

Experimental procedures and characterization data

for

**Thiazolium-Derived *N*-Heterocyclic Carbene-Catalyzed
Cross-Coupling of Aldehydes with Unactivated Imines**

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General Methods. Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use.

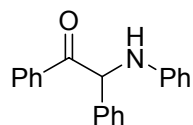
¹H NMR spectra were recorded on a VARIAN Mercury 300 MHz spectrometer in chloroform-d₃. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data are reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration).

¹³C NMR spectra were recorded on a VARIAN Mercury 75 MHz spectrometer in chloroform-d₃. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard.

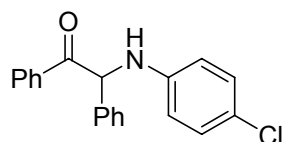
Substrates **3a-3i**¹ and **1c**² were prepared by known literature methods.

General Procedure of the Cross-Coupling of Aldehydes with Imines (4a): To a solution of 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride (**1a**, 0.054 g, 0.2 mmol) in ethanol (1.0 mL), Et₃N (28 μL, 0.2 mmol) was added. After the mixture was stirring for 5 min, benzaldehyde **2a** (0.12 mL, 1.2 mmol) and *N*-benzylidenebenzenamine

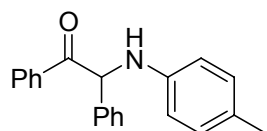
3a (0.181 g, 1.0 mmol) were added. The mixture was stirred for 2 days at 70°C. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (PE : EtOAc = 150 : 1), affording the title compound as a yellow solid (235 mg, 82%).



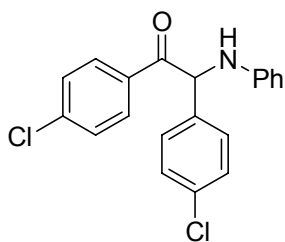
4a: ^1H NMR (CDCl_3 , 300 MHz) δ 5.42 (d, 1 H, $J = 6.0$ Hz), 6.03 (d, 1 H, $J = 6.0$ Hz), 6.68 (m, 3 H), 7.10-7.30 (m, 5 H), 7.40-7.46 (m, 4 H), 7.53 (m, 1 H), 8.00 (d, 2 H, $J = 7.5$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 62.6, 113.4, 117.8, 128.1, 128.1, 128.7, 128.8, 129.0, 129.2, 133.5, 135.0, 137.6, 146.0, 197.0.



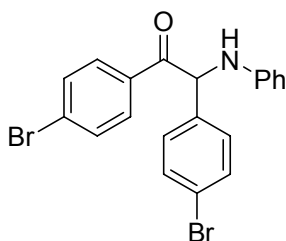
4b: ^1H NMR (CDCl_3 , 300 MHz) δ 5.46 (d, 1 H, $J = 6.0$ Hz), 5.97 (d, 1 H, $J = 6.0$ Hz), 6.57 (d, 2 H, $J = 8.7$ Hz), 7.06 (d, 2 H, $J = 8.7$ Hz), 7.16-7.30 (m, 3 H), 7.39-7.55 (m, 5 H), 7.98 (d, 2 H, $J = 7.2$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 62.6, 114.6, 122.4, 128.0, 128.2, 128.7, 128.8, 129.0, 129.1, 133.6, 134.8, 137.2, 144.5, 196.7.



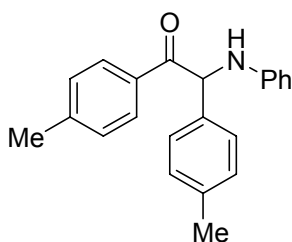
4c: ^1H NMR (CDCl_3 , 300 MHz) δ 2.18 (s, 3 H), 5.25 (br, 1 H), 6.00 (s, 1 H), 6.59 (d, 2 H, $J = 8.1$ Hz), 6.93 (d, 2 H, $J = 8.4$ Hz), 7.15-7.28 (m, 3 H), 7.38-7.53 (m, 5 H), 7.98 (d, 2 H, $J = 8.1$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 20.2, 62.8, 113.5, 126.9, 127.9, 127.9, 128.5, 128.5, 128.7, 128.8, 128.9, 129.6, 133.3, 135.0, 137.7, 143.7, 197.1; IR (thin film): ν_{max} (cm^{-1}) = 3396, 3022, 2852, 1674, 1617, 1524, 1450, 799, 699, 602; Anal. calcd for $\text{C}_{21}\text{H}_{19}\text{NO}$: C, 83.69; H, 6.35; N, 4.65; Found: C, 83.61; H, 6.40; N, 4.58.



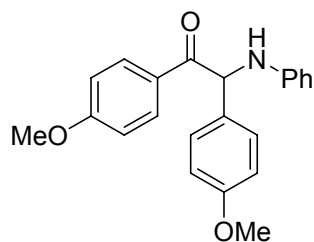
4d: ^1H NMR (CDCl_3 , 300 MHz) δ 5.37 (d, 1 H, $J = 6.3$ Hz), 5.94 (d, 1 H, $J = 6.0$ Hz), 6.64 (d, 2 H, $J = 7.8$ Hz), 6.71 (t, 1 H, $J = 7.5$ Hz), 7.14 (t, 2 H, $J = 7.8$ Hz), 7.26 (d, 2 H, $J = 8.4$ Hz), 7.40-7.56 (m, 4 H), 7.91 (d, 2 H, $J = 9.0$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 62.0, 113.4, 118.1, 129.1, 129.2, 129.3, 129.3, 130.1, 133.0, 134.1, 136.0, 140.2, 145.5, 195.4.



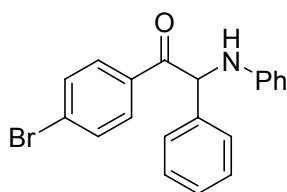
4e: ^1H NMR (CDCl_3 , 300 MHz) δ 5.37 (br, 1 H), 5.91 (s, 1 H), 6.63 (d, 2 H, $J = 8.7$ Hz), 6.71 (t, 1 H, $J = 7.5$ Hz), 7.14 (t, 2 H, $J = 7.8$ Hz), 7.27 (m, 2 H), 7.41 (d, 2 H, $J = 8.1$ Hz), 7.58 (d, 2 H, $J = 8.7$ Hz), 7.82 (d, 2 H, $J = 8.7$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 62.0, 113.1, 118.2, 122.3, 129.0, 129.3, 129.6, 130.2, 132.1, 132.3, 133.4, 136.5, 145.5, 195.5; m.p. 128-131 $^\circ$.



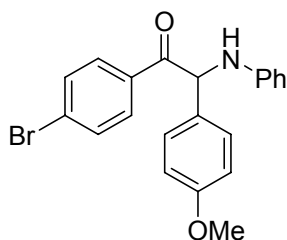
4f: ^1H NMR (CDCl_3 , 300 MHz) δ 2.18 (s, 3 H), 2.37 (s, 3 H), 5.25 (d, 2 H, $J = 6.6$ Hz), 5.98 (d, 1 H, $J = 6.3$ Hz), 6.58 (d, 2 H, $J = 8.7$ Hz), 6.93 (d, 2 H, $J = 8.1$ Hz), 7.18-7.30 (m, 4 H), 7.43 (dd, 2 H, $J_1 = 1.8$ Hz, $J_2 = 6.9$ Hz), 7.91 (d, 2 H, $J = 8.1$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 20.3, 21.6, 62.7, 113.6, 126.9, 127.9, 128.0, 128.1, 128.9, 129.0, 129.3, 129.7, 132.5, 138.1, 143.9, 144.4, 196.7;



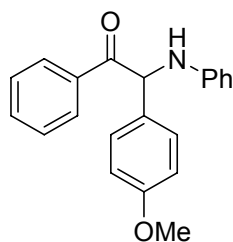
4g: ^1H NMR (CDCl_3 , 300 MHz) δ 3.72 (s, 3 H), 3.84 (s, 3 H), 5.34 (br, 1 H), 5.93 (s, 1 H), 6.67 (m, 3 H), 6.81 (d, 2 H, $J = 8.7$ Hz), 6.90 (d, 2 H, $J = 8.7$ Hz), 7.12 (t, 2 H, $J = 7.5$ Hz), 7.37 (d, 2 H, $J = 8.4$ Hz), 8.00 (d, 2 H, $J = 8.7$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 55.0, 55.3, 61.3, 113.4, 113.8, 114.3, 117.5, 127.7, 129.1, 130.0, 131.1, 132.2, 146.2, 159.1, 163.6, 195.3.



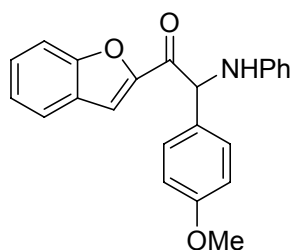
4h: ^1H NMR (CDCl_3 , 300 MHz) δ 5.36 (br, 1 H), 5.96 (br, 1 H), 6.64-6.71 (m, 3 H), 7.10-7.32 (m, 5 H), 7.42 (d, 2 H, $J = 7.5$ Hz), 7.56 (d, 2 H, $J = 8.4$ Hz), 7.85 (d, 2 H, $J = 8.1$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 62.8, 113.5, 118.0, 128.0, 128.3, 128.8, 129.2, 129.2, 130.3, 132.0, 133.7, 137.3, 145.9, 196.1; IR (thin film): ν_{max} (cm^{-1}) = 3397, 3018, 1670, 1602, 1504, 997, 746, 697; Anal. calcd for $\text{C}_{20}\text{H}_{16}\text{BrNO}$: C, 65.59; H, 4.40; N, 3.82; Found: C, 65.21; H, 4.34; N, 3.62; m.p. 160-162 $^\circ$.



