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Supporting Information

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Pd(Ar-BIAN)(Alkene)-Catalyzed Highly Chemo-, Positional- and Stereoselective Semi-Hydrogenation of 1,2-Allenylphosphonates and Related Compounds

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The catalysts **1a-b** were prepared according to the literature procedure.[1]

The following compounds were prepared according to the Typical Procedure in the text.

(1) **Diethyl (but-2(*Z*)-en-2-yl)phosphonate (*Z*-3b):** The reaction of **1b** (1 mg, 0.002 mmol) and **2b** (38 mg, 0.2 mmol) in THF (3 mL) under H_2 (1 atm) afforded 35 mg (91%) of ***Z*-3b**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.26 (dqq, J = 50.4, 6.9, 1.5 Hz, 1 H), 4.14-3.99 (m, 4 H), 2.04-1.99 (m, 3 H), 1.86 (dm, J = 12.9 Hz, 3 H), 1.31 (t, J = 7.2 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 142.8 (d, J_{PC} = 12.1 Hz), 124.6 (d, J_{PC} = 172.6 Hz), 61.1 (d, J_{PC} = 5.2 Hz), 21.6 (d, J_{PC} = 12.7 Hz), 16.2 (d, J_{PC} = 6.3 Hz), 16.1 (d, J_{PC} = 7.5 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 20.5; MS (m/z) 192 (M^+, 9.52), 44 (100); IR (neat) 1638, 1454, 1391, 1248, 1025 cm^{-1}; HRMS m/z (MALDI) calcd for $C_8H_{17}O_3P^+$ [M^+]: 192.0915; Found: 192.0925.

(2) **Diethyl (4,4-dimethylpent-2(*Z*)-en-3-yl)phosphonate (*Z*-3c):** The reaction of **1b** (1 mg, 0.002 mmol) and **2c** (46 mg, 0.2 mmol) in THF (3 mL) under H_2 (1 atm) afforded 42 mg (90%) of ***Z*-3c**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.35 (dq, J = 50.1, 7.2 Hz, 1 H), 4.12-3.97 (m, 4 H), 1.95 (dd, J = 7.2, 3.3 Hz, 3 H), 1.30 (t, J = 7.2 Hz, 6 H), 1.22 (s, 9 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 139.4 (d, J_{PC} = 161.7 Hz), 138.6 (d, J_{PC} = 9.2 Hz), 60.8 (d, J_{PC} = 5.2 Hz), 36.8 (d, J_{PC} = 13.8 Hz), 30.1 (d, J_{PC} = 4.6 Hz), 16.7 (d, J_{PC} = 7.5 Hz), 16.3 (d, J_{PC} = 6.9 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 21.4; MS (m/z) 234 (M^+, 13.10), 163 (100); IR (neat) 1614, 1483, 1444, 1392, 1243, 1026 cm^{-1}; HRMS m/z (ESI) calcd for $C_{11}H_{23}O_3PNa^+$ [M^++Na]: 257.1277; Found: 257.1273.

(3) **Diethyl (dec-2(*Z*)-en-3-yl)phosphonate (*Z*-3d):** The reaction of **1b** (1 mg, 0.002

mmol) and **2d** (55 mg, 0.2 mmol) in THF (3 mL) under H_2 (1 atm) afforded 52 mg (94%) of ***Z*-3d**: liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.24 (dqt, *J* = 51.0, 7.0, 1.0 Hz, 1 H), 4.09-4.01 (m, 4 H), 2.17-2.06 (m, 2 H), 2.01 (ddt, *J* = 7.0, 3.5, 1.0 Hz, 3 H), 1.49-1.34 (m, 2 H), 1.32-1.15 (m, 14 H), 0.86 (t, *J* = 7.0 Hz, 3 H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 20.9; MS (m/z) 276 (M^+, 6.39), 135 (100); IR (neat) 1633, 1444, 1391, 1247, 1027 cm^{-1}; HRMS m/z (ESI) calcd for $C_{14}H_{29}O_3PNa^+$ [M^++Na]: 299.1747; Found: 299.1746.

(4) **Diethyl (1-phenylprop-1(*Z*)-en-1-yl)phosphonate (*Z*-3e):**[2] The reaction of **1b** (1 mg, 0.002 mmol) and **2e** (50 mg, 0.2 mmol) in THF (3 mL) under H_2 (1 atm) afforded 48 mg (95%) of ***Z*-3e**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29-7.22 (m, 5 H), 6.51 (dq, *J* = 48.3, 7.5 Hz, 1 H), 4.10-3.94 (m, 4 H), 2.22 (dd, *J* = 7.5, 3.6 Hz, 3 H), 1.22 (t, *J* = 6.9 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 147.1 (d, J_{PC} = 10.4 Hz), 140.0 (d, J_{PC} = 12.1 Hz), 132.3 (d, J_{PC} = 175.0 Hz), 128.2 (d, J_{PC} = 4.6 Hz) (2C), 128.0 (2C), 127.1 (d, J_{PC} = 1.2 Hz), 61.6 (d, J_{PC} = 5.7 Hz), 16.9 (d, J_{PC} = 6.3 Hz), 16.2 (d, J_{PC} = 6.9 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 17.6; MS (m/z) 254 (M^+, 25.58), 84 (100); IR (neat) 1614, 1491, 1443, 1391, 1252, 1024 cm^{-1}.

(5) **Diethyl (1-(4-methoxyphenyl)prop-1(*Z*)-en-1-yl)phosphonate (*Z*-3f):** The reaction of **1b** (1 mg, 0.002 mmol) and **2f** (56 mg, 0.2 mmol) in THF (3 mL) under H_2 (1 atm) afforded 56 mg (99%) of ***Z*-3f**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.1 Hz, 2 H), 6.79 (d, *J* = 8.1 Hz, 2 H), 6.45 (dq, *J* = 48.6, 7.5 Hz, 1 H), 4.09-3.89 (m, 4 H), 3.74 (s, 3 H), 2.17 (dd, *J* = 7.5, 3.6 Hz, 3 H), 1.20 (t, *J* = 7.2 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 158.8 (2C), 146.2 (d, J_{PC} = 10.9 Hz), 132.4 (d, J_{PC} = 12.1 Hz),

131.4 (d, J_{PC} = 174.4 Hz), 129.4 (d, J_{PC} = 4.6 Hz) (2C), 113.3 (2C), 61.5 (d, J_{PC} = 5.2 Hz), 55.2 (2C), 16.8 (d, J_{PC} = 6.9 Hz), 16.2 (d, J_{PC} = 6.3 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 17.9; MS (m/z) 284 (M^+, 94.97), 145 (100); IR (neat) 1608, 1509, 1464, 1444, 1391, 1251, 1025 cm^{-1}; HRMS m/z (ESI) calcd for $C_{14}H_{21}O_4PNa^+$ [M^++Na]: 307.1070; Found: 307.1069.

(6) **Diethyl (1-(4'-methylphenyl)prop-1(*Z*)-en-1-yl)phosphonate (*Z*-3g):** The reaction of **1b** (1 mg, 0.002 mmol) and **2g** (53 mg, 0.2 mmol) in THF (3 mL) under H_2 (1 atm) afforded 50 mg (93%) of ***Z*-3g**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, *J* = 7.7 Hz, 2 H), 7.10 (d, *J* = 7.7 Hz, 2 H), 6.50 (dq, *J* = 48.9, 7.5 Hz, 1 H), 4.13-3.93 (m, 4 H), 2.32 (s, 3 H), 2.22 (dd, *J* = 7.5, 4.2 Hz, 3 H), 1.24 (t, *J* = 7.2 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 146.6 (d, J_{PC} = 10.8 Hz), 137.1 (d, J_{PC} = 12.4 Hz), 136.8 (d, J_{PC} = 1.7 Hz), 132.0 (d, J_{PC} = 174.4 Hz), 128.7 (2C), 128.1 (d, J_{PC} = 5.4 Hz) (2C), 61.5 (d, J_{PC} = 6.0 Hz), 21.0 (2C), 16.9 (d, J_{PC} = 6.7 Hz), 16.2 (d, J_{PC} = 6.6 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 17.9; MS (m/z) 268 (M^+, 73.26), 269 (100); IR (neat) 1612, 1510, 1444, 1391, 1253, 1023 cm^{-1}; HRMS m/z (ESI) calcd for $C_{14}H_{21}O_3PNa^+$ [M^++Na]: 291.1121; Found: 291.1120.

(7) **Diethyl (1-(4'-nitrophenyl)prop-1(*Z*)-en-1-yl)phosphonate (*Z*-3h):** The reaction of **1b** (1 mg, 0.002 mmol) and **2h** (59 mg, 0.2 mmol) in THF (3 mL) under H_2 (1 atm) afforded 54 mg (90%) of ***Z*-3h**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.9 Hz, 2 H), 7.47 (d, *J* = 8.9 Hz, 2 H), 6.61 (dq, *J* = 47.7, 7.5 Hz, 1 H), 4.16-3.99 (m, 4 H), 2.26 (dd, *J* = 7.5, 3.3 Hz, 3 H), 1.25 (t, *J* = 7.2 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 149.2 (d, J_{PC} = 9.3 Hz), 146.9 (d, J_{PC} = 5.6 Hz), 146.8 (2C), 131.2 (d, J_{PC} = 178.4 Hz),

129.1 (d, J_{PC} = 4.5 Hz) (2C), 123.2 (2C), 61.9 (d, J_{PC} = 5.7 Hz), 17.1 (d, J_{PC} = 6.3 Hz), 16.2 (d, J_{PC} = 6.2 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 15.8; MS (m/z) 299 (M^+, 56.60), 115 (100); IR (neat) 1593, 1518, 1443, 1392, 1348, 1257, 1021 cm^{-1}; HRMS m/z (ESI) calcd for $C_{13}H_{18}O_5PNNa^+$ [M^++Na]: 322.0815; Found: 322.0817.

(8) **Diethyl (1-(4'-methoxycarbonylphenyl)prop-1(*Z*)-en-1-yl)phosphonate (*Z*-3i):** The reaction of **1b** (1 mg, 0.002 mmol) and **2i** (62 mg, 0.2 mmol) in THF (3 mL) under H_2 (1 atm) afforded 58 mg (93%) of ***Z*-3i**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2 H), 7.38 (d, *J* = 8.3 Hz, 2 H), 6.58 (dq, *J* = 48.0, 7.2 Hz, 1 H), 4.14-3.94 (m, 4 H), 3.90 (s, 3 H), 2.25 (dd, *J* = 7.2, 3.6 Hz, 3 H), 1.23 (t, *J* = 7.2 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 166.9 (2C), 148.2 (d, J_{PC} = 9.4 Hz), 144.8 (d, J_{PC} = 12.1 Hz), 131.9 (d, J_{PC} = 176.7 Hz), 129.3 (2C), 128.8 (d, J_{PC} = 1.4 Hz), 128.2 (d, J_{PC} = 4.9 Hz) (2C), 61.7 (d, J_{PC} = 6.6 Hz), 52.1 (2C), 17.0 (d, J_{PC} = 6.5 Hz), 16.2 (d, J_{PC} = 6.9 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 14.7; MS (m/z) 312 (M^+, 53.72), 115 (100); IR (neat) 1723, 1608, 1437, 1393, 1278, 1256, 1105, 1021 cm^{-1}; HRMS m/z (ESI) calcd for $C_{15}H_{21}O_5PNa^+$ [M^++Na]: 335.1019; Found: 335.1016.

(9) **Diethyl (prop-1(*Z*)-en-1-yl)phosphonate (*Z*-3j):**[2] The reaction of **1b** (1 mg, 0.002 mmol) and **2j** (34 mg, 0.2 mmol) in THF (3 mL) under H_2 (1 atm) afforded 31 mg (91%) of ***Z*-3j**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.56 (ddq, *J* = 52.8, 12.9, 6.9 Hz, 1 H), 5.59 (ddq, *J* = 19.5, 12.9, 1.8 Hz, 1 H), 4.11-4.01 (m, 4 H), 2.07 (ddd, *J* = 6.9, 3.9, 1.8 Hz, 3 H), 1.31 (t, *J* = 6.9 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 148.8 (d, J_{PC} = 4.5 Hz), 117.5 (d, J_{PC} = 183.1 Hz), 61.3 (d, J_{PC} = 6.0 Hz), 16.8 (d, J_{PC} = 8.9 Hz), 16.3 (d, J_{PC} = 6.6 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 18.3; MS (m/z) 179 (M^++1, 79.74),

122 (100); IR (neat) 1632, 1444, 1391, 1246, 1027 cm^{-1}.

(10) **Diethyl (hex-2(*Z*)-en-3-yl)phosphonate (*Z*-3k):** The reaction of **1b** (1 mg, 0.002 mmol) and **2k** (44 mg, 0.2 mmol) in THF (3 mL) under H_2 (1 atm) afforded 41 mg (93%) of ***Z*-3k**: liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.25 (dqt, *J* = 50.5, 7.5, 1.5 Hz, 1 H), 4.09-4.04 (m, 4 H), 2.19-2.09 (m, 2 H), 2.03 (ddt, *J* = 7.5, 4.0, 1.5 Hz, 3 H), 1.53-1.43 (m, 2 H), 1.32 (t, *J* = 7.5 Hz, 6 H), 0.90 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 142.4 (d, J_{PC} = 11.5 Hz), 129.6 (d, J_{PC} = 169.7 Hz), 61.1 (d, J_{PC} = 5.5 Hz), 37.4 (d, J_{PC} = 12.1 Hz), 22.7 (d, J_{PC} = 3.2 Hz), 16.31 (d, J_{PC} = 7.5 Hz), 16.28 (d, J_{PC} = 6.6 Hz), 13.6 (2C); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 20.9; MS (m/z) 220 (M^+, 14.38), 135 (100); IR (neat) 1633, 1444, 1391, 1245, 1026 cm^{-1}; HRMS m/z (ESI) calcd for $C_{10}H_{22}O_3P^+$ [M^++H]: 221.1301; Found: 221.1301.

(11) **Diethyl (dec-5(*Z*)-en-5-yl)phosphonate (*Z*-3l):** The reaction of **1b** (1 mg, 0.002 mmol) and **2l** (55 mg, 0.2 mmol) in THF (3 mL) under H_2 (1 atm) afforded 51 mg (92%) of ***Z*-3l**: liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13 (dtt, *J* = 50.8, 6.8, 1.2 Hz, 1 H), 4.09-4.02 (m, 4 H), 2.52-2.45 (m, 2 H), 2.23-2.15 (m, 2 H), 1.47-1.25 (m, 14 H), 0.92-0.88 (m, 6 H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 21.1; MS (m/z) 276 (M^+, 18.03), 95 (100); IR (neat) 1629, 1466, 1391, 1245, 1028 cm^{-1}; HRMS m/z (EI) calcd for $C_{14}H_{29}O_3P^+$ [M^+]: 276.1854; Found: 276.1857.

(12) **Diethyl (2-methyloct-3(*Z*)-en-4-yl)phosphonate (*Z*-3m):** The reaction of **1b** (1 mg, 0.002 mmol) and **2m** (52 mg, 0.2 mmol) in THF (3 mL) under H_2 (1 atm) afforded 50 mg (95%) of ***Z*-3m**: liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (ddt, *J* = 51.6, 10.4, 1.2 Hz, 1 H), 4.09-4.03 (m, 4 H), 3.30-3.23 (m, 1 H), 2.24-2.15 (m, 2 H), 1.50-1.43 (m,

2 H), 1.42-1.28 (m, 8 H), 0.98 (d, J = 6.8 Hz, 6 H), 0.91 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 154.7 (d, J_{PC} = 12.4 Hz), 126.0 (d, J_{PC} = 170.6 Hz), 61.1 (d, J_{PC} = 5.4 Hz), 34.8 (d, J_{PC} = 12.1 Hz), 31.8 (d, J_{PC} = 3.5 Hz), 29.1 (d, J_{PC} = 6.6 Hz), 22.6 (d, J_{PC} = 2.4 Hz), 22.2 (2C), 16.3 (d, J_{PC} = 6.5 Hz), 13.9 (2C); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 21.3; MS (m/z) 262 (M^+, 17.43), 81 (100); IR (neat) 1629, 1466, 1391, 1244, 1027 cm^{-1}; HRMS m/z (ESI) calcd for $C_{13}H_{28}O_3P^+$ [M^++H]: 263.1771; Found: 263.1767.

(13) **Diethyl (3-methylnon-4(*Z*)-en-5-yl)phosphonate (*Z*-3n):** The reaction of **1b** (1 mg, 0.002 mmol) and **2n** (55 mg, 0.2 mmol) in THF (3 mL) under H_2 (1 atm) afforded 47 mg (85%) of ***Z*-3n**: liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.84 (ddt, J = 51.0, 10.5, 1.0 Hz, 1 H), 4.07-4.01 (m, 4 H), 3.06-3.00 (m, 1 H), 2.20-2.10 (m, 2 H), 1.47-1.40 (m, 2 H), 1.36-1.22 (m, 10 H), 0.94 (d, J = 6.5 Hz, 3 H), 0.89 (t, J = 7.0 Hz, 3 H), 0.85 (t, J = 7.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 153.9 (d, J_{PC} = 13.3 Hz), 127.1 (d, J_{PC} = 171.1 Hz), 61.0 (d, J_{PC} = 3.2 Hz), 35.7 (d, J_{PC} = 6.4 Hz), 34.9 (d, J_{PC} = 11.8 Hz), 31.9 (d, J_{PC} = 3.0 Hz), 29.9 (d, J_{PC} = 1.7 Hz), 22.1 (2C), 20.2 (d, J_{PC} = 2.9 Hz), 16.3 (d, J_{PC} = 6.8 Hz), 13.8 (2C), 11.7 (2C); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 21.3; MS (m/z) 276 (M^+, 13.97), 95 (100); IR (neat) 1629, 1459, 1391, 1239, 1027 cm^{-1}; HRMS m/z (MALDI) calcd for $C_{14}H_{30}O_3P^+$ [M^++H]: 277.1927; Found: 277.1934.

