Supplementary Material (ESI) for Chemical Communications

Oxidative decarboxylative synthesis of 2-H-imidazolines from glyoxylic acid and 1,2-diamines

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Experimental Section

Typical procedure

The mixture of diamine (1 mmol) and glyoxylic acid monohydrate (1.1 mmol) in dry MeOH (10 mL) were stirred at r.t. for 1 h under N_2. NBS (1.1 mmol) was added to the mixture and the resulting solution was stirred overnight at r.t. Reaction was quenched by the addition of sat. $Na_2S_2O_5$ aq., and MeOH was evaporated in vacuo. 5 % NaOH aq. was added to the residue, and the solution was extracted with AcOEt. Organic layer was dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by SiO_2 column chromatography to give imidazoline (yields are shown in tables). Compounds **2a**,[1] **2c**,[2] and **2f**[3] were reported. And spectral data of novel compounds were shown as follows.

1-Ethyl-4,5-*trans*-diphenyl-4,5-dihydro-1*H*-imidazole (2b): yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37-7.17 (m, 11H), 4.93 (dd, 1H, *J* = 9.6, 1.4 Hz), 4.26 (d, 1H, *J* = 9.6 Hz), 3.20-3.08 (m, 1H), 3.04-2.92 (m, 1H), 1.05 ppm (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 155.6, 143.2, 140.8, 128.5, 126.1, 127.5, 126.82, 126.80, 126.4, 80.0, 72.7, 40.0, 13.5 ppm; IR (KBr): 3659, 2843, 2201, 1950, 1809, 1611, 912, 743 cm^{-1}.; HRMS (FAB): calcd for $C_{17}H_{19}N_2$ [*M*+H]$^+$: 251.1548, found 251.1563.

1-Isopropyl-4-phenyl-4,5-dihydro-1*H*-imidazole (2d): yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27-7.12 (m, 5H), 6.97 (d, 1H, *J* = 1.2 Hz); 5.01 (ddd, 1H, *J* = 10.8, 9.3, 1.2 Hz), 3.59 (dd, 1H, *J* = 10.8, 9.3 Hz), 3.49-3.40 (m, 1H), 3.01 (dd, 1H, *J* = 9.3, 9.3 Hz), 1.13 (d, 3H, *J* = 6.6 Hz) 1.10 ppm (d, 3H, *J* = 6.6 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 155.2, 143.9, 128.2, 126.7, 126.3, 68.7, 52.5, 47.6, 21.2, 21.1 ppm; IR (KBr): 3666, 2847, 2201, 912, 743 cm^{-1}; HRMS (FAB): calcd for $C_{12}H_{17}N_2$ [*M*+H]$^+$: 189.1392, found 189.1391. (**2d** was very unstable and tended to cause partial decomposition.)

1-Cyclohexyl-4-benzyl-4,5-dihydro-1*H*-imidazole (2e): yellow oil; ^{1}H NMR (300 MHz,

$CDCl_3$): δ = 7.30-7.16 (m, 5H), 6.91 (s, 1H), 4.30-4.25 (m, 1H), 3.22 (t, 1H, *J* = 9.6 Hz), 3.09 (dd, 1H, *J* = 13.5, 5.1 Hz), 3.02-2.95 (m, 1H), 2.94 (t, 1H, *J* = 8.7 Hz), 2.63 (dd, 1H, *J* = 13.5, 8.7 Hz) 1.82-1.60 (m, 5H), 1.28-1.07 ppm (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 154.3, 138.8, 129.0, 128.1, 125.9, 66.5, 55.3, 49.6, 42.2, 31.6, 31.5, 25.3, 25.0, 24.9 ppm; IR (KBr): 2934, 2856, 2253, 1593, 912, 743 cm^{-1}; HRMS (FAB): calcd for $C_{16}H_{23}N_2$ [*M*+H]$^+$: 243.1861, found 243.1871.

