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Supporting Information

A New Pd^0-Cu^I Bimetallic Catalyst for the Synthesis of Indoles from Isocyanates and Allyl Carbonates

Shin Kamijo and Yoshinori Yamamoto*

Department of Chemistry, Graduate School of Science
Tohoku University
Sendai 980-8578, Japan

Experimental

General Information. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM LA-300 (300 MHz). The ^{1}H NMR chemical shifts are reported in ppm (δ) downfield from tetramethylsilane as an internal standard; the following abbreviation for multiplicities is used (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, and br=broadened). ^{13}C NMR spectra are reported in ppm (δ) relative to the central line of triplet for $CDCl_3$ at 77 ppm. IR spectra were recorded on a SHIMADZU FTIR-8200A spectrometer, and absorptions are reported in cm^{-1}. High resolution mass spectra were obtained on a HITACHI M-2500S and JEOL HX110 spectrometer. Column chromatography was carried out employing Silica gel 60 N (spherical, neutral, 40~100 μm and 100~210 μm, KANTO Chemical Co. Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F_{254} (Merck).

Materials. Anhydrous THF (KANTO), CuCl (Nacalai), 2-iodoaniline (TCI), and methyl 2-iodobenzoate (KANTO) were purchased and used as received. $Pd(PPh_3)_4$ was prepared according to the literature procedure.[1] Isocyanates were synthesized from the corresponding anilines or methyl benzoates. Allyl carbonates were synthesized from allyl chloroformate and the corresponding alcohols. All other compounds used were commercially available.

Representative procedure for the preparation of isocyanate 1

Synthesis of 2-(1-pentynyl)aniline

To a mixture of 2-iodoaniline (11.0 g, 50 mmol), $Pd(PPh_3)_4$ (0.58 g, 0.5 mmol), and CuI

(0.2 g, 1.0 mmol) in DMF (10 ml) were added 1-pentyne (6 ml, 60 mmol) and Et_2NH (40 ml) at room temperature under an argon atmosphere. The mixture was stirred at room temperature. After the reaction was completed, NH_3/NH_4Cl aqueous solution was added and the product was extracted with ether. Then the organic phase was dried with $MgSO_4$ and concentrated. The residue was purified by column chromatography (silica gel, hexane/AcOEt = 50/1~4/1) to give_2-(1-pentynyl)aniline in almost quantitative yield.

Synthesis of 2-(1-pentynyl)phenyl-1-isocyanate (1a)[2]

To a benzene solution (20 ml) of triphosgene (1.09 g, 3.67 mmol) was added dropwise a solution of benzene (30 ml), Et_3N (20 ml), and 2-(1-pentynyl)aniline (1.6 g, 10 mmol). After the mixture was stirred at 70 ˚C for 2 h, the mixture was filtered though celite pad using hexane as an eluent and evaporated. Then the residue was filtered though Florisil short column using hexane as an eluent to give 2-(1-pentynyl)phenyl-1-isocyanate **1a** in 69% yield (1.28 g). The product was used without further purification.

Synthesis of 2-(1-pentynyl)benzoic acid

To a mixture of methyl 2-iodobenzoate (13.2 g, 50 mmol), $PdCl_2(PPh_3)_2$ (0.70 g, 1.0 mmol), and CuI (0.96 g, 5.0 mmol) in DMF (150 ml) were added 1-pentyne (5.9 ml, 60 mmol) and $^{i}Pr_2NEt$ (27 ml, 150 mmol) at room temperature under an argon atmosphere. The mixture was stirred at room temperature. After the reaction was completed, NH_3/NH_4Cl aqueous solution was added and the product was extracted with ether. Then the organic phase was dried with $MgSO_4$ and concentrated. The residue was purified by column chromatography (silica gel, hexane/AcOEt = 100/1~8/1) to give_methyl 2-(1-pentynyl)benzoate in 95% yield (9.59 g).

A THF solution (20 ml) of methyl 2-(1-pentynyl)benzoate (4.23g, 21 mmol) was added 5N NaOH aqueous solution (20 ml) and the mixture was stirred at 60 ˚C for overnight. After the reaction was completed, the mixture was acidified by the addition of HCl aqueous solution and extracted with ether. Then the organic phase was dried with $MgSO_4$ and concentrated to give 2-(1-pentynyl)benzoic acid in almost quantitative yield (4.07 g). The product was used without further purification.

Synthesis of 2-(1-pentynyl)phenyl-1-isocyanate (1a)[3]

To a benzene solution (20 ml) of 2-(1-pentynyl)benzoic acid (4.07 g, 21 mmol) were added Et_3N (3.3 ml, 23 mmol) and diphenylphosphoryl azide (5.0 ml, 23 mmol). After

the mixture was stirred at room temperature for 3 h, the mixture was heated at 80 ˚C for 1.5 h. After the reaction was complete, volatile materials were removed by evaporation. The residue was filtered though Florisil short column using hexane as an eluent to give 2-(1-pentynyl)phenyl-1-isocyanate **1a** in 68% yield (2.64 g). The product was used without further purification.

Typical procedure for the palladium-catalyzed synthesis of indoles

To a THF solution (0.5 ml) of 2-(1-pentynyl)phenyl-1-isocyanate **1a** (92.7 mg, 0.5 mmol), $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol), and CuCl (2.0 mg, 0.02 mmol) was added allyl methyl carbonate **2a** (69 μl, 0.6 mmol) under an argon atmosphere. The solution was stirred at 100 ˚C for 1 h. The reaction mixture was cooled to room temperature and filtered through a short Florisil pad and concentrated. The residue was purified by column chromatography (silica gel, hexane-AcOEt 100/1~20/1) to afford 3-allyl-N-(methoxycarbonyl)-2-propylindole **(3aa)** in 81% yield (104.2 mg).

Analytical Data

2-(1-pentynyl)phenyl-1-isocyanate (1a)

yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.03 (3H, t, *J* = 7.5 Hz), 1.66 (2H, sextet, *J* = 7.5 Hz), 2.44 (2H, t, *J* = 7.5 Hz), 6.99 (1H, dd, *J* = 7.5, 1.5 Hz), 7.08 (1H, td, *J* = 7.5, 1.5 Hz), 7.18 (1H, td, *J* = 7.5, 1.5 Hz), 7.36 (1H, dd, *J* = 7.5, 1.5 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 13.57, 21.57, 21.67, 76.39, 99.49, 121.56, 123.32, 125.23, 128.49, 132.05, 135.14; IR (neat) 2246 (NCO), 1598, 1506, 756 cm^{-1}; Anal. Calcd for $C_{12}H_{11}NO$: C, 77.81; H, 5.98; N, 7.56. Found: C, 78.06; H, 6.14; N, 7.54; HRMS (EI) Calcd for $C_{12}H_{11}NO$ (M^+) 185.0840. Found 185.0845.

