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Supporting Information

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Synthesis and Study of Janus Bis(carbene)s and Their Transition-Metal Complexes

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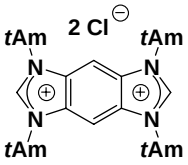
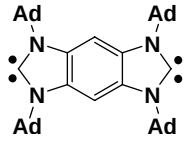
SUPPORTING INFORMATION

General Considerations. Compounds **1a-e** were prepared according to our previously reported procedures.[1] All reactions were conducted under an atmosphere of dry nitrogen using standard Schlenk techniques or in a nitrogen filled glove-box. CH_2Cl_2 was distilled from CaH_2 under nitrogen and degassed by three freeze-pump-thaw cycles. THF and toluene were distilled from Na/benzophenone under nitrogen and degassed by three freeze-pump-thaw cycles. $[(COD)RhCl]_2$ and 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride were purchased from Strem and used without further purification. All other reagents were purchased from Aldrich or Acros and were used without further purification. ^{1}H NMR spectra were recorded using a Varian Gemini (300 MHz or 400 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using the residual protonated solvent as an internal standard ($CDCl_3$, 7.24 ppm; C_6D_6, 7.15 ppm, DMSO-d_6, 2.49 ppm). ^{13}C NMR spectra were recorded using a Varian Gemini (75 MHz or 100 MHz) spectrometer and were routinely run with broadband decoupling. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using the residual protio solvent as an internal standard ($CDCl_3$, 77.0 ppm; C_6D_6, 128.0 ppm, DMSO-d_6, 39.5 ppm). High-resolution mass spectra (HRMS) were obtained with a VG analytical ZAB2-E or a Karatos MS9 instrument and are reported as m/z (relative intensity). X-ray crystal structure data was collected for compounds **1a** (CCDC 605308), **2a** (CCDC 605309), **2b** (CCDC 605310), **3a** (CCDC 605311), **3c** (CCDC 605312), **3d** (CCDC 605313), **5** (CCDC 605314), and (COD)RhCl(1,3-diadamantylbenzimidazolylidene) (CCDC 605315) and deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

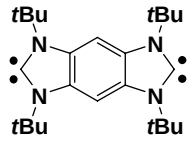


Tetrakis-*N*-*t*-amylbenzobis(imidazolium) dichloride (1c). 1,2,4,5-Tetrakis-*N*-*t*-amylaminobenzene was first prepared according to literature procedure[1a] using 1,2,4,5-tetrabromobenzene and *t*-amylamine. ^{1}H NMR (C_6D_6): δ 6.65 (s, 2H), 3.57 (br, 4H), 1.62 (q, J = 7.6 Hz, 8H), 1.22, (s, 24H) 0.95 (t, J = 7.6 Hz, 12H); ^{13}C NMR (C_6D_6): δ 132.0, 114.8, 54.3, 35.4, 27.5, 8.9. A 25 mL flask was charged with triethylorthoformate (10 mL), 1,2,4,5-tetrakis-*N*-*t*-amylaminobenzene (610 mg, 1.46 mmol), conc. HCl (1 mL), and a stir bar. The mixture was stirred vigorously at RT until complete dissolution of all solids was observed. The reaction was then heated at 60 °C for 10 h. Ethanol was partially removed from the solution by evaporation under reduced pressure. Precipitated solids were

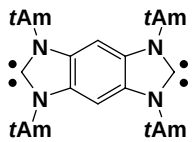
collected by filtration and dried under vacuum to afford 484 mg (65%) of the desired product as a white powder. ^{1}H NMR (DMSO-d_6): δ 9.23 (s, 2H), 8.55 (s, 2H), 2.28 (q, J = 7.2, 8H), 1.93 (s, 24H), 0.73 (t, J = 7.2 Hz, 12H); ^{13}C NMR (DMSO-d_6): δ 144.3, 128.9, 102.5, 65.6, 31.9, 25.9, 8.2.



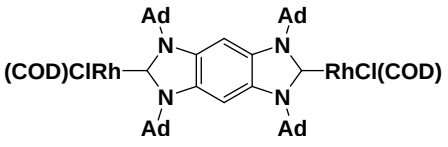
Tetrakis-*N*-adamantylbenzobis(imidazolylidene) (2a). In a nitrogen-filled drybox, a 20 mL flask was charged with bis(azolium) salt **1a** (680 mg, 0.78 mmol), THF (10 mL), LDA (1.83 M in THF/hexanes, 0.93 mL, 1.70 mmol), and a stir bar. The flask was sealed and the resulting slurry was stirred for 10 h at RT. Precipitated solids were collected by filtration, washed with THF (5 mL) and dried under reduced pressure to afford 450 mg (83%) of the desired product as a white solid. Crystals suitable for X-ray analysis were obtained by solvent diffusion of pentane into a saturated solution of **2a** in toluene/THF (1:1 v/v) (CCDC 605309). ^{1}H NMR (C_6D_6): δ 8.37 (s, 2H), 2.81 (s, 24H), 2.15 (s, 12H), 1.81-1.67 (br, 24H); ^{13}C NMR (C_6D_6): δ 227.6, 130.5, 98.5, 58.3, 43.6, 37.2, 30.5.



Tetrakis-*N*-*t*-butylbenzobis(imidazolylidene) (2b). In a nitrogen-filled drybox, a 20 mL flask was charged with bis(azolium) salt **1b** (1.27 g, 2.3 mmol), THF (10 mL), LDA (1.80 M in THF/hexanes, 2.8 mL, 5.05 mmol), and a stir bar. The flask was sealed and the resulting slurry was stirred for 10 h at RT. Precipitated solids were collected by filtration, washed with THF (5 mL) and dried under vacuum to afford 870 mg (99%) of the desired product as a light gray solid. Crystals suitable for X-ray analysis were obtained by slow cooling of a hot, saturated toluene solution (CCDC 605310). ^{1}H NMR (C_6D_6): δ 7.79 (s, 2H), 1.78 (s, 36H); ^{13}C NMR (C_6D_6): δ 228.3, 130.9, 97.5, 57.2, 30.5; HRMS calcd. for $C_{24}H_{34}N_4$ [M+H$^+$]: 383.3175, found: 383.3177.

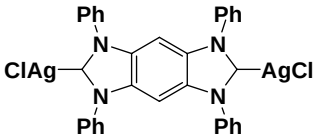


Tetrakis-*N*-*t*-amylbenzobis(imidazolylidene) (2c). In a nitrogen-filled drybox, a 10 mL flask was charged with bis(azolium) salt **1c** (50 mg, 0.098 mmol), LDA (0.41 M in THF/hexanes, 0.48 mL, 0.195 mmol), and a stir bar. The resulting slurry was stirred for 15 minutes at RT, then toluene (1 mL) was added. The reaction mixture was filtered through Celite and the solvent was removed under reduced pressure to afford 22 mg (99%) of the desired product as a white solid. ^{1}H NMR (C_6D_6): δ 7.89 (s, 2H), 2.14 (q, J = 7.2 Hz, 8H), 1.85 (s, 24H), 0.76 (t, J = 7.2 Hz, 12H); ^{13}C NMR (C_6D_6): δ 230.2, 131.1, 96.9, 60.1, 33.7, 29.0, 8.5; HRMS calcd. for $C_{26}H_{46}N_4$ [M+H$^+$]: 438.3722, found: 438.3722.

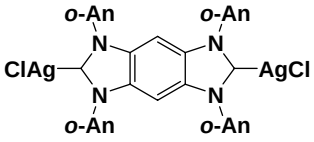


Bimetallic Rhodium Complex 3a. In a nitrogen-filled drybox, a 10 mL flask was charged with bis(carbene) **2a** (70 mg, 0.1 mmol), [(COD)RhCl]$_2$ (50 mg, 0.1 mmol), THF (2 mL), and a stir bar. The resulting slurry became homogeneous after stirring for 5 min at RT. Product precipitation began within 30 min and the reaction was stirred for an additional 2 h. Precipitated solids were collected by filtration, washed with THF (3 mL), and dried under vacuum to afford 100 mg (77%) of the desired product as a yellow powder. Crystals suitable for X-ray analysis were obtained by slow evaporation of a saturated $CHCl_3$ solution (CCDC

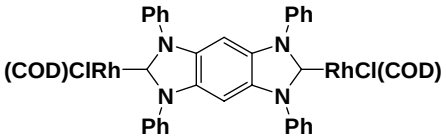
605311). ^{1}H NMR ($CDCl_3$): δ 8.20 (s, 2H), 4.98 (s, 2H), 3.50-3.47 (m, 12H), 3.00-2.97 (m, 16H), 2.47-2.41 (m, 22H), 1.67-1.61 (m, 36H); ^{13}C NMR ($CDCl_3$): δ 198 (d), 129.5, 109.7, 99.9, 92.5 (d, J = 6.9 Hz), 67.7 (d, J = 14.8 Hz), 62.2, 43.2, 36.6, 32.3, 30.4, 28.8.



Diargento Complex 3b. Bis(azolium) salt **1d** (535 mg, 1.0 mmol) was dissolved in CH_3CN (10 mL) and Ag_2O (243 mg, 1.05 mmol) was added. The resulting suspension was stirred at 40 °C for 2 h. The cooled reaction mixture was filtered through Celite and concentrated to give 726 mg (97%) of **3b** as a brown powder. ^{1}H and ^{13}C NMR analysis revealed broad peaks indicative of aggregation/oligomerization. ^{1}H NMR (DMSO-d_6) δ 7.82-7.78 (m, 8H), 7.73-7.60 (m, 12H), 7.45 (s, 2H).

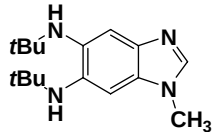


Diargento Complex 3c. Bis(azolium) salt **1e** (1.20 g, 1.82 mmol) was suspended in CH_2Cl_2 (100 mL). To the mixture was added Ag_2O (423 mg, 1.82 mmol) and the flask was protected from light using Al foil. After stirring for 2 h at room RT, a brown suspension formed which was filtered over Celite and concentrated to a brown glassy solid (1.49 g, 94%). ^{1}H and ^{13}C NMR analysis revealed broad peaks indicative of aggregation/oligomerization. Crystals suitable for X-ray analysis were obtained by diffusion of hexanes into a solution of **3c** in CH_2Cl_2 (CCDC 605312).

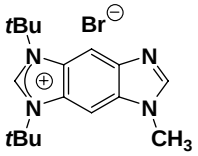


Bimetallic Rhodium Complex 3d. From bis(azolium) salt **1d·BF$_4$**: The bis(azolium) salt (100 mg, 0.157 mmol) was added to THF (3 mL) followed by NaHMDS (0.16 mL, 0.32 mmol, 2.0 M in THF). The slurry was stirred for 1 h, then $[(COD)RhCl]_2$ (77 mg, 0.157 mmol) was added and the solution was heated to 50 °C in a sealed vial for 10 h. The cooled reaction mixture was diluted with hexanes (6 mL) and solids were collected by filtration, washed with toluene (5 mL) and hexanes (5 mL). Solvent was removed under reduced pressure. Residual inorganic salts were removed by treating the crude solid with chloroform and filtering through a 0.45 μm PTFE filter, followed by removal of solvent under reduced pressure to obtain the product as a tan solid (51 mg, 34%).

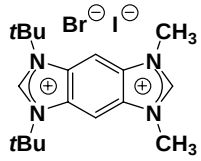
From diargento complex **3b**: The diargento complex **3b** (373 mg, 0.50 mmol) and $[(COD)RhCl]_2$ (258 mg, 0.52 mmol) were partially dissolved in CH_2Cl_2 (12 mL) in a screw-cap vial under an atmosphere of dry nitrogen. The vial was sealed with a Teflon-coated cap and stirred at 50 °C for 20 h protected from light with Al foil. The cooled reaction mixture was then filtered through Celite and concentrated to give 191 mg (40%) of the desired product. Crystals suitable for X-ray analysis were obtained by slow diffusion of hexanes into a saturated CH_2Cl_2 solution (CCDC 605313). ^{1}H NMR ($CDCl_3$): δ 8.13 (br, 8H), 7.64-7.52 (br, 12H), 7.13 (s, 2H), 4.89 (br, 4H), 2.73 (br, 4H), 1.8-1.46 (br, 16H); ^{13}C NMR ($CDCl_3$): δ 137.7, 132.7, 129.3, 128.9, 127.8, 127.4, 109.7, 99.3, 91.9, 68.5 (d, J = 13.9 Hz), 32.0, 28.2.



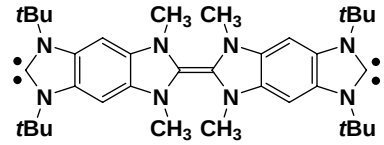
5,6-Bis(*t*-butylamino)-1-methylbenzimidazole. Under an atmosphere of nitrogen, a 10 mL vial was charged with 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (17 mg, 0.04 mmol), NaO*t*Bu (2 mg, 0.02 mmol), $Pd(OAc)_2$ (5 mg, 0.02 mmol), toluene (5 mL), and a stir bar. The resulting mixture was stirred at 80 °C for 5 minutes. Then, 5,6-dichloro-1-methylbenzimidazole[2] (101 mg, 0.50 mmol) was added, followed by *t*-butyl amine (146 mg, 2.0 mmol) and NaO*t*Bu (101 mg, 1.05 mmol). The resulting mixture was sealed and stirred at 150 °C for 24 h. After cooling to RT, precipitated solids were removed by filtration and solvent was removed to obtain a brown solid which was used in the next step without additional purification. ^{1}H NMR ($CDCl_3$): δ 7.57 (s, 1H), 7.32 (s, 1H), 6.70 (s, 1H), 3.70 (s, 3H), 1.34 (s, 9H), 1.21 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 141.2, 140.0, 136.1, 131.9, 131.4, 115.6, 95.6, 52.8, 51.3, 38.5, 29.8, 29.7.



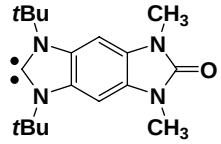
Desymmetrized Benzimidazolium Salt. Crude 5,6-bis(*t*-butylamino)-1-methylbenzimidazole was partially dissolved in $HC(OEt)_3$ and HBr (48%). The resulting slurry was stirred for 3 h at 65 °C. After cooling to RT, the solids were collected by vacuum filtration. The crude product was then dissolved in *i*PrOH and stirred with excess Na_2CO_3 for 2 h. Filtration through Celite followed by removal of solvent under reduced pressure provided the desired product as a golden solid in 65% yield from 5,6-dichloro-1-methylbenzimidazole. ^{1}H NMR (DMSO-d_6): δ 8.83 (s, 1H), 8.53 (s, 1H), 8.5 (s, 1H), 8.39 (s, 1H). 4.0 (s, 3H), 1.88 (s, 9H), 1.85 (s, 9H); ^{13}C NMR (DMSO-d_6): δ 148.8, 141.8, 139.1, 133.5, 127.5, 127.0, 105.4, 96.9, 60.72, 60.68, 31.4, 27.9, 27.8; HRMS calcd for $C_{17}H_{25}N_4$: 285.2079, found: 285.2079.



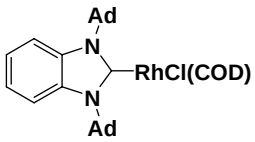
Desymmetrized Benzobisbis(imidazolium) Salt 4. The desymmetrized benzimidazolium salt (3.00 g, 8.21 mmol) was dissolved in CH_3CN (100 mL) and MeI (5 mL, 78.0 mmol) was added. The solution was stirred in a sealed vessel at 60 °C for 3 h. The cooled reaction mixture was then concentrated under vaccum to obtain 4.17 g (99%) of **4** as a brown powder. ^{1}H NMR (DMSO-d_6): δ 9.96 (s, 2H), 9.05 (s, 2H), 8.85 (s, 2H), 4.24 (s, 6H), 1.93 (s, 18H); ^{13}C NMR (DMSO-d_6): δ 147.0, 142.4, 130.0, 129.4, 100.9, 61.8, 34.1, 27.7.



Enetetraamine 5. A 10 mL vial was charged with desymmetrized salt **4** (100 mg 0.197 mmol), NaH (12 mg 0.48 mmol), a catalytic amount of KO*t*Bu (ca. 1 mg) and toluene (2 mL). The vial was then sealed and the reaction mixture was heated to 120 °C for 2 h. The cooled solution was then filtered through a 0.2 μm PTFE filter and solvent was removed under vacuum to obtain 55 mg (94%) of the desired product as a dark red powder. Crystals suitable for X-ray analysis were obtained by slowly cooling of a saturated toluene solution (CCDC 605314). ^{1}H NMR (C_6D_6): δ 6.84 (s, 2H), 2.84 (s, 6H), 1.82 (s, 18H); ^{13}C NMR (C_6D_6): 221.2, 138.7, 130.8, 125.9, 94.7, 57.0, 36.9, 30.7.

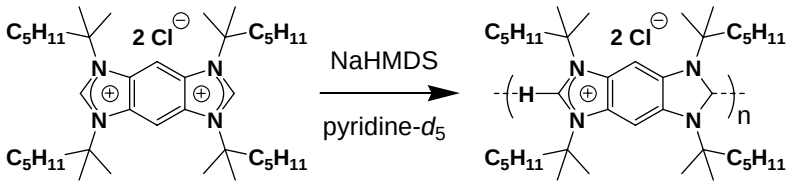


Urea 6. Enetetraamine **5** (0.05 g, 0.168 mmol) was dissolved in benzene and exposed to an atmosphere of oxygen for < 1 minute. After the color of the solution changed from red to brown, the solvent was removed under vacuum to obtain 51 mg (99%) of product as a brown powder. ^{1}H NMR (C_6D_6): δ 6.83 (s, 2H), 2.91 (s, 6H), 1.79 (s, 18H); ^{13}C NMR (C_6D_6): δ 223.0, 155.0, 130.6, 125.8, 92.7, 57.2, 20.5, 26.5; HRMS calcd. for $C_{18}H_{28}N_4O$ [M+H$^+$]: 315.2185; found, 315.2185.



(COD)RhCl(1,3-diadamantylbenzimidazolylidene). 1,3-Diadamantylbenzimidazolylidene was first prepared by deprotonating the corresponding salt[3] using standard methods. ^{1}H NMR (C_6D_6): δ 7.68-7.64 (m, 2H), 7.07-7.04 (m, 2H), 2.56 (s, 12H), 2.07 (s, 6H), 1.69-1.60 (m, 12H); ^{13}C NMR (C_6D_6): δ 224.0, 135.6, 120.0, 114.5, 58.3, 43.4, 36.9, 30.4. In a nitrogen-filled drybox, a 10 mL flask was charged with 1,3-diadamantylbenzimidazolylidene (120 mg, 0.31 mmol), $[(COD)RhCl]_2$ (76 mg, 0.15 mmol), THF (4 mL), and a stir bar. After stirring solution at 60 °C, product began to precipitate within 30 min. After an additional 1 h, the solution was cooled to 23 °C and hexanes (2 mL) were added. Precipitated solids were collected by filtration and dried under vacuum to afford 135 mg (69%) of the desired product as a yellow powder. Crystals suitable for X-ray analysis were obtained by slow evaporation of a saturated CH_2Cl_2/CH_3OH solution (2:1 v/v) (CCDC 605315). ^{1}H NMR ($CDCl_3$): δ 7.81-7.78 (m, 2H), 7.08-7.06 (m, 2H), 4.95 (s, 2H), 3.47-3.44 (m, 6H), 2.99 (m, 8H), 2.41 (s, 10H), 1.94-1.68 (m, 16H); ^{13}C NMR ($CDCl_3$): δ 194.1 (d, J = 49.1 Hz), 135.0, 120.3, 115.3, 92.0 (d, J = 8.5 Hz), 67.2 (d, J = 15.3 Hz), 62.0, 42.9, 36.4, 32.3, 30.3, 28.7.

