Copper-Mediated N-Alkynylation of Carbamates, Ureas, and Sulfonamides. A General Method for the Synthesis of Ynamides

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Supporting Information

General Procedures. All reactions were performed in flame-dried or oven-dried glassware under a positive pressure of argon. Reaction mixtures were stirred magnetically unless otherwise indicated. Air- and moisture-sensitive liquids and solutions were transferred by syringe or cannula and were introduced into reaction vessels through rubber septa. Reaction product solutions and chromatography fractions were concentrated by rotary evaporation at ca. 20 mmHg and then at ca. 0.1 mmHg (vacuum pump) unless otherwise indicated. Thin layer chromatography was performed on Merck precoated glass-backed silica gel 60 F-254 0.25 mm plates. Column chromatography was performed on EM Science silica gel 60 or Silicycle silica gel 60 (230-400 mesh).

Materials. Commercial grade reagents and solvents were used without further purification except as indicated below. Pyridine was distilled under argon from potassium hydroxide and degassed with argon bubbling prior to use. Copper(I) iodide was extracted with THF for 24 h in a Soxhlet extractor and then dried under vacuum (0.1 mmHg). Carbamates **8a**, **8b**, and **8c** were prepared by reaction of the corresponding amines with 1.1 equiv of pyridine and 1.1 equiv of methyl chloroformate in CH_2Cl_2 (rt, 1 h). Carbamate **8d** was prepared by reaction of benzylamine with 1.1 equiv of triethylamine and 1.1 equiv of di-*tert*-butyl dicarbonate in CH_2Cl_2 (rt, 14 h). Sulfonamide **13** was prepared by treatment of benzylamine with 1.1 equiv of triethylamine and 1.1 equiv of *p*-toluenesulfonyl chloride in CH_2Cl_2 (rt, 8

h). Alkynyl bromides **10a**[1] and **10f**[2] and were prepared as previously reported by reaction with $AgNO_3$ and NBS using the general method of Hofmeister and co-workers.[3] Alkynyl bromides **10c**,[4] **10e**,[5] and **10g**[6] were prepared from the corresponding terminal alkynes using the method of Hofmeister and co-workers ($AgNO_3$, NBS).[3] Alkynyl bromides **10b**[7] and **10d**[8] were prepared by bromination of the corresponding alkynylsilanes as previously reported using the general method of Miller and Zweifel (MeLi-LiBr, Br_2).[7] Halo alkynes were stored at –20 °C as 0.6 M stock solutions in benzene.[9] *Caution: Alkynyl bromides are strong lachrymators!*

Instrumentation. Melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were obtained using a Perkin Elmer 2000 FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were measured with an Inova 500 spectrometer. ^{1}H NMR chemical shifts are expressed in parts per million (δ) downfield from tetramethylsilane (with the $CHCl_3$ peak at 7.27 ppm used as a standard. ^{13}C NMR chemical shifts are expressed in parts per million (δ) downfield from tetramethylsilane (with the central peak of $CHCl_3$ at 77.23 ppm used as a standard). High resolution mass spectra (HRMS) were measured on a Bruker Daltonics APEXII 3 telsa fourier transform mass spectrometer. Elemental analyses were performed by E&R Microanalytical Laboratory, Inc. of Parsippany, NJ.

General Procedure for the Coupling of Amides with Bromo Alkynes. *N*-Methoxycarbonyl-*N*-(2-phenylethyl)-2-phenylethynylamine (9a). A 250-mL, two-necked, round-bottomed flask equipped with a rubber septum and addition funnel fitted with a rubber septum and argon inlet needle was charged with carbamate **8a** (1.951 g, 10.89 mmol) and 44 mL of pyridine. The solution was cooled at 0 °C while

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3 Hofmeister, H.; Annen, K.; Laurent, H.; Wiechert, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 727.

4 Early preparation of this compound involved the elimination of 3,4-dibromostyrene as reported by A. A. Petrov in *Chem. Abstr.* **1944**, 1466.

5 For a previous synthesis of this compound from 1-octyne with AgOAc and NBS, see Chen, C.; Crich, D. *J. Chem. Soc., Chem. Commun.* **1991**, *18*, 1289.

6 For a previous synthesis of this compound, see Stefani, H. A.; Menezes, P. H.; Costa, I. M.; Silva, D. O.; Petragnani, N. *Synlett* **2002**, *8*, 1335.

7 Miller, J. A.; Zweifel, G. *Synthesis* **1983**, 128.

8 Basak, S.; Srivastava, S.; le Noble, W. J. *J. Org. Chem.* **1987**, *52*, 5095.

9 Alkynyl bromide **10d** stored as 0.4 M stock solution in benzene.

12.0 mL of KHMDS solution (0.91 M in THF, 11 mmol) was added via syringe over 4 min. The reaction mixture was stirred at 0 °C for 10 min and then a solution of CuI (2.073 g, 10.89 mmol) in 22 mL of pyridine was added via cannula in one portion (10-mL pyridine rinse). The ice bath was removed, and the resulting solution was stirred at room temperature for 2 h. A solution of bromo alkyne **10a** (36 mL, 0.60 M in benzene, 22 mmol) was then added via the addition funnel over 1 h, and the resulting mixture was stirred at room temperature for 20 h. The reaction mixture was diluted with 300 mL of Et_2O and washed with three 100-mL portions of a 2:1 mixture of saturated NaCl and concentrated NH_4OH. The combined aqueous layers were extracted with three 75-mL portions of Et_2O, and the combined organic layers were washed with 300 mL of saturated NaCl, dried over $MgSO_4$, filtered, and concentrated to provide 4.397 g of a dark red oil. Column chromatography on 120 g of silica gel (gradient elution with 0-3% EtOAc-hexanes) provided 2.309 g (76%) of ynamide **9a** as a yellow oil: IR (neat): 3028, 2953, 2245, 1729, 1600, 1496, 1442, 1395, 1363, 1307, 1245, and 1147 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, J = 6.7 Hz, 2H), 7.28-7.39 (m, 8H), 3.88 (t, J = 7.5 Hz, 2H), 3.84 (s, 3H), and 3.11 (t, J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.6, 138.0, 131.4, 129.0, 128.6, 128.3, 127.7, 126.7, 123.2, 82.7, 71.0, 54.1, 51.4, and 34.2; HRMS-ESI *m/z*: $[M+Na]^+$ calcd for $C_{18}H_{17}NO_2$, 302.1151; found, 302.1141. Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.26; H, 6.23; N, 5.32.

