Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers

Regiocontrolled 1,2-Migration in Cyclization of 1-(Indol-2-yl)-3-alkyn-1-ols: $(Ph_3P)Au^+$ vs $PtCl_4$

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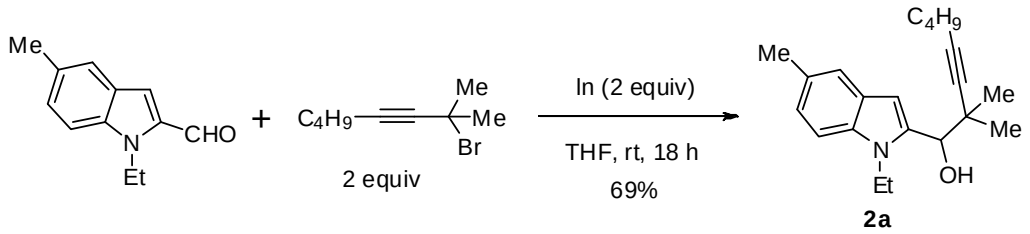
Supporting Information

General: ^1H and ^{13}C NMR spectra were recorded with a Bruker AM 300 MHz. IR spectra were recorded with a Perkin–Elmer 983G instrument. Elemental analyses were measured with a Carlo-Erba EA1110 elementary analysis instrument. Mass spectrometry was performed with an HP 5989A system. High-resolution mass spectrometry was determined with a Finnigan MAT 8430 or Bruker APEXIII instrument. Toluene was distilled from Na/benzophenone before use. Unless otherwise indicated, chemicals and solvents were purchased from commercial suppliers.

1. The Synthesis of 1-(Indol-2-yl)-2,2-dialkyl-3-alkyn-1-ols 2a-2j:

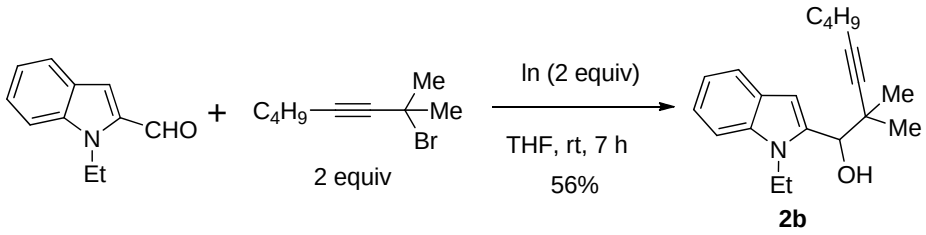
(1) **1-(1-Ethyl-5-methyl-1*H*-indol-2-yl)-2,2-dimethyloct-3-yn-1-ol (2a)**(qya-4-054)



Typical procedure: To a mixture of 1-ethyl-5-methyl-1*H*-indole-2-carbaldehyde (1.5060 g, 8 mmol) and 2-bromo-2-methyl-3-octyne (3.2539 g, 16 mmol) in THF (30 mL) was added indium powder (1.8426 g, 16 mmol) with vigorous stirring. After 18 h, the reaction was complete as monitored by TLC. The mixture was quenched with 20 mL of H_2O, extracted with diethyl ether (20 mL×3), washed with water (20 mL) and dried over anhydrous Na_2SO_4. Filtration, evaporation and column chromatography on silica gel (petroleum ether/ethyl acetate = 50/l~20/1) afforded **2a** (1.7376 g, 69%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (s, 1H, ArH), 7.25 (d, J = 8.4 Hz, 1H, ArH), 7.06 (dd, J_1 = 8.3 Hz and J_2 = 1.4 Hz, 1H, ArH), 6.78 (s, 1H, ArH), 4.53 (d, J = 8.1 Hz, 1H, CH), 4.40-4.13 (m, 2H, NCH_2), 2.47 (s, 3H, CH_3), 2.33-2.19 (m, 3H, CH_2 + OH), 1.63-1.34 (m, 10H, 2 × CH_2 + 2 × CH_3), 1.27 (s, 3H, CH_3), 0.96 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.9, 134.3, 128.6, 127.8, 123.1, 120.5, 109.0, 99.8, 84.2, 83.6, 73.0, 38.2, 37.6, 31.0, 28.0, 26.1, 22.0, 21.3, 18.5, 15.5, 13.6; IR (neat) ν (cm^{-1}) 3452, 2964, 2931, 2871, 1482, 1467, 1380, 1341, 1299, 1223, 1184, 1159, 1126, 1034, 1004; MS (70 ev, EI) *m/z* (%) 311 (M^+, 4.45), 188 (100); HRMS Calcd for $C_{21}H_{29}NO$ (M^+): 311.2249, Found: 311.2240.

The following compounds **2b-2h** were prepared according to this procedure.

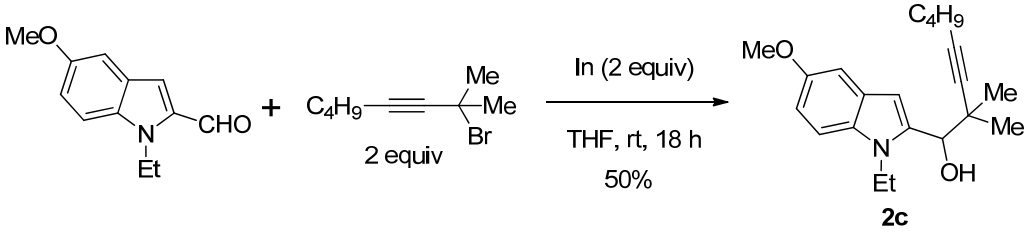
(2) **1-(1-Ethyl-1*H*-indol-2-yl)-2,2-dimethyloct-3-yn-1-ol (2b)** (qya-5-043)



2b

The reaction of 1-ethyl-1*H*-indole-2-carbaldehyde (0.6926 g, 4 mmol), indium powder (0.9238 g, 8 mmol), and 2-bromo-2-methyl-3-octyne (1.6269 g, 8 mmol) in THF (30 mL) for 7 h afforded **2b** (0.6614 g, 56%) (petroleum ether/ethyl acetate = 50/1~30/l~20/1) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, J = 7.8 Hz, 1H, ArH), 7.32 (d, J = 8.1 Hz, 1H, ArH), 7.19 (t, J = 7.7 Hz, 1H, ArH), 7.09 (t, J = 7.7 Hz, 1H, ArH), 6.84 (s, 1H, ArH), 4.52 (d, J = 8.1 Hz, 1H, CH), 4.40-4.15 (m, 2H, NCH_2), 2.30-2.15 (m, 3H, CH_2 + OH), 1.63-1.32 (m, 10H, 2 × CH_2 + 2 × CH_3), 1.25 (s, 3H, CH_3), 0.92 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 135.8, 127.4, 121.3, 120.7, 119.3, 109.2, 100.3, 84.2, 83.4, 72.8, 38.0, 37.4, 30.9, 27.7, 26.2, 21.8, 18.4, 15.3, 13.5; IR (neat) ν (cm^{-1}) 3541, 3060, 3024, 2964, 2932, 2871, 1534, 1462, 1381, 1348, 1319, 1257, 1220, 1169, 1139, 1126, 1028, 1004; MS (70 ev, EI) *m/z* (%) 297 (M^+, 7.72), 174 (100); HRMS Calcd for $C_{20}H_{27}NO$ (M^+): 297.2093, Found: 297.2097.

(3) **1-(1-Ethyl-5-methoxy-1*H*-indol-2-yl)-2,2-dimethyloct-3-yn-1-ol (2c)** (qya-5-040)

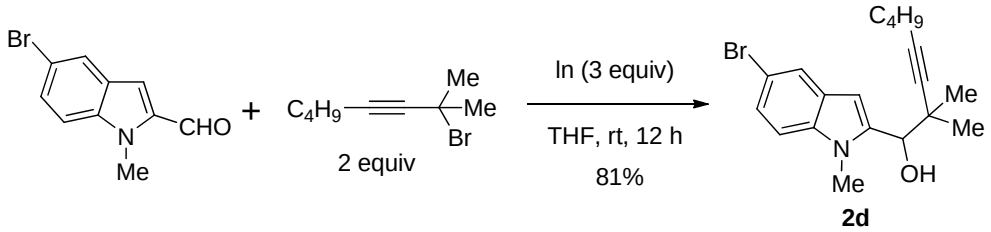


2c

The reaction of 1-ethyl-5-methoxy-1*H*-indole-2-carbaldehyde (1.6206 g, 8 mmol), indium powder (1.8467 g, 16 mmol), and 2-bromo-2-methyl-3-octyne (3.2561 g, 16 mmol) in THF (30 mL) for 18 h afforded **2c** (1.3071 g, 50%) (petroleum ether/ethyl acetate = 30/l~10/1) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, J = 8.7 Hz,1H, ArH), 7.09 (d, J = 2.4 Hz, 1H, ArH), 6.89 (dd, J_1 = 8.9 Hz and J_2 = 2.6 Hz, 1H, ArH), 6.78 (s, 1H, ArH), 4.52 (d, J = 8.4 Hz, 1H, CH), 4.37-4.15 (m, 2H, NCH_2), 3.86 (s, 3H, OCH_3), 2.36-2.18 (m, 3H, CH_2 + OH), 1.62-1.33 (m, 10H, 2 × CH_2 + 2 × CH_3), 1.27 (s, 3H, CH_3), 0.95 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.0, 139.4, 131.3, 127.8, 111.8, 110.0, 102.5, 100.0, 84.2, 83.6, 73.0, 55.8, 38.3, 37.6, 31.0, 27.9, 26.1, 22.0, 18.5, 15.5, 13.6; IR (neat) ν (cm^{-1}) 3476, 2962, 2932, 2871, 2832, 1621, 1578, 1533, 1481, 1453, 1380, 1318, 1208, 1177, 1152, 1108, 1034, 1005; MS (70 ev, EI) *m/z* (%) 327 (M^+, 12.43), 204 (100); HRMS Calcd for $C_{21}H_{29}NO_2$ (M^+): 327.2198, Found: 327.2194.

(4) **1-(5-Bromo-1-methyl-1*H*-indol-2-yl)-2,2-dimethyloct-3-yn-1-ol (2d)**

(qya-5-086)

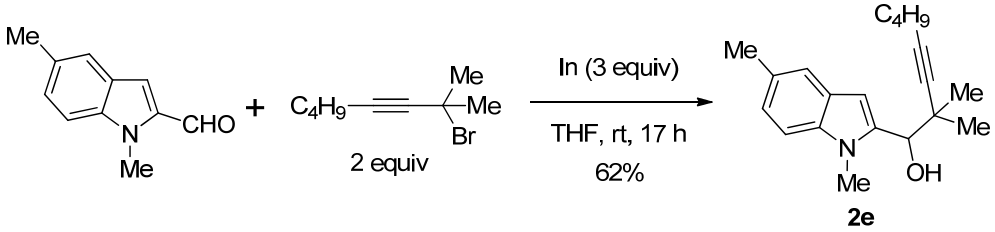


2d

The reaction of 5-bromo-1-methyl-1*H*-indole-2-carbaldehyde (0.5956 g, 2.5 mmol), indium powder (0.8656 g, 7.5 mmol), and 2-bromo-2-methyl-3-octyne (1.0239 g, 5 mmol) in THF (30 mL) for 12 h afforded **2d** (0.7311 g, 81%) (petroleum ether/ethyl acetate = 30/1~20/l~5/1) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) 7.69 (d,

J = 1.8 Hz, 1H, ArH), 7.25 (dd, J_1 = 8.7 Hz and J_2 = 1.8 Hz, 1H, ArH), 7.13 (d, J = 8.7 Hz, 1H, ArH), 6.65 (s, 1H, ArH), 4.56 (d, J = 6.0 Hz, 1H, CH), 3.71 (s, 3H, NCH_3), 2.39 (d, J = 6.3 Hz, 1H, OH), 2.20 (t, J = 7.1 Hz, 2H, CH_2), 1.54-1.31 (m, 7H, 2 × CH_2 + CH_3), 1.22 (s, 3H, CH_3), 0.90 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.6, 135.9, 128.8, 124.2, 123.0, 112.6, 110.6, 100.1, 83.9, 83.7, 73.2, 37.7, 30.9, 30.5, 27.2, 25.9, 21.9, 18.4, 13.6; IR (neat) ν (cm^{-1}) 3536, 2959, 2931, 2871, 1468, 1382, 1308, 1271, 1230, 1145, 1125, 1051, 1006; MS (70 ev, EI) *m/z* (%) 363 (M^+ (^{81}Br), 2.20), 361 (M^+ (^{79}Br), 2.24), 131 (100); HRMS Calcd for $C_{19}H_{24}NOBr$ (M^+): 361.1041, Found: 361.1037.

(5) **1-(1,5-Dimethyl-1*H*-indol-2-yl)-2,2-dimethyloct-3-yn-1-ol (2e)** (qya-5-062)

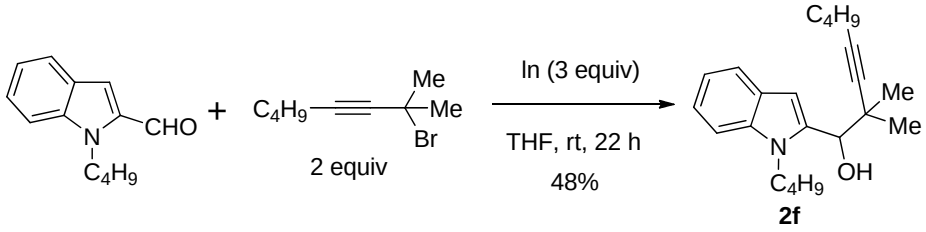


2e

The reaction of 1,5-dimethyl-1*H*-indole-2-carbaldehyde (0.8646 g, 5 mmol), indium powder (1.7319 g, 15 mmol), and 2-bromo-2-methyl-3-octyne (2.0531 g, 10 mmol) in THF (30 mL) for 17 h afforded **2e** (0.9212 g, 62%) (petroleum ether/ethyl acetate = 50/1~30/l) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (s, 1H, ArH), 7.21 (d, J = 8.1 Hz, 1H, ArH), 7.04 (d, J = 8.4 Hz, 1H, ArH), 6.67 (s, 1H, ArH), 4.61 (d, J = 6.6 Hz, 1H, CH), 3.77 (s, 3H, NCH_3), 2.45 (s, 3H, CH_3), 2.30-2.17 (m, 3H, CH_2 + OH), 1.55-1.40 (m, 4H, 2 × CH_2), 1.38 (s, 3H, CH_3), 1.25 (s, 3H, CH_3), 0.93 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.5, 135.8, 128.7, 127.5, 123.1, 120.3, 108.9, 100.0, 84.3, 83.5, 73.4, 37.9, 31.0, 30.4, 27.4, 25.8, 22.0, 21.4, 18.5,

13.6; IR (neat) ν (cm^{-1}) 3534, 2960, 2931, 2871, 1381, 1359, 1344, 1236, 1186, 1125, 1038, 1005; MS (70 ev, EI) *m/z* (%) 298 (M^+, 1.44), 297 (M^+, 6.96), 174 (100); HRMS Calcd for $C_{20}H_{27}NO$ (M^+): 297.2093, Found: 297.2090.

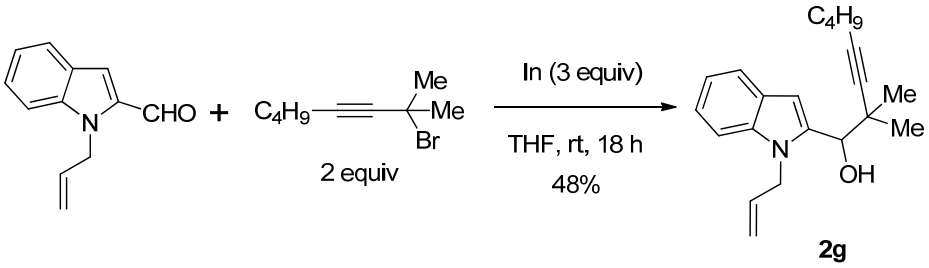
(6) **1-(1-Butyl-1*H*-indol-2-yl)-2,2-dimethyloct-3-yn-1-ol (2f)** (qya-5-078)



2f

The reaction of 1-butyl-1*H*-indole-2-carbaldehyde (1.0112 g, 5 mmol), indium powder (1.7116 g, 15 mmol), and 2-bromo-2-methyl-3-octyne (2.0219 g, 10 mmol) in THF (30 mL) for 22 h afforded **2f** (0.7909 g, 48%) (petroleum ether/ethyl acetate = 50/1~30/l) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.8 Hz, 1H, ArH), 7.30 (d, *J* = 8.1 Hz, 1H, ArH), 7.18 (t, *J* = 7.7 Hz, 1H, ArH), 7.07 (t, *J* = 7.5 Hz, 1H, ArH), 6.84 (s, 1H, ArH), 4.52 (d, *J* = 7.2 Hz, 1H, CH), 4.31-4.07 (m, 2H, NCH_2), 2.30-2.13 (m, 3H, CH_2 + OH), 1.83-1.65 (m, 2H, CH_2), 1.58-1.30 (m, 9H, 3 × CH_2 + CH_3), 1.24 (s, 3H, CH_3), 1.00-0.82 (m, 6H, 2 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.3, 136.3, 127.4, 121.4, 120.8, 119.3, 109.5, 100.2, 84.2, 83.6, 72.9, 43.4, 37.6, 32.5, 31.0, 27.9, 26.2, 21.9, 20.3, 18.5, 13.8, 13.6; IR (neat) ν (cm^{-1}) 3542, 3055, 3030, 2959, 2931, 2872, 1461, 1380, 1361, 1347, 1317, 1238, 1204, 1168, 1132, 1028, 1004; MS (70 ev, EI) *m/z* (%) 326 (M^++1, 2.84), 325 (M^+, 10.37), 202 (100); HRMS Calcd for $C_{22}H_{31}NO$ (M^+): 325.2406, Found: 325.2403.

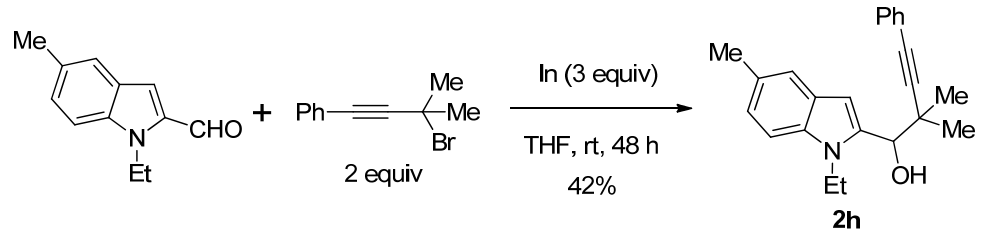
(7) **1-(1-Allyl-1*H*-indol-2-yl)-2,2-dimethyloct-3-yn-1-ol (2g)** (qya-5-097)



2g

The reaction of 1-allyl-1*H*-indole-2-carbaldehyde (0.7406 g, 4 mmol), indium powder (1.3829 g, 12 mmol), and 2-bromo-2-methyl-3-octyne (1.6229 g, 8 mmol) in THF (30 mL) for 18 h afforded **2g** (0.5908 g, 48%) (petroleum ether/ethyl acetate = 50/1~30/l) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.5 Hz, 1H, ArH), 7.38 (d, *J* = 7.8 Hz, 1H, ArH), 7.31 (t, *J* = 7.5 Hz, 1H, ArH), 7.23 (t, *J* = 7.5 Hz, 1H, ArH), 7.01 (s, 1H, ArH), 6.13-5.95 (m, 1H, =CH), 5.20 (d, *J* = 10.5 Hz, 1H, one proton of $=CH_2$), 5.07-4.82 (m, 3H, one proton of $=CH_2$ + NCH_2), 4.59 (d, *J* = 6.3 Hz, 1H, OCH), 2.51 (d, *J* = 6.9 Hz, 1H, OH), 2.35 (t, *J* = 6.9 Hz, 2H, CH_2), 1.72-1.45 (m, 7H, 2 × CH_2 + CH_3), 1.39 (s, 3H, CH_3), 1.05 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.2, 136.5, 133.8, 127.4, 121.6, 120.7, 119.6, 115.9, 109.5, 100.7, 84.2, 83.6, 73.0, 45.5, 37.3, 30.9, 27.8, 26.3, 21.9, 18.4, 13.6; IR (neat) ν (cm^{-1}) 3547, 2961, 2931, 2871, 1644, 1611, 1537, 1462, 1381, 1357, 1318, 1253, 1168, 1135, 1029, 1001; MS (70 ev, EI) *m/z* (%) 310 (M^++1, 2.02), 309 (M^+, 9.14), 158 (100); HRMS Calcd for $C_{21}H_{27}NO$ (M^+): 309.2093, Found: 309.2095.

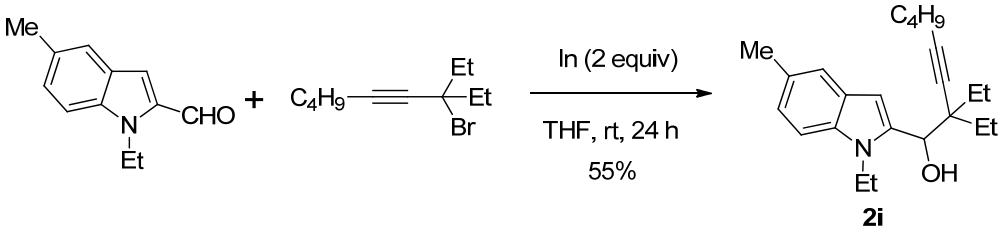
(8) **1-(1-Ethyl-5-methyl-1*H*-indol-2-yl)-2,2-dimethyl-4-phenylbut-3-yn-1-ol (2h)** (qya-5-074)



2h

The reaction of 1-ethyl-5-methyl-1*H*-indole-2-carbaldehyde (0.3741 g, 2 mmol), indium powder (0.6926 g, 6 mmol), and 2-bromo-2-methyl-4-phenyl-3-butyne (0.8926 g, 4 mmol) in THF (10 mL) for 48 h afforded **2h** (0.2813 g, 42%) (petroleum ether/ethyl acetate = 50/1~30/l~10/1) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52-7.42 (m, 3H, ArH), 7.37-7.32 (m, 3H, ArH), 7.28 (d, *J* = 8.1 Hz, 1H, ArH), 7.10 (d, *J* = 8.4 Hz, 1H, ArH), 6.88 (s, 1H, ArH), 4.69 (d, *J* = 7.5 Hz, 1H, CH), 4.44-4.22 (m, 2H, NCH_2), 2.50 (s, 3H, CH_3), 2.31 (d, *J* = 7.5 Hz, 1H, OH), 1.59 (s, 3H, CH_3), 1.50-1.36 (m, 6H, 2 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.8, 134.4, 131.6, 128.7, 128.2, 127.9, 127.8, 123.32, 123.26, 120.6, 109.1, 99.9, 94.0, 83.4, 73.1, 38.3, 38.2, 27.4, 26.1, 21.3, 15.5; IR (neat) ν (cm^{-1}) 3440, 2972, 2934, 2863, 1598, 1483, 1381, 1340, 1299, 1224, 1126, 1030, 1005; MS (70 ev, EI) *m/z* (%) 332 (M^+ +1, 2.07), 331 (M^+, 8.39), 188 (100); HRMS Calcd for $C_{23}H_{25}NO$ (M^+): 331.1936, Found: 331.1935.

(9) **1-(1-Ethyl-5-methyl-1*H*-indol-2-yl)-2,2-diethyloct-3-yn-1-ol (2i)** (qya-5-019)



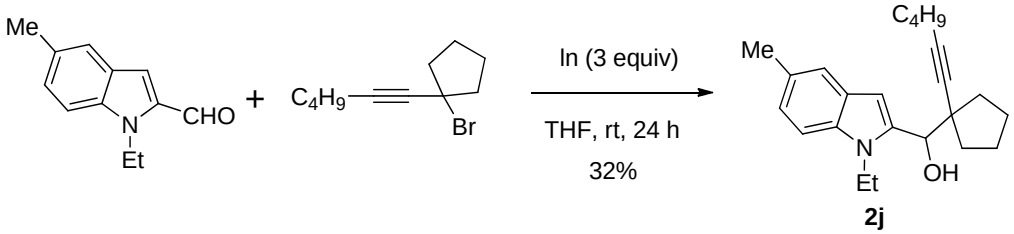
2i

The reaction of 1-ethyl-5-methyl-1*H*-indole-2-carbaldehyde (0.3741 g, 2 mmol), indium powder (0.4816 g, 4 mmol), and 3-bromo-3-ethyl-4-nonyne (0.9243 g, 4 mmol) in THF (20 mL) for 24 h afforded **2i** (0.3710 g, 55%) (petroleum ether/ethyl

acetate = 50/1~30/l): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (s, 1H, ArH), 7.26-7.18 (m, 1H, ArH), 7.03 (d, *J* = 8.1 Hz, 1H, ArH), 6.81 (s, 1H, ArH), 4.62 (d, *J* = 9.3 Hz, 1H, CH), 4.39-4.12 (m, 2H, NCH_2), 2.44 (s, 3H, CH_3), 2.27 (t, *J* = 7.1 Hz, 2H, CH_2), 2.11 (d, *J* = 9.0 Hz, 1H, OH), 1.91-1.75 (m, 2H, CH_2), 1.68-1.32 (m, 9H, 3× CH_2+CH_3), 0.99 (t, *J* = 7.5 Hz, 3H, CH_3), 0.93 (t, *J* = 7.4 Hz, 3H, CH_3), 0.84 (t, *J* = 7.4 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.1, 134.3, 128.6, 127.8, 123.0, 120.4, 109.0, 100.0, 85.7, 82.4, 69.2, 45.4, 38.1, 31.1, 27.8, 26.6, 22.0, 21.4, 18.5, 15.5, 13.6, 8.60, 8.59; IR (neat) ν (cm^{-1}) 3540, 3015, 2964, 2933, 2874, 1482, 1457, 1378, 1343, 1299, 1223, 1185, 1158, 1127, 1078, 1017; MS (70 ev, EI) *m/z* (%) 339 (M^+, 6.24), 188 (100); HRMS Calcd for $C_{23}H_{33}NO$ (M^+): 339.2562, Found: 339.2558.

(10) **1-(1-Ethyl-5-methyl-1*H*-indol-2-yl)-2,2-tetramethyleneoct-3-yn-1-ol (2j)**

(qya-5-103)



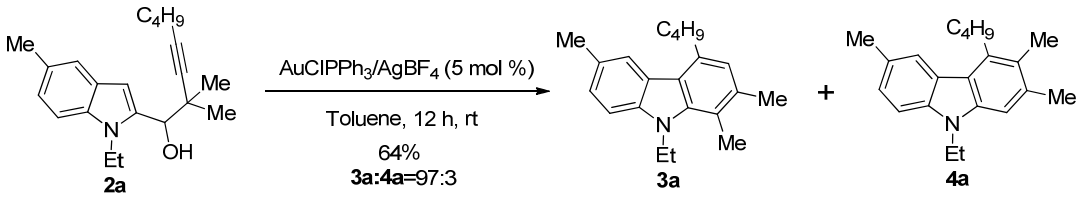
2j

The reaction of 1-ethyl-5-methyl-1*H*-indole-2-carbaldehyde (0.5616 g, 3 mmol), indium powder (1.0416 g, 9 mmol), and 1-bromo-1-(hex-1-yn-1-yl)cyclopentane (1.3762 g, 6 mmol) in THF (30 mL) for 24 h afforded **2j** (0.3281 g, 32%) (petroleum ether/ethyl acetate = 50/1~30/l): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (s, 1H, ArH), 7.21 (d, *J* = 8.1 Hz, 1H, ArH), 7.02 (d, *J* = 8.1 Hz, 1H, ArH), 6.83 (s, 1H, ArH), 4.45 (d, *J* = 9.9 Hz, 1H, CH), 4.38-4.11 (m, 2H, NCH_2), 2.44 (s, 3H, CH_3), 2.34-2.17 (m, 3H, CH_2 + OH), 2.17-2.03 (m, 1H, one proton of CH_2), 2.03-1.30 (m, 14H, one

proton of CH_2 + 5 × CH_2 + CH_3), 0.92 (t, J = 7.4 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.3, 134.4, 128.5, 127.6, 123.2, 120.6, 109.0, 100.1, 84.4, 84.0, 72.1, 48.5, 40.5, 38.1, 37.8, 31.0, 24.9, 24.5, 22.0, 21.3, 18.6, 15.5, 13.6; IR (neat) ν (cm^{-1}) 3451, 2956, 2929, 2870, 1483, 1451, 1378, 1343, 1299, 1218, 1189, 1131, 1076, 1022; MS (70 ev, EI) *m/z* (%) 337 (M^+, 8.52), 188 (100); HRMS Calcd for $C_{23}H_{31}NO$ (M^+): 337.2406, Found: 337.2399.

2. AuCl(PPh$_3$)/AgBF$_4$-catalyzed Cyclization Reaction of 1-(Indol-2yl)-2,2-dialkyl-3-alkyn-1-ols

(1) **4-Butyl-9-ethyl-1,2,6-trimethyl-9*H*-carbazole** (**3a**) **qya-5-058**

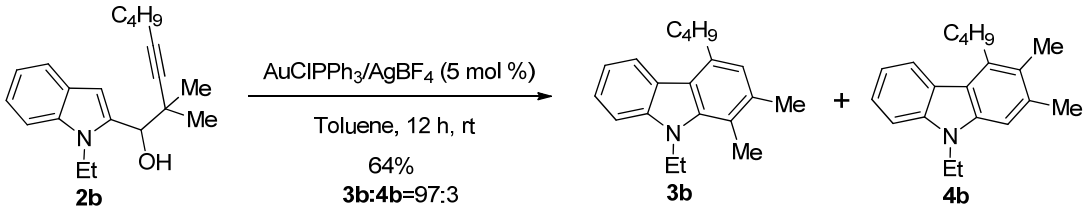


Typical Procedure: To a dry Schlenk tube were added $AgBF_4$ (10.8 mg, 0.055 mmol, weighed in glove box), $AuCl(PPh_3)$ (24.6 mg, 0.05 mmol), **2a** (310.2 mg, 1.0 mmol), and toluene (10 mL) under N_2. After continuous stirring for 12 h at rt, the reaction was complete as monitored by TLC. Filtration through a short pad of silica gel (eluent: Et_2O (20 mL × 3)), evaporation (the ratio of **3a** : **4a** (97 : 3) was determined by ^{1}H NMR analysis of the crude product), column chromatography on silica gel (petroleum ether/dichloromethane = 30/l for the first round, petroleum ether/dichloromethane = 30/l for the second round (impure part)) afforded **3a** (188.1 mg, 64%), which was further purified by recrystallization to afford pure **3a** (152.8 mg, 52%) as a solid: m. p. 80~82 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (s, 1H, ArH), 7.34 (d, J = 8.4 Hz, 1H, ArH), 7.31 (d, J = 8.4 Hz, 1H, ArH), 6.92 (s, 1H, ArH), 4.61

(q, J = 7.1 Hz, 2H, NCH_2), 3.22 (t, J = 7.8 Hz, 2H, $ArCH_2$), 2.73 (s, 3H, CH_3), 2.62 (s, 3H, CH_3), 2.53 (s, 3H, CH_3), 1.96-1.82 (m, 2H, CH_2), 1.71-1.58 (m, 2H, CH_2), 1.48 (t, J = 6.9 Hz, 3H, CH_3), 1.10 (t, J = 7.4 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.3, 139.7, 135.2, 134.2, 127.9, 125.7, 123.4, 122.7, 122.4, 120.0, 115.7, 108.2, 39.9, 33.9, 31.9, 23.0, 21.6, 20.9, 15.5, 14.8, 14.1; IR (KBr) ν (cm^{-1}) 3011, 2955, 2928, 2862, 1592, 1574, 1484, 1377, 1343, 1308, 1229, 1172, 1150, 1081; MS (70 ev, EI) *m/z* (%) 294 (M^++1, 21.92), 293 (M^+, 100); Elemental analysis calcd (%) for $C_{21}H_{27}N$: C, 85.95; H, 9.27; N, 4.77; Found: C, 85.64, H, 9.31; N, 4.84.

The following compounds **3b-3h** were prepared according to this procedure.

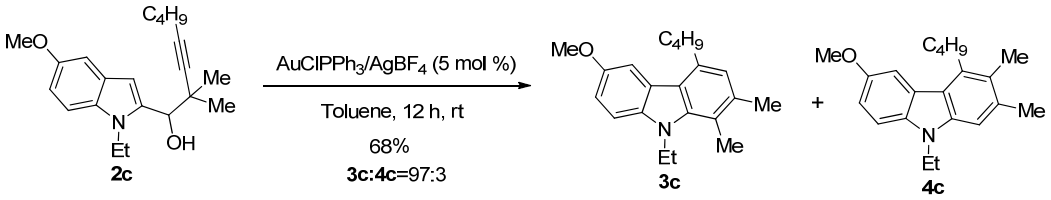
(2) **4-Butyl-9-ethyl-1,2-dimethyl-9*H*-carbazole (3b) qya-5-055**



The reaction of $AgBF_4$ (10.6 mg, 0.054 mmol), $AuCl(PPh_3)$ (25.0 mg, 0.051 mmol), and **2b** (297.8 mg, 1.0 mmol) in toluene (10 mL) at rt for 12 h afforded **3b** (178.2 mg, 64%) (petroleum ether/dichloromethane = 20/l) (the ratio of **3b** : **4b** (97 : 3) was determined by ^{1}H NMR analysis of the crude product), which was further purified by recrystallization to afford pure **3b** (125.4 mg, 45%) as a solid: m. p. 62~64 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, J = 7.8 Hz, 1H, ArH), 7.60-7.44 (m, 2H, ArH), 7.35-7.26 (m, 1H, ArH), 6.98 (s, 1H, ArH), 4.64 (q, J = 7.1 Hz, 2H, NCH_2), 3.27 (t, J = 7.8 Hz, 2H, $ArCH_2$), 2.76 (s, 3H, $ArCH_3$), 2.57 (s, 3H, $ArCH_3$), 2.00-1.82 (m, 2H, CH_2), 1.72-1.48 (m, 2H, CH_2), 1.53 (t, J = 7.2 Hz, 3H,

CH_3), 1.12 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.3, 140.0, 135.2, 134.4, 124.4, 123.2, 123.0, 122.2, 120.1, 118.8, 115.7, 108.4, 39.8, 33.9, 32.0, 23.0, 20.9, 15.5, 14.7, 14.1; IR (neat) ν (cm^{-1}) 2956, 2929, 2863, 1594, 1574, 1502, 1463, 1393, 1378, 1328, 1266, 1229, 1159, 1082, 1029; MS (70 ev, EI) *m/z* (%) 280 (M^++1, 22.45), 279 (M^+, 100); Elemental analysis calcd (%) for $C_{20}H_{25}N$: C, 85.97; H, 9.02; N, 5.01; Found: C, 85.73, H, 9.19; N, 5.06.

