Supporting Information

Zinc-Alkynylide Additions to Acyl Iminiums

Christian Fischer and Erick M. Carreira

Laboratorium für Organische Chemie, ETH Hönggerberg, CH-8093 Zürich, Switzerland

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General. All reactions were carried out in oven dried glassware under an atmosphere of argon. Toluene and acetonitrile were passed through two 4 x 36 inch columns of anhydrous neutral A-2 alumina (8 x 14 mesh; Macherey und Nagel; activated under a flow of N₂ at 300° over night) to remove water; for flash chromatography technical grade solvents were used, which were distilled prior to use. All chemicals were purchased from Acros, Aldrich, Avocado, Fluka or Lancaster and used as such.

NEt₃ was distilled from KOH and TMPDA (*N,N,N',N'*-tetramethyl-1,3-propanediamine) from CaH₂.

Chromatographic purification was performed as flash chromatography using Brunschwig silica 32-63, 60Å, using hexanes/ethyl acetate as eluent with 0.5 bar nitrogen pressure.

TLC was performed on Merck silica gel 60 F₂₅₄ TLC glass plates and visualized with UV light or permanganate stain.

Melting points were measured on a Büchi 510 melting point apparatus using open glass capillaries, the data is uncorrected.

¹H-NMR spectra were recorded on a VARIAN Mercury 300 MHz spectrometer in chloroform-d, all signals are reported in ppm with the internal chloroform signal at 7.26 ppm as standard. The data is being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration, interpretation).

¹³C-NMR spectra were recorded with ¹H-decoupling on a VARIAN Mercury 75 MHz spectrometer in chloroform-d, all signals are reported in ppm with the internal chloroform signal at 77.0 ppm as standard.

³¹F-NMR spectra were recorded with ¹H-decoupling on a VARIAN Mercury XXX MHz spectrometer in chloroform-d without standard.

Infrared spectra were recorded on a Perkin Elmer Spectrum RX-I FT-IR spectrophotometer as thin films.

High resolution mass spectrometric measurements were performed by the mass spectrometry service of the LOC at the ETHZ on an Ion Spec Ultima HR FT-ICR MS MALDI-FT-ICR MS using the DHB-tl (2,5-Dihydroxy-benzoic acid-two layers) method at 4.7 Tesla. EI measurements were performed on a VG Tribrid spectrometer, 70 eV.

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High resolution EI mass spectra were performed on a Micromass AutoSpec Ultima and were calibrated with perfluorotributylamine (PFTBA) prior to data acquisition

Elemental analysis was performed by the Mikroelementaranalytisches Laboratorium der ETHZ.

GP: Addition of Zinc-Alkynylides to N-Acyl iminium salts (Table 1)

In a 10-mL flask was placed 218 mg $\text{Zn}(\text{OTf})_2$ (0.500 mmol) under argon and dried under high vacuum. Toluene (1 mL), the alkyne (0.66 mmol), 92 μL NEt_3 (0.66 mmol) and 110 μL TMPDA (660 μmol) were added and the suspension stirred at rt. Depending on the alkyne used, a slightly milky or almost clear solution was obtained. In a separate 10-mL Schlenk flask was added the imine (0.5 mmol) and 1 mL toluene. The solution was cooled to 0°C and the acyl halide (0.5 mmol) was added. The solution was allowed to warm to rt and stirred at rt for 1 h. In most cases precipitation was observed. Then the acyl iminium salt solution was cooled to -78°C and the alkynylide solution was added via canula. The alkynylide flask was washed with additional 0.5 mL toluene. After the addition of the 0.5 mL toluene solution the cold bath was removed and the reaction allowed to warm to rt. After 8 h saturated aqueous NH_4Cl -solution was added and the mixture extracted 3 times with CH_2Cl_2 . The combined organic layers were washed with brine and dried over Na_2SO_4 . Solvent evaporation gave an oil which was purified by flash chromatography (*n*hexane/EtOAc (H/E)). The pure products were obtained as colorless oils unless indicated otherwise. To remove solvent traces some oils were redissolved in benzene and subsequently lyophilized which removed residual solvents in all cases.

***N*-(4-Methoxy-phenyl)-*N*-(1-phenyl-3-trimethylsilanyl-prop-2-ynyl)-acetamide
(Table 1, entry 1)**

The title compound was prepared according to the GP using 94 μ L trimethylsilylacetylene (0.66 mmol), 37 μ L acetyl bromide (0.50 mmol) and 106 mg benzyldiene-(4-methoxy-phenyl)-amine (0.50 mmol). The title compound (123 mg, 70%) was obtained after flash chromatography (H/E 3:1) as a slightly yellow oil.

