Supplementary Information
for

Catalyst–free synthesis of cycloalkenyl phosphonates

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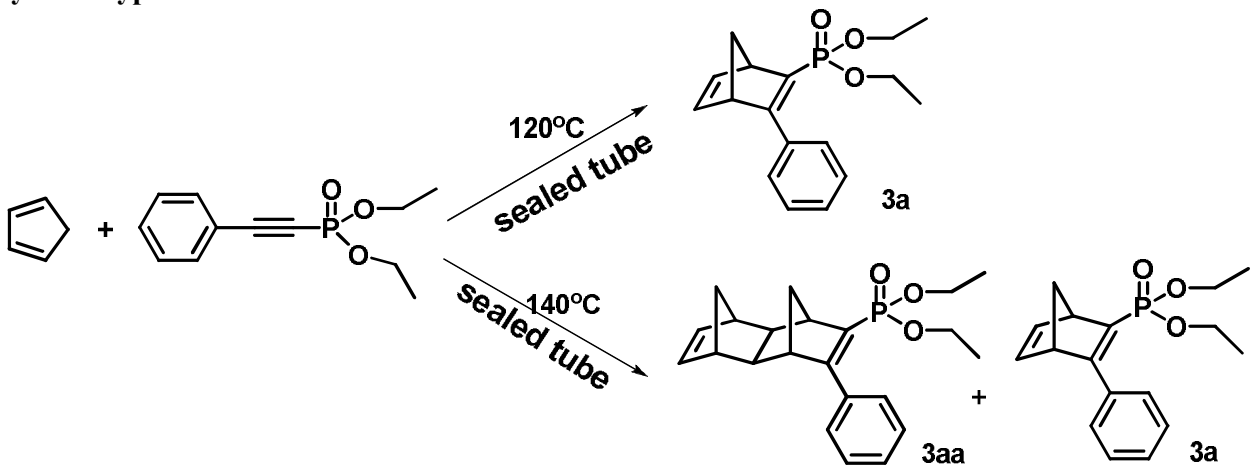
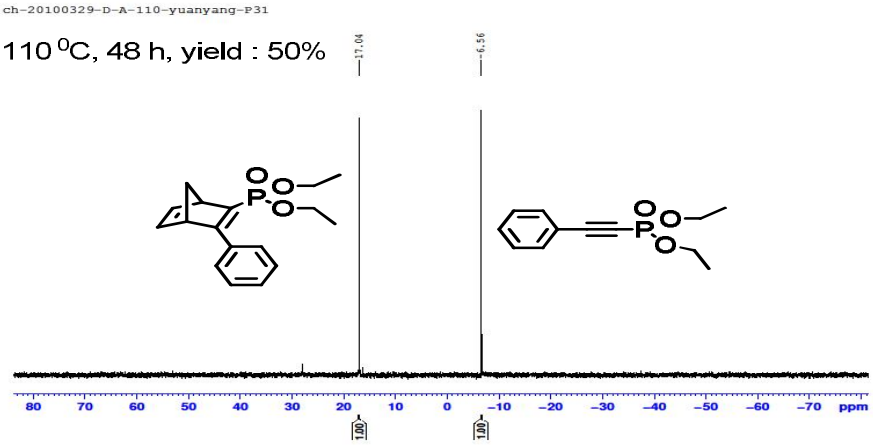
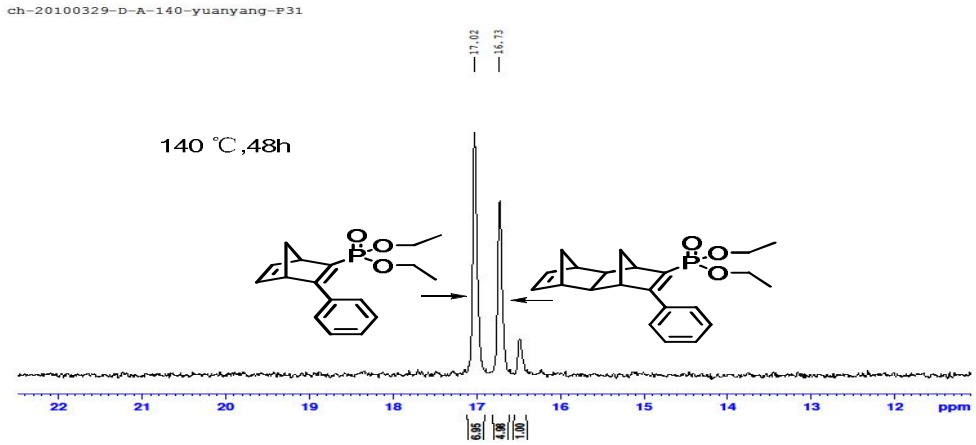
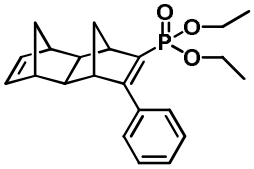
Analysis of byproduct 3aa

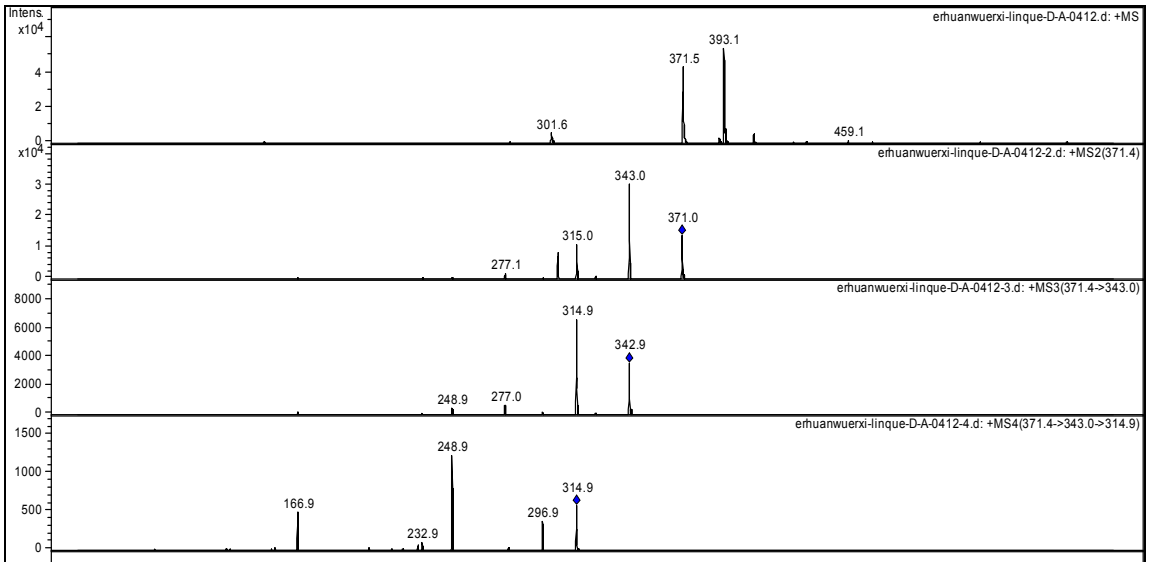






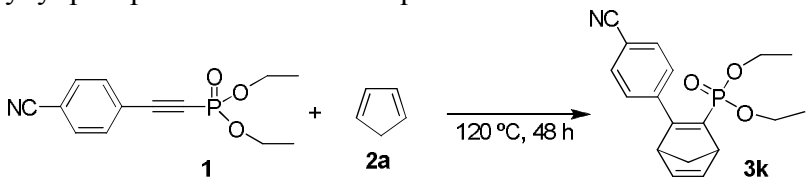


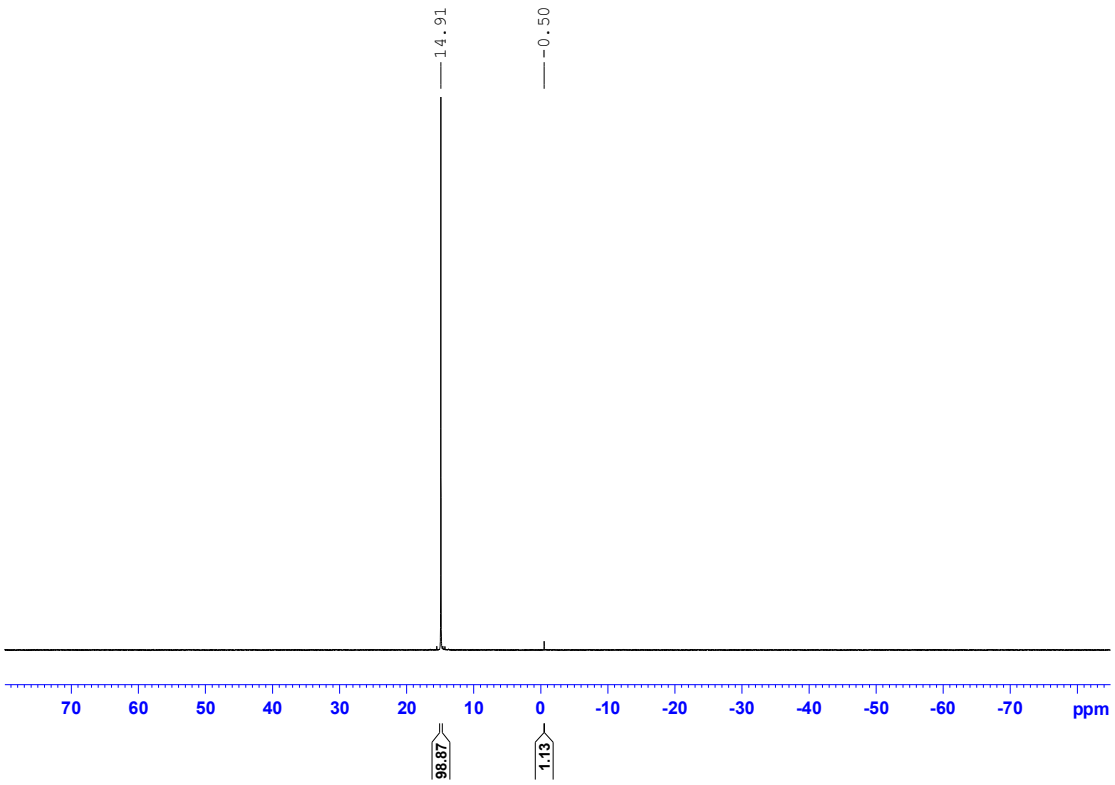
[M+Na] *m/z* : 393.0



^{31}P NMR spectra for the synthesis of 3k.

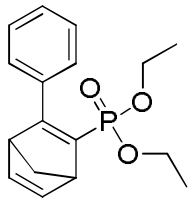
The yield of the crude product **3k** was determined by ^{31}P NMR spectrum after reaction at 120 °C for 48 h. The conversion of alkynyl phosphonate was almost quantitative.





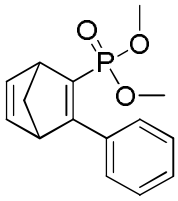
Spectral Data

Diethyl 3-phenylbicyclo[2.2.1]hepta-2,5-dien-2-ylphosphonate(3a)



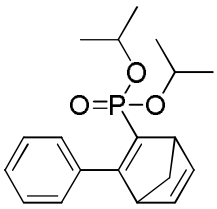
Yellow oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.49 (m, 2H), 7.43 – 7.23 (m, 3H), 6.96 (m, 2H), 4.14 – 4.05 (m, 1H), 4.05 – 3.72 (m, 5H), 2.27 (dt, J = 6.6, 1.4 Hz, 1H), 2.06 (dq, J = 6.6, 1.5 Hz, 1H), 1.17 (td, 7.0, 0.4 Hz, 3H), 1.12 (td, 7.2, 0.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6 (d, J_{PC} = 14.3 Hz), 143.5, 140.9 (d, J_{PC} = 2.1 Hz), 135.6 (d, J_{PC} = 3.5 Hz), 134.5 (d, J_{PC} = 201.9 Hz), 128.7, 127.9, 127.5 (d, J_{PC} = 1.6 Hz), 71.4 (d, J_{PC} = 6.2 Hz), 61.5 (d, J_{PC} = 5.5 Hz), 61.3 (d, J_{PC} = 5.4 Hz), 58.4 (d, J_{PC} = 16.3 Hz), 55.2 (d, J_{PC} = 12.2 Hz), 16.1 (d, J_{PC} = 7.2 Hz), 16.0 (d, J_{PC} = 7.3 Hz). ^{31}P NMR (160 MHz, $CDCl_3$) δ 17.6. IR (film): 3062, 2982, 2937, 2905, 2869, 1591, 1557, 1492, 1445, 1391, 1293, 1245, 1162, 1095, 1052, 1025, 965, 795, 766, 724, 698, 661, 604, 577, 546, 508 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{22}NaO_3P$, 328.1204; found 328.1209.

Dimethyl 3-phenylbicyclo[2.2.1]hepta-2,5-dien-2-ylphosphonate(3b)



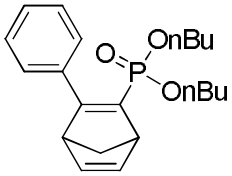
Yellow oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.44 (m, 2H), 7.35 (m, 3H), 7.04 – 6.86 (m, 2H), 4.17 – 4.02 (m, 1H), 3.95 (d, J = 1.4 Hz, 1H), 3.57 (d, J = 11.2 Hz, 3H), 3.47 (d, J = 11.4 Hz, 3H), 2.32 – 2.20 (m, 1H), 2.08-2.05 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7 (d, J_{PC} = 14.7 Hz), 143.5, 140.9 (d, J_{PC} = 2.3 Hz), 135.3(d, J_{PC} = 3.8 Hz), 133.4(d, J_{PC} = 201.6 Hz), 128.9, 128.0, 127.3 (d, J_{PC} = 1.7 Hz), 71.4 (d, J_{PC} = 6.2 Hz), 58.5 (d, J_{PC} = 16.4 Hz), 55.2 (d, J_{PC} = 12.1 Hz), 52.1 (d, J_{PC} = 5.5 Hz), 51.8 (d, J_{PC} = 5.5 Hz). ^{31}P NMR (160 MHz, $CDCl_3$) δ 20.6. IR (film): 3062, 2988, 2950, 2849, 1590, 1492, 1447, 1293, 1247, 1183, 1052, 1028, 930, 825, 795, 767, 725, 698, 661, 602, 575, 545 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{17}NaO_3P$, 299.0813; found 299.0800.

Diisopropyl (3-phenylbicyclo[2.2.1]hepta-2,5-dien-2-yl)phosphonate(3c)



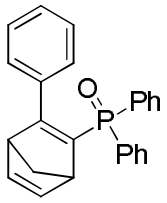
Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.55 (m, 2H), 7.37– 7.27 (m, 3H), 6.96 (dd, J = 4.8, 3.1 Hz, 1H), 6.90 (dd, J = 4.8, 3.2 Hz, 1H), 4.58 – 4.45 (m, 5H), 4.09 (d, J = 1.2 Hz, 1H), 3.93 - 3.92(m, 1H), 2.24 - 2.22 (m, 1H), 2.04 - 2.01 (m, 1H), 1.26 (d, J = 6.2 Hz, 3H), 1.21 (d, J = 6.2 Hz, 3H), 1.11 (d, J = 6.2 Hz, 3H), 1.07 (d, J = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2 (d, J_{PC} = 15.0 Hz), 143.5 (d, J_{PC} = 1.3 Hz), 140.6 (d, J_{PC} = 2.0 Hz), 135.8 (d, J_{PC} = 201.7 Hz), 135.7 (d, J_{PC} = 3.8 Hz), 128.4, 127.8, 127.7 (d, J_{PC} = 1.5 Hz), 71.2 (d, J_{PC} = 6.0 Hz), 70.1 (d, J_{PC} = 5.7 Hz), 70.0 (d, J_{PC} = 5.5 Hz), 58.4 (d, J_{PC} = 16.3 Hz), 55.5 (d, J_{PC} = 12.3 Hz), 24.0 (d, J_{PC} = 4.0 Hz), 23.9 (d, J_{PC} = 4.2 Hz), 23.7 (d, J_{PC} = 4.9 Hz), 23.5 (d, J_{PC} = 5.1 Hz). ^{31}P NMR (160 MHz, $CDCl_3$) δ 15.0. IR (film): 3060, 2978, 2935, 2871, 1721, 1657, 1594, 1492, 1466, 1448, 1385, 1374, 1242, 1177, 1141, 1105, 986, 896, 766, 722, 697, 660, 605, 579, 549 cm^{-1}. HRMS (ESI) calcd for $C_{19}H_{25}NaO_3P$, 355.1439; found 355.1440.

