

PtCl₄-catalyzed Skeleton Rearrangement- Cyclization of Tertiary Indolyl-3-alkynols

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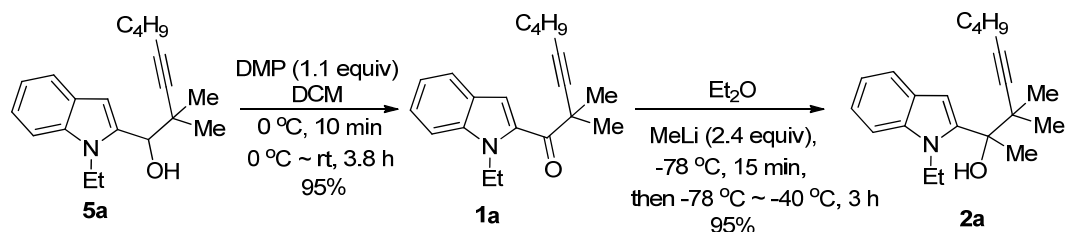
General Information

^1H and ^{13}C nuclear magnetic resonance spectra were recorded with an instrument operated at 300 MHz for ^1H NMR and 75 MHz for ^{13}C NMR spectra. CDCl_3 was used as solvent in all NMR experiments. Chemical shifts (δ) are given in parts per million (ppm). Infrared spectra were recorded on a FT-IR spectrometer. Mass spectra were carried out in EI mode. HRMS spectra were carried out in EI mode. Flash column chromatography was performed on silica gel. Et_2O and toluene was refluxed over sodium wire using diphenyl ketone as indicator and distilled right before use. PtCl_4 was purchased from Alfa Aesar. Other reagents were used as received without further treatment.

1. Synthesis of starting materials 2a~2n.

The starting materials **2a~2n** were prepared according to the literatures.¹

(1) 2-(1-Ethyl-1*H*-indol-2-yl)-3,3-dimethylnon-4-yn-2-ol (**2a**) (zj-1-032, 1-036)



Typical Procedure I: To a solution of **5a**² (2.9879 g, 10.0 mmol) and DCM (80 mL) was added DMP (4.6596 g, 11.0 mmol)/DCM (20 mL) at 0 °C within 10 min. Then the mixture was allowed to warm up to room temperature. After 3.8 h, the reaction was complete as monitored by TLC, and the resulting mixture was concentrated in vacuo. Column chromatography on silica gel (eluent: petroleum ether /ethyl acetate = 50/1 ~ 30/1) afforded **1a** (2.8271 g, 95%) as a liquid, which was then submitted to next step.

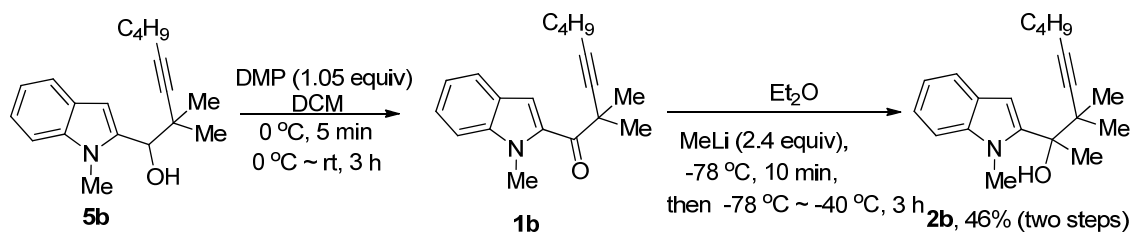
To a solution of **1a** (2.0717 g, 7.0 mmol, prepared above) in diethyl ether (50 mL) was added MeLi (10.5 mL, 1.6 M in Et₂O, 16.8 mmol) at -78 °C with stirring under nitrogen atmosphere within 15 min. Then the mixture was allowed to warm up to -40 °C. After 3 h, the reaction was complete as monitored by TLC, the resulting mixture was quenched with a saturated aqueous solution of NH₄Cl (10 mL), extracted with diethyl ether (20 mL×3), and washed with water and brine. The combined ether layer was dried over anhydrous Na₂SO₄, filtration, evaporation, and column chromatography on silica gel to give **2a** (2.0793 g, 95%) (eluent: petroleum ether/ethyl acetate = 50/1) as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.59-7.50 (m, 1H,

ArH), 7.38-7.27 (m, 1H, ArH), 7.23-7.12 (m, 1H, ArH), 7.11-7.03 (m, 1H, ArH), 6.34 (s, 1H, ArH), 5.01-4.86 (m, 1H, one proton of NCH₂), 4.34-4.16 (m, 1H, one proton of NCH₂), 2.50 (s, 1H, OH), 2.22 (t, *J* = 7.1 Hz, 2H, CH₂), 1.81 (s, 3H, CH₃), 1.57-1.33 (m, 7H, 2 × CH₂ + CH₃), 1.24 (s, 3H, CH₃), 1.17 (s, 3H, CH₃), 0.93 (t, *J* = 7.2 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 139.5, 136.9, 127.2, 121.0, 120.1, 119.2, 109.6, 102.5, 85.0, 83.6, 78.5, 42.9, 41.4, 31.1, 28.7, 25.9, 25.5, 22.0, 18.4, 15.7, 13.6; IR (neat) ν (cm⁻¹) 3540, 3047, 2961, 2933, 2872, 2231, 1463, 1371, 1344, 1311, 1225, 1181, 1133, 1108, ; MS (70 ev, EI) *m/z* (%) 312 (M⁺+1, 7.88), 311 (M⁺, 21.69), 188 (100), 146 (100); HRMS Calcd for C₂₁H₂₉NO (M⁺): 311.2249, Found: 311.2248.

The following compounds **2b~2l** were prepared according to **Typical Procedure**

I.

(2) 3,3-Dimethyl-2-(1-methyl-1*H*-indol-2-yl)non-4-yn-2-ol (**2b**) (zj-1-100, 1-112)

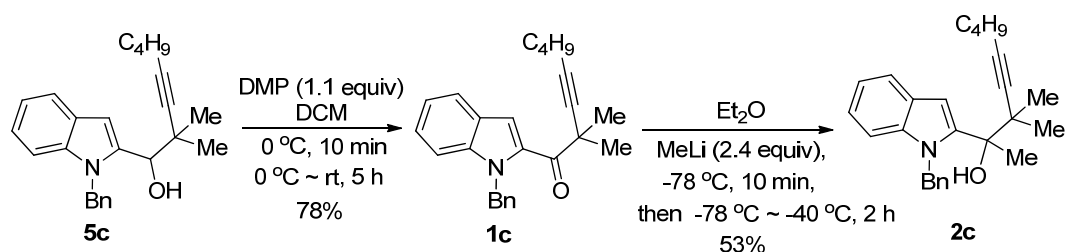


The reaction of **5b** (3.0077 g, 11.0 mmol), DMP (4.8925 g, 11.5 mmol)/DCM (20 mL), and DCM (80 mL) afforded **1b** (1.9562 g) (eluent: petroleum ether/ethyl acetate = 100/1~50/1) as a liquid.

The reaction of **1b** (1.9518 g, 7 mmol, prepared above)/diethyl ether (30 mL) and

MeLi (10.5 mL, 1.6 M in Et₂O, 16.8 mmol) afforded **2b** (1.4647 g, 46%, two steps) (eluent: petroleum ether/ethyl acetate = 100/1~50/1) as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.53 (d, *J* = 7.5 Hz, 1H, ArH), 7.28 (d, *J* = 8.1 Hz, 1H, ArH), 7.18 (t, *J* = 7.7 Hz, 1H, ArH), 7.07 (t, *J* = 7.4 Hz, 1H, ArH), 6.38 (s, 1H, ArH), 4.04 (s, 3H, NCH₃), 2.54 (s, 1H, OH), 2.21 (t, *J* = 6.8 Hz, 2H, CH₂), 1.80 (s, 3H, CH₃), 1.57-1.33 (m, 4H, 2 × CH₂), 1.24 (s, 3H, CH₃), 1.19 (s, 3H, CH₃), 0.92 (t, *J* = 7.1 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 140.1, 138.3, 126.8, 121.1, 120.0, 119.3, 109.3, 102.7, 85.0, 83.7, 78.5, 43.0, 33.4, 31.1, 28.4, 26.0, 25.6, 22.0, 18.4, 13.6; IR (neat) ν (cm⁻¹) 3539, 2957, 2933, 2872, 2230, 1469, 1371, 1358, 1316, 1236, 1176, 1143, 1104, 1055, 1010; MS (70 ev, EI) *m/z* (%) 298 (M⁺+1, 4.60), 297 (M⁺, 11.30), 174 (100), 132 (100); HRMS Calcd for C₂₀H₂₇NO (M⁺): 297.2093, Found: 297.2098.

(3) 2-(1-Benzyl-1*H*-indol-2-yl)-3,3-dimethylnon-4-yn-2-ol (2c) (qya-9-062, 9-068)

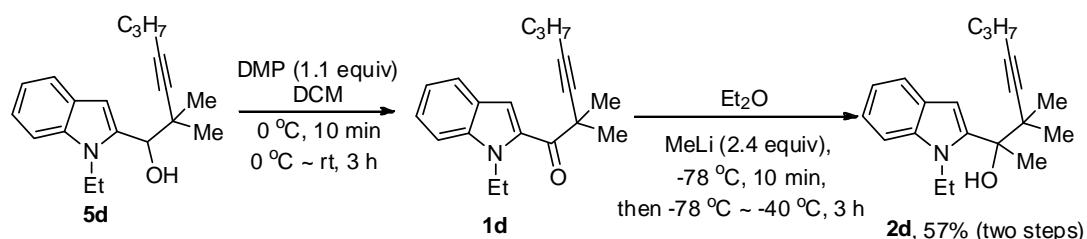


The reaction of **5c** (2.1567 g, 6 mmol), DMP (2.8027 g, 6.6 mmol)/DCM (20 mL), and DCM (80 mL) afforded **1c** (1.6708 g, 78%) (eluent: petroleum ether/ethyl acetate = 50/1~30/1) as a liquid.

The reaction of **1c** (1.4280 g, 4 mmol, prepared above)/diethyl ether (25 mL) and MeLi (6.0 mL, 1.6 M in Et₂O, 9.6 mmol) afforded **2c** (0.7915 g, 53%) (eluent: petroleum ether/ethyl acetate = 20/1) as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.63-7.51 (m, 1H, ArH), 7.27-7.00 (m, 6H, ArH), 6.98-6.86 (m, 2H, ArH), 6.49 (s, 1H,

ArH), 6.33 (d, $J = 16.5$ Hz, 1H, one proton of NCH₂), 5.38 (d, $J = 17.1$ Hz, 1H, one proton of NCH₂), 2.36 (s, 1H, OH), 2.19 (t, $J = 6.9$ Hz, 2H, CH₂), 1.82 (s, 3H, CH₃), 1.54-1.33 (m, 4H, 2 × CH₂), 1.29 (s, 3H, CH₃), 1.23 (s, 3H, CH₃), 0.91 (t, $J = 6.9$ Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 140.4, 139.8, 137.7, 128.4, 127.1, 126.5, 125.6, 121.4, 120.0, 119.6, 110.3, 103.0, 85.1, 83.4, 78.5, 49.9, 42.6, 31.1, 28.7, 25.8, 25.6, 22.0, 18.4, 13.6; IR (neat) ν (cm⁻¹) 3540, 3057, 3030, 2957, 2931, 2872, 2242, 1496, 1463, 1453, 1371, 1347, 1313, 1252, 1212, 1171, 1142, 1111, 1093, 1066, 1029, 1016; MS (70 ev, EI) m/z (%) 373 (M⁺, 5.03), 91 (100); HRMS Calcd for C₂₆H₃₁NO (M⁺): 373.2406, Found: 373.2404.

(4) 2-(1-Ethyl-1*H*-indol-2-yl)-3,3-dimethyloct-4-yn-2-ol (2d) (zj-1-069, 1-087)



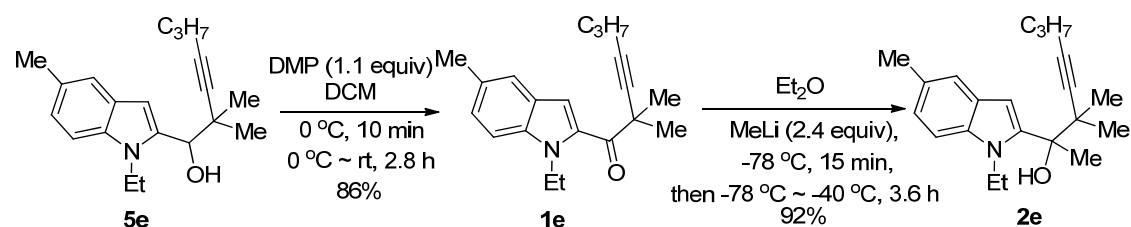
The reaction of **5d** (3.5406 g, 12.5 mmol), DMP (5.8378 g, 13.8 mmol)/DCM (25 mL), and DCM (75 mL) afforded crude **1d** (2.4774 g) (eluent: petroleum ether/ethyl acetate = 100/1~50/1) as a liquid.

The reaction of **1d** (2.4046 g, 8.6 mmol, prepared above)/diethyl ether (50 mL) and MeLi (13.0 mL, 1.6 M in Et₂O, 20.6 mmol) afforded **2d** (2.0387 g, 57%, two steps) (eluent: petroleum ether ~ petroleum ether/ethyl acetate = 100/1 for the first round afforded 0.5413 g of pure **2d** and 1.5478 g of impure **2d**, which was further purified by chromatography on silica gel (eluent: petroleum ether ~ ether/ethyl acetate = 100/1) to afford **2d** 1.4974 g, combined weight 2.0387 g as a liquid: ¹H NMR (300

MHz, CDCl₃) δ 7.54 (d, J = 8.1 Hz, 1H, ArH), 7.32 (d, J = 7.5 Hz, 1H, ArH), 7.17 (t, J = 7.7 Hz, 1H, ArH), 7.07 (t, J = 7.4 Hz, 1H, ArH), 6.34 (s, 1H, ArH), 5.02-4.86 (m, 1H, one proton of NCH₂), 4.36-4.18 (m, 1H, one proton of NCH₂), 2.49 (s, 1H, OH), 2.20 (t, J = 7.1 Hz, 2H, CH₂), 1.81 (s, 3H, CH₃), 1.63-1.47 (m, 2H, CH₂), 1.38 (t, J = 6.9 Hz, 3H, CH₃), 1.25 (s, 3H, CH₃), 1.18 (s, 3H, CH₃), 1.00 (t, J = 7.4 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 139.6, 136.9, 127.2, 121.0, 120.1, 119.2, 109.6, 102.6, 85.3, 83.5, 78.5, 42.9, 41.4, 28.7, 25.9, 25.6, 22.4, 20.7, 15.6, 13.5; IR (neat) ν (cm⁻¹) 3546, 3046, 2967, 2933, 2872, 2186, 1461, 1371, 1344, 1310, 1275, 1225, 1180, 1133, 1108, 1096; MS (70 ev, EI) m/z (%) 298 (M⁺+1, 5.82), 297 (M⁺, 15.90), 188 (100), 188 (100), 146 (100); HRMS Calcd for C₂₀H₂₇NO (M⁺): 297.2093, Found: 297.2095.

(5) 2-(1-Ethyl-5-methyl-1*H*-indol-2-yl)-3,3-dimethylnon-4-yn-2-ol (2e)

(zj-1-010,1-012)

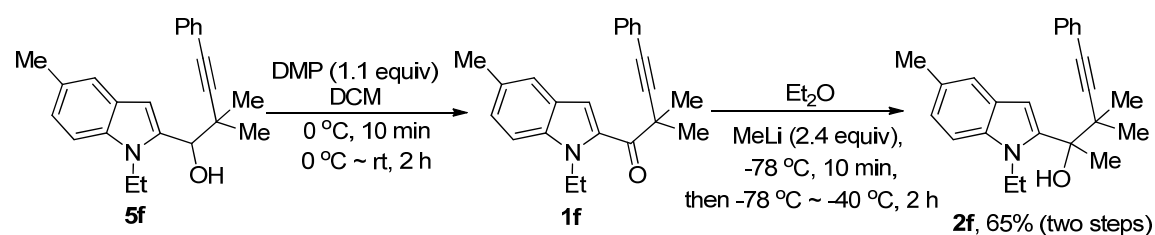


The reaction of **5e** (2.1125 g, 7.1 mmol), DMP (3.3165 g, 7.8 mmol)/DCM (20 mL), and DCM (80 mL) afforded **1e** (1.7911 g, 86%) (eluent: petroleum ether/ethyl acetate = 100/1~50/l) as a liquid.

The reaction of **1e** (1.5293 g, 5.2 mmol, prepared above)/diethyl ether (50 mL) and MeLi (4.2 mL, 3.0 M in Et₂O, 12.6 mmol) afforded **2e** (1.4814 g, 92%,) (eluent: petroleum ether/ethyl acetate = 30/l) as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.33 (s, 1H, ArH), 7.20 (d, J = 8.4 Hz, 1H, ArH), 6.99 (d, J = 8.4 Hz, 1H, ArH), 6.24 (s, 1H,

ArH), 4.98-4.82 (m, 1H, one proton of NCH₂), 4.30-4.13 (m, 1H, one proton of NCH₂), 2.49 (s, 1H, OH), 2.43 (s, 3H, CH₃), 2.18 (t, *J* = 7.1 Hz, 2H, CH₂), 1.79 (s, 3H, CH₃), 1.61-1.42 (m, 2H, CH₂), 1.35 (t, *J* = 7.1 Hz, 3H, CH₃), 1.23 (s, 3H, CH₃), 1.16 (s, 3H, CH₃), 0.99 (t, *J* = 7.4 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 139.4, 135.3, 128.3, 127.4, 122.5, 119.7, 109.3, 102.0, 85.3, 83.4, 78.4, 42.9, 41.4, 28.6, 25.8, 25.5, 22.4, 21.3, 20.7, 15.7, 13.5; IR (neat) ν (cm⁻¹) 3543, 2967, 2933, 2871, 2221, 1478, 1463, 1370, 1336, 1320, 1298, 1275, 1190, 1229, 1159, 1139, 1112, 1096, 1079, 1056, 1004; MS (70 ev, EI) *m/z* (%) 312 (M⁺+1, 6.02), 311 (M⁺, 16.56), 202 (100), 160 (100); HRMS Calcd for C₂₁H₂₉NO (M⁺): 311.2249, Found: 311.2247.

(6) 2-(1-Ethyl-5-methyl-1*H*-indol-2-yl)-3,3-dimethyl-5-phenylpent-4-yn-2-ol (2f)
(qya-9-127, 9-132)

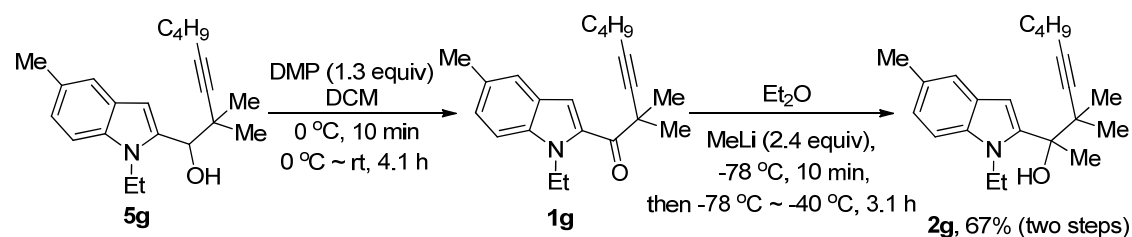


The reaction of **5f** (1.2916 g, 3.9 mmol), DMP (1.8213 g, 4.3 mmol)/DCM (10 mL), and DCM (50 mL) afforded crude **1f** (1.0625 g,) (eluent: petroleum ether/ethyl acetate = 100/1~50/1) as a liquid.

The reaction of **1f** (1.0513 g, 3.2 mmol, prepared above)/diethyl ether (20 mL) and MeLi (4.8 mL, 1.6 M in Et₂O, 7.7 mmol) afforded **2f** (0.8625 g, 65%, two steps) (eluent: petroleum ether/ethyl acetate = 50/1) as a solid; m.p. 104.9~106.2 °C (*n*-hexane/ethyl acetate); ¹H NMR (300 MHz, CDCl₃) δ 7.51-7.15 (m, 7H, ArH), 7.07-6.96 (m, 1H, ArH), 6.32 (d, *J* = 1.8 Hz, 1H, ArH), 5.04-4.82 (m, 1H, one proton

of NCH₂), 4.35-4.16 (m, 1H, one proton of NCH₂), 2.44 (s, 3H, CH₃), 2.34 (s, 1H, OH), 1.89 (d, *J* = 1.8 Hz, 3H, CH₃), 1.44-1.19 (m, 9H, 3 × CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 139.6, 135.5, 131.6, 128.5, 128.3, 128.0, 127.5, 123.4, 122.8, 119.9, 109.4, 102.2, 95.0, 83.4, 78.7, 43.3, 41.4, 28.7, 25.7, 25.3, 21.3, 15.7; IR (KBr) ν (cm⁻¹) 3554, 2977, 2935, 2866, 2218, 1597, 1477, 1459, 1371, 1335, 1298, 1269, 1229, 1191, 1136, 1107; MS (70 ev, EI) *m/z* (%) 346 (M⁺+1, 6.61), 345 (M⁺, 15.62), 202 (100), 160 (100); Elemental analysis calcd (%) for C₂₄H₂₇NO: C, 83.44; H, 7.88; N, 4.05; Found: C, 83.46, H, 8.06; N, 3.80.

(7) 2-(1-Ethyl-5-methyl-1*H*-indol-2-yl)-3,3-dimethylnon-4-yn-2-ol (2g) (zj-1-023, 1-024)

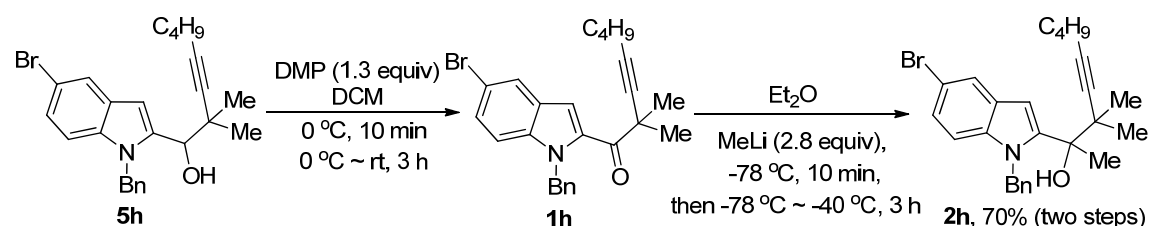


The reaction of **5g** (1.2536 g, 4.0 mmol), DMP (2.1553 g, 5.1 mmol)/DCM (20 mL), and DCM (80 mL) afforded crude **1g** (0.9215 g) (eluent: petroleum ether/ethyl acetate = 50/1~30/1) as a liquid.

The reaction of **1g** (0.8840 g, 2.9 mmol, prepared above)/diethyl ether (30 mL), and MeLi (4.4 mL, 1.6 M in Et₂O, 7.0 mmol) afforded **2g** (0.8362 g, 67%, two steps) (eluent: petroleum ether/ethyl acetate = 50/1~30/1) as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.36-7.30 (m, 1H, ArH), 7.21 (d, *J* = 8.4 Hz, 1H, ArH), 7.00 (d, *J* = 8.4, 1H, ArH), 6.24 (s, 1H, ArH), 4.99-4.83 (m, 1H, one proton of NCH₂), 4.30-4.15 (m, 1H, one proton of NCH₂), 2.49 (s, 1H, OH), 2.43 (s, 3H, CH₃), 2.21 (t, *J* = 7.1 Hz, 2H,

CH₂), 1.79 (s, 3H, CH₃), 1.57-1.30 (m, 7H, 2 × CH₂ + CH₃), 1.23 (s, 3H, CH₃), 1.16 (s, 3H, CH₃), 0.93 (t, *J* = 7.4 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 139.4, 135.3, 128.4, 127.4, 122.6, 119.7, 109.3, 102.0, 85.1, 83.6, 78.5, 42.9, 41.4, 31.1, 28.7, 25.9, 25.5, 22.0, 21.3, 18.4, 15.7, 13.6; IR (neat) ν (cm⁻¹) 3546, 2961, 2932, 2871, 2230, 1477, 1459, 1370, 1335, 1298, 1229, 1189, 1138, 1111, 1096; MS (70 ev, EI) *m/z* (%) 326 (M⁺+1, 11.07), 325 (M⁺, 13.79), 202 (100), 160 (100); HRMS Calcd for C₂₂H₃₁NO (M⁺): 325.2406, Found: 325.2404.

(8) 2-(1-Benzyl-5-bromo-1*H*-indol-2-yl)-3,3-dimethylnon-4-yn-2-ol (2h) (zj-1-055, 1-056)

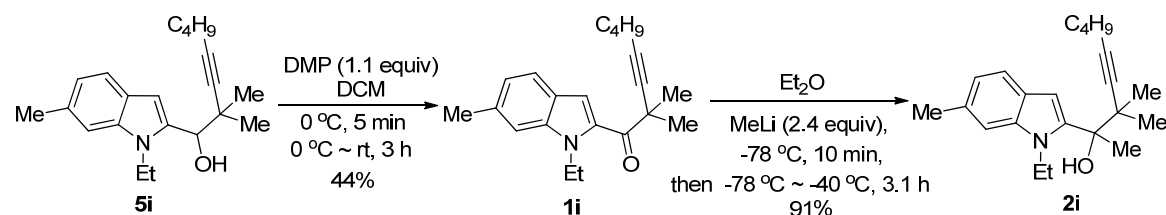


The reaction of **5h** (2.8472 g, 6.5 mmol), DMP (3.5460 g, 8.4 mmol)/DCM (20 mL), and DCM (80 mL) afforded crude **1h** (2.0670 g) (eluent: petroleum ether/ethyl acetate = 50/1~30/1) as a liquid.

The reaction of **1h** (2.0343 g, 4.7 mmol, prepared above)/diethyl ether (50 mL) and MeLi (8.2 mL, 1.6 M in Et₂O, 13.1 mmol) afforded **2h** (2.0169 g, 70%, two steps) (eluent: petroleum ether/ethyl acetate = 50/1~30/1) as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.68 (s, 1H, ArH), 7.26-7.09 (m, 4H, ArH), 6.97 (d, *J* = 8.7 Hz, 1H, ArH), 6.94-6.85 (m, 2H, ArH), 6.42 (s, 1H, ArH), 6.32 (d, *J* = 16.5 Hz, 1H, one proton of NCH₂), 5.33 (d, *J* = 16.5 Hz, 1H, one proton of NCH₂), 2.34 (s, 1H, OH), 2.19 (t, *J* =

6.9 Hz, 2H, CH₂), 1.80 (s, 3H, CH₃), 1.55-1.33 (m, 4H, 2 × CH₂), 1.27 (s, 3H, CH₃), 1.21 (s, 3H, CH₃), 0.91 (t, *J* = 7.2 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 142.0, 139.4, 136.4, 128.8, 128.5, 126.7, 125.6, 124.2, 122.5, 112.9, 111.8, 102.5, 84.9, 83.7, 78.5, 50.1, 42.7, 31.1, 28.6, 25.8, 25.6, 22.0, 18.4, 13.6; IR (neat) ν (cm⁻¹) 3537, 3060, 3027, 2956, 2931, 2871, 2227, 1604, 1496, 1463, 1382, 1370, 1328, 1314, 1271, 1207, 1171, 1144, 1105, 1055, 1029; MS (70 ev, EI) *m/z* (%) 453 (M(⁸¹Br)⁺, 5.31), 451 (M(⁷⁹Br)⁺, 5.22), 91 (100); HRMS Calcd for C₂₆H₃₀NO⁷⁹Br (M⁺): 451.1511, Found: 451.1508.

(9) 2-(1-Ethyl-6-methyl-1*H*-indol-2-yl)-3,3-dimethylnon-4-yn-2-ol (2i) (zj-1-089, 1-108)

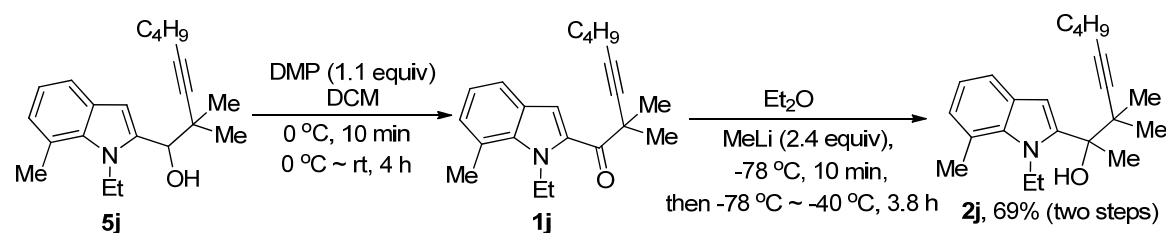


The reaction of **5i** (3.4728 g, 11.2 mmol), DMP (5.2395 g, 12.4 mmol)/DCM (25 mL), and DCM (75 mL) afforded **1i** (1.5249 g, 44%) (eluent: petroleum ether ~ petroleum ether/ethyl acetate = 100/1) as a liquid.

The reaction of **1i** (1.4329 g, 4.6 mmol, prepared above)/diethyl ether (30 mL) and MeLi (6.9 mL, 1.6 M in Et₂O, 11.0 mmol) afforded **2i** (1.3653 g, 91%) (eluent: petroleum ether/ethyl acetate = 50/1~30/1) as a solid; m.p. 78.1~79.3 °C (*n*-hexane/diethyl ether): ¹H NMR (300 MHz, CD₃COCD₃) δ 7.35 (d, *J* = 7.8 Hz, 1H, ArH), 7.16 (s, 1H, ArH), 6.83 (d, *J* = 7.2 Hz, 1H, ArH), 6.33 (s, 1H, ArH), 5.08-4.92 (m, 1H, one proton of NCH₂), 4.32-4.20 (m, 1H, one proton of NCH₂), 4.19 (s, 1H,

OH), 2.43 (s, 3H, CH₃), 2.18 (t, *J* = 6.6 Hz, 2H, CH₂), 1.82 (s, 3H, CH₃), 1.52-1.35 (m, 4H, 2 × CH₂), 1.32 (t, *J* = 7.1 Hz, 3H, CH₃), 1.26 (s, 3H, CH₃), 1.21 (s, 3H, CH₃), 0.90 (t, *J* = 7.2 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CD₃COCD₃) δ 142.0, 138.2, 130.8, 126.4, 121.5, 120.6, 110.4, 102.7, 87.3, 82.6, 78.6, 42.7, 41.7, 31.9, 28.4, 26.5, 26.3, 22.6, 22.1, 19.0, 15.9, 13.9; IR (KBr) ν (cm⁻¹) 3542, 3024, 2961, 2932, 2872, 2227, 1617, 1521, 1489, 1467, 1371, 1339, 1311, 1269, 1225, 1180, 1139, 1105, 1058; MS (70 ev, EI) *m/z* (%) 326 (M⁺+1, 3.06), 325 (M⁺, 7.27), 202 (100), 160 (100); Elemental analysis calcd (%) for C₂₂H₃₁NO: C, 81.18; H, 9.60; N, 4.30; Found: C, 81.24; H, 9.53; N, 4.11.

(10) 2-(1-Ethyl-7-methyl-1*H*-indol-2-yl)-3,3-dimethylnon-4-yn-2-ol (2j) (zj-1-046, 1-049)

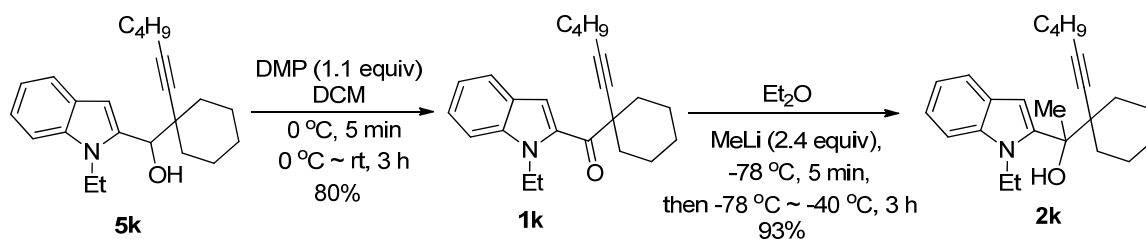


The reaction of **5j** (4.1782 g, 13.4 mmol), DMP (6.3333 g, 14.9 mmol)/DCM (20 mL), and DCM (80 mL) afforded crude **1j** (3.0237 g) (eluent: petroleum ether/ethyl acetate = 100/1~50/l) as a liquid.

The reaction of **1j** (2.9784 g, 9.6 mmol, prepared above)/diethyl ether (50 mL) and MeLi (14.5 mL, 1.6 M in Et₂O, 23.2 mmol) afforded **2j** (2.9697 g, 69%, two steps) (eluent: petroleum ether/ethyl acetate = 50/l) as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.40 (dd, *J*₁ = 7.5 and *J*₂ = 0.6 Hz, 1H, ArH), 6.95 (t, *J* = 7.4 Hz, 1H, ArH), 6.89 (dd,

$J_1 = 7.4$ and $J_2 = 0.6$ Hz, 1H, ArH), 6.38 (s, 1H, ArH), 5.28-4.90 (m, 1H, one proton of NCH₂), 4.63-4.43 (m, 1H, one proton of NCH₂), 2.75 (s, 3H, CH₃), 2.48 (s, 1H, OH), 2.22 (t, $J = 6.9$ Hz, 2H, CH₂), 1.83 (s, 3H, CH₃), 1.55-1.38 (m, 4H, 2 × CH₂), 1.29 (t, $J = 6.9$ Hz, 3H, CH₃), 1.23 (s, 3H, CH₃), 1.19 (s, 3H, CH₃), 0.93 (t, $J = 7.2$ Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 139.2, 136.1, 128.3, 125.0, 120.8, 119.4, 118.5, 104.6, 85.2, 83.6, 78.6, 43.0, 42.5, 31.1, 28.6, 26.0, 25.5, 22.0, 20.8, 18.4, 18.0, 13.6; IR (neat) ν (cm⁻¹) 3546, 3043, 2960, 2931, 2872, 2230, 1486, 1459, 1409, 1371, 1319, 1303, 1237, 1177, 1141, 1109, 1093, 1049; MS (70 ev, EI) m/z (%) 325 (M⁺, 3.52), 202 (100); HRMS Calcd for C₂₂H₃₁NO (M⁺): 325.2406, Found: 325.2408.

(11) 1-(1-Ethyl-1*H*-indol-2-yl)-3,3-pentamethylenon-4-yn-2-ol (2k) (zj-1-072, 1-173)

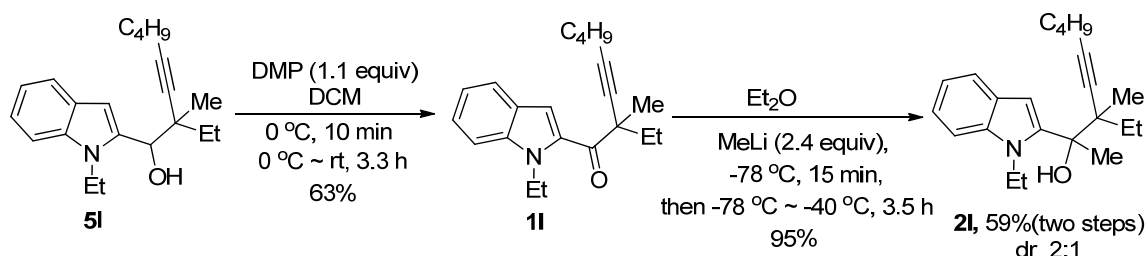


The reaction of **5k** (1.7757 g, 5.3 mmol), DMP (2.5471 g, 6.0 mmol)/DCM (15 mL), and DCM (60 mL) afforded **1k** (1.4110 g, 80%) (eluent: petroleum ether/ethyl acetate = 100/1~50/l) as a liquid.

The reaction of **1k** (1.2480 g, 3.7 mmol, prepared above)/diethyl ether (30 mL) and MeLi (3.0 mL, 3.0 M in Et₂O, 9.0 mmol) afforded **2k** (1.2188 g, 93%) (eluent: petroleum ether/ethyl acetate = 100/1~50/l) as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.55 (d, $J = 7.5$ Hz, 1H, ArH), 7.33 (d, $J = 7.8$ Hz, 1H, ArH), 7.23-7.13 (m, 1H, ArH),

7.12-7.02 (m, 1H, ArH), 6.29 (s, 1H, ArH), 5.02-4.82 (m, 1H, one proton of NCH₂), 4.33-4.10 (m, 1H, one proton of NCH₂), 2.61 (s, 1H, OH), 2.27 (t, *J* = 6.9 Hz, 2H, CH₂), 2.13-1.96 (m, 1H, one proton of CH₂), 1.78 (s, 3H, CH₃), 1.84-1.67 (m, 1H, one proton of CH₂), 1.66-1.31 (m, 13H, 5 × CH₂ + CH₃), 1.01-0.69 (m, 5H, CH₂ + CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 140.0, 136.9, 127.2, 120.9, 120.1, 119.1, 109.6, 102.6, 87.1, 82.5, 78.9, 49.4, 41.5, 32.4, 32.2, 31.3, 28.4, 25.3, 23.6, 23.2, 22.1, 18.5, 15.6, 13.6; IR (neat) ν (cm⁻¹) 3538, 3046, 3032, 2932, 2858, 2226, 1463, 1373, 1345, 1311, 1276, 1224, 1202, 1172, 1147, 1110, 1082, 1045, 1015; MS (70 ev, EI) *m/z* (%) 352 (M⁺+1, 6.75), 351 (M⁺, 3.00), 188 (100); HRMS Calcd for C₂₄H₃₃NO (M⁺): 351.2562, Found: 351.2563.

(12) 3-Ethyl-2-(1-ethyl-1*H*-indol-2-yl)-3-methylnon-4-yn-2-ol (2I) (zj-1-019, 1-021)

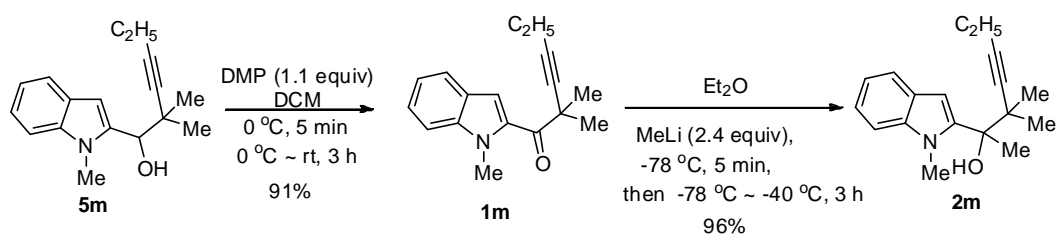


The reaction of **5I** (2.3447 g, 7.9 mmol), DMP (3.6815 g, 8.69 mmol)/DCM (25 mL), and DCM (75 mL) afforded crude **1I** (1.4618 g) (petroleum ether/ethyl acetate = 50/1~30/1) as a liquid.

The reaction of **1I** (1.3854 g, 4.5 mmol, prepared above)/diethyl ether (30 mL) and MeLi (6.8 mL, 1.6 M in Et₂O, 10.9 mmol) afforded **2I** (1.3803 g, 59%, two steps) (petroleum ether/ethyl acetate = 30/1) as a liquid (dr 2:1): ¹H NMR (300 MHz, CDCl₃)

δ 7.54 (d, $J = 7.5$ Hz, 1H, ArH), 7.32 (d, $J = 7.8$ Hz, 1H, ArH), 7.21-7.13 (m, 1H, ArH), 7.10-7.02 (m, 1H, ArH), [6.31 (s, 0.65H), 6.30 (s, 0.33H), ArH], 5.06-4.86 (m, 1H, one proton of NCH₂), 4.35-4.19 (m, 1H, one proton of NCH₂), 2.54 (s, 1H, OH), 2.23 (t, $J = 6.9$ Hz, 2H, CH₂), [2.04-1.91 (m, 0.35H), 1.73-1.59 (m, 0.72H), one proton of CH₂], [1.82 (s, 1.01H), 1.80 (s, 1.96H), CH₃], 1.57-1.32 (m, 8H, 2 \times CH₂ + CH₃ + one proton of CH₂), [1.18 (s, 1.00H), 1.10 (s, 1.99H), CH₃], 0.99-0.85 (m, 6H, 2 \times CH₃); IR (neat) ν (cm⁻¹) 3540, 2964, 2933, 2874, 2224, 1523, 1463, 1377, 1344, 1310, 1275, 1225, 1180, 1133, 1108, 1015; MS (70 eV, EI) m/z (%) 325 (M⁺, 6.69), 326 (M⁺+1, 3.60), 188 (100), 146(100); HRMS Calcd for C₂₂H₃₁NO (M⁺): 325.2406, Found: 325.2400.

(13) 3,3-Dimethyl-2-(1-methyl-1H-indol-2-yl)hept-4-yn-2-ol (2m) (zj-8-008, 8-009)

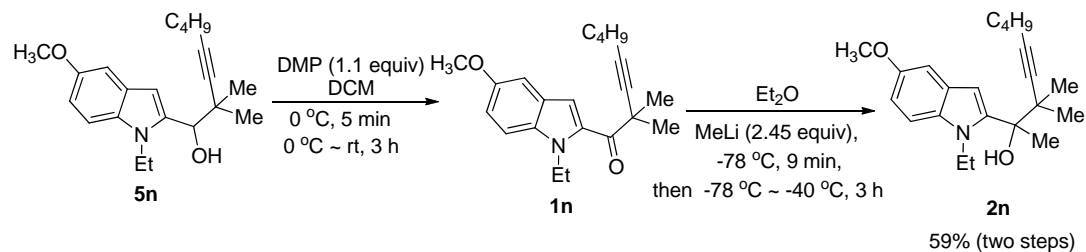


The reaction of **5m** (0.3561 g, 1.4 mmol), DMP (0.6875 g, 1.54 mmol)/DCM (5 mL), and DCM (35 mL) afforded **1m** (0.3211 g, 91%) [eluent: petroleum ether/ethyl acetate = 100/1 (500 mL) ~ 50/1 (400 mL)] as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 8.02 (s, 1H, ArH), 7.75-7.65 (m, 1H, ArH), 7.40-7.29 (m, 2H, ArH), 7.18-7.08 (m, 1H, ArH), 4.00 (s, 3H, NCH₃), 2.22 (q, $J = 7.4$ Hz, 2H, CH₂), 1.59 (s, 6H, CH₃ \times 2), 1.13 (t, $J = 7.5$ Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 194.3, 139.4, 131.9, 125.64, 125.55, 123.0, 120.5, 113.1, 110.2, 85.5, 84.4, 42.3, 32.5, 28.8, 13.7, 12.6; IR (neat) ν (cm⁻¹) 2975, 2936, 2876, 2236, 1660, 1614, 1511, 1462, 1385, 1374, 1360, 1321,

1243, 1218, 1152, 1121, 1101; MS (70 ev, EI) m/z (%) 254 ($M^+ + 1$, 2.58), 253 (M^+ , 12.81), 158 (100); HRMS Calcd for $C_{17}H_{19}NO$ (M^+): 253.1467, Found: 253.1469.

