Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Synthesis of 1,3,5-Trisubstituted Pyrazolines via Zn(II)-Catalyzed Double Hydroamination of Enynes with Aryl Hydrazines

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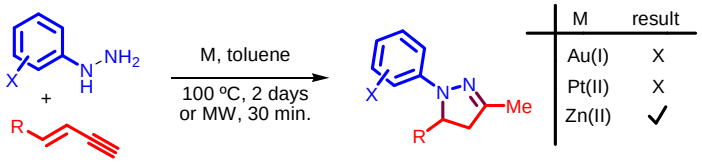


1. General Information

All reactions were carried out in oven or flame dried flasks and vials with magnetic stirring under nitrogen atmosphere. The microwave reactions were carried out in a microwave reactor (Biotage, initiator 8, single-mode reactor). Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringe cooled to ambient temperature in a desiccators. The chemicals such as phenyl hydrazine (**1a**), cinnamaldehyde (**I**) and 1-ethynylcyclohexene (**4**) and metal catalysts such as AuCl, Ph_3PAuCl, Ph_3AuNTf_2, AgOTf, $PtCl_2$, PtI_2, $PtCl_4$, $ZnCl_2$, ZnI_2 and $Zn(OTf)_2$ were commercially available and used as recieved. All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated silica gel aluminium/glass plates. After elution, plate was visualized under UV illumination at 254 nm for UV active materials. Further visualization was achieved by staining with $KMnO_4$ and charring on a hot plate. Solvents were removed in vacuum with a water bath at 35 °C. Silica gel finer than 200 mesh was used for flash column chromatography. Columns were packed with slurry of silica gel in hexane and equilibrated with the appropriate solvent/solvent mixture prior to use. The compounds were loaded neat or as a concentrated solution using the appropriate solvent system. The elution was assisted by applying pressure with an air pump. Yields refer to chromatographically and spectroscopically homogeneous materials unless otherwise stated.

Melting points are uncorrected. IR spectra were recorded as neat liquids or KBr pellets and absorptions are reported in cm^{-1}. ^1H NMR spectra were recorded on 300 and 500 MHz spectrometers in appropriate solvents ($CDCl_3$/DMSO-d_6) using TMS as internal standard or the solvent signals as secondary standards and the chemical shifts are shown in δ scales. Multiplicities of NMR signals are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet, for unresolved lines), etc. ^{13}C NMR spectra were recorded on 75 MHz spectrometer. High-resolution mass spectra were obtained by using ESI-QTOF mass spectrometry

2. Synthesis and Characterization of Starting Materials

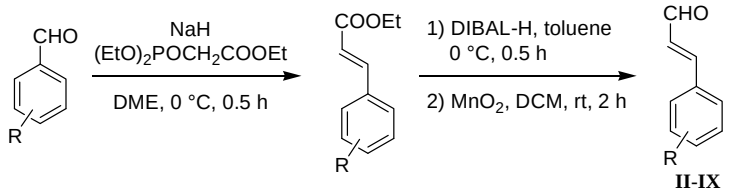
2.1. Preparation of Aryl Hydrazines

Aryl hydrazines **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **1i**, **1j**, **1k**, **1l** and **1m** were prepared by literature known procedure.[1]

2.2. Preparation of Enynes

Aromatic enynes **2a-i** were synthesized from corresponding cinnamaldehydes adopting literature known procedures.[2] The aliphatic enynes **2j**[3] and **2k**[4] were synthesized by literature known methods.

General Procedure for the Preparation of Cinnamaldehydes II-IX[5]



II-IX

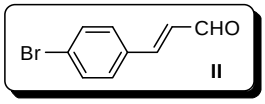
Triethyl phosphonoacetate (2 equiv.) was added drop wise to a stirred suspension of sodium hydride [55% mineral oil dispersion (2 equiv.), washed with hexane] in DME (5 mL) at 0 °C. After the solution was stirred for 15 min at 0 °C, benzaldehyde was added and stirred at same temperature for 30 min. After the completion of reation, as indicated by TLC, the reaction mixture was diluted with EtOAc and water. The aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, concentrated under vacuum and the crude product was purified by column chromatography using hexane/EtOAc as eluent to afford (*E*)-ethylcinnamate. The obtained cinnamate, thus obtained, was reduced to cinnamyl alcohol by following the procedure described below.

A solution of DIBAL–H (1M in toluene, 2 equiv.) was added drop wise to a stirred solution of (*E*)-ethylcinnmate in toluene at 0 °C. After the completion of reation as indicated by TLC the reaction mixture was diluted with EtOAc and water. The aqueous layer was extracted twice with

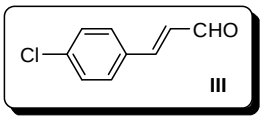
[1] A.-R. Lee, W.-H. Huang, T.-L. Lin, K.-M, Shih, H.-F. Lee, *J. Heterocycl. Chem.*, 1995, **32**, 1-11.
[2] P. Michel, D. Gennet, A. Rassat, *Tetrahedron Lett.,* 1999, **40**, 8575-8578.
[3] M. A. Tius, H. Hu, J. K. Kawakami, J. Busch-Peterson, *J. Org. Chem.,* 1998, **63**, 5971-5976.
[4] I. E. Markó, T. Giard, S. Sumida, A.-E. Gies, *Tetrahedron Lett.,* 2002, **43**, 2317-2320.
[5] S. Oida, Y. Tajima, T. Konosu, Y. Nakamura, A. Somada, T. Tanaka, S. Habuki, T. Harasaki, Y. Kamai, T. Fukuoka, S. Ohya, H. Yasuda, *Chem. Pharm. Bull.,* 2000, **48**, 694-707.

EtOAc. The combined organic layers were dried over Na_2SO_4, concentrated under vacuum and the crude product was purified by column chromatography using hexane/EtOAc as eluent to afford (*E*)-ethylcinnamyl alcohol. The alcohol was oxidized to (*E*)-cinnamaldehyde according to the procedure described below.

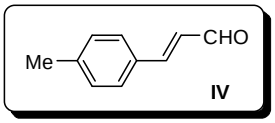
Activated MnO_2 (10 equiv.) was added to the solution of (*E*)-cinnamyl alcohol in DCM (5 mL) and stirred at room temperature for 2 h. Upon completion of reaction, the suspension was filtered through celite and the filtrate was concentrated. The crude product was purified by column chromatography using hexane/EtOAc as eluent to afford (*E*)-cinnamaldehyde.



(*E*)-4-Bromocinnamaldehyde (**II**):[6] solid; M.p. 78–80 °C (ref. M.p. 78–79 °C); overall yield 65%; R_f = 0.61 (hexane/EtOAc = 95/05); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.68 (d, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.43-7.34 (m, 3H), 6.68 (dd, *J* = 16.1, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 193.2, 150.9, 132.8, 132.3, 129.7, 128.9, 125.6.



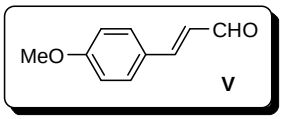
(*E*)-4-Chloroocinnamaldehyde (**III**):[7] solid; M.p. 59–61 °C (ref. M.p. 59–60 °C); overall yield 70%; R_f = 0.65 (hexane/EtOAc = 95/05); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.68 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 8.9 Hz, 2H), 7.40-7.36 (m, 3H), 6.65 (dd, *J* = 16.8, 7.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 193.2, 150.9, 137.2, 132.5, 129.5, 129.4, 128.9.



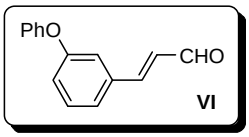
(*E*)-4-Methylcinnamaldehyde (**IV**):[7] solid; M.p. 43–45 °C (ref. M.p. 45–47 °C); overall yield 58%; R_f = 0.70 (hexane/EtOAc = 95/05); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.65 (d, *J* = 7.5 Hz,

[6] O. V. Maltsev, A. S. Kucherenko, I. P. Beletskaya, V. A. Tartakovsky, S. G. Zlotin, *Eur. J. Org. Chem.*, 2010, 2927-2933.
[7] J. Li, J. Zhu, H. Jiang, W. Wang, J. Li, *Chem. Commun.*, 2010, 415-417.

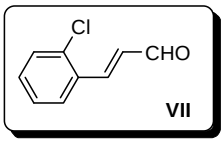
1H), 7.44-7.36 (m, 3H), 7.29 (d, *J* = 7.5 Hz, 2H), 6.32 (dd, *J* = 15.8, 7.5 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 193.8, 152.9, 141.9, 131.3, 129.8, 128.5, 127.7, 21.6.



(*E*)-4-Methoxycinnamaldehyde (**V**):[8] solid; M.p. 63–65 °C (ref. M.p. 58.5–59.8 °C); overall yield 72%; R_f = 0.58 (hexane/EtOAc = 95/05); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.59 (d, *J* = 7.55 Hz, 1H), 7.48-7.45 (m, 2H), 7.32 (d, *J* = 1.51 Hz, 1H), 6.90-6.86 (m, 2H), 6.54 (dd, *J* = 15.8, 7.5 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 193.6, 162.2, 152.7, 152.6, 130.4, 126.4, 114.6, 55.5.

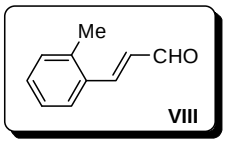


(*E*)-3-Phenoxycinnamaldehyde (**VI**): solid; M.p. 55–57 °C; overall yield 63%; R_f = 0.66 (hexane/EtOAc = 95/05); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.65 (d, *J* = 7.5 Hz, 1H), 7.39-7.24 (m, 4H), 7.26-7.24 (m, 1H), 7.14-7.09 (m, 2H), 7.06-6.98 (m, 3H), 6.62 (dd, *J* = 15.6, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 193.5, 158.1, 156.3, 151.9, 135.7, 130.4, 129.9, 129.1, 123.9, 123.1, 121.2, 119.2, 117.7; IR (KBr): ν_{max} 3292, 3058, 1670, 1480, 1233, 822, 753, 692; HRMS calcd for $C_{15}H_{12}O_2Na$ (M^+ + Na) 247.0734, found 247.0736.

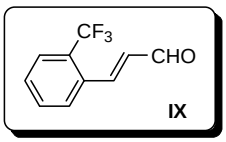


(*E*)-2-Chlorocinnamaldehyde (**VII**):[7] solid; M.p. 52–54 °C (ref. M.p. 49–51°C); overall yield 55%; R_f = 0.56 (hexane/EtOAc = 95/05); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.75 (d, *J* = 7.5 Hz, 1H), 7.90 (d, *J* = 16.1 Hz, 7.4, 1H), 7.66 (dd, *J* = 7.2, 1.5 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.38-7.25 (m, 2H), 6.67 (dd, *J* = 16.1, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 193.4, 147.8, 135.0, 131.8, 130.3, 130.2, 127.7, 127.2.

[8] E. Artuso, M. Barbero, I. Degani, S. Dughera, R. Fochi, *Tetrahedron*, 2006, **62**, 3146-3157.

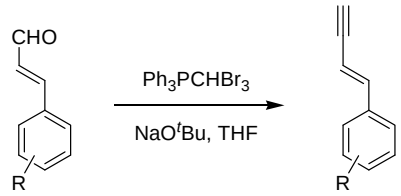


(*E*)-2-Methylcinnamaldehyde (**VIII**):[7] thick liquid; overall yield 68%; R_f = 0.65 (hexane/EtOAc = 95/05); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.70 (d, *J* = 7.5 Hz, 1H), 7.73 (d, *J* = 15.8 Hz, 1H), 7.32-7.17 (m, 4H), 6.61 (dd, *J* = 15.8, 7.5 Hz, 1H), 2.06 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 193.9, 150.4, 144.7, 137.9, 131.0, 126.6, 118.1, 19.7.



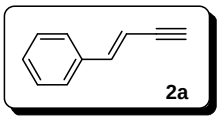
(*E*)-2-Trifluoromethylcinnamaldehyde (**IX**):[9] solid; M.p. 43–45 °C (ref. M.p. 37–39 °C); overall yield 40%; R_f = 52 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.73 (d, *J* = 7.5 Hz, 1H), 8.12-8.09 (m, 1H), 7.99-7.96 (m, 2H), 7.94-7.91 (m, 2H), 6.72 (dd, *J* = 15.5, 7.5 Hz, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 194.6, 166.9, 138.2, 134.3, 132.9, 132.4, 130.2, 128.4, 125.9, 123.8.

General Procedure for the Preparation of Enynes 2a-i

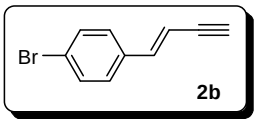


Under nitrogen atmosphere dibromomethyltriphenylphosphoniumbromide (2 equiv.) was added to the stirred suspension of NaO^{t}Bu (1.9 equiv.) in THF (10 mL). The solution was stirred for 20 minutes then cinnamaldehyde was added. After 30 min, the solution was cooled to –78 °C and NaO^{t}Bu (5 equiv.) was added. After 2 h the reaction mixture was quenched with saturated brine and extracted twice with ethyl acetate. The combined organic layers were dried over Na_2SO_4, concentrated under vacuum and the crude product was purified by column chromatography using hexane/EtOAc as eluent to afford enyne.

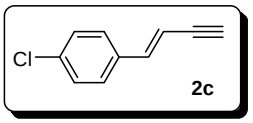
[9] A. Nudelman, Y. Binnes, N. Shmueli-Broide, Y. Odessa, J. P. Hieble, A. C. Sulpizio, *Arch. Pharm. Pharm. Med. Chem.,* 1996, **329**, 125-132.



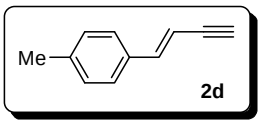
(*E*)-1-(But-1-en-3-ynyl)benzene (2a):[10] thick liquid; 60% yield. R_f = 0.76 (hexane/EtOAc = 95/05); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.38-7.21 (m, 5H), 6.98 (d, *J* = 16.2 Hz, 1H), 6.17 (dd, *J* = 16.4, 2.2 Hz, 1H), 2.96 (d, *J* = 2.2Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.2, 135.8, 132.8, 128.9, 128.7, 127.6, 126.4, 107.0, 82.9, 79.3.



(*E*)-1-(But-1-en-3-ynyl)-4-bromoobenzene (2b):[11] thick liquid; yield 63%; R_f = 0.62 (hexane/EtOAc = 95/05); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 16.2 Hz, 1H), 6.09 (dd, *J* = 16.2, 2.2 Hz, 1H), 2.99 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 141.7, 134.7, 131.8, 127.7, 122.8, 107.7, 82.5, 79.8.

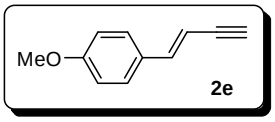


(*E*)-1-(But-1-en-3-ynyl)-4-chlorobenzene (2c):[12] solid; M.p. 55–57 °C (ref. M.p. 51–53 °C); yield 65%; R_f = 0.78 (hexane/EtOAc = 95/05); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.35-7.25 (m, 4H), 6.94 (d, *J* = 16.2 Hz, 1H), 6.06 (dd, *J* = 16.2, 2.3 Hz, 1H), 2.98 (d, *J* = 2.2, Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 141.6, 134.6, 134.2, 128.9, 127.4, 107.6, 82.5, 79.8.

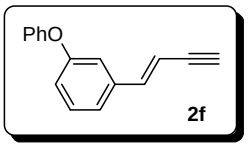


[10] B. J. Albert, A. Sivaramakrishnan, T. Naka, N. L. Czaicki, K. Koide, *J. Am. Chem. Soc.*, 2007, **129**, 2648-2659.
[11] K. Tohdo, Y. Hamada, T. Shioiri, *Tetrahedron Lett.*, 1992, **33**, 2031-2034.
[12] E. N. Marvell, G. Caple, C. Delphey, J. Platt, N. Polston, J. Tashiro, *Tetrahedron,* 1973, **29**, 3797-3806.

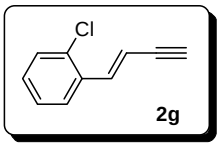
(*E*)-1-(But-1-en-3-ynyl)-4-methylbenzene (2d):[13] thick liquid; yield 55%; R_f = 0.75 (hexane/EtOAc = 95/05); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.27-7.23 (m, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 6.97 (d, *J* = 15.8 Hz, 1H), 6.04 (dd, *J* = 15.8, 2.2 Hz, 1H), 2.94 (d, *J* = 2.2 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.0, 138.9, 133.1, 131.4, 129.4, 126.2, 105.8, 83.1, 78.8, 21.3.



(*E*)-1-(But-1-en-3-ynyl)-4-methoxybenzene (2e):[13] solid; M.p. 45–47 °C (ref. M.p. 45–47); yield 67%; R_f = 0.75 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.31-7.25 (m, 2H), 6.94 (d, *J* = 16.6 Hz, 1H), 6.80 (d, *J* = 9.1 Hz, 2H), 5.93 (dd, *J* = 16.6, 2.2 Hz, 1H), 3.79 (s, 3H), 2.90 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 142.7, 127.7, 126.5, 114.1, 104.5, 78.4, 55.3.

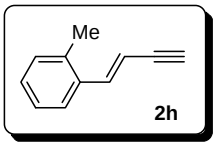


(*E*)-1-(But-1-en-3-ynyl)-3-phenoxybenzene (2f): thick liquid; yield 55%; R_f = 0.73 (hexane/EtOAc = 95/05); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.34-7.29 (m, 3H), 7.26-7.23 (m, 1H), 7.11-7.06 (m, 2H), 6.99-6.97 (m, 3H), 6.92 (s, 1H), 6.05 (dd, *J* = 16.6, 2.2 Hz, 1H), 2.98 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 157.7, 156.8, 142.4, 137.6, 129.9, 129.7, 123.5, 121.3, 119.2, 118.9, 116.2, 107.8, 82.6, 79.6; IR (film): ν_{max} 3291, 3038, 2923, 1695, 1575, 1487, 1378, 1241, 1072, 954, 769, 691; HRMS calcd for $C_{16}H_{13}O$ (M^+ + H) 221.1123, found 221.1127.

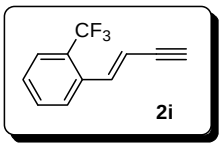


[13] A. W. Gibson, G. R. Humphrey, D. J. Kennedy, S. H. B. Stanley, *Synthesis*, 1991, 414-416.

(*E*)-1-(But-1-en-3-ynyl)-2-chlorobenzene (2g): thick liquid; yield 59%; R_f = 0.70 (hexane/EtOAc = 95/05); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.51-7.47 (m, 1H), 7.37-7.31 (m, 2H), 7.24-7.15 (m, 2H), 6.08 (dd, *J* = 16.6, 2.2 Hz, 1H), 3.02 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 139.0, 129.9, 129.7, 129.2, 128.5, 126.9, 126.2, 109.6, 82.6, 80.1; IR (film): ν_{max} 3240, 2948, 2835, 1656, 1454, 1113, 1032, 750; HRMS calcd for $C_{10}H_8Cl$ (M^+ + H) 163.0287, found 163.0285.



(*E*)-1-(But-1-en-3-ynyl)-2-methylbenzene (2h):[14] solid; M.p. 37–39 °C (ref. M.p. 49–42 °C); yield 52%; R_f = 0.76 (hexane/EtOAc = 95/05); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.42-7.37 (m, 1H), 7.24 (d, *J* = 16.2 Hz, 1H), 7.16-7.09 (m 3H), 6.01 (dd, *J* = 16.2, 2.1 Hz, 1H), 2.95 (d, *J* = 2.1 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 140.9, 130.6, 128.8, 127.5, 126.3, 125.1, 108.1, 83.3, 78.9, 19.7.



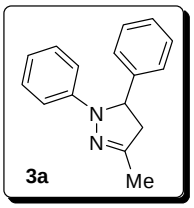
(*E*)-1-(But-1-en-3-ynyl)-2-trifuromethylbenzene (2i): thick liquid; yield 30%; R_f = 0.43 (hexane/EtOAc = 70/30); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.66-7.60 (m, 2H), 7.52-7.45 (m, 1H), 7.40-7.30 (m, 2H), 6.09 (dd, *J* = 16.1, 2.1 Hz, 1H), 3.04 (d, *J* = 2.1 Hz, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 134.1, 132.8, 131.4, 128.7, 127.1, 125.8, 122.0, 113.0, 88.5, 66.9; IR (film): ν_{max} 3028, 2917, 1597, 1499, 1355, 1097, 872, 752, 659; HRMS calcd for $C_{11}H_8F_3$ (M^+ + H) 197.0573, found 197.0576.

3. General Procedure and Characterization Data for Pyrazolines

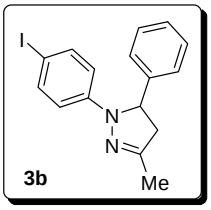
A solution of enyne (0.391 mmol), aryl hydrazine (1.172 mmol) and $Zn(OTf)_2$ (3 equiv.) in toluene (2 mL) was sealed under nitrogen in reaction vials and irradiated in a microwave reactor (Biotage, initiator 8, single-mode reactor) at 150 °C for 1 h. On cooling of the reaction mixture

[14] G. Okusa, M. Kumagai, T. Itai, *Chem. Pharm. Bull.*, 1969, **17**, 2502-2506.

to ambient temperature the solvent was removed under reduced pressure and the residue was purified by column chromatography using hexane/EtOAc as eluent to afford pyrrazoline.

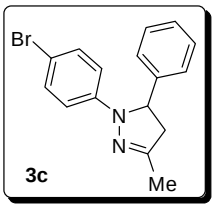


3-Methyl-1,5-diphenyl-4,5-dihydro-1H-pyrazole (**3a**):[15] thick liquid; yield 76%; R_f = 0.63 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.32-7.18 (m, 5H), 7.06 (t, *J* = 7.5 Hz, 2H), 6.83 (d, *J* = 9.1 Hz, 1H), 6.67 (t, *J* = 7.5 Hz, 1H), 4.97 (dd, *J* = 12.1, 8.3 Hz, 1H), 3.38 (dd, *J* = 17.4, 12.1 Hz, 1H), 2.68 (dd, *J* = 17.4, 8.3 Hz, 1H), 2.05 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 148.5, 146.1, 143.0, 129.1, 128.9, 127.4, 125.9, 118.6, 113.1, 107.8, 64.7, 47.8, 15.9; IR (film): ν_{max} 3146, 2925, 1597, 1504, 1365, 1010, 764, 695; HRMS calcd for $C_{16}H_{17}N_2$ (M^+ + H) 237.1391, found 237.1382.

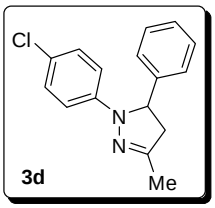


1-(4-Iodophenyl)-3-methyl-5-phenyl-4,5-dihydro-1H-pyrazole (**3b**): thick liquid; yield 74%; R_f = 0.61 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.29-7.15 (m, 4H), 7.06 (t, *J* = 7.2 Hz, 2H), 6.84 (d, *J* = 7.7 Hz, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 4.98 (dd, *J* = 11.9, 8.1 Hz, 1H), 3.38 (dd, *J* = 17.4, 11.9 Hz, 1H), 2.69 (dd, *J* = 17.4, 8.1 Hz, 1H), 2.06 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 129.0, 128.8, 128.6, 127.3, 125.9, 125.1, 118.6, 113.1, 64.7, 47.8, 15.9; IR (film): ν_{max} 3202, 2930, 1510, 1210, 1051, 772; HRMS calcd for $C_{16}H_{16}N_2I$ (M^+ + H) 363.0358, found 363.0361.

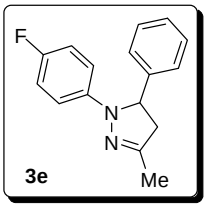
[15] X. Zhu, Z. Li, C. Jin, L. Xu, Q. Wu, W. Su, *Green Chem.*, 2009, 163-165.



1-(4-Bromophenyl)-3-methyl-5-phenyl-4,5-dihydro-1H-pyrazole (**3c**):[16] thick liquid; yield 76%; R_f = 0.66 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.35-7.12 (m, 7 H), 6.72 (d, *J* = 9.3 Hz, 2H), 4.96 (dd, *J* = 11.8, 7.6 Hz, 1H), 3.40 (dd, *J* = 17.8, 11.8 Hz, 1H), 2.79 (dd, *J* = 17.8, 7.6 Hz, 1H), 2.05 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 145.9, 144.4, 139.3, 138.6, 138.4, 129.4, 128.7, 128.5, 126.3, 121.4, 120.7, 114.3, 113.8, 82.2, 25.1, 16.0; IR (film): ν_{max} 3220, 2924, 1732, 1590, 1402, 1365, 1072, 968, 829; HRMS calcd for $C_{16}H_{16}N_2Br$ (M^+ + H) 315.0494, found 315.0496



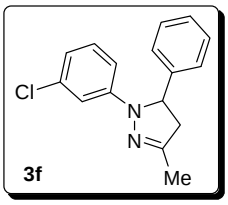
1-(4-Chlorophenyl)-3-methyl-5-phenyl-4,5-dihydro-1H-pyrazole (**3d**): thick liquid; yield 71%; R_f = 0.62 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.33-7.16 (m, 5H), 7.02 (d, *J* = 9.1 Hz, 2H), 6.77 (d, *J* = 9.1 Hz, 2H), 4.95 (dd, *J* = 12.1, 8.3 Hz, 1H), 3.39 (dd, *J* = 17.4, 12.1 Hz, 1H), 2.70 (dd, *J* = 17.4, 8.3 Hz, 1H), 2.06 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 148.9, 144.4, 142.4, 129.1, 128.6, 127.5, 125.7, 123.2, 114.1, 64.6, 47.8, 15.8; IR (film): ν_{max} 3231, 2924, 1710, 1494, 1093, 831, 758, 696; HRMS calcd for $C_{16}H_{16}N_2Cl$ (M^+ + H) 271.1010, found 271.1001.



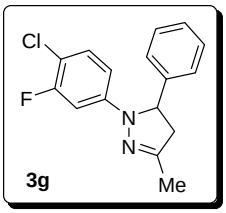
1-(4-Fluorophenyl)-3-methyl-5-phenyl-4,5-dihydro-1H-pyrazole (**3e**): thick liquid; yield 69%; R_f = 0.53 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.21-7.19 (m, 2H),

[16] US2002/156081 A1, 2002

7.17-7.14 (m, 4H), 6.97 (t, *J* = 7.3 Hz, 2H), 6.77 (d, *J* = 6.5 Hz, 1H), 4.88 (dd, *J* = 12.2, 8.9 Hz, 1H), 3.37 (dd *J* = 17.1, 12.2 Hz, 1H), 2.70 (dd, *J* = 17.1, 8.9 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 158.1, 154.9, 148.7, 142.8, 142.6, 129.0, 128.5, 127.5, 126.7, 125.9, 125.6, 116.1, 115.7, 115.3, 115.0, 114.3, 114.2, 104.2, 65.6, 47.9, 15.8; IR (film): ν_{max} 3214, 2923, 1620, 1502, 1493, 1370, 1160, 750; HRMS calcd for $C_{16}H_{16}N_2F$ (M^+ + H) 255.1297, found 255.1300.

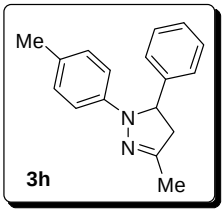


1-(3-Chlorophenyl)-3-methyl-5-phenyl-4,5-dihydro-1H-pyrazole (**3f**): thick liquid; yield 68%; R_f = 0.61 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.33-7.28 (m, 2H), 7.24-7.20 (m, 3H), 6.97-6.92 (m, 2H), 6.63 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.56 (dd, *J* = 8.3, 2.6 Hz, 1H), 4.97 (dd, *J* = 12.1, 7.5 Hz, 1H), 3.40 (dd, *J* = 17.4, 12.1 Hz, 1H), 2.69 (dd, *J* = 17.4, 7.5 Hz, 1H), 2.05 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 149.2, 146.7, 142.3, 134.6, 129.7, 129.1, 127.5, 125.7, 118.2, 113.1, 110.7, 64.3, 47.8, 15.7; IR (film): ν_{max} 3072, 2932, 2853, 1713, 1592, 1490, 1439, 1376, 1115, 780; HRMS calcd for $C_{16}H_{16}ClN_2$ (M^+ + H) 271.1218, found 271.1215.

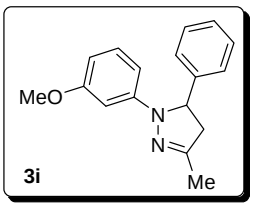


1-(4-Chloro-3-fluorophenyl)-3-methyl-5-phenyl-4,5-dihydro-1H-pyrazole (**3g**): thick liquid; yield 65%; R_f = 0.48 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.32-7.28 (m, 2H), 7.27-7.21 (m, 3H), 7.01-6.98 (m, 1H), 6.81 (t, *J* = 9.1 Hz, 1H), 6.65-6.51 (m, 1H), 4.89 (dd, *J* = 11.3, 8.3 Hz, 1H), 3.38 (dd, *J* = 17.3, 11.3 Hz, 1H), 2.69 (dd, *J* = 17.3, 8.3 Hz, 1H), 2.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 153.2, 149.5, 142.2, 131.2, 129.2, 127.7, 125.8,

116.4, 116.2, 114.8, 111.9, 65.1, 48.1, 15.8; IR (film): ν_{max} 3061, 2934, 1742, 1507, 1489, 1363, 1261, 1042, 758; HRMS calcd for $C_{18}H_{15}N_2ClF$ (M^+ + H) 289.0767, found 289.0754.

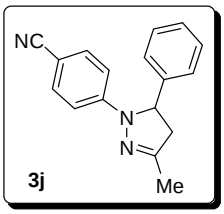


3-Methyl-5-phenyl-1-p-tolyl-4,5-dihydro-1H-pyrazole (**3h**):[17] thick liquid; yield 72%; R_f = 0.61 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.31-7.19 (m, 5H), 6.87 (d, J = 8.1 Hz, 2H), 6.74 (d, J = 8.1 Hz, 2H), 4.93 (dd, J = 12.2, 8.9 Hz, 1H), 3.36 (dd, J = 17.9, 12.2 Hz, 1H), 2.68 (dd, J = 17.9, 8.9 Hz, 1H), 2.21 (s, 3H), 2.06 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 148.2, 144.1, 143.1, 129.4, 128.9, 127.3, 125.9, 113.3, 109.8, 107.5, 104.1, 65.3, 47.8, 20.4, 15.9; IR (KBr): ν_{max} 3052, 2924, 2836, 1605, 1518, 1410, 1350, 1011, 762; HRMS calcd for $C_{17}H_{19}N_2$ (M^+ + H) 251.1407, found 251.1418.

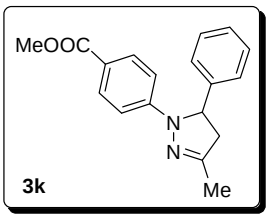


1-(3-methoxyphenyl)-3-methyl-5-phenyl-4,5-dihydro-1H-pyrazole (**3i**): thick liquid; yield 80%; R_f = 0.61 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.32-7.20 (m, 5H), 6.93 (t, J = 8.31 Hz, 1H), 6.52 (d, J = 2.3 Hz, 1H), 6.35-6.17 (m, 2H), 4.96 (dd, J = 12.1, 8.3 Hz, 1H), 3.69 (s, 3H), 3.37 (dd, J = 17.4, 12.1 Hz, 1H), 2.67 (dd, J = 17.4, 8.3 Hz, 1H), 2.05 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 160.3, 148.6, 147.3, 143.0, 129.6, 129.0, 127.4, 125.8, 110.8, 105.7, 104.4, 98.9, 64.7, 55.1, 47.8, 15.9; IR (film): ν_{max} 3062, 2923, 1729, 1587, 1492, 1367, 1236, 886, 757, 691; HRMS calcd for $C_{17}H_{19}N_2O$ (M^+ + H) 267.1356, found 267.1358.

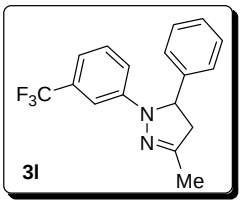
[17] US3013015, 1959



4-(3-Methyl-5-phenyl-4,5-dihydropyrazol-1-yl)benzonitrile (**3j**):[18] thick liquid; yield 62%; R_f = 0.42 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.35-7.24 (m, 5H), 7.15 (d, *J* = 6.8 Hz, 2H), 6.84 (d, *J* = 9.1 Hz, 2H), 5.09 (dd, *J* = 12.1, 6.1 Hz, 1H), 3.48 (dd, *J* = 18.8, 12.1 Hz, 1H), 2.74 (dd, *J* = 18.8, 6.1 Hz, 1H), 2.09 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 151.3, 147.4, 141.3, 133.1, 129.2, 127.8, 125.4, 120.3, 112.2, 99.4, 63.1, 47.7, 15.8; IR (film): ν_{max} 3135, 2925, 2226, 1605, 1512, 1405, 1200, 890, 753; HRMS calcd for $C_{17}H_{16}N_3$ (M^+ + H) 262.1193, found 262.1206.

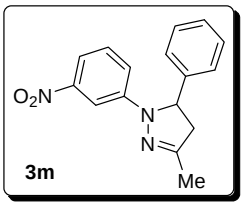


Methyl 4-(3-methyl-5-phenyl-4,5-dihydropyrazol-1-yl)benzoate (**3k**): thick liquid; yield 71%; R_f = 0.63 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.83 (d, *J* = 9.1 Hz, 1H), 7.75 (d, *J* = 9.1 Hz, 2H), 7.21-7.11 (m, 4H), 6.81 (d, *J* = 8.3 Hz, 2H), 5.11 (dd, *J* = 12.1, 6.1 Hz, 1H), 3.80 (s, 3H), 3.45 (dd, *J* = 17.4, 12.1 Hz, 1H), 2.72 (dd, *J* = 17.4, 6.1 Hz, 1H), 2.08 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 167.3, 150.5, 148.3, 141.9, 131.1, 129.2, 127.7, 125.6, 113.7, 111.6, 63.3, 47.7, 26.3, 15.9; IR (film): ν_{max} 3164, 2925, 2872, 1704, 1673, 1615, 1514, 1393, 1141, 925, 809, 715; HRMS calcd for $C_{18}H_{19}N_2O_2$ (M^+ + H) 295.1446, found 295.1450.

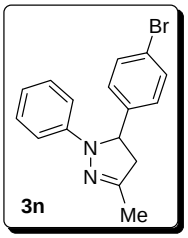


[18] D. N. Dhar, R. Raghunathan, *Indian J. Chem.*, 1984, **23B**, 1187-1189.

3-Methyl-5-phenyl-1-(3-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrazole (**3l**): thick liquid; yield 78%; R_f = 0.45 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.32 (t, *J* = 7.3 Hz, 2H), 7.26-7.23 (m, 4H), 7.14 (t, *J* = 8.2 Hz, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 5.01 (dd, *J* = 11.9, 7.3 Hz, 1H), 3.43 (dd, *J* = 17.4, 11.9 Hz, 1H), 2.76 (dd, *J* = 17.4, 7.3 Hz, 1H), 2.14 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 149.6, 142.2, 129.2, 128.6, 125.7, 123.6, 115.3, 114.7, 109.8, 108.5, 64.3, 47.8, 15.8; IR (film): ν_{max} 3170, 2932, 2862, 1590, 1490, 1443, 1117, 1072, 781; HRMS calcd for $C_{17}H_{16}N_2F_3$ (M^+ + H) 305.1125, found 305.1114.

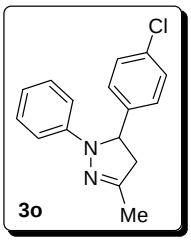


3-Methyl-1-(3-nitrophenyl)-5-phenyl-4,5-dihydro-1H-pyrazole (**3m**):[19] solid; M.p. 92–94 °C (ref. M.p. 86–88 °C); yield 52%; R_f = 0.44 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.71 (s, 1H), 7.50 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.26-7.23 (m, 3H), 7.19 (t, *J* = 7.9, 1.9 Hz, 1H), 7.06 (dd, *J* = 7.9, 1.9 Hz, 1H), 5.06 (dd, *J* = 11.9, 6.9 Hz, 1H), 3.47 (dd, *J* = 17.8, 11.9 Hz, 1H), 2.77 (dd, *J* = 17.8, 6.9 Hz, 1H), 2.10 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 150.4, 149.1, 146.1, 141.6, 129.4, 129.3, 127.8, 125.7, 118.2, 112.7, 107.4, 64.1, 47.9, 15.8; IR (KBr): ν_{max} 3296, 3047, 1617, 1526, 1493, 1365, 1334, 1263, 1092, 958, 745; HRMS calcd for $C_{16}H_{16}N_3O_2$ (M^+ + H) 282.1242 found 282.1246.

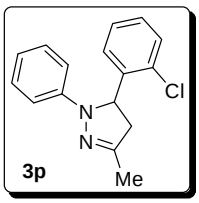


[19] H. Ferres, M. S. Hamdam, W. R. Jackson, *J. Chem. Soc. (B): Phys. Org.*, 1971, 1892-1898.

5-(4-Bromophenyl)-3-methyl-1-phenyl-4,5-dihydro-1H-pyrazole (**3n**):[20] thick liquid; yield 72%; R_f = 0.63 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.44-7.32 (m, 3H), 7.29-7.22 (m, 3H), 6.81 (d, *J* = 7.7 Hz, 2H), 6.69 (t, *J* = 7.3 Hz, 1H), 4.94 (dd, *J* = 11.9, 7.9 Hz, 1H), 3.38 (dd, *J* = 17.4, 11.9 Hz, 1H), 2.64 (dd, *J* = 17.4, 7.9 Hz, 1H), 2.06 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 148.4, 145.7, 141.9, 132.1, 131.6, 130.1, 128.9, 127.6, 125.1, 121.1, 118.8, 113.1, 107.8, 64.1, 47.6, 15.8; IR (film): ν_{max} 3208, 3056, 2966, 1628, 1592, 1312, 1102, 992, 770 ; HRMS calcd for $C_{16}H_{16}N_2Br$ (M^+ + H) 315.0356, found 315.0353.



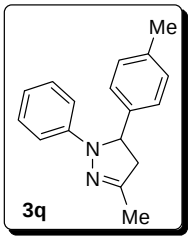
5-(4-Chlorophenyl)-3-methyl-1-phenyl-4,5-dihydro-1H-pyrazole (**3o**): thick liquid; yield 75%; R_f = 0.64 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.29-7.19 (m, 4H), 7.10-7.05 (m, 2H), 6.81 (d, *J* = 9.1 Hz, 2H), 6.69 (t, *J* = 6.8 Hz, 1H), 4.95 (dd, *J* = 12.1, 8.3 Hz, 1H), 3.38 (dd, *J* = 17.4, 12.1 Hz, 1H), 2.64 (dd, *J* = 17.4, 8.3 Hz, 1H), 2.05 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 148.4, 145.7, 141.4, 132.9, 129.1, 128.8, 127.3, 118.8, 113.1, 64.1, 47.6, 15.8; IR (film): ν_{max} 3185, 2925, 1564, 1241, 1020, 771; HRMS calcd for $C_{16}H_{16}N_2Cl$ (M^+ + H) 271.0861, found 271.0855.



5-(2-Chlorophenyl)-3-methyl-1-phenyl-4,5-dihydro-1H-pyrazole (**3p**):[21] thick liquid; yield 76%; R_f = 0.63 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.41-7.37 (m, 1H), 7.22-7.04 (m, 5H), 6.78 (d, *J* = 7.5 Hz, 2H), 6.70 (t, *J* = 6.8 Hz, 1H), 5.34 (dd, *J* = 12.1, 7.5 Hz, 1H), 3.56 (dd, *J* = 17.4, 12.1 Hz, 1H), 2.59 (dd, *J* = 17.4, 7.5 Hz, 1H), 2.06 (s, 3H); ^{13}C

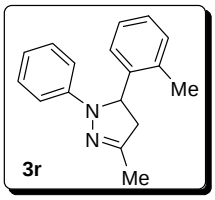
[20] Y. Chen, Y. Lam, Y.-H. Lai, *Org. Lett.*, 2003, **5**, 1067-1069.
[21] W. J. Begley, J. Grimshaw, J. Trocha-Grimshow, *J. Chem. Soc., Perkin Transaction I,* 1974, 2633-2637.

NMR ($CDCl_3$, 75 MHz): δ 148.8, 145.5, 139.7, 131.7, 129.7, 129.3, 128.9, 128.5, 127.5, 127.4, 118.7, 112.8, 61.5, 45.9, 15.8; IR (film): ν_{max} 3060, 2924, 1699, 1597, 1438, 1367, 1155, 968, 759; HRMS calcd for $C_{16}H_{16}N_2Cl$ (M^+ + H) 271.0861, found 271.0873.



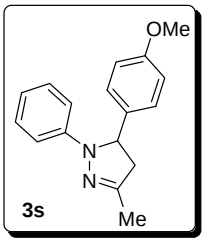
3q

3-Methyl-1-phenyl-5-p-tolyl-4,5-dihydro-1H-pyrazole (**3q**): solid; M.p. 93–95 °C; yield 73%; R_f = 0.63 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.29-7.22 (m, 1H), 7.15-7.04 (m, 5H), 6.83 (d, *J* = 7.9 Hz, 2H), 6.66 (t, *J* = 7.2 Hz, 1H), 4.93 (dd, *J* = 11.9, 8.1 Hz, 1H), 3.35 (dd, *J* = 17.2, 11.9 Hz, 1H), 2.65 (dd, *J* = 17.2, 8.1 Hz, 1H), 2.32 (s, 3H), 2.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 148.4, 146.0, 139.9, 136.8, 136.8, 129.6, 128.7, 128.4, 127.1, 125.7, 125.1, 118.4, 112.9, 107.4, 64.4, 47.8, 21.0, 15.8; IR (KBr): ν_{max} 3126, 2953, 1630, 1502, 1260, 1027, 780; HRMS calcd for $C_{17}H_{19}N_2$ (M^+ + H) 251.1415, found 251.1418.

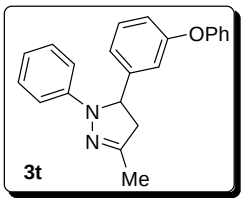


3r

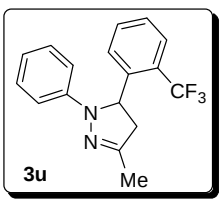
3-Methyl-1-phenyl-5-o-tolyl-4,5-dihydro-1H-pyrazole (**3r**): thick liquid; yield 71%; R_f = 0.58 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.22-7.05 (m, 6H), 6.76 (d, *J* = 7.7 Hz, 2H), 6.67 (t, *J* = 7.2 Hz, 1H), 5.10 (dd, *J* = 11.9, 8.3 Hz, 1H), 3.45 (dd, *J* = 16.6, 11.9 Hz, 1H), 2.57 (dd, *J* = 16.8, 8.3 Hz, 1H), 2.41 (s, 3H), 2.06 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 150.5, 141.3, 130.1, 127.5, 111.8, 110.8, 107.5, 104.6, 55.5, 29.7, 14.2, 13.7; IR (film): ν_{max} 3029, 2928, 1736, 1607, 1534, 1465, 1372, 1240, 1047, 913, 748; HRMS calcd for $C_{17}H_{19}N_2$ (M^+ + H) 251.1407, found 251.1420.



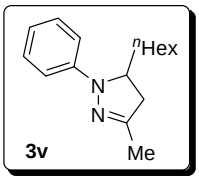
5-(4-Methoxyphenyl)-3-methyl-1-phenyl-4,5-dihydro-1H-pyrazole (**3s**):[20] thick liquid; yield 72%; R_f = 0.64 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.36-7.27 (m, 2H), 7.16 (d, *J* = 8.3 Hz, 2H), 7.11-7.06 (m, 2H), 6.81-6.77 (m, 2H), 6.67 (t, *J* = 7.5 Hz, 1H), 4.92 (dd, *J* = 11.3, 8.3 Hz, 1H), 3.76 (s, 3H), 3.34 (dd, *J* = 17.4, 11.3 Hz, 1H), 2.65 (dd, *J* = 17.4, 8.3 Hz, 1H), 2.06 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 148.5, 146.0, 140.1, 135.0, 129.8, 128.7, 126.9, 125.1, 118.5, 114.3, 113.8, 113.1, 107.2, 64.2, 55.2, 47.8, 15.9; IR (film): ν_{max} 3046, 2930, 1630, 123, 1027, 750; HRMS calcd for $C_{17}H_{19}N_2O$ (M^+ + H) 267.1356, found 267.1367.



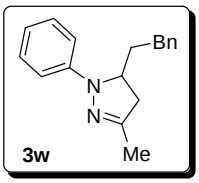
3-Methyl-5-(3-phenoxyphenyl)-1-phenyl-4,5-dihydro-1H-pyrazole (**3t**): thick liquid; yield 69%; R_f = 0.62 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.32-7.19 (m, 5H), 7.12-6.97 (m, 3H), 6.93-6.90 (m, 2H), 6.85-6.80 (m, 3H), 6.70 (t, *J* = 7.2, 1H), 4.95 (dd, *J* = 11.9, 7.9 Hz, 1H), 3.37 (dd, *J* = 17.4, 11.9 Hz, 1H), 2.71 (dd, *J* = 17.4, 7.9 Hz, 1H), 2.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 148.5, 145.9, 145.2, 138.8, 129.7, 128.8, 125.3, 123.3, 120.7, 119.1, 118.8, 117.6, 116.5, 113.4, 113.2, 107.8, 64.5, 47.7, 14.2; IR (film): ν_{max} 3085, 2926, 1582, 1488, 1237, 889, 758, 692; HRMS calcd for $C_{22}H_{21}N_2O$ (M^+ + H) 329.1653, found 329.1669.



3-Methyl-1-phenyl-5-(2-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrazole (**3u**): thick liquid; yield 60%; R_f = 0.51 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.69 (d, *J* = 7.6 Hz, 1H), 7.46-7.43 (m, 2H), 7.36-7.30 (m, 1H), 7.07 (t, *J* = 8.3 Hz, 2H), 6.77 (d, *J* = 8.3 Hz, 2H), 6.67 (t, *J* = 7.6 Hz, 1H), 5.43 (dd, *J* = 12.1, 7.5 Hz, 1H), 3.47 (dd, *J* = 18.2, 12.1 Hz, 1H), 2.62 (dd, *J* = 18.2, 7.5 Hz, 1H), 2.05, (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 147.9, 145.2, 141.3, 133.0, 128.9, 127.4, 127.2, 126.1, 118.6, 112.7, 60.5, 47.8, 15.7; IR (film): ν_{max} 3102, 2925, 2854, 1735, 1599, 1501, 1314, 1167, 1127, 967, 765; HRMS calcd for $C_{17}H_{16}N_2F_3$ (M^+ + H) 305.1115, found 305.1120.

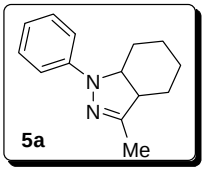


5-Hexyl-3-methyl-1-phenyl-4,5-dihydro-1H-pyrazole (**3v**): thick liquid; yield 53%; R_f = 0.65 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.56 (d, *J* = 7.5 Hz, 1H), 7.47-7.36 (m, 2H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.09 (m, 1H), 2.73 (t, *J* = 7.5 Hz, 1H), 2.61 (dd, *J* = 17.4, 9.1 Hz, 1H), 2.33 (d, *J* = 5.3 Hz, 1H), 1.76-143 (m, 2H), 1.44-1.14 (m, 10 H), 0.95-0.78 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 129.1, 124.9, 121.8, 120.9, 119.0, 113.0, 111.0, 42.7, 32.8, 31.8, 29.7, 25.1, 22.6, 16.1, 14.1, 12.4; IR (film): ν_{max} 3055, 2924, 1728, 1597, 1241, 1020, 771; HRMS calcd for $C_{16}H_{25}N_2$ (M^+ + H) 245.1877, found 245.1867.

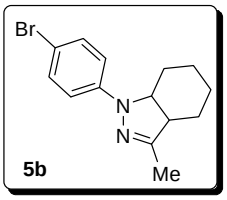


3-Methyl-5-phenethyl-1-phenyl-4,5-dihydro-1H-pyrazole (**3w**): thick liquid; yield 62%; R_f = 0.63 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.26-7.21 (m, 2H), 7.17-7.11 (m, 5H), 6.86 (d, *J* = 7.5 Hz, 2H), 6.71 (t, *J* = 7.5 Hz, 1H), 3.02 (dd, *J* = 17.4, 11.3 Hz, 1H), 2.72-2.63 (m, 1H), 2.61-2.51 (m, 2H), 1.19-2.05 (m, 1H), 2.03 (s, 3H), 1.87-1.74 (m, 1H), 1.09-0.78 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 149.1, 145.5, 141.1, 128.9, 128.4, 128.3, 126.0,

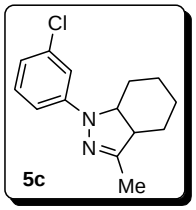
118.4, 113.1, 59.4, 42.6, 34.3, 31.3, 16.0; IR (film): ν_{max} 3027, 2926, 1722, 1598, 1503, 1454, 1383, 1287, 1073, 912; HRMS calcd for $C_{18}H_{21}N_2$ (M^+ + H) 265.1345, found 265.1342.



3-Methyl-1-phenyl-3a,4,5,6,7,7a-hexahydro-1H-indazole (**5a**):[22] thick liquid; yield 71%; R_f = 0.67 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.29 (t, J = 7.9 Hz, 2H), 7.23 (t, J = 7.9 Hz, 2H), 6.98 (t, J = 6.9 Hz, 1H), 2.21-2.14 (m, 6H), 2.11-2.02 (m, 5H), 1.93-1.88 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 129.3, 128.9, 122.5, 119.1, 116.3, 114.9, 60.0, 47.3, 34.7, 26.1, 23.3, 21.7, 14.1; IR (film): ν_{max} 3061, 2926, 2858, 1725, 1598, 1437, 1280, 1025, 762; HRMS calcd for $C_{14}H_{19}N_2$ (M^+ + H) 215.1543, found 215.1547.

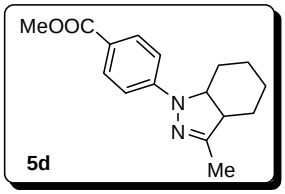


1-(4-Bromophenyl)-3-methyl-3a,4,5,6,7,7a-hexahydro-1H-indazole (**5b**): thick liquid; yield 74%; R_f = 0.64 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.55-7.49 (m, 2H), 7.35 (d, J = 9.1 Hz, 1H), 6.88 (d, J = 9.1 Hz, 1H), 2.69 (m, 1H), 2.44 (m, 1H), 2.20 (s, 3H), 2.02-1.54 (m, 6H), 1.33-0.88 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 132.2, 132.1, 131.7, 123.9, 117.4, 116.3, 59.7, 47.3, 34.4, 26.1, 23.1, 22.5, 14.1; IR (film): ν_{max} 3020, 2933, 2854, 1711, 1590, 1488, 1445, 1384, 1070, 922, 863; HRMS calcd for $C_{14}H_{18}N_2Br$ (M^+ + H) 293.0673, found 293.0679.



[22] C. W. Alexander, M. S. Hamdam, W. R. Jackson, *J. Chem. Soc., Chemical Communications,* 1972, 94-95.

