Divalent Lanthanide Complexes: Highly Active Precatalysts for the Addition of N-H and C-H Bonds to Carbodiimides

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Experimental Section

All manipulations and reactions were performed under a purified argon atmosphere using standard Schlenk techniques or under a nitrogen atmosphere in a glovebox. Solvents were

degassed and distilled from sodium benzophenone ketyl under argon prior to use. $Sm[N(TMS)_2]_2(THF)_3$ **I**; $Eu[N(TMS)_2]_2(THF)_3$ **II;** $Yb[N(TMS)_2]_2(THF)_3$ **III** $(MeCp)_2Sm(THF)_2$ **IV,** $Sm(ArO)_2(THF)_2$(ArO=2,6-(^{t}Bu)$_2$-4-MeC_6H_2) **V,** SmI_2 **VI. A** and **A′ w**ere prepared according to the literature procedure.[1] All carbodiimides and amines were pre-dried, sublimed, recrystallized or redistilled before use. Melting points were determined in sealed Ar-filled capillary tube, and uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz or 400 MHz spectrometer. Chemical shifts (δ) were reported in ppm. HRMS were recorded on a GCT-TOF instrument.

Procedures:

General procedure 1: for the direct synthesis of guanidines from reaction of aromatic amines with carbodiimides catalyzed by I (product 3 as an Example). A 30 mL of Schlenk tube under dried argon was charged with **I** (0.006 g, 0.009 mmol). To the flask were added the *N, N′*-diisopropylcarbodiimide (0.239 g, 1.9 mmol), aniline (0.177 g, 1.9 mmol). The resulting mixture was stirred at room temperature for 3 min. The reaction mixture was then hydrolyzed with water (0.5 mL), extracted with dichloromethane (3 ×10 mL), dried over anhydrous Na_2SO_4 and filtered. After the solvent was removed under reduced pressure, the residue was recrystallized in hexane to provide a white solid **3** in 98% yield.

General procedure 2: for the direct synthesis of guanidines from reaction of secondary amines with carbodiimides catalyzed by I (product 18 as an Example).

A 30 mL of Schlenk tube under dried argon was charged with **I** (0.011 g, 0.018 mmol). To the flask were added the *N, N′*-diisopropylcarbodiimide (0.441 g, 3.5 mmol), pyrrolidine (0.248 g, 3.5 mmol). The resulting mixture was stirred at 80 ^{o}C for 3 h. The reaction mixture was then

hydrolyzed with water (0.5 mL), extracted with hexane (3 ×10 mL), dried over anhydrous Na_2SO_4 and filtered. After the solvent was removed under vacuum, the final product **18** was obtained in 98% yield.

General procedure 3 : for the direct synthesis of propiolamidines from reaction of terminal alkynes with carbodiimides catalyzed by I (product 28 as an Example).

A 30.0 ml of Schlenk tube under dried argon was charged with **I** (0.010 g, 0.015 mmol). phenylacetylene (0.153 g, 1.5 mmol) and THF (1.20 mL). To the mixture was added the *N, N′*-diisopropylcarbodiimide (0.189 g, 1.5 mmol).The Schlenk tube was taken outside and the mixture was stirred at 80 ^{o}C for 3 h. After the solvent was removed under reduced pressure, the residue was extracted with hexane and filtered to give a clean solution. The solvent was evaporated under vacuum; recrystallization of the crude from n-hexane afforded the product as yellow solid (94 %).

General procedure 4 : for Synthesis and characterization of A (A = [{$(Me_3Si)_2N$}$_2$Sm(μ-$C_2N_4{}^{i}Pr_4$)Sm{$N(SiMe_3)_2$}$_2$])

Sythesis: A solution of *N*, *N′*-diisopropylcarbodiimide (0.204 g, 2.0 mmol) in THF (20 mL) was added at ambient temperature with stirring to a purple solution of [Sm{$N(SiMe_3)_2$}$_2$$(THF)_3$] (0.1M, 20 mL, 2.0 mmol) in hexane. The color turned gradually to light yellow, and the mixture was stirred continuously for 1 h . The volume of solvent was reduced to 20 mL and stored at -10 ^{o}C for two days. light-yellow powders of A were collected (1.03 g, 43 %).

Characterization: Element Analysis and IR

A = [{$(Me_3Si)_2N$}$_2$Sm(μ-$C_2N_4{}^{i}Pr_4$)Sm{$N(SiMe_3)_2$}$_2$]: Found: C, 37.59; H, 8.26; N, 9.11. Anal.

Calcd for $C_{38}H_{102}N_8Si_8Sm_2$: C, 38.14; H, 8.59; N, 9.36. IR (KBr), ν = 2966(s), 2933(w), 1646(s), 1496(m), 1384(m), 1364(m), 1248(w), 1176(m), 1128(w), 843(w) cm^{-1}.

Isolation of diketone $O_2C_2H_2N_2{}^iPr_2$ from the mixture of A and two equiv. of aniline. A solution of **A** (1.196 g, 1.0 mmol) in THF (10 mL) was added to aniline (0.186 g, 2.0 mmol) in THF (5 mL) with stirring at room temperature. After stirring for 1 h, distilled water (10 mL) was added to the system and extracted with dichloromethane (3 × 10 mL), the organic phase dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure, then washed with OEt_2, the white solid was obtained (0.160 g, 93 %). ^{1}H NMR ($CDCl_3$): δ =1.12-1.13(12H), 3.78-3.88(2H), 4.07-4.08(2H). ^{13}C NMR ($CDCl_3$): δ = 157.4, 42.6, 24.0.

for Synthesis and characterization of A′ (A′ = $(MeCp)_2Sm(\mu\text{-}C_2N_4{}^iPr_4)Sm(CpMe)_2$)

Sythesis: A solution of *N*, *N*′-diisopropylcarbodiimide (0.153 g, 1.5 mmol) in THF (20 mL) was added at ambient temperature with stirring to a purple solution of $Sm(CpMe)_2(THF)_2$ (0.1 M, 15 mL, 1.5 mmol) in THF. The color turned gradually to light yellow, and the mixture was stirred continuously for 1.5 h . The volume of solvent was reduced to 10 mL and stored at -20 °C for one week. light-yellow powders of A′ were collected (0.731 g, 56 %).

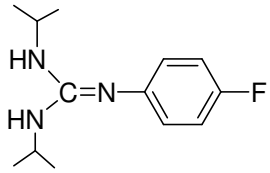
Characterization: Element Analysis and IR

A′ = $(MeCp)_2Sm(\mu\text{-}C_2N_4{}^iPr_4)Sm(CpMe)_2$: Found: C, 51.66; H, 6.54; N, 6.31. Anal. Calcd for $C_{38}H_{58}N_4Sm_2$: C, 52.36; H, 6.71; N, 6.43. IR (KBr), ν = 2965(m), 2925(m), 1642(m), 1298(m), 1197(s), 1173(s), 987(s), 747(s) cm^{-1}.

Isolation of diketone $O_2C_2H_2N_2{}^iPr_2$ from the mixture of A′ and two equiv. of aniline. A solution of **A′** (0.871 g, 1.0 mmol) in THF (10 mL) was added to aniline (0.186 g, 2.0 mmol) in THF (5 mL) with stirring at room temperature. After stirring for 1 h, distilled water (10 mL) was

added to the system and extracted with dichloromethane (3 ×10 mL), the organic phase dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure, then washed with OEt_2, the white solid was obtained (0.153 g, 89 %).^{1}H NMR ($CDCl_3$): δ =1.12-1.13(12H), 3.78-3.88(2H), 4.07-4.08(2H). ^{13}C NMR ($CDCl_3$): δ = 157.4, 42.6, 24.0.

Spectroscopic data for the products



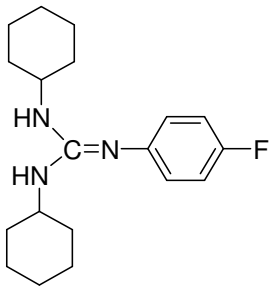
***N-p*-flurophenyl-*N′, N′′*-diisopropylguanidine (1):** product 1 was obtained following the procedure 1 catalyzed by catalysts **I** and isolated as a white solid in 98 % yields.

Mp□130-131 ^{o}C.

^{1}H NMR ($CDCl_3$): δ =6.95-6.91 (2H), 6.79-6.75 (2H), 3.74(2H), 3.52(2H), 1.16-1.14(12H).

^{13}C NMR ($CDCl_3$): δ = 148.0, 144.6, 141.8, 123.4, 122.5, 28.3, 24.2.

HRMS (ESI): m/z calcd for $C_{13}H_{20}FN_3$: 237.1641, found: 237.1653.



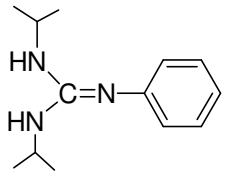
***N-p*-flurophenyl-*N′, N′′*-dicyclohexylguanidine (2):** product 2 was obtained following the procedure 1 catalyzed by catalysts **I** and isolated as a white solid in 99 % yields.

Mp□168-169 ^{o}C.

^{1}H NMR ($CDCl_3$): δ =6.94-6.90 (2H), 6.78-6.75 (2H), 3.59 (2H), 3.38 (2H), 1.99-1.03(20H).

^{13}C NMR ($CDCl_3$): δ = 150.6, 124.9, 124.8, 116.1, 115.9, 50.4, 34.0, 25.9, 25.2.

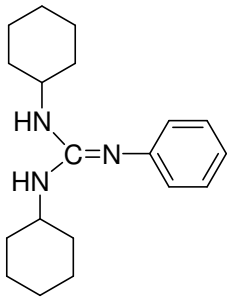
HRMS (ESI): m/z calcd for $C_{19}H_{28}FN_3$: 317.2267, found: 317.2276



***N*-phenyl-*N′, N′′*-diisopropylguanidine (3):** product 3 was obtained following the procedure 1 catalyzed by catalysts **I** and isolated as a white solid in 98 % yields□Known compound.[2]

^{1}H NMR ($CDCl_3$): δ = 7.22 (2H), 6.95-6.91 (1H), 6.86-6.84(2H),3.77 (2H), 3.61(2H), 1.17-1.15 (12H).

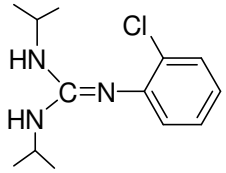
^{13}C NMR ($CDCl_3$): δ = 150.5, 150.4, 129.5, 123.7, 121.5, 43.4, 23.6.



***N*-phenyl-*N′, N″*-dicyclohexylguanidine(4):** product 4 was obtained following the procedure 1 catalyzed by catalysts **I** and isolated as a white solid in 99 % yields, Known compound.[2]

^{1}H NMR ($CDCl_3$): δ = 7.25-7.23 (2H), 6.95-6.91 (1H),6.88-6.86(2H), 3.64 (2H), 3.42 (2H), 2.03-1.05 (20H).

^{13}C NMR ($CDCl_3$): δ = 150.7, 150.7, 129.5, 123.9, 121.6, 50.5, 34.1, 26.0, 25.2.



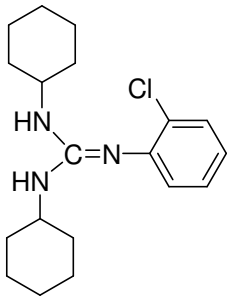
***N*-*o*-chlorophenyl-*N′, N″*-diisopropylguanidine (5):** product 5 was obtained following the procedure 1 catalyzed by catalysts **I** and isolated as a white solid in 99 % yields,

Mp:137-138 °C.

^{1}H NMR ($CDCl_3$): δ = 7.35-7.33 (1H), 7.15-7.11(1H), 6.91-6.85 (2H), 3.79-3.77 (2H),3.48 (2H), 1.19-1.17 (12H).

^{13}C NMR ($CDCl_3$): δ = 150.1, 147.2, 130.1, 128.5, 127.8, 125.5, 122.7, 43.6, 23.6.

HRMS (ESI): m/z calcd for$C_{13}H_{20}ClN_3$: 253.1346, found: 253.1356.



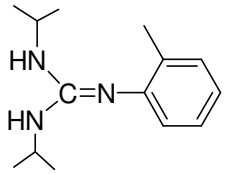
***N*-*o*-chlorophenyl-*N′, N″*-dicyclohexylguanidine (6):** product 6 was obtained following the procedure 1 catalyzed by catalysts **I** and isolated as a white solid in 99.3 % yields.

Mp:137-138 °C.

^{1}H NMR ($CDCl_3$): δ =7.34-7.33(1H), 7.15-7.11(1H), 6.92-6.85 (2H), 3.56 (2H), 3.42 (2H), 2.05-1.06(20H).

^{13}C NMR ($CDCl_3$): δ = 150.1, 147.6, 130.1, 128.7, 127.8, 125.6, 122.6, 50.5, 34.1, 26.0, 25.2.

HRMS (ESI): m/z calcd for$C_{19}H_{28}ClN_3$: 333.1972,found:333.1963.

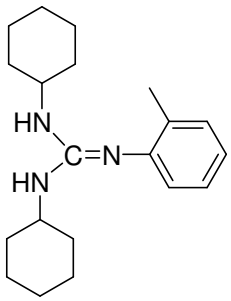


***N-o*-methylphenyl-*N′, N″*-diisopropylguanidine (7):** product 7 was obtained following the procedure 1 catalyzed by catalysts **I** and isolated as a white solid in 95 % yields. Known compound.[3]

Mp□124-125 ^{o}C.

^{1}H NMR ($CDCl_3$): δ = 7.15-7.14(1H), 7.11-7.07(1H), 6.90-6.86(1H), 6.78-6.76 (1H), 3.76 (2H), 3.46 (2H), 2.14 (3H), 1.17-1.15(12H).

^{13}C NMR ($CDCl_3$): δ = 149.1, 148.6, 131.8, 130.6, 126.8, 123.4, 121.9, 43.4, 23.7, 18.4

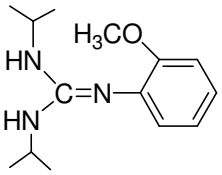


***N-o*-methylphenyl-*N′, N″*-dicyclohexylguanidine (8):** product 8 was obtained following the procedure 1 catalyzed by catalysts **I** and isolated as a white solid in 98 % yields. Known compound.[3]

Mp□134-135 ^{o}C

^{1}H NMR ($CDCl_3$): δ = 6.95-6.91(2H), 6.80-6.76 (2H), 3.62 (2H), 3.40 (2H), 2.00(3H), 1.97-1.03 (20H).

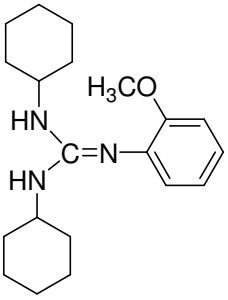
^{13}C NMR ($CDCl_3$): δ = 148.9, 148.7, 131.9, 130.6, 126.8, 123.5, 121.9, 50.4, 34.2, 25.9, 25.2, 18.4.



***N*-o-methoxyphenyl-*N′, N″*-diisopropylguanidine (9):** product 9 was obtained following the procedure 1 catalyzed by catalysts **I** and isolated as a white solid in 98 % yields, Known compound.[4]

^{1}H NMR ($CDCl_3$): δ = 6.94-6.86(4H), 3.78 (5H), 3.56 (2H), 2.00(3H), 1.17-1.15(12H).

^{13}C NMR ($CDCl_3$): δ = 152.4, 150.7, 139.2, 124.7, 122.2, 121.3, 111.8, 55.6, 43.3, 23.4.



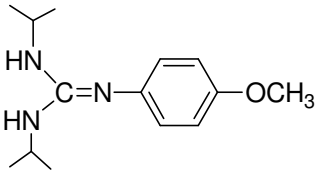
***N*-o-methoxyphenyl-*N′, N″*-dicyclohexylguanidine (10):** product 10 was obtained following the procedure 1 catalyzed by catalysts **I** and isolated as a white solid in 92 % yields.

Mp: 122-123 ^{o}C.

^{1}H NMR ($CDCl_3$): δ = 6.96-6.85(4H), 3.79 (3H), 3.60 (2H),3.45 (2H), 2.04-1.04(20H).

^{13}C NMR ($CDCl_3$): δ = 152.6, 150.5, 139.3, 125.0, 122.4, 121.4, 111.9, 55.7, 50.4, 34.0, 25.9, 25.1.

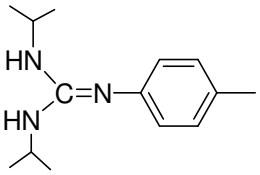
HRMS (ESI): m/z calcd for$C_{20}H_{31}N_3O$: 329.2467, found: 329.2458.



***N*-p-methoxyphenyl-*N′, N″*-diisopropylguanidine(11):** product 11 was obtained following the procedure 1 catalyzed by catalysts **I** and isolated as a white solid in 95 % yields. Known compound.[5]

^{1}H NMR ($CDCl_3$): δ = 6.83-6.76(4H), 3.77 (5H), 3.57 (2H), 1.16-1.14(12H).

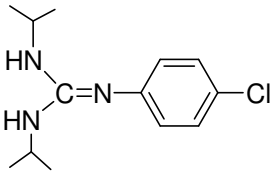
^{13}C NMR ($CDCl_3$): δ = 154.7, 150.9, 143.4, 124.5, 114.8, 55.6, 43.4, 23.6.



***N-p*-methylphenyl-*N′, N″*-diisopropylguanidine (12):** product 12 was obtained following the procedure 1 catalyzed by catalysts **I** and isolated as a white solid in 90 % yields. Known compound.[3]

^{1}H NMR ($CDCl_3$): δ =7.05-7.03(2H), 6.75-6.73(2H), 3.75 (2H), 3.58 (2H),2.27(3H), 1.16-1.14(12H).

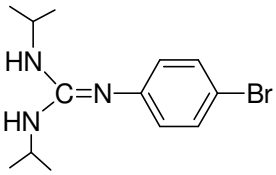
^{13}C NMR ($CDCl_3$): δ = 150.6, 147.6, 130.7, 130.1, 123.5, 43.4, 23.6, 21.1.



***N-p*-chlorophenyl-*N′, N″*-diisopropylguanidine (13):** product 13 was obtained following the procedure 1 catalyzed by catalysts **I** and isolated as a white solid in 98 % yields. Known compound.[5]

^{1}H NMR ($CDCl_3$): δ =7.20-7.18(2H), 6.79-6.77(2H), 3.75 (2H), 3.60 (2H), 1.17-1.15(12H).

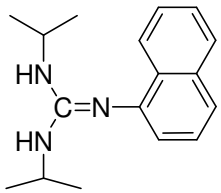
^{13}C NMR ($CDCl_3$): δ = 150.5, 149.2, 129.4, 126.4, 125.1, 43.5, 23.6.



***N-p*-bromophenyl-*N′, N″*-diisopropylguanidine (14):** product 14 was obtained following the procedure 1 catalyzed by catalysts **I** and isolated as a white solid in 99 % yields. Known compound.[2]

^{1}H NMR ($CDCl_3$): δ =7.33-7.31(2H), 6.73-6.71(2H), 3.74 (2H), 3.56 (2H), 1.15-1.14(12H).

^{13}C NMR ($CDCl_3$): δ = 150.4, 149.7, 132.4, 125.6, 114.0, 43.5, 23.6.

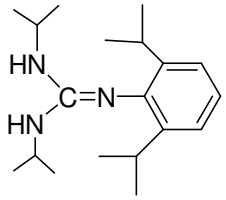


***N*-(1-naphthyl)-*N′, N″*-diisopropylguanidine (15)** product 15 was obtained following the

procedure 1 catalyzed by catalysts **I** and isolated as a white solid in 96 % yields. Known compound.[2]

^{1}H NMR ($CDCl_3$): δ =8.08-8.06(1H), 7.80-7.78(1H),7.47-7.35(4H), 6.93-6.91(1H), 3.88 (2H), 3.63 (2H), 1.19-1.17(12H).

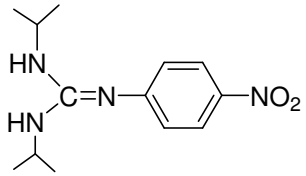
^{13}C NMR ($CDCl_3$): δ = 150.2, 147.1, 135.1, 129.9, 128.1, 126.8, 126.1, 125.0, 124.7, 121.7, 118.1, 43.6, 23.7.



***N, N′′*-diisopropyl-*N′*-2, 6-diisopropylphenylguanidine (16):** product 16 was obtained following the procedure 1 catalyzed by catalysts **I** and isolated as a white solid in 95 % yields. Known compound.[3]

^{1}H NMR ($CDCl_3$): δ =7.07-7.05(2H), 6.98-6.94(1H), 4.19(1H), 3.43-3.19(3H), 3.11-3.04 (2H). 3.56 (2H), 1.25-1.04(24H).

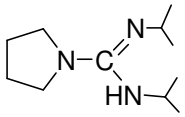
^{13}C NMR ($CDCl_3$): δ = 147.7, 144.3, 141.6, 123.2, 122.3, 43.5, 42.7, 28.0, 23.9.



***N-p*-nitrophenyl-*N′, N′′*-diisopropylguanidine(17):** product 17 was obtained following the procedure 1 catalyzed by catalysts **I** and isolated as a yellow solid in 95 % yields. Known compound.[2]

^{1}H NMR ($CDCl_3$): δ =8.11-8.09(2H), 6.90-6.88(2H), 4.19(1H), 3.83-3.78(4H), 1.19-1.18(12H).

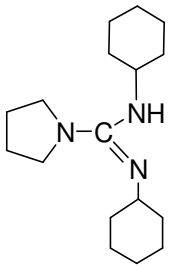
^{13}C NMR ($CDCl_3$): δ = 158.6, 150.8, 141.1, 125.9, 123.1, 43.7, 23.6.



***N, N′*-diisopropylpyrrolidine-1-carboximidamide (18):** product 18 was obtained following the procedure 2 catalyzed by catalysts **I** and isolated as a colorless liquid in 98 % yields. Known compound.[6]

^{1}H NMR ($CDCl_3$): δ =3.38(2H), 3.26(4H), 1.80(4H), 1.11-1.10(12H).

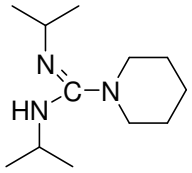
^{13}C NMR ($CDCl_3$): δ = 153.7, 47.9, 46.8, 26.3, 24.8.



***N, N′*-dicyclohexylpyrrolidine-1-carboximidamide (19):** product 19 was obtained following the procedure 2 catalyzed by catalysts **I** and isolated as a white solid in 98 % yields. Known compound.[6]

^{1}H NMR ($CDCl_3$): δ =3.21(4H), 2.89(2H),1.75-1.08(24H).

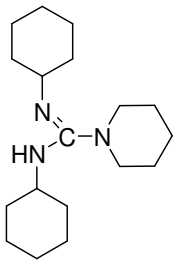
^{13}C NMR ($CDCl_3$): δ = 154.0, 55.3, 48.3, 35.4, 26.0, 25.9, 25.5.



***N, N′*-diisopropylpiperidine-1-carboximidamide (20):** product 20 was obtained following the procedure 2 catalyzed by catalysts **I** and isolated as a colorless liquid in 97 % yields. Known compound.[6]

^{1}H NMR ($CDCl_3$): δ =3.40-3.30(2H), 3.03(4H),1.53(6H), 1.10-1.08(12H).

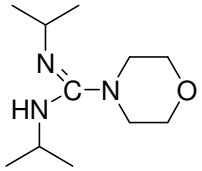
^{13}C NMR ($CDCl_3$): δ = 156.3, 49.2, 46.6, 45.7, 26.3, 26.3, 24.8, 24.0.



N, N'-dicyclohexylpiperidine-1-carboximidamide (21): product 21 was obtained following the procedure 2 catalyzed by catalysts **I** and isolated as a white solid in 98 % yields. Known compound.[6]

^{1}H NMR ($CDCl_3$): δ =3.02(4H), 2.87(2H), 1.90-1.05(26H).

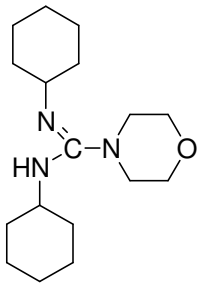
^{13}C NMR ($CDCl_3$): δ = 156.0, 55.9, 53.7, 49.2, 34.9, 34.9, 26.3, 26.0, 25.7, 25.4.



***N, N′*-diisopropylmorpholine-4-carboximidamide (22):** product 22 was obtained following the procedure 2 catalyzed by catalysts **I** and isolated as a white solid in 93 % yields. Known compound[6].

^{1}H NMR ($CDCl_3$): δ =3.69-3.67(4H), 3.42-3.39(1H), 3.32-3.29(1H), 3.08-3.06(4H), 1.14-1.06(12H).

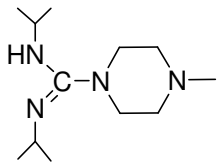
^{13}C NMR ($CDCl_3$): δ = 155.5, 67.3, 48.9, 47.4, 46.6, 23.9, 23.8.



***N, N′*-dicyclohexylmorpholine-4-carboximidamide (23):** product 23 was obtained following the procedure 2 catalyzed by catalysts **I** and isolated as a white solid in 99 % yields. Known compound.[6]

^{1}H NMR ($CDCl_3$): δ =3.66(4H), 3.06(4H), 2.97-2.88(2H), 1.90-1.02(20H).

^{13}C NMR ($CDCl_3$): δ = 155.2, 67.5, 56.7, 54.0, 49.1, 35.6, 34.9, 26.3 ,26.1 , 25.9.

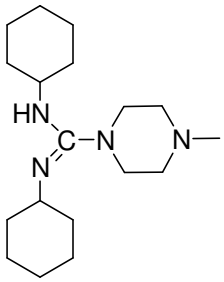


***N, N′*-diisopropyl -4-methylpiperazine-1-carboxamidine (24):** product 24 was obtained following the procedure 2 catalyzed by catalysts **I** and isolated as a colorless liquid in 87 % yields.

^{1}H NMR ($CDCl_3$): δ =3.12(2H), 2.88(4H),2.16(4H), 2.05(3H), 0.86-0.84(12H).

^{13}C NMR ($CDCl_3$): δ = 154.9, 55.2, 47.7, 46.6, 46.1, 24.2.

HRMS (ESI): m/z calcd for$C_{12}H_{26}N_4$: 226.2157, found: 226.2151.

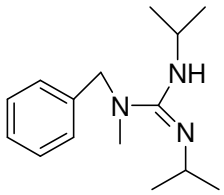


***N, N′*-dicyclohexyl -4-methylpiperazine-1-carboxamidine (25):** product 25 was obtained following the procedure 2 catalyzed by catalysts **I** and isolated as a colorless liquid in 90 % yields.

^{1}H NMR ($CDCl_3$): δ =3.10(4H), 2.95-2.87(2H),2.36(4H), 2.27(3H), 1.88-1.01(20H).

^{13}C NMR ($CDCl_3$): δ = 152.4, 52.9, 45.2, 43.8, 32.4, 23.3, 23.0, 22.2.

HRMS (ESI): m/z calcd for$C_{18}H_{34}N_4$: 306.2783, found: 306.2781.

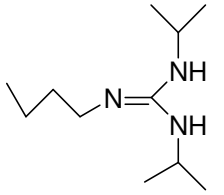


***N –benzyl-N-methyl-N′,N″*- diisopropylguanidine (26):** product 26 was obtained following the procedure 2 catalyzed by catalysts **I** and isolated as a colorless liquid in 95 % yields.

^{1}H NMR ($CDCl_3$): δ =7.32-7.29(3H), 7.24-7.20(2H),4.30(2H), 3.50-3.35(2H), 2.61(3H). 1.12 (12H)

^{13}C NMR ($CDCl_3$): δ = 155.9, 139.7, 128.5, 128.0, 126.9, 55.4, 37.1, 24.9.

HRMS (ESI): m/z calcd for$C_{15}H_{25}N_3$: 247.2048, found: 247.2049.

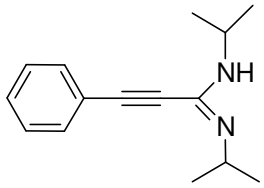


***N-butyl-N′,N″*- diisopropylguanidine (27):** product 27 was obtained following the procedure 2 catalyzed by catalysts **I** and isolated as a colorless liquid in 94 % yields.

^{1}H NMR ($CDCl_3$): δ =3.57-3.48(2H), 3.05-2.98(2H),1.53-1.48(2H), 1.42-1.34(2H), 1.15-1.07(12) ,0.94-0.91(3H).

^{13}C NMR ($CDCl_3$): δ = 151.8, 44.7, 34.0, 33.7, 24.6, 21.2, 14.7,.

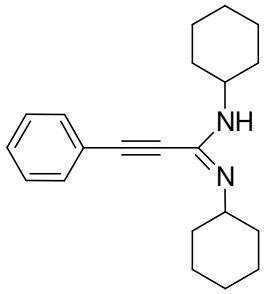
HRMS (ESI): m/z calcd for$C_{11}H_{25}N_3$: 199.2048, found: 199.2050.