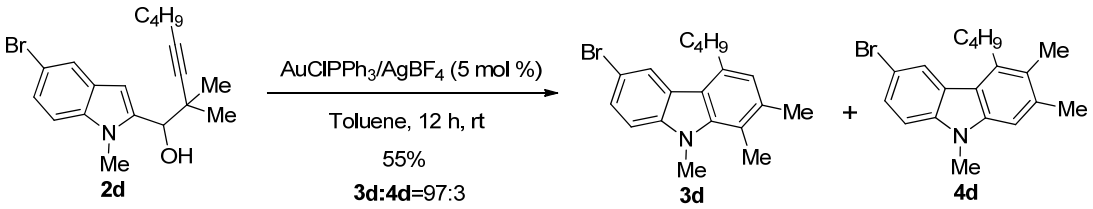
(3) **4-Butyl-9-ethyl-1,2-dimethyl-6-methoxy-9*H*-carbazole (3c) qya-5-059**



The reaction of $AgBF_4$ (10.7 mg, 0.055 mmol), $AuCl(PPh_3)$ (24.7 mg, 0.05 mmol), and **2c** (327.3 mg, 1.0 mmol) in toluene (10 mL) at rt for 12 h afforded **3c** (211.6 mg, 68%) (petroleum ether/dichloromethane = 5/l) (the ratio of **3c** : **4c** (97 : 3) was determined by ^{1}H NMR analysis of the crude product), which was further purified by recrystallization to afford pure **3c** (180.6 mg, 58%) as a solid: m. p. 93~94 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, J = 2.1 Hz, 1H, ArH), 7.32 (d, J = 9.0 Hz, 1H, ArH), 7.11 (dd, J_1 = 9.0 Hz and J_2 = 2.4 Hz, 1H, ArH), 6.86 (s, 1H, ArH), 4.56 (q, J = 7.1 Hz, 2H, NCH_2), 3.96 (s, 3H, OCH_3), 3.16 (t, J = 7.8 Hz, 2H, $ArCH_2$), 2.69 (s, 3H, $ArCH_3$), 2.49 (s, 3H, $ArCH_3$), 1.93-1.77 (m, 2H, CH_2), 1.67-1.50 (m, 2H, CH_2), 1.44 (t, J = 7.2 Hz, 3H, $ArCH_3$), 1.04 (t, J = 7.4 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 140.7, 136.5, 135.2, 134.5, 123.6, 122.7, 120.0, 115.9, 112.8, 109.0, 106.1, 56.1, 40.0, 33.9, 32.1, 23.1, 20.9, 15.5, 14.7, 14.1; IR (neat) ν (cm^{-1}) 2954, 2930, 2864, 2829, 1619, 1579, 1482, 1377, 1349, 1311, 1296,

1213, 1172, 1075, 1039; MS (70 ev, EI) *m/z* (%) 310 (M^++1, 23.44), 309 (M^+, 100); Elemental analysis calcd (%) for $C_{21}H_{27}NO$: C, 81.51; H, 8.79; N, 4.53; Found: C, 81.40, H, 8.89; N, 4.56.

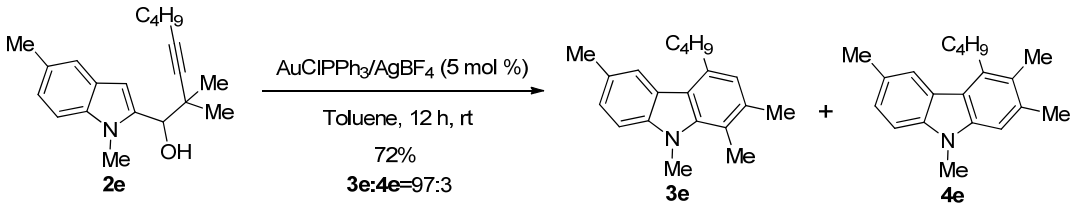
(4) **6-Bromo-4-butyl-1,2,9-trimethyl-9*H*-carbazole (3d) qya-5-088**



The reaction of $AgBF_4$ (5.3 mg, 0.027 mmol), $AuCl(PPh_3)$ (12.6 mg, 0.025 mmol), and **2d** (181.3 mg, 0.5 mmol) in toluene (5 mL) at rt for 12 h afforded **3d** (94.6 mg, 55%) (petroleum ether/dichloromethane = 30/l) (the ratio of **3d** : **4d** (97 : 3) was determined by ^{1}H NMR analysis of the crude product), which was further purified by recrystallization to afford pure **3d** (81.6 mg, 47%) as a solid: m. p. 103~104 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, J = 1.8 Hz, 1H, ArH), 7.50 (dd, J_1 = 8.7 Hz and J_2 = 1.8 Hz, 1H, ArH), 7.22 (d, J = 8.7 Hz, 1H, ArH), 6.87 (s, 1H, ArH), 4.06 (s, 3H, NCH_3), 3.09 (t, J = 7.8 Hz, 2H, $ArCH_2$), 2.70 (s, 3H, $ArCH_3$), 2.45 (s, 3H, $ArCH_3$), 1.86-1.71 (m, 2H, CH_2), 1.62-1.47 (m, 2H, CH_2), 1.02 (t, J = 7.4 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.4, 141.0, 135.4, 135.3, 127.0, 124.6, 123.4, 119.0, 116.4, 111.6, 109.8, 33.6, 33.5, 31.7, 22.9, 20.8, 15.2, 14.0; IR (neat) ν (cm^{-1}) 2955, 2928, 2870, 1622, 1597, 1465, 1417, 1377, 1293, 1143, 1110, 1067; MS (70 ev, EI) *m/z* (%) 346 (M^+ (^{81}Br) + 1, 21.67), 345 (M^+ (^{81}Br), 95.07), 344 (M^+ (^{79}Br) + 1, 25.18), 343 (M^+ (^{79}Br), 100); Elemental analysis calcd (%) for $C_{19}H_{22}BrN$: C, 66.28; H, 6.44; N, 4.07; Found: C, 66.20; H, 6.43; N,

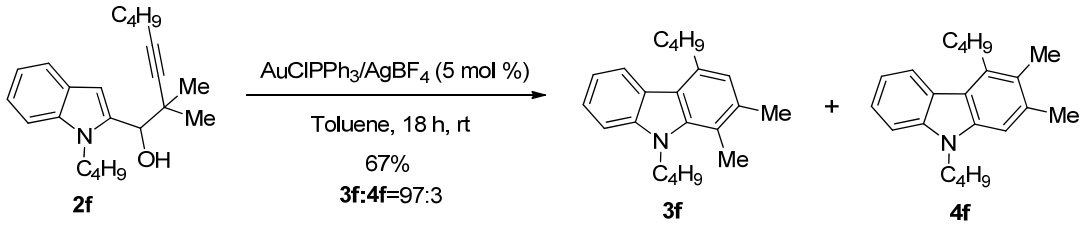
4.19.

(5) **4-Butyl-1,2,6,9-tetramethyl-9*H*-carbazole (3e) qya-5-072**



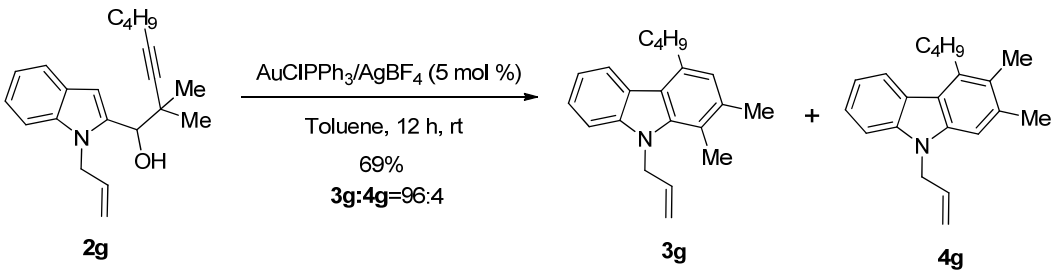
The reaction of $AgBF_4$ (10.8 mg, 0.055 mmol), $AuCl(PPh_3)$ (25.0 mg, 0.051 mmol), and **2e** (297.8 mg, 1.0 mmol) in toluene (10 mL) at rt for 12 h afforded **3e** (200.6 mg, 72%) (petroleum ether/dichloromethane = 30/l~15/1) (the ratio of **3e** : **4e** (97 : 3) was determined by ^{1}H NMR analysis of the crude product), which was further purified by recrystallization to afford pure **3e** (165.0 mg, 59%) as a solid: m. p. 105~106 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (s, 1H, ArH), 7.28-7.21 (m, 2H, ArH), 6.82 (s, 1H, ArH), 4.06 (s, 3H, NCH_3), 3.13 (t, J = 7.8 Hz, 2H, $ArCH_2$), 2.70 (s, 3H, $ArCH_3$), 2.54 (s, 3H, $ArCH_3$), 2.44 (s, 3H, $ArCH_3$), 1.86-1.72 (m, 2H, CH_2), 1.62-1.47 (m, 2H, CH_2), 1.01 (t, J = 7.4 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.5, 140.9, 135.2, 134.3, 127.9, 125.7, 123.2, 122.8, 122.3, 119.9, 116.1, 108.2, 33.8, 33.5, 31.9, 23.0, 21.7, 20.7, 15.2, 14.1; IR (neat) ν (cm^{-1}) 2923, 1594, 1573, 1463, 1388, 1315, 1299, 1233, 1174, 1147, 1091, 1048; MS (70 ev, EI) *m/z* (%) 280 (M^++1, 23.69); 279 (M^+, 100); Elemental analysis calcd (%) for $C_{20}H_{25}N$: C, 85.97; H, 9.02; N, 5.01; Found: C, 85.72; H, 9.10; N, 5.06.

(6) **4,9-Dibutyl-1,2-dimethyl-9*H*-carbazole (3f) qya-5-085**



The reaction of $AgBF_4$ (10.7 mg, 0.055 mmol), $AuCl(PPh_3)$ (24.6 mg, 0.05 mmol), and **2f** (325.2 mg, 1.0 mmol) in toluene (10 mL) at rt for 18 h afforded **3f** (205.7 mg, 67%) (petroleum ether/dichloromethane = 30/l) (the ratio of **3f** : **4f** (97 : 3) was determined by ^{1}H NMR analysis of the crude product) as a solid: m. p. 67~68 °C (*n*-hexane/ethyl acetate); ^{1}H NMR of **3f** (300 MHz, $CDCl_3$) δ 8.05 (d, J = 8.1 Hz, 1H, ArH), 7.36 (t, J = 7.4 Hz, 1H, ArH), 7.28 (d, J = 7.8 Hz, 1H, ArH), 7.17 (t, J = 7.2 Hz, 1H, ArH), 6.82 (s, 1H, ArH), 4.30 (t, 2H, J = 8.0 Hz, NCH_2), 3.12 (t, J = 7.4 Hz, 2H, $ArCH_2$), 2.53 (s, 3H, $ArCH_3$), 2.39 (s, 3H, $ArCH_3$), 1.87-1.64 (m, 4H, 2 × CH_2), 1.61-1.44 (m, 2H, CH_2), 1.42-1.26 (m, 2H, CH_2), 1.03-0.85 (m, 6H, 2 × CH_3); the following signals are discernible for **4f**: 6.96 (s, 1H, ArH), 4.10 (t, J = 6.9 Hz, 2H, NCH_2), 2.32 (s, 3H, $ArCH_3$); ^{13}C NMR of **3f** (75 MHz, $CDCl_3$) δ 141.7, 140.1, 135.1, 134.4, 124.3, 123.1, 122.9, 122.1, 120.1, 118.7, 115.7, 108.6, 45.0, 33.9, 32.6, 32.0, 23.0, 20.9, 20.2, 14.7, 14.1, 13.8; IR (neat) ν (cm^{-1}) 2957, 2929, 2863, 1594, 1574, 1502, 1463, 1456, 1393, 1328, 1218, 1159, 1113, 1085, 1029; MS (70 ev, EI) *m/z* (%) 308 (M^++1, 16.67), 307 (M^+, 64.64), 264 (100); Elemental analysis calcd (%) for $C_{22}H_{29}N$: C, 85.94; H, 9.51; N, 4.56; Found: C, 85.70; H, 9.61; N, 4.70.

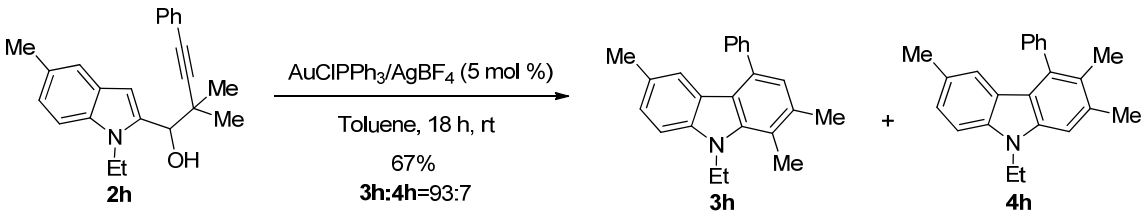
(7) **9-Allyl-4-butyl-1,2-dimethyl-9*H*-carbazole (3g) qya-5-105**



2g **3g** **4g**

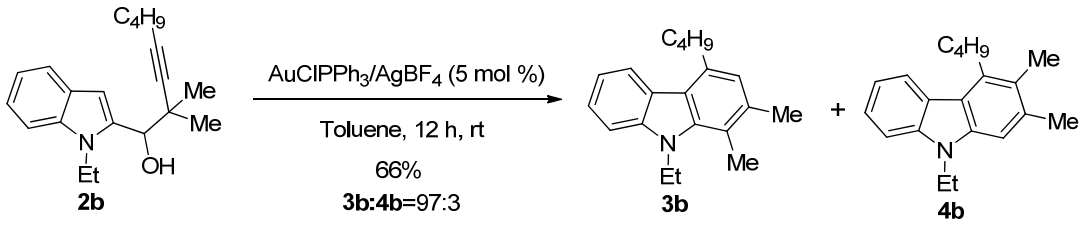
The reaction of $AgBF_4$ (10.8 mg, 0.055 mmol), $AuCl(PPh_3)$ (25.0 mg, 0.05 mmol), and **2g** (311.2 mg, 1.0 mmol) in toluene (10 mL) at rt for 12 h afforded **3g** (202.8 mg, 69%, **3g** : **4g** = 96 : 4 as determined by ^{1}H NMR analysis) (petroleum ether/dichloromethane = 30/l~20/1) (the ratio of **3g** : **4g** (95 : 5) was determined by ^{1}H NMR analysis of the crude product), which was further purified by recrystallization to afford pure **3g** (158.6 mg, 54%) as a solid: m. p. 101~102 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.5 Hz, 1H, ArH), 7.42 (t, *J* = 7.5 Hz, 1H, ArH), 7.32 (d, *J* = 7.8 Hz, 1H, ArH), 7.27-7.20 (m, 1H, ArH), 6.89 (s, 1H, ArH), 6.23-6.07 (m, 1H, =CH), 5.23 (d, *J* = 11.7 Hz, 1H, one proton of $=CH_2$), 5.14-5.07 (m, 2H, NCH_2), 5.01 (d, *J* = 17.1 Hz, 1H, one proton of $=CH_2$), 3.17 (t, *J* = 7.8 Hz, 2H, $ArCH_2$), 2.64 (s, 3H, $ArCH_3$), 2.46 (s, 3H, $ArCH_3$), 1.91-1.73 (m, 2H, CH_2), 1.63-1.48 (m, 2H, CH_2), 1.02 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.0, 140.7, 135.2, 134.6, 134.2, 124.6, 123.2, 123.1, 122.1, 120.1, 119.1, 116.2, 116.0, 108.8, 47.7, 33.9, 32.0, 23.0, 20.8, 14.5, 14.1; IR (neat) ν (cm^{-1}) 2955, 2928, 2862, 1645, 1595, 1574, 1502, 1463, 1392, 1354, 1327, 1302, 1225, 1162, 1118, 1029; MS (70 ev, EI) *m/z* (%) 292 (M^++1, 26.18), 291 (M^+, 100); Elemental analysis calcd (%) for $C_{21}H_{25}N$: C, 86.55; H, 8.65; N, 4.81; Found: C, 86.38; H, 8.70; N, 4.89.

(8) **9-Ethyl-1,2,6-trimethyl-4-phenyl-9*H*-carbazole (3h) qya-5-096**



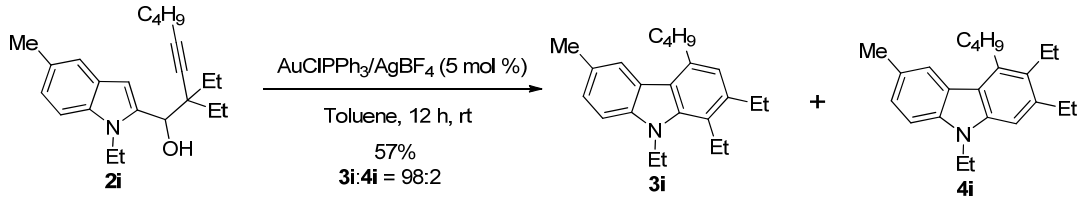
The reaction of $AgBF_4$ (10.6 mg, 0.054 mmol), $AuCl(PPh_3)$ (24.5 mg, 0.05 mmol), and **2h** (165.9 mg, 0.5 mmol) in toluene (5 mL) at rt for 18 h afforded **3h** (104.7 mg, 67%) (petroleum ether/dichloromethane = 20/l) (the ratio of **3h** : **4h** (93 : 7) was determined by ^{1}H NMR analysis of the crude product) , which was further purified by recrystallization to afford pure **3h** (88.9 mg, 57%) as a solid: m. p. 156~157 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61-7.40 (m, 5H, ArH), 7.26 (d, *J* = 8.7 Hz, 1H, ArH), 7.16 (d, *J* = 8.1 Hz, 1H, ArH), 7.07 (s, 1H, ArH), 6.91 (s, 1H, ArH), 4.59 (q, *J* = 7.2 Hz, 2H, CH_2), 2.74 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 1.45 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.6, 140.1, 139.9, 134.9, 134.2, 129.3, 128.2, 127.5, 127.2, 126.2, 123.5, 123.0, 122.1, 119.7, 117.3, 108.2, 40.0, 21.4, 20.9, 15.5, 14.9; IR (neat) ν (cm^{-1}) 3069, 3014, 2977, 2957, 2922, 2864, 1599, 1590, 1564, 1478, 1463, 1443, 1373, 1354, 1309, 1269, 1209, 1185, 1150, 1170; 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 **4h**: T_R 6.1 min: 314 (M^+ + 1, 27.05), 313 (M^+, 95.88), 298 (100), for **3h**: T_R 6.3 min: 314 (M^+ + 1, 24.46), 313 (M^+, 99.01), 298 (100); Elemental analysis calcd (%) for $C_{23}H_{23}N$: C, 88.13; H, 7.40; N, 4.47; Found: C, 88.04; H, 7.43; N, 4.63.

(9) **4-Butyl-9-ethyl-1,2-dimethyl-9*H*-carbazole (3b) qya-7-101**



The reaction of $AgBF_4$ (33.9 mg, 0.175 mmol), $AuCl(PPh_3)$ (87.0 mg, 0.175 mmol), and **2b** (1040.1 mg, 3.5 mmol) in toluene (35 mL) at rt for 12 h afforded **3b** (645.3 mg, 66%) (petroleum ether/dichloromethane = 20/l) (the ratio of **3b** : **4b** (97 : 3) was determined by ^{1}H NMR analysis of the crude product), which was further purified by recrystallization to afford pure **3b** (496.3 mg, 51%) as a solid: m. p. 62~64 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.8 Hz, 1H, ArH), 7.63-7.47 (m, 2H, ArH), 7.39 (t, *J* = 7.4 Hz, 1H, ArH), 7.03 (s, 1H, ArH), 4.67 (q, *J* = 7.1 Hz, 2H, NCH_2), 3.32 (t, *J* = 7.8 Hz, 2H, $ArCH_2$), 2.80 (s, 3H, $ArCH_3$), 2.62 (s, 3H, $ArCH_3$), 2.05-1.90 (m, 2H, CH_2), 1.80-1.63 (m, 2H, CH_2), 1.57 (t, *J* = 7.2 Hz, 3H, CH_3), 1.18 (t, *J* = 7.4 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.3, 140.0, 135.2, 134.4, 124.4, 123.2, 123.0, 122.2, 120.1, 118.8, 115.7, 108.4, 39.8, 33.9, 32.0, 23.0, 20.9, 15.5, 14.7, 14.1.

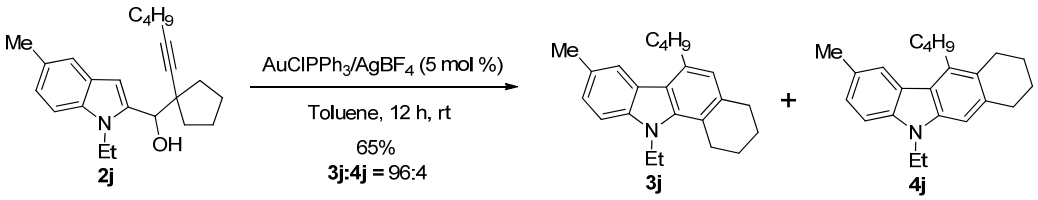
(10) **4-Butyl-1,2,9-triethyl-6-methyl-9*H*-carbazole (3i) qya-5-099**



The reaction of $AgBF_4$ (10.1 mg, 0.052 mmol), $AuCl(PPh_3)$ (24.6 mg, 0.05 mmol), and **2i** (339.6 mg, 1.0 mmol) in toluene (10 mL) at rt for 12 h afforded **3i** (183.1 mg, 57%, **3i** : **4i** = 98 : 2 as determined by ^{1}H NMR analysis) (petroleum ether/dichloromethane = 40/l~20/1): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (s, 1H,

ArH), 7.46-7.30 (m, 2H, ArH), 7.00 (s, 1H, ArH), 4.62 (q, J = 7.1 Hz, 2H, NCH_2), 3.30 (t, J = 7.8 Hz, 2H, $ArCH_2$), 3.19 (q, J = 7.5 Hz, 2H, $ArCH_2$), 2.96 (q, J = 7.6 Hz, 2H, $ArCH_2$), 2.67 (s, 3H, CH_3), 2.03-1.87 (m, 2H, CH_2), 1.77-1.62 (m, 2H, CH_2), 1.55-1.37 (m, 9H, 3× CH_3), 1.16 (t, J = 7.5 Hz, 3H, CH_3); the following signals are discernible for **4i**: 7.21 (s, 1H, ArH), 4.40 (q, J = 7.1 Hz, 2H, NCH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.9, 139.5, 139.1, 135.6, 127.8, 125.6, 123.5, 122.4, 121.6, 121.5, 120.3, 108.2, 39.4, 34.1, 31.8, 26.1, 23.0, 21.6, 20.4, 16.6, 16.4, 15.2, 14.1; IR (neat) ν (cm^{-1}) 3006, 2962, 2930, 2869, 1591, 1574, 1479, 1378, 1348, 1305, 1229, 1170, 1054; MS (70 ev, EI) *m/z* (%) 322 (M^++1, 26.18), 321 (M^+, 100); HRMS Calcd for $C_{23}H_{31}N$ (M^+): 321.2457, Found: 321.2452.

(11) **6-Butyl-11-ethyl-8-methyl-1,2,3,4-tetrahydro-11*H*-benzo[*a*]carbazole (3j) qya-5-098**

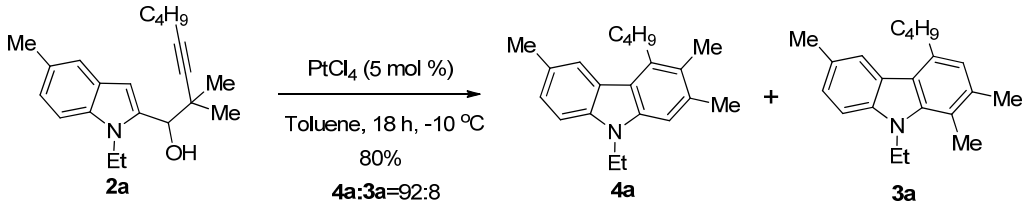


The reaction of $AgBF_4$ (10.5 mg, 0.054 mmol), $AuCl(PPh_3)$ (25.0 mg, 0.05 mmol), and **2j** (336.5 mg, 1.0 mmol) in toluene (10 mL) at rt for 12 h afforded **3j** (207.2 mg, 68%, **3j** : **4j** = 96 : 4 as determined by ^{1}H NMR analysis) (petroleum ether/dichloromethane = 100/l~40/1): solid; m. p. 103~104 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (s, 1H, ArH), 7.49-7.31 (m, 2H, ArH), 6.91 (s, 1H, ArH), 4.68 (q, J = 7.1 Hz, 2H, NCH_2), 3.40 (t, J = 5.7 Hz, 2H, $ArCH_2$), 3.31 (t, J = 7.8 Hz, 2H, $ArCH_2$), 3.13 (t, J = 5.7 Hz, 2H, $ArCH_2$), 2.72 (s, 3H, CH_3), 2.16-1.89 (m, 6H, 3 × CH_2), 1.82-1.65 (m, 2H, CH_2), 1.52 (t, J = 7.2 Hz, 3H, CH_3);

1.20 (t, J = 7.2 Hz, 3H, CH_3); the following signals are discernible for **4j**: 7.12 (s, 1H, ArH), 4.39 (q, J = 6.9 Hz, 2H, NCH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.7, 139.3, 135.3, 134.8, 127.9, 125.4, 123.5, 122.3, 121.8, 119.3, 117.6, 108.2, 39.9, 33.9, 31.9, 30.7, 26.3, 23.7, 23.0, 22.8, 21.6, 15.5, 14.1; IR (neat) ν (cm^{-1}) 3008, 2952, 2928, 2859, 1593, 1574, 1483, 1439, 1376, 1347, 1308, 1262, 1236, 1172, 1075, 1030; MS (70 ev, EI) *m/z* (%) 320 (M^++1, 26.15), 319 (M^+, 100); Elemental analysis calcd (%) for $C_{23}H_{29}N$: C, 86.47; H, 9.15; N, 4.38; Found: C, 86.19; H, 9.27; N, 4.52.

3. $PtCl_4$-catalyzed cyclization reaction of 1-(indol-2-yl)-2,2-dimethyl-3-alkyn-1-ols

(1) **4-Butyl-9-ethyl-2,3,6-trimethyl-9*H*-carbazole** (**4a**) **qya-5-038**

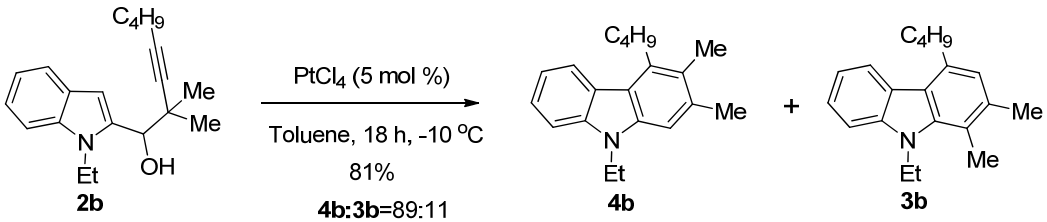


Typical Procedure: To a dry Schlenk tube were added $PtCl_4$ (17.1 mg, 0.05 mmol, weighed inside a glove box), **2a** (311.6 mg, 1.0 mmol), and toluene (10 mL) under N_2. After continuous stirring for 18 h at -10 °C, the reaction was complete as monitored by TLC. Filtration through a short pad of silica gel (eluent: Et_2O (20 mL × 3)), evaporation (the ratio of **4a** : **3a** (92 : 8) was determined by ^1H NMR analysis of the crude product), and column chromatography on silica gel (petroleum ether/ethyl acetate = 100/l) afforded **4a** and **3a** (235.0 mg, 80%), which was further purified by recrystallization to afford **4a** (179.3 mg, 61%, **4a** : **3a** = 96 : 4) as a solid: m. p. 84~86 °C (*n*-hexane/ethyl acetate); ^1H NMR of **4a** (300 MHz, $CDCl_3$) δ 7.99 (s, 1H, ArH), 7.37-7.27 (m, 2H, ArH), 7.14 (s, 1H, ArH), 4.34 (q, J = 7.1 Hz, 2H, NCH_2),

3.33 (t, J = 8.0 Hz, 2H, $ArCH_2$), 2.62 (s, 3H, $ArCH_3$), 2.56 (s, 3H, $ArCH_3$), 2.43 (s, 3H, $ArCH_3$), 1.92-1.62 (m, 4H, 2 × CH_2), 1.44 (t, J = 7.1 Hz, 3H, CH_3), 1.13 (t, J = 7.2 Hz, 3H, CH_3); the following signals are discernible for **3a**: 7.93 (s, 1H, ArH), 6.91 (s, 1H, ArH), 4.60 (q, J = 7.1 Hz, 2H, NCH_2), 3.21 (t, J = 7.7 Hz, 2H, $ArCH_2$), 2.73 (s, 3H, $ArCH_3$); ^{13}C NMR of **4a** (75 MHz, $CDCl_3$) δ 138.8, 138.2, 136.4, 134.8, 127.4, 125.4, 124.6, 123.2, 122.4, 119.1, 107.7, 107.1, 37.1, 31.4, 30.3, 23.4, 22.3, 21.7, 14.5, 14.1, 13.6; IR (neat) ν (cm^{-1}) 2956, 2929, 2871, 1623, 1605, 1576, 1487, 1471, 1377, 1349, 1307, 1266, 1192, 1147, 1015; 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 **4a**: T_R 5.290 min: 294 (M^++1, 22.77), 293 (M^+, 100), for **3a**: T_R 5.313 min: 294 (M^++1, 23.31), 293 (M^+, 100); Elemental analysis calcd (%) for $C_{21}H_{27}N$: C, 85.95; H, 9.27; N, 4.77; Found: C, 85.91; H, 9.46; N, 4.91.

The following compounds **4b**, **4c**, **4e**, **4f**, and **4h** were prepared according to this procedure.

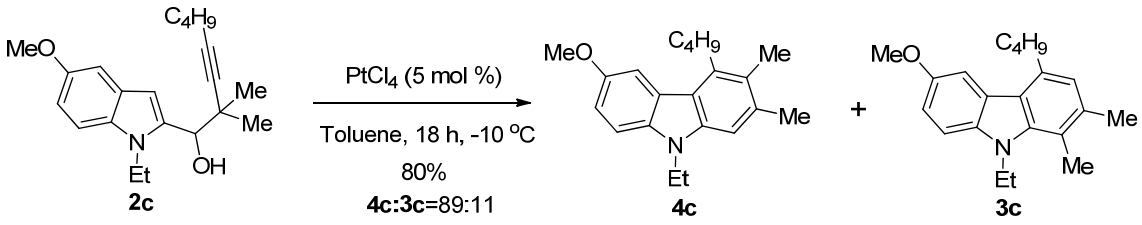
(2) **4-Butyl-9-ethyl-2,3-dimethyl-9*H*-carbazole (4b) qya-5-037**



The reaction of $PtCl_4$ (17.1 mg, 0.05 mmol) and **2b** (297.2 mg, 1.0 mmol) in toluene (10 mL) at -10 °C for 18 h afforded **4b** and **3b** (226.2 mg, 81%) (petroleum ether/ethyl acetate = 100/l) (the ratio of **4b** : **3b** (89 : 11) was determined by ^{1}H NMR

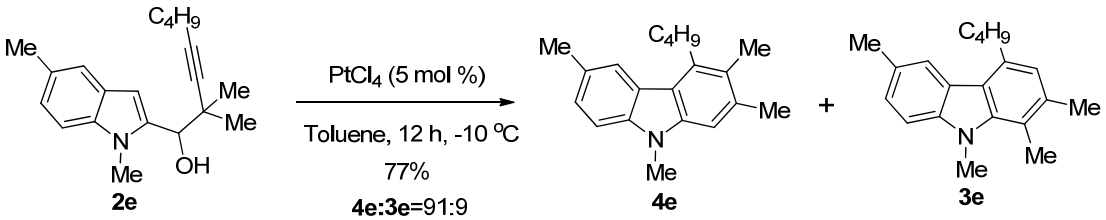
analysis of the crude product) as a liquid: ^{1}H NMR of **4b** (300 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.8 Hz, 1H, ArH), 7.57-7.43 (m, 2H, ArH), 7.37-7.27 (m, 1H, ArH), 7.20 (s, 1H, ArH), 4.39 (q, *J* = 7.2 Hz, 2H, NCH_2), 3.39 (t, *J* = 8.1 Hz, 2H, $ArCH_2$), 2.61 (s, 3H, $ArCH_3$), 2.49 (s, 3H, $ArCH_3$), 1.99-1.61 (m, 4H, 2 × CH_2), 1.49 (t, *J* = 7.2 Hz, 3H, CH_3), 1.16 (t, *J* = 7.2 Hz, 3H, CH_3); the following signals are discernible for **3b**: 8.20 (d, *J* = 8.1 Hz, 1H, ArH), 6.98 (s, 1H, ArH), 4.65 (q, *J* = 7.1 Hz, 2H, NCH_2), 3.27 (t, *J* = 7.8 Hz, 2H, $ArCH_2$), 2.77 (s, 3H, $ArCH_3$), 2.57 (s, 3H, $ArCH_3$); ^{13}C NMR of **4b** (75 MHz, $CDCl_3$) δ 139.9, 138.5, 136.4, 135.0, 124.9, 124.2, 123.1, 122.2, 119.3, 118.4, 108.3, 107.2, 37.1, 31.4, 30.4, 23.4, 22.3, 14.5, 14.1, 13.6; the following signals are discernible for **3b**: 141.4, 140.0, 135.2, 134.5, 124.4, 123.3, 123.0, 122.2, 120.2, 118.8, 115.7, 108.5, 39.8, 33.9, 32.0, 23.0, 21.0, 15.5, 14.8, 14.1; IR (neat) ν (cm^{-1}) 3049, 2956, 2929, 2871, 1620, 1598, 1572, 1470, 1378, 1330, 1314, 1264, 1207, 1180, 1111, 1082, 1030; 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 **4b**: T_R 5.13 min: 280 (M^++1, 22.45), 279 (M^+, 100), for **3b**: T_R 5.17 min: 280 (M^++1, 22.49), 279 (M^+, 100); Elemental analysis calcd (%) for $C_{20}H_{25}N$: C, 85.97; H, 9.02; N, 5.01; Found: C, 85.73; H, 9.19; N, 5.06.