The reaction of **1m** (0.2862 g, 1.13 mmol, prepared above)/diethyl ether (25 mL) MeLi (1.7 mL, 1.6 M in Et_2O , 2.712 mmol) afforded **2m** (0.2914 g, 96%) [eluent: petroleum ether/ethyl acetate = 50/1 (500 mL) \sim 30/1 (500 mL) \sim 20/1 (400 mL)] as a oil: 1H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, $J = 7.8$ Hz, 1H, ArH), 7.30 (d, $J = 8.1$ Hz, 1H, ArH), 7.23-7.15 (m, 1H, ArH), 7.13-7.01 (m, 1H, ArH), 6.38 (s, 1H, ArH), 4.05 (s, 3H, NCH_3), 2.55 (s, 1H, OH), 2.22 (q, $J = 7.5$ Hz, 2H, CH_2), 1.80 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 1.19 (s, 3H, CH_3), 1.16 (t, $J = 7.7$ Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.0, 138.3, 126.8, 121.1, 120.0, 119.3, 109.3, 102.7, 85.0, 84.3, 78.4, 42.9, 33.4, 28.4, 25.9, 25.6, 14.2, 12.4; IR (neat) ν (cm^{-1}) 3538, 2976, 2937, 2874, 2233, 1522, 1468, 1371, 1356, 1315, 1236, 1176, 1143, 1069, 1048, 1012; MS (70 ev, EI) m/z (%) 270 ($M^+ + 1$, 1.89), 269 (M^+ , 8.50), 174 (100); HRMS Calcd for $C_{18}H_{23}NO$ (M^+): 269.1780, Found: 269.1776.

(14) 2-(1-Ethyl-5-methoxy-1H-indol-2-yl)-3,3-dimethylnon-4-yn-2-ol (2n)
(zj-1-084, 1-107)

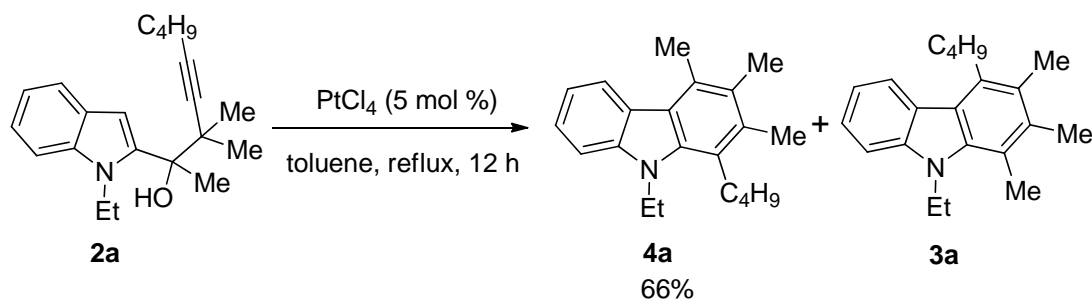


The reaction of **5n** (1.5959 g, 4.9 mmol), DMP (2.3105 g, 5.39 mmol)/DCM (20 mL), and DCM (55 mL) afforded **1n** (1.2898 g) (eluent: petroleum ether/ethyl acetate = 50/1) as a liquid.

The reaction of **1n** (1.2523 g, 3.85 mmol, prepared above)/diethyl ether (30 mL) and MeLi (5.9 mL, 1.6 M in Et₂O, 9.44 mmol) afforded **2n** (0.9582 g, 59%, two steps) (eluent: petroleum ether/ethyl acetate = 50/1~30/1) as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.20 (d, *J* = 8.7 Hz, 1H, ArH), 7.01 (d, *J* = 2.4 Hz, 1H, ArH), 6.83 (dd, *J*₁ = 9.0 Hz, *J*₂ = 2.4 Hz, 1H, ArH), 6.26 (s, 1H, ArH), 4.97-4.83 (m, 1H, one proton of NCH₂), 4.28-4.14 (m, 1H, one proton of NCH₂), 3.83 (s, 3H, OCH₃), 2.49 (s, 1H, OH), 2.21 (t, *J* = 7.1 Hz, 2H, CH₂), 1.79 (s, 3H, CH₃), 1.58-1.39 (m, 4H, 2 × CH₂), 1.36 (t, *J* = 7.1 Hz, 3H, CH₃), 1.24 (s, 3H, CH₃), 1.17 (s, 3H, CH₃), 0.93 (t, *J* = 7.1 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 153.9, 140.1, 132.3, 127.4, 111.2, 110.3, 102.1, 101.9, 85.1, 83.6, 78.4, 55.9, 42.9, 41.4, 31.1, 28.6, 25.9, 25.5, 22.0, 18.4, 15.7, 13.6; IR (neat) ν (cm⁻¹) 3539, 2955, 2933, 2872, 2831, 2226, 1620, 1581, 1522, 1476, 1455, 1400, 1371, 1319, 1299, 1271, 1228, 1210, 1181, 1151, 1110; MS (70 ev, EI) *m/z* (%) 342 (M⁺+1, 6.95), 341 (M⁺, 17.00), 218 (100), 176 (100); HRMS Calcd for C₂₂H₃₁NO₂ (M⁺): 341.2355, Found: 341.2356.

2. Synthesis of 4a~4n and 3o.

(1) 1-Butyl-9-ethyl-2,3,4-trimethyl-9H-carbazole (4a) (zj-1-113)

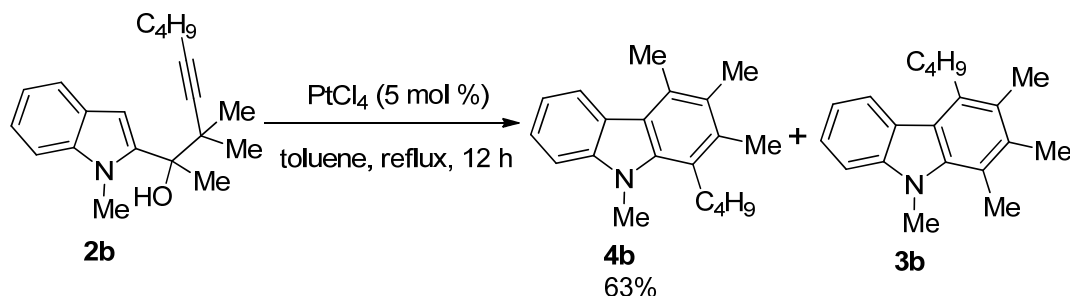


Typical Procedure II: To a dry Schlenk tube were added sequentially PtCl_4 (17.0 mg, 0.05 mmol, weighed in glove box), **2a** (311.7 mg, 1.0 mmol), and toluene (50 mL) under N_2 . After continuous stirring for 12 h under reflux, the reaction was complete as monitored by TLC. Filtration through a short column of silica gel (eluent: Et_2O (20 mL \times 3)) and evaporation afforded a crude mixture of **4a** and **3a** (98 : 2, as determined by ^1H NMR analysis). Column chromatography on silica gel (eluent: petroleum ether/dichloromethane = 50:1) afforded **4a** (193.6 mg, 66%) as a liquid; ^1H NMR (300 MHz, CDCl_3) δ 8.20 (d, $J = 7.8$ Hz, 1H, ArH), 7.37-7.30 (m, 1H, ArH), 7.28 (d, $J = 7.5$ Hz, 1H, ArH), 7.18-7.10 (m, 1H, ArH), 4.37 (q, $J = 7.1$ Hz, 2H, NCH_2), 3.06-2.95 (m, 2H, ArCH_2), 2.77 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 1.70-1.42 (m, 4H, $2 \times \text{CH}_2$), 1.33 (t, $J = 7.1$ Hz, 3H, CH_3), 0.98 (t, $J = 7.2$ Hz, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 141.4, 137.0, 133.3, 128.9, 126.2, 124.3, 124.1, 122.6, 121.1, 120.9, 118.5, 108.3, 39.5, 33.5, 28.5, 22.9, 17.2, 16.5, 16.1, 15.1, 13.9; IR (neat) ν (cm^{-1}) 3047, 2957, 2927, 2871, 2727, 1608, 1581, 1483, 1455, 1397, 1377, 1333, 1303, 1261, 1247, 1198, 1176, 1152, 1138, 1104, 1077, 1033, 1008; MS (70 ev, EI) m/z (%) 294 ($\text{M}^+ + 1$, 13.59), 293 (M^+ , 55.90), 250 (100); HRMS Calcd for $\text{C}_{21}\text{H}_{27}\text{N}$

(M⁺): 293.2144, Found: 293.2144.

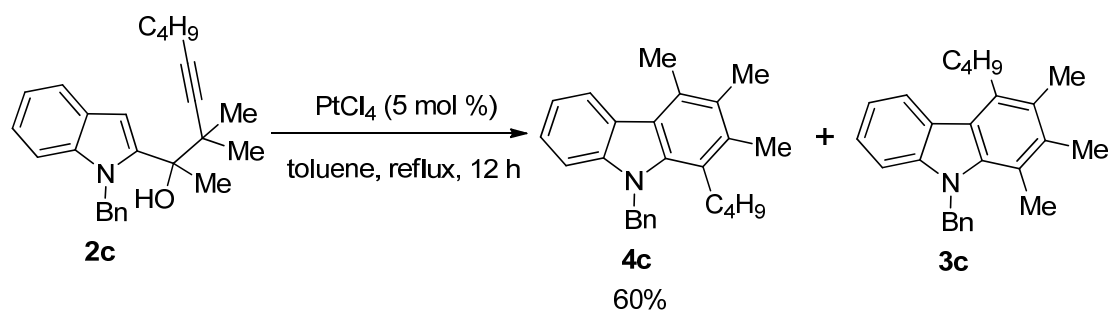
The compounds **4b~4l** and **3m** were prepared according to **Typical Procedure II**.

(2) 1-Butyl-2,3,4,9-tetramethyl-9H-carbazole (4b) (zj-1-141-2)



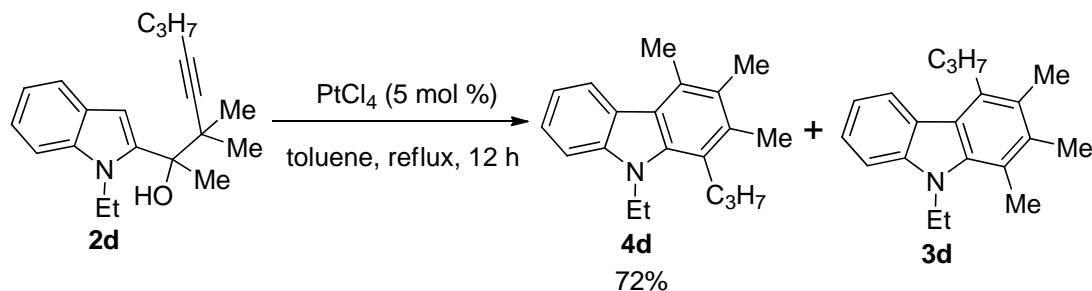
The reaction of PtCl₄ (17.1 mg, 0.05 mmol) and **2b** (295.4 mg, 1.0 mmol) in toluene (50 mL) under reflux for 12 h afforded **4b** (175.4 mg, 63%) (eluent: petroleum ether) (**4b** : **3b** = 96 : 4 as determined by ¹H NMR analysis of the crude product) as a solid: m. p. 119.6~120.7 °C (*n*-hexane/dichloromethane); ¹H NMR (300 MHz, CDCl₃) δ 8.20 (d, *J* = 7.8 Hz, 1H, ArH), 7.43-7.33 (m, 1H, ArH), 7.29 (d, *J* = 8.4 Hz, 1H, ArH), 7.19-7.10 (m, 1H, ArH), 3.93 (s, 3H, NCH₃), 3.13-2.96 (m, 2H, CH₂), 2.79 (s, 3H, CH₃), 2.36 (s, 3H, CH₃), 2.34 (s, 3H, CH₃), 1.71-1.41 (m, 4H, 2 × CH₂), 0.99 (t, *J* = 7.2 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 142.5, 138.4, 133.4, 128.8, 126.4, 124.3, 123.8, 122.5, 121.3, 120.9, 118.4, 108.3, 34.0, 32.9, 28.5, 23.0, 17.2, 16.4, 16.1, 13.9; IR (KBr) ν (cm⁻¹) 2958, 2913, 2871, 2854, 1577, 1482, 1459, 1431, 1390, 1339, 1304, 1290, 1240, 1202, 1184, 1175, 1150, 1099, 1057, 1029; MS (70 ev, EI) *m/z* (%) 280 (M⁺+1, 12.85), 279 (M⁺, 52.36), 236 (100); Elemental analysis calcd (%) for C₂₀H₂₅N: C, 85.97; H, 9.02; N, 5.01; Found: C, 85.95; H, 9.18; N, 4.77.

(3) 9-Benzyl-1-butyl-2,3,4-trimethyl-9H-carbazole (4c) (qya-12-176)



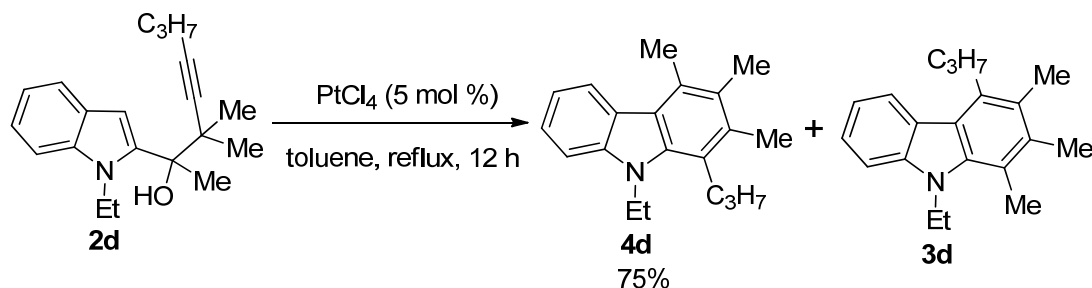
The reaction of PtCl_4 (8.6 mg, 0.025 mmol) and **2c** (186.8 mg, 0.5 mmol) in toluene (25 mL) under reflux for 12 h afforded **4c** (106.4 mg, 60%) (eluent: petroleum ether/ dichloromethane = 100/1~50/1) (**4c** : **3c** = 96 : 4 as determined by ^1H NMR analysis of the crude product) as a solid: m. p. 102.4~103.4 °C (*n*-hexane/ethyl acetate); ^1H NMR (300 MHz, CDCl_3) δ 8.28 (d, $J = 7.8$ Hz, 1H, ArH), 7.37-7.28 (m, 1H, ArH), 7.27-7.13 (m, 5H, ArH), 7.07-6.97 (m, 2H, ArH), 5.65 (s, 2H, NCH_2), 2.93-2.73 (m, 2H, CH_2), 2.87 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 1.67-1.51 (m, 2H, CH_2), 1.43-1.28 (m, 2H, CH_2), 0.90 (t, $J = 7.2$ Hz, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 142.2, 138.7, 137.8, 133.7, 129.0, 128.8, 127.0, 126.8, 125.4, 124.6, 124.0, 122.6, 121.3, 121.0, 119.0, 108.6, 48.9, 34.2, 28.3, 22.9, 17.4, 16.5, 16.2, 14.0; IR (KBr) ν (cm^{-1}) 3027, 2955, 2926, 2870, 1605, 1582, 1495, 1461, 1396, 1376, 1355, 1330, 1295, 1235, 1171, 1160, 1117, 1068; MS (70 eV, EI) m/z (%) 356 ($\text{M}^+ + 1$, 6.85), 355 (M^+ , 24.38), 91 (100); Elemental analysis calcd (%) for $\text{C}_{26}\text{H}_{29}\text{N}$: C, 87.84; H, 8.22; N, 3.94; Found: C, 87.77; H, 8.31; N, 3.70.

(4) 9-Ethyl-2,3,4-trimethyl-1-propyl-9H-carbazole (4d) (zj-1-190)



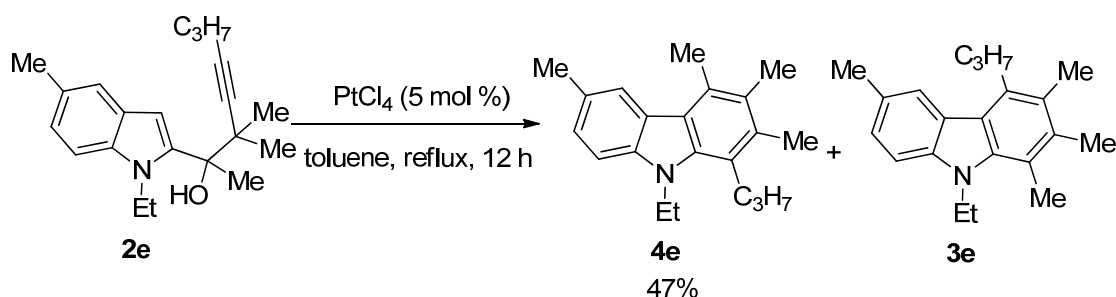
The reaction of PtCl_4 (17.1 mg, 0.05 mmol) and **2d** (296.1 mg, 1.0 mmol) in toluene (50 mL) under reflux for 12 h afforded **4d** (201.5 mg, 72%) (eluent: petroleum ether/ dichloromethane = 100/1~50/1) (**4d** : **3d** = 93 : 7 as determined by ^1H NMR analysis of the crude product) as a liquid; ^1H NMR (300 MHz, CDCl_3) δ 8.21 (d, $J = 7.8$ Hz, 1H, ArH), 7.39-7.31 (m, 1H, ArH), 7.29 (d, $J = 7.8$ Hz, 1H, ArH), 7.21-7.12 (m, 1H, ArH), 4.36 (q, $J = 7.1$ Hz, 2H, NCH_2), 3.03-2.90 (m, 2H, ArCH_2), 2.78 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 1.73-1.55 (m, 2H, CH_2), 1.34 (t, $J = 7.1$ Hz, 3H, CH_3), 1.06 (t, $J = 7.2$ Hz, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 141.3, 137.0, 133.3, 128.9, 126.2, 124.3, 124.1, 122.6, 121.0, 120.9, 118.5, 108.3, 39.5, 30.9, 24.5, 17.3, 16.5, 16.1, 15.1, 14.2; IR (neat) ν (cm^{-1}) 3046, 2958, 2928, 2869, 2728, 1607, 1579, 1455, 1397, 1377, 1332, 1302, 1259, 1240, 1222, 1177, 1152, 1138, 1104, 1077, 1033, 1008; MS (70 ev, EI) m/z (%) 280 ($\text{M}^+ + 1$, 19.63), 279 (M^+ , 77.18), 250 (100); HRMS Calcd for $\text{C}_{20}\text{H}_{25}\text{N}$ (M^+): 279.1987, Found: 279.1990.

3.5 mmol scale (zj-2-185)



The reaction of PtCl₄ (59.1 mg, 0.15 mmol) and **2d** (1054.7 mg, 3.5 mmol) in toluene (175 mL) under reflux for 12 h afforded **4d** (746.2 mg, 75%) (eluent: petroleum ether/ dichloromethane = 100/1) (**4d** : **3d** = 93 : 7 as determined by ¹H NMR analysis of the crude product) as a liquid; ¹H NMR (300 MHz, CDCl₃) δ 8.17 (d, *J* = 8.1 Hz, 1H, ArH), 7.35-7.26 (m, 1H, ArH), 7.18 (d, *J* = 8.1 Hz, 1H, ArH), 7.16-7.07 (m, 1H, ArH), 4.23 (q, *J* = 7.1 Hz, 2H, NCH₂), 2.99-2.84 (m, 2H, ArCH₂), 2.72 (s, 3H, CH₃), 2.31 (s, 3H, CH₃), 2.27 (s, 3H, CH₃), 1.70-1.50 (m, 2H, CH₂), 1.24 (t, *J* = 7.1 Hz, 3H, CH₃), 1.01 (t, *J* = 7.4 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 141.3, 137.0, 133.2, 128.8, 126.1, 124.3, 124.1, 122.6, 121.0, 120.8, 118.5, 108.2, 39.4, 30.8, 24.5, 17.2, 16.4, 16.0, 15.0, 14.1.

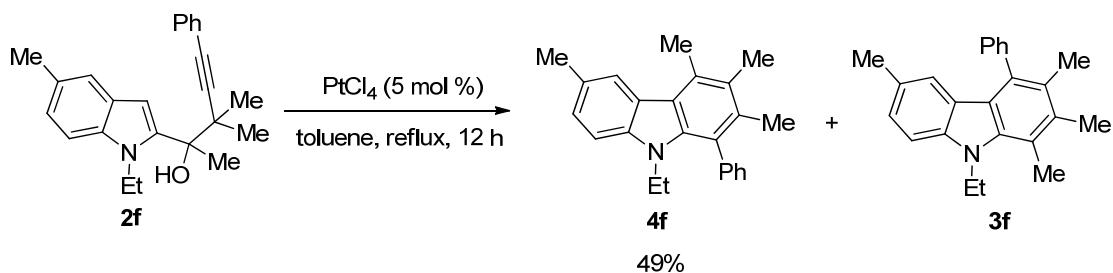
(5) 9-Ethyl-2,3,4,6-tetramethyl-1-propyl-9H-carbazole (4e) (zj-1-037)



The reaction of PtCl₄ (16.8 mg, 0.05 mmol) and **2e** (311.4 mg, 1.0 mmol) in toluene (50 mL) under reflux for 12 h afforded **4e** (137.7 mg, 47%) (eluent: petroleum ether/ dichloromethane = 50/1 for the first round afforded 135.3 mg of pure **4e** and the impure part, which was further purified by chromatography on silica gel (eluent: petroleum ether/ dichloromethane = 50/1) to afford **4e** (2.4 mg, combined weight 137.7 mg) (**4e** : **3e** = 96 : 4 as determined by ¹H NMR analysis of the crude product) as a solid: m. p. 94.9~95.9 °C (*n*-hexane/ dichloromethane); ¹H

NMR (300 MHz, CDCl₃) δ 8.02 (s, 1H, ArH), 7.27-7.12 (m, 2H, ArH), 4.37 (q, J = 7.0 Hz, 2H, NCH₂), 3.06-2.91 (m, 2H, CH₂), 2.79 (s, 3H, CH₃), 2.51 (s, 3H, CH₃), 2.38 (s, 3H, CH₃), 2.35 (s, 3H, CH₃), 1.75-1.52 (m, 2H, CH₂), 1.34 (t, J = 7.1 Hz, 3H, CH₃), 1.07 (t, J = 7.4 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 139.7, 137.3, 133.2, 129.0, 127.5, 126.0, 125.6, 124.3, 122.8, 120.91, 120.88, 108.0, 39.6, 30.9, 24.5, 21.6, 17.4, 16.5, 16.1, 15.1, 14.2; IR (KBr) ν (cm⁻¹) 2959, 2927, 2869, 1583, 1488, 1470, 1447, 1376, 1335, 1308, 1261, 1240, 1178, 1149, 1102, 1077; MS (70 ev, EI) m/z (%) 293 (M⁺, 67.29), 264 (100); Elemental analysis calcd (%) for C₂₁H₂₇N: C, 85.95; H, 9.27; N, 4.77; Found: C, 86.06; H, 9.23; N, 4.60.

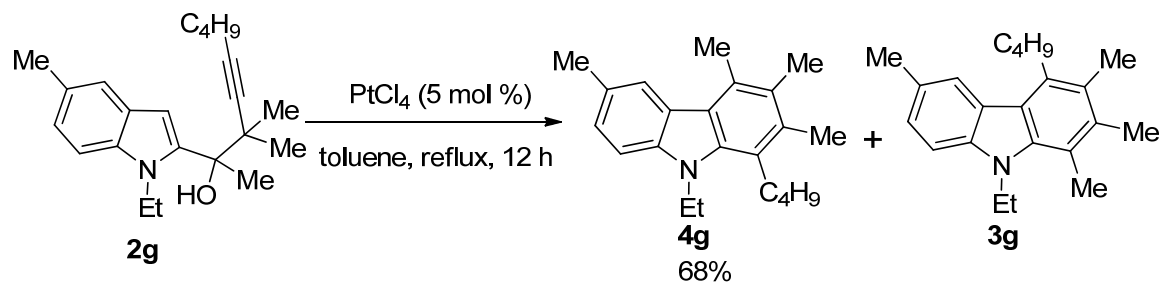
(6) 9-Ethyl-2,3,4,6-tetramethyl-1-phenyl-9H-carbazole (4f) (zj-1-158)



The reaction of PtCl₄ (17.0 mg, 0.05 mmol) and **2f** (345.9 mg, 1.0 mmol) in toluene (50 mL) under reflux for 12 h afforded **4f** (167.0 mg, 49%, purity: 97%) (eluent: petroleum ether) (**4f** : **3f** = 97 : 3 as determined by ¹H NMR analysis of the crude product) as a solid: m. p. 112.7~113.5 °C (*n*-hexane/ ether); ¹H NMR (300 MHz, CDCl₃) δ 8.07 (s, 1H, ArH), 7.48-7.26 (m, 5H, ArH), 7.23-7.07 (m, 2H, ArH), 3.52 (q, J = 7.0 Hz, 2H, NCH₂), 2.87 (s, 3H, CH₃), 2.52 (s, 3H, CH₃), 2.38 (s, 3H, CH₃), 2.07 (s, 3H, CH₃), 0.83 (t, J = 6.9 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 140.5, 139.3, 136.4, 133.0, 130.5, 130.4, 128.2, 127.6, 127.2, 125.6, 125.3, 123.9, 122.8, 122.7, 120.5, 108.3, 38.2, 21.7, 18.2, 17.4, 15.8, 13.8; IR (KBr) ν (cm⁻¹) 2923,

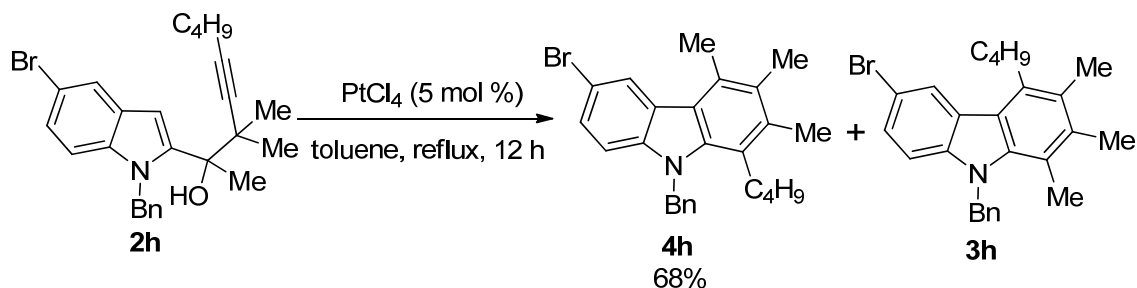
1601, 1580, 1481, 1494, 1484, 1470, 1442, 1374, 1351, 13363, 1311, 1298, 1270, 1250, 1180, 1147, 1123, 1094, 1075, 1003; MS (70 ev, EI) m/z (%) 328 (M^{+1} , 31.11), 327 (100); Elemental analysis calcd (%) for $C_{24}H_{25}N$: C, 88.03; H, 7.70; N, 4.28; Found: C, 87.75; H, 7.83; N, 4.01.

(7) 1-Butyl-9-ethyl-2,3,4,6-tetramethyl-9H-carbazole (4g) (zj-1-033)



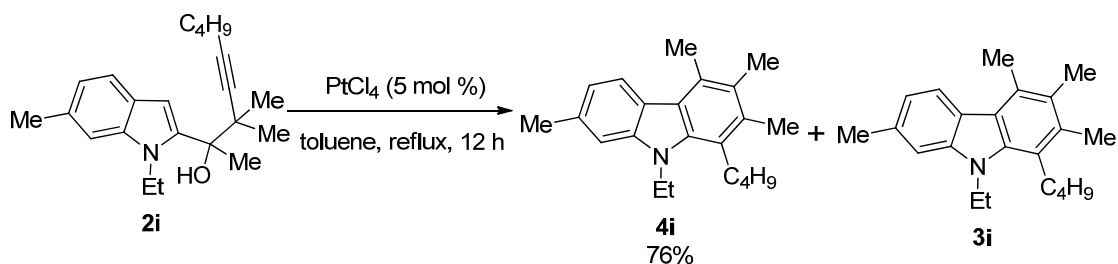
The reaction of $PtCl_4$ (16.5 mg, 0.05 mmol) and **2g** (325.5 mg, 1.0 mmol) in toluene (50 mL) under reflux for 12 h afforded **4g** (209.1 mg, 68%) (eluent: petroleum ether/ dichloromethane = 40/1) (**4g** : **3g** = 95 : 5 as determined by 1H NMR analysis of the crude product) as a liquid; 1H NMR (300 MHz, $CDCl_3$) δ 8.02 (s, 1H, ArH), 7.27 (d, $J = 8.4$ Hz, 1H, ArH), 7.22 (d, $J = 8.4$ Hz, 1H, ArH), 4.44 (q, $J = 7.1$ Hz, 2H, NCH_2), 3.09-2.98 (m, 2H, CH_2), 2.82 (s, 3H, CH_3), 2.53 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 1.73-1.46 (m, 4H, $2 \times CH_2$), 1.38 (t, $J = 7.1$ Hz, 3H, CH_3), 1.01 (t, $J = 7.4$ Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.8, 137.4, 133.2, 129.0, 127.5, 126.1, 125.6, 124.3, 122.9, 120.99, 120.96, 108.1, 39.7, 33.5, 28.6, 23.0, 21.6, 17.4, 16.5, 16.1, 15.1, 13.9; IR (neat) ν (cm^{-1}) 2959, 2925, 2871, 1583, 1489, 1464, 1376, 1335, 1309, 1262, 1176, 1150, 1104, 1077; MS (70 ev, EI) m/z (%) 308 (M^{+1} , 16.46), 307 (M^+ , 66.58), 264 (100); HRMS Calcd for $C_{22}H_{29}N$ (M^+): 307.2300, Found: 307.2296.

(8) 6-Bromo-1-butyl-9-benzyl-2,3,4-trimethyl-9H-carbazole (4h) (zj-1-062)



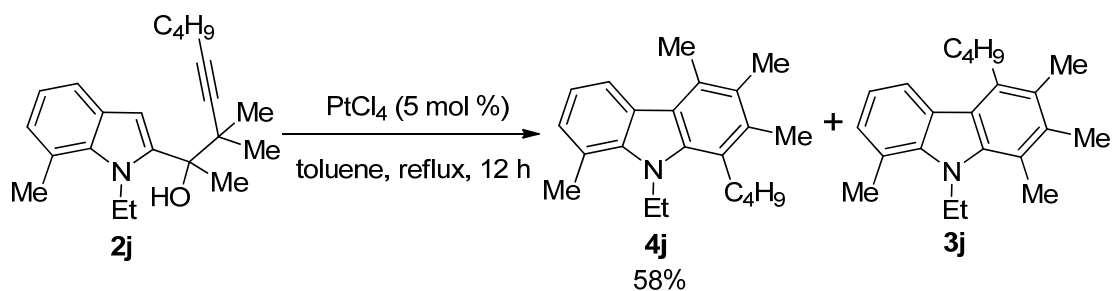
The reaction of PtCl_4 (16.4 mg, 0.05 mmol) and **2h** (457.0 mg, 1.0 mmol) in toluene (50 mL) under reflux for 12 h afforded **4h** (297.8 mg, 68%) (eluent: petroleum ether, then petroleum ether / dichloromethane = 100/1) (**4h** : **3h** = 92 : 8 as determined by ^1H NMR analysis of the crude product) as a solid: m. p. 122.4~123.9 °C (*n*-hexane/ dichloromethane); ^1H NMR (300 MHz, CDCl_3) δ 8.31 (d, $J = 2.1$ Hz, 1H, ArH), 7.29 (dd, $J_1 = 8.7$ and $J_2 = 1.8$ Hz, 1H, ArH), 7.22-7.07 (m, 3H, ArH), 6.97-6.87 (m, 3H, ArH), 5.47 (s, 2H, NCH_2), 2.82-2.65 (m, 2H, CH_2), 2.70 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 1.62-1.43 (m, 2H, CH_2), 1.40-1.19 (m, 2H, CH_2), 0.87 (t, $J = 7.4$ Hz, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 140.7, 138.1, 138.0, 134.6, 129.0, 128.8, 127.2, 127.1, 125.5, 125.2, 124.9, 121.3, 120.0, 111.8, 109.9, 48.8, 34.0, 28.2, 22.8, 17.2, 16.5, 16.1, 13.9; IR (KBr) ν (cm^{-1}) 3063, 3024, 2956, 2926, 2871, 2725, 1604, 1582, 1495, 1485, 1454, 1391, 1355, 1296, 1236, 1194, 1156, 1127, 1103, 1074, 1029, 1002; MS (70 ev, EI) m/z (%) 435 ($\text{M}(\text{Br}^{81})^+$, 99.54), 433 ($\text{M}(\text{Br}^{79})^+$, 100); Elemental analysis calcd (%) for $\text{C}_{26}\text{H}_{28}\text{BrN}$: C, 71.89; H, 6.50; N, 3.22; Found: C, 71.55; H, 6.49; N, 3.13.

(9) 1-Butyl-9-ethyl-2,3,4,7-tetramethyl-9H-carbazole (4i) (zj-1-126)



The reaction of PtCl_4 (16.7 mg, 0.05 mmol) and **2i** (324.9 mg, 1.0 mmol) in toluene (50 mL) under reflux for 12 h afforded **4i** (231.9 mg, 76%) (eluent: petroleum ether/ dichloromethane = 50/1) (**4i** : **3i** = 95 : 5 as determined by ^1H NMR analysis of the crude product) as a oil; ^1H NMR (300 MHz, CDCl_3) δ 8.07 (d, $J = 7.8$ Hz, 1H, ArH), 7.14 (s, 1H, ArH), 6.98 (dd, $J_1 = 8.1$ and $J_2 = 0.9$ Hz, 1H, ArH), 4.40 (q, $J = 7.1$ Hz, 2H, NCH_2), 3.07-2.94 (m, 2H, CH_2), 2.77 (s, 3H, CH_3), 2.52 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 1.72-1.43 (m, 4H, $2 \times \text{CH}_2$), 1.38 (t, $J = 7.1$ Hz, 3H, CH_3), 1.00 (t, $J = 7.2$ Hz, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 141.9, 137.1, 134.2, 132.7, 128.6, 126.1, 122.4, 121.9, 121.2, 120.9, 120.0, 108.6, 39.5, 33.5, 28.5, 23.0, 22.1, 17.2, 16.4, 16.1, 15.2, 13.9; IR (neat) ν (cm^{-1}) 2956, 2924, 2871, 1617, 1583, 1489, 1455, 1397, 1377, 1332, 1302, 1287, 1264, 1247, 1193, 1170, 1103, 1077, 1013; MS (70 eV, EI) m/z (%) 308 ($\text{M}^+ + 1$, 16.31), 307 (M^+ , 60.42), 264 (100); HRMS Calcd for $\text{C}_{22}\text{H}_{29}\text{N}$ (M^+): 307.2300, Found: 307.2307.

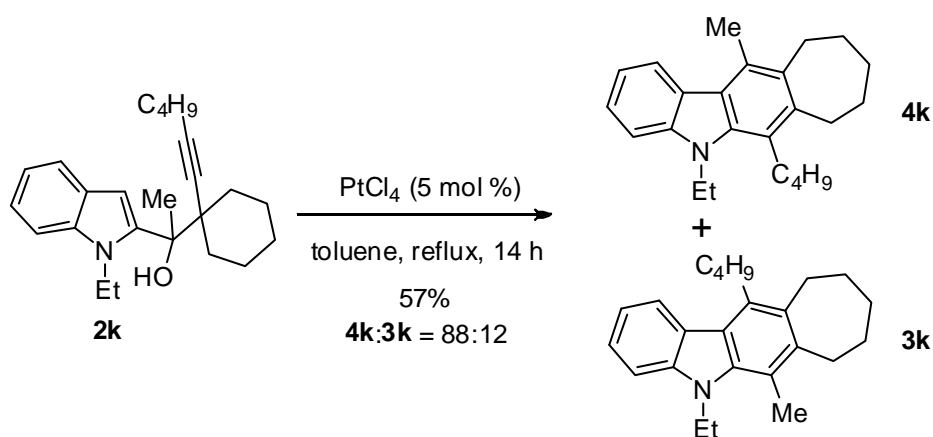
(10) 1-Butyl-9-ethyl-2,3,4,8-tetramethyl-9H-carbazole (4j) (zj-1-078)



The reaction of PtCl_4 (17.1 mg, 0.05 mmol) and **2j** (327.7 mg, 1.0 mmol) in

toluene (50 mL) under reflux for 12 h afforded **4j** (178.3 mg, 58%) (eluent: petroleum ether ~ petroleum ether/ dichloromethane = 100/1) (**4j** : **3j** = 94: 6 as determined by ¹H NMR analysis of the crude product) as a oil; ¹H NMR (300 MHz, CDCl₃) δ 8.11-7.98 (m, 1H, ArH), 7.12-7.02 (m, 2H, ArH), 4.52 (q, *J* = 7.1 Hz, 2H, NCH₂), 3.07-2.92 (m, 2H, CH₂), 2.74 (s, 3H, CH₃), 2.68 (s, 3H, CH₃), 2.36 (s, 3H, CH₃), 2.32 (s, 3H, CH₃), 1.74-1.60 (m, 2H, CH₂), 1.58-1.42 (m, 2H, CH₂), 1.00 (t, *J* = 7.4 Hz, 3H, CH₃), 0.88 (t, *J* = 7.1 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 142.4, 140.2, 133.5, 128.5, 128.1, 127.6, 127.4, 123.3, 122.6, 121.2, 120.6, 119.7, 41.5, 32.2, 29.3, 23.2, 21.1, 17.3, 16.7, 16.2, 14.02, 13.96; IR (neat) ν (cm⁻¹) 3093, 3042, 2957, 2870, 2731, 1575, 1455, 1407, 1377, 1327, 1297, 1254, 1236, 1206, 1162, 1117, 1091, 1077, 1050; MS (70 ev, EI) *m/z* (%) 308 (M⁺+1, 21.86), 307 (M⁺, 88.14), 264 (100); HRMS Calcd for C₂₂H₂₉N (M⁺): 307.2300, Found: 307.2304.

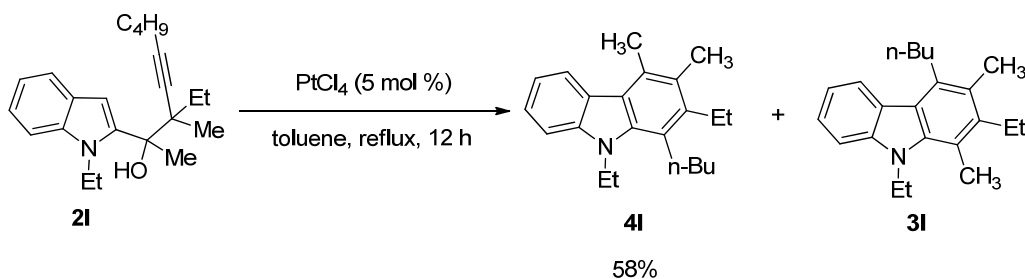
(11) 1-Butyl-9-ethyl-4-methyl-2,3-pentamethylene-9H-carbazole (4k) (zj-2-007)



The reaction of PtCl₄ (17.0 mg, 0.05 mmol) and **2k** (352.7 mg, 1.0 mmol) in toluene (50 mL) under reflux for 12 h afforded **4k** and **3k** (190.2 mg, 57%, **4k** : **3k** = 88:12 as determined by ¹H NMR analysis of the crude product) (eluent: petroleum ether/ dichloromethane = 50/1~30/1 for the first round, petroleum ether/

dichloromethane = 50/1~30/1 for the second round (impure part)) as a liquid; ^1H NMR (300 MHz, CDCl_3) δ 8.32-8.15 (m, 1H, ArH), 7.45-7.26 (m, 2H, ArH), 7.23-7.07 (m, 1H, ArH), 4.53-4.29 (m, 2H, NCH_2), 3.11-2.88 (m, 6H, $3 \times \text{CH}_2$), 2.82 (s, 3H, CH_3), 1.88-1.45 (m, 10H, $5 \times \text{CH}_2$), 1.41 (t, $J = 7.1$ Hz, 3H, CH_3), 1.01 (t, $J = 7.1$ Hz, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 141.4, 1406, 137.2, 133.2, 127.8, 124.2, 122.7, 120.9, 119.8, 118.5, 108.3, 39.8, 34.5, 31.0, 29.0, 28.7, 28.3, 28.1, 27.6, 23.0, 17.1, 15.3, 14.0; the following signals are discernible for **3k**: 3.56-3.44 (m, 2H, CH_2), 2.42 (s, 3H, CH_3), 1.31 (t, $J = 7.1$ Hz, 3H, CH_3); IR (neat) ν (cm^{-1}) 3045, 2957, 2929, 2852, 1607, 1577, 1483, 1452, 1397, 1377, 1350, 1333, 1350, 1293, 1261, 1201, 1173, 1137, 1104, 1075, 1033, 1007; GC-MS (GC condition: injector: 280°C ; column: DB5 column $30 \text{ m} \times 0.25 \text{ mm}$, temperature programming: 60°C (2 min), $20^\circ\text{C}/\text{min}$ to 280°C , 280°C (30 min); detector: 280°C) (70 ev, EI) m/z (%) for **3k**: T_R 4.9 min: 334 ($M^+ + 1$, 20.68), 333 (M^+ , 79.60), 290 (100); for **4k**: T_R 5.0 min: 334 ($M^+ + 1$, 26.13), 333 (M^+ , 95.56), 290 (100); HRMS Calcd for $\text{C}_{24}\text{H}_{31}\text{N}$ (M^+): 333.2457, Found: 333.2454.