(*E*)-*N, N'*-diisopropyl-3-phenylpropiolamidine (28): product 28 was obtained following the procedure 3 catalyzed by catalysts **I** and isolated as a colorless solid in 94 % yields. Known compound[7].

^{1}H NMR ($CDCl_3$): δ =7.51-7.48(2H), 7.39-7.33(3H),3.99-3.93(2H), 1.17-1.16(12H),

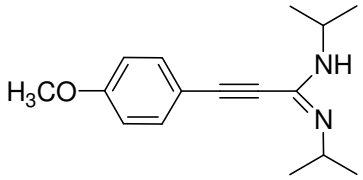
^{13}C NMR ($CDCl_3$): δ = 141.0, 131.7, 129.1, 128.2, 121.2, 91.6, 91.4,.79.0, 45.8, 23.7.



(*E*)-*N, N'*- dicyclohexyl-3-phenylpropiolamidine (29): product 29 was obtained following the procedure 3 catalyzed by catalysts **I** and isolated as a colorless solid in 95 % yields. Known compound[7].

^{1}H NMR ($CDCl_3$): δ =7.52-7.26(5H), 3.60(2H),1.89-1.18(20H).

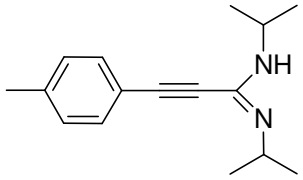
^{13}C NMR ($CDCl_3$): δ = 141.9, 132.2, 129.6, 92.3, 79.6, 55.8, 53.0, 34.5, 33.4, 26.4, 26.0, 25.3, 22.9



(*E*)-*N, N'*- diisopropyl-3-(4-methoxyphenyl)propiolamidine (30):): product 30 was obtained following the procedure 3 catalyzed by catalysts **I** and isolated as a light yellow solid in 96 % yields. Known compound[7].

^{1}H NMR ($CDCl_3$): δ =7.43-7.41(2H), 6.87-6.85(2H),3.95-3.92(2H), 3.82(3H), 1.16-1.14(12H).

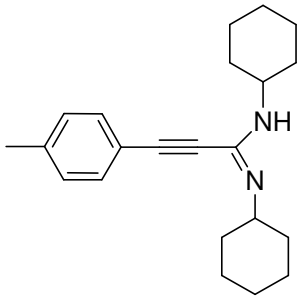
^{13}C NMR ($CDCl_3$): δ = 160.6, 141.6, 122.6, 114.3, 113.5, 92.0, 78.6,.55.4, 47.1, 24.0.



(E)-N,N'-diisopropyl-3-p-tolylpropiolamidine (31): product 32 was obtained following the procedure 3 catalyzed by catalysts **I** and isolated as a colorless solid in 95 % yields. Known compound[7].

^{1}H NMR ($CDCl_3$): δ =7.38-7.37(2H), 7.16-7.14(2H),3.96-3.93(2H),2.36(3H),1.16-1.14(12H).

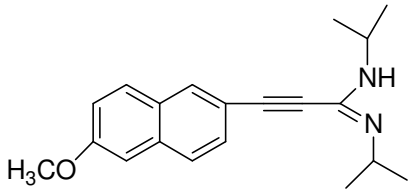
^{13}C NMR ($CDCl_3$): δ = 141.7, 139.9, 132.1, 129.4, 118.6, 92.3, 79.0,.47.2, 24.1 21.8



(E)-N,N'-dicyclohexyl -3-p-tolylpropiolamidine(32): product 33 was obtained following the procedure 3 catalyzed by catalysts **I** and isolated as a colorless solid in 90% yields. Known compound[7].

^{1}H NMR ($CDCl_3$): δ =7.37-7.35(2H), 7.16-7.14(2H),3.60-3.47(2H),2.36(3H),1.88-1.21(20H).

^{13}C NMR ($CDCl_3$): δ = 159.5, 132.9, 130.2, 129.6, 127.8, 120.5, 106.6,.56.1, 47.9 35.1, 26.6, 25.9.

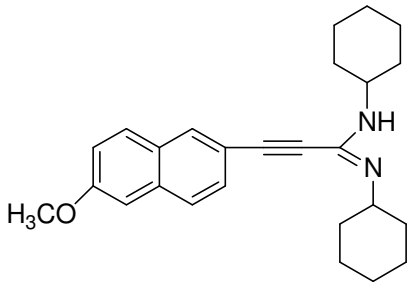


(E)-N,N'-diisopropyl-3-(6-methoxynaphthalen-2-yl)propiolamidine(33): product 34 was obtained following the procedure 3 catalyzed by catalysts **I** and isolated as a colorless solid in 98% yields.

^{1}H NMR ($CDCl_3$): δ =7.94(1H), 7.72-7.68(2H),7.48-7.46(1H),7.18-7.16(1H),7.11(1H), 4.03-3.97(2H), 3.92(3H),1.19-1.17(12H).

^{13}C NMR ($CDCl_3$): δ = 159.1, 141.9, 135.0,132.5, 129.8, 128.7, 127.4,.120.1, 116.6 106.2, 92.9,79.5, 55.8, 44.0, 24.5

HRMS (ESI): m/z calcd for$C_{20}H_{24}N_2O$: 308.1889, found: 308.1903.

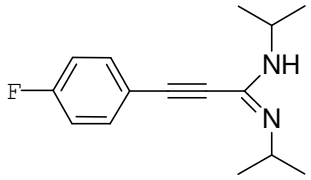


(E)-N,N'-dicyclohexyl -3-(6-methoxynaphthalen-2-yl)propiolamidine(34): product 35 was obtained following the procedure 3 catalyzed by catalysts **I** and isolated as a colorless solid in 97% yields.

^{1}H NMR ($CDCl_3$): δ =7.92(1H), 7.73-7.69(2H),7.48-7.45(1H),7.19-7.12(2H), 3.93(3H), 3.65-3.64(2H),1.92-1.21(20H).

^{13}C NMR ($CDCl_3$): δ = 159.0, 142.2, 134.9,132.4, 129.7,129.1,128.5,.127.3, 112.0 116.5, 106.1,93.1, 79.3, 55.6, 49.2, 34.6, 26.1, 25.4.

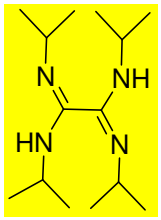
HRMS (ESI): m/z calcd for$C_{26}H_{32}N_2O$: 388.2515 , found: 388.2520.



(E)-3-(4-fluorophenyl)- N,N'-diisopropylpropiolamidine(35): product 36 was obtained following the procedure 3 catalyzed by catalysts **I** and isolated as a colorless solid in 90% yields. Known compound [8].

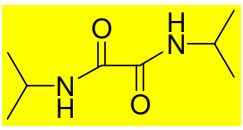
^{1}H NMR ($CDCl_3$): δ =7.53-7.50(2H), 7.11-7.07(2H),3.99-3.96(2H),1.21-1.19(12H).

^{13}C NMR ($CDCl_3$): δ = 165.0, 161.7, 141.3,134.3, 134.2,117.8,116.3,.116.0, 90.8 79.3, 48.6, 24.2.



□1E,2E□-N^1,N$^{1\prime}$,N^{2}N$^{2\prime}$-tetraisopropyloxalamidine(36):product 36 was obtained following the procedure 4 catalyzed by catalysts **I** or **IV** and isolate as a white solid. Known compound.[9]

^{1}H NMR ($CDCl_3$): δ =1.14-1.16(24H), 3.77-3.86(4H).



N^1,N^2-diisopropyloxalamide(37):product 37 was obtained following the procedure 4 catalyzed by catalysts **I** or **IV** and isolate as a white solid. Known compound.[10]

^{1}H NMR ($CDCl_3$): δ =1.12-1.13(12H), 3.78-3.88(2H), 4.07-4.08(2H).

^{13}C NMR ($CDCl_3$): δ = 157.4,42.6, 24.0.

Reference

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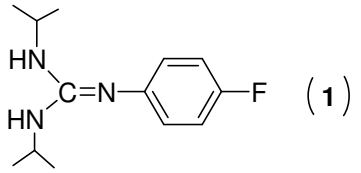
Copy of ^{1}H and ^{13}C NMR spectra



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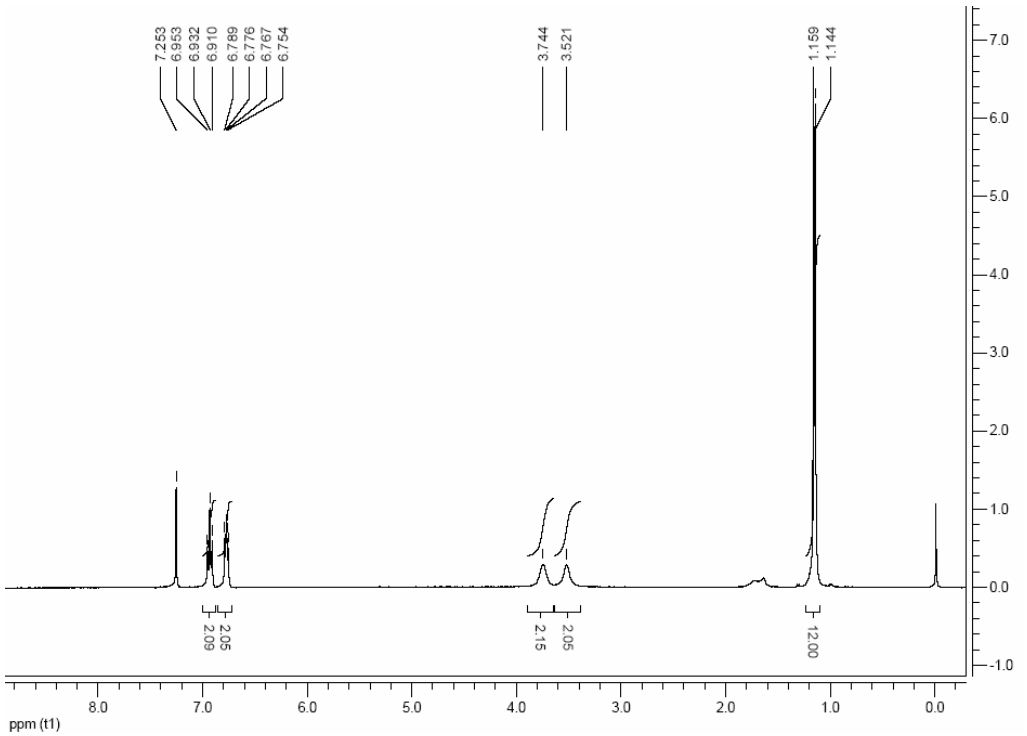

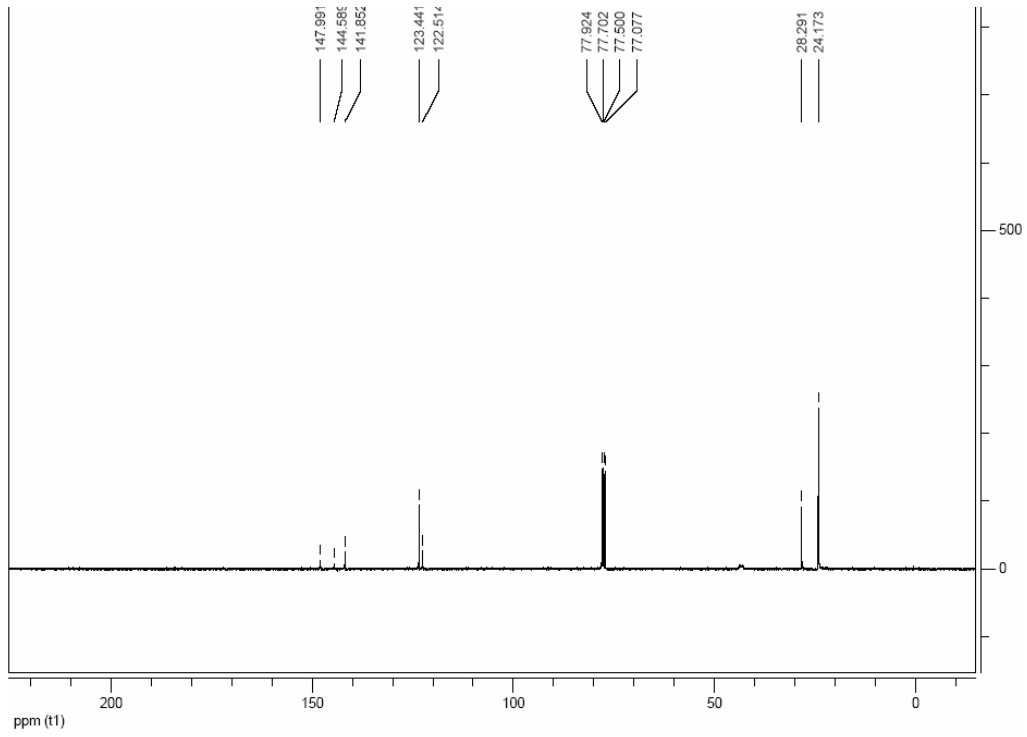

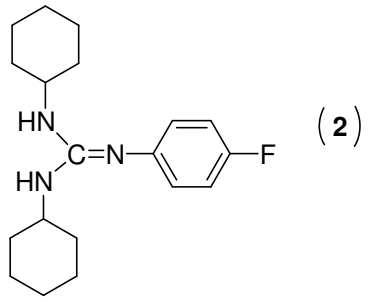
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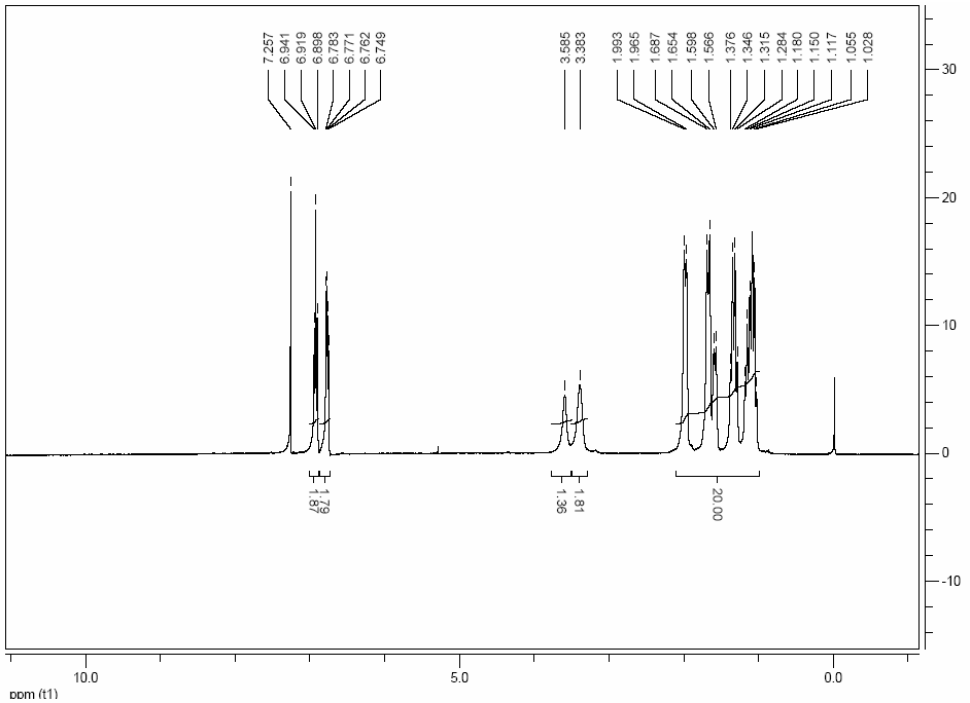
HN
F

(**2**)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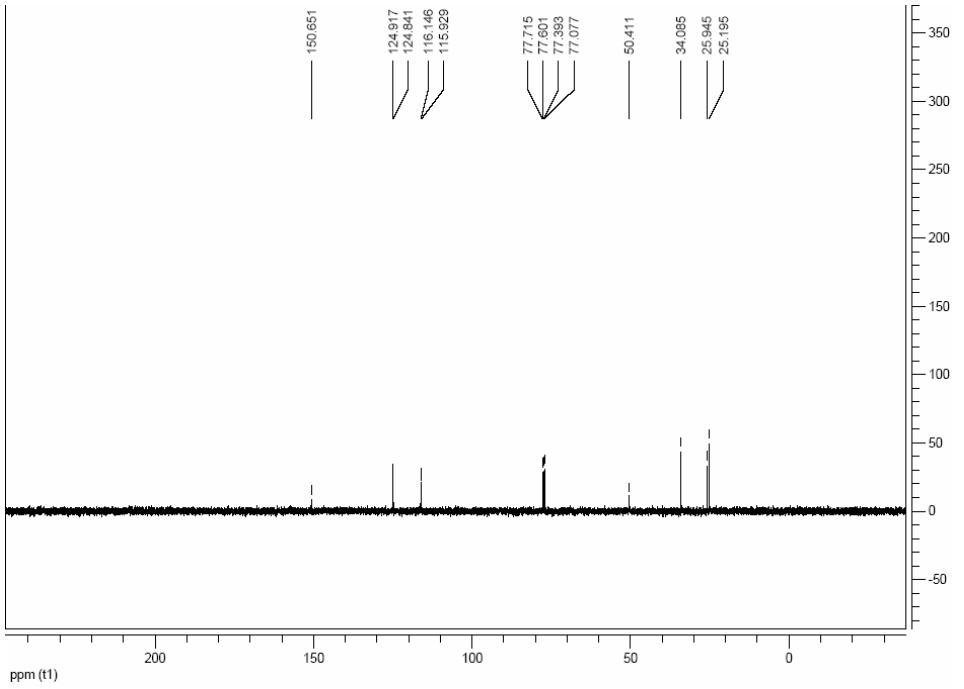
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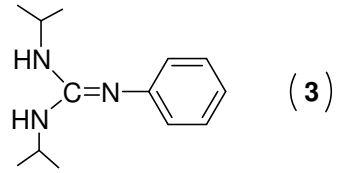
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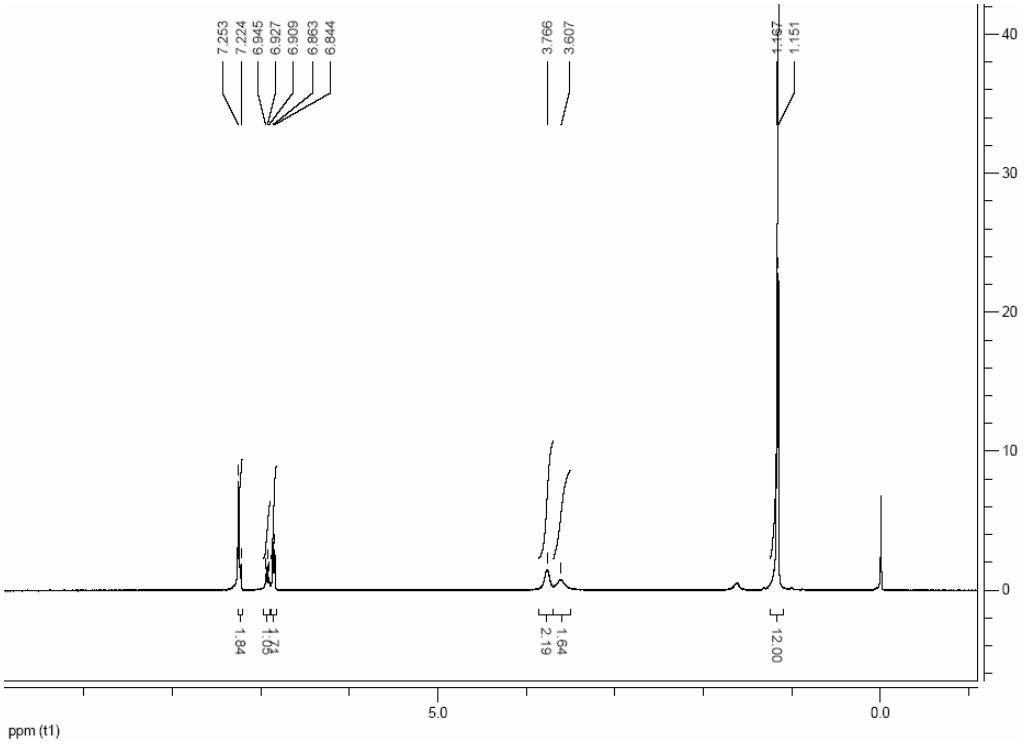
(**3**)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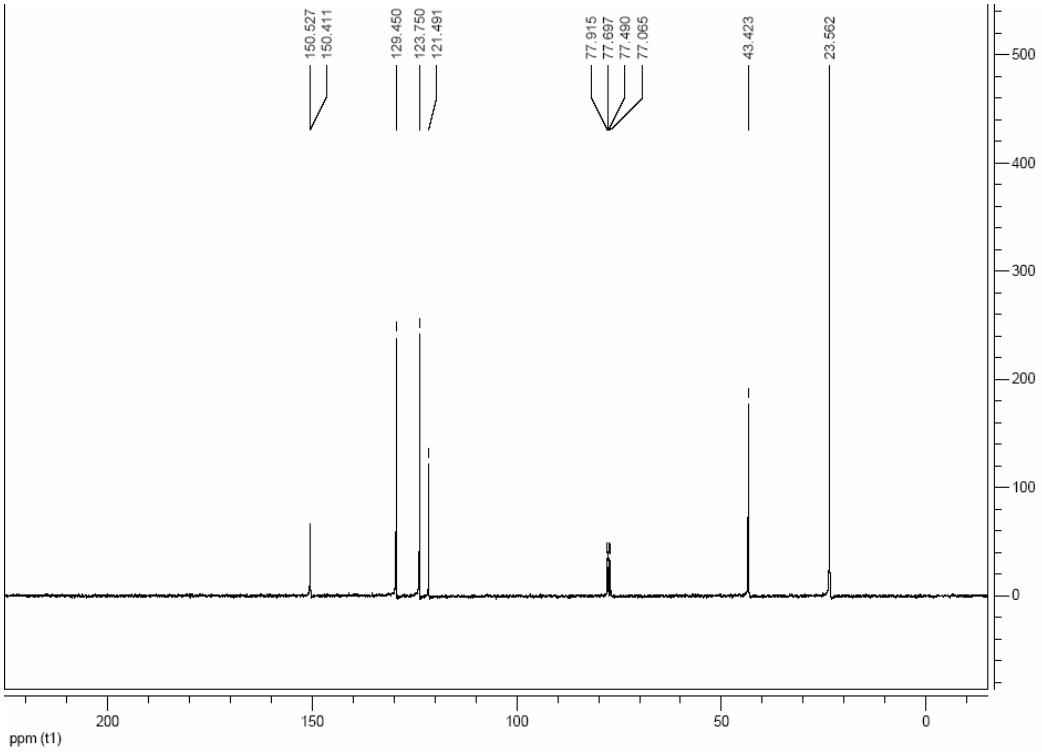
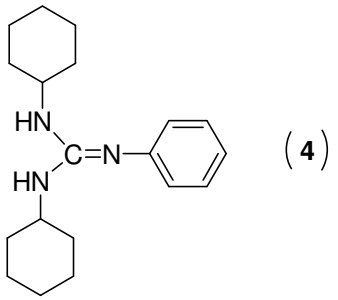
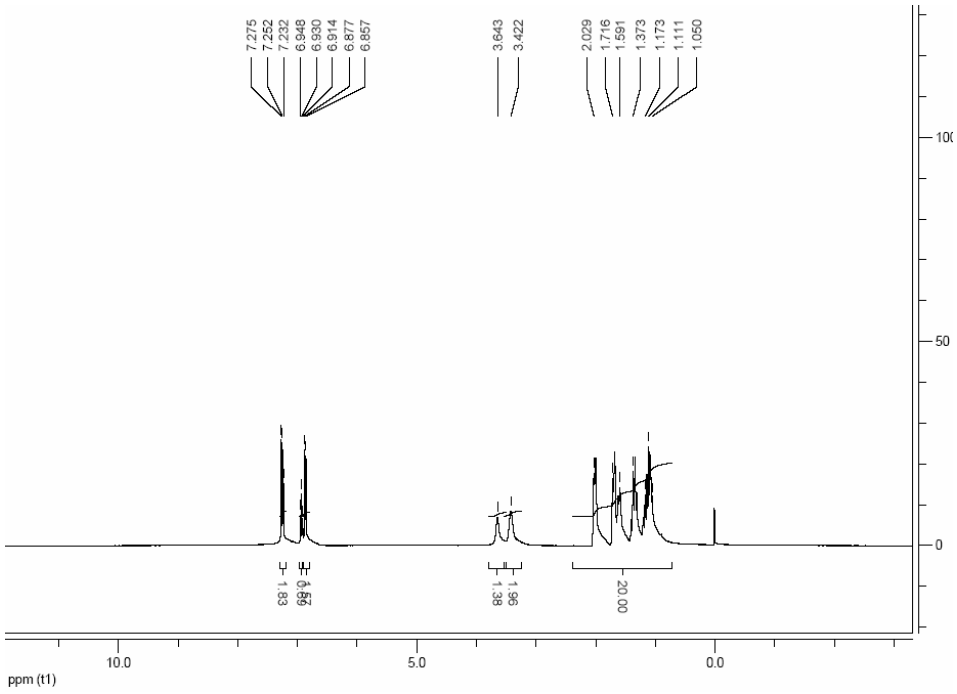
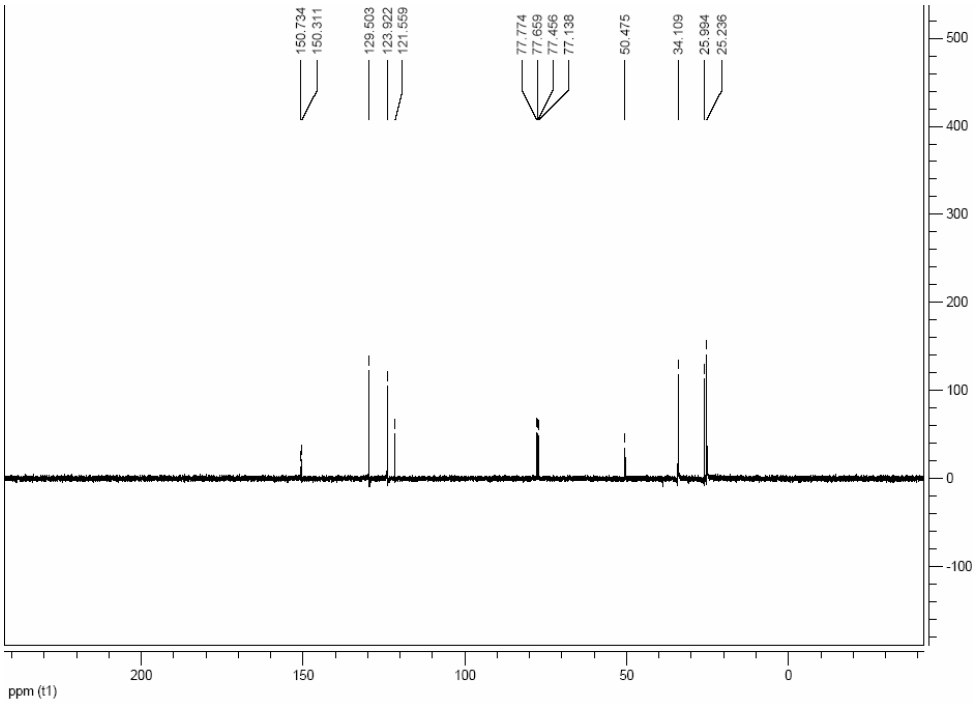
0.0
ppm (t1)

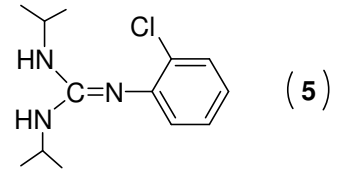

150.527
150.411
129.450
123.750
121.491
77.915
77.697
77.490
77.065
43.423
23.562
200
150
100
50
0
ppm (t1)