1-(3-Chlorophenyl)-3-methyl-3a,4,5,6,7,7a-hexahydro-1H-indazole (**5c**): thick liquid; yield 73%; R_f = 0.67 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.07 (t, *J* = 7.9 Hz, 1H), 7.00 (t, *J* = 1.8 Hz, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 6.69 (dd, *J* = 7.7, 1.1 Hz, 1H), 3.02 (m, 1H), 2.04 (s, 3H), 2.00-1.85 (m, 2H), 1.84-1.69 (m, 1H), 1.68-151 (m, 2H), 1.33-0.96 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 154.5, 146.7, 134.8, 129.9, 118.4, 114.2, 112.4, 59.5, 47.2, 24.2, 22.9, 22.3, 21.5, 13.9; IR (film): ν_{max} 3191, 2924, 1704, 1615, 1514, 1450, 1393, 1242, 1141, 925, 809; HRMS calcd for $C_{14}H_{18}N_2Cl$ (M^+ + H) 249.1148, found 249.1142.

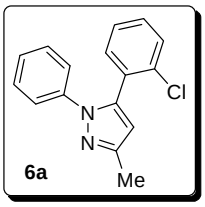


Methyl 4-(3-methyl-3a,4,5,6,7,7a-hexahydroindazol-1-yl)benzoate (**5d**): thick liquid; yield 63%; R_f = 0.53 (hexane/EtOAc = 90/10); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.04 (d, *J* = 8.9 Hz, 1H), 7.83, (d, *J* = 8.9 Hz, 1H), 7.55 (d, *J* = 8.9 Hz, 1H); 6.95 (d, *J* = 8.9 Hz, 1H), 3.9 (s, 3H), 2.78-2.76 (m, 1H), 2.45-2.43 (m, 1H), 2.20 (s, 3H), 2.09-1.93 (m, 2H), 1.91-1.69 (m, 4H), 1.66-1.56 (m, 1H), 1.36-1.10 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 167.4. 155.5, 148.4, 140.7, 131.2, 130.5, 112.3, 58.6, 51.5, 47.1, 24.4, 22.6, 22.1, 21.3, 14.0; IR (film): ν_{max} 3032, 2981, 1725, 1590, 1462, 1357, 1124, 752; HRMS calcd for $C_{16}H_{21}N_2O_2$ (M^+ + H) 273.1462, found 273.1469.

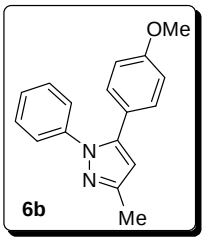
4. General Procedure for Aromatization of Pyrazolines to Pyrazoles[23]

To a solution of pyrrazoline 0.0746 mmol in 1 mL acetic acid 20 wt.% of Pd/C(10%) was added and heated to 100 °C for 6 h. After completion of reaction as indicated by TLC catalyst Pd/C was filtered off by using celite. A saturated $NaHCO_3$ solution was added to the filtrate and product was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, concentrated under vacuum and the crude product was purified by column chromatography using hexane/EtOAc as eluent to afford the pyrazole.

[23] N. Nakamichi, Y. Kawashita, M. Hayashi, *Org. Lett.*, 2002, **4**, 3955-3957.



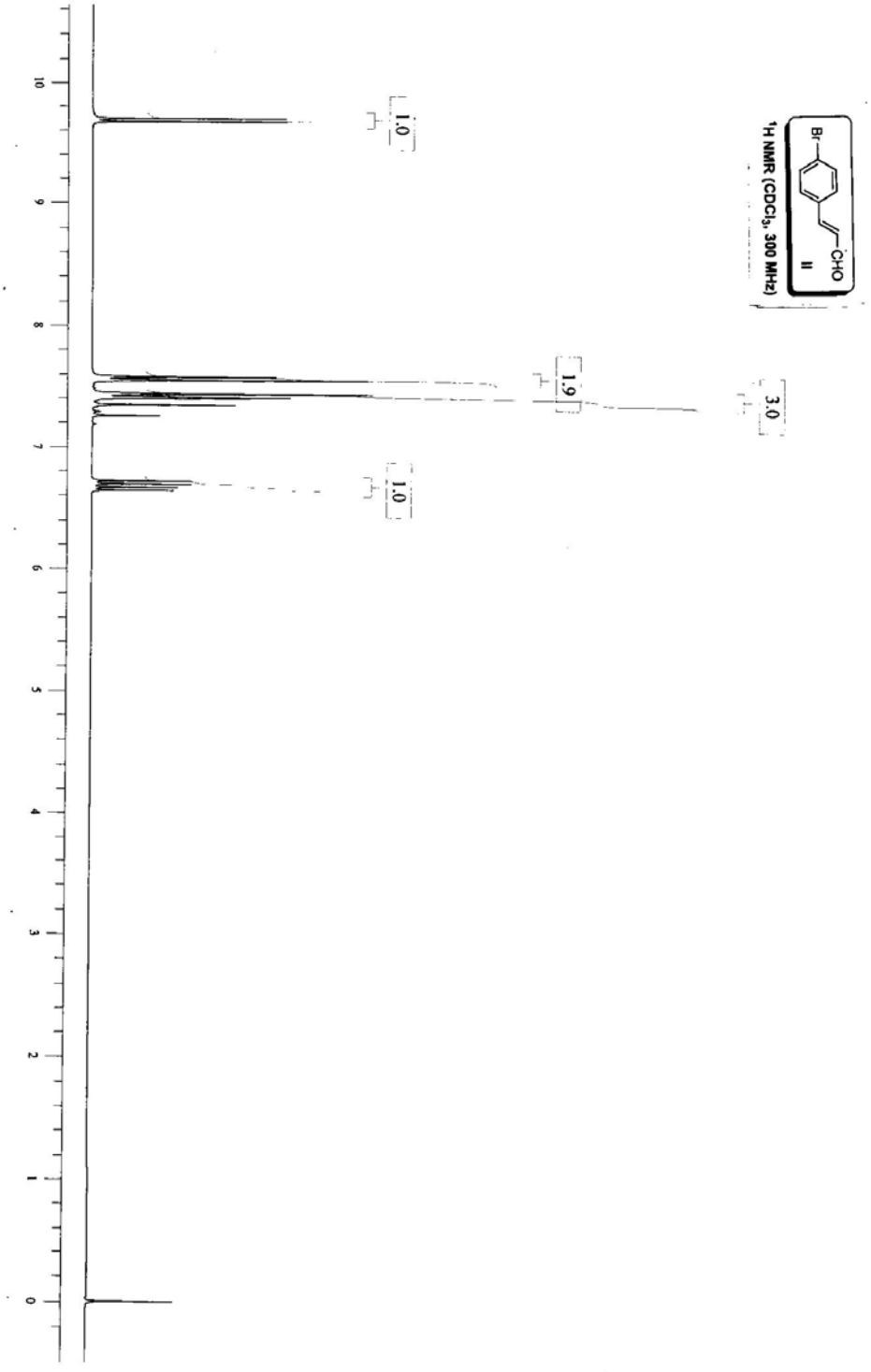
5-(2-chlorophenyl)-3-methyl-1-phenyl-1H-pyrazole (**6a**):[21] thick liquid; yield 95%; R_f = 0.72 (hexane/EtOAc = 95/05); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.38 (d, J = 7.9 Hz, 1H), 7.28-7.16 (m, 8H), 6.26 (s, 1H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 149.1, 140.2, 140.1, 133.8, 132.0, 130.5, 129.9, 129.8, 128.7, 126.7, 126.6, 123.8, 109.3, 13.6; IR (film): ν_{max} 3018, 3060, 2926, 2856, 1727, 1598, 1501, 1439, 1369, 1282, 1060, 971, 760; HRMS calcd for $C_{16}H_{14}N_2Cl$ (M^+ + H) 269.0731, found 269.0736.

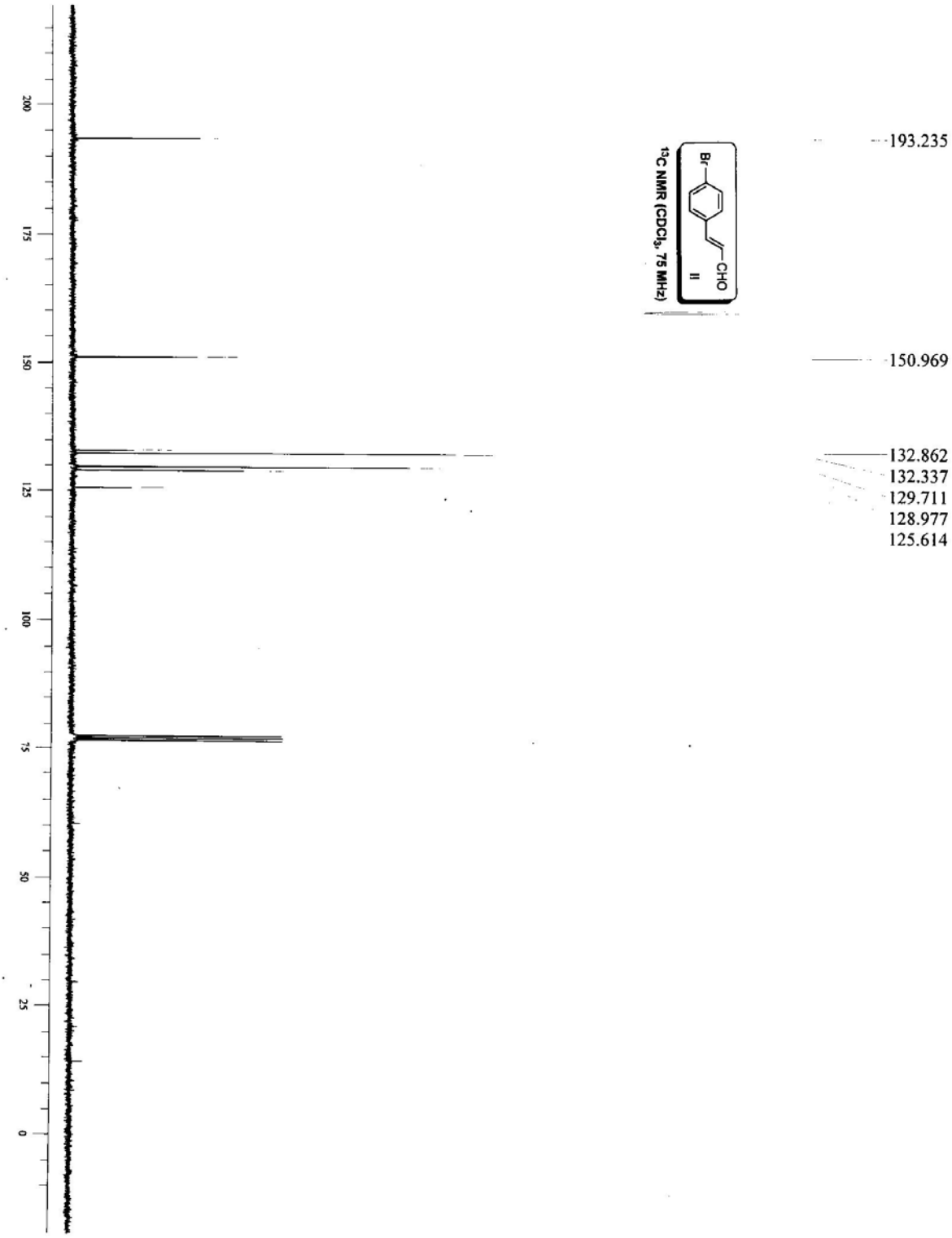


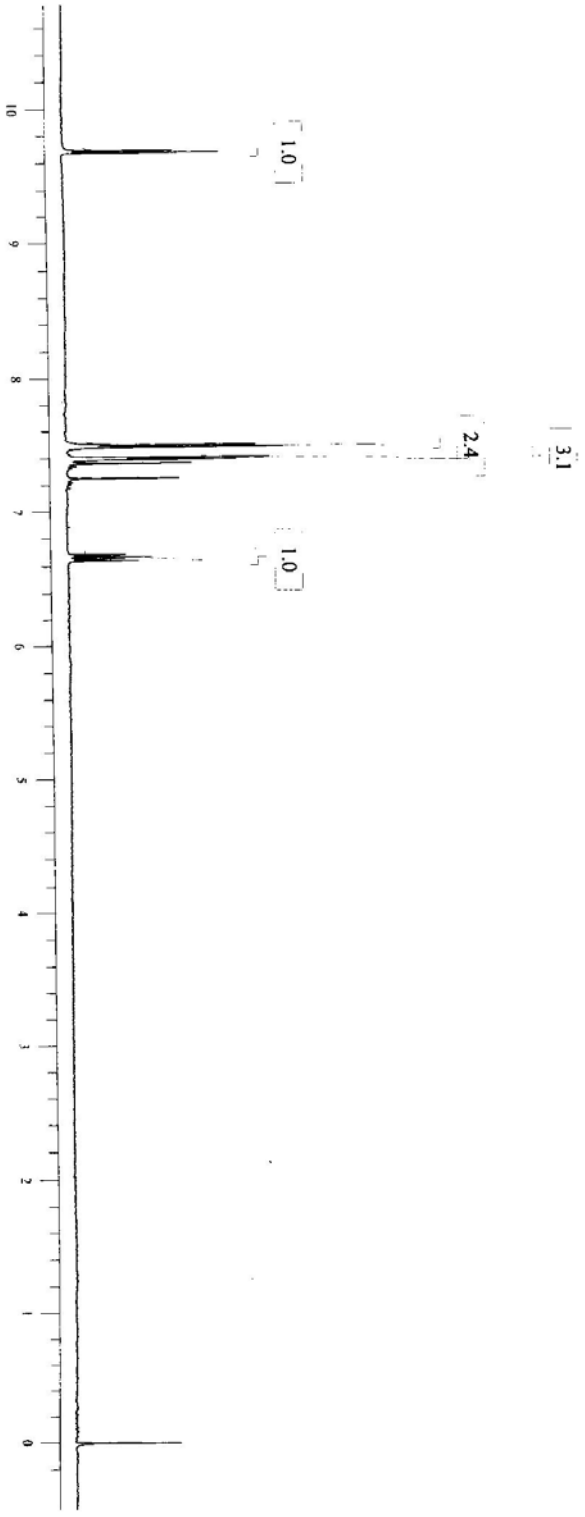
5-(4-methoxyphenyl)-3-methyl-1-phenyl-1H-pyrazole (**6b**):[24] thick liquid; yield 96%; R_f = 0.72 (hexane/EtOAc = 95/05); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.30-7.19 (m, 5H), 7.09 (d, J = 8.8 Hz, 2H), 6.76 (d, J = 7.9 Hz, 2H), 6.17 (s, 1H), 3.78 (s, 3H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.3, 149.3, 143.5, 140.2, 129.8, 128.7, 126.9, 125.1, 123.1, 113.8, 107.1, 55.2, 13.5; IR (film): ν_{max} 3046, 2925, 2853, 1727, 1606, 1507, 1460, 1250, 1032, 763; HRMS calcd for $C_{17}H_{17}N_2O$ (M^+ + H) 265.1342, found 265.1353.

[24] C. A. Dvorak, D. A. Rudolph, S. Ma, N. I. Carruthers, *J. Org. Chem.*, 2005, **70**, 4188-4190.

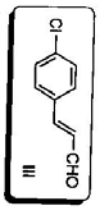
5. ^{1}H NMR and ^{13}C NMR Spectra of Compounds



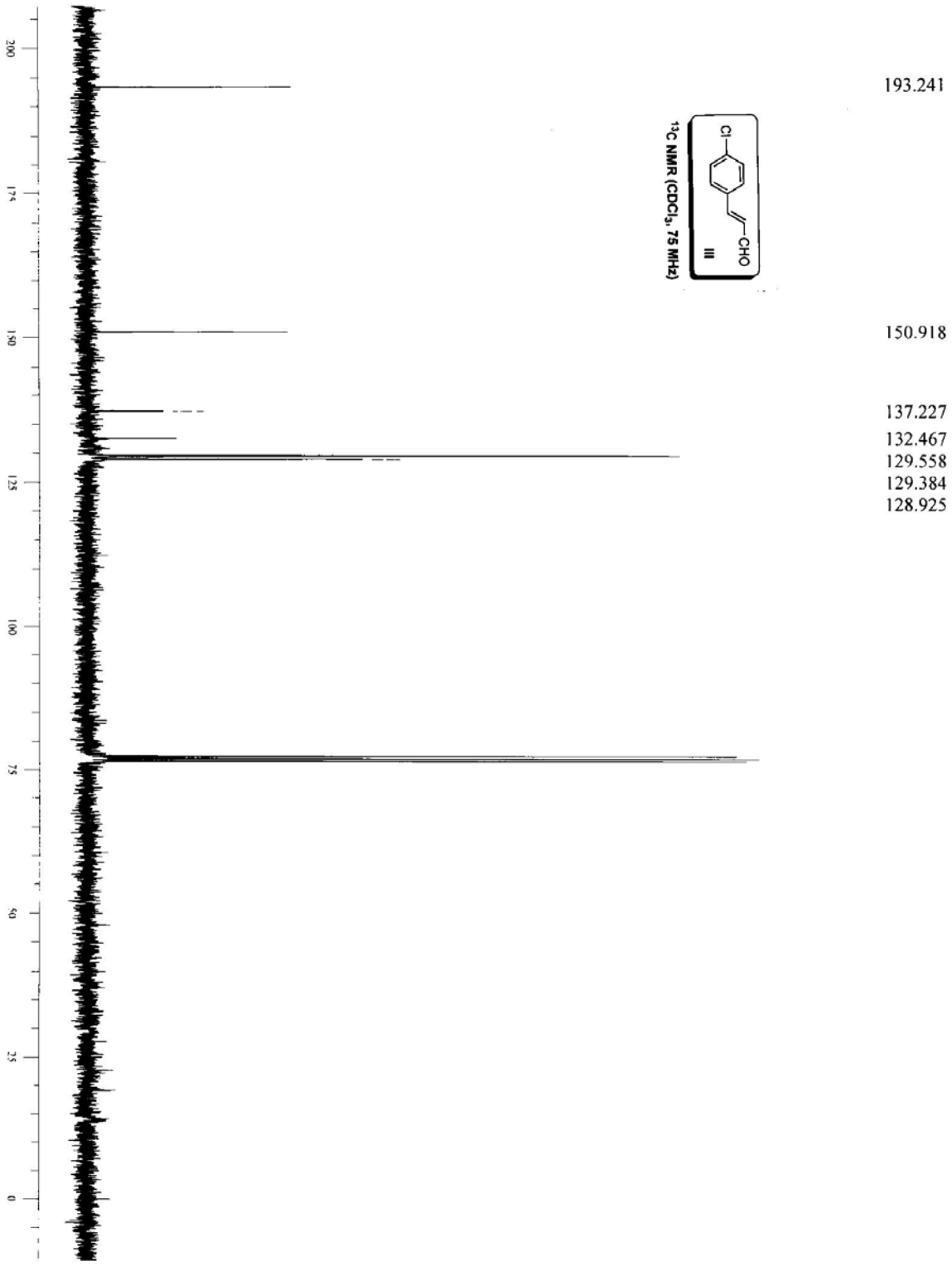

^{13}C NMR ($CDCl_3$, 75 MHz)
Br
CHO
O
193.235
150.969
132.862
132.337
129.711
128.977
125.614
200
175
150
125
100
75
50
25
0

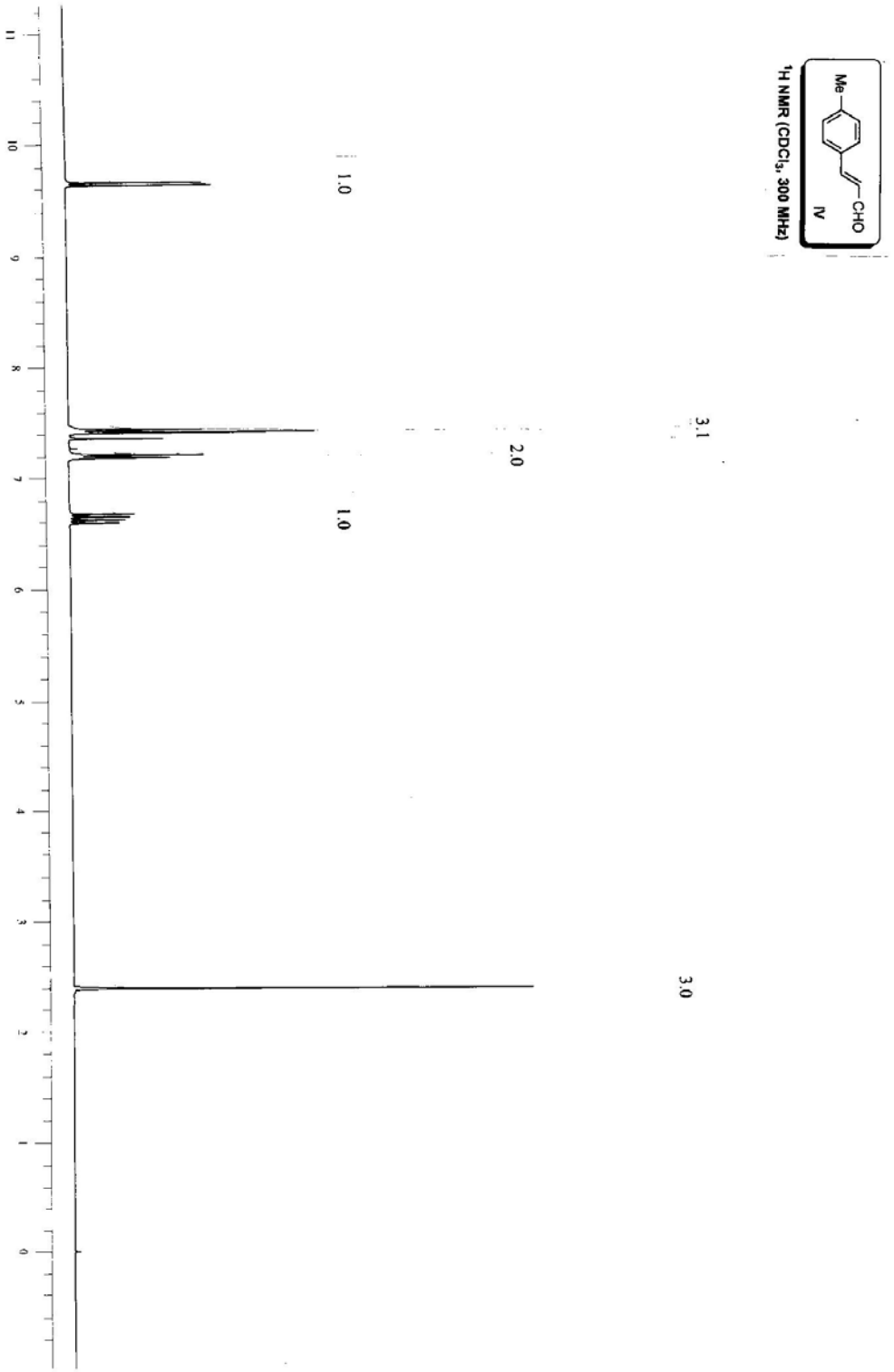


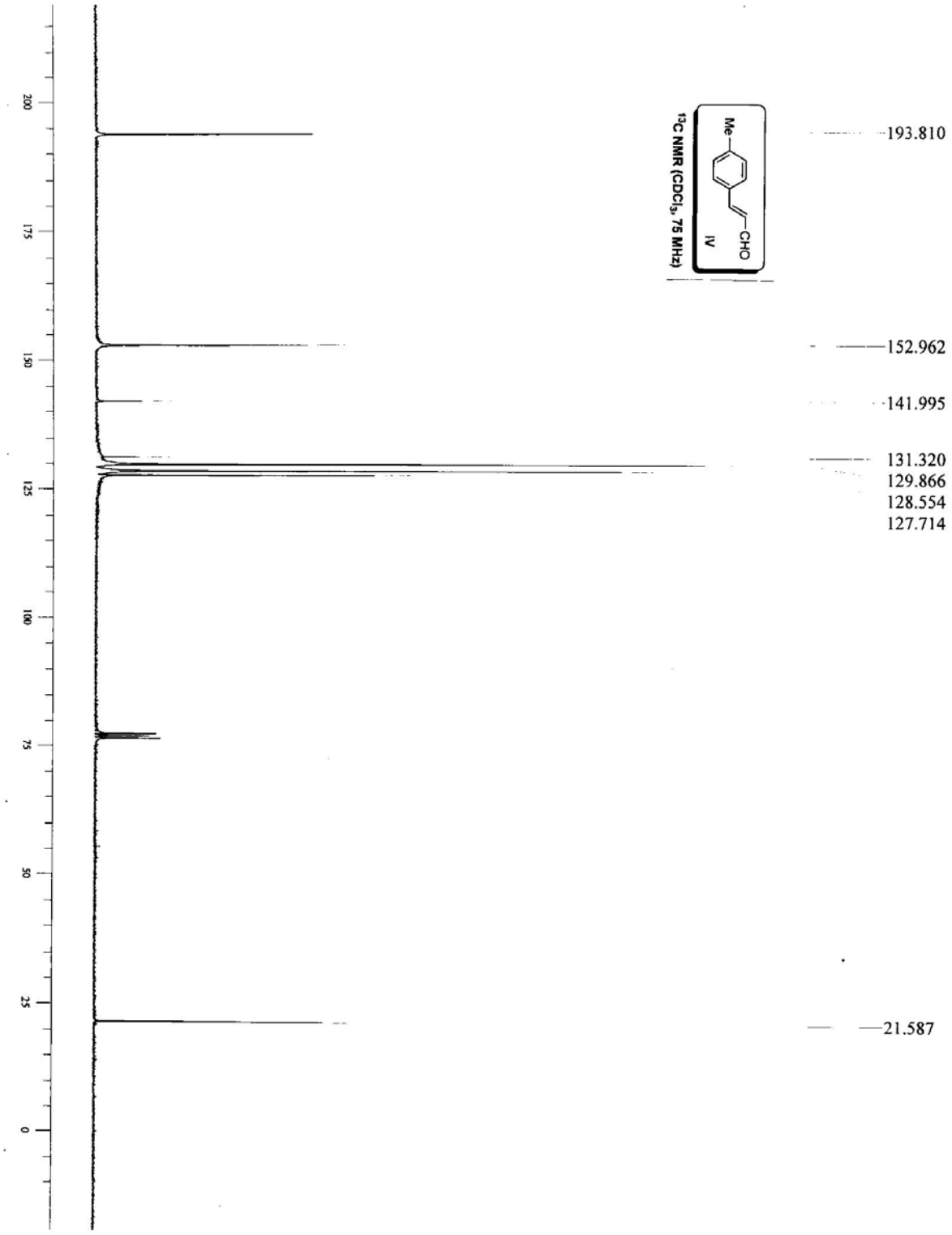
^{1}H NMR (CDCl$_3$,500 MHz)

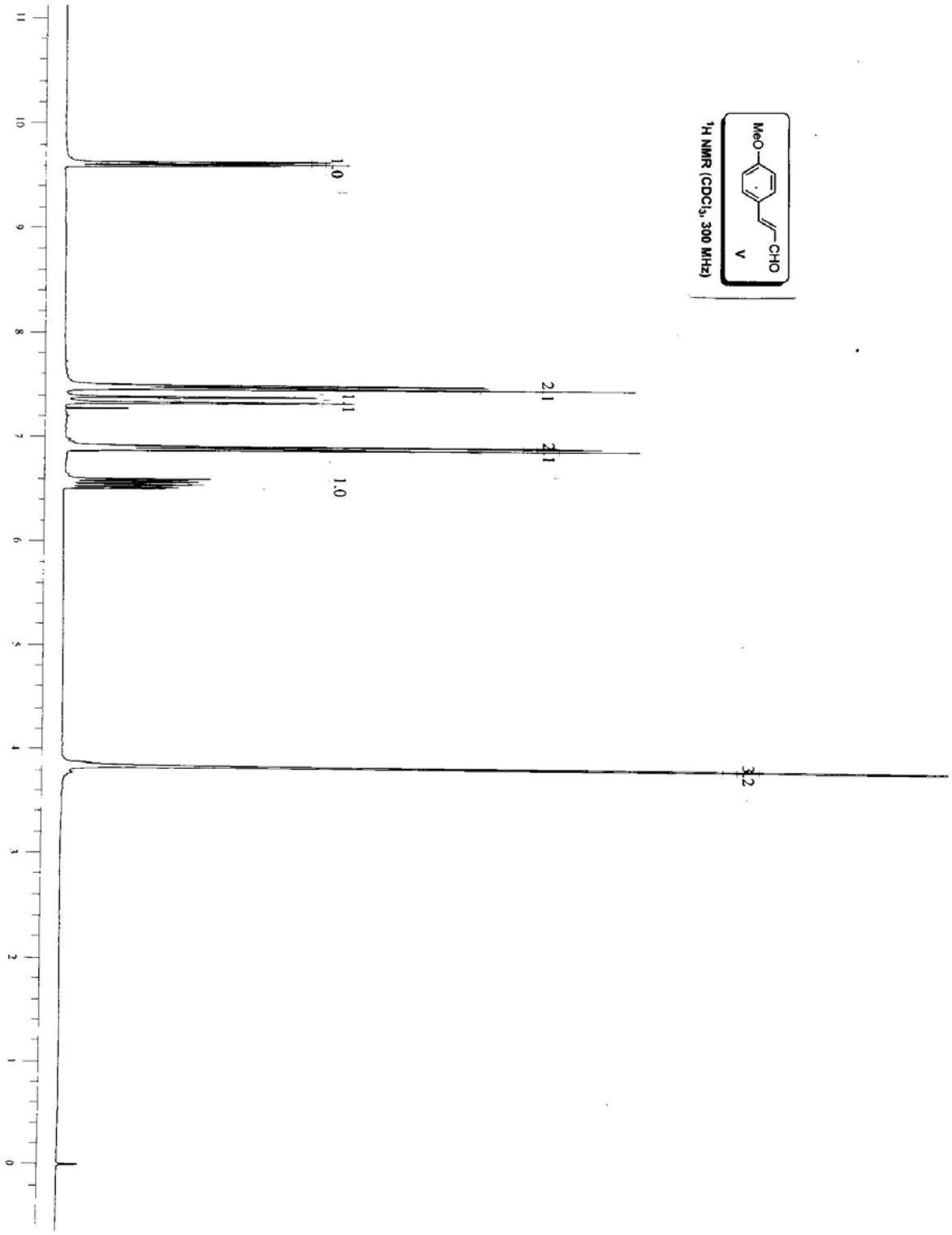


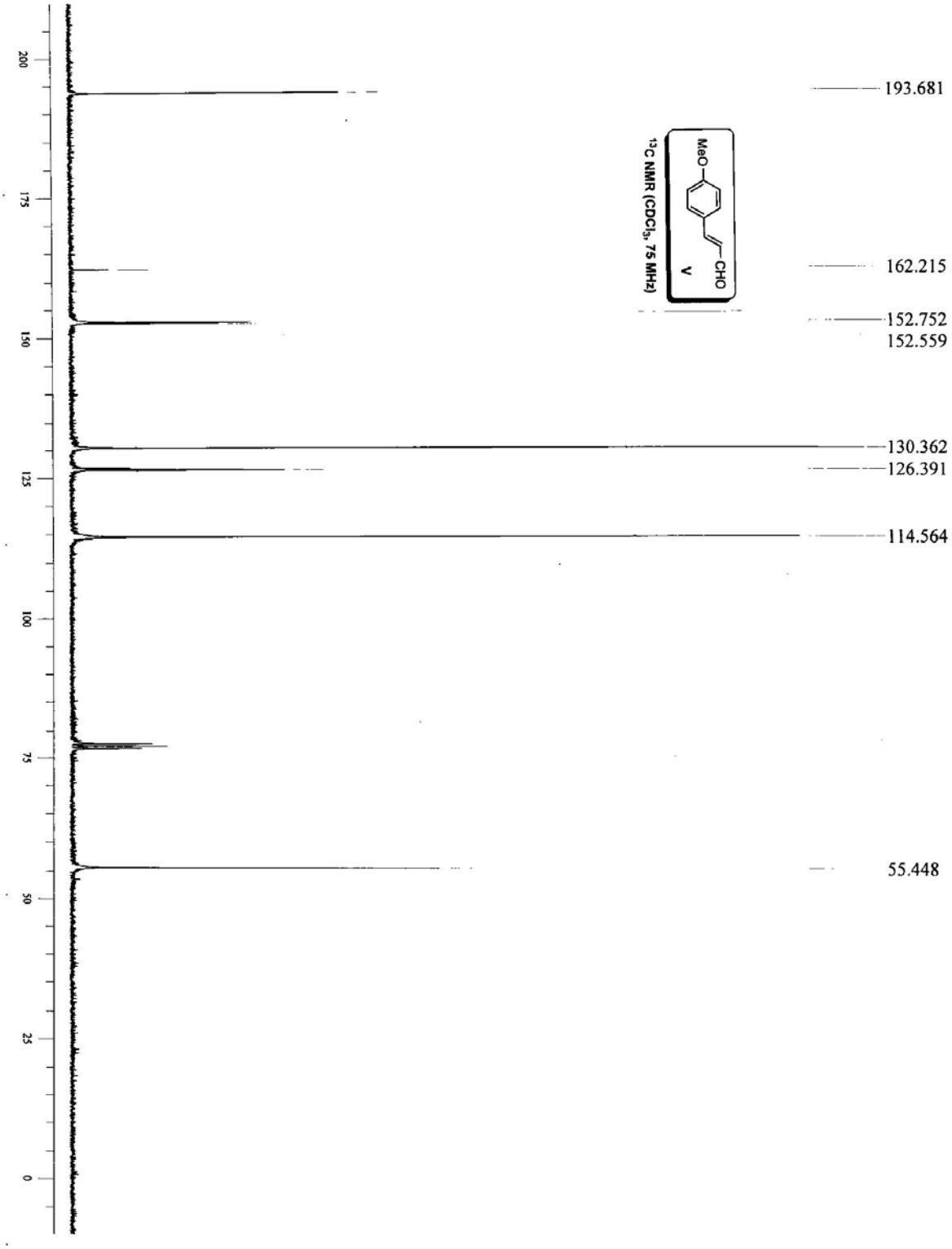
III

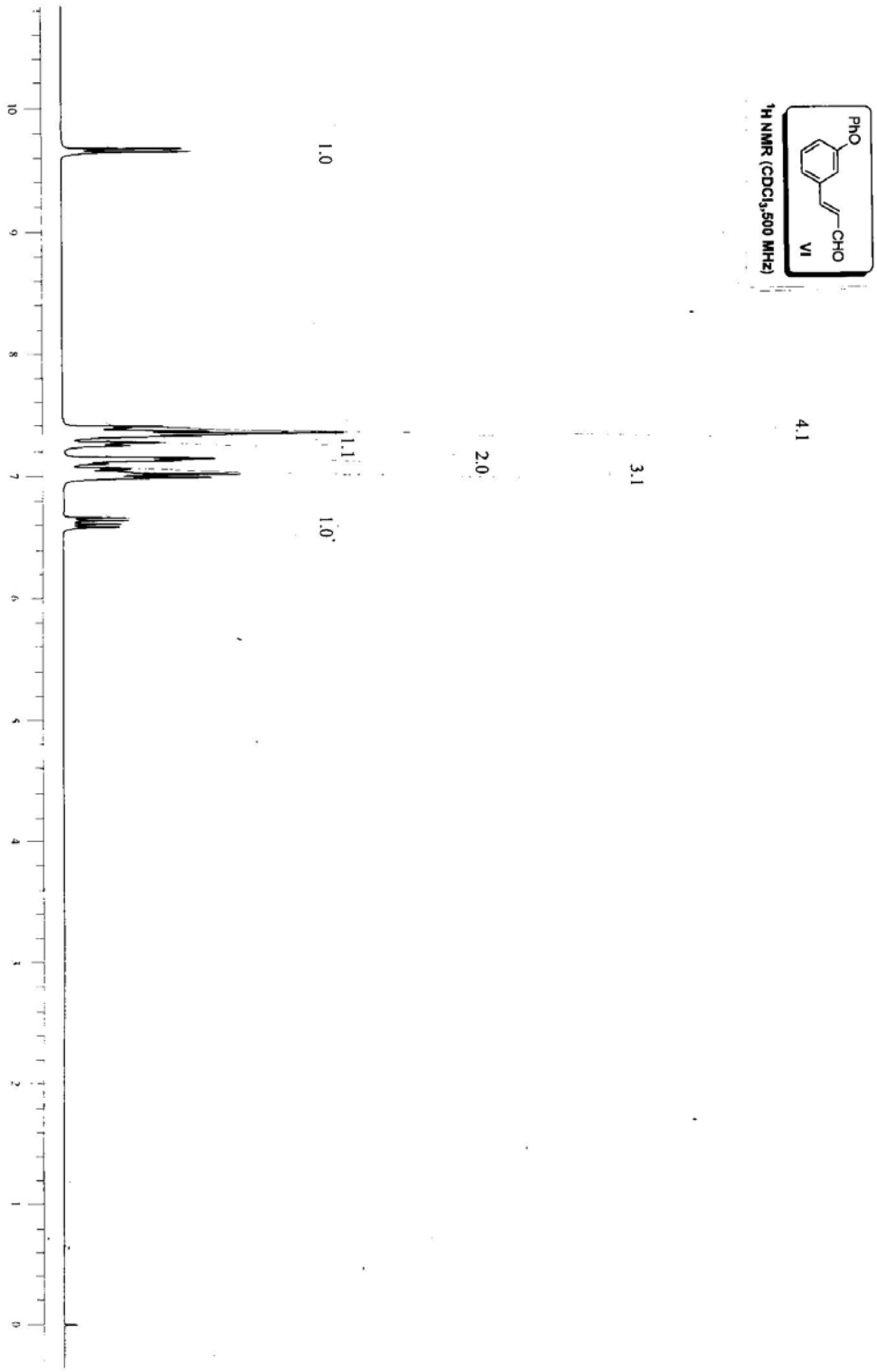

^{13}C NMR ($CDCl_3$, 75 MHz)
Cl
CHO
III
193.241
150.918
137.227
132.467
129.558
129.384
128.925
200
175
150
125
100
75
50
25
0

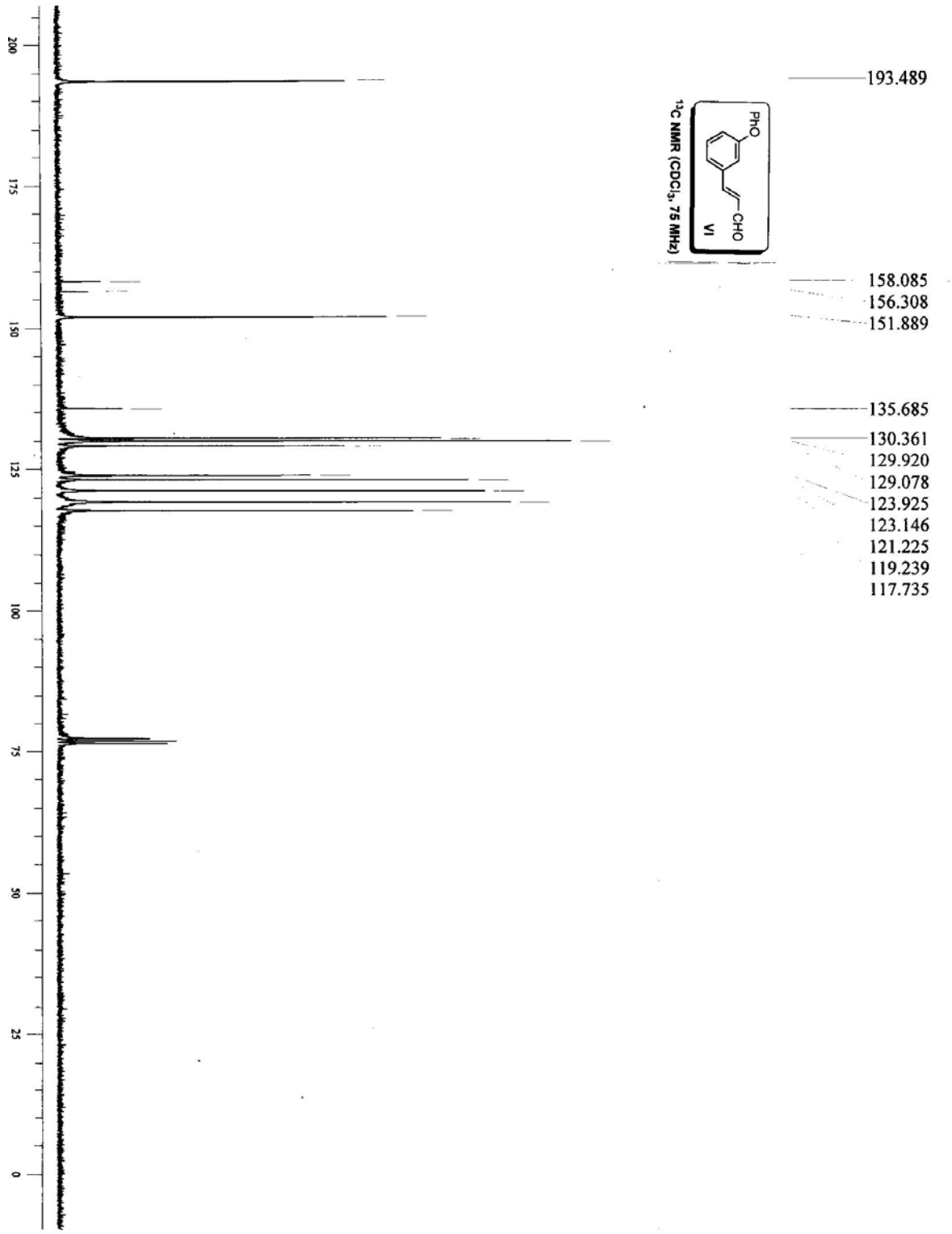

Me
CHO
IV
^{1}H NMR ($CDCl_3$, 300 MHz)
1.0
2.0
1.0
3.1
3.0

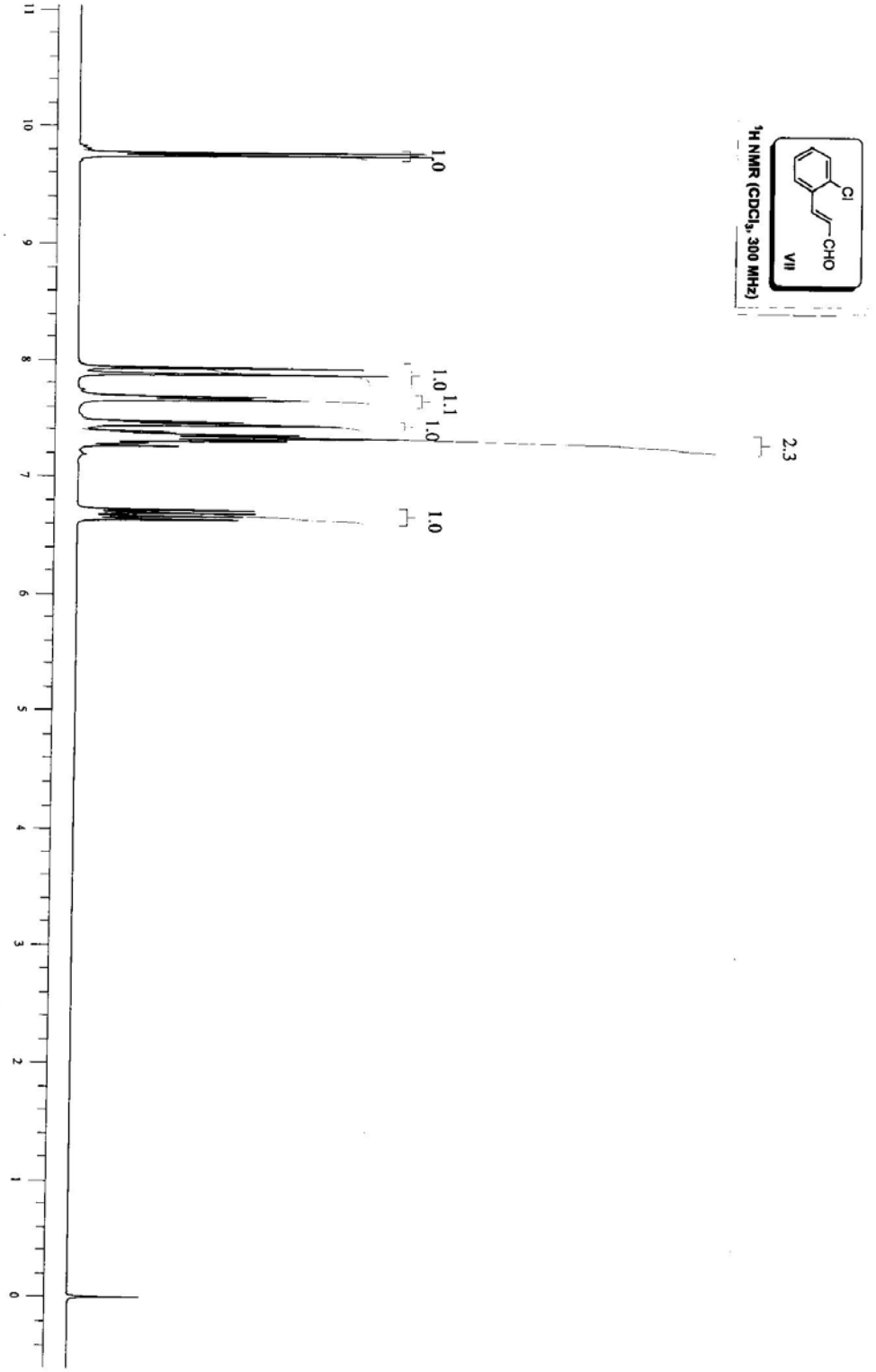

^{13}C NMR (CDCl$_3$, 75 MHz)
Me
CHO
IV
193.810
152.962
141.995
131.320
129.866
128.554
127.714
21.587
200
175
150
125
100
75
50
25
0

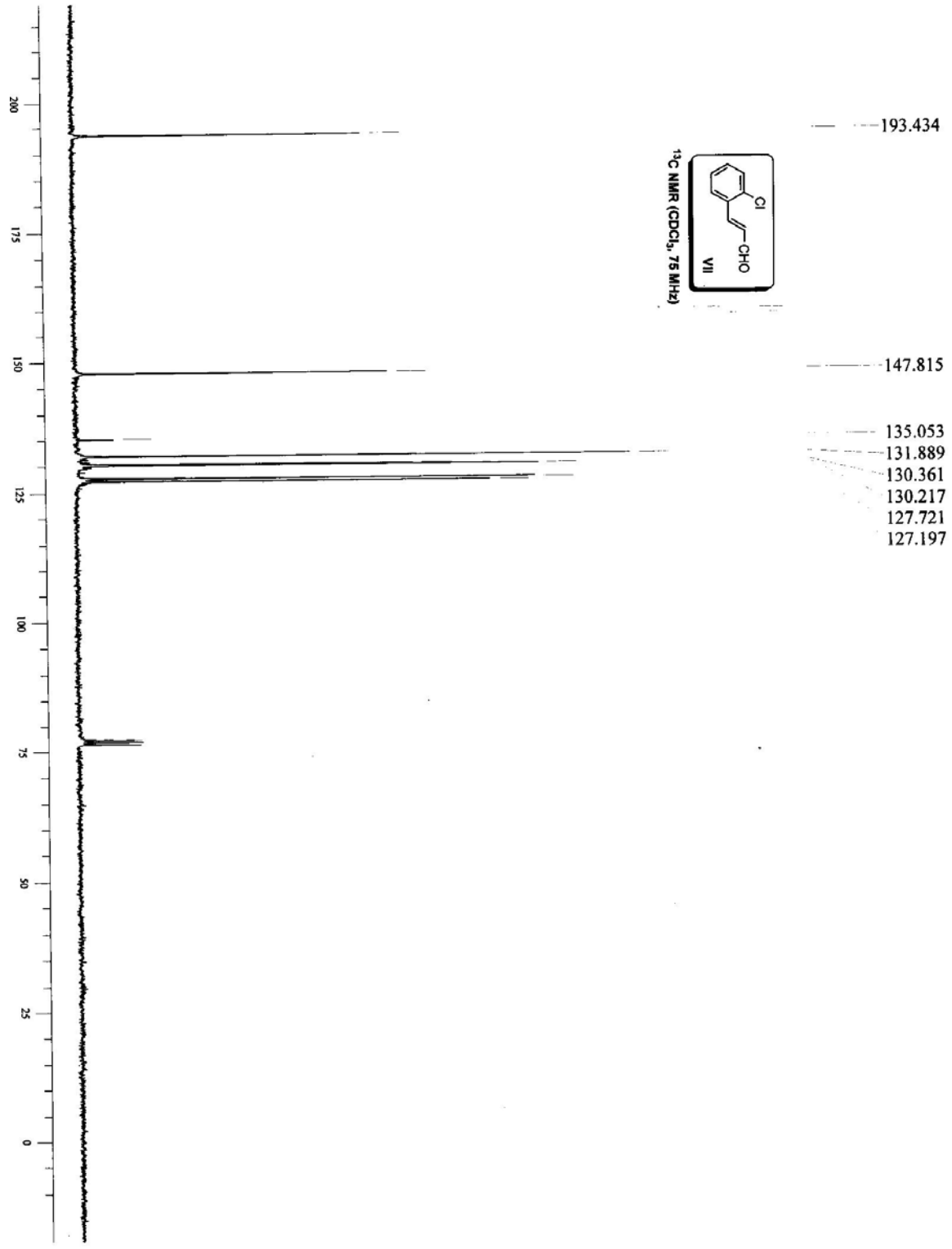

MeO
CHO
v
^{1}H NMR (CDCl$_3$, 300 MHz)
1.0
1.1
2.1
2.1
1.0
3.2

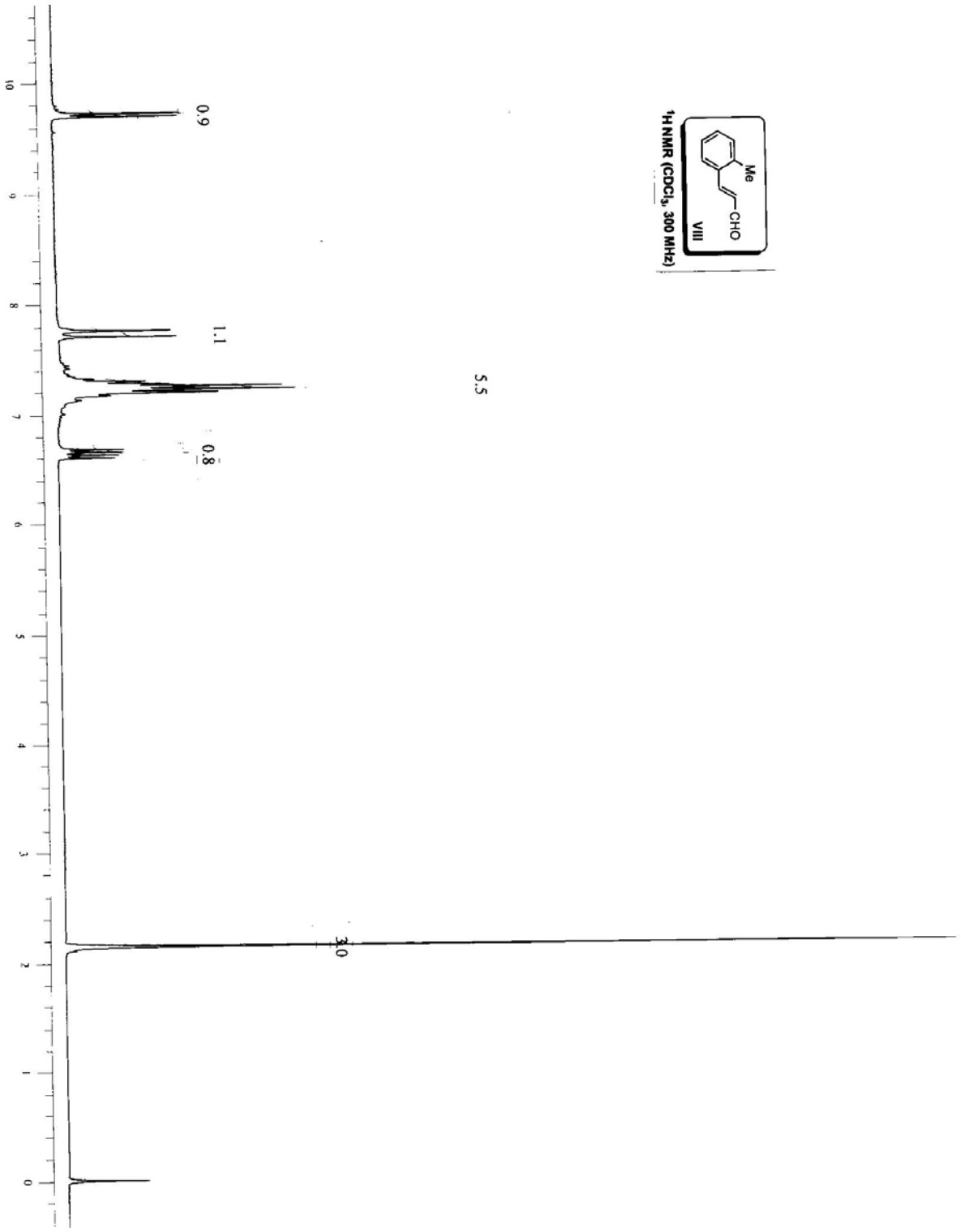

^{13}C NMR ($CDCl_3$, 75 MHz)
MeO
CHO
v
193.681
162.215
152.752
152.559
130.362
126.391
114.564
55.448
200
175
150
125
100
75
50
25
0