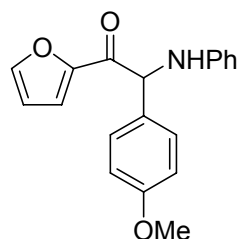
4i: ^1H NMR (CDCl_3 , 300 MHz) δ 3.73 (s, 3 H), 5.29 (d, 1 H, $J = 4.8$ Hz), 5.91 (d, 1 H, $J = 4.8$ Hz), 6.29-6.71 (m, 3 H), 6.80-6.84 (m, 2 H), 7.10-7.16 (m, 2 H), 7.30-7.35 (m, 2 H), 7.55-7.59 (m, 2 H), 7.82-7.87 (m, 2 H); ^{13}C NMR (75 MHz, CDCl_3): δ 55.2, 62.1, 113.5, 114.6, 117.9, 128.6, 129.1, 129.2, 129.3, 130.2, 132.0, 133.7, 146.0, 159.4, 196.1; IR (thin film): ν_{max} (cm^{-1}) = 3402, 2925, 1673, 1605, 1509, 1257, 997, 750, 692; Anal. calcd for $\text{C}_{21}\text{H}_{18}\text{BrNO}_2$: C, 63.65; H, 4.58; N, 3.53; Found: C, 63.78; H, 4.69; N, 3.31; m.p.: 152-153 $^\circ$.



4j: ^1H NMR (CDCl_3 , 300 MHz) δ 3.72 (s, 3 H), 5.35 (d, 1 H, $J = 5.1$ Hz), 5.98 (d, 1 H, $J = 5.1$ Hz), 6.64-6.670 (m, 3 H), 6.81 (d, 2 H, $J = 8.1$ Hz), 7.13 (t, 2 H, $J = 7.5$ Hz), 7.35 (d, 2 H, $J = 8.4$ Hz), 7.43 (m, 2 H), 7.53 (t, 1 H, $J = 7.4$ Hz), 7.99 (d, 2 H, $J = 7.8$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 55.1, 61.9, 113.4, 114.4, 117.7, 128.6, 128.7, 129.1, 129.2, 129.4, 133.3, 135.0, 146.1, 159.2, 197.0; MS (ESI, m/z , rel. intensity) 318 ($\text{M}+\text{H}^+$, 100). HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{19}\text{NO}_2$ (M^+): 317.1416; Found: 317.1423; m.p. 114-115°C.

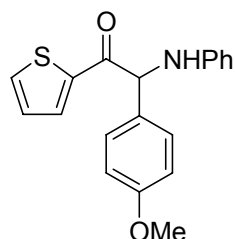


4k: ^1H NMR (CDCl_3 , 300 MHz) δ 3.73 (s, 3 H), 5.31 (d, 1 H, $J = 3.6$ Hz), 5.95 (d, 1 H, $J = 5.1$ Hz), 6.67-6.71 (m, 3 H), 6.84 (d, 2 H, $J = 8.7$ Hz), 7.14 (m, 2 H), 7.30 (m, 1 H), 7.46-7.51 (m, 3 H), 7.60 (d, 2 H, $J = 9.9$ Hz), 7.68 (d, 1 H, $J = 7.8$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 55.2, 62.6, 112.4, 113.5, 114.5, 114.5, 117.9, 123.4, 124.1, 126.9, 128.6, 129.0, 129.2, 129.4, 145.9, 150.8, 155.6, 159.5, 187.8; IR (thin film): ν_{max} (cm^{-1}) = 3391, 2926, 1676, 1604, 1562, 1506, 1315, 1253, 1163, 1024, 870, 751, 690, 605; MS (ESI, m/z , rel. intensity) 358 ($\text{M}+\text{H}^+$, 100); HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{19}\text{NO}_3$ (M^+): 357.1365; Found: 357.1361; b.p. 161-163°C.

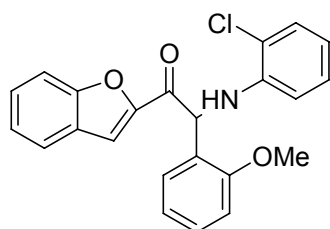


4l: ^1H NMR (CDCl_3 , 300 MHz) δ 3.74 (s, 3 H), 5.80 (s, 1 H), 6.52 (dd, 1 H, $J_1 = 1.5$ Hz, $J_2 = 4.1$ Hz), 6.63-6.67 (m, 3 H), 6.84 (d, 2 H, $J = 8.7$ Hz), 7.12 (dd, 2 H, $J_1 = 7.2$ Hz, $J_2 = 8.4$ Hz), 7.29 (d, 1 H, $J = 3.6$ Hz), 7.43 (d, 2 H, $J = 8.4$ Hz), 7.60 (s, 1 H); ^{13}C NMR (75

MHz, CDCl₃): δ 55.1, 62.1, 112.6, 113.4, 114.3, 117.7, 118.9, 129.1, 129.2, 129.3, 145.9, 146.8, 150.8, 159.4, 185.7; IR (thin film): ν_{\max} (cm⁻¹) = 3406, 2970, 1662, 1603, 1509, 1462, 1257, 1028, 996, 794, 767, 692, 594; MS (ESI, *m/z*, rel. intensity) 308 (M+H⁺, 100); m.p.110-112°C.



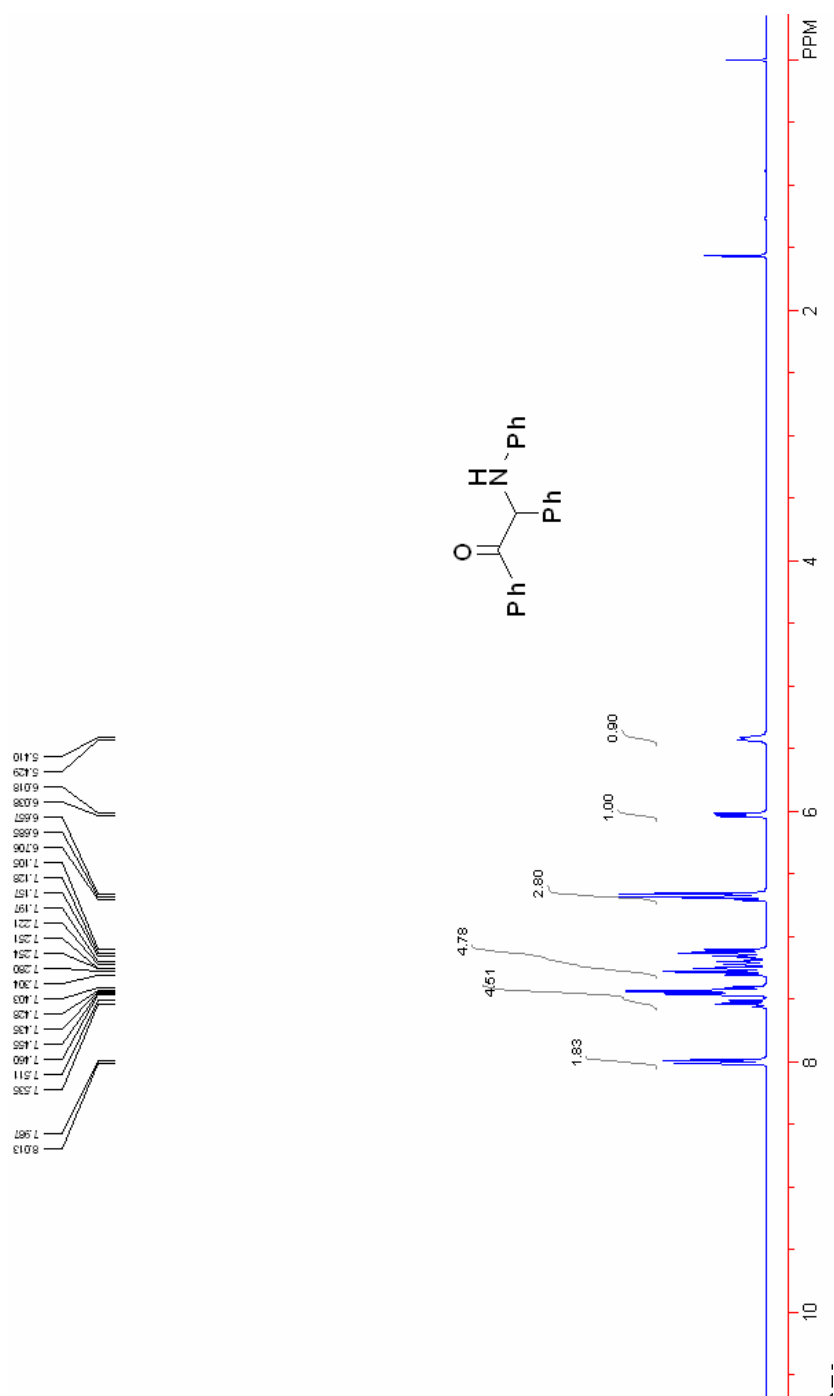
4m: ¹H NMR (CDCl₃, 300 MHz) δ 3.75 (s, 3 H), 5.21 (br, 1 H), 5.74 (s, 1 H), 6.64-6.72 (m, 3 H), 6.85 (d, 2 H, *J* = 5.1 Hz), 7.13 (t, 3 H, *J* = 7.1 Hz), 7.42 (d, 2 H, *J* = 8.4 Hz), 7.64 (d, 1 H, *J* = 4.2 Hz), 7.86 (s, 1 H); ¹³C NMR (75 MHz, CDCl₃): δ 55.2, 63.5, 113.5, 114.5, 117.9, 128.2, 129.2, 129.3, 129.8, 133.1, 134.4, 141.2, 146.1, 159.5, 189.9; IR (thin film): ν_{\max} (cm⁻¹) = 3404, 2933, 1645, 1602, 1509, 1411, 1253, 1028, 791, 749, 690; Anal. calcd for C₁₉H₁₇NO₂S: C, 70.56; H, 5.30; N, 4.33; Found: C, 70.35; H, 5.24; N, 4.12; m.p.108-110°C.