HN
C=N
HN

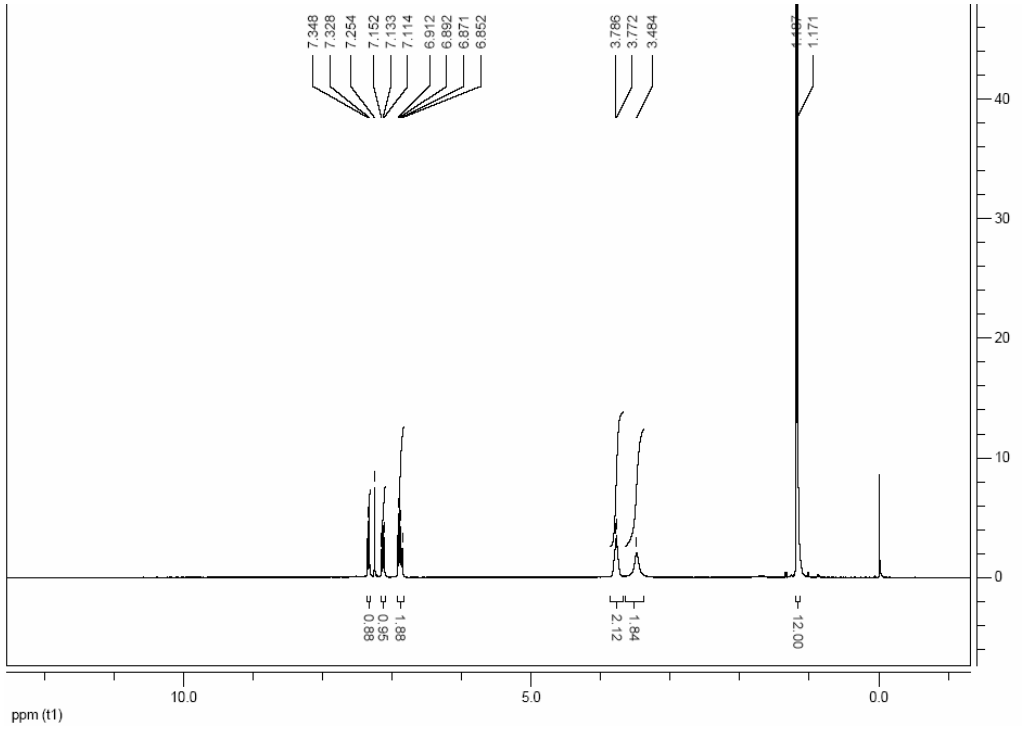
(**4**)

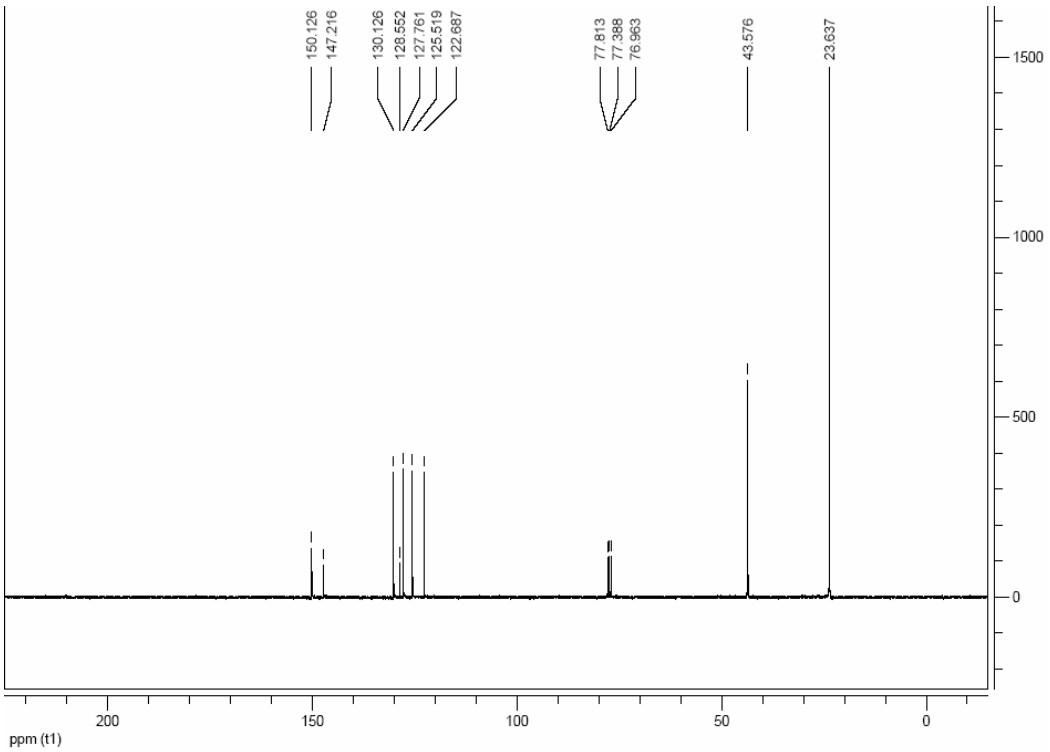

7.275
7.252
7.232
6.948
6.930
6.914
6.877
6.857
3.643
3.422
2.029
1.716
1.591
1.373
1.173
1.111
1.050
1.83
6.66
1.38
1.96
20.00
10.0
5.0
0.0
ppm (t1)

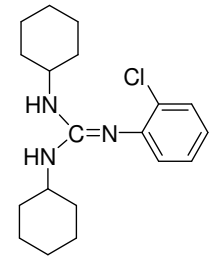

150.734
150.311
129.503
123.922
121.559
77.774
77.659
77.456
77.138
50.475
34.109
25.994
25.236
200
150
100
50
0
ppm (t1)


Cl
HN
C=N
HN

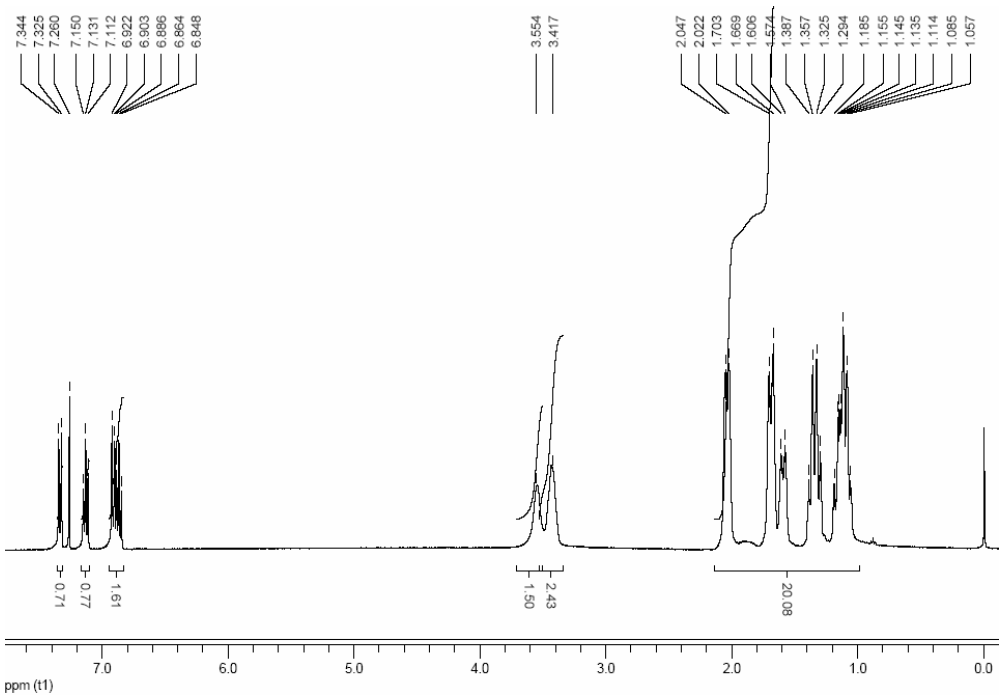
(**5**)

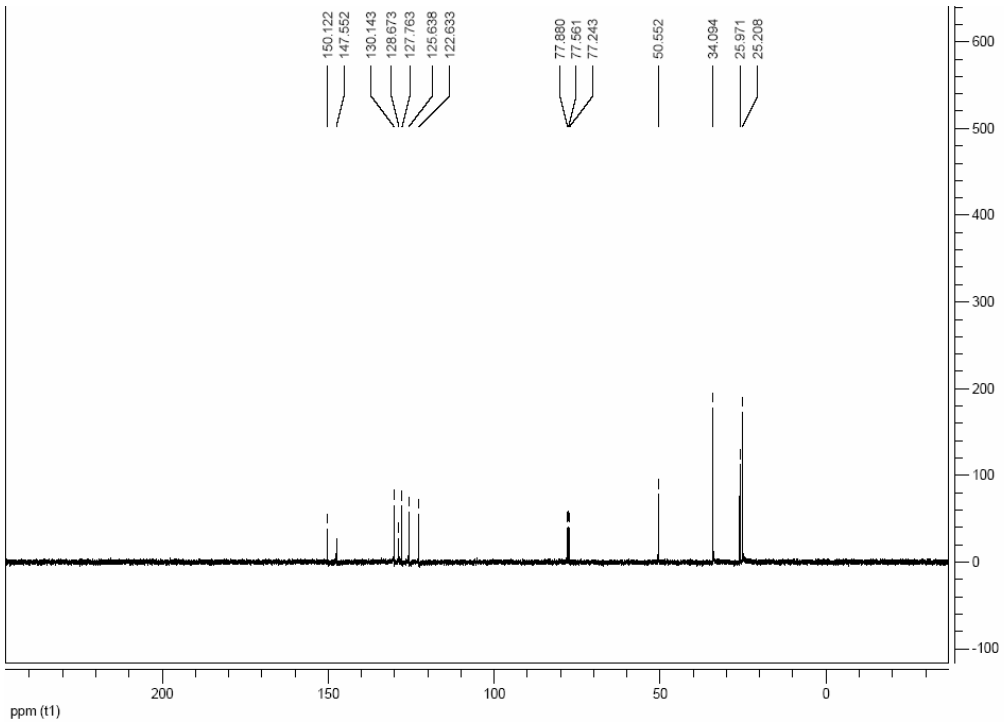

7.348
7.328
7.254
7.152
7.133
7.114
6.912
6.892
6.871
6.852
3.786
3.772
3.484
1.187
1.171
0.88
0.96
1.88
2.12
1.84
12.00
40
30
20
10
0
10.0
5.0
0.0
ppm (t1)

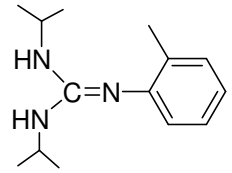

150.126
147.216
130.126
128.552
127.761
125.519
122.687
77.813
77.388
76.963
43.576
23.637
1500
1000
500
0
200
150
100
50
0
ppm (t1)


Cl
HN
C=N
HN

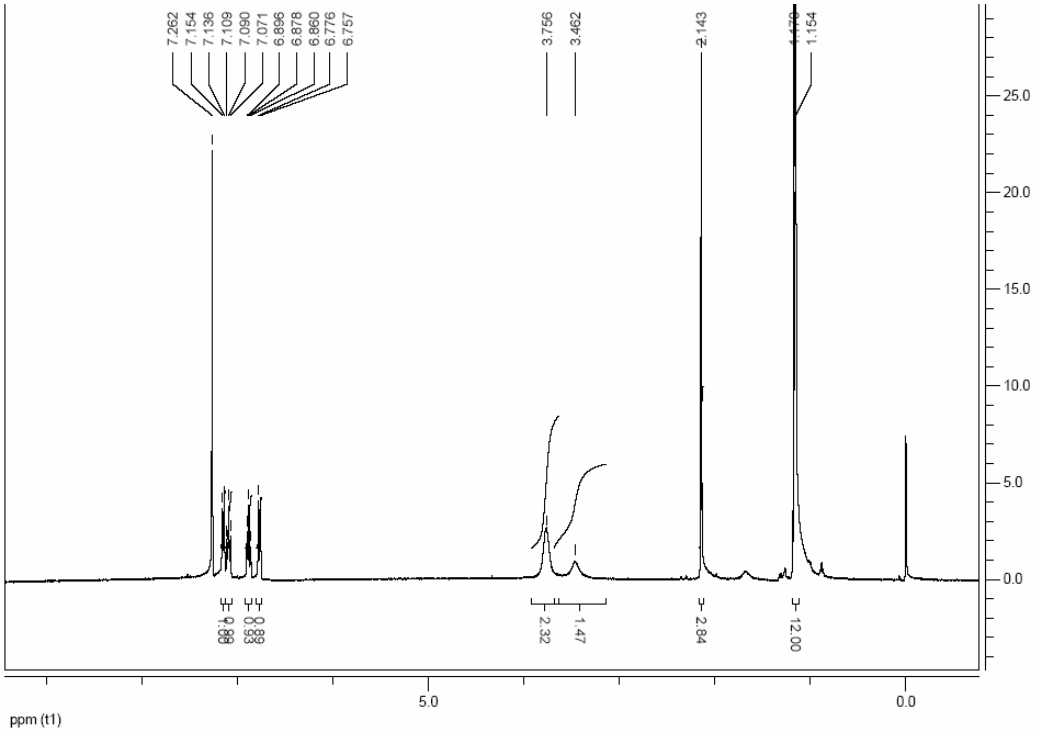
(**6**)

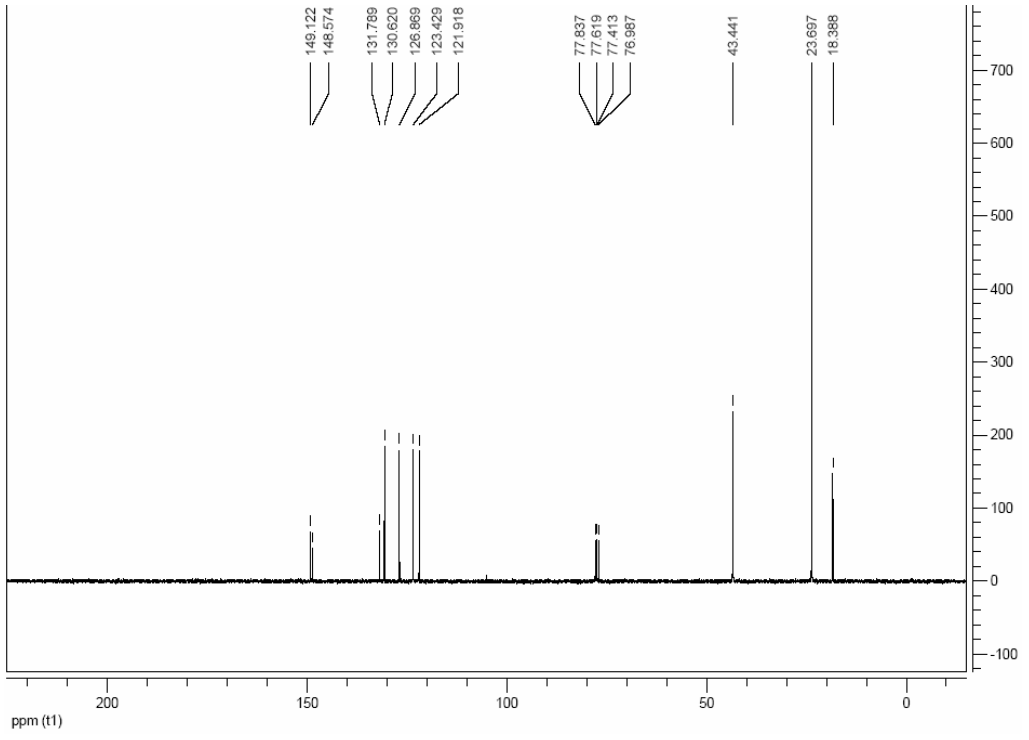

7.344
7.325
7.260
7.150
7.131
7.112
6.922
6.903
6.886
6.864
6.848
3.554
3.417
2.047
2.022
1.703
1.669
1.606
1.574
1.387
1.357
1.325
1.294
1.185
1.155
1.145
1.135
1.114
1.085
1.057
0.71
0.77
1.61
1.50
2.43
20.08
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

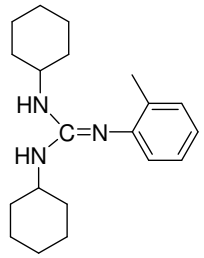

150.122
147.552
130.143
128.673
127.763
125.638
122.633
77.880
77.561
77.243
50.552
34.094
25.971
25.208
600
500
400
300
200
100
0
-100
200
150
100
50
0
ppm (t1)


HN
C=N
HN

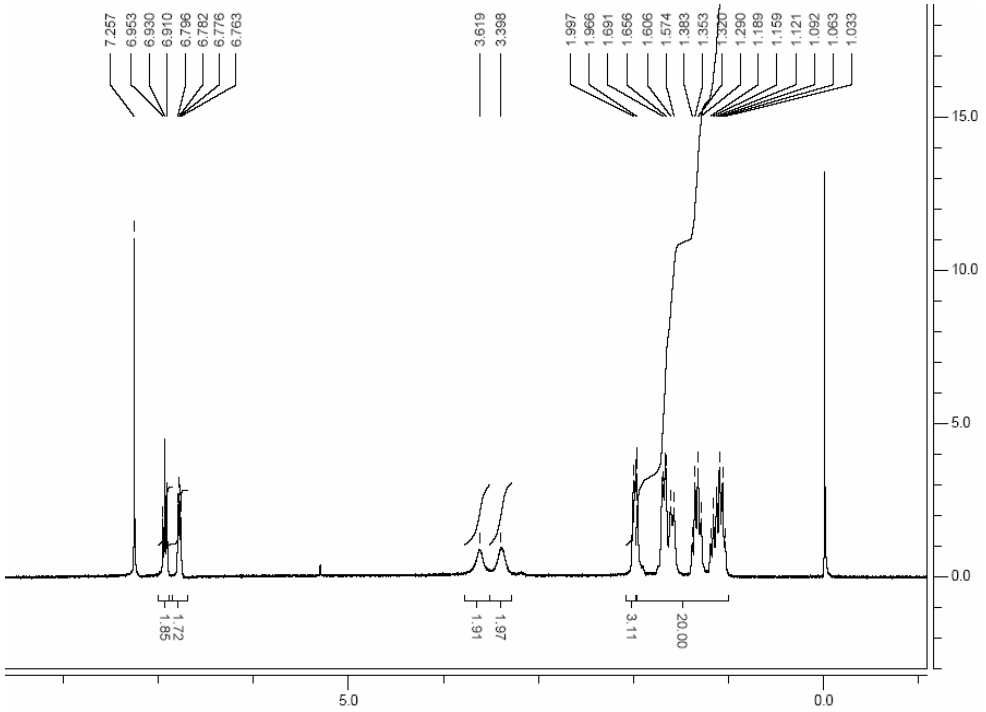
(**7**)

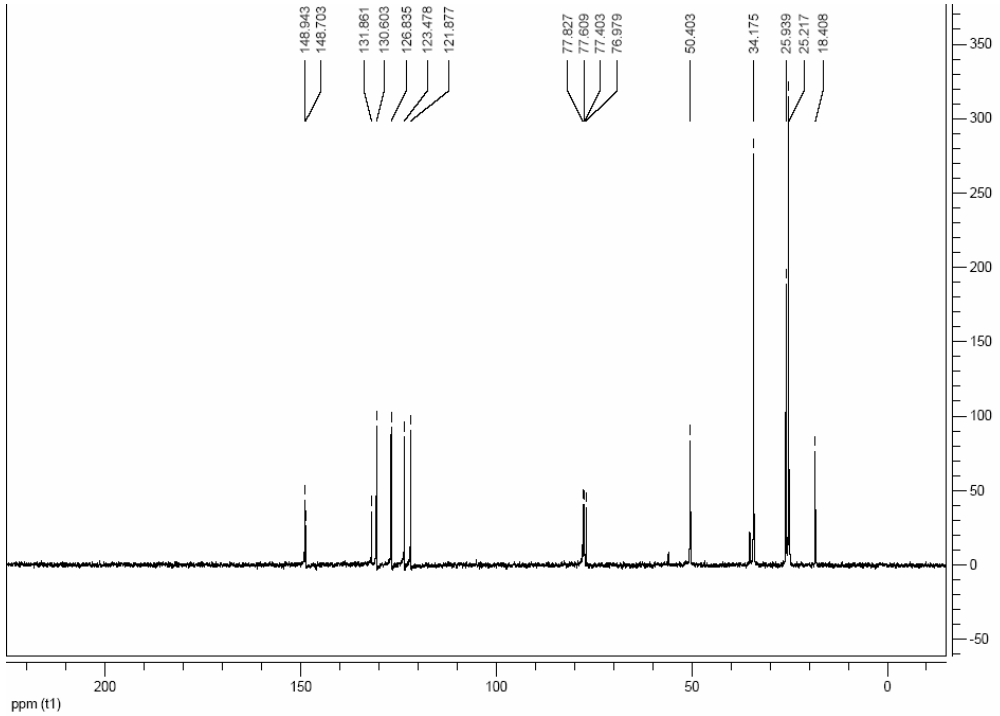

7.262
7.154
7.136
7.109
7.090
7.071
6.896
6.878
6.860
6.776
6.757
3.756
3.462
2.143
1.154
25.0
20.0
15.0
10.0
5.0
0.0
2.32
1.47
2.84
12.00
5.0
0.0
ppm (t1)

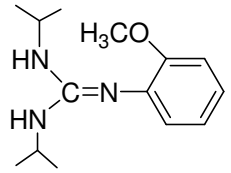

149.122
148.574
131.789
130.620
126.869
123.429
121.918
77.837
77.619
77.413
76.987
43.441
23.697
18.388
700
600
500
400
300
200
100
0
-100
200
150
100
50
0
ppm (t1)


HN
C=N
HN

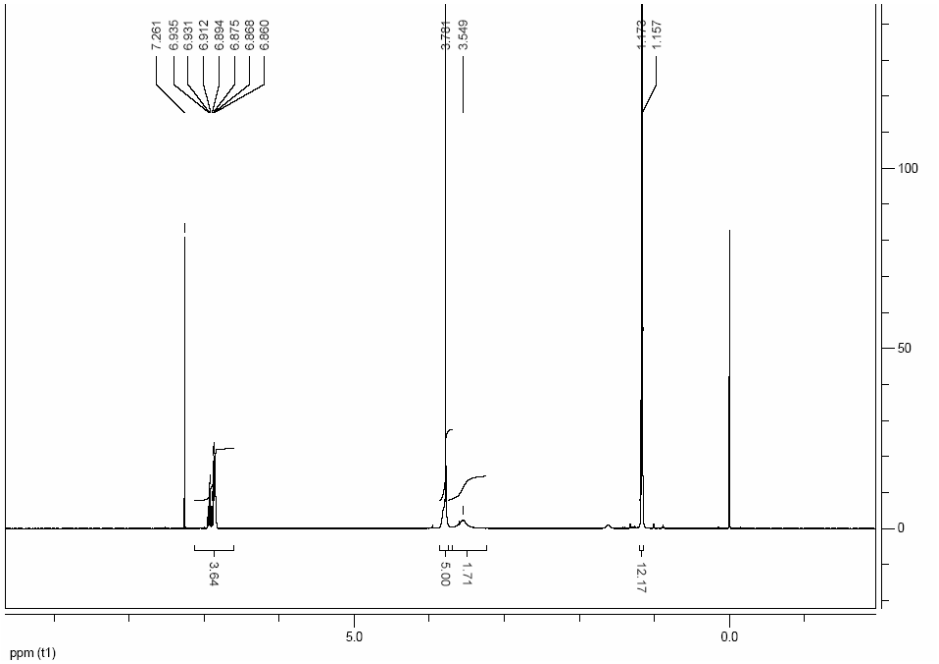
(**8**)

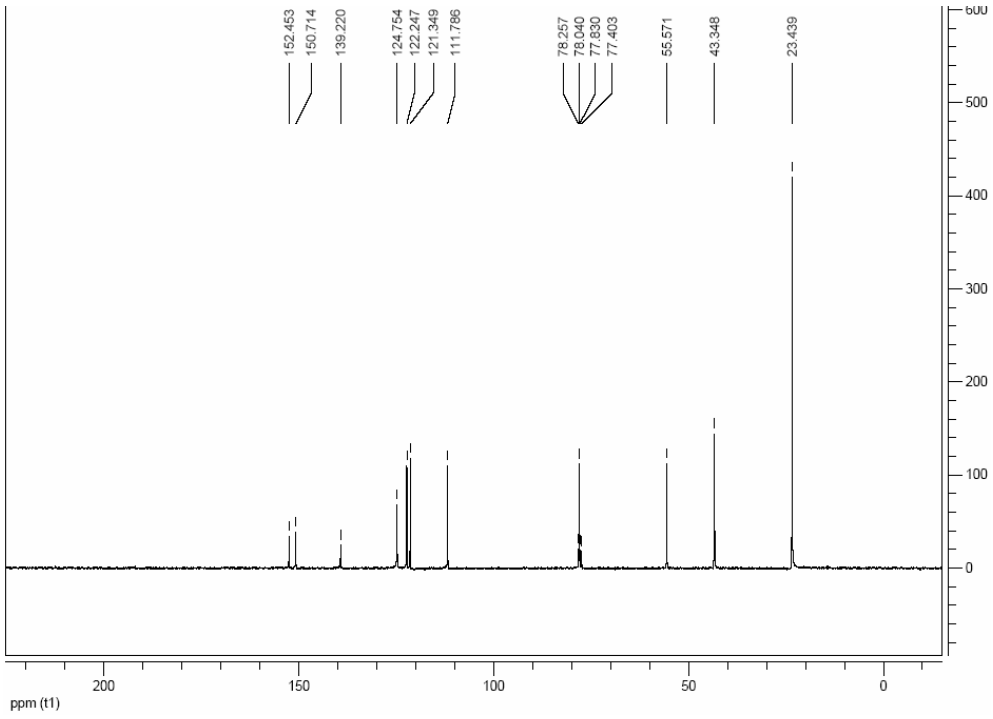

7.257
6.953
6.930
6.910
6.796
6.782
6.776
6.763
3.619
3.398
1.997
1.966
1.691
1.656
1.606
1.574
1.383
1.353
1.320
1.290
1.189
1.159
1.121
1.092
1.063
1.033
15.0
10.0
5.0
0.0
1.72
1.85
1.91
1.97
3.11
20.00
5.0
0.0

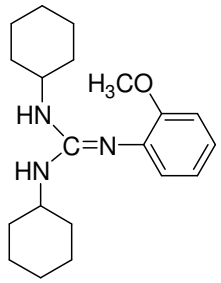

148.943
148.703
131.861
130.603
126.835
123.478
121.877
77.827
77.609
77.403
76.979
50.403
34.175
25.939
25.217
18.408
350
300
250
200
150
100
50
0
-50
200
150
100
50
0
ppm (t1)


H3CO
HN
C=N
HN

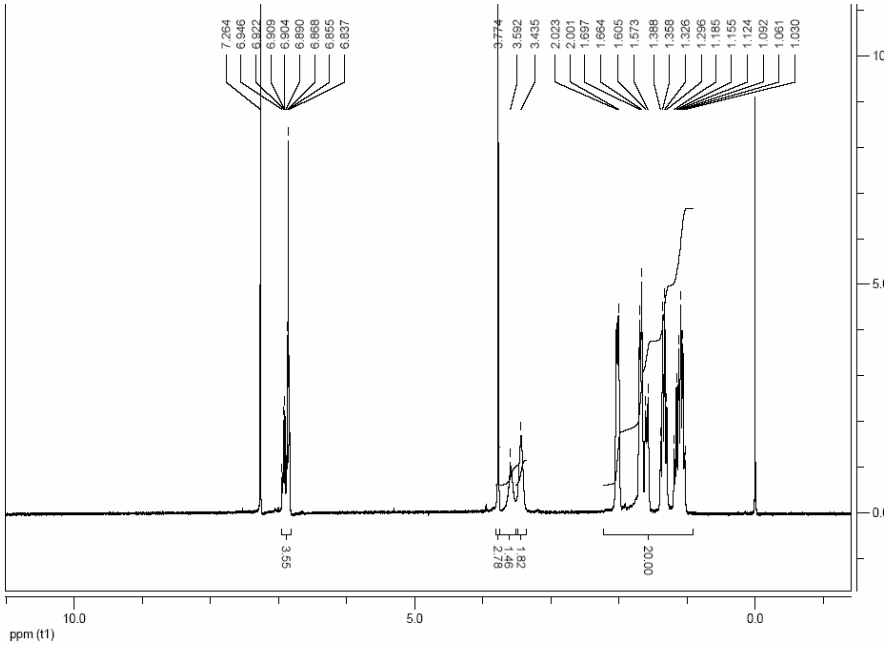
(**9**)

