Supporting information for
Synthesis of a Triphenylphophine Reagent on Non-Cross-Linked Polystyrene Support: Application to the Staudinger/Aza-Wittig Reaction

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General Methods and Materials. NMR spectra were recorded on a Bruker ARX-400 spectrometer operated at 400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR and 162 MHz for ^{31}P. NMR. IR spectra were recorded on a Perkin Elmer 783 FT-IR. Carbon tetrachloride (ACP Chemical inc.), *N*,*N*-dimethylformamide (Anachemia) and *p*-dioxane (Anachemia) were dried on 4Å molecular sieves for 15 hours prior to use. Tetrahydrofuran (BDH) was glass distilled over sodium/benzophenone under argon atmosphere. Methylene chloride (BDH) was glass distilled over calcium hydride under argon atmosphere. All reactions were carried out in flame dried flasks under argon or nitrogen atmosphere.

Poly(styrene-*co*-4-vinylbenzyl chloride) or non-cross-linked chloromethylated polystyrene (NCPS) (2). [1] NCPS **2** was prepared by adding tin(IV) chloride (8 mL, 68 mmol) to a solution of linear polystyrene (Mw = 230 000, Mn = 140 000), (100 g, 960 mmol) and chloromethyl methyl ether (200 mL, 274 mmol) in carbon tetrachloride (800 mL). *Warning: Extreme care should be taken while manipulating MOMCl which is a suspected carcinogen.* The reaction mixture was stirred vigorously using a mechanical stirrer for exactly 2 hours. The solution was then poured on methyl alcohol (4 L) under vigorous magnetic stirring thus precipitating the polymer. The polymer suspension was then filtered using a corse sintered glass filter, dissolved in a minimum of benzene (about 1.5 L) and precipitated drop by drop in methyl alcohol (8 L) under vigorous magnetic stirring. Filter polymer as above and place in a vacuum oven at 70 °C for 15 hours. The title compound was obtained as a white solid (106.1 g, 99%). A loading of 1,36 mmol/g was determined by ^{1}H NMR (10 s relaxation time). ^{1}H NMR ($CDCl_3$) δ 7.30-6. 88 (bm, aromatic), 4.62-4.38 (bm, benzylic), 2.31-1.70 (bm, PS-α-methylenes), 1.70-1.16 (bm, PS-β-methylenes); ^{13}C NMR ($CDCl_3$) δ 145.2, 134.9, 127.9, 127.5, 125.6, 46.2, 43.6, 40. IR (KBr) 3025, 2921, 1942, 1871, 1802, 1746, 1601, 1493, 1452, 757, 698 cm^{-1}. Anal. calcd.: C, 87.83; H, 7.37.; found: C, 86.84; H, 7.55.

Poly(styrene-*co*-diphenyl-[4-(4-vinyl-benzyloxy)-phenyl]-phosphine oxyde (3). Polymer **3** was prepared by adding *p*-methoxyphenyldiphenylphosphine oxyde [2] (31.1 g, 110 mmol) to a solution of NCPS **2** (65 g, 88.4 mmol) in DMF (1 L). Cesium carbonate (57.4 g, 88.4 mmol) was then added to the reaction mixture and heated to 60 °C for 15 hours under vigorous magnetic stirring. The solution was then poured on methyl alcohol (5 L) under vigorous magnetic stirring thus precipitating the polymer. The polymer suspension was then filtered using a corse sintered glass filter, rinsed with water and methyl alcohol to be subsequently placed in a vacuum oven at 70 °C for 15 hours. The title compound **3** was obtained as an off-white solid (87.8 g, 100%). A loading of 0.96 mmol/g was determined by ^{1}H NMR (10 s relaxation time). ^{1}H NMR ($CDCl_3$) δ 7.85-7.33 (bm, aromatic), 7.33-6.82 (bm, aromatic), 6.82-6.25 (bm, aromatic) 5.01-4.82 (bm, benzylic), 2.39-1.70 (bm, PS-α-methylenes), 1.70-1.16 (bm, PS-β-methylenes); ^{13}C NMR ($CDCl_3$) δ 145.1, 134.0, 133.8, 133.5, 132.4, 132.0, 131.9, 131.7, 128.4, 128.3, 127.9, 127.5, 124.3, 114.8, 114.7, 70.0, 42.5, 40.3; ^{31}P NMR ($CDCl_3$) δ 29.35; IR (KBr) 3025, 2921, 1943,

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[1] Modified procedure from: Green, B.; Garson, L. R. *J. Chem. Soc.* **1969**, *C*, 401-406.

[2] Senear, A. E.; Valient, W.; Wirth, J. *J. Org. Chem.* **1960**, *25*, 2001-2006.

1873, 1596, 1493, 1451, 1197, 1178, 1118, 751, 697, 546 cm^{-1}; Anal. calcd.: C, 87.04; H, 6.92; found: C, 85.95; H, 6.88.