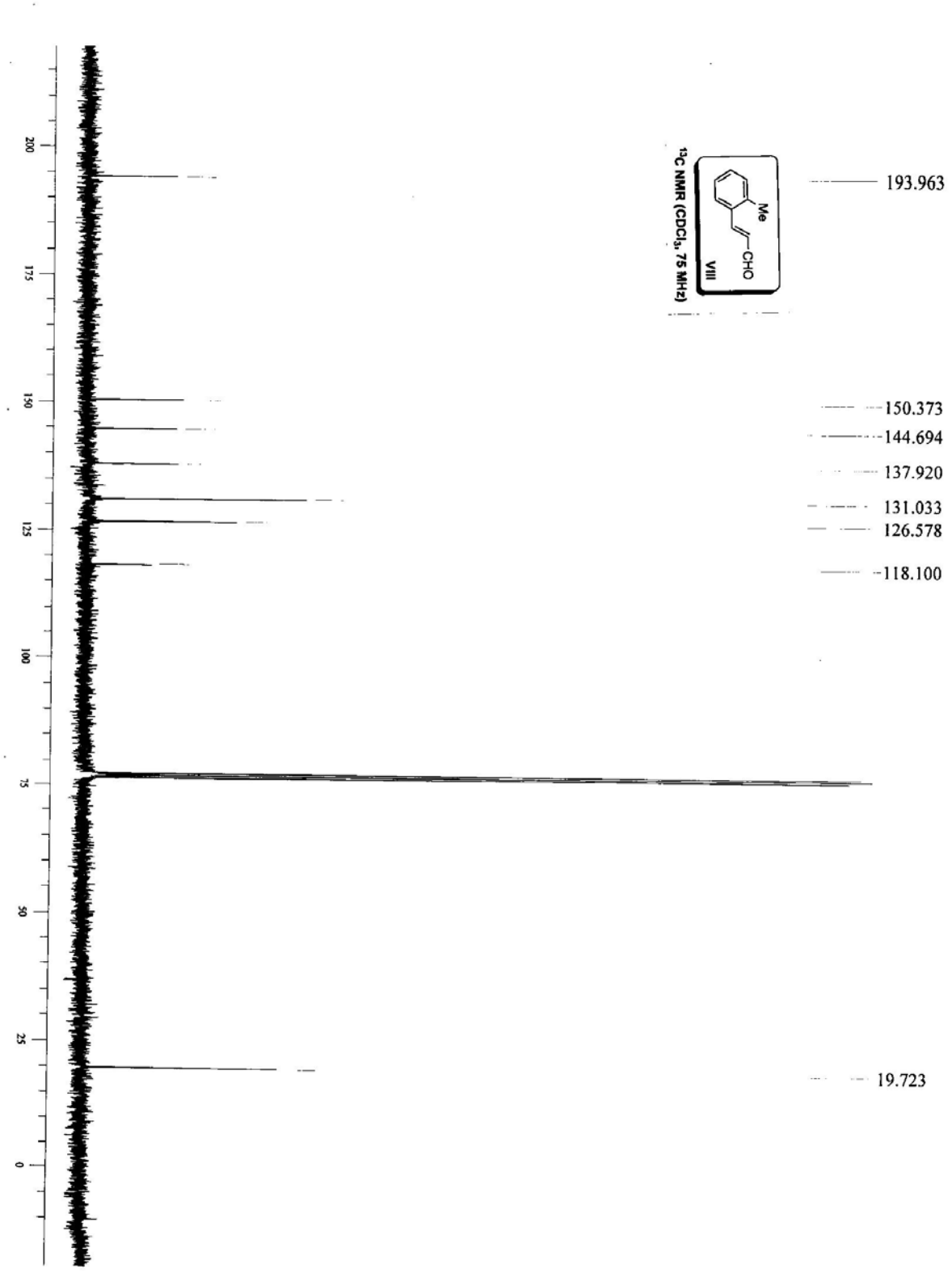

PhO
CHO
VI
¹H NMR (CDCl₃,500 MHz)
1.0
1.1
2.0
3.1
4.1
1.0

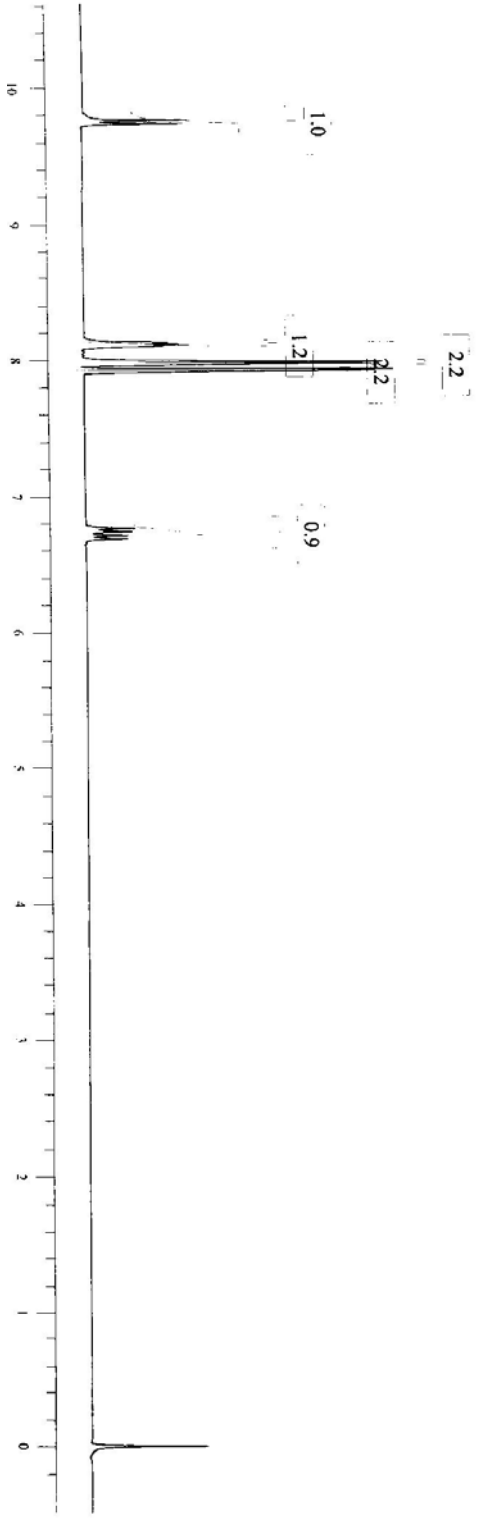

^{13}C NMR (CDCl$_3$, 75 MHz)
PhO
CHO
VI
193.489
158.085
156.308
151.889
135.685
130.361
129.920
129.078
123.925
123.146
121.225
119.239
117.735
200
175
150
125
100
75
50
25
0


VII
^{1}H NMR (CDCl$_3$, 300 MHz)
1.0
1.0
1.1
1.0
2.3
1.0

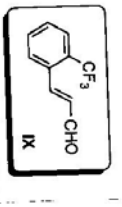

193.434
147.815
135.053
131.889
130.361
130.217
127.721
127.197
^{13}C NMR (CDCl$_3$, 75 MHz)
Cl
CHO
VII
200
175
150
125
100
75
50
25
0

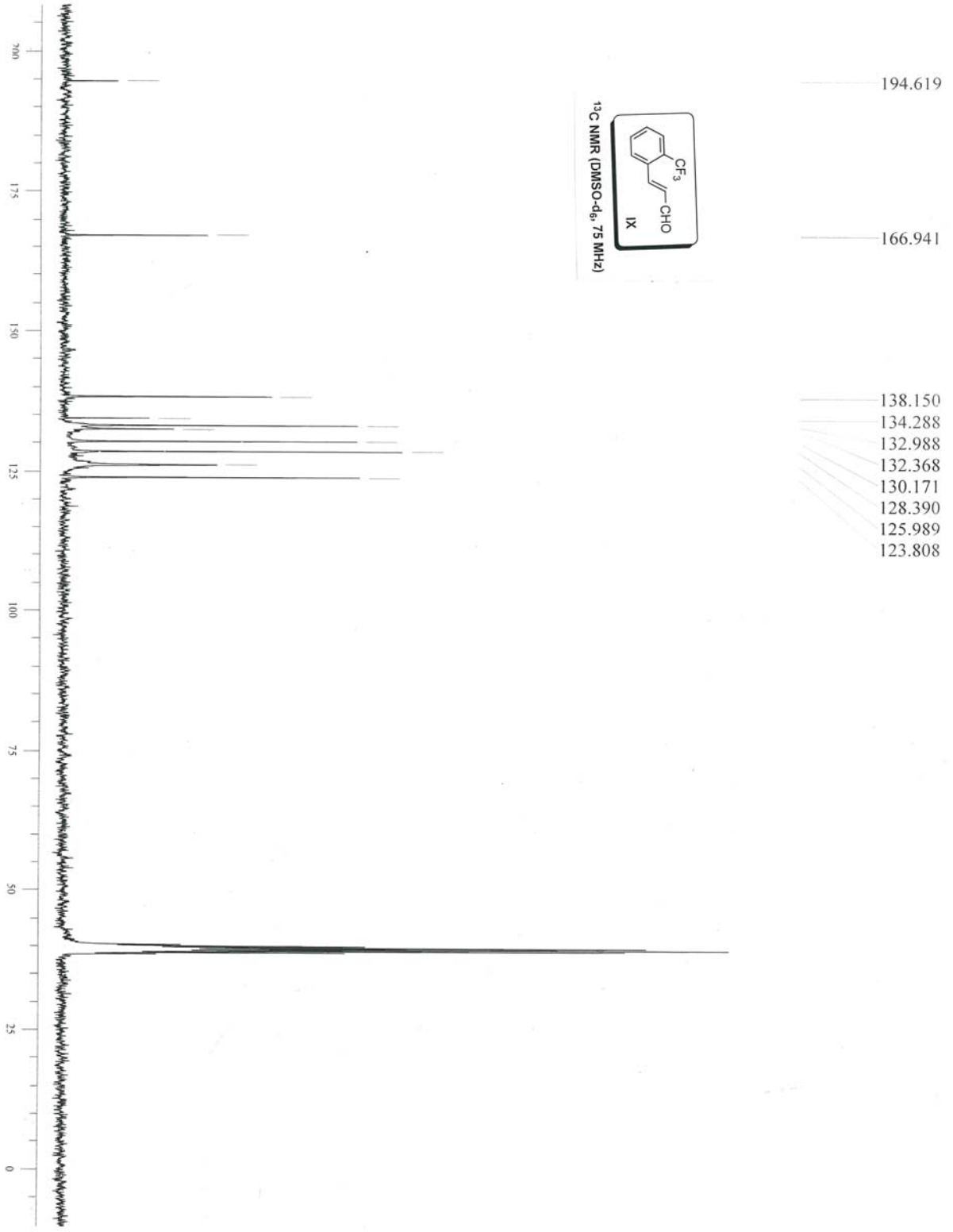

Me
CHO
VIII
^{1}H NMR (CDCl$_3$, 300 MHz)
0.9
1.1
0.8
5.5
30

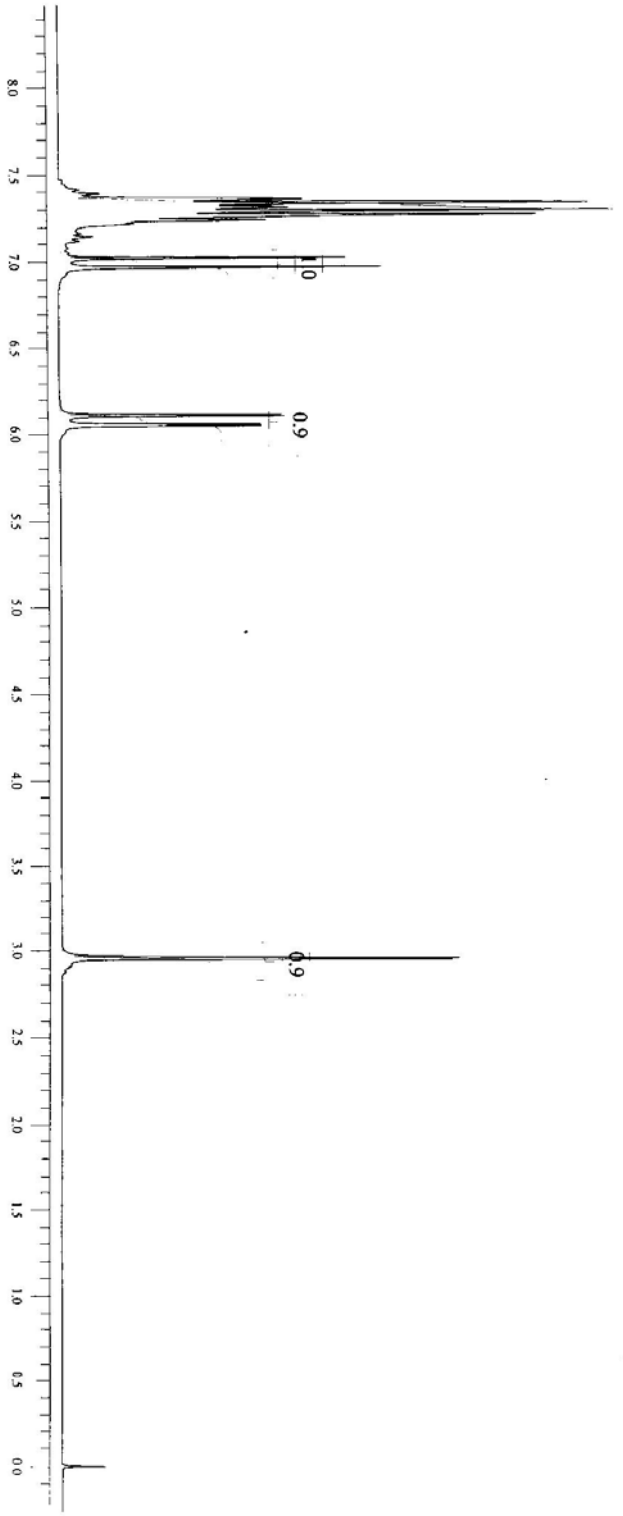

^{13}C NMR (CDCl$_3$, 75 MHz)
Me
CHO
VIII
193.963
150.373
144.694
137.920
131.033
126.578
118.100
19.723
200
175
150
125
100
75
50
25
0



^{1}H NMR ($CDCl_3$, 300 MHz)



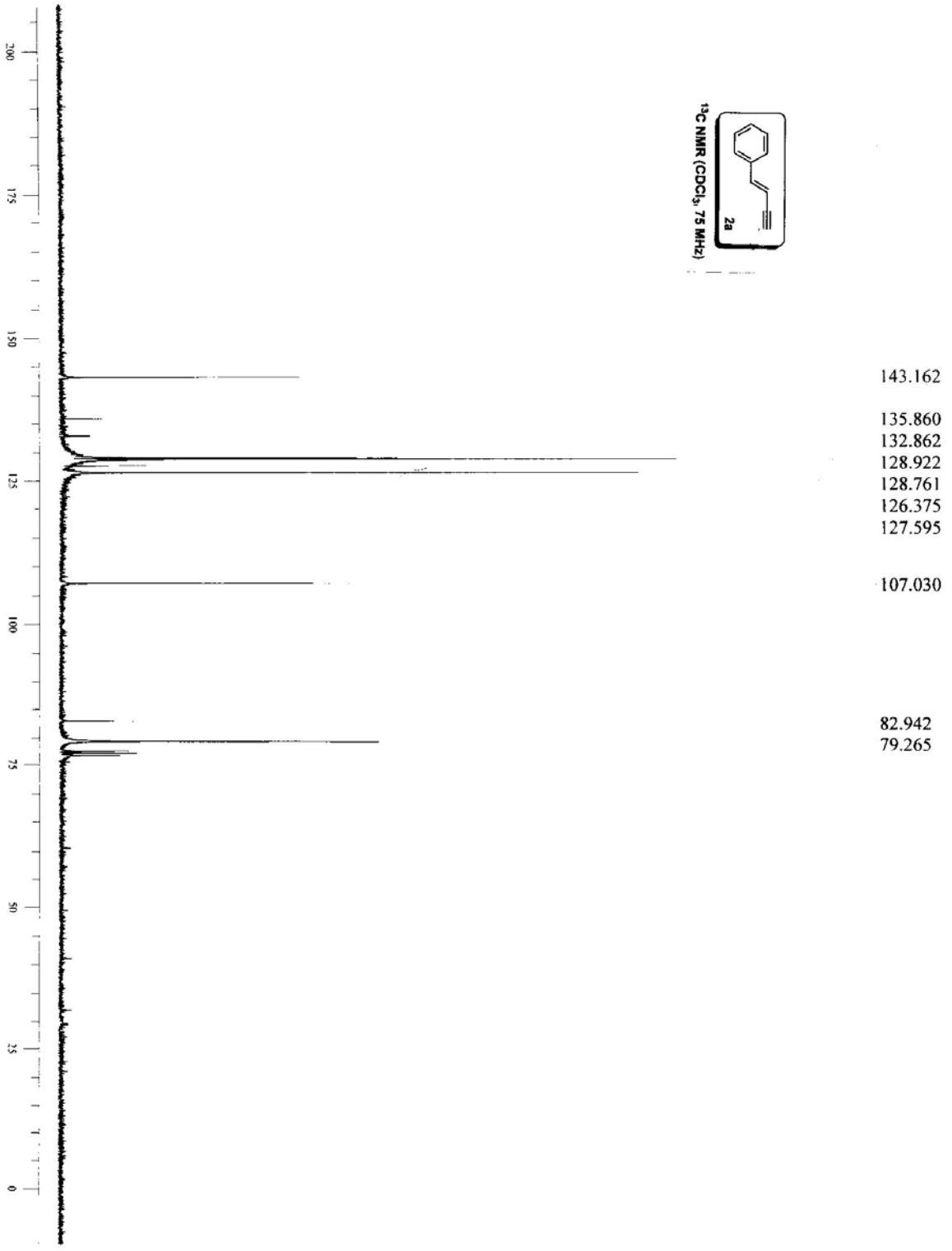

194.619
166.941
138.150
134.288
132.988
132.368
130.171
128.390
125.989
123.808
^{13}C NMR (DMSO-d_6, 75 MHz)
CF$_3$
CHO
IX
200
175
150
125
100
75
50
25
0

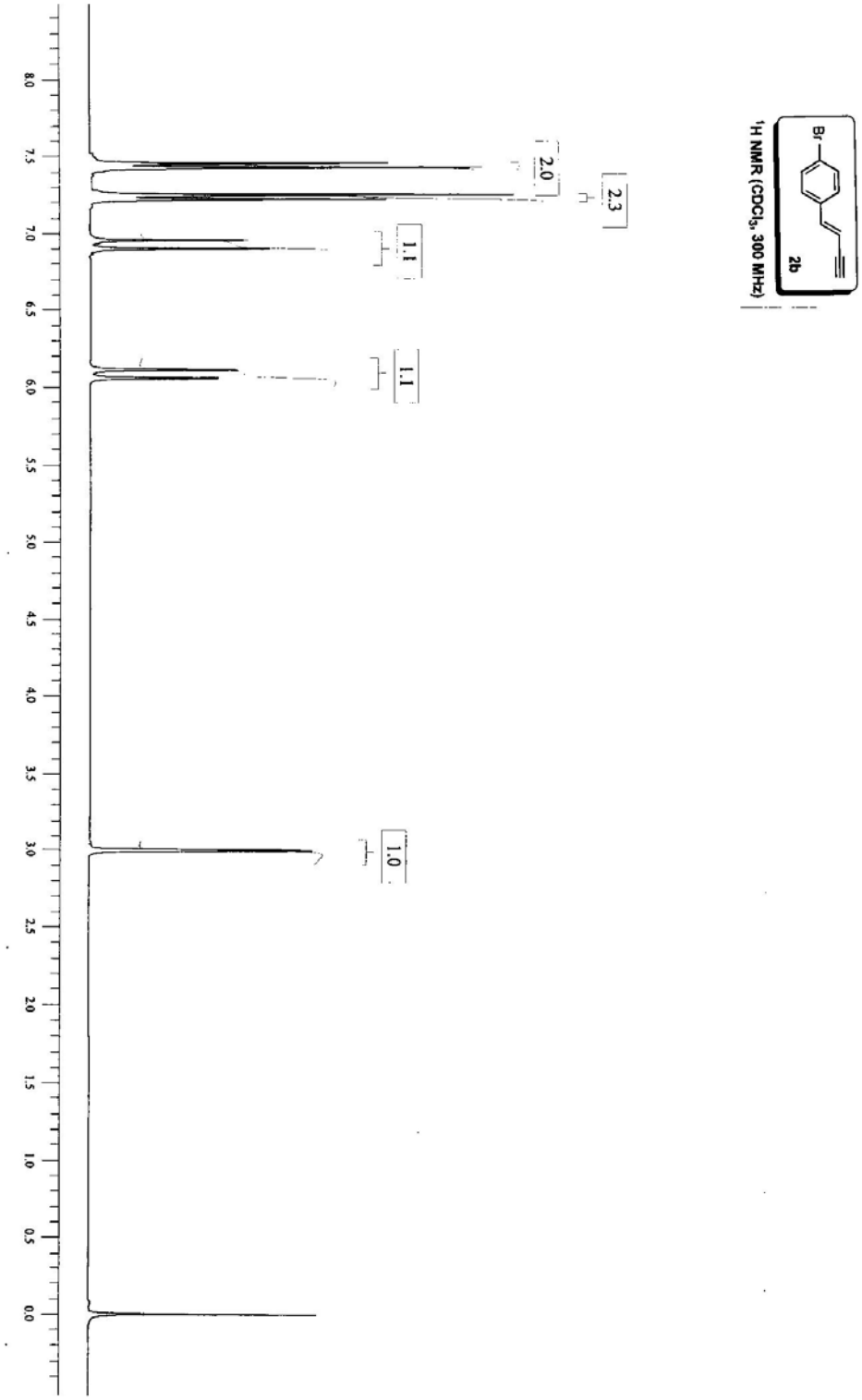


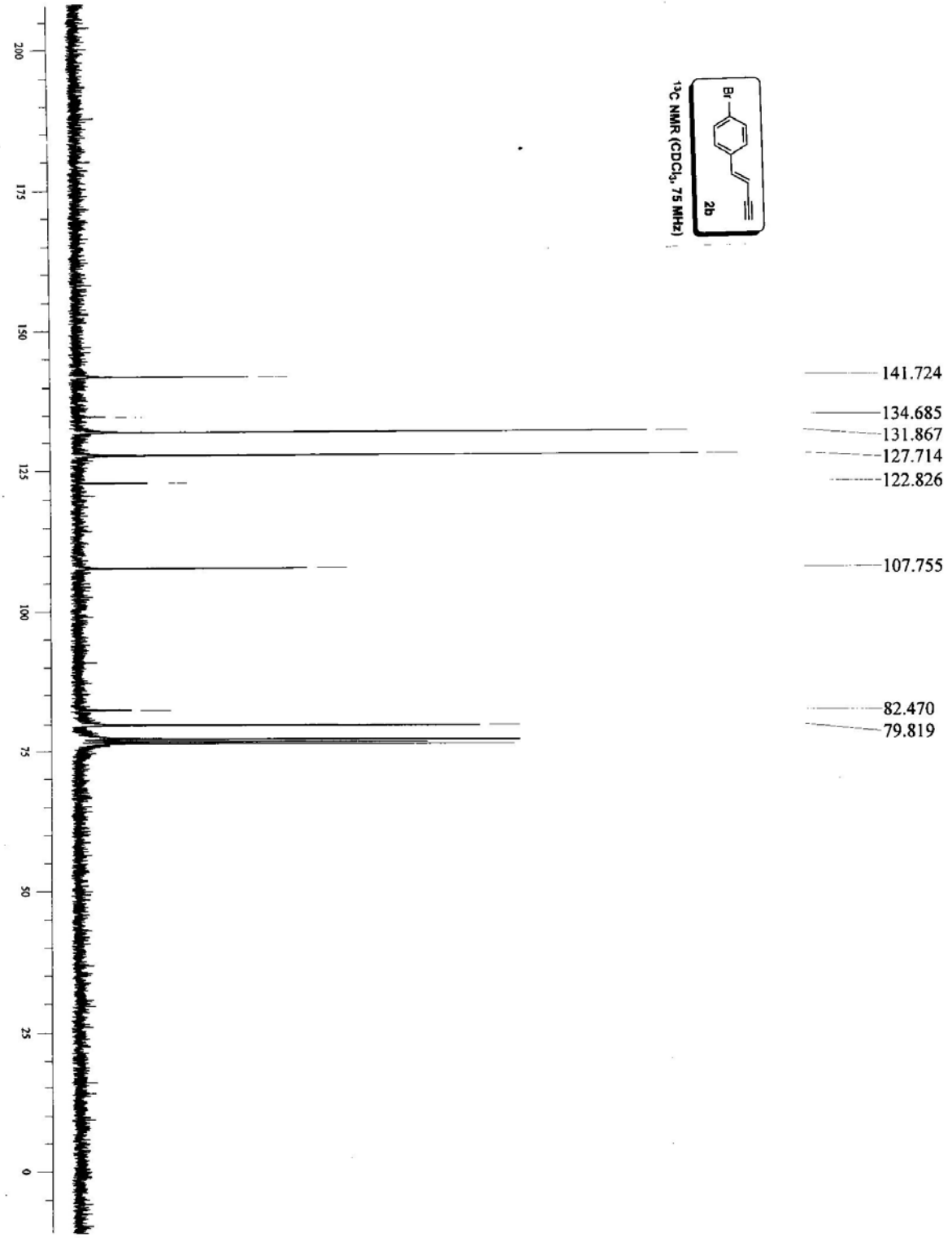
2a

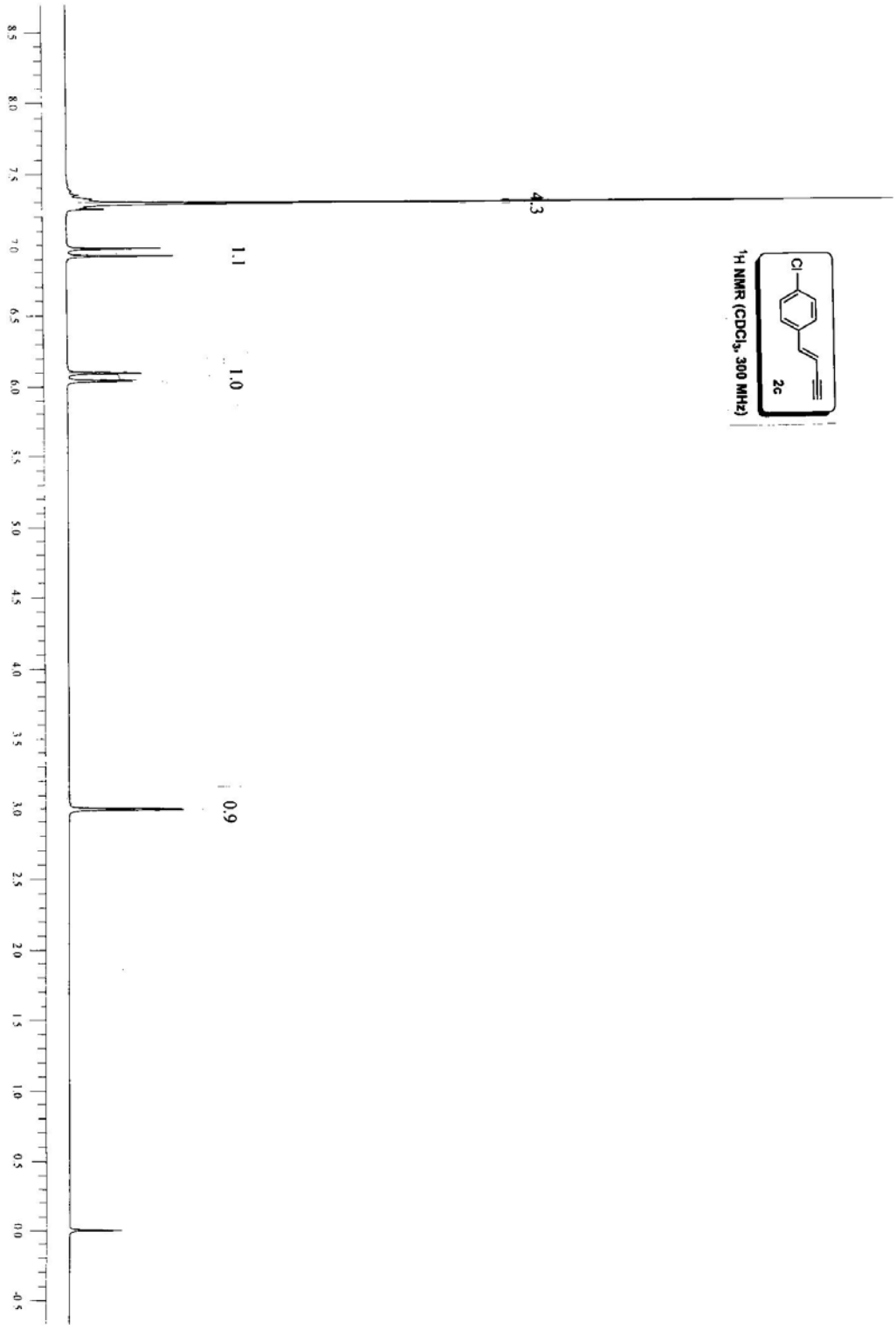
^{1}H NMR ($CDCl_3$, 300 MHz)

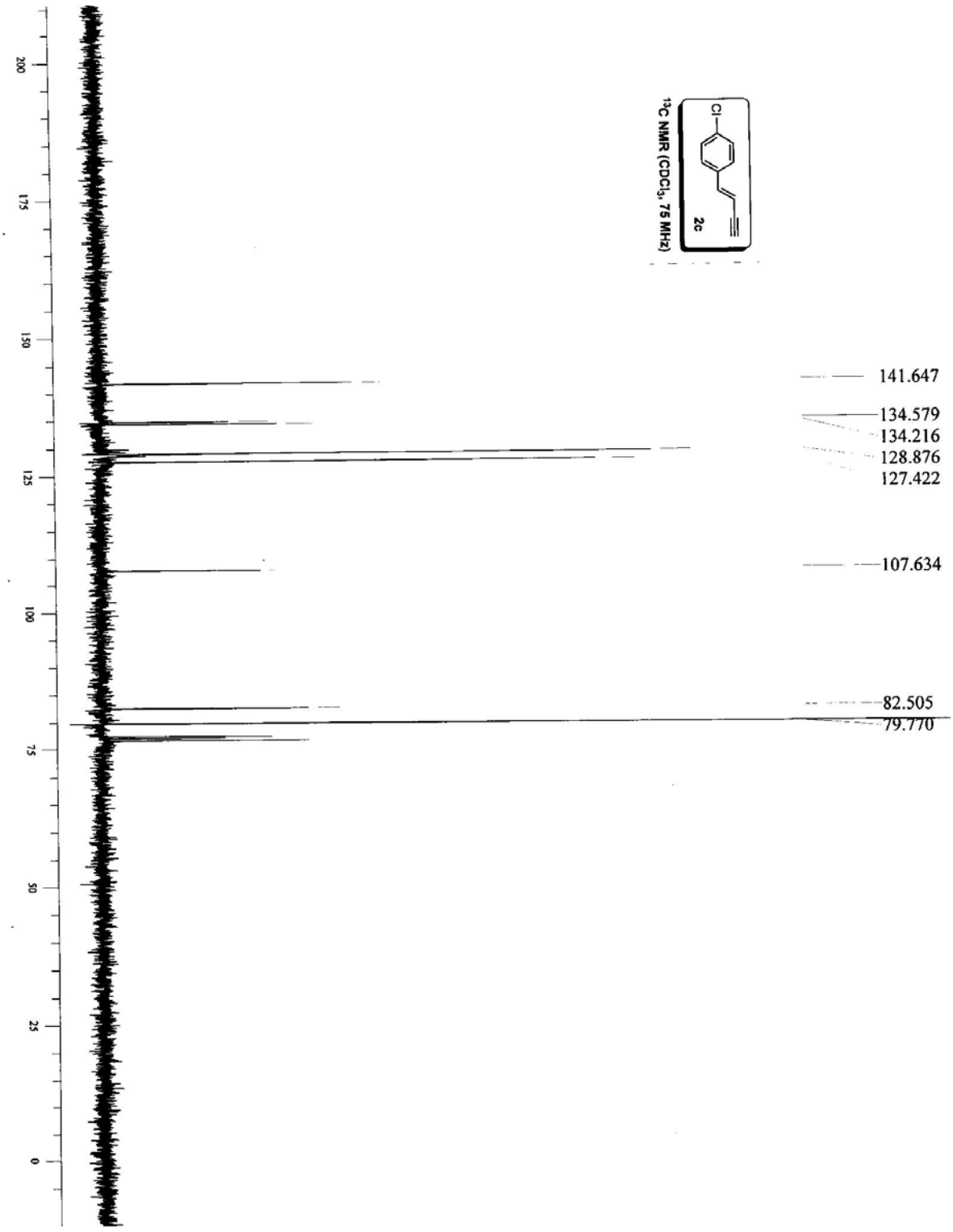
5.2

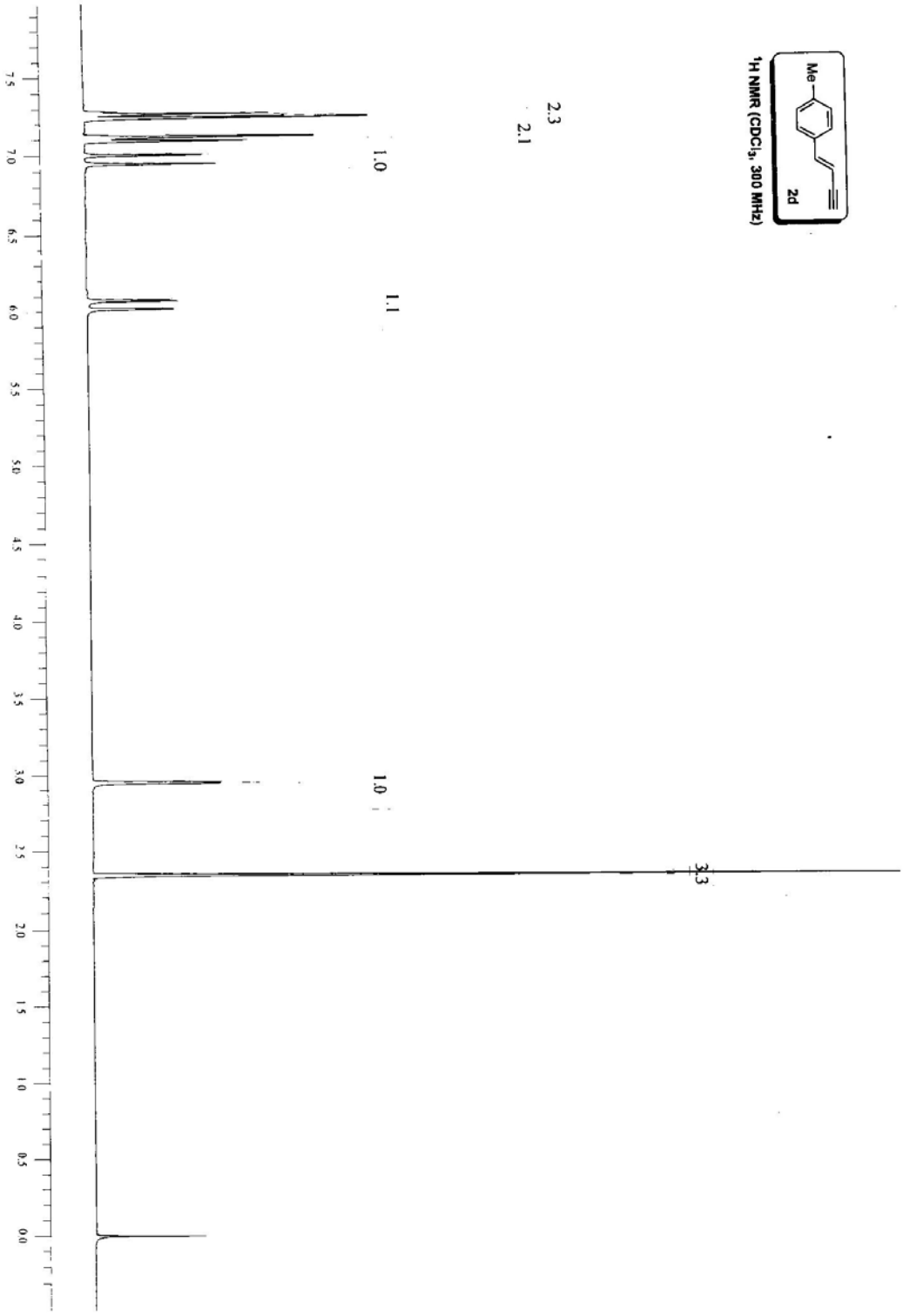

^{13}C NMR (CDCl$_3$, 75 MHz)
2a
143.162
135.860
132.862
128.922
128.761
126.375
127.595
107.030
82.942
79.265
200
175
150
125
100
75
50
25
0

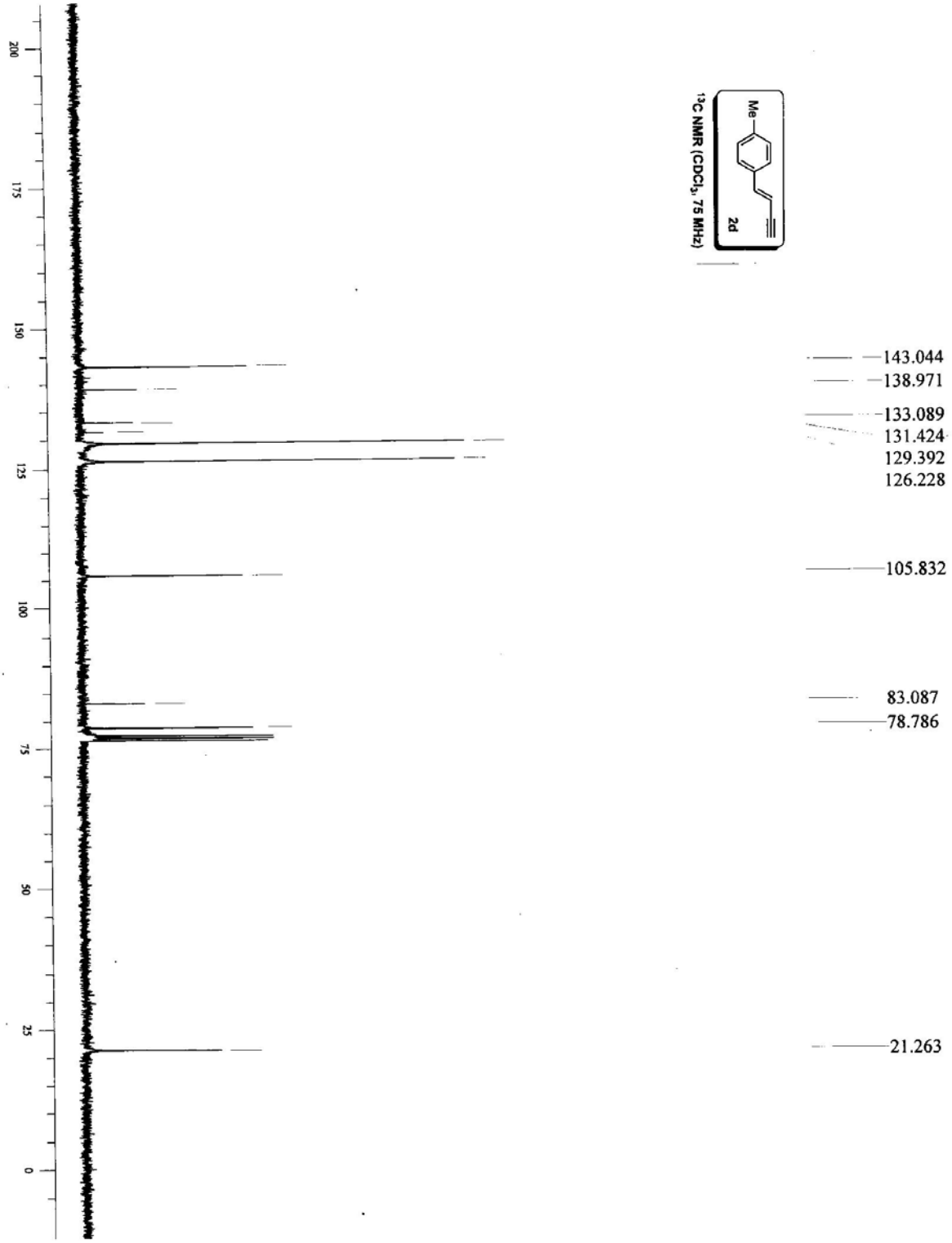

Br
2b
^{1}H NMR ($CDCl_3$, 300 MHz)
2.0
2.3
1.1
1.1
1.0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

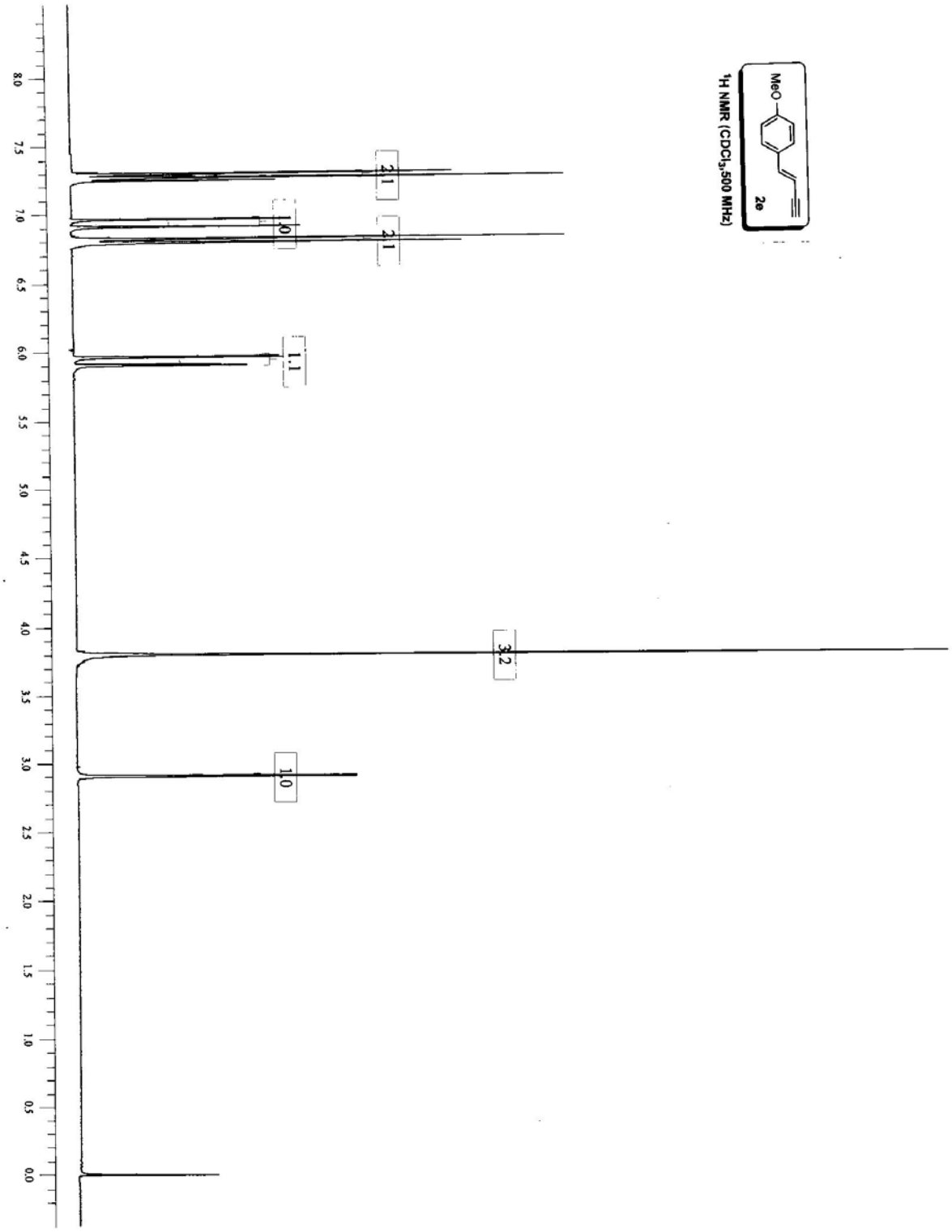

^{13}C NMR ($CDCl_3$, 75 MHz)
Br
2b
200
175
150
125
100
75
50
25
0
141.724
134.685
131.867
127.714
122.826
107.755
82.470
79.819

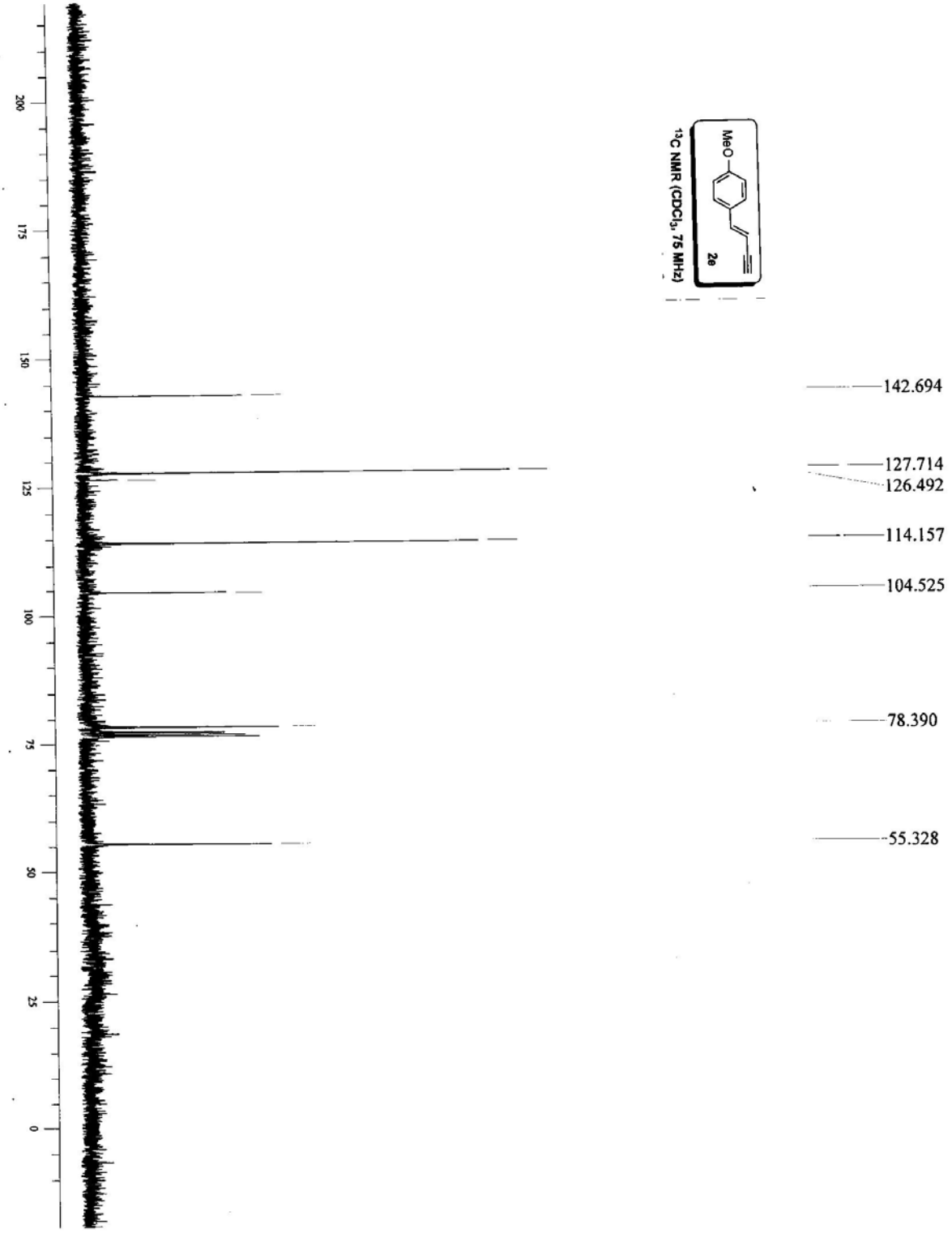

Cl
2c
^{1}H NMR (CDCl$_3$, 300 MHz)
4.3
1.1
1.0
0.9

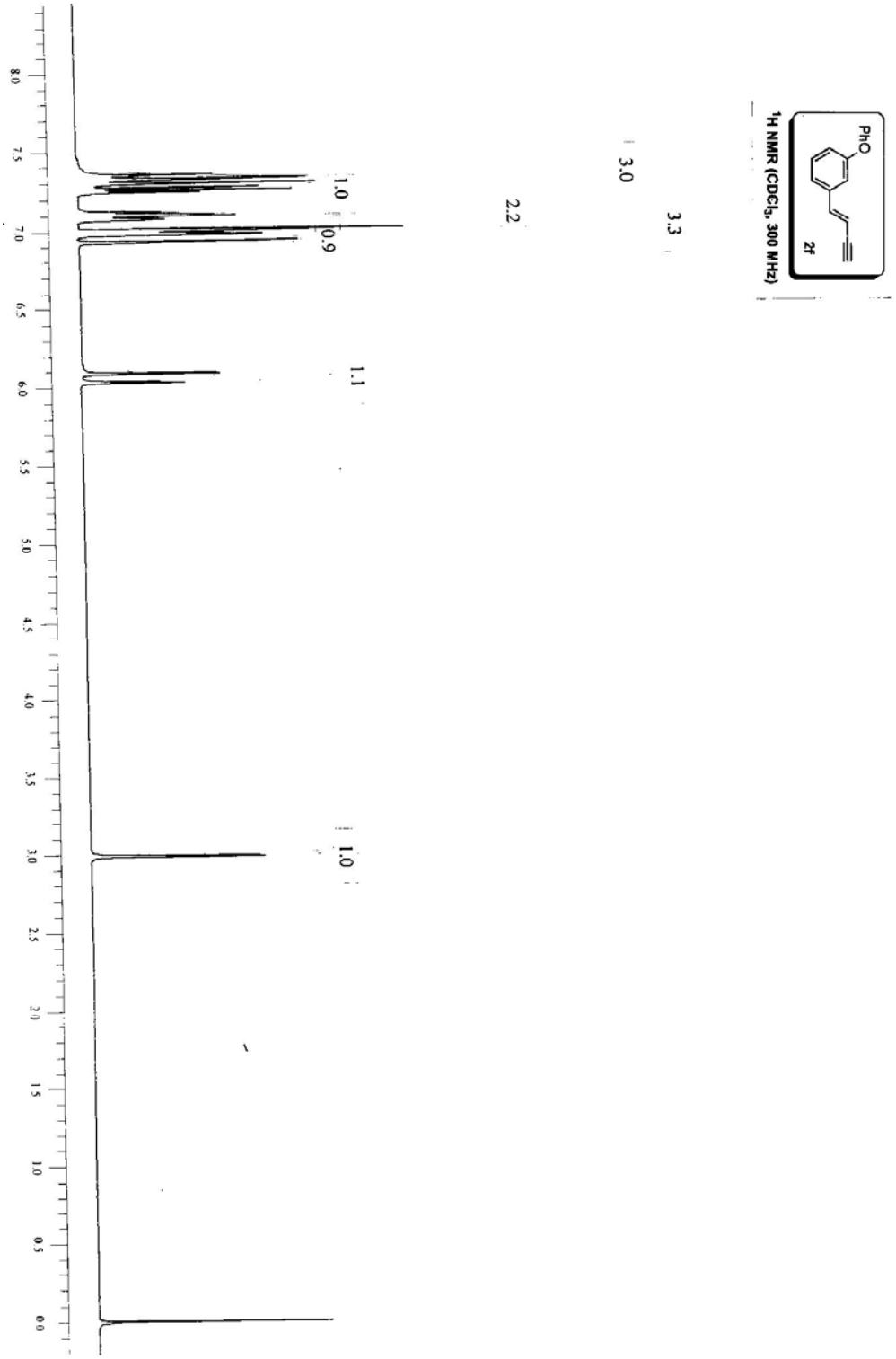

^{13}C NMR ($CDCl_3$, 75 MHz)
Cl
2c
141.647
134.579
134.216
128.876
127.422
107.634
82.505
79.770
200
175
150
125
100
75
50
25
0

