
Supporting Information for

Allylation of Aldehydes and Imines: Promoted by Reuseable Polymer-Supported Sulfonamide of *N*-Glycine

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General experimental methods and data of the corresponding compounds -----S2-S14

Spectra of the corresponding compounds -----S15-S35

General: Melting point data were measured on Mettler FP62. All the ^1H NMR spectra were recorded with TMS as an internal standard on a Bruker AM-300 or Varian EM-360 (300 MHz). IR spectra were recorded on a Nicolet -AV360 spectrometer. EI Mass spectra were determined on an HP-5989A spectrometer. Elemental analysis for carbon and hydrogen were performed on a Rapid CHN-O analyzer. Optical rotations were obtained on a Perkin-Elmer 241 Autopol polarimeter.

Allyltributyltin 1 (**2**) was prepared according to the reported procedure. All aldehydes, amines, and solvents are commercially available and were used after standard purification.

Typical procedure for preparation of *N*-Tosyl α -amino acids: 2

To a stirred solution of *D*(+)-phenylalanine (2.5g, 15 mmol) dissolved in 25 mL of 1.5 M NaOH at room temperature was added *p*-toluenesulfonyl chloride (3.4g, 18 mmol) in Et₂O (15 mL). White solid appeared after stirring for overnight. Concentrated HCl was added to the solution until pH = 2. The Et₂O layer was separated and aqueous layer was extracted with Et₂O (3 x 20 mL). The combined extracts were dried over Na₂SO₄ and concentrated. The crude product was recrystallized from Et₂O giving pure *N*-Tosyl-*D*-phenylalanine (3.8g), 79% yield. The other *N*-Tosyl α -amino acids were prepared according to a similar method.

***N*-Tosyl-*D*-phenylalanine** 2 m.p. 164 °C; $[\alpha]_{\text{D}}^{20} = +2.61$ (*c* 4.82, acetone); ^1H NMR(CDCl₃) δ 7.56 (d, 2 H, *J* = 7.7 Hz), 7.19(m, 5 H), 7.06(d, 2 H, *J* = 3.4 Hz), 5.17(s, 1 H), 4.18(d, 1 H, *J* = 7.1 Hz), 2.94(dq, 2 H, *J* = 7.0, 6.5, 14.1, 4.9, Hz), 2.39(s, 3 H); IR (KBr) ν 3353, 3334, 3172, 3058, 2968, 1734, 1697, 1598, 1454, 1376, 1348, 1168, 1093, 811 cm⁻¹.

***N*-Tosyl-*L*-proline** 3 m.p. 96 °C; $[\alpha]_{\text{D}}^{20} = -77.7$ (*c* 1.90, EtOH); ^1H NMR(CDCl₃) δ 7.75 (d, 2 H, *J* = 8.2 Hz), 7.34(d, 2 H, *J* = 8.4 Hz), 4.24(dd, 1 H, *J* = 3.6, 4.6 Hz), 3.50-3.57(m, 1 H), 3.21(q, 1 H, *J* = 9.2, 8.3, 7.1 Hz), 2.45(s, 3 H), 2.14-2.19(m, 1 H), 1.90-1.97(m, 2 H), 1.74-1.77(m, 1 H); IR (KBr) ν 3437, 3040, 2986, 1716, 1341, 1161, 1096, 1010, 820 cm⁻¹.

***N*-Tosyl-*L*-valine** 4 m.p. 167.3 °C; $[\alpha]_{\text{D}}^{20} = +26.8$ (*c* 1.15, EtOH); ^1H NMR(CDCl₃) δ

7.69(d, 2 H, $J = 8.7$), 7.26(d, 2H, $J = 7.2$ Hz), 5.22(d, 1 H, $J = 9.9$ Hz), 2.40(s, 3 H), 2.06-2.12(m, 1 H), 0.93 (d, 3 H, $J = 6.9$ Hz), 0.84 (d, 3 H, $J = 6.6$ Hz); IR (KBr) ν 3292, 3050, 2970, 2879, 1708, 1333, 1161, 1069, 809 cm^{-1} .

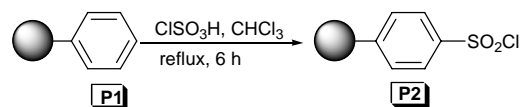
***N*-Tosyl-*L*-2-phenylglycine**⁵ m.p. 177.1 °C; $[\alpha]_{\text{D}}^{20} = + 106.1$ (c 2.25, EtOH); ^1H NMR (d^6 - acetone) δ 7.66(d, 2 H, $J = 8.6$ Hz), 7.27-7.35 (m, 7 H), 5.02(s, 1 H), 2.37(s, 3 H); IR (KBr) ν 3391, 3331, 3293, 3077, 2981, 1724, 1600, 1461, 1325, 1166, 1090, 925 cm^{-1} .

***N*-Tosyl-glycine**⁶ m.p. 147.6 °C; ^1H NMR (d^6 - acetone) δ 7.75 (d, 2 H, $J = 8.0$ Hz), 7.37(d, 2 H, $J = 7.8$ Hz), 6.65 (d, 1 H, $J = 5.4$ Hz) 3.75 (d, 2 H, $J = 5.8$ Hz), 2.41 (s, 3 H). IR (KBr): ν 3429, 3272, 2976, 1719, 1631, 1415, 1336, 1231, 1157, 1093, 821 cm^{-1} .

Typical procedure for the allylation promoted by *N*-tosylglycine:

To a solution of *N*-tosylglycine (115 mg, 0.5 mmol) in acetonitrile (2.0 mL) were added successively benzaldehyde (53 mg, 0.5 mmol) and allyltributyltin (198 mg, 0.6 mmol) at room temperature. The reaction was quenched with NaOH (2 M, 2 mL) after 23 h. The solution was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to furnish the crude product, which was purified by silica gel chromatography (typical eluent: petroleum ether / EtOAc 14:1(v/v)) to afford **3a** (68mg, 92%).

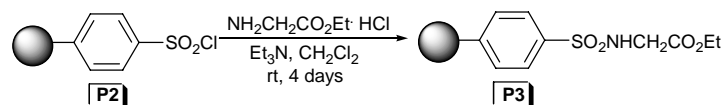
The preparation of **P2**:⁷



Chlorosulfonic acid (20 mL) was added dropwise to a suspension of polystyrene (**P1**, 2.0 g) in CHCl_3 (40 mL). After refluxed for 6h, the reaction solution was carefully poured into icewater (30 mL). The solid polymer was filtered and washed with distilled water (3 x 10 mL), CH_2Cl_2 (3 x 10 mL), CH_2Cl_2 /THF (V/V = 4/1, 3/2; 3 x 10 mL), THF (3 x 10 mL), CH_2Cl_2 (3 x 10 mL), respectively. After dried in vacuum (8mmHg, 50 °C, overnight). The **P2** was obtained as a golden powder (3.9g). Elemental analysis: 4.61 mmol/g Cl and 4.80 mmol/g S. IR (KBr): ν 2932, 2831, 1598,

1366, 1166, 971, 775cm⁻¹.

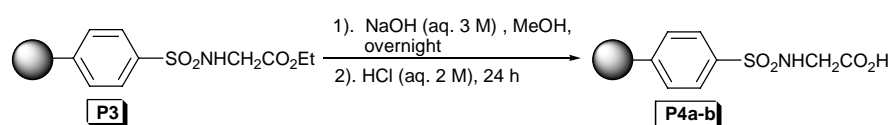
The preparation of **P3**:⁷



Et_3N (6.3 mL, 4.5 mmol) was added to the mixture of **P2** (1.84g, 9.0 mmol) and glycine ethyl ester (5.0 g, 36.0 mmol) in anhydrous CH_2Cl_2 (100 mL). The mixture was stirred at room temperature for 4 days. Then removed the solvent under reduced pressure and the resulted solid was immersed in MeOH (200 mL) overnight. The solid polymer was filtered and washed with distilled water (2 x 60 mL), CH_2Cl_2 (2 x 60 mL), MeOH/ distilled water (v/v = 1/1, 2 x 60 mL), MeOH (2 x 60 mL), respectively.

After dried (in vacuum, 8mmHg, 50 °C, 16 h). The **P3** was obtained as a golden powder (2.2g). Elemental analysis: Cl < 0.5%. IR (KBr): ν 3292, 2983, 2931, 1747, 1597, 1415, 1332, 1209, 1159, 1094, 1031, 970, 832cm⁻¹.

The preparation of **P4**:



P3 (2.2 g) was added to a solution of NaOH (6.0 g, 0.15 mol) in MeOH- H_2O (MeOH/ H_2O = 40/10 mL). The mixture was stirred at room temperature overnight. IR showed that the saponification was completed. The solid was filtered and washed with distilled water (3 x 50 mL), MeOH/ distilled water (v/v = 1/1, 2 x 50 mL), MeOH (2 x 50 mL). The resulted solid was treated with aqueous HCl (2 M, 100 mL) and stirred for 24 h, then filtered and washed with distilled water to neutral. The solid was stirred in distilled water for 48 h to remove the trace hydrochloric acid and dried in vacuum (1mmHg, P_2O_5 , 50°C overnight). Then the PS-supported *N*-tosylglycine **P4a** was obtained. Elemental analysis: 3.65mmol/g N, 3.89 mmol/g S. IR (KBr): ν 3284, 2926, 1732, 1597, 1415, 1324, 1156, 1093, 834 cm⁻¹.

Typical procedure for the allylation of aldehydes promoted by P4a:

To a suspension of **P4a** (164 mg, 0.6 mmol) in acetonitrile (1.5 mL) were added successively benzaldehyde (53 mg, 0.5 mmol) and allyltributyltin (198 mg, 0.6 mmol)

at room temperature. After stirred for 3 h (TLC showed the reaction was completed). The suspension was filtered and washed with CH₃CN (3 x 5 mL). The filtrate was concentrated under reduced pressure to furnish the pure product, **3a** (71mg, 96%). The resulted polymer **P5a** (320 mg) was stirred in a solution of HCl (2 M, 15 mL) and Et₂O (5 mL) at room temperature for 24 h. Then filtered and washed with Et₂O (3 x 15 mL) to recover **P4a**. The Et₂O layer was dried and concentrated under reduced pressure to recover Bu₃SnCl (180 mg, 92% based on allyltributyltin).

1-Phenyl-3-buten-1-ol (3a)⁸ ¹H NMR (300MHz, CDCl₃): δ 7.37-7.26(m, 5H), 5.87-5.78(m, 1H), 5.14(t, 2H, J = 9.1, 9.6 Hz), 4.73(t, 1H, J = 5.4, 7.3 Hz), 2.54-2.49(m, 2H), 2.03(s, 1H); IR (KBr, film): ν 3383, 3076, 3030, 2978, 2906, 1642, 1494, 1455, 1435, 1048, 916, 700 cm⁻¹.

1-(4-Nitrophenyl)-3-buten-1-ol (3b)⁹ ¹H NMR (300MHz, CDCl₃): δ 8.19(dd, 2H, J = 1.8, 8.8 Hz), 7.52(d, 2H, J = 8.5 Hz), 5.58-5.72(m, 1H), 5.23-5.17(m, 2H), 4.86(t, 1H, J = 3.6 Hz), 2.61-2.38(m, 2H), 2.24(d, 1H, J = 3.0 Hz); IR (KBr, film): ν 3416, 3078, 2911, 1641, 1604, 1591, 1347, 1055 cm⁻¹.

