F1 = 100.520805 MHz
F2 = 399.722015 MHz

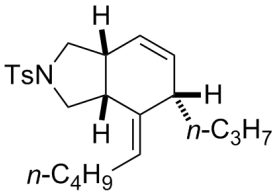


(3a*R**,5*S**,7a*R**,*Z*)-**2c**

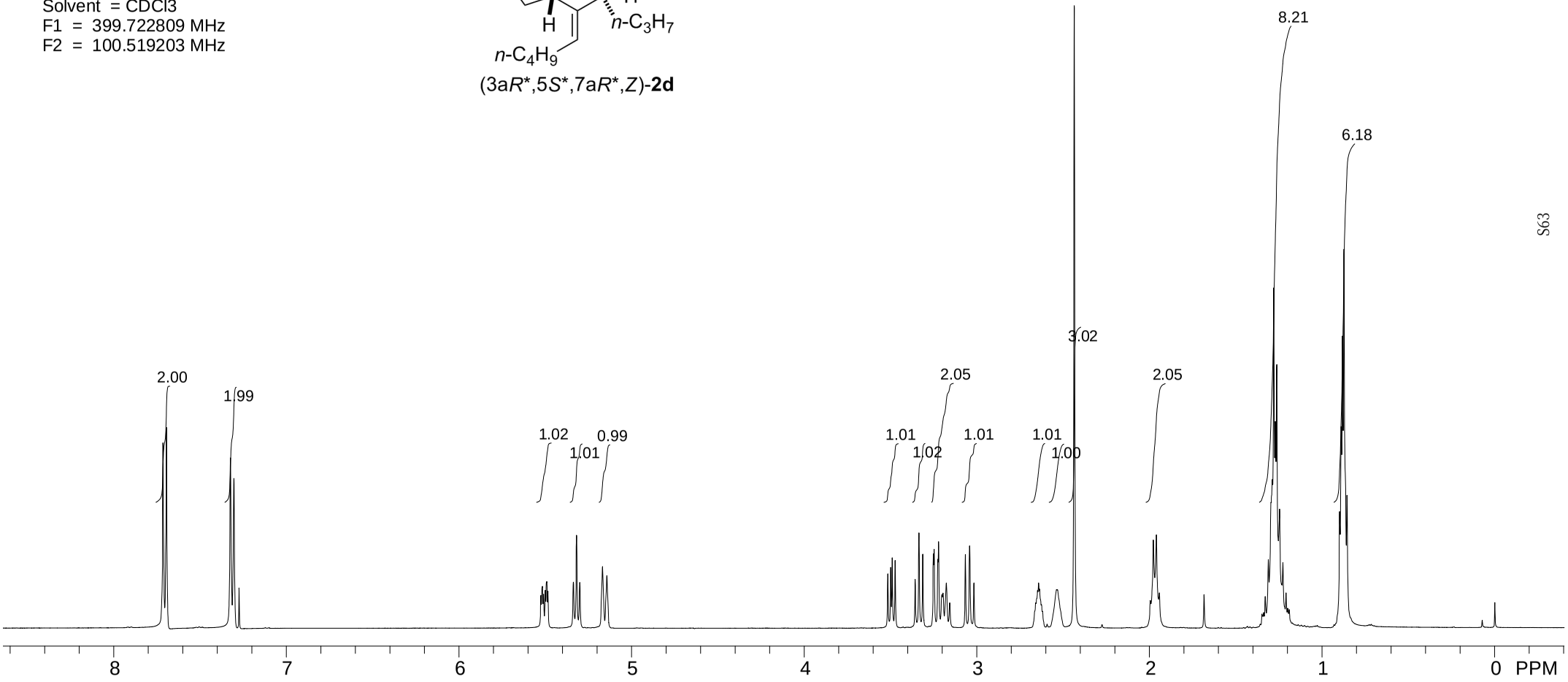
200 150 100 50 0 PPM

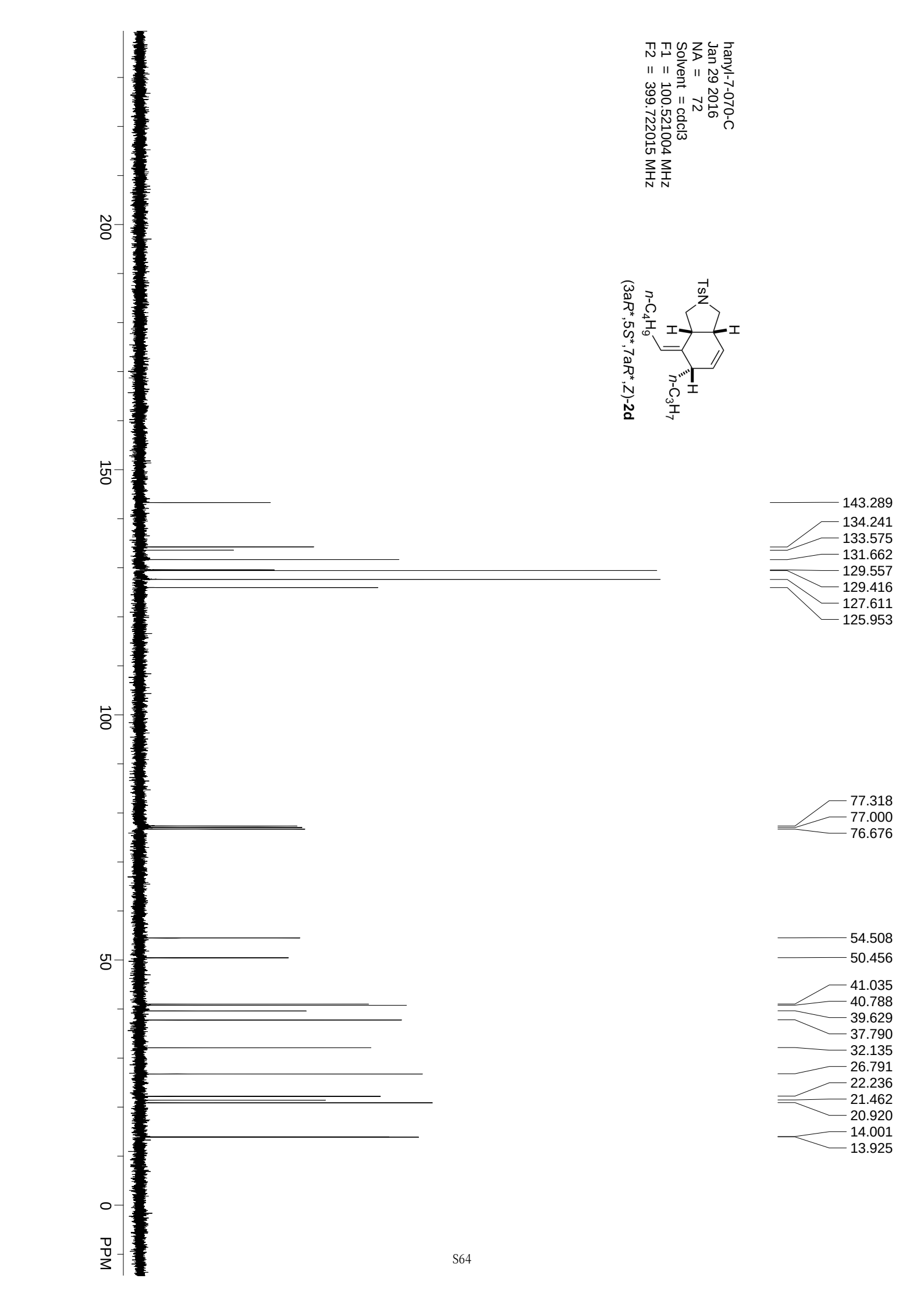


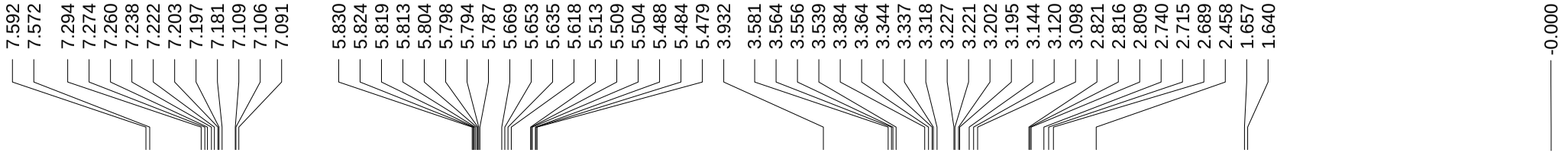
hanyl-7-070-H
Jan 29 2016
NA = 8
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz



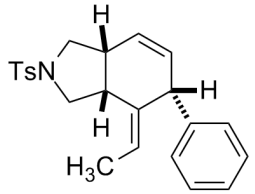
(3a*R**,5*S**,7a*R**,*Z*)-**2d**



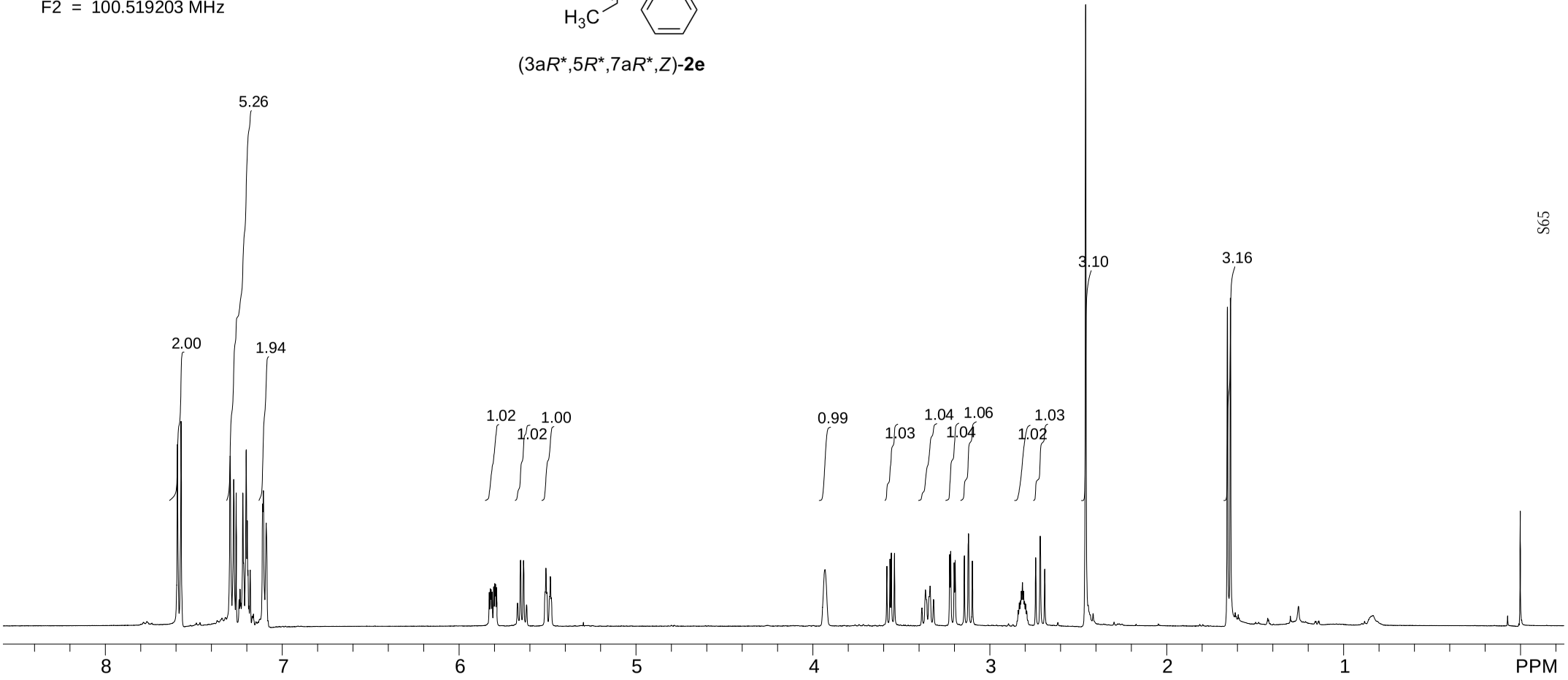

hanyl-7-070-C
Jan 29 2016
NA = 72
Solvent = cdcl3
F1 = 100.521004 MHz
F2 = 399.722015 MHz
TsN
H
H
H
n-C4H9
n-C3H7
(3aR*,5S*,7aR*,Z)-2d
143.289
134.241
133.575
131.662
129.557
129.416
127.611
125.953
77.318
77.000
76.676
54.508
50.456
41.035
40.788
39.629
37.790
32.135
26.791
22.236
21.462
20.920
14.001
13.925
200
150
100
50
0
PPM

