

**Efficient Synthesis of 1,2-Bis(alkoxycarbonyl)pyrazol-3-ones from 2,3-Allenic
Acids, Azodicarboxylates and PPh₃**

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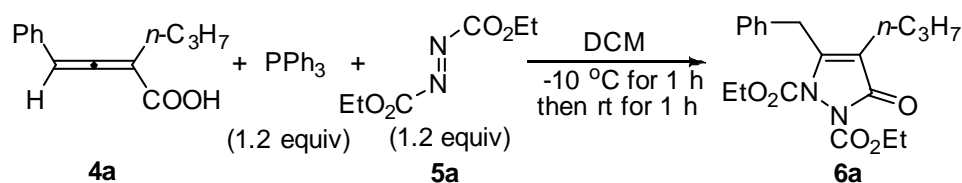
1. General Information:

The NMR spectra were recorded with a Bruker AM-300 instrument. Chemical shifts are reported in relative to TMS [^1H : $\delta = 0.00$ ppm (TMS)], solvent residual peaks [^{13}C : $\delta = 77.0$ ppm (CDCl_3)]. IR spectra were measured with a Bruker Tensor 27 instrument. MS analyses were performed with an Agilent Technologies 5975C instrument. HRMS analyses were performed with a Waters GCT Premier instrument. All reactions were carried out in oven dried Schlenk tubes. Methylene dichloride was dried over CaH_2 and distilled freshly before use. Other reagents were used as received from commercial sources. The petroleum ether (30-60 °C) for chromatography was distilled before use. All the temperatures unless otherwise specified are referred to the ice-salt baths used.

2. Experimental details:

(1) Diethyl 3-oxo-4-(*n*-propyl)-5-benzyl-1*H*-pyrazole-1,2(3*H*)-dicarboxylate (6a)

(entry 1, Table 2) (Irz-5-87).



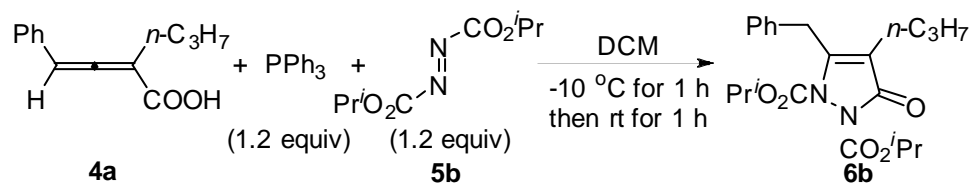
Typical procedure: Under an atmosphere of argon, a solution of **5a** (63.2 mg, 0.36 mmol) in 1 mL of DCM was added dropwise to a solution of triphenyl phosphine (94.7 mg, 0.36 mmol) and **4a** (60.6 mg, 0.30 mmol) in 3 mL of DCM at the bath temperature of -10 °C with stirring in 1 min. After being stirred at -10 °C for 1 h and then at room temperature for an additional 1 h, the reaction mixture was evaporated and the residue was purified by flash chromatography on silica gel (Φ 20 mm x 13 cm,

eluent: petroleum ether (30-60 °C)/ethyl acetate = 5:1) at the gauge pressure of 0.1 MPa to afford 79.4 mg (73%) of **6a** as oil: ^1H NMR (300 MHz, CDCl_3) δ 7.37-7.21 (m, 3 H, ArH), 7.20-7.11 (m, 2 H, ArH), 4.41 (q, $J = 7.1$ Hz, 2 H, OCH_2), 4.23 (s, 2 H, PhCH_2), 4.13 (q, $J = 7.2$ Hz, 2 H, OCH_2), 2.27 (t, $J = 7.8$ Hz, 2 H, $=\text{CCH}_2$), 1.56-1.41 (m, 2 H, CH_2), 1.40 (t, $J = 7.1$ Hz, 3 H, CH_3 (in COOEt)), 1.17 (t, $J = 7.1$ Hz, 3 H, CH_3 (in COOEt)), 0.90 (t, $J = 7.4$ Hz, 3 H, CH_3); ^{13}C NMR (75.4 MHz, CDCl_3) δ 164.2, 152.5, 149.7, 149.0, 135.8, 128.7, 127.6, 126.8, 115.0, 64.4, 64.3, 32.0, 24.3, 21.7, 14.1, 13.8, 13.7; MS (EI) m/z (%) 360 (M^+ , 0.53), 187 (100); IR (neat) 2963, 1787, 1748, 1725, 1636, 1603, 1496, 1370, 1264, 1053 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_5$ (M^+): 360.1685; Found: 360.1680.

The following compounds were prepared according to this procedure.

(2) Diisopropyl 3-oxo-4-(*n*-propyl)-5-benzyl-1*H*-pyrazole-1,2(3*H*)-dicarboxylate

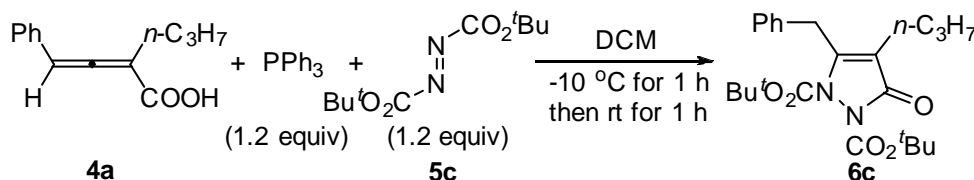
(6b) (entry 2, Table 2) (lrz-4-128).



The reaction of **5b** (72.9 mg, 0.36 mmol), triphenyl phosphine (94.2 mg, 0.36 mmol), and **4a** (60.2 mg, 0.30 mmol) in DCM (4 mL) afforded 97.4 mg (84%) of **6b** as oil (eluent: petroleum ether (30-60 °C)/ethyl acetate = 6:1): ^1H NMR (300 MHz, CDCl_3) δ 7.37-7.22 (m, 3 H, ArH), 7.22-7.12 (m, 2 H, ArH), 5.12 (septet, $J = 6.3$ Hz, 1 H, OCH), 4.93 (septet, $J = 6.3$ Hz, 1 H, OCH), 4.23 (s, 2 H, PhCH_2), 2.25 (t, $J = 7.8$ Hz, 2 H, $=\text{CCH}_2$), 1.57-1.43 (m, 2 H, CH_2), 1.41 (d, $J = 6.3$ Hz, 6 H, 2 x CH_3 (^iPr)),

1.15 (d, $J = 6.3$ Hz, 6 H, 2 x CH₃ (^{*i*}Pr)), 0.90 (t, $J = 7.5$ Hz, 3 H, CH₃); ¹³C NMR (75.4 MHz, CDCl₃) δ 164.4, 152.5, 149.2, 148.8, 136.0, 128.7, 127.7, 126.8, 114.8, 73.3, 72.9, 32.0, 24.4, 21.7, 21.3, 13.9; MS (ESI) m/z (%) 389 (M⁺+H); IR (neat) 2983, 1784, 1746, 1724, 1634, 1603, 1496, 1376, 1264, 1103, 1051 cm⁻¹; HRMS (MALDI/DHB) calcd. for C₂₁H₂₈N₂O₅Na (M+Na⁺): 411.1890; Found: 411.1910.

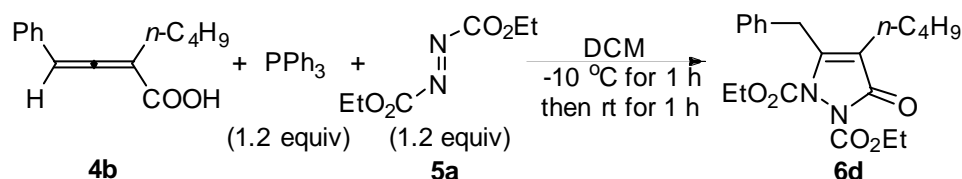
(3) Di-*tert*-butyl 3-oxo-4-(*n*-propyl)-5-benzyl-1*H*-pyrazole-1,2(3*H*)-dicarboxylate (6c) (entry 3, Table 2) (lrz-5-129).



The reaction of **5c** (83.1 mg, 0.36 mmol), triphenyl phosphine (94.7 mg, 0.36 mmol), and **4a** (60.4 mg, 0.30 mmol) in DCM (4 mL) afforded 88.3 mg (71%) of **6c** as solid (Φ 20 mm x 11 cm, eluent: petroleum ether (30-60 °C)/ethyl acetate = 10:1); m.p. 117-118 °C (petroleum ether/ethyl acetate); ¹H NMR (300 MHz, CDCl₃) δ 7.34-7.21 (m, 3 H, ArH), 7.21-7.10 (m, 2 H, ArH), 4.22 (s, 2 H, PhCH₂), 2.28-2.17 (m, 2 H, =CCH₂), 1.60 (s, 9 H, C(CH₃)₃), 1.54-1.44 (m, 2 H, CH₂), 1.33 (s, 9 H, C(CH₃)₃), 0.89 (t, $J = 7.4$ Hz, 3 H, CH₃); ¹³C NMR (75.4 MHz, CDCl₃) δ 164.4, 151.9, 148.0, 147.5, 136.0, 128.6, 127.7, 126.7, 114.2, 85.6, 84.9, 31.7, 27.9, 27.4, 24.4, 21.7, 13.9; MS (ESI) m/z (%) 439 (M+Na⁺); IR (KBr) 2981, 1783, 1744, 1720, 1633, 1603, 1496, 1395, 1371, 1284, 1256, 1146, 1054 cm⁻¹; Anal Calcd for C₂₃H₃₂N₂O₅: C, 66.32; H, 7.74; N 6.73. Found: C, 66.28; H, 7.67; N 6.52.

(4) Diethyl 3-oxo-4-(*n*-butyl)-5-benzyl-1*H*-pyrazole-1,2(3*H*)-dicarboxylate (6d)

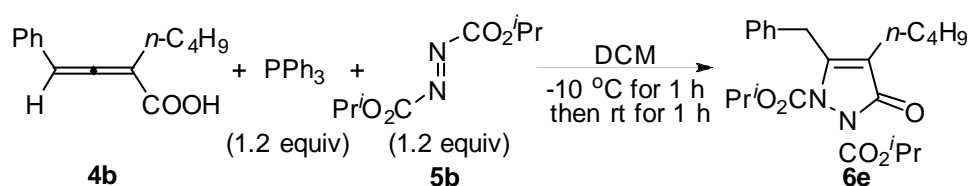
(entry 4, Table 2) (lrz-6-124).



The reaction of **5a** (62.8 mg, 0.36 mmol), triphenyl phosphine (94.9 mg, 0.36 mmol), and **4b** (65.2 mg, 0.30 mmol) in DCM (4 mL) afforded 75.4 mg (67%) of **6d** as oil (eluent: petroleum ether (30-60 °C)/ethyl acetate = 5:1): ^1H NMR (300 MHz, CDCl_3) δ 7.40-7.20 (m, 3 H, ArH), 7.20-7.11 (m, 2 H, ArH), 4.41 (q, $J = 7.2$ Hz, 2 H, OCH_2), 4.22 (s, 2 H, PhCH_2), 4.13 (q, $J = 7.2$ Hz, 2 H, OCH_2), 2.29 (t, $J = 7.7$ Hz, 2 H, $=\text{CCH}_2$), 1.53-1.23 (m, 7 H, $2 \times \text{CH}_2 + \text{CH}_3$ (in COOEt)), 1.17 (t, $J = 7.1$ Hz, 3 H, CH_3 (in COOEt)), 0.87 (t, $J = 7.2$ Hz, 3 H, CH_3); ^{13}C NMR (75.4 MHz, CDCl_3) δ 164.2, 152.5, 149.8, 149.1, 135.9, 128.8, 127.7, 126.9, 115.3, 64.5, 64.3, 32.1, 30.5, 22.5, 22.1, 14.2, 13.8, 13.7; MS (EI) m/z (%) 374 (M^+ , 4.29), 187 (100); IR (neat) 2959, 2932, 1787, 1748, 1727, 1636, 1603, 1496, 1370, 1267, 1056, 1025 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_5$ (M^+): 374.1842; Found: 374.1840.

(5) Diisopropyl 3-oxo-4-(*n*-butyl)-5-benzyl-1*H*-pyrazole-1,2(3*H*)-dicarboxylate

(6e) (entry 5, Table 2) (lrz-6-111).

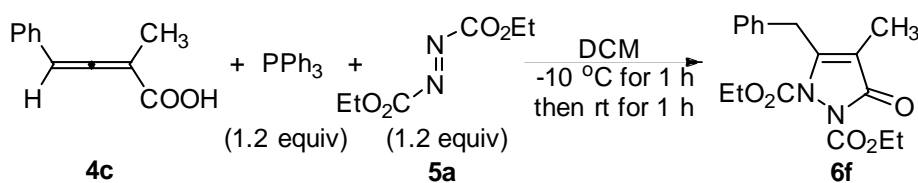


The reaction of **5b** (72.9 mg, 0.37 mmol), triphenyl phosphine (94.7 mg, 0.36

mmol), and **4b** (64.7 mg, 0.31 mmol) in DCM (4 mL) afforded 78.5 mg (65%) of **6e** as oil (Φ 20 mm \times 18 cm, eluent: petroleum ether (30-60 °C)/ethyl acetate = 6:1): ^1H NMR (300 MHz, CDCl_3) δ 7.36-7.19 (m, 3 H, ArH), 7.19-7.10 (m, 2 H, ArH), 5.12 (septet, $J = 6.3$ Hz, 1 H, OCH), 4.93 (septet, $J = 6.3$ Hz, 1 H, OCH), 4.23 (s, 2 H, PhCH_2), 2.27 (t, $J = 7.7$ Hz, 2 H, $=\text{CCH}_2$), 1.51-1.23 (m, 10 H, $2 \times \text{CH}_2 + 2 \times \text{CH}_3$ (^iPr)), 1.15 (d, $J = 6.3$ Hz, 6 H, $2 \times \text{CH}_3$ (^iPr)), 0.87 (t, $J = 7.2$ Hz, 3 H, CH_3); ^{13}C NMR (75.4 MHz, CDCl_3) δ 164.4, 152.3, 149.2, 148.8, 136.0, 128.7, 127.7, 126.8, 114.9, 73.3, 72.9, 32.0, 30.5, 22.5, 22.2, 21.7, 21.3, 13.7; MS (ESI) m/z (%) 457 ($\text{M}+\text{Na}^++\text{MeOH}$), 425 ($\text{M}+\text{Na}^+$); IR (neat) 2984, 1784, 1746, 1724, 1635, 1603, 1496, 1455, 1376, 1263, 1103, 1054 cm^{-1} ; HRMS (MALDI/DHB) calcd. for $\text{C}_{22}\text{H}_{30}\text{N}_2\text{O}_5\text{Na}$ ($\text{M}+\text{Na}^+$): 425.2047; Found: 425.2049.

(6) Diethyl 3-oxo-4-methyl-5-benzyl-1H-pyrazole-1,2(3H)-dicarboxylate (6f)

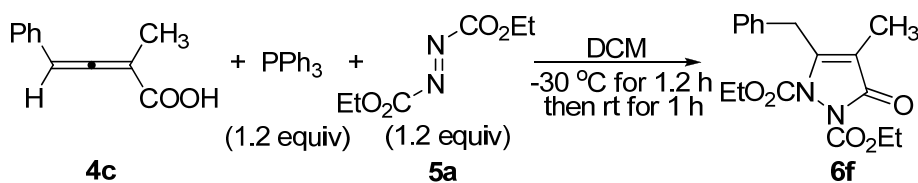
(entry 6, Table 2) (lrz-5-113).



The reaction of **5a** (62.8 mg, 0.37 mmol), triphenyl phosphine (94.4 mg, 0.36 mmol), and **4c** (52.5 mg, 0.30 mmol) in DCM (4 mL) afforded 60.6 mg (61%) of **6f** as oil (Φ 20 mm \times 10 cm, eluent: petroleum ether (30-60 °C)/ethyl acetate = 5:1): ^1H NMR (300 MHz, CDCl_3) δ 7.37-7.21 (m, 3 H, ArH), 7.21-7.14 (m, 2 H, ArH), 4.41 (q, $J = 7.1$ Hz, 2 H, OCH_2), 4.23 (s, 2 H, PhCH_2), 4.16 (q, $J = 7.2$ Hz, 2 H, OCH_2), 1.87 (s, 3 H, CH_3), 1.40 (t, $J = 7.1$ Hz, 3 H, CH_3), 1.19 (t, $J = 7.2$ Hz, 3 H, CH_3); ^{13}C NMR

(75.4 MHz, CDCl₃) δ 163.8, 152.3, 149.3, 148.3, 135.1, 128.2, 127.3, 126.3, 110.0, 64.0, 63.7, 31.6, 13.6, 13.2, 6.5; MS (EI) *m/z* (%) 332 (M⁺, 0.87), 288 (M⁺-CH₃CHO, 3.89), 188 (100); IR (neat) 2984, 1787, 1748, 1727, 1643, 1602, 1496, 1369, 1265, 1029 cm⁻¹; HRMS (EI) calcd. for C₁₇H₂₀N₂O₅ (M⁺): 332.1372; Found: 332.1379.

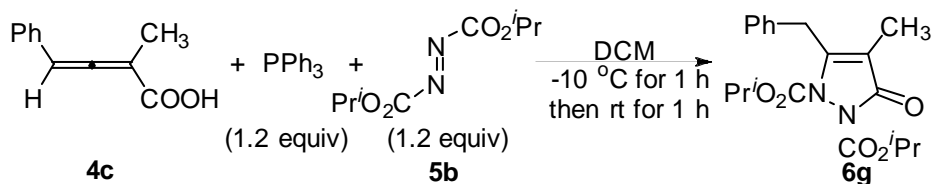
Synthesis of 6f on one gram scale (entry 6, Table 2) (lrz-6-19).



Under an atmosphere of argon, a solution of **5a** (1.250 g, 7.2 mmol) in 20 mL of DCM was added to a solution of triphenyl phosphine (1.891 g, 7.2 mmol) and **4c** (1.047 g, 6.0 mmol) in 60 mL of DCM at the inner temperature of -30 °C in 1 minute with stirring. After being stirred for 1.2 h with the inner temperature of -30 °C, and then at room temperature for an additional 1 h, the reaction mixture was evaporated and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether (30-60 °C)/ethyl acetate = 5:1) to afford 1.212 g (61%) of **6f** as oil: ¹H NMR (300 MHz, CDCl₃) δ 7.37-7.22 (m, 3 H, ArH), 7.22-7.13 (m, 2 H, ArH), 4.40 (q, *J* = 7.1 Hz, 2 H, OCH₂), 4.22 (s, 2 H, PhCH₂), 4.16 (q, *J* = 7.1 Hz, 2 H, OCH₂), 1.86 (s, 3 H, CH₃), 1.39 (t, *J* = 7.1 Hz, 3 H, CH₃), 1.18 (t, *J* = 7.2 Hz, 3 H, CH₃); ¹³C NMR (75.4 MHz, CDCl₃) δ 164.5, 152.8, 149.8, 149.0, 135.5, 128.8, 127.8, 126.9, 110.7, 64.5, 64.3, 32.2, 14.1, 13.8, 7.1.

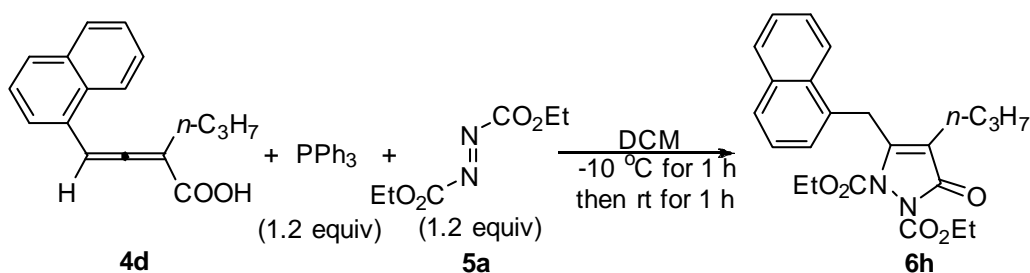
(7) Diisopropyl 3-oxo-4-methyl-5-benzyl-1H-pyrazole-1,2(3H)-dicarboxylate (6g)

(entry 7, Table 2) (lrz-5-115).



The reaction of **5b** (73.1 mg, 0.36 mmol), triphenyl phosphine (94.9 mg, 0.36 mmol), and **4c** (52.5 mg, 0.30 mmol) in DCM (4 mL) afforded 60.5 mg (61%) of **6g** as oil (Φ 20 mm \times 10 cm, eluent: petroleum ether (30-60 °C)/ethyl acetate = 5:1): ^1H NMR (300 MHz, CDCl_3) δ 7.37-7.20 (m, 3 H, ArH), 7.20-7.12 (m, 2 H, ArH), 5.12 (septet, $J = 6.3$ Hz, 1 H, OCH), 4.94 (septet, $J = 6.3$ Hz, 1 H, OCH), 4.23 (s, 2 H, PhCH_2), 1.85 (s, 3 H, CH_3), 1.40 (d, $J = 6.3$ Hz, 6 H, $2 \times \text{CH}_3$ (^iPr)), 1.16 (d, $J = 6.0$ Hz, 6 H, $2 \times \text{CH}_3$ (^iPr)); ^{13}C NMR (75.4 MHz, CDCl_3) δ 164.6, 152.6, 149.3, 148.7, 135.6, 128.8, 127.8, 126.8, 110.5, 73.3, 72.9, 32.2, 21.7, 21.3, 7.0; IR (neat) 2984, 1785, 1747, 1724, 1643, 1599, 1496, 1355, 1376, 1355, 1262, 1168, 1101, 1018 cm^{-1} ; MS (ESI) m/z (%) 361 ($\text{M}^+\text{+H}$); HRMS (MALDI/DHB) calcd. for $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_5\text{Na}$ ($\text{M}+\text{Na}^+$): 383.1577; Found: 383.1588.

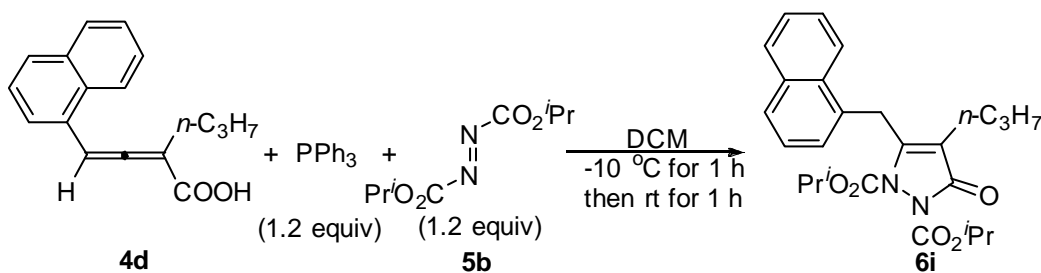
(8) Diethyl 3-oxo-4-(*n*-propyl)-5-(1'-naphthylmethyl)1*H*-pyrazole-1,2(3*H*)-dicarboxylate (**6h**) (entry 8, Table 2) (lrz-5-29).



The reaction of **5a** (62.7 mg, 0.37 mmol), triphenyl phosphine (94.9 mg, 0.36

mmol), and **4d** (75.6 mg, 0.30 mmol) in DCM (4 mL) afforded 106.4 mg (86%) of **6h** as oil (Φ 20 mm x 11 cm, eluent: petroleum ether (30-60 °C)/ethyl acetate = 5:1): ^1H NMR (300 MHz, CDCl_3) δ 8.04 (d, $J = 8.4$ Hz, 1 H, Naph-H), 7.95-7.86 (m, 1 H, Naph-H), 7.77 (d, $J = 8.1$ Hz, 1 H, Naph-H), 7.65-7.48 (m, 2 H, Naph-H), 7.37 (t, $J = 7.7$ Hz, 1 H, Naph-H), 7.04-6.95 (m, 1 H, Naph-H), 4.64 (s, 2 H, ArCH_2), 4.45 (q, $J = 7.1$ Hz, 2 H, OCH_2), 3.85 (q, $J = 7.2$ Hz, 2 H, OCH_2), 2.20 (t, $J = 7.7$ Hz, 2 H, $=\text{CCH}_2$), 1.56-1.37 (m, 5 H, $\text{CH}_2 + \text{CH}_3$), 0.85 (t, $J = 7.4$ Hz, 3 H, CH_3), 0.78 (t, $J = 7.4$ Hz, 3 H, CH_3); ^{13}C NMR (75.4 MHz, CDCl_3) δ 164.2, 152.0, 149.8, 149.0, 133.6, 131.7, 131.2, 128.9, 127.6, 126.5, 126.0, 125.5, 123.3, 122.6, 115.9, 64.45, 64.44, 29.3, 24.2, 21.7, 14.2, 13.9, 13.3; MS (EI) m/z (%) 410 (M^+ , 26.27), 265 (100); IR (neat) 2963, 2933, 2872, 1786, 1748, 1723, 1635, 1599, 1511, 1465, 1399, 1370, 1259, 1177, 1056, 1021 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_5$ (M^+): 410.1842; Found: 410.1848.