(3) **4-Butyl-9-ethyl-2,3-dimethyl-6-methoxy-9*H*-carbazole (4c)** qya-5-054



The reaction of $PtCl_4$ (17.0 mg, 0.05 mmol) and **2c** (327.2 mg, 1.0 mmol) in toluene (10 mL) at -10 ^oC for 18 h afforded **4c** and **3c** (246.0 mg, 80%) (petroleum ether/ethyl acetate = 50/l) (the ratio of **4c** : **3c** (89 : 11) as determined by ^1H NMR analysis of the crude product), which was further purified by recrystallization to afford **4c** and **3c** (201.6 mg, 65%, **4c** : **3c** = 98:2 as determined by ^1H NMR analysis) as a solid: m. p. 100~102 °C (*n*-hexane/ethyl acetate); ^1H NMR of **4c** (300 MHz, $CDCl_3$) δ 7.67 (d, J = 2.1 Hz, 1H, ArH), 7.29 (d, J = 9.0 Hz, 1H, ArH), 7.14-7.05 (m, 2H, ArH), 4.30 (q, J = 7.1 Hz, 2H, NCH_2), 3.95 (s, 3H, OCH_3), 3.26 (t, J = 8.1 Hz, 2H, $ArCH_2$), 2.51 (s, 3H, $ArCH_3$), 2.38 (s, 3H, $ArCH_3$), 1.83-1.60 (m, 4H, 2 × CH_2), 1.39 (t, J = 7.2 Hz, 3H, CH_3), 1.06 (t, J = 7.1 Hz, 3H, CH_3); the following signals are discernible for **3c**: 2.68 (s, 3H, $ArCH_3$); ^{13}C NMR of **4c** (75 MHz, $CDCl_3$) δ 153.1, 139.2, 136.2, 135.1, 124.4, 123.3, 119.1, 112.7, 108.3, 107.3, 106.3, 56.2, 37.2, 31.5, 30.3, 23.5, 22.3, 14.5, 14.1, 13.7; IR (neat) ν (cm^{-1}) 2955, 2931, 2871, 2829, 1625, 1607, 1578, 1486, 1435, 1350, 1309, 1215, 1170, 1081, 1047; GC-MS (GC condition: injector: 280 ^oC; column: DB5 column 30 m × 0.25 mm, temperature programming: 60 ^oC (2 min), 20 ^oC/min to 280 ^oC, 280 ^oC (30 min); detector: 280 ^oC) (70 ev, EI) *m/z* (%) for **4c**: T_R 6.0 min: 310 (M^++1, 23.11), 309 (M^+, 100), for **3c**: T_R 6.1 min: 310 (M^++1, 26.36), 309 (M^+, 100); Elemental analysis calcd (%) for $C_{21}H_{27}NO$: C, 81.51; H, 8.79; N, 4.53; Found: C, 81.47; H, 8.85; N, 4.56.

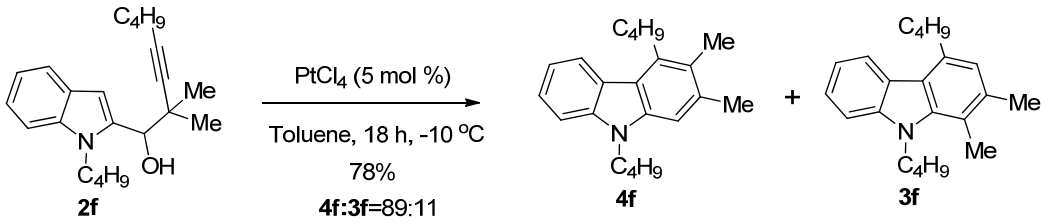
(4) **4-Butyl-2,3,6,9-tetramethyl-9*H*-carbazole (4e)** qya-5-068



The reaction of $PtCl_4$ (17.1 mg, 0.05 mmol) and **2e** (297.6 mg, 1.0 mmol) in toluene (10 mL) at -10 °C for 12 h afforded **4e** and **3e** (215.1 mg, 77%, petroleum ether/ethyl acetate = 50/l) (the ratio of **4e** : **3e** (91 : 9) as determined by ^{1}H NMR analysis of the crude product) as a solid: m. p. 72~74 °C (*n*-hexane/ethyl acetate); ^{1}H NMR of **4e** (300 MHz, $CDCl_3$) δ 7.90 (s, 1H, ArH), 7.25-7.20 (m, 2H, ArH), 7.03 (s, 1H, ArH), 3.71 (s, 3H, NCH_3), 3.25 (t, *J* = 8.1 Hz, 2H, $ArCH_2$), 2.54 (s, 3H, $ArCH_3$), 2.47 (s, 3H, $ArCH_3$), 2.35 (s, 3H, $ArCH_3$), 1.83-1.51 (m, 4H, 2 × CH_2), 1.05 (t, *J* = 7.2 Hz, 3H, CH_3); the following signals are discernible for **3e**: 7.83 (s, 1H, ArH), 7.20-7.17 (m, 2H, ArH), 6.81 (s, 1H, ArH), 4.01 (s, 3H, NCH_3), 3.12 (t, *J* = 8.0 Hz, 2H, $ArCH_2$), 2.67 (s, 3H, $ArCH_3$), 2.42 (s, 3H, $ArCH_3$); ^{13}C NMR of **4e** (75 MHz, $CDCl_3$) δ 139.9, 139.4, 136.2, 134.9, 127.5, 125.5, 124.7, 123.1, 122.3, 119.0, 107.7, 107.2, 31.4, 30.3, 28.8, 23.4, 22.2, 21.7, 14.5, 14.1; the following signals are discernible for **3e**: 141.5, 140.9, 135.2, 134.3, 127.9, 125.7, 123.2, 122.8, 119.9, 116.1, 108.2, 38.8, 33.4, 32.0, 23.0, 21.6, 20.7, 15.2; IR (neat) ν (cm^{-1}) 2955, 2923, 2871, 2858, 1625, 1606, 1576, 1488, 1376, 1365, 1303, 1281, 1213, 1146, 1109, 1005; 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 **4e**: T_R 7.2 min: 280 (M^++1, 22.58), 279 (M^+, 100), for **3e**: T_R 7.3 min: 280 (M^++1, 21.54), 279 (M^+, 100); Elemental analysis calcd

(%) for $C_{20}H_{25}N$: C, 85.97; H, 9.02; N, 5.01; Found: C, 85.63; H, 9.13; N, 5.15.

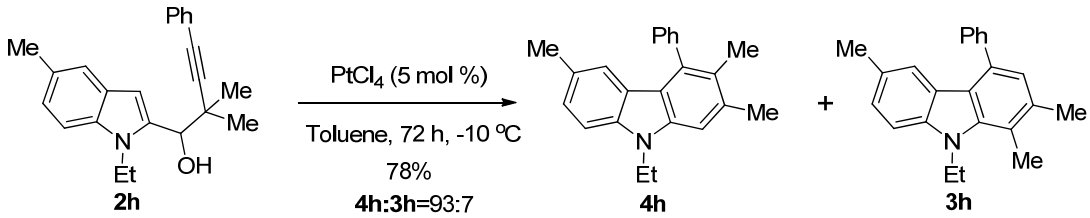
(5) **4,9-Dibutyl-2,3-dimethyl-9*H*-carbazole (4f) qya-5-084**



The reaction of $PtCl_4$ (17.1 mg, 0.05 mmol) and **2f** (325.6 mg, 1.0 mmol) in toluene (10 mL) at -10 °C for 18 h afforded **4f** and **3f** (239.4 mg, 78%) (petroleum ether/dichloromethane = 30/l) (the ratio of **4f** : **3f** (89 : 11) as determined by ^{1}H NMR analysis of the crude product) as a solid; m. p. 62~64 °C (*n*-hexane/ethyl acetate); ^{1}H NMR of **4f** (300 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.1 Hz, 1H, ArH), 7.44-7.33 (m, 2H, ArH), 7.23-7.16 (m, 1H, ArH), 7.07 (s, 1H, ArH), 4.22 (t, *J* = 7.2 Hz, 2H, NCH_2), 3.26 (t, *J* = 8.3 Hz, 2H, $ArCH_2$), 2.48 (s, 3H, $ArCH_3$), 2.36 (s, 3H, $ArCH_3$), 1.88-1.50 (m, 6H, 2 × CH_2), 1.49-1.31 (m, 2H, CH_2), 1.03 (t, *J* = 7.2 Hz, 3H, CH_3), 0.93 (t, *J* = 7.4 Hz, 3H, CH_3), the following signals are discernible for **3f**: 8.06 (d, *J* = 7.8 Hz, 1H, ArH), 6.85 (s, 1H, ArH), 4.45 (t, *J* = 7.8 Hz, 2H, NCH_2), 3.14 (t, *J* = 7.8 Hz, 2H, $ArCH_2$), 2.64 (s, 3H, $ArCH_3$), 2.45 (s, 3H, $ArCH_3$); ^{13}C NMR of **4f** (75 MHz, $CDCl_3$) δ 140.5, 139.0, 136.3, 134.9, 124.8, 124.2, 123.0, 122.1, 119.2, 118.3, 108.3, 107.4, 42.5, 31.4, 31.0, 30.4, 23.4, 22.3, 20.6, 14.5, 14.1, 13.9, the following signals are discernible for **3f**: 141.7, 140.1, 135.2, 134.4, 124.3, 123.1, 122.2, 120.1, 118.8, 115.7, 108.7, 45.1, 33.9, 32.6, 32.0, 23.0, 21.0, 20.2, 14.8; IR (KBr) ν (cm^{-1}) 2956, 2929, 2871, 1621, 1598, 1481, 1464, 1377, 1359, 1329, 1314, 1275, 1174, 1112, 1030, 1004; GC-MS (GC condition: injector: 280 °C; column: DB5 column 30 m × 0.25 mm,

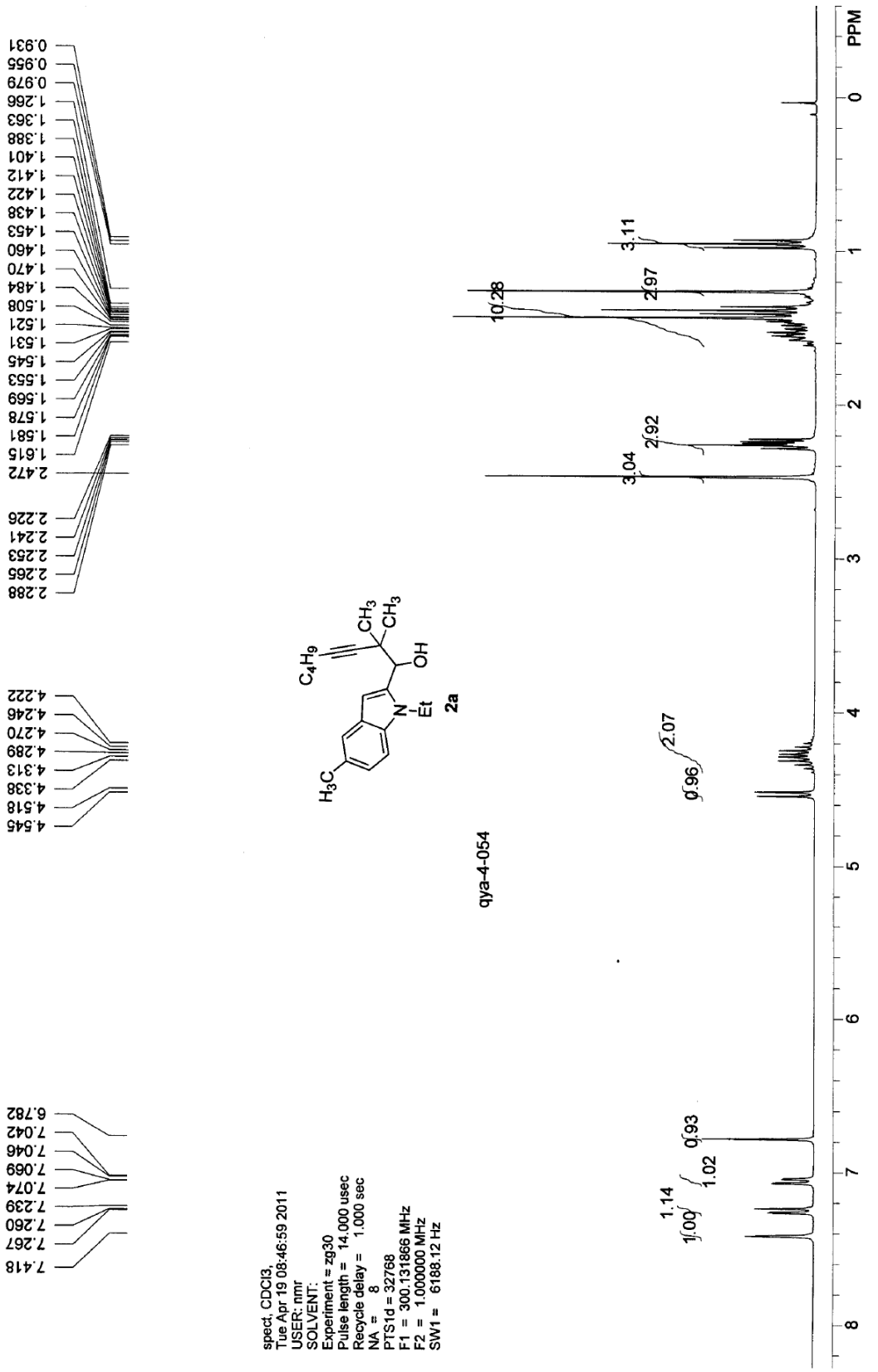
temperature programming: 60 °C (2 min), 20 °C/min to 280 °C, 280 °C (30 min); detector: 280 °C) (70 ev, EI) *m/z* (%) for **4f**: T_R 5.80 min: 308 (M^++1, 20.06), 307 (M^+, 81.77), 264 (100), for **3f**: T_R 5.82 min: 308 (M^++1, 13.60), 307 (M^+, 55.51), 264 (100); Elemental analysis calcd (%) for $C_{22}H_{29}N$: C, 85.94; H, 9.51; N, 4.56; Found: C, 85.64; H, 9.67; N, 4.74.

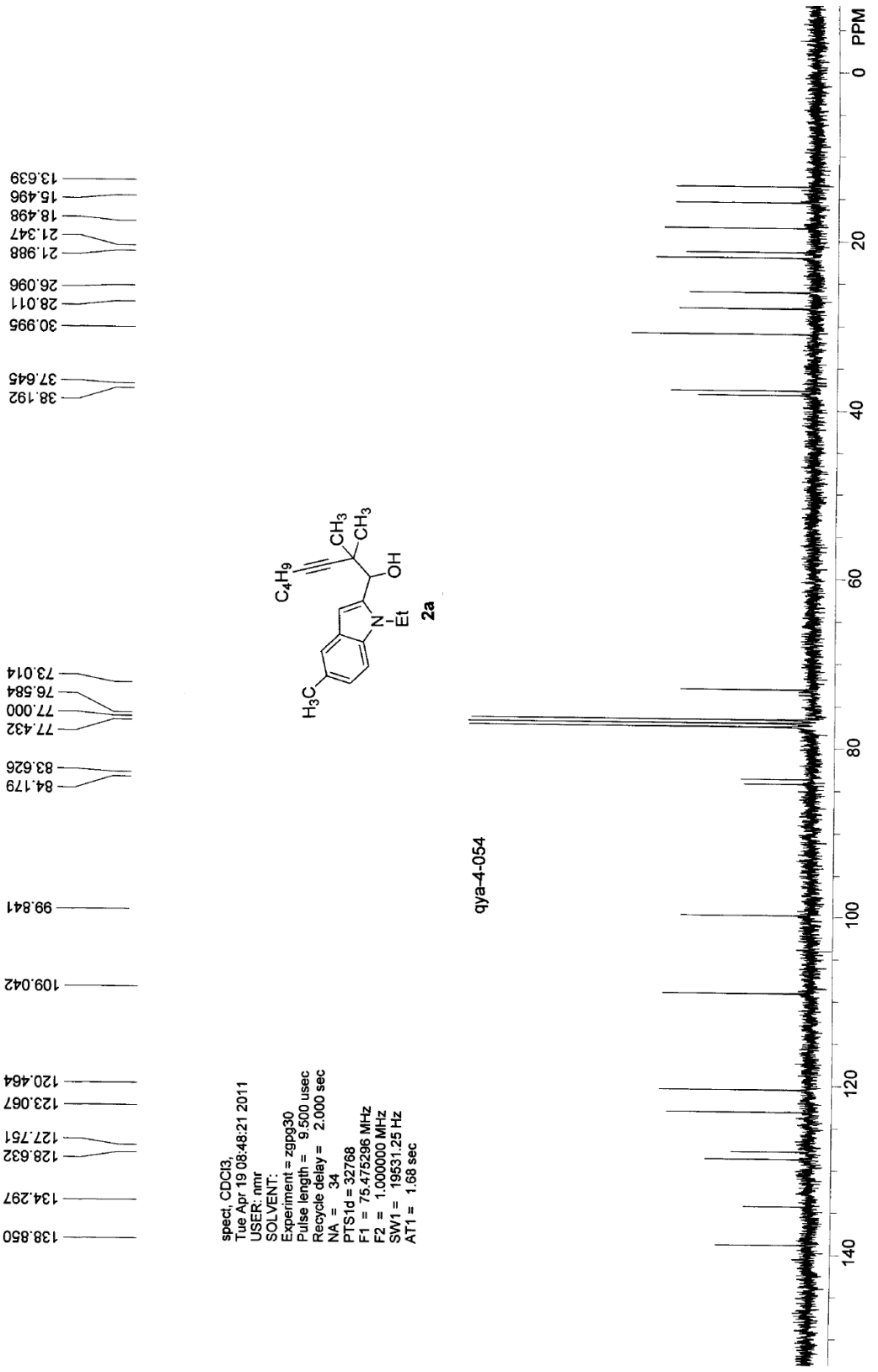
(6) **9-Ethyl-2,3,6-trimethyl-4-phenyl-9*H*-carbazole (4h) qya-5-071**

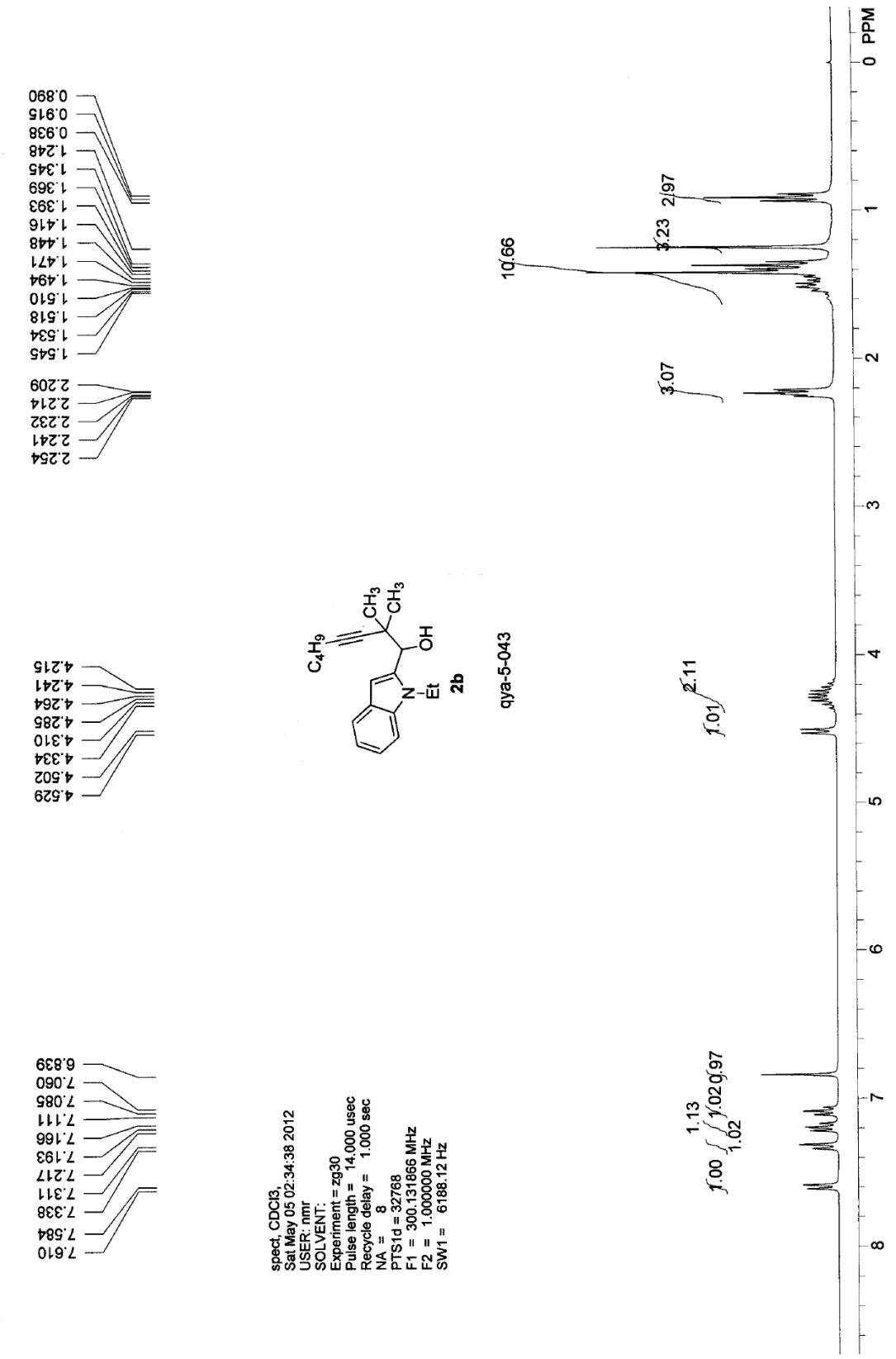


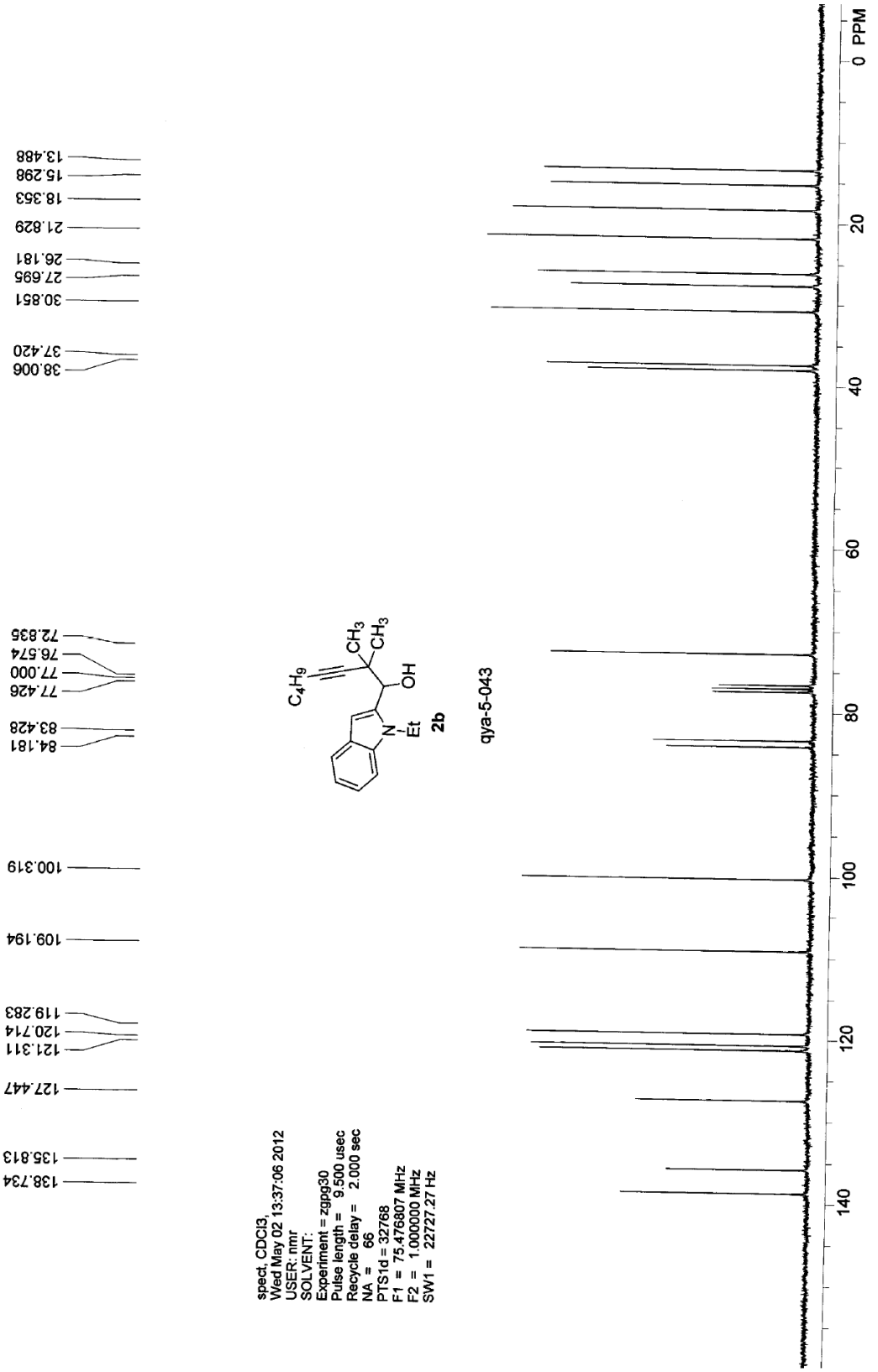
The reaction of $PtCl_4$ (8.9 mg, 0.026 mmol) and **2h** (166.0 mg, 0.5 mmol) in toluene (5 mL) at -10 °C for 72 h afforded **4h** and **3h** (121.8 mg, 78%) (petroleum ether/ethyl acetate = 50/l) (the ratio of **4h** : **3h** (93 : 7) as determined by ^{1}H NMR analysis of the crude product), which was further purified by recrystallization to afford **4h** and **3h** (95.3 mg, 61%, **4h** : **3h** = 97 : 3 as determined by ^{1}H NMR analysis) as a solid; m. p. 164~166 °C (*n*-hexane/ethyl acetate); ^{1}H NMR of **4h** (300 MHz, $CDCl_3$) δ 7.58-7.45 (m, 3H, ArH), 7.42-7.33 (m, 2H, ArH), 7.25-7.18 (m, 2H, ArH), 7.12 (d, *J* = 9.0 Hz, 1H, ArH), 6.40 (s, 1H, ArH), 4.33 (q, *J* = 7.2 Hz, 2H, NCH_2), 2.53 (s, 3H, $ArCH_3$), 2.21 (s, 3H, $ArCH_3$), 2.14 (s, 3H, $ArCH_3$), 1.42 (t, *J* = 7.2 Hz, 3H, CH_3); the following signals are discernible for **3h**: 2.75 (s, 3H, $ArCH_3$), 2.27 (s, 3H, $ArCH_3$); ^{13}C NMR of **4h** (75 MHz, $CDCl_3$) δ 141.2, 138.4, 138.3, 136.4, 134.7, 129.4, 128.6, 127.2, 127.0, 125.8, 124.8, 123.2, 121.9, 119.6, 108.4, 107.5, 37.3, 21.8, 21.4, 16.1, 13.7; IR (KBr) ν (cm^{-1}) 3054, 3024, 2973, 2919, 1622, 1603, 1575, 1486, 1471,

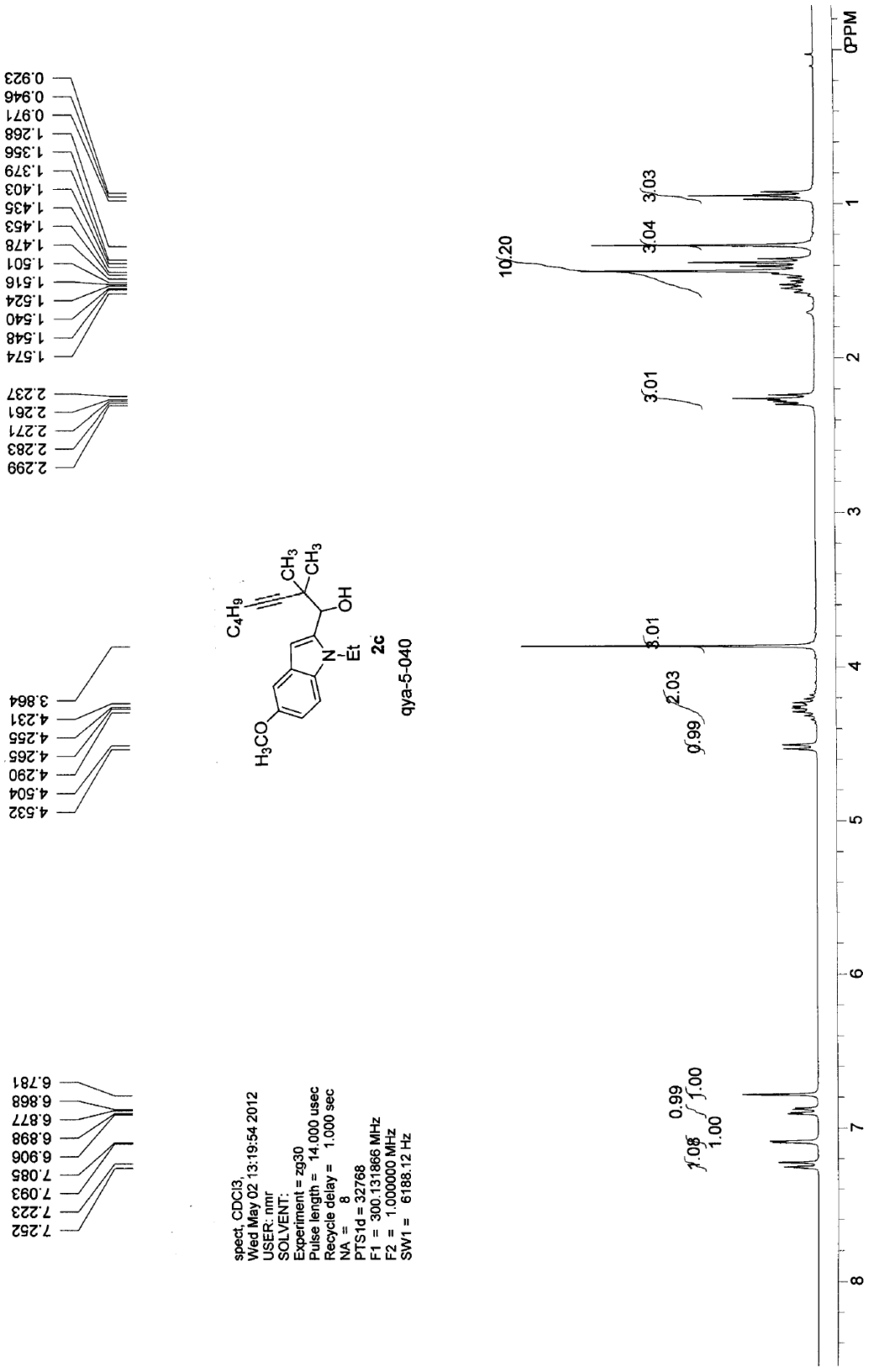
1379, 1349, 1305, 1219, 1146, 1082, 1065, 1023; GC-MS (GC condition: injector: 280 °C; column: DB5 column 30 m × 0.25 mm, temperature programming: 60 °C (2 min), 20 °C/min to 280 °C, 280 °C (30 min); detector: 280 °C) (70 ev, EI) *m/z* (%) for **4h**: T_R 7.6 min: 314 (M^++1, 25.95), 313 (M^+, 100), for **3h**: T_R 7.8 min: 314 (M^++1, 26.03), 313 (M^+, 100); Elemental analysis calcd (%) for $C_{23}H_{23}N$: C, 88.13; H, 7.40; N, 4.47; Found: C, 87.82; H, 7.45; N, 4.55.