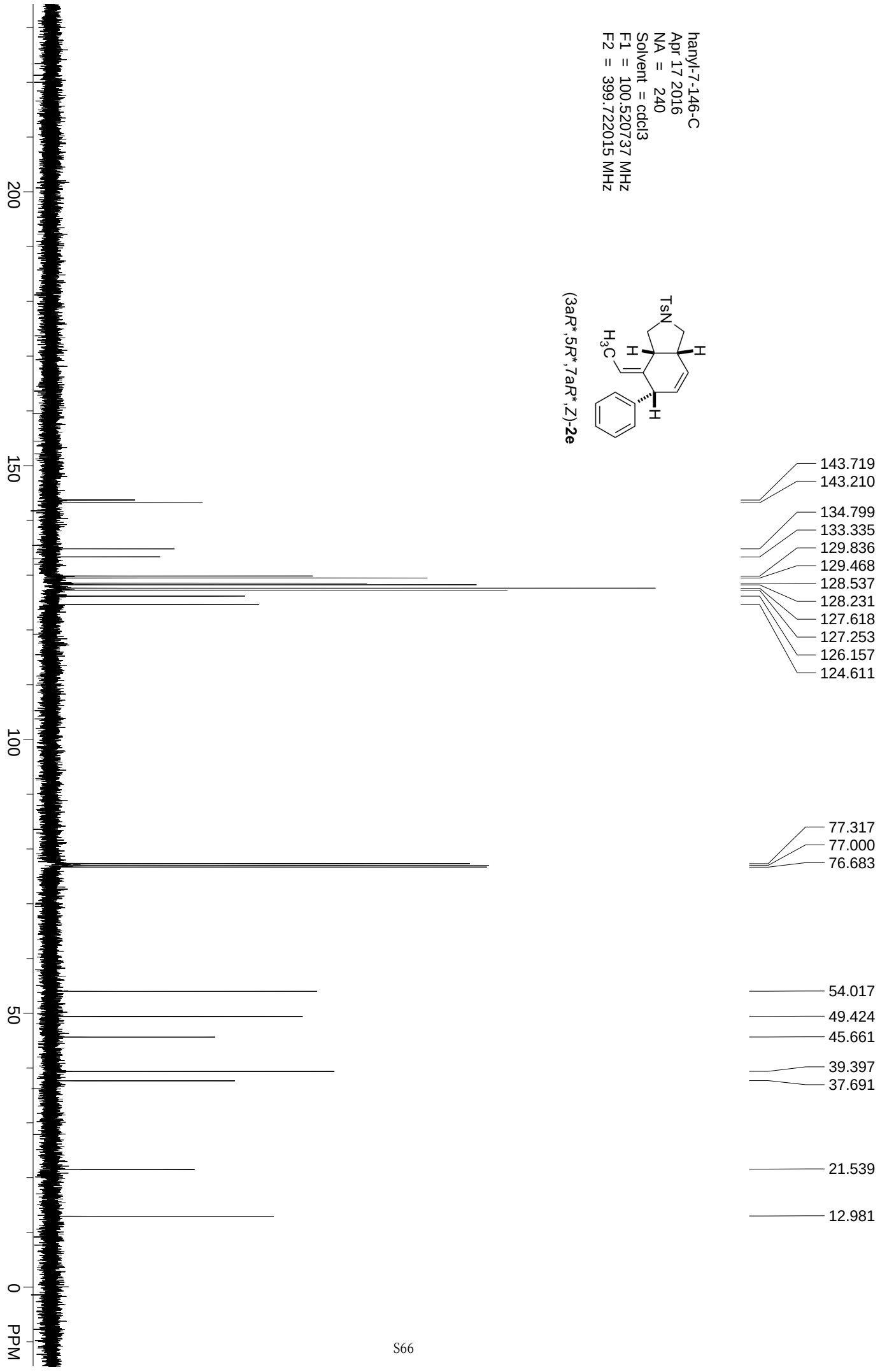


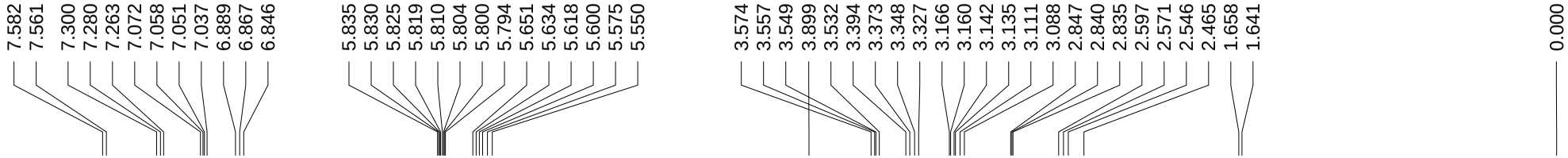
hanyl-7-146-H
Mar 29 2016
NA = 8
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz



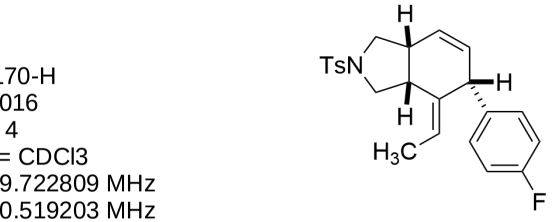
(3a*R**,5*R**,7a*R**,*Z*)-**2e**



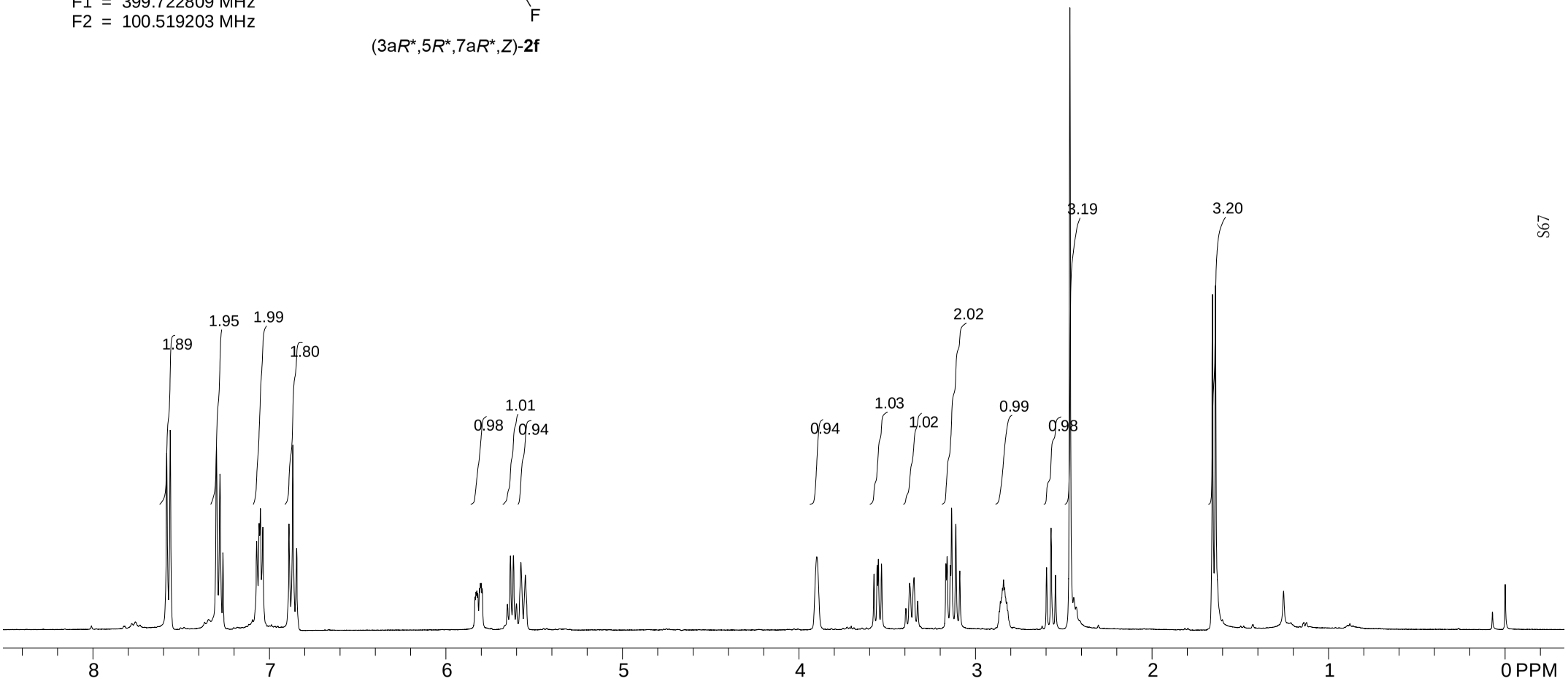

hanyl-7-146-C
Apr 17 2016
NA = 240
Solvent = cdcl3
F1 = 100.520737 MHz
F2 = 399.722015 MHz
(3aR*,5R*,7aR*,Z)-2e
TsN
H3C
H
H
H
143.719
143.210
134.799
133.335
129.836
129.468
128.537
128.231
127.618
127.253
126.157
124.611
77.317
77.000
76.683
54.017
49.424
45.661
39.397
37.691
21.539
12.981
200
150
100
50
0
PPM

