Supplementary Material (ESI) for Organic and Biomolecular Chemistry

Supporting Information

Lewis acid catalyzed ring-opening reactions of methylenecyclopropanes with diphenylphosphine oxide in the presence of sulfur or selenium

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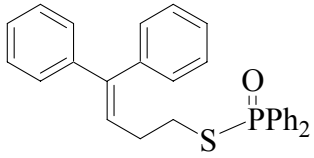
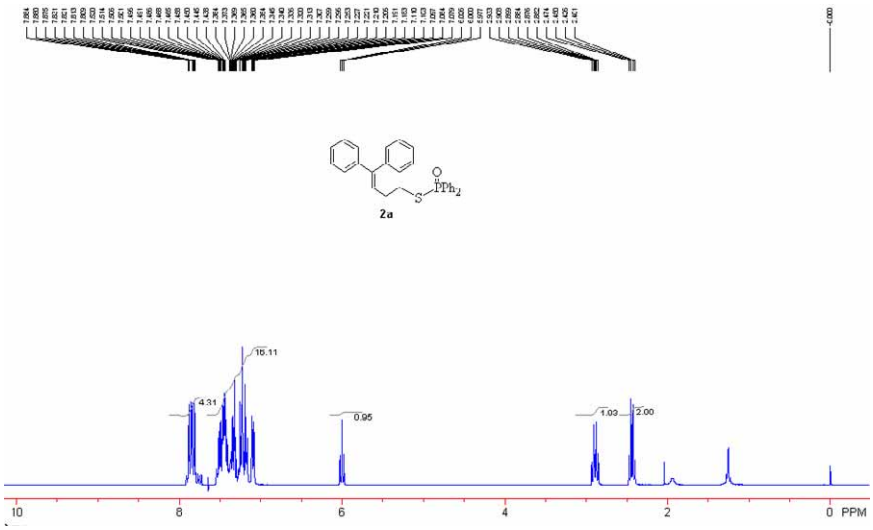
General Remarks. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; *J*-values are in Hz. Mass spectra were recorded by ESI and MALDI methods, and HRMS was measured on a Finnigan MA^+ mass spectrometer. CHN microanalyses were recorded on a Carlo-Erba 1106 analyzer. THF and toluene were distilled from sodium (Na) under argon (Ar) atmosphere. CH_3CN and 1,2-dichloroethane were distilled from CaH_2 under argon (Ar) atmosphere. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure.

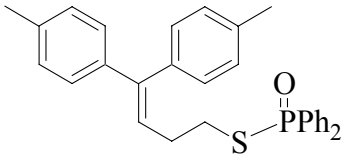
General procedure for the Lewis acid-catalyzed reaction of MCPs with diphenylphosphine oxide in the presence of sulfur or selenium. Under an argon atmosphere, to a solution of 1,1-diphenylmethylenecyclopropane **1a** (62 mg, 0.3 mmol) in DCE (2.0 mL) was added diphenylphosphine oxide (91 mg, 0.45 mmol), sulfur (14 mg, 0.45 mmol) or selenium powder (34 mg, 0.45 mmol) and $Sn(OTf)_2$ (12 mg, 0.03 mmol). The reaction mixture was stirred at 85 ^{o}C for 1 h (monitored by TLC). Then the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding products **2a** (113 mg, 86%) as a white solid.



2a

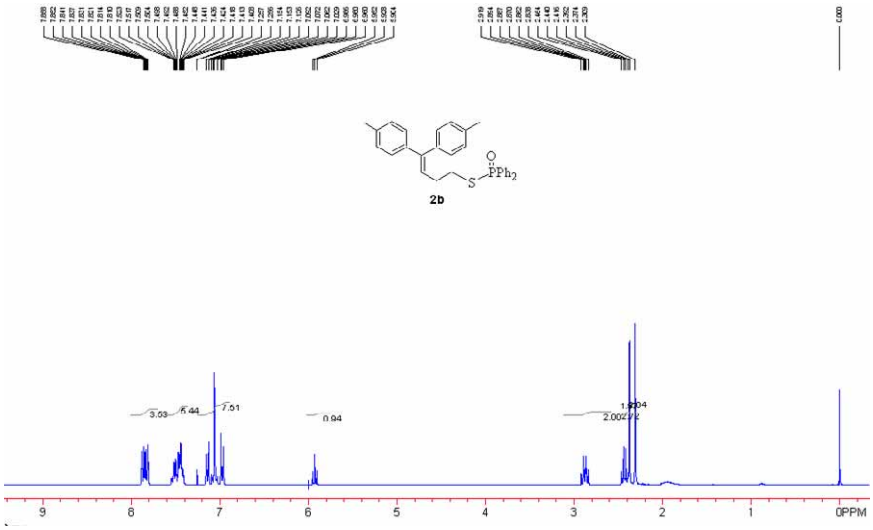
Diphenylphosphinothioic acid S-(4,4-diphenylbut-3-enyl) ester (2a). A white solid, m.p. 102-104 ^{o}C; IR (CH_2Cl_2): ν 3075, 3023, 1655, 1596, 1494, 1438, 1200, 1115, 926, 753, 724, 698, 568 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 2.43 (2H, dt, J = 7.2, 7.2 Hz, CH_2), 2.89 (2H, dt, J = 7.2, 10.2 Hz, CH_2), 6.01 (1H, t, J = 7.2 Hz, =CH), 7.08-7.51 (16H, m, ArH), 7.81-7.88 (4H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 29.1 (d, $J_{C\text{-}P}$ = 2.3 Hz), 30.4 (d, $J_{C\text{-}P}$ = 5.2 Hz), 126.1, 127.0, 127.2, 128.0, 128.4, 128.6, 129.6, 131.4, 132.2, 132.4, 133.8, 139.4, 142.0, 143.7; ^{31}P NMR (121.45 MHz, $CDCl_3$, TMS): δ 44.50; MS (ESI) *m/z* (%): 441 (47) [M^++1]; HRMS (MALDI) Calcd. for $C_{28}H_{26}POS^{+1}$(M^++1) requires 441.1442, Found: 441.1436.