Dibutyl 3-phenylbicyclo[2.2.1]hepta-2,5-dien-2-ylphosphonate(3d)



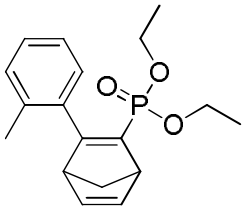
Yellow oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 2H), 7.41 – 7.25 (m, 3H), 6.98 – 6.91 (m, 2H), 4.10 (s, 1H), 4.09-3.73 (m, 5H), 2.26 (dt, J = 6.6, 1.4 Hz, 1H), 2.10 – 1.98 (m, 1H), 1.56 – 1.35 (m, 4H), 1.35 – 1.16 (m, 4H), 0.85 (dt, J = 14.5, 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5 (d, J_{PC} = 14.4 Hz), 143.5, 140.9(d, J_{PC} = 2.1 Hz), 135.6(d, J_{PC} = 3.7 Hz), 134.5(d, J_{PC} = 201.9 Hz), 128.6, 127.9, 127.5 (d, J_{PC} = 1.6 Hz), 71.4 (d, J_{PC} = 6.2 Hz), 65.2 (d, J_{PC} = 5.8 Hz), 64.9 (d, J_{PC} = 5.6 Hz), 58.4 (d, J_{PC} = 16.2 Hz), 55.3 (d, J_{PC} = 12.1 Hz), 32.3 (d, J_{PC} = 6.8 Hz), 32.2 (d, J_{PC} = 7.0 Hz), 18.7 (d, J_{PC} = 6.6 Hz), 13.6 (d, J_{PC} = 3.2 Hz). ^{31}P NMR (160 MHz, $CDCl_3$) δ 17.7. IR (film): 3063, 2960, 2933, 2872, 1591, 1492, 1461, 1295, 1247, 1065, 1023, 980, 902, 765, 723, 697, 605, 579, 548 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{30}O_3P$, 361.1927; found 361.1925.

Diphenyl 3-phenylbicyclo[2.2.1]hepta-2,5-dien-2-ylphosphine oxide(3e)



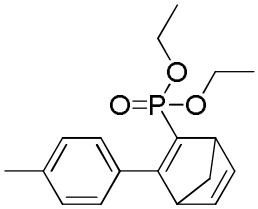
White solid, m.p. 85-87 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.61 (m, 2H), 7.53 – 7.38 (m, 5H), 7.38 – 7.27 (m, 3H), 7.21 (m, 2H), 7.11 – 7.05 (m, 3H), 7.01 (dd, *J* = 4.9, 3.2 Hz, 1H), 6.73 (dd, *J* = 4.7, 3.0 Hz, 1H), 4.03 – 3.93 (m, 1H), 3.71 – 3.60 (m, 1H), 2.39 (dt, *J* = 6.6, 1.4 Hz, 1H), 2.02 (dd, *J* = 6.6, 1.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1 (d, *J* = 9.1 Hz), 143.1, 141.0(d, J_{PC} = 2.1 Hz), 138.2(d, J_{PC} = 108.6 Hz), 135.5(d, J_{PC} = 3.1Hz), 133.3(d, J_{PC} = 108.9 Hz), 132.0 (d, J_{PC} = 106.4 Hz), 131.4(d, J_{PC} = 9.8 Hz),131.3 (d, J_{PC} = 3.1 Hz), 131.2(d, J_{PC} = 9.6 Hz), 131.1(d, J_{PC} = 3.0 Hz), 128.4(d, J_{PC} = 11.7Hz), 128.3, 128.0(d, J_{PC} = 12.3 Hz), 127.6, 127.4 (d, J_{PC} = 1.3 Hz), 71.3 (d, J_{PC} = 5.1 Hz), 59.2 (d, J_{PC} = 11.6 Hz), 55.8 (d, J_{PC} = 11.9 Hz). ^{31}P NMR (160 MHz, $CDCl_3$) δ 22.8. IR (film): 3057, 2967, 2939, 2869, 1717, 1586, 1556, 1489, 1438, 1296, 1261, 1182, 1115, 1025, 927, 808, 754, 721, 698, 661, 591, 573, 545, 523 cm^{-1}. HRMS (ESI) calcd for $C_{25}H_{21}NaOP$, 391.1222; found 391.1230.

Diethyl 3-*o*-tolylbicyclo[2.2.1]hepta-2,5-dien-2-ylphosphonate(3f)



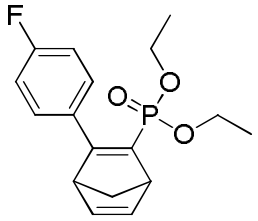
Yellow oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.11 (m, 3H), 7.00 (dd, *J* = 5.1, 3.0 Hz, 2H), 6.88 (dd, *J* = 4.9, 3.2 Hz, 1H), 4.07 (s, 1H), 3.94 – 3.68 (m, 5H), 2.38 (d, *J* = 6.5 Hz, 1H), 2.23 (s, 3H), 2.12 – 1.99 (m, 1H), 1.08 (dt, *J* = 19.3, 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6 (d, J_{PC} = 14.1 Hz), 143.6, 141.1 (d, J_{PC} = 2.4 Hz), 137.2 (d, J_{PC} = 3.5 Hz), 137.0(d, J_{PC} = 204.0 Hz), 135.1 (d, J_{PC} = 2.0 Hz),129.7,127.9,127.4,125.3, 72.6 (d, J_{PC} = 6.0 Hz), 61.4 (d, J_{PC} = 6.1 Hz), 61.3 (d, J_{PC} = 6.8 Hz), 59.1 (d, J_{PC} = 16.5 Hz), 53.8 (d, J_{PC} = 13.3 Hz), 20.2, 16.1 (d, J_{PC} = 6.8 Hz), 16.0 (d, J_{PC} = 7.0 Hz). ^{31}P NMR (160 MHz, $CDCl_3$) δ 17.1. IR (film): 3065, 2982, 2935, 2900, 2868, 1620, 1596, 1558, 1482, 1453, 1391, 1296, 1244, 1199, 1162, 1095, 1052, 1027, 964, 868, 795, 755, 728, 654, 609, 582, 560 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{23}NaO_3P$, 341.1277; found 341.1276.

Diethyl (3-(p-tolyl)bicyclo[2.2.1]hepta-2,5-dien-2-yl)phosphonate(3g)



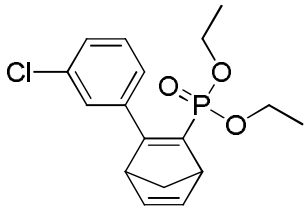
Yellow oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, J = 6.4, 1.7 Hz, 2H), 6.15 (d, J = 7.9 Hz, 2H), 6.93 – 6.87 (m, 2H),4.04 – 3.76 (m, 6H), 2.33 (s, 3H), 2.22 – 2.20 (m, 1H), 2.01 – 1.99 (m, 1H), 1.13 (dt, J = 21.8, 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6 (d, J_{PC} = 14.1 Hz), 143.4, 140.7 (d, J_{PC} = 2.1 Hz), 138.7, 133.1 (d, J_{PC} = 200.7 Hz), 132.5 (d, J_{PC} = 3.8 Hz), 128.5, 127.4 (d, J_{PC} = 1.4 Hz), 71.1 (d, J_{PC} = 6.3 Hz), 61.3 (d, J_{PC} = 5.2 Hz), 61.1 (d, J_{PC} = 5.3 Hz), 58.3 (d, J_{PC} = 16.5 Hz), 55.1 (d, J_{PC} = 12.1 Hz), 21.2, 16.1 (d, J_{PC} = 6.6 Hz), 16.0 (d, J_{PC} = 7.2 Hz). ^{31}P NMR (160 MHz, $CDCl_3$) δ 17.1. IR (film): 2982, 2935, 1508, 1443, 1391, 1290, 1231, 1163, 1095, 1052, 1024, 967, 820, 603, 573, 537 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{23}NaO_3P$, 341.1283; found 341.1278.

Diethyl 3-(4-fluorophenyl)bicyclo[2.2.1]hepta-2,5-dien-2-ylphosphonate(3h)



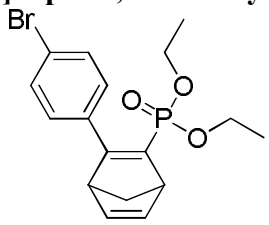
Yellow oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.47 (m, 2H), 7.13 – 7.00 (m, 2H), 6.99 – 6.85 (m, 2H), 4.07 (d, J = 0.9 Hz, 1H), 4.03 – 3.69 (m, 5H), 2.25 (dd, J = 6.6, 1.4 Hz, 1H), 2.05 (dd, J = 6.6, 1.5 Hz, 1H), 1.25 – 1.18 (m, 3H), 1.17 – 1.09 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5 (d, J_{PC} = 14.2 Hz), 164.2, 161.7, 143.6 (d, J_{PC} = 1.0 Hz),, 140.6 (d, J_{PC} = 2.3 Hz), 133.4(d, J_{PC} = 201.0 Hz), 131.6, 129.5 (d, J_{PC} = 1.7 Hz), 129.4 (d, J_{PC} = 1.6 Hz), 114.9 (d, J_{PC} = 21.6 Hz), 71.4 (d, J_{PC} = 6.2 Hz), 61.5 (d, J_{PC} = 5.4 Hz), 61.3 (d, J_{PC} = 5.3 Hz), 58.5 (d, J_{PC} = 16.2 Hz), 55.3 (d, J_{PC} = 11.9 Hz), 16.2 (d, J_{PC} = 6.7 Hz), 16.1 (d, J_{PC} = 6.9 Hz). ^{31}P NMR (160 MHz, $CDCl_3$) δ 17.3. IR (film): 3068, 2983, 2938, 2906, 2871, 1717, 1666, 1600, 1506, 1445, 1392, 1293, 1235, 1162, 1097, 1052, 1025, 966, 840, 794, 732, 603, 575, 539 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{20}FNaO_3P$, 345.1026; found 345.1026.

Diethyl 3-(3-chlorophenyl)bicyclo[2.2.1]hepta-2,5-dien-2-ylphosphonate(3i)



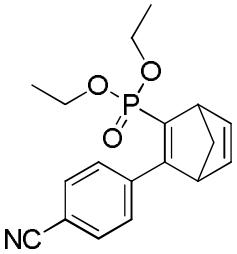
Yellow oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 1H), 7.48 – 7.41 (m, 1H), 7.33 – 7.25 (m, 2H), 6.95 (ddt, *J* = 8.0, 7.4, 3.8 Hz, 2H), 4.13 – 4.06 (m, 1H), 4.05 – 3.79 (m, 5H), 2.26 (dt, *J* = 6.7, 1.5 Hz, 1H), 2.06 (dt, *J* = 6.7, 1.5 Hz, 1H), 1.24 – 1.09 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8 (d, J_{PC} = 13.9 Hz), 143.6, 140.8 (d, J_{PC} = 2.3 Hz), 137.4 (d, J_{PC} = 5.2 Hz), 136.5(d, J_{PC} = 201.0 Hz), 133.8, 129.2, 128.5, 127.3 (d, J_{PC} = 1.7 Hz), 125.9, 71.6 (d, J_{PC} = 6.2 Hz), 61.6 (d, J_{PC} = 5.7 Hz), 61.4 (d, J_{PC} = 5.5 Hz), 58.4 (d, J_{PC} = 16.0 Hz), 55.4 (d, J_{PC} = 12.0 Hz), 16.2 (d, J_{PC} = 4.7 Hz), 16.1 (d, J_{PC} = 4.8 Hz). ^{31}P NMR (160 MHz, $CDCl_3$) δ 16.7. IR (film): 3067, 2982, 2937, 2906, 2869, 1586, 1559, 1474, 1392, 1296, 1246, 1162, 1096, 1052, 1025, 965, 790, 713, 696, 611, 580 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{20}ClNaO_3P$, 361.0731; found 361.0739.

Diethyl (3-(4-bromophenyl)bicyclo[2.2.1]hepta-2,5-dien-2-yl)phosphonate(3j)



Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.46 (m, 2H), 7.41 – 7.39 (m, 2H), 6.94 – 6.89(m, 2H), 4.06 – 3.76 (m, 6H), 2.23 (d, *J* = 6.6 , 1H), 2.03 (dd, *J* = 6.7, 1.3 Hz, 1H), 1.21 – 1.17 (m, 3H), 1.15 – 1.11 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3 (d, J_{PC} = 14.3 Hz), 143.5, 140.7 (d, J_{PC} = 2.2 Hz), 135.5 (d, J_{PC} = 200.2 Hz), 134.3 (d, J_{PC} = 4.1 Hz), 131.0, 129.1 (d, J_{PC} = 1.3 Hz), 122.8, 71.4 (d, J_{PC} = 6.2 Hz), 61.5 (d, J_{PC} = 5.4 Hz), 61.4 (d, J_{PC} = 5.4 Hz), 58.3 (d, J_{PC} = 16.1 Hz), 55.3 (d, J_{PC} = 11.9 Hz), 16.2 (d, J_{PC} = 7.1 Hz), 16.1 (d, J_{PC} = 7.8 Hz). ^{31}P NMR (160 MHz, $CDCl_3$) δ 17.0. IR (film): 2981, 2934, 1584, 1485, 1443, 1394, 1287, 1244, 1163, 1024, 971, 827, 796, 730, 602, 577, 553 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{20}BrNaO_3P$, 405.0231; found 405.0240.

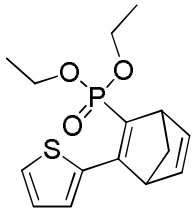
Diethyl (3-(4-cyanophenyl)bicyclo[2.2.1]hepta-2,5-dien-2-yl)phosphonate(3k)



Deep yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 4H), 6.96 – 6.92 (m, 2H), 4.08 – 3.79 (m, 6H) , 2.26 – 2.24 (m, 1H), 2.09 – 2.07 (m, 1H), 1.17 (dt, *J* = 32.9, 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.3 (d, J_{PC} = 13.9 Hz), 143.5 (d, J_{PC} = 1.5 Hz), 140.7 (d, J_{PC} = 2.2 Hz), 140.0 (d, J_{PC} = 3.9 Hz), 138.9 (d, J_{PC} = 199.7 Hz), 131.6, 128.1 (d, J_{PC} = 1.4 Hz), 118.7, 111.9, 71.7 (d, J_{PC} = 6.1 Hz), 61.7 (d, J_{PC} = 5.5 Hz), 61.6 (d, J_{PC} = 5.6 Hz), 58.2 (d, J_{PC} = 15.8 Hz), 55.6 (d, J_{PC} = 11.4 Hz), 16.2 (d, J_{PC} = 6.7 Hz), 16.1 (d,

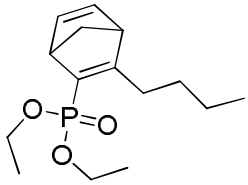
J_{PC} = 6.6 Hz). ^{31}P NMR (160 MHz, $CDCl_3$) δ 15.8. IR (film): 2983, 2937, 2869, 2226, 1605, 1500, 1391, 1290, 1246, 1163, 1095, 1054, 1025, 965, 842, 797, 719, 603, 573, 551, 518 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{20}NNaO_3P$, 352.1078; found 352.1081.

Diethyl (3-(thiophen-2-yl)bicyclo[2.2.1]hepta-2,5-dien-2-yl)phosphonate(3l)



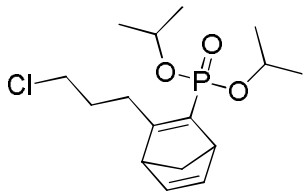
Pale yellow oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 3.7 Hz, 1H), 7.39 (d, *J* = 4.6 Hz, 1H), 7.09 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.91 – 6.90 (m, 1H), 6.84 – 6.83 (m, 1H), 4.11 –3.86 (m, 6H), 2.20 (d, *J* = 6.7 Hz, 1H), 2.01 (dd, *J* = 6.7, 1.4 Hz, 1H), 1.25 (dt, *J* = 16.6, 7.1Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, J_{PC} = 14.1 Hz), 143.6, 139.8 (d, J_{PC} = 2.0 Hz), 137.9 (d, J_{PC} = 4.7 Hz), 130.3 (d, J_{PC} = 201.9 Hz), 129.3, 128.2, 127.9,70.1 (d, J_{PC} = 6.0 Hz), 61.5 (d, J_{PC} = 5.0 Hz), 61.4 (d, J_{PC} = 5.1Hz), 59.0 (d, J_{PC} = 11.4 Hz), 55.8 (d, J_{PC} = 11.4 Hz), 16.2 (d, J_{PC} = 6.5 Hz), 16.2 (d, J_{PC} = 6.7 Hz). ^{31}P NMR (160 MHz, $CDCl_3$) δ 17.1. IR (film): 2963, 2934, 2870, 1729, 1616, 1452, 1384, 1374, 1260, 1177, 1105, 1018, 981, 799, 595 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{19}NaO_3PS$, 333.0690; found 333.0691.