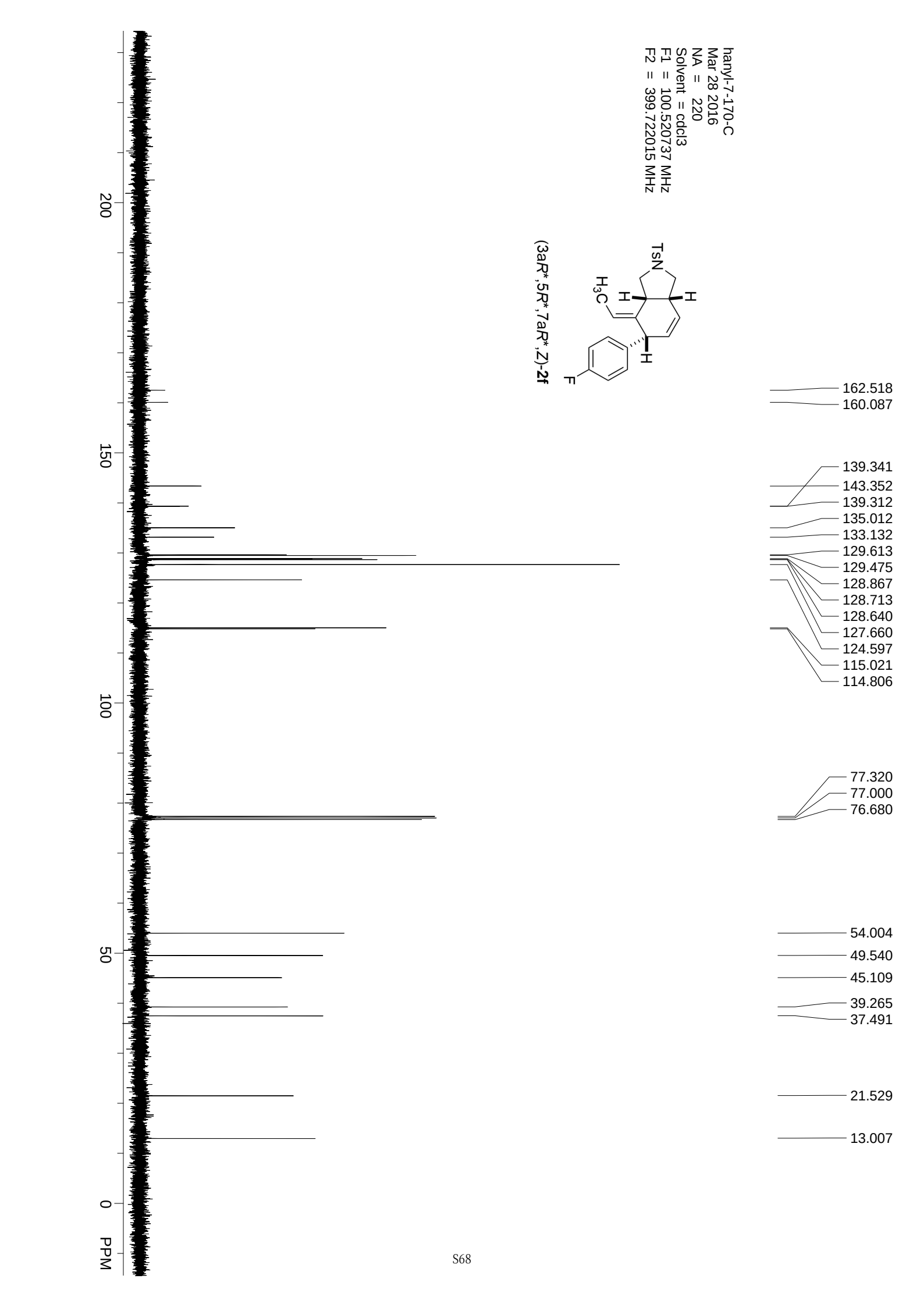


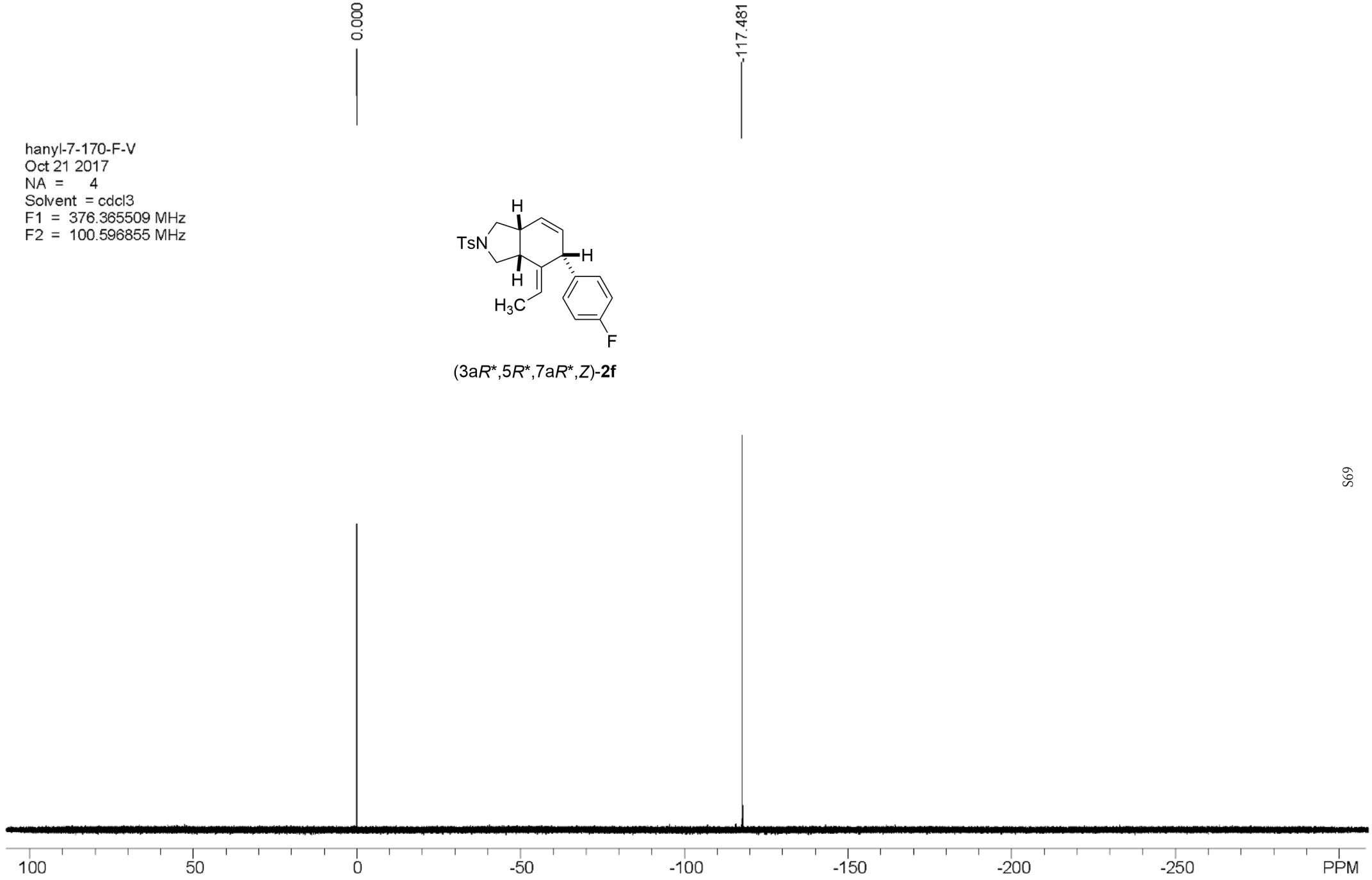
hanyl-7-170-H
Mar 28 2016
NA = 4
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz



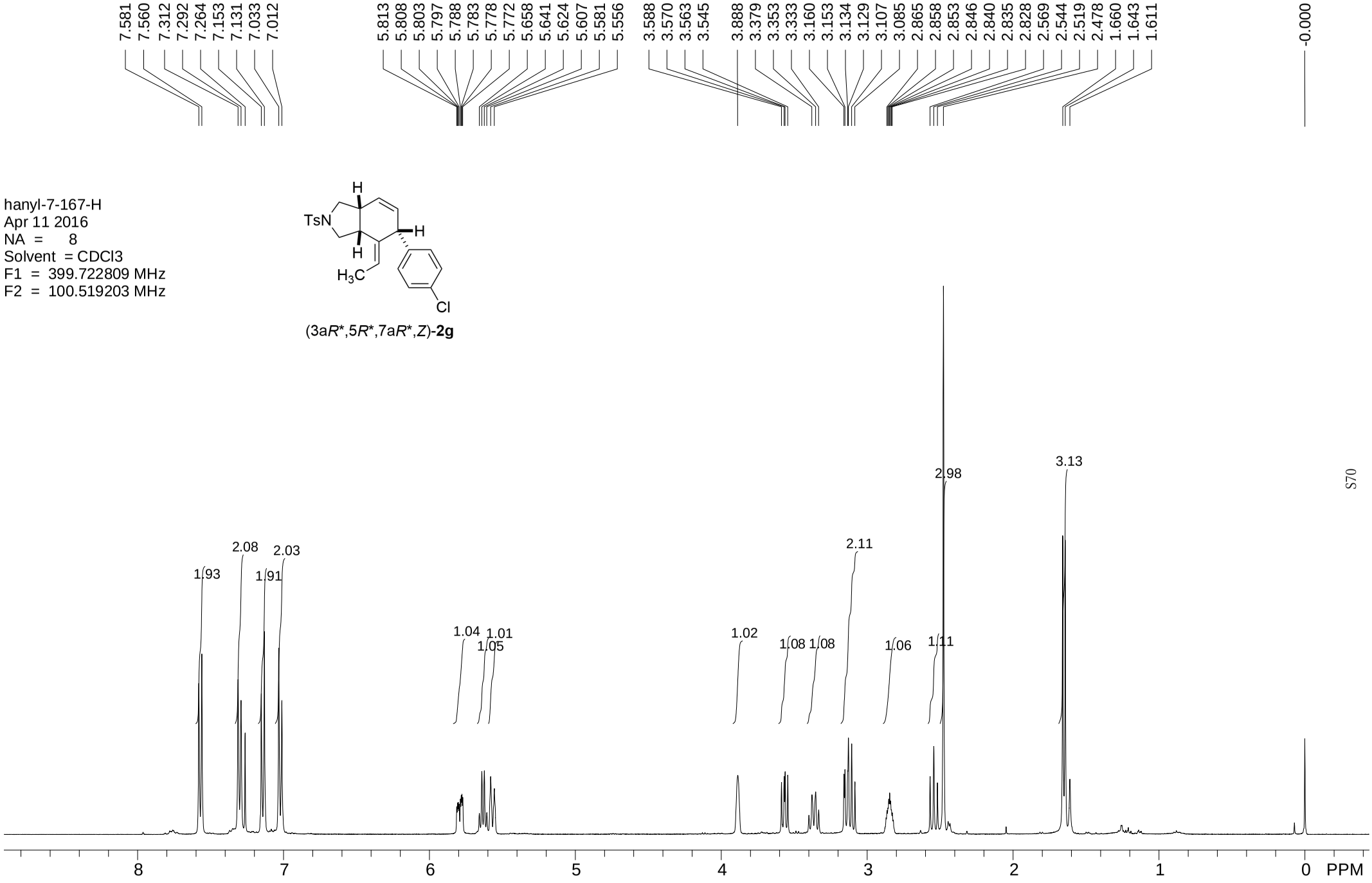
(3a*R**,5*R**,7a*R**,*Z*)-**2f**

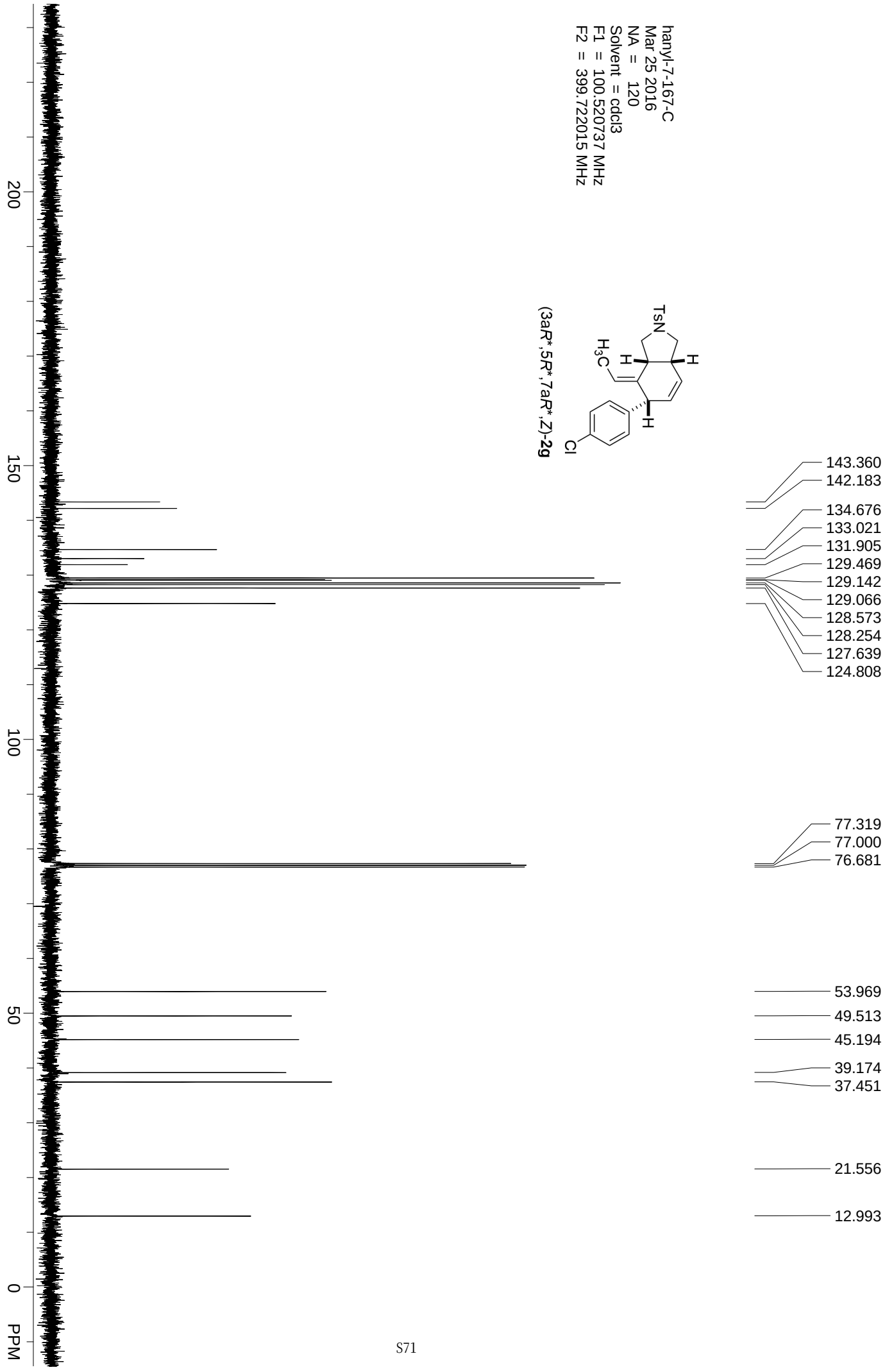


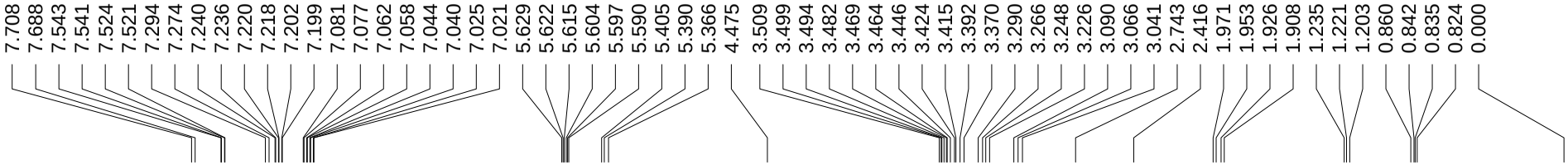

hanyl-7-170-C
Mar 28 2016
NA = 220
Solvent = cdcl3
F1 = 100.520737 MHz
F2 = 399.722015 MHz
(3aR*,5R*,7aR*,Z)-2f
TsN
H3C
H
H
H
F
162.518
160.087
139.341
143.352
139.312
135.012
133.132
129.613
129.475
128.867
128.713
128.640
127.660
124.597
115.021
114.806
77.320
77.000
76.680
54.004
49.540
45.109
39.265
37.491
21.529
13.007
200
150
100
50
0
PPM



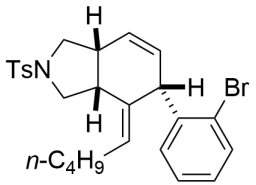
(3a*R**,5*R**,7a*R**,*Z*)-**2f**


7.581
7.560
7.312
7.292
7.264
7.153
7.131
7.033
7.012
5.813
5.808
5.803
5.797
5.788
5.783
5.778
5.772
5.658
5.641
5.624
5.607
5.581
5.556
3.588
3.570
3.563
3.545
3.888
3.379
3.353
3.333
3.160
3.153
3.134
3.129
3.107
3.085
2.865
2.858
2.853
2.846
2.840
2.835
2.828
2.569
2.544
2.519
2.478
1.660
1.643
1.611
-0.000
hanyl-7-167-H
Apr 11 2016
NA = 8
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz
TsN
H
H
H
H3C
Cl
(3aR*,5R*,7aR*,Z)-2g
1.93
2.08
1.91
2.03
1.04
1.01
1.05
1.02
1.08
1.08
2.11
1.06
1.11
2.98
3.13
S70
8
7
6
5
4
3
2
1
0
PPM

