Electronic Supplementary Material (ESI) for Chemical Communications.

Copper-Mediated Pyrazole Synthesis from 2,3-Allenoates or 2-Alkynoates, Amines and Nitriles

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Supporting Information

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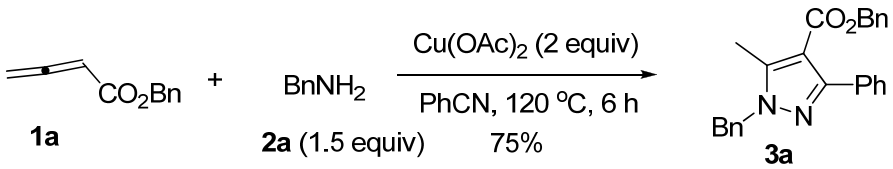
General Information: All reactions were carried out in oven-dried Schlenk tubes. PhCN, CH_3CN, and *n*-BuCN were dried over calcium hydride before distillation. All the temperatures are referred to the bath temperature. All ^1H NMR experiments were measured in relative to the signal of tetramethylsilane (0 ppm) in $CDCl_3$ and ^{13}C NMR experiments were measured in relative to the signal of $CDCl_3$ (77.00 ppm) in $CDCl_3$. ^{19}F NMR experiments were measured with trifluoroacetic acid as the external reference. IR spectra were recorded on the Bruker Tensor 27 infrared spectrometer with the major peaks listed. Melting points were measured without correction. Copper(II) acetate anhydrous (98.5%) was purchased from J&K, other common reagents were purchased from commercial sources and used without further purification unless noted otherwise. 2,3-Allenoates were prepared according to the known procedure.[1] Column chromatography was performed using silica gel (H) eluting with ethyl acetate and petroleum ether. TLC was performed on glass-backed silica plates.

Synthesis of pyrazoles from 2,3-allenoates with amines in nitriles.

1. Benzyl 1-benzyl-5-methyl-3-phenyl-1*H*-pyrazole-4-carboxylate (3a) (cb-9-198).

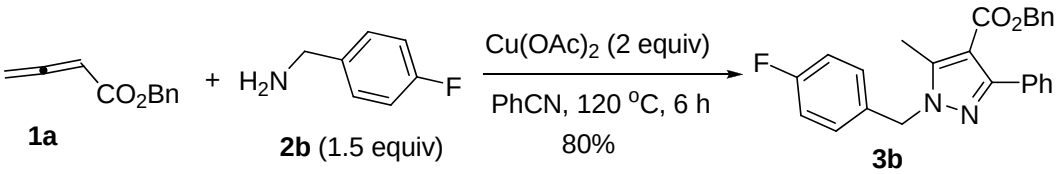


Typical procedure I: To a dried Schlenk tube equipped with a Teflon-coated magnetic stirring bar were added **1a** (35.1 mg, 0.2 mmol)/benzonitrile (1 mL) and **2a** (33.2 mg, 0.3 mmol)/benzonitrile (1 mL) under an argon atmosphere at room temperature. After being vigrously stirred for 0.5 h, $Cu(OAc)_2$ (72.9 mg, 0.4 mmol) was added. The reaction mixture was heated to 120 ^oC. After 6 h the reaction was complete as monitored by TLC, the resulting mixture was diluted with 50 mL of Et_2O and filtered through a short pad (3 cm) of silica gel. Evaporation and column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) afforded **3a**

(57.9 mg, 75%): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63-7.52 (m, 2 H, ArH), 7.38-7.22 (m, 9 H, ArH), 7.19-7.10 (m, 4 H, ArH), 5.33 (s, 2 H, $ArCH_2$), 5.18 (s, 2 H, $ArCH_2$), 2.47 (s, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8, 152.9, 144.6, 135.81, 135.77, 133.3, 129.4, 128.8, 128.3, 128.1, 128.0, 127.8, 127.7, 126.8, 109.6, 65.6, 53.3, 11.5; IR (neat) 1702, 1539, 1454, 1293, 1209, 1158, 1130, 1066 cm^{-1}; MS (EI) (*m/z*) 383 ($(M+1)^+$, 14.27), 382 (M^+, 51.56), 91 (100); HRMS calcd. for $C_{25}H_{22}N_2O_2$ [M^+]: 382.1681; Found: 382.1679.

The following compounds **3b**-**3o** were prepared according to **Typical Procedure I**.

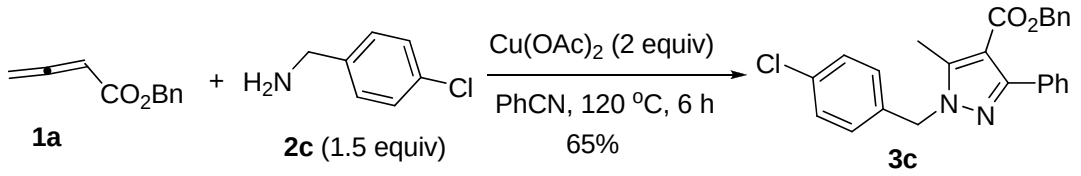
2. Benzyl 1-(4-fluorobenzyl)-5-methyl-3-phenyl-1*H*-pyrazole-4-carboxylate (3b) (cb-11-40).



1a **2b** (1.5 equiv) **3b**

The reaction of **1a** (35.1 mg, 0.2 mmol)/benzonitrile (1 mL), **2b** (37.5 mg, 0.3 mmol)/benzonitrile (1 mL), and $Cu(OAc)_2$ (73.1 mg, 0.4 mmol) afforded **3b** (64.8 mg, 80%) (petroleum ether/ethyl acetate = 10/1): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.54 (m, 2 H, ArH), 7.40-7.24 (m, 6 H, ArH), 7.20-7.11 (m, 4 H, ArH), 7.04-6.93 (m, 2 H, ArH), 5.29 (s, 2 H, $ArCH_2$), 5.18 (s, 2 H, $ArCH_2$), 2.47 (s, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.7, 162.3 (d, *J* = 245.0 Hz), 152.9, 144.4, 135.7, 133.2, 131.5 (d, *J* = 3.4 Hz), 129.3, 128.6 (d, *J* = 8.1 Hz), 128.3, 128.1, 128.0, 127.9, 127.7, 115.7 (d, *J* = 21.8 Hz), 109.7, 65.6, 52.5, 11.4; ^{19}F NMR ($CDCl_3$, 376 MHz) -114.0; IR (neat) 2925, 2853, 1705, 1606, 1538, 1510, 1481, 1450, 1427, 1375, 1356, 1318, 1298, 1215, 1143, 1111, 1076 cm^{-1}; MS (EI) (*m/z*) 401 ($(M+1)^+$, 11.06), 400 (M^+, 39.29), 109 (100); HRMS calcd. for $C_{25}H_{21}N_2O_2F$ [M^+]: 400.1587; Found: 400.1589.

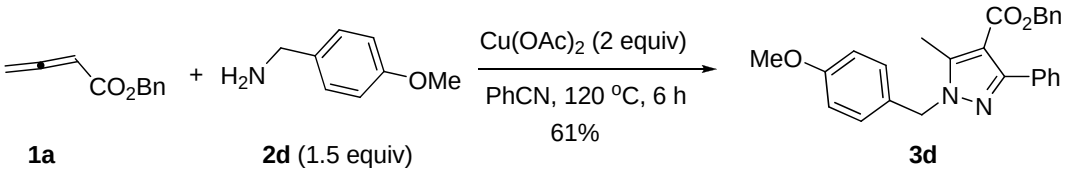
3. Benzyl 1-(4-chlorobenzyl)-5-methyl-3-phenyl-1*H*-pyrazole-4-carboxylate (3c) (cb-11-39).



1a **2c** (1.5 equiv) **3c**

The reaction of **1a** (34.4 mg, 0.2 mmol)/benzonitrile (1 mL), **2c** (42.7 mg, 0.3 mmol)/benzonitrile (1 mL), and $Cu(OAc)_2$ (72.7 mg, 0.4 mmol) afforded **3c** (53.9 mg, 65%) (petroleum ether/ethyl acetate = 20/1 to 10/1): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65-7.53 (m, 2 H, ArH), 7.41-7.22 (m, 8 H, ArH), 7.20-7.05 (m, 4 H, ArH), 5.28 (s, 2 H, $ArCH_2$), 5.18 (s, 2 H, $ArCH_2$), 2.46 (s, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.7, 153.0, 144.5, 135.7, 134.2, 133.7, 133.1, 129.3, 128.9, 128.3, 128.2, 128.1, 127.9, 127.7, 109.7, 65.7, 52.5, 11.4; IR (neat) 2923, 2851, 1693, 1489, 1453, 1291, 1215, 1162, 1092, 1065, 1013 cm^{-1}; MS (EI) (*m/z*) 419 ((M(^{37}Cl)+1)$^+$, 3.18), 418 (M(^{37}Cl)$^+$, 11.66), 417 ((M(^{35}Cl)+1)$^+$, 9.49), 416 (M(^{35}Cl)$^+$, 32.75), 91 (100); HRMS calcd. for $C_{25}H_{21}N_2O_2{}^{35}Cl$ [M$^+$]: 416.1292; Found: 416.1289.

4. Benzyl 1-(4-methoxybenzyl)-5-methyl-3-phenyl-1*H*-pyrazole-4-carboxylate (3d) (cb-10-143).

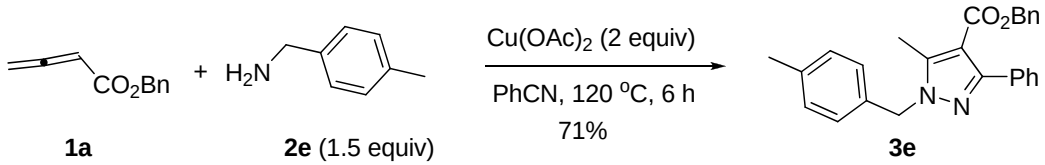


1a **2d** (1.5 equiv) **3d**

The reaction of **1a** (33.8 mg, 0.2 mmol)/benzonitrile (1 mL), **2d** (41.5 mg, 0.3 mmol)/benzonitrile (1 mL), and $Cu(OAc)_2$ (72.8 mg, 0.4 mmol) afforded **3d** (48.7 mg, 61%) (petroleum ether/ethyl acetate = 10/1): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65-7.53 (m, 2 H, ArH), 7.37-7.29 (m, 3 H, ArH), 7.29-7.20 (m, 3 H, ArH), 7.20-7.08 (m, 4 H, ArH), 6.89-6.78 (m, 2 H, ArH), 5.26 (s, 2 H, $ArCH_2$), 5.17 (s, 2 H, $ArCH_2$), 3.75 (s, 3 H, OMe), 2.47 (s, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8, 159.2, 152.7, 144.3, 135.8, 133.4, 129.4, 128.28, 128.26, 128.0, 127.9,

127.8, 127.6, 114.1, 109.6, 65.6, 55.2, 52.8, 11.4; IR (neat) 1701, 1612, 1586, 1539, 1513, 1484, 1453, 1295, 1248, 1210, 1129, 1067, 1030 cm^{-1}; MS (EI) (*m/z*) 413 ($(M+1)^+$, 3.77), 412 (M^+, 13.05), 121 (100); HRMS calcd. for $C_{26}H_{24}N_2O_3$ [M^+]: 412.1787; Found: 412.1789.

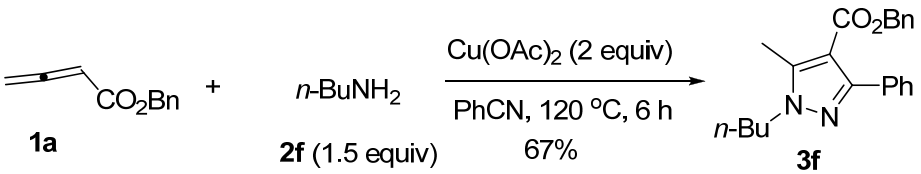
5. Benzyl 1-(4-methylbenzyl)-5-methyl-3-phenyl-1*H*-pyrazole-4-carboxylate (3e) (cb-11-36).



1a **2e** (1.5 equiv) **3e**

The reaction of **1a** (35.1 mg, 0.2 mmol)/benzonitrile (1 mL), **2e** (37.0 mg, 0.3 mmol)/benzonitrile (1 mL), and $Cu(OAc)_2$ (72.5 mg, 0.4 mmol) afforded **3e** (56.9 mg, 71%) (petroleum ether/ethyl acetate = 20/1): solid; m.p. 86-87 °C (hexane/Et_2O); ^1H NMR (300 MHz, $CDCl_3$) δ 7.65-7.53 (m, 2 H, ArH), 7.39-7.26 (m, 6 H, ArH), 7.20-7.03 (m, 6 H, ArH), 5.29 (s, 2 H, $ArCH_2$), 5.17 (s, 2 H, $ArCH_2$), 2.47 (s, 3 H, CH_3), 2.30 (s, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8, 152.8, 144.4, 137.6, 135.8, 133.3, 132.7, 129.40, 129.36, 128.3, 128.1, 128.0, 127.8, 127.7, 126.8, 109.5, 65.6, 53.2, 21.0, 11.5; IR (neat) 1695, 1541, 1515, 1486, 1451, 1432, 1291, 1214, 1158, 1064 cm^{-1}; MS (EI) (*m/z*) 397 ($(M+1)^+$, 12.20), 396 (M^+, 41.13), 105 (100); elemental analysis calcd (%) for $C_{26}H_{24}N_2O_2$: C 78.76, H 6.10, N 7.07; found: C 78.44, H 6.16, N 6.97.

6. Benzyl 1-butyl-5-methyl-3-phenyl-1*H*-pyrazole-4-carboxylate (3f) (cb-11-42).

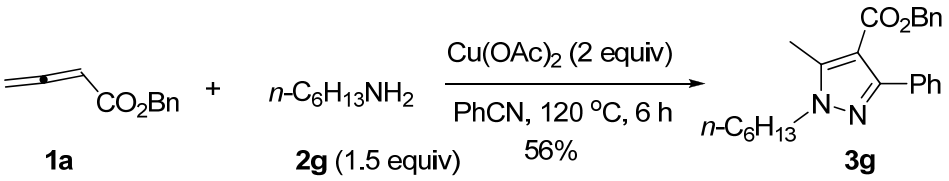


1a **2f** (1.5 equiv) **3f**

The reaction of **1a** (35.8 mg, 0.2 mmol)/benzonitrile (1 mL), **2f** (22.5 mg, 0.3 mmol)/benzonitrile (1 mL), and $Cu(OAc)_2$ (72.7 mg, 0.4 mmol) afforded **3f** (47.9 mg, 67%) (petroleum ether/ethyl acetate = 15/1 to 10/1): oil; ^1H NMR (400 MHz, $CDCl_3$)

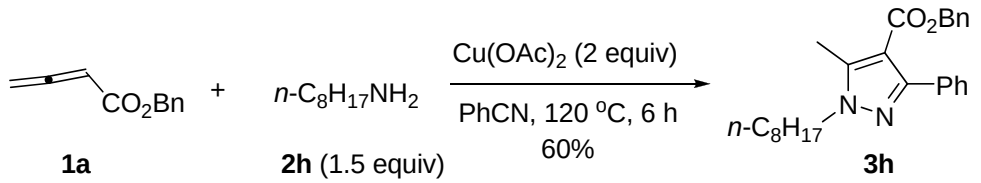
δ 7.58-7.51 (m, 2 H, ArH), 7.35-7.23 (m, 6 H, ArH), 7.20-7.11 (m, 2 H, ArH), 5.18 (s, 2 H, OCH_2), 4.08 (t, J = 7.4 Hz, 2 H, NCH_2), 2.55 (s, 3 H, Me), 1.87-1.75 (m, 2 H, CH_2), 1.41-1.30 (m, 2 H, CH_2), 0.94 (t, J = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 152.6, 143.8, 135.9, 133.5, 129.3, 128.2, 128.0, 127.84, 127.78, 127.6, 108.8, 65.5, 49.0, 31.9, 19.8, 13.6, 11.3; IR (neat) 1699, 1606, 1537, 1514, 1485, 1453, 1386, 1296, 1208, 1160, 1127, 1066, 1029 cm^{-1}; MS (EI) (*m/z*) 349 ($(M+1)^+$, 13.05), 348 (M^+, 53.02), 305 (100); HRMS calcd. for $C_{22}H_{24}N_2O_2$ [M^+]: 348.1838; Found: 348.1840.

7. Benzyl 1-hexyl-5-methyl-3-phenyl-1*H*-pyrazole-4-carboxylate (3g) (cb-10-134).



The reaction of **1a** (36.6 mg, 0.2 mmol)/benzonitrile (1 mL), **2g** (31.7 mg, 0.3 mmol)/benzonitrile (1 mL), and $Cu(OAc)_2$ (72.4 mg, 0.4 mmol) afforded **3g** (44.4 mg, 56%), the crude product contained a trace amount of benzyl 3-oxobutanoate according to the reported data,[2] which has the same R_f value as pyrazole **3g**, so we treated the crude product with 20 mg of $NaBH_4$ in MeOH (1 mL), then evaporation and column chromatography on silica gel using petroleum ether/ethyl acetate = 20/1): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61-7.48 (m, 2 H, ArH), 7.35-7.23 (m, 6 H, ArH), 7.20-7.11 (m, 2 H, ArH), 5.18 (s, 2 H, OCH_2), 4.07 (t, J = 7.4 Hz, 2 H, NCH_2), 2.55 (s, 3 H, Me), 1.87-1.75 (m, 2 H, CH_2), 1.40-1.23 (m, 6 H, $(CH_2)_3$), 0.88 (t, J = 6.9 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9, 152.6, 143.8, 135.9, 133.6, 129.3, 128.3, 128.0, 127.84, 127.78, 127.6, 108.8, 65.5, 49.3, 31.3, 29.9, 26.2, 22.4, 13.9, 11.3; IR (neat) 1699, 1537, 1514, 1485, 1453, 1375, 1296, 1260, 1211, 1193, 1158, 1127, 1065, 1028 cm^{-1}; MS (EI) (*m/z*) 377 ($(M+1)^+$, 8.67), 376 (M^+, 32.26), 91 (100); HRMS calcd. for $C_{24}H_{28}N_2O_2$ [M^+]: 376.2151; Found: 376.2150.

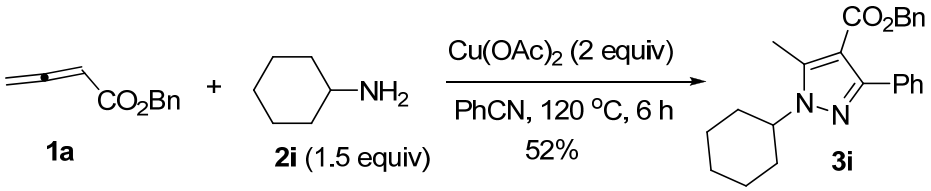
8. Benzyl 1-octyl-5-methyl-3-phenyl-1*H*-pyrazole-4-carboxylate (3h) (cb-10-99).



1a **2h** (1.5 equiv) **3h**

The reaction of **1a** (35.4 mg, 0.2 mmol)/benzonitrile (1 mL), **2h** (39.0 mg, 0.3 mmol)/benzonitrile (1 mL), and $Cu(OAc)_2$ (72.7 mg, 0.4 mmol) afforded **3h** (49.3 mg, 60%) (petroleum ether/ethyl acetate = 20/1 for twice): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59-7.48 (m, 2 H, ArH), 7.37-7.23 (m, 6 H, ArH), 7.20-7.09 (m, 2 H, ArH), 5.18 (s, 2 H, OCH_2), 4.08 (t, J = 7.2 Hz, 2 H, NCH_2), 2.56 (s, 3 H, Me), 1.92-1.75 (m, 2 H, CH_2), 1.40-1.23 (m, 10 H, $(CH_2)_5$), 0.87 (t, J = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9, 152.7, 143.8, 135.9, 133.5, 129.3, 128.3, 128.0, 127.9, 127.8, 127.7, 108.8, 65.5, 49.3, 31.7, 30.0, 29.09, 29.07, 26.6, 22.6, 14.0, 11.3; IR (neat) 1700, 1537, 1514, 1485, 1453, 1374, 1296, 1261, 1211, 1158, 1127, 1066, 1029, 1003 cm^{-1}; MS (EI) (*m/z*) 405 ($(M+1)^+$, 7.52), 404 (M^+, 24.60), 91 (100); HRMS calcd. for $C_{26}H_{32}N_2O_2$ [M^+]: 404.2464; Found: 404.2463.

9. Benzyl 1-cyclohexyl-5-methyl-3-phenyl-1*H*-pyrazole-4-carboxylate (3i) (cb-11-52).

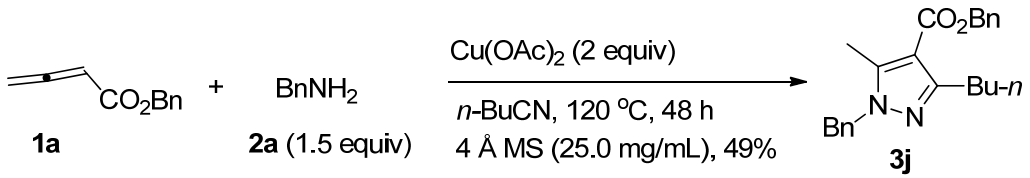


1a **2i** (1.5 equiv) **3i**

The reaction of **1a** (33.8 mg, 0.2 mmol)/benzonitrile (1 mL), **2i** (30.0 mg, 0.3 mmol)/benzonitrile (1 mL), and $Cu(OAc)_2$ (72.9 mg, 0.4 mmol) afforded **3i** (37.6 mg, 52%) (petroleum ether/ethyl acetate = 20/1 for twice): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58-7.48 (m, 2 H, ArH), 7.36-7.22 (m, 6 H, ArH), 7.16-7.09 (m, 2 H, ArH), 5.17 (s, 2 H, OCH_2), 4.05 (tt, J = 11.6, 3.8 Hz, 1 H, NCH), 2.57 (s, 3 H, Me), 2.11-1.83 (m, 6 H, $(CH_2)_3$), 1.75-1.64 (m, 1 H, one proton in CH_2), 1.50-1.20 (m, 3 H, three proton in $(CH_2)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 152.3, 143.0, 136.0, 133.9, 129.4, 128.3, 128.0, 127.8, 127.6, 108.6, 65.5, 57.7, 32.3, 25.5, 25.0,

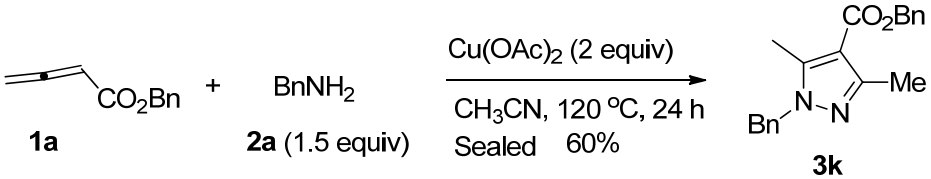
11.0; IR (neat) 2932, 2856, 1700, 1537, 1498, 1451, 1426, 1299, 1259, 1221, 1160, 1151, 1128, 1091, 1029 cm^{-1}; MS (EI) (*m/z*) 375 ($(M+1)^+$, 8.73), 374 (M^+, 32.55), 185 (100); HRMS calcd. for $C_{24}H_{26}N_2O_2$ [M^+]: 374.1994; Found: 374.1993.

10. Benzyl 1-benzyl-3-butyl-5-methyl-1*H*-pyrazole-4-carboxylate (3j) (cb-11-81).



The reaction of **1a** (34.9 mg, 0.2 mmol)/*n*-BuCN (1 mL), **2a** (32.3 mg, 0.3 mmol)/*n*-BuCN (1 mL), 4Å Molecular Sieve (50.0 mg) and $Cu(OAc)_2$ (72.9 mg, 0.4 mmol) afforded **3j** (35.4 mg, 49%) (petroleum ether/ethyl acetate = 10/1): oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.50-7.22 (m, 8 H, ArH), 7.15-7.04 (m, 2 H, ArH), 5.27 (s, 2 H, $ArCH_2$), 5.25 (s, 2 H, $ArCH_2$), 2.90-2.78 (m, 2 H, CH_2), 2.42 (s, 3 H, Me), 1.68-1.52 (m, 2 H, CH_2), 1.40-1.22 (m, 2 H, CH_2), 0.87 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 154.9, 144.4, 136.2, 136.1, 128.7, 128.5, 128.3, 128.1, 127.7, 126.6, 109.1, 65.6, 52.9, 31.7, 28.2, 22.7, 13.9, 11.4; IR (neat) 2956, 2930, 1702, 1546, 1496, 1455, 1305, 1235, 1211, 1189, 1113, 1086, 1029 cm^{-1}; MS (EI) (*m/z*) 362 (M^+, 2.90), 91 (100); HRMS calcd. for $C_{23}H_{26}N_2O_2$ [M^+]: 362.1994; Found: 362.1996.

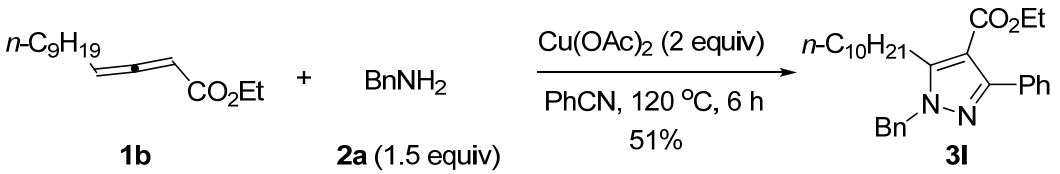
11. Benzyl 1-benzyl-3,5-dimethyl-1*H*-pyrazole-4-carboxylate (3k) (cb-11-55).



The reaction of **1a** (34.7 mg, 0.2 mmol)/MeCN (1mL), **2a** (32.4 mg, 0.3 mmol)/MeCN (1mL), and $Cu(OAc)_2$ (72.8 mg, 0.4 mmol) afforded **3k** (38.3 mg, 60%) (petroleum ether/ethyl acetate = 10/1 to 5/1): oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45-7.24 (m, 8 H, ArH), 7.13-7.04 (m, 2 H, ArH), 5.28 (s, 2 H, $ArCH_2$), 5.24 (s, 2 H, $ArCH_2$), 2.45 (s, 3 H, CH_3), 2.43 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ

164.2, 150.7, 144.4, 136.3, 136.0, 128.8, 128.5, 128.03, 127.98, 127.8, 126.6, 109.7, 65.5, 52.8, 14.5, 11.4; IR (neat) 1685, 1549, 1495, 1452, 1430, 1372, 1295, 1271, 1205, 1194, 1115 cm^{-1}; MS (EI) (*m/z*) 320 (M^+, 15.65), 91 (100); HRMS calcd. for $C_{20}H_{20}N_2O_2$ [M^+]: 320.1525; Found: 320.1526.

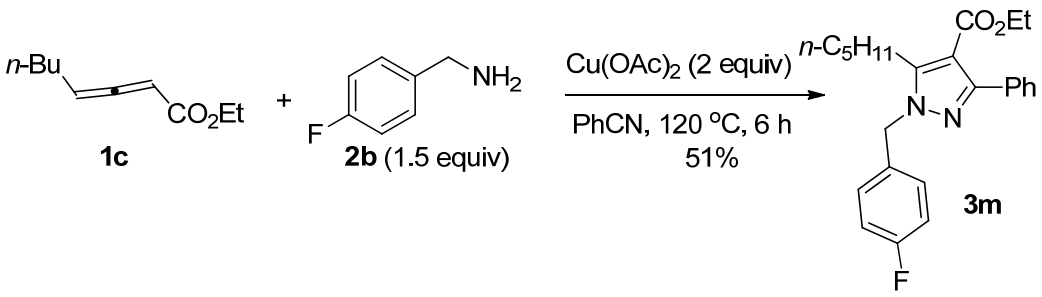
12. Benzyl 1-benzyl-5-decyl-3-phenyl-1*H*-pyrazole-4-carboxylate (3l) (cb-11-53).



1b **2a** (1.5 equiv) **3l**

The reaction of **1b** (47.8 mg, 0.2 mmol)/PhCN (1 mL), **2a** (32.5 mg, 0.3 mmol)/PhCN (1 mL), and $Cu(OAc)_2$ (72.7 mg, 0.4 mmol) afforded **3l** (45.6 mg, 51%) (petroleum ether/ethyl acetate = 20/1): oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.70-7.59 (m, 2 H, ArH), 7.45-7.27 (m, 6 H, ArH), 7.23-7.14 (m, 2 H, ArH), 5.37 (s, 2 H, NCH_2), 4.19 (q, *J* = 7.2 Hz, 2 H, OCH_2), 2.89-2.80 (m, 2 H, CH_2), 1.50-1.38 (m, 2 H, CH_2), 1.37-1.15 (m, 17 H, CH_3 and $(CH_2)_7$), 0.89 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9, 152.9, 148.8, 136.4, 133.4, 129.4, 128.7, 128.0, 127.8, 127.6, 126.8, 109.2, 59.8, 53.3, 31.8, 29.7, 29.5, 29.4, 29.3, 29.2, 29.0, 25.6, 22.6, 14.1, 14.0; IR (neat) 2925, 2854, 1702, 1534, 1478, 1454, 1296, 1170, 1137, 1075, 1038, 1028 cm^{-1}; MS (EI) (*m/z*) 320 (M^+, 26.56), 91 (100); HRMS calcd. for $C_{29}H_{38}N_2O_2$ [M^+]: 446.2933; Found: 446.2935.

13. Ethyl 1-(4-fluorobenzyl)-5-pentyl-3-phenyl-1*H*-pyrazole-4-carboxylate (3m) (cb-12-53).

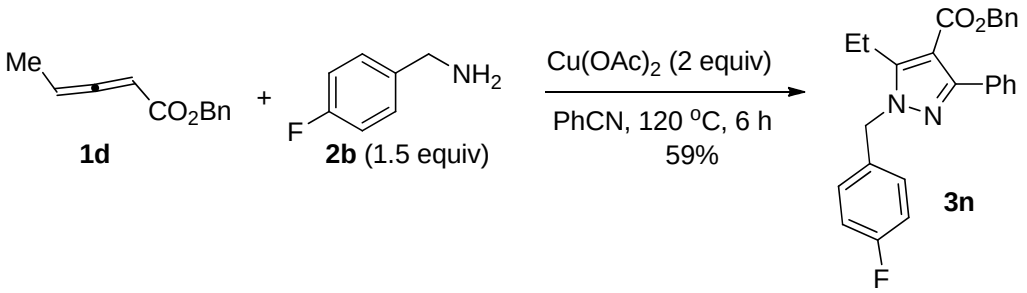


1c **2b** (1.5 equiv) **3m**

The reaction of **1c** (32.8 mg, 0.2 mmol)/PhCN (1 mL), **2b** (37.6 mg, 0.3

mmol)/PhCN (1 mL), and $Cu(OAc)_2$ (72.8 mg, 0.4 mmol) afforded **3m** (39.6 mg, 51%) (petroleum ether/ethyl acetate = 15/1 for twice): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66-7.58 (m, 2 H, ArH), 7.45-7.30 (m, 3 H, ArH), 7.23-7.14 (m, 2 H, ArH), 7.01 (t, *J* = 8.6 Hz, 2 H), 5.32 (s, 2 H, NCH_2), 4.19 (q, *J* = 7.1 Hz, 2 H, OCH_2), 2.88 (t, *J* = 8.0 Hz, 2 H, CH_2), 1.53-1.21 (m, 6 H, there CH_2), 1.18 (t, *J* = 7.1 Hz, 3 H, CH_3), 0.86 (t, *J* = 6.9 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8, 162.3 (d, *J* = 245.2 Hz), 153.0, 148.7, 133.3, 132.1 (d, *J* = 3.3 Hz), 129.3, 128.6 (d, *J* = 8.3 Hz), 128.1, 127.6, 115.7 (d, *J* = 21.7 Hz), 109.4, 59.8, 52.5, 31.8, 28.7, 25.6, 22.3, 14.0, 13.9; ^{19}F NMR ($CDCl_3$, 282 MHz) -114.3; IR (neat) 2956, 2931, 2860, 1700, 1606, 1533, 1510, 1477, 1449, 1379, 1365, 1295, 1223, 1170, 1156, 1137, 1115, 1097, 1038 cm^{-1}; MS (EI) (*m/z*) 394 (M^+, 35.09), 109 (100); HRMS calcd. for $C_{24}H_{27}N_2O_2F$ [M^+]: 394.2057; Found: 394.2055.

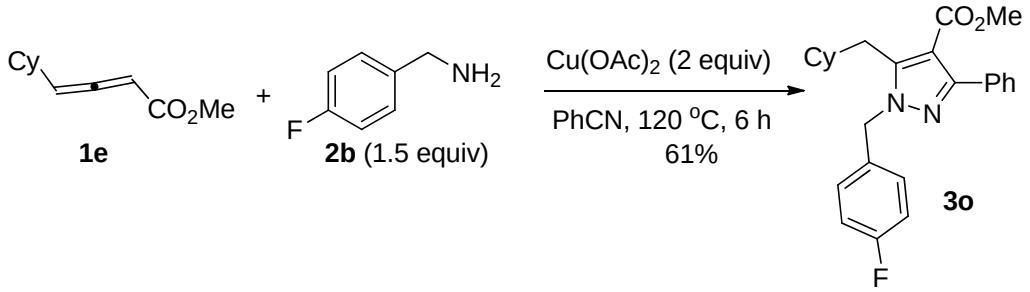
14. Ethyl 1-(4-fluorobenzyl)-5-ethyl-3-phenyl-1*H*-pyrazole-4-carboxylate (3n) (cb-12-57).



The reaction of **1d** (37.1 mg, 0.2 mmol)/PhCN (1 mL), **2b** (38.0 mg, 0.3 mmol)/PhCN (1 mL), and $Cu(OAc)_2$ (73.0 mg, 0.4 mmol) afforded **3n** (47.9 mg, 59%) (petroleum ether 30-60 °C/ethyl acetate = 15/1): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62-7.54 (m, 2 H, ArH), 7.37-7.30 (m, 3 H, ArH), 7.29-7.24 (m, 3 H, ArH), 7.20-7.12 (m, 4 H, ArH), 7.06-6.95 (m, 2 H, ArH), 5.31 (s, 2 H, CH_2), 5.18 (s, 2 H, CH_2), 2.91 (q, *J* = 7.6 Hz, 2 H, CH_2), 1.06 (t, *J* = 7.5 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5, 162.3 (d, *J* = 244.6 Hz), 153.2, 150.0, 135.7, 133.3, 132.0 (d, *J* = 2.8 Hz), 129.4, 128.6 (d, *J* = 8.3 Hz), 128.3, 128.2, 128.0, 127.9, 127.7, 115.7 (d, *J* = 21.6 Hz), 108.9, 65.7, 52.4, 18.9, 13.3; ^{19}F NMR ($CDCl_3$, 282 MHz)

–114.1; IR (neat) 1701, 1605, 1535, 1509, 1478, 1451, 1373, 1354, 1325, 1290, 1223, 1189, 1155, 1130, 1089, 1059, 1032, 1010 cm^{-1}; MS (EI) (*m/z*) 414 (M^+, 31.31), 109 (100); HRMS calcd. for $C_{26}H_{23}N_2O_2F$ [M^+]: 414.1744; Found: 414.1743.