1-(2,4-Dichlorophenyl)-3-buten-1-ol (3c)¹⁰ m.p.59.5 °C; ¹H NMR (300MHz, CDCl₃): δ 7.5(d, 1H, J = 8.7 Hz), 7.35(d, 1H, J = 2.2 Hz), 7.26(d, 1H, J = 5.3 Hz), 5.86-5.80(m, 1H), 5.23-5.10(m, 3 H), 2.64-2.59(m, 1H), 2.39-2.33(m, 1H), 2.16(d, 1H, J = 3.3 Hz); IR (KBr): ν 3283, 3080, 2977, 1639, 1591, 1471, 1070 cm⁻¹.

1-(4-Fluorophenyl)-3-buten-1-ol (3d)¹ ¹H NMR (300MHz, CDCl₃): δ 7.30(t, 2H, J = 7.0 Hz), 7.00(t, 2H, J = 8.7 Hz), 5.87-5.72(m, 1H), 5.20-5.13 (m, 2H), 4.70(t, 1H, J = 6.4 Hz), 2.51-2.45(m, 2H), 2.07(s, 1H); IR (KBr, film): ν 3388, 3077, 2980, 2930, 1641, 1605, 1510, 1224 cm⁻¹.

1-(4-Methoxyphenyl)-3-buten-1-ol (3e)¹¹ ¹H NMR (300MHz, CDCl₃): δ 7.27(d, 2H, J = 8.3 Hz), 6.87(dd, 2H, J = 2.6, 7.1 Hz), 5.87-5.73(m, 1 H), 5.19-5.11(m, 2H), 4.67(t, 1H, J = 6.3 Hz), 3.80(s, 3H), 2.52-2.48(t, 2H, J = 7.2 Hz), 2.00(s, 1H); IR (KBr): ν 3407, 3075, 3002, 2933, 2836, 1640, 1612, 1513, 1247 cm⁻¹.

1-(3-Methoxyphenyl)-3-buten-1-ol (3f)¹² ¹H NMR (300MHz, CDCl₃): δ 7.29-7.24(m, 1H), 6.94-6.92(m, 2H), 6.84-6.80(m, 1H), 5.88-5.75(m, 1H), 5.21-5.14(m, 1H), 4.73-4.70(m, 1H), 3.82(S, 3H), 2.53-2.48(m, 2H), 2.04(d, 1H, J =

3.4 Hz); IR (KBr, film): ν 3415, 3075, 2936, 2836, 1641, 1602, 1586, 1489, 1264 cm^{-1} .

1-Phenylhexa-1, 5-dien-3-ol (3g)¹³ ^1H NMR (300MHz, CDCl_3): δ 7.40-7.22(m, 5H), 6.59(d, 1H, J = 15.8 Hz), 6.29-6.21(m, 1H), 5.91-5.82(m, 1H), 5.22-5.15(m, 2H), 4.39-4.35(m, 1H), 2.45-2.38(m, 2H), 1.78(d, 1H, J = 5.0 Hz); IR (KBr, film): ν 3366, 3026, 2978, 2928, 1641, 1599, 1494, 1030 cm^{-1} .

1-(2-Naphthyl)-3-buten-1-ol (3h)¹⁰ ^1H NMR (300MHz, CDCl_3): δ 7.77-7.82 (m, 4 H), 7.44-7.48(m, 3 H), 5.75-5.85(m, 1 H), 5.10-5.19(m, 2 H), 4.84-4.89(m, 1 H), 2.54-2.59(m, 2 H), 2.30(d, 1 H, J = 3.3 Hz). IR (KBr, film): ν 3384, 3072, 3033, 2975, 1638, 1490, 1451, 915, 700 cm^{-1} .

1-(4-Bromophenyl)-3-buten-1-ol (3i)¹⁴ ^1H NMR (300MHz, CDCl_3): δ 7.44-7.48 (m, 2 H), 7.20(d, 2 H, J = 8.1 Hz), 5.71-5.80(m, 1H), 5.11-5.17(m, 2 H), 4.65(t, 1H, J = 5.9 Hz), 2.42-2.48(m, 2 H), 2.26(s, 1 H); IR (KBr, film): ν 3388, 3077, 2978, 2906, 1641, 1591, 1488, 1405, 1068, 1010, 919, 826 cm^{-1} .

1-Undecen-4-ol (3j)¹⁵ ^1H NMR (300MHz, CDCl_3): δ 5.76-5.90 (m, 1 H), 5.10-5.16(m, 2 H), 3.60-3.66(m, 1 H), 2.08-2.34(m, 2 H), 1.74(s, 1 H), 1.28-1.46(m, 12 H), 0.86 (t, 3 H, J = 6.2 Hz); IR (KBr, film): ν 3358, 3077, 2956, 2927, 2856, 1641, 1466, 994, 912 cm^{-1} .

1-cyclohexyl-3-buten-1-ol (3k)⁹ ^1H NMR (300MHz, CDCl_3): δ 5.91-5.77(m, 1H), 5.16-5.11(m, 2H), 3.40-3.37(m, 1H), 2.38-2.30(m, 1H), 2.17-2.07(m, 1H), 1.88-0.99(m, 12H); IR (KBr, film): ν 3391, 3075, 2925, 2853, 1640, 1450 cm^{-1} .

Typical procedure for the three-component reaction promoted by P4a:

To a suspension of **P4a** (66 mg, 0.24 mmol) in acetonitrile (0.8 mL) were added successively benzaldehyde (22 mg, 0.2 mmol), aniline (18 mg, 0.2 mmol) and allyltributyltin (66 mg, 0.2 mmol) at room temperature. After stirred for 5 h (TLC showed the reaction was completed). The suspension was filtered and washed with CH_3CN (3 x 5 mL). The filtrate was concentrated under reduced pressure to furnish the desired product **5a** (44 mg, 99%).

N-(1-Phenylbut-3-enyl)benzenamine (5a)¹⁶ ^1H NMR (300MHz, CDCl_3): δ 7.38-7.20(m, 5H), 7.10-7.04(M, 2H), 6.66-6.61(m, 1H), 6.50-6.47(m, 2H),

5.77-5.71(m, 1H), 5.21-5.12(m, 2H), 4.35(s, 1H), 4.15(s, 1H), 2.45-2.61(m, 2H); IR (KBr, film): ν 3412, 3054, 2914, 1639, 1602, 1504, 1316, 920, 749 cm^{-1} .

***N*-(1-(4-Nitrophenyl)but-3-enyl)benzenamine (5b)**¹⁶ ^1H NMR (300MHz, CDCl_3): δ 8.19-8.15(m, 2H), 7.55-7.51(m, 2H), 7.10-7.05(m, 3H), 6.70-6.65(m, 1H), 6.44-6.41(dd, 2H, $J = 7.5, 1.5$ Hz), 5.80-5.66(m, 1H), 5.24-5.17(m, 2H), 4.47(s, 1H), 4.24(s, 1H), 2.65-2.57(m, 2H); IR (KBr, film): ν 3410, 3077, 3021, 2979, 2914, 2853, 1640, 1603, 1518, 1344, 1289, 1108, 993, 854, 750 cm^{-1} .

***N*-(1-(3-Methoxyphenyl)but-3-enyl)benzenamine (5c)** ^1H NMR (300MHz, CDCl_3): δ 7.26-7.24(m, 2H), 7.11-7.05 (m, 2H), 6.97-6.92 (m, 2H), 6.78-6.75(m, 1H), 6.66-6.61(m, 1H), 6.51-6.47(m, 1H), 5.81-5.71(m, 1H), 5.22-5.12(m, 2H), 4.31(q, 1H, $J = 5.1, 2.7, 5.3$ Hz), 4.13(m, 1H), 3.80(s, 3H), 2.63-2.56(m, 1H), 2.52-2.45(m, 1H); IR (KBr, film): ν 3048, 3015, 2935, 1639, 1602, 1501, 1266, 750 cm^{-1} ; MS (70 eV, EI): 253(M^+ , 3.04), 212(100); Anal. Calcd for $\text{C}_{17}\text{H}_{19}\text{NO}$ (253.15): C 80.60, H 7.56, N 5.53; found C 80.25, H 7.56, N 5.65.

***N*-(1-(Furan-2-yl)but-3-enyl)benzenamine (5d)**¹⁶ ^1H NMR (300MHz, CDCl_3): δ 7.34(s, 1H), 7.16-7.11(m, 2H), 6.67(t, 1H, $J = 7.5$ Hz), 6.59(d, 2H, $J = 7.3$ Hz), 6.27(d, 1H, $J = 1.8$ Hz), 6.15(s, 1H), 5.79-5.70(m, 1H), 5.11(t, 2H, $J = 8.9, 15.9$ Hz), 4.53(t, 1H, $J = 6.0$ Hz), 3.98 (s, 1H), 2.63 (t, 2H, $J = 4.1, 7.1$ Hz); IR (KBr, film): ν 3411, 3035, 2921, 1640, 1603, 1504, 922, 749 cm^{-1} .

***N*-(1-Cyclohexylbut-3-enyl)benzenamine (5e)**¹⁷ ^1H NMR (300MHz, CDCl_3): δ 7.16(td, 2H, $J = 2.1, 5.2, 1.1, 5.7, 2.3$ Hz), 6.65-6.54(m, 3H), 5.85-5.73(m, 1H), 5.08-5.02(m, 2H), 3.52(s, 1H), 3.28(q, 1H, $J = 5.4, 6.9, 5.3$ Hz), 2.37-2.32(m, 1H), 2.22-2.12(m, 1H), 1.85-1.04(m, 11H); IR (KBr, film): ν 3412, 3053, 2961, 2926, 2853, 1640, 1601, 1505, 1259, 1005, 789, 691 cm^{-1} .

***N*-(1-(4-(Benzyloxy)phenyl)but-3-enyl)benzenamine (5f)** m.p. 253.9 $^{\circ}\text{C}$; ^1H NMR (300MHz, CDCl_3): δ 7.44-7.25(m, 7H), 7.11-7.05(m, 2H), 6.92(t, 2H, $J = 6.9, 1.0$ Hz), 6.67-6.61(m, 1H), 6.51-6.48(m, 2H), 5.80-5.71(m, 1H), 5.20-5.12(m, 2H), 5.03(s, 2H), 4.31(t, 1H, $J = 5.8, 6.9$ Hz), 4.12(s, 1H), 2.60-2.44(m, 2H); IR (KBr): ν 3405, 3056, 2931, 1604, 1504, 1242, 747 cm^{-1} . MS (70 eV, EI): 329(M^+ , 0.81), 288(90.91), 91(100); Anal. Calcd for $\text{C}_{23}\text{H}_{23}\text{NO}$ (329.18): C 83.85, H 7.04, N 4.25; found: C

83.55, H 7.17, N 3.96.