(9) Diisopropyl 3-oxo-4-(*n*-propyl)-5-(1'-naphthylmethyl)-1*H*-pyrazole-1,2(3*H*)-dicarboxylate (6i**) (entry 9, Table 2) (lrz-6-112).**

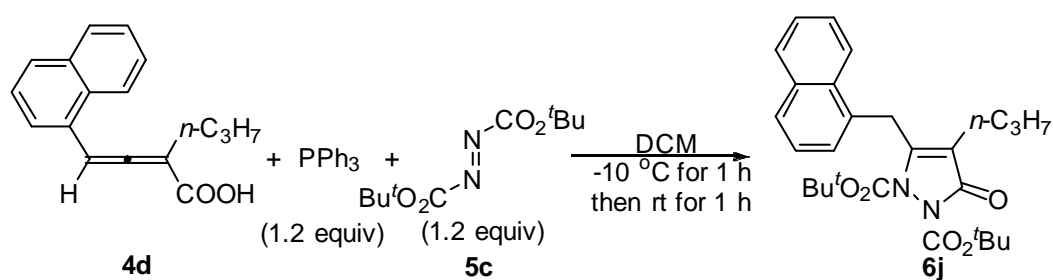


The reaction of **5b** (73.1, 0.36 mmol), triphenyl phosphine (94.4 mg, 0.36 mmol), and **4d** (76.3, 0.30 mmol) in DCM (4 mL) afforded 113.1 mg (86%) of **6i** as oil (Φ 20 mm \times 9 cm, eluent: petroleum ether (30-60 °C)/ethyl acetate = 5:1): ^1H NMR (300

MHz, CDCl₃) δ 8.03 (d, *J* = 8.4 Hz, 1 H, Naph-H), 7.94-7.86 (m, 1 H, Naph-H), 7.76 (d, *J* = 8.1 Hz, 1 H, Naph-H), 7.67-7.50 (m, 2 H, Naph-H), 7.36 (t, *J* = 7.7 Hz, 1 H, Naph-H), 6.70 (dd, *J*₁ = 7.2 Hz, *J*₂ = 1.2 Hz, 1 H, Naph-H), 5.17 (septet, *J* = 6.3 Hz, 1 H, OCH), 4.75 (septet, *J* = 6.3 Hz, 1 H, OCH), 4.64 (s, 2 H, ArCH₂), 2.18 (t, *J* = 7.7 Hz, 2 H, =CCH₂), 1.54-1.36 (m, 8 H, CH₂ + 2 × CH₃), 0.90-0.78 (m, 9 H, CH₃ + 2 × CH₃); ¹³C NMR (75.4 MHz, CDCl₃) δ 164.4, 151.8, 149.2, 148.8, 133.7, 131.8, 131.4, 128.9, 127.5, 126.5, 126.0, 125.5, 123.5, 122.6, 115.7, 73.2, 73.0, 29.4, 24.3, 21.7, 21.0, 13.9; MS (ESI) *m/z* (%) 461 (M+Na⁺), 439 (M⁺+H); IR (neat) 2983, 2935, 2872, 1783, 1744, 1724, 1634, 1599, 1512, 1466, 1376, 1357, 1262, 1103, 1054 cm⁻¹; HRMS (MALDI/DHB) calcd. for C₂₅H₃₀N₂O₅Na (M+Na⁺): 461.2047; Found: 461.2061.

(10) Di-*tert*-butyl 3-oxo-4-(*n*-propyl)-5-(1'-naphthylmethyl)-1*H*-pyrazole-

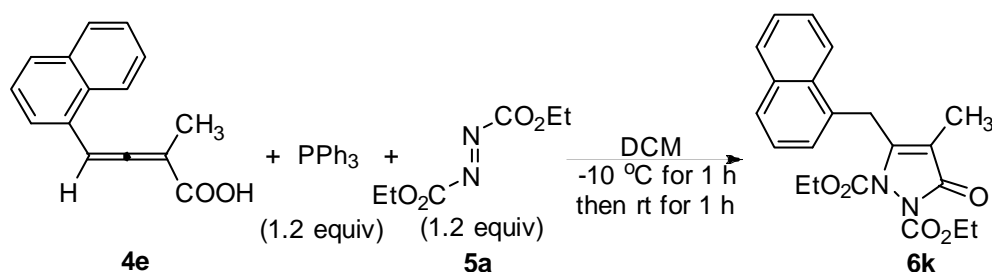
1,2(3*H*)-dicarboxylate (6j) (entry 10, Table 2) (lrz-5-142).



The reaction of **5c** (83.2 mg, 0.36 mmol), triphenyl phosphine (94.7 mg, 0.36 mmol), and **4d** (75.5 mg, 0.30 mmol) in DCM (4 mL) afforded 103.3 mg (74%) of **6j** as solid (Φ 20 mm x 11 cm, eluent: petroleum ether (30-60 °C)/ethyl acetate = 10:1); m.p. 143-144 °C (petroleum ether/ethyl acetate); ¹H NMR (300 MHz, CDCl₃) δ 8.02 (d, *J* = 7.8 Hz, 1 H, Naph-H), 7.89 (d, *J* = 7.8 Hz, 1 H, Naph-H), 7.76 (d, *J* = 8.1 Hz, 1

H, Naph-H), 7.69-7.47 (m, 2 H, Naph-H), 7.36 (t, $J = 7.7$ Hz, 1 H, Naph-H), 6.97 (d, $J = 6.9$ Hz, 1 H, Naph-H), 4.61 (s, 2 H, ArCH₂), 2.16 (t, $J = 7.7$ Hz, 2 H, =CCH₂), 1.62 (s, 9 H, C(CH₃)₃), 1.50-1.37 (m, 2 H, CH₂), 1.07 (s, 9 H, C(CH₃)₃), 0.83 (t, $J = 7.4$ Hz, 3 H, CH₃); ¹³C NMR (75.4 MHz, CDCl₃) δ 164.4, 151.2, 148.1, 147.4, 133.6, 132.0, 131.4, 128.9, 127.5, 126.5, 126.0, 125.5, 123.5, 122.7, 115.1, 85.5, 85.0, 29.3, 27.9, 27.2, 24.3, 21.8, 13.9; MS (ESI) m/z (%) 521 (M+Na⁺+MeOH), 489 (M+Na⁺); IR (neat) 2980, 2933, 2872, 1783, 1744, 1717, 1633, 1599, 1512, 1457, 1396, 1370, 1284, 1256, 1147, 1057, 1011 cm⁻¹; Anal Calcd for C₂₇H₃₄N₂O₅: C, 69.50; H, 7.35; N 6.00. Found: C, 69.41; H, 7.34; N 5.78.

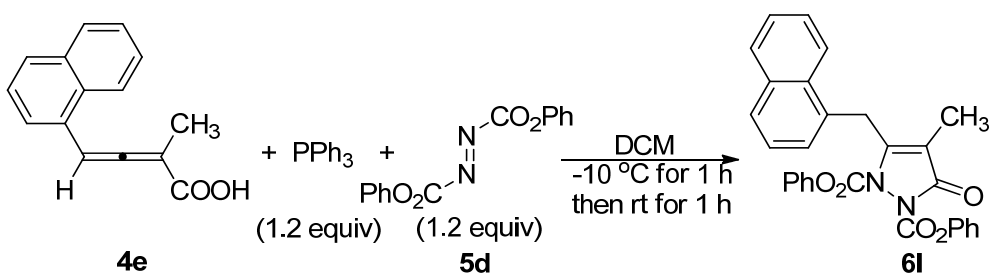
(11) Diethyl 3-oxo-4-methyl-5-(1'-naphthylmethyl)-1H-pyrazole-1,2(3H)-dicarboxylate (6k) (entry 11, Table 2) (lrz-6-114).



The reaction of **5a** (63.2 mg, 0.36 mmol), triphenyl phosphine (94.7 mg, 0.36 mmol), and **4e** (67.4 mg, 0.3 mmol) in DCM (4 mL) afforded 73.1 mg (64%) of **6k** as oil (Φ 20 mm \times 10 cm, eluent: petroleum ether (30-60 °C)/ethyl acetate = 5:1): ¹H NMR (300 MHz, CDCl₃) δ 8.02 (d, $J = 8.4$ Hz, 1 H, Naph-H), 7.94-7.86 (m, 1 H, Naph-H), 7.77 (d, $J = 8.4$ Hz, 1 H, Naph-H), 7.65-7.46 (m, 2 H, Naph-H), 7.38 (t, $J = 7.7$ Hz, 1 H, Naph-H), 7.02 (dd, $J_1 = 7.1$ Hz, $J_2 = 0.75$ Hz, 1 H, Naph-H), 4.65 (s, 2 H, ArCH₂), 4.45 (q, $J = 7.1$ Hz, 2 H, OCH₂), 3.92 (q, $J = 7.1$ Hz, 2 H, OCH₂), 1.75 (s, 3

H, CH₃), 1.42 (t, *J* = 7.2 Hz, 3 H, CH₃), 0.84 (t, *J* = 7.2 Hz, 3 H, CH₃); ¹³C NMR (75.4 MHz, CDCl₃) δ 164.5, 152.3, 149.9, 149.0, 133.7, 131.4, 131.2, 128.9, 127.6, 126.5, 126.0, 125.5, 123.6, 122.6, 111.8, 64.5, 64.4, 29.7, 14.2, 13.3, 6.8; MS (ESI) *m/z* (%) 437 (M+Na⁺+MeOH), 405 (M+Na⁺), 383 (M⁺+H); IR (neat) 2984, 2927, 1786, 1747, 1721, 1645, 1598, 1511, 1399, 1370, 1257, 1027, cm⁻¹; HRMS (MALDI/DHB) calcd. for C₂₁H₂₃N₂O₅ (M⁺+H): 383.1602; Found: 383.1600.

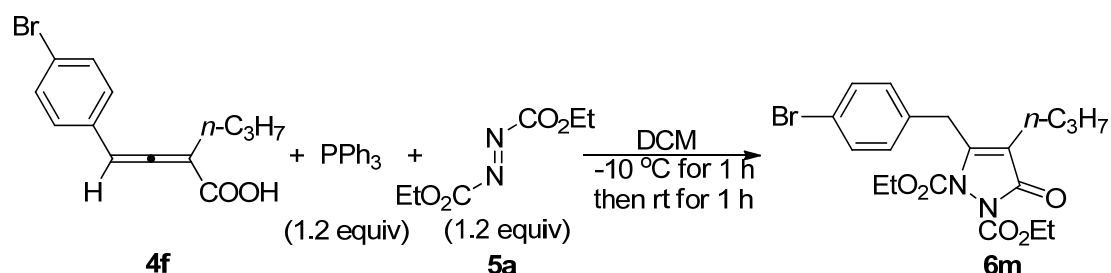
(12) 1,2-Diphenyl 3-oxo-4-methyl-5- (1'-naphthylmethyl)-1H-pyrazole-1,2(3H)-dicarboxylate (6l) (entry 12, Table 2) (lrz-9-144).



The reaction of **5d** (97.7 mg, 0.36 mmol), triphenyl phosphine (94.3 mg, 0.36 mmol), and **4e** (67.6 mg, 0.3 mmol) in DCM (4 mL) afforded 94.9 mg (66%) of **6l** as oil (Φ 20 mm x 9 cm, eluent: petroleum ether (30-60 °C)/ethyl acetate = 7:1): ¹H NMR (300 MHz, CDCl₃) δ 8.00 (d, *J* = 8.1 Hz, 1 H, Ar-H), 7.88 (d, *J* = 7.2 Hz, 1 H, Ar-H), 7.80 (d, *J* = 7.8 Hz, 1 H, Ar-H), 7.60-7.05 (m, 12 H, Ar-H and Ph-H), 6.72 (d, *J* = 7.8 Hz, 2 H, Ar-H), 4.78 (s, 2 H, ArCH₂), 1.83 (s, 3 H, CH₃); ¹³C NMR (75.4 MHz, CDCl₃) δ 164.3, 153.1, 150.3, 149.8, 148.4, 147.7, 133.8, 131.5, 130.9, 129.6, 129.5, 128.9, 127.9, 126.62, 126.57, 126.1, 125.5, 123.9, 122.7, 121.2, 120.6, 112.6, 29.9, 7.1; MS (SI) *m/z* (%) 478 (M⁺, 6.62), 77 (100); IR (neat) 2927, 2854, 1796, 1730, 1645, 1592, 1490, 1247, 1183, 1023, cm⁻¹; HRMS (ESI) calcd. for C₂₉H₂₃N₂O₅

(M⁺+H): 479.1601; Found: 479.1600.

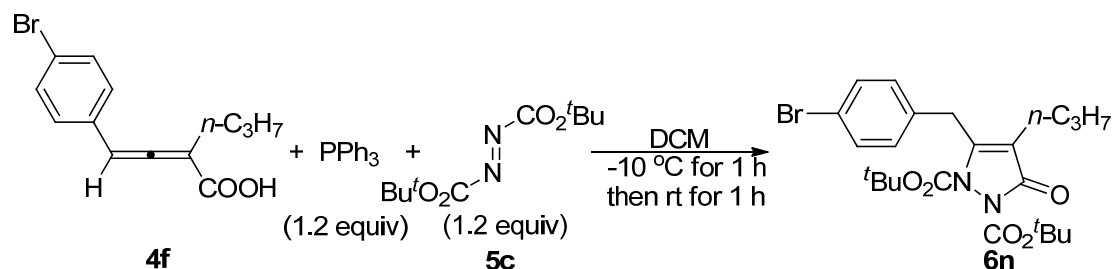
(13) Diethyl 3-oxo-4-(*n*-propyl)-5-(4'-bromobenzyl)-1*H*-pyrazole-1,2(3*H*)-dicarboxylate (6m) (entry 13, Table 2) (lrz-5-88).



The reaction of **5a** (63.3 mg, 0.36 mmol), triphenyl phosphine (94.4 mg, 0.36 mmol), and **4f** (84.4 mg, 0.30 mmol) in DCM (4 mL) afforded 85.8 mg (65%) of **6m** as oil (Φ 20 mm×13 cm, eluent: petroleum ether (30-60 °C)/ethyl acetate = 5:1): ¹H NMR (300 MHz, CDCl₃) δ 7.44 (d, J = 8.4 Hz, 2 H, ArH), 7.07 (d, J = 8.4 Hz, 2 H, ArH (Ph)), 4.41 (q, J = 7.1 Hz, 2 H, OCH₂), 4.28-4.10 (m, 4 H, ArCH₂ + OCH₂), 2.27 (t, J = 7.8 Hz, 2 H, =CCH₂), 1.60-1.44 (m, 2 H, CH₂), 1.40 (t, J = 7.2 Hz, 3 H, CH₃), 1.21 (t, J = 7.2 Hz, 3 H, CH₃), 0.91 (t, J = 7.4 Hz, 3 H, CH₃); ¹³C NMR (75.4 MHz, CDCl₃) δ 164.1, 152.1, 149.7, 149.0, 135.0, 131.8, 129.5, 120.8, 115.2, 64.6, 64.4, 31.6, 24.3, 21.7, 14.1, 13.9, 13.8; MS (ESI) m/z (%): 495 (M(⁸¹Br)+Na⁺+MeOH), 493 (M(⁷⁹Br)+Na⁺+MeOH), 463 (M(⁸¹Br)+Na⁺), 461 (M(⁷⁹Br)+Na⁺), 441 (M(⁸¹Br)+H), 439 (M(⁷⁹Br)+H); IR (neat) 2962, 2933, 1786, 1750, 1727, 1636, 1488, 1370, 1264, 1232, 1176, 1053, 1012 cm⁻¹; HRMS (ESI): C₁₉H₂₃N₂O₅⁷⁹BrNa (M+Na⁺): 461.0683; Found: 461.0686.

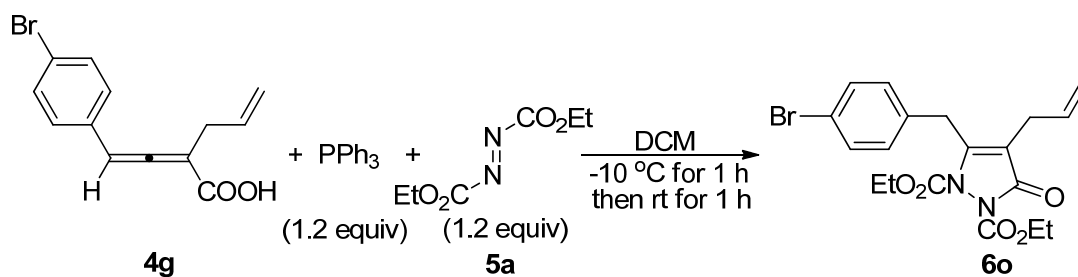
(14) Di-*tert*-butyl 3-oxo-4-(*n*-propyl)-5-(4'-bromobenzyl)-1*H*-pyrazole-1,2(3*H*)-

dicarboxylate (6n) (entry 14, Table 2) (lrz-5-89).



The reaction of **5c** (83.3 mg, 0.36 mmol), triphenyl phosphine (94.9 mg, 0.36 mmol), and **4f** (84.5 mg, 0.30 mmol) in DCM (4 mL) afforded 82.6 mg (56%) of **6n** as solid (Φ 20 mm x 17 cm, eluent: petroleum ether (30-60 °C)/ethyl acetate = 10:1); m.p. 125-126 °C (petroleum ether/ethyl acetate); ^1H NMR (300 MHz, CDCl_3) δ 7.42 (d, $J = 8.1$ Hz, 2 H, ArH), 7.07 (d, $J = 8.4$ Hz, 2 H, ArH), 4.16 (s, 2 H, PhCH_2), 2.23 (t, $J = 7.7$ Hz, 2 H, $=\text{CCH}_2$), 1.60 (s, 9 H, $(\text{CH}_3)_3$), 1.54-1.44 (m, 2 H, CH_2), 1.38 (s, 9 H, $(\text{CH}_3)_3$), 0.90 (t, $J = 7.5$ Hz, 3 H, CH_3); ^{13}C NMR (75.4 MHz, CDCl_3) δ 164.3, 151.5, 148.0, 147.5, 135.2, 131.7, 129.6, 120.6, 114.3, 85.8, 85.1, 31.3, 27.9, 27.5, 24.4, 21.8, 14.0; MS (ESI) m/z (%) 551 ($\text{M}^{(81}\text{Br})+\text{Na}^++\text{MeOH}$), 549 ($\text{M}^{(79}\text{Br})+\text{Na}^++\text{MeOH}$), 519 ($\text{M}^{(81}\text{Br})+\text{Na}^+$), 517 ($\text{M}^{(79}\text{Br})+\text{Na}^+$); IR (KBr) 2980, 2933, 2837, 1783, 1746, 1720, 1635, 1489, 1458, 1394, 1370, 1283, 1256, 1012, 1147 cm^{-1} ; Anal Calcd for $\text{C}_{23}\text{H}_{31}\text{N}_2\text{O}_5\text{Br}$: C, 55.76; H, 6.31; N 5.65. Found: C, 55.84; H, 6.39; N 5.74.

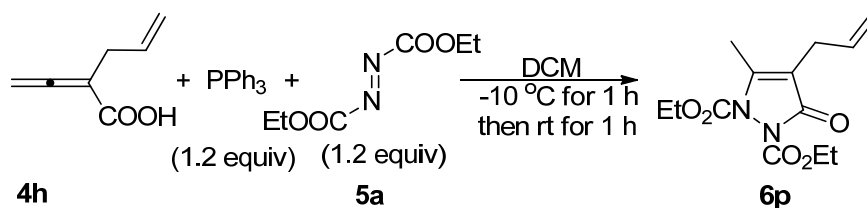
(15) Diethyl 3-oxo-4-allyl-5-(4'-bromobenzyl)-1H-pyrazole-1,2(3H)-dicarboxylate (6o) (entry 15, Table 2) (lrz-6-109).



The reaction of **5a** (63.1 mg, 0.36 mmol), triphenyl phosphine (95.1 mg, 0.36 mmol), and **4g** (83.9 mg, 0.30 mmol) in DCM (4 mL) afforded 72.0 mg (55%) of **6o** as oil (Φ 20 mm x 9 cm, eluent: petroleum ether (30-60 $^\circ\text{C}$)/ethyl acetate = 5:1): ^1H NMR (300 MHz, CDCl_3) δ 7.48-7.39 (m, 2 H, ArH), 7.12-7.03 (m, 2 H, ArH), 5.87-5.71 (m, 1 H, CH (in allyl)), 5.13-4.99 (m, 2 H, =CH₂), 4.41 (q, $J = 7.1$ Hz, 2 H, OCH₂), 4.27-4.14 (m, 4 H, OCH₂ + PhCH₂), 3.07 (dt, $J_1 = 6.4$ Hz, $J_2 = 1.7$ Hz, 2 H, =CCH₂), 1.40 (t, $J = 7.2$ Hz, 3 H, CH₃), 1.22 (t, $J = 7.2$ Hz, 3 H, CH₃); ^{13}C NMR (75.4 MHz, CDCl_3) δ 163.7, 153.0, 149.6, 149.0, 134.6, 133.4, 131.8, 129.7, 120.8, 116.7, 112.8, 64.7, 64.5, 31.6, 26.4, 14.2, 13.8; MS (ESI) m/z (%) 493 ($\text{M}^{(81}\text{Br})+\text{Na}^+\text{+MeOH}$), 491 ($\text{M}^{(79}\text{Br})+\text{Na}^+\text{+MeOH}$), 461 ($\text{M}^{(81}\text{Br})+\text{Na}^+$), 459 ($\text{M}^{(79}\text{Br})+\text{Na}^+$), 439 ($\text{M}^{(81}\text{Br})+\text{H}$), 437 ($\text{M}^{(79}\text{Br})+\text{H}$); IR (neat) 2983, 1787, 1751, 1728, 1640, 1489, 1370, 1265, 1227, 1012 cm^{-1} ; HRMS (MALDI/DHB) $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_5^{79}\text{Br}$ ($\text{M}^+\text{+H}$): 437.0707; Found: 437.0721.

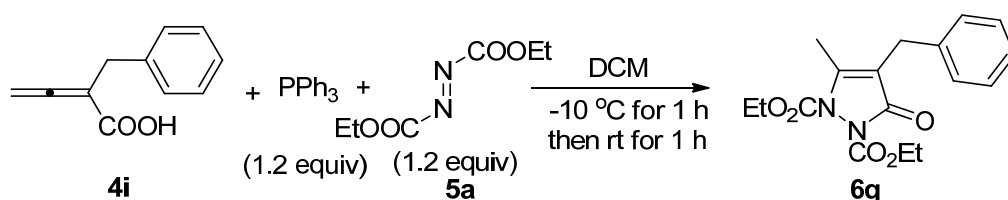
(16) Diethyl 3-oxo-4-allyl-5-methyl-1*H*-pyrazole-1,2(3*H*)-dicarboxylate (**6p**)

(entry 16, Table 2) (lrz-4-162):



The reaction of **5a** (62.3 mg, 0.36 mmol), triphenyl phosphine (94.7 mg, 0.36 mmol), and **4h** (37.3 mg, 0.30 mmol) in DCM (4 mL) afforded 49.1 mg (58%) of **6p** as oil (eluent: petroleum ether (30-60 °C)/ethyl acetate = 5:1): ^1H NMR (300 MHz, CDCl_3) δ 5.88-5.70 (m, 1 H, CH (in ally)), 5.15-4.97 (m, 2 H, =CH₂), 4.42 (q, J = 7.1 Hz, 2 H, OCH₂), 4.34 (q, J = 7.2 Hz, 2 H, OCH₂), 3.02 (d, J = 6.3 Hz, 2 H, =CCH₂), 2.41 (s, 3 H, CH₃), 1.41 (t, J = 7.1 Hz, 3 H, CH₃), 1.35 (t, J = 7.2 Hz, 3 H, CH₃); ^{13}C NMR (75.4 MHz, CDCl_3) δ 163.9, 152.9, 149.8, 149.1, 133.6, 116.0, 110.9, 64.4, 64.3, 26.0, 14.1, 13.9, 13.5; IR (neat) 2984, 1786, 1747, 1722, 1640, 1398, 1370, 1250, 1209, 1065, 1011; MS (EI) m/z (%) 282 (M^+ , 2.00), 79 (100); HRMS (EI) calcd. for $\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_5$ (M^+): 282.1216; Found: 282.1216.

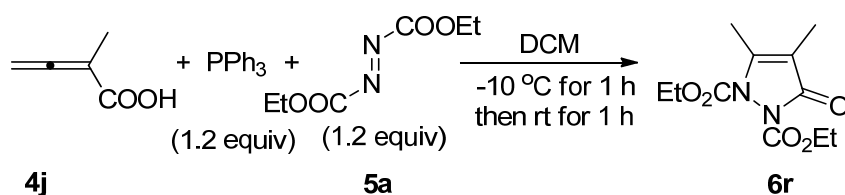
(17) Diethyl 3-oxo-4-benzyl-5-methyl-1H-pyrazole-1,2(3H)-dicarboxylate (6q)
(entry 17, Table 2) (lrz-4-159).



The reaction of **5a** (62.6 mg, 0.36 mmol), triphenyl phosphine (94.2 mg, 0.36 mmol), and **4i** (52.4 mg, 0.30 mmol) in DCM (4 mL) afforded 54.2 mg (54%) of **6q** as oil (eluent: petroleum ether (30-60 °C)/ethyl acetate = 6:1): ^1H NMR (300 MHz, CDCl_3) δ 7.33-7.11 (m, 5 H, Ar-H) 4.41 (q, J = 7.1 Hz, 2 H, OCH₂), 4.32 (q, J = 7.2 Hz, 2 H, OCH₂), 3.60 (s, 2 H, =CCH₂), 2.43 (s, 3 H, CH₃), 1.41 (t, J = 7.1 Hz, 3 H, CH₃), 1.33 (t, J = 7.1 Hz, 3 H, CH₃); ^{13}C NMR (75.4 MHz, CDCl_3) δ 164.2, 152.7, 149.8, 149.2, 138.4, 128.6, 128.3, 126.4, 112.7, 64.5, 64.4, 27.9, 14.2, 14.0, 13.7; IR

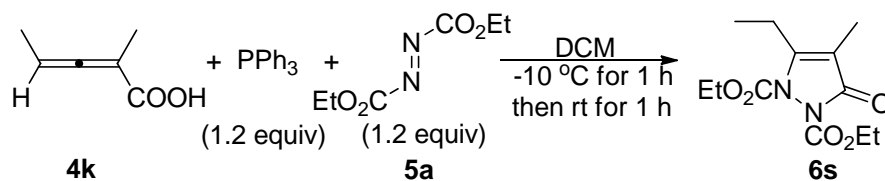
(neat) 3061, 2986, 1785, 1748, 1637, 1397, 1370, 1259, 1209, 1085, 1067, 1013; MS (EI) m/z (%) 332 (M^+ , 10.07), 187 (100); HRMS (EI) calcd. for $C_{17}H_{20}N_2O_5$ (M^+): 332.1372; Found: 332.1373.