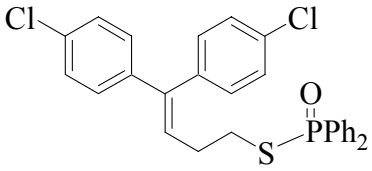




2b

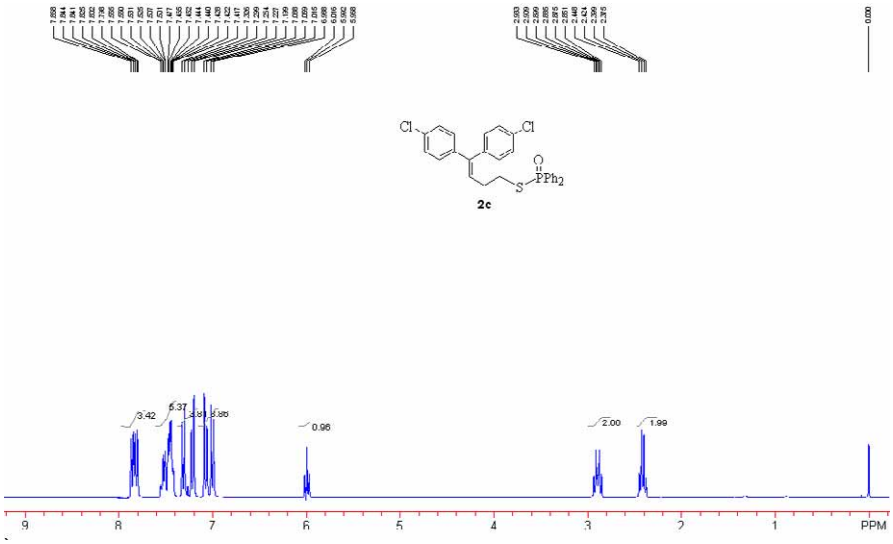
Diphenylphosphinothioic acid S-(4,4-di-p-tolyl-but-3-enyl) ester (2b). A yellow oil; IR (CH_2Cl_2): ν 3022, 2920, 1510, 1437, 1200, 1114, 1097, 820, 698, 751, 723, 567 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.04 (3H, s, CH_3), 2.31 (3H, s, CH_3), 2.43 (2H, dt, J = 7.2, 7.2 Hz, CH_2), 2.88 (2H, dt, J = 7.2, 9.6 Hz, CH_2), 5.93 (1H, t, J = 7.2 Hz, =CH), 6.96-7.25 (8H, m, ArH), 7.41-7.52 (6H, m, ArH), 7.81-7.88 (4H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 21.0, 21.2, 29.2 (d, J_{C-P} = 2.3 Hz), 30.5 (d, J_{C-P} = 5.2 Hz), 125.1, 127.2, 128.2, 128.6, 128.8, 129.6, 131.4, 132.2, 132.5, 134.0, 136.6, 136.8, 139.6, 143.5; ^{31}P NMR (121.45 MHz, $CDCl_3$, TMS): δ 44.47; MS (ESI) *m/z* (%): 485 (100.00) [M^++17]; HRMS (MALDI) Calcd. for $C_{30}H_{29}PONaS^{+1}$(M^++Na) requires 491.1588, Found: 491.1569.

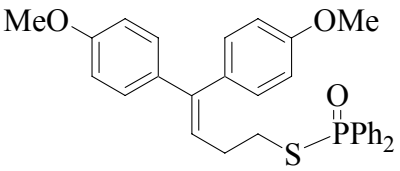




2c

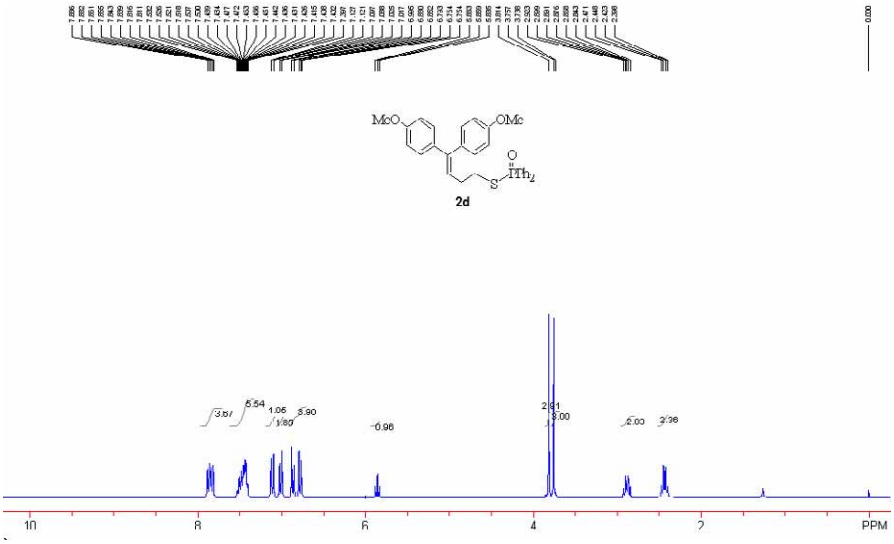
Diphenylphosphinothioic acid S-[4,4-bis(4-chlorophenyl)but-3-enyl] ester (2c). A colorless oil; IR (CH_2Cl_2): ν 3057, 2920, 1713, 1661, 1589, 1491, 1437, 1400, 1198, 1115, 1092, 1071, 1027, 998, 698, 567 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.42 (2H, dt, J = 7.2, 7.2 Hz, CH_2), 2.90 (2H, dt, J = 7.2, 9.9 Hz,CH_2), 6.0 (1H, t, J = 7.2 Hz, =CH), 7.01 (2H, d, J = 7.8 Hz, ArH), 7.08 (2H, d, J = 7.8 Hz, ArH), 7.22 (2H, d, J = 8.7 Hz, ArH), 7.32 (2H, d, J = 8.7 Hz, ArH), 7.42-7.56 (6H, m, ArH), 7.81-7.88 (4H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 28.9 (d, J_{C-P} = 2.3 Hz), 30.7 (d, J_{C-P} = 5.2 Hz), 127.3, 128.3, 128.5, 128.6, 131.0, 131.4, 132.3, 132.4, 133.2, 133.3, 133.8, 137.4, 140.1, 141.5; ^{31}P NMR (121.45 MHz, $CDCl_3$, TMS): δ 44.40; MS (ESI) *m/z* (%): 509 (15) [M^++1]; HRMS (MALDI) Calcd. for $C_{28}H_{24}Cl_2POS^{+1}$(M^++1) requires 509.0639, Found: 509.0657.