2-Fluoro-5-methyl-*N*-(1-phenylbut-3-enyl)benzenamine (5g) R_f 0.89 (petroleum ether/EtOAc 6:1); ^1H NMR (300MHz, CDCl_3): δ 7.36-7.22(m, 5H), 6.85-6.78(m, 1H), 6.36-6.31(m, 1H), 6.21(dd, 1H, $J = 1.9, 6.6$ Hz), 5.76-5.70(m, 1H), 5.21-5.12(m, 2H), 4.39(t, 2H, $J = 5.3, 4.1$ Hz), 2.59-2.54(m, 2h), 2.08(s, 1H); ^{13}C NMR (75MHz, CDCl_3): δ 143.2, 134.2, 128.6, 127.0, 126.2, 118.4, 116.96, 116.90, 113.96, 113.94, 113.87, 113.72, 56.9, 43.1, 21.1; IR (KBr, film): ν 3428, 3062, 3028, 2978, 2923, 2864, 1639, 1619, 1525, 1454, 1328, 1206, 921, 794 cm^{-1} ; MS (70 eV, EI): 255(M^+ , 1.86), 214(100.00); HRMS (EI) calcd for $\text{C}_{14}\text{H}_{13}\text{N}_1\text{F}_1$ (- 41, allyl): 214.10320 found: 214.10282.

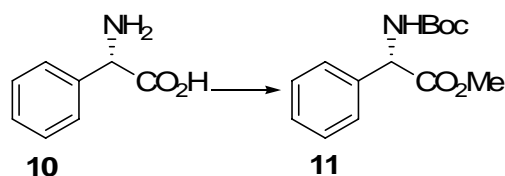
***N*-(1-Phenylbut-3-enyl)-2-(trifluoromethyl)benzenamine (5h)** R_f 0.75 (petroleum ether/EtOAc 6:1); ^1H NMR (300MHz, CDCl_3): δ 7.36-7.22(m, 5H), 7.14(t, 1H, $J = 7.8, 7.9$ Hz), 6.87(d, 1H, $J = 7.1$ Hz), 6.74(s, 1H), 6.58(dd, 1Hz, $J = 2.3, 5.7, 2.0$ Hz), 5.79-5.70(m, 1H), 5.22-5.14(m, 2H), 4.40-4.36(m, 2H), 2.62-2.46(m, 2H); ^{13}C NMR (75MHz, CDCl_3): δ 147.4, 142.6, 134.2, 129.5, 128.7, 127.2, 126.2, 118.6, 116.0, 113.8(q), 110.1(q), 57.0, 43.1; IR (KBr, film): ν 3418, 3064, 3030, 2981, 2916, 1640, 1616, 1516, 1494, 1437, 1345, 1164, 1123, 1069, 994, 698 cm^{-1} ; MS (70 eV, EI): 291(M^+ , 1.11), 250(100.00); HRMS (EI) calcd for $\text{C}_{14}\text{H}_{11}\text{N}_1\text{F}_3$ (- 41, allyl): 250.08436. found: 250.08367.

3,4,5-Trimethoxy-*N*-(1-phenylbut-3-enyl)benzenamine (5i) R_f 0.24 (petroleum ether/EtOAc 6:1); ^1H NMR (300MHz, CDCl_3): δ 7.39-7.21(m, 5H), 5.84-5.73(m, 1H), 5.72(s, 2H), 5.23-5.15(m, 2H), 4.30(q, 1H, $J = 4.8, 3.2, 5.1$ Hz), 4.09(s, 1H), 3.70(s, 3H), 3.66(s, 6H), 2.63-2.56(m, 1H), 2.52-2.45(m, 1H); IR (KBr): ν 3384, 3062, 2998, 2934, 2840, 1639, 1611, 1510, 1453, 1237, 1127, 1010, 911, 732 cm^{-1} ; MS (70 eV, EI): 313(M^+ , 15.7), 272 (100); Anal. calcd for $\text{C}_{19}\text{H}_{23}\text{NO}_3$ (313.17): C 72.82, H 7.40, N 4.47; found C 72.55, H 7.47, N 4.38.

Tributyltin Chloride (6) (the ^1H NMR, GC, and IR spectra are the same with the standard spectra of Tributyltin Chloride). ^1H NMR (300MHz, CDCl_3): δ 1.57-1.69(m, 6 H), 1.27-1.42(m, 12 H), 0.89(t, 9 H, $J = 7.2$ Hz); IR (KBr, film): ν 2957, 2923, 2872, 1464, 1378, 1067, 877, 698, 673 cm^{-1} ; EIMS m/z : 325(M-H^+), 291, 269, 213, 177,

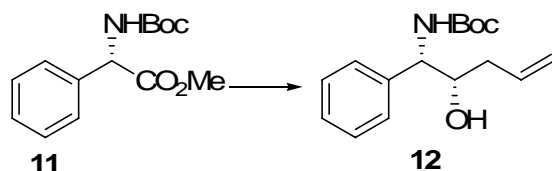
155, 57, 41.

The preparation of **Methyl (S)-2-tert-butoxycarbonylamino-2-phenylacetate (11)**.¹⁸



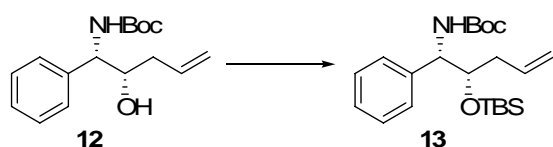
To a solution of L-phenylglycine (7.6g, 50 mmol) in anhydrous MeOH (40 mL) was added SOCl₂ (9 mL) dropwise. After the addition was completed, the mixture was refluxed overnight. The solution was cooled to rt, then ether (30 mL) was added in and white solid was appeared. The solid was filtrated out and dried in vacuum (50°C, 20 mmHg, under P₂O₅) to give **(S)-amino-phenyl-acetic acid methyl ester hydrochloride**, white solid, 7.78g, 78% yield. $[\alpha]_D^{24.1} = +136.0$ ($c = 2.17$, CH₃OH); ¹H NMR (300MHz, D₂O): δ 7.39-7.31 (m, 5H), 5.14 (d, 1H, $J = 3.0$ Hz), 3.67(s, 3 H). To a suspension of **(S)-amino-phenyl-acetic acid methyl ester hydrochloride** (5.29 g, 26 mmol) in 60 mL CH₂Cl₂ was added in Et₃N (7.3 mL, 52mmol). The mixture was cooled to 0 °C and (Boc)₂O (6.0g, 26 mmol, dissolved in 30mL CH₂Cl₂) was added dropwise in with stirring. Then the mixture was warmed to rt and stirred for 38h. The reaction was quenched with saturated NH₄Cl (100mL) and extracted with CH₂Cl₂(2x150 mL). The organic layer was washed with NH₄Cl (1x150mL), then dried with anhydrous Na₂SO₄. After concentration under reduced pressure, compound **11** was obtained, white solid, 7.1g, 99% yield. ¹H NMR (300MHz, CDCl₃): δ 7.37-7.31(m, 5H), 5.54(br s, 1H), 5.33(d, 1H, $J = 7.4$ Hz), 3.71(s, 3H), 1.43(s, 9H); IR (KBr): 3404, 3064,3010, 2983, 2935, 1739, 1730, 1701, 1505, 1441, 1322, 1167, 1053, 1026, 996, 730 cm⁻¹.

The preparation of **tert-butyl (1S, 2S)-2-hydroxy-1-phenylpent-4-enylcarbamate (12)**.¹⁹



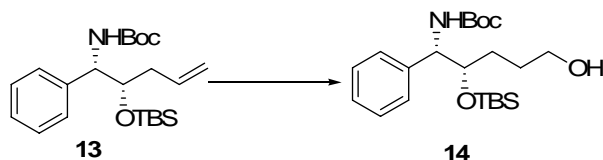
Compound **11** (1.53g, 6 mmol) was dissolved in CH_2Cl_2 (32 mL) and the mixture was cooled to -78°C . DIBAH (13.2 mL, 13.2 mmol, 1.0mol/L in toluene) was added dropwise under -78°C . After the addition completed, the mixture was stirred for 3.5h until material **11** was disappeared. Cooled Methanol (5 mL) was added slowly to quench the excessive DIBAH under -78°C . Saturated ice-cooled NH_4Cl (18mL) was added in slowly at this temperature. Then the mixture was warm to rt and filtered. The filtration residue was wash with CH_2Cl_2 (2x 10 mL). The aqueous phase was extracted with CH_2Cl_2 (3x 20 mL). The combined organic layer was dried over anhydrous Na_2SO_4 for 10 min and then dried again over anhydrous MgSO_4 for another 20min. After the solvent was concentrated under reduced pressure, crude Boc-L-phenylglycinal was obtained. Colorless syrup 1.35g. Crude Boc-L-phenylglycinal was dissolved in CH_2Cl_2 (30 mL) for further use. The solution of Boc-L-phenylglycinal in CH_2Cl_2 (7.5 mL, 1.5mmol) was concentrated under reduced pressure to remove CH_2Cl_2 . Then **P4a** (0.41g, 1.5 mmol, 3.65mmol/g), CH_3CN (3mL), and allyltributyltin (496.5mg, 1.5mmol) were added in successively. The mixture was stirred overnight and the insoluble polymer was filtrated off. The filtrate was concentrated under reduced pressure to afford crude product **12** without further purification, white solid, 379mg, 91% yield. $[\alpha]_{\text{D}}^{23.7} = +13.41$ (c 1.05, CHCl_3); ^1H NMR (300MHz, CDCl_3): δ 7.38-7.24(m, 5H), 5.88-5.81(m, 1H), 5.38(d, 1H, $J = 6.5\text{Hz}$), 5.18-5.10(m, 2H), 4.67(br s, 1H), 3.87(br d, 1H, $J = 6.5\text{Hz}$), 2.34-2.27(m, 2H), 1.97 (br s, 1H), 1.42(s, 9H); IR (KBr, film): 3386, 2976, 2932, 1685, 1638, 1517, 1391, 1169, 1021, 911 cm^{-1} ; MS (ESI): 300 ($\text{M} + \text{Na}^+$); HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{23}\text{NO}_3\text{Na}$: 300.1565; found 300.1570.

The preparation of **tert-butyl (1S, 2S)-2-(tert-butyldimethylsilyloxy)-1-phenylpent-4-enylcarbamate (13)**.²⁰



12 (223mg, 0.81mmol) and 2, 6-lutidine (188μL, 1.61mmol) were dissolved in anhydrous CH₂Cl₂ (7mL) with stirring. After the solution was cooled to 0 °C with an ice-bath, TBSOTf (1.21mmol, 277μL) was added in. The mixture was stirred overnight, then was quenched with saturated NH₄Cl (10mL), extracted with Et₂O (3 x 15mL), and dried over anhydrous Na₂SO₄. After concentration, the crude product was purified by silica gel chromatography (eluent: petroleum ether / EtOAc 30:1(v/v)) to afford compound **13**, 250mg, colorless syrup, 89% yield. ¹H NMR (300MHz, CDCl₃): δ 7.31-7.19(m, 5H), 5.94-5.80(m, 1H), 5.39(br d, 1H, *J* = 8.3Hz), 5.17-5.12(m, 2H), 4.79(d, 1H, *J* = 8.7Hz), 3.83(br s, 1H), 2.43-2.24(m, 2H), 1.46(s, 9H), 0.78(s, 9H), -0.17(s, 3H), -0.54(s, 3H); IR (KBr, film): 3451, 3065, 2929, 2857, 1722, 1641, 1492, 1365, 1171, 1086, 836 cm⁻¹.