(14) **Diphenyl (hept-2(*Z*)-en-3-yl)phosphine oxide (10):** The reaction of **1b** (1 mg, 0.002 mmol) and **9** (59 mg, 0.2 mmol) in THF (3 mL) under H_2 (1 atm) afforded 40 mg (68%) of **10**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71-7.64 (m, 4 H), 7.52-7.39 (m, 6 H), 6.49 (dq, J = 38.4, 7.2 Hz, 1 H), 2.04-1.95 (m, 2 H), 1.82 (dd, J = 7.2, 3.0 Hz, 3 H),

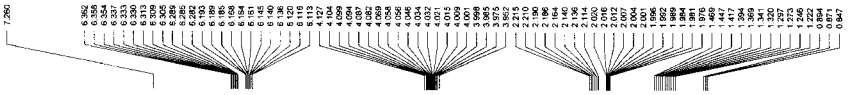
1.25-1.15 (m, 2 H), 1.12-1.00 (m, 2 H), 0.66 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 143.0 (d, J_{PC} = 8.1 Hz), 133.5 (d, J_{PC} = 100.7 Hz) (2C), 133.1 (d, J_{PC} = 92.1 Hz), 131.50 (d, J_{PC} = 9.8 Hz) (4C), 131.48 (2C), 128.3 (d, J_{PC} = 12.1 Hz) (4C), 35.3 (d, J_{PC} = 12.7 Hz), 31.8 (d, J_{PC} = 3.5 Hz), 22.1 (2C), 17.2 (d, J_{PC} = 8.1 Hz), 13.5 (2C); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 30.5; MS (m/z) 298 (M^+, 22.61), 44 (100); IR (neat) 1622, 1590, 1482, 1455, 1437, 1189, 1116 cm^{-1}; HRMS m/z (ESI) calcd for $C_{19}H_{24}OP^+$ [M^++H]: 299.1559; Found: 299.1548.

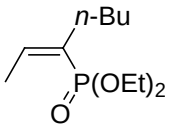
(15) **Phenyl propenyl sulfone (12):**[3] The reaction of **1b** (1 mg, 0.002 mmol) and **11** (35 mg, 0.2 mmol) in THF (2 mL) under H_2 (1 atm) afforded 28 mg (77%) of **12** (***Z*-12**:***E*-12** = 94:6). ***Z*-12**: liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94-7.92 (m, 2 H), 7.63-7.61 (m, 1 H), 7.57-7.53 (m, 2 H), 6.41 (dq, J = 11.0, 7.0 Hz, 1 H), 6.35 (dq, J = 11.0, 1.5 Hz, 1 H), 2.17 (dd, J = 7.0, 1.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 142.3, 141.6, 133.3, 131.2, 129.2, 127.1, 14.0; MS (m/z) 182 (M^+, 19.45), 77 (100); IR (neat) 1628, 1585, 1477, 1446, 1305, 1147, 1086 cm^{-1}.

(16) **2-benzylbut-2-enoic acid ethyl ester (14):** The reaction of **1b** (1 mg, 0.002 mmol) and **13** (39 mg, 0.2 mmol) in toluene (2 mL) under H_2 (1 atm) afforded 31 mg (80%) of **14** (***Z*-14**:***E*-14** = 94:6). ***Z*-14**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23-7.10 (m, 5 H), 5.96 (q, J = 7.5 Hz, 1 H), 4.07 (q, J = 7.5 Hz, 2 H), 3.51 (s, 2 H), 1.95 (d, J = 7.5 Hz, 3 H), 1.15 (t, J = 7.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 167.6, 139.6, 138.2, 132.2, 128.8, 128.3, 126.1, 60.1, 40.4, 15.8, 14.2; MS (m/z) 204 (M^+, 10.30), 129 (100); IR (neat) 1716, 1647, 1603, 1495, 1453, 1234, 1031 cm^{-1}; Anal. cacld for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90; Found: C, 76.25; H, 8.13. ***E*-14**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ

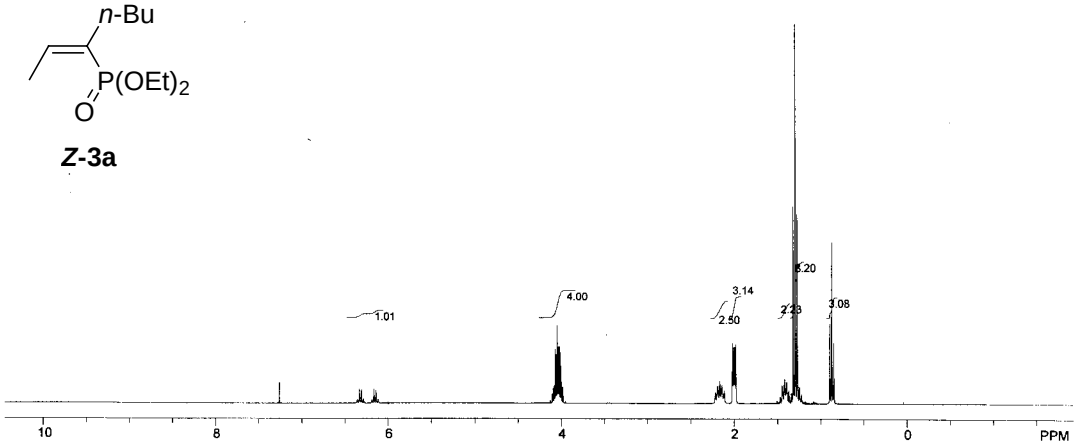
7.30-7.16 (m, 5 H), 7.06 (q, *J* = 7.5 Hz, 1 H), 4.16 (q, *J* = 7.2 Hz, 2 H), 3.71 (s, 2 H), 1.91 (d, *J* = 7.5 Hz, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 167.5, 139.7, 138.4, 132.2, 128.23, 128.19, 125.8, 60.4, 31.9, 14.6, 14.1; MS (m/z) 204 (M^+, 9.73), 91 (100); IR (neat) 1710, 1648, 1601, 1495, 1453, 1274, 1054 cm^{-1}; Anal. cacld for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90; Found: C, 76.19; H, 7.96.

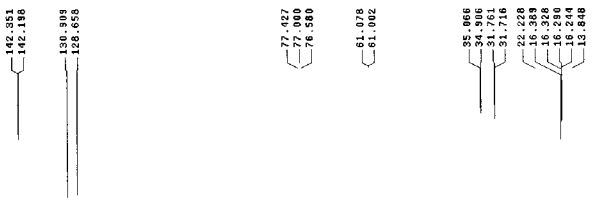
The ^{1}H, ^{13}C, and ^{31}P NMR spectra of all the new compounds.

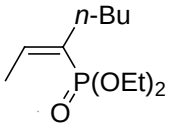




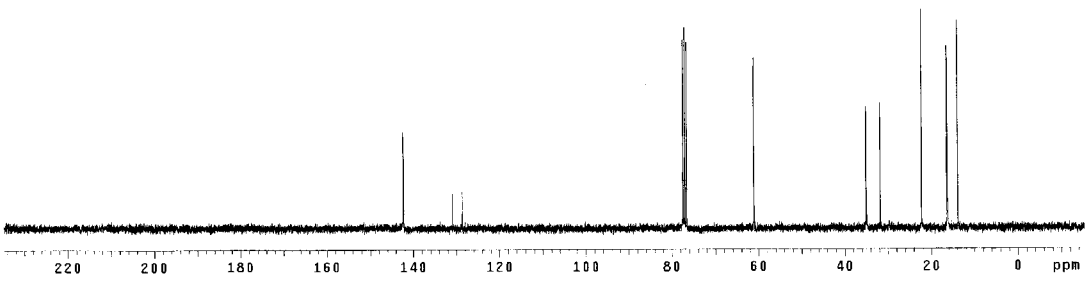
***Z*-3a**





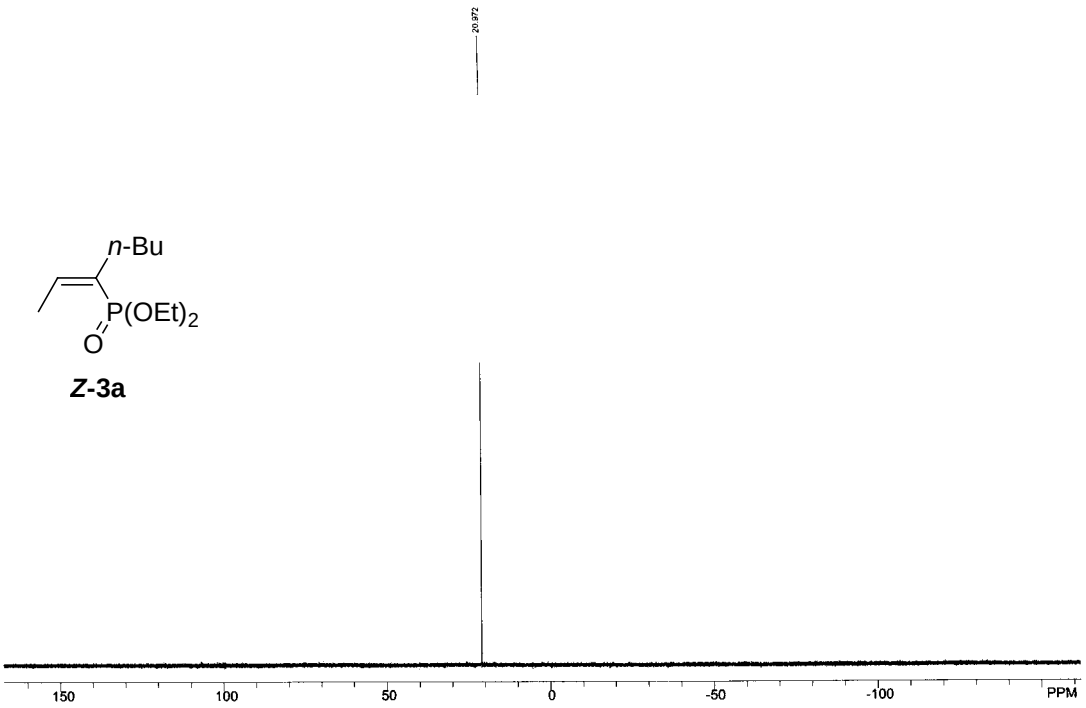


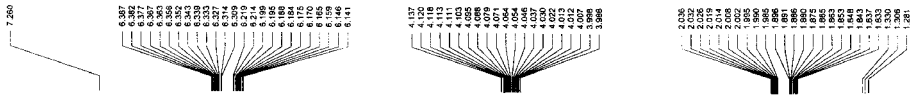
***Z*-3a**



n-Bu
P(OEt)2
O

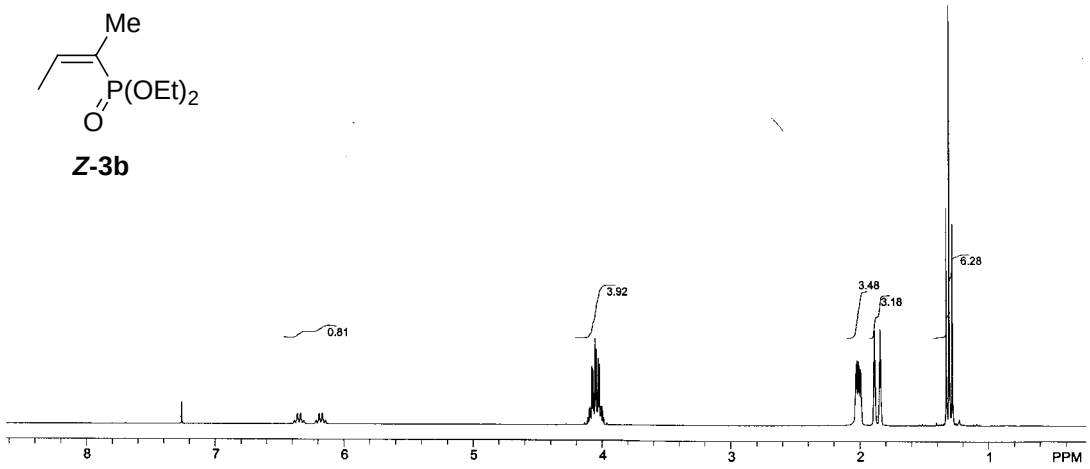
***Z*-3a**

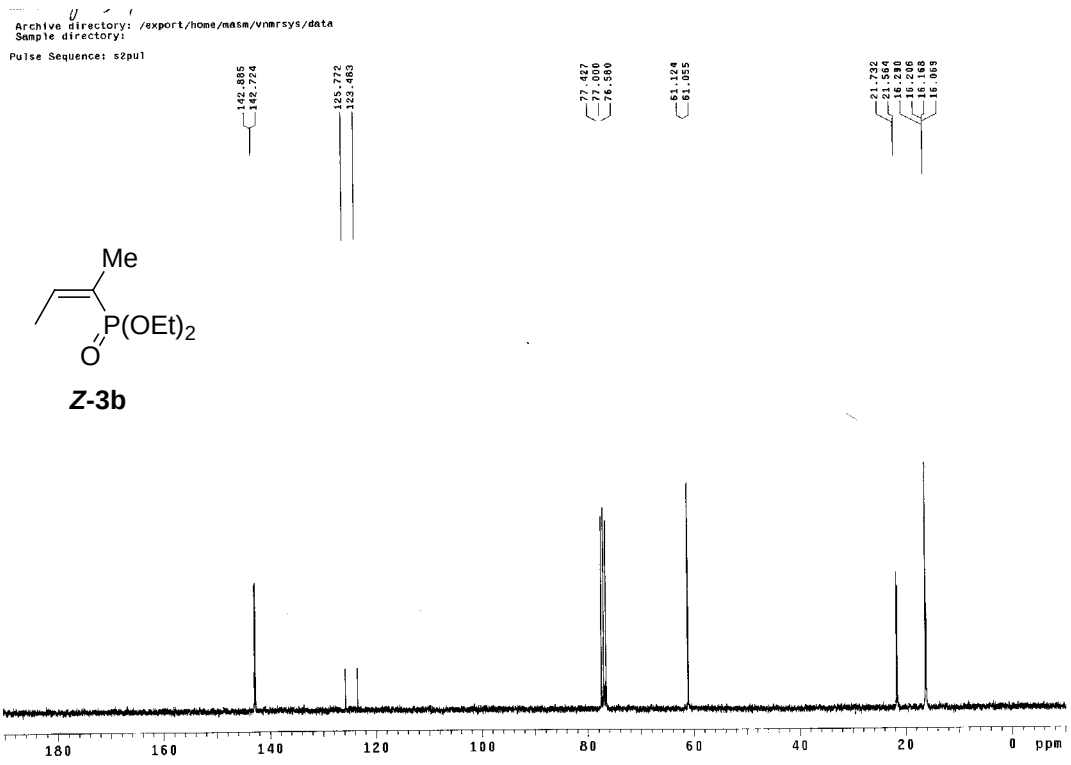

20.972
150
100
50
0
-50
-100
PPM


7.260

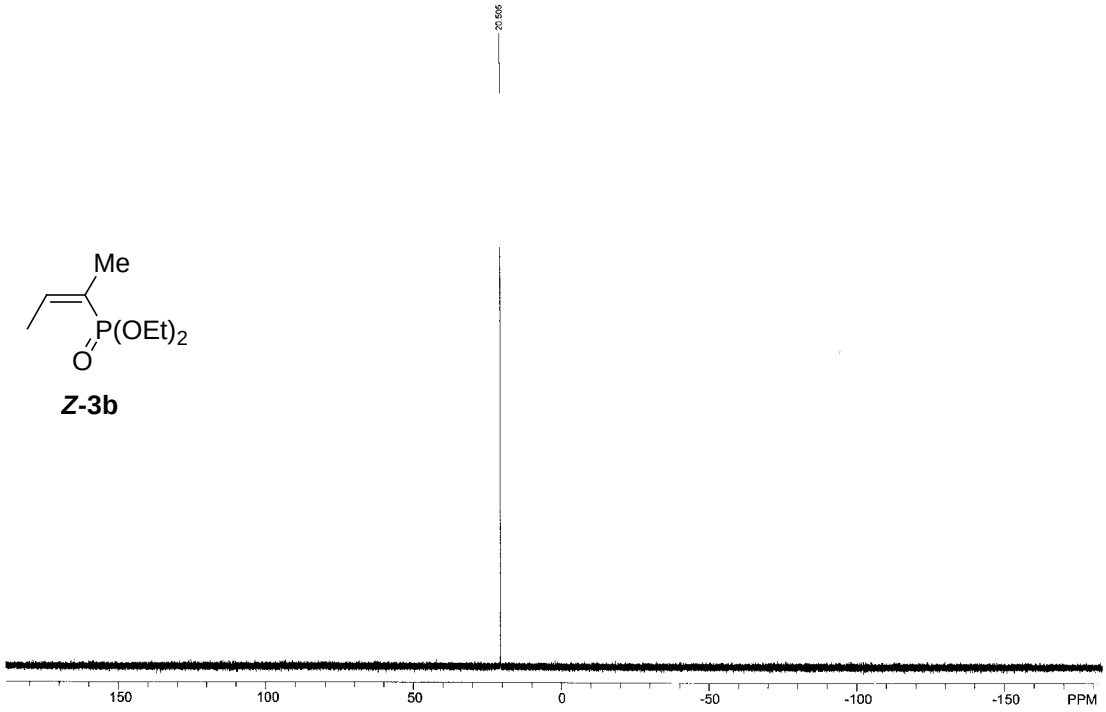
Me
P(OEt)2
O

***Z*-3b**

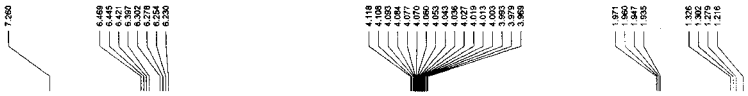

0.81
3.92
3.48
3.18
6.28
8
7
6
5
4
3
2
1
PPM

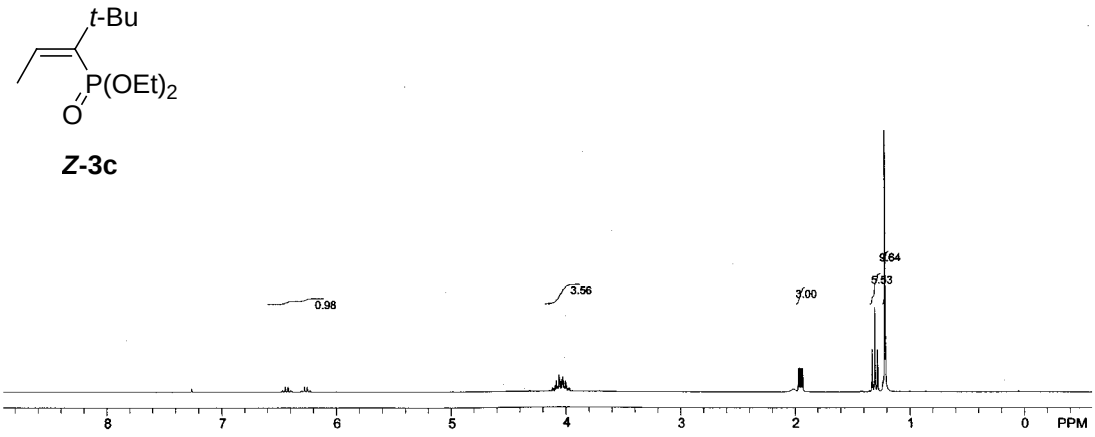

Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
142.885
142.724
125.772
123.483
77.427
77.000
76.580
61.124
61.055
21.732
21.564
16.290
16.206
16.168
16.069
Me
P(OEt)2
O
180
160
140
120
100
80
60
40
20
0
ppm