Poly(styrene-*co*-diphenyl-[4-(4-vinyl-benzyloxy)-phenyl]-phosphine (4). Polymer **4** was prepared by adding *N*,*N*-dimethylaniline (100 mL, 790 mmol) to a solution of **3** (82 g, 78.7 mmol) in *p*-dioxane (800 mL). Trichlorosilane (80 g, 790 mmol) was then added to the reaction mixture through a reflux condenser (condenser temperature: -10 ^{o}C) and subsequently heated at 100 ^{o}C for 15 hours under vigorous magnetic stirring (maintaining the condenser temperature at –10 ^{o}C). The solution was then poured on methyl alcohol (5 L) under vigorous magnetic stirring thus precipitating the polymer. The polymer suspension was then filtered using a corse sintered glass filter, rinsed with water and methyl alcohol to be subsequently placed in a vacuum oven at 70 ^{o}C for 15 hours. The title compound **4** was obtained as a white solid (80.7 g, 100%). A loading of 0.96 mmol/g was determined by ^{1}H NMR (10 s relaxation time). ^{1}H NMR (CDCl$_3$) δ 7.46-7.27 (bm, aromatic), 7.27-6.86 (bm, aromatic), 6.86-6.30 (bm, aromatic) 5.09-4.84 (bm, benzylic), 2.34-1.72 (bm, PS-α-methylenes), 1.72-1.25 (bm, PS-β-methylenes); ^{13}C NMR (CDCl$_3$) δ 145.1, 137.6, 135.6, 135.5, 133.5, 133.3, 128.5, 128.4, 128.3, 127.9, 127.5, 125.6, 115.0, 69.9, 40.2, 43.0; ^{31}P NMR (CDCl$_3$) δ -6.36. IR (KBr) 3058, 3024, 2921, 1944, 1881, 1805, 1790, 1593, 1494, 1452, 1434, 1242, 1177, 1027, 744, 697, 532 cm^{-1}; Anal. calcd.: C, 88.46; H, 7.04; found: C, 87.33; H, 7.22.

Standard Procedure for the formation of imines (7a). The aldehyde **5a** (38 mg, 0.36 mmol), was added to a stirred solution of the phosphine polymer **4** (435 mg, 0.42 mmol) in THF (5 mL). The azide **6a** (47 mg, 0.36 mmol) was then added to the reaction mixture (gas evolution is observed). Stirring is continued for 24 hours (48 hours for the cinnamyl derivatives **5d**). Volatiles were evaporated under reduced pressure. The residue was suspended in methyl alcohol (75 mL) and reflux overnight (use of a soxhlet extractor does not affect yield). The polymer suspension was then filtered, solvent was evaporated and imine **7a** was obtained (63 mg, 89%). All spectroscopic and physical properties were consistent with those reported in the literature.[3]

Benzylidene-phenethyl-amine (7b). The reaction was carried out according to standard procedure using aldehyde **5a** (40 mg, 0.38 mmol) and azide **6b** (56 mg, 0.38 mmol) and phosphine polymer **4** (435 mg, 0.42 mmol). The imine **7b** was obtained (76 mg, 96%). All spectroscopic and physical properties were consistent with those reported in the literature.[3]

3-[(Benzylidene-amino)-methly]-oxazolidin-2-one (7c). The reaction was carried out according to standard procedure (Et_2O at rt instead of MeOH for extraction) using aldehyde **5a** (38 mg, 0.36 mmol) and azide **6c** (56 mg, 0.39 mmol) and phosphine polymer **4** (446.2 mg, 0.43 mmol). The imine **7c** was obtained (71 mg, 97%). ^1H NMR ($CDCl_3$) δ 8.40 (t, *J* = 1 Hz, 1H), 7.77 (dd, *J* = 6, 2 Hz, 2H), 7.44 (m, 3H), 5.03 (s, 2H), 4.41 (t, *J* = 8 Hz, 2H), 3.79 (t, *J* = 8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 162.7, 158.2, 135.0, 131.3, 128.5, 128.4, 67.7, 62.0, 43.8; IR (KBr) 2913, 1737, 1643, 1485, 1439, 1386, 1260, 1041, 972, 762, 695 cm^{-1}.