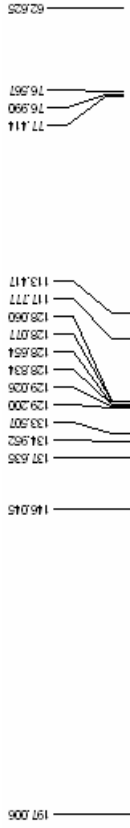
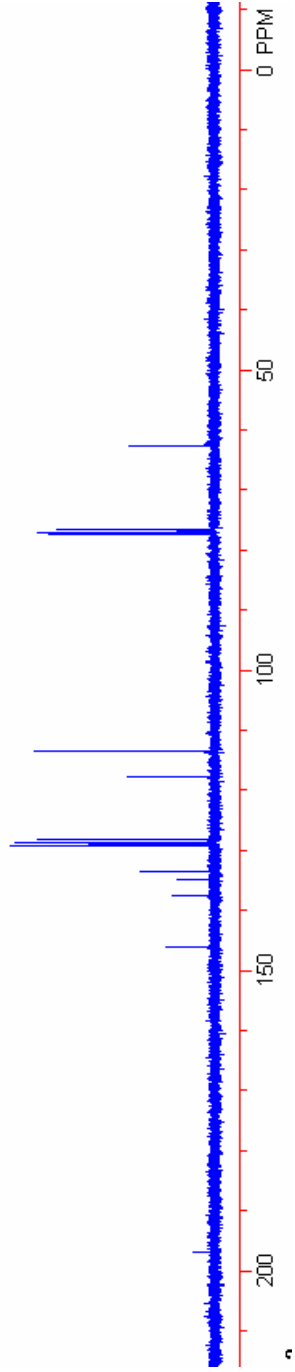
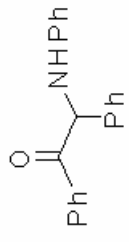


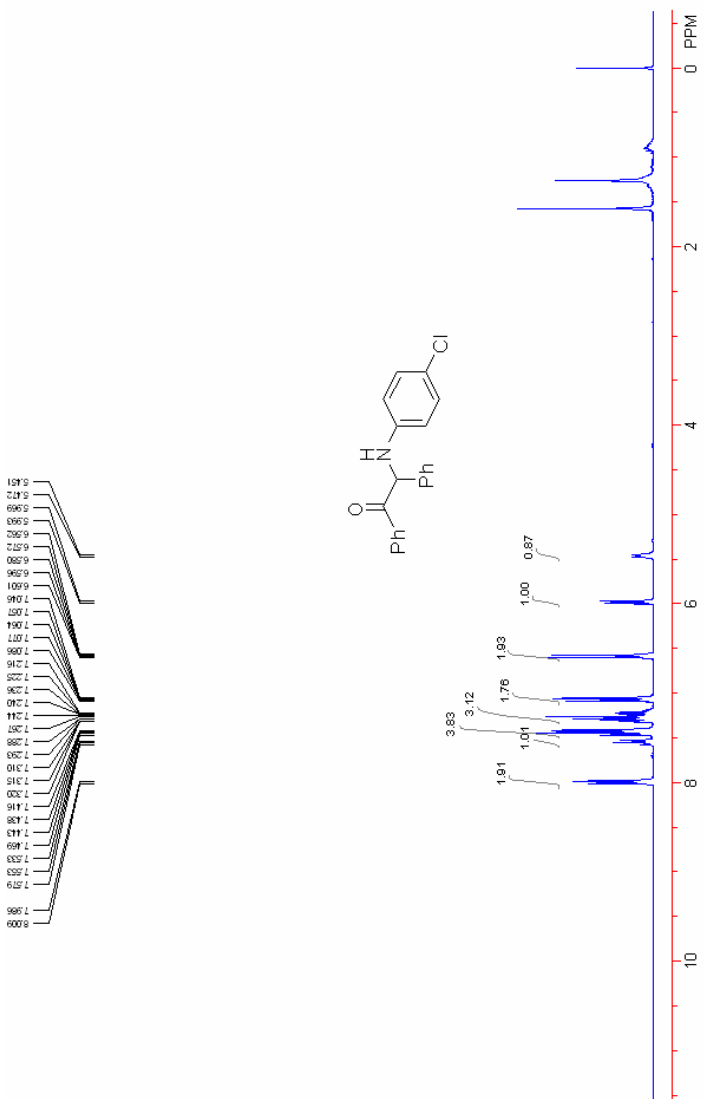
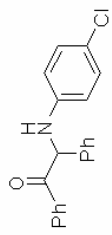
4n: ¹H NMR (CDCl₃, 300 MHz) δ 4.08 (s, 3 H), 6.07 (d, 1 H, *J* = 6.0 Hz), 6.43 (d, 1 H, *J* = 6.6 Hz), 6.60 (t, 1 H, *J* = 7.2 Hz), 6.74 (d, 1 H, *J* = 8.1 Hz), 6.91 (t, 2 H, *J* = 8.1 Hz), 7.04 (t, 1 H, *J* = 7.5 Hz), 7.20-7.56 (m, 6 H), 7.68 (d, 1 H, *J* = 7.5 Hz), 7.77 (s, 1 H); ¹³C NMR (75 MHz, CDCl₃): δ 55.5, 55.7, 111.1, 112.1, 112.4, 114.5, 117.7, 119.7, 121.6, 123.4, 123.9, 125.3, 126.8, 127.6, 128.5, 128.6, 129.2, 129.8, 142.0, 150.5, 155.8, 156.6, 185.6; IR (thin film): ν_{\max} (cm⁻¹) = 3385, 2919, 1678, 1597, 1513, 1329, 1293, 1248, 1135, 1088, 1032, 1020, 753, 743; Anal. calcd for C₂₃H₁₈ClNO₃: C, 70.50; H, 4.63; N, 3.57; Found: C, 70.57; H, 4.66; N, 3.43. m.p.111-114°C

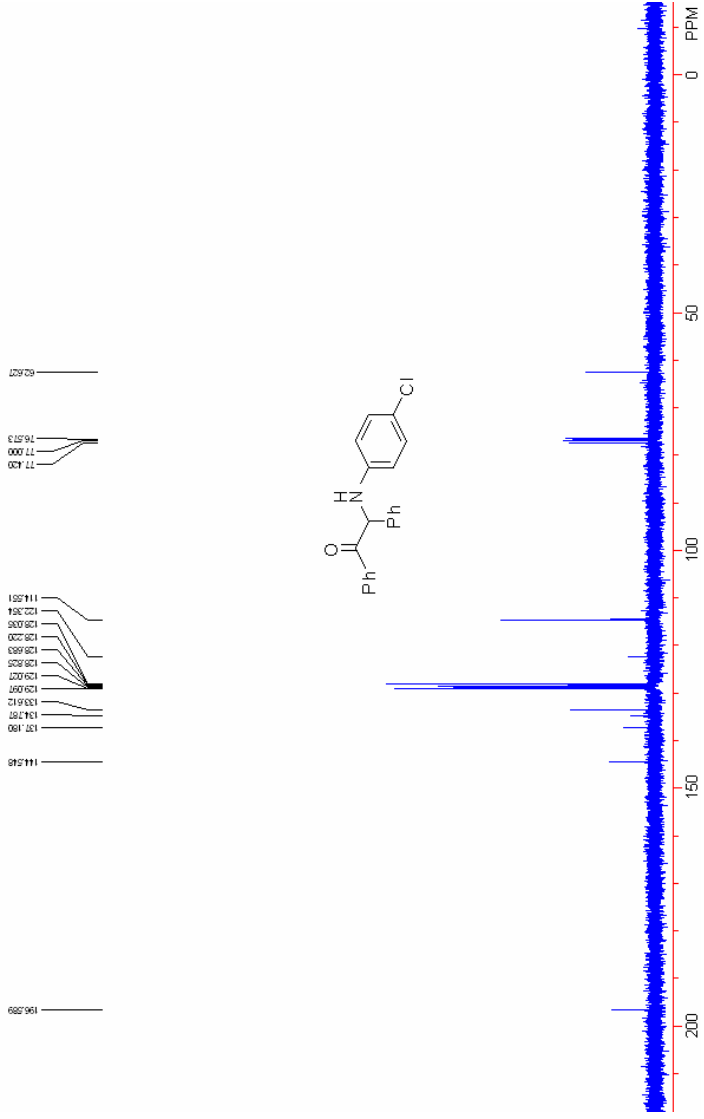
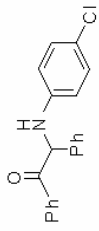
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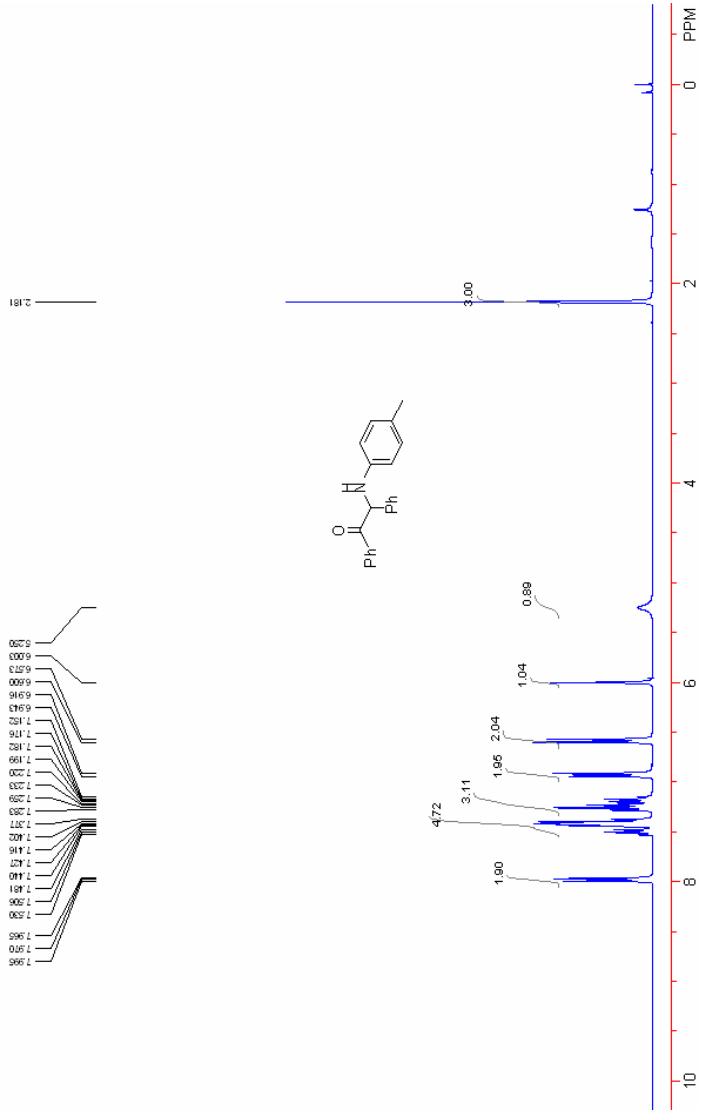
1. Nongkunsarn, P.; Ramsden, C. A. *Tetrahedron*, **1997**, *53*, 3805-3830.
2. Enders, D.; Breuer, K.; Kalfass, U.; Balensiefer, T. *Synthesis*, **2003**, 1292-1295.