Ethyl methyl 3-butylbicyclo[2.2.1]hepta-2,5-dien-2-ylphosphonate(3m)



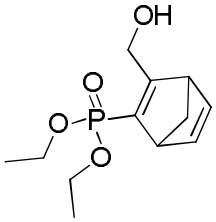
Yellow oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (dd, *J* = 4.8, 3.1Hz, 1H), 6.69 (dd, *J* = 4.8, 3.1Hz 1H), 4.08 - 3.84 (m, 4H), 3.79 (s, 1H), 3.56 (s, 1H), 2.70 - 2.57 (m, 2H), 2.01 (d, *J* = 6.3 Hz, 1H), 1.93 (dd, *J* = 6.4, 1.2 Hz, 1H), 1.51 - 1.25 (m,10H), 0.91 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0 (d, J_{PC} = 17.8 Hz), 143.3, 140.8, 132.4 (d, J_{PC} = 202.5 Hz), 71.8 (d, J_{PC} = 6.0 Hz), 61.0, 60.9, 56.0 (d, J_{PC} = 17.7 Hz), 53.0 (d, J_{PC} =13.1 Hz), 30.1 (d, J_{PC} = 2.7 Hz), 29.2 (d, J_{PC} = 2.1 Hz), 22.5, 16.3 (d, J_{PC} = 5.7 Hz), 16.3 (d, J_{PC} = 6.3Hz), 13.9. ^{31}P NMR (160 MHz, $CDCl_3$) δ 18.7. IR (film): 3070, 2980, 2936, 2903, 2868, 1573, 1556, 1477, 1443, 1419, 1390, 1364, 1298, 1276, 1246,1193, 1163, 1095, 1050, 1024, 961, 863, 847, 792, 720, 673, 635, 597, 579, 535, 506 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{17}NaO_3P$, 299.0808; found 299.0800.

Diisopropyl (3-(3-chloropropyl)bicyclo[2.2.1]hepta-2,5-dien-2-yl)phosphonate(3n)



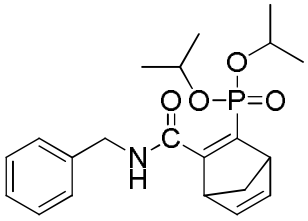
Yellow oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (dd, J = 5.0, 3.0Hz, 1H), 6.68 (dd, J = 4.9, 3.2Hz 1H), 4.66-4.43 (m, 2H), 3.76 (s, 1H), 3.53 (s, 1H), 3.51 – 3.43 (m, 2H), 2.88 – 2.80 (m, 1H), 2.78 – 2.70 (m, 1H), 2.00 – 1.82 (m, 4H), 1.33(d, J = 6.2Hz, 3H), 1.30 (d, J = 6.2Hz, 3H), 1.27 (d, J = 6.2Hz, 3H), 1.19 (d, J = 6.2Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0 (d, J_{PC} = 17.4 Hz), 143.5, 140.4 (d, J_{PC} = 2.1 Hz), 135.6 (d, J_{PC} = 203.4 Hz), 71.9 (d, J_{PC} = 5.9 Hz), 69.7, 69.6, 56.0 (d, J_{PC} = 17.5 Hz), 53.1 (d, J_{PC} =12.4 Hz), 44.3, 30.4 (d, J_{PC} = 2.0 Hz), 27.9 (d, J_{PC} = 2.7 Hz), 24.1 (d, J_{PC} = 3.7 Hz), 24.1 (d, J_{PC} = 3.5 Hz), 24.0 (d, J_{PC} = 4.4 Hz), 23.9 (d, J_{PC} = 4.4 Hz). ^{31}P NMR (160 MHz, $CDCl_3$) δ 15.2. IR (film): 3067, 2976, 2935, 2869, 1726, 1616, 1557, 1451, 1373, 1385, 1302, 1283, 1240, 1178, 1140, 1107, 1042, 979, 849, 882, 798, 772, 723, 649, 596, 523 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{26}ClNaO_3P$, 355.1206; found 355.1212.

Diethyl (3-(hydroxymethyl)bicyclo[2.2.1]hepta-2,5-dien-2-yl)phosphonate(3o)



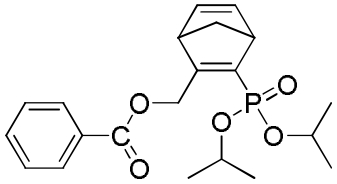
Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (dd, J = 5.0,3.0Hz, 1H), 6.69 (dd, J = 4.9,3.3Hz 1H), 5.52 (s, 1H), 4.63 (dd, J = 17.8,3.5Hz 1H), 6.69 (dd, J = 17.8,4.0Hz 1H), 4.13 – 3.78 (m, 4H), 3.75 (s, 1H), 3.50 (s, 1H), 2.03 (d, J = 6.6 Hz, 1H), 1.91 (dd, J = 6.6,1.1 Hz, 1H), 1.31 (t, J = 7.1 Hz, 3H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5 (d, J_{PC} = 18.2 Hz), 143.3, 140.5 (d, J_{PC} = 2.3 Hz), 132.2 (d, J_{PC} = 201.1 Hz), 71.6 (d, J_{PC} = 5.8 Hz), 62.5 (d, J_{PC} = 4.2 Hz), 61.8 (d, J_{PC} = 5.1 Hz), 61.7 (d, J_{PC} =5.1 Hz), 55.5 (d, J_{PC} = 16.6 Hz), 53.5 (d, J_{PC} = 11.3 Hz), 16.2(d, J_{PC} = 6.4 Hz), 16.1 (d, J_{PC} = 6.7Hz). ^{31}P NMR (160 MHz, $CDCl_3$) δ 19.7. IR (film): 2983, 2938, 2870, 1725, 1669, 1392, 1281, 1226, 1164, 1095, 1024, 971, 796, 587 cm^{-1}. HRMS (ESI) calcd for $C_{12}H_{19}NaO_4P$, 281.0919; found 281.0925.

Diethyl (3-(thiophen-2-yl)bicyclo[2.2.1]hepta-2,5-dien-2-yl)phosphonate(3p)



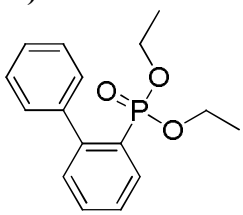
Yellow oil;[1]H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.36 -7.19 (m,5H), 6.89 (dd, *J* = 4.1, 4.1Hz, 1H), 6.879 (dd, *J* = 4.8, 3.2Hz, 1H), 4.71 - 4.63 (m, 1H), 4.55 - 4.45 (m, 2H), 4.44 - 4.34 (m, 2H), 3.93 (s, 1H), 2.06 (d, *J* = 6.8 Hz, 1H), 1.94 (d, *J* = 6.8Hz, 1H), 1.36 (d, *J* = 6.2Hz, 3H), 1.30 (d, *J* = 6.2Hz, 3H), 1.26 (d, *J* = 6.2Hz, 3H), 1.11 (d, *J* = 6.2Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2 (d, J_{PC} = 15.4 Hz), 163.0 (d, J_{PC} = 4.6 Hz), 143.7 (d, J_{PC} = 194.2 Hz), 142.6 (d, J_{PC} = 2.4 Hz), 141.6 (d, J_{PC} = 1.3 Hz), 138.9, 128.4, 127.9, 127.0, 71.5 (d, J_{PC} = 6.9 Hz), 71.4 (d, J_{PC} = 9.5 Hz), 56.3 (d, J_{PC} = 9.3 Hz), 54.8 (d, J_{PC} =15.8 Hz), 43.7, 24.0 (d, J_{PC} = 3.8 Hz), 23.9 (d, J_{PC} = 4.3 Hz), 23.8 (d, J_{PC} =4.2 Hz), 23.7 (d, J_{PC} = 5.2 Hz). ^{31}P NMR (160 MHz, $CDCl_3$) δ 13.9. IR (film): 3064, 2979, 2935, 1657, 1538, 1497, 1453, 1386, 1375, 1232, 1177, 1142, 1103, 988, 897, 700, 585 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{28}NNaO_4P$, 412.1654; found412.1654.

Diethyl (3-(thiophen-2-yl)bicyclo[2.2.1]hepta-2,5-dien-2-yl)phosphonate(3q)



Pale yellow oil;[1]H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.4 Hz, 2H), 7.57 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.45 (dd, *J* = 7.7, 7.7 Hz, 2H), 4.86 - 4.84 (m, 1H), 6.74 - 4.72 (m, 1H), 5.49 (dd, *J* = 13.7, 2.4 Hz, 1H), 5.30 (dd, *J* = 13.7, 2.8 Hz, 1H), 4.72 - 4.53 (m, 2H), 3.86 (s, 1H), 3.77 (s, 1H), 2.10 (d, *J* = 6.5 Hz, 1H), 1.98 (d, *J* = 6.4Hz, 1H), 1.36(d, *J* = 6.2Hz, 3H), 1.33 (d, *J* = 6.2Hz, 3H), 1.30 (d, *J* = 6.2 Hz, 3H), 1.21 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3 (d, J_{PC}= 15.5 Hz), 166.2, 143.0 (d, J_{PC} = 1.4 Hz), 141.1 (d, J_{PC} = 2.3 Hz), 139.9 (d, J_{PC} = 200.5 Hz), 133.0, 130.1, 129.7, 128.4, 72.2 (d, J_{PC} = 5.8 Hz), 70.3 (d, J_{PC} = 5.3Hz), 70.2 (d, J_{PC} = 5.3Hz), 61.5 (d, J_{PC} = 2.2 Hz), 54.1 (d, J_{PC} = 16.2 Hz), 53.5 (d, J_{PC} =11.6 Hz), 24.1 (d, J_{PC} = 1.9 Hz), 24.1 (d, J_{PC} = 1.4 Hz), 24.0 (d, J_{PC} = 3.0 Hz), 23.9 (d, J_{PC} = 3.6 Hz). ^{31}P NMR (160 MHz, $CDCl_3$) δ 13.5. IR (film): 2977, 2935, 1722, 1451, 1385, 1269, 1176, 1106, 1069, 1045, 1021, 979, 712,594 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{27}NaO_5P$, 413.1494; found 413.1493.

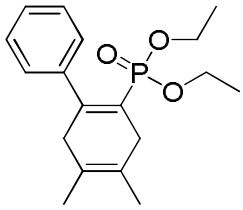
Diethyl [1,1'-biphenyl]-2-ylphosphonate(3r)



Pale yellow oil;[1]H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 14.2,7.7Hz, 1H), 7.55 (dd, *J* = 7.1,7.1Hz 1H), 7.44-7.31 (m, 7H), 3.97-3.78 (m, 4H), 1.12 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0 (d, J_{PC} = 9.7 Hz), 141.4 (d, J_{PC} = 4.2 Hz), 133.8 (d, J_{PC} = 9.8 Hz), 131.9 (d, J_{PC} = 3.0 Hz), 131.3 (d, J_{PC} =

14.1 Hz) ,129.3, 127.5, 127.4, 127.0 (d, J_{PC} = 187.3 Hz), 126.8 (d, J_{PC} = 14.7 Hz), 61.8 (d, J_{PC} = 6.0 Hz), 16.0 (d, J_{PC} =6.9Hz). ^{31}P NMR (160 MHz, $CDCl_3$) δ 18.2. IR (film): 3056, 2981, 2929, 1467, 1444, 1390, 1242, 1163, 1139, 1094, 1056, 1024, 965, 777, 756, 701, 569, 552, 523 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{19}NaO_3P$, 313.0970; found 313.0978.

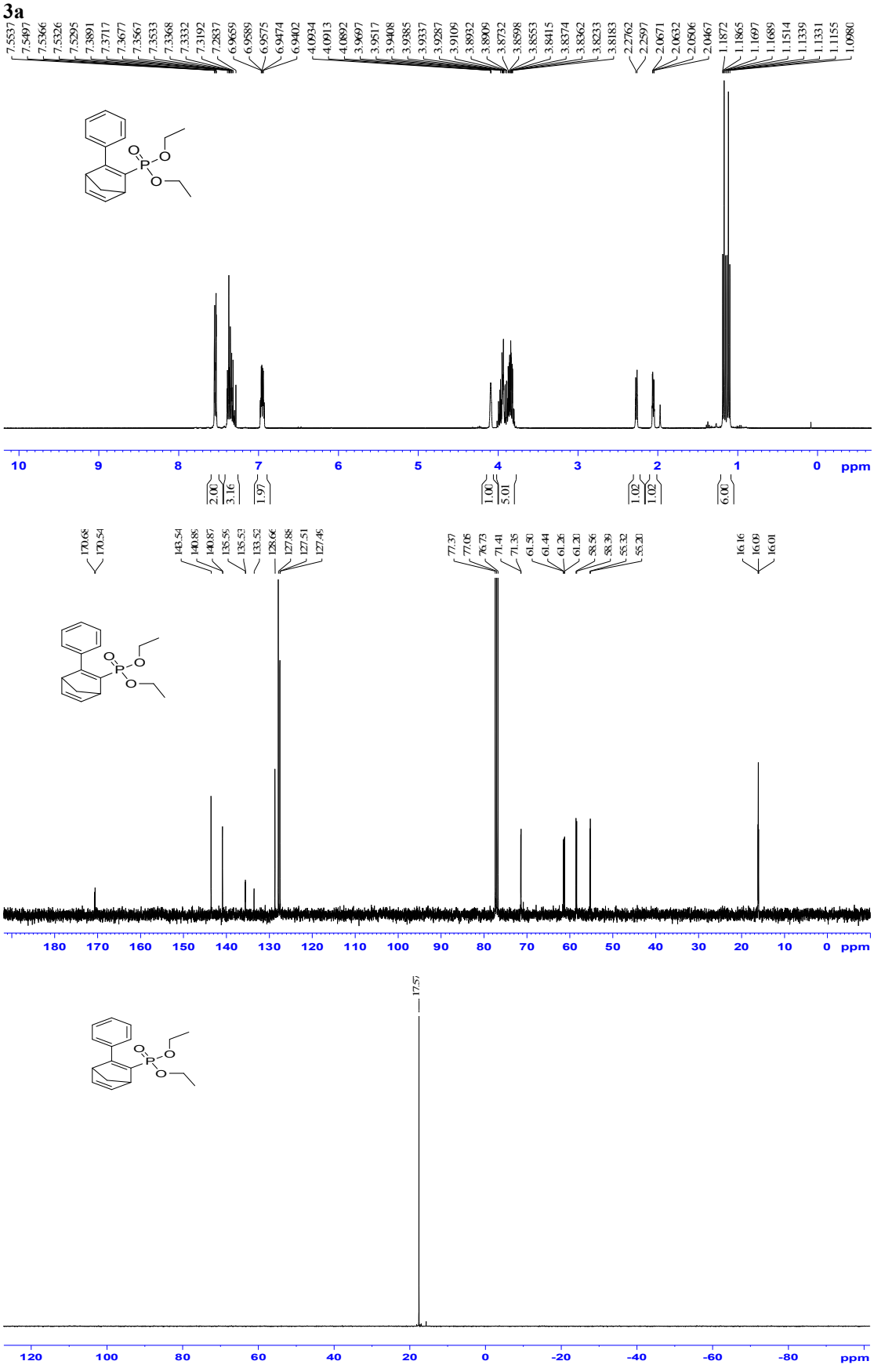
Diethyl (4,5-dimethyl-3,6-dihydro-[1,1'-biphenyl]-2-yl)phosphonate(3s)