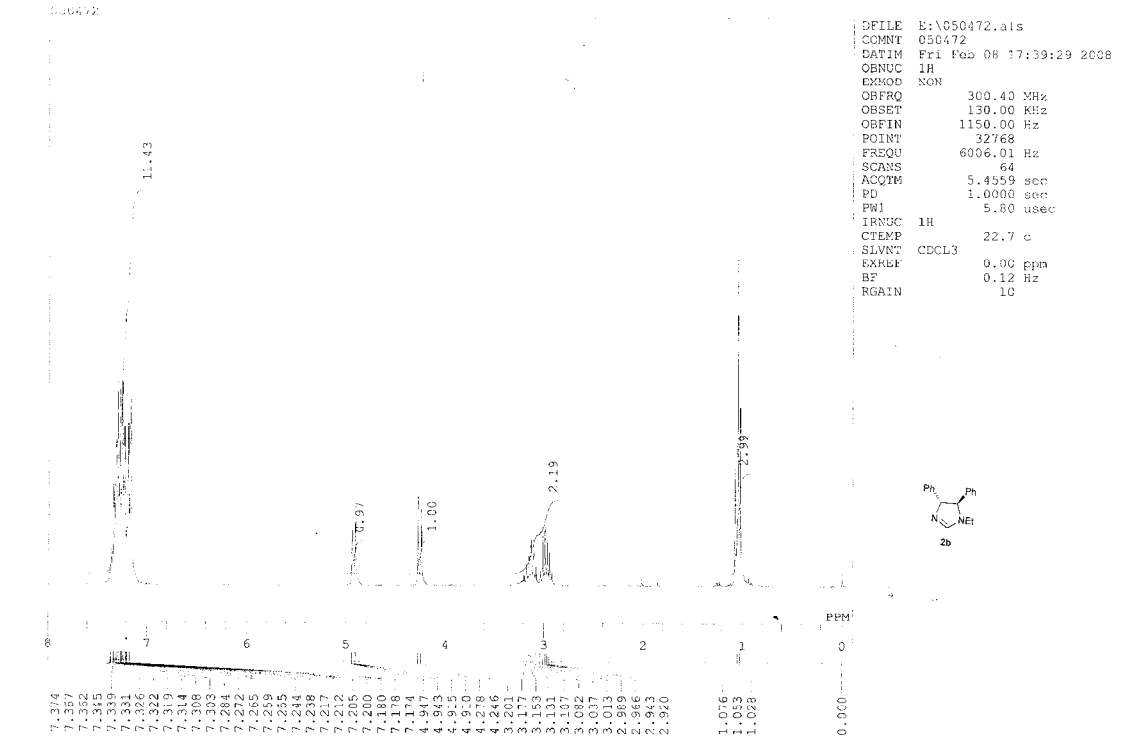
5,6-*trans*-Diphenyl-5,6-dihydro-2-(*1H*)-pyrazinone (3)

Ethyl glyoxylate (50 % in toluene, 0.10 mL, 0.50 mmol) was added to the solution of *(dl)*-1,2 –diphenylethylenediamine (**1a**) (95 mg, 0.448 mmol) in MeOH (4.5 mL) at r.t. under N_2. The reaction mixture was stirred for 2.5 h and solvent was removed in vacuo. The residue was purified by SiO_2 column chromatography (Hex/AcOEt = 2/3) to give **3** (58.7 mg, 52 %) as colorless solid. m.p. 181 ^oC; ^1H NMR (270 MHz, $CDCl_3$): δ = 7.96 (m, 1H, *J* = 2.4 Hz), 7.28-7.20 (m, 6H), 7.05-7.02 (m, 2H), 6.92-6.90 (m, 2H), 6.58 (brs, 1H), 4.70 (dd, 1H, *J* = 10.8, 3.0 Hz), 4.56 ppm (d, 1H, *J* = 10.8 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 156.6, 156.3, 138.1, 137.2, 128.7, 128.6, 128.1, 127.8, 127.7, 127.3, 68.7, 61.6 ppm; IR (KBr): 3053, 2986, 2304, 1692, 1626, 1265, 910, 748 cm^{-1}; HRMS (FAB): calcd for $C_{16}H_{15}N_2O$ [*M*+H]$^+$: 251.1184, found 251.1173.