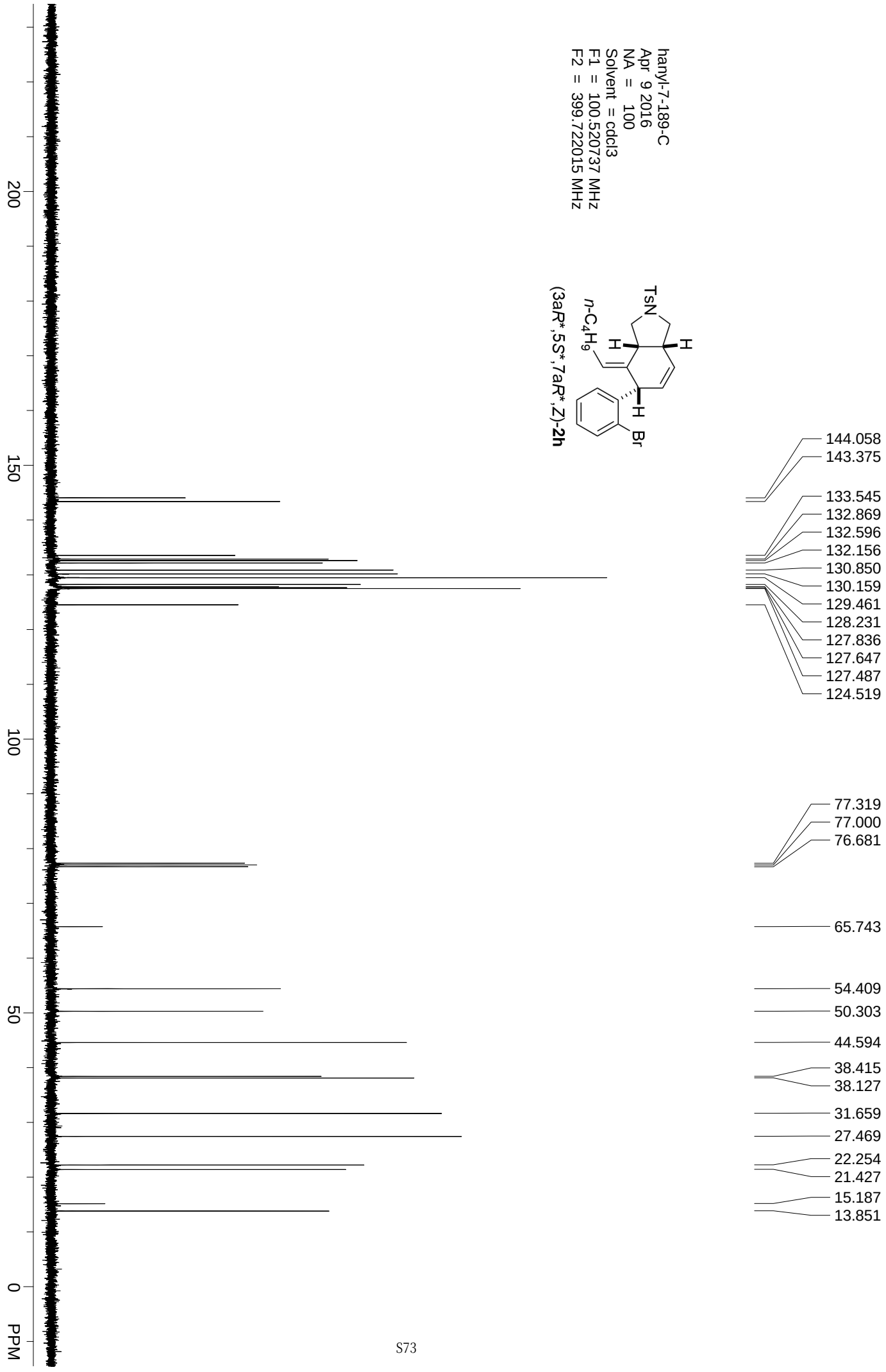

hanyl-7-167-C
Mar 25 2016
NA = 120
Solvent = cdcl3
F1 = 100.520737 MHz
F2 = 399.722015 MHz
(3aR*,5R*,7aR*,Z)-2g
TsN
H
H3C
H
H
Cl
143.360
142.183
134.676
133.021
131.905
129.469
129.142
129.066
128.573
128.254
127.639
124.808
77.319
77.000
76.681
53.969
49.513
45.194
39.174
37.451
21.556
12.993
200
150
100
50
0
PPM

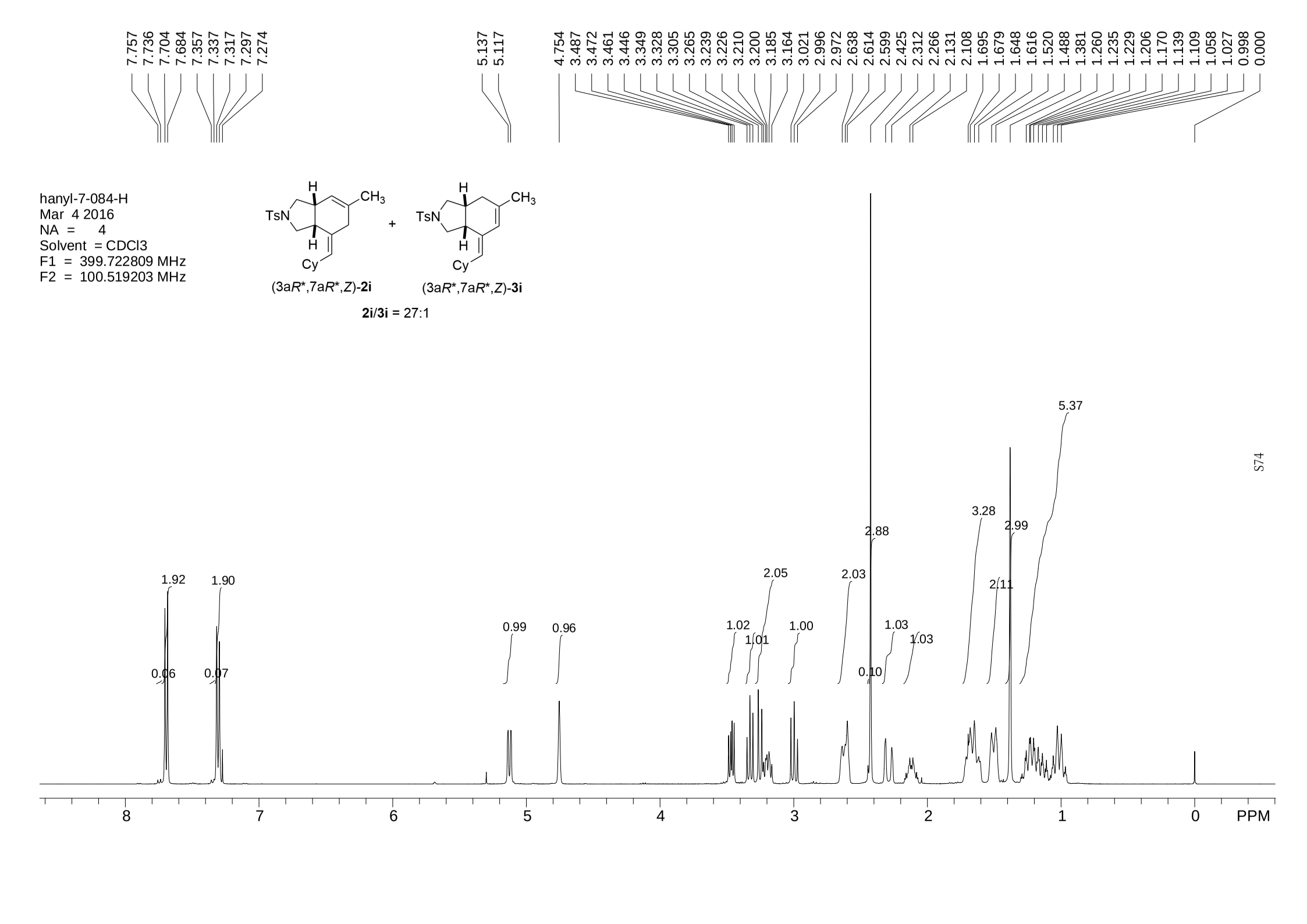


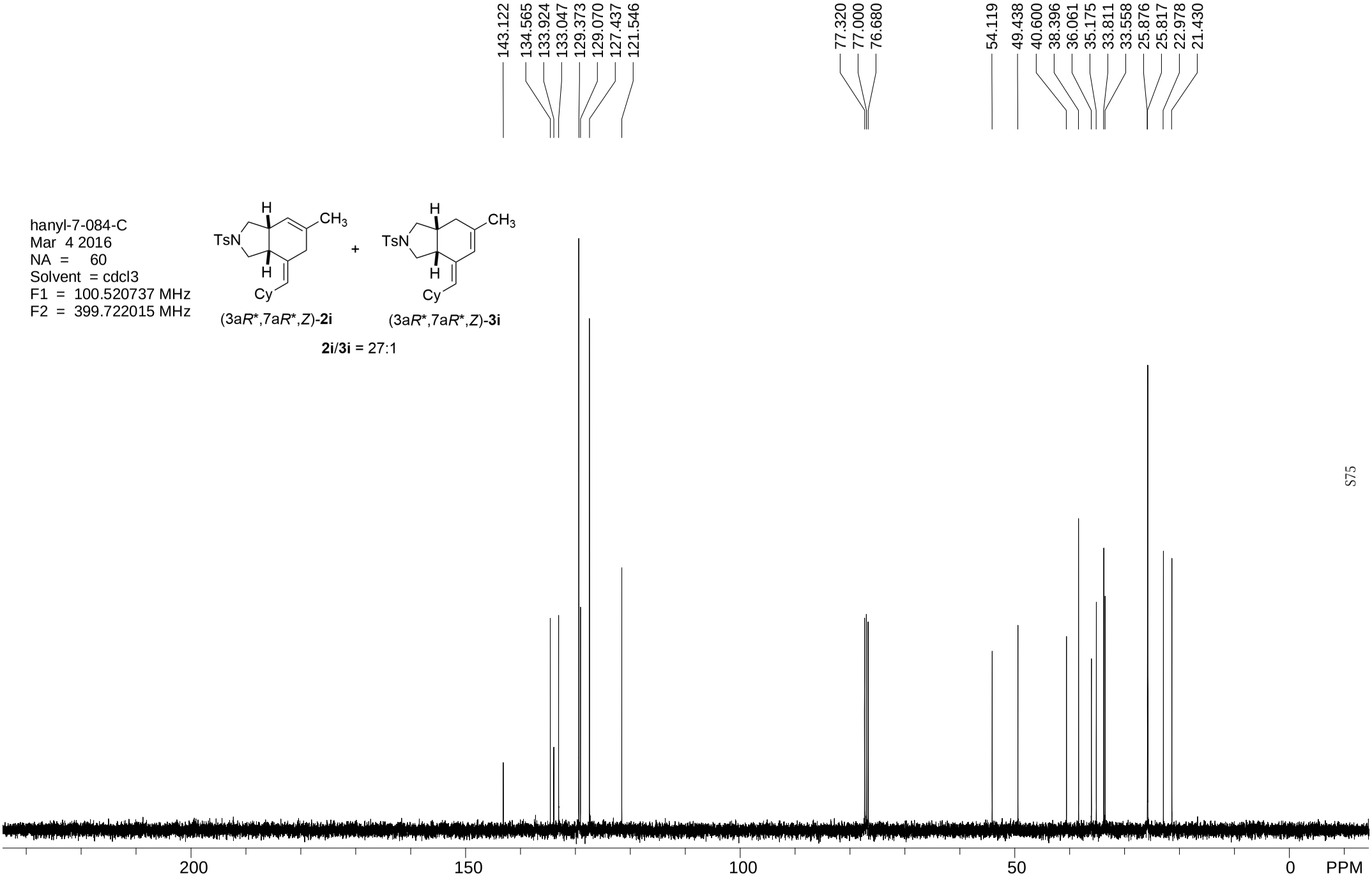
hanyl-7-189-H
Apr 9 2016
NA = 8
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz

