Efficient Synthesis of 2,3-Dihydro-1*H*-pyrazoles via a Highly Selective Pd(0)-Catalyzed Coupling-Cyclization Reaction of Terminal 2-Substituted 2,3-Allenyl Hydrazines with Aryl Iodides

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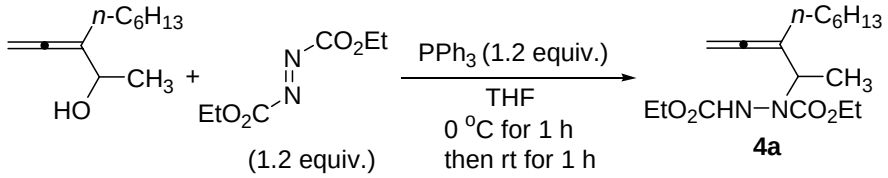
Synthesis of racemic 4-non-substituted 2-substituted 2,3-allenyl hydrazines.

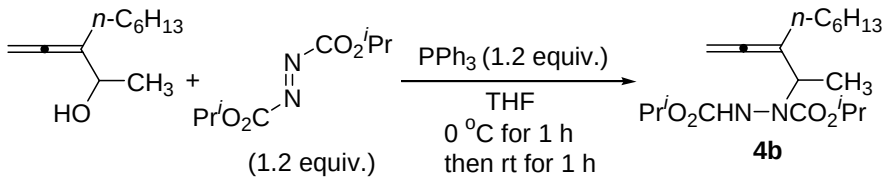
Racemic 4-non-substituted 2-substituted 2,3-allenyl hydrazines **4** were prepared according to the procedure described in the Supporting Information of our previous report[1] by the reaction of dialkyl azodicarboxylates with the corresponding 2,3-allenols.

(1) 3-(*n*-Hexyl)penta-3,4-dien-2-yl *N*,*N*-bis(ethoxycarbonyl)hydrazine (4a)



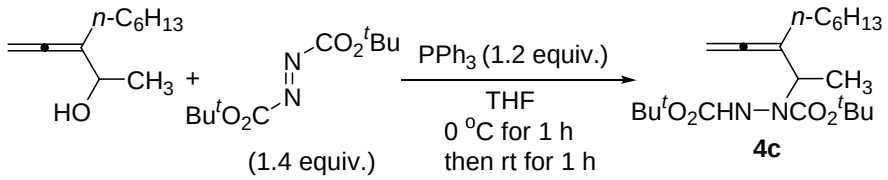
Under an atmosphere of argon, a solution of diethyl azodicarboxylate (1.675 g, 9.62 mmol) in 6 mL of THF was added dropwise to a solution of triphenyl phosphine (2.520 g, 9.61 mmol) and 3-(*n*-hexyl)penta-3,4-dien-2-ol (1.346 g, 8.00 mmol) in 25 mL of THF at 0 °C with stirring. After being stirred at 0 °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 (eluent: petroleum ether/ether = 6:1) to afford 1.823 g (70%) of **4a**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ [6.32 (bs), 6.16 (bs), 1 H], 4.91-4.52 (m, 3 H), 4.31-3.99 (m, 4 H), 2.16-1.74 (m, 2 H), 1.47-1.09 (m, 17 H), 0.83 (t, *J* = 6.6 Hz, 3 H); MS (ESI) *m/z* (%) 327 ($[M+H]^+$); IR (neat) 3297, 2930, 1956, 1758, 1712, 1518, 1467, 1412, 1383, 1310, 1222, 1064 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{30}N_2O_4$ (M^+) 326.2206; Found 326.2190.

(2) 3-(*n*-Hexyl)penta-3,4-dien-2-yl *N*,*N*-bis(isopropoxycarbonyl)hydrazine (4b)



The reaction of diisopropyl azodicarboxylate (260 mg, 94%, 1.21 mmol), triphenyl phosphine (317 mg, 1.21 mmol), and 3-(*n*-hexyl)penta-3,4-dien-2-ol (169 mg, 1.00 mmol) in THF (2+4 mL) afforded 221 mg (62%) of **4b**: Eluent for chromatography on silica gel: petroleum ether/ether = 6:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ [6.11 (bs), 5.93 (bs), 1 H], 5.04-4.87 (m, 2 H), 4.87-4.53 (m, 3 H), 2.17-1.75 (m, 2 H), 1.48-1.10 (m, 23 H), 0.86 (t, *J* = 6.8 Hz, 3 H); MS (ESI) *m/z* (%) 355 ($[M+H]^+$), 377 ($[M+Na]^+$), 409 ($[M+MeOH+Na]^+$); IR (neat) 3303, 2932, 1956, 1753, 1709, 1468, 1404, 1386, 1305, 1225, 1110 cm^{-1}; HRMS (MALDI/DHB) calcd for $C_{19}H_{34}N_2O_4Na$ ($[M+Na]^+$) 377.2411; Found 377.2418.

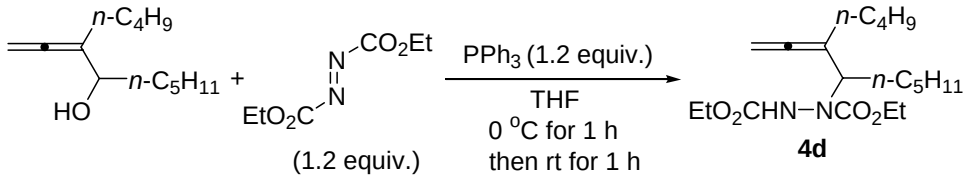
(3) 3-(*n*-Hexyl)penta-3,4-dien-2-yl *N*,*N*-bis(*tert*-butoxycarbonyl)hydrazine (4c)



The reaction of di-*tert*-butyl azodicarboxylate (330 mg, 1.43 mmol), triphenyl phosphine (315 mg, 1.20 mmol), and 3-(*n*-hexyl)penta-3,4-dien-2-ol (169 mg, 1.00 mmol) in THF (2+4 mL) afforded 236 mg (61%) of **4c**: Eluent for chromatography on silica gel: petroleum ether/ether = 20:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ [6.00 (bs), 5.72 (bs), 1 H], 4.90-4.48 (m, 3 H), 2.15-1.75 (m, 2 H), 1.55-1.16 (m, 29 H), 0.87 (t, *J* = 6.8 Hz, 3 H); MS (ESI) *m/z* (%) 405 ($[M+Na]^+$) , 437 ($[M+MeOH+Na]^+$);

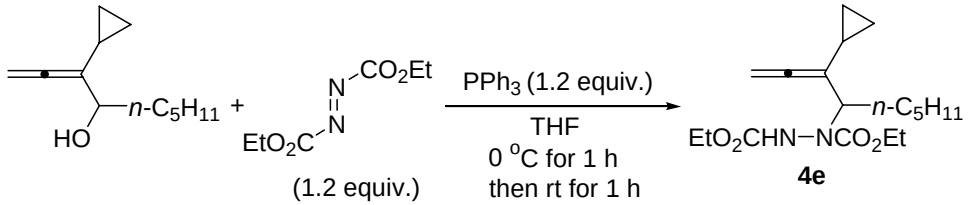
IR (neat) 3319, 2930, 1956, 1749, 1705, 1478, 1392, 1367, 1318, 1164 cm^{-1}; HRMS (MALDI/DHB) calcd for $C_{21}H_{38}N_2O_4Na$ ($[M+Na]^+$) 405.2724; Found 405.2740.

(4) 3-(*n*-Butyl)nona-1,2-dien-4-yl *N,N*-bis(ethoxycarbonyl)hydrazine (4d)



The reaction of diethyl azodicarboxylate (214 mg, 1.23 mmol), triphenyl phosphine (315 mg, 1.20 mmol), and 3-(*n*-butyl)nona-1,2-dien-4-ol (196 mg, 1.00 mmol) in THF (2+4 mL) afforded 147 mg (42%) of **4d**: Eluent for chromatography on silica gel: petroleum ether/ether = 7:1; solid; m.p. 50-52 ^oC (petroleum ether/ether); ^1H NMR (300 MHz, $CDCl_3$) δ [6.14 (bs), 5.97 (bs), 1 H], 4.85-4.68 (m, 2 H), 4.68-4.34 (m, 1 H), 4.33-4.05 (m, 4 H), 2.20-1.78 (m, 2 H), 1.77-1.52 (m, 2 H), 1.52-1.07 (m, 16 H), 0.94-0.80 (m, 6 H); MS (EI) *m/z* (%) 354 (M^+, 1.97), 355 (M^+, 0.63), 81 (100); IR (neat) 3291, 2932, 1956, 1760, 1711, 1467, 1411, 1381, 1300, 1221, 1062 cm^{-1}; Anal. Calcd. for $C_{19}H_{34}N_2O_4$: C, 64.38; H, 9.67; N, 7.90. Found: C, 64.45; H, 9.82; N, 7.64.

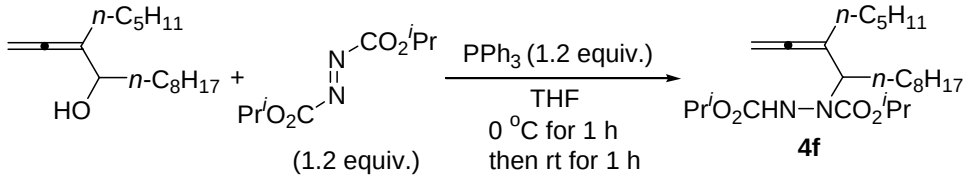
(5) 3-Cyclopropylnona-1,2-dien-4-yl *N,N*-bis(ethoxycarbonyl)hydrazine (4e)



The reaction of diethyl azodicarboxylate (629 mg, 3.61 mmol), triphenyl phosphine (953 mg, 3.63 mmol), and 3-cyclopropylnona-1,2-dien-4-ol (541 mg, 3.00 mmol) in

THF (5+12 mL) afforded 559 mg (55%) of **4e**: Eluent for chromatography on silica gel: petroleum ether/ether = 5:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ [6.15 (bs), 5.98 (bs), 1 H], 4.95-4.54 (m, 3 H), 4.33-4.07 (m, 4 H), 1.71-1.58 (m, 2 H), 1.58-1.03 (m, 13 H), 0.87 (t, *J* = 6.5 Hz, 3 H), 0.74-0.58 (m, 2 H), 0.47-0.21 (m, 2 H); MS (ESI) *m/z* (%) 339 ($[M+H]^+$), 361 ($[M+Na]^+$), 393 ($[M+MeOH+Na]^+$); IR (neat) 3293, 2932, 1953, 1760, 1712, 1467, 1409, 1381, 1301, 1217, 1062 cm^{-1}; HRMS (MALDI/DHB) calcd for $C_{18}H_{30}N_2O_4Na$ ($[M+Na]^+$) 361.2098; Found 361.2107.

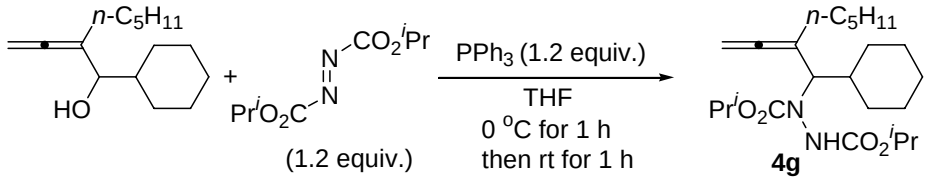
(6) 3-(*n*-Pentyl)dodeca-1,2-dien-4-yl *N*,*N*-bis(isopropoxycarbonyl)hydrazine (4f)



The reaction of diisopropyl azodicarboxylate (265 mg, 94%, 1.23 mmol), triphenyl phosphine (315 mg, 1.20 mmol), and 3-(*n*-pentyl)dodeca-1,2-dien-4-ol (252 mg, 1.00 mmol) in THF (2+4 mL) afforded 217 mg (50%) of **4f**: Eluent for chromatography on silica gel: petroleum ether/ether = 6:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.13-5.81 (m, 1 H), 5.07-4.87 (m, 2 H), 4.85-4.68 (m, 2 H), 4.64-4.36 (m, 1 H), 2.15-1.76 (m, 2 H), 1.69-1.06 (m, 32 H), 0.96-0.78 (m, 6 H); MS (ESI) *m/z* (%) 439 ($[M+H]^+$), 461 ($[M+Na]^+$), 493 ($[M+MeOH+Na]^+$); IR (neat) 3281, 2927, 1956, 1759, 1710, 1467, 1385, 1295, 1110 cm^{-1}; HRMS (MALDI/DHB) calcd for $C_{25}H_{46}N_2O_4Na$ ($[M+Na]^+$) 461.3350; Found 461.3353.

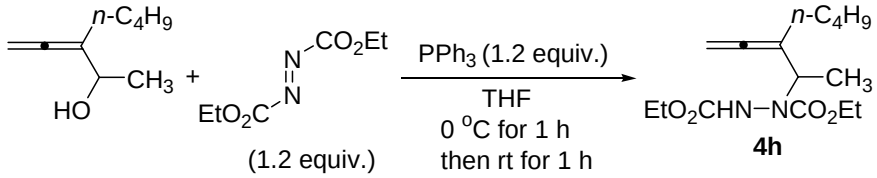
(7) 1-Cyclohexyl-2-(*n*-pentyl)buta-2,3-dien-1-yl *N*,*N*-bis(isopropoxycarbonyl)-

hydrazine (4g)



The reaction of diisopropyl azodicarboxylate (260 mg, 94%, 1.21 mmol), triphenyl phosphine (315 mg, 1.20 mmol), and 2-(*n*-pentyl)-1-cyclohexylbuta-2,3-dien-1-ol (223 mg, 1.00 mmol) in THF (2+4 mL) afforded 85 mg (21%) of **4g**: Eluent for chromatography on silica gel: petroleum ether/ether = 6:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.10-5.75 (m, 1 H), 5.06-4.85 (m, 2 H), 4.82-4.60 (m, 2 H), 432-3.99 (m, 1 H), 2.17-1.90 (m, 2 H), 1.85-1.53 (m, 6 H), 1.49-0.76 (m, 26 H); MS (ESI) *m/z* (%) 431 ($[M+Na]^+$), 463 ($[M+MeOH+Na]^+$); IR (neat) 3272, 2926, 1957, 1756, 1709, 1468, 1404, 1385, 1292, 1110 cm^{-1}; HRMS (MALDI/DHB) calcd for $C_{23}H_{40}N_2O_4Na$ ($[M+Na]^+$) 431.2880; Found 431.2889.

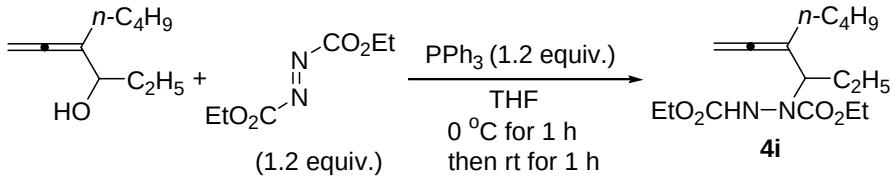
(8) 3-(*n*-Butyl)penta-3,4-dien-2-yl *N,N*-bis(ethoxycarbonyl)hydrazine (4h)



The reaction of diethyl azodicarboxylate (219 mg, 1.26 mmol), triphenyl phosphine (317 mg, 1.21 mmol), and 3-(*n*-butyl)penta-3,4-dien-2-ol (145 mg, 1.03 mmol) in THF (2+4 mL) afforded 183 mg (59%) of **4h**: Eluent for chromatography on silica gel: petroleum ether/ether = 6:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ [6.22 (bs), 6.03 (bs), 1 H], 4.93-4.56 (m, 3 H), 4.33-4.06 (m, 4 H), 2.10-1.79 (m, 2 H), 1.50-1.16 (m,

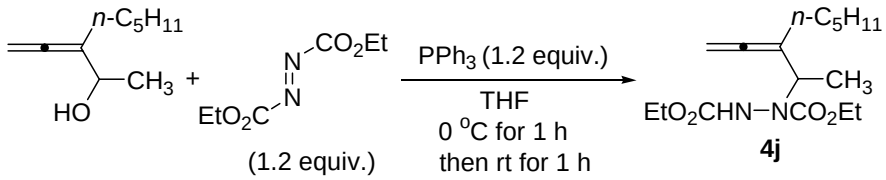
13 H), 0.88 (t, J = 7.1 Hz, 3 H); MS (EI) *m/z* (%) 298 (M^+, 2.72), 299 (M^++1, 2.18), 81 (100); IR (neat) 3298, 2934, 1956, 1758, 1712, 1467, 1412, 1383, 1311, 1222, 1064 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{26}N_2O_4$ (M^+) 298.1893; Found 298.1902.

(9) 4-(*n*-Butyl)hexa-4,5-dien-3-yl *N*,*N*-bis(ethoxycarbonyl)hydrazine (4i)



The reaction of diethyl azodicarboxylate (215 mg, 1.23 mmol), triphenyl phosphine (317 mg, 1.21 mmol), and 4-(*n*-butyl)hexa-4,5-dien-3-ol (155 mg, 1.00 mmol) in THF (2+4 mL) afforded 147 mg (47%) of **4i**: Eluent for chromatography on silica gel: petroleum ether/ether = 5:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ [6.15 (bs), 5.97 (bs), 1 H], 4.87-4.68 (m, 2 H), 4.64-4.30 (m, 1 H), 4.30-4.05 (m, 4 H), 2.20-1.79 (m, 2 H), 1.70-1.53 (m, 2 H), 1.51-1.08 (m, 10 H), 1.04-0.78 (m, 6 H); MS (ESI) *m/z* (%) 313 ($[M+H]^+$), 335 ($[M+Na]^+$), 367 ($[M+MeOH+Na]^+$); IR (neat) 3297, 2960, 1956, 1759, 1711, 1466, 1411, 1382, 1300, 1218, 1061 cm^{-1}; HRMS (MALDI/DHB) calcd for $C_{16}H_{28}N_2O_4Na$ ($[M+Na]^+$) 335.1941; Found 335.1956.

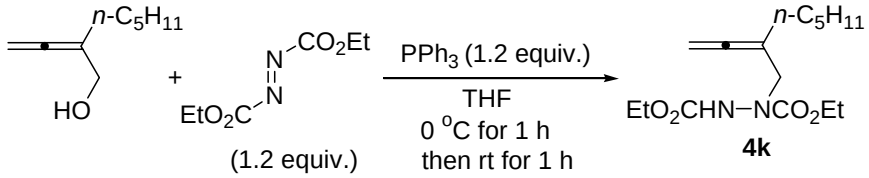
(10) 3-(*n*-Pentyl)penta-3,4-dien-2-yl *N*,*N*-bis(ethoxycarbonyl)hydrazine (4j)



The reaction of diethyl azodicarboxylate (315 mg, 1.81 mmol), triphenyl phosphine

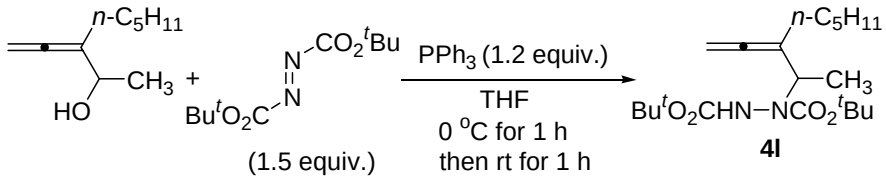
(480 mg, 1.83 mmol), and 3-(*n*-pentyl)penta-3,4-dien-2-ol (234 mg, 1.52 mmol) in THF (3+5 mL) afforded 341 mg (72%) of **4j**: Eluent for chromatography on silica gel: petroleum ether/ether = 5:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ [6.22 (bs), 6.02 (bs), 1 H], 4.91-4.58 (m, 3 H), 4.31-4.06 (m, 4 H), 2.06-1.77 (m, 2 H), 1.49-1.14 (m, 15 H), 0.87 (t, *J* = 6.8 Hz, 3 H);; MS (EI) *m/z* (%) 312 (M^+, 2.29), 313 (M^++1, 0.99), 95 (100); IR (neat) 3300, 2933, 1956, 1759, 1712, 1467, 1411, 1383, 1310, 1221, 1064 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{28}N_2O_4$ (M^+) 312.2049; Found 312.2048.

(11) 2-(*n*-Pentyl)buta-2,3-dien-1-yl *N,N*-bis(ethoxycarbonyl)hydrazine (4k)



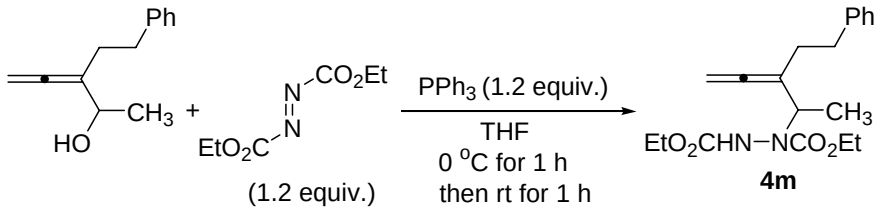
The reaction of diethyl azodicarboxylate (323 mg, 1.85 mmol), triphenyl phosphine (482 mg, 1.84 mmol), and 2-(*n*-pentyl)buta-2,3-dien-1-ol (217 mg, 1.55 mmol) in THF (3+6 mL) afforded 340 mg (74%) of **4k**: Eluent for chromatography on silica gel: petroleum ether/ether = 5:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ [6.55 (bs), 6.35 (bs), 1 H], 4.84-4.72 (m, 2 H), 4.31-4.15 (m, 4 H), 4.12-3.90 (m, 2 H), 1.97-1.83 (m, 2 H), 1.50-1.35 (m, 2 H), 1.32-1.18 (m, 10 H), 0.87 (t, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 205.9, 156.8, 155.8, 104.5, 78.0, 62.2, 61.6, 53.8, 31.3, 29.4, 27.0, 22.3, 16.0, 14.3, 13.9; MS (ESI) *m/z* (%) 299 ($[M+H]^+$), 321 ($[M+Na]^+$), 353 ($[M+MeOH+Na]^+$); IR (neat) 3305, 2930, 1959, 1716, 1468, 1445, 1414, 1382, 1263, 1216, 1061 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{15}H_{27}N_2O_4$ ($[M+H]^+$) 299.1965; Found: 299.1975.

(12) 3-(*n*-Pentyl)penta-3,4-dien-2-yl *N*,*N*-bis(*tert*-butoxycarbonyl)hydrazine (4l)



The reaction of di-*tert*-butyl azodicarboxylate (528 mg, 2.29 mmol), triphenyl phosphine (481 mg, 1.83 mmol), and 3-(*n*-pentyl)penta-3,4-dien-2-ol (236 mg, 1.53 mmol) in THF (3+5 mL) afforded 415 mg (74%) of **4l**: Eluent for chromatography on silica gel: petroleum ether/ether = 10:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ [6.00 (bs), 5.72 (bs), 1 H], 4.85-4.50 (m, 3 H), 2.12-1.79 (m, 2 H), 1.54-1.13 (m, 27 H), 0.87 (t, *J* = 6.9 Hz, 3 H); MS (ESI) *m/z* (%) 391 ([M+Na]$^+$); IR (neat) 3318, 2979, 1956, 1753, 1705, 1392, 1367, 1318, 1250, 1155, 1054 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{36}N_2O_4Na$ ([M+Na]$^+$) 391.2567; Found 391.2585.

(13) 3-Phenethylpenta-3,4-dien-2-yl *N*,*N*-bis(ethoxycarbonyl)hydrazine (4m)

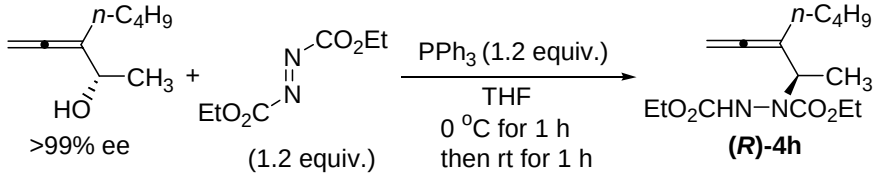


The reaction of diethyl azodicarboxylate (637 mg, 3.66 mmol), triphenyl phosphine (954 mg, 3.64 mmol), and 3-phenethylpenta-3,4-dien-2-ol (570 mg, 3.03 mmol) in THF (5+12 mL) afforded 781 mg (74%) of **4m**: Eluent for chromatography on silica gel: petroleum ether/ether = 4:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.08 (m, 5 H), 6.22-5.54 (m, 1 H), 5.01-4.58 (m, 3 H), 4.35-4.04 (m, 4 H), 2.88-2.61 (m, 2 H), 2.44-2.03 (m, 2 H), 1.41-1.10 (m, 9 H); MS (ESI) *m/z* (%) 369 ([M+Na]$^+$); IR (neat)

3297, 2982, 1955, 1757, 1709, 1602, 1496, 1467, 1411, 1383, 1310, 1222, 1063 cm^{-1}; HRMS (MALDI/DHB) calcd for $C_{19}H_{27}N_2O_4$ ($[M+H]^+$) 347.1965; Found 347.1969.

Synthesis of optically active terminal 2-substituted 2,3-allenyl hydrazines. Optically active 2,3-allenyl hydrazines (*R*)- or (*S*)-**4** were prepared according to the procedure described above for the racemic **4** by the reaction of diethyl azodicarboxylate with the corresponding optically pure (*S*)- or (*R*)-2,3-allenols, which were easily obtained from the kinetic enzymatic resolution of the racemic 2,3-allenols.[2]

(1) 2(*R*)-3-(*n*-Butyl)penta-3,4-dien-2-yl *N*,*N*-bis(ethoxycarbonyl)hydrazine (*R*)-(4h)

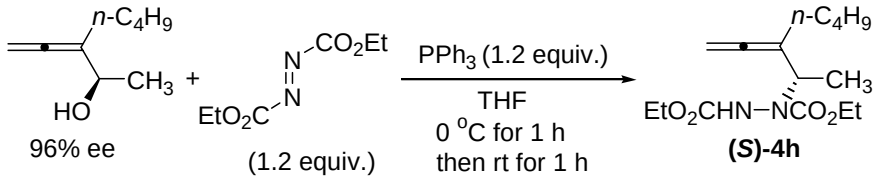


The reaction of diethyl azodicarboxylate (140 mg, 0.80 mmol), triphenyl phosphine (209 mg, 0.80 mmol), and (*S*)-3-(*n*-butyl)penta-3,4-dien-2-ol (92 mg, 0.66 mmol, >99% ee) in THF (1+3 mL) afforded 147 mg (75%) of (*R*)-**4h**: Eluent for chromatography on silica gel: petroleum ether/ether = 5:1; liquid; $[\alpha]^{20}_D$ = + 85.2 (*c* = 0.9, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ [6.26 (bs), 6.10 (bs), 1 H], 4.91-4.57 (m, 3 H), 4.28-4.05 (m, 4 H), 2.10-1.77 (m, 2 H), 1.47-1.12 (m, 13 H), 0.87 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 205.9, 156.8, 156.0, 104.6, 78.0, 62.4, 61.8, 54.1, 29.6, 29.3, 22.3, 16.1, 14.4, 13.8; MS (ESI) *m/z* (%) 177 ($[M-C_9H_{15}+2H]^+$), 299 ($[M+H]^+$); IR (neat) 3294, 2933, 1957, 1758, 1710, 1412, 1384, 1311, 1223, 1065

cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{15}H_{27}N_2O_4$ ([M+H]$^+$) 299.1965; Found: 299.1977.

(2) 2(*S*)-3-(*n*-Butyl)penta-3,4-dien-2-yl *N*,*N*-bis(ethoxycarbonyl)hydrazine

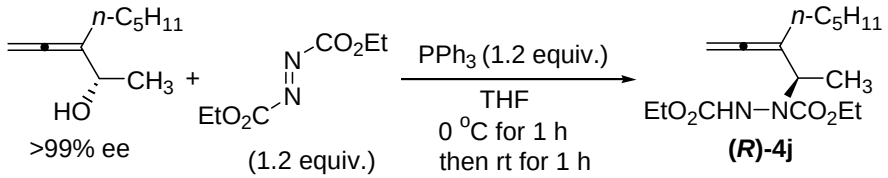
(*S*)-(4h)



The reaction of diethyl azodicarboxylate (120 mg, 0.69 mmol), triphenyl phosphine (180 mg, 0.69 mmol), and (*R*)-3-(*n*-butyl)penta-3,4-dien-2-ol (80 mg, 0.57 mmol, 96% ee) in THF (1+3 mL) afforded 133 mg (78%) of (*S*)-**4h**: Eluent for chromatography on silica gel: petroleum ether/ether = 5:1; liquid; $[\alpha]^{20}_D$ = – 74.2 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ [6.22 (bs), 6.03 (bs), 1 H], 4.93-4.56 (m, 3 H), 4.33-4.06 (m, 4 H), 2.10-1.79 (m, 2 H), 1.50-1.16 (m, 13 H), 0.88 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 205.9, 156.9, 156.0, 104.6, 78.1, 62.4, 61.8, 53.9, 29.5, 29.3, 22.3, 16.0, 14.4, 13.8; MS (ESI) *m/z* (%) 177 ([M-C_9H_{15}+2H]$^+$), 299 ([M+H]$^+$); IR (neat) 3297, 2933, 1957, 1757, 1711, 1414, 1383, 1311, 1223, 1065 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{15}H_{27}N_2O_4$ ([M+H]$^+$) 299.1965; Found: 299.1973.

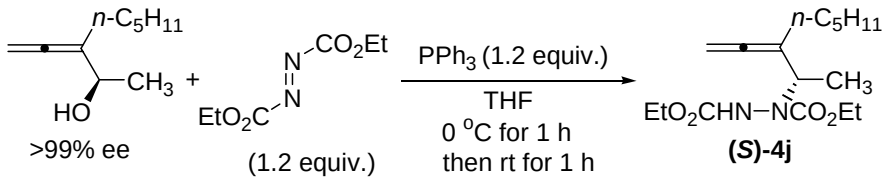
(3) 2(*R*)-3-(*n*-Pentyl)penta-3,4-dien-2-yl *N*,*N*-bis(ethoxycarbonyl)hydrazine

(*R*)-(4j)



The reaction of diethyl azodicarboxylate (142 mg, 0.82 mmol), triphenyl phosphine (213 mg, 0.81 mmol), and (*S*)-3-(*n*-pentyl)penta-3,4-dien-2-ol (103 mg, 0.67 mmol, >99% ee) in THF (1+3 mL) afforded 154 mg (74%) of (*R*)-**4j**: Eluent for chromatography on silica gel: petroleum ether/ether = 5:1; liquid; $[\alpha]^{20}_{D}$ = + 96.5 (*c* = 0.65, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ [6.21 (bs), 6.01 (bs), 1 H], 4.91-4.58 (m, 3 H), 4.31-4.06 (m, 4 H), 2.06-1.77 (m, 2 H), 1.49-1.14 (m, 15 H), 0.87 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 205.9, 156.8, 155.8, 104.5, 78.0, 62.2, 61.6, 53.8, 31.3, 29.4, 27.0, 22.3, 16.0, 14.3, 13.9; MS (ESI) *m/z* (%) 177 ($[M-C_{10}H_{17}+2H]^+$), 313 ($[M+H]^+$); IR (neat) 3298, 2932, 1956, 1758, 1711, 1411, 1383, 1311, 1222, 1064 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{16}H_{29}N_2O_4$ ($[M+H]^+$) 313.2122; Found: 313.2118.

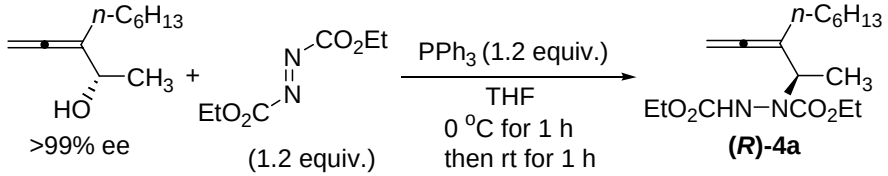
(4) 2(*S*)-3-(*n*-Pentyl)penta-3,4-dien-2-yl *N,N*-bis(ethoxycarbonyl)hydrazine (*S*)-(4j)



The reaction of diethyl azodicarboxylate (150 mg, 0.86 mmol), triphenyl phosphine (225 mg, 0.86 mmol), and (*R*)-3-(*n*-pentyl)penta-3,4-dien-2-ol (110 mg, 0.71 mmol, >99% ee) in THF (1+3 mL) afforded 173 mg (78%) of (*S*)-**4j**: Eluent for

chromatography on silica gel: petroleum ether/ether = 5:1; liquid; $[\alpha]^{20}_{D} = -92.0$ (*c* = 0.75, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ [6.21 (bs), 6.02 (bs), 1 H], 4.90-4.52 (m, 3 H), 4.31-4.08 (m, 4 H), 2.20-1.79 (m, 2 H), 1.49-1.14 (m, 15 H), 0.87 (t, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 205.9, 156.8, 155.9, 104.5, 77.9, 62.2, 61.6, 53.9, 31.3, 29.5, 27.0, 22.3, 16.0, 14.3, 13.9; MS (ESI) *m/z* (%) 177 ($[M-C_{10}H_{17}+2H]^+$), 313 ($[M+H]^+$); IR (neat) 3298, 2932, 1956, 1758, 1712, 1412, 1383, 1311, 1222, 1064 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{16}H_{29}N_2O_4$ ($[M+H]^+$) 313.2122; Found: 313.2118.

(5) 2(*R*)-3-(*n*-Hexyl)penta-3,4-dien-2-yl *N*,*N*-bis(ethoxycarbonyl)hydrazine (*R*)-(4a)



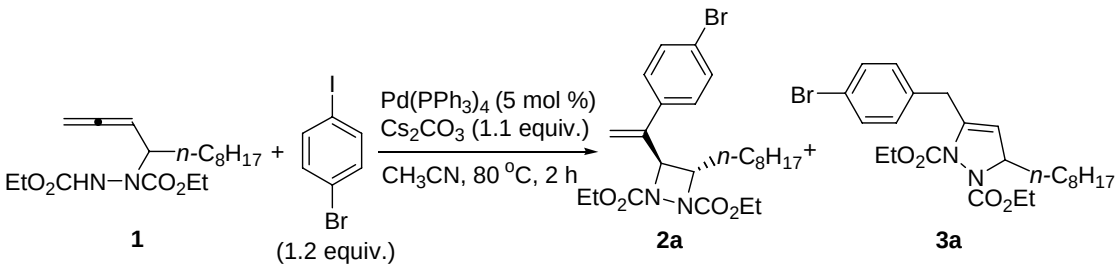
The reaction of diethyl azodicarboxylate (125 mg, 0.72 mmol), triphenyl phosphine (188 mg, 0.72 mmol), and (*S*)-3-(*n*-hexyl)penta-3,4-dien-2-ol (107 mg, 0.64 mmol, >99% ee) in THF (1+3 mL) afforded 132 mg (64%) of (*R*)-**4a**: Eluent for chromatography on silica gel: petroleum ether/ether = 5:1; liquid; $[\alpha]^{20}_{D} = +69.8$ (*c* = 0.85, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ [6.22 (bs), 6.03 (bs), 1 H], 4.90-4.52 (m, 3 H), 4.31-4.13 (m, 4 H), 2.20-1.79 (m, 2 H), 1.49-1.14 (m, 17 H), 0.87 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 206.0, 156.8, 155.9, 104.5, 78.0, 62.3, 61.7, 53.9, 31.6, 29.5, 28.8, 27.3, 22.5, 16.1, 14.4, 14.3, 13.9; MS (ESI) *m/z* (%) 177 ($[M-C_{11}H_{19}+2H]^+$), 327 ($[M+H]^+$); IR (neat) 3297, 2930, 1957, 1758, 1712, 1413,

1383, 1310, 1222, 1064 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{17}H_{31}N_2O_4$ ($[M+H]^+$) 327.2278; Found: 327.2274.

$Pd(PPh_3)_4$-catalyzed coupling-cyclization reaction of 4-non-substituted 2,3-allenyl hydrazines with aryl iodides. General procedure: Under an atmosphere of argon, Cs_2CO_3 (1.1 equiv.), aryl iodide (1.2 equiv.), $Pd(PPh_3)_4$ (5 mol %), **1** or **4** (0.2 or 0.25 mmol), and CH_3CN (2.5 or 3 mL) were added sequentially to an oven-dried Schlenk tube equipped with a stirring bar and the resulting reaction mixture was stirred at 80 °C. When the reaction was complete as determined by TLC analysis, ether was added and the mixture was filtered to remove the solid. After adding some silica gel and evaporation, the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ether) to afford the product.

The reaction of 2,4-non-substituted 2,3-allenyl hydrazine 1 with 4-bromoiodobenzene or 4-cyanoiodobenzene.

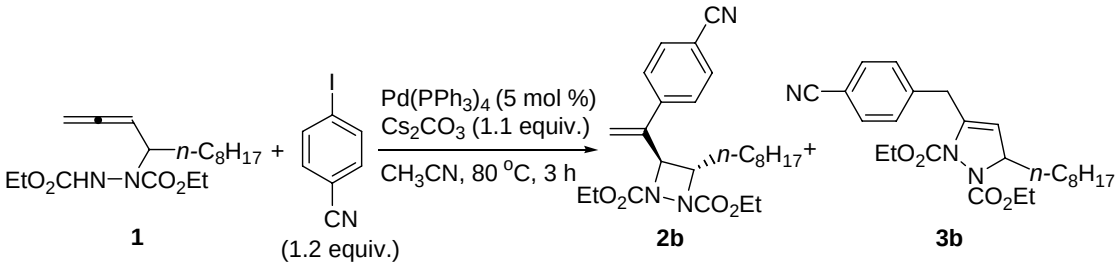
(1) 3-(*n*-Octyl)-4-(1'-(4''-bromophenyl)vinyl)-1,2-bis(ethoxycarbonyl)-1,2-diazetidine (2a) and 3-(*n*-octyl)-5-(4'-bromobenzyl)-1,2-bis(ethoxycarbonyl)-2,3-dihydro-1*H*-pyrazole (3a) (Scheme 1)



The reaction of **1** (85 mg, 0.25 mmol), 4-bromoiodobenzene (85 mg, 0.30 mmol),

$Pd(PPh_3)_4$ (15 mg, 0.013 mmol), and Cs_2CO_3 (90 mg, 0.28 mmol) in 3 mL of CH_3CN afforded 55 mg (44%) of **2a** (more polar) and 44 mg (36%) of **3a** (less polar). Eluent for chromatography on silica gel: petroleum ether/ether = 15:1. **2a**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.6 Hz, 2 H), 7.22 (d, *J* = 8.6 Hz, 2 H), 5.65 (s, 1 H), 5.45 (s, 1 H), 4.75 (d, *J* = 5.1 Hz, 1 H), 4.36-4.15 (m, 4 H), 3.87-3.78 (m, 1 H), 1.86-1.62 (m, 2 H), 1.36-1.12 (m, 18 H), 0.86 (t, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 161.0, 160.6, 143.7, 136.6, 131.6, 128.4, 122.3, 115.7, 69.1, 69.0, 62.7, 62.4, 34.6, 31.7, 29.3, 29.11, 29.08, 24.4, 22.6, 14.4, 14.3, 14.0; MS (ESI) *m/z* (%) 497 ($[M(^{81}Br)+H]^+$), 495 ($[M(^{79}Br)+H]^+$), 519 ($[M(^{81}Br)+Na]^+$), 517 ($[M(^{79}Br)+Na]^+$); IR (neat) 2928, 1753, 1713, 1629, 1588, 1489, 1373, 1322, 1099, 1009 cm^{-1}; HRMS (MALDI/DHB) $C_{24}H_{35}N_2O_4{}^{79}BrNa$ ($[M+Na]^+$) 517.1672; Found 517.1656. **3a**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 2 H), 7.11 (d, *J* = 8.4 Hz, 2 H), 4.88 (bs, 1 H), 4.63-4.55 (m, 1 H), 4.26-4.13 (m, 4 H), 3.89 (bs, 2 H), 1.47-1.18 (m, 20 H), 0.86 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 158.0, 155.2, 141.9, 136.6, 131.4, 130.7, 120.4, 112.2, 63.9, 62.3, 34.6, 31.8, 29.4, 29.3, 29.2, 29.1, 24.8, 22.6, 14.4, 14.1; MS (ESI) *m/z* (%) 497 ($[M(^{81}Br)+H]^+$), 495 ($[M(^{79}Br)+H]^+$); IR (neat) 2927, 1715, 1657, 1488, 1373, 1317, 1012 cm^{-1}; HRMS (MALDI/DHB) $C_{24}H_{35}N_2O_4{}^{79}BrNa$ ($[M+Na]^+$) 517.1672; Found 517.1662.

(2) 3-(*n*-Octyl)-4-(1'-(4''-cyanophenyl)vinyl)-1,2-bis(ethoxycarbonyl)-1,2-diazetidine (2b) and 3-(*n*-octyl)-5-(4'-cyanobenzyl)-1,2-bis(ethoxycarbonyl)-2,3-dihydro-1*H*-pyrazole (3b) (Scheme 1)



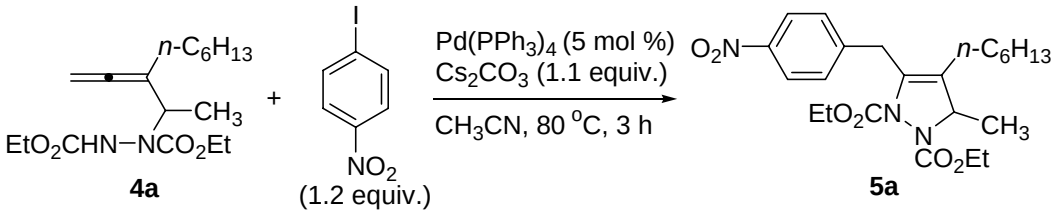
1 **2b** **3b**

The reaction of **1** (85 mg, 0.25 mmol), 4-cyanoiodobenzene (69 mg, 0.30 mmol), $Pd(PPh_3)_4$ (15 mg, 0.013 mmol), and Cs_2CO_3 (90 mg, 0.28 mmol) in 3 mL of CH_3CN afforded 18 mg (16%) of **2b** (more polar) and 65 mg (59%) of **3b** (less polar). Eluent for chromatography on silica gel: petroleum ether/ether = 5:1. **2b**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.6 Hz, 2 H), 7.47 (d, *J* = 8.6 Hz, 2 H), 5.76 (s, 1 H), 5.55 (s, 1 H), 4.78 (d, *J* = 4.8 Hz, 1 H), 4.37-4.13 (m, 4 H), 3.88-3.77 (m, 1 H), 1.90-1.76 (m, 1 H), 1.73-1.60 (m, 1 H), 1.39-1.12 (m, 18 H), 0.86 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 160.9, 160.6, 143.5, 142.4, 132.3, 127.5, 118.4, 118.0, 111.9, 68.9, 68.8, 62.8, 62.5, 34.6, 31.7, 29.3, 29.1, 24.4, 22.6, 14.4, 14.3, 14.0; MS (ESI) *m/z* (%) 442 ($[M+H]^+$), 464 ($[M+Na]^+$); IR (neat) 2927, 2228, 1753, 1714, 1606, 1505, 1373, 1322, 1098 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{25}H_{35}N_3O_4Na$ ($[M+Na]^+$) 464.2520; Found: 464.2508. **3b**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.1 Hz, 2 H), 7.33 (d, *J* = 8.1 Hz, 2 H), 4.97 (bs, 1 H), 4.66-4.55 (m, 1 H), 4.25-4.10 (m, 4 H), 4.07 (d, *J* = 16.5 Hz, 1 H), 3.93 (d, *J* = 16.5 Hz, 1 H), 1.50-1.15 (m, 20 H), 0.84 (t, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 157.9, 155.0, 143.2, 140.6, 132.1, 129.5, 118.8, 112.7, 110.3, 63.9, 62.4, 62.3, 35.1, 34.5, 31.7, 29.3, 29.2, 29.1, 24.8, 22.5, 14.33, 14.28, 14.0; MS (ESI) *m/z* (%) 442 ($[M+H]^+$), 464 ($[M+Na]^+$), 496 ($[M+MeOH+Na]^+$); IR (neat) 2928, 2228, 1714, 1657, 1608, 1505, 1466, 1374, 1317, 1176, 1070 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{25}H_{35}N_3O_4Na$

([M+Na]$^+$) 464.2520; Found: 464.2537.

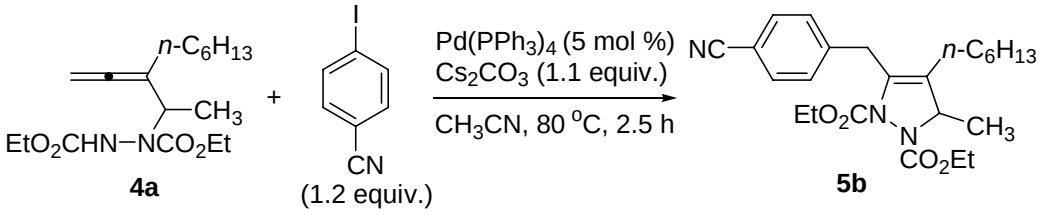
The reaction of 4-non-substituted 2-substituted 2,3-allenyl hydrazines with aryl iodides.

(1) 3-Methyl-4-(*n*-hexyl)-5-(4'-nitrobenzyl)-1,2-bis(ethoxycarbonyl)-2,3-dihydro-1*H*-pyrazole (5a) (Scheme 2)



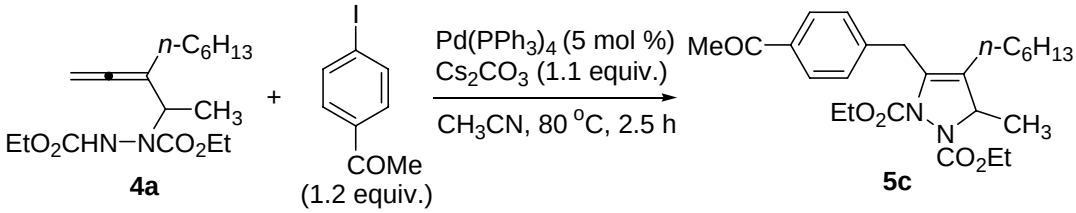
The reaction of **4a** (82 mg, 0.25 mmol), 4-nitroiodobenzene (75 mg, 0.30 mmol), $Pd(PPh_3)_4$ (15 mg, 0.013 mmol), and Cs_2CO_3 (90 mg, 0.28 mmol) in 3 mL of CH_3CN afforded 83 mg (74%) of **5a**: Eluent for chromatography on silica gel: petroleum ether/ether = 8:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.6 Hz, 2 H), 7.34 (d, *J* = 8.6 Hz, 2 H), 4.69 (q, *J* = 6.5 Hz, 1 H), 4.23 (d, *J* = 16.8 Hz, 1 H), 4.20-4.06 (m, 4 H), 3.83 (d, *J* = 16.8 Hz, 1 H), 2.25-2.12 (m, 1 H), 2.08-1.96 (m, 1 H), 1.53-1.37 (m, 1 H), 1.36-1.09 (m, 16 H), 0.81 (t, *J* = 6.3 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 157.7, 155.5, 146.4, 146.2, 132.0, 128.8, 127.6, 123.4, 62.3, 62.2, 61.2, 31.8, 31.3, 29.0, 28.4, 24.6, 22.4, 18.6, 14.4, 14.2, 13.9; MS (ESI) *m/z* (%) 448 ([M+H]$^+$), 470 ([M+Na]$^+$), 502 ([M+MeOH+Na]$^+$); IR (neat) 2931, 1712, 1679, 1599, 1522, 1375, 1346, 1046 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{23}H_{34}N_3O_6$ ([M+H]$^+$) 448.2442; Found: 448.2444.

(2) 3-Methyl-4-(*n*-hexyl)-5-(4'-cyanobenzyl)-1,2-bis(ethoxycarbonyl)-2,3-dihydro-1*H*-pyrazole (5b) (entry 1, Table 1)



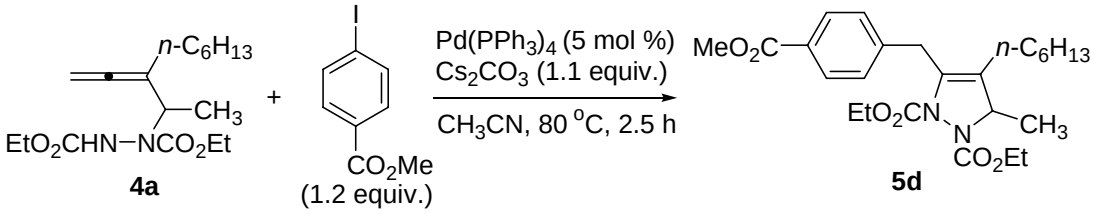
The reaction of **4a** (67 mg, 0.21 mmol), 4-cyanoiodobenzene (55 mg, 0.24 mmol), $Pd(PPh_3)_4$ (12 mg, 0.010 mmol), and Cs_2CO_3 (72 mg, 0.22 mmol) in 2.5 mL of CH_3CN afforded 69 mg (79%) of **5b**: Eluent for chromatography on silica gel: petroleum ether/ether = 7:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2 H), 7.32 (d, *J* = 8.3 Hz, 2 H), 4.71 (q, *J* = 6.5 Hz, 1 H), 4.29-4.07 (m, 5 H), 3.82 (d, *J* = 16.2 Hz, 1 H), 2.24-2.14 (m, 1 H), 2.10-2.00 (m, 1 H), 1.53-1.38 (m, 1 H), 1.35-1.13 (m, 16 H), 0.85 (t, *J* = 6.5 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 157.7, 155.5, 144.0, 132.1, 131.9, 128.8, 127.5, 118.9, 109.9, 62.24, 62.19, 61.1, 32.0, 31.3, 29.0, 28.4, 24.5, 22.4, 18.6, 14.3, 14.2, 13.9; MS (ESI) *m/z* (%) 428 ($[M+H]^+$), 450 ($[M+Na]^+$), 466 ($M+K^+$), 482 ($[M+MeOH+Na]^+$); IR (neat) 2931, 2228, 1712, 1678, 1608, 1375, 1318, 1047 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{24}H_{34}N_3O_4$ ($[M+H]^+$) 428.2544; Found: 428.2548.

(3) 3-Methyl-4-(*n*-hexyl)-5-(4'-acetylbenzyl)-1,2-bis(ethoxycarbonyl)-2,3-dihydro-1*H*-pyrazole (5c) (entry 2, Table 1)



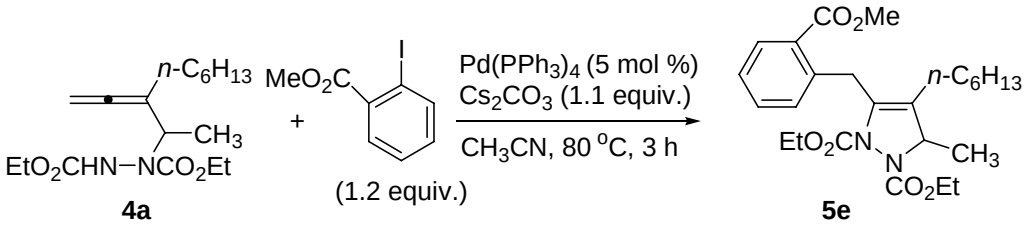
The reaction of **4a** (82 mg, 0.25 mmol), 4-acetyliodobenzene (74 mg, 0.30 mmol), $Pd(PPh_3)_4$ (15 mg, 0.013 mmol), and Cs_2CO_3 (90 mg, 0.28 mmol) in 3 mL of CH_3CN afforded 81 mg (73%) of **5c**: Eluent for chromatography on silica gel: petroleum ether/ether = 8:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 2 H), 7.30 (d, *J* = 8.4 Hz, 2 H), 4.71 (q, *J* = 6.5 Hz, 1 H), 4.26-4.09 (m, 5 H), 3.83 (d, *J* = 16.5 Hz, 1 H), 2.57 (s, 3 H), 2.25-2.15 (m, 1 H), 2.09-1.99 (m, 1 H), 1.53-1.39 (m, 1 H), 1.35-1.13 (m, 16 H), 0.84 (t, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 197.7, 157.7, 155.5, 144.1, 135.1, 132.5, 128.3, 128.1, 127.1, 62.2, 62.1, 61.0, 31.9, 31.3, 29.0, 28.4, 26.5, 24.5, 22.4, 18.6, 14.3, 14.2, 13.9; MS (EI) *m/z* (%) 444 (M^+, 3.65), 385 (M^+-2xCH_3-C_2H_5, 19.21), 371 (M^+-CH_3-2xC_2H_5, 15.59), 357 (M^+-CH_3-C_2H_5-C_3H_7, 100); IR (neat) 2930, 1739, 1712, 1683, 1607, 1375, 1318, 1267, 1047 cm^{-1}; HRMS (EI) calcd. for $C_{25}H_{36}N_2O_5$ (M^+) 444.2624; Found: 444.2619.