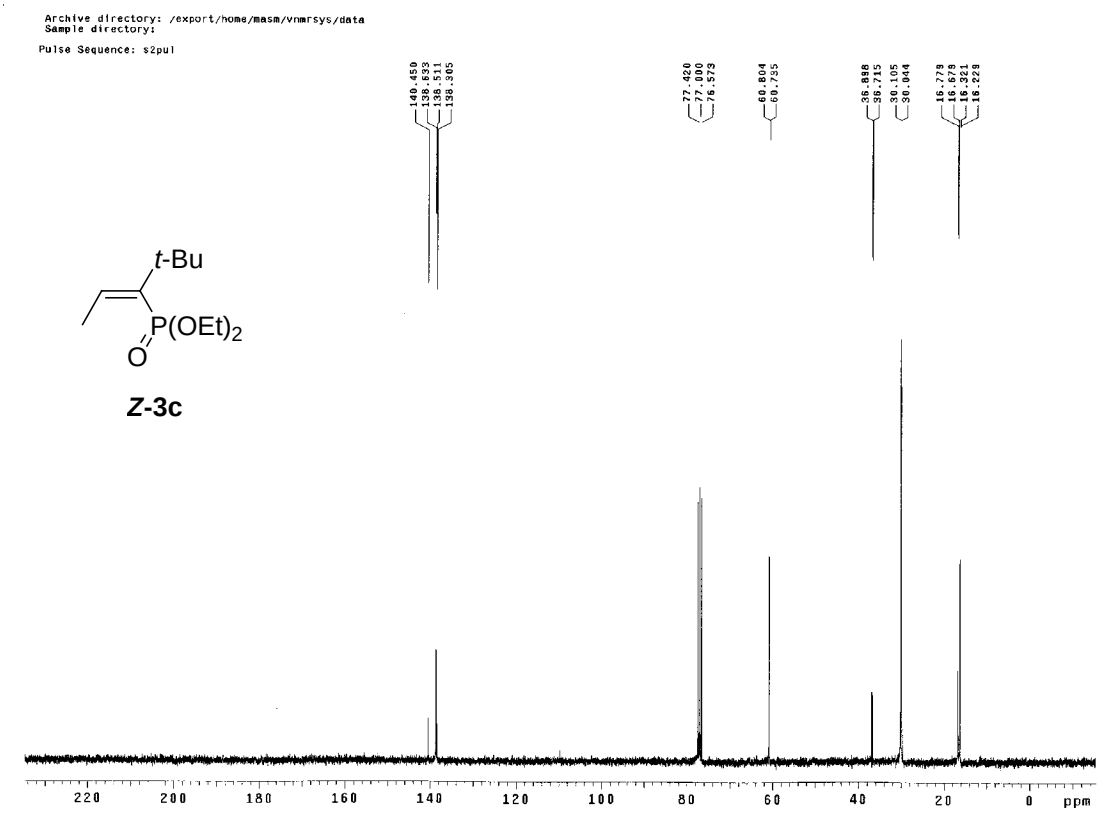
***Z*-3b**

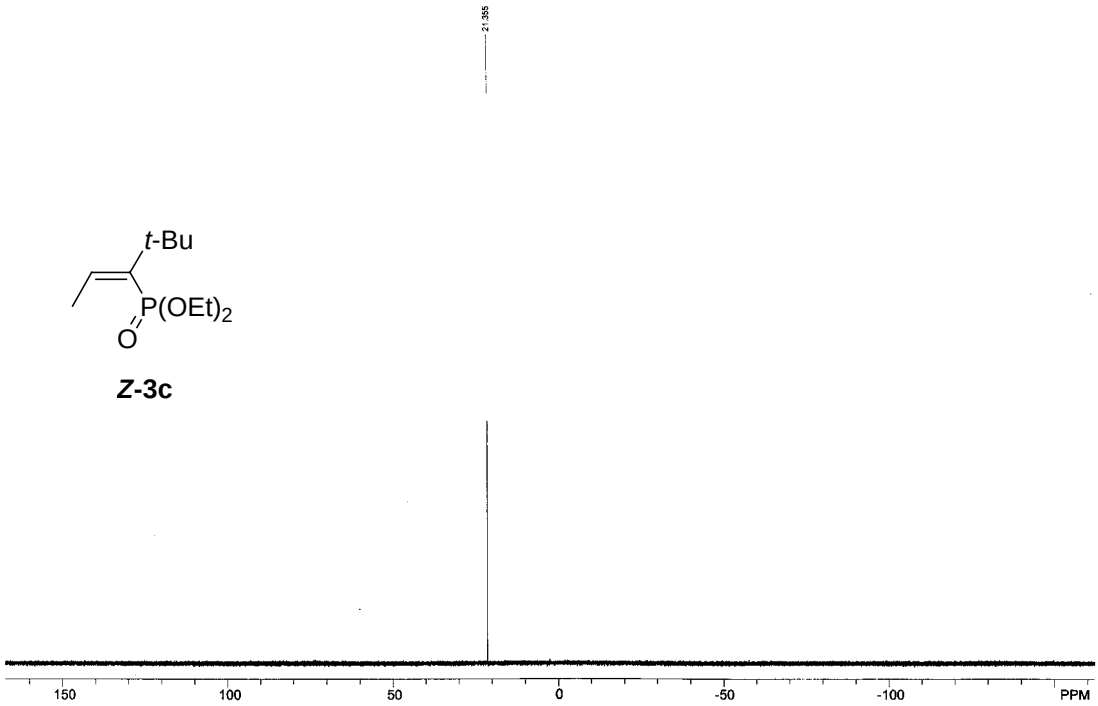

20.556
Me
P(OEt)2
O
150
100
50
0
-50
-100
-150
PPM

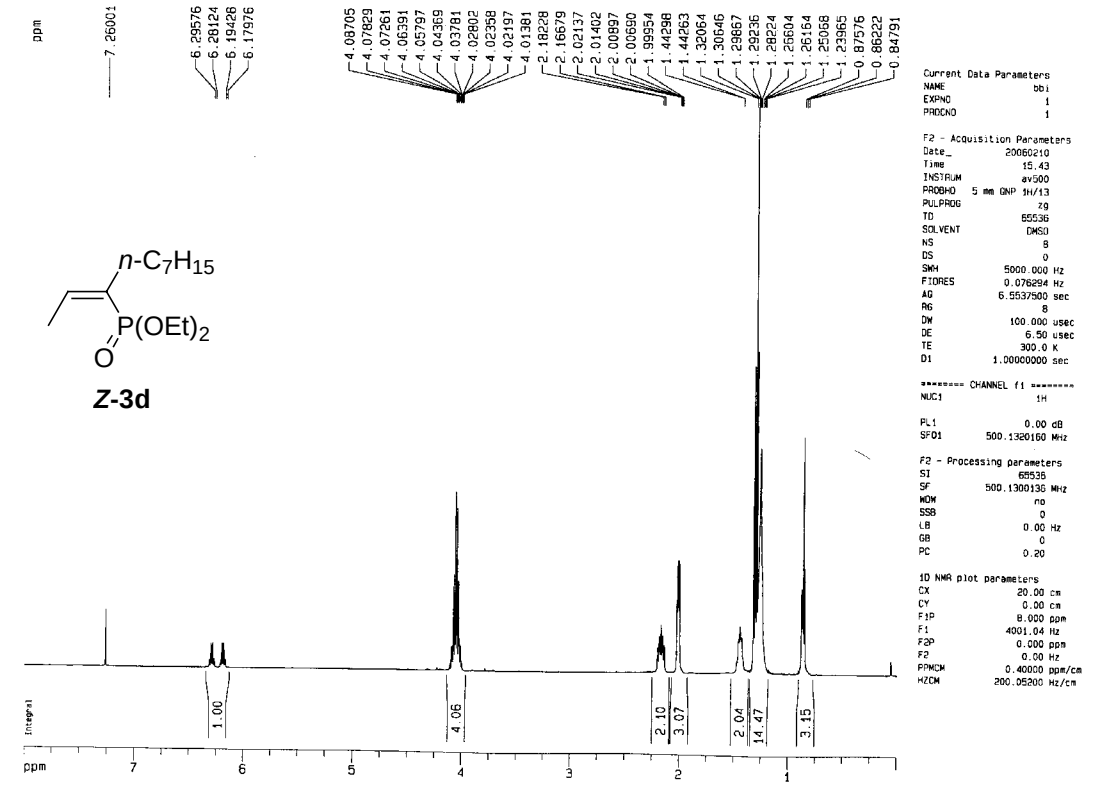
***Z*-3b**

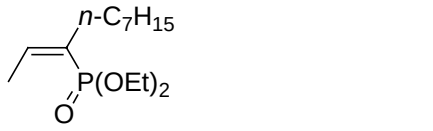



t-Bu
P(OEt)2
O
Z-3c
0.98
3.56
3.00
9.64
5.53
8
7
6
5
4
3
2
1
0
PPM

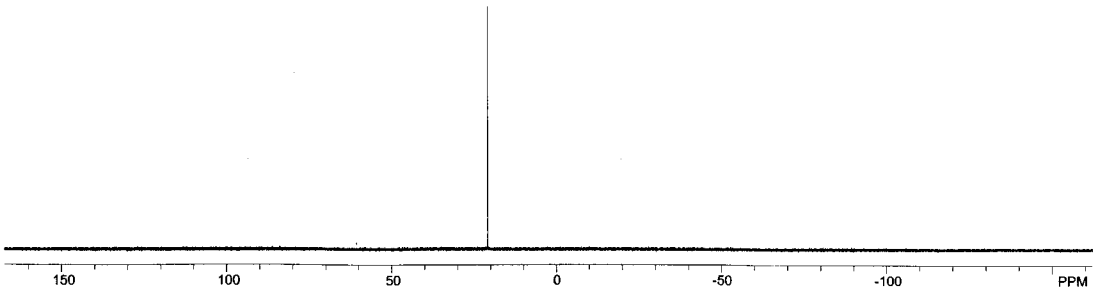

Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
140.450
138.633
138.511
138.385
77.420
77.000
76.579
60.804
60.735
36.888
36.715
30.105
30.044
16.278
16.178
16.321
16.229
t-Bu
P(OEt)2
O
Z-3c
220
200
180
160
140
120
100
80
60
40
20
0
ppm