Footnote 11: Addition of 1.0 equivalent of base to benzobis(imidazolium) salts 1 afforded polymeric materials. The feasibility of selectively monodeprotonating the bis(azolium) salts described above was studied using ^{1}H NMR spectroscopy. Addition of 1.0 equiv of NaHMDS to a suspension of bis(azolium) salts **1c** in common solvents (C_6D_6, toluene-d_8, CD_2Cl_2, pyridine-d_5, THF-d_8) resulted in formation of the respective bis(carbene) leaving an equivalent amount of bis(azolium) salt; mono(azolium) species were not detected. We believed this process was driven by the high solubility of the bis(carbene)s facilitated by the insolubility of the bis(azolium) salts in these solvents. To overcome this limitation, a highly soluble variant featuring *N*-(1,1-dimethylhexyl) groups was synthesized as described below. Addition of 1.0 equiv of NaHMDS to a pyridine-d_5 solution of this compound revealed signals indicative of coordination-type polymers in the ^{1}H NMR spectrum (see Eq. 1). Similar coordination phenomena with mixtures of imidazolylidenes and their respective imidazolium salts has been reported.[4]



(1)

Tetrakis[*N*-(1,1-dimethylhexyl)]benzobis(imidazolium) dichloride. The tetrakis[*N*-(1,1-dimethylhexyl)]benzobis(imidazolium) dichloride salt was prepared according to our previously reported procedure using 1,1-dimethylhexylamine.[1a] ^{1}H NMR (DMSO-d_6): δ 9.15 (s, 2H), 8.60 (s, 2H), 2.24 (br, 8H), 1.94 (s, 24H), 1.12-1.03 (br, 24H), 0.68 (br, 12H); ^{13}C NMR (DMSO-d_6): δ 128.8, 102.5, 65.3, 31.1, 26.4, 22.7, 21.7, 13.6.

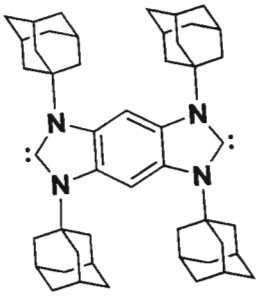
Monodeprotonation Experiment. In a drybox, tetrakis[*N*-(1,1-dimethylhexyl)]benzobis(imidazolium) dichloride (72 mg, 0.11 mmol) was dissolved in pyridine-d_5 (1.0 mL). To the solution was added NaHMDS in THF (2.0 M, 55 μL, 0.11 mmol). The mixture was stirred for 1 h then filtered through 0.2 μm PTFE filter. ^{1}H NMR analysis revealed significantly broadened signals indicative of polymer formation. Notably, the resonances for imidazolium (NC*H*N) and arene (C_6H_2) protons were shifted upfield (δ = 10.88 and 8.42 ppm, respectively) relative to the bis(azolium) salt (corresponding signals at δ = 10.95 and 8.95; solvent = pyridine-d_5).

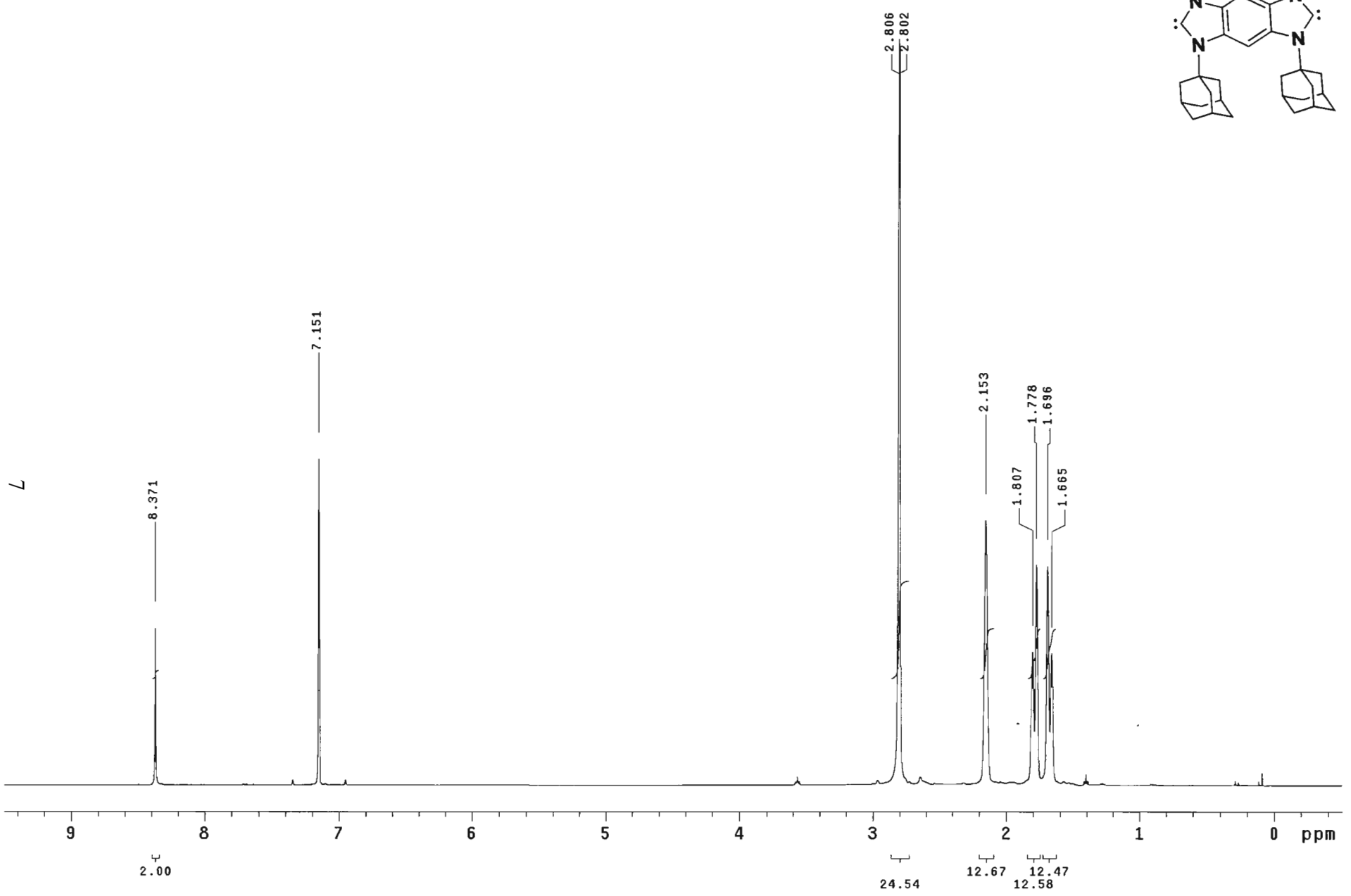
[1] a) D. M. Khramov, A. J. Boydston, C. W. Bielawski, *Org. Lett.* **2006**, 8, 1831. b) A. J. Boydston, D. M. Khramov, C. W. Bielawski, *Tetrahedron Lett.* **2006**, *47*, 5123.

[2] B. N. Feitelson, P. Mamalis, R. J. Moualim, V. Petrow, O. Stephenson, B. Sturgeon, *J. Chem. Soc.* **1952**, 2389.

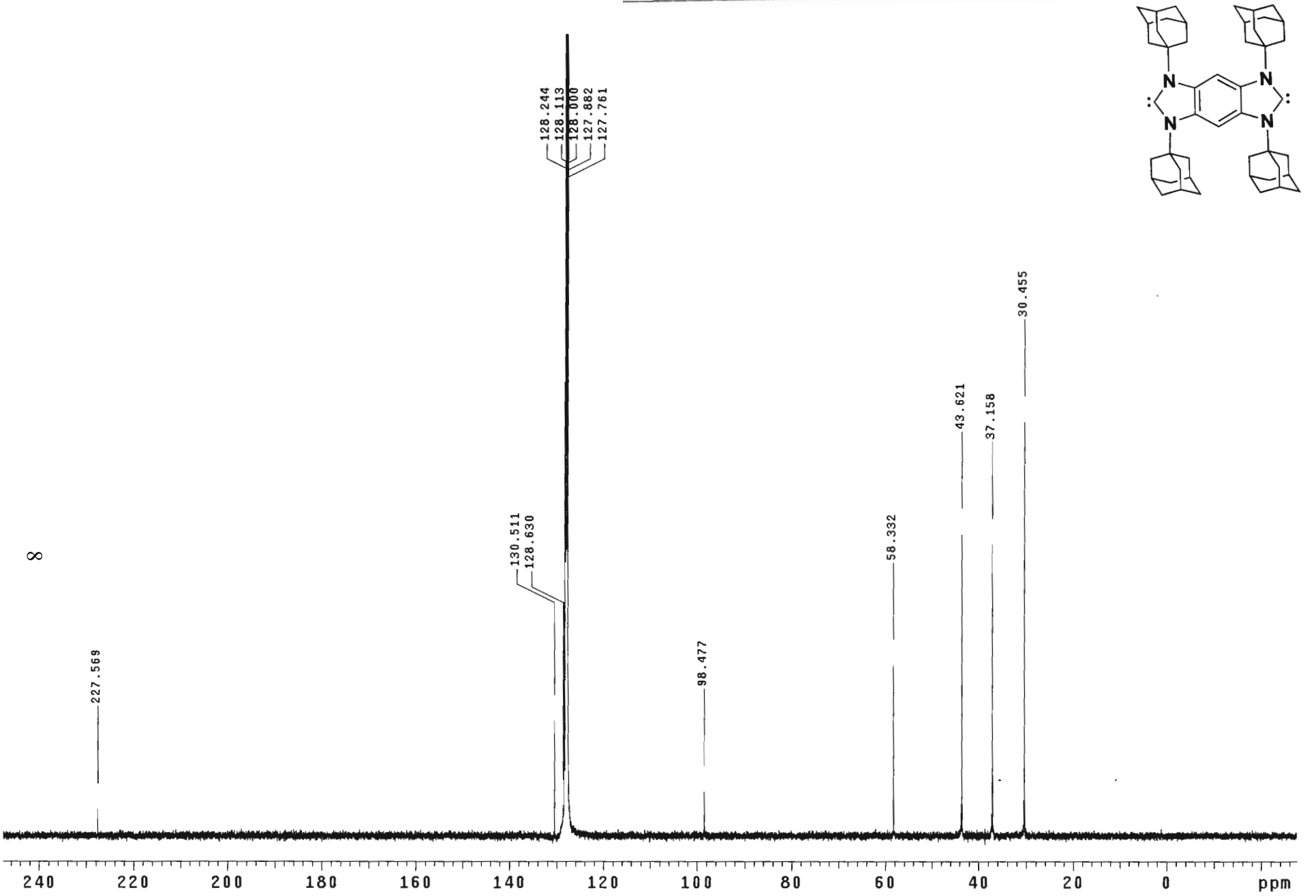
[3] N. Hadei, E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, *Org. Lett.* **2005**, *7*, 1991.

[4] A. J. Arduengo, III, S. F. Gamper, M. Tamm, J. C. Calabrese, F. Davidson, H. A. Craig, *J. Am. Chem. Soc.* **1995**, *117*, 572.

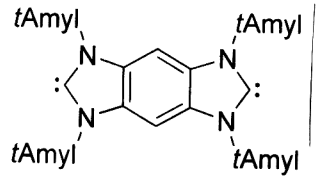


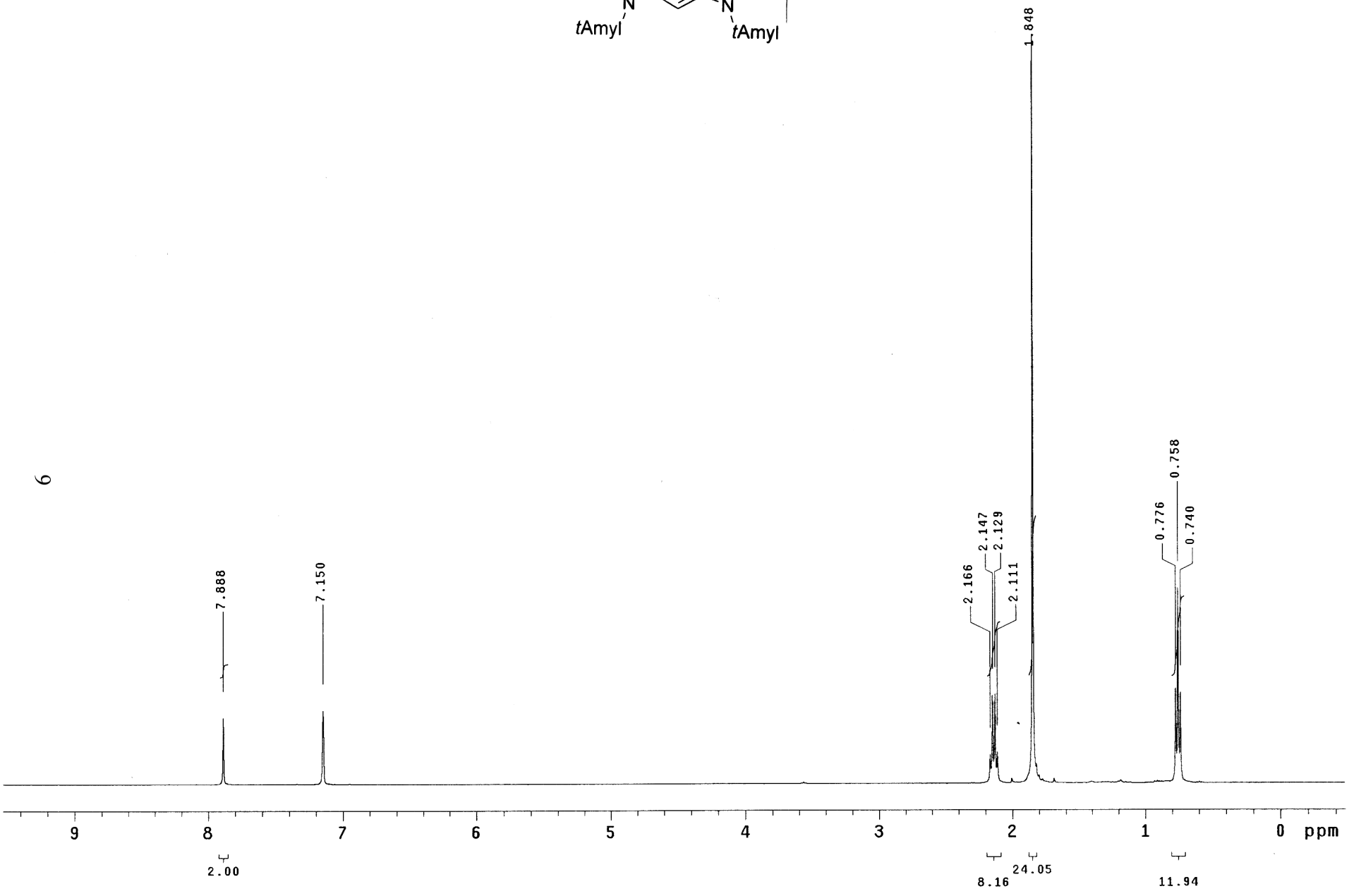


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 24.5 degrees Acq. time 2.856 sec Width 5602.2 Hz 49 repetitions	OBSERVE H1, 400.2670009	DATA PROCESSING Line broadening 0.1 Hz FT size 32768 Total time 3 minutes			dmk120305-1 4Ad carbene Pulse Sequence: s2pul Solvent: Benzene Ambient temperature Mercury-400 "nmr6"

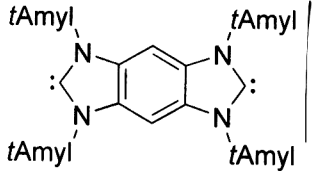


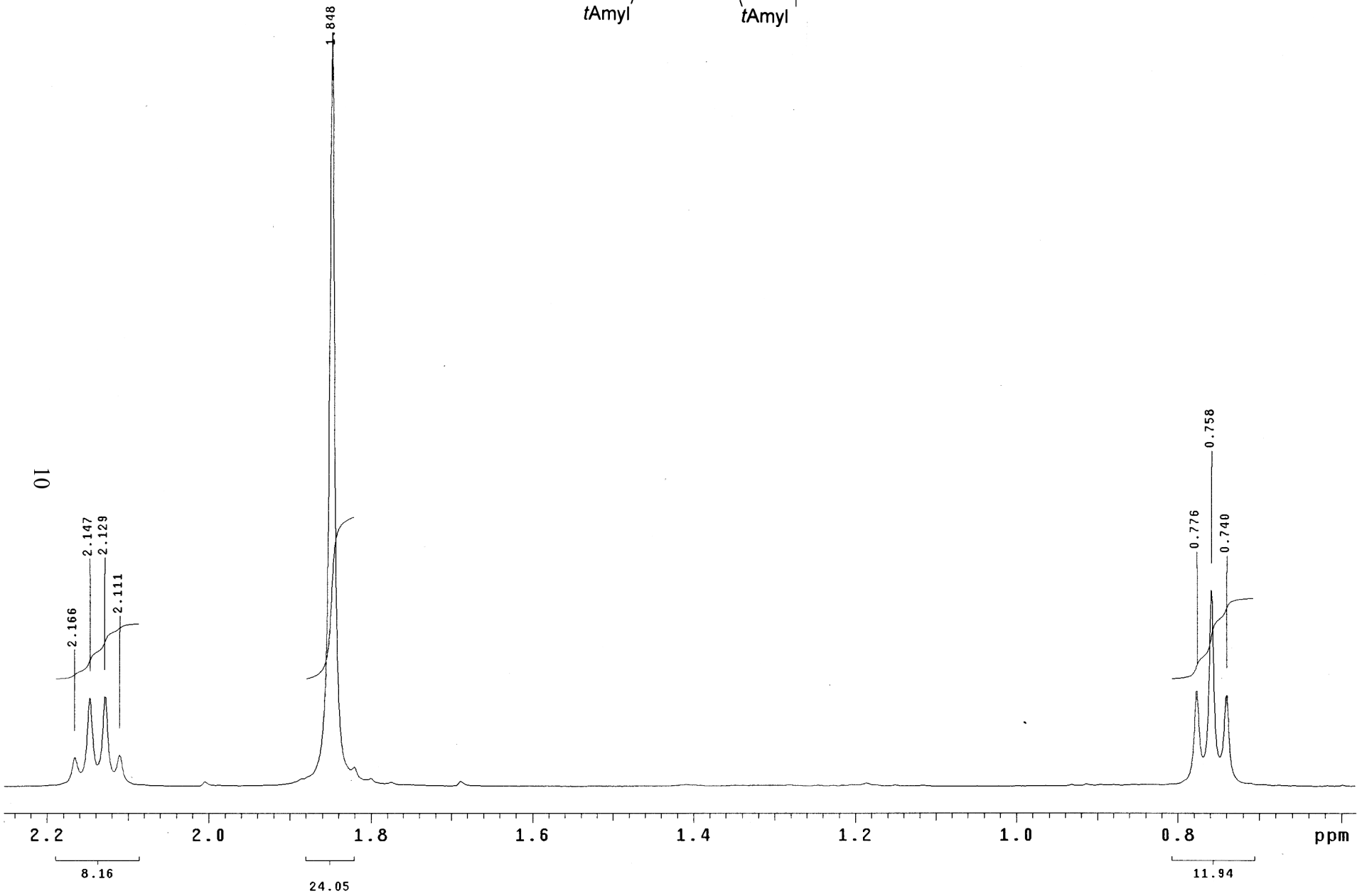
PULSE SEQUENCE Relax. delay 1.000 sec Pulse 22.5 degrees Acq. time 1.280 sec Width 27700.8 Hz 13736 repetitions	OBSERVE C13, 100.6471863 DECOUPLE H1, 400.2690316 Power 38 dB continuously on WALTZ-16 modulated	DATA PROCESSING Line broadening 1.0 Hz FT size 131072 Total time 8.7 hours			dmk120305-2 4Ad carbene Pulse Sequence: s2pul Solvent: Benzene Ambient temperature Mercury-400 "nmr6"