Benzylidene-(4-methoxy-phenyl)-amine (7d). The reaction was carried out according to standard procedure using aldehyde **5a** (37 mg, 0.35 mmol) and azide **6d** (52 mg, 0.35 mmol) and phosphine polymer **4** (396 mg, 0.38 mmol). The imine **7d** was obtained (56 mg, 75%). All spectroscopique and physical properties were consistent with those reported in the literature.[3]

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[3] (a) Saoudi, A.; Benguedach, A.; Benhaoua, H. *Synth. Commun.* **1995**, *25*, 2349-2354 (**7a, 7m, 7o**); (b) Enholm, E. J.; Forbes, D. C.; Holub, D. P. *Synth. Commun.* **1990**, *20,* 981-987 (**7a, 7e**); (c) Ojima, I.; et *al*, *Tetrahedron*, **1992**, *48*, 6985-7012 (**7d, 7p**); (d) Echevarria, A.; Miller, J.; Nascimento, M. G. *Magn. Reson. Chem.* **1985**, *23*, 809-813 (**7a**); (e) Ratcliff, Jr. M. A.; Kochi, J. K. *Tetrahedron* **1972**, *28*, 4467-4481 (**7a**); (f) Zajac, Jr. W. W.; Walters, T. R.; Darcy, M. G. *J. Org. Chem.* **1988**, *53*, 5856-5860 (**7a**); (g) O'Donnell, M. J.; Bennett, W. D.; Bruder, W. A.; Jacobsen, W. N.; Knuth, K.; LeClef, B.; Polt, R.L.; Bordwell, F. G.; Mrozack, S. *J. Am. Chem. Soc.* **1988**, *110,* 8520-8525 (**7a**); (h) Denecke, E.; Müller, K.; Bluhm, T. *Org. Magn. Res.* **1982**, *18*, 68-70 (**7k**). (i) Ciufolini, M.A.; Spencer, G.O. *J.Org. Chem*. **1989**, *54,* 4739-4741 (**7q**); (j) Afarinkia, K.; Rees, C. W. *Tetrahedron* **1990**, *46*, 7175-

Benzyl-cyclohexylmethylene-amine (7e). The reaction was carried out according to standard procedure using aldehyde **5b** (39 mg, 0.35 mmol) and azide **6a** (46 mg, 0.35 mmol) and phosphine polymer **4** (382 mg, 0.38 mmol). The imine **7e** was obtained (63 mg, 90%). All spectroscopique and physical properties were consistent with those reported in the literature.[3]

Cyclohexylmethylene-phenethyl-amine (7f). The reaction was carried out according to standard procedure using aldehyde **5b** (43 mg, 0.38 mmol) and azide **6b** (56 mg, 0.38 mmol) and phosphine polymer **4** (440 mg, 0.42 mmol). The imine **7f** was obtained (80 mg, 98%). All spectroscopique and physical properties were consistent with those reported in the literature.[3]

Cyclohexylmethylene-(4-methoxy-phenyl)-amine (7g). The reaction was carried out according to standard procedure using aldehyde **5b** (40 mg, 0.36 mmol) and azide **6d** (53 mg, 0.36 mmol) and phosphine polymer **4** (411 mg, 0.39 mmol). The imine **7g** was obtained (60 mg, 76%). All spectroscopique and physical properties were consistent with those reported in the literature.[3]

Benzyl-pyridin-3-ylmethylene-amine (7h). The reaction was carried out according to standard procedure using aldehyde **5c** (45 mg, 0.42 mmol) and azide **6a** (56 mg, 0.42 mmol) and phosphine polymer **4** (460 mg, 0.46 mmol). The imine **7h** was obtained (78 mg, 94%). All spectroscopic and physical properties were consistent with those reported in the literature.[3]

Phenethyl-pyridin-3-ylmethylene-amine (7i). The reaction was carried out according to standard procedure using aldehyde **5c** (44 mg, 0.41 mmol) and azide **6b** (60 mg, 0.41 mmol) and

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7196 (**7o**, **7p**); (k) Tomaszewski, M. J.; Warkentin, J.; Werstiuk, N.H. *Aust. J. Chem*. **1995**, *48*, 291-321 (**7b, 7f, 7I, 7n**); (l) Castonguay, A.; Vunakis, H. V. *J. Org. Chem.* **1979**, *44*, 4332-4337 (**7h**);

phosphine polymer **4** (470 mg, 0.45 mmol). The imine **7i** was obtained (86 mg, 100%). All spectroscopic and physical properties were consistent with those reported in the literature. [3]

3-{[(Pyridin-3-ylmethylene)-amino]-methyl}-oxazolidin-2-one (7j). The reaction was carried out according to standard procedure (Et_2O at RT instead of MeOH for extraction) using aldehyde **5c** (43 mg, 0.40 mmol) and azide **6c** (63 mg, 0.44 mmol) and phosphine polymer **4** (502 mg, 0.48 mmol). The imine **7j** was obtained (76 mg, 92%). RMN ^1H ($CDCl_3$) δ 8.83 (d, *J* = 1.5 Hz, 1H), 8.60 (dd, *J* = 4.8, 1.5 Hz, 1H), 8.36 (s, 1H), 8.05 (dt, J = 7.9, 1.9 Hz, 1H), 7.30 (dd *J* = 7.9, 4.8 Hz, 1H), 4.97 (s, 2H), 4.34 (t, *J* = 8.2 Hz, 2H), 3.72 (t, *J* = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 159.6, 158.1, 151.9, 150.2, 134.8, 130.7, 123.6, 67.5, 62.0, 43.8; IR (KBr) 3345, 2917, 1736, 1647, 1484, 1424, 1328, 1258, 1116, 1040, 974, 812, 765, 707, 628 cm^{-1}.