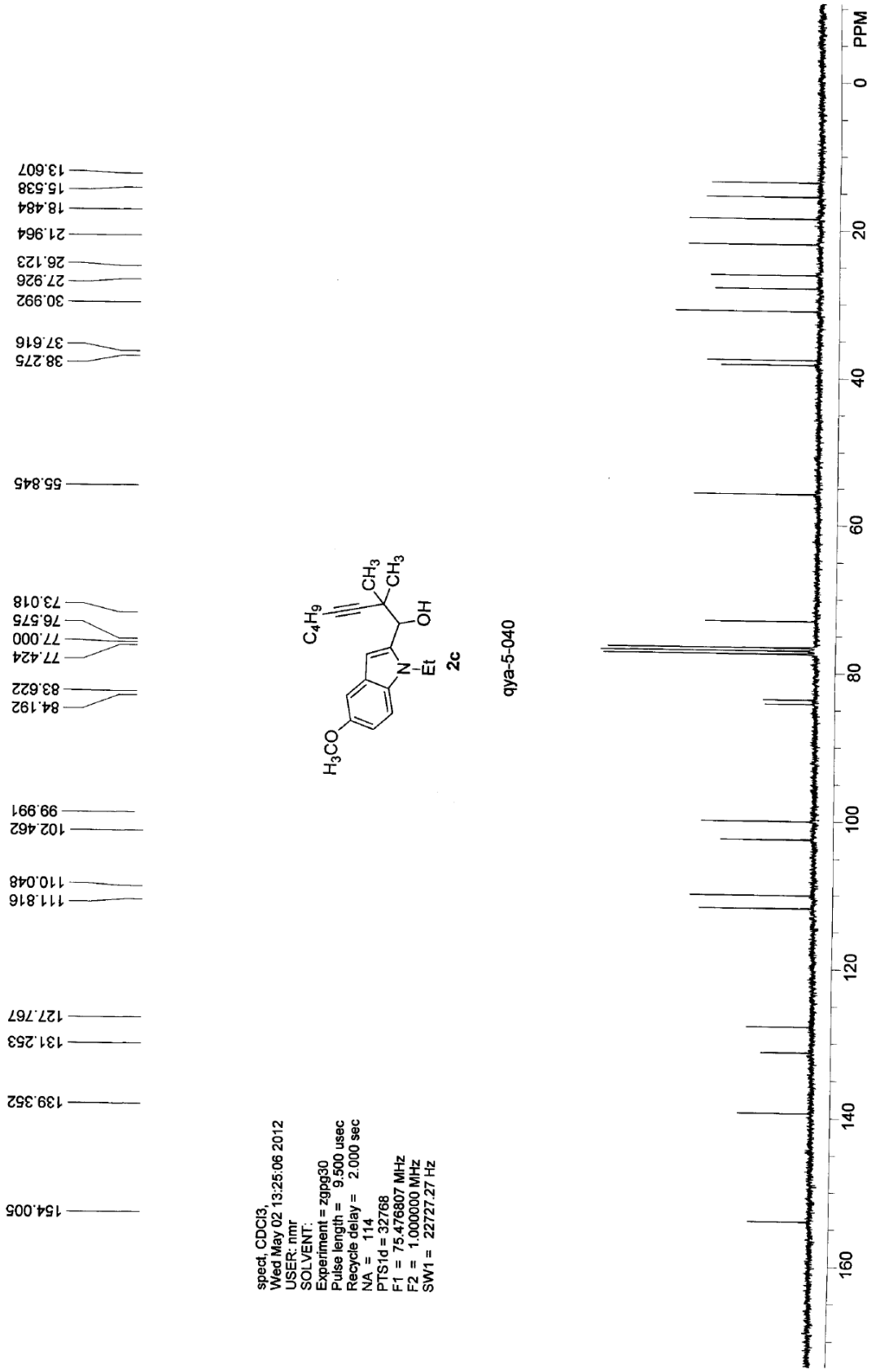


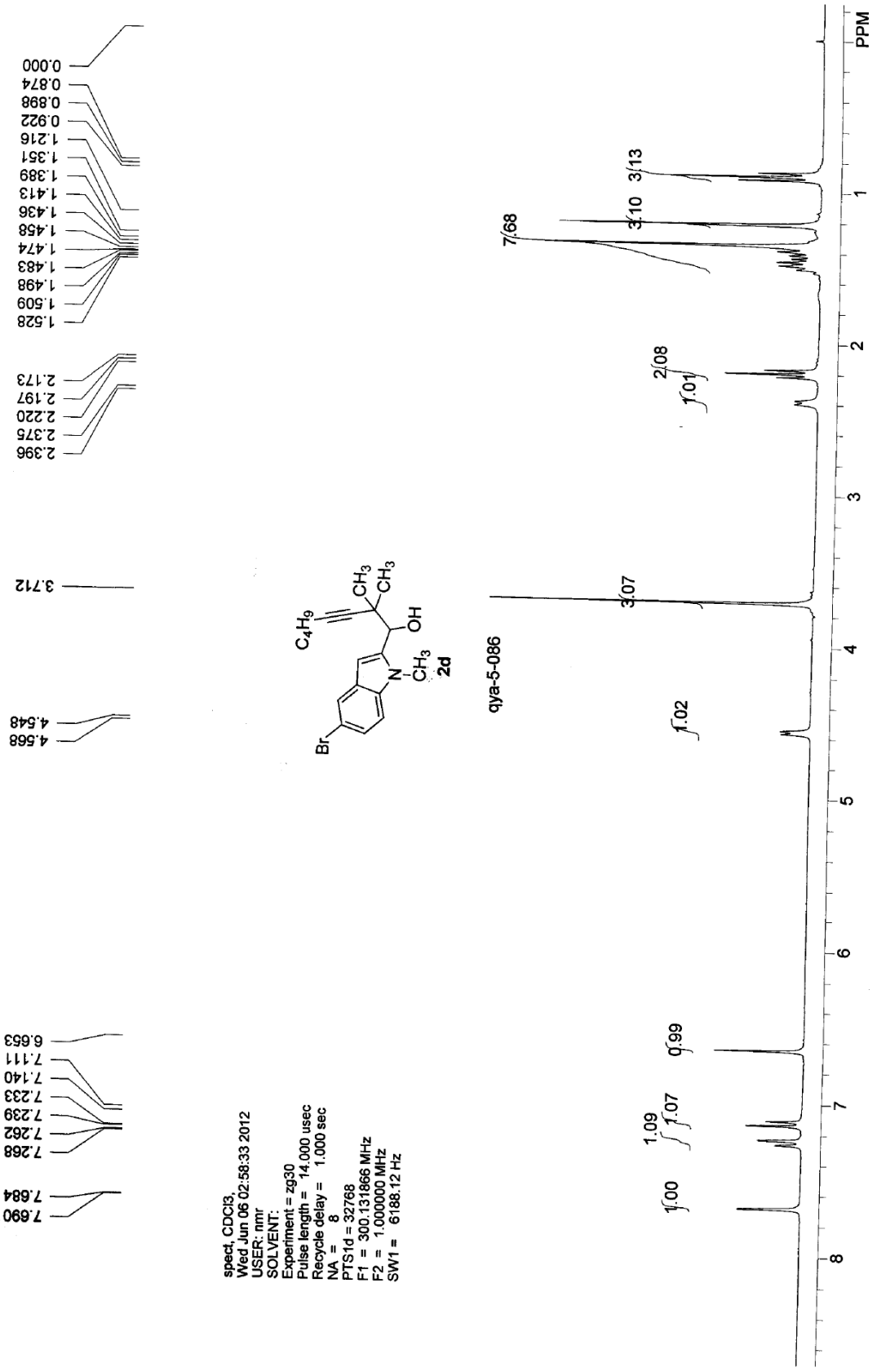


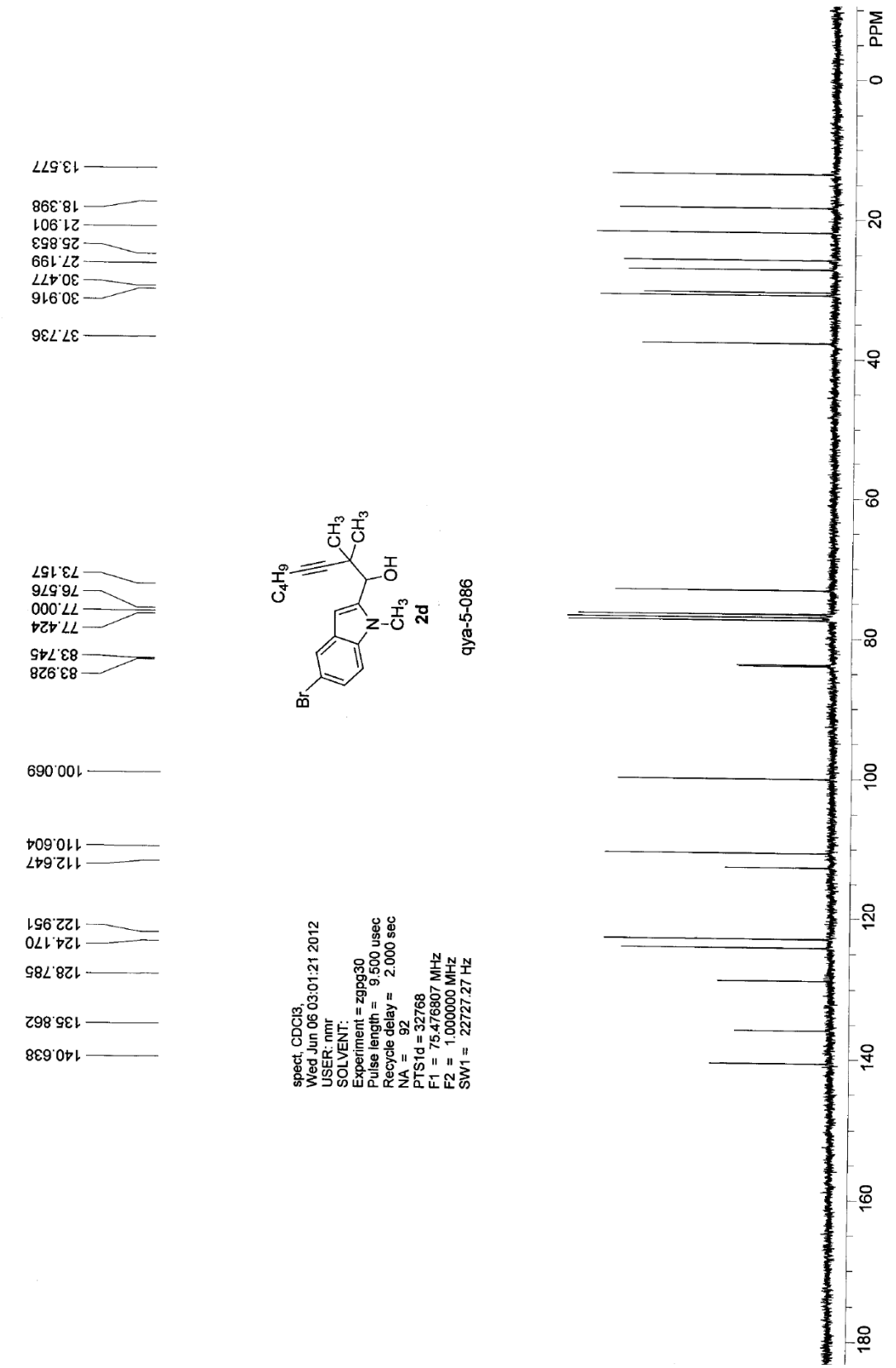


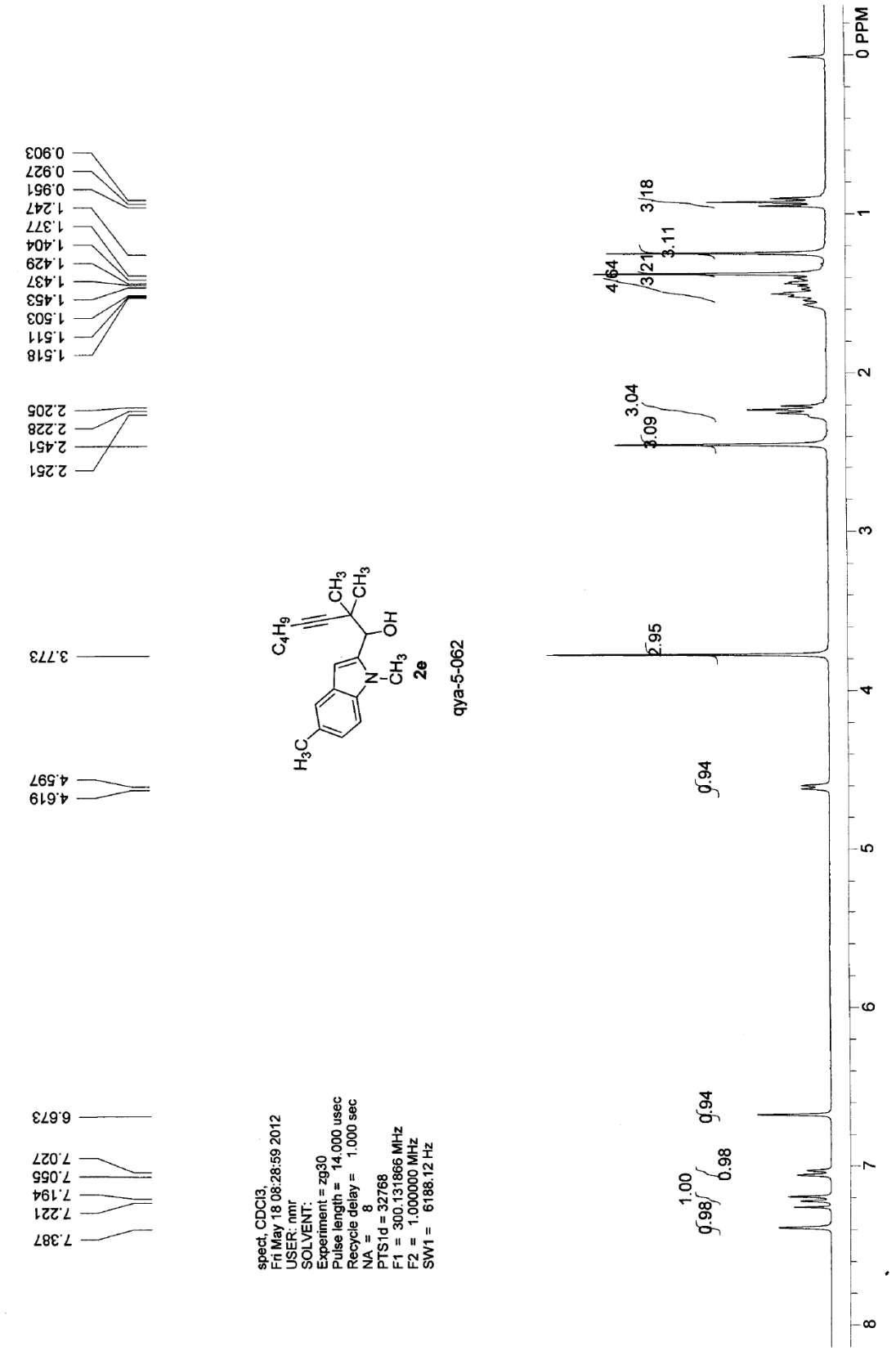


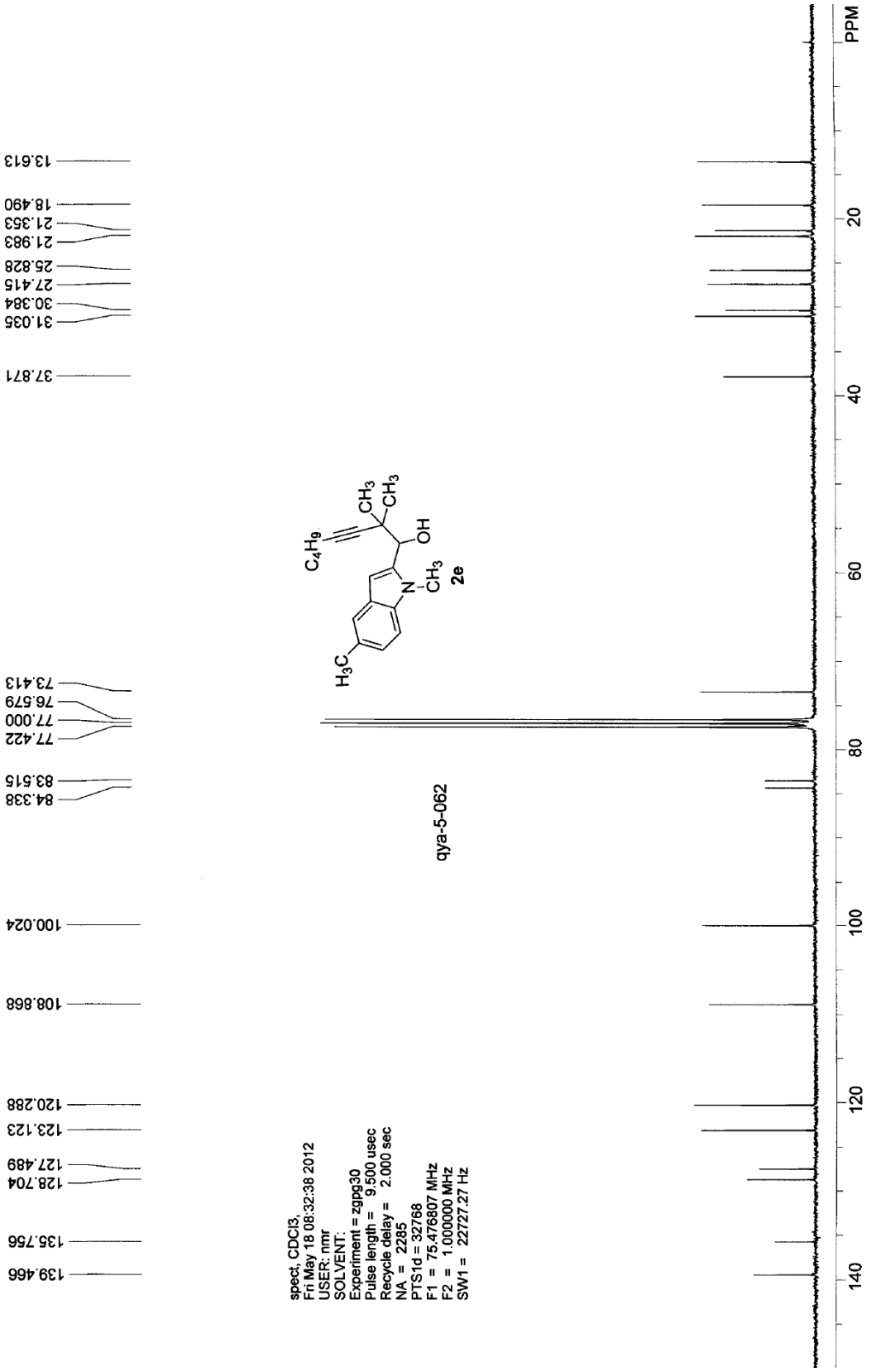


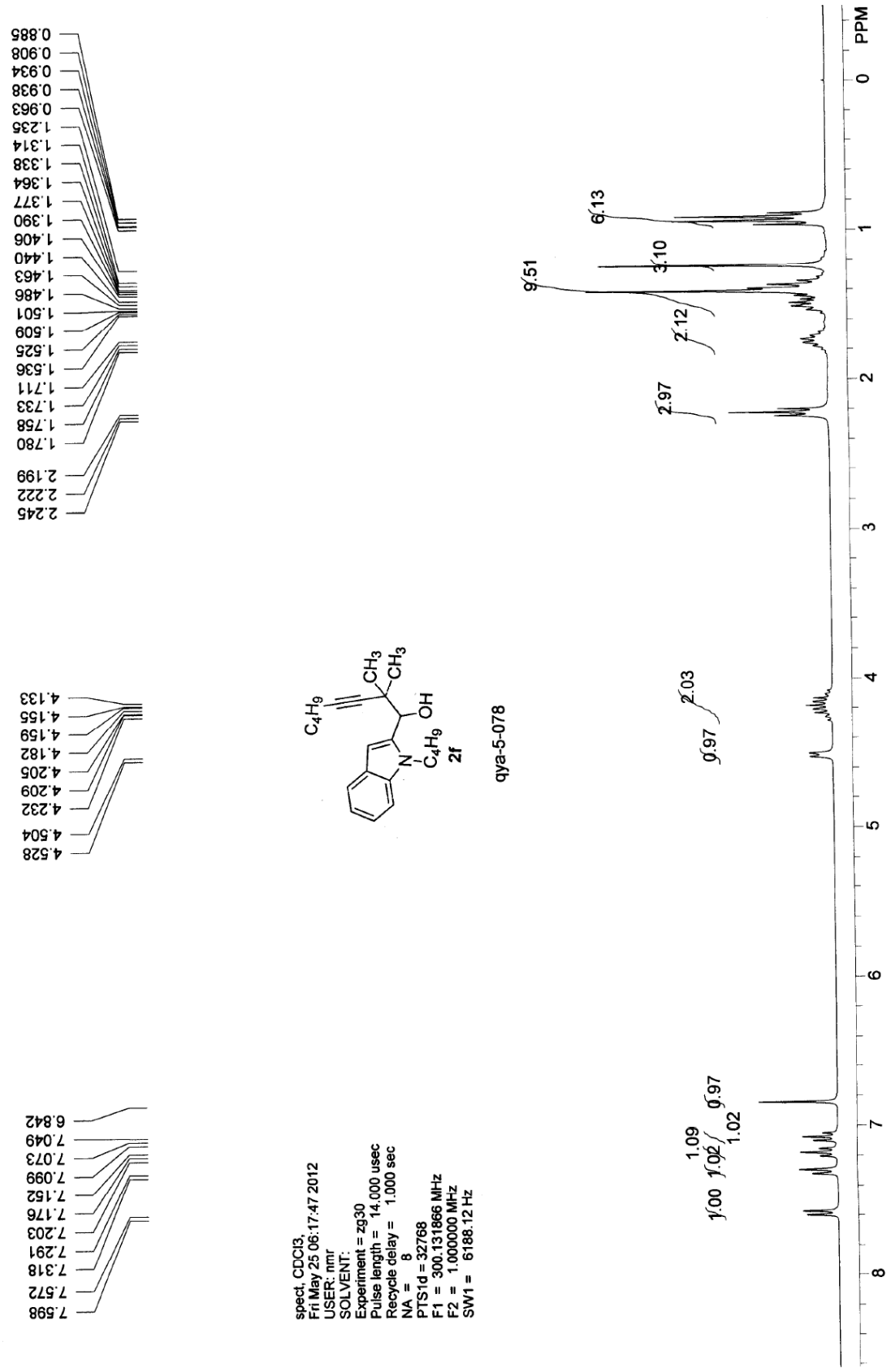


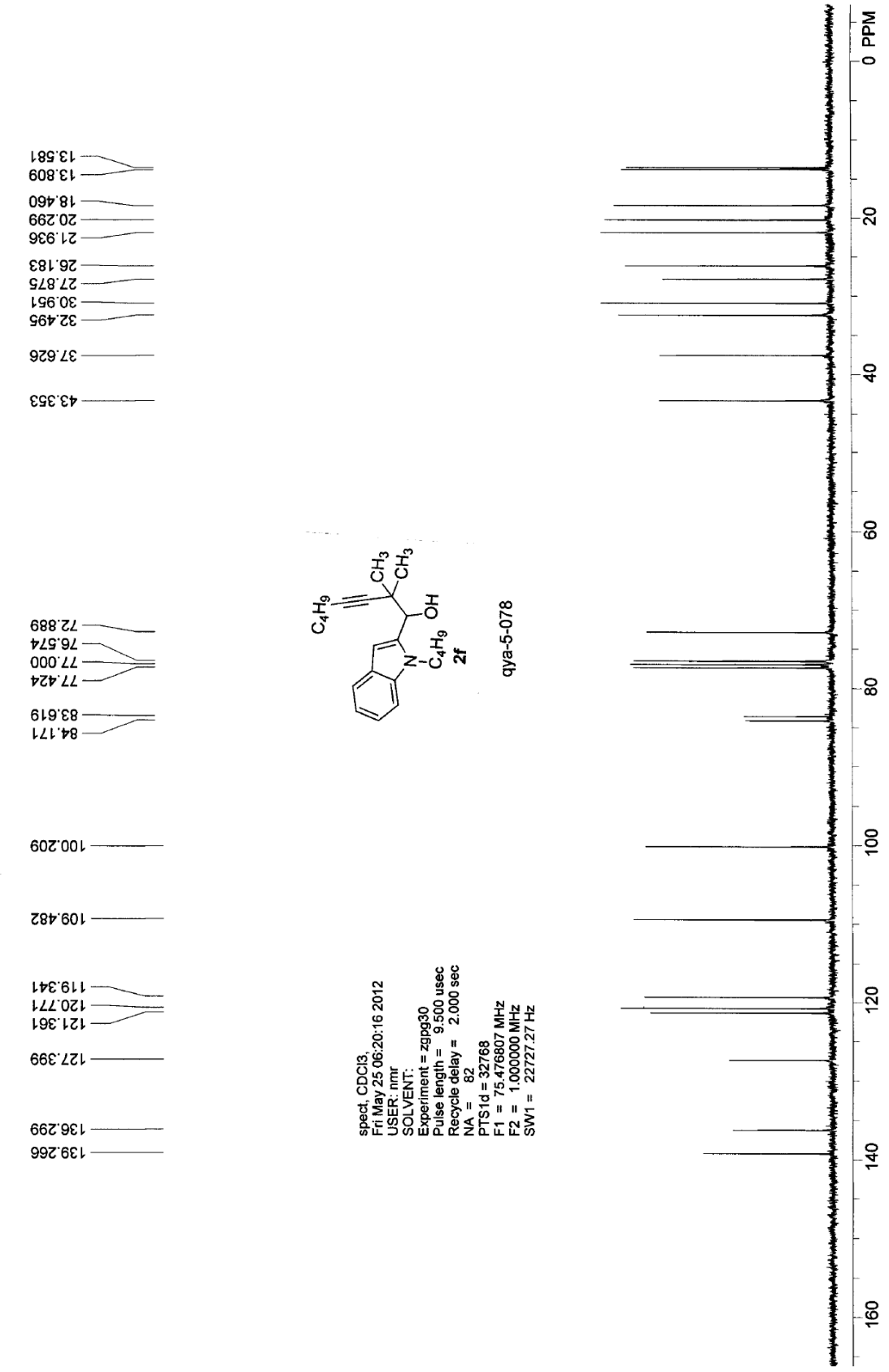

qya-5-086
spect, CDCl3,
Wed Jun 06 02:58:33 2012
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
2d
PPM

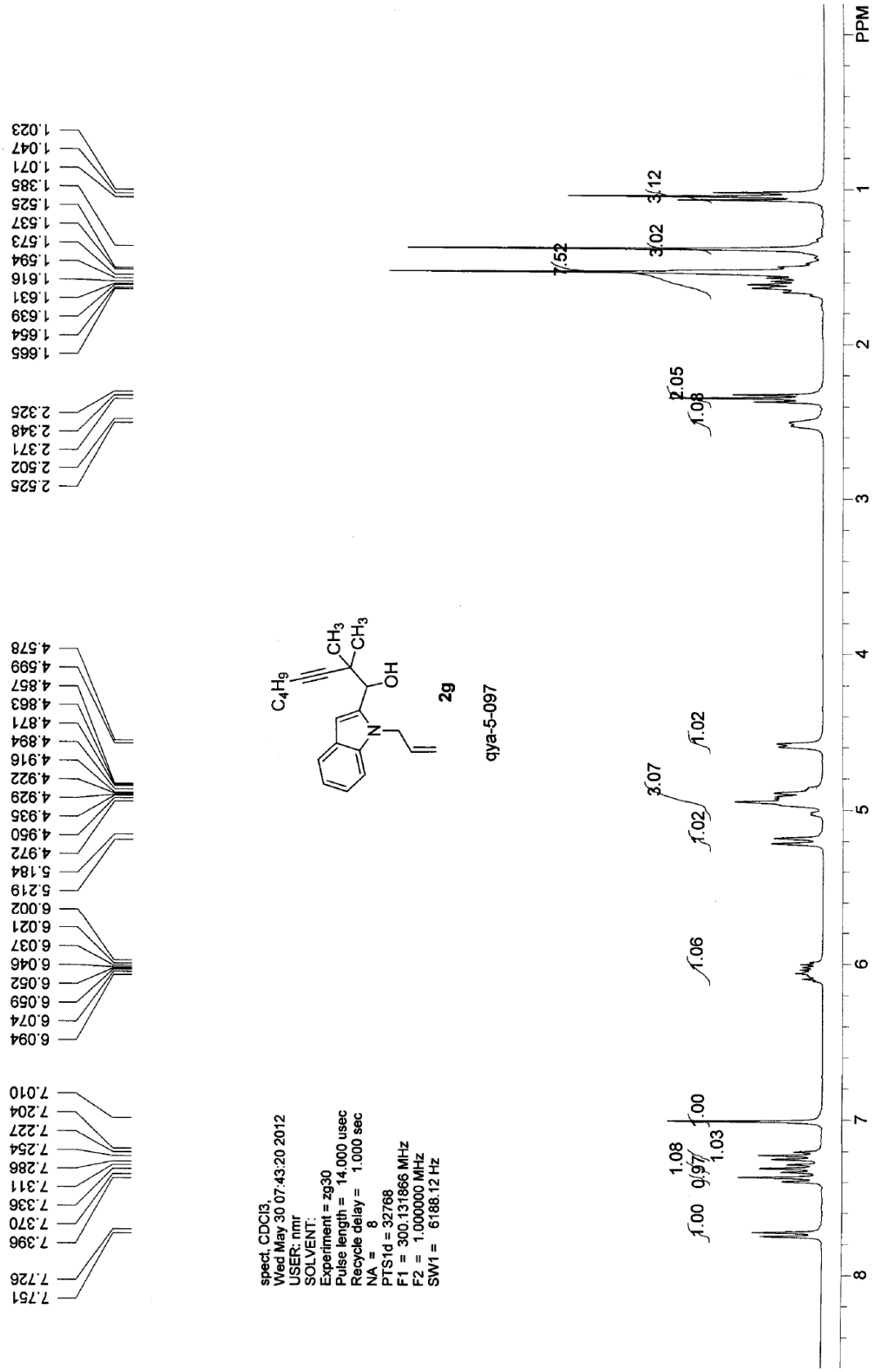


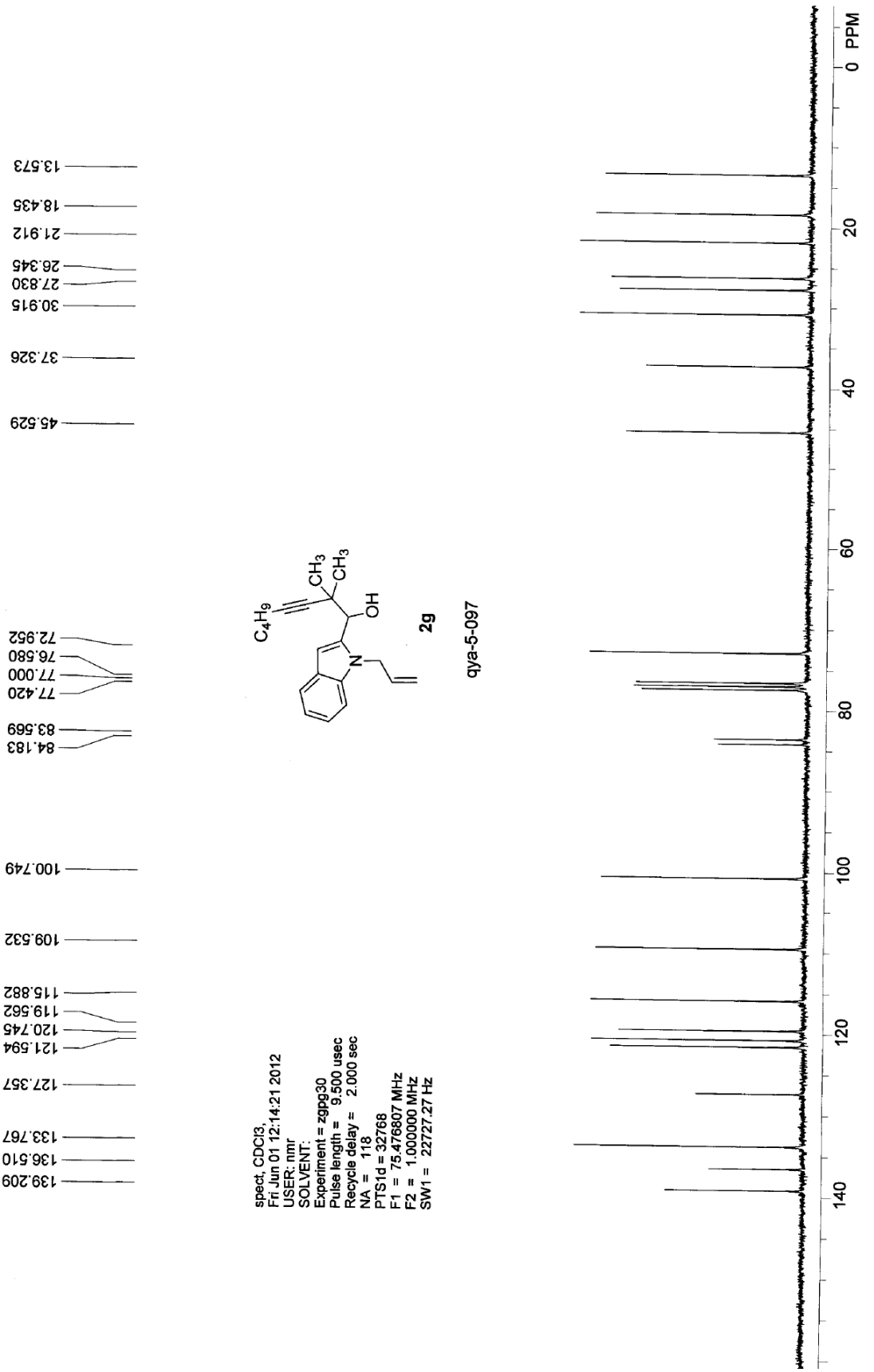


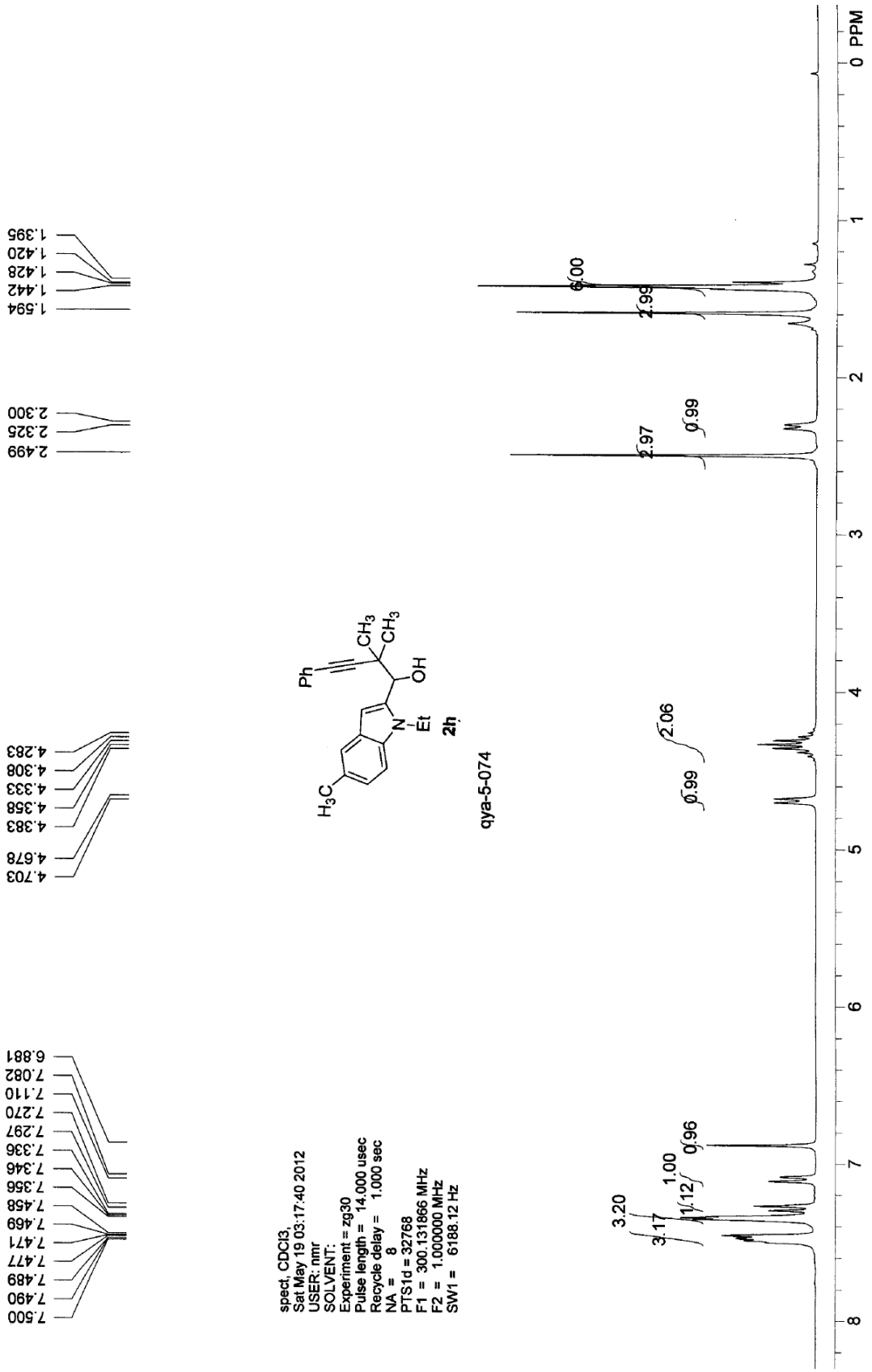


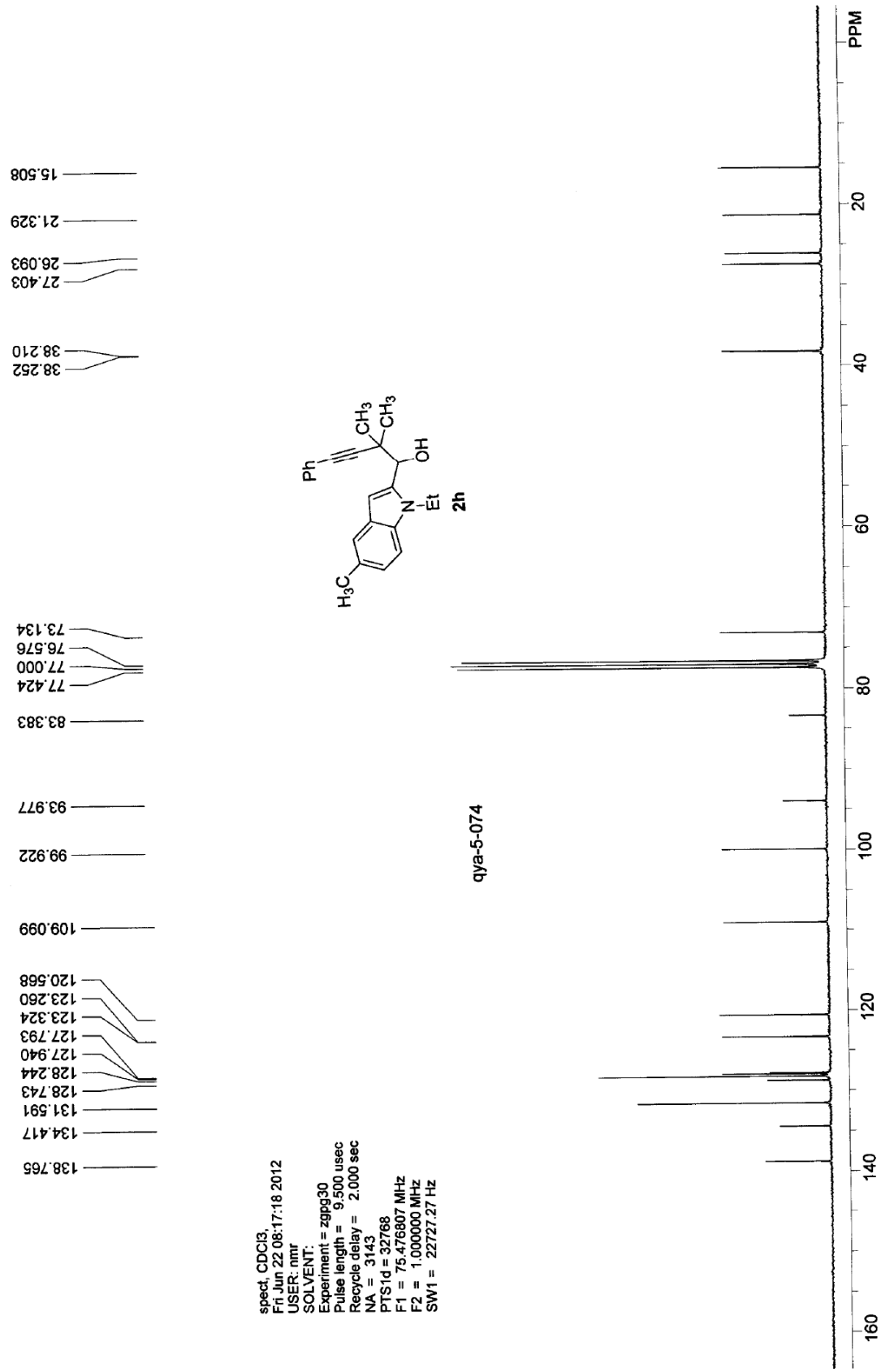

0.885
0.908
0.934
0.938
0.963
1.235
1.314
1.338
1.364
1.377
1.390
1.406
1.440
1.463
1.486
1.501
1.509
1.525
1.536
1.711
1.733
1.758
1.780
2.199
2.222
2.245
4.133
4.155
4.159
4.182
4.205
4.209
4.232
4.504
4.528
6.842
7.049
7.073
7.099
7.152
7.176
7.203
7.291
7.318
7.572
7.598
spect, CDCl3,
Fri May 25 06:17:47 2012
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
C_4H_9
CH_3
CH_3
OH
N
C_4H_9
2f
qya-5-078
9.51
6.13
3.10
2.12
2.97
2.03
0.97
1.09
1.00
1.02
1.02
0.97
PPM
0
1
2
3
4
5
6
7
8