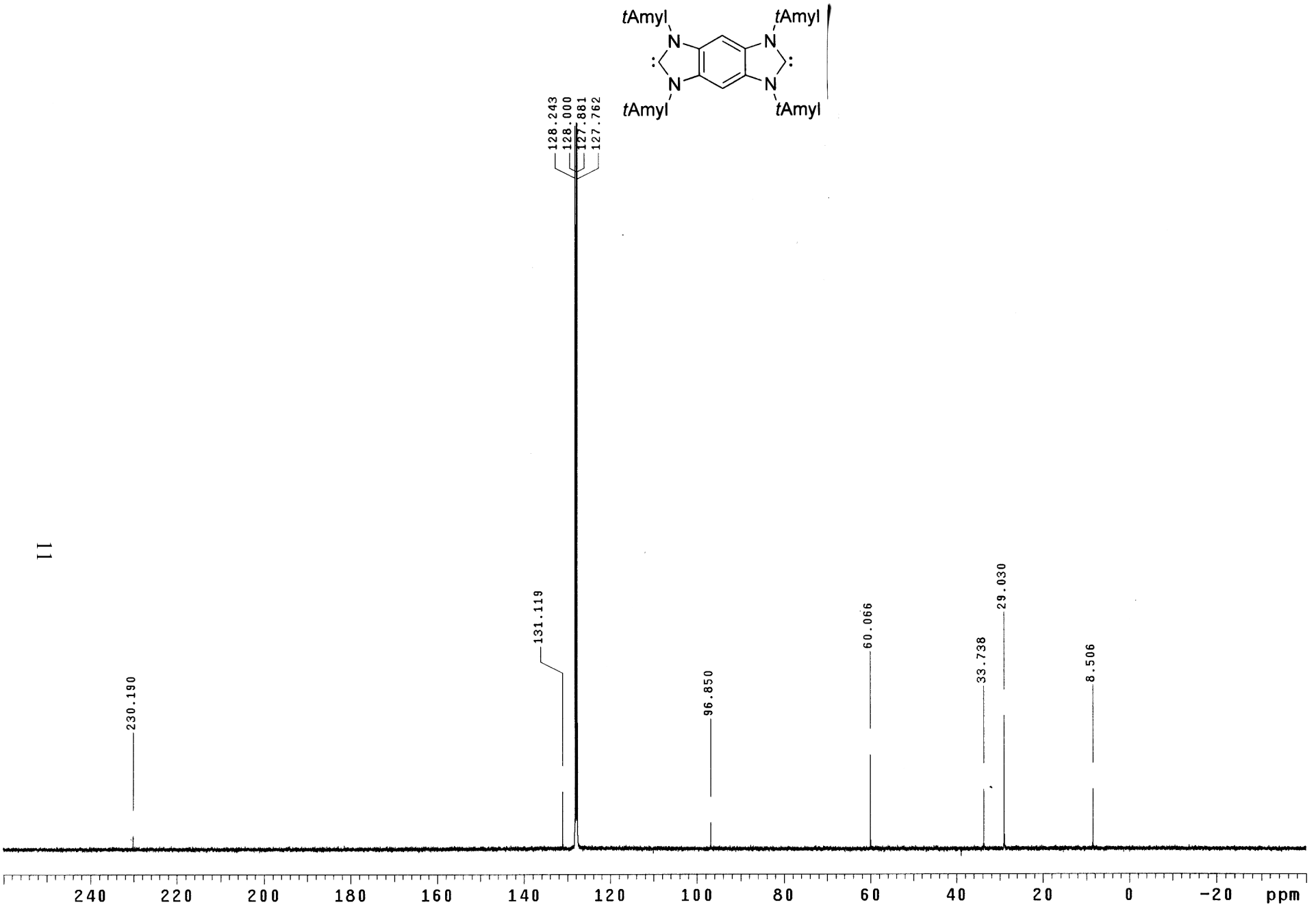


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 32.7 degrees Acq. time 2.856 sec Width 5602.2 Hz 4 repetitions	OBSERVE H1, 400.2670009	DATA PROCESSING Line broadening 0.1 Hz FT size 32768 Total time 1 minute			dmk032306-3 tAmyl biscarbene Pulse Sequence: s2pul Solvent: Benzene Ambient temperature Mercury-400 "nmr6"



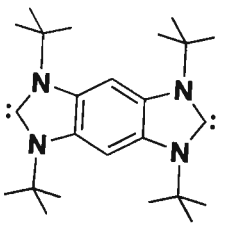


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 32.7 degrees Acq. time 2.856 sec Width 5602.2 Hz 4 repetitions	OBSERVE H1, 400.2670009	DATA PROCESSING Line broadening 0.1 Hz FT size 32768 Total time 1 minute			dmk032306-3 tAmyl biscarbene Pulse Sequence: s2pul Solvent: Benzene Ambient temperature Mercury-400 "nmr6"

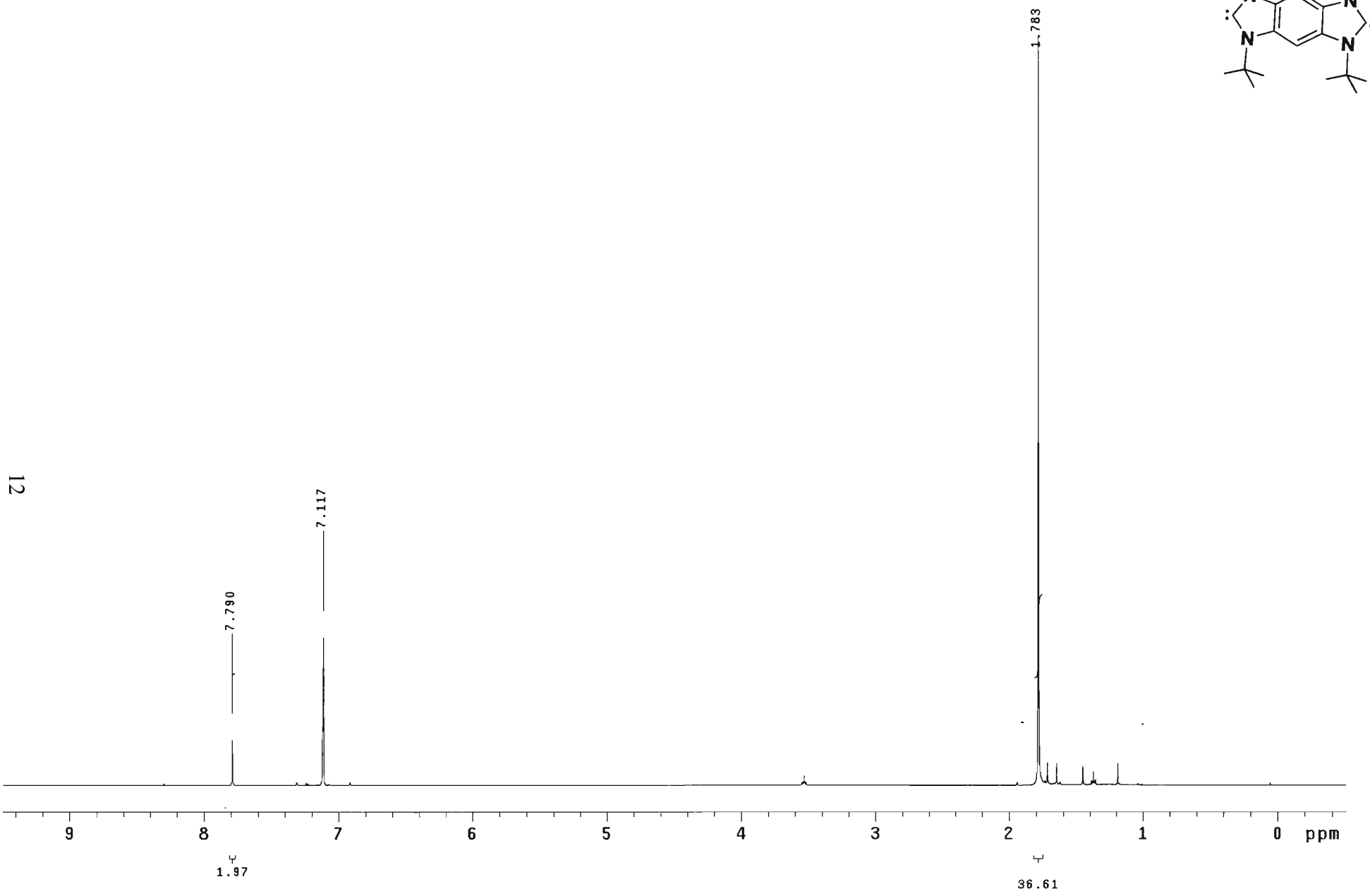


11

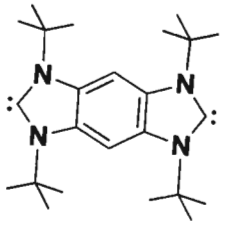
PULSE SEQUENCE Relax. delay 1.000 sec Pulse 30.0 degrees Acq. time 1.280 sec Width 30211.5 Hz 244 repetitions	OBSERVE C13, 100.6471862 DECOUPLE H1, 400.2690316 Power 38 dB continuously on WALTZ-16 modulated	DATA PROCESSING Line broadening 1.0 Hz FT size 131072 Total time 9 minutes			dmk032306-4 tAmyl biscarbene Pulse Sequence: s2pul Solvent: Benzene Ambient temperature Mercury-400 "nmr6"

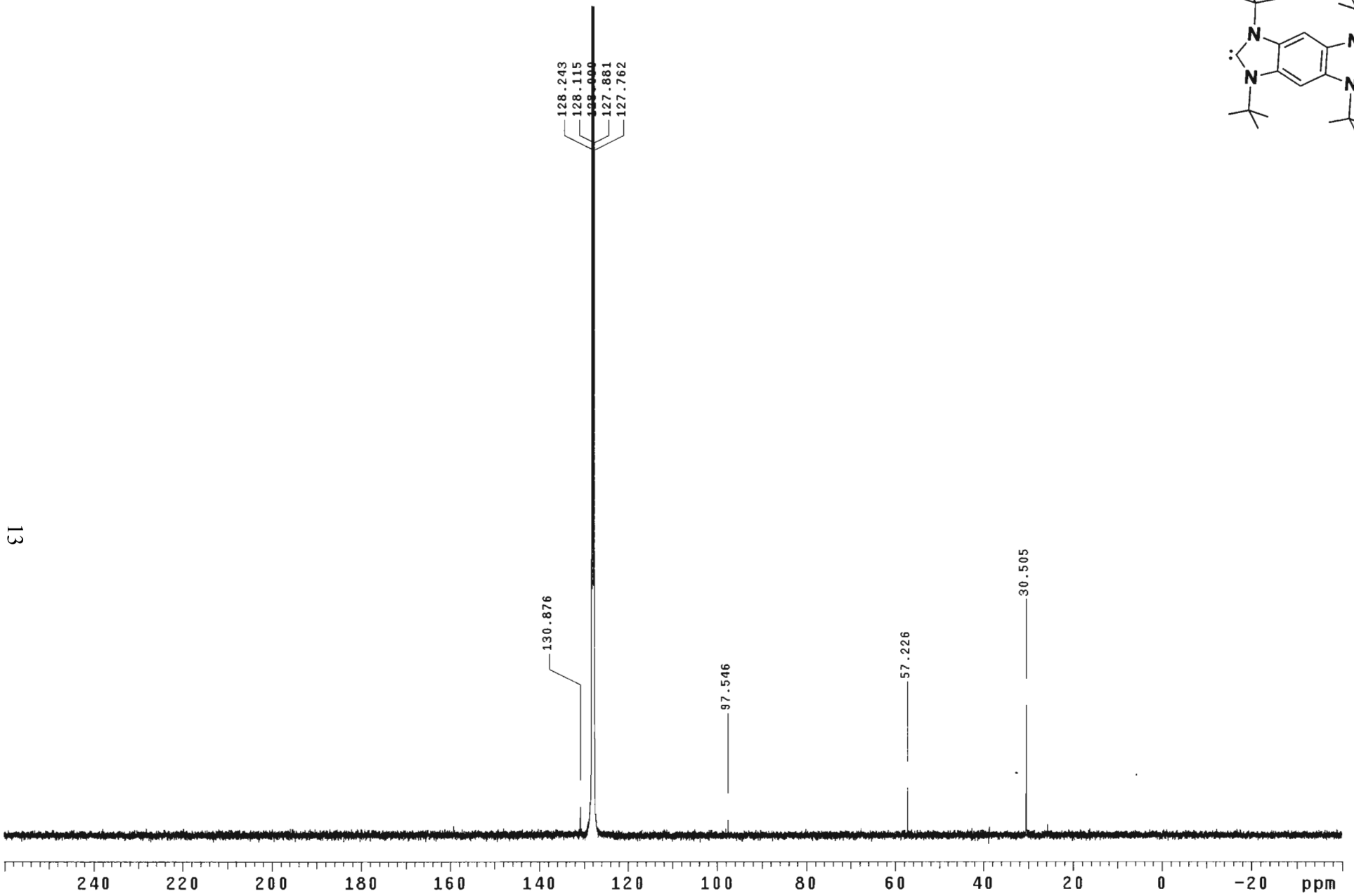


12

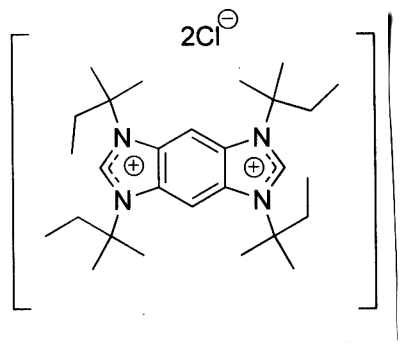


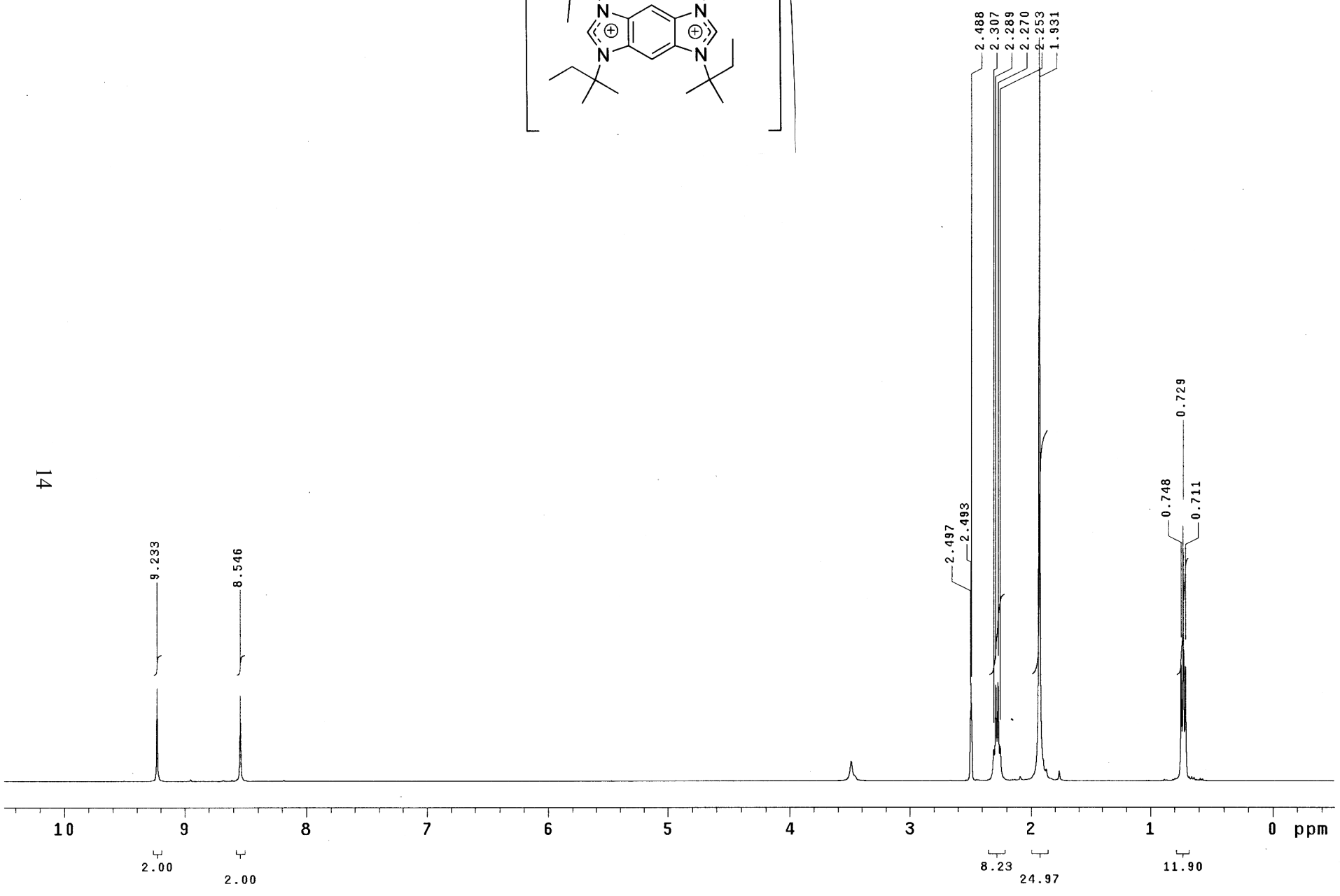
PULSE SEQUENCE Relax. delay 1.000 sec Pulse 32.7 degrees Acq. time 2.856 sec Width 5602.2 Hz 9 repetitions	OBSERVE H1, 400.2670144	DATA PROCESSING Line broadening 0.1 Hz FT size 32768 Total time 1 minute			dmk120605-1 4tBu carbene Pulse Sequence: s2pul Solvent: Benzene Ambient temperature Mercury-400 "nmr6"