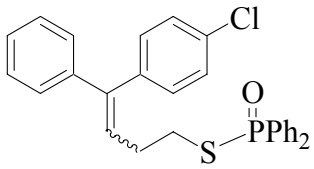




2d

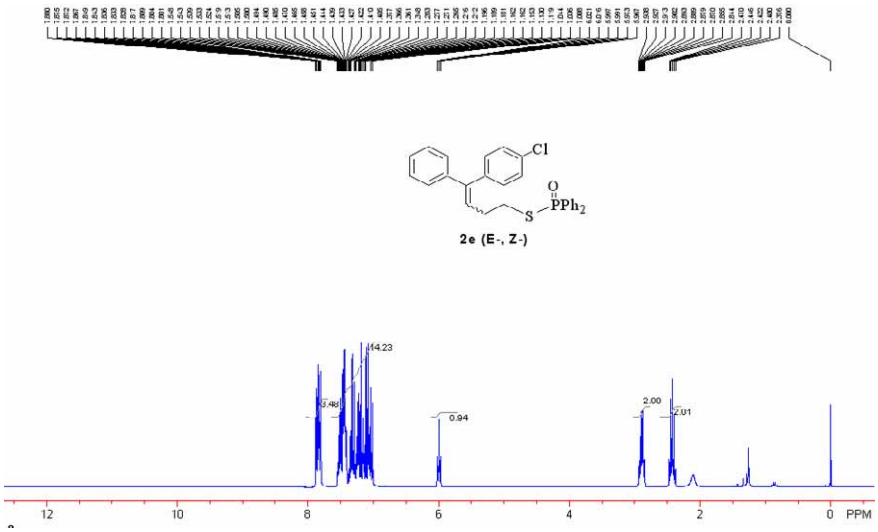
Diphenylphosphinothioic acid S-[4,4-bis(4-methoxyphenyl)but-3-enyl] ester (2d). A colorless oil; IR (CH_2Cl_2): ν 3056, 3002, 2953, 1712, 1646, 1605, 1574, 1509, 1438, 1287, 1178, 1114, 1097, 1032, 822, 568 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.43 (2H, dt, *J* = 7.2, 7.2 Hz, CH_2), 2.88 (2H, dt, *J* = 7.2, 9.6 Hz, CH_2), 3.76 (3H, s, OCH_3), 3.81 (3H, s, OCH_3), 5.86 (1H, t, *J* = 7.2 Hz, =CH), 6.78 (2H, d, *J* = 8.7 Hz, ArH), 6.87 (2H, d, *J* = 8.7 Hz, ArH), 7.01 (2H, d, *J* = 9.0 Hz, ArH), 7.11 (2H, d, *J* = 9.0 Hz, ArH), 7.40-7.51 (6H, m, ArH), 7.81-7.88 (6H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 29.2 (d, $J_{C\text{-}P}$ = 1.8 Hz), 30.5 (d, $J_{C\text{-}P}$ = 5.4 Hz), 55.0, 55.1, 113.3, 124.0, 128.3, 128.6, 130.7, 131.4, 131.9, 132.1, , 132.4, 133.8, 135.1, 142.7, 158.5, 158.8; ^{31}P NMR (121.45 MHz, $CDCl_3$, TMS): δ 44.57; MS (EI) *m/z* (%): 501 (2.63) [M^+], 387 (2.03), 268 (6.04), 267 (38.37), 266 (100), 265 (2.26); HRMS (MALDI) Calcd. for $C_{30}H_{30}O_3PS^{+1}(M^+)$ requires 501.1619, Found: 501.1647.

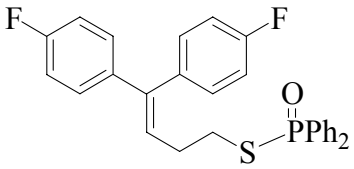




2e (E-, Z-)

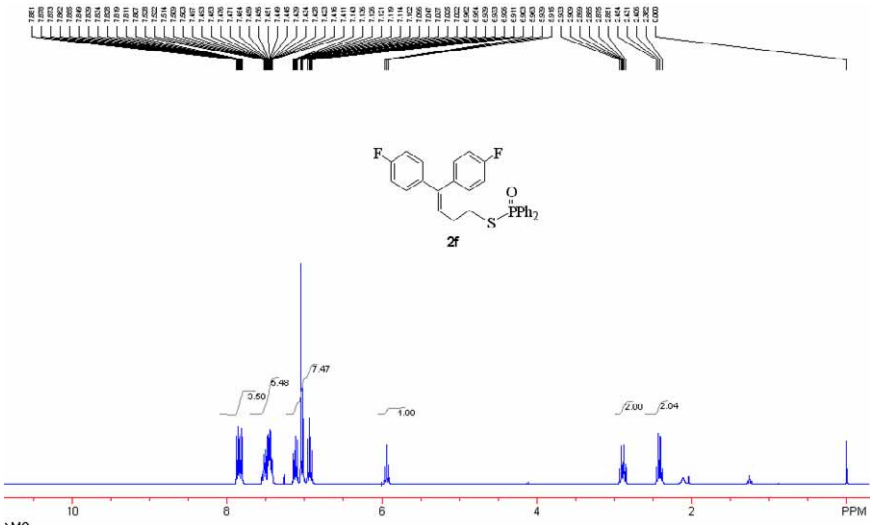
Diphenylphosphinothioic acid S-[4-(4-chlorophenyl)-4-phenylbut-3-enyl] ester (2e) (E/Z = 1:1). A colorless oil; IR (CH_2Cl_2): ν 3056, 1660, 1589, 1489, 1438, 1199, 1115, 1093, 1070, 1027, 1014, 998, 698, 567 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.37-2.47 (2H, m, CH_2), 2.84-2.94 (2H, m, CH_2), 5.97-6.02 (1H, m, =CH), 7.01-7.55 (14H, m, ArH), 7.80-7.88 (4H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 28.9 (d, J_{C-P} = 2.3 Hz), 29.0 (d, J_{C-P} = 2.3 Hz), 30.4 (d, J_{C-P} = 5.2 Hz), 30.6 (d, J_{C-P} = 5.1 Hz), 126.6, 127.1, 127.30, 127.34, 128.11, 128.13, 128.3, 128.40, 128.46, 128.5, 128.7, 129.6, 131.0, 131.3, 131.4, 132.2, 132.3, 132.4, 132.9, 133.0, 133.8, 137.8, 139.0, 140.5, 140.6, 141.5, 142.6, 142.7; ^{31}P NMR (121.45 MHz, $CDCl_3$, TMS): δ 44.54, 44.47; MS (ESI) *m/z* (%): 475 (100) $[M^+ +1]$; HRMS (MALDI) Calcd. for $C_{28}H_{25}ClOPS^{+1}(M^+ +1)$ requires 475.1065, Found: 475.1047.