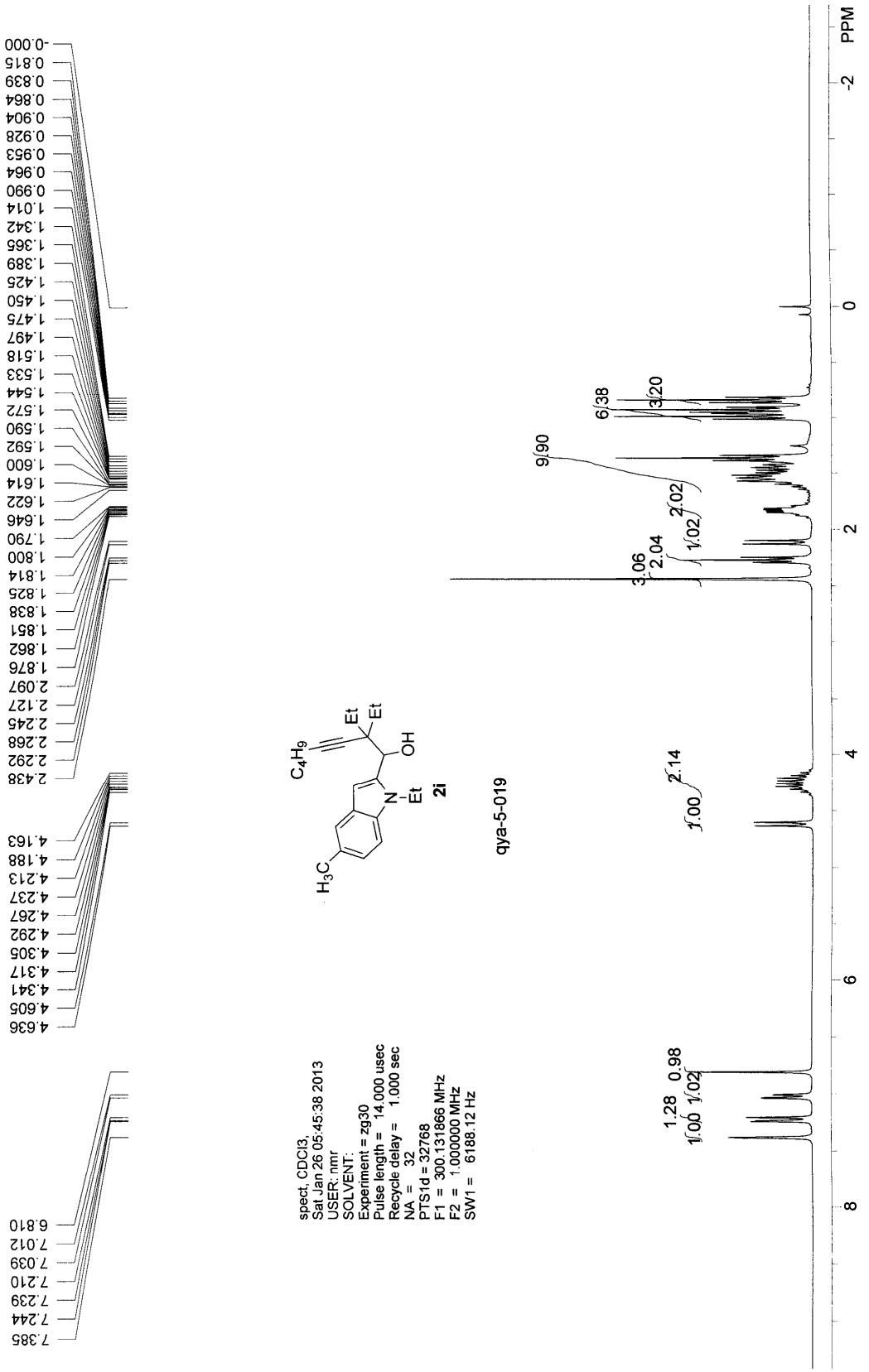

13.581
13.809
18.460
20.299
21.936
26.183
27.875
30.961
32.495
37.626
43.353
72.889
76.574
77.000
77.424
83.619
84.171
100.209
109.482
119.341
120.771
121.361
127.399
136.299
139.266
spect, CDCl3,
Fri May 25 06:20:16 2012
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 82
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
qya-5-078
2f
0 PPM
20
40
60
80
100
120
140
160

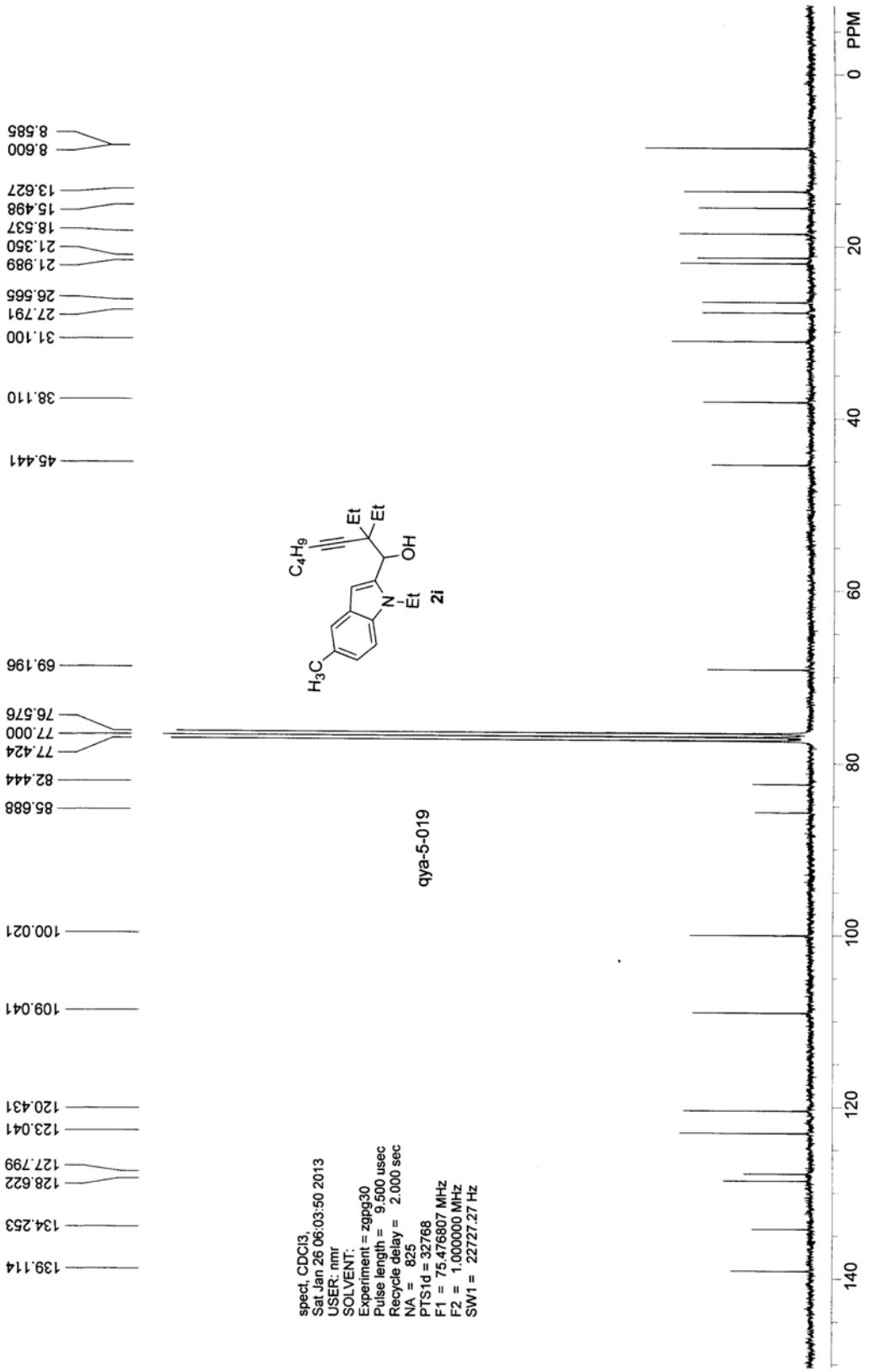


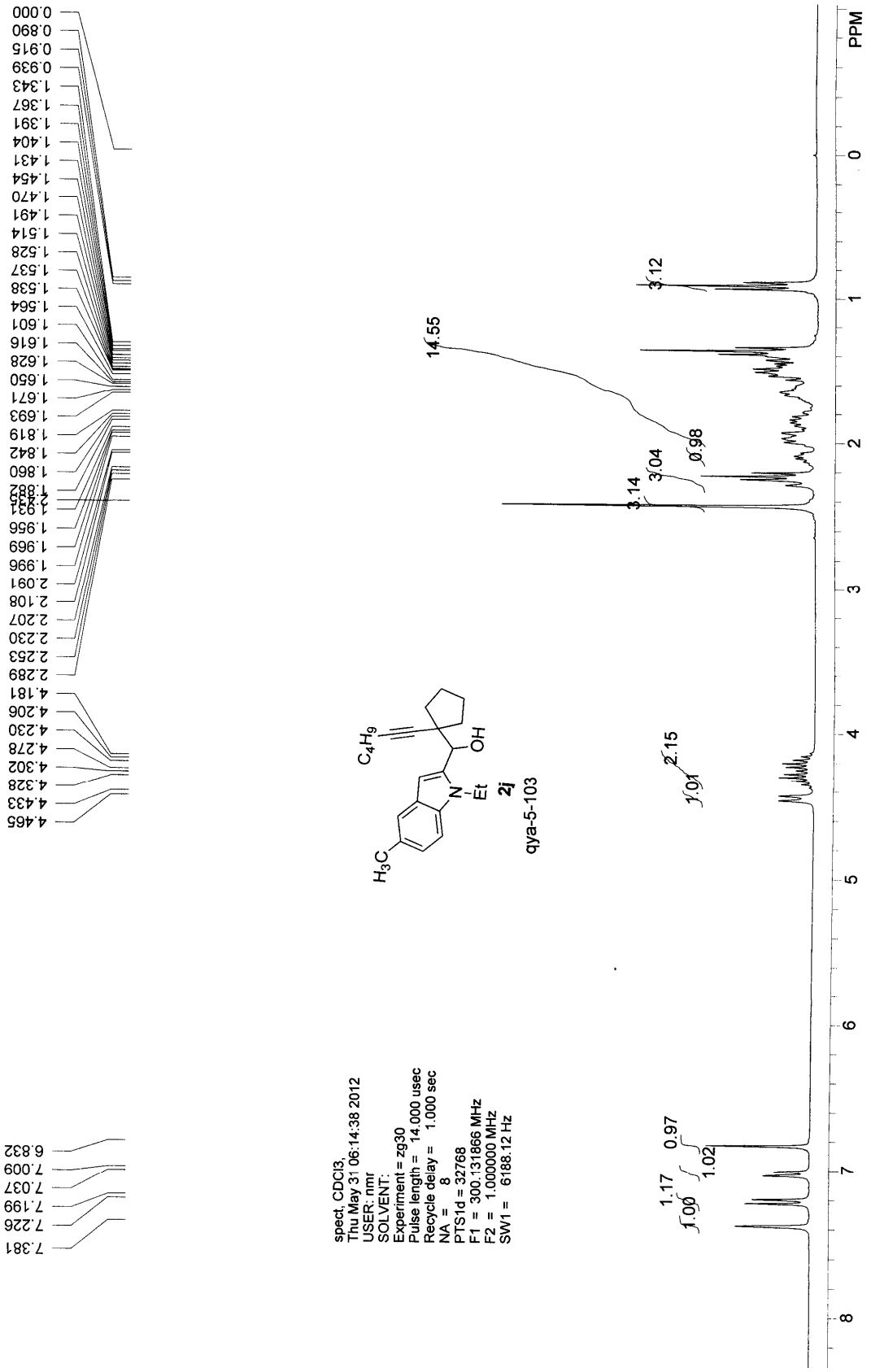


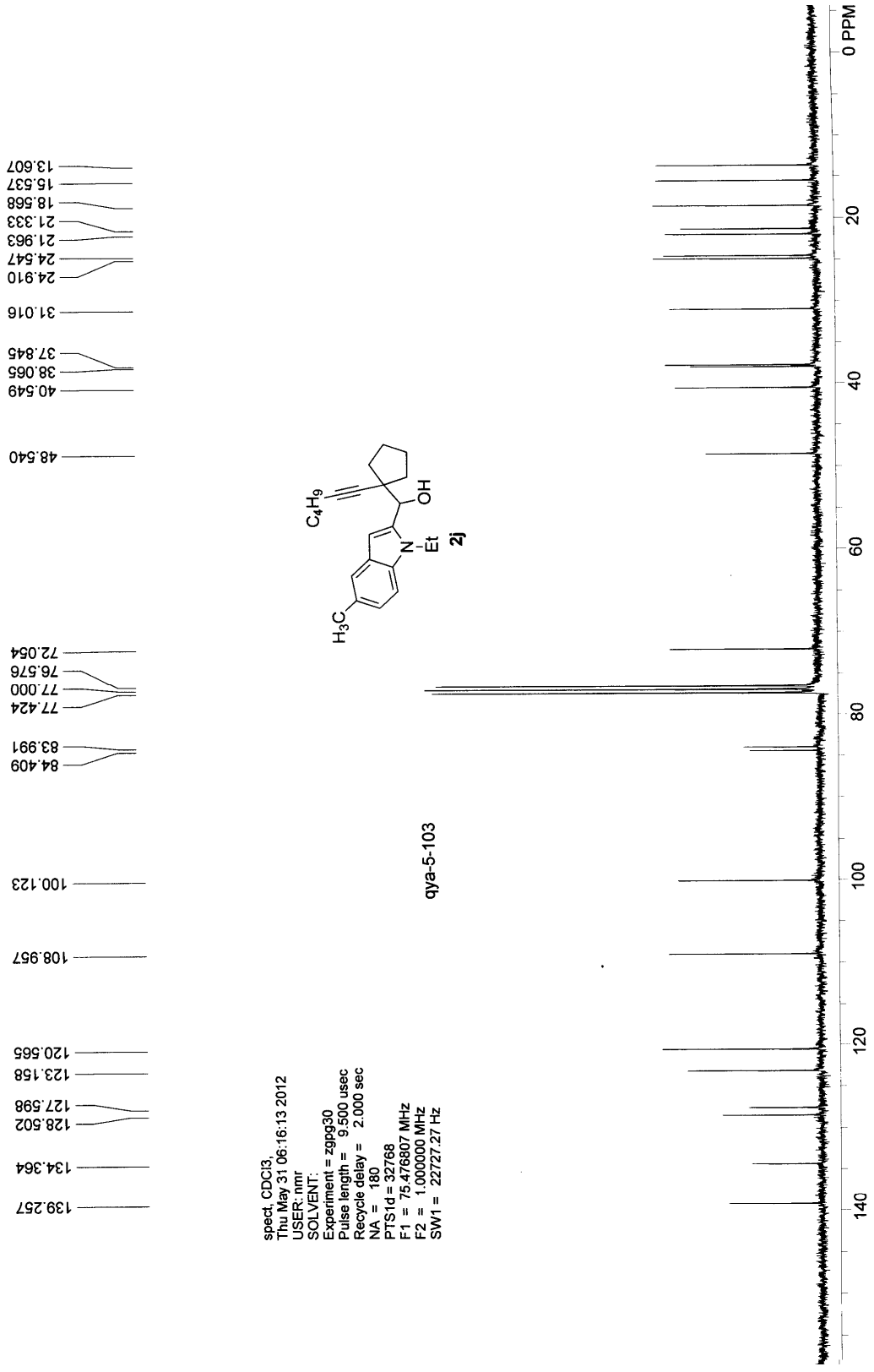

1.395
1.420
1.428
1.442
1.594
2.300
2.325
2.499
4.283
4.308
4.333
4.358
4.383
4.678
4.703
6.881
7.082
7.110
7.270
7.297
7.336
7.346
7.356
7.458
7.469
7.471
7.477
7.489
7.490
7.500
spect, CDCl3,
Sat May 19 03:17:40 2012
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
Ph
CH3
CH3
OH
N
Et
H3C
2h
qya-5-074
3.20
3.17
1.12
1.00
0.96
0.99
2.06
0.99
2.97
0.99
2.99
6.00
0 PPM

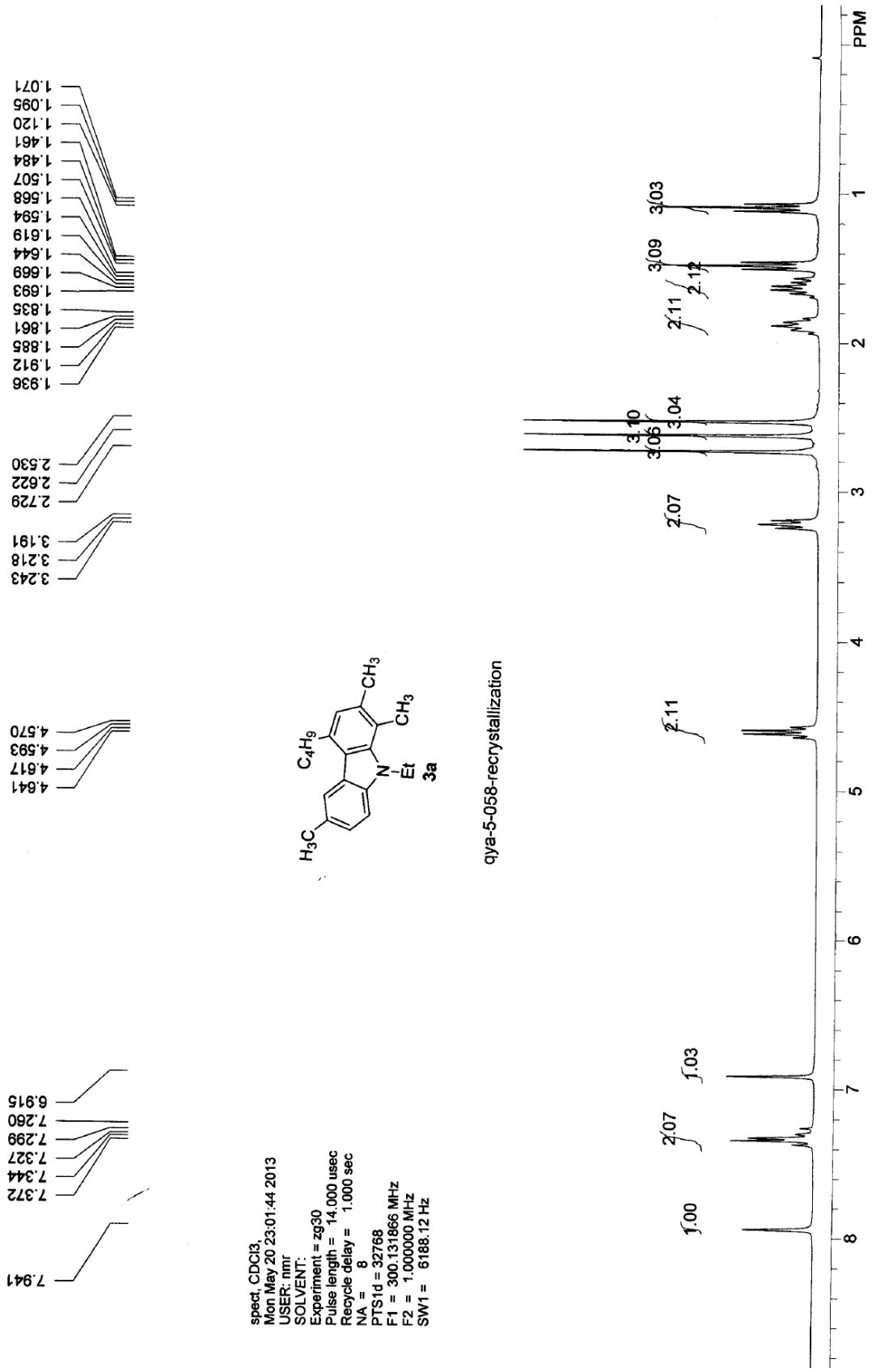


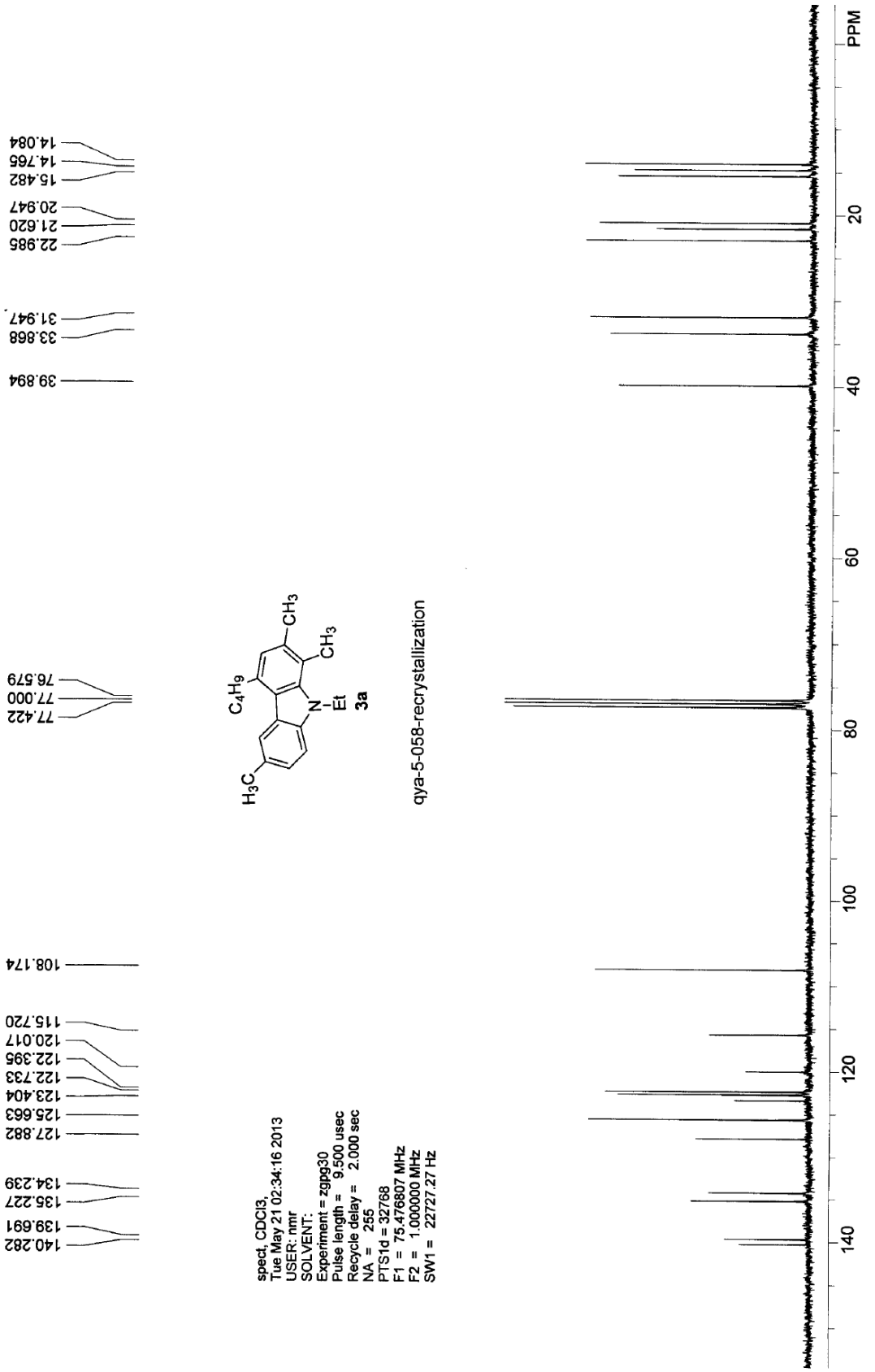

-0.000
0.815
0.839
0.864
0.904
0.928
0.953
0.964
0.990
1.014
1.342
1.365
1.389
1.425
1.450
1.475
1.497
1.518
1.533
1.544
1.572
1.590
1.592
1.600
1.614
1.622
1.646
1.790
1.800
1.814
1.825
1.838
1.851
1.862
1.876
2.097
2.127
2.245
2.268
2.292
2.438
4.163
4.188
4.213
4.237
4.267
4.292
4.305
4.317
4.341
4.605
4.636
6.810
7.012
7.039
7.210
7.239
7.244
7.385
spect, CDCl3,
Sat Jan 26 05:45:38 2013
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 32
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
qya-5-019
2i
PPM
-2
0
2
4
6
8
9.90
6.38
3.20
3.06
2.04
2.02
1.02
2.14
1.00
1.28
0.98
1.00
1.02

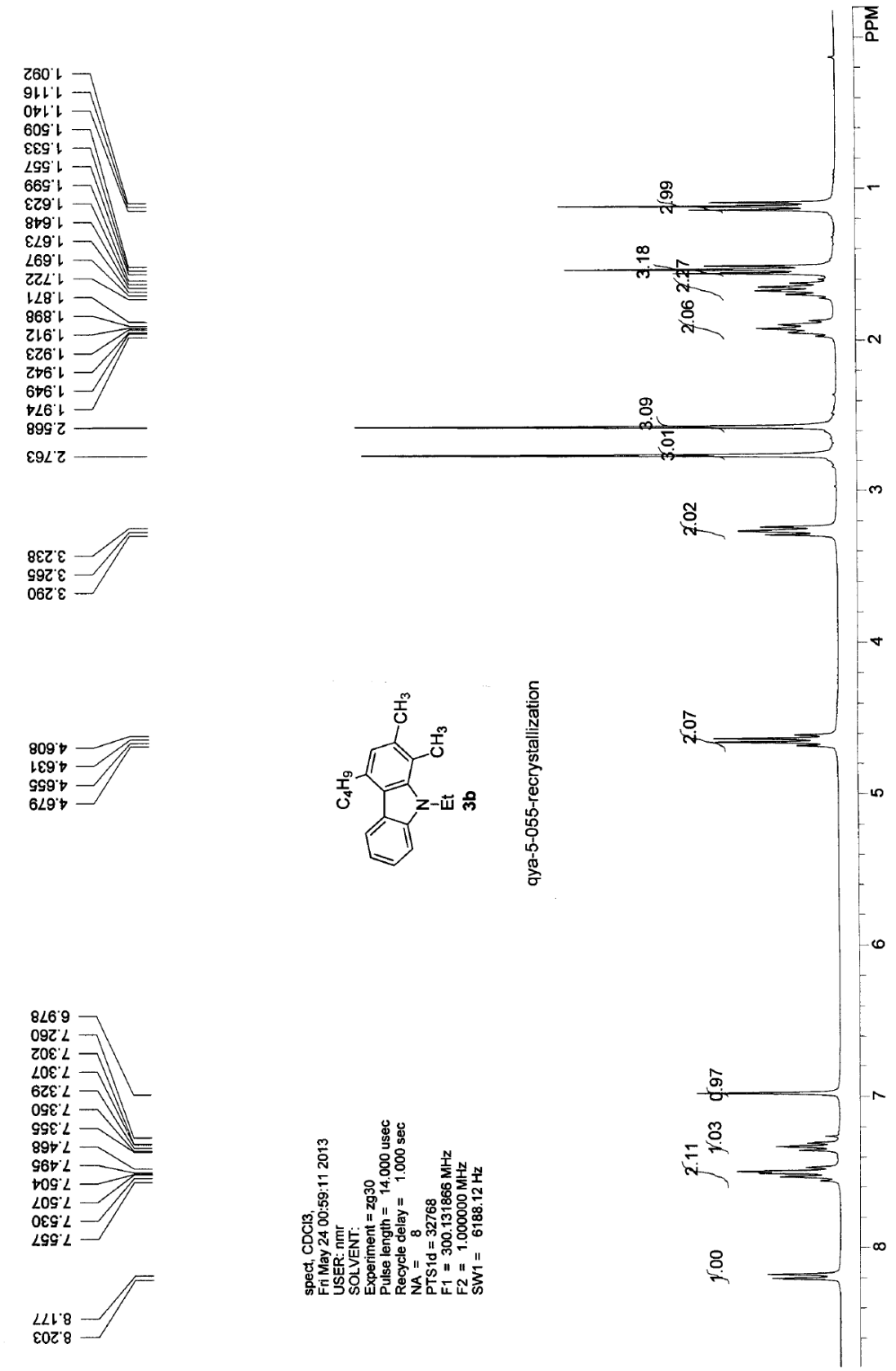

8.585
8.600
13.627
15.498
18.537
21.350
21.989
26.565
27.791
31.100
38.110
45.441
69.196
76.576
77.000
77.424
82.444
85.688
100.021
109.041
120.431
123.041
127.799
128.622
134.253
139.114
PPM
0
20
40
60
80
100
120
140
Et
Et
OH
N
Et
C_4H_9
H_3C
2i
qya-5-019
spect, CDCl3,
Sat Jan 26 06:03:50 2013
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 825
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz

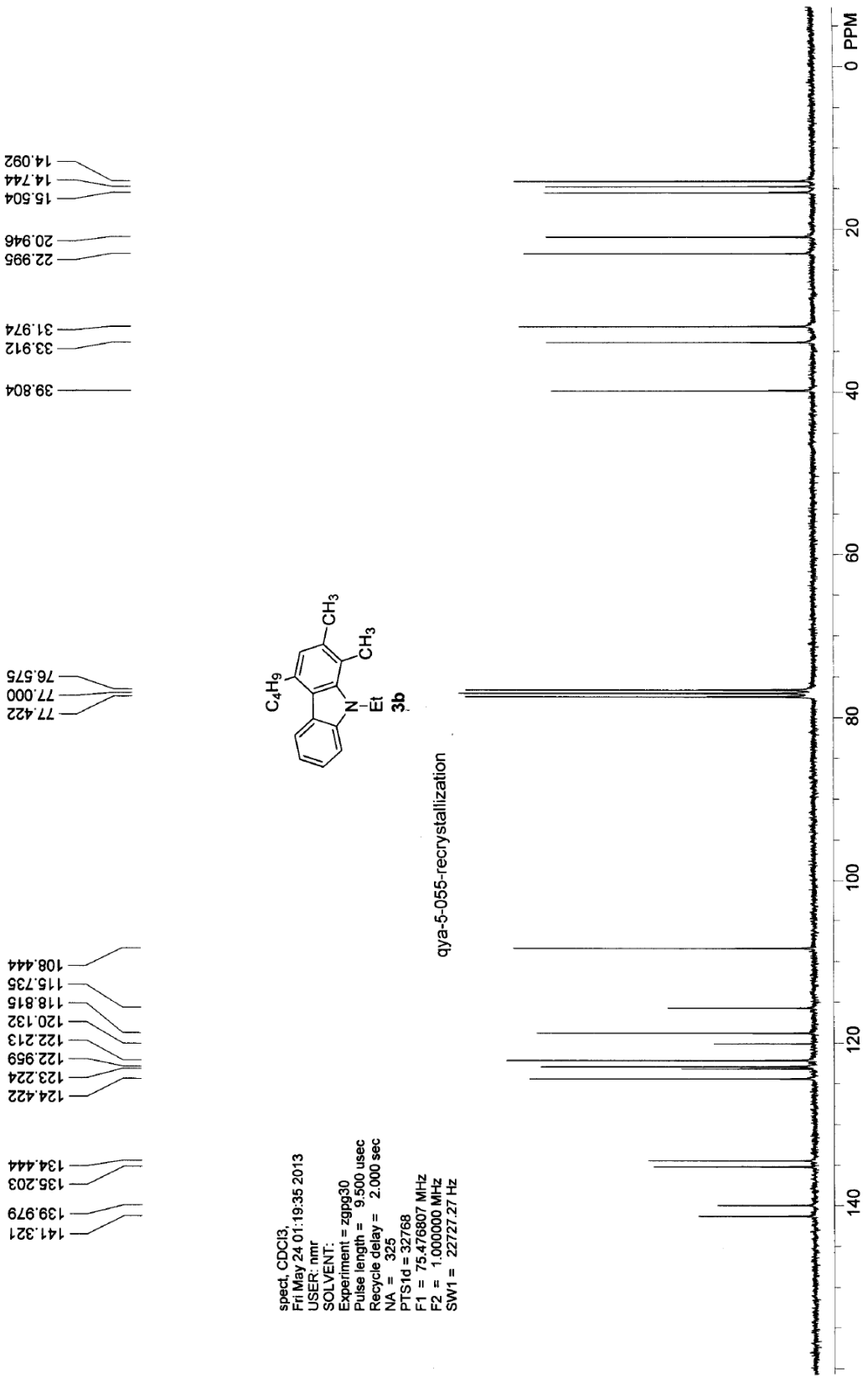

0.000
0.890
0.915
0.939
1.343
1.367
1.391
1.404
1.431
1.454
1.470
1.491
1.514
1.528
1.537
1.538
1.564
1.601
1.616
1.628
1.650
1.671
1.693
1.819
1.842
1.860
1.882
1.931
1.956
1.969
1.996
2.091
2.108
2.207
2.230
2.253
2.289
4.181
4.206
4.230
4.278
4.302
4.328
4.433
4.465
6.832
7.009
7.037
7.199
7.226
7.381
spect, CDCl3,
Thu May 31 06:14:38 2012
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
C_4H_9
OH
N
Et
H_3C
2j
qya-5-103
14.55
3.12
3.14
3.04
0.98
2.15
1.01
1.17
0.97
1.00
1.02
PPM
0
1
2
3
4
5
6
7
8