***N*-Methoxycarbonyl-*N*-(2-phenylethyl)-2-(trimethylsilyl)ethynylamine (9b).** Reaction of a solution of carbamate **8a** (0.157 g, 0.876 mmol) in 3.5 mL of pyridine with KHMDS (0.97 mL, 0.91 M in THF, 0.88 mmol), CuI (0.167 g, 0.877 mmol) in 2.3 mL of pyridine, and bromo alkyne **10b** (2.9 mL, 0.60 M in benzene, 1.7 mmol) according to the general procedure gave 0.282 g of a dark red oil. Column chromatography on 25 g of silica gel (gradient elution with 0-5% EtOAc-hexanes) provided 0.135 g (56%) of ynamide **9b** as a pale yellow oil: IR (neat): 3029, 2956, 2898, 2176, 1736, 1604, 1498, 1443, 1375, 1282, 1249, 1202, and 1124 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32 (m, 2H), 7.25 (m, 3H), 3.78 (s, 3H), 3.72 (t, J = 7.6 Hz, 2H), 2.99 (t, J = 7.6 Hz, 2H), and 0.22 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.5, 138.0, 128.9, 128.6, 126.6, 95.4, 72.9, 54.0, 51.2, 33.9, and 0.3; HRMS-EI *m/z*: $[M]^+$ calcd for $C_{15}H_{21}NO_2Si$, 275.1337; found, 275.1341.

***N*-Methoxycarbonyl-*N*-(2-phenylethyl)-3-methyl-3-buten-1-ynylamine (9c).** Reaction of a solution of carbamate **8a** (0.244 g, 1.36 mmol) in 5.4 mL of pyridine with KHMDS (1.5 mL, 0.91 M in THF, 1.4 mmol), CuI (0.260 g, 1.37 mmol) in 3.7 mL of pyridine, and bromo alkyne **10c** (4.7 mL, 0.58 M

in benzene, 2.7 mmol) according to the general procedure gave 0.486 g of a dark red oil. Column chromatography on 35 g of silica gel (gradient elution with 0-3% EtOAc-hexanes) afforded 0.216 g (65%) of ynamide **9c** as a pale yellow oil: IR (neat): 3028, 2954, 2234, 1730, 1614, 1497, 1444, 1402, 1367, 1309, 1280, 1251, and 1177 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32 (m, 2H), 7.25 (m, 3H), 5.23 (s, 1H), 5.17 (s, 1H), 3.77 (s, 3H), 3.76 (t, J = 7.5 Hz, 2H), 3.00 (t, J = 7.5 Hz, 2H), and 1.94 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.4, 137.9, 128.9, 128.5, 126.6, 126.3, 119.5, 82.0, 72.3, 53.9, 51.2, 34.1, and 23.7; HRMS-ESI *m/z*: $[M+Na]^+$ calcd for $C_{15}H_{17}NO_2$, 266.1151; found, 266.1155.

***N*-Methoxycarbonyl-*N*-(2-phenylethyl)-4-(trimethylsilyl)-1,3-butadiynylamine (9d).** Reaction of a solution of carbamate **8a** (0.195 g, 1.08 mmol) in 4.3 mL of pyridine with KHMDS (1.2 mL, 0.91 M in THF, 1.1 mmol), CuI (0.209 g, 1.10 mmol) in 3.2 mL of pyridine, and bromo alkyne **10d** (5.4 mL, 0.40 M in benzene, 2.2 mmol) according to the general procedure gave 0.451 g of a dark red oil. Column chromatography on 40 g of silica gel (gradient elution with 0-2% EtOAc-hexanes) provided 0.128 g (40%) of ynamide **9d** as a yellow oil: IR (neat): 3029, 2957, 2232, 2113, 1741, 1604, 1497, 1440, 1396, 1359, 1293, 1250, 1205, and 1131 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31 (m, 2H), 7.23 (m, 3H), 3.77 (s, 3H), 3.71 (t, J = 7.8 Hz, 2H), 2.97 (t, J = 7.8 Hz, 2H), and 0.23 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.6, 137.5, 129.0, 128.7, 126.9, 90.0, 87.6, 69.5, 58.7, 54.5, 51.2, 34.2, and –0.2; HRMS-ESI *m/z*: $[M+H]^+$ calcd for $C_{17}H_{21}NO_2Si$, 300.1414; found, 300.1424.

***N*-Benzyl-*N*-methoxycarbonyl-1-octynylamine (9e).** Reaction of a solution of carbamate **8b** (0.150 g, 0.908 mmol) in 3.6 mL of pyridine with KHMDS (1.0 mL, 0.91 M in THF, 0.91 mmol), CuI (0.174 g, 0.914 mmol) in 2.8 mL of pyridine, and bromo alkyne **10e** (3.0 mL, 0.60 M in benzene, 1.8 mmol) according to the general procedure gave 0.402 g of a dark brown oil. Column chromatography on 25 g of silica gel (gradient elution with 0-5% EtOAc-hexanes) provided 0.123 g (50%) of ynamide **9e** as a red oil: IR (neat): 3033, 2931, 2858, 2263, 1728, 1606, 1497, 1444, 1389, 1360, 1286, 1219, and 1128 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.30-7.37 (m, 5H), 4.60 (s, 2H), 3.80 (s, 3H), 2.25 (t, J = 7.0 Hz, 2H), 1.45 (app quintet, J = 7.0 Hz, 2H), 1.22-1.35 (m, 6H), and 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.3, 136.4, 128.5, 128.5, 128.0, 73.9, 70.7, 54.0, 54.0, 31.5, 29.0, 28.5, 22.7, 18.5, and 14.2; HRMS-ESI *m/z*: $[M+Na]^+$ calcd for $C_{17}H_{23}NO_2$, 296.1621; found, 296.1608.