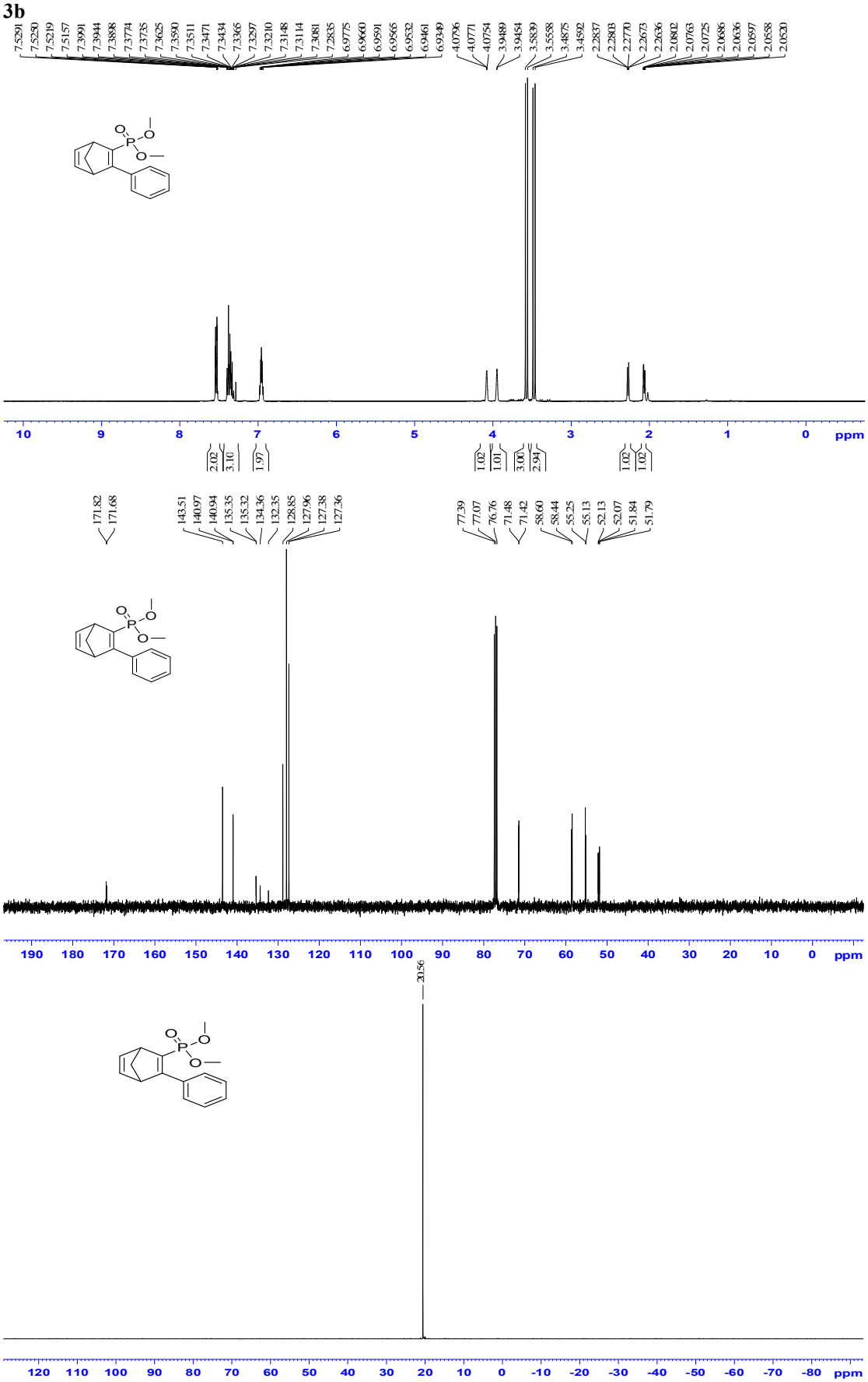
Pale yellow oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 5H), 3.90 – 3.81 (m, 2H), 3.77 – 3.68 (m, 2H), 3.03 (d, *J* = 5.8 Hz, 2H), 2.93 (d, *J* = 6.8 Hz, 2H), 1.71 (s, 3 H), 1.64 (s, 3 H), 1.10 (t, *J* =7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1 (d, J_{PC} = 8.6 Hz), 142.3 (d, J_{PC} = 8.2 Hz), 127.8, 127.3 (d, J_{PC} = 1.4 Hz), 122.7 (d, J_{PC} = 11.0 Hz), 121.8(d, J_{PC} = 1.8Hz), 121.5 (d, J_{PC} = 183.6 Hz), 61.1 (d, J_{PC} = 6.1 Hz), 42.3 (d, J_{PC} = 16.1 Hz), 35.4 (d, J_{PC} = 10.9 Hz), 17.8 (d, J_{PC} = 8.6 Hz), 16.0 (d, J_{PC} = 6.7 Hz). ^{31}P NMR (160 MHz, $CDCl_3$) δ 18.8. IR (film): 3055, 2980, 2927, 2862, 1601, 1479, 1443, 1390, 1367, 1287, 1239, 1166, 1137, 1096, 1026, 966, 887, 781, 767, 751, 723, 700, 651, 635, 582, 571, 527 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{25}NaO_3P$, 343.1439; found 343.1444.

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

3a



3b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7.3991
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7.3434
7.3366
7.3297
7.3210
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2.2673
2.2636
2.0802
2.0763
2.0725
2.0686
2.0636
2.0597
2.0558
2.0520
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171.68
143.51
140.97
140.94
135.35
135.32
134.36
132.35
128.85
127.96
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127.36
77.39
77.07
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58.60
58.44
55.25
55.13
52.13
52.07
51.84
51.79
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
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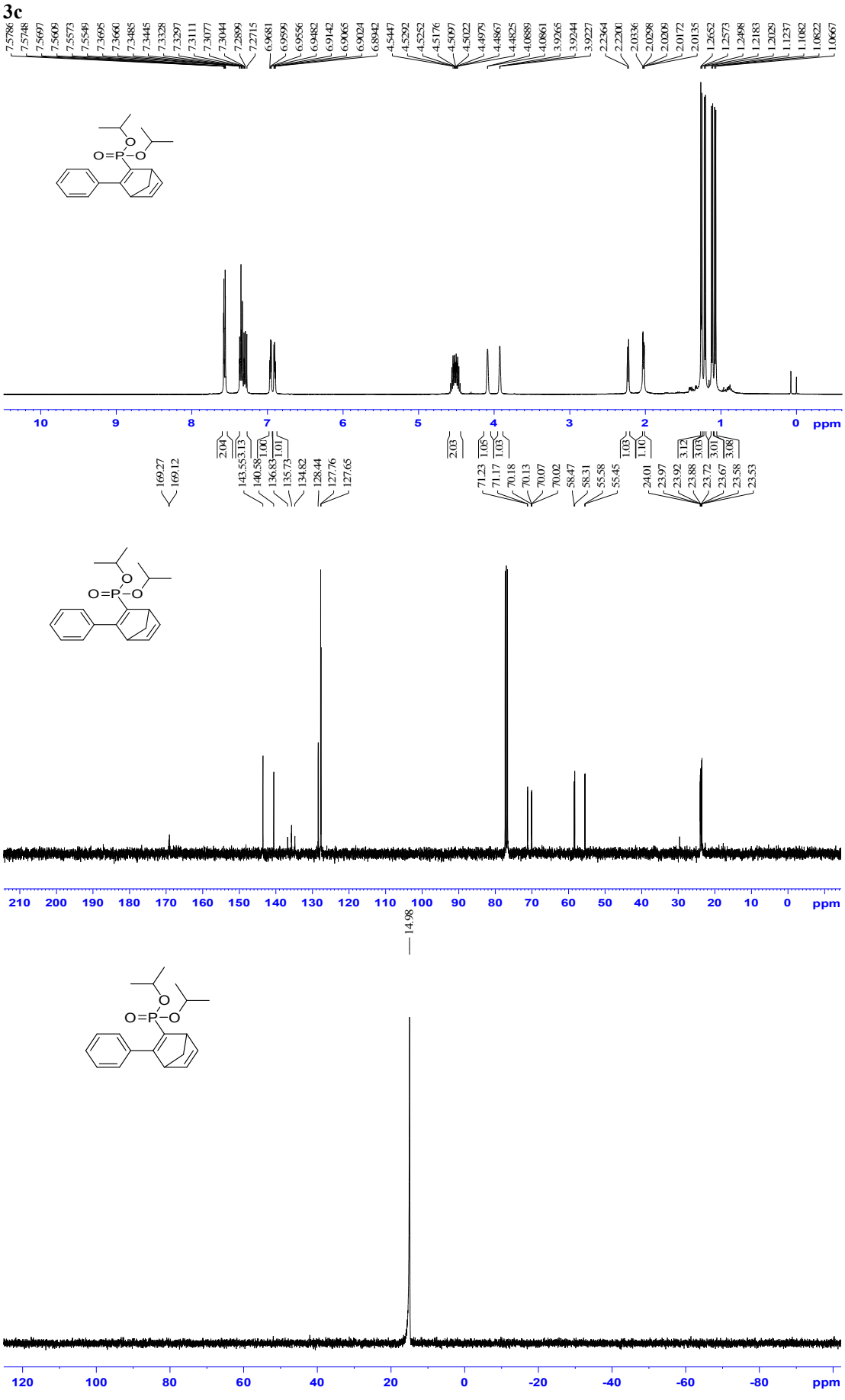
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm

3c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O=P
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2.03
1.06 1.03
1.03 1.16
3.12 3.03 3.01 3.08
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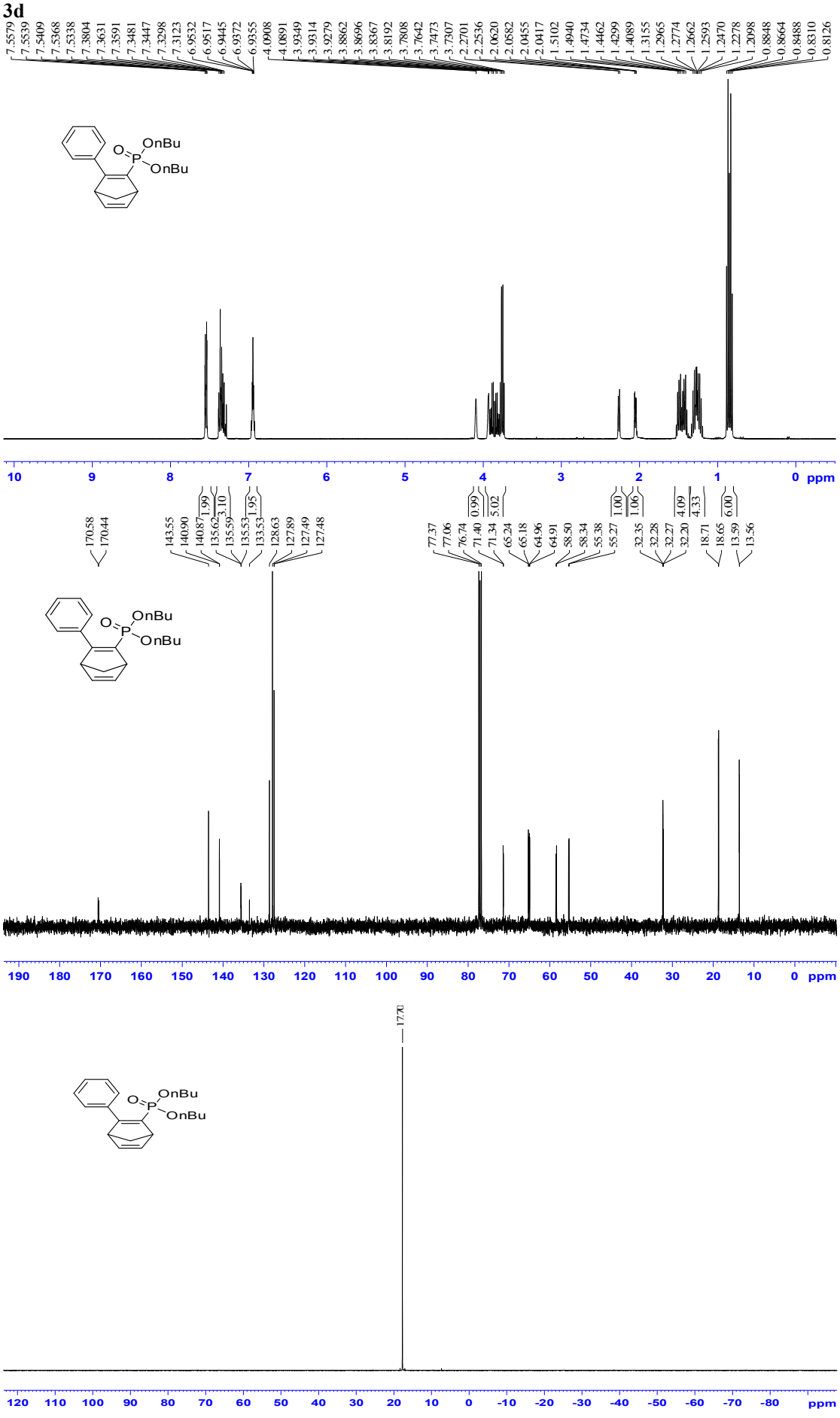
169.12
143.53
140.58
136.83
135.73
134.82
128.44
127.76
127.65
71.23
71.17
70.18
70.13
70.07
70.02
58.47
58.31
55.58
55.45
24.01
23.97
23.92
23.88
23.72
23.67
23.58
23.53
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
14.98
120 100 80 60 40 20 0 -20 -40 -60 -80 ppm

3d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7.3631
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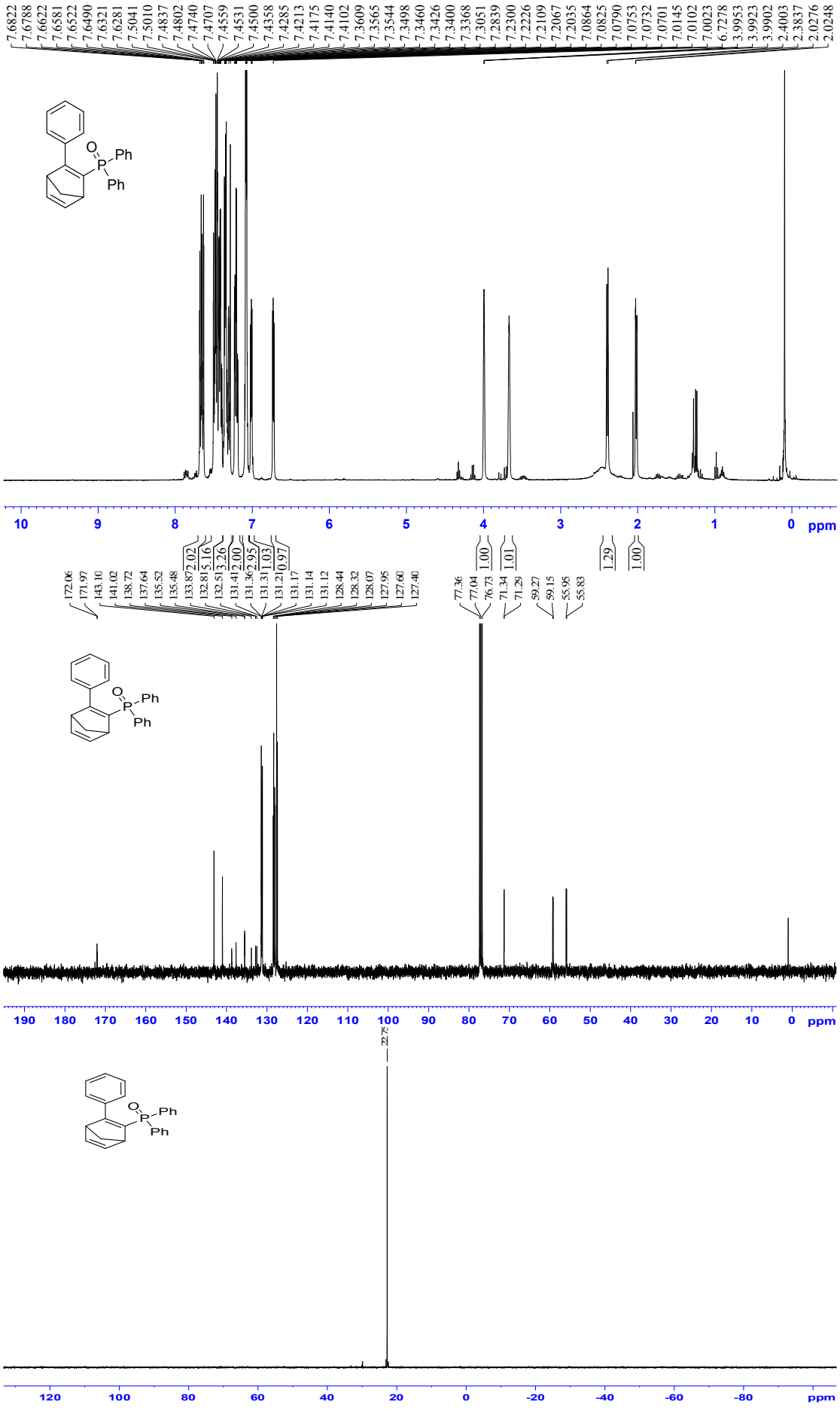
7.3481
7.3447
7.3298
7.3123
6.9532
6.9517
6.9445
6.9372
6.9355
4.0908
4.0891
3.9349
3.9314
3.9279
3.8862
3.8696
3.8367
3.8192
3.7808
3.7642
3.7473
3.7307
2.2701
2.2536
2.0620
2.0582
2.0455
2.0417
1.5102
1.4940
1.4734
1.4462
1.4299
1.4089
1.3155
1.2965
1.2774
1.2662
1.2593
1.2470
1.2278
1.2098
0.8848
0.8664
0.8488
0.8310
0.8126
OnBu
OnBu
10 9 8 7 6 5 4 3 2 1 0 ppm
170.58
170.44
143.55
140.90
140.87
135.62
135.59
135.53
133.53
128.63
127.89
127.49
127.48
77.37
77.06
76.74
71.40
71.34
65.24
65.18
64.96
64.91
58.50
58.34
55.38
55.27
32.35
32.28
32.27
32.20
18.71
18.65
13.59
13.56
1.99
3.10
1.95
0.99
5.02
1.00
1.06
4.09
4.33
6.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
17.70
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm