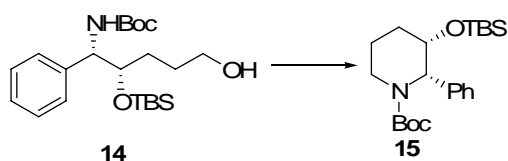
The preparation of **tert-butyl (1*S*, 2*S*)-2-(tert-butyldimethylsilyloxy)-5-hydroxy-1-phenylpentylcarbamate (14)**.²⁰



A solution of borane-dimethyl sulfide (0.3mL, 0.6mmol, 2M in THF) was added into the solution of **13** (78.3mg, 0.2mmol) in dry THF (8mL) under 0 °C with stirring. The mixture was then stirred for 4h at rt. The excess B₂H₆ was quenched carefully with water (0.2mL). Then NaOH (2.3mL, 3M) and H₂O₂ (1.3mL, 30%) were added in successively. The mixture was stirred overnight at rt. THF was removed under reduced pressure and the residue was extracted by EtOAc (3 x 15mL), dried over anhydrous Na₂SO₄. After concentration, the crude product was purified by silica gel chromatography (eluent: petroleum ether / EtOAc 7:1 to 1:1 (v/v)) to afford product **14**, 61mg, Colorless oil, 74.5%. [α]_D^{27.4} = +4.66 (*c* 1.42, CHCl₃); ¹H NMR (300MHz, CDCl₃): δ 7.27-7.15 (m, 5H), 5.37(d, 1H, *J* = 9.0Hz), 4.76(d, 1H, *J* = 8.7Hz), 3.80(br d, 1H, *J* = 7.2Hz), 3.63(t, 2H, *J* = 5.6, 6.0Hz), 1.99(br s, 1H), 1.70-1.50(m, 4H), 1.40(s,

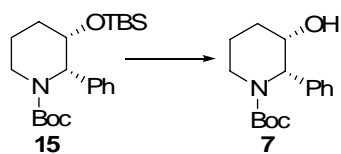
9H), 0.72(s, 9H), -0.21(s, 3H), -0.59(s, 3H); ^{13}C NMR (75MHz, CDCl_3): δ 155.94, 128.15, 126.85, 126.45, 79.57, 76.53, 62.66, 56.25, 31.55, 28.86, 28.39, 25.87, 17.93, -4.83, -5.64; IR (KBr, film): 3445, 3063, 2953, 2930, 2857, 1702, 1496, 1366, 1171, 1066, 836 cm^{-1} ; MS(ESI): 432.1(M + Na) $^{+}$; HRMS(ESI)calcd for $\text{C}_{22}\text{H}_{39}\text{NO}_4\text{SiNa}$: 432.2543; found 432.2540.

The preparation of **(2*S*,3*S*)-tert-butyl 3-(tert-butyldimethylsilyloxy)-2-phenylpiperidine-1-carboxylate (15)**.²⁰



To a solution of **14** (47mg, 0.12mmol) in anhydrous CH_2Cl_2 (3mL) was added MsCl (26mg, 0.23mmol) at -78°C with stirring. Then Et_3N was added in slowly at this temperature. The mixture was stirred for 3 h at -78°C , then was quenched with saturated NH_4Cl (1mL), and warmed to room temperature. The mixture was extracted with CH_2Cl_2 (3 x 5mL). The combined organic layer was washed with saturated NaHCO_3 (1 x 5mL), dried over anhydrous Na_2SO_4 and concentrated to afforded a colorless oil, 50mg. The oil was dissolved in anhydrous THF (2.5mL) and cooled with an ice-bath. $t\text{-BuOK}$ (22mg, 0.2mmol) was added at 0°C with stirring, then warmed to room temperature and stirred overnight. The reaction was quenched with saturated NH_4Cl (4mL), extracted with CH_2Cl_2 (3 x 8mL), and dried over anhydrous Na_2SO_4 . After concentration, the crude product was purified by silica gel chromatography (eluent: petroleum ether / EtOAc 30:1 (v/v)) to afford product **15**, 45mg, pale yellow oil, 99% yield. $[\alpha]_{\text{D}}^{27.1} = +16.28$ (c 1.27, CHCl_3); ^1H NMR (300MHz, CDCl_3): δ 7.59-7.56(m, 2H), 7.34(m, 3H), 5.39(d, 1H, $J = 5.0\text{Hz}$), 4.10-4.03(m, 1H), 3.97(d, 1H, $J = 13.6\text{Hz}$), 2.77-2.67(m, 1H), 2.00-1.87(m, 1H), 1.79-1.60(m, 3H), 1.48(s, 9H), 0.90(s, 9H), 0.12(s, 3H), 0.03(s, 3H); ^{13}C NMR (75MHz, CDCl_3): δ 155.29, 138.89, 128.50, 127.91, 126.46, 126.41, 79.71, 71.90, 30.86, 28.71, 28.42, 25.79, 24.01, 18.03, -4.89, -5.04; IR (KBr, film): 3092, 3060, 2931, 2858, 1693, 1462, 1410, 1365, 1254, 1174, 1143, 1090, 977, 838; MS(ESI): 414.2(M+Na) $^{+}$; HRMS(ESI) calcd for $\text{C}_{22}\text{H}_{37}\text{NO}_3\text{SiNa}$: 414.2438; found 414.2434.

The preparation of *N*-Boc-(2*S*,3*S*)-3-hydroxy-2-phenylpiperidine (**7**)^{20, 21, 22}

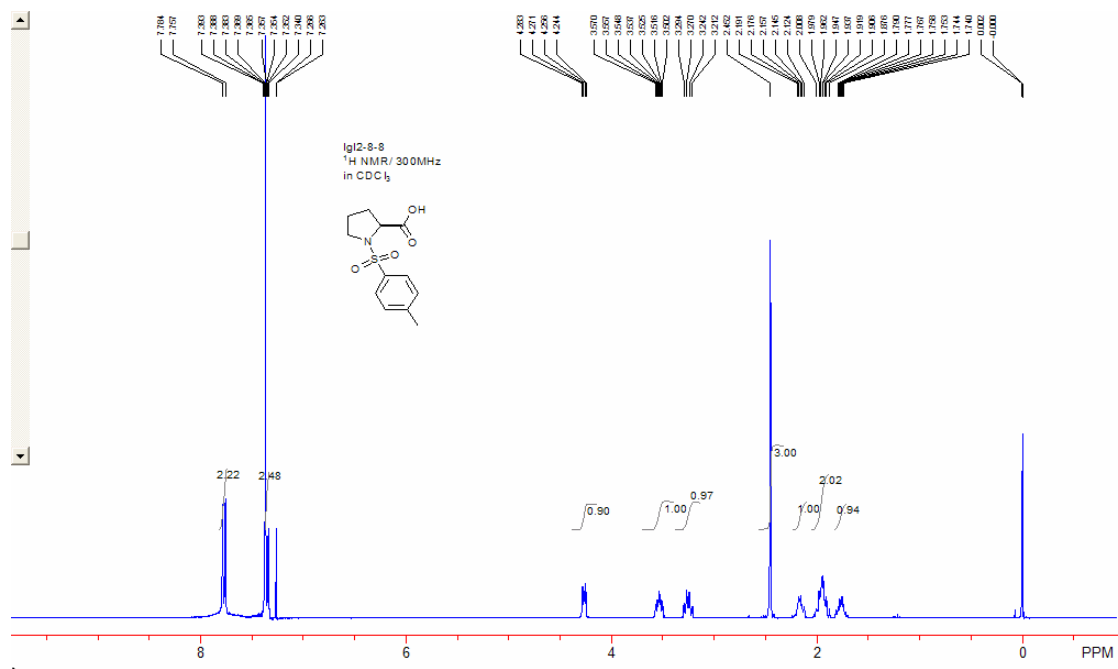


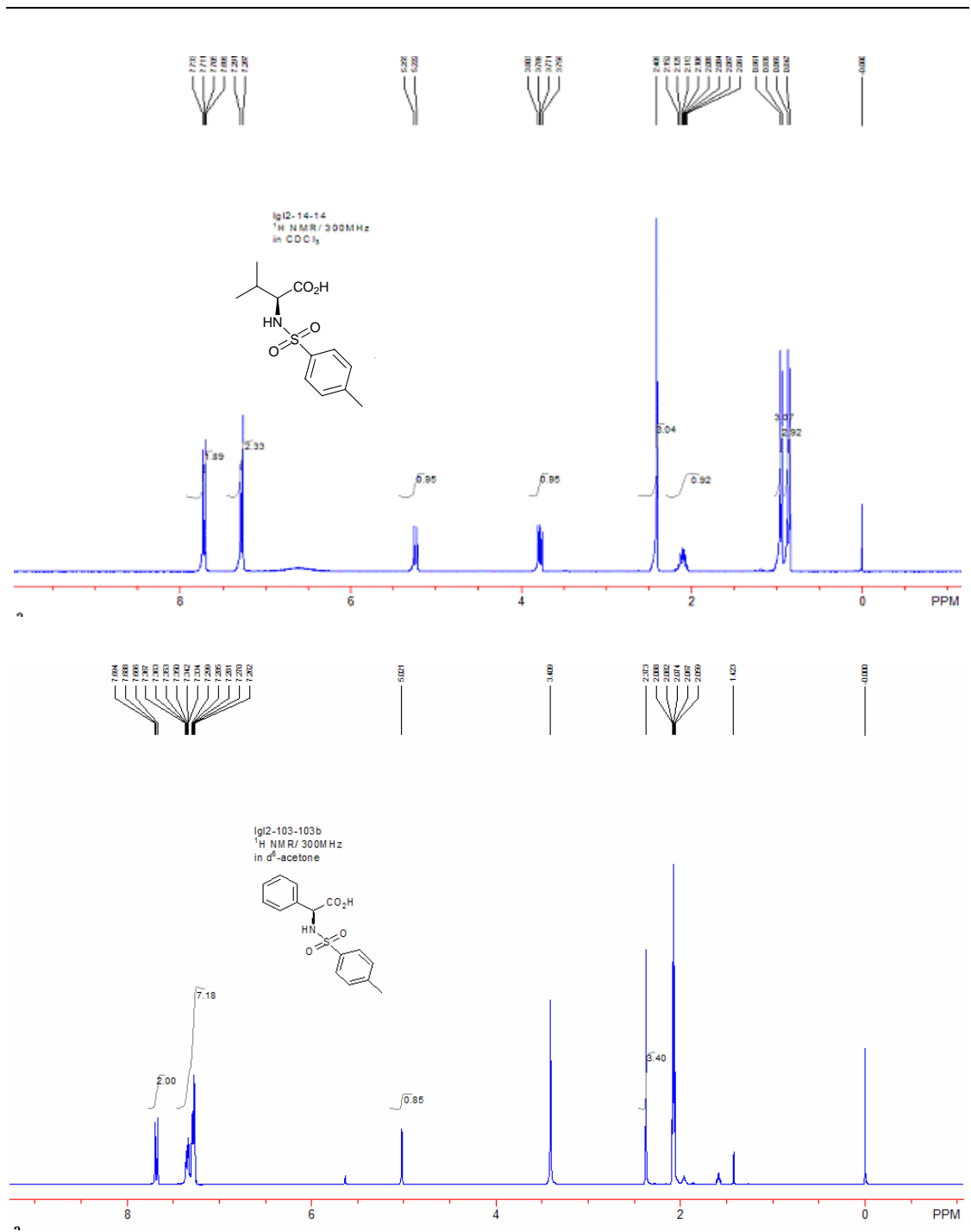
To a solution of **15** (30mg, 0.076mmol) in anhydrous THF (1.5mL) was added 4 Å molecular sieve (15mg) and TBAF (120μL, 0.12mmol, 1M in THF) successively with stirring. The mixture was stirred overnight, then was quenched with water (2mL) at 0 °C and diluted with CH₂Cl₂ (5mL). After being stirred for about 10 minutes, the mixture was filtered, washed and extracted with CH₂Cl₂ (3 x 8mL), dried over anhydrous Na₂SO₄. After concentration, the crude product was purified by silica gel chromatography (eluent: petroleum ether / EtOAc 8:1 (v/v)) to afford product **7**, pale yellow oil, 20mg, 95% yield. $[\alpha]_D^{25.7} = +33.17$ (*c* 0.50, CHCl₃); ¹H NMR (300MHz, CDCl₃): δ 7.46(d, 2H, *J* = 7.4Hz), 7.35-7.23(m, 3H), 5.33(d, 1H, *J* = 5.8Hz), 4.11-4.04(m, 1H), 4.02(dd, 1H, *J* = 5.3, 7.7Hz), 3.06-2.97(ddd, 1H, *J* = 4.3, 9.6, 12.4, 3.3Hz), 1.85-1.66(m, 5H), 1.37(s, 9H); ¹³C NMR (75MHz, CDCl₃): δ 155.41, 138.51, 128.39, 128.34, 127.14, 79.88, 70.07, 59.26, 39.47, 28.32, 27.72, 23.10; IR (KBr, film): 3437, 3060, 2939, 2868, 1690, 1666, 1451, 1414, 1366, 1253, 1171, 1147, 1082, 964, 700; MS(ESI): 300.1(M+Na)⁺; HRMS(ESI) calcd for C₁₆H₂₃NO₃Na: 300.1570; found 300.1570.