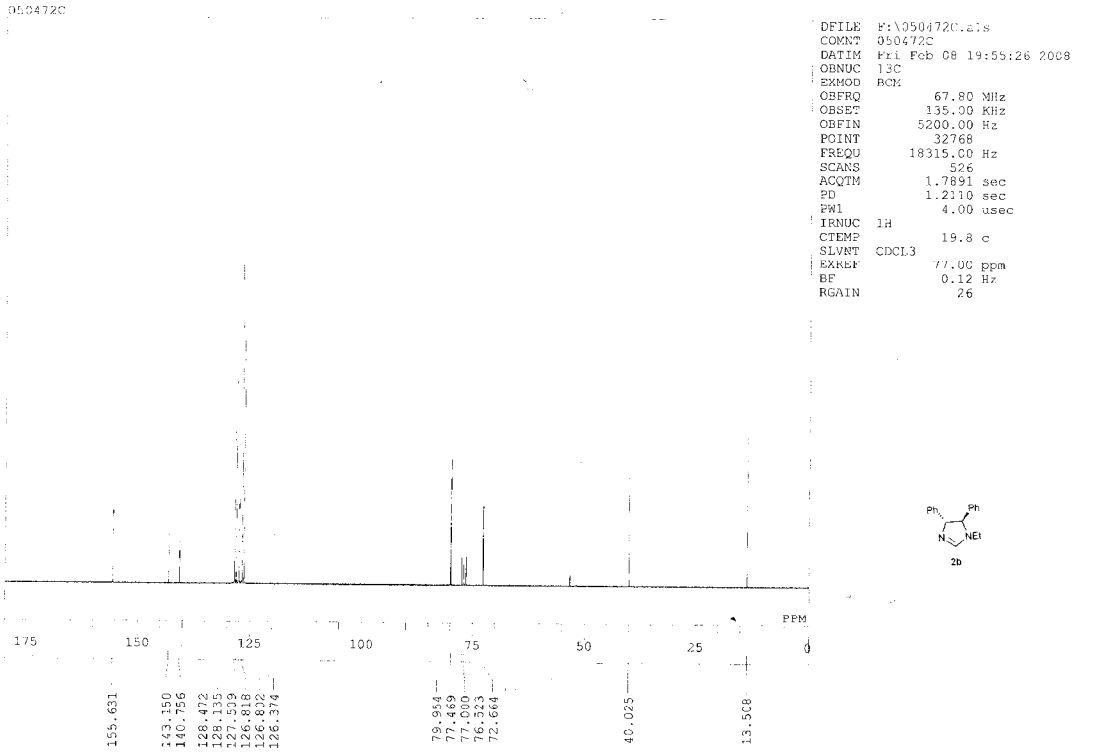
References

1) Díaz, D. D., Finn, M. G. *Org., Lett.* 2004, **6**, 43-46.
2) Jones, R. C. F., Nichols, J. R. *Tetrahedron Lett.* 1990, **31**, 1767-1770.
3) Ronan, B., Hegedus, L. S. *Tetrahedron* 1993, **49**, 5549-5564.