3e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7.6581
7.6522
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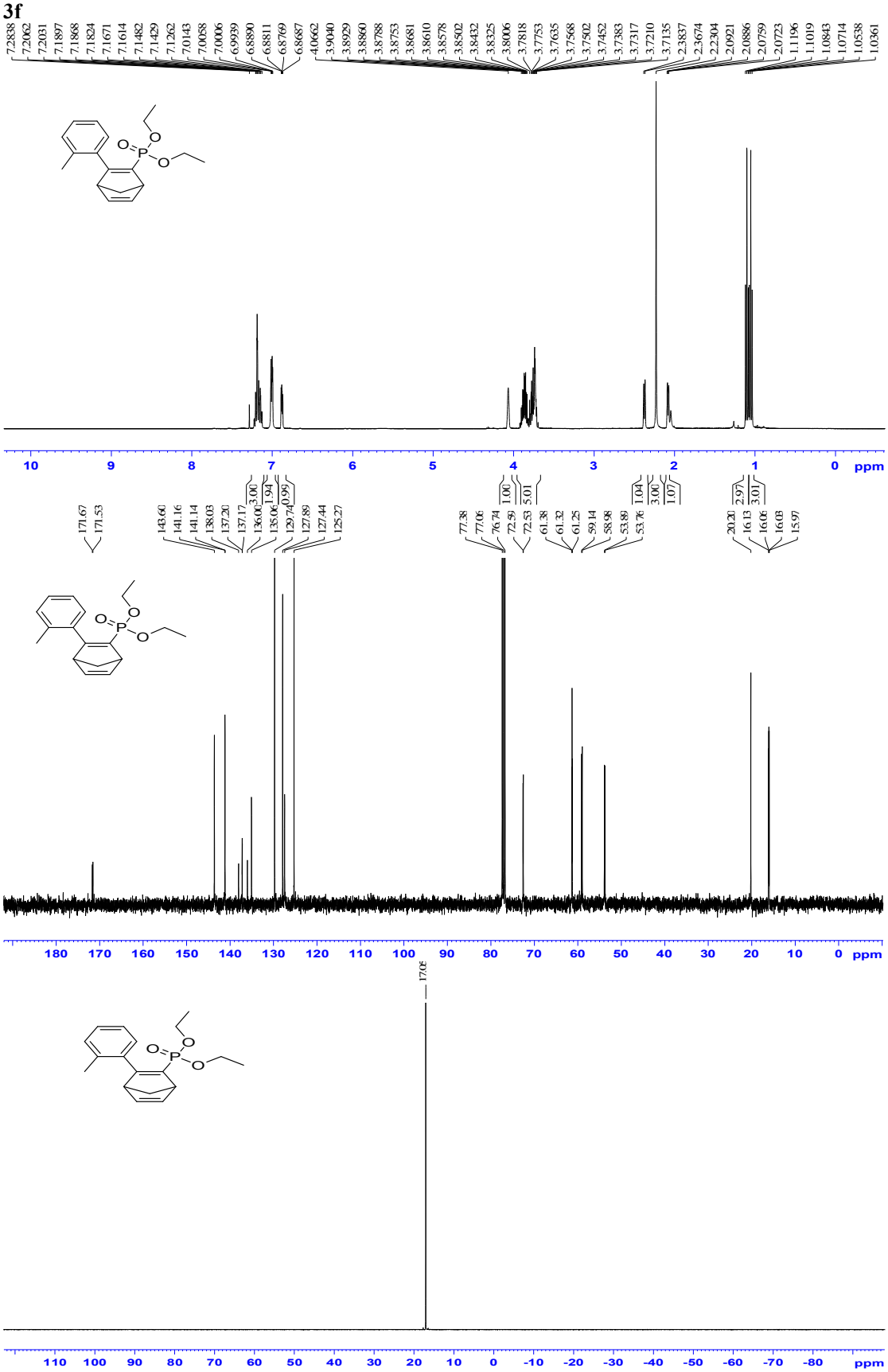
7.6321
7.6281
7.5041
7.5010
7.4837
7.4802
7.4740
7.4707
7.4559
7.4531
7.4500
7.4358
7.4285
7.4213
7.4175
7.4140
7.4102
7.3609
7.3565
7.3544
7.3498
7.3460
7.3426
7.3400
7.3368
7.3051
7.2839
7.2300
7.2226
7.2109
7.2067
7.2035
7.0864
7.0825
7.0790
7.0753
7.0732
7.0701
7.0145
7.0102
7.0023
6.7278
3.9953
3.9923
3.9902
2.4003
2.3837
2.0276
2.0248
O
P
Ph
Ph
10 9 8 7 6 5 4 3 2 1 0 ppm
2.02
5.16
3.26
2.00
2.95
1.03
0.97
1.00
1.01
1.29
1.00
172.06
171.97
143.10
141.02
138.72
137.64
135.52
135.48
133.87
132.81
132.51
131.41
131.36
131.31
131.20
131.17
131.14
131.12
128.44
128.32
128.07
127.95
127.60
127.40
77.36
77.04
76.73
71.34
71.29
59.27
59.15
55.95
55.83
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
22.
120 100 80 60 40 20 0 -20 -40 -60 -80 ppm

3f



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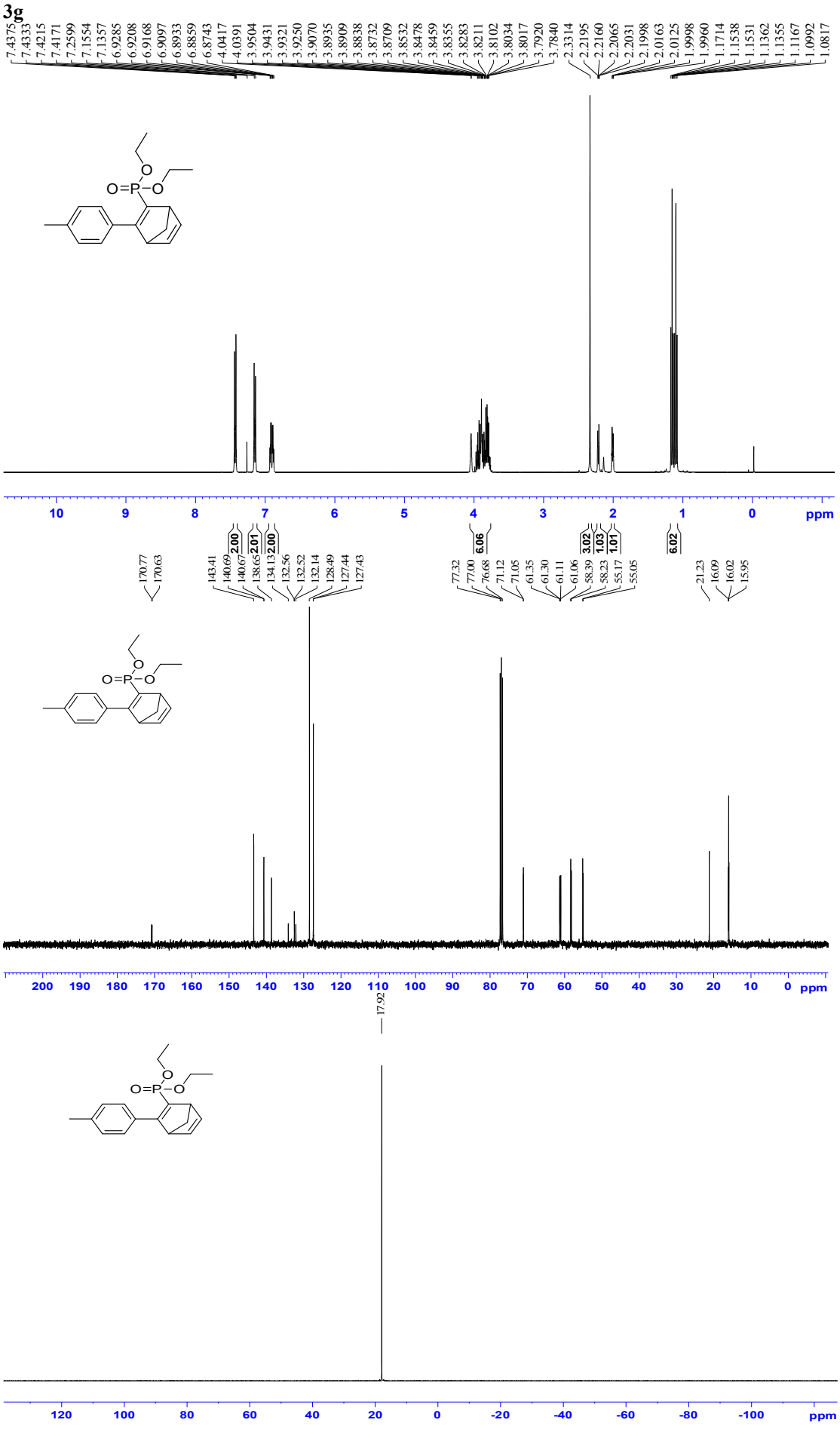
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7.1357
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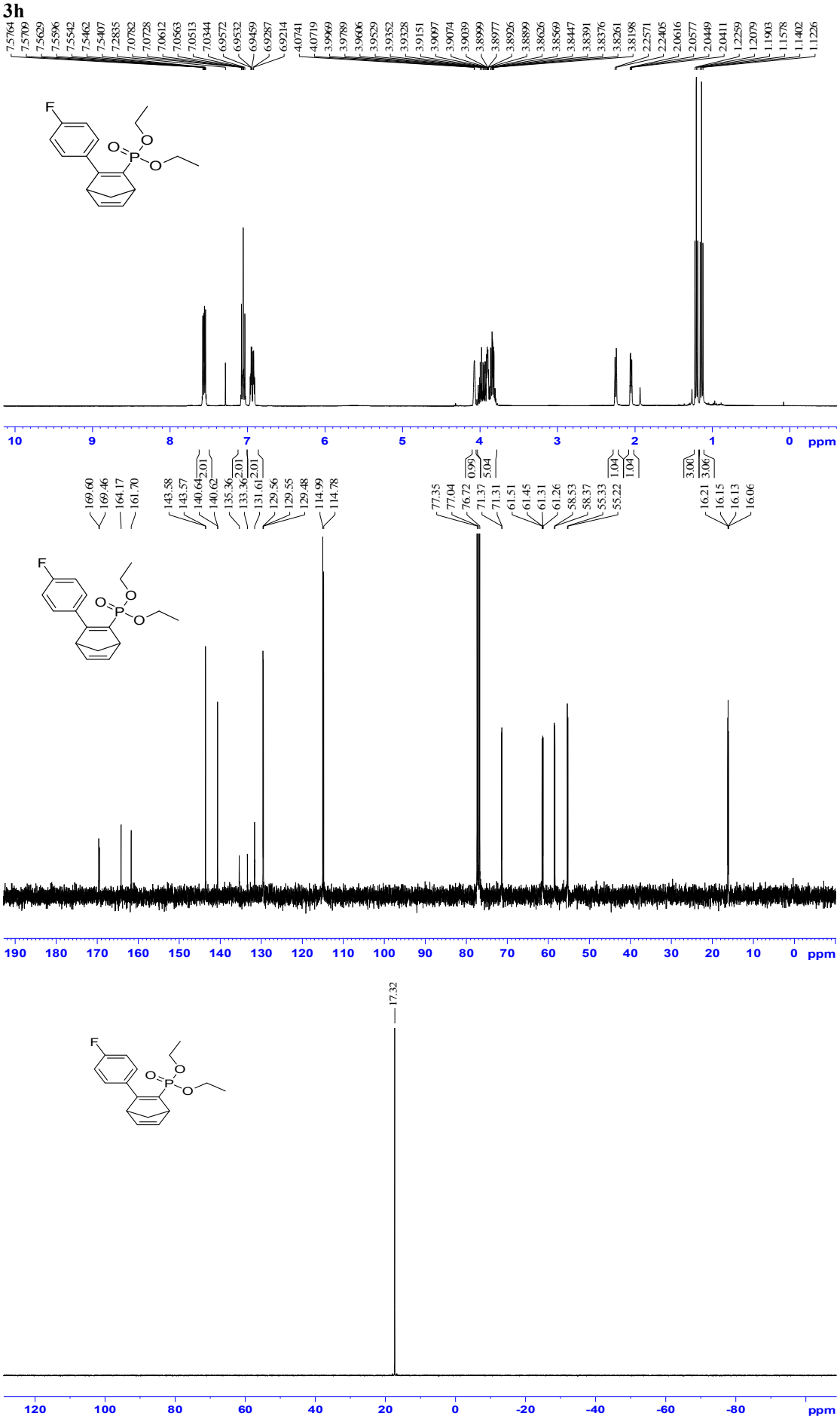
6.9208
6.9168
6.9097
6.8933
6.8859
6.8743
4.0417
4.0391
3.9504
3.9431
3.9321
3.9250
3.9070
3.8935
3.8909
3.8838
3.8732
3.8709
3.8532
3.8478
3.8459
3.8355
3.8283
3.8211
3.8102
3.8034
3.8017
3.7920
3.7840
2.3314
2.2195
2.2160
2.2065
2.2031
2.1998
2.0163
2.0125
1.9998
1.9960
1.1714
1.1538
1.1531
1.1362
1.1355
1.1167
1.0992
1.0817
O=P
ppm
2.00
2.01
2.00
6.06
3.02
1.03
1.01
6.02
170.77
170.63
143.41
140.69
140.67
138.65
134.13
132.56
132.52
132.14
128.49
127.44
127.43
77.32
77.00
76.68
71.12
71.05
61.35
61.30
61.11
61.06
58.39
58.23
55.17
55.05
21.23
16.09
16.02
15.95
17.92

3h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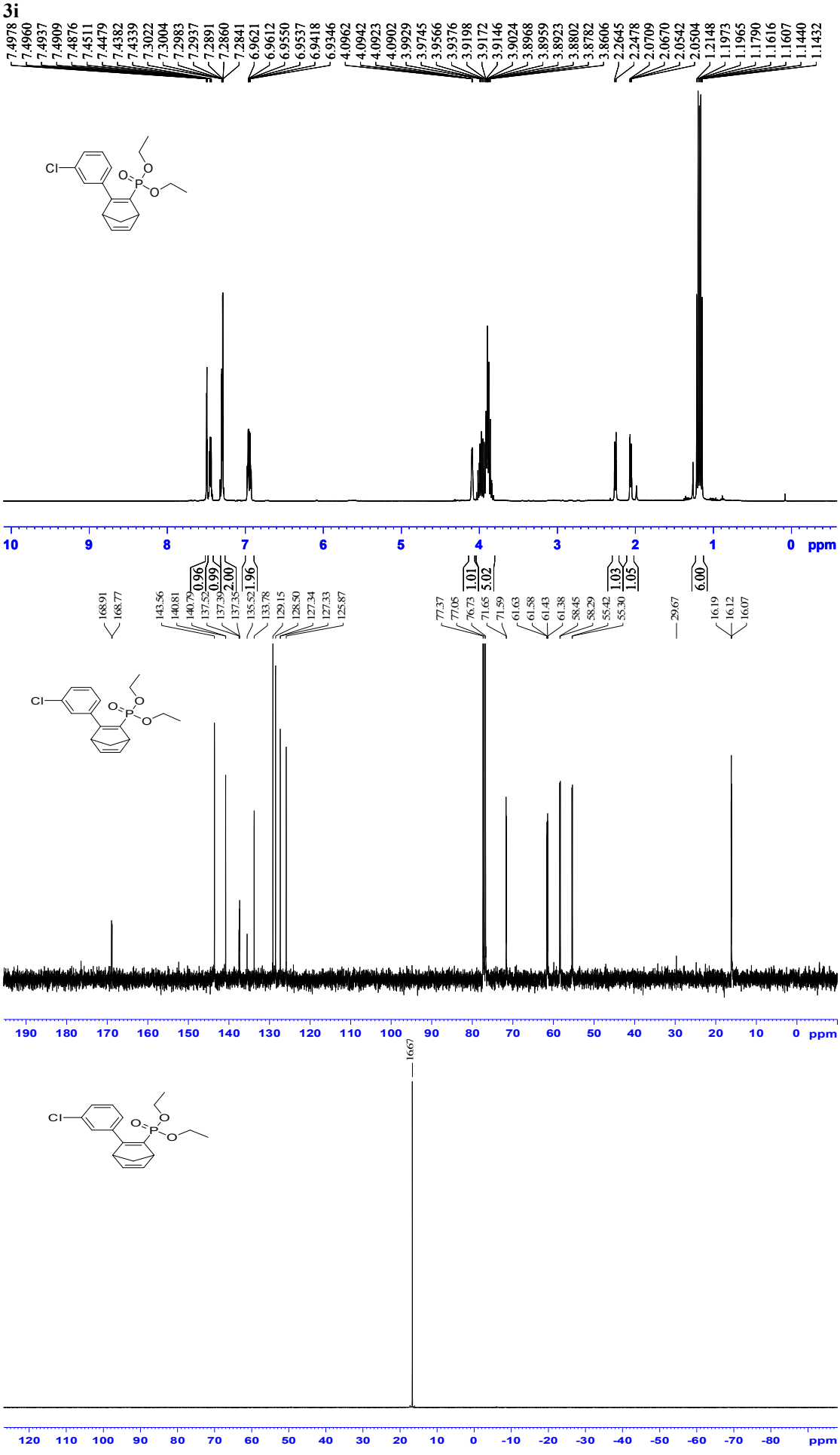
7.5629
7.5596
7.5542
7.5462
7.5407
7.2835
7.0782
7.0728
7.0612
7.0563
7.0513
7.0344
6.9572
6.9532
6.9459
6.9287
6.9214
4.0741
4.0719
3.9969
3.9789
3.9606
3.9529
3.9352
3.9328
3.9151
3.9097
3.9074
3.9039
3.8999
3.8977
3.8926
3.8899
3.8626
3.8569
3.8447
3.8391
3.8376
3.8261
3.8198
2.2571
2.2405
2.0616
2.0577
2.0449
2.0411
1.2259
1.2079
1.1903
1.1578
1.1402
1.1226
F
O
P
O
O
10
9
8
7
6
5
4
3
2
1
0
ppm
2.01
2.01
2.01
0.99
5.04
1.04
1.04
3.00
3.06
169.60
169.46
164.17
161.70
143.58
143.57
140.64
140.62
135.36
133.36
131.61
129.56
129.55
129.48
114.99
114.78
77.35
77.04
76.72
71.37
71.31
61.51
61.45
61.31
61.26
58.53
58.37
55.33
55.22
16.21
16.15
16.13
16.06
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
17.32
120
100
80
60
40
20
0
-20
-40
-60
-80
ppm