***N*-Benzyl-*N*-methoxycarbonyl-(2-triisopropylsilyl)ethynylamine (9f).** Reaction of a solution of carbamate **8b** (0.205 g, 1.24 mmol) in 5.0 mL of pyridine with KHMDS (1.4 mL, 0.91 M in THF, 1.3

mmol), CuI (0.244 g, 1.28 mmol) in 3.5 mL of pyridine, and bromo alkyne **10f** (4.1 mL, 0.60 M in benzene, 2.5 mmol) according to the general procedure gave 0.909 g of a dark red oil. Column chromatography on 35 g of silica gel (gradient elution with 0-5% EtOAc-hexanes) provided 0.317 g (74%) of ynamide **9f** as a yellow oil: IR (neat): 3033, 2943, 2865, 2176, 1733, 1606, 1497, 1442, 1370, 1271, 1225, and 1123 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.41 (m, 2H), 7.30-7.36 (m, 3H), 4.64 (s, 2H), 3.80 (s, 3H), and 1.06-1.08 (app s, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.8, 135.9, 128.6, 128.5, 128.0, 97.0, 69.2, 53.9, 53.7, 18.6, and 11.4; HRMS-EI *m/z*: $[M]^+$ calcd for $C_{20}H_{31}NO_2Si$, 345.2119; found, 345.2107.

***N*-Cyclohexyl-*N*-methoxycarbonyl-2-phenylethynylamine (9g).** Reaction of a solution of carbamate **8c** (0.170 g, 1.08 mmol) in 4.4 mL of pyridine with KHMDS (1.2 mL, 0.91 M in THF, 1.1 mmol), CuI (0.209 g, 1.10 mmol) in 3.2 mL of pyridine, and bromo alkyne **10a** (3.6 mL, 0.60 M in benzene, 2.2 mmol) according to the general procedure gave 0.501 g of a dark red oil. Column chromatography on 35 g of silica gel (gradient elution with 0-3% EtOAc-hexanes) provided 0.118 g (42%) of ynamide **9g** as a yellow oil: IR (neat): 2933, 2857, 2247, 1728, 1599, 1440, 1402, 1357, 1295, and 1245 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.43 (m, 2H), 7.25-7.32 (m, 3H), 3.99 (m, 1H), 3.84 (s, 3H), 1.83-1.91 (m, 4H), 1.60-1.68 (m, 3H), 1.39 (app ddt, J = 3.3, 3.3, 13.1 Hz, 2H), and 1.14 (app ddt, J = 3.7, 3.7, 13.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.6, 131.2, 128.4, 127.5, 123.6, 80.7, 72.4, 56.6, 54.0, 30.7, 25.5, and 25.3; HRMS-EI *m/z*: $[M]^+$ calcd for $C_{16}H_{19}NO_2$, 257.1411; found, 257.1414.

***N*-Benzyl-*N*-*tert*-butoxycarbonyl-2-phenylethynylamine (9h).** Reaction of a solution of carbamate **8d** (0.189 g, 0.912 mmol) in 3.6 mL of pyridine with KHMDS (1.0 mL, 0.91 M in THF, 0.91 mmol), CuI (0.174 g, 0.914 mmol) in 2.8 mL of pyridine, and bromo alkyne **10a** (3.0 mL, 0.60 M in benzene, 1.8 mmol) according to the general procedure gave 0.457 g of a dark red oil. Column chromatography on 50 g of silica gel (elution with benzene) provided 0.171 g (61%) of ynamide **9h** as an orange oil: IR (neat): 3033, 2979, 2242, 1721, 1600, 1496, 1454, 1393, 1369, 1301, 1242, and 1155 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.49 (m, 2H), 7.43 (m, 2H), 7.38 (m, 3H), 7.32 (m, 2H), 7.28 (m, 1H), 4.74 (s, 2H), and 1.60 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.9, 136.5, 130.6, 128.6, 128.4, 128.3, 128.0, 127.2, 123.7, 84.2, 82.7, 71.2, 53.1, and 28.1; HRMS-ESI *m/z*: $[M+Na]^+$ calcd for $C_{20}H_{21}NO_2$, 330.1465; found, 330.1452.

***N*-Benzyl-*N*-*tert*-butoxycarbonyl-5-(*tert*-butyldimethylsiloxy)-1-pentynylamine (9i).** Reaction of a solution of carbamate **8d** (0.207 g, 0.999 mmol) in 4.0 mL of pyridine with KHMDS (1.1 mL, 0.91 M in THF, 1.0 mmol), CuI (0.191 g, 1.00 mmol) in 3.0 mL of pyridine, and bromo alkyne **10g** (3.3 mL, 0.60 M in benzene, 2.0 mmol) according to the general procedure gave 0.706 g of a dark red oil. Column chromatography on 40 g of silica gel (gradient elution with 0.5-2% EtOAc-hexanes) provided 0.213 g (53%) of ynamide **9i** as a yellow oil: IR (neat): 3033, 2954, 2929, 2857, 2264, 1720, 1606, 1497, 1471, 1455, 1391, 1368, 1295, 1256, 1162, 1105, and 836 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 (app d, J = 4.6 Hz, 2H), 7.29 (m, 3H), 4.54 (s, 2H), 3.64 (t, J = 6.1 Hz, 2H), 2.33 (m, 2H), 1.66 (m, 2H), 1.48 (br s, 9H), 0.90 (s, 9H), and 0.04 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.7, 137.0, 128.5, 128.2, 127.7, 82.1, 74.7, 69.4, 61.6, 53.0, 32.2, 28.2, 26.0, 18.4, 15.0, and -5.2; HRMS-ESI *m/z*: $[M+Na]^+$ calcd for $C_{23}H_{37}NO_3Si$, 426.2435; found, 426.2425.

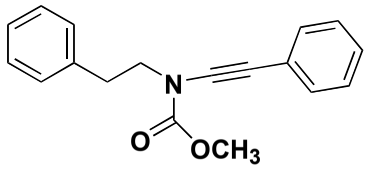
(*R*)-(+)-4-Benzyl-3-(2-phenylethynyl)-2-oxazolidinone (14). Reaction of a solution of oxazolidinone **11** (0.225 g, 1.27 mmol) in 5.1 mL of pyridine with KHMDS (1.4 mL, 0.91 M in THF, 1.3 mmol), CuI (0.243 g, 1.28 mmol) in 3.6 mL of pyridine, and bromo alkyne **10a** (4.2 mL, 0.60 M in benzene, 2.5 mmol) according to the general procedure gave 0.555 g of a dark red oil. Column chromatography on 40 g of silica gel (gradient elution with 0-10% EtOAc-hexanes) provided 0.262 g (74%) of ynamide **14** as a light tan solid: mp 87-88 °C; IR (CH_2Cl_2): 3060, 3029, 2917, 2256, 1777, 1602, 1497, 1476, 1454, 1442, 1411, 1285, 1210, 1158, and 1088 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.49 (m, 2H), 7.24-7.36 (m, 8H), 4.31 (m, 2H), 4.12 (m, 1H), 3.21 (m, 1H), and 3.00 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.4, 134.2, 131.4, 129.3, 128.8, 128.2, 128.1, 127.3, 122.1, 78.2, 73.0, 67.3, 58.1, and 37.6; HRMS-EI *m/z*: $[M]^+$ calcd for $C_{18}H_{15}NO_2$, 277.1097; found, 277.1107.