(4) 3-Methyl-4-(*n*-hexyl)-5-(4'-(methoxycarbonyl)benzyl)-1,2-bis(ethoxy-carbonyl)-2,3-dihydro-1*H*-pyrazole (5d) (entry 3, Table 1)



The reaction of **4a** (66 mg, 0.20 mmol), 4-iodobenzoic acid methyl ester (63 mg, 0.24 mmol), $Pd(PPh_3)_4$ (12 mg, 0.010 mmol), and Cs_2CO_3 (72 mg, 0.22 mmol) in 2.5 mL of CH_3CN afforded 72 mg (77%) of **5d**: Eluent for chromatography on silica gel: petroleum ether/ether = 7:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2 H), 7.23 (d, *J* = 8.4 Hz, 2 H), 4.68 (q, *J* = 6.5 Hz, 1 H), 4.23-4.05 (m, 5 H), 3.87 (s, 3 H), 3.79 (d, *J* = 16.5 Hz, 1 H), 2.22-2.10 (m, 1 H), 2.06-1.94 (m, 1 H), 1.50-1.36 (m, 1 H), 1.35-1.07 (m, 16 H), 0.81 (t, *J* = 6.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 167.0, 157.8, 155.5, 143.8, 132.6, 129.5, 128.0, 127.2, 62.2, 62.1, 61.0, 51.9, 31.9, 31.3, 29.0, 28.4, 24.6, 22.4, 18.6, 14.3, 14.2, 13.9; MS (ESI) *m/z* (%) 461 ($[M+H]^+$), 483 ($[M+Na]^+$), 499 ($[M+K]^+$), 515 ($[M+MeOH+Na]^+$); IR (neat) 2931, 1721, 1678, 1611, 1375, 1317, 1279, 1107 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{25}H_{37}N_2O_6$ ($[M+H]^+$) 461.2646; Found: 461.2643.

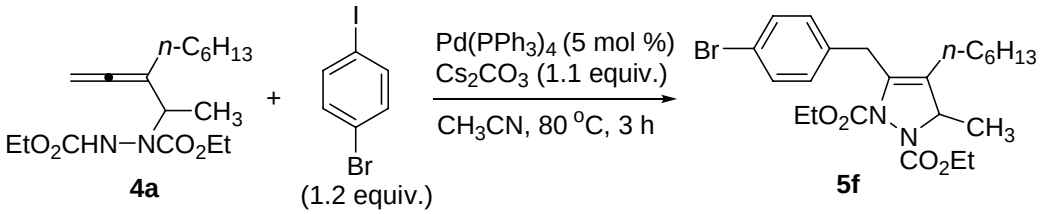
(5) 3-Methyl-4-(*n*-hexyl)-5-(2'-(methoxycarbonyl)benzyl)-1,2-bis(ethoxy-carbonyl)-2,3-dihydro-1*H*-pyrazole (5e) (entry 4, Table 1)



The reaction of **4a** (65 mg, 0.20 mmol), 2-iodobenzoic acid methyl ester (65 mg, 0.25 mmol), $Pd(PPh_3)_4$ (12 mg, 0.010 mmol), and Cs_2CO_3 (72 mg, 0.22 mmol) in 2.5 mL of CH_3CN afforded 70 mg (76%) of **5e**: Eluent for chromatography on silica gel: petroleum ether/ether = 7:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.8 Hz,

1 H), 7.45-7.33 (m, 1 H), 7.31-7.19 (m, 2 H), 4.73 (q, *J* = 6.5 Hz, 1 H), 4.49 (d, *J* = 17.7 Hz, 1 H), 4.29-4.15 (m, 3 H), 4.06 (q, *J* = 7.1 Hz, 2 H), 3.90 (s, 3 H), 2.23-2.10 (m, 1 H), 2.05-1.92 (m, 1 H), 1.51-1.36 (m, 1 H), 1.34-1.12 (m, 13 H), 1.07 (t, *J* = 7.1 Hz, 3 H), 0.83 (t, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 167.9, 157.7, 155.2, 139.8, 132.6, 131.7, 130.3, 129.2, 128.7, 127.3, 125.9, 62.2, 62.0, 61.0, 51.9, 31.4, 29.9, 29.0, 28.3, 24.5, 22.4, 18.8, 14.4, 14.0, 13.9; MS (ESI) *m/z* (%) 483 ($[M+Na]^+$); IR (neat) 2930, 1717, 1676, 1375, 1318, 1262, 1077, 1048 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{25}H_{36}N_2O_6Na$ ($[M+Na]^+$) 483.2466; Found: 483.2454.

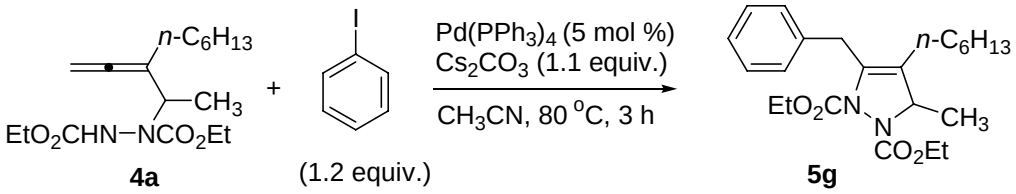
(6) 3-Methyl-4-(*n*-hexyl)-5-(4'-bromobenzyl)-1,2-bis(ethoxycarbonyl)-2,3-dihydro-1*H*-pyrazole (5f) (entry 5, Table 1)



The reaction of **4a** (82 mg, 0.25 mmol), 4-bromoiodobenzene (85 mg, 0.30 mmol), $Pd(PPh_3)_4$ (15 mg, 0.013 mmol), and Cs_2CO_3 (90 mg, 0.28 mmol) in 3 mL of CH_3CN afforded 87 mg (72%) of **5f**: Eluent for chromatography on silica gel: petroleum ether/ether = 10:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.3 Hz, 2 H), 7.05 (d, *J* = 8.3 Hz, 2 H), 4.67 (q, *J* = 6.4 Hz, 1 H), 4.20-4.08 (m, 4 H), 4.07 (d, *J* = 16.5 Hz, 1 H), 3.69 (d, *J* = 16.5 Hz, 1 H), 2.22-2.10 (m, 1 H), 2.08-1.95 (m, 1 H), 1.49-1.37 (m, 1 H), 1.37-1.07 (m, 16 H), 0.84 (t, *J* = 6.5 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 157.8, 155.6, 137.3, 133.0, 131.2, 129.8, 126.9, 119.8, 62.2, 62.1,

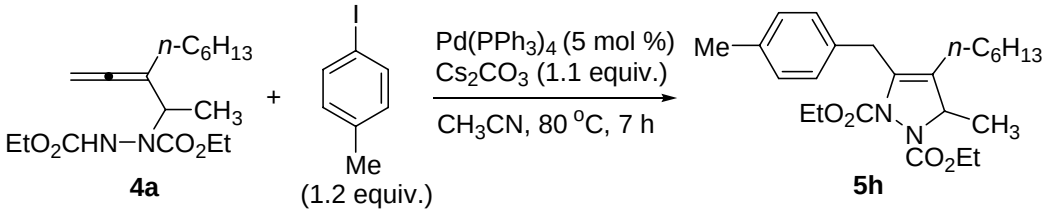
61.1, 31.4, 31.3, 29.1, 28.4, 24.6, 22.4, 18.6, 14.34, 14.26, 13.9; MS (ESI) *m/z* (%) 483 ([M(^{81}Br)+H]$^+$), 481 ([M(^{79}Br)+H]$^+$), 505 ([M(^{81}Br)+Na]$^+$), 503 (M([^{79}Br)+Na]$^+$), 537 ([M(^{81}Br)+MeOH+Na]$^+$), 535 ([M(^{79}Br)+MeOH+Na]$^+$); IR (neat) 2930, 1739, 1712, 1678, 1488, 1375, 1318, 1047, 1012 cm^{-1}; HRMS (ESI) $C_{23}H_{33}N_2O_4{}^{79}BrNa$ ([M+Na]$^+$) 503.1516; Found 503.1509.

(7) 3-Methyl-4-(*n*-hexyl)-5-benzyl-1,2-bis(ethoxycarbonyl)-2,3-dihydro-1*H*-pyrazole (5g) (entry 6, Table 1)



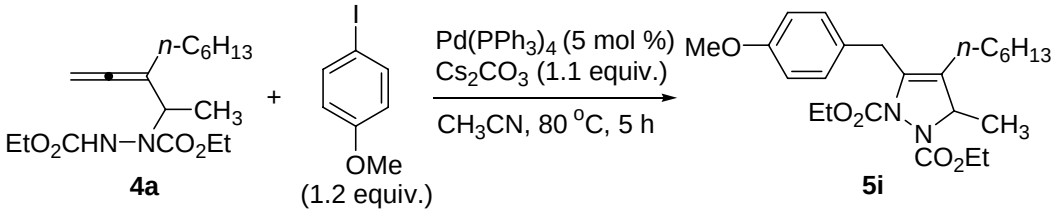
The reaction of **4a** (82 mg, 0.25 mmol), iodobenzene (62 mg, 0.30 mmol), $Pd(PPh_3)_4$ (15 mg, 0.013 mmol), and Cs_2CO_3 (90 mg, 0.28 mmol) in 3 mL of CH_3CN afforded 69 mg (68%) of **5g**: Eluent for chromatography on silica gel: petroleum ether/ether = 10:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28-7.14 (m, 5 H), 4.69 (q, *J* = 6.4 Hz, 1 H), 4.20-4.07 (m, 5 H), 3.77 (d, *J* = 16.2 Hz, 1 H), 2.25-2.13 (m, 1 H), 2.10-1.97 (m, 1 H), 1.51-1.39 (m, 1 H), 1.37-1.13 (m, 16 H), 0.85 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 157.9, 155.7, 138.3, 133.5, 128.1, 128.0, 126.7, 126.0, 62.12, 62.07, 61.0, 31.9, 31.4, 29.1, 28.5, 24.6, 22.5, 18.7, 14.3, 14.2, 13.9; MS (ESI) *m/z* (%) 403 ([M+H]$^+$), 425 ([M+Na]$^+$); IR (neat) 2930, 1739, 1713, 1678, 1599, 1496, 1375, 1318, 1047 cm^{-1}; HRMS (ESI) calcd. for $C_{23}H_{35}N_2O_4$ ([M+H]$^+$) 403.2591; Found: 403.2595.

(8) 3-Methyl-4-(*n*-hexyl)-5-(4'-methylbenzyl)-1,2-bis(ethoxycarbonyl)-2,3-dihydro-1*H*-pyrazole (5h) (entry 7, Table 1)



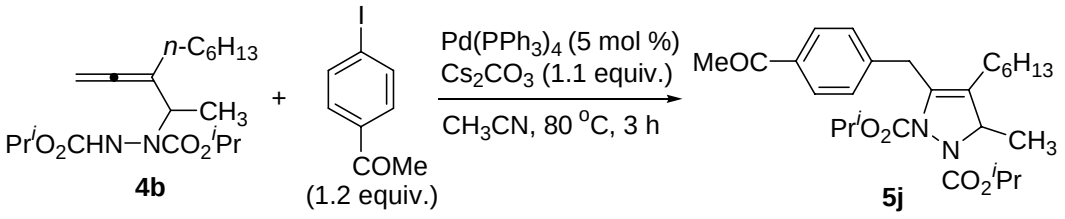
The reaction of **4a** (83 mg, 0.25 mmol), 4-methyliodobenzene (65 mg, 0.30 mmol), $Pd(PPh_3)_4$ (15 mg, 0.013 mmol), and Cs_2CO_3 (90 mg, 0.28 mmol) in 3 mL of CH_3CN afforded 52 mg (49%) of **5h**: Eluent for chromatography on silica gel: petroleum ether/ether = 10:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11-6.99 (bs, 4 H), 4.68 (q, *J* = 6.4 Hz, 1 H), 4.23-4.09 (m, 4 H), 4.08 (d, *J* = 15.9 Hz, 1 H), 3.73 (d, *J* = 15.9 Hz, 1 H), 2.30 (s, 3 H), 2.23-2.13 (m, 1 H), 2.05-1.95 (m, 1 H), 1.49-1.38 (m, 1 H), 1.36-1.12 (m, 16 H), 0.85 (t, *J* = 6.5 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 157.9, 155.7, 135.4, 135.2, 133.7, 128.8, 127.8, 126.5, 62.1, 62.0, 61.0, 31.4, 29.1, 28.4, 24.6, 22.4, 20.9, 18.6, 14.3, 14.2, 13.9; MS (ESI) *m/z* (%) 417 ($[M+H]^+$); IR (neat) 2929, 1742, 1713, 1678, 1515, 1375, 1318, 1253, 1047 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{24}H_{36}N_2O_4Na$ ($[M+Na]^+$) 439.2567; Found: 439.2559.

(9) 3-Methyl-4-(*n*-hexyl)-5-(4'-methoxybenzyl)-1,2-bis(ethoxycarbonyl)-2,3-dihydro-1*H*-pyrazole (5i) (entry 8, Table 1)



The reaction of **4a** (83 mg, 0.25 mmol), 4-iodoanisole (70 mg, 0.30 mmol), $Pd(PPh_3)_4$ (15 mg, 0.013 mmol), and Cs_2CO_3 (90 mg, 0.28 mmol) in 3 mL of CH_3CN afforded 42 mg (38%) of **5i**: Eluent for chromatography on silica gel: petroleum ether/ether = 5:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.9 Hz, 2 H), 6.78 (d, *J* = 8.9 Hz, 2 H), 4.67 (q, *J* = 6.4 Hz, 1 H), 4.144 (q, *J* = 7.2 Hz, 2 H), 4.141 (q, *J* = 7.1 Hz, 2 H), 4.04 (d, *J* = 15.9 Hz, 1 H), 3.76 (s, 3 H), 3.70 (d, *J* = 15.9 Hz, 1 H), 2.23-2.12 (m, 1 H), 2.06-1.93 (m, 1 H), 1.50-1.36 (m, 1 H), 1.35-1.11 (m, 16 H), 0.84 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 157.9, 155.7, 133.9, 130.4, 128.9, 126.3, 113.5, 62.11, 62.06, 61.0, 55.1, 31.4, 31.0, 29.1, 28.5, 24.6, 22.5, 18.6, 14.4, 14.3, 13.9; MS (ESI) *m/z* (%) 433 ($[M+H]^+$), 455 ($[M+Na]^+$), 487 ($[M+MeOH+Na]^+$); IR (neat) 2931, 1739, 1712, 1678, 1613, 1512, 1375, 1318, 1248, 1039 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_{36}N_2O_5Na$ ($[M+Na]^+$) 455.2516; Found: 455.2518.

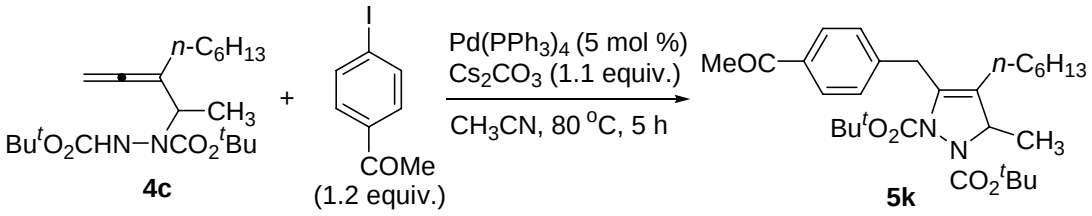
(10) 3-Methyl-4-(*n*-hexyl)-5-(4'-acetylbenzyl)-1,2-bis(isopropoxycarbonyl)-2,3-dihydro-1*H*-pyrazole (5j) (entry 1, Table 2)



The reaction of **4b** (71 mg, 0.20 mmol), 4-acetyliodobenzene (59 mg, 0.24 mmol), $Pd(PPh_3)_4$ (12 mg, 0.010 mmol), and Cs_2CO_3 (72 mg, 0.22 mmol) in 2.5 mL of CH_3CN afforded 72 mg (76%) of **5j**: Eluent for chromatography on silica gel: petroleum ether/ether = 5:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz,

2 H), 7.30 (d, *J* = 8.4 Hz, 2 H), 5.02-4.85 (m, 2 H), 4.69 (q, *J* = 6.5 Hz, 1 H), 4.23 (d, *J* = 16.5 Hz, 1 H), 3.80 (d, *J* = 16.5 Hz, 1 H), 2.57 (s, 3 H), 2.26-2.14 (m, 1 H), 2.10-1.97 (m, 1 H), 1.53-1.39 (m, 1 H), 1.37-1.07 (m, 22 H), 0.84 (t, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 197.7, 157.5, 155.3, 144.3, 135.1, 132.7, 128.24, 128.23, 127.1, 69.7, 60.8, 31.9, 31.4, 29.0, 28.4, 26.5, 24.6, 22.4, 21.81, 21.79, 21.7, 21.6, 18.5, 13.9; MS (ESI) *m/z* (%) 473 ($[M+H]^+$), 495 ($[M+Na]^+$); IR (neat) 2931, 1708, 1685, 1607, 1375, 1310, 1266, 1109 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{27}H_{40}N_2O_5Na$ ($[M+Na]^+$) 495.2829; Found: 495.2822.

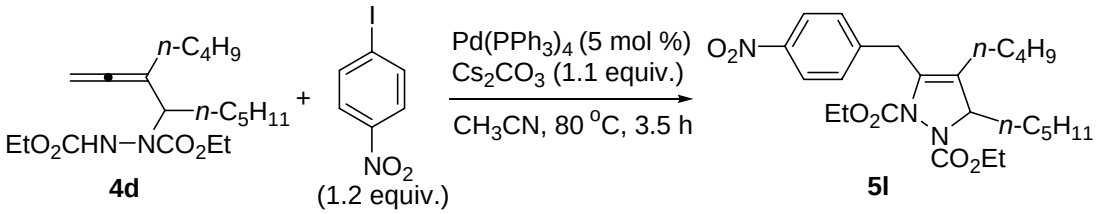
(11) 3-Methyl-4-(*n*-hexyl)-5-(4'-acetylbenzyl)-1,2-bis(*tert*-butoxycarbonyl)-2,3-dihydro-1*H*-pyrazole (5k) (entry 2, Table 2)



The reaction of **4c** (77 mg, 0.20 mmol), 4-acetyliodobenzene (59 mg, 0.24 mmol), $Pd(PPh_3)_4$ (12 mg, 0.010 mmol), and Cs_2CO_3 (72 mg, 0.22 mmol) in 2.5 mL of CH_3CN afforded 71 mg (70%) of **5k**: Eluent for chromatography on silica gel: petroleum ether/ether = 7:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 2 H), 7.29 (d, *J* = 8.1 Hz, 2 H), 4.59 (q, *J* = 6.5 Hz, 1 H), 4.17 (d, *J* = 16.7 Hz, 1 H), 3.75 (d, *J* = 16.7 Hz, 1 H), 2.55 (s, 3 H), 2.20-2.08 (m, 1 H), 2.07-1.94 (m, 1 H), 1.50-1.04 (m, 29 H), 0.79 (t, *J* = 6.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 197.7, 156.8, 154.5, 144.6, 135.1, 132.7, 128.3, 128.2, 126.8, 81.4, 80.9, 60.4, 31.9, 31.4,

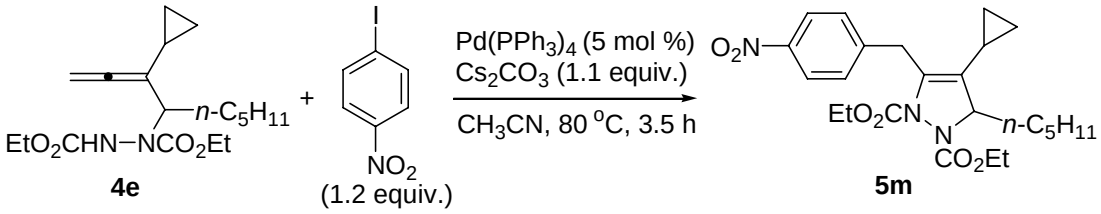
29.0, 28.4, 28.0, 26.5, 24.6, 22.4, 18.6, 13.9; MS (ESI) *m/z* (%) 523 ($[M+Na]^+$); IR (neat) 2930, 1707, 1685, 1607, 1572, 1367, 1266, 1155 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{29}H_{44}N_2O_5Na$ ($[M+Na]^+$) 523.3142; Found: 523.3148.

(12) 3-(*n*-Pentyl)-4-(*n*-butyl)-5-(4'-nitrobenzyl)-1,2-bis(ethoxycarbonyl)-2,3-dihydro-1*H*-pyrazole (5l) (entry 3, Table 2)



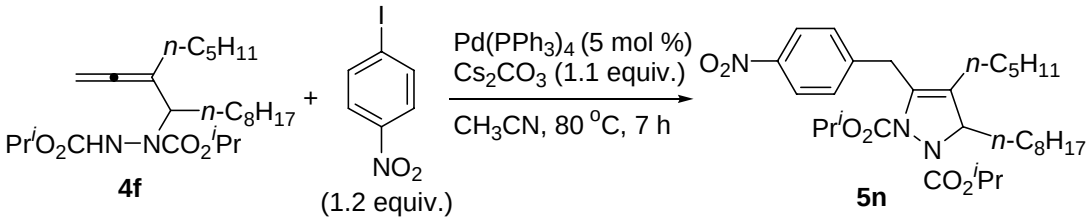
The reaction of **4d** (71 mg, 0.20 mmol), 4-nitroiodobenzene (60 mg, 0.24 mmol), $Pd(PPh_3)_4$ (12 mg, 0.010 mmol), and Cs_2CO_3 (72 mg, 0.22 mmol) in 2.5 mL of CH_3CN afforded 63 mg (66%) of **5l**: Eluent for chromatography on silica gel: petroleum ether/ether = 7:1; liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 2 H), 7.35 (d, *J* = 8.4 Hz, 2 H), 4.65-4.56 (m, 1 H), 4.25 (d, *J* = 16.4 Hz, 1 H), 4.22-4.03 (m, 4 H), 3.84 (d, *J* = 16.4 Hz, 1 H), 2.24-2.12 (m, 1 H), 2.08-1.96 (m, 1 H), 1.68-1.55 (m, 1 H), 1.50-1.09 (m, 17 H), 0.88 (t, *J* = 6.8 Hz, 3 H), 0.82 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 158.3, 155.5, 146.5 146.3, 132.5, 128.9, 126.6, 123.4, 65.6, 62.3, 62.1, 31.93, 31.90, 31.6, 28.2, 27.1, 24.7, 22.4, 22.2, 14.4, 14.3, 13.93, 13.86; MS (ESI) *m/z* (%) 476 ($[M+H]^+$), 498 ($[M+Na]^+$), 530 ($[M+MeOH+Na]^+$); IR (neat) 2932, 1713, 1679, 1599, 1522, 1375, 1346, 1316, 1049 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{25}H_{38}N_3O_6$ ($[M+H]^+$) 476.2755; Found: 476.2770.

(13) 3-(*n*-Pentyl)-4-cyclopropyl-5-(4'-nitrobenzyl)-1,2-bis(ethoxycarbonyl)-2,3-dihydro-1*H*-pyrazole (5m) (entry 4, Table 2)



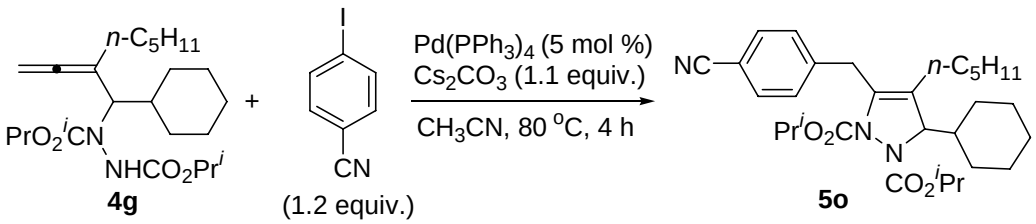
The reaction of **4e** (68 mg, 0.20 mmol), 4-nitroiodobenzene (60 mg, 0.24 mmol), $Pd(PPh_3)_4$ (12 mg, 0.010 mmol), and Cs_2CO_3 (72 mg, 0.22 mmol) in 2.5 mL of CH_3CN afforded 58 mg (63%) of **5m**: Eluent for chromatography on silica gel: petroleum ether/ether = 8:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.7 Hz, 2 H), 7.36 (d, *J* = 8.7 Hz, 2 H), 4.40-4.31 (m, 1 H), 4.26 (d, *J* = 16.5 Hz, 1 H), 4.19-4.01 (m, 5 H), 1.65-1.51 (m, 1 H), 1.48-1.12 (m, 14 H), 0.86 (t, *J* = 6.8 Hz, 3 H), 0.82-0.70 (m, 2 H), 0.56-0.47 (m, 1 H), 0.45-0.37 (m, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 158.1, 155.3, 146.4, 146.2, 134.4, 128.9, 126.8, 123.4, 65.3, 62.3, 62.1, 33.1, 32.1, 31.4, 24.7, 22.4, 14.31, 14.28, 13.9, 6.4, 6.0, 4.9; MS (ESI) *m/z* (%) 460 ($[M+H]^+$), 482 ($[M+Na]^+$); IR (neat) 2932, 1712, 1599, 1523, 1372, 1346, 1316, 1252, 1110, 1022 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{24}H_{33}N_3O_6Na$ ($[M+Na]^+$) 482.2262; Found: 482.2257.

(14) 3-(*n*-Octyl)-4-(*n*-pentyl)-5-(4'-nitrobenzyl)-1,2-bis(isopropoxycarbonyl)-2,3-dihydro-1*H*-pyrazole (5n) (entry 5, Table 2)



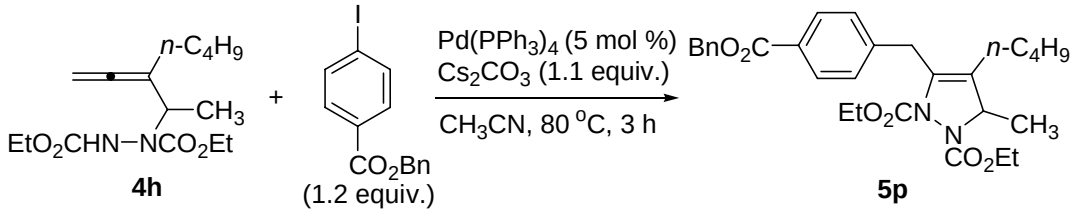
The reaction of **4f** (88 mg, 0.20 mmol), 4-nitroiodobenzene (60 mg, 0.24 mmol), $Pd(PPh_3)_4$ (12 mg, 0.010 mmol), and Cs_2CO_3 (72 mg, 0.22 mmol) in 2.5 mL of CH_3CN afforded 81 mg (72%) of **5n**: Eluent for chromatography on silica gel: petroleum ether/ether = 8:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.6 Hz, 2 H), 7.36 (d, *J* = 8.6 Hz, 2 H), 5.01-4.82 (m, 2 H), 4.66-4.53 (m, 1 H), 4.27 (d, *J* = 16.7 Hz, 1 H), 3.82 (d, *J* = 16.7 Hz, 1 H), 2.25-2.12 (m, 1 H), 2.08-1.96 (m, 1 H), 1.69-1.53 (m, 1 H), 1.48-1.08 (m, 31 H), 0.89-0.77 (m, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 157.9, 155.2, 146.5 146.4, 132.5, 128.9, 126.5, 123.3, 69.8, 69.7, 65.3, 32.3, 31.9, 31.8, 31.5, 29.45, 29.42, 29.2, 28.2, 24.9, 24.7, 22.6, 22.3, 21.9, 21.8, 21.7, 14.0, 13.9; MS (ESI) *m/z* (%) 439 ($[M-C_6H_4NO_2+2H]^+$), 461 ($[M-C_6H_4NO_2+H+Na]^+$), 560 ($[M+H]^+$), 582 ($[M+Na]^+$), 614 ($[M+MeOH+Na]^+$); IR (neat) 2930, 1709, 1678, 1600, 1523, 1375, 1345, 1310, 1108 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{31}H_{49}N_3O_6Na$ ($[M+Na]^+$) 582.3514; Found: 582.3519.

(15) 3-Cyclohexyl-4-(*n*-pentyl)-5-(4'-cyanobenzyl)-1,2-bis(isopropoxycarbonyl)-2,3-dihydro-1*H*-pyrazole (5o) (entry 6, Table 2)



The reaction of **4g** (78 mg, 0.19 mmol), 4-cyanoiodobenzene (52 mg, 0.23 mmol), $Pd(PPh_3)_4$ (11 mg, 0.0095 mmol), and Cs_2CO_3 (68 mg, 0.21 mmol) in 2.5 mL of CH_3CN afforded 74 mg (76%) of **5o**: Eluent for chromatography on silica gel: petroleum ether/ether = 7:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.1 Hz, 2 H), 7.29 (d, *J* = 8.1 Hz, 2 H), 4.98-4.84 (m, 2 H), 4.47 (bs, 1 H), 4.25 (d, *J* = 16.5 Hz, 1 H), 3.79 (d, *J* = 16.5 Hz, 1 H), 2.23-2.11 (m, 1 H), 2.07-1.95 (m, 1 H), 1.80-1.58 (m, 4 H), 1.56-0.82 (m, 25 H), 0.80 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 158.6, 154.7, 144.3, 132.8, 131.8, 128.9, 124.1, 119.0, 109.8, 70.2, 69.8, 69.7, 69.5, 39.7, 32.0, 31.5, 30.6, 28.2, 26.3, 26.1, 25.7, 25.0, 22.2, 21.9, 21.85, 21.79, 21.75, 13.8; MS (ESI) *m/z* (%) 510 ($[M+H]^+$), 532 ($[M+Na]^+$), 564 ($[M+MeOH+Na]^+$); IR (neat) 2929, 2228, 1709, 1679, 1608, 1506, 1373, 1311, 1108 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{30}H_{43}N_3O_4Na$ ($[M+Na]^+$) 532.3146; Found: 532.3156.

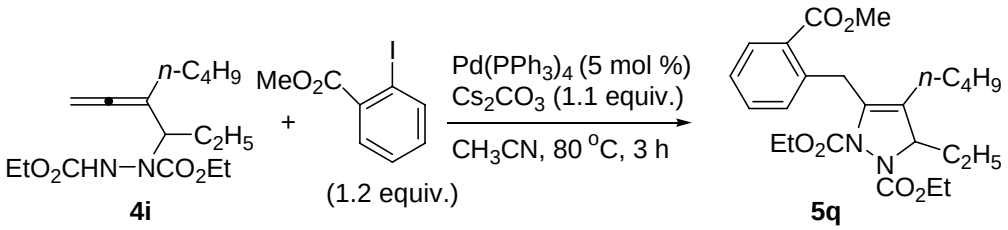
(16) 3-Methyl-4-(*n*-butyl)-5-((4'-benzyloxycarbonyl)benzyl)-1,2-bis(ethoxy-carbonyl)-2,3-dihydro-1*H*-pyrazole (5p) (entry 7, Table 2)



The reaction of **4h** (60 mg, 0.20 mmol), 4-iodobenzoic acid benzyl ester (81 mg, 0.24 mmol), $Pd(PPh_3)_4$ (12 mg, 0.010 mmol), and Cs_2CO_3 (72 mg, 0.22 mmol) in 2.5 mL of CH_3CN afforded 80 mg (78%) of **5p**: Eluent for chromatography on silica gel: petroleum ether/ether = 7:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.1 Hz,

2 H), 7.45-7.31 (m, 5 H), 7.26 (d, *J* = 8.1 Hz, 2 H), 5.35 (s, 2 H), 4.71 (q, *J* = 6.5 Hz, 1 H), 4.27-4.04 (m, 5 H), 3.82 (d, *J* = 16.2 Hz, 1 H), 2.28-2.13 (m, 1 H), 2.09-1.95 (m, 1 H), 1.52-1.11 (m, 13 H), 0.87 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 166.3, 157.7, 155.5, 144.0, 136.0, 132.6, 129.6, 128.5, 128.1, 128.02, 127.97, 127.1, 66.4, 62.2, 62.1, 61.1, 31.9, 30.6, 24.3, 22.5, 18.6, 14.3, 14.2, 13.7; MS (ESI) *m/z* (%) 509 ($[M+H]^+$), 532 ($[M+Na]^+$); IR (neat) 2931, 1716, 1678, 1610, 1375, 1316, 1271, 1100 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{29}H_{36}N_2O_6Na$ ($[M+Na]^+$) 531.2466; Found: 531.2471.

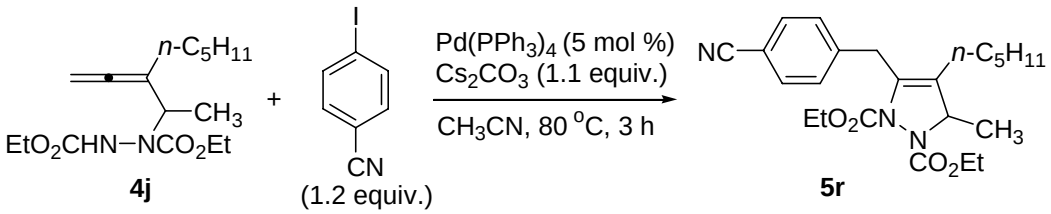
(17) 3-Ethyl-4-(*n*-butyl)-5-(2'-(methoxycarbonyl)benzyl)-1,2-bis(ethoxycarbonyl)-2,3-dihydro-1*H*-pyrazole (5q) (entry 8, Table 2)



The reaction of **4i** (75 mg, 0.24 mmol), 2-iodobenzoic acid methyl ester (75 mg, 0.29 mmol), $Pd(PPh_3)_4$ (14 mg, 0.012 mmol), and Cs_2CO_3 (86 mg, 0.26 mmol) in 3 mL of CH_3CN afforded 82 mg (76%) of **5q**: Eluent for chromatography on silica gel: petroleum ether/ether = 7:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.5 Hz, 1 H), 7.44-7.33 (m, 1 H), 7.31-7.19 (m, 2 H), 4.65 (dd, *J* = 6.8 and 3.5 Hz, 1 H), 4.51 (d, *J* = 17.7 Hz, 1 H), 4.29-4.16 (m, 3 H), 4.11-4.00 (m, 2 H), 3.90 (s, 3 H), 2.23-2.11 (m, 1 H), 2.04-1.92 (m, 1 H), 1.82-1.68 (m, 1 H), 1.49-1.35 (m, 2 H), 1.34-1.15 (m, 6 H), 1.07 (t, *J* = 7.1 Hz, 3 H), 0.96 (t, *J* = 7.4 Hz, 3 H), 0.84 (t, *J* = 6.9 Hz, 3 H); ^{13}C

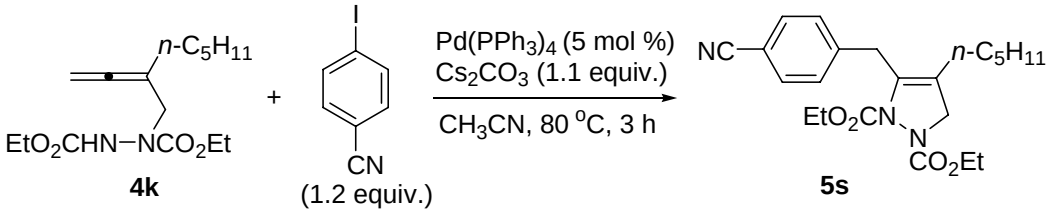
NMR (75.4 MHz, $CDCl_3$) δ 167.9, 158.3, 155.0, 139.8, 133.1, 131.7, 130.3, 129.3, 128.7, 125.8, 125.4, 66.4, 62.1, 61.9, 51.8, 30.5, 29.9, 25.3, 24.4, 22.5, 14.4, 14.0, 13.7, 9.1; MS (ESI) *m/z* (%) 447 ($[M+H]^+$), 469 ($[M+Na]^+$); IR (neat) 2933, 1716, 1678, 1601, 1576, 1375, 1303, 1271, 1079 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{24}H_{34}N_2O_6Na$ ($[M+Na]^+$) 469.2309; Found: 469.2321.

(18) 3-Methyl-4-(*n*-pentyl)-5-(4'-cyanobenzyl)-1,2-bis(ethoxycarbonyl)-2,3-dihydro-1*H*-pyrazole (5r) (entry 9, Table 2)



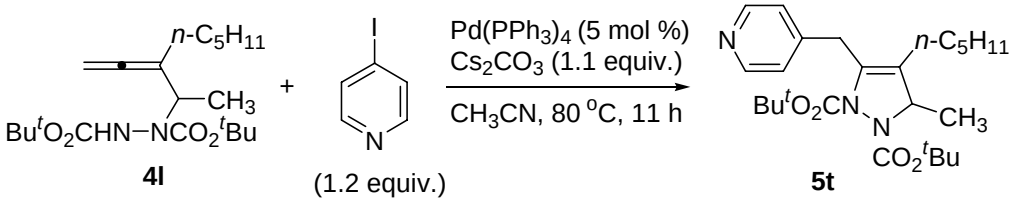
The reaction of **4j** (78 mg, 0.25 mmol), 4-cyanoiodobenzene (69 mg, 0.30 mmol), $Pd(PPh_3)_4$ (15 mg, 0.013 mmol), and Cs_2CO_3 (90 mg, 0.28 mmol) in 3 mL of CH_3CN afforded 85 mg (82%) of **5r**: Eluent for chromatography on silica gel: petroleum ether/ether = 7:1; liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, J = 8.1 Hz, 2 H), 7.32 (d, J = 8.1 Hz, 2 H), 4.71 (q, J = 6.6 Hz, 1 H), 4.29-4.09 (m, 5 H), 3.82 (d, J = 16.8 Hz, 1 H), 2.26-2.13 (m, 1 H), 2.11-1.98 (m, 1 H), 1.55-1.41 (m, 1 H), 1.37-1.14 (m, 14 H), 0.85 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 157.6, 155.5, 144.0, 132.1, 131.9, 128.8, 127.5, 118.9, 109.9, 62.22, 62.17, 61.1, 32.0, 31.5, 28.1, 24.5, 22.2, 18.6, 14.3, 14.2, 13.8; MS (ESI) *m/z* (%) 414 ($[M+H]^+$), 436 ($[M+Na]^+$); IR (neat) 2932, 2228, 1712, 1678, 1608, 1506, 1375, 1318, 1253, 1046 cm^{-1}; HRMS (ESI) calcd. for $C_{23}H_{32}N_3O_4$ ($[M+H]^+$) 414.2387; Found: 414.2394.

(19) 4-(*n*-Pentyl)-5-(4'-cyanobenzyl)-1,2-bis(ethoxycarbonyl)-2,3-dihydro-1*H*-pyrazole (5s) (entry 10, Table 2)



The reaction of **4k** (75 mg, 0.25 mmol), 4-cyanoiodobenzene (69 mg, 0.30 mmol), $Pd(PPh_3)_4$ (15 mg, 0.013 mmol), and Cs_2CO_3 (90 mg, 0.28 mmol) in 3 mL of CH_3CN afforded 73 mg (73%) of **5s**: Eluent for chromatography on silica gel: petroleum ether/ether = 7:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, J = 8.3 Hz, 2 H), 7.31 (d, J = 8.3 Hz, 2 H), 4.59-4.37 (bs, 1 H), 4.32-4.06 (m, 6 H), 3.99-3.74 (bs, 1 H), 2.18 (t, J = 7.4 Hz, 2 H), 1.46-1.36 (m, 2 H), 1.34-1.16 (m, 10 H), 0.87 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 158.1, 155.1, 143.9, 132.7, 131.9, 128.9, 122.5, 118.9, 110.0, 62.5, 62.2, 54.6, 31.9, 31.4, 27.5, 25.4, 22.2, 14.3, 14.2, 13.8; MS (ESI) *m/z* (%) 400 ($[M+H]^+$), 422 ($[M+Na]^+$); IR (neat) 2931, 2227, 1712, 1681, 1608, 1505, 1375, 1320, 1224, 1020 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{22}H_{30}N_3O_4$ ($[M+H]^+$) 400.2231; Found: 400.2235.

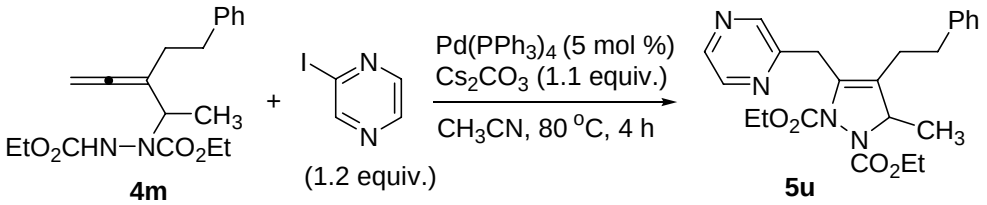
(20) 3-Methyl-4-(*n*-pentyl)-5-(4'-pyridinylmethyl)-1,2-bis(*tert*-butoxycarbonyl)-2,3-dihydro-1*H*-pyrazole (5t) (entry 11, Table 2)



The reaction of **4l** (75 mg, 0.20 mmol), 4-iodopyridine (50 mg, 0.24 mmol),

$Pd(PPh_3)_4$ (12 mg, 0.010 mmol), and Cs_2CO_3 (72 mg, 0.22 mmol) in 2.5 mL of CH_3CN afforded 78 mg (86%) of **5t**: Eluent for chromatography on silica gel: petroleum ether/ethyl acetate = 3:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 (d, *J* = 5.9 Hz, 2 H), 7.13 (d, *J* = 5.9 Hz, 2 H), 4.59 (q, *J* = 6.5 Hz, 1 H), 4.11 (d, *J* = 16.7 Hz, 1 H), 3.68 (d, *J* = 16.7 Hz, 1 H), 2.19-2.07 (m, 1 H), 2.06-1.94 (m, 1 H), 1.49-1.11 (m, 27 H), 0.79 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 156.8, 154.4, 149.4, 147.9, 131.8, 127.3, 123.5, 81.5, 81.1, 60.4, 31.5, 31.3, 28.1, 28.0, 24.6, 22.2, 18.6, 13.9; MS (ESI) *m/z* (%) 446 ($[M+H]^+$); IR (neat) 2931, 1708, 1678, 1599, 1368, 1335, 1256, 1156 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{40}N_3O_4$ ($[M+H]^+$) 446.3013; Found: 446.3031.

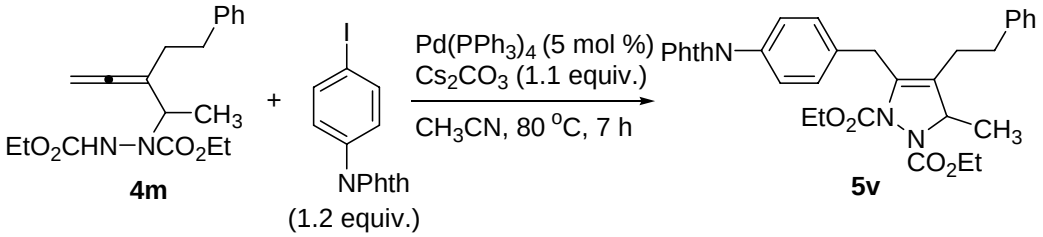
(21) 3-Methyl-4-phenethyl-5-pyrazinylmethyl-1,2-bis(ethoxycarbonyl)-2,3-dihydro-1*H*-pyrazole (5u) (entry 12, Table 2)



The reaction of **4m** (70 mg, 0.20 mmol), iodopyrazine (50 mg, 0.24 mmol), $Pd(PPh_3)_4$ (12 mg, 0.010 mmol), and Cs_2CO_3 (72 mg, 0.22 mmol) in 2.5 mL of CH_3CN afforded 72 mg (84%) of **5u**: Eluent for chromatography on silica gel: petroleum ether/ether = 1:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 (s, 1 H), 8.35 (s, 1 H), 8.18 (s, 1 H), 7.22-7.00 (m, 5 H), 4.71 (q, *J* = 6.3 Hz, 1 H), 4.25-4.02 (m, 5 H), 3.79 (d, *J* = 16.5 Hz, 1 H), 2.85-2.72 (m, 1 H), 2.71-2.47 (m, 2 H), 2.44-2.28 (m, 1 H), 1.25 (d, *J* = 7.5 Hz, 3 H), 1.21 (t, *J* = 7.5 Hz, 3 H), 1.13 (t, *J* = 7.1 Hz, 3 H); ^{13}C

NMR (75.4 MHz, $CDCl_3$) δ 157.8, 155.2, 153.8, 144.0, 143.5, 142.2, 140.3, 131.8, 128.3, 128.2, 126.6, 126.2, 62.4, 62.2, 61.0, 34.4, 32.6, 26.6, 18.5, 14.3, 14.2; MS (ESI) *m/z* (%) 425 ($[M+H]^+$); IR (neat) 2979, 1711, 1681, 1402, 1375, 1319, 1254, 1050 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{23}H_{28}N_4O_4Na$ ($[M+Na]^+$) 447.2003; Found: 447.1997.

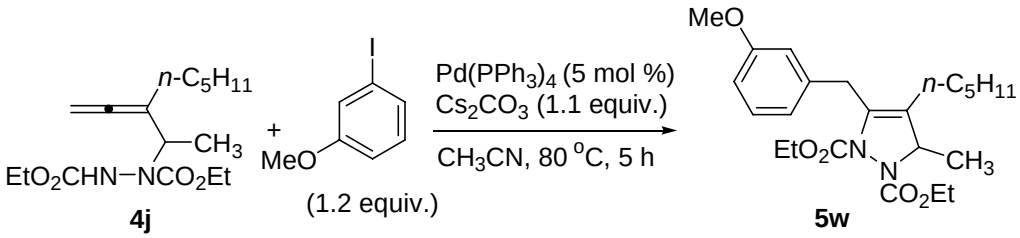
(22) 3-Methyl-4-phenethyl-5-(4'-phthalimidobenzyl)-1,2-bis(ethoxycarbonyl)-2,3-dihydro-1*H*-pyrazole (5v) (entry 13, Table 2)



The reaction of **4m** (88 mg, 0.25 mmol), 4-phthalimidoiodobenzene (106 mg, 0.30 mmol), $Pd(PPh_3)_4$ (15 mg, 0.013 mmol), and Cs_2CO_3 (90 mg, 0.28 mmol) in 2.5 mL of CH_3CN afforded 68 mg (47%) of **5v**: Eluent for chromatography on silica gel: petroleum ether/ether = 1:1; solid; m.p. 123-124 °C (petroleum ether/ethyl acetate); ^1H NMR (300 MHz, $CDCl_3$) δ 7.97-7.92 (m, 2 H), 7.81-7.76 (m, 2 H), 7.30-7.16 (m, 5 H), 7.11 (d, *J* = 8.4 Hz, 2 H), 7.04 (d, *J* = 8.4 Hz, 2 H), 4.81 (q, *J* = 6.4 Hz, 1 H), 4.22-4.11 (m, 4 H), 4.04 (d, *J* = 16.2 Hz, 1 H), 3.67 (d, *J* = 16.2 Hz, 1 H), 2.87-2.76 (m, 1 H), 2.72-2.50 (m, 2 H), 2.44-2.33 (m, 1 H), 1.28 (d, *J* = 6.3 Hz, 3 H), 1.20 (t, *J* = 6.9 Hz, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 167.3, 158.1, 155.4, 140.4, 138.0, 134.3, 134.1, 131.6, 129.5, 128.7, 128.5, 128.3, 126.2, 126.1, 125.7, 123.6, 62.3, 62.2, 60.8, 34.4, 31.4, 26.7, 18.5, 14.4, 14.2; MS (ESI) *m/z* (%) 568 ($[M+H]^+$), 585 ($[M+NH_4]^+$),

590 ([M+Na]$^+$), 606 ([M+K]$^+$); IR (neat) 2980, 1783, 1719, 1676, 1606, 1514, 1378, 1317, 1254, 1220, 1049 cm^{-1}; Anal. Calcd. for $C_{33}H_{33}N_3O_6$: C, 69.83; H, 5.86; N 7.40. Found: C, 69.69; H, 5.93; N 7.23.

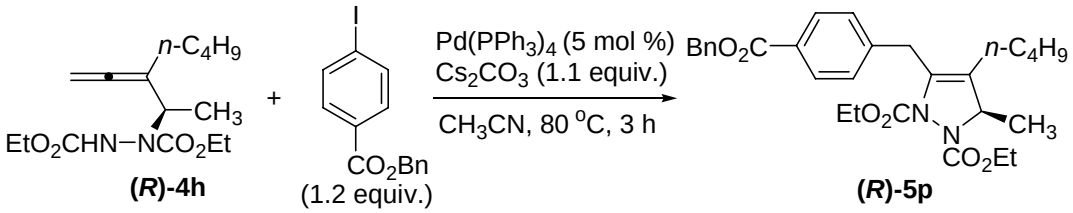
(23) 3-Methyl-4-(*n*-pentyl)-5-(3'-methoxybenzyl)-1,2-bis(ethoxycarbonyl)-2,3-dihydro-1*H*-pyrazole (5w) (entry 14, Table 2)



The reaction of **4j** (133 mg, 0.43 mmol), 3-methoxyiodobenzene (120 mg, 0.51 mmol), $Pd(PPh_3)_4$ (25 mg, 0.022 mmol), and Cs_2CO_3 (154 mg, 0.47 mmol) in 4 mL of CH_3CN afforded 129 mg (72%) of **5w**: Eluent for chromatography on silica gel: petroleum ether/ether = 7:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.8 Hz, 1 H), 6.82-6.65 (m, 3 H), 4.68 (q, *J* = 6.4 Hz, 1 H), 4.22-4.03 (m, 5 H), 3.73 (d, *J* = 16.2 Hz, 1 H), 3.73 (s, 3 H), 2.25-2.09 (m, 1 H), 2.08-1.92 (m, 1 H), 1.50-1.36 (m, 1 H), 1.36-1.09 (m, 14 H), 0.82 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 159.4, 157.7, 155.6, 139.8, 133.3, 128.9, 126.6, 120.3, 113.5, 111.3, 62.1, 62.0, 60.9, 54.8, 31.7, 31.5, 28.0, 24.5, 22.2, 18.5, 14.2, 13.8; MS (ESI) *m/z* (%) 419 ([M+H]$^+$), 441 ([M+Na]$^+$); IR (neat) 2932, 2228, 1712, 1678, 1601, 1375, 1318, 1258, 1047 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{23}H_{34}N_2O_5Na$ ([M+Na]$^+$) 441.2360; Found: 441.2347.

Synthesis of optically active 2,3-dihydro-1*H*-pyrazoles.

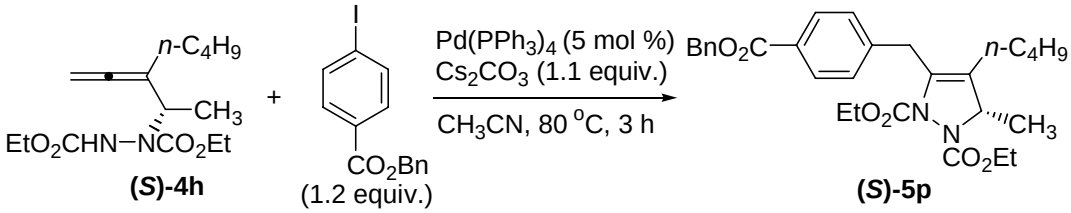
(1) 3(*R*)-Methyl-4-(*n*-butyl)-5-((4'-benzyloxycarbonyl)benzyl)-1,2-bis(ethoxycarbonyl)-2,3-dihydro-1*H*-pyrazole (*R*)-(5p) (entry 1, Table 3)



The reaction of (*R*)-**4h** (69 mg, 0.23 mmol, >99% ee), 4-iodobenzoic acid benzyl ester (93 mg, 0.28 mmol), $Pd(PPh_3)_4$ (14 mg, 0.012 mmol), and Cs_2CO_3 (82 mg, 0.25 mmol) in 3 mL of CH_3CN afforded 91 mg (77%) of (*R*)-**5p** with 99% ee as determined by HPLC analysis (Chiralcel AD-H, *n*-Hexane : *i*-PrOH = 85 : 15, 0.7 mL/min, 254 nm, t_r 9.5 min (major), 12.5 min (minor)); $[\alpha]^{20}_D$ = + 46.7 (*c* = 1.00, $CHCl_3$); Eluent for chromatography on silica gel: petroleum ether/ether = 6:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 2 H), 7.49-7.32 (m, 5 H), 7.27 (d, *J* = 8.0 Hz, 2 H), 5.35 (s, 2 H), 4.71 (q, *J* = 6.3 Hz, 1 H), 4.26-4.06 (m, 5 H), 3.82 (d, *J* = 16.5 Hz, 1 H), 2.28-2.14 (m, 1 H), 2.09-1.95 (m, 1 H), 1.51-1.12 (m, 13 H), 0.87 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 166.3, 157.7, 155.5, 144.0, 136.0, 132.6, 129.6, 128.5, 128.03, 127.97, 127.1, 66.4, 62.2, 62.1, 61.1, 31.9, 30.6, 24.3, 22.5, 18.6, 14.3, 14.2, 13.7; MS (ESI) *m/z* (%) 509 ($[M+H]^+$); IR (neat) 2932, 1714, 1679, 1611, 1375, 1316, 1271, 1101, 1044 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{29}H_{36}N_2O_6Na$ ($[M+Na]^+$) 531.2466; Found: 531.2460.