3i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7.4876
7.4511
7.4479
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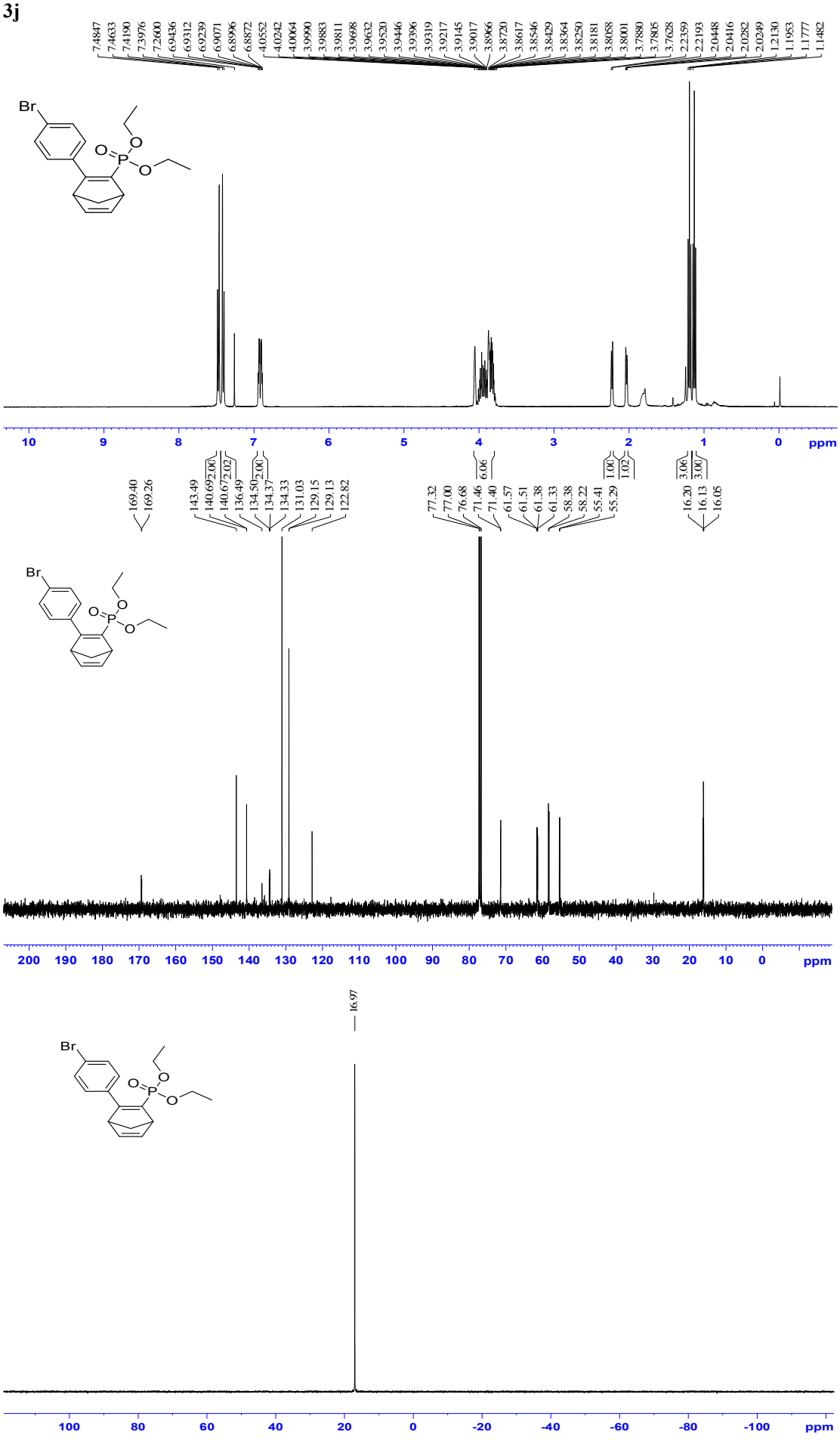
7.4339
7.3022
7.3004
7.2983
7.2937
7.2891
7.2860
7.2841
6.9621
6.9612
6.9550
6.9537
6.9418
6.9346
4.0962
4.0942
4.0923
4.0902
3.9929
3.9745
3.9566
3.9376
3.9198
3.9172
3.9146
3.9024
3.8968
3.8959
3.8923
3.8802
3.8782
3.8606
2.2645
2.2478
2.0709
2.0670
2.0542
2.0504
1.2148
1.1973
1.1965
1.1790
1.1616
1.1607
1.1440
1.1432
Cl
O
P
10 9 8 7 6 5 4 3 2 1 0 ppm
0.96
0.99
2.00
1.96
1.01
5.02
1.03
1.05
6.00
168.91
168.77
143.56
140.81
140.79
137.52
137.39
137.35
135.52
133.78
129.15
128.50
127.34
127.33
125.87
77.37
77.05
76.73
71.65
71.59
61.63
61.58
61.43
61.38
58.45
58.29
55.42
55.30
29.67
16.19
16.12
16.07
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
16.67
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm

3j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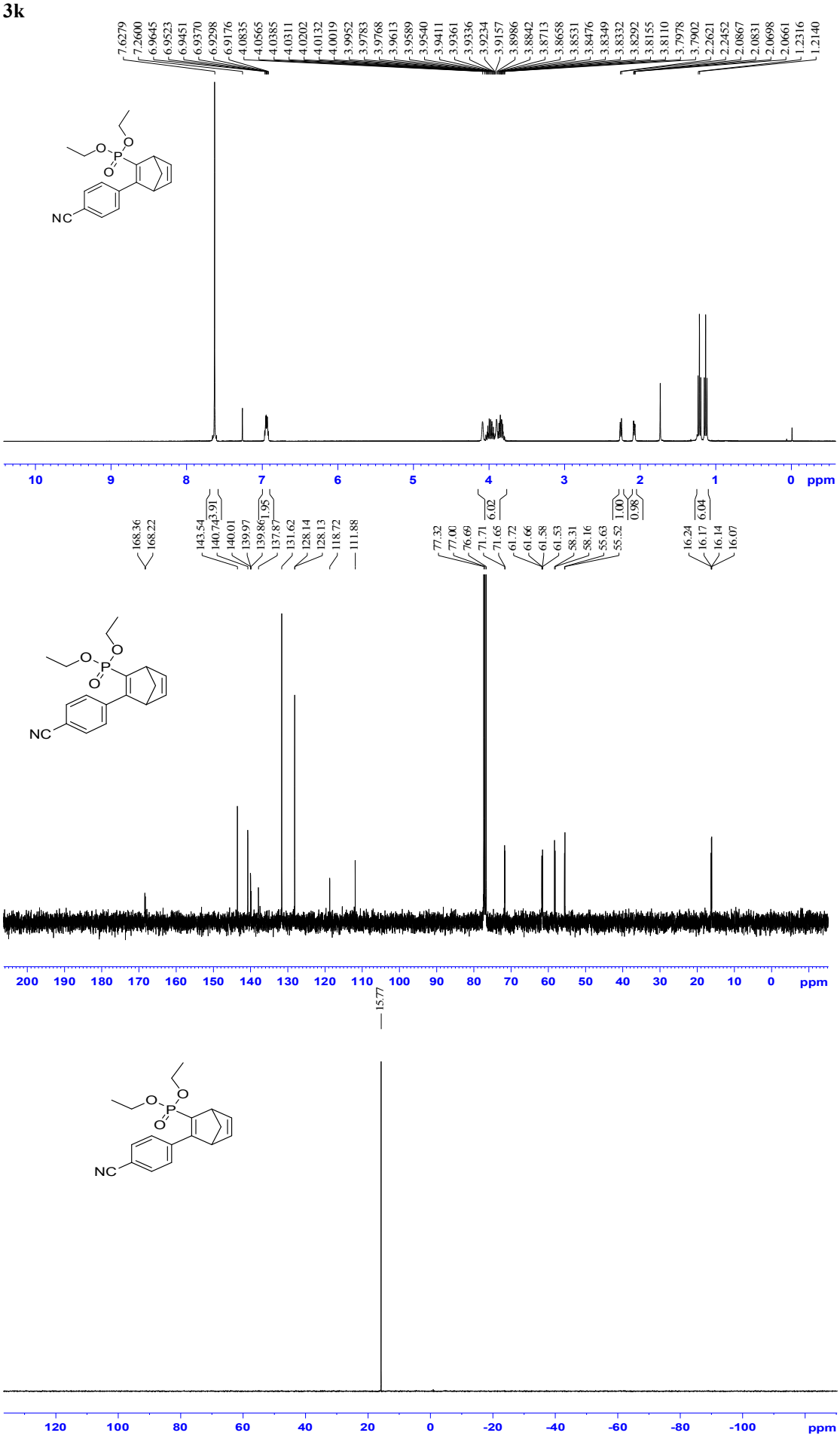
6.9312
6.9239
6.9071
6.8996
6.8872
4.0552
4.0242
4.0064
3.9990
3.9883
3.9811
3.9698
3.9632
3.9520
3.9446
3.9396
3.9319
3.9217
3.9145
3.9017
3.8966
3.8720
3.8617
3.8546
3.8429
3.8364
3.8250
3.8181
3.8058
3.8001
3.7880
3.7805
3.7628
2.2359
2.2193
2.0448
2.0416
2.0282
2.0249
1.2130
1.1953
1.1777
1.1482
Br
O
P
O
O
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.02
2.00
6.06
1.00
1.02
3.06
3.00
169.40
169.26
143.49
140.69
140.67
136.49
134.50
134.37
134.33
131.03
129.15
129.13
122.82
77.32
77.00
76.68
71.46
71.40
61.57
61.51
61.38
61.33
58.38
58.22
55.41
55.29
16.20
16.13
16.05
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
16.97
100
80
60
40
20
0
-20
-40
-60
-80
-100
ppm

3k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6.9451
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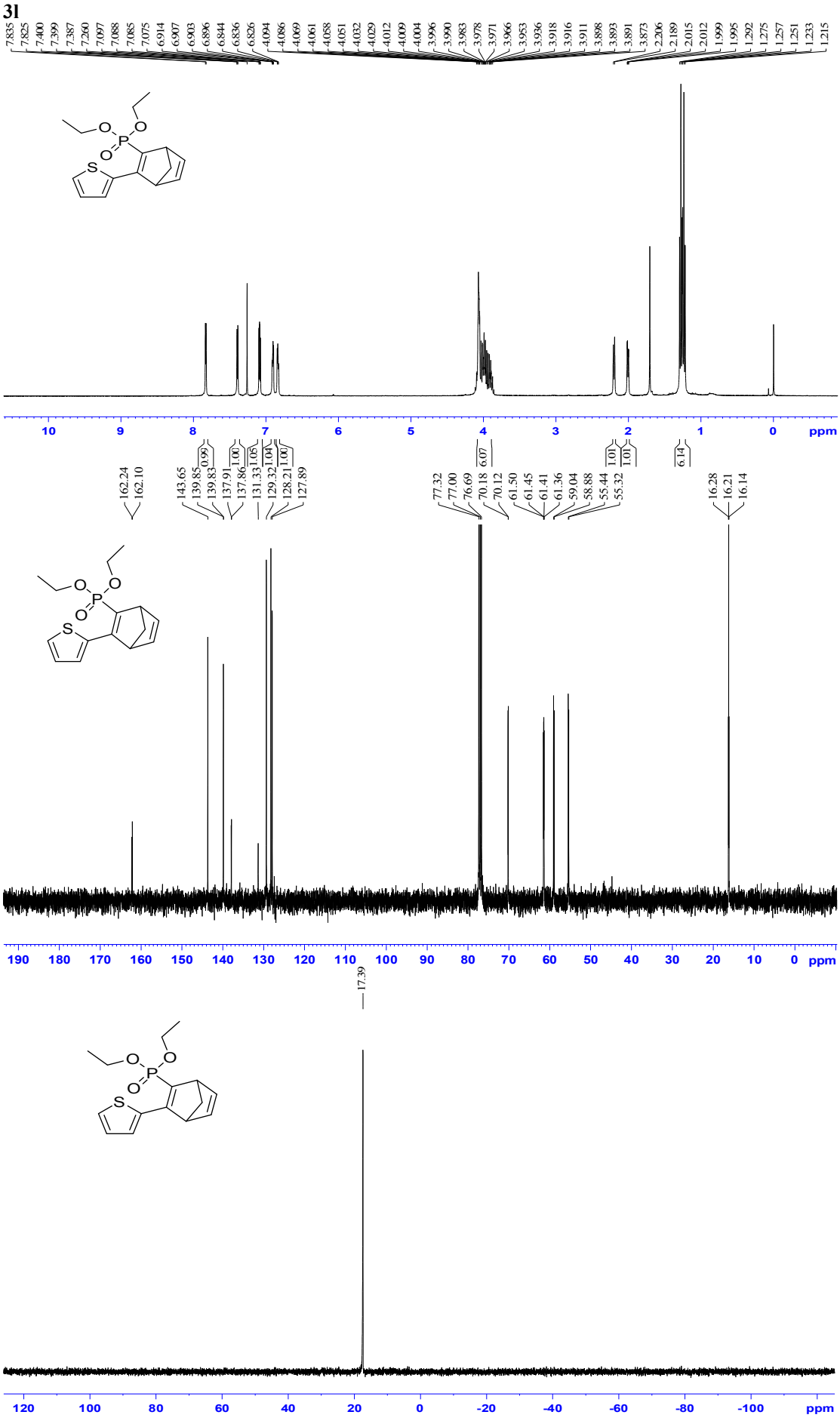
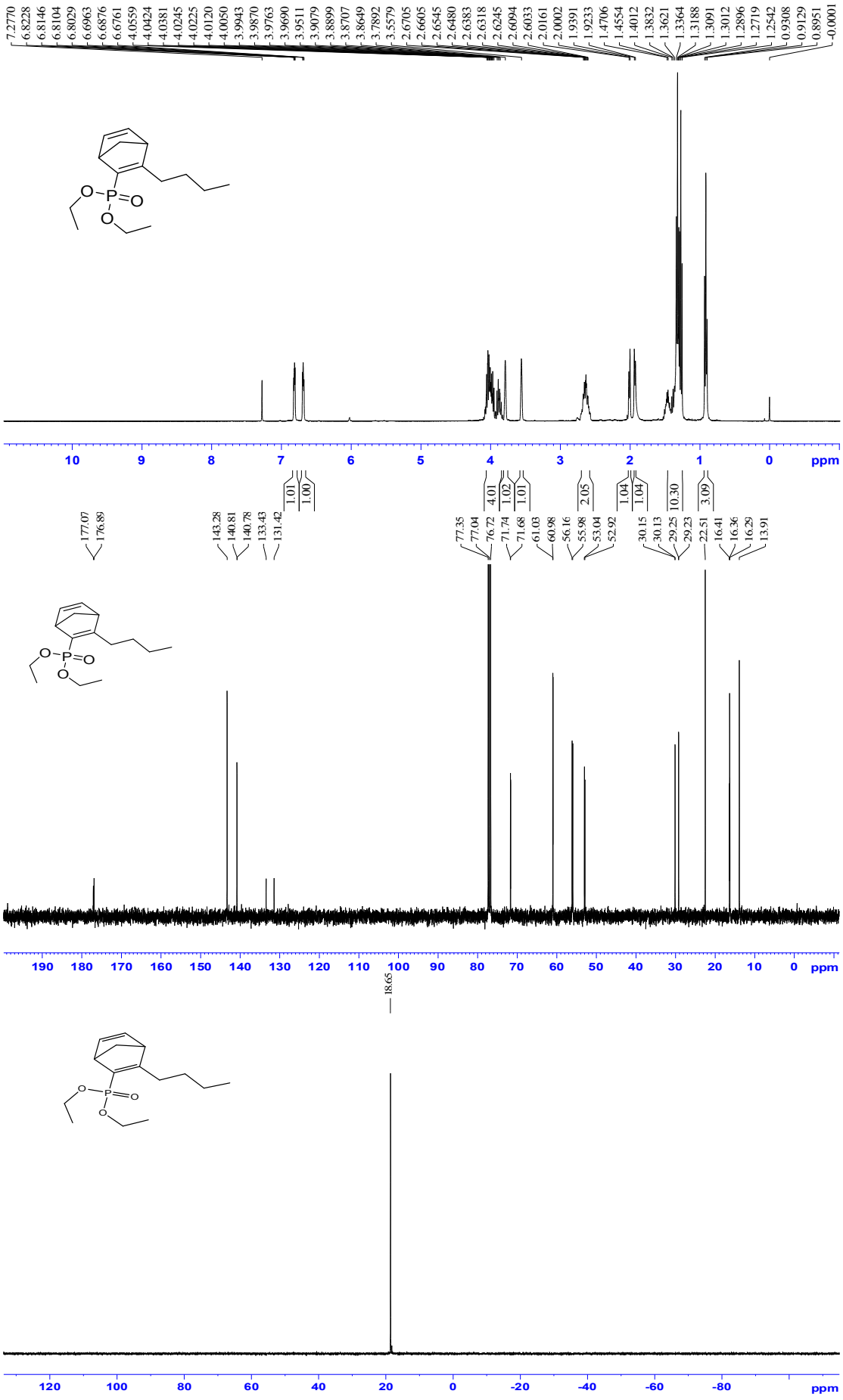
6.9298
6.9176
4.0835
4.0565
4.0385
4.0311
4.0202
4.0132
4.0019
3.9952
3.9783
3.9768
3.9613
3.9589
3.9540
3.9411
3.9361
3.9336
3.9234
3.9157
3.8986
3.8842
3.8713
3.8658
3.8531
3.8476
3.8349
3.8332
3.8292
3.8155
3.8110
3.7978
3.7902
2.2621
2.2452
2.0867
2.0831
2.0698
2.0661
1.2316
1.2140
NC
10 9 8 7 6 5 4 3 2 1 0 ppm
3.91
1.95
6.02
1.00
0.98
6.04
168.36
168.22
143.54
140.74
140.01
139.97
139.86
137.87
131.62
128.14
128.13
118.72
111.88
77.32
77.00
76.69
71.71
71.65
61.72
61.66
61.58
61.53
58.31
58.16
55.63
55.52
16.24
16.17
16.14
16.07
NC
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
15.77
NC
120 100 80 60 40 20 0 -20 -40 -60 -80 -100 ppm