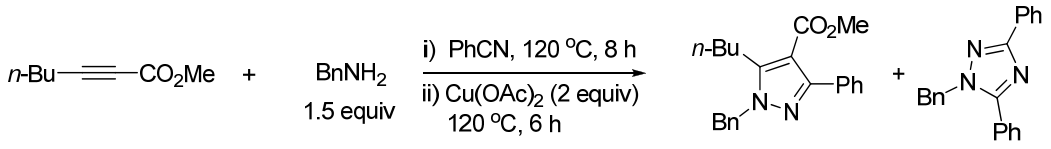
15. Methyl 5-(cyclohexylmethyl)-1-(4-fluorobenzyl)-3-phenyl-1*H*-pyrazole-4-carboxylate (3o) (cb-12-54).



The reaction of **1e** (36.1 mg, 0.2 mmol)/PhCN (1 mL), **2b** (37.4 mg, 0.3 mmol)/PhCN (1 mL), and $Cu(OAc)_2$ (72.7 mg, 0.4 mmol) afforded **3o** (49.6 mg, 61%) (petroleum ether /ethyl acetate = 15/1): oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.63-7.56 (m, 2 H, ArH), 7.45-7.30 (m, 3 H, ArH), 7.20-7.09 (m, 2 H, ArH), 7.01 (t, *J* = 8.4 Hz, 2 H, ArH), 5.33 (s, 2 H, CH_2), 3.70 (s, 3 H, CH_3), 2.81 (d, *J* = 7.2 Hz, 2 H, CH_2), 1.78-1.44 (m, 6 H, three CH_2), 1.20-0.98 (m, 5 H, five protons in Cy); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.5, 162.3 (d, *J* = 245.0 Hz), 152.9, 147.6, 133.3, 132.1 (d, *J* = 3.0 Hz), 129.2, 128.5 (d, *J* = 7.7 Hz), 128.1, 127.7, 115.7 (d, *J* = 22.1 Hz), 109.8, 52.6, 50.8 (d, *J* = 2.5 Hz), 38.4, 33.1, 32.5, 26.2, 26.1; ^{19}F NMR ($CDCl_3$, 282 MHz) –114.3; IR (neat) 2923, 2851, 1706, 1606, 1537, 1508, 1474, 1447, 1378, 1332, 1321, 1296, 1279, 1223, 1195, 1154, 1132, 1107, 1091, 1074, 1058, 1035, 1018 cm^{-1}; MS (EI) (*m/z*) 406 (M^+, 38.46), 109 (100); HRMS calcd. for $C_{25}H_{27}N_2O_2F$ [M^+]: 406.2057; Found: 406.2060.

Synthesis of pyrazoles from 2-alkynoates with amines in nitriles.

1. Methyl 1-benzyl-5-butyl-3-phenyl-1*H*-pyrazole-4-carboxylate (3p) (zhucan-9-123)



4a **2a** **3p** **6**

ratio of **3p**:**6** = 2.3:1

yield of **3p** = 50%

Typical procedure II: To a dried Schlenk tube equipped with a Teflon-coated magnetic stirring bar were added 2-alkynoate **4a** (28.1 mg, 0.2 mmol)/benzonitrile (0.25 mL), and amine **2a** (32.3 mg, 0.3 mmol)/benzonitrile (0.25 mL) under an argon atmosphere at room temperature. After being vigrously stirred for 8 h at 120 ^{o}C, $Cu(OAc)_2$ (72.5 mg, 0.4 mmol) was added. After the mixture was stirred at 120 ^{o}C for another 6 h, the reaction was complete as monitored by TLC, the resulting mixture was diluted with 50 mL of Et_2O and filtered through a short pad (3 cm) of silica gel. Evaporation and column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) afforded a mixture of **3p** and **6**[5] (48.2 mg). The ratio (**3p**:**6** = 2.3:1) was determined by ^{1}H NMR analysis, and yield of **3p** is 50% was based on the ratio: oil.

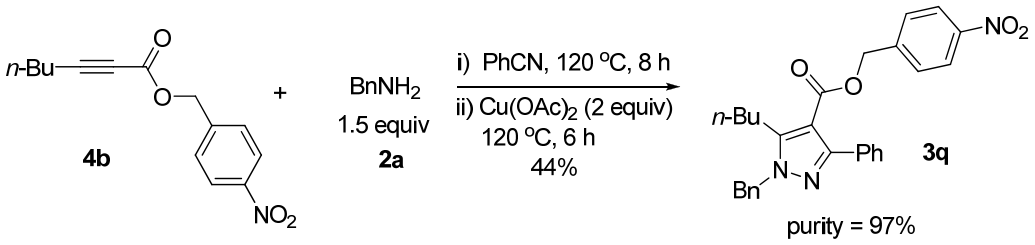
the following signals are discernible for **3p**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 6.4 Hz, 2 H, ArH), 7.50-7.23 (m, 6 H, ArH), 7.17 (d, *J* = 7.2 Hz, 2 H, ArH), 5.36 (s, 2 H, $ArCH_2$), 3.70 (s, 3 H, CO_2CH_3), 2.88 (t, *J* = 7.8 Hz, 2 H, $ArCH_2$), 1.48-1.30 (m, 4 H, CH_2CH_2), 0.88 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 152.8, 149.0, 136.3, 133.4, 129.2, 128.8, 127.9, 127.8, 127.6, 109.0, 53.3, 50.8, 31.0, 25.2, 22.7, 13.6; GC-MS (GC condition: injector: 300 ^{o}C; column: HP-5MS column 30 m × 0.25 mm, temperature programming: 20 ^{o}C/min to 300 ^{o}C, 300 ^{o}C (50 min); detector: 300 ^{o}C) (70 ev, EI) m/z (%) (retention time: 15.8 min): 349 ($(M+1)^+$, 24.71), 348 (M^+, 100); HRMS calcd. for $C_{22}H_{24}N_2O_2$ [M^+]: 348.1838; Found: 348.1839.

The following signals are discernible for **6**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.2 Hz, 2 H, ArH), 5.45 (s, 2 H, $ArCH_2$); GC-MS (GC condition: injector:

300 °C; column: HP-5MS column 30 m × 0.25 mm, temperature programming: 20 °C/min to 300 °C, 300 °C (50 min); detector: 300 °C) (70 ev, EI) m/z (%) (retention time: 16.5 min): 312 ($(M+1)^+$, 23.92), 311 (M^+, 100).

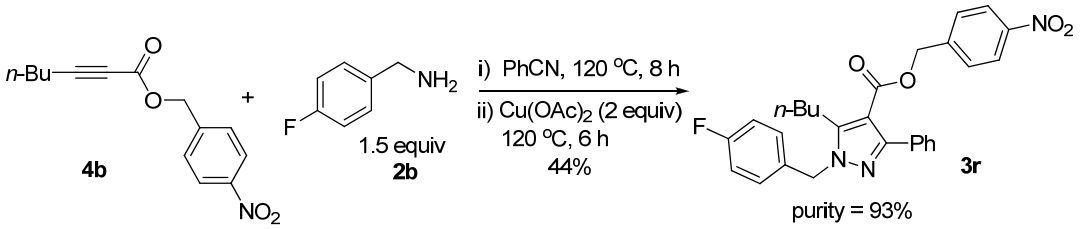
The following compounds **3q-3t** were prepared according to **Typical Procedure II**.

2. 4-Nitrobenzyl 1-benzyl-5-butyl-3-phenyl-1*H*-pyrazole-4-carboxylate (3q) (zhucan-9-116)



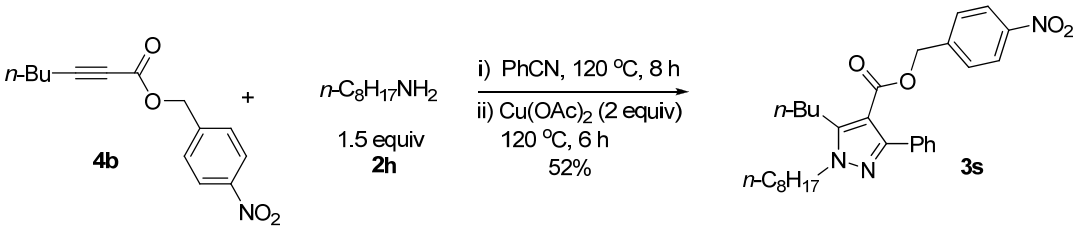
The reaction of 2-alkynoate **4b** (52.8 mg, 0.2 mmol)/benzonitrile (0.25 mL), amine **2a** (32.4 mg, 0.3 mmol)/benzonitrile (0.25 mL), and $Cu(OAc)_2$ (72.9 mg, 0.4 mmol) afforded **3q** (42.6 mg, purity = 97% based on the ^1H NMR analysis with CH_3NO_2 as the internal standard, 44%) (petroleum ether/ethyl acetate = 20/1 then petroleum ether/ethyl acetate = 10/1): oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 2 H, ArH), 7.59-7.54 (m, 2 H, ArH), 7.42-7.27 (m, 6 H, ArH), 7.19 (d, *J* = 6.4 Hz, 2 H, ArH), 7.13 (d, *J* = 8.8 Hz, 2 H, ArH), 5.38 (s, 2 H, $ArCH_2$), 5.23 (s, 2 H, $ArCH_2$), 2.90 (t, *J* = 7.8 Hz, 2 H, $ArCH_2$), 1.48-1.37 (m, 2 H, CH_2), 1.37-1.25 (m, 2 H, CH_2), 0.85 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 153.0, 149.6, 147.3, 143.1, 136.1, 133.7, 129.4, 128.8, 128.2, 128.03, 127.97, 127.8, 126.9, 123.5, 108.5, 64.2, 53.4, 30.9, 25.2, 22.7, 13.7; IR (neat) 3065, 3031, 2957, 2928, 2871, 1708, 1606, 1522, 1497, 1478, 1455, 1380, 1347, 1315, 1290, 1255, 1221, 1179, 1157, 1130, 1107, 1092, 1175, 1035, 1015 cm^{-1}; MS (EI) (*m/z*) 470 ($(M+1)^+$, 17.16), 469 (M^+, 49.38), 91 (100); HRMS calcd. for $C_{28}H_{27}N_3O_4$ [M^+]: 469.2002; Found: 469.2005.

3. 4-Nitrobenzyl 5-butyl-1-(4-fluorobenzyl)-3-phenyl-1*H*-pyrazole-4-carboxylate (3r) (zhucan-9-134)



The reaction of 2-alkynoate **4b** (51.9 mg, 0.2 mmol)/benzonitrile (0.25 mL), amine **2b** (38.2 mg, 0.3 mmol)/benzonitrile (0.25 mL), and $Cu(OAc)_2$ (73.0 mg, 0.4 mmol) afforded **3r** (46.0 mg, purity = 93% based on the ^1H NMR analysis with CH_3NO_2 as the internal standard, 44%) (petroleum ether/ethyl acetate = 10/1 then petroleum ether/ethyl acetate = 5/1): oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 2 H, ArH), 7.58-7.51 (m, 2 H, ArH), 7.42-7.33 (m, 3 H, ArH), 7.22-7.15 (m, 2 H, ArH), 7.13 (d, *J* = 8.4 Hz, 2 H, ArH), 7.03 (t, *J* = 8.6 Hz, 2 H, ArH), 5.34 (s, 2 H, $ArCH_2$), 5.23 (s, 2 H, $ArCH_2$), 2.90 (t, *J* = 8.0 Hz, 2 H, $ArCH_2$), 1.49-1.39 (m, 2 H, CH_2), 1.39-1.28 (m, 2 H, CH_2), 0.87 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 162.4 (d, *J* = 245.3 Hz), 153.2, 149.5, 147.3, 143.0, 133.6, 131.9 (d, *J* = 3.2 Hz), 129.4, 128.7 (d, *J* = 8.1 Hz), 128.2, 128.0, 127.9, 123.5, 115.7 (d, *J* = 21.6 Hz), 108.6, 64.2, 52.5, 31.0, 25.2, 22.7, 13.7; ^{19}F NMR ($CDCl_3$, 282 MHz) -112.8; IR (neat) 3068, 2958, 2932, 2871, 1710, 1607, 1522, 1479, 1453, 1381, 1347, 1316, 1292, 1225, 1156, 1131, 1107, 1092, 1036, 1015 cm^{-1}; MS (EI) (*m/z*) 488 ($(M+1)^+$, 10.60), 487 (M^+, 35.27), 109 (100); HRMS calcd. for $C_{28}H_{26}FN_3O_4$ [M^+]: 487.1907; Found: 487.1911.

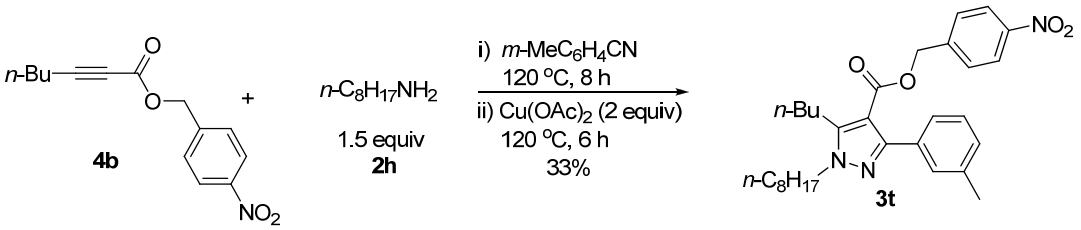
4. 4-Nitrobenzyl 5-butyl-1-octyl-3-phenyl-1*H*-pyrazole-4-carboxylate (3s) (zhucan-9-143)



The reaction of 2-alkynoate **4b** (52.0 mg, 0.2 mmol)/benzonitrile (0.25 mL), amine **2h** (37.9 mg, 0.3 mmol)/benzonitrile (0.25 mL), and $Cu(OAc)_2$ (72.7 mg, 0.4 mmol) afforded **3s** (50.5 mg, 52%) (petroleum ether/ethyl acetate = 20/1): oil;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 2 H, ArH), 7.54-7.48 (m, 2 H, ArH), 7.40-7.32 (m, 3 H, ArH), 7.11 (d, *J* = 8.4 Hz, 2 H, ArH), 5.23 (s, 2 H, $ArCH_2$), 4.08 (t, *J* = 7.8 Hz, 2 H, NCH_2), 2.96 (t, *J* = 7.8 Hz, 2 H, $ArCH_2$), 1.95-1.84 (m, 2 H, CH_2), 1.66-1.56 (m, 2 H, CH_2), 1.48-1.19 (m, 12 H, 6×CH_2), 0.95 (t, *J* = 7.2 Hz, 3 H, CH_3), 0.88 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 152.9, 148.9, 147.3, 143.2, 134.0, 129.4, 128.04, 127.96, 127.8, 123.5, 107.7, 64.1, 49.2, 31.7, 31.4, 30.3, 29.11, 29.08, 26.7, 25.0, 22.7, 22.6, 14.0, 13.8; IR (neat) 3066, 3032, 2956, 2929, 2857, 1709, 1607, 1525, 1480, 1467, 1455, 1378, 1347, 1314, 1294, 1253, 1228, 1158, 1128, 1105, 1036, 1016 cm^{-1}; MS (EI) (*m/z*) 492 ($(M+1)^+$, 3.60), 491 (M^+, 11.56), 337 (100); HRMS calcd. for $C_{29}H_{37}N_3O_4$ [M^+]: 491.2784; Found: 491.2786.

5. 4-Nitrobenzyl 5-butyl-1-octyl-3-*m*-tolyl-1*H*-pyrazole-4-carboxylate (3t) (zhucan-9-145)

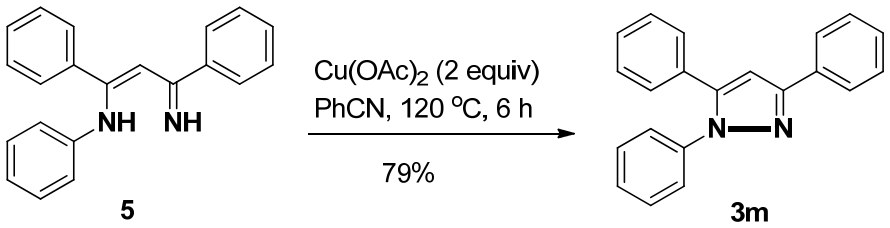


The reaction of 2-alkynoate **4b** (53.8 mg, 0.2 mmol)/3-methylbenzonitrile (0.25 mL), amine **2h** (39.5 mg, 0.3 mmol)/3-methylbenzonitrile (0.25 mL), and $Cu(OAc)_2$ (72.7 mg, 0.4 mmol) afforded **3t** (34.0 mg, 33%) (petroleum ether/ethyl acetate = 20/1): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 2 H, ArH), 7.35-7.16 (m, 4 H, ArH), 7.12 (d, *J* = 8.8 Hz, 2 H, ArH), 5.23 (s, 2 H, $ArCH_2$), 4.07 (t, *J* = 7.8 Hz, 2 H, NCH_2), 2.96 (t, *J* = 7.8 Hz, 2 H, $ArCH_2$), 2.31 (s, 3 H, $ArCH_3$), 1.95-1.83 (m, 2 H, CH_2), 1.67-1.55 (m, 2 H, CH_2), 1.48-1.20 (m, 12 H, 6×CH_2), 0.95 (t, *J* = 7.4 Hz, 3 H, CH_3), 0.88 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 153.0, 148.8, 147.3, 143.3, 137.4, 133.8, 129.9, 128.7, 127.9, 127.7, 126.6, 123.4, 107.7, 64.1, 49.2, 31.7, 31.4, 30.3, 29.10, 29.07, 26.7, 24.9, 22.7, 22.6, 21.3, 14.0, 13.8; IR (neat) 2956, 2928, 2857, 1708, 1608, 1524, 1481, 1465, 1378, 1347, 1295, 1217, 1178, 1144, 1124, 1104, 1036, 1016 cm^{-1}; MS (ESI)

(*m/z*) 506 ($M+H^+$); HRMS (ESI) calcd. for $C_{30}H_{40}N_3O_4$ [$M+H^+$]: 506.3013; Found: 506.3014.

Mechanistic study.

Synthesis of 1,3,5-triphenyl-1*H*-pyrazole (3u) (cb-12-39)



5 **3m**

To a dried Schlenk tube were added **5** (58.1 mg, 0.2 mmol), PhCN (2 mL) and $Cu(OAc)_2$ (72.5 mg, 0.4 mmol) at room temperature. After being stirred at 120 °C (oil bath) for 6 h, the resulting mixture was diluted with 50 mL of Et_2O, filtered through a short pad of silica gel and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford **3m**[4] (45.6 mg, 79%): yellow solid; m.p. 142-143 °C (*n*-hexane/Et_2O) (lit. m.p. 142-146 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.2 Hz, 2 H, ArH), 7.46-7.20 (m, 13 H, ArH), 6.82 (s, 1 H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 151.9, 144.4, 140.1, 133.0, 130.6, 128.9, 128.7, 128.6, 128.4, 128.3, 128.0, 127.4, 125.8, 125.3, 105.2; IR (neat) 1723, 1596, 1546, 1496, 1482, 1456, 1434, 1414, 1363, 1313, 1262, 1214, 1175, 1158, 1107, 1067, 1025, 1001 cm^{-1}; MS (EI) (*m/z*) 297 ($(M+1)^+$, 21.53), 296 (M^+, 100).

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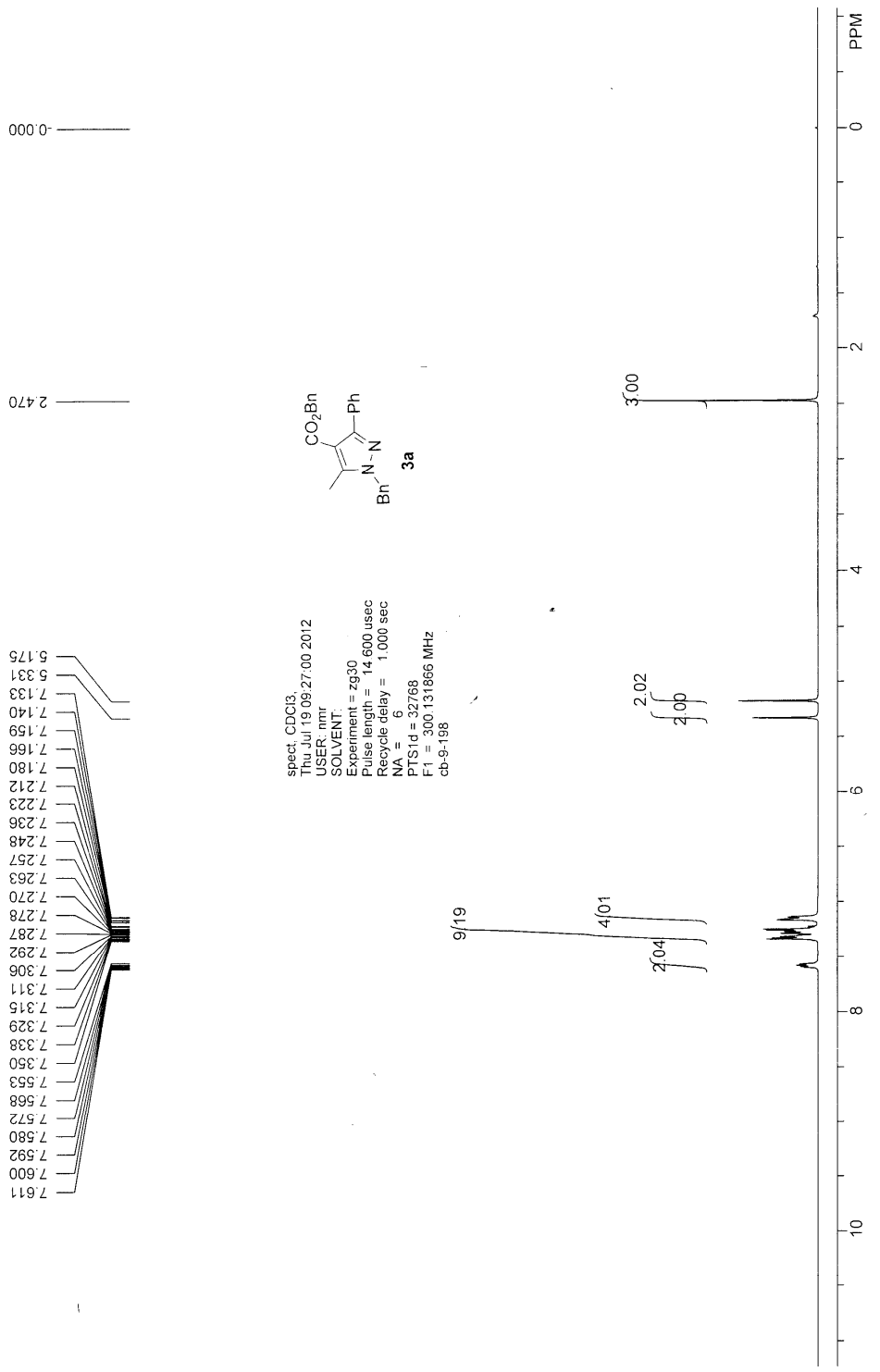
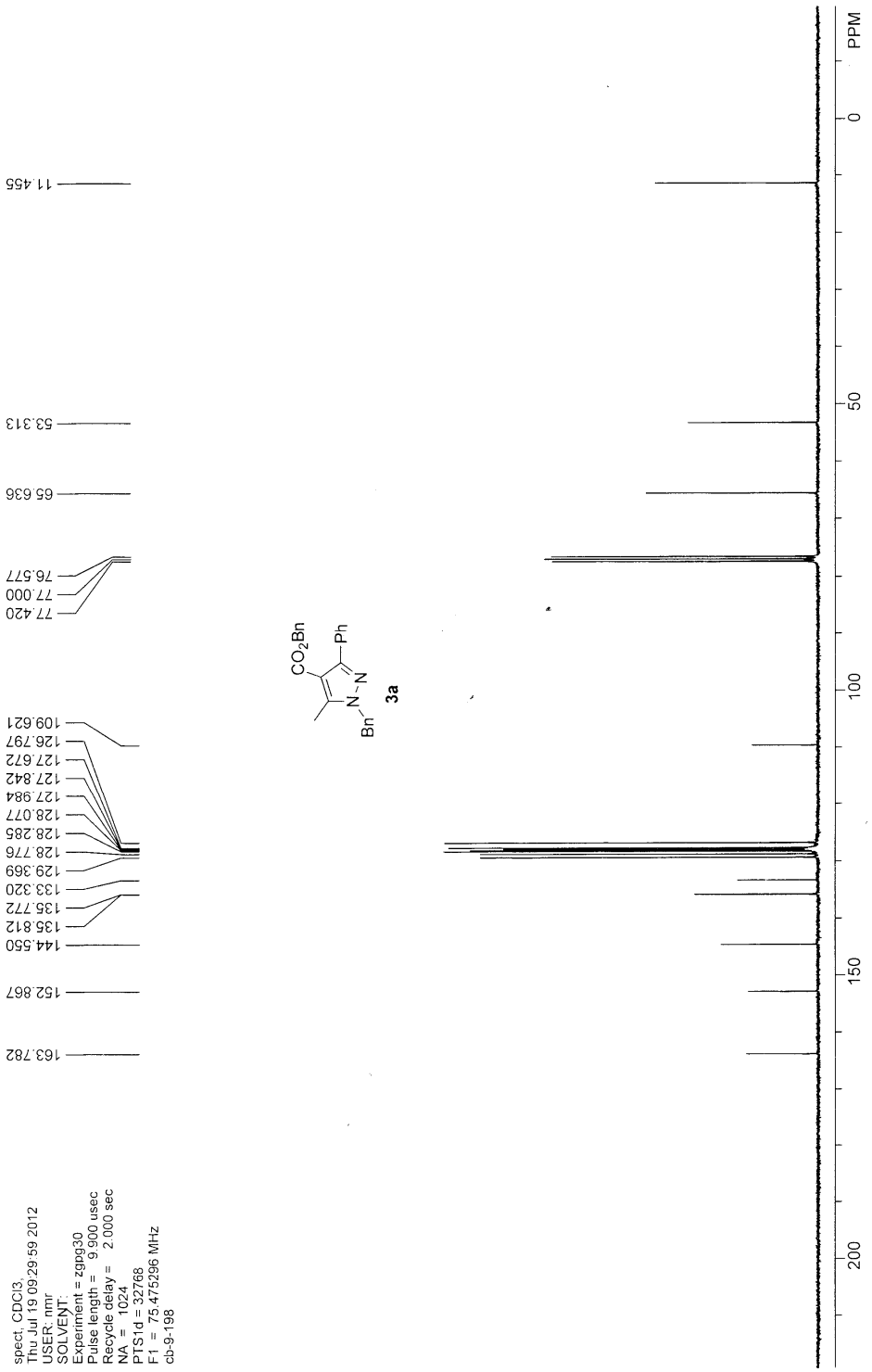
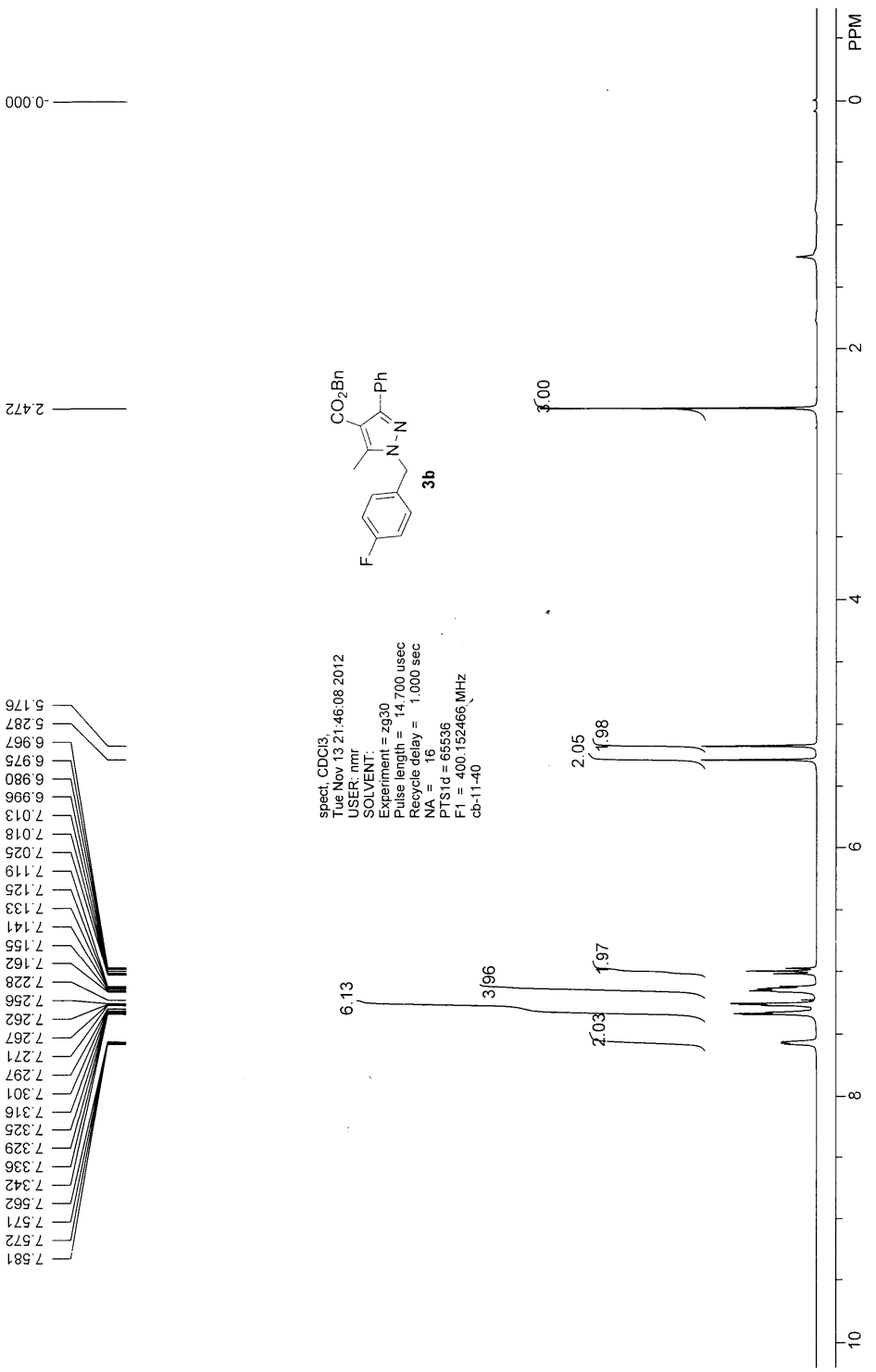
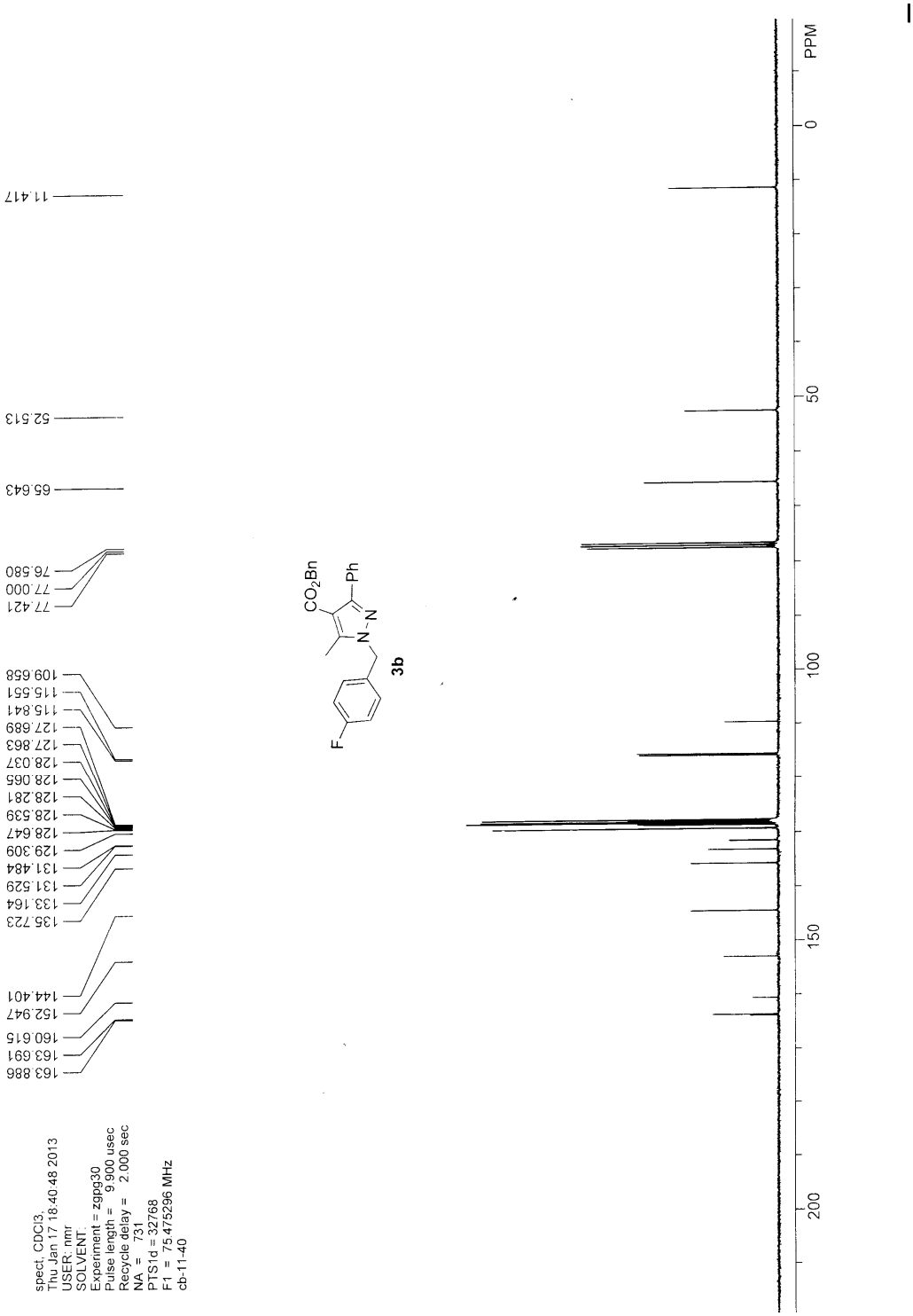
4) S. V. Gamapwar, N. P. Tale, N. N. Karade, *Synth. Commun.* **2012**, *42*, 2617-2623.