^1H NMR (CDCl_3 , 300 MHz) δ 7.35-7.25 (m, 5H, Ph H), 6.73 (br m, 4H, PMP), 3.78 (s, 3H, OMe), 1.81 (s, 3H, Ac), 0.17 (s, 9H, TMS); ^{13}C NMR (CDCl_3 , 75 MHz) δ 169.9, 159.0, 137.2, 131.2, 129.3, 128.0, 127.7, 113.4, 102.0, 92.2, 55.2, 50.4, 22.8, -0.2; IR (thin film) ν 3064, 3032, 3005, 2959, 2935, 2901, 2838, 2179, 1660, 1607, 1582, 1511, 1494, 1464, 1455, 1443, 1380, 1300, 1249, 1225, 1182, 1170, 1106, 1086, 1066, 1036, 995, 958, 918, 843, 808, 762, 736, 702 cm^{-1} ; HRMS (MALDI) calcd for $\text{C}_{21}\text{H}_{25}\text{NO}_2\text{SiNa}$ ($\text{M}+\text{Na}$) 374.1547, found 374.1544; Anal. Calcd for $\text{C}_{21}\text{H}_{25}\text{NO}_2\text{Si}$: C, 71.75; H, 7.17; N, 3.98. Found: C, 71.81; H, 7.35; N, 3.99.

***N*-(1-Furan-2-yl-3-phenyl-prop-2-ynyl)-*N*-(4-methoxy-phenyl)-acetamide (Table 1, entry 2)**

The title compound was prepared according to the GP using 72 μ L phenylacetylene (0.66 mmol), 37 μ L acetyl bromide (0.50 mmol) and 101 mg furan-2-ylmethylene-(4-methoxy-phenyl)-amine (0.50 mmol). The title compound (126 mg, 73%) was obtained after flash chromatography (H/E 3:1) as a yellow, gummy oil.

^1H NMR (CDCl_3 , 300 MHz) δ 7.40-7.14 (m, 7H, Ar H), 6.79 (br m, 3H, PMP), 6.25-6.24 (m, 2H, Furan H), 3.77 (s, 3H, OMe), 1.84 (s, 3H, Ac); ^{13}C NMR (CDCl_3 , 75 MHz) δ 170.2, 159.2, 150.2, 142.5, 131.6, 131.4, 130.7, 128.9, 128.4, 128.2, 122.3, 113.9,

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110.2, 110.2, 85.4, 84.1, 55.4, 45.2, 22.9; IR (thin film) ν 3082, 3062, 3031, 2984, 1929, 1652, 1599, 1492, 1454, 1444, 1405, 1360, 1340, 1303, 1256, 1188, 1170, 1134, 1070, 1050, 1029, 1008, 994, 970, 922, 758, 696 cm^{-1} ; HRMS (MALDI) calcd for $\text{C}_{22}\text{H}_{19}\text{NO}_3\text{Na}$ ($\text{M}+\text{Na}$) 368.1257, found 368.1250;

N-Allyl-*N*-(1,3-diphenyl-prop-2-ynyl)-benzamide (Table 1, entry 3)

The title compound was prepared according to the GP using 72 μL phenylacetylene (0.66 mmol), 58 μL benzoyl chloride (0.50 mmol) and 73 mg allyl-benzylidene-amine (0.50 mmol). The title compound (145 mg, 83%) was obtained after flash chromatography (H/E 3:1) as a light yellow solid.

MP (nhexane/EtOAc): 76°C; ^1H NMR (CDCl_3 , 300 MHz, -20°C) δ 7.68-7.61 (m, 2H, Ar H), 7.55-7.35 (m, 13H, Ar H), 7.25 (s, 1H, C(N)H major), 6.11 (s, 1H, C(N)H minor), 5.93-5.82 (m, 1H, vinyl H major), 5.59-5.50 (m, 1H, vinyl H minor), 5.19-5.06 (m, 2H, 2 vinyl H major), 4.85-4.81 (m, 1H, vinyl H minor), 4.66 (d, $J = 16.8$ Hz, 1H, vinyl H minor), 4.27-4.20 (m, 1H, 1 CH_2 major), 4.01-3.94 (m, 1H, 1 CH_2 minor), 3.80-3.74 (m, 1H, 1 CH_2 major and minor); ^{13}C NMR (CDCl_3 , 75 MHz, -20°C) δ major and minor 171.9, 171.1, 137.0, 136.0, 135.6, 135.3, 134.2, 133.3, 131.5, 131.5, 130.0, 129.5, 128.7, 128.5, 128.3, 128.1, 128.0, 127.8, 127.2, 126.7, 126.5, 122.2, 121.8, 117.0, 116.6, 87.4, 86.7, 85.2, 84.6, 55.6, 49.1 (2C), 46.2; IR (thin film) ν 3060, 3030, 2923, 1640, 1600, 1577, 1491, 1444, 1399, 1306, 1266, 1178, 1157, 1104, 1074, 1028, 990, 967, 919, 830, 790, 757, 734, 698 cm^{-1} ; HRMS (MALDI) calcd for $\text{C}_{25}\text{H}_{21}\text{NONa}$ ($\text{M}+\text{Na}$) 374.1515, found 374.1520.