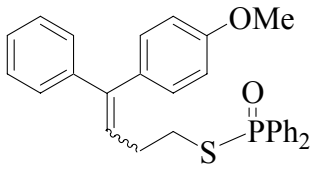




2f

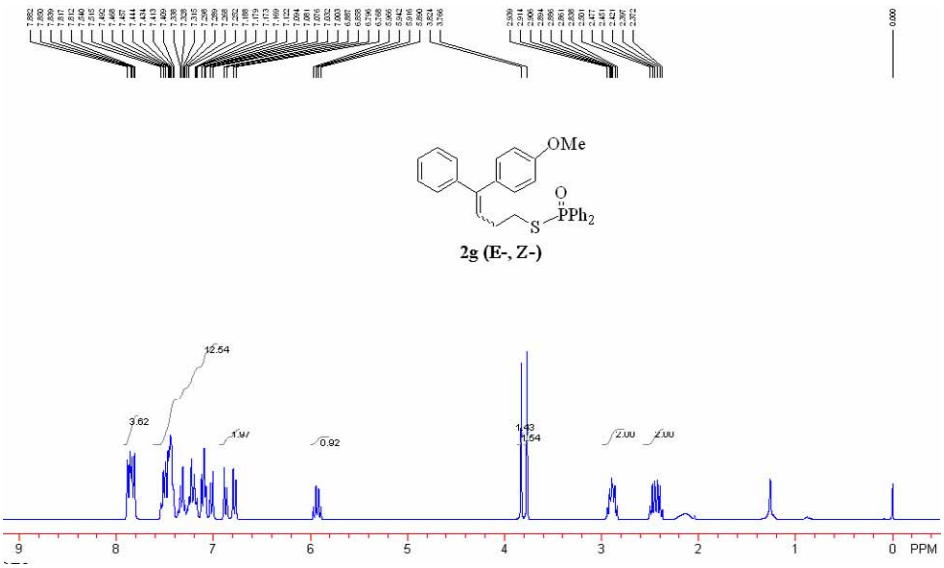
Diphenylphosphinothioic acid S-[4,4-bis(4-fluorophenyl)but-3-enyl] ester (2f). A colorless oil; IR (CH_2Cl_2): ν 3057, 1660, 1601, 1507, 1438, 1224, 1198, 1115, 1071, 1015, 838, 698, 569 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.42 (2H, dt, J = 7.2, 7.2 Hz, CH_2), 2.89 (2H, dt, J = 7.2, 10.5 Hz, CH_2), 5.94 (1H, t, J = 7.2 Hz, =CH), 6.90-7.14 (8H, m, ArH), 7.41-7.53 (6H, m, ArH), 7.80-7.88 (4H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 29.0 (d, $J_{C\text{-}P}$ = 2.3 Hz), 30.5 (d, $J_{C\text{-}P}$ = 4.6 Hz), 114.8, 115.0, 115.1, 115.4, 126.4 (d, $J_{C\text{-}F}$ = 1.2 Hz), 128.5, 128.7 (d, $J_{C\text{-}F}$ = 2.9 Hz), 128.8, 131.2 (d, $J_{C\text{-}F}$ = 1.2 Hz), 131.4, 132.3 (d, $J_{C\text{-}F}$ = 4.2 Hz), 132.4, 133.8, 135.1 (d, $J_{C\text{-}F}$ = 3.5 Hz), 138.1 (d, $J_{C\text{-}F}$ = 4.0 Hz), 141.7, 160.4 (d, $J_{C\text{-}F}$ = 245.0 Hz), 163.6 (d, $J_{C\text{-}F}$ = 245.0 Hz); ^{31}P NMR (121.45 MHz, $CDCl_3$, TMS): δ 44.56; MS (ESI) *m/z* (%): 477 (100) [M^++1]; HRMS (MALDI) Calcd. for $C_{28}H_{24}F_2OPS^{+1}$(M^++1) requires 477.1266, Found: 477.1248.

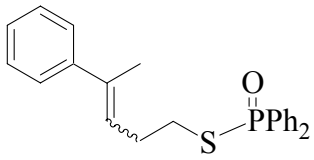




2g (E-, Z-)

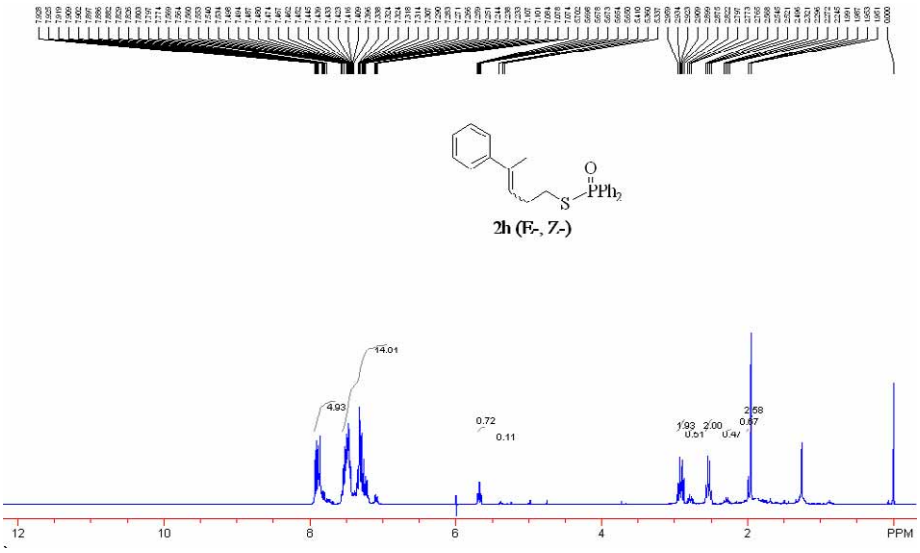
Diphenylphosphinothioic acid S-[4-(4-methoxyphenyl)-4-phenylbut-3-enyl] ester (2g) (E/Z = 1:1). A colorless oil; IR (CH_2Cl_2): ν 3055, 2927, 1606, 1574, 1510, 1493, 1298, 1199, 1114, 1070, 1032, 832, 698, 568 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.37-2.50 (4H, m, CH_2), 2.84-2.94 (4H, m, CH_2), 3.76 (3H, s, CH_3), 3.82 (3H, s, CH_3), 5.93 (1H, m, =CH), 6.78-7.54 (30H, m, ArH), 7.81-7.88 (8H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 29.1 (d, J_{C-P} = 2.5 Hz), 29.2 (d, J_{C-P} = 2.6 Hz), 30.4 (d, J_{C-P} = 6.0 Hz), 30.6 (d, J_{C-P} = 5.2 Hz), 55.1, 55.2, 113.4, 113.5, 124.3, 125.8, 127.0, 127.1, 127.3, 128.0, 128.1, 128.3, 128.5, 128.6, 129.6, 130.8, 131.3, 131.4, 131.7, 132.1, 132.2, 132.4, 133.8, 134.7, 139.7, 142.5, 143.1, 143.3, 158.5, 158.8; ^{31}P NMR (121.45 MHz, $CDCl_3$, TMS): δ 44.54, 44.57; MS (ESI) *m/z* (%): 487 (100) [M^++17], 471 (10) [M^++1]; HRMS (MALDI) Calcd. for $C_{29}H_{27}O_2PSNa^{+1}$(M^++Na) requires 493.1373, Found: 493.1361.

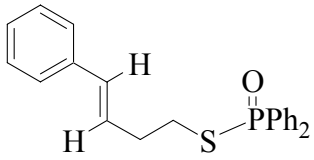




2h (E-, Z-)

