

**Direct sp^3 C-H Bond Arylation, Alkylation, and Amidation of Tetrahydroisoquinolines
Mediated by Hypervalent Iodine(III) under Mild Conditions**

Supporting Information

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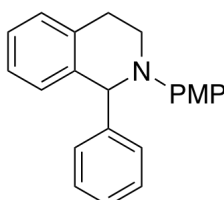
1. General

NMR spectra were recorded on a JEOL JNM-AL400 spectrometer operating at 400 MHz and 100 MHz for ^1H and ^{13}C acquisitions, respectively. Chemical shifts are reported in ppm with a solvent resonance as an internal standard (^1H -NMR; tetramethylsilane or chloroform as internal standards, indicating 0 or 7.26, respectively, ^{13}C -NMR; chloroform as internal standard, indicating 77.00). Data is reported as follows: s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants in Hz; integration. IR spectra were recorded with a SHIMADZU IRAffinity-1 spectrometer. Specific rotation was measured with a JASCO DIP-1000 digital polarimeter. MS spectra were recorded with a JEOL JMS-700N mass spectrometer with fast atom bombardment (FAB) and a double-focusing magnetic sector mass analyzer for MS and HRMS measurements. TLC analysis for the sp^3 C–H bond arylation and alkylation was performed on commercial glass plates bearing a 0.25 mm layer of Merck TLC Silica gel 60 F₂₅₄. TLC analysis for the sp^3 C–H bond amidation was performed on commercial glass plates bearing a 0.25 mm layer of Merck TLC Aluminium oxide 60 F₂₅₄, basic. Silica gel chromatography for the sp^3 C–H bond arylation and alkylation was carried out Merck Silica gel 60 (70-230 mesh). Silica gel chromatography for the sp^3 C–H bond amidation was carried out Merck Aluminium oxide 90 active neutral (70-230 mesh).

2. Experimental details and characterization data for all compounds

2-1. sp^3 C-H bond arylation and alkylation of THIQs

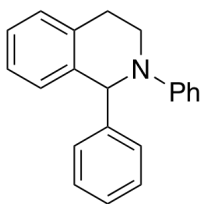
1-Phenyl-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (1)¹



After stirring the mixture of 2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (95.7 mg, 0.4 mmol) and [bis(trifluoroacetoxy)iodo]benzene (172.1 mg, 0.40 mmol) in 2-MeTHF or 1,2-dichloroethane (4.0 mL) in a vial at room temperature for 10 min under Ar atmosphere, phenylmagnesium bromide (1.0 M in THF, 8.0 mL, 0.80 mmol) was added to the solution at 0 °C. After stirring vigorously for 3 hours at 0 °C, the reaction mixture was quenched with saturated aqueous NH_4Cl and saturated aqueous NaHCO_3 , then extracted with ethyl acetate. The organic layer was washed with water and brine, dried over MgSO_4 , filtrated, and concentrated in *vacuo*. The residue was purified by SiO_2 column chromatography (*n*-hexane/ether = 100/0-100/5) to give 1-phenyl-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline **1** (125.2 mg, 99%) as pale yellow solid.

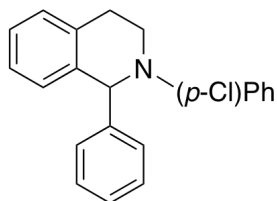
125.2 mg (99%). Pale yellow solid. R_f = 0.29 (AcOEt/*n*-Hexane, 1 : 10). M.p. 128–129 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.30-7.10 (9H, m), 6.90-6.75 (4H, m), 5.66 (1H, s), 3.74 (3H, s), 3.65-3.53 (1H, m), 3.50-3.35 (1H, m), 3.05-2.85 (2H, m). ^{13}C NMR (100 MHz, CDCl_3) δ 152.9, 144.4, 143.2, 137.7, 135.5, 128.4, 128.1, 128.1, 128.0 (2C), 126.8, 126.7 (2C), 126.0, 117.7 (2C), 114.5 (2C), 64.3, 55.6, 44.5, 28.1. IR (solid) 3022, 2918, 2822, 1606, 1506, 1450, 1032, 826 cm^{-1} . MS (FAB) m/z (rel intensity) 316 ($\text{M}+\text{H}^+$, 25), 315 (M^+ , 45), 307 (25), 289 (15), 238 (20), 154 (100), 136 (70), 107 (20). HRMS (FAB) Calcd for $\text{C}_{22}\text{H}_{22}\text{NO}$ ($\text{M}+\text{H}^+$): 316.1696, found, 316.1726. Anal Calcd for $\text{C}_{22}\text{H}_{21}\text{NO}$: C, 83.78; H, 6.71. Found: C, 83.70; H, 7.00.

1-Phenyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (2)¹



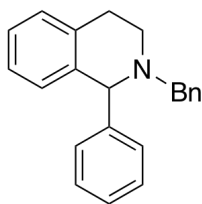
113.1 mg (99%). White solid. $R_f = 0.27$ (Et₂O/*n*-Hexane, 1 : 20). M.p. 62–64 °C (lit.¹ M.p. 62–64 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.35–7.10 (11H, m), 6.85 (2H, d, $J = 8.8$ Hz), 6.75 (1H, t, $J = 7.3$ Hz), 5.83 (1H, s), 3.80–3.67 (1H, m), 3.55–3.45 (1H, m), 3.00–2.85 (2H, m). ¹³C NMR (100 MHz, CDCl₃) δ 149.5, 143.1, 137.9, 135.7, 129.1 (3C), 128.2 (2C), 128.1, 127.8, 127.3 (2C), 127.0, 126.8, 126.1, 117.4, 113.8, 62.8, 43.8, 28.0. IR (solid) 3020, 2916, 2853, 1593, 1503, 1381, 1250, 746 cm⁻¹. MS (FAB) m/z (rel intensity) 286 (M+H⁺, 40), 285 (M⁺, 60), 208 (45), 154 (100), 136 (65), 107 (15). HRMS (FAB) Calcd for C₂₁H₂₀N (M+H⁺): 286.1590, found, 286.1574.

1-Phenyl-2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (3)²



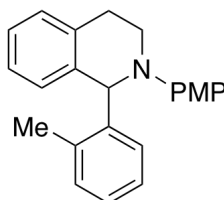
127.0 mg (>99%). Colorless viscous oil. $R_f = 0.53$ (EtOAc/*n*-Hexane, 1 : 9). ¹H NMR (400 MHz, CDCl₃) δ 7.35–7.10 (11H, m), 6.74 (2H, d, $J = 9.0$ Hz), 5.75 (1H, s), 3.69 (1H, dt, $J = 11.2$, 5.4 Hz), 3.46 (1H, ddd, $J = 11.2$, 8.3, 5.9 Hz), 3.00–2.85 (2H, m). ¹³C NMR (100 MHz, CDCl₃) δ 148.1, 142.6, 137.6, 135.5, 128.2 (2C), 128.3, 128.1, 127.7, 127.2, 127.1 (2C), 126.9, 126.3 (2C), 122.2, 115.0 (2C), 62.9, 44.1, 28.0. IR (neat) 3024, 2909, 2843, 1593, 1491, 1383, 1331, 1217 cm⁻¹. MS (FAB) m/z (rel intensity) 320 (M+H⁺, 65), 319 (M⁺, 100), 242 (80), 179 (15), 165 (15), 115 (10). HRMS (FAB) Calcd for C₂₁H₁₉ClN (M+H⁺): 320.1201, found, 320.1207.

1-Phenyl-2-benzyl-1,2,3,4-tetrahydroisoquinoline (4)¹



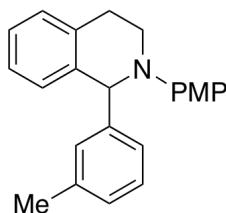
97.8 mg (82%). White solid. $R_f = 0.48$ (AcOEt/*n*-Hexane, 1 : 10). M.p. 106–109 °C (lit.¹ M.p. 106–109 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.50–7.17 (10H, m), 7.17–7.05 (2H, m), 6.99 (1H, t, $J = 7.8$ Hz), 6.72 (1H, d, $J = 7.8$ Hz), 4.60 (1H, s), 3.81 (1H, d, $J = 13.6$ Hz), 3.24 (1H, d, $J = 13.6$ Hz), 3.15–3.00 (2H, m), 2.82–2.70 (1H, m), 2.60–2.45 (1H, m). ¹³C NMR (100 MHz, CDCl₃) δ 144.4, 139.6, 138.5, 134.8, 129.6 (2C), 128.8, 128.7 (2C), 128.4, 128.3 (2C), 128.1 (2C), 127.2, 126.8, 125.9, 125.6, 68.8, 58.8, 47.3, 29.2. IR (solid) 3027, 2930, 2808, 1598, 1489, 1450, 1256, 1123 cm⁻¹. MS (FAB) m/z (rel intensity) 300 (M+H⁺, 40), 298 (65), 222 (95), 154 (20), 136 (20), 91 (100). HRMS (FAB) Calcd for C₂₂H₂₂N (M+H⁺): 300.1747, found, 300.1777.

1-(2-Tolyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (5)¹



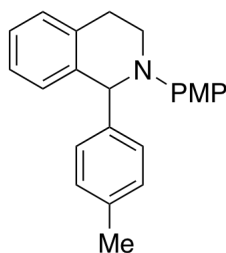
125.7 mg (95%). White solid. $R_f = 0.40$ (EtOAc/*n*-Hexane, 1 : 10). M.p. 124–126 °C (lit.¹ M.p. 124–126 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.20–7.05 (5H, m), 7.05–6.97 (1H, m), 6.97–6.90 (1H, m), 6.92 (2H, d, $J = 8.9$ Hz), 6.80–6.70 (1H, m), 6.74 (2H, d, $J = 8.9$ Hz), 5.65 (1H, s), 3.72 (3H, s), 3.52–3.35 (2H, m), 2.87 (1H, ddd, $J = 16.4, 8.8, 5.9$ Hz), 2.76 (1H, dt, $J = 16.4, 4.4$ Hz), 2.30 (3H, s). ¹³C NMR (100 MHz, CDCl₃) δ 154.1, 144.7, 142.2, 137.7, 136.9, 135.9, 130.5, 130.1, 128.9, 128.5, 126.9, 126.3, 125.9, 125.2, 121.3 (2C), 114.2 (2C), 61.5, 55.4, 46.0, 26.3, 19.6. IR (solid) 3015, 2928, 2833, 1580, 1504, 1240, 1194, 1128 cm⁻¹. MS (FAB) m/z (rel intensity) 330 (M+H⁺, 45), 329 (M⁺, 100), 238 (60), 154 (25), 136 (20). HRMS (FAB) Calcd for C₂₃H₂₄NO (M+H⁺): 330.1852, found, 330.1860. Anal Calcd for C₂₃H₂₃NO: C, 83.85; H, 7.04. Found: C, 83.60; H, 7.38.

1-(3-Tolyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (6)¹



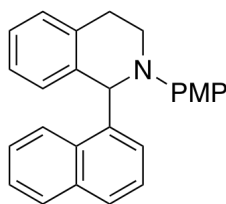
131.0 mg (99%). Colorless viscous oil. $R_f = 0.39$ (EtOAc/*n*-Hexane, 1 : 9). ^1H NMR (400 MHz, CDCl_3) δ 7.22-7.05 (5H, m), 7.05-6.90 (3H, m), 6.85-6.75 (4H, m), 5.62 (1H, s), 3.74 (3H, s), 3.59 (1H, ddd, $J = 11.7, 6.3, 5.6$ Hz), 3.41 (1H, ddd, $J = 11.7, 6.8, 5.4$ Hz), 3.05-2.85 (2H, m), 2.25 (3H, s). ^{13}C NMR (100 MHz, CDCl_3) δ 152.7, 144.4, 143.4, 137.7, 137.6, 135.5, 128.6, 128.3, 128.1, 127.9, 127.6, 126.6, 126.0, 125.1, 117.4 (2C), 114.5 (2C), 64.2, 55.6, 44.5, 28.0, 21.5. IR (neat) 3020, 2907, 2830, 1603, 1508, 1240, 1180, 1036 cm^{-1} . MS (FAB) m/z (rel intensity) 330 ($\text{M}+\text{H}^+$, 55), 329 (M^+ , 100), 238 (65), 136 (10), 105 (5). HRMS (FAB) Calcd for $\text{C}_{23}\text{H}_{24}\text{NO}$ ($\text{M}+\text{H}^+$): 330.1852, found, 330.1829. Anal Calcd for $\text{C}_{23}\text{H}_{23}\text{NO}$: C, 83.85; H, 7.04. Found: C, 84.15; H, 7.13.

1-(4-Tolyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (7)¹



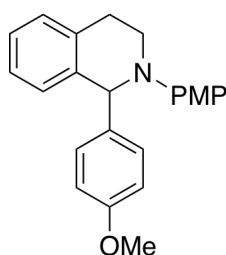
130.9 mg (99%). Colorless viscous oil. $R_f = 0.45$ ($\text{Et}_2\text{O}/n$ -Hexane, 1 : 10). ^1H NMR (400 MHz, CDCl_3) δ 7.22-7.10 (4H, m), 7.02 (4H, s), 6.85-6.75 (4H, m), 5.64 (1H, s), 3.74 (3H, s), 3.57 (1H, ddd, $J = 11.7, 6.6, 5.4$ Hz), 3.40 (1H, ddd, $J = 11.7, 6.6, 5.4$ Hz), 3.05-2.85 (2H, m), 2.27 (3H, s). ^{13}C NMR (100 MHz, CDCl_3) δ 152.8, 144.5, 140.2, 137.8, 136.3, 135.4, 128.7 (2C), 128.3, 128.1, 128.0, 126.6, 125.9 (2C), 117.7 (2C), 114.4 (2C), 64.0, 55.6, 44.4, 28.1, 21.0. IR (neat) 3022, 2926, 2841, 1665, 1510, 1258, 1175, 1130 cm^{-1} . MS (FAB) m/z (rel intensity) 330 ($\text{M}+\text{H}^+$, 65), 329 (M^+ , 100), 238 (75), 147 (20), 73 (50). HRMS (FAB) Calcd for $\text{C}_{23}\text{H}_{24}\text{NO}$ ($\text{M}+\text{H}^+$): 330.1852, found, 330.1845.

1-(1-Naphthyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (8)¹



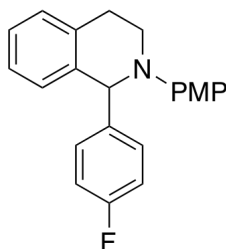
97.8 mg (67%). White solid. R_f = 0.31 (EtOAc/*n*-Hexane, 1 : 10). M.p. 172–174 °C (lit.¹ M.p. 172–174 °C). ¹H NMR (400 MHz, CDCl₃) δ 8.11 (1H, dd, J = 7.7, 1.7 Hz), 7.84 (1H, dd, J = 6.8, 2.4 Hz), 7.72 (1H, d, J = 8.1 Hz), 7.50–7.35 (2H, m), 7.30–7.10 (5H, m), 7.02 (1H, d, J = 8.1 Hz), 6.99 (2H, d, J = 9.0 Hz), 6.76 (2H, d, J = 9.0 Hz), 6.23 (1H, s), 3.74 (3H, s), 3.60–3.40 (2H, m), 2.91 (1H, dt, J = 16.6, 8.3 Hz), 2.76 (1H, dt, J = 16.6, 3.9 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 154.0, 144.3, 139.9, 136.7, 136.1, 134.0, 132.3, 129.0, 128.7, 128.6, 128.2, 128.0, 126.6, 126.1, 126.0, 125.5, 124.8, 124.7, 120.9 (2C), 114.4 (2C), 60.8, 55.4, 45.9, 25.8. IR (solid) 3046, 2914, 2830, 1595, 1510, 1506, 1238, 1032 cm⁻¹. MS (FAB) m/z (rel intensity) 366 (M+H⁺, 5), 365 (M⁺, 20), 307 (25), 154 (100), 136 (65). HRMS (FAB) Calcd for C₂₆H₂₄NO (M+H⁺): 366.1852, found, 366.1860.

1-(4-Methoxyphenyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (9)¹



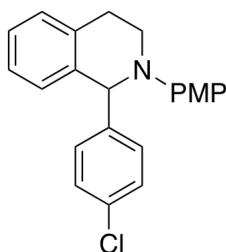
123.4 mg (89%). Colorless viscous oil. R_f = 0.24 (EtOAc/*n*-Hexane, 1 : 10). ¹H NMR (400 MHz, CDCl₃) δ 7.20–7.05 (4H, m), 7.02 (2H, d, J = 8.5 Hz), 6.85–6.74 (4H, m), 6.72 (2H, d, J = 8.5 Hz), 5.61 (1H, s), 3.70 (3H, s), 3.69 (3H, s), 3.51 (1H, ddd, J = 12.0, 6.8, 5.1 Hz), 3.36 (1H, ddd, J = 12.0, 6.6, 5.4 Hz), 3.00–2.83 (2H, m). ¹³C NMR (100 MHz, CDCl₃) δ 158.4, 152.9, 144.5, 137.8, 135.3, 135.2, 129.2 (2C), 128.4, 128.0, 126.5, 125.8, 118.2 (2C), 114.4 (2C), 113.2 (2C), 63.9, 55.5, 55.1, 44.3, 28.1. IR (neat) 2995, 2930, 2832, 1607, 1504, 1238, 1169, 1032 cm⁻¹. MS (FAB) m/z (rel intensity) 346 (M+H⁺, 65), 345 (M⁺, 100), 344 (40), 238 (90), 136 (10). HRMS (FAB) Calcd for C₂₃H₂₄NO₂ (M+H⁺): 346.1802, found, 346.1802. Anal Calcd for C₂₃H₂₃NO₂: C, 79.97; H, 6.71. Found: C, 74.66; H, 6.74.

1-(4-Fluorophenyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (10)¹



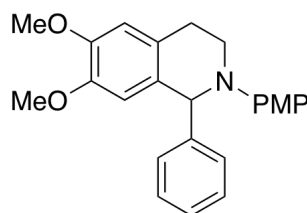
130.3 mg (98%). White solid. R_f = 0.50 (EtOAc/*n*-Hexane, 1 : 9). M.p. 107–109 °C (lit.¹ M.p. 107–109 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.25–7.10 (3H, m), 7.10–7.00 (3H, m), 6.90–6.75 (6H, m), 5.61 (1H, s), 3.74 (3H, s), 3.50 (1H, dd, J = 12.0, 6.8, 5.1 Hz), 3.38 (1H, ddd, J = 12.0, 6.6, 5.4 Hz), 3.05–2.85 (2H, m). ¹³C NMR (100 MHz, CDCl₃) δ 161.7 (d, J = 245.0 Hz), 153.2, 144.3, 138.8 (d, J = 2.5 Hz), 137.4, 135.4, 129.7 (2C, d, J = 8.3 Hz), 128.5, 128.1, 126.8, 126.0, 118.5 (2C), 114.7 (2C, d, J = 21.5 Hz), 114.4 (2C), 64.0, 55.6, 44.6, 28.2. IR (solid) 3036, 2926, 2820, 1601, 1502, 1452, 1225, 1032 cm⁻¹. MS (FAB) m/z (rel intensity) 334 (M+H⁺, 35), 333 (M⁺, 100), 332 (20), 238 (40), 136 (5). HRMS (FAB) Calcd for C₂₂H₂₁FNO (M+H⁺): 334.1602, found, 334.1607. Anal Calcd for C₂₂H₂₀FNO · 1/4 H₂O: C, 78.20; H, 6.12. Found: C, 78.33; H, 6.18.

1-(4-Chlorophenyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (11)¹



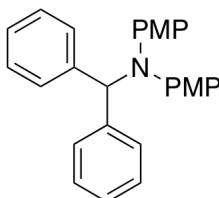
131.7 mg (94%). Colorless viscous oil. R_f = 0.30 (EtOAc/*n*-Hexane, 1 : 9). ¹H NMR (400 MHz, CDCl₃) δ 7.22–7.00 (8H, m), 6.80 (4H, d, J = 1.5 Hz), 5.60 (1H, s), 3.74 (3H, s), 3.51 (1H, ddd, J = 11.7, 6.6, 5.4 Hz), 3.38 (1H, ddd, J = 11.7, 6.6, 5.4 Hz), 3.05–2.85 (2H, m). ¹³C NMR (100 MHz, CDCl₃) δ 153.2, 144.2, 141.7, 137.2, 135.4, 132.6, 129.5 (2C), 128.5, 128.1 (2C), 128.0, 126.9, 126.1, 118.3 (2C), 114.5 (2C), 64.0, 55.6, 44.7, 28.2. IR (neat) 3025, 2930, 2832, 1508, 1487, 1240, 1090, 1036 cm⁻¹. MS (FAB) m/z (rel intensity) 350 (M+H⁺, 60), 349 (M⁺, 100), 238 (75), 154 (20), 136 (20). HRMS (FAB) Calcd for C₂₂H₂₁ClNO (M+H⁺): 350.1306, found, 350.1327. Anal Calcd for C₂₂H₂₀ClNO: C, 75.53; H, 5.76. Found: C, 75.80; H, 5.78.

1-Phenyl-2-(4-methoxyphenyl)-1,2,3,4-tetrahydro-6,7-dimethoxyisoquinoline (12)¹



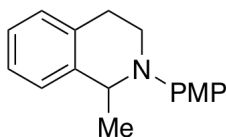
148.8 mg (99%). White solid. $R_f = 0.24$ (EtOAc/*n*-Hexane, 1 : 5). M.p. 112–114 °C (lit.¹ M.p. 112–114 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.30–7.05 (5H, m), 6.85 (2H, d, $J = 9.2$ Hz), 6.78 (2H, d, $J = 9.2$ Hz), 6.65 (1H, s), 6.59 (1H, s), 5.58 (1H, s), 3.87 (3H, s), 3.79 (3H, s), 3.74 (3H, s), 3.50–3.30 (2H, m), 2.90 (1H, ddd, $J = 15.9, 8.1, 5.9$ Hz), 2.77 (1H, dt, $J = 15.9, 5.1$ Hz). ¹³C NMR (100 MHz, CDCl₃) δ 153.2, 147.8, 147.2, 144.6, 143.2, 129.0, 128.4 (2C), 127.9 (2C), 127.6, 126.8, 118.7 (2C), 114.4 (2C), 111.3, 111.2, 64.0, 56.0, 55.9, 55.6, 44.1, 27.2. IR (solid) 2905, 2828, 1609, 1506, 1449, 1373, 1236, 1118 cm⁻¹. MS (FAB) m/z (rel intensity) 376 ($M+H^+$, 45), 375 (M^+ , 100), 298 (70), 154 (10), 136 (10). HRMS (FAB) Calcd for C₂₄H₂₆NO₃ ($M+H^+$): 376.1907, found, 376.1919.

N,N-Di-(4-methoxyphenyl)-1,1-diphenylmethanamine (13)¹



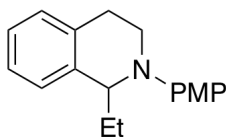
152.3 mg (96%). Pale yellow viscous oil. $R_f = 0.28$ (EtOAc/*n*-Hexane, 1 : 10). ¹H NMR (400 MHz, CDCl₃) δ 7.30–7.10 (10H, m), 6.75 (4H, d, $J = 7.7$ Hz), 6.65 (4H, d, $J = 7.7$ Hz), 6.17 (1H, s), 3.69 (6H, s). ¹³C NMR (100 MHz, CDCl₃) δ 154.4 (2C), 141.7 (4C), 129.3 (4C), 128.0 (4C), 126.8 (2C), 124.5 (4C), 114.0 (4C), 69.5, 55.4 (2C). IR (neat) 3390, 3028, 2951, 2833, 1501, 1236, 1179, 1030 cm⁻¹. MS (FAB) m/z (rel intensity) 396 ($M+H^+$, 30), 395 (M^+ , 70), 319 (30), 228 (100), 167 (65). HRMS (FAB) Calcd for C₂₇H₂₆NO₂ ($M+H^+$): 396.1958, found, 396.1928. Anal Calcd for C₂₇H₂₅NO₂•1/3H₂O: C, 80.77; H, 6.44. Found: C, 81.02; H, 6.38.

1-Methyl-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (14)³



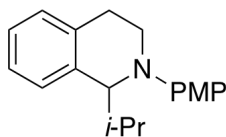
99.7 mg (98%). Colorless oil. $R_f = 0.39$ (EtOAc/*n*-Hexane, 1 : 9). ^1H NMR (400 MHz, CDCl_3) δ 7.20-7.10 (4H, m), 6.92 (2H, d, $J = 9.0$ Hz), 6.85 (2H, d, $J = 9.0$ Hz), 4.77 (1H, q, $J = 6.6$ Hz), 3.77 (3H, s), 3.49 (1H, ddd, $J = 12.5, 6.1, 3.9$ Hz), 3.42 (1H, ddd, $J = 12.5, 9.5, 4.2$ Hz), 3.01 (1H, ddd, $J = 16.1, 9.5, 6.1$ Hz), 2.83 (1H, ddd, $J = 16.1, 4.2, 3.9$ Hz), 1.33 (3H, d, $J = 6.6$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ 153.0, 144.5, 140.1, 134.3, 128.8, 126.9, 126.1, 125.8, 118.4 (2C), 114.6 (2C), 55.6 (2C), 42.0, 28.4, 20.1. IR (neat) 2967, 2830, 1508, 1464, 1383, 1240, 1180, 1036 cm^{-1} . MS (FAB) m/z (rel intensity) 254 ($\text{M}+\text{H}^+$, 50), 253 (M^+ , 100), 252 (25), 238 (75), 136 (10). HRMS (FAB) Calcd for $\text{C}_{17}\text{H}_{20}\text{NO}$ ($\text{M}+\text{H}^+$): 254.1539, found, 254.1546.