(12) 1-Butyl-2,9-diethyl-3,4-dimethyl-9H-carbazole (4l) (zj-5-176-2)

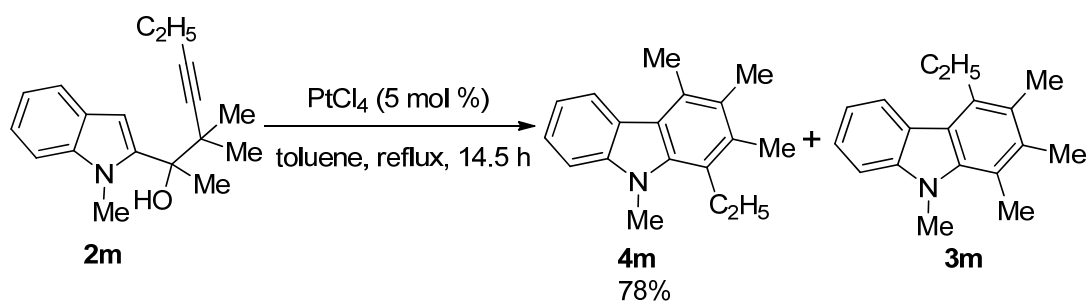


The reaction of PtCl_4 (16.9 mg, 0.05 mmol) and **2l** (324.8 mg, 1.0 mmol) in toluene (50 mL) under reflux for 12 h afforded a mixture of **4l** and **3l** (**4l** : **3l** = 98 : 2 as determined by ^1H NMR analysis of the crude product) with an impurity. Purification by column chromatography afforded **4l** (195.1 mg, 58%, purity: 92%)

[eluent: petroleum ether (500 mL) ~ petroleum ether/dichloromethane = 100/1 (500 mL × 4) ~ 30/1 (310 mL)].

After repeated recrystallization from the *n*-hexane/ dichloromethane, pure **4l** was afforded as a solid: m. p. 98.1~99.2 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.23 (d, *J* = 7.8 Hz, 1H, ArH), 7.45-7.34 (m, 2H, ArH), 7.23-7.11 (m, 1H, ArH), 4.48 (q, *J* = 7.2 Hz, 2H, NCH₂), 3.12-2.95 (m, 2H, CH₂), 2.88 (q, *J* = 7.5 Hz, 2H, CH₂), 2.82 (s, 3H, CH₃), 2.43 (s, 3H, CH₃), 1.75-1.47 (m, 4H, 2 × CH₂), 1.38 (t, *J* = 7.1 Hz, 3H, CH₃), 1.23 (t, *J* = 7.5 Hz, 3H, CH₃), 1.02 (t, *J* = 7.2 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 141.4, 139.2, 137.1, 129.7, 125.6, 124.4, 124.2, 122.7, 121.3, 120.6, 118.5, 108.3, 39.4, 34.5, 28.0, 23.1, 17.3, 15.5, 15.1, 15.0, 13.9; IR (neat) ν (cm⁻¹) 3048, 2959, 2927, 2870, 1608, 1580, 1447, 1397, 1377, 1352, 1332, 1307, 1263, 1248, 1231, 1194, 1175, 1152, 1136, 1104, 1073, 1052, 1034, 1016; MS (70 ev, EI) *m/z* (%) 308 (M⁺+1, 19.79), 307 (M⁺, 75.30), 264 (100); Elemental analysis calcd (%) for C₂₂H₂₉N: C, 85.94; H, 9.51; N, 4.56; Found: C, 85.99 ; H, 9.35 ; N, 4.33.

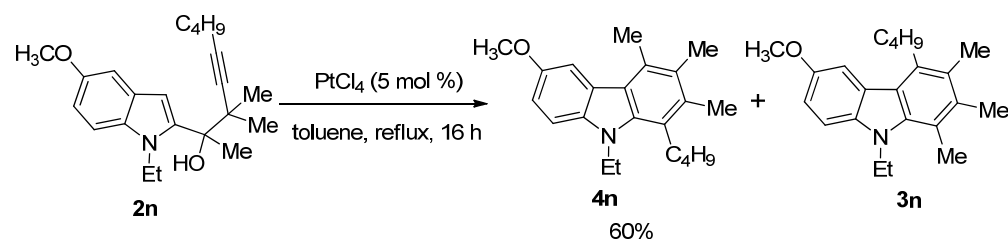
(13) 1-Ethyl-2,3,4,9-tetramethyl-9H-carbazole (4m) (zj-8-010-2)



The reaction of PtCl₄ (16.9 mg, 0.05 mmol) and **2m** (268.7 mg, 1.0 mmol) in toluene (50 mL) under reflux for 14.5 h afforded **4m** (196.1 mg, 78%) [eluent: petroleum ether (500 mL × 5) (**4m** : **3m** = 97 : 3 as determined by ¹H NMR analysis

of the crude product) as a solid: m. p. 94.6 ~ 95.7 °C (*n*-hexane/ diethyl ether); ¹H NMR (300 MHz, CDCl₃) δ 8.22 (d, *J* = 7.8 Hz, 1H, ArH), 7.44-7.31 (m, 2H, ArH), 7.22-7.12 (m, 1H, ArH), 4.00 (s, 3H, NCH₃), 3.15 (q, *J* = 7.5 Hz, 2H, CH₂), 2.81 (s, 3H, CH₃), 2.40 (s, 3H, CH₃), 2.37 (s, 3H, CH₃), 1.32 (t, *J* = 7.5 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 142.4, 138.2, 133.3, 128.9, 126.4, 124.3, 123.8, 122.51, 122.47, 120.9, 118.4, 108.3, 32.9, 21.6, 17.2, 16.2, 16.10, 16.06; IR (KBr) ν (cm⁻¹) 2957, 2927, 2867, 1607, 1582, 1462, 1393, 1328, 1304, 1284, 1241, 1188, 1152, 1105, 1092, 1050, 1030; MS (70 ev, EI) *m/z* (%) 252 (M⁺+1, 19.31), 251 (M⁺, 82.06), 236 (100); Elemental analysis calcd (%) for C₁₈H₂₁N: C, 86.01; H, 8.42; N, 5.57; Found: C, 86.11; H, 8.30; N, 5.37.

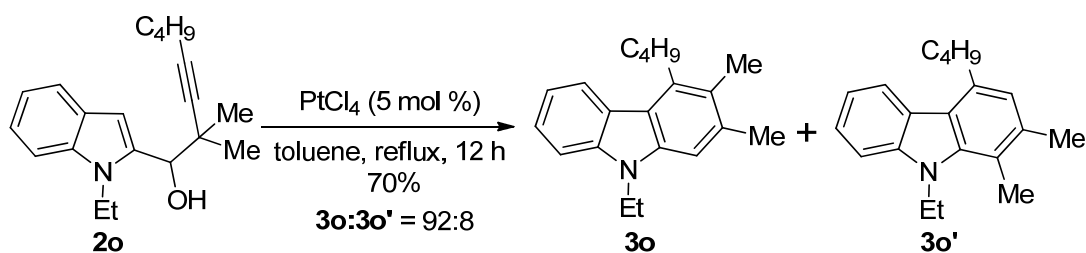
(14) 1-Butyl-9-ethyl-6-methoxy-2,3,4-trimethyl-9H-carbazole (4n) (zj-1-123-2)



The reaction of PtCl₄ (17.0 mg, 0.05 mmol) and **2n** (341.2 mg, 1.0 mmol) in toluene (50 mL) under reflux for 16 h afforded **4n** (194.0 mg, 60%) (eluent: petroleum ether/ dichloromethane = 50/1~30/1~10:1) (**4n** : **3n** = 98 : 2 as determined by ¹H NMR analysis of the crude product) as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.77 (d, *J* = 2.1 Hz, 1H, ArH), 7.28 (d, *J* = 8.7 Hz, 1H, ArH), 7.06 (dd, *J*₁ = 8.7 Hz, *J*₂ = 2.4 Hz, 1H, ArH), 4.43 (q, *J* = 7.1 Hz, 2H, NCH₂), 3.91 (s, 3H, CH₃), 3.11-2.92 (m, 2H, CH₂), 2.81 (s, 3H, CH₃), 2.41 (s, 3H, CH₃), 2.37 (s, 3H, CH₃), 1.71-1.45 (m, 4H, 2 × CH₂), 1.38 (t, *J* = 7.1 Hz, 3H, CH₃), 1.01 (t, *J* = 7.2 Hz, 3H, CH₃); ¹³C NMR (75

MHz, CDCl₃) δ 153.0, 137.7, 136.6, 133.5, 128.9, 125.9, 124.5, 121.1, 120.9, 112.3, 108.7, 107.1, 56.2, 39.7, 33.4, 28.5, 23.0, 17.2, 16.5, 16.1, 15.1, 13.9; IR (neat) ν (cm⁻¹) 2953, 2928, 2869, 2827, 1617, 1581, 1487, 1377, 1353, 1311, 1296, 1259, 1219, 1175, 1143, 1105, 1077, 1041; GC-MS (GC condition: injector: 280 °C; column: DB5 column 30 m \times 0.25 mm, temperature programming: 60 °C (2 min), 20 °C/min to 280 °C, 280 °C (30 min); detector: 280 °C) (70 ev, EI) m/z (%) for **4n**: T_R 6.4 min: 324 (M⁺+1, 24.29), 323 (M⁺, 94.81), 280 (100); HRMS Calcd for C₂₂H₂₉NO (M⁺): 323.2249, Found: 323.2254.

(15) 4-Butyl-9-ethyl-2,3-dimethyl-9H-carbazole (3o) (zj-2-117)



The reaction of PtCl₄ (3.5 mg, 0.01 mmol) and **2o** (58.4 mg, 0.2 mmol) in toluene (10 mL) under reflux for 12 h afforded **3o** and **3o'** (38.5 mg, 70%, **3o** : **3o'** = 92 : 8 as determined by ¹H NMR analysis of the crude product) (petroleum ether/dichloromethane = 50/1~30/1) (**3o** : **3o'** = 91 : 9 determined by ¹H NMR of crude product) as a liquid: ¹H NMR of **3o**^{2b} (300 MHz, CDCl₃) δ 8.12 (d, J = 8.1 Hz, 1H, ArH), 7.46-7.33 (m, 2H, ArH), 7.25-7.15 (m, 1H, ArH), 7.09 (s, 1H, ArH), 4.31 (q, J = 7.2 Hz, 2H, NCH₂), 3.33-3.19 (m, 2H, ArCH₂), 2.49 (s, 3H, ArCH₃), 2.37 (s, 3H, ArCH₃), 1.85-1.52 (m, 4H, 2 \times CH₂), 1.39 (t, J = 7.4 Hz, 3H, CH₃), 1.03 (t, J = 7.1 Hz, 3H, CH₃); the following signals are discernible for **3o'**: 8.07 (d, J = 8.1 Hz, 1H, ArH), 6.86 (s, 1H, ArH), 4.58 (q, J = 7.1 Hz, 2H, NCH₂), 3.17-3.10 (m, 2H, ArCH₂), 2.68 (s,

3H, ArCH₃), 2.46 (s, 3H, ArCH₃); ¹³C NMR of **3o** (75 MHz, CDCl₃) δ 140.0, 138.6, 136.4, 135.0, 124.9, 124.2, 123.1, 122.2, 119.3, 118.4, 108.0, 107.2, 37.1, 31.4, 30.4, 23.4, 22.3, 14.5, 14.1, 13.6; the following signals are discernible for **3o'**: 135.3, 134.5, 124.4, 123.0, 118.8, 115.8, 108.5, 39.9, 33.9, 32.0, 29.7, 23.0, 20.915.5, 14.8; IR (neat) ν (cm⁻¹) 3048, 2955, 2929, 2872, 2852, 1619, 1598, 1569, 1469, 1456, 1377, 1349, 1330, 1314, 1264, 1239, 1207, 1180, 1153, 1132, 1110, 1082, 1029, 1004; GC-MS (GC condition: injector: 280 °C; column: DB5 column 30 m × 0.25 mm, temperature programming: 60 °C (2 min), 20 °C/min to 280 °C, 280 °C (30 min); detector: 280 °C) (70 eV, EI) *m/z* (%) for **3o**: T_R 3.8 min: 280 (M⁺+1, 21.34), 279 (M⁺, 100), for **3o'**: T_R 3.9 min: 280 (M⁺+1, 22.20), 279 (M⁺, 100).

3. Computational details

All calculations were performed with the Gaussian 09 program.³ Geometries have been fully optimized with the density functional theory of B3LYP method.^{4,5} The 6-31G(d) basis set was used for C, H, O, N, and Cl atoms and LANL2DZ basis set⁶ with effective core potential (ECP) for Pt atom. Harmonic vibration frequency calculations were carried out for all the stationary points to confirm each structure being either a minimum (no imaginary frequency) or a transition structure (one imaginary frequency). Solvent effect has been considered by using the CPCM⁷(UAHF atomic radii) model based on the gas-phase-optimized structures. The reported relative energies are free energies (ΔG_{sol}) in toluene (dielectric constant $\epsilon = 2.37$).

Table S1. Electronic energies (E_{elec}), Gibbs free energies (G_{298}), enthalpies (H_{298}) and free energies ($\text{delt } G_{\text{sol}}$) in toluene ($\epsilon = 2.37$) for all stationary points.

species	E_{elec}	H_{298}	G_{298}	$\text{delt } G_{\text{sol}}$	G_{sol}
M1_1	-2789.672282	-2789.263502	-2789.350036	-18.42	-2789.37939
TS1	-2789.663559	-2789.255900	-2789.341829	-16.50	-2789.368123
M2_1	-2789.69833	-2789.287797	-2789.374180	-19.94	-2789.405956
TS2	-2789.646753	-2789.238215	-2789.324259	-15.81	-2789.349454
M2_2	-2789.672632	-2789.262542	-2789.348296	-24.46	-2789.387275

S2. Calculated Cartesian coordinates of all stationary points **M1_1**.

C	1.40650900	1.90811300	0.10155800
C	-0.04318000	1.80243400	-0.53366600
C	2.95852000	0.41431800	-1.22345300
C	4.20136100	0.03342600	-0.79962600
C	1.99654500	0.43842700	-0.08346100
C	4.09672400	-0.24988300	0.62094800
C	5.45274900	-0.13020000	-1.47617000
C	5.22898500	-0.71126700	1.34407400
C	6.52827200	-0.56793500	-0.75685800
H	5.52665900	0.09214900	-2.53603000

C	6.40385200	-0.85704000	0.64568700
H	5.17224500	-0.92961300	2.40428200
H	7.49322800	-0.70401600	-1.23371500
H	7.28655400	-1.20437800	1.17585900
N	2.85323100	-0.03294600	1.04738100
C	2.34498400	-0.45502400	2.35345300
H	1.26172000	-0.57847500	2.29269100
H	2.78663500	-1.41892600	2.62040000
H	2.58399600	0.28163600	3.12589400
C	-0.35992900	0.33191700	-0.21300100
C	0.73811500	-0.45317800	-0.20325100
H	2.68202200	0.72676800	-2.21972800
O	2.27762600	2.78810200	-0.60832900
H	1.93501000	3.69076000	-0.49966200
C	-0.95192000	2.92450900	-0.00927800
H	-1.92070600	2.88409700	-0.50807000
H	-1.13604600	2.87240600	1.06132700
H	-0.49438500	3.89538200	-0.24934800
C	-0.00015500	1.94636400	-2.07824600
H	0.35354800	2.94276600	-2.36225400
H	0.63780900	1.19925700	-2.55733500
H	-1.01037000	1.80888100	-2.47026800
Cl	-1.56671700	-1.88197600	1.81109200
C	0.94577500	-1.94281700	-0.31828600
H	1.69411300	-2.27505200	0.41401900
H	0.01756900	-2.45046000	-0.06546900
Pt	-2.23785400	-0.35958400	0.08496500
Cl	-2.88696100	1.09351900	1.86148000
C	1.36810000	2.34890000	1.56902200
H	2.37497500	2.32957500	1.99447600
H	1.00945800	3.38100100	1.62096900
H	0.69061600	1.74345000	2.17589100
Cl	-2.10850700	-2.03020100	-1.60296200
Cl	-3.39478000	0.98835800	-1.50039800
C	1.38589100	-2.38920000	-1.72563400
H	0.62403600	-2.12396400	-2.46285600
H	2.34322500	-1.94796800	-2.03050300
H	1.50830500	-3.47804000	-1.74234700
TS1			
C	1.50623500	1.84743000	0.16141500
C	0.08963100	1.72725300	-0.42096900
C	2.96957100	0.16968700	-1.28883700
C	4.27523900	0.02853000	-0.80946900
C	2.05241500	-0.11181100	-0.23508000

C	4.16537400	-0.47264900	0.53285000
C	5.55803300	0.24899000	-1.37649600
C	5.31159800	-0.75825200	1.30232200
C	6.67041300	-0.03840500	-0.61775000
H	5.64953300	0.62670300	-2.39056800
C	6.54155200	-0.53880900	0.70955300
H	5.23521100	-1.14248100	2.31396600
H	7.66380400	0.11319000	-1.02805800
H	7.44406300	-0.75596300	1.27392100
N	2.85075300	-0.59079200	0.85292300
C	2.35327100	-1.18425800	2.09078800
H	1.26247000	-1.20609000	2.07190500
H	2.72030900	-2.21116900	2.18536400
H	2.68711900	-0.60547800	2.95856300
C	-0.32811000	0.25474200	-0.20530100
C	0.65574600	-0.66065800	-0.33490400
H	2.67630300	0.53236600	-2.26324100
O	2.25913300	2.75580100	-0.49337900
H	3.03113600	3.00449700	0.04437900
C	-0.71296900	2.86222000	0.27165100
H	-1.71251100	2.90689900	-0.16129800
H	-0.82539600	2.71064000	1.34298100
H	-0.20550400	3.81450700	0.07925500
C	0.06525800	2.01175600	-1.94369300
H	0.39528300	3.03356200	-2.15154000
H	0.69200000	1.31416500	-2.50457600
H	-0.96086800	1.89481400	-2.29822300
Cl	-2.39710700	-1.67320600	-1.79628600
C	0.62084300	-2.15718400	-0.59106700
H	1.25639700	-2.67406900	0.13924700
H	-0.38810000	-2.53191400	-0.45067800
Pt	-2.27588200	-0.24173600	0.09831500
Cl	-1.75046000	-2.02713600	1.60642000
Cl	-3.36918900	1.39176900	-1.25132800
Cl	-2.67753400	1.03986400	2.07399100
C	1.67571100	1.90344800	1.66241900
H	2.71693000	1.71994700	1.94913100
H	1.40674200	2.91481400	1.98918900
H	1.02117500	1.19953200	2.17601300
C	1.09706600	-2.51378800	-2.01052800
H	0.44691100	-2.05047300	-2.75827900
H	2.13289900	-2.20535000	-2.20061600
H	1.04620300	-3.59949500	-2.14785500

M2_1

C	-1.77759800	-1.75691100	-0.00810100
C	-0.25167900	-1.60660300	-0.47063800
C	-2.59123500	-0.63111100	-0.68310000
C	-4.04282400	-0.47725900	-0.33588500
C	-1.98510900	0.66762200	-0.25938000
C	-4.21545100	0.80361200	0.19547700
C	-5.13598400	-1.32158500	-0.48420100
C	-5.45803000	1.29576100	0.57915900
C	-6.39645500	-0.85115600	-0.09552600
H	-5.00530100	-2.32037400	-0.88593300
C	-6.55318000	0.43854000	0.42342400
H	-5.59378200	2.29786300	0.97142000
H	-7.26497100	-1.49389200	-0.20286300
H	-7.54087900	0.78723300	0.70932400
N	-2.93994600	1.44967400	0.26075300
C	-2.75642100	2.69602200	1.01201200
H	-1.83510900	2.63894900	1.59144200
H	-2.72462600	3.55881700	0.34174000
H	-3.59589700	2.80108600	1.69919700
C	0.24721800	-0.15719900	-0.23009000
C	-0.57840700	0.95165700	-0.35621200
H	-2.46747600	-0.75916500	-1.76546300
O	-2.35141900	-2.94570400	-0.53555800
H	-2.09493900	-3.68840300	0.03312800
C	0.50489200	-2.76896200	0.20347700
H	1.53196600	-2.83190900	-0.14609800
H	0.53088100	-2.68854800	1.28763900
H	0.01084500	-3.70520000	-0.08148500
C	-0.12740600	-1.81195400	-2.01105800
H	-0.61471800	-2.75218500	-2.28362500
H	-0.57547100	-1.00055700	-2.59343800
H	0.92855900	-1.86367100	-2.28465500
Cl	2.69311400	1.42309200	-1.77865000
C	-0.20911400	2.39411500	-0.69609600
H	-0.51269000	3.09195400	0.08336900
H	0.86708200	2.48395000	-0.76446500
Pt	2.22638000	0.12076300	0.17081500
Cl	1.84238200	2.00966500	1.60033700
Cl	3.37188100	-1.60877700	-1.01155600
Cl	2.37869000	-1.10483100	2.21189100
C	-1.93011600	-1.73034500	1.52196600
H	-2.98763900	-1.67039000	1.79492400
H	-1.52378300	-2.64474700	1.96214400
H	-1.39064800	-0.89450800	1.97715300

C	-0.81232000	2.80842900	-2.05125700
H	-0.43212000	2.16654700	-2.85275300
H	-1.90962600	2.76728300	-2.07107200
H	-0.51412300	3.83671700	-2.28224900
TS2			
C	1.12091900	2.27894400	-0.16280800
C	-0.16904100	1.72102400	-0.95601800
C	2.38417600	0.28614100	-1.10970400
C	3.67281100	-0.29289400	-0.82443300
C	1.98299400	1.03426700	0.05663400
C	4.02227000	0.11197400	0.48489100
C	4.56191600	-1.05065100	-1.59922900
C	5.23683400	-0.27837000	1.06299200
C	5.78026400	-1.41332700	-1.04081500
H	4.29654400	-1.34916000	-2.60904600
C	6.10115500	-1.03746400	0.27951200
H	5.51429500	0.01777000	2.06891900
H	6.49153300	-1.99437600	-1.61892300
H	7.05798400	-1.33913900	0.69606500
N	3.01004300	0.90345300	1.01586000
C	2.86729400	1.12301700	2.45540500
H	1.81890800	1.03114600	2.74353300
H	3.42796000	0.35183900	2.98894900
H	3.24574100	2.10491400	2.75665100
C	-0.26114700	0.30914700	-0.36111900
C	0.95175700	-0.30086700	-0.08313000
H	2.01959100	0.48253700	-2.10186500
O	1.92148200	3.14855400	-0.95057800
H	1.56222600	4.04700500	-0.87307000
C	-1.33271400	2.71091800	-0.77657100
H	-2.21714600	2.35823400	-1.30571700
H	-1.61437600	2.88101100	0.25843000
H	-1.02762900	3.66551600	-1.22755200
C	0.03388000	1.61348100	-2.50851900
H	0.80722500	2.31512300	-2.83267500
H	0.28030500	0.60536300	-2.84995000
H	-0.90383900	1.86821400	-3.00313900
Cl	-1.44348800	-0.97964200	2.38966900
C	1.27956800	-1.62574100	0.57632000
H	2.07224400	-1.45665700	1.31478400
H	0.40275300	-1.91957300	1.14968200
Pt	-2.05575600	-0.46497400	0.13098500
Cl	-3.39804400	1.24926900	1.10552600
C	0.74171900	2.98364800	1.14486500

H	1.64718500	3.27692400	1.68001100
H	0.18038000	3.89637700	0.92789600
H	0.11553700	2.36338200	1.79290500
Cl	-1.57655900	-2.65569000	-0.64967100
Cl	-3.02954900	-0.05408200	-2.00494300
C	1.69051700	-2.78675100	-0.34968300
H	1.02434900	-2.86013800	-1.21033500
H	2.72079700	-2.70346300	-0.69964800
H	1.60311000	-3.72401300	0.20942300
M2_2			
C	-1.38821400	2.08691200	1.00425300
C	-0.24191400	1.72722900	-0.07215300
C	-2.21585200	-0.30107200	0.89043300
C	-3.39266900	-0.98942500	0.22529000
C	-2.48730400	1.13755700	0.62641500
C	-4.21226700	0.01036300	-0.30503400
C	-3.82215200	-2.31212600	0.14082500
C	-5.41725000	-0.23406000	-0.95265500
C	-5.02837300	-2.59058700	-0.51282200
H	-3.24418100	-3.12128300	0.56893100
C	-5.81274100	-1.56985100	-1.05830200
H	-6.03072700	0.56128900	-1.36151900
H	-5.35939600	-3.62120100	-0.59526500
H	-6.74256700	-1.81221000	-1.56312600
N	-3.61317700	1.28646200	-0.03745200
C	-4.26314100	2.49666200	-0.55032100
H	-4.26925700	2.45438800	-1.64284400
H	-5.29184200	2.51875700	-0.18233200
H	-3.74149500	3.38484400	-0.21893200
C	0.15071800	0.22902700	0.17083400
C	-0.75255600	-0.71441900	0.52505700
H	-2.29069000	-0.43237000	1.98207500
O	-0.98158300	1.74467400	2.32492500
H	-0.24405700	1.10863000	2.26974500
Pt	2.11653700	-0.30284200	-0.23774500
C	-0.59465500	-2.21111200	0.70494600
H	0.40747900	-2.51529400	0.43192000
H	-1.25507100	-2.70263100	-0.01922300
C	-0.76232400	1.84340600	-1.52721100
H	0.07554500	1.67497100	-2.20714900
H	-1.52625100	1.09742600	-1.76859900
H	-1.15951500	2.84654500	-1.72631900
C	0.84609900	2.79935600	0.13494400
H	1.17227300	2.86110600	1.17352400

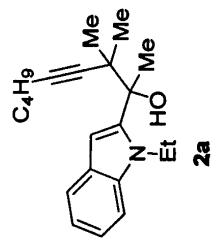
H	1.71419300	2.59401200	-0.48465300
H	0.44747900	3.76985500	-0.17493100
Cl	2.56288400	1.04442900	-2.16630800
Cl	3.34603500	1.18808700	1.16250000
Cl	2.42487700	-1.84068500	1.56535200
Cl	1.42786400	-1.97241800	-1.80152000
C	-1.75501100	3.57439400	1.08276100
H	-1.89139200	4.04325500	0.10567500
H	-2.65857300	3.70788200	1.68708300
H	-0.94557200	4.08990200	1.59816000
C	-0.88731900	-2.71504600	2.12860900
H	-1.91813800	-2.53772800	2.46343200
H	-0.71523200	-3.79587700	2.17060600
H	-0.20466600	-2.24847300	2.84497400

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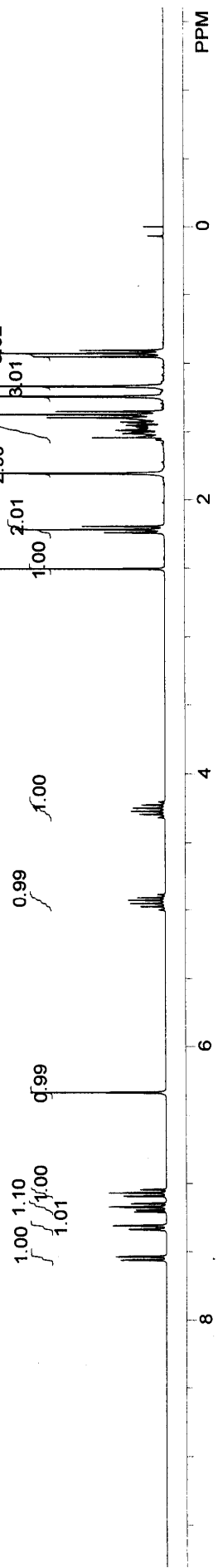
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7.043
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4.224
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2.218
2.194
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0.929
0.905
0.000

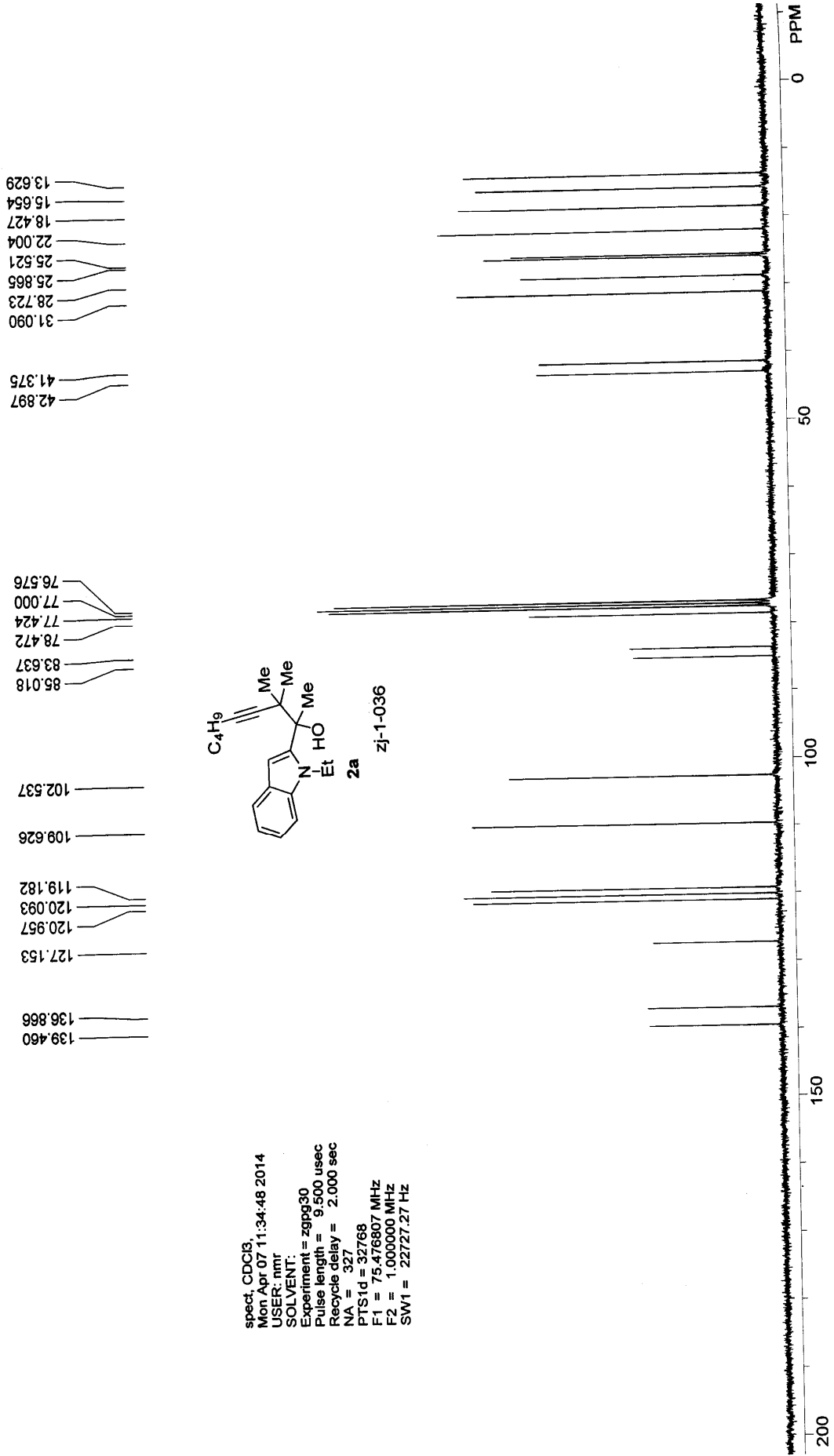
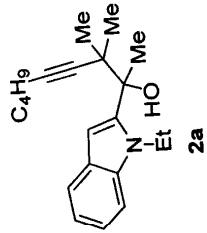


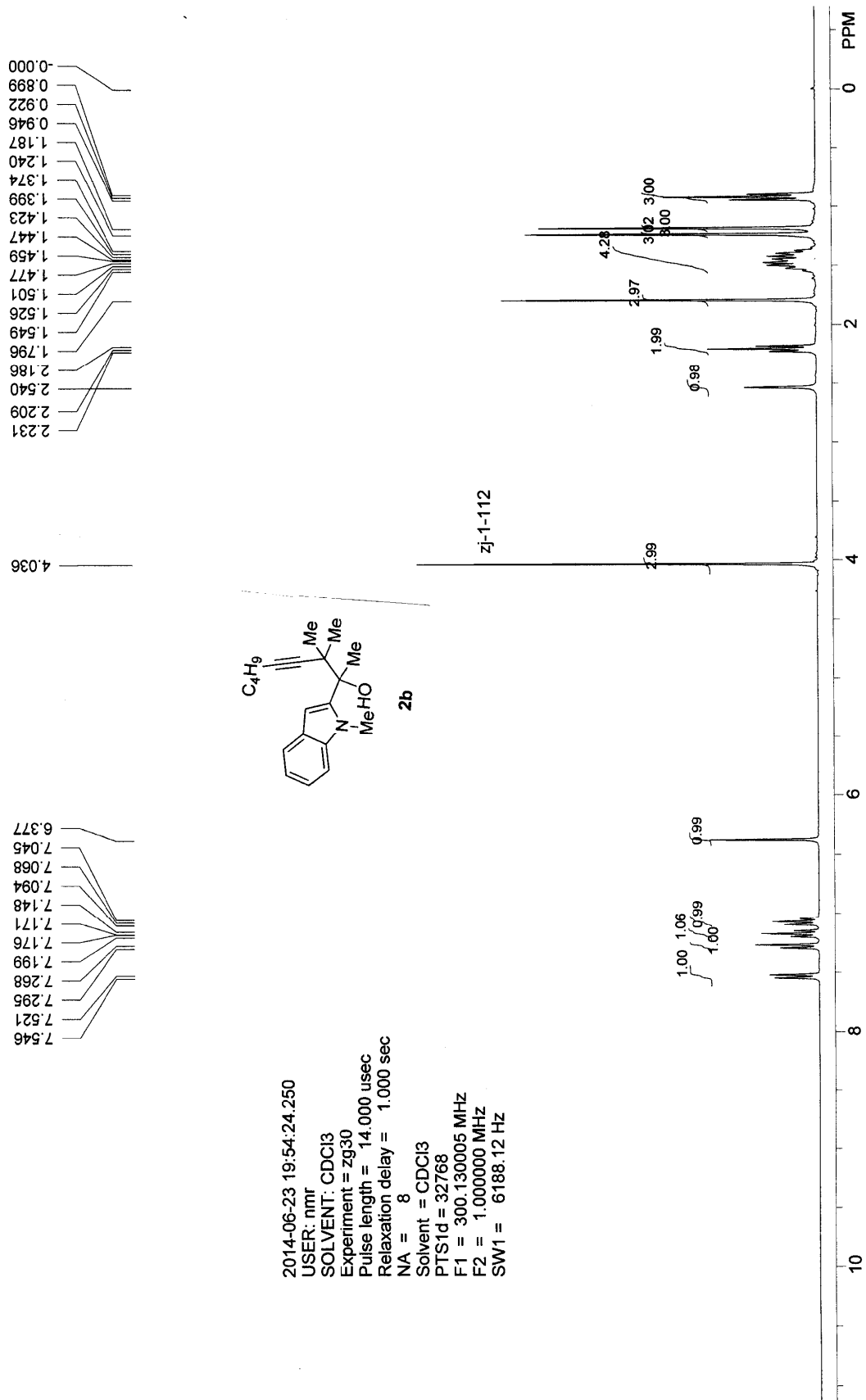
spect, CDCl3,
Mon Apr 07 11:33:04 2014
USER: nmr
SOLVENT:
Experiment = z930
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz

zj-1-036

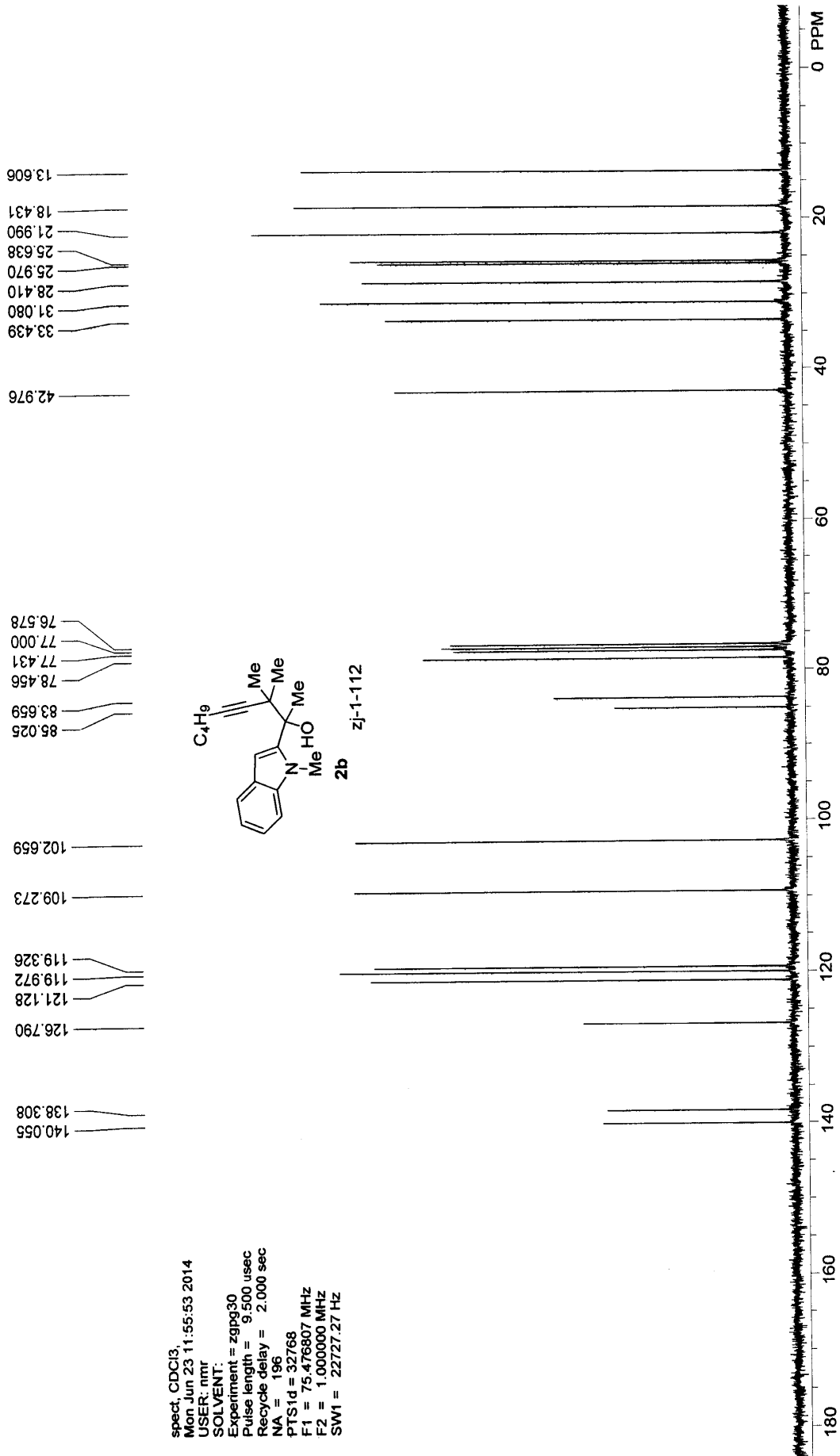


spect. CDCl3,
 Mon Apr 07 11:34:48 2014
 USER: nmr
 SOLVENT:
 Experiment = zgpg30
 Pulse length = 9.500 usec
 Recycle delay = 2.000 sec
 NA = 327
 PTS1d = 32768
 F1 = 75.476807 MHz
 F2 = 1.000000 MHz
 SW1 = 22727.27 Hz

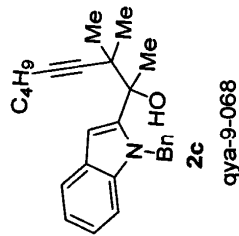
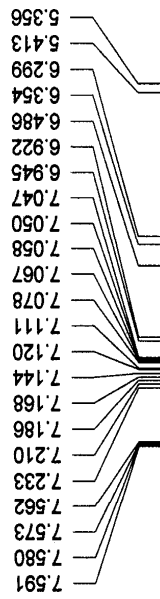
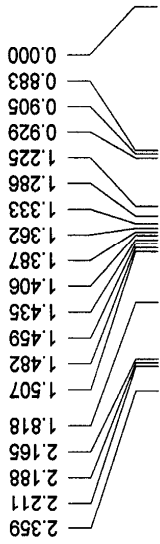




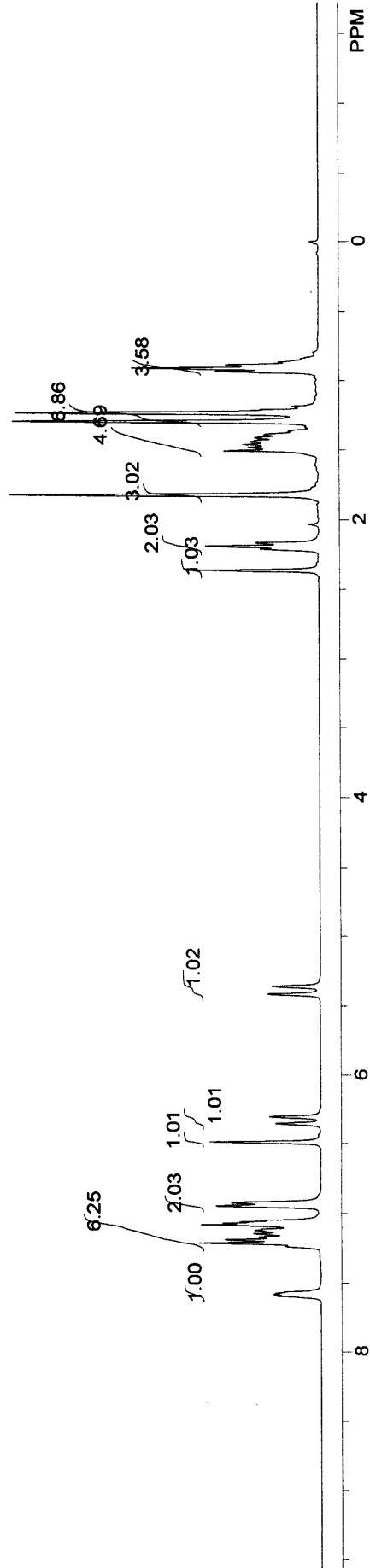
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 USER: nmr
 SOLVENT: CDCl3
 Experiment = zg30
 Pulse length = 14.000 usec
 Relaxation delay = 1.000 sec
 NA = 8
 Solvent = CDCl3
 PTS1d = 32768
 F1 = 300.130005 MHz
 F2 = 1.000000 MHz
 SW1 = 6188.12 Hz