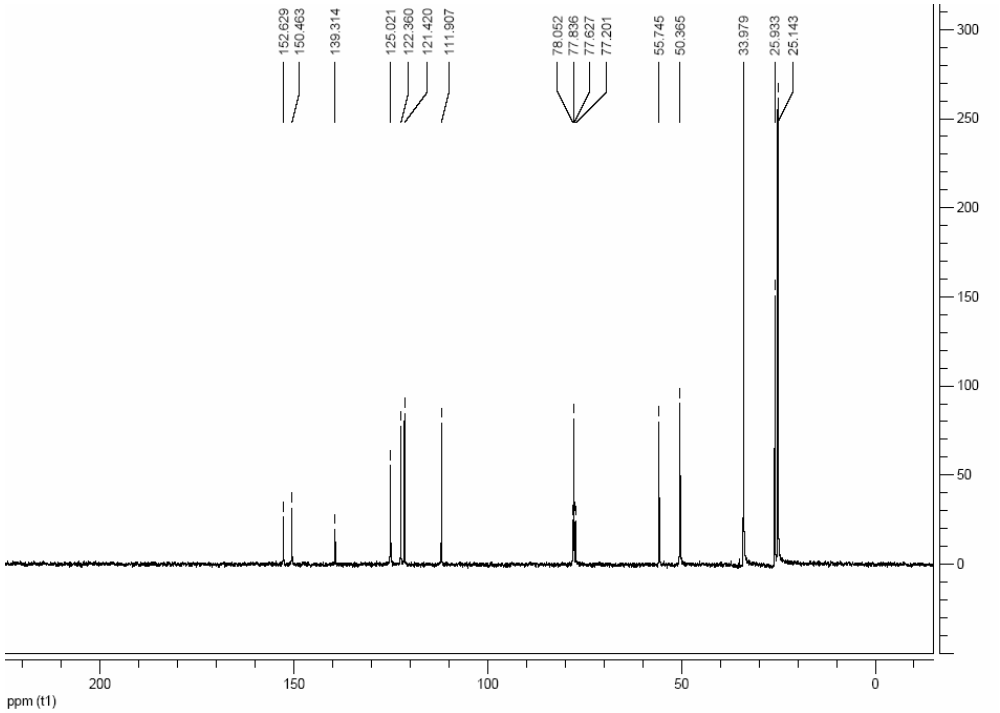

7.261
6.935
6.931
6.912
6.894
6.875
6.868
6.860
3.761
3.549
1.173
1.157
3.64
5.00
1.71
12.17
ppm (t1)

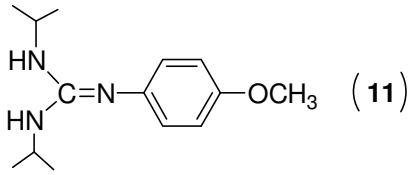

152.453
150.714
139.220
124.754
122.247
121.349
111.786
78.257
78.040
77.830
77.403
55.571
43.348
23.439
ppm (t1)


H3CO
HN
C=N
HN

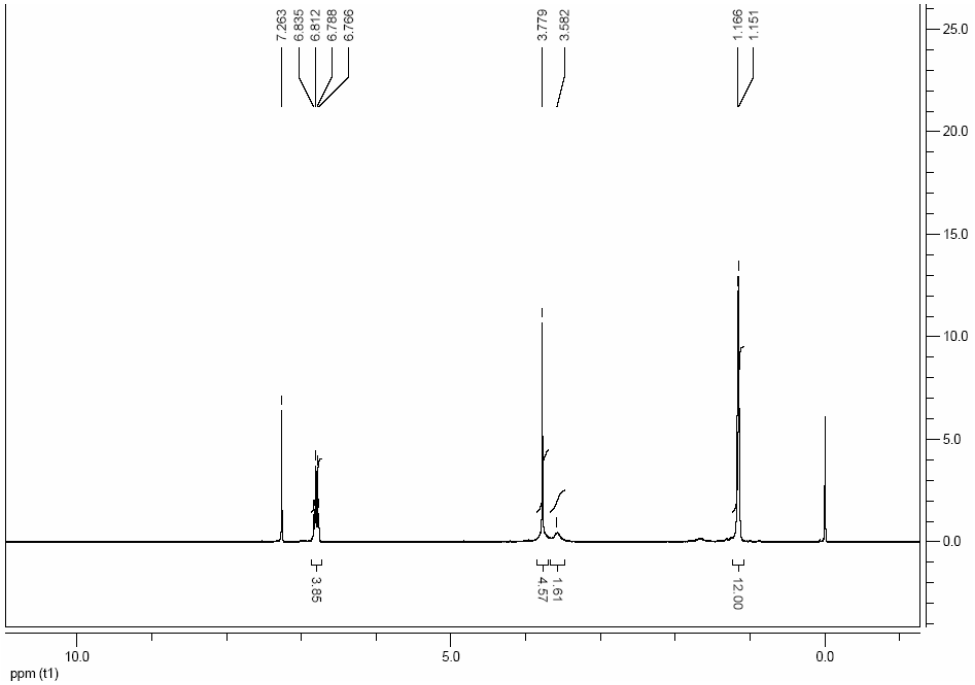
(**10**)

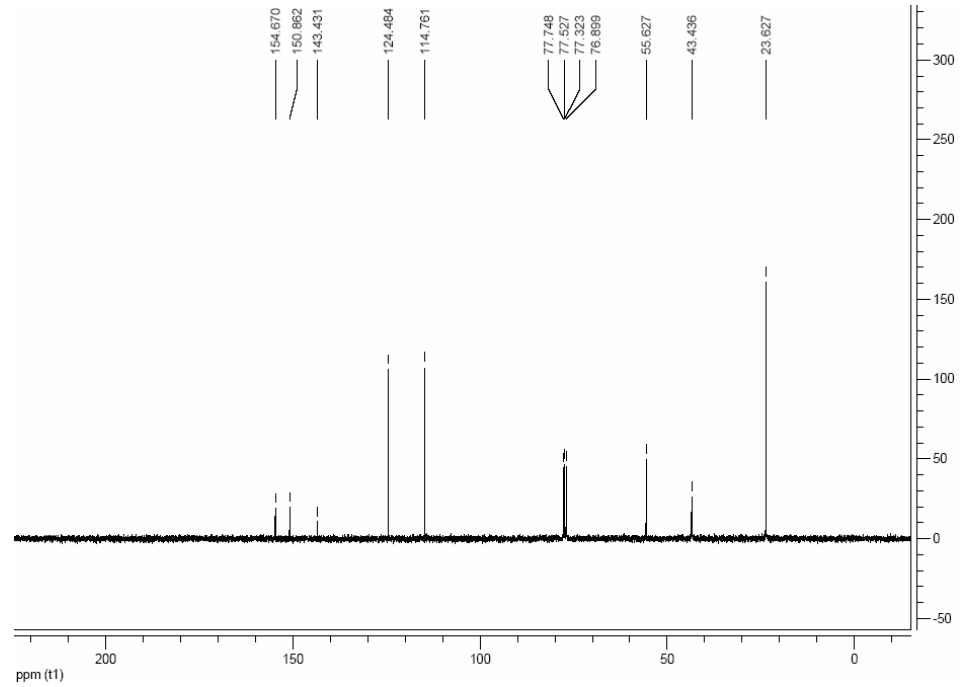

7.264
6.946
6.922
6.909
6.904
6.890
6.868
6.855
6.837
3.774
3.592
3.435
2.023
2.001
1.697
1.664
1.605
1.573
1.388
1.358
1.326
1.296
1.185
1.155
1.124
1.092
1.061
1.030
3.56
2.78
1.99
1.82
20.00
10.0
5.0
0.0
ppm (t1)

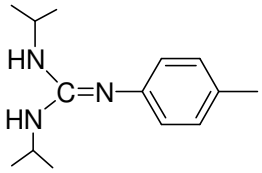

152.629
150.463
139.314
125.021
122.360
121.420
111.907
78.052
77.836
77.627
77.201
55.745
50.365
33.979
25.933
25.143
300
250
200
150
100
50
0
200
150
100
50
0
ppm (t1)


HN
C=N
HN
OCH3

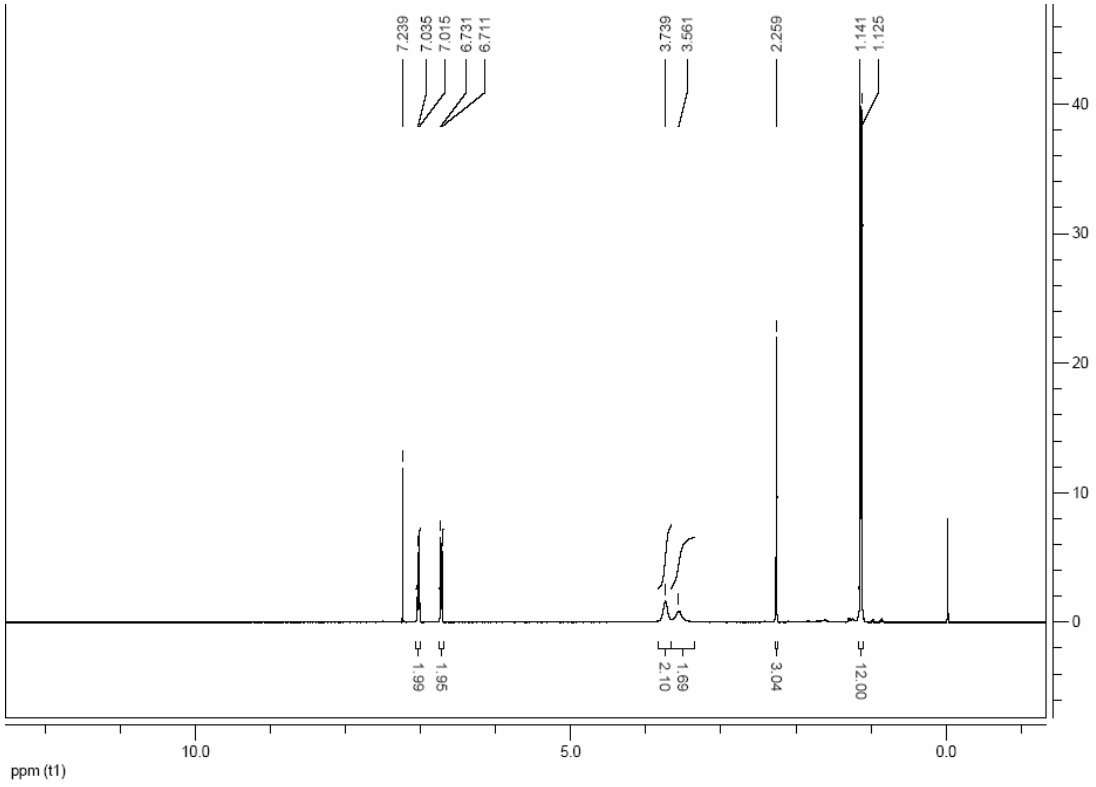
(**11**)

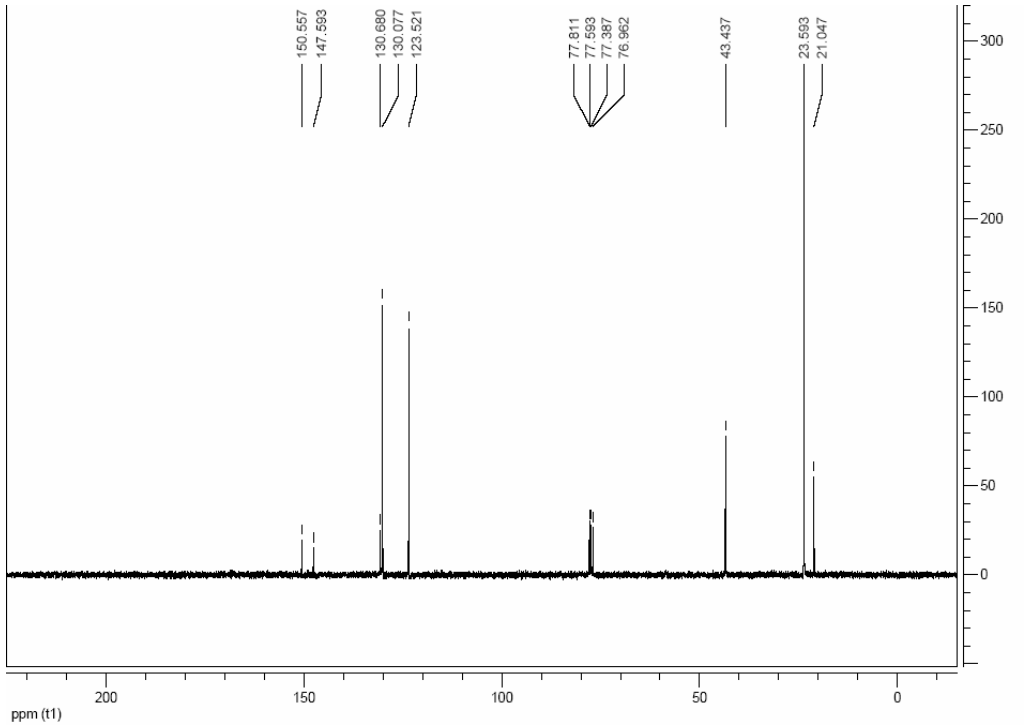

7.263
6.835
6.812
6.788
6.766
3.779
3.582
1.166
1.151
3.86
4.57
1.91
12.00
10.0
5.0
0.0
ppm (t1)

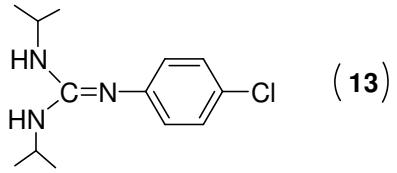

154.670
150.862
143.431
124.484
114.761
77.748
77.527
77.323
76.899
55.627
43.436
23.627
200
150
100
50
0
ppm (t1)


HN
C=N
HN

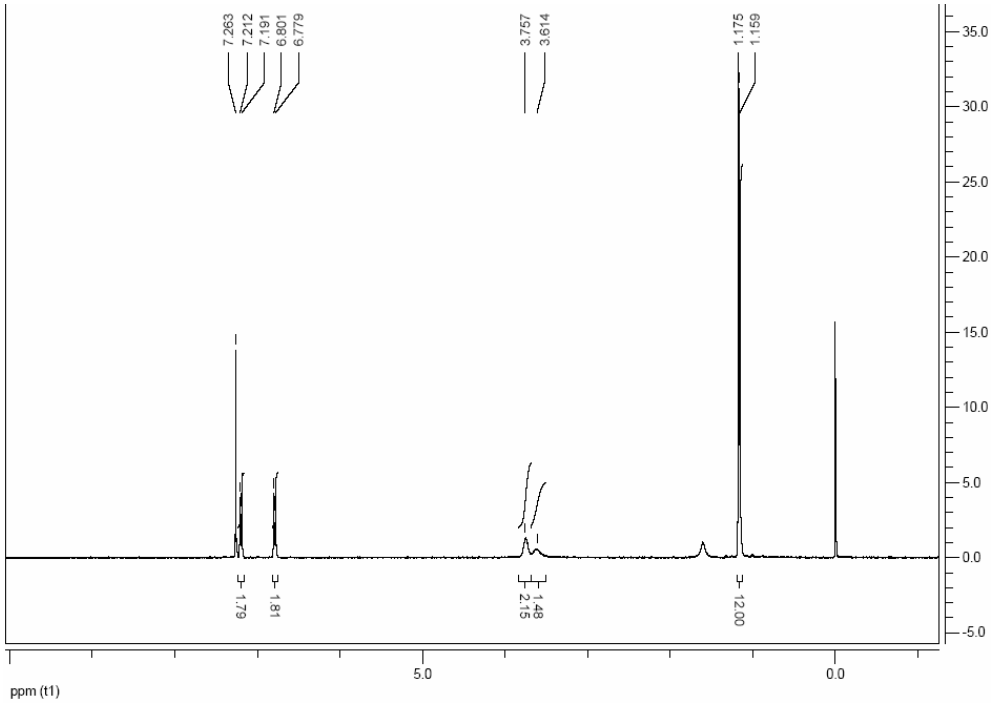
(**12**)

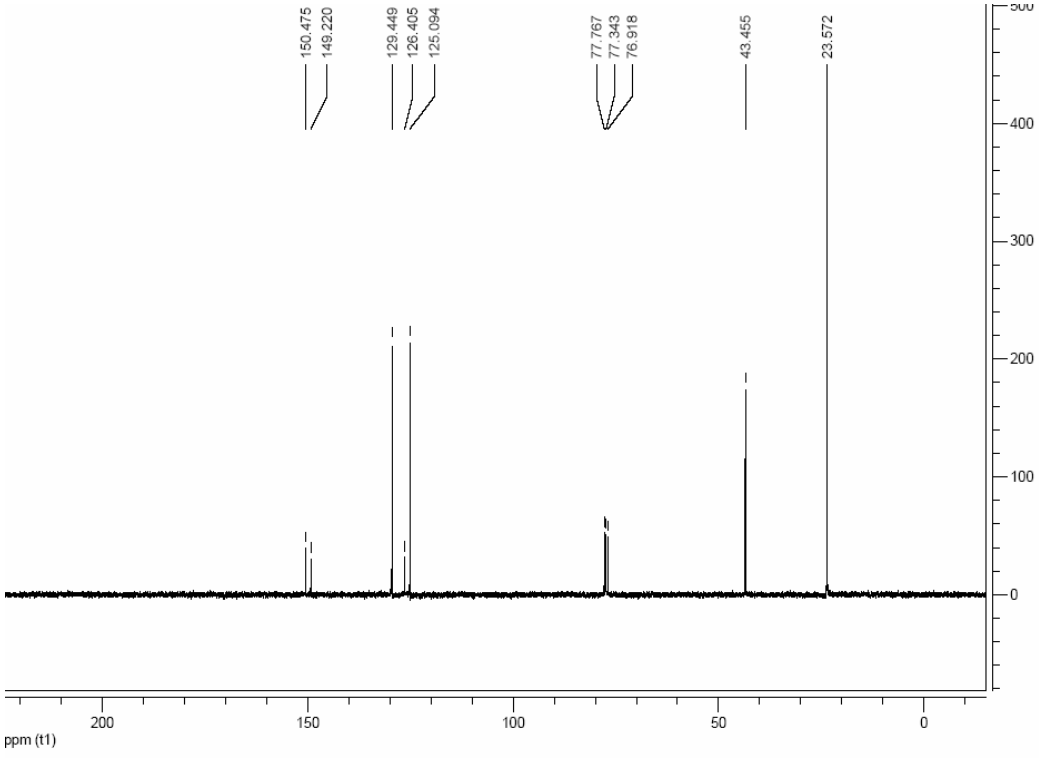

7.239
7.035
7.015
6.731
6.711
3.739
3.561
2.259
1.141
1.125
1.99
1.95
2.10
1.69
3.04
12.00
ppm (t1)

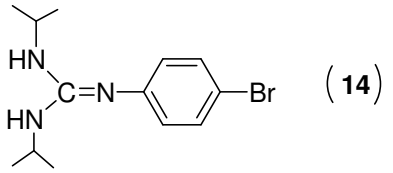

150.557
147.593
130.680
130.077
123.521
77.811
77.593
77.387
76.962
43.437
23.593
21.047
ppm (t1)


HN
C=N
HN
Cl

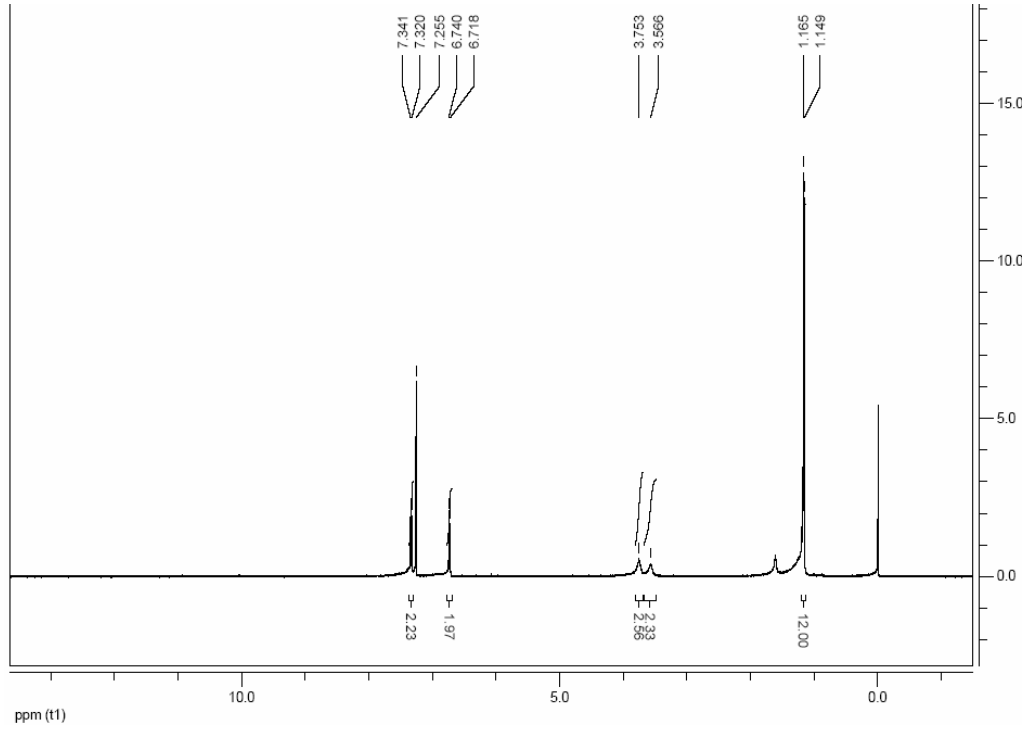
(**13**)

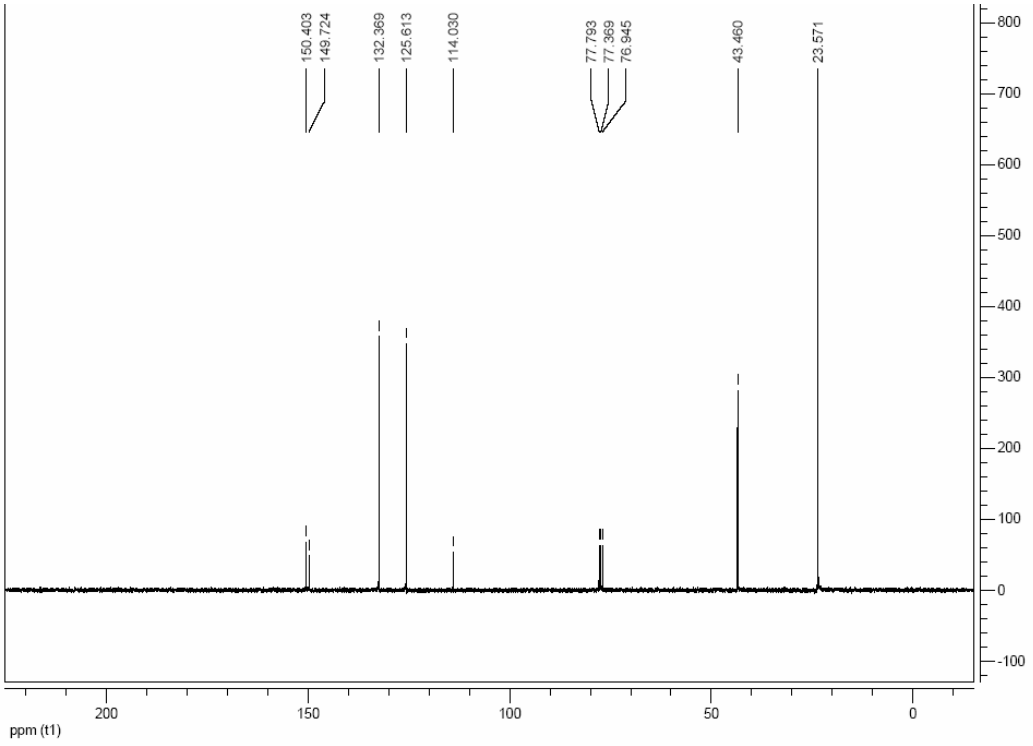

7.263
7.212
7.191
6.801
6.779
3.757
3.614
1.175
1.159
1.79
1.81
1.48
2.15
12.00
ppm (t1)

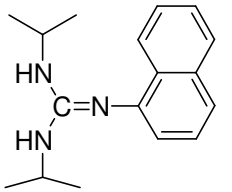

150.475
149.220
129.449
126.405
125.094
77.767
77.343
76.918
43.455
23.572
ppm (t1)


HN
C=N
HN
Br

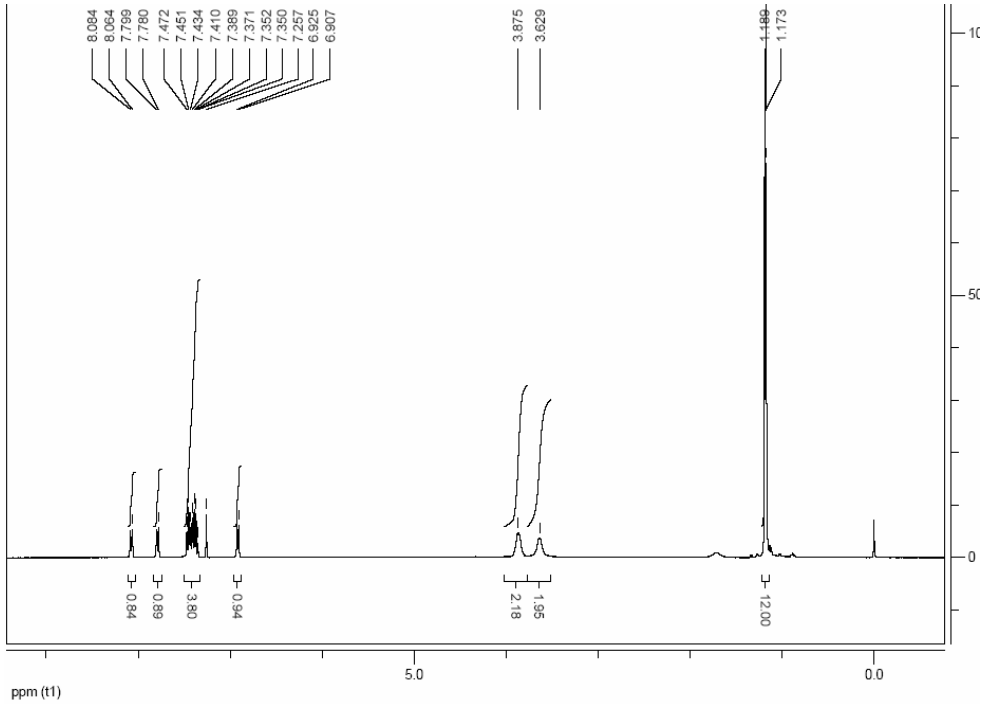
(**14**)

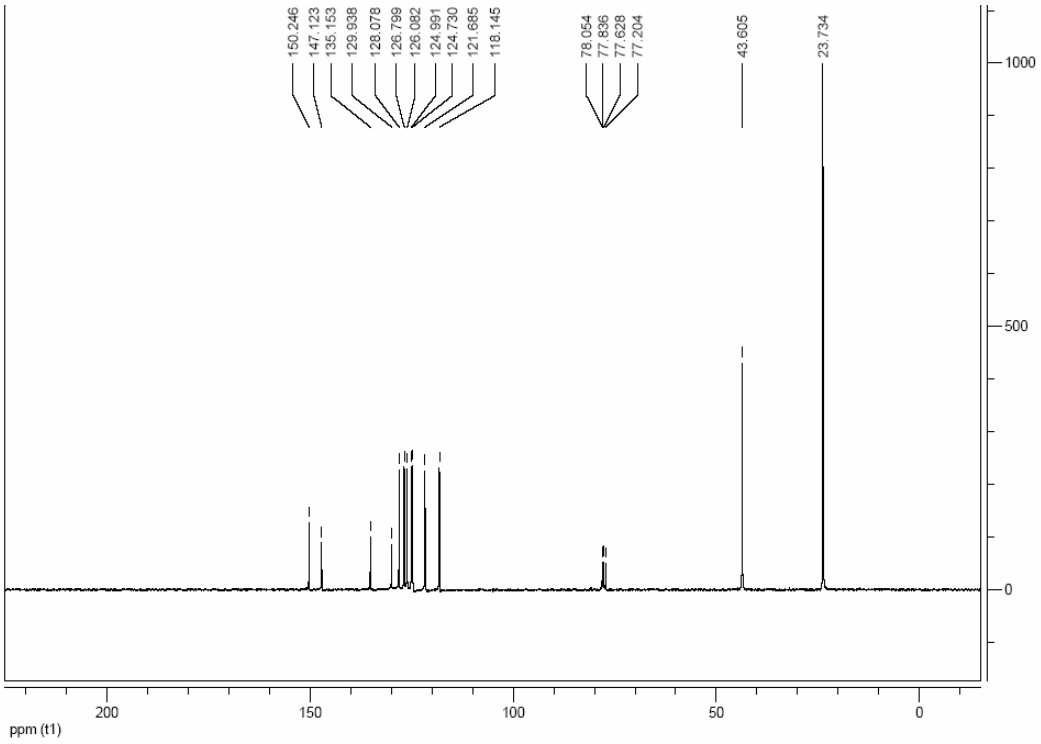

7.341
7.320
7.255
6.740
6.718
3.753
3.566
1.165
1.149
2.23
1.97
2.33
2.56
12.00
ppm (t1)