t-Bu
P(OEt)2
O
Z-3c
150
100
50
0
-50
-100
PPM


n-C7H15
P(OEt)2
O
Z-3d
ppm
Integral
1.00
4.06
2.10
3.07
2.04
14.47
3.15

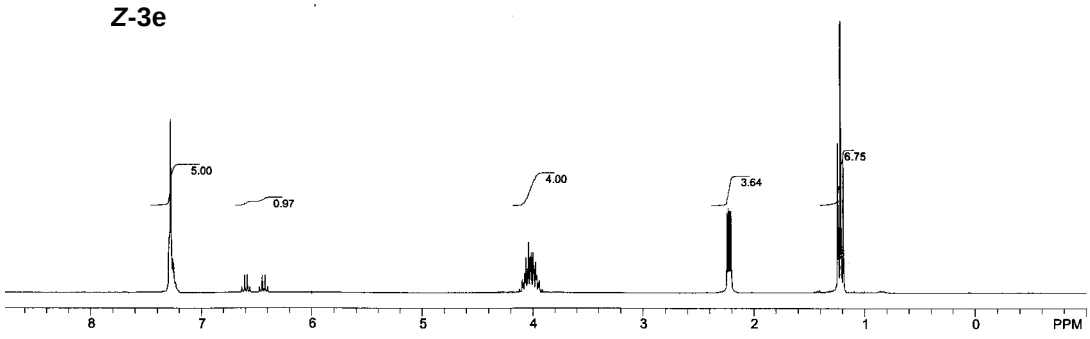

n-C7H15
P(OEt)2
O

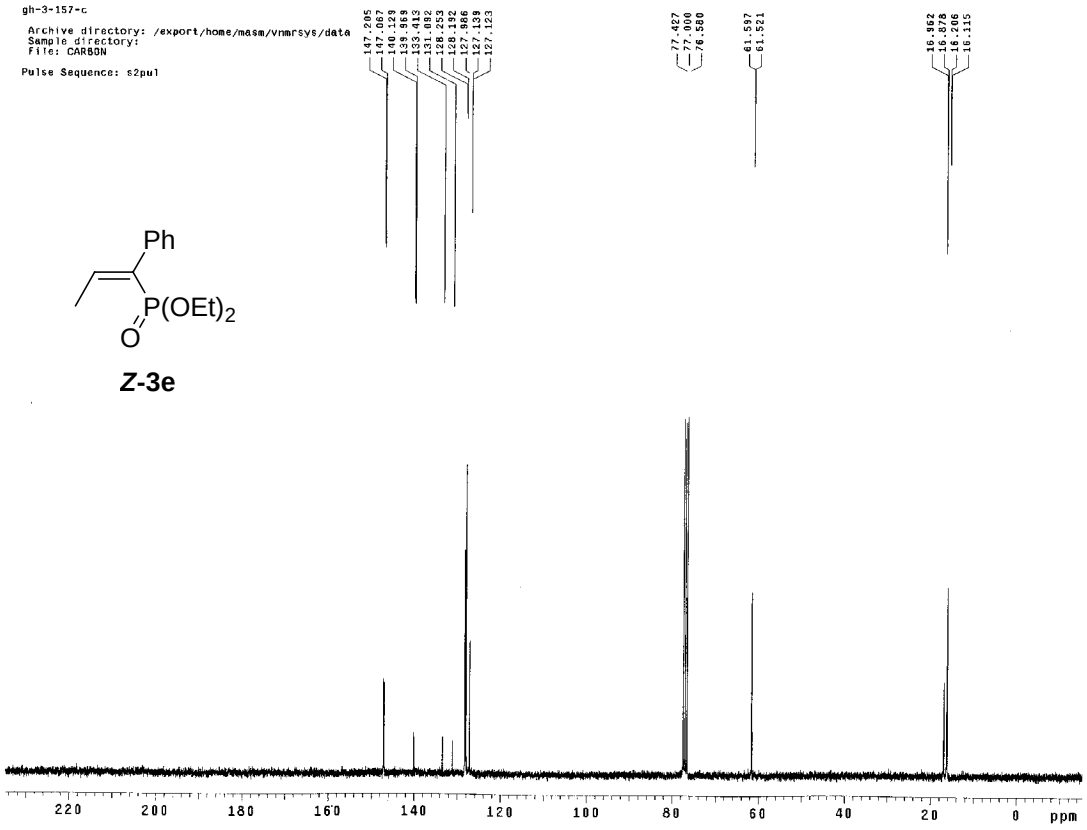
***Z*-3d**

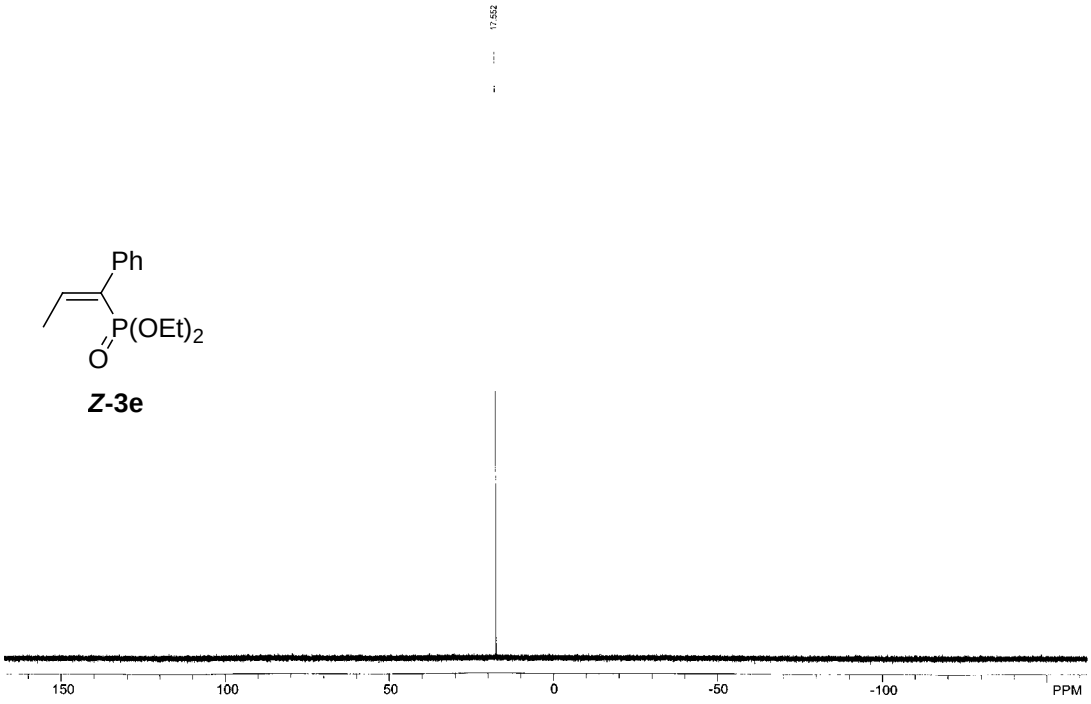

150
100
50
0
-50
-100
PPM

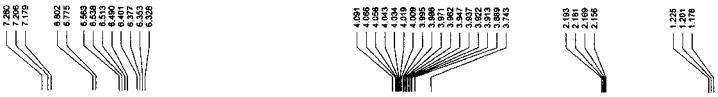
Ph
P(OEt)2
O

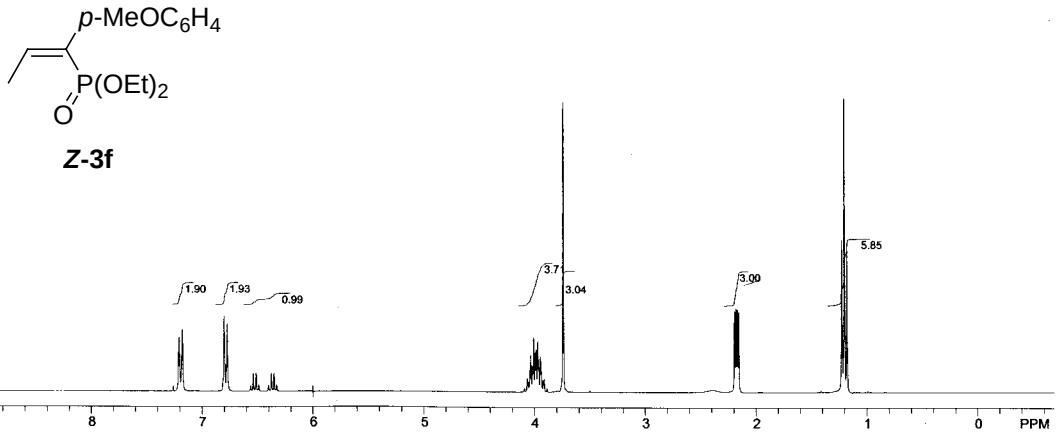
***Z*-3e**

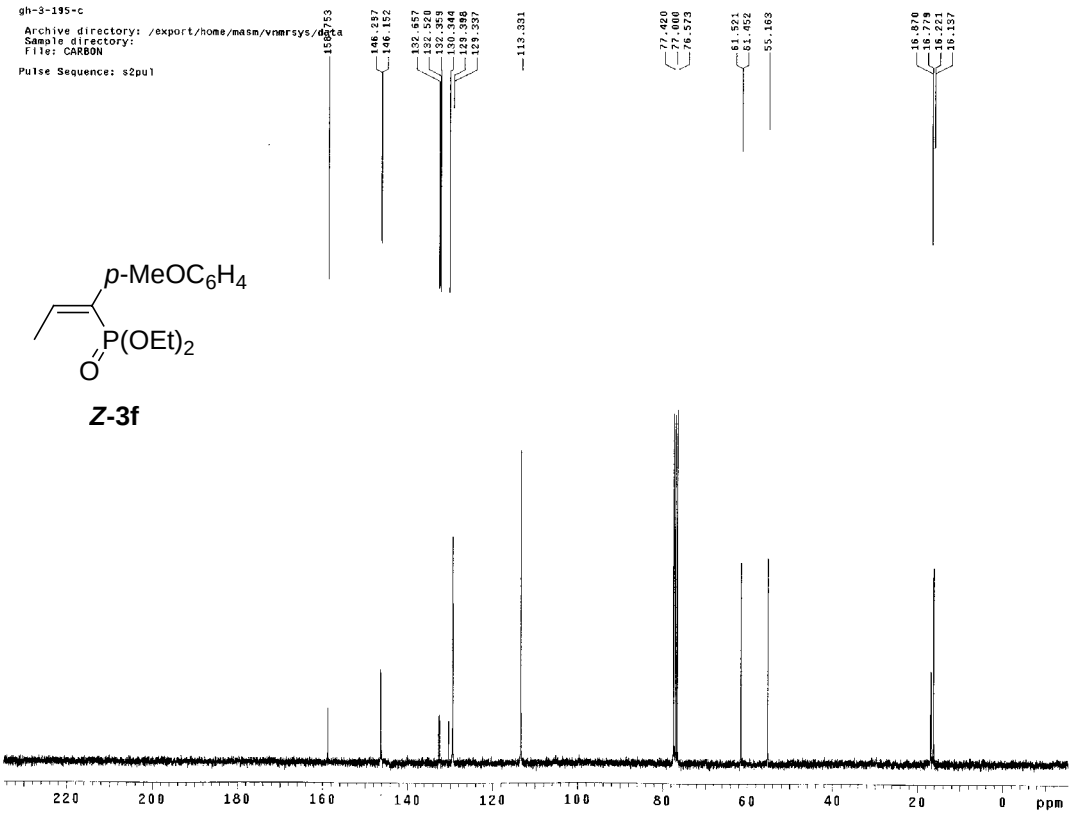

5.00
0.97
4.00
3.64
6.75
8
7
6
5
4
3
2
1
0
PPM

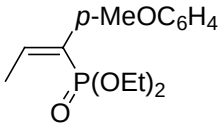

gh-3-157-c
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
147.205
147.067
140.129
139.968
133.413
131.092
128.253
128.192
127.986
127.139
127.123
77.427
77.000
76.580
61.597
61.521
16.962
16.878
16.206
16.115
Ph
P(OEt)2
O
Z-3e
220
200
180
160
140
120
100
80
60
40
20
0
ppm


Ph
P(OEt)2
O
Z-3e
150
100
50
0
-50
-100
PPM

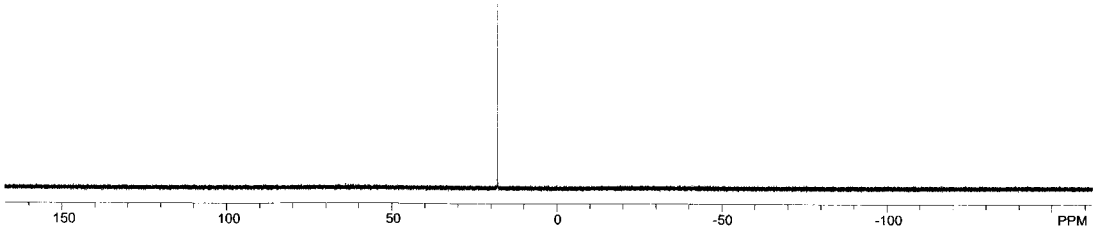


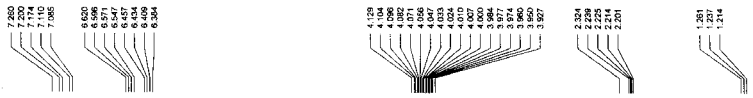

p-MeOC6H4
P(OEt)2
O
Z-3f
1.90
1.93
0.99
3.71
3.04
3.00
5.85
8
7
6
5
4
3
2
1
0
PPM

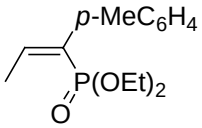

gh-3-195-c
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
p-MeOC6H4
P(OEt)2
O
Z-3f
220
200
180
160
140
120
100
80
60
40
20
0
ppm