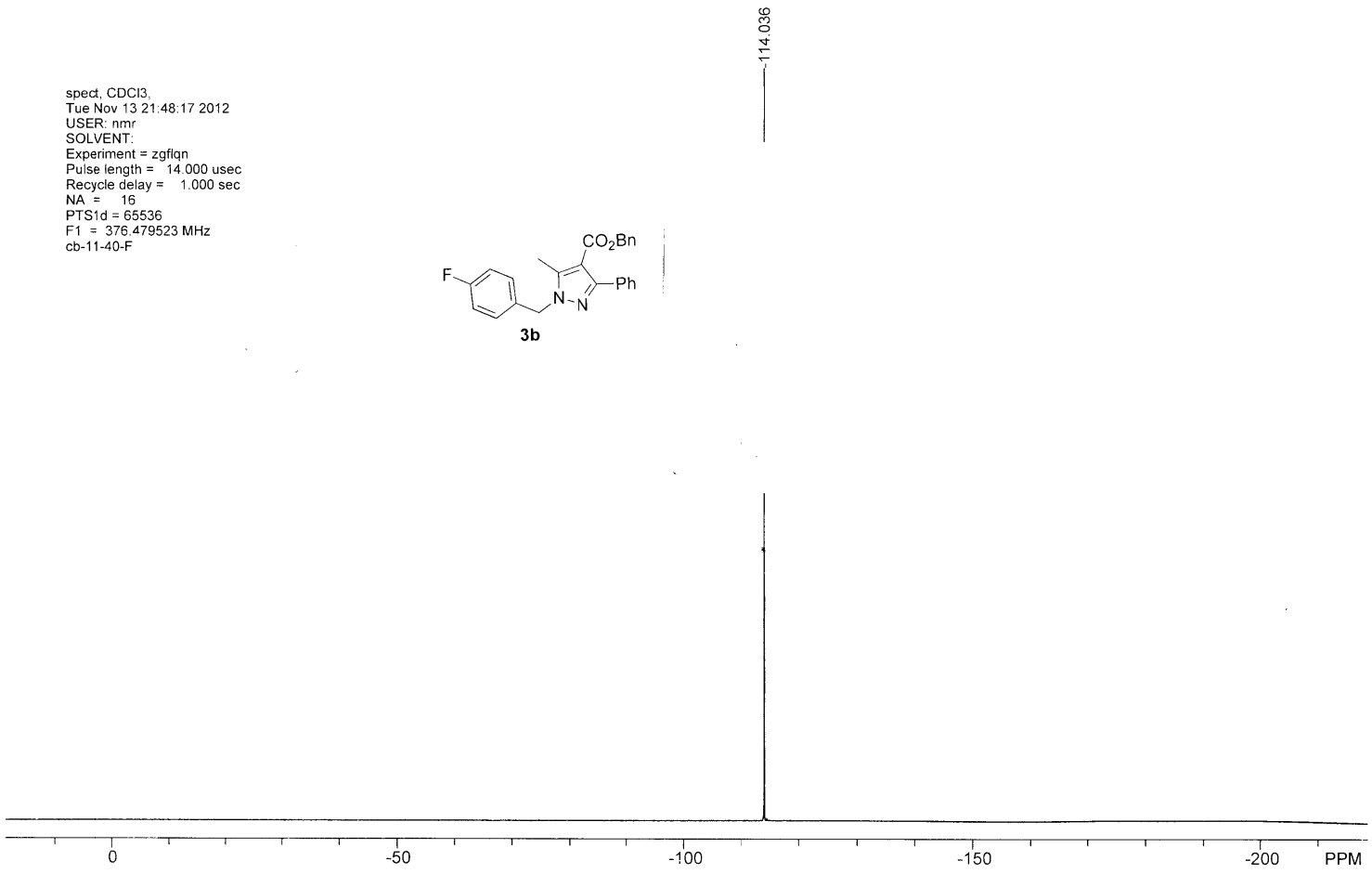
5) J. Kuang, B. Chen, S. Ma, *Org. Chem. Front*. **2014**, *1*, 186-189.

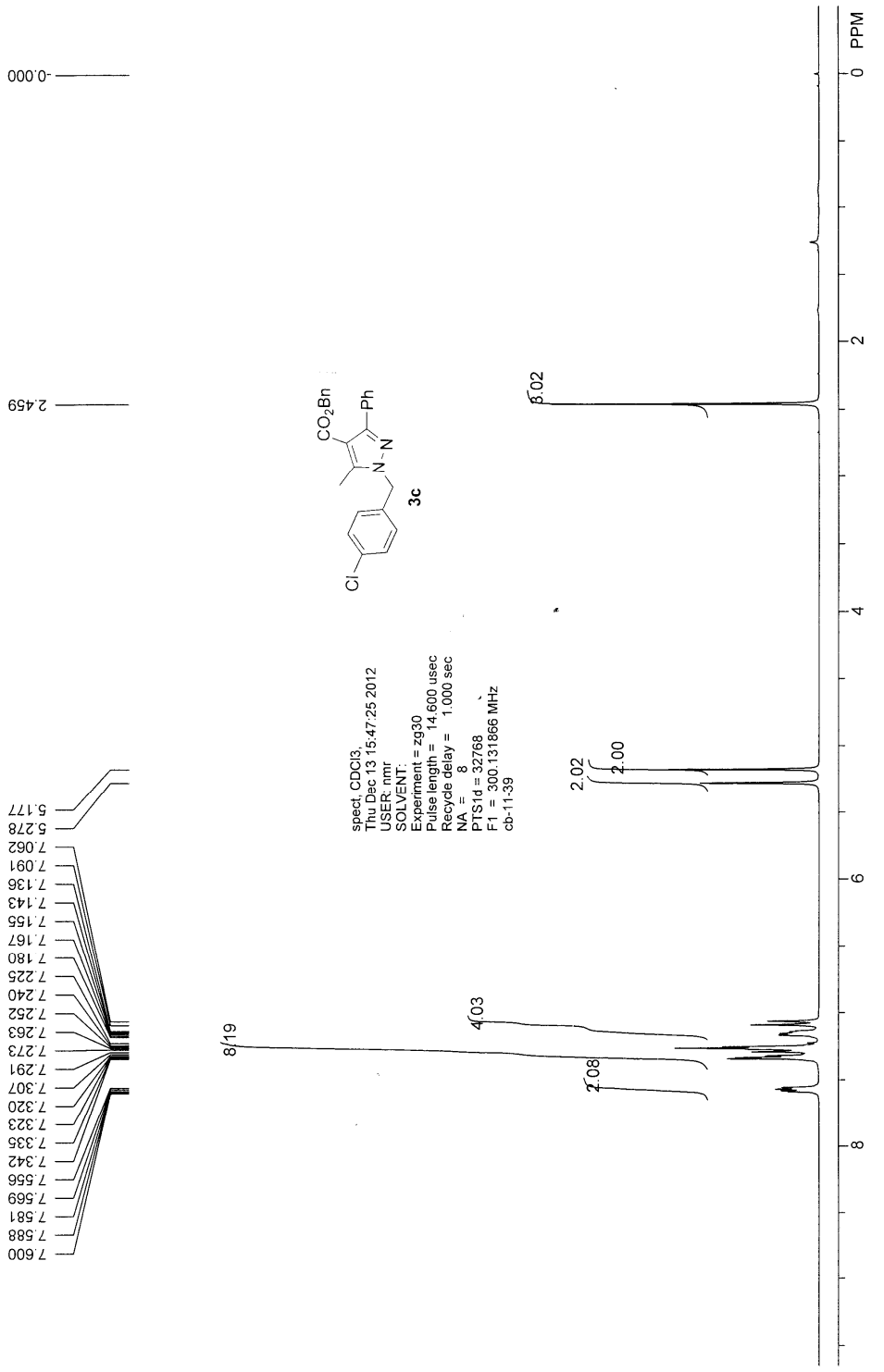

spect. CDCl3.
Thu Jul 19 09:27:00 2012
USER: nmr
SOLVENT
Experiment = zg30
Pulse length = 14.600 usec
Recycle delay = 1.000 sec
NA = 6
PTS1d = 32768
F1 = 300.131866 MHz
cb-9-198
CO2Bn
Ph
N
N
Bn
3a
9.19
4.01
2.04
2.02
2.00
3.00
PPM
0
2
4
6
8
10
-0.000
2.470
5.175
5.331
7.133
7.140
7.159
7.166
7.180
7.212
7.223
7.236
7.248
7.257
7.263
7.270
7.278
7.287
7.292
7.306
7.311
7.315
7.329
7.338
7.350
7.553
7.568
7.572
7.580
7.592
7.600
7.611

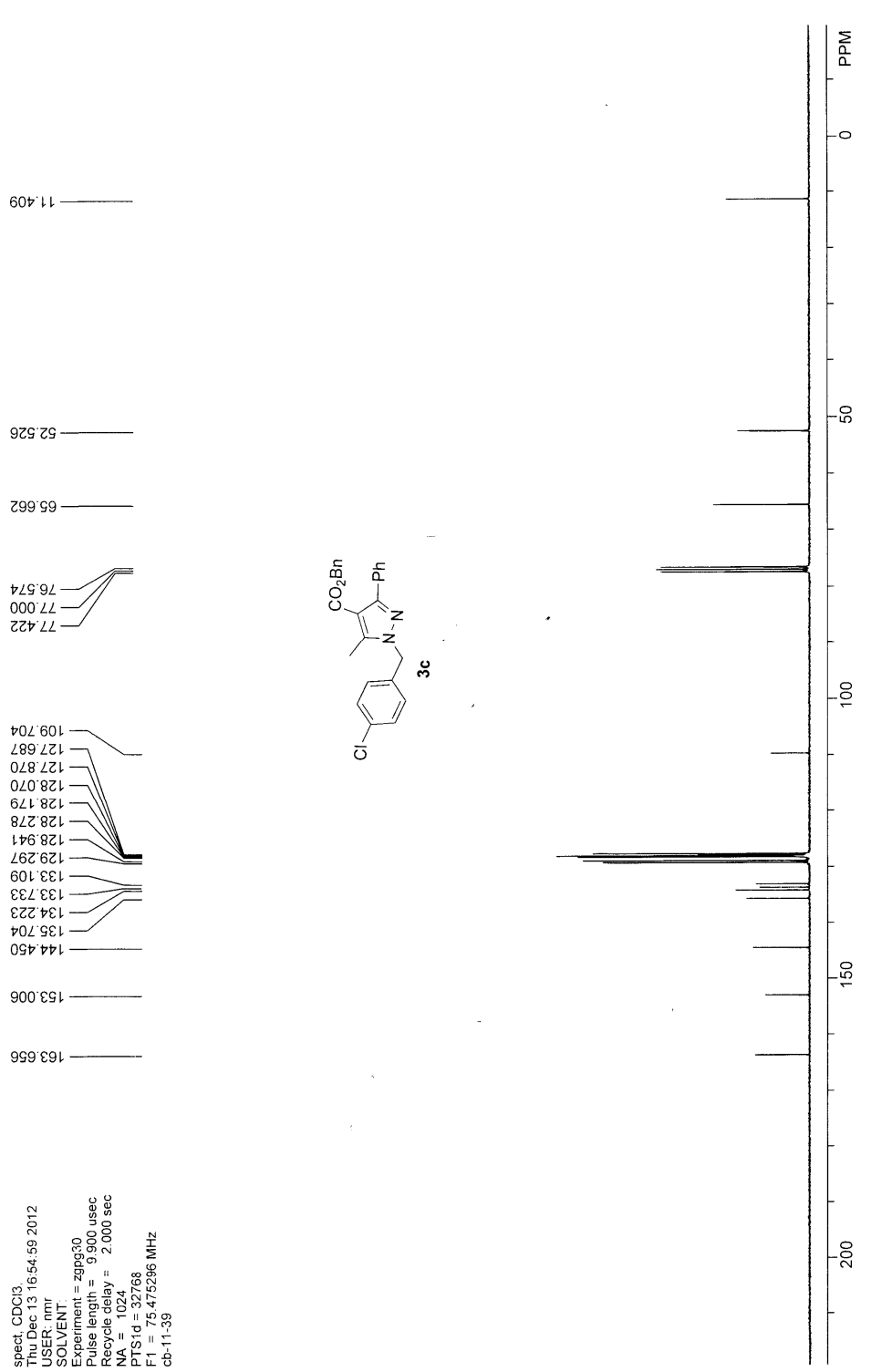

spect, CDCl3,
Thu Jul 19 09:29:59 2012
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.900 usec
Recycle delay = 2.000 sec
NA = 1024
PTS1d = 32768
F1 = 75.475296 MHz
cb-9-198
11.455
53.313
65.636
76.577
77.000
77.420
109.621
126.797
127.672
127.842
127.984
128.077
128.285
128.776
129.369
133.320
135.772
135.812
144.550
152.867
163.782
CO2Bn
Ph
N
N
Bn
3a
PPM
0
50
100
150
200

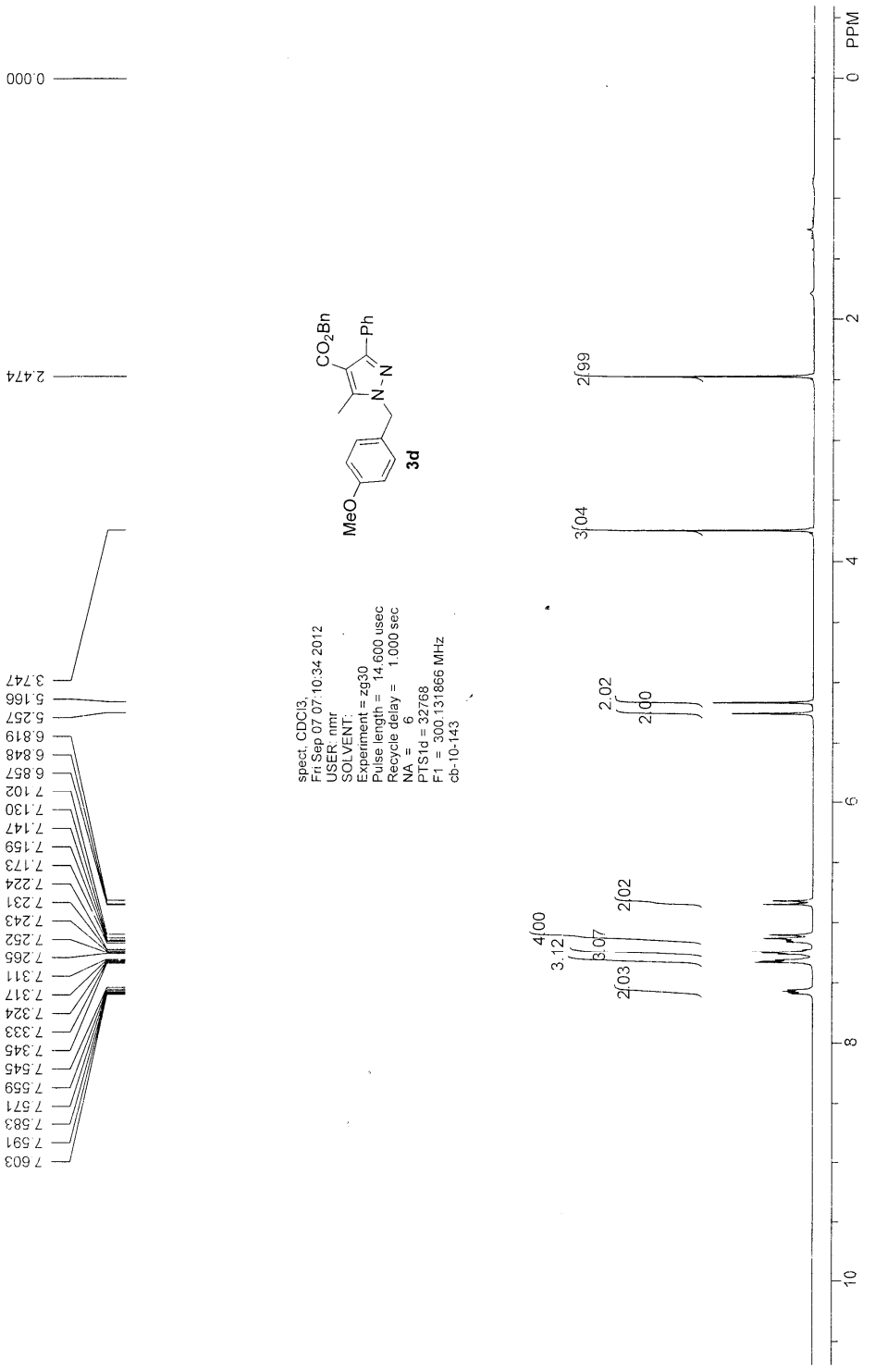

spect, CDCl3,
Tue Nov 13 21:46:08 2012
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.700 usec
Recycle delay = 1.000 sec
NA = 16
PTS1d = 65536
F1 = 400.152466 MHz
cb-11-40
CO2Bn
Ph
N
N
F
3b
6.13
3.96
1.97
2.03
3.00
2.05
1.98
PPM
0
2
4
6
8
10
-0.000
2.472
5.176
5.287
6.967
6.975
6.980
6.996
7.013
7.018
7.025
7.119
7.125
7.133
7.141
7.155
7.162
7.228
7.256
7.262
7.267
7.271
7.297
7.301
7.316
7.325
7.329
7.336
7.342
7.562
7.571
7.572
7.581

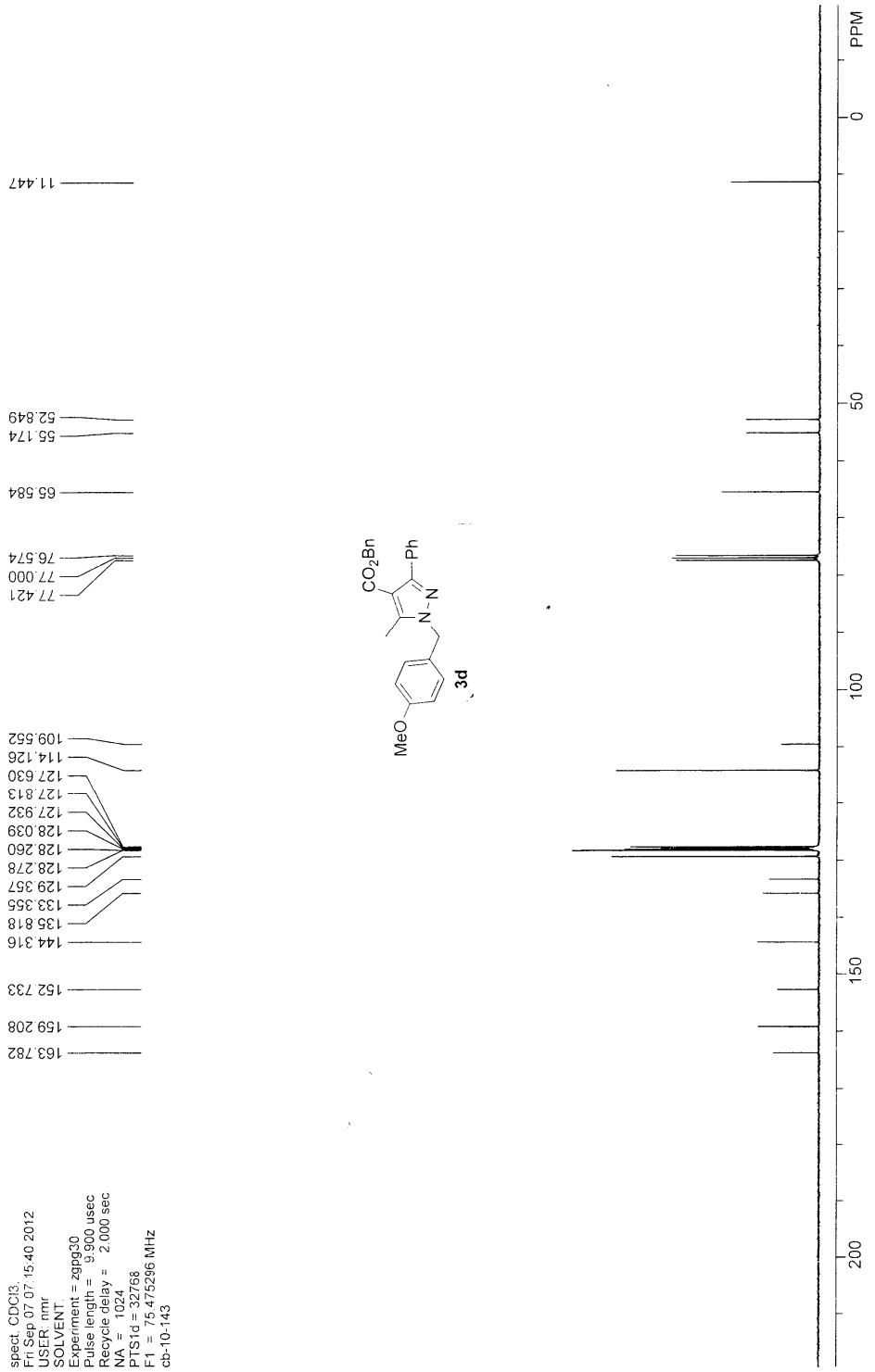

11.417
52.513
65.643
76.580
77.000
77.421
109.658
115.551
115.841
127.689
127.863
128.037
128.065
128.281
128.539
128.647
129.309
131.484
131.529
133.164
135.723
144.401
152.947
160.615
163.691
163.886
spect, CDCl3,
Thu Jan 17 18:40:48 2013
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.900 usec
Recycle delay = 2.000 sec
NA = 731
PTS1d = 32768
F1 = 75.475296 MHz
cb-11-40
CO2Bn
Ph
N
N
F
3b
PPM
0
50
100
150
200

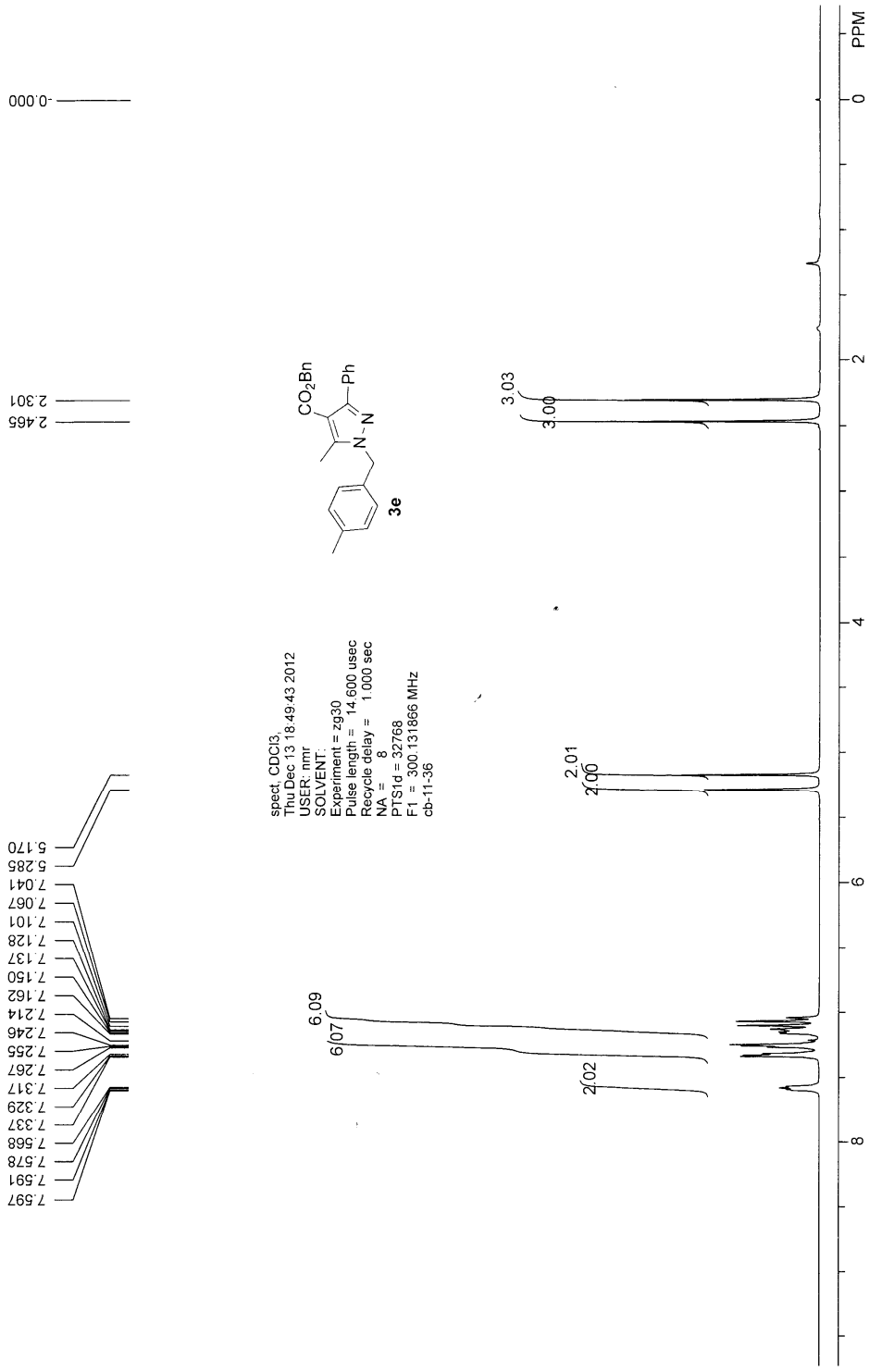

spect, CDCl3,
Tue Nov 13 21:48:17 2012
USER: nmr
SOLVENT:
Experiment = zgflqn
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 16
PTS1d = 65536
F1 = 376.479523 MHz
cb-11-40-F
-114.036
CO2Bn
F
Ph
N
N
3b
0
-50
-100
-150
-200
PPM

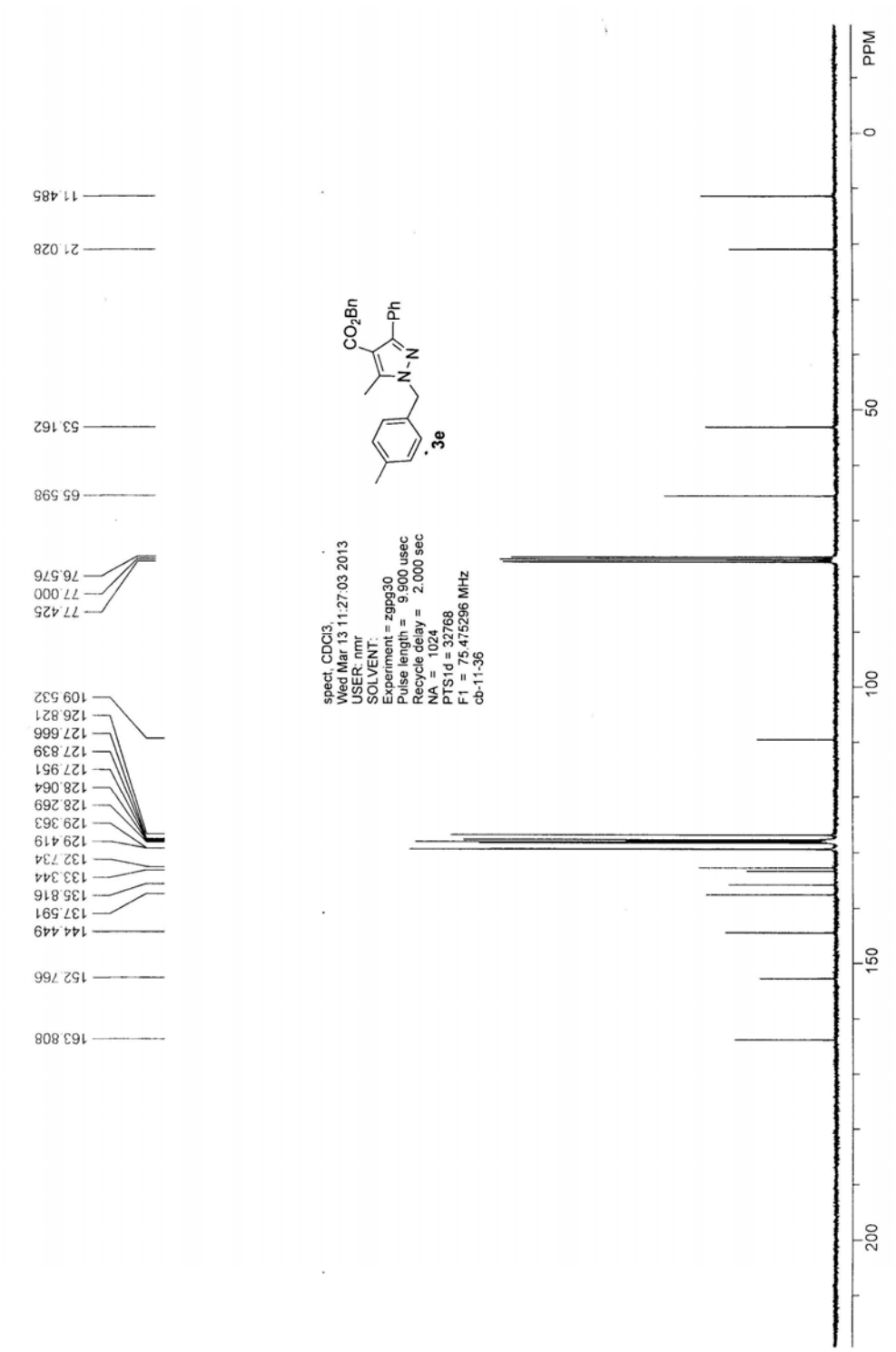

spect_CDCl3
Thu Dec 13 15:47:25 2012
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.600 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
cb-11-39
3c
Ph
CO2Bn
Cl
N
N
8.19
4.03
3.02
2.08
2.02
2.00
PPM
0
2
4
6
8
-0.000
2.459
5.177
5.278
7.062
7.091
7.136
7.143
7.155
7.167
7.180
7.225
7.240
7.252
7.263
7.273
7.291
7.307
7.320
7.323
7.335
7.342
7.556
7.569
7.581
7.588
7.600

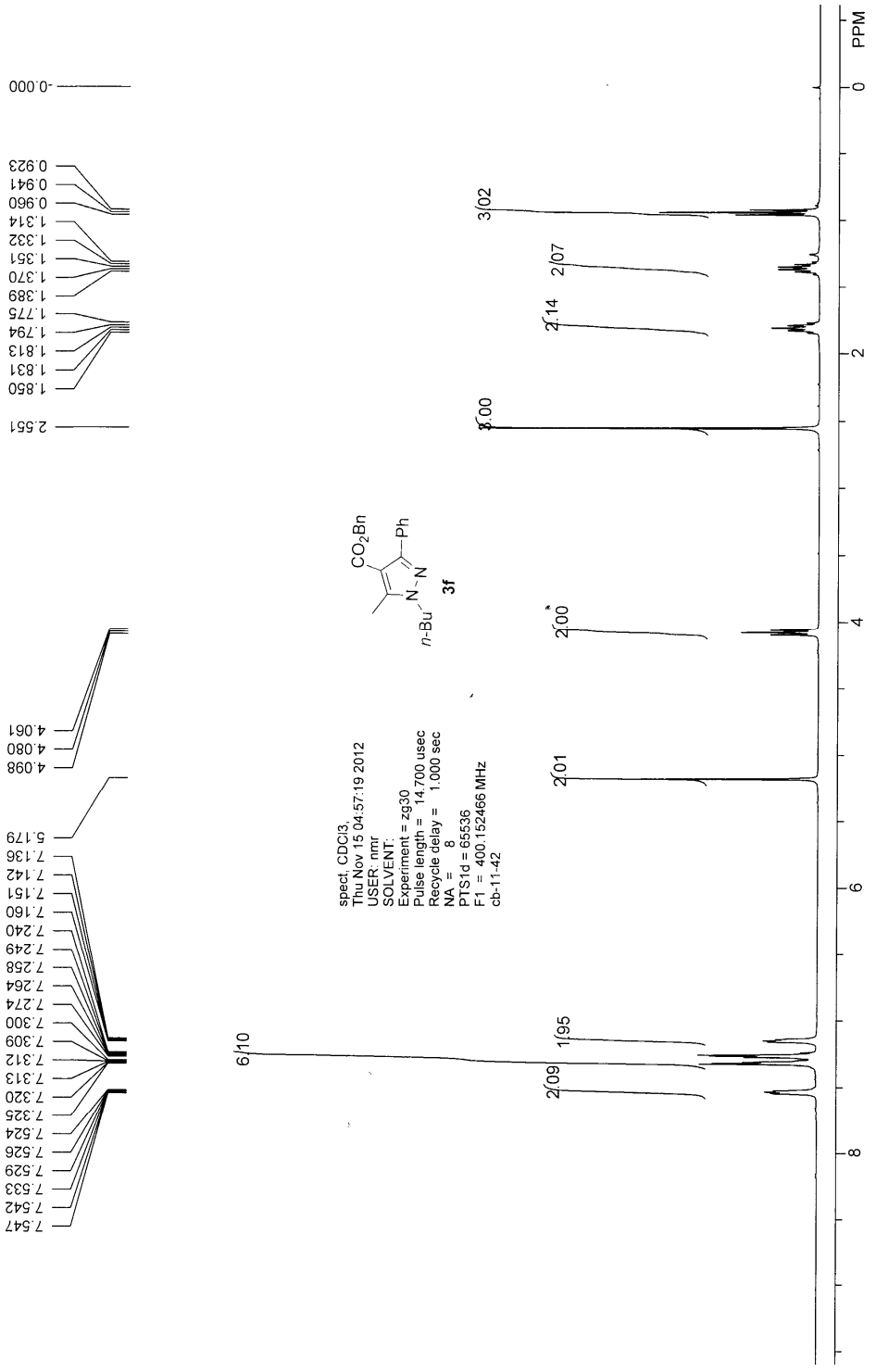

spect_CDCl3
Thu Dec 13 16:54:59 2012
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.900 usec
Recycle delay = 2.000 sec
NA = 1024
PTS1d = 32768
F1 = 75.475296 MHz
cb-11-39
163.656
153.006
144.450
135.704
134.223
133.733
133.109
129.297
128.941
128.278
128.179
128.070
127.870
127.687
109.704
77.422
77.000
76.574
65.662
52.526
11.409
CO2Bn
Ph
N
N
Cl
3c
PPM
0
50
100
150
200