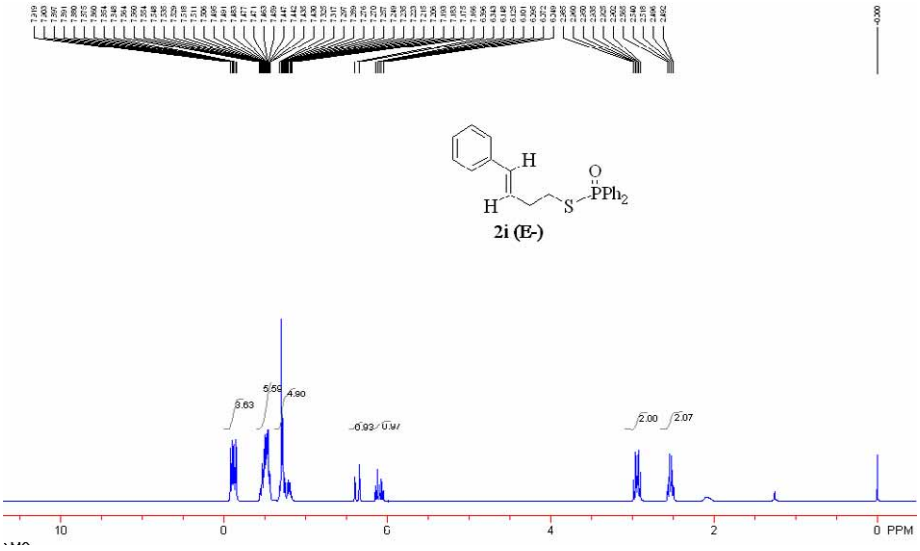
Diphenylphosphinothioic acid S-(4-phenylpent-3-enyl) ester (2h) (E/Z = 4:1). A yellow oil; IR (CH_2Cl_2): ν 3055, 2922, 1714, 1493, 1438, 1200, 1114, 1070, 1027, 997, 698, 567 cm^{-1}; E-isomer: ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.95 (3H, s, CH_3), 2.53 (2H, dt, J = 7.2, 7.2 Hz, CH_2), 2.90 (2H, dt, J = 7.2, 10.8 Hz, CH_2), 5.67 (1H, t, J = 7.2 Hz, =CH), 7.18-7.57 (16H, m, ArH), 7.72-7.92 (4H, m, ArH); Z-isomer: ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.99 (3H, s, CH_3), 2.29 (2H, dt, J = 7.2, 7.2 Hz, CH_2), 2.78 (2H, dt, J = 7.2, 10.8 Hz, CH_2), 5.33 (1H, t, J = 7.2 Hz, =CH), 7.18-7.57 (16H, m, ArH), 7.72-7.92 (4H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 15.9, 16.0, 28.9 (d, J_{C-P} = 2.1 Hz), 29.0 (d, J_{C-P} = 2.2 Hz), 29.8 (d, J_{C-P} = 5.2 Hz), 29.9 (d, J_{C-P} = 5.2 Hz), 124.9, 125.6, 126.6, 127.7, 128.1, 128.2, 128.4, 128.5, 128.6, 128.7, 129.1, 131.34, 131.39, 131.4, 131.5, 131.7, 132.2, 132.3, 137.2, 143.3; ^{31}P NMR (121.45 MHz, $CDCl_3$, TMS): δ 45.20, 45.29; MS (ESI) *m/z* (%): 379 (100) [M^++1]; HRMS (MALDI) Calcd. for $C_{23}H_{29}OPS^{+1}(M^+)$ requires 379.1296, Found: 379.1280.

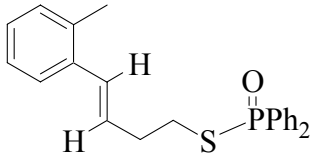




2i (E-)

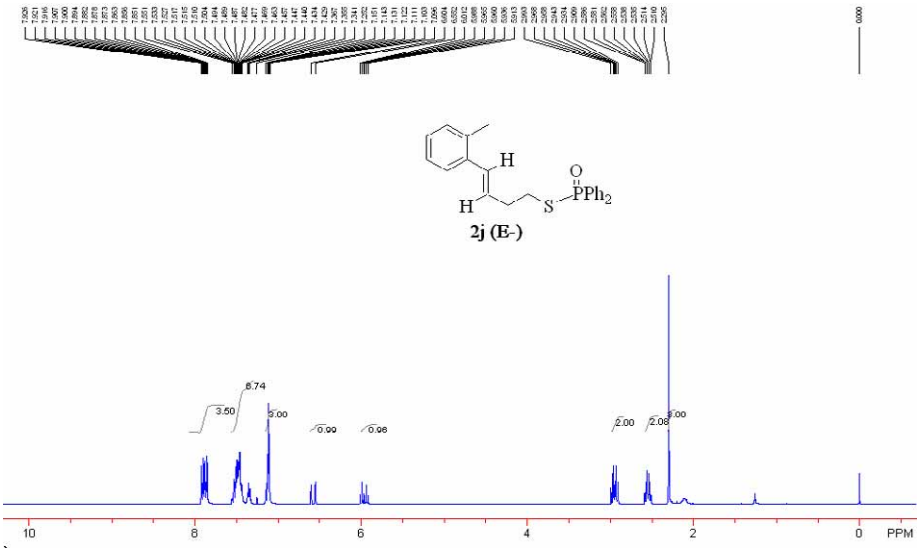
Diphenylphosphinothioic acid S-(4-phenylbut-3-enyl) ester (2i). A white solid, m.p. 98-100 ^{o}C; IR (CH_2Cl_2): ν 3056, 3025, 2927, 1589, 1492, 1481, 1437, 1309, 1199, 1114, 1070, 1027, 966, 698, 567 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 2.53 (2H, dt, J = 7.5, 7.5 Hz, CH_2), 2.94 (2H, dt, J = 7.5, 10.2 Hz, CH_2), 6.10 (1H, dt, J = 7.5, 15.9 Hz, =CH), 6.37 (1H, d, J = 15.9 Hz, =CH), 7.18-7.30 (5H, m, ArH), 7.32-7.56 (6H, m, ArH), 7.85-7.92 (4H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 28.8 (d, $J_{C\text{-}P}$ = 2.3 Hz), 33.9 (d, $J_{C\text{-}P}$ = 4.6 Hz), 126.1, 127.2, 128.4, 128.7, 131.3, 131.5, 132.1, 132.5, 134.0, 137.0; ^{31}P NMR (121.45 MHz, $CDCl_3$, TMS): δ 44.48; MS (ESI) *m/z* (%): 365 (100) [M^{+}+1]; Anal. Calcd. for $C_{22}H_{21}OPS$ requires C, 72.50; H, 5.81%. Found: C, 72.57; H, 5.95%.

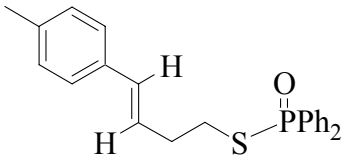




2j (E-)