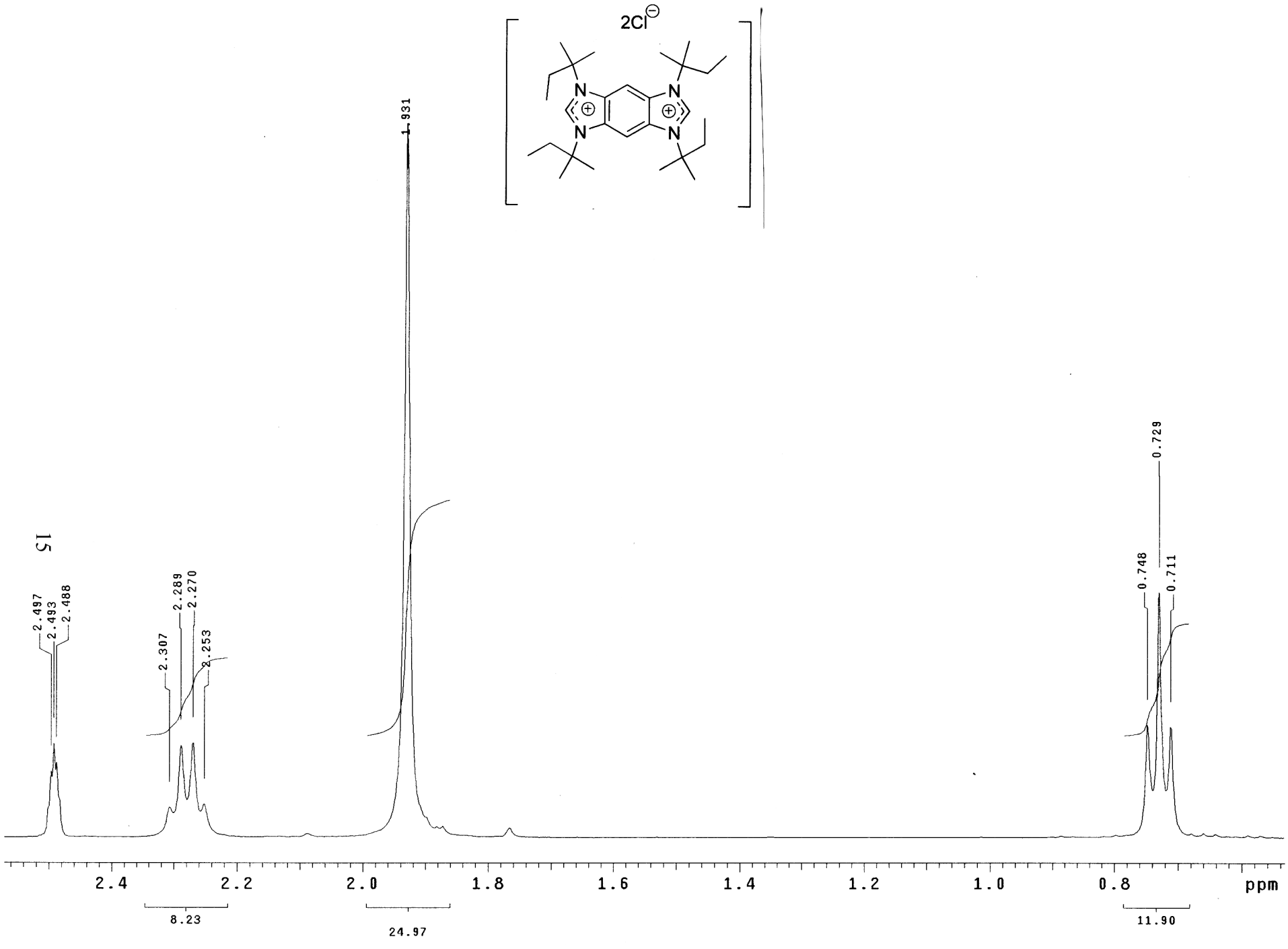


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 22.5 degrees Acq. time 1.280 sec Width 30211.5 Hz 13231 repetitions	OBSERVE C13, 100.6471862 DECOUPLE H1, 400.2690316 Power 38 dB continuously on WALTZ-16 modulated	DATA PROCESSING Line broadening 1.0 Hz FT size 131072 Total time 8.4 hours			dmk120605-2 4tBu carbene Pulse Sequence: s2pul Solvent: Benzene Ambient temperature Mercury-400 "nmr6"



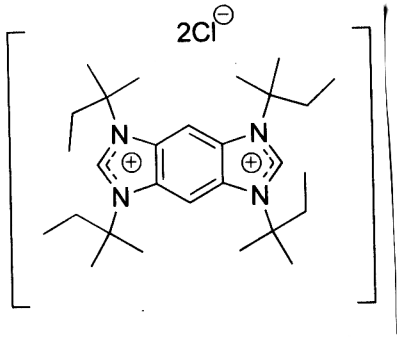


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 32.7 degrees Acq. time 2.856 sec Width 5602.2 Hz 3 repetitions	OBSERVE H1, 400.2688771	DATA PROCESSING Line broadening 0.1 Hz FT size 32768 Total time 1 minute			dmk032306-1 tAmyl salt Pulse Sequence: s2pul Solvent: DMSO Ambient temperature Mercury-400 "nmr6"

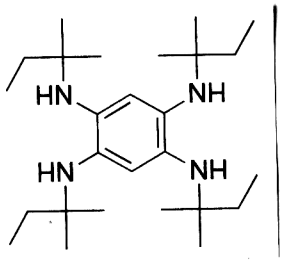


15

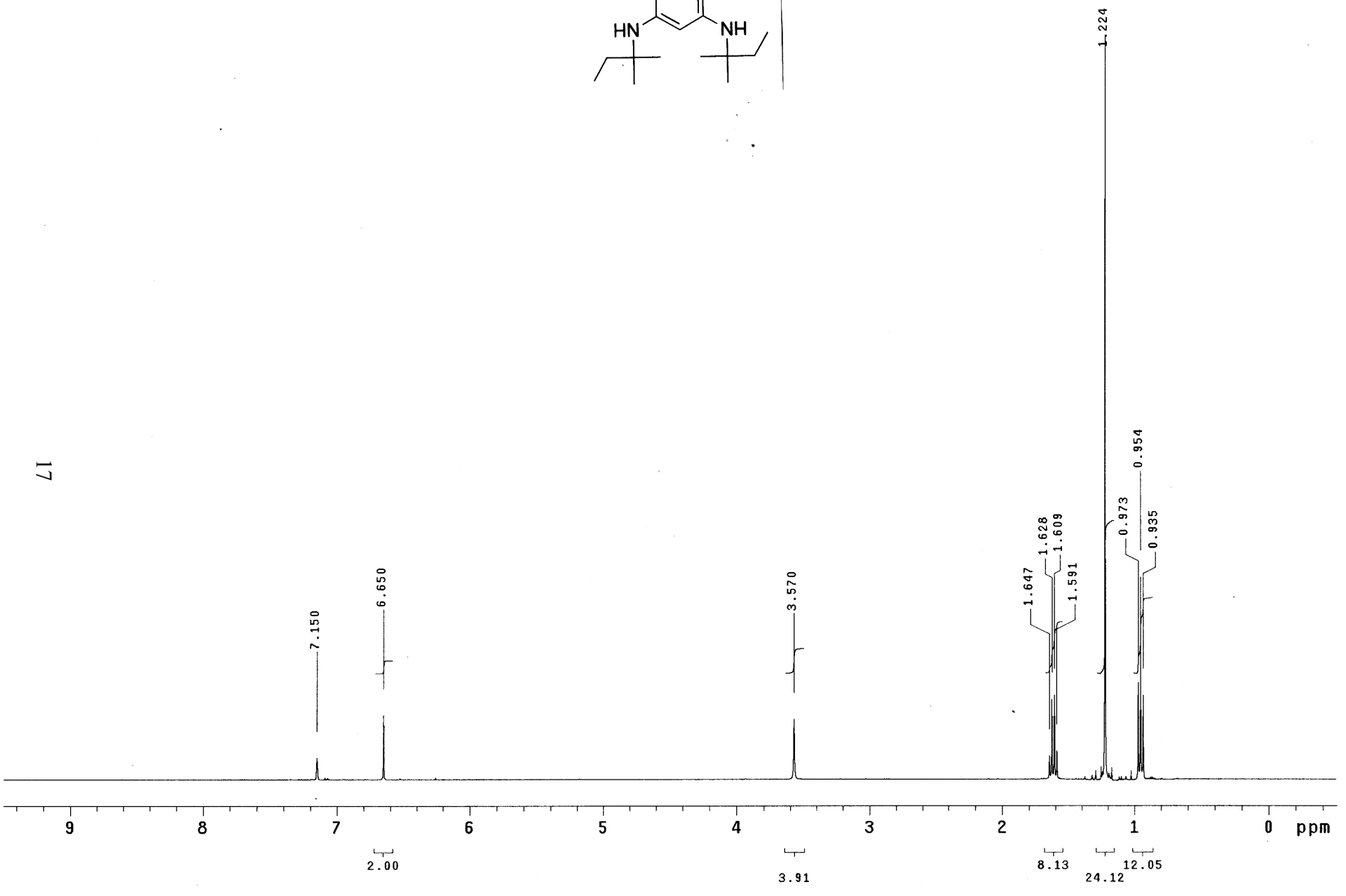
PULSE SEQUENCE Relax. delay 1.000 sec Pulse 32.7 degrees Acq. time 2.856 sec Width 5602.2 Hz 3 repetitions	OBSERVE H1, 400.2688771	DATA PROCESSING Line broadening 0.1 Hz FT size 32768 Total time 1 minute			dmk032306-1 tAmyl salt Pulse Sequence: s2pul Solvent: DMSO Ambient temperature Mercury-400 "nmr6"



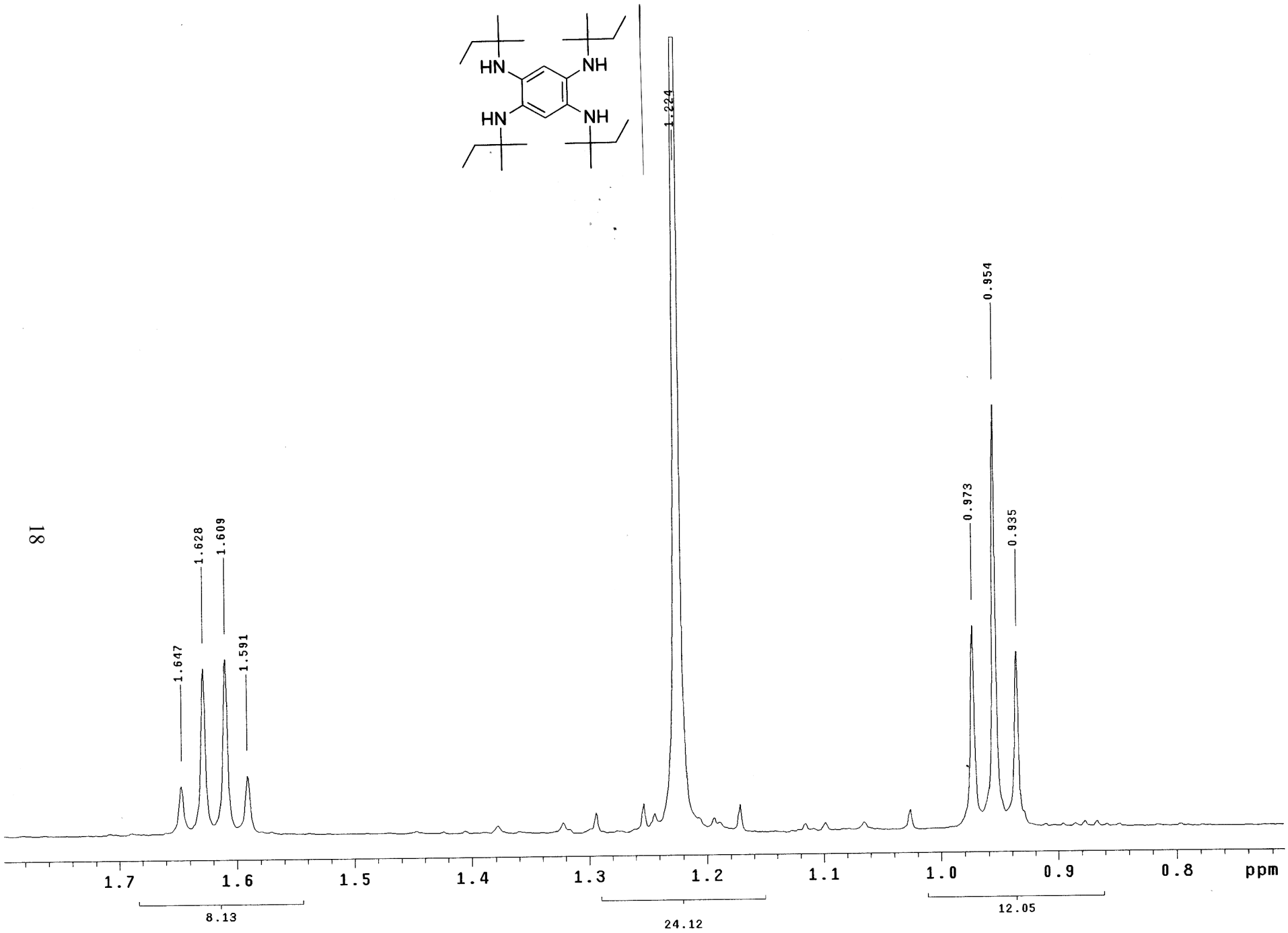
PULSE SEQUENCE Relax. delay 1.000 sec Pulse 30.0 degrees Acq. time 1.280 sec Width 25188.9 Hz 104 repetitions	OBSERVE C13, 100.6477380 DECOUPLE H1, 400.2708968 Power 38 dB continuously on WALTZ-16 modulated	DATA PROCESSING Line broadening 1.0 Hz FT size 65536 Total time 3 minutes			dmk032306-2 tAmyl salt Pulse Sequence: s2pul Solvent: DMSO Ambient temperature Mercury-400 "nmr6"



17

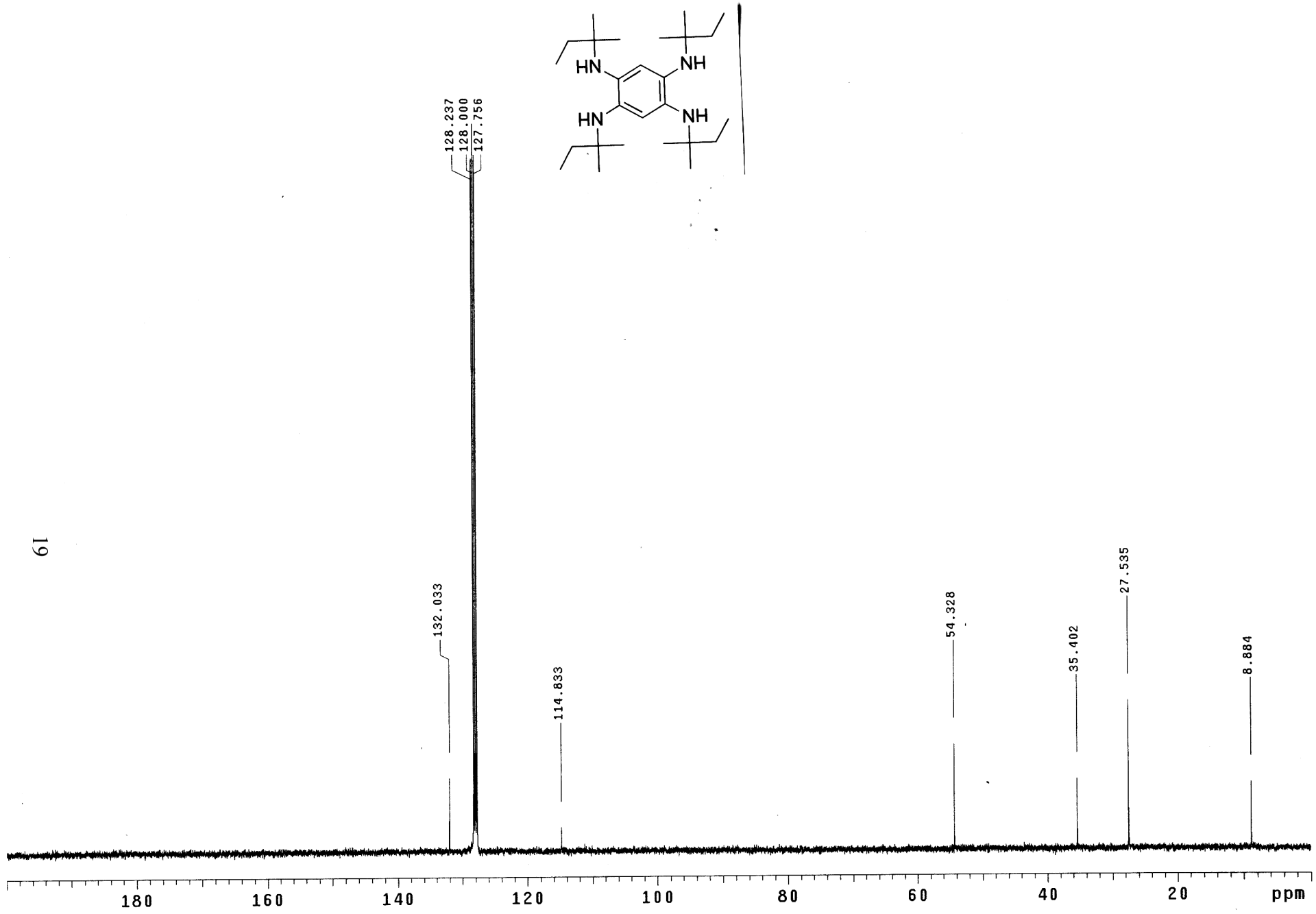


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 32.7 degrees Acq. time 2.856 sec Width 5602.2 Hz 3 repetitions	OBSERVE H1, 400.2670012	DATA PROCESSING Line broadening 0.1 Hz FT size 32768 Total time 1 minute			dmk032205-1 aryl amination tAmyl Pulse Sequence: s2pul Solvent: Benzene Ambient temperature Mercury-400 "nmr6"