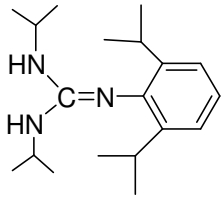

150.403
149.724
132.369
125.613
114.030
77.793
77.369
76.945
43.460
23.571
ppm (t1)



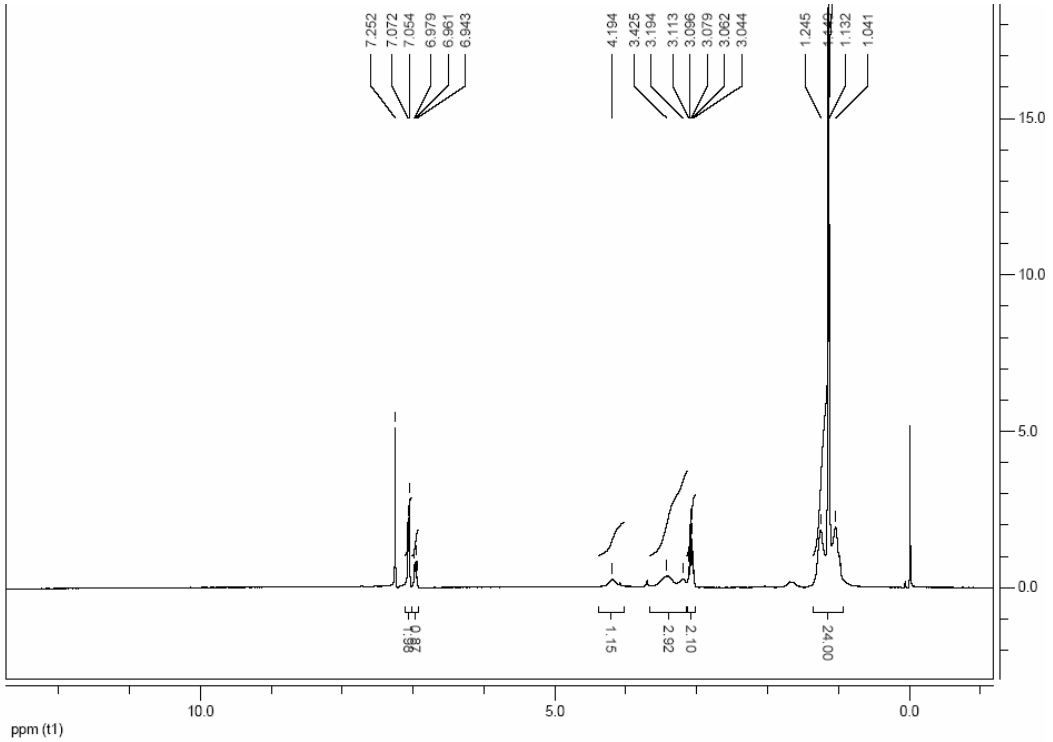
(**15**)

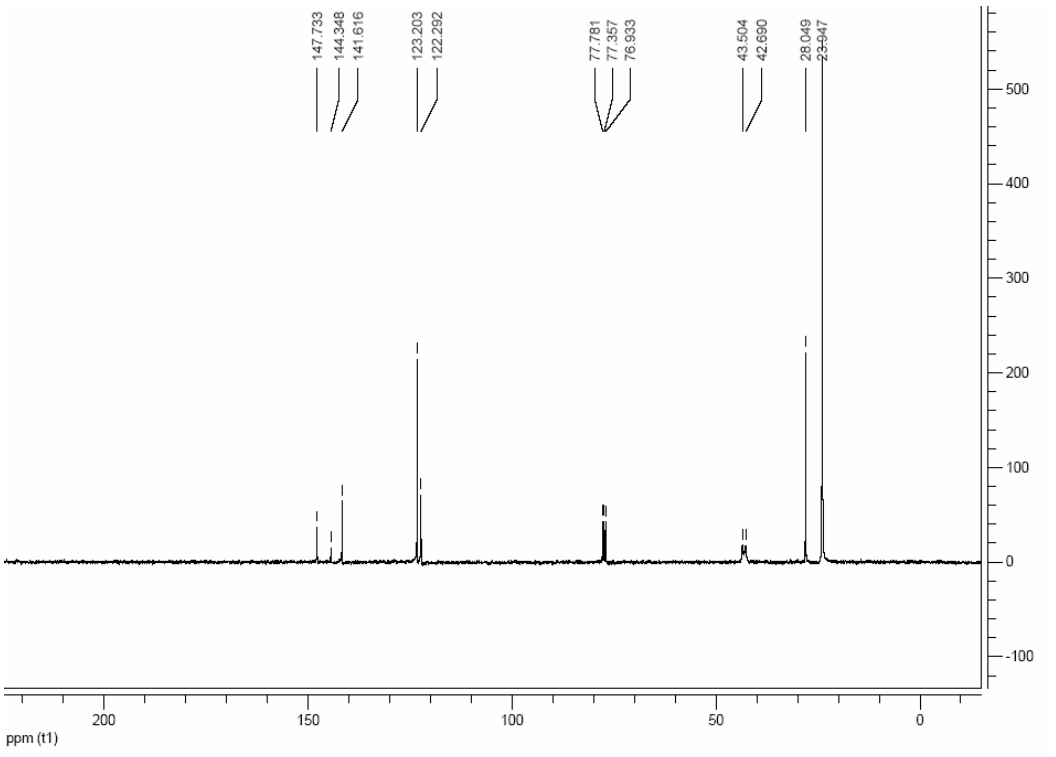

8.084
8.064
7.799
7.780
7.472
7.451
7.434
7.410
7.389
7.371
7.352
7.350
7.257
6.925
6.907
3.875
3.629
1.188
1.173
0.84
0.89
3.80
0.94
2.18
1.95
12.00
5.0
0.0
ppm (t1)

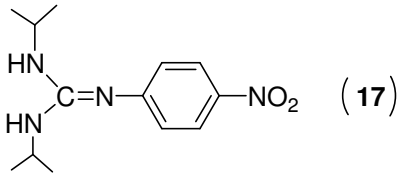

150.246
147.123
135.153
129.938
128.078
126.799
126.082
124.991
124.730
121.685
118.145
78.054
77.836
77.628
77.204
43.605
23.734
1000
500
0
200
150
100
50
0
ppm (t1)


HN
C=N
HN

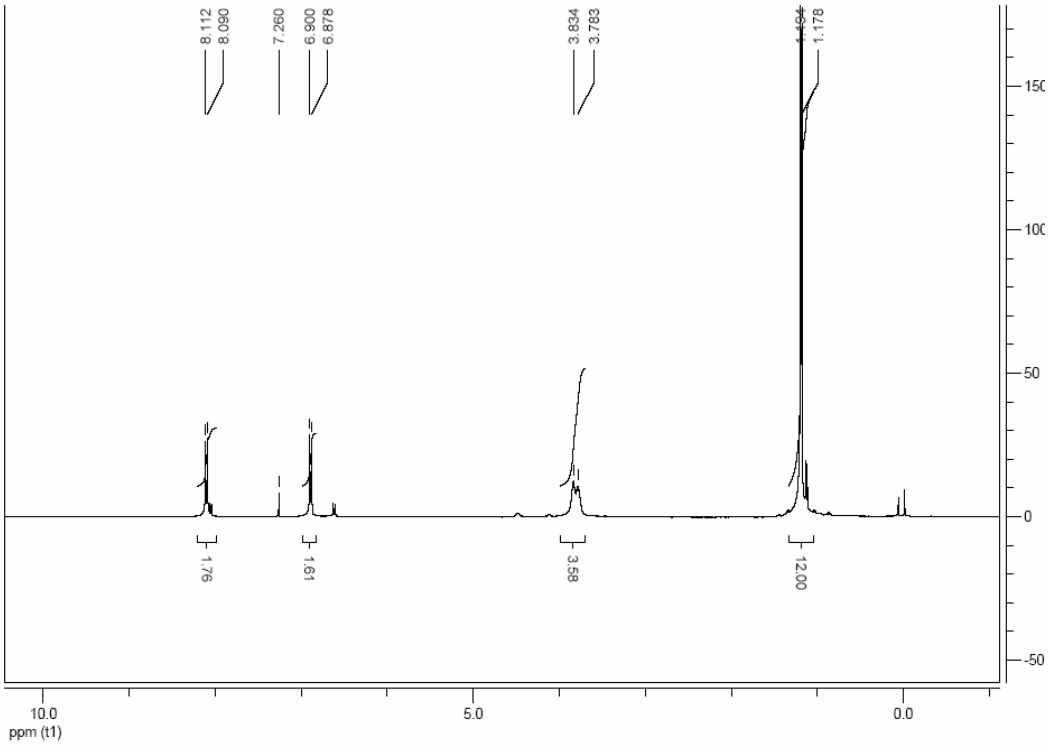
(**16**)

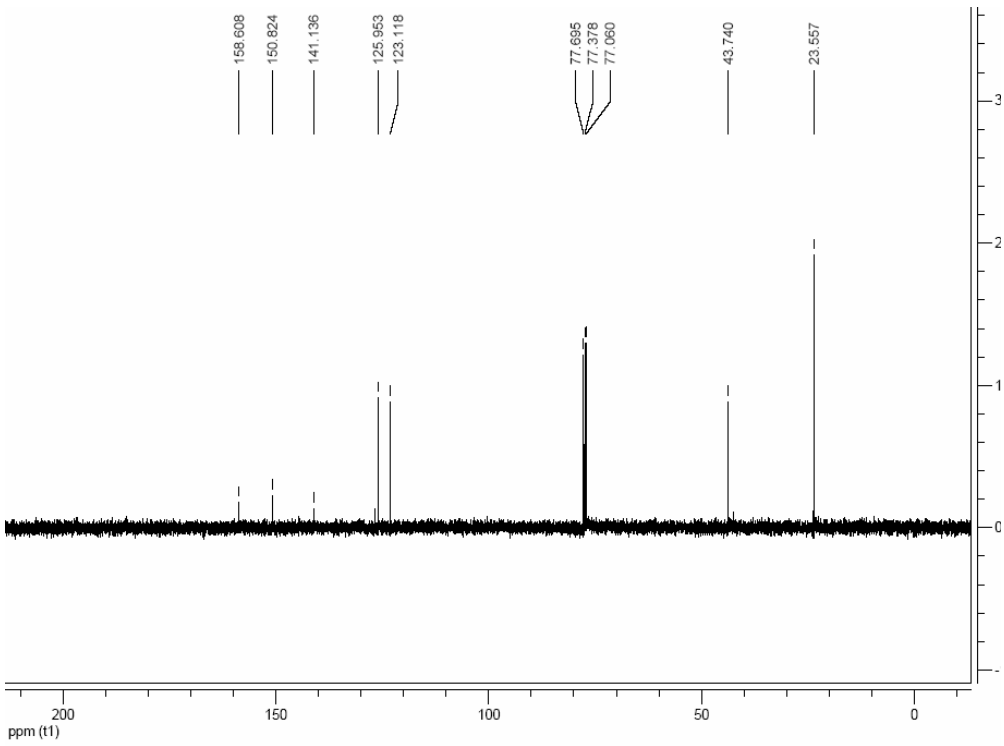

7.252
7.072
7.054
6.979
6.961
6.943
4.194
3.425
3.194
3.113
3.096
3.079
3.062
3.044
1.245
1.132
1.041
1.15
2.92
2.10
24.00
15.0
10.0
5.0
0.0
10.0
5.0
0.0
ppm (t1)

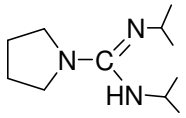

147.733
144.348
141.616
123.203
122.292
77.781
77.357
76.933
43.504
42.690
28.049
23.947
500
400
300
200
100
0
-100
200
150
100
50
0
ppm (t1)


HN
C=N
HN
NO2

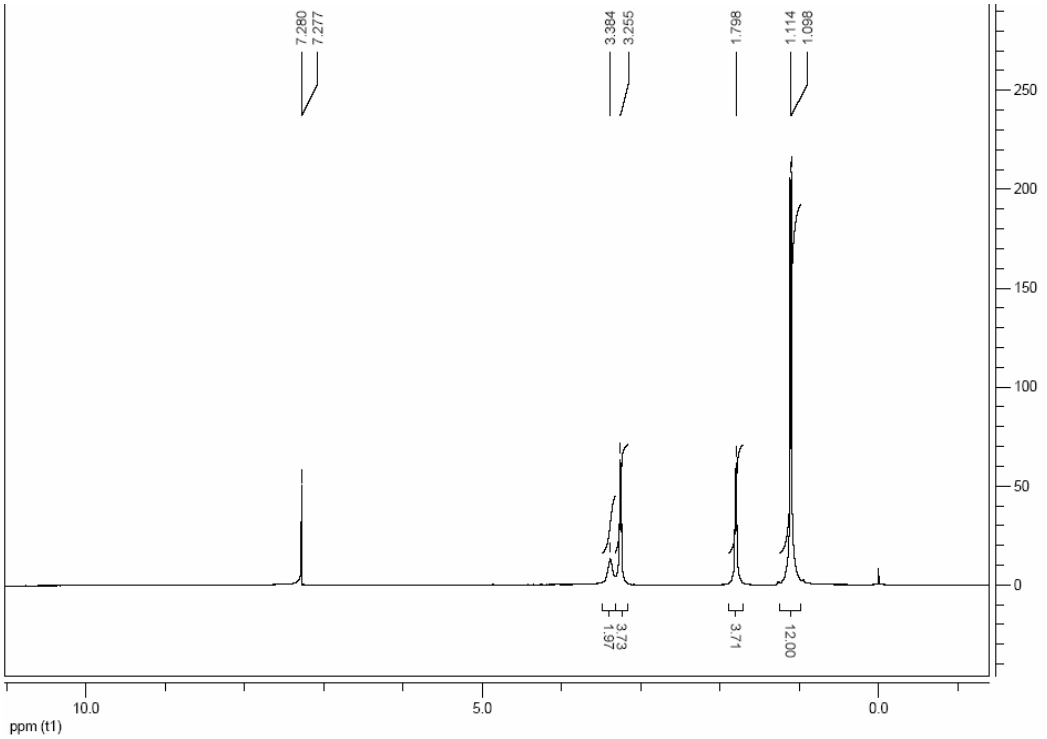
(**17**)

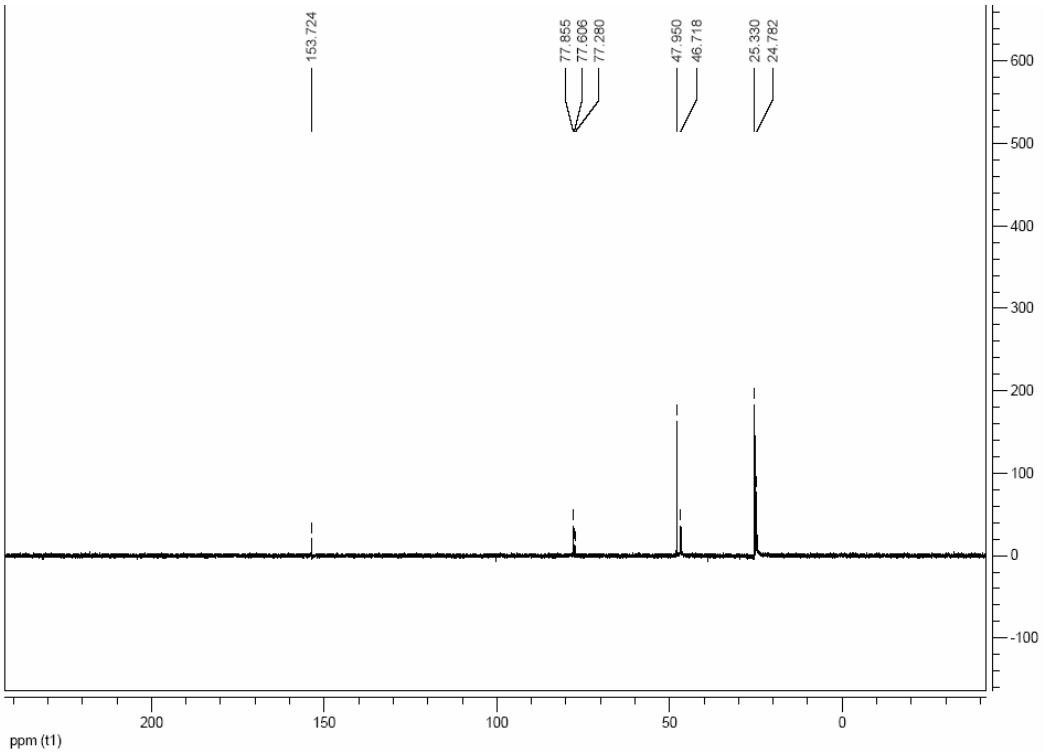

8.112
8.090
7.260
6.900
6.878
3.834
3.783
1.178
1.76
1.61
3.58
12.00
ppm (t1)

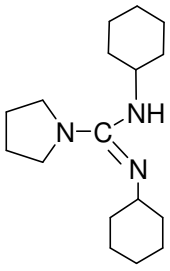

158.608
150.824
141.136
125.953
123.118
77.695
77.378
77.060
43.740
23.557
ppm (t1)



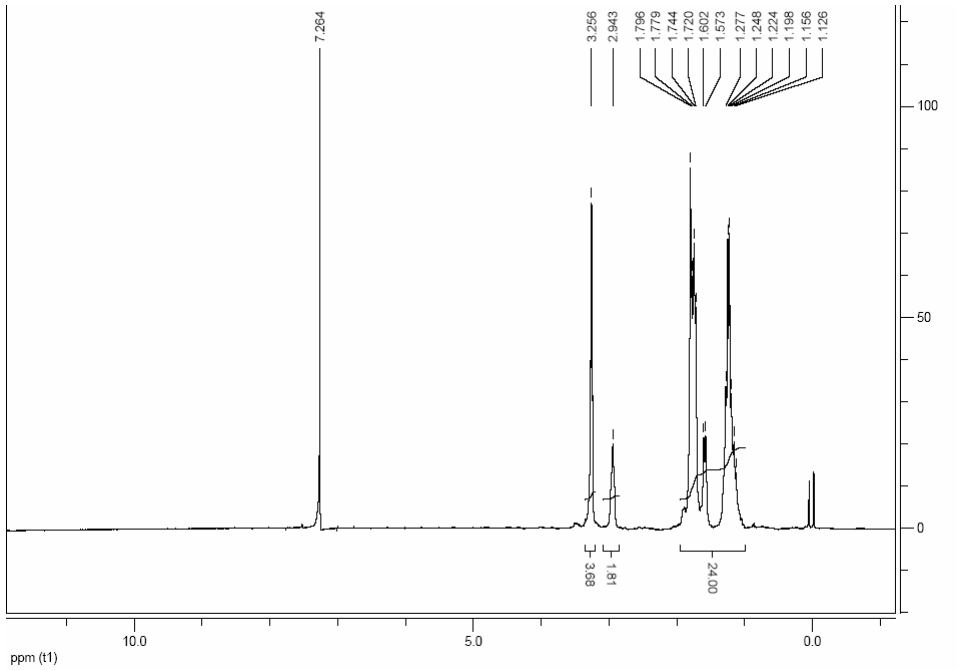
(**18**)

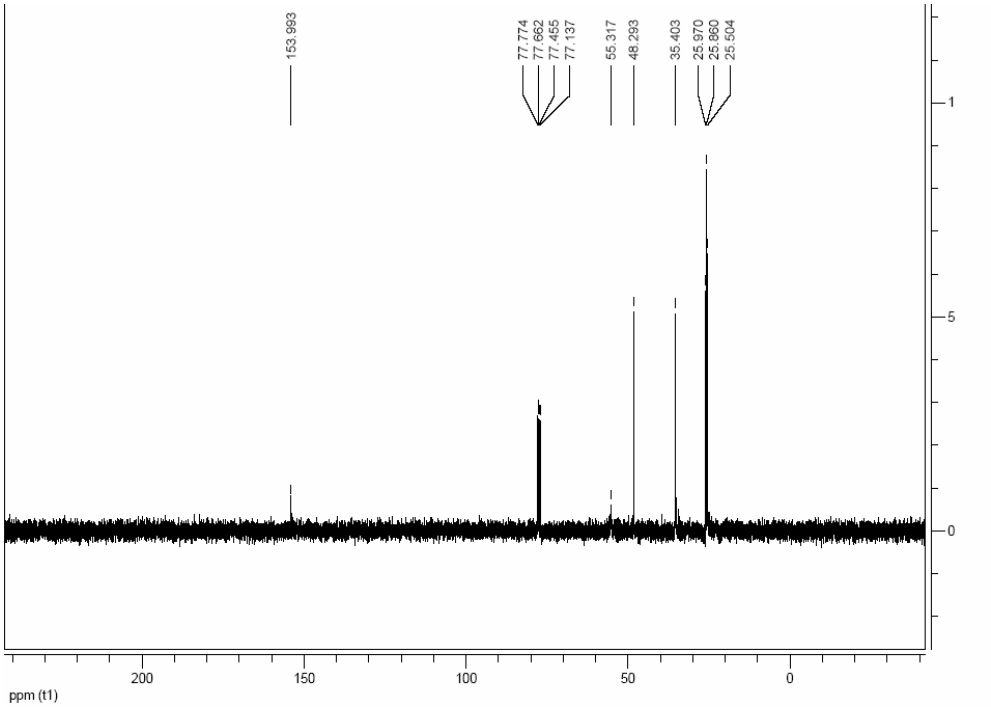

7.280
7.277
3.384
3.255
1.798
1.114
1.098
1.97
3.73
3.71
12.00
10.0
5.0
0.0
ppm (t1)

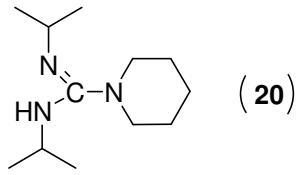

153.724
77.855
77.606
77.280
47.950
46.718
25.330
24.782
200
150
100
50
0
ppm (t1)



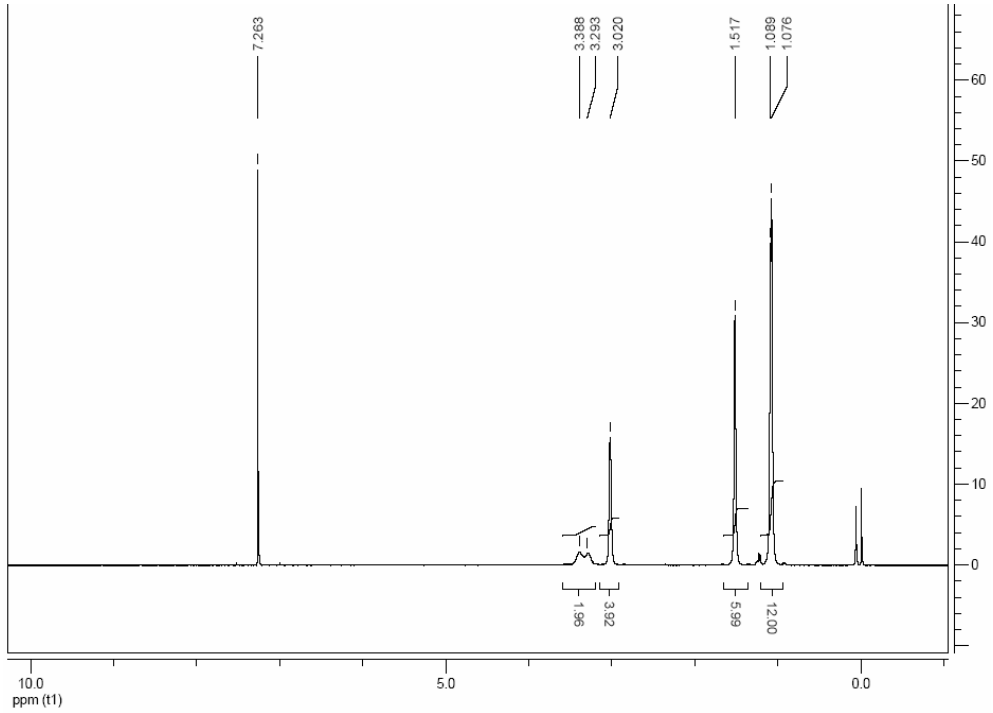
(**19**)

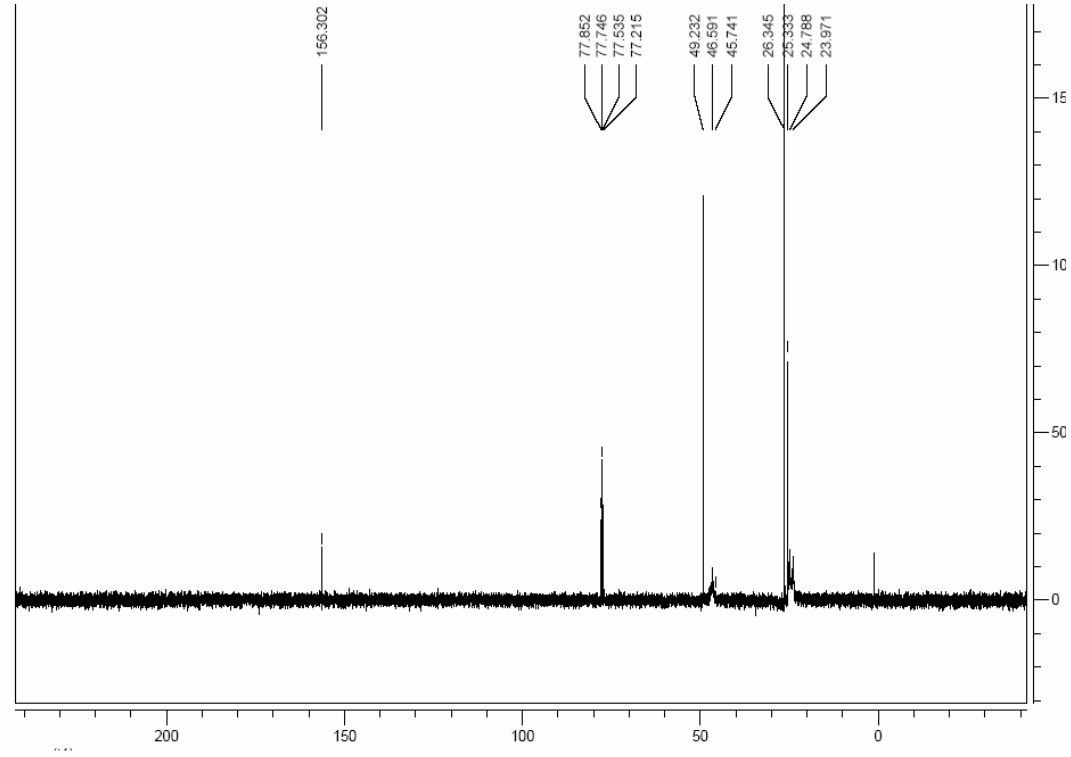

7.264
3.256
2.943
1.796
1.779
1.744
1.720
1.602
1.573
1.277
1.248
1.224
1.198
1.156
1.126
100
50
0
3.89
1.81
24.00
10.0
5.0
0.0
ppm (t1)

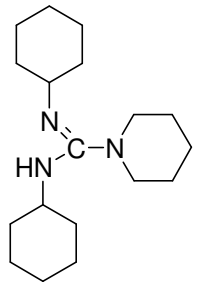

153.993
77.774
77.662
77.455
77.137
55.317
48.293
35.403
25.970
25.860
25.504
1
5
0
200
150
100
50
0
ppm (t1)



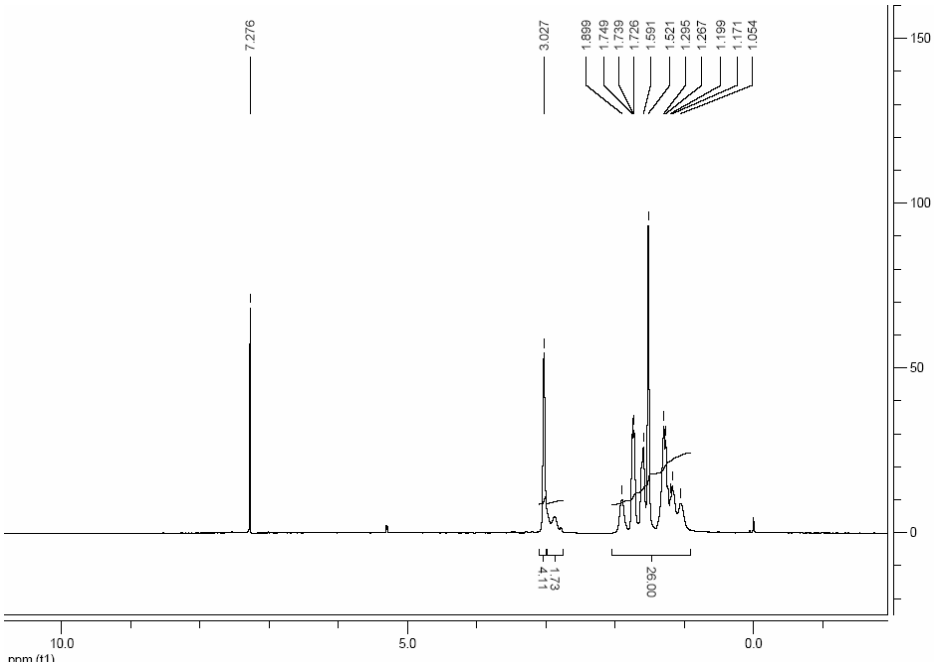
(**20**)