1-Ethyl-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (15)



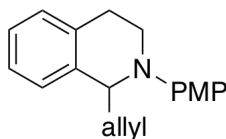
106.3 mg (99%). Colorless oil. $R_f = 0.55$ (EtOAc/*n*-Hexane, 1 : 9). ^1H NMR (400 MHz, CDCl_3) δ 7.20-7.05 (4H, m), 6.90-6.75 (4H, m), 4.40 (1H, t, $J = 6.8$ Hz), 3.74 (3H, s), 3.60-3.45 (2H, m), 2.95 (1H, ddd, $J = 16.1, 8.9, 5.7$ Hz), 2.75 (1H, dm, $J = 16.1$ Hz), 2.00-1.85 (1H, m), 1.80-1.65 (1H, m), 0.98 (3H, t, $J = 7.3$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ 152.2, 144.7, 139.0, 134.9, 128.6, 127.3, 126.1, 125.6, 116.9 (2C), 114.6 (2C), 61.3, 55.7, 42.9, 29.4, 26.8, 11.4. IR (neat) 2930, 2830, 1506, 1464, 1391, 1238, 1180, 1036 cm^{-1} . MS (FAB) m/z (rel intensity) 268 ($\text{M}+\text{H}^+$, 30), 267 (M^+ , 50), 266 (25), 238 (100), 136 (5). HRMS (FAB) Calcd for $\text{C}_{18}\text{H}_{22}\text{NO}$ ($\text{M}+\text{H}^+$): 268.1696, found, 268.1699.

1-Isopropyl-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (16)



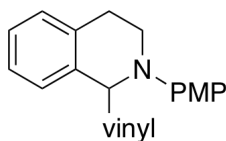
108.9 mg (97%). Colorless oil. $R_f = 0.58$ (EtOAc/*n*-Hexane, 1 : 9). M.p. 59–60 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.20–7.00 (4H, m), 6.90–6.70 (4H, m), 4.20 (1H, d, $J = 8.1$ Hz), 3.73 (3H, s), 3.69 (1H, ddd, $J = 12.7, 6.6, 6.1$ Hz), 3.44 (1H, ddd, $J = 12.7, 6.3, 6.1$ Hz), 3.00–2.80 (2H, m), 2.10 (1H, dq, $J = 8.1, 6.8$ Hz), 1.06 (3H, d, $J = 6.8$ Hz), 0.93 (3H, d, $J = 6.8$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ 151.7, 145.1, 137.8, 135.4, 128.4, 128.4, 126.4, 125.1, 115.8 (2C), 114.6 (2C), 65.4, 55.7, 43.6, 34.3, 26.9, 20.6, 20.2. IR (neat) 2953, 2830, 1506, 1464, 1382, 1240, 1180, 1038 cm^{-1} . MS (FAB) m/z (rel intensity) 282 ($\text{M}+\text{H}^+$, 20), 281 (M^+ , 20), 280 (20), 238 (100), 236 (10). HRMS (FAB) Calcd for $\text{C}_{19}\text{H}_{24}\text{NO}$ ($\text{M}+\text{H}^+$): 282.1852, found, 282.1852.

1-Allyl-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (17)⁴



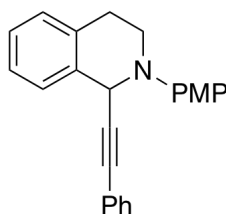
79.6 mg (71%). Colorless oil. $R_f = 0.44$ (EtOAc/*n*-Hexane, 1 : 10). ^1H NMR (400 MHz, CDCl_3) δ 7.20–7.00 (4H, m), 6.88 (2H, d, $J = 9.0$ Hz), 6.82 (2H, d, $J = 9.0$ Hz), 5.95–5.75 (1H, m), 5.10–4.95 (2H, m), 4.61 (1H, t, $J = 6.6$ Hz), 3.75 (3H, s), 3.65–3.45 (2H, m), 2.98 (1H, ddd, $J = 16.1, 9.3, 6.1$ Hz), 2.78 (1H, ddd, $J = 16.1, 4.6, 4.4$ Hz), 2.72–2.60 (1H, m), 2.53–2.40 (1H, m). ^{13}C NMR (100 MHz, CDCl_3) δ 152.5, 144.4, 138.3, 136.1, 134.9, 128.7, 127.3, 126.3, 125.6, 117.3 (2C), 116.6, 114.6 (2C), 60.1, 55.7, 42.8, 40.6, 27.1. IR (neat) 3022, 2909, 2832, 1506, 1464, 1240, 1180, 1036 cm^{-1} . MS (FAB) m/z (rel intensity) 280 ($\text{M}+\text{H}^+$, 15), 279 (M^+ , 15), 238 (100), 154 (15), 136 (10). HRMS (FAB) Calcd for $\text{C}_{19}\text{H}_{22}\text{NO}$ ($\text{M}+\text{H}^+$): 280.1696, found, 280.1696.

1-Vinyl-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (18)



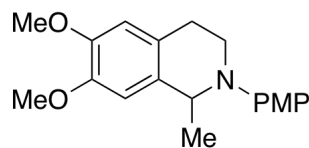
103.9 mg (98%). Colorless oil. $R_f = 0.40$ (EtOAc/*n*-Hexane, 1 : 90). ^1H NMR (400 MHz, CDCl_3) δ 7.22-7.10 (4H, m), 6.89 (2H, d, $J = 9.0$ Hz), 6.83 (2H, d, $J = 9.0$ Hz), 5.94 (1H, ddd, $J = 17.1, 10.3, 5.6$ Hz), 5.11 (1H, d, $J = 10.3$ Hz), 5.07 (1H, d, $J = 5.6$ Hz), 5.04 (1H, d, $J = 17.1$ Hz), 3.76 (3H, m), 3.60-3.40 (2H, m), 2.98 (1H, ddd, $J = 15.9, 8.1, 5.6$ Hz), 2.86 (1H, dt, $J = 15.9, 5.1$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ 152.8, 144.3, 138.6, 136.3, 135.2, 128.5, 127.8, 126.6, 125.9, 117.6 (2C), 116.1, 114.5 (2C), 63.0, 55.6, 43.7, 28.3. IR (neat) 3001, 2905, 2830, 1508, 1462, 1240, 1180, 1036 cm^{-1} . MS (FAB) m/z (rel intensity) 266 ($\text{M}+\text{H}^+$, 40), 265 (M^+ , 100), 238 (55), 136 (10), 91 (5). HRMS (FAB) Calcd for $\text{C}_{18}\text{H}_{20}\text{NO}$ ($\text{M}+\text{H}^+$): 266.1539, found, 266.1540.

1-Phenylethynyl-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (19)⁵



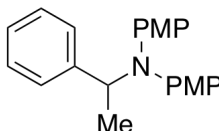
62.6 mg (46%). Pale yellow solid. $R_f = 0.30$ (EtOAc/*n*-Hexane, 1 : 10). M.p. 103–104 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.40-7.15 (9H, m), 7.11 (2H, d, $J = 9.0$ Hz), 6.89 (2H, d, $J = 9.0$ Hz), 5.50 (1H, s), 3.78 (3H, s), 3.63 (1H, ddd, $J = 12.2, 10.7, 4.2$ Hz), 3.54 (1H, ddd, $J = 12.2, 6.1, 3.2$ Hz), 3.14 (3H, ddd, $J = 15.6, 10.7, 6.1$ Hz), 2.92 (1H, ddd, $J = 15.6, 4.2, 3.2$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ 154.2, 144.1, 135.4, 134.0, 131.7 (2C), 129.0, 128.0 (2C), 127.9, 127.5, 127.1, 126.1, 123.0, 120.2 (2C), 114.3 (2C), 88.4, 85.5, 55.5, 54.4, 44.2, 20.0. IR (solid) 3022, 2907, 2832, 1506, 1441, 1240, 1180, 1034 cm^{-1} . MS (FAB) m/z (rel intensity) 340 ($\text{M}+\text{H}^+$, 45), 339 (M^+ , 100), 238 (15), 154 (45), 136 (30). HRMS (FAB) Calcd for $\text{C}_{24}\text{H}_{22}\text{NO}$ ($\text{M}+\text{H}^+$): 340.1696, found, 340.1693.

1-Methyl-2-(4-methoxyphenyl)-1,2,3,4-tetrahydro-6,7-dimethoxyisoquinoline (20)



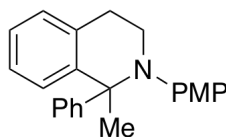
119.5 mg (95%). White solid. $R_f = 0.33$ (EtOAc/*n*-Hexane, 1 : 3). M.p. 83–85 °C. ^1H NMR (400 MHz, CDCl_3) δ 6.92 (2H, d, $J = 9.0$ Hz), 6.84 (2H, d, $J = 9.0$ Hz), 6.61 (2H, d, $J = 3.7$ Hz), 4.69 (1H, q, $J = 6.8$ Hz), 3.87 (3H, s), 3.85 (3H, s), 3.76 (3H, s), 3.48 (1H, ddd, $J = 12.4, 5.9, 3.4$ Hz), 3.40 (1H, ddd, $J = 12.4, 10.3, 4.2$ Hz), 2.92 (1H, ddd, $J = 15.9, 10.3, 5.9$ Hz), 2.70 (1H, ddd, $J = 15.9, 4.2, 3.4$ Hz), 1.32 (3H, d, $J = 6.8$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ 153.0, 147.4, 147.2, 144.5, 131.9, 126.1, 118.7 (2C), 114.5 (2C), 111.3, 109.8, 55.9, 55.8, 55.6, 55.2, 42.0, 27.8, 20.0. IR (solid) 2961, 2832, 1611, 1508, 1464, 1383, 1244, 1126 cm^{-1} . MS (FAB) m/z (rel intensity) 314 ($\text{M}+\text{H}^+$, 40), 313 (M^+ , 50), 298 (50), 154 (100), 137 (70). HRMS (FAB) Calcd for $\text{C}_{19}\text{H}_{24}\text{NO}_3$ ($\text{M}+\text{H}^+$): 314.1751, found, 314.1758. Anal Calcd for $\text{C}_{19}\text{H}_{23}\text{NO}_3 \cdot 1/4\text{H}_2\text{O}$: C, 71.79; H, 7.45. Found: C, 72.00; H, 7.69.

N,N-Di-(4-methoxyphenyl)-1-phenylethylamine (21)



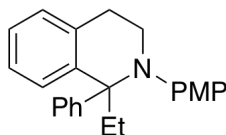
127.0 mg (95%). Colorless oil. $R_f = 0.38$ (EtOAc/*n*-Hexane, 1 : 9). ^1H NMR (400 MHz, CDCl_3) δ 7.40-7.15 (5H, m), 7.85-7.70 (8H, m), 5.13 (1H, q, $J = 6.8$ Hz), 3.75 (6H, s), 1.42 (3H, d, $J = 6.8$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ 154.5 (2C), 144.5, 141.2 (2C), 128.3 (2C), 127.0 (2C), 126.6, 124.1 (4C), 114.2 (4C), 58.0 (2C), 55.5, 20.2. IR (neat) 3040, 2932, 2833, 1501, 1464, 1281, 1236, 1034 cm^{-1} . MS (FAB) m/z (rel intensity) 334 ($\text{M}+\text{H}^+$, 30), 333 (M^+ , 100), 228 (55), 214 (5), 105 (30). HRMS (FAB) Calcd for $\text{C}_{22}\text{H}_{24}\text{NO}_2$ ($\text{M}+\text{H}^+$): 334.1802, found, 334.1807. Anal Calcd for $\text{C}_{22}\text{H}_{23}\text{NO}_2 \cdot 1/4\text{H}_2\text{O}$: C, 78.19; H, 7.01. Found: C, 78.33; H, 7.10.

1-Methyl-1-phenyl-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (22)



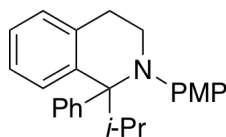
130.1 mg (99%). White solid. $R_f = 0.53$ (EtOAc/*n*-Hexane, 1 : 10). M.p. 107–108 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.25–7.00 (8H, m), 6.83 (1H, d, $J = 7.8$ Hz), 6.60 (2H, d, $J = 9.0$ Hz), 6.53 (2H, d, $J = 9.0$ Hz), 3.72 (3H, s), 3.44 (1H, ddd, $J = 12.0, 8.8, 4.2$ Hz), 3.32 (1H, ddd, $J = 12.0, 5.1, 4.9$ Hz), 3.17 (1H, ddd, $J = 16.1, 8.8, 4.9$ Hz), 2.97 (1H, ddd, $J = 16.1, 5.1, 4.2$ Hz), 1.70 (3H, s). ^{13}C NMR (100 MHz, CDCl_3) δ 155.8, 148.4, 144.5, 143.2, 134.5, 129.0, 128.7 (2C), 128.4, 127.8 (2C), 127.4 (2C), 126.4, 125.7, 125.6, 112.8 (2C), 64.9, 55.2, 46.6, 30.6, 23.3. IR (solid) 2930, 2832, 1508, 1443, 1373, 1244, 1179, 1036 cm^{-1} . MS (FAB) m/z (rel intensity) 330 ($\text{M}+\text{H}^+$, 60), 329 (M^+ , 100), 252 (35), 154 (35), 136 (50). HRMS (FAB) Calcd for $\text{C}_{23}\text{H}_{24}\text{NO}$ ($\text{M}+\text{H}^+$): 330.1852, found, 330.1857.

1-Ethyl-1-phenyl-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (23)



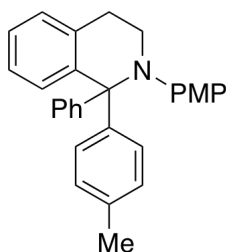
134.8 mg (98%). Colorless oil. $R_f = 0.55$ (EtOAc/*n*-Hexane, 1 : 10). ^1H NMR (400 MHz, CDCl_3) δ 7.20–7.00 (6H, m), 6.95–6.85 (3H, m), 6.62 (2H, d, $J = 9.0$ Hz), 6.49 (2H, d, $J = 9.0$ Hz), 3.74 (3H, s), 3.52 (1H, ddd, $J = 11.6, 10.3, 3.2$ Hz), 3.18 (1H, ddd, $J = 11.5, 10.3, 5.1$ Hz), 3.04 (1H, ddd, $J = 11.6, 5.1, 3.4$ Hz), 2.85 (1H, ddd, $J = 11.5, 3.4, 3.2$ Hz), 2.56 (1H, dq, $J = 13.9, 7.1$ Hz), 2.05 (1H, dq, $J = 13.9, 7.1$ Hz), 0.86 (3H, d, $J = 7.1$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ 156.0, 145.6, 143.0, 141.5, 136.8, 128.5 (2C), 128.4, 128.1, 128.1 (2C), 126.9 (2C), 126.2, 125.9, 125.5, 112.8 (2C), 67.8, 55.3, 46.7, 31.2, 31.0, 8.7. IR (neat) 2932, 2832, 1506, 1443, 1368, 1242, 1180, 1036 cm^{-1} . MS (FAB) m/z (rel intensity) 344 ($\text{M}+\text{H}^+$, 35), 343 (M^+ , 50), 314 (100), 266 (20), 136 (20). HRMS (FAB) Calcd for $\text{C}_{24}\text{H}_{26}\text{NO}$ ($\text{M}+\text{H}^+$): 344.2009, found, 344.2011.

1-Isopropyl-1-phenyl-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (24)



93.8 mg (66%). White Solid. $R_f = 0.63$ (EtOAc/*n*-Hexane, 1 : 10). M.p. 119–122 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.25–7.00 (6H, m), 6.89 (1H, d, $J = 8.1$ Hz), 6.74 (2H, d, $J = 7.1$ Hz), 6.56 (2H, d, $J = 9.0$ Hz), 6.41 (2H, d, $J = 8.8$ Hz), 3.73 (3H, s), 3.40–3.20 (2H, m), 2.94 (1H, septet, $J = 7.1$ Hz), 2.90–2.80 (1H, m), 2.75–2.65 (1H, m), 0.99 (3H, d, $J = 7.1$ Hz), 0.99 (3H, d, $J = 7.1$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ 156.4, 143.1, 142.1, 139.1, 138.8, 130.2, 129.5 (2C), 129.4 (2C), 128.0, 126.6 (2C), 126.0, 125.7, 124.1, 112.6 (2C), 72.4, 55.3, 47.7, 33.3, 32.4, 19.5, 17.9. IR (solid) 2949, 2832, 1504, 1443, 1362, 1242, 1182, 1036 cm^{-1} . MS (FAB) m/z (rel intensity) 358 ($\text{M}+\text{H}^+$, 15), 357 (M^+ , 10), 314 (100), 154 (35), 136 (30). HRMS (FAB) Calcd for $\text{C}_{25}\text{H}_{28}\text{NO}$ ($\text{M}+\text{H}^+$): 358.2165, found, 358.2162.

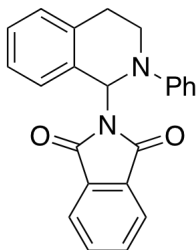
1-(4-Tolyl)-1-phenyl-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (25)



82.8 mg (51%). Colorless oil. $R_f = 0.60$ (EtOAc/*n*-Hexane, 1 : 10). ^1H NMR (400 MHz, CDCl_3) δ 7.25–7.00 (9H, m), 7.00–6.90 (3H, m), 6.64 (1H, d, $J = 7.3$ Hz), 6.48 (2H, d, $J = 8.9$ Hz), 6.42 (2H, d, $J = 8.9$ Hz), 3.67 (3H, s), 3.42 (2H, t, $J = 5.6$ Hz), 3.10 (2H, t, $J = 5.6$ Hz), 2.30 (3H, s). ^{13}C NMR (100 MHz, CDCl_3) δ 154.3, 144.5, 144.0, 143.9, 140.6, 135.9, 135.1, 130.8 (2C), 130.7 (2C), 130.7, 127.9, 127.6 (2C), 126.8 (2C), 126.4, 125.7, 125.5, 125.0 (2C), 112.7 (2C), 74.5, 55.3, 47.2, 31.0, 21.0. IR (neat) 3021, 2918, 2832, 1609, 1506, 1443, 1244, 1180, 1036 cm^{-1} . MS (FAB) m/z (rel intensity) 406 ($\text{M}+\text{H}^+$, 35), 405 (M^+ , 75), 307 (20), 154 (100), 136 (70). HRMS (FAB) Calcd for $\text{C}_{29}\text{H}_{28}\text{NO}$ ($\text{M}+\text{H}^+$): 406.2165, found, 406.2175.

2-2. sp³ C-H bond amidation of THIQs

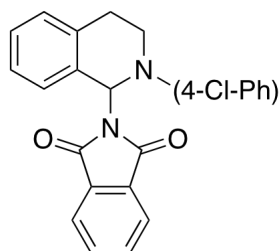
1-(Indene-1,3-dionyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (26)



After stirring the mixture of 2-phenyl-1,2,3,4-tetrahydroisoquinoline (83.7 mg, 0.4 mmol) and [bis(trifluoroacetoxy)iodo]benzene (172.1 mg, 0.40 mmol) in 2-MeTHF (4.0 mL) in a vial at room temperature for 10 min under Ar atmosphere, phthalimide (61.8 mg, 0.42 mmol) was added to the solution at room temperature. After stirring vigorously for 3 hours at room temperature, the reaction mixture was quenched with saturated aqueous NaHCO₃, and extracted with ethyl acetate. The organic layer was washed with water and brine, dried over Na₂SO₄, filtrated, and concentrated in *vacuo*. The residue was purified by Al₂O₃ column chromatography (*n*-hexane/ethyl acetate = 90/10-70/30) to give 1-(indene-1,3-dionyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline **26** (141.5 mg, >99%) as pale yellow solid.

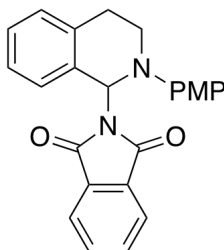
141.5 mg (>99%). Pale yellow solid. *R*_f = 0.59 (EtOAc/*n*-Hexane, 3 : 7). M.p. 138–139 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.80-7.70 (2H, m), 7.70-7.60 (2H, m), 7.30-7.05 (9H, m), 6.82 (1H, d, *J* = 7.3 Hz), 4.11 (2H, ddd, *J* = 12.0, 9.0, 5.9 Hz), 3.82 (1H, ddd, *J* = 12.0, 5.1, 3.9 Hz), 2.20-2.05 (2H, m). ¹³C NMR (100 MHz, CDCl₃) δ 168.5 (2C), 147.8, 135.8, 134.0 (2C), 132.6, 131.8 (2C), 129.1 (2C), 128.5, 127.9, 126.4, 126.4, 123.6, 123.3, 119.8, 116.4 (2C), 63.7, 42.1, 29.0. IR (solid) 3059, 2922, 2851, 1701, 1599, 1497, 1342, 1308, 1219 cm⁻¹. MS (FAB) *m/z* (rel intensity) 355 (M+H⁺, 5), 354 (M⁺, 10), 208 (100), 136 (10), 77 (10). HRMS (FAB) Calcd for C₂₃H₁₉N₂O₂ (M+H⁺): 355.1441, found, 355.1434.

1-(Indene-1,3-dionyl)-2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (27)



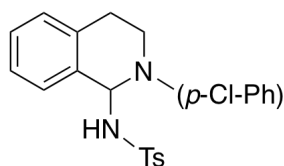
152.9 mg (98%). Pale yellow solid. $R_f = 0.47$ (EtOAc/*n*-Hexane, 1 : 3). M.p. 57–60 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.74 (2H, d, $J = 5.4, 2.9$ Hz), 7.65 (2H, d, $J = 5.4, 2.9$ Hz), 7.30-6.95 (9H, m), 4.07 (1H, ddd, $J = 11.7, 7.3, 4.6$ Hz), 3.74 (1H, dt, $J = 11.7, 4.3$ Hz), 3.20-3.00 (2H, m). ^{13}C NMR (100 MHz, CDCl_3) δ 168.4 (2C), 146.4, 135.5, 134.1 (2C), 132.2, 131.6 (2C), 129.0 (2C), 128.5, 128.0, 126.5, 126.3, 124.7, 123.4 (2C), 117.7 (2C), 63.4, 42.3, 28.9. IR (solid) 3028, 2926, 1705, 1595, 1495, 1346, 1288, 1225, 1103 cm^{-1} . MS (FAB) m/z (rel intensity) 389 ($\text{M}+\text{H}^+$, 2), 388 (M^+ , 5), 242 (100), 154 (30), 136 (30). HRMS (FAB) Calcd for $\text{C}_{23}\text{H}_{18}\text{ClN}_2\text{O}_2$ ($\text{M}+\text{H}^+$): 389.1051, found, 389.1039.

1-(Indene-1,3-dionyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (28)



>99% (NMR yield). ^1H NMR (400 MHz, CDCl_3) δ 7.80-7.60 (4H, m), 7.30-7.20 (2H, m), 7.20-7.05 (4H, m), 7.00 (1H, s), 6.79 (2H, d, $J = 9.0$ Hz), 4.10-4.00 (1H, m), 3.71 (3H, s), 3.65-3.55 (1H, m), 3.20-3.05 (2H, m). ^{13}C NMR (100 MHz, CDCl_3) δ 168.6 (2C), 154.1, 142.0, 137.4, 135.8, 133.9 (2C), 130.2 (2C), 128.5, 127.8, 126.4, 126.2, 123.3 (2C), 119.7 (2C), 114.3 (2C), 64.9, 55.4, 43.2, 29.3. IR (neat) 2928, 2833, 1709, 1508, 1464, 1398, 1242, 1036, 941 cm^{-1} . MS (FAB) m/z (rel intensity) 385 ($\text{M}+\text{H}^+$, 5), 384 (M^+ , 10), 239 (25), 238 (100), 136 (5). HRMS (FAB) Calcd for $\text{C}_{24}\text{H}_{21}\text{N}_2\text{O}_3$ ($\text{M}+\text{H}^+$): 385.1547, found, 385.1542.