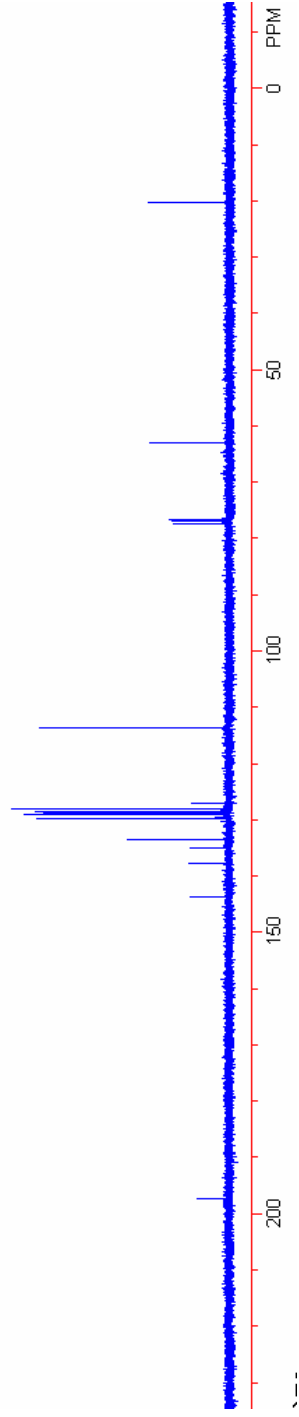
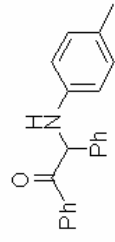


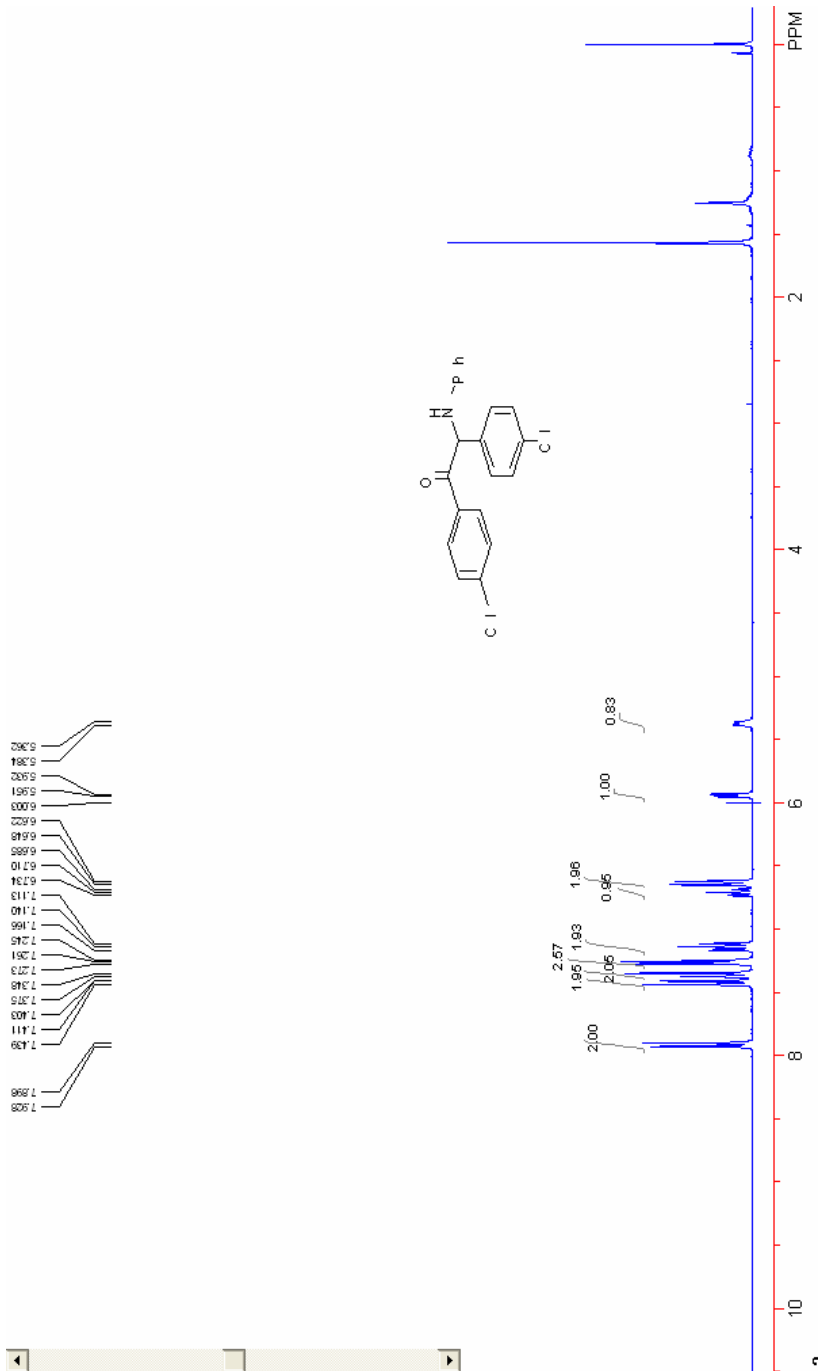


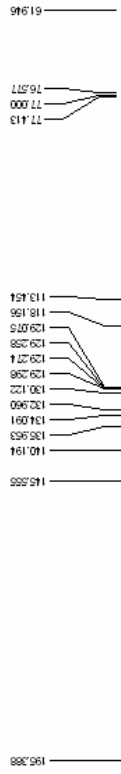
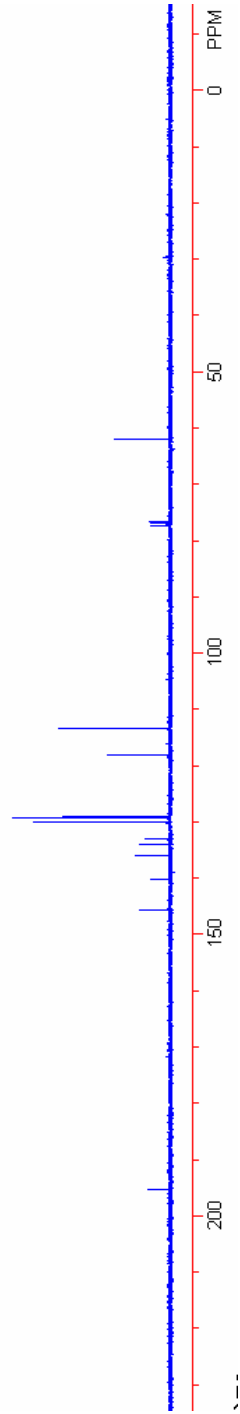
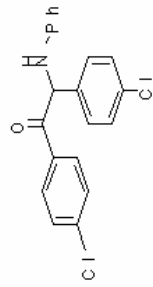