p-MeOC6H4
P(OEt)2
O

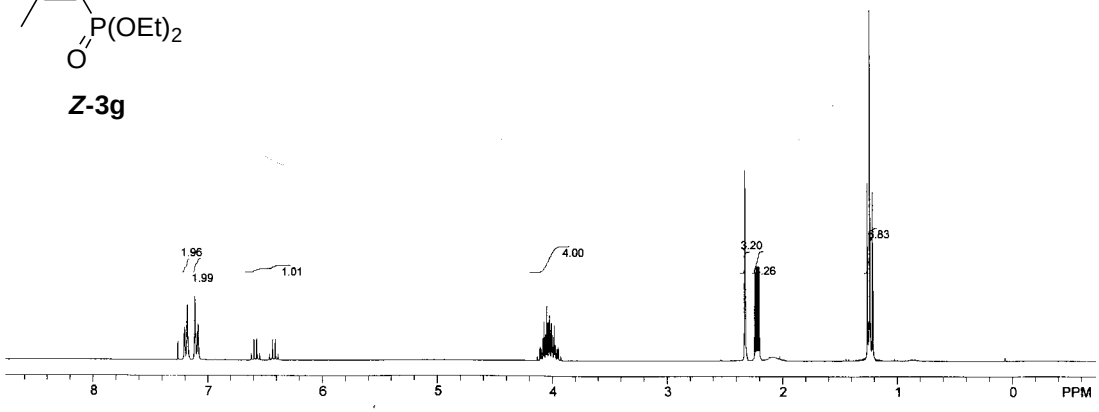
***Z*-3f**

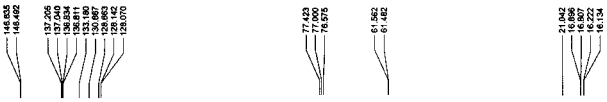

150
100
50
0
-50
-100
PPM

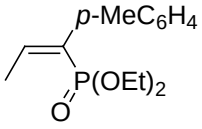



p-MeC6H4
P(OEt)2
O

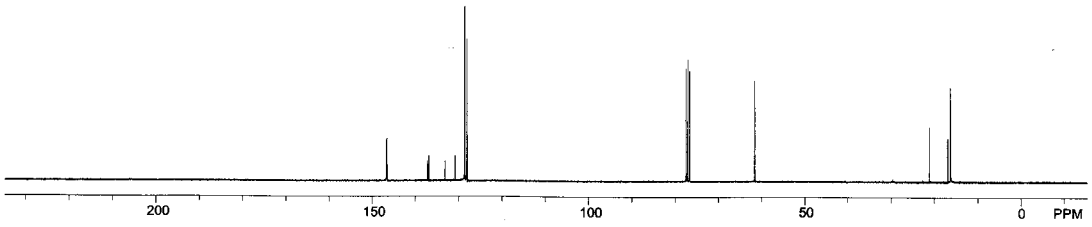
***Z*-3g**

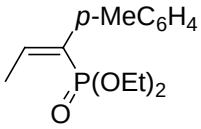

1.96
1.99
1.01
4.00
3.20
3.26
5.83
8
7
6
5
4
3
2
1
0
PPM



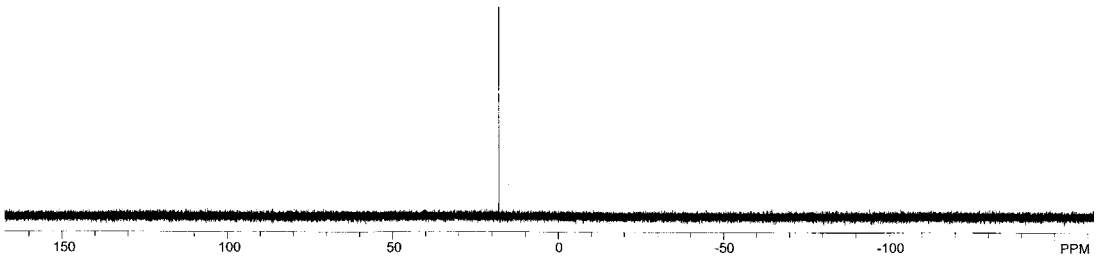

p-MeC6H4
P(OEt)2
O

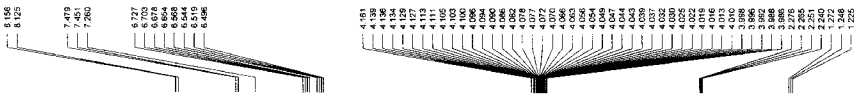
***Z*-3g**

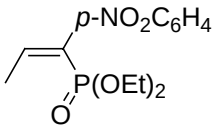

200
150
100
50
0
PPM


p-MeC6H4
P(OEt)2
O

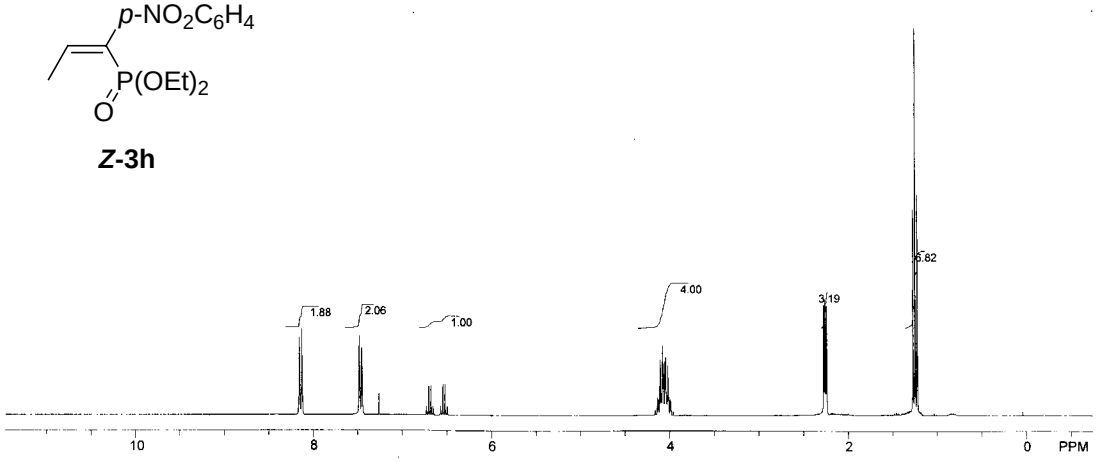
***Z*-3g**

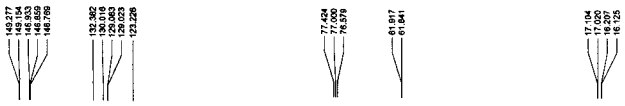

150
100
50
0
-50
-100
PPM

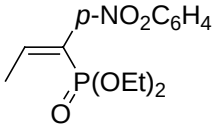



p-NO2C6H4
P(OEt)2
O

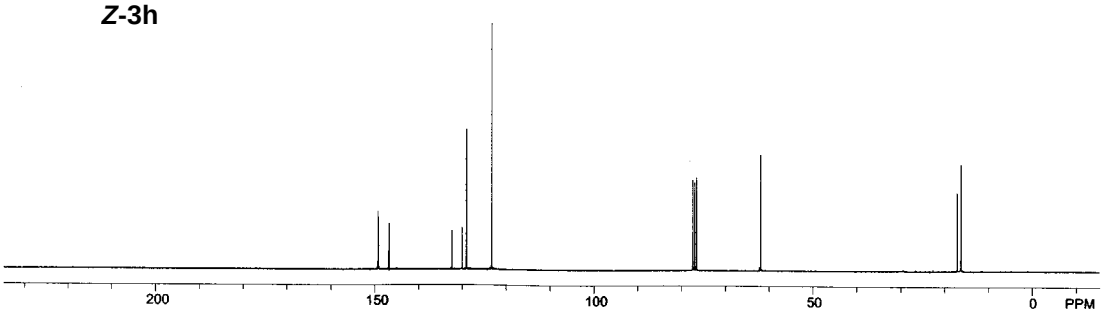
***Z*-3h**


1.88
2.06
1.00
4.00
3.19
6.82
10
8
6
4
2
0
PPM



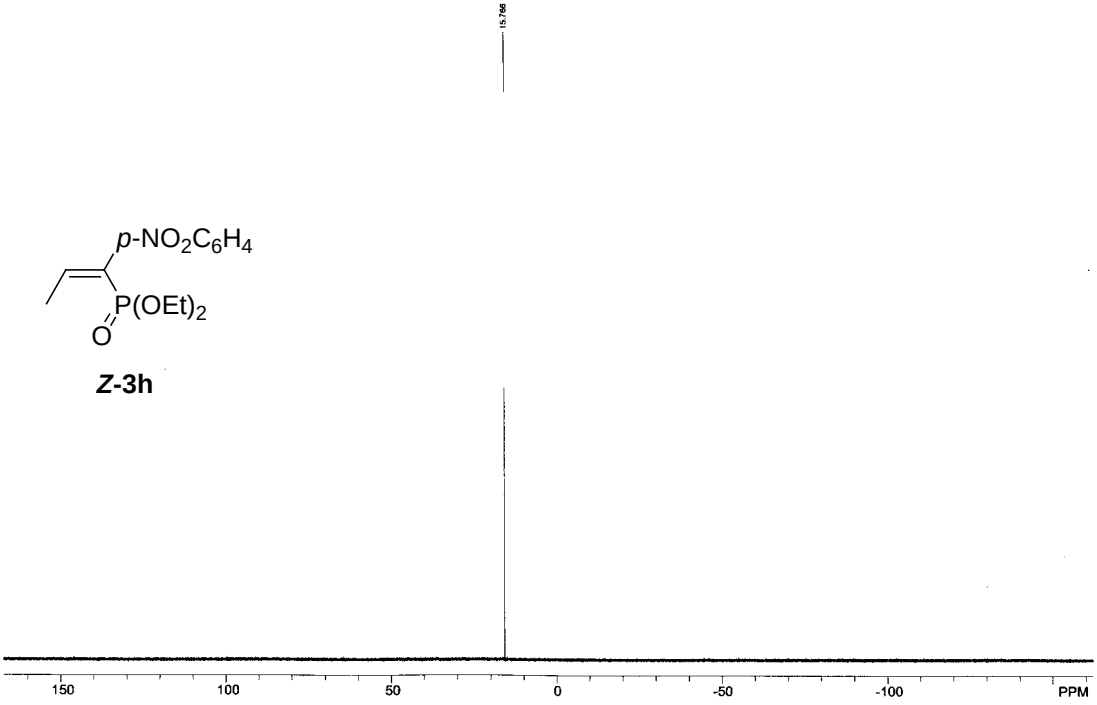

p-NO2C6H4
P(OEt)2
O

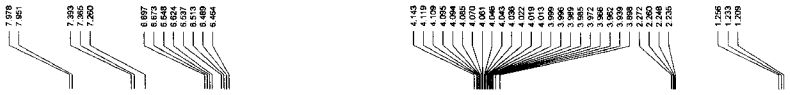
***Z*-3h**

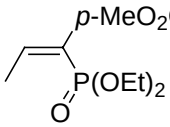

200
150
100
50
0
PPM

p-NO2C6H4
P(OEt)2
O

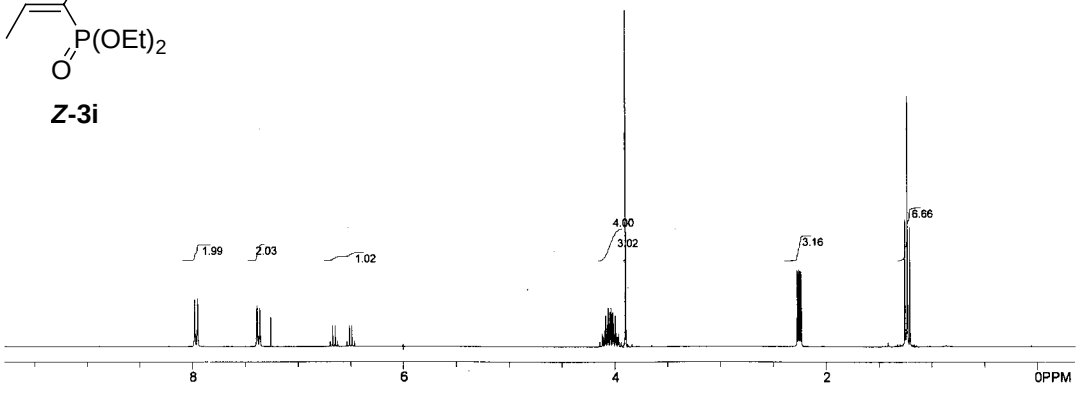
***Z*-3h**

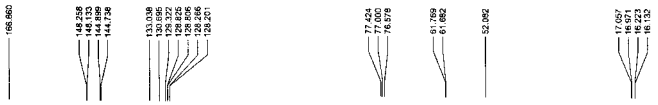

15.768
150
100
50
0
-50
-100
PPM

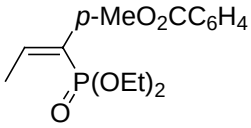



p-MeO2CC6H4
P(OEt)2
O

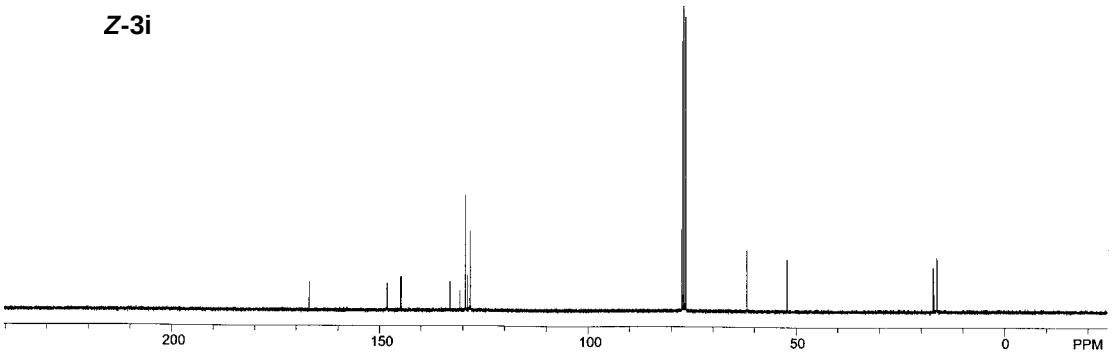
***Z*-3i**


1.99
2.03
1.02
4.00
3.02
3.16
6.66
8
6
4
2
0PPM

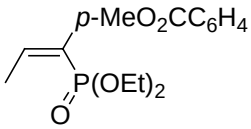

166.660
148.358
148.133
144.899
144.738
133.038
130.696
129.322
128.825
128.656
128.266
128.201
77.424
77.000
76.578
61.789
61.662
52.062
17.057
16.971
16.727
16.132


p-MeO2CC6H4
P(OEt)2
O

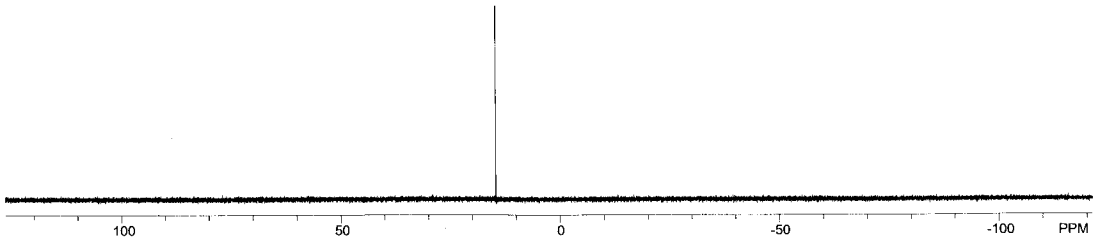
***Z*-3i**

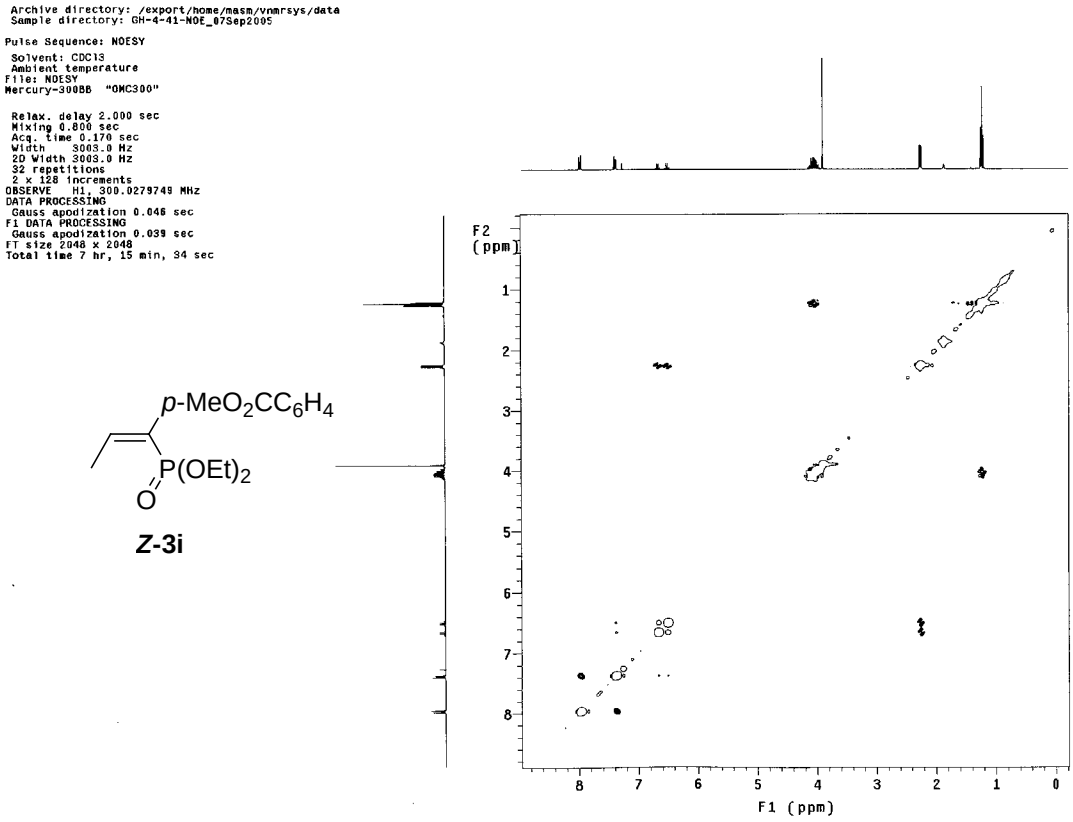

200
150
100
50
0
PPM

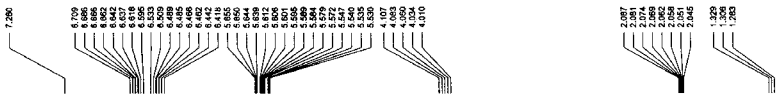
14.680

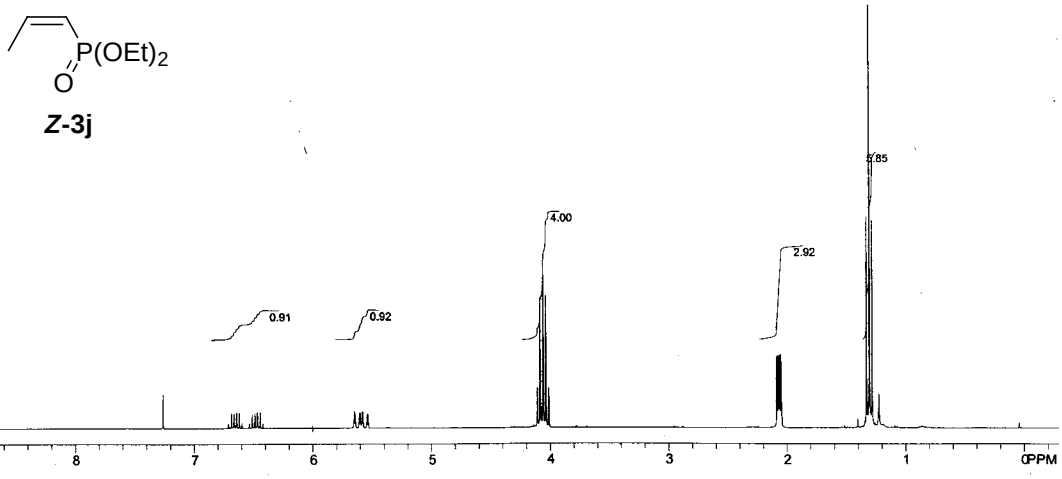

p-MeO2CC6H4
P(OEt)2
O

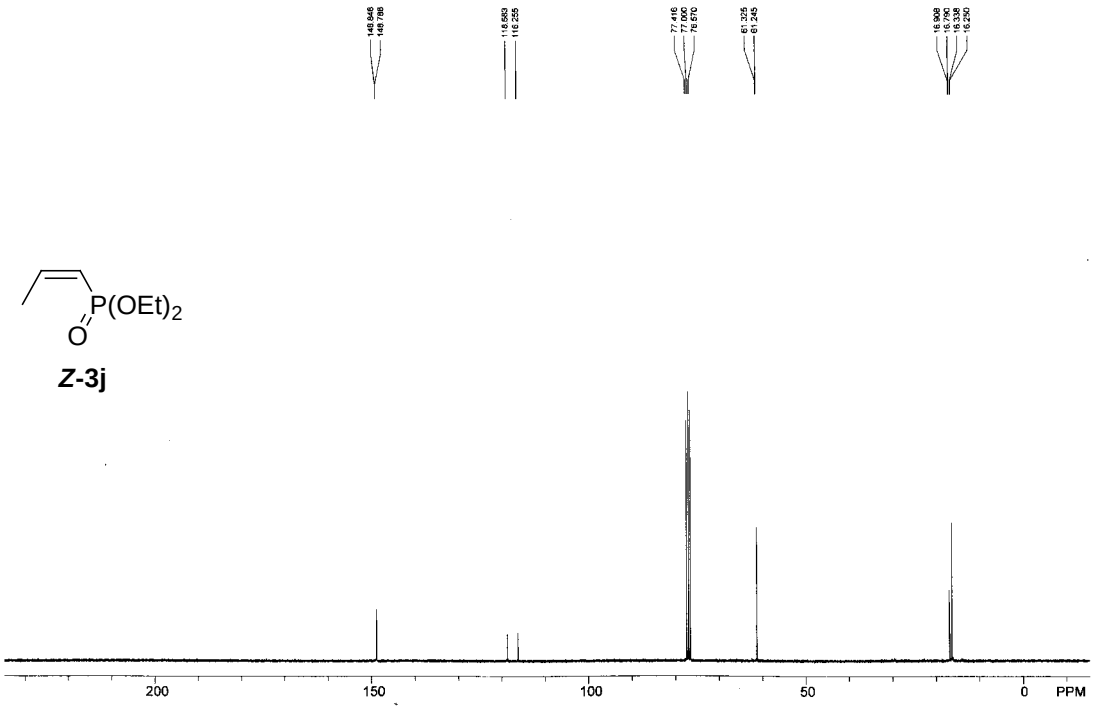
***Z*-3i**


100
50
0
-50
-100
PPM

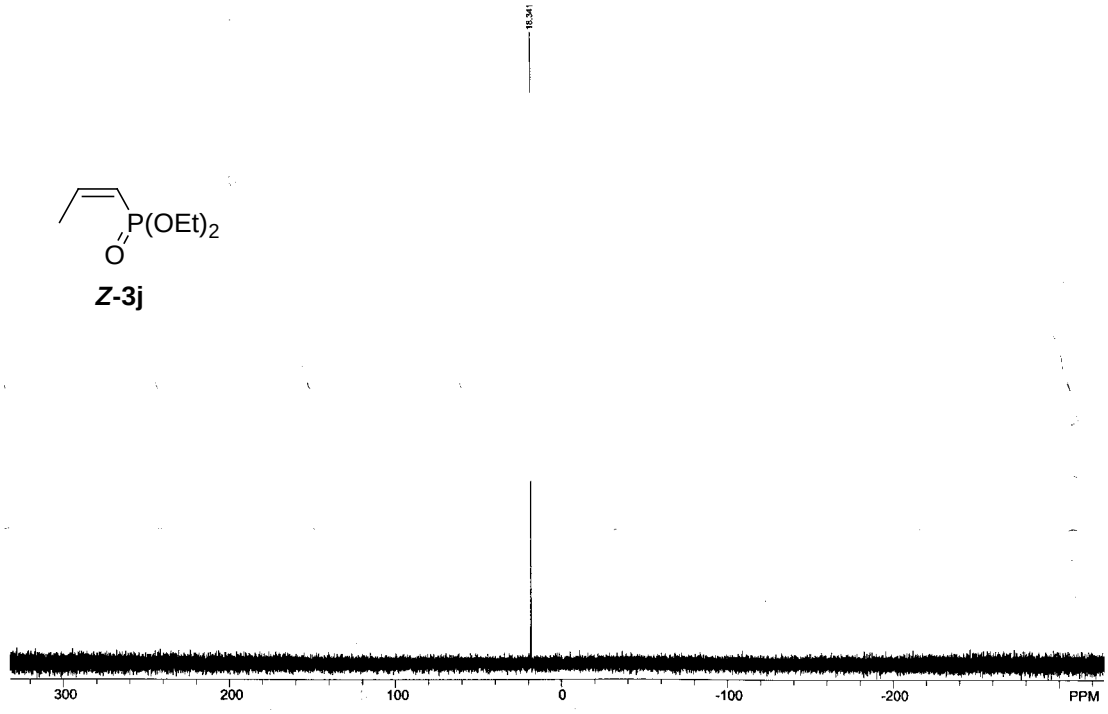

Archive directory: /export/home/masm/vnmrsys/data
Sample directory: GH-4-41-NOE_07Sep2005
Pulse Sequence: NOESY
Solvent: CDCl3
Ambient temperature
File: NOESY
Mercury-300BB "OMC300"
Relax. delay 2.000 sec
Mixing 0.800 sec
Acq. time 0.170 sec
Width 3003.0 Hz
2D Width 3003.0 Hz
32 repetitions
2 x 128 increments
OBSERVE H1, 300.0279749 MHz
DATA PROCESSING
Gauss apodization 0.046 sec
F1 DATA PROCESSING
Gauss apodization 0.039 sec
FT size 2048 x 2048
Total time 7 hr, 15 min, 34 sec
p-MeO2CC6H4
P(OEt)2
O
Z-3i
F2 (ppm)
F1 (ppm)