***N*-Allyl-*N*-(1,3-diphenyl-prop-2-ynyl)-acetamide (Table 1, entry 4)**

The title compound was prepared according to the GP using 72 μ L phenylacetylene (0.66 mmol), 36 μ L acetyl chloride (0.50 mmol) and 73 mg allyl-benzylidene-amine (0.50 mmol). The title compound (119 mg, 82%) was obtained after flash chromatography (H/E 3:1) as a colorless oil.

^1H NMR (CDCl_3 , 300 MHz) δ 7.60-7.43 (m, 4H, Ar H), 7.40-7.23 (m, 6H, Ar H), 7.18 (s, 1H, C(N)H major), 6.01 (s, 1H, C(N)H minor), 5.90-5.79 (m, 1H, allyl H minor), 5.73-5.90 (m, 1H, allyl H, major), 5.13-5.03 (m, 2H, allyl H major and minor), 4.16-4.09 (m, 2H, CH_2 minor), 4.00-3.84 (m, 2H, CH_2 major), 2.30 (s, 3H, Me minor), 2.17 (s, 3H, Me major); ^{13}C NMR (CDCl_3 , 75 MHz) δ (major only) 170.8, 137.6, 134.3, 131.6, 128.4, 128.2, 128.0, 127.7, 122.5, 116.7, 86.3, 85.6, 49.0, 48.0, 22.1; IR (thin film) ν 3062, 3031, 2984, 1925, 1651, 1599, 1492, 1453, 1444, 1409, 1359, 1339, 1302, 1256, 1188, 1170, 1070, 1049, 1029, 993, 969, 914, 757, 692 cm^{-1} ; HRMS (MALDI) calcd for $\text{C}_{20}\text{H}_{19}\text{NONa}$ ($\text{M}+\text{Na}$) 312.1359, found 312.1353.

***N*-Allyl-*N*-(4,4-dimethyl-1-phenyl-pent-2-ynyl)-benzamide (Table 1, entry 5)**

The title compound was prepared according to the GP using 72 μ L 3,3-dimethyl-1-butyne (0.66 mmol), 58 μ L benzoyl chloride (0.50 mmol) and 73 mg allyl-benzylidene-amine (0.50 mmol). The title compound (131 mg, 79%) was obtained after flash chromatography (H/E 4:1) as a colorless oil.

^1H NMR (CDCl_3 , 300 MHz, -20°C) δ 7.66-7.60 (m, 2H, Ar H), 7.46-7.25 (m, 8H, Ar H), 7.04 (s, 1H, C(N)H minor), 5.90-5.78 (m, 2H, C(N)H and vinyl H both major), 5.56-5.45 (m, 1H, vinyl H minor), 5.16-5.03 (m, 2H, vinyl H major), 4.79 (d, $J = 9.7$ Hz, 1H, vinyl H minor), 4.60 (d, $J = 17.1$ Hz, 1H, vinyl H minor), 4.19-4.12 (m, 1H, 1 CH_2 major),

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3.72-3.62 (m, 1H, 1 CH₂ minor), 3.72-3.62 (m, 1H, 1 CH₂ major and minor), 1.33 (s, 9H, tBu minor), 1.32 (s, 9H, tBu major); ¹³C NMR (CDCl₃, 75 MHz, -20°C) δ major and minor 171.7, 170.9, 137.7, 136.5, 135.8, 135.4, 134.3, 133.4, 129.7, 129.2, 128.5, 128.2, 128.2, 128.0, 127.7, 127.5, 127.0, 126.5, 126.3, 116.6, 116.3, 96.4, 95.6, 74.1, 73.9, 55.0, 48.7, 48.4, 45.9, 30.8, 27.6; IR (thin film) ν 3084, 3062, 3030, 2969, 2929, 2902, 2868, 2242, 1715, 1643, 1602, 1578, 1494, 1475, 1451, 1400, 1363, 1341, 1304, 1268, 1204, 1178, 1157, 1106, 1076, 1029, 991, 969, 920, 857, 829, 788, 739, 699, 661, 634, 614 cm⁻¹; HRMS (MALDI) calcd for C₂₃H₂₅NONa (M+Na) 354.1828, found 354.1829.