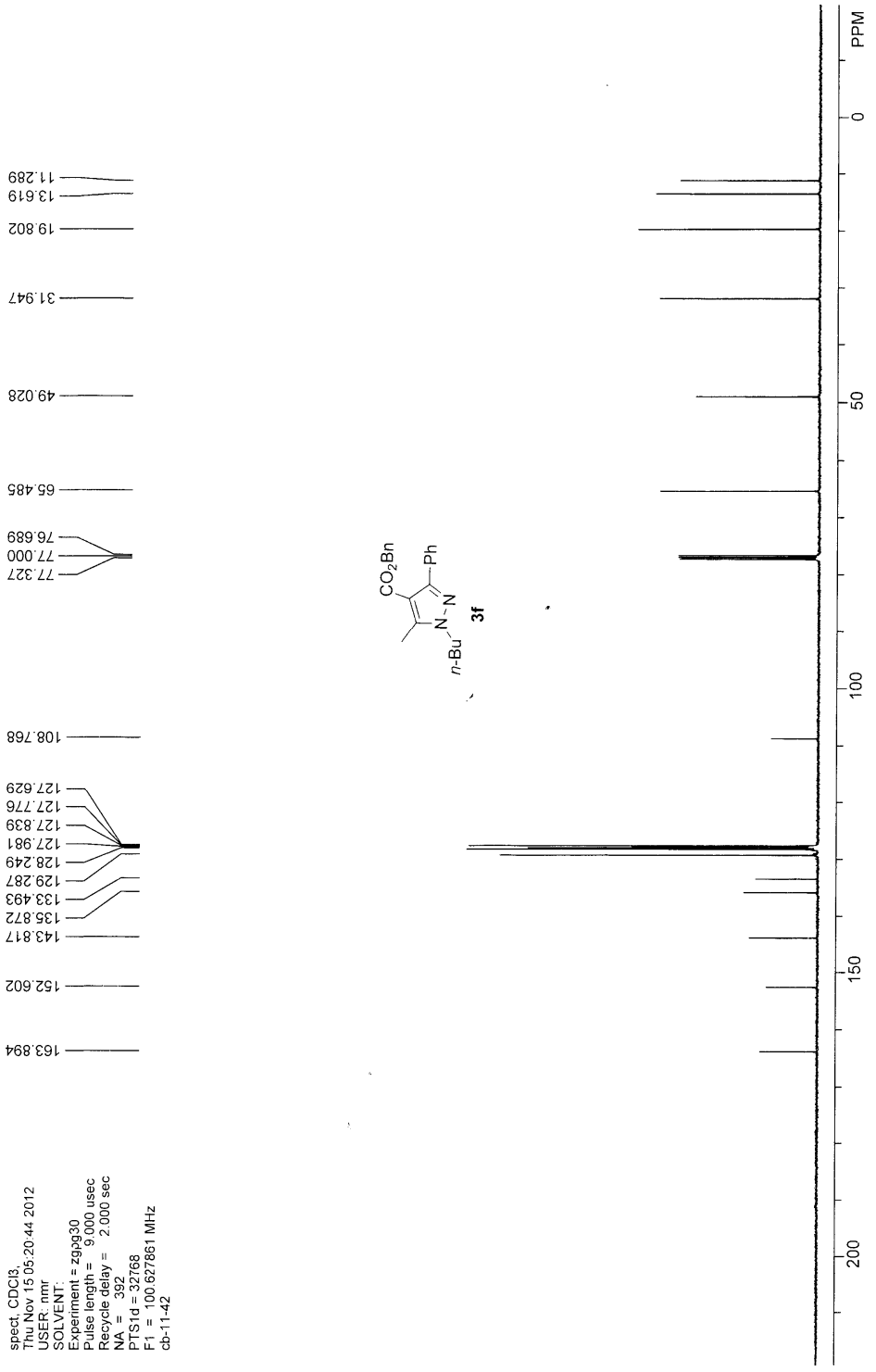

spect. CDCl3,
Fri Sep 07 07:10:34 2012
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.600 usec
Recycle delay = 1.000 sec
NA = 6
PTS1d = 32768
F1 = 300.131866 MHz
cb-10-143
CO2Bn
Ph
N
N
MeO
3d
0.000
2.474
3.747
5.166
5.257
6.819
6.848
6.857
7.102
7.130
7.147
7.159
7.173
7.224
7.231
7.243
7.252
7.265
7.311
7.317
7.324
7.333
7.345
7.545
7.559
7.571
7.583
7.591
7.603
4.00
3.12
3.07
2.03
2.02
2.02
2.00
3.04
2.99
PPM
10
8
6
4
2
0

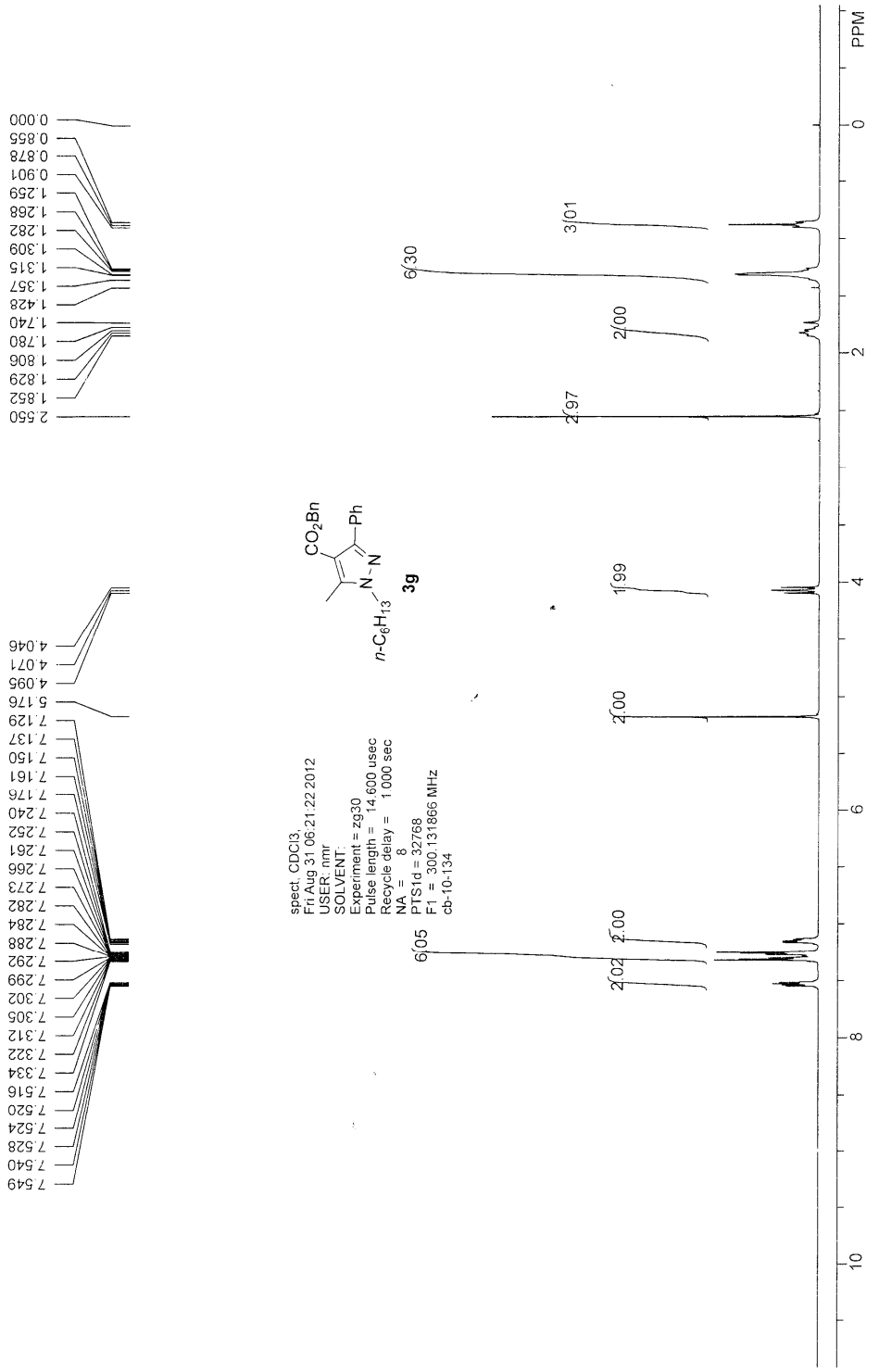

spect_CDCl3.
Fri Sep 07 07:15:40 2012
USER: nmr
SOLVENT
Experiment = zgpg30
Pulse length = 9.900 usec
Recycle delay = 2.000 sec
NA = 1024
PTS1d = 32768
F1 = 75.475296 MHz
cb-10-143
163.782
159.208
152.733
144.316
135.818
133.355
129.357
128.278
128.260
128.039
127.932
127.813
127.630
114.126
109.552
77.421
77.000
76.574
65.584
55.174
52.849
11.447
CO2Bn
Ph
N
N
MeO
3d
PPM
0
50
100
150
200

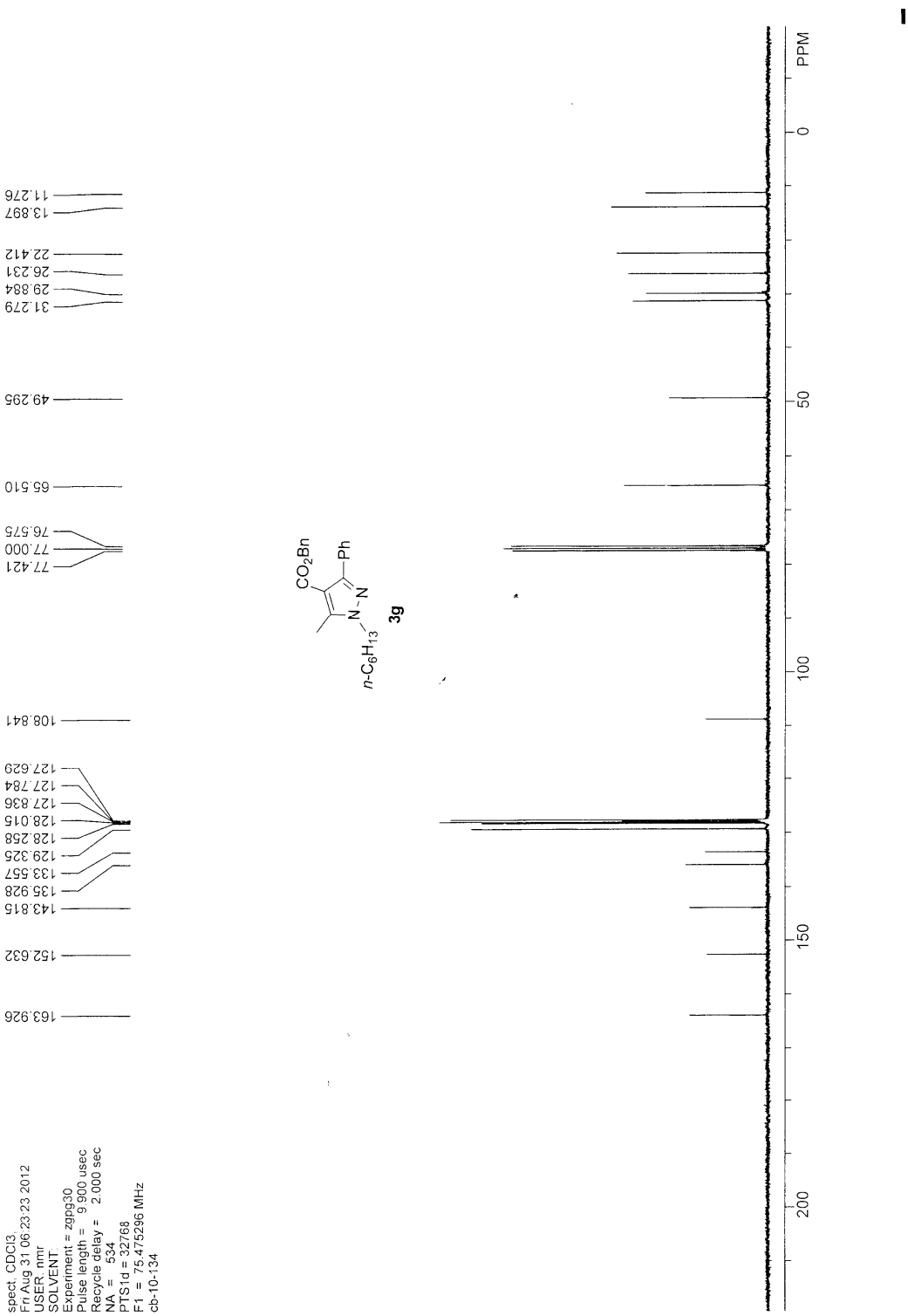

spect. CDCl3,
Thu Dec 13 18:49:43 2012
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.600 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
cb-11-36
CO2Bn
Ph
N
N
3e
PPM
0
2
4
6
8
3.03
3.00
2.01
2.00
6.09
6.07
2.02
-0.000
2.301
2.465
5.170
5.285
7.041
7.067
7.101
7.128
7.137
7.150
7.162
7.214
7.246
7.255
7.267
7.317
7.329
7.337
7.568
7.578
7.591
7.597

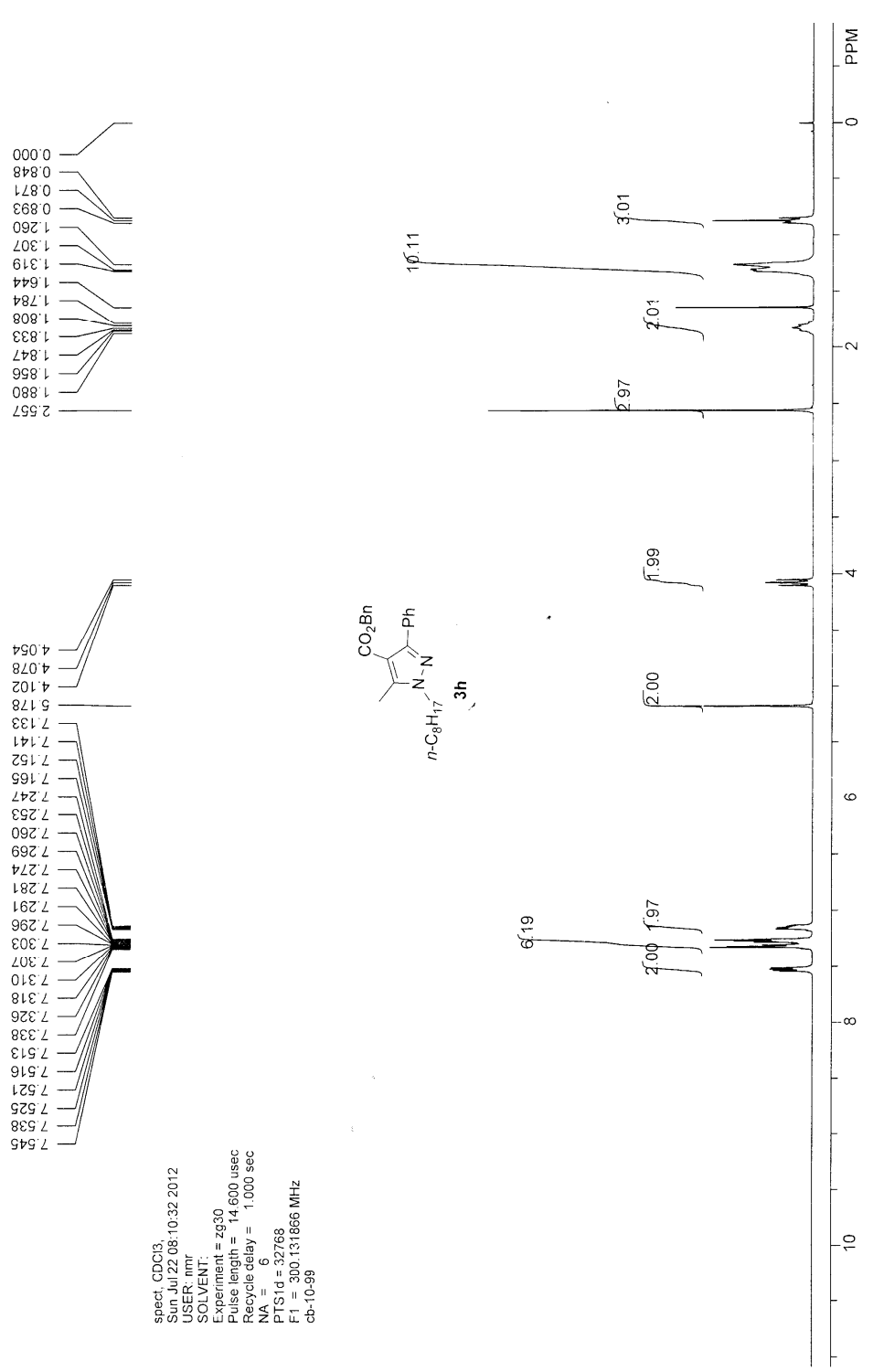

11.485
21.028
53.162
65.598
76.576
77.000
77.425
109.532
126.821
127.666
127.839
127.951
128.064
128.269
129.363
129.419
132.734
133.344
135.816
137.591
144.449
152.766
163.808
spect, CDCl3,
Wed Mar 13 11:27:03 2013
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.900 usec
Recycle delay = 2.000 sec
NA = 1024
PTS1d = 32768
F1 = 75.475296 MHz
cb-11-36
CO2Bn
Ph
N
N
3e
PPM
0
50
100
150
200

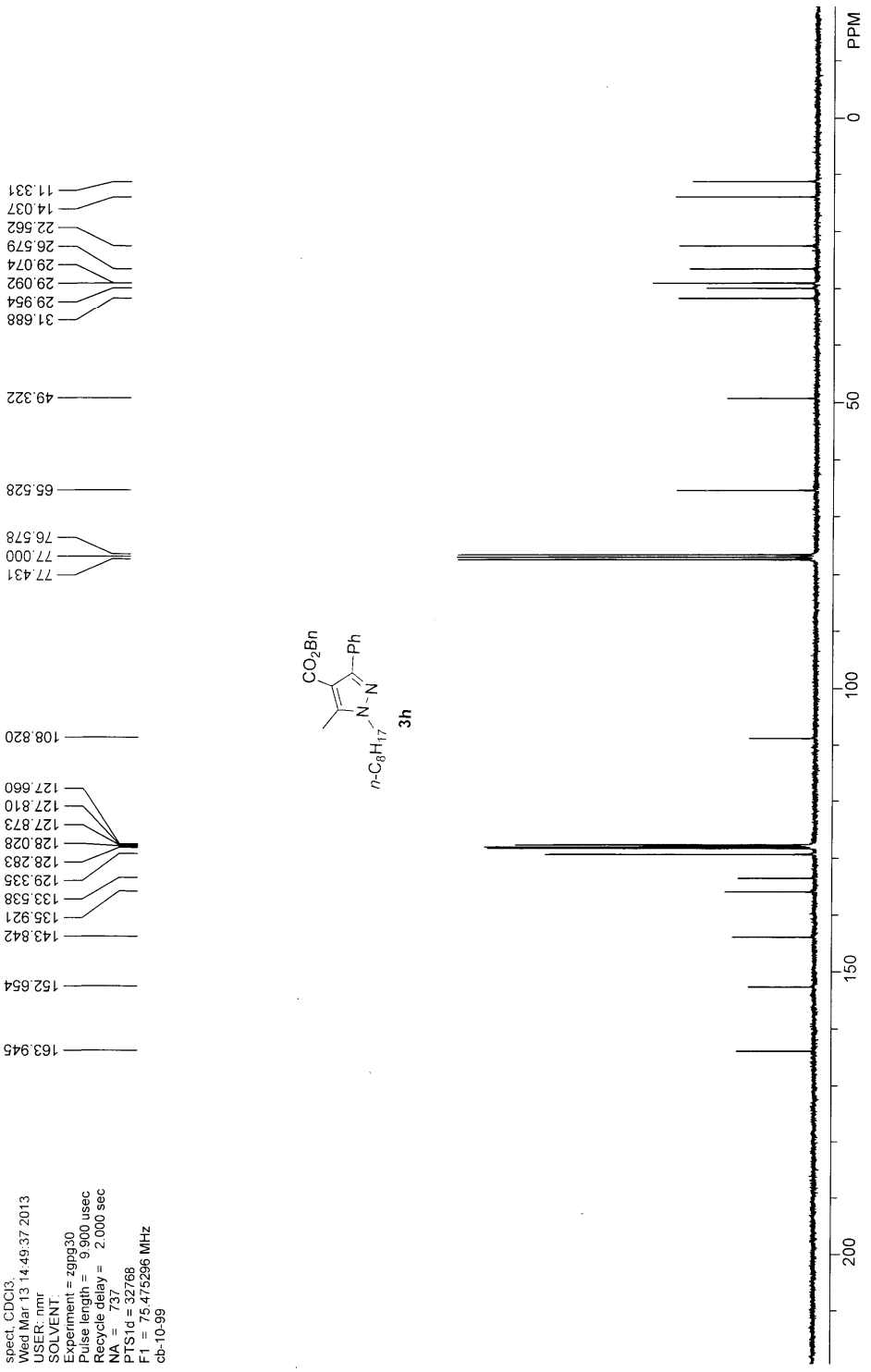

spect. CDCl3,
Thu Nov 15 04:57:19 2012
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.700 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 65536
F1 = 400.152466 MHz
cb-11-42
CO2Bn
Ph
n-Bu
3f
6.10
1.95
2.09
2.01
2.00
3.00
2.14
2.07
3.02
PPM
0
2
4
6
8
-0.000
0.923
0.941
0.960
1.314
1.332
1.351
1.370
1.389
1.775
1.794
1.813
1.831
1.850
2.551
4.061
4.080
4.098
5.179
7.136
7.142
7.151
7.160
7.240
7.249
7.258
7.264
7.274
7.300
7.309
7.312
7.313
7.320
7.325
7.524
7.526
7.529
7.533
7.542
7.547

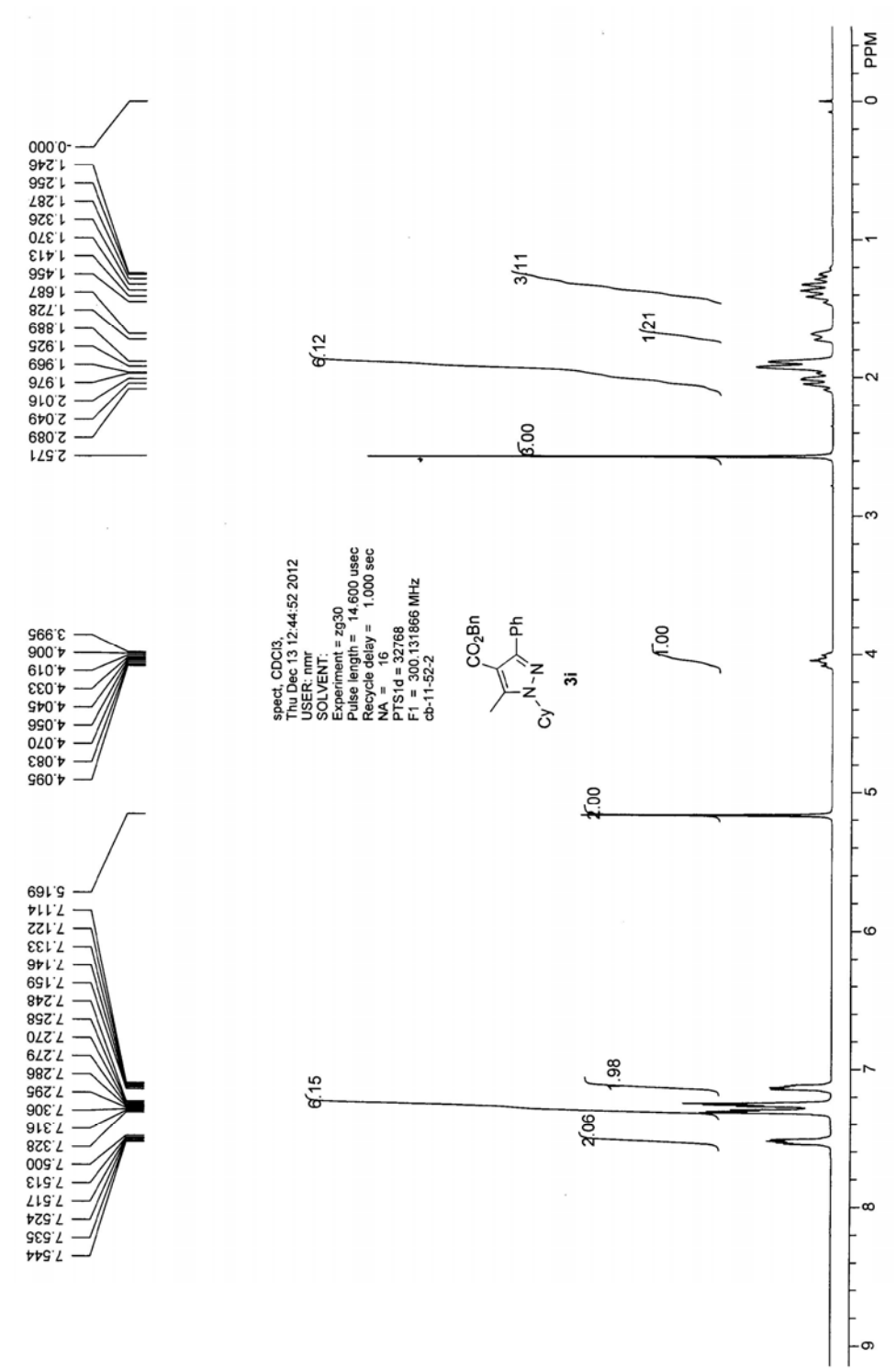

spect, CDCl3,
Thu Nov 15 05:20:44 2012
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.000 usec
Recycle delay = 2.000 sec
NA = 392
PTS1d = 32768
F1 = 100.627861 MHz
cb-11-42
11.289
13.619
19.802
31.947
49.028
65.485
76.689
77.000
77.327
108.768
127.629
127.776
127.839
127.981
128.249
129.287
133.493
135.872
143.817
152.602
163.894
CO2Bn
Ph
N
N
n-Bu
3f
PPM
0
50
100
150
200

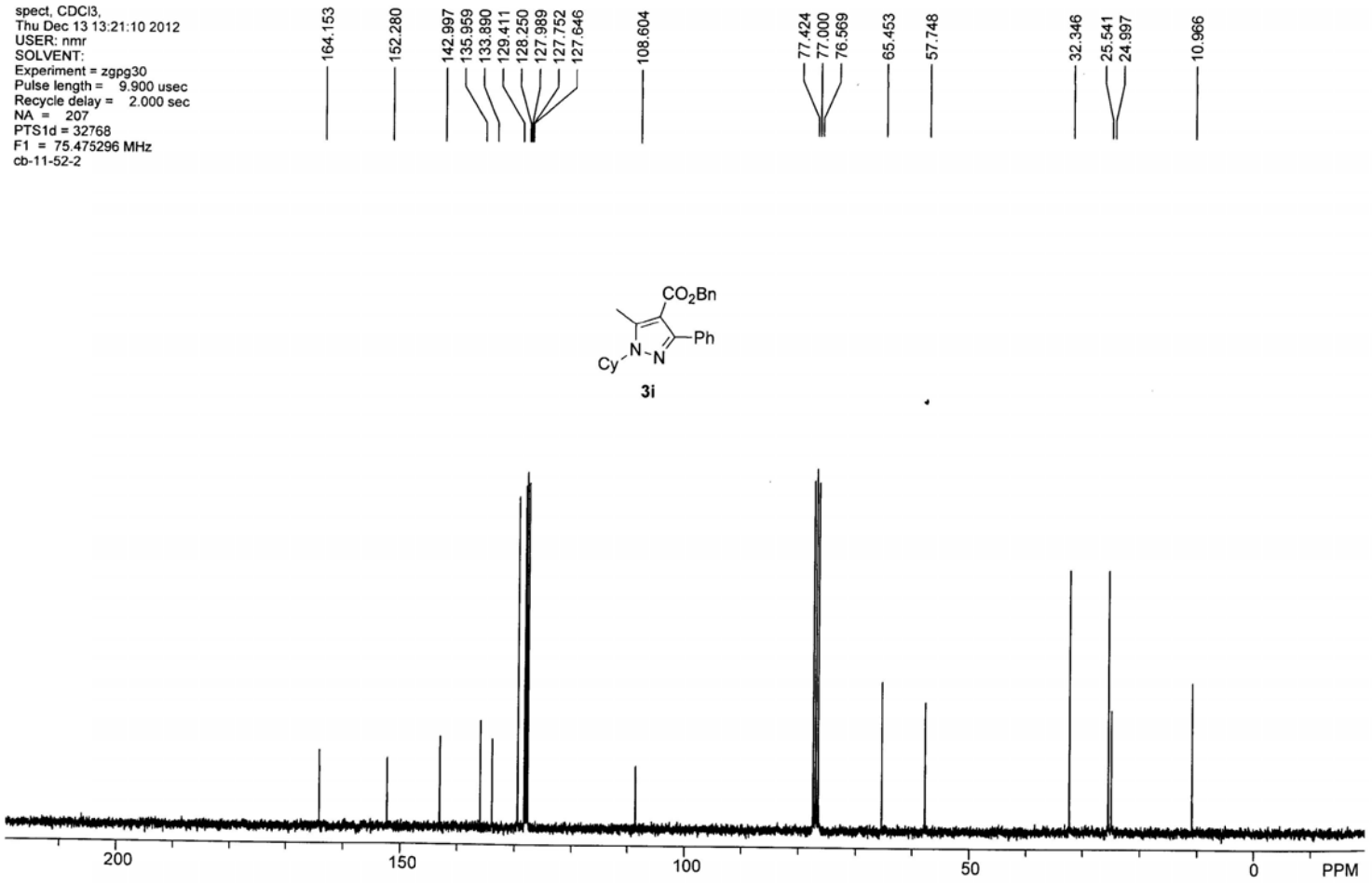

spect. CDCl3,
Fri Aug 31 06:21:22 2012
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.600 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
cb-10-134
CO2Bn
Ph
N
N
n-C6H13
3g
6.05
2.02
2.00
2.00
1.99
2.00
2.97
6.30
3.01
PPM
0
2
4
6
8
10
7.549
7.540
7.528
7.524
7.520
7.516
7.334
7.322
7.312
7.305
7.302
7.299
7.292
7.288
7.284
7.282
7.273
7.266
7.261
7.252
7.240
7.176
7.161
7.150
7.137
7.129
5.176
4.095
4.071
4.046
2.550
1.852
1.829
1.806
1.780
1.740
1.428
1.357
1.315
1.309
1.282
1.268
1.259
0.901
0.878
0.855
0.000

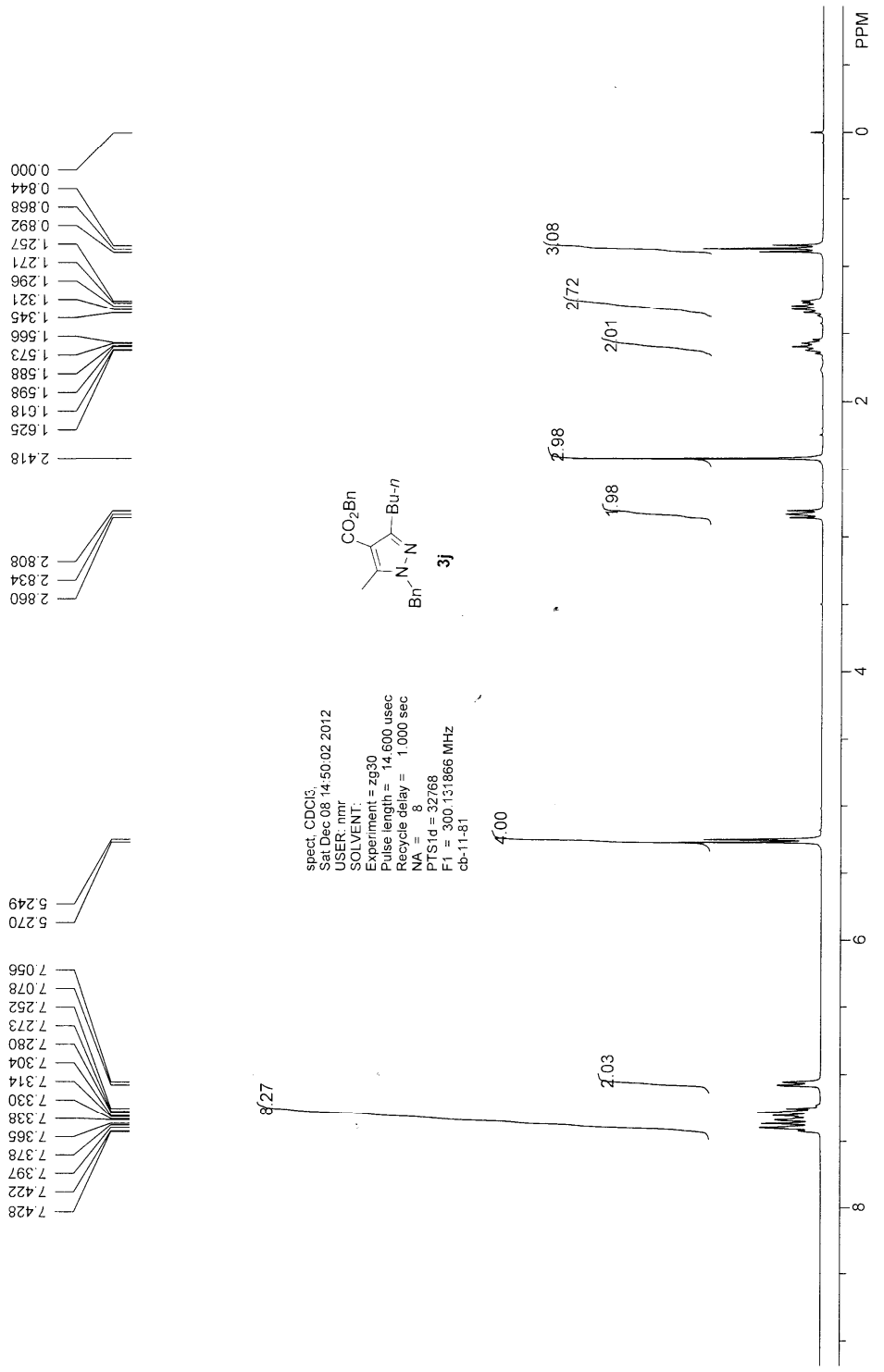

spect. CDCl3.
Fri Aug 31 06:23:23 2012
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.900 usec
Recycle delay = 2.000 sec
NA = 534
PTS1d = 32768
F1 = 75.475296 MHz
cb-10-134
11.276
13.897
22.412
26.231
29.884
31.279
49.295
65.510
76.675
77.000
77.421
108.841
127.629
127.784
127.836
128.015
128.258
129.325
133.557
135.928
143.815
152.632
163.926
CO2Bn
Ph
N
N
n-C6H13
3g
PPM
0
50
100
150
200