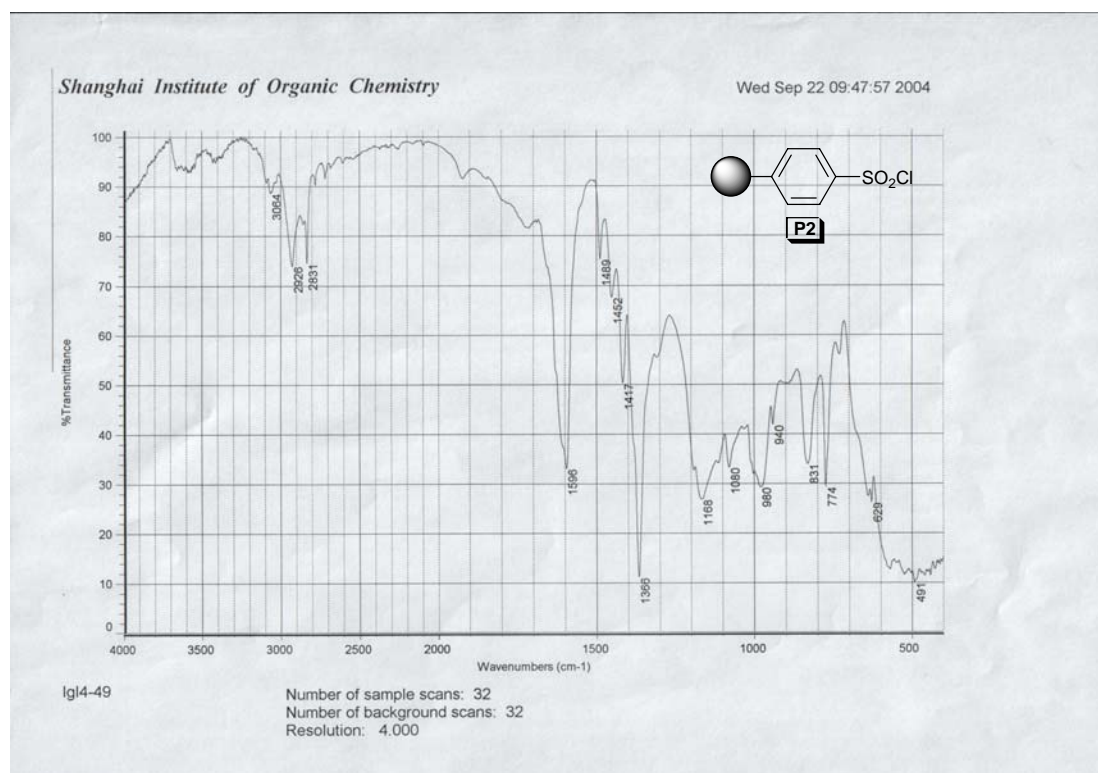
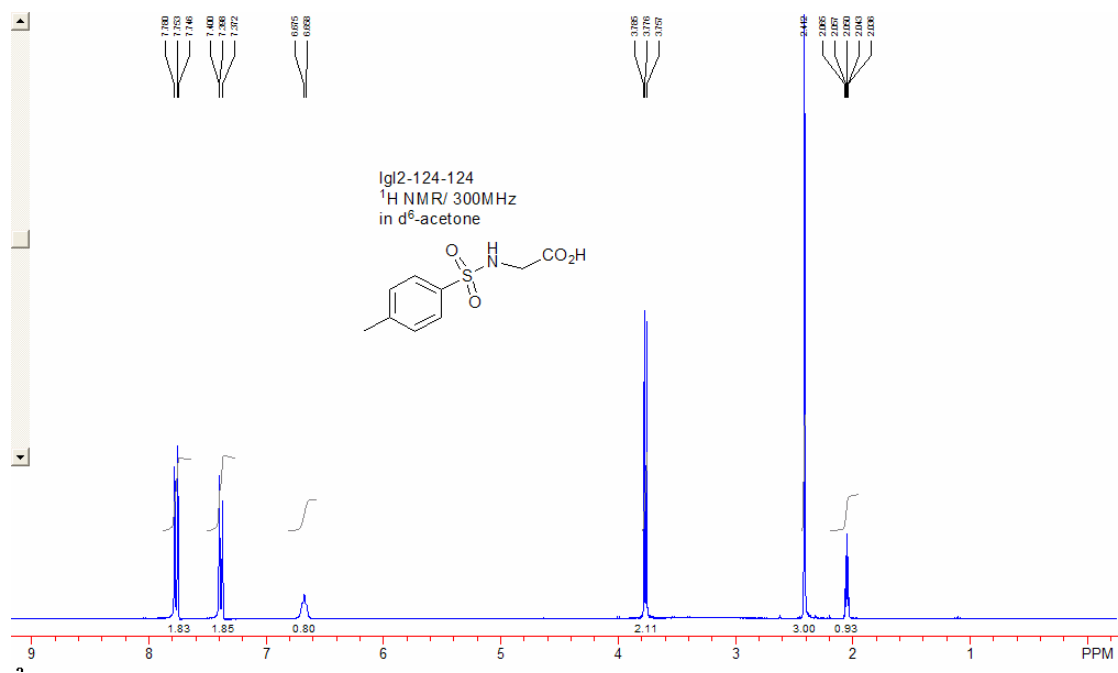
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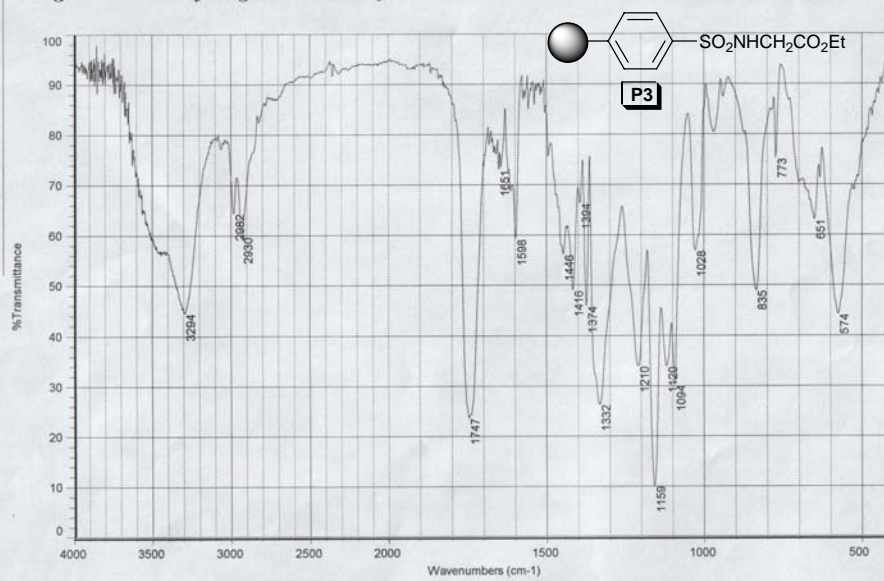
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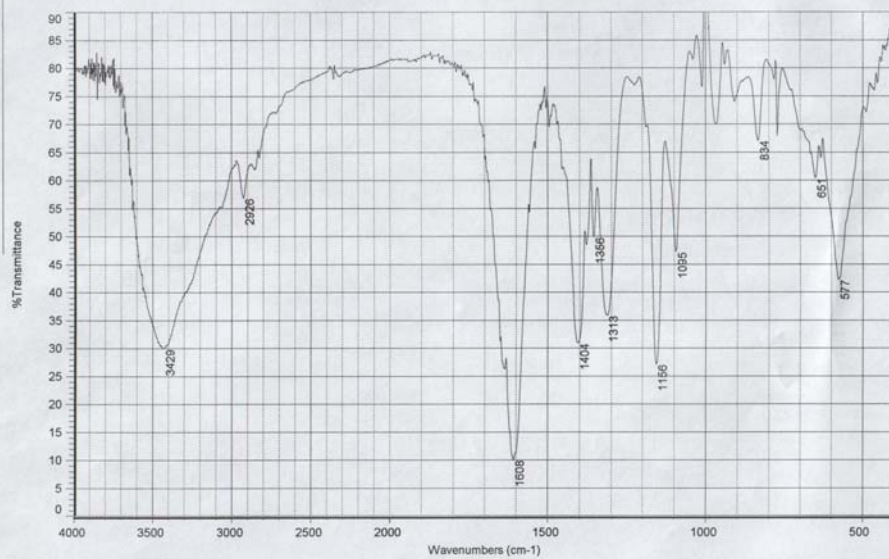