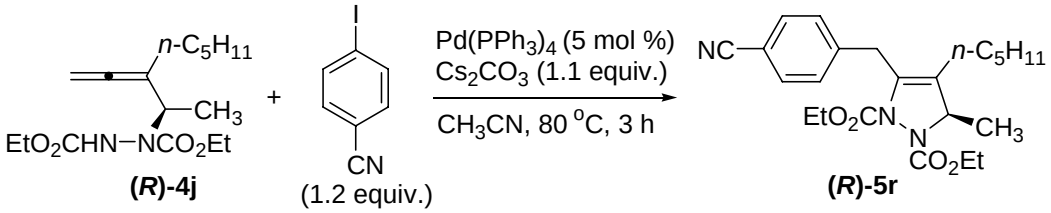
(2) 3(*S*)-Methyl-4-(*n*-butyl)-5-(4'-(benzyloxycarbonyl)benzyl)-1,2-bis(ethoxy-

carbonyl)-2,3-dihydro-1*H*-pyrazole (*S*)-(5p) (entry 2, Table 3)



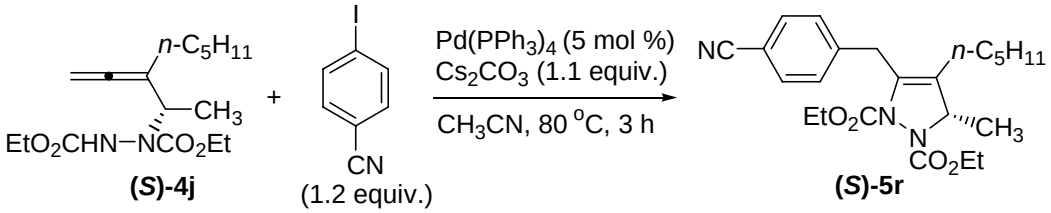
The reaction of (*S*)-**4h** (62 mg, 0.21 mmol, 96% ee), 4-iodobenzoic acid benzyl ester (85 mg, 0.25 mmol), $Pd(PPh_3)_4$ (12 mg, 0.011 mmol), and Cs_2CO_3 (75 mg, 0.23 mmol) in 3 mL of CH_3CN afforded 81 mg (77%) of (*S*)-**5p** with 95% ee as determined by HPLC analysis (Chiralcel AD-H, *n*-Hexane : *i*-PrOH = 85 : 15, 0.7 mL/min, 254 nm, t_r 9.5 min (minor), 12.4 min (major)); $[\alpha]^{20}_D$ = – 45.8 (*c* = 1.05, $CHCl_3$); Eluent for chromatography on silica gel: petroleum ether/ether = 6:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 2 H), 7.48-7.31 (m, 5 H), 7.27 (d, *J* = 8.3 Hz, 2 H), 5.35 (s, 2 H), 4.71 (q, *J* = 6.4 Hz, 1 H), 4.25-4.08 (m, 5 H), 3.82 (d, *J* = 16.5 Hz, 1 H), 2.26-2.14 (m, 1 H), 2.09-1.97 (m, 1 H), 1.50-1.11 (m, 13 H), 0.87 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 166.3, 157.8, 155.5, 144.0, 136.0, 132.6, 129.6, 128.5, 128.1, 128.04, 127.99, 127.1, 66.4, 62.2, 62.1, 61.1, 31.9, 30.6, 24.3, 22.5, 18.6, 14.3, 14.2, 13.7; MS (ESI) *m/z* (%) 509 ($[M+H]^+$); IR (neat) 2932, 1714, 1679, 1611, 1375, 1316, 1271, 1101, 1044 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{29}H_{36}N_2O_6Na$ ($[M+Na]^+$) 531.2466; Found: 531.2462.

(3) 3(*R*)-Methyl-4-(*n*-pentyl)-5-(4'-cyanobenzyl)-1,2-bis(ethoxycarbonyl)-2,3-dihydro-1*H*-pyrazole (*R*)-(5r) (entry 3, Table 3)



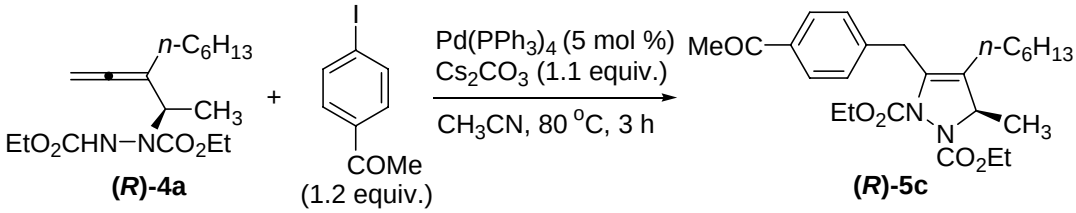
The reaction of (*R*)-**4j** (81 mg, 0.26 mmol, >99% ee), 4-cyanoiodobenzene (71 mg, 0.31 mmol), $Pd(PPh_3)_4$ (15 mg, 0.013 mmol), and Cs_2CO_3 (93 mg, 0.29 mmol) in 3 mL of CH_3CN afforded 88 mg (82%) of (*R*)-**5r** with 98% ee as determined by HPLC analysis (Chiralcel OD-H, *n*-Hexane : *i*-PrOH = 90 : 10, 0.7 mL/min, 254 nm, t_r 4.4 min (minor), 6.2 min (major)); $[\alpha]^{20}_D$ = + 55.5 (*c* = 1.05, $CHCl_3$); Eluent for chromatography on silica gel: petroleum ether/ether = 6:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.1 Hz, 2 H), 7.32 (d, *J* = 8.1 Hz, 2 H), 4.71 (q, *J* = 6.4 Hz, 1 H), 4.29-4.06 (m, 5 H), 3.82 (d, *J* = 16.5 Hz, 1 H), 2.28-2.14 (m, 1 H), 2.11-1.97 (m, 1 H), 1.56-1.40 (m, 1 H), 1.39-1.11 (m, 14 H), 0.85 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 157.6, 155.5, 144.0, 132.1, 131.9, 128.8, 127.5, 118.9, 109.9, 62.2, 62.1, 61.1, 32.0, 31.5, 28.1, 24.5, 22.2, 18.6, 14.3, 14.2, 13.8; MS (ESI) *m/z* (%) 414 ($[M+H]^+$); IR (neat) 2931, 2228, 1712, 1679, 1608, 1505, 1402, 1375, 1319, 1254, 1046 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{23}H_{32}N_3O_4$ ($[M+H]^+$) 414.2387; Found: 414.2388.

(4) 3(*S*)-Methyl-4-(*n*-pentyl)-5-(4'-cyanobenzyl)-1,2-bis(ethoxycarbonyl)-2,3-dihydro-1*H*-pyrazole (*S*)-(5r) (entry 4, Table 3)



The reaction of (*S*)-**4j** (97 mg, 0.31 mmol, >99% ee), 4-cyanoiodobenzene (85 mg, 0.37 mmol), $Pd(PPh_3)_4$ (18 mg, 0.016 mmol), and Cs_2CO_3 (112 mg, 0.34 mmol) in 4 mL of CH_3CN afforded 107 mg (83%) of (*S*)-**5r** with 96% ee as determined by HPLC analysis (Chiralcel OD-H, *n*-Hexane : *i*-PrOH = 90 : 10, 0.7 mL/min, 254 nm, t_r 4.4 min (major), 6.3 min (minor)); $[\alpha]^{20}_D$ = – 62.5 (*c* = 1.10, $CHCl_3$); Eluent for chromatography on silica gel: petroleum ether/ether = 6:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 4.71 (q, *J* = 6.5 Hz, 1 H), 4.29-4.08 (m, 5 H), 3.83 (d, *J* = 16.8 Hz, 1 H), 2.26-2.14 (m, 1 H), 2.11-1.98 (m, 1 H), 1.54-1.40 (m, 1 H), 1.38-1.12 (m, 14 H), 0.85 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 157.6, 155.4, 144.0, 132.1, 131.9, 128.8, 127.4, 118.8, 109.9, 62.2, 62.1, 61.1, 31.9, 31.4, 28.0, 24.4, 22.1, 18.5, 14.3, 14.1, 13.8; MS (ESI) *m/z* (%) 414 ($[M+H]^+$); IR (neat) 2932, 2228, 1712, 1679, 1608, 1505, 1402, 1375, 1319, 1254, 1046 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{23}H_{32}N_3O_4$ ($[M+H]^+$) 414.2387; Found: 414.2385.

(5) 3(*R*)-Methyl-4-(*n*-hexyl)-5-(4'-acetylbenzyl)-1,2-bis(ethoxycarbonyl)-2,3-dihydro-1*H*-pyrazole (*R*)-(5c) (entry 5, Table 3)



The reaction of (*R*)-**4a** (55 mg, 0.17 mmol, >99% ee), 4-acetyliodobenzene (50 mg, 0.20 mmol), $Pd(PPh_3)_4$ (10 mg, 0.0087 mmol), and Cs_2CO_3 (61 mg, 0.19 mmol) in 2 mL of CH_3CN afforded 53 mg (71%) of (*R*)-**5c** with 97% ee as determined by HPLC analysis (Chiralcel AD-H, *n*-Hexane : *i*-PrOH = 80 : 20, 0.7 mL/min, 254 nm, t_r 7.4 min (major), 7.9 min (minor)); $[\alpha]^{20}_D$ = + 54.0 (*c* = 0.95, $CHCl_3$); Eluent for chromatography on silica gel: petroleum ether/ether = 5:1; liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 2 H), 7.29 (d, *J* = 8.1 Hz, 2 H), 4.71 (q, *J* = 6.4 Hz, 1 H), 4.26-4.08 (m, 5 H), 3.83 (d, *J* = 16.5 Hz, 1 H), 2.58 (s, 3 H), 2.27-2.14 (m, 1 H), 2.10-1.97 (m, 1 H), 1.52-1.38 (m, 1 H), 1.36-1.12 (m, 16 H), 0.84 (t, *J* = 6.3 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 197.7, 157.7, 155.6, 144.1, 135.2, 132.6, 128.3, 128.2, 127.2, 62.22, 62.16, 61.1, 31.9, 31.4, 29.0, 28.4, 26.5, 24.6, 22.4, 18.6, 14.4, 14.2, 13.9; MS (ESI) *m/z* (%) 445 ($[M+H]^+$), 467 ($[M+Na]^+$); IR (neat) 2930, 1712, 1683, 1607, 1375, 1318, 1267, 1047 cm^{-1}; HRMS (MALDI/DHB) calcd. for $C_{25}H_{36}N_2O_5Na$ ($[M+Na]^+$) 467.2516; Found: 467.2528.

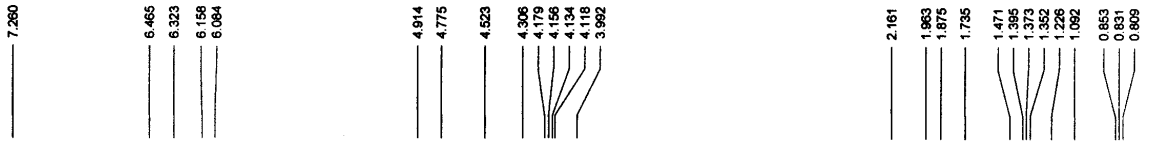
References:

(1) X. Cheng and S. Ma, *Angew. Chem., Int. Ed.*, **2008**, *47*, 4581.

(2) (a) D. Xu, Z. Li and S. Ma, *Chem. Eur. J.*, **2002**, *21*, 5012; (b) D. Xu, Z. Li and S. Ma, *Tetrahedron: Asymmetry*, **2003**, *14*, 3657; (c) D. Xu, Z. Li and S. Ma,

Tetrahedron Lett., **2003**, *44*, 6343; (d) D. Xu, Z. Lu, Z. Li and S. Ma, *Tetrahedron*, **2004**, *60*, 11879.

The following $^{1}H/^{13}C$ NMR spectra (pp S43-S70) display very broad multi peaks due to the presence of rotamers and conformers, etc. For a similar report, see: F. Menard, M. Latutens *Angew. Chem. Int. Ed*. **2007**, *8*, 47, 2085.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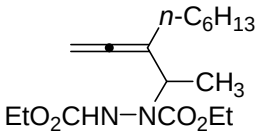
6.323
6.158
6.084
4.914
4.775
4.523
4.306
4.179
4.156
4.134
4.118
3.992
2.161
1.963
1.875
1.735
1.471
1.395
1.373
1.352
1.226
1.092
0.853
0.831
0.809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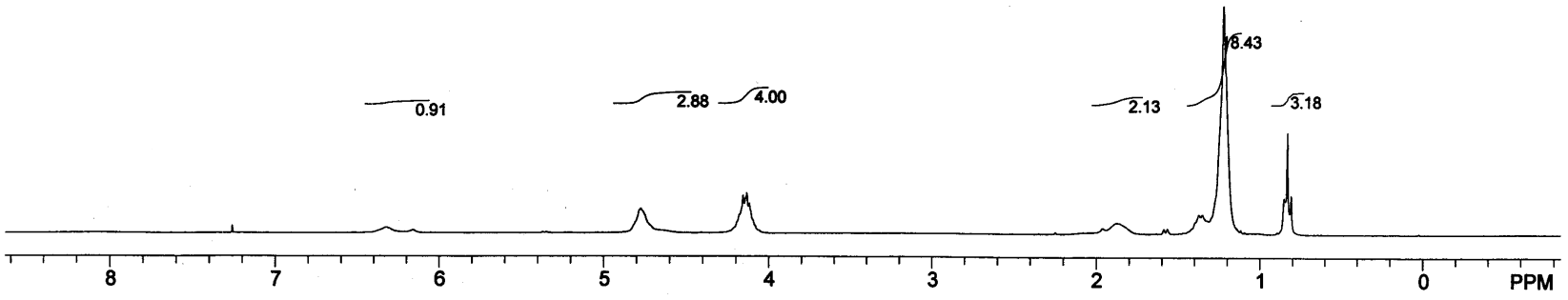
EtO2CHN−NCO2Et

4a

cx-3-015-h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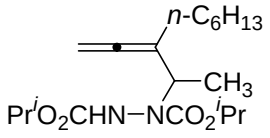
6.43
3.18
8
7
6
5
4
3
2
1
0
PPM


7.260
6.114
5.930
4.958
4.939
4.917
4.899
4.802
1.899
1.403
1.395
1.386
1.342
1.257
1.241
0.886
0.863
0.841

cx-3-200-h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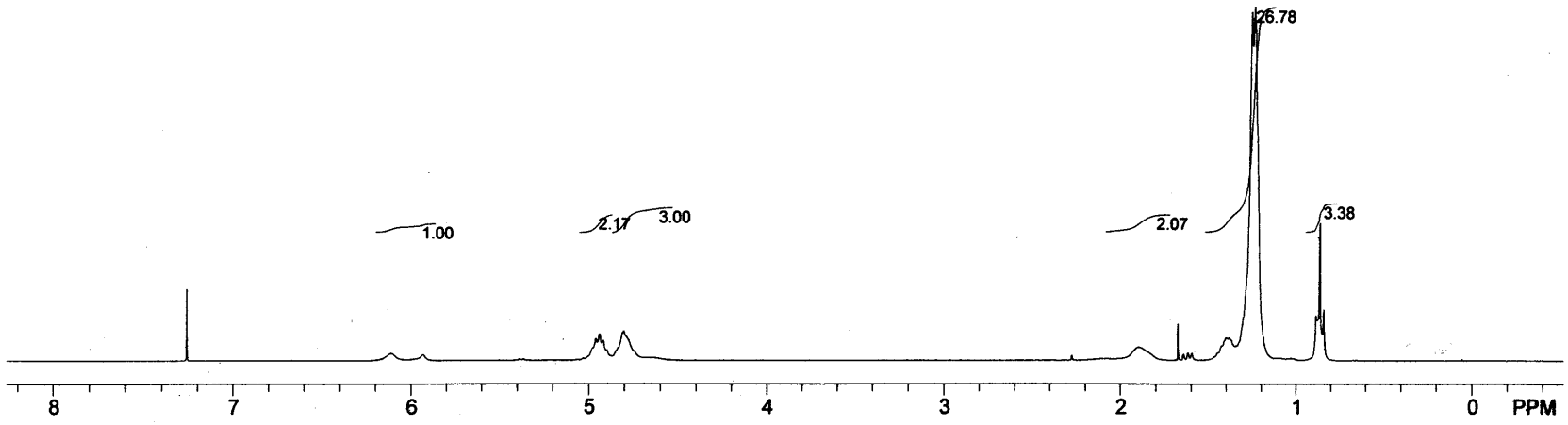
PriO2CHN–NCO2iPr

4b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6
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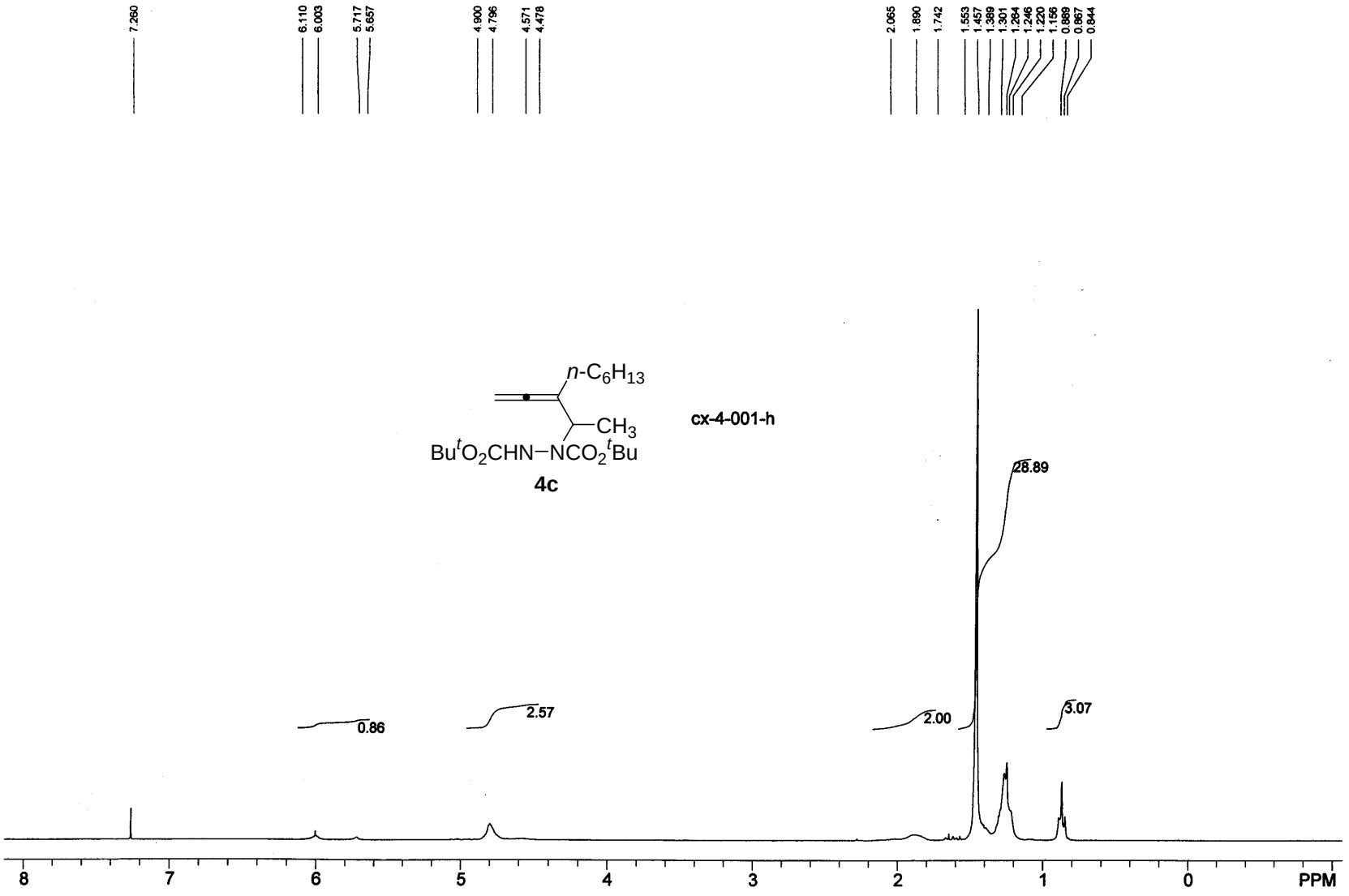
4
3
2
1
0
PPM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5.717
5.657
4.900
4.796
4.571
4.478
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1.742
1.553
1.457
1.389
1.301
1.264
1.246
1.220
1.156
0.889
0.867
0.844
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ButO2CHN−NCO2tBu
4c
cx-4-001-h
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3
2
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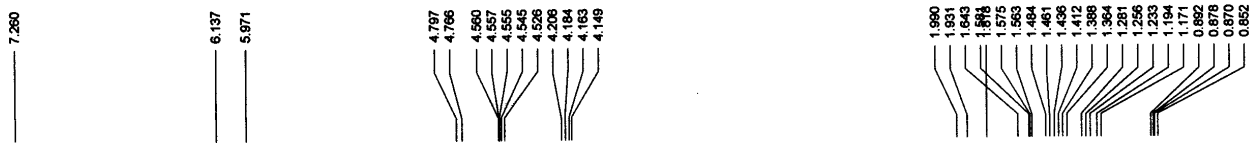
PPM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4.526
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4.163
4.149
1.990
1.931
1.643
1.575
1.563
1.484
1.461
1.436
1.412
1.388
1.364
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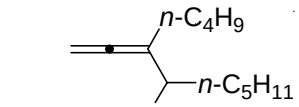
0.870
0.852

cx-4-005-h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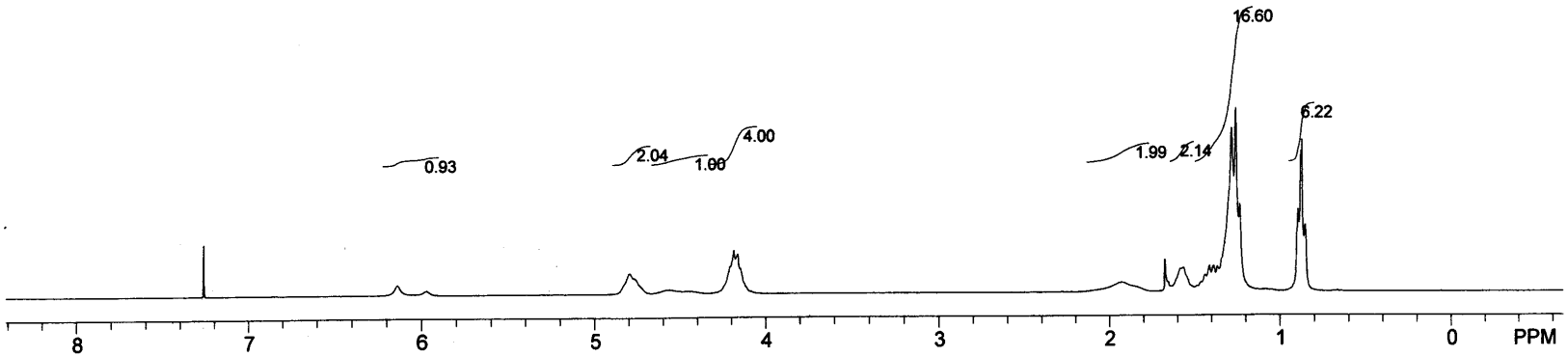
4d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4
3
2
1
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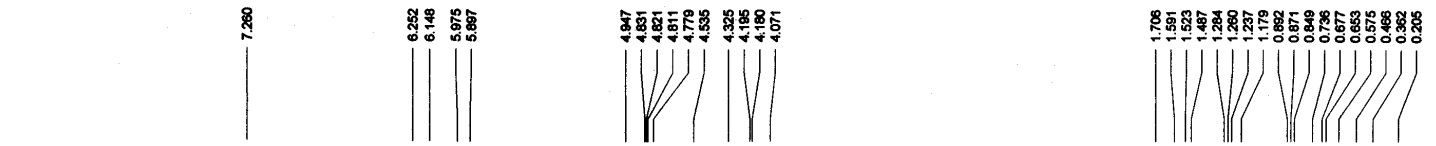
PPM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1.706
1.591
1.523
1.487
1.284
1.260
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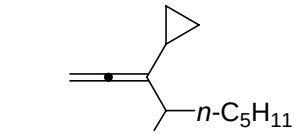
0.205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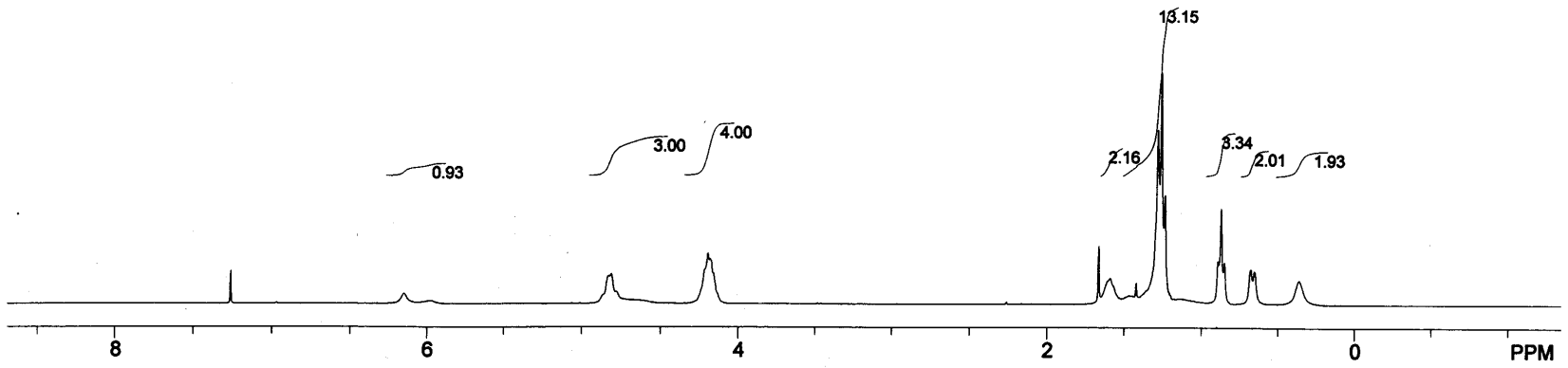
4e

cx-6-087-h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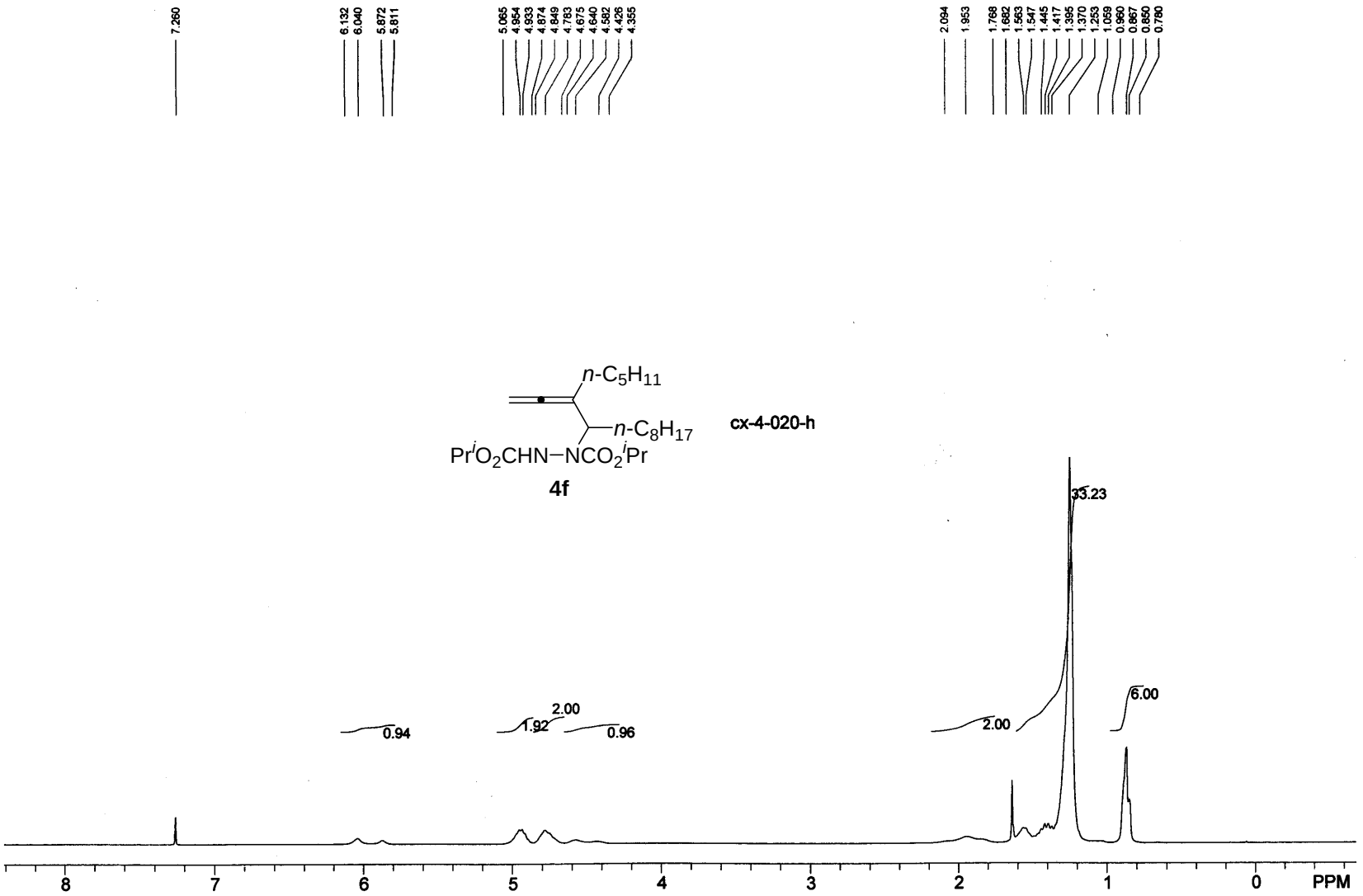
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2.094
1.953
1.768
1.682
1.563
1.547
1.445
1.417
1.395
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n-C8H17
PriO2CHN−NCO2iPr
4f
cx-4-020-h
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6
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2
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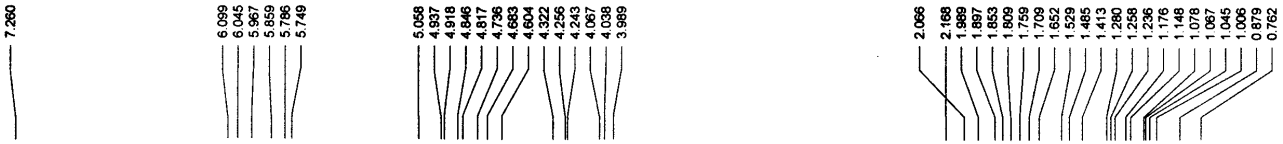
0
PPM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4.736
4.683
4.604
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4.256
4.243
4.067
4.038
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2.168
1.988
1.897
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1.709
1.652
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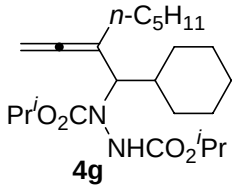
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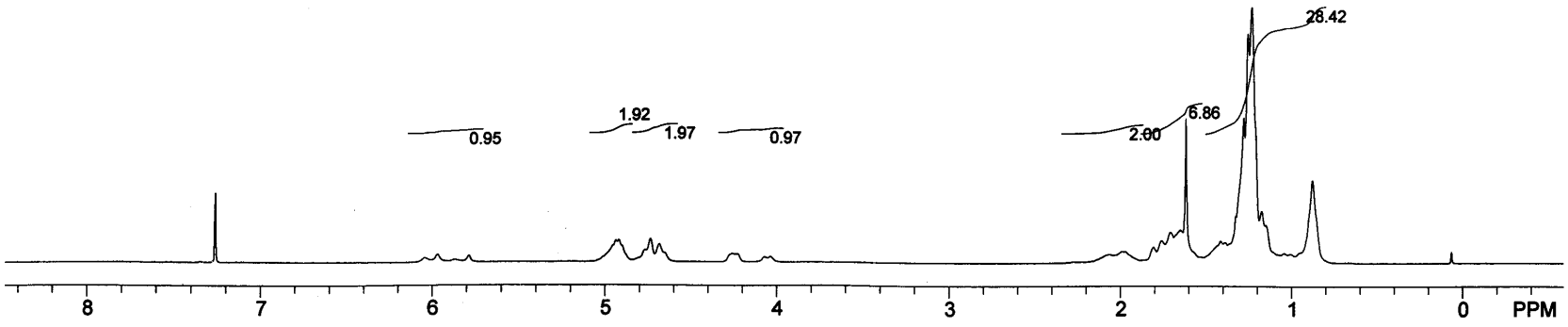
NHCO2iPr

4g

cx-4-021-h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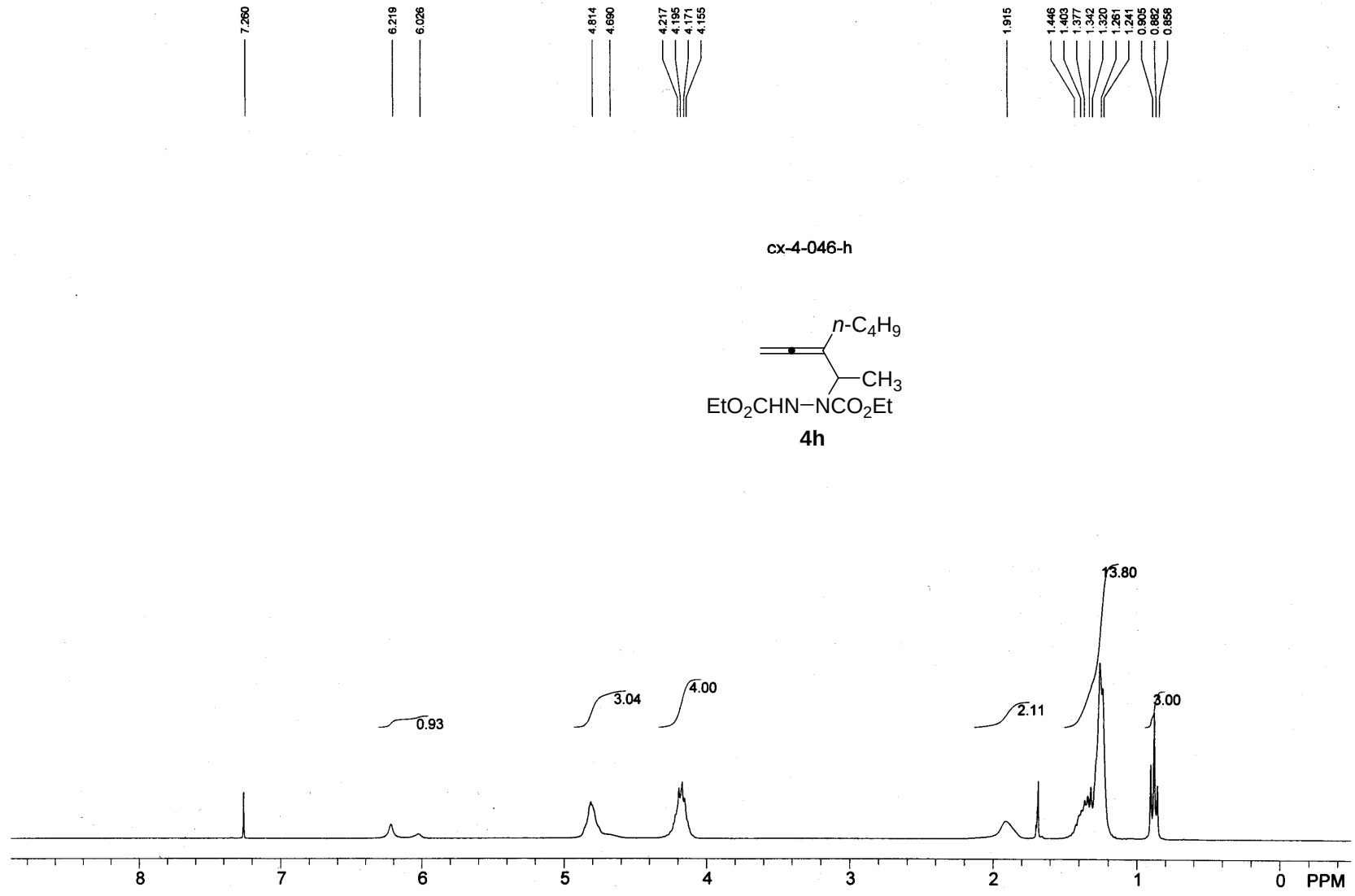
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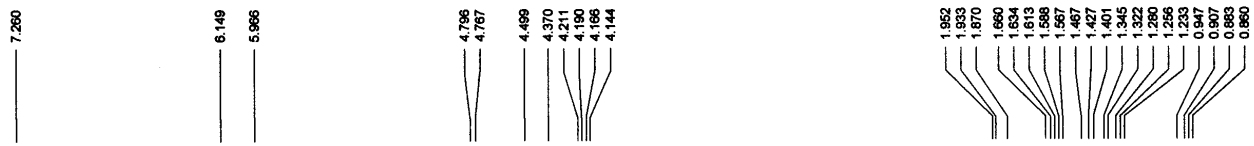
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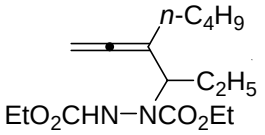
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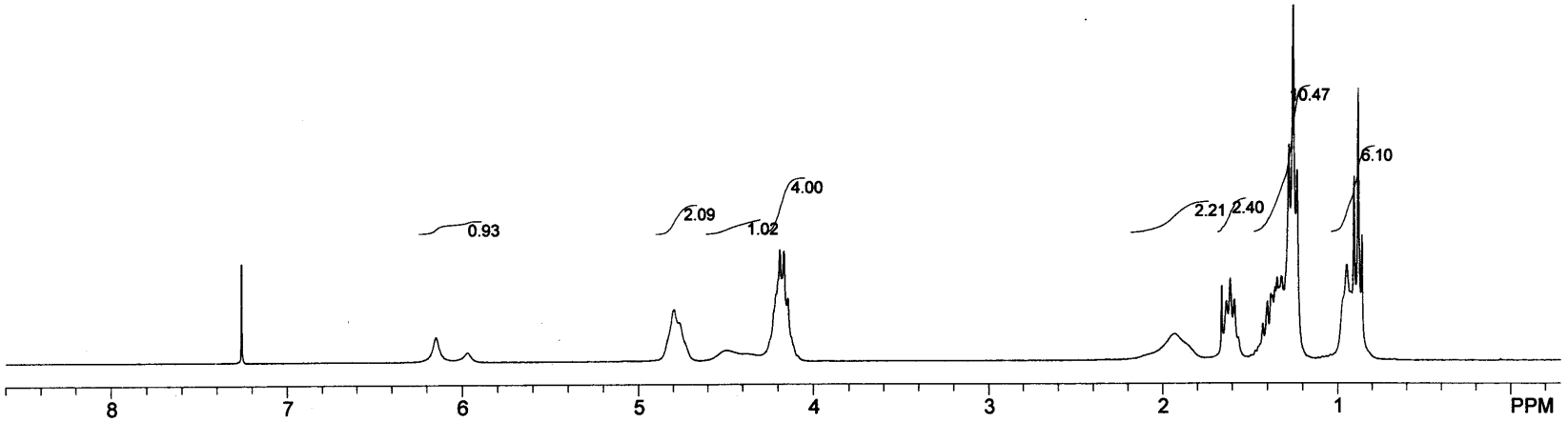
4i

cx-4-031-h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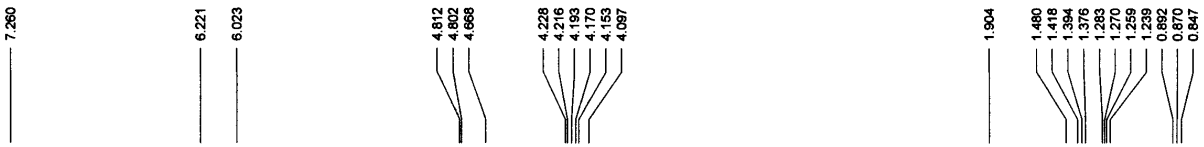
1
PPM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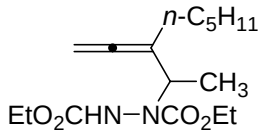
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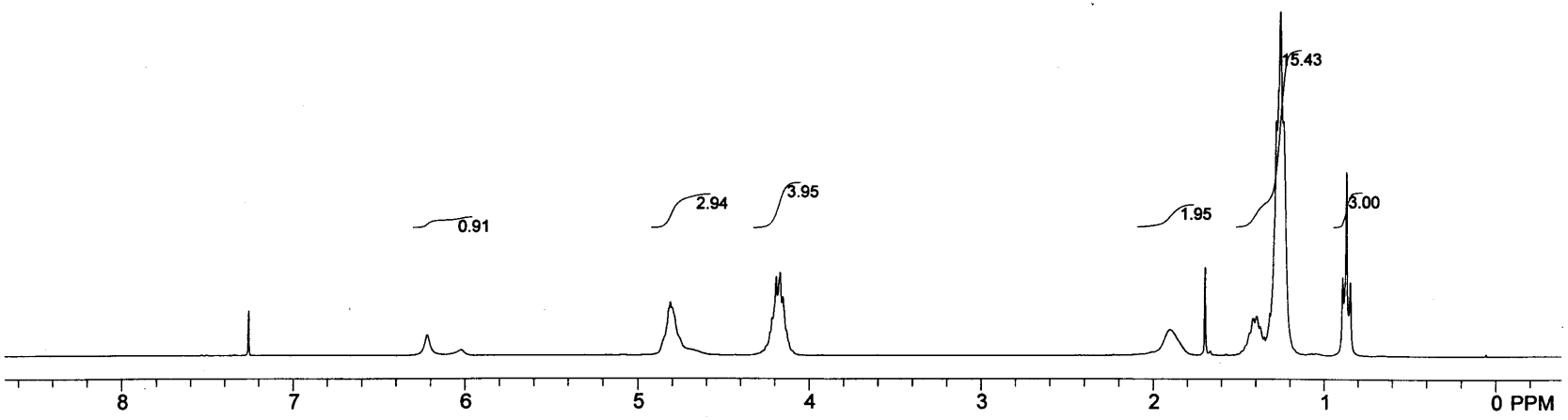
4j

cx-4-173-h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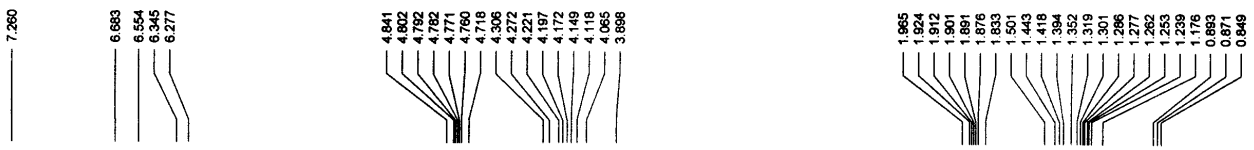
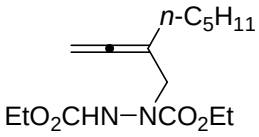
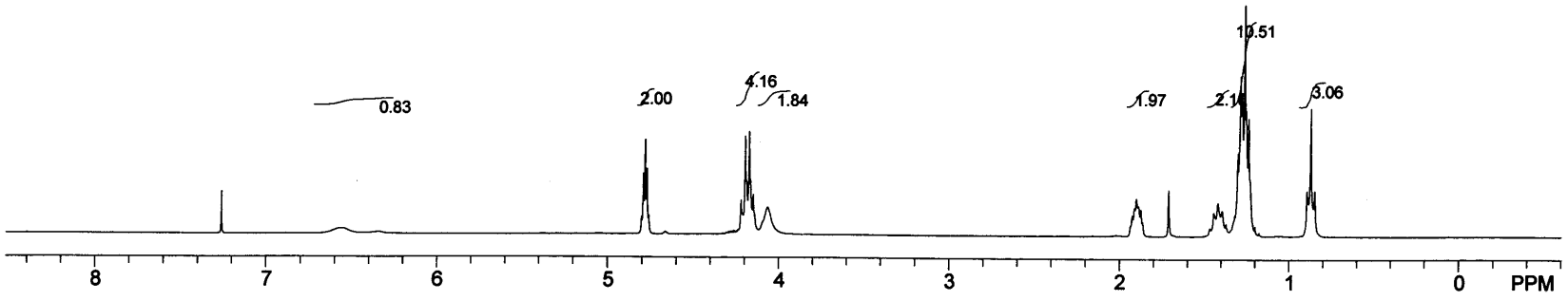
3
2
1
0 PPM

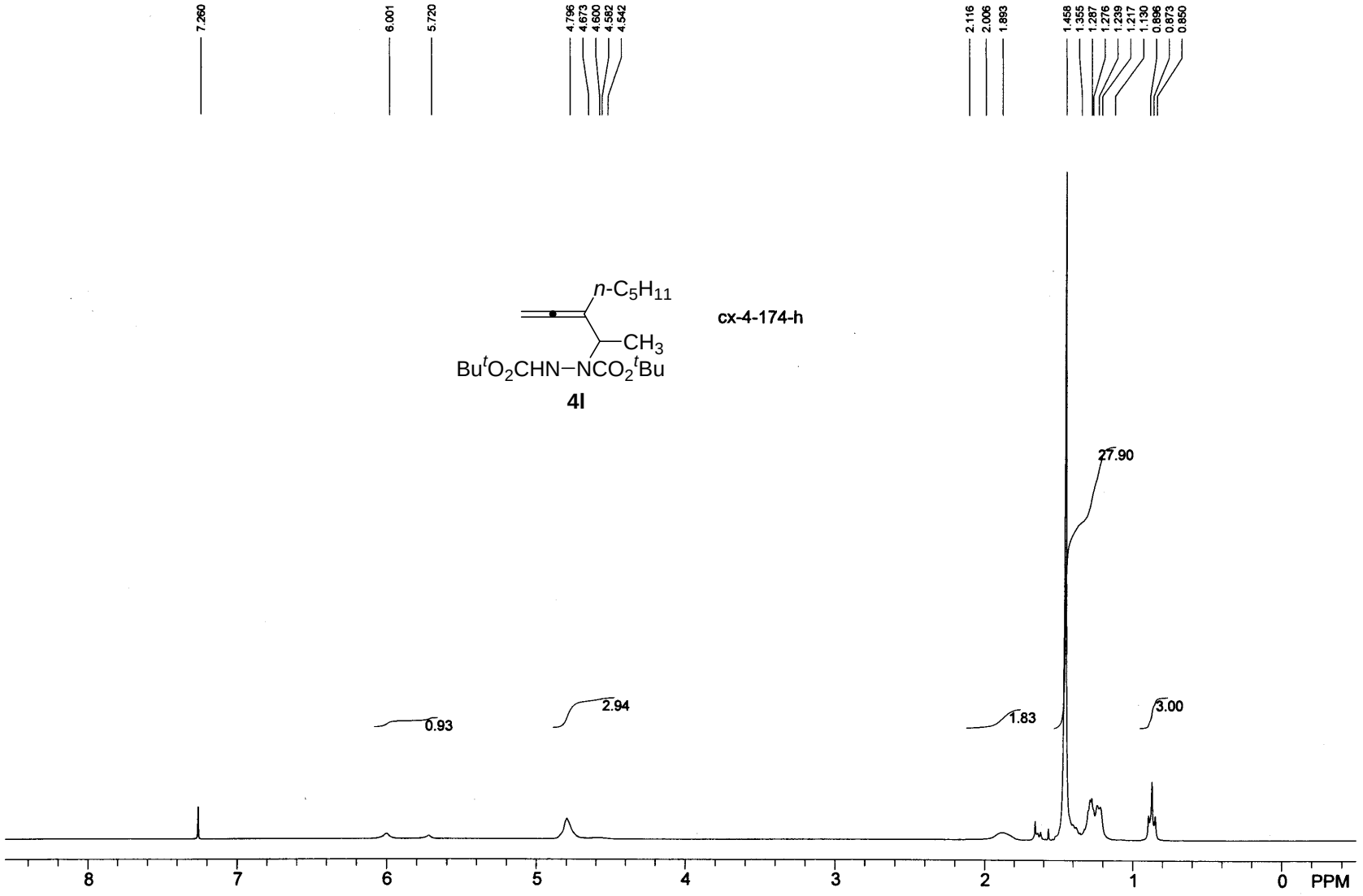

7.260
6.683
6.554
6.345
6.277
4.841
4.802
4.792
4.782
4.771
4.760
4.718
4.306
4.272
4.221
4.197
4.172
4.149
4.118
4.065
3.898
1.965
1.924
1.912
1.901
1.891
1.876
1.833
1.501
1.443
1.418
1.394
1.352
1.319
1.301
1.286
1.277
1.262
1.253
1.239
1.176
0.893
0.871
0.849

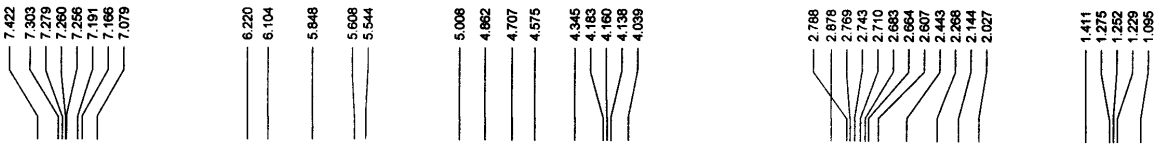

n-C5H11
EtO2CHN−NCO2Et

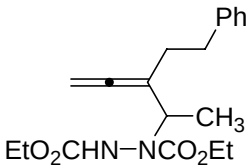
4k

cx-6-107-h


0.83
2.00
4.16
1.84
1.97
2.1
10.51
3.06
8
7
6
5
4
3
2
1
0
PPM

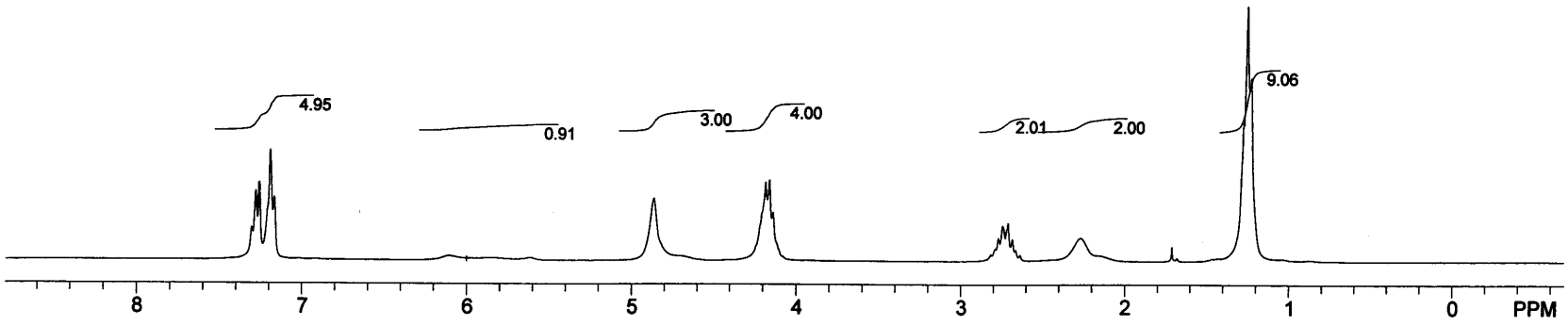

7.260
6.001
5.720
4.796
4.673
4.600
4.582
4.542
2.116
2.006
1.893
1.456
1.355
1.287
1.276
1.239
1.217
1.130
0.896
0.873
0.850
n-C5H11
CH3
ButO2CHN−NCO2tBu
4l
cx-4-174-h
27.90
0.93
2.94
1.83
3.00
8
7
6
5
4
3
2
1
0
PPM

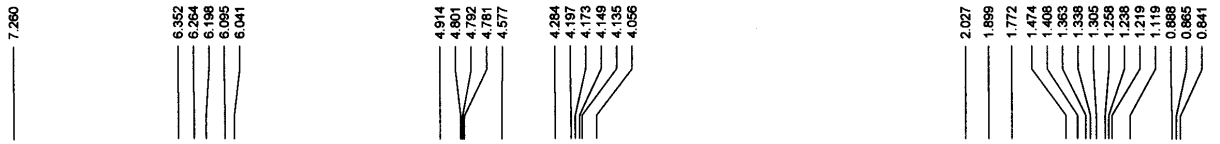

7.422
7.303
7.279
7.260
7.256
7.191
7.166
7.079
6.220
6.104
5.848
5.608
5.544
5.008
4.862
4.707
4.575
4.345
4.183
4.160
4.138
4.039
2.788
2.678
2.769
2.743
2.710
2.683
2.664
2.607
2.443
2.268
2.144
2.027
1.411
1.275
1.252
1.229
1.095