(4*R*,5*S*)-(-)-1,5-Dimethyl-4-phenyl-3-(2-phenylethynyl)-2-imidazolidinone (15). Reaction of a solution of imidazolidinone **12** (0.242 g, 1.27 mmol) in 5.0 mL of pyridine with KHMDS (1.4 mL, 0.91 M in THF, 1.3 mmol), CuI (0.243 g, 1.28 mmol) in 3.5 mL of pyridine, and bromo alkyne **10a** (4.2 mL, 0.60 M in benzene, 2.5 mmol) according to the general procedure gave 0.563 g of a dark red solid. Column chromatography on 40 g of silica gel (gradient elution with 0-30% EtOAc-hexanes) provided 0.222 g (60%) of ynamide **15** as a light purple solid: mp 187-188 °C; IR (CH_2Cl_2): 3054, 2986, 2240, 1726, 1599, 1441, 1403, 1265, 1167, 896, and 739 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31-7.39 (m, 3H), 7.24 (m, 4H), 7.17 (m, 3H), 5.02 (d, J = 8.9 Hz, 1H), 3.91 (dq, J = 6.6, 8.9 Hz, 1H), 2.83 (s, 3H), and

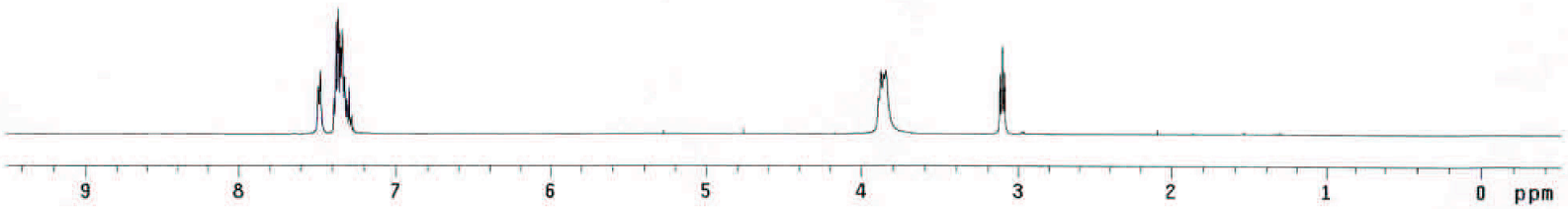
0.76 (d, J = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 157.6, 134.7, 131.2, 128.5, 128.5, 128.0, 127.7, 127.2, 123.4, 81.7, 71.4, 64.1, 55.6, 28.9, and 14.8; HRMS-ESI *m/z*: $[M+H]^+$ calcd for $C_{19}H_{18}N_2O$, 291.1492; found, 291.1490.

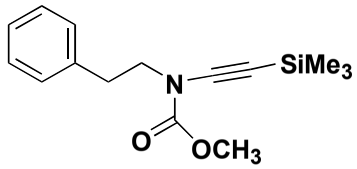
***N*-Benzyl-*N*-(*p*-toluenesulfonyl)-2-phenylethynylamine (16).** Reaction of a solution of sulfonamide **13** (0.268 g, 1.03 mmol) in 4.1 mL of pyridine with KHMDS (1.1 mL, 0.91 M in THF, 1.0 mmol), CuI (0.197 g, 1.03 mmol) in 3.1 mL of pyridine, and bromo alkyne **10a** (3.4 mL, 0.60 M in benzene, 2.0 mmol) according to the general procedure gave 0.561 g of a dark red oil. Column chromatography on 35 g of silica gel (gradient elution with 0-10% EtOAc-hexanes) provided 0.291 g (78%) of ynamide **16** as a pale yellow solid: mp 82-83 °C; IR (CH_2Cl_2): 3035, 2928, 2235, 1598, 1495, 1456, 1443, 1366, 1171, and 1090 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 7.89 (d, J = 8.2 Hz, 2H), 7.41 (m, 2H), 7.36 (m, 5H), 7.28-7.33 (m, 5H), 4.65 (s, 2H), and 2.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 144.8, 134.5, 134.4, 131.1, 129.8, 128.9, 128.5, 128.4, 128.2, 127.7, 127.7, 122.7, 82.7, 71.4, 55.7, and 21.6; HRMS-EI *m/z*: $[M]^+$ calcd for $C_{22}H_{19}NO_2S$, 361.1131; found, 361.1135.

***N*-Benzyl-*N*-(*p*-toluenesulfonyl)-1-octynylamine (17).** Reaction of a solution of sulfonamide **13** (0.260 g, 0.995 mmol) in 4.0 mL of pyridine with KHMDS (1.1 mL, 0.91 M in THF, 1.0 mmol), CuI (0.191 g, 1.00 mmol) in 3.0 mL of pyridine, and bromo alkyne **10e** (3.3 mL, 0.60 M in benzene, 2.0 mmol) according to the general procedure gave 0.453 g of a dark red oil. Column chromatography on 35 g of silica gel (gradient elution with 0-5% EtOAc-hexanes) provided 0.155 g (42%) of ynamide **17** as a yellow oil: IR (neat): 3033, 2930, 2858, 2254, 1597, 1497, 1455, 1365, 1169, 1091 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 7.77 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 7.29 (m, 5H), 4.46 (s, 2H), 2.44 (s, 3H), 2.18 (t, J = 7.0 Hz, 2H), 1.38 (app quartet, J = 7.0 Hz, 2H), 1.19-1.29 (m, 6H), and 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 144.4, 134.9, 134.7, 129.7, 128.8, 128.5, 128.2, 127.7, 73.4, 70.9, 55.6, 31.4, 28.8, 28.4, 22.6, 21.7, 18.4, and 14.2; HRMS-ESI *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{27}NO_2S$, 392.1655; found, 392.1645.