(18) Diethyl 3-oxo-4,5-dimethyl-1H-pyrazole-1,2(3H)-dicarboxylate (6r) (entry 18, Table 2) (lrz-5-116).



The reaction of **5a** (62.9 mg, 0.36 mmol), triphenyl phosphine (94.7 mg, 0.36 mmol) and **4j** (29.0 mg, 0.30 mmol) in DCM (4 mL) afforded 29.7 mg (39%) of **6r** as oil (ϕ 20 mm x 12 cm, eluent: petroleum ether (30-60 $^\circ\text{C}$)/ethyl acetate = 10:1): ^1H NMR (300 MHz, CDCl_3) δ 4.42 (q, $J = 7.1$ Hz, 2 H, OCH_2), 4.33 (q, $J = 7.0$ Hz, 2 H, OCH_2), 2.42 (s, 3 H, $=\text{CCH}_3$), 1.81 (s, 3 H, CH_3), 1.41 (t, $J = 6.9$ Hz, 3 H, CH_3), 1.35 (t, $J = 7.1$ Hz, 3 H, CH_3); ^{13}C NMR (75.4 MHz, CDCl_3) δ 164.7, 151.9, 150.0, 149.2, 109.2, 64.35, 64.29, 14.2, 14.0, 13.6, 6.8; IR (neat) 2984, 2929, 1785, 1722, 1645, 1370, 1258, 1210, 1018; MS (EI) m/z (%) 256 (M^+ , 0.59), 54 (100); HRMS (EI) calcd. for $C_{11}H_{16}N_2O_5$ (M^+): 256.1059; Found: 256.1061.

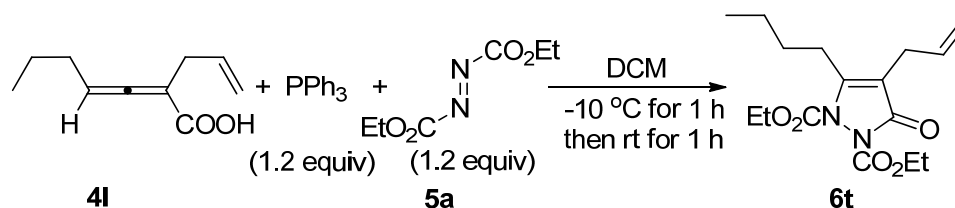
(19) Diethyl 3-oxo-4-methyl-5-ethyl-1H-pyrazole-1,2(3H)-dicarboxylate (6s) (entry 19, Table 2) (lrz-5-123).



The reaction of **5a** (62.6 mg, 0.36 mmol), triphenyl phosphine (94.7 mg, 0.36 mmol), and **4k** (33.1 mg, 0.30 mmol) in DCM (4 mL) afforded 40.2 mg (50%) of **6s** as oil (Φ 20 mm \times 11 cm, eluent: petroleum ether (30-60 °C)/ethyl acetate = 7:1): ^1H NMR (300 MHz, CDCl_3) δ 4.42 (q, $J = 7.2$ Hz, 2 H, OCH_2), 4.34 (q, $J = 7.2$ Hz, 2 H, OCH_2), 2.83 (q, $J = 7.4$ Hz, 2 H, CH_2), 1.82 (s, 3 H, $=\text{CCH}_3$), 1.41 (t, $J = 7.2$ Hz, 3 H, CH_3), 1.35 (t, $J = 7.2$ Hz, 3 H, CH_3), 1.27 (t, $J = 7.5$ Hz, 3 H, CH_3); ^{13}C NMR (75.4 MHz, CDCl_3) δ 164.8, 157.2, 149.8, 149.2, 108.4, 64.4, 64.2, 20.5, 14.2, 13.9, 12.7, 6.7; IR (neat) 2984, 1786, 1747, 1722, 1640, 1465, 1369, 1259, 1016 cm^{-1} ; MS (EI) m/z (%) 270 (M^+ , 2.86), 67 (100); HRMS (EI) calcd. for $\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_5$ (M^+): 270.1216; Found: 270.1219.

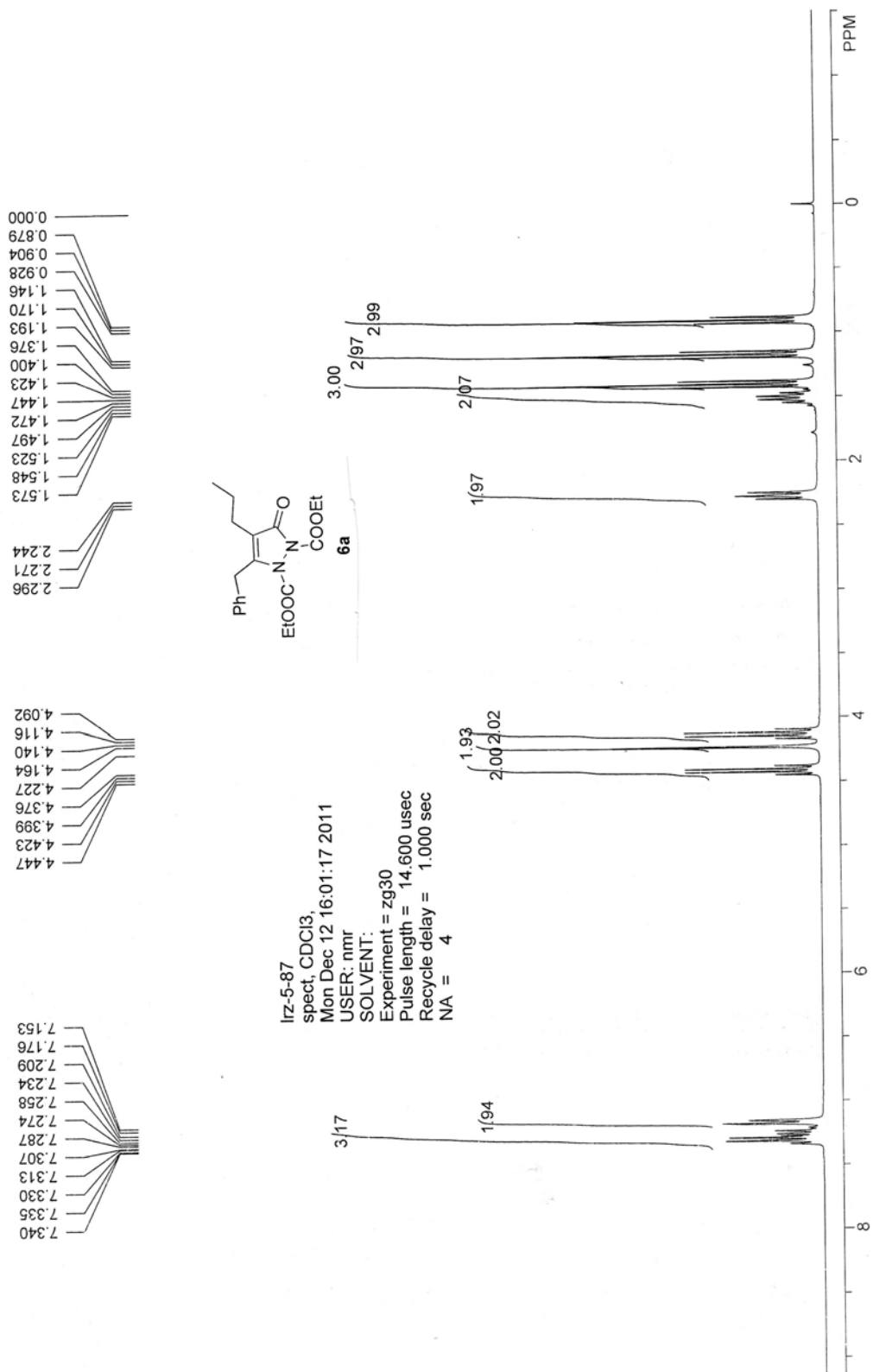
(20) Diethyl 3-oxo-4-allyl-5-(*n*-butyl)-1*H*-pyrazole-1,2(3*H*)-dicarboxylate (6t)

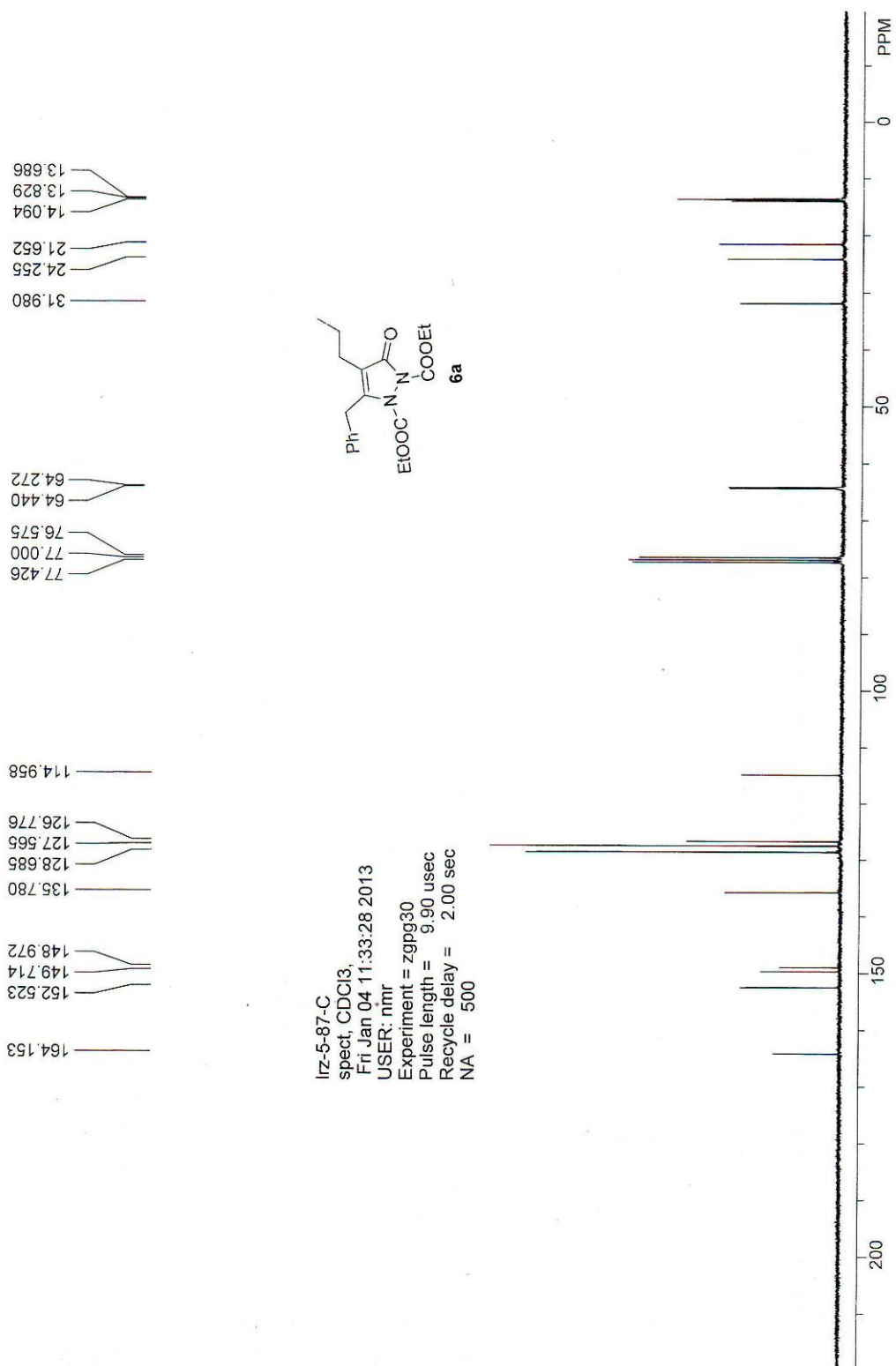
(entry 20, Table 2) (lrz-5-126).

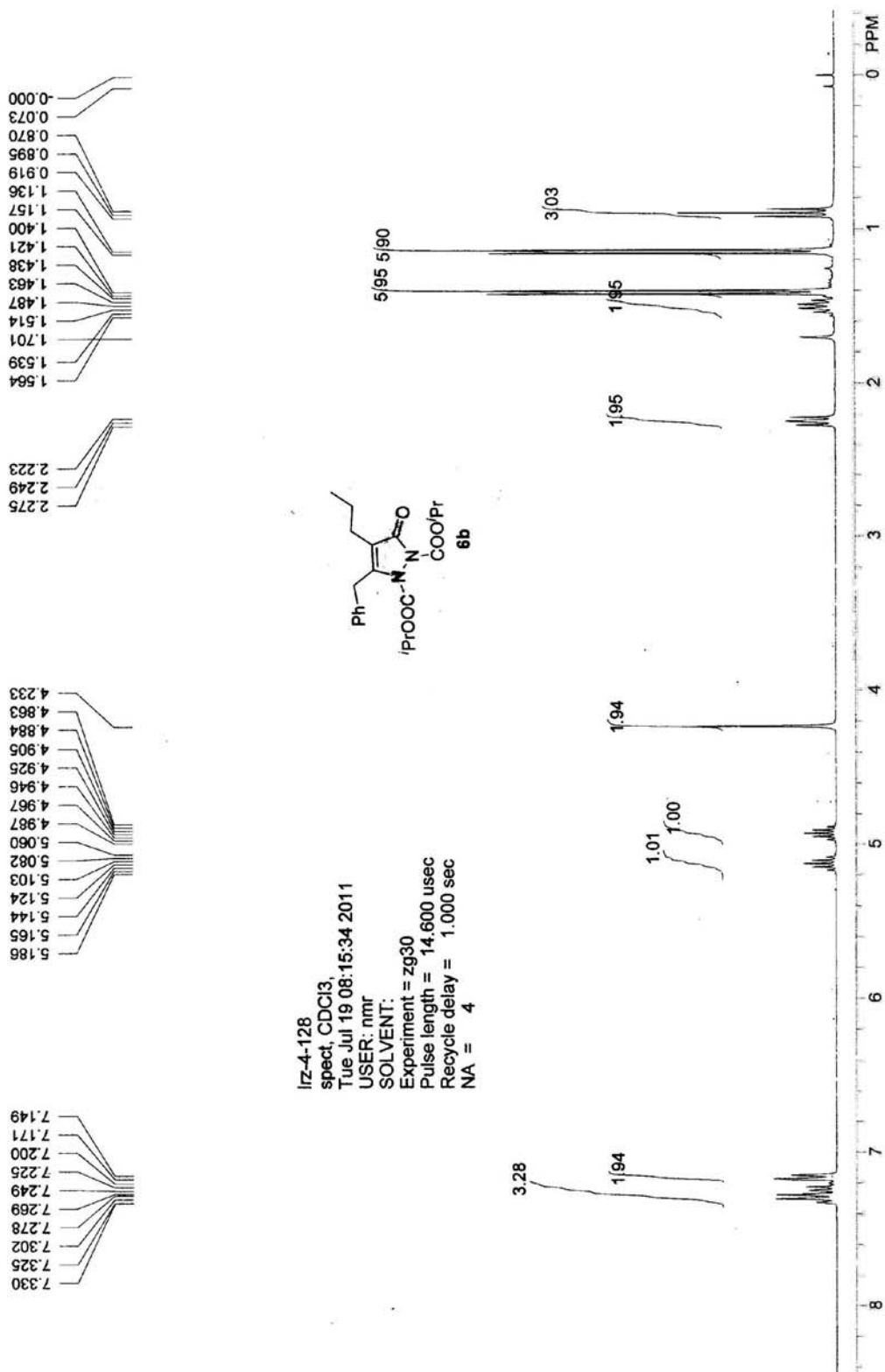


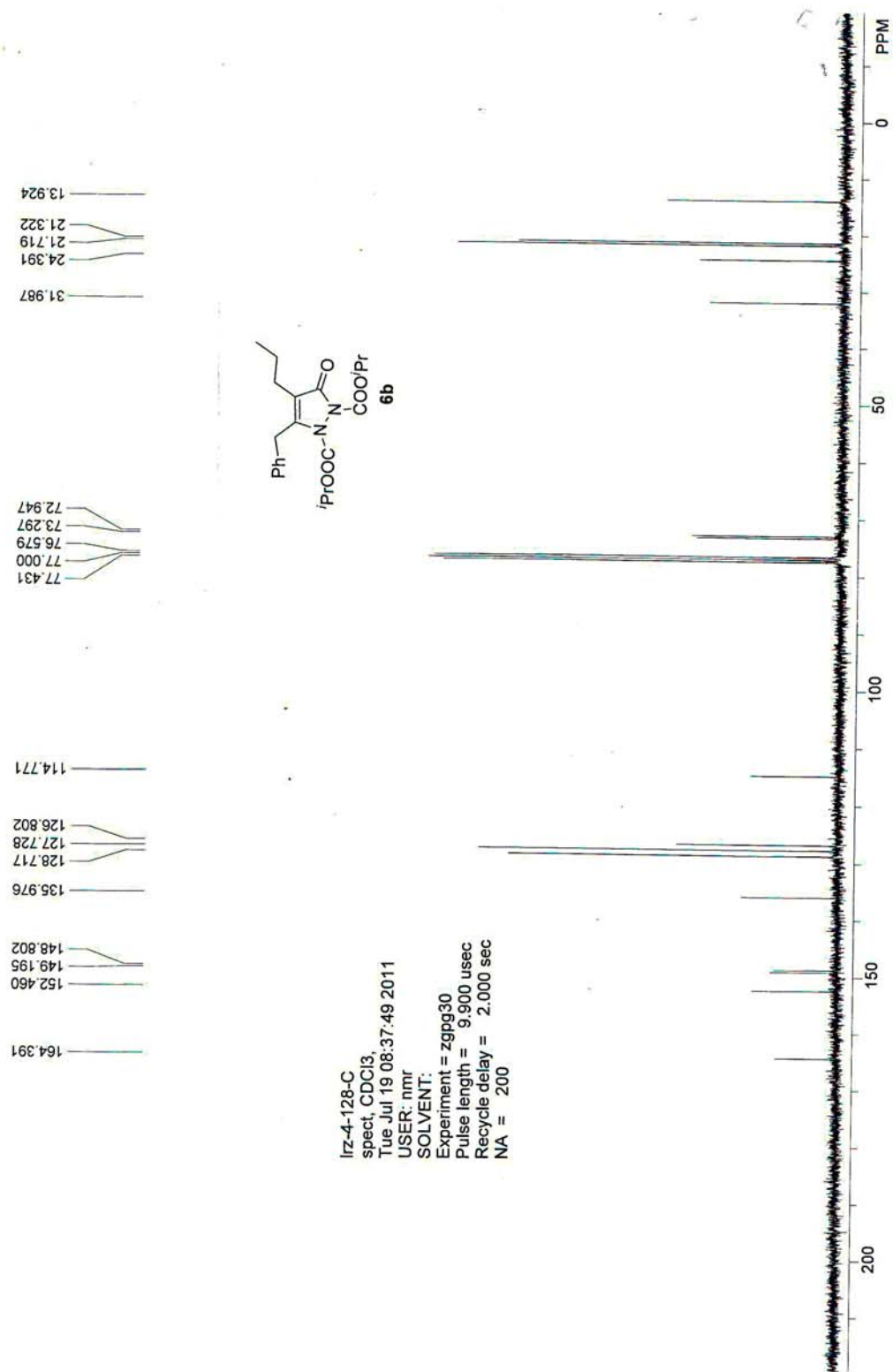
The reaction of **5a** (62.8 mg, 0.36 mmol), triphenyl phosphine (94.9 mg, 0.36 mmol), and **4l** (50.3 mg, 0.30 mmol) in DCM (4 mL) afforded 63.5 mg (65%) of **6t** as oil (Φ 20 mm \times 11 cm, eluent: petroleum ether(30-60 °C)/ethyl acetate = 7:1): ^1H NMR (300 MHz, CDCl_3) δ 5.89-5.73 (m, 1 H, $\text{CH}=\text{}$), 5.15-4.99 (m, 2 H, $=\text{CH}_2$), 4.42

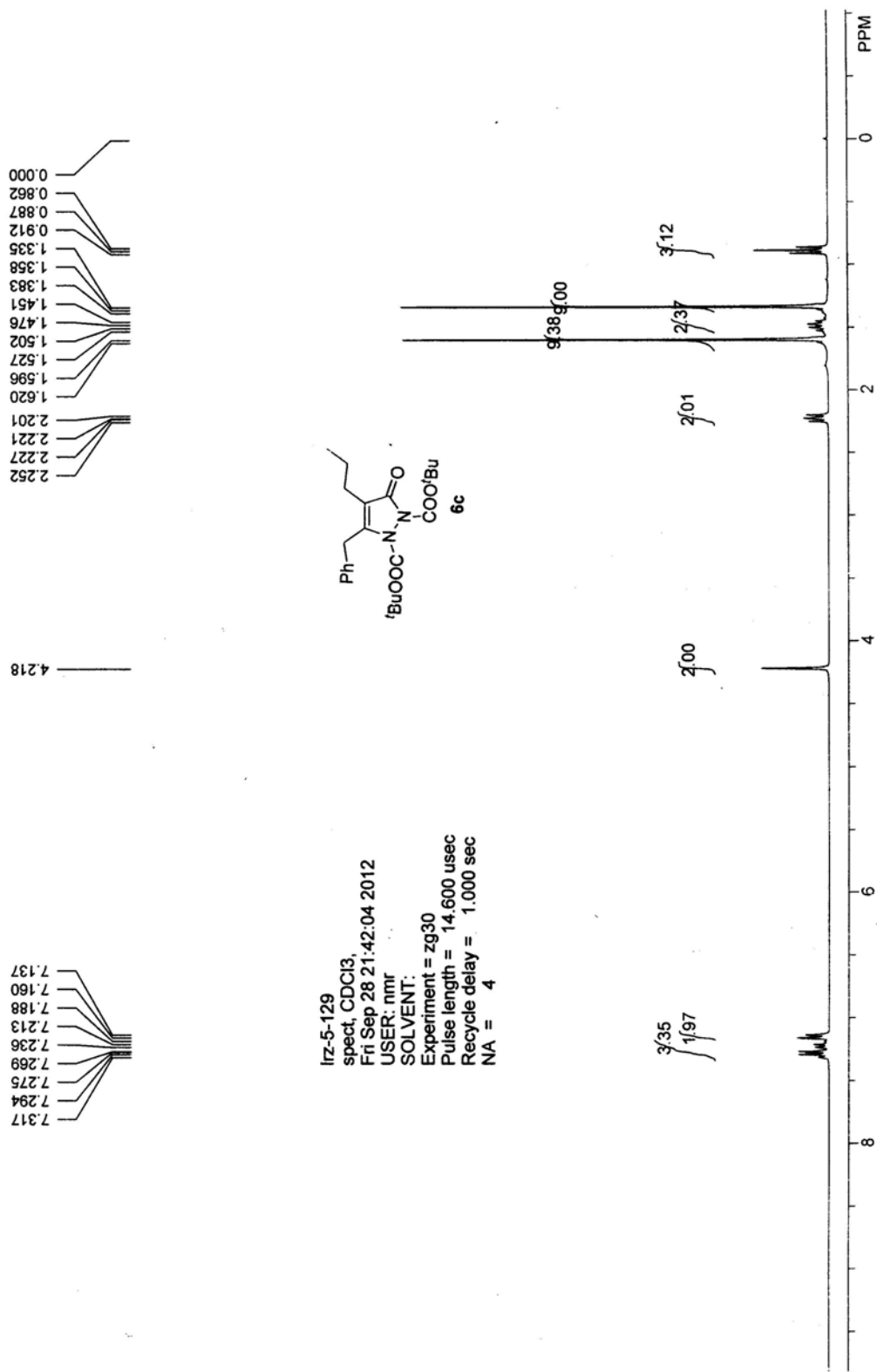
(q, $J = 7.1$ Hz, 2 H, OCH₂), 4.33 (q, $J = 7.1$ Hz, 2 H, OCH₂), 3.02 (dt, $J_1 = 6.0$ Hz, $J_2 = 1.5$ Hz, 2 H, CH₂), 2.78 (t, $J = 7.8$ Hz, 2 H, =CCH₂), 1.72-1.59 (m, 2 H, CH₂) 1.46-1.29 (m, 8 H, 2 x CH₃ + CH₂), 0.95 (t, $J = 7.4$ Hz, 3 H, CH₃); ¹³C NMR (75.4 MHz, CDCl₃) δ 164.0, 157.1, 149.6, 149.2, 134.0, 116.0, 110.7, 64.5, 64.3, 30.7, 26.6, 26.3, 22.6, 14.2, 13.9, 13.7; IR (neat) 2961, 2873, 1788, 1749, 1724, 1637, 1370, 1263, 1224, 1019 cm⁻¹; MS (EI) m/z (%) 324 (M⁺, 3.54), 151 (100); HRMS (EI) calcd. for C₁₆H₂₄N₂O₅ (M⁺): 324.1685; Found 324.1683.