1-(*N*-*p*-Tosyl)-2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (29)

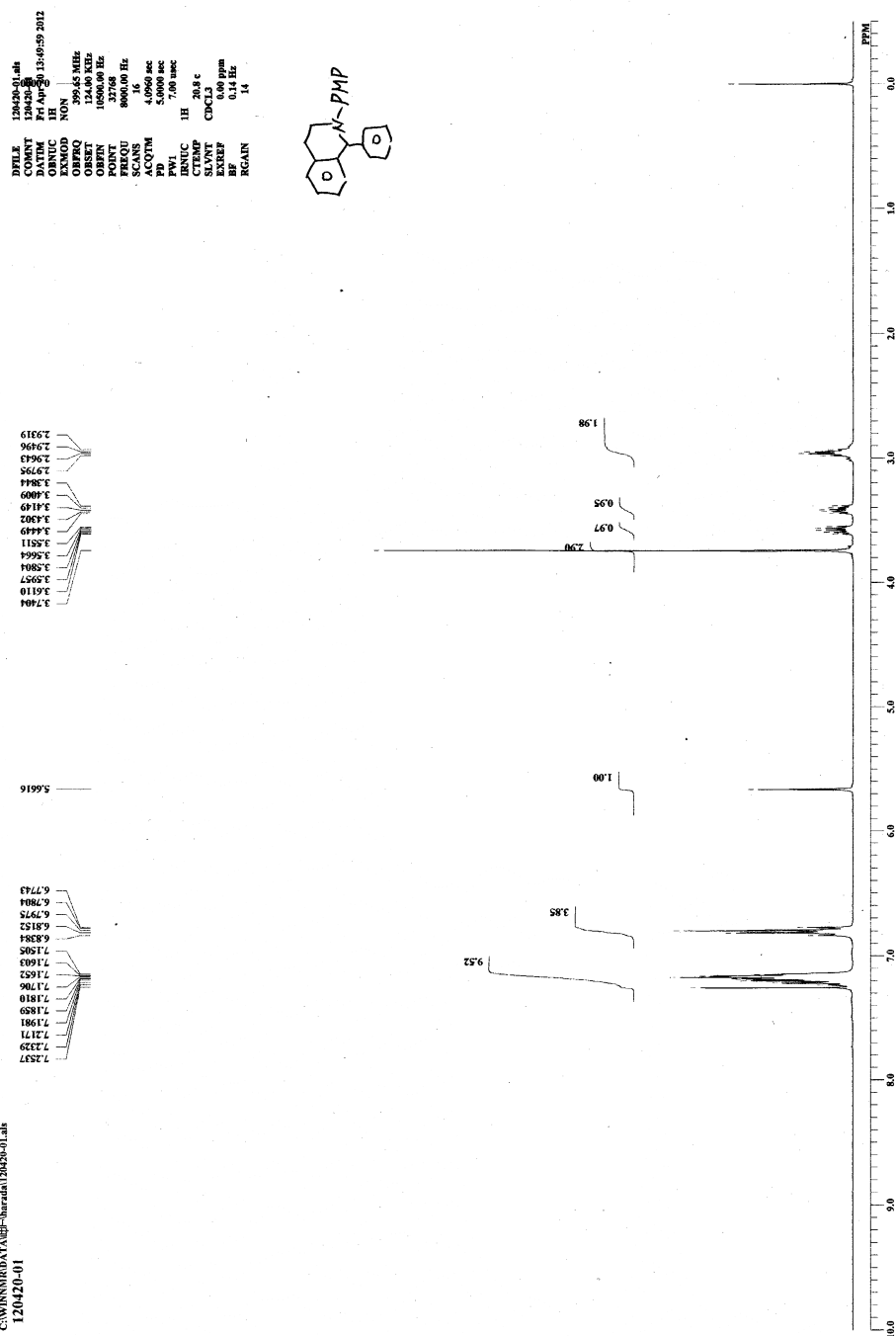


95% (NMR yield). ^1H NMR (400 MHz, CDCl_3) δ 7.40-7.00 (10H, m), 6.76 (2H, d, $J = 9.3$ Hz), 6.22 (1H, d, $J = 7.1$ Hz), 5.48 (1H, d, $J = 7.1$ Hz), 3.30-3.20 (2H, m), 2.95 (1H, ddd, $J = 16.6$, 8.5, 7.6 Hz), 2.67 (1H, dt, $J = 16.6$, 3.4 Hz), 2.38 (3H, s). ^{13}C NMR (100 MHz, CDCl_3) δ 146.7, 142.8, 138.4, 134.6, 133.9, 129.1 (2C), 128.9 (2C), 128.8, 128.4, 128.2, 126.7, 126.5 (2C), 125.5, 119.0 (2C), 69.6, 40.4, 26.8, 21.5. IR (solid) 3265, 3026, 2933, 2859, 1595, 1493, 1425, 1327, 1144 cm^{-1} . MS (FAB) m/z (rel intensity) 413 ($\text{M}+\text{H}^+$, 1), 394 (15), 244 (40), 242 (100), 136 (15). HRMS (FAB) Calcd for $\text{C}_{22}\text{H}_{22}\text{ClN}_2\text{O}_2\text{S}$ ($\text{M}+\text{H}^+$): 413.1085, found, 413.1089.

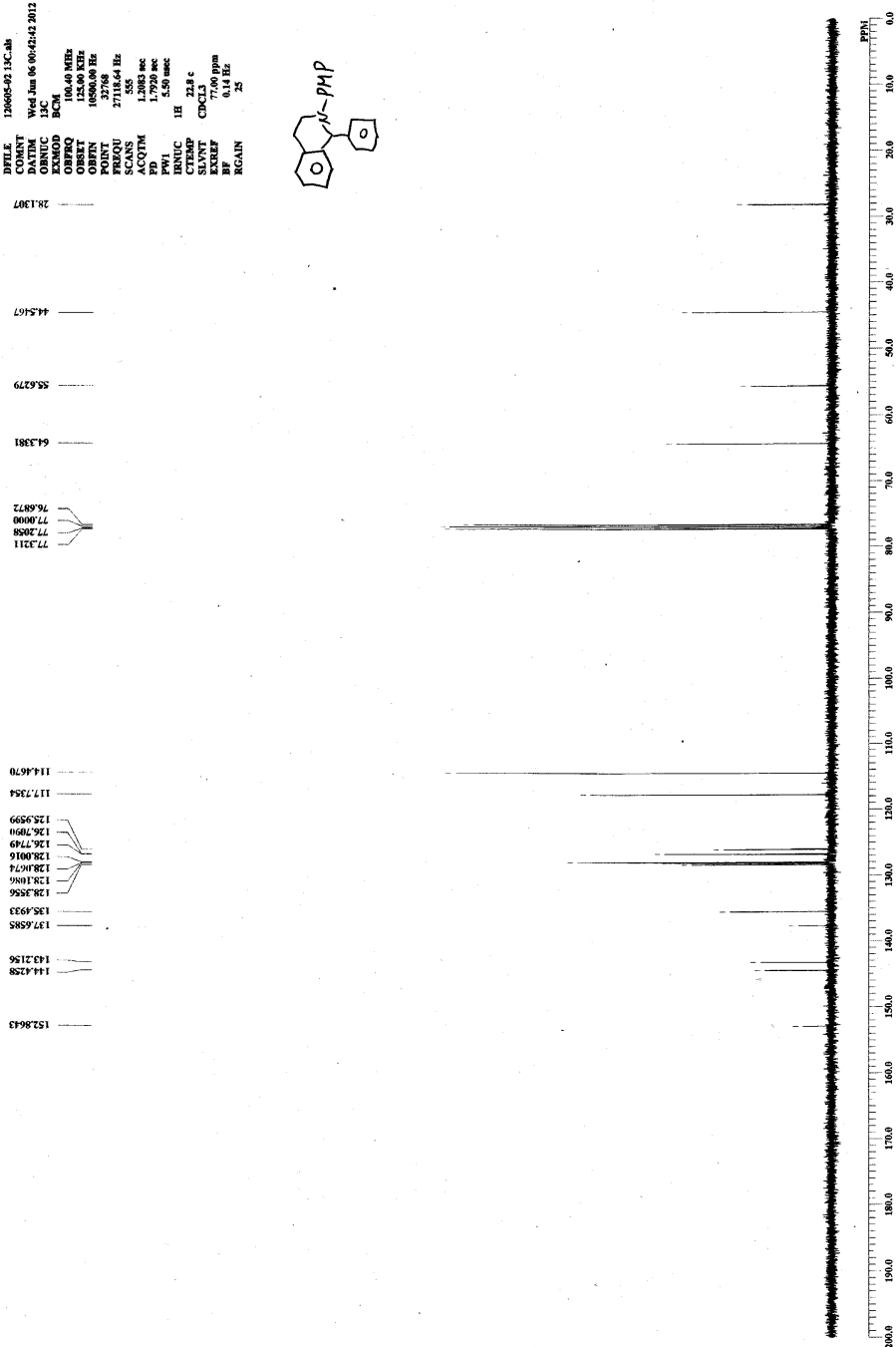
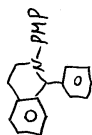
Reference

1. W. Muramatsu, K. Nakano, C.-J. Li, *Org. Lett.*, 2013, **15**, 3650.
2. J. A. Cambell, T. D. Greenwood, S. B. Hendi, M. S. Hendi, P. Hguyen, J. F. Wolfe, *Heterocycl. Comm.*, 1996, **2**, 339.
3. D. Taniyama, M. Hasegawa, K. Tomioka, *Tetrahedron: Asymmetry*, 1999, **10**, 221.
4. G. Kumaraswamy, A. N. Murthy, A. Pitchaiah, *A. J. Org. Chem.*, 2010, **75**, 3916.
5. Z. Li, C.-J. Li. *Org. Lett.*, 2004, **6**, 4997.

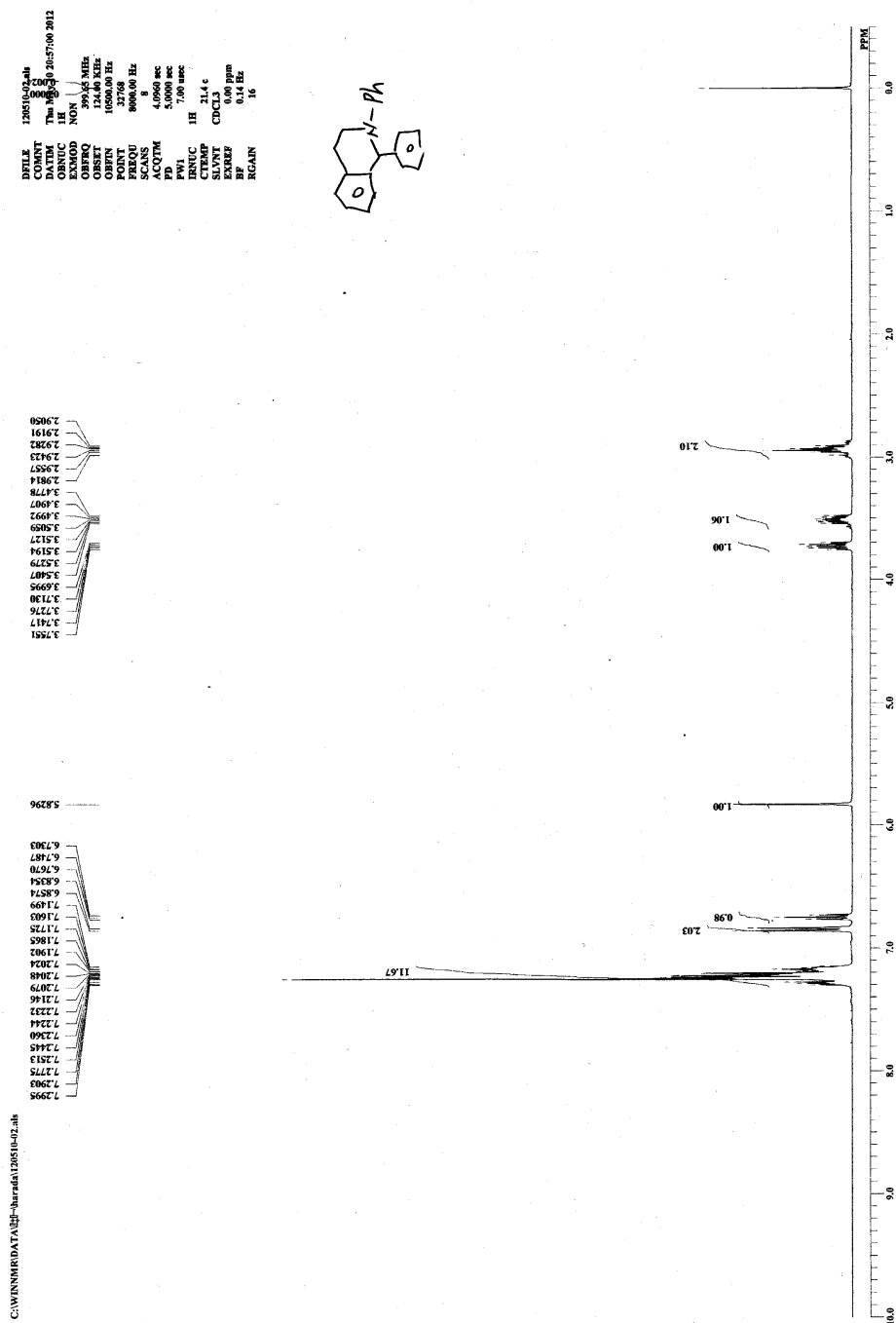
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1-Phenyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (2)

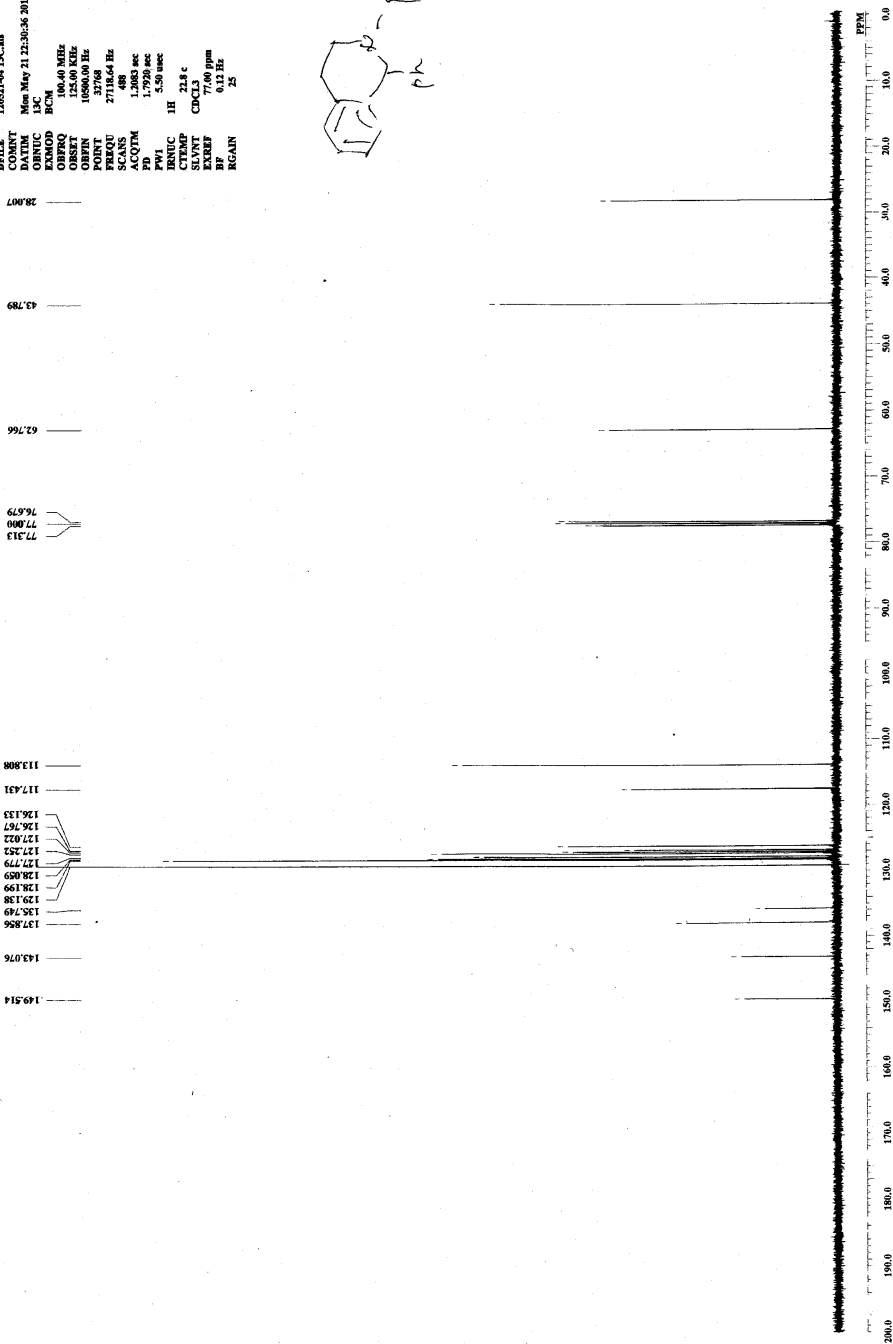


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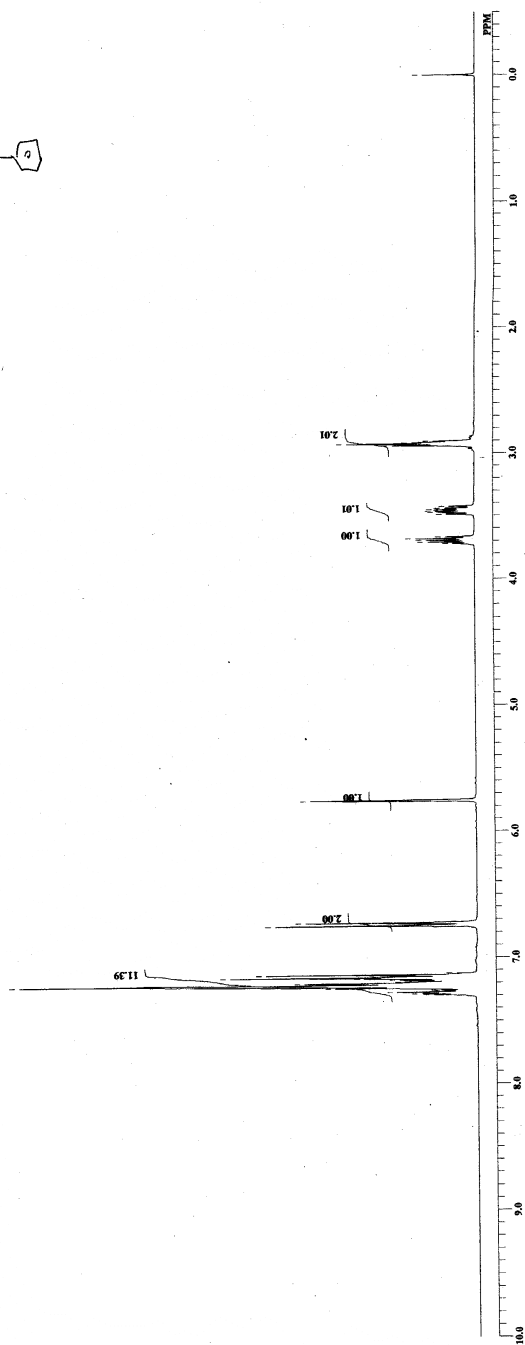
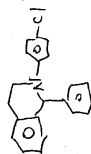
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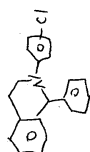
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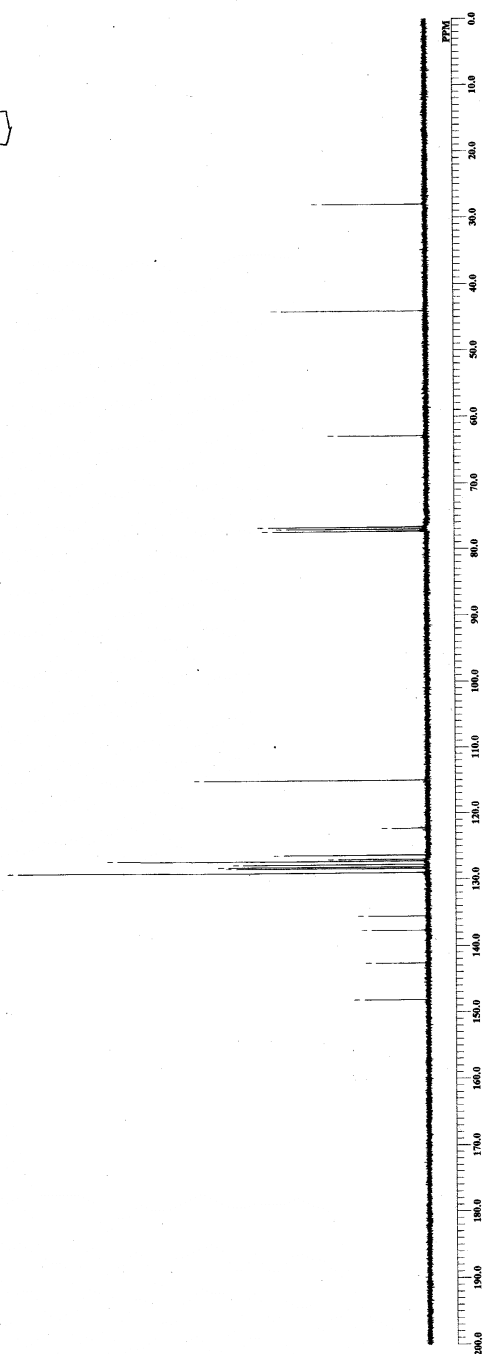


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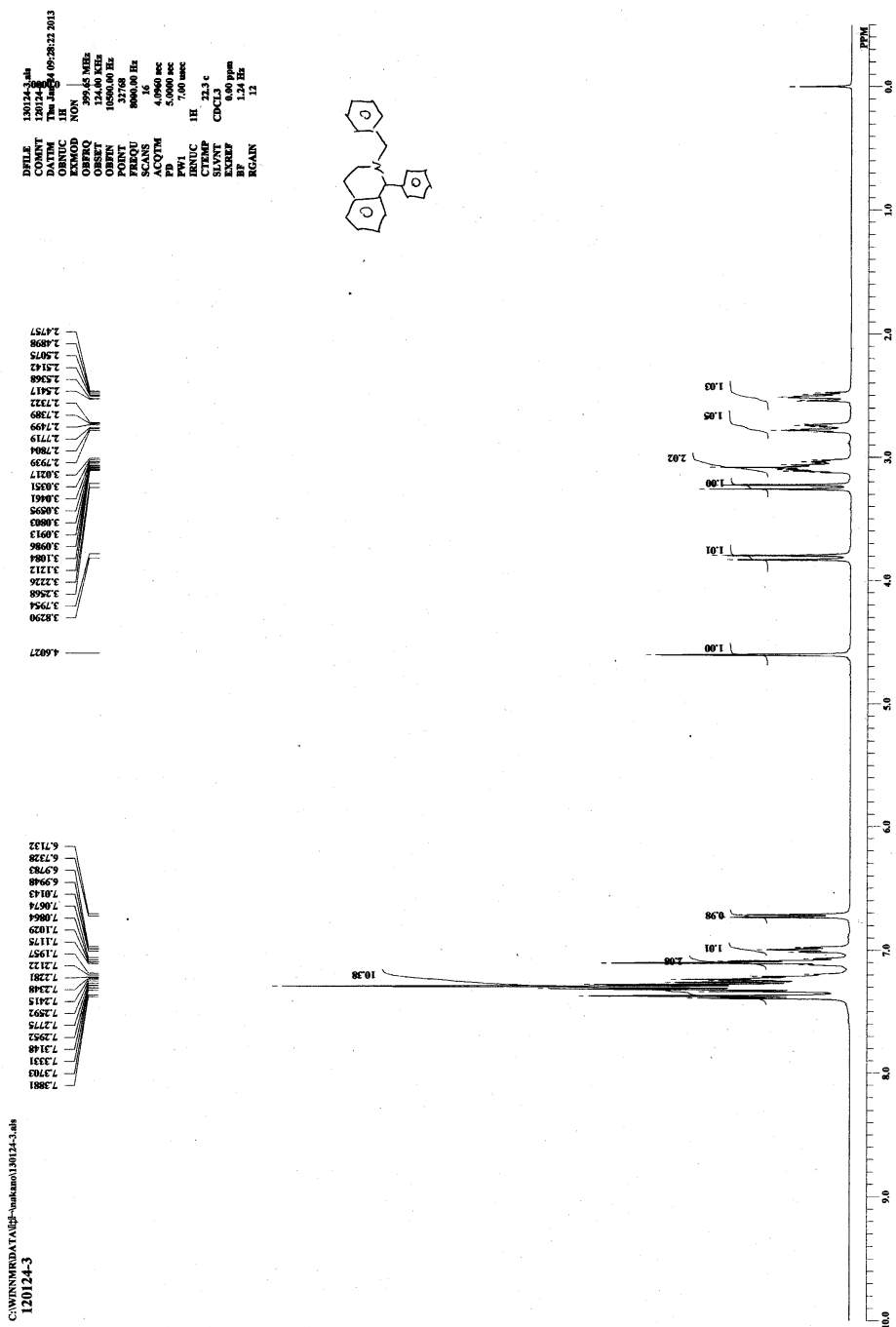