Ph
CH3
EtO2CHN–NCO2Et

4m

cx-6-020-h

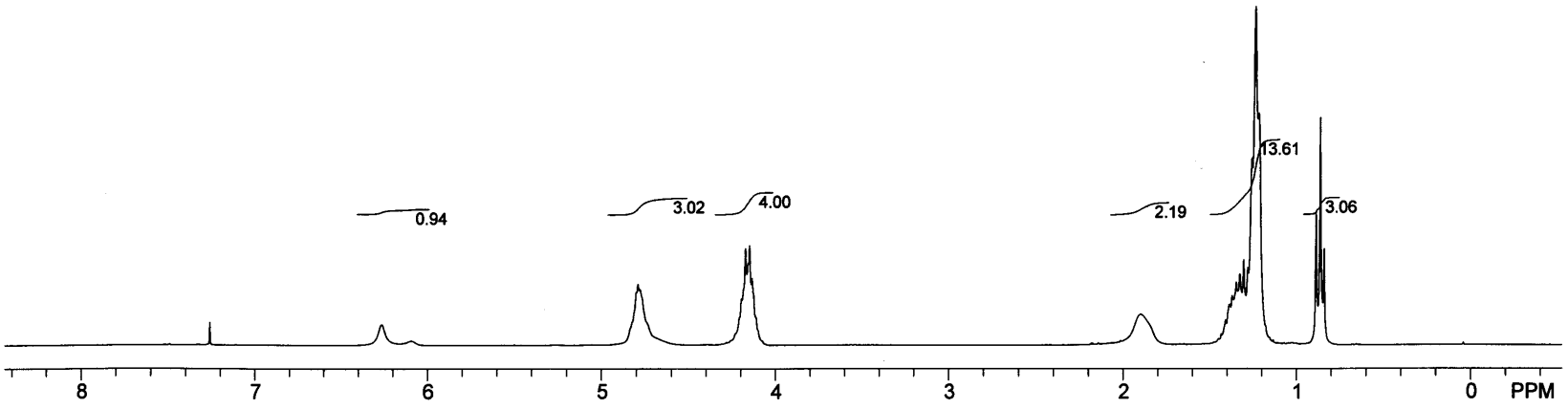

4.95
0.91
3.00
4.00
2.01
2.00
9.06
8
7
6
5
4
3
2
1
0
PPM

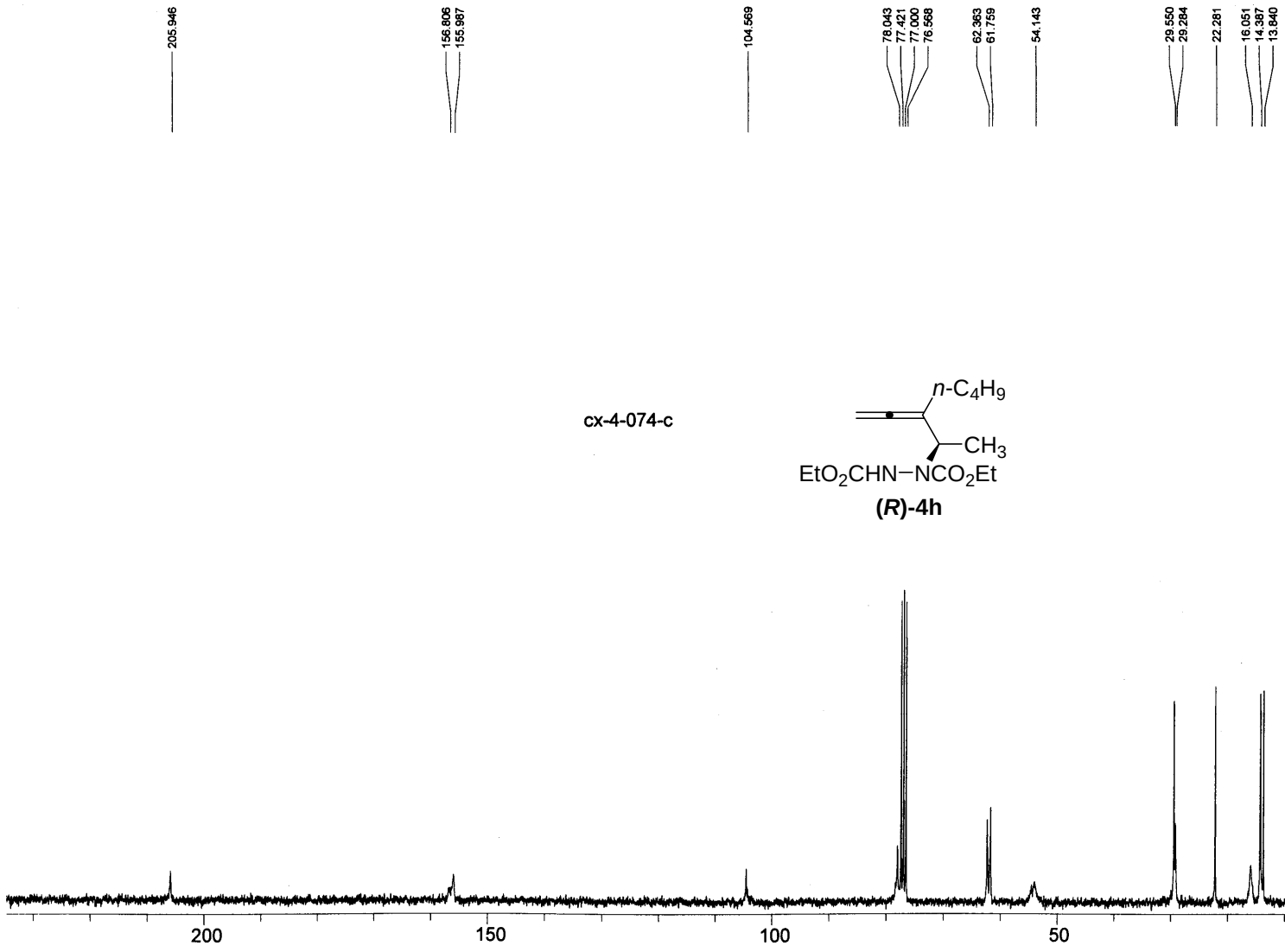

7.260
6.352
6.264
6.198
6.095
6.041
4.914
4.801
4.792
4.781
4.577
4.284
4.197
4.173
4.149
4.135
4.056
2.027
1.899
1.772
1.474
1.406
1.363
1.338
1.305
1.258
1.238
1.219
1.119
0.888
0.865
0.841


n-C4H9
CH3
EtO2CHN−NCO2Et

(*R*)-4h

cx-4-074-h


0.94
3.02
4.00
2.19
13.61
3.06
8
7
6
5
4
3
2
1
0
PPM


205.946
156.806
155.987
104.569
78.043
77.421
77.000
76.568
62.363
61.759
54.143
29.550
29.284
22.281
16.051
14.387
13.840
cx-4-074-c
n-C4H9
CH3
EtO2CHN−NCO2Et
(R)-4h
200
150
100
50
0
PPM

PERKIN–ELMER Polarimeter 341
Serial No. 7413

RESULTS TABLE Date: 12/09/2007 22:10:25

Operator: _____

Sample No.: 0001

Sample ID: _____

(*R*)-4h

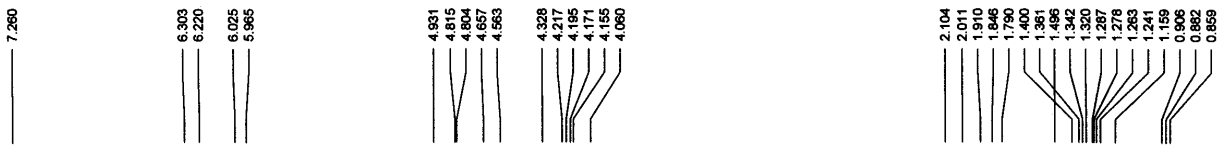
Sample Name: CX-4-074

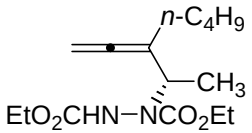
Comment: 18mg, c=0.9, $CHCl_3$

Integration Time: 5.0 s

Cell Path: 100.00 mm

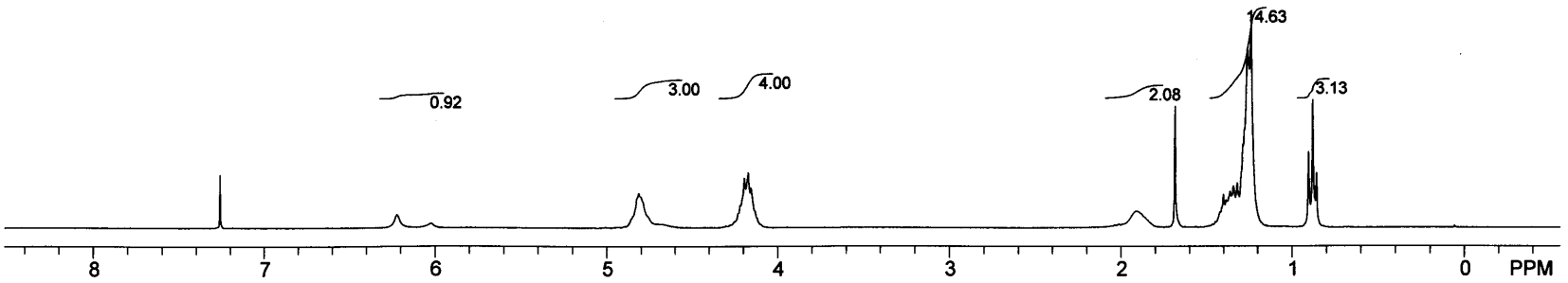
Sample	Wavelength	Temperature	Concentration	Rotation	Spec.Rotation	
0001	589 nm	20.0°C	0.90000	+0.764°	+84.9 °	
0002	589 nm	20.0°C	0.90000	+0.764°	+84.9 °	
0003	589 nm	20.0°C	0.90000	+0.764°	+84.9 °	+85.2
0004	589 nm	20.0°C	0.90000	+0.766°	+85.1 °	
0005	589 nm	20.0°C	0.90000	+0.768°	+85.4 °	
0006	589 nm	20.0°C	0.90000	+0.769°	+85.4 °	
0007	589 nm	20.0°C	0.90000	+0.768°	+85.4 °	
0008	589 nm	20.0°C	0.90000	+0.769°	+85.4 °	
0009	589 nm	20.0°C	0.90000	+0.769°	+85.4 °	
0010	589 nm	20.0°C	0.90000	+0.769°	+85.4 °	

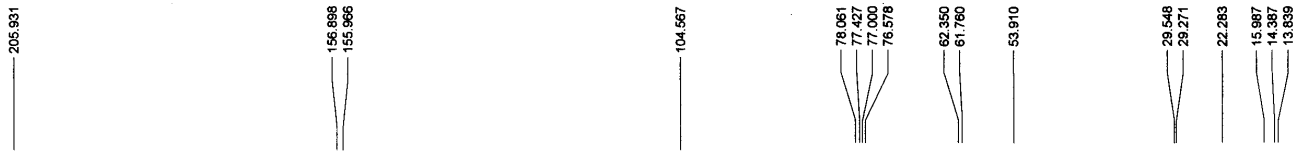

7.260
6.303
6.220
6.025
5.965
4.931
4.815
4.804
4.657
4.563
4.328
4.217
4.195
4.171
4.155
4.060
2.104
2.011
1.910
1.846
1.790
1.400
1.361
1.496
1.342
1.320
1.287
1.278
1.263
1.241
1.159
0.906
0.882
0.859


n-C4H9
CH3
EtO2CHN–NCO2Et

(*S*)-4h

cx-4-075-h

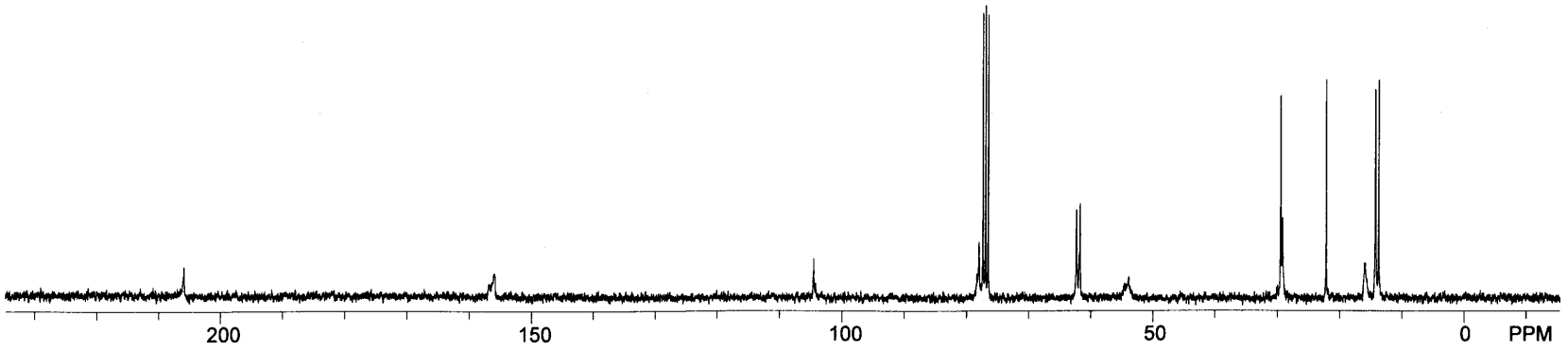

0.92
3.00
4.00
2.08
14.63
3.13
8
7
6
5
4
3
2
1
0
PPM

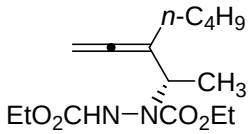

205.931
156.898
155.966
104.567
78.061
77.427
77.000
76.578
62.350
61.760
53.910
29.548
29.271
22.283
15.987
14.387
13.839

cx-4-075-c


n-C4H9
CH3
EtO2CHN–NCO2Et

(*S*)-4h


200
150
100
50
0
PPM



(*S*)-4h

PERKIN–ELMER Polarimeter 341
Serial No. 7413

RESULTS TABLE Date: 12/09/2007 22:32:52

Operator: _____

Sample No.: 0001

Sample ID: _____

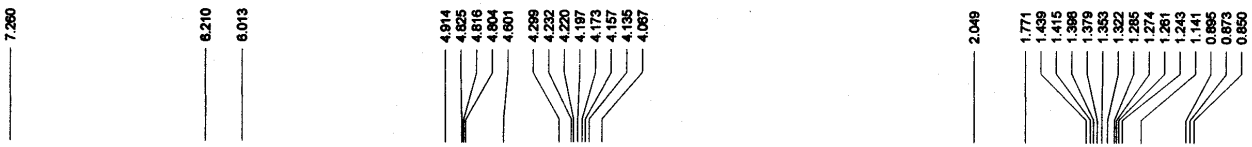
Sample Name: CX-4-075

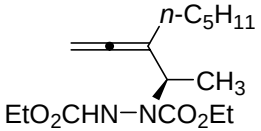
Comment: 10 mg, c = 0.5, $CHCl_3$

Integration Time: 5.0 s

Cell Path: 100.00 mm

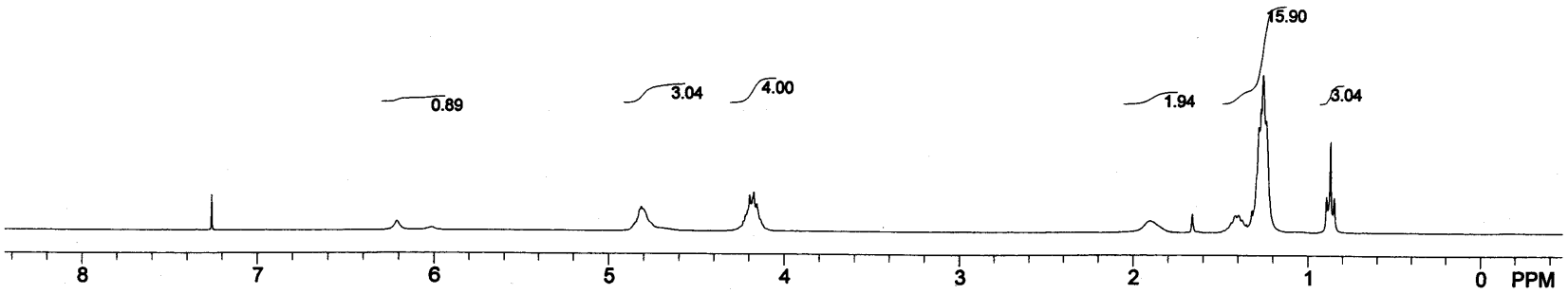
Sample	Wavelength	Temperature	Concentration	Rotation	Spec.Rotation	
0001	589 nm	20.0°C	0.50000	-0.369°	-73.7 °	
0002	589 nm	20.0°C	0.50000	-0.373°	-74.5 °	
0003	589 nm	20.0°C	0.50000	-0.371°	-74.2 °	-74.2
0004	589 nm	20.0°C	0.50000	-0.370°	-74.0 °	
0005	589 nm	20.0°C	0.50000	-0.369°	-73.8 °	
0006	589 nm	20.0°C	0.50000	-0.372°	-74.3 °	
0007	589 nm	20.0°C	0.50000	-0.366°	-73.2 °	
0008	589 nm	20.0°C	0.50000	-0.371°	-74.1 °	
0009	589 nm	20.0°C	0.50000	-0.375°	-75.1 °	
0010	589 nm	20.0°C	0.50000	-0.374°	-74.8 °	

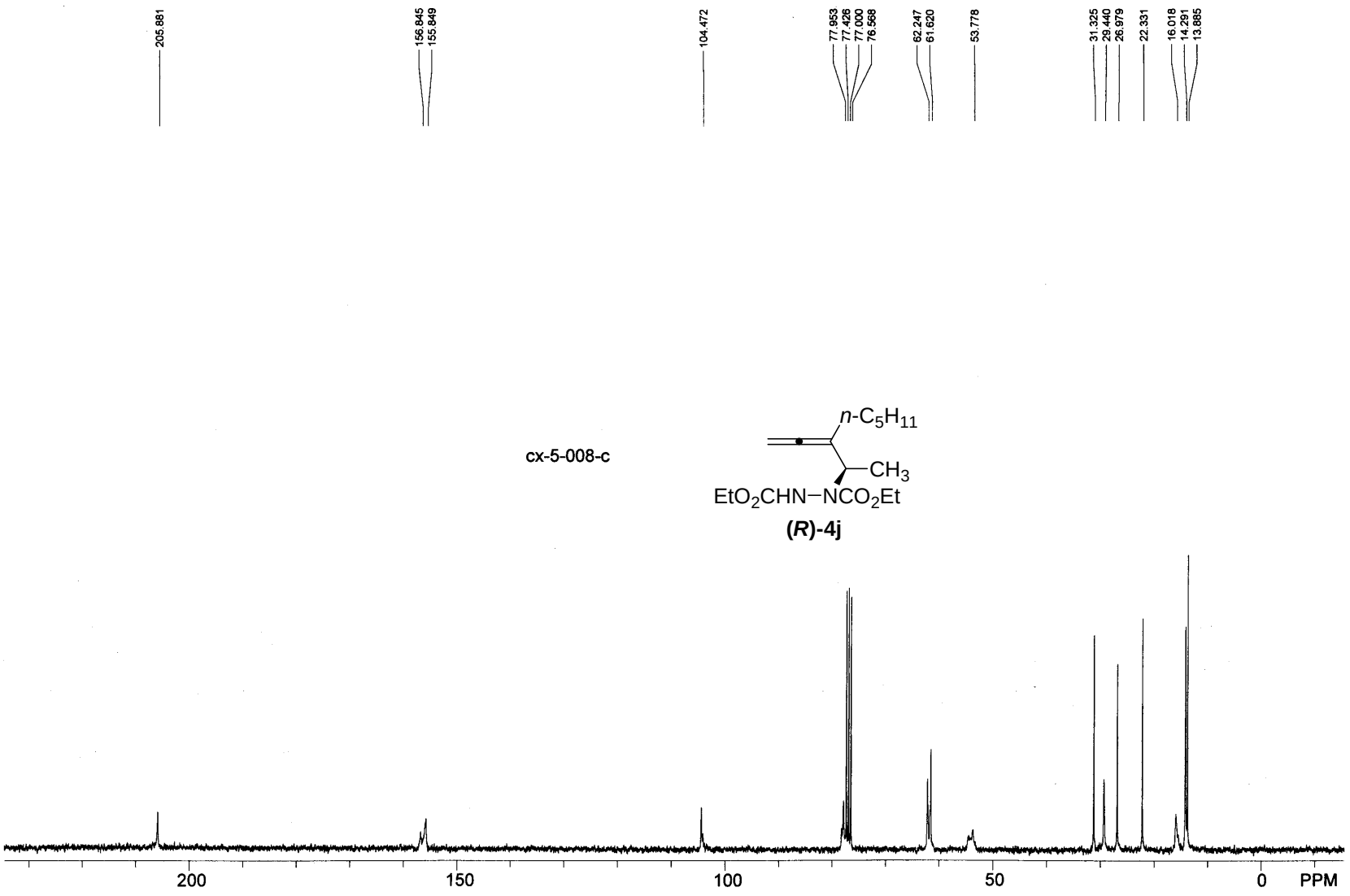

7.260
8.210
8.013
4.914
4.825
4.816
4.804
4.801
4.299
4.232
4.220
4.197
4.173
4.157
4.135
4.087
2.049
1.771
1.439
1.415
1.398
1.379
1.353
1.322
1.285
1.274
1.261
1.243
1.141
0.895
0.873
0.850


n-C5H11
CH3
EtO2CHN−NCO2Et

(*R*)-4j

cx-5-008-h


0.89
3.04
4.00
1.94
15.90
3.04
8
7
6
5
4
3
2
1
0
PPM


205.881
156.845
155.849
104.472
77.953
77.426
77.000
76.568
62.247
61.620
53.778
31.325
29.440
26.979
22.331
16.018
14.291
13.885
cx-5-008-c
n-C5H11
CH3
EtO2CHN−NCO2Et
(R)-4j
200
150
100
50
0
PPM

PERKIN–ELMER

Polarimeter 341
Serial No. 7413

Date: 12/09/2007 23:24:55

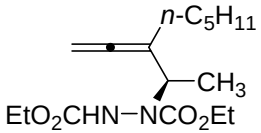
Operator: _____

Sample#1

Sample ID: _____

Sample Name: CX-5-008

Comment: 13mg, c=0.65, CHCl3



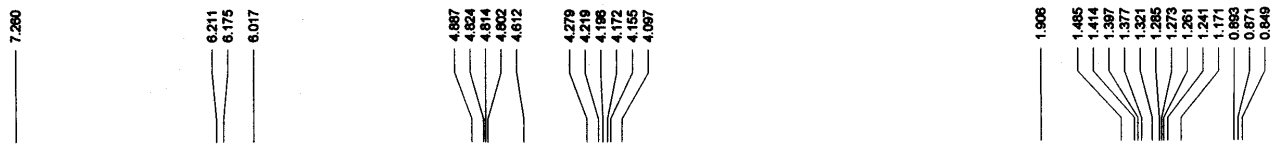
(*R*)-4j

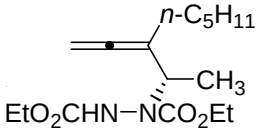
Integration Time: 5.0 s

Cell Path: 100.00 mm

Sample	Wavelength	Temperature	Concentration	Rotation	Spec.Rotation
0001	589 nm	20.0°C	0.65000	+0.627°	+96.5 °
0002	589 nm	20.0°C	0.65000	+0.629°	+96.8 °
0003	589 nm	20.0°C	0.65000	+0.629°	+96.7 °
0004	589 nm	20.0°C	0.65000	+0.627°	+96.5 °
0005	589 nm	20.0°C	0.65000	+0.627°	+96.5 °
0006	589 nm	20.0°C	0.65000	+0.625°	+96.2 °
0007	589 nm	20.0°C	0.65000	+0.625°	+96.2 °
0008	589 nm	20.0°C	0.65000	+0.628°	+96.7 °
0009	589 nm	20.0°C	0.65000	+0.627°	+96.4 °
0010	589 nm	20.0°C	0.65000	+0.626°	+96.3 °

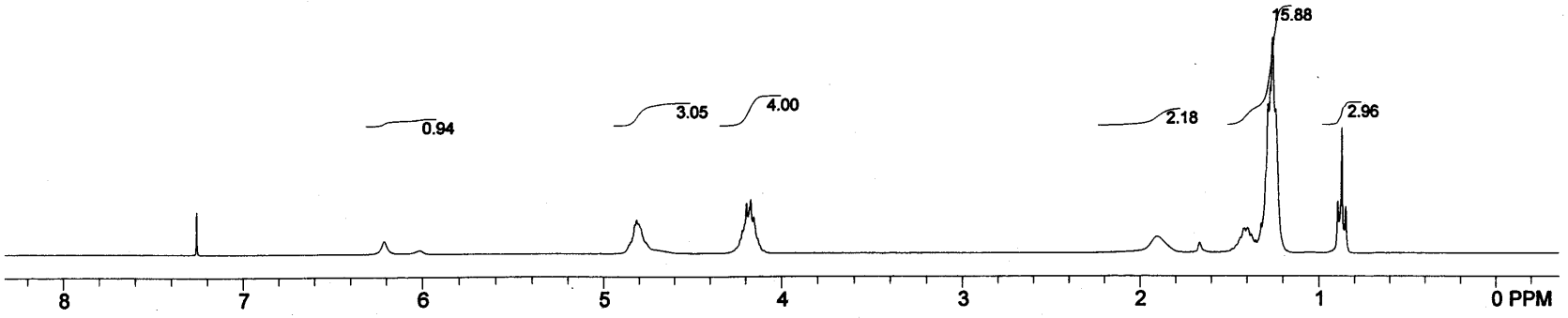
+96.5

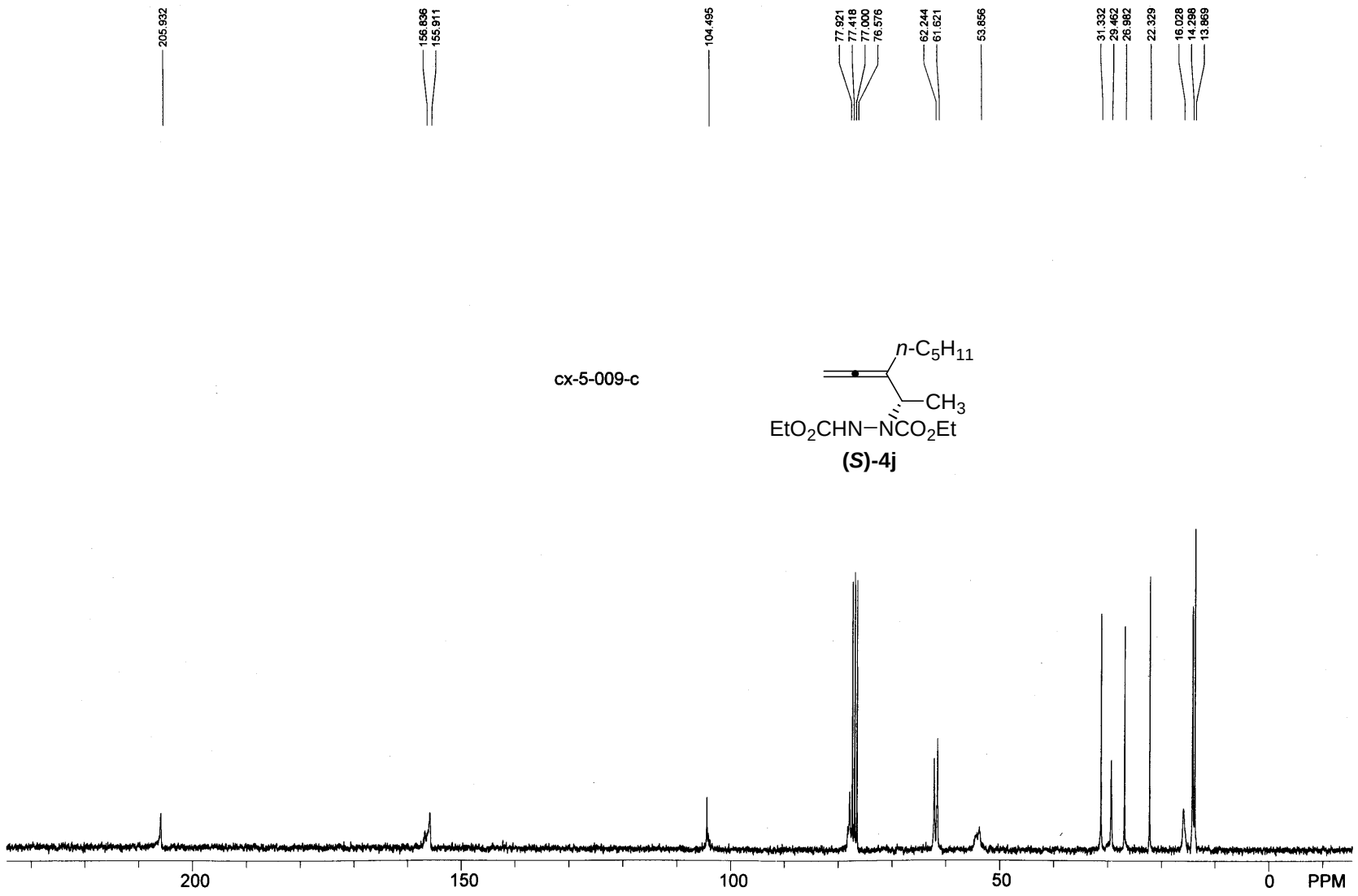

7.280
6.211
6.175
6.017
4.887
4.824
4.814
4.802
4.612
4.279
4.219
4.198
4.172
4.155
4.097
1.906
1.485
1.414
1.397
1.377
1.321
1.285
1.273
1.261
1.241
1.171
0.893
0.871
0.849


n-C5H11
CH3
EtO2CHN−NCO2Et

(*S*)-4j

cx-5-009-h


15.88
0.94
3.05
4.00
2.18
2.96
8
7
6
5
4
3
2
1
0 PPM


205.932
156.836
155.911
104.495
77.921
77.418
77.000
76.576
62.244
61.621
53.856
31.332
29.462
26.982
22.329
16.028
14.298
13.869
cx-5-009-c
n-C5H11
CH3
EtO2CHN−NCO2Et
(S)-4j
200
150
100
50
0
PPM

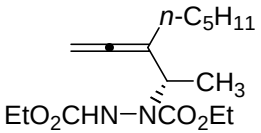
PERKIN–ELMER Polarimeter 341
Serial No. 7413

RESULTS TABLE Date: 12/10/2007 00:29:20

Operator: _____

Sample No.: 01

Sample ID: __



(*S*)-4j

Sample Name: CX-5-009

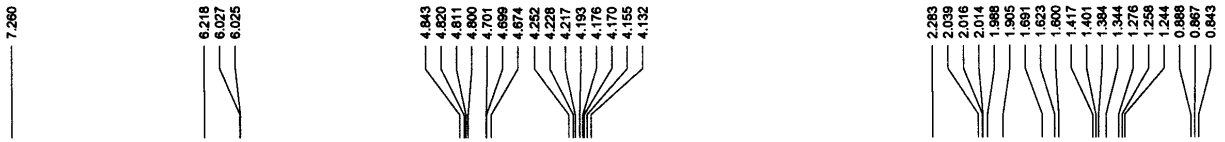
Comment: 15mg 5=0.75, CHCl3

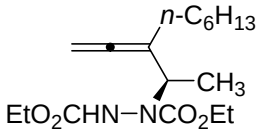
Integration Time: 5.0 s

Cell Path: 100.00 mm

Sample	Wavelength	Temperature	Concentration	Rotation	Spec.Rotation
0001	589 nm	20.0°C	0.75000	-0.691°	-92.2 °
0002	589 nm	20.0°C	0.75000	-0.690°	-92.0 °
0003	589 nm	20.0°C	0.75000	-0.690°	-92.0 °
0004	589 nm	20.0°C	0.75000	-0.690°	-91.9 °
0005	589 nm	20.0°C	0.75000	-0.690°	-91.9 °
0006	589 nm	20.0°C	0.75000	-0.690°	-91.9 °
0007	589 nm	20.0°C	0.75000	-0.690°	-92.0 °
0008	589 nm	20.0°C	0.75000	-0.690°	-92.0 °
0009	589 nm	20.0°C	0.75000	-0.689°	-91.9 °
0010	589 nm	20.0°C	0.75000	-0.690°	-91.9 °

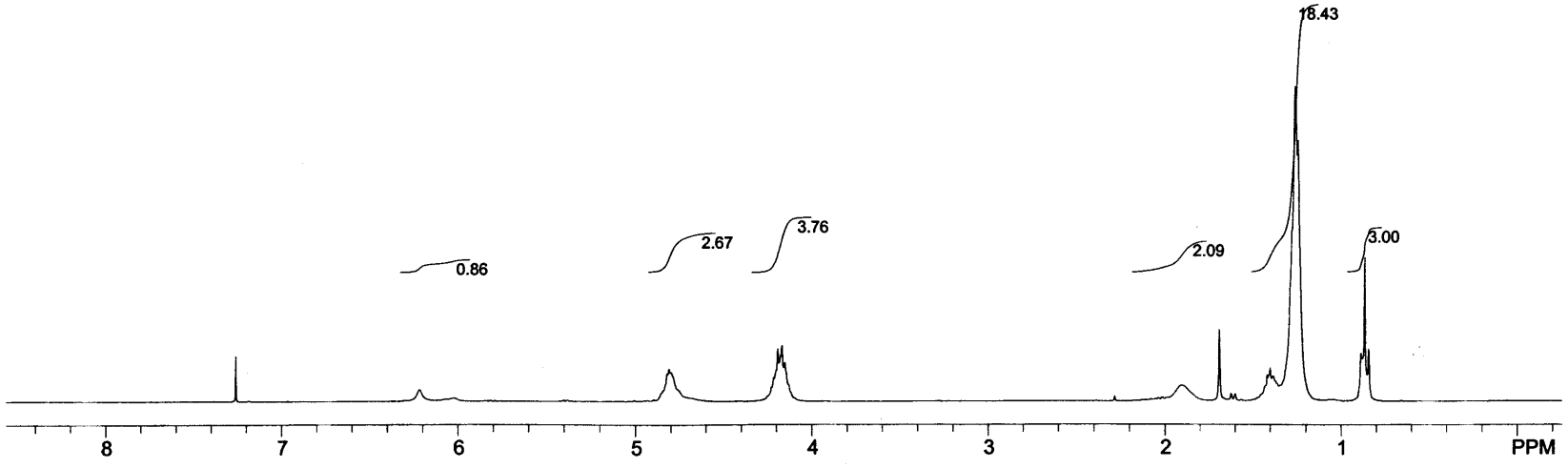
-92.0

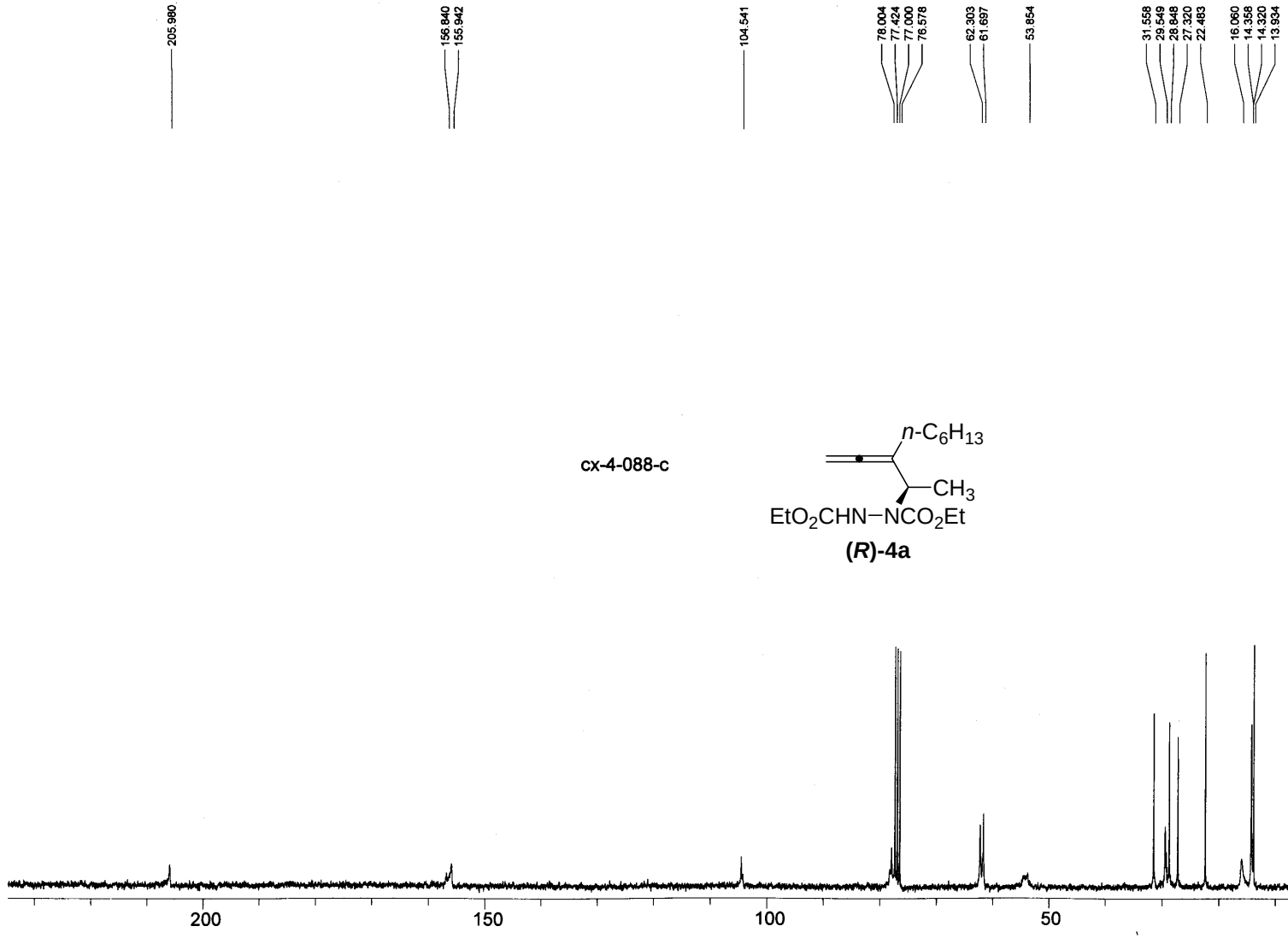

7.260
6.218
6.027
6.025
4.843
4.820
4.811
4.800
4.701
4.699
4.674
4.252
4.228
4.217
4.193
4.176
4.170
4.155
4.132
2.283
2.039
2.016
2.014
1.988
1.905
1.691
1.623
1.600
1.417
1.401
1.384
1.344
1.276
1.258
1.244
0.888
0.867
0.843


n-C6H13
CH3
EtO2CHN–NCO2Et

(*R*)-4a

cx-4-088-h


18.43
0.86
2.67
3.76
2.09
3.00
8
7
6
5
4
3
2
1
PPM


205.980
156.840
155.942
104.541
78.004
77.424
77.000
76.578
62.303
61.697
53.854
31.558
29.549
28.848
27.320
22.483
16.060
14.358
14.320
13.934
cx-4-088-c
n-C6H13
CH3
EtO2CHN−NCO2Et
(R)-4a
200
150
100
50
0
PPM

PERKIN–ELMER

Polarimeter 341
Serial No. 7413

RESULTS TABLE

Date: 12/09/2007 22:54:45

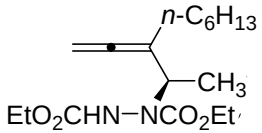
Operator: _____

Sample No.: 0001

Sample ID: _____

Sample Name: CX-4-088

Comment: 17 mg, c=0.85, CHCl3



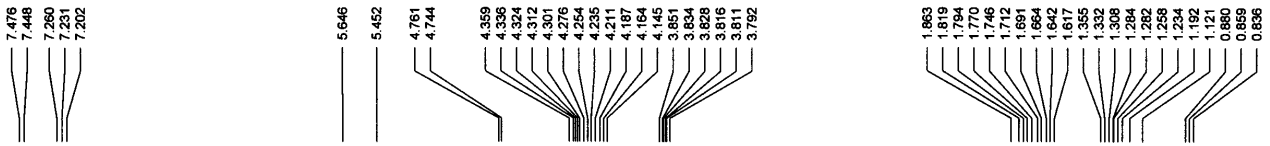
(*R*)-4a

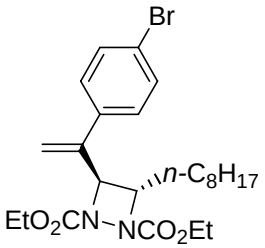
Integration Time: 5.0 s

Cell Path: 100.00 mm

Sample	Wavelength	Temperature	Concentration	Rotation	Spec.Rotation
0001	589 nm	20.0°C	0.85000	+0.598°	+70.3 °
0002	589 nm	20.0°C	0.85000	+0.593°	+69.8 °
0003	589 nm	20.0°C	0.85000	+0.595°	+70.0 °
0004	589 nm	20.0°C	0.85000	+0.593°	+69.8 °
0005	589 nm	20.0°C	0.85000	+0.593°	+69.8 °
0006	589 nm	20.0°C	0.85000	+0.593°	+69.8 °
0007	589 nm	20.0°C	0.85000	+0.594°	+69.9 °
0008	589 nm	20.0°C	0.85000	+0.594°	+69.9 °
0009	589 nm	20.0°C	0.85000	+0.596°	+70.1 °
0010	589 nm	20.0°C	0.85000	+0.586°	+69.0 °

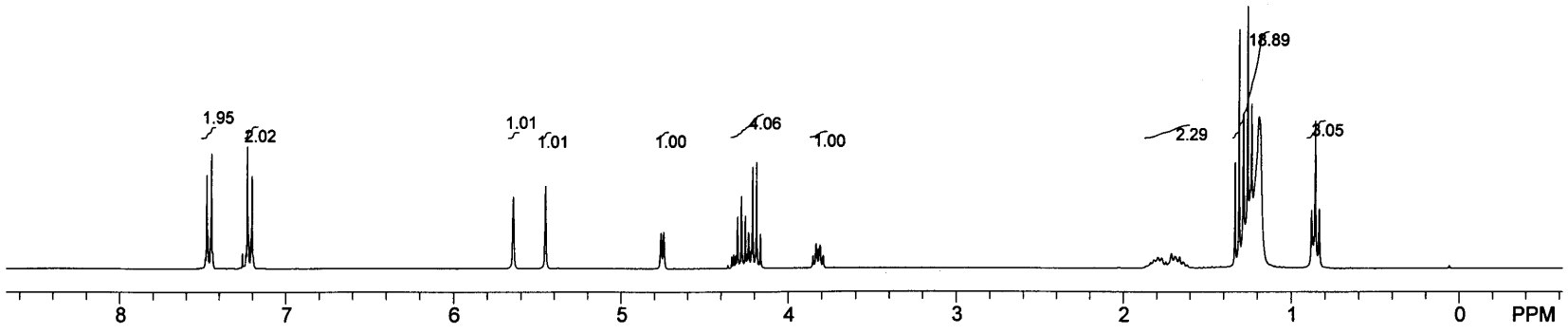
+69.8

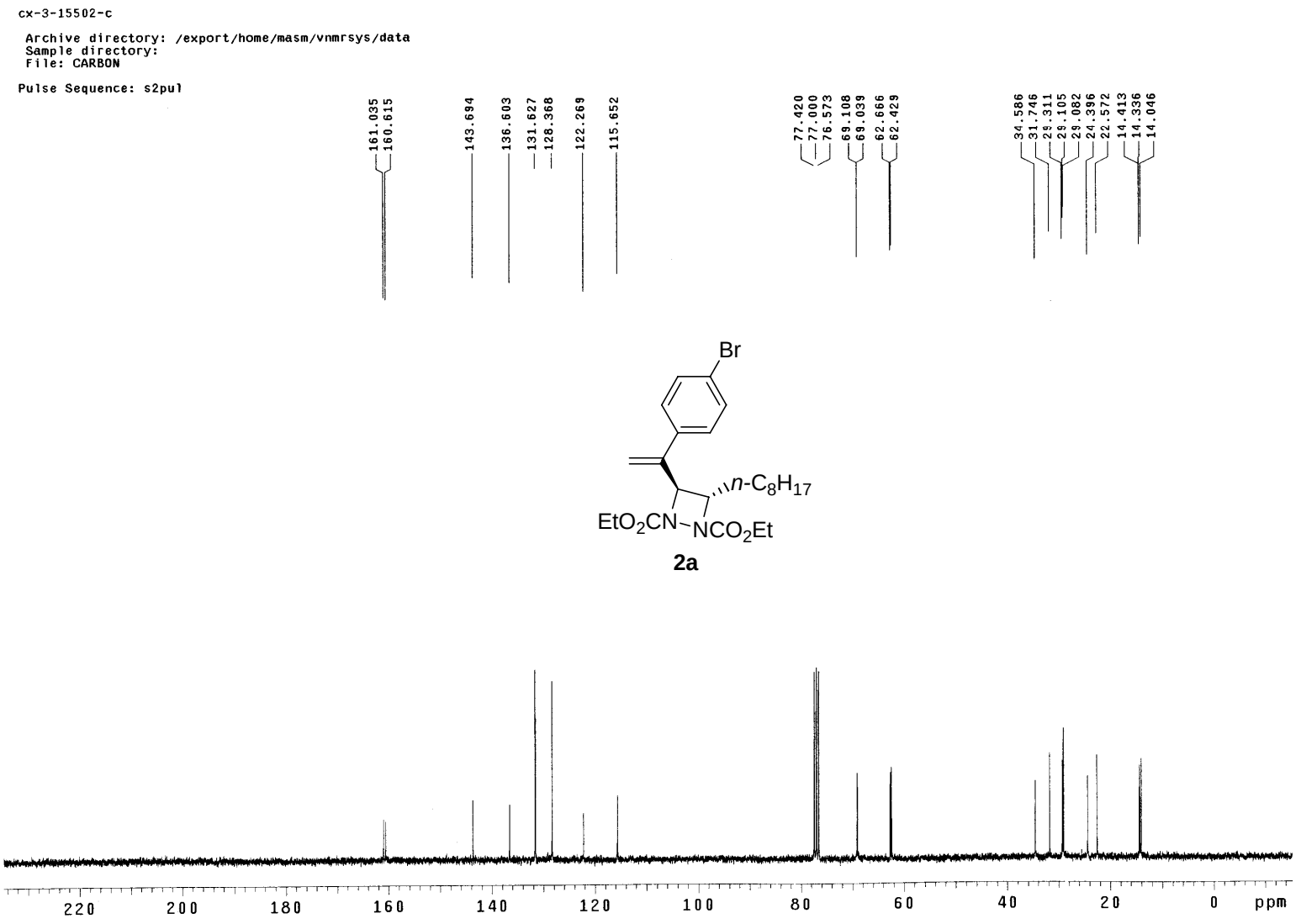


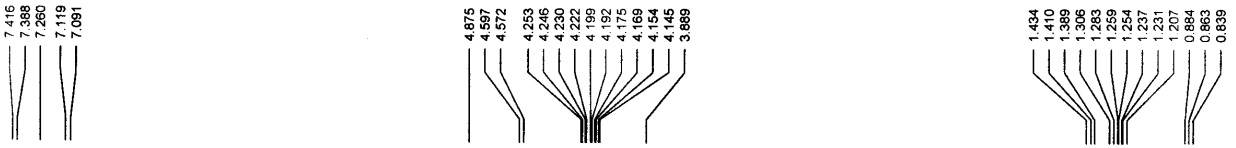


2a

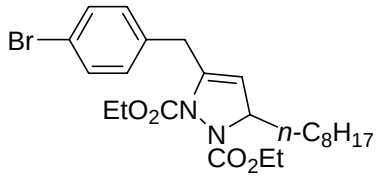
cx-3-15502-h



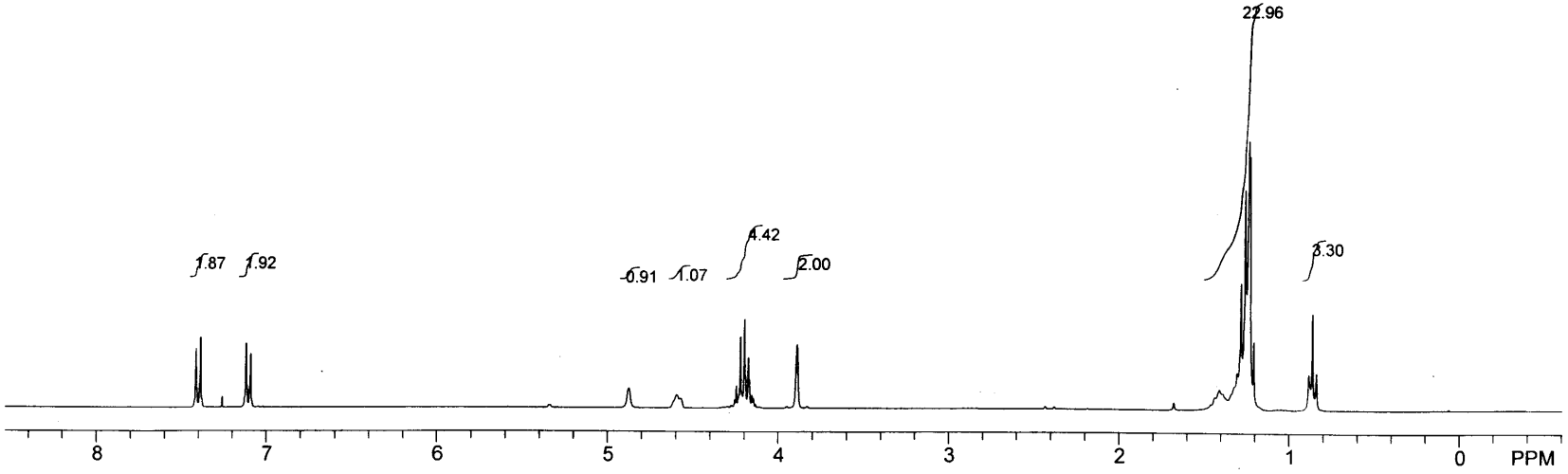

cx-3-15502-c
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
161.035
160.615
143.694
136.603
131.627
128.368
122.269
115.652
77.420
77.000
76.573
69.108
68.039
62.666
62.429
34.586
31.746
29.311
29.105
29.082
24.396
22.572
14.413
14.336
14.046
Br
n-C8H17
EtO2CN
NCO2Et
2a
220
200
180
160
140
120
100
80
60
40
20
0
ppm