2-(2-cyclopentyethynyl)phenyl-1-isocyanate (1b)

colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.55-1.70 (2H, m), 1.70-1.85 (4H, m), 1.97-2.10 (2H, m), 2.89 (1H, br quintet, *J* = 7.5 Hz), 6.99 (1H, dd, *J* = 7.5, 1.0 Hz), 7.09 (1H, td, *J* = 7.5, 1.0 Hz), 7.18 (1H, td, *J* = 7.5, 1.5 Hz), 7.37 (1H, dd, *J* = 7.5, 1.5 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 25.08, 30.92, 33.31, 75.72, 103.51, 121.73, 123.26, 125.20, 128.37, 132.12, 134.86; IR (neat) 2250 (NCO), 1598, 1506, 756 cm^{-1}; HRMS (EI) Calcd for $C_{14}H_{13}NO$ (M^+) 211.0997. Found 211.0997.

2-(2-*tert*-butylethynyl)phenyl-1-isocyanate (1c)

slightly yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (9H, s), 6.99 (1H, dd, *J* = 7.5, 1.5 Hz), 7.09 (1H, td, *J* = 7.5, 1.5 Hz), 7.18 (1H, td, *J* = 7.5, 1.5 Hz), 7.37 (1H, dd, *J* = 7.5, 1.5 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 28.30, 30.41, 74.70, 106.95, 121.67, 123.26, 125.18, 128.42, 132.32, 134.62; IR (neat) 2268 (NCO), 2245 (NCO), 1598, 1514, 756 cm^{-1}; Anal. Calcd for $C_{13}H_{13}NO$: C, 78.36; H, 6.57; N, 7.02. Found: C, 78.40; H, 6.96; N, 7.00; HRMS (EI) Calcd for $C_{13}H_{13}NO$ (M^+) 199.0997. Found 199.0996.

2-(2-phenylethynyl)phenyl-1-isocyanate (1d)

yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.97 (1H, dd, *J* = 7.5, 1.0 Hz), 7.18 (1H, td, *J* = 7.5, 1.0 Hz), 7.28 (1H, td, *J* = 7.5, 1.5 Hz), 7.37 (3H, m), 7.53 (1H, dd, *J* = 7.5, 1.5 Hz), 7.62 (2H, m); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 84.75, 97.41, 120.97, 122.37, 123.59, 125.44, 128.40, 128.87, 129.29, 131.47, 132.28, 134.79; IR (neat) 2273 (NCO), 2245 (NCO), 1595, 1508, 752 cm^{-1}; HRMS (EI) Calcd for $C_{15}H_9NO$ (M^+) 219.0684. Found 219.0682.

2-(2-(4-methoxyphenyl)ethynyl)phenyl-1-isocyanate (1e)

slightly yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.84 (3H, s), 6.90 (2H, br d, *J* = 8.5 Hz), 7.06 (1H, br d, *J* = 7.5 Hz), 7.16 (1H, br t, *J* = 7.5 Hz), 7.24 (1H, td, *J* = 7.5, 1.5 Hz), 7.50 (1H, dd, *J* = 7.5, 1.5 Hz), 7.56 (2H, br d, *J* = 8.5 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 55.22, 83.61, 97.66, 114.03, 114.40, 121.32, 123.45, 125.37, 128.84, 131.94, 132.98, 134.51, 160.04; IR (neat) 2264 (NCO), 2238 (NCO), 1606, 1514, 1249 (C-O), 1031 (C-O), 756 cm^{-1}; HRMS (EI) Calcd for $C_{16}H_{11}NO$ (M^+) 249.0789. Found 249.0784.

2-(2-(4-trifluoromethylphenyl)ethynyl)phenyl-1-isocyanate (1f)

white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (1H, br d, *J* = 8.0 Hz), 7.18 (1H, td, *J* = 8.0, 1.0 Hz), 7.30 (1H, td, *J* = 7.5, 1.5 Hz), 7.53 (1H, dd, *J* = 7.5, 1.5 Hz), 7.61 (2H, br d, *J* = 8.5 Hz), 7.69 (2H, br d, *J* = 8.5 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 86.96, 95.76, 120.29, 122.03, 123.76, 125.36, 125.58, 126.16, 129.97, 131.58, 131.69, 132.49, 135.02; IR (neat) 2273 (NCO), 2248 (NCO), 1610, 1595, 1508, 1325 (CF_3), 759 cm^{-1}; HRMS (EI) Calcd for $C_{16}H_8F_3NO$ (M^+) 287.0557. Found 287.0562.

3-allyl-*N*-(methoxycarbonyl)-2-propylindole (3aa)

slightly yellow oil; 1H NMR (300 MHz, CDCl3) δ 0.96 (3H, t, *J* = 7.5 Hz), 1.61 (2H,

sextet, J = 7.5 Hz), 2.95 (2H, t, J = 7.5 Hz), 3.42 (2H, ddd, J = 6.0, 1.0, 1.0 Hz), 4.03 (3H, s), 5.01 (1H, ddd, J = 10.0, 1.5, 1.5 Hz), 5.05 (1H, ddd, J = 17.0, 1.5, 1.5 Hz), 5.92 (1H, ddd, J = 17.0, 10.0, 6.0 Hz), 7.17-7.27 (2H, m), 7.44 (2H, br dd, J = 7.0, 2.0 Hz), 8.05 (1H, br dd, J = 8.0, 1.5 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 14.12, 23.27, 28.39, 28.56, 53.32, 115.34, 115.57, 116.65, 118.40, 122.65, 123.59, 130.09, 135.69, 136.10, 137.93, 152.45 (C=O); IR (neat) 1739 (C=O), 1637, 1577, 1460, 1230 (C-O), 1022 (C-O), 993, 912, 746 cm^{-1}; HRMS (EI) Calcd for $C_{16}H_{19}NO_2$ (M^+) 257.1415. Found 257.1417.

3-allyl-*N*-(isopropoxycarbonyl)-2-propylindole (3ab)

yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.98 (3H, t, J = 7.5 Hz), 1.47 (6H, d, J = 6.5 Hz), 1.63 (2H, sextet, J = 7.5 Hz), 2.96 (2H, br t, J = 7.5 Hz), 3.43 (2H, br d, J = 6.0 Hz), 5.02 (1H, br dd, J = 10.0, 1.5 Hz), 5.07 (1H, br dd, J = 17.0, 1.5 Hz), 5.92 (1H, septet, J = 6.5 Hz), 5.94 (1H, ddd, J = 17.0, 10.0, 6.0 Hz), 20 (1H, br t, J = 7.0 Hz), 7.24 (1H, br t, J = 7.0 Hz), 7.44 (1H, br dd, J = 7.0, 2.0 Hz), 8.13 (1H, br d, J = 7.0 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 14.06, 21.94, 23.38, 28.39, 28.70, 70.93, 115.24, 115.62, 116.31, 118.29, 122.46, 123.48, 129.98, 135.93, 136.15, 137.80, 151.42 (C=O); IR (neat) 1782 (C=O), 1639, 1458, 1230 (C-O), 1105 (C-O), 1012, 910, 744 cm^{-1}; HRMS (EI) Calcd for $C_{18}H_{23}NO_2$ (M^+) 285.1728. Found 285.1729.