***N*-Allyl-*N*-(1-phenyl-4-trimethylsilyl-but-2-ynyl)-benzamide (Table 1, entry 6)**

The title compound was prepared according to the GP using 106 μL propargyltrimethylsilane (tech., ~80%, 0.660 mmol), 58 μL benzoyl chloride (0.50 mmol) and 73 mg allyl-benzylidene-amine (0.50 mmol). The title compound (140 mg, 77%) was obtained after flash chromatography (H/E 4:1) as a colorless oil.

¹H NMR (CDCl₃, 300 MHz, -20°C) δ 7.69-7.62 (m, 2H, Ar H), 7.46-7.30 (m, 8H, Ar H), 7.02 (s, 1H, C(N)H minor), 5.87 (s, 1H, C(N)H major), 5.81-5.68 (m, 1H, vinyl H major), 5.43-5.30 (m, 1H, vinyl H minor), 5.09-4.97 (m, 2H, vinyl H major), 4.72 (d, *J* = 10.3 Hz, 1H, vinyl H minor), 4.50 (d, *J* = 17.1 Hz, 1H, vinyl H minor), 4.09-3.71 (m, 2H, NCH₂ major and minor), 1.66-1.63 (m, 2H, TMSCH₂ major and minor), 0.18 (s, 9H, TMS major), 0.17 (s, 9H, TMS minor); ¹³C NMR (CDCl₃, 75 MHz, -20°C) δ major and minor 171.6, 170.9, 137.9, 136.8, 135.8, 135.5, 134.2, 133.4, 129.7, 129.2, 128.4, 128.1, 127.9, 127.8, 127.7, 127.6, 127.1, 126.6, 126.3, 116.4, 116.2, 86.2, 85.3, 74.2, 73.9, 55.5, 49.1, 48.8, 46.0, 7.0, -1.5, -1.9; IR (thin film) ν 3083, 3062, 3029, 2956, 2898, 2220, 1642, 1602, 1578, 1493, 1450, 1438, 1400, 1340, 1305, 1362, 1250, 1177, 1156, 1128, 1101, 1075, 1028, 992, 970, 920, 853, 789, 761, 737, 699, 672, 664, 638, 612 cm⁻¹; HRMS (MALDI) calcd for C₂₃H₂₇NOSiNa (M+Na) 384.1754, found 384.1753.

***N*-Allyl-*N*-(1-phenyl-3-triethylsilylprop-2-ynyl)-benzamide (Table 1, entry 7)**

The title compound was prepared according to the GP using 118 μL triethylsilylacetylene (0.660 mmol), 58 μL benzoyl chloride (0.50 mmol) and 73 mg allyl-benzylidene-amine (0.50 mmol). The title compound (136 mg, 70%) was obtained after flash chromatography (H/E 8:1) as a colorless oil.

^1H NMR (CDCl_3 , 300 MHz, -20°C) δ 7.70-7.64 (m, 2H, Ar H), 7.53-7.28 (m, 8H, Ar H), 7.11 (s, 1H, C(N)H minor), 5.91 (s, 1H, C(N)H major), 5.87-5.75 (m, 1H, vinyl H major), 5.54-5.41 (m, 1H, vinyl H minor), 5.14-5.01 (m, 2H, vinyl H major), 4.77 (d, $J = 10.3$ Hz, 1H, vinyl H minor), 4.58 (d, $J = 17.1$ Hz, 1H, vinyl H minor), 4.14 (dd, $J = 5.9, 15.3$ Hz, 1H, 1 CH_2 major), 3.94 (dd, $J = 6.2, 16.8$ Hz, 1H, 1 NCH_2 minor), 3.81-3.71 (m, 1H, 1 NCH_2 major and minor), 1.10-1.03 (m, 9H, 3 Me major and minor), 0.90-0.65 (m, 6H, 3 SiCH_2 major and minor); ^{13}C NMR (CDCl_3 , 75 MHz, -20°C) δ major and minor 171.7, 171.0, 136.9, 135.6, 135.3, 133.9, 133.1, 129.8, 129.3, 128.7, 128.5, 128.3, 128.3, 128.1, 128.0, 127.8, 127.6, 127.1, 126.5, 126.3, 116.8, 116.5, 102.0, 101.7, 90.3, 89.6, 55.7, 49.2, 48.9, 46.1, 7.6, 4.4, 4.1, 3.7; IR (thin film) ν 3084, 3062, 3030, 2955, 2935, 2912, 2875, 2174, 1645, 1602, 1579, 1494, 1452, 1398, 1339, 1302, 1264, 1239, 1178, 1157, 1106, 1076, 1038, 1021, 968, 920, 787, 738, 728, 699, 676, 657, 615 cm^{-1} ; HRMS (MALDI) calcd for $\text{C}_{23}\text{H}_{32}\text{NOSi}$ (M+H) 390.2248, found 390.2251.