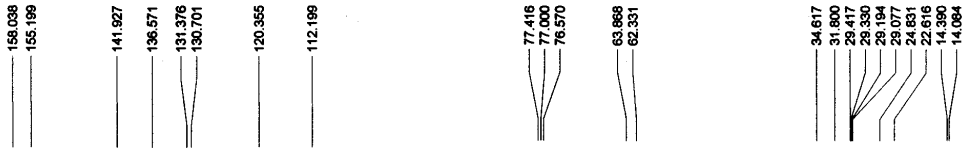


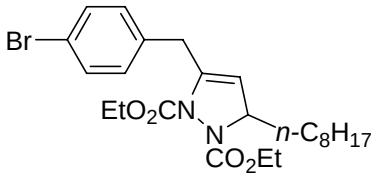
cx-3-15501-h



3a

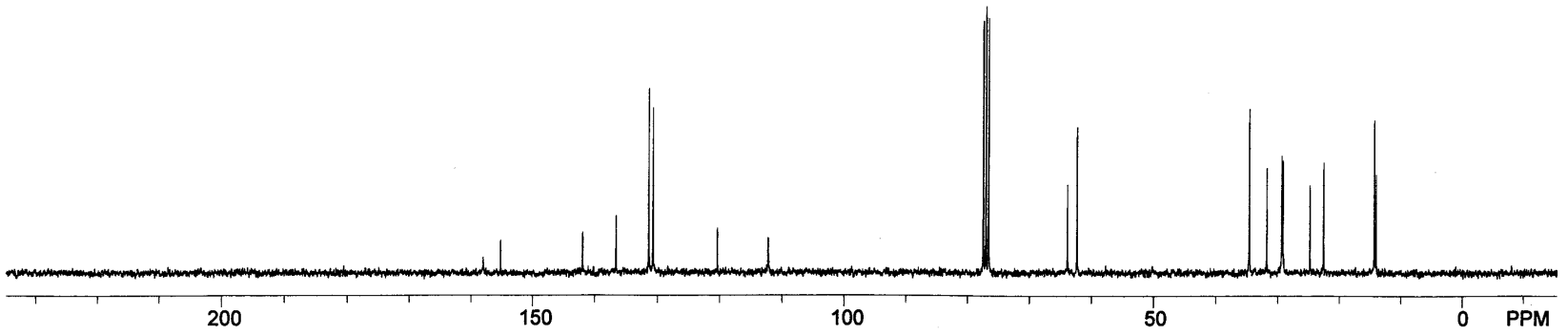


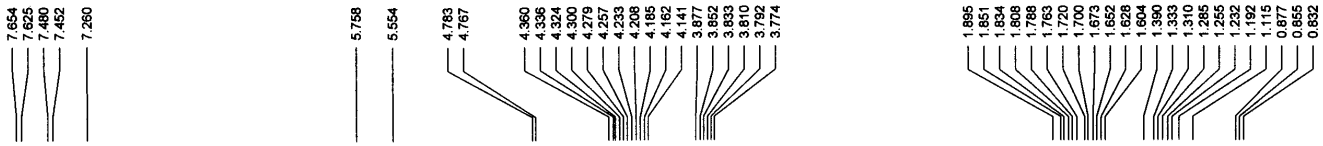


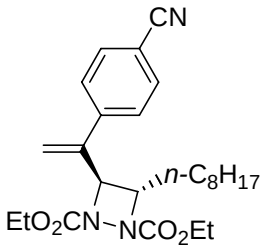


3a

cx-3-15501-c

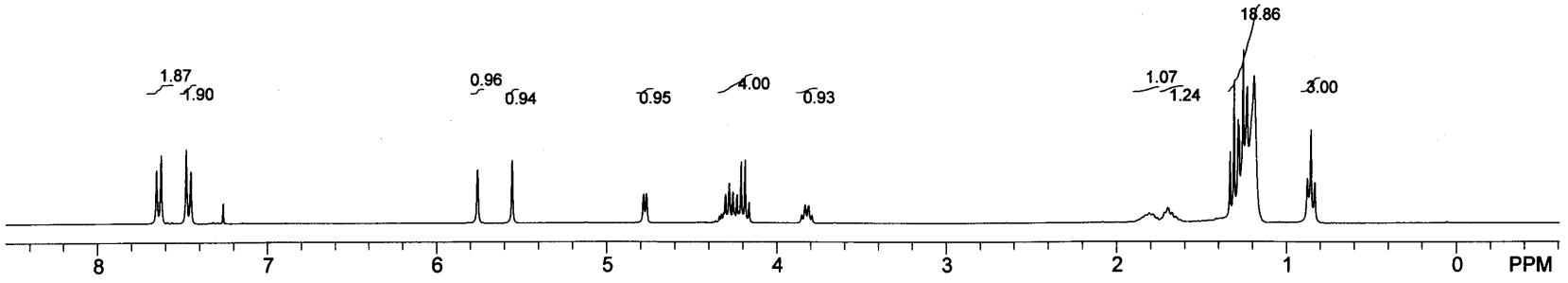




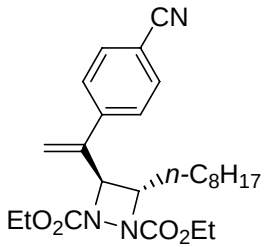


2b

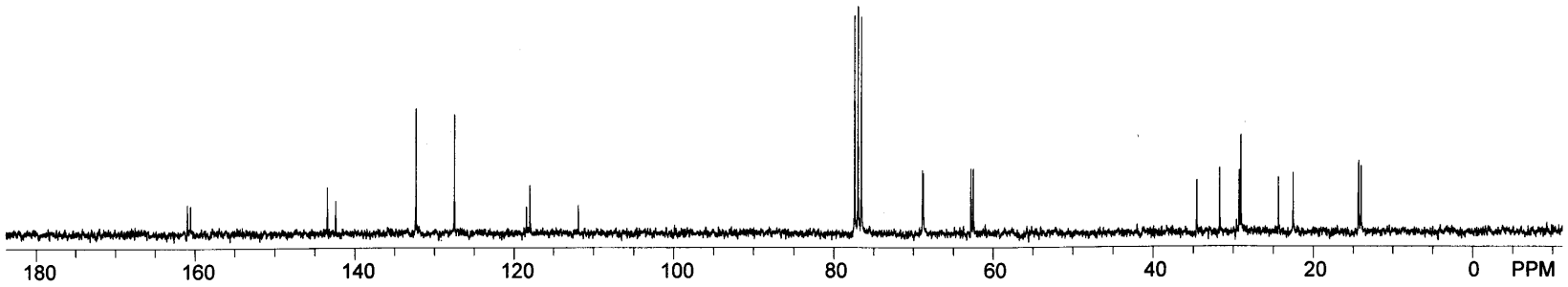
cx-6-11802-h

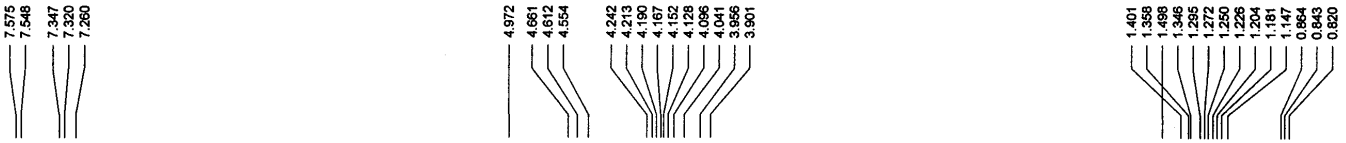


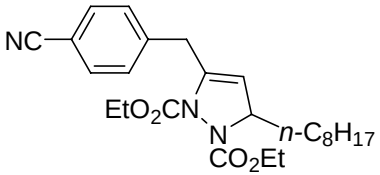
cx-6-11802-c



2b

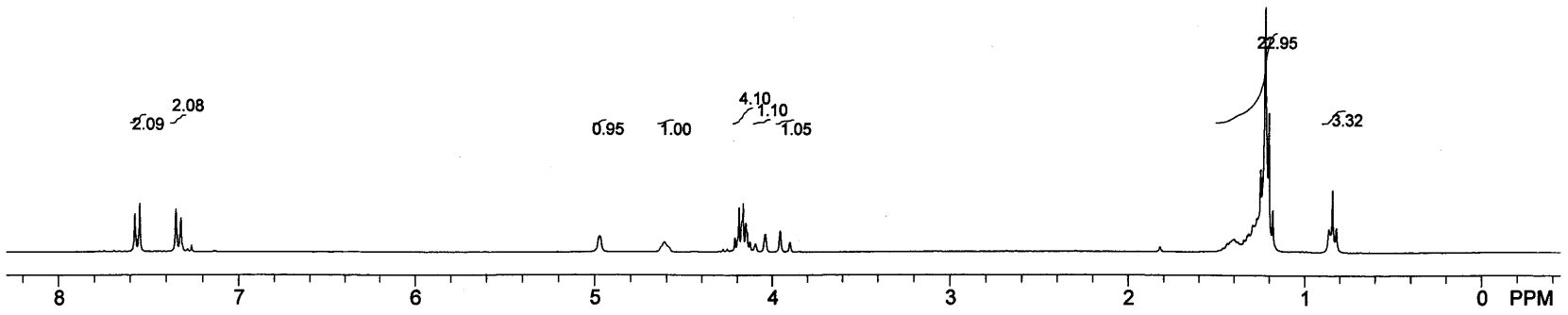




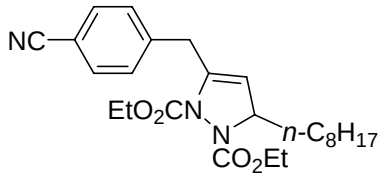


3b

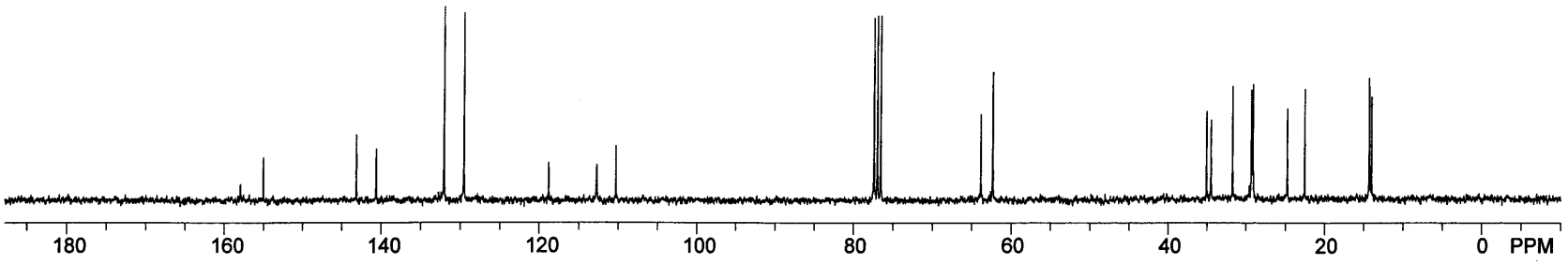
cx-6-11502-h

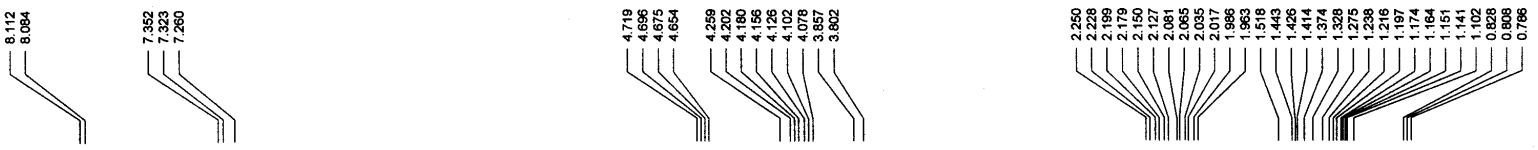


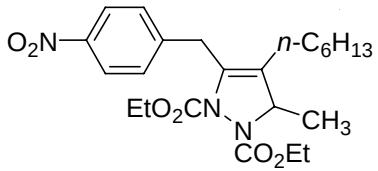
cx-6-11502-c



3b

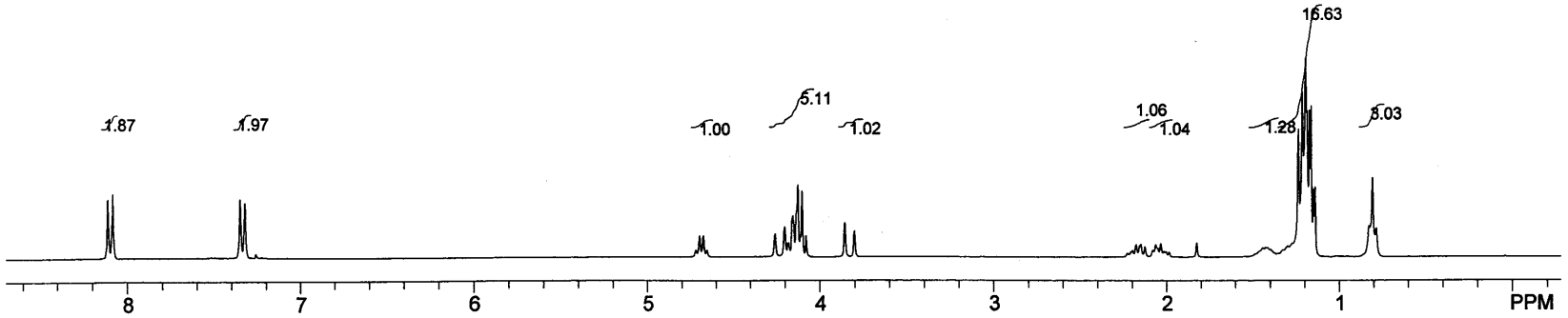


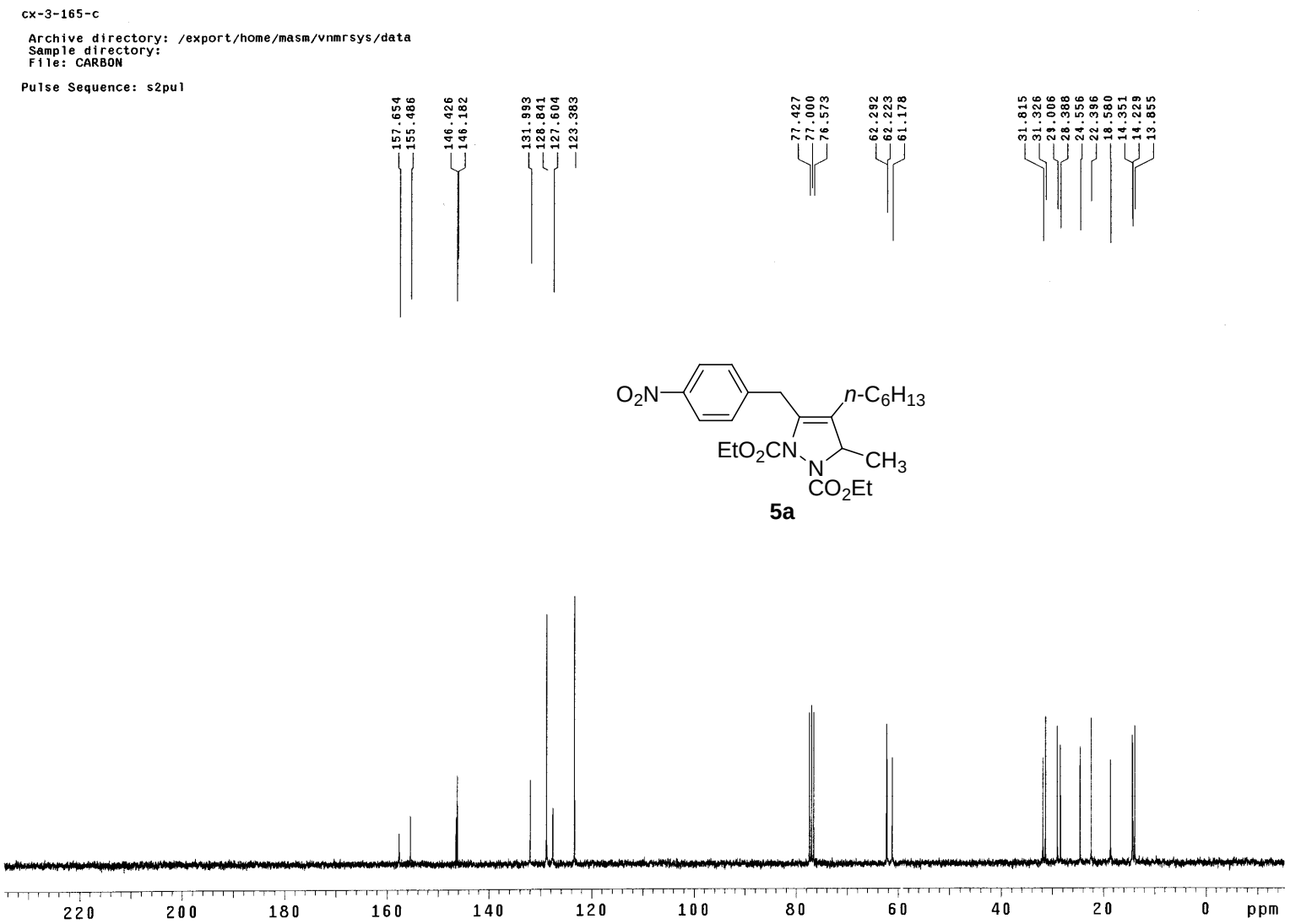

8.112
8.084
7.352
7.323
7.260
4.719
4.696
4.675
4.654
4.259
4.202
4.180
4.156
4.126
4.102
4.078
3.857
3.802
2.250
2.228
2.199
2.179
2.150
2.127
2.081
2.065
2.035
2.017
1.986
1.963
1.518
1.443
1.426
1.414
1.374
1.328
1.275
1.238
1.216
1.197
1.174
1.164
1.151
1.141
1.102
0.828
0.808
0.786


O2N
n-C6H13
EtO2CN
N
CH3
CO2Et

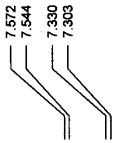
5a

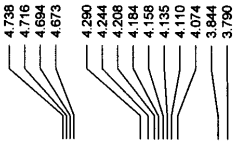
cx-3-165-h

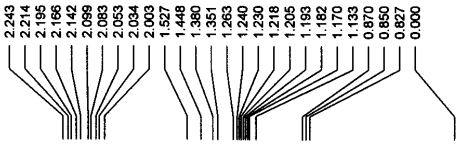

1.87
1.97
1.00
5.11
1.02
1.06
1.04
1.28
16.63
3.03
8
7
6
5
4
3
2
1
PPM

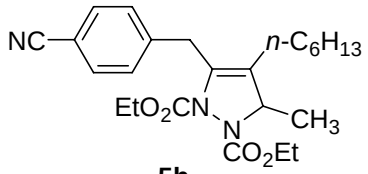

cx-3-165-c
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
157.654
155.486
146.426
146.182
131.893
128.841
127.604
123.383
77.427
77.000
76.573
62.292
62.223
61.178
31.815
31.326
29.006
28.388
24.556
22.396
18.580
14.351
14.229
13.855
O2N
n-C6H13
EtO2CN
N
CH3
CO2Et
220
200
180
160
140
120
100
80
60
40
20
0
ppm

5a


7.572
7.544
7.330
7.303

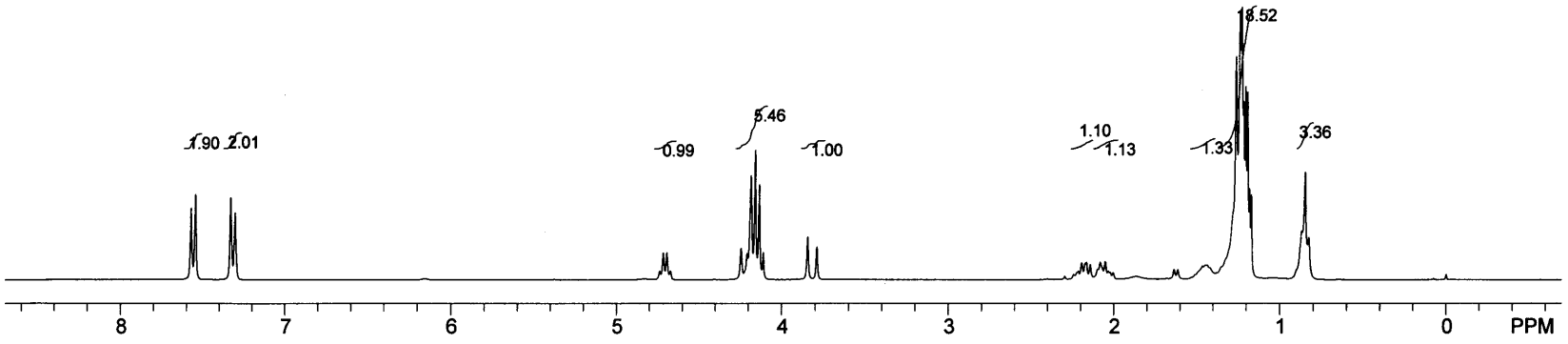

4.738
4.716
4.694
4.673
4.290
4.244
4.208
4.184
4.158
4.135
4.110
4.074
3.844
3.790

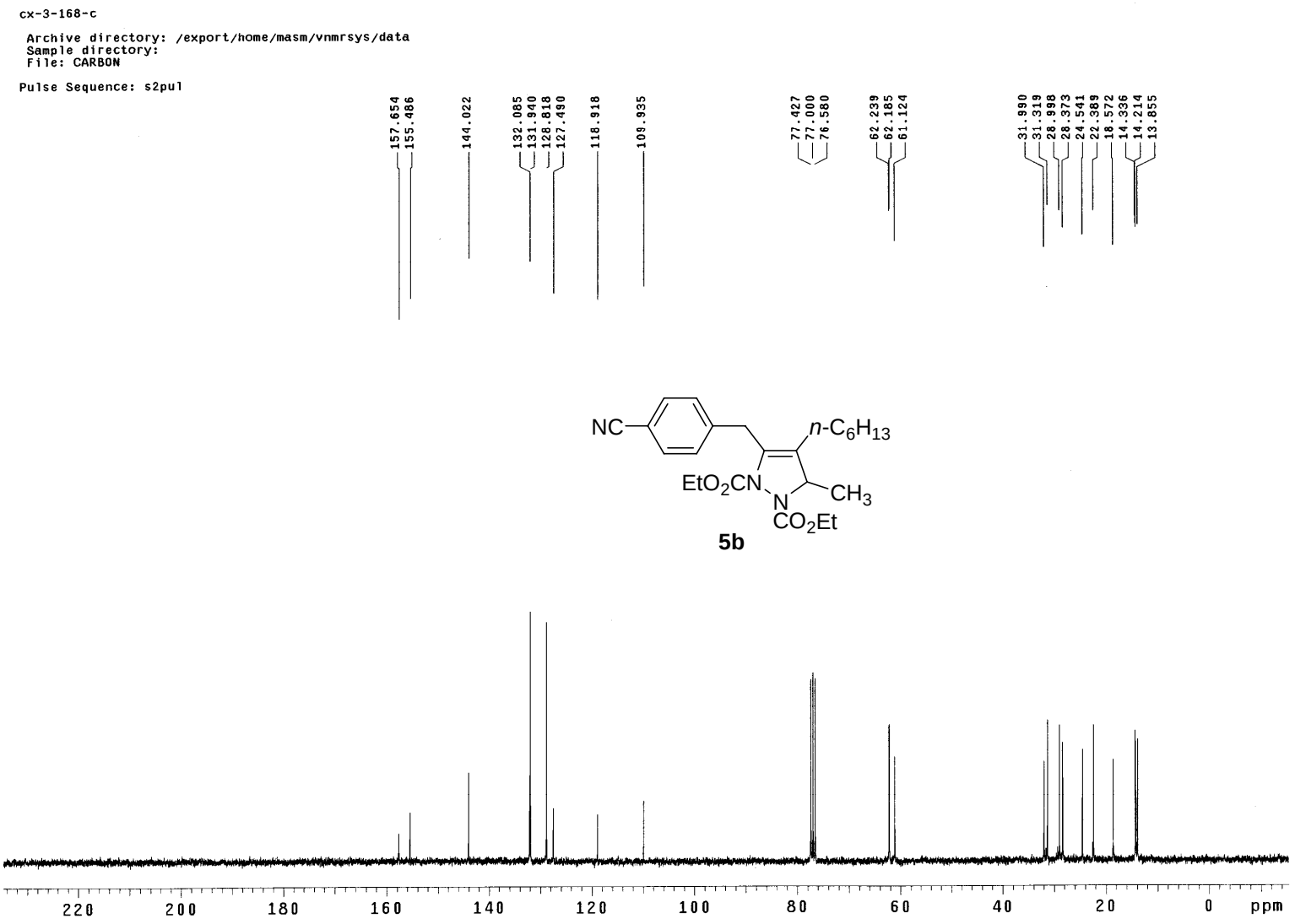

2.243
2.214
2.195
2.166
2.142
2.096
2.083
2.053
2.034
2.003
1.527
1.448
1.380
1.351
1.263
1.240
1.230
1.218
1.205
1.193
1.182
1.170
1.133
0.870
0.850
0.827
0.000

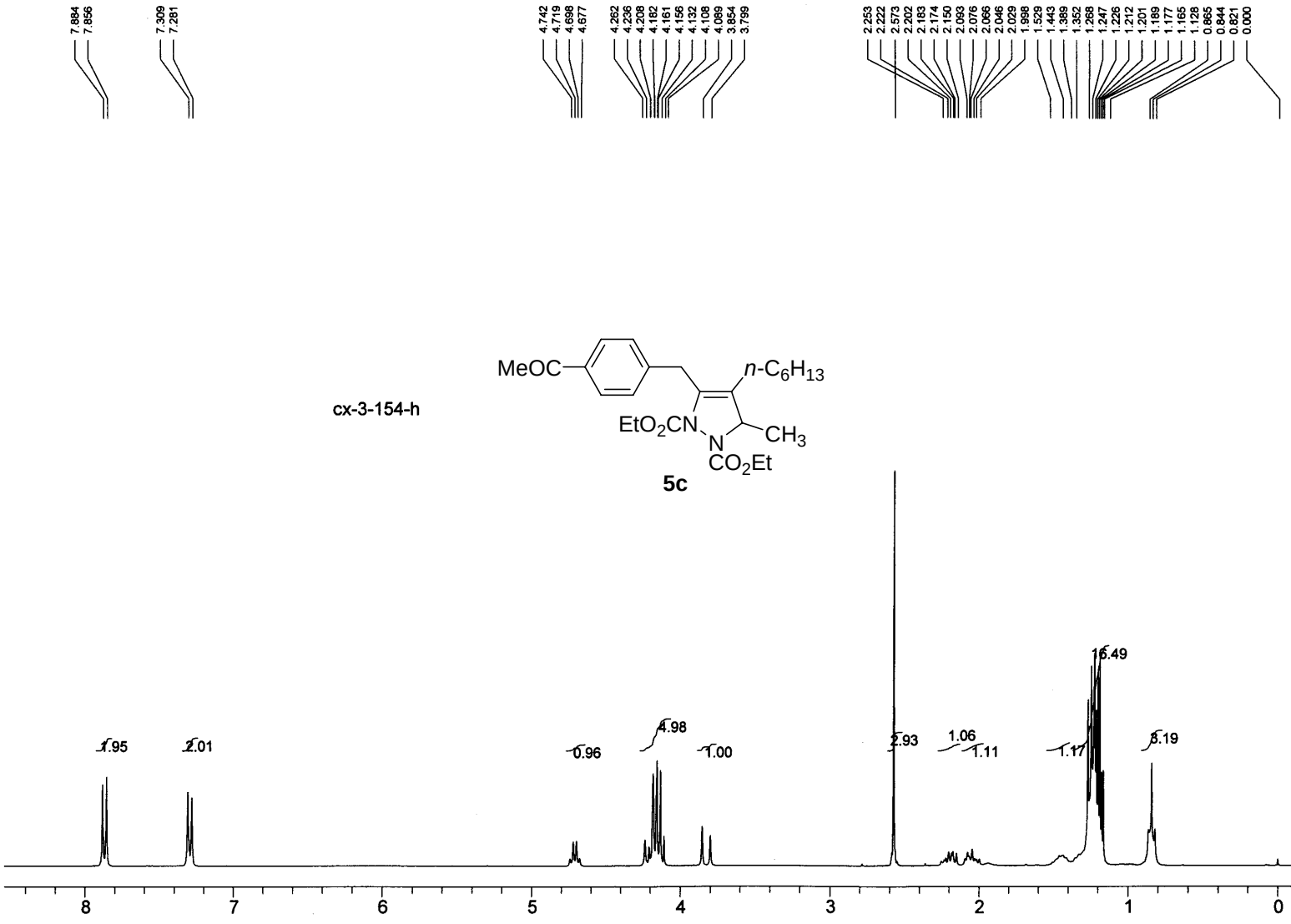

NC
n-C6H13
EtO2CN
N
CH3
CO2Et

5b

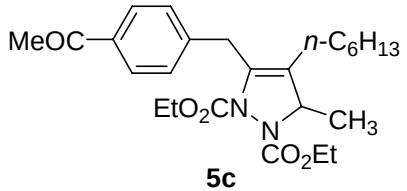
cx-3-168-h


1.90
2.01
0.99
5.46
1.00
1.10
1.13
1.33
18.52
3.36
8
7
6
5
4
3
2
1
0
PPM


cx-3-168-c
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
157.654
155.486
144.022
132.085
131.940
128.818
127.490
118.918
109.935
77.427
77.000
76.580
62.239
62.185
61.124
31.990
31.319
28.998
28.373
24.541
22.389
18.572
14.336
14.214
13.855
NC
n-C6H13
EtO2CN
N
CH3
CO2Et
5b
220
200
180
160
140
120
100
80
60
40
20
0
ppm

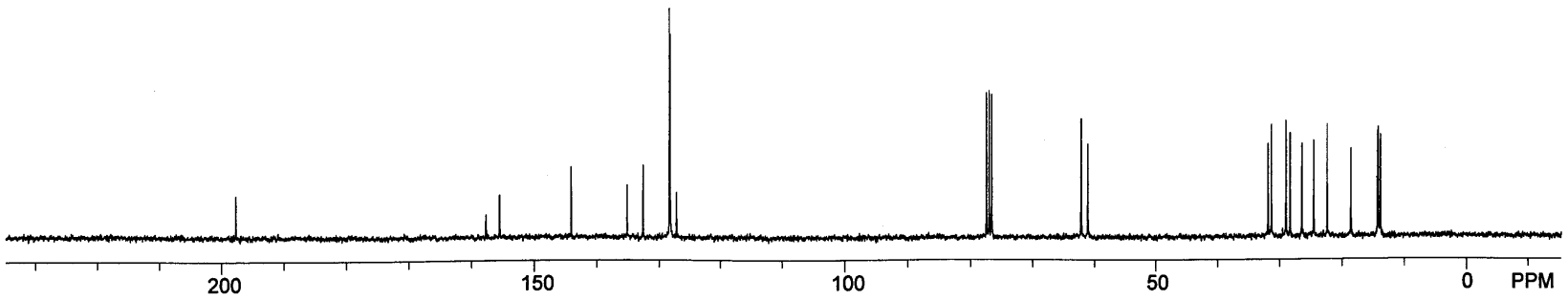

7.884
7.856
7.309
7.281
4.742
4.719
4.698
4.677
4.262
4.236
4.208
4.182
4.161
4.156
4.132
4.108
4.089
3.854
3.799
2.253
2.222
2.573
2.202
2.183
2.174
2.150
2.093
2.076
2.066
2.046
2.029
1.998
1.529
1.443
1.389
1.352
1.268
1.247
1.226
1.212
1.201
1.189
1.177
1.165
1.128
0.865
0.844
0.821
0.000
cx-3-154-h
MeOC
n-C6H13
EtO2CN
N
CH3
CO2Et
5c
1.95
2.01
0.96
4.98
1.00
2.93
1.06
1.11
1.17
6.49
3.19
8
7
6
5
4
3
2
1
0
PPM

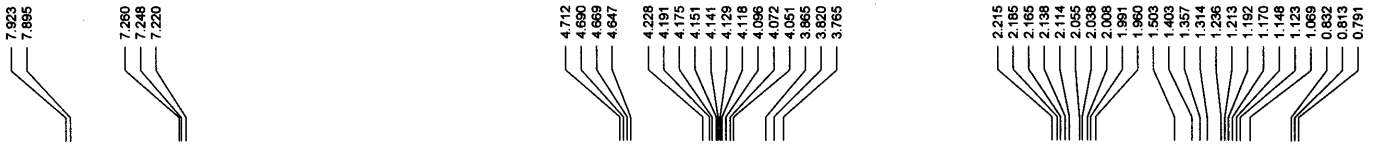

197.684
157.687
155.505
144.078
135.143
132.549
128.283
128.142
127.120
77.423
77.000
76.567
62.176
62.119
61.039
31.878
31.325
28.997
28.350
26.456
24.549
22.382
18.588
14.324
14.204
13.858


MeOC
n-C6H13
EtO2CN
N
CH3
CO2Et

5c

cx-3-154-c


200
150
100
50
0
PPM


7.923
7.895
7.260
7.248
7.220
4.712
4.690
4.669
4.647
4.228
4.191
4.175
4.151
4.141
4.129
4.118
4.096
4.072
4.051
3.865
3.820
3.765
2.215
2.185
2.165
2.138
2.114
2.055
2.038
2.008
1.991
1.960
1.503
1.403
1.357
1.314
1.236
1.213
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1.123
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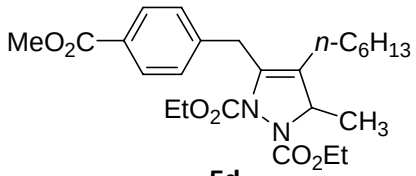
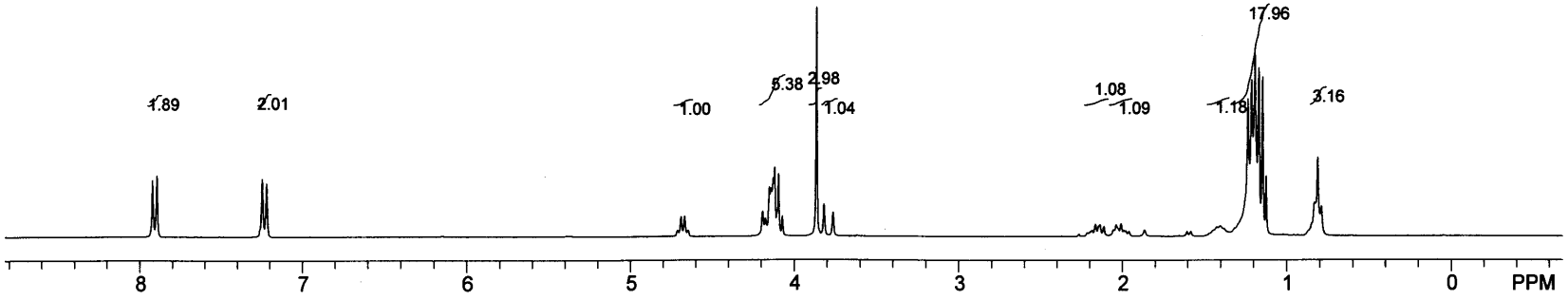
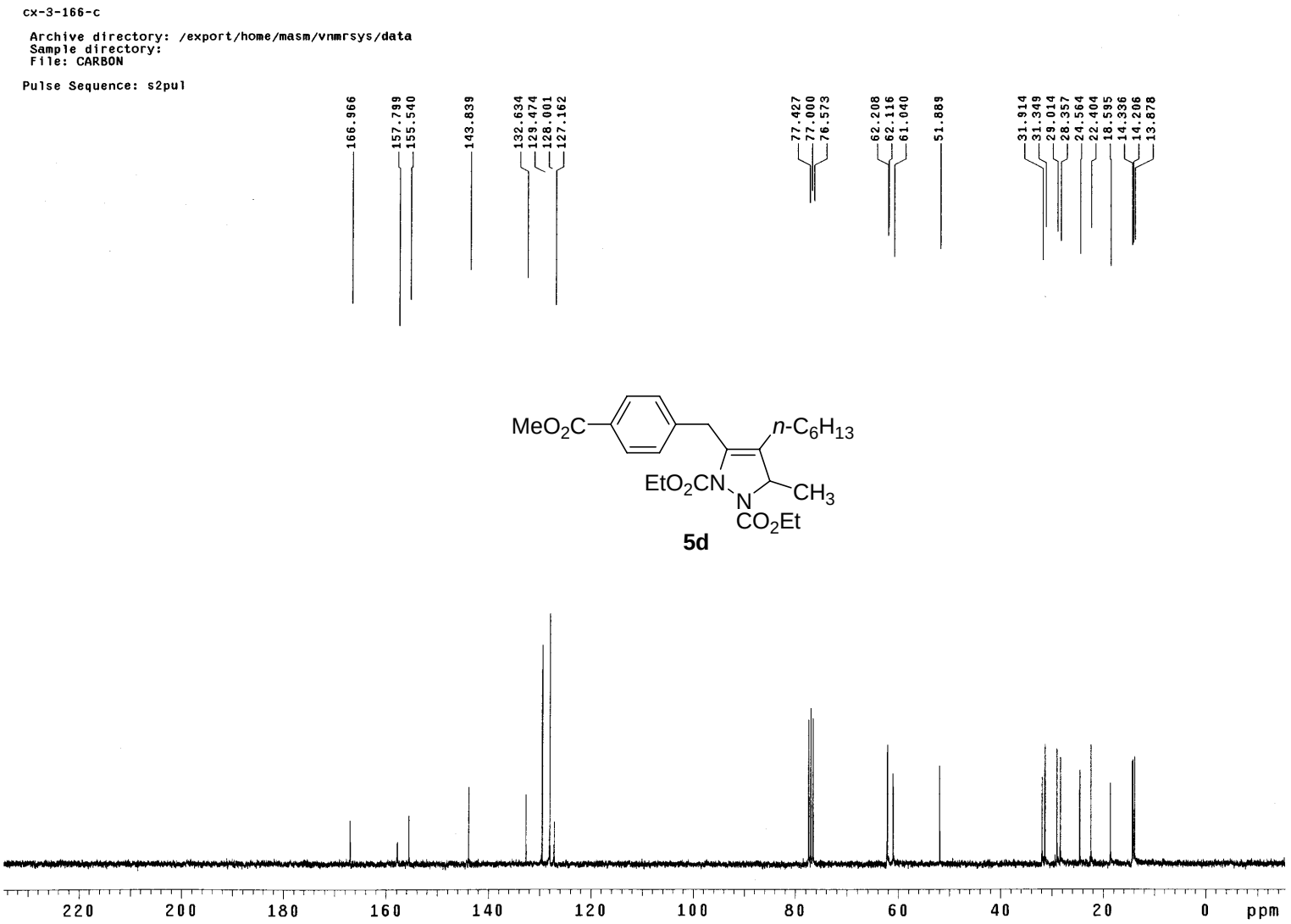
0.832
0.813
0.791

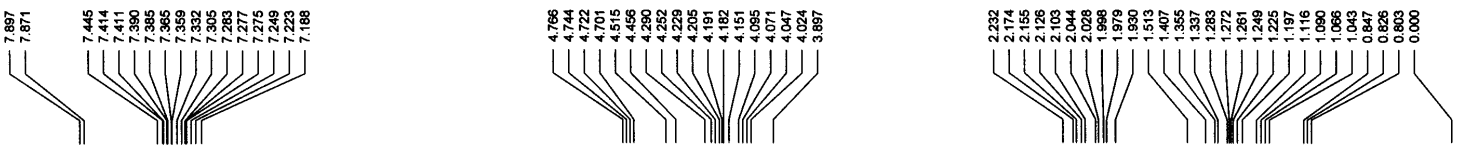

MeO2C
n-C6H13
EtO2CN
N
CH3
CO2Et

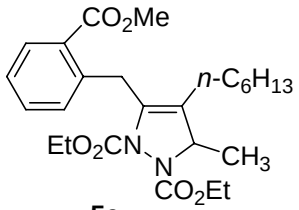
5d

cx-3-166-h


1.89
2.01
1.00
5.38
2.98
1.04
1.08
1.09
1.18
17.96
3.16
8
7
6
5
4
3
2
1
0
PPM

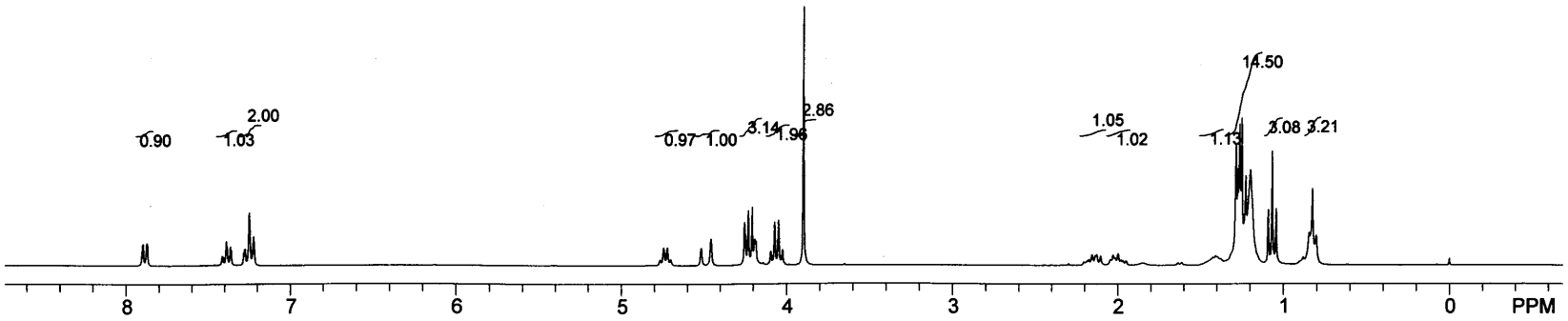

cx-3-166-c
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
166.966
157.799
155.540
143.839
132.634
129.474
128.001
127.162
77.427
77.000
76.573
62.208
62.116
61.040
51.889
31.914
31.349
29.014
28.357
24.564
22.404
18.595
14.336
14.206
13.878
MeO2C
n-C6H13
EtO2CN
N
CH3
CO2Et
5d
220
200
180
160
140
120
100
80
60
40
20
0
ppm


7.897
7.871
7.445
7.414
7.411
7.390
7.385
7.365
7.359
7.332
7.305
7.283
7.277
7.275
7.249
7.223
7.188
4.766
4.744
4.722
4.701
4.515
4.456
4.290
4.252
4.229
4.205
4.191
4.182
4.151
4.095
4.071
4.047
4.024
3.897
2.232
2.174
2.155
2.126
2.103
2.044
2.028
1.998
1.979
1.930
1.513
1.407
1.355
1.337
1.283
1.272
1.261
1.249
1.225
1.197
1.116
1.090
1.066
1.043
0.847
0.826
0.803
0.000


CO2Me
n-C6H13
EtO2CN
N
CH3
CO2Et

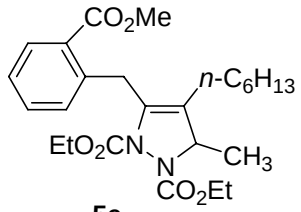
5e

cx-3-198-h

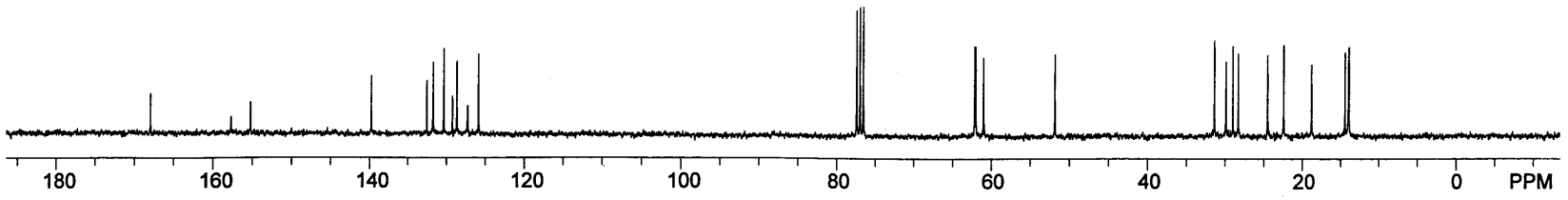

0.90
2.00
1.03
0.97
1.00
3.14
1.96
2.86
1.05
1.02
1.13
14.50
3.08
3.21
8
7
6
5
4
3
2
1
0
PPM

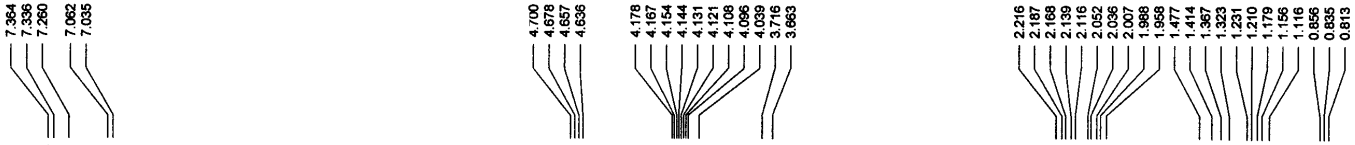

167.929
157.693
155.210
139.763
132.538
131.727
130.338
129.240
128.651
127.275
125.877
77.422
77.000
76.577
62.192
62.027
61.029
51.869
31.371
29.900
29.001
28.294
24.507
22.416
18.778
14.407
13.966
13.690

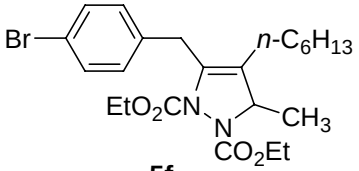
cx-3-198-c


CO2Me
n-C6H13
EtO2CN
N
CH3
CO2Et

5e

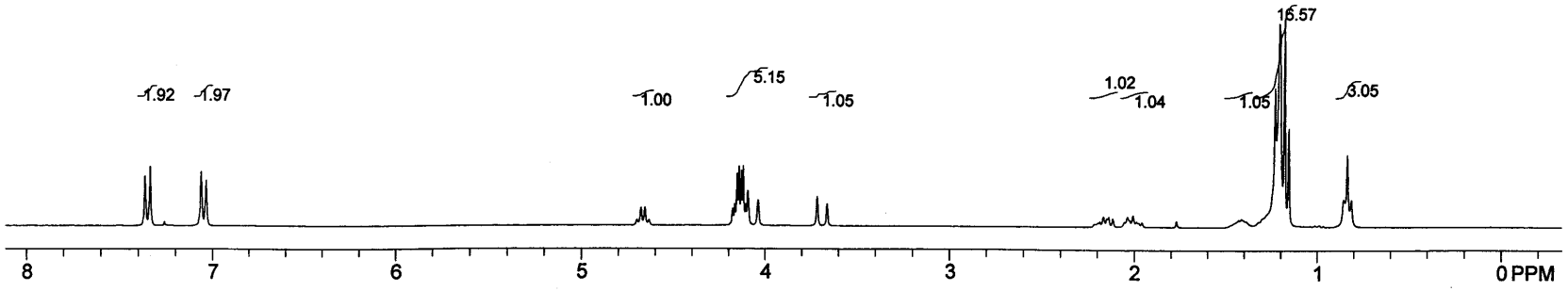

180
160
140
120
100
80
60
40
20
0
PPM

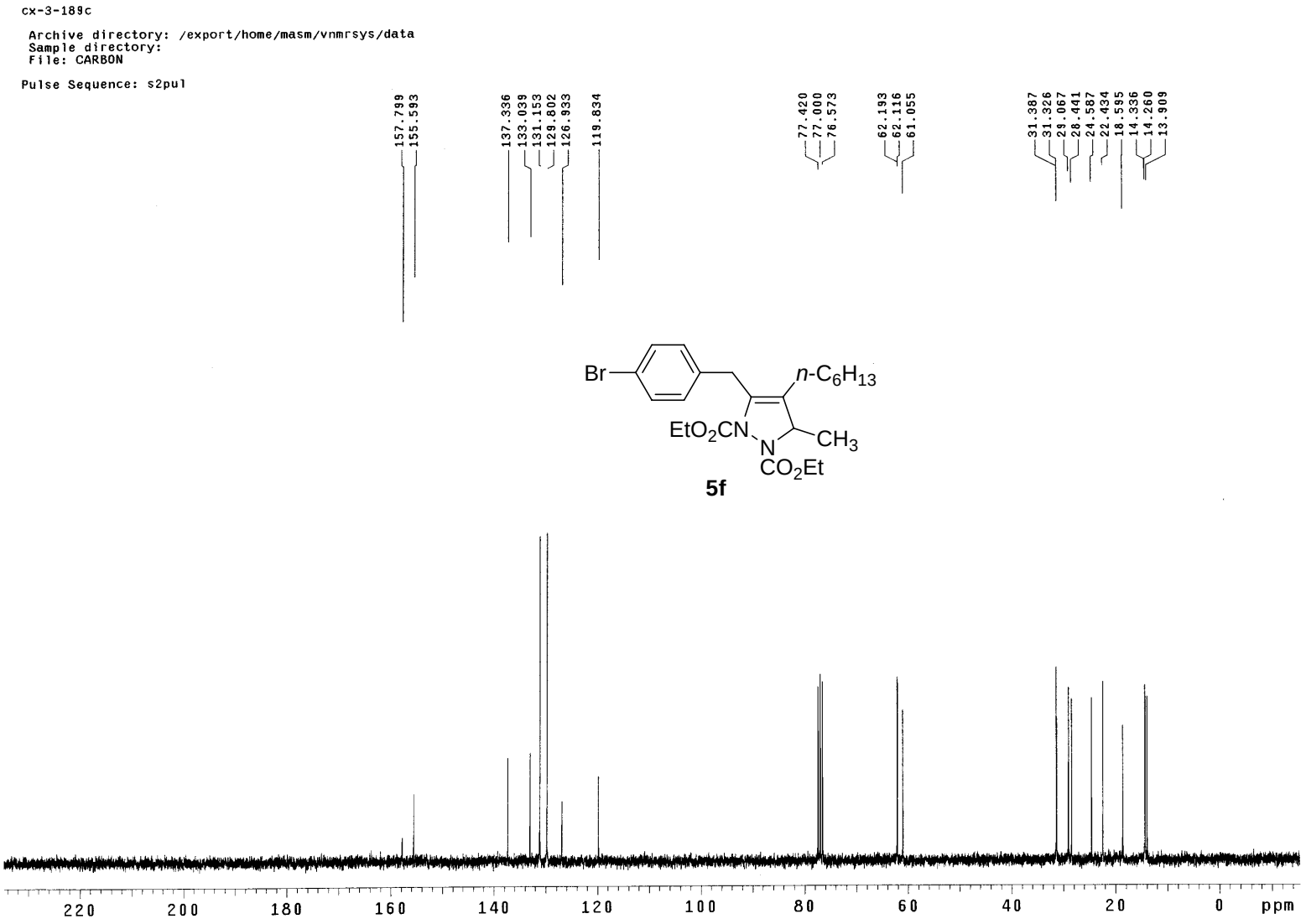

7.364
7.336
7.260
7.062
7.035
4.700
4.678
4.657
4.636
4.178
4.167
4.154
4.144
4.131
4.121
4.108
4.096
4.039
3.716
3.663
2.216
2.187
2.168
2.139
2.116
2.052
2.036
2.007
1.988
1.958
1.477
1.414
1.367
1.323
1.231
1.210
1.179
1.156
1.116
0.856
0.835
0.813

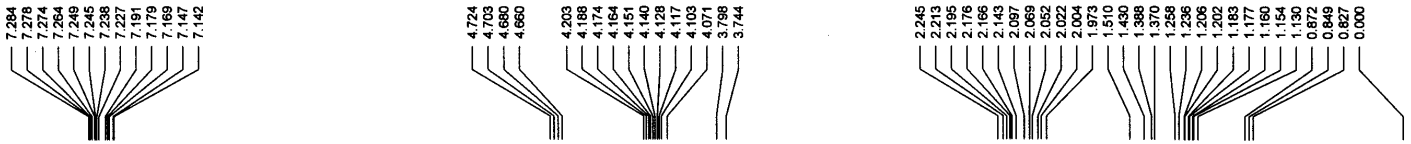

Br
n-C6H13
EtO2CN
N
CH3
CO2Et

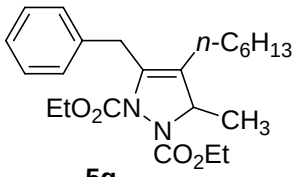
5f

cx-3-189-h


1.92
1.97
1.00
5.15
1.05
1.02
1.04
1.05
16.57
3.05
8
7
6
5
4
3
2
1
0 PPM

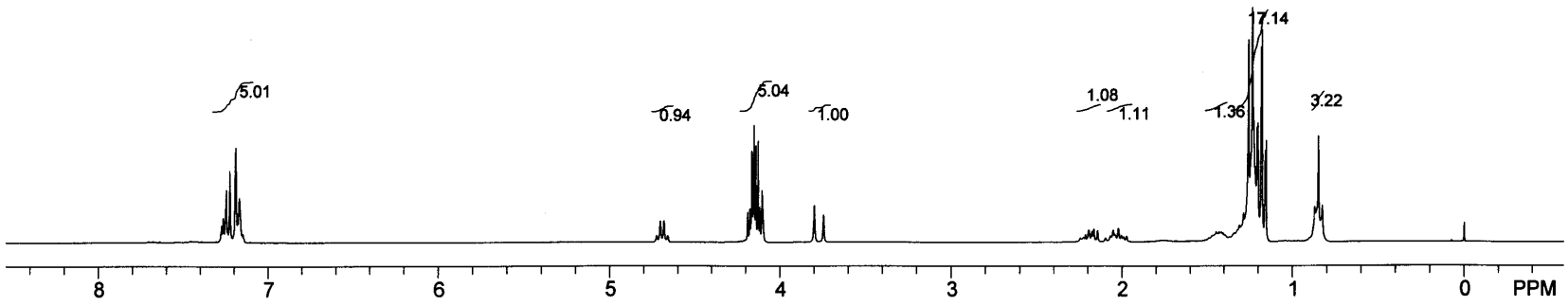

cx-3-189c
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
157.799
155.593
137.336
133.039
131.153
129.802
126.933
119.834
77.420
77.000
76.573
62.193
62.116
61.055
31.387
31.326
29.067
28.441
24.587
22.434
18.595
14.336
14.260
13.909
Br
n-C6H13
EtO2CN
N
CH3
CO2Et
5f
220
200
180
160
140
120
100
80
60
40
20
0
ppm

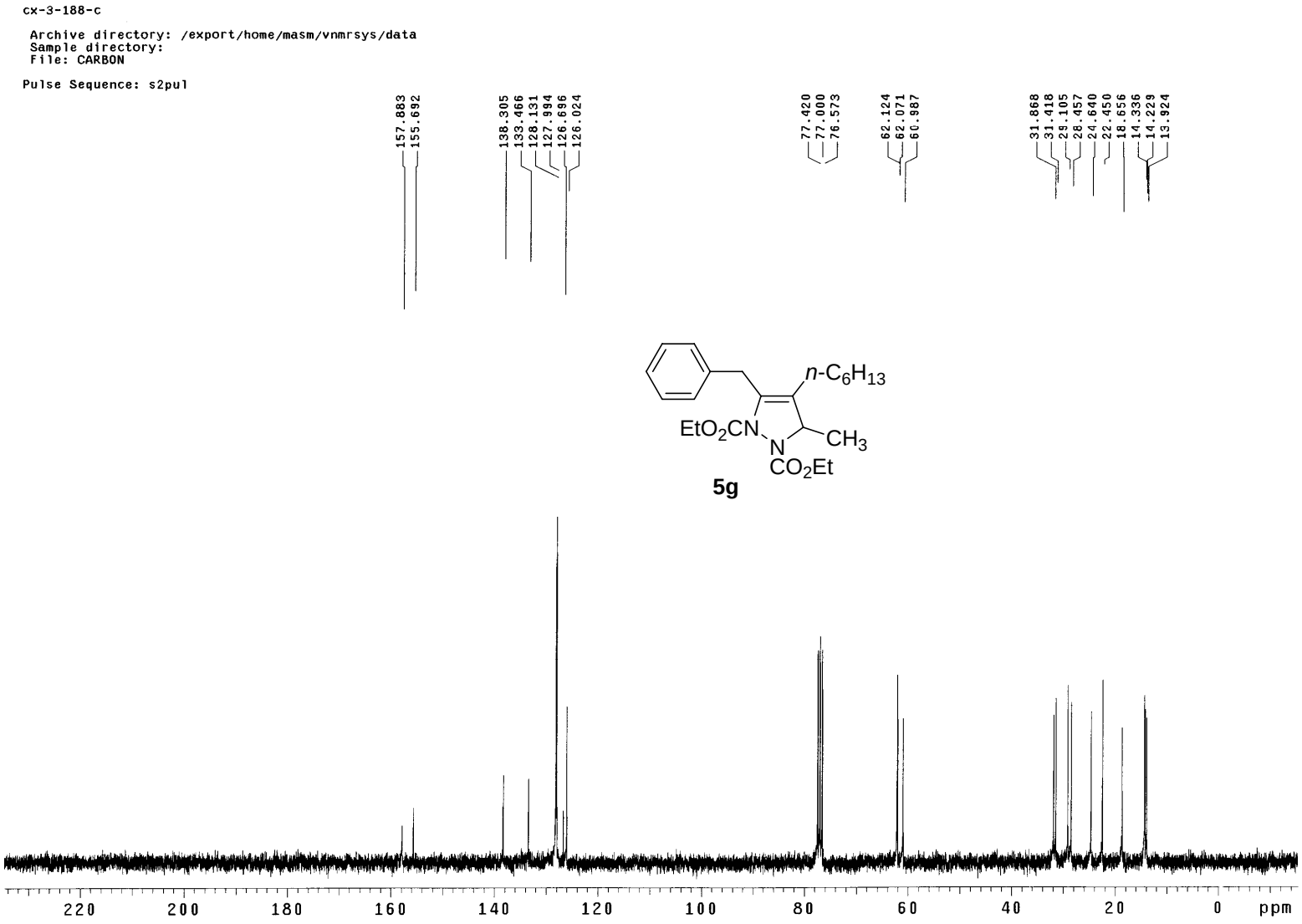

7.284
7.278
7.274
7.264
7.249
7.245
7.238
7.227
7.191
7.179
7.169
7.147
7.142
4.724
4.703
4.680
4.660
4.203
4.188
4.174
4.164
4.151
4.140
4.128
4.117
4.103
4.071
3.798
3.744
2.245
2.213
2.195
2.176
2.166
2.143
2.097
2.069
2.052
2.022
2.004
1.973
1.510
1.430
1.388
1.370
1.258
1.236
1.206
1.202
1.183
1.177
1.160
1.154
1.130
0.872
0.849
0.827
0.000