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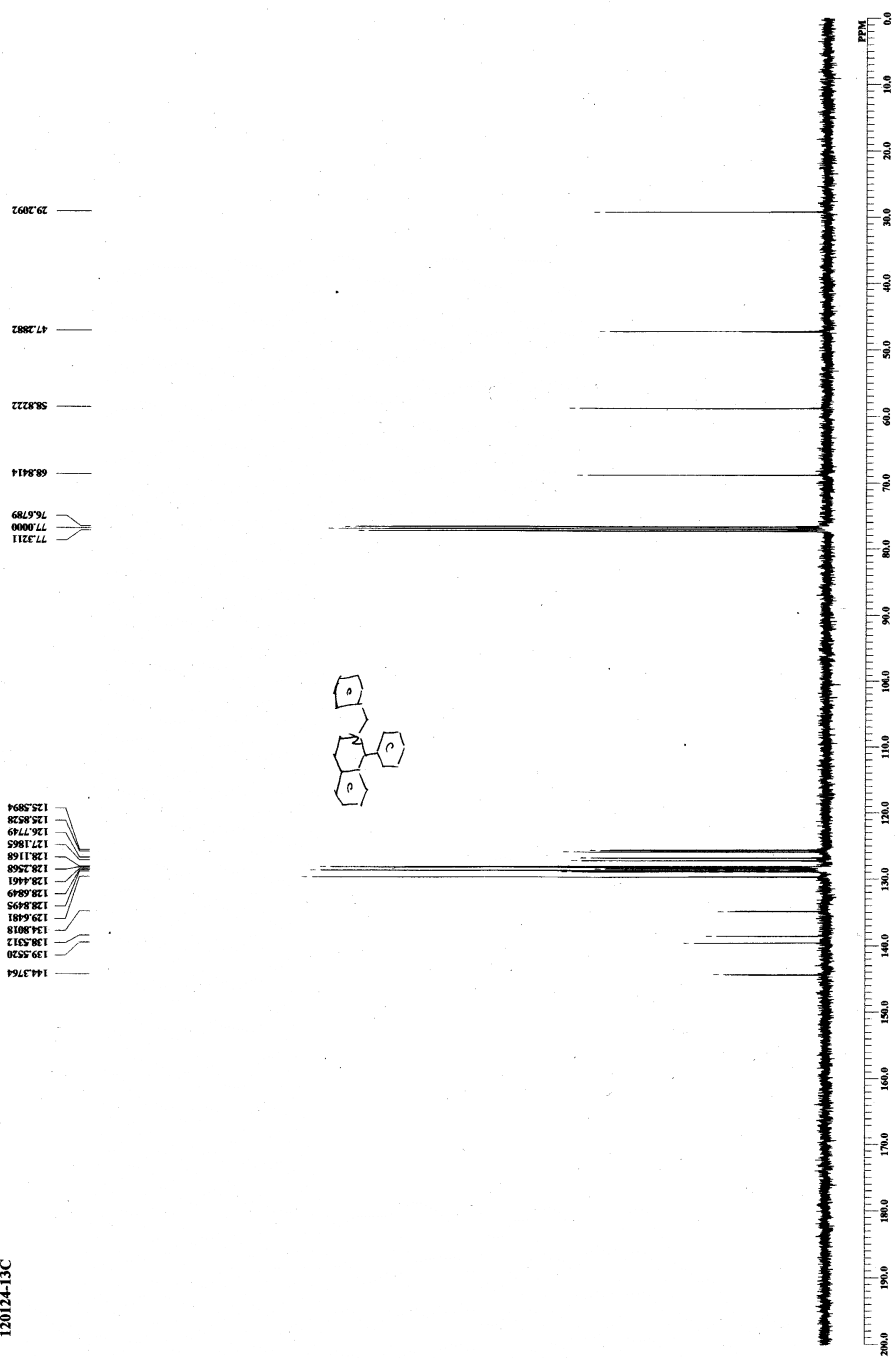
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1-Phenyl-2-benzyl-1,2,3,4-tetrahydroisoquinoline (4)



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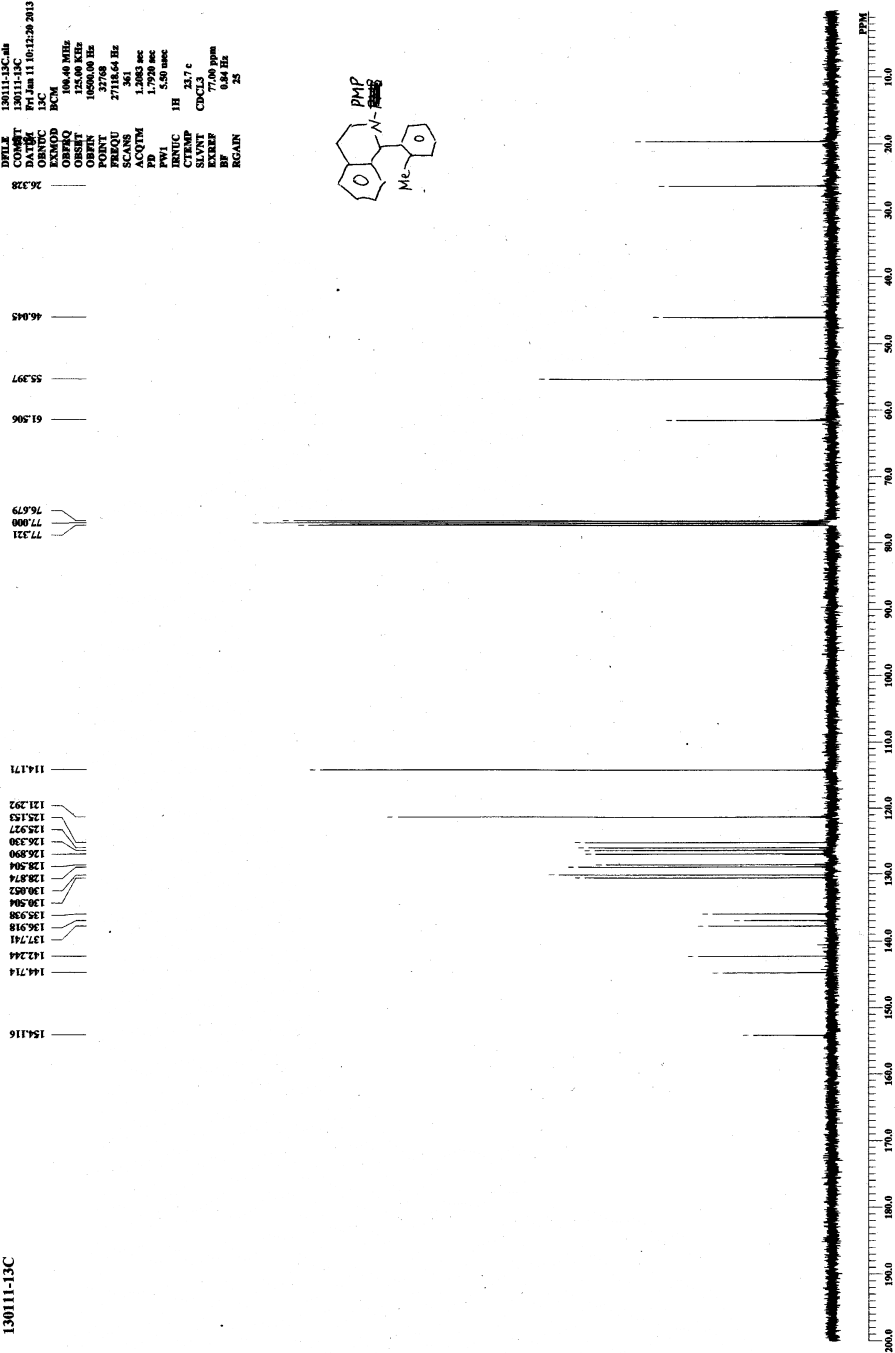
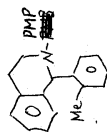


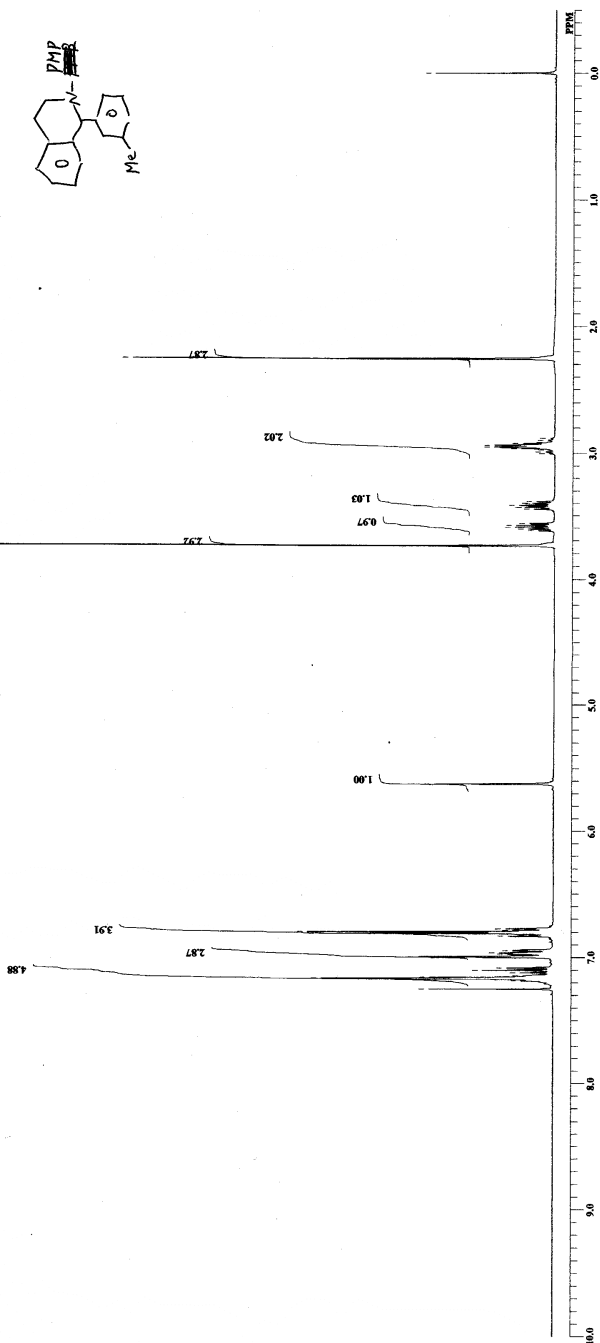
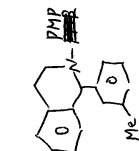
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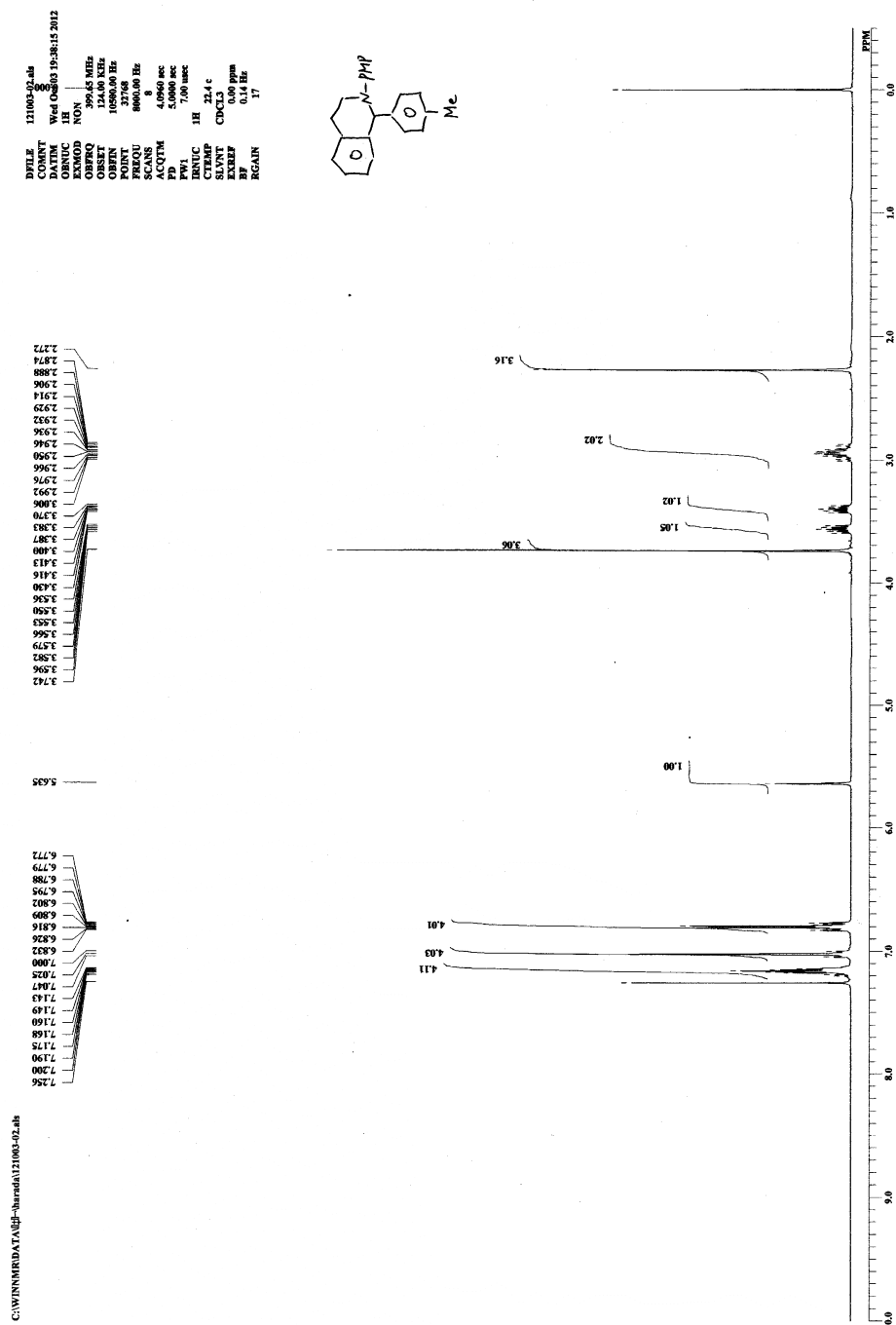
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130111-13C

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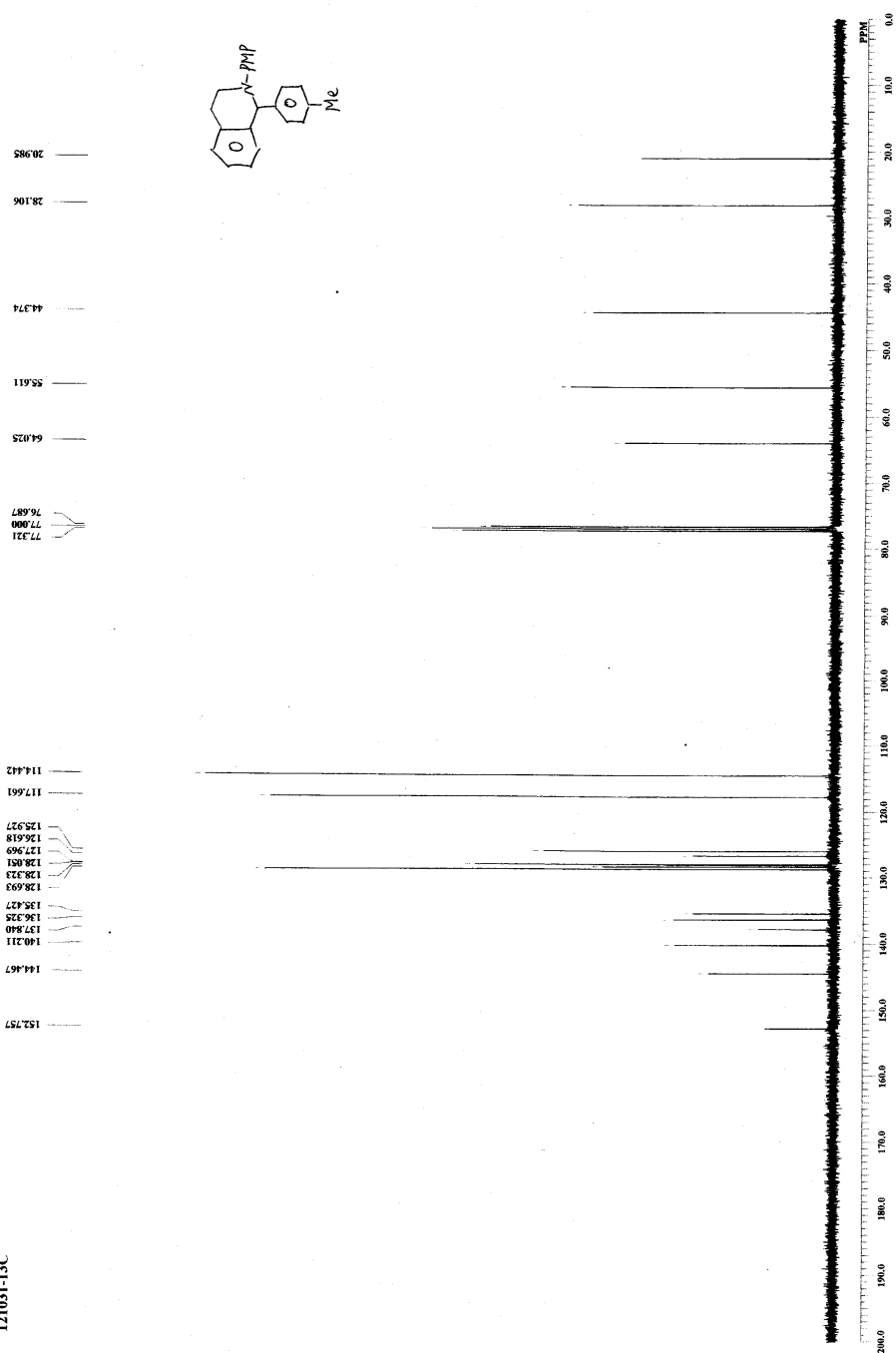


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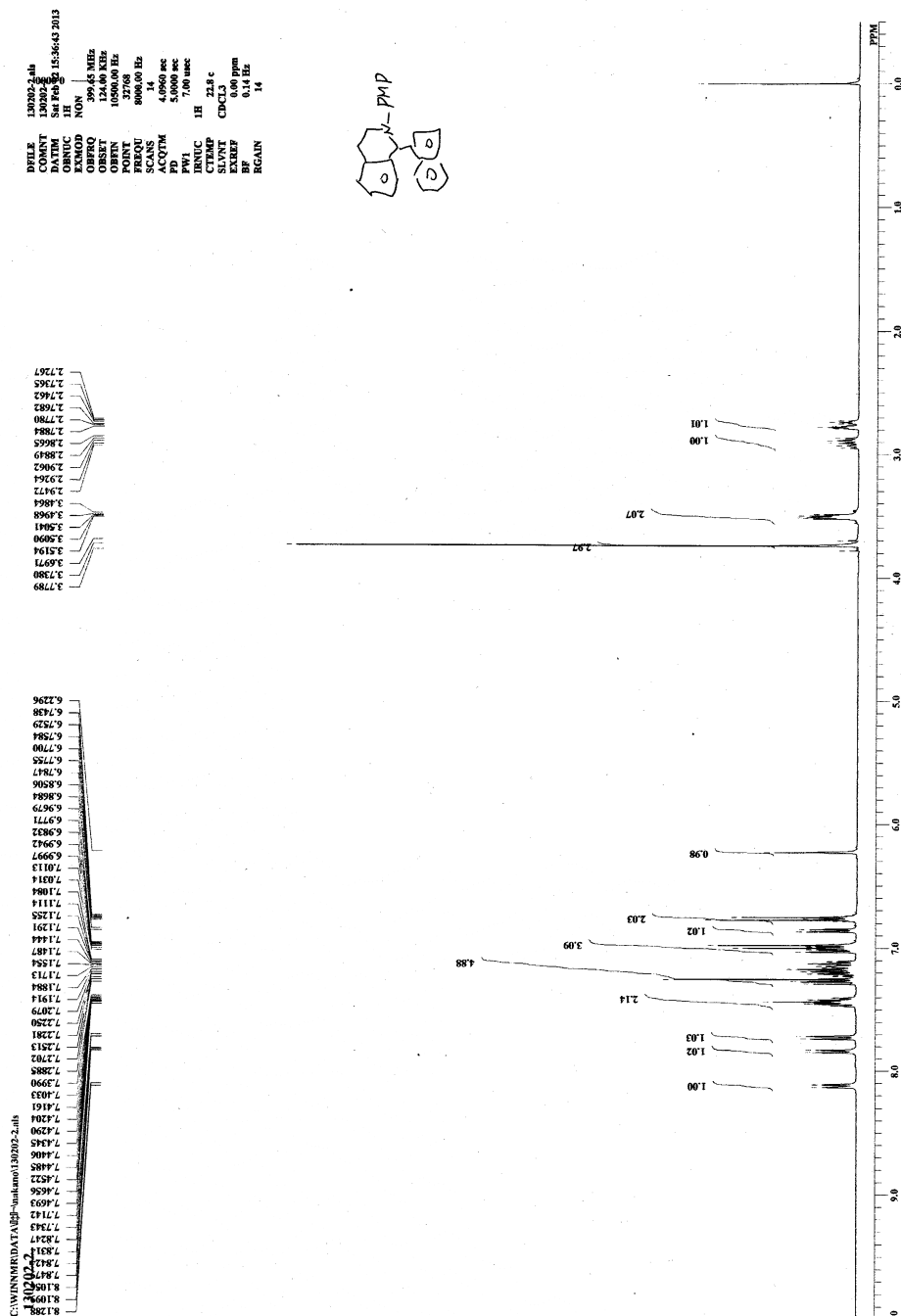
1-(4-Tolyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (7)



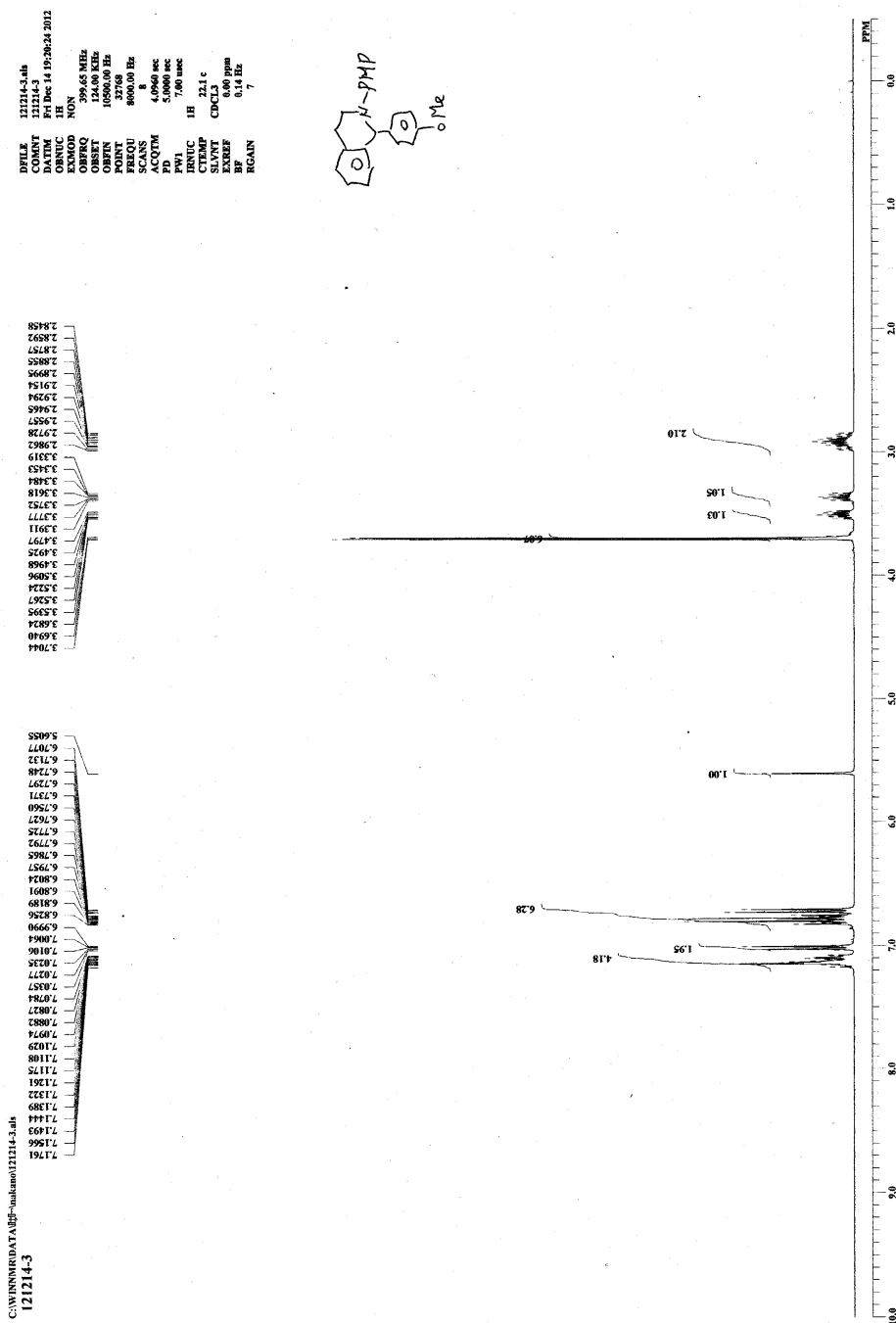
121031-13C



1-(1-Naphthyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (8)