^{1}H NMR of **2b**



^{13}C NMR of **2b**



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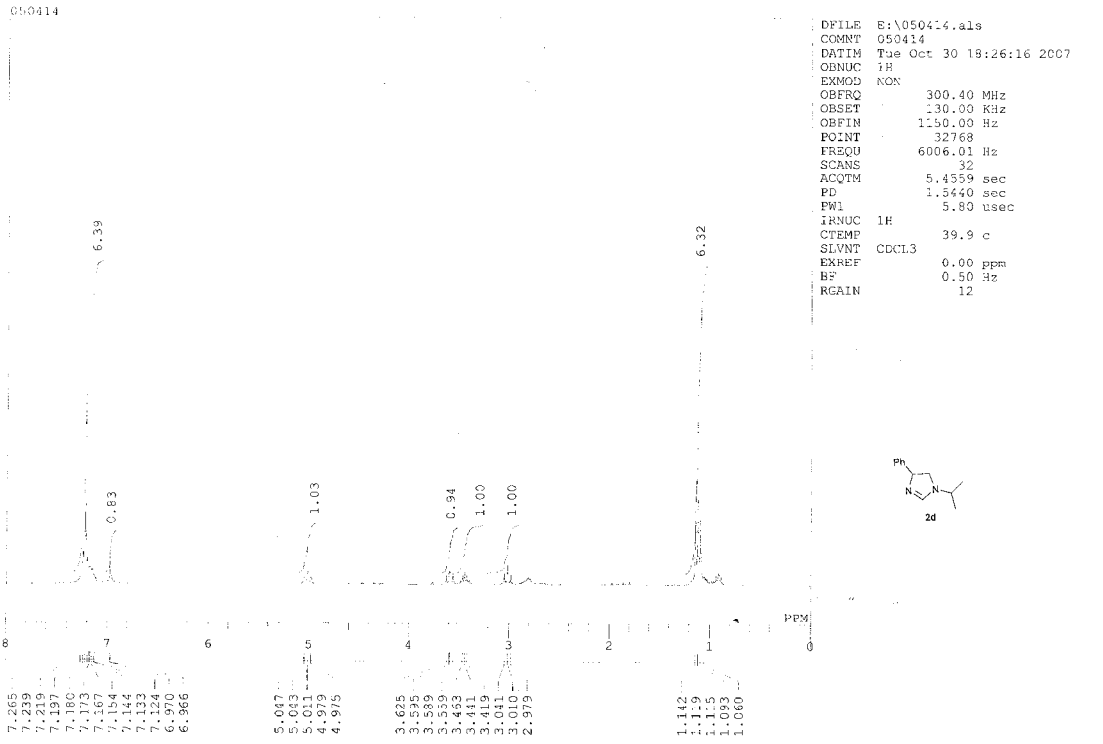

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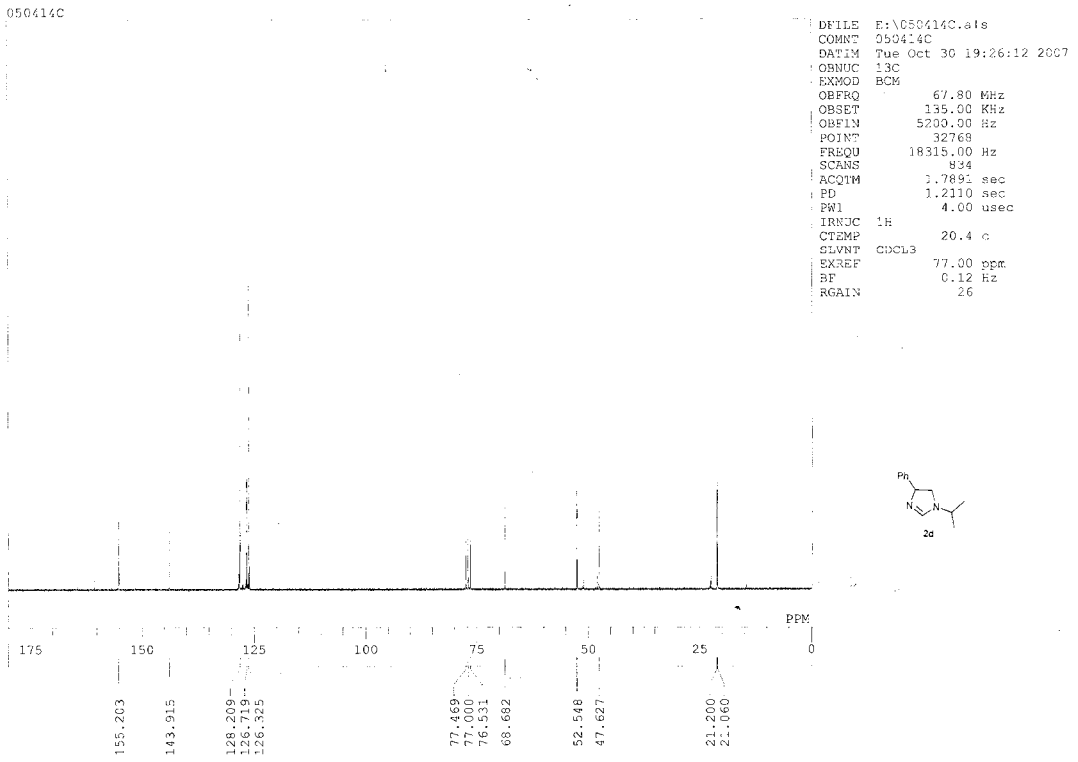