3l


7.835 7.825 7.400 7.399 7.387 7.260 7.097 7.088 7.085 7.075 6.914 6.907 6.903 6.896 6.844 6.836 6.826 4.094 4.086 4.069 4.061 4.058 4.051 4.032 4.029 4.012 4.009 4.004 3.996 3.990 3.983 3.978 3.971 3.966 3.953 3.936 3.918 3.916 3.911 3.898 3.893 3.891 3.873 2.206 2.189 2.015 2.012 1.999 1.995 1.292 1.275 1.257 1.251 1.233 1.215
10 9 8 7 6 5 4 3 2 1 0 ppm
0.99 1.00 1.05 1.04 1.00 6.07 1.01 1.01 6.14
162.24 162.10 143.65 139.85 139.83 137.91 137.86 131.33 129.32 128.21 127.89 77.32 77.00 76.69 70.18 70.12 61.50 61.45 61.41 61.36 59.04 58.88 55.44 55.32 16.28 16.21 16.14
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
17.39
120 100 80 60 40 20 0 -20 -40 -60 -80 -100 ppm

3m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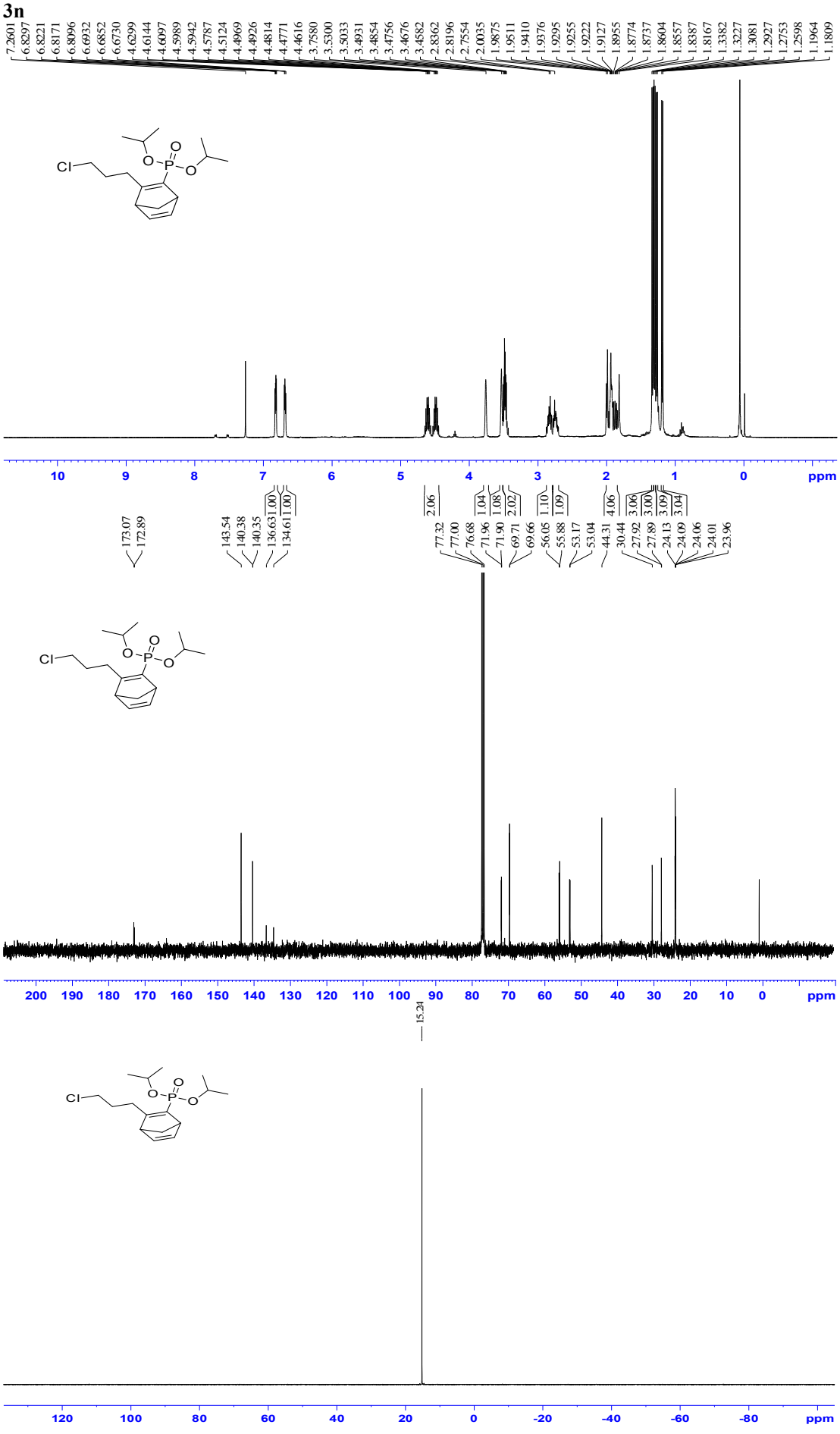
6.8029
6.6963
6.6876
6.6761
4.0559
4.0424
4.0381
4.0245
4.0225
4.0120
4.0050
3.9943
3.9870
3.9763
3.9690
3.9511
3.9079
3.8899
3.8707
3.8649
3.7892
3.5579
2.6705
2.6605
2.6545
2.6480
2.6383
2.6318
2.6245
2.6094
2.6033
2.0161
2.0002
1.9391
1.9233
1.4706
1.4554
1.4012
1.3832
1.3621
1.3364
1.3188
1.3091
1.3012
1.2896
1.2719
1.2542
0.9308
0.9129
0.8951
-0.0001
10 9 8 7 6 5 4 3 2 1 0 ppm
1.01
1.00
4.01
1.02
1.01
2.05
1.04
1.04
10.30
3.09
177.07
176.89
143.28
140.81
140.78
133.43
131.42
77.35
77.04
76.72
71.74
71.68
61.03
60.98
56.16
55.98
53.04
52.92
30.15
30.13
29.25
29.23
22.51
16.41
16.36
16.29
13.91
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
18.65
120 100 80 60 40 20 0 -20 -40 -60 -80 ppm

3n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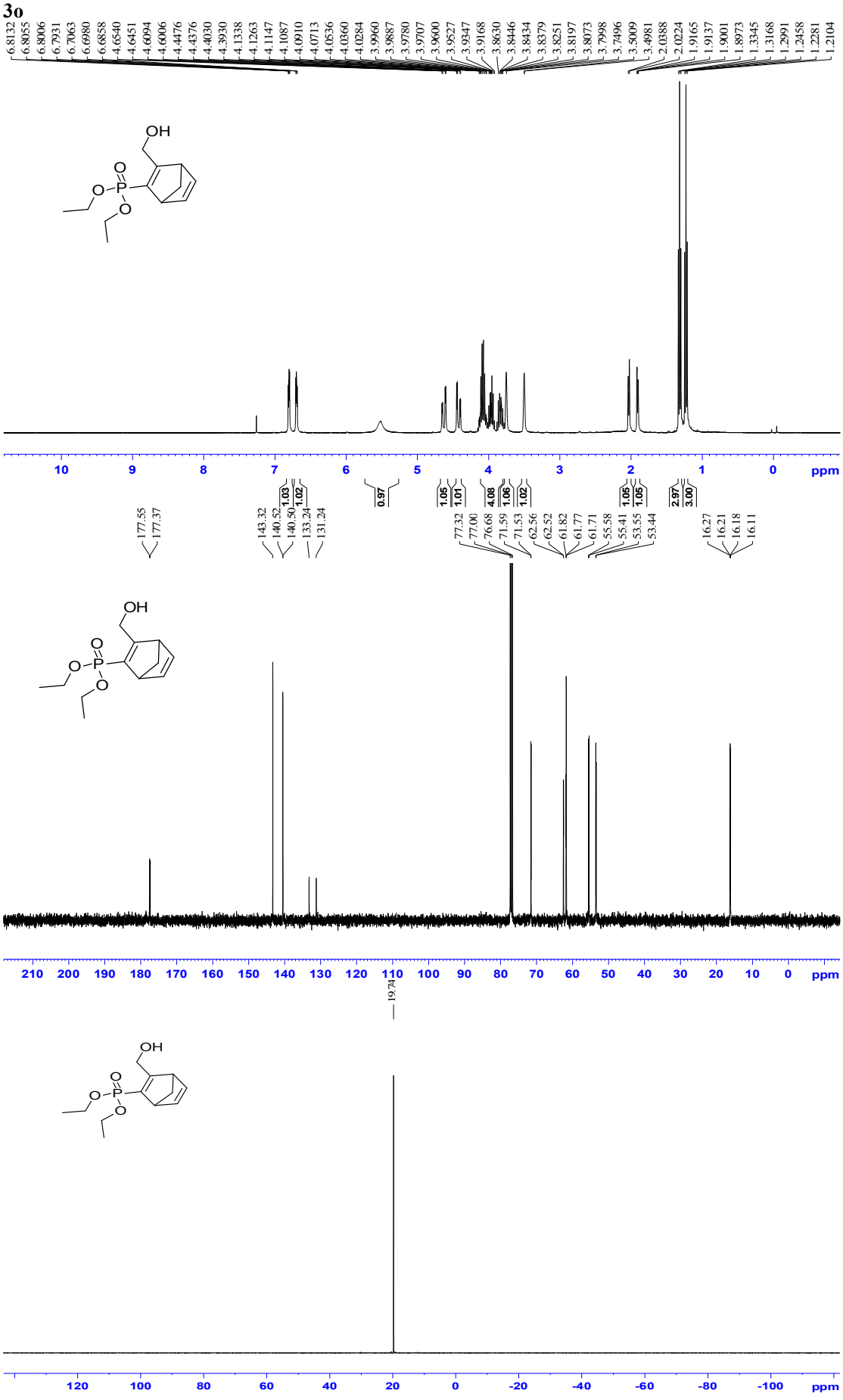
4.6299
4.6144
4.6097
4.5989
4.5942
4.5787
4.5124
4.4969
4.4926
4.4814
4.4771
4.4616
3.7580
3.5300
3.5033
3.4931
3.4854
3.4756
3.4676
3.4582
2.8362
2.8196
2.7554
2.0035
1.9875
1.9511
1.9410
1.9376
1.9295
1.9255
1.9222
1.9127
1.8955
1.8774
1.8737
1.8604
1.8557
1.8387
1.8167
1.3382
1.3227
1.3081
1.2927
1.2753
1.2598
1.1964
1.1809
Cl
O
P
O
O
10
9
8
7
6
5
4
3
2
1
0
ppm
2.06
1.04
1.08
2.02
1.10
1.09
4.06
3.06
3.00
3.09
3.04
136.63
1.00
134.61
1.00
173.07
172.89
143.54
140.38
140.35
77.32
77.00
76.68
71.96
71.90
69.71
69.66
56.05
55.88
53.17
53.04
44.31
30.44
27.92
27.89
24.13
24.09
24.06
24.01
23.96
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
15.24
120
100
80
60
40
20
0
-20
-40
-60
-80
ppm