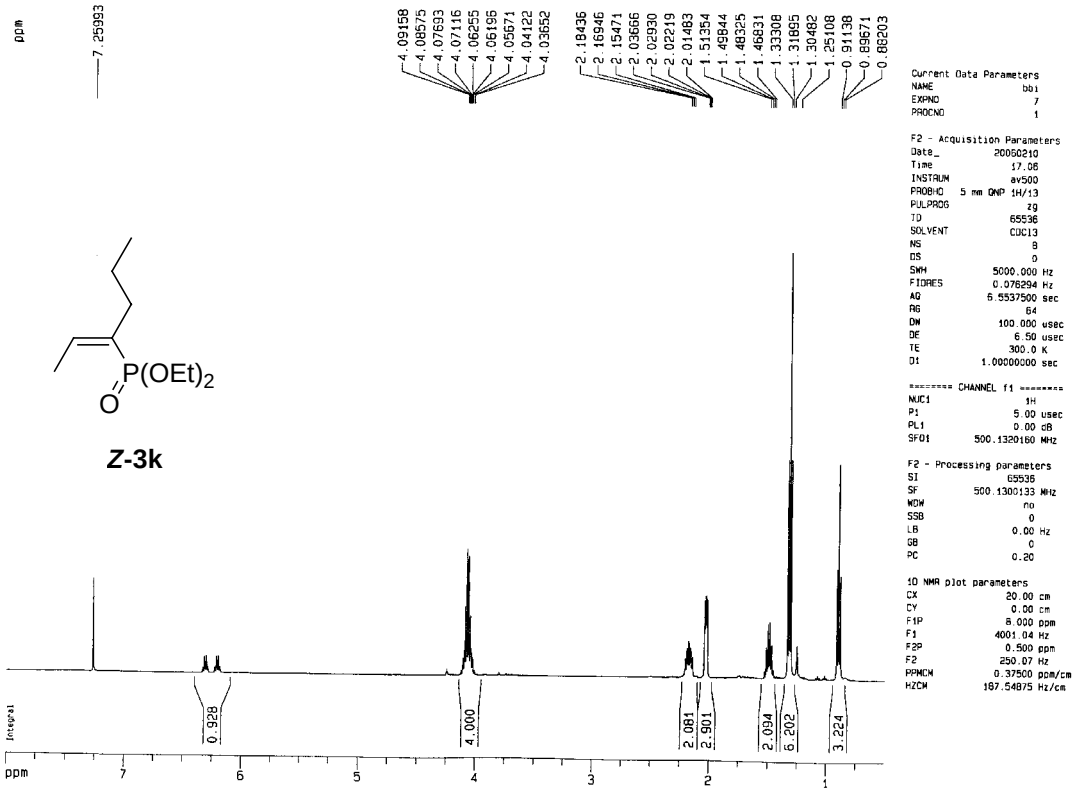

P(OEt)2
O
Z-3j
0.91
0.92
4.00
2.92
7.85
PPM

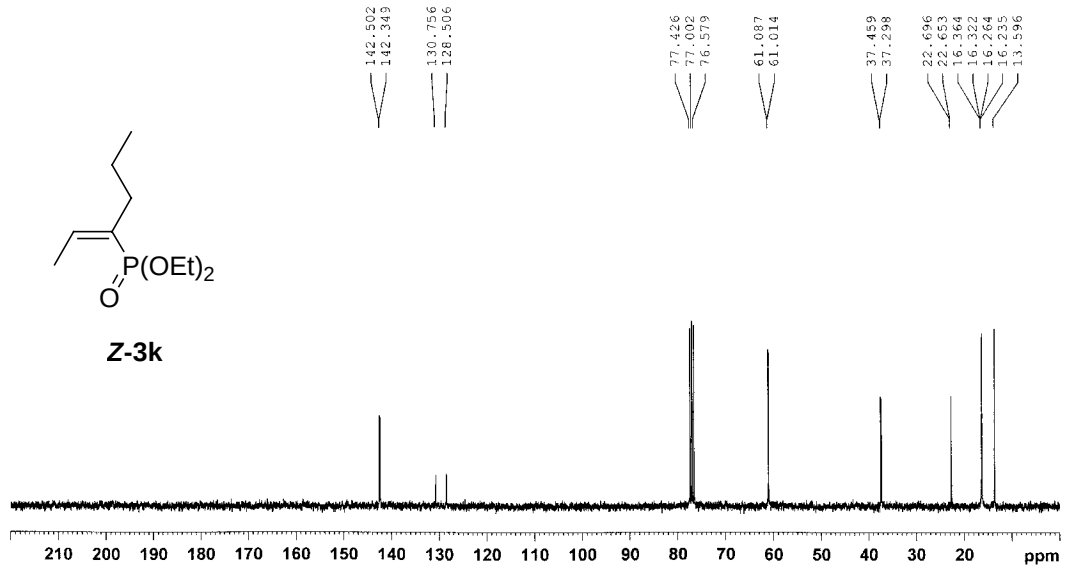

148.946
148.788
118.583
118.255
77.416
77.000
76.670
61.325
61.245
16.908
16.790
16.338
16.250
P(OEt)2
O
200
150
100
50
0
PPM

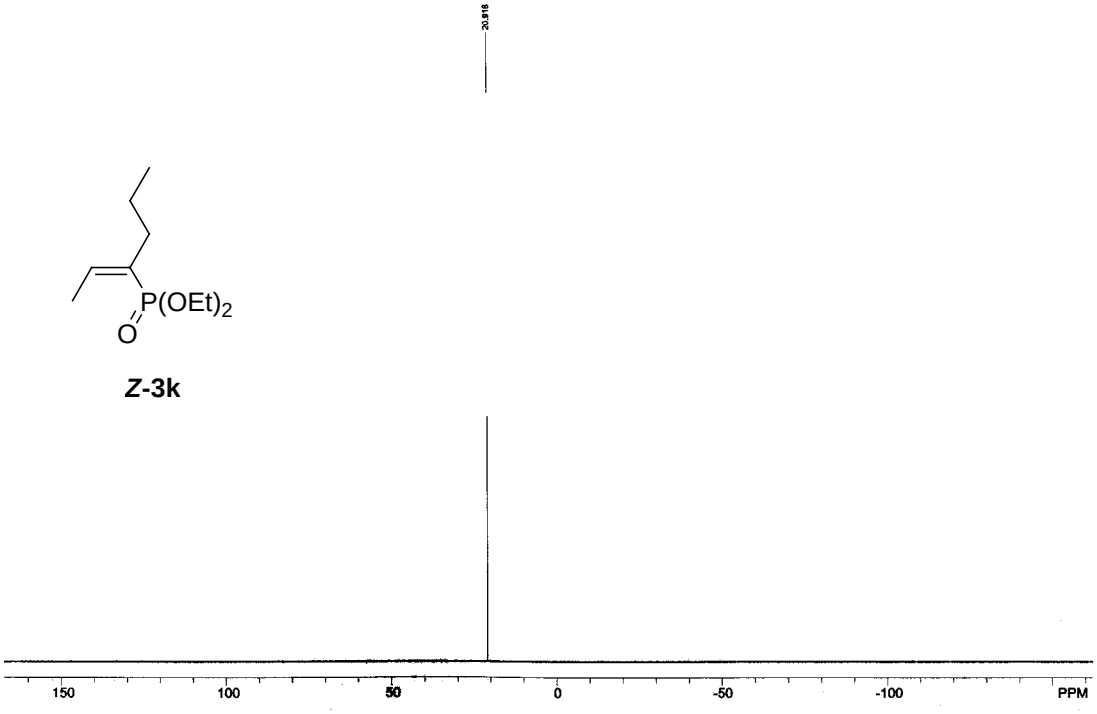
***Z*-3j**

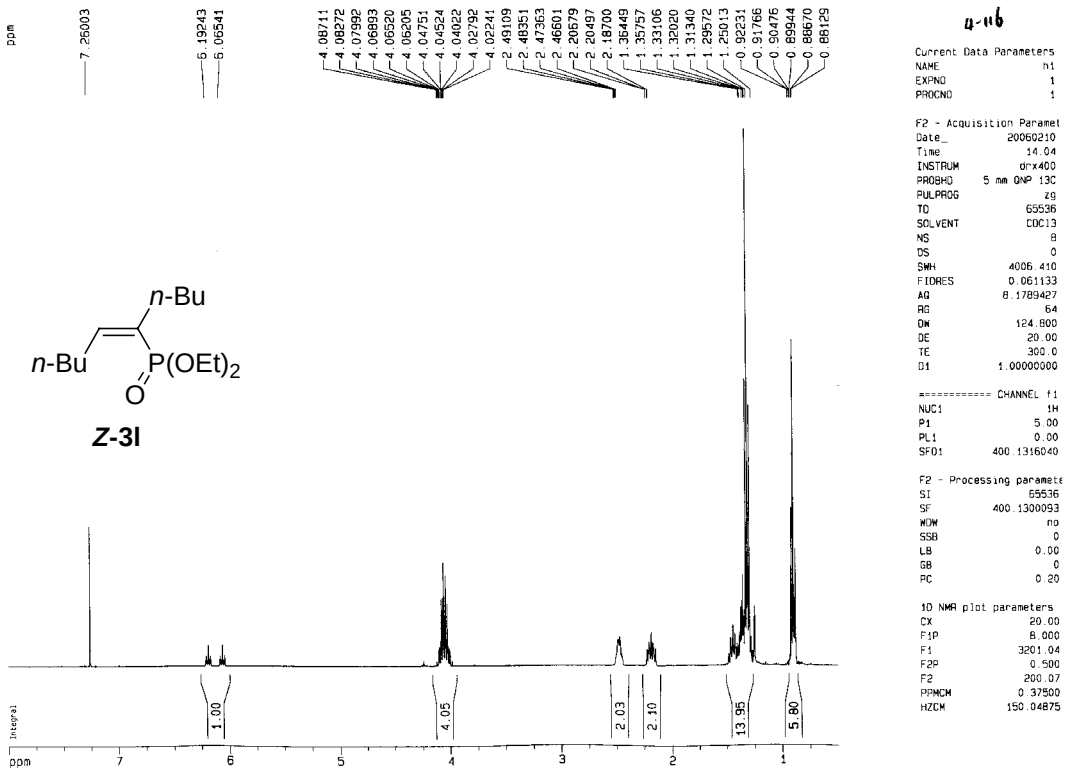

18.341
P(OEt)2
O
300
200
100
0
-100
-200
PPM

***Z*-3j**

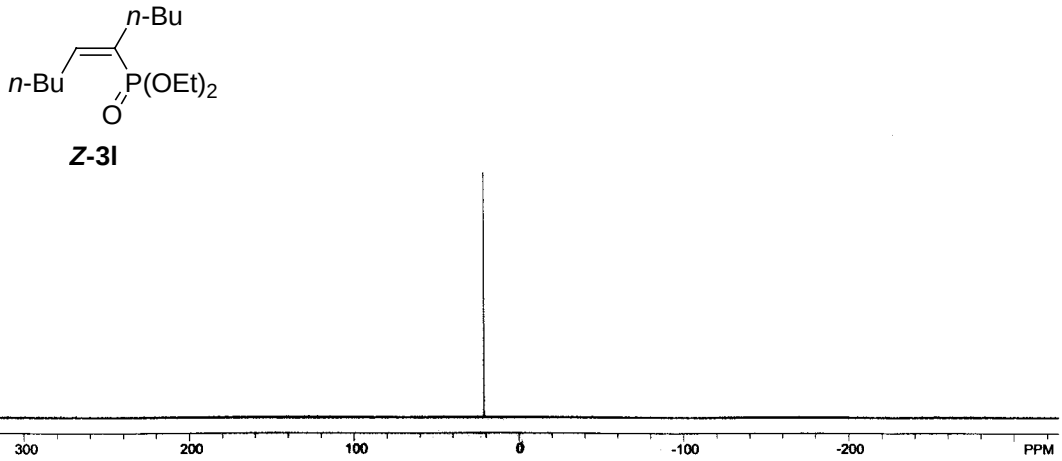

ppm
7.25993
4.09158
4.08575
4.07693
4.07116
4.06255
4.06195
4.05671
4.04122
4.03652
2.18436
2.16946
2.15471
2.03666
2.02930
2.02219
2.01483
1.51354
1.49844
1.48325
1.46831
1.33308
1.31895
1.30482
1.25108
0.91138
0.89671
0.88203
P(OEt)2
O
Z-3k
Integral
0.928
4.000
2.081
2.901
2.094
6.202
3.224
ppm
7
6
5
4
3
2
1
Current Data Parameters
NAME bbi
EXPNO 7
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060210
Time 17.06
INSTRUM av500
PROBHD 5 mm DNP 1H/13
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 5000.000 Hz
FIDRES 0.076294 Hz
AQ 6.5537500 sec
RG 64
DW 100.000 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 0.00 dB
SFO1 500.1320160 MHz
F2 - Processing parameters
SI 65536
SF 500.1300133 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 0.20
1D NMR plot parameters
CX 20.00 cm
CY 0.00 cm
F1P 8.000 ppm
F1 4001.04 Hz
F2P 0.500 ppm
F2 250.07 Hz
PPMCM 0.37500 ppm/cm
HZCM 187.54875 Hz/cm


142.502
142.349
130.756
128.506
77.426
77.002
76.579
61.087
61.014
37.459
37.298
22.696
22.653
16.364
16.322
16.264
16.235
13.596
P(OEt)2
O
Z-3k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

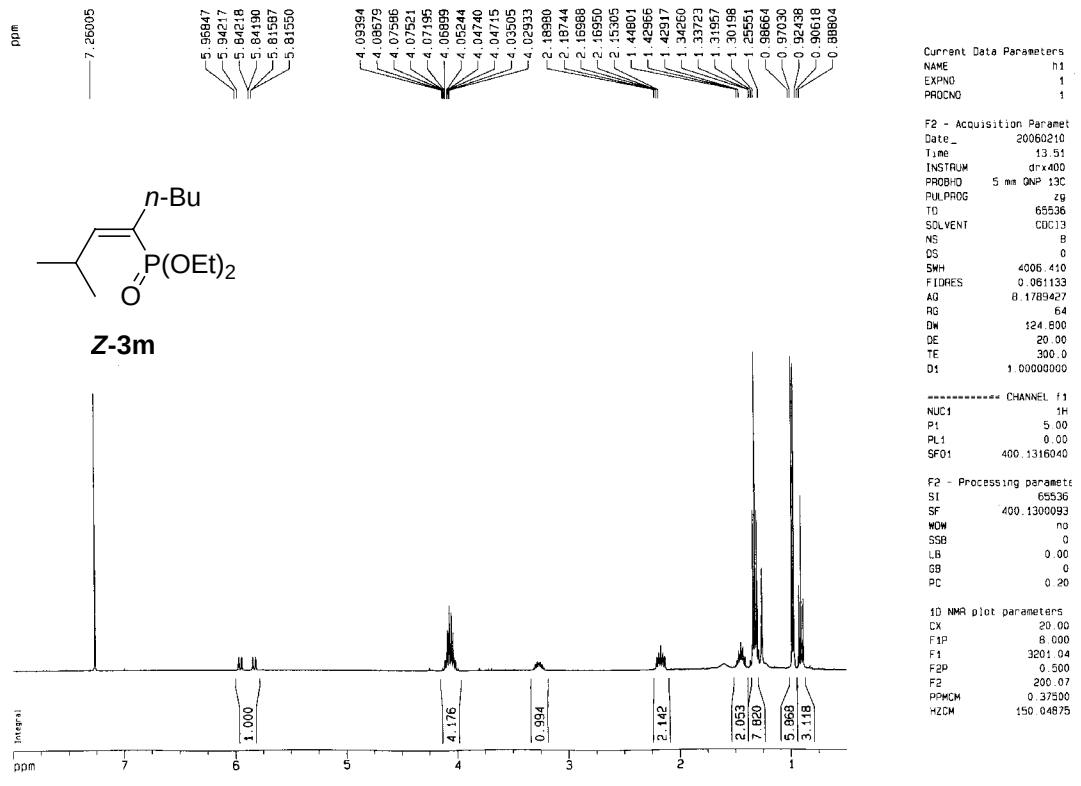





```
Current Data Parameters
NAME                  h1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Paramet
Date_           20060210
Time               14.04
INSTRUM          drx400
PROBHD     5 mm QNP 13C
PULPROG              zg
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH             4006.410
FIDRES          0.061133
AQ              8.1789427
RG                   64
DW               124.800
DE                20.00
TE                300.0
D1             1.00000000

============ CHANNEL f1
NUC1                 1H
P1                 5.00
PL1                0.00
SFO1         400.1316040

F2 - Processing paramete
SI                65536
SF          400.1300093
WDW                  no
SSB                   0
LB                 0.00
GB                    0
PC                 0.20

1D NMR plot parameters
CX                20.00
F1P                8.000
F1                3201.04
F2P                0.500
F2                200.07
PPMCM             0.37500
HZCM            150.04875
```