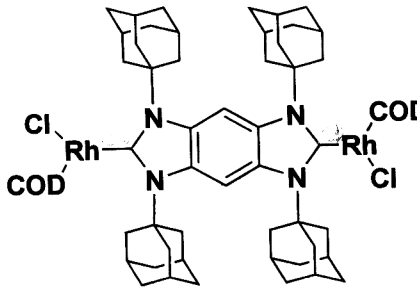


18

PULSE SEQUENCE Relax. delay 1.000 sec Pulse 32.7 degrees Acq. time 2.856 sec Width 5602.2 Hz 3 repetitions	OBSERVE H1, 400.2670012	DATA PROCESSING Line broadening 0.1 Hz FT size 32768 Total time 1 minute			dmk032205-1 aryl amination tAmyl Pulse Sequence: s2pul Solvent: Benzene Ambient temperature Mercury-400 "nmr6"



PULSE SEQUENCE Relax. delay 1.000 sec Pulse 37.5 degrees Acq. time 1.280 sec Width 25188.9 Hz 74 repetitions	OBSERVE C13, 100.6471864 DECOUPLE H1, 400.2690316 Power 38 dB continuously on WALTZ-16 modulated	DATA PROCESSING Line broadening 1.0 Hz FT size 65536 Total time 2 minutes			dmk032205-2 aryl amination tAmyl Pulse Sequence: s2pul Solvent: Benzene Ambient temperature Mercury-400 "nmr6"

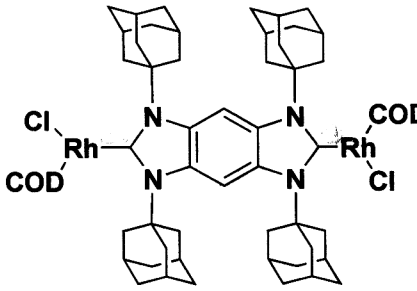


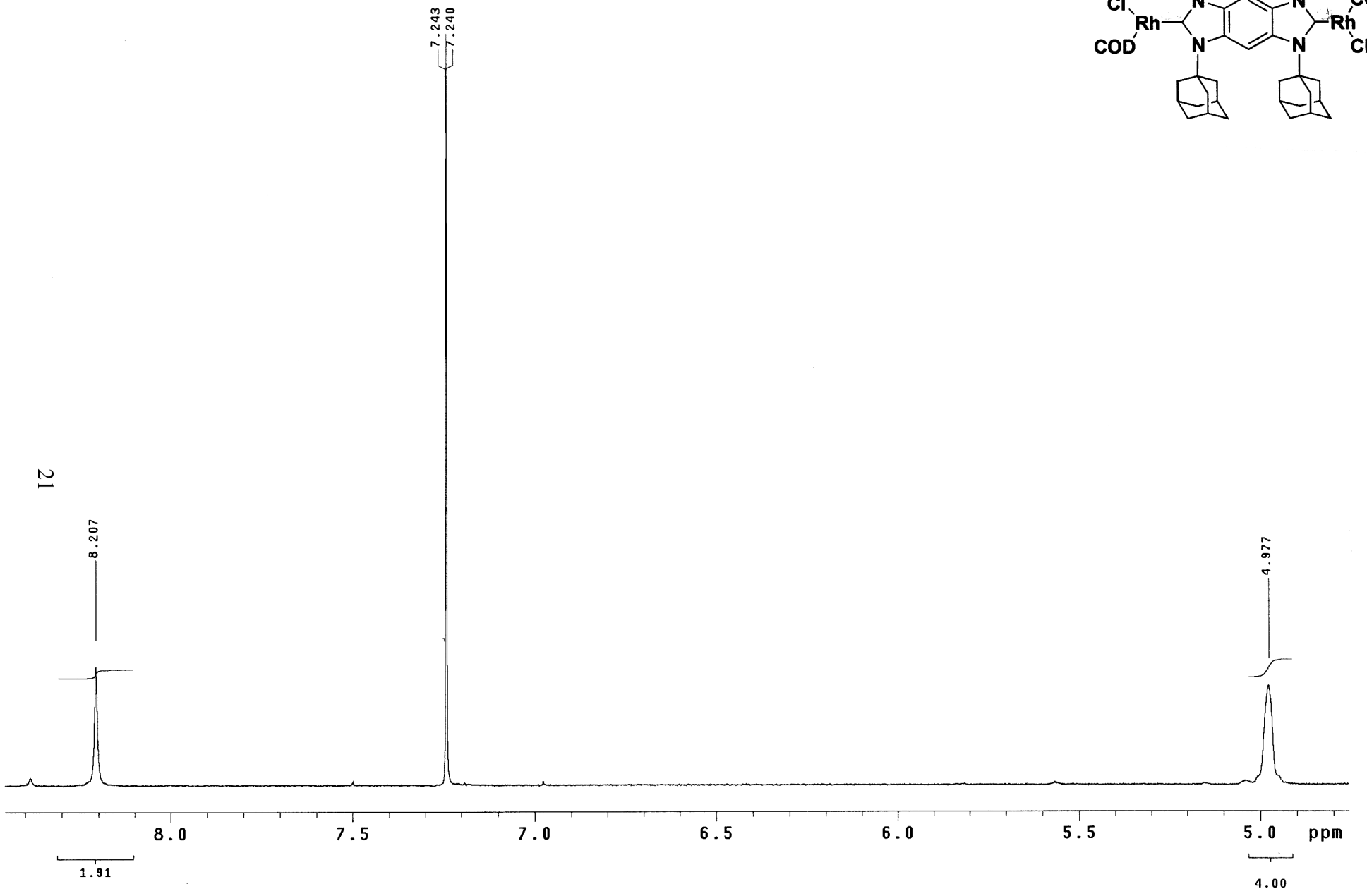
20

9 8 7 6 5 4 3 2 1 0 ppm

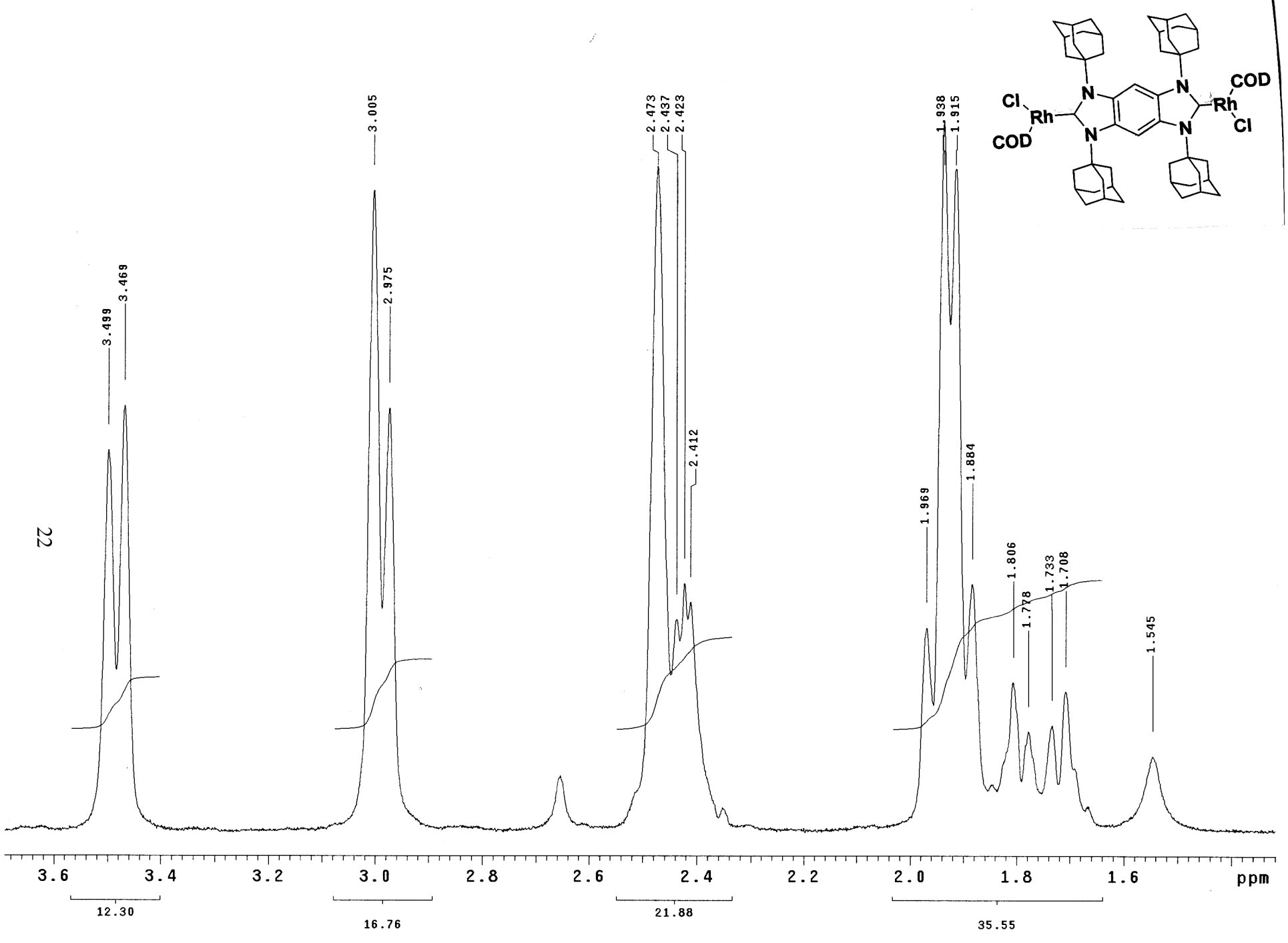
1.91 4.00 12.30 16.76 21.88 35.55

PULSE SEQUENCE Relax. delay 2.000 sec Pulse 24.5 degrees Acq. time 2.856 sec Width 5602.2 Hz 58 repetitions	OBSERVE H1, 400.2669856	DATA PROCESSING Line broadening 0.1 Hz FT size 32768 Total time 4 minutes			dmk120405-4 4Ad carbene RhClCOD complex Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-400 "nmr6"



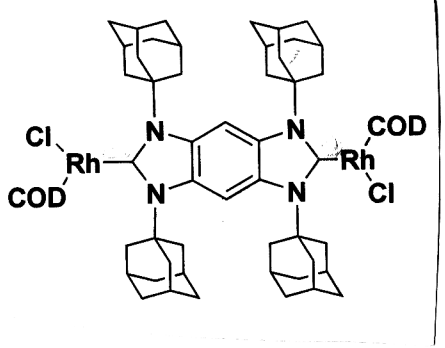


PULSE SEQUENCE Relax. delay 2.000 sec Pulse 24.5 degrees Acq. time 2.856 sec Width 5602.2 Hz 58 repetitions	OBSERVE H1, 400.2669856	DATA PROCESSING Line broadening 0.1 Hz FT size 32768 Total time 4 minutes			dmk120405-4 4Ad carbene RhClCOD complex Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-400 "nmr6"

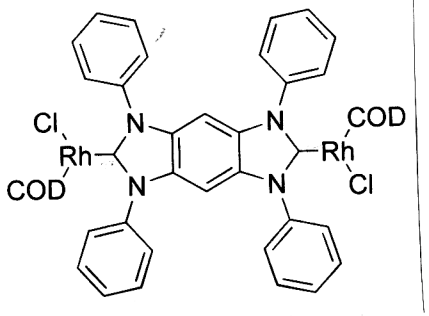


22

PULSE SEQUENCE Relax. delay 2.000 sec Pulse 24.5 degrees Acq. time 2.856 sec Width 5602.2 Hz 58 repetitions	OBSERVE H1, 400.2669856	DATA PROCESSING Line broadening 0.1 Hz FT size 32768 Total time 4 minutes			dmk120405-4 4Ad carbene RhClCOD complex Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-400 "nmr6"



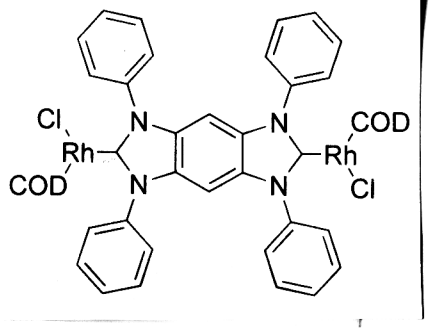
PULSE SEQUENCE Relax. delay 2.000 sec Pulse 22.5 degrees Acq. time 1.280 sec Width 30211.5 Hz 21502 repetitions	OBSERVE C13, 100.6472121 DECOUPLE H1, 400.2689955 Power 38 dB continuously on WALTZ-16 modulated	DATA PROCESSING Line broadening 1.0 Hz FT size 131072 Total time 19.6 hours			dmk120405-5 4Ad carbene RhClCOD complex Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-400 "nmr6"

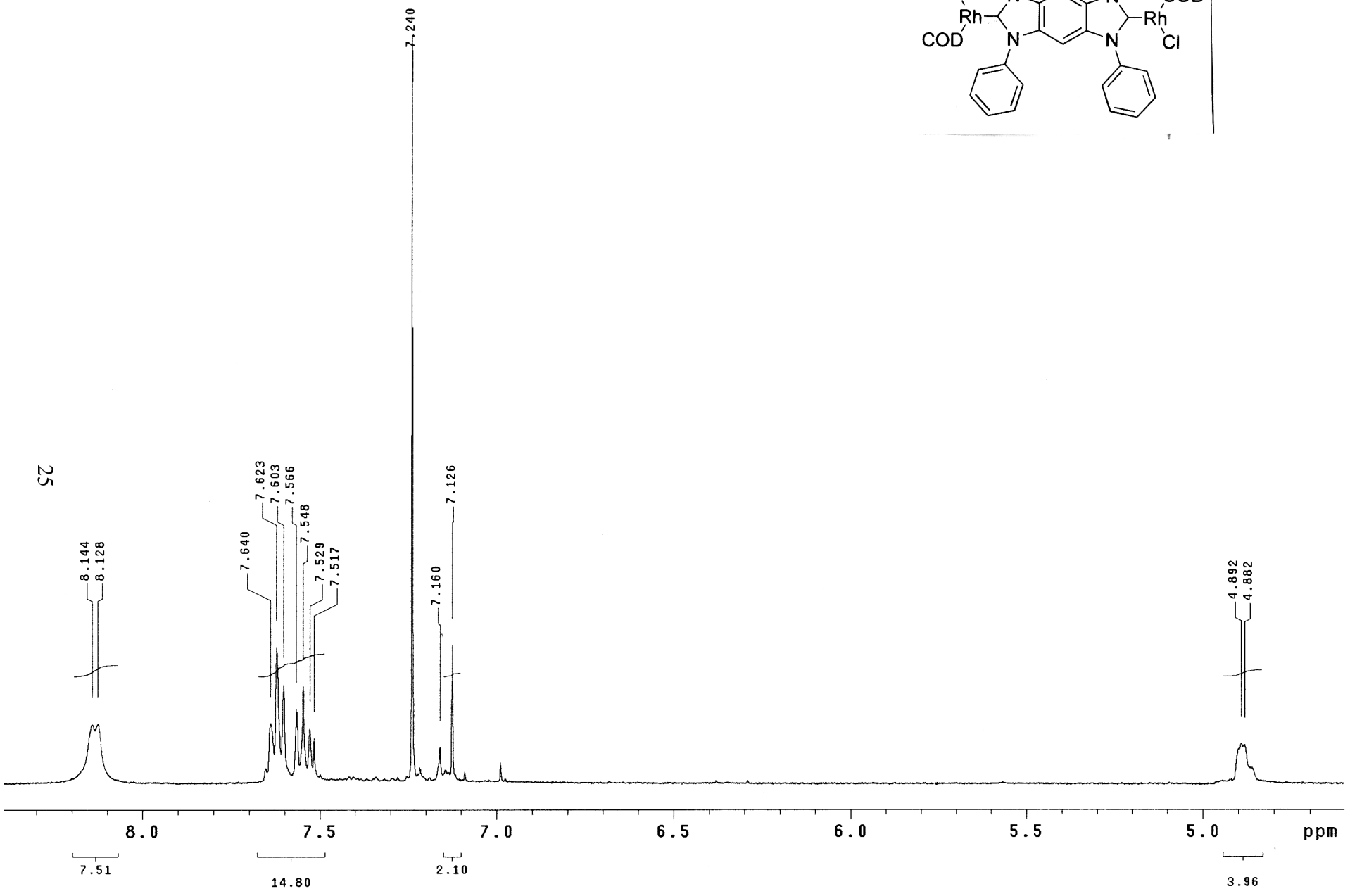


9 8 7 6 5 4 3 2 1 0 ppm

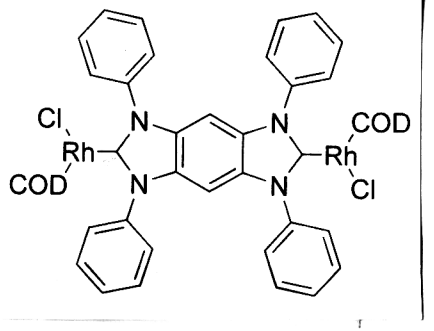
7.51 14.80 2.10 3.96 3.70 21.14

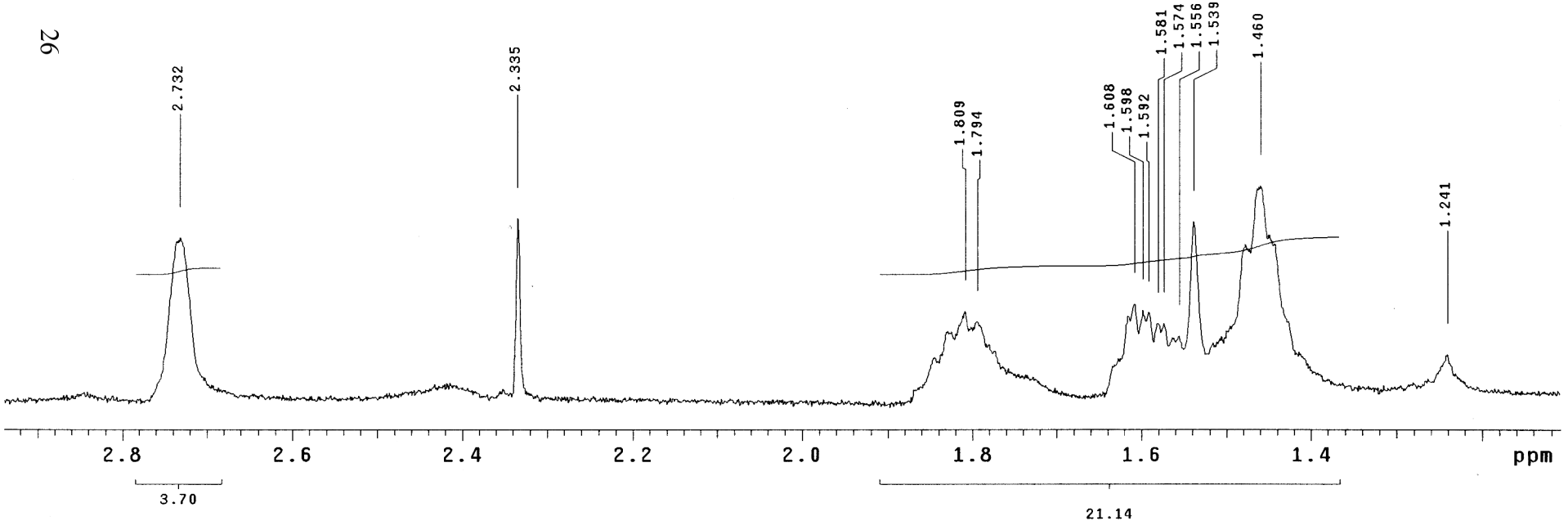
PULSE SEQUENCE Relax. delay 1.000 sec Pulse 32.7 degrees Acq. time 2.856 sec Width 5602.2 Hz 20 repetitions	OBSERVE H1, 400.2669859	DATA PROCESSING Line broadening 0.1 Hz FT size 32768 Total time 1 minute			dmk022206-8 4Ph-Rh(COD)Cl complex Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-400 "nmr6"