***N*-Allyl-*N*-(1,5-diphenylpent-2-ynyl)-benzamide (Table 1, entry 8)**

The title compound was prepared according to the GP using 93 μL 4-phenyl-1-butyne (0.66 mmol), 58 μL benzoyl chloride (0.50 mmol) and 73 mg allyl-benzylidene-amine (0.50 mmol). The title compound (152 mg, 80%) was obtained after flash chromatography (H/E 4:1) as a colorless oil.

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^1H NMR (CDCl_3 , 300 MHz, -20°C) δ 7.65-7.62 (m, 1H, Ar H major), 7.54-7.26 (m, 14 H, Ar H), 7.01 (s, 1H, C(N)H minor), 5.85 (s, 1H, C(N)H major), 5.81-5.70 (m, 1H, vinyl H major), 5.34 (ddd, $J = 5.6, 10.3, 17.1$ Hz, 1H, vinyl H minor), 5.11-5.01 (m, 2H, vinyl H major), 4.74 (d, $J = 10.3$ Hz, 1H, vinyl H minor), 4.52 (d, $J = 17.1$ Hz, 1H, vinyl H minor), 4.05 (dd, $J = 5.9, 15.3$ Hz, 1H, 1 NCH_2 major), 3.89-3.64 (m, 1H+2H, 1 NCH_2 major and NCH_2 minor), 2.98-2.93 (m, 2H, CH_2), 2.75-2.69 (m, 2H, CH_2); ^{13}C NMR (CDCl_3 , 75 MHz, -20°C) δ : major and minor 171.7, 170.8, 140.1, 139.9, 137.2, 136.2, 135.7, 135.3, 134.1, 133.3, 129.7, 129.3, 128.5, 128.3, 128.2, 128.1, 127.9, 127.7, 127.1, 126.6, 126.4, 126.2, 126.1, 116.5, 116.2, 87.2, 86.4, 76.6, 76.3, 55.1, 48.8, 48.7, 46.0, 34.5, 34.4, 20.9, 20.8; IR (thin film) ν 3084, 3062, 3028, 2985, 2926, 2861, 2232, 1640, 1602, 1578, 1494, 1452, 1400, 1340, 1306, 1265, 1178, 1157, 1134, 1102, 1076, 1029, 1001, 992, 971, 921, 789, 739, 699, 664, 639, 613 cm^{-1} ; HRMS (MALDI) calcd for $\text{C}_{27}\text{H}_{25}\text{NONa}$ ($\text{M}+\text{Na}$) 402.1828, found 402.1832.

***N*-Allyl-*N*-[1-(4-methoxy-phenyl)-3-phenyl-prop-2-ynyl]-benzamide (Table 1, entry 9)**

The title compound was prepared according to the GP using 72 μL phenylacetylene (0.66 mmol), 58 μL benzoyl chloride (0.50 mmol) and 73 mg allyl-(4-methoxy-benzylidene)-amine (0.50 mmol). The title compound (152 mg, 80%) was obtained after flash chromatography (H/E 3:1) as an orange solid.

MP (nhexane/EtOAc: 94°C ; ^1H NMR (CDCl_3 , 300 MHz, -20°C) δ 7.71-7.37 (m, 12H, Ar H), 7.24 (s, 1H, C(N)H minor), 6.96-6.88 (m, 2H, Ar H), 6.09 (s, 1H, C(N)H major), 5.95-5.83 (m, 1H, vinyl H major), 5.62-5.49 (m, 1H, vinyl H minor), 5.22-5.09 (m, 2H, vinyl H major), 4.86 (d, $J = 10.3$ Hz, 1H, vinyl H minor), 4.68 (d, $J = 17.1$ Hz, 1H, vinyl H minor), 4.24 (dd, $J = 5.3, 15.6$ Hz, 1H, 1 CH_2 major), 4.02-3.95 (m, 1H, 1 CH_2 minor), 3.84 (s, 3H, OMe minor), 3.81 (s, 3H, OMe major) and 1 CH_2 major and minor

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underneath the OMe; ^{13}C NMR (CDCl_3 , 75 MHz, -20°C) δ major and minor 171.7, 170.8, 159.0, 158.9, 135.6, 135.3, 134.2, 133.3, 131.4, 131.3, 129.8, 129.4, 129.0, 128.6, 128.4, 128.2, 128.1, 128.0, 127.9, 126.6, 126.3, 122.1, 121.8, 116.8, 116.4, 113.5, 87.2, 86.3, 85.5, 84.9, 55.1, 55.0, 48.8, 48.5, 45.8; IR (thin film) ν 3080, 3061, 3032, 3002, 2955, 2931, 2836, 2227, 1640, 1611, 1584, 1511, 1491, 1444, 1418, 1399, 1305, 1252, 1174, 1109, 1072, 1032, 992, 968, 921, 852, 834, 783, 759, 730, 700, 693, 663, 631 cm^{-1} ; HRMS (MALDI) calcd for $\text{C}_{26}\text{H}_{23}\text{NO}_2\text{Na}$ ($\text{M}+\text{Na}$) 404.1621, found 404.1622.