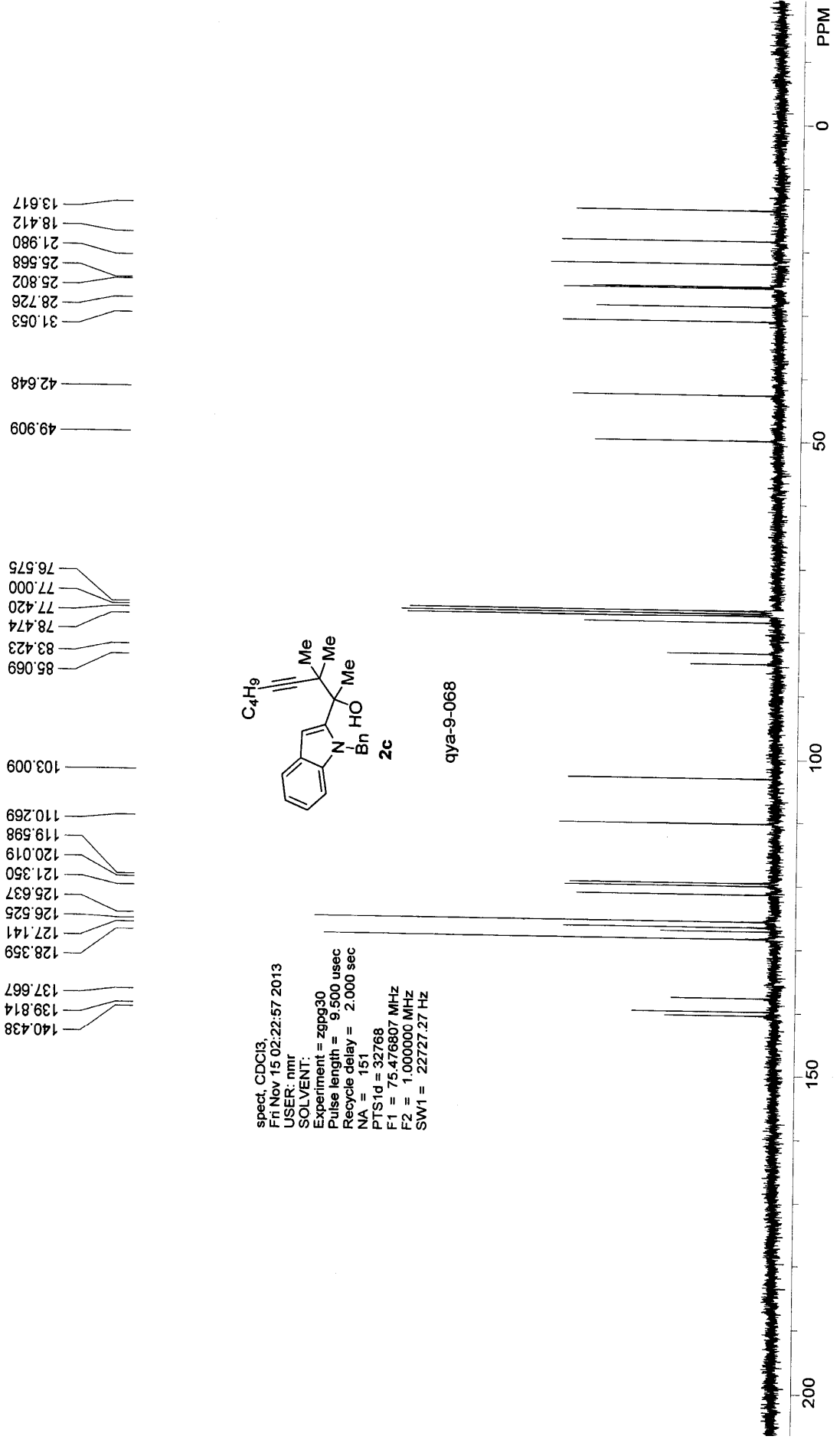


spect, CDCI3
 Mon Jun 23 11:55:53 2014
 USER: nmr
 SOLVENT:
 Experiment = zgpg30
 Pulse length = 9.500 usec
 Recycle delay = 2.000 sec
 NA = 196
 P1 = 32768
 F1 = 75.476807 MHz
 F2 = 1.000000 MHz
 SW1 = 22727.27 Hz



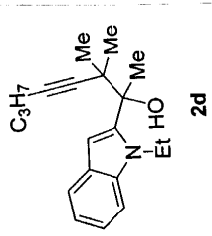
spect, CDCl3,
 Fri Nov 15 02:35:26 2013
 USER: nmr
 SOLVENT:
 Experiment = zg30
 Pulse length = 14.000 usec
 Recycle delay = 1.000 sec
 NA = 8
 PTS1d = 32768
 F1 = 300.131866 MHz
 F2 = 1.000000 MHz
 SW1 = 6188.12 Hz



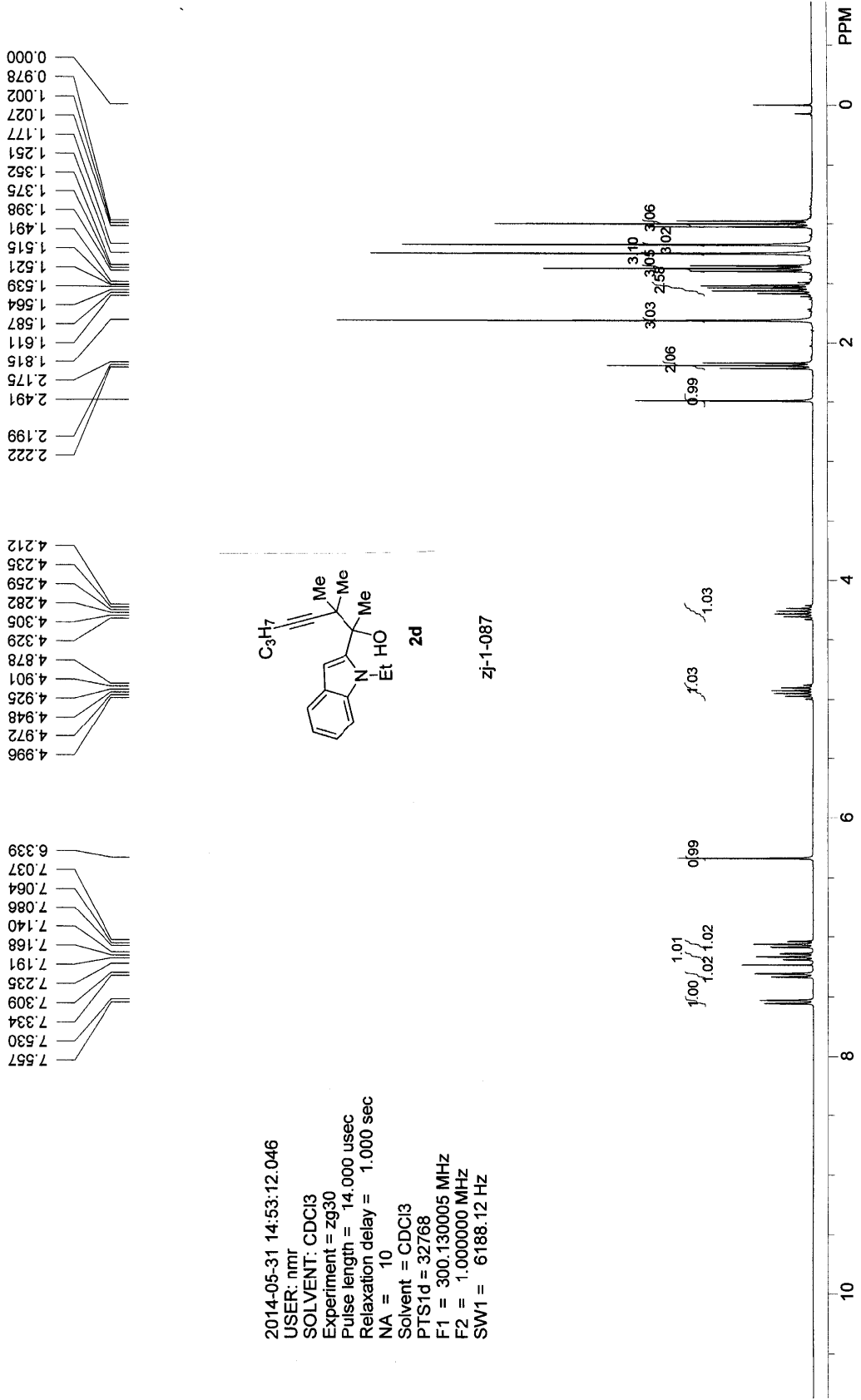


spect, CDCl3
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 USER: nmr
 SOLVENT:
 Experiment = zgpg30
 Pulse length = 9.500 usec
 Recycle delay = 2.000 sec
 NA = 151
 PTS1d = 32768
 F1 = 75.476807 MHz
 F2 = 1.000000 MHz
 SW1 = 22727.27 Hz

2014-05-31 14:53:12.046
 USER: nmr
 SOLVENT: CDCl3
 Experiment = zg30
 Pulse length = 14.000 usec
 Relaxation delay = 1.000 sec
 NA = 10
 Solvent = CDCl3
 PTS1d = 32768
 F1 = 300.130005 MHz
 F2 = 1.000000 MHz
 SW1 = 6188.12 Hz



zj-1-087



28.739
25.906
25.579
22.434
20.748
15.648
13.522

42.948
41.391

85.312
83.523
78.505
77.424
77.000
76.576

102.587

109.648

119.214

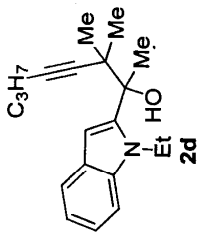
120.120

120.985

127.231

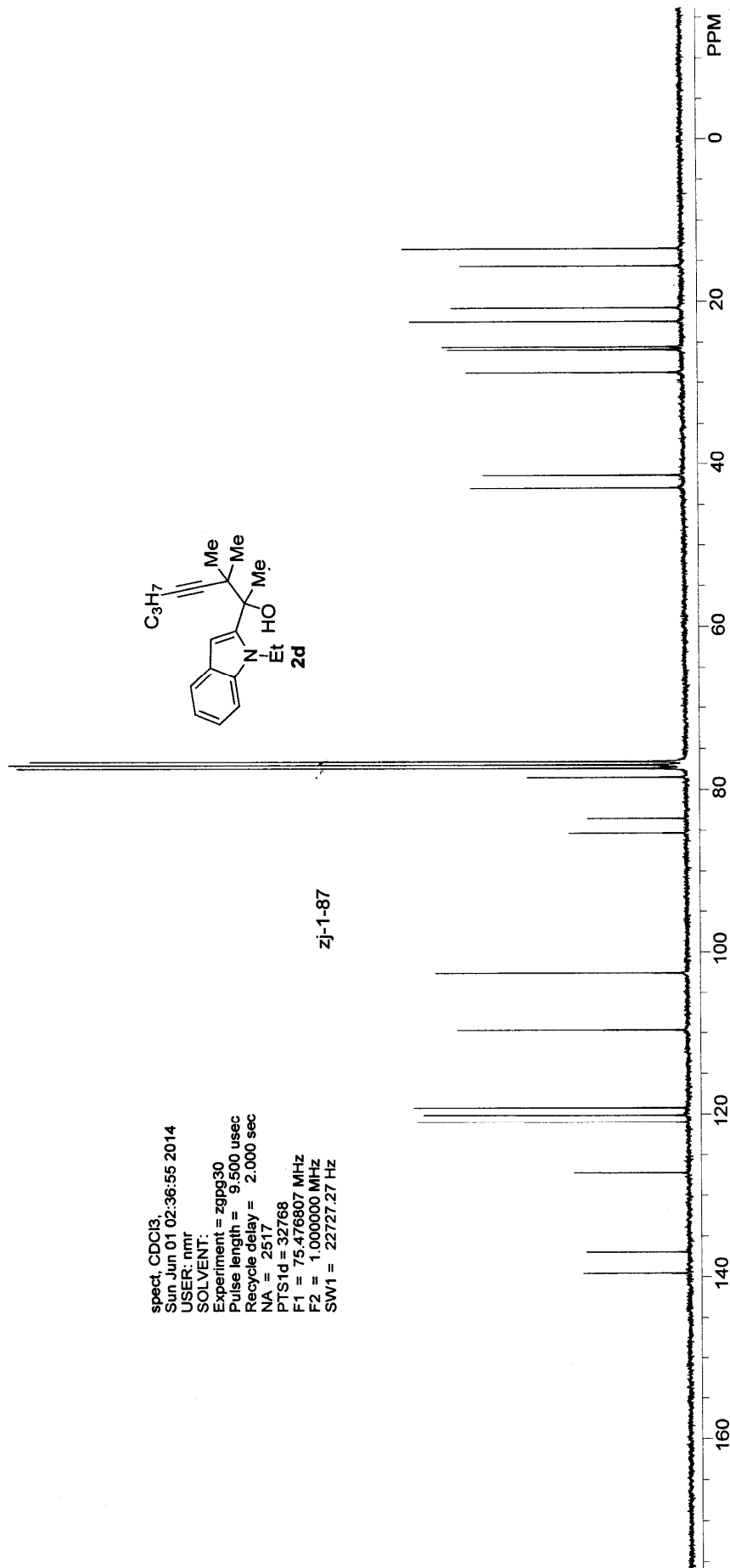
136.946

139.554

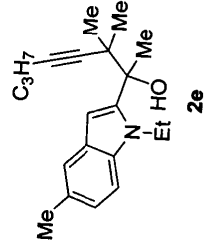
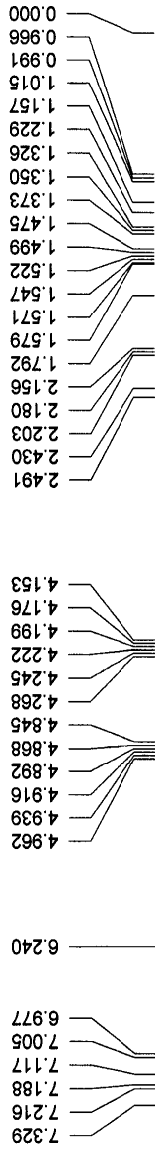


spect. CDCl3,
Sun Jun 01 02:36:55 2014
USER: nmr
SOLVENT:
Experiment = zgpg30
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Recycle delay = 2.000 sec
NA = 2517
PTSD = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz

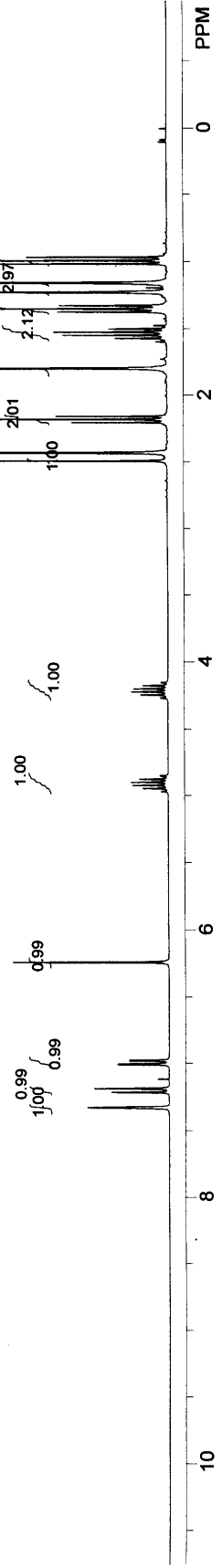
zj-1-87



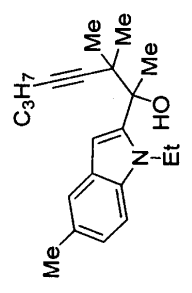
2014-03-17 21:08:40.625
 USER: nmr
 SOLVENT: CDCl3
 Experiment = zg30
 Pulse length = 14.000 usec
 Relaxation delay = 1.000 sec
 NA = 8
 Solvent = CDCl3
 PTS1d = 32768
 F1 = 300.130005 MHz
 F2 = 1.000000 MHz
 SW1 = 6188.12 Hz



zi-1-012

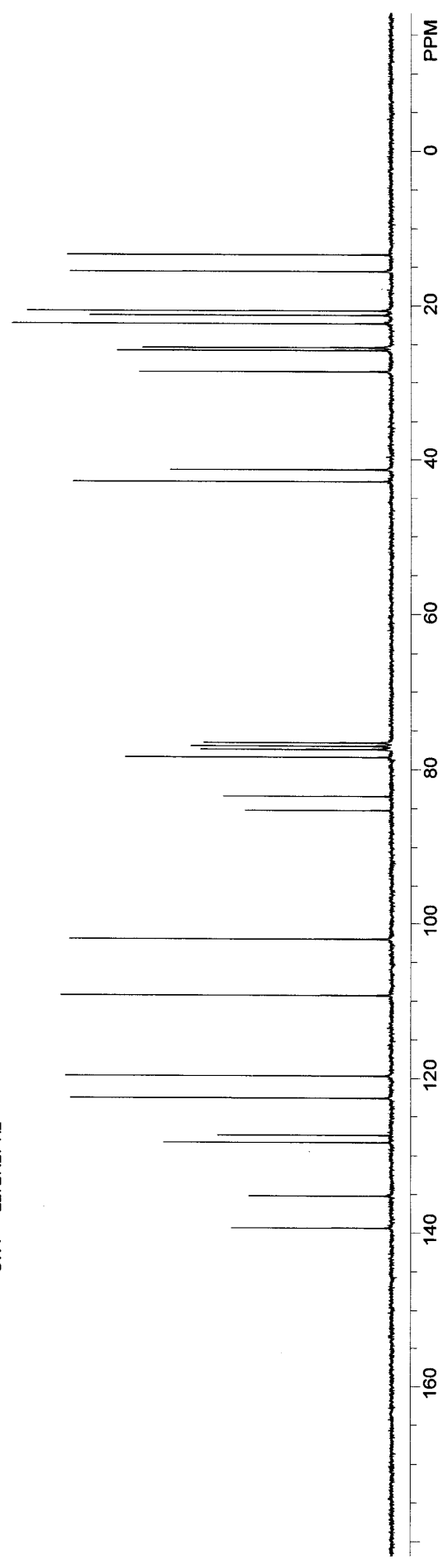


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 128.326
 127.367
 122.545
 119.704
 109.313
 102.009
 85.260
 83.408
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 77.425
 77.000
 76.575
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 41.350
 28.633
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 15.653
 13.499

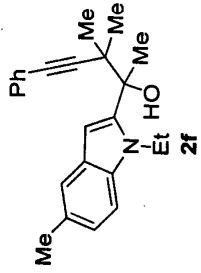


2e
 zj-1-012

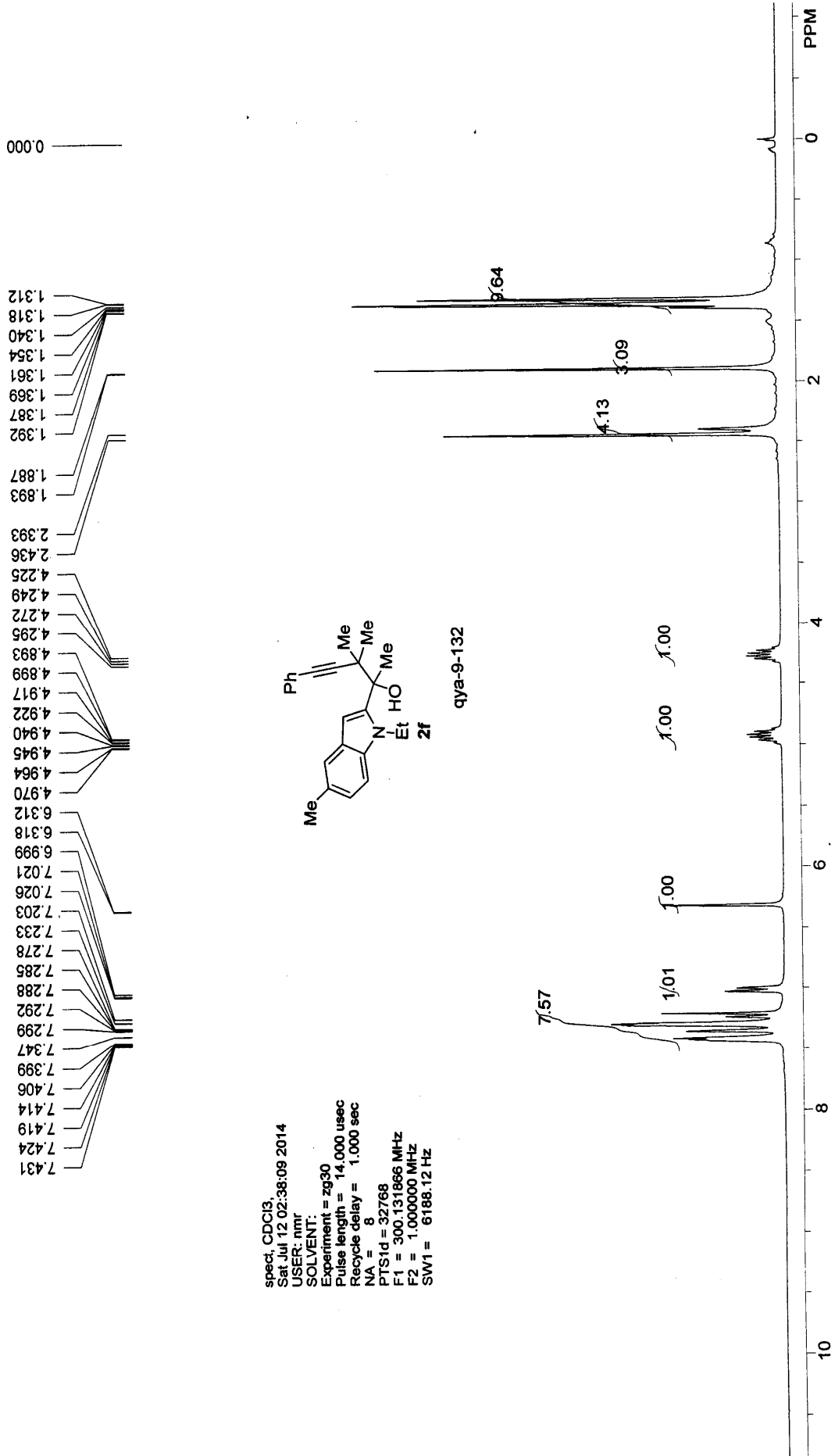
spect. CDCl₃
 Mon Mar 17 13:11:08 2014
 USER: nmr
 SOLVENT: zppg30
 Experiment = zppg30
 Pulse length = 9.500 usec
 Recycle delay = 2.000 sec
 NA = 184
 PTS1d = 32768
 F1 = 75.476807 MHz
 F2 = 1.000000 MHz
 SW1 = 22727.27 Hz



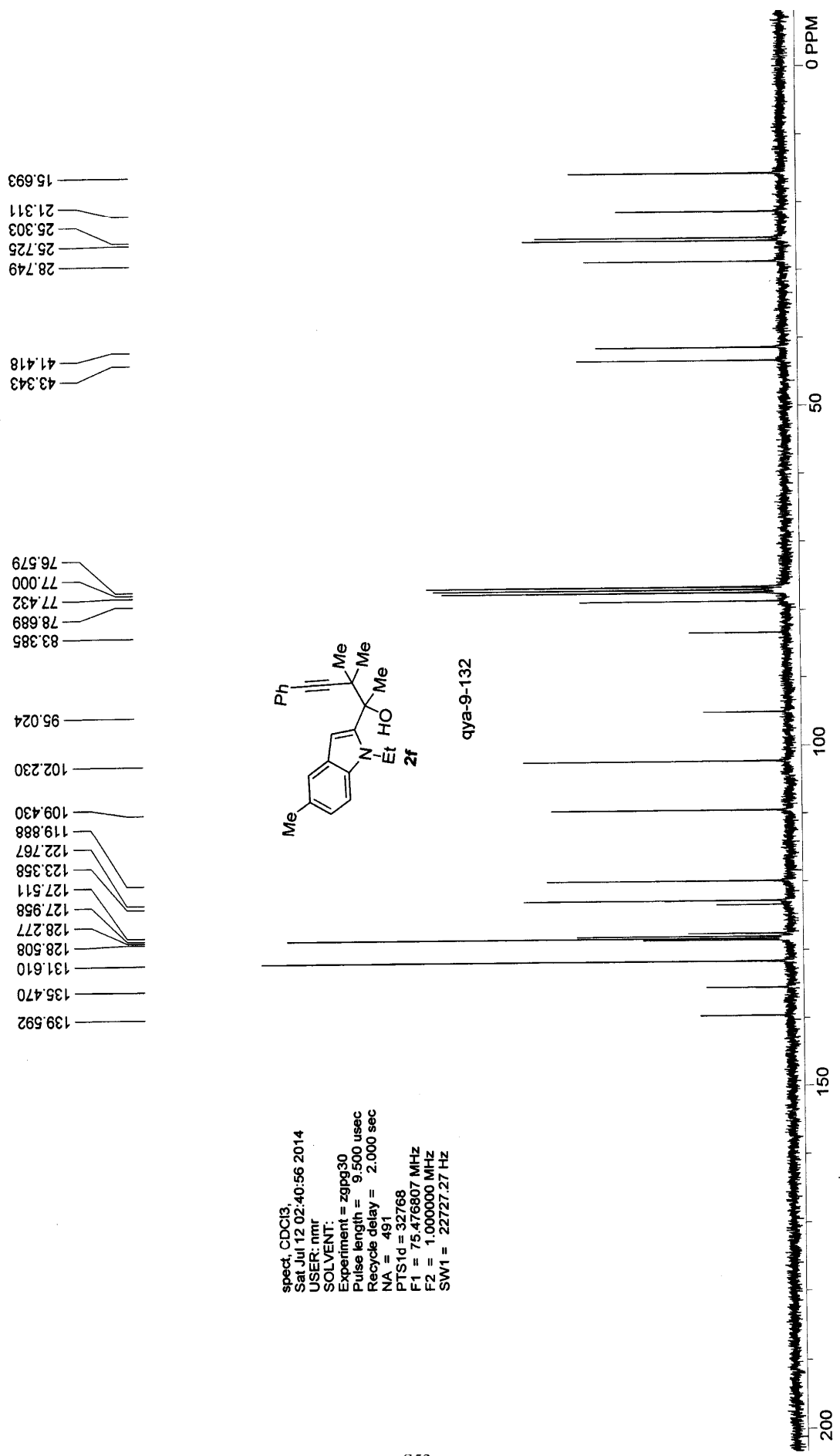
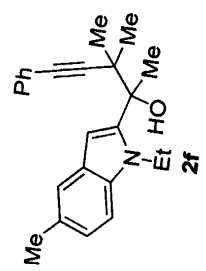
specd, CDC13,
 Sat Jul 12 02:38:09 2014
 USER: nmr
 SOLVENT:
 Experiment = zg30
 Pulse length = 14.000 usec
 Recycle delay = 1.000 sec
 NA = 8
 P1 = 32768
 F1 = 300.131866 MHz
 F2 = 1.000000 MHz
 SW1 = 6188.12 Hz

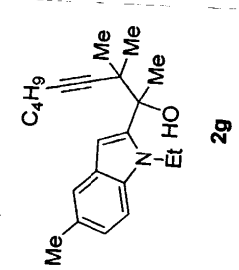
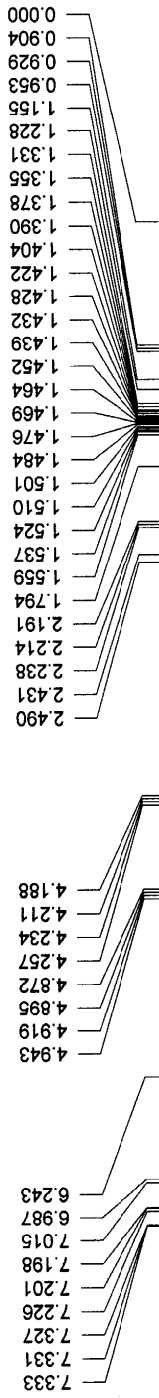


qya-9-132



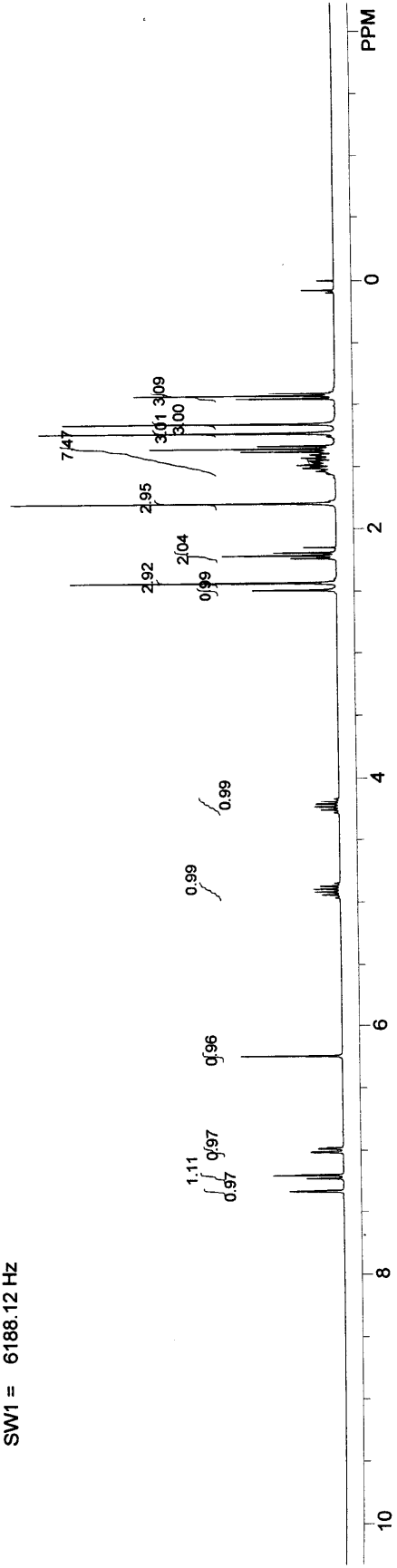
spect, CDC13,
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 USER: nmr
 SOLVENT:
 Experiment = zgpg30
 Pulse length = 9.500 usec
 Recycle delay = 2.000 sec
 NA = 491
 PTS1d = 32768
 F1 = 75.476807 MHz
 F2 = 1.000000 MHz
 SW1 = 22727.27 Hz

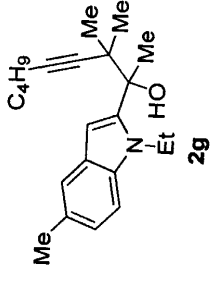
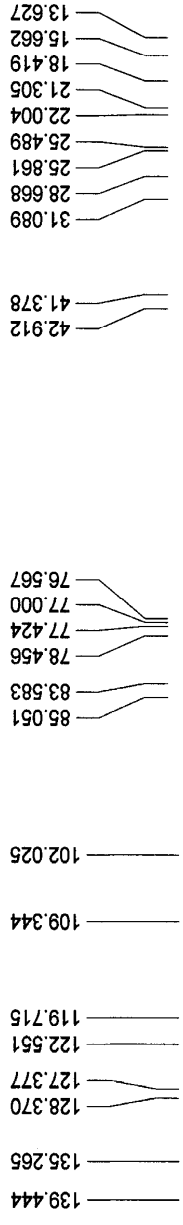




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 SOLVENT: CDCl3
 Experiment = zg30
 Pulse length = 14.000 usec
 Relaxation delay = 1.000 sec
 NA = 8
 Solvent = CDCl3
 PTS1d = 32768
 F1 = 300.130005 MHz
 F2 = 1.000000 MHz
 SW1 = 6188.12 Hz

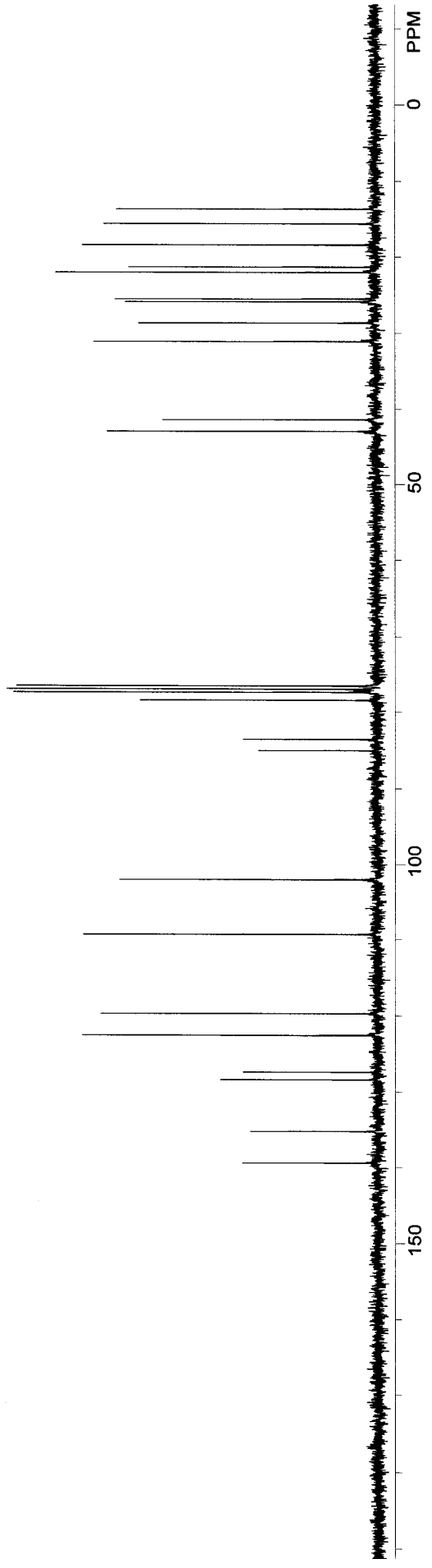
zj-1-024





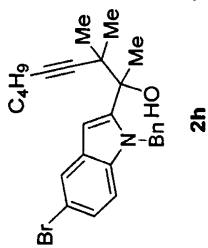
zj-1-024

spect, CDCl3,
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USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 96
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz



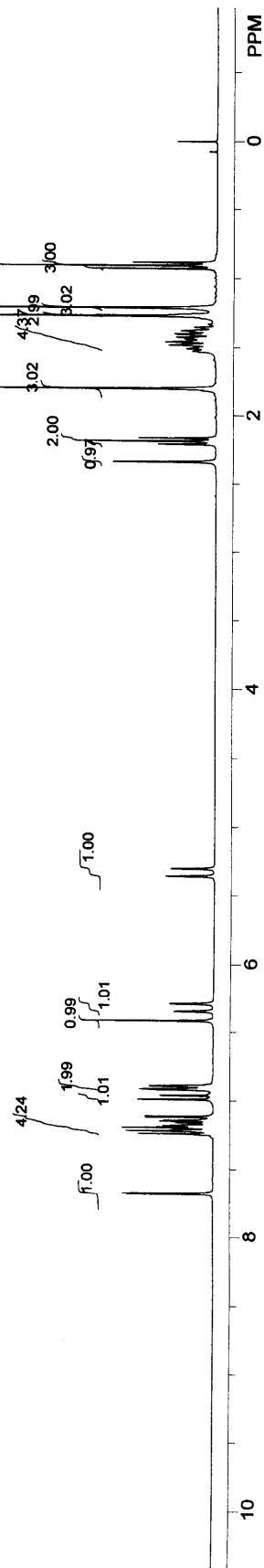
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1.472
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1.435
1.423
1.409
1.399
1.385
1.376
1.350
1.270
1.211
0.929
0.905
0.882
-0.000

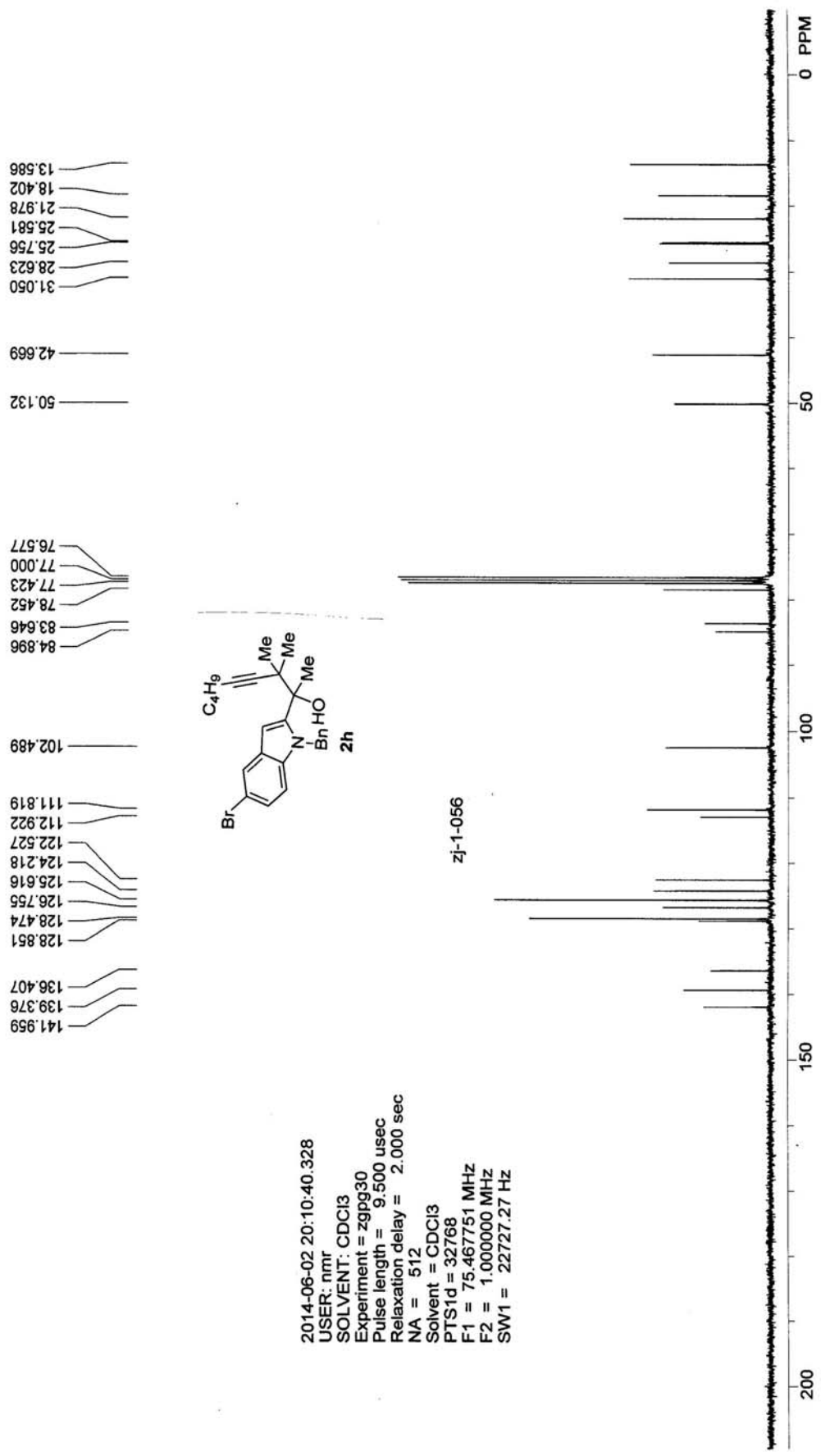
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7.213
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7.194
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7.175
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7.140
7.117
7.110
6.989
6.960
6.918
6.913
6.891
6.418
6.349
6.294
5.361
5.306



2014-06-02 19:39:36.437
 USER: nmr
 SOLVENT: CDCl3
 Experiment = zg30
 Pulse length = 14,000 usec
 Relaxation delay = 1,000 sec
 NA = 8
 Solvent = CDCl3
 PTS1d = 32768
 F1 = 300.130005 MHz
 F2 = 1,000000 MHz
 SW1 = 6188.12 Hz