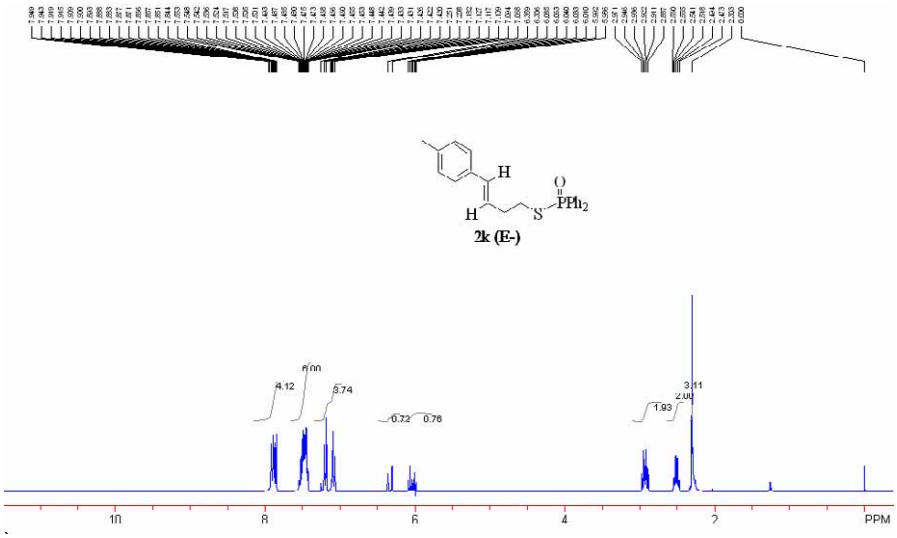
Diphenylphosphinothioic acid S-(4-o-tolyl-but-3-enyl) ester (2j). A yellow oil; IR (CH_2Cl_2): ν 3056, 3022, 2928, 1438, 1460, 1437, 1200, 1114, 1070, 1027, 967, 698, 567 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.30 (3H, s, CH_3), 2.56 (2H, dt, J = 7.2, 7.2 Hz, CH_2), 2.95 (2H, dt, J = 7.2, 10.2 Hz, CH_2), 5.97 (1H, dt, J = 7.2, 15.3 Hz, =CH), 6.58 (1H, d, J = 15.3 Hz, =CH), 7.11-7.15 (3H, m, ArH), 7.35-7.54 (7H, m, ArH), 7.85-7.93 (4H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 19.8, 28.9 (d, $J_{C\text{-}P}$ = 2.3 Hz), 34.1 (d, $J_{C\text{-}P}$ = 5.1 Hz), 125.5, 125.9, 127.2, 128.4, 128.5, 130.0, 131.3, 131.5, 132.5, 133.9, 135.0, 136.2; ^{31}P NMR (121.45 MHz, $CDCl_3$, TMS): δ 44.50; MS (ESI) *m/z* (%): 379 (100) [M^++1]; HRMS (MALDI) Calcd. for $C_{23}H_{24}OPS^{+1}$(M^++1) requires 379.1298, Found: 379.1280.

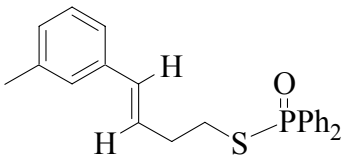




2k (E-)

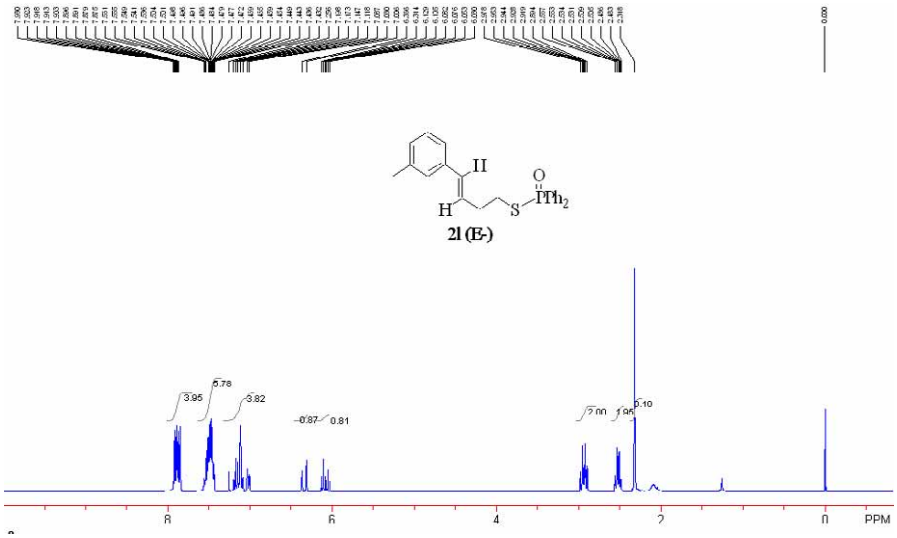
Diphenylphosphinothioic acid S-(4-p-tolyl-but-3-enyl) ester (2k). A yellow oil; IR (CH_2Cl_2): ν 3023, 2920, 1512, 1437, 1309, 1200, 1114, 1098, 1070, 1027, 968, 698, 567 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.30 (3H, s, CH_3), 2.50 (2H, dt, J = 7.2, 7.2 Hz, CH_2), 2.93 (2H, dt, J =7.2, 10.2 Hz, CH_2), 6.04 (1H, dt, J = 7.2, 15.9 Hz, =CH), 6.33 (1H, d, J = 15.9 Hz, =CH), 7.07-7.25 (4H, m, ArH), 7.42-7.55 (6H, m, ArH), 7.84-7.92 (4H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 21.05, 28.8 (d, $J_{C\text{-}P}$ = 2.3 Hz), 33.9 (d, $J_{C\text{-}P}$ = 5.2 Hz), 125.9, 128.5, 129.1, 131.3, 131.9, 132.2, 132.5, 133.9, 134.2, 136.9; ^{31}P NMR (121.45 MHz, $CDCl_3$, TMS): δ 44.50; MS (ESI) *m/z* (%): 379 (100) [M^++1]; HRMS (MALDI) Calcd. for $C_{23}H_{24}OPS^{+1}$(M^++1) requires 379.1288, Found: 379.1280.

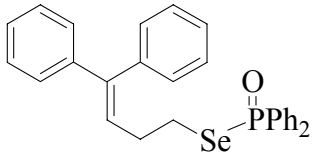




2l (E-)

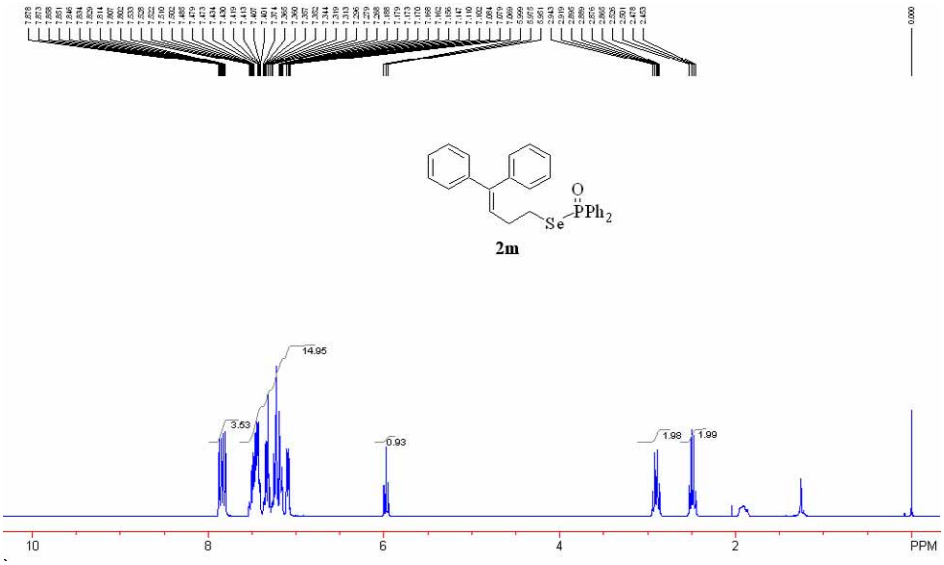
Diphenylphosphinothioic acid S-(4-m-tolyl-but-3-enyl) ester (2l). A yellow oil; IR (CH_2Cl_2): ν 3023, 2920, 1603, 1482, 1437, 1200, 1114, 1098, 1070, 965, 698, 567 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.32 (3H, s, CH_3), 2.52 (2H, dt, J = 7.2, 7.2 Hz, CH_2), 2.93 (2H, dt, J = 7.2, 10.2 Hz, CH_2), 6.08 (1H, dt, J = 7.2, 12.0 Hz, =CH), 6.34 (1H, d, J = 12.0 Hz, =CH), 7.01-7.26 (4H, m, ArH), 7.43-7.56 (6H, m, ArH), 7.85-7.93 (4H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 21.05, 28.8 (d, $J_{C\text{-}P}$ = 2.3 Hz), 33.9 (d, $J_{C\text{-}P}$ = 5.2 Hz), 123.2, 125.9, 128.5, 128.6, 129.1, 131.3, 131.9, 132.1, 132.5, 133.9, 134.2, 136.9; ^{31}P NMR (121.45 MHz, $CDCl_3$, TMS): δ 44.54; MS (ESI) *m/z* (%): 379 (100) [M^++1]; HRMS (MALDI) Calcd. for $C_{23}H_{24}OPS^{+1}$(M^++1) requires 379.1299, Found: 379.1280.