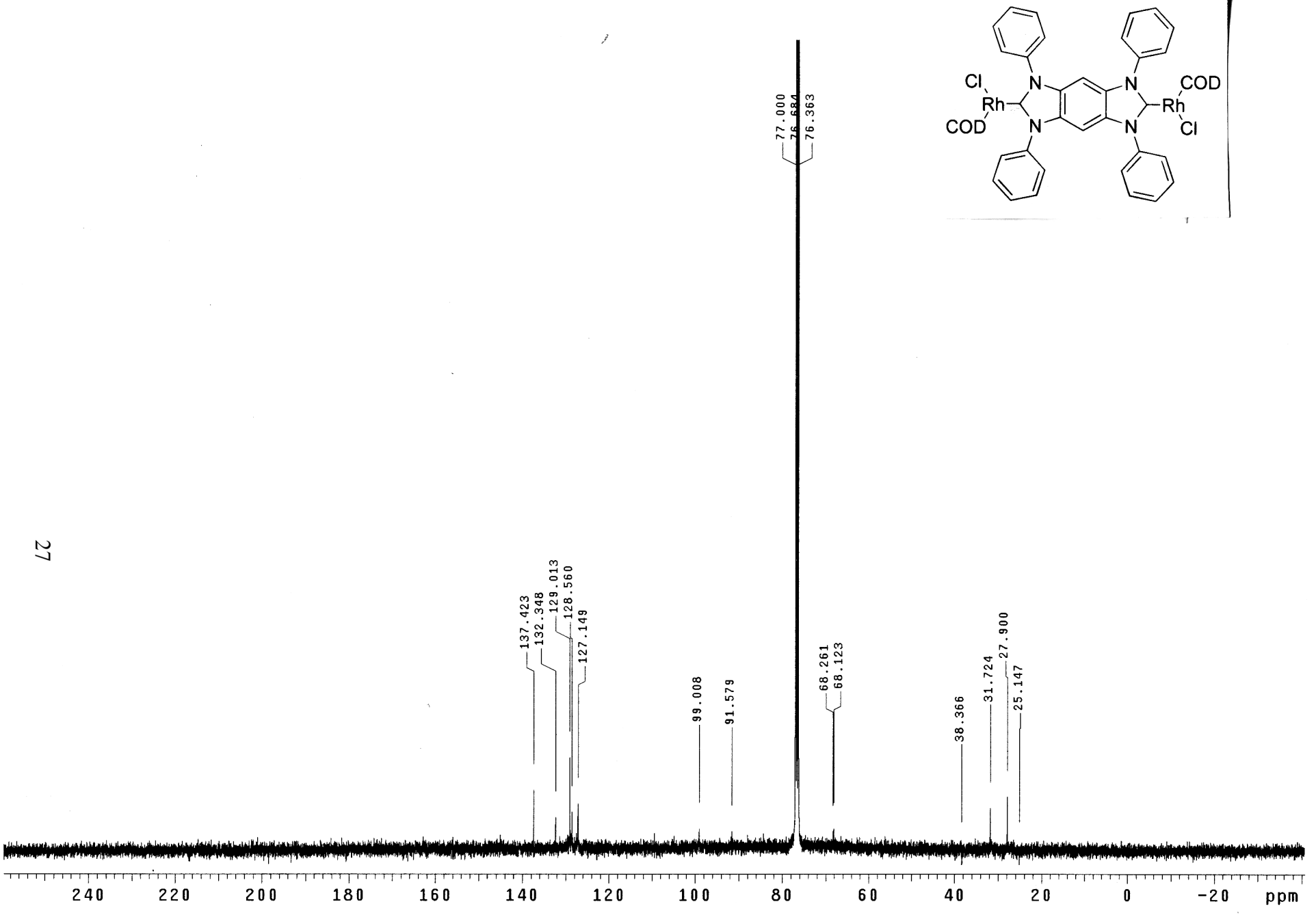


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 32.7 degrees Acq. time 2.856 sec Width 5602.2 Hz 20 repetitions	OBSERVE H1, 400.2669859	DATA PROCESSING Line broadening 0.1 Hz FT size 32768 Total time 1 minute			dmk022206-8 4Ph-Rh(COD)Cl complex Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-400 "nmr6"



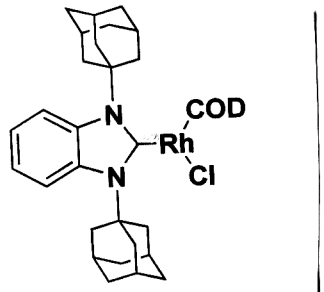


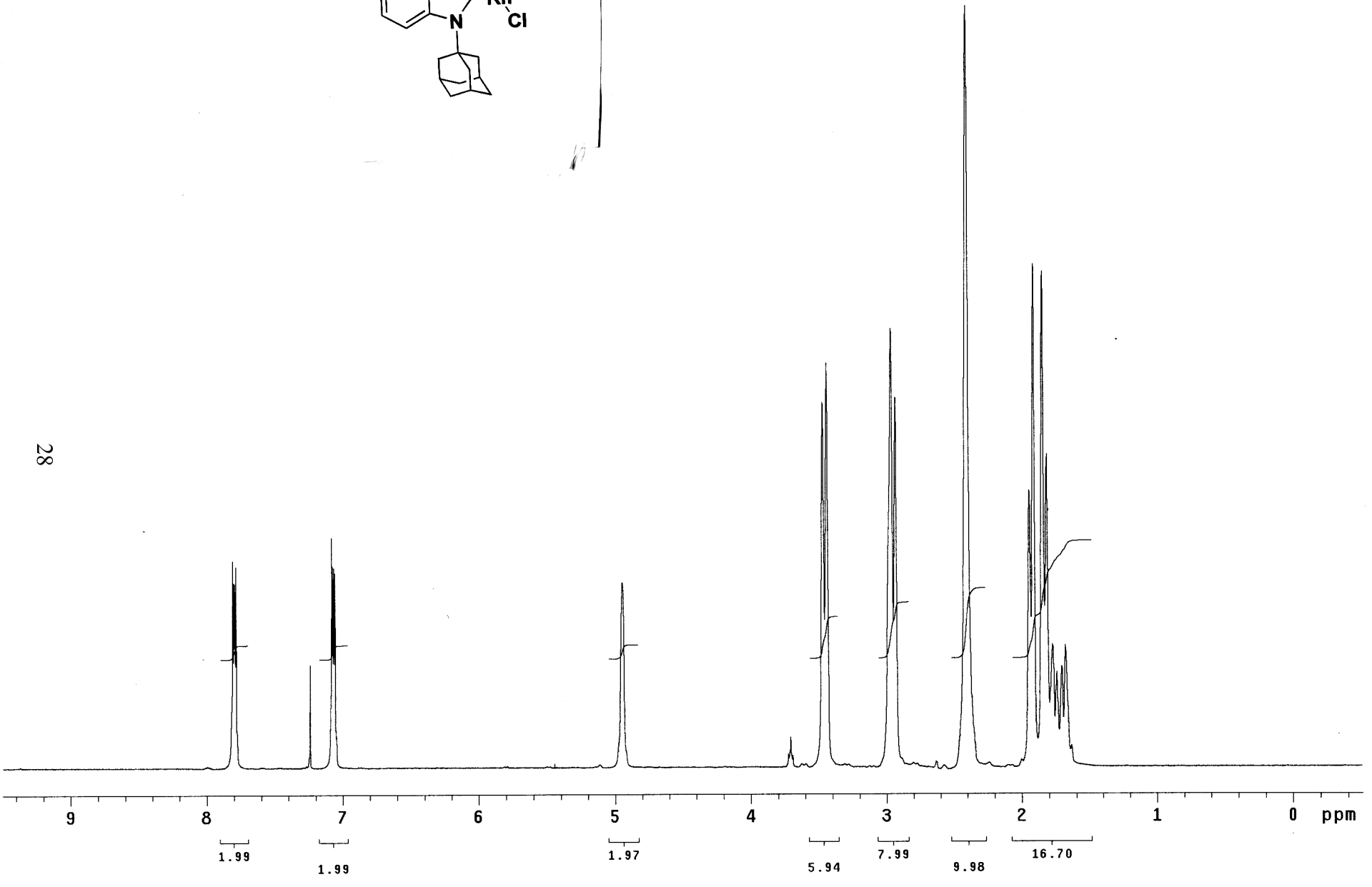
PULSE SEQUENCE Relax. delay 1.000 sec Pulse 32.7 degrees Acq. time 2.856 sec Width 5602.2 Hz 20 repetitions	OBSERVE H1, 400.2669859	DATA PROCESSING Line broadening 0.1 Hz FT size 32768 Total time 1 minute			dmk022206-8 4Ph-Rh(COD)Cl complex Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-400 "nmr6"



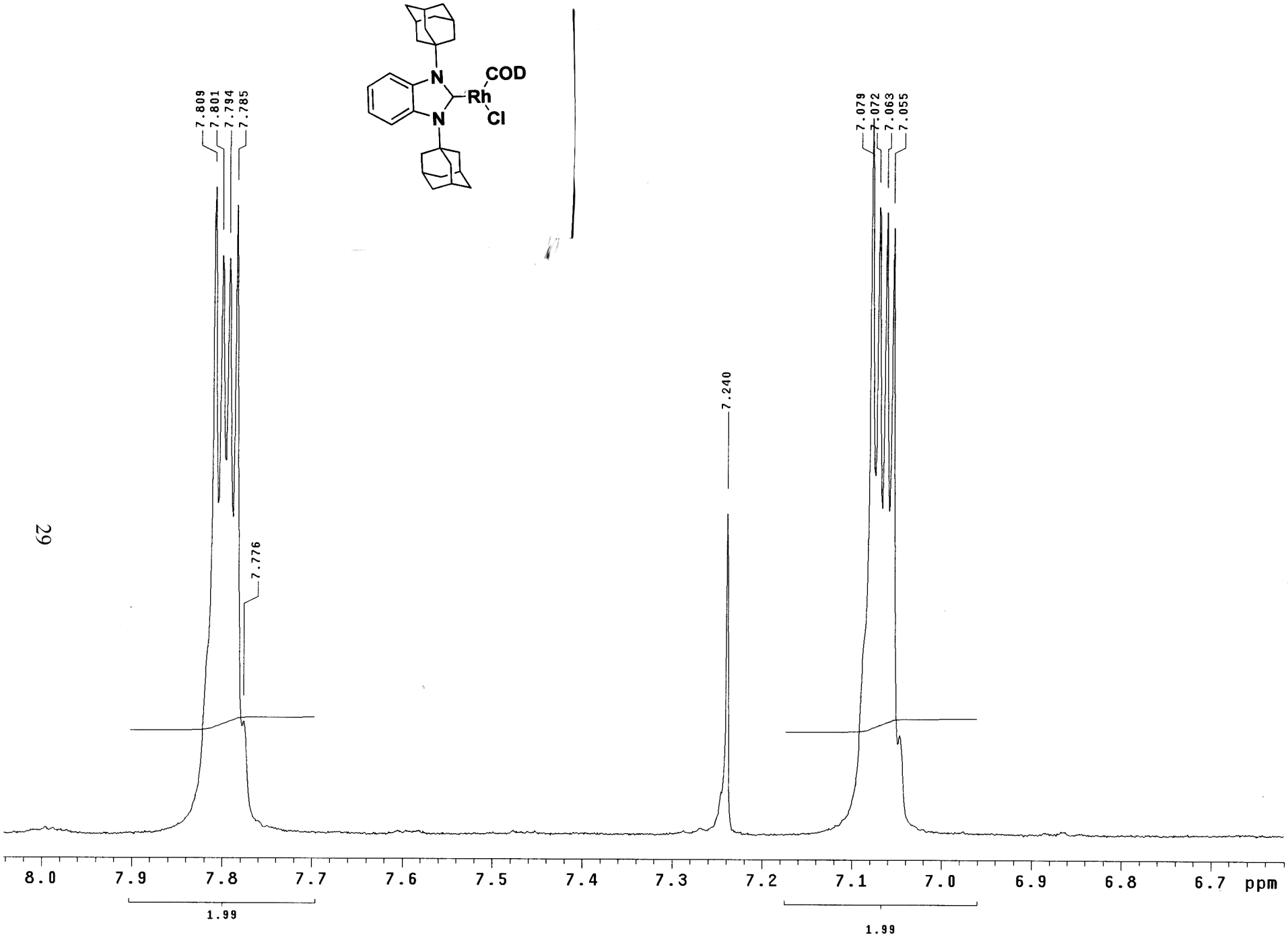
27

PULSE SEQUENCE Relax. delay 1.000 sec Pulse 30.0 degrees Acq. time 1.280 sec Width 30211.5 Hz 11019 repetitions	OBSERVE C13, 100.6472444 DECOUPLE H1, 400.2689955 Power 38 dB continuously on WALTZ-16 modulated	DATA PROCESSING Line broadening 1.0 Hz FT size 131072 Total time 7.0 hours			dmk022206-9 4Ph-Rh(COD)Cl complex Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature File: dmk022206-9 Mercury-400 "nmr6"

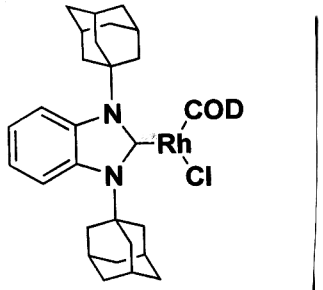




PULSE SEQUENCE Relax. delay 1.000 sec Pulse 32.7 degrees Acq. time 2.856 sec Width 5602.2 Hz 14 repetitions	OBSERVE H1, 400.2669863	DATA PROCESSING Line broadening 0.1 Hz FT size 32768 Total time 1 minute			dmk121805-1 2Ad benzimid. carbene RhClCOD complex Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-400 "nmr6"



PULSE SEQUENCE Relax. delay 1.000 sec Pulse 32.7 degrees Acq. time 2.856 sec Width 5602.2 Hz 14 repetitions	OBSERVE H1, 400.2669863	DATA PROCESSING Line broadening 0.1 Hz FT size 32768 Total time 1 minute			dmk121805-1 2Ad benzimid. carbene RhClCOD complex Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-400 "nmr6"

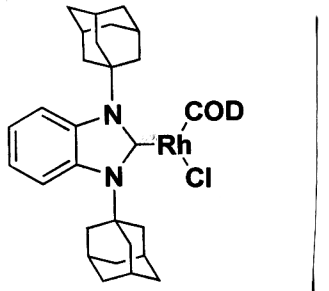


4.947
3.470
3.440
2.986
2.964
2.935
2.407
2.364
1.944
1.914
1.848
1.815
1.774
1.743
1.706
1.680

5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm

1.97 5.94 7.99 9.98 16.70

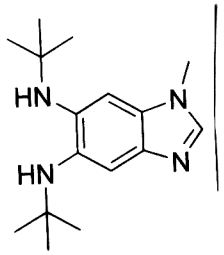
PULSE SEQUENCE Relax. delay 1.000 sec Pulse 32.7 degrees Acq. time 2.856 sec Width 5602.2 Hz 14 repetitions	OBSERVE H1, 400.2669863	DATA PROCESSING Line broadening 0.1 Hz FT size 32768 Total time 1 minute			dmk121805-1 2Ad benzimid. carbene RhClCOD complex Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-400 "nmr6"

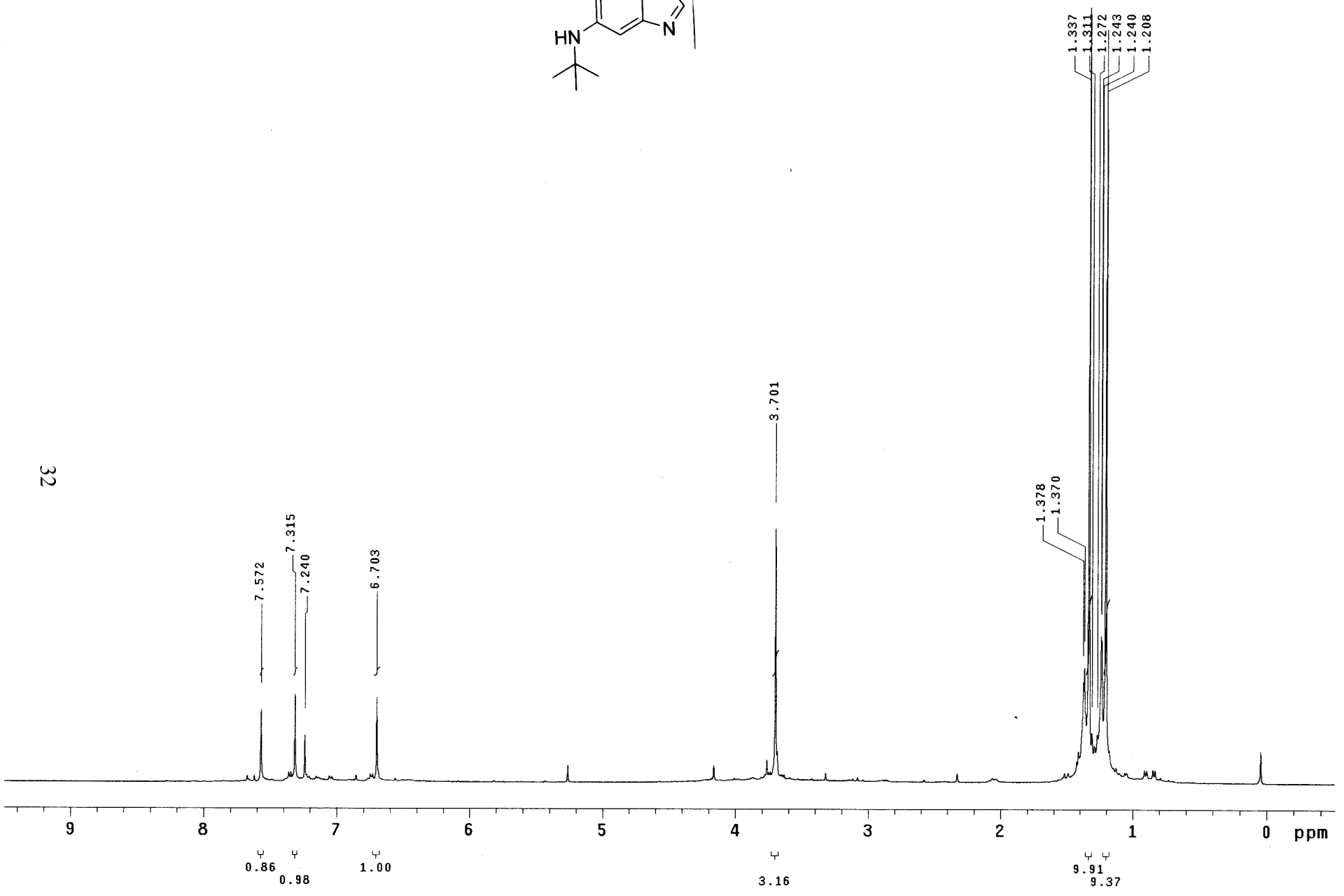


194.321
193.833
134.962
120.267
115.303
92.046
91.962
77.313
77.000
76.679
67.277
67.125
62.046
42.898
36.376
32.259
30.319
28.700