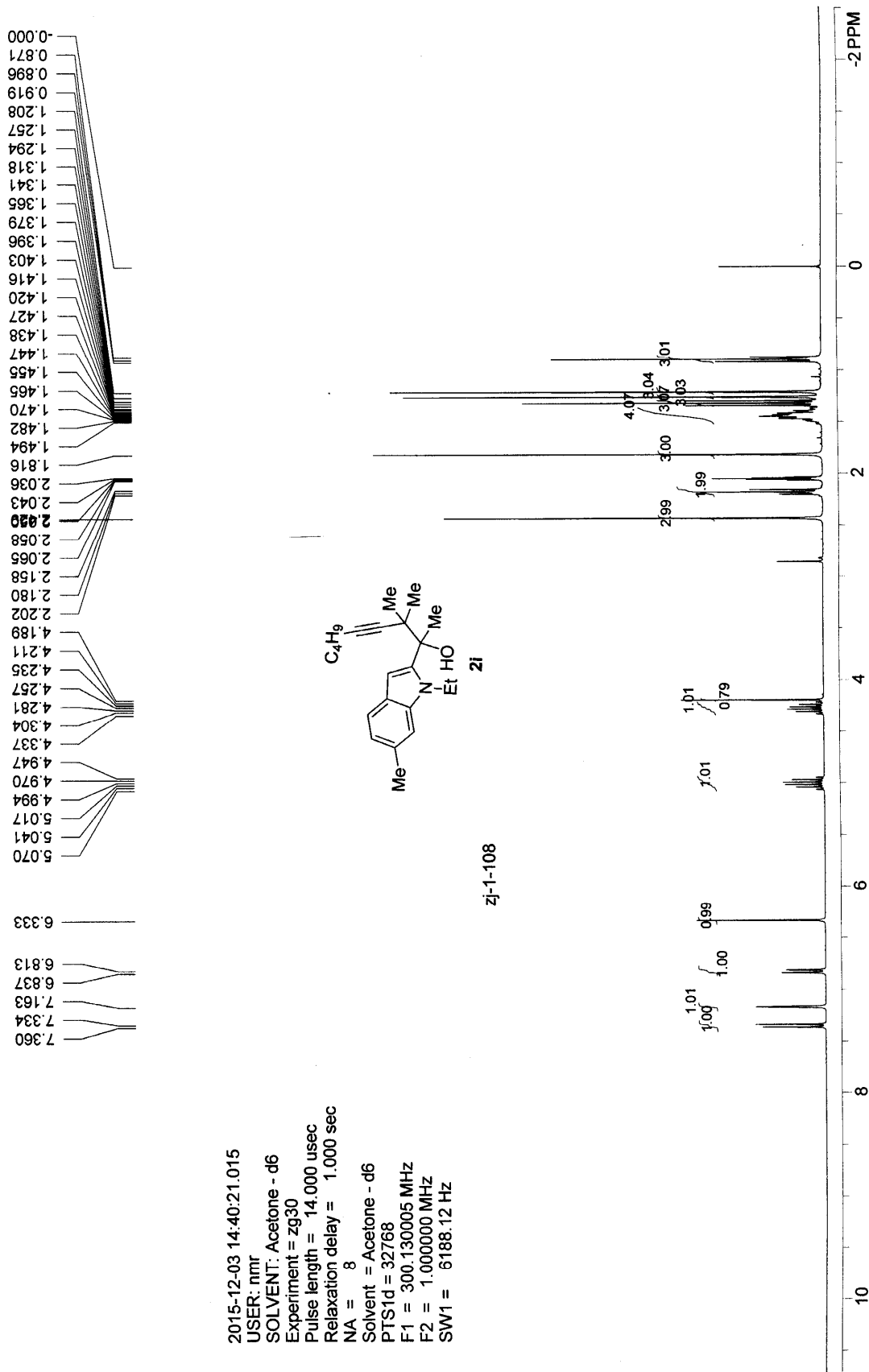
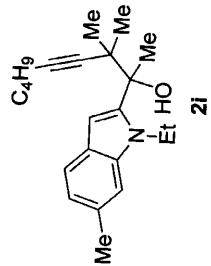
zj-1-056

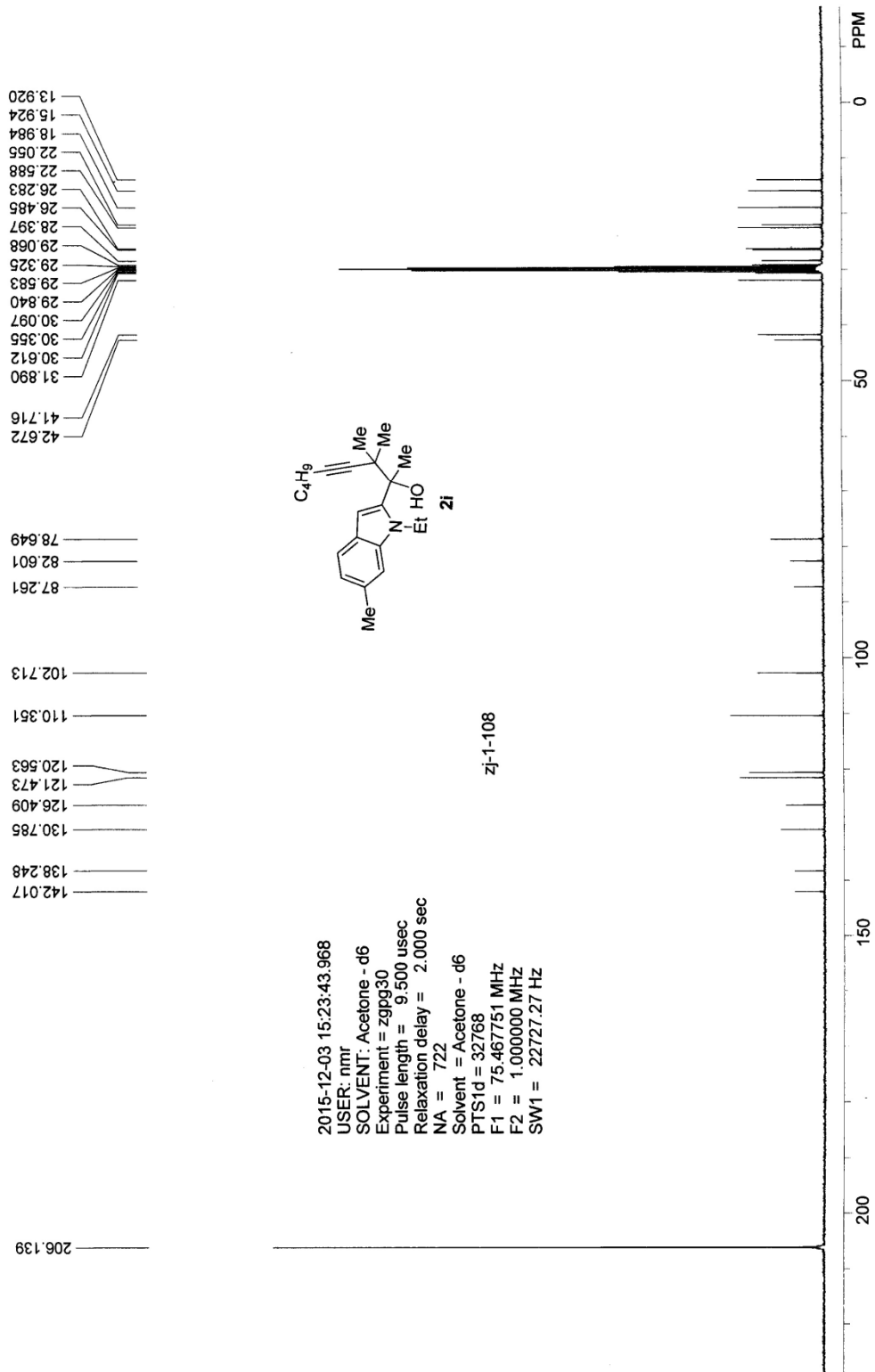


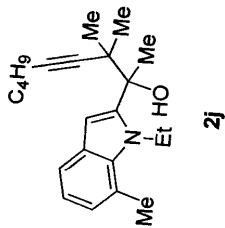
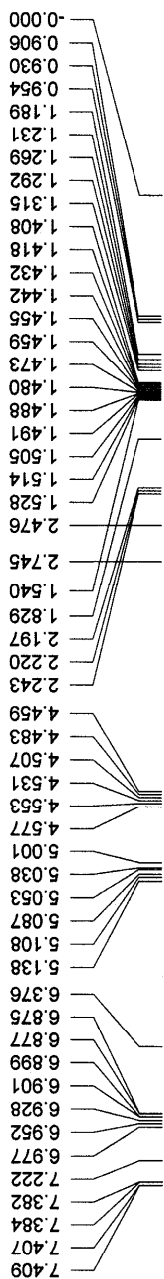


2014-06-02 20:10:40.328
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 SOLVENT: CDCl3
 Experiment = zgpg30
 Pulse length = 9.500 usec
 Relaxation delay = 2.000 sec
 NA = 512
 Solvent = CDCl3
 PTS1d = 32768
 F1 = 75.467751 MHz
 F2 = 1.000000 MHz
 SW1 = 22727.27 Hz

2015-12-03 14:40:21.015
 USER: nmr
 SOLVENT: Acetone - d6
 Experiment = zg30
 Pulse length = 14.000 usec
 Relaxation delay = 1.000 sec
 NA = 8
 Solvent = Acetone - d6
 PTS1d = 32768
 F1 = 300.130005 MHz
 F2 = 1.000000 MHz
 SW1 = 6188.12 Hz



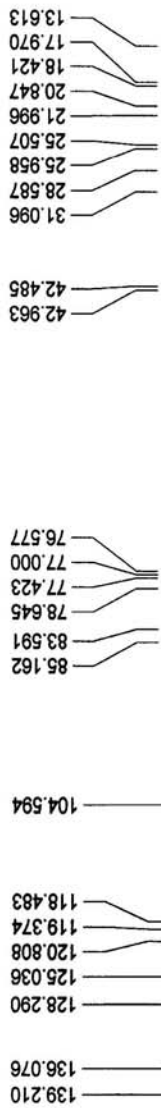
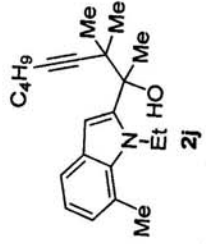




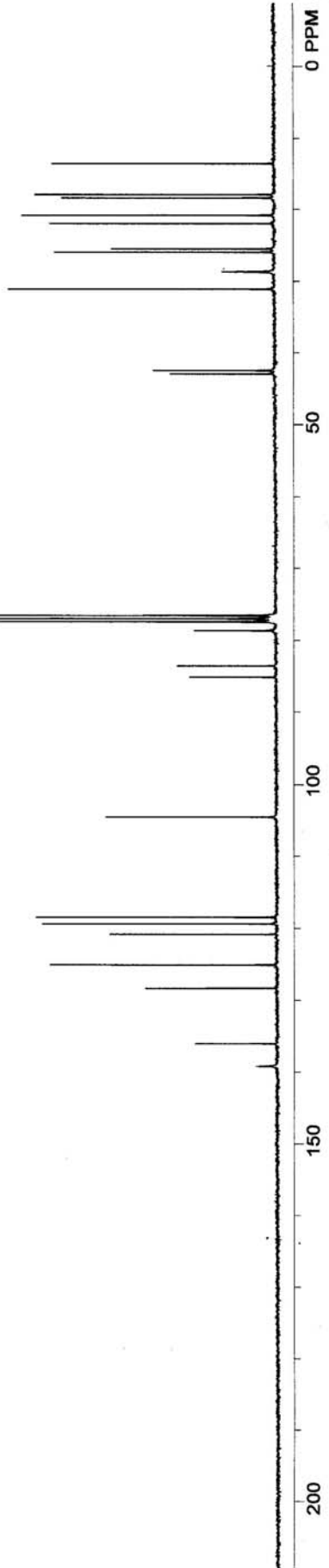
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 SOLVENT: CDCl₃
 Experiment = zg30
 Pulse length = 14.000 usec
 Relaxation delay = 1.000 sec
 NA = 8
 Solvent = CDCl₃
 PTS1d = 32768
 F1 = 300.130005 MHz
 F2 = 1.000000 MHz
 SW1 = 6188.12 Hz

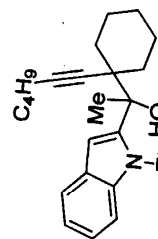
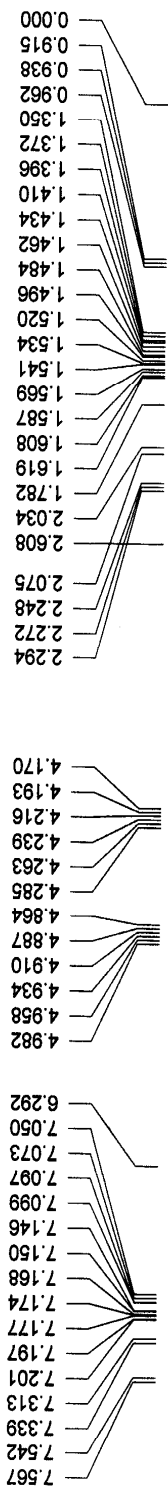
zj-1-049

2014-04-26 18:50:57.703
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 SOLVENT: CDCl3
 Experiment = zgpg30
 Pulse length = 9.500 usec
 Relaxation delay = 2.000 sec
 NA = 1967
 Solvent = CDCl3
 PTS1d = 32768
 F1 = 75.467751 MHz
 F2 = 1,000000 MHz
 SW1 = 22727.27 Hz



zj-1-049

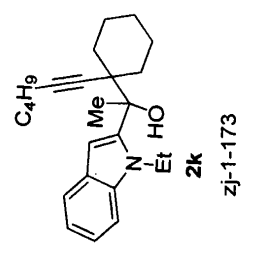
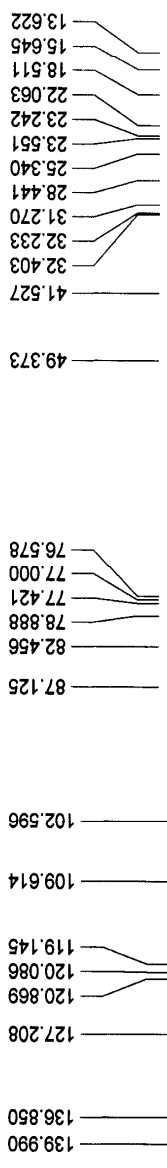




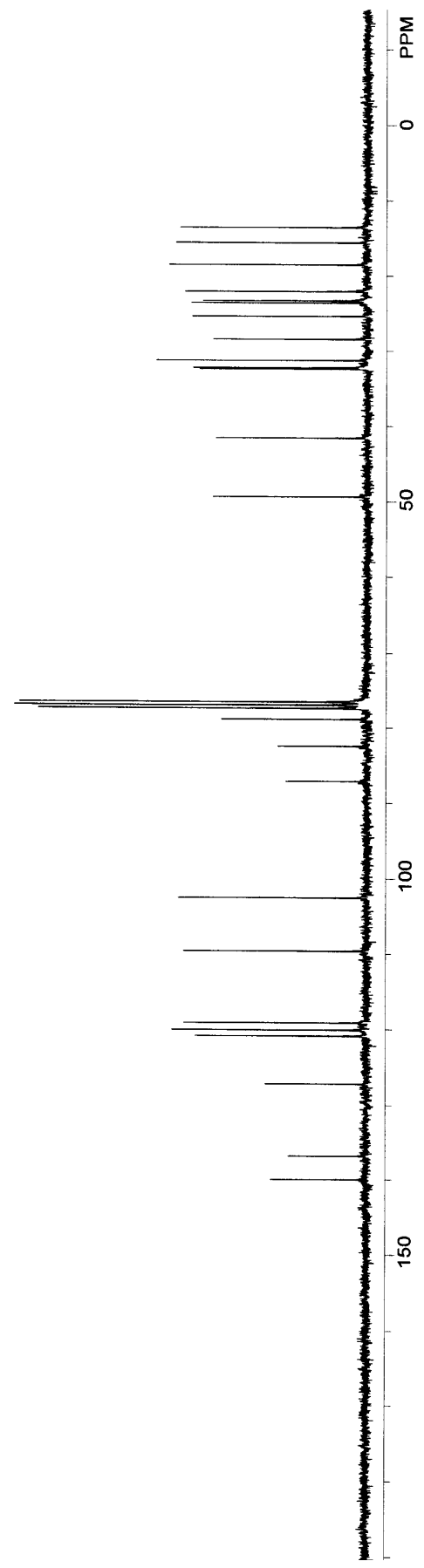
spect, CDCI3,
 Mon Feb 02 07:03:42 2015
 USER: nmr
 SOLVENT:
 Experiment = zg30
 Pulse length = 14.000 usec
 Recycle delay = 1.000 sec
 NA = 8
 PTS1d = 32768
 F1 = 300.131866 MHz
 F2 = 1.000000 MHz
 SW1 = 6188.12 Hz

zj-1-173

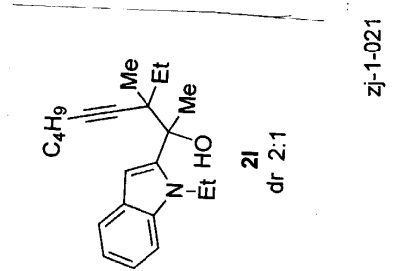




spec: CDCl3
 Wed Sep 24 02:33:28 2014
 USER: nmr
 SOLVENT:
 Experiment = zgg930
 Pulse length = 9.500 usec
 Recycle delay = 2.000 sec
 NA = 6383
 PTS1d = 32768
 F1 = 75.476807 MHz
 F2 = 1.000000 MHz
 SW1 = 22727.27 Hz



7.551
7.526
7.329
7.303
7.190
7.182
7.167
7.163
7.140
7.136
7.089
7.085
7.063
7.059
7.039
7.036
6.312
6.299
5.025
5.001
4.978
4.955
4.931
4.908
4.320
4.298
4.274
4.251
4.228
4.205
2.539
2.252
2.229
2.206
2.012
1.935
1.954
1.972
1.992
1.922
1.972
1.657
1.632
1.608
1.564
1.542
1.529
1.515
1.505
1.491
1.457
1.438
1.409
1.390
1.367
1.343
1.178
1.101
0.964
0.950
0.939
0.926
0.914
0.902
0.872
-0.000



2014-03-28 21:18:10.890
 USER: nmr
 SOLVENT: CDCl3
 Experiment = zg30
 Pulse length = 14.000 usec
 Relaxation delay = 1.000 sec
 NA = 8
 Solvent = CDCl3
 PTS1d = 32768
 F1 = 300.130005 MHz
 F2 = 1.000000 MHz
 SW1 = 6188.12 Hz

zj-1-021

6.30

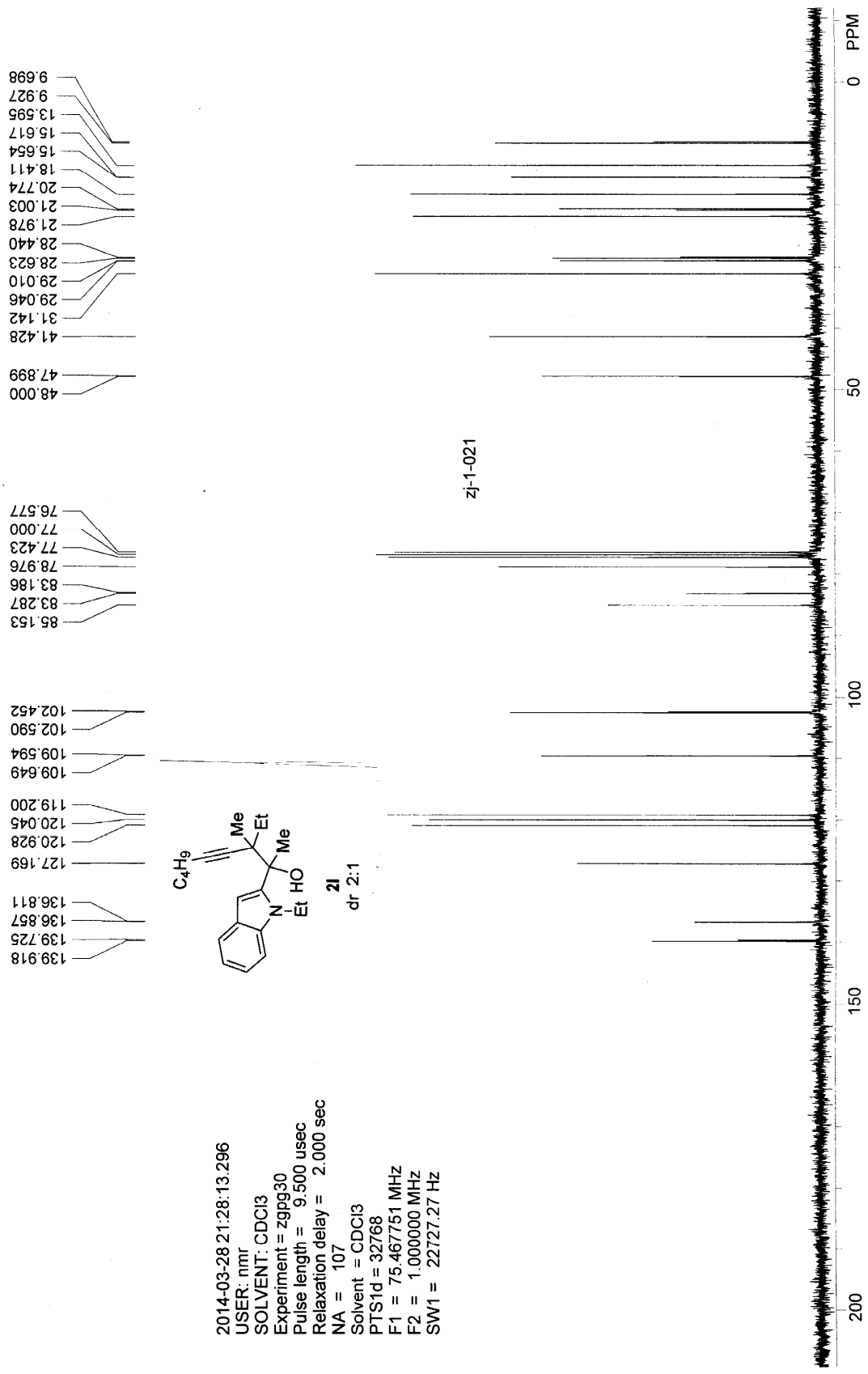
1.00
1.00
1.05
0.65
0.33

1.00
1.00

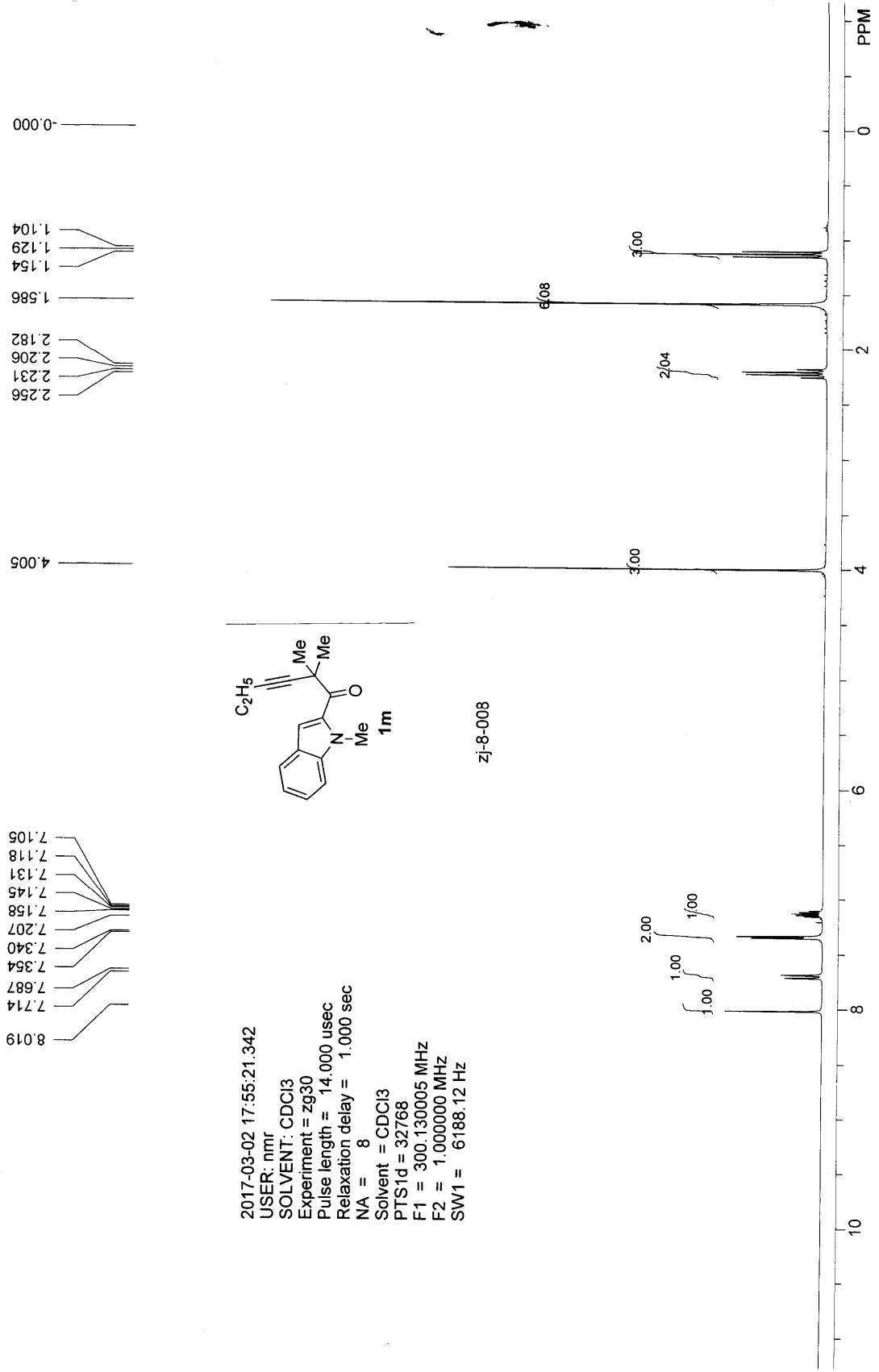
2.00
1.96
1.00
0.72
0.35

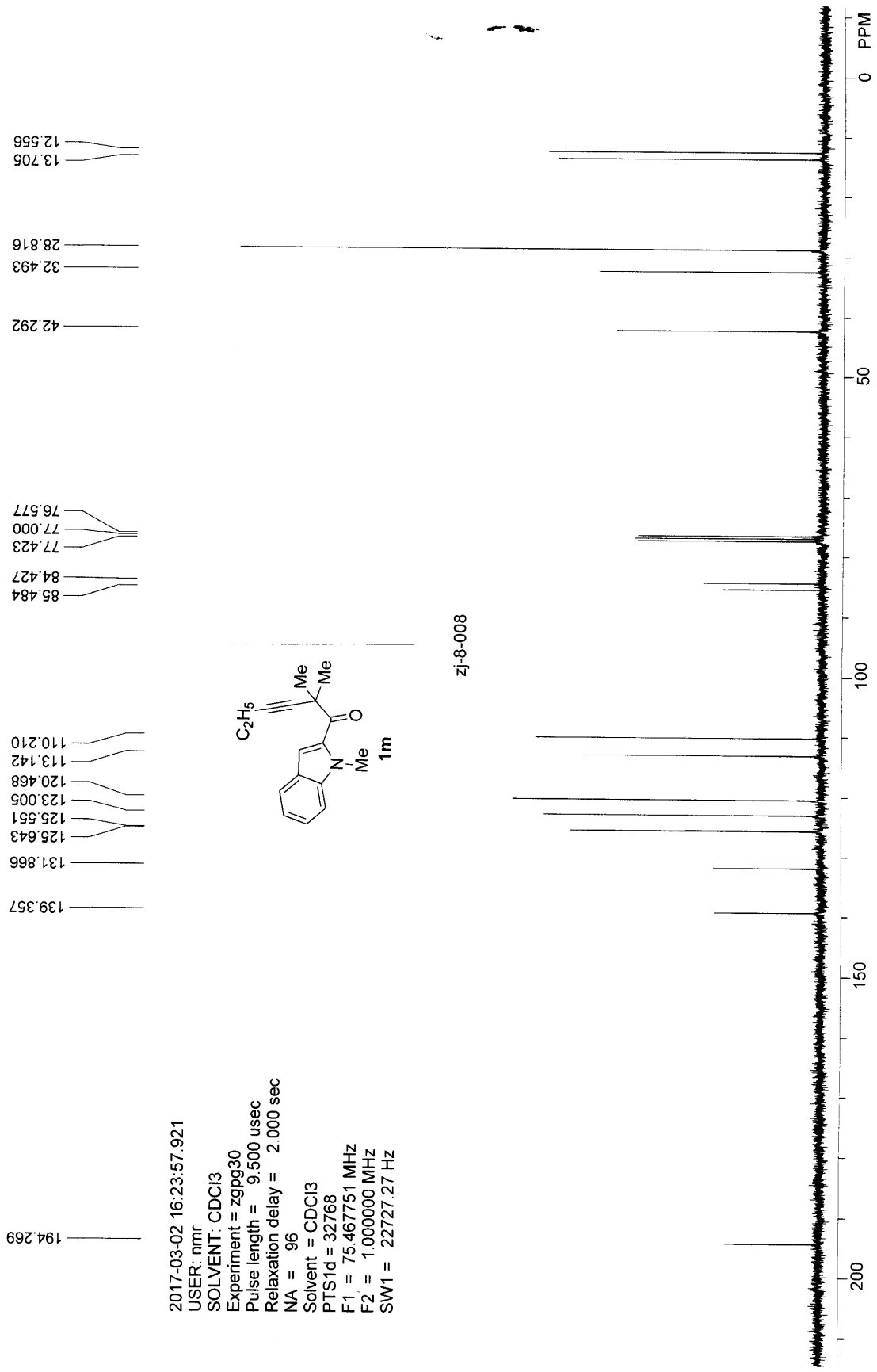
1.04
1.99

10 8 6 4 2 0 -2 -4 PPM

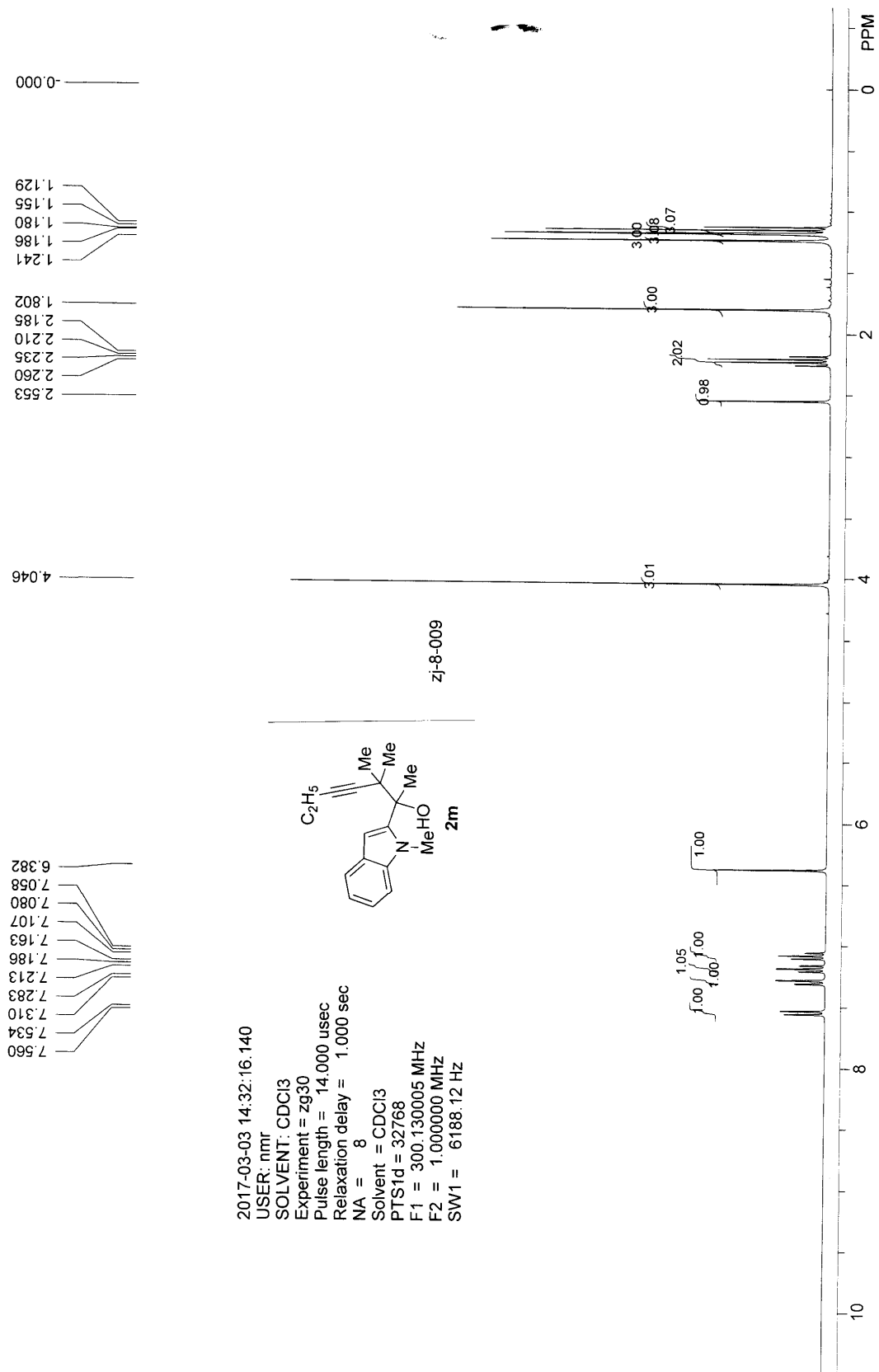


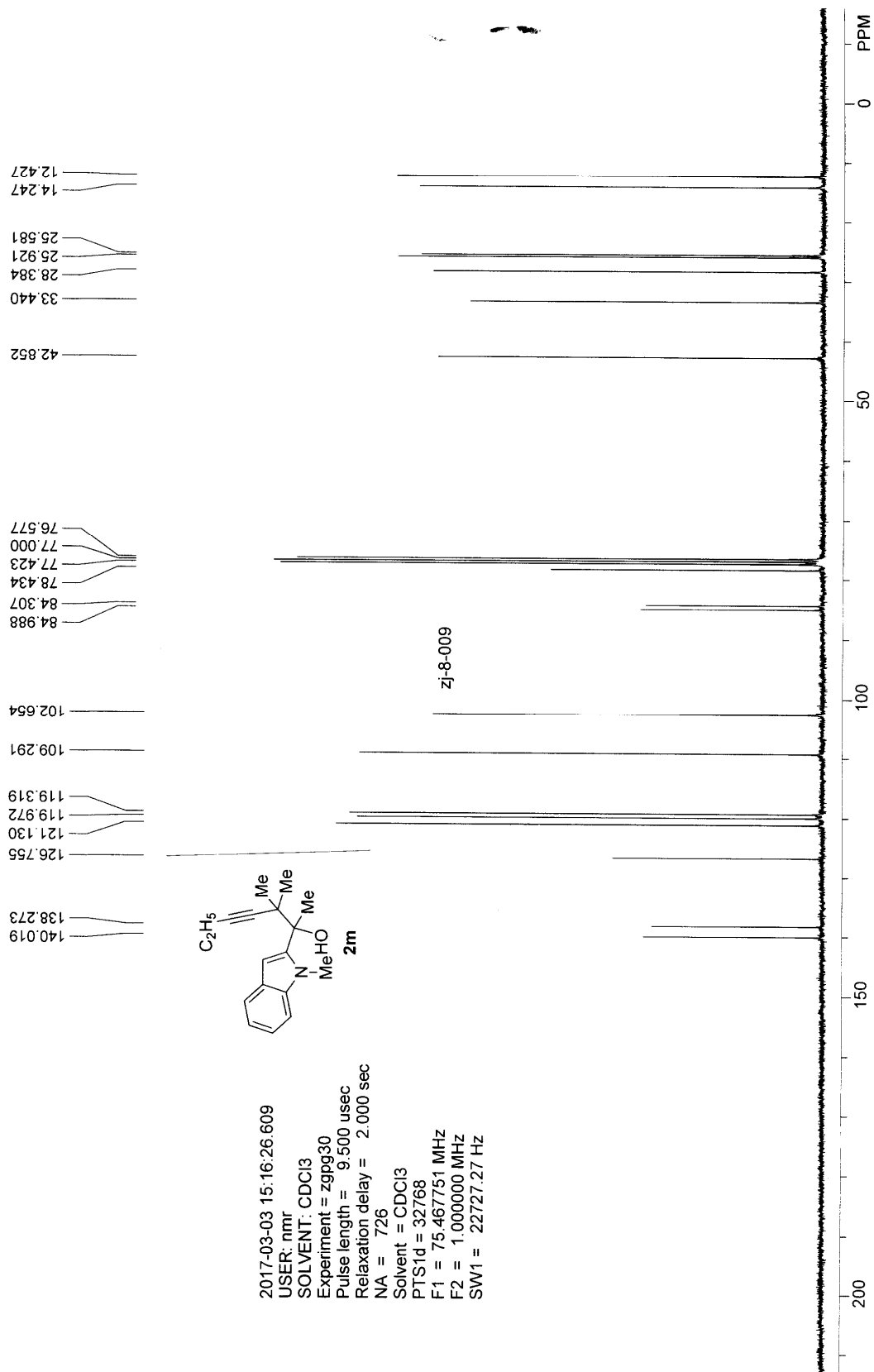
2014-03-28 21:28:13.296
 USER: nmr
 SOLVENT: CDCl3
 Experiment = z9p930
 Pulse length = 9.500 usec
 Relaxation delay = 2.000 sec
 NA = 107
 Solvent = CDCl3
 PTS1d = 32768
 F1 = 75.467751 MHz
 F2 = 1.000000 MHz
 SW1 = 22727.27 Hz

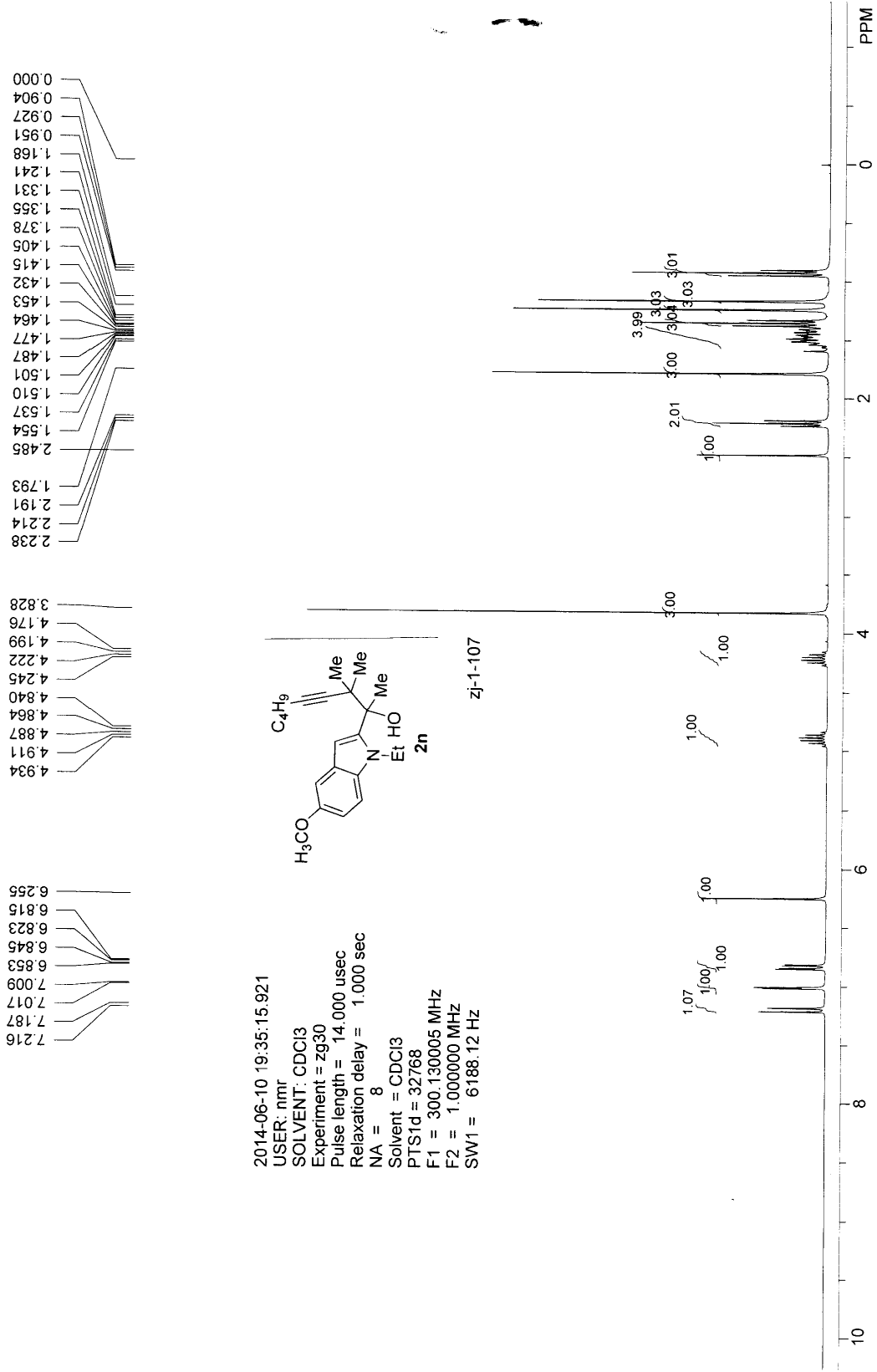


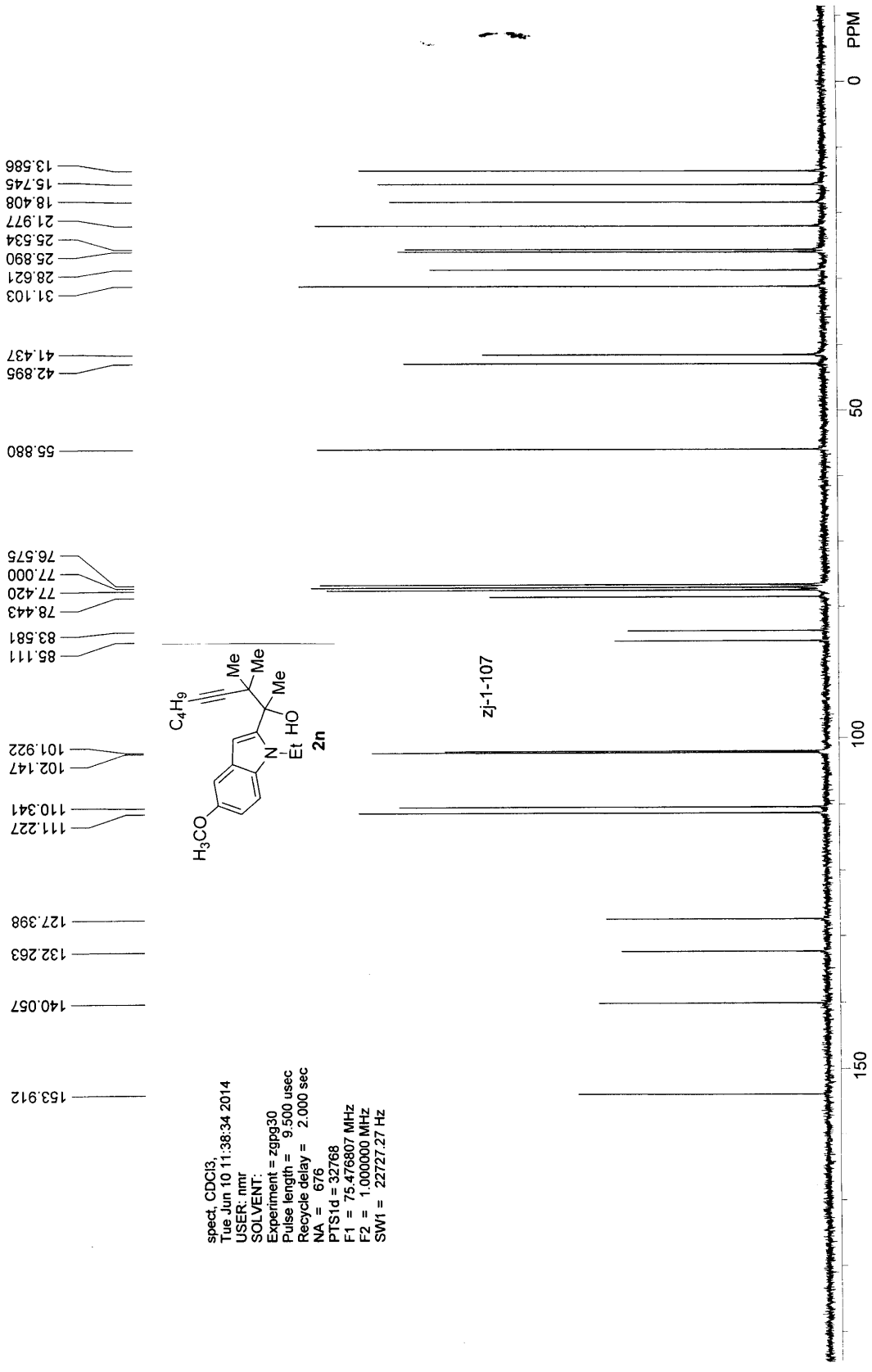


2017-03-02 16:23:57.921
 USER: nmr
 SOLVENT: CDCl3
 Experiment = zgpg30
 Pulse length = 9.500 usec
 Relaxation delay = 2.000 sec
 NA = 96
 Solvent = CDCl3
 PTS1d = 32768
 F1 = 75.467751 MHz
 F2 = 1.000000 MHz
 SW1 = 22727.27 Hz