3-allyl-*N*-(*tert*-butoxycarbonyl)-2-propylindole (3ac)

slightly yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97 (3H, t, J = 7.5 Hz), 1.63 (2H, sextet, J = 7.5 Hz), 1.68 (9H, s), 2.96 (2H, t, J = 7.5 Hz), 3.43 (2H, ddd, J = 6.0, 1.0, 1.0 Hz), 5.02 (1H, ddd, J = 10.0, 1.5, 1.5 Hz), 5.07 (1H, ddd, J = 17.0, 1.5, 1.5 Hz), 5.94 (1H, ddd, J = 17.0, 10.0, 6.0 Hz), 7.19 (1H, br dd, J = 7.0, 1.5 Hz), 7.23 (1H, br dd, J = 7.0, 1.5 Hz), 7.44 (1H, br dd, J = 7.0, 2.0 Hz), 8.10 (1H, br d, J = 7.0 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 14.00, 23.41, 28.17, 28.44, 28.60, 83.28, 115.17, 115.49, 115.96, 118.23, 122.24, 123.32, 129.84, 136.01, 136.26, 137.77, 150.49 (C=O); IR (neat) 1732 (C=O), 1637, 1456, 1232 (C-O), 1136 (C-O), 912, 744 cm^{-1}; HRMS (EI) Calcd for $C_{19}H_{25}NO_2$ (M^+) 299.1885. Found 299.1884.

3-allyl-*N*-(phenoxycarbonyl)-2-propylindole (3ad)

slightly yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86 (3H, t, J = 7.5 Hz), 1.56 (2H, sextet, J = 7.5 Hz), 2.92 (2H, t, J = 7.5 Hz), 3.41 (2H, ddd, J = 6.0, 1.5, 1.5 Hz), 5.01 (1H, ddd, J = 10.0, 1.5, 1.5 Hz), 5.05 (1H, ddd, J = 17.0, 1.5, 1.5 Hz), 5.45 (2H, s), 5.92

(1H, ddd, *J* = 17.0, 10.0, 6.0 Hz), 7.28-7.23 (2H, m), 7.35-7.53 (6H, m), 8.07-8.12 (1H, m); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 13.95, 23.33, 28.38, 28.61, 68.60, 115.32, 115.68, 116.69, 118.35, 122.65, 123.65, 128.67, 128.70, 128.74, 130.07, 134.97, 135.83, 136.05, 137.86, 151.73 (C=O); IR (neat) 1747 (C=O), 1639, 1593, 1458, 1217 (C-O), 1188 (C-O), 996, 912, 752 cm^{-1}; HRMS (EI) Calcd for $C_{21}H_{21}NO_2$ (M^+) 319.1572. Found 319.1575.

3-allyl-*N*-(benzyloxycarbonyl)-2-propylindole (3ae)

colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97 (3H, t, *J* = 7.5 Hz), 1.69 (2H, sextet, *J* = 7.5 Hz), 3.03 (2H, t, *J* = 7.5 Hz), 3.47 (2H, br d, *J* = 6.0 Hz), 5.06 (1H, ddd, *J* = 10.0, 1.5, 1.5 Hz), 5.10 (1H, ddd, *J* = 17.0, 1.5, 1.5 Hz), 5.96 (1H, ddd, *J* = 17.0, 10.0, 6.0 Hz), 7.24-7.36 (4H, m), 7.44-7.52 (3H, m), 8.15-8.20 (2H, m); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 14.10, 23.37, 28.42, 28.61, 115.52, 115.86, 117.54, 118.60, 121.59, 123.11, 123.96, 126.33, 129.68, 130.34, 135.79, 135.89, 138.00, 150.14, 150.28 (C=O); IR (neat) 1732 (C=O), 1637, 1458, 1226 (C-O), 1016 (C-O), 991, 912, 746 cm^{-1}; HRMS (EI) Calcd for $C_{22}H_{23}NO_2$ (M^+) 333.1728. Found 333.1730.

3-allyl-*N*-(methoxycarbonyl)-2-cyclopentylindole (3ba)

slightly yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.63-1.80 (2H, m), 1.80-2.03 (6H, m), 3.50 (2H, ddd, *J* = 5.5, 1.5 Hz), 3.83 (1H, br quintet, *J* = 8.5 Hz), 4.04 (3H, s), 5.02 (1H, ddd, *J* = 16.5, 1.5, 1.5 Hz), 5.04 (1H, ddd, *J* = 10.5, 1.5, 1.5 Hz), 5.97 (1H, ddd, *J* = 16.5, 10.5, 5.5 Hz), 7.19 (1H, br td, *J* = 6.5, 1.5 Hz), 7.24 (1H, br td, *J* = 6.5, 1.5 Hz), 7.42 (1H, br dd, *J* = 6.5, 2.0 Hz), 7.97 (1H, br dd, *J* = 6.5, 2.0 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 26.38, 28.73, 32.15, 37.77, 53.37, 115.19, 115.46, 116.65, 118.22, 122.50, 123.56, 130.38, 135.72, 136.03, 140.58, 152.65 (C=O); IR (neat) 1739 (C=O), 1637, 1458, 1230 (C-O), 1132 (C-O), 993, 912, 744 cm^{-1}; HRMS (EI) Calcd for $C_{18}H_{21}NO_2$ (M^+) 283.1572. Found 283.1576.

3-allyl-*N*-(methoxycarbonyl)-2-phenylindole (3da)

yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.28 (2H, ddd, *J* = 6.0, 1.5, 1.5 Hz), 3.74 (3H, s), 4.98-5.05 (2H, m), 5.99 (1H, ddt, *J* = 17.0, 10.0, 6.0 Hz), 7.28-7.45 (7H, m), 7.55 (1H, br d, *J* = 7.5 Hz), 8.17 (1H, br d, *J* = 8.0 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 28.63, 53.16, 115.43, 115.55, 118.79, 119.30, 122.91, 124.60, 127.65, 127.76, 129.54, 129.84, 133.22, 136.09, 136.20, 136.28, 152.17 (C=O); IR (neat) 1739 (C=O), 1637, 1579, 1456, 1234 (C-O), 1072 (C-O), 993, 914, 765, 748, 702 cm^{-1}; HRMS (EI) Calcd

for $C_{19}H_{17}NO_2$ (M^+) 291.1259. Found 291.1252.