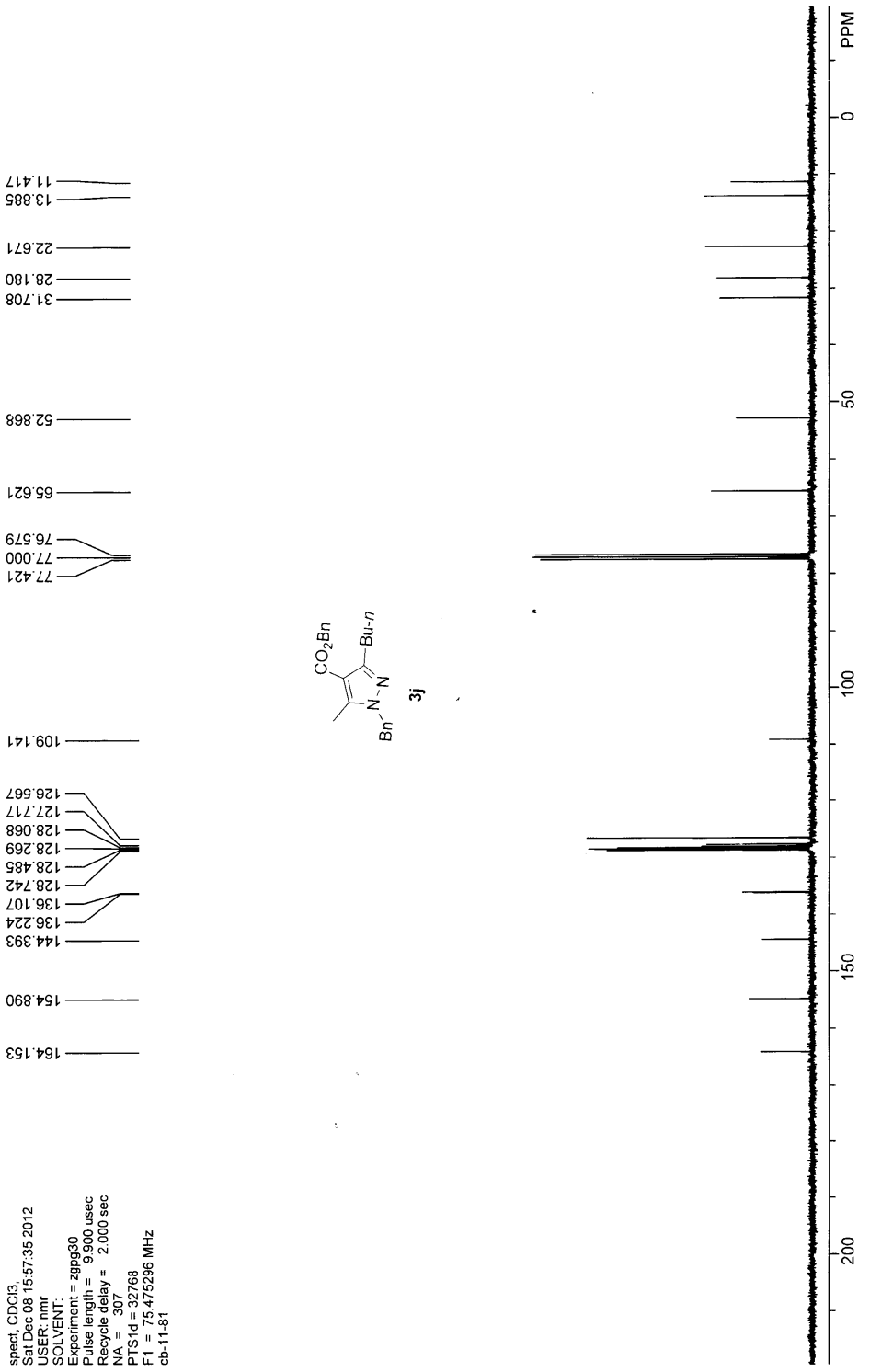

spect_CDCl3
Sun Jul 22 08:10:32 2012
USER nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.600 usec
Recycle delay = 1.000 sec
NA = 6
PTS1d = 32768
F1 = 300.131866 MHz
cb-10-99
CO2Bn
Ph
n-C8H17
3h
PPM

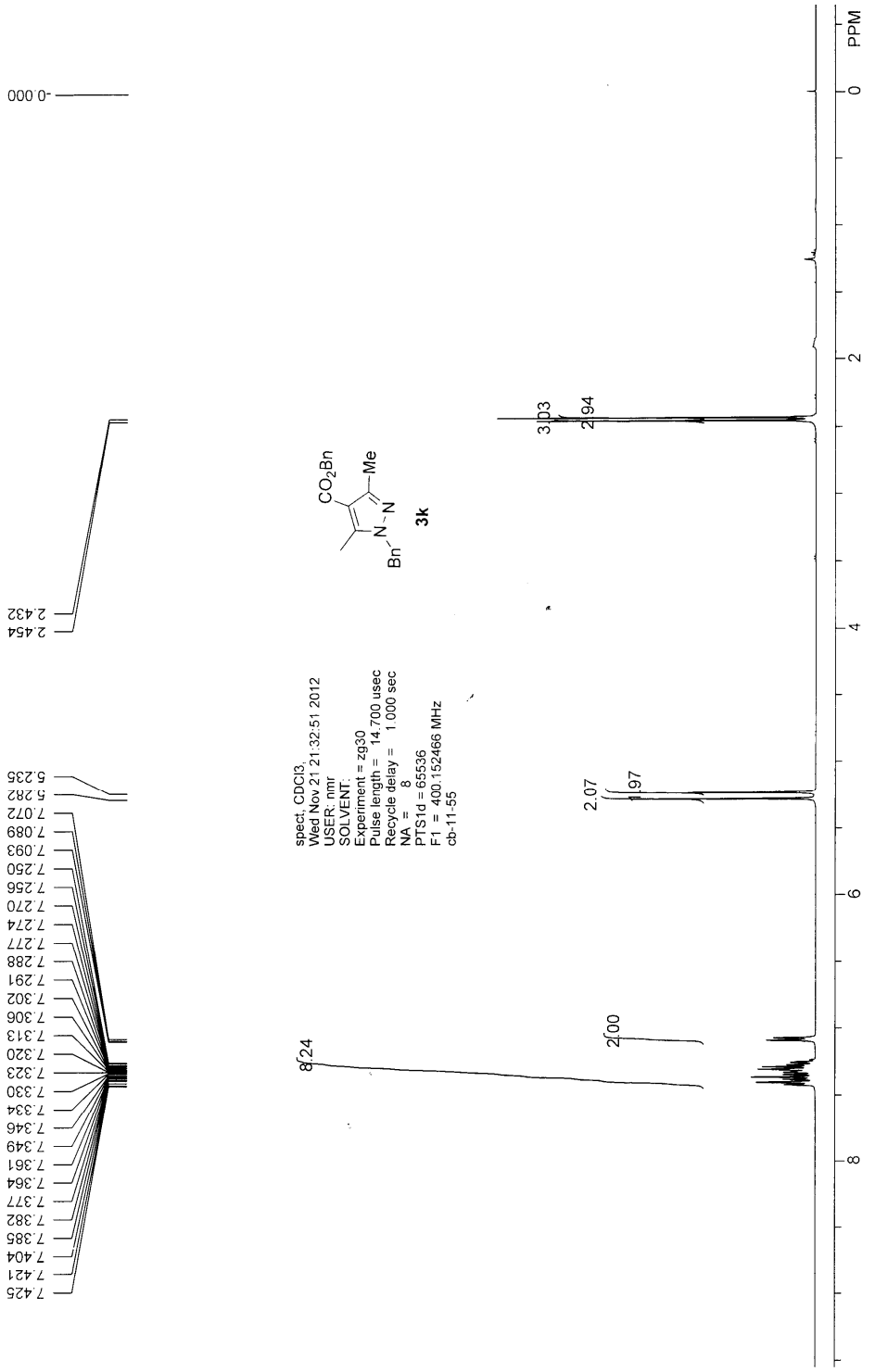

spect_CDCl3
Wed Mar 13 14:49:37 2013
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.900 usec
Recycle delay = 2.000 sec
NA = 737
PTS1d = 32768
F1 = 75.475296 MHz
cb-10-99
11.331
14.037
22.562
26.579
29.074
29.092
29.954
31.688
49.322
65.528
76.578
77.000
77.431
108.820
127.660
127.810
127.873
128.028
128.283
129.335
133.538
135.921
143.842
152.654
163.945
CO2Bn
Ph
n-C8H17
3h
PPM
0
50
100
150
200

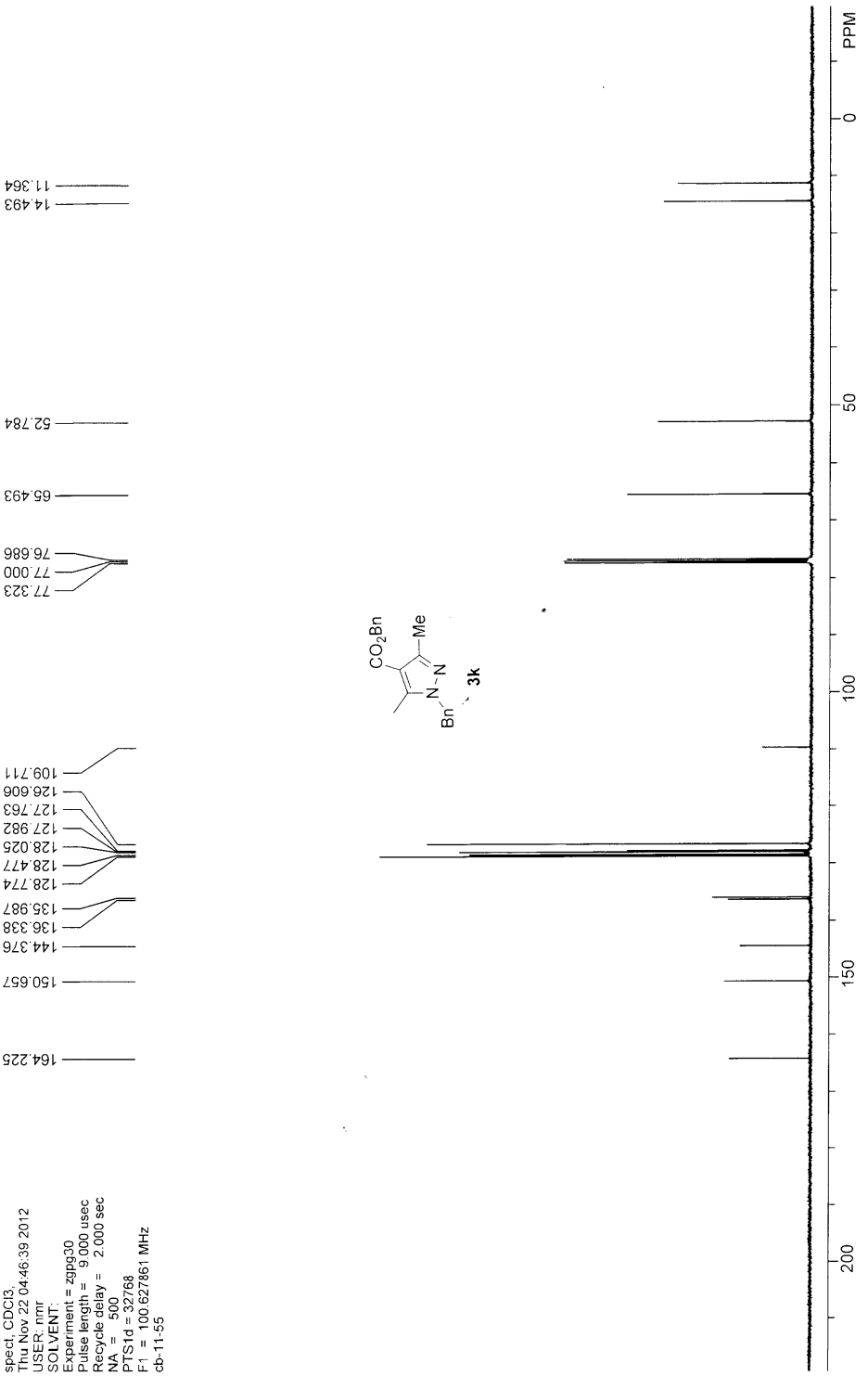

spect, CDCl3,
Thu Dec 13 12:44:52 2012
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.600 usec
Recycle delay = 1.000 sec
NA = 16
PTS1d = 32768
F1 = 300.131866 MHz
cb-11-52-2
CO2Bn
Ph
Cy
N
N
3i
6.15
1.98
2.06
2.00
1.00
6.12
3.00
1.21
3.11
PPM

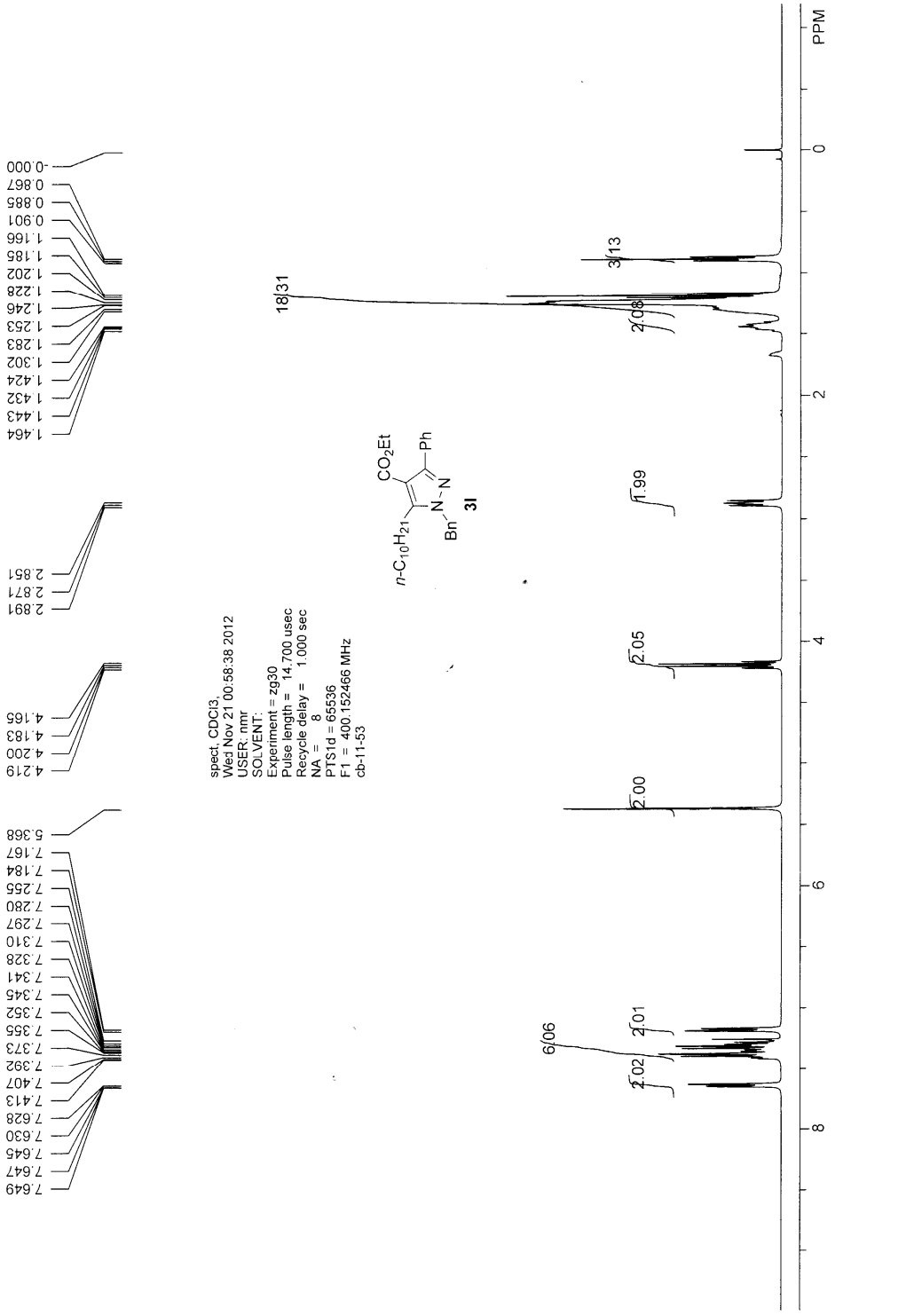

spect, CDCl3,
Thu Dec 13 13:21:10 2012
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.900 usec
Recycle delay = 2.000 sec
NA = 207
PTS1d = 32768
F1 = 75.475296 MHz
cb-11-52-2
164.153
152.280
142.997
135.959
133.890
129.411
128.250
127.989
127.752
127.646
108.604
77.424
77.000
76.569
65.453
57.748
32.346
25.541
24.997
10.966
CO2Bn
Ph
Cy
N
N
3i
200
150
100
50
0
PPM

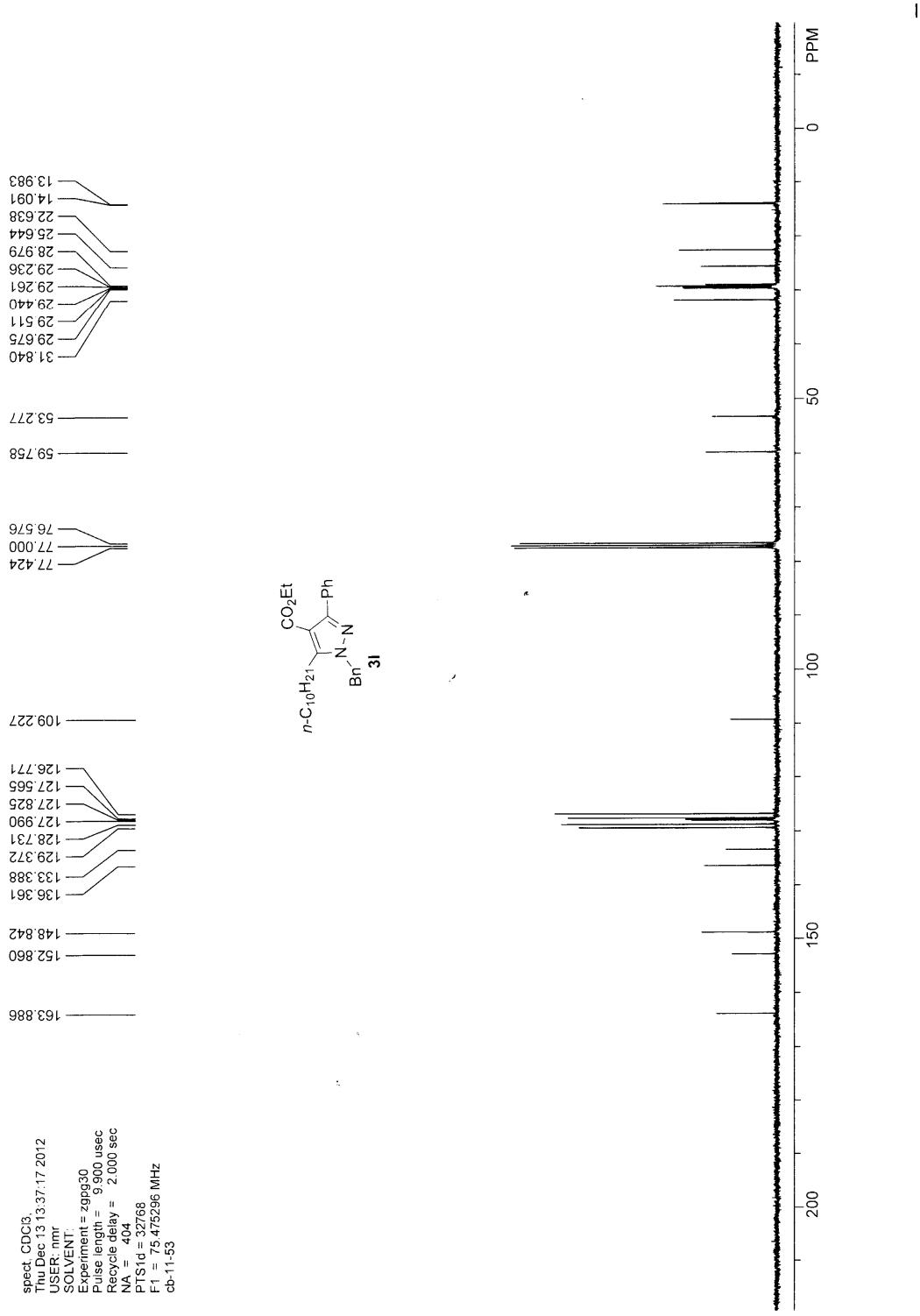

spect. CDCl3.
Sat Dec 08 14:50:02 2012
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.600 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
cb-11-81
CO2Bn
Bu-n
N
N
Bn
3j
8.27
2.03
4.00
1.98
2.98
2.01
2.72
3.08
PPM
0
2
4
6
8
7.428
7.422
7.397
7.378
7.365
7.338
7.330
7.314
7.304
7.280
7.273
7.262
7.078
7.056
5.270
5.249
2.860
2.834
2.808
2.418
1.625
1.618
1.598
1.588
1.573
1.566
1.345
1.321
1.296
1.271
1.257
0.892
0.868
0.844
0.000

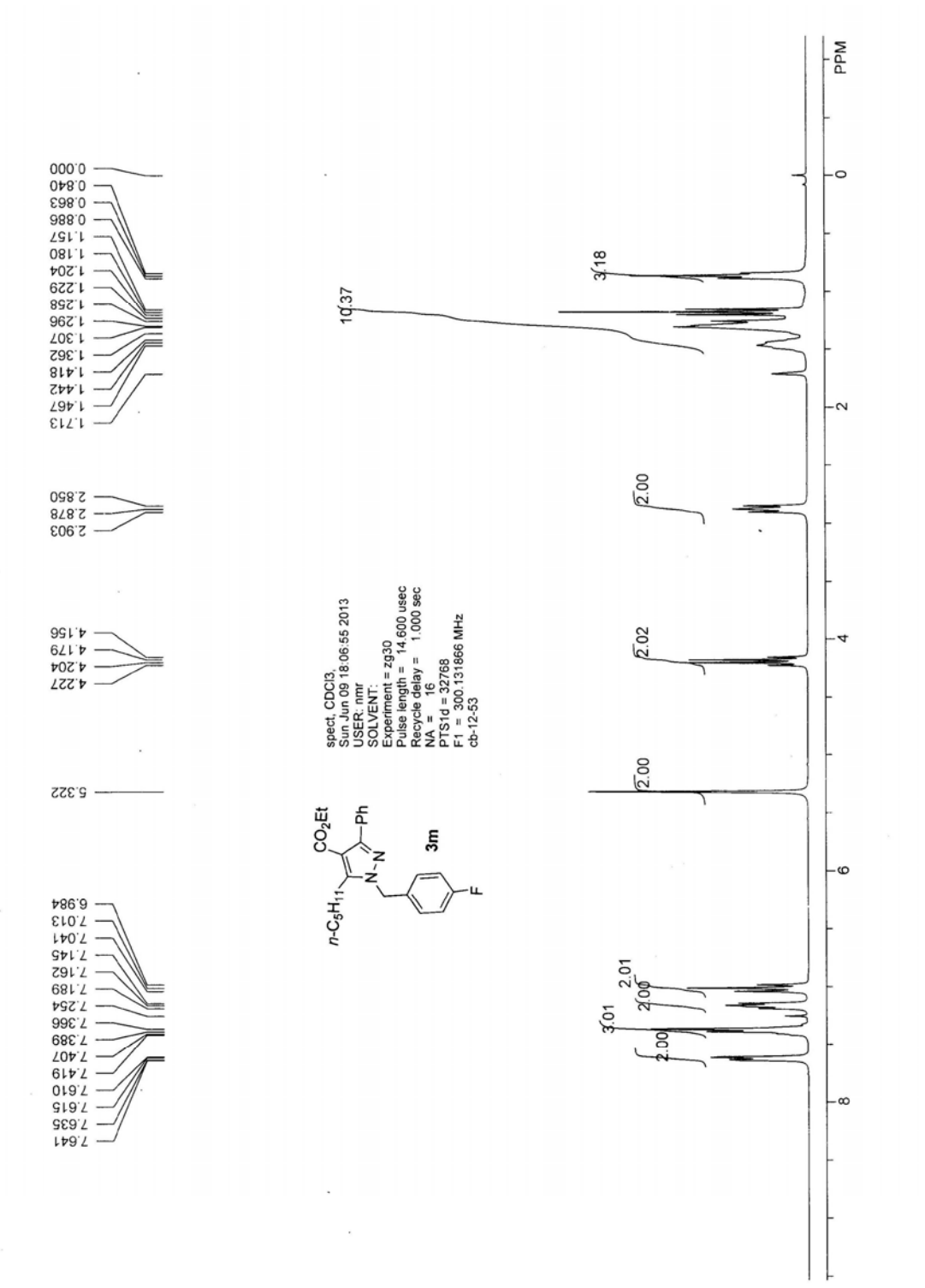

spect, CDCl3,
Sat Dec 08 15:57:35 2012
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.900 usec
Recycle delay = 2.000 sec
NA = 307
PTS1d = 32768
F1 = 75.475296 MHz
cb-11-81
164.153
154.890
144.393
136.224
136.107
128.742
128.485
128.269
128.068
127.717
126.567
109.141
77.421
77.000
76.579
65.621
52.868
31.708
28.180
22.671
13.885
11.417
CO2Bn
Bu-n
Bn
N
N
3j
PPM
0
50
100
150
200

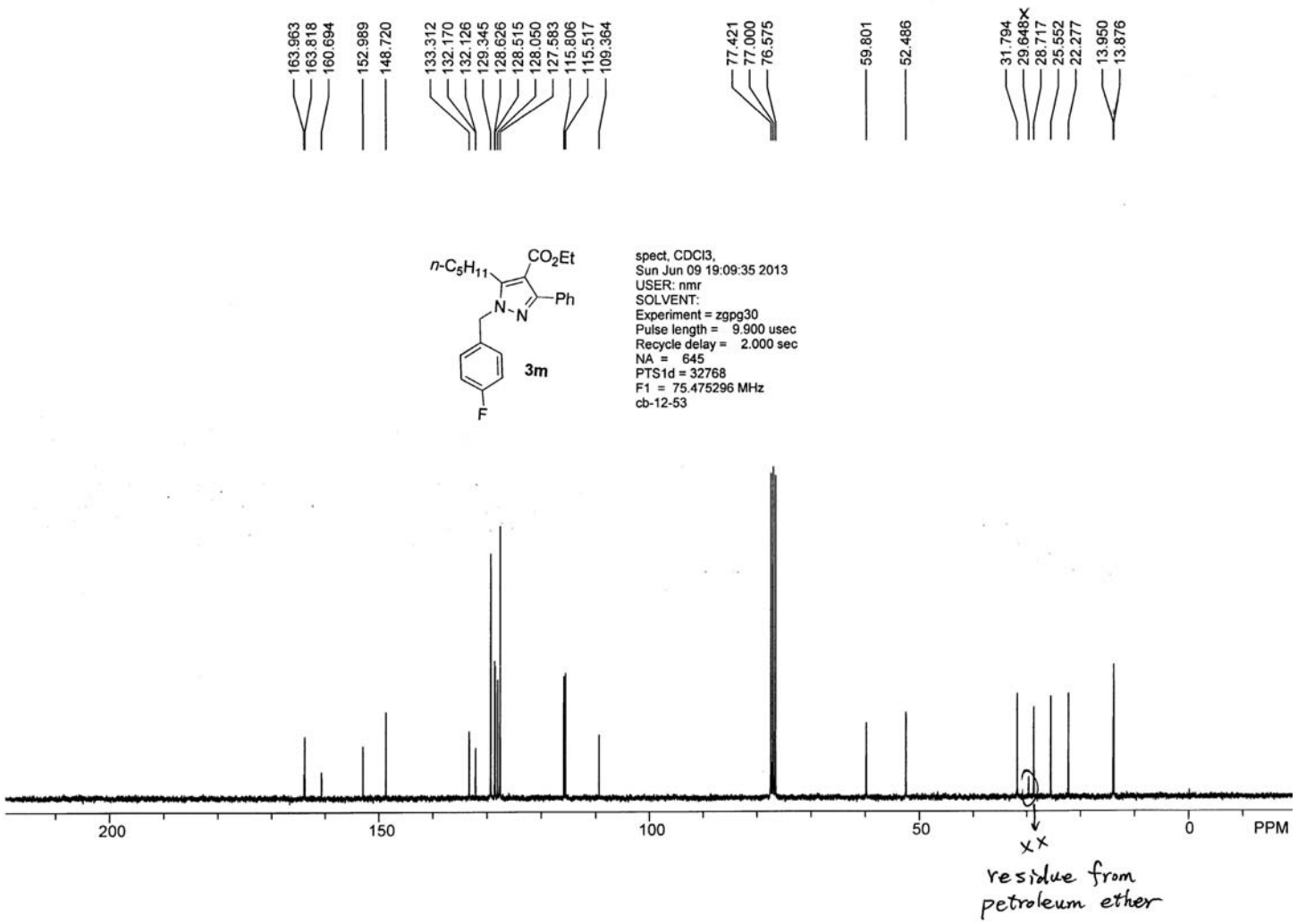

spect, CDCl3,
Wed Nov 21 21:32:51 2012
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.700 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 65536
F1 = 400.152466 MHz
cb-11-55
CO2Bn
Me
Bn
N
N
3k
PPM
0
2
4
6
8
8.24
2.00
2.07
1.97
3.03
2.94
7.425
7.421
7.404
7.385
7.382
7.377
7.364
7.361
7.349
7.346
7.334
7.330
7.323
7.320
7.313
7.306
7.302
7.291
7.288
7.277
7.274
7.270
7.256
7.250
7.093
7.089
7.072
5.282
5.235
2.454
2.432
-0.000


spect, CDCl3,
Thu Nov 22 04:46:39 2012
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.000 usec
Recycle delay = 2.000 sec
NA = 500
PTS1d = 32768
F1 = 100.627861 MHz
cb-11-55
164.225
150.657
144.376
136.338
135.987
128.774
128.477
128.025
127.982
127.763
126.606
109.711
77.323
77.000
76.686
65.493
52.784
14.493
11.364
CO2Bn
Me
N
N
Bn
3k
PPM
0
50
100
150
200

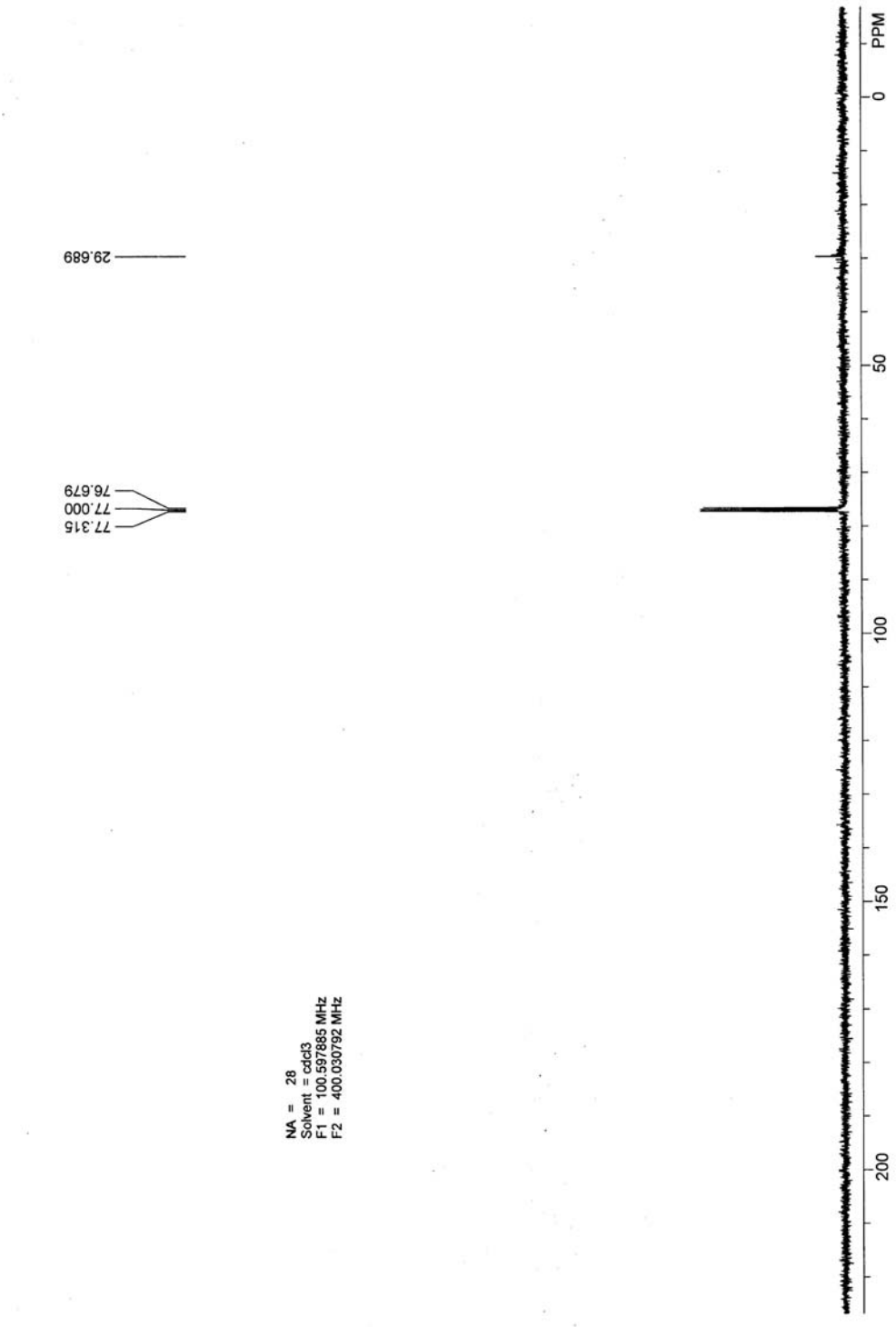

0.000
0.867
0.885
0.901
1.166
1.185
1.202
1.228
1.246
1.253
1.283
1.302
1.424
1.432
1.443
1.464
2.851
2.871
2.891
4.165
4.183
4.200
4.219
5.368
7.167
7.184
7.255
7.280
7.297
7.310
7.328
7.341
7.345
7.352
7.355
7.373
7.392
7.407
7.413
7.628
7.630
7.645
7.647
7.649
spect, CDCl3,
Wed Nov 21 00:58:38 2012
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.700 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 65536
F1 = 400.152466 MHz
cb-11-53
CO2Et
Ph
n-C10H21
N
N
Bn
3l
18.31
3.13
2.08
1.99
2.05
2.00
6.06
2.01
2.02
8
6
4
2
0
PPM