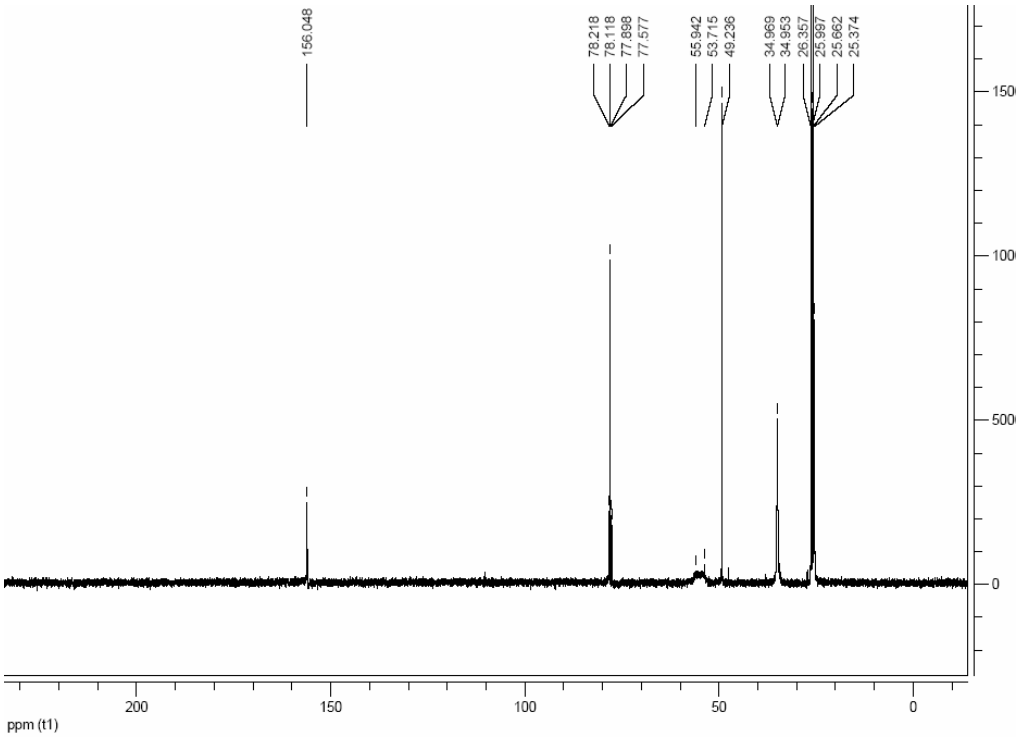

7.263
3.388
3.293
3.020
1.517
1.089
1.076
1.96
3.92
5.99
12.00
10.0
ppm (t1)
5.0
0.0

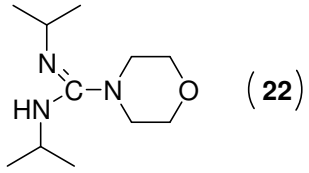

156.302
77.852
77.746
77.535
77.215
49.232
46.591
45.741
26.345
25.333
24.788
23.971
200
150
100
50
0


N
C
N
HN

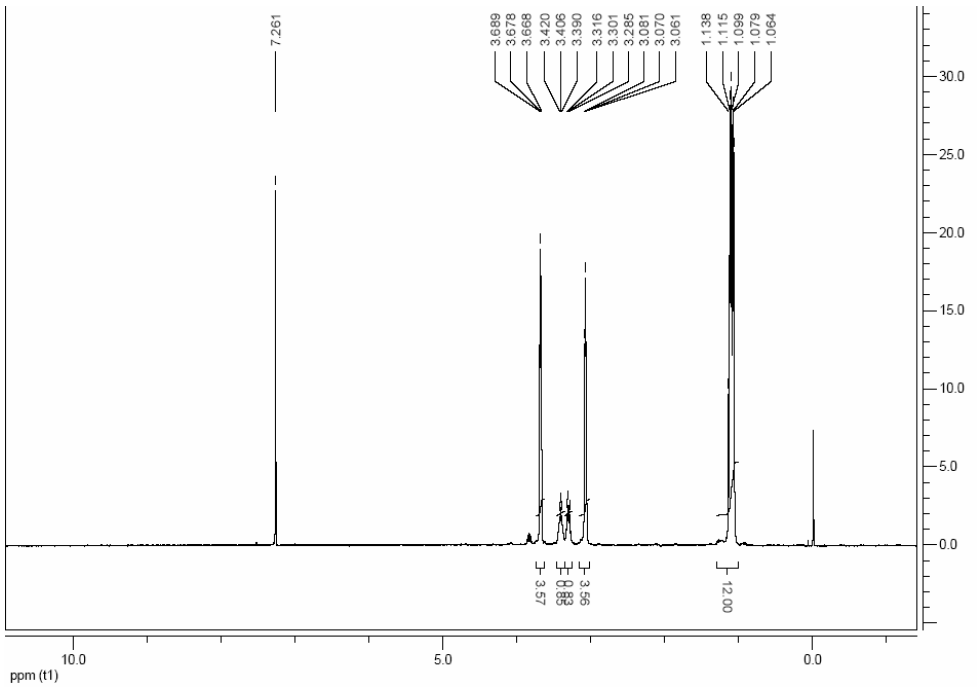
(**21**)

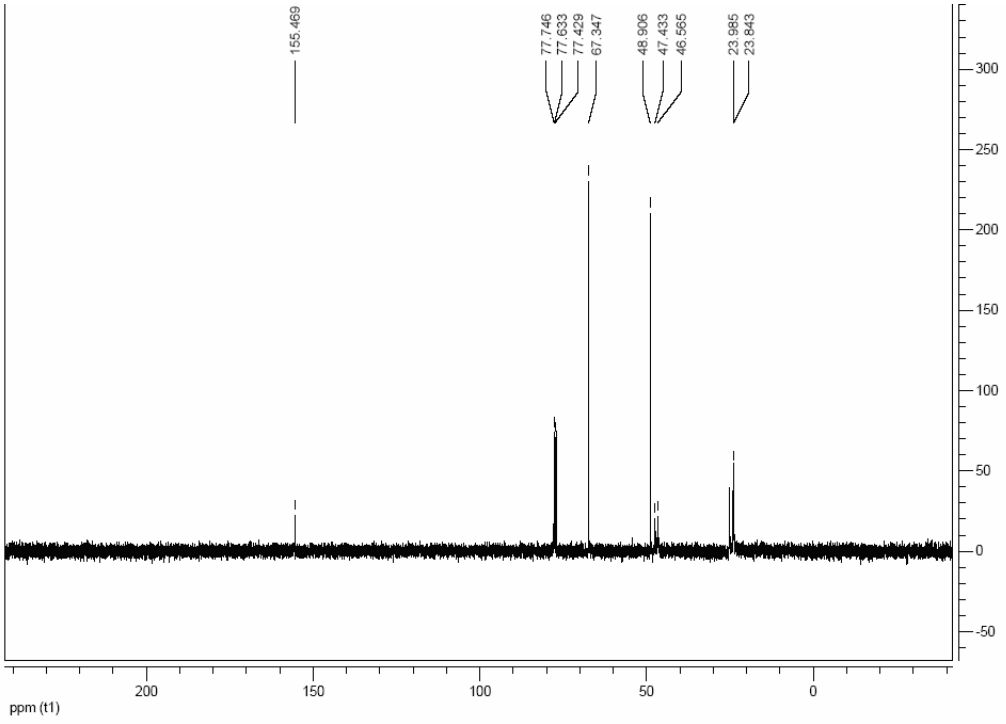

7.276
3.027
1.899
1.749
1.739
1.726
1.591
1.521
1.295
1.267
1.199
1.171
1.054
1.73
4.11
26.00
150
100
50
0
10.0
5.0
0.0
ppm (t1)

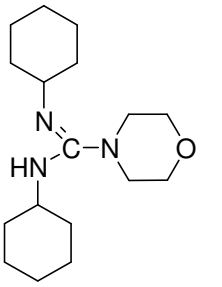

156.048
78.218
78.118
77.898
77.577
55.942
53.715
49.236
34.969
34.953
26.357
25.997
25.662
25.374
150
100
500
0
200
150
100
50
0
ppm (t1)



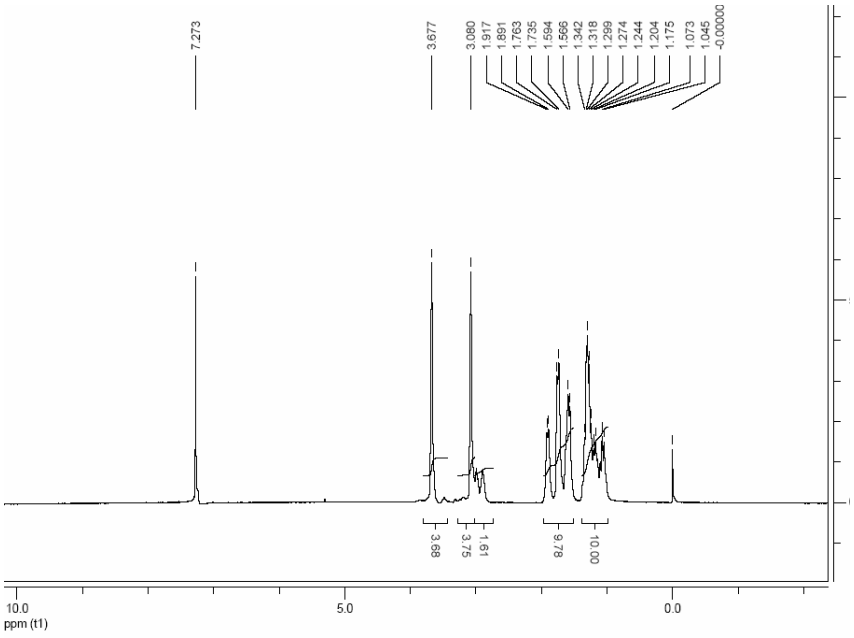
(**22**)

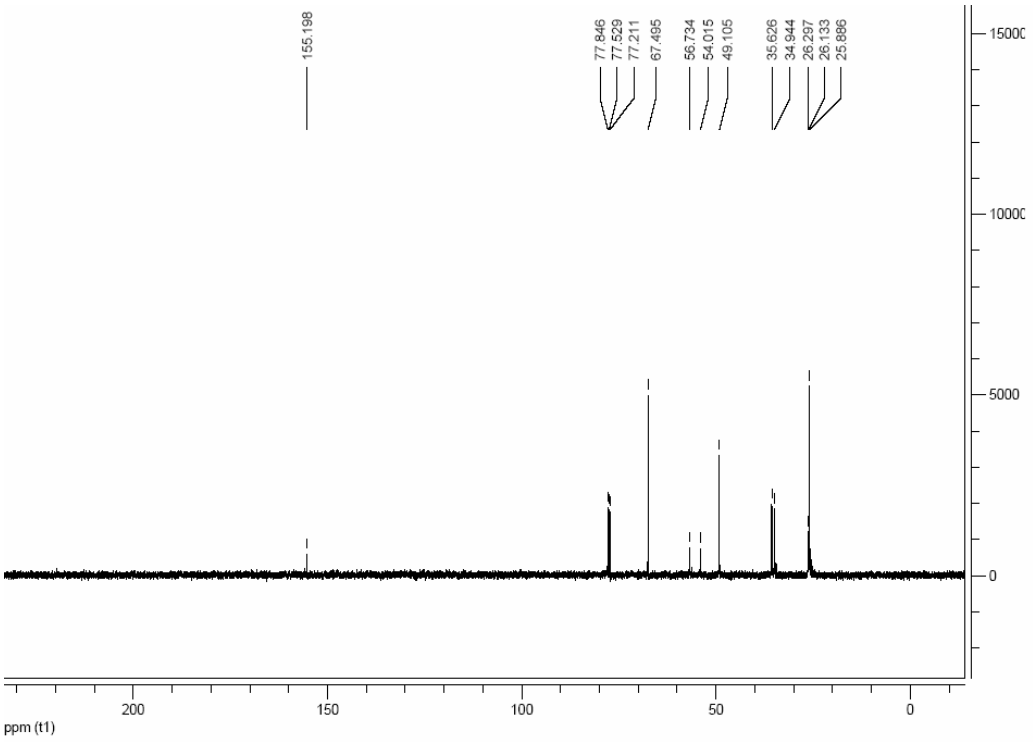

7.261
3.689
3.678
3.668
3.420
3.406
3.390
3.316
3.301
3.285
3.081
3.070
3.061
1.138
1.115
1.099
1.079
1.064
3.57
3.96
12.00
ppm (t1)

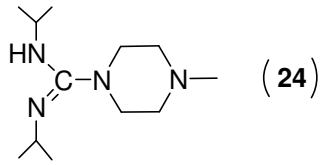

155.469
77.746
77.633
77.429
67.347
48.906
47.433
46.565
23.985
23.843
ppm (t1)


N
C
N
O
HN

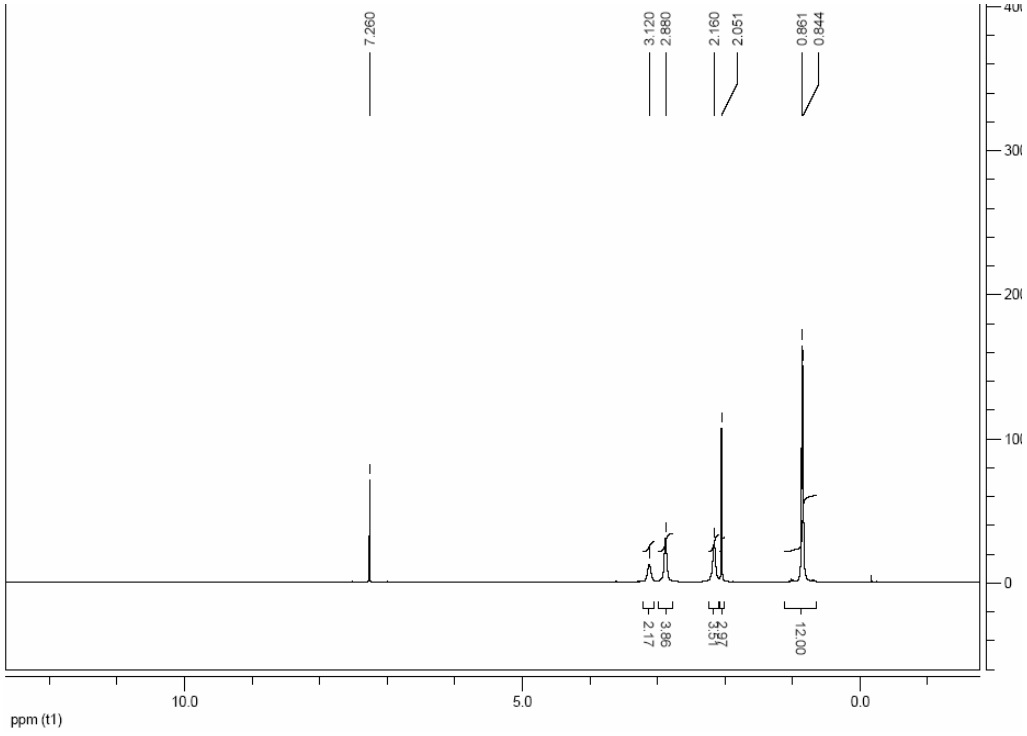
(**23**)

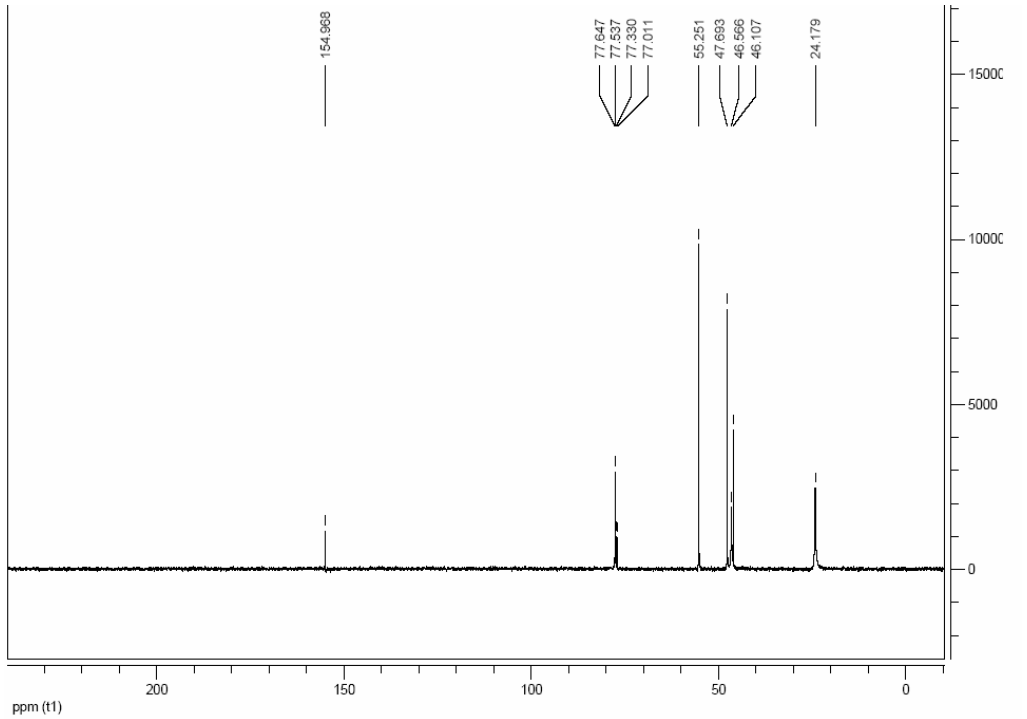

7.273
3.677
3.080
1.917
1.891
1.763
1.735
1.594
1.566
1.342
1.318
1.299
1.274
1.244
1.204
1.175
1.073
1.045
-0.00000
3.68
3.75
1.61
6.78
10.00
10.0
5.0
0.0
ppm (t1)

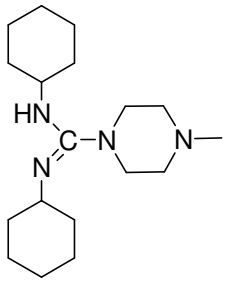

155.198
77.846
77.529
77.211
67.495
56.734
54.015
49.105
35.626
34.944
26.297
26.133
25.886
15000
10000
5000
0
200
150
100
50
0
ppm (t1)



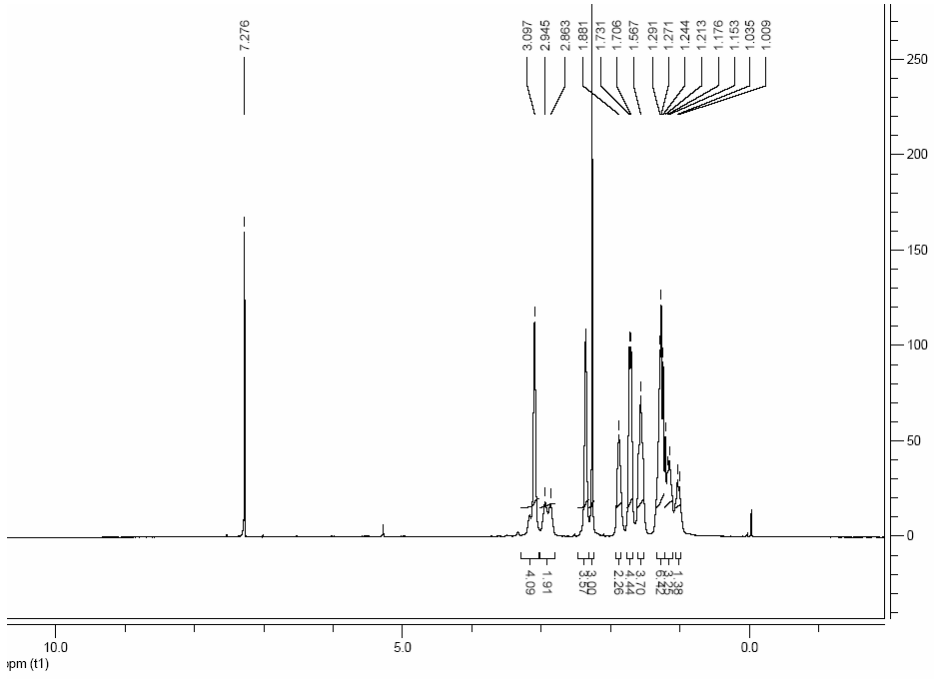
(**24**)

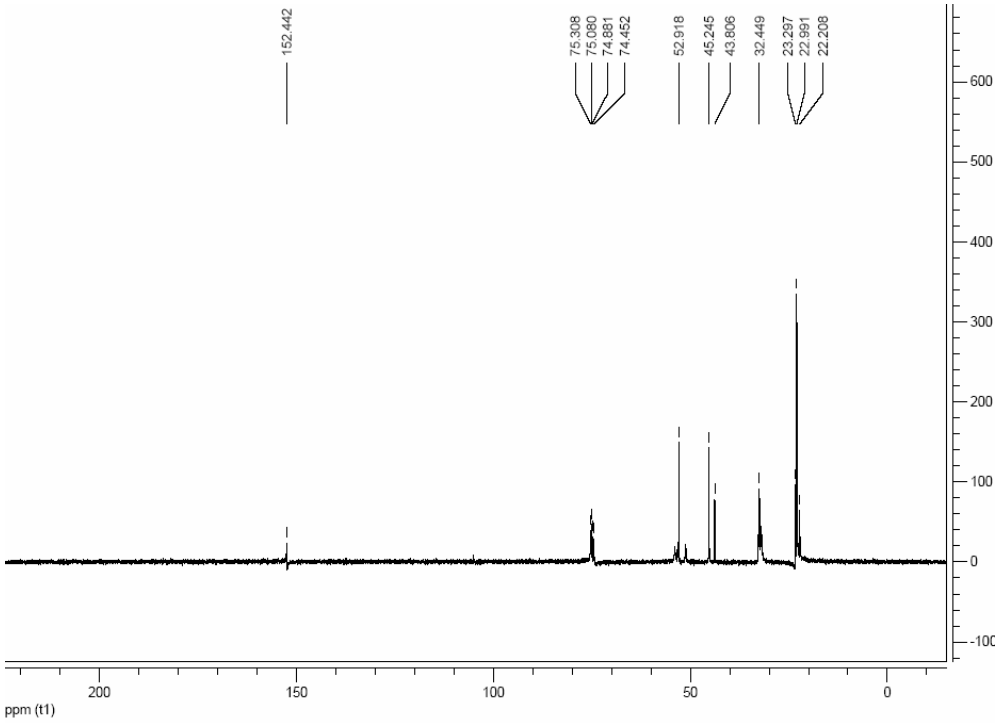

7.260
3.120
2.880
2.160
2.051
0.861
0.844
2.17
3.86
3.97
12.00
10.0
5.0
0.0
ppm (t1)

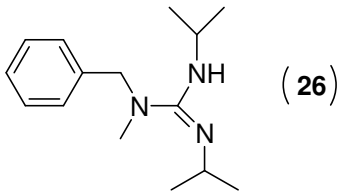

154.968
77.647
77.537
77.330
77.011
55.251
47.693
46.566
46.107
24.179
200
150
100
50
0
ppm (t1)



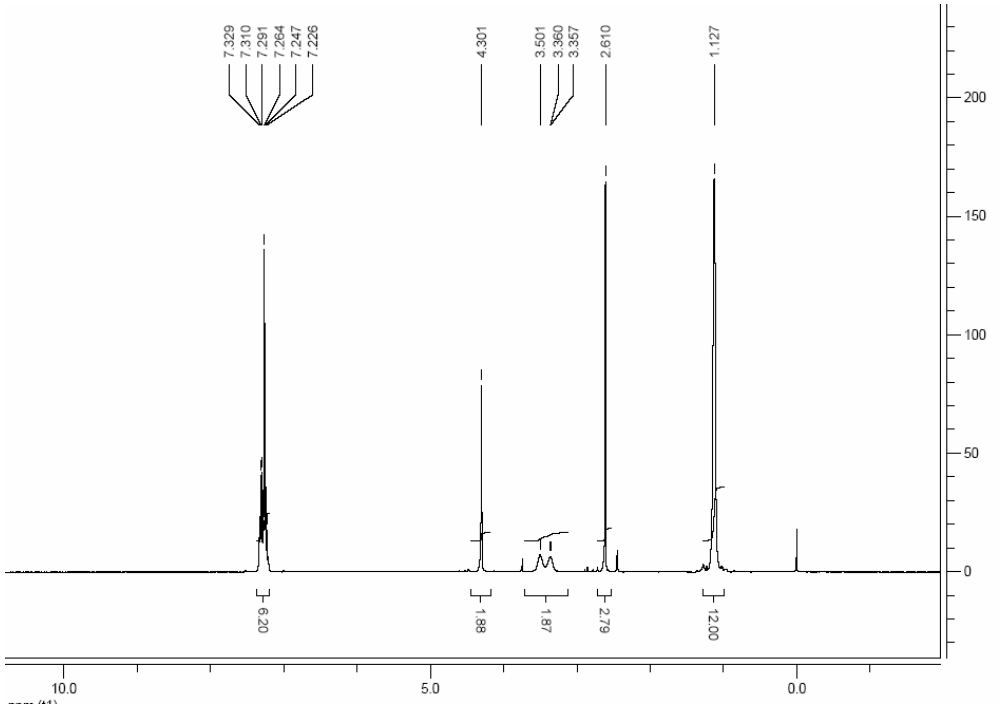
(**25**)

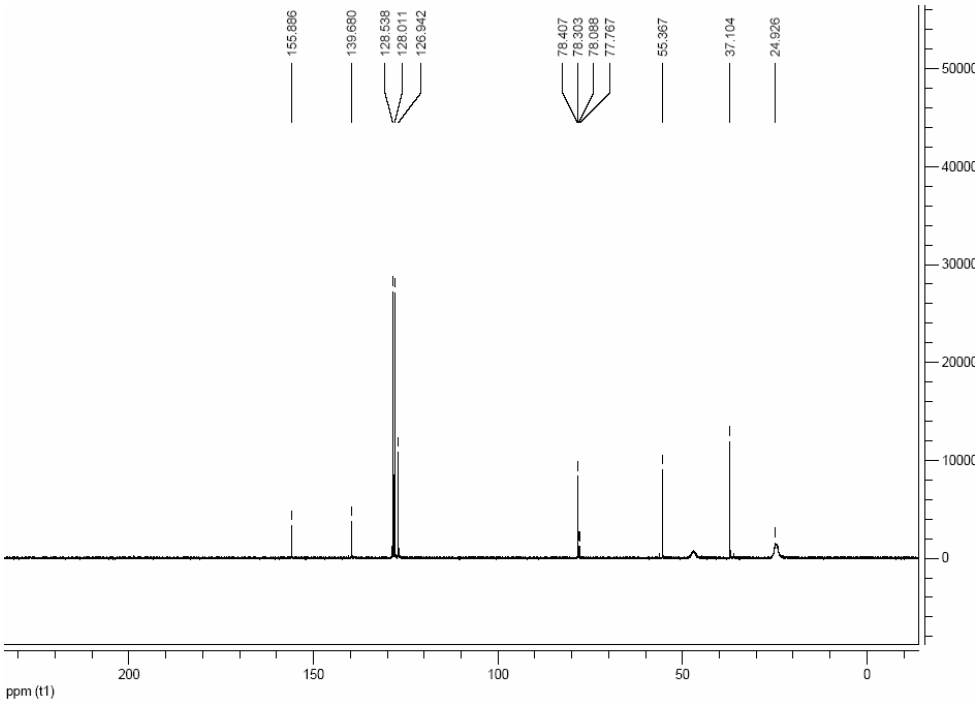

7.276
3.097
2.945
2.863
1.881
1.731
1.706
1.567
1.291
1.271
1.244
1.213
1.176
1.153
1.035
1.009
4.09
1.91
3.00
3.97
2.27
2.44
2.70
1.88
10.0
5.0
0.0
ppm (t1)

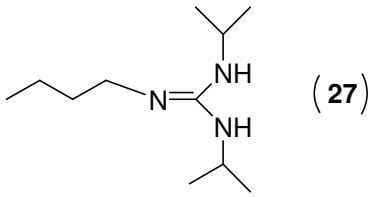

152.442
75.308
75.080
74.881
74.452
52.918
45.245
43.806
32.449
23.297
22.991
22.208
200
150
100
50
0
ppm (t1)