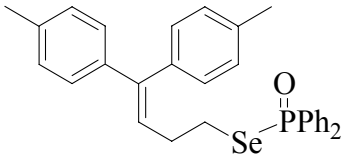




2m

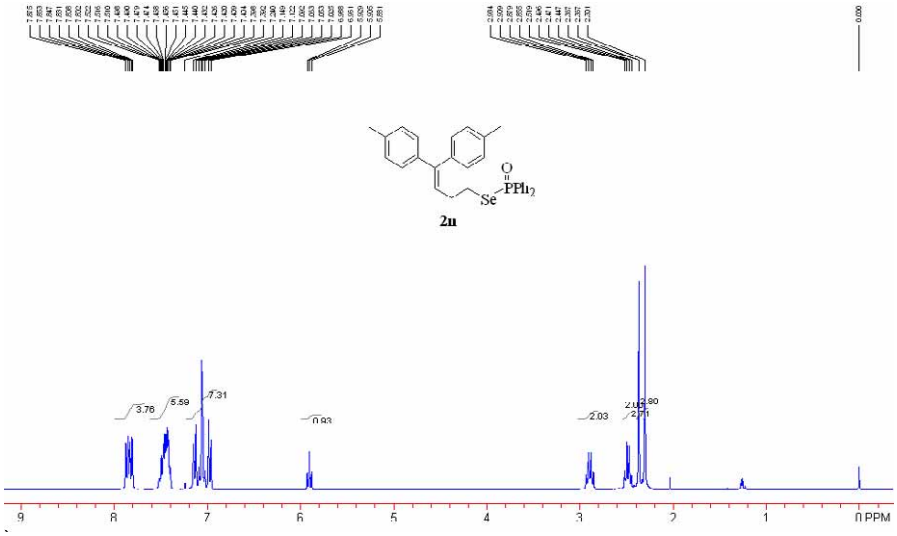
Diphenylphosphinoselenoic acid Se-(4-m-tolyl-but-3-enyl) ester 2m. A colorless oil; IR (CH_2Cl_2): ν 3054, 3023, 2932, 1597, 1493, 1437, 1363, 1198, 1114, 1096, 1071, 1027, 998, 754, 696, 538 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.49 (2H, dt, J = 7.2, 7.2 Hz, CH_2), 2.90 (2H,dt, J = 7.2, 7.5 Hz, CH_2), 5.97 (1H, t, J = 7.2 Hz, =CH), 7.08-7.53 (16H, m, ArH), 7.80-7.88 (4H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 24.9 (d, J_{C-P} = 1.8 Hz), 30.5 (d, J_{C-P} = 4.8 Hz), 127.0, 127.1, 128.0, 128.2, 128.5, 128.7, 129.7, 131.1, 132.1, 133.5, 134.8, 139.5, 142.1, 143.5; ^{31}P NMR (75 MHz, $CDCl_3$, TMS): δ 41.18; MS (ESI) *m/z* (%): 489 (100) [M^++1]; HRMS (MALDI) Calcd. for $C_{28}H_{26}OPSe^{+1}$(M^++1) requires 489.0891, Found: 489.0881.

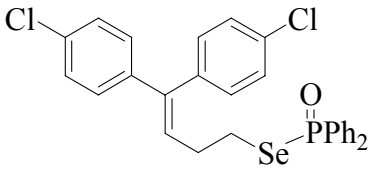




2n

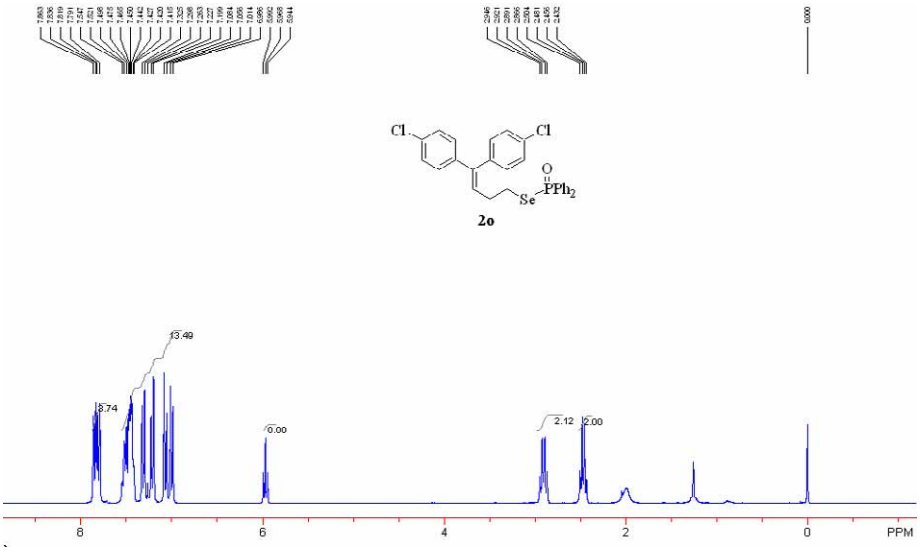
Diphenylphosphinoselenoic acid Se-[4,4-bis(4-chlorophenyl)but-3-enyl] ester 2n. A yellow oil; IR (CH_2Cl_2): ν 3052, 2919, 1511, 1481, 1437, 1199, 1113, 1096, 1070, 1021, 821, 696, 539 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.30 (3H, s, CH_3), 2.37 (3H, s, CH_3), 2.48 (2H,dt, J = 7.2, 7.2 Hz, CH_2), 2.89 (2H, dt, J = 7.2, 7.2 Hz,CH_2), 5.90 (1H, t, J = 7.2 Hz, =CH), 6.96-7.15 (8H, m, ArH), 7.40-7.50 (6H, m, ArH), 7.80-7.87 (4H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 21.0, 21.2, 25.0 (d, J_{C-P} = 2.3 Hz), 30.5 (d, J_{C-P} = 4.1 Hz), 125.9, 127.1, 128.4, 128.6, 128.8, 129.5, 131.2, 132.0, 133.5, 134.8, 136.5, 136.7, 139.5, 143.2; ^{31}P NMR (75 MHz, $CDCl_3$, TMS): δ 41.22; MS (ESI) *m/z* (%): 517 (23) [M^++1]; HRMS (MALDI) Calcd. for $C_{30}H_{29}PONaSe^{+1}$(M^++Na) requires 539.1041, Found: 539.1013.