3-allyl-*N*-(methoxycarbonyl)-2-(4-methoxyphenyl)indole (3ea)

colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.26 (2H, br d, *J* = 6.0 Hz), 3.76 (3H, s), 3.84 (3H, s), 4.96-5.04 (2H, m), 5.93 (1H, ddt, *J* = 17.5, 10.0, 6.0 Hz), 6.93 (2H, br d, *J* = 8.5 Hz), 7.22-7.35 (4H, m), 7.52 (1H, br d, *J* = 7.5 Hz), 8.13 (1H, br d, *J* = 8.0 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 28.64, 53.17, 55.11, 113.09, 115.42, 115.45, 118.59, 119.14,122.83, 124.39, 125.37, 129.84, 130.77, 135.96, 136.20, 136.27, 152.23 (C=O), 159.11; IR (neat) 1737 (C=O), 1616, 1508, 1456, 1247 (C-O), 1031 (C-O), 914, 748 cm^{-1}; HRMS (EI) Calcd for $C_{20}H_{19}NO_3$ (M^+) 321.1365. Found 321.1367.

3-allyl-*N*-(methoxycarbonyl)-2-(4-trifluoromethylphenyl)indole (3fa)

yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.27 (2H, dt, *J* = 6.0, 1.5 Hz), 3.78 (3H, s), 5.01 (1H, ddd, *J* = 17.0, 2.0, 2.0 Hz), 5.05 (1H, *J* = 10.0, 2.0, 2.0 Hz), 5.94 (1H, ddt, *J* = 17.0, 10.0, 6.0 Hz), 7.31 (1H, br t, *J* = 7.5 Hz), 7.38 (1H, br t, *J* = 8.0 Hz), 7.47 (2H, br d, *J* = 8.0 Hz), 7.57 (1H, br d, *J* = 7.5 Hz), 7.68 (2H, br d, *J* = 8.0 Hz), 8.17 (1H, br d, *J* = 8.0 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 28.49, 53.36, 115.59, 115.87, 118.41, 119.54, 118.87, 123.20, 124.65, 125.16, 128.23, 129.71, 129.93, 131.39, 134.63, 135.79, 136.19, 152.03 (C=O); IR (neat) 1745 (C=O), 1620, 1456, 1325 (CF_3), 993, 916, 748 cm^{-1}; HRMS (EI) Calcd for $C_{20}H_{16}F_3NO_2$ (M^+) 359.1133. Found 359.1136.

***N*-allyl-*N*-(methoxycarbonyl)-2-(1-pentynyl)aniline (4aa)**

yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.03 (3H, t, *J* = 7.5 Hz), 1.61 (2H, sextet, *J* = 7.5 Hz), 2.39 (2H, t, *J* = 7.5 Hz), 3.64 (3H, s), 3.75-4.60 (2H, broad peaks), 5.03 (1H, ddd, *J* = 10.0, 1.5, 1.5 Hz), 5.10 (1H, ddd, *J* = 17.0, 1.5, 1.5 Hz), 5.91 (1H, br ddd, *J* = 17.0, 10.0, 6.5 Hz), 7.12 (1H, br d, *J* = 7.5 Hz), 7.17-7.28 (2H, m), 7.43 (1H, dd, *J* = 7.5, 1.5 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 13.40, 21.38, 22.07, 52.77, 77.07, 95.11, 117.38, 123.35, 127.00, 127.96, 128.45, 132.63, 133.49, 142.65, 155.94 (C=O); IR (neat) 1712 (C=O), 1645, 1596, 1488, 752 cm^{-1}; Anal. Calcd for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44. Found: C, 74.39; H, 7.75; N, 5.39; HRMS (EI) Calcd for $C_{16}H_{19}NO_2$ (M^+) 257.1415. Found 257.1415.

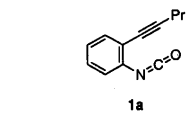
***N*-allyl-*N*-(methoxycarbonyl)-2-(2-*tert*-butylethynyl)aniline (4ca)**

slightly yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30 (9H, s), 3.65 (3H, s), 3.75-4.50 (2H, broad peaks), 5.07 (1H, br d, J = 10.0 Hz), 5.11 (1H, br d, J = 17.0 Hz), 5.92 (1H,

br ddd, J = 17.0, 10.0, 6.5 Hz), 7.12 (1H, br d, J = 7.5 Hz), 7.17-7.28 (2H, m), 7.41 (1H, br dd, *J* = 7.5, 1.5 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 30.88, 31.47, 52.82, 52.93, 75.58, 103.42, 117.44, 123.55, 127.05, 128.04, 128.32, 132.36, 133.63, 142.88, 156.01 (C=O); IR (neat) 1714 (C=O), 1643, 1596, 1488, 1298 (C-O), 1151 (C-O), 989, 923, 752 cm^{-1}; HRMS (EI) Calcd for $C_{17}H_{21}NO_2$ (M^+) 271.1572. Found 271.1574.

References

1. Coulson, D. R. *Inorg. Synth.* 1972, 13, 121-124.
2. Zhang, Q.; Shi, C.; Zhang, H.-R.; Wang, K. K. *J. Org. Chem.* **2000**, *65*, 7977-7983.
3. Shi, C.; Zhang, Q.; Wang, K. K. *J. Org. Chem.* **1999**, *64*, 925-932.



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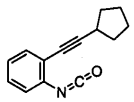