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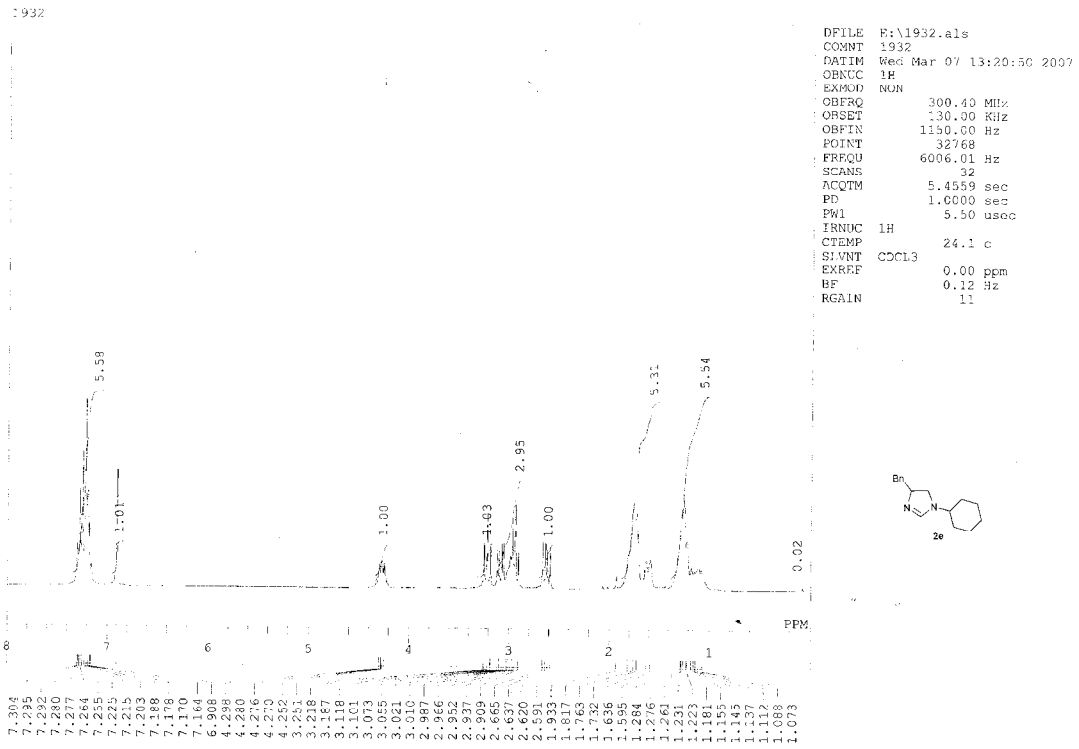