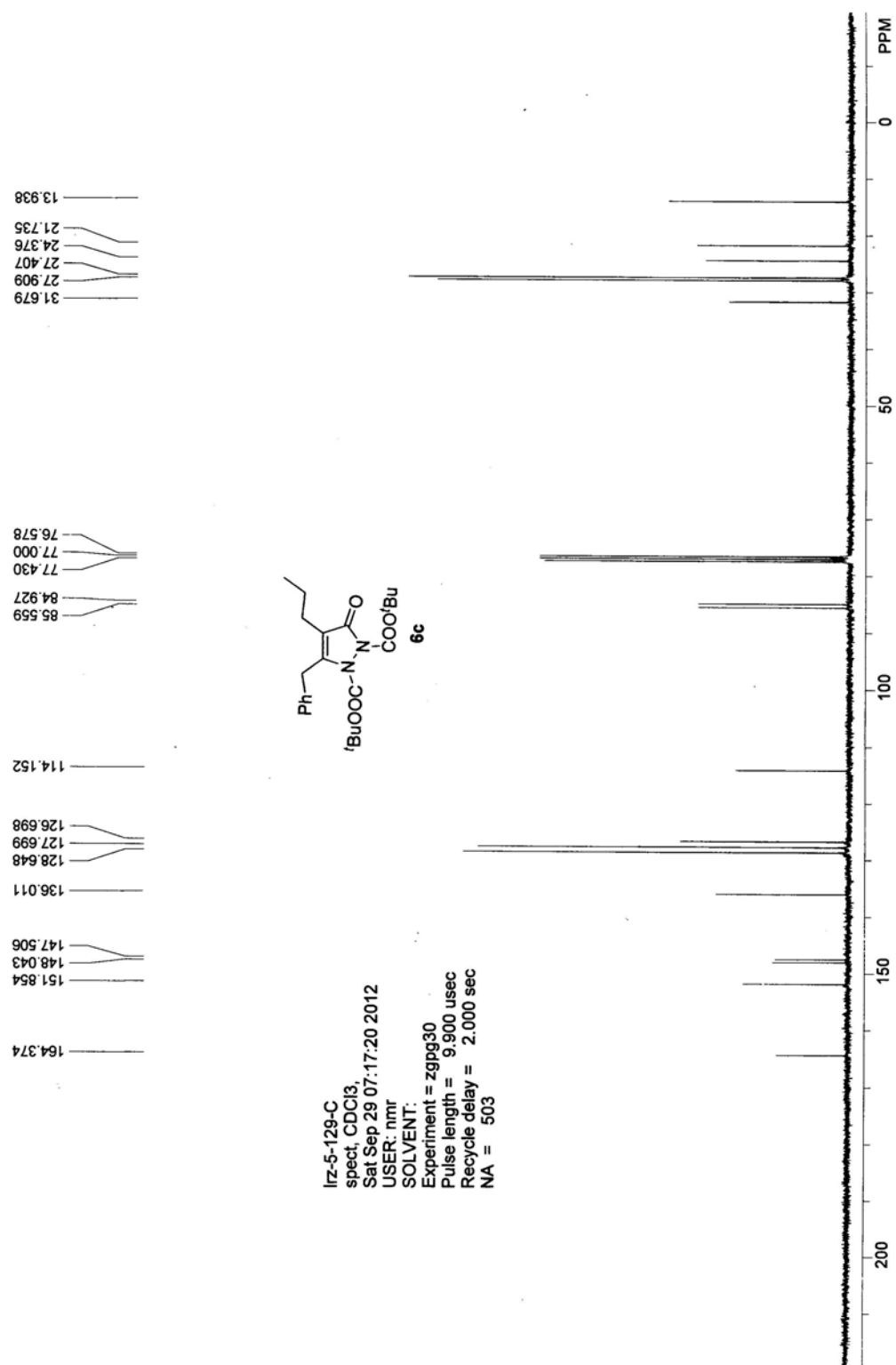


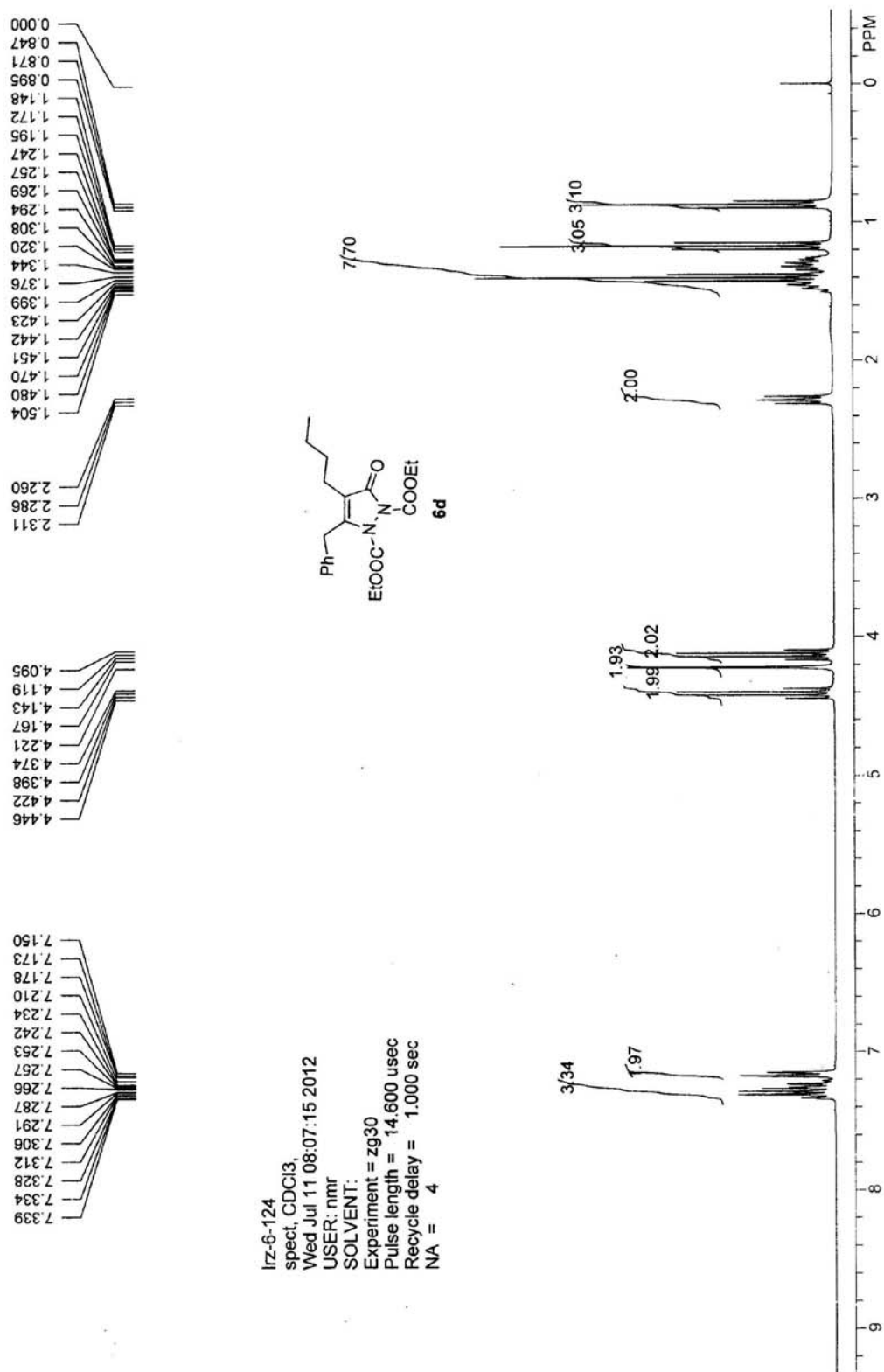




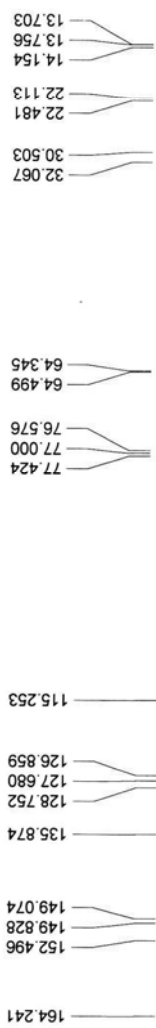




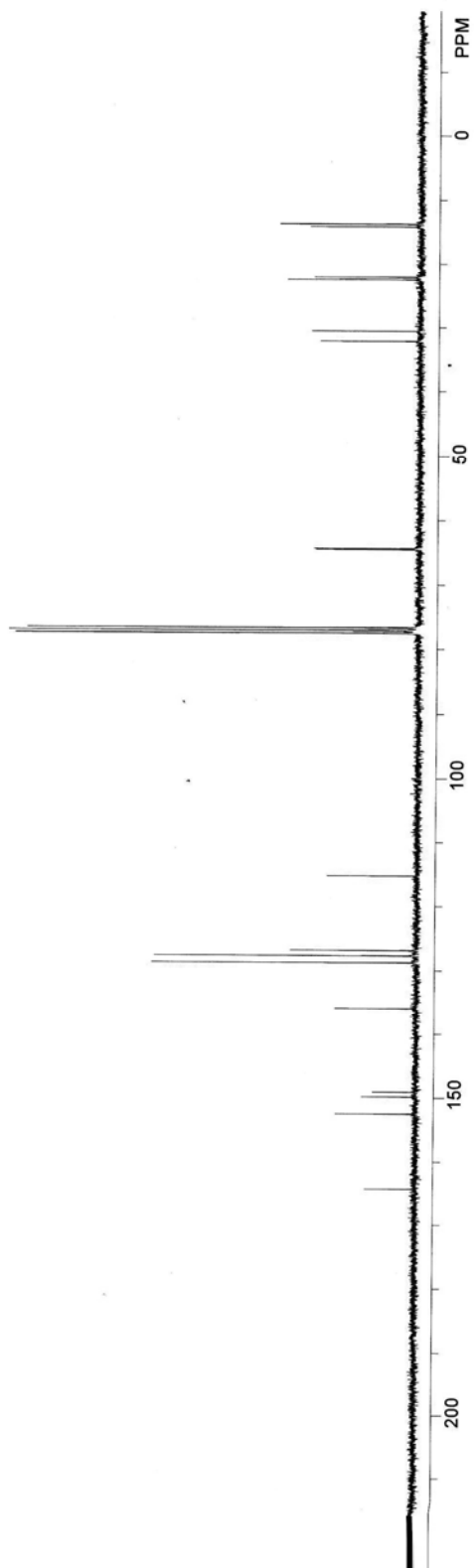
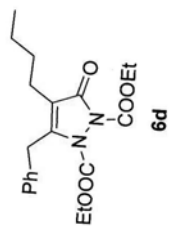


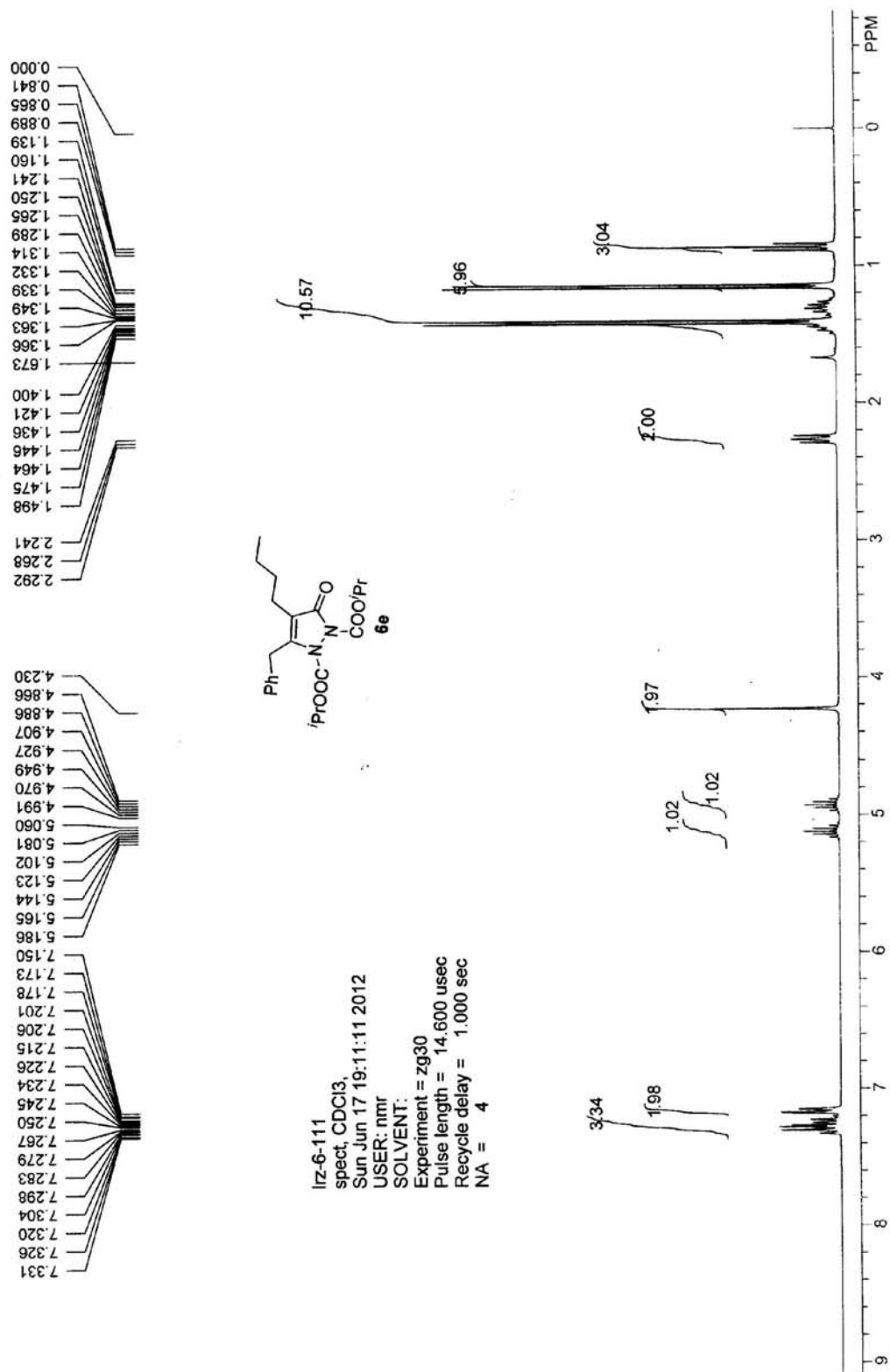


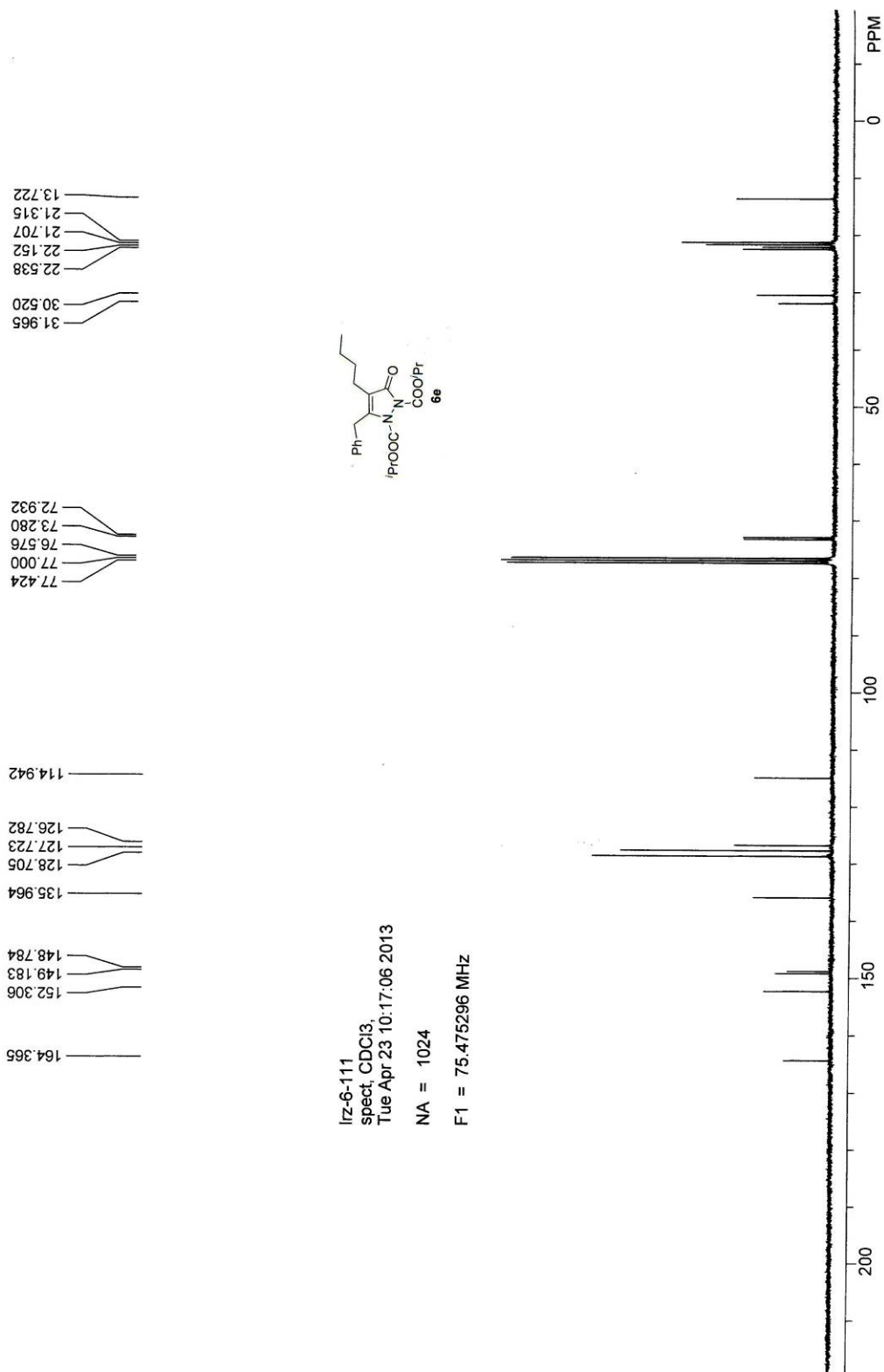
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SOLVENT:
Experiment = zg30
Pulse length = 14,600 usec
Recycle delay = 1,000 sec
NA = 4



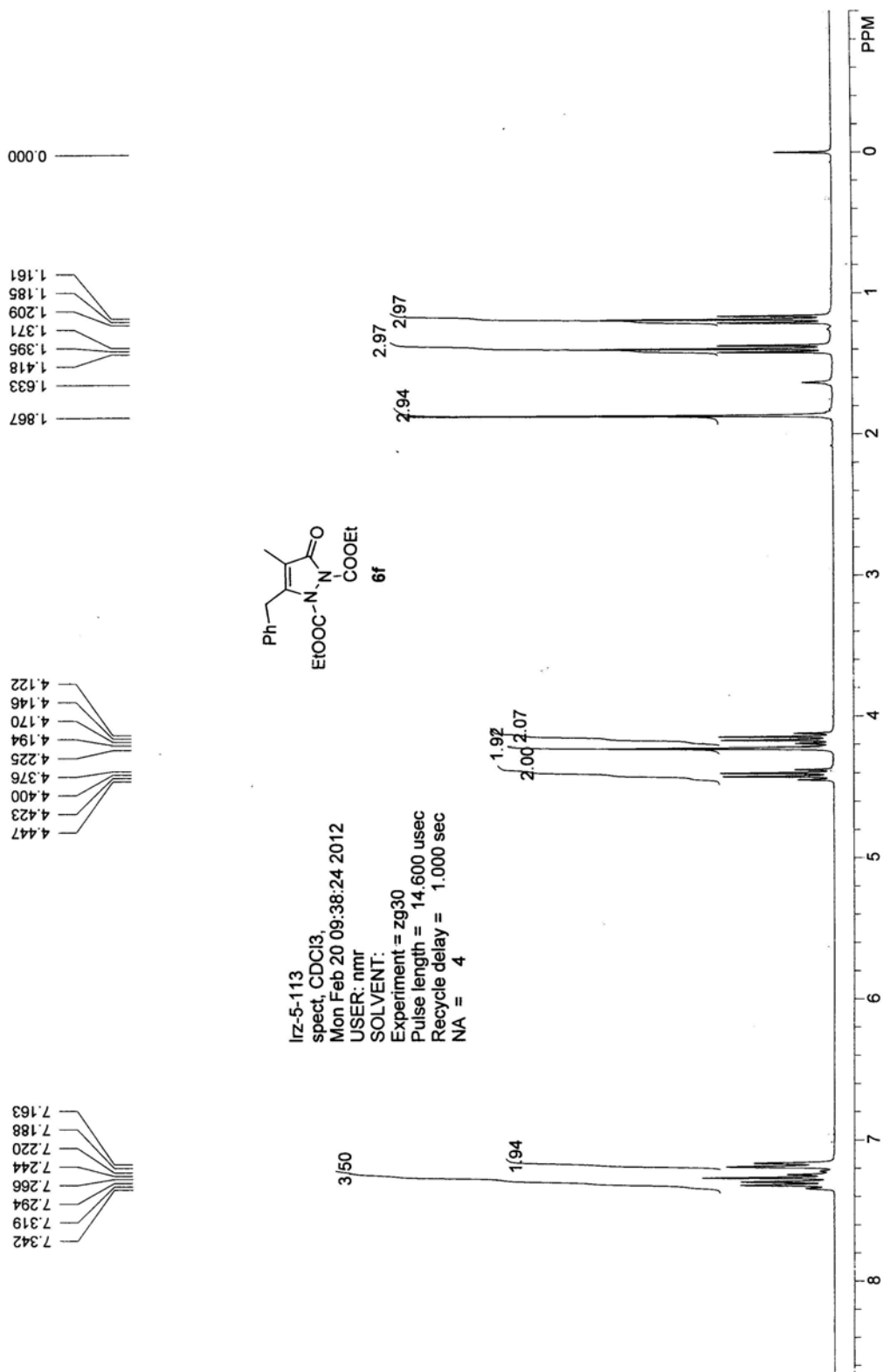
lrz-6-124-C
spect, CDCl3
Fri Jul 13 13:34:34 2012
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.900 usec
Recycle delay = 2.000 sec
NA = 395