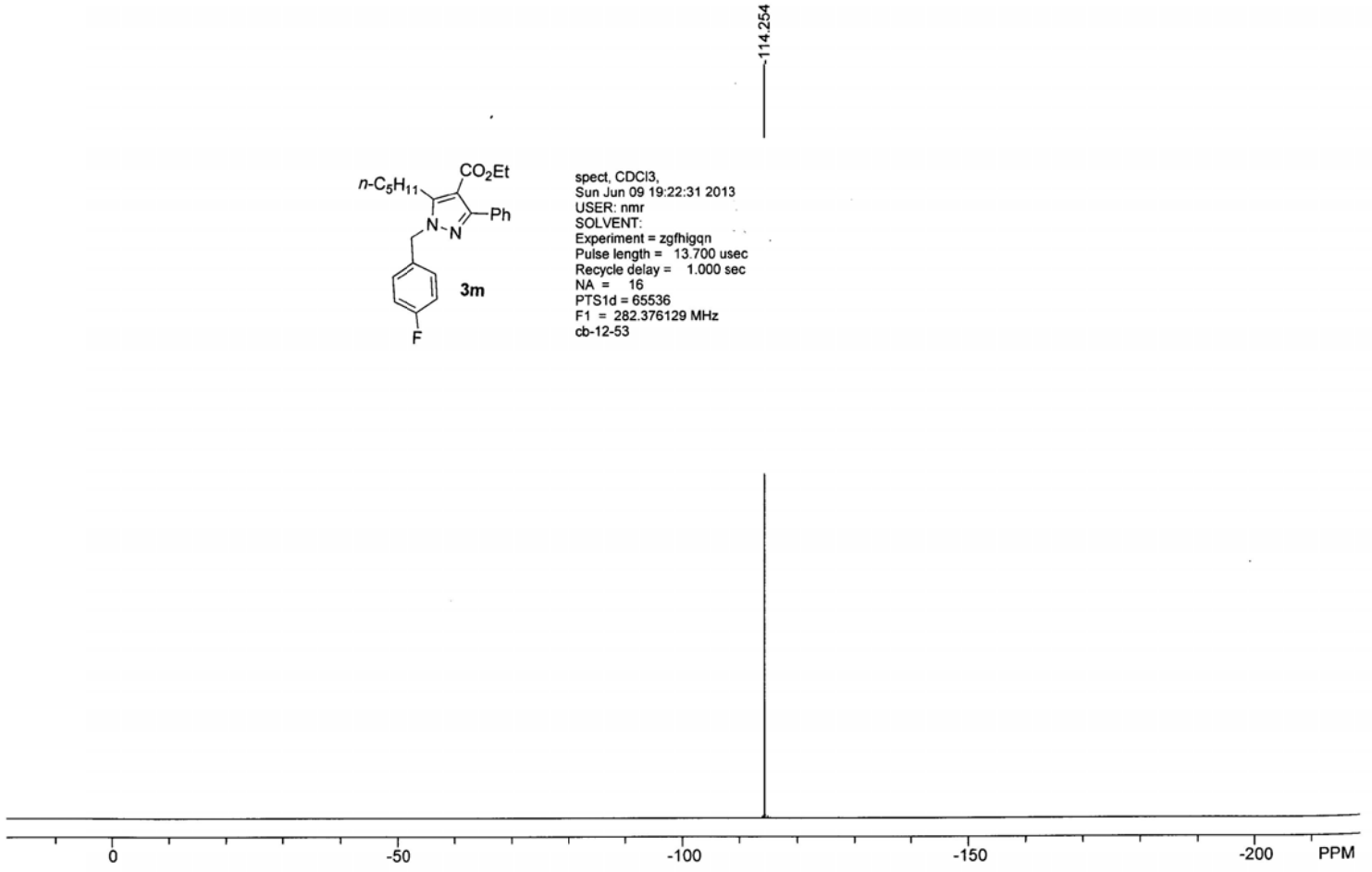

spect. CDCl3.
Thu Dec 13 13:37:17 2012
USER: nmr
SOLVENT
Experiment = zgpg30
Pulse length = 9.900 usec
Recycle delay = 2.000 sec
NA = 404
PTS1d = 32768
F1 = 75.475296 MHz
cb-11-53
163.886
152.860
148.842
136.361
133.388
129.372
128.731
127.990
127.825
127.565
126.771
109.227
77.424
77.000
76.576
59.758
53.277
31.840
29.675
29.511
29.440
29.261
29.236
28.979
25.644
22.638
14.091
13.983
CO2Et
Ph
n-C10H21
Bn
3l
PPM
200
150
100
50
0

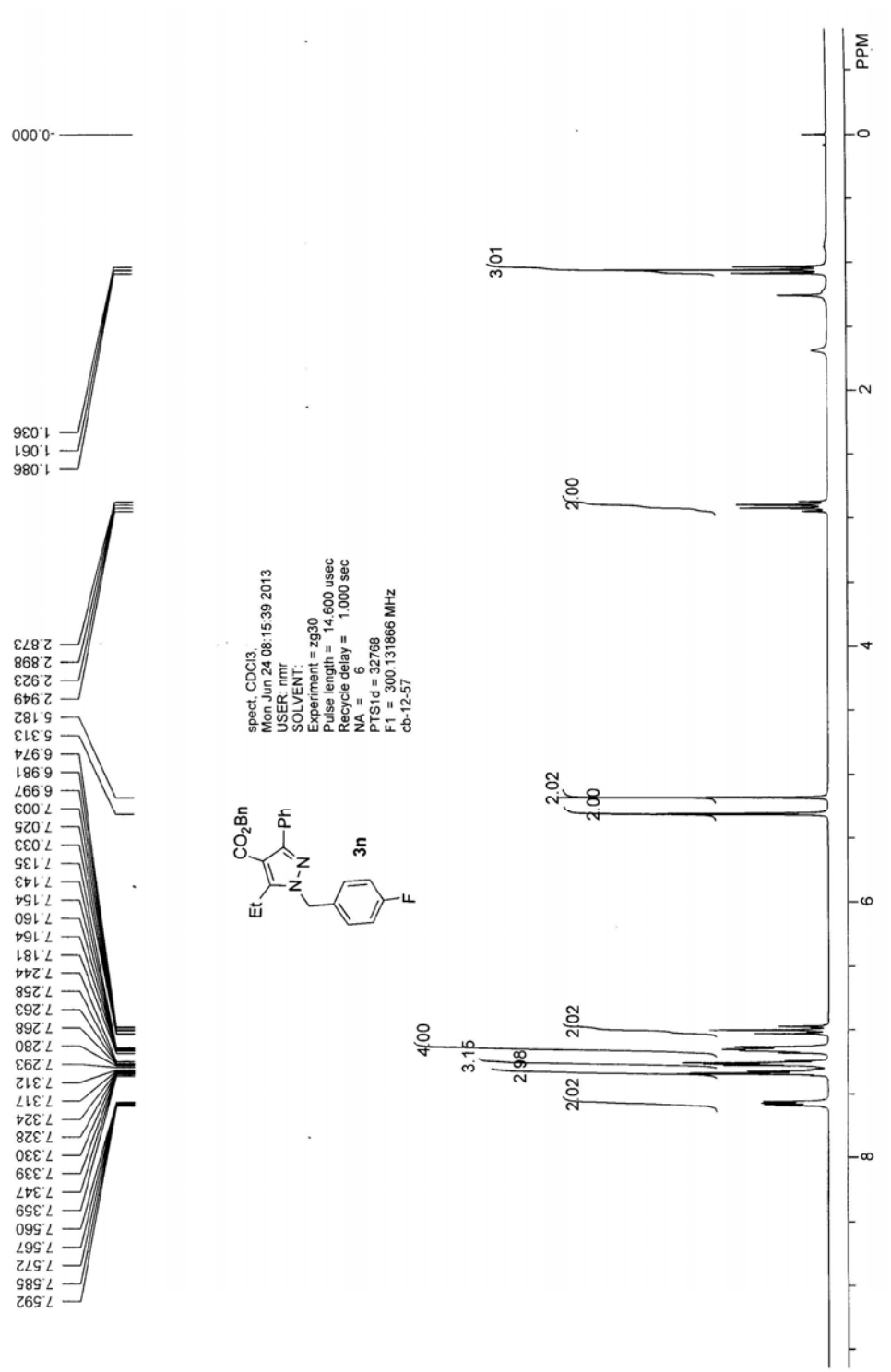

0.000
0.840
0.863
0.886
1.157
1.180
1.204
1.229
1.258
1.296
1.307
1.362
1.418
1.442
1.467
1.713
2.850
2.878
2.903
4.156
4.179
4.204
4.227
5.322
6.984
7.013
7.041
7.145
7.162
7.189
7.254
7.366
7.389
7.407
7.419
7.610
7.615
7.635
7.641
spect. CDCl3.
Sun Jun 09 18:06:55 2013
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.600 usec
Recycle delay = 1.000 sec
NA = 16
PTS1d = 32768
F1 = 300.131866 MHz
cb-12-53
CO2Et
Ph
n-C5H11
N-N
F
3m
10.37
3.18
2.00
2.02
2.00
3.01
2.01
2.00
2.00
PPM
0
2
4
6
8

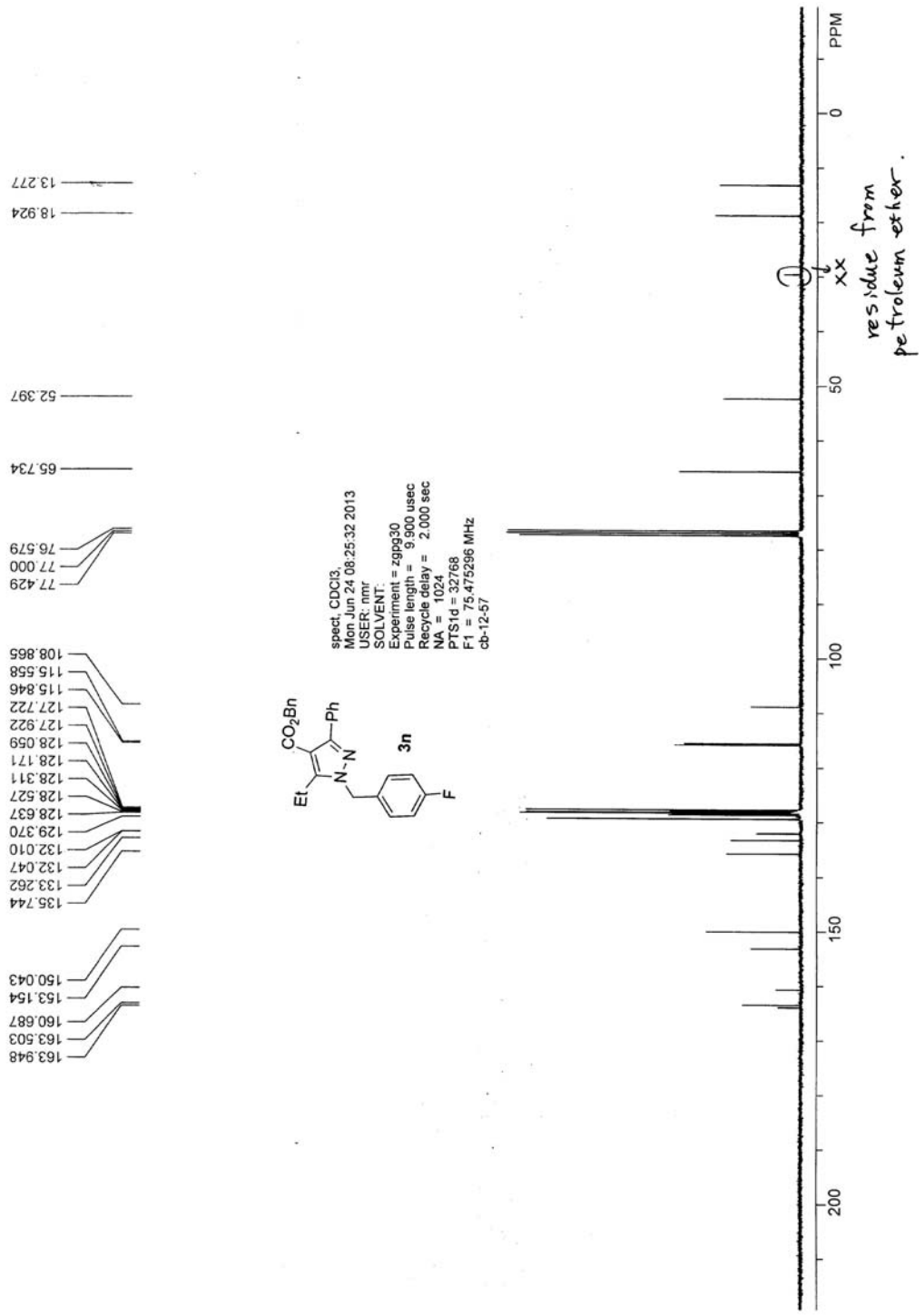

163.963
163.818
160.694
152.989
148.720
133.312
132.170
132.126
129.345
128.626
128.515
128.050
127.583
115.806
115.517
109.364
77.421
77.000
76.575
59.801
52.486
31.794
29.648
28.717
25.552
22.277
13.950
13.876
n-C5H11
CO2Et
Ph
N
N
3m
F
spect, CDCl3,
Sun Jun 09 19:09:35 2013
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.900 usec
Recycle delay = 2.000 sec
NA = 645
PTS1d = 32768
F1 = 75.475296 MHz
cb-12-53
200
150
100
50
0
PPM
x x
residue from
petroleum ether

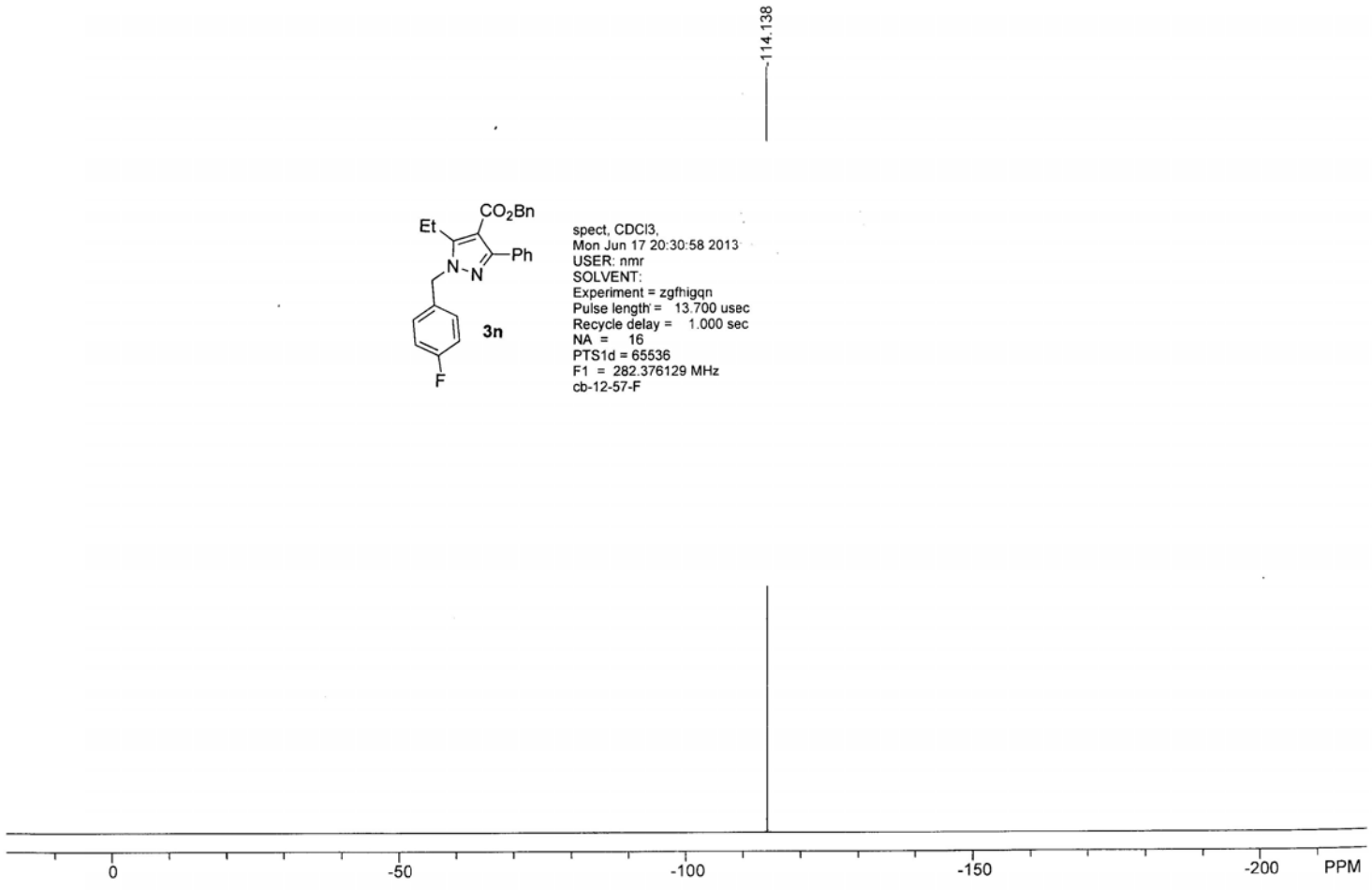
^{13}C NMR spectrum for the residue from petroleum ether:

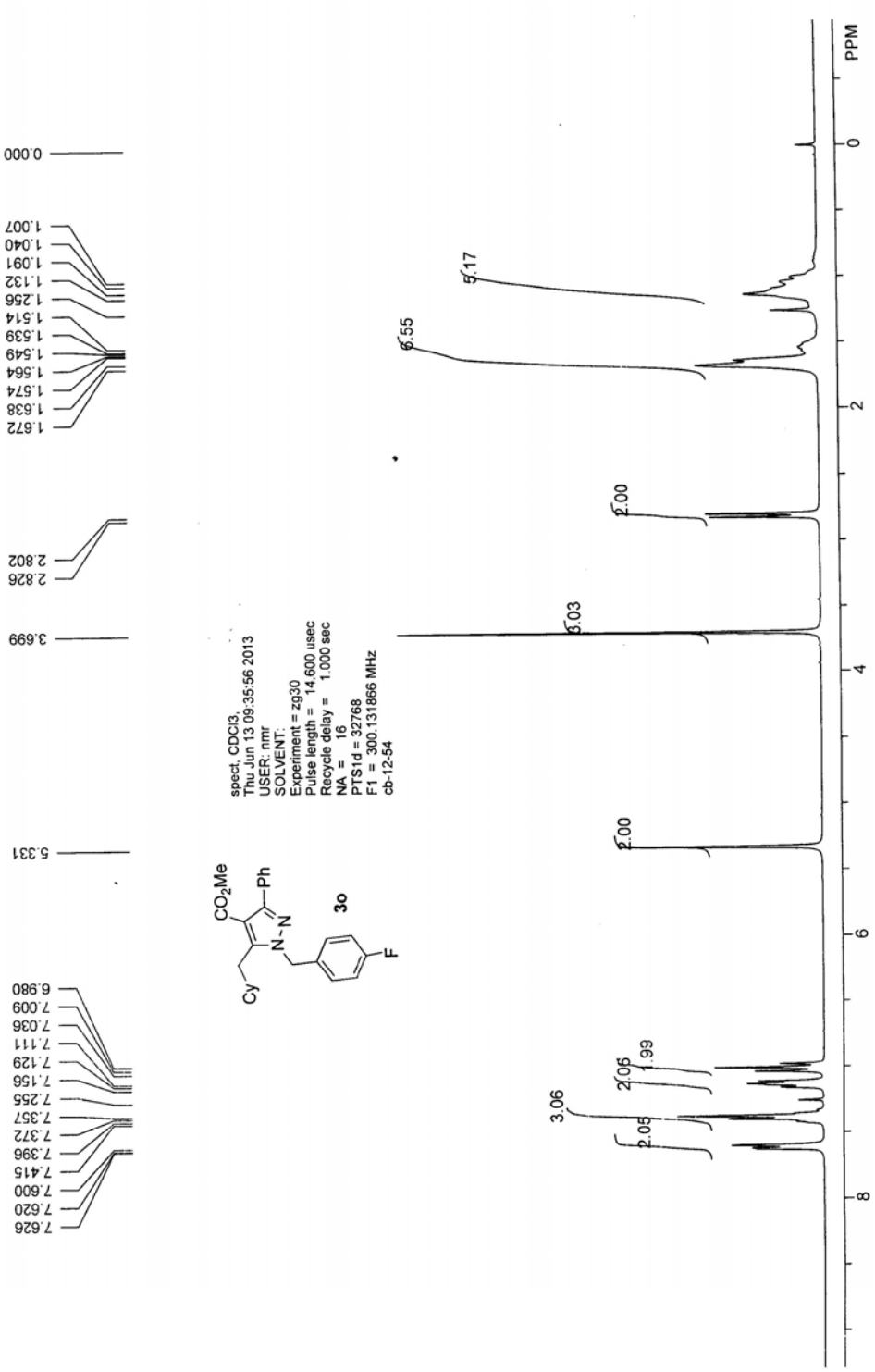


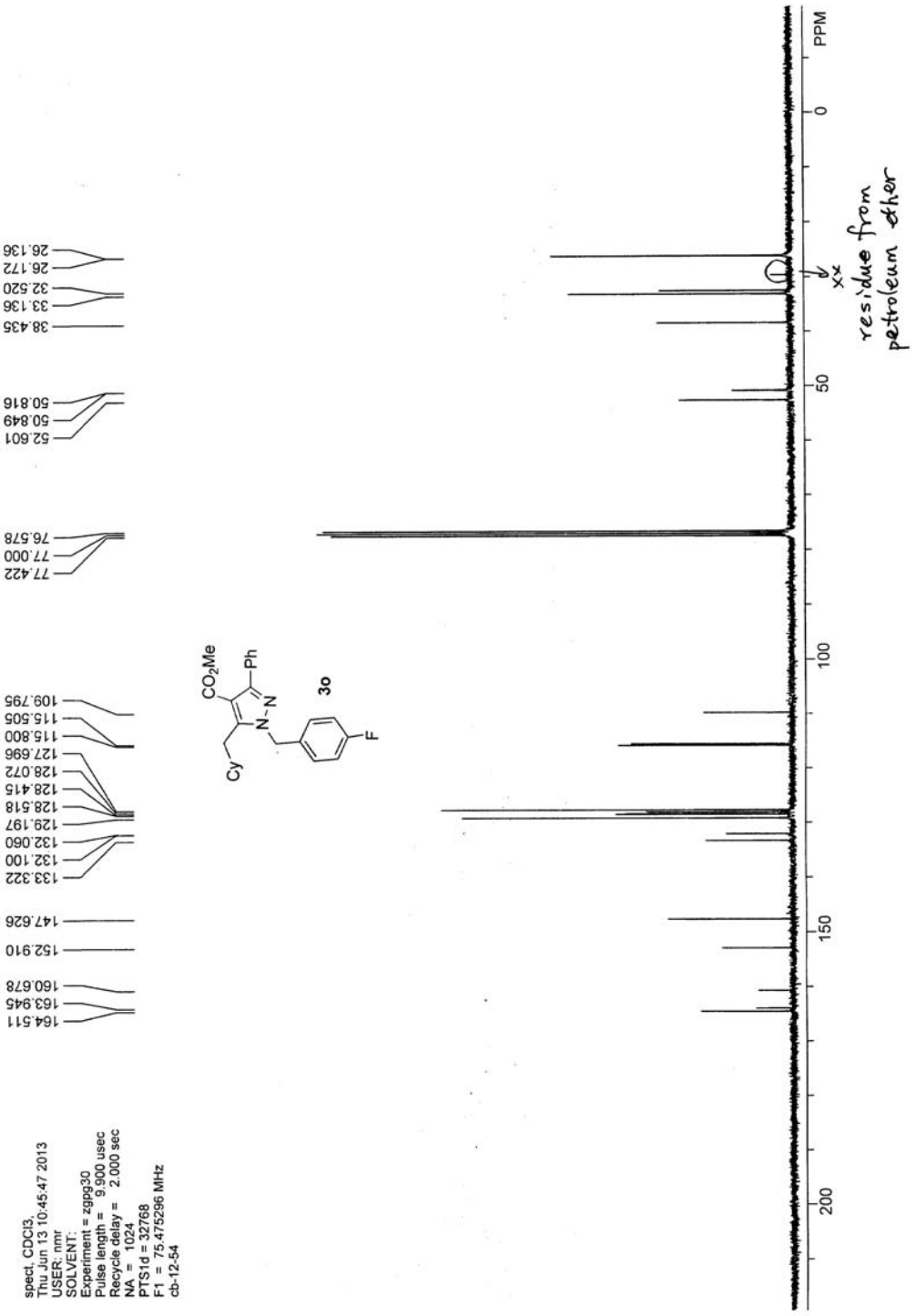

114.254
CO2Et
n-C5H11
Ph
N
N
3m
F
spect, CDCl3,
Sun Jun 09 19:22:31 2013
USER: nmr
SOLVENT:
Experiment = zgfhigqn
Pulse length = 13.700 usec
Recycle delay = 1.000 sec
NA = 16
PTS1d = 65536
F1 = 282.376129 MHz
cb-12-53
0
-50
-100
-150
-200
PPM

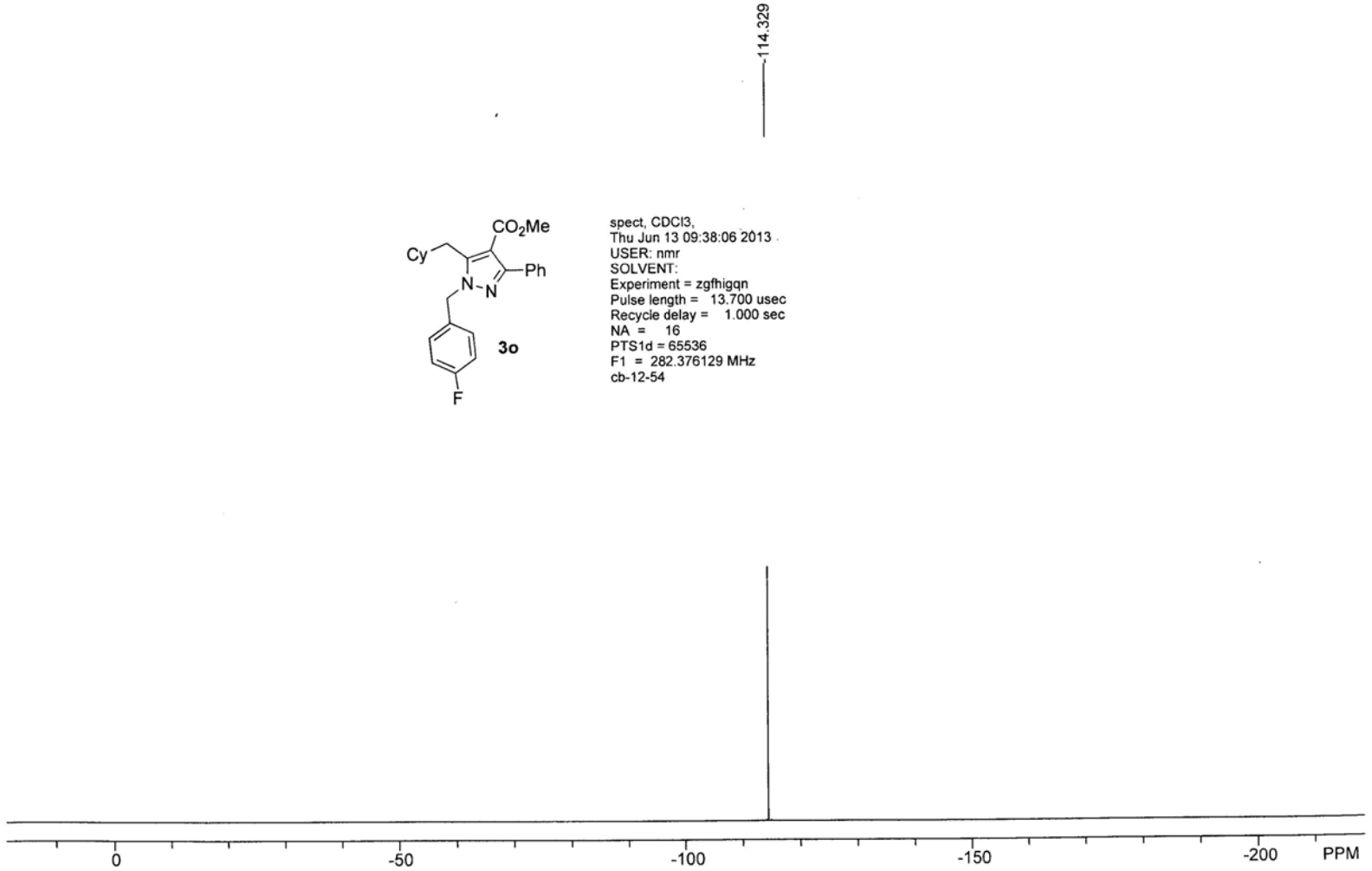

spect. CDCl3
Mon Jun 24 08:15:39 2013
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.600 usec
Recycle delay = 1.000 sec
NA = 6
PTS1d = 32768
F1 = 300.131866 MHz
cb-12-57
CO2Bn
Et
Ph
N
N
F
3n
PPM
0
2
4
6
8
4.00
3.15
2.98
2.02
2.02
2.02
2.00
2.00
3.01
-0.000
1.036
1.061
1.086
2.873
2.898
2.923
2.949
5.182
5.313
6.974
6.981
6.997
7.003
7.025
7.033
7.135
7.143
7.154
7.160
7.164
7.181
7.244
7.258
7.263
7.268
7.280
7.293
7.312
7.317
7.324
7.328
7.330
7.339
7.347
7.359
7.560
7.567
7.572
7.585
7.592

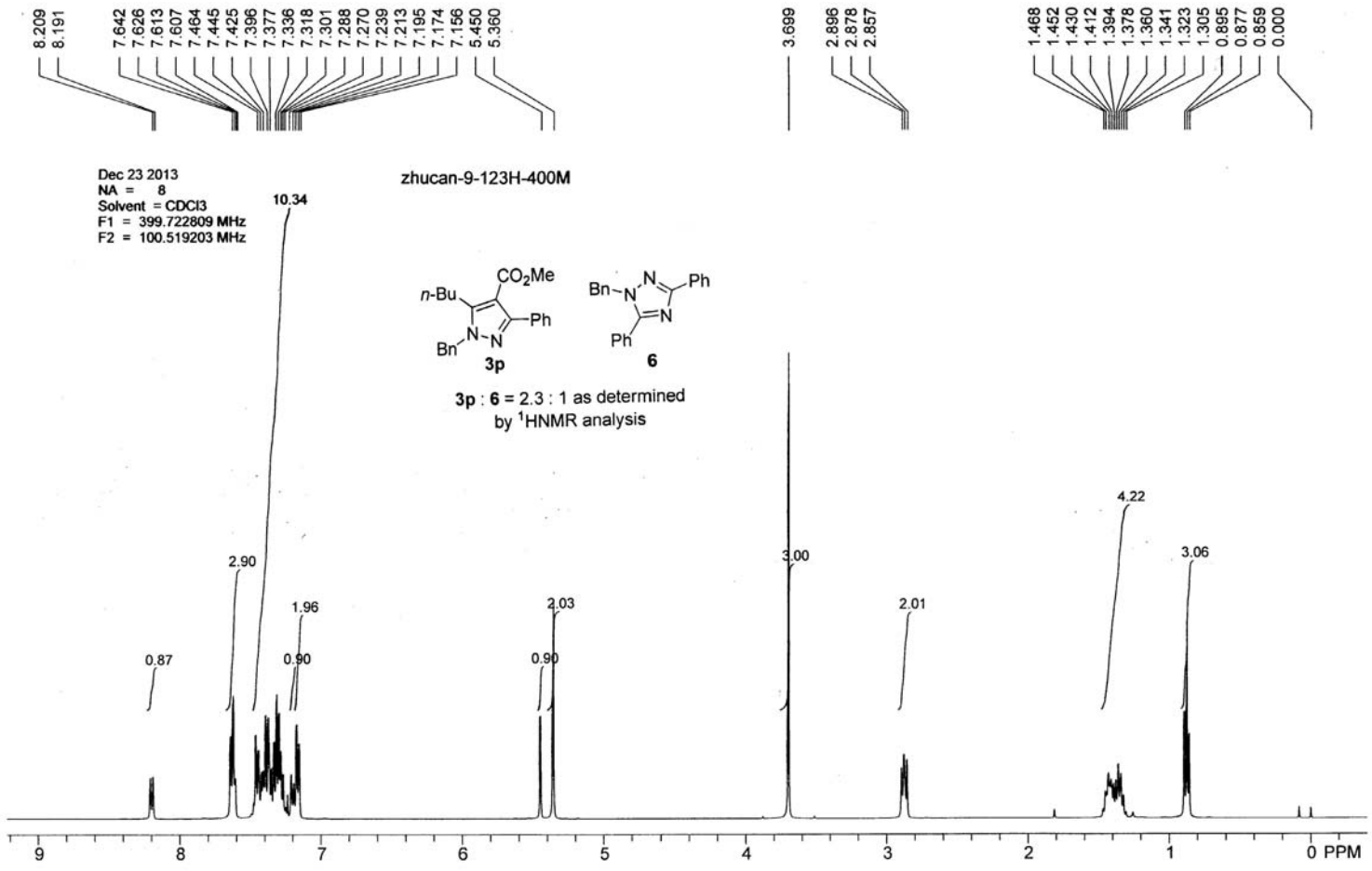

13.277
18.924
52.397
65.734
76.579
77.000
77.429
108.865
115.558
115.846
127.722
127.922
128.059
128.171
128.311
128.527
128.637
129.370
132.010
132.047
133.262
135.744
150.043
153.154
160.687
163.503
163.948
spect, CDCl3,
Mon Jun 24 08:25:32 2013
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.900 usec
Recycle delay = 2.000 sec
NA = 1024
PTS1d = 32768
F1 = 75.475296 MHz
cb-12-57
CO2Bn
Ph
Et
N
N
F
3n
PPM
0
50
100
150
200
xx
residue from
petroleum ether.