9a





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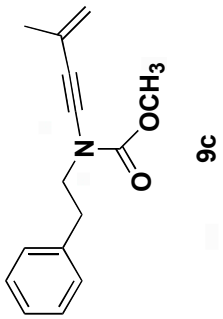

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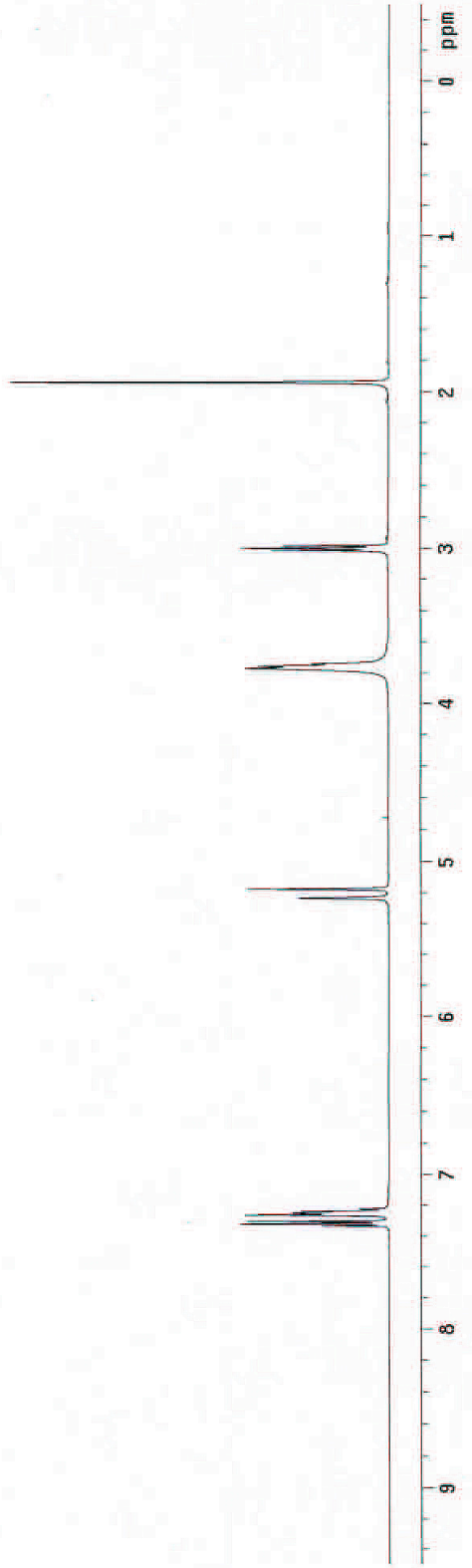

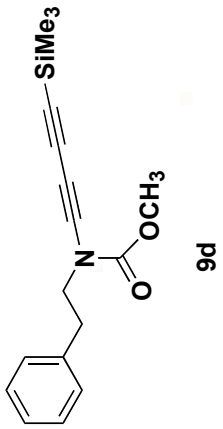

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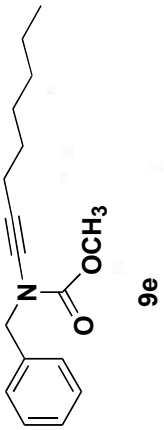

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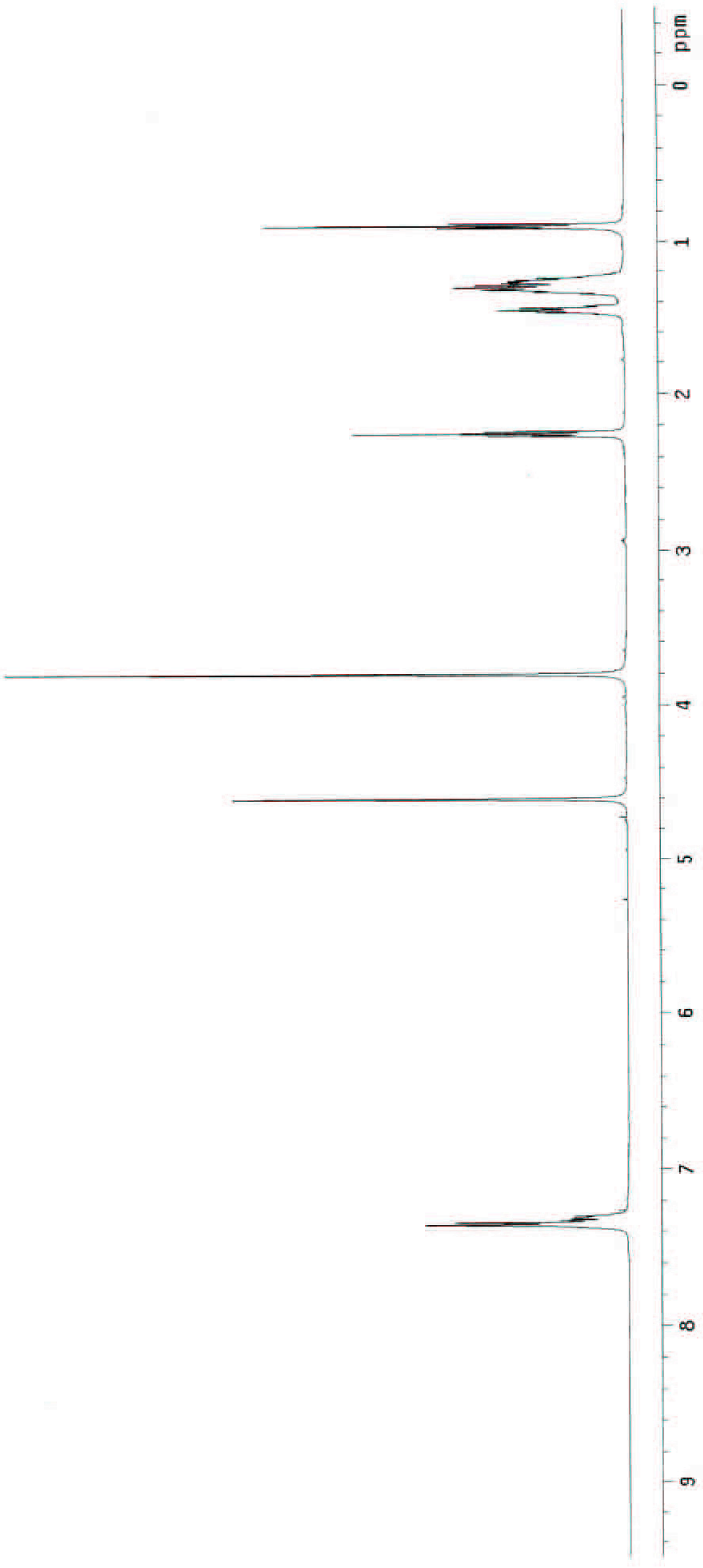