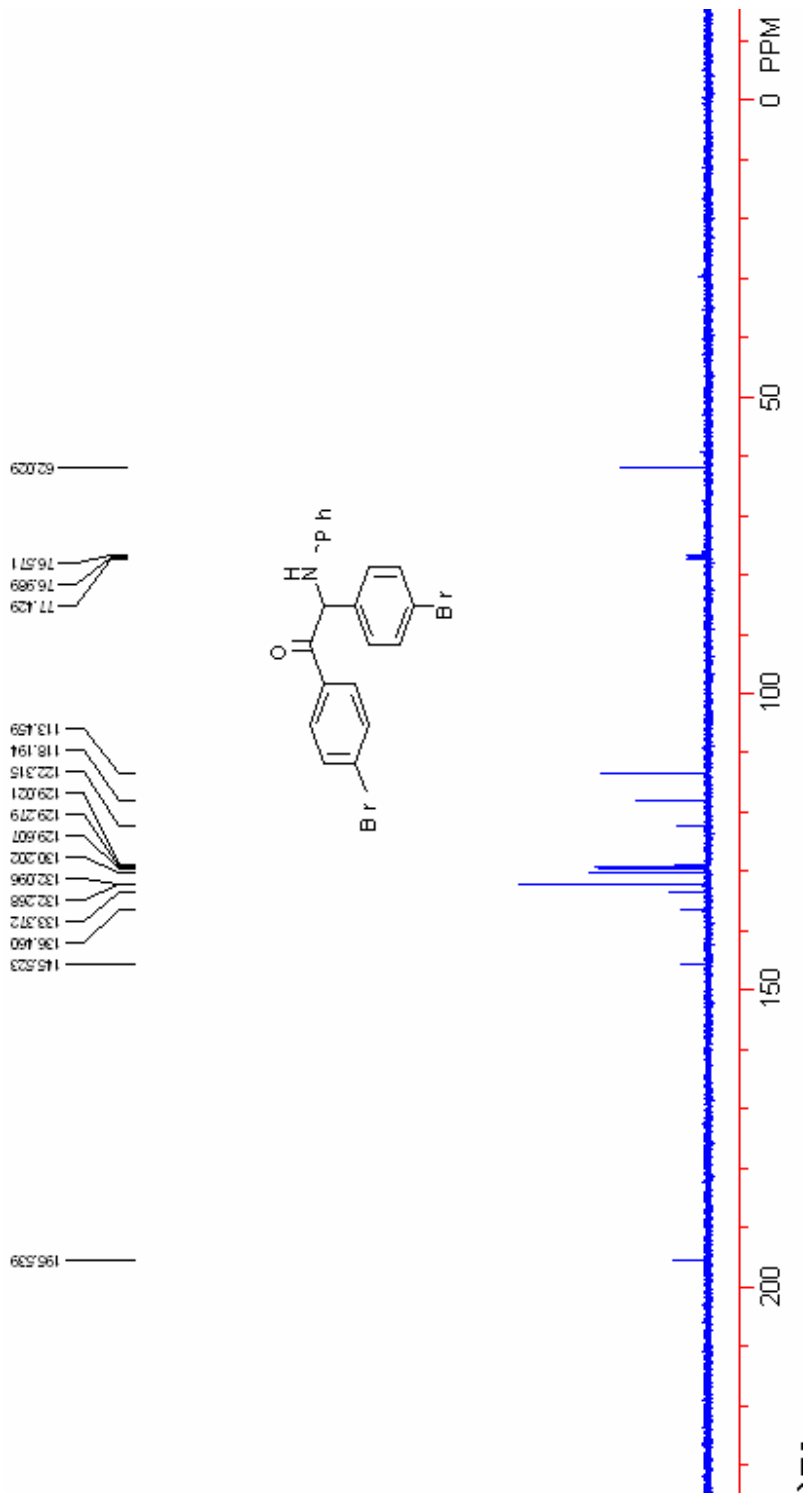








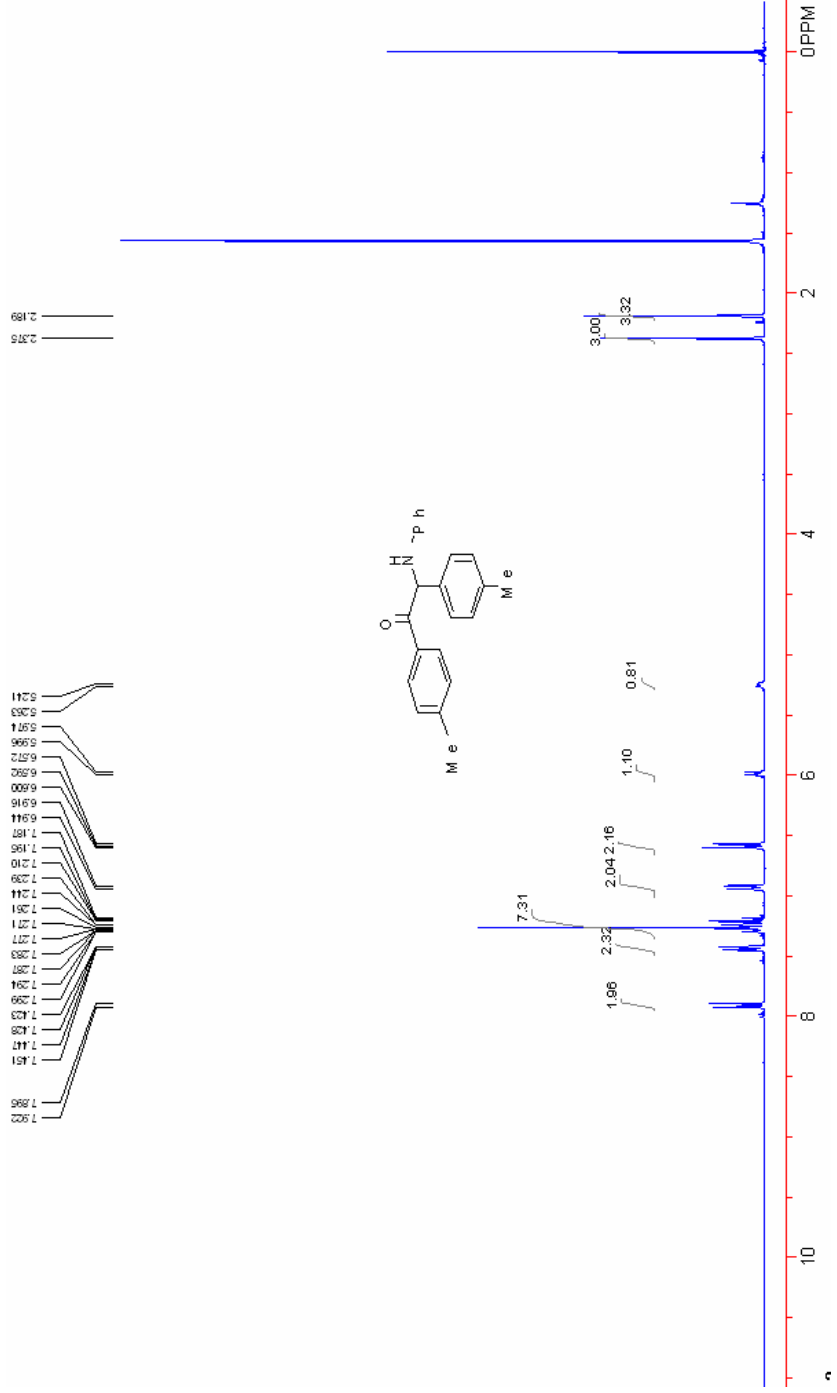




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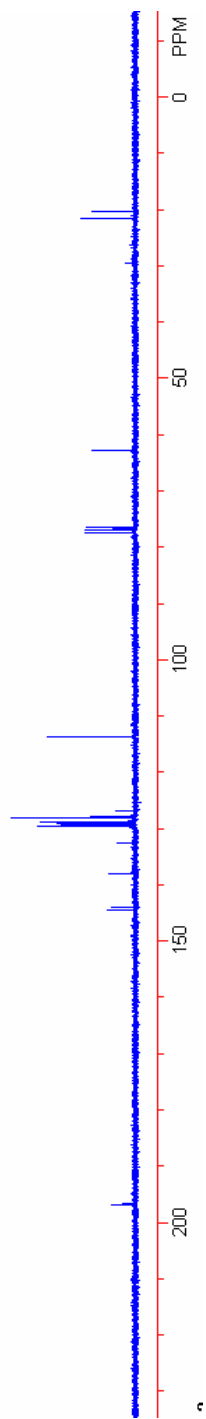
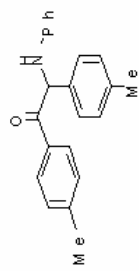
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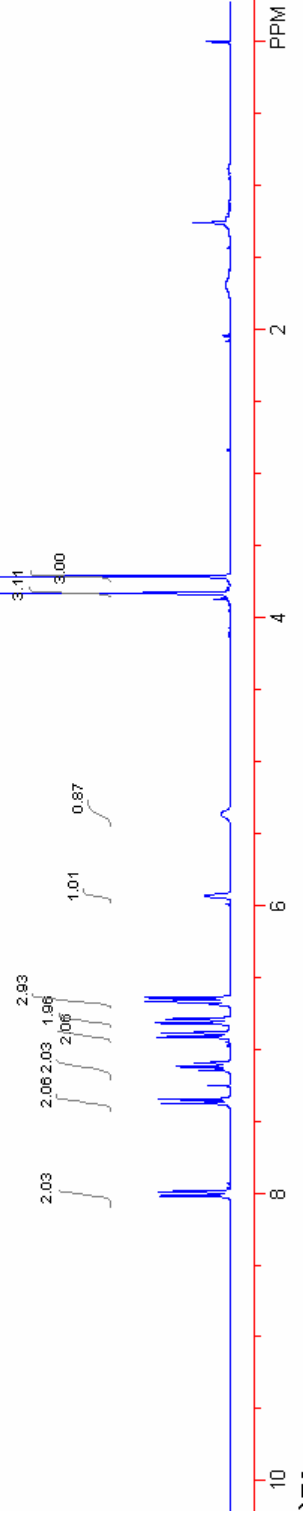
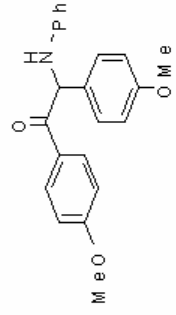
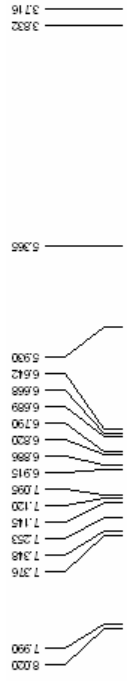
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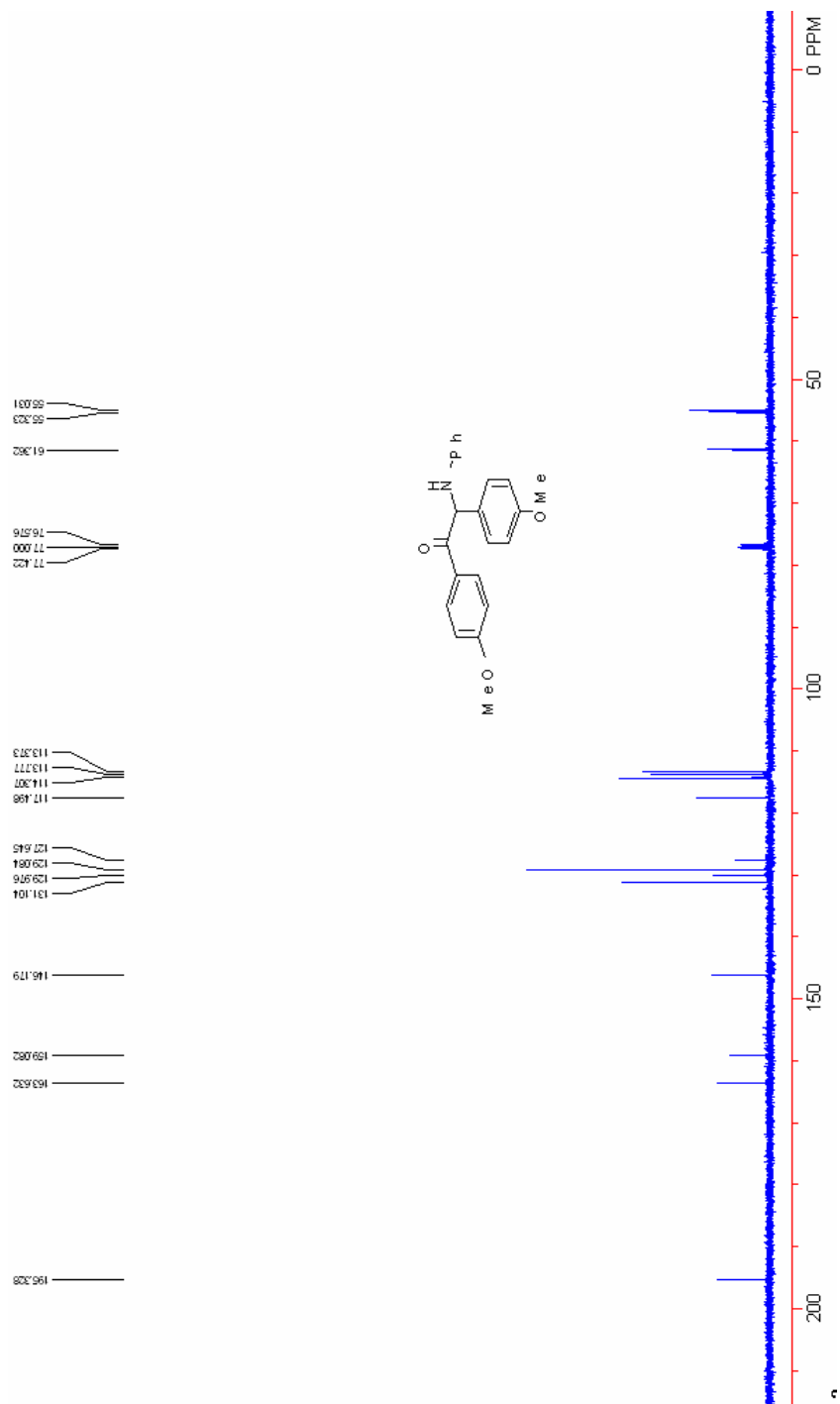
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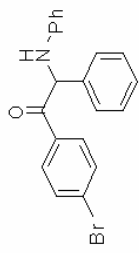
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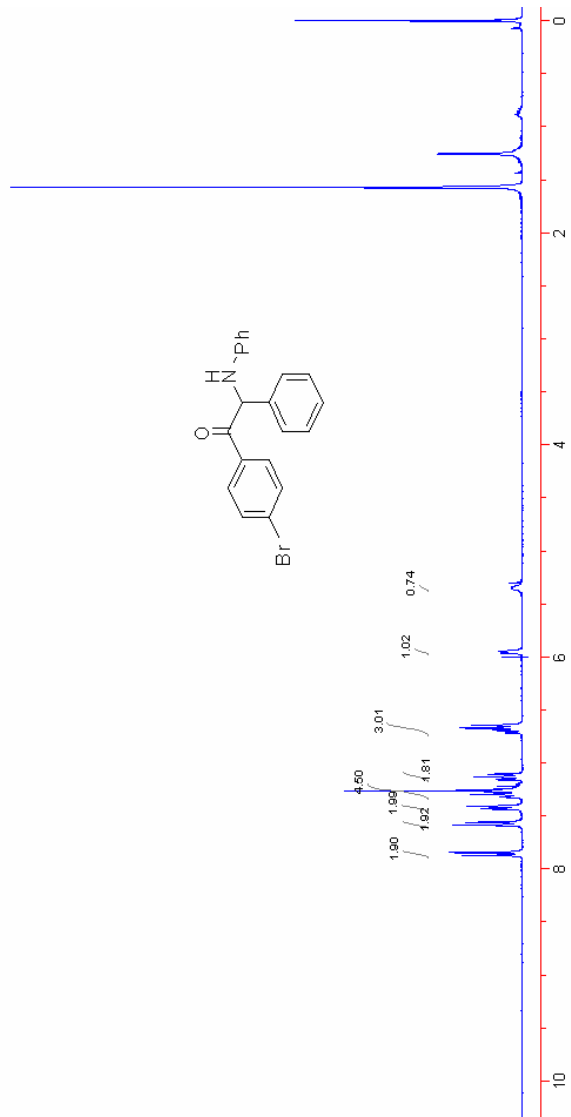