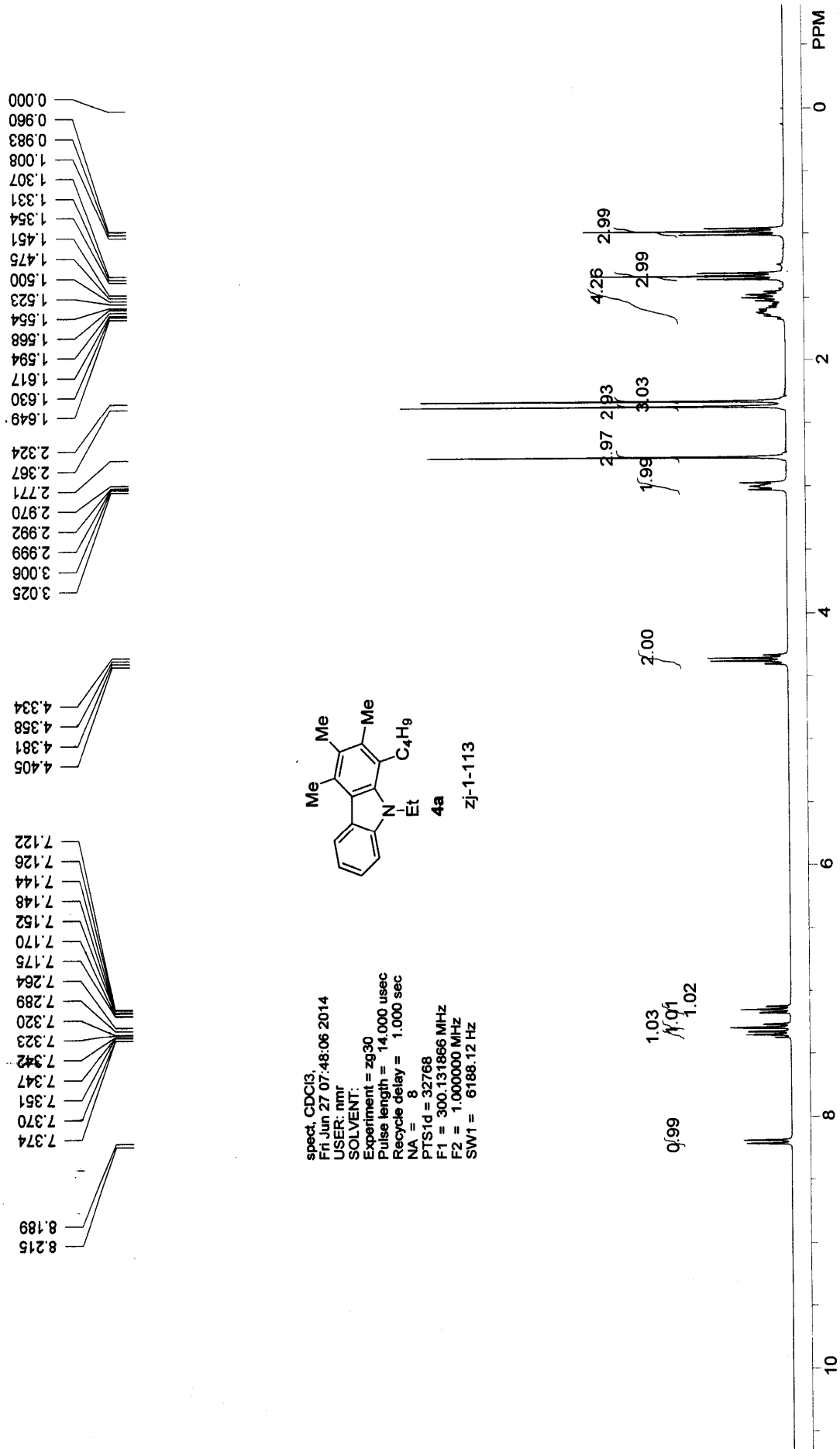


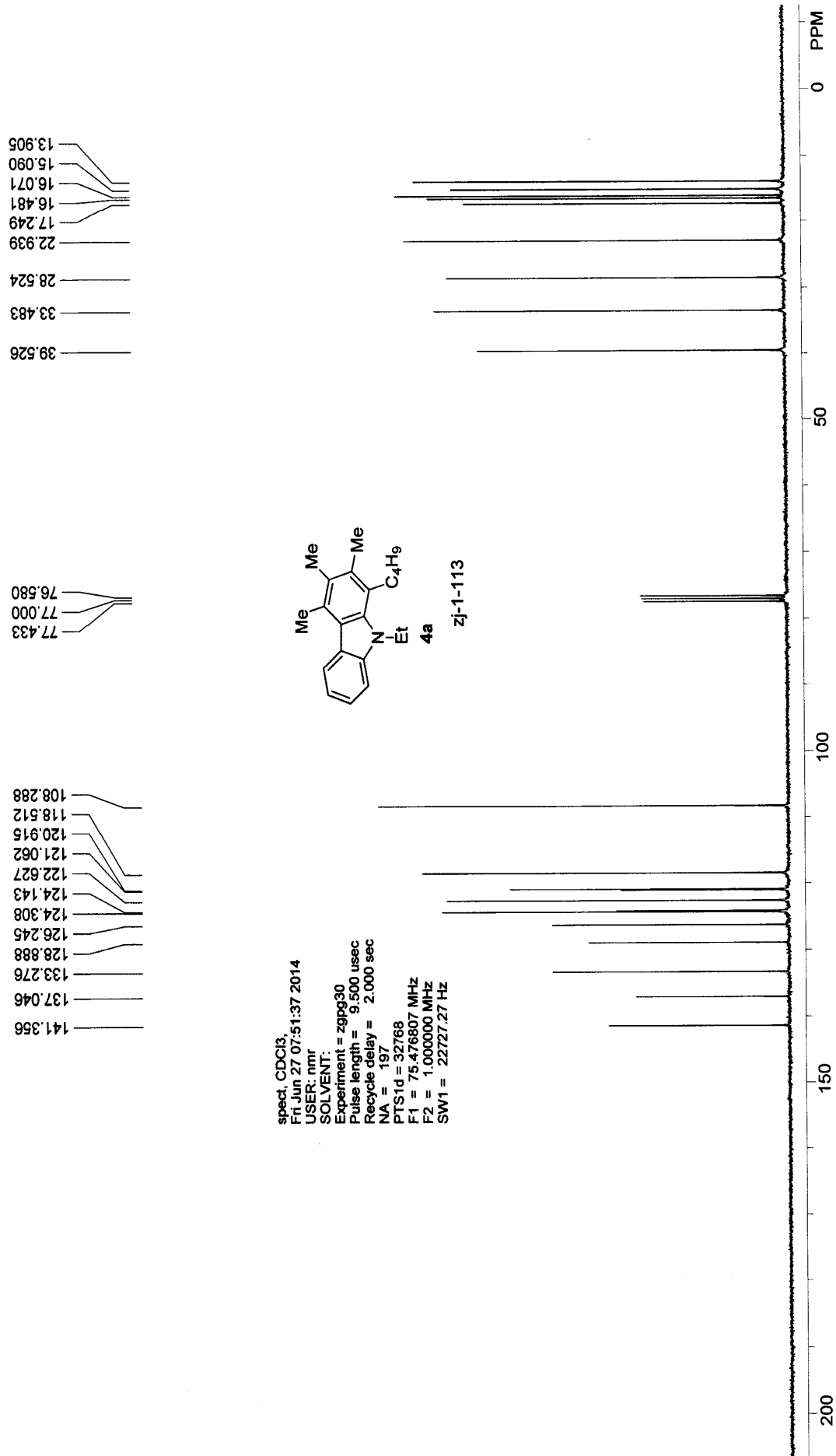






spect. CDCl₃,
 Tue, Jun 10 11:38:34 2014
 USER: nmr
 SOLVENT:
 Experiment = zgpg30
 Pulse length = 9.500 usec
 Recycle delay = 2.000 sec
 NA = 676
 P1S1d = 32768
 F1 = 75.476807 MHz
 F2 = 1.000000 MHz
 SW1 = 22727.27 Hz





spect. CDCl3,
 Fri Jun 27 07:51:37 2014
 USER: nmr
 SOLVENT:
 Experiment = zgpg30
 Pulse length = 9.500 usec
 Recycle delay = 2.000 sec
 NA = 197
 PTS1d = 32768
 F1 = 75.476807 MHz
 F2 = 1.000000 MHz
 SW1 = 22727.27 Hz

13.905
 15.090
 16.071
 16.481
 17.249
 22.939
 28.524
 33.483
 39.526

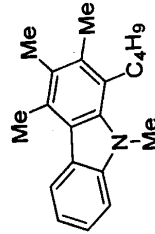
76.580
 77.000
 77.433

108.288
 118.512
 120.915
 121.062
 122.627
 124.143
 124.308
 126.245
 128.888
 133.276
 137.046
 141.356

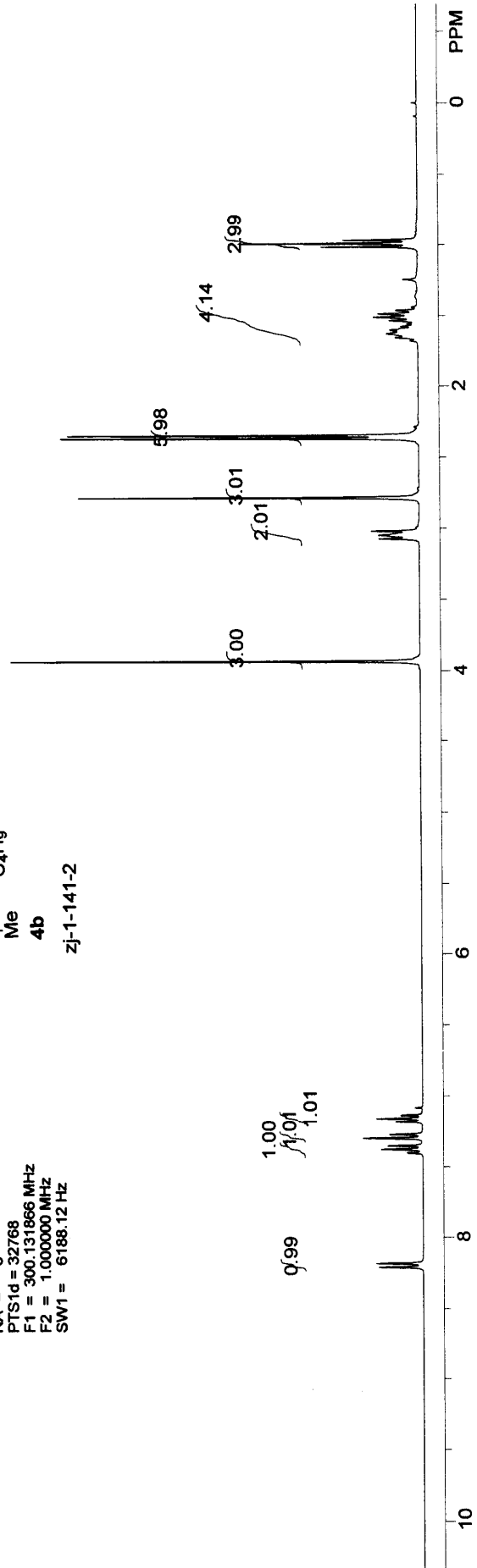
3.931
3.075
3.048
3.019
2.785
2.364
2.344
1.658
1.648
1.629
1.614
1.603
1.593
1.578
1.560
1.535
1.512
1.487
1.464
1.439
1.016
0.992
0.968
0.000

8.209
8.183
7.406
7.403
7.378
7.355
7.352
7.301
7.273
7.185
7.182
7.158
7.135
7.132

spect, CDCl3,
Thu Jul 10 01:52:16 2014
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz



zj-1-141-2

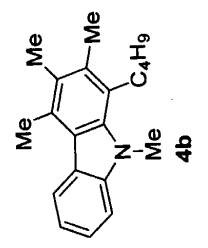


13.948
16.064
16.436
17.227
23.026
28.514
32.889
34.039

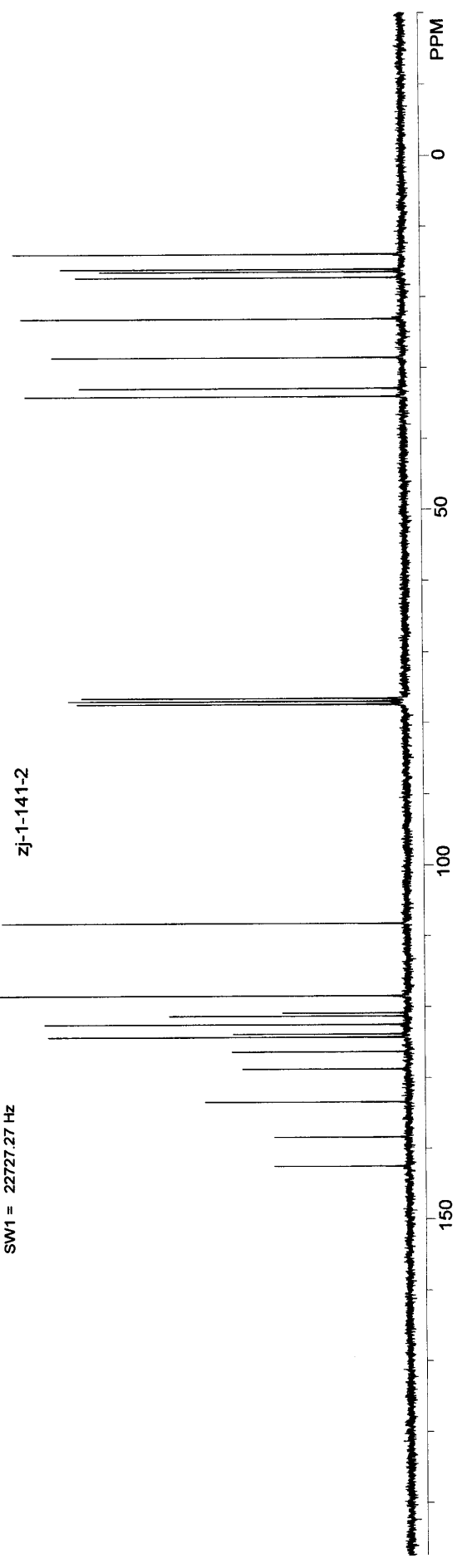
76.575
77.000
77.425

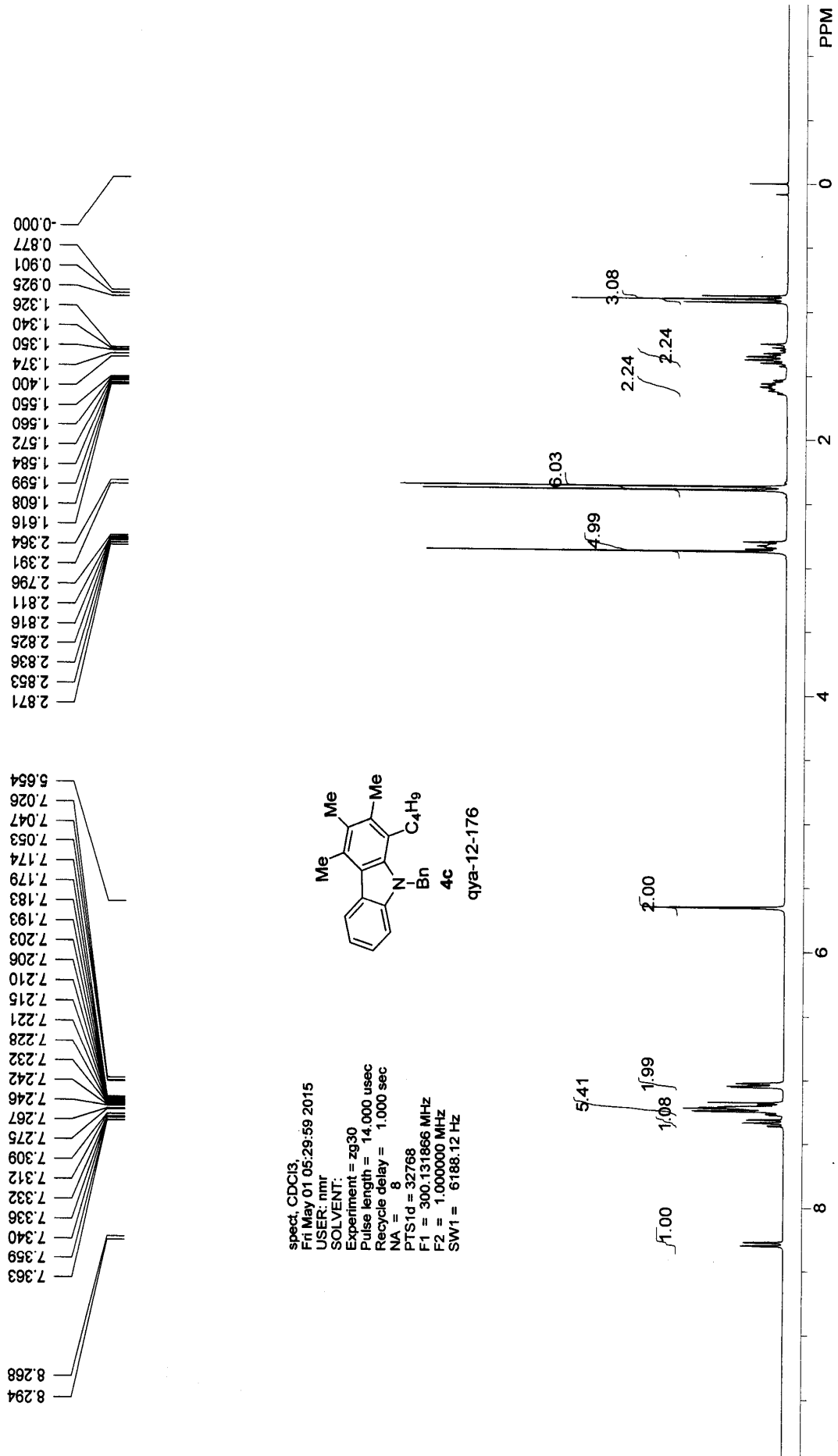
108.273
118.448
120.860
121.314
122.494
123.833
124.266
126.364
128.761
133.370
138.369
142.489

specd, CDCI3,
Thu Jul 10 01:55:18 2014
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 165
PTStd = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz



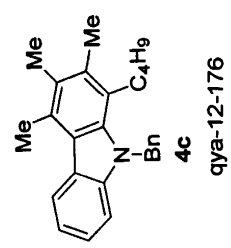
zj-1-141-2



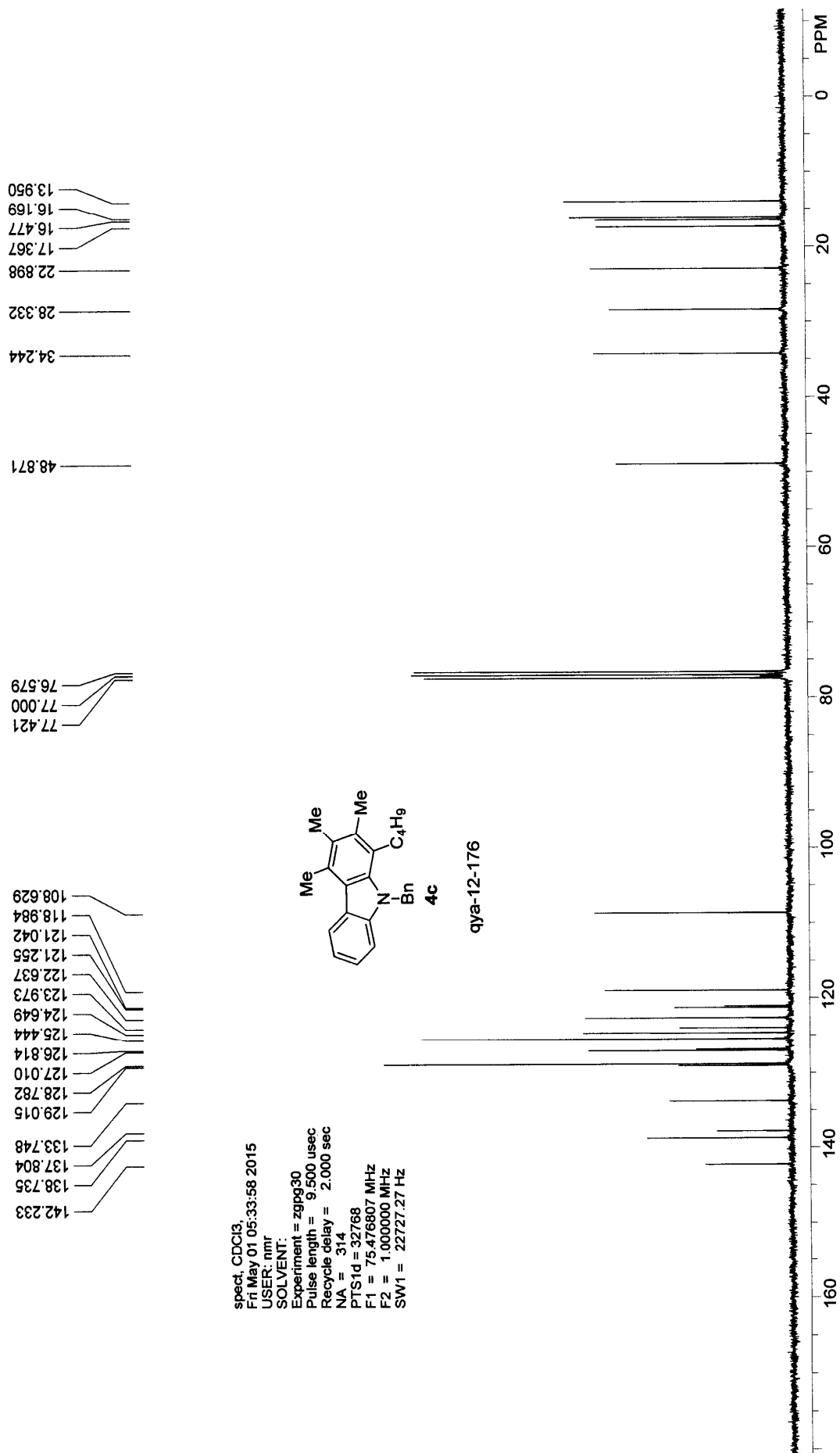


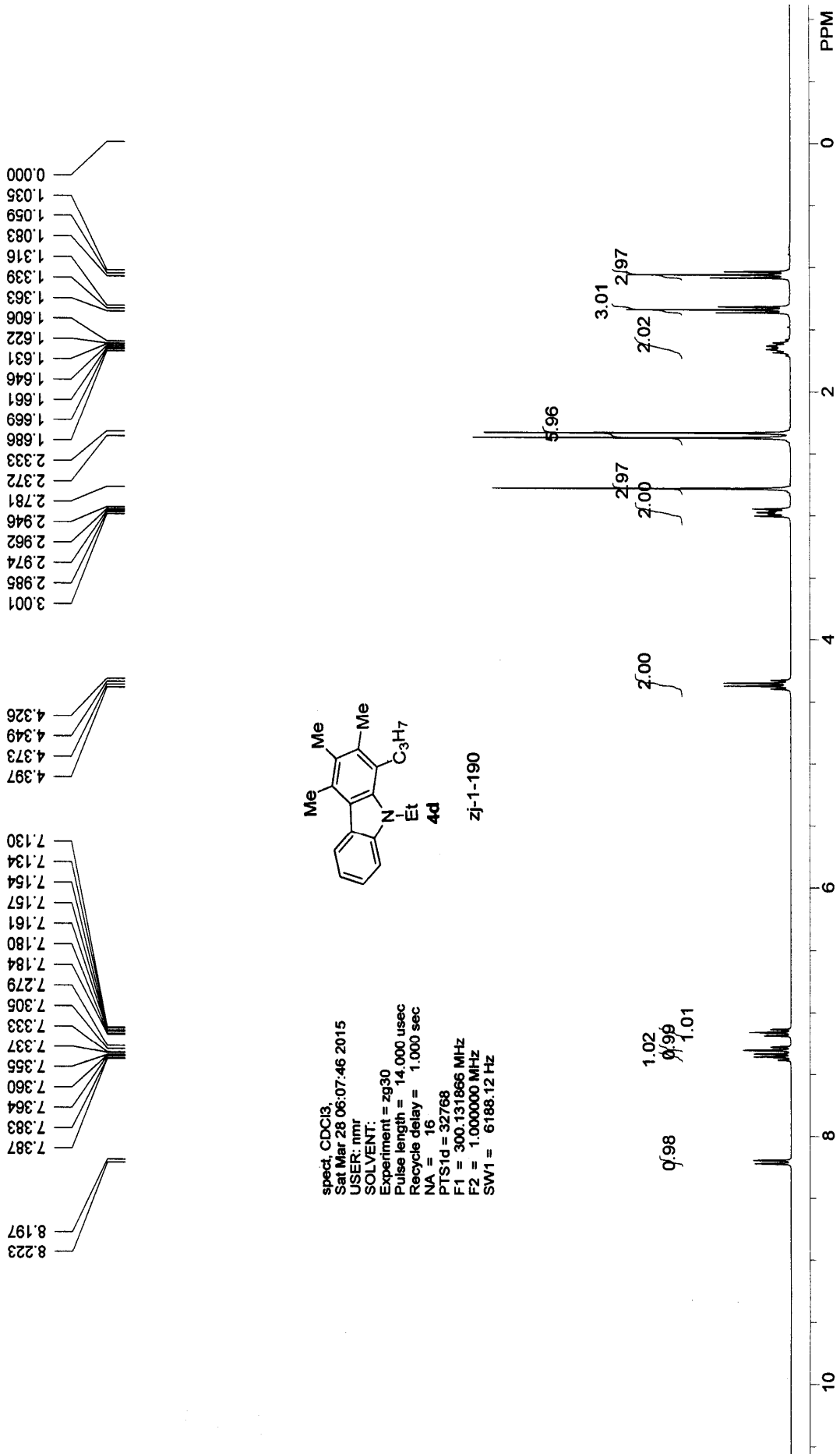
2.871
2.853
2.836
2.825
2.816
2.811
2.796
2.391
2.364
1.616
1.608
1.599
1.584
1.572
1.560
1.550
1.400
1.374
1.350
1.340
1.326
0.925
0.901
0.877
-0.000

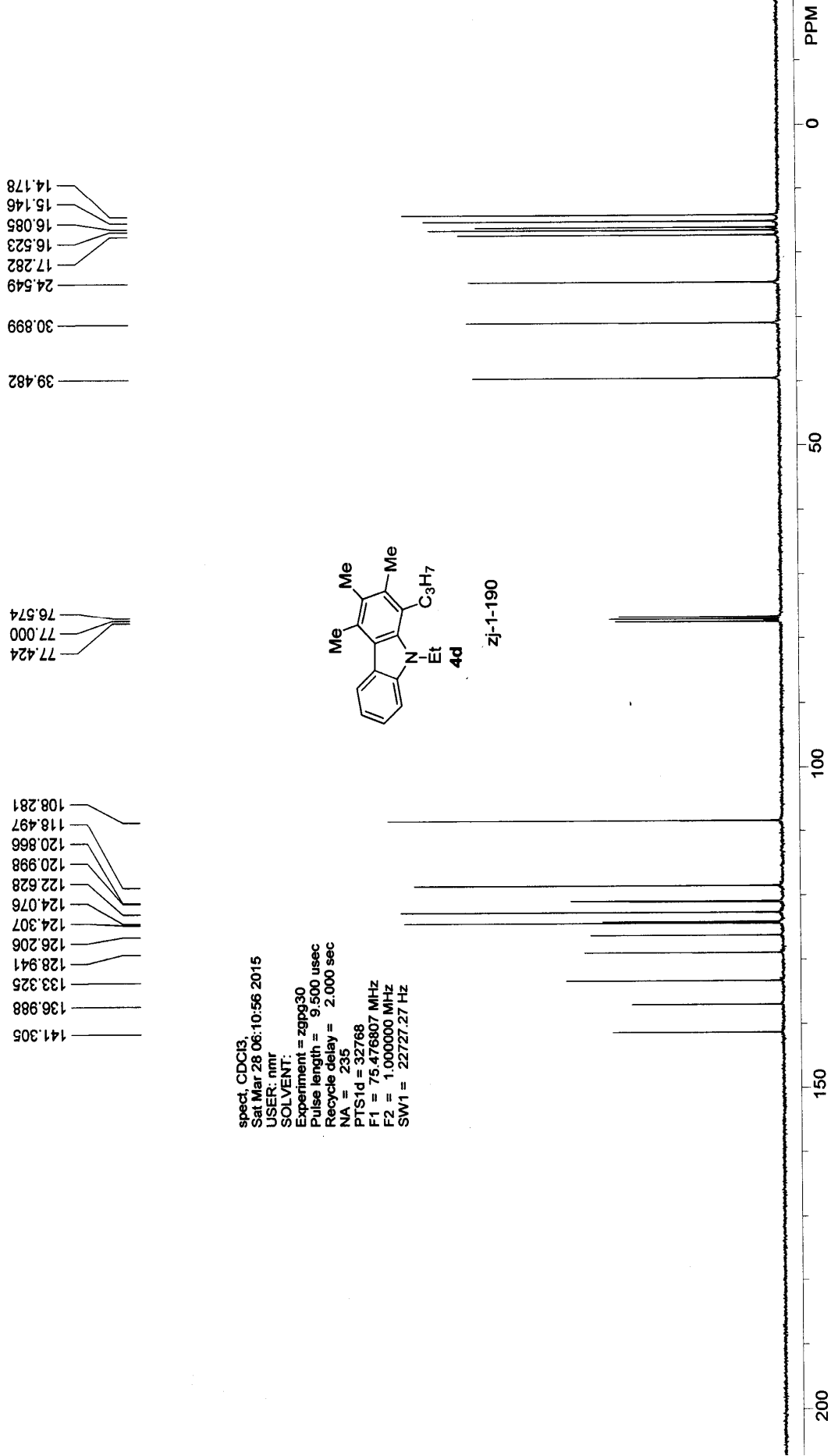
8.294
8.268
7.363
7.359
7.340
7.336
7.332
7.312
7.309
7.275
7.267
7.246
7.242
7.232
7.228
7.221
7.215
7.210
7.206
7.203
7.193
7.183
7.179
7.174
7.053
7.047
7.026
5.654



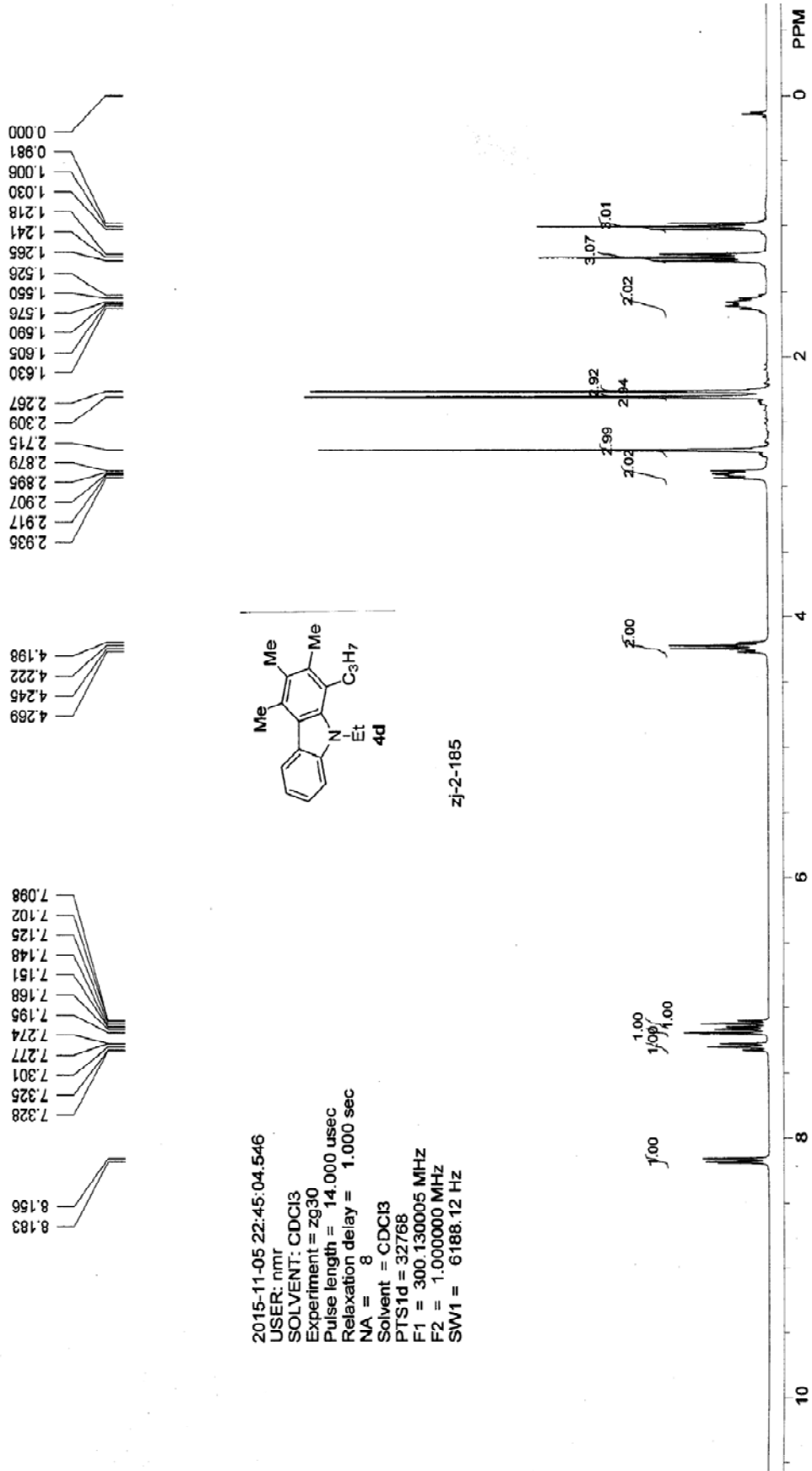
spect, CDCl3,
 Fri May 01 05:29:59 2015
 USER: nmr
 SOLVENT:
 Experiment = zg30
 Pulse length = 14,000 usec
 Recycle delay = 1,000 sec
 NA = 8
 P1 = 32768
 F1 = 300.131866 MHz
 F2 = 1,000,000 MHz
 SW1 = 6188.12 Hz







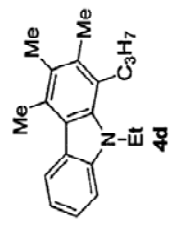
spect, CDCl₃,
 Sat Mar 28 06:10:56 2015
 USER: nmr
 SOLVENT:
 Experiment = zpgg30
 Pulse length = 9.500 usec
 Recycle delay = 2.000 sec
 NA = 235
 PTS1d = 32768
 F1 = 75.476807 MHz
 F2 = 1.000000 MHz
 SW1 = 22727.27 Hz



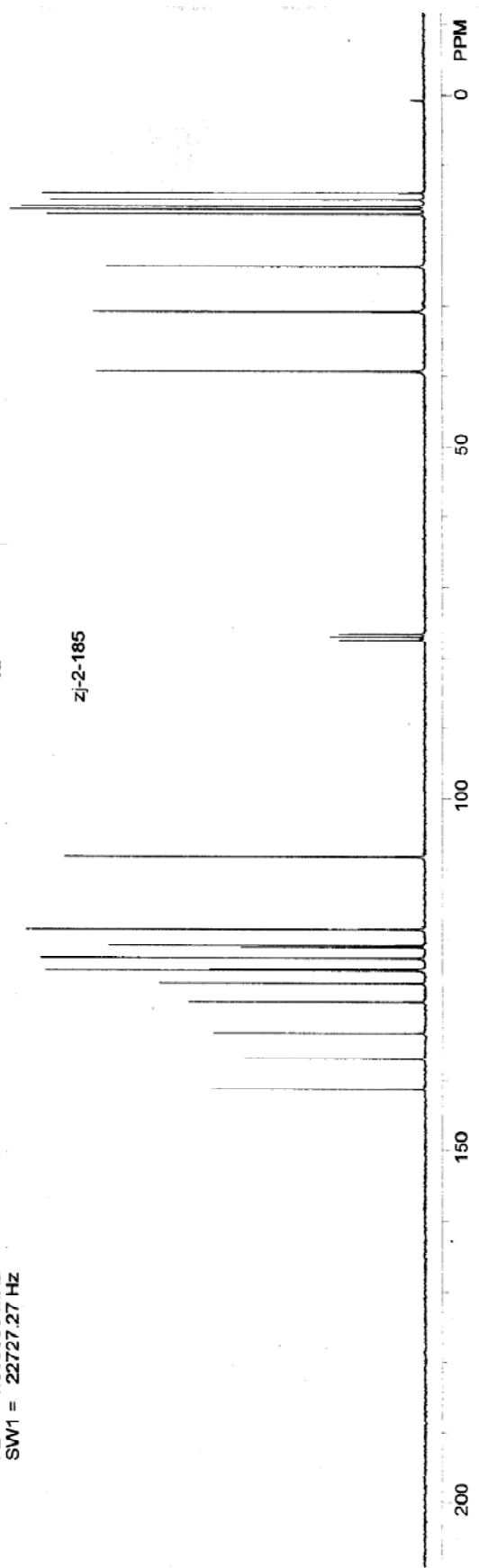
14.091
15.010
16.957
16.398
17.161
24.478
30.829
39.350

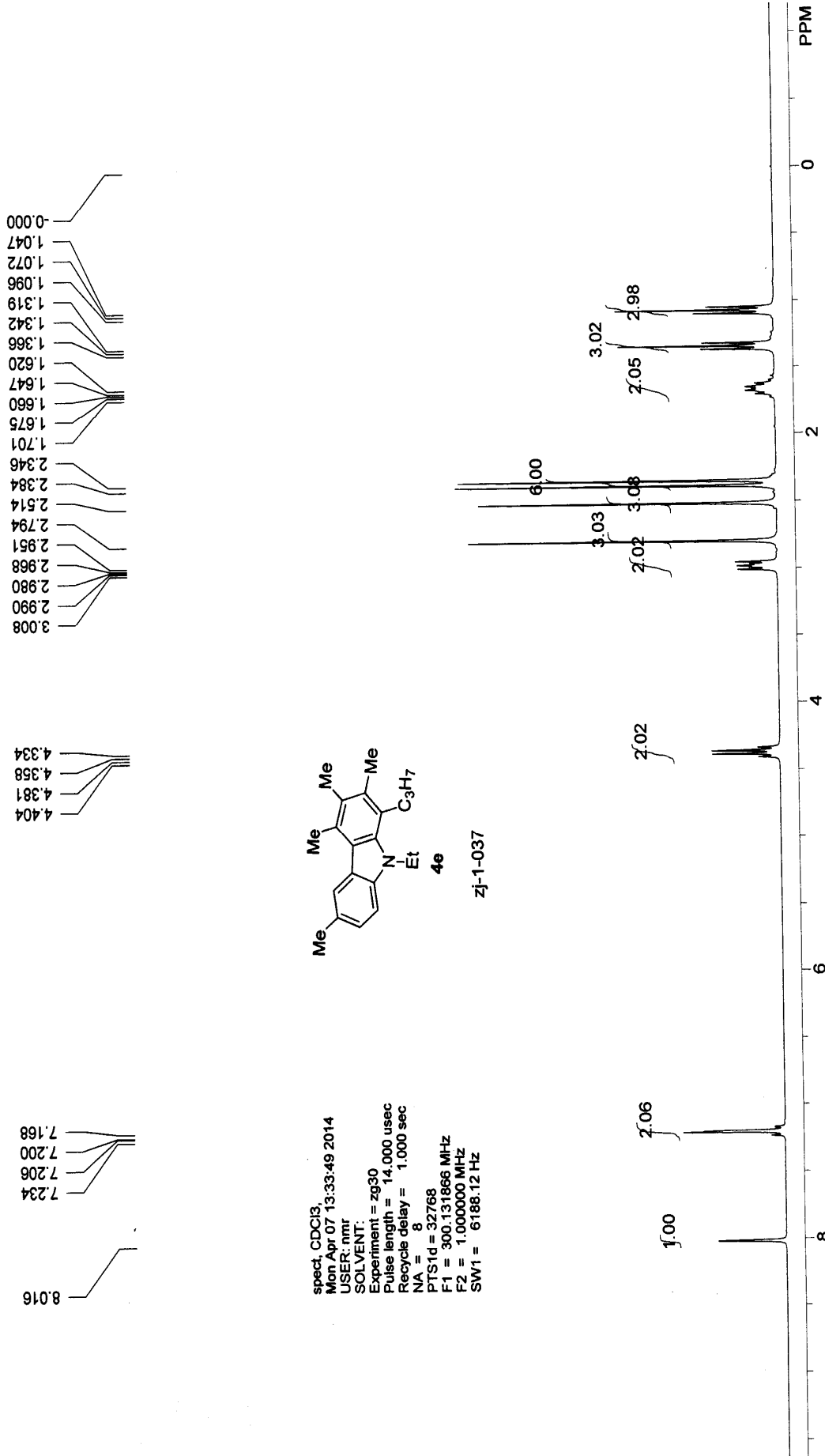
76.577
77.000
77.423

108.234
118.501
120.762
121.029
122.564
124.108
124.273
126.103
128.842
133.199
136.995
141.306