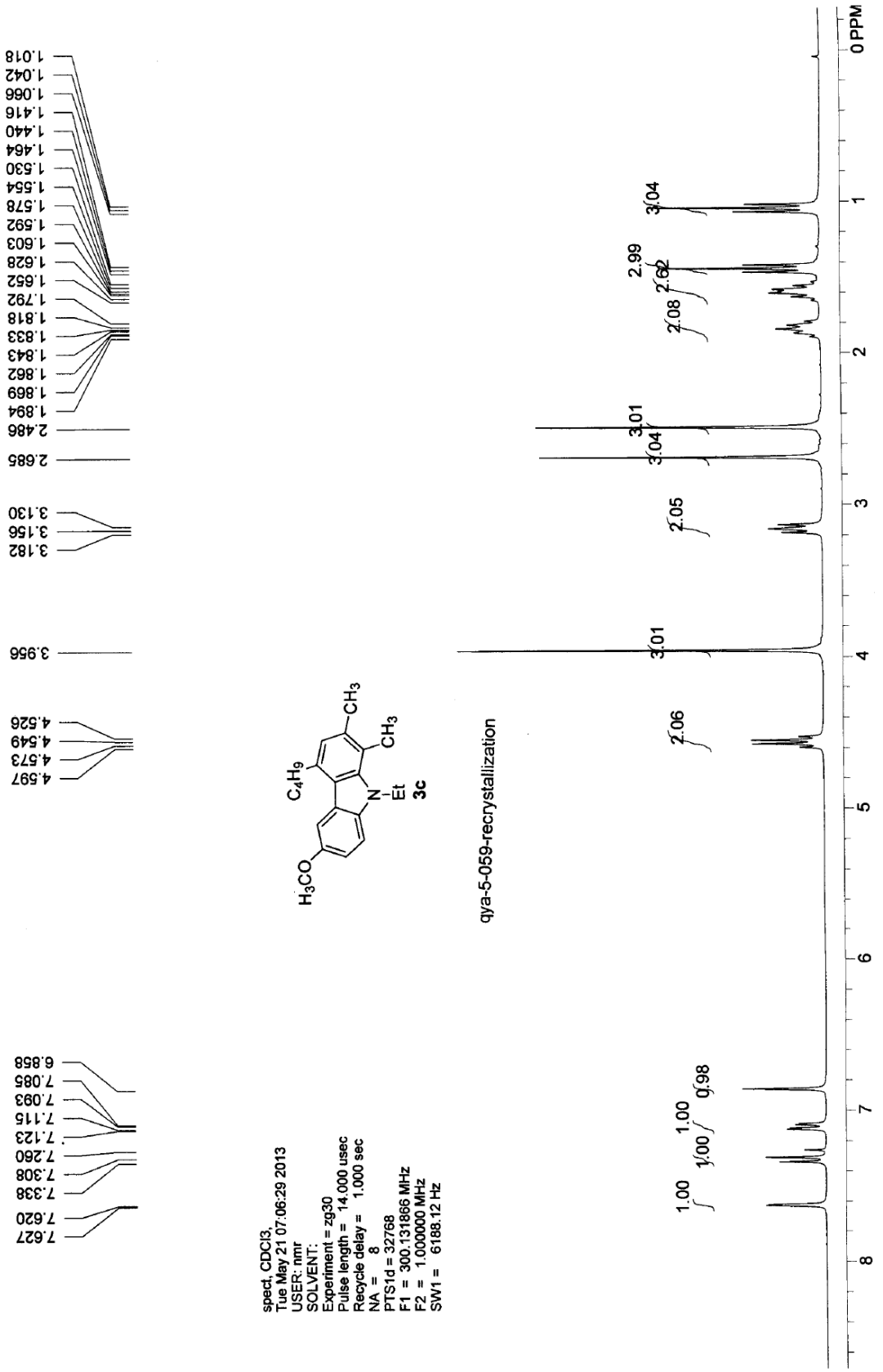


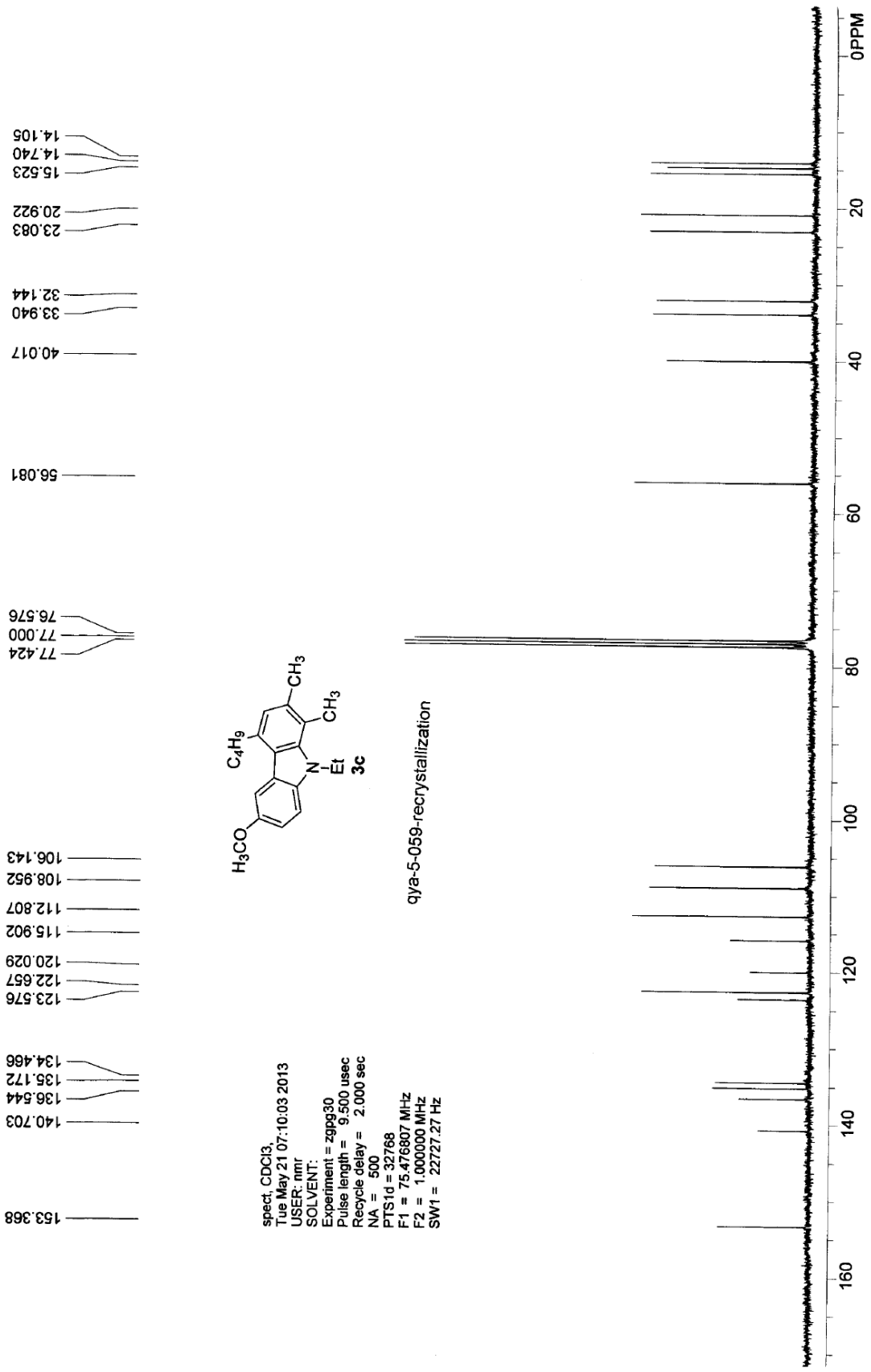

1.071
1.095
1.120
1.461
1.484
1.507
1.568
1.594
1.619
1.644
1.669
1.693
1.835
1.861
1.885
1.912
1.936
2.530
2.622
2.729
3.191
3.218
3.243
4.570
4.593
4.617
4.641
7.372
7.344
7.327
7.299
7.260
6.915
7.941
spect, CDCl3,
Mon May 20 23:01:44 2013
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
C_4H_9
CH_3
CH_3
H_3C
N
Et
3a
qya-5-058-recrystallization
1.00
2.07
1.03
2.11
2.07
3.06
3.10
3.04
2.11
2.12
3.09
3.03
PPM

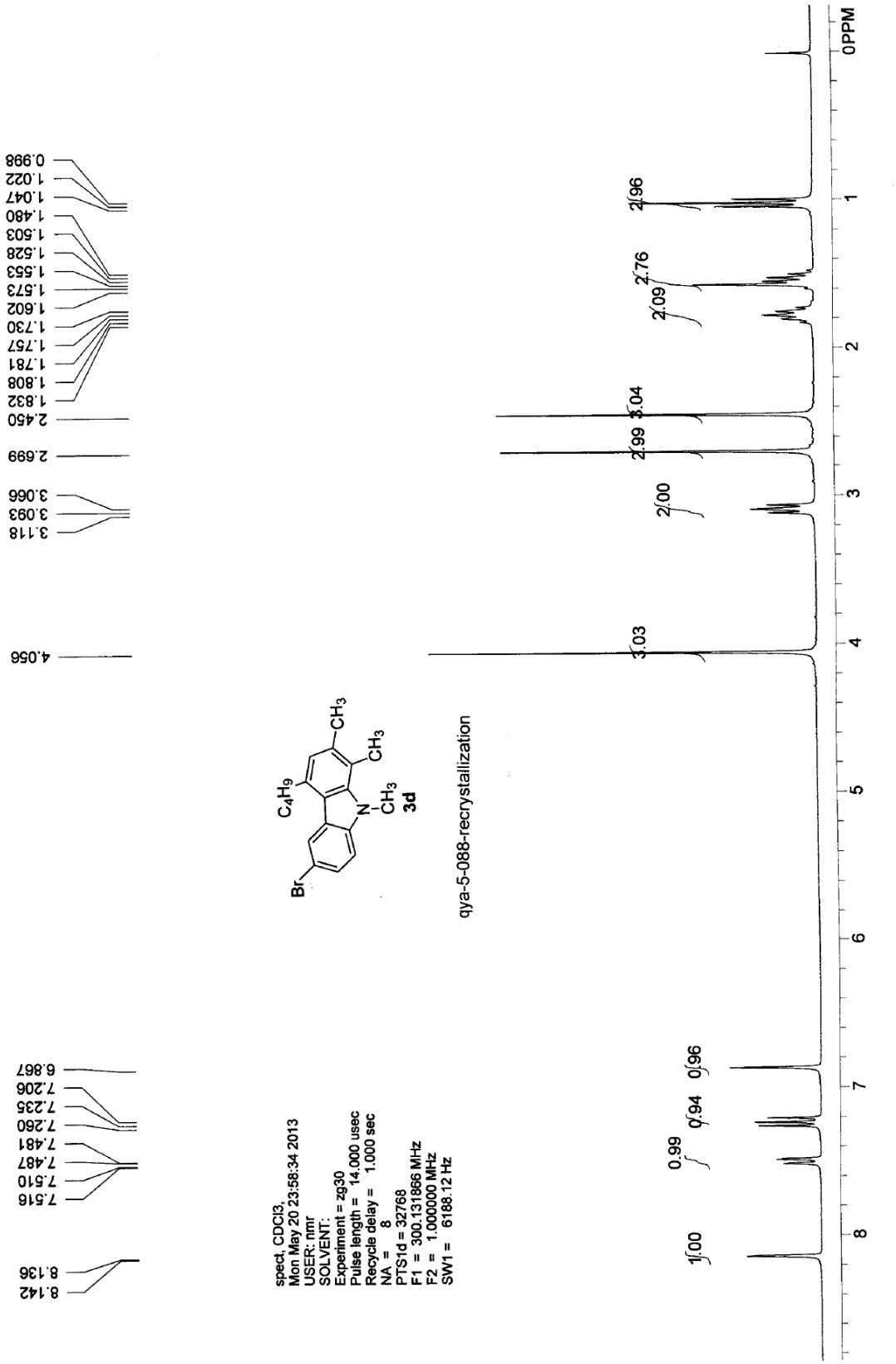


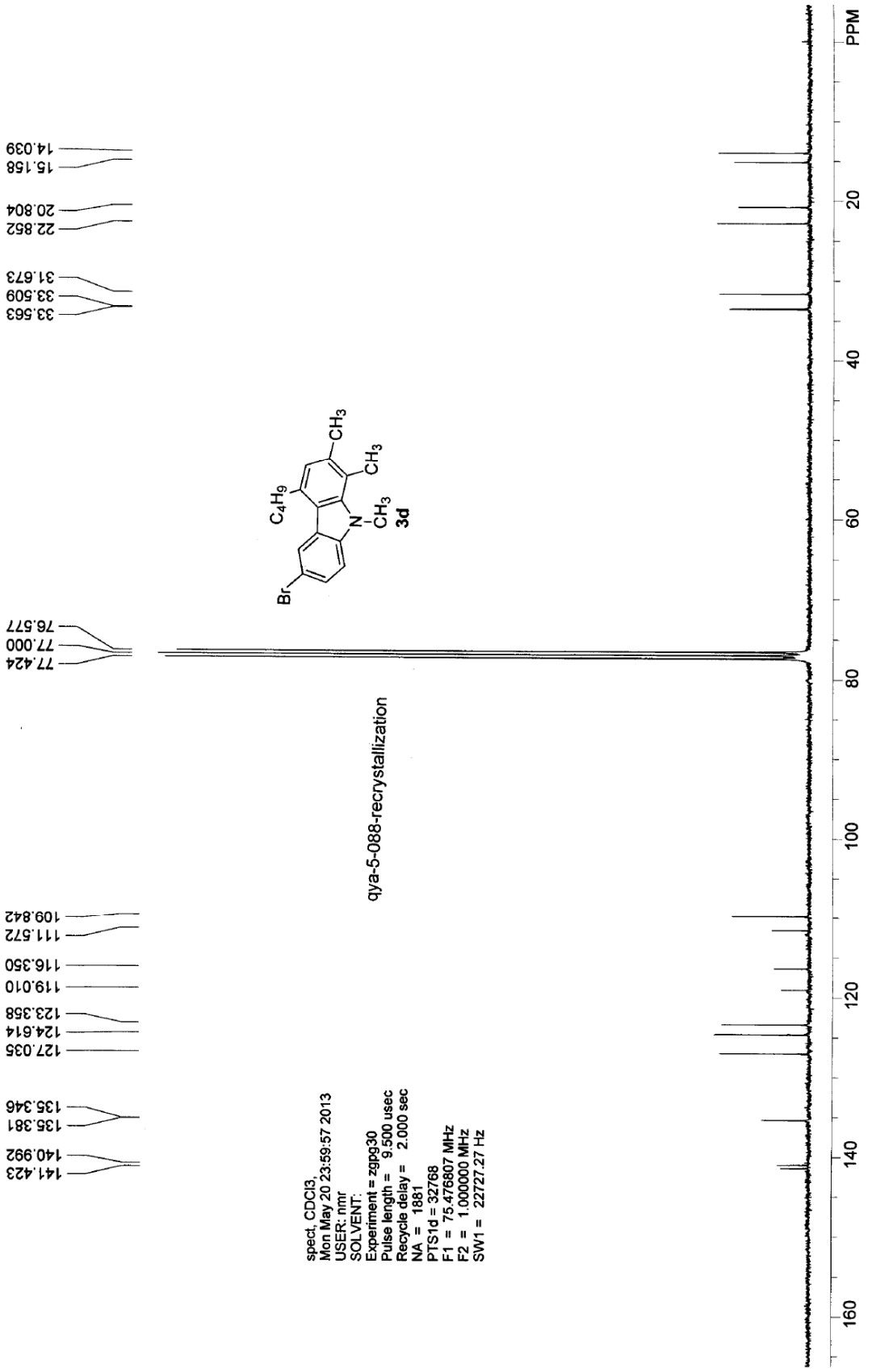


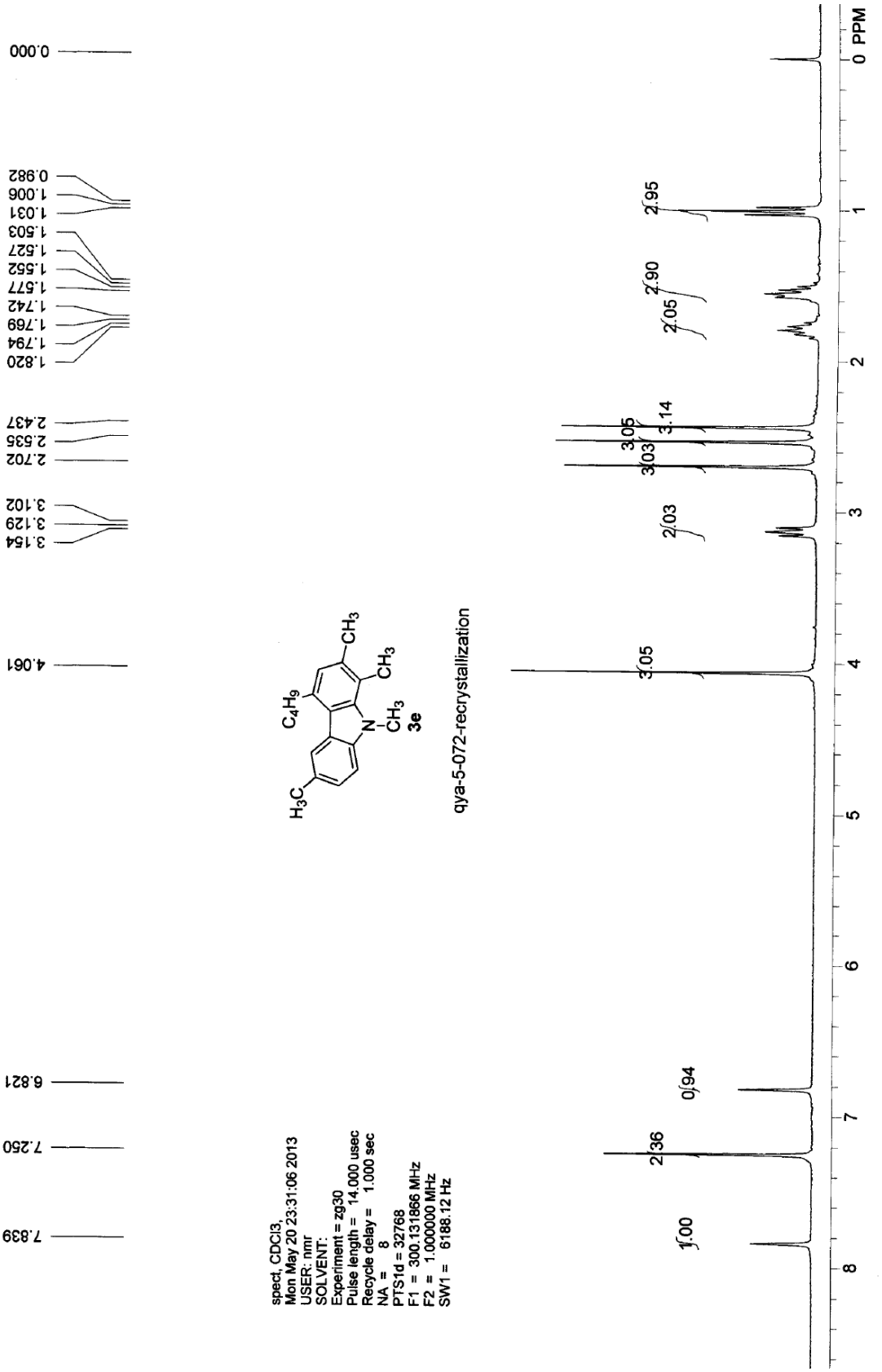


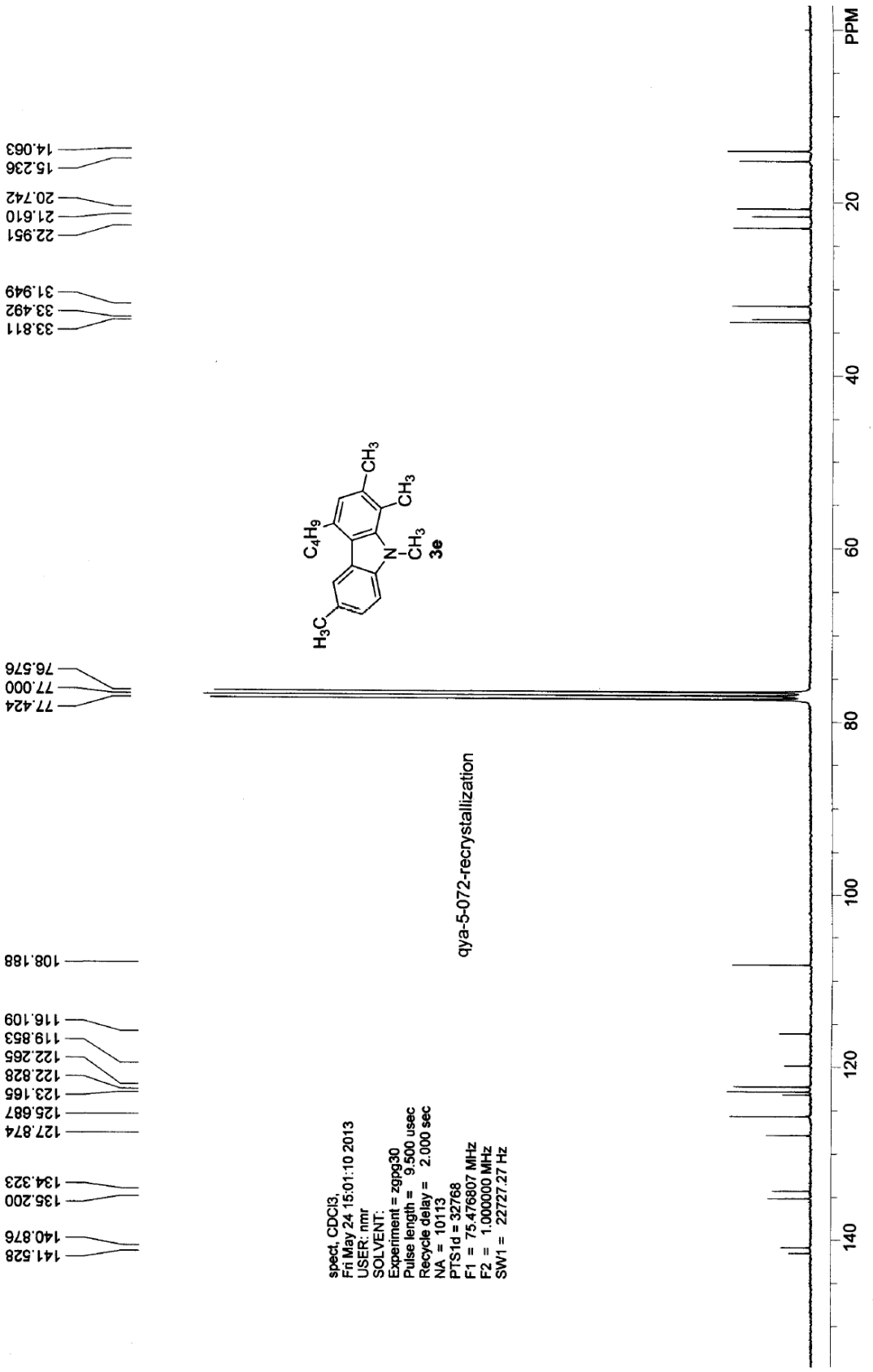

1.018
1.042
1.066
1.416
1.440
1.464
1.530
1.554
1.578
1.592
1.603
1.628
1.652
1.792
1.818
1.833
1.843
1.862
1.869
1.894
2.486
2.685
3.130
3.156
3.182
3.956
4.526
4.549
4.573
4.597
6.858
7.085
7.093
7.115
7.123
7.260
7.308
7.338
7.620
7.627
spect, CDCl3,
Tue May 21 07:06:29 2013
USER: nmr
SOLVENT:
Experiment = 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
C_4H_9
CH_3
CH_3
N–Et
H_3CO
3c
qya-5-059-recrystallization
1.00
1.00
1.00
0.98
2.06
3.01
2.05
3.01
3.04
2.08
2.02
2.99
3.04
0 PPM

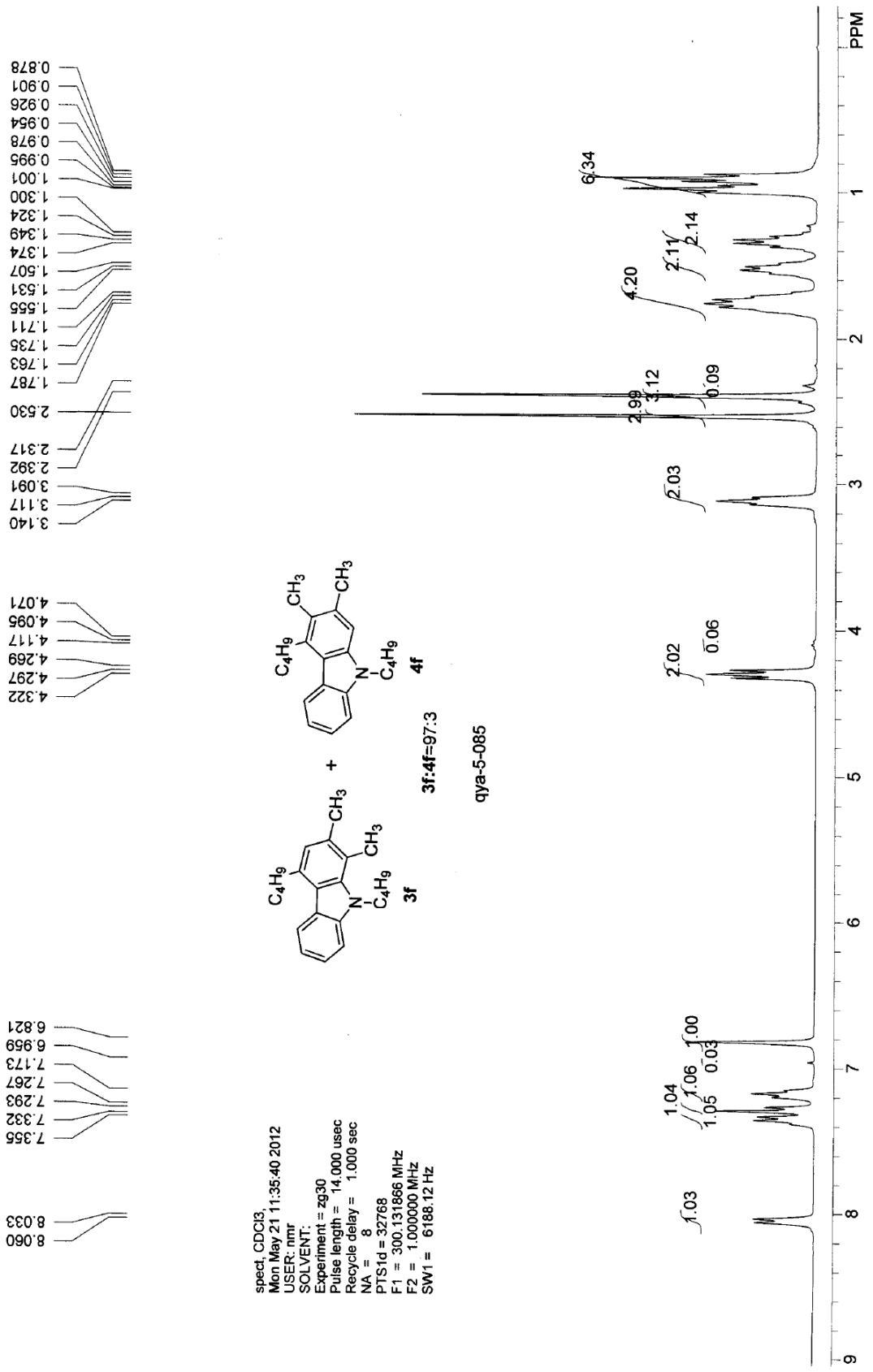


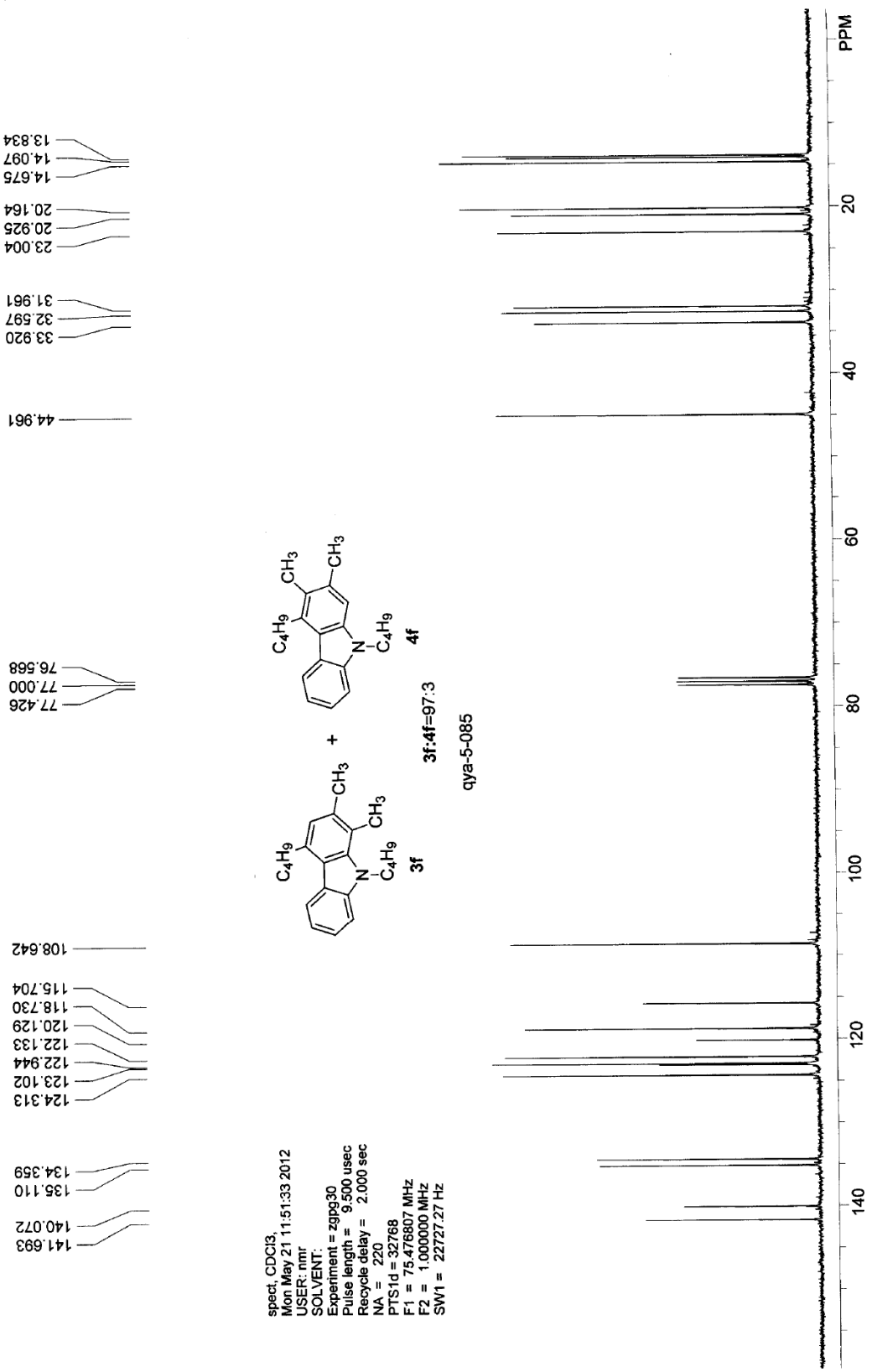


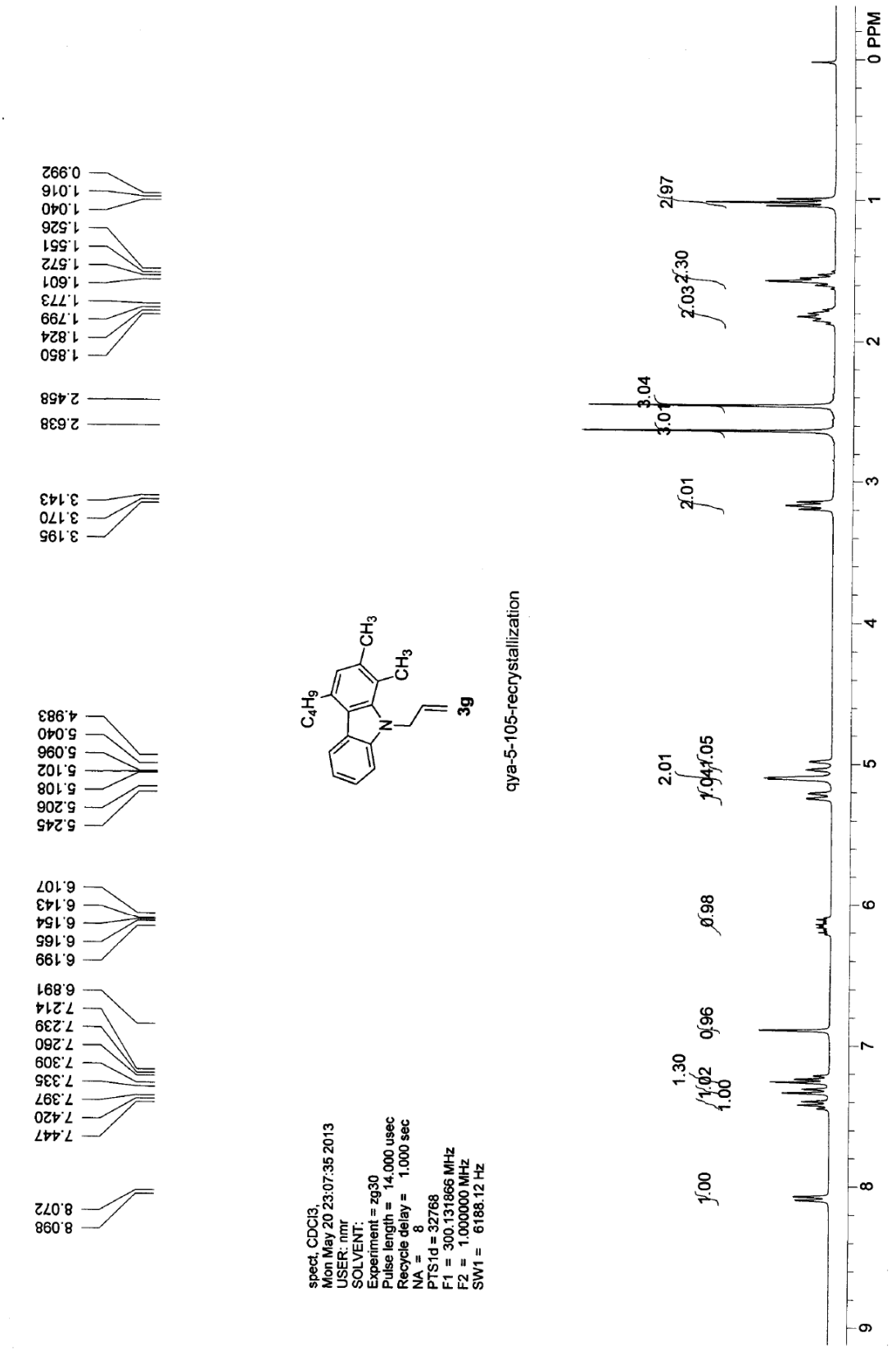

14.039
15.158
20.804
22.852
31.673
33.509
33.563
76.577
77.000
77.424
109.842
111.572
116.350
119.010
123.358
124.614
127.035
135.346
135.381
140.992
141.423
CH3
CH3
C4H9
N
CH3
Br
3d
qya-5-088-recrystallization
spect, CDCl3,
Mon May 20 23:59:57 2013
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 1881
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
PPM
20
40
60
80
100
120
140
160