Phenyl-pyridin-3-ylmethylene-amine (7k). The reaction was carried out according to standard procedure using aldehyde **5c** (40 mg, 0.37 mmol) and azide **6e** (44 mg, 0.37 mmol) and phosphine polymer **4** (405 mg, 0.41 mmol). The imine **7k** was obtained (45 mg, 66%). All spectroscopic and physical properties were consistent with those reported in the literature. [3]

(4-Methoxy-phenyl)-pyridin-3-ylmethylene-amine (7l) The reaction was carried out according to standard procedure using aldehyde **5c** (38 mg, 0.36 mmol) and azide **6d** (53 mg, 0.36 mmol) and phosphine polymer **4** (411 mg, 0.40 mmol). The imine **7l** was obtained (76 mg, 100%). All spectroscopic and physical properties were consistent with those reported in the literature. [3]

Benzyl-(3-phenyl-allylidene)-amine (7m). The reaction was carried out according to standard procedure using aldehyde **5d** (42 mg, 0.32 mmol) and azide **6a** (42.1 mmol, 0.32 mmol) and phosphine polymer **4** (348 mg, 0.35 mmol). The imine **7m** was obtained (70 mg, 99%). All spectroscopic and physical properties were consistent with those reported in the literature. [3]

Phenethyl-(3-phenyl-allylidene)-amine (7n). The reaction was carried out according to standard procedure using aldehyde **5d** (53 mg, 0.40 mmol) and azide **6b** (59 mg, 0.40 mmol) and phosphine polymer **4** (460 mg, 0.44 mmol). The imine **7n** was obtained (90 mg, 96%). All spectroscopic and physical properties were consistent with those reported in the literature. [3]

Phenyl-(3-phenyl-allylidene)-amine (7o). The reaction was carried out according to standard procedure using aldehyde **5d** (54 mg, 0.41 mmol) and azide **6e** (49 mg, 0.41 mmol) and phosphine polymer **4** (452 mg, 0.45 mmol). The imine **7o** was obtained (64 mg, 75%). All spectroscopic and physical properties were consistent with those reported in the literature. [3]

(4-Methoxy-phenyl)-(3-phenyl-allylidene)-amine (7p). The reaction was carried out according to standard procedure using aldehyde **5d** (52 mg, 0.39 mmol) and azide **6d** (59 mg, 0.39 mmol) and phosphine polymer **4** (452 mg, 0.43 mmol). The imine **7p** was obtained (91 mg, 98%). All spectroscopic and physical properties were consistent with those reported in the literature. [3]

3-Azidomethyl-2-oxazolidone (6c).[4] 2-oxazolidone (1.00 g, 11.48 mmol) is dissolved in a 1.59 M magneticaly stirred solution (22 ml, 34.44 mol) of HN_3 in methylene chloride. Paraformaldehyde (380 mg, 12.63 mmol) and a catalytic amount of *p*-TsOH were subsequently added and stirring was continued for 18 hours at room temperature. The reaction mixture was filtered on a pad (2 cm by 4 cm) of neutral alumina that was rinsed using methylene chloride. Solvent was evaporated under reduced pressure and the crude oil was purified by column chromatography on silica gel (1:1, Ethyl acetate : Hexanes) affording the title compound as a

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[4] Azide (**6a**): Alvarez, S. G.; Alvarez, M. T. *Synthesis*, **1997**, 413-414.; azide (**6b**): Hudlicky, T.; Endoma, M. A. A.; Butora, G. *J. Chem. Soc. Perkin Trans. 1*, **1996**, 2187-2192.; azide (**6c**): Lindsay, R.O.; Allen, C. F. H. *Org. Synth.* Coll. Vol. III, 710-711.; azide (**6d**): Dyall, L. K.; Suffolk, P. M.; Dehaen, W.; L'abbé, G. *J. Chem. Soc. Perkin Trans. 2*, **1994**, 2115-2118.

colorless oil (1.45 g, 89%). ^{1}H NMR (CDCl$_3$) δ 4.86 (s, 2H), 4.38 (t, *J* = 8 Hz, 2H), 3.69 (t, *J* = 8 Hz); ^{13}C NMR (CDCl$_3$) δ 157.8, 62.1, 60.2, 43.3; IR (KBr) 2922, 2111, 1748, 1642, 1484, 1427, 1370, 1235, 1038, 875, 765 cm^{-1}.