***N*-Butyl-2,2,2-trichloro-*N*-(1,3-diphenyl-prop-2-ynyl)-acetamide (Table 1, entry 10)**

The title compound was prepared according to the GP using 72 μL phenylacetylene (0.66 mmol), 56 μL trichloroacetyl chloride (0.50 mmol) and 81 mg benzylidene-butyl-amine (0.50 mmol). The title compound (172 mg, 84%) was obtained after flash chromatography (H/E 4:1) as a colorless oil.

^1H NMR (CDCl_3 , 300 MHz, -20°C) δ 7.75-7.17 (m, 10H, Ar H), 3.83 (s, 1H, C(N)H major), 5.13-5.10 (m, 1H, C(N)H minor), 3.99-3.89 (m, 1H, 1 NCH₂ minor), 3.65-3.55 (m, 1H, 1 NCH₂ minor), 3.47 (dt, $J = 4.6, 12.2\text{ Hz}$, 1H, 1 NCH₂ major), 3.10 (dt, $J = 4.4, 12.2\text{ Hz}$, 1H, 1 NCH₂ major), 1.81-1.75 (m, 1H, 1 NCH₂CH₂ major and minor), 1.56-1.45 (m, 1H, 1 NCH₂CH₂ major and minor), 1.38-1.12 (m, 2H, CH₃CH₂ major and minor), 0.90-0.72 (m, 3H, Me major and minor); ^{13}C NMR (CDCl_3 , 75 MHz, -20°C) δ major and minor 160.5, 159.4, 139.4, 136.0, 135.1, 131.6, 131.5, 131.4, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.4, 127.1, 127.0, 121.9, 121.6, 93.1, 92.9, 87.5, 87.0, 84.2, 84.0, 57.5, 55.4, 53.2, 48.2, 47.8, 30.8, 29.3, 20.3, 20.1, 14.0, 13.9, 13.8; IR (thin film) ν 3082, 3063, 3033, 2959, 2933, 2873, 2227, 1678, 1599, 1491, 1466, 1450, 1444, 1404, 1373, 1325, 1286, 1266, 1242, 1181, 1109, 1070, 1030, 1006, 988, 919, 854, 839, 811, 757, 733, 701, 691, 668, 639 cm^{-1} ; HRMS (MALDI) calcd for $\text{C}_{21}\text{H}_{20}\text{Cl}_3\text{NONa}$ ($\text{M}+\text{Na}$) 430.0503, found 430.0510.

***N*-Allyl-*N*-(1-*tert*-butyl-3-phenyl-prop-2-ynyl)-2,2,2-trichloro-acetamide (Table 1, entry 11)**

The title compound was prepared according to the GP using 72 μL phenylacetylene (0.66 mmol), 56 μL trichloroacetyl chloride (0.50 mmol) and 63 mg allyl-(2,2-dimethyl-propylidene)-amine (0.50 mmol). The title compound (155 mg, 83%) was obtained after flash chromatography (H/E 4:1) as a colorless oil.

^1H NMR (CDCl_3 , 300 MHz, -20°C) δ 7.41-7.24 (m, 5H, Ph H), 6.08-3.83 (br m, 6H, C(N)H and allyl both isomers, not resolved), 1.22 (s, 9H, tBu minor), 1.13 (s, 9H, tBu major); ^{13}C NMR (CDCl_3 , 75 MHz, -30°C) δ major and minor 161.4, 160.2, 136.9, 132.4, 131.3, 131.0, 128.4, 128.2, 128.1, 128.1, 122.2, 121.8, 117.7, 114.4, 93.1, 93.0, 87.8, 86.2, 85.0, 84.3, 60.5, 58.6, 50.2, 39.3, 37.3, 28.4, 28.0, 27.1; IR (thin film) ν 3082, 3064, 3022, 2968, 2910, 2871, 2678, 1599, 1490, 1479, 1467, 1444, 1393, 1367, 1340, 1327, 1268, 1234, 1188, 1158, 1126, 1070, 1058, 989, 938, 926, 872, 843, 812, 757, 719, 690, 668, 622 cm^{-1} ; HRMS (MALDI) calcd for $\text{C}_{18}\text{H}_{20}\text{Cl}_3\text{NONa}$ ($\text{M}+\text{Na}$) 394.0508, found 394.0490.