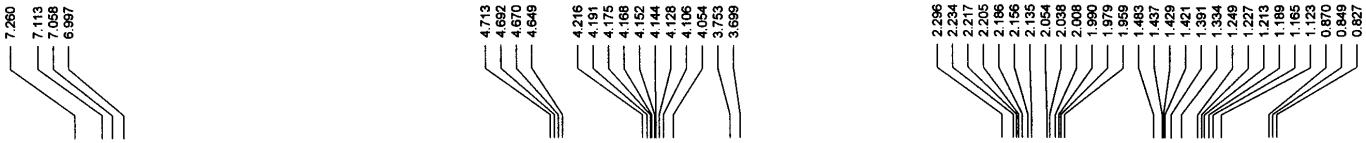

n-C6H13
EtO2CN
N
CH3
CO2Et

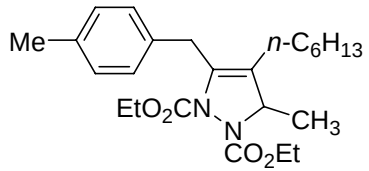
5g

cx-3-188-h


5.01
0.94
5.04
1.00
1.08
1.11
1.36
7.14
3.22
8
7
6
5
4
3
2
1
0
PPM

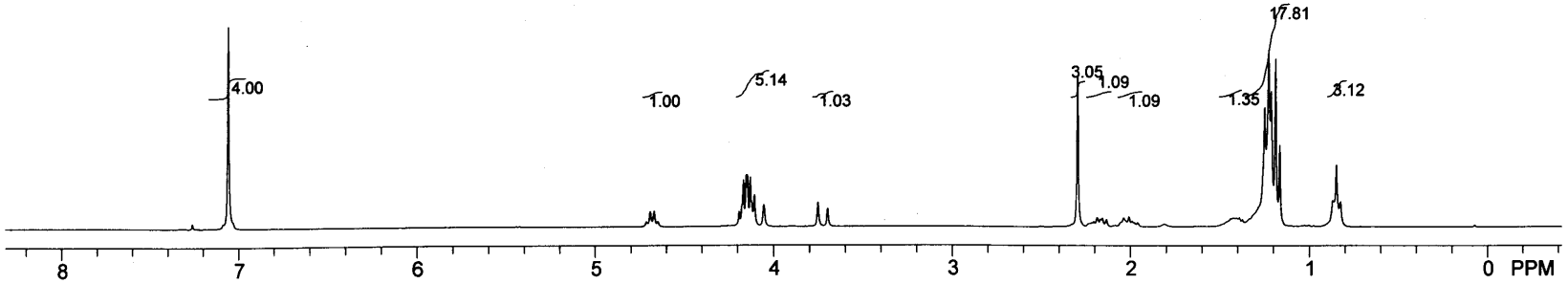

cx-3-188-c
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
157.883
155.692
138.305
133.466
128.131
127.994
126.696
126.024
77.420
77.000
76.573
62.124
62.071
60.987
31.868
31.418
29.105
28.457
24.640
22.450
18.656
14.336
14.229
13.924
n-C6H13
EtO2CN
CH3
N
CO2Et
5g
220
200
180
160
140
120
100
80
60
40
20
0
ppm

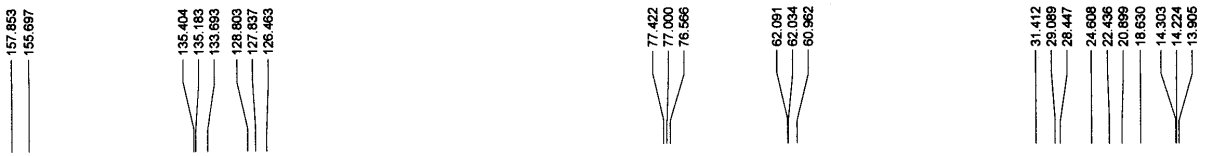

7.260
7.113
7.058
6.997
4.713
4.692
4.670
4.649
4.216
4.191
4.175
4.168
4.152
4.144
4.128
4.106
4.054
3.753
3.699
2.296
2.234
2.217
2.205
2.186
2.156
2.135
2.054
2.038
2.008
1.990
1.979
1.959
1.483
1.437
1.429
1.421
1.391
1.334
1.249
1.227
1.213
1.189
1.165
1.123
0.870
0.849
0.827

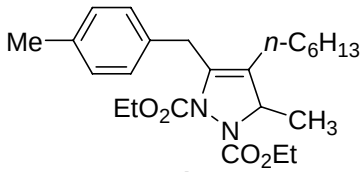

Me
n-C6H13
EtO2CN
N
CH3
CO2Et

5h

cx-6-119-h

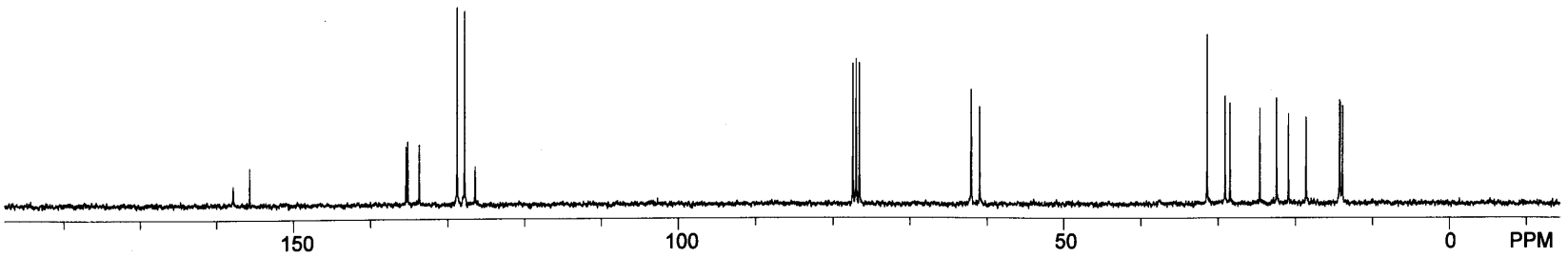

4.00
1.00
5.14
1.03
3.05
1.09
1.09
1.35
17.81
3.12
8
7
6
5
4
3
2
1
0 PPM

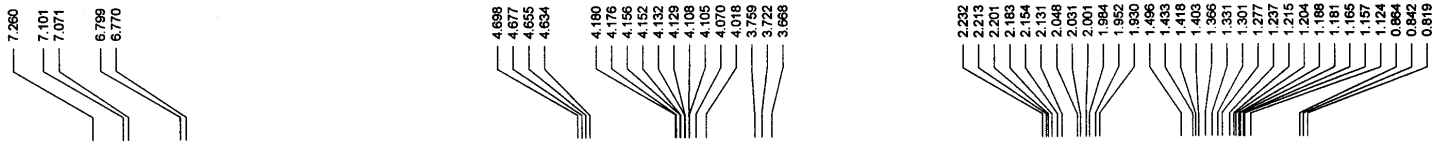

157.853
155.697
135.404
135.183
133.693
128.803
127.837
126.463
77.422
77.000
76.566
62.091
62.034
60.962
31.412
29.089
28.447
24.608
22.436
20.899
18.630
14.303
14.224
13.905

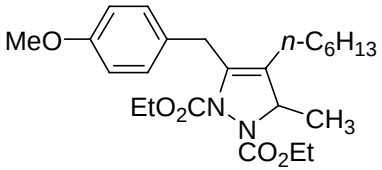

Me
n-C6H13
EtO2CN
N
CH3
CO2Et

5h

cx-6-119-c

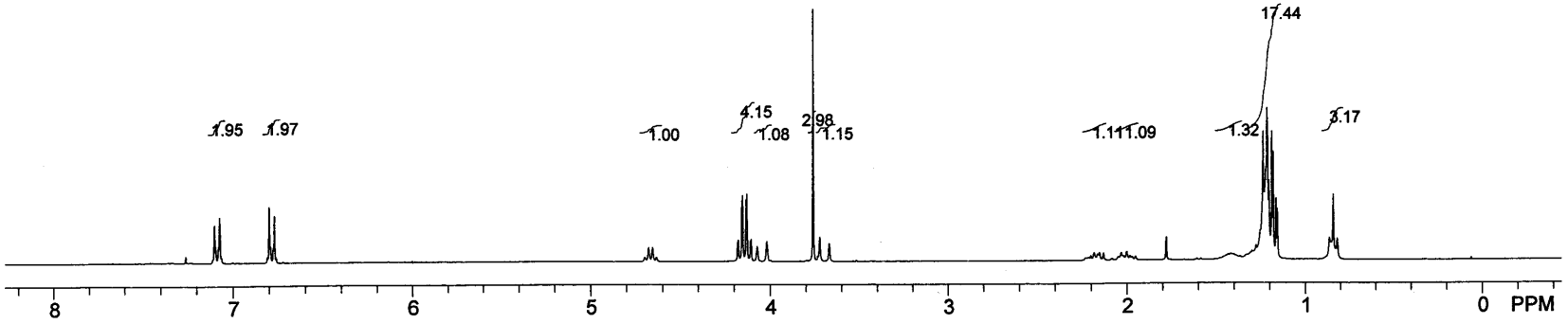

150
100
50
0
PPM

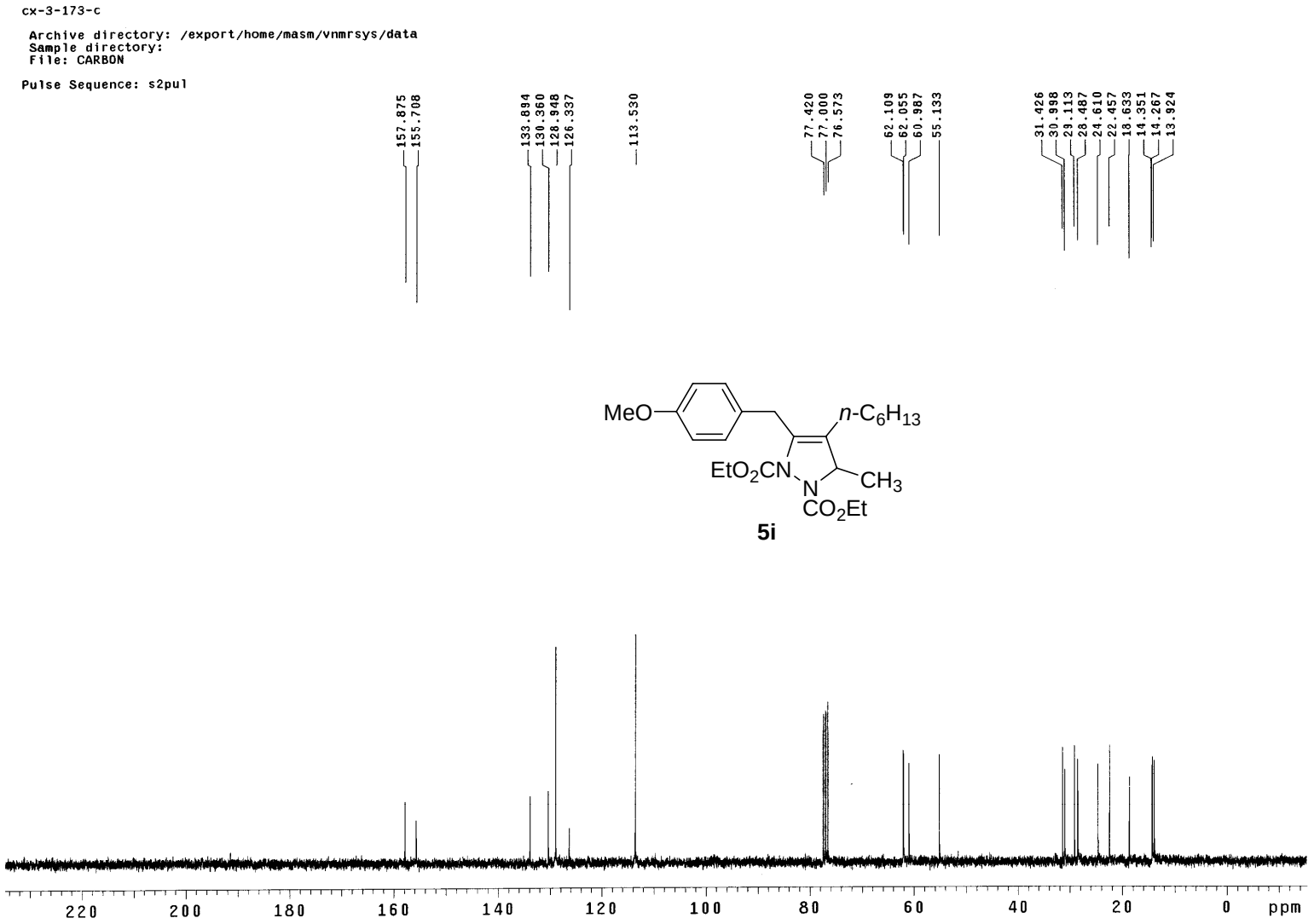

7.260
7.101
7.071
6.799
6.770
4.698
4.677
4.655
4.634
4.180
4.176
4.156
4.152
4.132
4.129
4.108
4.105
4.070
4.018
3.759
3.722
3.668
2.232
2.213
2.201
2.183
2.154
2.131
2.048
2.031
2.001
1.984
1.952
1.930
1.496
1.433
1.418
1.403
1.366
1.331
1.301
1.277
1.237
1.215
1.204
1.188
1.181
1.165
1.157
1.124
0.884
0.842
0.819


MeO
n-C6H13
EtO2CN
CH3
N
CO2Et

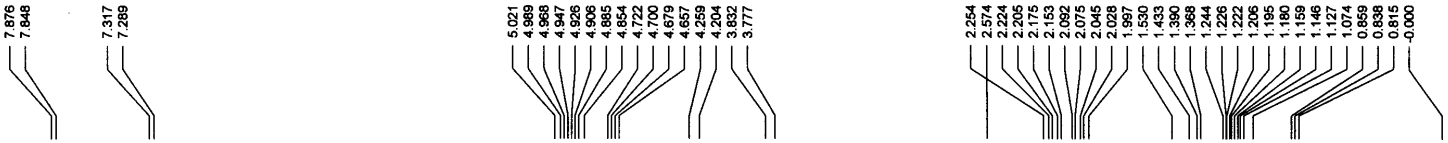
5i

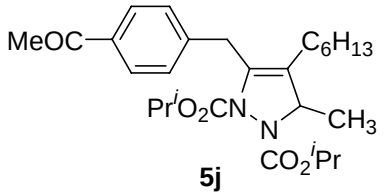
cx-3-173-h


17.44
1.95
1.97
1.00
3.15
1.08
2.98
1.15
1.111.09
1.32
3.17
8
7
6
5
4
3
2
1
0
PPM


cx-3-173-c
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
157.875
155.708
133.894
130.360
128.948
126.337
113.530
77.420
77.000
76.573
62.109
62.055
60.987
55.133
31.426
30.998
29.113
28.487
24.610
22.457
18.633
14.351
14.267
13.924
MeO
n-C6H13
EtO2CN
N
CH3
CO2Et
220
200
180
160
140
120
100
80
60
40
20
0
ppm

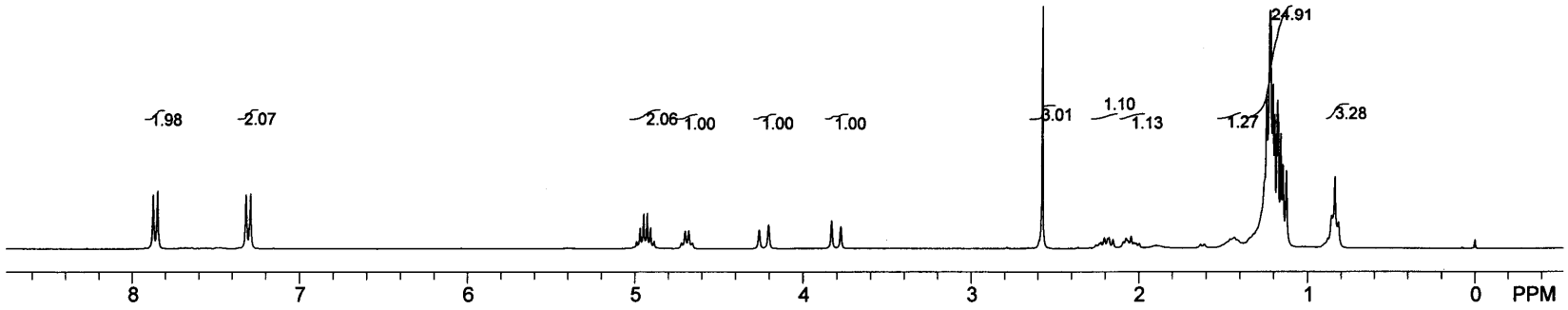
5i


7.876
7.848
7.317
7.289
5.021
4.989
4.968
4.947
4.926
4.906
4.885
4.854
4.722
4.700
4.679
4.657
4.259
4.204
3.832
3.777
2.254
2.574
2.224
2.205
2.175
2.153
2.092
2.075
2.045
2.028
1.997
1.530
1.433
1.390
1.368
1.244
1.226
1.222
1.206
1.195
1.180
1.159
1.146
1.127
1.074
0.859
0.838
0.815
-0.000

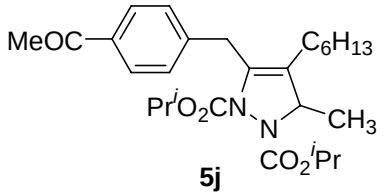

MeOC
C6H13
PriO2CN
CH3
N
CO2iPr

5j

cx-4-010-h

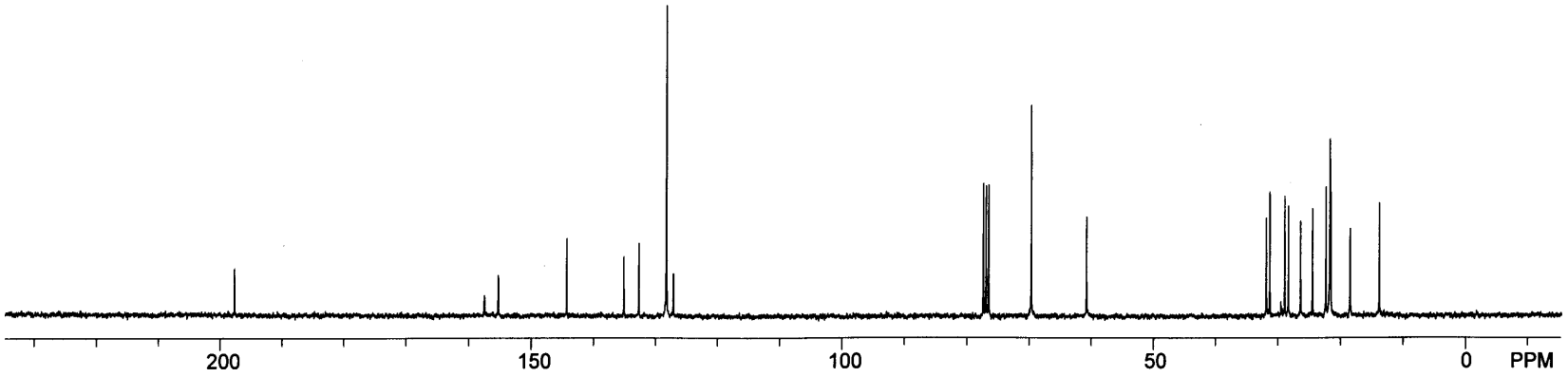

1.98
2.07
2.06
1.00
1.00
1.00
3.01
1.10
1.13
1.27
24.91
3.28
8
7
6
5
4
3
2
1
0
PPM

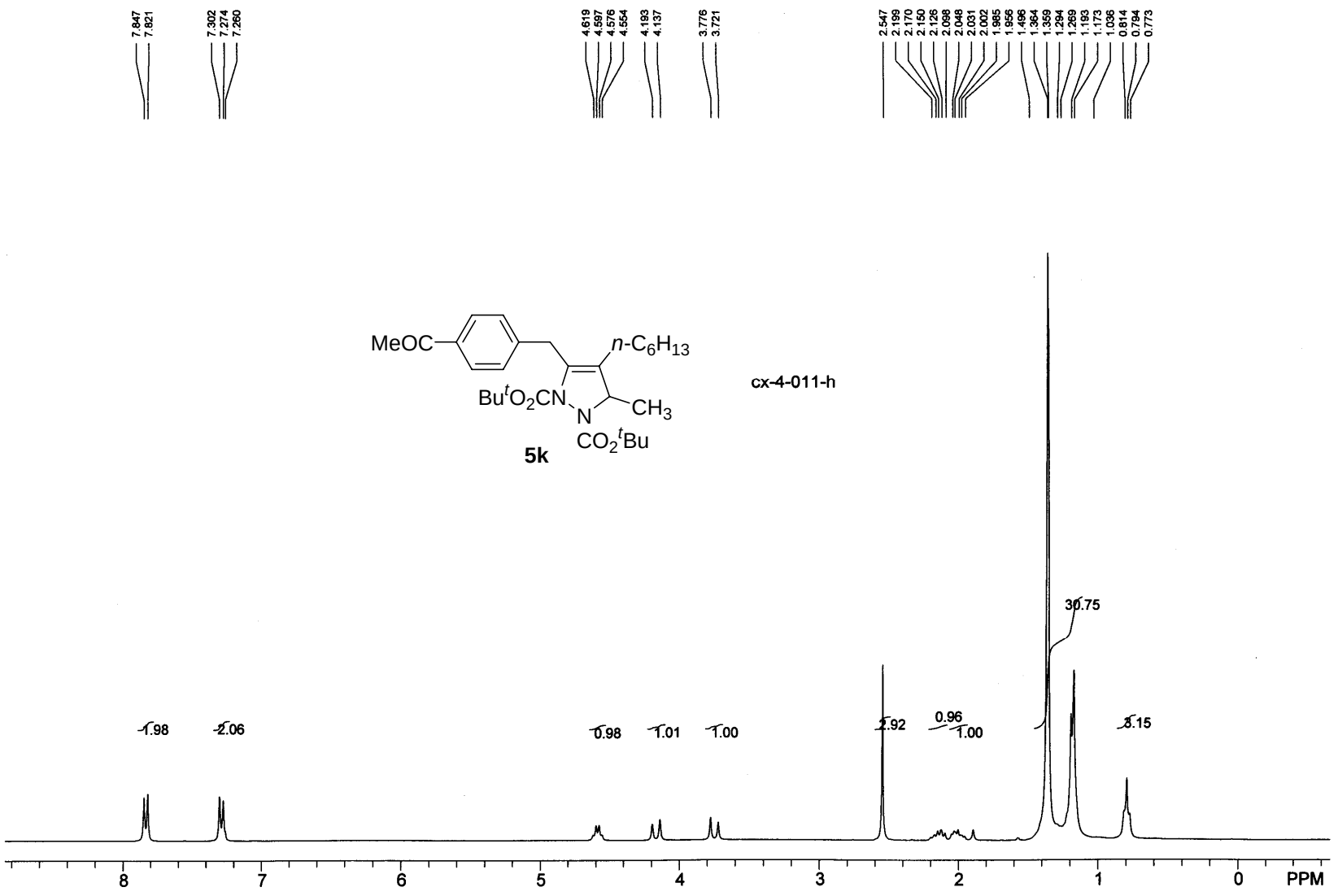

197.691
157.481
155.250
144.285
135.113
132.701
128.242
128.232
127.118
77.434
77.000
76.585
69.732
60.814
31.929
31.356
28.986
28.390
26.456
24.562
22.415
21.812
21.791
21.747
21.640
18.534
13.874

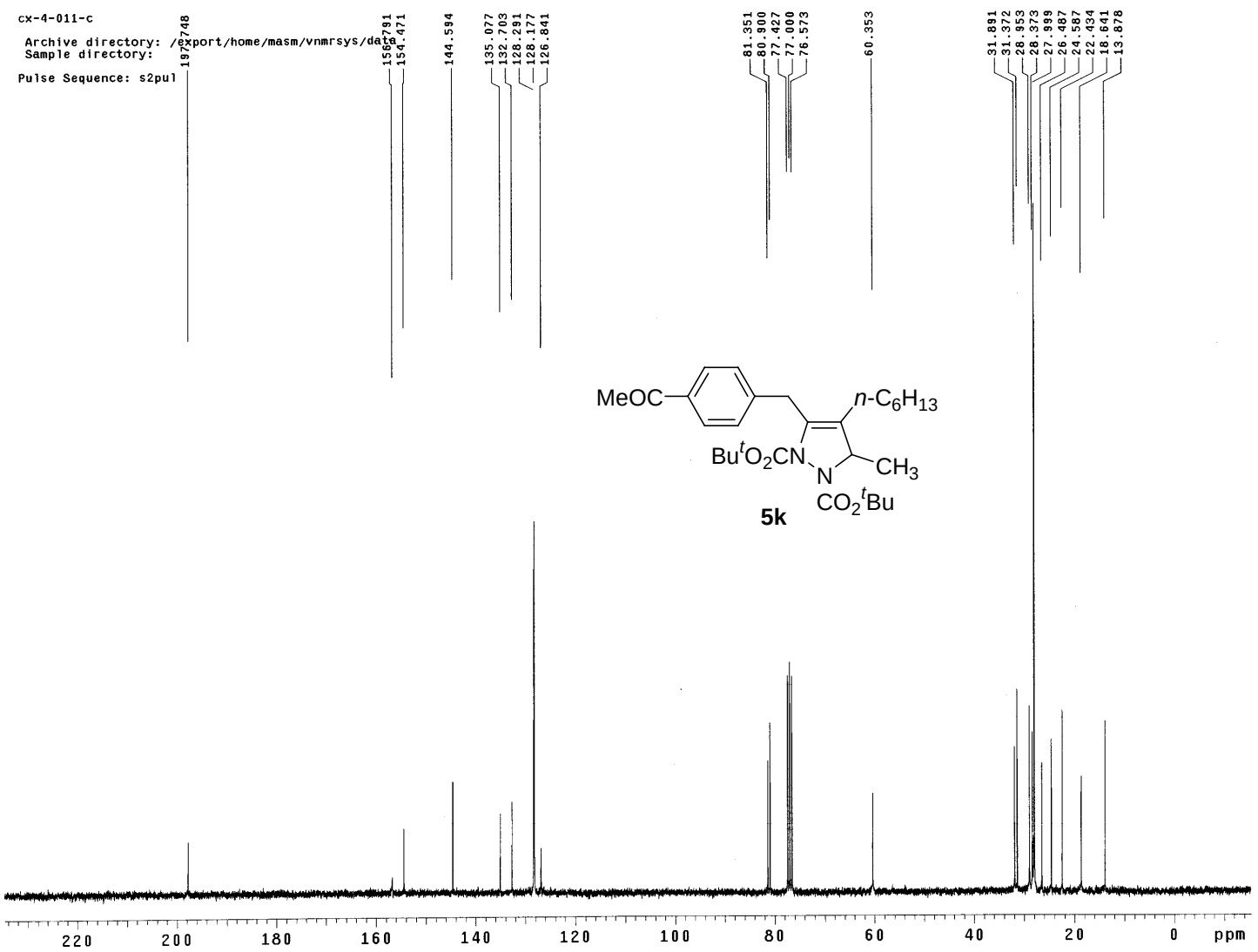

MeOC
C6H13
PriO2CN
N
CH3
CO2iPr

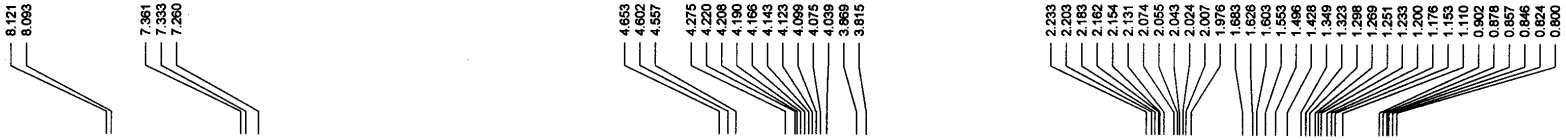
5j

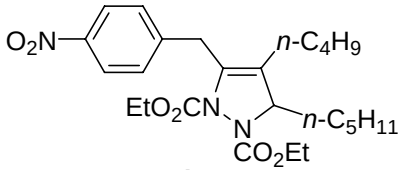
cx-4-010-c


200
150
100
50
0
PPM


7.847
7.821
7.302
7.274
7.260
4.619
4.597
4.576
4.554
4.193
4.137
3.776
3.721
2.547
2.199
2.170
2.150
2.126
2.098
2.048
2.031
2.002
1.985
1.956
1.496
1.364
1.359
1.294
1.269
1.193
1.173
1.036
0.814
0.794
0.773
MeOC
n-C6H13
Bu^tO2CN
CH3
N
CO2^tBu
5k
cx-4-011-h
1.98
2.06
0.98
1.01
1.00
2.92
0.96
1.00
3.15
30.75
8
7
6
5
4
3
2
1
0
PPM

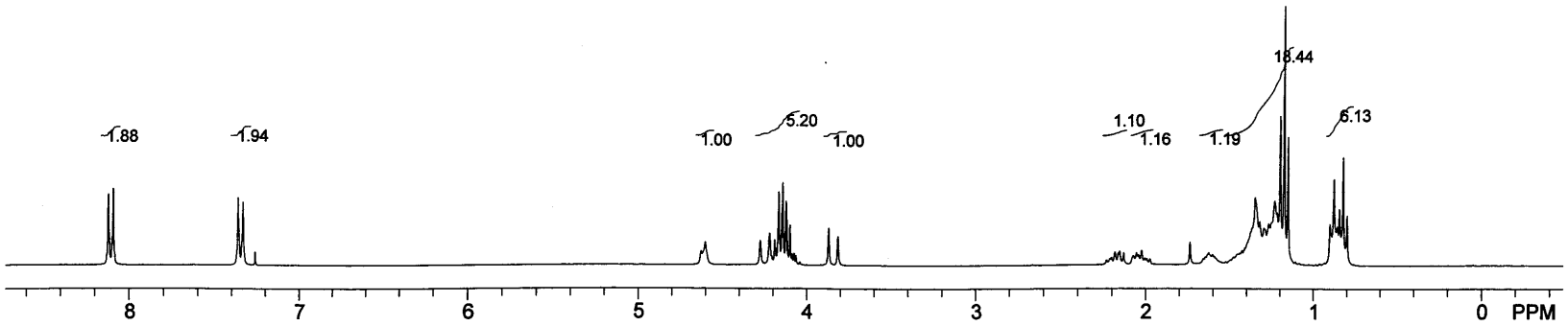

cx-4-011-c
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
197.748
156.791
154.471
144.594
135.077
132.703
128.291
128.177
126.841
81.351
80.900
77.427
77.000
76.573
60.353
31.881
31.372
28.953
28.373
27.999
26.487
24.587
22.434
18.641
13.878
MeOC
n-C6H13
ButO2CN
CH3
N
CO2tBu
5k
220
200
180
160
140
120
100
80
60
40
20
0
ppm

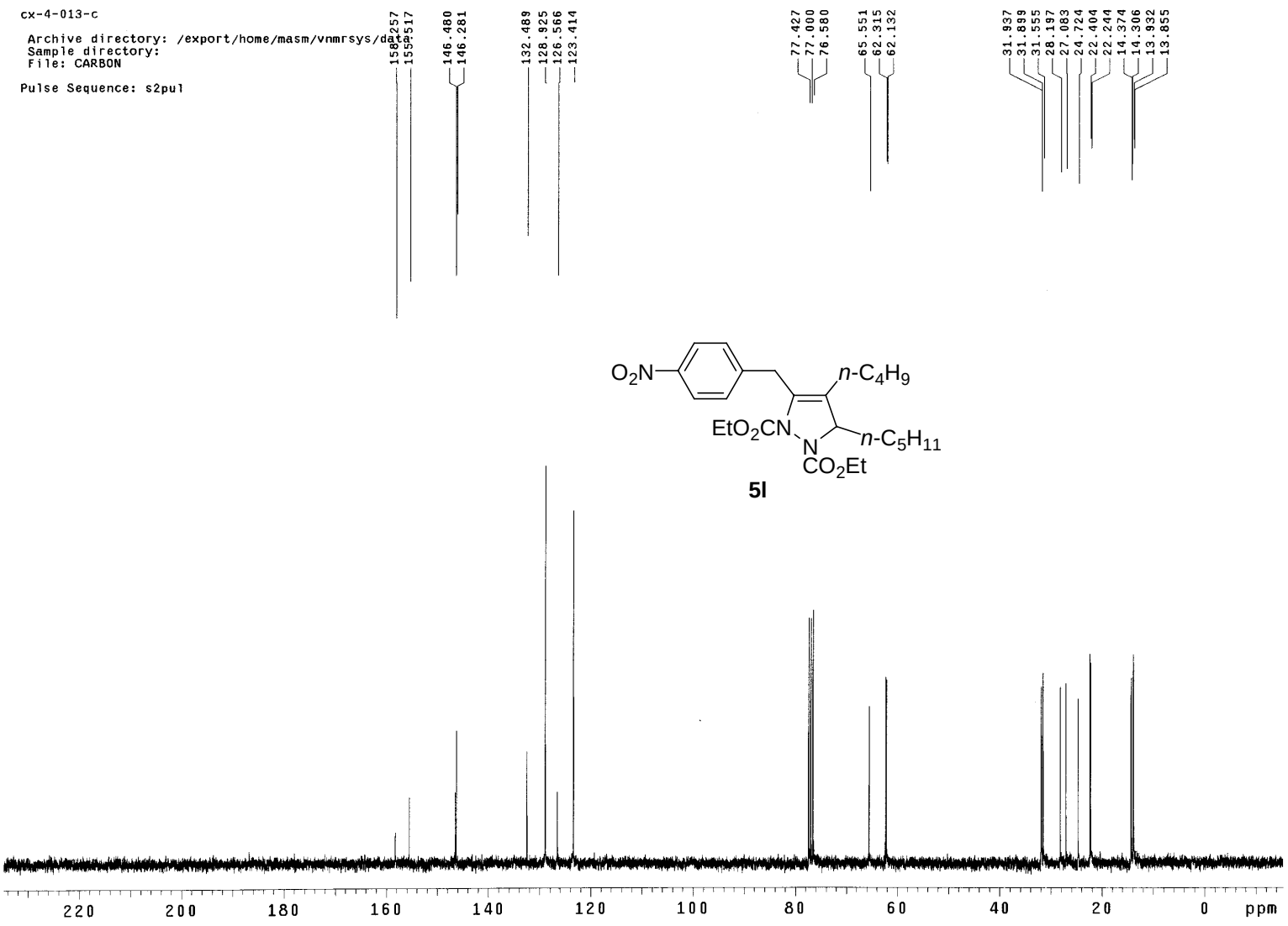

8.121
8.093
7.361
7.333
7.260
4.653
4.602
4.557
4.275
4.220
4.208
4.190
4.166
4.143
4.123
4.099
4.075
4.039
3.869
3.815
2.233
2.203
2.183
2.162
2.154
2.131
2.074
2.055
2.043
2.024
2.007
1.976
1.683
1.626
1.603
1.553
1.496
1.428
1.349
1.323
1.298
1.269
1.251
1.233
1.200
1.176
1.153
1.110
0.902
0.878
0.857
0.846
0.824
0.800


O2N
n-C4H9
EtO2CN
N
n-C5H11
CO2Et

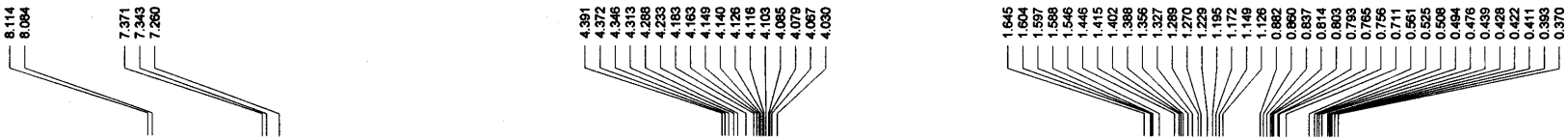
5l

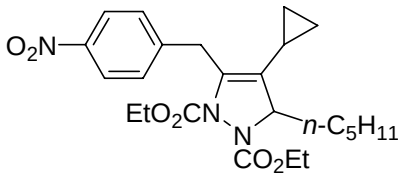
cx-4-013-h


1.88
1.94
1.00
5.20
1.00
1.10
1.16
1.19
18.44
5.13
8
7
6
5
4
3
2
1
0
PPM


cx-4-013-c
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
158.257
155.517
146.480
146.281
132.489
128.925
126.566
123.414
77.427
77.000
76.580
65.551
62.315
62.132
31.937
31.899
31.555
28.197
27.083
24.724
22.404
22.244
14.374
14.306
13.932
13.855
O2N
n-C4H9
EtO2CN
N
n-C5H11
CO2Et
220
200
180
160
140
120
100
80
60
40
20
0
ppm

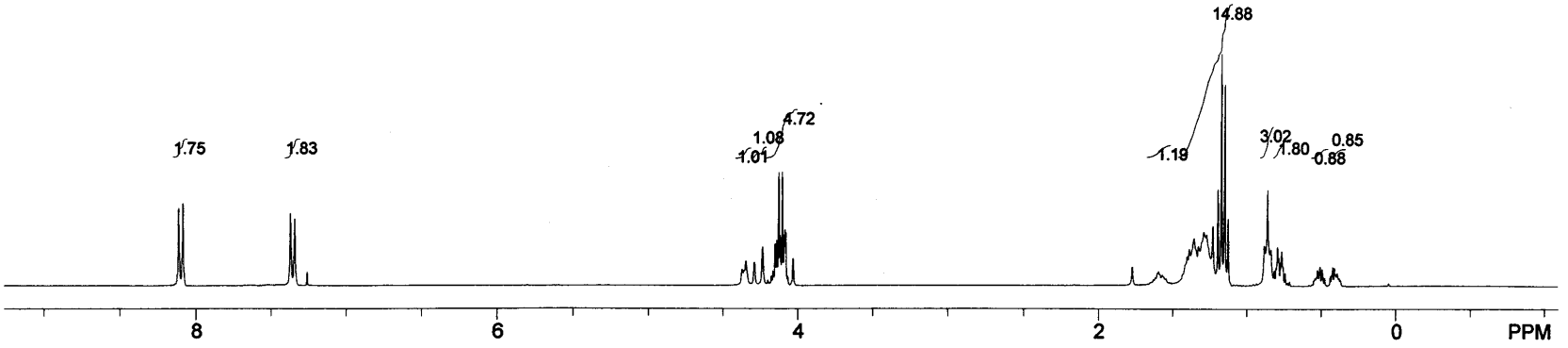
5l

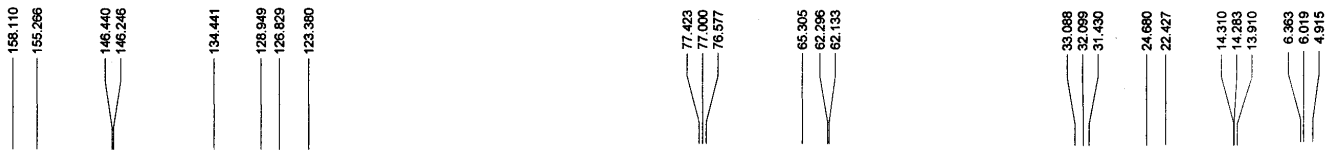

8.114
8.084
7.371
7.343
7.260
4.391
4.372
4.346
4.313
4.288
4.233
4.183
4.163
4.149
4.140
4.126
4.116
4.103
4.085
4.079
4.067
4.030
1.645
1.604
1.597
1.588
1.546
1.446
1.415
1.402
1.388
1.356
1.327
1.289
1.270
1.229
1.195
1.172
1.149
1.126
0.882
0.860
0.837
0.814
0.803
0.793
0.765
0.756
0.711
0.561
0.525
0.508
0.494
0.476
0.439
0.428
0.422
0.411
0.393
0.370


O2N
EtO2CN
N
n-C5H11
CO2Et

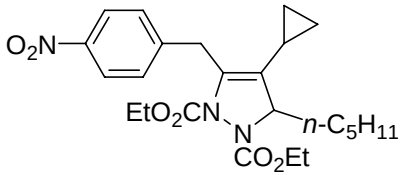
5m

cx-6-088-h

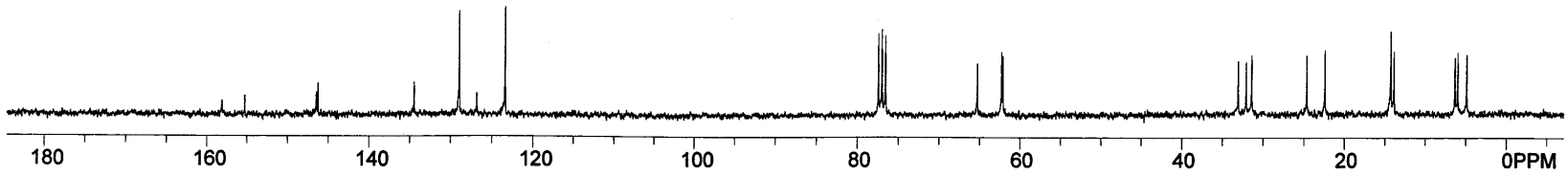

1.75
1.83
1.01
1.08
4.72
1.19
14.88
3.02
1.80
0.88
0.85
8
6
4
2
0
PPM

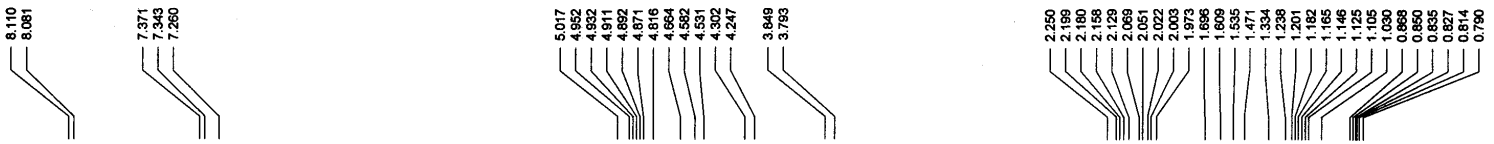

158.110
155.266
146.440
146.246
134.441
128.949
128.829
123.380
77.423
77.000
76.577
65.305
62.296
62.133
33.088
32.099
31.430
24.680
22.427
14.310
14.283
13.910
6.363
6.019
4.915

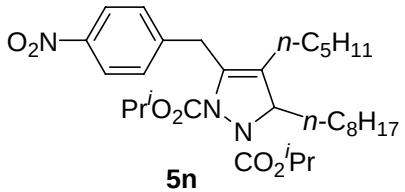
cx-6-088-c


O2N
EtO2CN
N
n-C5H11
CO2Et

5m

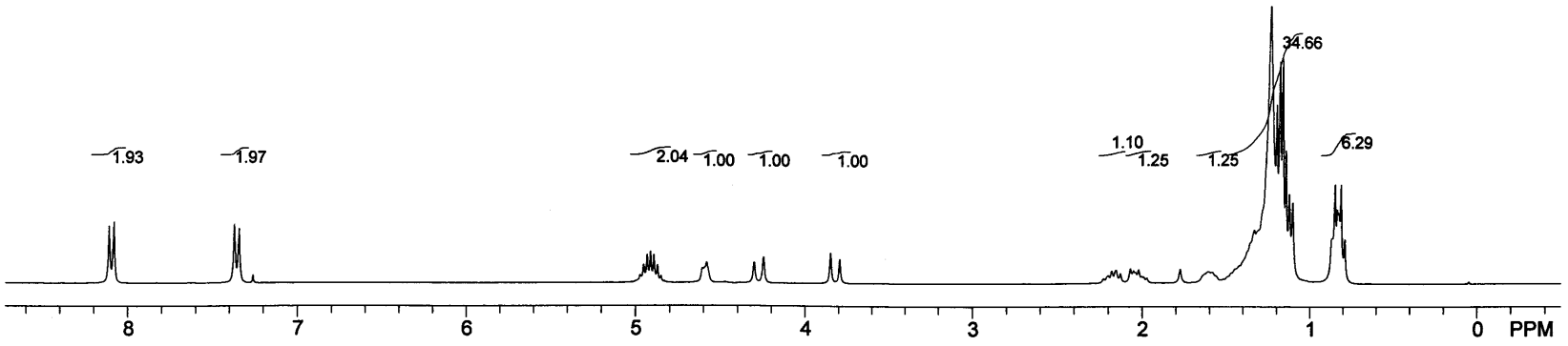

180
160
140
120
100
80
60
40
20
0PPM

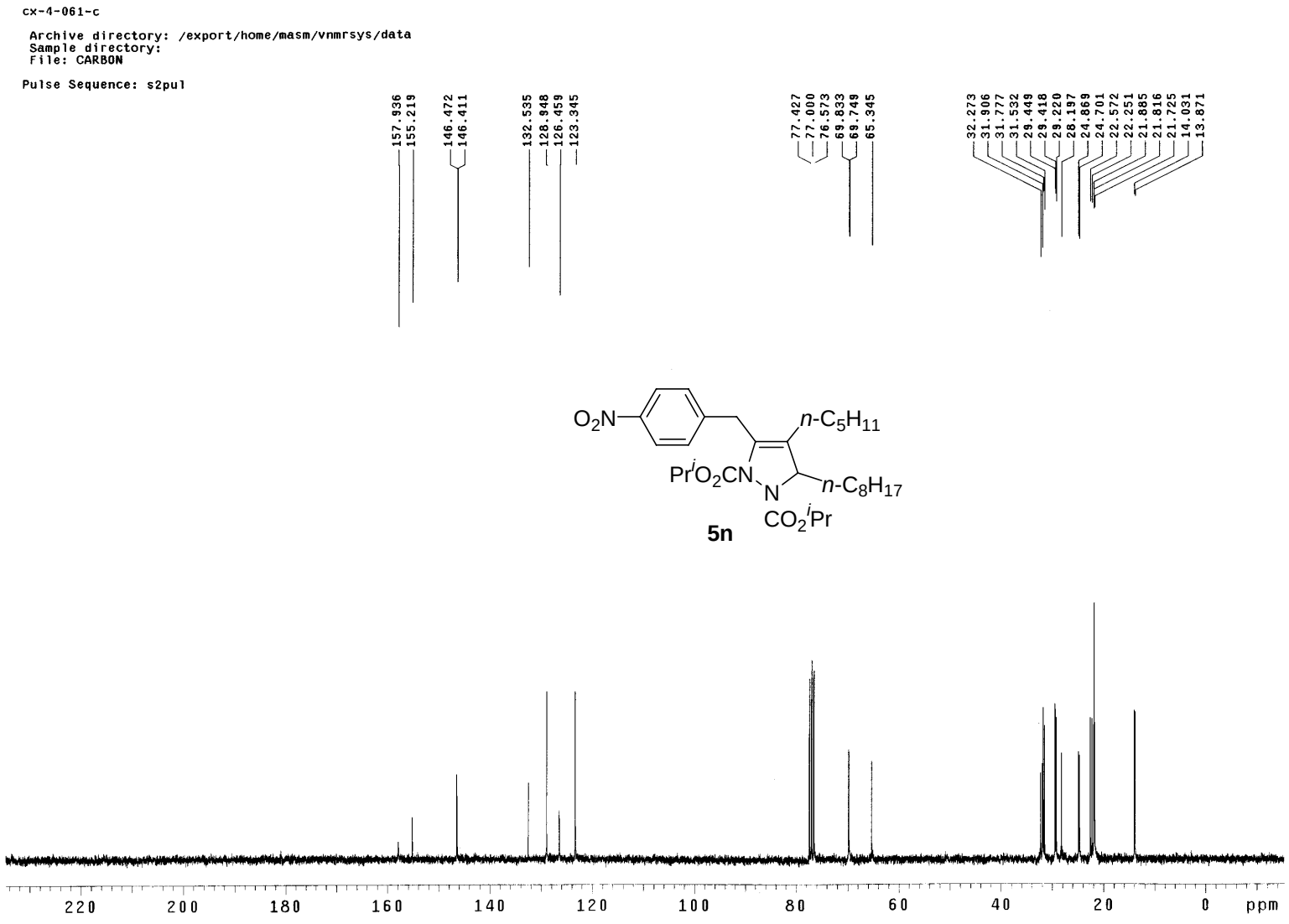

8.110
8.081
7.371
7.343
7.260
5.017
4.952
4.932
4.911
4.892
4.871
4.816
4.664
4.582
4.531
4.302
4.247
3.849
3.793
2.250
2.199
2.180
2.158
2.129
2.069
2.051
2.022
2.003
1.973
1.698
1.609
1.535
1.471
1.334
1.238
1.201
1.182
1.165
1.146
1.125
1.105
1.080
0.888
0.850
0.835
0.827
0.814
0.790

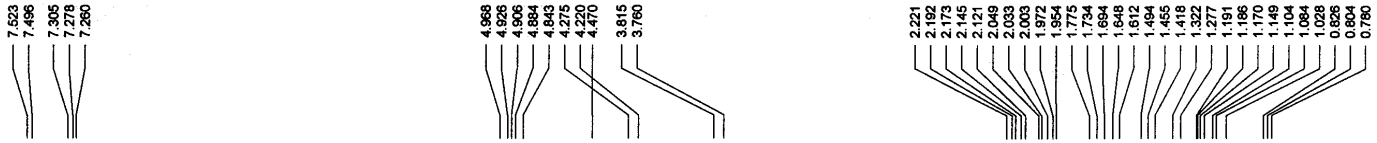

O2N
n-C5H11
PriO2CN
N
n-C8H17
CO2iPr

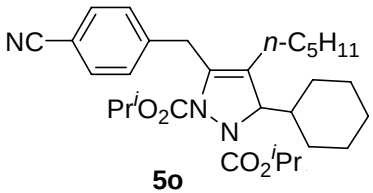
5n

cx-4-061-h


1.93
1.97
2.04
1.00
1.00
1.00
1.10
1.25
1.25
34.66
6.29
8
7
6
5
4
3
2
1
0
PPM

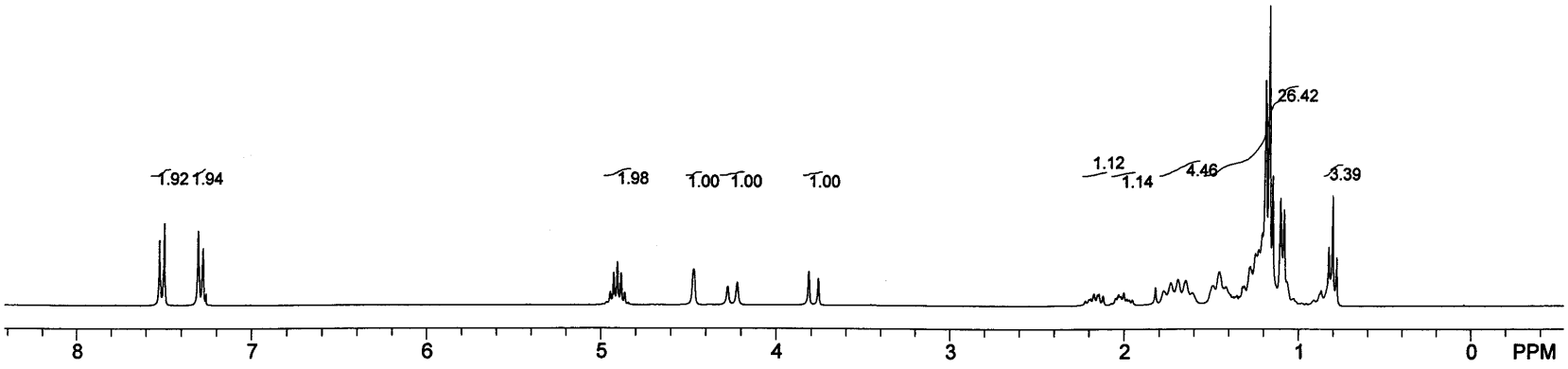

cx-4-061-c
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
157.936
155.219
146.472
146.411
132.535
128.948
126.459
123.345
77.427
77.000
76.573
69.833
69.749
65.345
32.273
31.906
31.777
31.532
29.449
29.418
29.220
28.197
24.869
24.701
22.572
22.251
21.885
21.816
21.725
14.031
13.871
O2N
n-C5H11
PriO2CN
N
n-C8H17
CO2iPr
5n
220
200
180
160
140
120
100
80
60
40
20
0
ppm