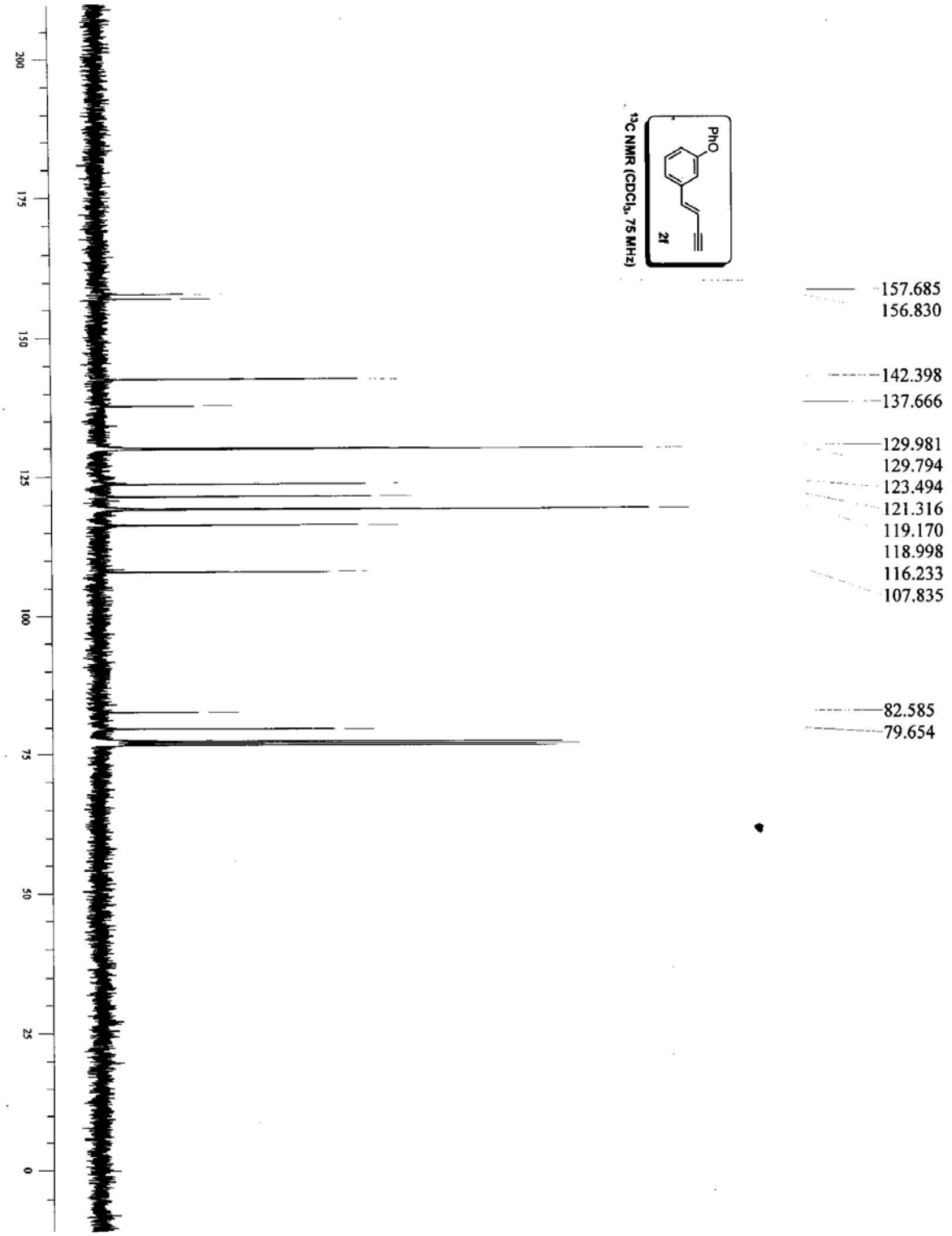

Me
2d
¹H NMR (CDCl₃, 300 MHz)
2.3
2.1
1.0
1.1
1.0
3.3
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

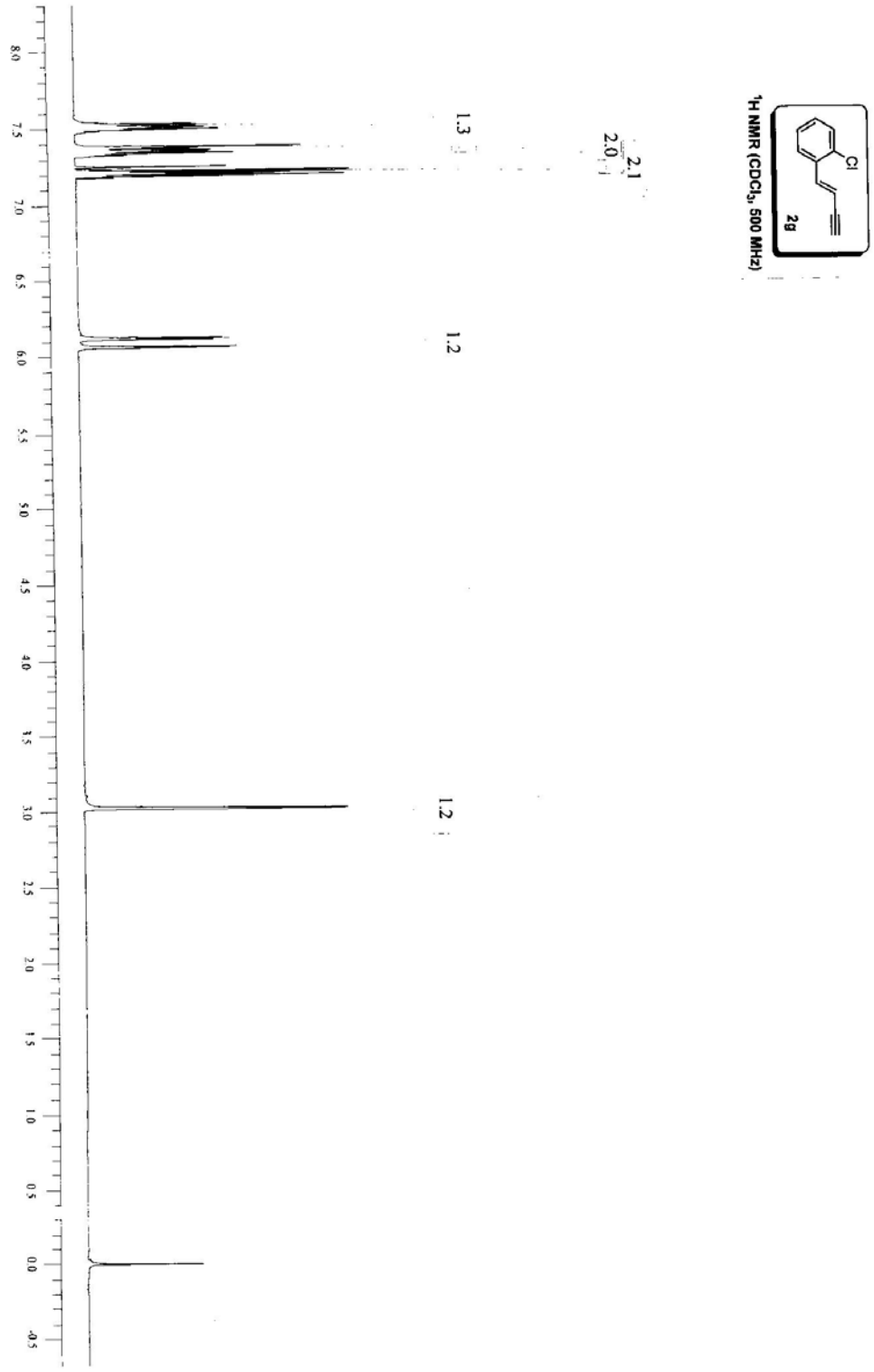

^{13}C NMR (CDCl$_3$, 75 MHz)
Me
2d
143.044
138.971
133.089
131.424
129.392
126.228
105.832
83.087
78.786
21.263
200
175
150
125
100
75
50
25
0

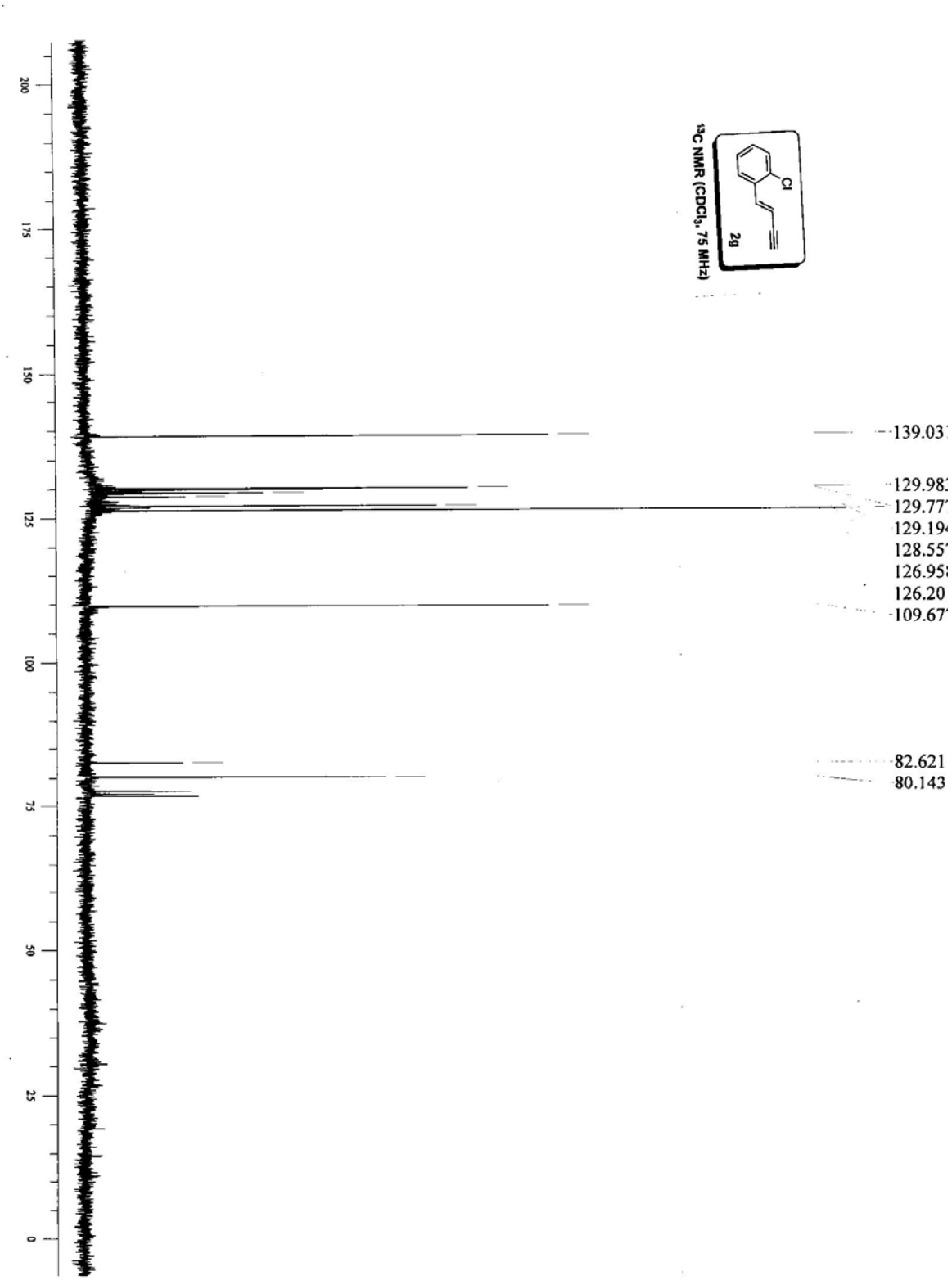

MeO
2e
^{1}H NMR (CDCl$_3$,500 MHz)
2.1
1.0
2.1
1.1
3.2
1.0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

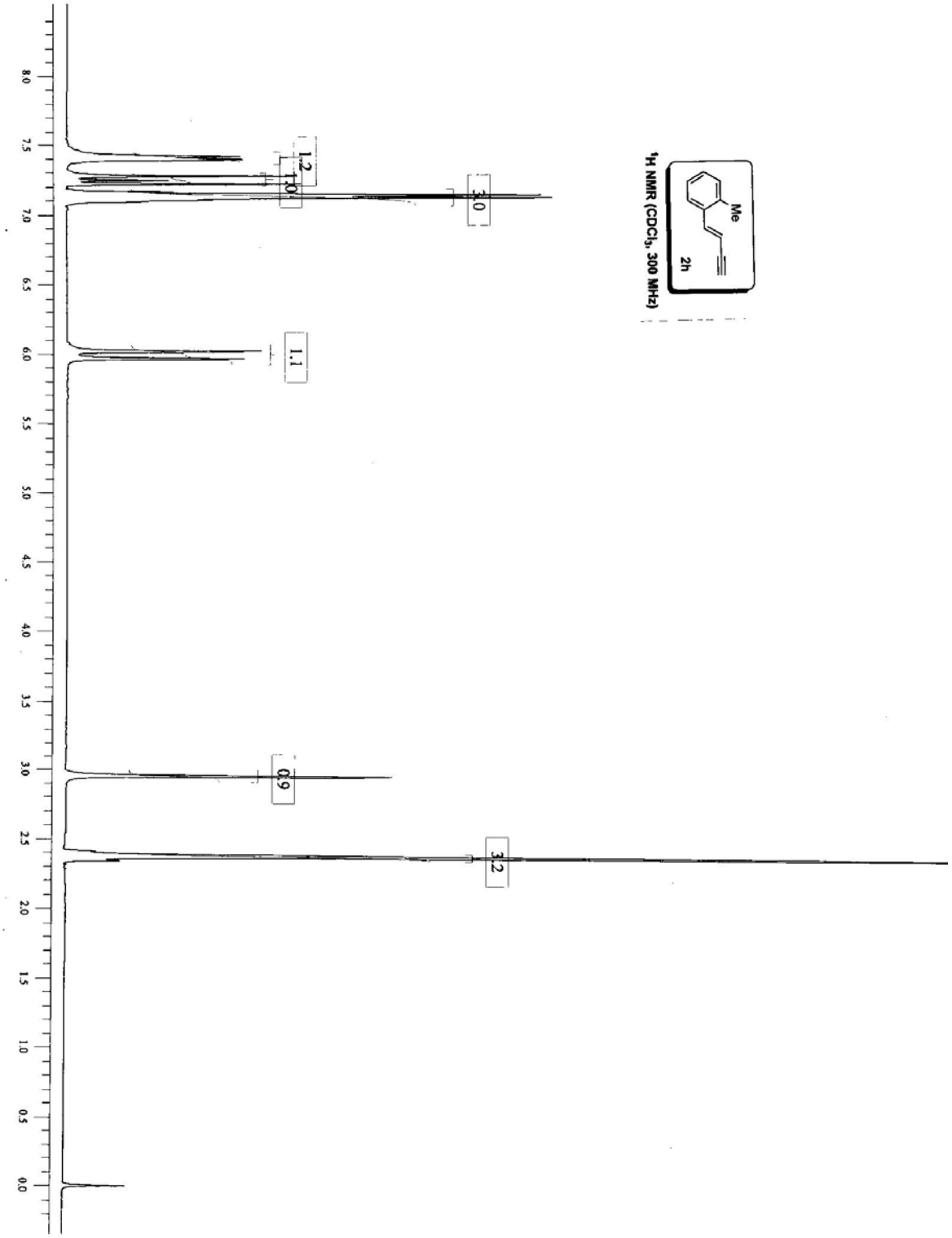

^{13}C NMR ($CDCl_3$, 75 MHz)
MeO
2e
142.694
127.714
126.492
114.157
104.525
78.390
55.328
200
175
150
125
100
75
50
25
0

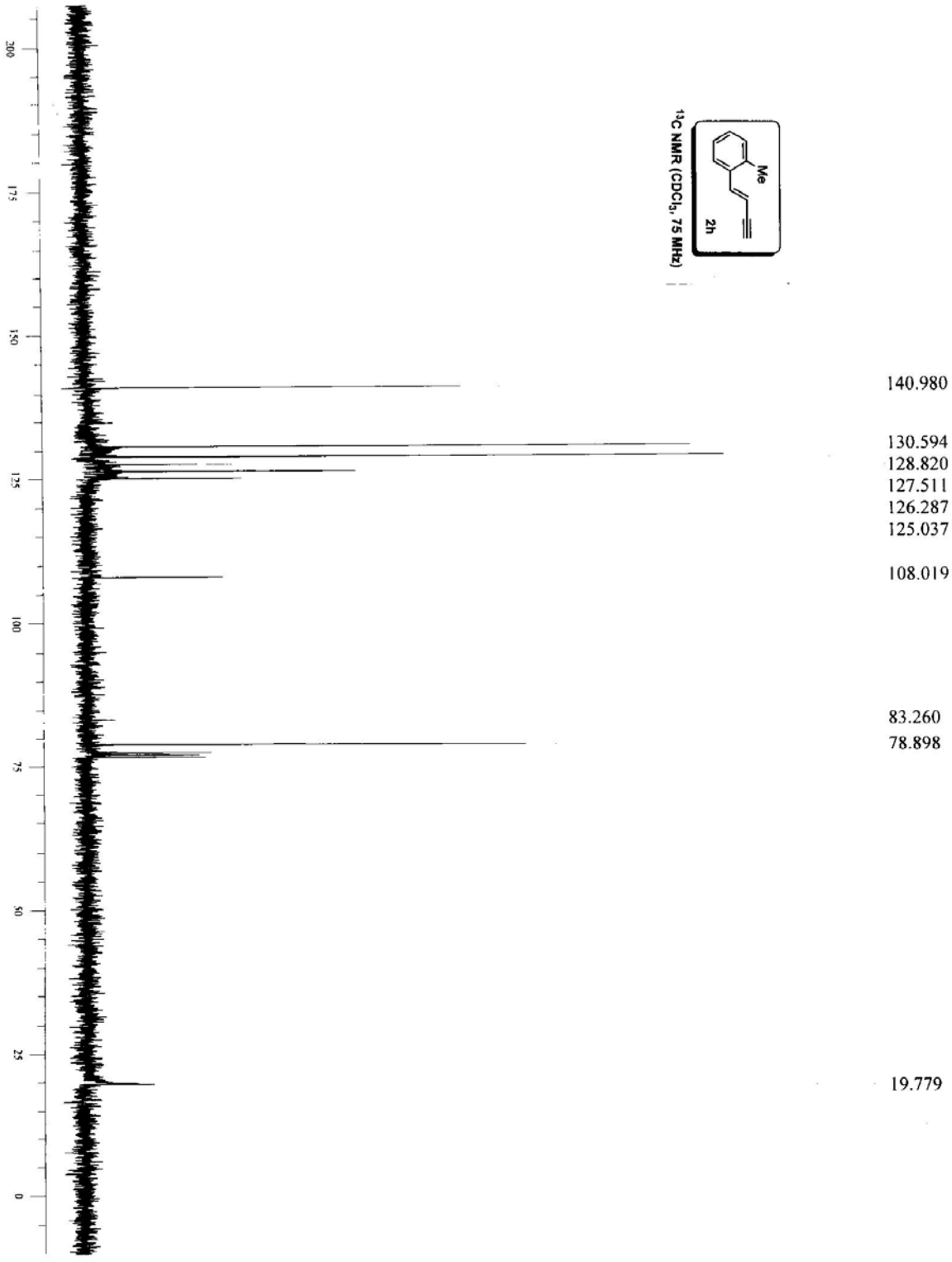

PhO
2f
^{1}H NMR (CDCl$_3$, 300 MHz)
3.3
3.0
2.2
1.0
0.9
1.1
1.0

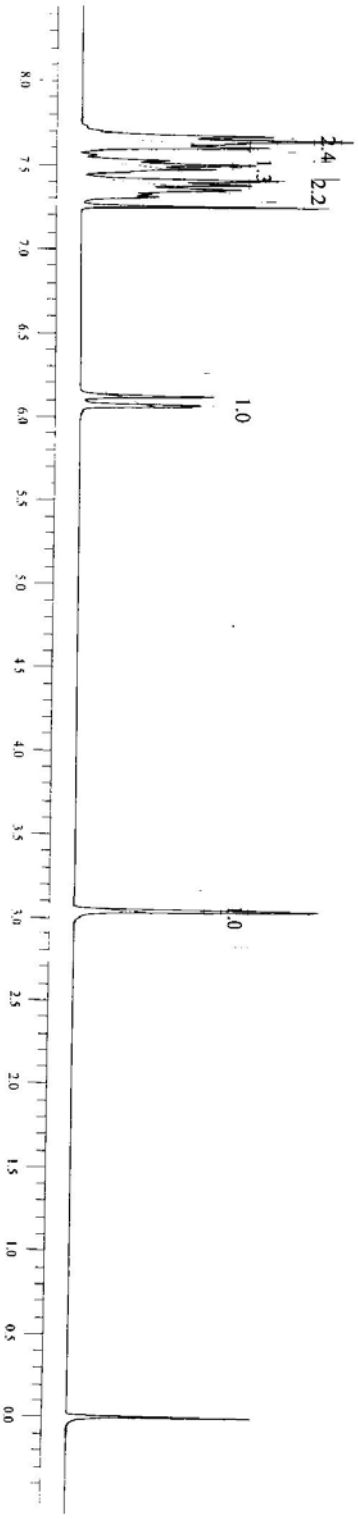

^{13}C NMR (CDCl$_3$, 75 MHz)
PhO
2f
157.685
156.830
142.398
137.666
129.981
129.794
123.494
121.316
119.170
118.998
116.233
107.835
82.585
79.654
200
175
150
125
100
75
50
25
0


1H NMR (CDCl3, 500 MHz)
Cl
2g
1.3
2.1
2.0
1.2
1.2
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

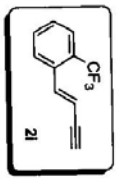

^{13}C NMR (CDCl$_3$, 75 MHz)
Cl
2g
139.03
129.98
129.77
129.19
128.55
126.95
126.20
109.67
82.621
80.143
200
175
150
125
100
75
50
25
0

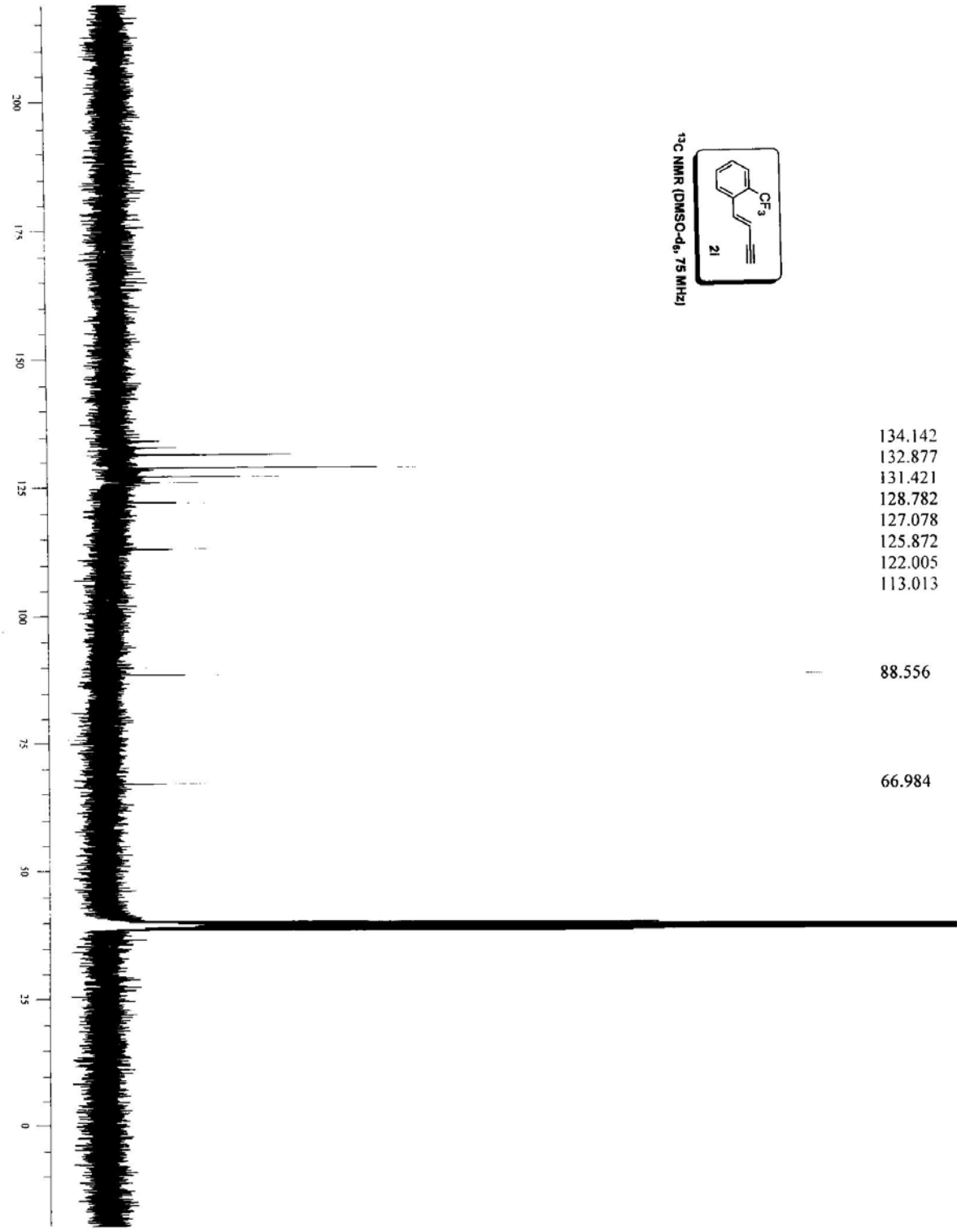

Me
2h
^{1}H NMR (CDCl$_3$, 300 MHz)
1.2
1.0
3.0
1.1
0.9
3.2
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

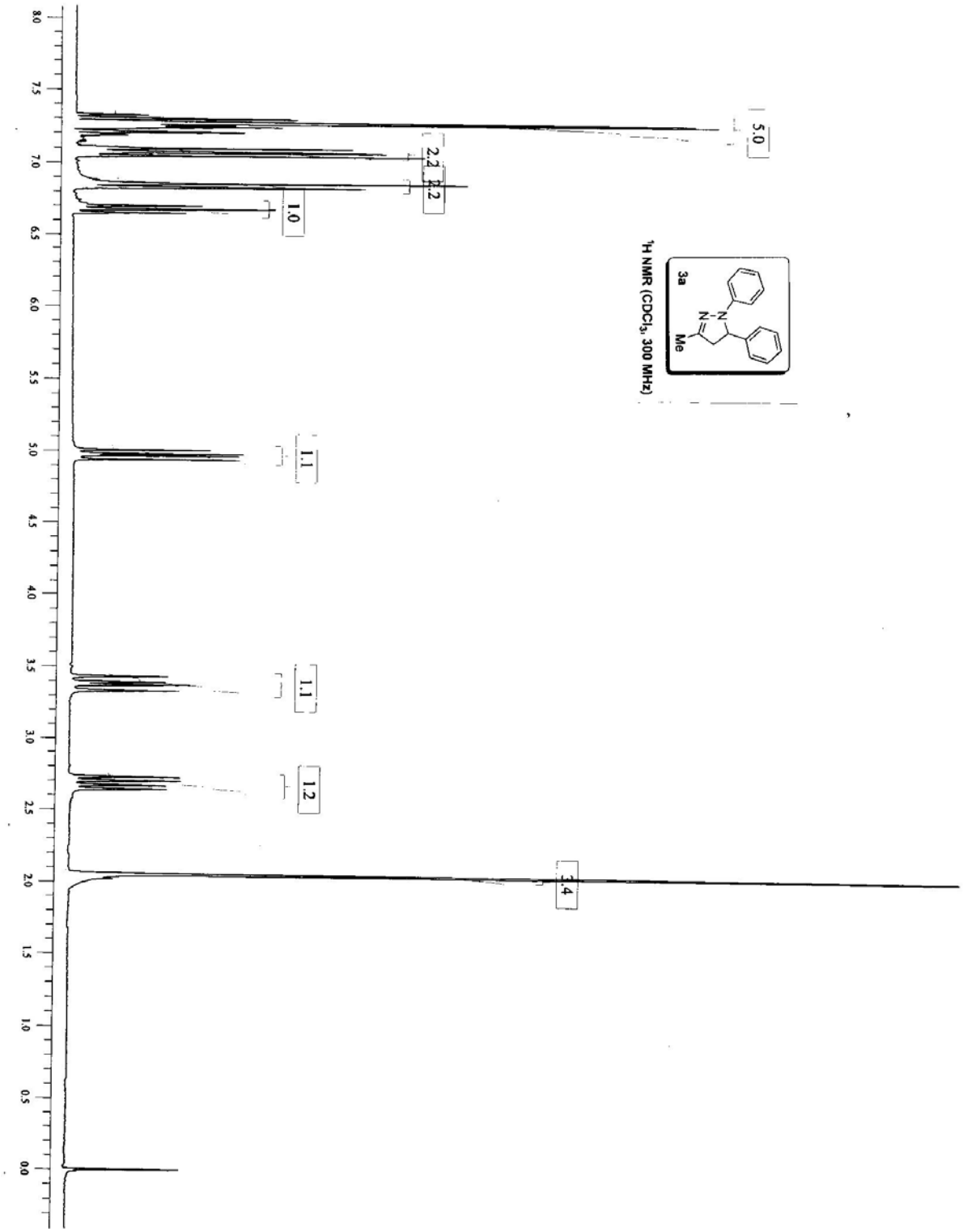

^{13}C NMR ($CDCl_3$, 75 MHz)
Me
2h
200
175
150
125
100
75
50
25
0
140.980
130.594
128.820
127.511
126.287
125.037
108.019
83.260
78.898
19.779

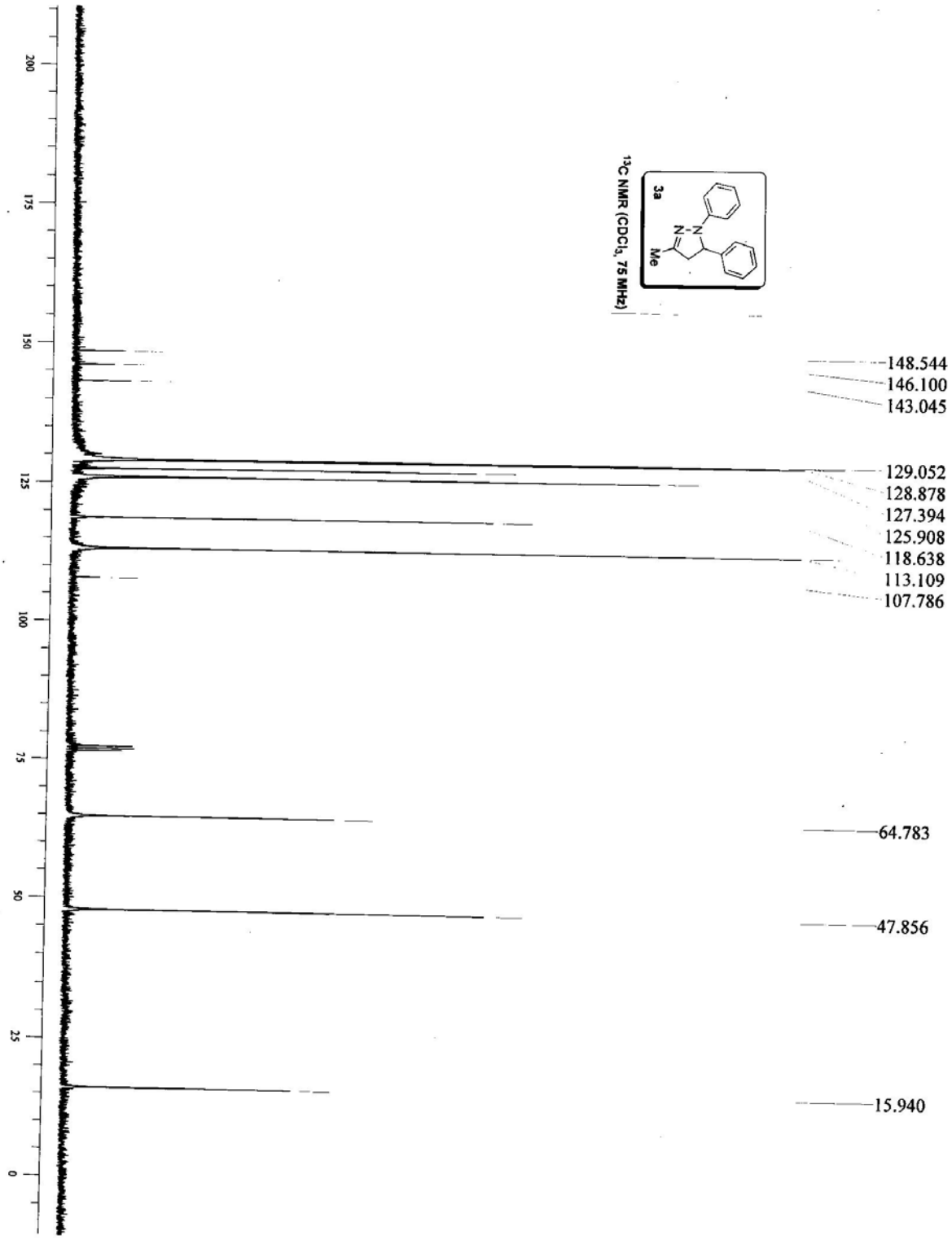


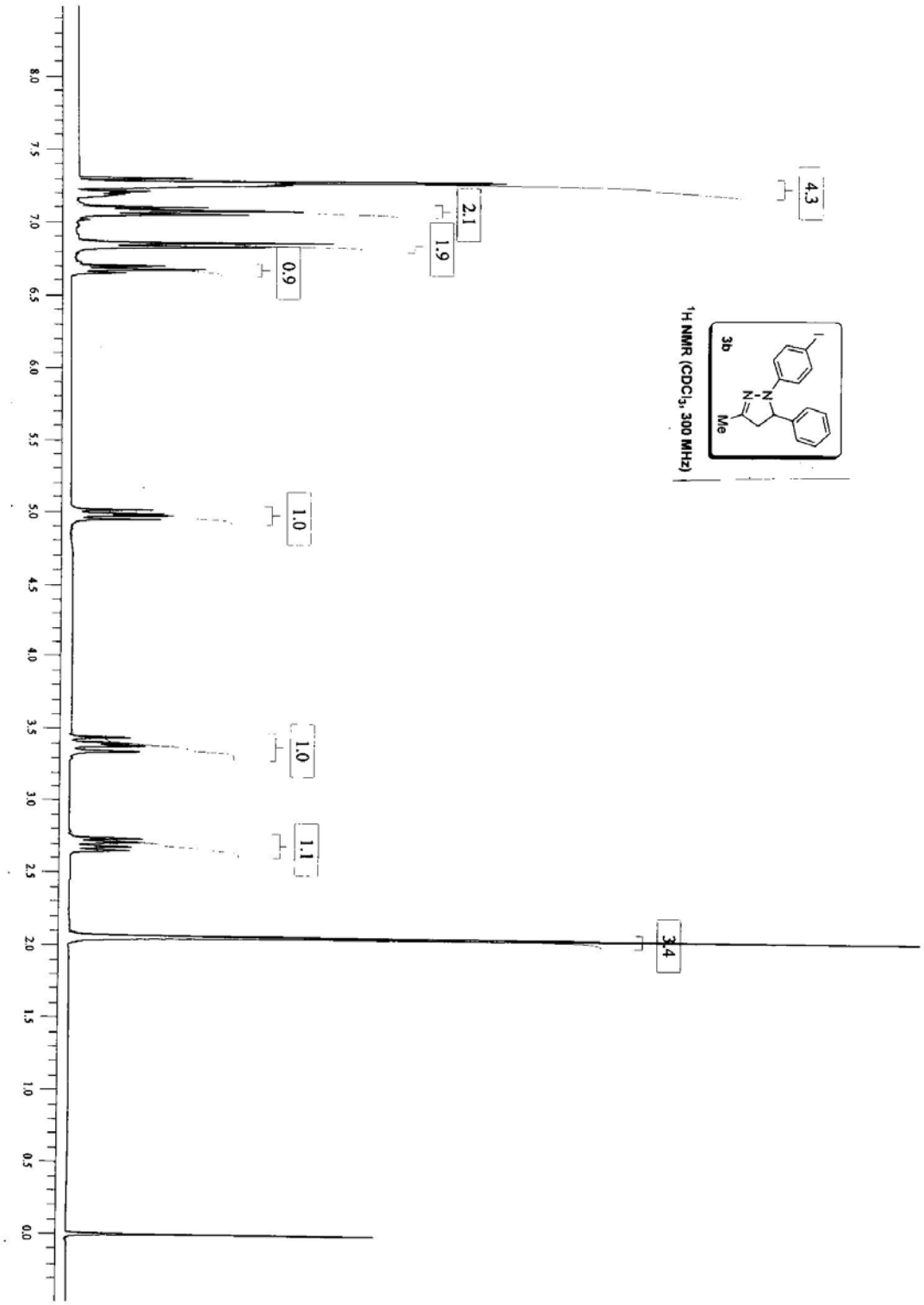
^{1}H NMR ($CDCl_3$, 300 MHz)

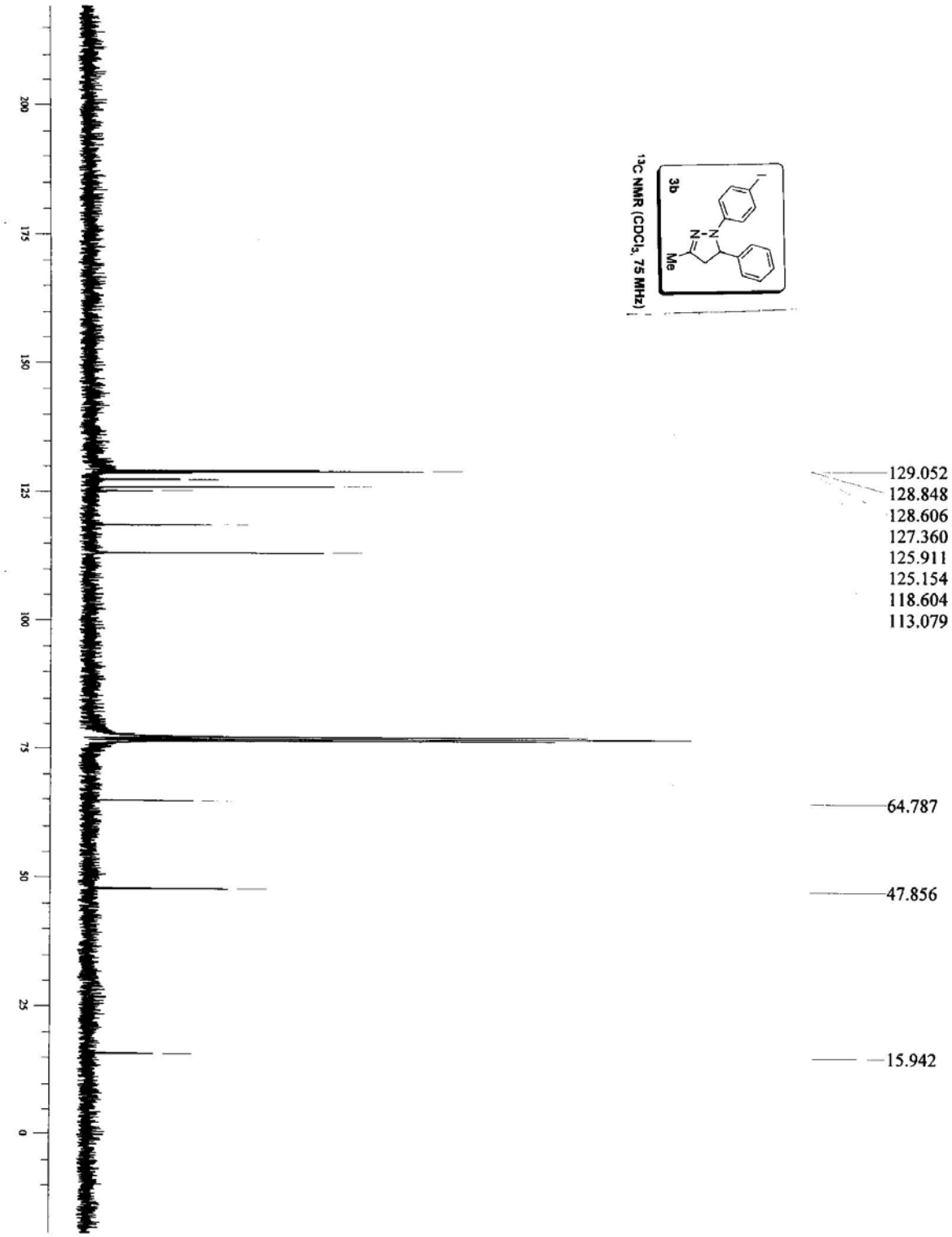


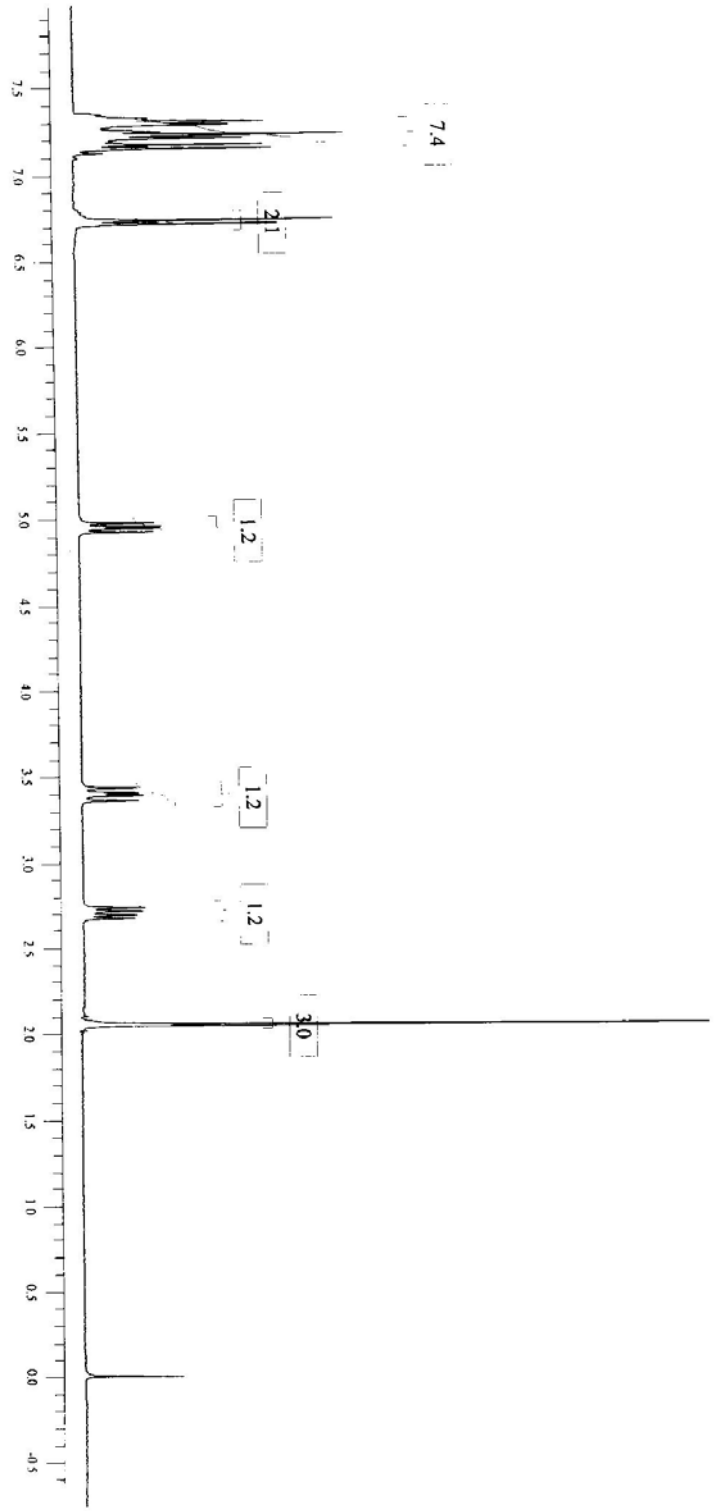

^{13}C NMR (DMSO-d_6, 75 MHz)
CF_3
21
134.142
132.877
131.421
128.782
127.078
125.872
122.005
113.013
88.556
66.984
200
175
150
125
100
75
50
25
0


^{1}H NMR (CDCl$_3$, 300 MHz)
3a
Me
5.0
2.2
1.2
1.0
1.1
1.1
1.2
3.4

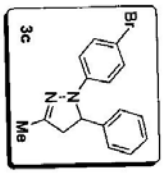

^{13}C NMR (CDCl$_3$, 75 MHz)
3a
Me
148.544
146.100
143.045
129.052
128.878
127.394
125.908
118.638
113.109
107.786
64.783
47.856
15.940