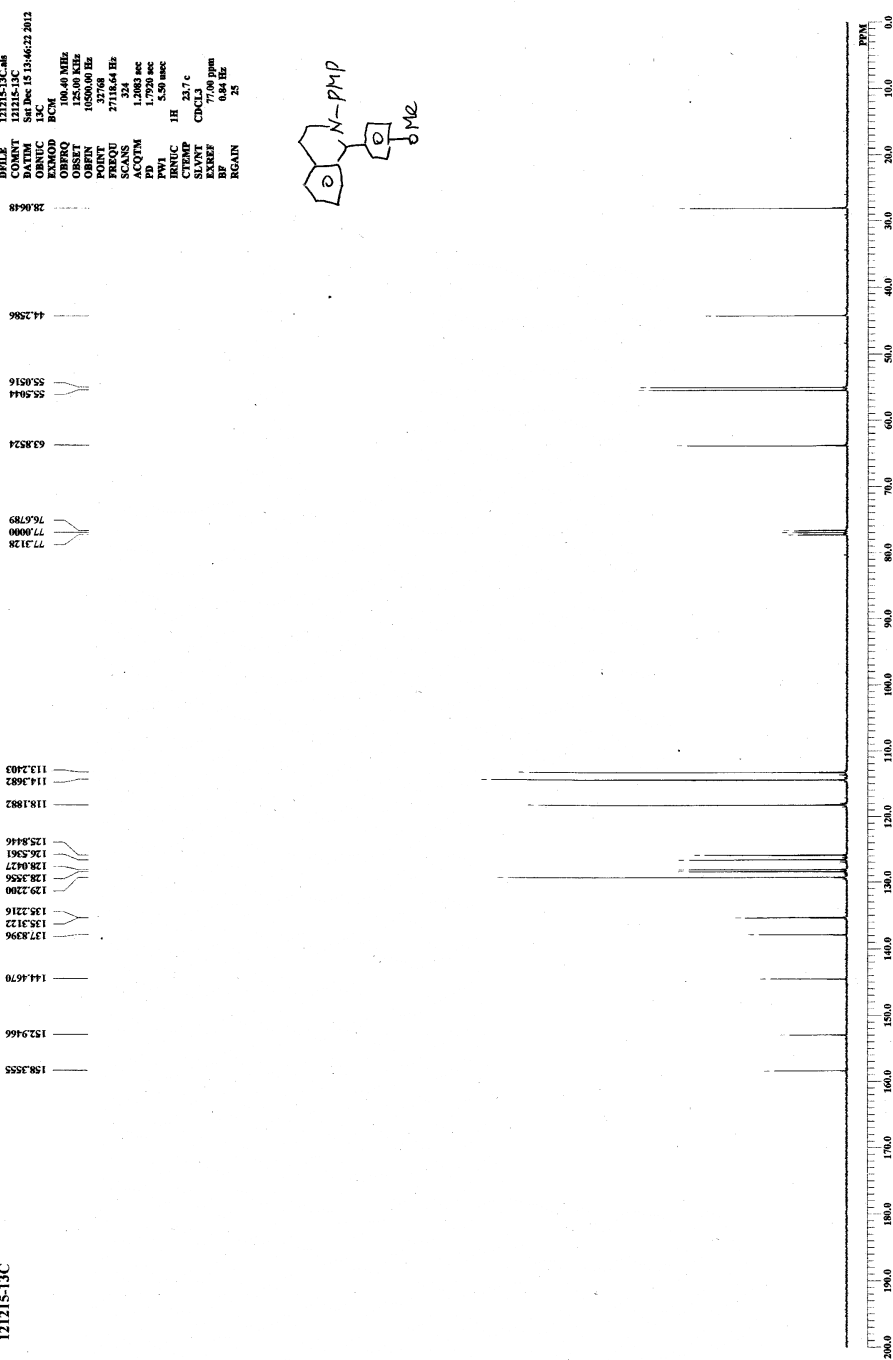
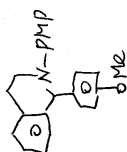


1-(4-Methoxyphenyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (9)



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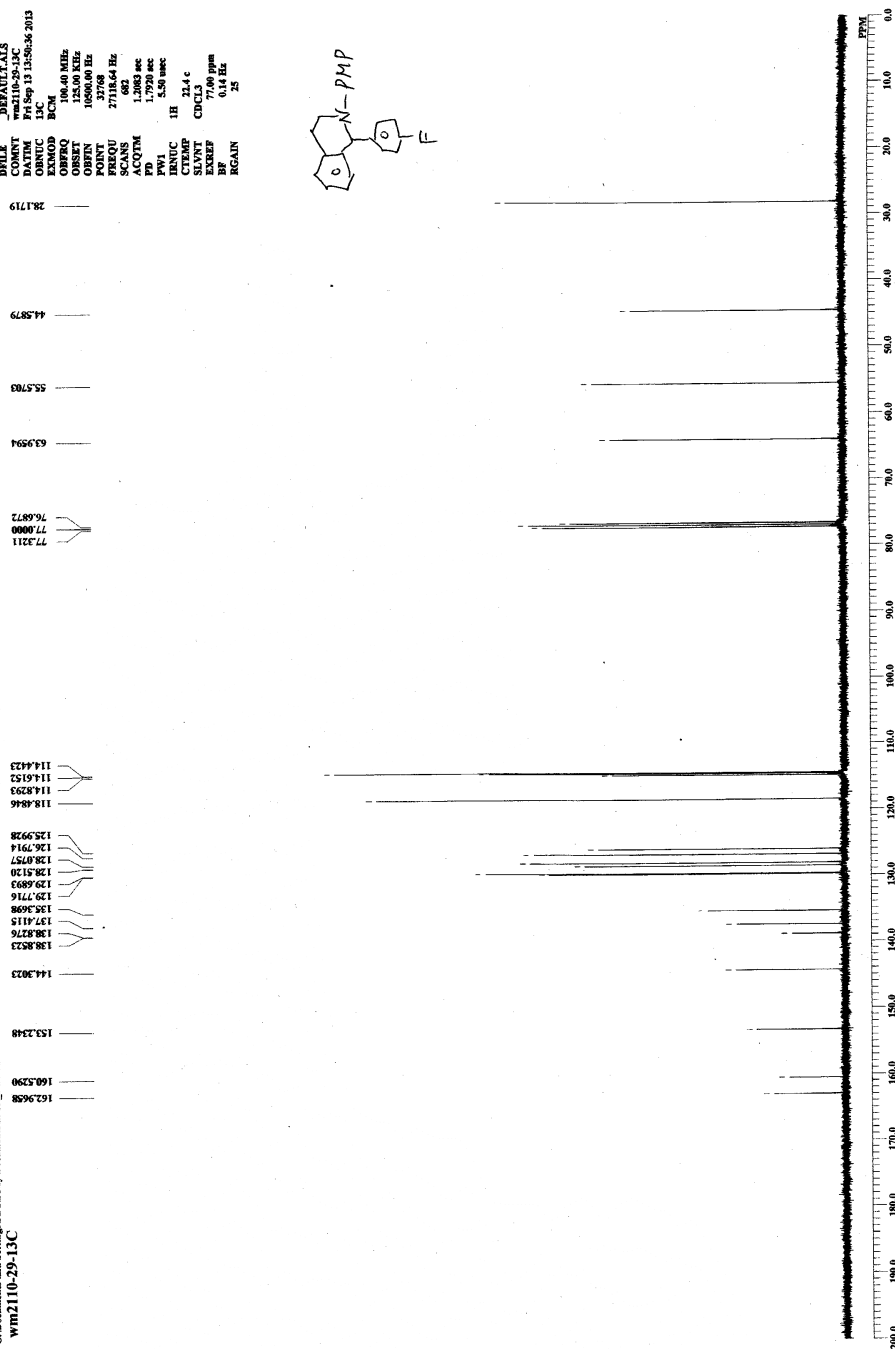
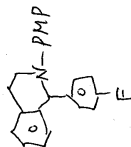
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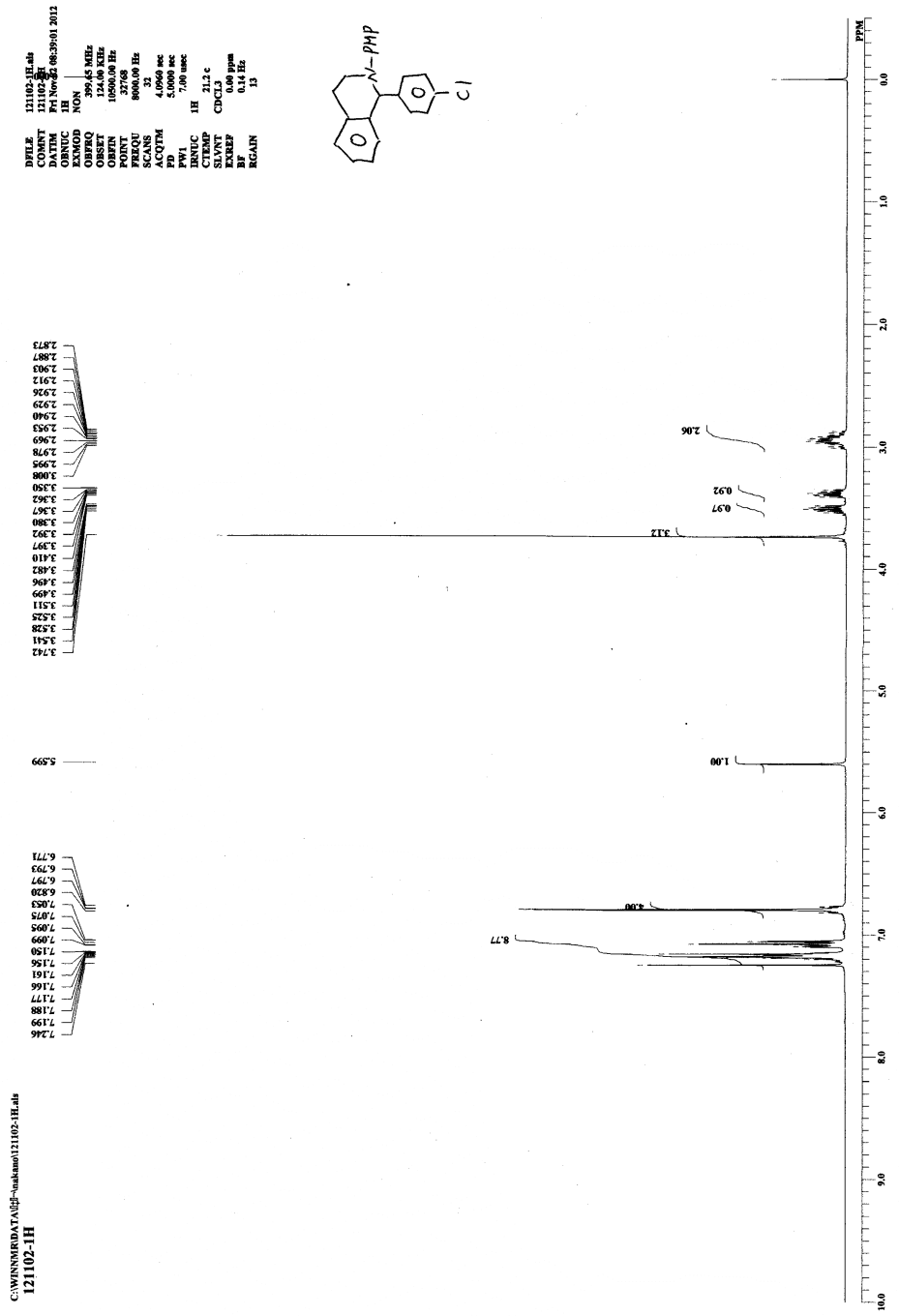
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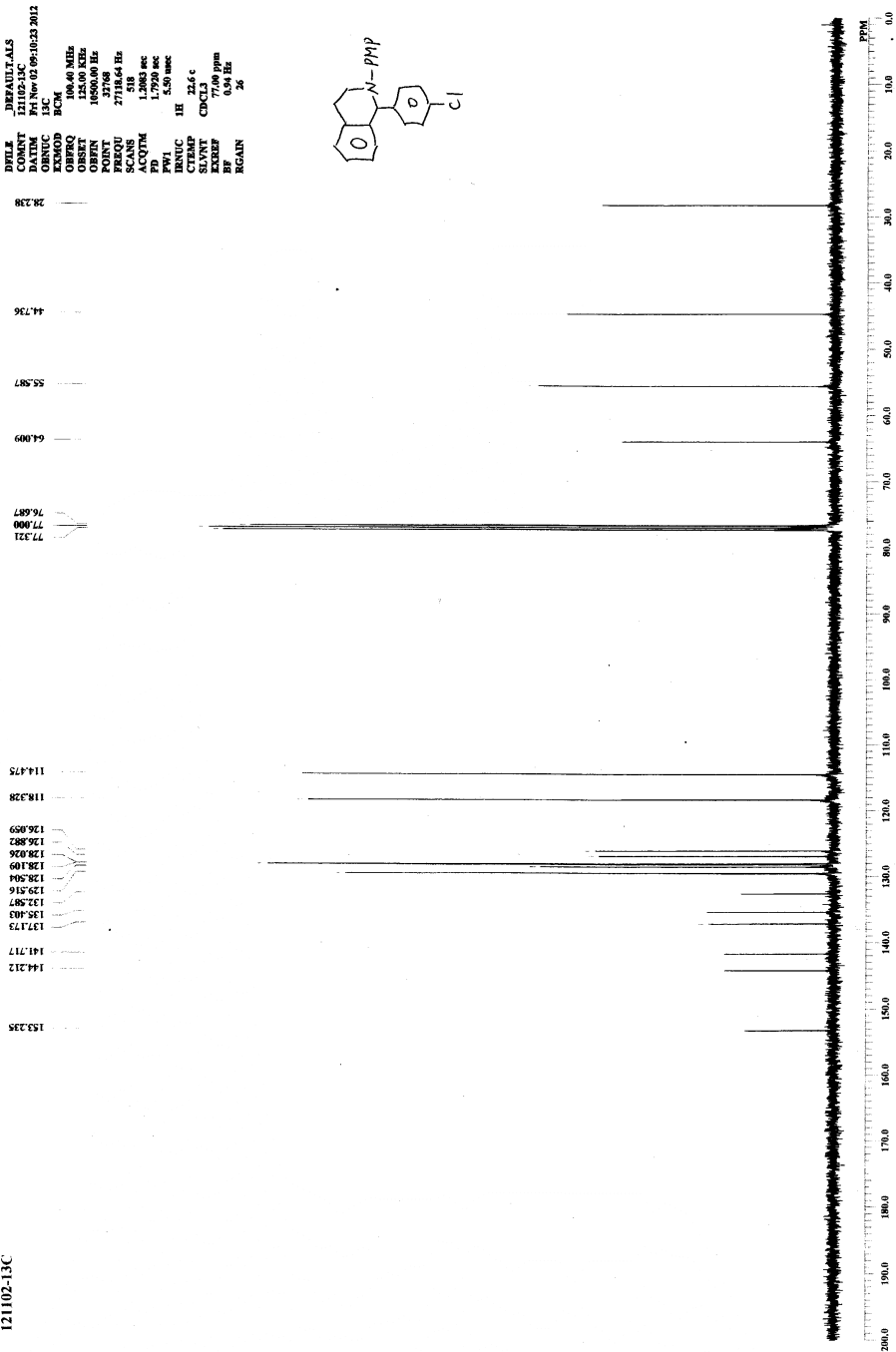
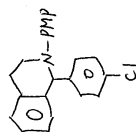


1-(4-Chlorophenyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (11)

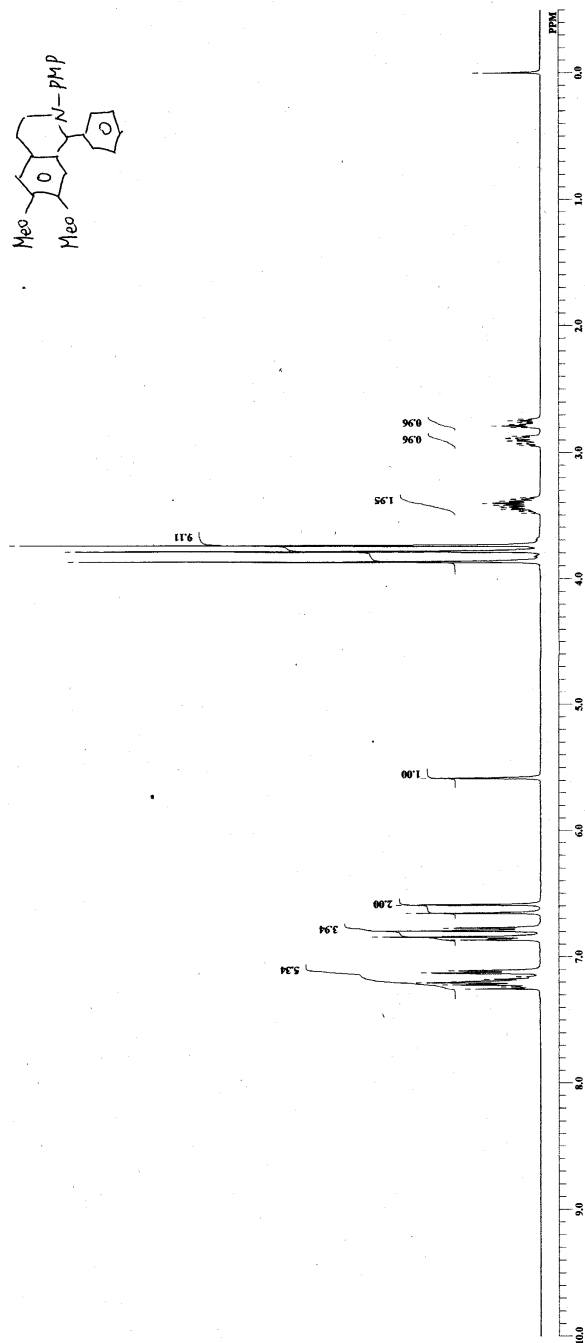
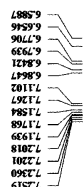
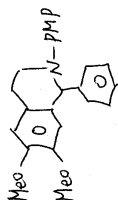


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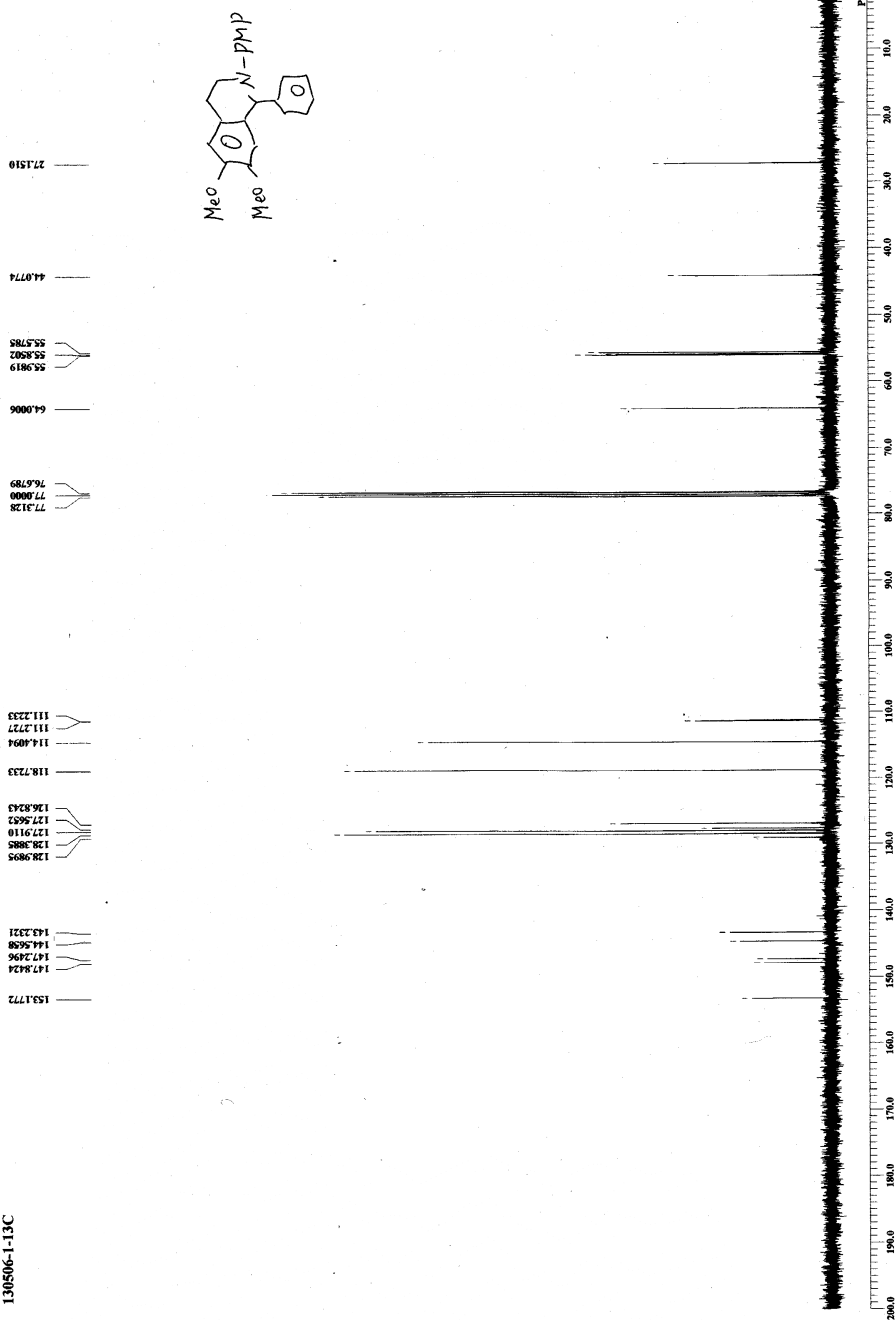
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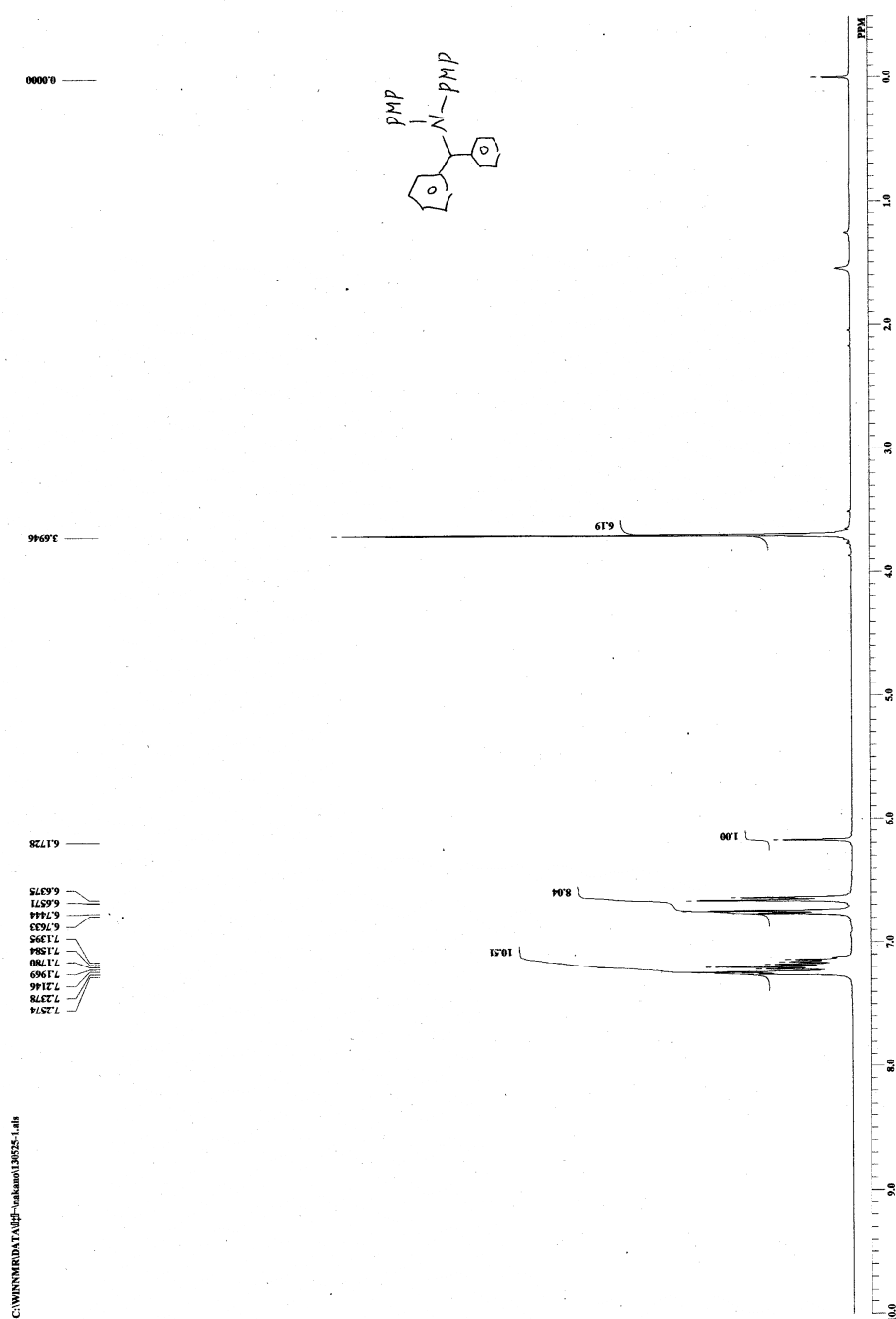
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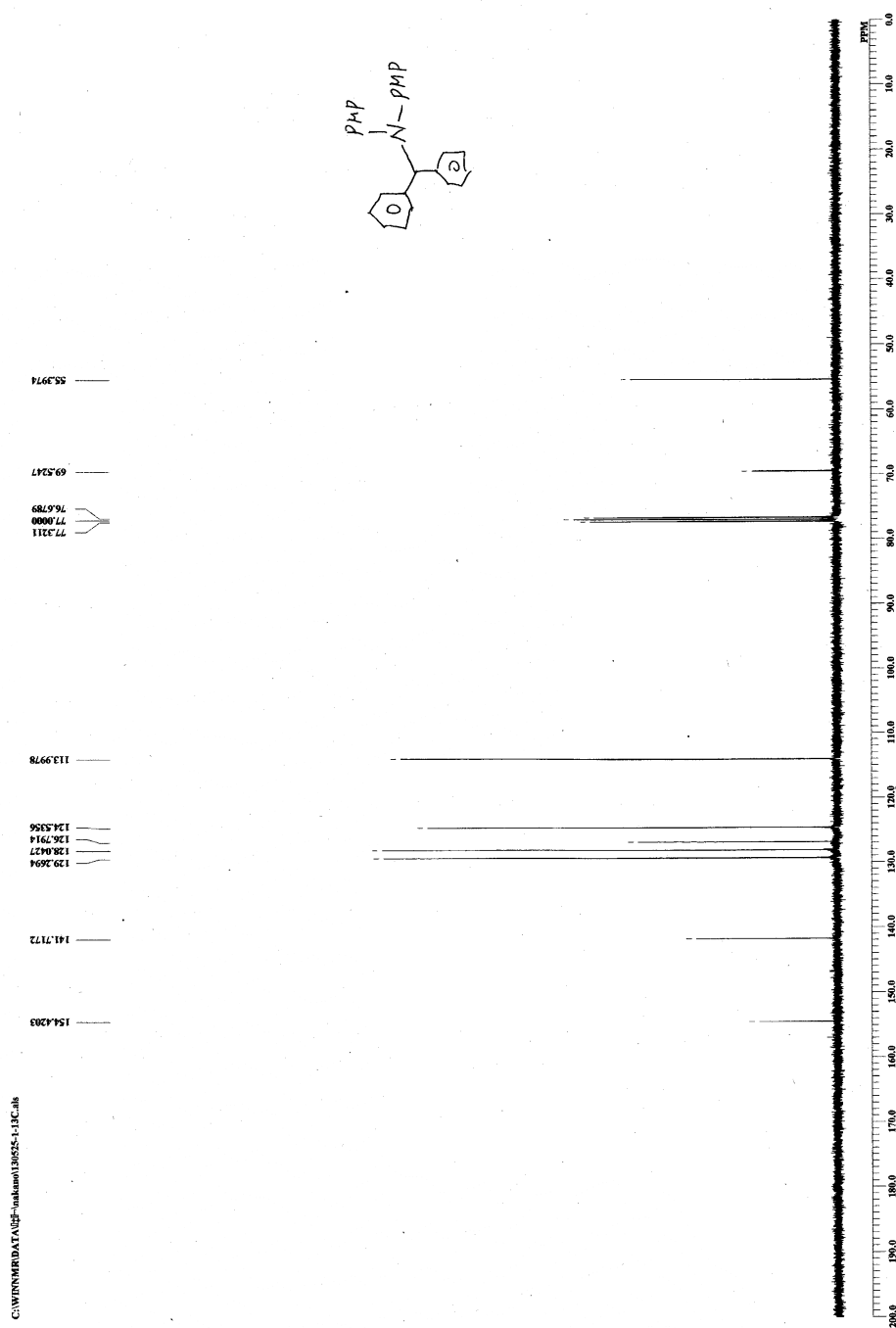