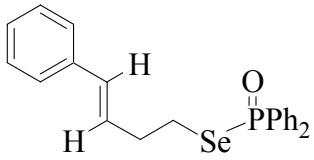




2o

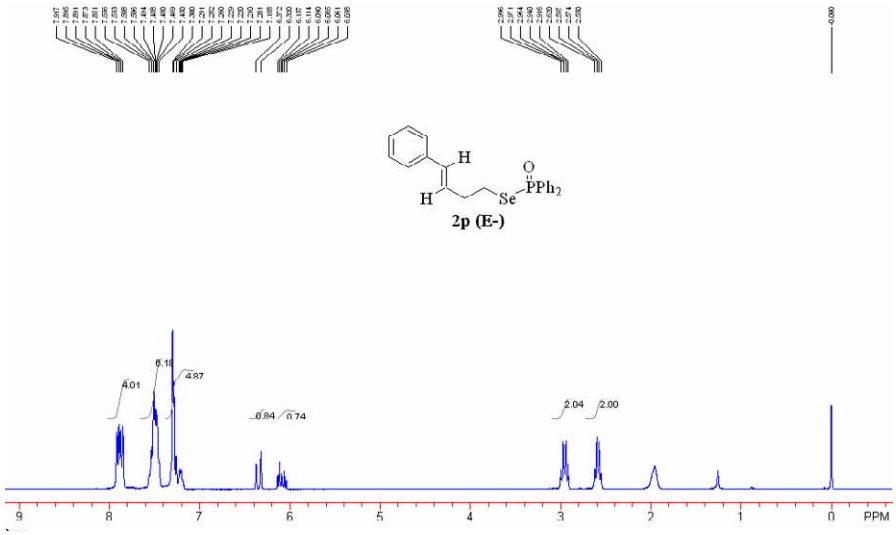
Diphenylphosphinoselenoic acid Se-[4,4-bis(4-chlorophenyl)but-3-enyl] ester (2o). A yellow oil; IR (CH_2Cl_2): ν 3056, 2930, 1590, 1491, 1437, 1400, 1263, 1198, 1092, 1070, 1014, 831, 721, 696, 539 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.47 (2H, dt, J = 7.2, 7.2 Hz, CH_2), 2.91 (2H, dt, J = 7.2, 7.2 Hz,CH_2), 5.97 (1H, t, J = 7.2 Hz, =CH), 7.0 (2H, d, J = 8.4 Hz, ArH), 7.06 (2H, d, J = 8.1 Hz, ArH), 7.21 (2H, d, J = 8.1 Hz, ArH), 7.31 (2H, d, J = 8.4 Hz, ArH), 7.42-7.52 (6H, m, ArH), 7.79-7.86 (4H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 24.5 (d, $J_{C\text{-}P}$ = 2.3 Hz), 30.7 (d, $J_{C\text{-}P}$ = 4.0 Hz), 127.3, 128.3, 128.5, 128.7, 131.0, 131.3, 132.3, 132.4, 133.2, 133.3, 133.8, 137.4, 140.1, 141.5; ^{31}P NMR (121.45 MHz, $CDCl_3$, TMS): δ 41.12; MS (MALDI) *m/z* (%): 557 (100) [M^++1]; HRMS (MALDI) Calcd. for $C_{28}H_{23}Cl_2POSe^{+1}(M^+)$ requires 556.0007, Found: 556.0023.

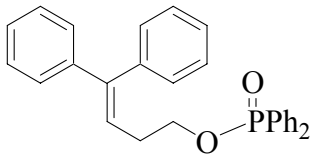




2p (E-)

Diphenylphosphinoselenoic acid Se-(4-phenylbut-3-enyl) ester (2p). A yellow solid, m.p. 106-108 ^{o}C; IR (CH_2Cl_2): ν 3056, 3025, 1589, 1492, 1437, 1196, 1113, 1096, 1070, 1027, 966, 696, 539 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 2.59 (2H, dt, J = 7.2, 7.2 Hz, CH_2), 2.96 (2H, dt, J = 7.2, 7.2 Hz, CH_2), 6.09 (1H, dt, J = 7.2, 15.6 Hz, =CH), 6.35 (1H, d, J = 15.6 Hz, =CH), 7.18-7.30 (5H, m, ArH), 7.45-7.56 (6H, m, ArH), 7.85-7.92 (4H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 24.6 (d, $J_{C\text{-}P}$ = 2.7 Hz), 34.1 (d, $J_{C\text{-}P}$ =3.7 Hz), 126.1, 128.0, 128.5, 128.7, 131.1, 131.3, 131.9, 132.2, 132.3, 137.1; ^{31}P NMR (121.45 MHz, $CDCl_3$, TMS): δ 41.16; MS (ESI) *m/z* (%): 429 (100) [M^++17]; HRMS (MALDI) Calcd. for $C_{22}H_{22}POSe^{+1}$(M^++1) requires 413.0577, Found: 413.0568.





3a

Diphenylphosphinic acid 4,4-diphenylbut-3-enyl ester (3a). A colorless oil; IR (CH_2Cl_2): ν 3056, 3025, 1593, 1494, 1439, 1228, 1130, 1113, 1012, 996, 697, 561 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.55 (2H, dt, J = 6.3, 6.3 Hz, CH_2), 4.10 (2H, dt, J = 6.3, 6.3 Hz, CH_2), 6.08 (1H, t, J = 6.3 Hz, =CH), 7.11-7.51 (16H, m, ArH), 7.75-7.82 (4H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 31.0 (d, $J_{C\text{-}P}$ = 6.8 Hz), 64.2 (d, $J_{C\text{-}P}$ = 7.8 Hz), 124.1, 127.0, 127.2, 128.0, 128.3, 128.5, 130.3, 131.5, 131.6, 132.0, 132.1, 139.5, 142.1, 144.2; ^{31}P NMR (121.45 MHz, $CDCl_3$, TMS): δ 32.79; MS (ESI) *m/z* (%): 425 (18) [M^++1]; HRMS (MALDI) Calcd. for $C_{28}H_{25}O_2PNa^{+1}$(M^++Na) requires 447.1503, Found: 447.1508.