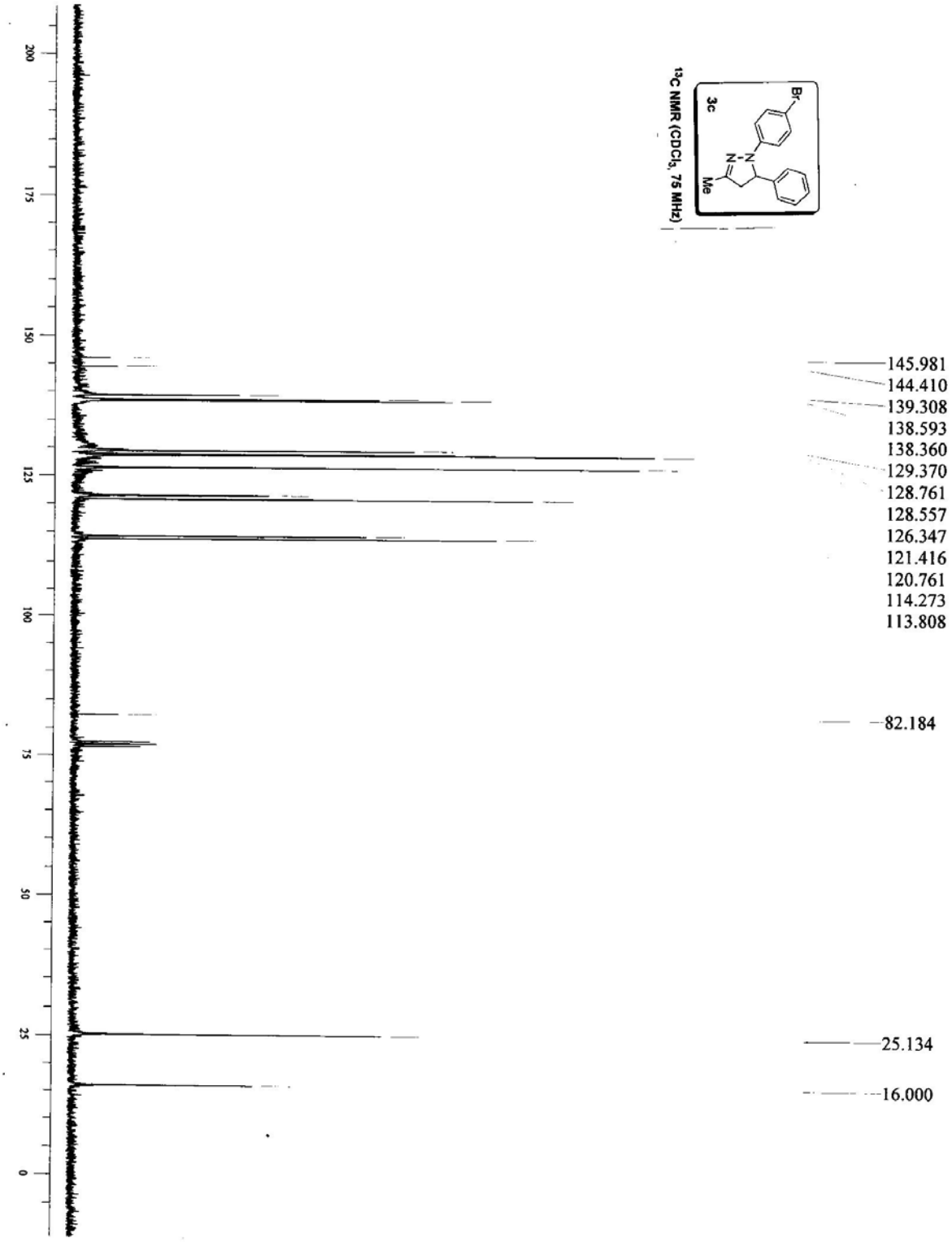

4.3
2.1
1.9
0.9
1.0
1.0
1.1
3.4
^{1}H NMR (CDCl$_3$, 300 MHz)
3b
Me

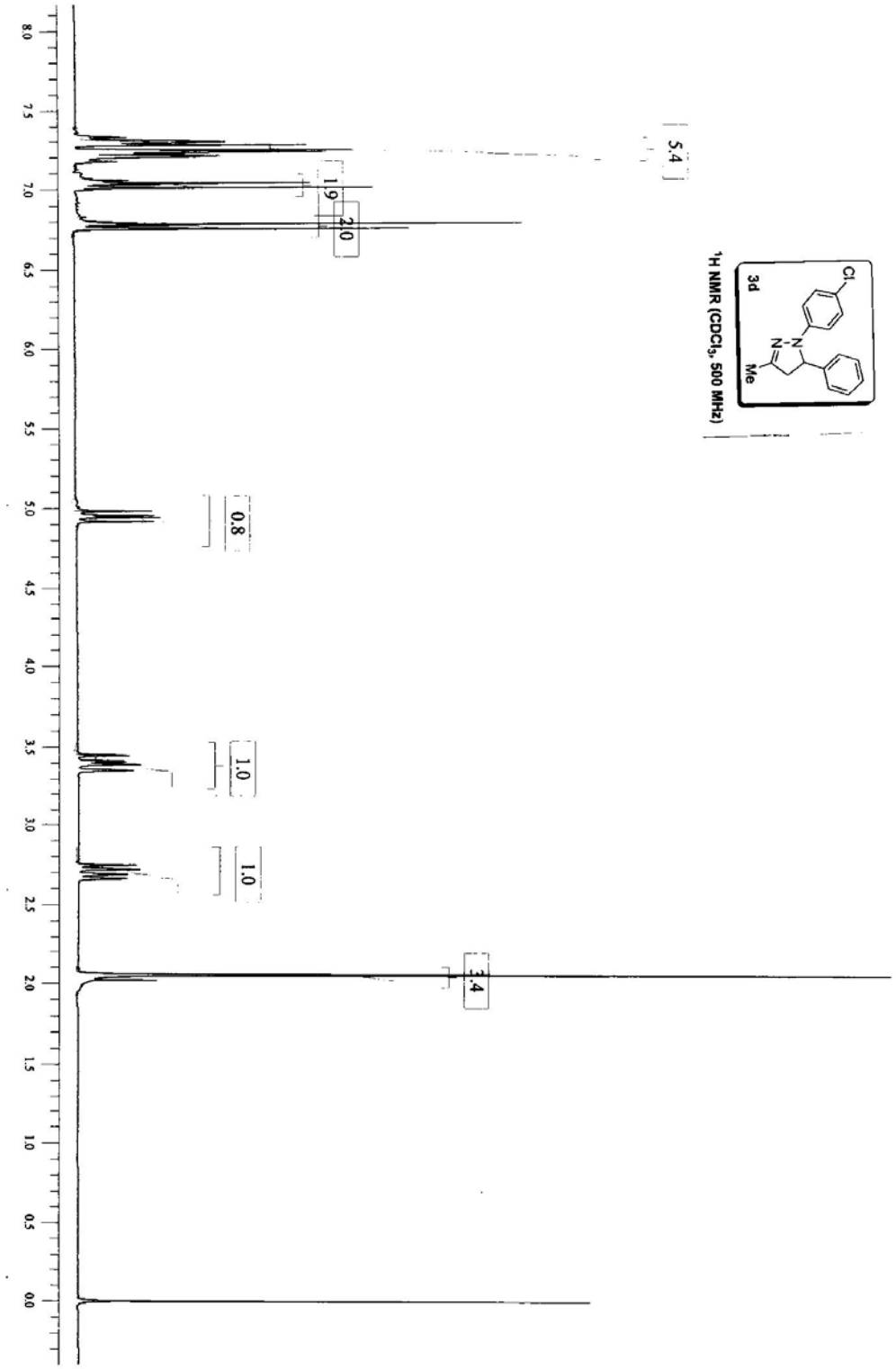


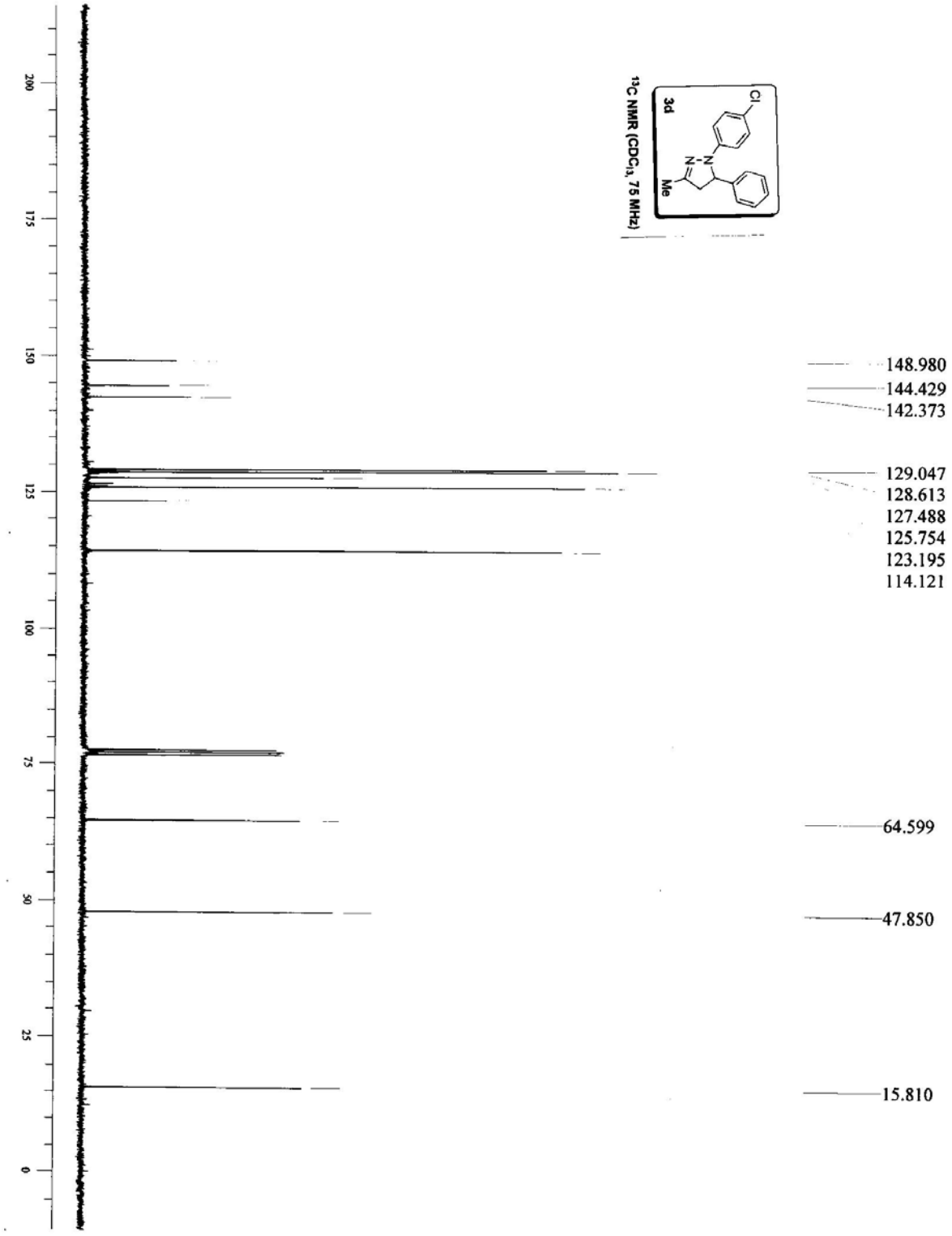


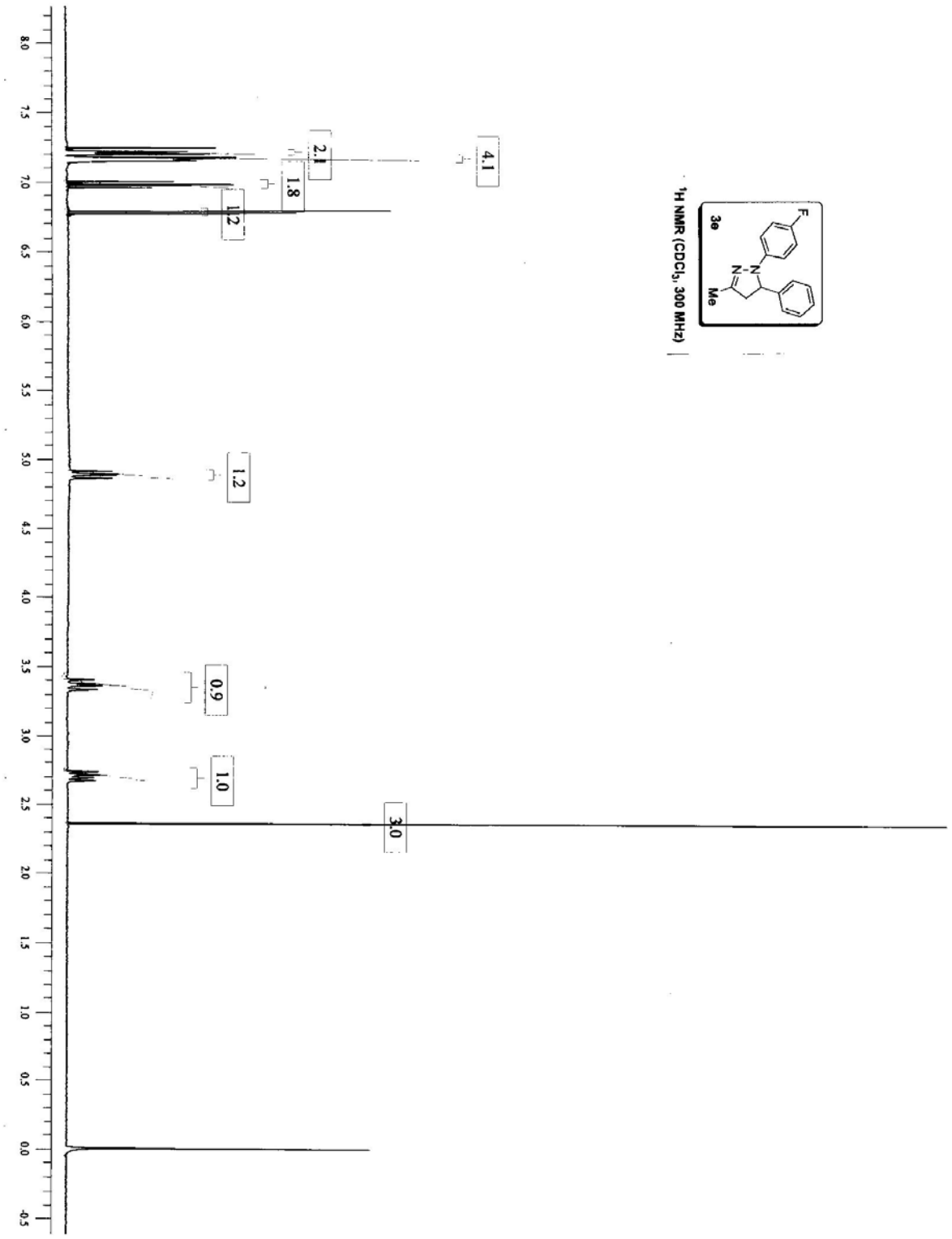
^{1}H NMR ($CDCl_3$, 500 MHz)

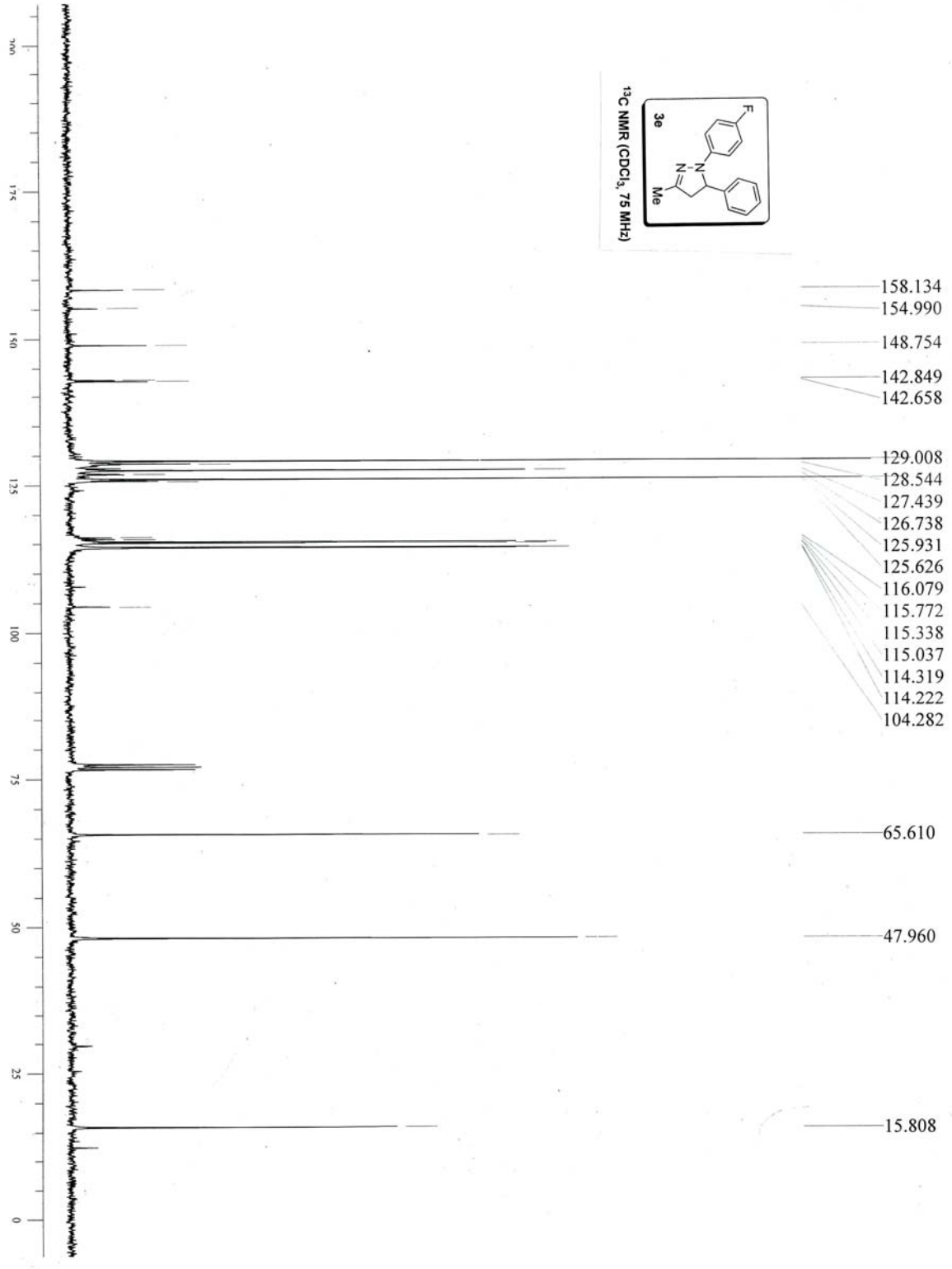


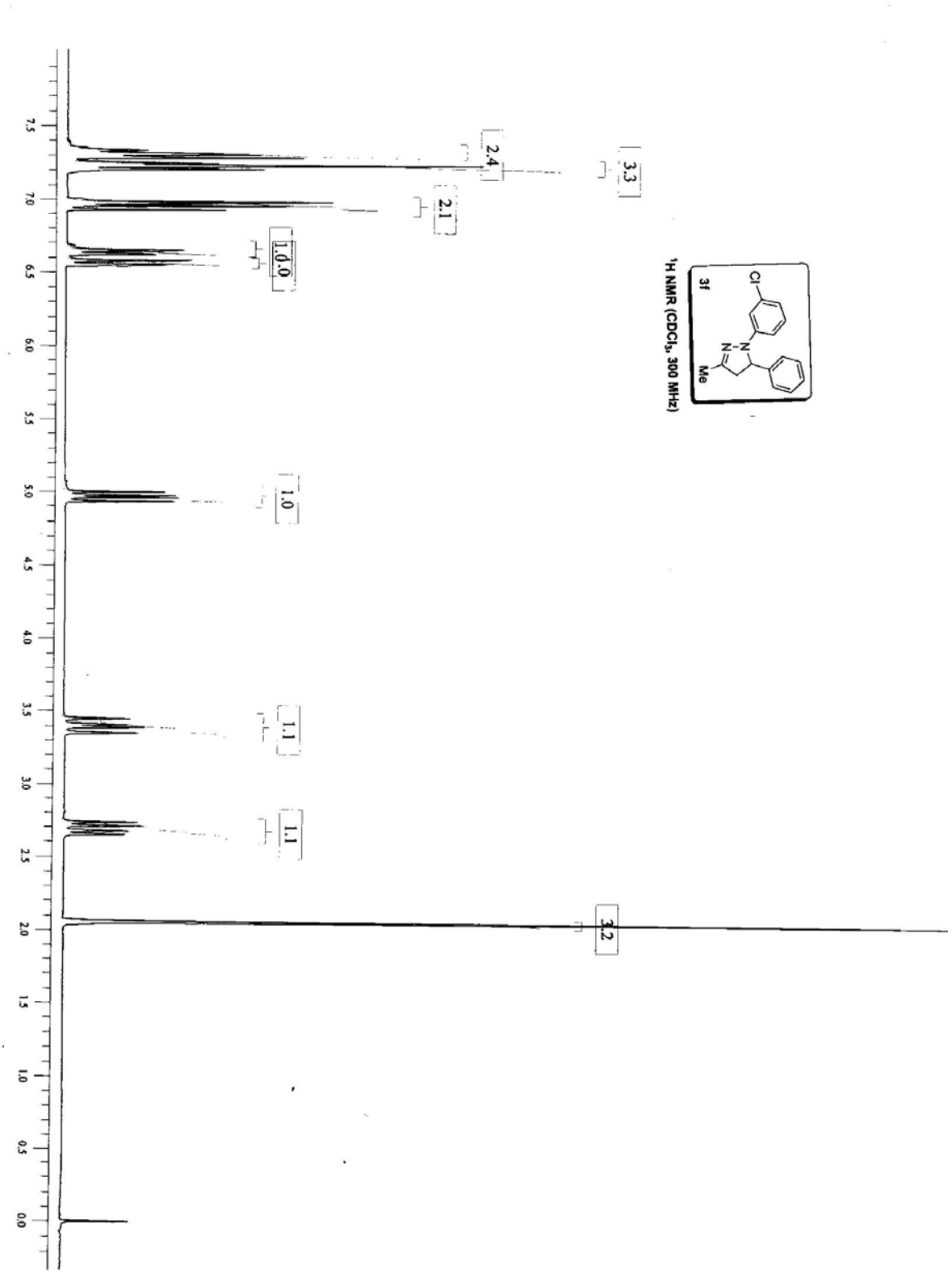

^{13}C NMR (CDCl$_3$, 75 MHz)
3c
Br
N
N
Me
200
175
150
125
100
75
50
25
0
145.981
144.410
139.308
138.593
138.360
129.370
128.761
128.557
126.347
121.416
120.761
114.273
113.808
82.184
25.134
16.000

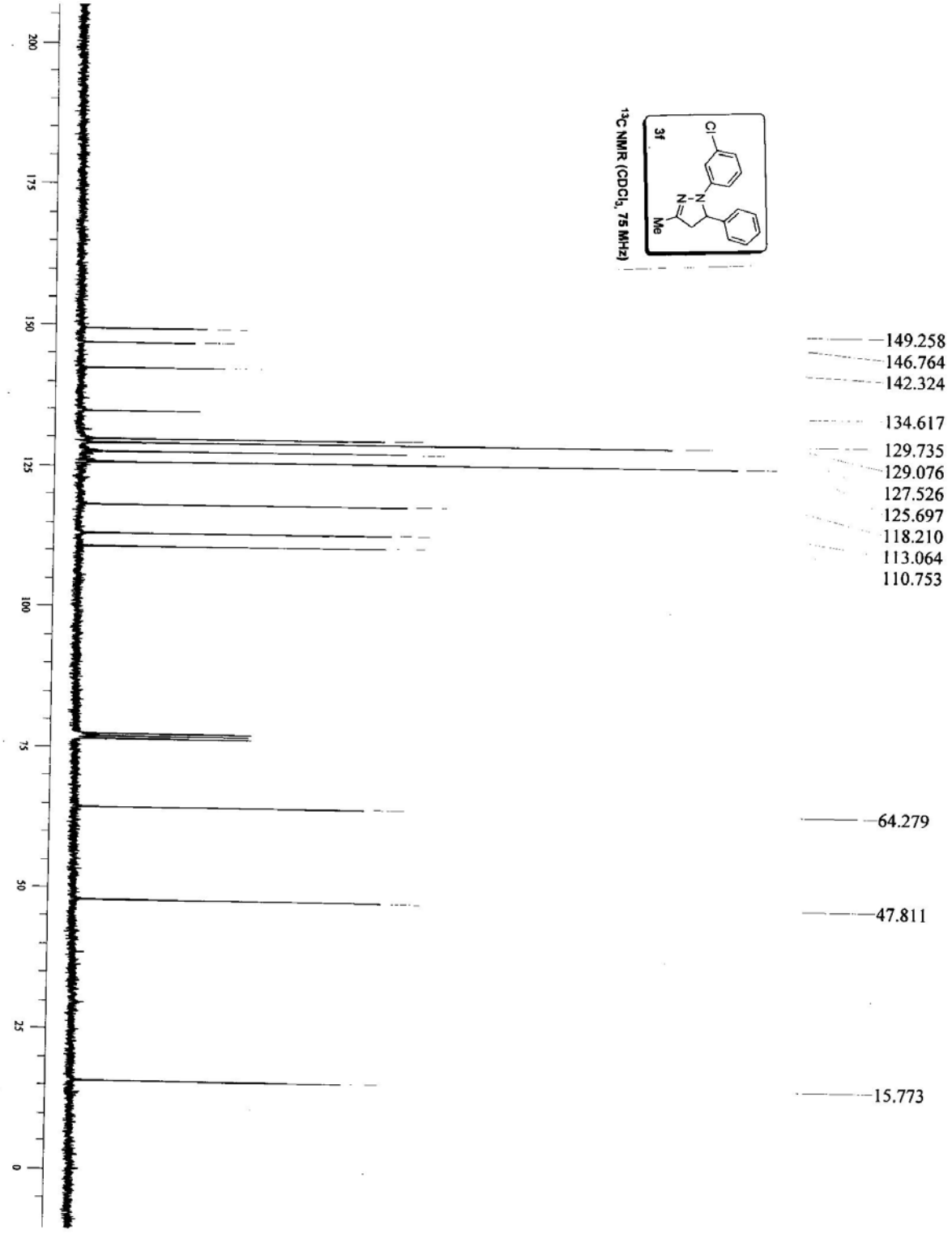

3d
Cl
Me
^{1}H NMR (CDCl$_3$, 500 MHz)
5.4
1.9
2.0
0.8
1.0
1.0
3.4

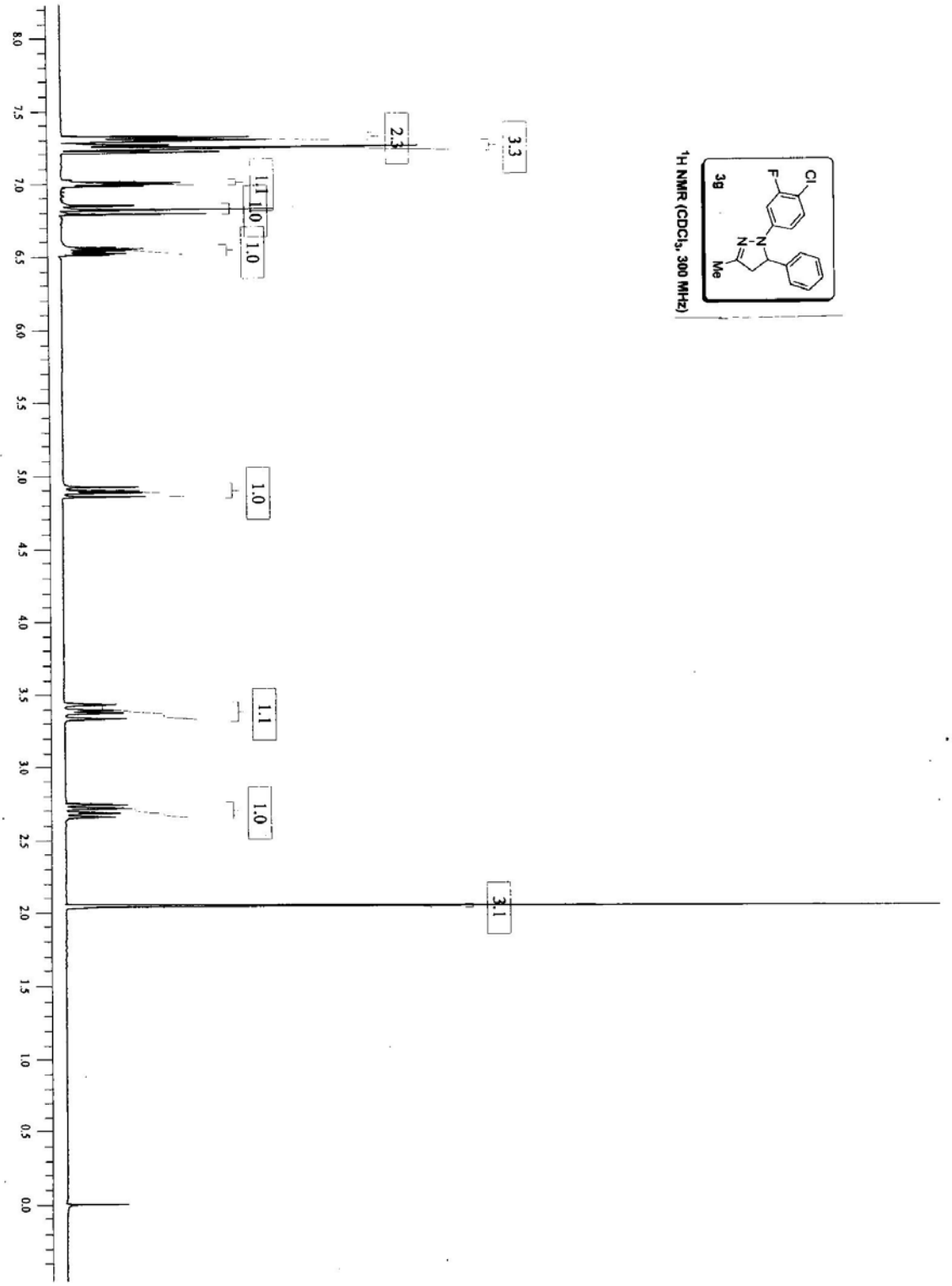

^{13}C NMR (CDCl$_3$, 75 MHz)
3d
Cl
Me
N
N
200
175
150
125
100
75
50
25
0
148.980
144.429
142.373
129.047
128.613
127.488
125.754
123.195
114.121
64.599
47.850
15.810

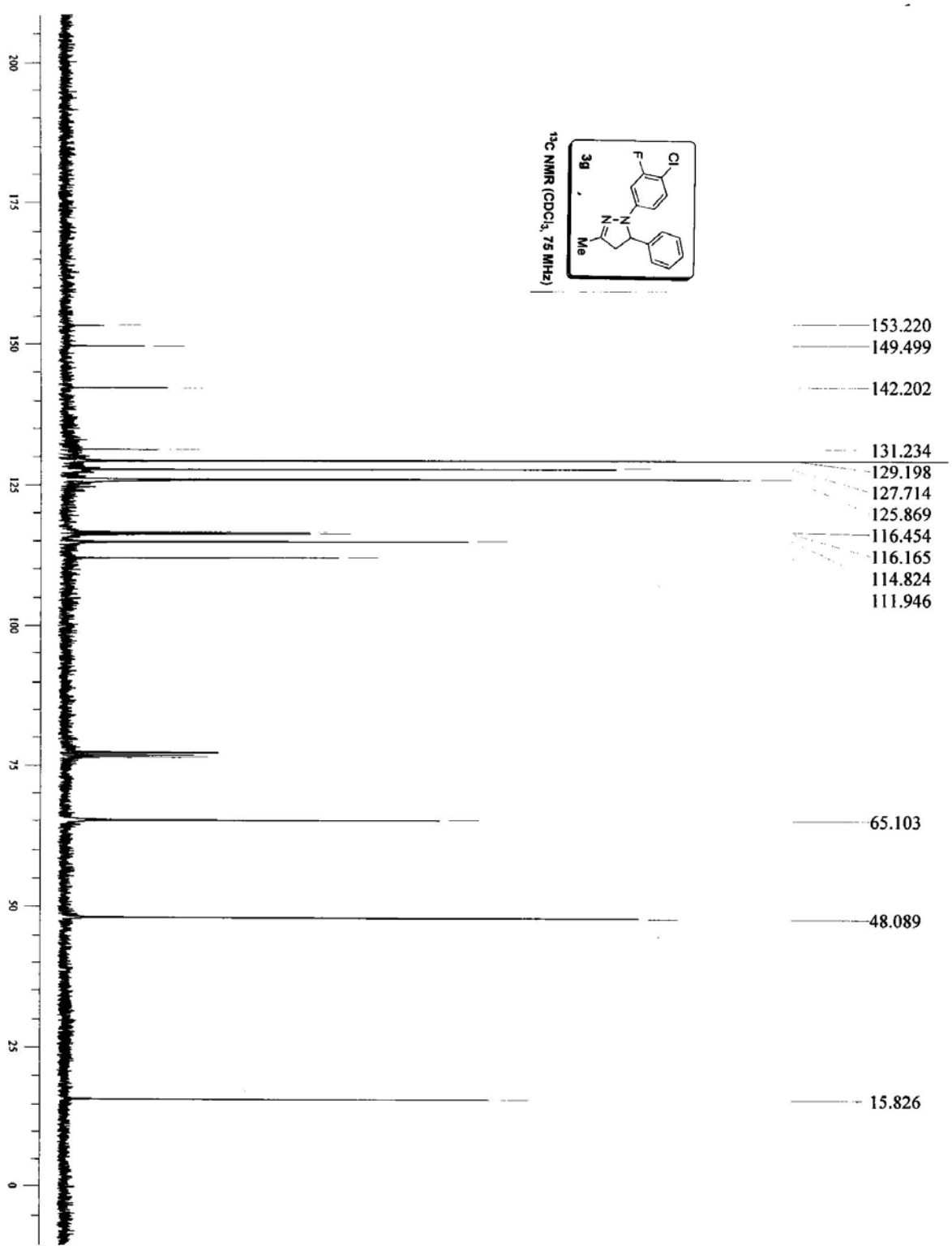

^{1}H NMR (CDCl$_3$, 300 MHz)
3e
F
N
N
Me
4.1
2.1
1.8
1.2
1.2
0.9
1.0
3.0

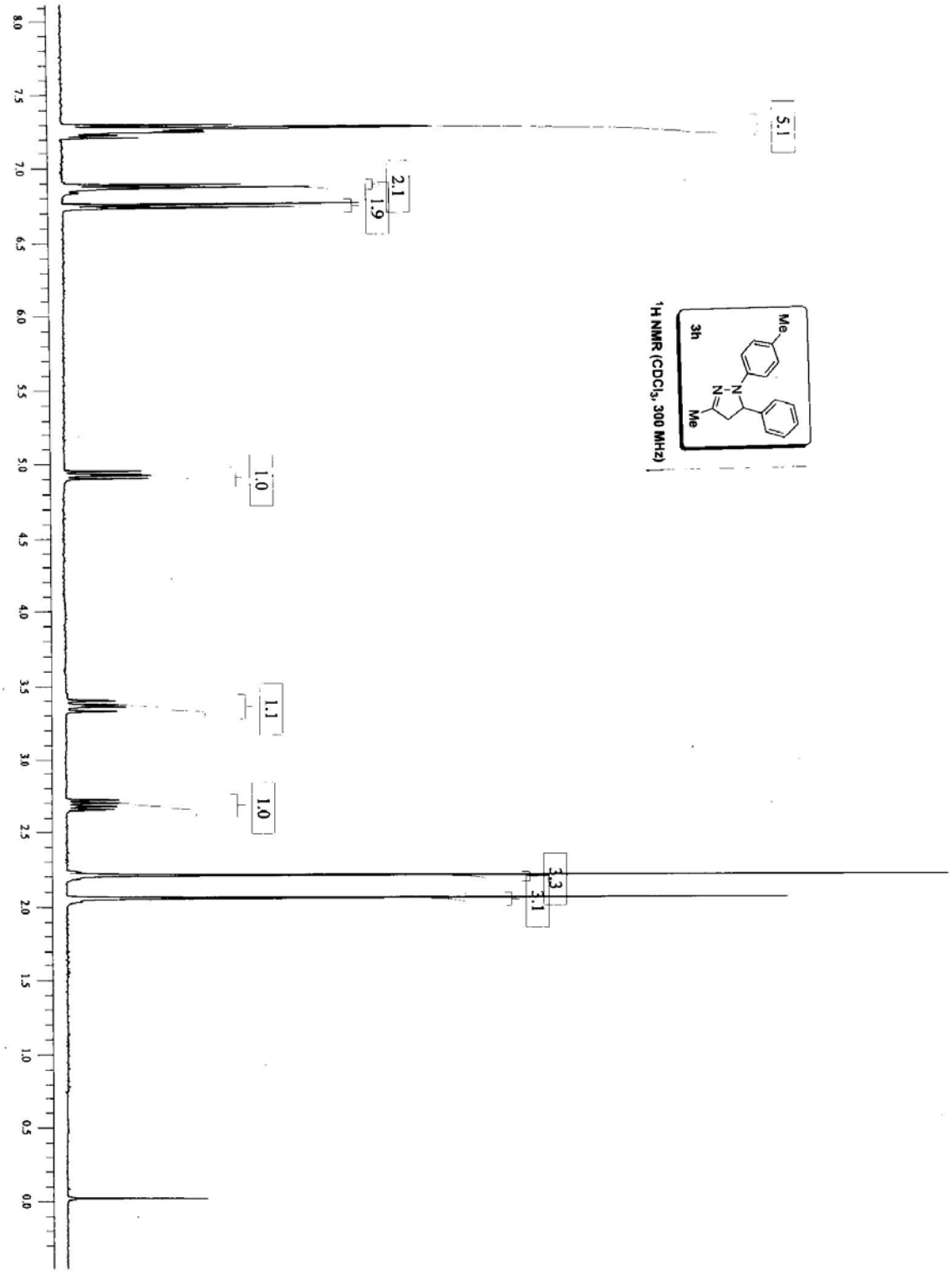

^{13}C NMR (CDCl$_3$, 75 MHz)
3e
F
N
N
Me
158.134
154.990
148.754
142.849
142.658
129.008
128.544
127.439
126.738
125.931
125.626
116.079
115.772
115.338
115.037
114.319
114.222
104.282
65.610
47.960
15.808
175
150
125
100
75
50
25
0

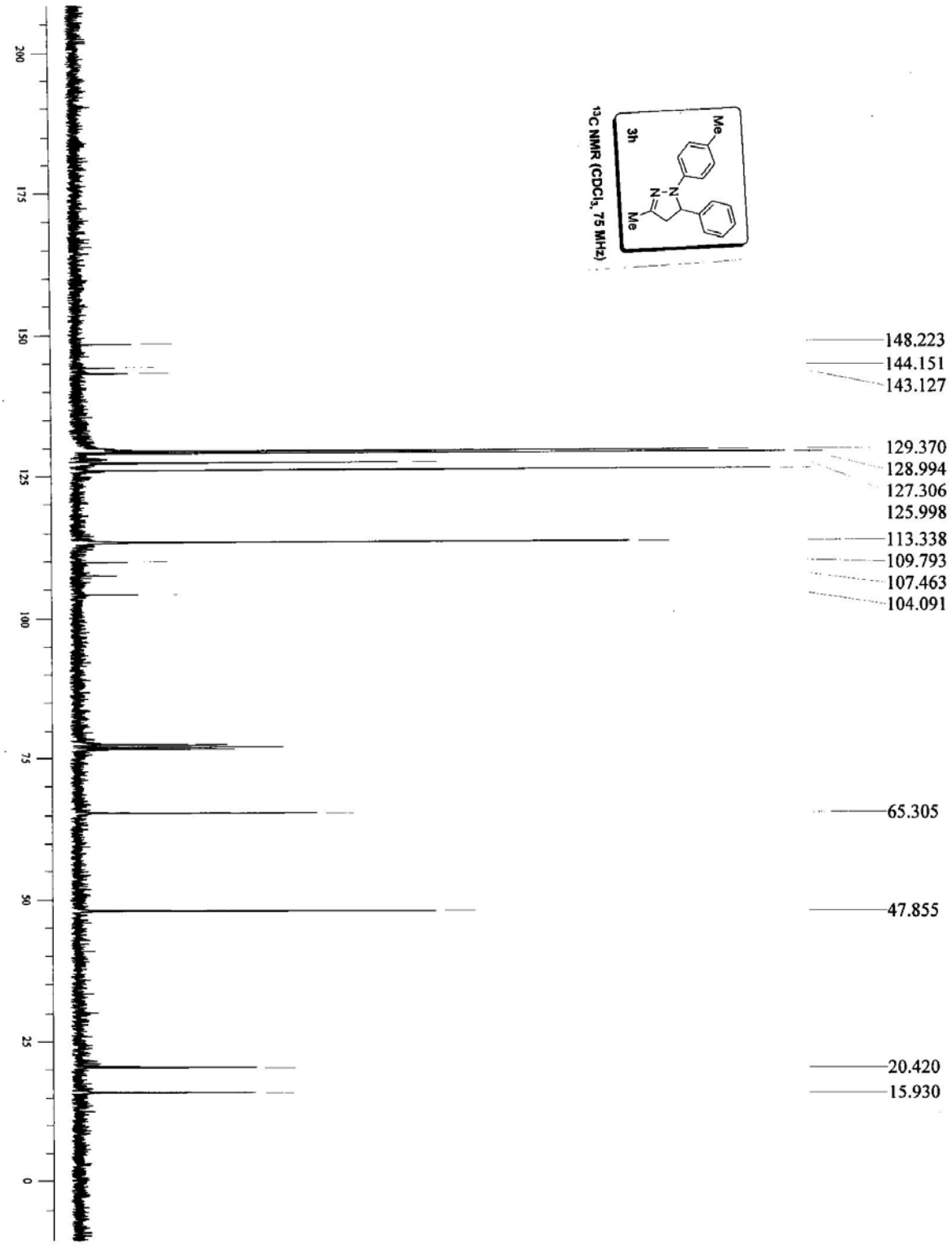

2.4
3.3
2.1
1.0.0
1.0
1.1
1.1
3.2
3f
Cl
N
N
Me
^{1}H NMR (CDCl$_3$, 300 MHz)

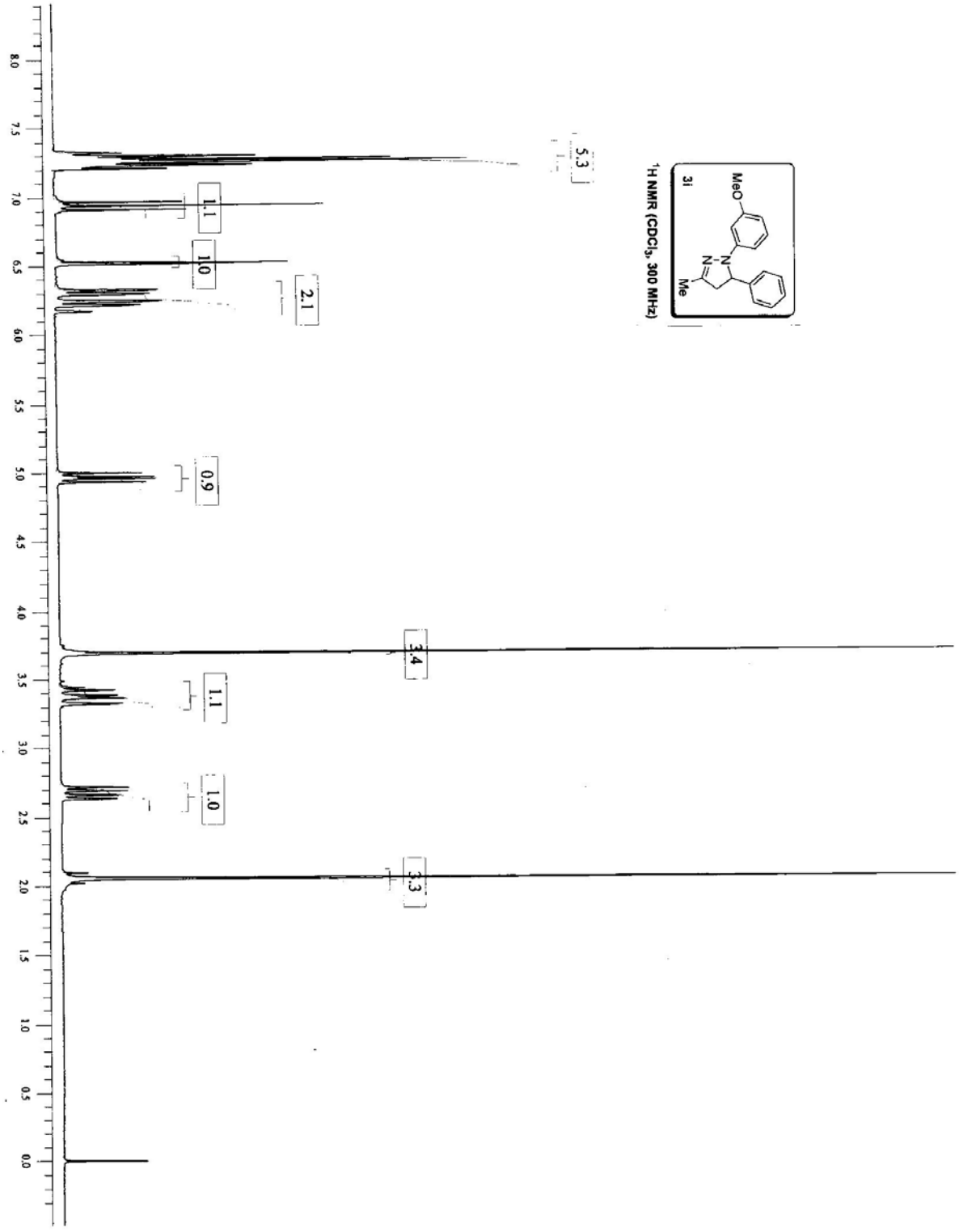

^{13}C NMR (CDCl$_3$, 75 MHz)
3f
Cl
N
N
Me
149.258
146.764
142.324
134.617
129.735
129.076
127.526
125.697
118.210
113.064
110.753
64.279
47.811
15.773
200
175
150
125
100
75
50
25
0

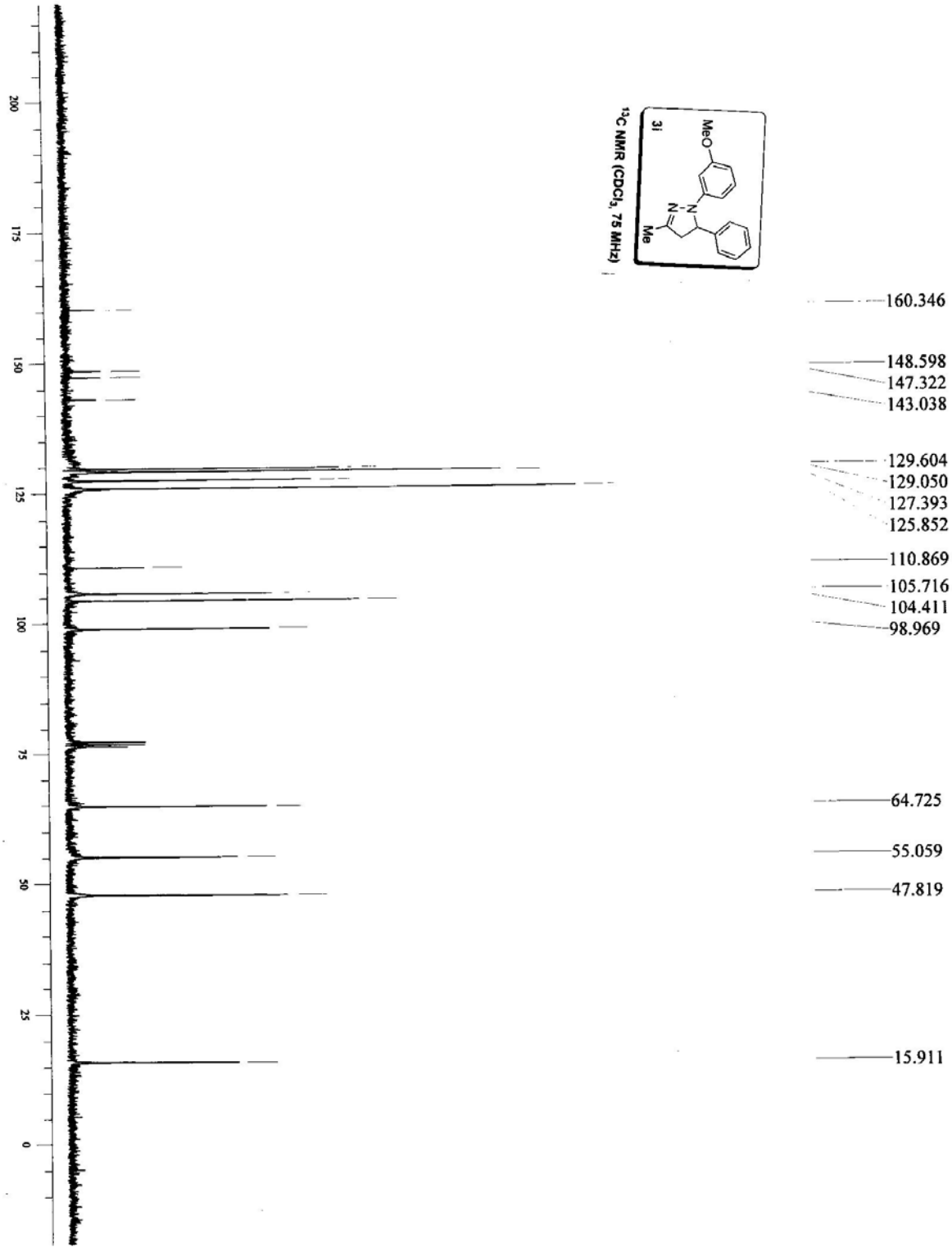

1H NMR (CDCl3, 300 MHz)
3g
Cl
F
N
N
Me
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
2.3
3.3
1.1
1.0
1.0
1.0
1.1
1.0
3.1

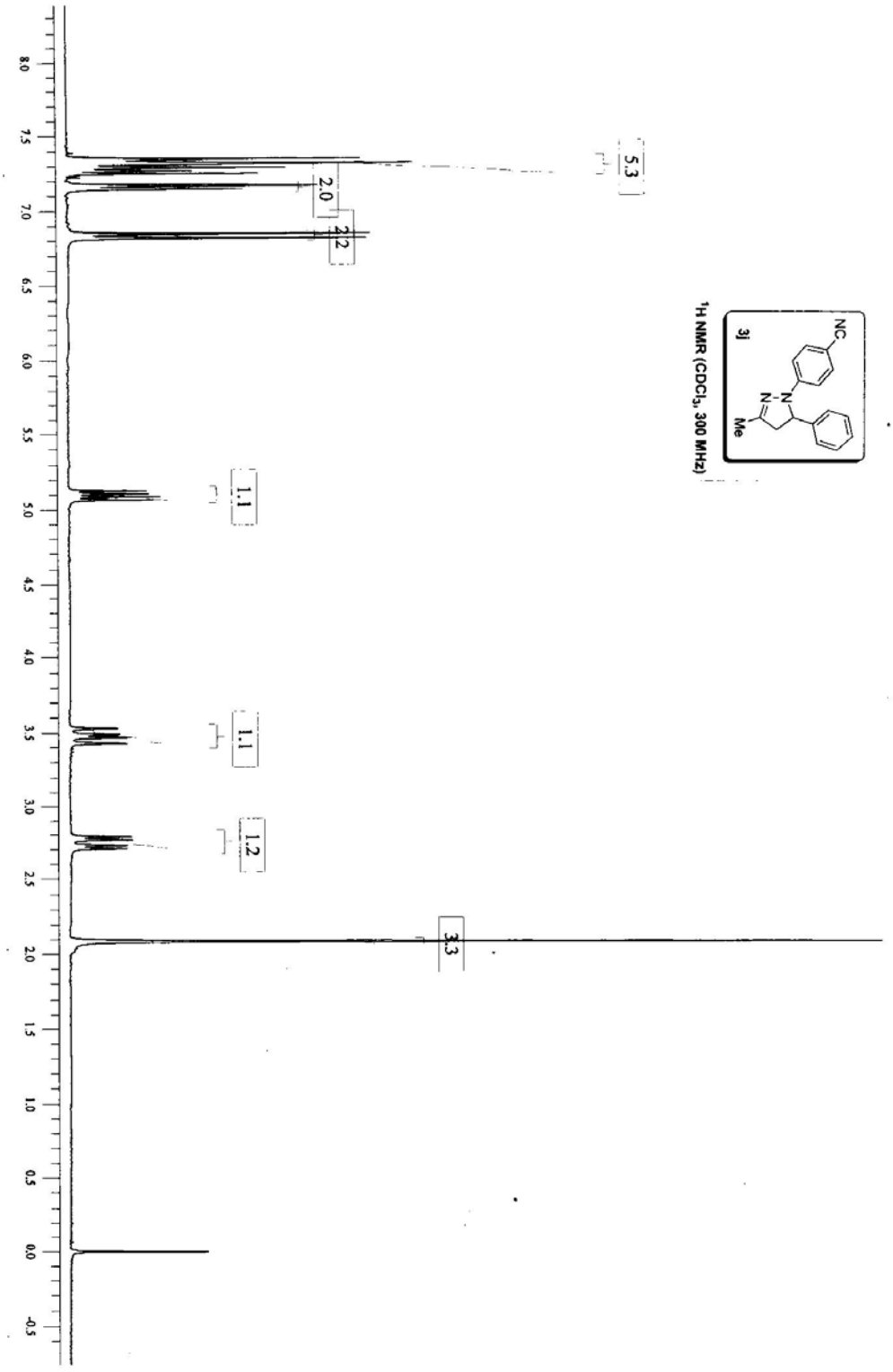

^{13}C NMR (CDCl$_3$, 75 MHz)
3g
Cl
F
N
N
Me
153.220
149.499
142.202
131.234
129.198
127.714
125.869
116.454
116.165
114.824
111.946
65.103
48.089
15.826
200
175
150
125
100
75
50
25
0