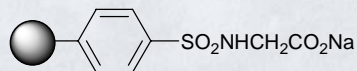
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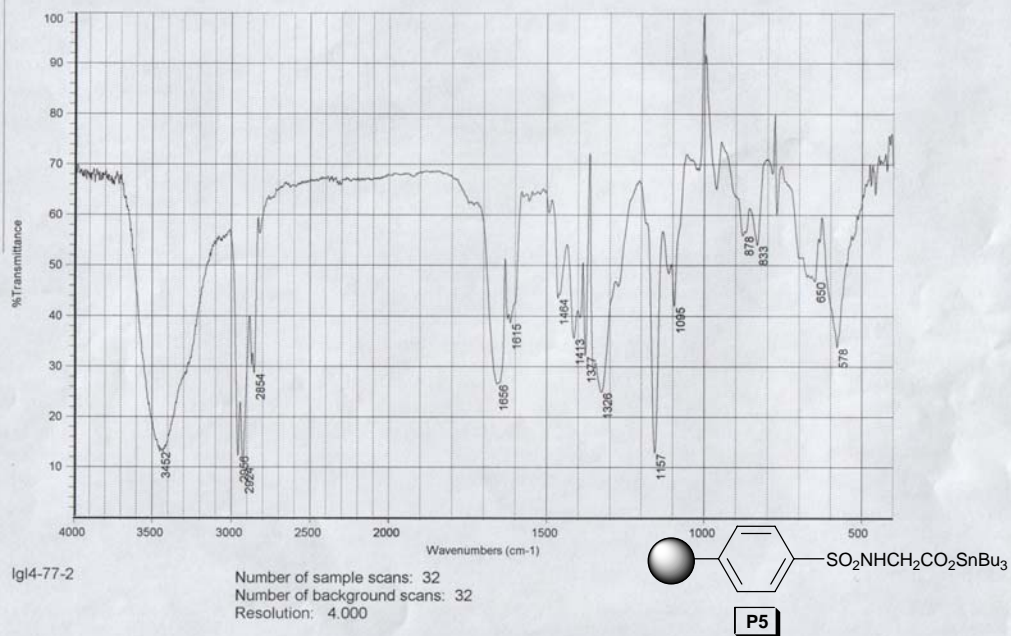
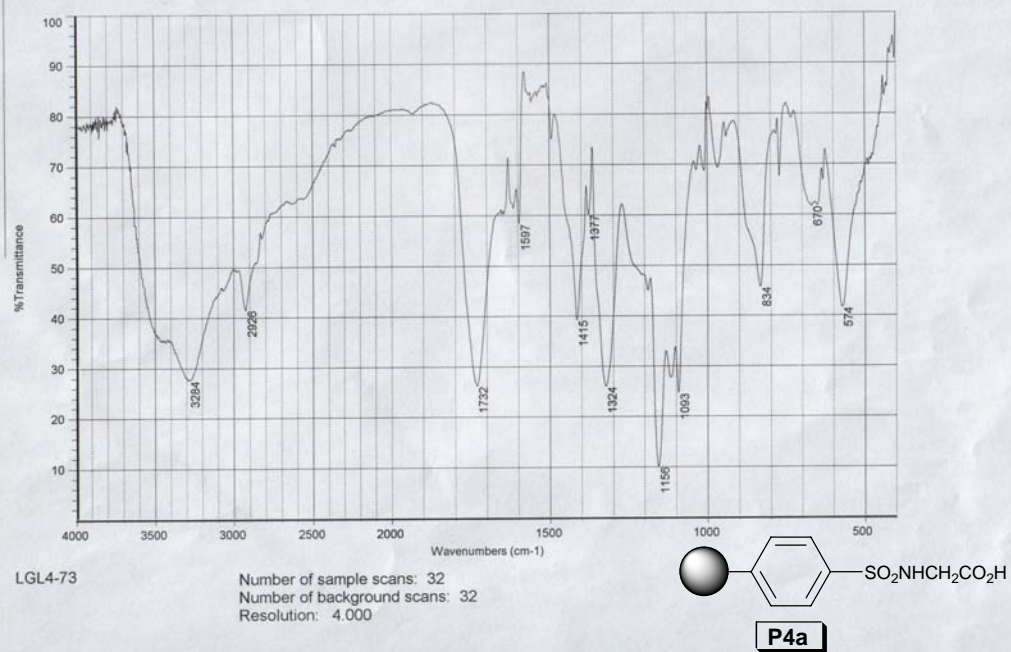
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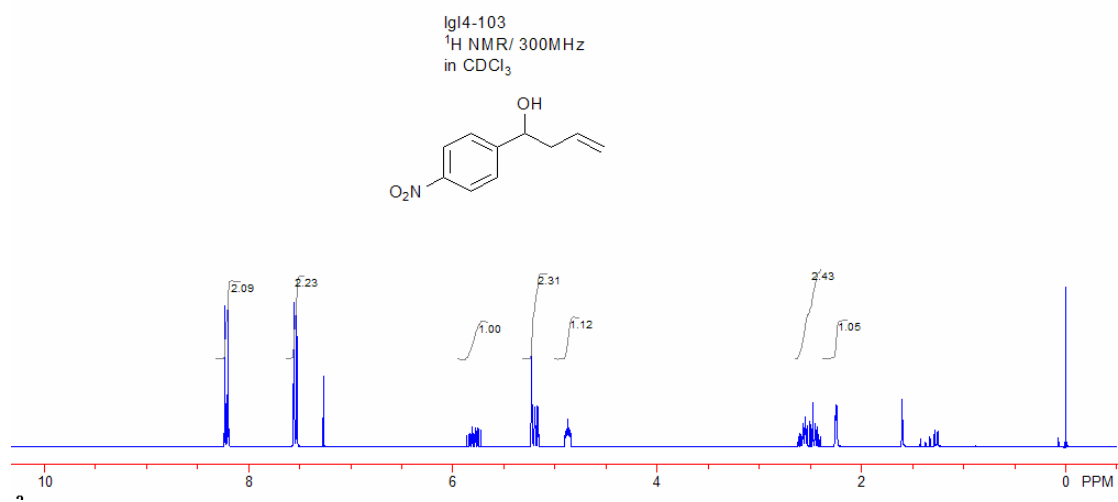
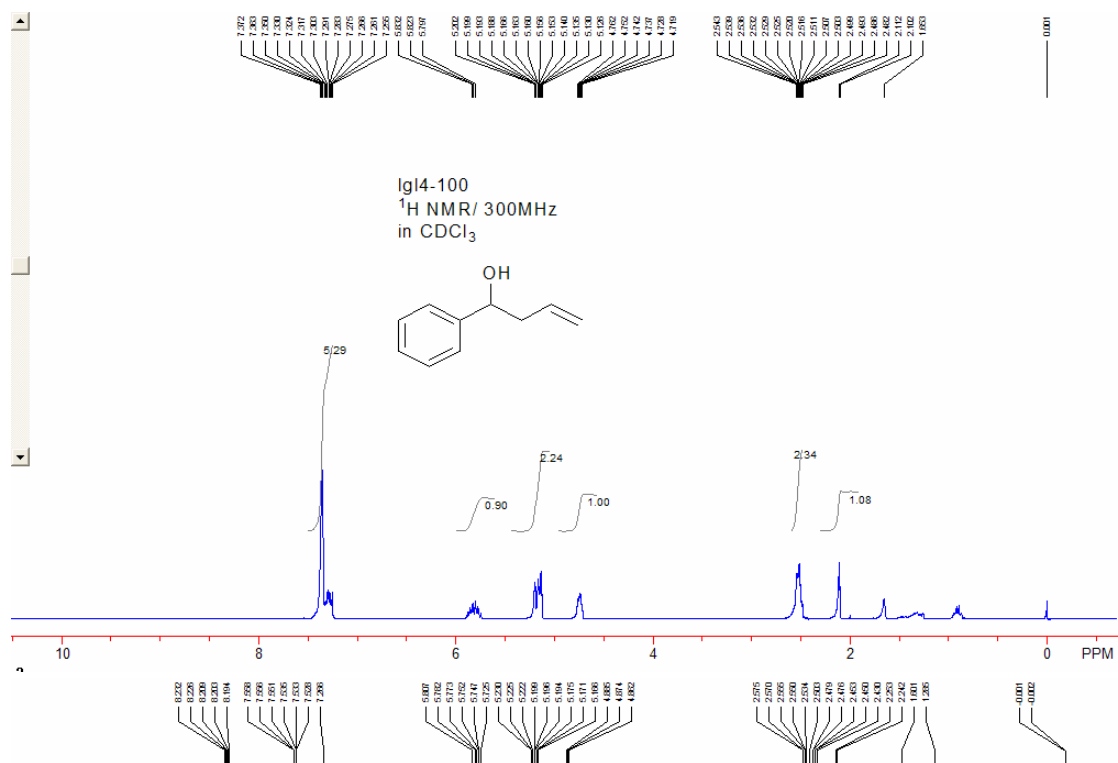