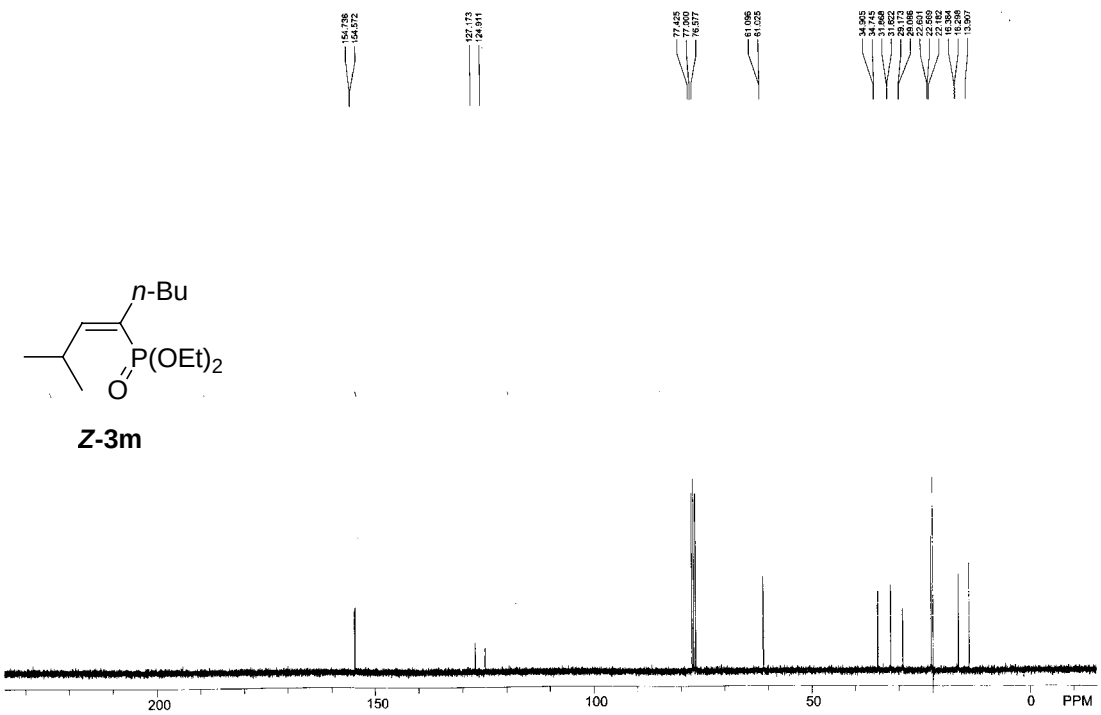


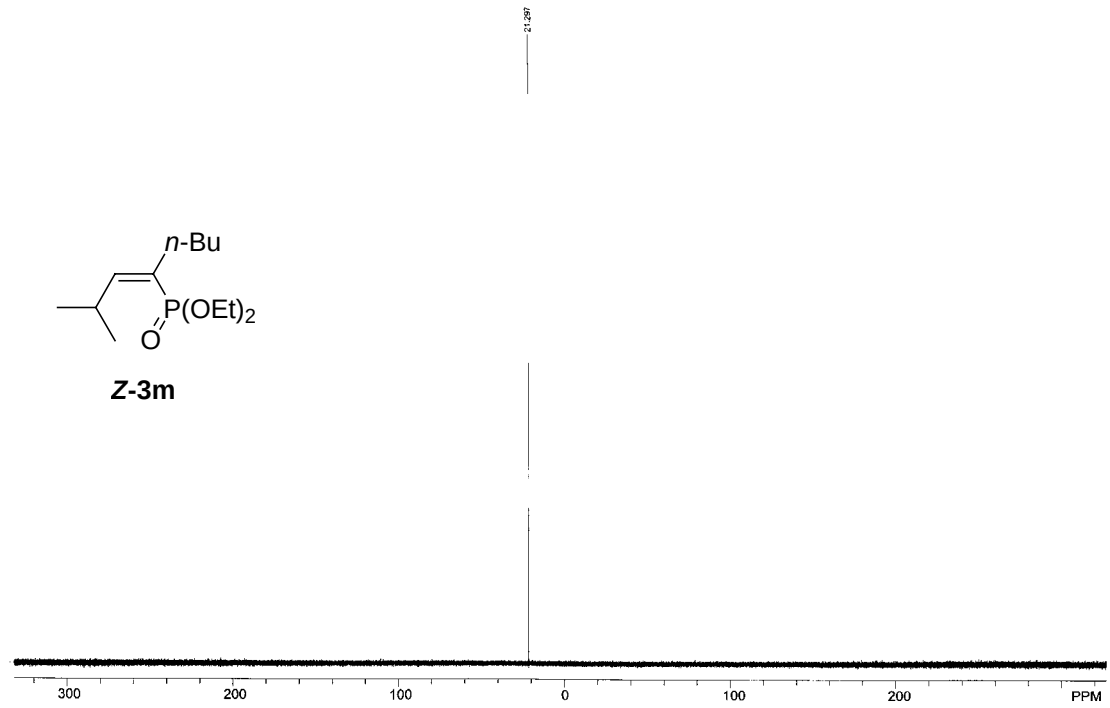
***Z*-3l**

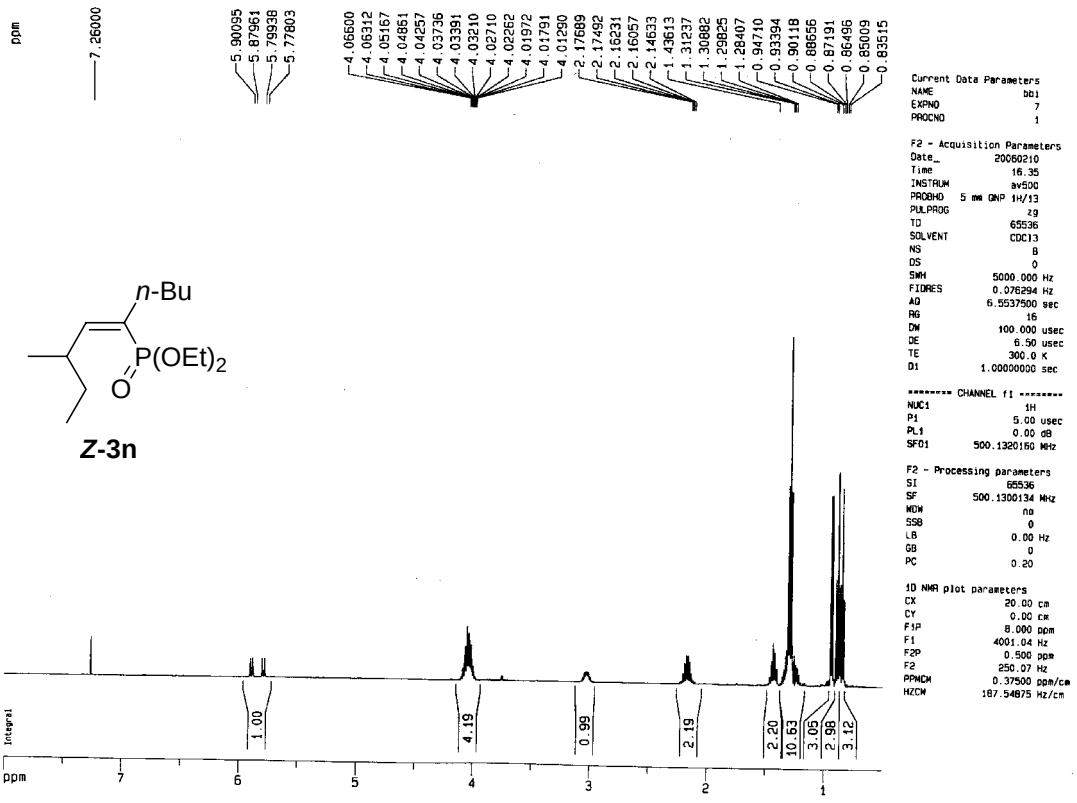


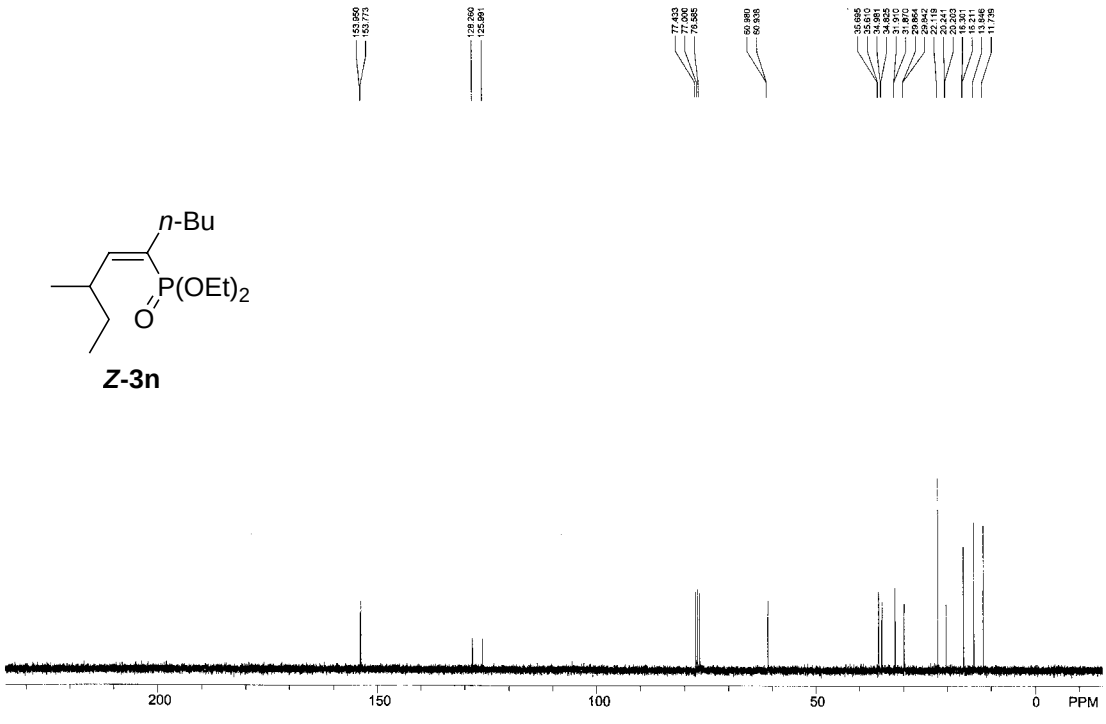
***Z*-3m**

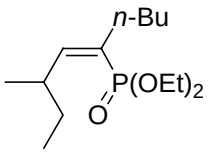
```
Current Data Parameters
NAME                  h1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Paramet
Date_           20060210
Time               13.51
INSTRUM          drx400
PROBHD     5 mm QNP 13C
PULPROG              zg
TD                65536
SOLVENT           CDCl3
NS                     8
DS                     0
SWH              4006.410
FIDRES           0.061133
AQ               8.1789427
RG                    64
DW                124.800
DE                 20.00
TE                 300.0
D1              1.00000000

============ CHANNEL f1
NUC1                  1H
P1                  5.00
PL1                 0.00
SF01          400.1316040

F2 - Processing paramete
SI                 65536
SF          400.1300093
WDW                   no
SSB                    0
LB                  0.00
GB                     0
PC                  0.20

1D NMR plot parameters
CX                 20.00
F1P                 8.000
F1                3201.04
F2P                 0.500
F2                200.07
PPMCM              0.37500
HZCM             150.04875
```


154.738
154.572
127.173
124.911
77.425
77.000
76.577
61.096
61.025
34.905
34.745
31.868
31.822
29.173
29.086
22.601
22.569
22.182
16.384
16.298
13.907
n-Bu
P(OEt)2
O
Z-3m
200
150
100
50
0
PPM

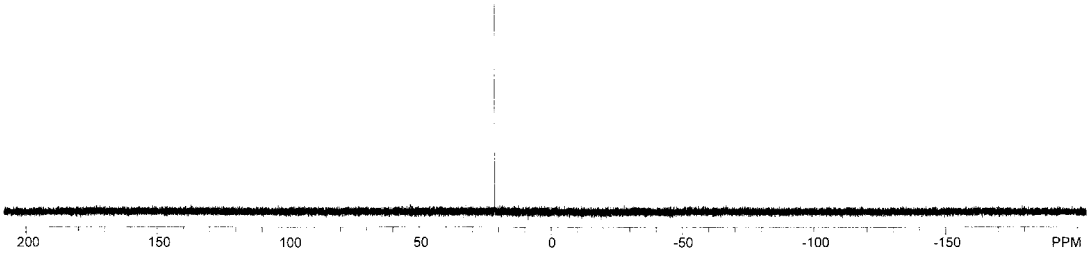

21.297
n-Bu
P(OEt)2
O
Z-3m
300
200
100
0
100
200
PPM

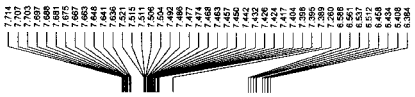

ppm
7.26000
5.90095
5.87961
5.79938
5.77803
4.06600
4.06312
4.05167
4.04861
4.04257
4.03736
4.03391
4.03210
4.02710
4.02262
4.01972
4.01791
4.01290
2.17689
2.17492
2.16231
2.16057
2.14633
1.43613
1.31237
1.30882
1.29825
1.28407
0.94710
0.93394
0.90118
0.88656
0.87191
0.86496
0.85009
0.83515
Current Data Parameters
NAME bbi
EXPNO 7
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060210
Time 16.35
INSTRUM av500
PROBHD 5 mm GNP 1H/13
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 5000.000 Hz
FIDRES 0.076294 Hz
AQ 6.5537500 sec
RG 16
DW 100.000 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 0.00 dB
SFO1 500.1320160 MHz
F2 - Processing parameters
SI 65536
SF 500.1300134 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 0.20
1D NMR plot parameters
CX 20.00 cm
CY 0.00 cm
F1P 8.000 ppm
F1 4001.04 Hz
F2P 0.500 ppm
F2 250.07 Hz
PPMCM 0.37500 ppm/cm
HZCM 187.54875 Hz/cm
n-Bu
P(OEt)2
O
Z-3n
Integral
1.00
4.19
0.99
2.19
2.20
10.63
3.05
2.98
3.12
ppm
7
6
5
4
3
2
1

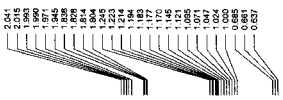

153.950
153.773
128.260
125.991
77.433
77.000
76.585
50.980
50.938
35.695
35.610
34.981
34.825
31.910
31.870
29.864
29.842
22.118
20.241
20.203
16.301
15.211
13.846
11.739
n-Bu
P(OEt)2
O
Z-3n
200
150
100
50
0
PPM