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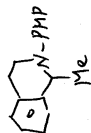
***N,N*-Di-(4-methoxyphenyl)-1,1-diphenylmethanamine (13)**





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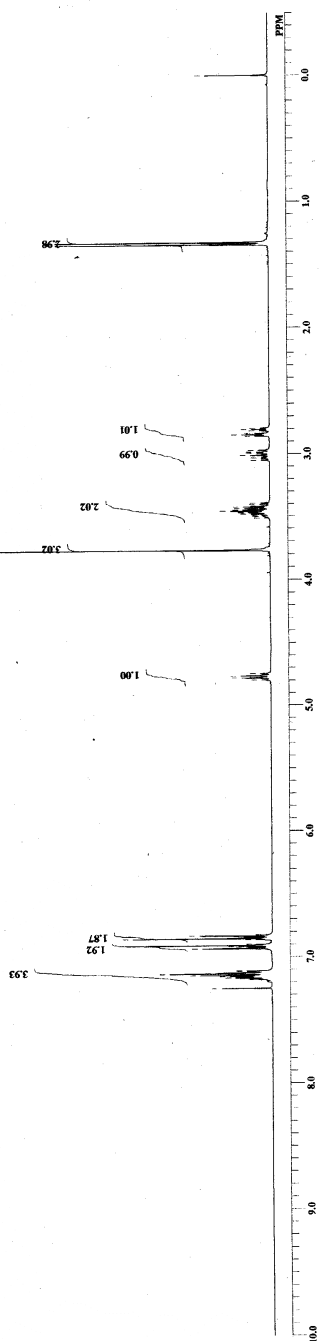


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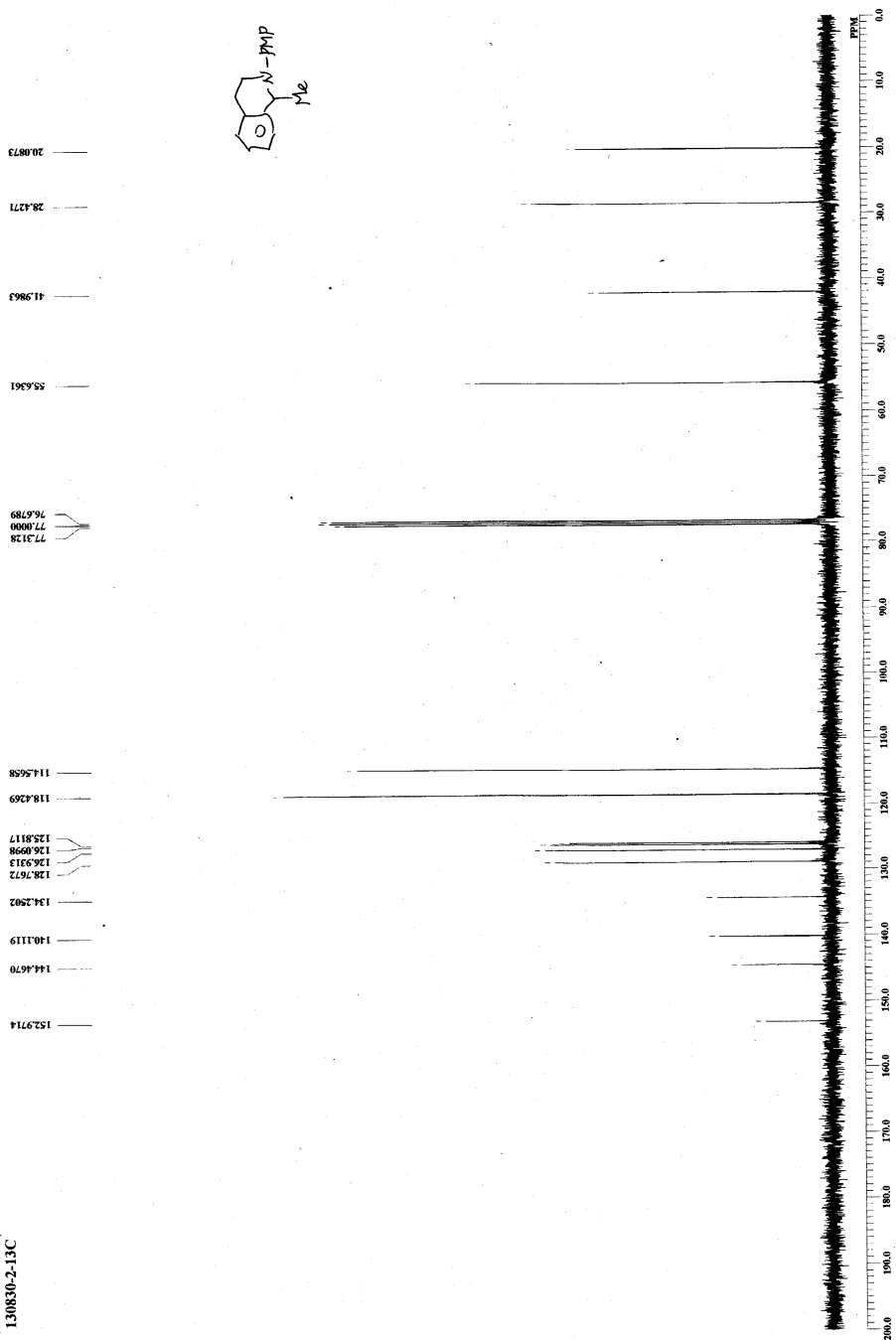
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7.1810
7.2494

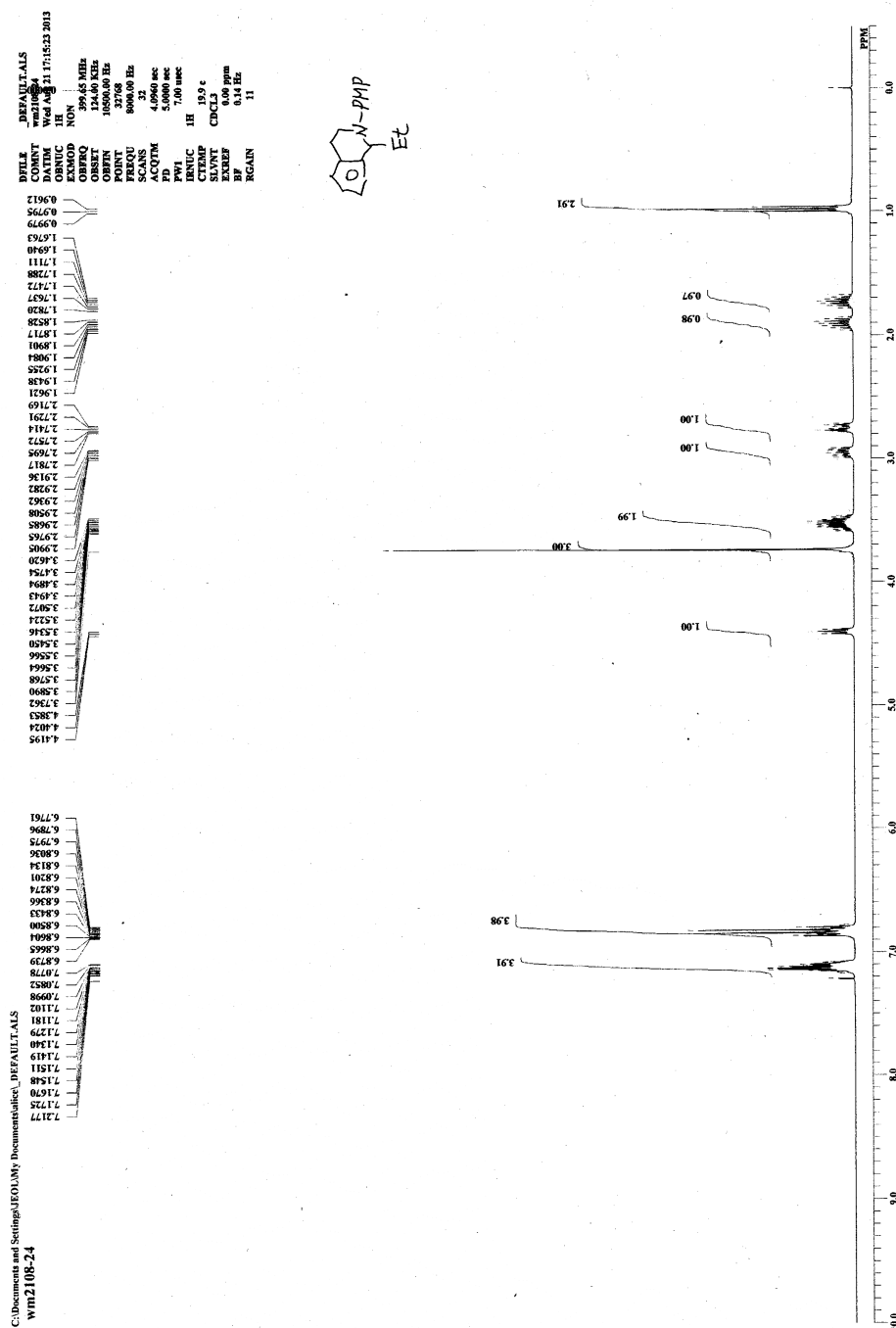
C:\WINNIR\DATA\130830-2.d
 130830-2



C:\WINNIR\DATA\08-11-01\130830-2-13C.ms
130830-2-13C

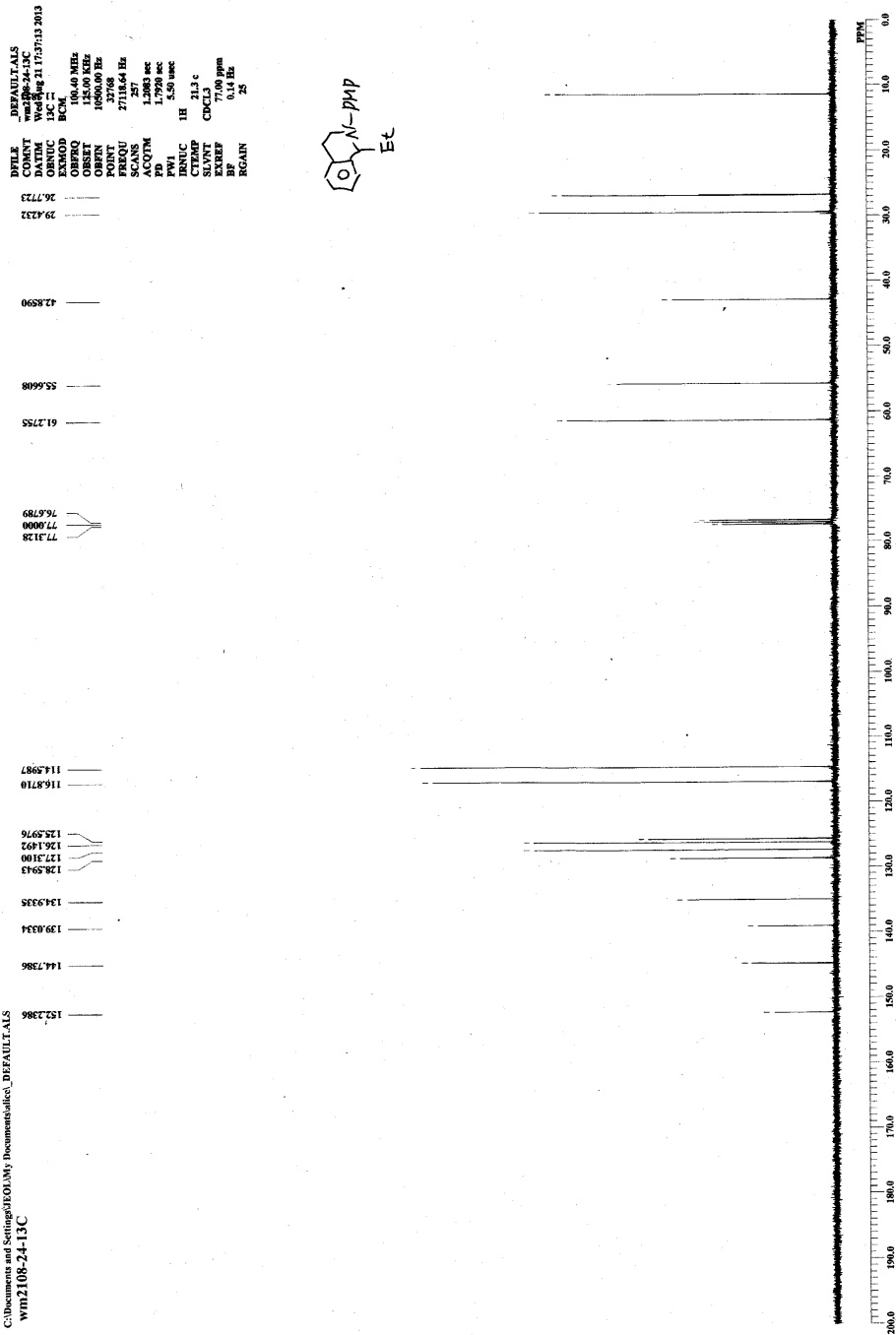
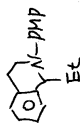


1-Ethyl-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (15)

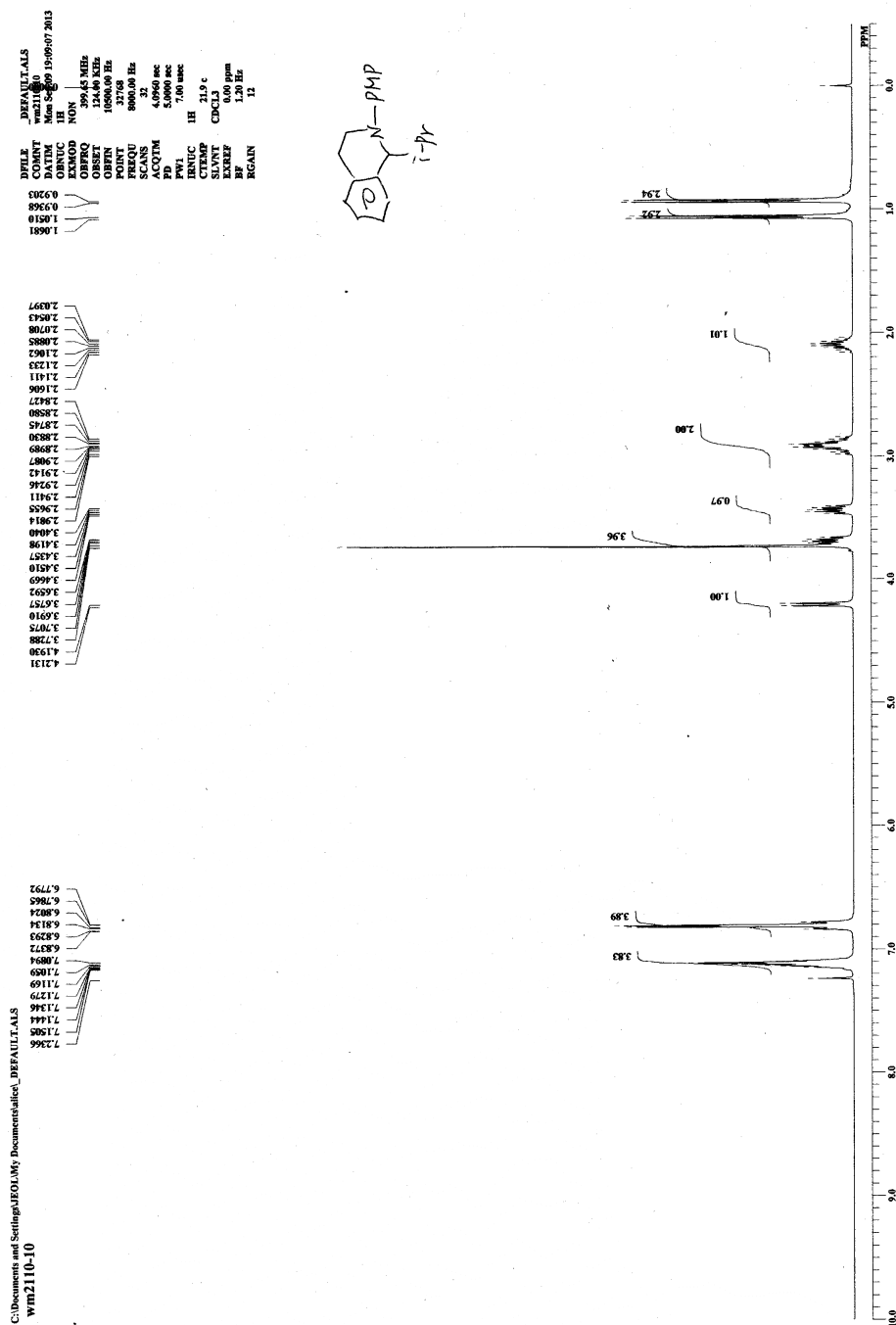


C:\Documents and Settings\TOD.M\My Documents\data\ct_DEFAULT.TALS
W12108-24-13C

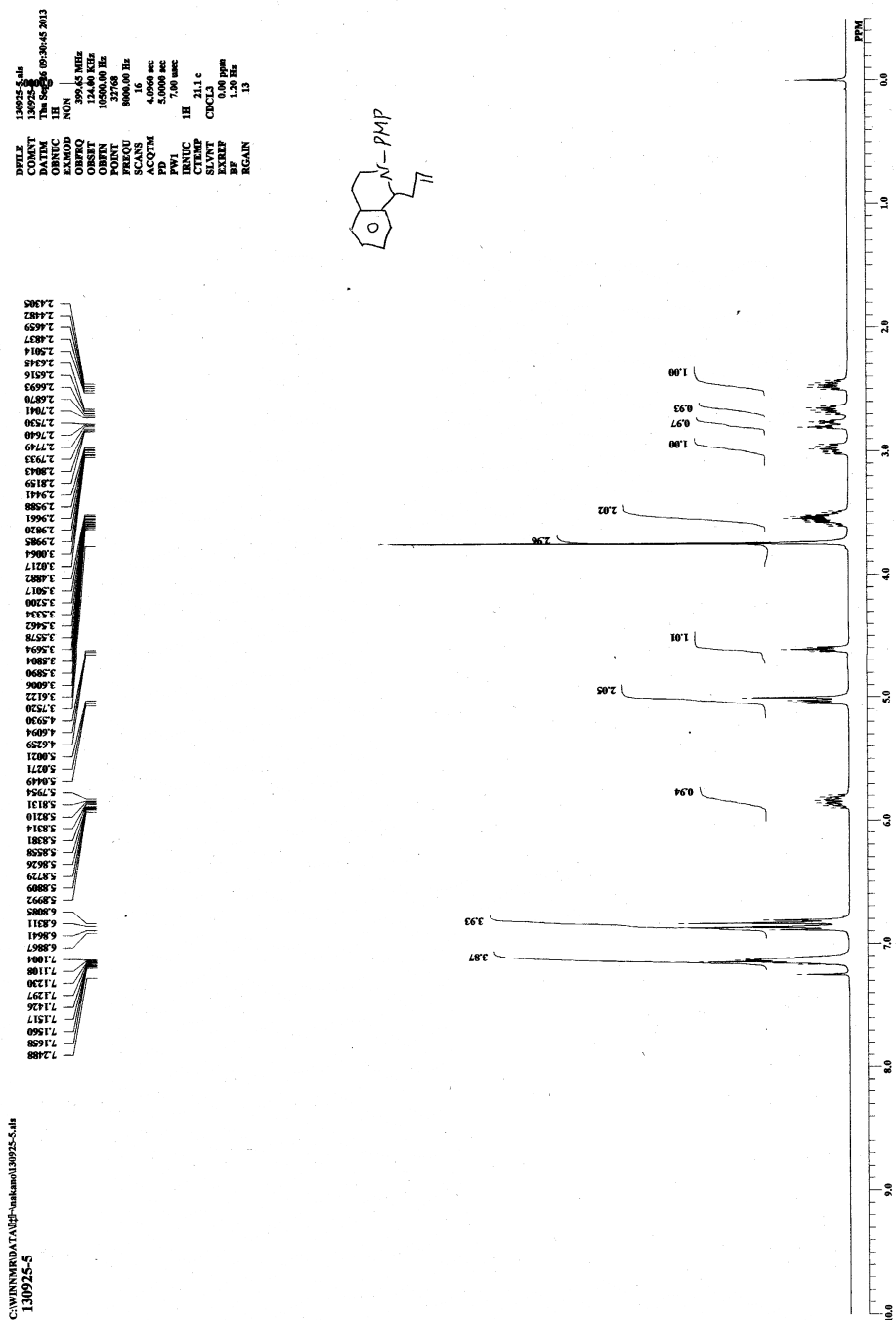
DFILE DEFAULT.TALS
 CONTC W12108-24-13C
 DATE 12/24/2013
 TIME 11:15:15
 INSTR 13C
 EXPROD BCC
 OBSRO 100.40 MHz
 OBSF 125.00 KHz
 OBSW 12500.0 Hz
 POINT 32768
 FREQU 271.184 Hz
 SCANS 257
 ACQTM 1.7200 sec
 PD 1.7200 sec
 FW1 5.50 sec
 IRNUC 1H 71.3 c
 CHANP 13C
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.14 Hz
 RGAIN 25



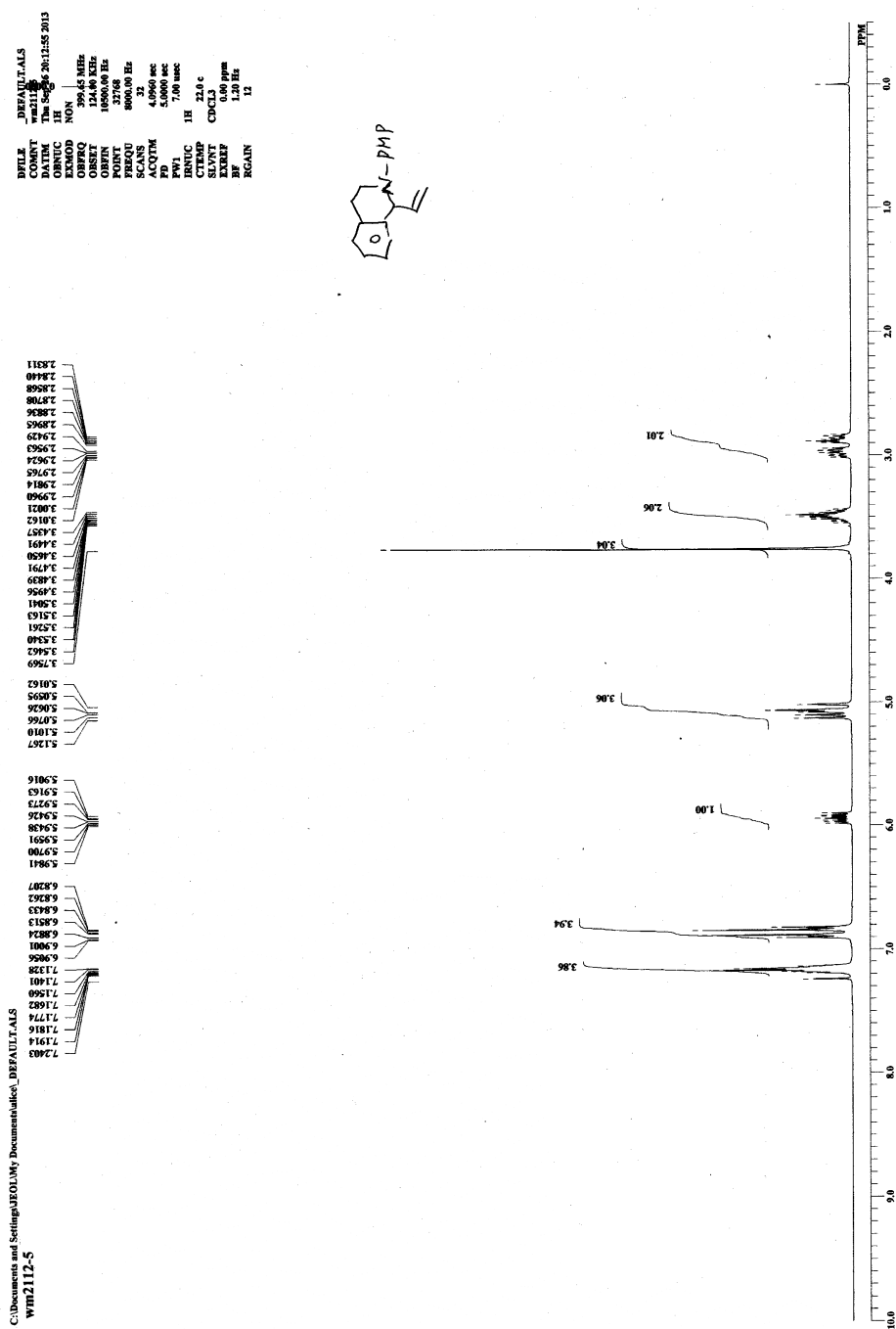
1-Isopropyl-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (16)