Phenyl-(1-phenylethynyl-1H-isoquinolin-2-yl)-methanone (Table 1, entry 12)

The title compound was prepared according to the GP using 72 μL phenylacetylene (0.66 mmol), 58 μL benzoyl chloride (0.50 mmol) and 59 mg isochinoline (0.50 mmol). The title compound (140 mg, 83%) was obtained after flash chromatography (H/E 3:1) as a colorless oil.

SUPPORTING INFORMATION

^1H NMR (CDCl_3 , 300 MHz, -20°C) δ 7.64-7.20 (m, 16H, Ar H), 6.74 (s, 1H, C(N)(Ar)H), 6.60 (d, $J = 7.5$ Hz, olefin H), 6.05 (d, $J = 7.9$ Hz, olefin H); ^{13}C NMR (CDCl_3 , 75 MHz, -20°C) δ 168.5, 133.0, 131.6, 131.1, 129.7, 129.4, 128.9, 128.3, 128.1, 128.1, 127.7, 127.6, 126.3, 126.1, 124.9, 121.9, 109.6, 86.4, 83.1, 46.0; IR (thin film) ν 3059, 3021, 1664, 1626, 1600, 1570, 1490, 1456, 1445, 1409, 1349, 1275, 1251, 1230, 1190, 1180, 1154, 1131, 1105, 1073, 1028, 1002, 985, 945, 913, 873, 848, 820, 776, 757, 726, 702, 692, 666, 622, 611 cm^{-1} ; HRMS (MALDI) calcd for $\text{C}_{24}\text{H}_{17}\text{NONa}$ ($\text{M}+\text{Na}$) 358.1202, found 358.1207.

***N*-Benzyl-*N*-(3,3-diphenyl-1-phenylethynyl-allyl)-benzamide (Table 1, entry 13)**

The title compound was prepared according to the GP using 72 μL phenylacetylene (0.66 mmol), 58 μL benzoyl chloride (0.50 mmol) and 149 mg benzyl-(3,3-diphenyl-allylidene)-amine (0.50 mmol). The title compound (216 mg, 86%) was obtained after flash chromatography (H/E 3:1) as a colorless oil.

^1H NMR (CDCl_3 , 300 MHz, -20°C) δ 7.61-7.17 (m, 21H, Ar H), 7.06 (d, $J = 7.5$ Hz, 1H, Ar H), 6.77 (d, $J = 7.8$ Hz, 1H, Ar H), 6.09 (d, $J = 9.7$ Hz, 1H, C(N)H or olefin H), 5.81 (d, $J = 9.6$ Hz, 1H, C(N)H or olefin H), 5.54 (d, $J = 15.9$ Hz, 1H, 1 CH_2), 4.94 (d, $J = 15.9$ Hz, 1H, 1 CH_2); ^{13}C NMR (CDCl_3 , 75 MHz, -20°C) δ 171.3, 143.5, 140.8, 138.8, 137.4, 134.5, 131.4, 129.4, 129.2, 128.9, 128.4, 128.1, 128.0, 127.7, 127.7, 127.6, 127.6, 127.4, 127.0, 126.7, 126.4, 125.9, 123.3, 121.7, 86.1, 85.5, 51.2, 46.2; IR (thin film) ν 3081, 3059, 3030, 2927, 2245, 1641, 1600, 1577, 1491, 1444, 1404, 1360, 1308, 1256, 1157, 1145, 1075, 1029, 976, 933, 910, 786, 758, 732, 697, 665, 647, 631, 618 cm^{-1} ; HRMS (MALDI) calcd for $\text{C}_{37}\text{H}_{29}\text{NONa}$ ($\text{M}+\text{Na}$) 526.2141, found 526.2145.

***N*-Butyl-*N*-(1,3-diphenyl-prop-2-ynyl)-diphenylphosphinic amide (Scheme 1)**

In a 10-mL flask was placed 218 mg $\text{Zn}(\text{OTf})_2$ (0.600 mmol) under argon and dried under high vacuum, then 1 mL toluene, 72 μL phenylacetylene (0.66 mmol), 92 μL NEt_3 (0.66 mmol) and 110 μL TMPDA (660 μmol) were added and the suspension stirred at rt for 2 h to give a slightly turbid, almost clear solution. To this solution, 81 mg benzylidene-butyl-amine (0.50 mmol) and 105 μL Ph_2POCl (0.550 mmol) and 1.5 mL toluene were added. The reaction turned slightly yellowish and was stirred at rt for 8 h when it was quenched by addition of a sat. NH_4Cl solution. After extraction with CH_2Cl_2 (3 times) the combined organic layers were washed with brine and dried over Na_2SO_4 . Solvent evaporation gave an oil, which was purified by flash chromatography (hexanes/ethyl acetate 1:1) to give the title compound (185 mg, 80%) as a colorless solid.