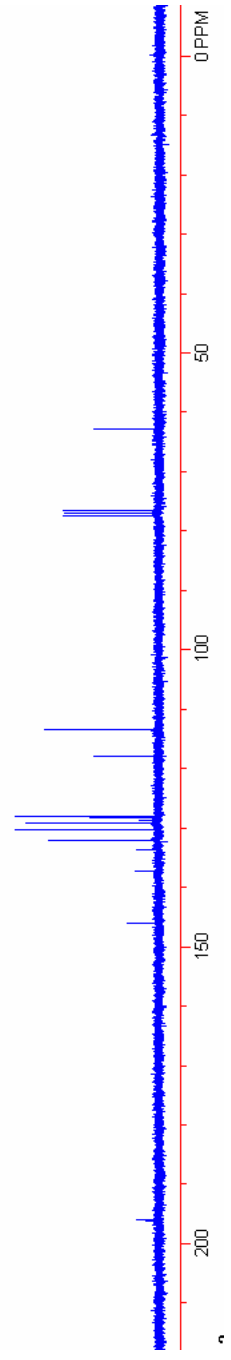
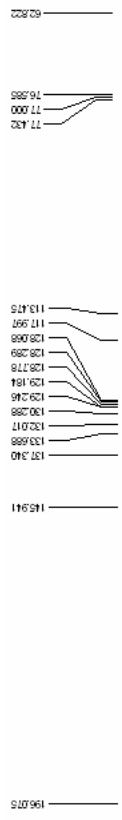
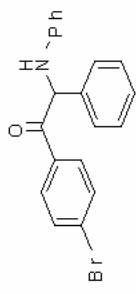


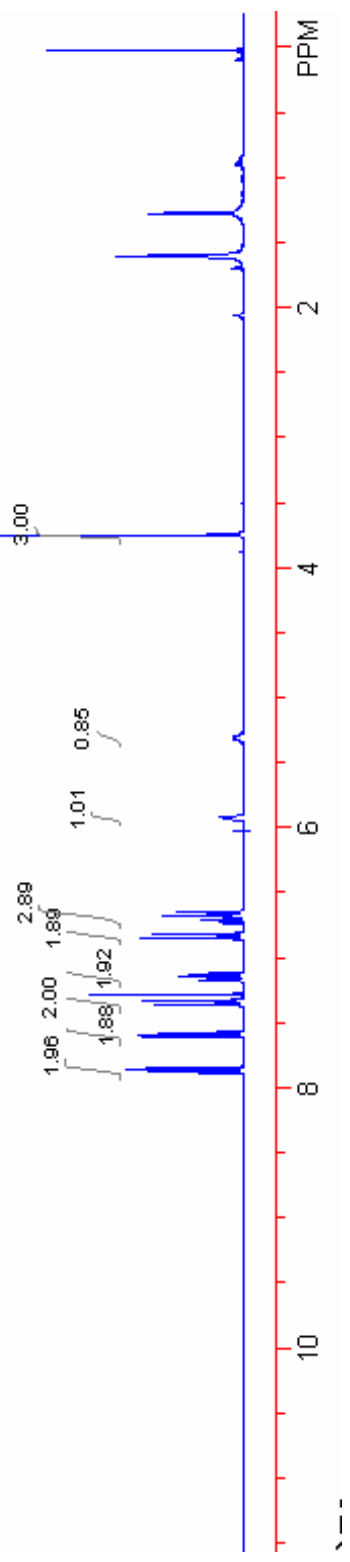
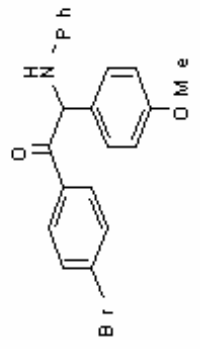
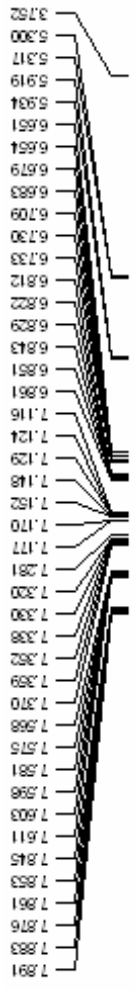