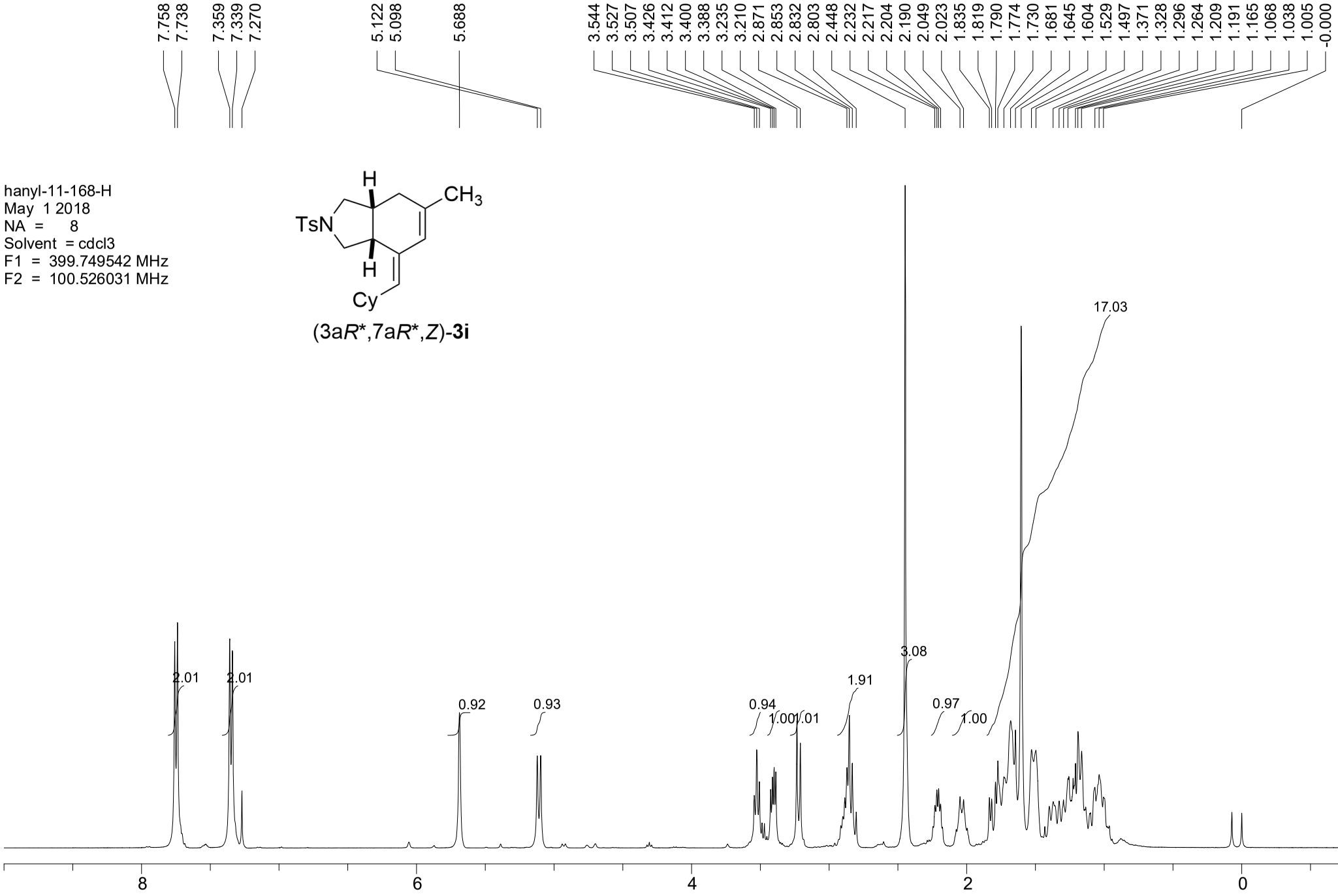


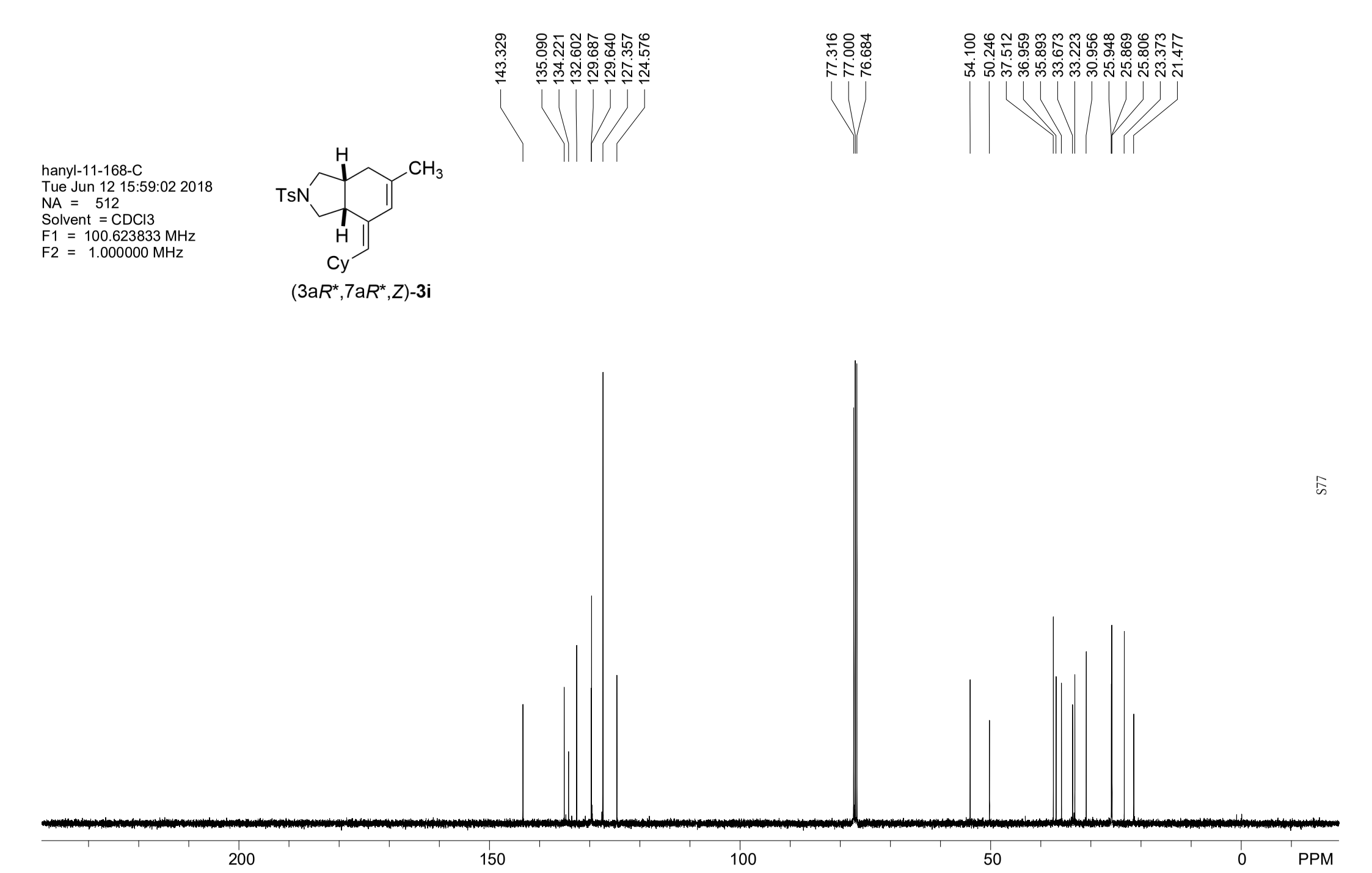
(3a*R**,5*S**,7a*R**,*Z*)-**2h**


hanyl-7-189-C
Apr 9 2016
NA = 100
Solvent = cdcl3
F1 = 100.520737 MHz
F2 = 399.722015 MHz
(3aR*,5S*,7aR*,Z)-2h
TsN
n-C4H9
H
H
H
Br
144.058
143.375
133.545
132.869
132.596
132.156
130.850
130.159
129.461
128.231
127.836
127.647
127.487
124.519
77.319
77.000
76.681
65.743
54.409
50.303
44.594
38.415
38.127
31.659
27.469
22.254
21.427
15.187
13.851
200
150
100
50
0
PPM

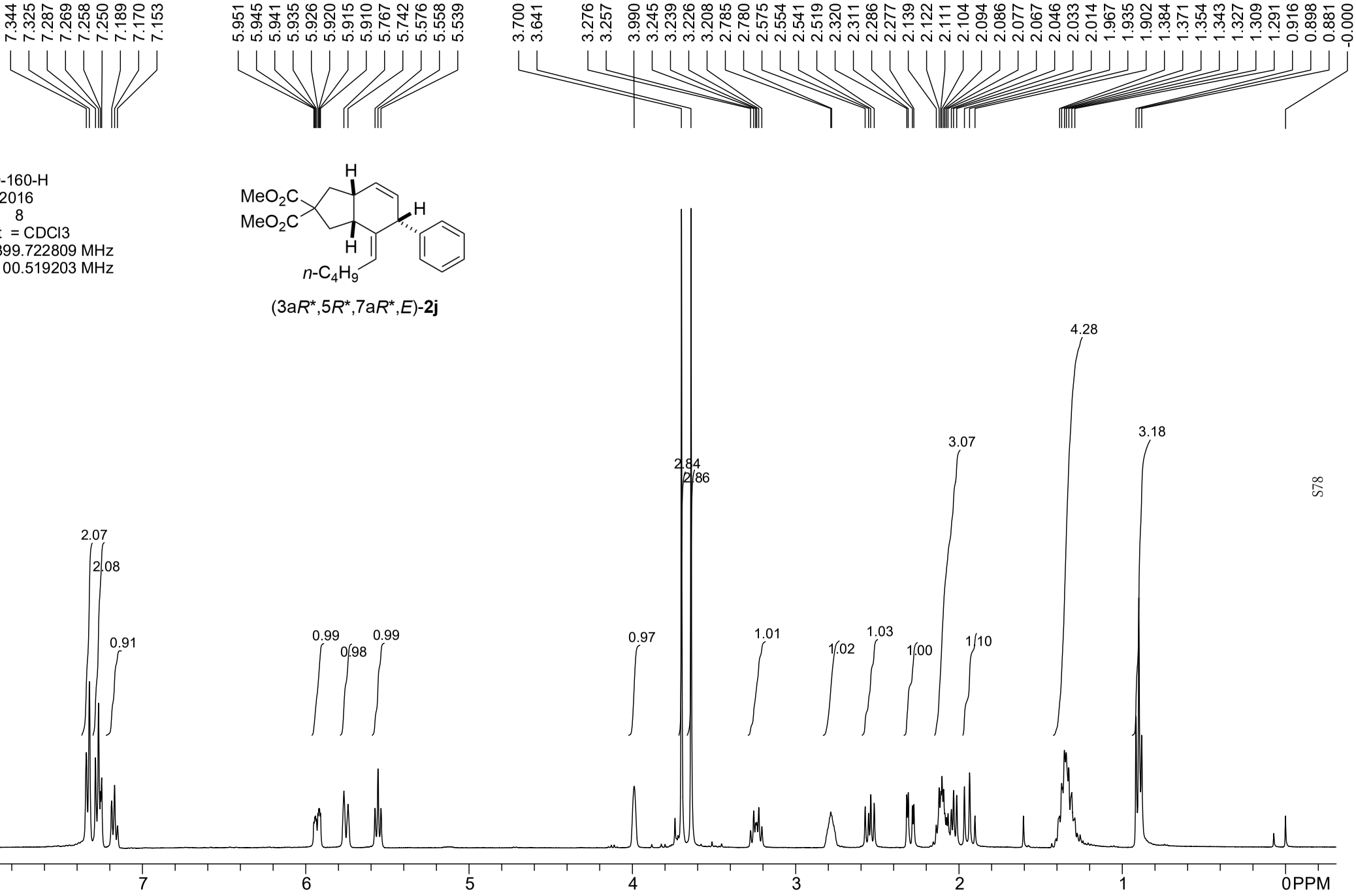

7.757
7.736
7.704
7.684
7.357
7.337
7.317
7.297
7.274
5.137
5.117
4.754
3.487
3.472
3.461
3.446
3.349
3.328
3.305
3.265
3.239
3.226
3.210
3.200
3.185
3.164
3.021
2.996
2.972
2.638
2.614
2.599
2.425
2.312
2.266
2.131
2.108
1.695
1.679
1.648
1.616
1.520
1.488
1.381
1.260
1.235
1.229
1.206
1.170
1.139
1.109
1.058
1.027
0.998
0.000
hanyl-7-084-H
Mar 4 2016
NA = 4
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz
TsN
H
CH3
Cy
+
(3aR*,7aR*,Z)-2i
(3aR*,7aR*,Z)-3i
2i/3i = 27:1
1.92
1.90
0.06
0.07
0.99
0.96
1.02
1.01
2.05
1.00
2.03
2.88
0.10
1.03
1.03
3.28
2.11
2.99
5.37
S74
8
7
6
5
4
3
2
1
0
PPM

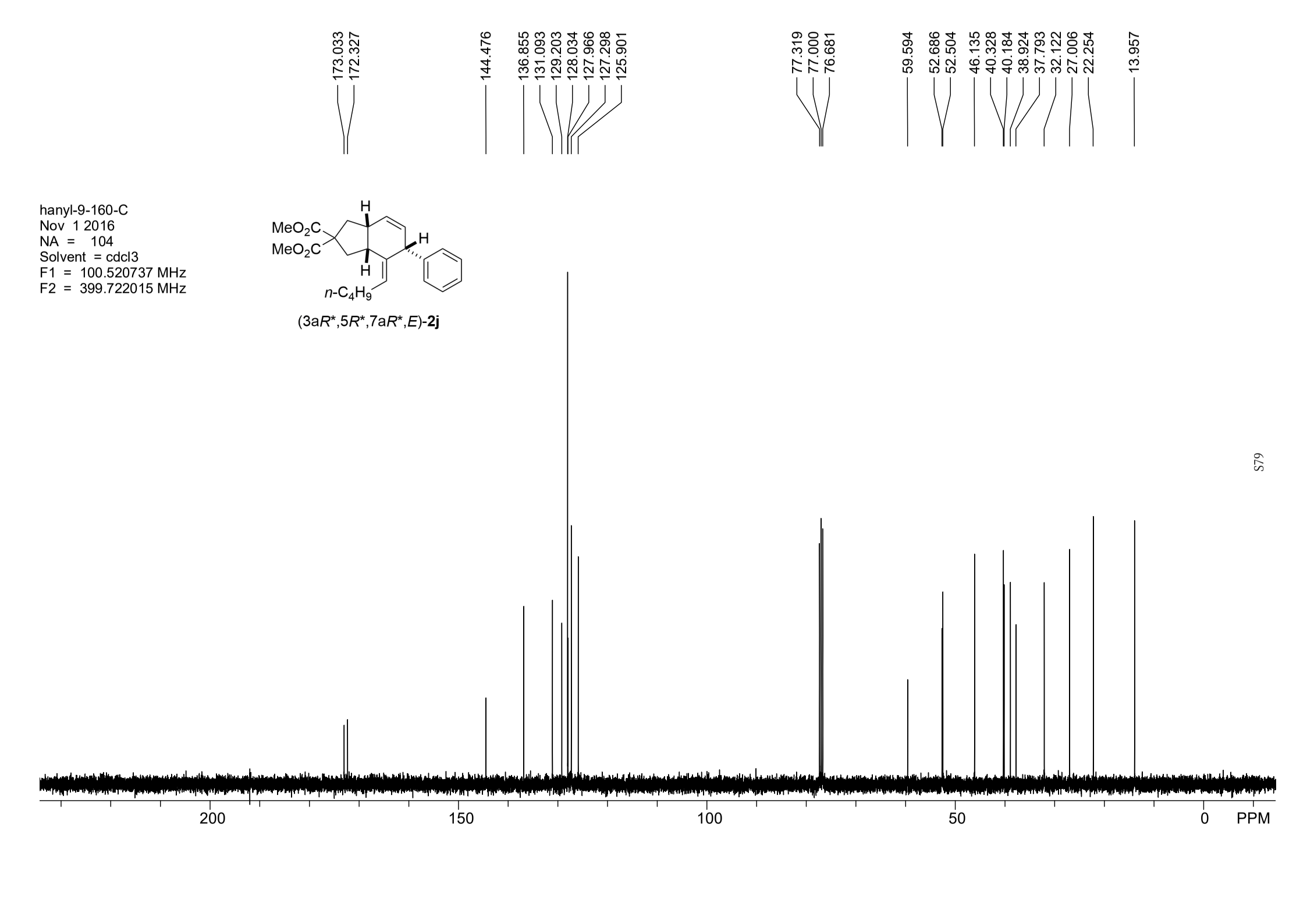

143.122
134.565
133.924
133.047
129.373
129.070
127.437
121.546
77.320
77.000
76.680
54.119
49.438
40.600
38.396
36.061
35.175
33.811
33.558
25.876
25.817
22.978
21.430
hanyl-7-084-C
Mar 4 2016
NA = 60
Solvent = cdcl3
F1 = 100.520737 MHz
F2 = 399.722015 MHz
TsN
CH3
H
Cy
+
(3aR*,7aR*,Z)-2i
(3aR*,7aR*,Z)-3i
2i/3i = 27:1
S75
200
150
100
50
0
PPM