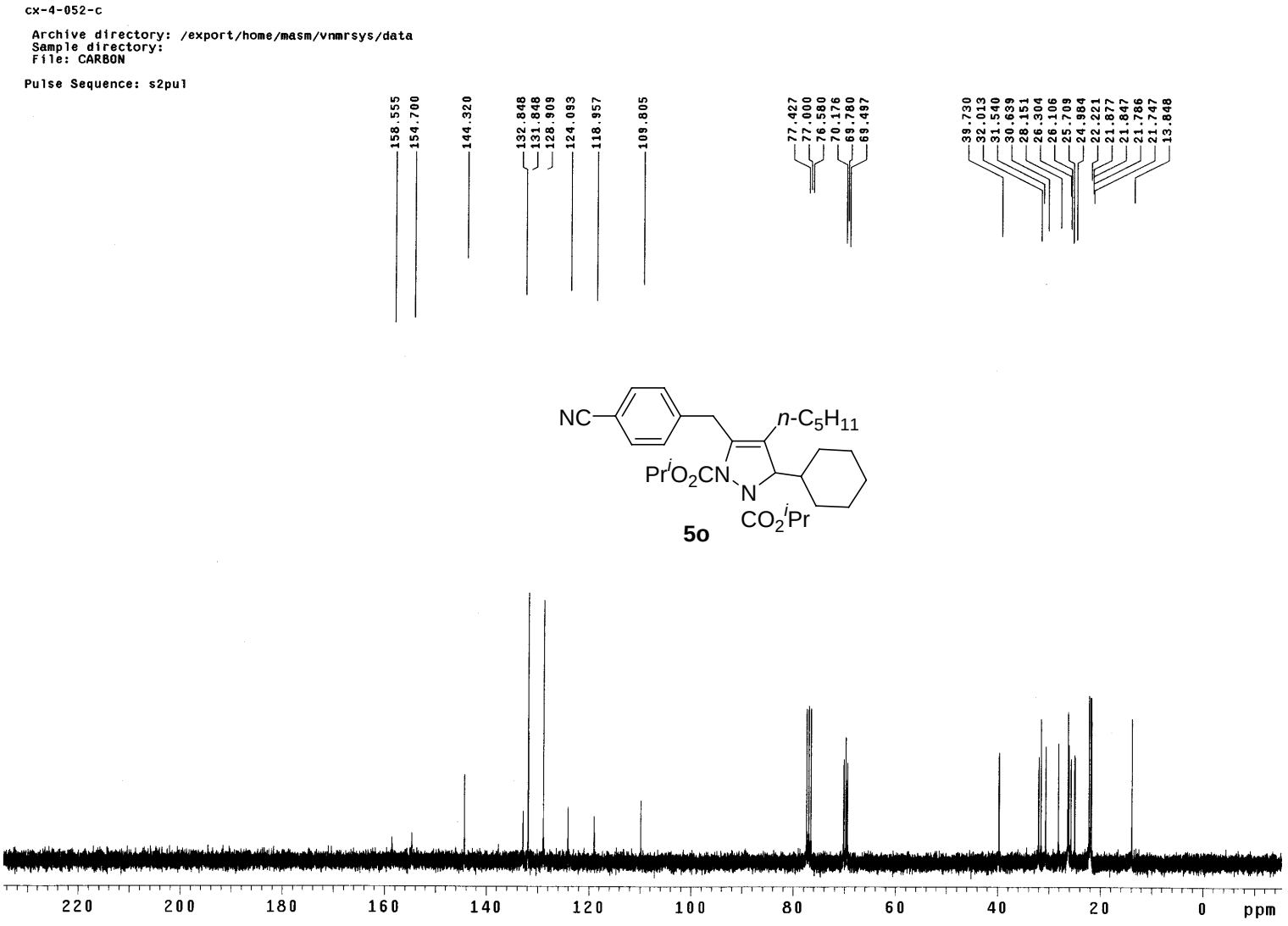

7.523
7.496
7.305
7.278
7.260
4.968
4.928
4.906
4.884
4.843
4.275
4.220
4.470
3.815
3.760
2.221
2.192
2.173
2.145
2.121
2.049
2.033
2.003
1.972
1.954
1.775
1.734
1.694
1.648
1.612
1.494
1.455
1.418
1.322
1.277
1.191
1.186
1.170
1.149
1.104
1.084
1.028
0.826
0.804
0.780

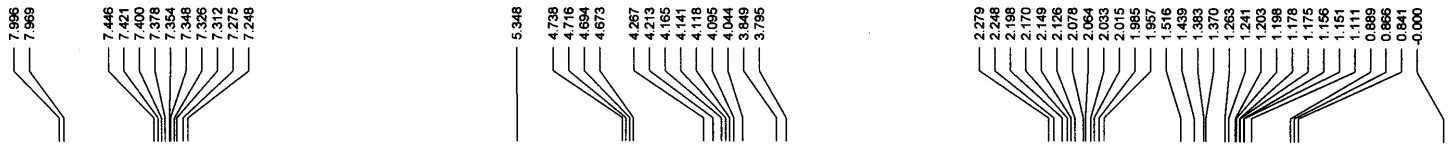

NC
n-C5H11
PriO2CN
N
CO2iPr

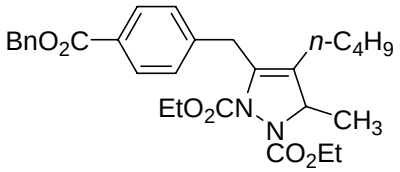
5o

cx-4-052-h


1.92
1.94
1.98
1.00
1.00
1.00
1.12
1.14
4.46
26.42
3.39
8
7
6
5
4
3
2
1
0
PPM

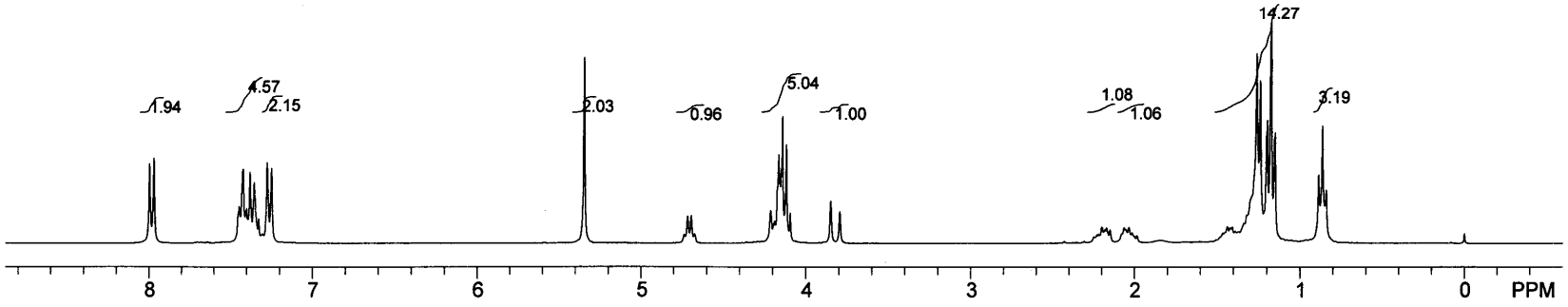

cx-4-052-c
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
158.555
154.700
144.320
132.848
131.848
128.909
124.093
118.957
109.805
77.427
77.000
76.580
70.176
69.780
69.497
39.730
32.013
31.540
30.639
28.151
26.304
26.106
25.709
24.984
22.221
21.877
21.847
21.786
21.747
13.848
NC
n-C5H11
PriO2CN
N
CO2iPr
5o
220
200
180
160
140
120
100
80
60
40
20
0
ppm

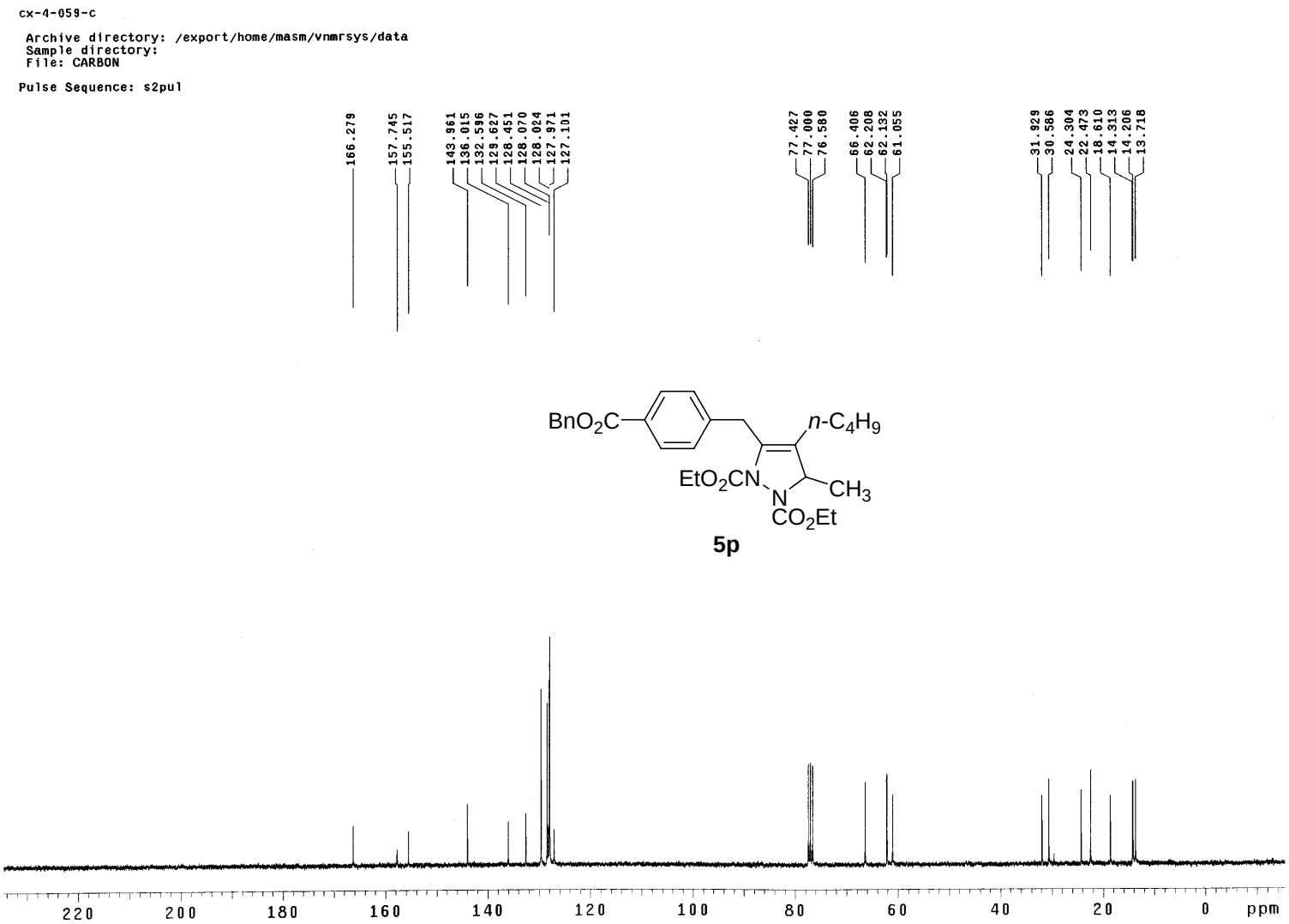

7.996
7.969
7.446
7.421
7.400
7.378
7.354
7.348
7.326
7.312
7.275
7.248
5.348
4.738
4.716
4.694
4.673
4.267
4.213
4.165
4.141
4.118
4.095
4.044
3.849
3.795
2.279
2.248
2.198
2.170
2.149
2.126
2.078
2.064
2.033
2.015
1.985
1.957
1.516
1.439
1.383
1.370
1.263
1.241
1.203
1.198
1.178
1.175
1.156
1.151
1.111
0.889
0.866
0.841
0.000

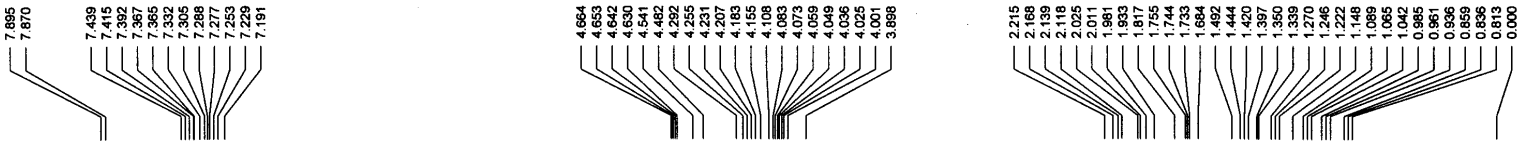

BnO2C
n-C4H9
EtO2CN
CH3
N
CO2Et

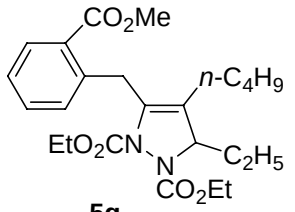
5p

cx-4-059-h


1.94
4.57
2.15
2.03
0.96
5.04
1.00
1.08
1.06
14.27
3.19
8
7
6
5
4
3
2
1
0
PPM

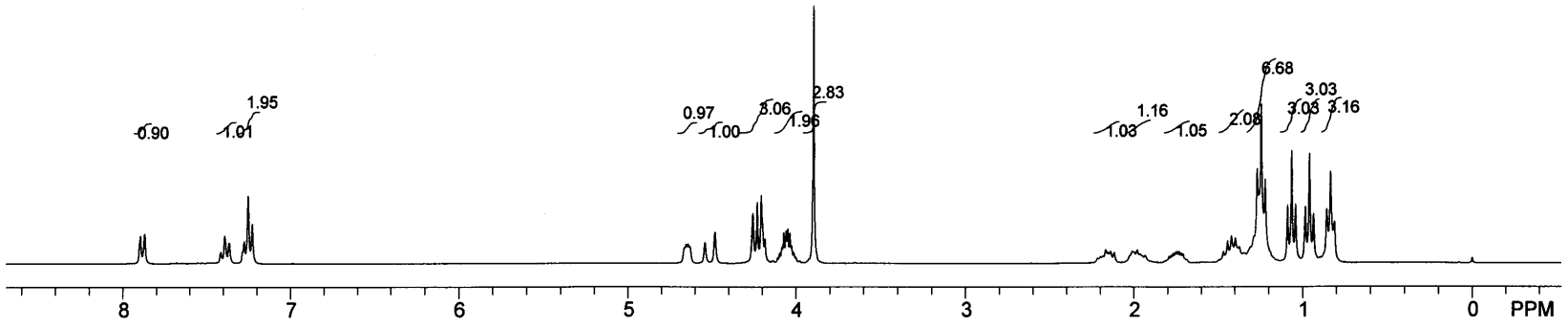

cx-4-059-c
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
166.279
157.745
155.517
143.961
136.015
132.596
129.627
128.451
128.070
128.024
127.971
127.101
77.427
77.000
76.580
66.406
62.208
62.132
61.055
31.929
30.586
24.304
22.473
18.610
14.313
14.206
13.718
BnO2C
n-C4H9
EtO2CN
CH3
N
CO2Et
5p
220
200
180
160
140
120
100
80
60
40
20
0
ppm

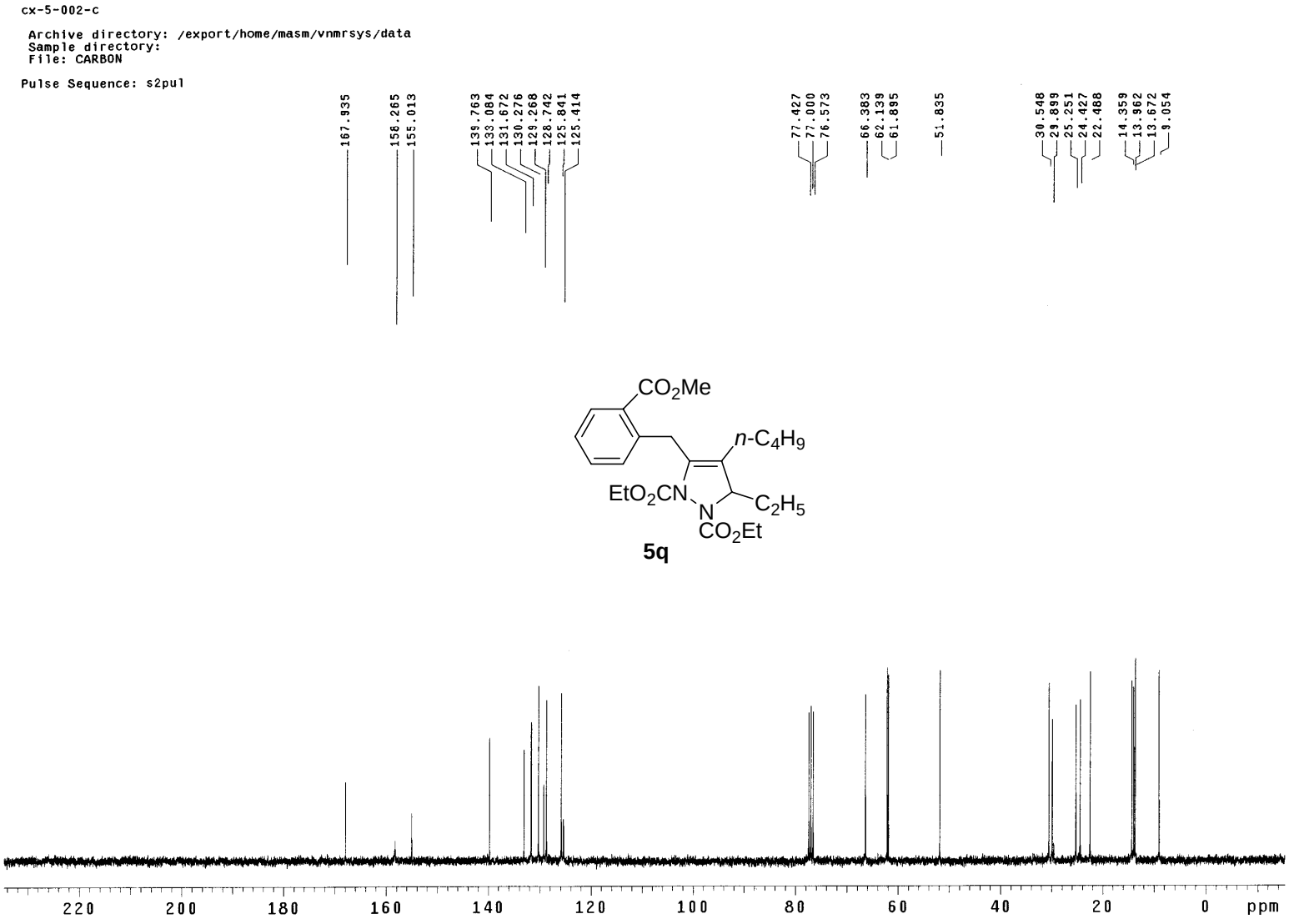

7.895
7.870
7.439
7.415
7.392
7.367
7.365
7.332
7.305
7.288
7.277
7.253
7.229
7.191
4.664
4.653
4.642
4.630
4.541
4.482
4.292
4.255
4.231
4.207
4.183
4.155
4.108
4.083
4.073
4.059
4.049
4.036
4.025
4.001
3.898
2.215
2.168
2.139
2.118
2.025
2.011
1.981
1.933
1.817
1.755
1.744
1.733
1.684
1.492
1.444
1.420
1.397
1.350
1.339
1.270
1.246
1.222
1.148
1.089
1.065
1.042
0.985
0.961
0.936
0.859
0.836
0.813
0.000

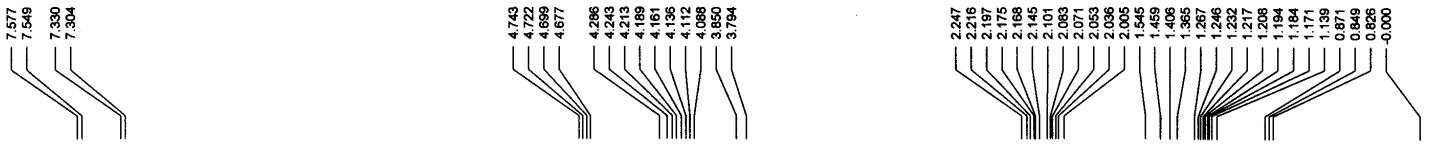

CO2Me
n-C4H9
EtO2CN
N
C2H5
CO2Et

5q

cx-5-002-h


0.90
1.91
1.95
0.97
1.00
3.06
1.96
2.83
1.03
1.16
1.05
2.08
6.68
3.03
3.05
3.16
8
7
6
5
4
3
2
1
0
PPM


cx-5-002-c
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
167.935
158.265
155.013
139.763
133.084
131.672
130.276
129.268
128.742
125.841
125.414
77.427
77.000
76.573
66.383
62.139
61.895
51.835
30.548
29.899
25.251
24.427
22.488
14.359
13.962
13.672
9.054
CO2Me
n-C4H9
EtO2CN
N
C2H5
CO2Et
5q
220
200
180
160
140
120
100
80
60
40
20
0
ppm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7.304
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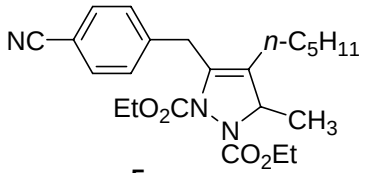
4.677
4.286
4.243
4.213
4.189
4.161
4.136
4.112
4.088
3.850
3.794
2.247
2.216
2.197
2.175
2.168
2.145
2.101
2.083
2.071
2.053
2.036
2.005
1.545
1.459
1.406
1.365
1.267
1.246
1.232
1.217
1.208
1.194
1.184
1.171
1.139
0.871
0.849
0.826
-0.000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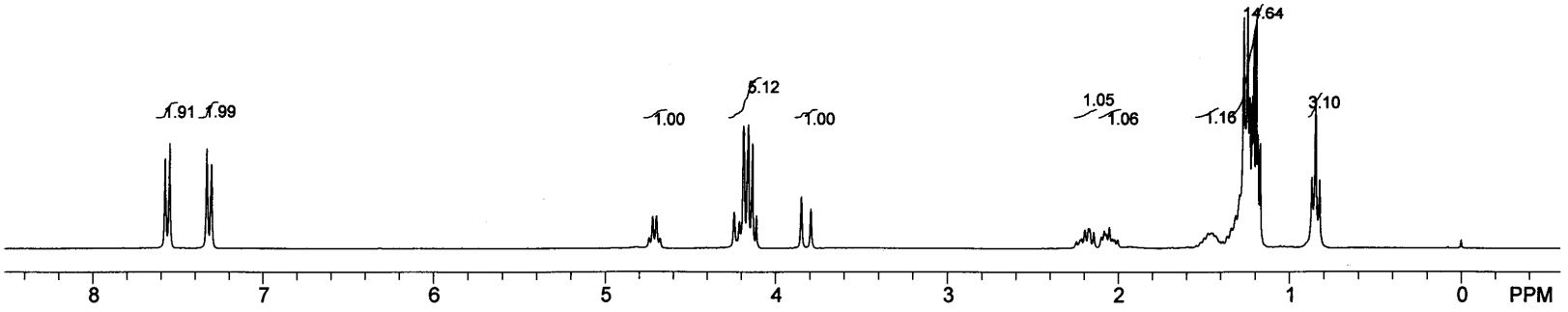
n-C5H11
EtO2CN
N
CH3
CO2Et

5r

cx-4-183-h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1.16
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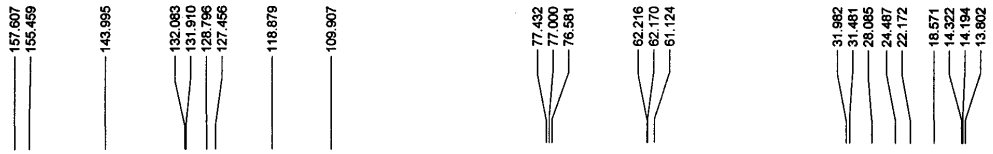
5
4
3
2
1
0
PPM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155.459
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128.796
127.456
118.879
109.907
77.432
77.000
76.581
62.216
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61.124
31.982
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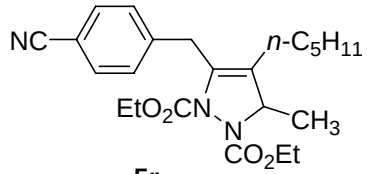
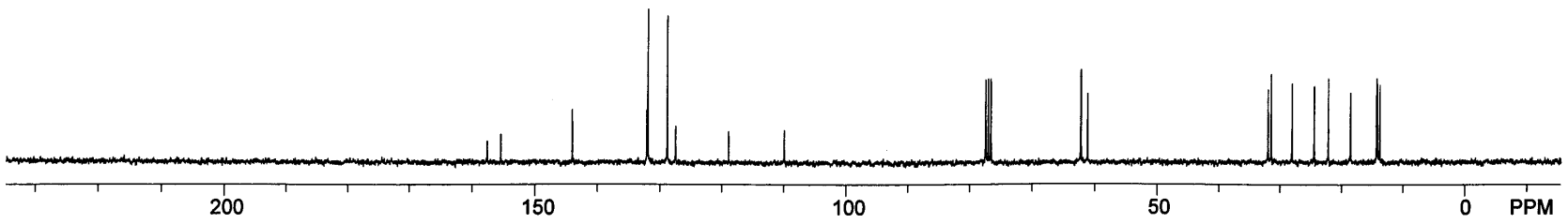
28.085
24.487
22.172
18.571
14.322
14.194
13.802


NC
n-C5H11
EtO2CN
N
CH3
CO2Et

5r

cx-4-183-c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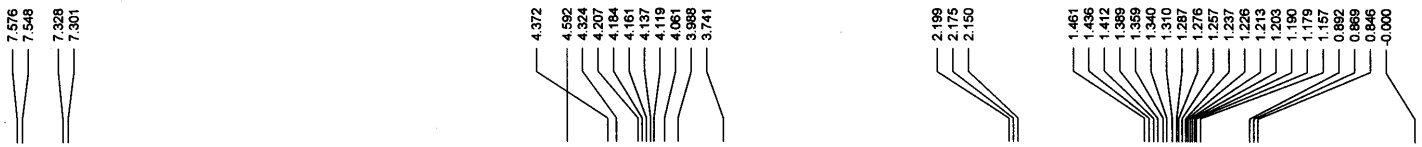
150
100
50
0
PPM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4.592
4.324
4.207
4.184
4.161
4.137
4.119
4.061
3.988
3.741
2.199
2.175
2.150
1.461
1.436
1.412
1.389
1.359
1.340
1.310
1.287
1.276
1.257
1.237
1.226
1.213
1.203
1.190
1.179
1.157
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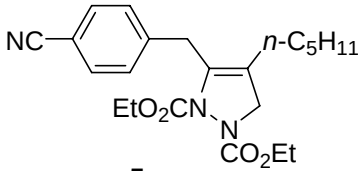
0.869
0.846
-0.000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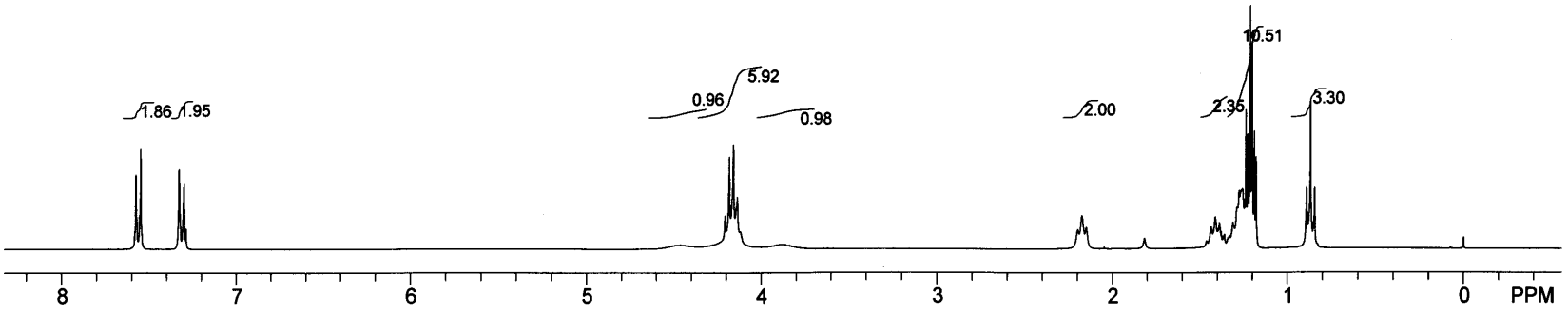
n-C5H11
EtO2CN
N
CO2Et

5s

cx-6-109-h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0.96
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0.98
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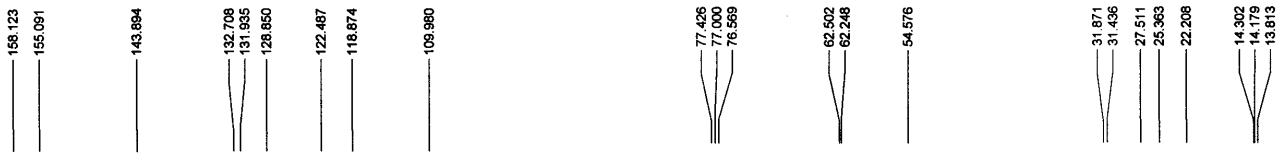
2.35
10.51
3.30
8
7
6
5
4
3
2
1
0
PPM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143.894
132.708
131.935
128.850
122.487
118.874
109.980
77.426
77.000
76.569
62.502
62.248
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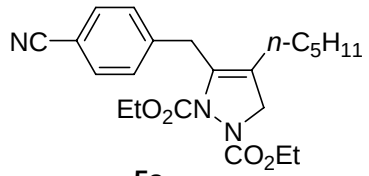
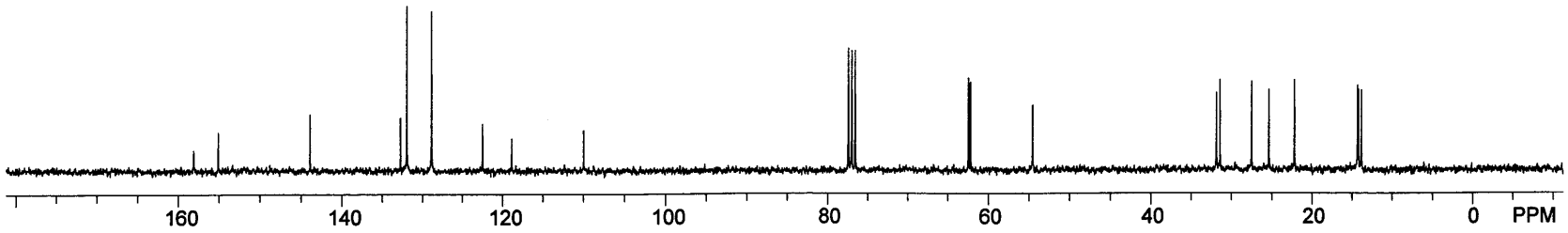
31.871
31.436
27.511
25.363
22.208
14.302
14.179
13.813

cx-6-109-c


NC
n-C5H11
EtO2CN
N
CO2Et

5s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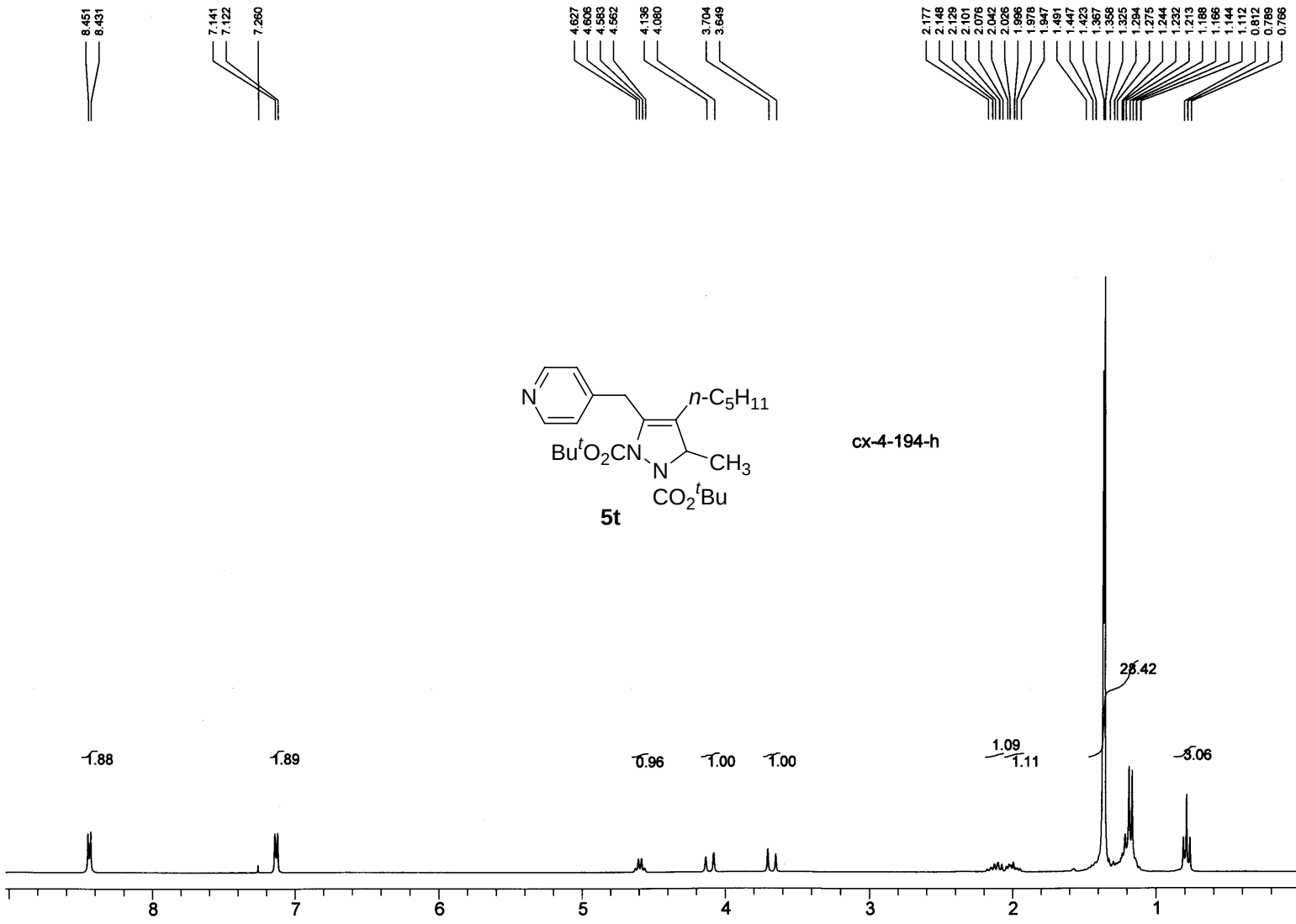
140
120
100
80
60
40
20
0
PPM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8.431
7.141
7.122
7.260
4.627
4.606
4.583
4.562
4.136
4.080
3.704
3.649
2.177
2.148
2.129
2.101
2.076
2.042
2.026
1.996
1.978
1.947
1.491
1.447
1.423
1.367
1.358
1.325
1.294
1.275
1.244
1.232
1.213
1.188
1.166
1.144
1.112
0.812
0.788
0.766
N
n-C5H11
ButO2CN
N
CH3
CO2tBu
5t
cx-4-194-h
1.88
1.89
0.96
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1.11
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3.06
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7
6
5
4
3
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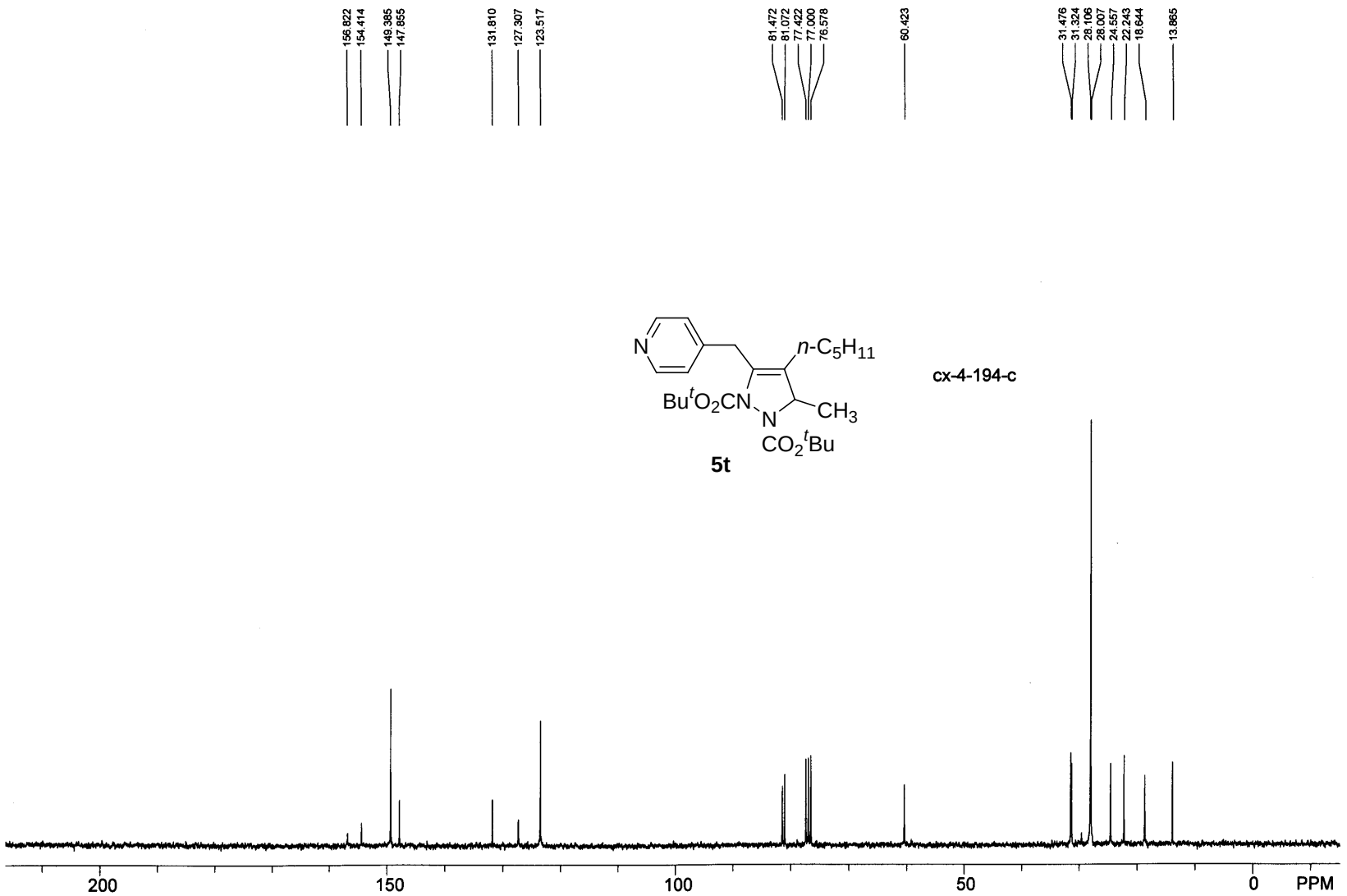
1
0
PPM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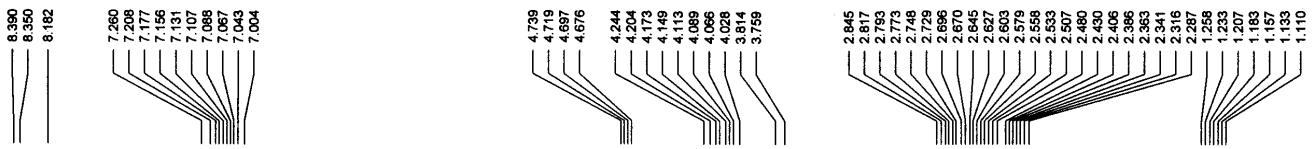
154.414
149.385
147.855
131.810
127.307
123.517
81.472
81.072
77.422
77.000
76.578
60.423
31.476
31.324
28.106
28.007
24.557
22.243
18.644
13.865
N
n-C5H11
ButO2CN
N
CH3
CO2tBu
5t
cx-4-194-c
200
150
100
50
0
PPM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8.350
8.182
7.260
7.208
7.177
7.156
7.131
7.107
7.088
7.067
7.043
7.004
4.739
4.719
4.697
4.676
4.244
4.204
4.173
4.149
4.113
4.089
4.066
4.028
3.814
3.759
2.845
2.817
2.793
2.773
2.748
2.729
2.696
2.670
2.645
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2.430
2.406
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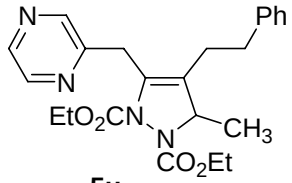
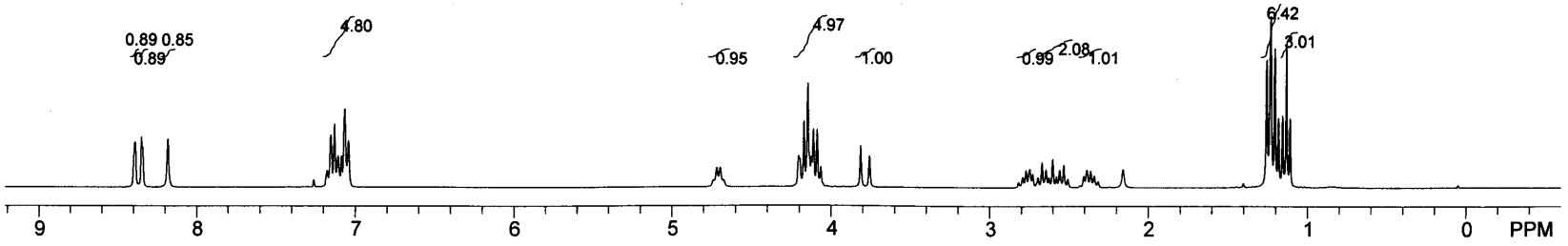
2.316
2.287
1.258
1.233
1.207
1.183
1.157
1.133
1.110


N
N
Ph
EtO2CN
N
CH3
CO2Et

5u

cx-6-068-h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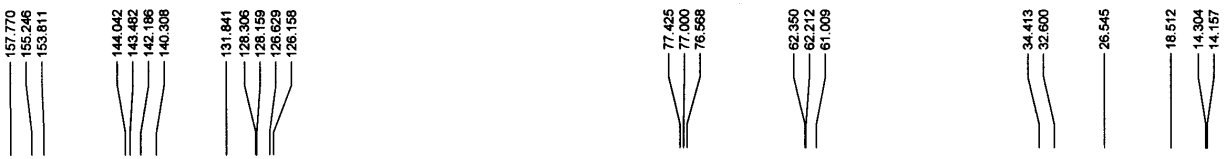
0.89
4.80
0.95
4.97
1.00
0.99
2.08
1.01
6.42
3.01
9
8
7
6
5
4
3
2
1
0
PPM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153.811
144.042
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142.186
140.308
131.841
128.306
128.159
126.629
126.158
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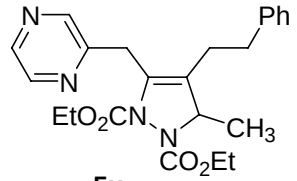
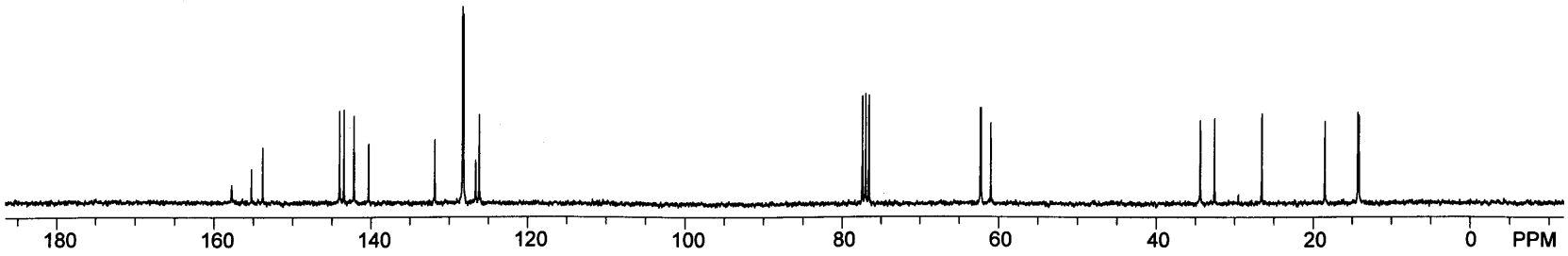
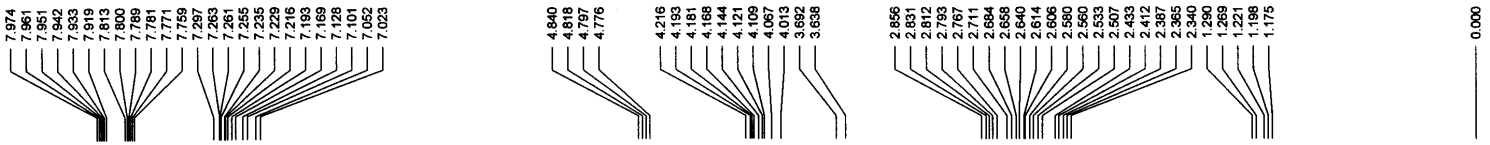
34.413
32.600
26.545
18.512
14.304
14.157


N
N
Ph
EtO2CN
N
CH3
CO2Et

5u

cx-6-068-c


180
160
140
120
100
80
60
40
20
0
PPM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7.813
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7.781
7.771
7.759
7.297
7.263
7.261
7.255
7.235
7.229
7.216
7.193
7.169
7.128
7.101
7.052
7.023
4.840
4.818
4.797
4.776
4.216
4.193
4.181
4.168
4.144
4.121
4.109
4.067
4.013
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2.831
2.812
2.793
2.767
2.711
2.684
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2.640
2.614
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2.580
2.560
2.533
2.507
2.433
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2.387
2.365
2.340
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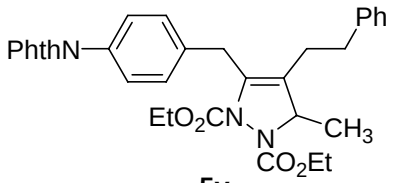
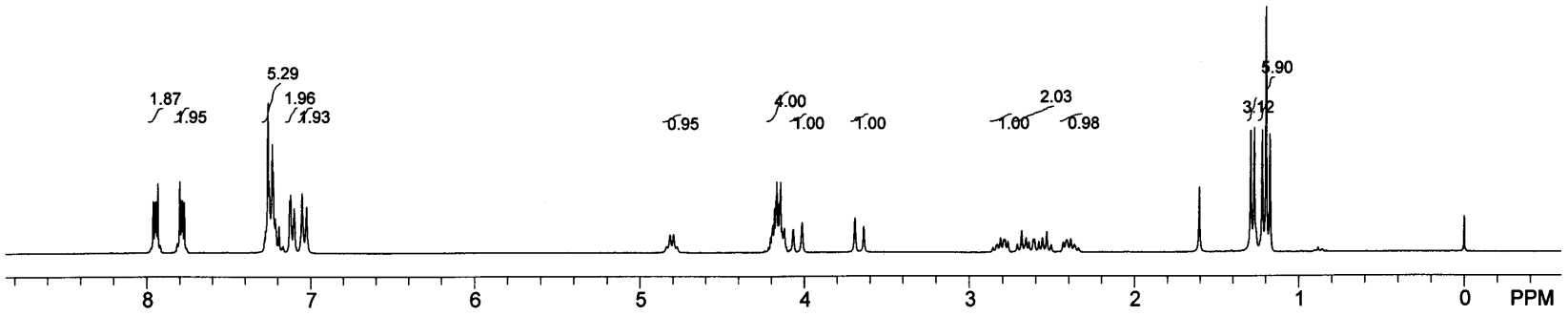
1.269
1.221
1.198
1.175
0.000

cx-6-116-h


PhthN
Ph
EtO2CN
N
CH3
CO2Et

5v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1.93
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1.00
1.00
2.03
1.00
0.98
5.90
3.12
8
7
6
5
4
3
2
1
0
PPM


167.254
158.131
155.404
140.446
137.965
134.273
134.073
131.626
129.460
128.658
128.502
128.322
126.235
126.123
125.698
123.576
77.426
77.000
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62.171
60.778
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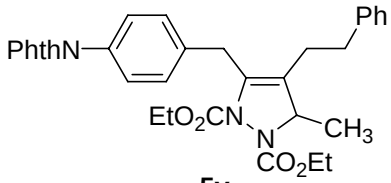
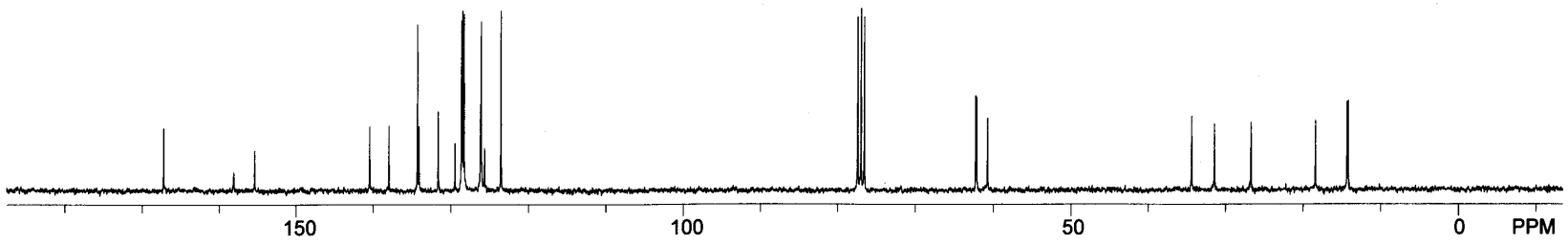
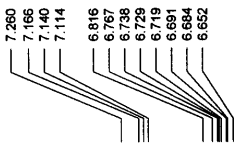
31.439
26.713
18.459
14.385
14.226

cx-6-116-c


PhthN
Ph
EtO2CN
N
CH3
CO2Et

5v


150
100
50
0
PPM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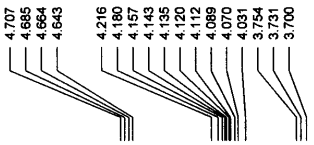
6.816
6.767
6.738
6.729
6.719
6.691
6.684
6.652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4.643
4.216
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4.135
4.120
4.112
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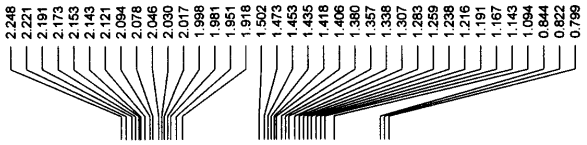
4.070
4.031
3.754
3.731
3.700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2.221
2.191
2.173
2.153
2.143
2.121
2.094
2.078
2.046
2.030
2.017
1.998
1.981
1.951
1.918
1.502
1.473
1.453
1.435
1.418
1.406
1.380
1.357
1.338
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1.238
1.216
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1.167
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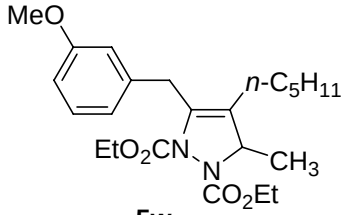
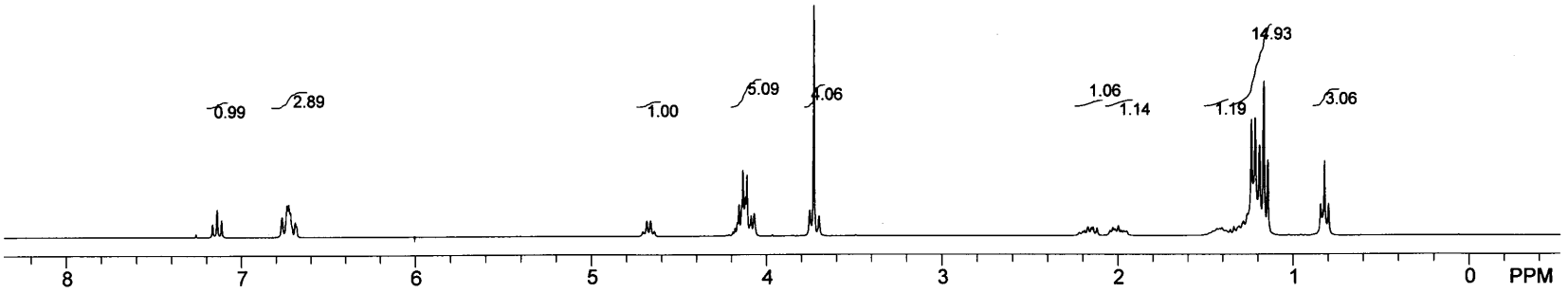
0.822
0.799