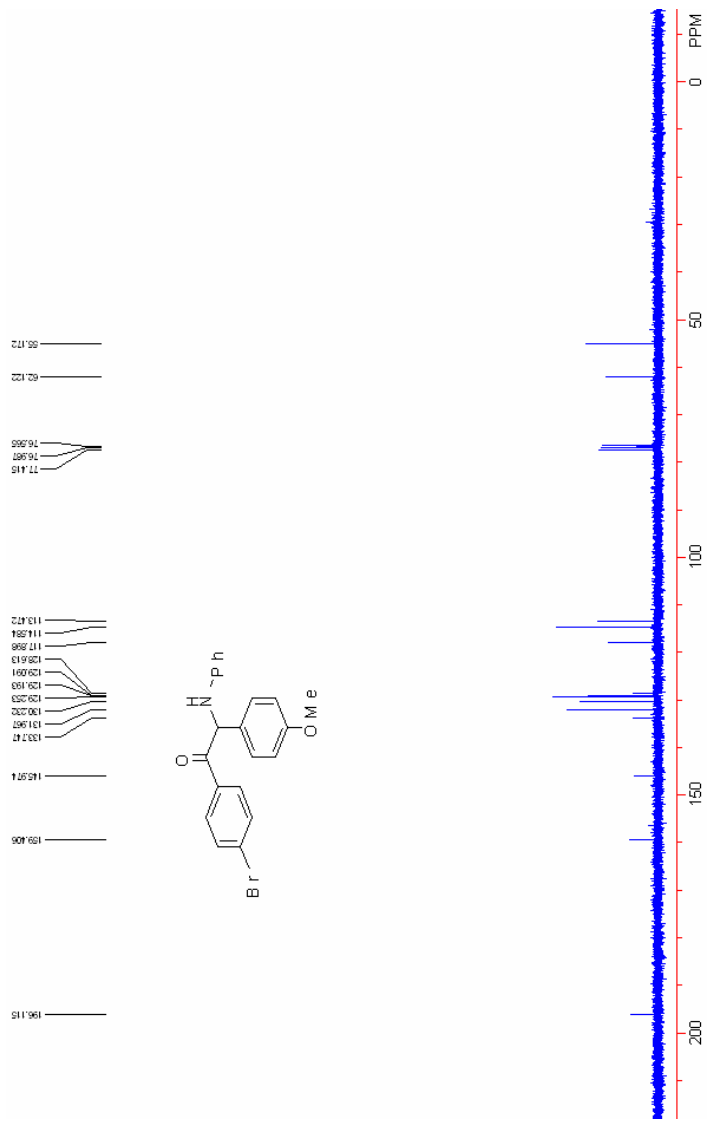


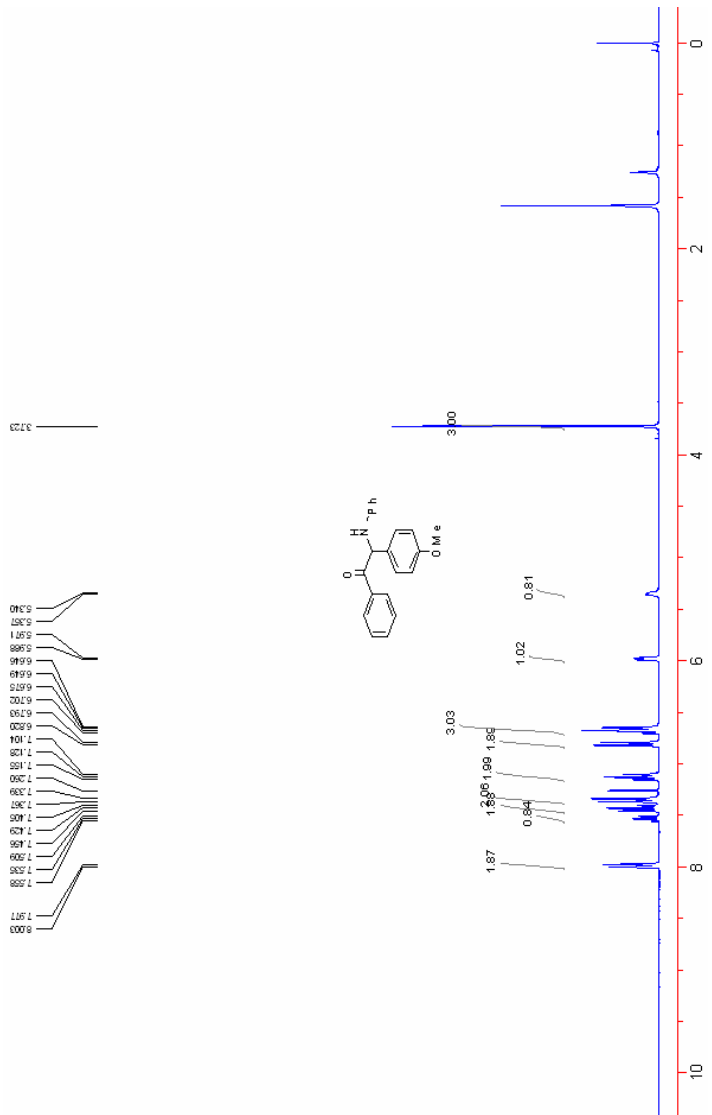
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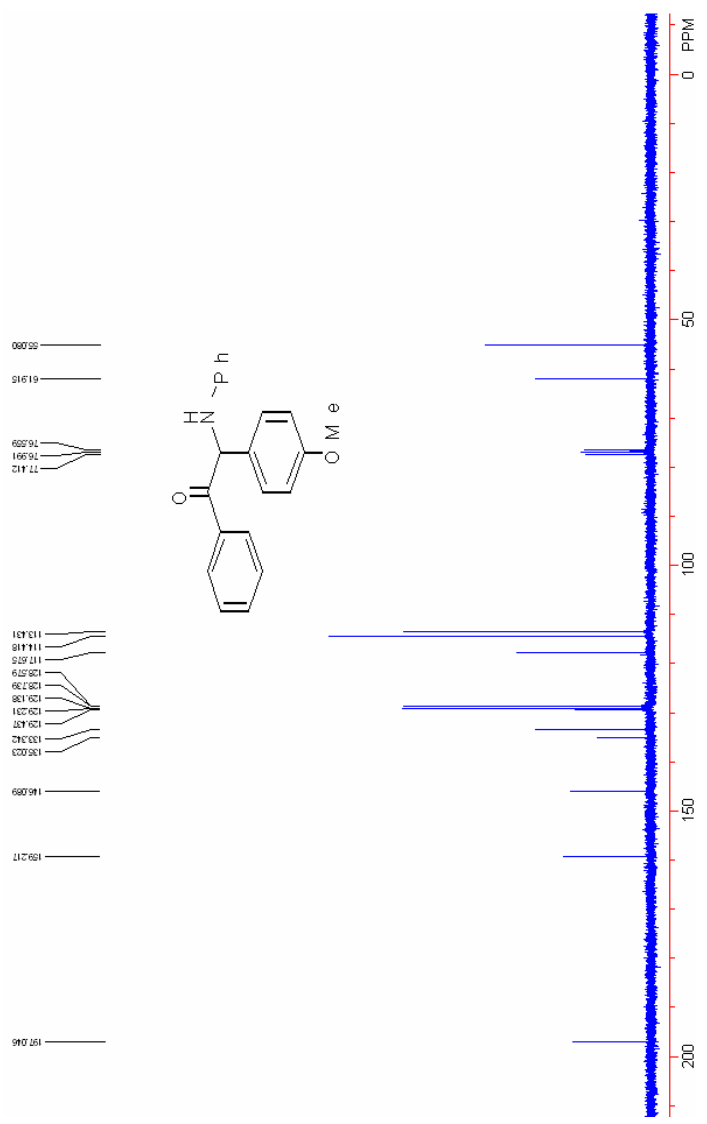