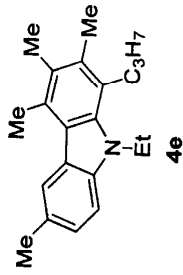


2015-11-05 22:55:25.156
USER: nmr
SOLVENT: CDCl₃
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 158
Solvent = CDCl₃
PTS1d = 32768
F1 = 75.467751 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz





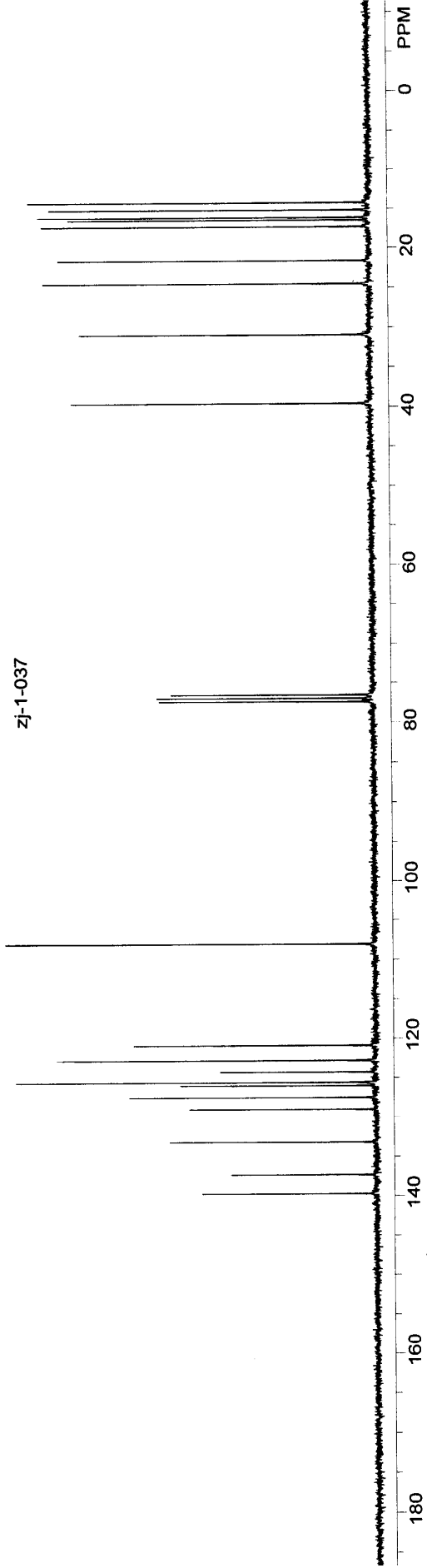
spect, CDCI3,
 Mon Apr 07 13:37:10 2014
 USER: nmr
 SOLVENT:
 Experiment = zgpg30
 Pulse length = 9.500 usec
 Recycle delay = 2.000 sec
 NA = 98
 P1 = 32768
 F1 = 75.476807 MHz
 F2 = 1.000000 MHz
 SW1 = 22727.27 Hz

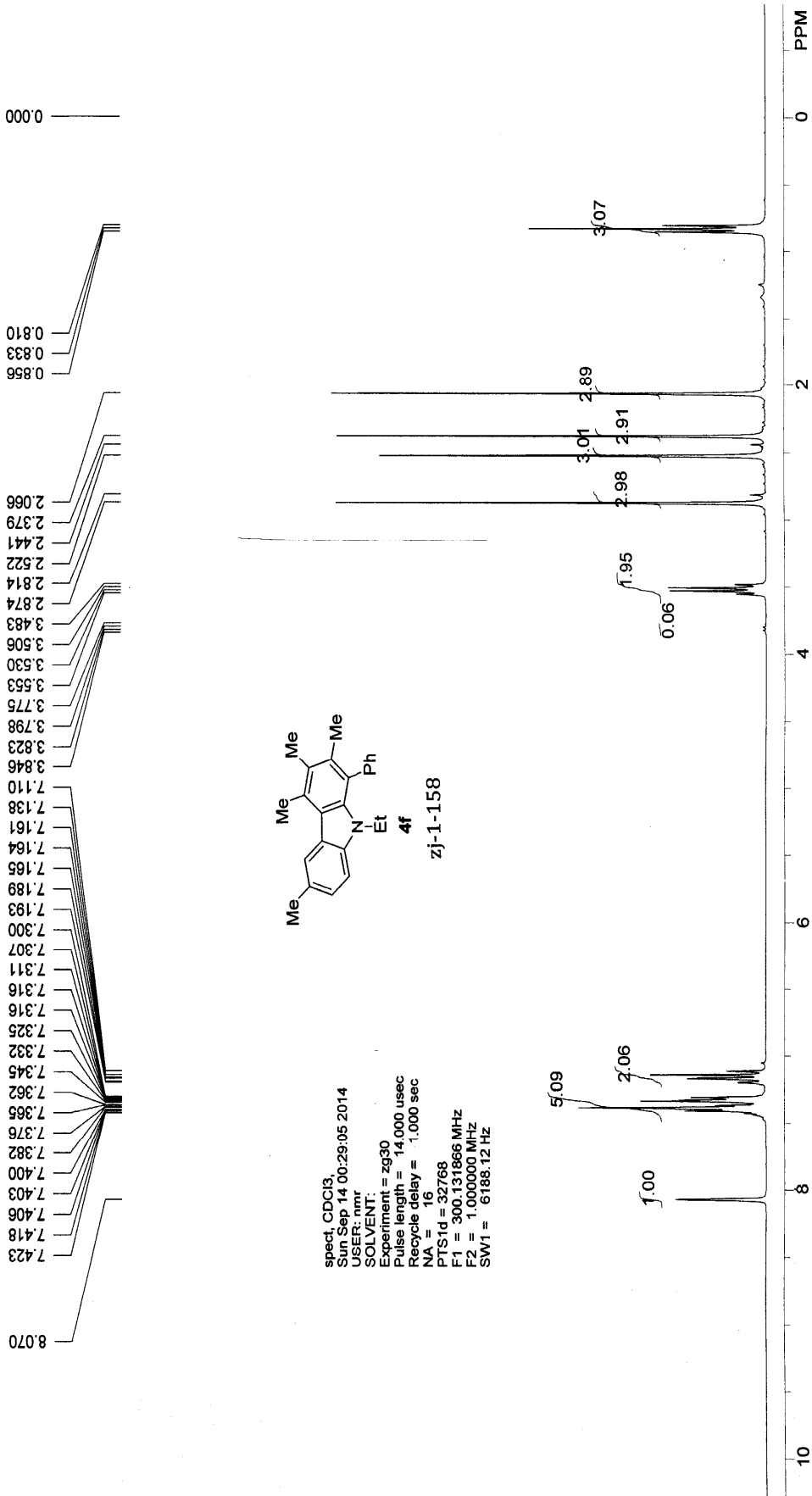


14.209
 15.135
 16.113
 16.531
 17.380
 21.624
 24.514
 30.930
 39.584

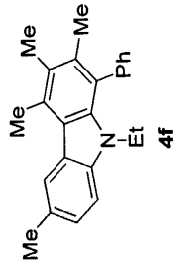
76.575
 77.000
 77.425

108.021
 120.882
 120.913
 122.799
 124.270
 125.560
 125.963
 127.473
 128.979
 133.153
 137.296
 139.703

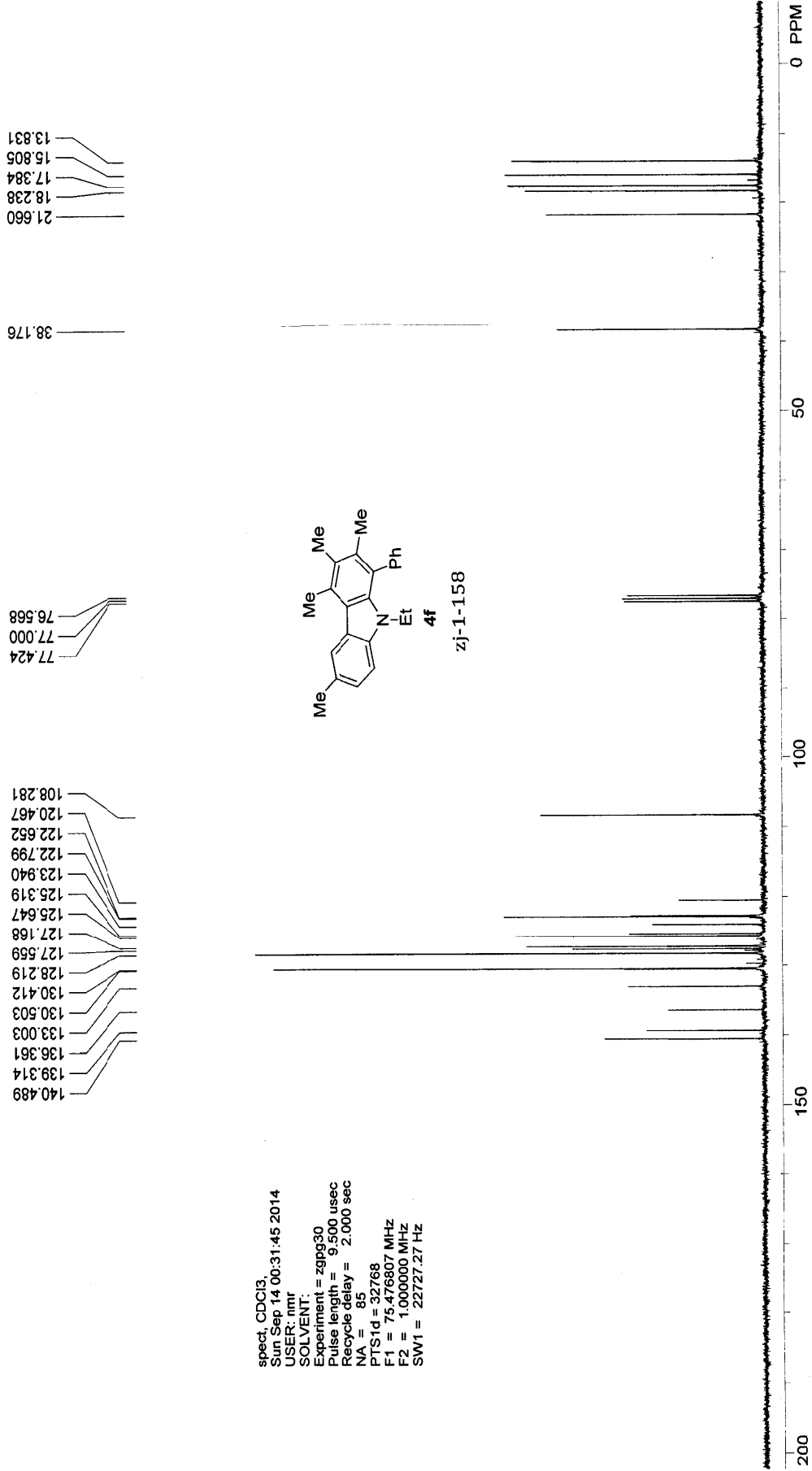


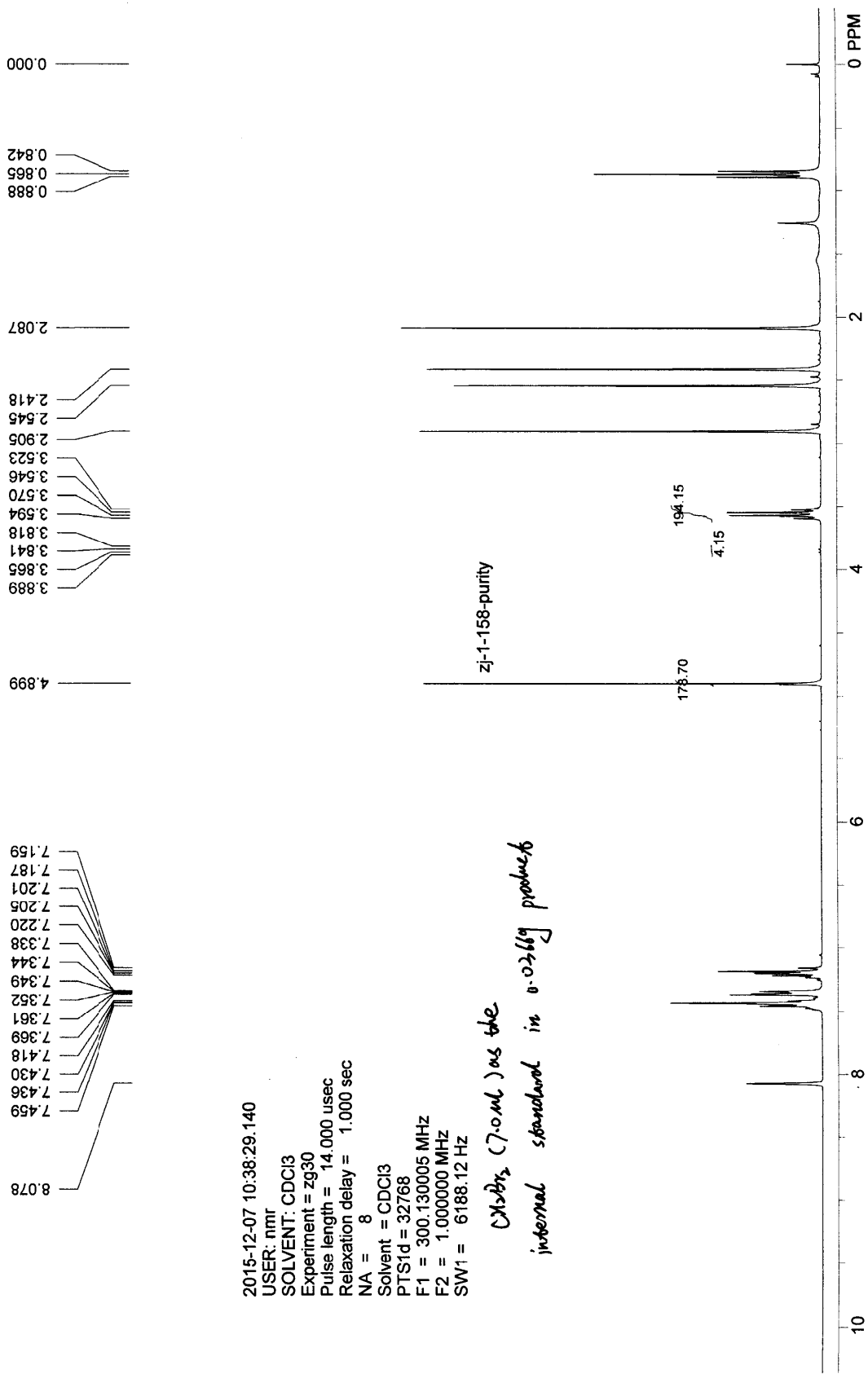


spect, CDCI3,
 Sun Sep 14 00:31:45 2014
 USER: nmr
 SOLVENT:
 Experiment = zgpg30
 Pulse length = 9.500 usec
 Recycle delay = 2.000 sec
 NA = 85
 P1 = 32768
 F1 = 75.476807 MHz
 F2 = 1.0000000 MHz
 SW1 = 222727.27 Hz



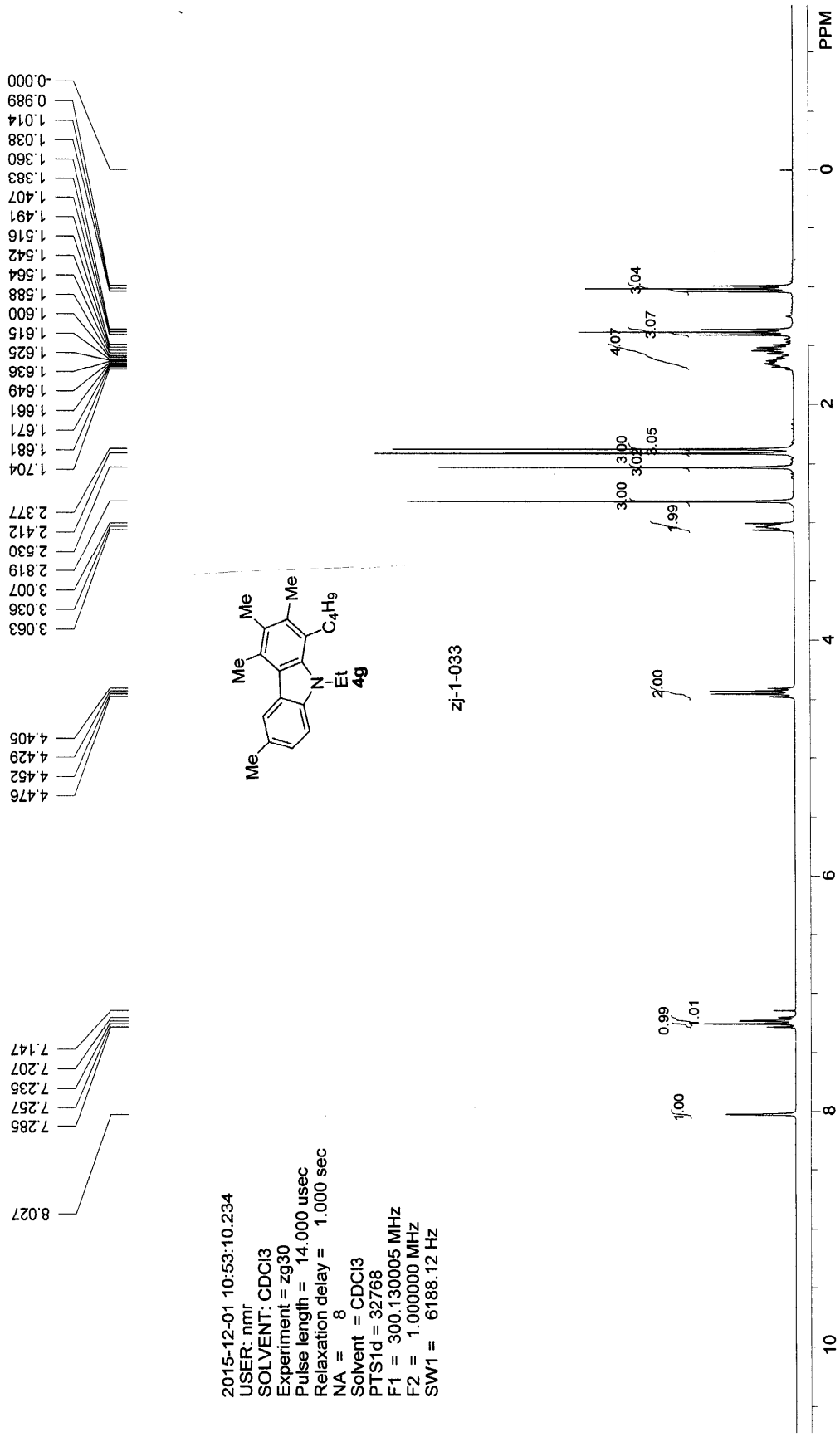
zj-1-158





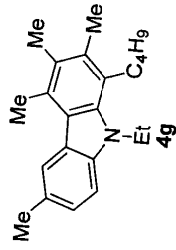
2015-12-07 10:38:29.140
 USER: nmr
 SOLVENT: CDCl3
 Experiment = zg30
 Pulse length = 14.000 usec
 Relaxation delay = 1.000 sec
 NA = 8
 Solvent = CDCl3
 PTS1d = 32768
 F1 = 300.130005 MHz
 F2 = 1.000000 MHz
 SW1 = 6188.12 Hz

*CDCl₃ (7.0 mL) as the
 internal standard in 0.0269 g products*



2015-12-01 10:53:10.234
 USER: nmr
 SOLVENT: CDCl3
 Experiment = zg30
 Pulse length = 14.000 usec
 Relaxation delay = 1.000 sec
 NA = 8
 Solvent = CDCl3
 P1 = 32768
 F1 = 300.130005 MHz
 F2 = 1.000000 MHz
 SW1 = 6188.12 Hz

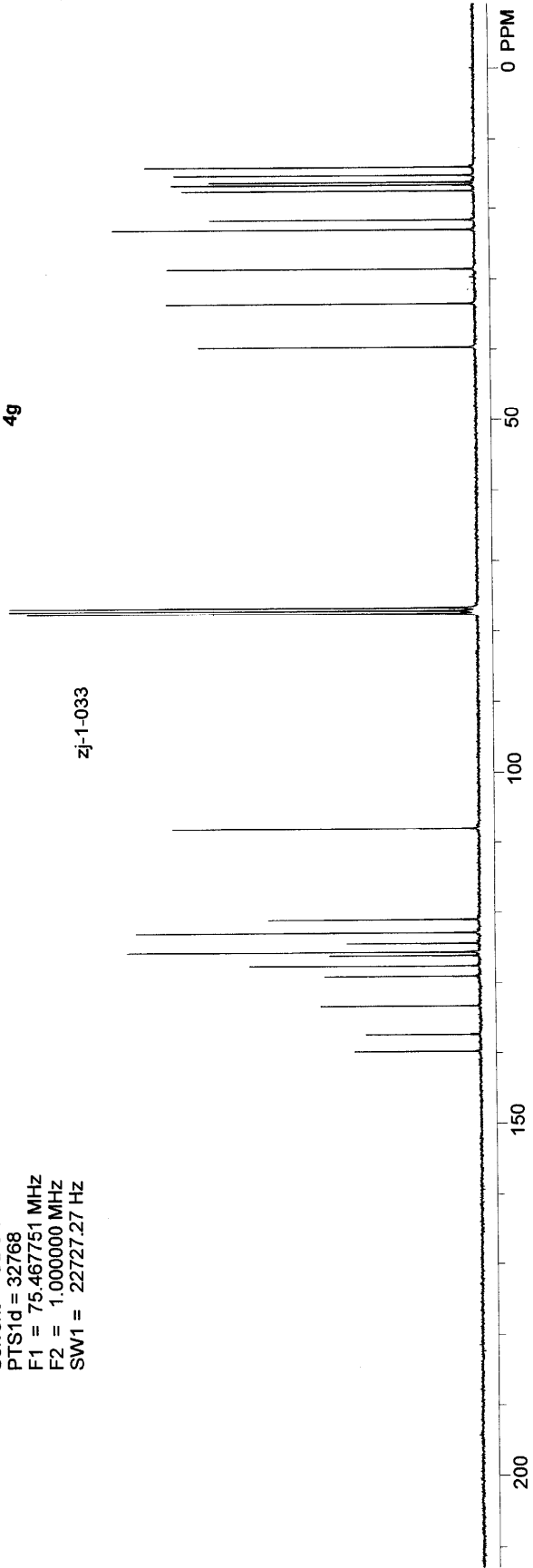
2015-12-01 13:29:41.609
 USER: nmr
 SOLVENT: CDCl3
 Experiment = zgpg30
 Pulse length = 9.500 usec
 Relaxation delay = 2.000 sec
 NA = 2253
 Solvent = CDCl3
 PTS1d = 32768
 F1 = 75.467751 MHz
 F2 = 1.000000 MHz
 SW1 = 22727.27 Hz

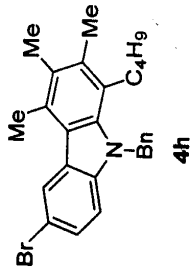
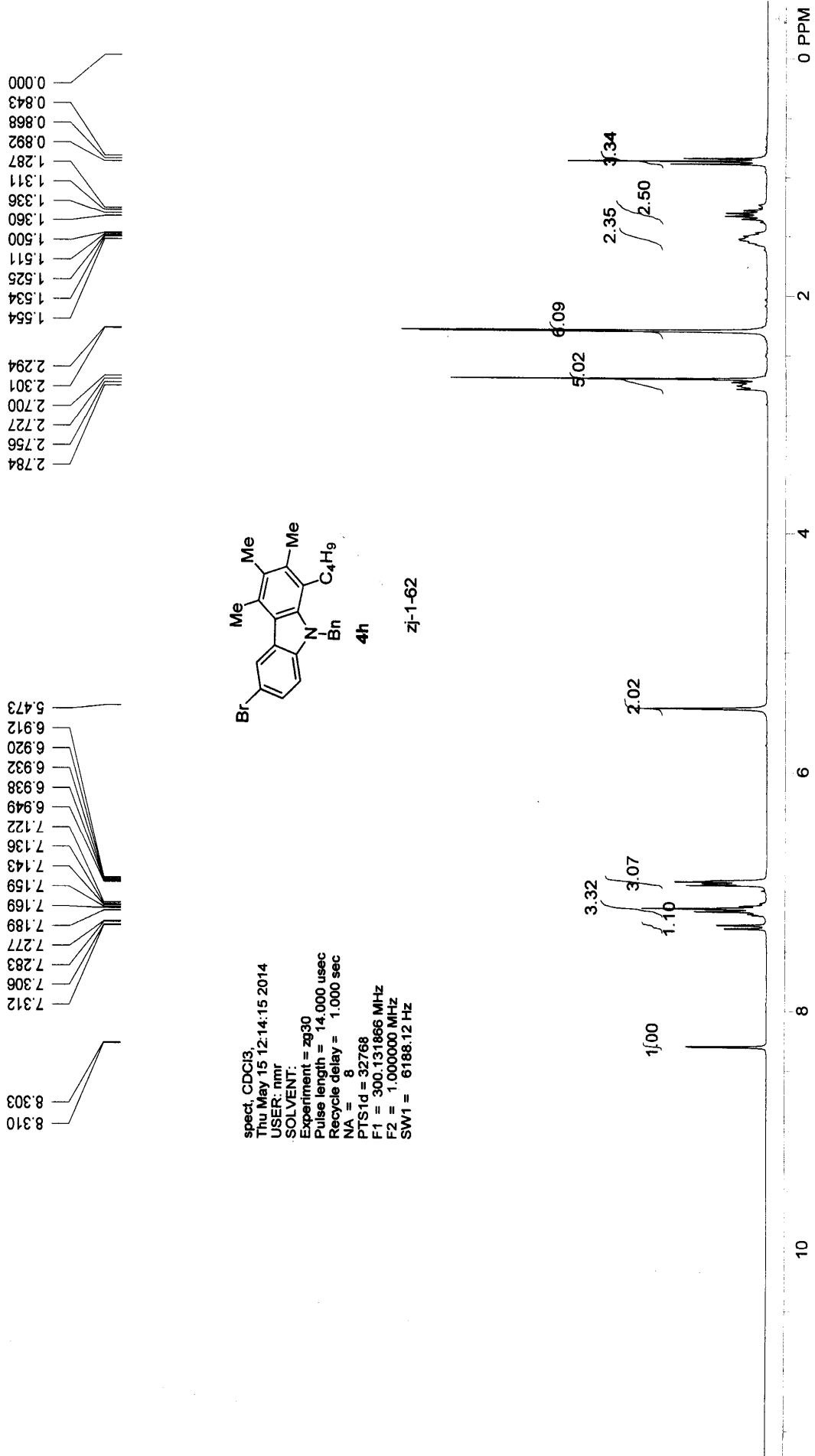


13.935
 15.121
 16.141
 16.527
 17.391
 21.619
 22.980
 28.559
 33.458
 39.672

76.577
 77.000
 77.423

108.050
 120.965
 120.992
 122.858
 124.338
 125.579
 126.075
 127.537
 128.989
 133.180
 137.363
 139.771





spect, CDCl3,
 Thu May 15 12:14:15 2014
 USER: nmr
 SOLVENT:
 Experiment = zg30
 Pulse length = 14.000 usec
 Recycle delay = 1.000 sec
 NA = 8
 PTS1d = 32768
 F1 = 300.131866 MHz
 F2 = 1.000000 MHz
 SW1 = 6188.12 Hz

2.784
 2.756
 2.727
 2.700
 2.301
 2.294
 1.554
 1.534
 1.525
 1.511
 1.500
 1.360
 1.336
 1.311
 1.287
 0.892
 0.868
 0.843
 0.000

7.312
 7.306
 7.283
 7.277
 7.189
 7.169
 7.169
 7.143
 7.136
 7.122
 6.949
 6.938
 6.932
 6.920
 6.912
 5.473

2.35
 3.34
 2.50

6.09

5.02

2.02

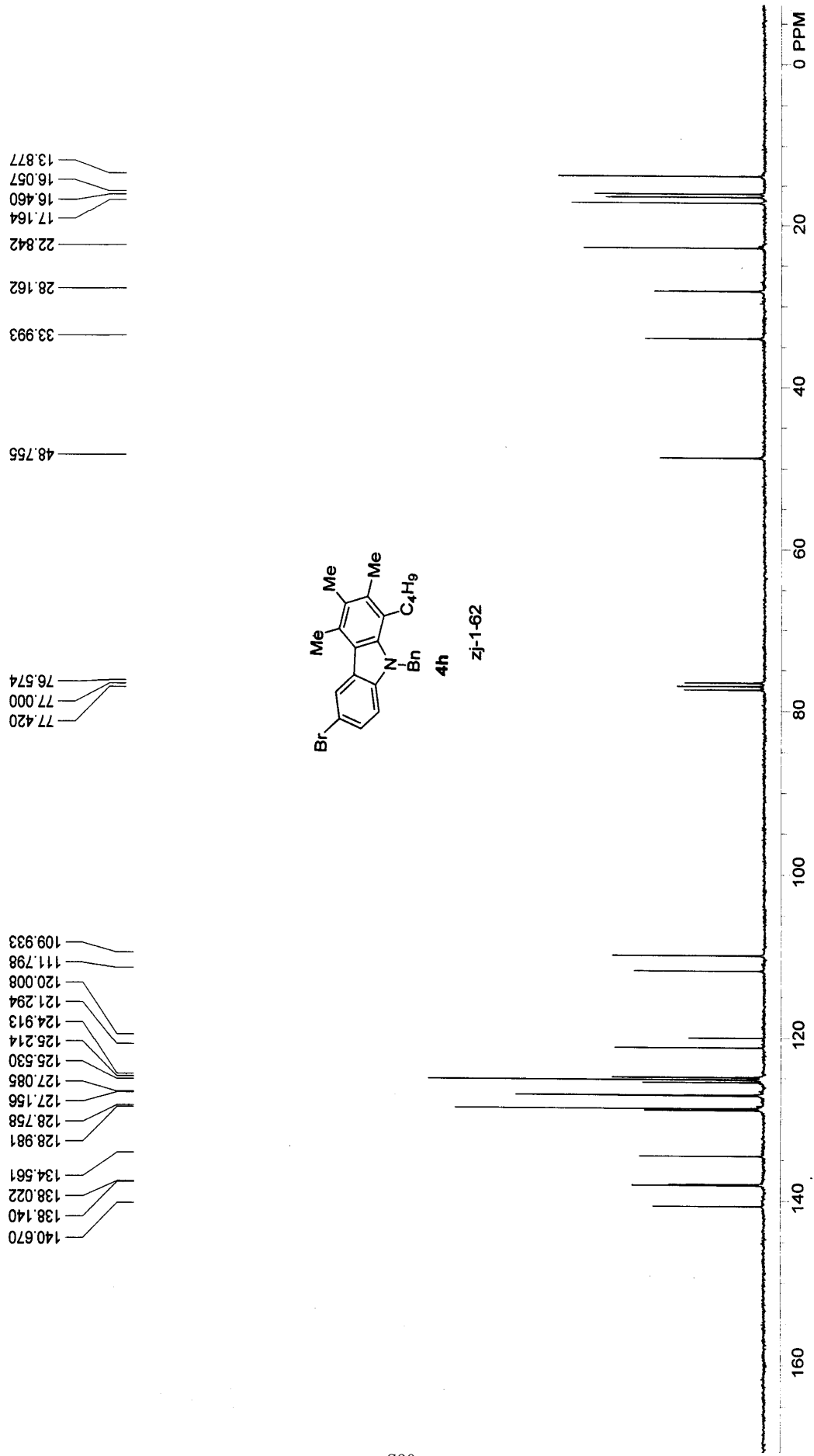
3.32

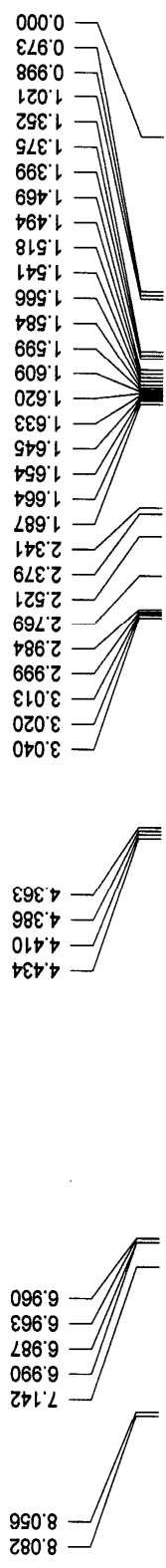
3.07

1.10

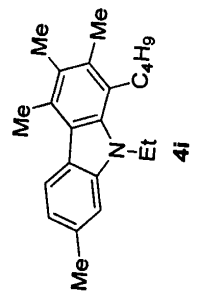
1.00

10 8 6 4 2 0 PPM

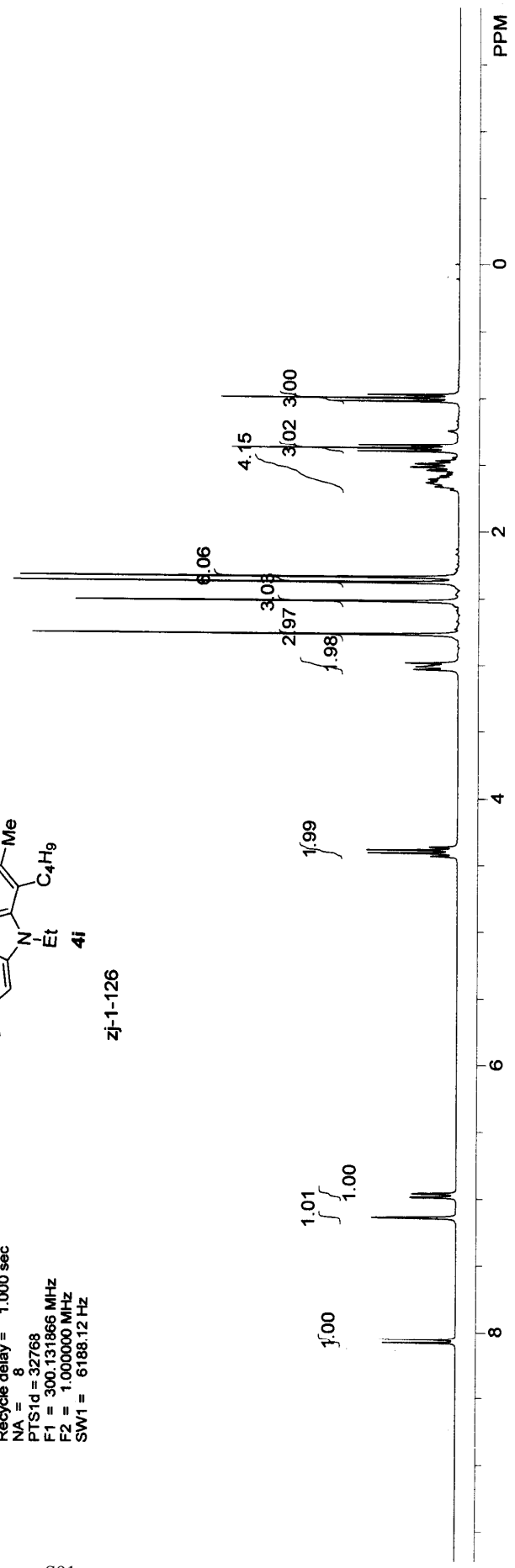


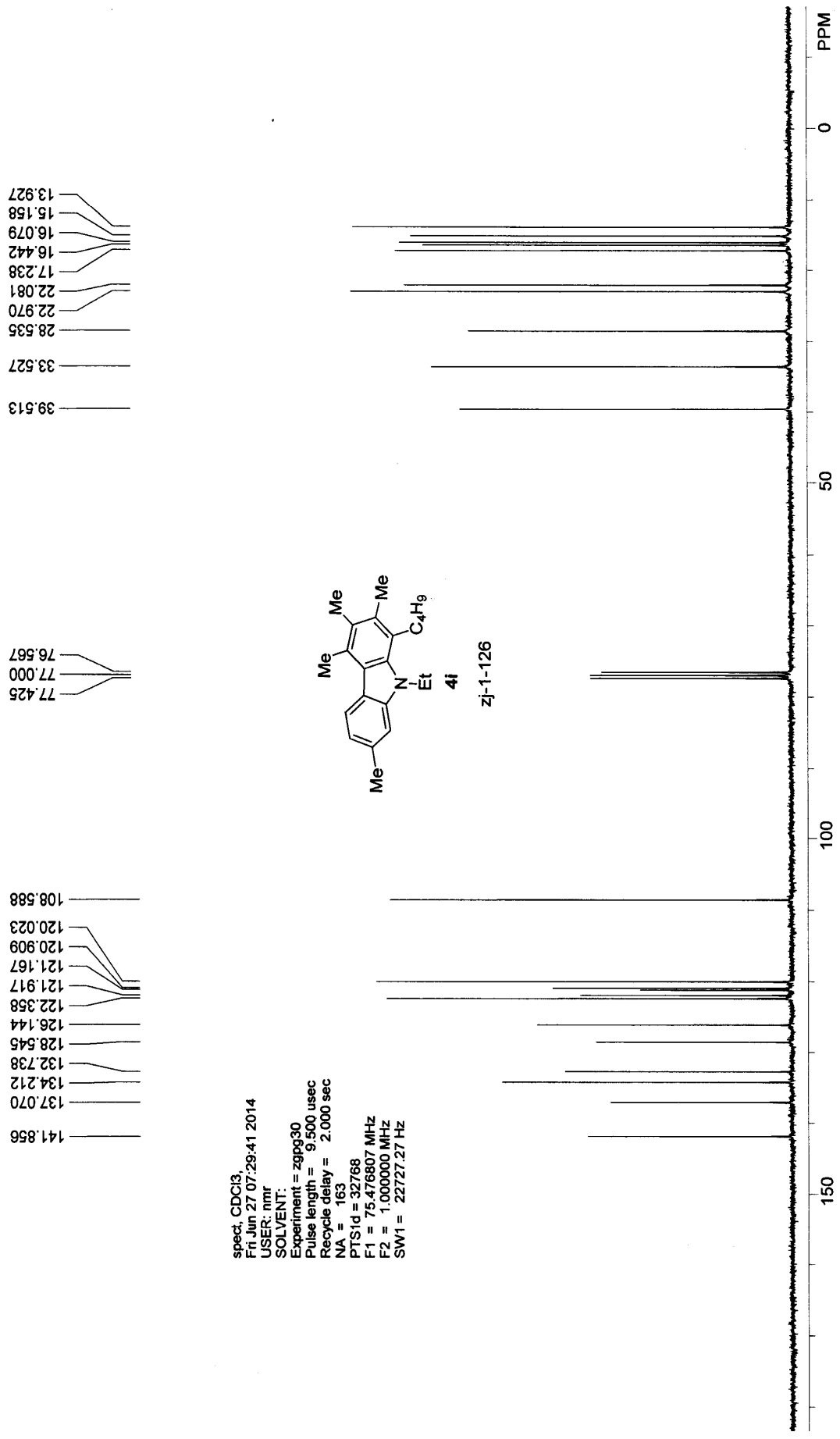


spect, CDCl3,
 Fri Jun 27 07:26:29 2014
 USER: nmr
 SOLVENT:
 Experiment = zg30
 Pulse length = 14.000 usec
 Recycle delay = 1.000 sec
 NA = 8
 P1 = 32768
 F1 = 300.131866 MHz
 F2 = 1.000000 MHz
 SW1 = 6188.12 Hz