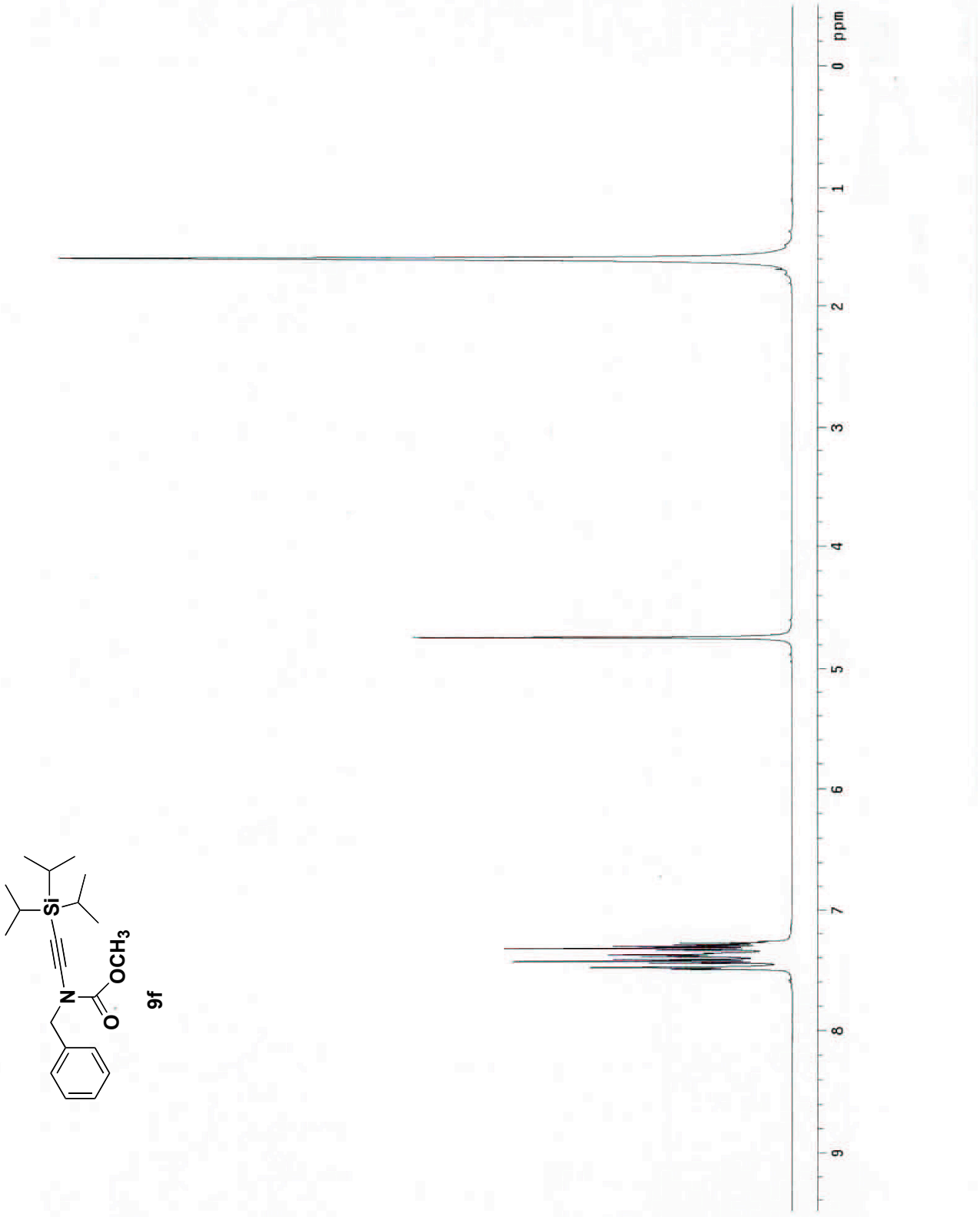
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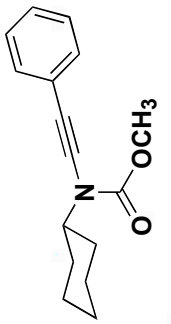

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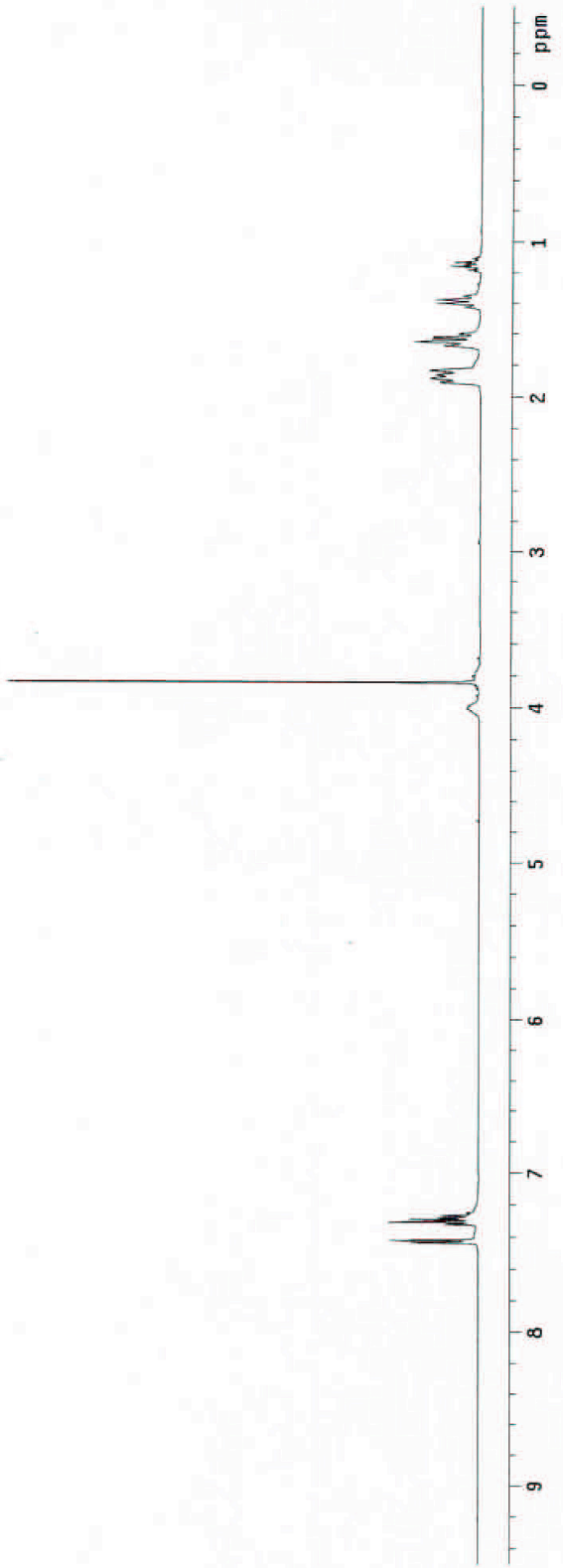