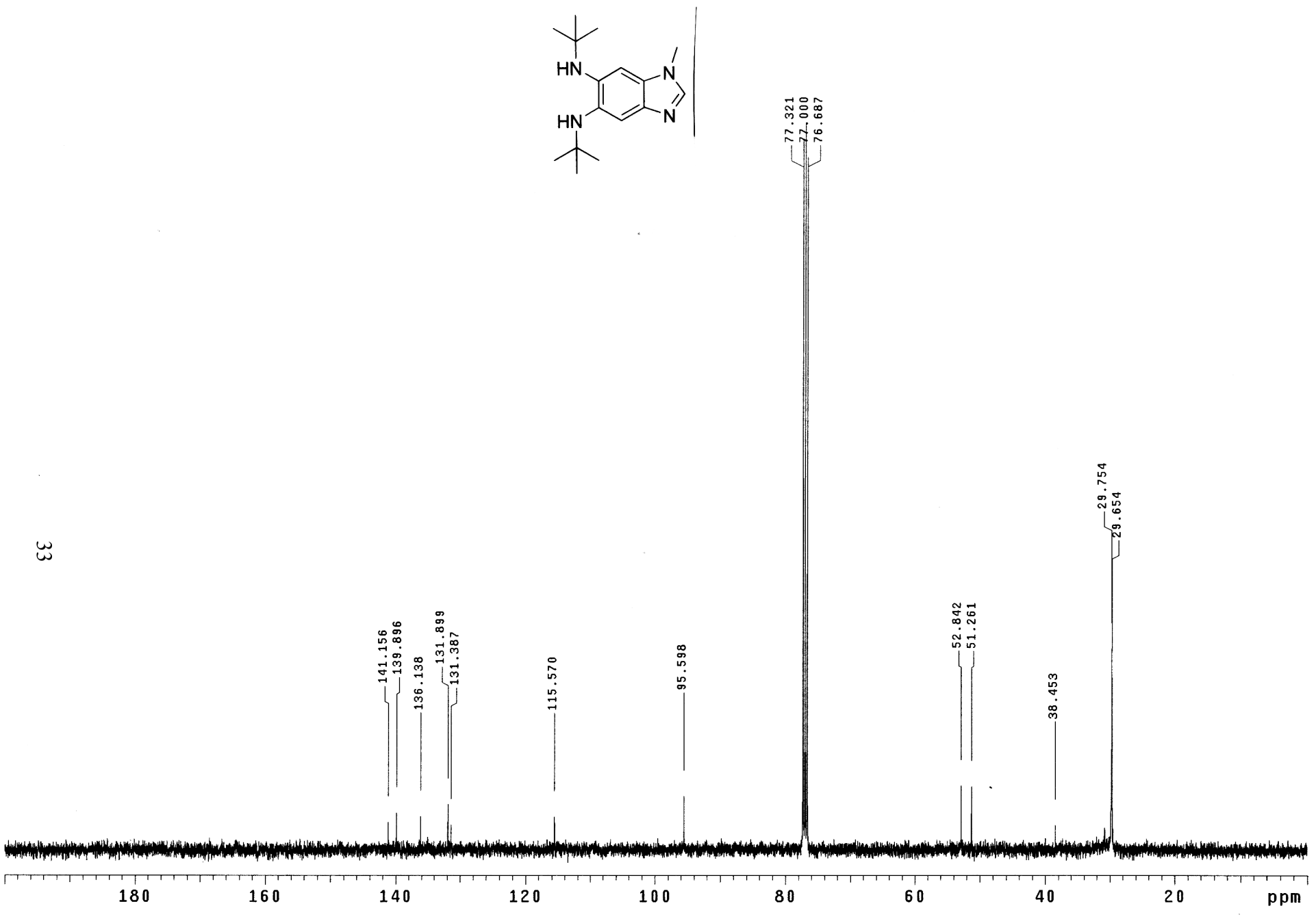
220 200 180 160 140 120 100 80 60 40 20 0 ppm

PULSE SEQUENCE Relax. delay 1.000 sec Pulse 22.5 degrees Acq. time 1.280 sec Width 25188.9 Hz 8052 repetitions	OBSERVE C13, 100.6472192 DECOUPLE H1, 400.2689955 Power 38 dB continuously on WALTZ-16 modulated	DATA PROCESSING Line broadening 1.0 Hz FT size 65536 Total time 5.1 hours			dmk121805-2 2Ad benzimid. carbene RhClCOD complex Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-400 "nmr6"

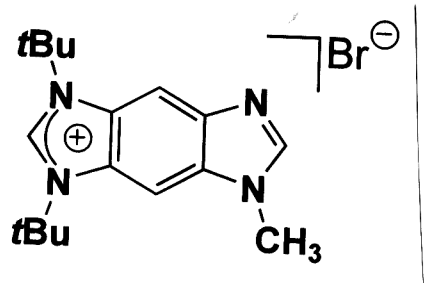




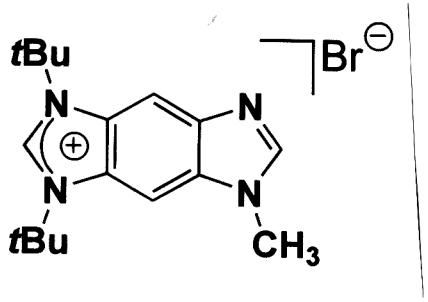
PULSE SEQUENCE Relax. delay 1.000 sec Pulse 32.7 degrees Acq. time 2.856 sec Width 5602.2 Hz 6 repetitions	OBSERVE H1, 400.2669856	DATA PROCESSING Line broadening 0.1 Hz FT size 32768 Total time 1 minute			dmk032206-4 diBr benzimidazole tBuNH2 coupling Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-400 "nmr6"

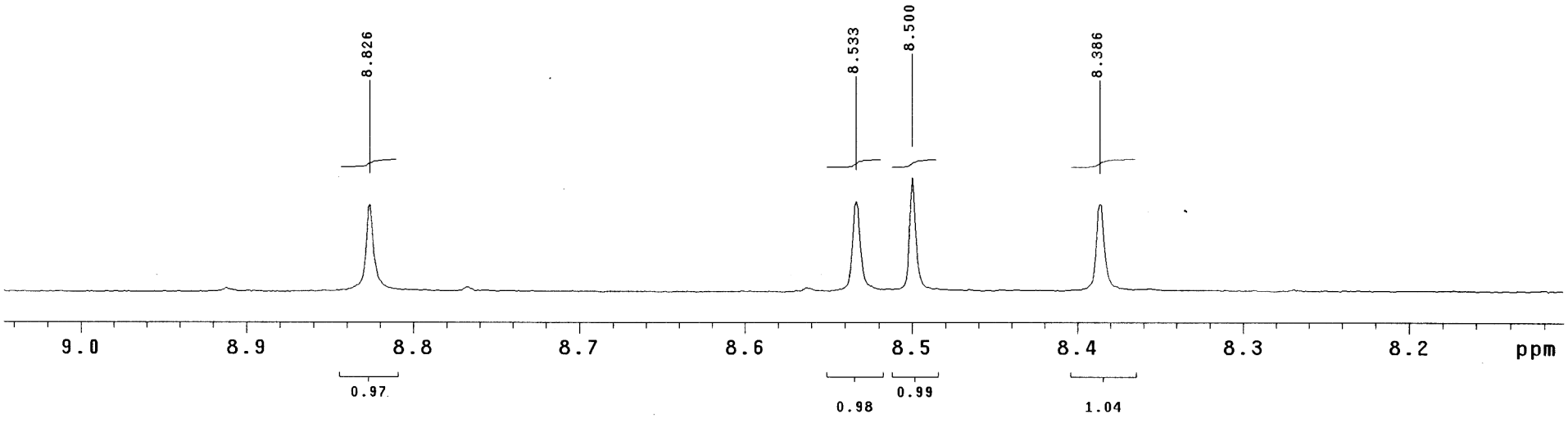


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 37.5 degrees Acq. time 1.280 sec Width 25188.9 Hz 332 repetitions	OBSERVE C13, 100.6472161 DECOUPLE H1, 400.2689955 Power 38 dB continuously on WALTZ-16 modulated	DATA PROCESSING Line broadening 1.0 Hz FT size 65536 Total time 12 minutes			dmk032206-5 diBr benzimidazole tBuNH2 coupling Pulse Sequence: s2pul Solvent: CDCl3 Ambient temperature Mercury-400 "nmr6"

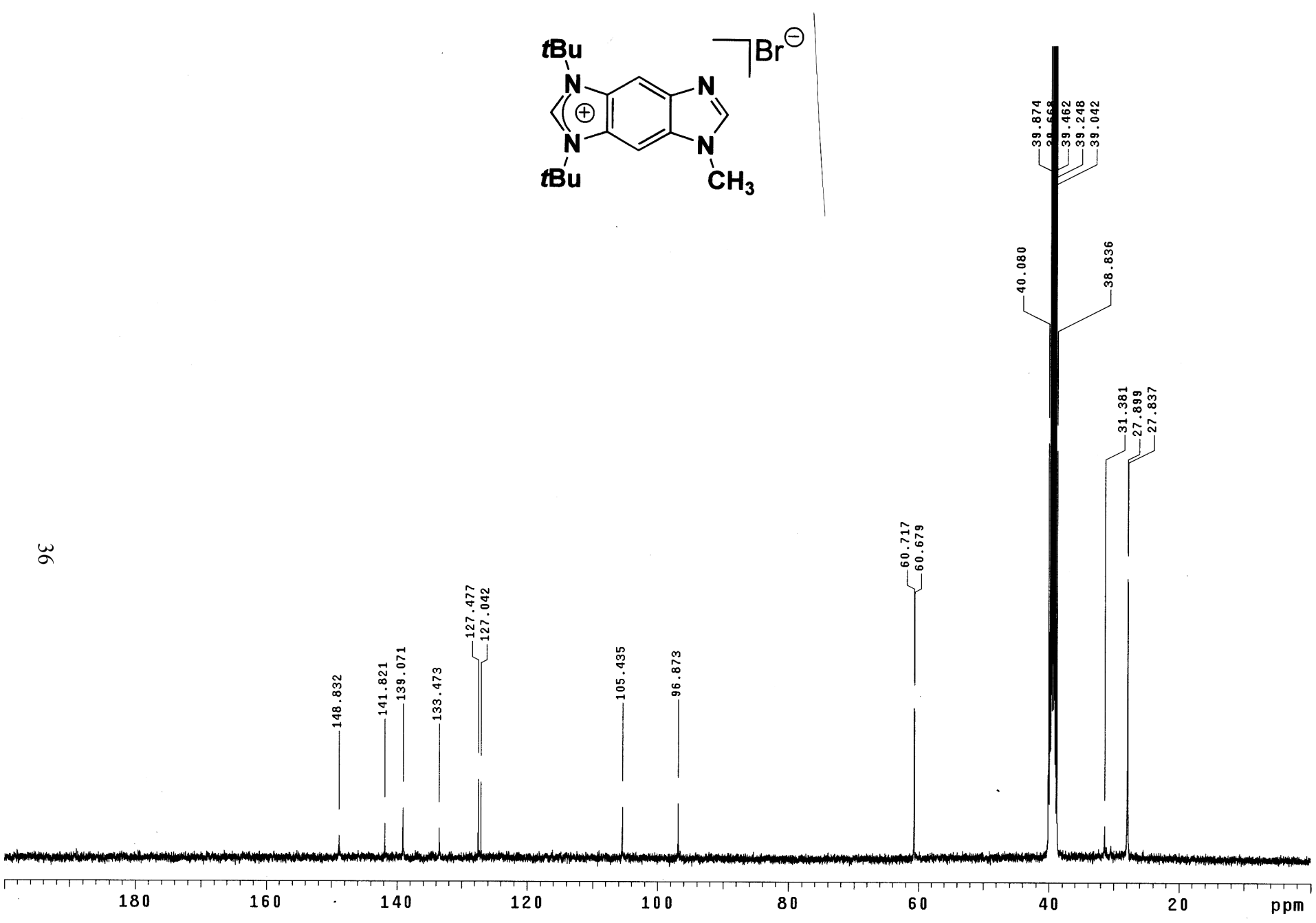


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 32.7 degrees Acq. time 2.856 sec Width 5602.2 Hz 6 repetitions	OBSERVE H1, 400.2688797	DATA PROCESSING Line broadening 0.1 Hz FT size 32768 Total time 1 minute			dmk032206-6 Janus cyclized Pulse Sequence: s2pul Solvent: DMSO Ambient temperature Mercury-400 "nmr6"

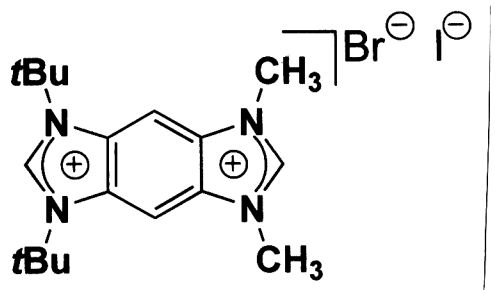


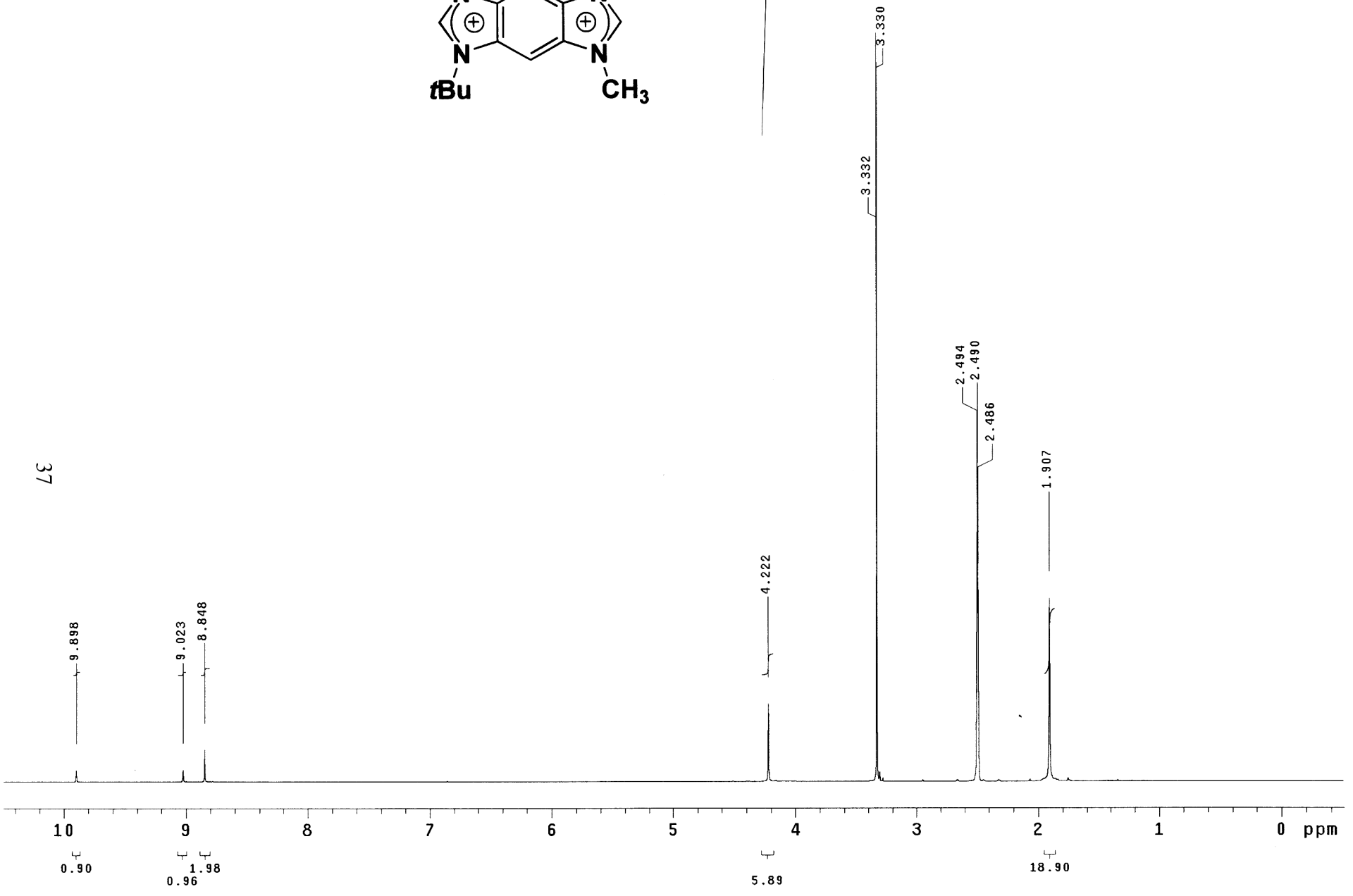


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 32.7 degrees Acq. time 2.856 sec Width 5602.2 Hz 6 repetitions	OBSERVE H1, 400.2688797	DATA PROCESSING Line broadening 0.1 Hz FT size 32768 Total time 1 minute			dmk032206-6 Janus cyclized Pulse Sequence: s2pul Solvent: DMSO Ambient temperature Mercury-400 "nmr6"

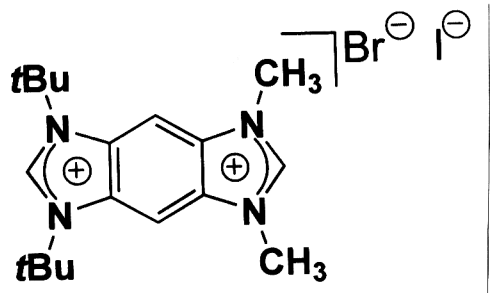


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 30.0 degrees Acq. time 1.280 sec Width 25188.9 Hz 5434 repetitions	OBSERVE C13, 100.6477410 DECOUPLE H1, 400.2708968 Power 38 dB continuously on WALTZ-16 modulated	DATA PROCESSING Line broadening 1.0 Hz FT size 65536 Total time 3.4 hours			dmk031506-2 asym. salt Cl anion Pulse Sequence: s2pul Solvent: DMSO Ambient temperature Mercury-400 "nmr6"