NH
N
N

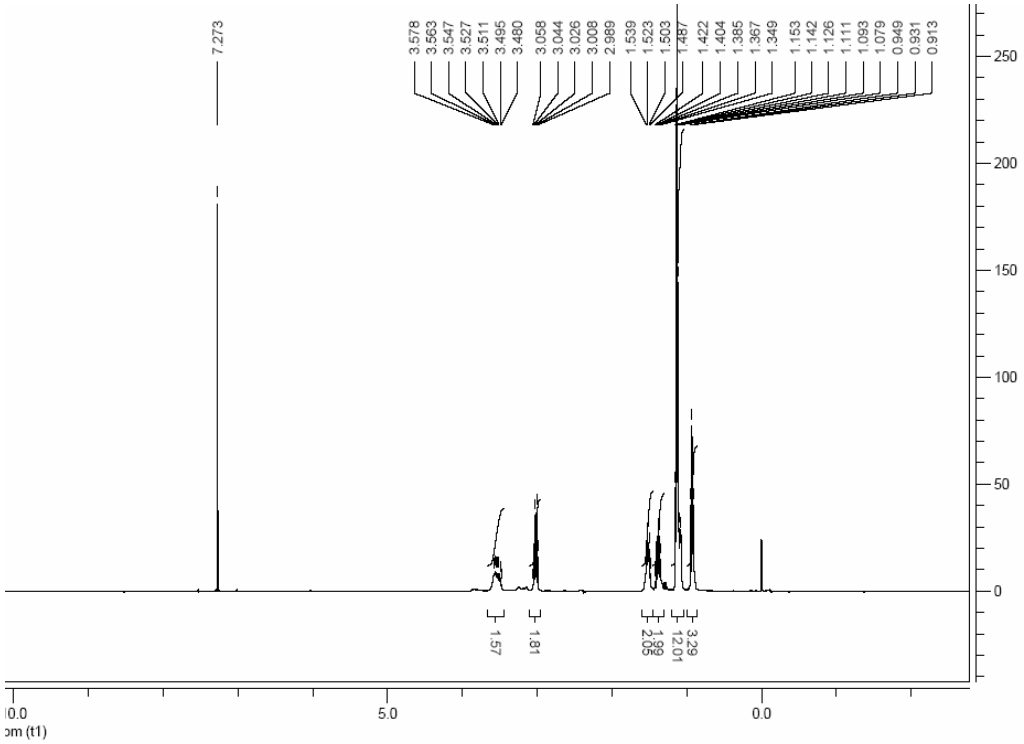
(**26**)

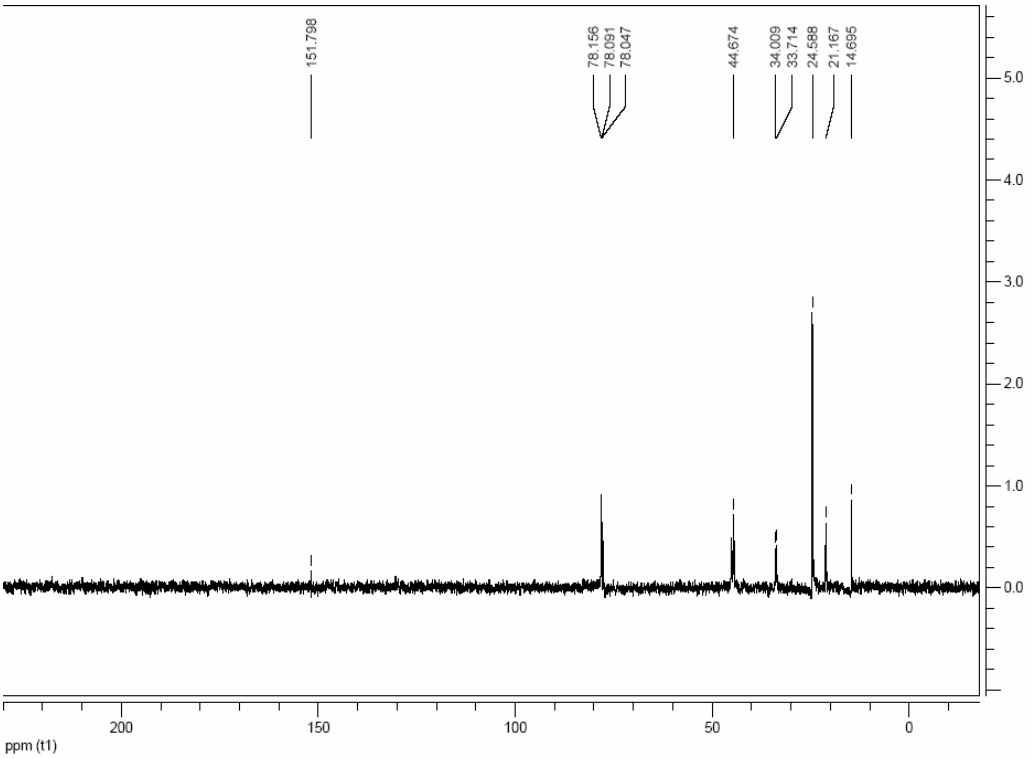

7.329
7.310
7.291
7.264
7.247
7.226
4.301
3.501
3.360
3.357
2.610
1.127
6.20
1.88
1.87
2.79
12.00
10.0
5.0
0.0

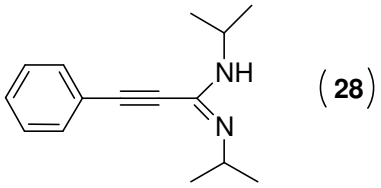

155.886
139.680
128.538
128.011
126.942
78.407
78.303
78.088
77.767
55.367
37.104
24.926
200
150
100
50
0
ppm (t1)


NH
N
NH

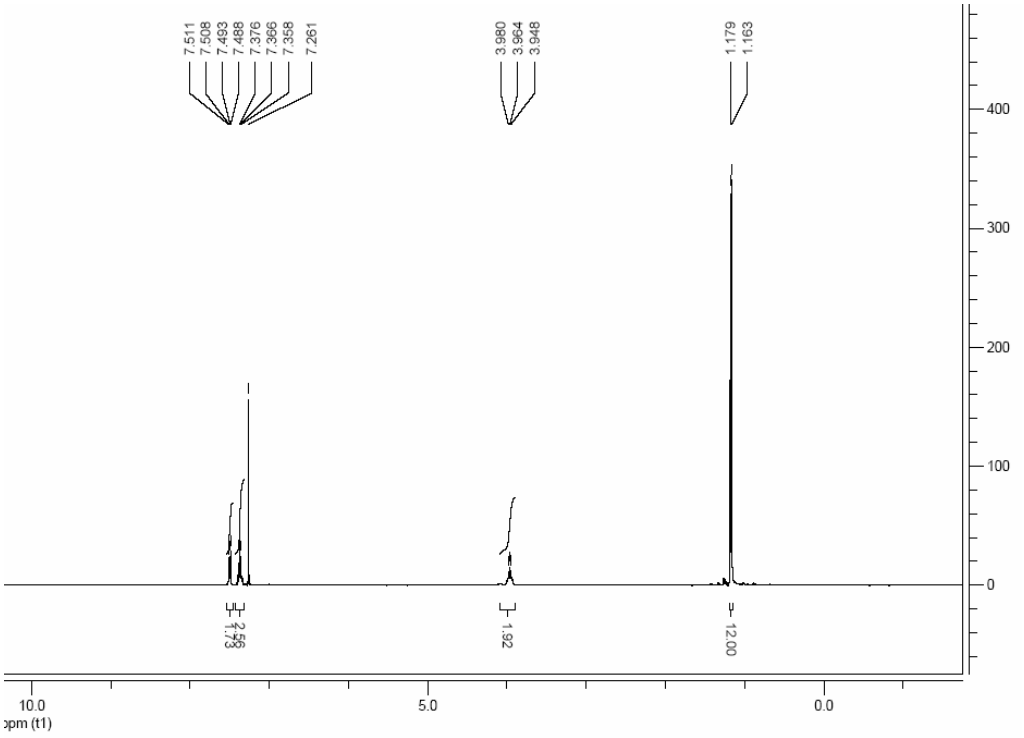
(**27**)

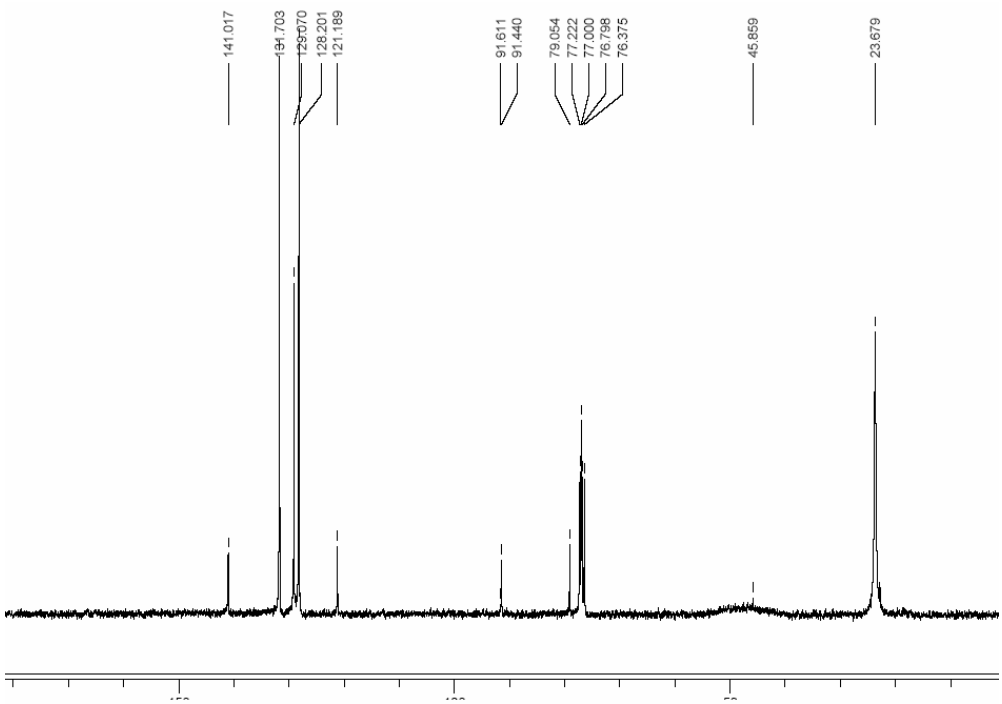

7.273
3.578
3.563
3.547
3.527
3.511
3.495
3.480
3.058
3.044
3.026
3.008
2.989
1.539
1.523
1.503
1.487
1.422
1.404
1.385
1.367
1.349
1.153
1.142
1.126
1.111
1.093
1.079
0.949
0.931
0.913
1.57
1.81
1.99
2.05
12.01
3.29
250
200
150
100
50
0
0.0
5.0
0.0
ppm (t1)

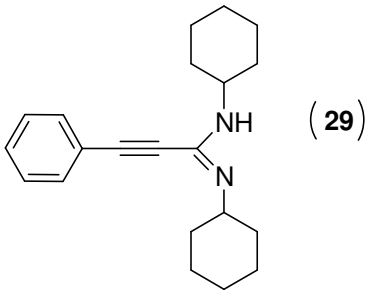

151.798
78.156
78.091
78.047
44.674
34.009
33.714
24.588
21.167
14.695
5.0
4.0
3.0
2.0
1.0
0.0
200
150
100
50
0
ppm (t1)


NH
N

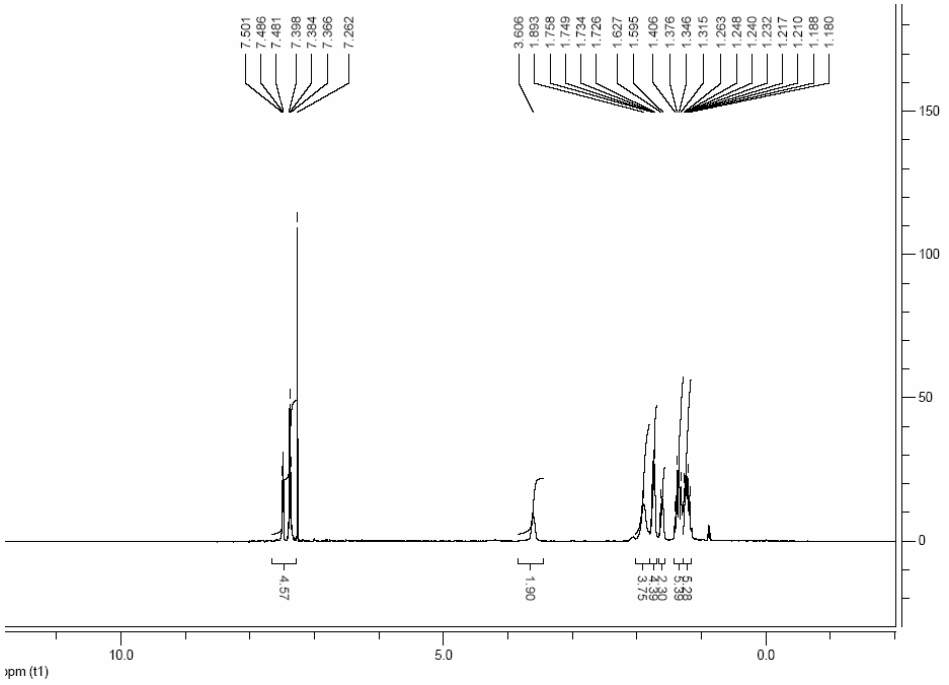
(**28**)

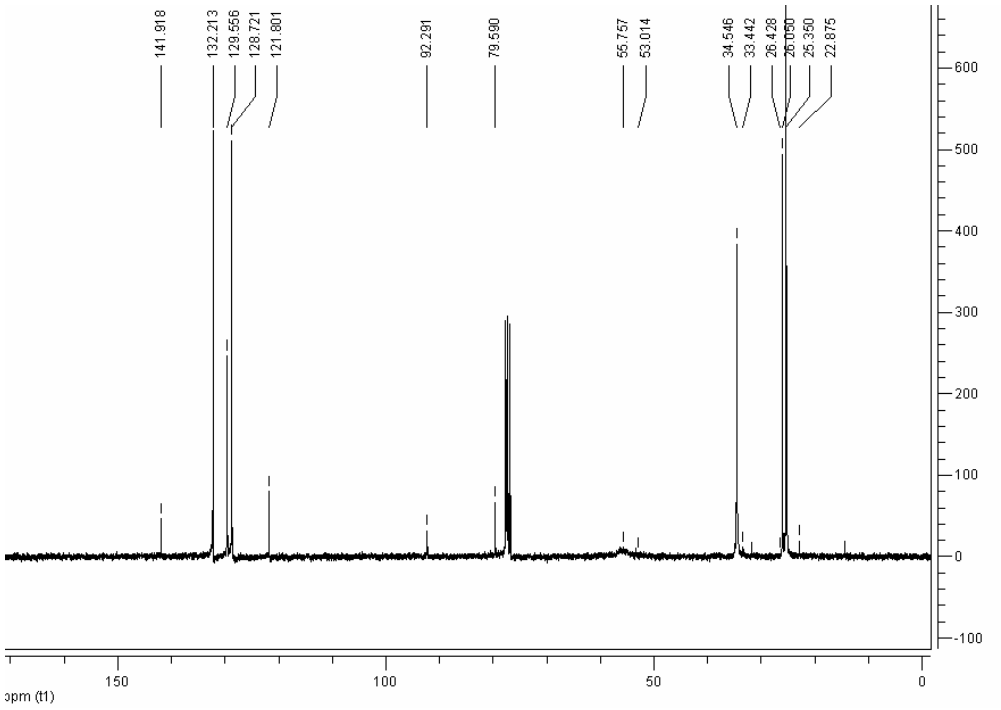

7.511
7.508
7.493
7.488
7.376
7.366
7.358
7.261
3.980
3.964
3.948
1.179
1.163
2.55
1.92
12.00
400
300
200
100
0
10.0
5.0
0.0
ppm (t1)

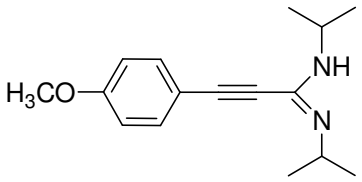

141.017
129.070
128.201
121.189
91.611
91.440
79.054
77.222
77.000
76.798
76.375
45.859
23.679


NH
N

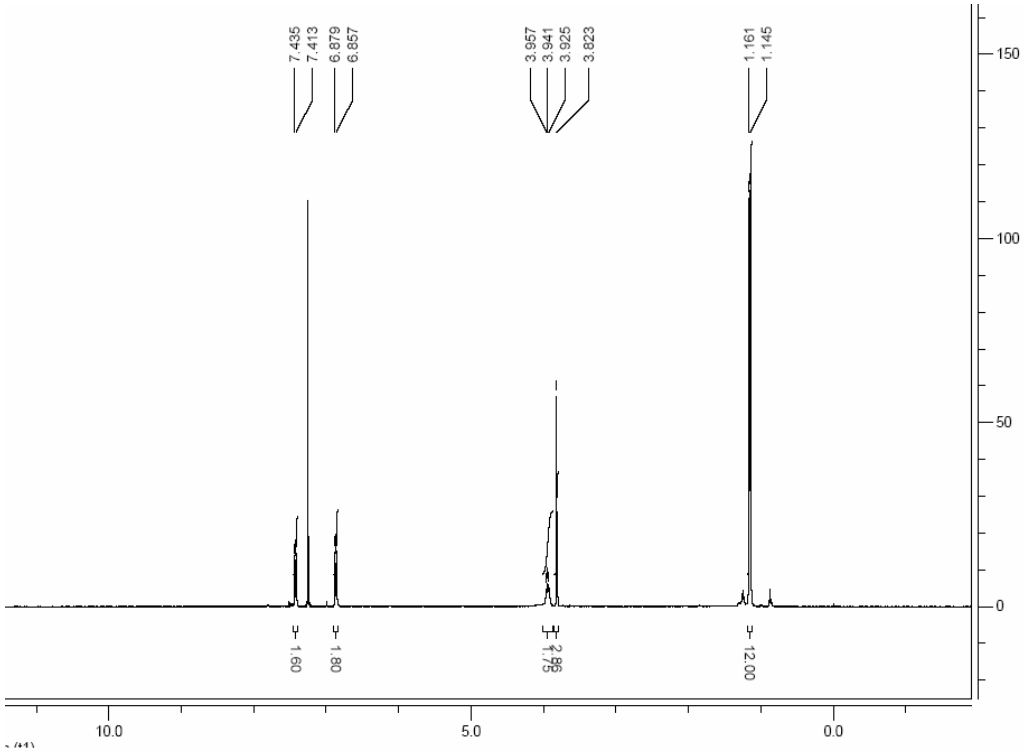
(**29**)

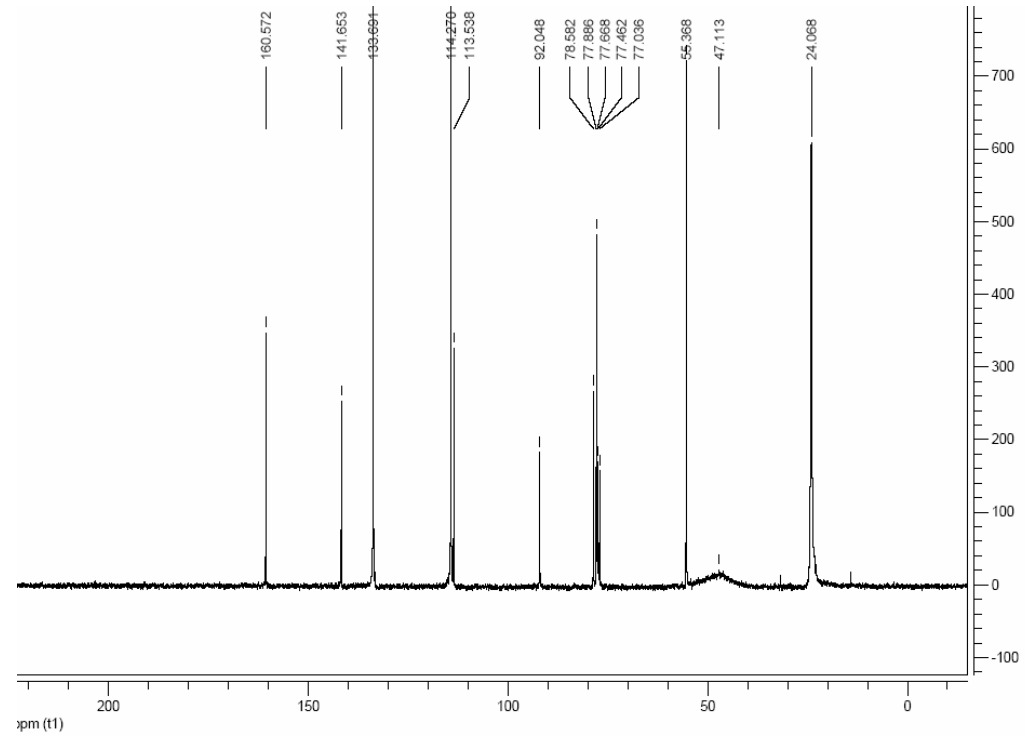

7.501
7.486
7.481
7.398
7.384
7.366
7.262
3.606
1.893
1.758
1.749
1.734
1.726
1.627
1.595
1.406
1.376
1.346
1.315
1.263
1.248
1.240
1.232
1.217
1.210
1.188
1.180
4.57
1.90
3.75
2.30
2.09
5.98
5.88
150
100
50
0
10.0
5.0
0.0
ppm (t1)

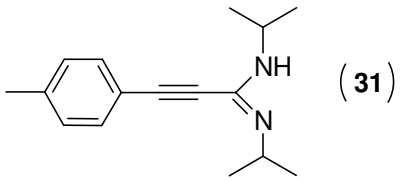

141.918
132.213
129.556
128.721
121.801
92.291
79.590
55.757
53.014
34.546
33.442
26.428
26.050
25.350
22.875
600
500
400
300
200
100
0
-100
150
100
50
0
ppm (t1)


H3CO
NH
N

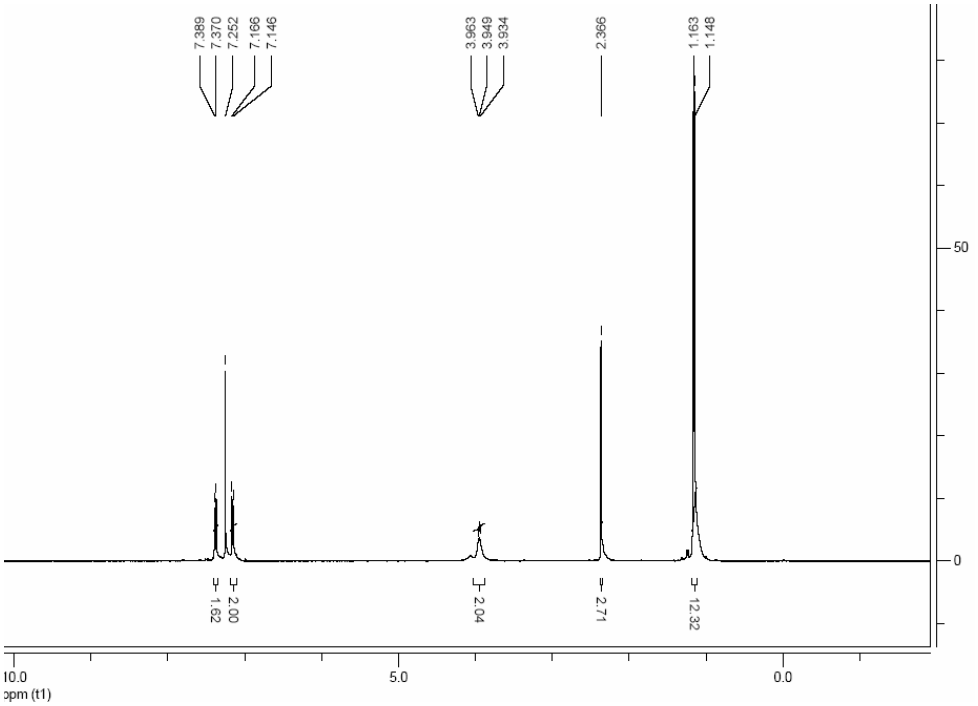
(**30**)

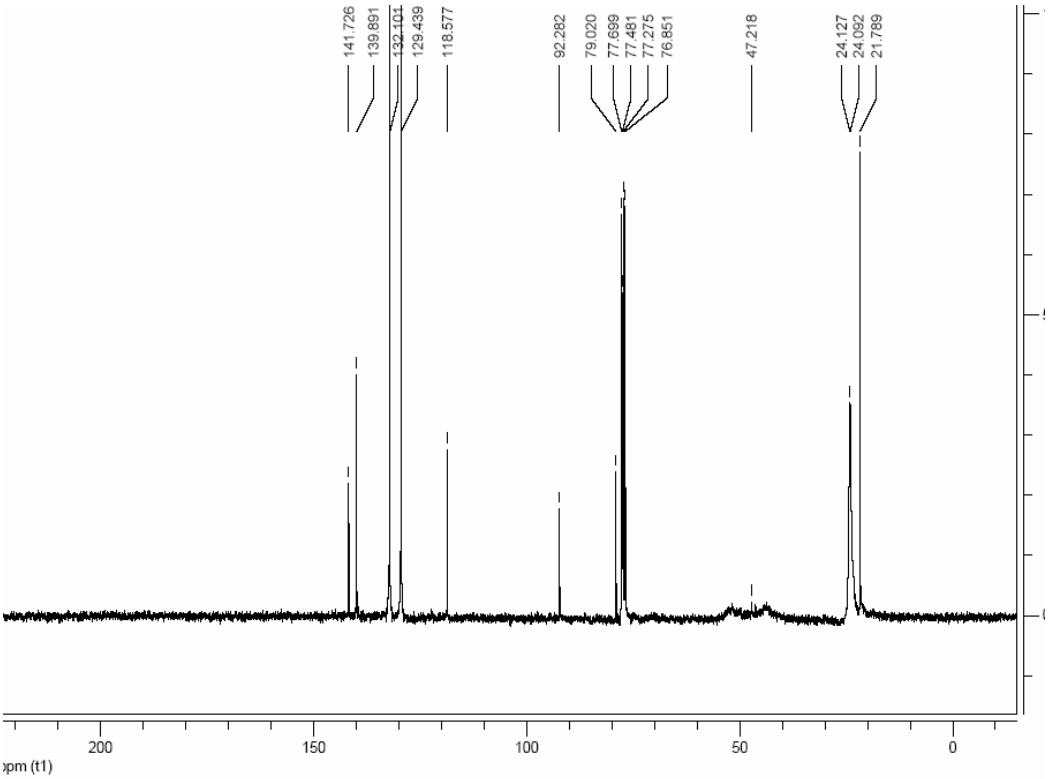

7.435
7.413
6.879
6.857
3.957
3.941
3.925
3.823
1.161
1.145
1.60
1.80
2.86
4.75
12.00
150
100
50
0
10.0
5.0
0.0

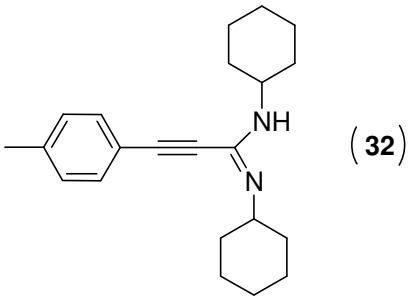

160.572
141.653
133.691
114.270
113.538
92.048
78.582
77.886
77.668
77.462
77.036
55.368
47.113
24.068
700
600
500
400
300
200
100
0
-100
200
150
100
50
0
ppm (t1)