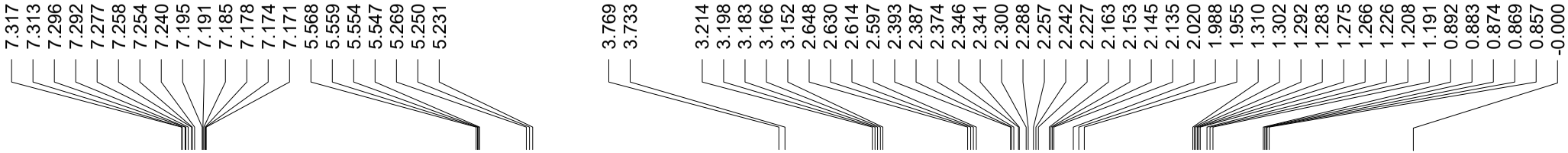

7.758
7.738
7.359
7.339
7.270
5.122
5.098
5.688
3.544
3.527
3.507
3.426
3.412
3.400
3.388
3.235
3.210
2.871
2.853
2.832
2.803
2.448
2.232
2.217
2.204
2.190
2.049
2.023
1.835
1.819
1.790
1.774
1.730
1.681
1.645
1.604
1.529
1.497
1.371
1.328
1.296
1.264
1.209
1.191
1.165
1.068
1.038
1.005
-0.000
hanyl-11-168-H
May 1 2018
NA = 8
Solvent = cdcl3
F1 = 399.749542 MHz
F2 = 100.526031 MHz
H
CH3
TsN
H
Cy
(3aR*,7aR*,Z)-3i
17.03
3.08
2.01
2.01
0.92
0.93
0.94
1.00
1.01
1.91
0.97
1.00
8
6
4
2
0
PPM


143.329
135.090
134.221
132.602
129.687
129.640
127.357
124.576
77.316
77.000
76.684
54.100
50.246
37.512
36.959
35.893
33.673
33.223
30.956
25.948
25.869
25.806
23.373
21.477
hanyl-11-168-C
Tue Jun 12 15:59:02 2018
NA = 512
Solvent = CDCl3
F1 = 100.623833 MHz
F2 = 1.000000 MHz
H
CH3
TsN
H
Cy
200
150
100
50
0
PPM

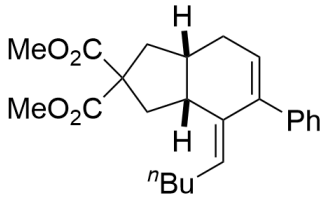
(3a*R**,7a*R**,*Z*)-**3i**


7.344
7.325
7.287
7.269
7.258
7.250
7.189
7.170
7.153
5.951
5.945
5.941
5.935
5.926
5.920
5.915
5.910
5.767
5.742
5.576
5.558
5.539
3.700
3.641
3.276
3.257
3.990
3.245
3.239
3.226
3.208
2.785
2.780
2.575
2.554
2.541
2.519
2.320
2.311
2.286
2.277
2.139
2.122
2.111
2.104
2.094
2.086
2.077
2.067
2.046
2.033
2.014
1.967
1.935
1.902
1.384
1.371
1.354
1.343
1.327
1.309
1.291
0.916
0.898
0.881
-0.000
hanyl-9-160-H
Nov 1 2016
NA = 8
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz
MeO2C
MeO2C
H
H
H
n-C4H9
(3aR*,5R*,7aR*,E)-2j
4.28
3.18
3.07
2.84
2.86
2.07
2.08
0.91
0.99
0.98
0.99
0.97
1.01
1.02
1.03
1.00
1.10
S78
8
7
6
5
4
3
2
1
0PPM

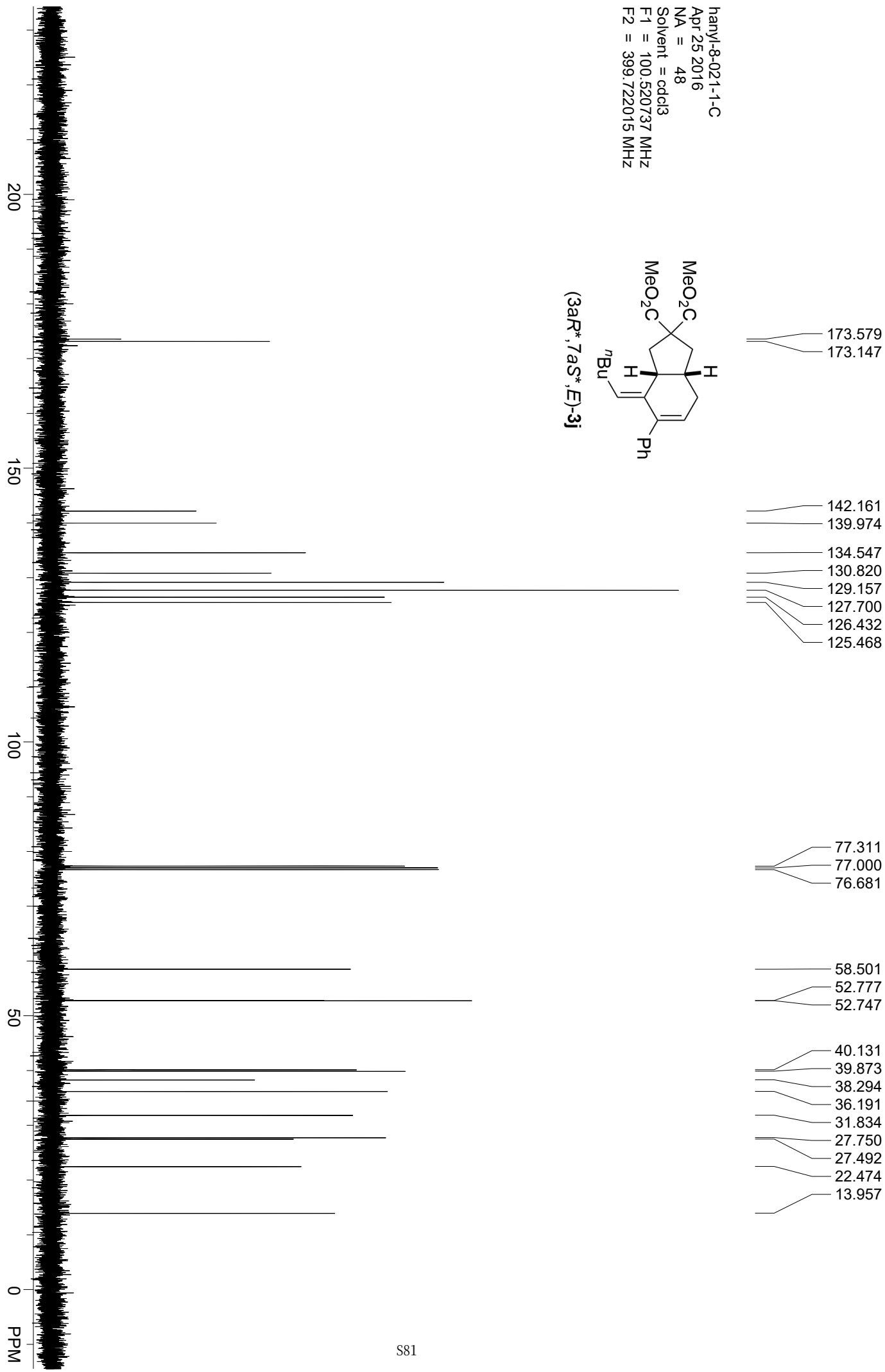

173.033
172.327
144.476
136.855
131.093
129.203
128.034
127.966
127.298
125.901
77.319
77.000
76.681
59.594
52.686
52.504
46.135
40.328
40.184
38.924
37.793
32.122
27.006
22.254
13.957
hanyl-9-160-C
Nov 1 2016
NA = 104
Solvent = cdcl3
F1 = 100.520737 MHz
F2 = 399.722015 MHz
MeO2C
MeO2C
H
H
H
n-C4H9
(3aR*,5R*,7aR*,E)-2j
200
150
100
50
0
PPM

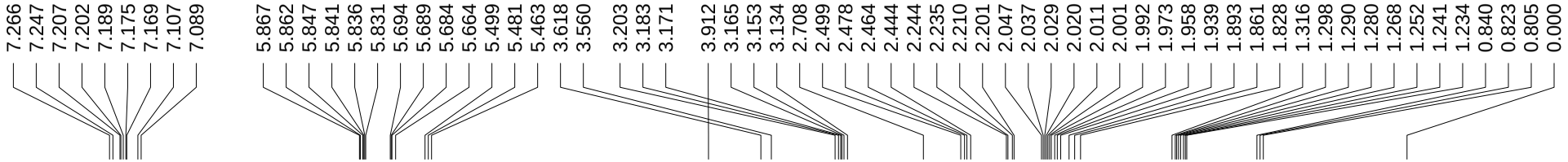


hanyl-8-021-1-H
Apr 25 2016
NA = 8
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz

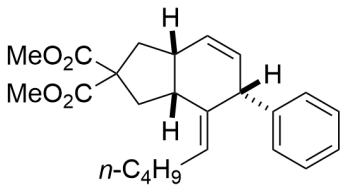


(3a*R**,7*aS**,*E*)-**3j**

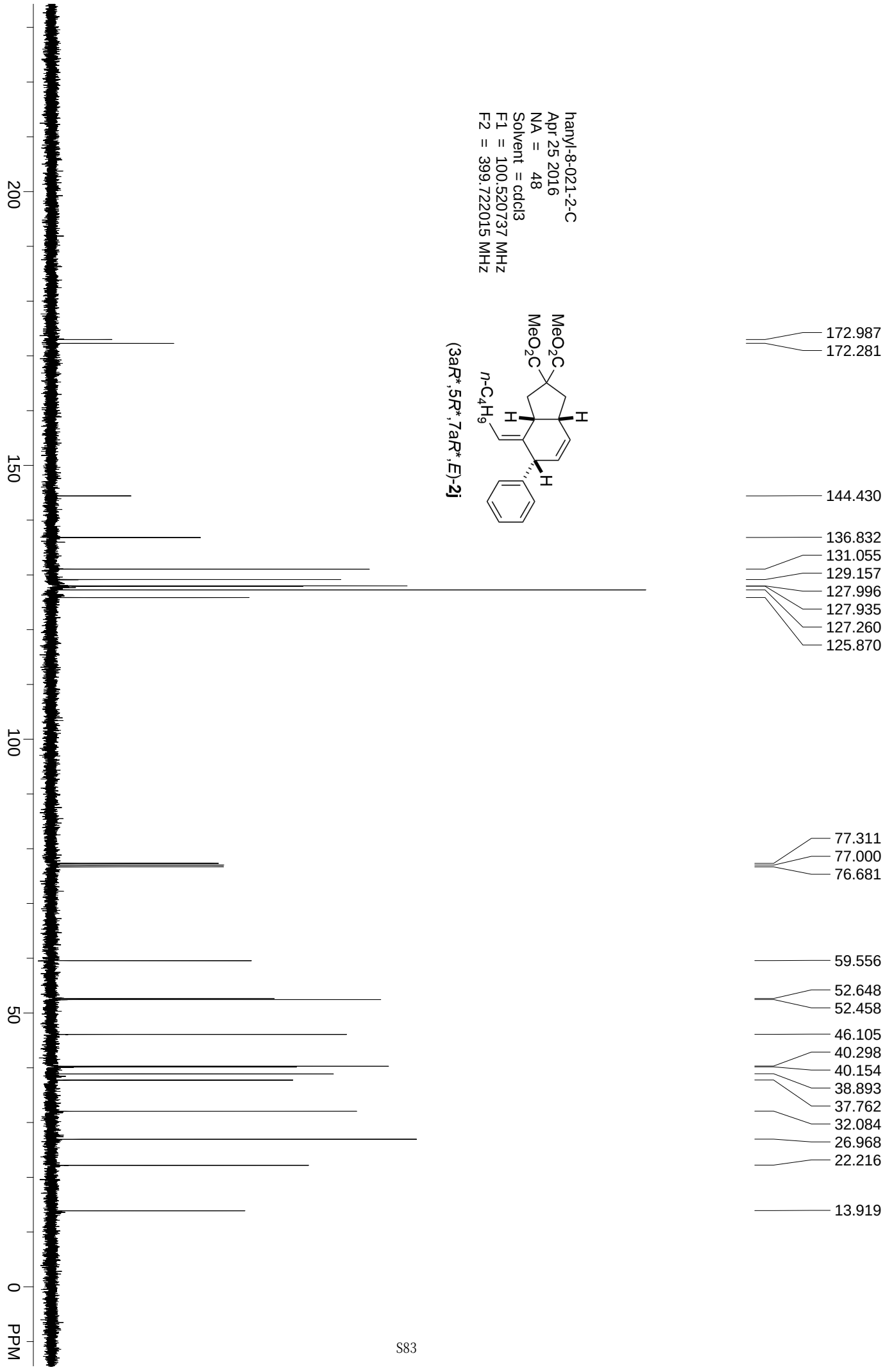

hanyl-8-021-1-C
Apr 25 2016
NA = 48
Solvent = cdcl3
F1 = 100.520737 MHz
F2 = 399.722015 MHz
MeO2C
MeO2C
nBu
H
H
Ph
(3aR*,7aS*,E)-3j
173.579
173.147
142.161
139.974
134.547
130.820
129.157
127.700
126.432
125.468
77.311
77.000
76.681
58.501
52.777
52.747
40.131
39.873
38.294
36.191
31.834
27.750
27.492
22.474
13.957
200
150
100
50
0
PPM