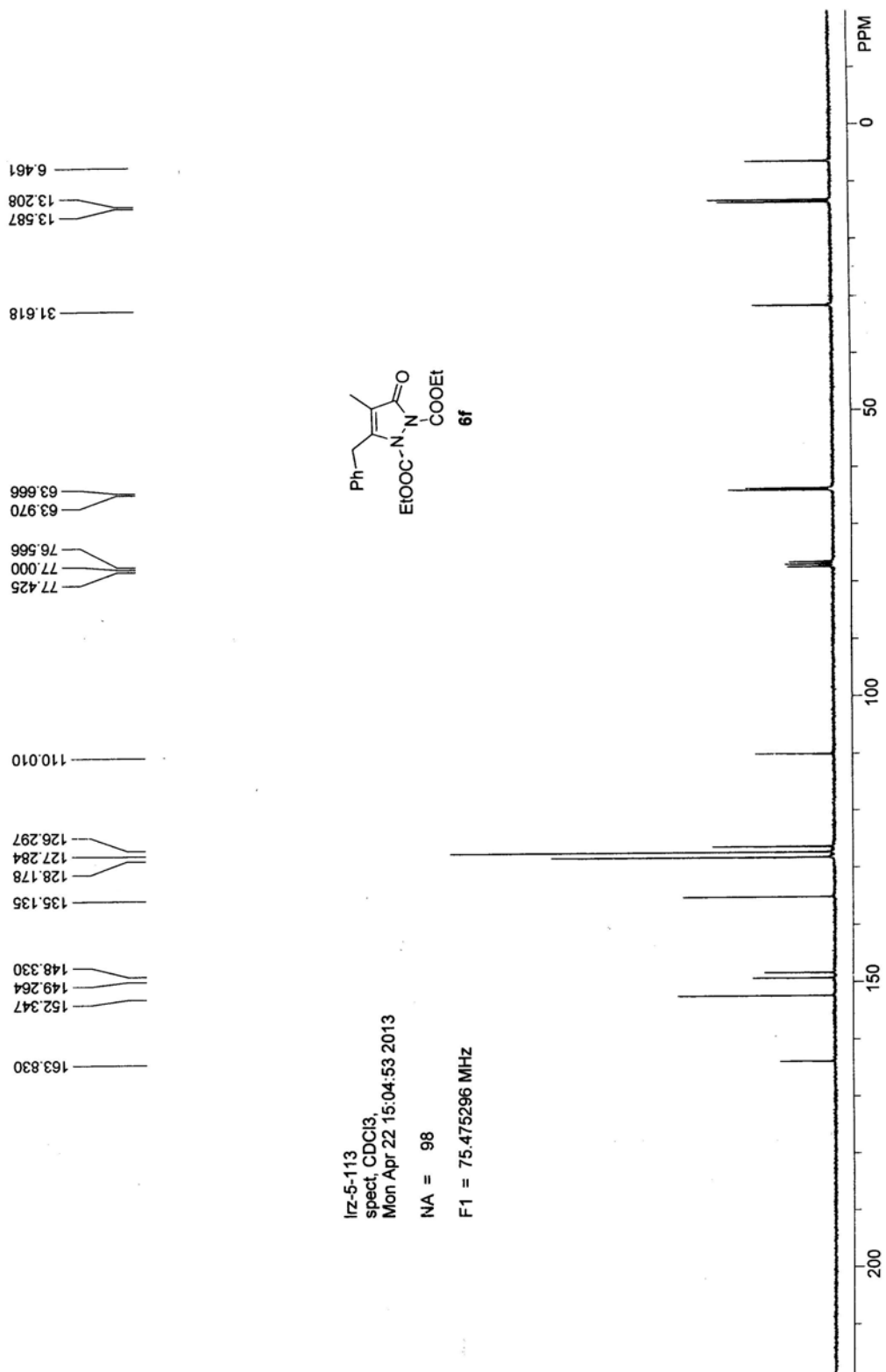




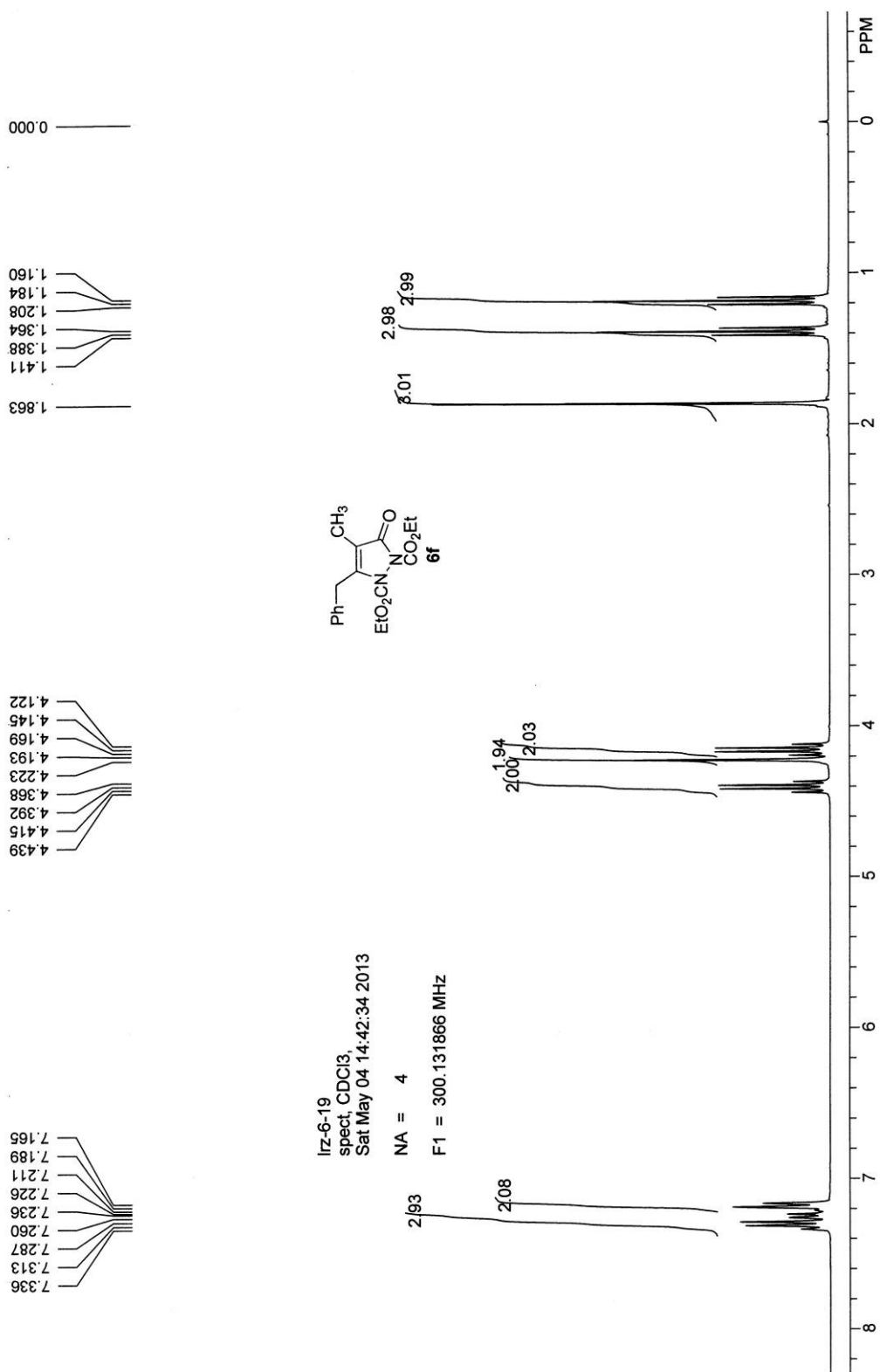


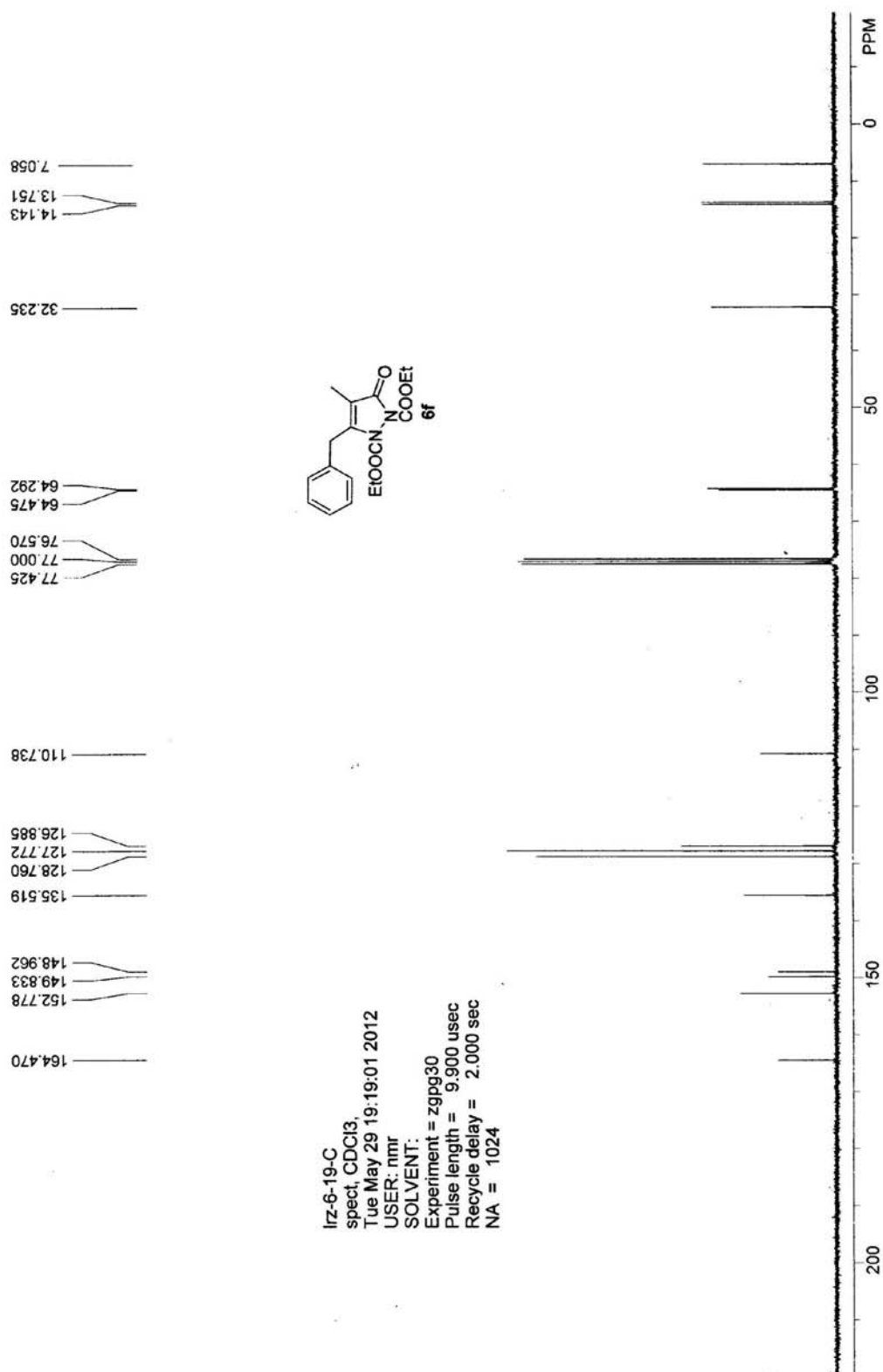
lhz-6-111
spect, CDCl₃,
Tue Apr 23 10:17:06 2013
NA = 1024
F1 = 75.475296 MHz

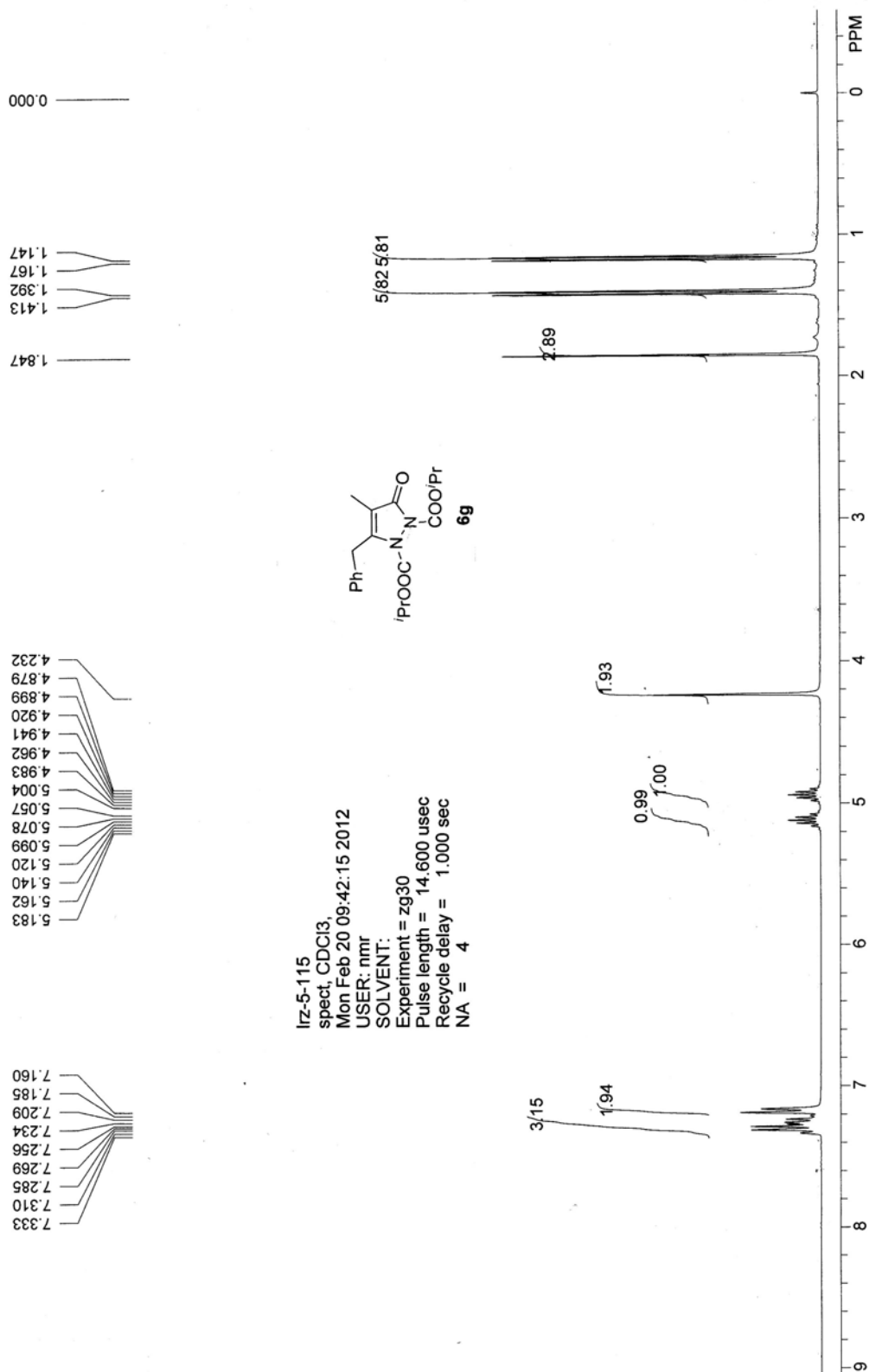


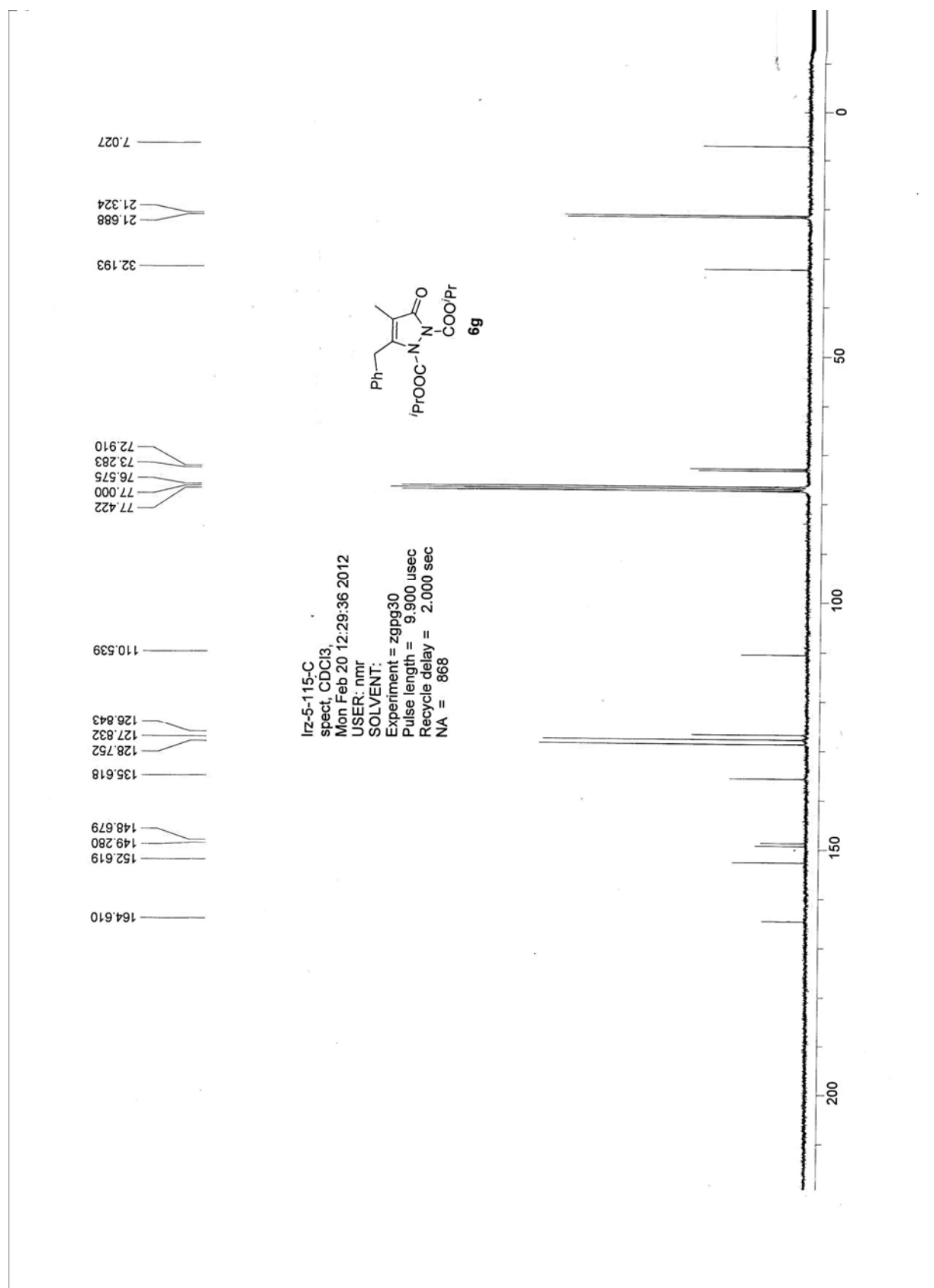


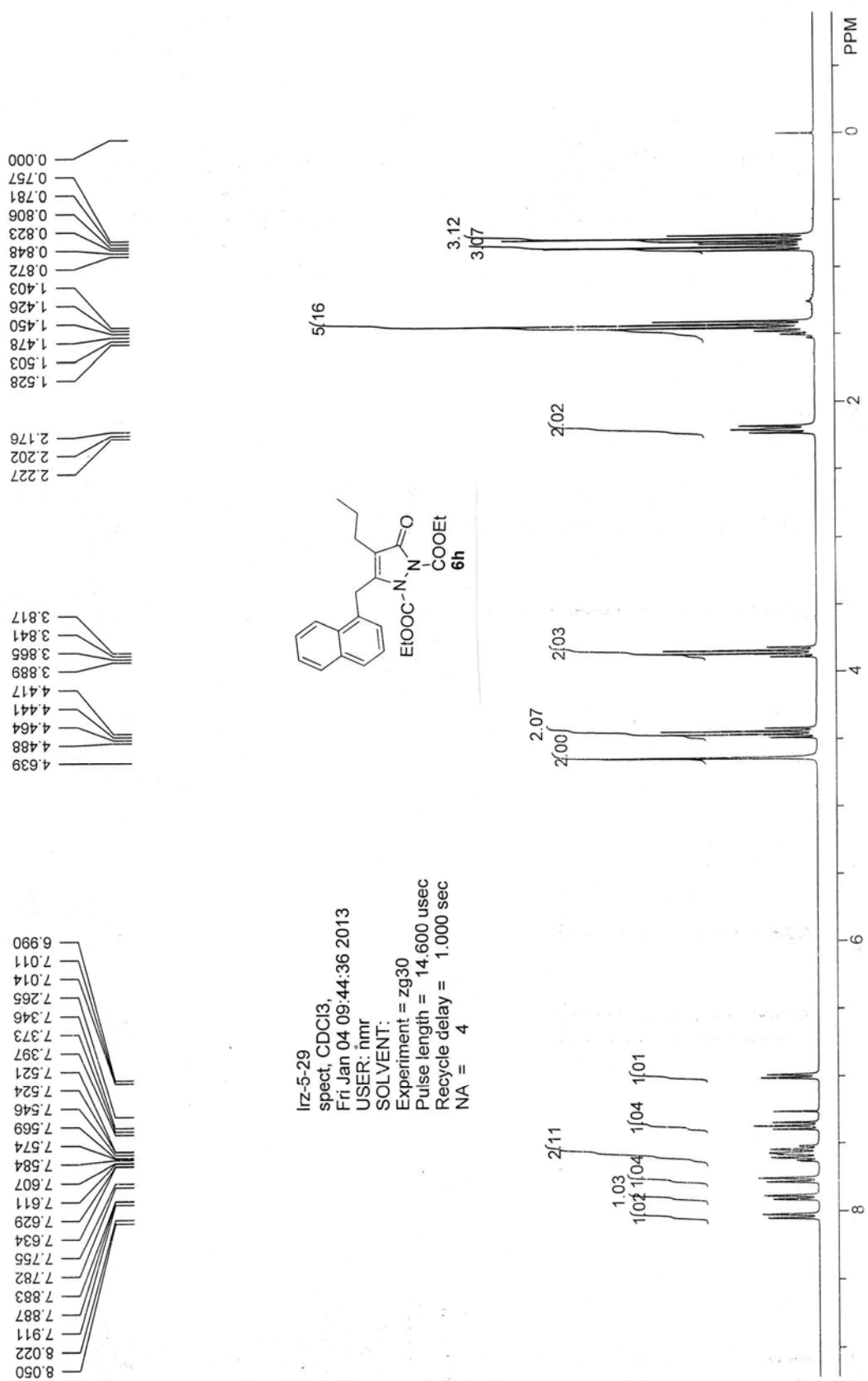
lrz-5-113
spect, CDCl₃,
Mon Apr 22 15:04:53 2013
NA = 98
F1 = 75.475296 MHz