NH
N

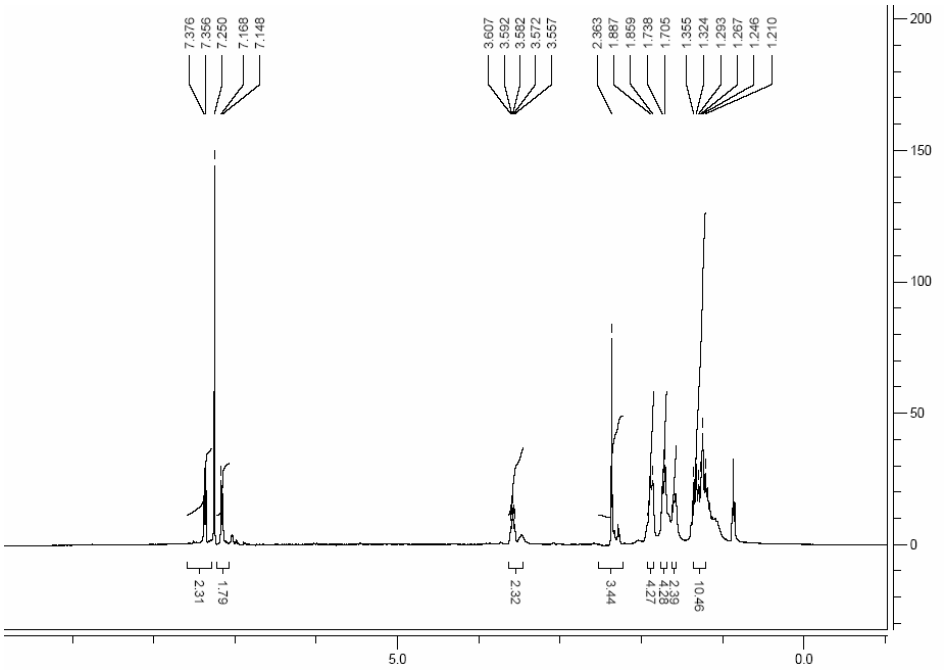
(**31**)

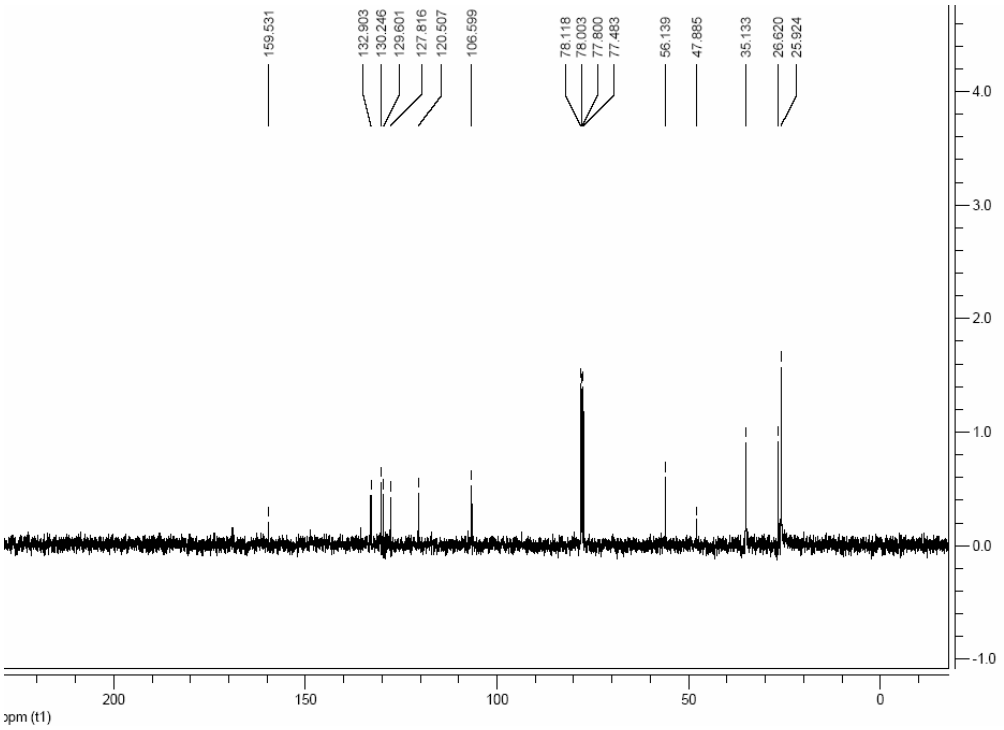

7.389
7.370
7.252
7.166
7.146
3.963
3.949
3.934
2.366
1.163
1.148
1.62
2.00
2.04
2.71
12.32
50
0
10.0
5.0
0.0
ppm (t1)

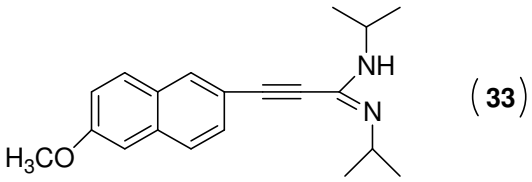

141.726
139.891
132.101
129.439
118.577
92.282
79.020
77.699
77.481
77.275
76.851
47.218
24.127
24.092
21.789
200
150
100
50
0
ppm (t1)


NH
N

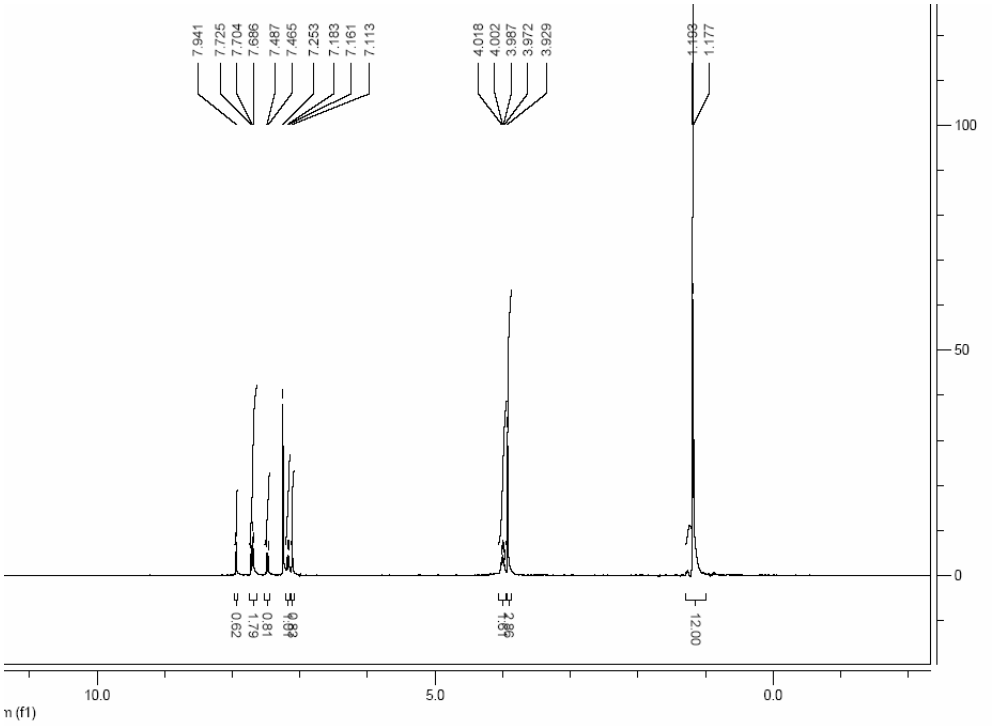
(**32**)

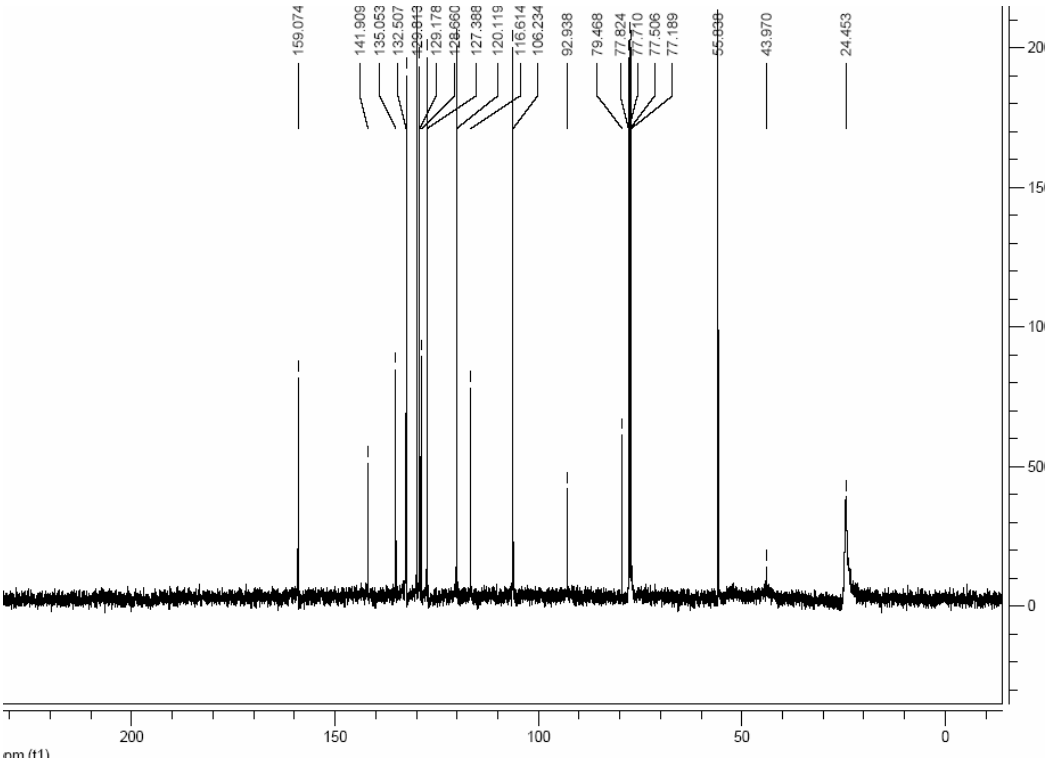

7.376
7.356
7.250
7.168
7.148
3.607
3.592
3.582
3.572
3.557
2.363
1.887
1.859
1.738
1.705
1.355
1.324
1.293
1.267
1.246
1.210
2.31
1.79
2.32
3.44
2.39
4.28
4.27
10.46
200
150
100
50
0
5.0
0.0

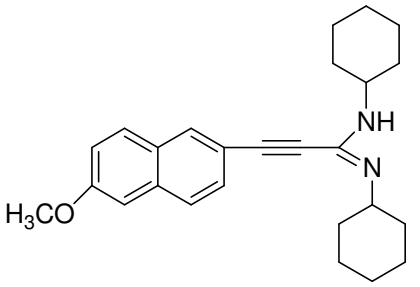

159.531
132.903
130.246
129.601
127.816
120.507
106.599
78.118
78.003
77.800
77.483
56.139
47.885
35.133
26.620
25.924
4.0
3.0
2.0
1.0
0.0
-1.0
200
150
100
50
0
ppm (t1)


NH
N
H_3CO

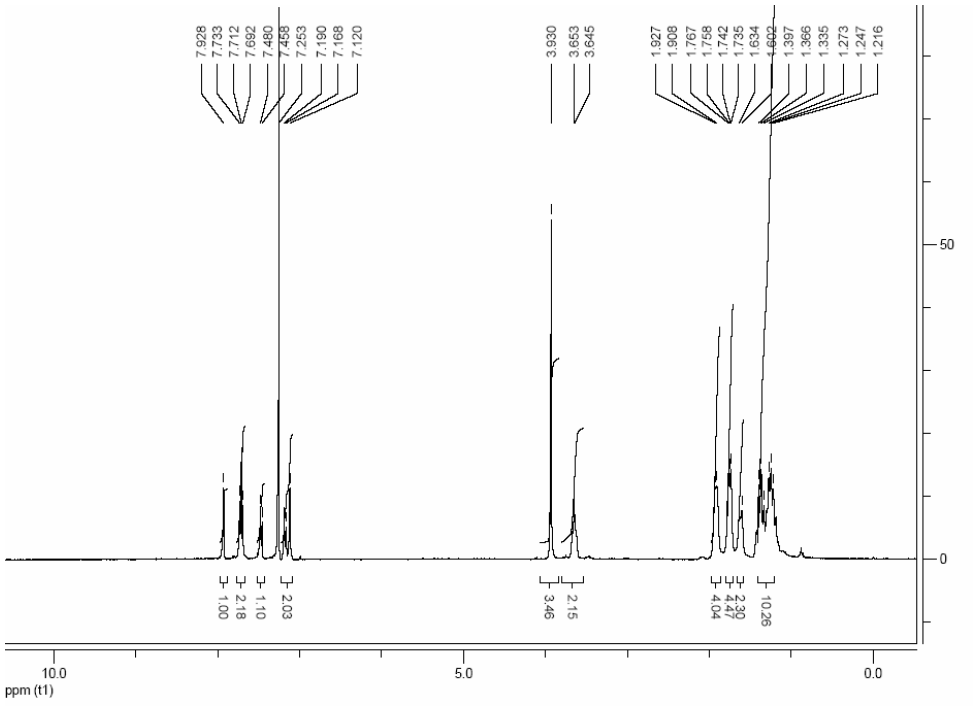
(**33**)

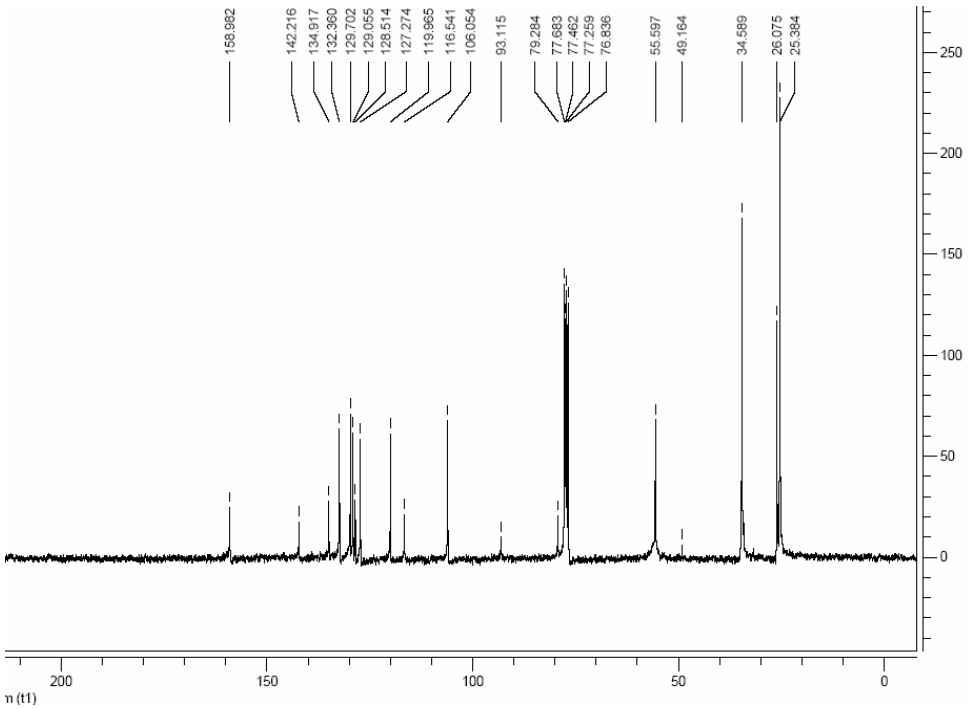

7.941
7.725
7.704
7.686
7.487
7.465
7.253
7.183
7.161
7.113
4.018
4.002
3.987
3.972
3.929
1.193
1.177
100
50
0
0.62
1.79
0.81
12.00
10.0
5.0
0.0

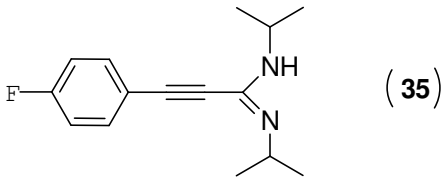

159.074
141.909
135.053
132.507
129.178
127.388
120.119
116.614
106.234
92.938
79.468
77.506
77.189
55.030
43.970
24.453
200
150
100
50
0


NH
N
H3CO

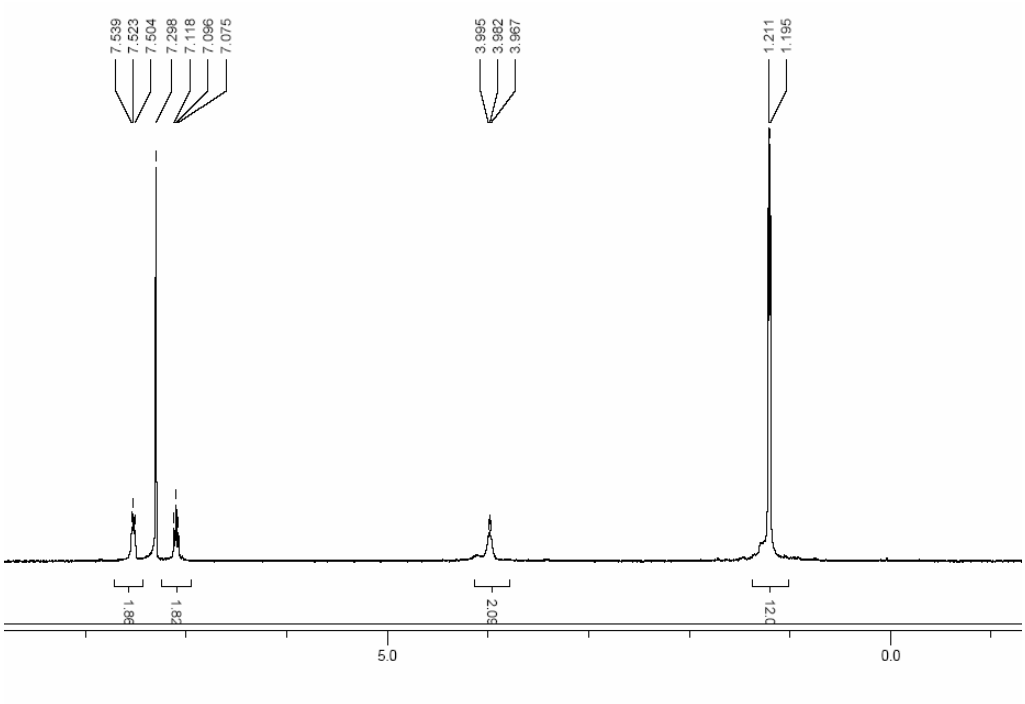
(**34**)

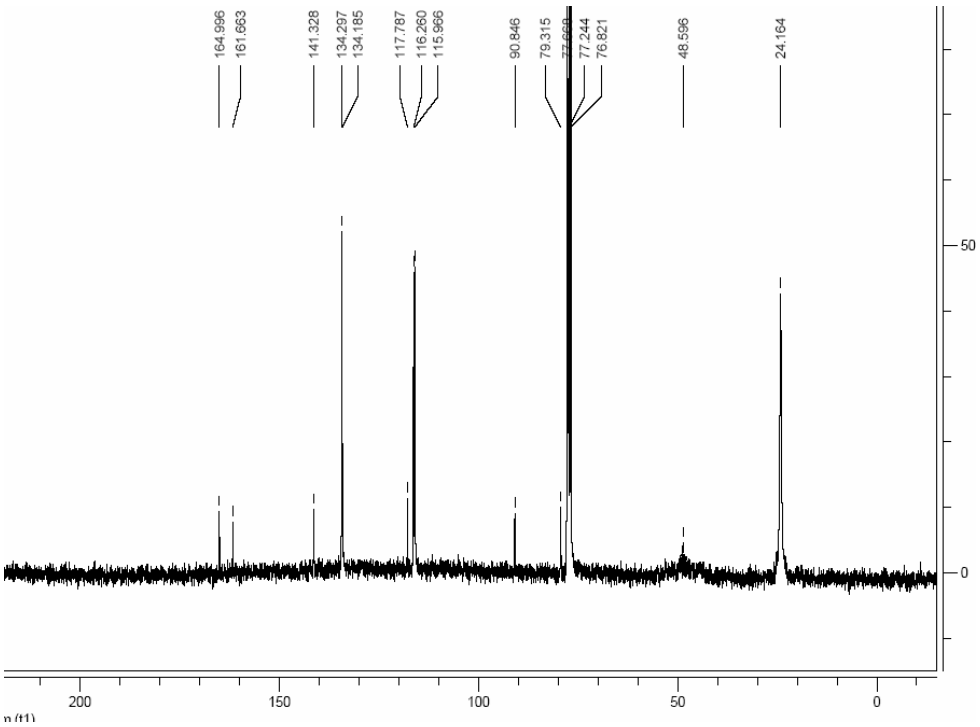

7.928
7.733
7.712
7.692
7.480
7.458
7.253
7.190
7.168
7.120
3.930
3.653
3.645
1.927
1.908
1.767
1.758
1.742
1.735
1.634
1.602
1.397
1.366
1.335
1.273
1.247
1.216
1.00
2.18
1.10
2.03
3.46
2.15
4.04
2.30
2.47
10.26
50
0
10.0
5.0
0.0
ppm (t1)

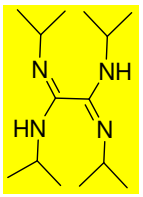

158.982
142.216
134.917
132.360
129.702
129.055
128.514
127.274
119.965
116.541
106.054
93.115
79.284
77.683
77.462
77.259
76.836
55.597
49.164
34.589
26.075
25.384
250
200
150
100
50
0
200
150
100
50
0
n (t1)


F
NH
N

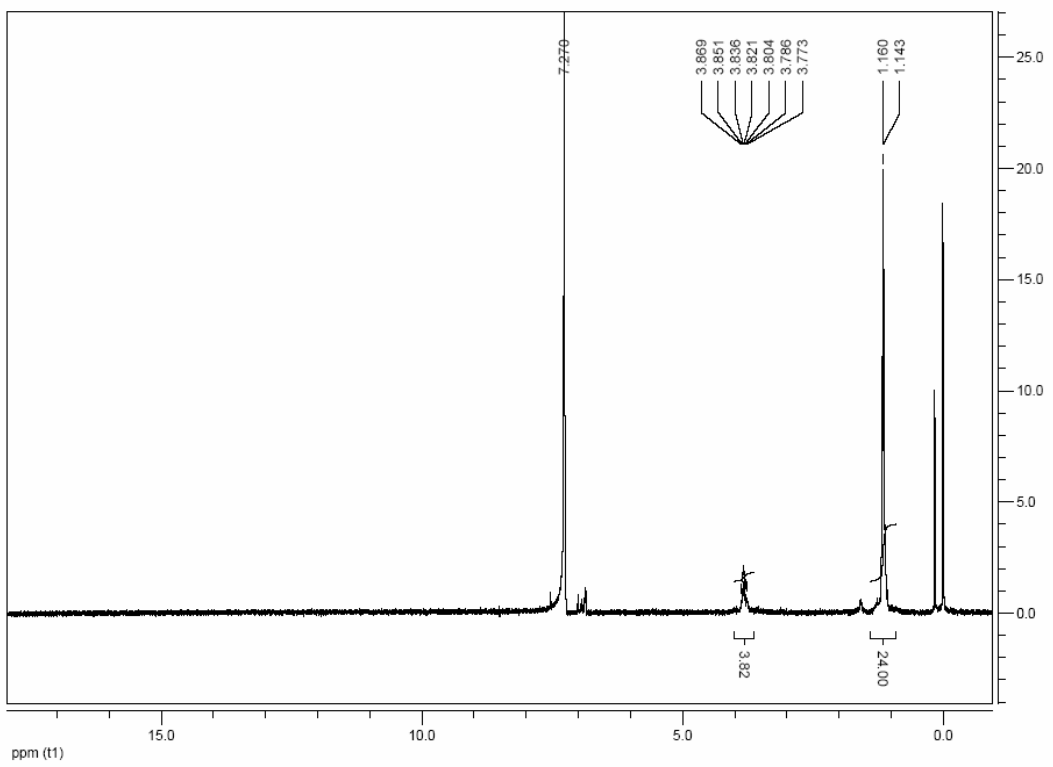
(**35**)

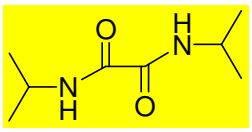

7.539
7.523
7.504
7.298
7.118
7.096
7.075
3.995
3.982
3.967
1.211
1.195
1.98
1.82
2.06
12.00
5.0
0.0


164.996
161.663
141.328
134.297
134.185
117.787
116.260
115.966
90.846
79.315
77.244
76.821
48.596
24.164
50
0
200
150
100
50
0

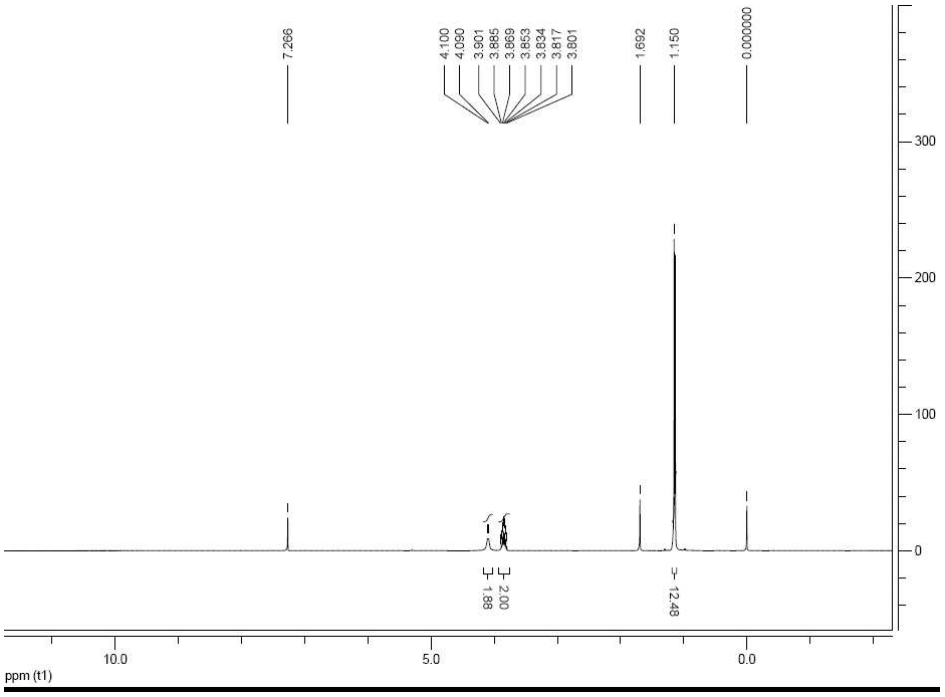


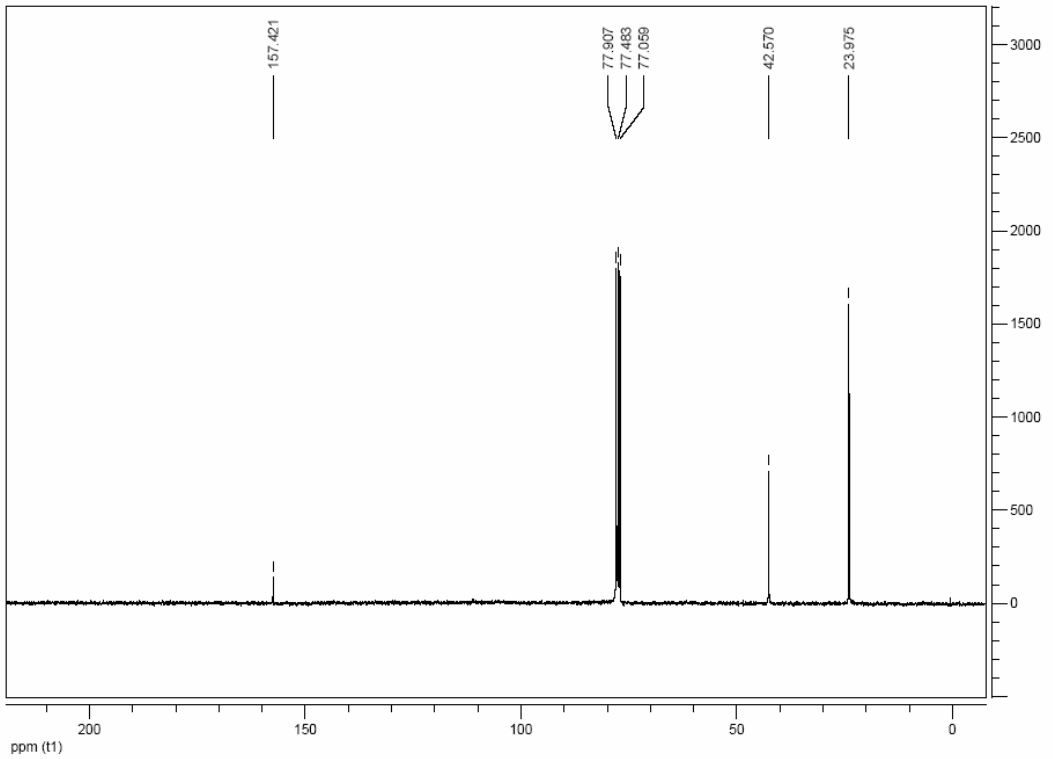
Biamidine (36)





Diketone (37)


7.266
4.100
4.090
3.901
3.885
3.869
3.853
3.834
3.817
3.801
1.692
1.150
0.000000
1.88
2.00
12.48
300
200
100
0
10.0
5.0
0.0
ppm (t1)


157.421
77.907
77.483
77.059
42.570
23.975
3000
2500
2000
1500
1000
500
0
200
150
100
50
0
ppm (t1)