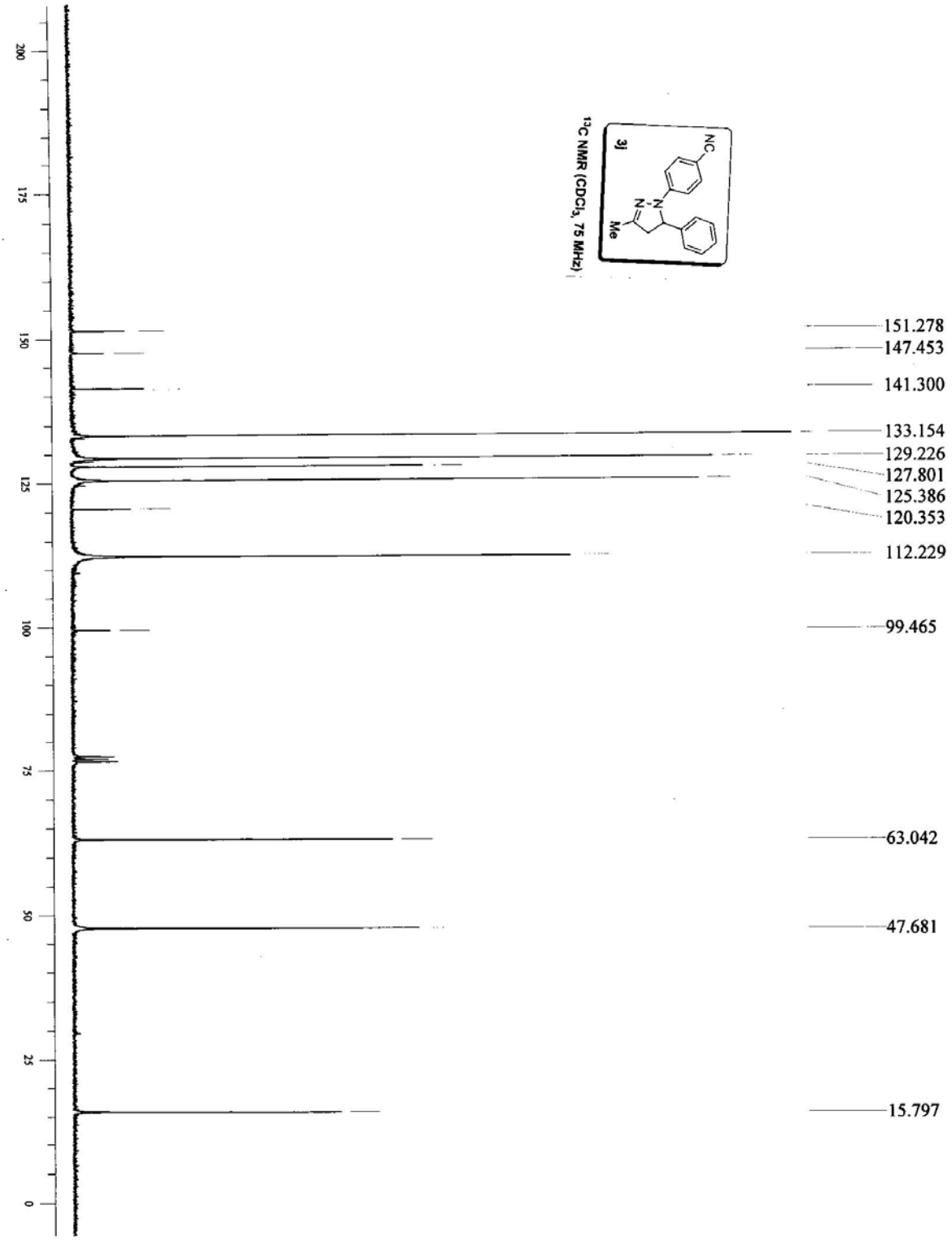

5.1
2.1
1.9
1.0
1.1
1.0
3.3
3.1
3h
Me
Me
N
N
^{1}H NMR (CDCl$_3$, 300 MHz)

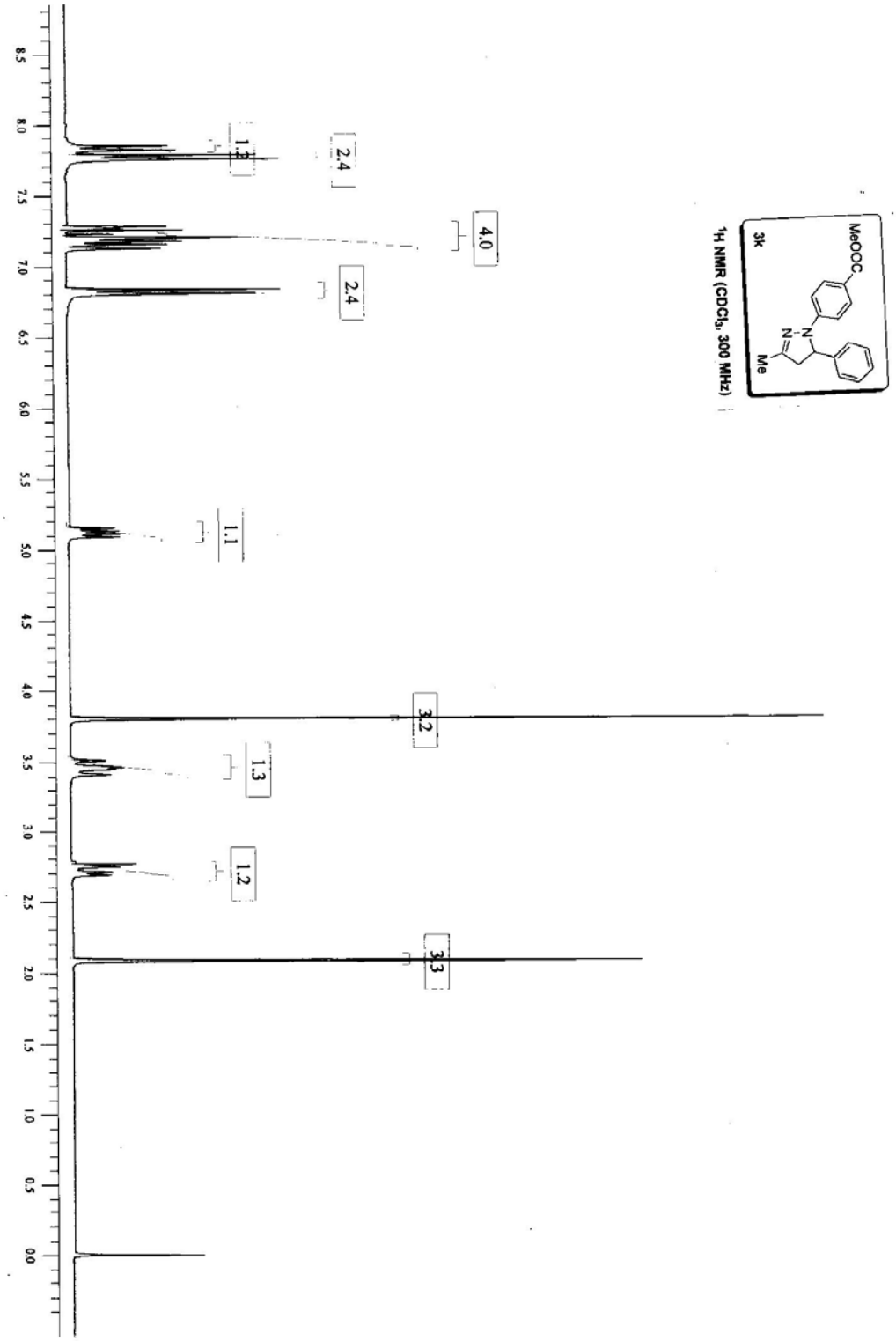

^{13}C NMR (CDCl$_3$, 75 MHz)
3h
Me
Me
148.223
144.151
143.127
129.370
128.994
127.306
125.998
113.338
109.793
107.463
104.091
65.305
47.855
20.420
15.930
200
175
150
125
100
75
50
25
0

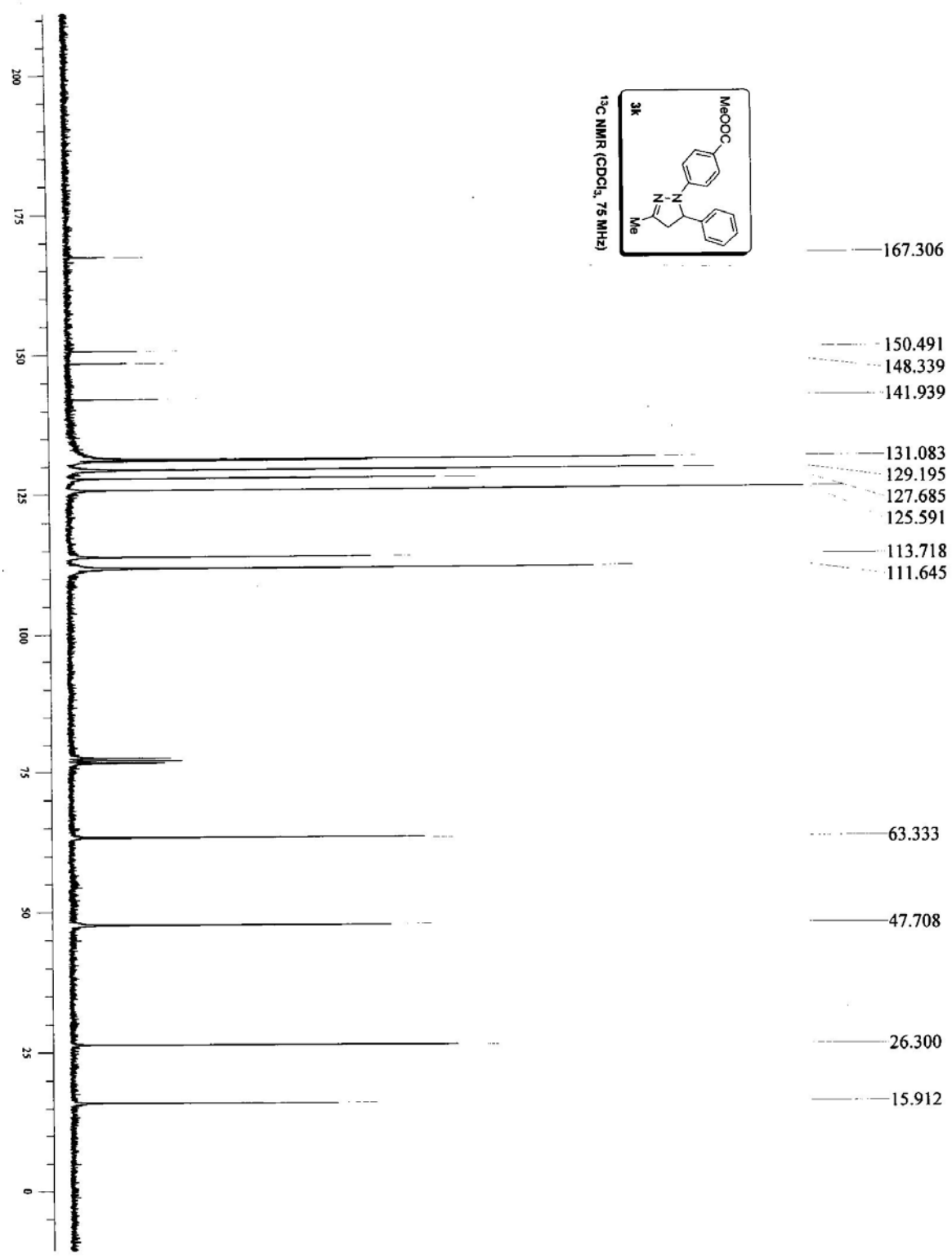

3i
MeO
Me
^{1}H NMR (CDCl$_3$, 300 MHz)
5.3
1.1
1.0
2.1
0.9
3.4
1.1
1.0
3.3

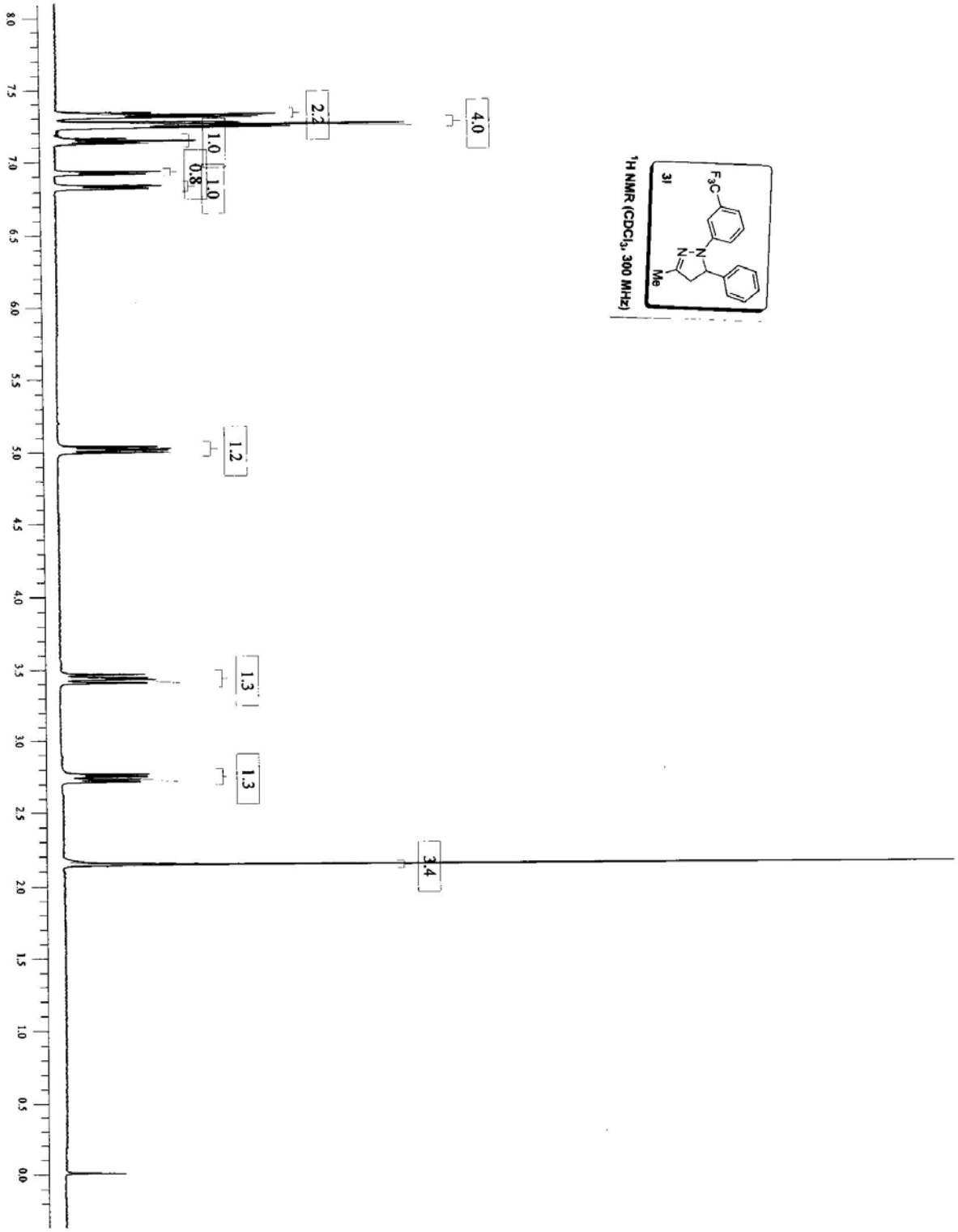

^{13}C NMR (CDCl$_3$, 75 MHz)
3i
MeO
Me
160.346
148.598
147.322
143.038
129.604
129.050
127.393
125.852
110.869
105.716
104.411
98.969
64.725
55.059
47.819
15.911

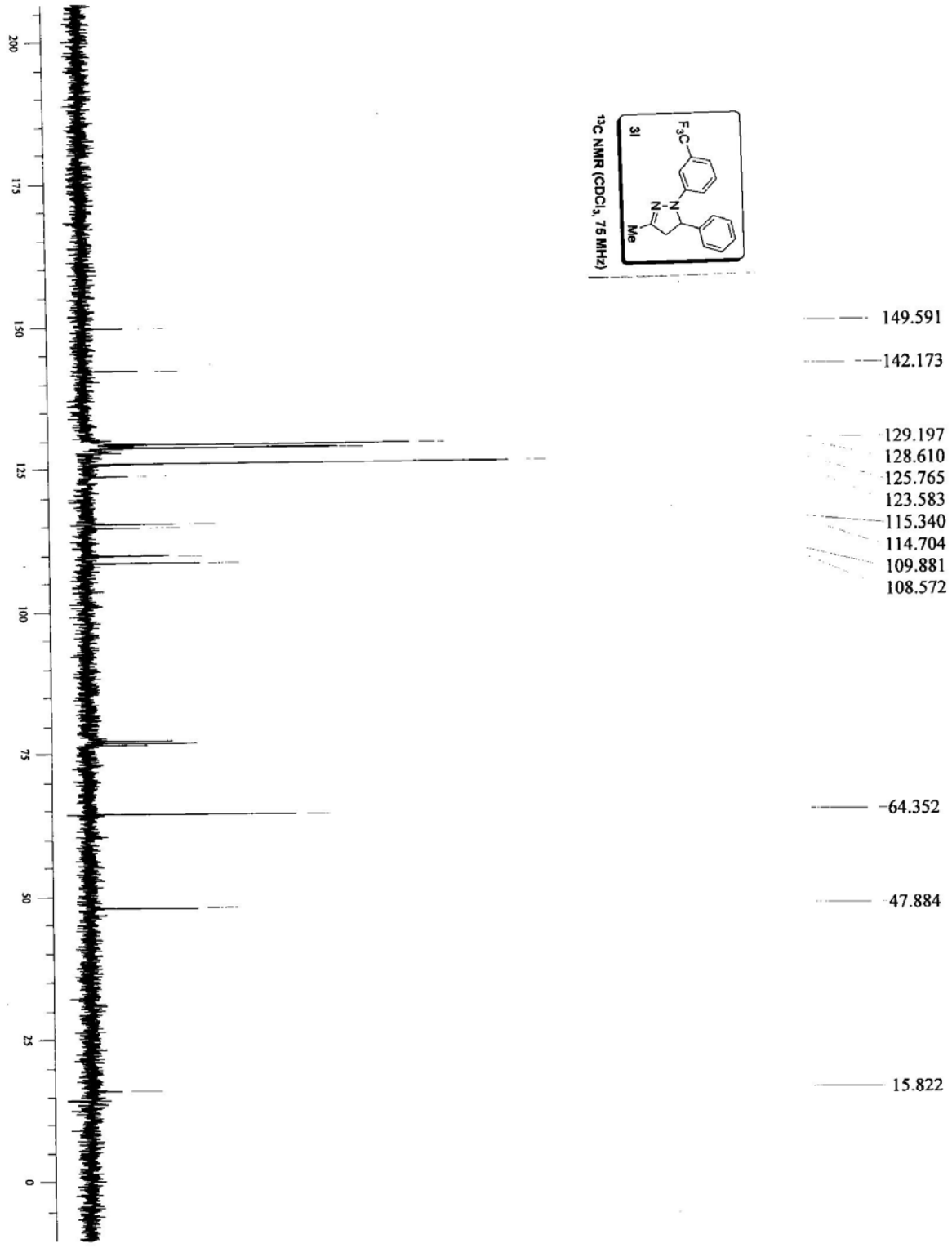

3j
NC
N
N
Me
^{1}H NMR (CDCl$_3$, 300 MHz)
5.3
2.0
2.2
1.1
1.1
1.2
3.3

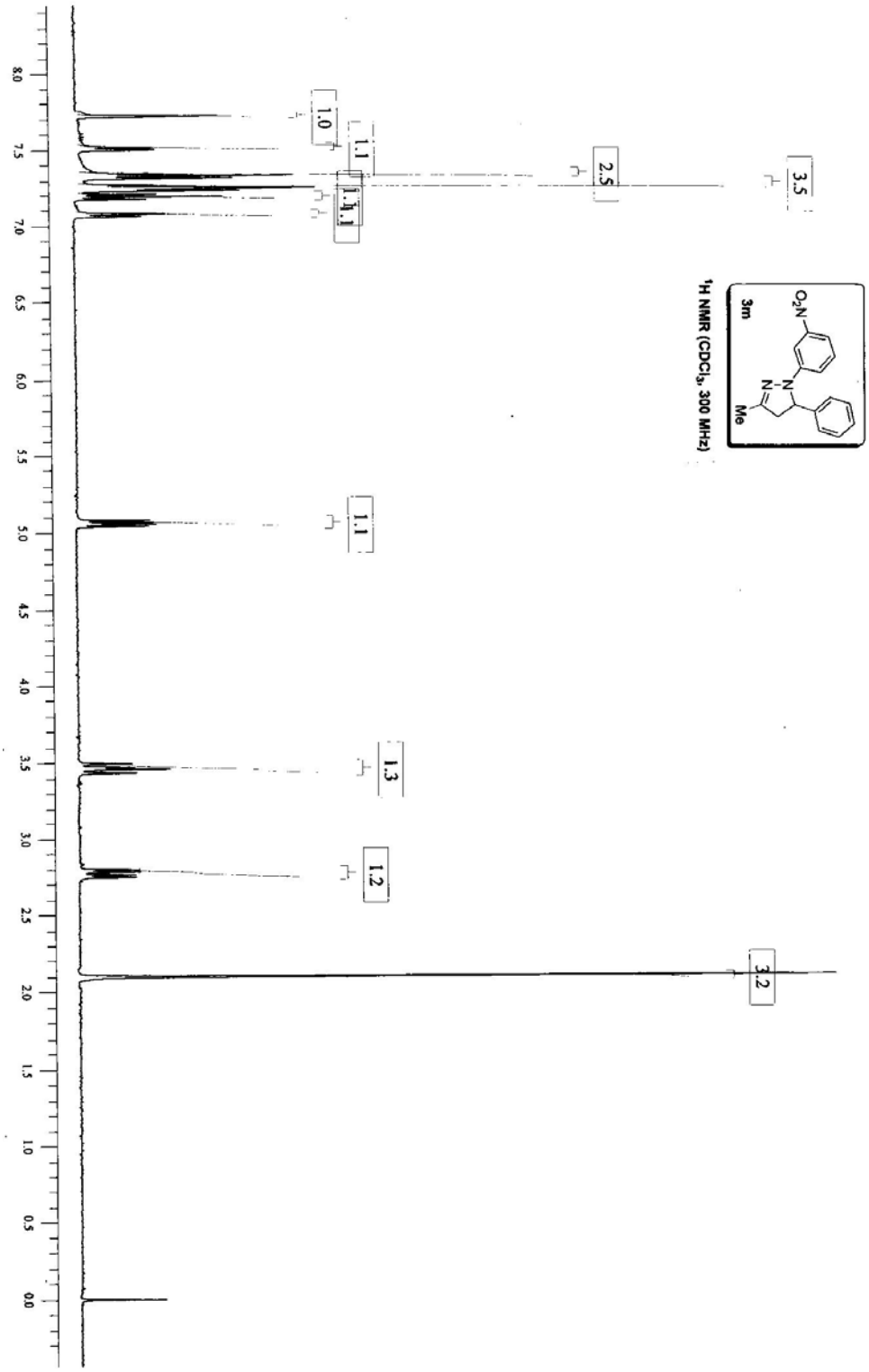

3j
NC
Me
^{13}C NMR (CDCl$_3$, 75 MHz)
200
175
150
125
100
75
50
25
0
151.278
147.453
141.300
133.154
129.226
127.801
125.386
120.353
112.229
99.465
63.042
47.681
15.797

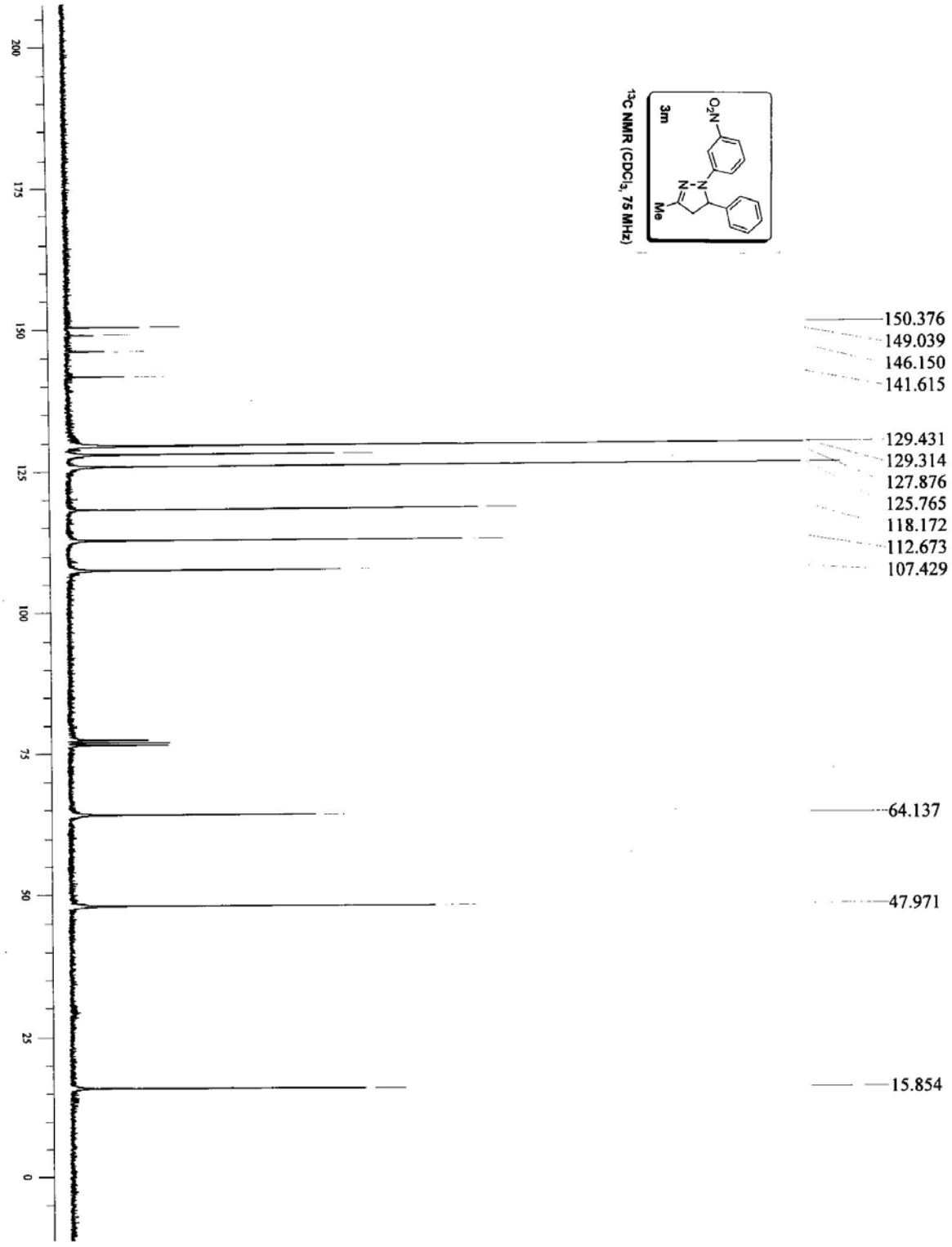

3k
MeOOC
Me
^{1}H NMR (CDCl$_3$, 300 MHz)
1.2
2.4
4.0
2.4
1.1
3.2
1.3
1.2
3.3

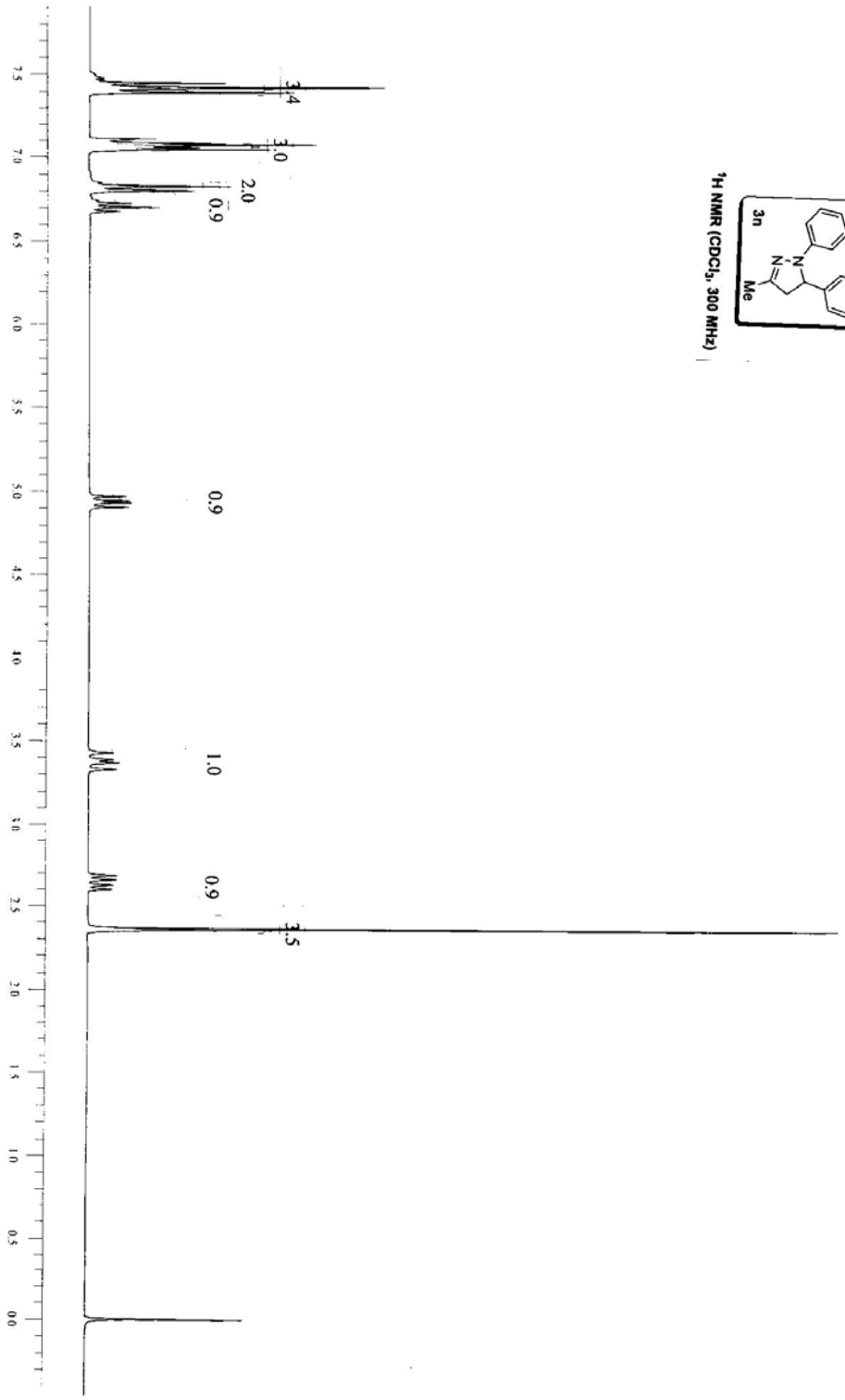

^{13}C NMR (CDCl$_3$, 75 MHz)
3k
MeOOC
Me
167.306
150.491
148.339
141.939
131.083
129.195
127.685
125.591
113.718
111.645
63.333
47.708
26.300
15.912
200
175
150
125
100
75
50
25
0


3l
^{1}H NMR ($CDCl_3$, 300 MHz)
F_3C
N
N
Me
2.2
4.0
1.0
0.8
1.0
1.2
1.3
1.3
3.4
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

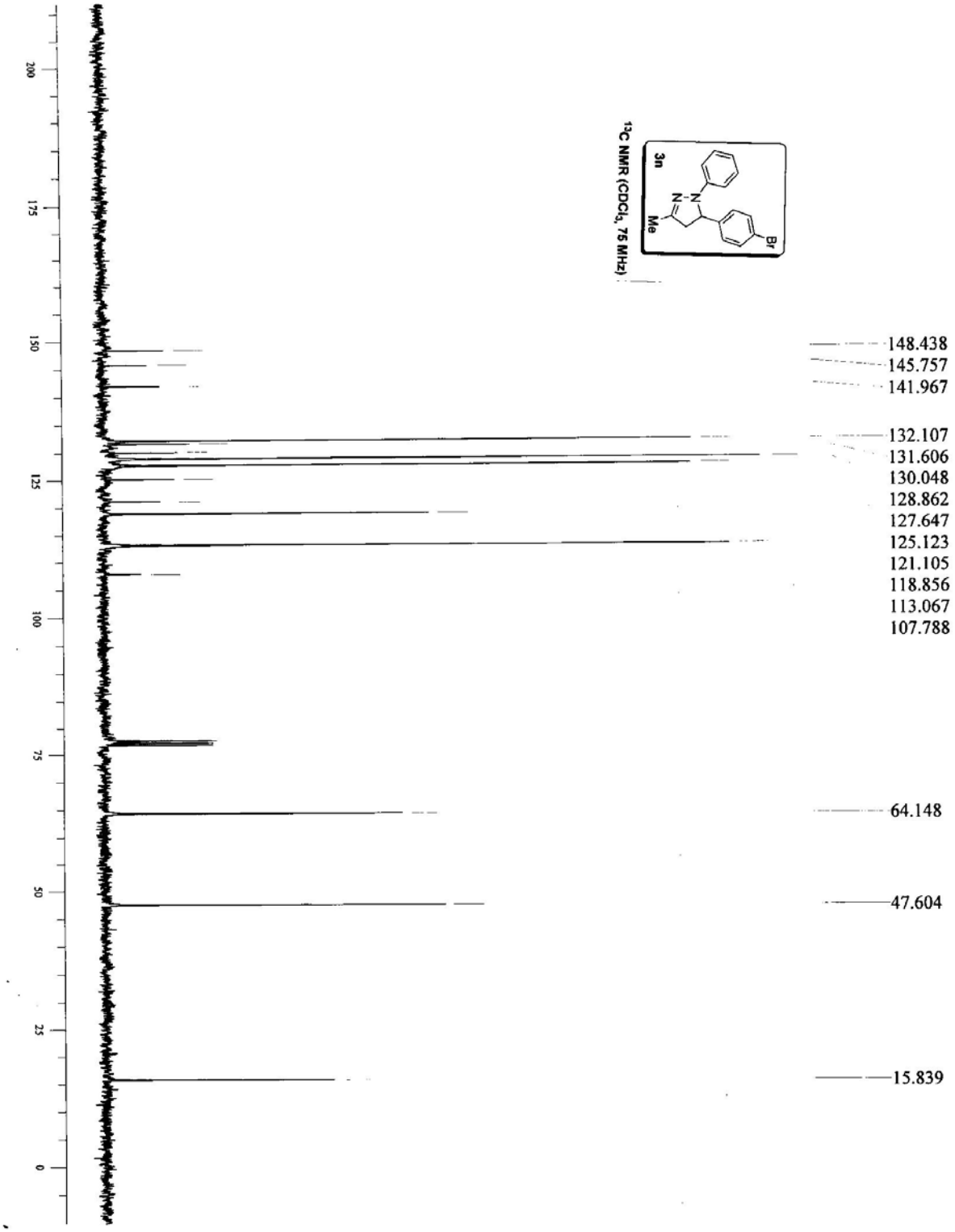

3l
^{13}C NMR (CDCl$_3$, 75 MHz)
149.591
142.173
129.197
128.610
125.765
123.583
115.340
114.704
109.881
108.572
64.352
47.884
15.822

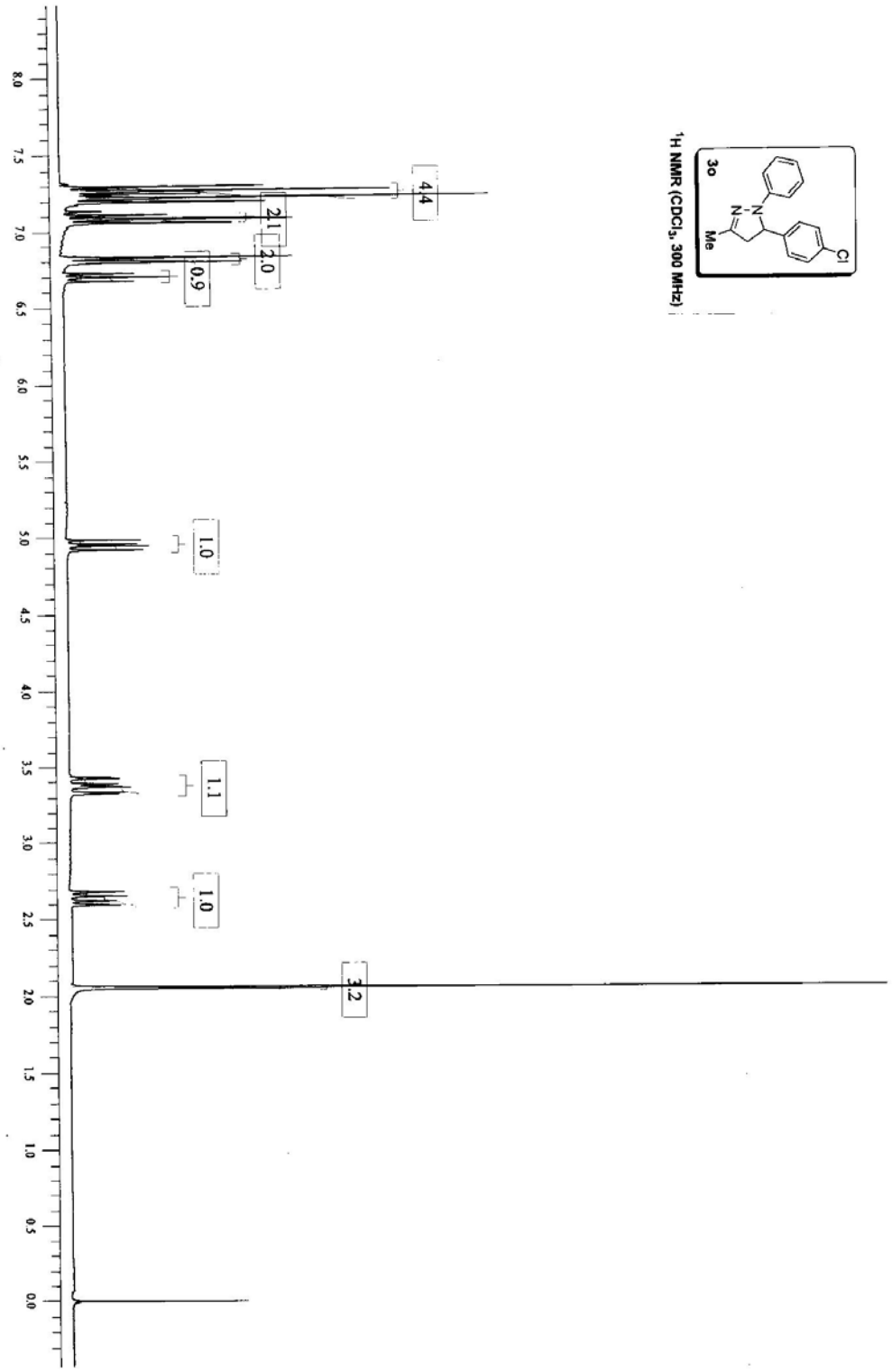

1.0
1.1
1.1
1.1
2.5
3.5
1.1
1.3
1.2
3.2
3m
Me
^{1}H NMR (CDCl$_3$, 300 MHz)

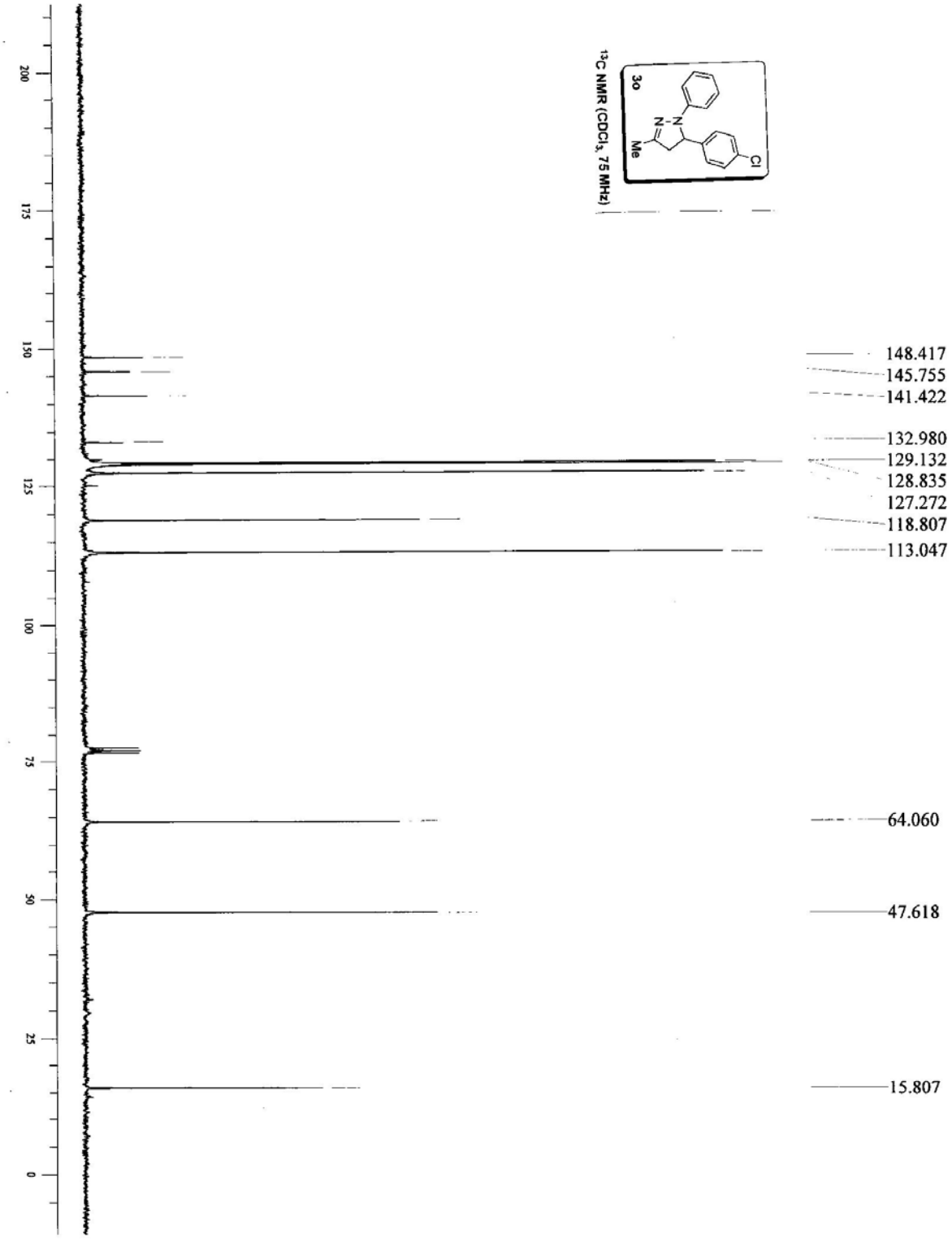

^{13}C NMR (CDCl$_3$, 75 MHz)
3m
O_2N
N
N
Me
200
175
150
125
100
75
50
25
0
150.376
149.039
146.150
141.615
129.431
129.314
127.876
125.765
118.172
112.673
107.429
64.137
47.971
15.854

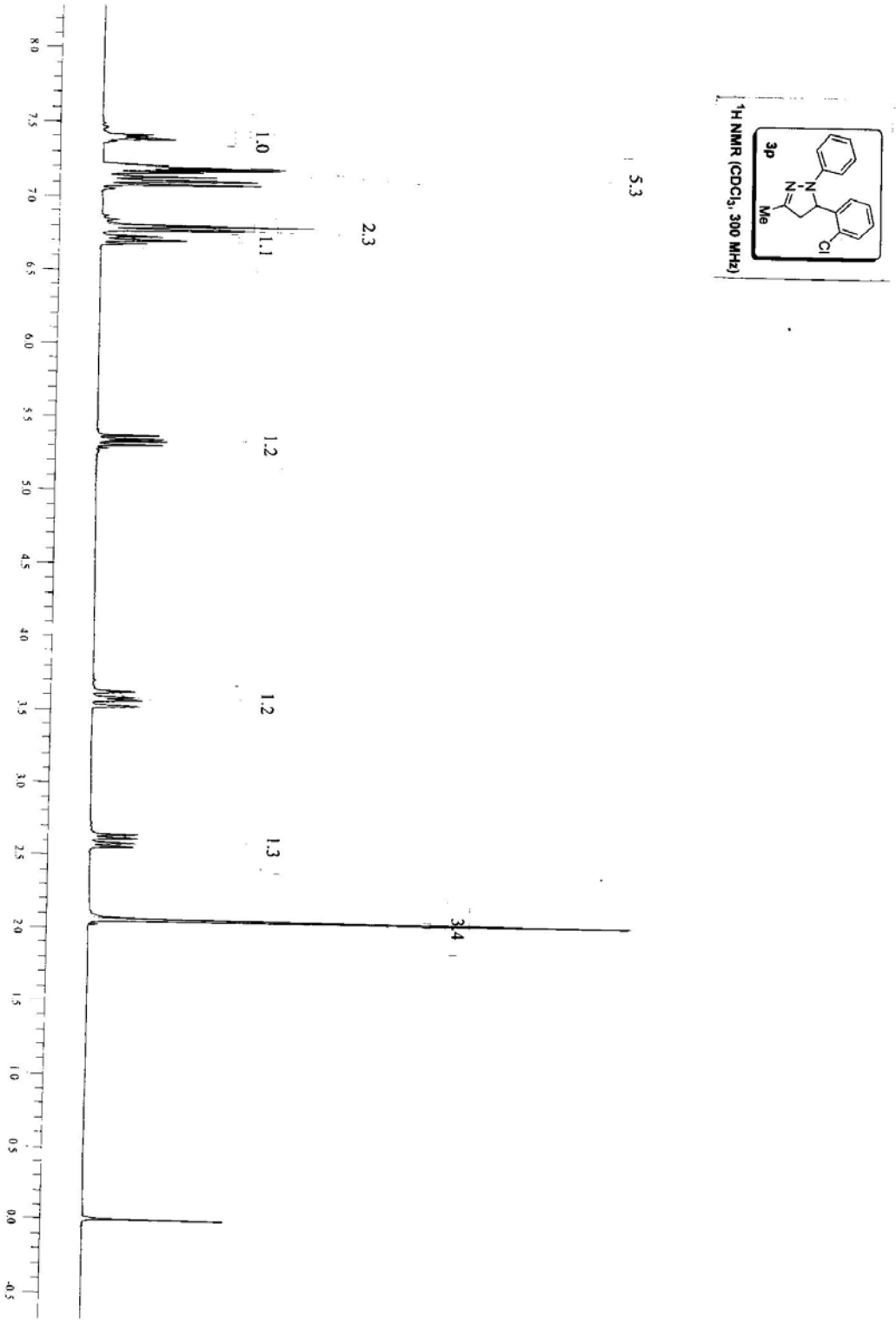


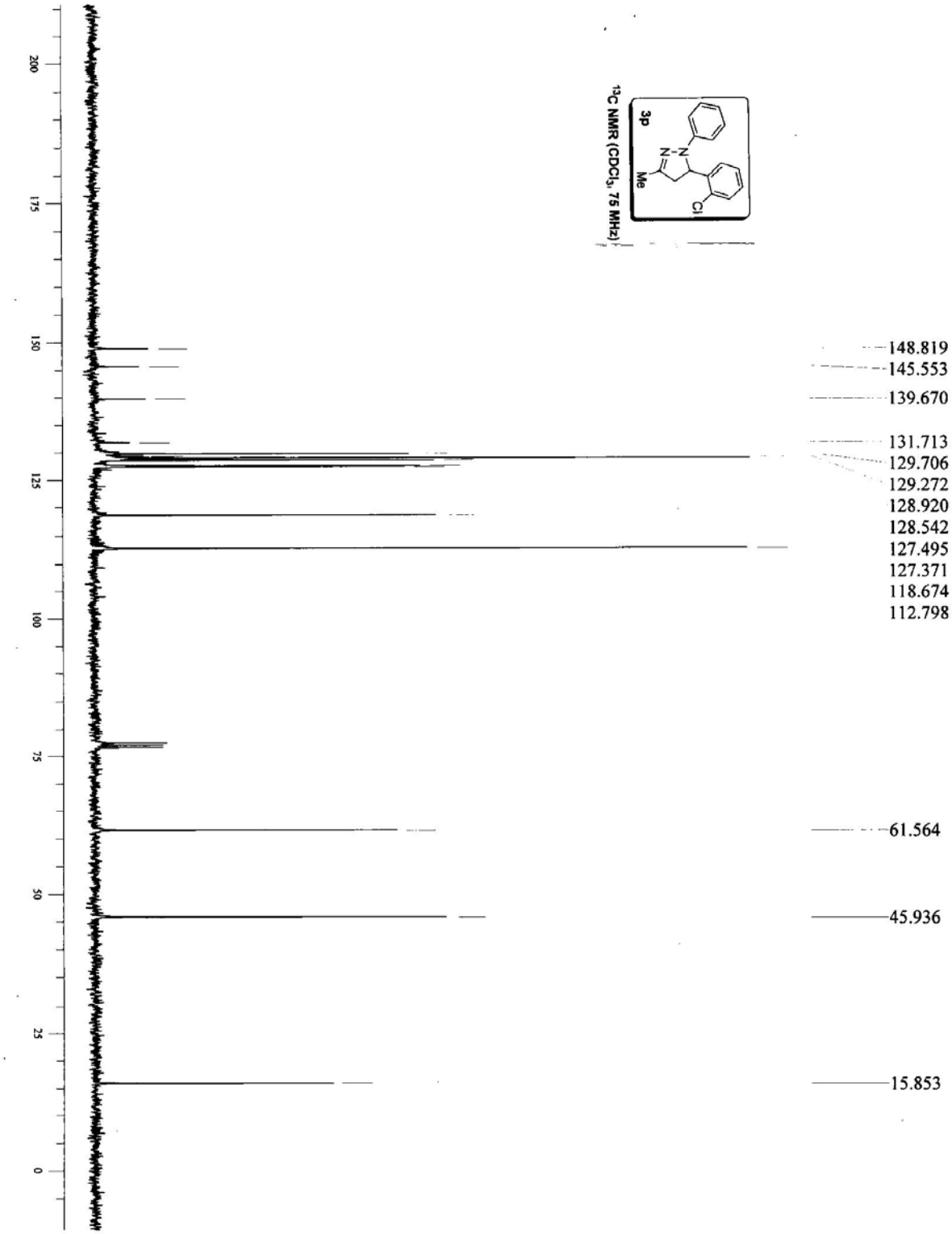
^{1}H NMR ($CDCl_3$, 300 MHz)