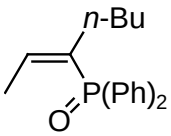

n-Bu
P(OEt)2
O

***Z*-3n**

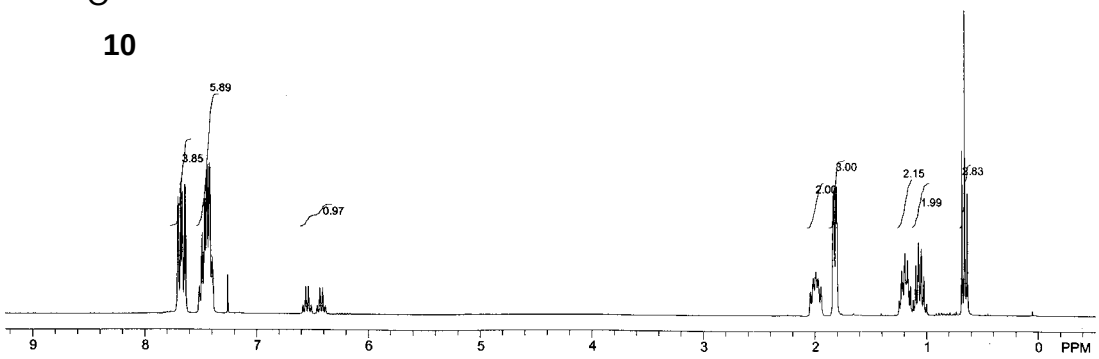

200
150
100
50
0
-50
-100
-150
PPM

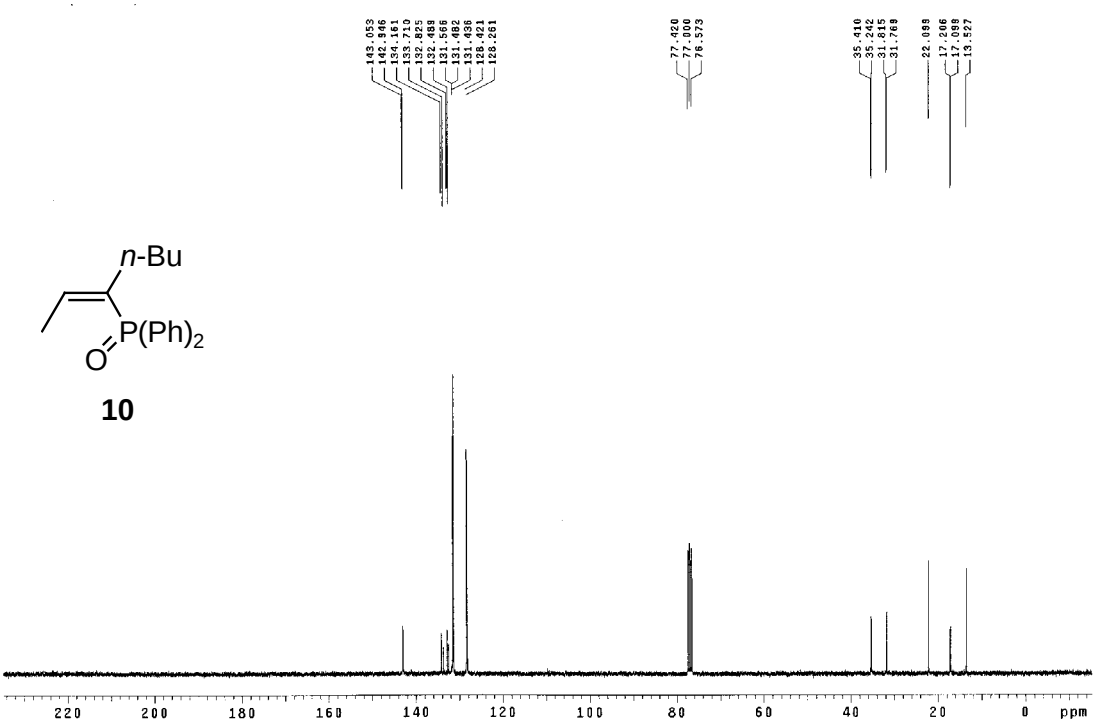




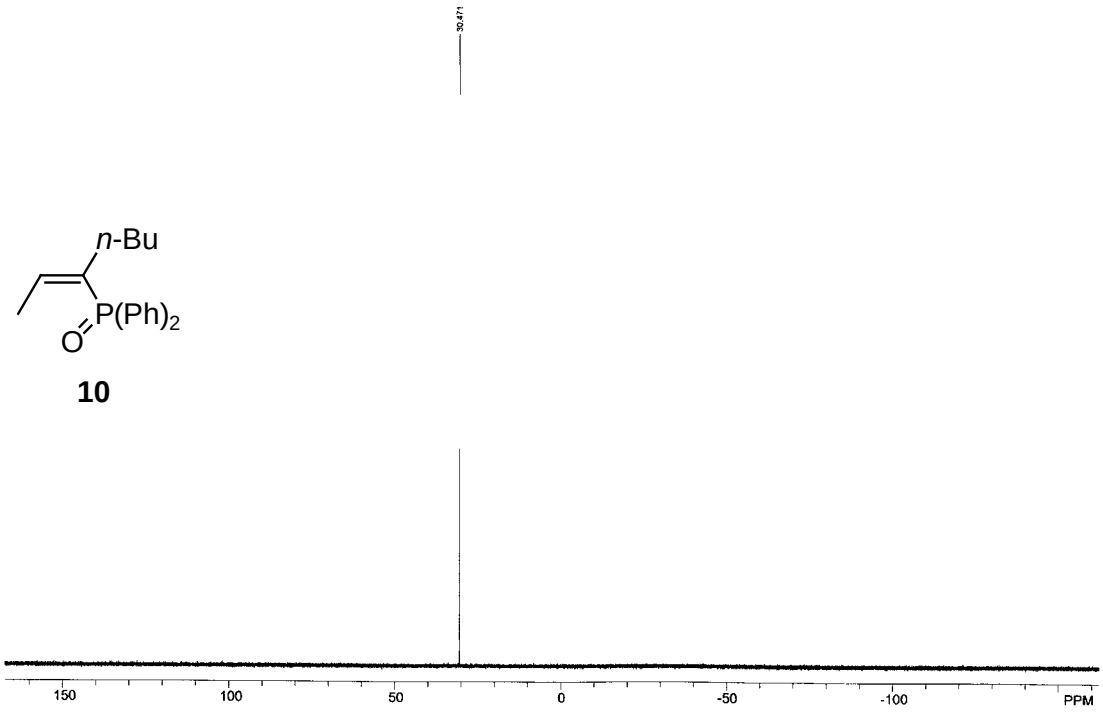

n-Bu
P(Ph)2
O

10

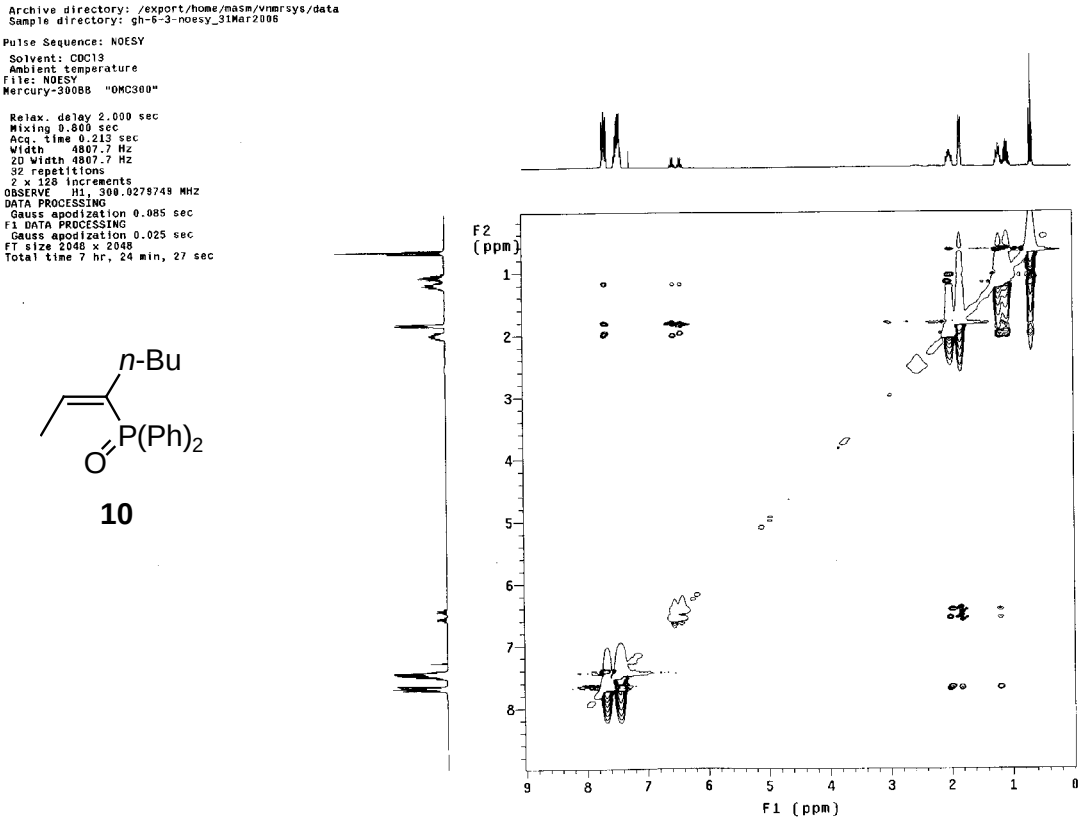

5.89
3.85
0.97
3.00
2.06
2.15
1.99
3.83
9
8
7
6
5
4
3
2
1
0
PPM


143.053
142.946
134.161
133.710
132.825
132.489
131.566
131.482
131.436
128.421
128.261
77.420
77.000
76.573
35.410
35.242
31.815
31.768
22.098
17.006
17.098
13.527
n-Bu
P(Ph)2
O
220
200
180
160
140
120
100
80
60
40
20
0
ppm

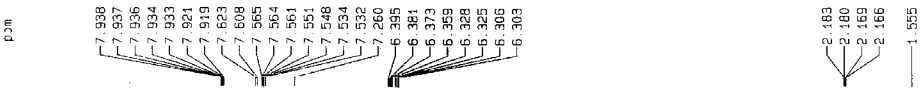
10

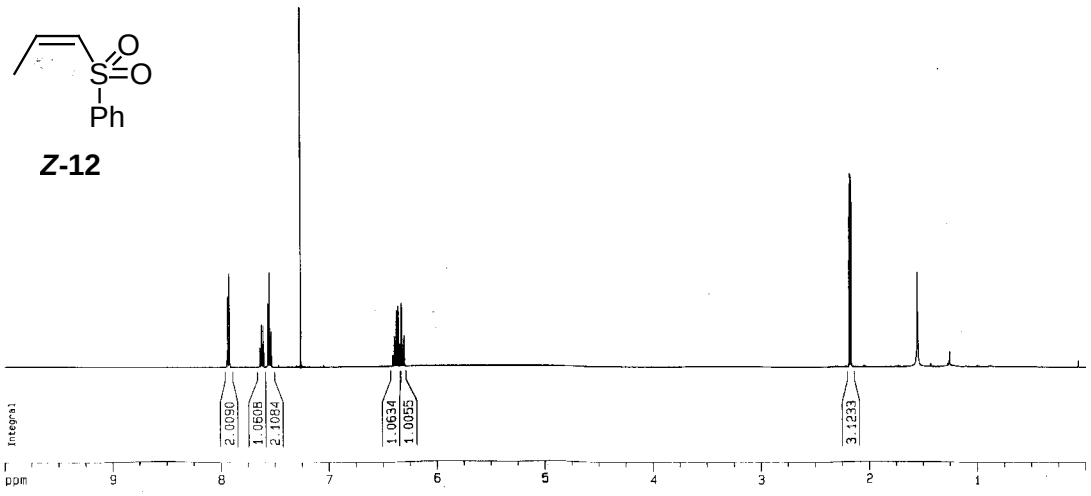

30.471
n-Bu
P(Ph)2
O
150
100
50
0
-50
-100
PPM

10

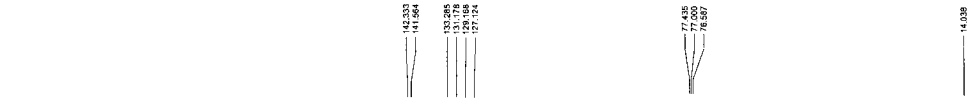

Archive directory: /export/home/masm/vnmrsys/data
Sample directory: gh-6-3-noesy_31Mar2006
Pulse Sequence: NOESY
Solvent: CDCl3
Ambient temperature
File: NOESY
Mercury-300BB "OMC300"
Relax. delay 2.000 sec
Mixing 0.800 sec
Acq. time 0.213 sec
Width 4807.7 Hz
2D Width 4807.7 Hz
32 repetitions
2 x 128 increments
OBSERVE H1, 300.0279748 MHZ
DATA PROCESSING
Gauss apodization 0.085 sec
F1 DATA PROCESSING
Gauss apodization 0.025 sec
FT size 2048 x 2048
Total time 7 hr, 24 min, 27 sec
n-Bu
P(Ph)2
O
F2 (ppm)
F1 (ppm)

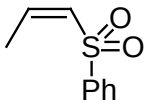
10


pjm
7.938
7.937
7.936
7.934
7.933
7.921
7.919
7.623
7.608
7.565
7.564
7.561
7.551
7.548
7.534
7.532
7.260
6.395
6.381
6.373
6.359
6.328
6.325
6.306
6.303
2.183
2.180
2.169
2.166
1.555


O
S
O
Ph
Integral
2.0090
1.0608
2.1084
1.0634
1.0055
3.1233
ppm

***Z*-12**





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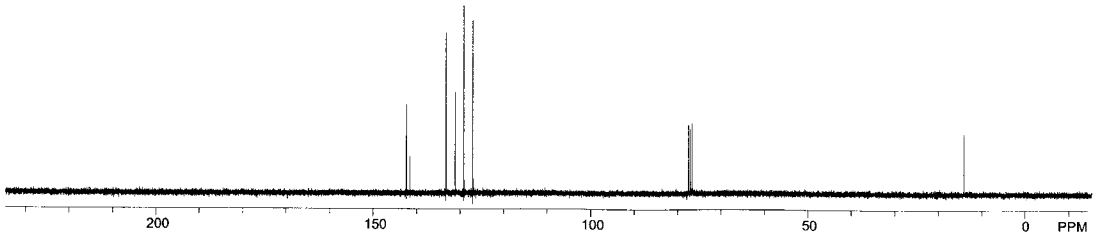

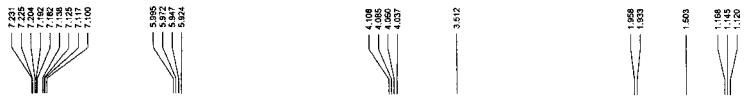

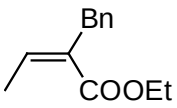

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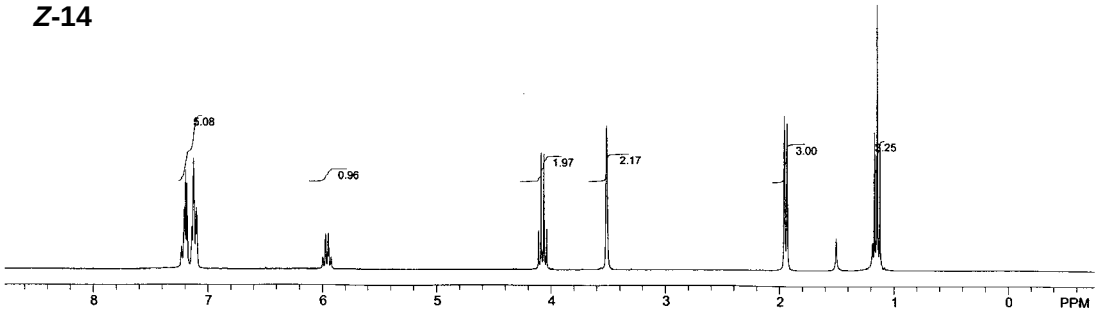

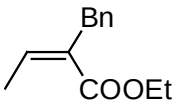

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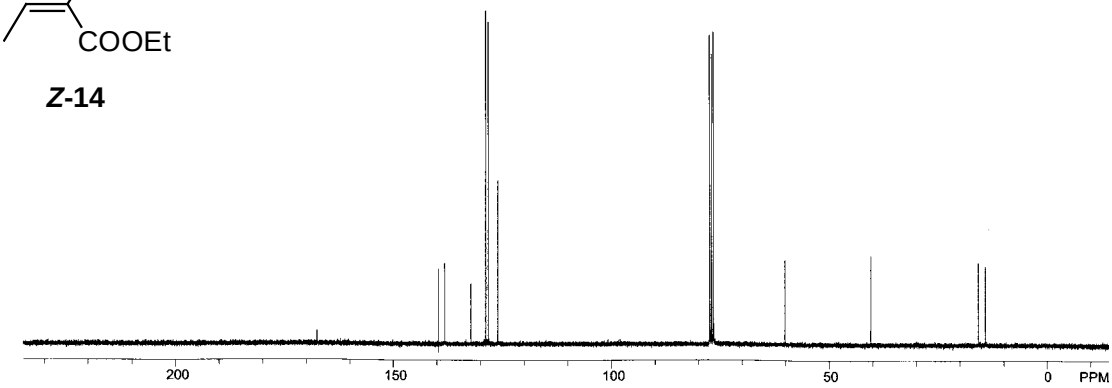
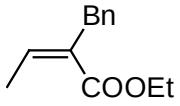



```
Archive directory: /export/home/masm/vnmrsys/data
Sample directory: gh-6-20-1-noesy_29Mar2006

Pulse Sequence: NOESY

 Solvent: CDCl3
 Ambient temperature
File: NOESY
Mercury-300BB  "OMC300"

 Relax. delay 2.000 sec
 Mixing 0.800 sec
 Acq. time 0.213 sec
 Width     4807.7 Hz
 2D Width 4807.7 Hz
  32 repetitions
  2 x 128 increments
OBSERVE   H1, 300.0280171 MHz
DATA PROCESSING
 Line broadening 3.0 Hz
 Gauss apodization 0.098 sec
F1 DATA PROCESSING
 Gauss apodization 0.025 sec
FT size 2048 x 2048
Total time 7 hr, 24 min, 27 sec
```



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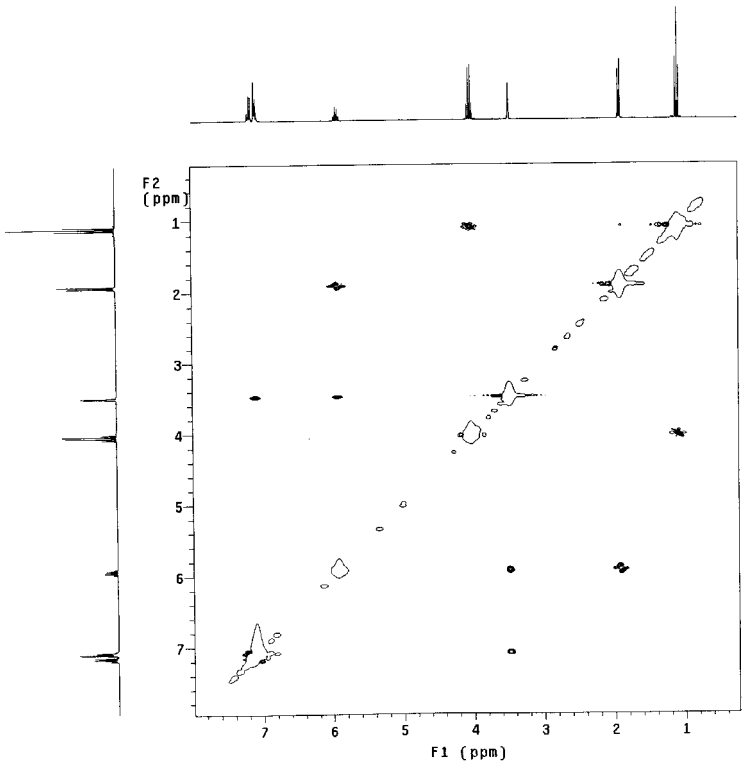
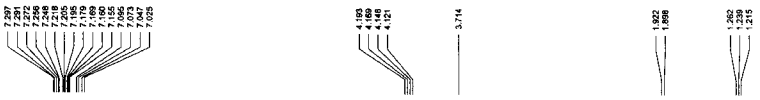
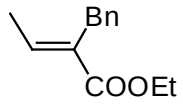
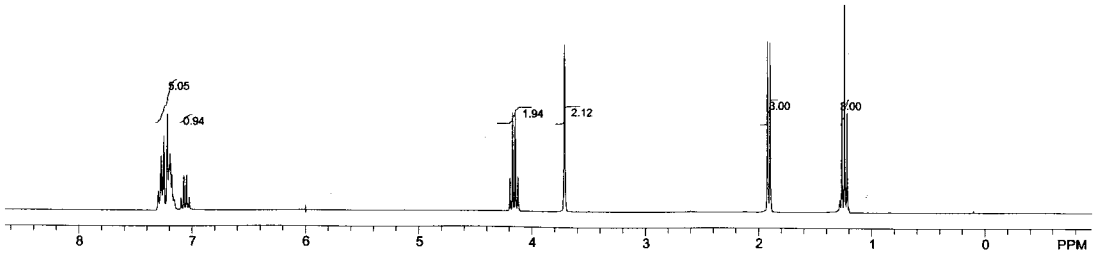
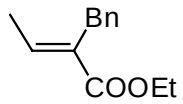




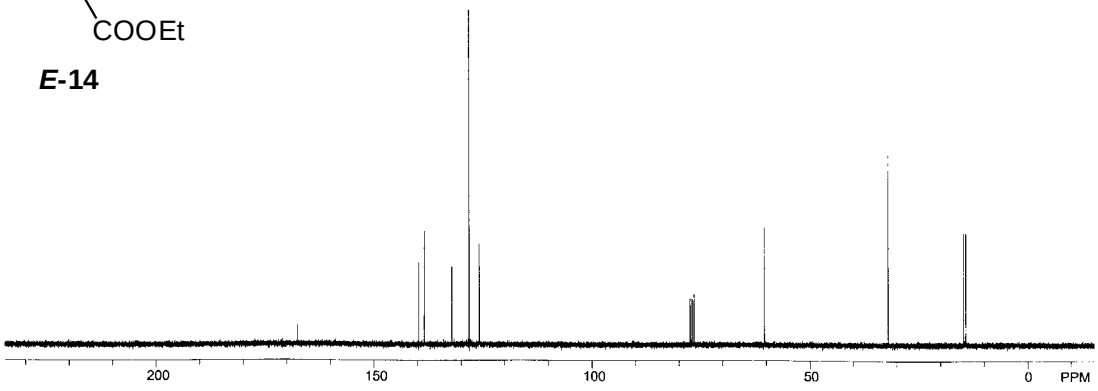

Bn
COOEt

***E*-14**


5.05
0.94
1.94
2.12
3.00
3.00
PPM


Bn
COOEt

***E*-14**


200
150
100
50
0
PPM

References

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