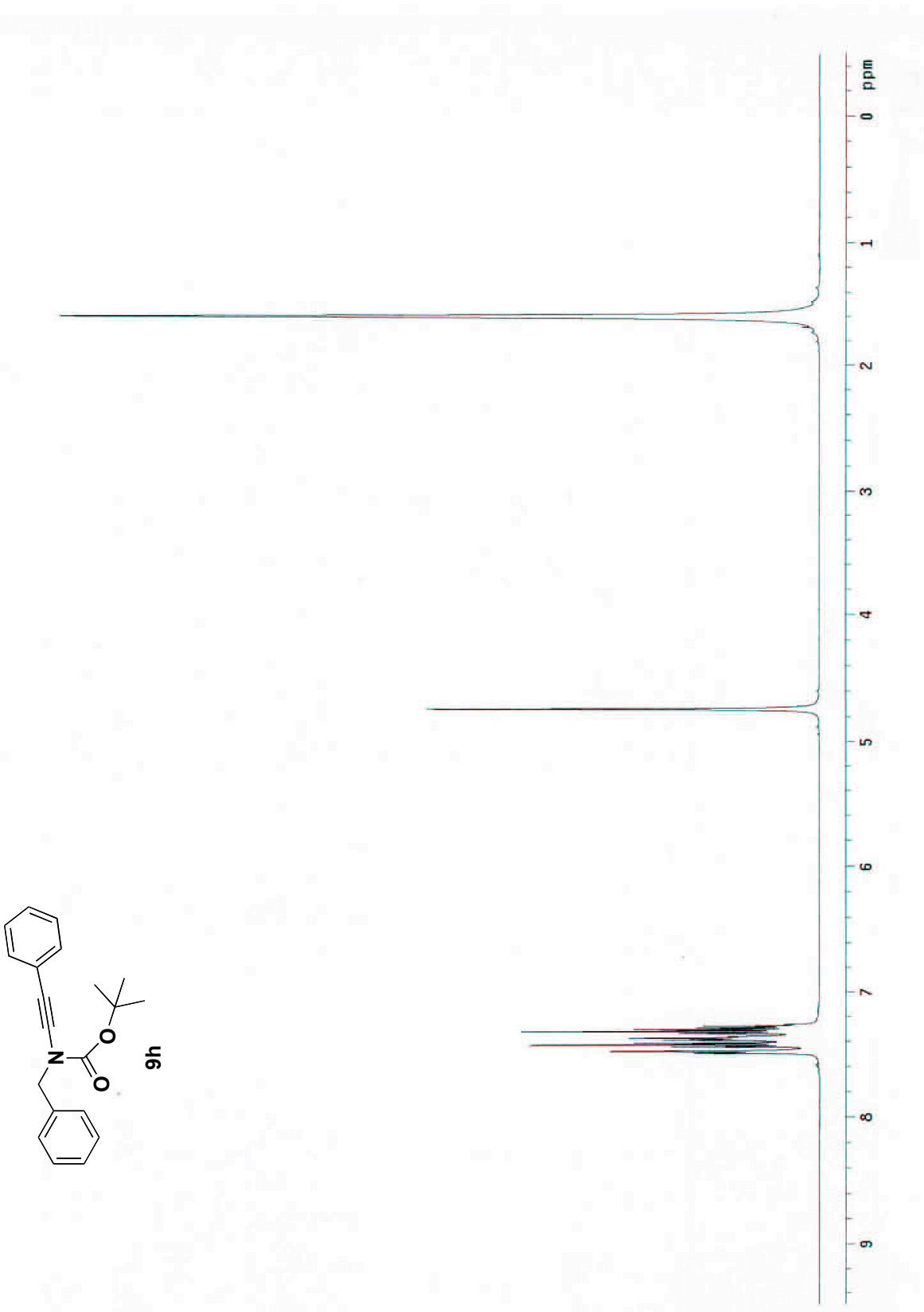
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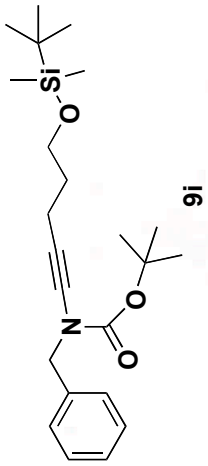