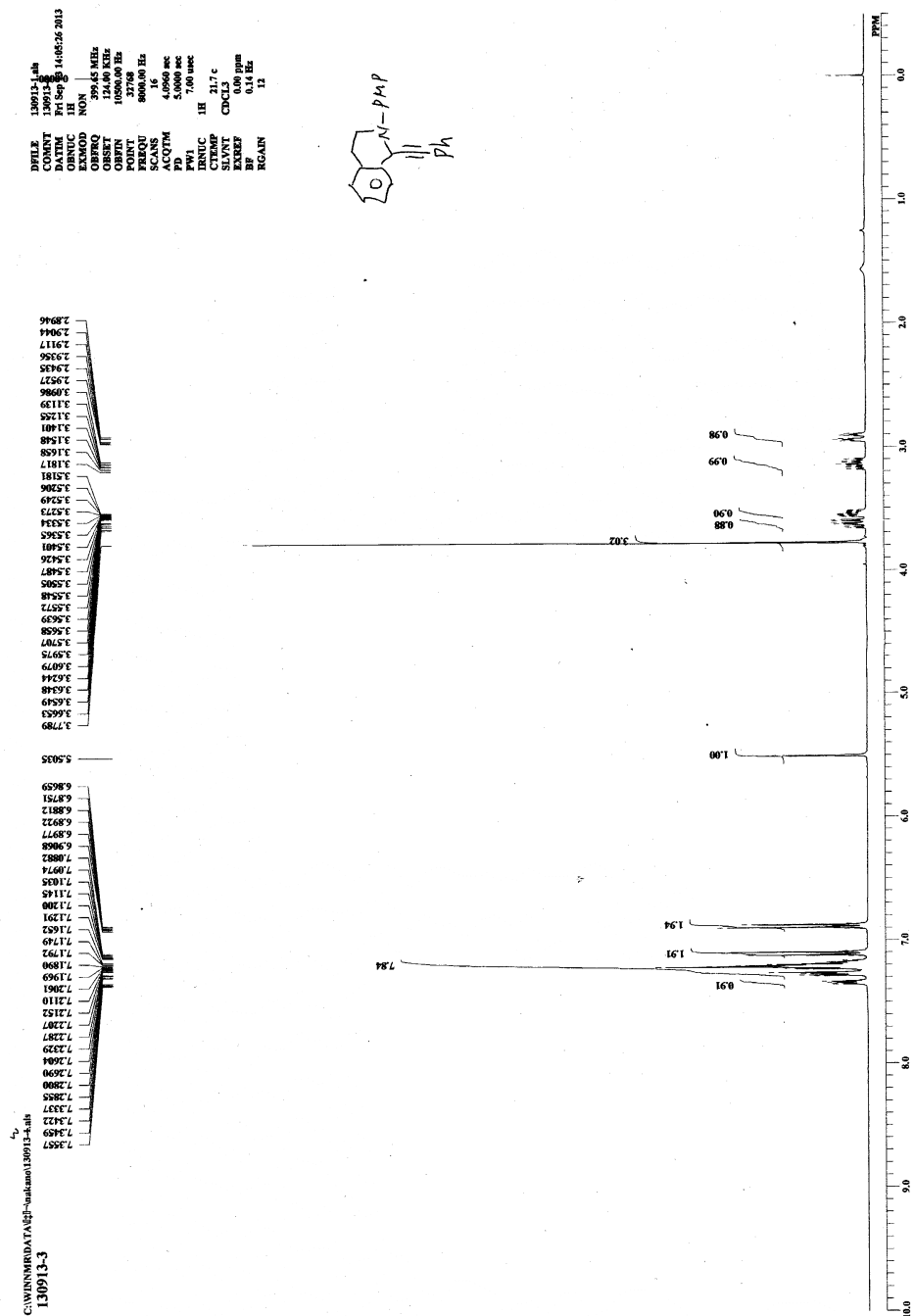
1-Allyl-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (17)



1-Vinyl-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (18)

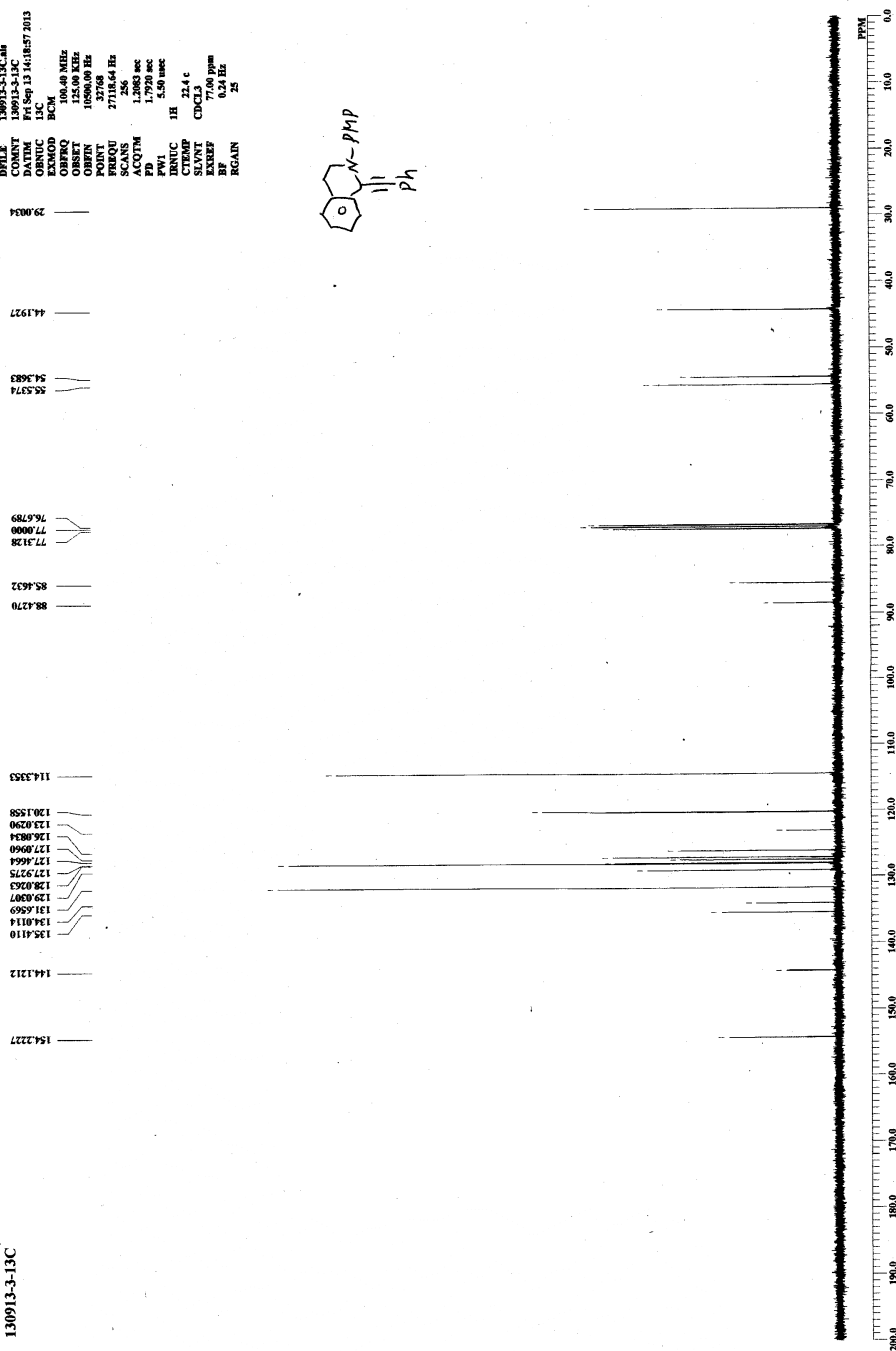
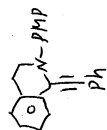


1-Phenylethynyl-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (19)



C:\WINNMR\DATA\2013-09-13\130913-3-13C-46
130913-3-13C

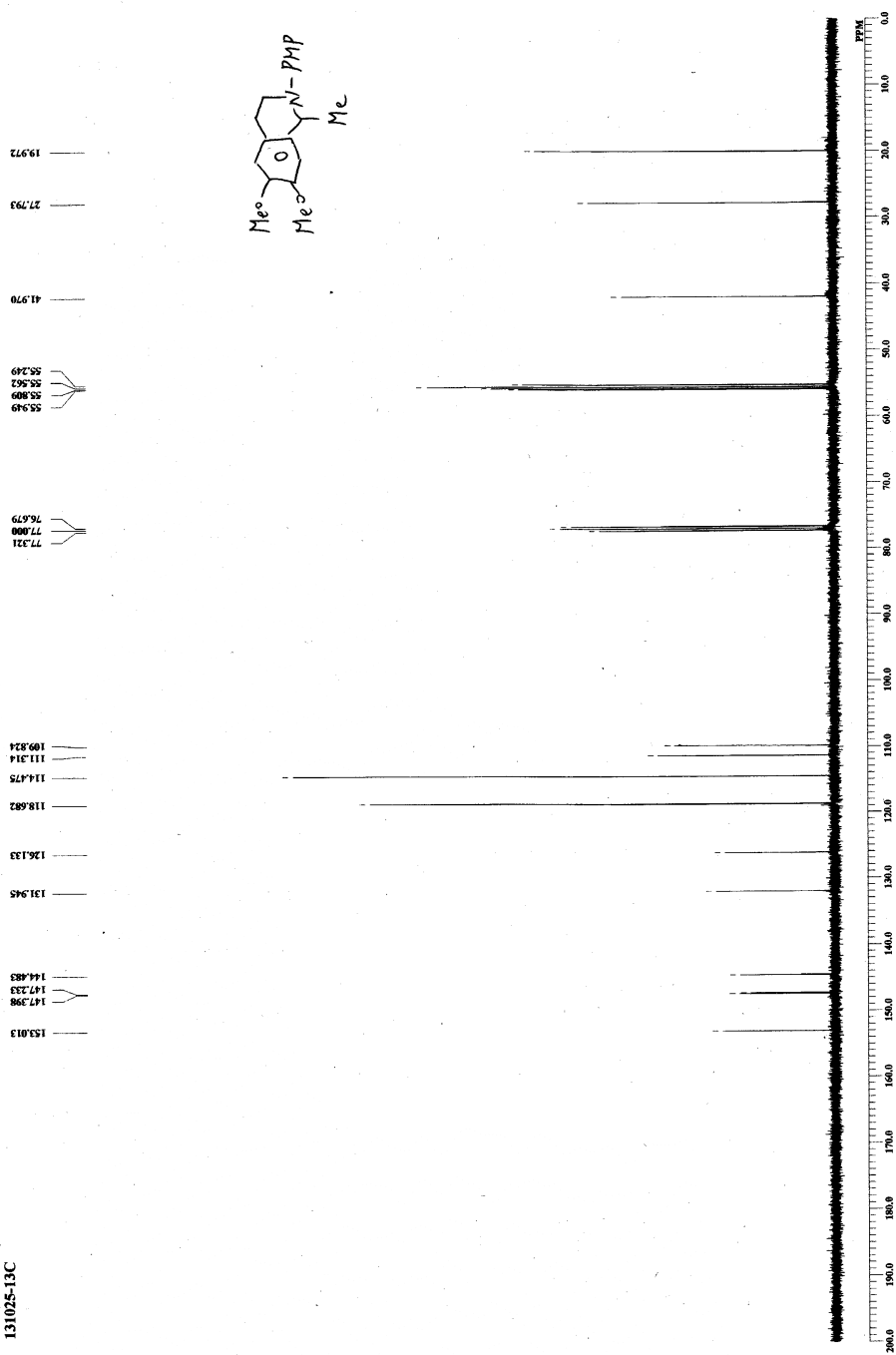
DTITLE 130913-3-13C-46
 CONENT 130913-3-13C
 DATIM 13 Sep 13 14:18:57 2013
 PROCES 1
 EXMODE ECM
 ORFREQ 100.60 MHz
 ORSET 125.00 MHz
 PULPROG zgpg30
 PULPRT 27116.44 Hz
 POINT 286
 SCANS 256
 AVCGTM 1.000 sec
 ACQTIM 1.200 sec
 FWH 5.50 msec
 INNUC 1H 22.4 c
 CTMP CD
 SFO 500.136 MHz
 EXREF 77.00 ppm
 RF 0.24 Hz
 RGAIN 25



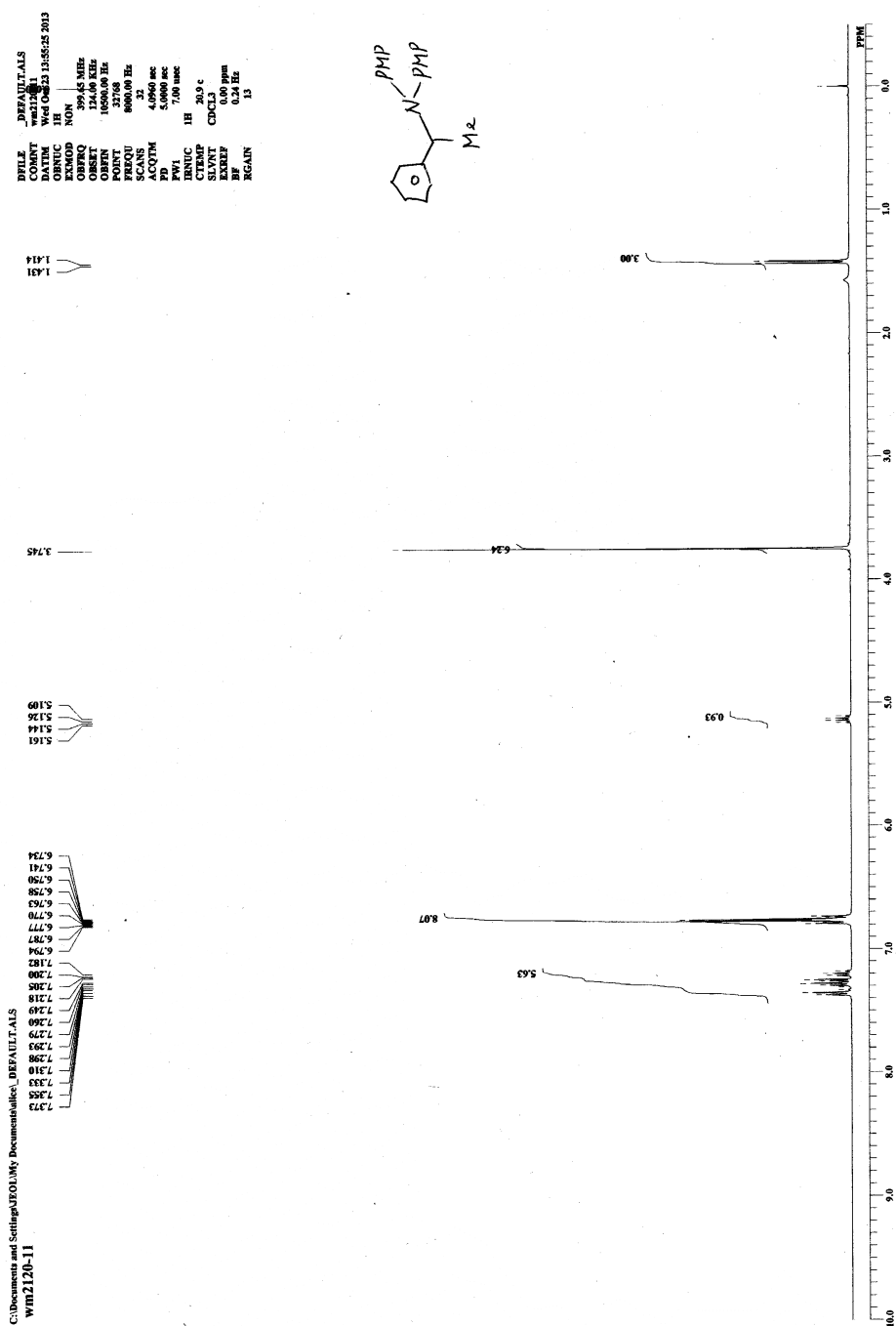
131025



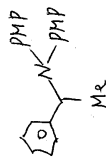
C:\WINNMR\DATA\H1-nakano131025-13C.sls
131025-13C



N,N-Di-(4-Methoxyphenyl)-1-phenylethylamine (21)

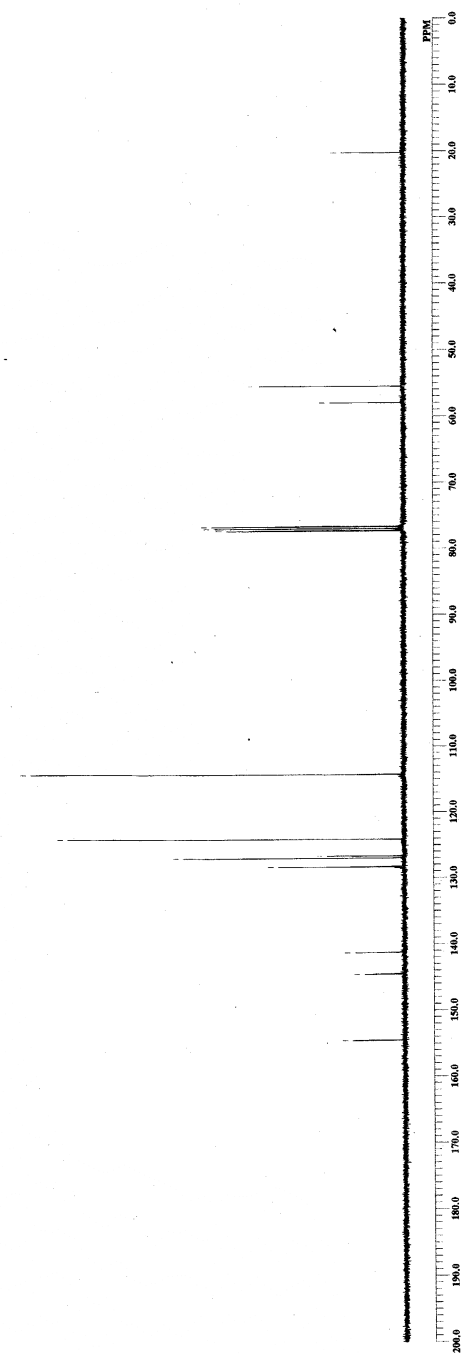


FILE wml2120-11-13C.mh
 COMMENT wml2120-11-13C
 DATE_1 Wed Oct 23 14:23:09 2013
 NAME
 EXMOD BCM
 OBSFQ 100.40 MHz
 OBSFQ 125.00 MHz
 OBSFQ 125.00 MHz
 POINT 271868
 FREQU 271864 Hz
 SCANS 457
 ACQTM 1.700 sec
 PR 1.700 sec
 PW1 5.50 usec
 INNUC 1H 33.3 c
 STTEMP 77.00 ppm
 SOLVENT CDCl3
 EXREF 0.24 Hz
 RGAIN 25



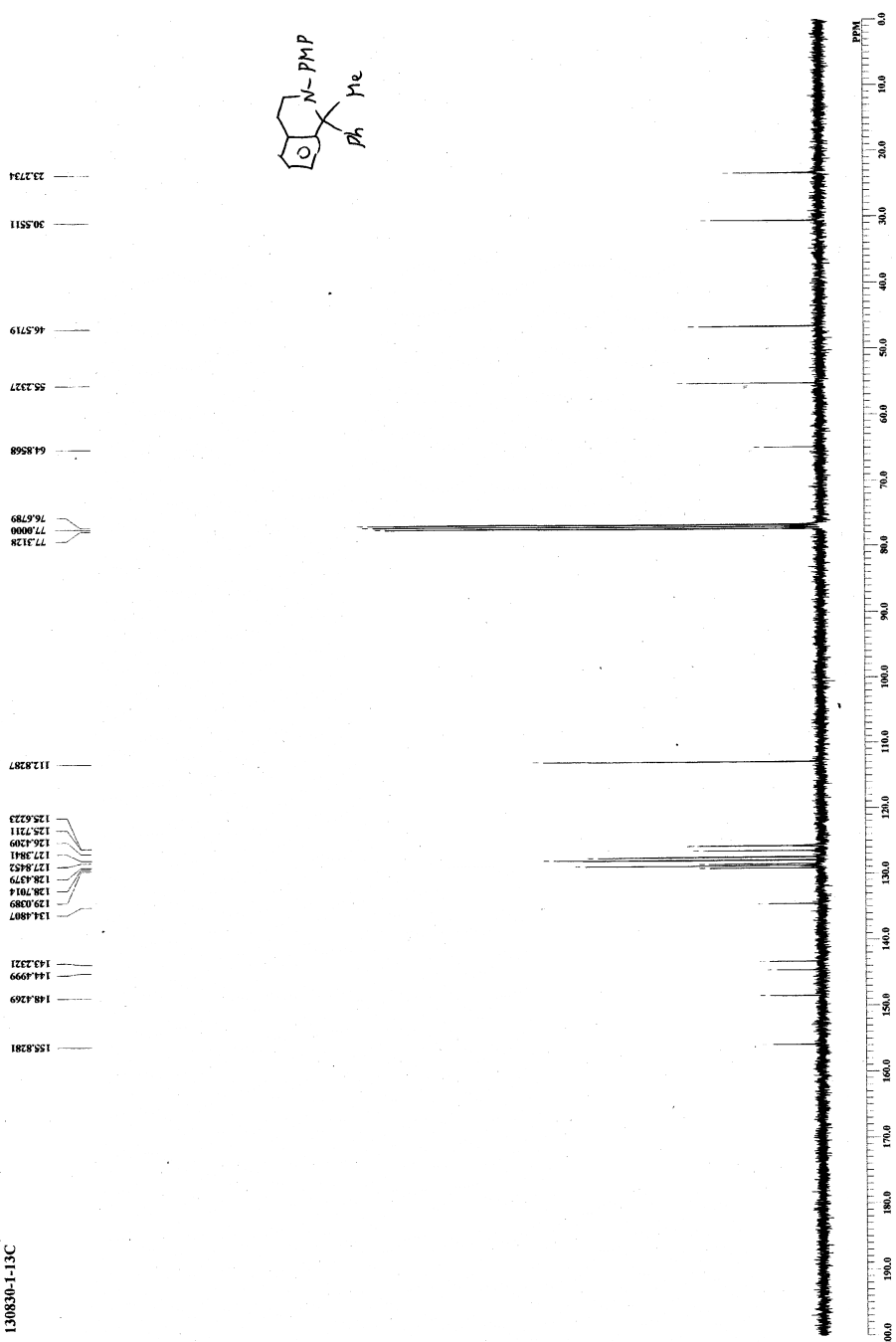
76.679
 77.000
 77.313
 114.228
 124.091
 126.635
 126.964
 128.281
 141.232
 144.483
 154.486