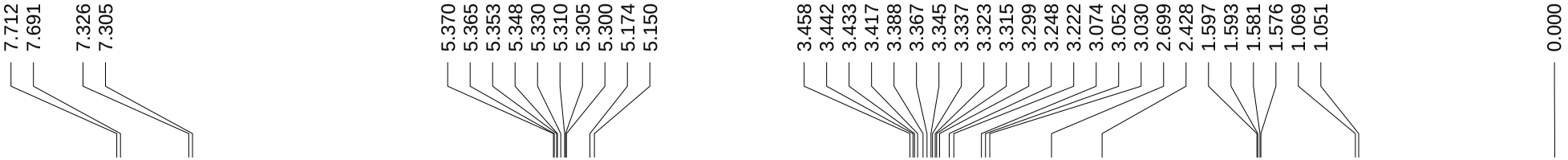


hanyl-8-021-2-H
Apr 25 2016
NA = 8
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz

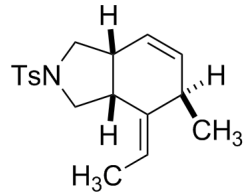


(3a*R**,5*R**,7a*R**,*E*)-**2j**

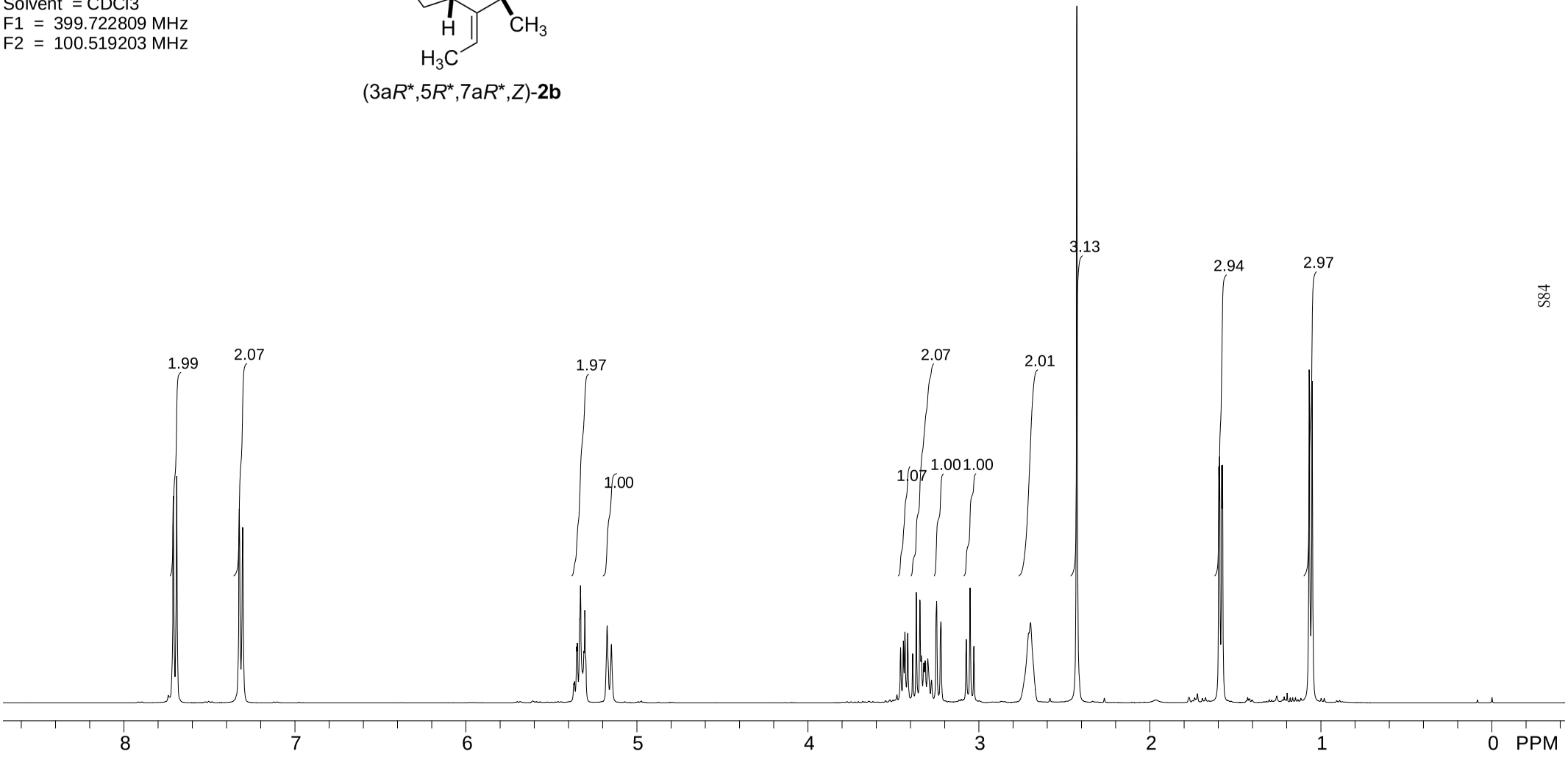

hanyl-8-021-2-C
Apr 25 2016
NA = 48
Solvent = cdcl3
F1 = 100.520737 MHz
F2 = 399.722015 MHz
(3aR*,5R*,7aR*,E)-2j
MeO2C
MeO2C
n-C4H9
H
H
H
172.987
172.281
144.430
136.832
131.055
129.157
127.996
127.935
127.260
125.870
77.311
77.000
76.681
59.556
52.648
52.458
46.105
40.298
40.154
38.893
37.762
32.084
26.968
22.216
13.919
200
150
100
50
0
PPM



hanyl-10-105-H
Apr 22 2017
NA = 8
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz

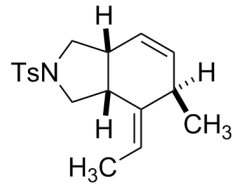


(3a*R**,5*R**,7a*R**,*Z*)-**2b**



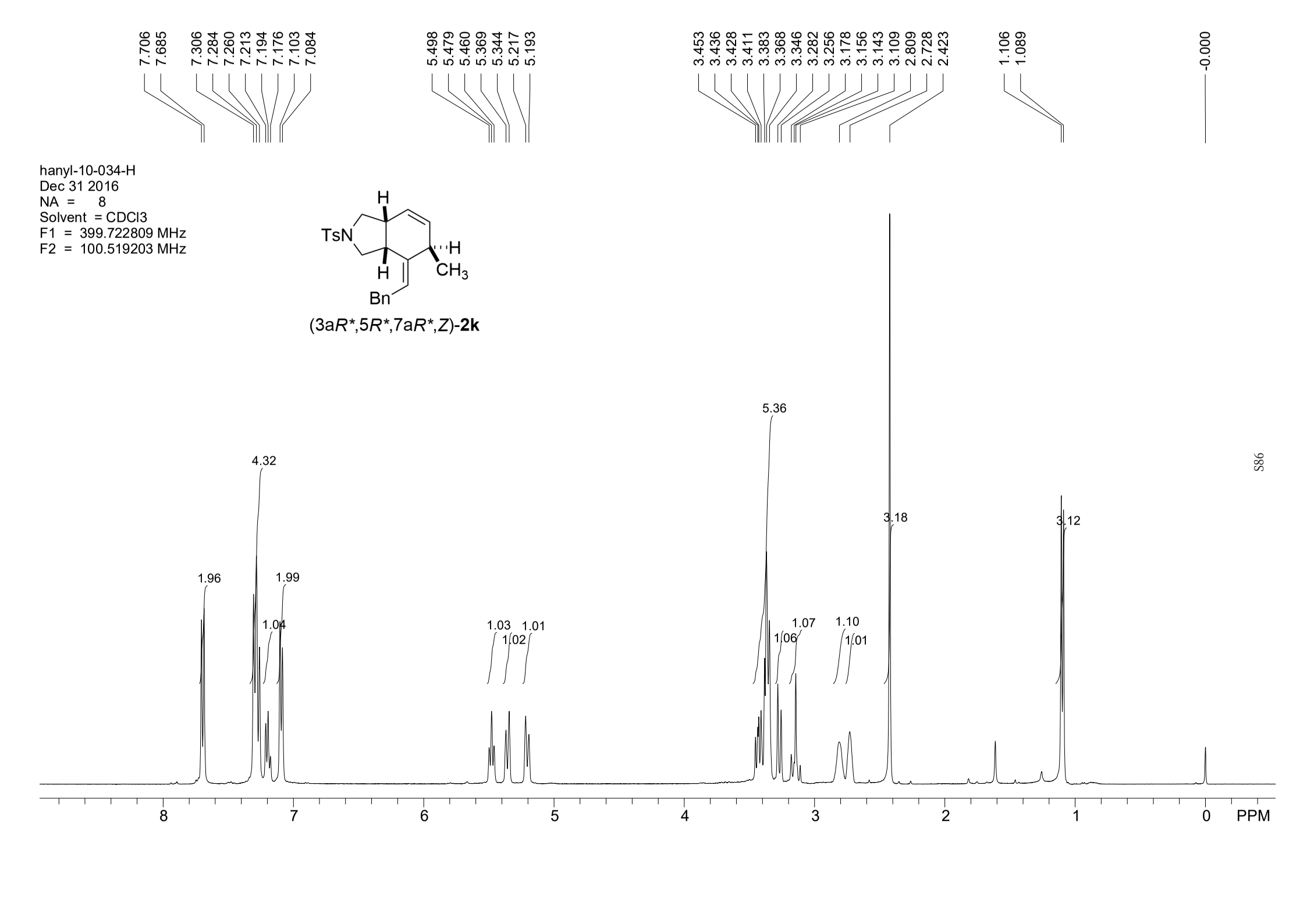
143.134
136.023
133.793
133.676
129.339
127.286
126.310
118.425
77.318
77.000
76.682
53.398
49.378
39.820
38.131
30.897
21.307
18.255
12.578

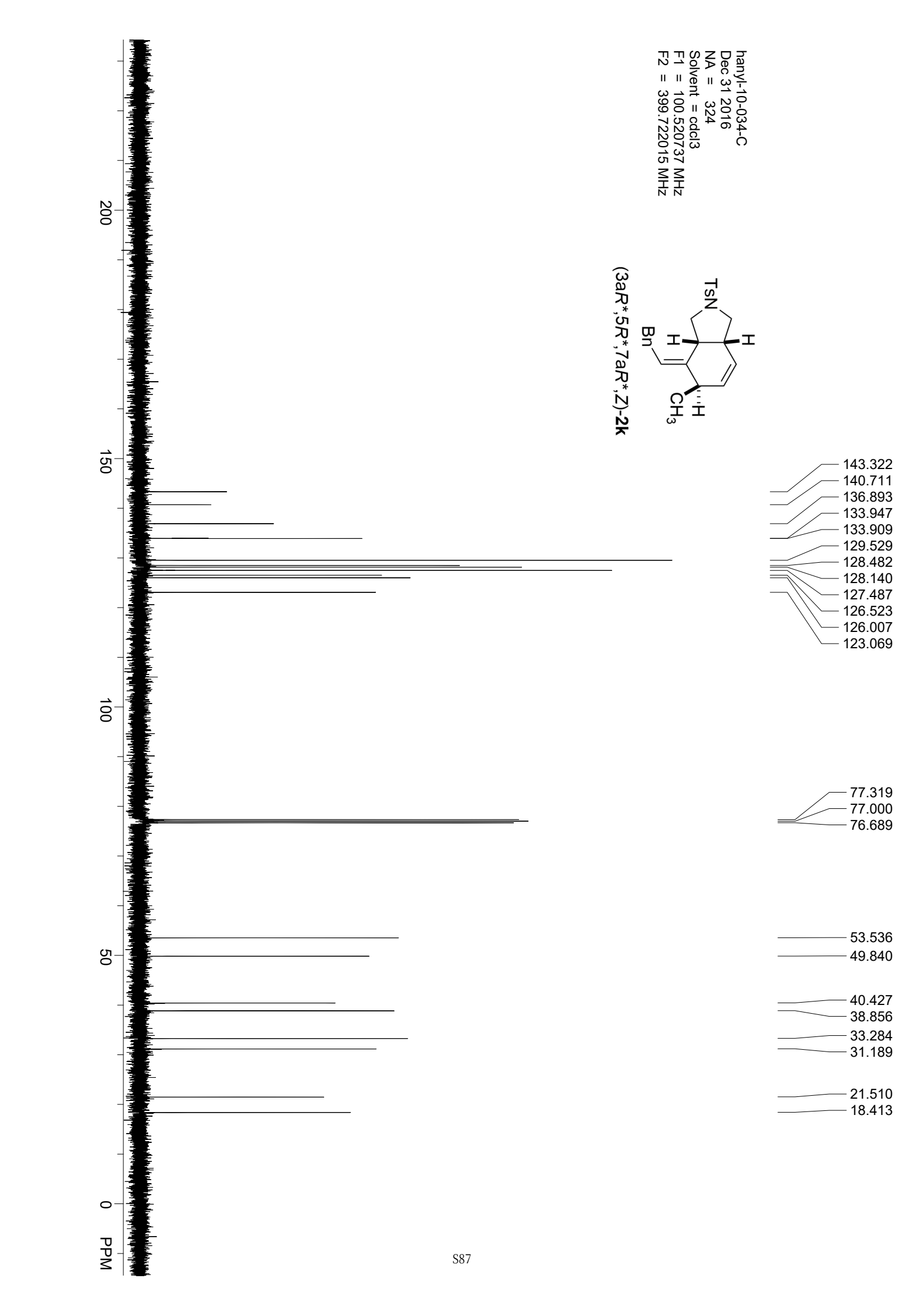
hanyl-10-105-C
Apr 22 2017
NA = 48
Solvent = cdcl3
F1 = 100.521141 MHz
F2 = 399.722015 MHz