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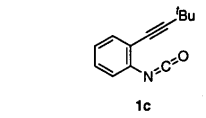
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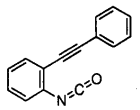
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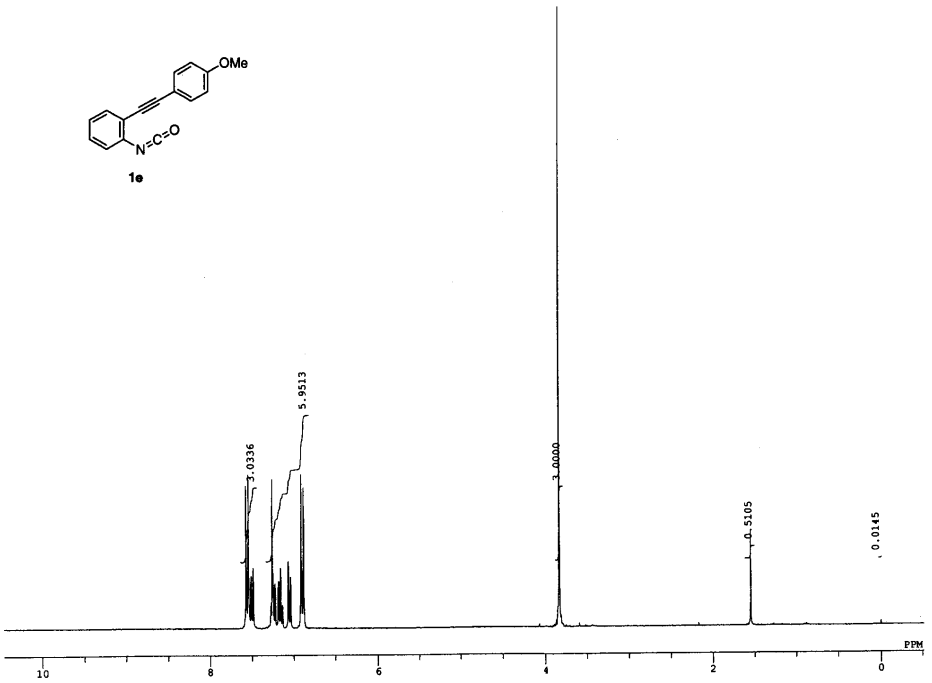
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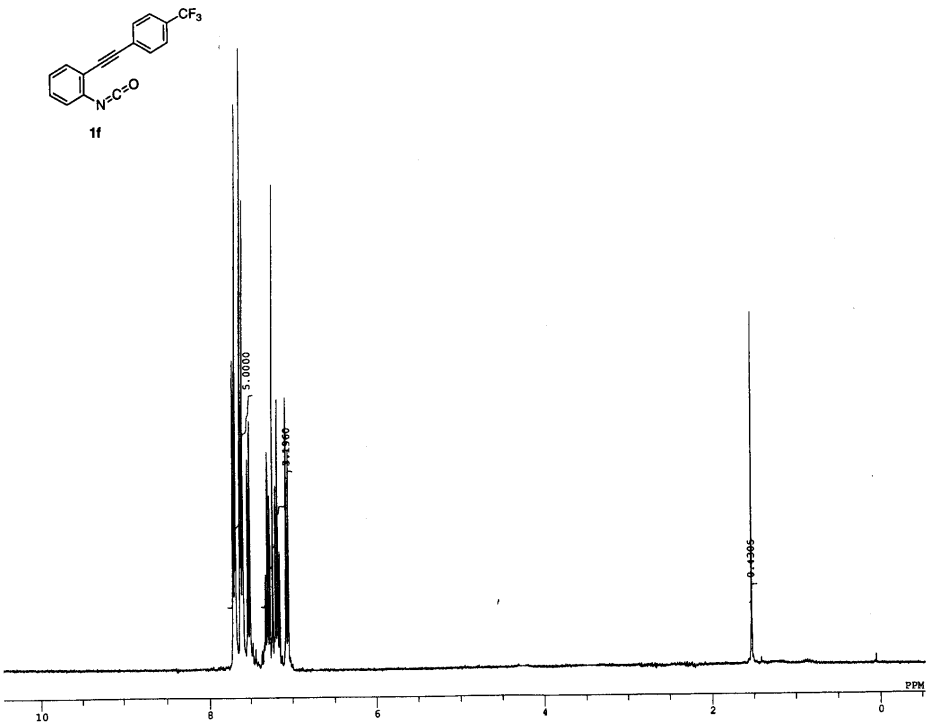