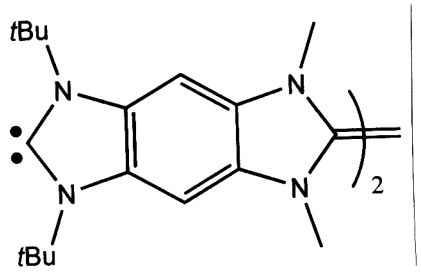


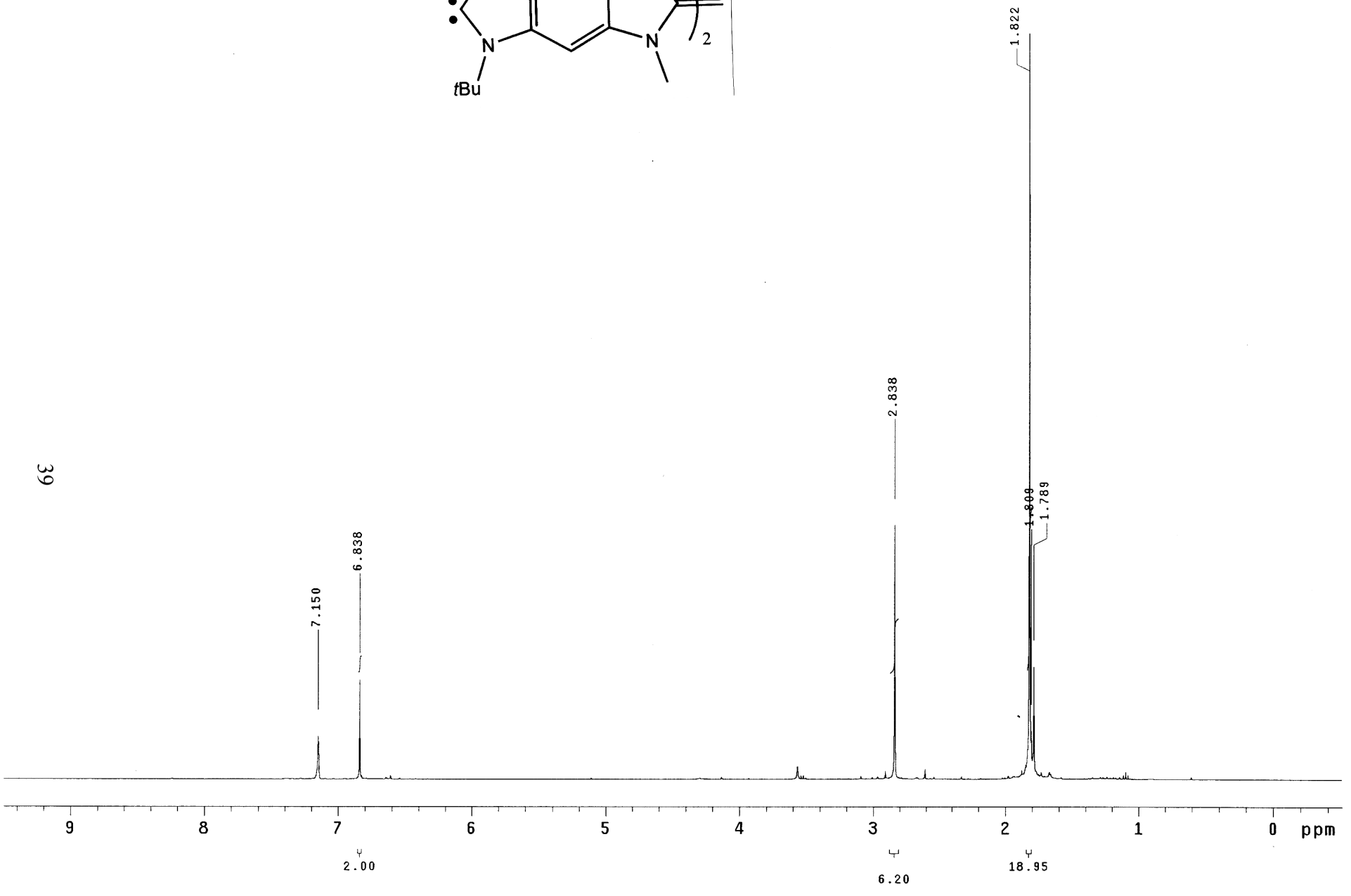


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 32.7 degrees Acq. time 2.856 sec Width 5602.2 Hz 46 repetitions	OBSERVE H1, 400.2688767	DATA PROCESSING Line broadening 0.1 Hz FT size 32768 Total time 2 minutes			dmk040606-1 Pulse Sequence: s2pul Solvent: DMSO Ambient temperature Mercury-400 "nmr6"

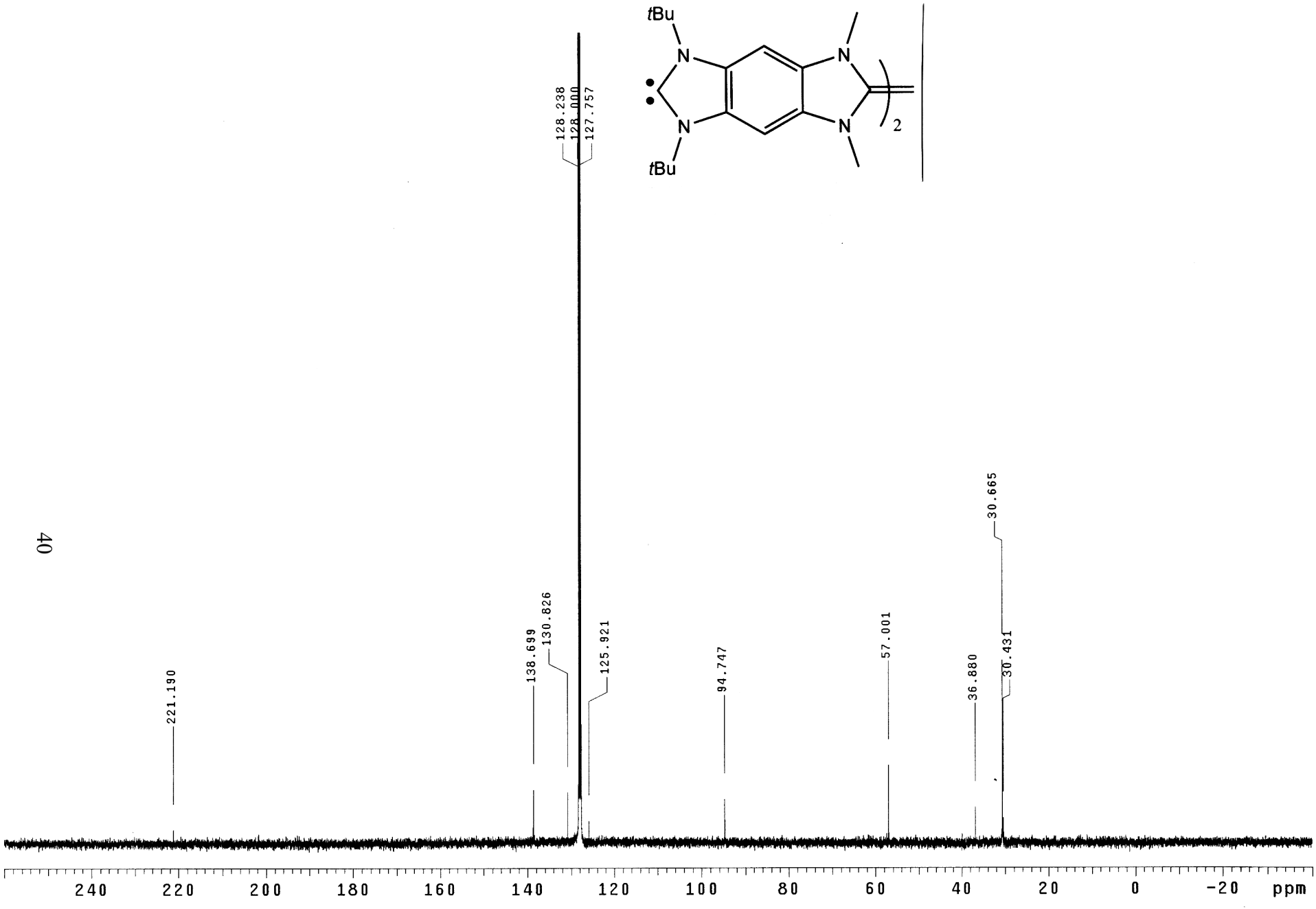


PULSE SEQUENCE Relax. delay 2.000 sec Pulse 22.5 degrees Acq. time 1.280 sec Width 25188.9 Hz 3507 repetitions	OBSERVE C13, 100.6477395 DECOUPLE H1, 400.2708968 Power 38 dB continuously on WALTZ-16 modulated	DATA PROCESSING Line broadening 1.0 Hz FT size 65536 Total time 3.2 hours			dmk031506-4 asym. bis salt Cl and I counterions Pulse Sequence: s2pul Solvent: DMSO Ambient temperature Mercury-400 "nmr6"

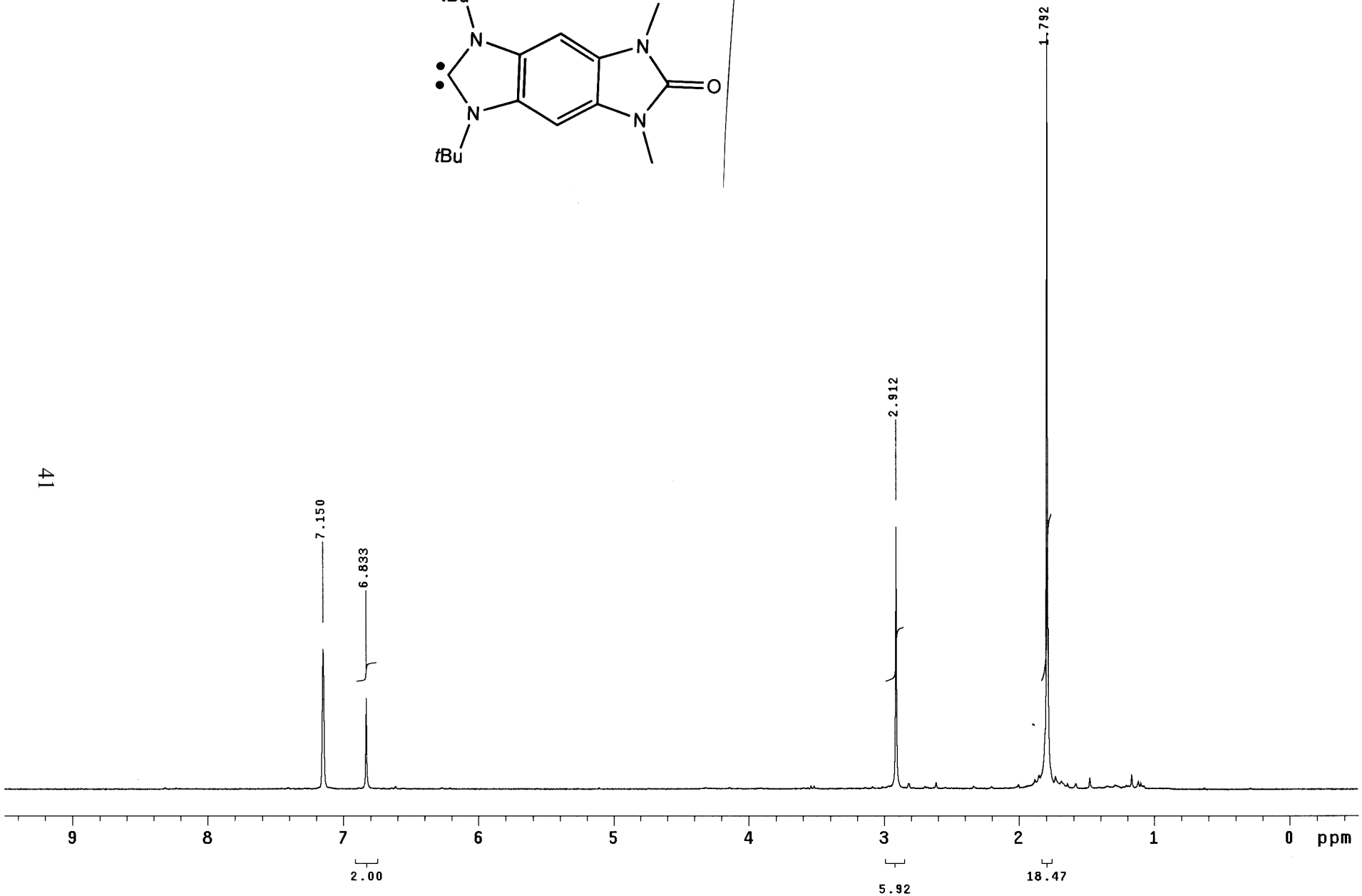




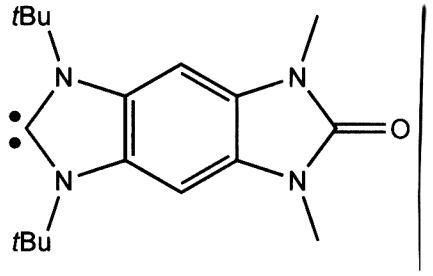
PULSE SEQUENCE Relax. delay 1.000 sec Pulse 32.7 degrees Acq. time 2.856 sec Width 5602.2 Hz 6 repetitions	OBSERVE H1, 400.2670009	DATA PROCESSING Line broadening 0.1 Hz FT size 32768 Total time 1 minute			dmk060706-1 Pulse Sequence: s2pul Solvent: Benzene Ambient temperature Mercury-400 "nmr6"

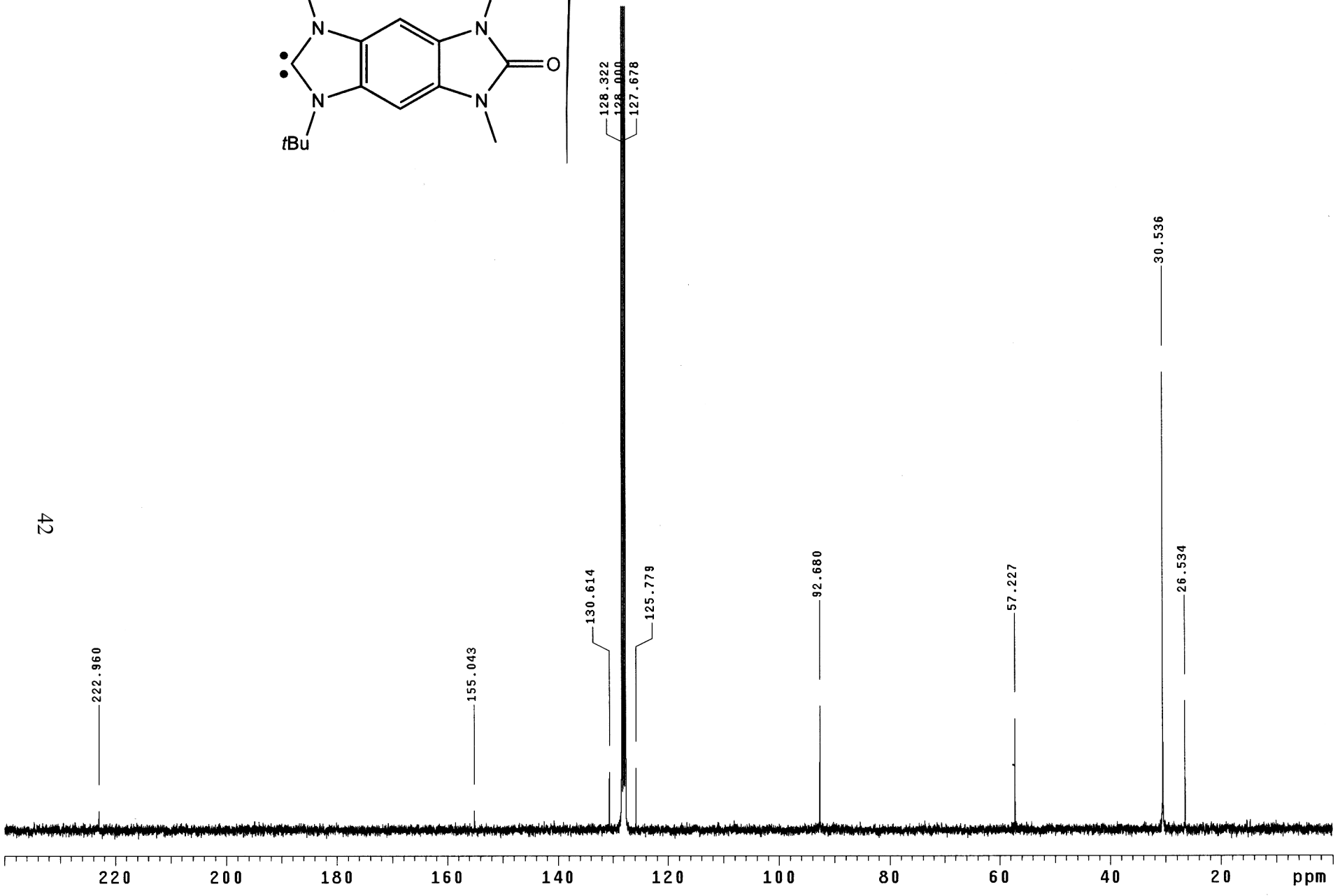


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 30.0 degrees Acq. time 1.280 sec Width 30211.5 Hz 167 repetitions	OBSERVE C13, 100.6471872 DECOUPLE H1, 400.2690316 Power 38 dB continuously on WALTZ-16 modulated	DATA PROCESSING Line broadening 1.0 Hz FT size 131072 Total time 6 minutes			dmk060706-2 Pulse Sequence: s2pul Solvent: Benzene Ambient temperature Mercury-400 "nmr6"



PULSE SEQUENCE Relax. delay 1.000 sec Pulse 25.0 degrees Acq. time 3.813 sec Width 4196.4 Hz 2 repetitions	OBSERVE H1, 300.1390491	DATA PROCESSING Line broadening 0.1 Hz FT size 32768 Total time 1 minute			dmk040806-1 Pulse Sequence: s2pul Solvent: Benzene Ambient temperature UNITYplus-300 "nmr2"





PULSE SEQUENCE	OBSERVE C13, 75.4700008	DATA PROCESSING			dmk040806-2
Relax. delay 1.000 sec Pulse 30.0 degrees Acq. time 1.777 sec Width 21798.4 Hz 449 repetitions	DECOUPLE H1, 300.1409529 Power 40 dB continuously on WALTZ-16 modulated Single precision data	Line broadening 1.0 Hz FT size 131072 Total time 20 minutes			Pulse Sequence: s2pul Solvent: Benzene Ambient temperature UNITYplus-300 "nmr2"