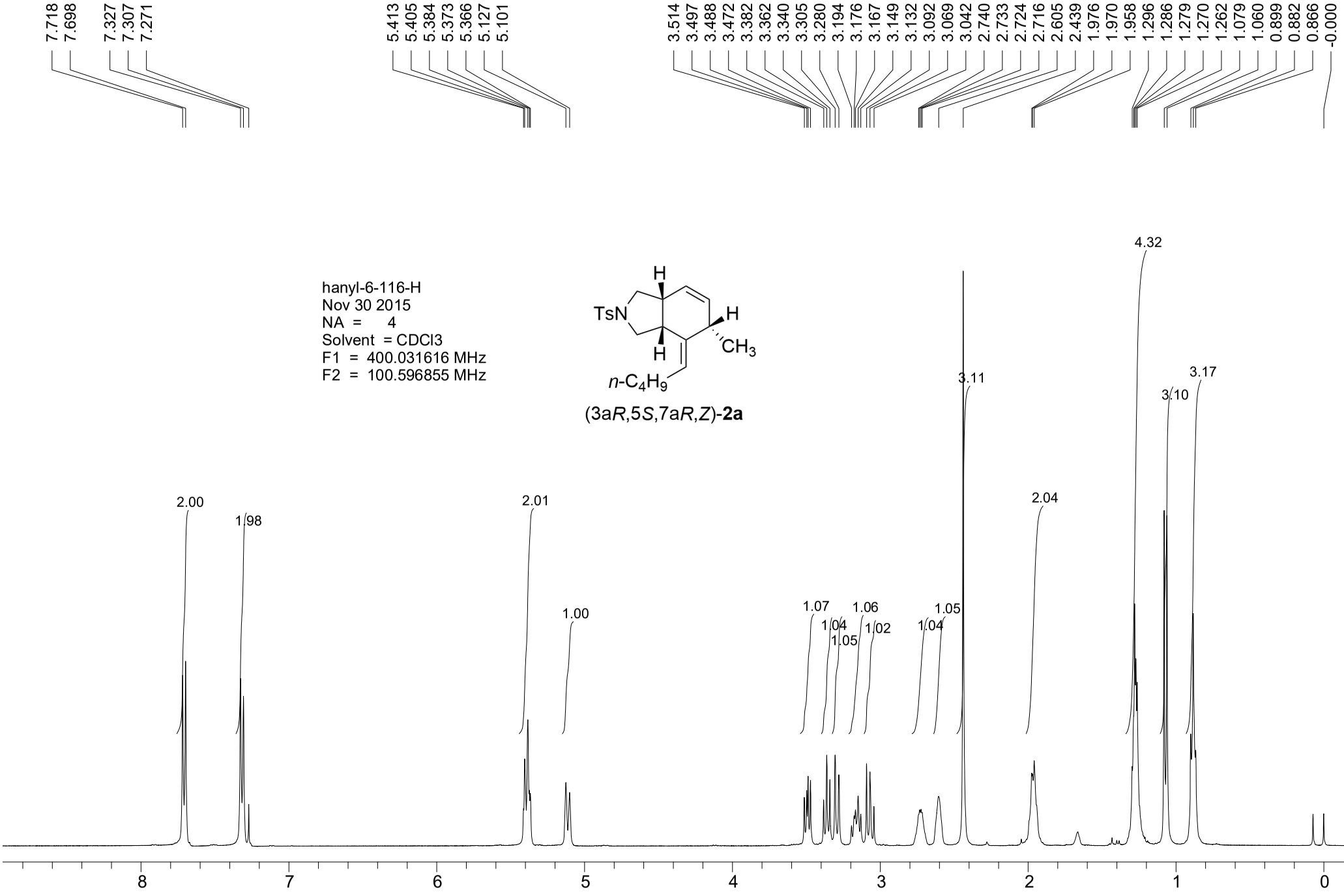


(3a*R**,5*R**,7a*R**,*Z*)-**2b**

200
150
100
50
0
PPM


7.706
7.685
7.306
7.284
7.260
7.213
7.194
7.176
7.103
7.084
5.498
5.479
5.460
5.369
5.344
5.217
5.193
3.453
3.436
3.428
3.411
3.383
3.368
3.346
3.282
3.256
3.178
3.156
3.143
3.109
2.809
2.728
2.423
1.106
1.089
-0.000
hanyl-10-034-H
Dec 31 2016
NA = 8
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz
TsN
H
H
H
CH3
Bn
(3aR*,5R*,7aR*,Z)-2k
1.96
4.32
1.04
1.99
1.03
1.02
1.01
5.36
1.06
1.07
1.10
1.01
3.18
3.12
S86
8
7
6
5
4
3
2
1
0
PPM

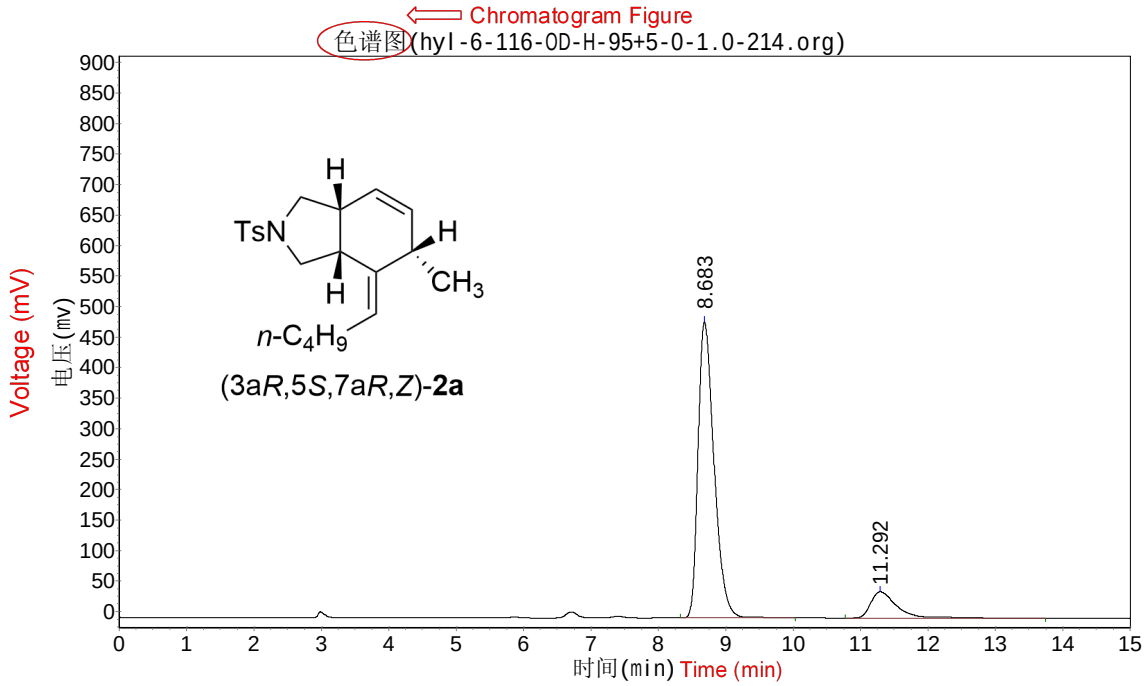

hanyl-10-034-C
Dec 31 2016
NA = 324
Solvent = cdcl3
F1 = 100.520737 MHz
F2 = 399.722015 MHz
(3aR*,5R*,7aR*,Z)-2k
TsN
H
H
Bn
CH3
H
143.322
140.711
136.893
133.947
133.909
129.529
128.482
128.140
127.487
126.523
126.007
123.069
77.319
77.000
76.689
53.536
49.840
40.427
38.856
33.284
31.189
21.510
18.413
200
150
100
50
0
PPM


7.718
7.698
7.327
7.307
7.271
5.413
5.405
5.384
5.373
5.366
5.127
5.101
3.514
3.497
3.488
3.472
3.382
3.362
3.340
3.305
3.280
3.194
3.176
3.167
3.149
3.132
3.092
3.069
3.042
2.740
2.733
2.724
2.716
2.605
2.439
1.976
1.970
1.958
1.296
1.286
1.279
1.270
1.262
1.079
1.060
0.899
0.882
0.866
-0.000
hanyl-6-116-H
Nov 30 2015
NA = 4
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz
TsN
H
H
H
CH3
n-C4H9
(3aR,5S,7aR,Z)-2a
2.00
1.98
2.01
1.00
1.07
1.04
1.05
1.06
1.02
1.04
1.05
3.11
2.04
4.32
3.10
3.17
S88
8
7
6
5
4
3
2
1
0
PPM

hyl-6-116

实验时间：2015-11-23,13:02:56　　报告时间：2015-11-23,13:04:29
谱图文件:F:\slf\韩玉林\2015-11-24\hyl-6-116\hyl-6-116-OD-H-95+5-0-1.0-214.org

实验内容简介：
OD-H　　95:5
214nm　　1.0ml/min



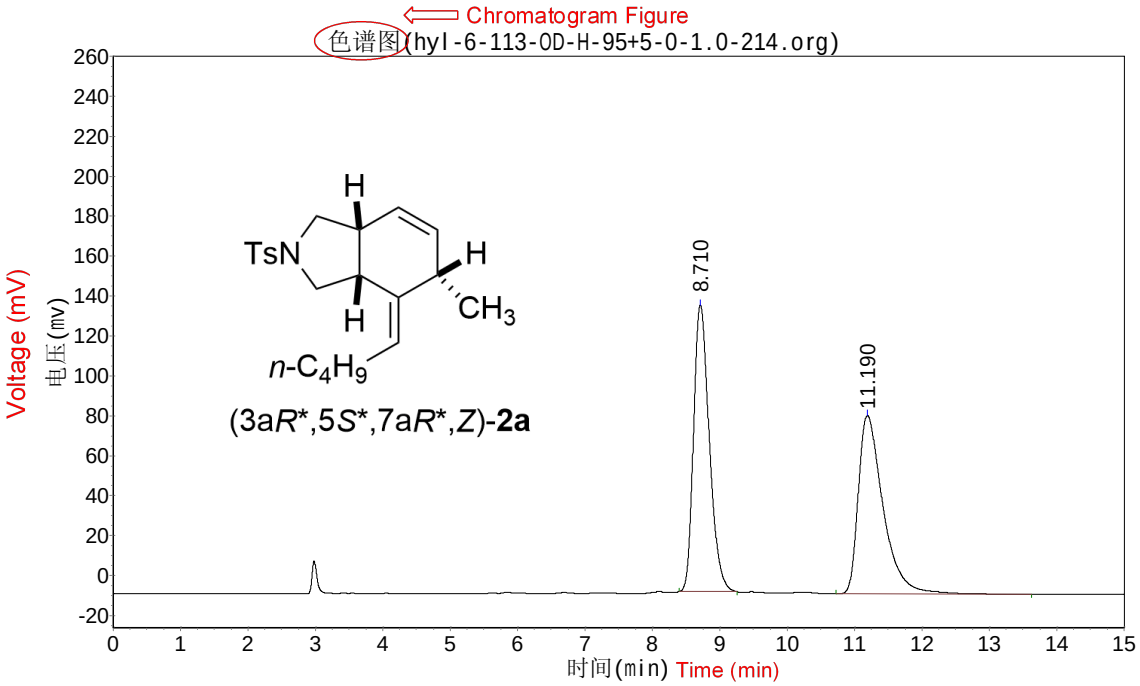
分析结果表

峰号(Peak No.)	峰名(Peak name)	保留时间(Retention time)	峰高(Peak height)	峰面积(Peak area)	含量(Content)
1		8.683	484604.219	7973202.000	87.4332
2		11.292	43067.367	1145991.250	12.5668
总计			527671.586	9119193.250	100.0000

hyl-6-113

实验时间：2015-11-23,13:18:39　　报告时间：2015-11-23,13:19:59
谱图文件:F:\slf\韩玉林\2015-11-24\hyl-6-113\hyl-6-113-OD-H-95+5-0-1.0-214.org

实验内容简介：
OD-H　　95:5
214nm　　1.0ml/min



分析结果表

峰号(Peak No.)	峰名(Peak name)	保留时间(Retention time)	峰高(Peak height)	峰面积(Peak area)	含量(Content)
1		8.710	143521.875	2329465.000	50.4172
2		11.190	89308.227	2290916.000	49.5828
总计			232830.102	4620381.000	100.0000