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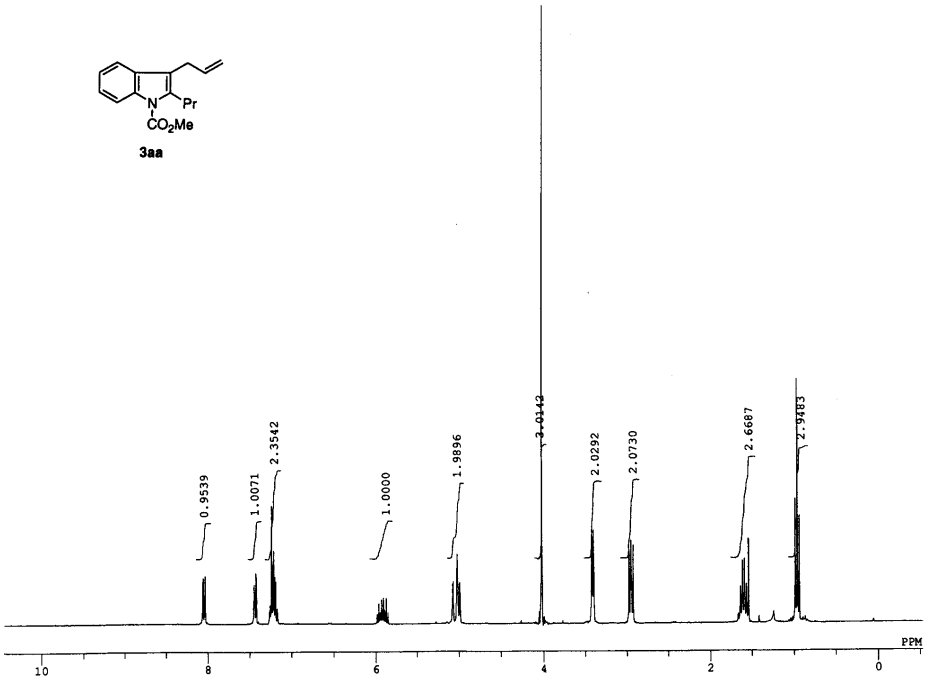
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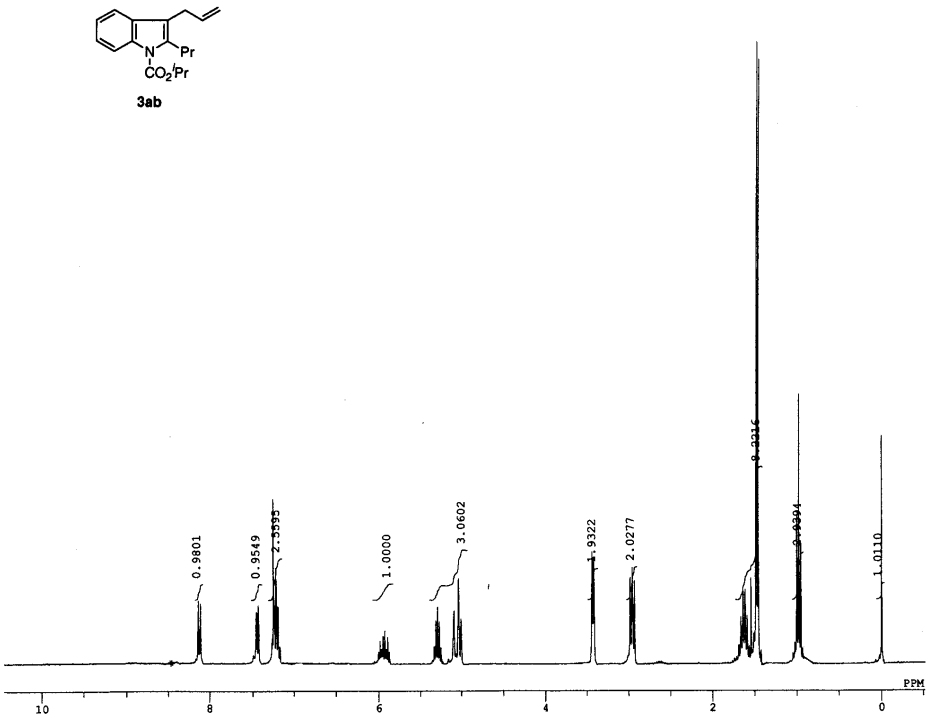
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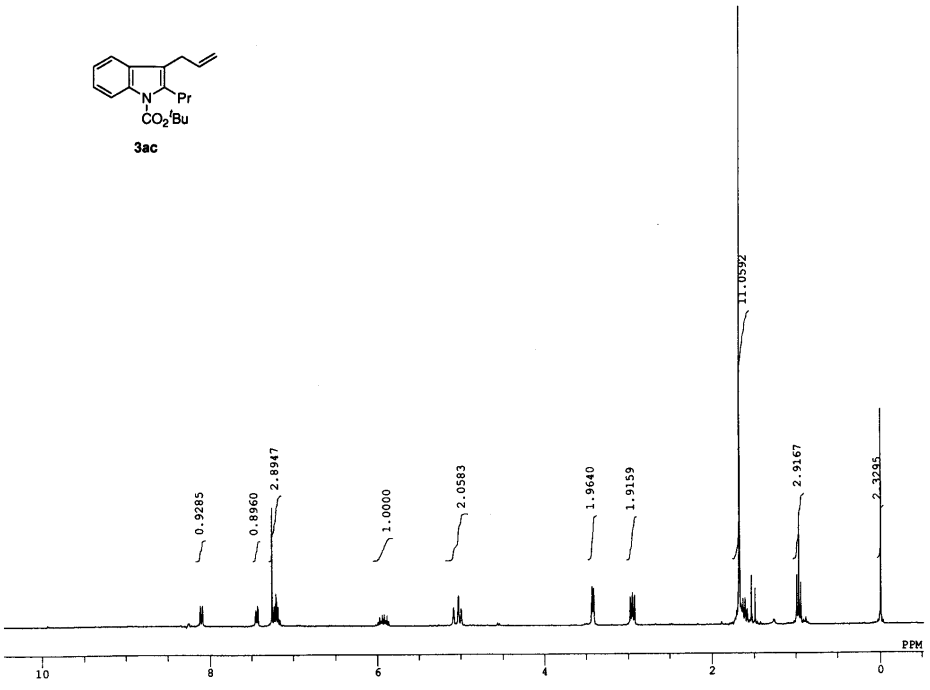
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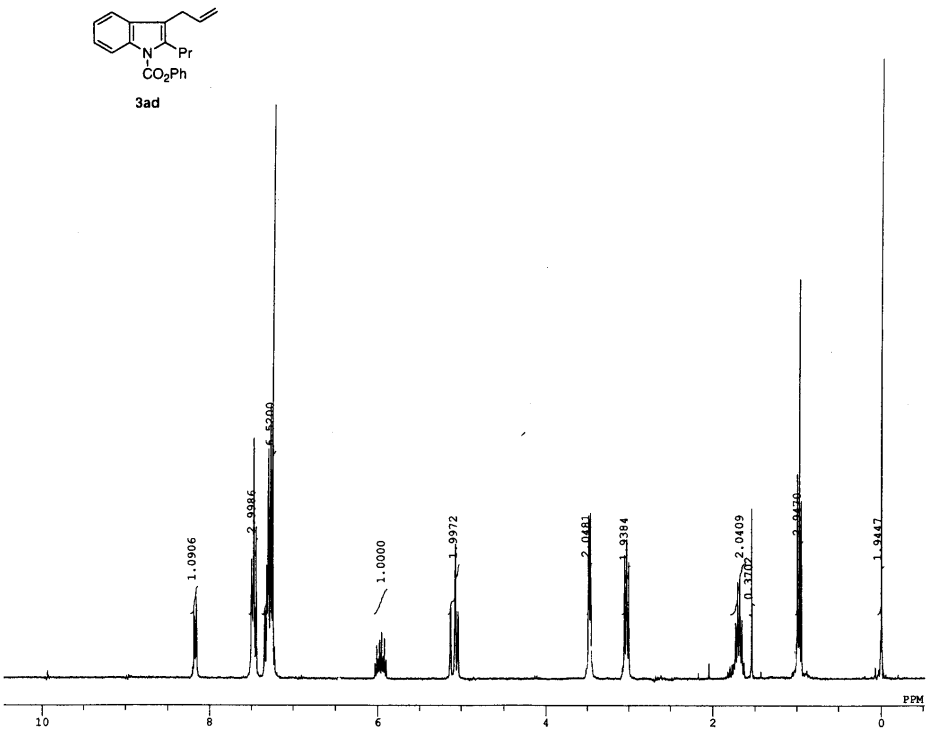