C:\WINNMR\DATA\ddp\wml2120-11-13C.mh
 wml2120-11-13C

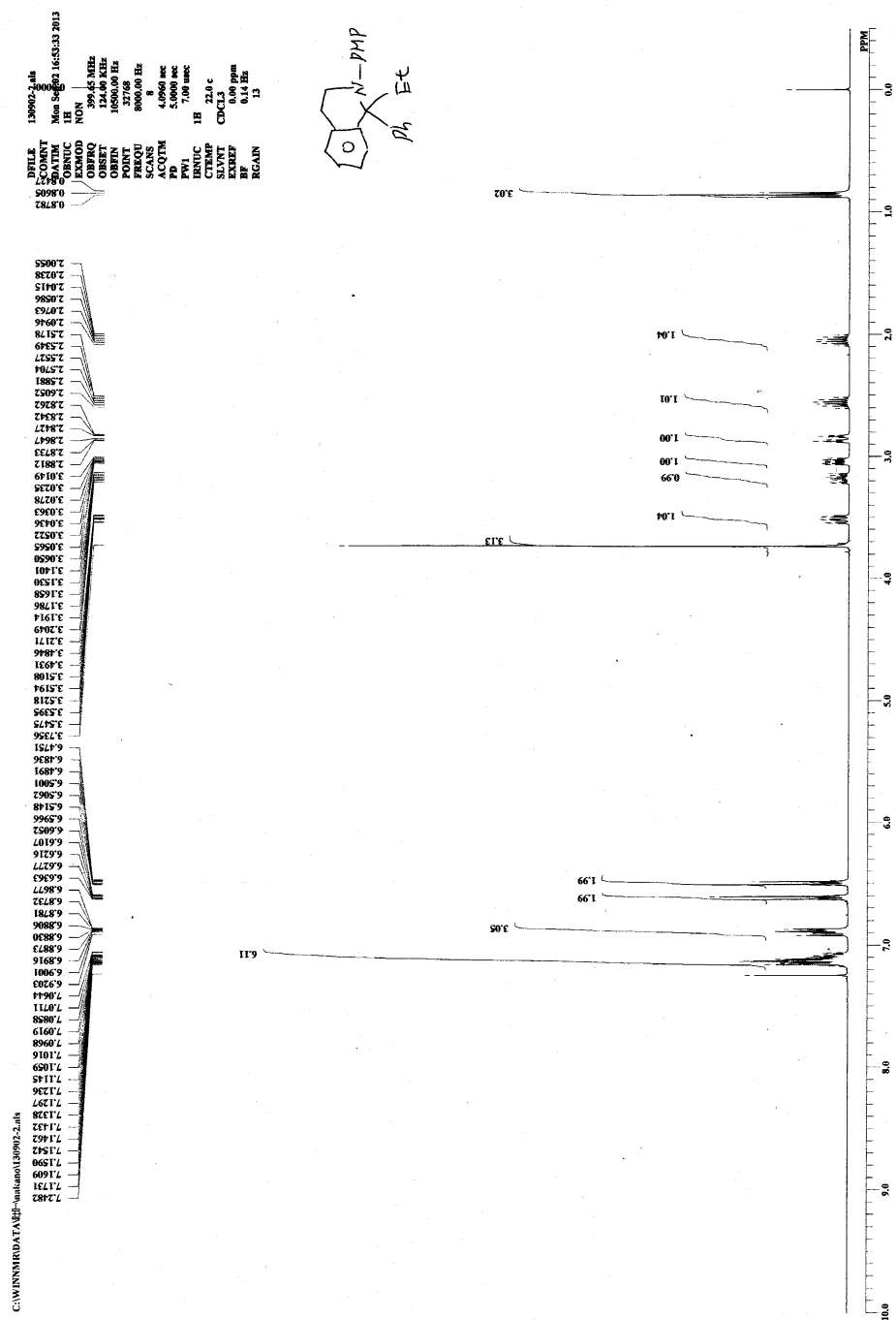


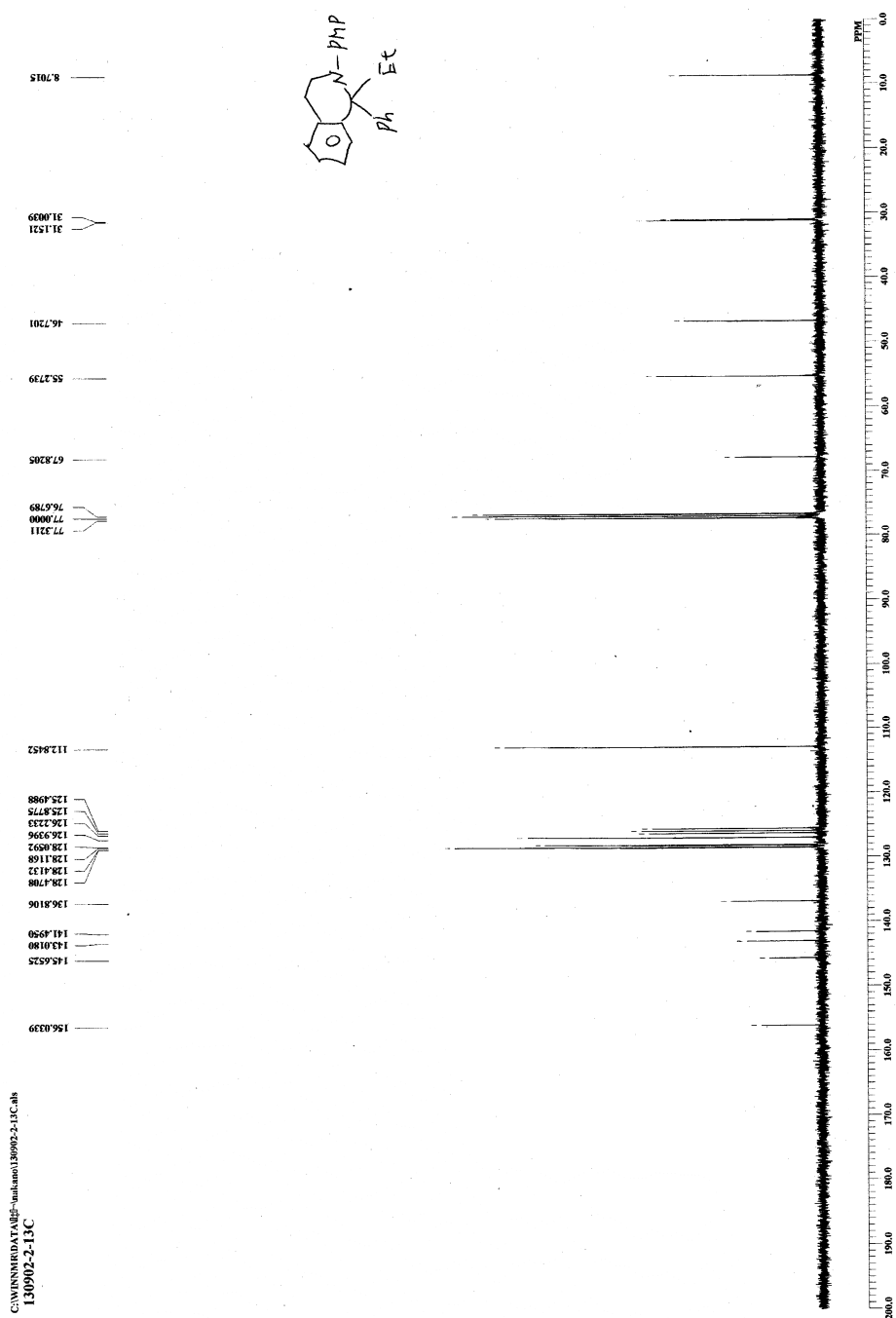
[illegible]

C:\WINNIR\DATA\MS-001\001308340-1-13C.mh
1308340-1-13C

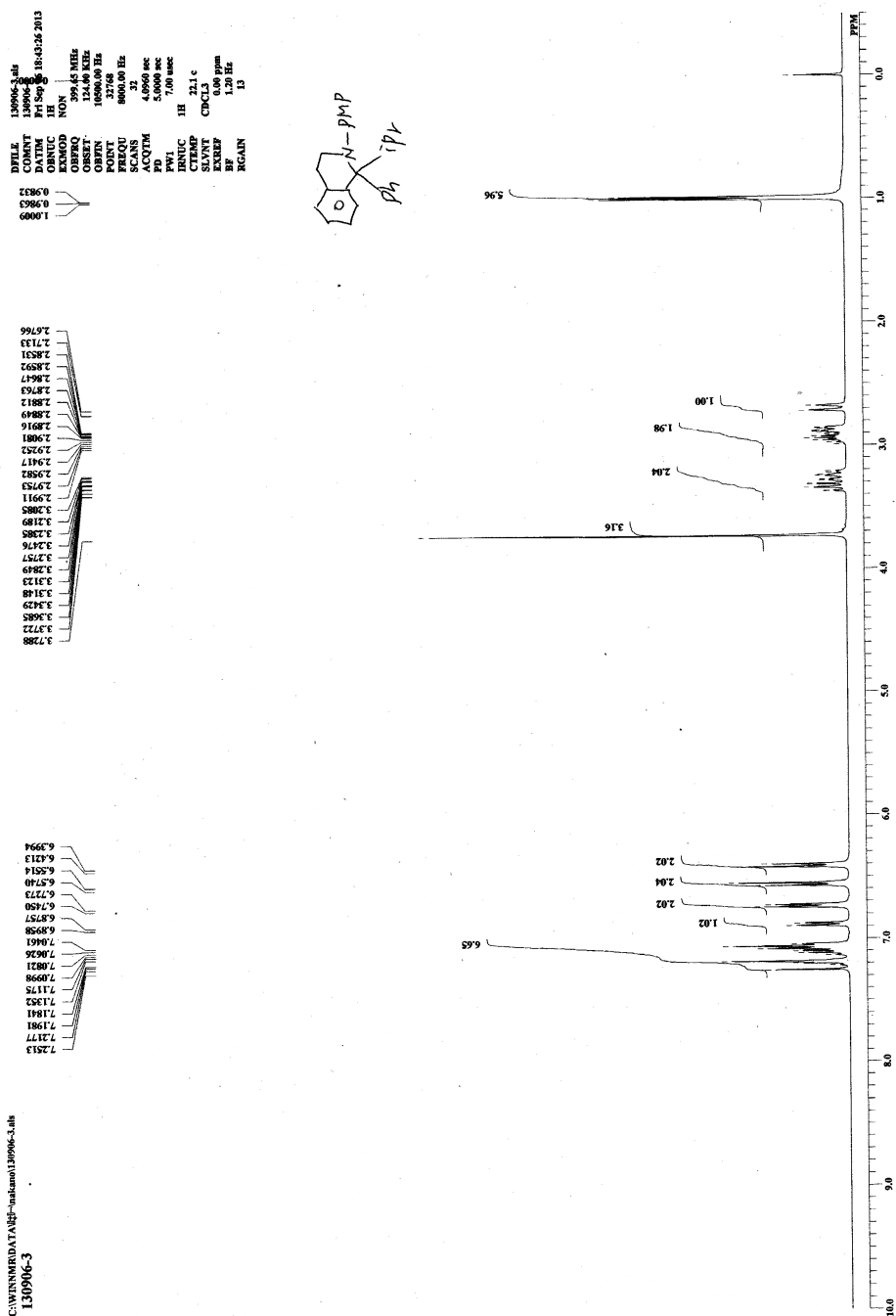


1-Ethyl-1-phenyl-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (23)



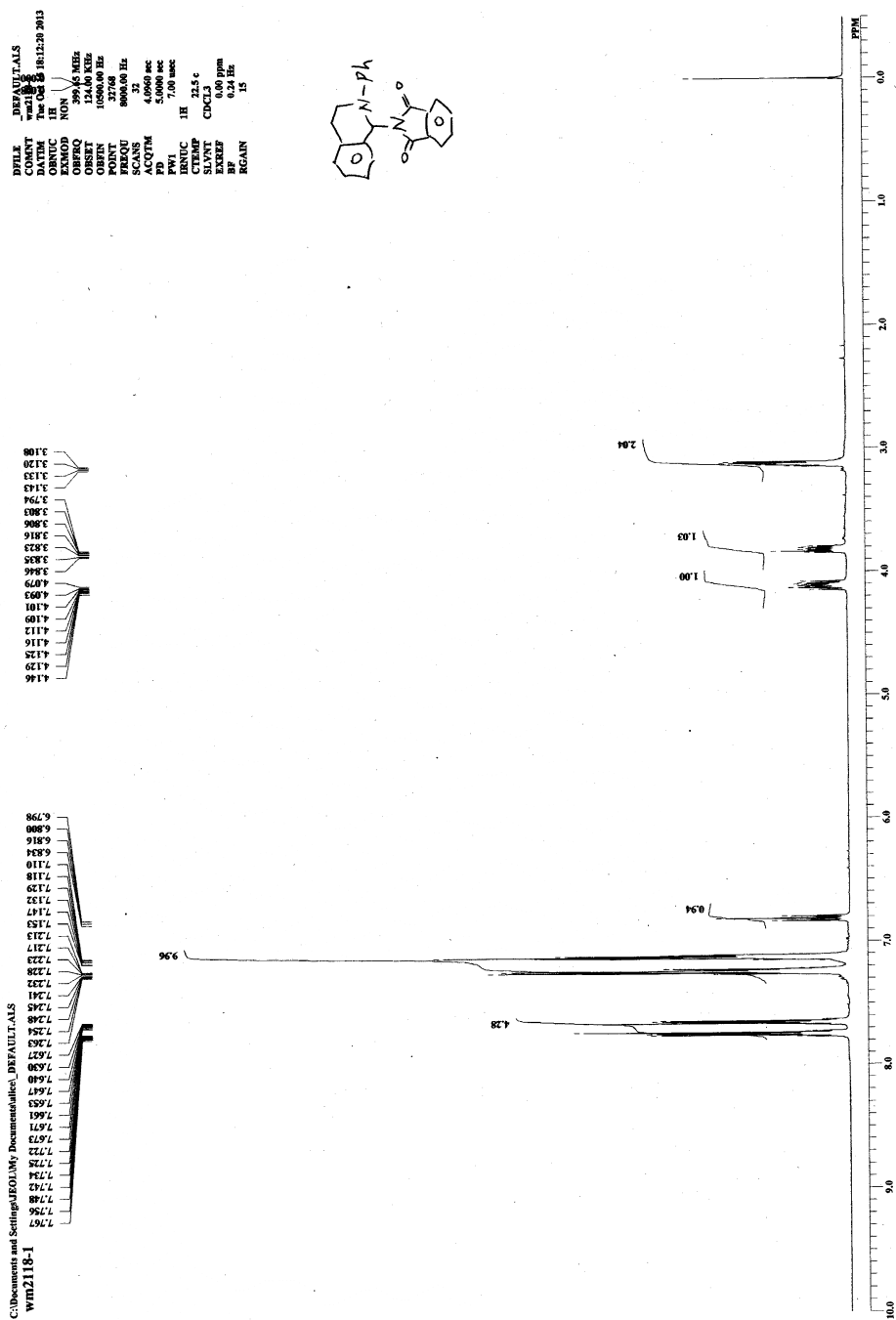


1-Isopropyl-1-phenyl-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (24)

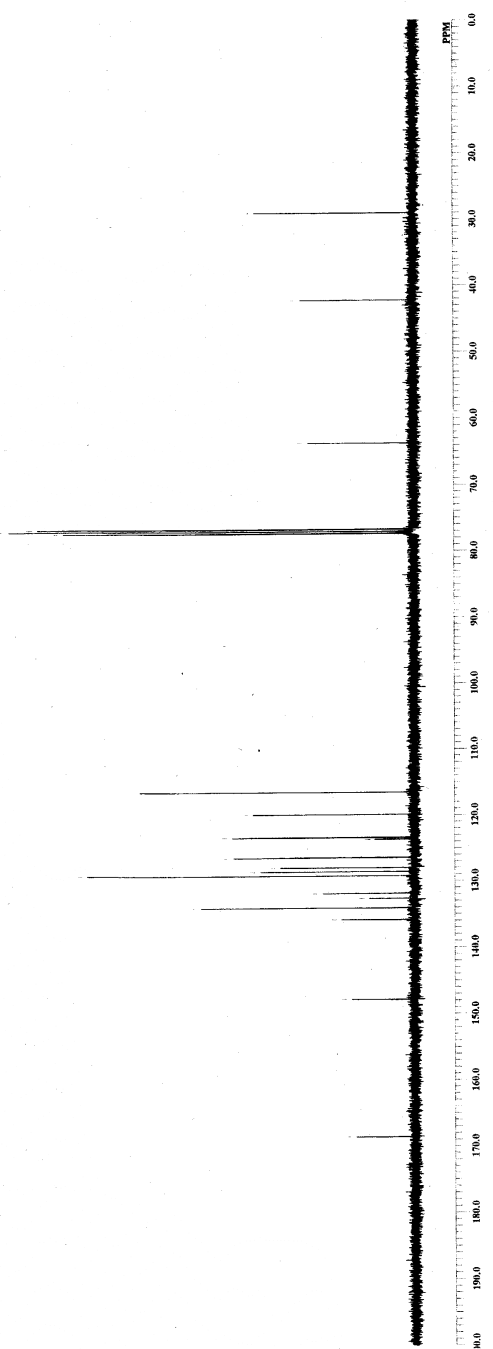
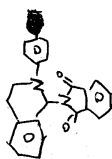


[illegible]

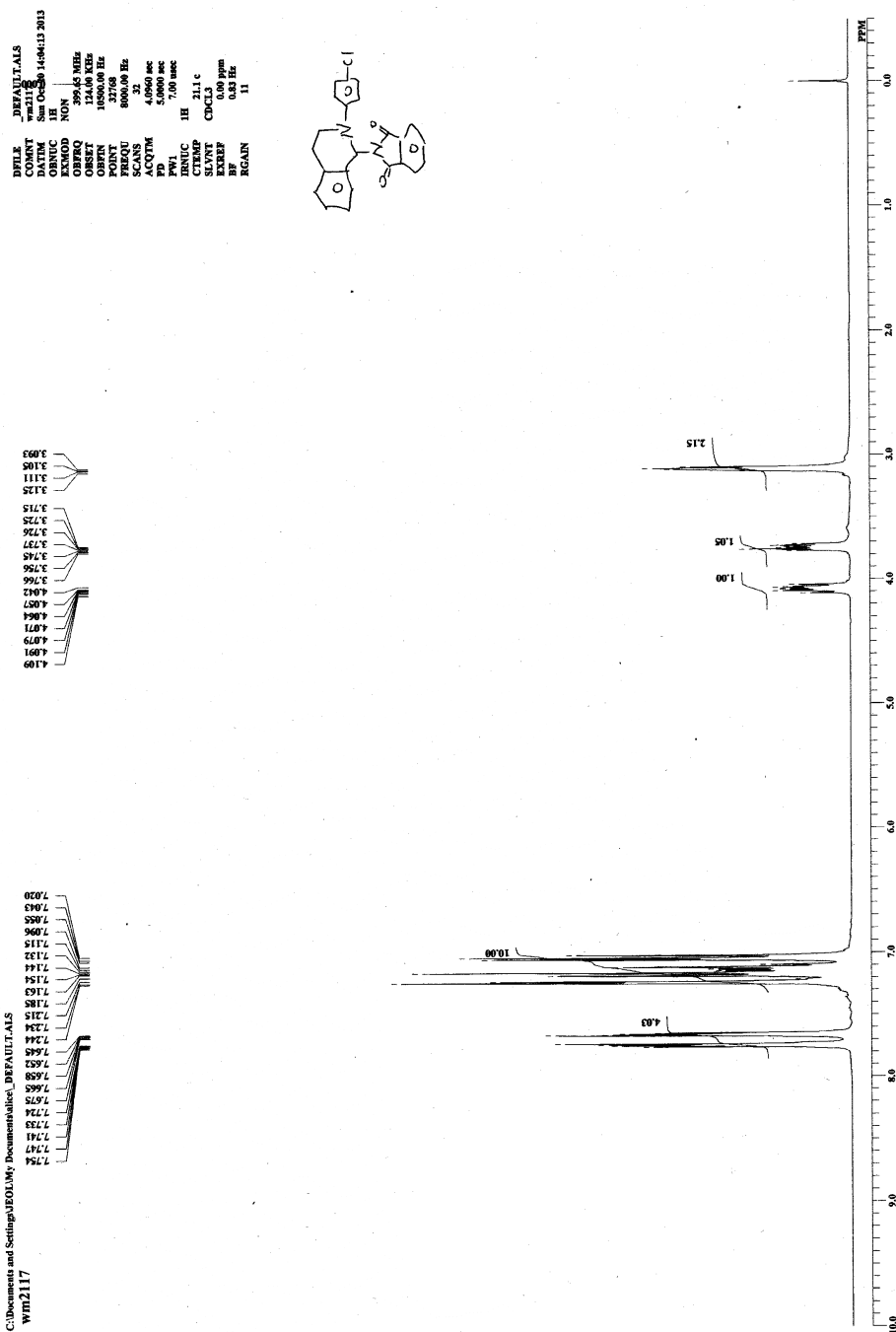
1-(Indene-1,3-dionyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (26)



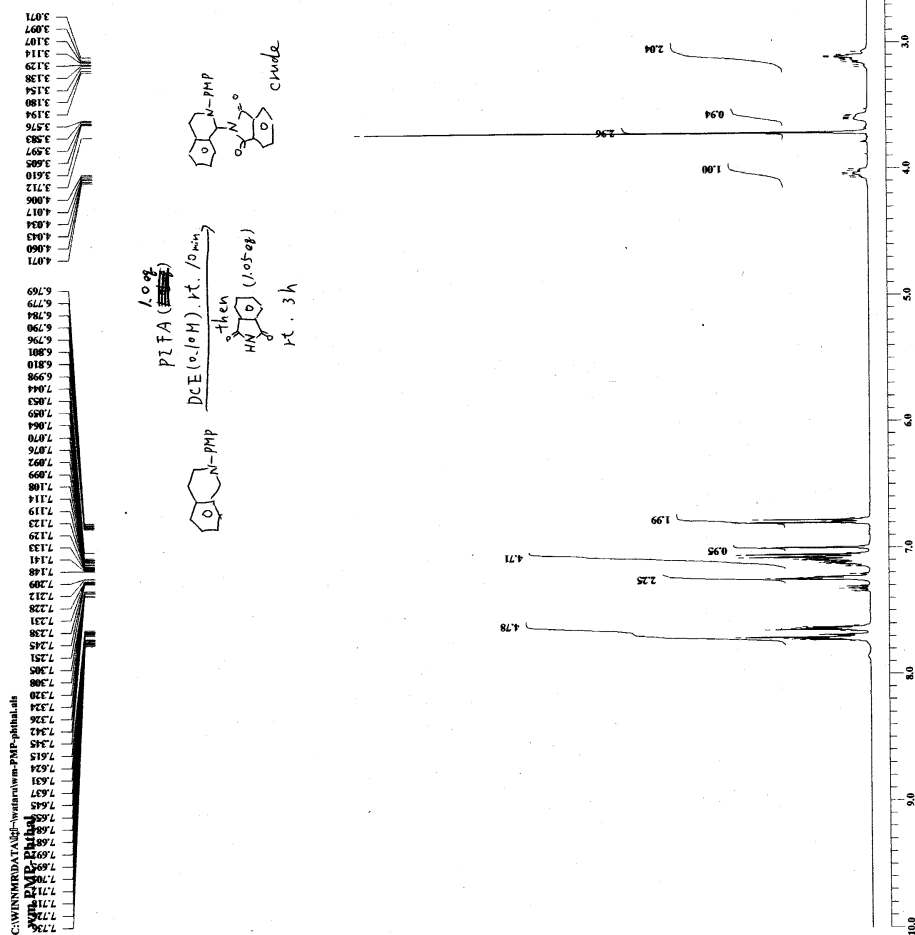
C:\WINNOR\DATA\AU\jswan\wm2118-1-13C.m
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 DATE: 11/15/2005
 TIME: 15:05:05
 INSTR: 13C
 PULPROG: zgpg30
 PROCNO: 1
 F2: 100.625 MHz
 F1: 500.136 MHz
 AQ: 1.720 sec
 SFO: 500.136 MHz
 ACQTM: 1.720 sec
 PD: 1.720 sec
 PWT: 1.720 sec
 FWHM: 1.720 sec
 CT: 1.720 sec
 SLANT: 0.000
 EXREF: 0.000
 BP: 0.000
 RGAIN: 1.000



1-(Indene-1,3-dionyl)-2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (27)



DFILE	wa-PAC-ahhhhhhh
COMMENT	wa-PAC-Final
DATE	Wed Oct 30 18:23:24 2013
OPERATION	1B
OBSCUR	NON
EXMOD	399.43 MHz
ORFREQ	399.43 MHz
ORBSRT	100000 Hz
ORBSRT	32768
POINT	8900.00 Hz
FREQ00	32
SCANS	4.0950 sec
ACQTIME	5.0000 sec
PDW	7.00 msec
FW1	1B
IRNUC	21.1 c
CTEMP	CDCL3
SLVNT	8.00 ppm
EXREF	0.14 Hz
BF	12
RGAIN	



C:\Documents and Settings\JFO\My Documents\data\ex_defaults
wim PMP-Phthal-13C

DEFAULTS
COMET wim PMP-Phthal-13C
DATE Wed Oct 30 18:52:30 2013
ORNUC 13C
PULPROG zgpg30
PROBHD 5mm QNP 1H/13C
P1 12.00
PC 100.00
PD 1.20
PE 0.00
PF 0.00
PG 0.00
PH 0.00
PI 0.00
PJ 0.00
PK 0.00
PL 0.00
PM 0.00
PN 0.00
PO 0.00
PP 0.00
PQ 0.00
PR 0.00
PS 0.00
PT 0.00
PU 0.00
PV 0.00
PW 0.00
PX 0.00
PY 0.00
PZ 0.00
RGAIN 25

29.259

43.729

55.406

64.881

76.679

77.313

114.311

119.654

123.251

126.397

126.396

127.417

127.837

128.530

130.200

131.747

132.538

133.954

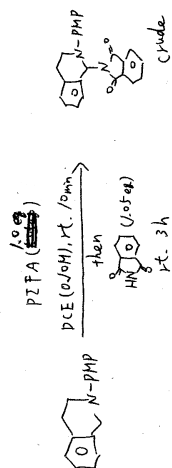
135.831

137.436

141.972

154.058

168.605



1-(*N*-*p*-Tosyl)-2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (29)