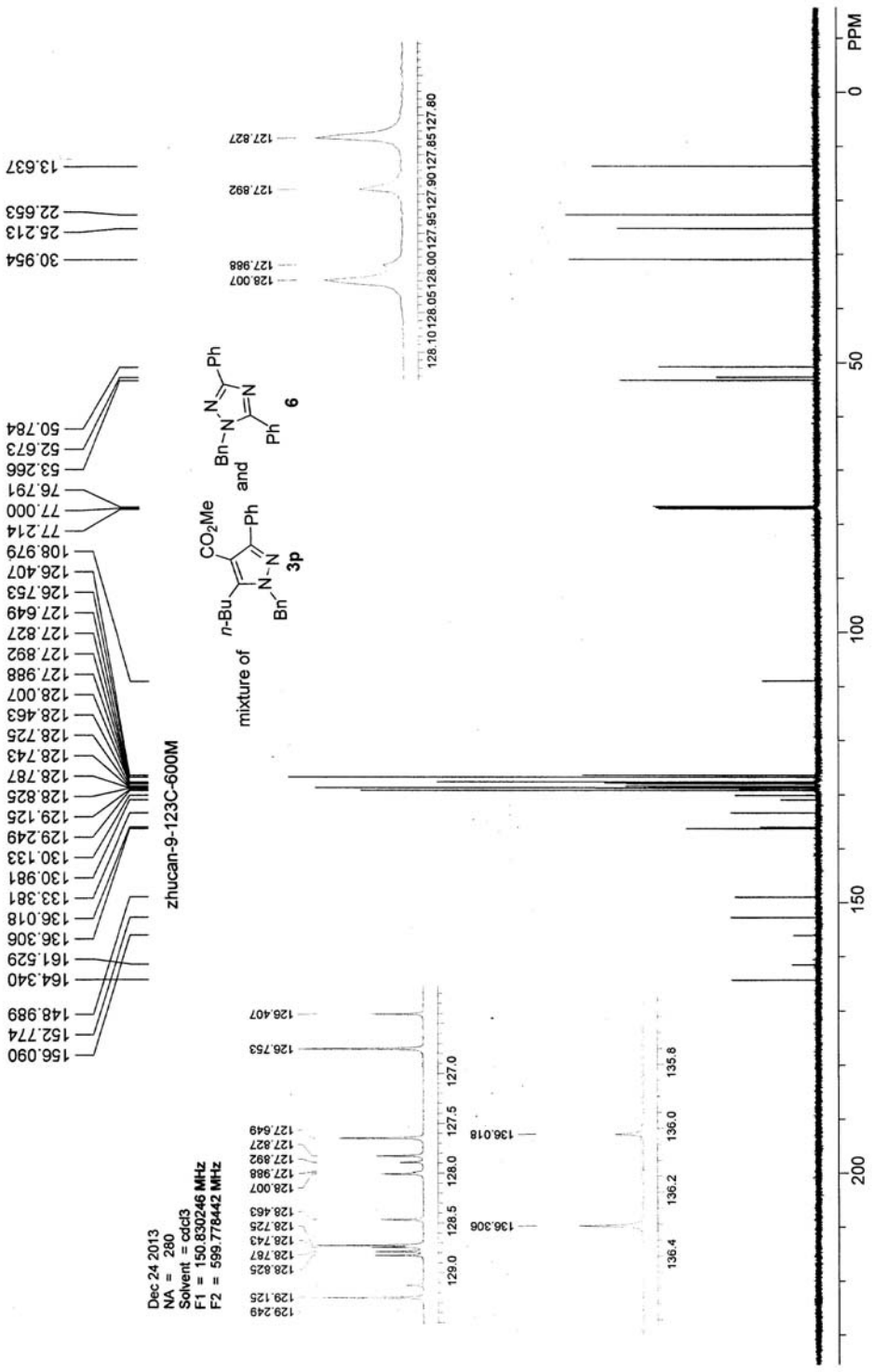

-114.138
Et
CO2Bn
Ph
N
N
3n
F
spect, CDCl3,
Mon Jun 17 20:30:58 2013
USER: nmr
SOLVENT:
Experiment = zgfhigqn
Pulse length = 13.700 usec
Recycle delay = 1.000 sec
NA = 16
PTS1d = 65536
F1 = 282.376129 MHz
cb-12-57-F
0
-50
-100
-150
-200
PPM


spect, CDCl3,
Thu Jun 13 09:35:56 2013
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.600 usec
Recycle delay = 1.000 sec
NA = 16
PTS1d = 32768
F1 = 300.131866 MHz
cb-12-54
3o
PPM
0.000
1.007
1.040
1.091
1.132
1.256
1.514
1.539
1.549
1.564
1.574
1.638
1.672
2.802
2.826
3.699
5.331
6.980
7.009
7.036
7.111
7.129
7.156
7.255
7.357
7.372
7.396
7.415
7.600
7.620
7.626
3.06
2.05
2.06
1.99
2.00
6.03
2.00
6.55
5.17

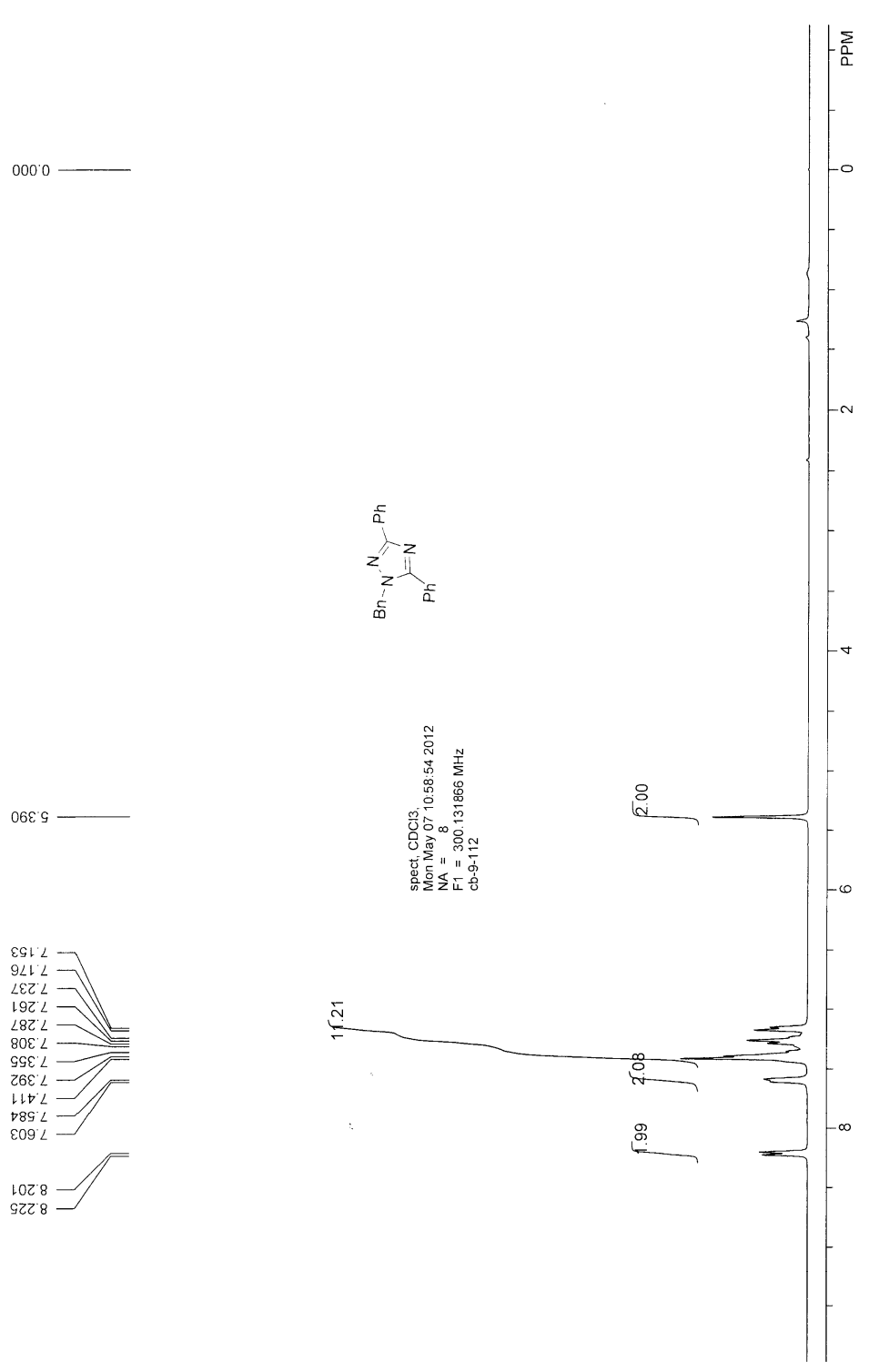

spect, CDCl3,
Thu Jun 13 10:45:47 2013
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.900 usec
Recycle delay = 2.000 sec
NA = 1024
PTS1d = 32768
F1 = 75.475296 MHz
cb-12-54
164.511
163.945
160.678
152.910
147.626
133.322
132.100
132.060
129.197
128.518
128.415
128.072
127.696
115.800
115.505
109.795
77.422
77.000
76.578
52.601
50.849
50.816
38.435
33.136
32.520
26.172
26.136
CO2Me
Ph
N
N
Cy
F
3o
PPM
0
50
100
150
200
xx
residue from
petroleum ether


114.329
CO2Me
Cy
Ph
N
N
3o
F
spect, CDCl3,
Thu Jun 13 09:38:06 2013
USER: nmr
SOLVENT:
Experiment = zgfhigqn
Pulse length = 13.700 usec
Recycle delay = 1.000 sec
NA = 16
PTS1d = 65536
F1 = 282.376129 MHz
cb-12-54
0
-50
-100
-150
-200
PPM

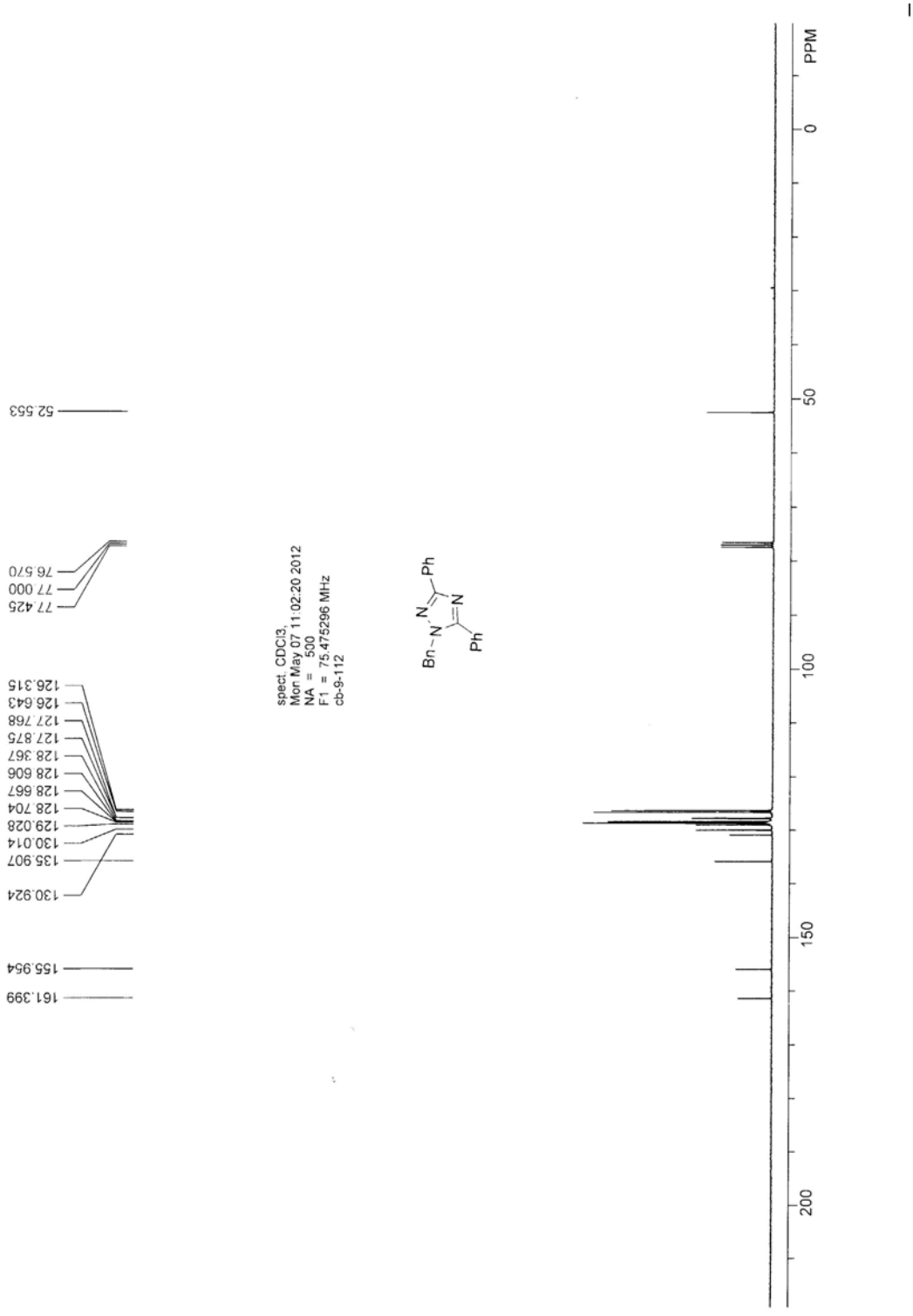

8.209
8.191
7.642
7.626
7.613
7.607
7.464
7.445
7.425
7.396
7.377
7.336
7.318
7.301
7.288
7.270
7.239
7.213
7.195
7.174
7.156
5.450
5.360
3.699
2.896
2.878
2.857
1.468
1.452
1.430
1.412
1.394
1.378
1.360
1.341
1.323
1.305
0.895
0.877
0.859
0.000
Dec 23 2013
NA = 8
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz
zhucan-9-123H-400M
10.34
2.90
1.96
0.87
0.90
2.03
0.90
3.00
2.01
4.22
3.06
n-Bu
CO2Me
Ph
Bn
N
3p
Bn
Ph
Ph
6
3p : 6 = 2.3 : 1 as determined
by 1HNMR analysis
9
8
7
6
5
4
3
2
1
0 PPM

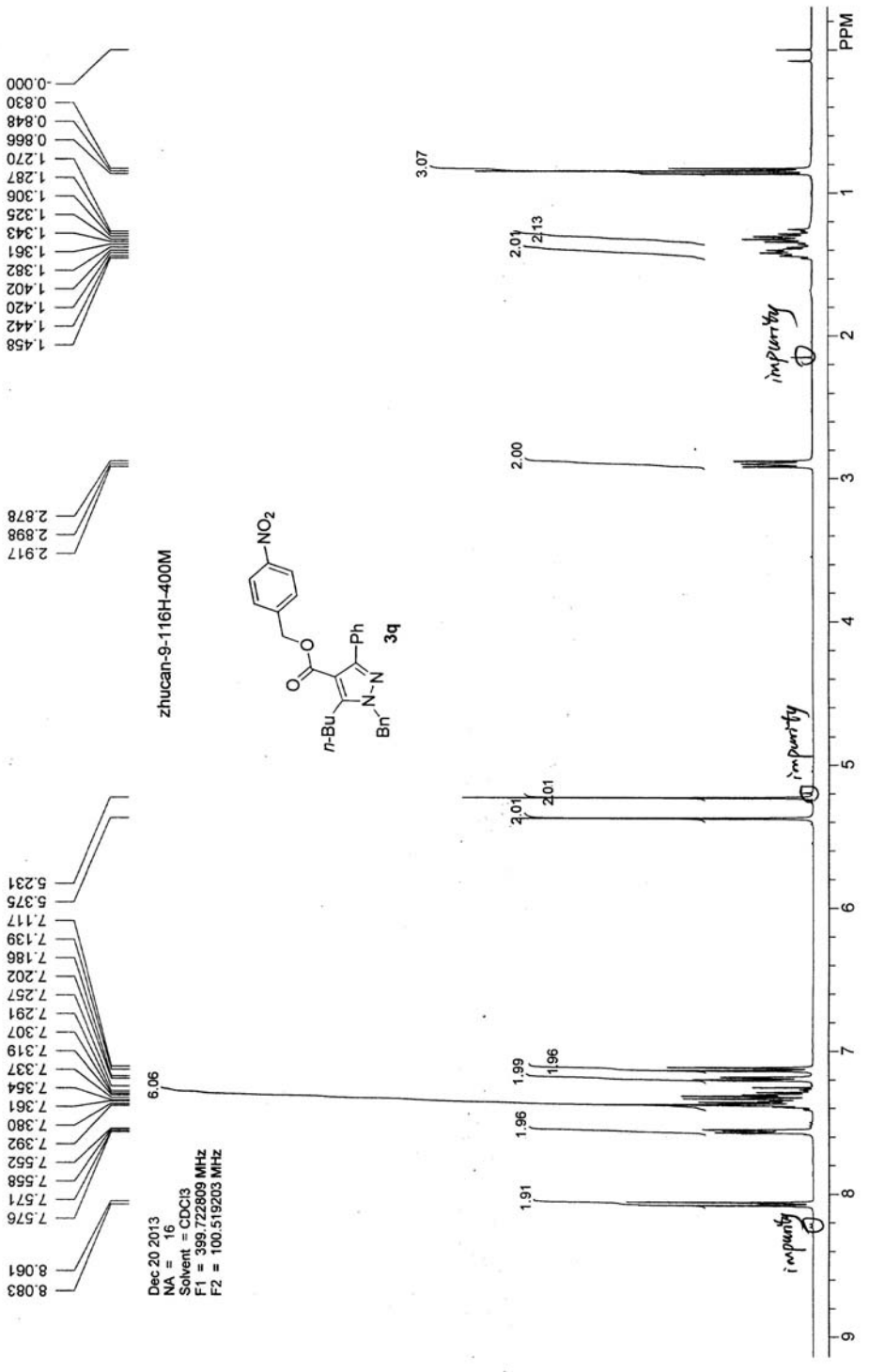

zhucan-9-123C-600M
Dec 24 2013
NA = 280
Solvent = cdcl3
F1 = 150.830246 MHz
F2 = 599.778442 MHz
mixture of
and
PPM

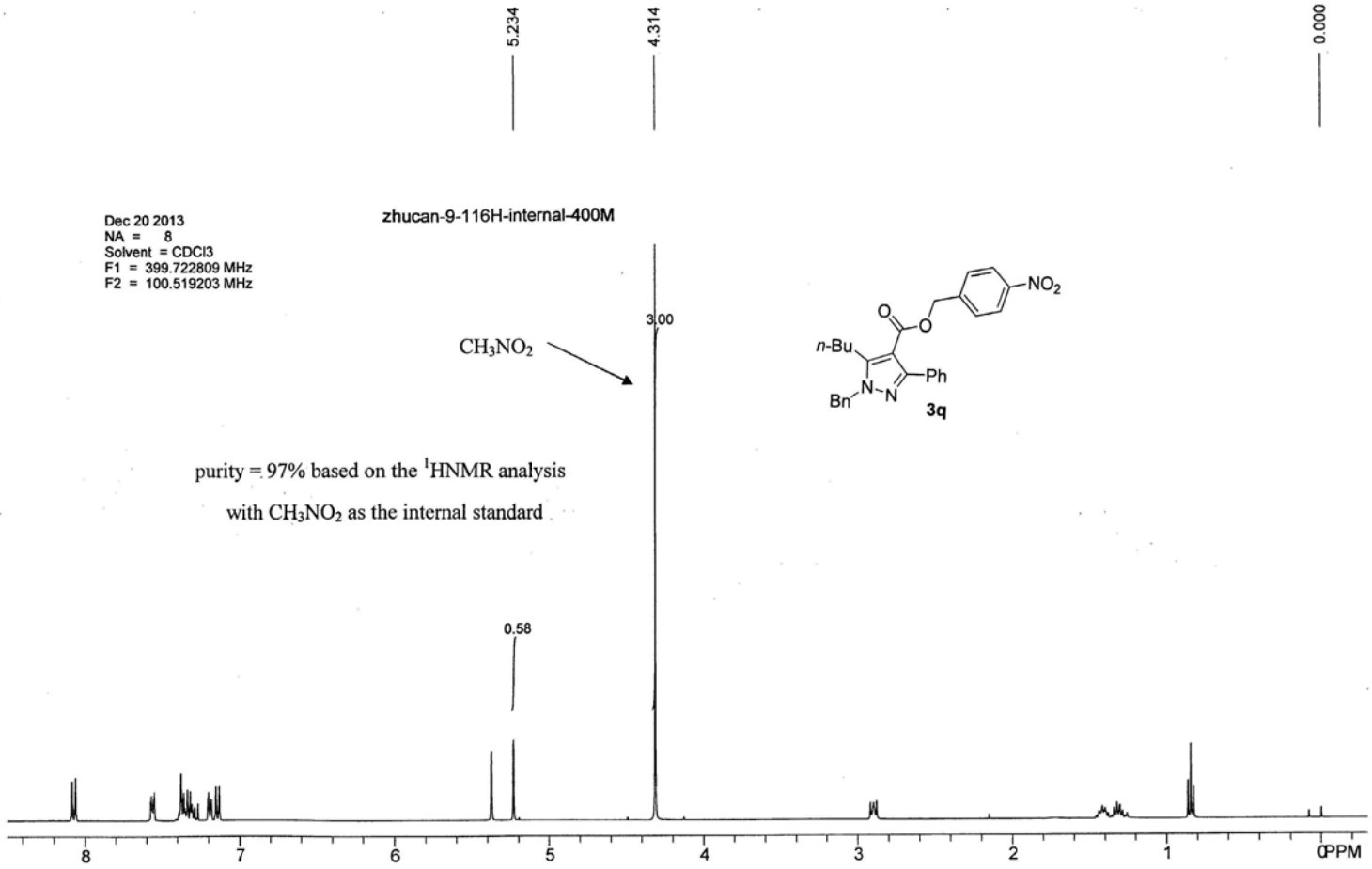
^{1}H NMR spectrum for **6**:

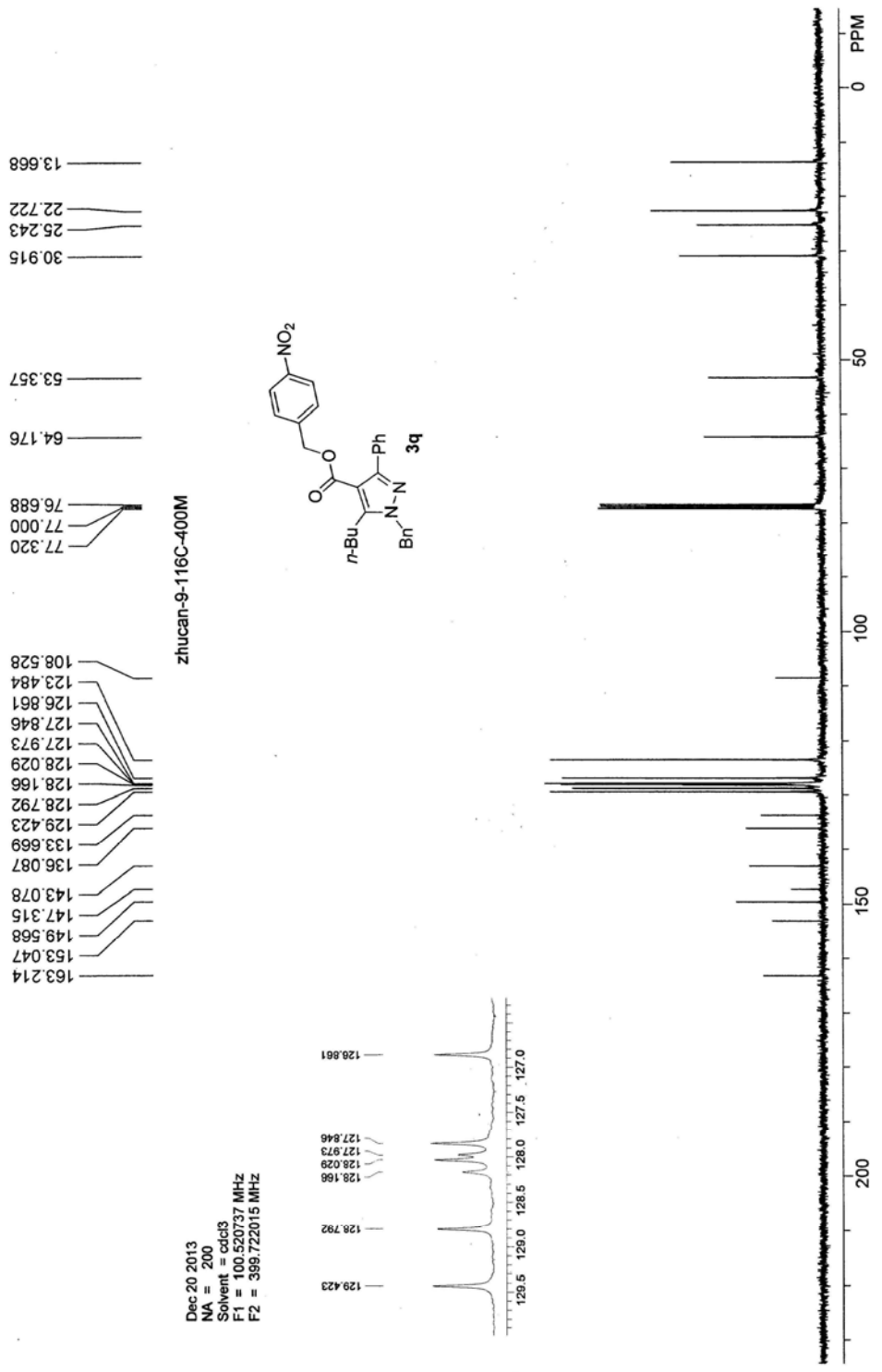


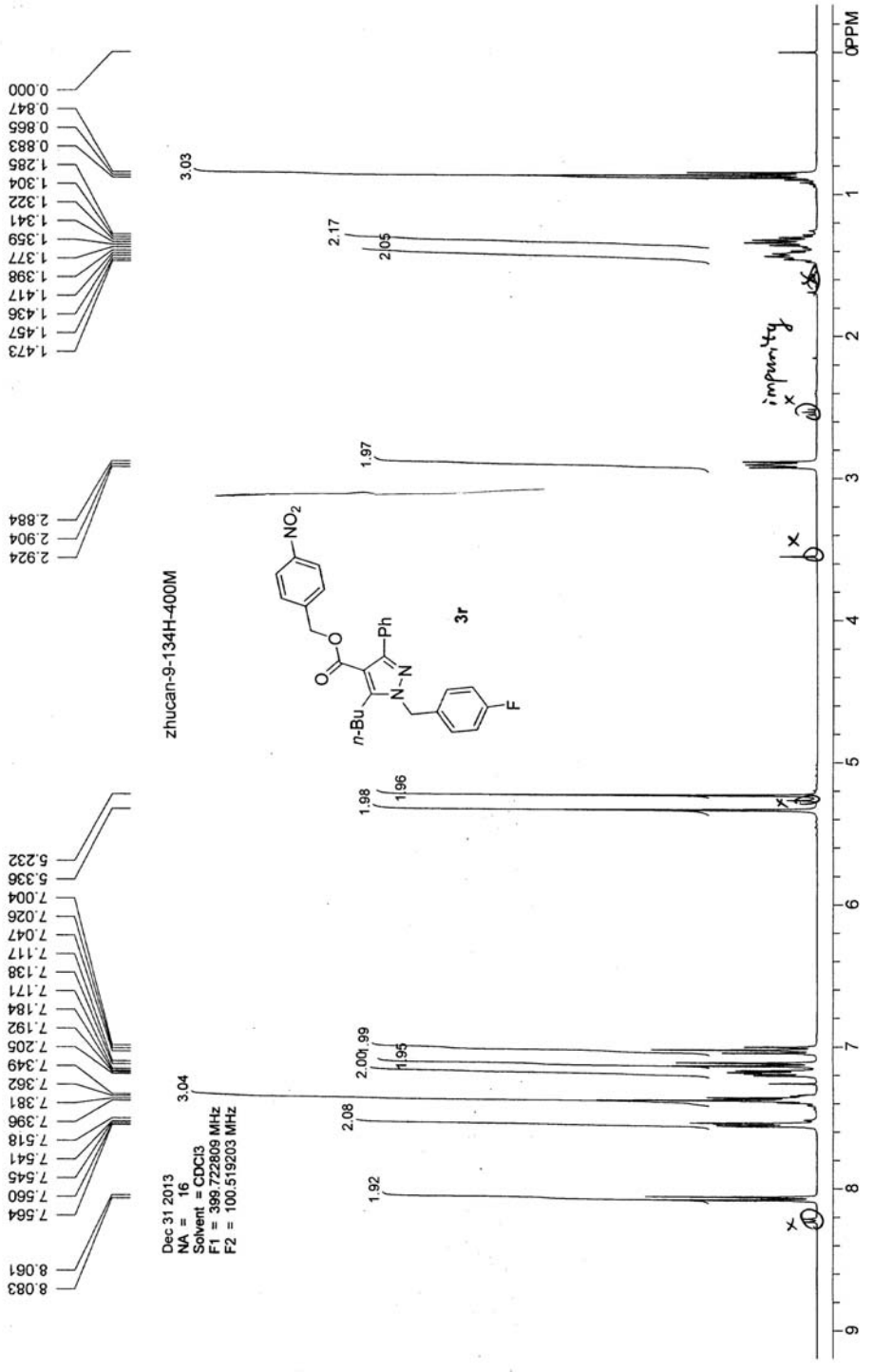
^{13}C NMR spectrum for **6**:

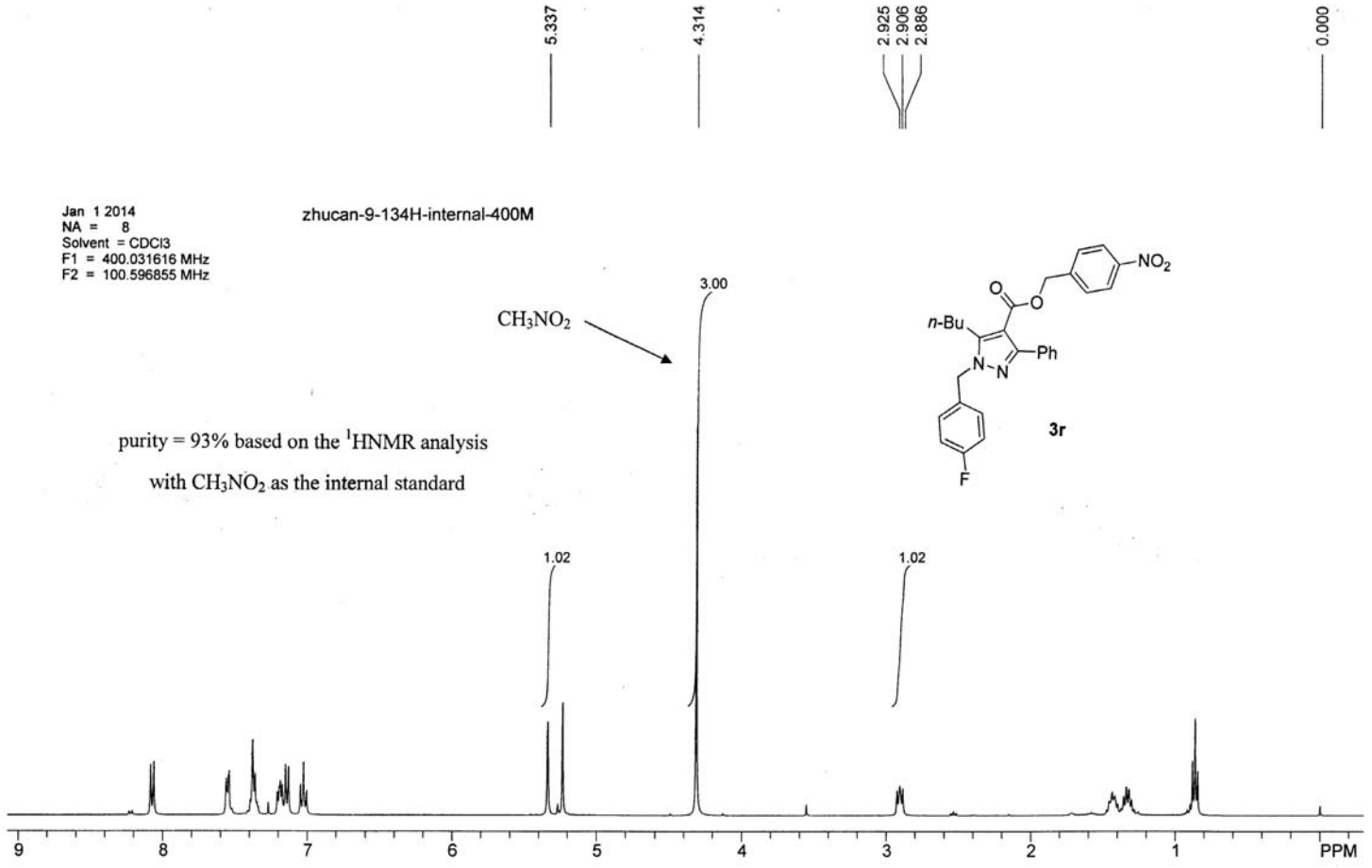


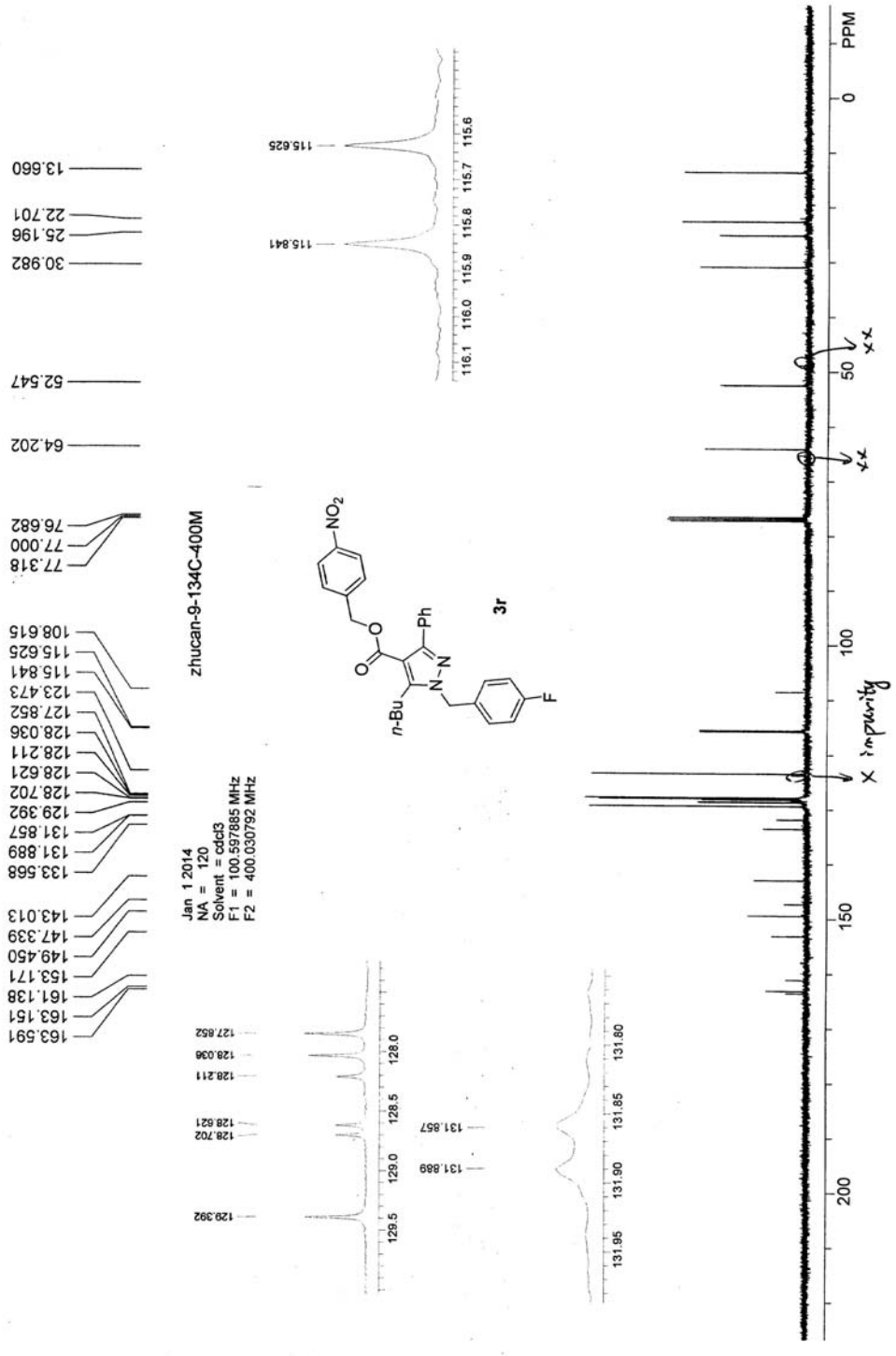

zhucan-9-116H-400M
Dec 20 2013
NA = 16
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz
3q
impurity
PPM

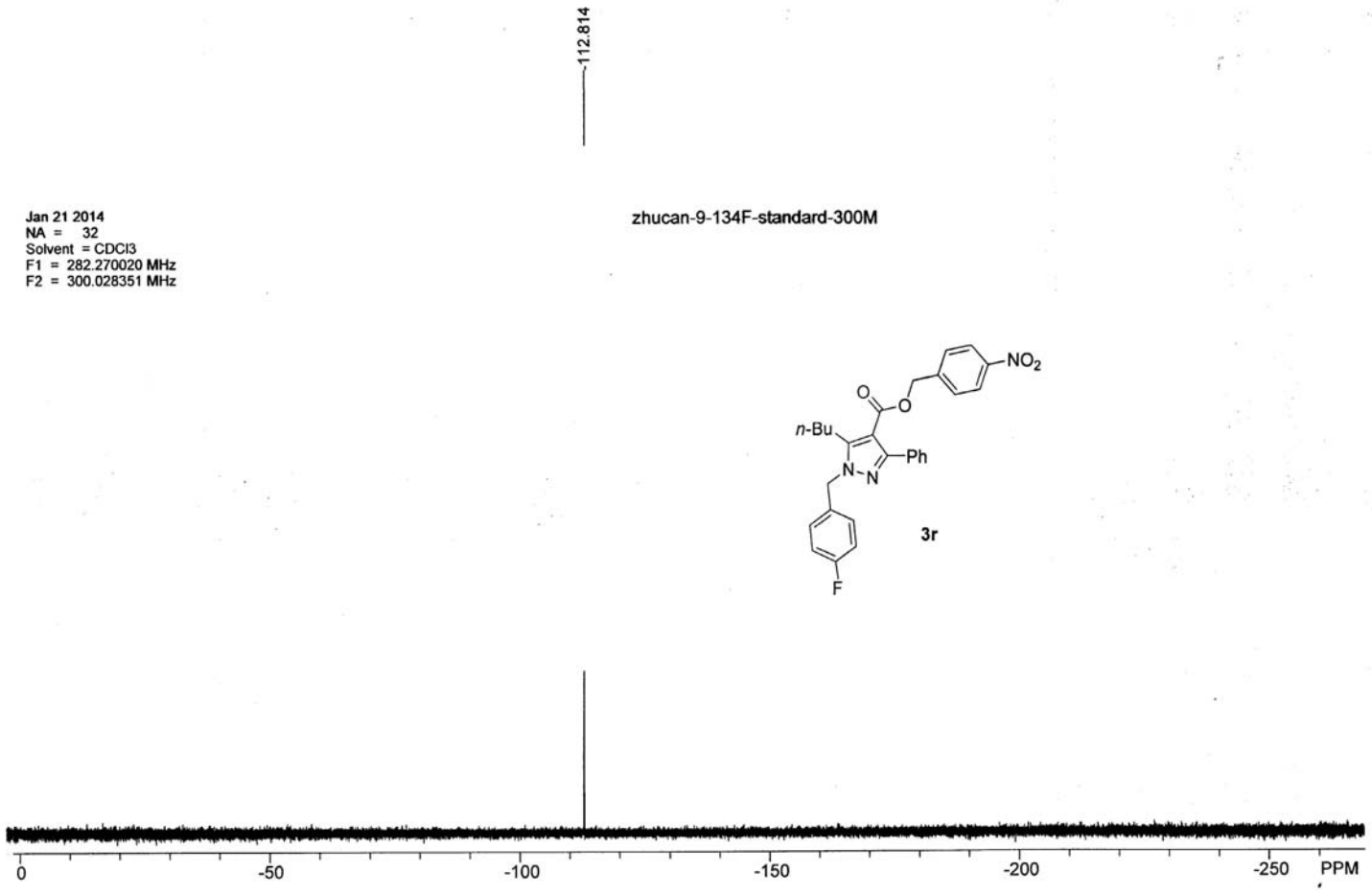

5.234
4.314
0.000
zhucan-9-116H-internal-400M
Dec 20 2013
NA = 8
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz
3.00
CH_3NO_2
NO_2
O
O
n-Bu
Ph
N
N
Bn
3q
purity = 97% based on the ^{1}HNMR analysis
with CH_3NO_2 as the internal standard
0.58
8
7
6
5
4
3
2
1
0
PPM

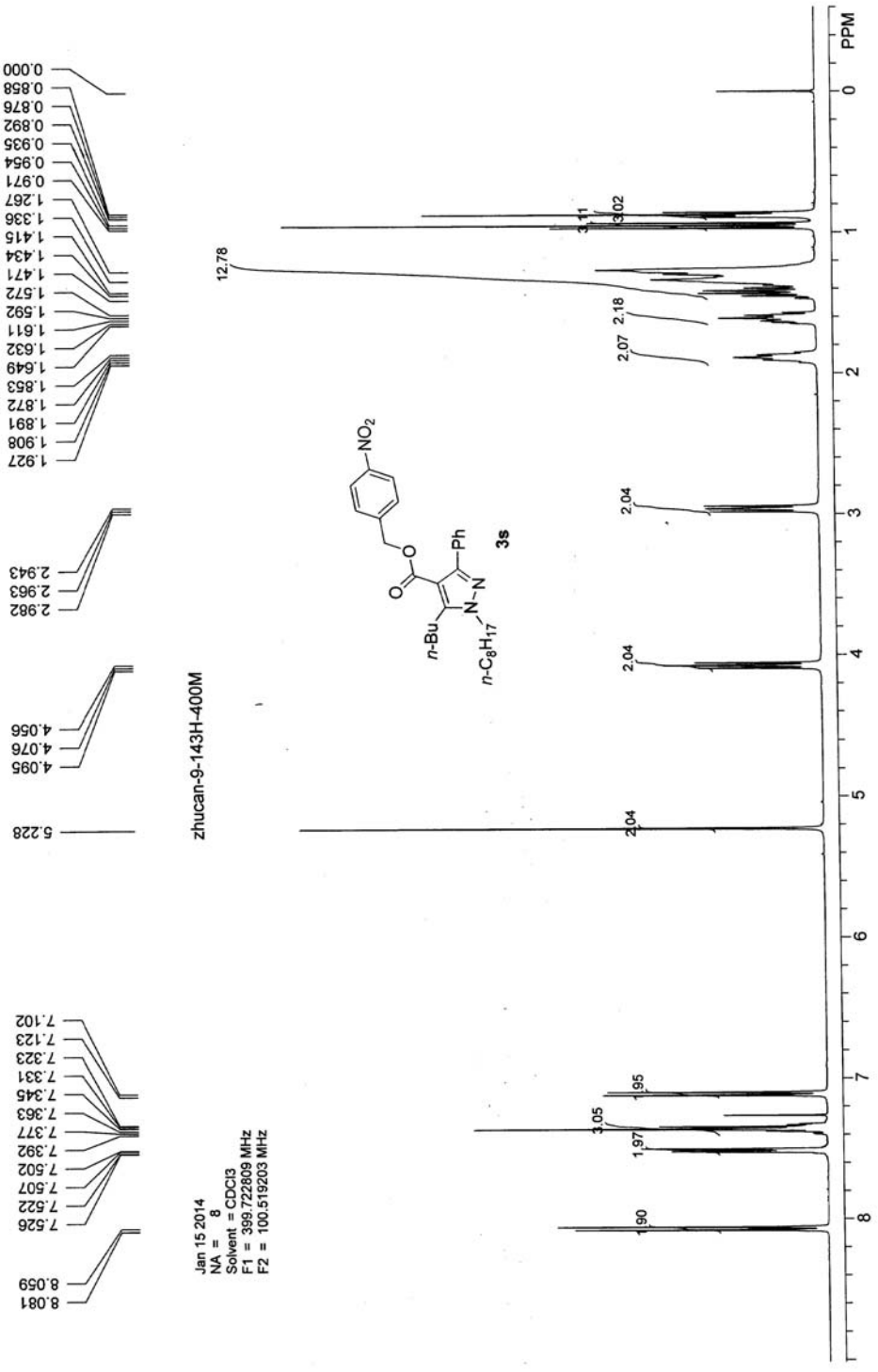

zhucan-9-116C-400M
Dec 20 2013
NA = 200
Solvent = cdcl3
F1 = 100.520737 MHz
F2 = 399.722015 MHz
3q
n-Bu
Bn
Ph
NO2
13.668
22.722
25.243
30.915
53.357
64.176
76.688
77.000
77.320
108.528
123.484
126.861
127.846
127.973
128.029
128.166
128.792
129.423
133.669
136.087
143.078
147.315
149.568
153.047
163.214
PPM

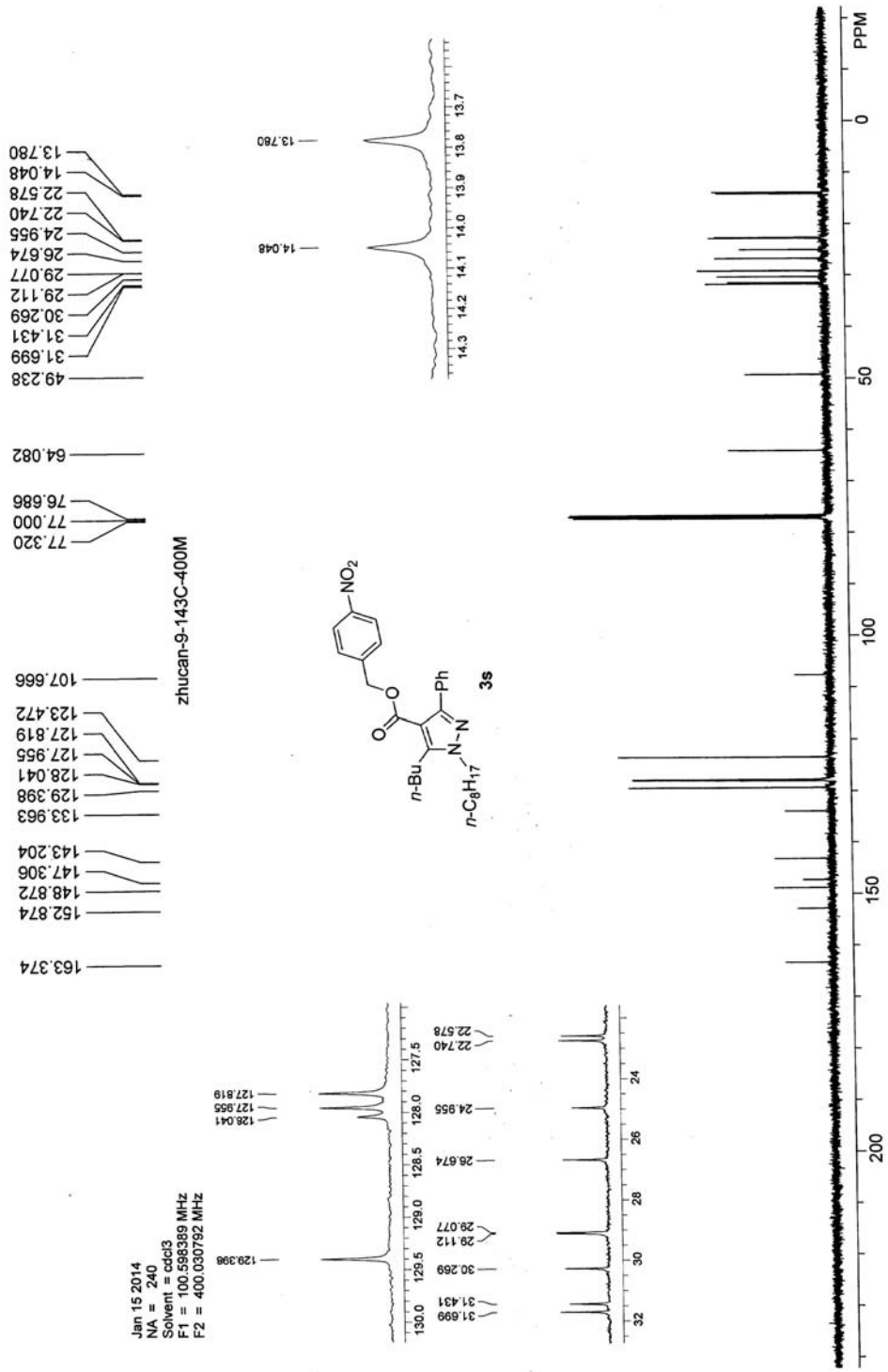

zhucan-9-134H-400M
Dec 31 2013
NA = 16
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz
3r
n-Bu
Ph
F
NO2
impurity
PPM

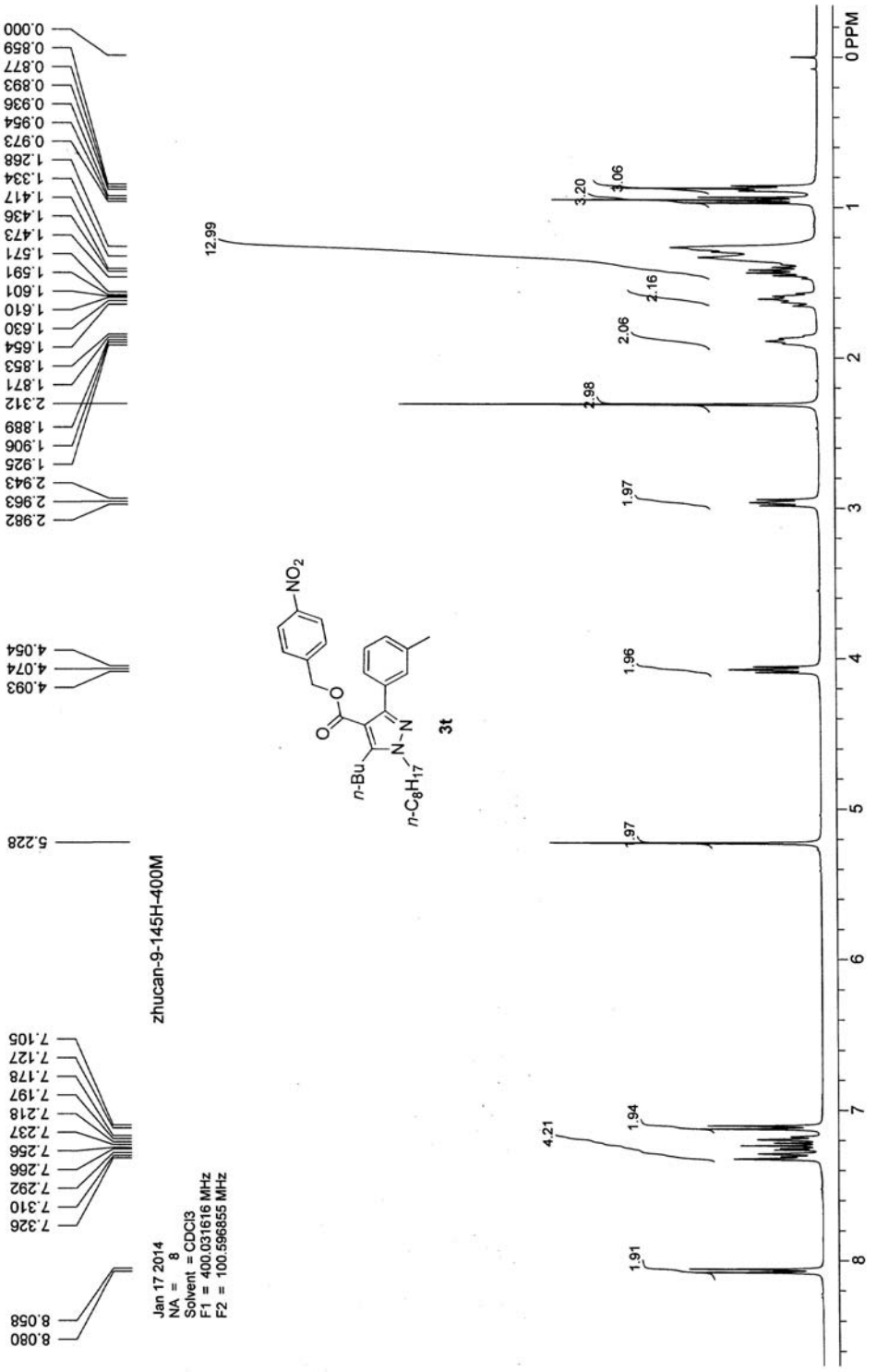

5.337
4.314
2.925
2.906
2.886
0.000
Jan 1 2014
NA = 8
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz
zhucan-9-134H-internal-400M
3.00
CH_3NO_2
purity = 93% based on the ^{1}HNMR analysis
with CH_3NO_2 as the internal standard
1.02
1.02
NO_2
O
O
n-Bu
Ph
N
N
F
3r
9
8
7
6
5
4
3
2
1
PPM

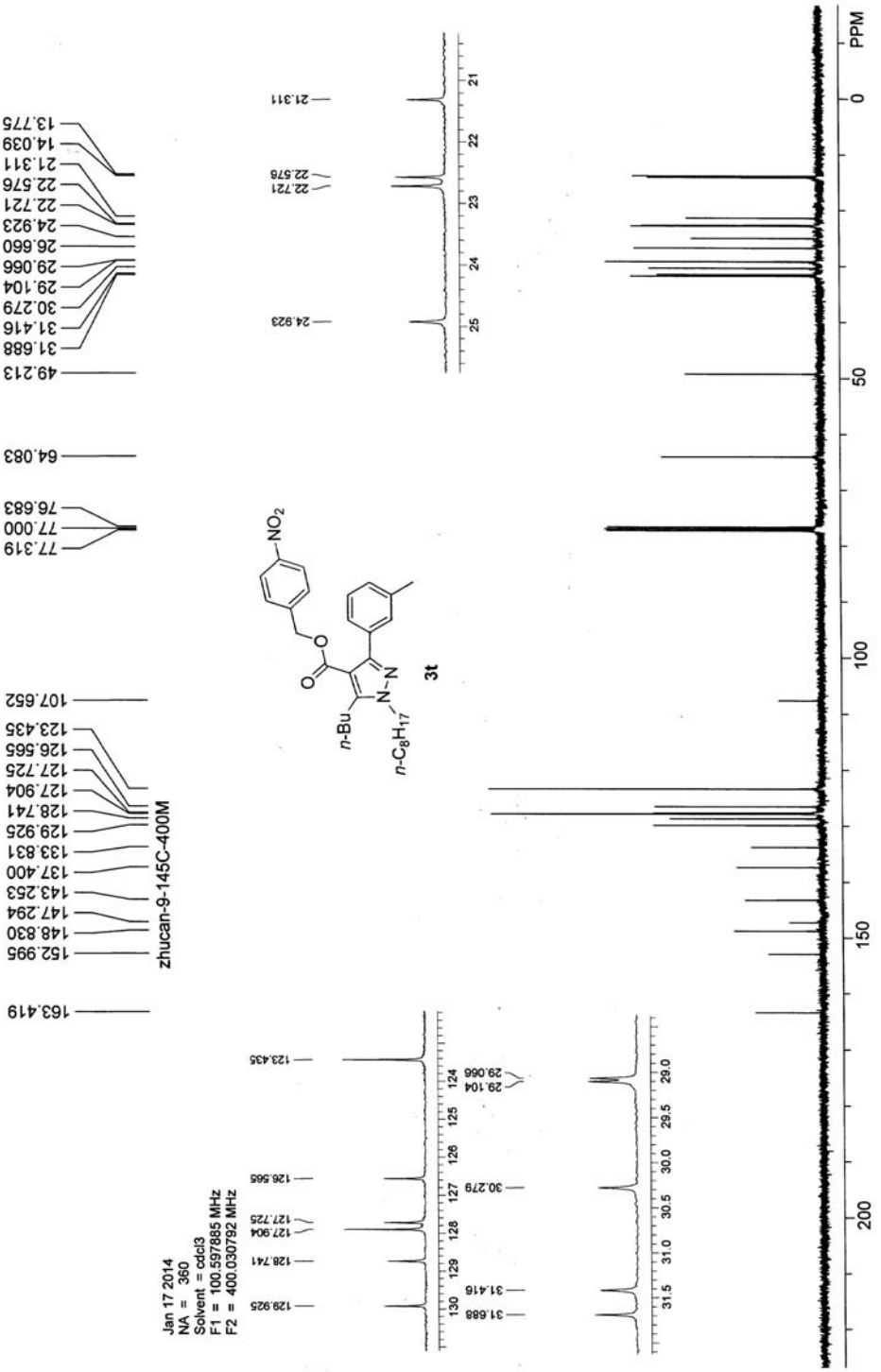

zhucan-9-134C-400M
Jan 1 2014
NA = 120
Solvent = cdcl3
F1 = 100.597885 MHz
F2 = 400.030792 MHz
3r
n-Bu
Ph
F
PPM
13.660
22.701
25.196
30.982
52.547
64.202
76.682
77.000
77.318
108.615
115.625
115.841
123.473
127.852
128.036
128.211
128.621
128.702
129.392
131.857
131.889
133.568
143.013
147.339
149.450
153.171
161.138
163.151
163.591

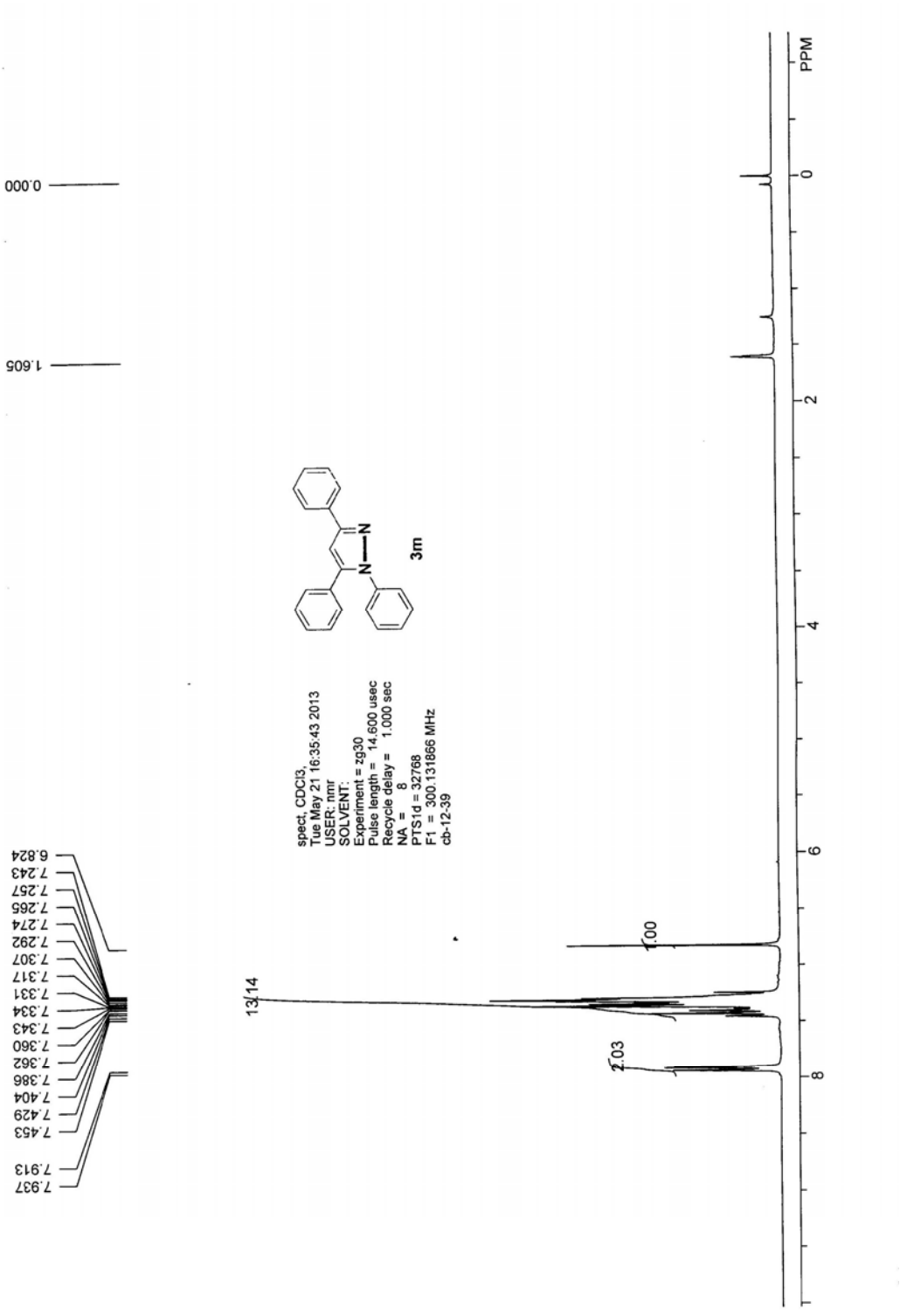

112.814
Jan 21 2014
NA = 32
Solvent = CDCl3
F1 = 282.270020 MHz
F2 = 300.028351 MHz
zhucan-9-134F-standard-300M
NO2
O
O
n-Bu
Ph
N
N
F
3r
0
-50
-100
-150
-200
-250
PPM

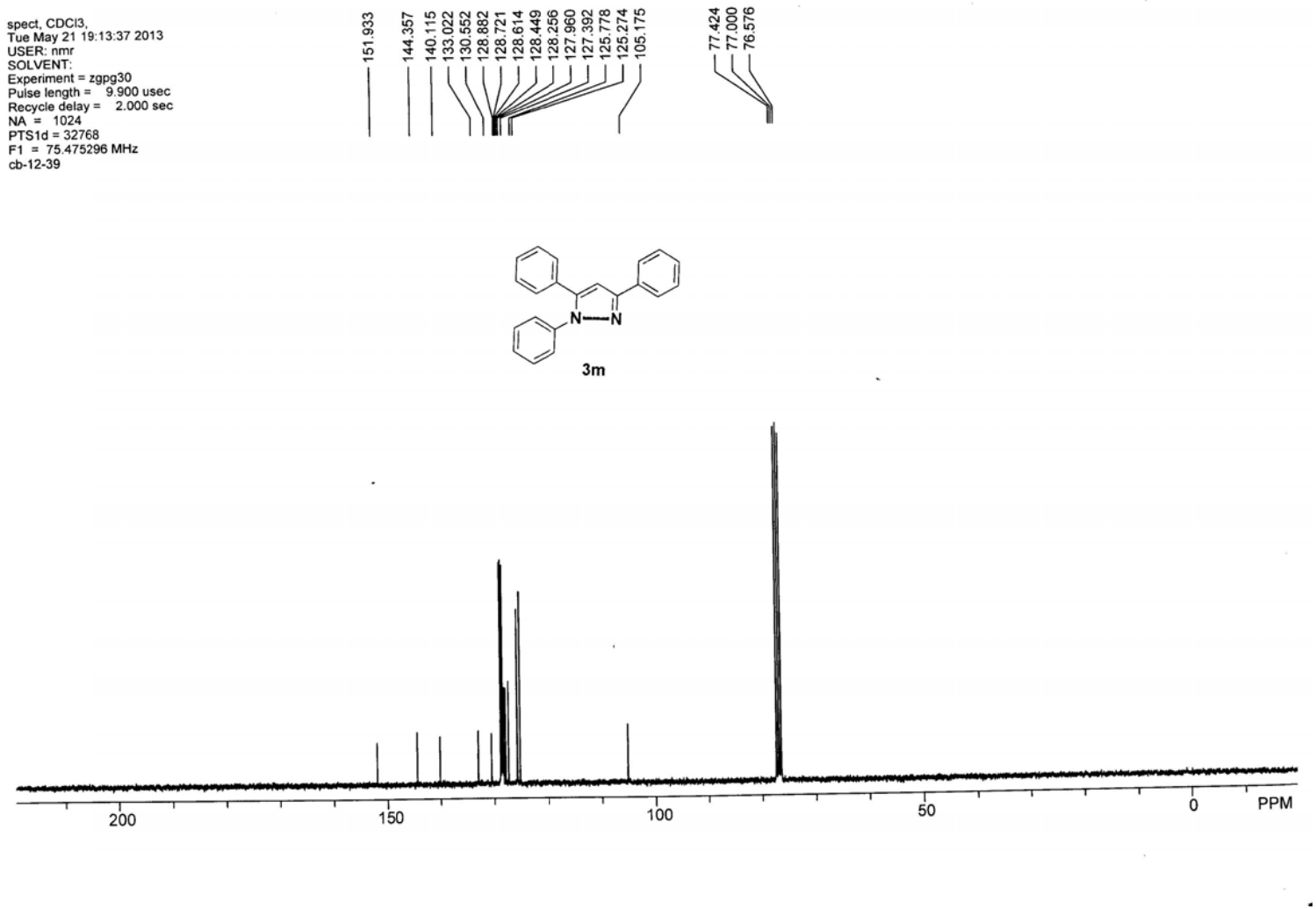

zhucan-9-143H-400M
Jan 15 2014
NA = 8
Solvent = CDCl3
F1 = 399.722809 MHz
F2 = 100.519203 MHz
3s
PPM


zhucan-9-143C-400M
Jan 15 2014
NA = 240
Solvent = cdcl3
F1 = 100.598389 MHz
F2 = 400.030792 MHz
13.780
14.048
22.578
22.740
24.955
26.674
29.077
29.112
30.269
31.431
31.699
49.238
64.082
76.686
77.000
77.320
107.666
123.472
127.819
127.955
128.041
129.398
133.963
143.204
147.306
148.872
152.874
163.374
n-Bu
Ph
n-C8H17
NO2
3s
PPM


zhucan-9-145H-400M
Jan 17 2014
NA = 8
Solvent = CDCl3
F1 = 400.031616 MHz
F2 = 100.596855 MHz
3t
n-Bu
n-C8H17
NO2
12.99
4.21
3.20
3.06
2.98
2.16
2.06
1.97
1.96
1.94
1.91
0 PPM


zhucan-9-145C-400M
Jan 17 2014
NA = 360
Solvent = cdcl3
F1 = 100.597885 MHz
F2 = 400.030792 MHz
3t
PPM


0.000
1.605
6.824
7.243
7.257
7.265
7.274
7.292
7.307
7.317
7.331
7.334
7.343
7.360
7.362
7.386
7.404
7.429
7.453
7.913
7.937
spect, CDCl3,
Tue May 21 16:35:43 2013
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.600 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
cb-12-39
3m
13.14
1.00
2.03
PPM
0
2
4
6
8


spect, CDCl3,
Tue May 21 19:13:37 2013
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.900 usec
Recycle delay = 2.000 sec
NA = 1024
PTS1d = 32768
F1 = 75.475296 MHz
cb-12-39
151.933
144.357
140.115
133.022
130.552
128.882
128.721
128.614
128.449
128.256
127.960
127.392
125.778
125.274
105.175
77.424
77.000
76.576
N
N
3m
200
150
100
50
0
PPM