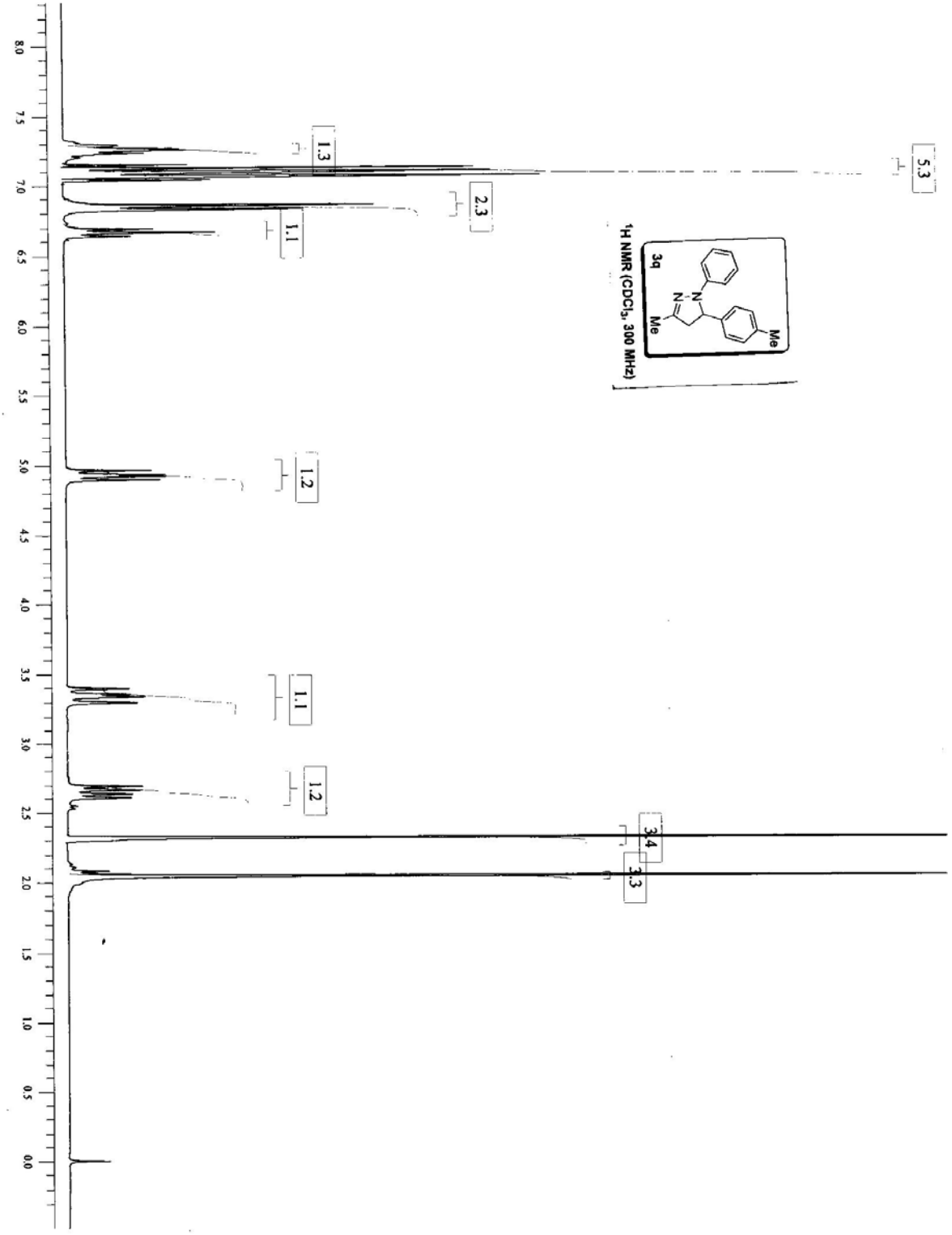

^{13}C NMR (CDCl$_3$, 75 MHz)
3n
Me
Br
148.438
145.757
141.967
132.107
131.606
130.048
128.862
127.647
125.123
121.105
118.856
113.067
107.788
64.148
47.604
15.839

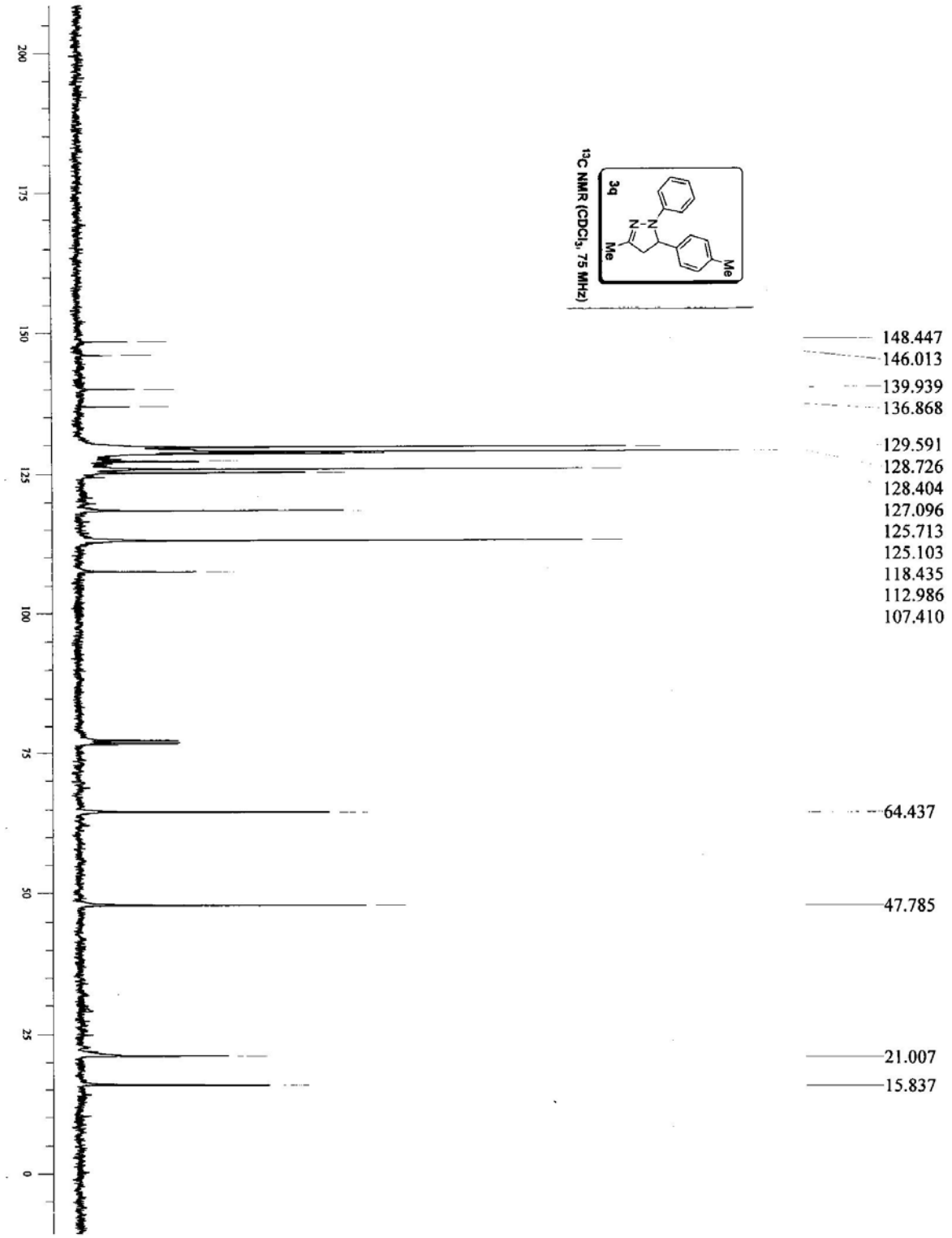

3o
Me
Cl
^{1}H NMR (CDCl$_3$, 300 MHz)
4.4
2.1
2.0
0.9
1.0
1.1
1.0
3.2

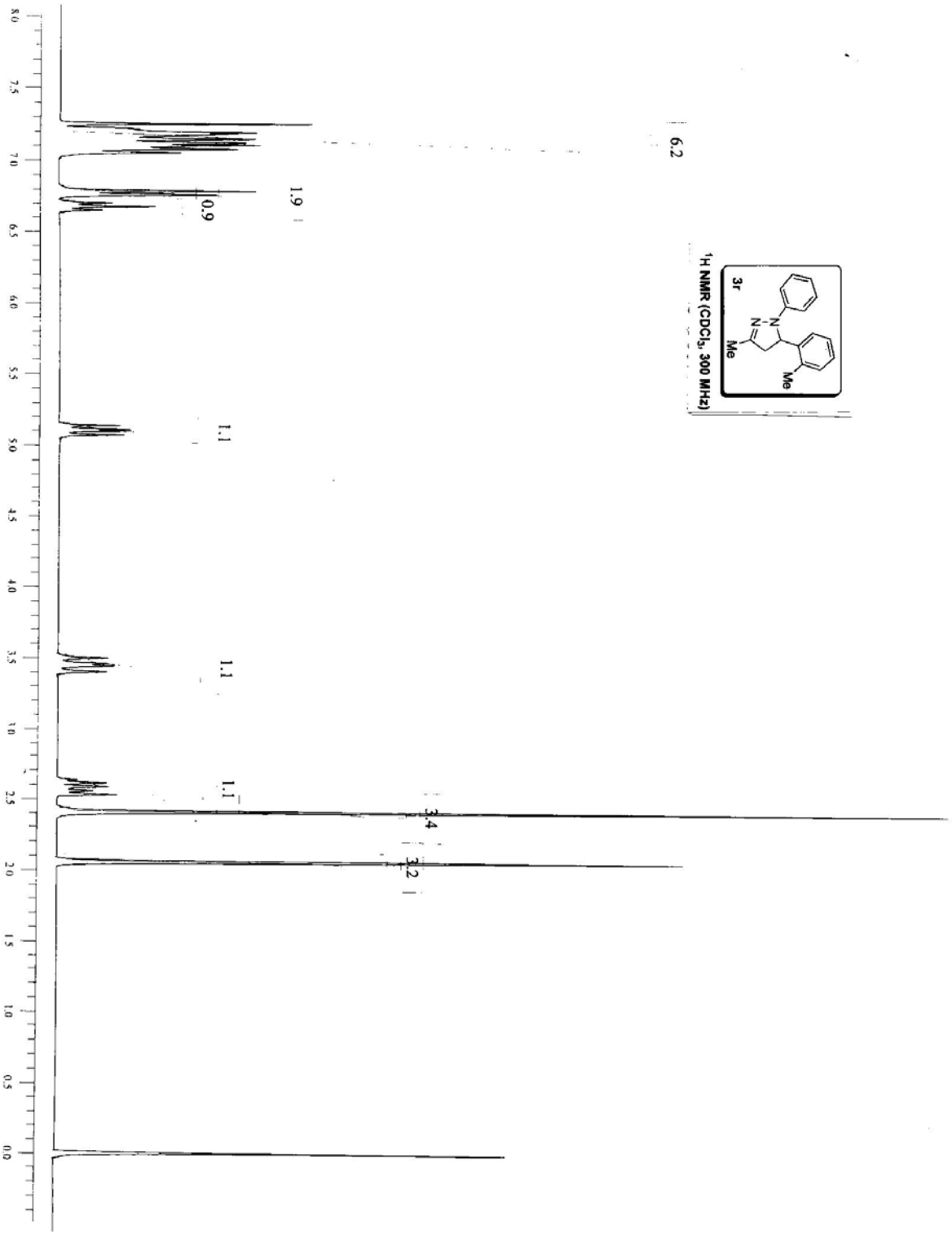

^{13}C NMR (CDCl$_3$, 75 MHz)
3o
Me
Cl
148.417
145.755
141.422
132.980
129.132
128.835
127.272
118.807
113.047
64.060
47.618
15.807
200
175
150
125
100
75
50
25
0

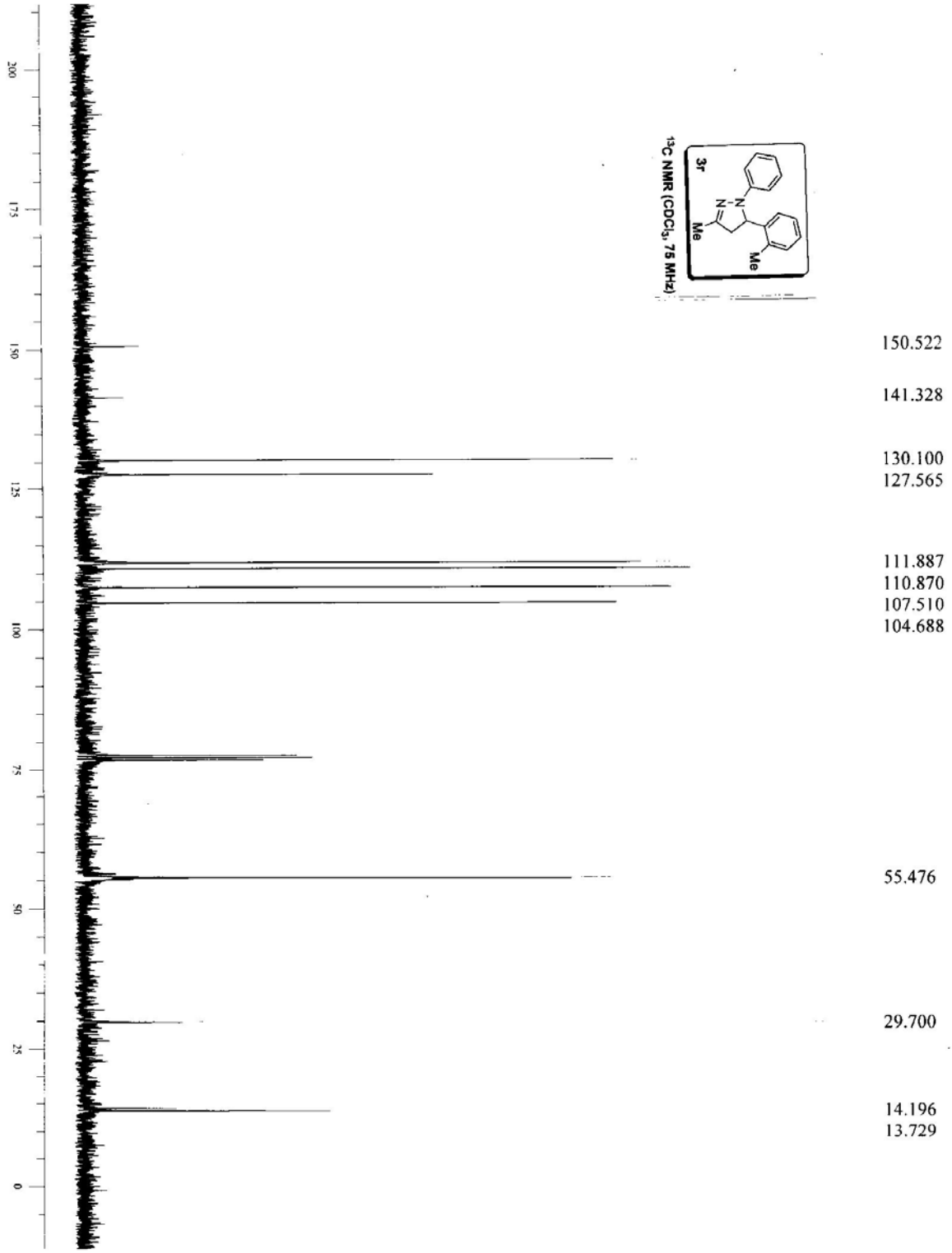

1H NMR (CDCl3, 300 MHz)
3p
Me
Cl
5.3
2.3
1.0
1.1
1.2
1.2
1.3
3.4

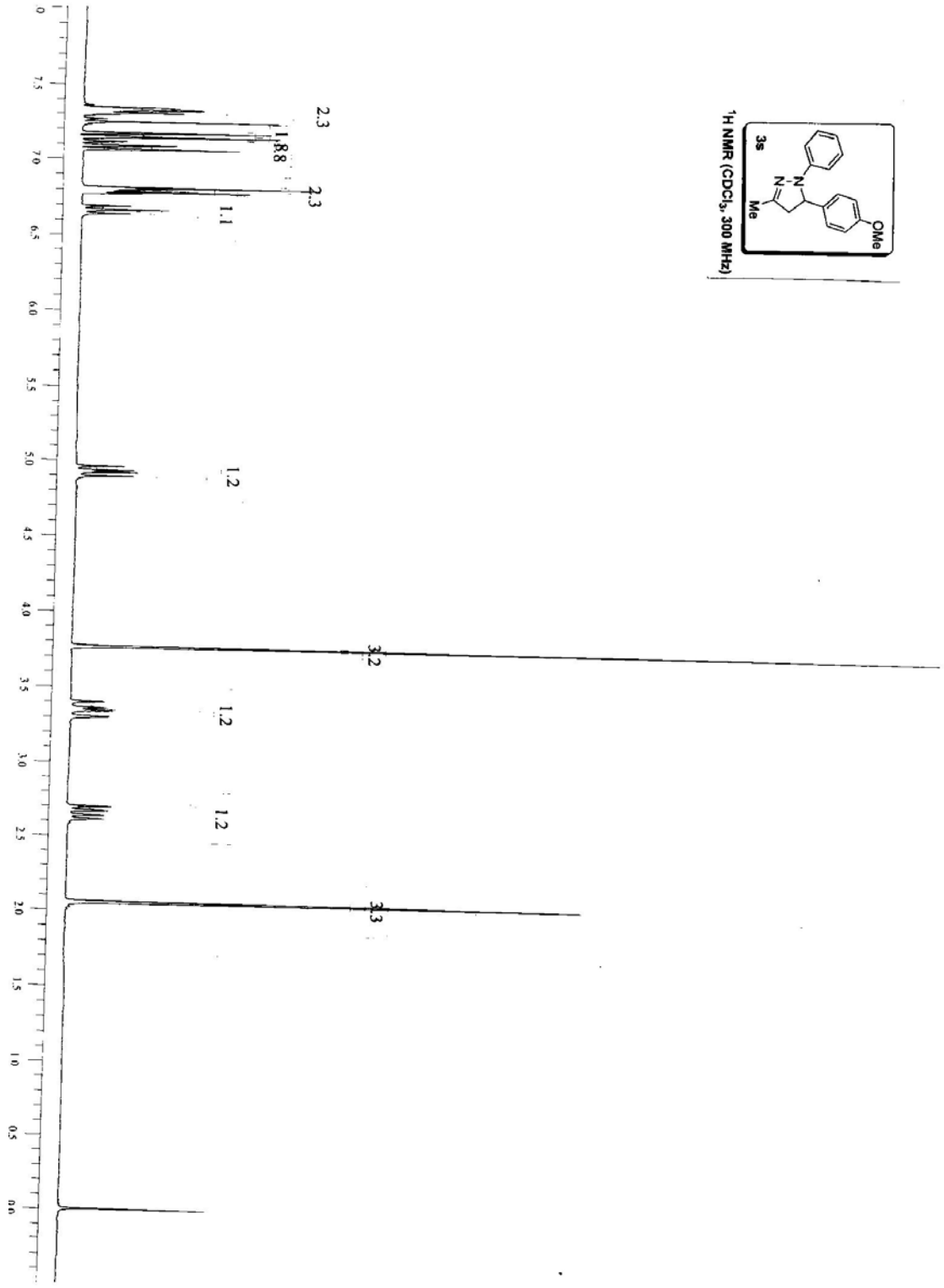

^{13}C NMR (CDCl$_3$, 75 MHz)
3p
Me
Cl
148.819
145.553
139.670
131.713
129.706
129.272
128.920
128.542
127.495
127.371
118.674
112.798
61.564
45.936
15.853

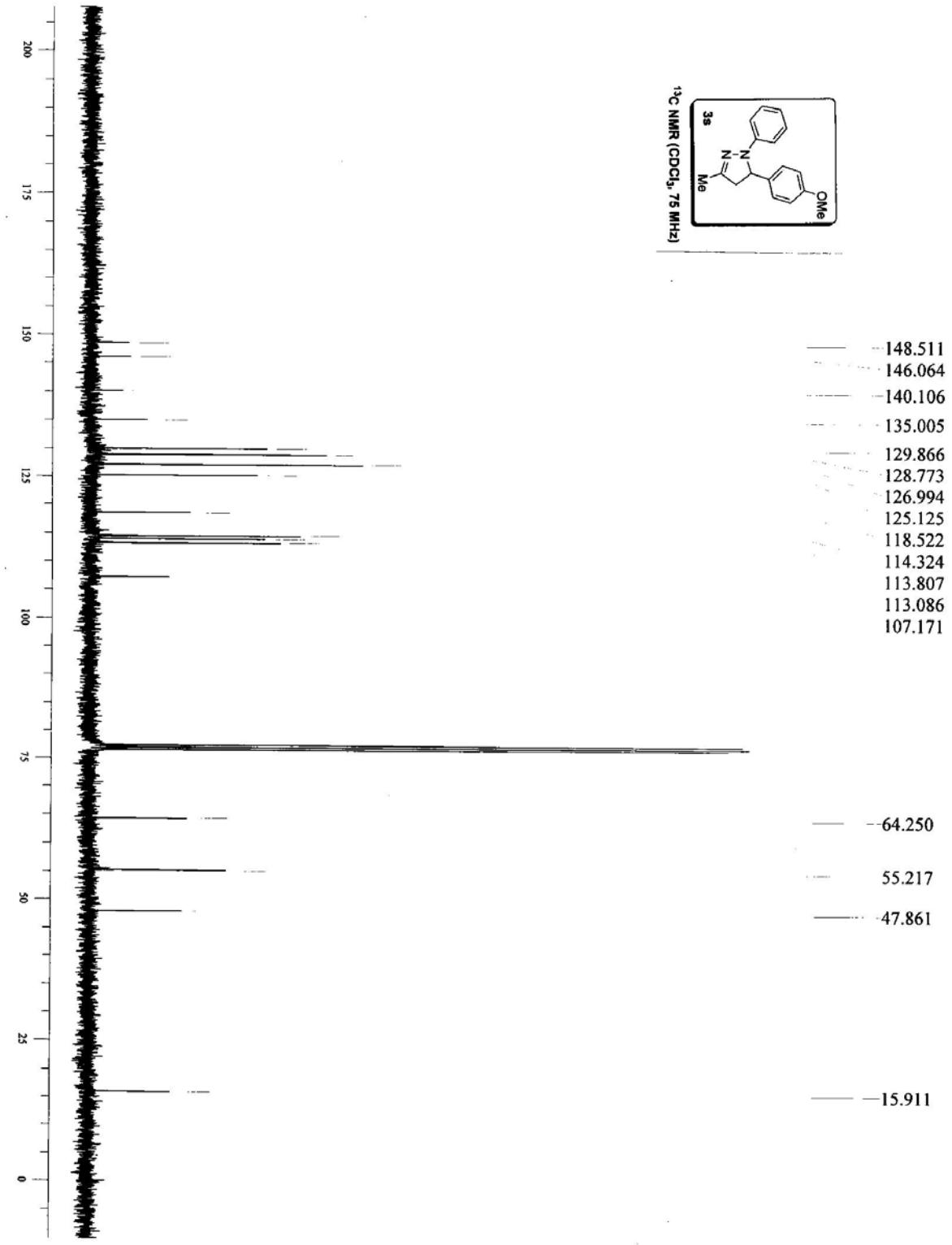

1.3
2.3
1.1
1.2
1.1
1.2
3.4
3.3
5.3
3q
Me
Me
Me
N
N
^{1}H NMR (CDCl$_3$, 300 MHz)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

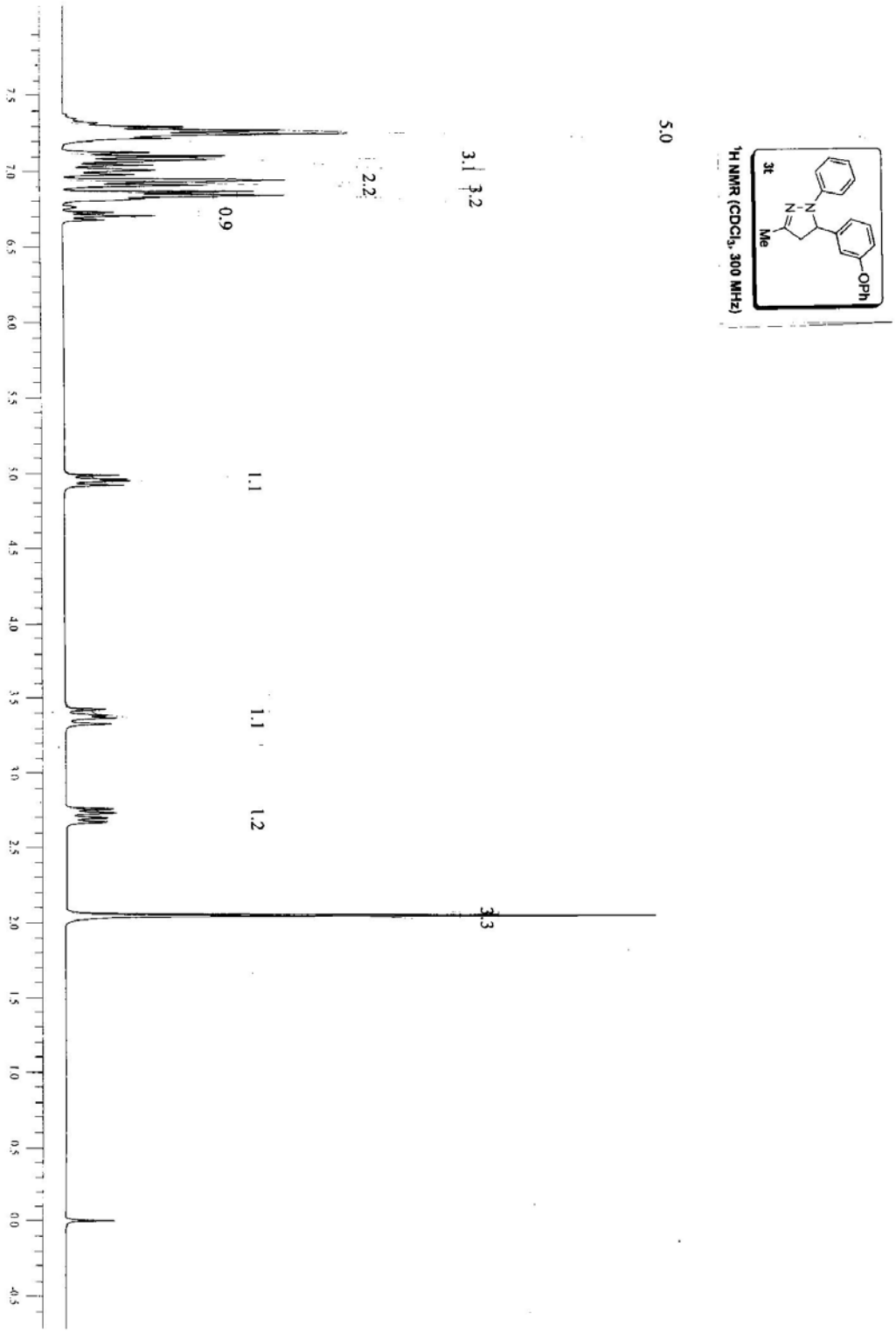

^{13}C NMR (CDCl$_3$, 75 MHz)
3q
Me
Me
148.447
146.013
139.939
136.868
129.591
128.726
128.404
127.096
125.713
125.103
118.435
112.986
107.410
64.437
47.785
21.007
15.837

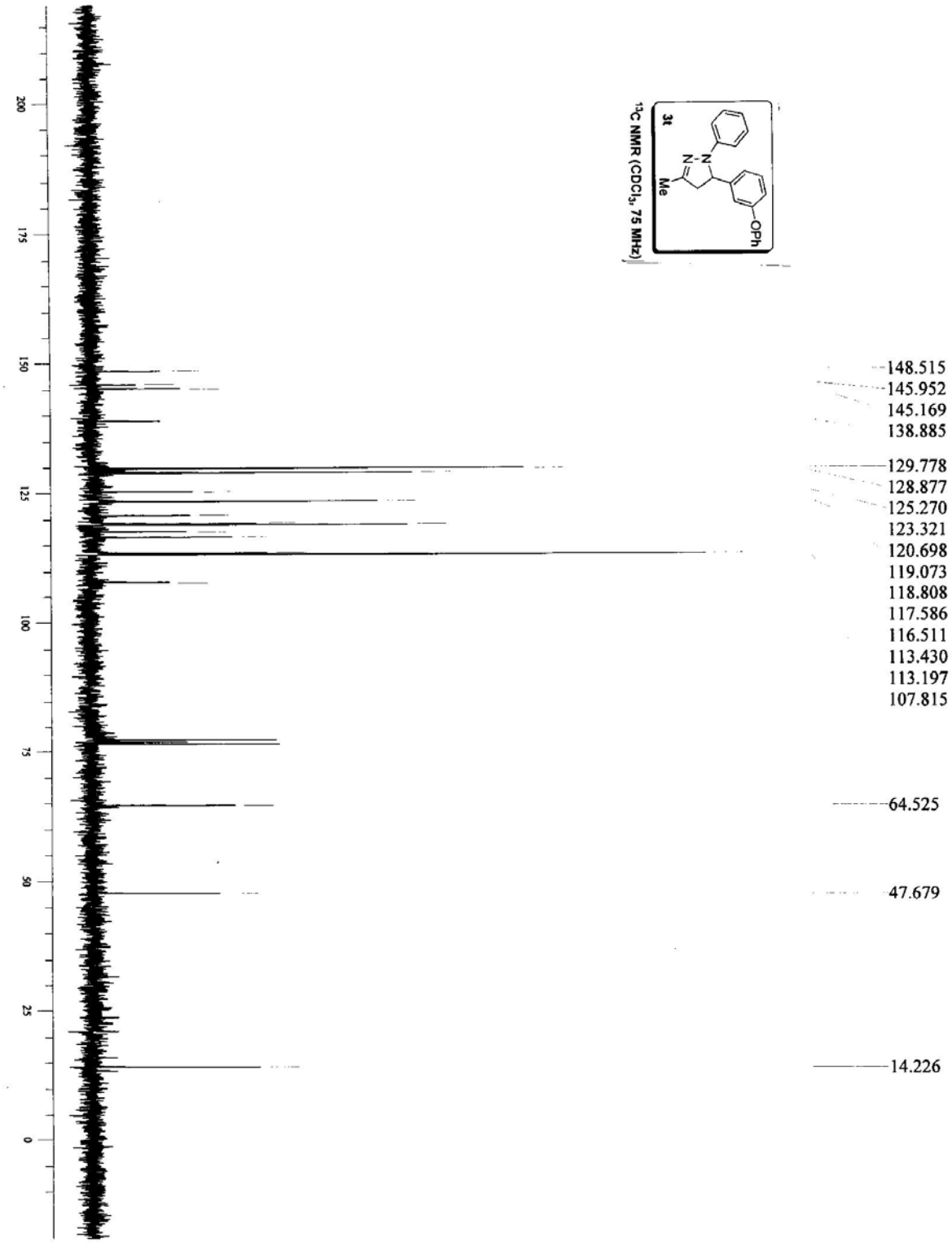

3r
Me
Me
^{1}H NMR (CDCl$_3$, 300 MHz)
6.2
1.9
0.9
1.1
1.1
1.1
3.4
3.2

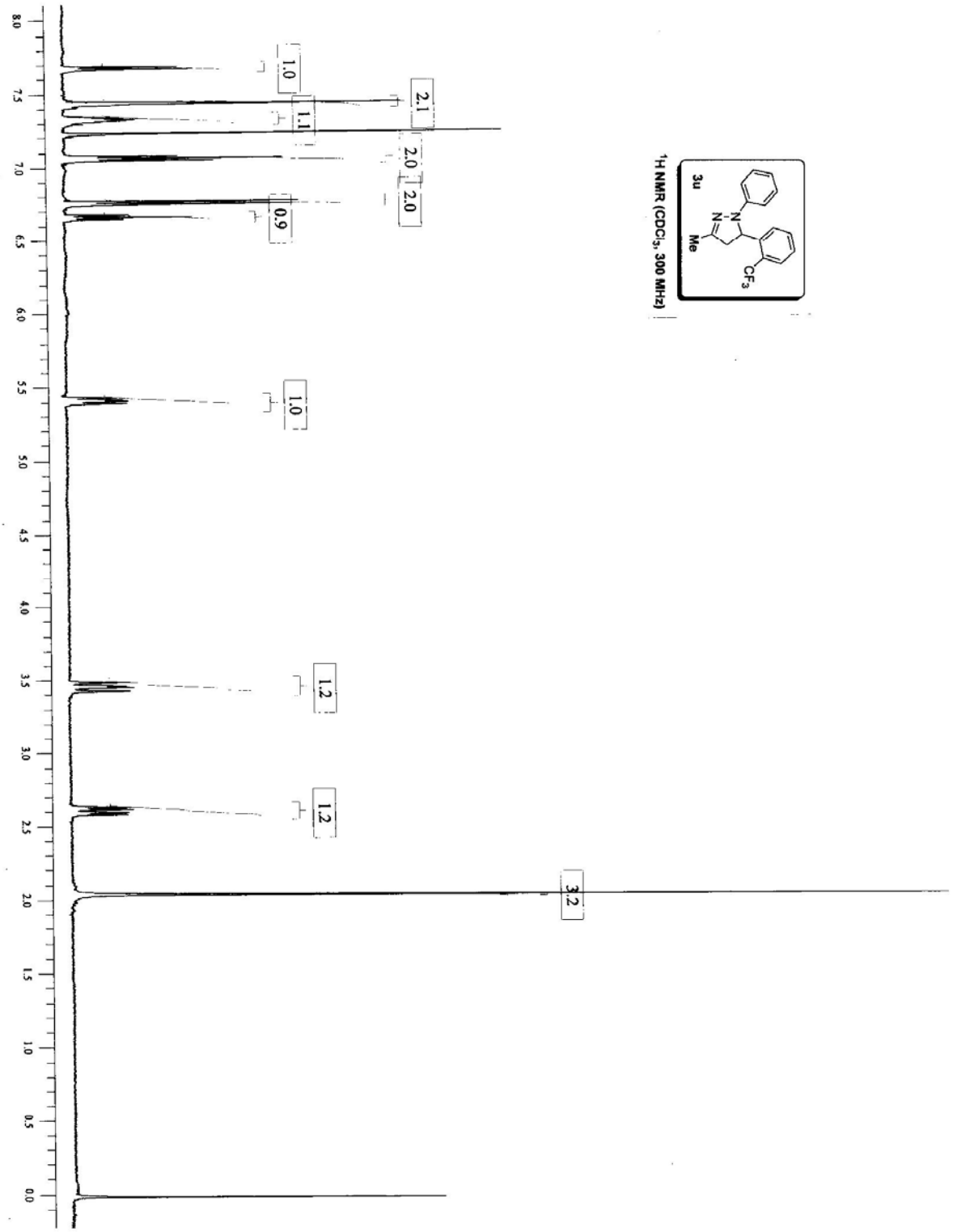

^{13}C NMR (CDCl$_3$, 75 MHz)
3r
Me
Me
150.522
141.328
130.100
127.565
111.887
110.870
107.510
104.688
55.476
29.700
14.196
13.729

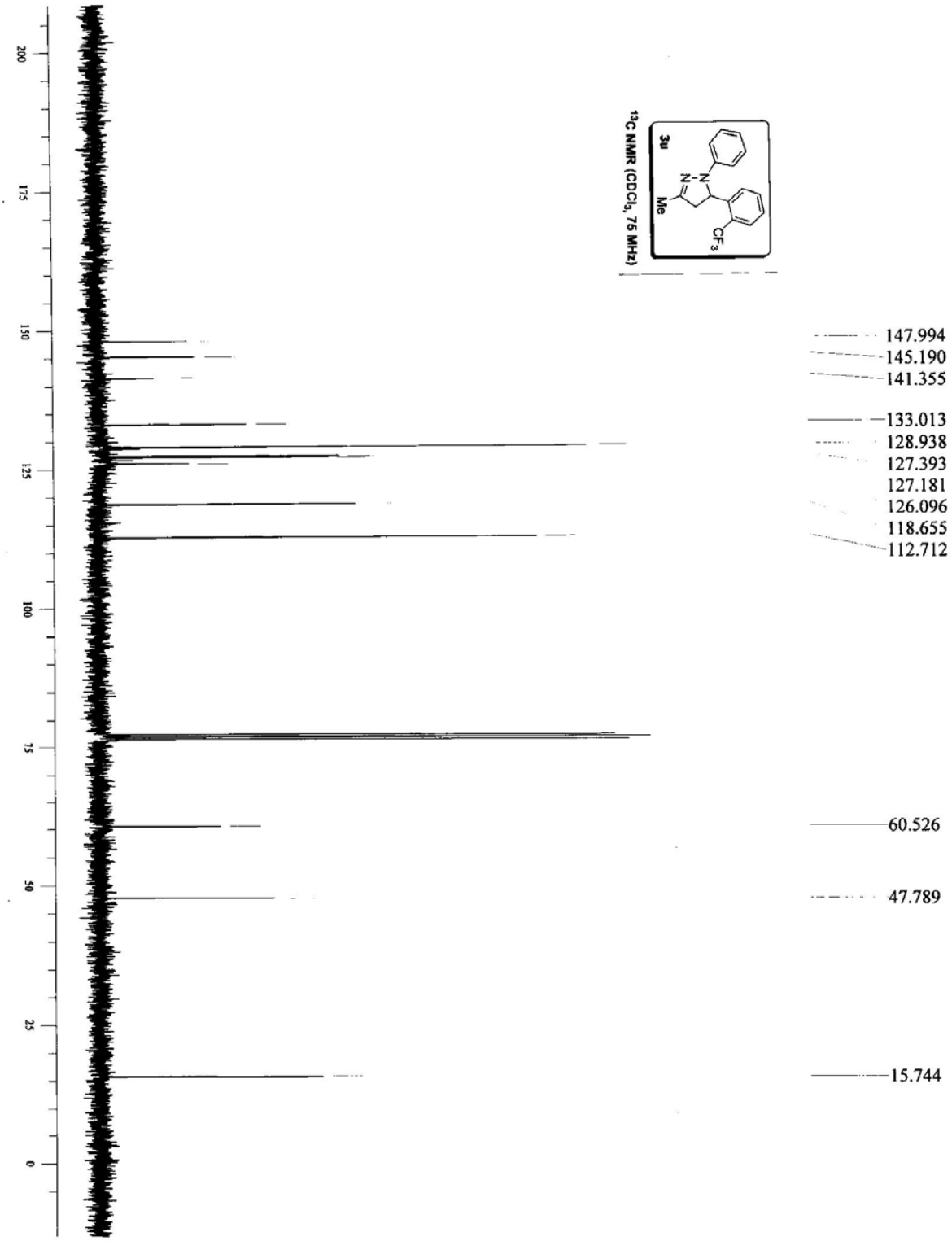

^{1}H NMR (CDCl$_3$, 300 MHz)
3s
Me
OMe
2.3
1.88
2.3
1.1
1.2
3.2
1.2
1.2
3.3

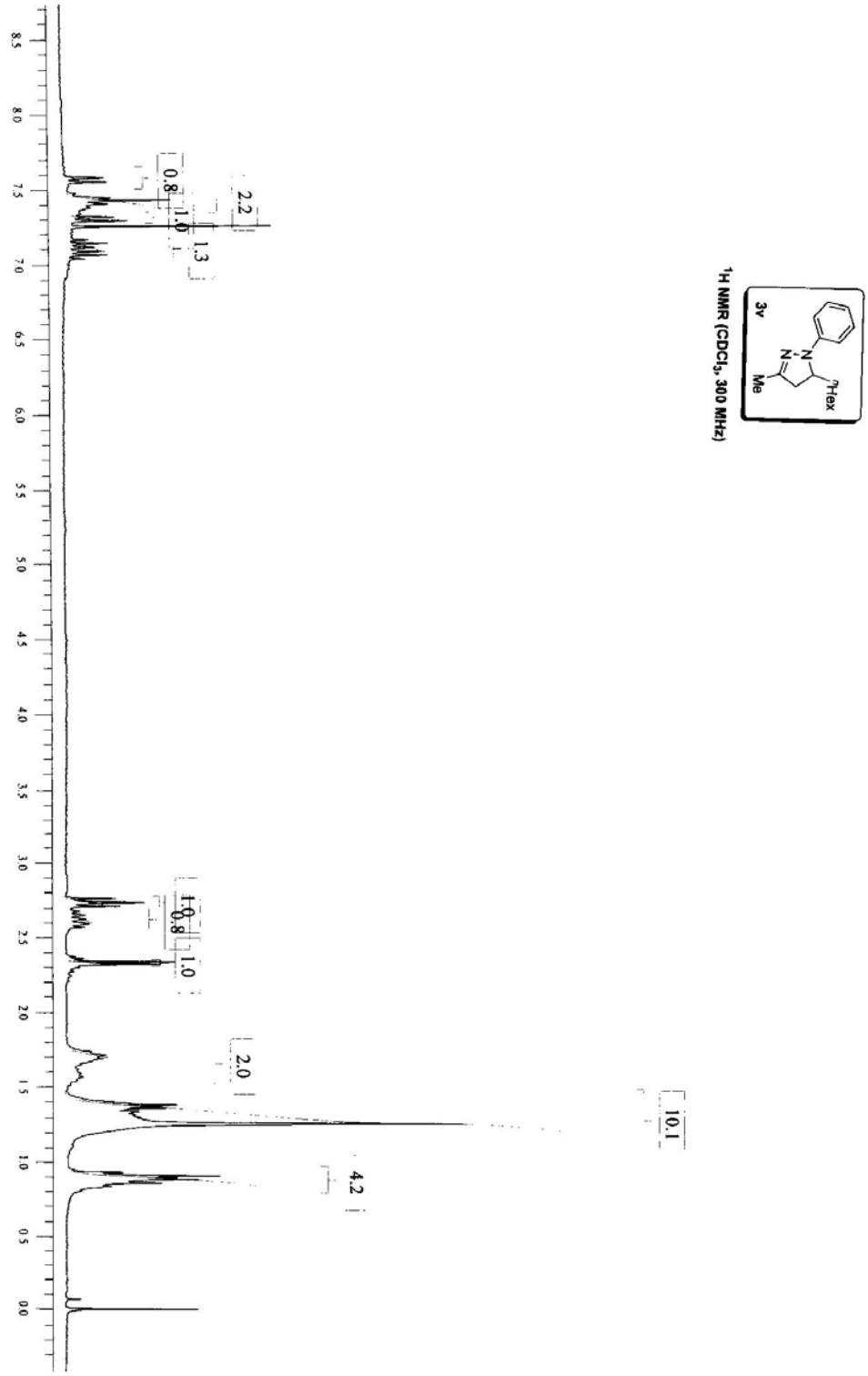

^{13}C NMR (CDCl$_3$, 75 MHz)
3s
Me
OMe
148.511
146.064
140.106
135.005
129.866
128.773
126.994
125.125
118.522
114.324
113.807
113.086
107.171
64.250
55.217
47.861
15.911
200
175
150
125
100
75
50
25
0

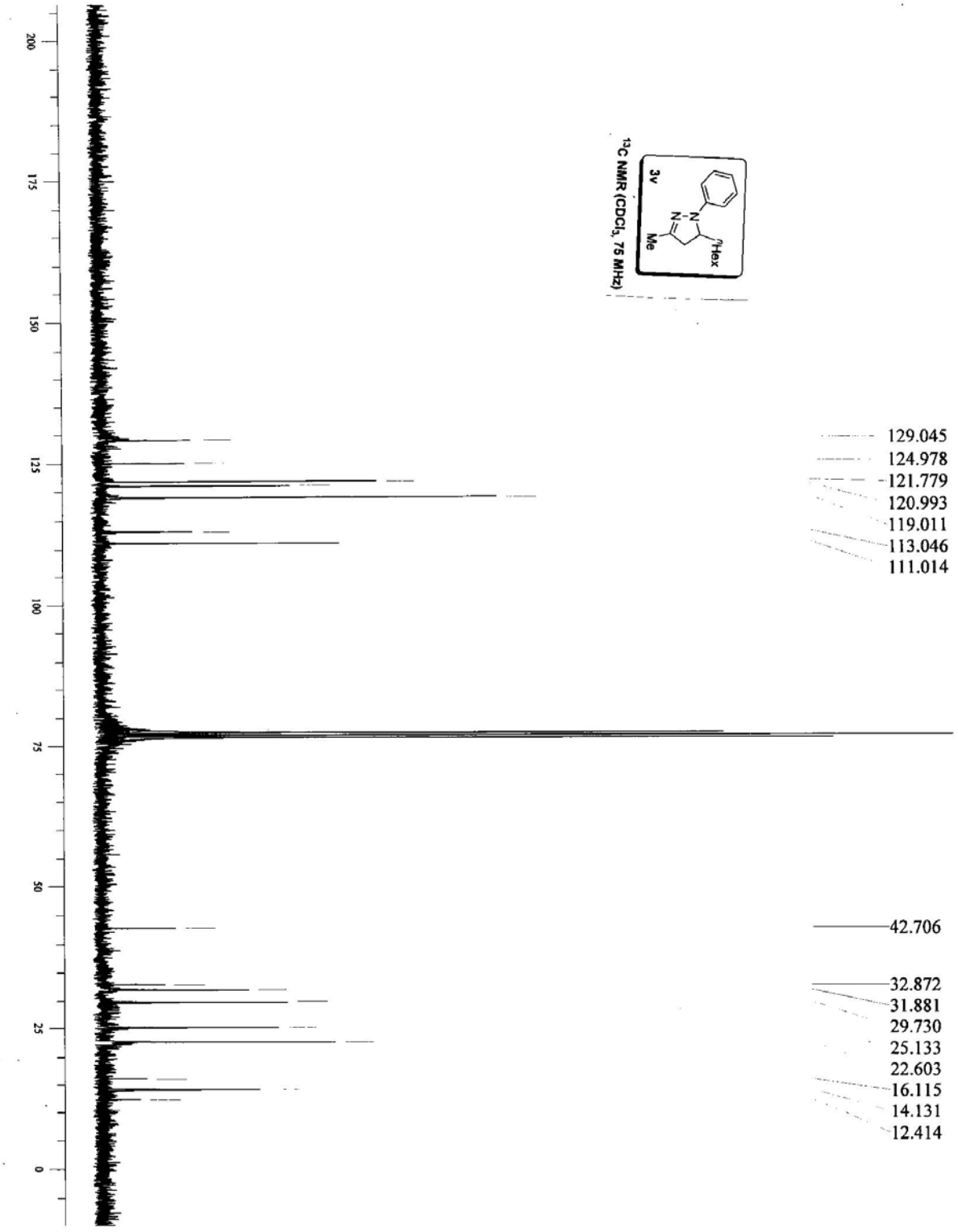

3t
Me
OPh
^{1}H NMR (CDCl$_3$, 300 MHz)
5.0
3.1
3.2
2.2
0.9
1.1
1.1
1.2
3.3

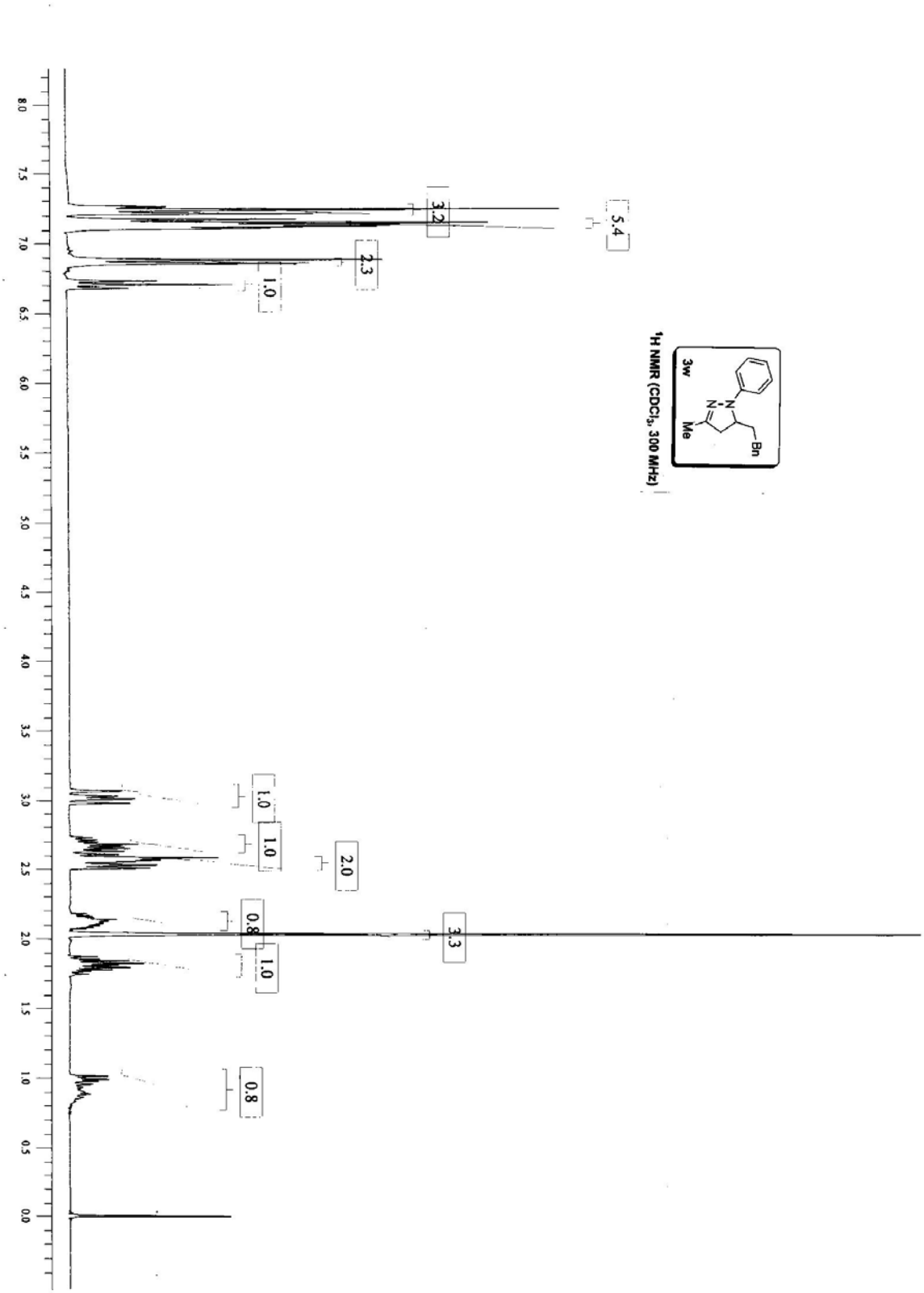

^{13}C NMR (CDCl$_3$, 75 MHz)
3t
Me
OPh
148.515
145.952
145.169
138.885
129.778
128.877
125.270
123.321
120.698
119.073
118.808
117.586
116.511
113.430
113.197
107.815
64.525
47.679
14.226