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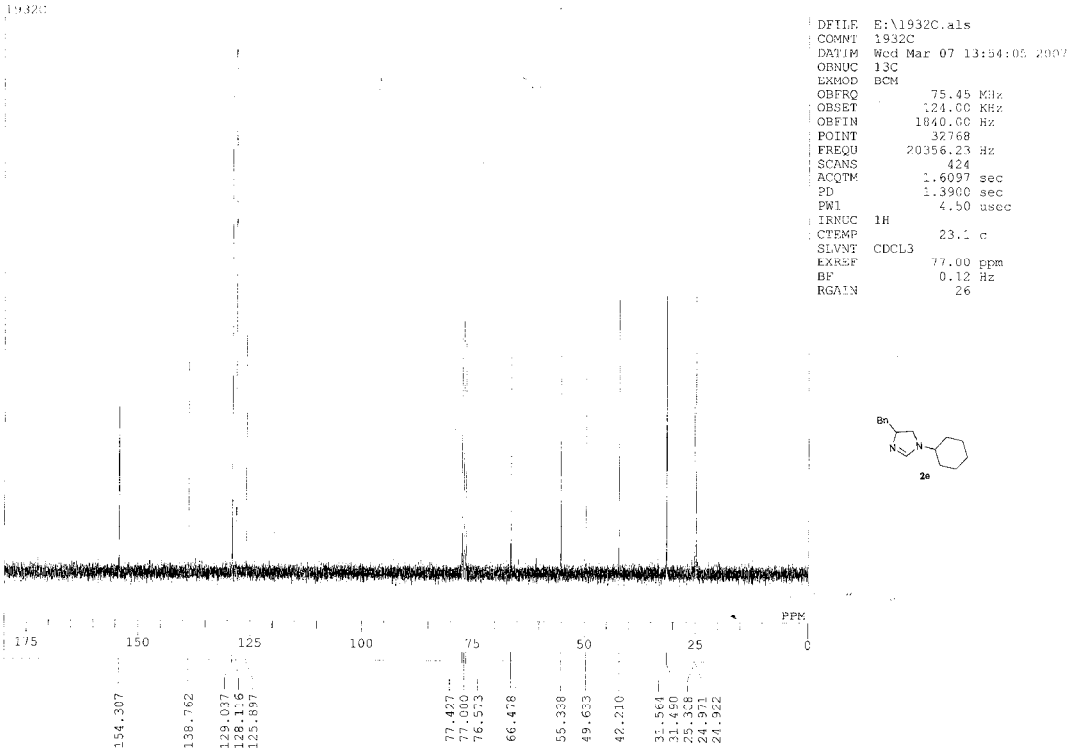

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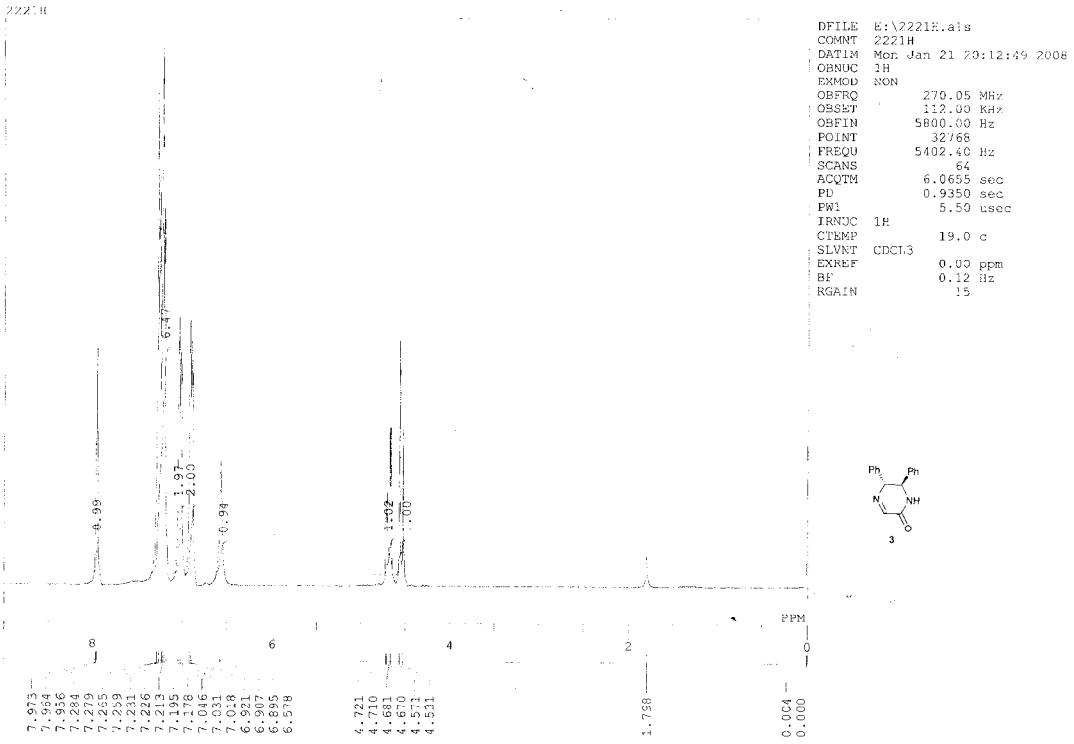