MeO
n-C5H11
EtO2CN
N
CH3
CO2Et

5w

cx-6-117-h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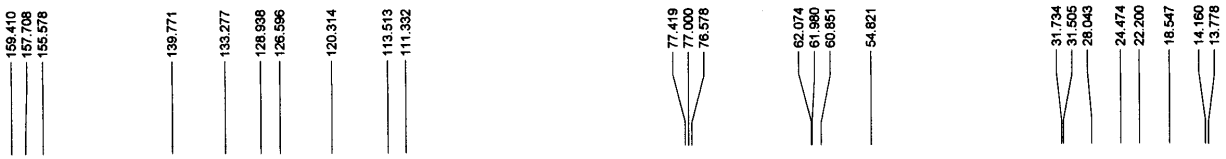
1.19
14.93
3.06
8
7
6
5
4
3
2
1
0
PPM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139.771
133.277
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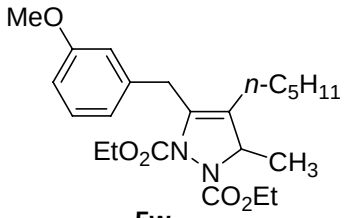
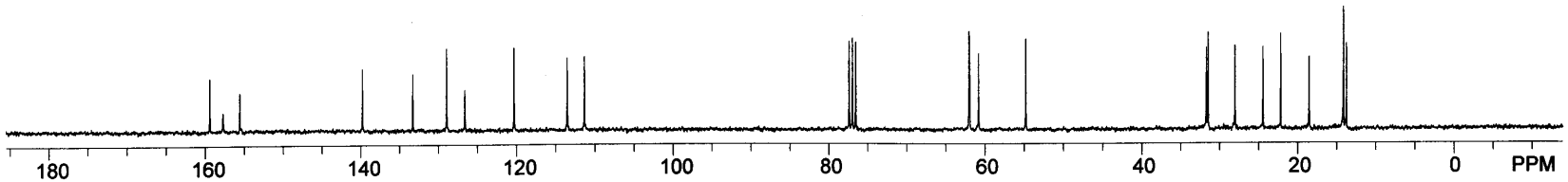
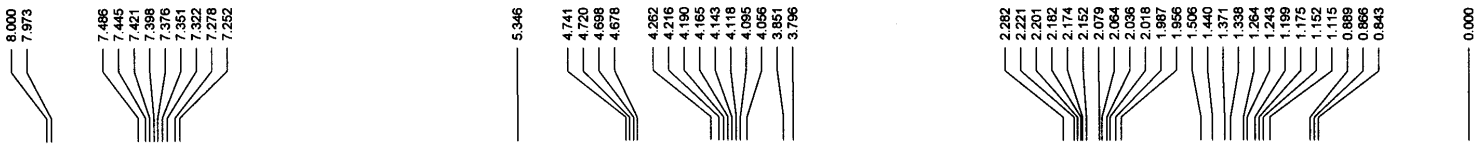
126.596
120.314
113.513
111.332
77.419
77.000
76.578
62.074
61.980
60.851
54.821
31.734
31.505
28.043
24.474
22.200
18.547
14.160
13.778

cx-6-117-c


MeO
n-C5H11
EtO2CN
N
CH3
CO2Et

5w


180
160
140
120
100
80
60
40
20
0
PPM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7.421
7.398
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7.278
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5.346
4.741
4.720
4.698
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4.216
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4.095
4.056
3.851
3.796
2.282
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2.182
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2.064
2.036
2.018
1.987
1.956
1.506
1.440
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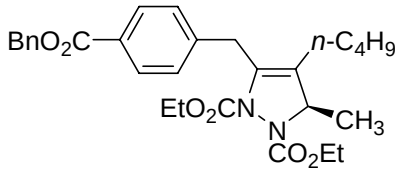
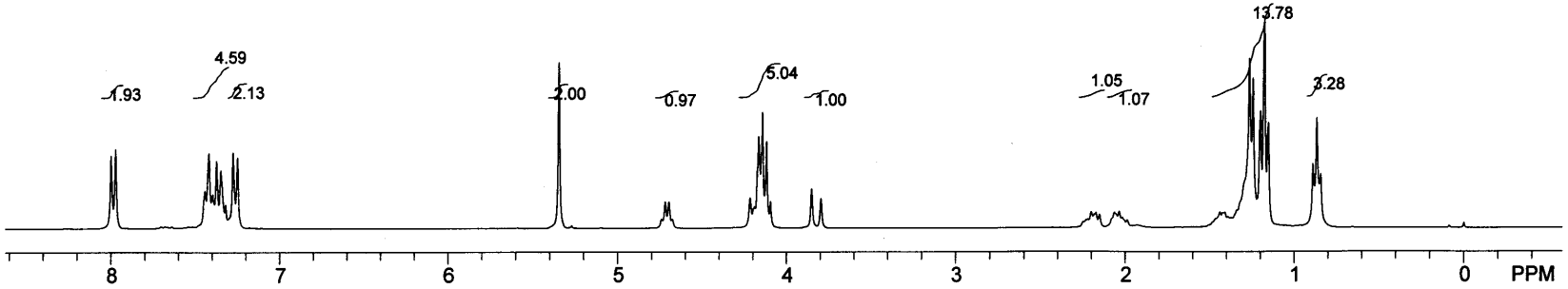
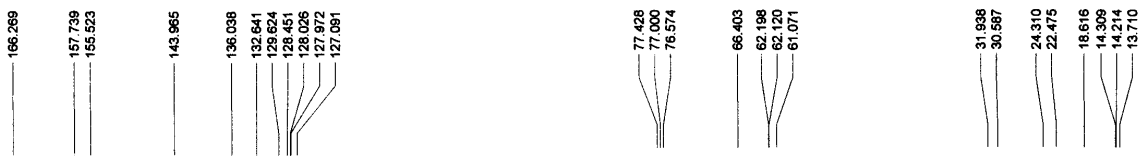
1.338
1.264
1.243
1.199
1.175
1.152
1.115
0.889
0.866
0.843
0.000

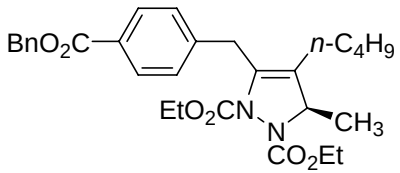

BnO2C
n-C4H9
EtO2CN
CH3
N
CO2Et

(*R*)-5p

cx-4-081-h

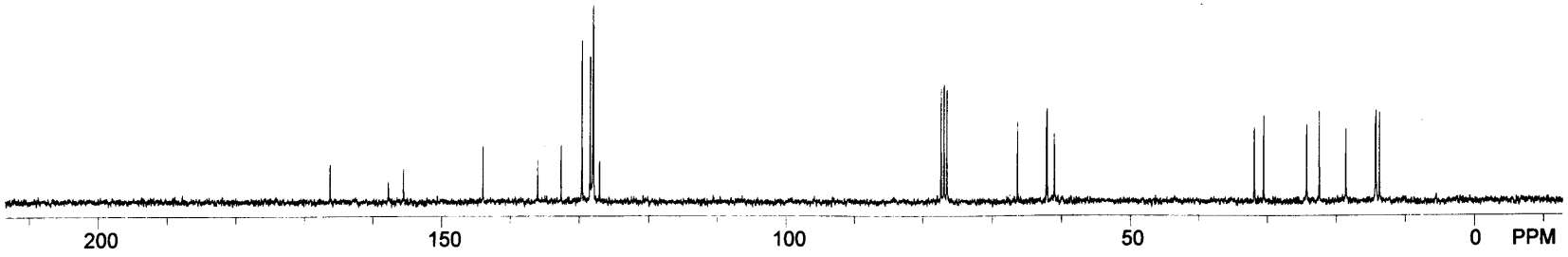

1.93
4.59
2.13
2.00
0.97
5.04
1.00
1.05
1.07
13.78
3.28
8
7
6
5
4
3
2
1
0
PPM


166.269
157.739
155.523
143.965
136.038
132.641
129.624
128.451
128.026
127.972
127.091
77.428
77.000
76.574
66.403
62.198
62.120
61.071
31.938
30.587
24.310
22.475
18.616
14.309
14.214
13.710


BnO2C
n-C4H9
EtO2CN
N
CH3
CO2Et

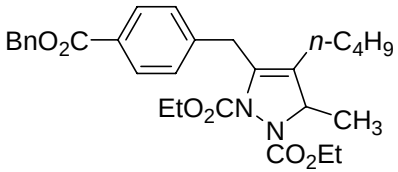
(*R*)-5p

cx-4-081-c

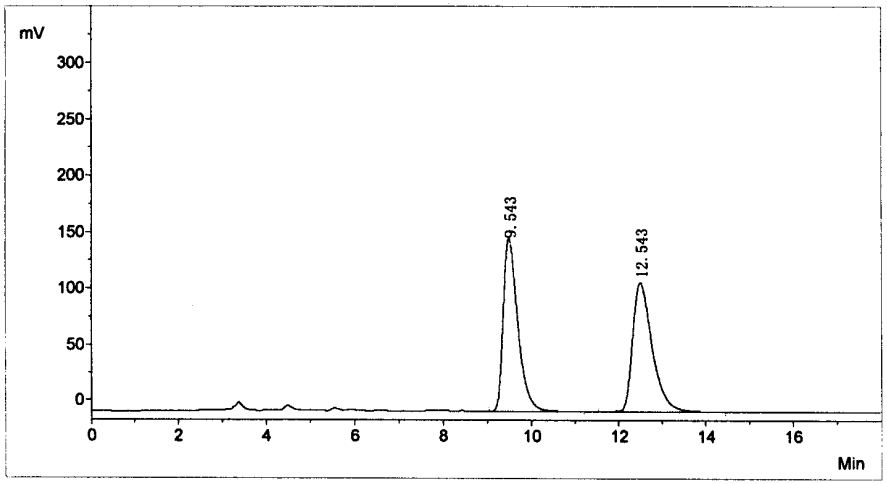

200
150
100
50
0
PPM

HPLC REPORT

Sample Name:cx-4-059-rac ad 85.che
Date:2007-06-22
Time:09:39
Method:
Column: AD-H
Flow Rate: 0.7 ml/min
Wave Length: 254 nm
Mobile Phase: 85/15



racemic 5p

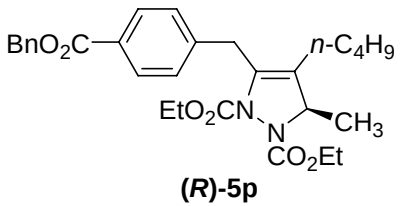


No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	9.543	148496.8	3564196.9	49.7609
2	2	Unknown	12.543	113102.5	3598441.9	50.2391
Total				261599.4	7162638.8	100.0000

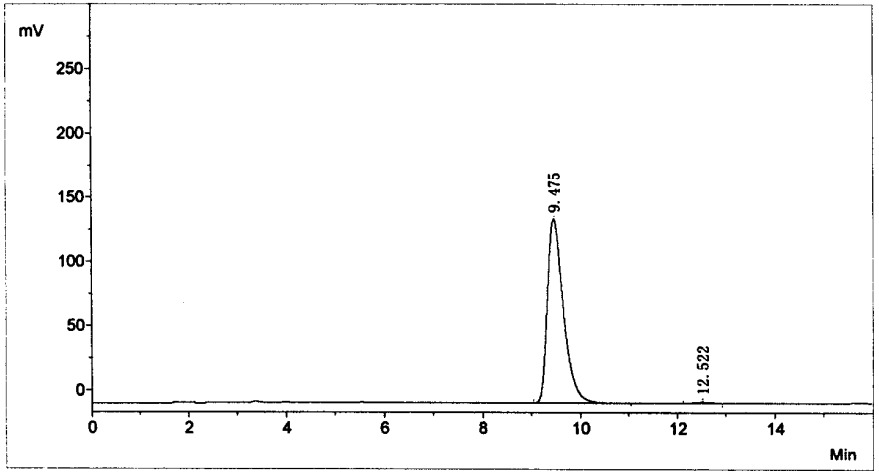
HPLC REPORT

Sample Name:cx-4-081.che
Time:10:26
Column: AD-H
Wave Length: 254nm

Date:2007-06-22
Method:
Flow Rate: 0.7ml/min
Mobile Phase: 85/15



(*R*)-5p



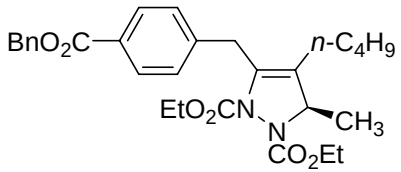
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	9.475	142625.8	3261817.3	99.3508
2	2	Unknown	12.522	897.6	21313.9	0.6492
Total				143523.3	3283131.2	100.0000

99%ee

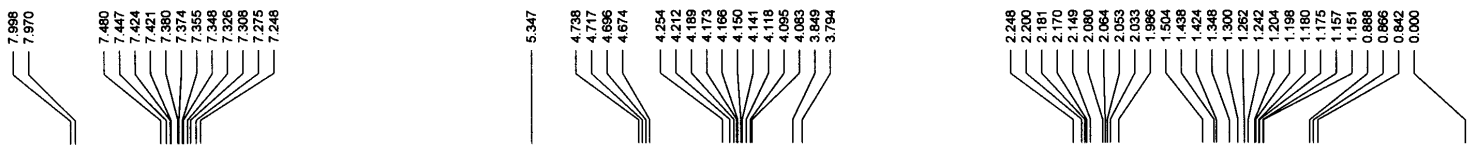
4-081
20mg, C=1.00, $CHCl_3$

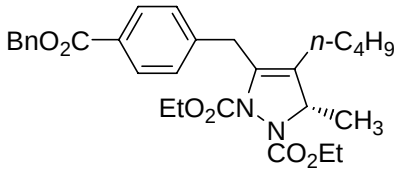
0040	589 nm	20.0	1.0000	+0.467	+46.7
0041	589 nm	20.0	1.0000	+0.465	+46.5
0042	589 nm	20.0	1.0000	+0.468	+46.8
0043	589 nm	20.0	1.0000	+0.468	+46.8
0044	589 nm	20.0	1.0000	+0.467	+46.7
0045	589 nm	20.0	1.0000	+0.468	+46.8
0046	589 nm	20.0	1.0000	+0.468	+46.8
0047	589 nm	20.0	1.0000	+0.468	+46.8

+46.7



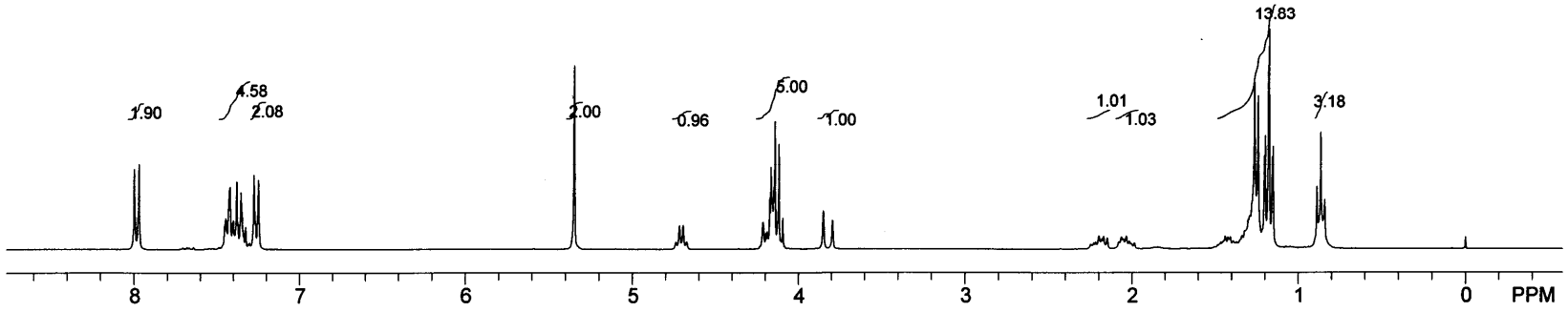
(*R*)-5p

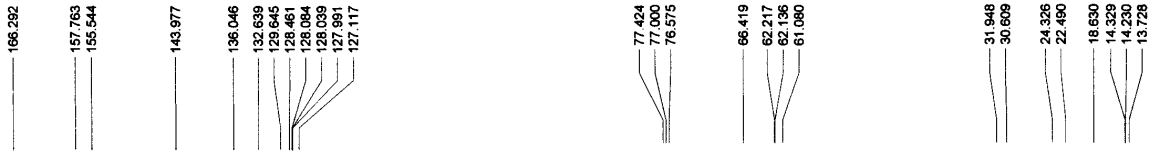

7.998
7.970
7.480
7.447
7.424
7.421
7.380
7.374
7.355
7.348
7.326
7.306
7.275
7.248
5.347
4.738
4.717
4.696
4.674
4.254
4.212
4.189
4.173
4.166
4.150
4.141
4.118
4.095
4.083
3.849
3.794
2.248
2.200
2.181
2.170
2.149
2.080
2.064
2.053
2.033
1.986
1.504
1.438
1.424
1.348
1.300
1.262
1.242
1.204
1.198
1.180
1.175
1.157
1.151
0.888
0.866
0.842
0.000

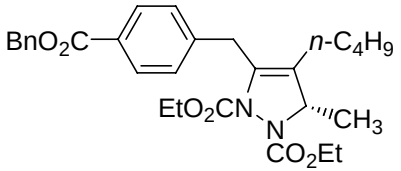

BnO2C
n-C4H9
EtO2CN
CH3
N
CO2Et

(*S*)-5p

cx-4-082-h

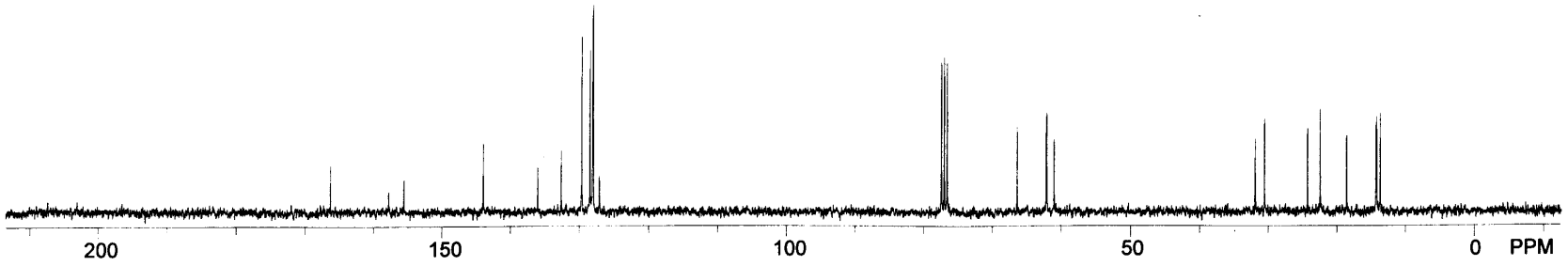

1.90
4.58
2.08
2.00
0.96
5.00
1.00
1.01
1.03
13.83
3.18
8
7
6
5
4
3
2
1
0
PPM


166.292
157.763
155.544
143.977
136.046
132.639
129.645
128.461
128.084
128.039
127.991
127.117
77.424
77.000
76.575
66.419
62.217
62.136
61.080
31.948
30.609
24.326
22.490
18.630
14.329
14.230
13.728


BnO2C
n-C4H9
EtO2CN
N
CH3
CO2Et

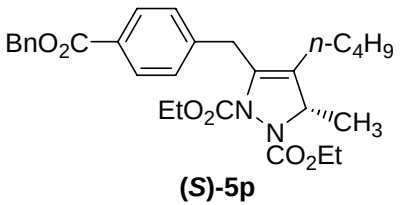
(*S*)-5p

cx-4-082-c

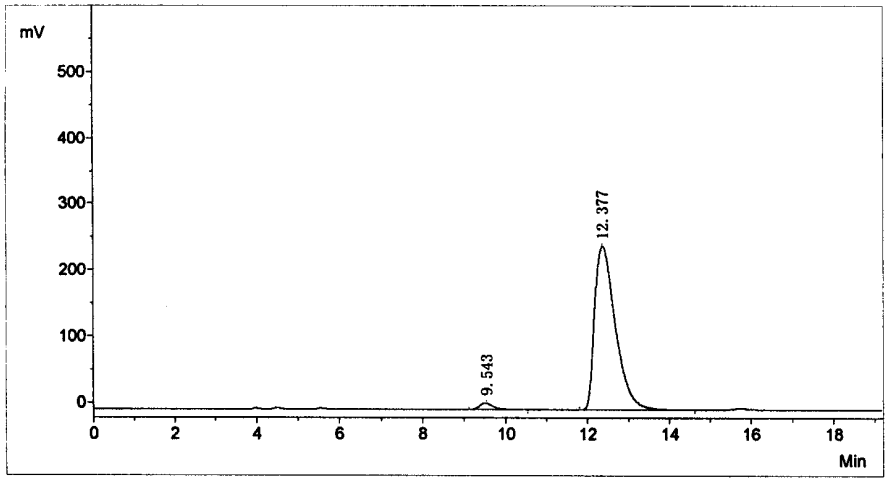

200
150
100
50
0
PPM

HPLC REPORT

Sample Name:cx-4-082.che
Date:2007-06-22
Time:10:05
Method:
Column: AD-H
Flow Rate: 0.7 ml/min
Wave Length: 254nm
Mobile Phase: 85/15



(*S*)-5p



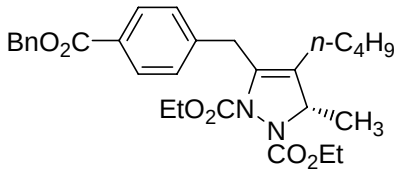
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	9.543	9585.0	213507.8	2.4012
2	2	Unknown	12.377	245719.9	8678101.4	97.5988
Total				255304.9	8891609.2	100.0000

95% ee

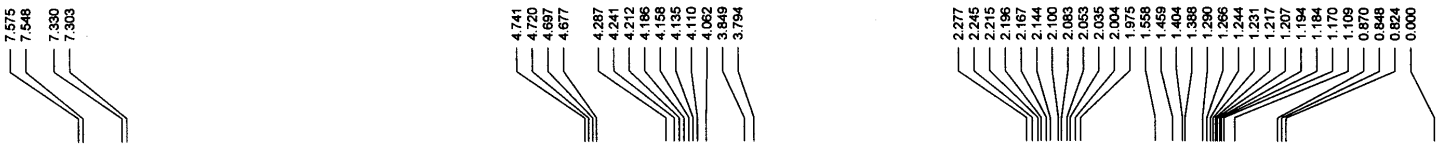
0049	589 nm	20.0	1.0500	-0.180	-15.8
0050	589 nm	20.0	1.0500	-0.181	-15.8
0051	589 nm	20.0	1.0500	-0.181	-15.8
0052	589 nm	20.0	1.0500	-0.183	-16.0
0053	589 nm	20.0	1.0500	-0.183	-16.0
0054	589 nm	20.0	1.0500	-0.183	-16.0
0055	589 nm	20.0	1.0500	-0.175	-15.3

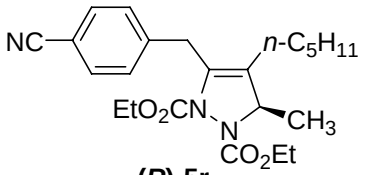
4-082
21mg, c=1.05, CH_2Cl_2

-45.8



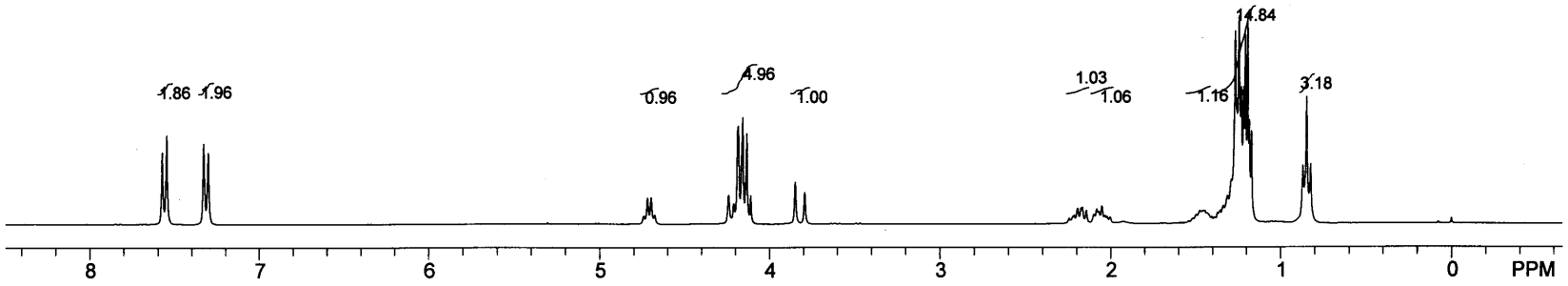
(*S*)-5p

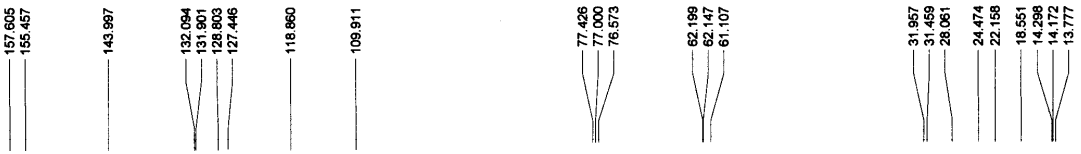

7.575
7.548
7.330
7.303
4.741
4.720
4.697
4.677
4.287
4.241
4.212
4.186
4.158
4.135
4.110
4.062
3.849
3.794
2.277
2.245
2.215
2.196
2.167
2.144
2.100
2.083
2.053
2.035
2.004
1.975
1.558
1.459
1.404
1.388
1.290
1.266
1.244
1.231
1.217
1.207
1.194
1.184
1.170
1.109
0.870
0.848
0.824
0.000

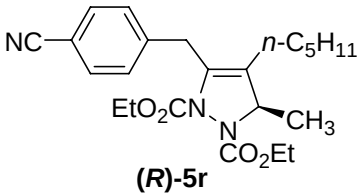

NC
n-C5H11
EtO2CN
N
CH3
CO2Et

(*R*)-5r

cx-5-026-h

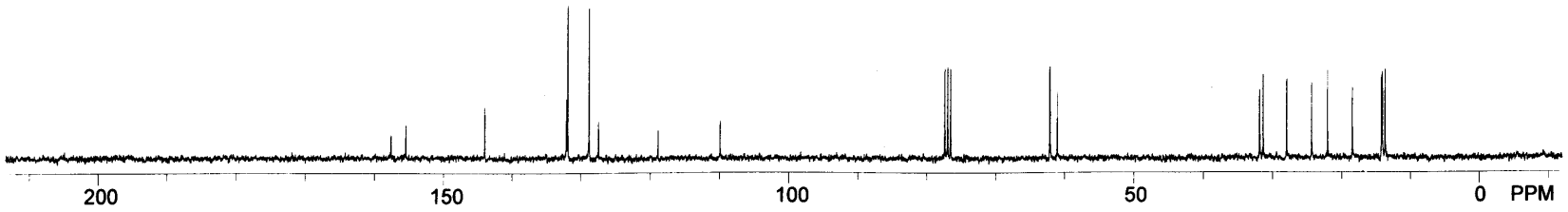

1.86
1.96
0.96
4.96
1.00
1.03
1.06
1.16
14.84
3.18
8
7
6
5
4
3
2
1
0
PPM


157.605
155.457
143.997
132.094
131.901
128.803
127.446
118.860
109.911
77.426
77.000
76.573
62.199
62.147
61.107
31.957
31.459
28.061
24.474
22.158
18.551
14.298
14.172
13.777


NC
n-C5H11
EtO2CN
N
CH3
CO2Et

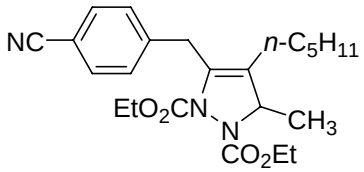
(*R*)-5r

cx-5-026-c

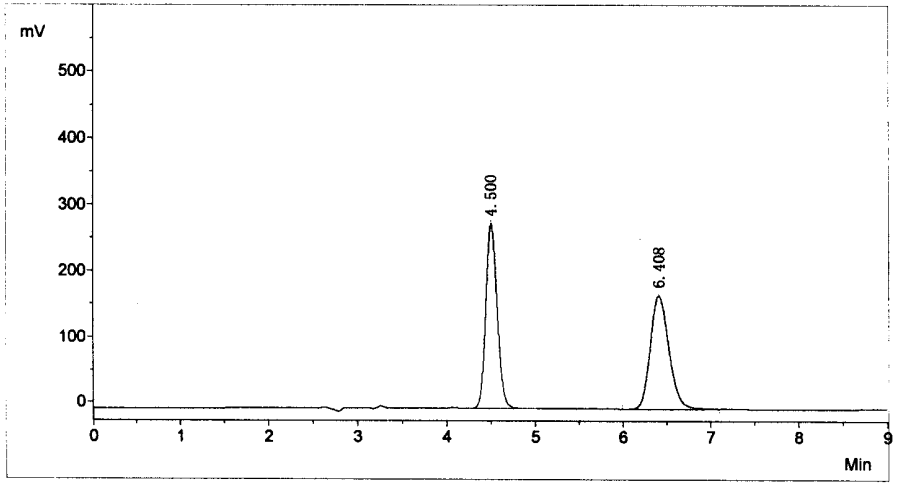

200
150
100
50
0
PPM

HPLC REPORT

Sample Name:cx-4-183-rac.che
Date:2007-11-09
Time:09:26
Method:
Column: OD-H
Flow Rate: 0.7 ml/min
Wave Length: 254 nm
Mobile Phase: 90/10



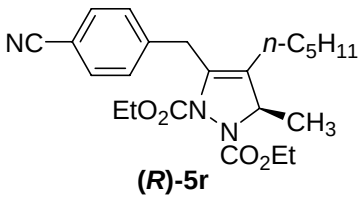
racemic 5r



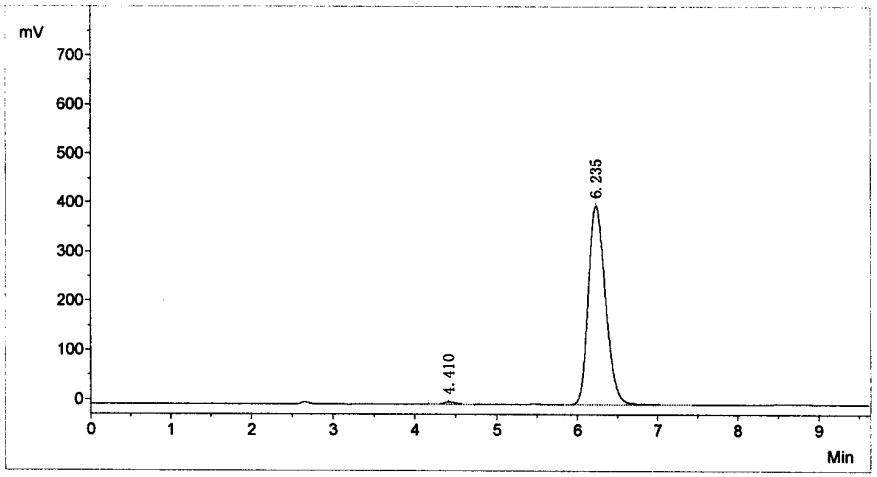
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	4.500	279678.9	2519592.4	49.8167
2	2	Unknown	6.408	171738.0	2538134.9	50.1833
Total				451416.9	5057727.3	100.0000

HPLC REPORT

Sample Name:cx-5-026.che
Date:2007-11-09
Time:10:23
Method:
Column: OD-H
Flow Rate: 0.7 mL/min
Wave Length: 254 nm
Mobile Phase: 90/10

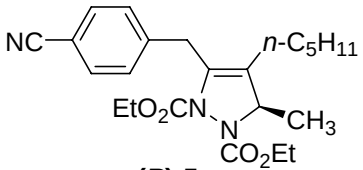


(*R*)-5r



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	4.410	4824.0	48328.3	0.7982
2	2	Unknown	6.235	381402.5	6006003.2	99.2018
Total				386226.5	6054331.5	100.0000

98% ee



(*R*)-5r

PERKIN–ELMER Polarimeter 341
Serial No. 7413

RESULTS TABLE Date: 12/10/2007 01:40:34

Operator: _____

Sample No.: 0001

Sample ID: _____

Sample Name: cx-5-026

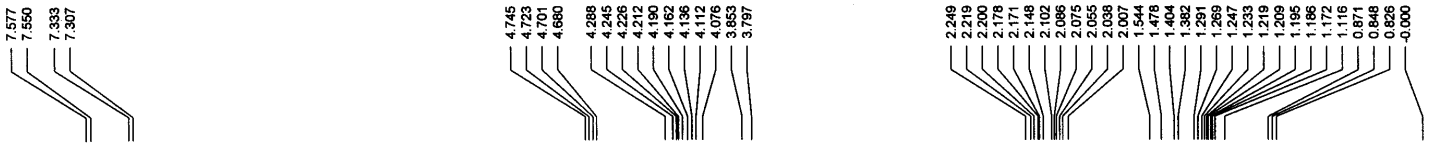
Comment: 21mg, c=1.05, CHCl3

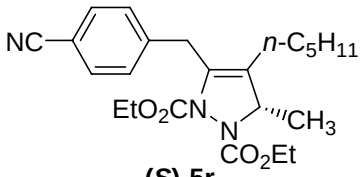
Integration Time: 5.0 s

Cell Path: 100.00 mm

Sample	Wavelength	Temperature	Concentration	Rotation	Spec.Rotation
0001	589 nm	20.0°C	1.0500	+0.583°	+55.6 °
0002	589 nm	20.0°C	1.0500	+0.584°	+55.7 °
0003	589 nm	20.0°C	1.0500	+0.584°	+55.7 °
0004	589 nm	20.0°C	1.0500	+0.582°	+55.5 °
0005	589 nm	20.0°C	1.0500	+0.582°	+55.5 °
0006	589 nm	20.0°C	1.0500	+0.582°	+55.5 °
0007	589 nm	20.0°C	1.0500	+0.583°	+55.5 °
0008	589 nm	20.0°C	1.0500	+0.583°	+55.5 °
0009	589 nm	20.0°C	1.0500	+0.582°	+55.4 °
0010	589 nm	20.0°C	1.0500	+0.582°	+55.4 °

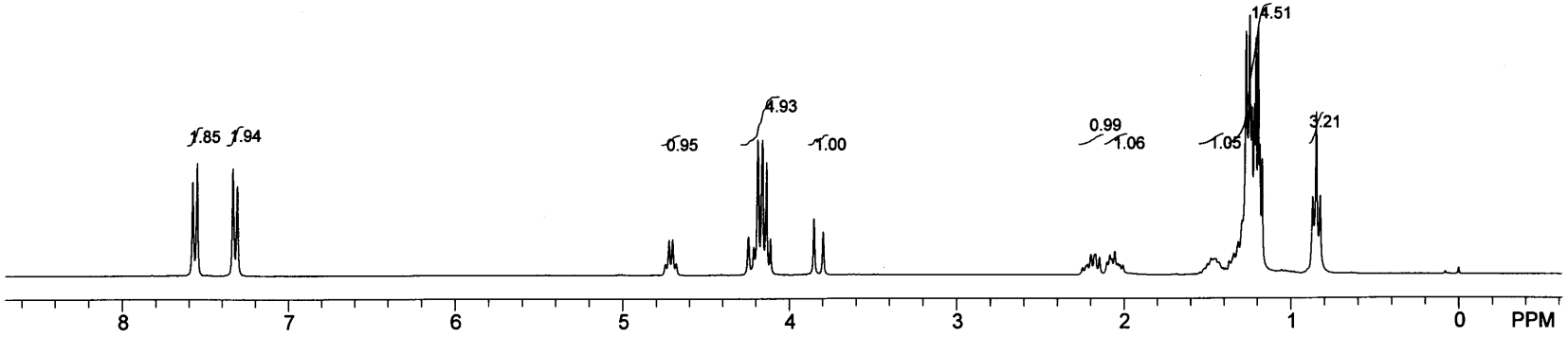
+55.5

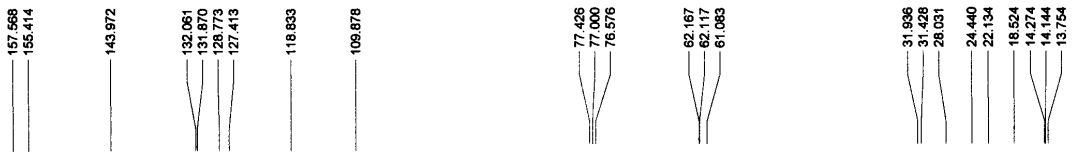

7.577
7.550
7.333
7.307
4.745
4.723
4.701
4.680
4.288
4.245
4.226
4.212
4.190
4.162
4.136
4.112
4.076
3.853
3.797
2.249
2.219
2.200
2.178
2.171
2.148
2.102
2.086
2.075
2.055
2.038
2.007
1.544
1.478
1.404
1.382
1.291
1.269
1.247
1.233
1.219
1.209
1.195
1.186
1.172
1.116
0.871
0.848
0.826
0.000

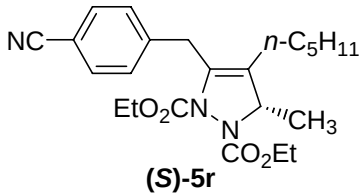

NC
n-C5H11
EtO2CN
N
CH3
CO2Et

(*S*)-5r

cx-5-027-h

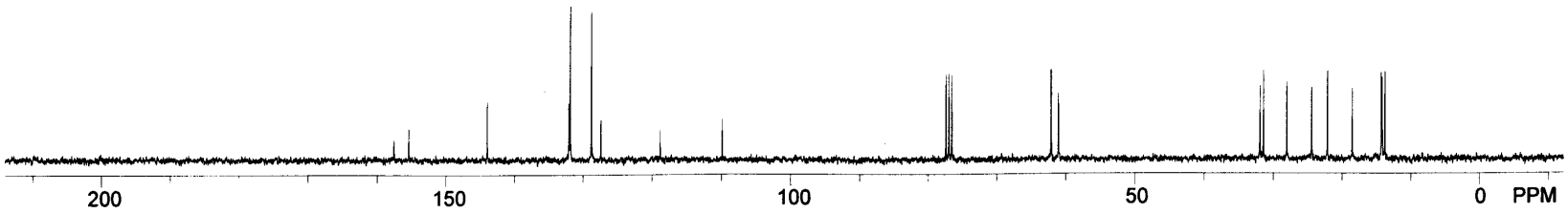

1.85
1.94
0.95
4.93
1.00
0.99
1.06
1.05
14.51
3.21
8
7
6
5
4
3
2
1
0
PPM


157.568
155.414
143.972
132.061
131.870
128.773
127.413
118.833
109.878
77.426
77.000
76.576
62.167
62.117
61.063
31.936
31.428
28.031
24.440
22.134
18.524
14.274
14.144
13.754


NC
n-C5H11
EtO2CN
N
CH3
CO2Et

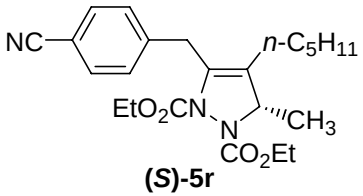
(*S*)-5r

cx-5-027-c

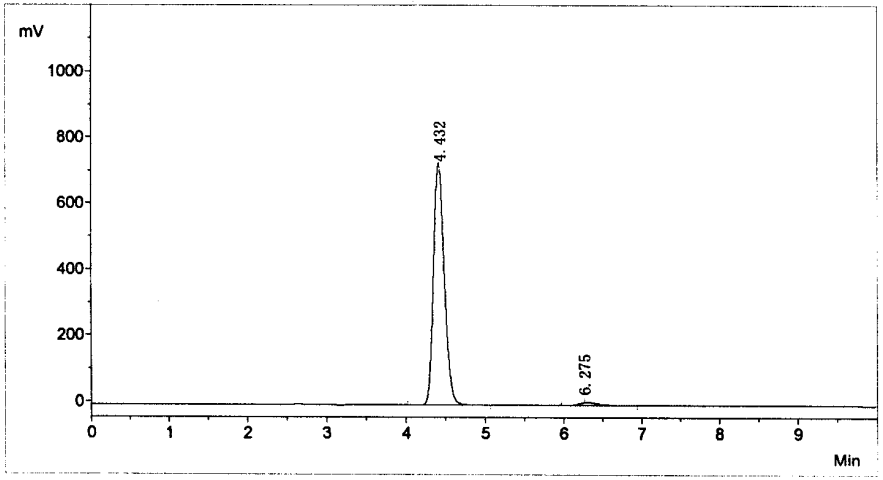

200
150
100
50
0
PPM

HPLC REPORT

Sample Name:cx-5-027.che
Date:2007-11-09
Time:09:49
Method:
Column: OD-H
Flow Rate: 0.7ml/min
Wave Length: 254nm
Mobile Phase: 90/10



(*S*)-5r



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	4.432	714295.6	6943184.4	97.8123
2	2	Unknown	6.275	8503.4	155296.7	2.1877
Total				722799.0	7098481.1	100.0000

96% ee

PERKIN-ELMER

Polarimeter 341
Serial No. 7413

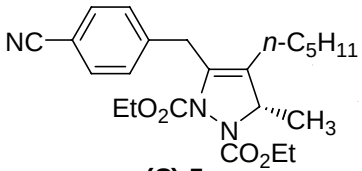
TABLE

Date: 12/10/2007 01:57:16

Operator: _____

Sample No.: ■

Sample ID:



(*S*)-5r

Sample Name: CX-5-027

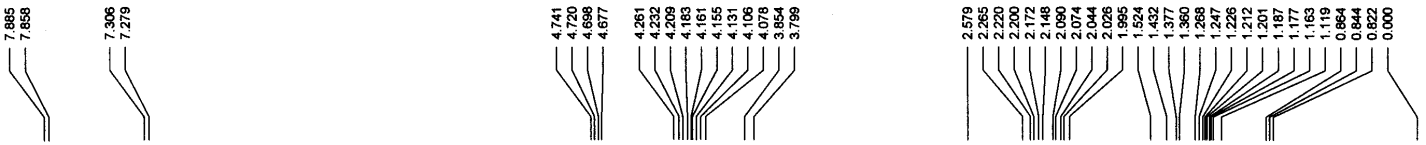
Comment: 22mg, c=1.1, CHCl3

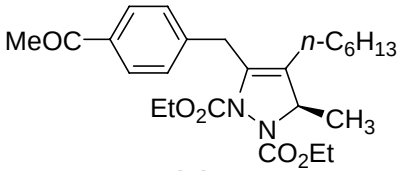
Integration Time: 5.0 s

Cell Path: 100.00 mm

Sample	Wavelength	Temperature	Concentration	Rotation	Spec.Rotation
0001	589 nm	20.0°C	1.1000	-0.689°	-62.7 °
0002	589 nm	20.0°C	1.1000	-0.688°	-62.6 °
0003	589 nm	20.0°C	1.1000	-0.688°	-62.6 °
0004	589 nm	20.0°C	1.1000	-0.688°	-62.6 °
0005	589 nm	20.0°C	1.1000	-0.686°	-62.4 °
0006	589 nm	20.0°C	1.1000	-0.686°	-62.4 °
0007	589 nm	20.0°C	1.1000	-0.686°	-62.4 °
0008	589 nm	20.0°C	1.1000	-0.686°	-62.4 °
0009	589 nm	20.0°C	1.1000	-0.686°	-62.4 °
0010	589 nm	20.0°C	1.1000	-0.688°	-62.5 °

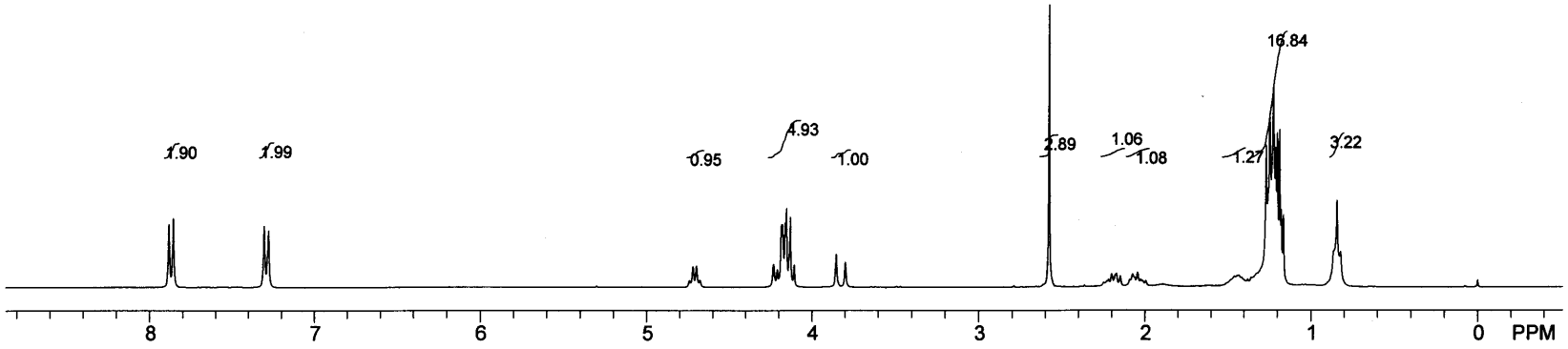
-62.5


7.885
7.858
7.306
7.279
4.741
4.720
4.698
4.677
4.261
4.232
4.209
4.183
4.161
4.155
4.131
4.106
4.078
3.854
3.799
2.579
2.265
2.220
2.200
2.172
2.148
2.090
2.074
2.044
2.026
1.995
1.524
1.432
1.377
1.360
1.268
1.247
1.226
1.212
1.201
1.187
1.177
1.163
1.119
0.864
0.844
0.822
0.000

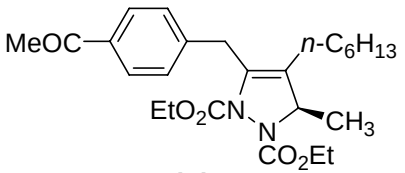

MeOC
n-C6H13
EtO2CN
N
CH3
CO2Et

(*R*)-5c

cx-4-092-h

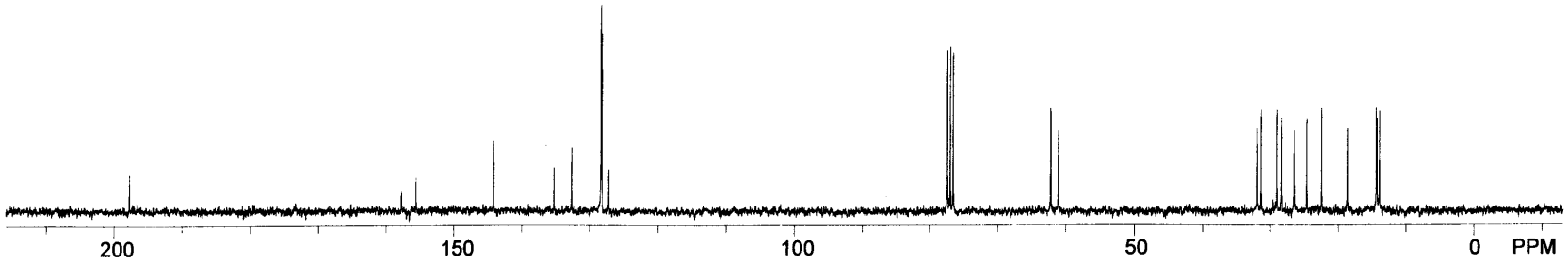

1.90
1.99
0.95
4.93
1.00
2.89
1.06
1.08
1.27
16.84
3.22
8
7
6
5
4
3
2
1
0
PPM


197.748
157.740
155.568
144.132
135.215
132.618
128.334
128.202
127.176
77.422
77.000
76.573
62.219
62.160
61.096
31.921
31.371
29.040
28.392
26.484
24.599
22.422
18.632
14.359
14.241
13.888


MeOC
n-C6H13
EtO2CN
CH3
N
CO2Et

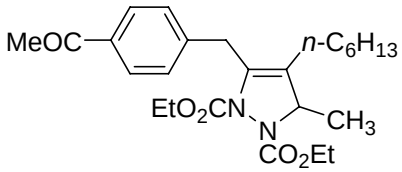
(*R*)-5c

cx4-092-c

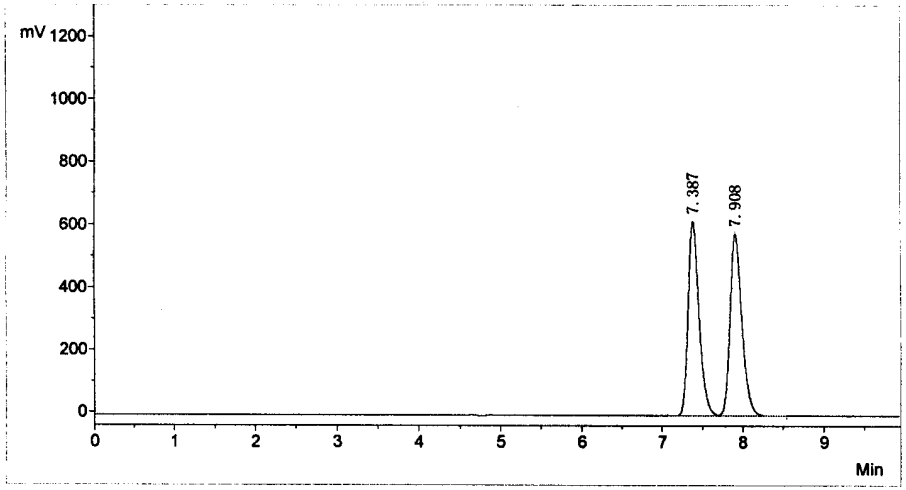

200
150
100
50
0
PPM

HPLC REPORT

Sample Name:cx-3-154-rac.che
Date:2007-07-02
Time:15:37
Method:
Column: AD-H
Flow Rate: 0.7 ml/mn
Wave Length: 254nm
Mobile Phase: 80/20



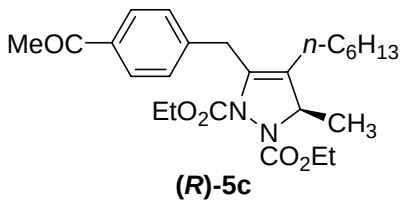
racemic 5c



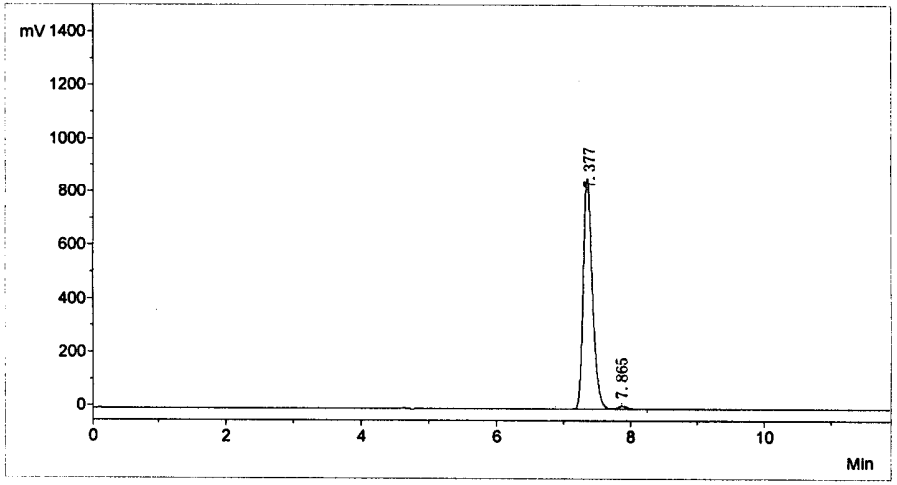
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	7.387	619271.5	5877528.1	49.8264
2	2	Unknown	7.908	542816.9	5918489.4	50.1736
Total				1162088.4	11796017.5	100.0000

HPLC REPORT

Sample Name:cx-4-092..che
Date:2007-07-02
Time:16:13
Method:
Column: AD-H
Flow Rate: 0.7 ml/min
Wave Length: 254nm
Mobile Phase: 80/20



(*R*)-5c



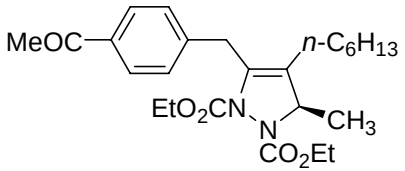
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	7.377	800650.5	8210120.1	98.6142
2	2	Unknown	7.865	11018.0	115374.7	1.3858
Total				811668.5	8325494.8	100.0000

97%ee

4-092
19mg, c=0.95, $CHCl_3$

0059	589 nm	20.0	0.95000	+0.513	+54.0
0060	589 nm	20.0	0.95000	+0.513	+54.0
0061	589 nm	20.0	0.95000	+0.511	+54.1
0062	589 nm	20.0	0.95000	+0.514	+54.1
0063	589 nm	20.0	0.95000	+0.511	+54.1

+54.0



(*R*)-5c