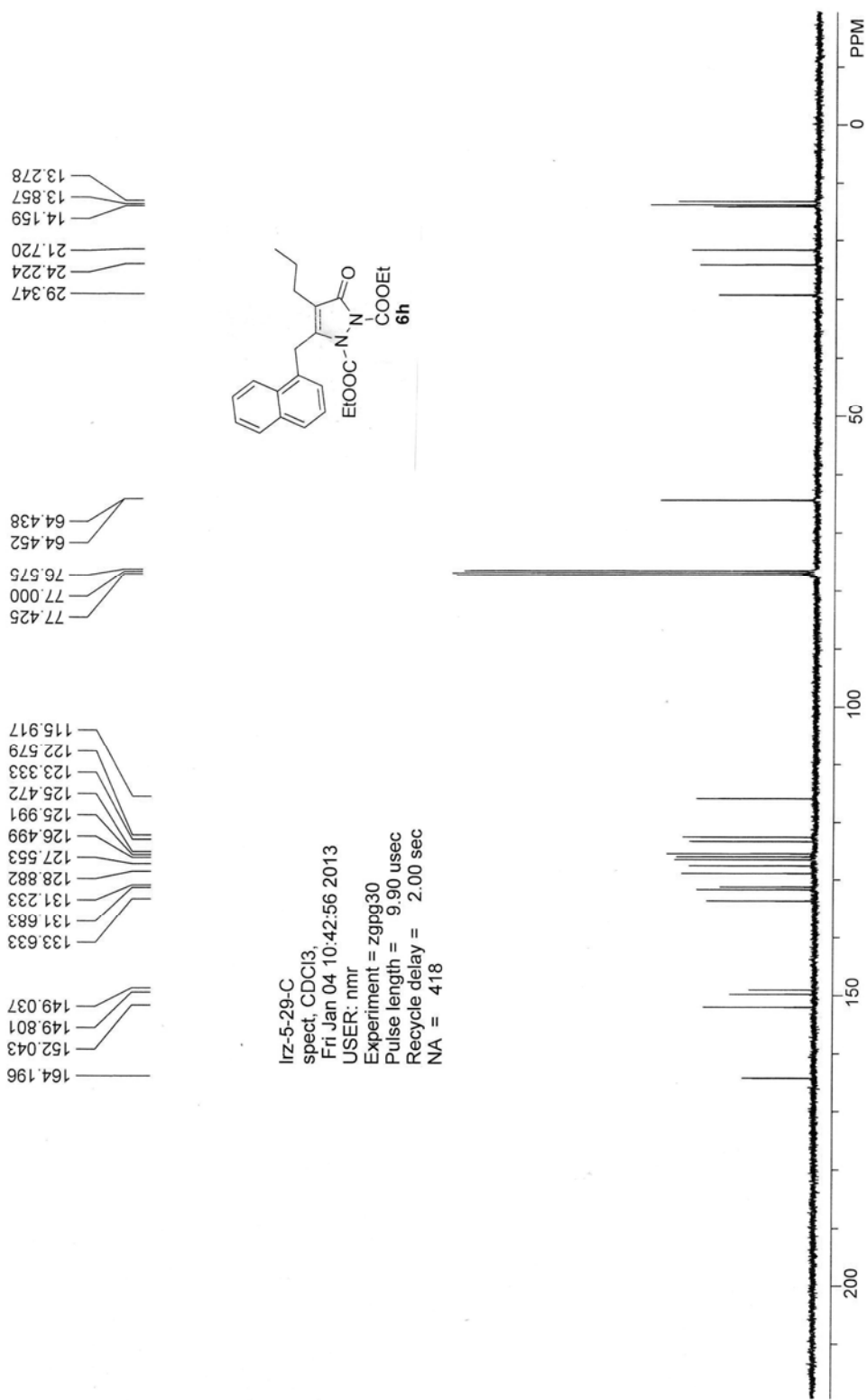


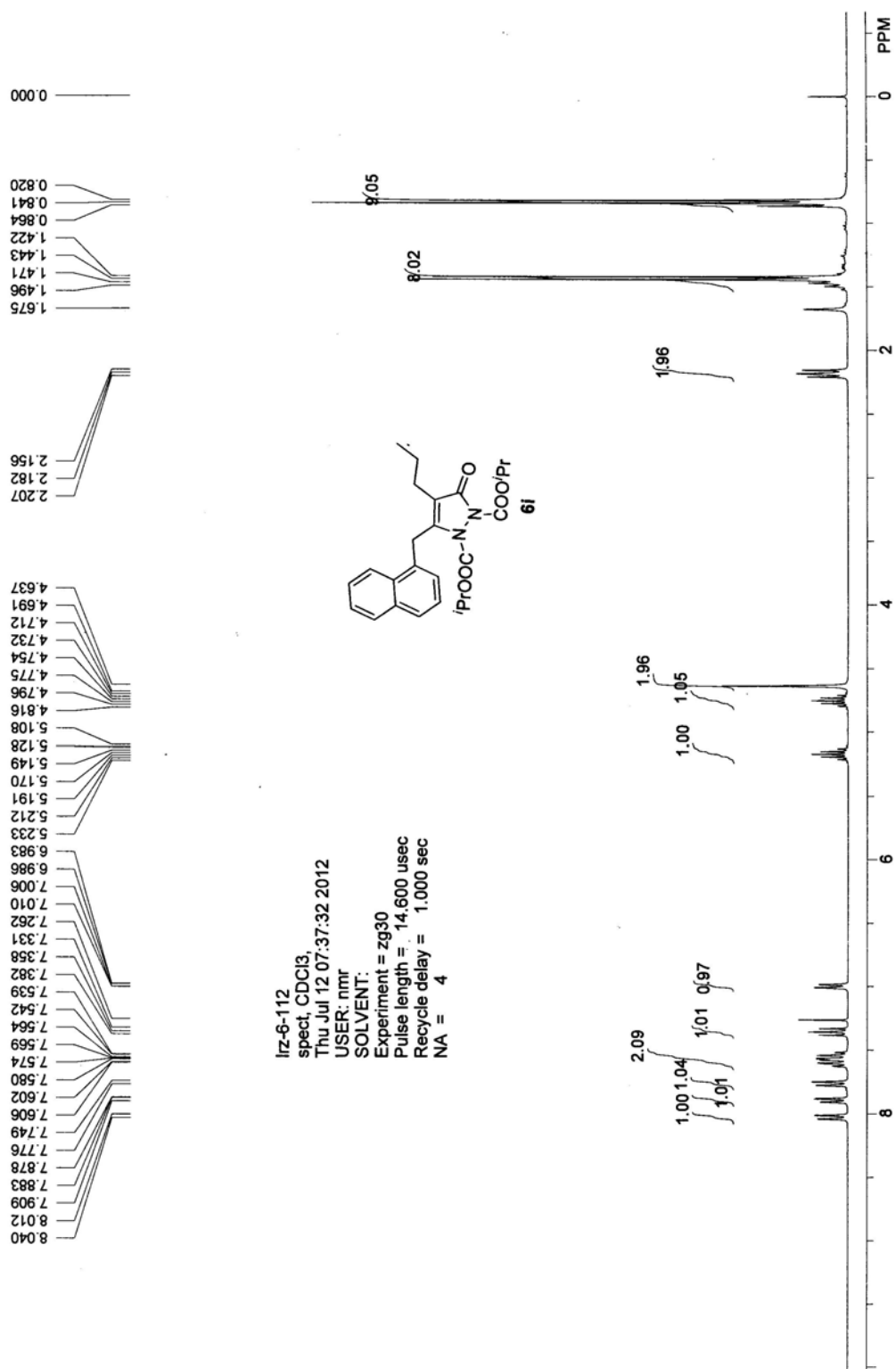


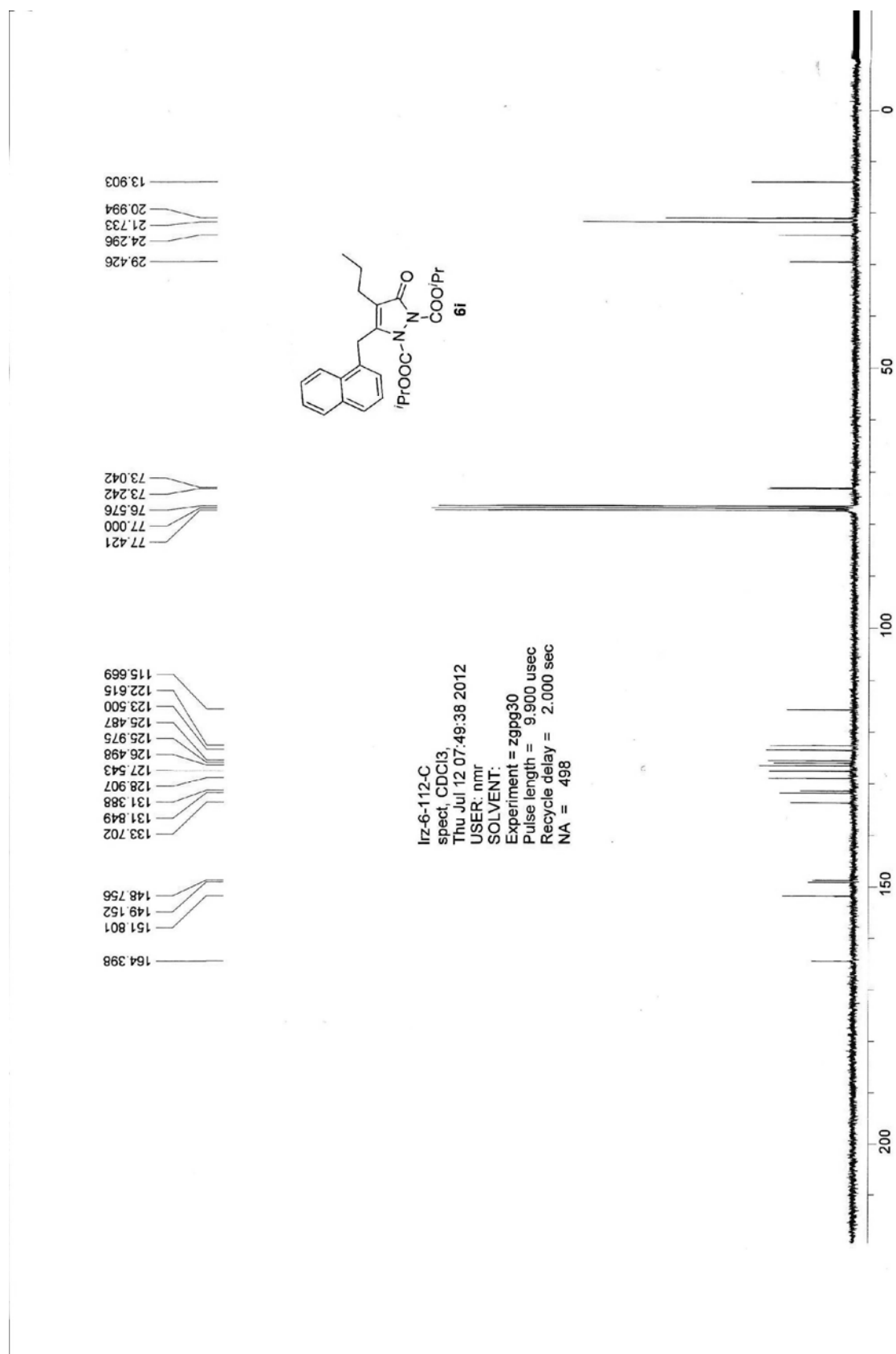


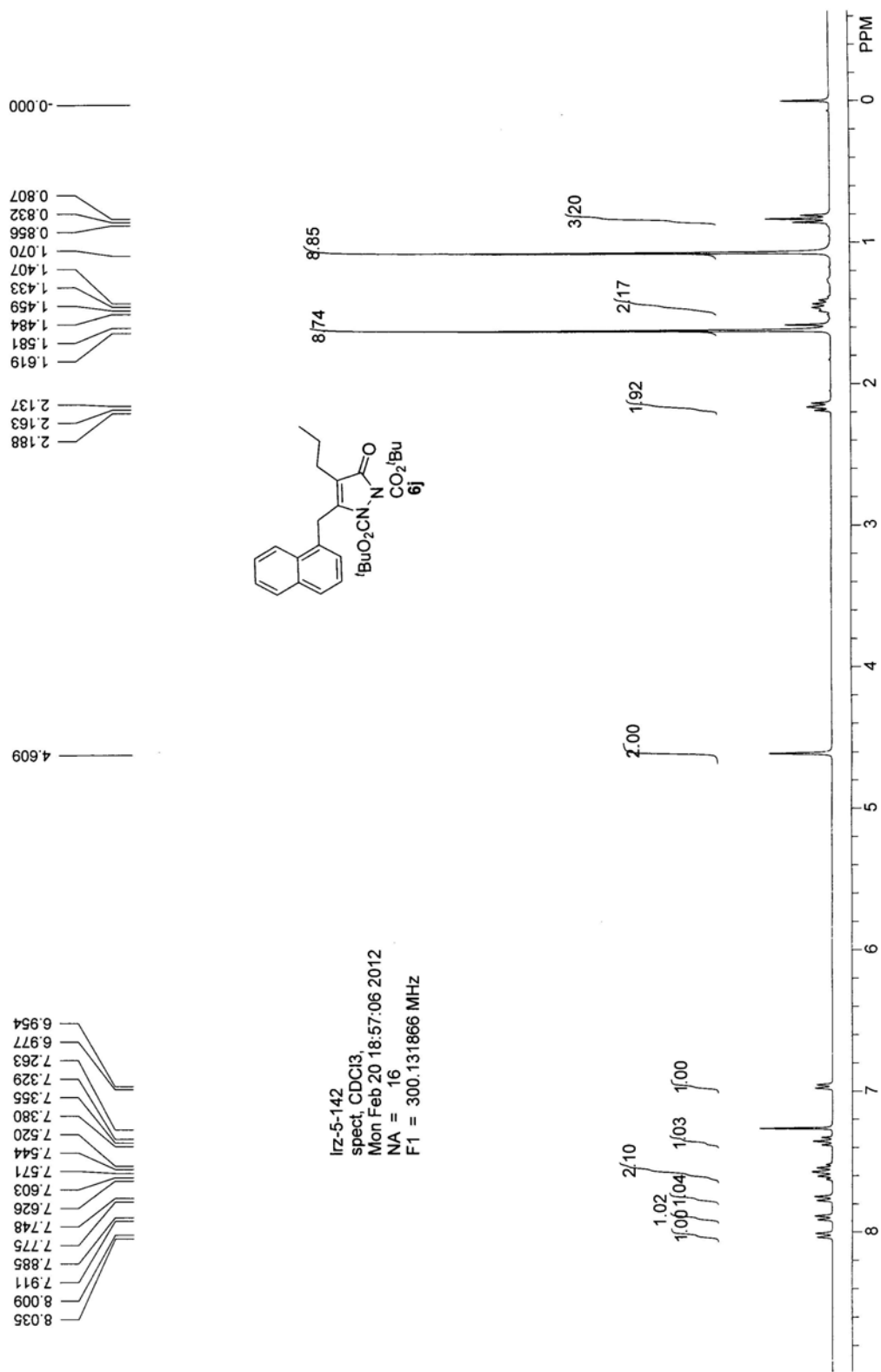


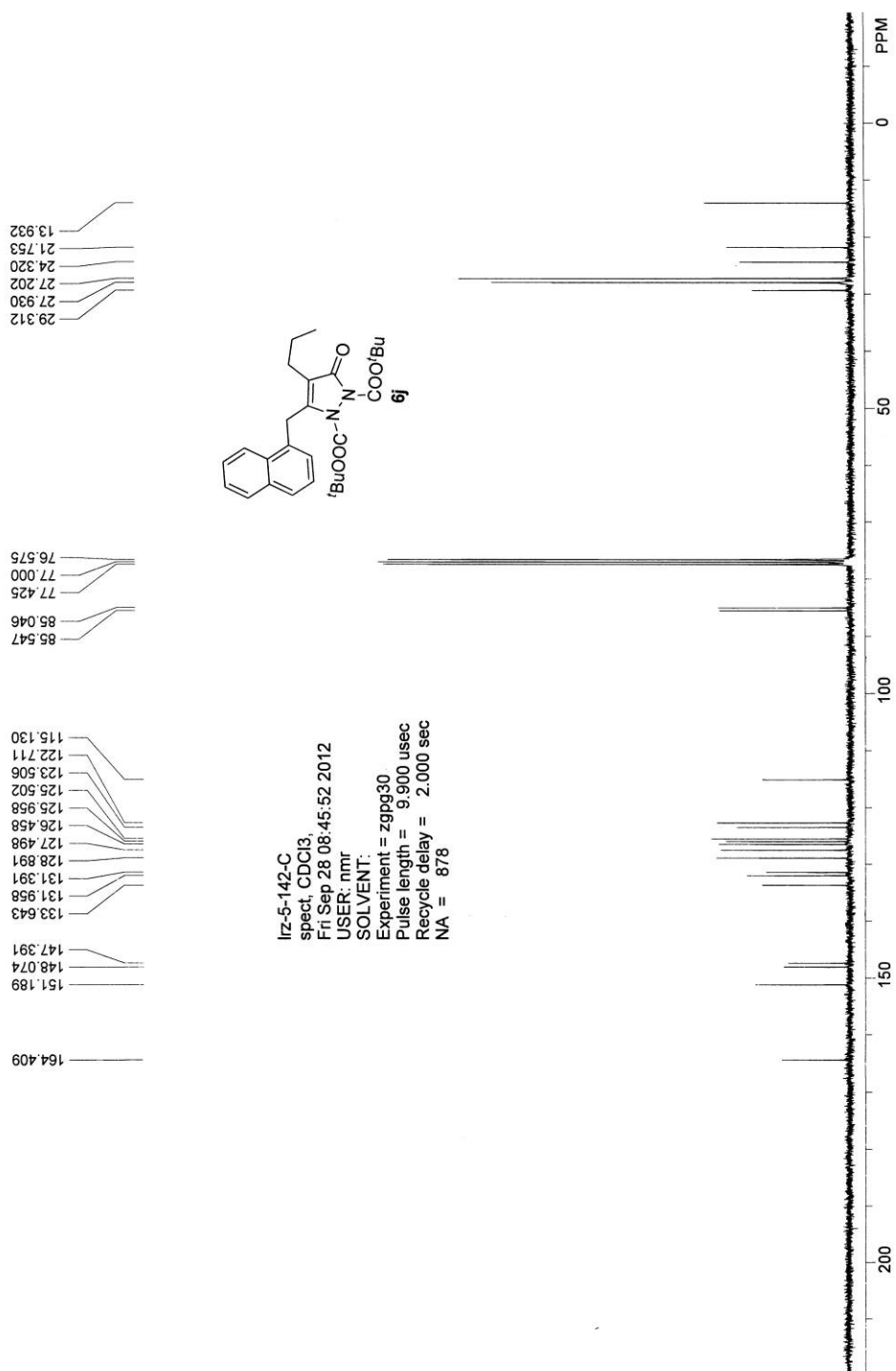
IZ-5-29
 spect, CDCl₃,
 Fri Jan 04 09:44:36 2013
 USER: hmr
 SOLVENT:
 Experiment = zg30
 Pulse length = 14.600 usec
 Recycle delay = 1.000 sec
 NA = 4