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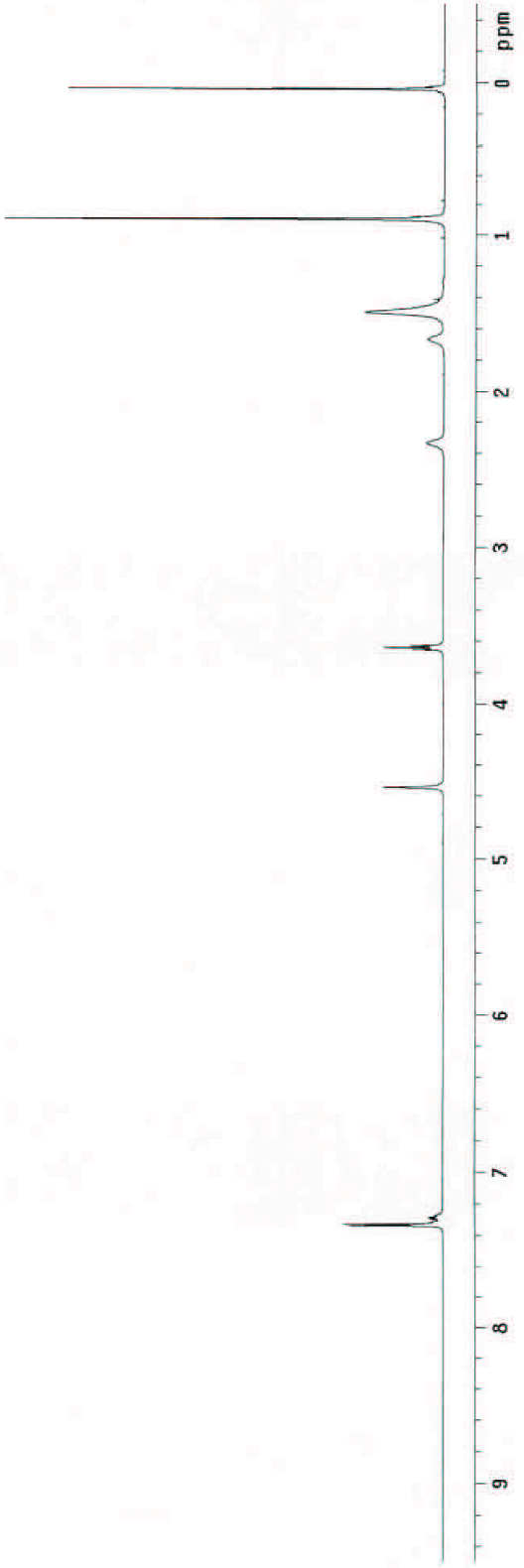

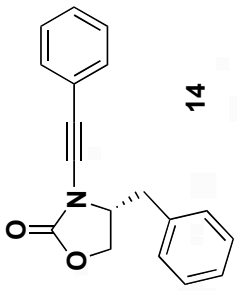

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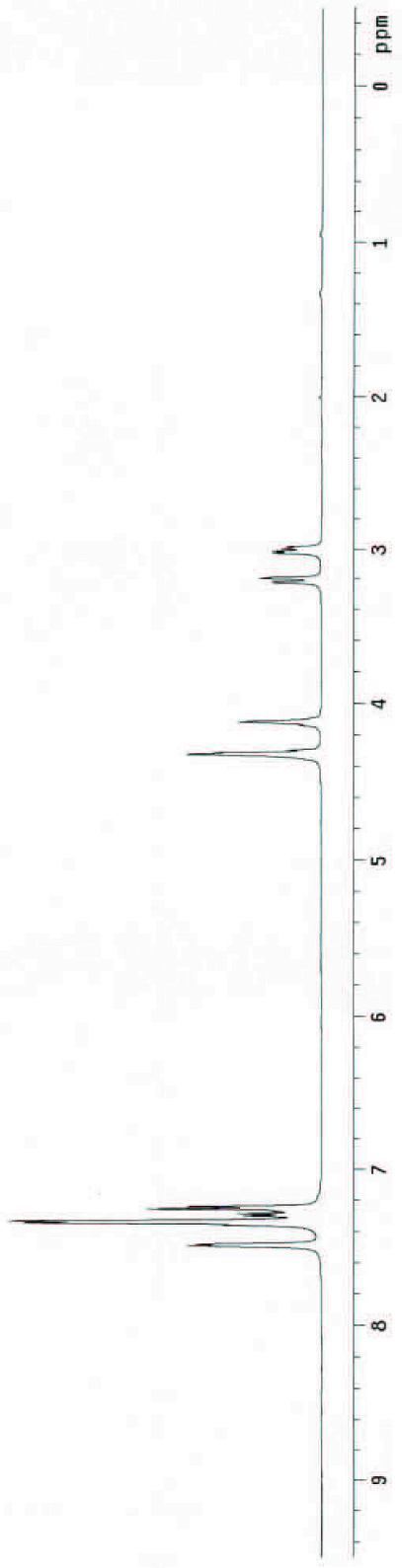

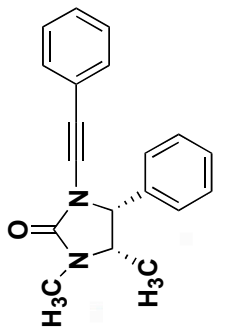

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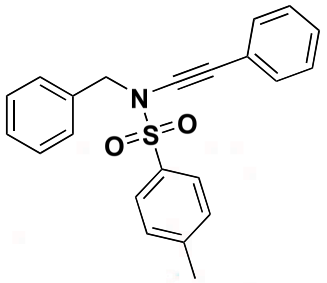

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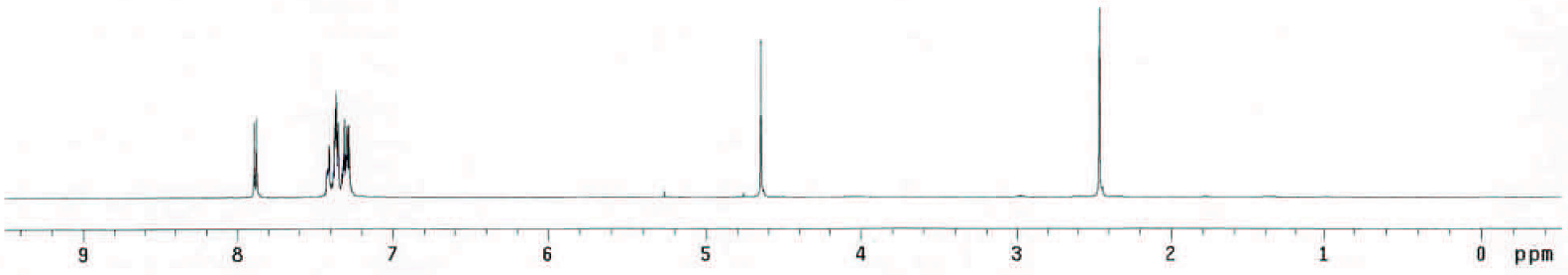

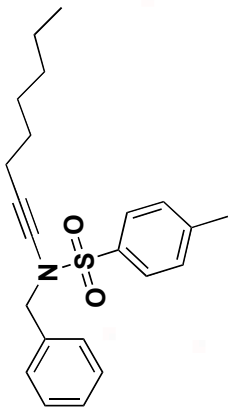

17