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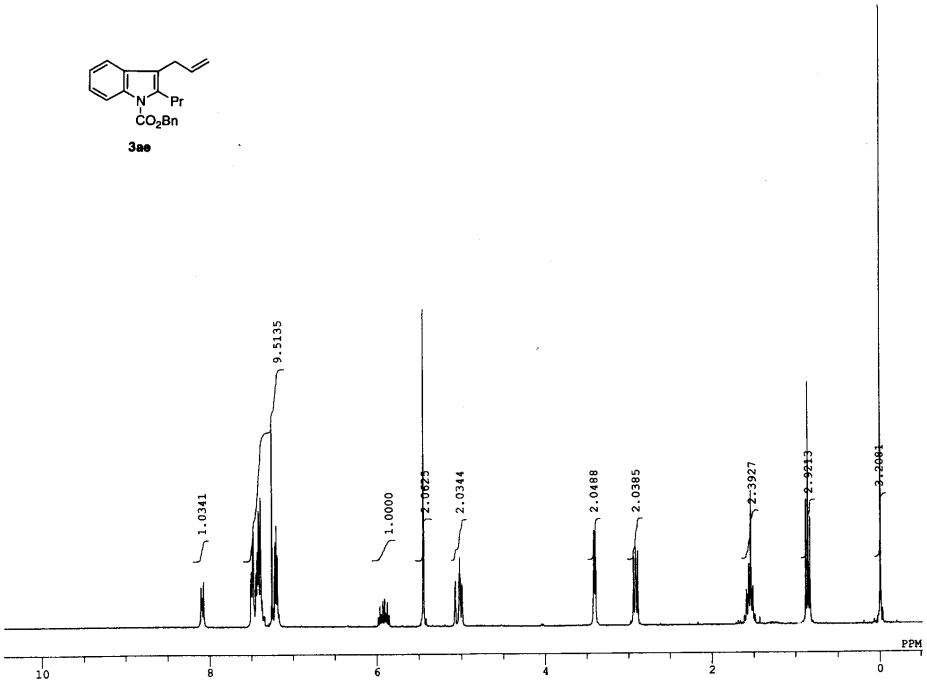
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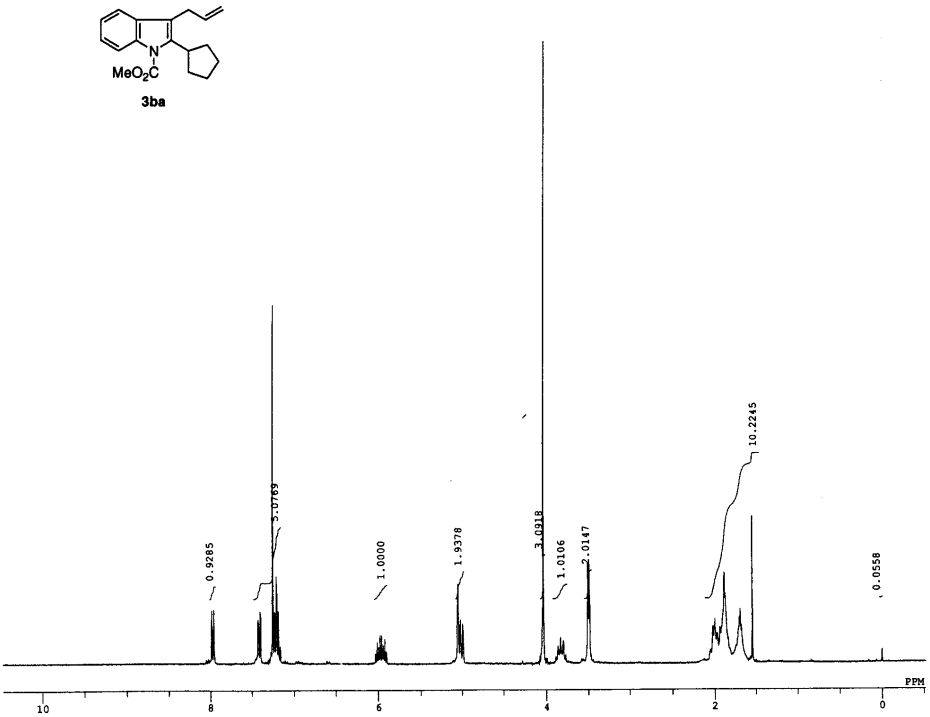
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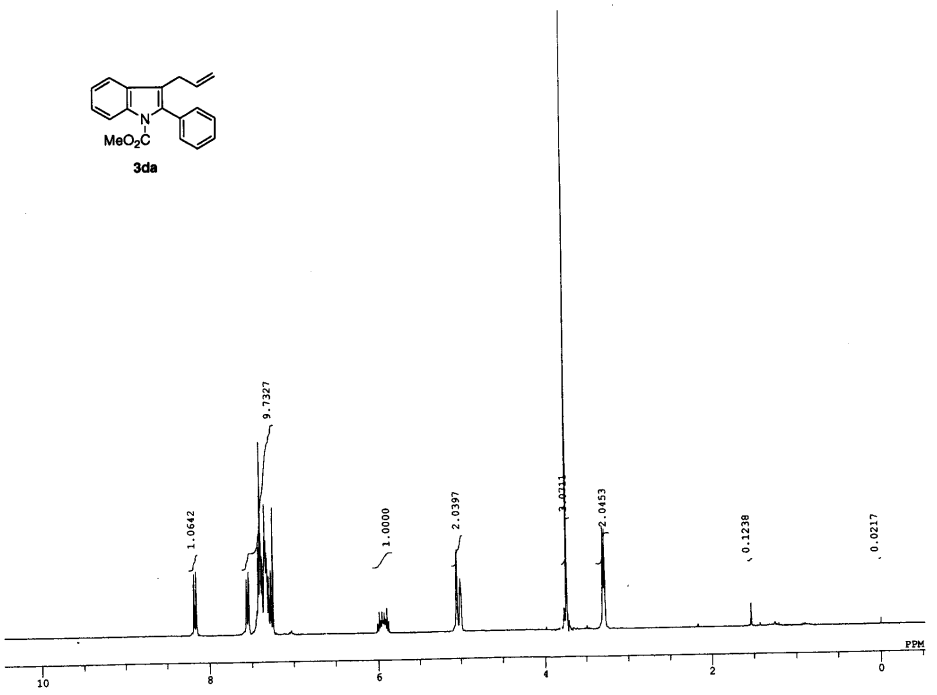
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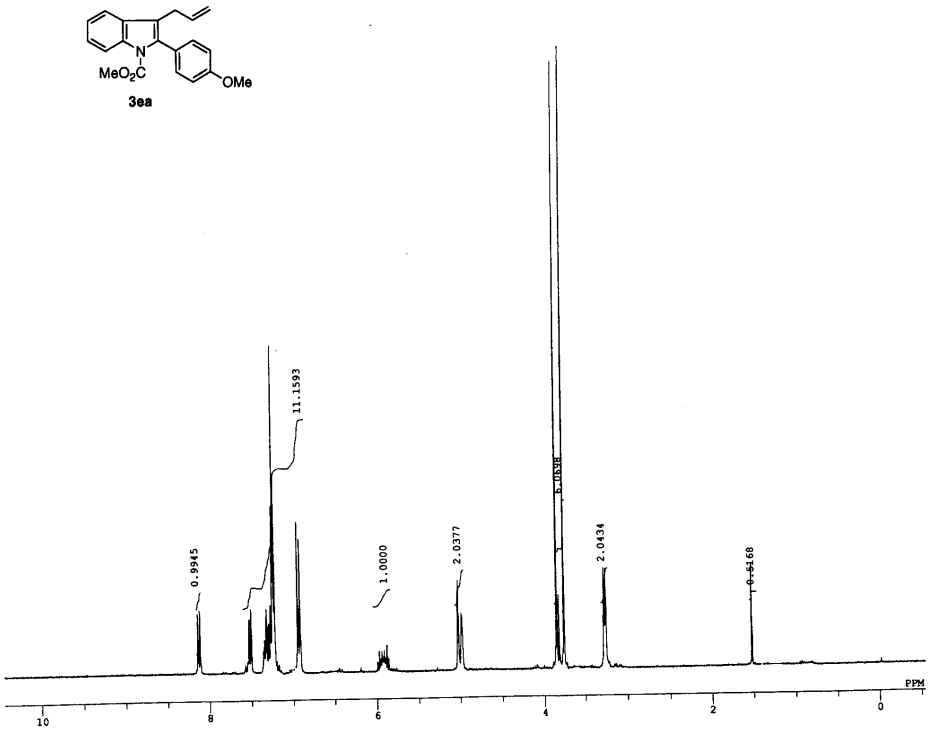