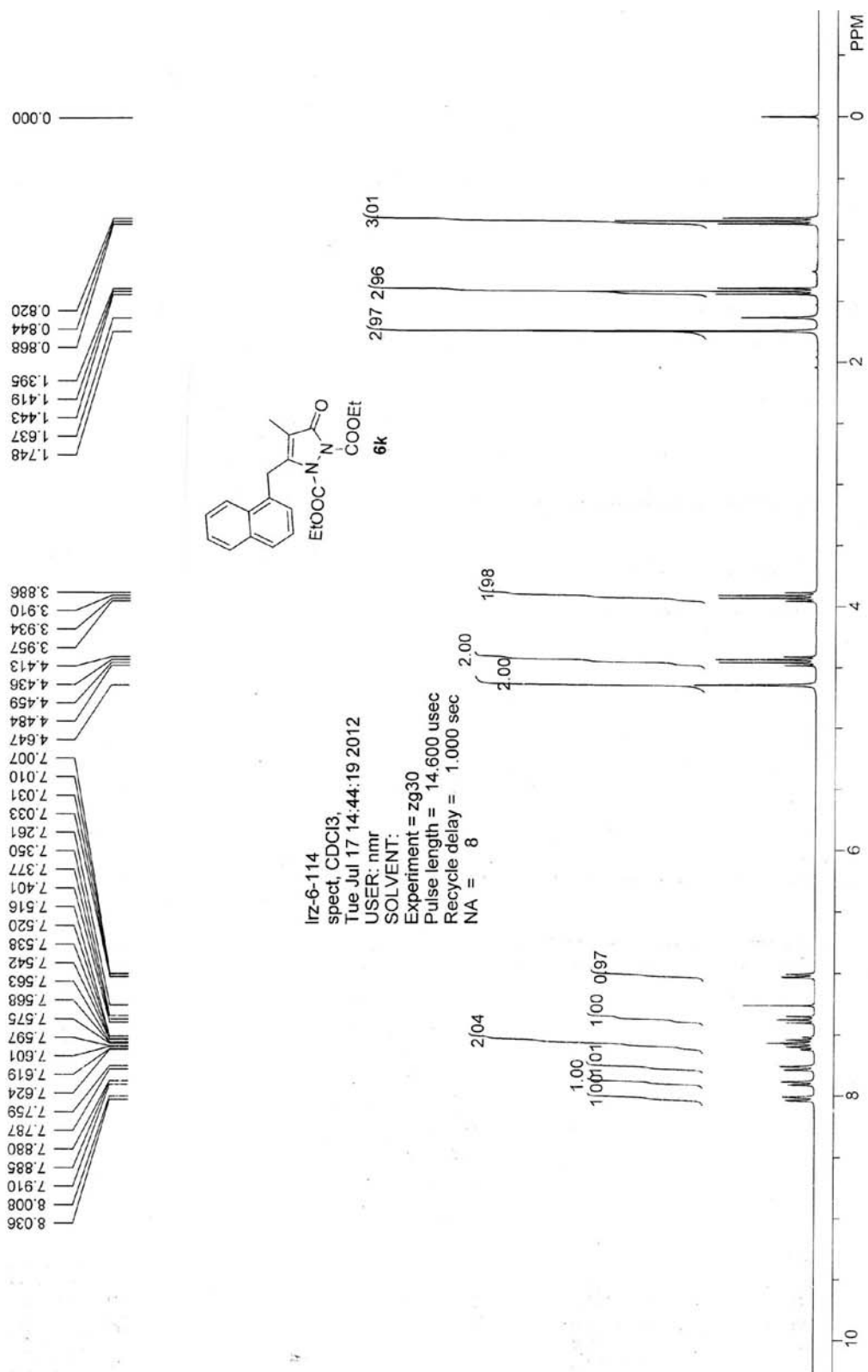


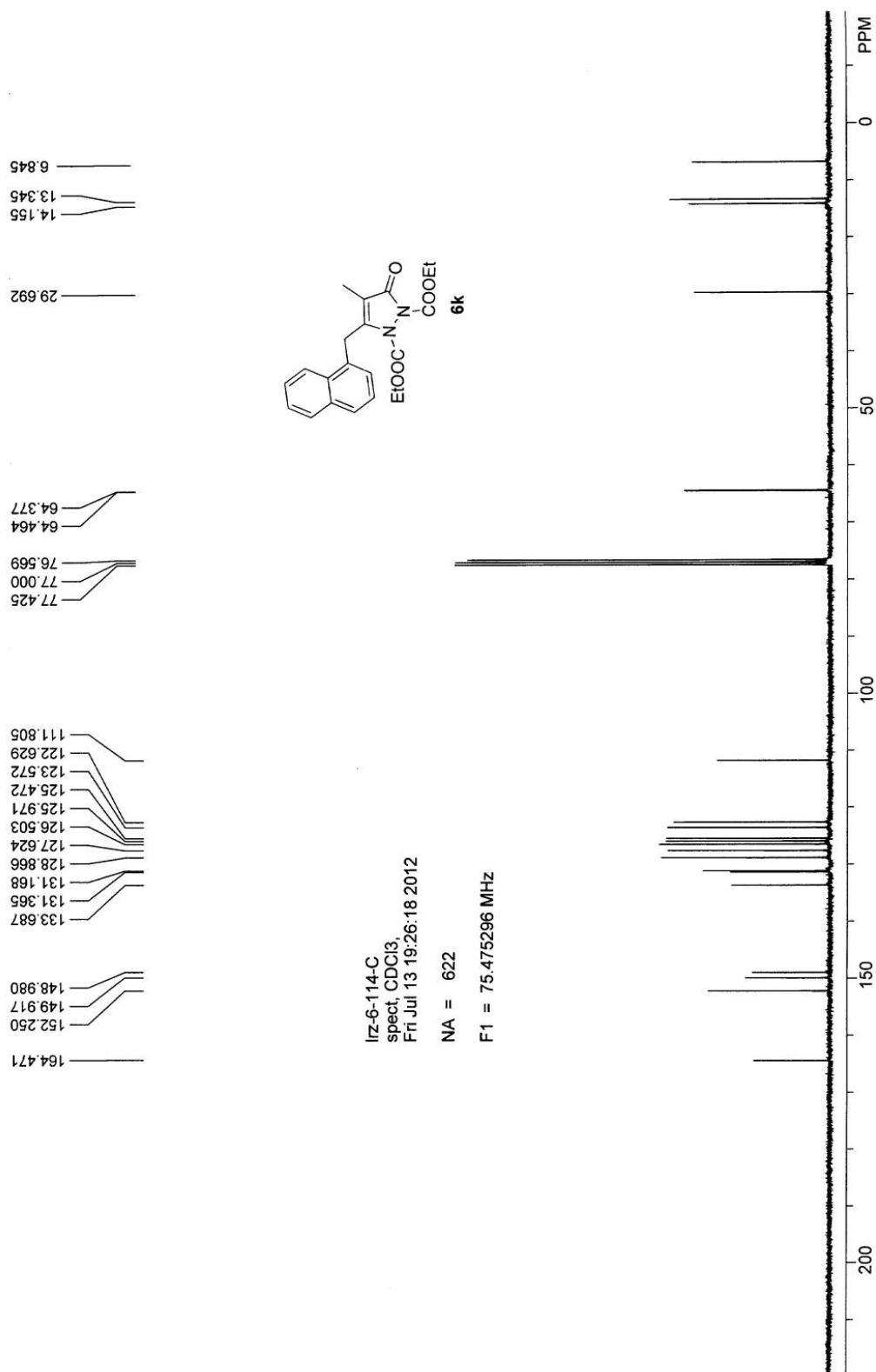


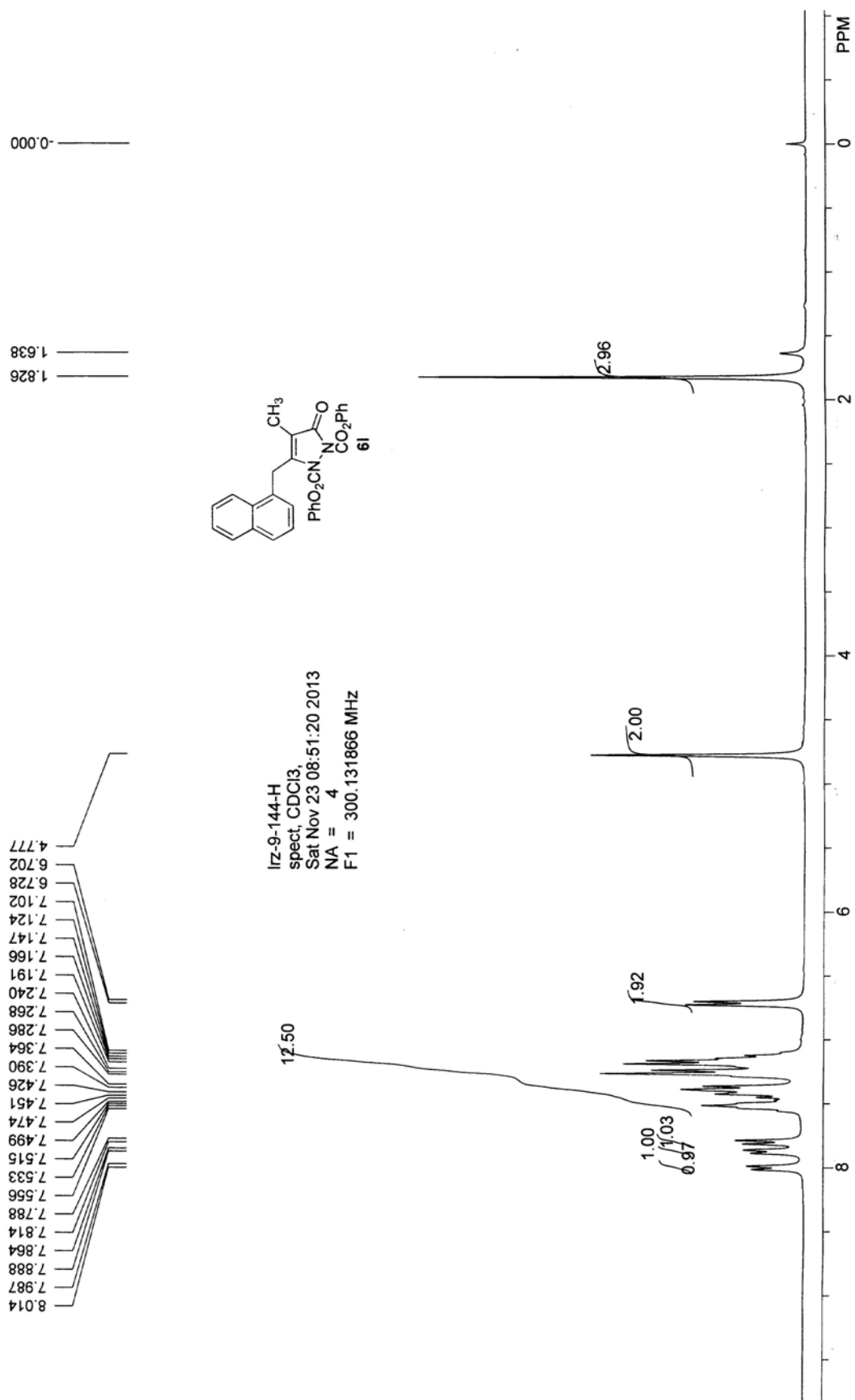


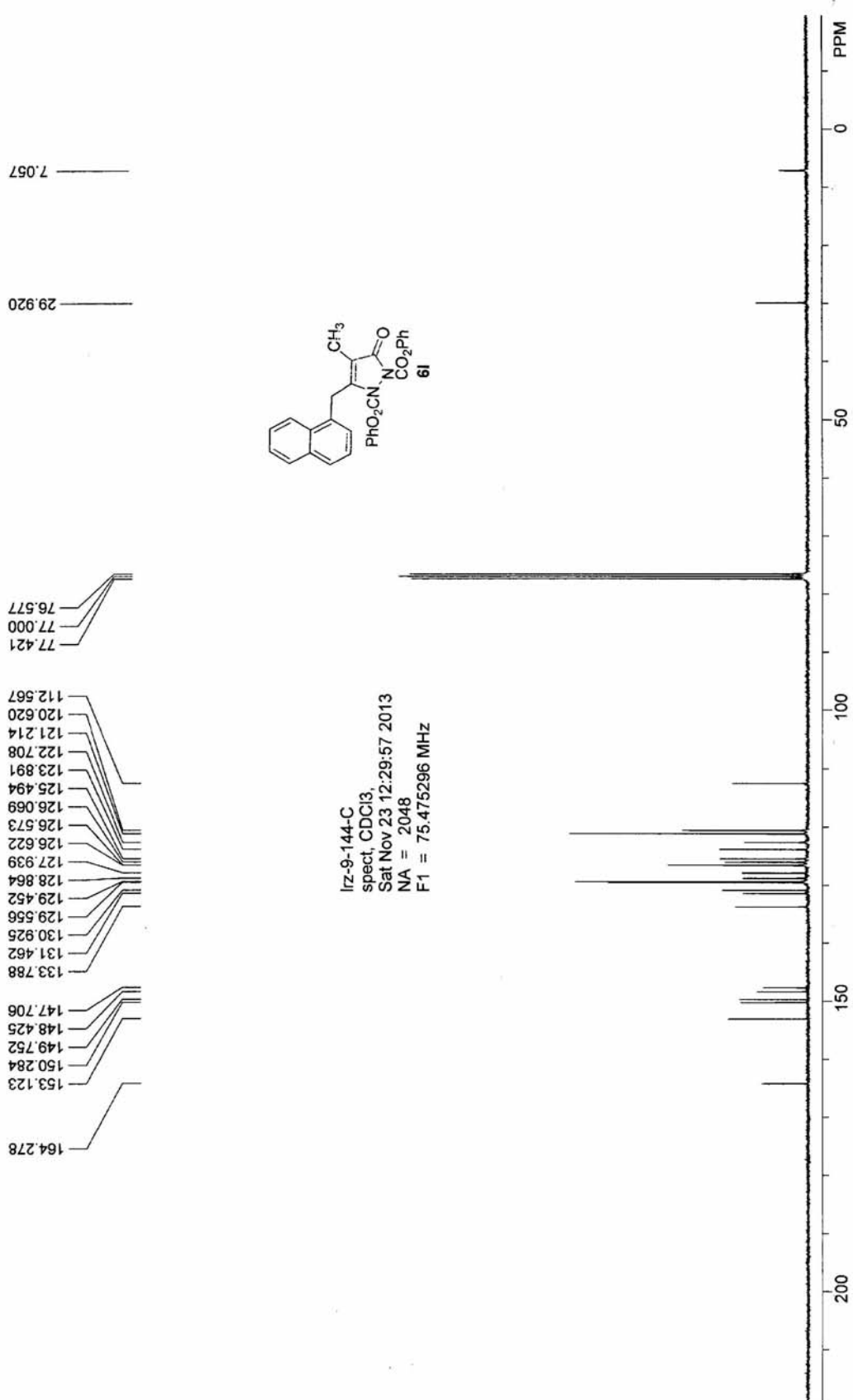


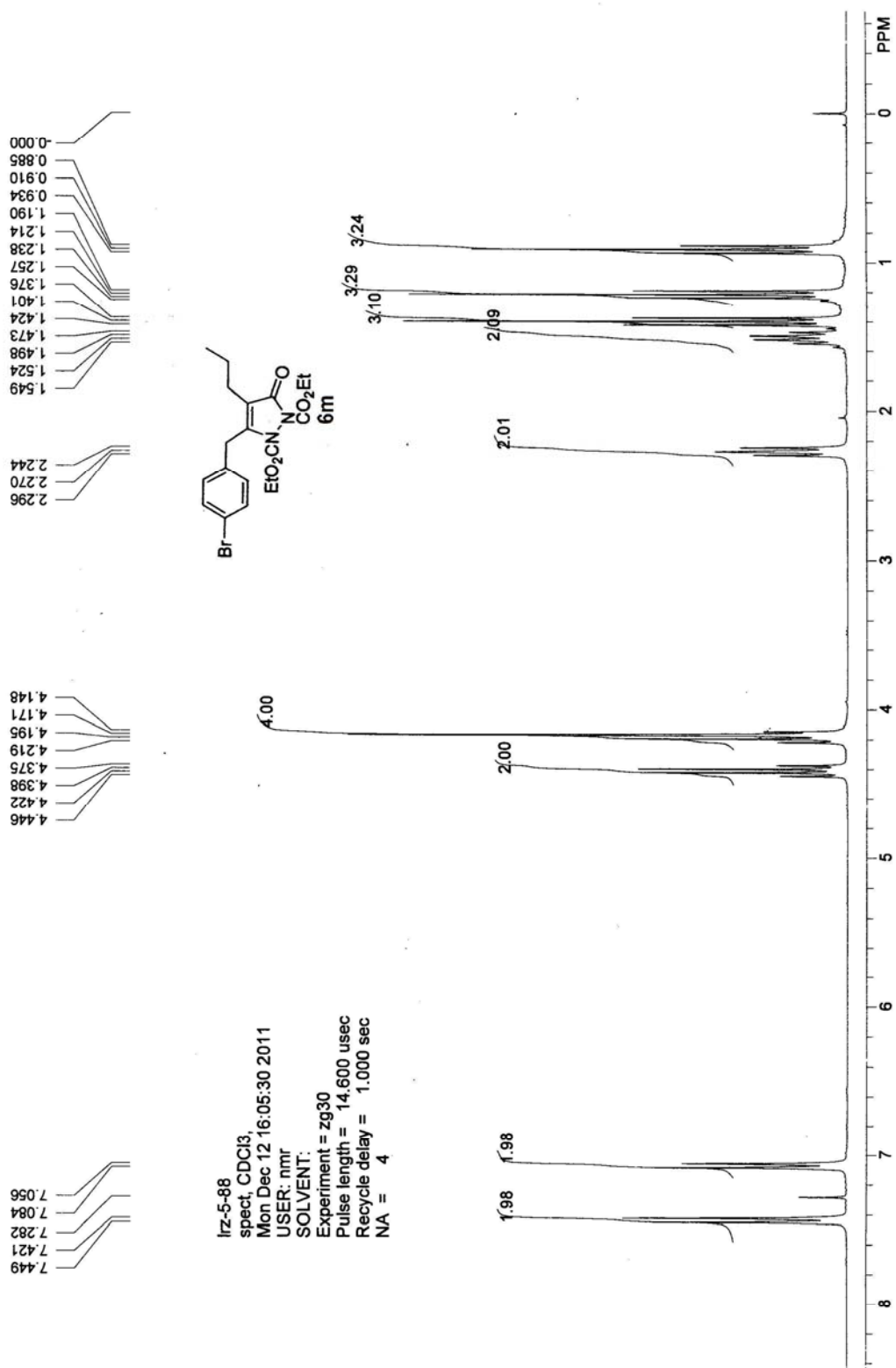


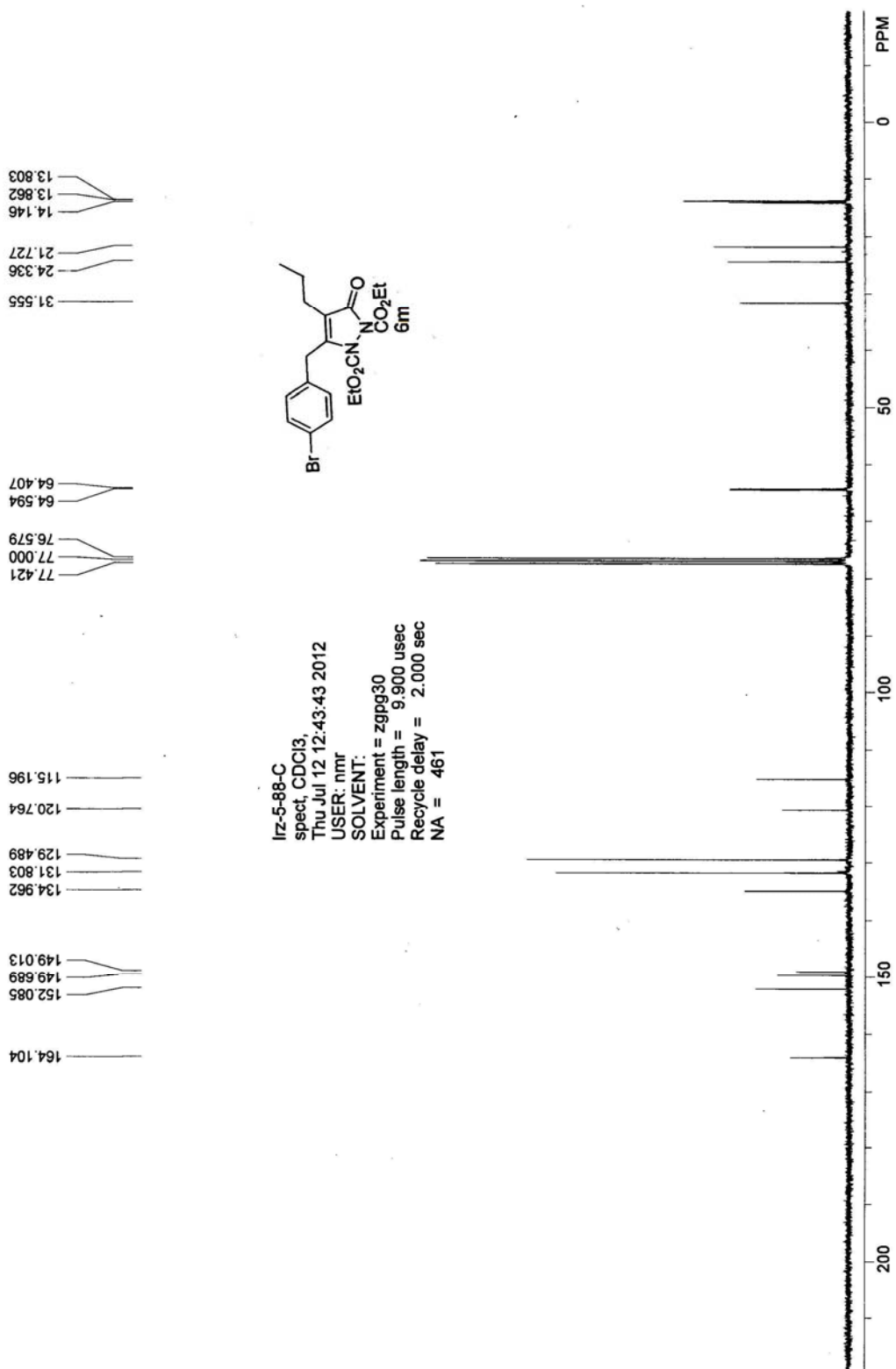


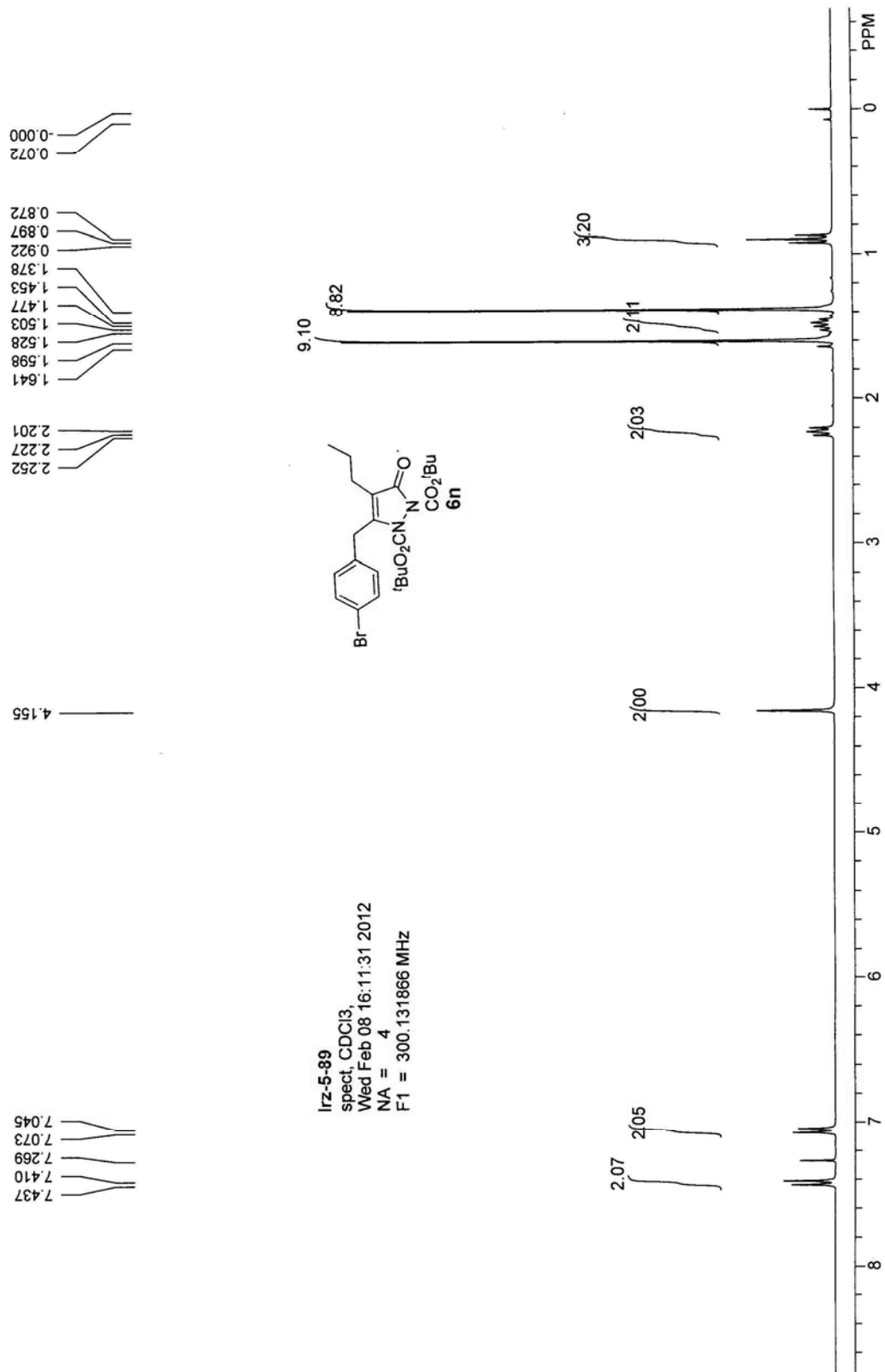


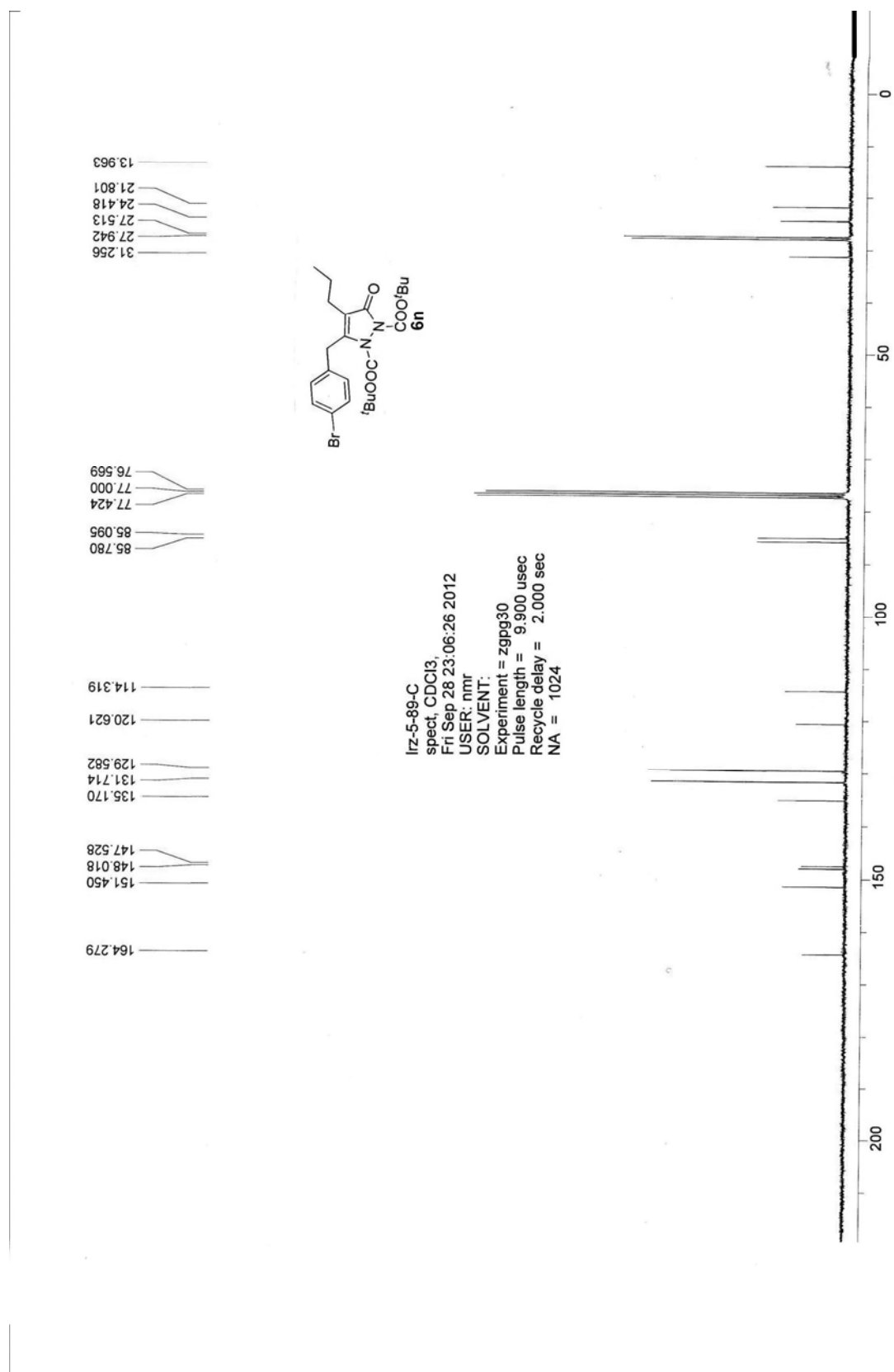


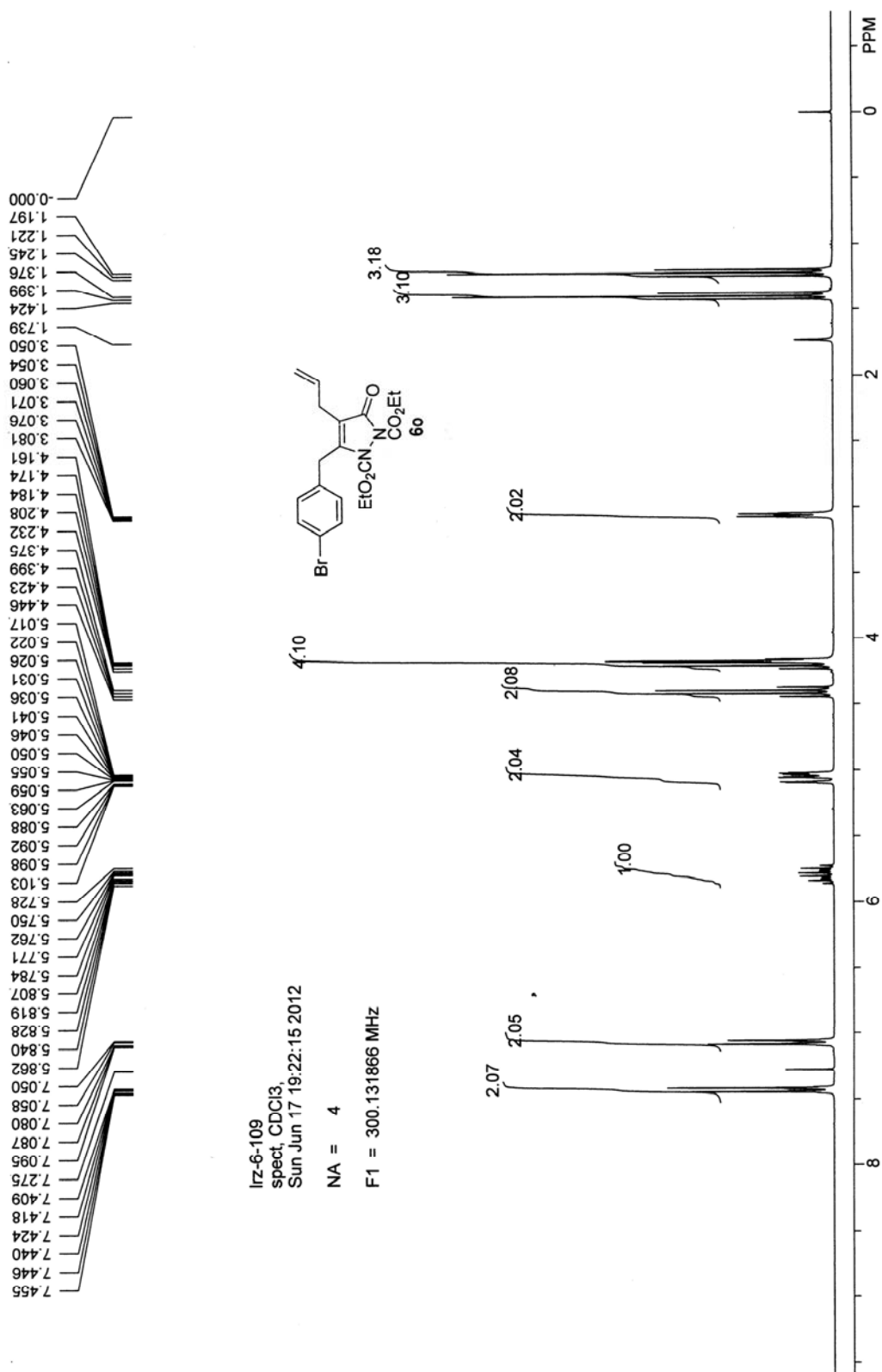


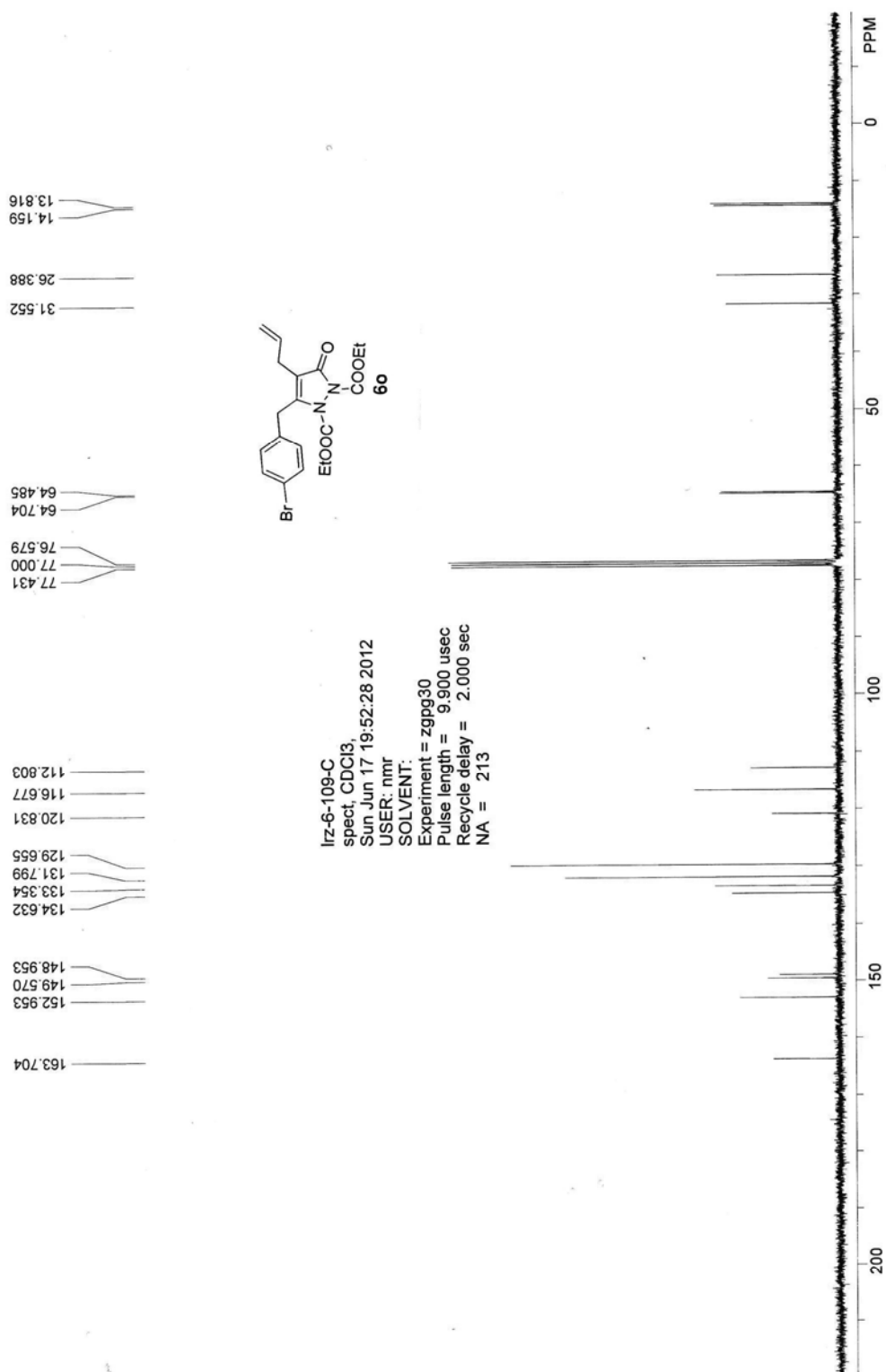


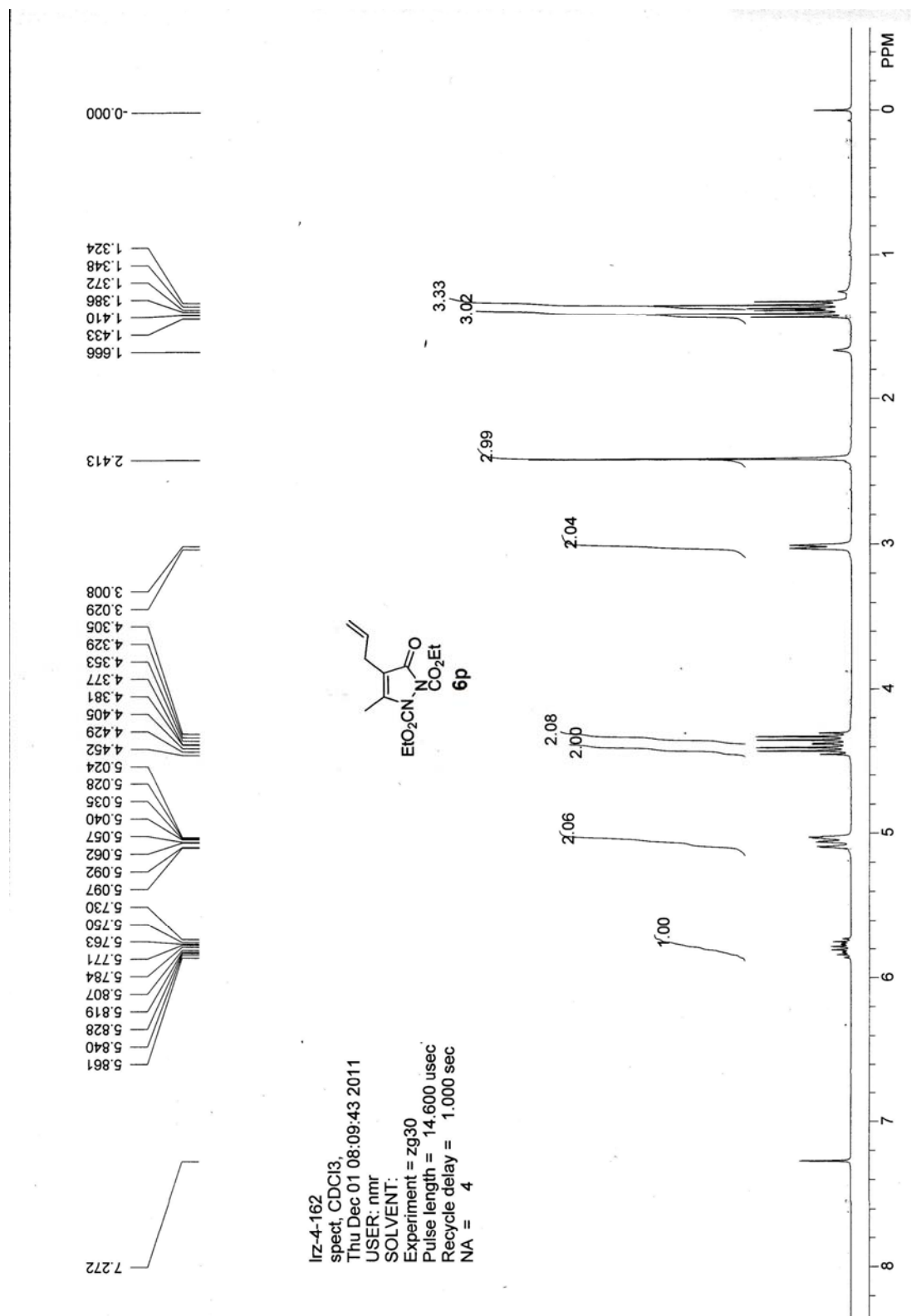


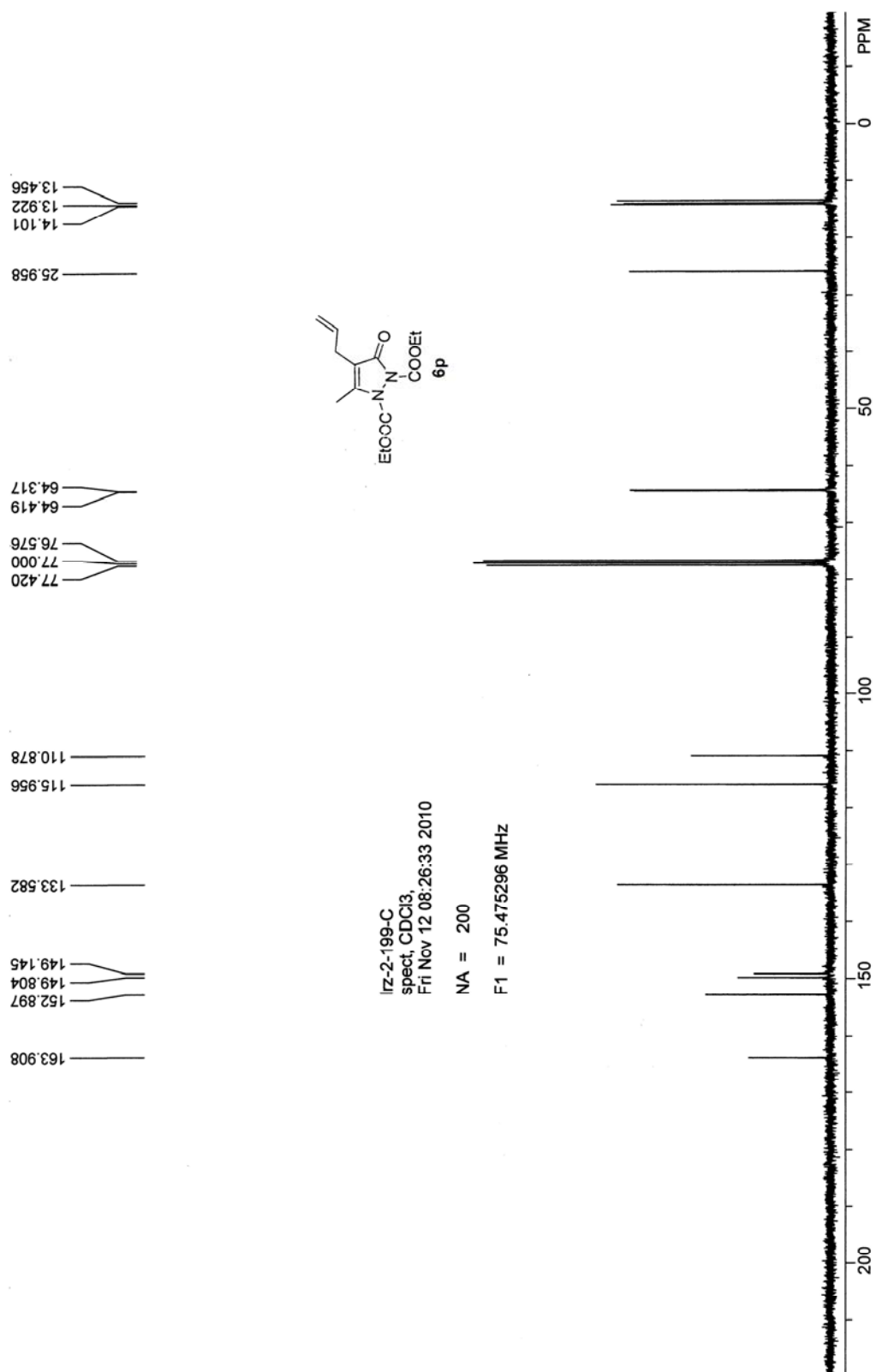