MP (nhexane/EtOAc): 85°C; ^1H NMR (CDCl_3 , 300 MHz) δ 8.11-8.03 (m, 2H, PPh H), 7.96-7.88 (m, 2H, PPh H), 7.89-7.79 (m, 2H, Ph H), 7.61-7.27 (m, 14H, Ar H), 5.83 (d, $J_{\text{P-H}} = 9.7$ Hz, 1H, C(N)H), 3.16-3.02 (m, 1H, 1 NCH_2), 2.88-2.75 (m, 1H, 1 NCH_2), 1.43-1.62 (m, 1H, 1 NCH_2CH_2), 1.06-0.89 (m, 1H, 1 NCH_2CH_2), 0.87-0.77 (m, 2H, CH_3CH_2), 0.53-0.48 (m, 3H, Me); ^{13}C NMR (CDCl_3 , 75 MHz) δ 137.8, 137.8, 132.5, 132.5, 132.4, 132.2, 132.1, 131.7, 131.6, 131.5, 131.3, 130.9, 130.8, 128.3, 128.2, 128.0, 127.5, 122.6, 87.5, 87.4, 86.7, 51.9, 51.8, 44.6, 32.1, 20.1, 13.4; ^{31}P NMR (CDCl_3 , 121 MHz) δ 32.7; IR (thin film) ν 3059, 3030, 2958, 2932, 2871, 2223, 1598, 1490, 1452, 1438, 1380, 1359, 1269, 1241, 1203, 1159, 1121, 1105, 1071, 1031, 1022, 998, 977, 922, 832, 755, 725, 696, 638 cm^{-1} ; HRMS (MALDI) calcd for $\text{C}_{31}\text{H}_{30}\text{NOPNa}$ ($\text{M}+\text{Na}$) 486.1957, found 486.1963.

***N*-Propyl-*N*-(1,3-diphenyl-prop-2-ynyl)-diphenylphosphinic amide (Scheme 1)**

In a 10-mL flask was placed 218 mg $\text{Zn}(\text{OTf})_2$ (0.600 mmol) under argon and dried under high vacuum, then 1 mL CH_3CN , 72 μL phenylacetylene (0.66 mmol) and 92 μL NEt_3 (0.66 mmol) were added and the suspension stirred at rt for 1 h to give a clear solution. To this solution, 77 mg butylidene-propyl-amine (0.50 mmol) and 142 mg Ph_2POCl (0.600 mmol) were added. The solution turned slightly yellow and was stirred at rt for 8 h when it was quenched by addition of a saturated NH_4Cl solution. After extraction with CH_2Cl_2 (3 times) the combined organic layers were washed with brine and dried over Na_2SO_4 . Solvent evaporation gave an oil, which was purified by flash chromatography (hexanes/ethyl acetate 1:1) to give the title compound (101 mg, 49%) as a colorless oil.

^1H NMR (CDCl_3 , 300 MHz) δ 7.92-7.85 (m, 4H, PPh H), 7.47-7.39 (m, 8H, Ar H), 7.34-7.30 (m, 3H, Ar H), 4.32 (ddd, $J = 6.3, 9.3, 15.6$ Hz, 1H, C(N)H), 3.27-3.13 (m, 1H, 1 NCH_2), 3.07-2.94 (m, 1H, 1 NCH_2), 1.94-1.27 (m, 6H, 3 CH_2), 0.82 (t, $J = 7.4$ Hz, 3H, Me), 0.67 (t, $J = 7.4$ Hz, 3H, Me); ^{13}C NMR (CDCl_3 , 75 MHz) δ 132.9, 132.8, 132.4, 132.4, 132.3, 132.3, 131.7, 131.7, 131.6, 131.6, 131.4, 131.2, 131.2, 128.4, 128.3, 128.3, 128.2, 128.2, 128.1, 122.9, 89.3, 89.2, 84.4, 49.4, 49.4, 46.2, 46.1, 38.3, 38.3, 24.9, 19.7, 13.4, 11.5; ^{31}P NMR (CDCl_3 , 121 MHz) δ 32.5; IR (thin film) ν 3057, 2961, 2933, 2873, 1966, 1899, 1824, 1598, 1490, 1466, 1483, 1379, 1312, 1262, 1206, 1173, 1121, 1105, 1071, 1028, 1013, 996, 936, 858, 756, 725, 695, 571, 549, 528; HRMS (MALDI) calcd for $\text{C}_{27}\text{H}_{30}\text{NOPNa}$ ($\text{M}+\text{Na}$) 438.1963, found 438.1959.