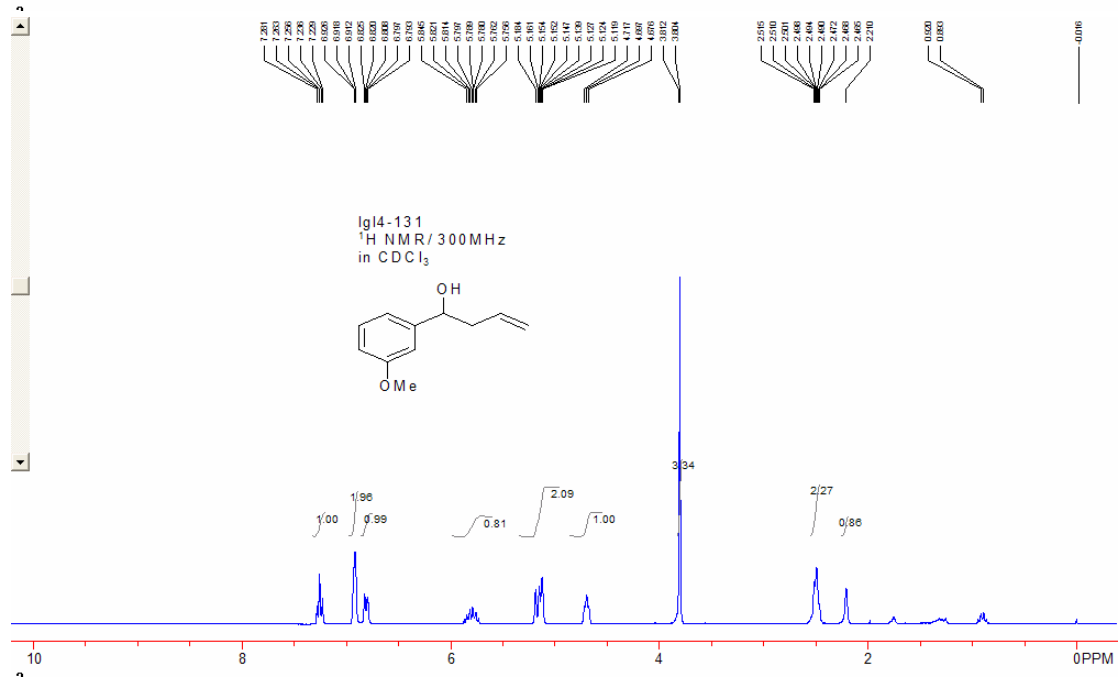
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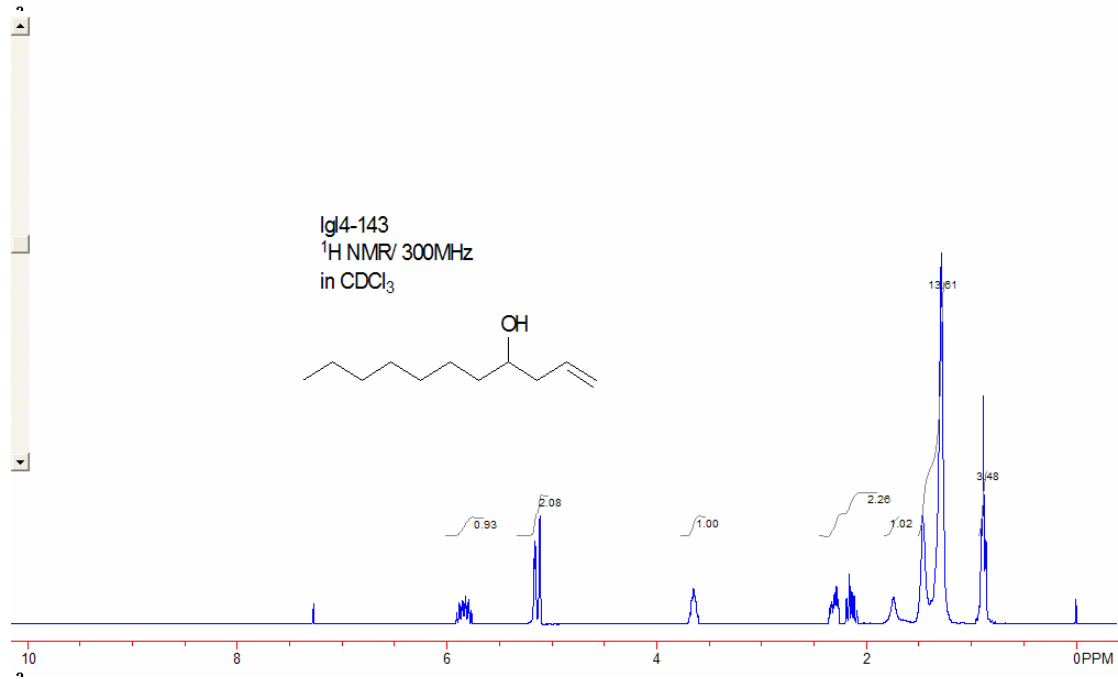
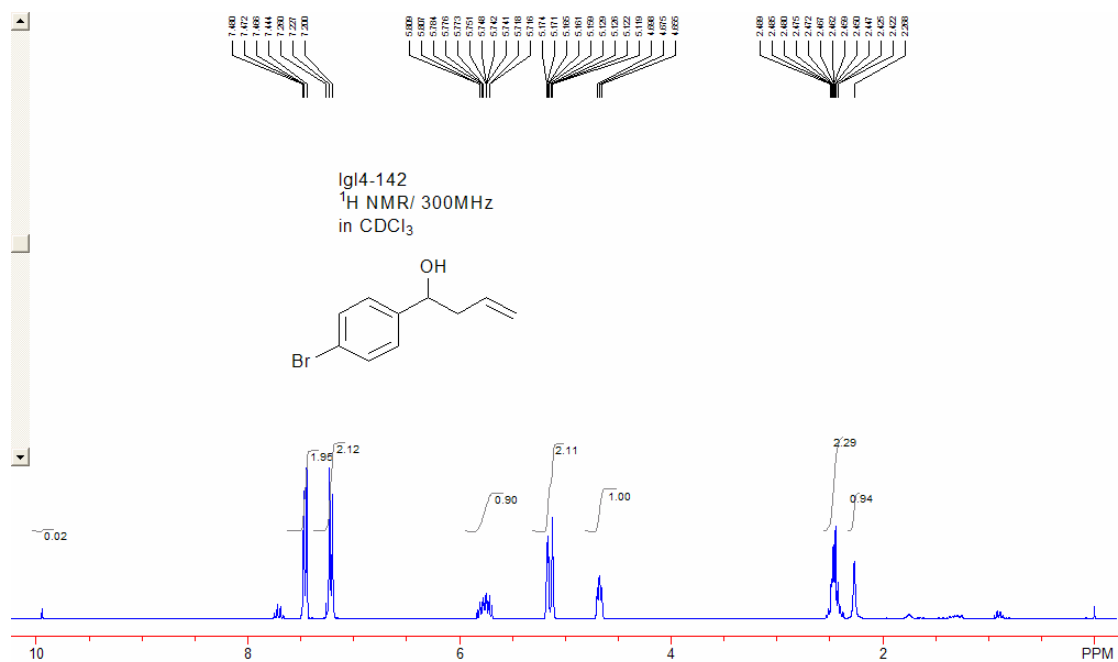
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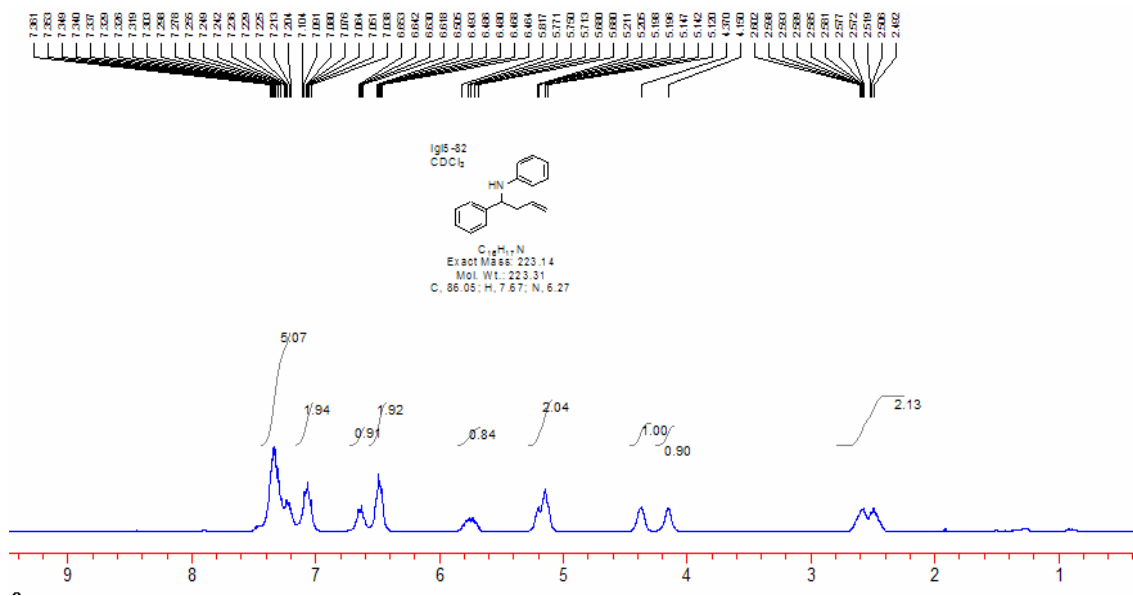


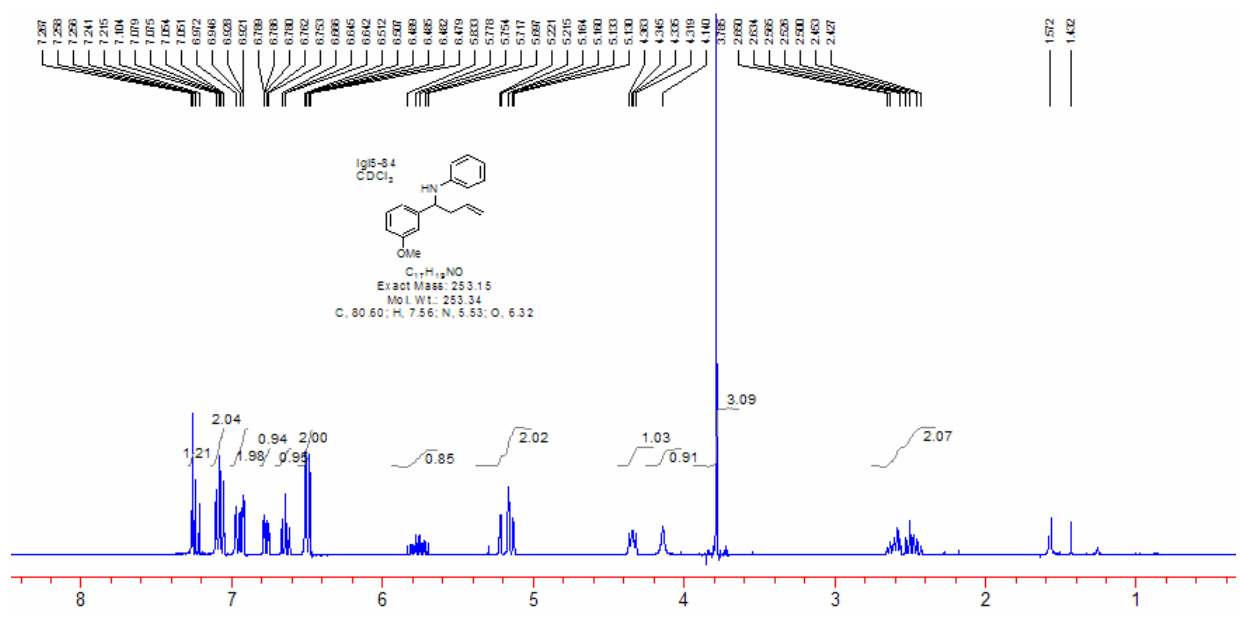
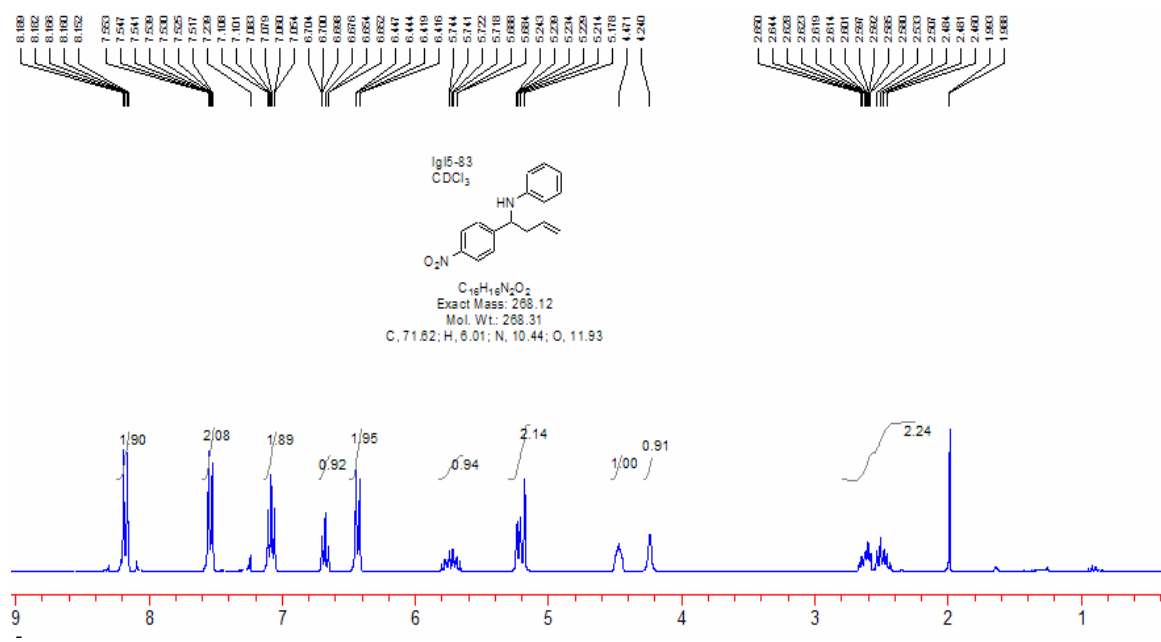