3o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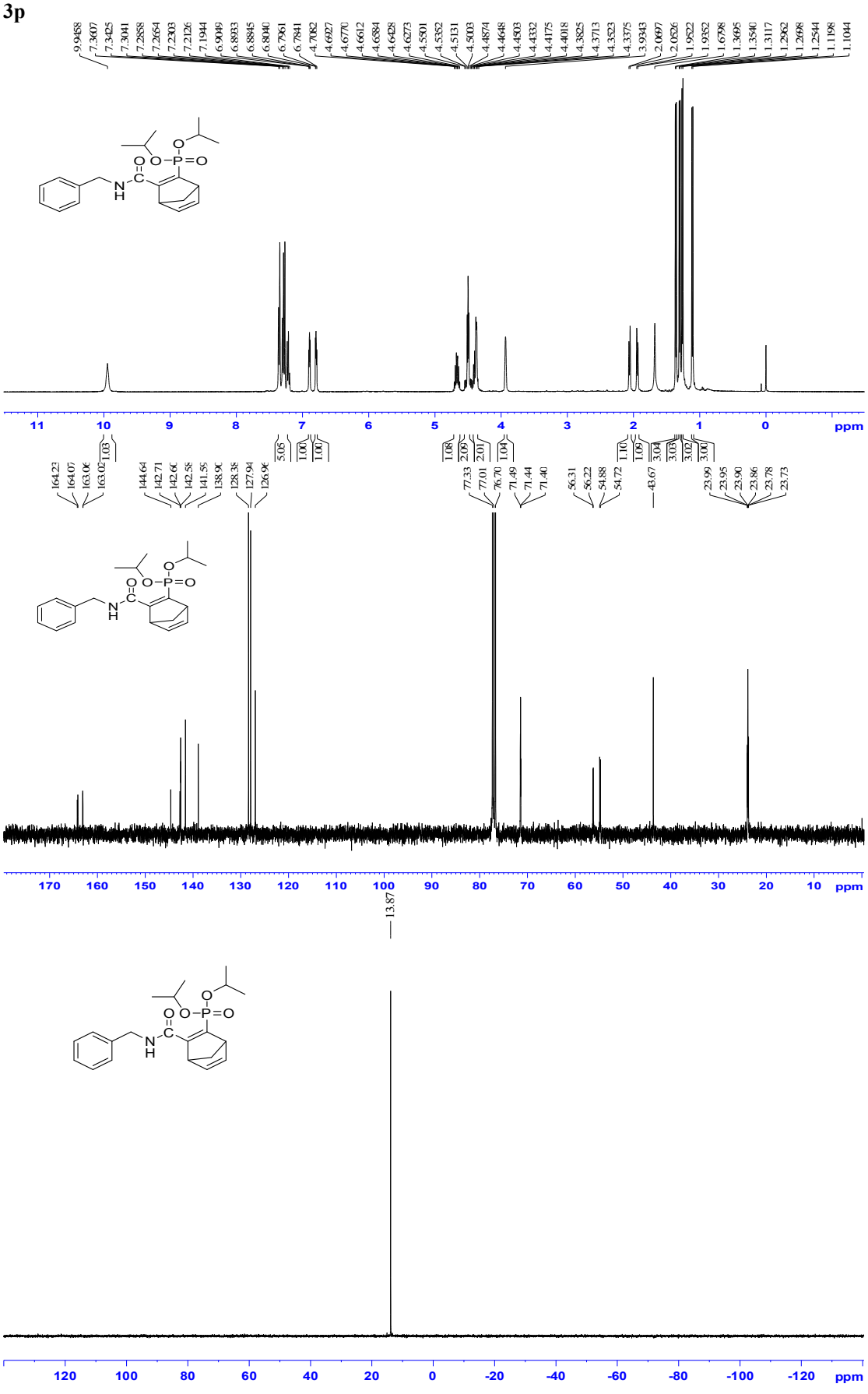
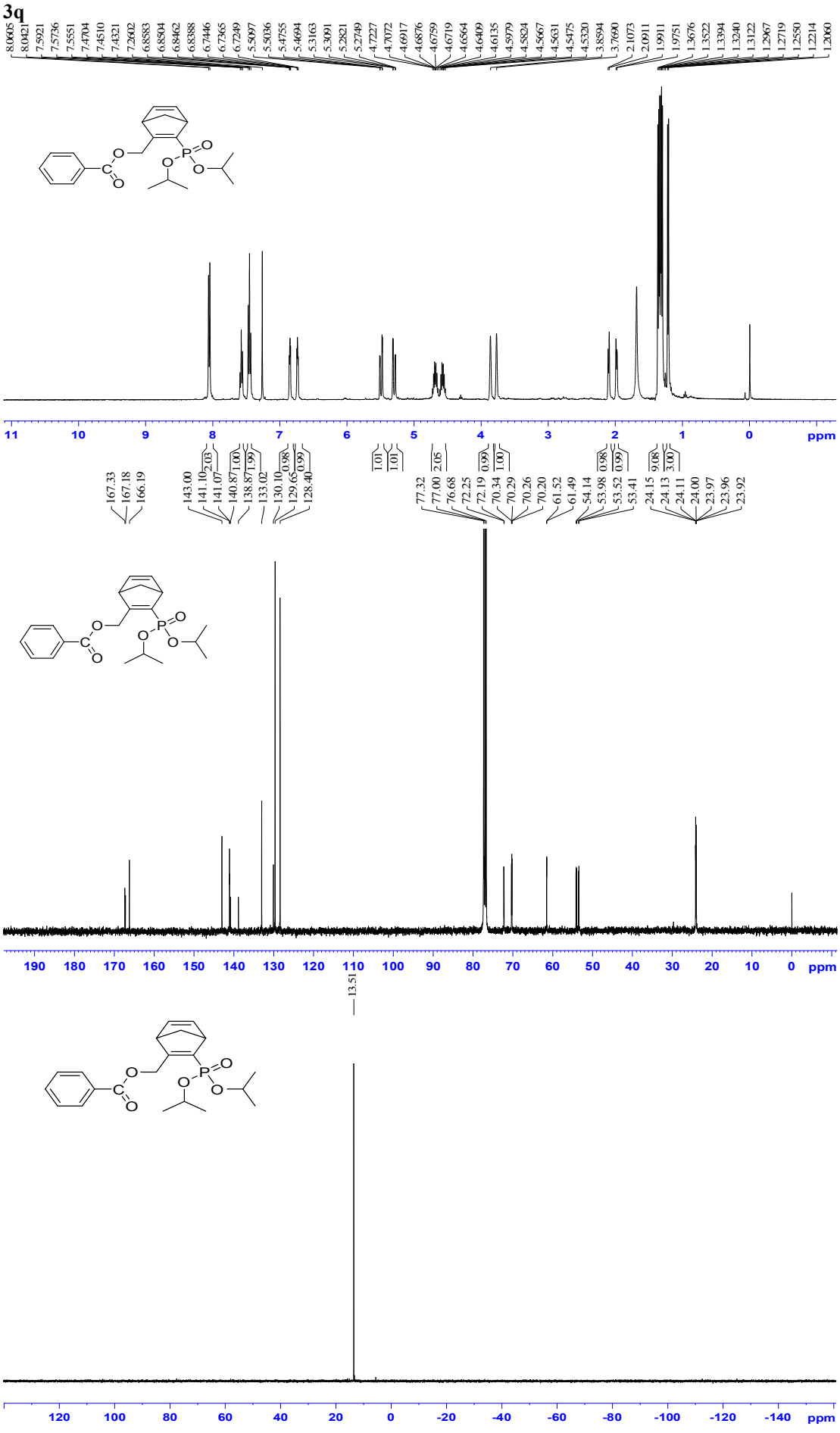
OH
O
P
O
O
10 9 8 7 6 5 4 3 2 1 0 ppm
1.03 1.02 0.97 1.05 1.01 4.08 1.06 1.02 1.05 1.05 2.97 3.00
177.55 177.37 143.32 140.52 140.50 133.24 131.24 77.32 77.00 76.68 71.59 71.53 62.56 62.52 61.82 61.77 61.71 55.58 55.41 53.55 53.44 16.27 16.21 16.18 16.11
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
19.74
120 100 80 60 40 20 0 -20 -40 -60 -80 -100 ppm

3p



3q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7.5921
7.5736
7.5551
7.4704
7.4510
7.4321
7.2602
6.8583
6.8504
6.8462
6.8388
6.7446
6.7365
6.7249
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5.5036
5.4755
5.4694
5.3163
5.3091
5.2821
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4.7227
4.7072
4.6917
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4.6759
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4.6135
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4.5824
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4.5631
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3.8594
3.7690
2.1073
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1.9911
1.9751
1.3676
1.3522
1.3394
1.3240
1.3122
1.2967
1.2719
1.2550
1.2214
1.2060
11 10 9 8 7 6 5 4 3 2 1 0 ppm
167.33
167.18
166.19
143.00
141.10
141.07
140.87
138.87
133.02
130.10
129.65
128.40
77.32
77.00
76.68
72.25
72.19
70.34
70.29
70.26
70.20
61.52
61.49
54.14
53.98
53.52
53.41
24.15
24.13
24.11
24.00
23.97
23.96
23.92
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
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120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 ppm

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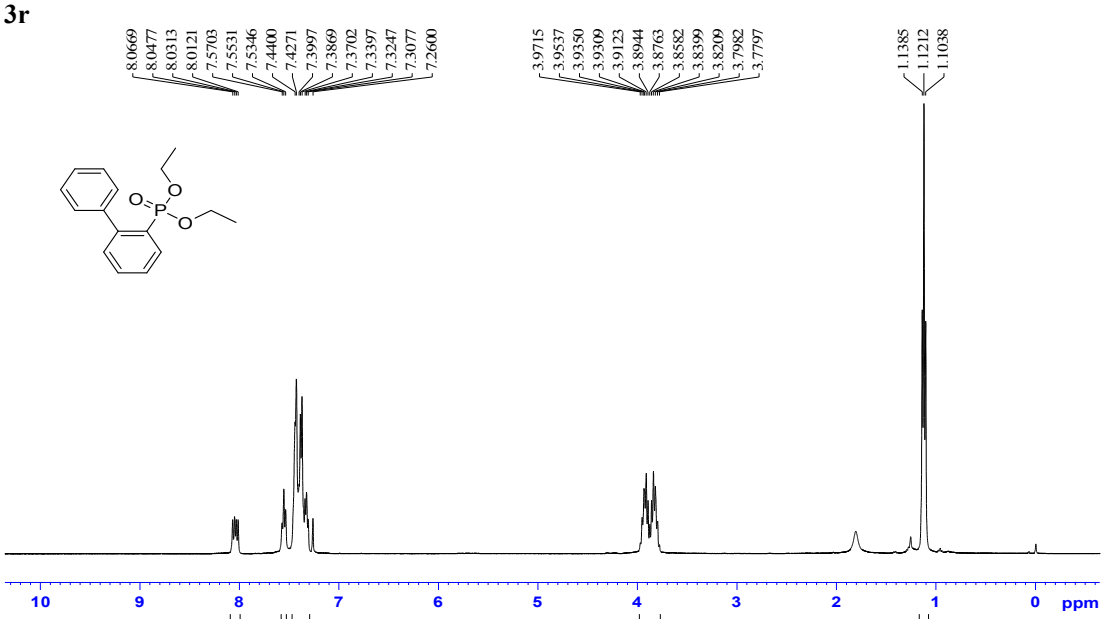
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8.0121
7.5703
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7.5346
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7.3869
7.3702
7.3397
7.3247
7.3077
7.2600
3.9715
3.9537
3.9350
3.9309
3.9123
3.8944
3.8763
3.8582
3.8399
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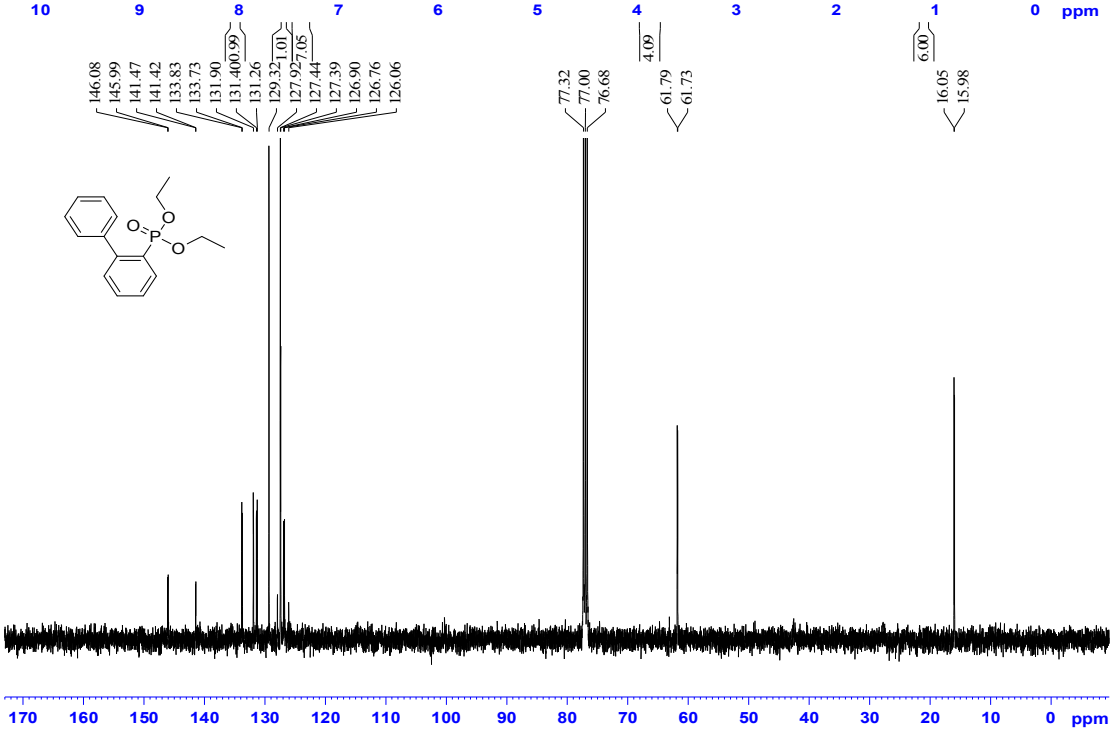
1.1038
4.00
6.00
10 9 8 7 6 5 4 3 2 1 0 ppm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145.99
141.47
141.42
133.83
133.73
131.90
131.40
131.26
129.32
127.92
127.44
127.39
126.90
126.76
126.06
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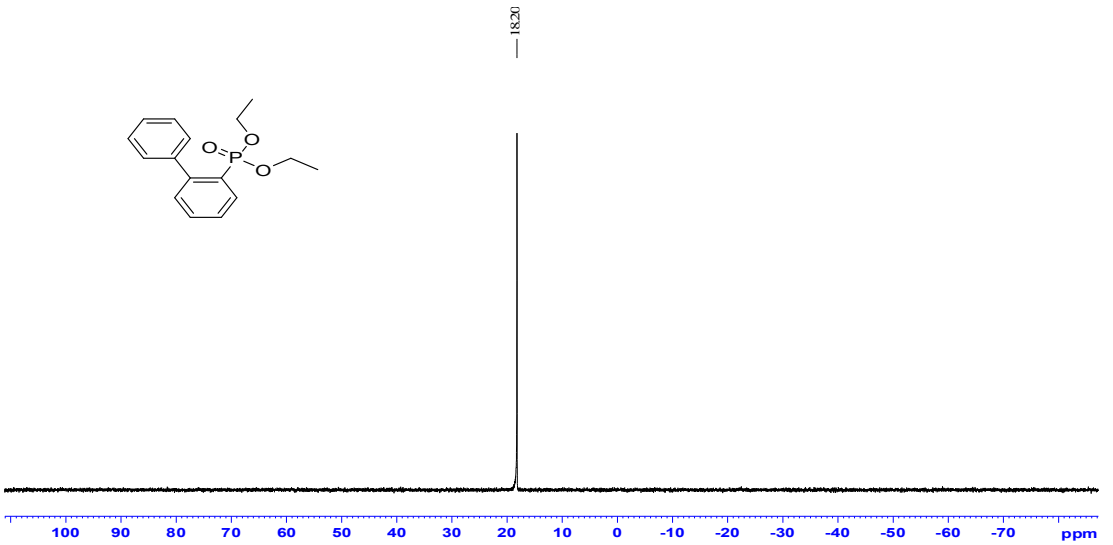
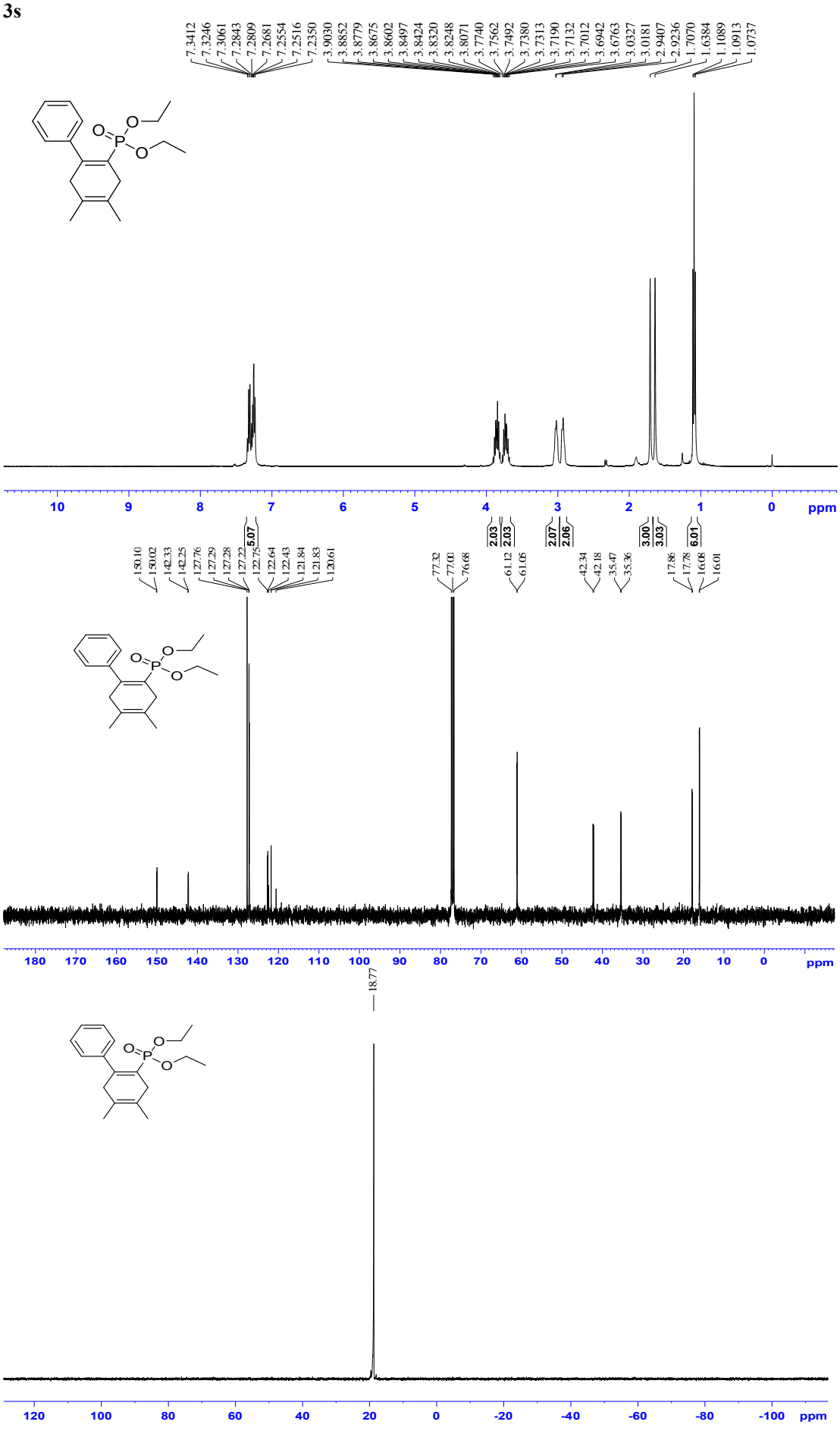
76.68
61.79
61.73
16.05
15.98
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


18.20
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 ppm

3s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3.8852
3.8779
3.8675
3.8602
3.8497
3.8424
3.8320
3.8248
3.8071
3.7740
3.7562
3.7492
3.7380
3.7313
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3.7132
3.7012
3.6942
3.6763
3.0327
3.0181
2.9407
2.9236
1.7070
1.6384
1.1089
1.0913
1.0737
ppm
150.10
150.02
142.33
142.25
127.76
127.29
127.28
127.22
122.75
122.64
122.43
121.84
121.83
120.61
77.32
77.00
76.68
61.12
61.05
42.34
42.18
35.47
35.36
17.86
17.78
16.08
16.01
5.07
2.03
2.03
2.07
2.06
3.00
3.03
6.01
ppm
18.77
ppm