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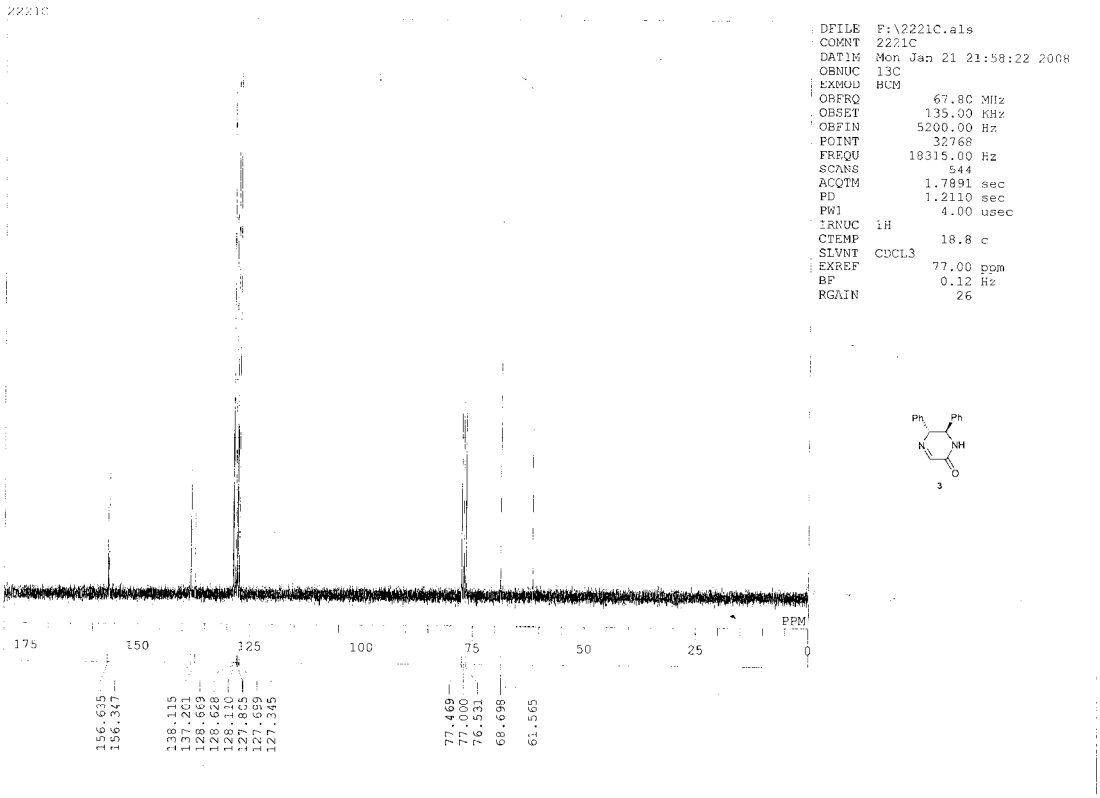
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