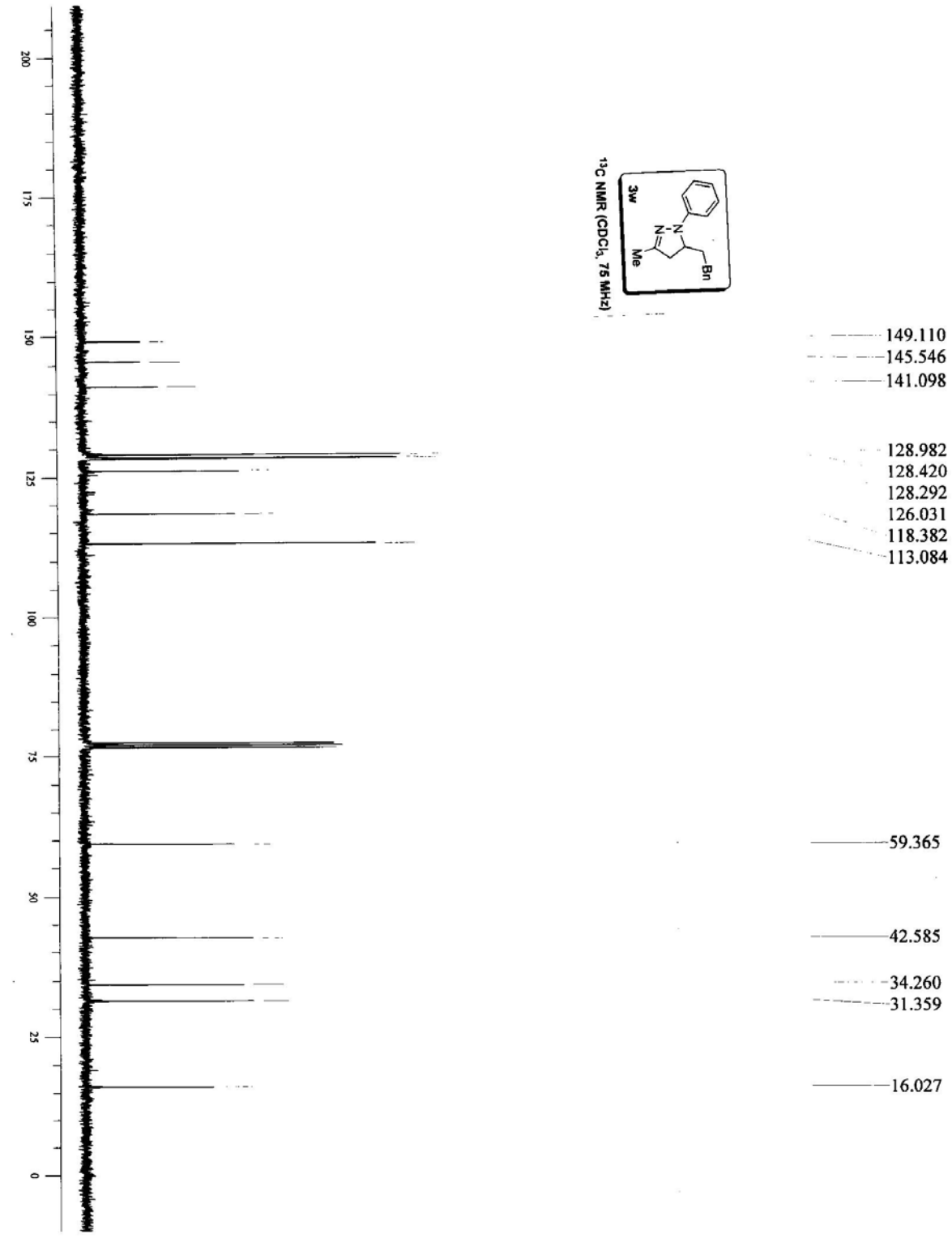

3u
Me
CF3
1H NMR (CDCl3, 300 MHz)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.0
1.1
2.1
2.0
2.0
0.9
1.0
1.2
1.2
3.2

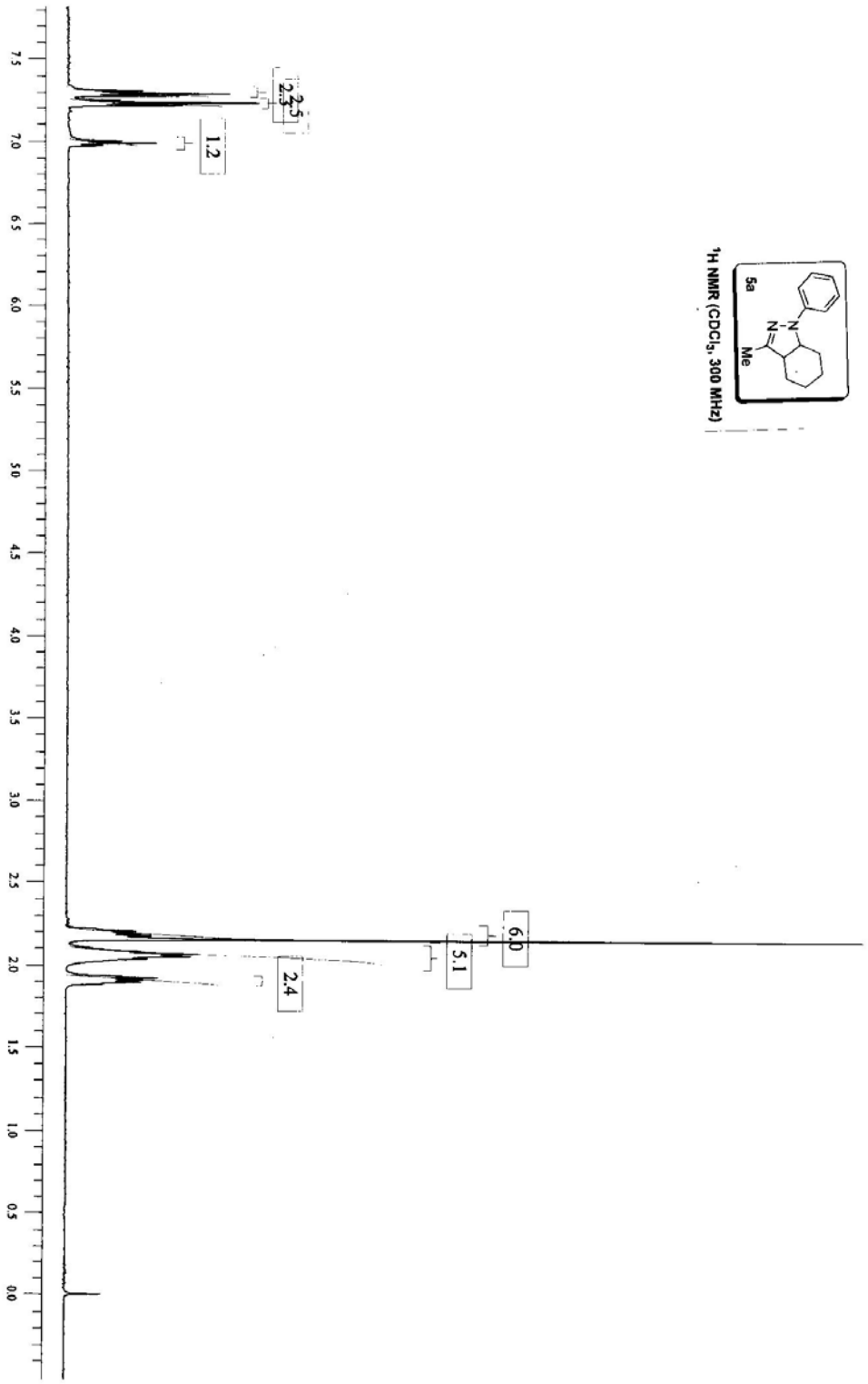

^{13}C NMR (CDCl$_3$, 75 MHz)
3u
Me
CF$_3$
147.994
145.190
141.355
133.013
128.938
127.393
127.181
126.096
118.655
112.712
60.526
47.789
15.744

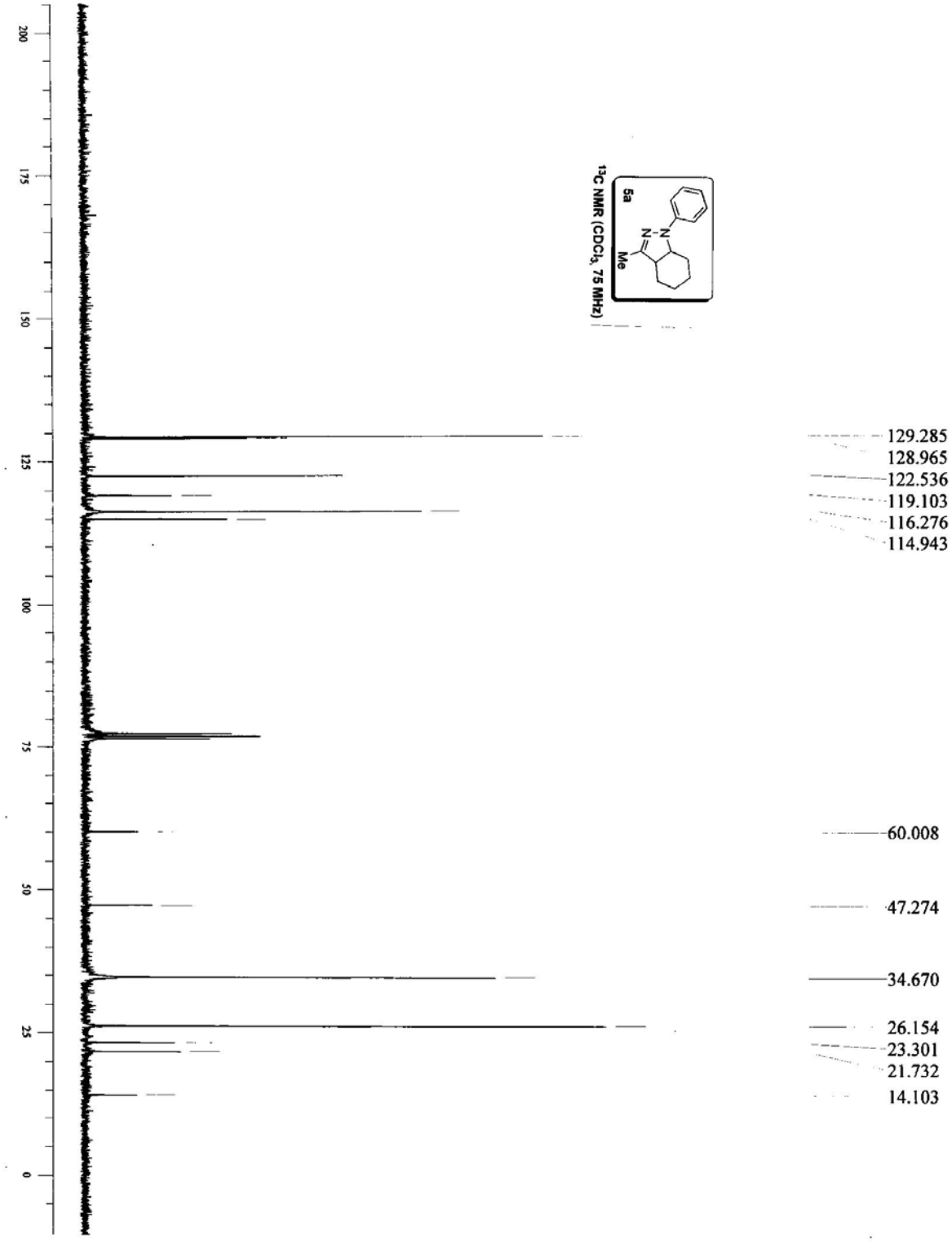

3v
Me
nHex
^{1}H NMR (CDCl$_3$, 300 MHz)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.8
1.0
1.3
2.2
1.0
0.8
1.0
2.0
4.2
10.1

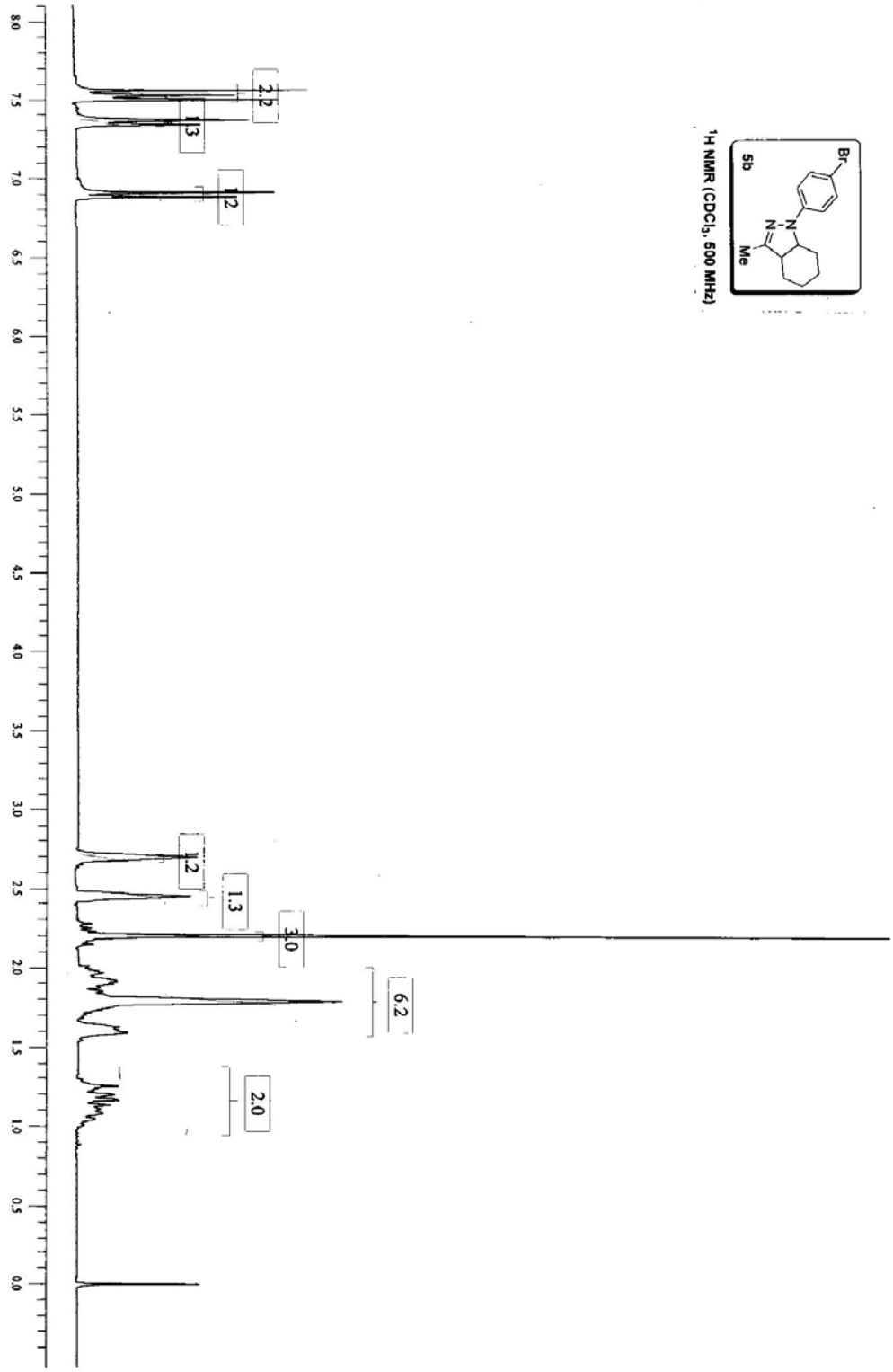

^{13}C NMR (CDCl$_3$, 75 MHz)
3v
Me
nHex
129.045
124.978
121.779
120.993
119.011
113.046
111.014
42.706
32.872
31.881
29.730
25.133
22.603
16.115
14.131
12.414

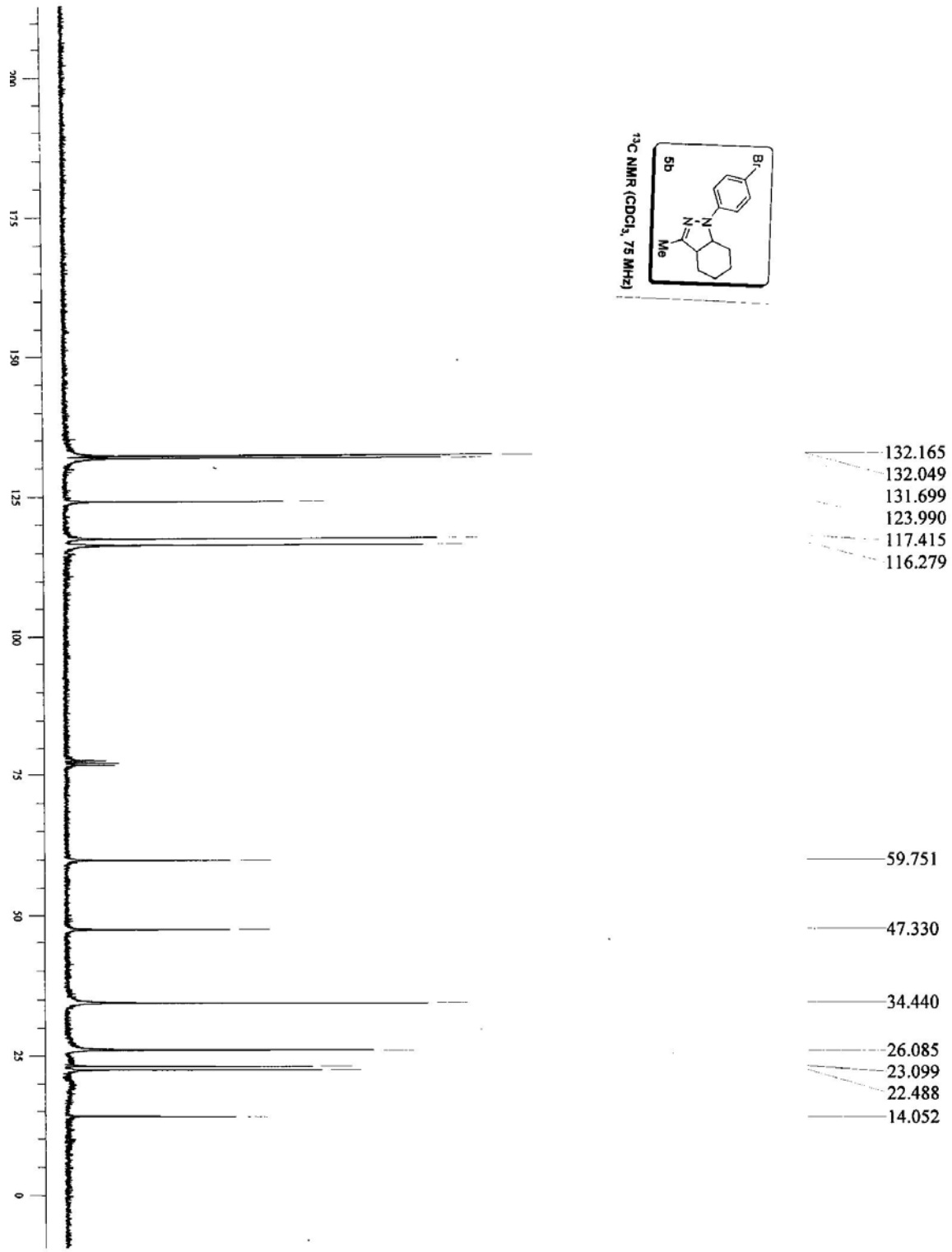

3w
Me
Bn
^{1}H NMR (CDCl$_3$, 300 MHz)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
3.2
5.4
2.3
1.0
1.0
1.0
2.0
0.8
3.3
1.0
0.8

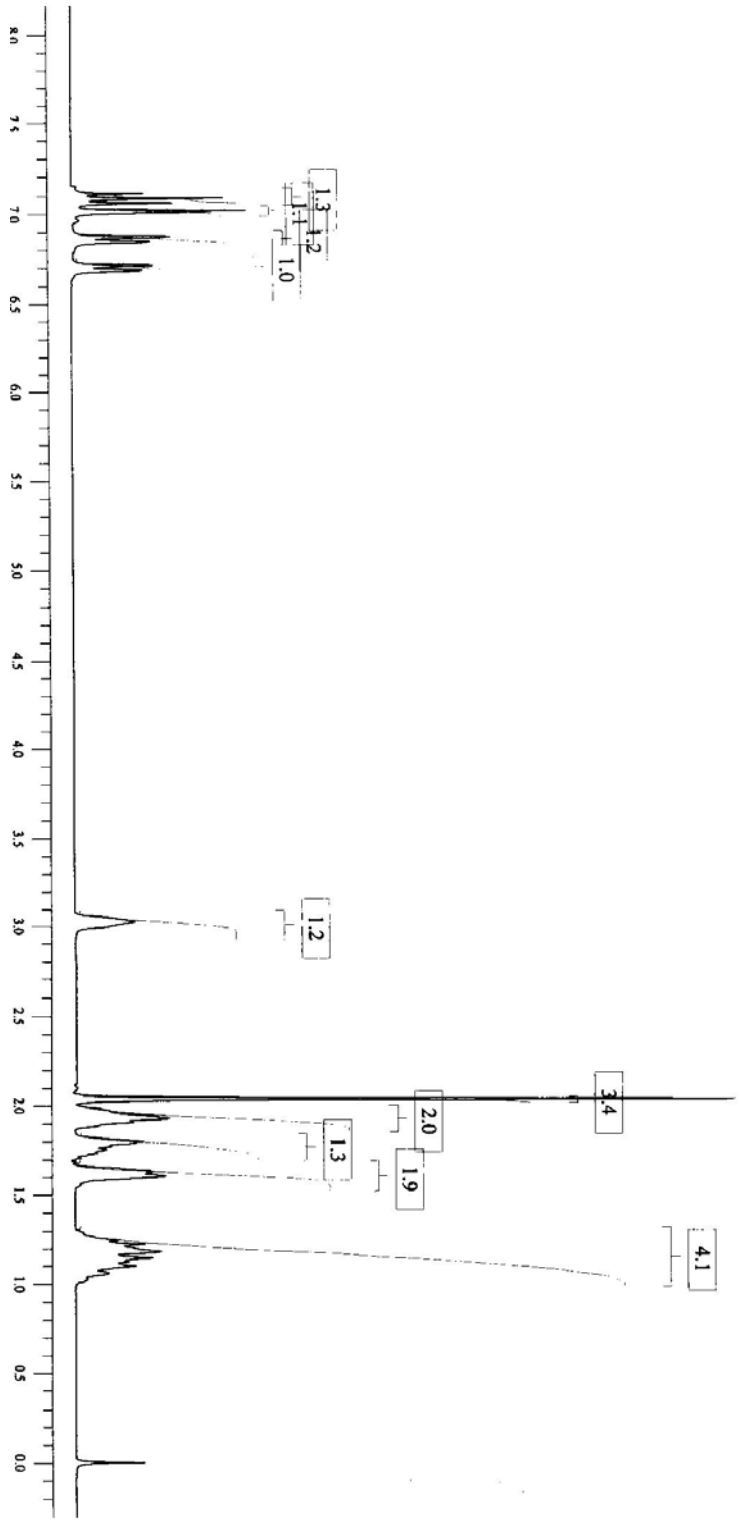

^{13}C NMR (CDCl$_3$, 75 MHz)
3w
Me
Bn
N
N
200
175
150
125
100
75
50
25
0
149.110
145.546
141.098
128.982
128.420
128.292
126.031
118.382
113.084
59.365
42.585
34.260
31.359
16.027


5a
Me
^{1}H NMR (CDCl$_3$, 300 MHz)
2.5
2.3
1.2
6.0
5.1
2.4
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


^{13}C NMR (CDCl$_3$, 75 MHz)
5a
Me
129.285
128.965
122.536
119.103
116.276
114.943
60.008
47.274
34.670
26.154
23.301
21.732
14.103
200
175
150
125
100
75
50
25
0

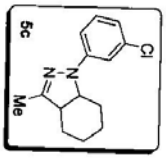

5b
Br
N
N
Me
^{1}H NMR (CDCl$_3$, 500 MHz)
2.2
1.3
1.2
1.2
1.3
3.0
6.2
2.0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

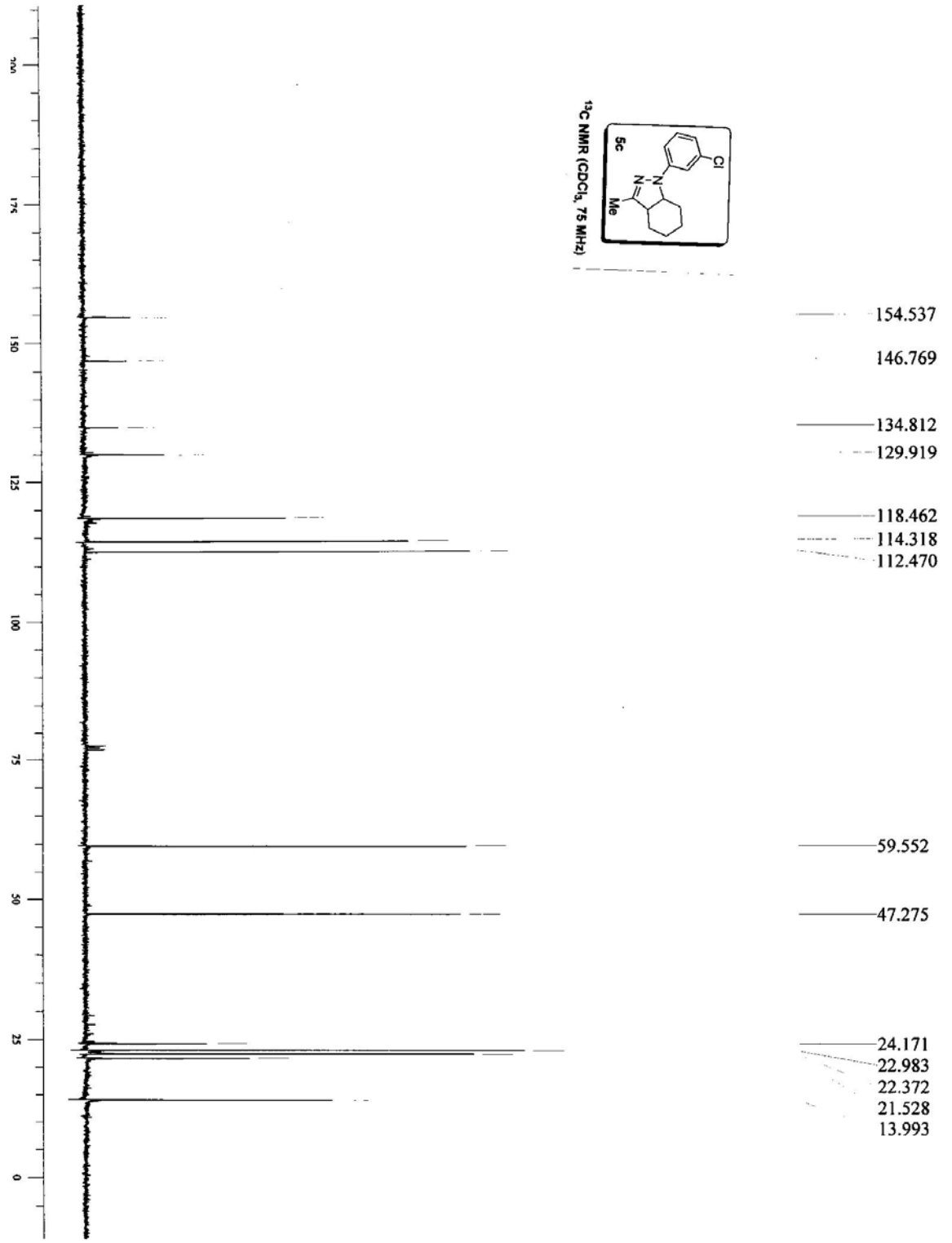

^{13}C NMR (CDCl$_3$, 75 MHz)
5b
Br
Me
N
N
200
175
150
125
100
75
50
25
0
132.165
132.049
131.699
123.990
117.415
116.279
59.751
47.330
34.440
26.085
23.099
22.488
14.052

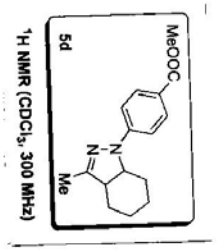


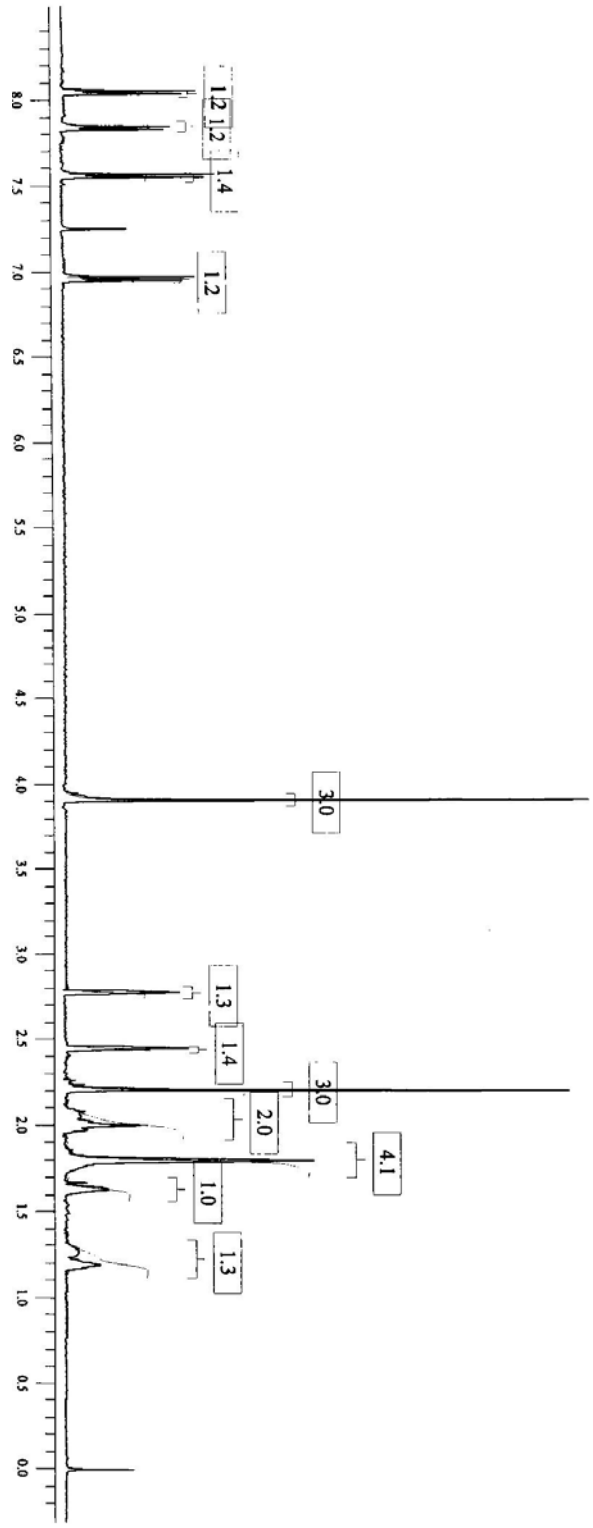
^{1}H NMR ($CDCl_3$, 300 MHz)

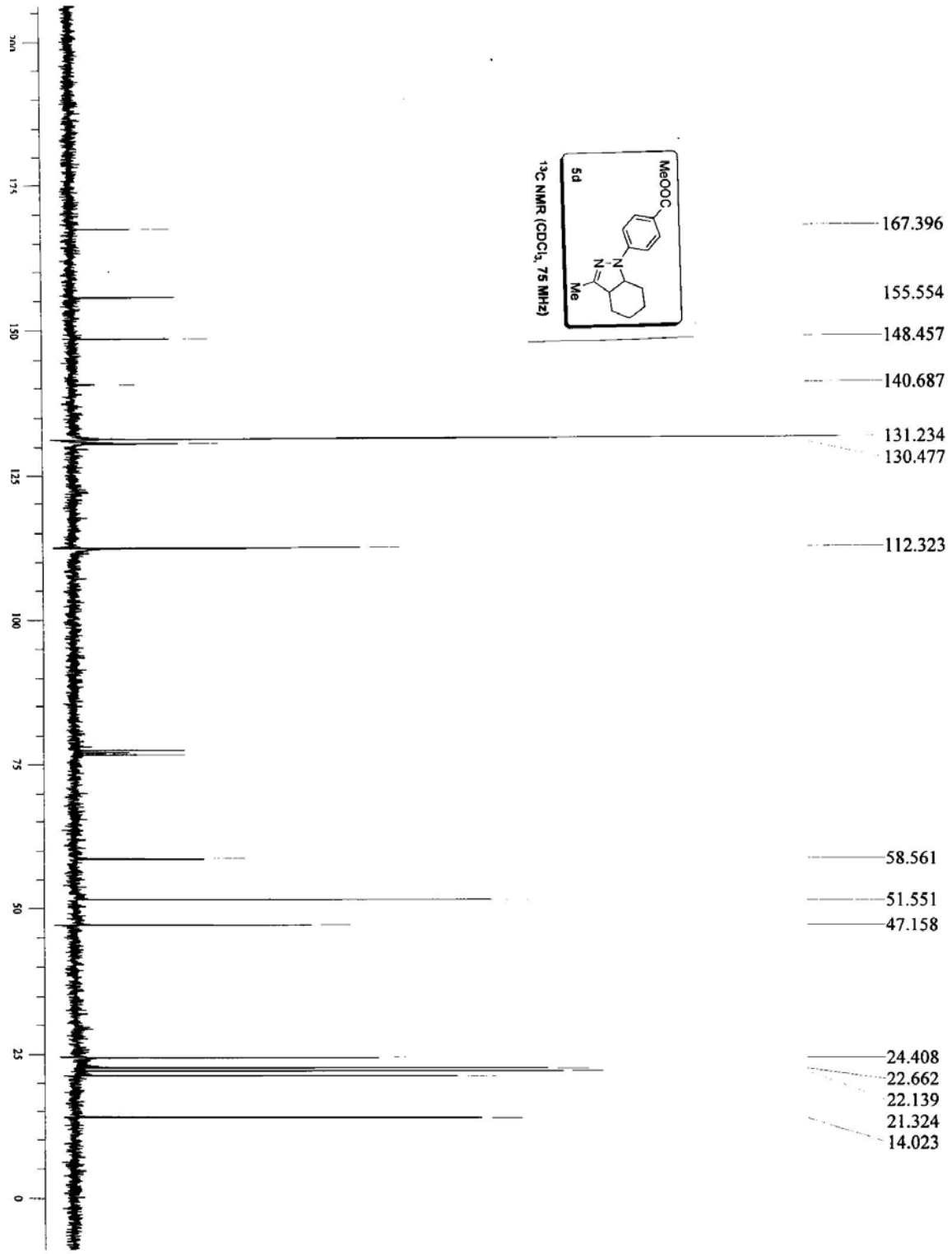
5c

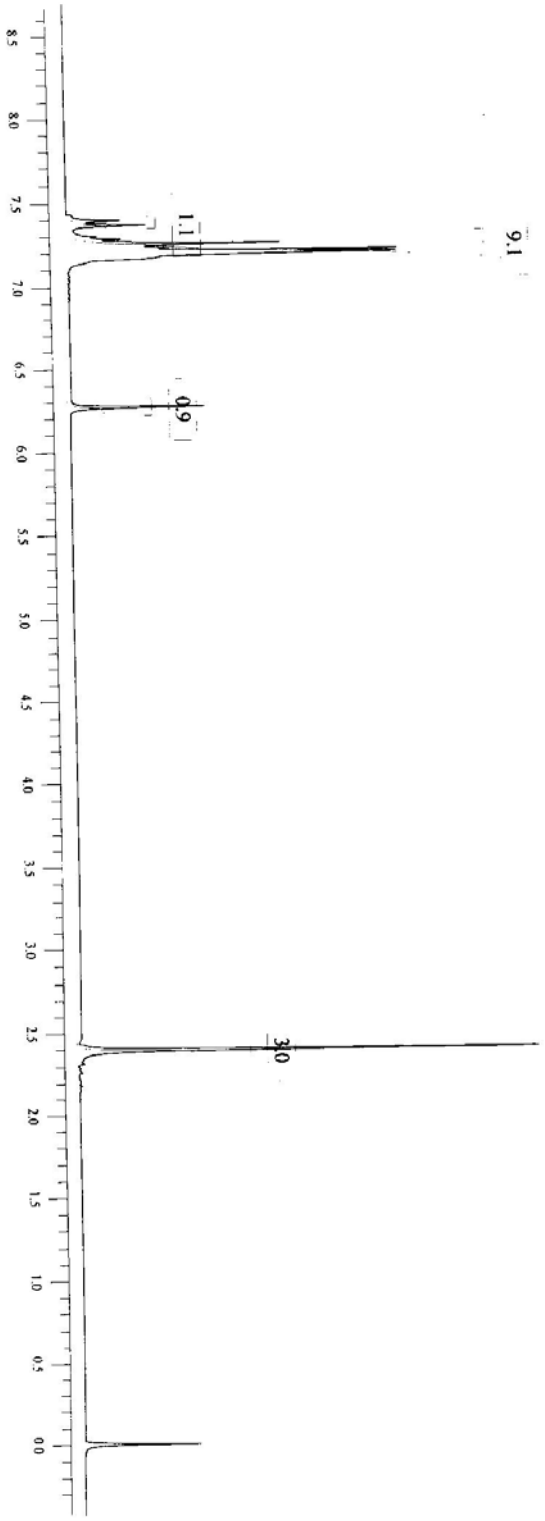


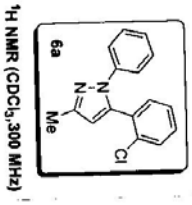

^{13}C NMR (CDCl$_3$, 75 MHz)
5c
Cl
N
N
Me
154.537
146.769
134.812
129.919
118.462
114.318
112.470
59.552
47.275
24.171
22.983
22.372
21.528
13.993
175
150
125
100
75
50
25
0


MeOOC
5d
Me
^{1}H NMR (CDCl$_3$, 300 MHz)

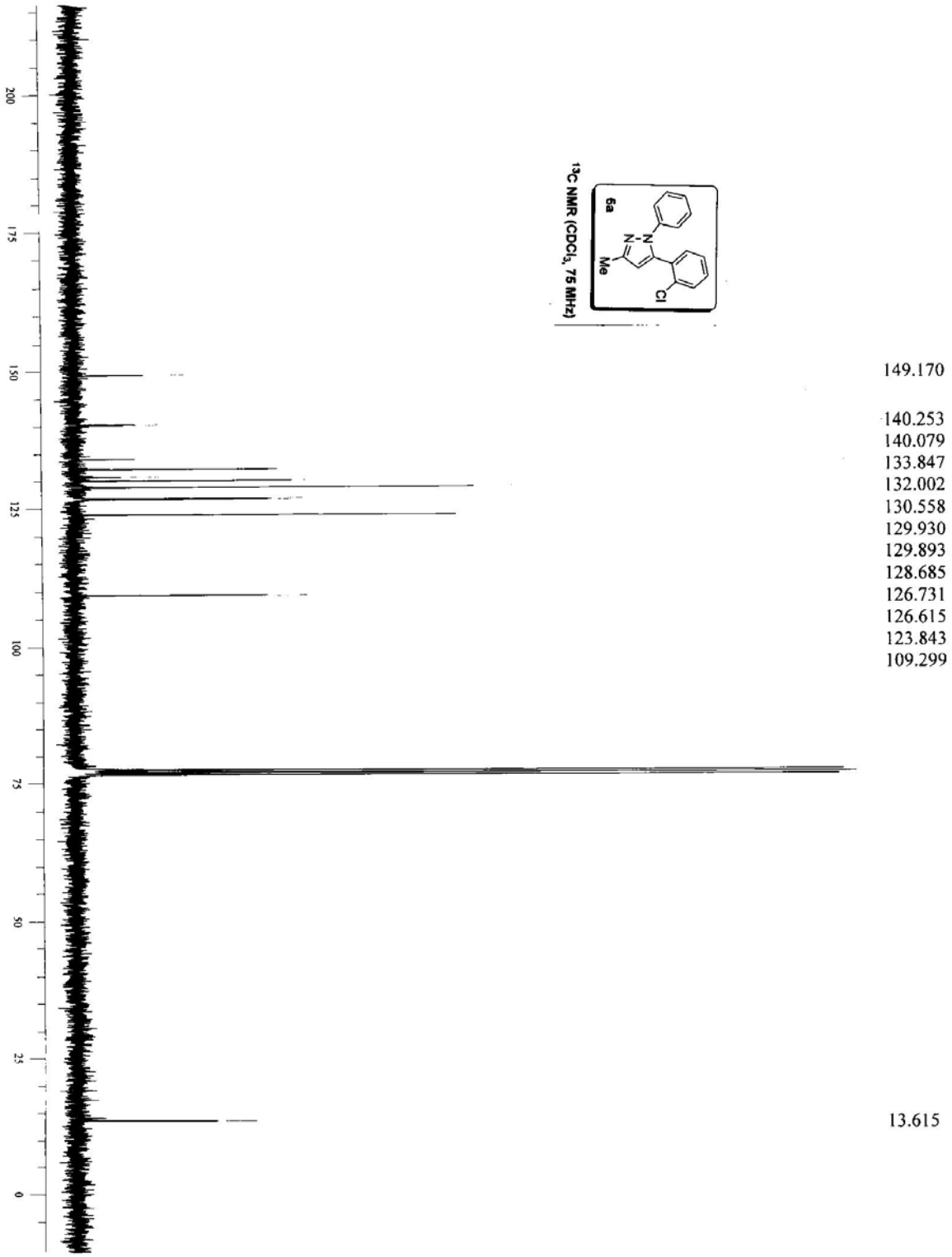

1.2
1.2
1.2
1.4
1.2
3.0
1.3
1.4
3.0
2.0
4.1
1.0
1.3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

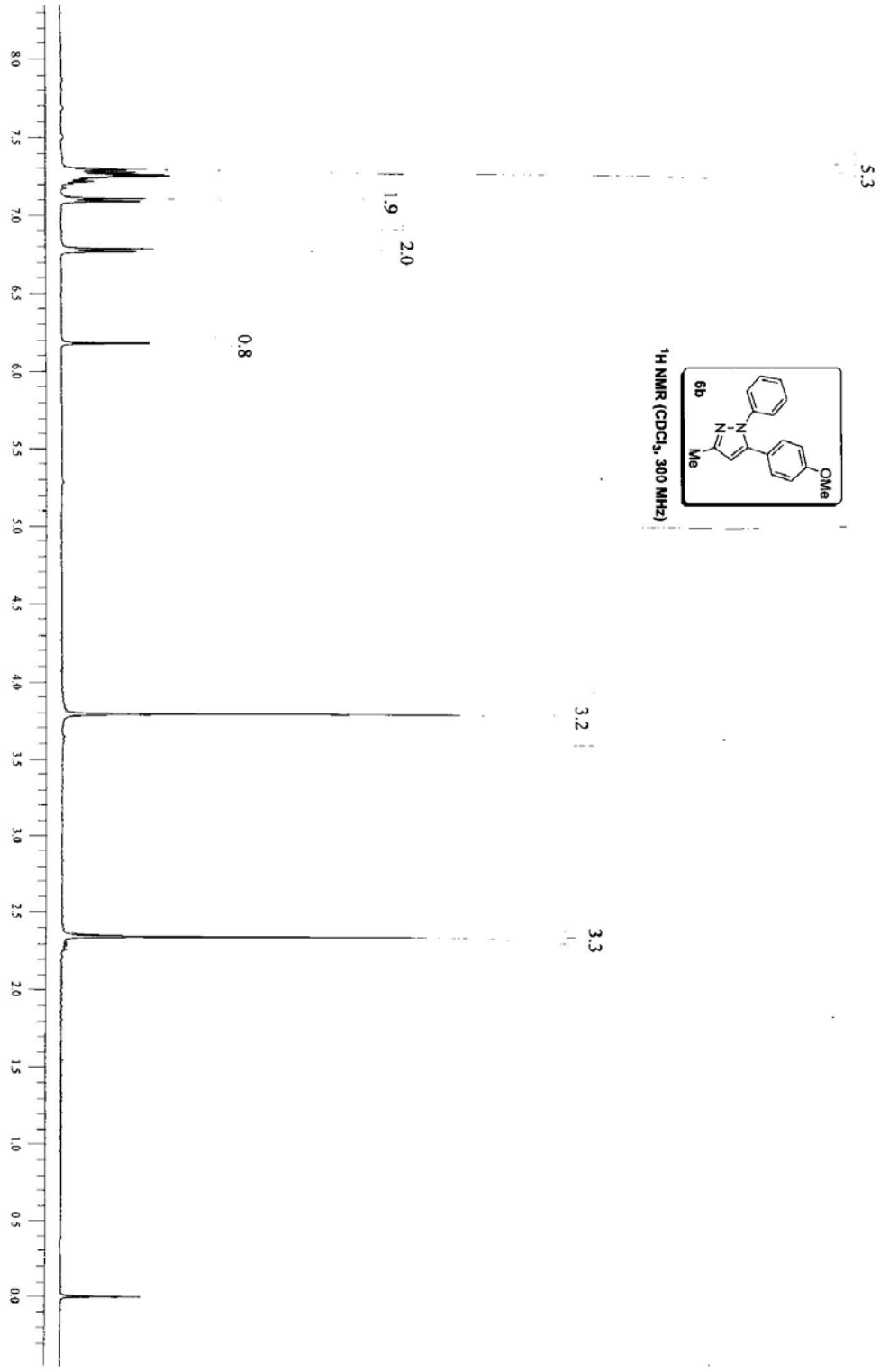

5d
MeOOC
Me
^{13}C NMR (CDCl$_3$, 75 MHz)
167.396
155.554
148.457
140.687
131.234
130.477
112.323
58.561
51.551
47.158
24.408
22.662
22.139
21.324
14.023

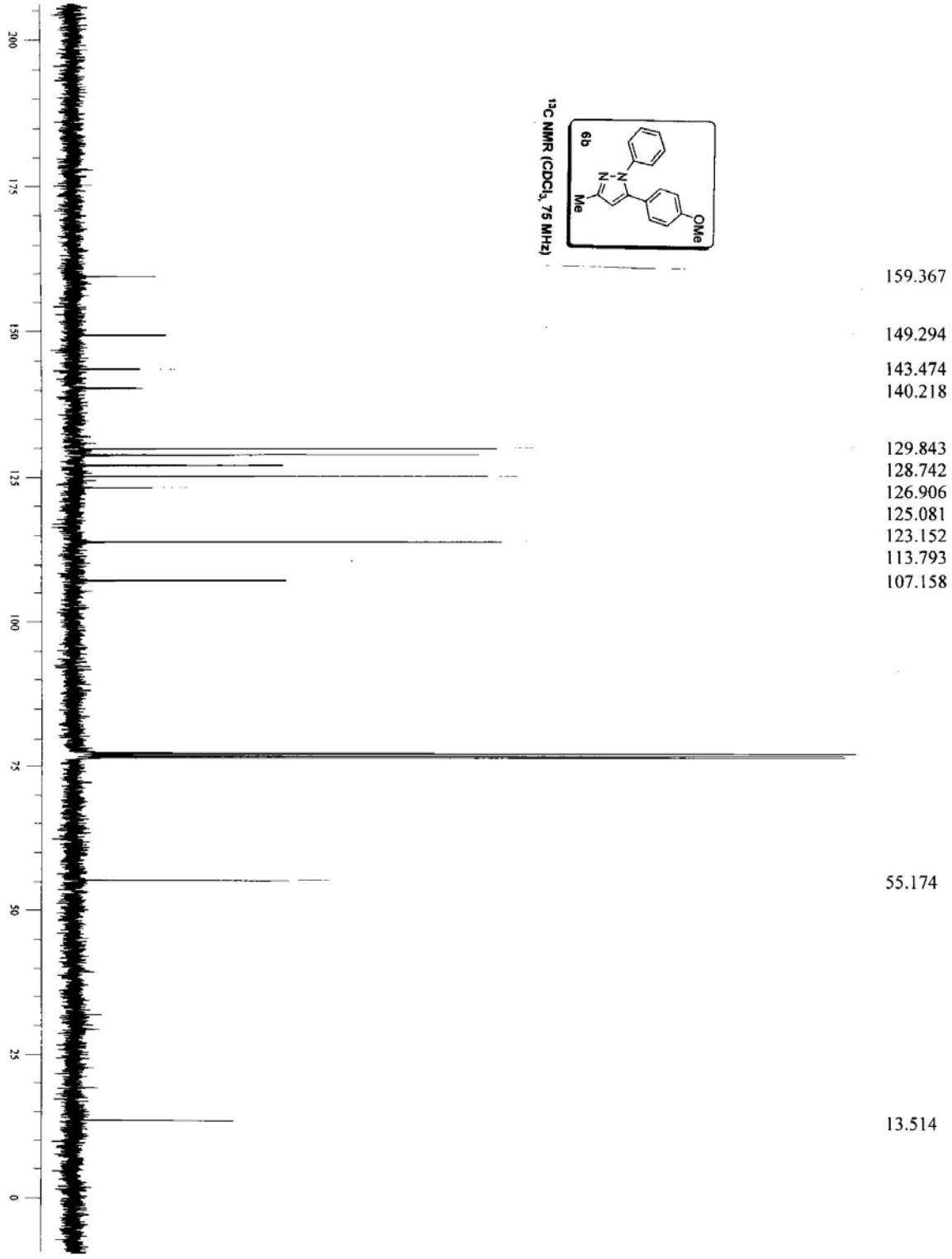




^{1}H NMR ($CDCl_3$,300 MHz)


^{13}C NMR (CDCl$_3$, 75 MHz)
6a
Me
Cl
149.170
140.253
140.079
133.847
132.002
130.558
129.930
129.893
128.685
126.731
126.615
123.843
109.299
13.615


5.3
1.9
2.0
0.8
3.2
3.3
6b
Me
OMe
^{1}H NMR (CDCl$_3$, 300 MHz)


^{13}C NMR (CDCl$_3$, 75 MHz)
6b
Me
OMe
159.367
149.294
143.474
140.218
129.843
128.742
126.906
125.081
123.152
113.793
107.158
55.174
13.514