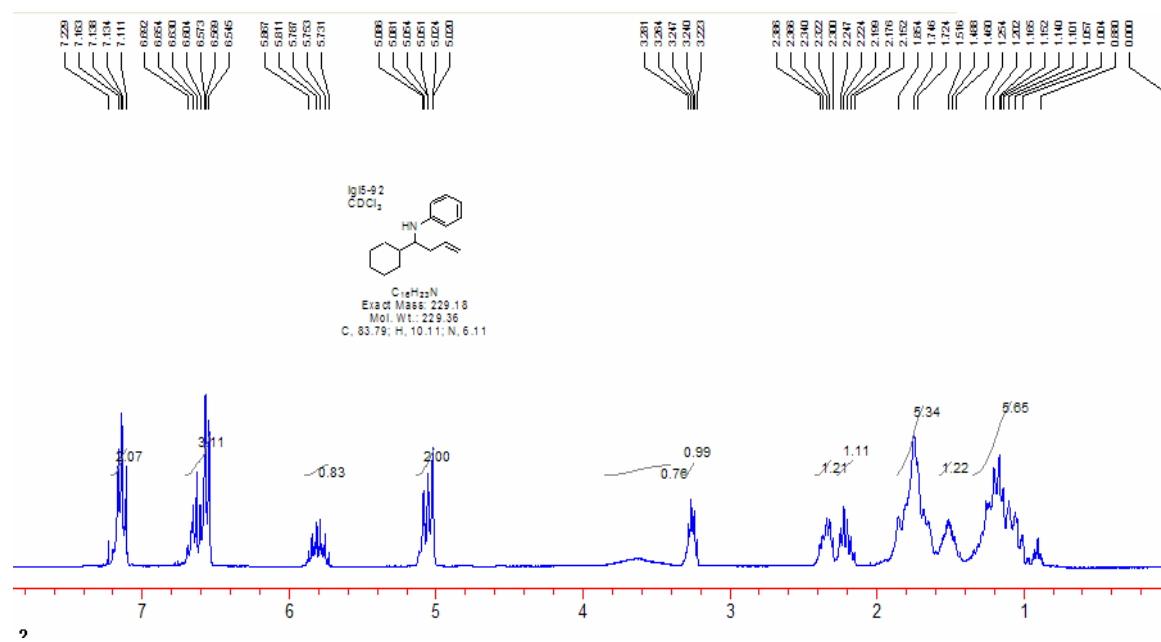
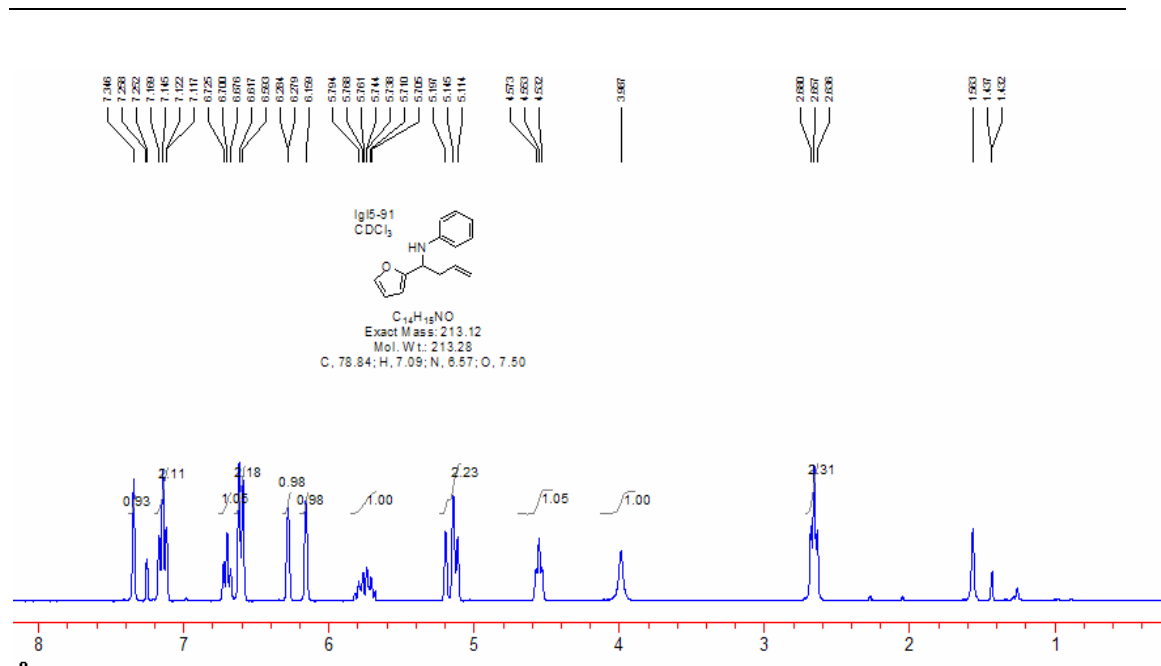


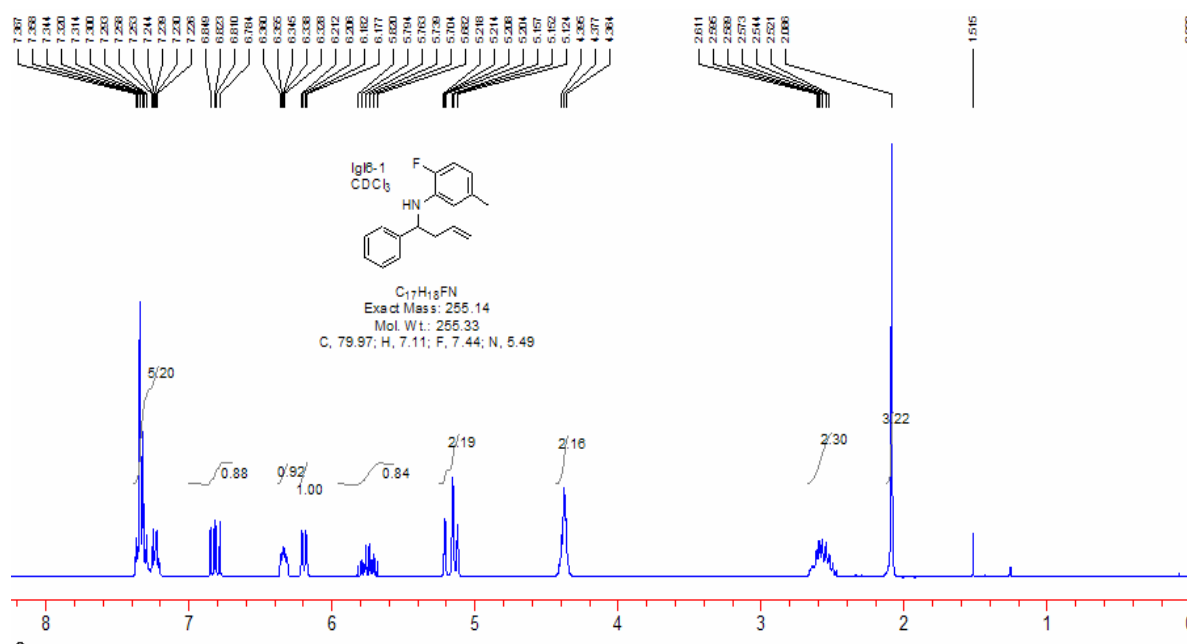
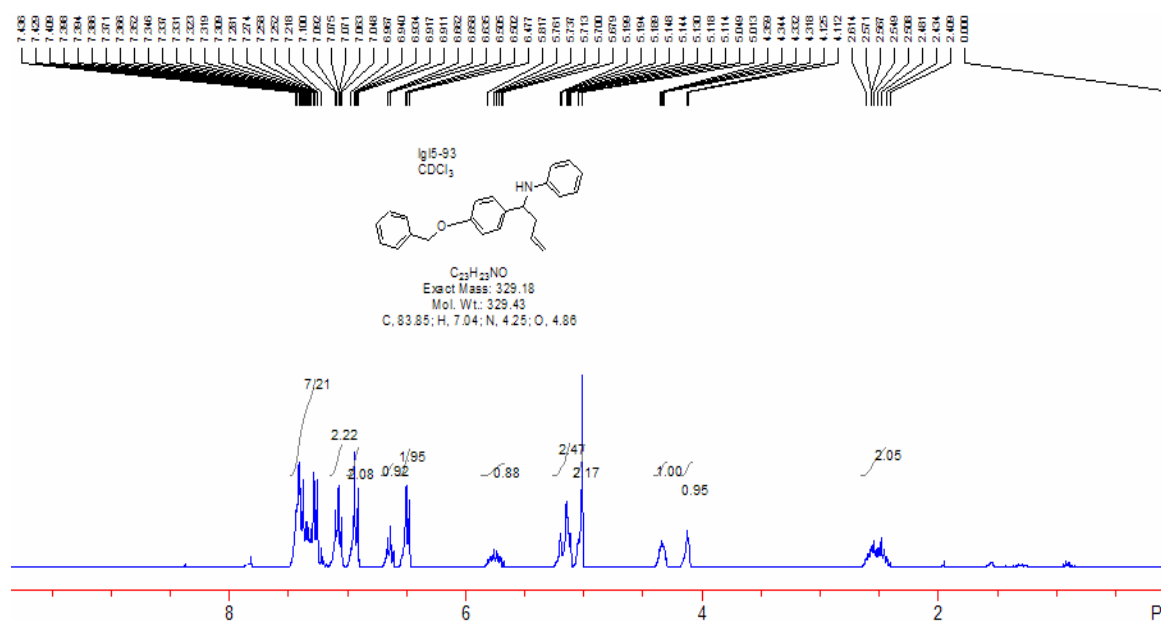


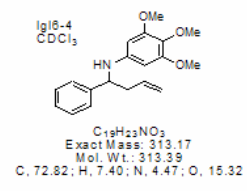
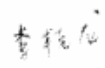


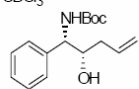
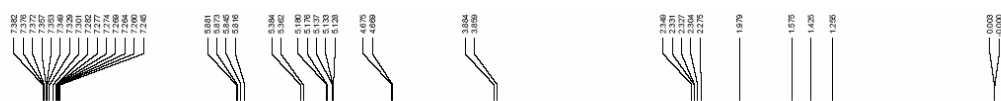












Chemical Formula: $C_{16}H_{23}NO_3$
Exact Mass: 277.17
Molecular Weight: 277.36