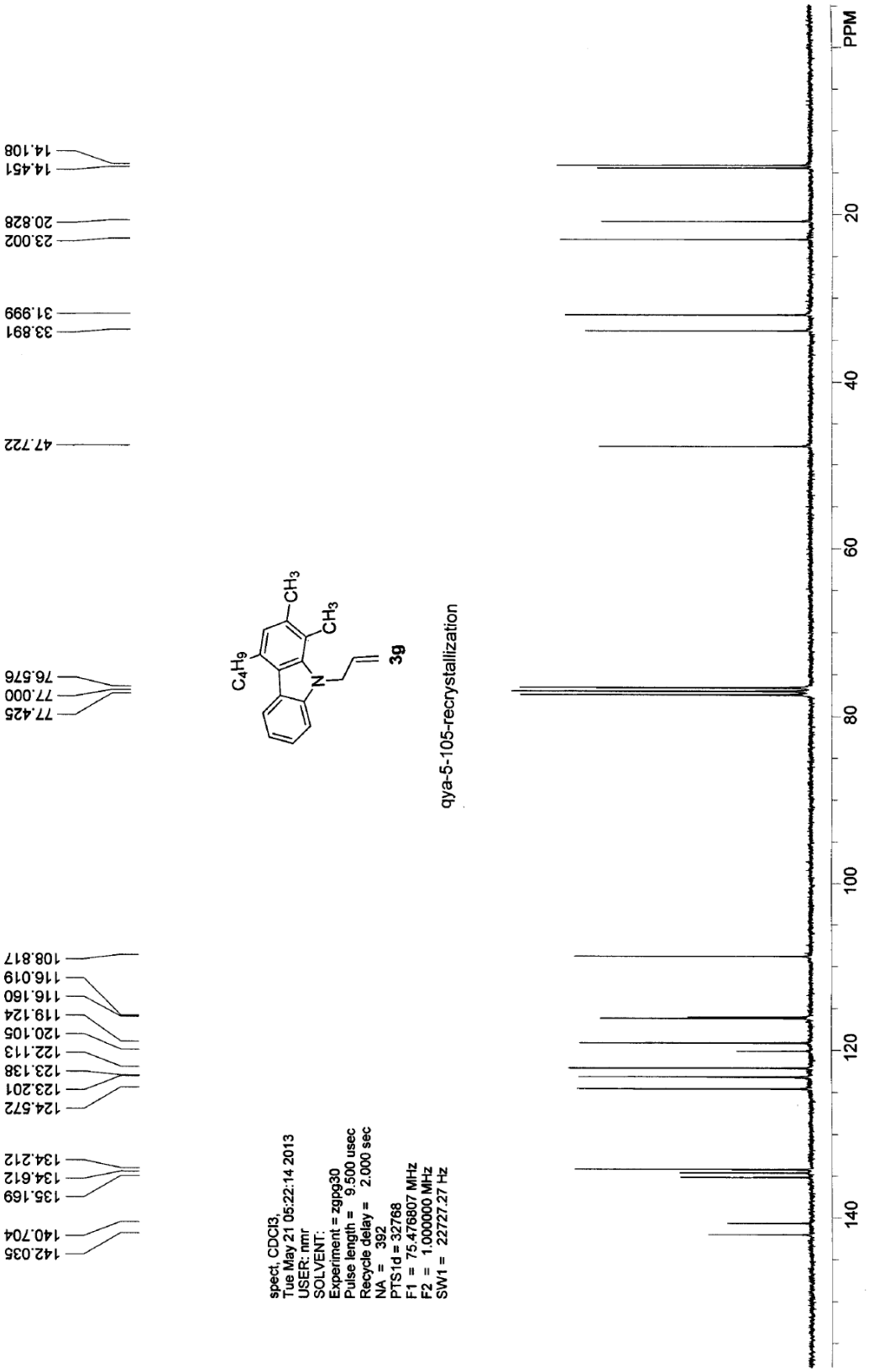


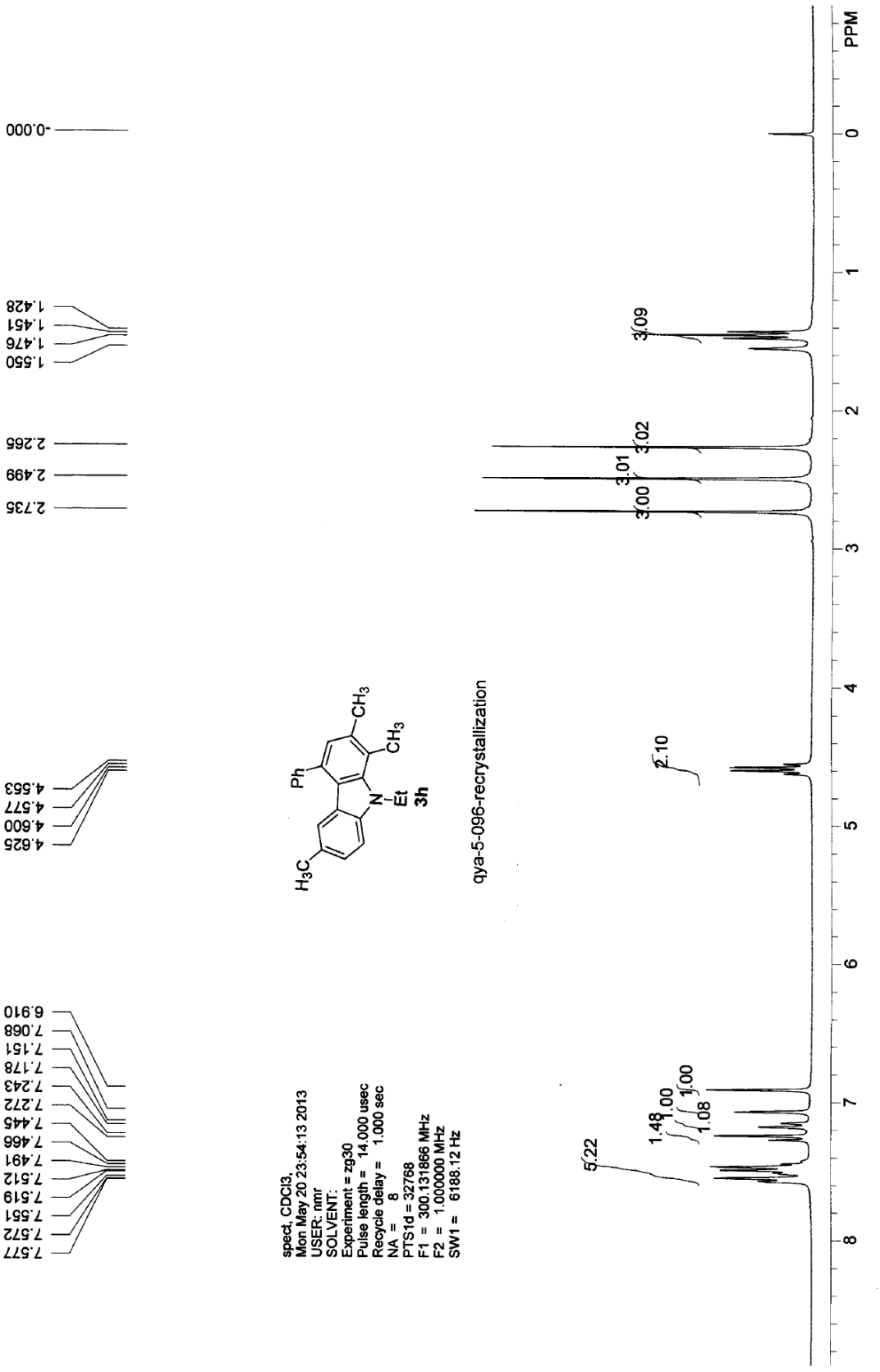

14.063
15.236
20.742
21.610
22.951
31.949
33.492
33.811
76.576
77.000
77.424
108.188
116.109
119.853
122.265
122.828
123.165
125.687
127.874
134.323
135.200
140.876
141.528
spect, CDCl3,
Fri May 24 15:01:10 2013
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 10113
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz
qya-5-072-recrystallization
C_4H_9
CH_3
CH_3
N
CH_3
H_3C
3e
PPM
20
40
60
80
100
120
140

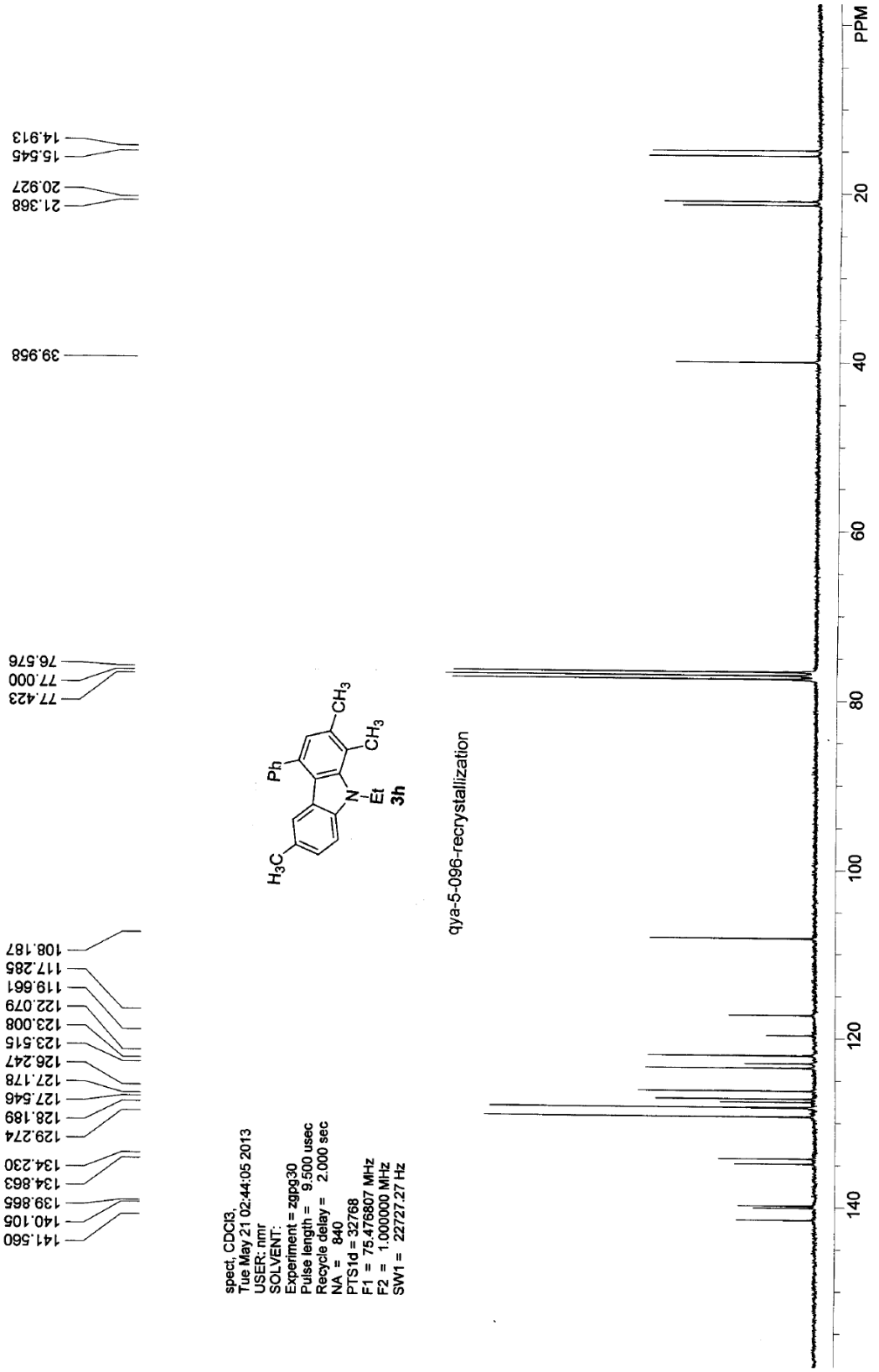

0.878
0.901
0.926
0.954
0.978
0.995
1.001
1.300
1.324
1.349
1.374
1.507
1.531
1.555
1.711
1.735
1.763
1.787
2.530
2.317
2.392
3.091
3.117
3.140
4.071
4.095
4.117
4.269
4.297
4.322
8.033
8.060
6.821
6.959
7.173
7.267
7.293
7.332
7.355
spect_CDCl3
Mon May 21 11:35:40 2012
USER: nmr
SOLVENT:
Experiment = 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
qya-5-085
3f:4f=97:3
4f
3f
PPM
1.03
1.04
1.05
1.06
0.03
1.00
2.02
0.06
2.03
2.99
3.12
0.09
4.20
2.11
2.14
6.34

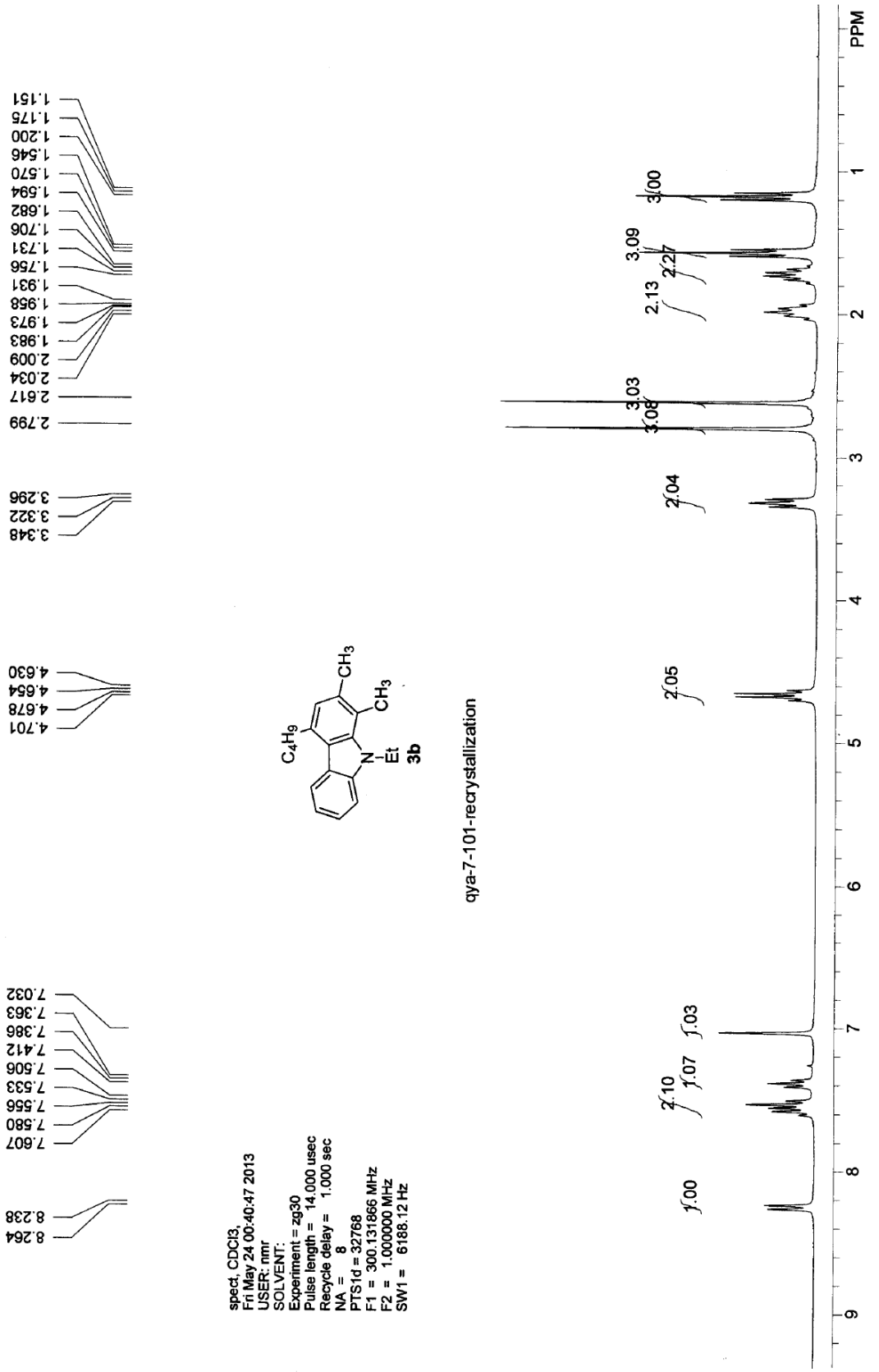

13.834
14.097
14.675
20.164
20.925
23.004
31.961
32.597
33.920
44.961
76.568
77.000
77.426
108.642
115.704
118.730
120.129
122.133
122.944
123.102
124.313
134.359
135.110
140.072
141.693
PPM
20
40
60
80
100
120
140
4f
3f
3f:4f=97:3
qya-5-085
spect, CDCl3,
Mon May 21 11:51:33 2012
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 220
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz

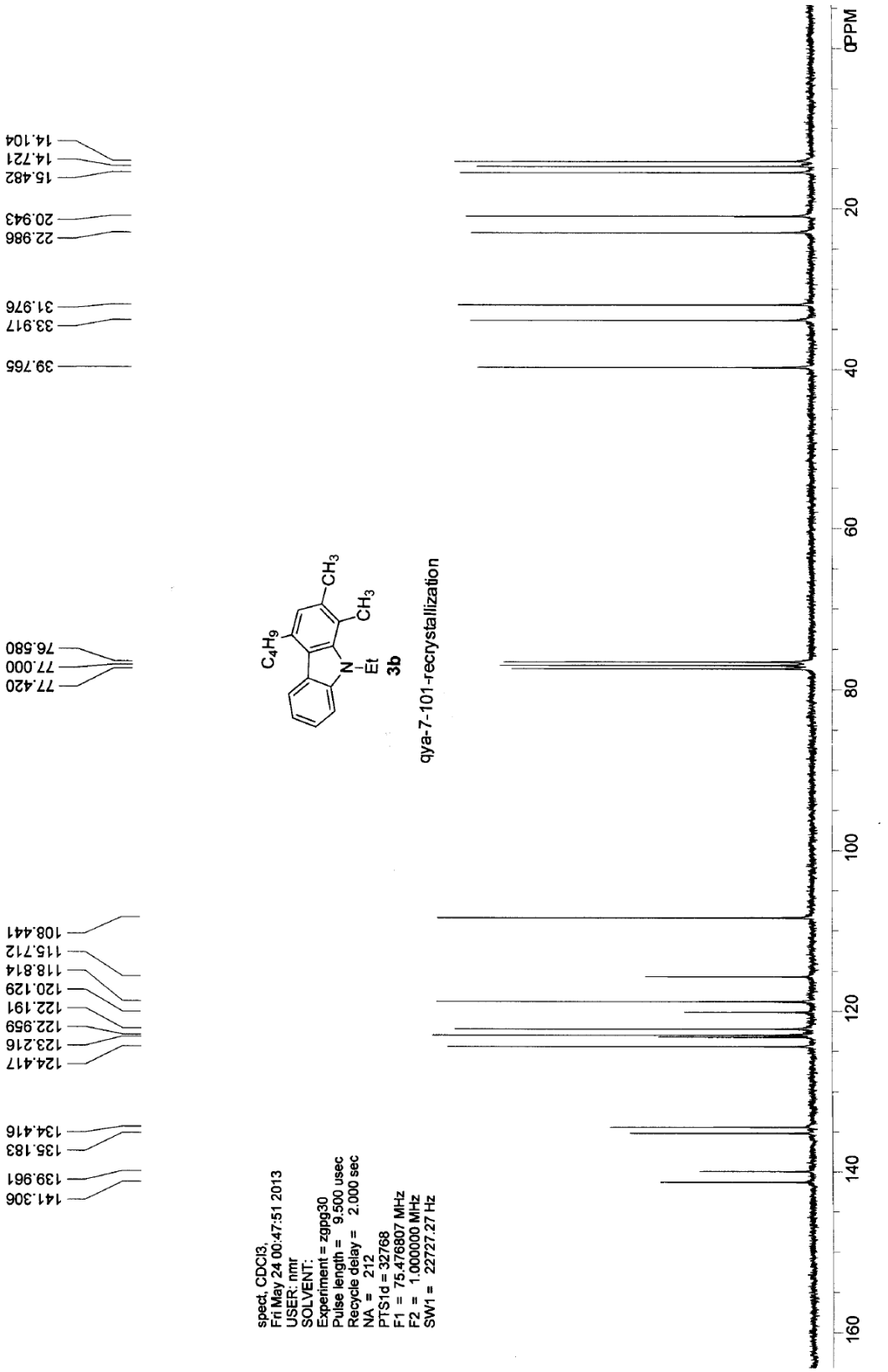


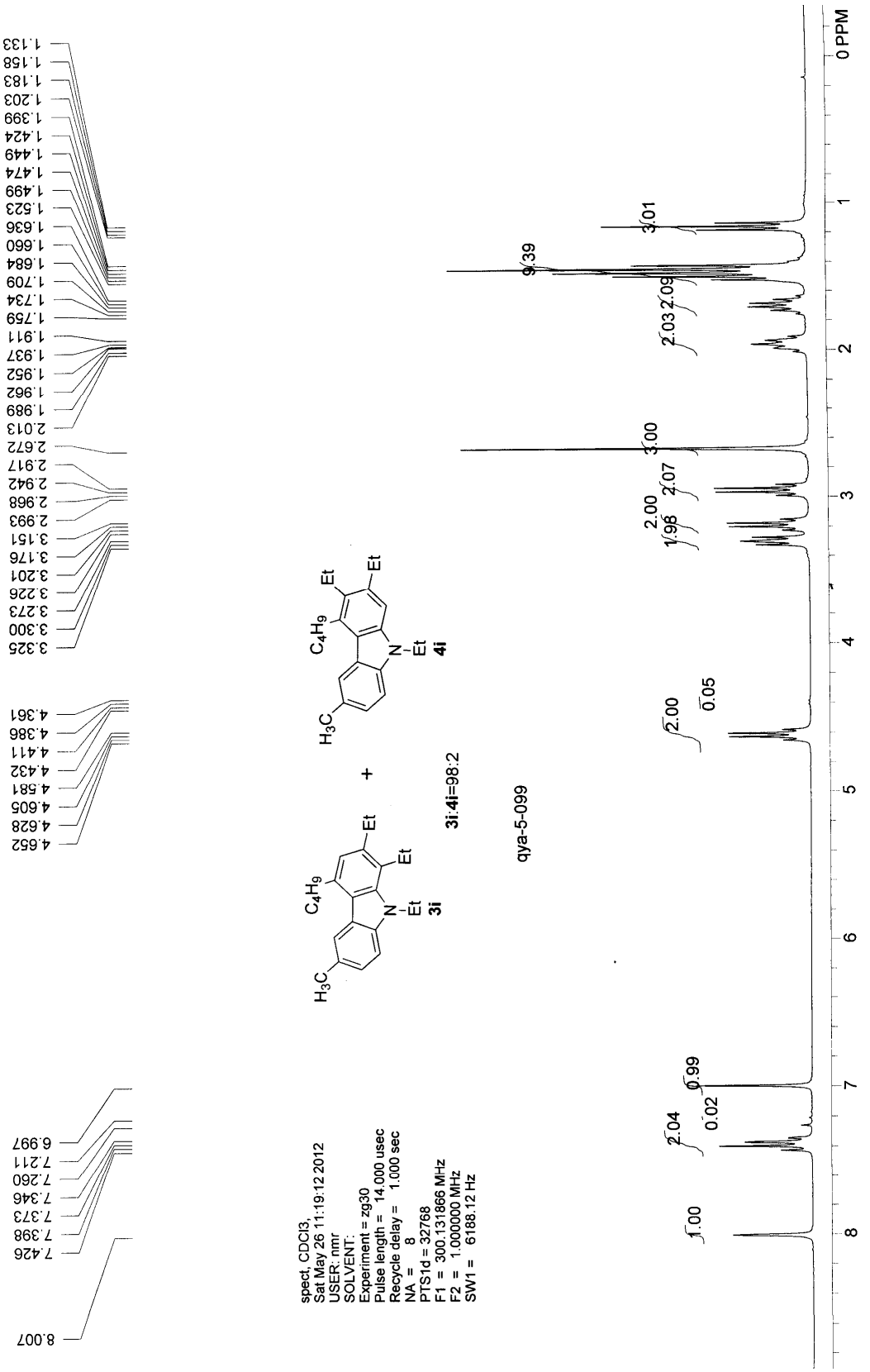


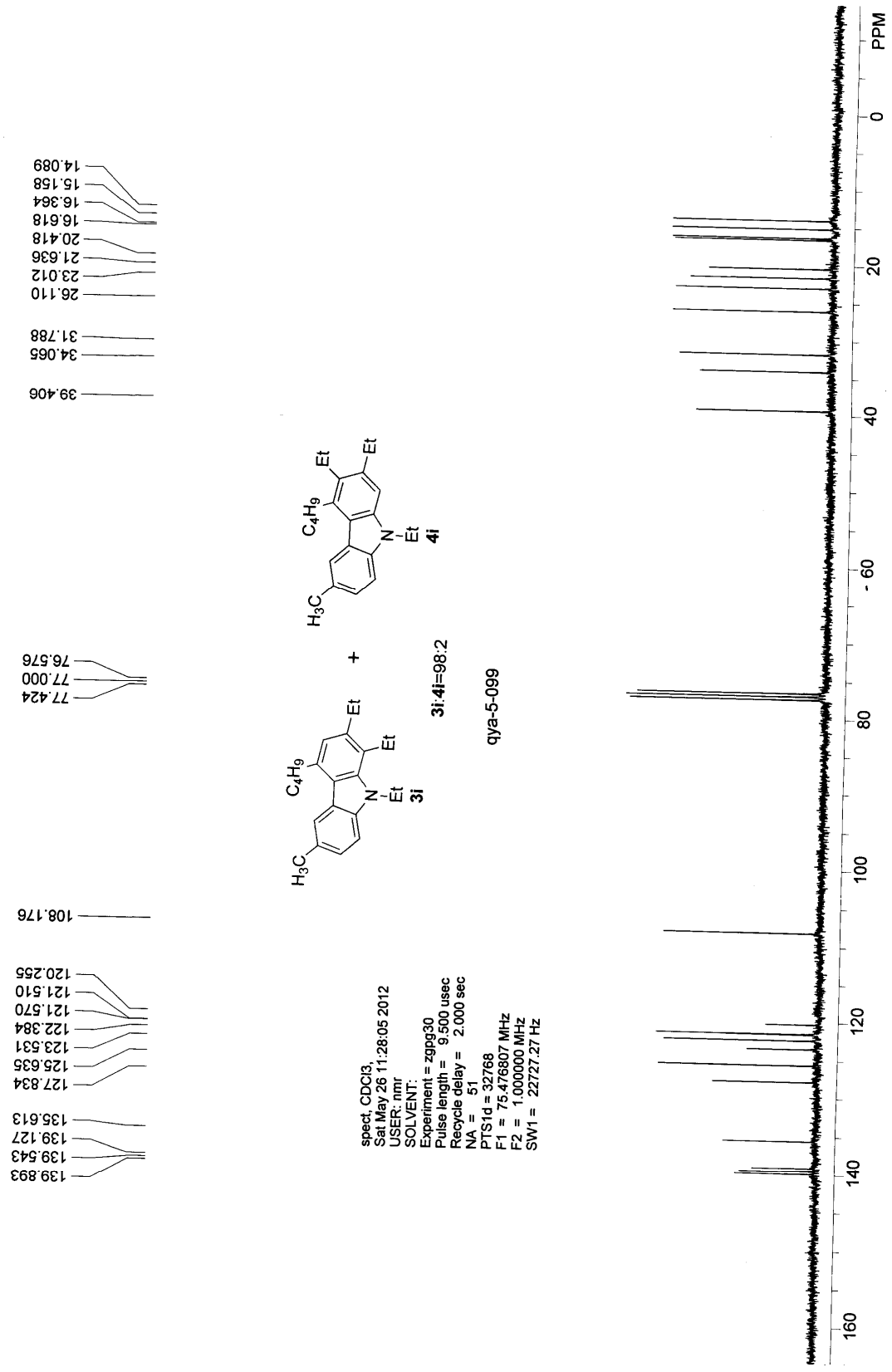


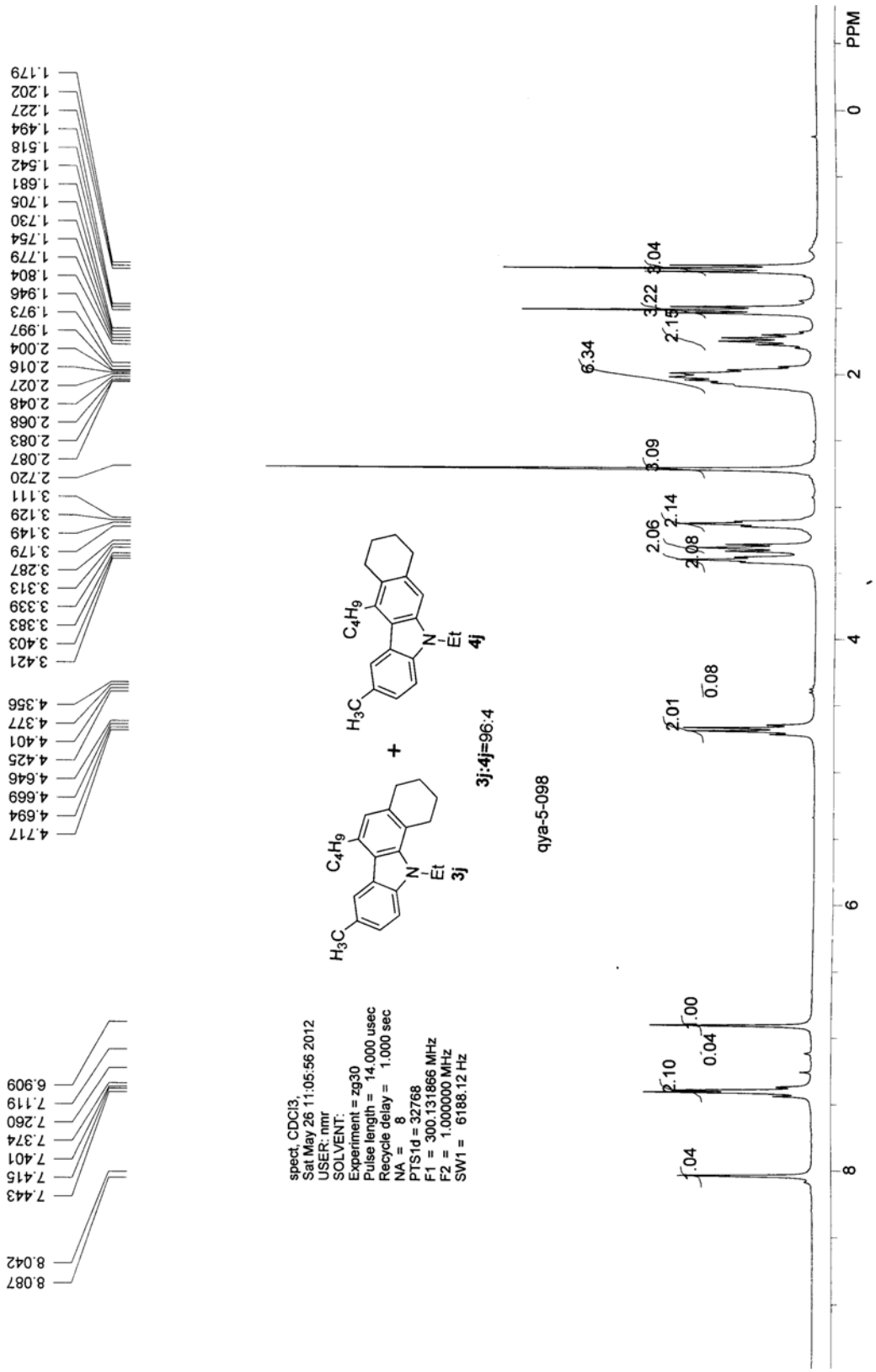


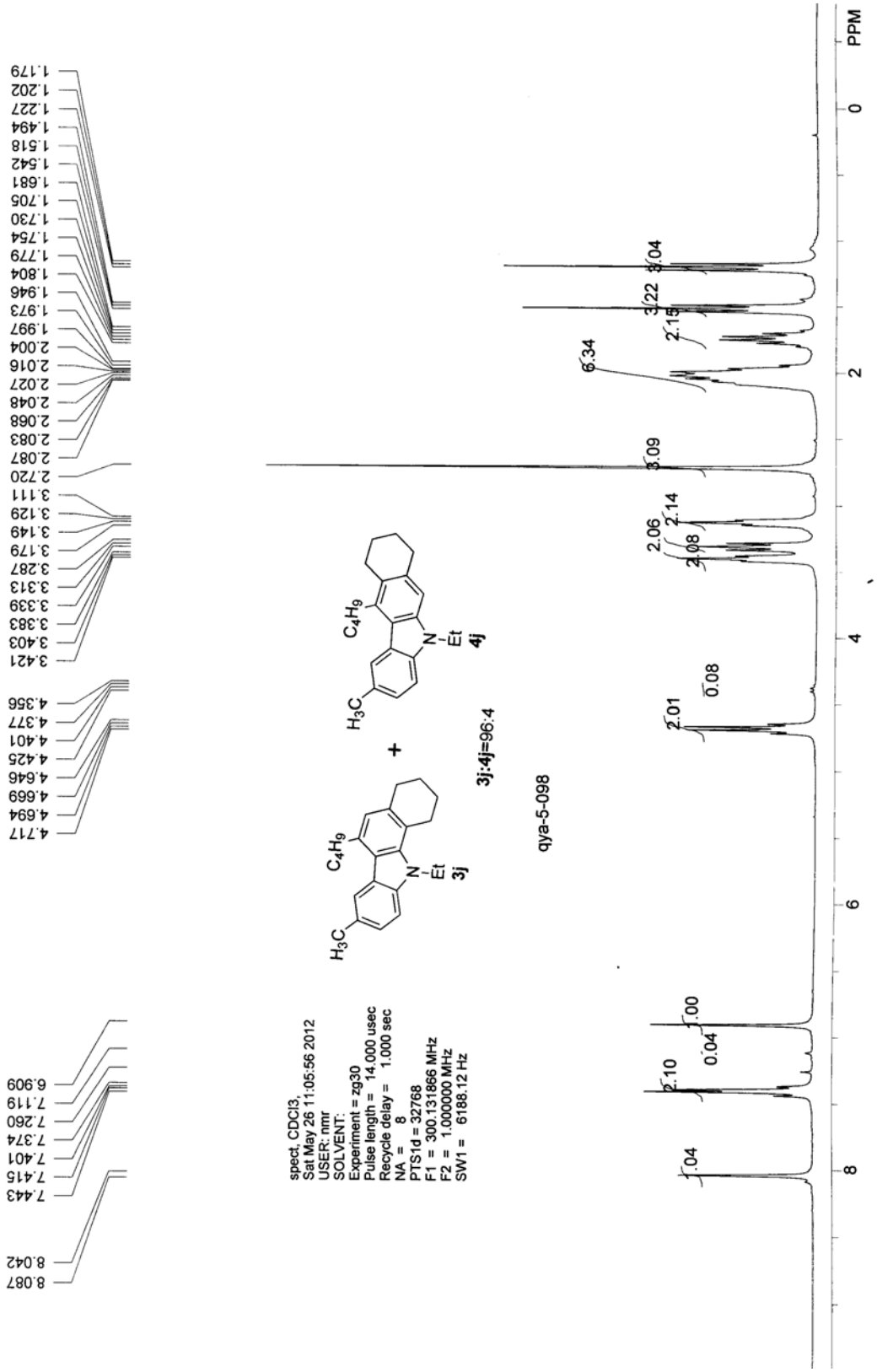


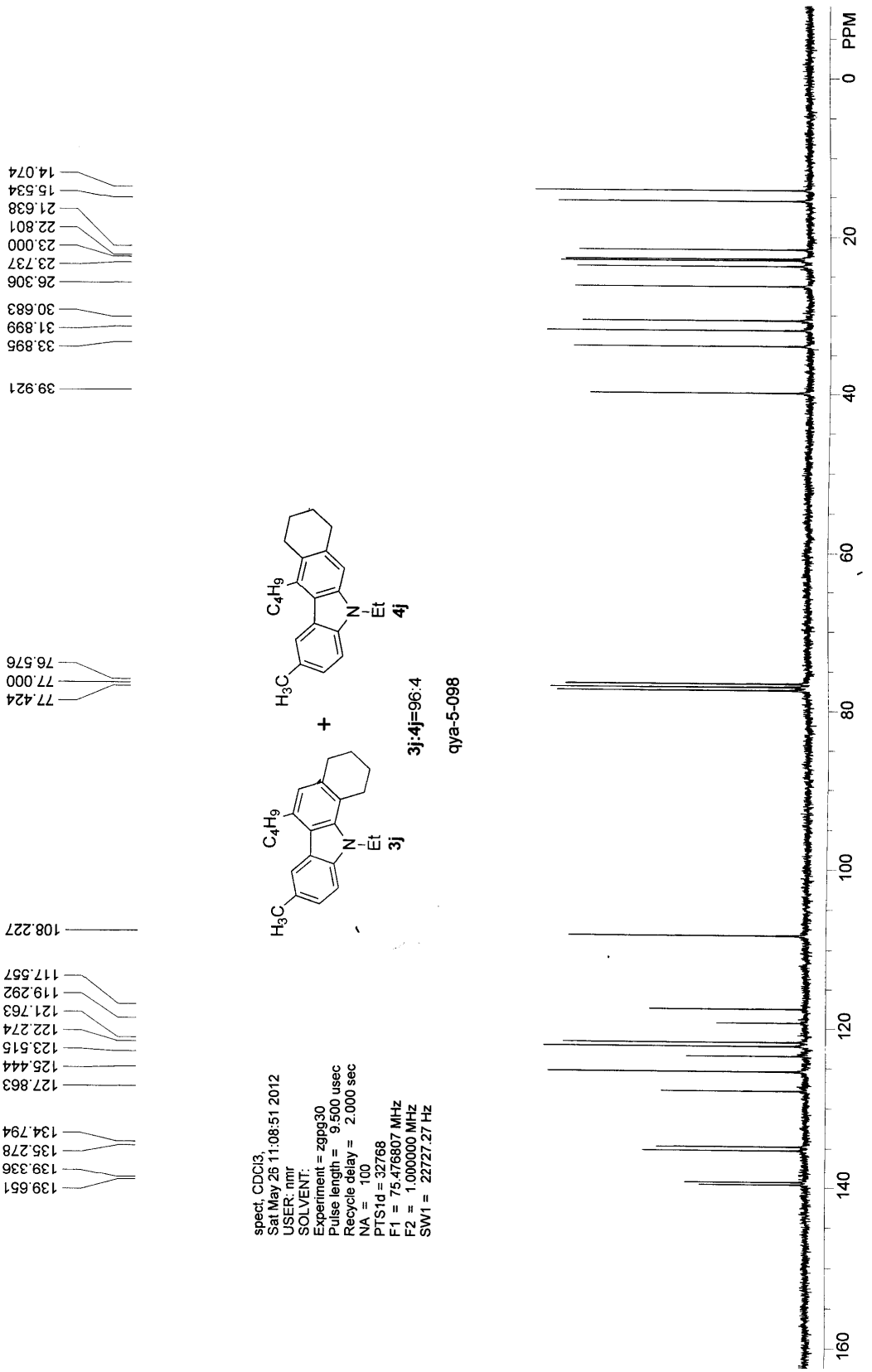


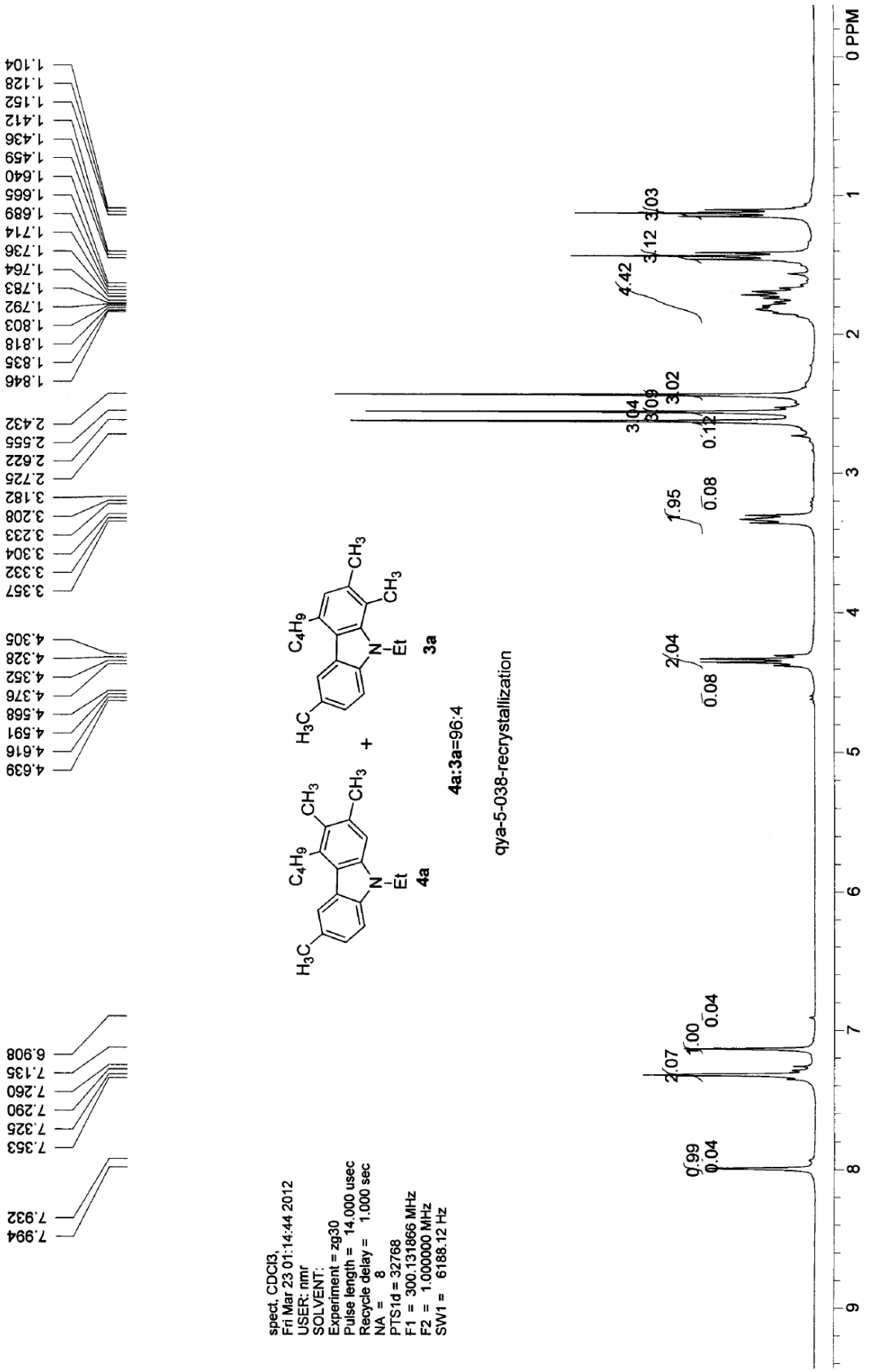


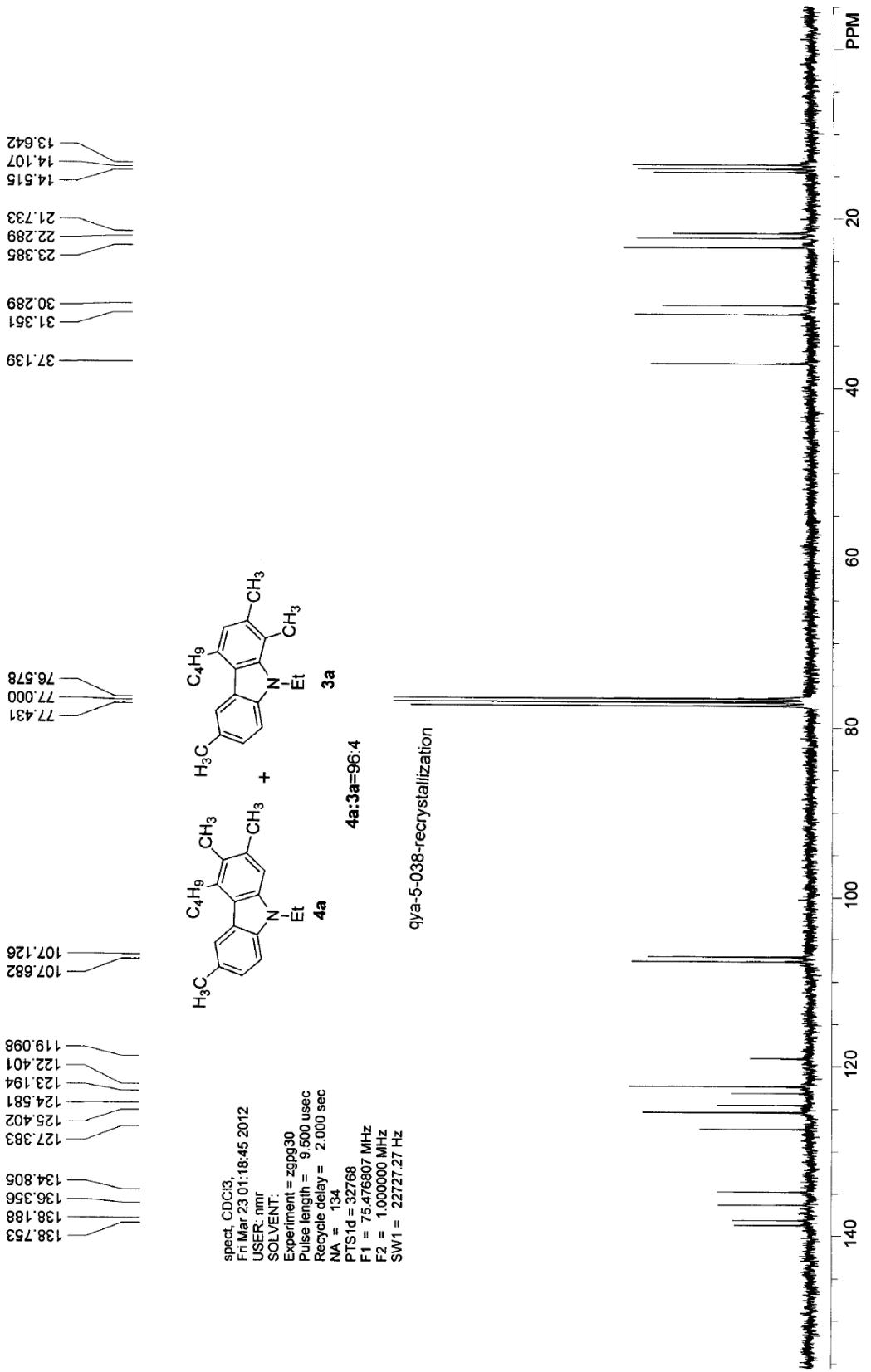


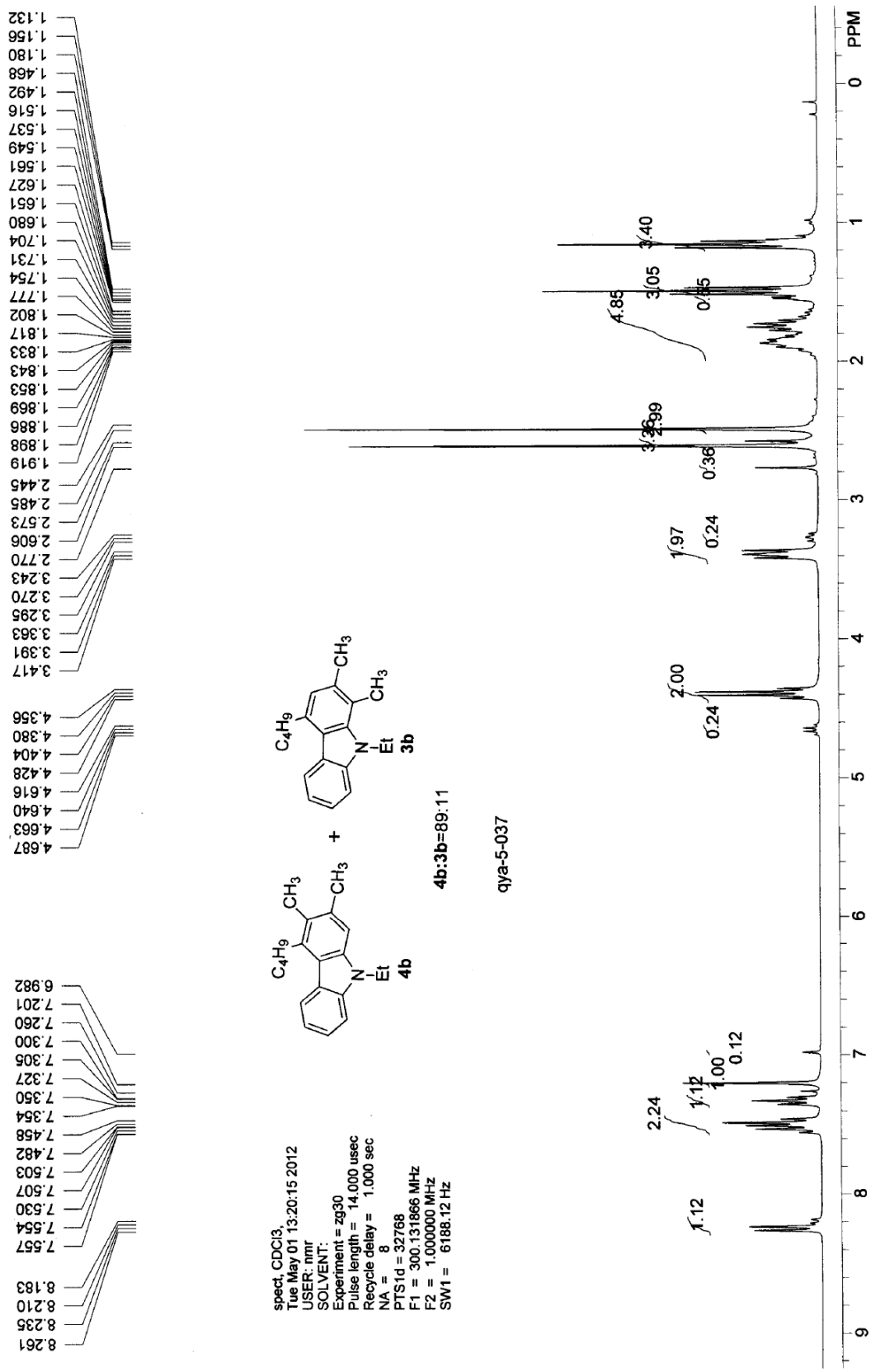


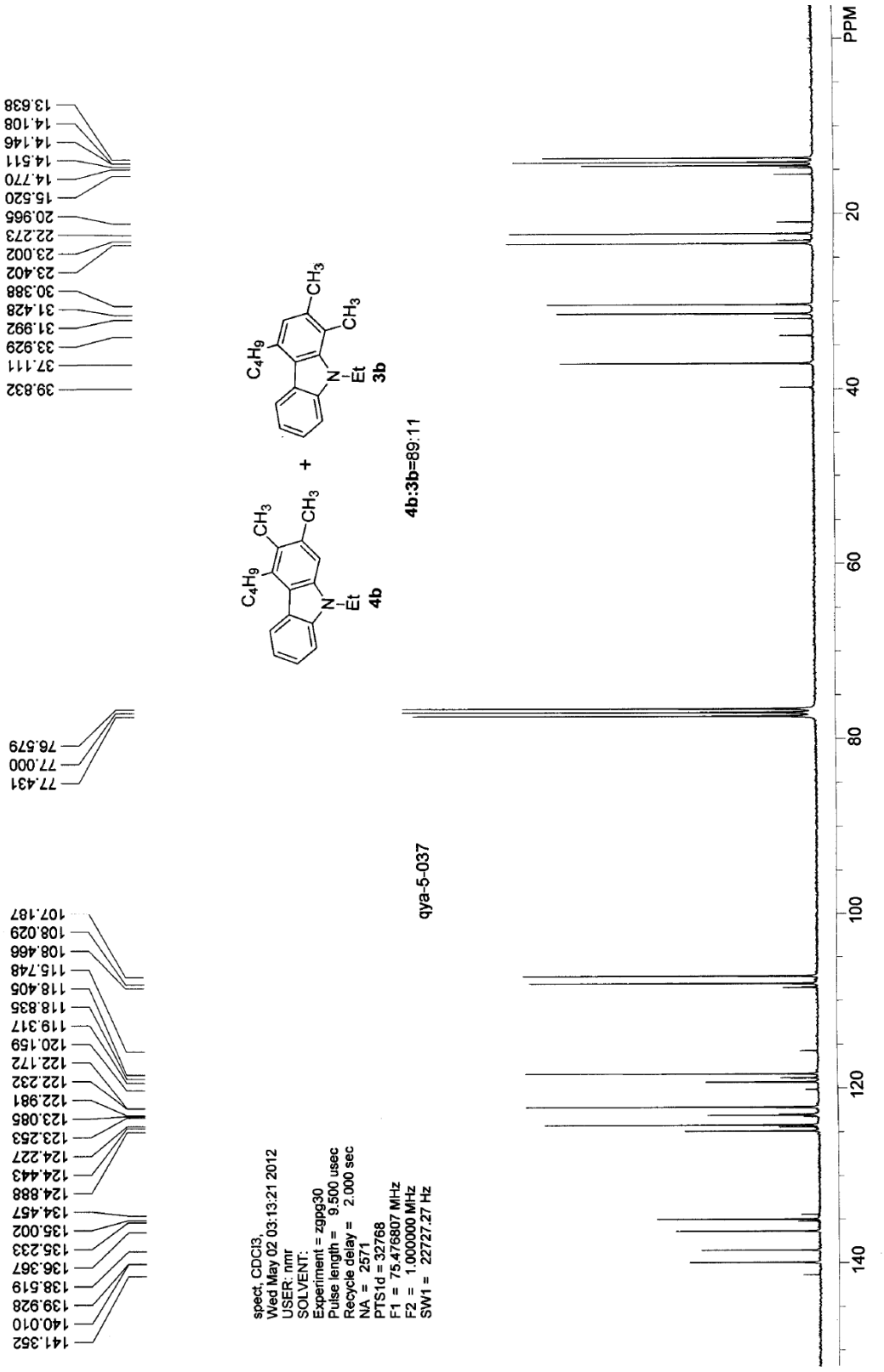

1.179
1.202
1.227
1.494
1.518
1.542
1.681
1.705
1.730
1.754
1.779
1.804
1.946
1.973
1.997
2.004
2.016
2.027
2.048
2.068
2.083
2.087
2.720
3.111
3.129
3.149
3.179
3.287
3.313
3.339
3.383
3.403
3.421
4.356
4.377
4.401
4.425
4.646
4.669
4.694
4.717
6.909
7.119
7.260
7.374
7.401
7.415
7.443
8.042
8.087
spect, CDCl3,
Sat May 26 11:05:56 2012
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
C_4H_9
H_3C
N
Et
3j
+
C_4H_9
H_3C
N
Et
4j
3j:4j=96:4
qya-5-098
1.04
2.10
0.04
1.00
2.01
0.08
2.06
2.14
2.08
3.09
6.34
3.22
2.15
3.04
PPM
0
2
4
6
8

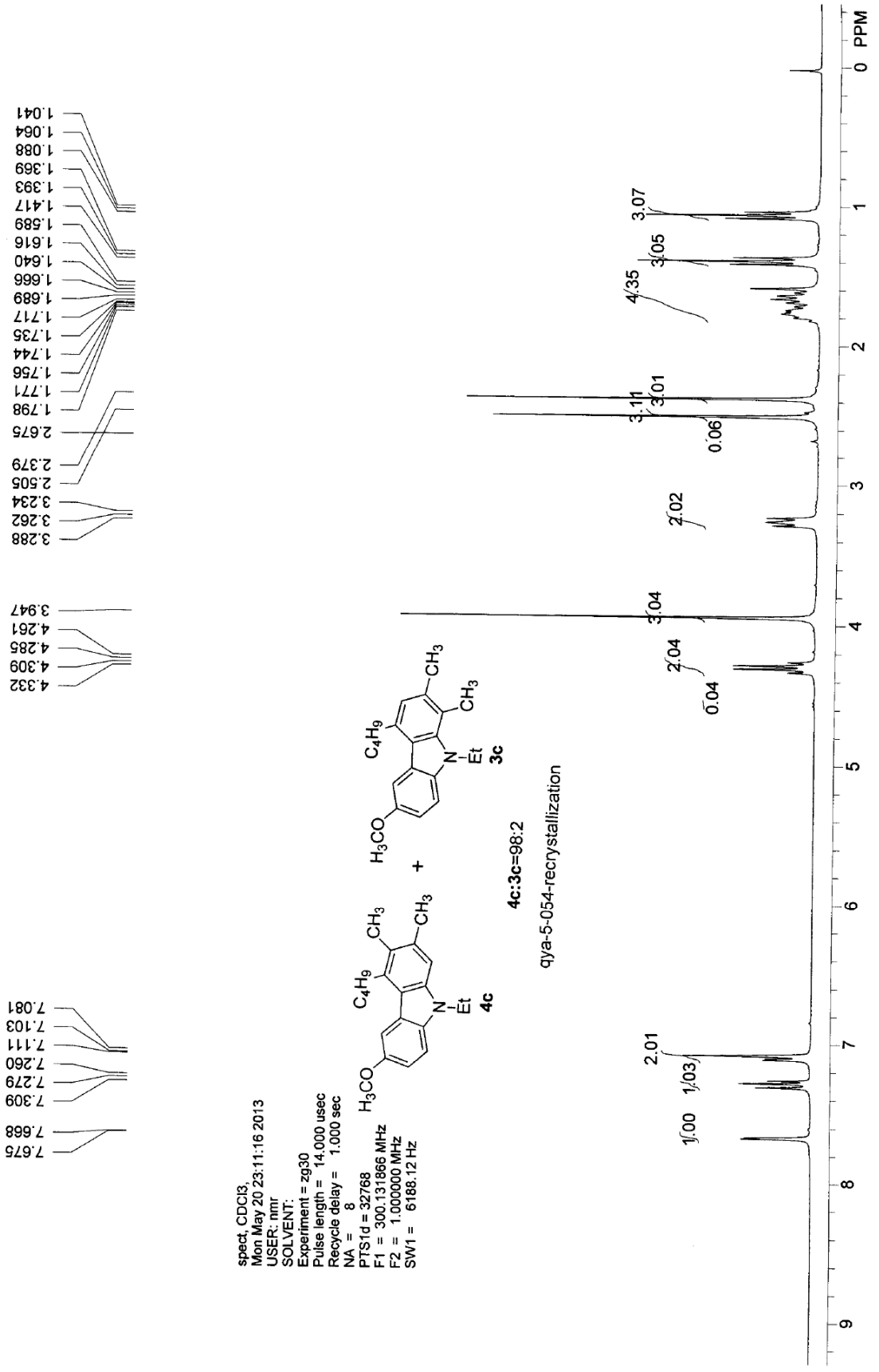

14.074
15.534
21.638
22.801
23.000
23.737
26.306
30.683
31.899
33.895
39.921
76.576
77.000
77.424
108.227
117.557
119.292
121.763
122.274
123.515
125.444
127.863
134.794
135.278
139.336
139.651
PPM
0
20
40
60
80
100
120
140
160
C4H9
H3C
N
Et
4j
+
3j
3j:4j=96:4
qya-5-098
spect, CDCl3,
Sat May 26 11:08:51 2012
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 100
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz

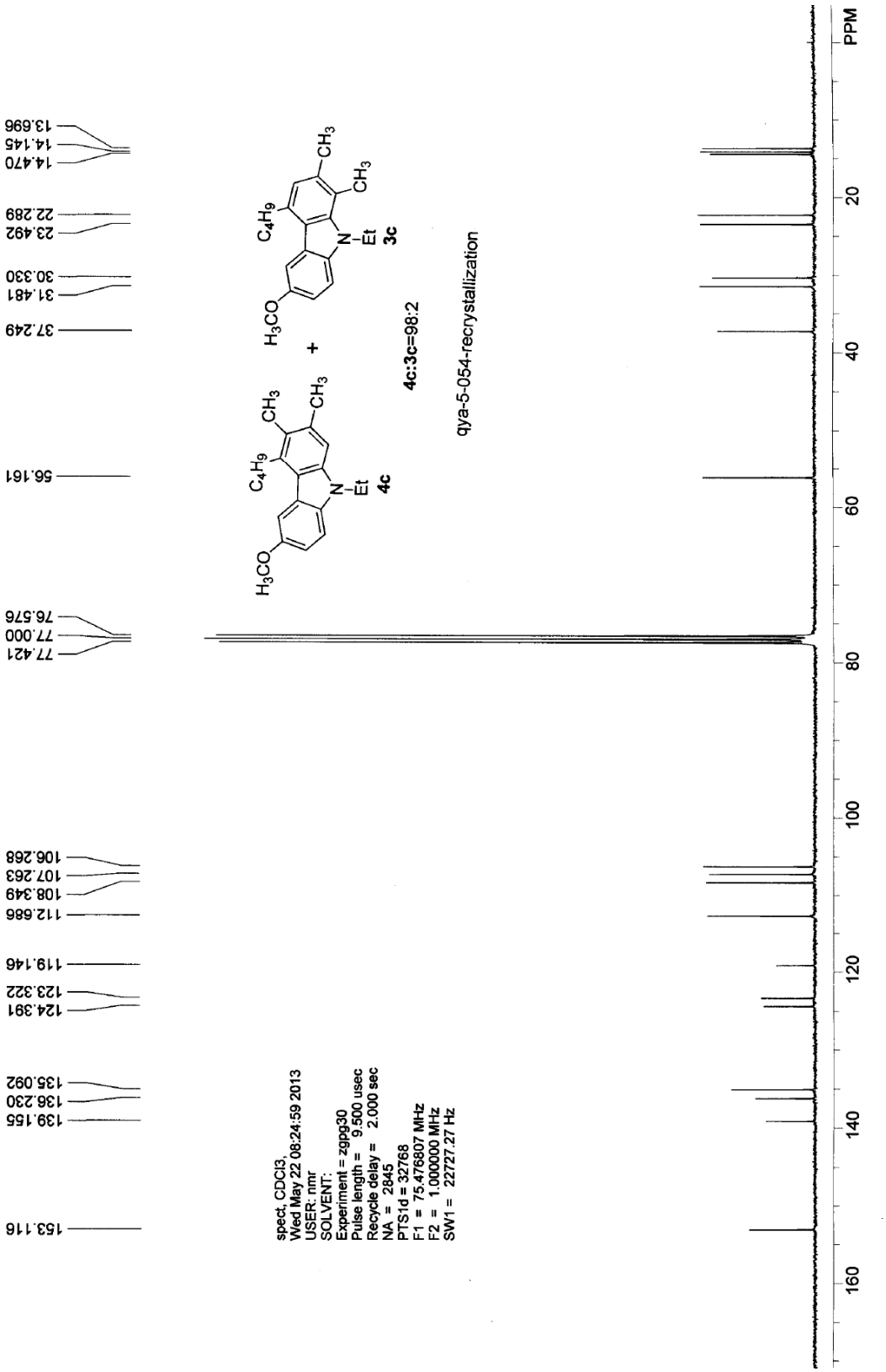


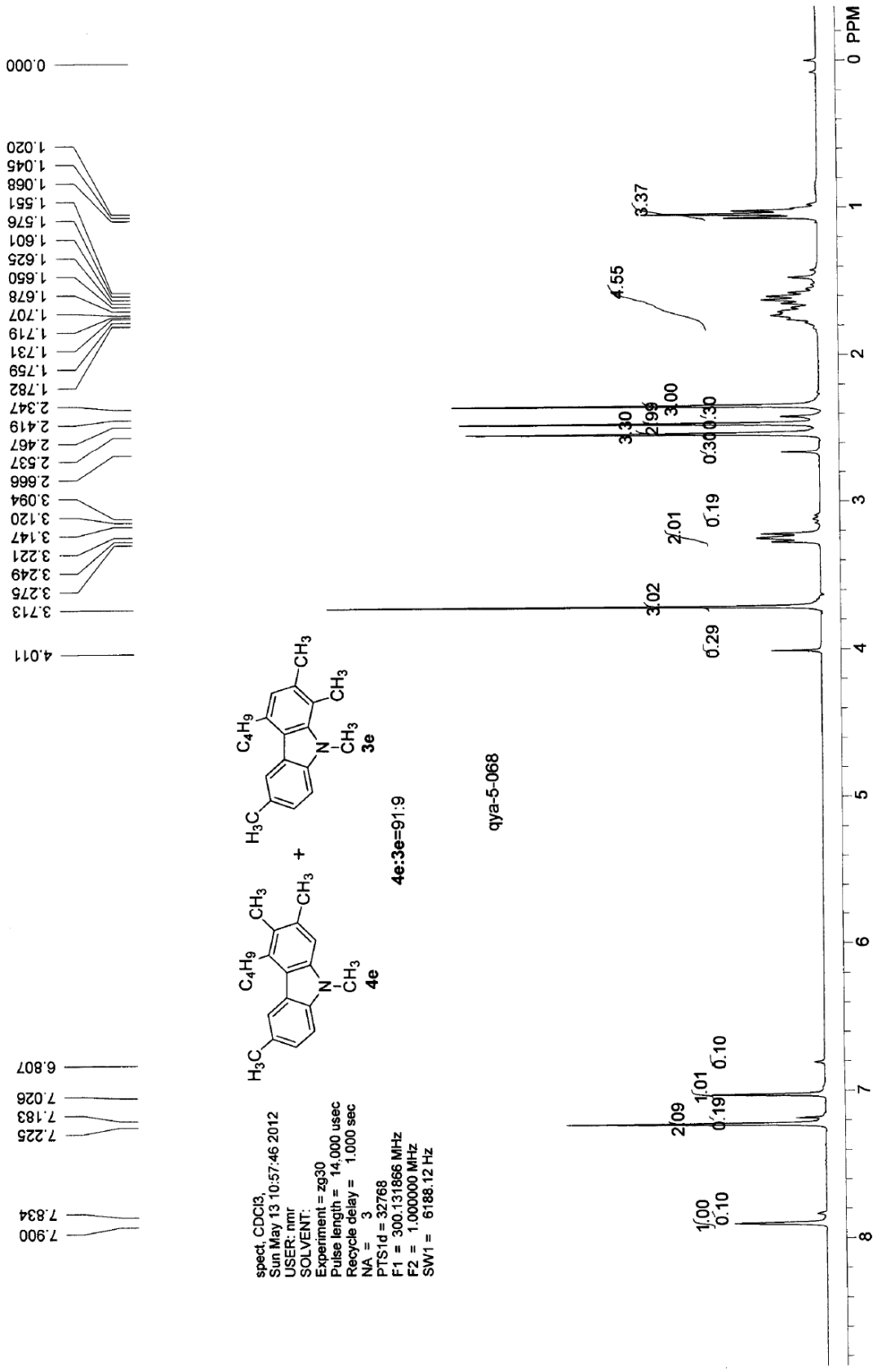



spect, CDCl3,
Tue May 01 13:20:15 2012
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
4b
3b
4b:3b=89:11
qya-5-037
PPM




spect, CDCl3,
Mon May 20 23:11:16 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
4c:3c=98:2
qya-5-054-recrystallization
4c
3c
PPM




spect, CDCl3,
Sun May 13 10:57:46 2012
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 3
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
qya-5-068
4e:3e=91:9
4e
3e
PPM