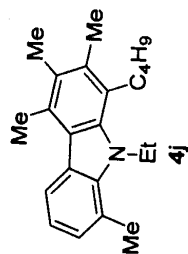
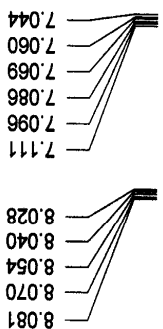
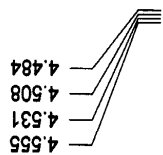
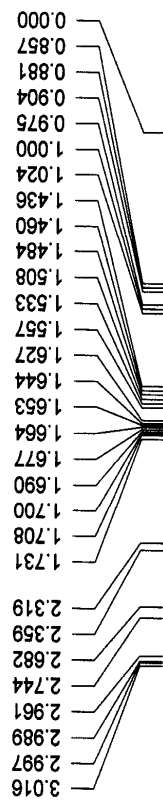


zj-1-126



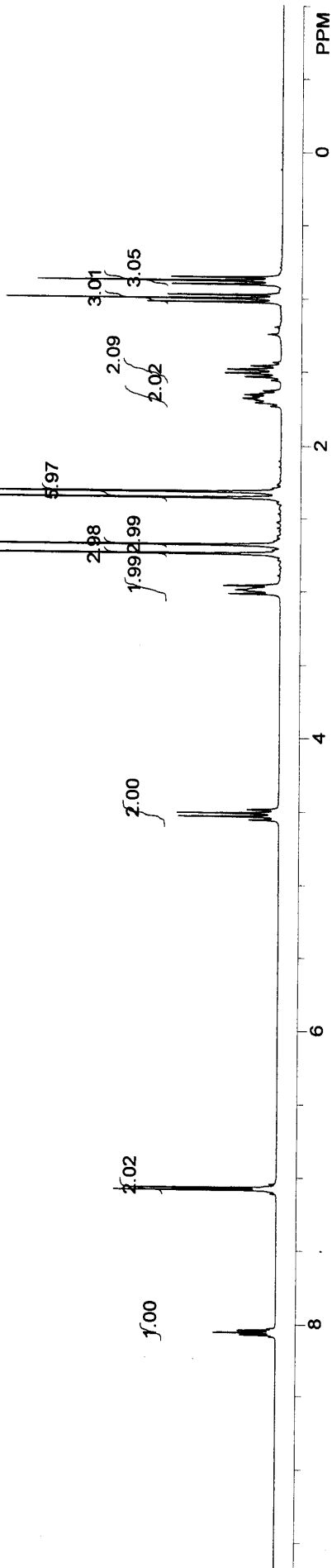


spect. CDC13
 Fri Jun 27 07:29:41 2014
 USER: nmr
 SOLVENT:
 Experiment = zqpg30
 Pulse length = 9.500 usec
 Recycle delay = 2.000 sec
 NA = 163
 PTS1d = 32768
 F1 = 75.476807 MHz
 F2 = 1.000000 MHz
 SW1 = 22727.27 Hz



zj-1-078

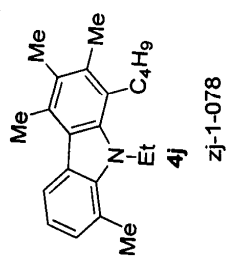
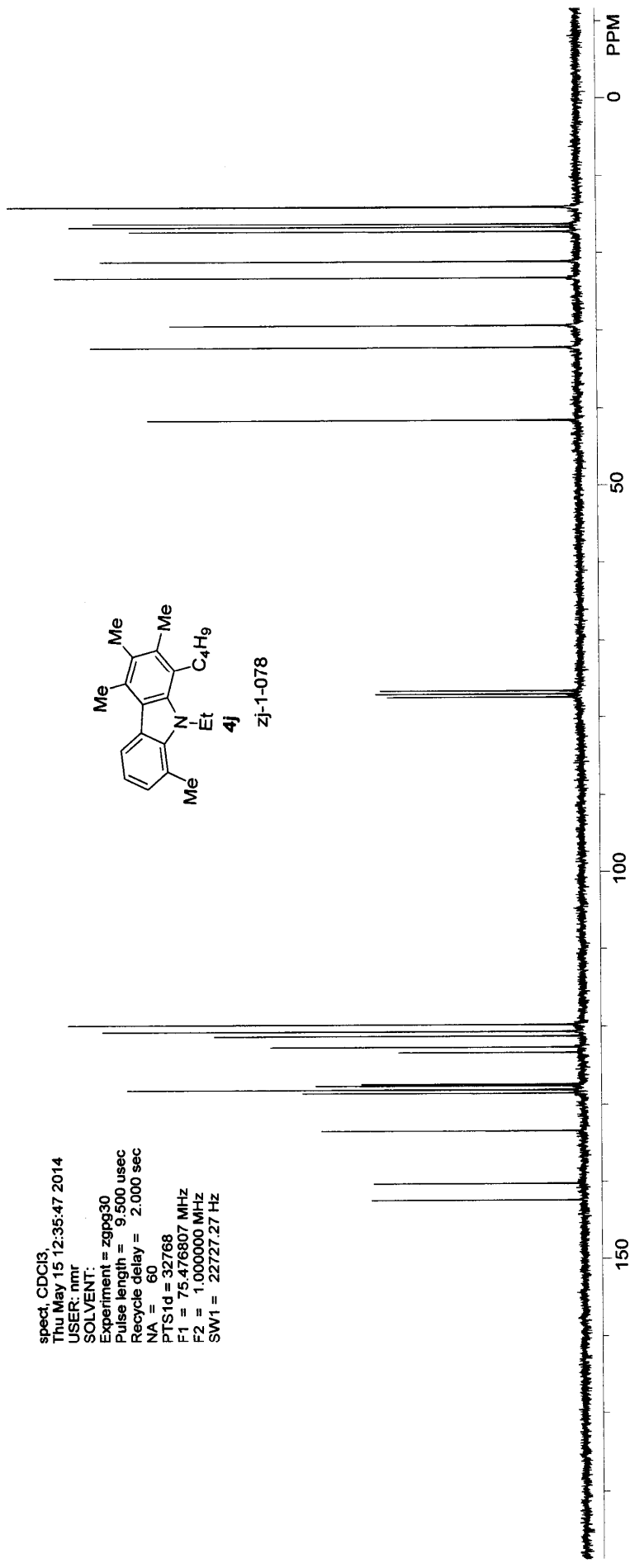
spect, CDC13,
Thu May 15 12:33:44 2014
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz



13.963
14.015
16.188
16.667
17.258
21.074
23.179
29.325
32.152
41.484

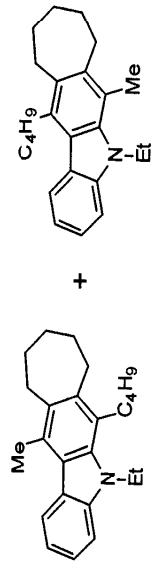
76.580
77.000
77.432

119.736
120.616
121.200
122.637
123.344
127.350
127.572
128.075
128.522
133.452
140.246
142.425



spect_CDCI3,
 Thu May 15 12:35:47 2014
 USER: nmr
 SOLVENT:
 Experiment = zgpg30
 Pulse length = 9.500 usec
 Recycle delay = 2.000 sec
 NA = 60
 PTS1d = 32768
 F1 = 75.476807 MHz
 F2 = 1.000000 MHz
 SW1 = 22727.27 Hz

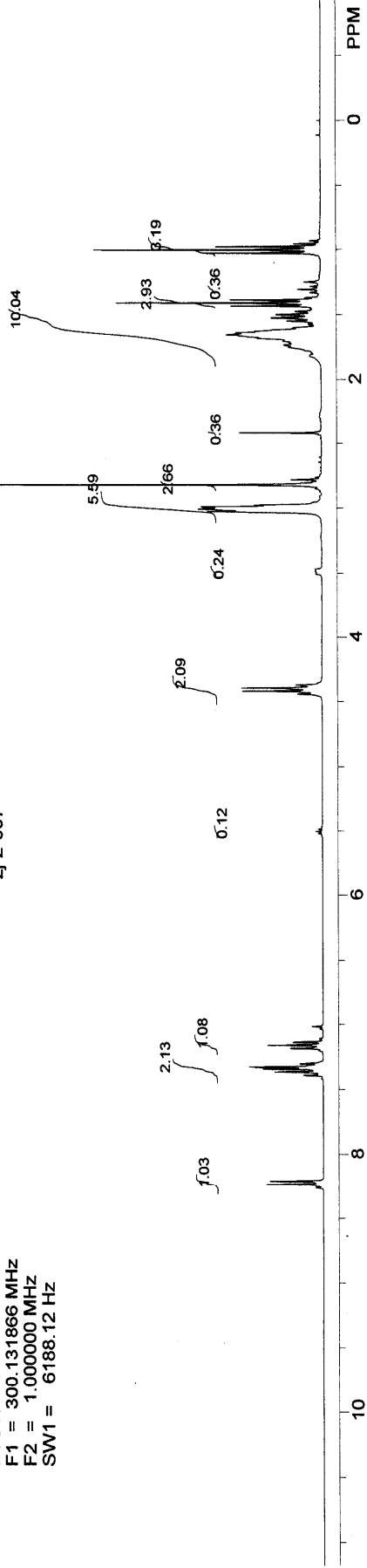
8.236
 8.209
 7.394
 7.391
 7.372
 7.367
 7.363
 7.355
 7.345
 7.341
 7.331
 7.328
 7.315
 7.304
 7.189
 7.184
 7.167
 7.162
 7.158
 7.141
 7.136
 4.443
 4.419
 4.395
 4.372
 3.506
 3.487
 3.473
 3.027
 3.008
 2.992
 2.978
 2.819
 2.806
 2.779
 2.418
 1.819
 1.736
 1.683
 1.657
 1.639
 1.574
 1.550
 1.526
 1.501
 1.477
 1.434
 1.410
 1.386
 1.330
 1.307
 1.283
 1.029
 1.005
 0.981
 0.000

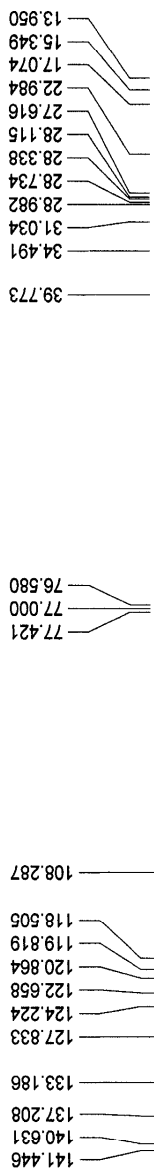


spect, CDCl₃,
 Sun Oct 19 03:04:00 2014
 USER: nmr
 SOLVENT:
 Experiment = zg30
 Pulse length = 14.000 usec
 Relaxation delay = 1.000 sec
 NA = 8
 PTS1d = 32768
 F1 = 300.131866 MHz
 F2 = 1.000000 MHz
 SW1 = 6188.12 Hz

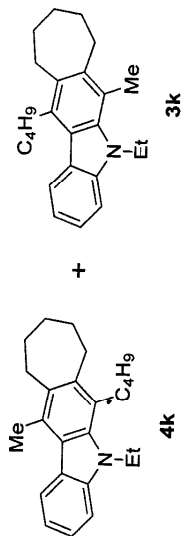
4k:3k=88:12

zj-2-007





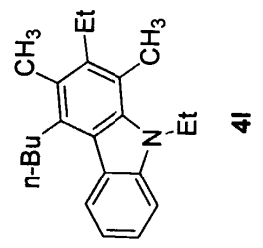
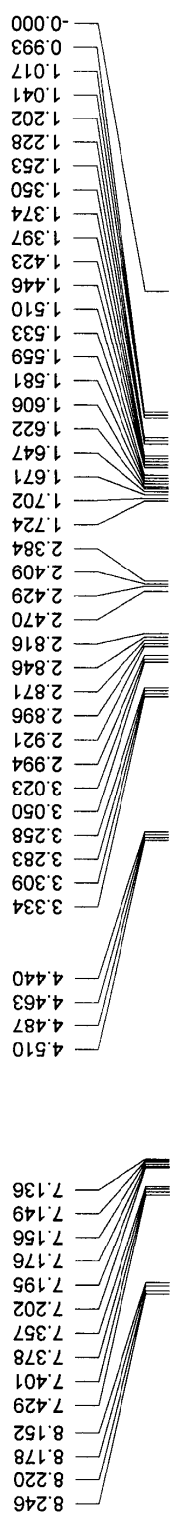
spect. CDCl₃
 Sun Oct 19 05:06:24 2014
 USER: nmr
 SOLVENT:
 Experiment = zgpg30
 Pulse length = 9.500 usec
 Recycle delay = 2.000 sec
 NA = 145
 P1 = 32768
 F1 = 75.476807 MHz
 F2 = 1.000000 MHz
 SW1 = 22727.27 Hz



4k:3k=88:12

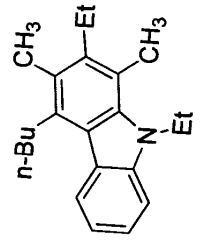
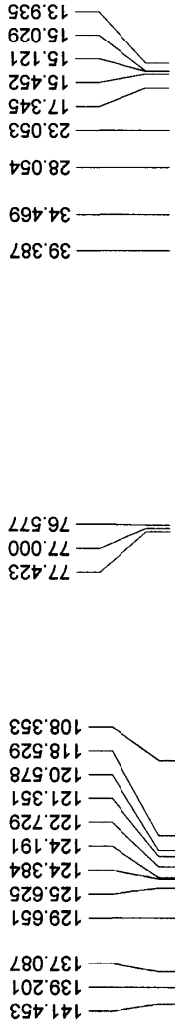
zj-2-007

150 100 50 0 PPM



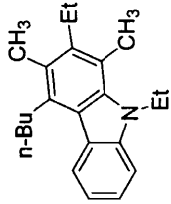
2016-04-01 22:36:55.015
 USER: nmr
 SOLVENT: CDCl₃
 Experiment = zg30
 Pulse length = 14.000 usec
 Relaxation delay = 1.000 sec
 NA = 34
 Solvent = CDCl₃
 PTS1d = 32768
 F1 = 300.130005 MHz
 F2 = 1.000000 MHz
 SW1 = 6188.12 Hz

zj-5-176-2



2016-04-02 09:41:21.234
 USER: nmr
 SOLVENT: CDCl3
 Experiment = zgpg30
 Pulse length = 9.500 usec
 Relaxation delay = 2.000 sec
 NA = 7323
 Solvent = CDCl3
 PTS1d = 32768
 F1 = 75.467751 MHz
 F2 = 1.000000 MHz
 SW1 = 22727.27 Hz

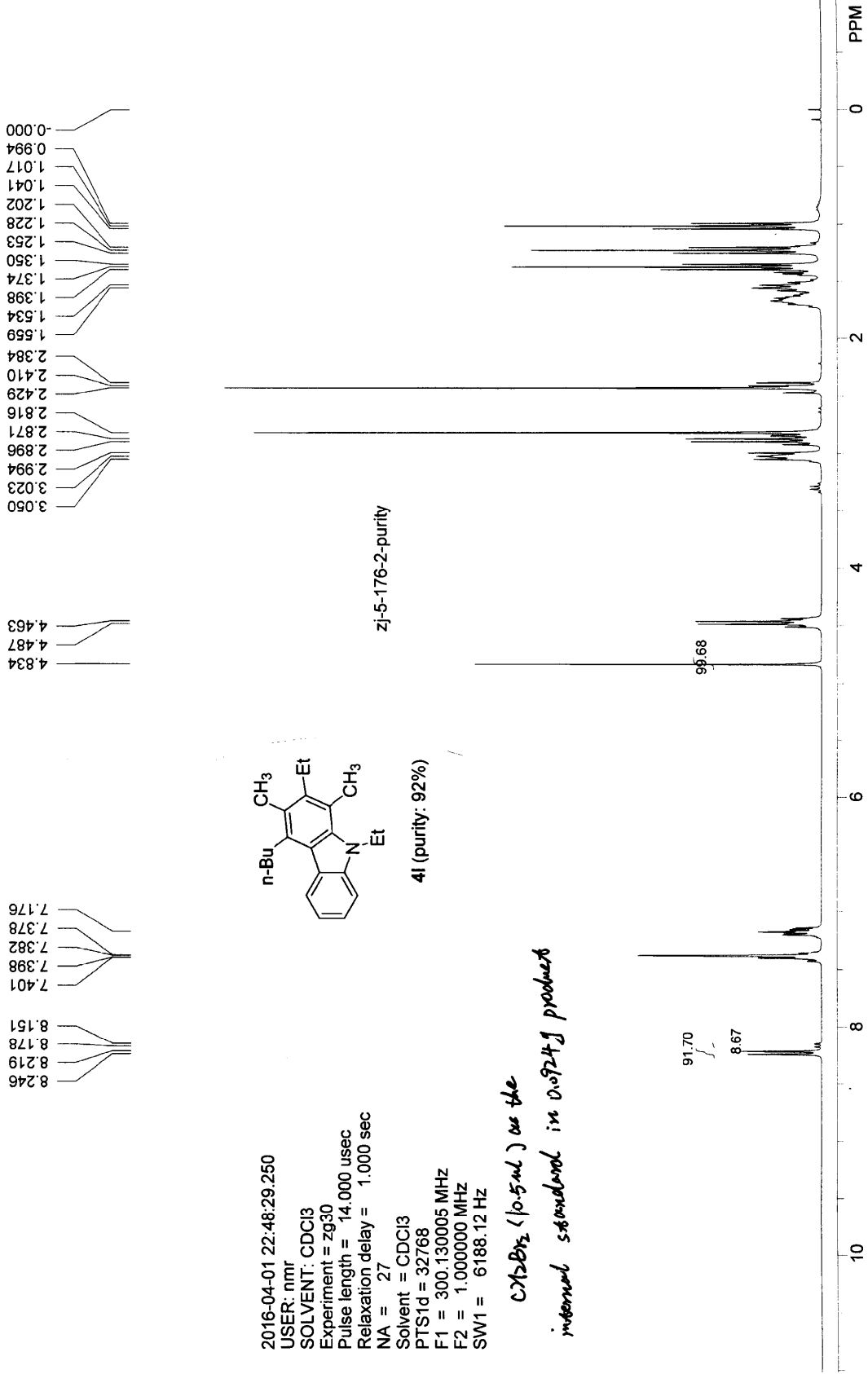
2016-04-01 22:48:29.250
 USER: nmr
 SOLVENT: CDCl3
 Experiment = zg30
 Pulse length = 14.000 usec
 Relaxation delay = 1.000 sec
 NA = 27
 Solvent = CDCl3
 PTS1d = 32768
 F1 = 300.130005 MHz
 F2 = 1.000000 MHz
 SW1 = 6188.12 Hz

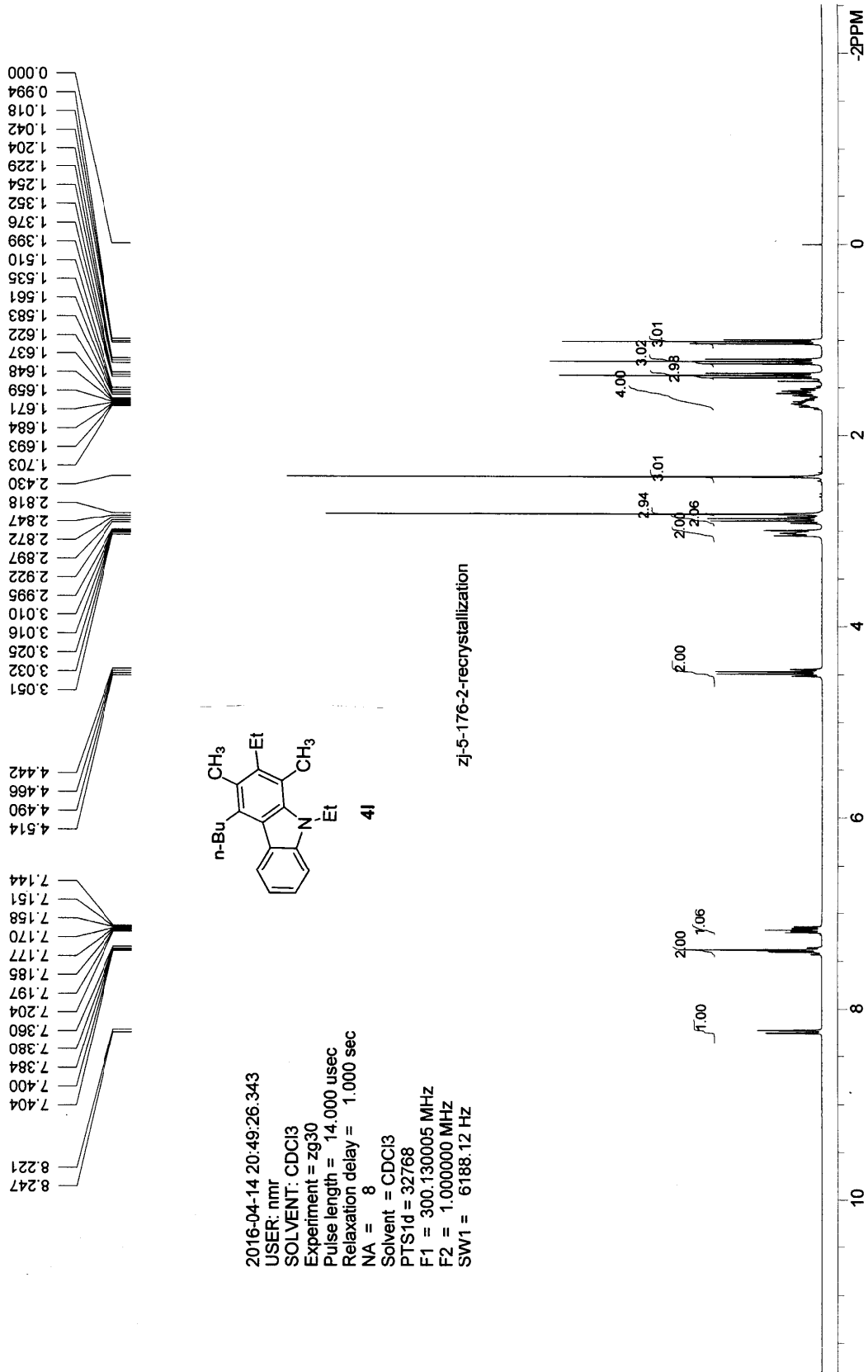


4l (purity: 92%)

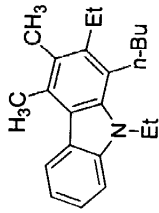
zj-5-176-2-purity

CDCl3 (10.5 ml) as the internal standard in 0.924 g product

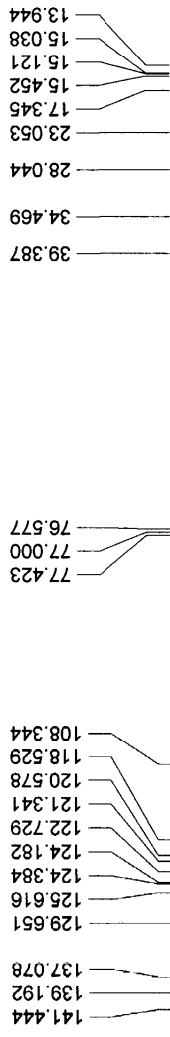


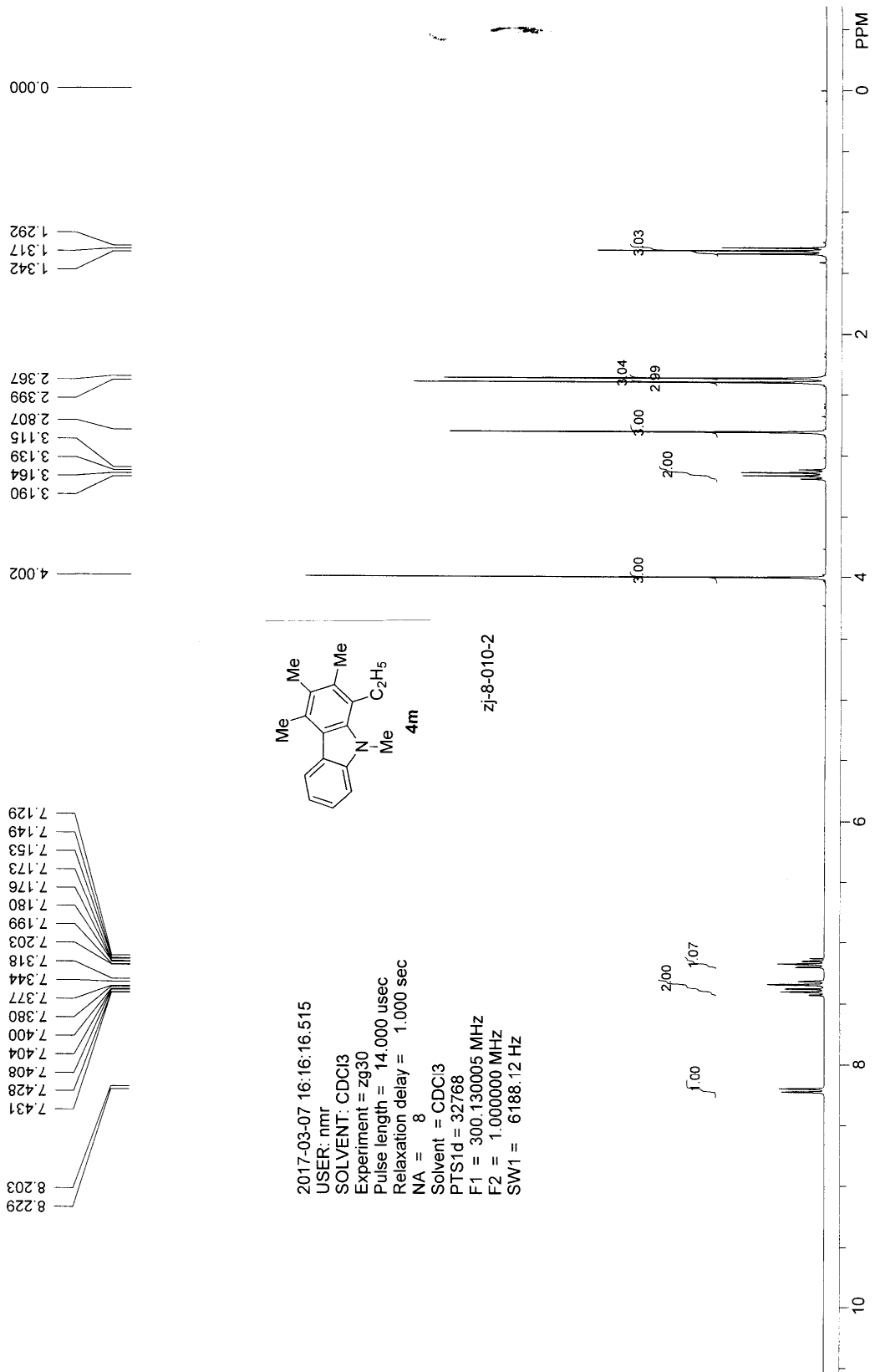


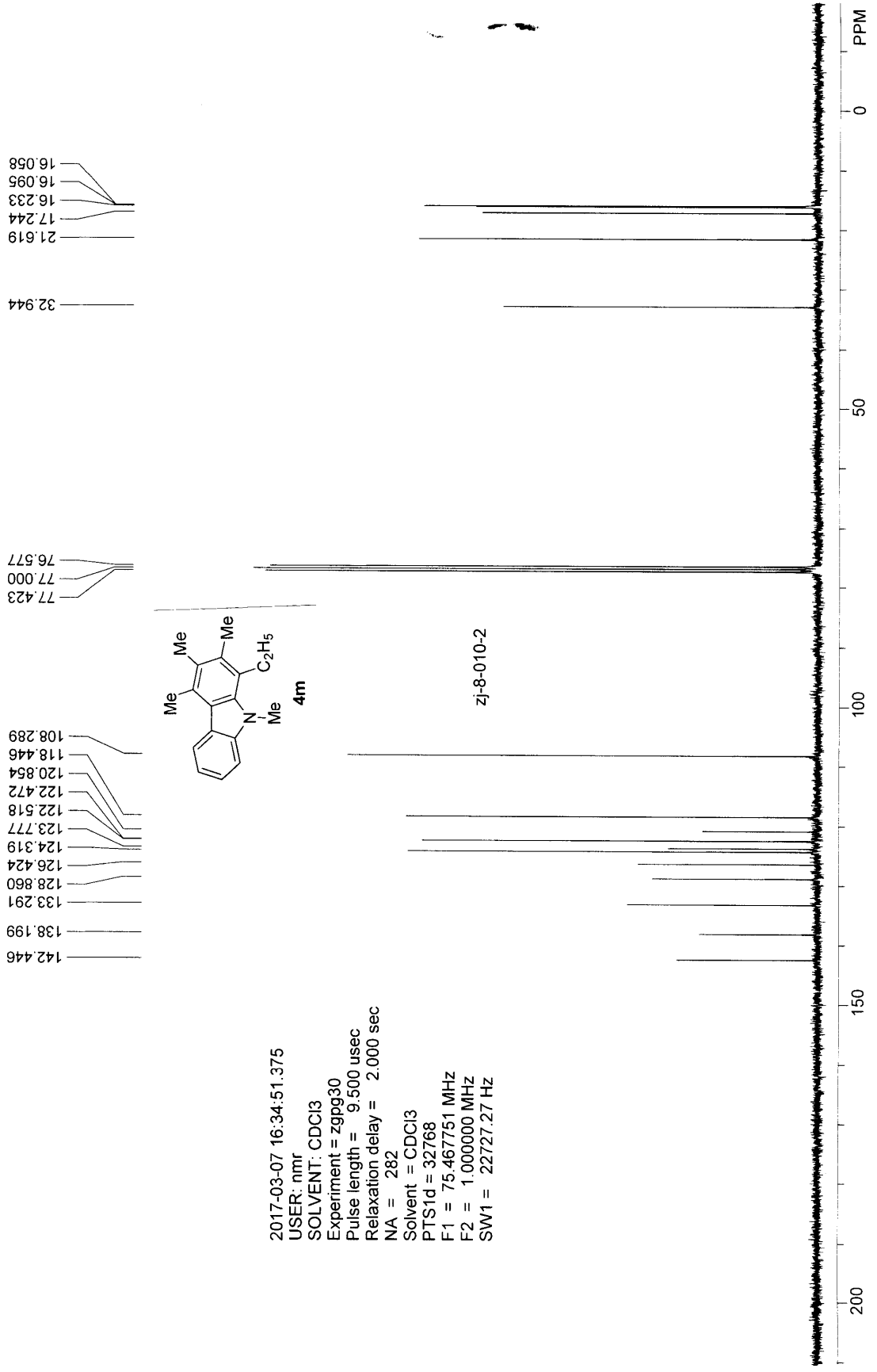
2016-04-16 16:11:13.750
 USER: nmr
 SOLVENT: CDCl3
 Experiment = zgpg30
 Pulse length = 9.500 usec
 Relaxation delay = 2.000 sec
 NA = 775
 Solvent = CDCl3
 PTS1d = 32768
 F1 = 75.467751 MHz
 F2 = 1.000000 MHz
 SW1 = 22727.27 Hz



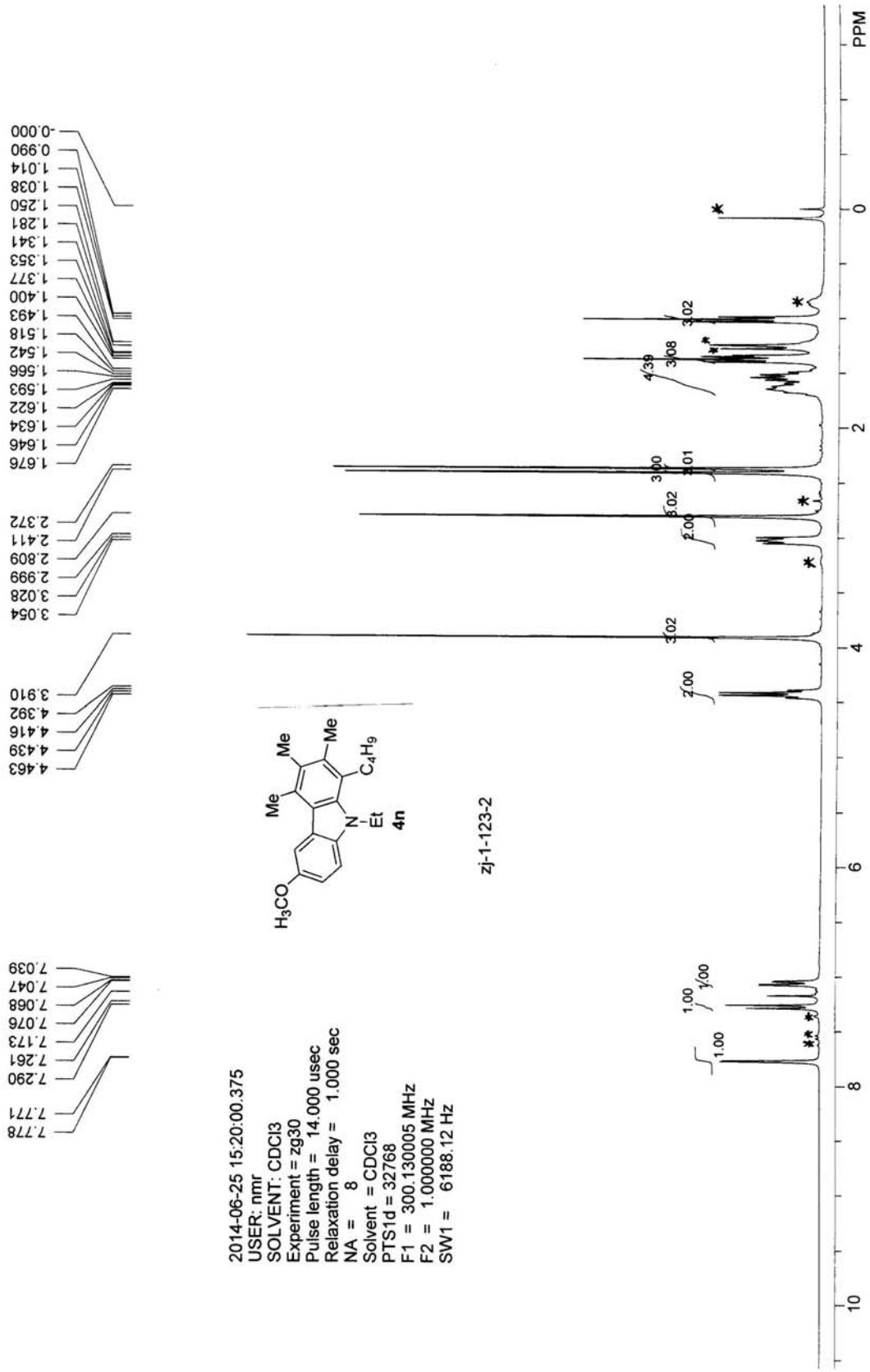
zj-5-176-2-recrystallization

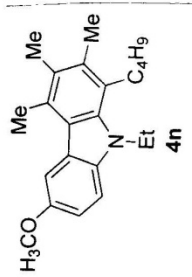
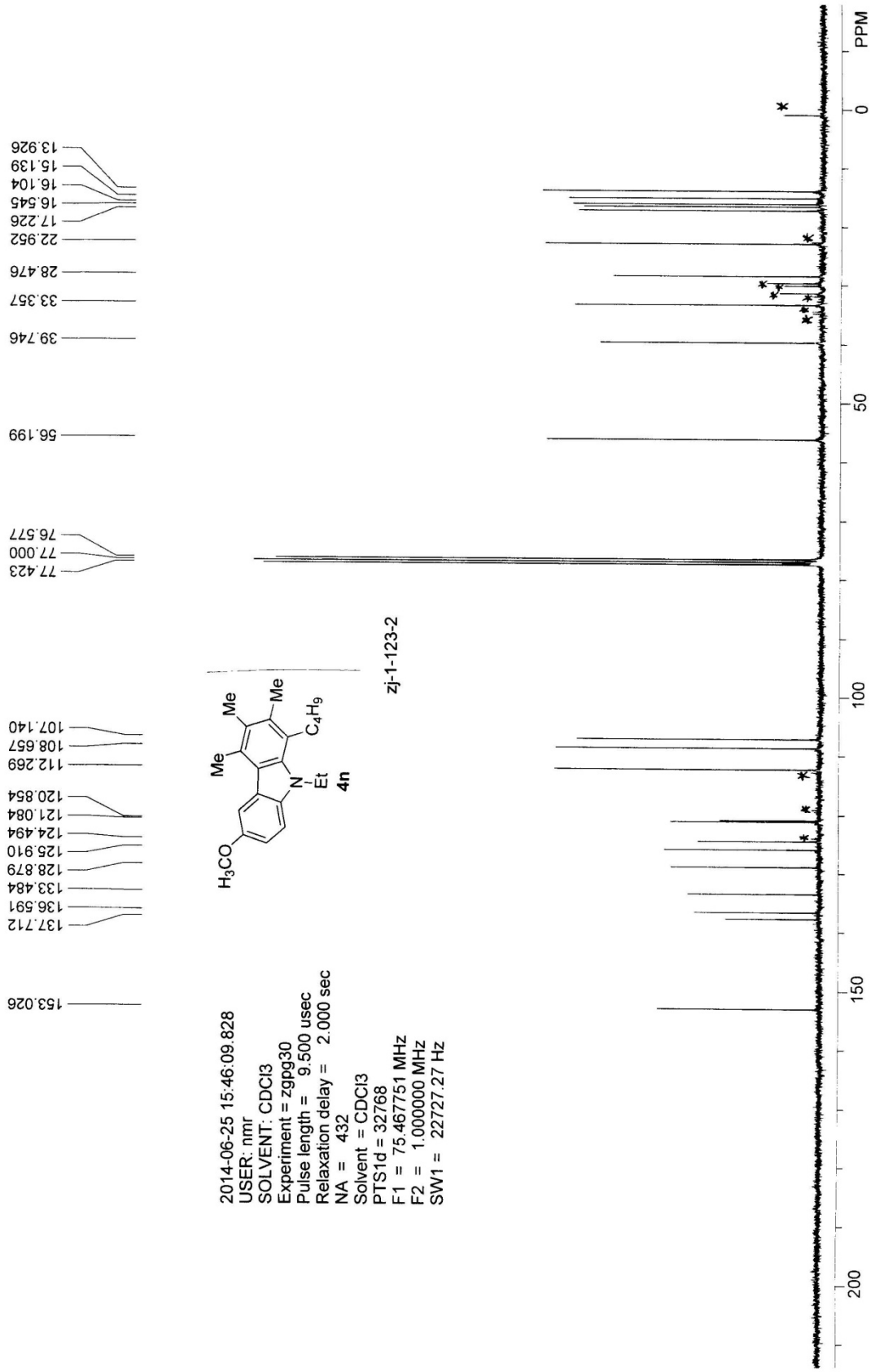






2017-03-07 16:34:51.375
 USER: nmr
 SOLVENT: CDCl3
 Experiment = zgpg30
 Pulse length = 9.500 usec
 Relaxation delay = 2.000 sec
 NA = 282
 Solvent = CDCl3
 PTD1d = 32768
 F1 = 75.467751 MHz
 F2 = 1.000000 MHz
 SW1 = 22727.27 Hz



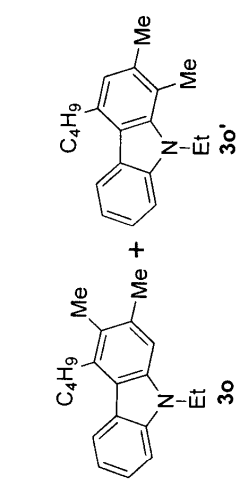


zj-1-123-2

2014-06-25 15:46:09.828
 USER: nmr
 SOLVENT: CDCl3
 Experiment = zgpg30
 Pulse length = 9.500 usec
 Relaxation delay = 2.000 sec
 NA = 432
 Solvent = CDCl3
 PTS1d = 32768
 F1 = 75.467751 MHz
 F2 = 1.000000 MHz
 SW1 = 22727.27 Hz

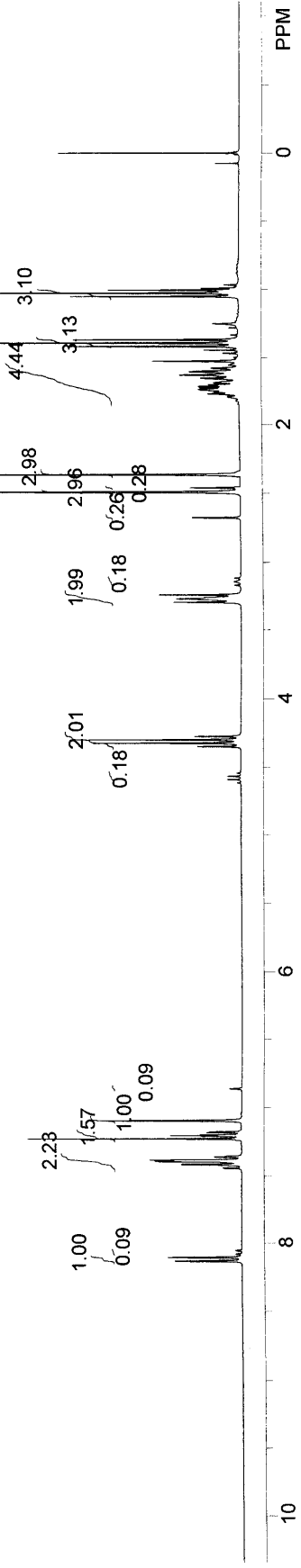
* impurity

8.130
8.103
8.079
8.052
7.418
7.415
7.396
7.392
7.388
7.384
7.361
7.229
7.226
7.207
7.202
7.198
7.181
7.175
7.094
6.860
4.613
4.589
4.565
4.541
4.346
4.321
4.298
4.274
3.291
3.265
3.237
3.168
3.143
3.116
2.677
2.491
2.460
2.365
1.766
1.734
1.720
1.710
1.699
1.685
1.651
1.629
1.605
1.577
1.527
1.418
1.393
1.369
1.052
1.029
1.005
-0.000



spect, CDCl3,
 Sat Jun 13 12:51:56 2015
 USER: nmr
 SOLVENT:
 Experiment = zg30
 Pulse length = 14.000 usec
 Recycle delay = 1.000 sec
 NA = 8
 P1 = 32768
 F1 = 300.131866 MHz
 F2 = 1.000000 MHz
 SW1 = 6188.12 Hz

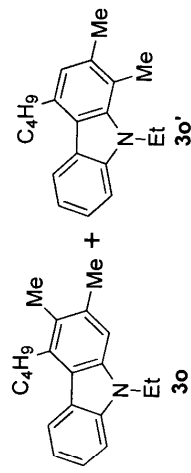
zj-2-117



13.647
14.123
14.510
14.784
15.514
20.948
22.259
23.002
23.396
29.709
30.393
31.442
31.992
33.917
37.143
39.875

76.578
77.000
77.422

107.191
108.039
108.479
115.758
118.415
118.849
119.342
122.183
122.243
122.995
123.112
124.225
124.449
124.908
134.484
135.019
135.255
136.384
138.556
139.957



30:30' = 92.8

spect, CDCl3,
Sun Jun 14 09:33:42 2015
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 3862
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz

zj-2-117

0 PPM
20
40
60
80
100
120
140
160