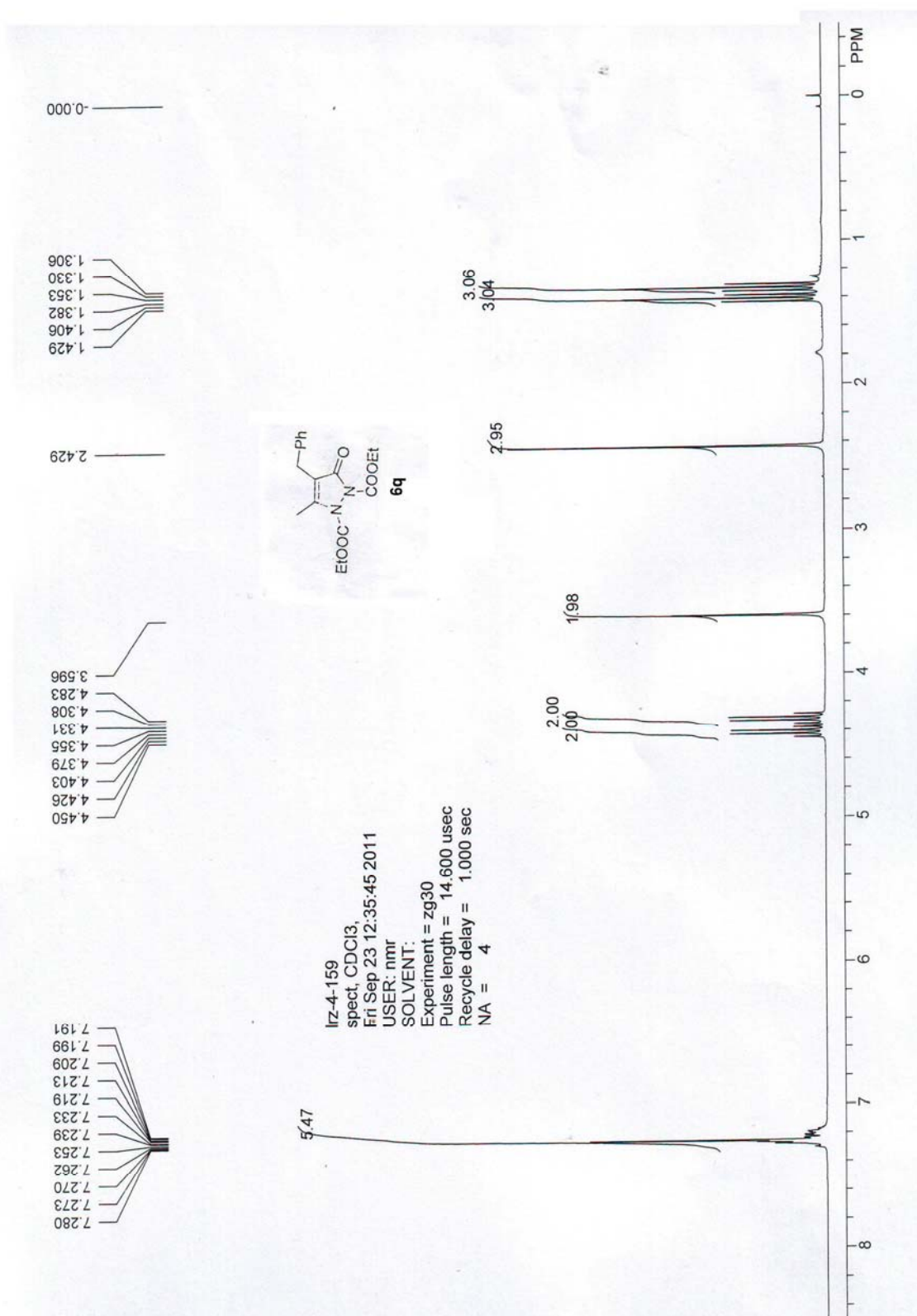


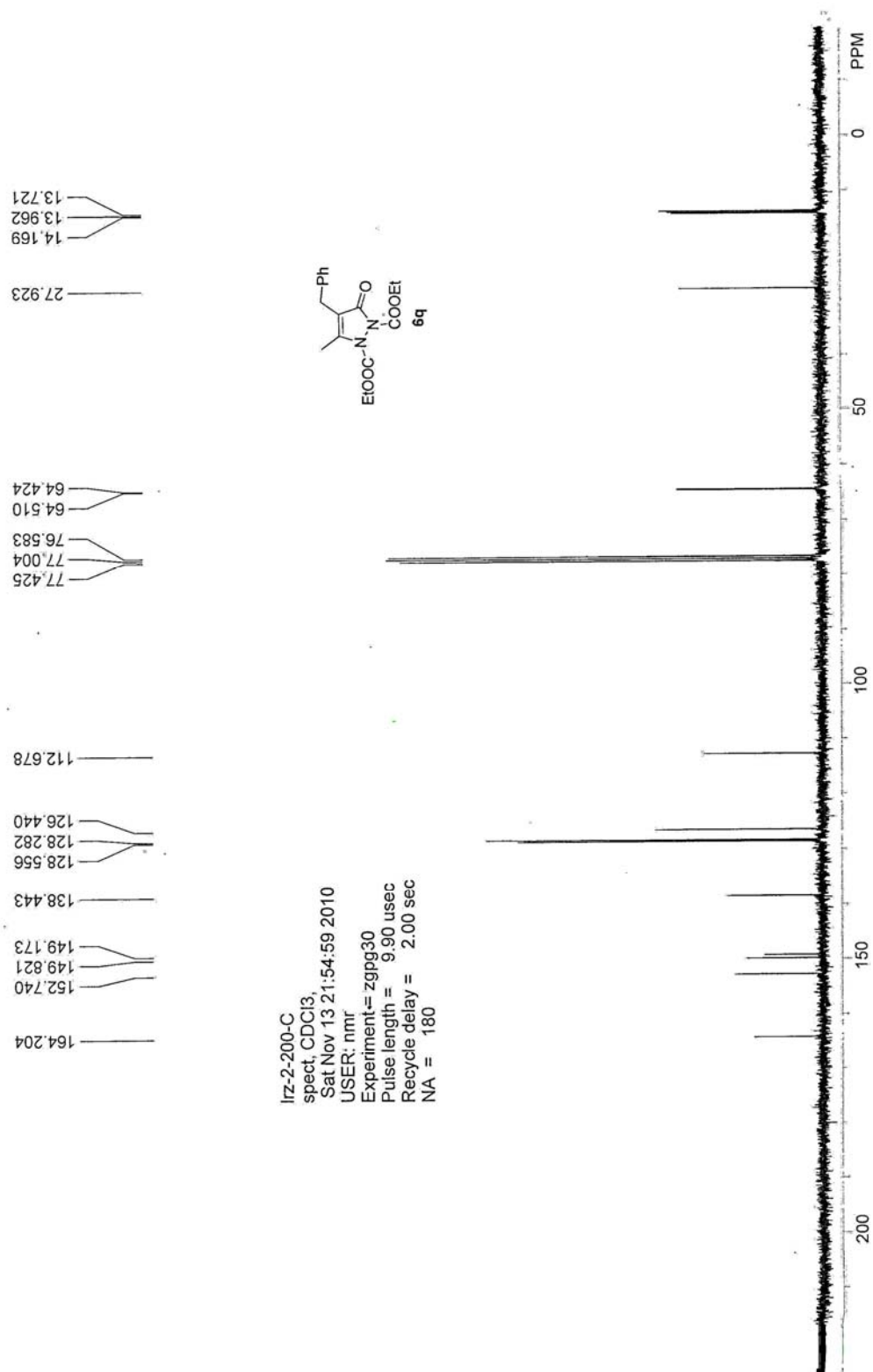


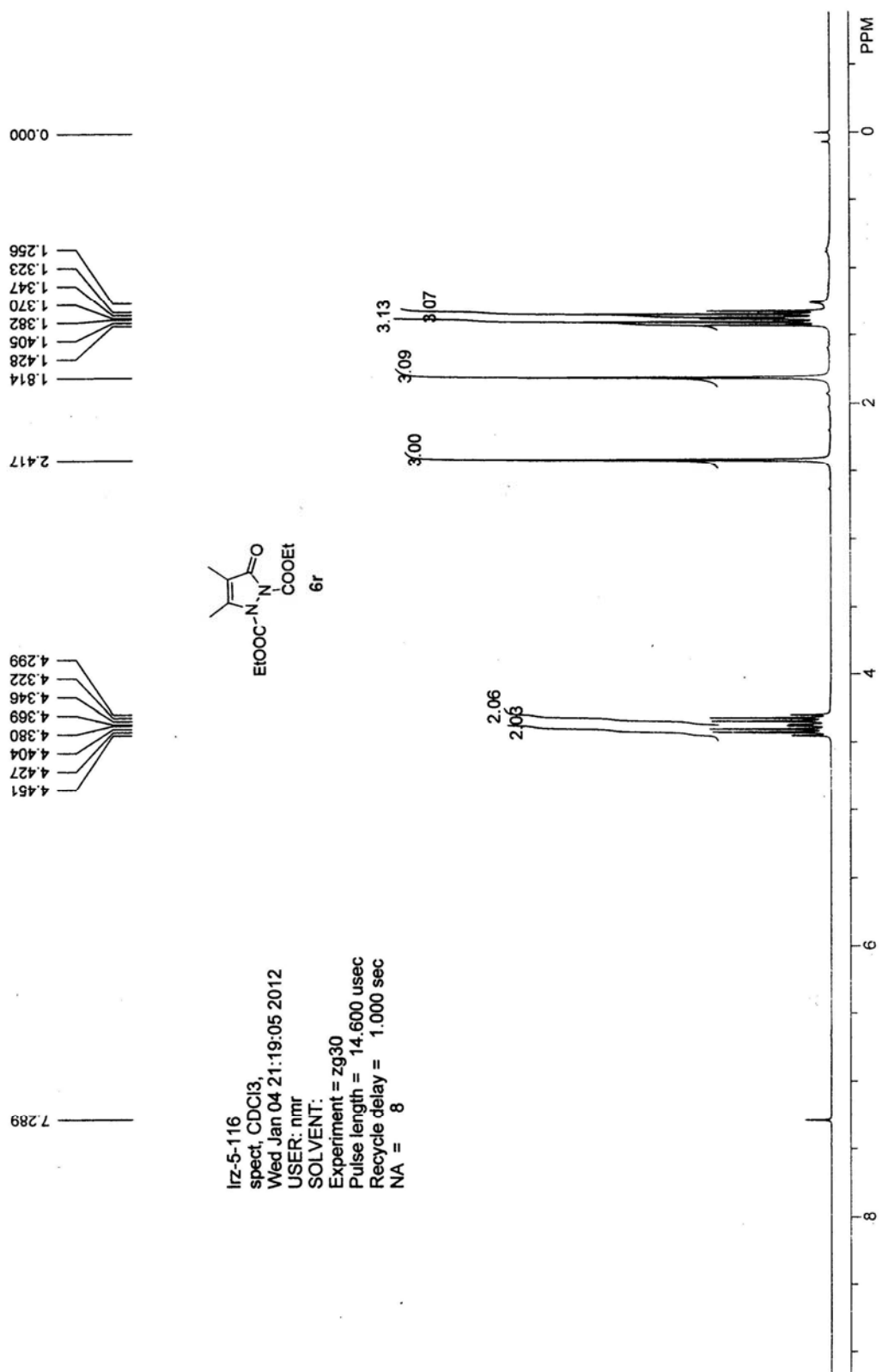


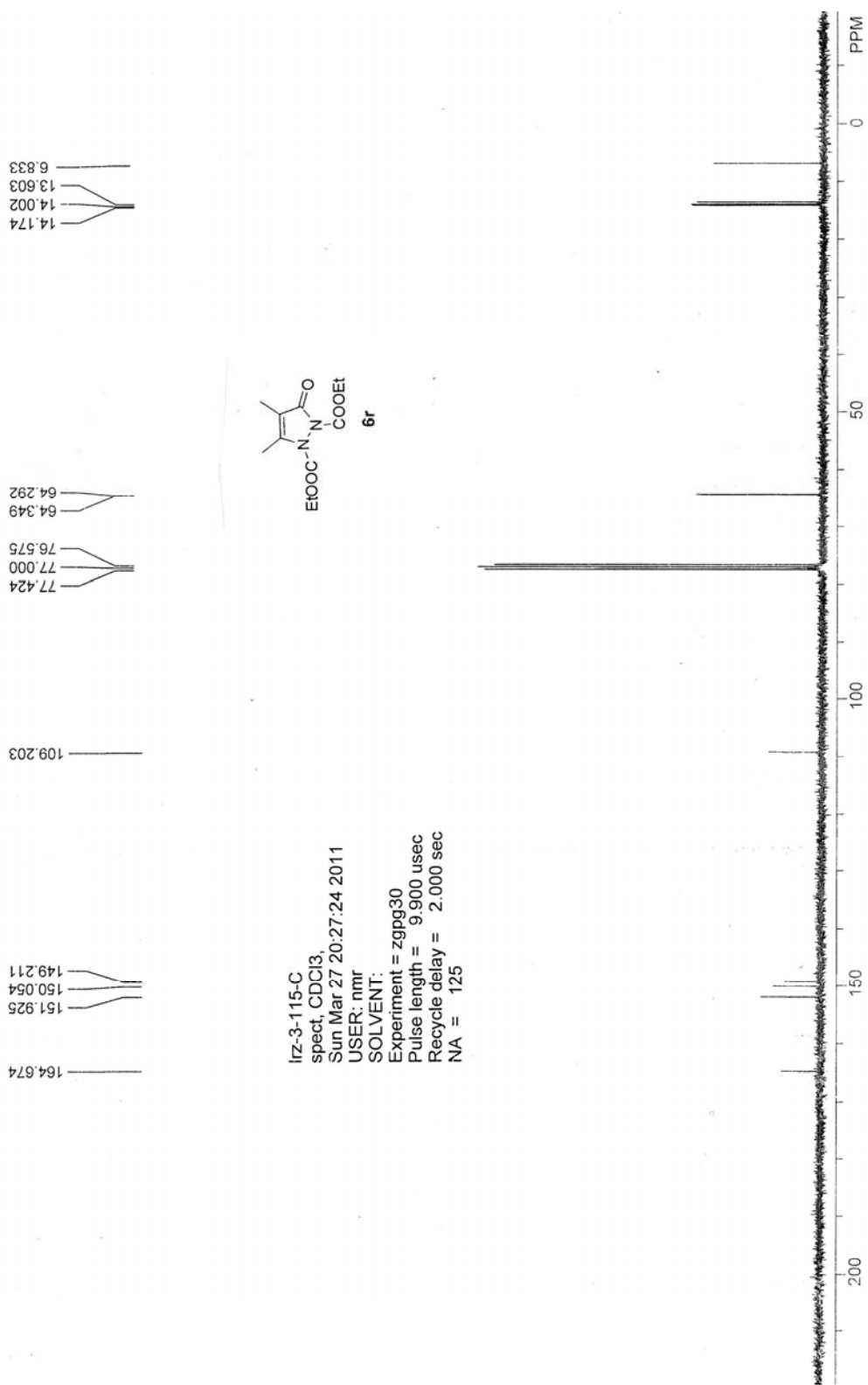


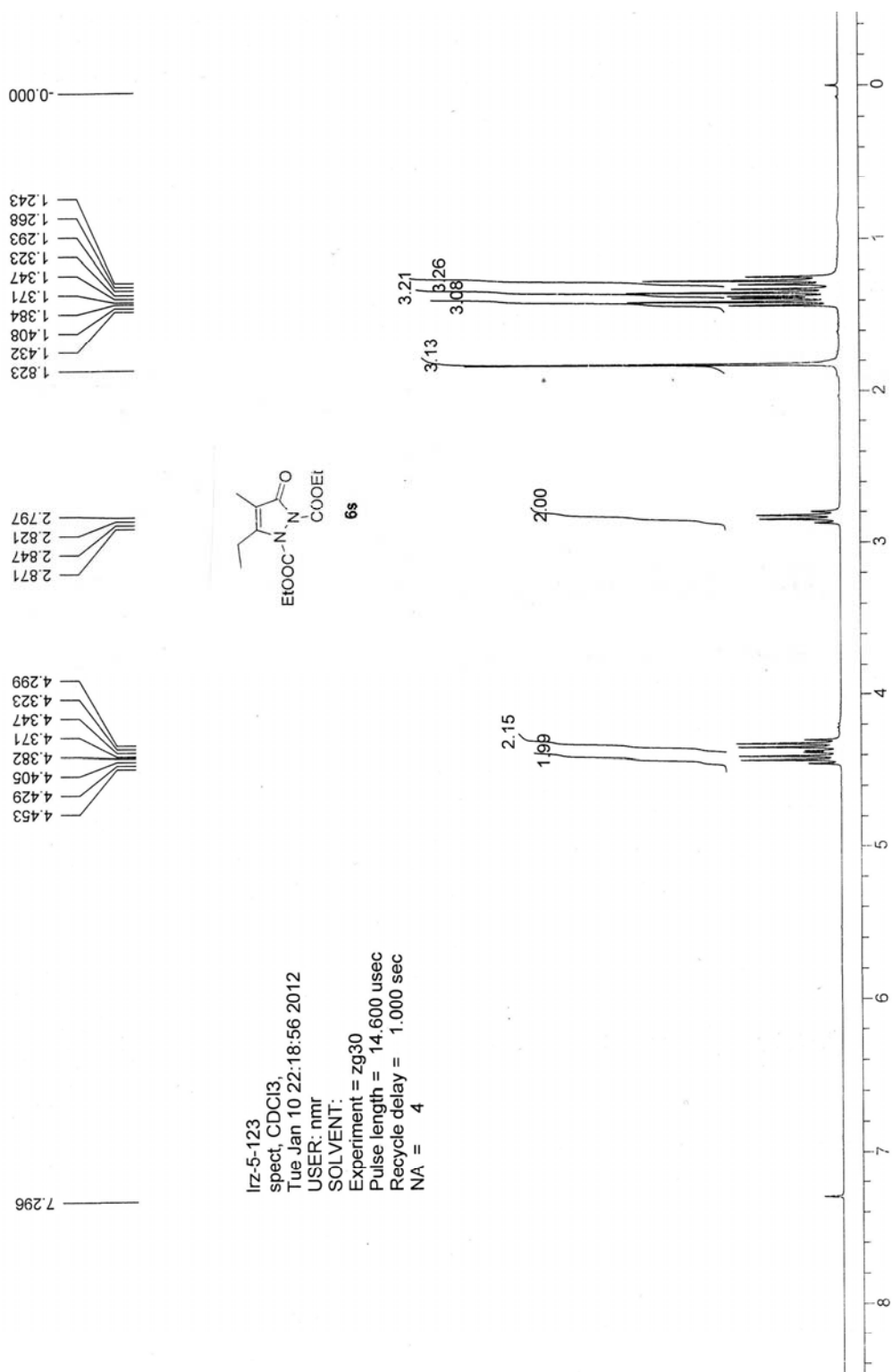










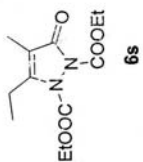


20.464
14.182
13.935
12.676
6.696

77.432
77.008
76.576
64.366
64.239

108.443

164.774
157.186
149.789
149.228



Irz-3-116-C
spect, CDCl₃,
Sun Mar 27 20:33:04 2011
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.900 usec
Recycle delay = 2.000 sec
NA = 101