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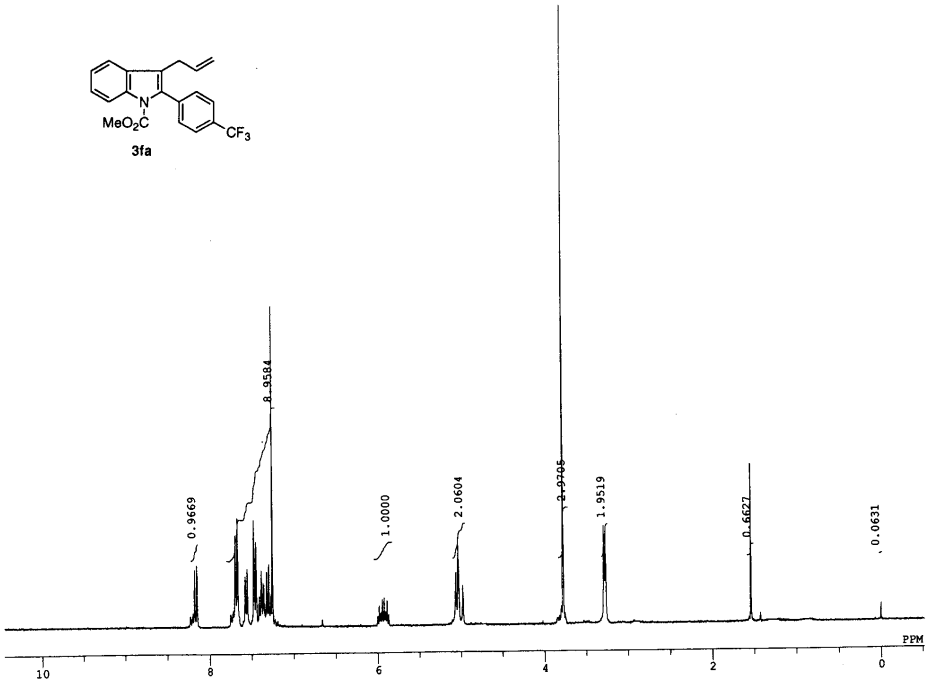
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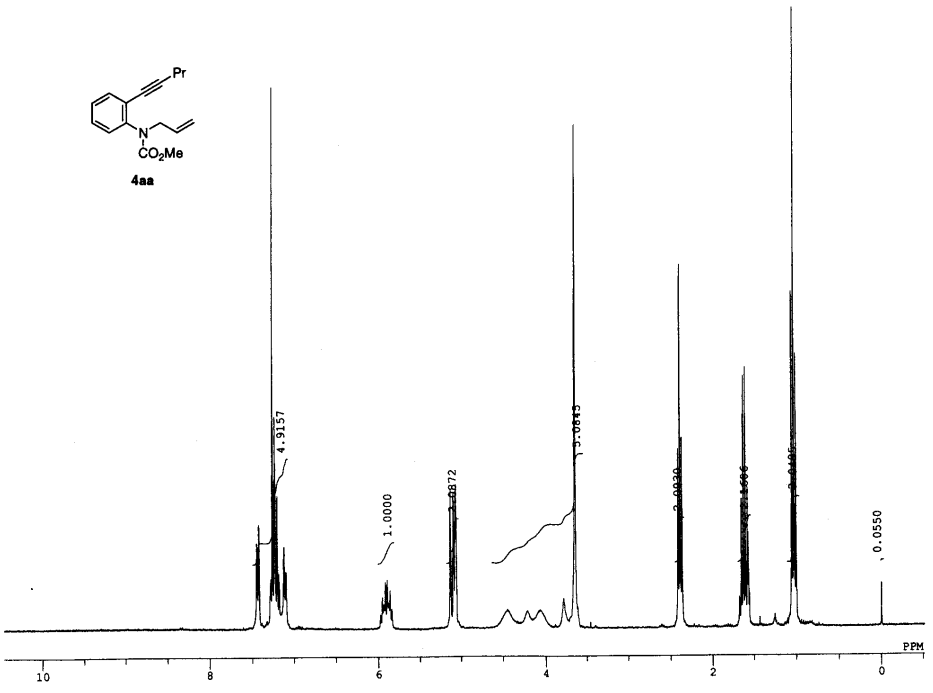
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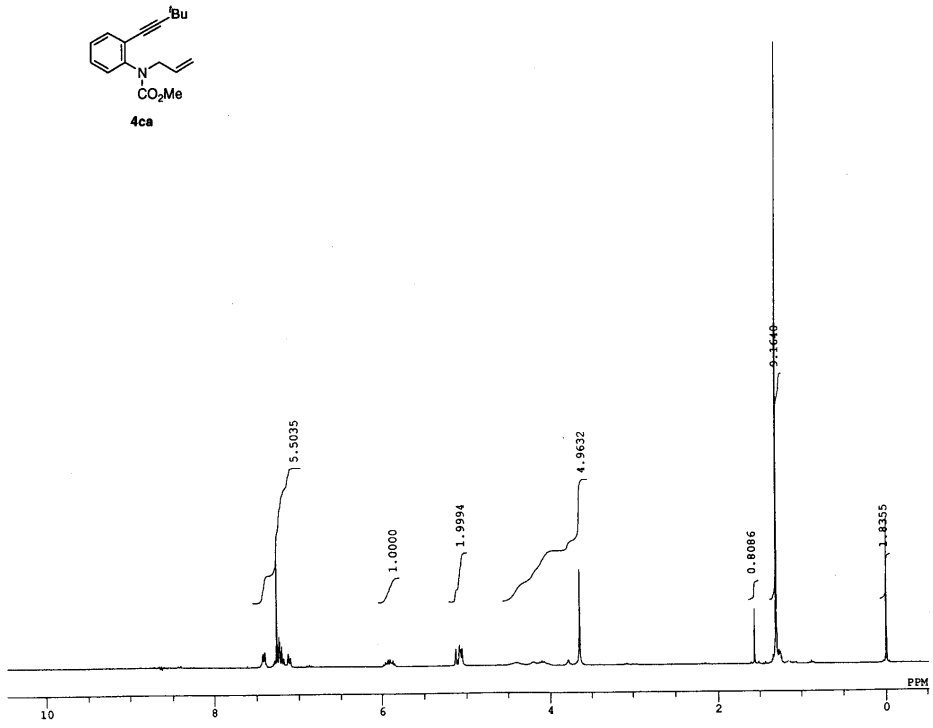
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