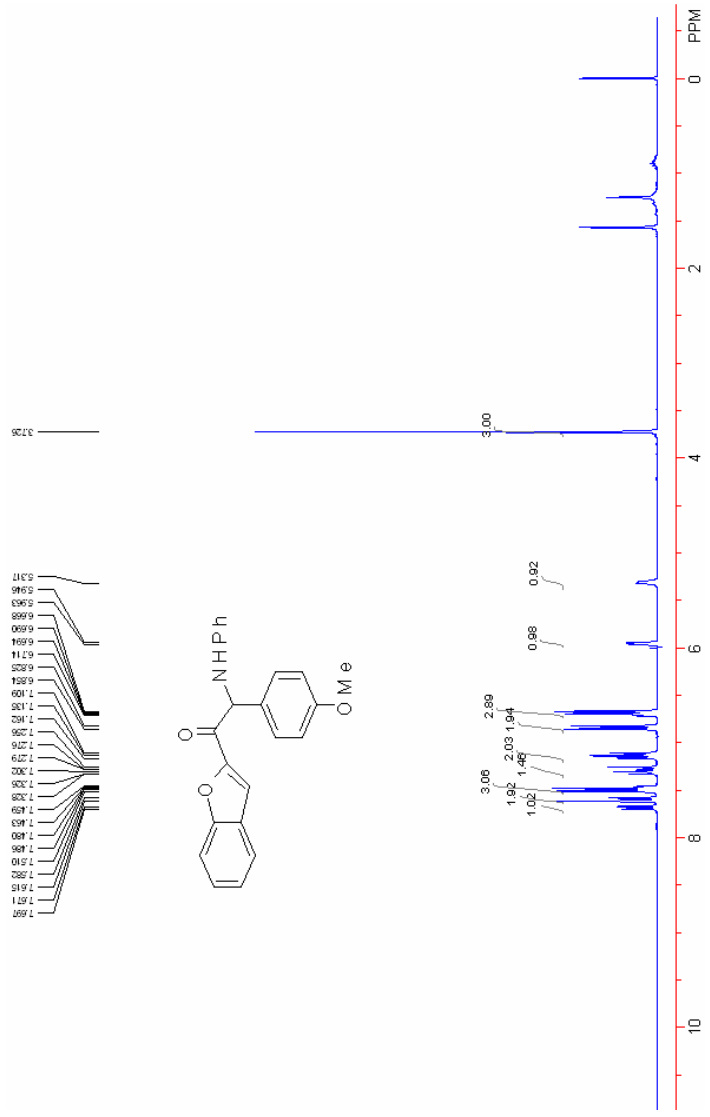


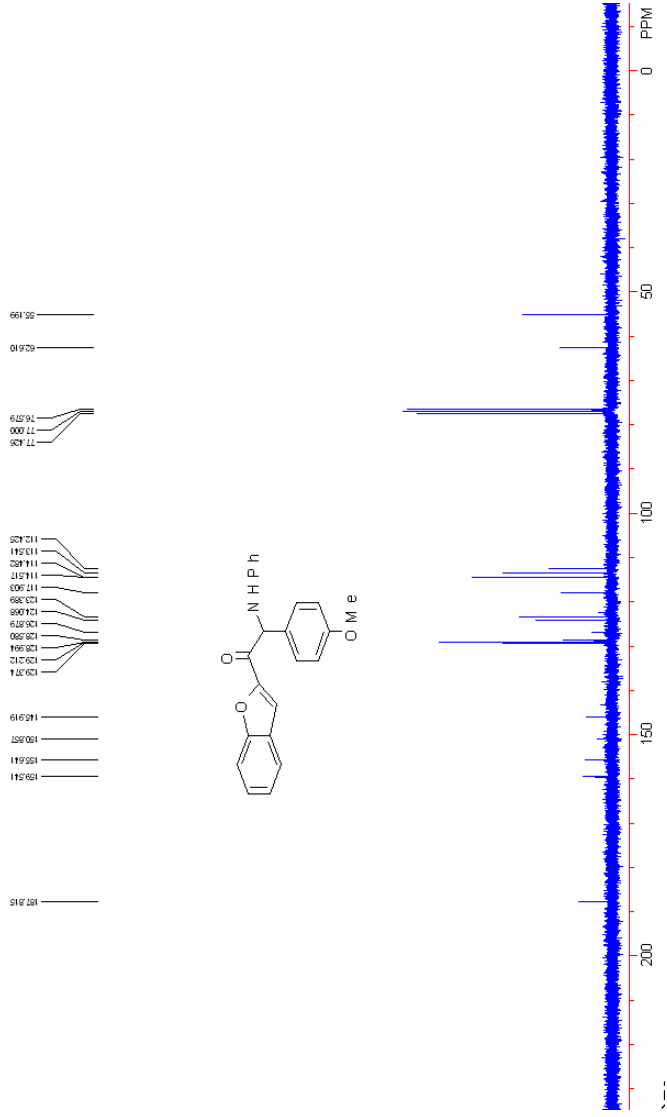


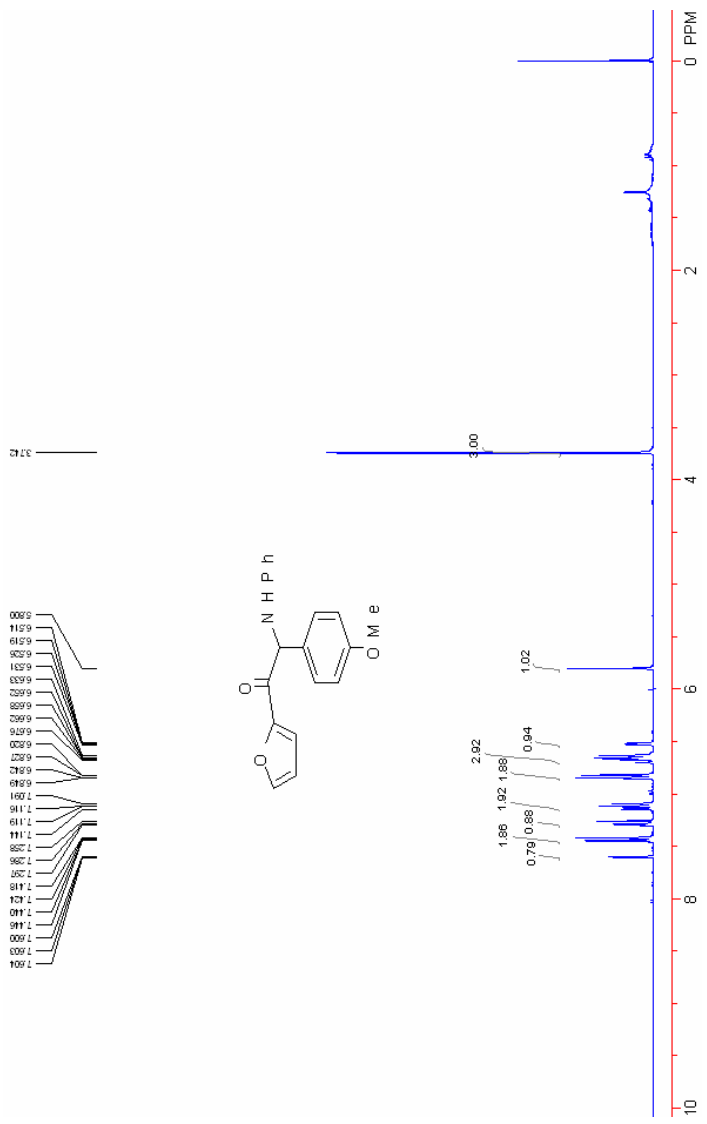


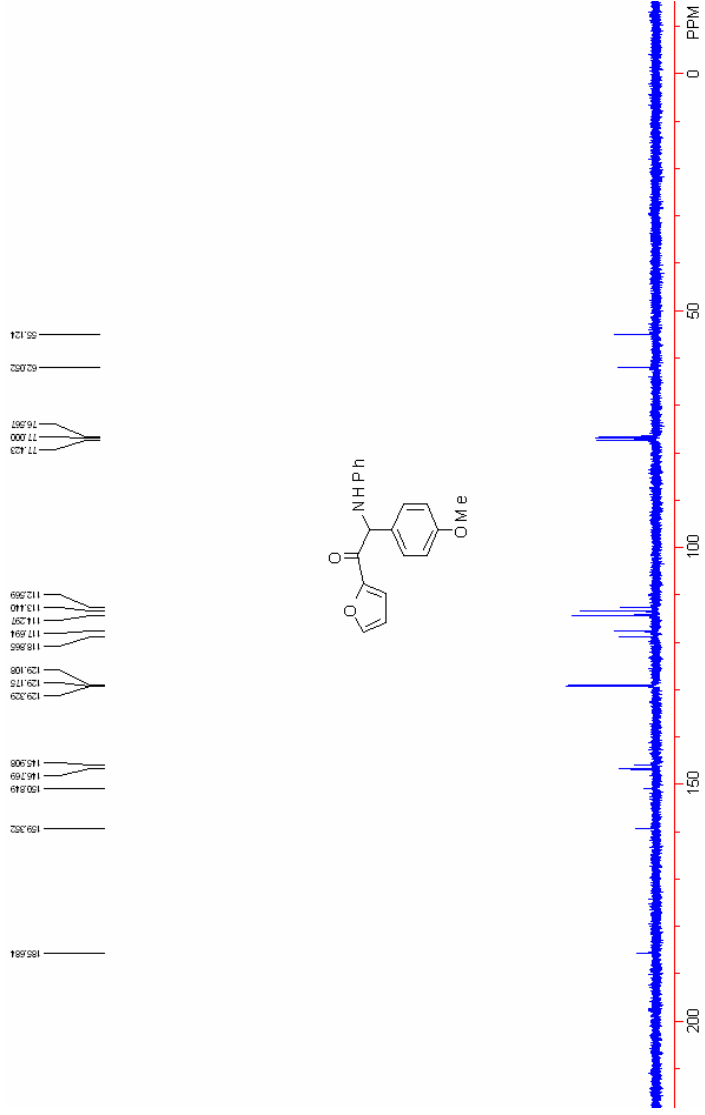
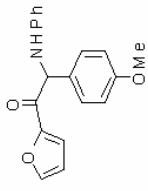


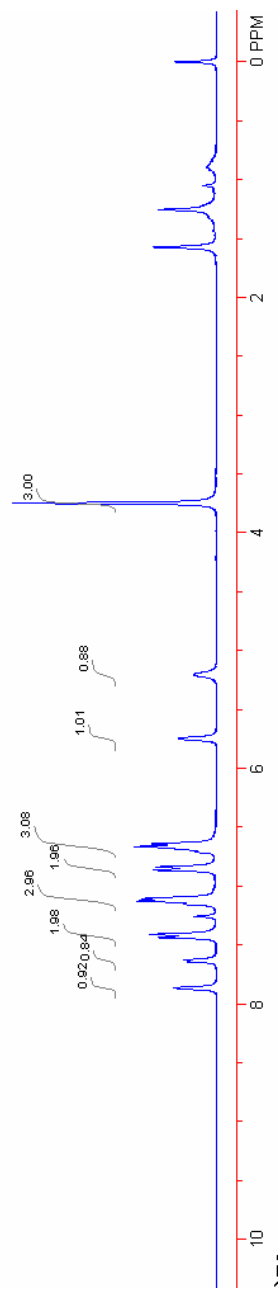
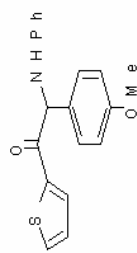
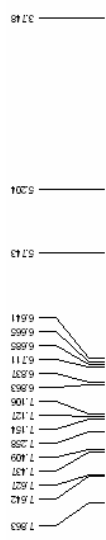


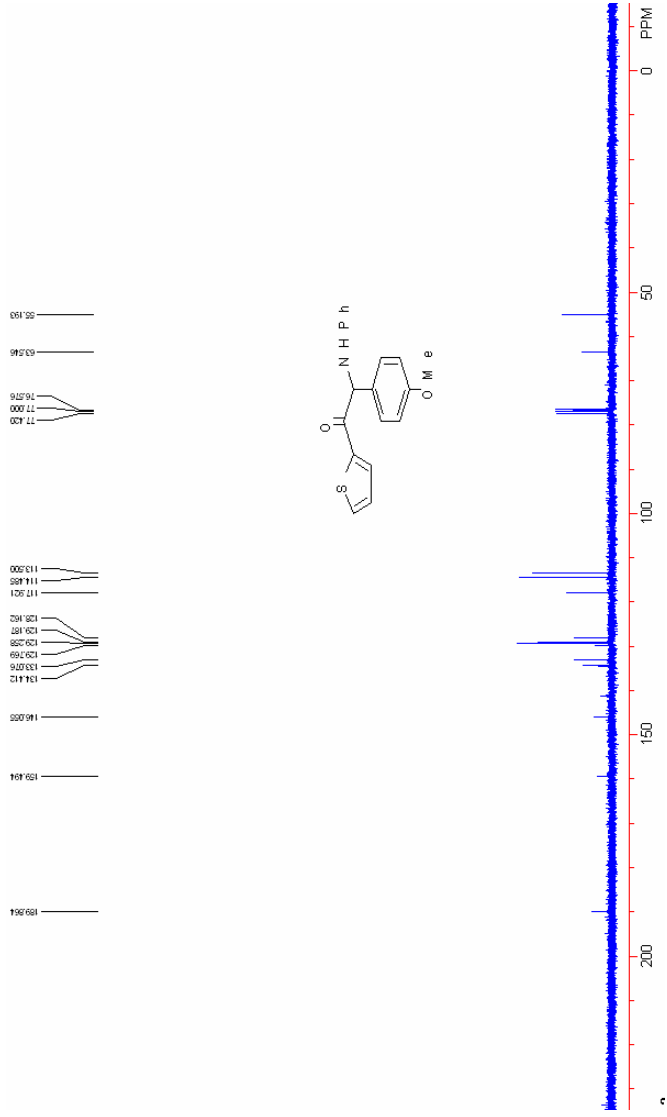












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