Supporting Information

Benzyne Click Chemistry:

Synthesis of Benzotriazoles from Benzynes and Azides

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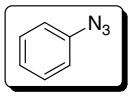
General information

All reactions were carried out in oven-dried glassware and monitored by thin layer chromatography (SiO_2, hexanes or hexanes/EtOAc). THF was distilled over Na. DCM was distilled over CaH_2. Anhydrous MeCN was used as received. Powered CsF and a TBAF solution (1 M in THF) were used as received. Benzyne precursor **2a** is commercially available and was used as received. Other benzyne precursors were prepared according to literature procedures.[1] Azides that are commercially available (**1a**, **1l**, **1r**, **1s**) were used as received. Non-commercial azides were prepared according to the following procedures.

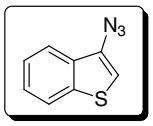
The ^1H and ^{13}C NMR spectra are referenced to the residual signals of $CDCl_3$ (7.24 ppm for ^1H and 77.0 ppm for ^{13}C). Melting points are uncorrected. The high resolution mass spectra were recorded using EI at 70 eV.

Preparation of non-commercial azides

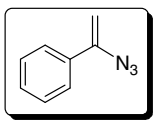
General procedure A (oxidation of the corresponding boronic acid, applied to the preparation of azides **1b**, **1i** and **1q**):[2] to a suspension of $CuSO_4 \cdot 5H_2O$ (10 mol %) and NaN_3 (1.2 equiv) in MeOH (0.3 M) was added the corresponding boronic acid in one portion. The suspension was stirred vigorously in an open flask for 1 day. The MeOH was evaporated and the residue was extracted with hexanes. The combined hexanes were evaporated and the residue was chromatographed (hexanes) to afford the azides.



Phenyl azide (**1b**). General procedure A was applied to 5.0 mmol of phenylboronic acid to afford **1b** in a 22% yield as a colorless oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.34 (t, J = 7.6 Hz, 2 H), 7.13 (t, J = 7.0 Hz, 2 H), 7.00-7.03 (m, 2 H). This compound has been fully characterized previously.[3]

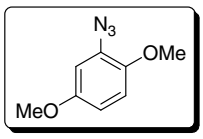


3-Azidobenzo[*b*]thiophene (**1i**). General procedure A was applied to 4.0 mmol of benzothiophene-3-boronic acid to afford **1i** in a 66% yield as a yellow solid: mp 50-51 ºC (dec); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.76-7.81 (m, 1 H), 7.69-7.73 (m, 1 H), 7.36-7.40 (m, 2 H), 6.96 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.8, 132.7, 131.9, 125.4, 124.4, 122.9, 121.0, 109.7.



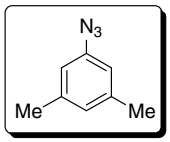
1-Azido-1-phenylethylene (**1q**). General procedure A was applied to 4.0 mmol of 1-phenylvinylboronic acid to afford **1q** in a 40% yield as a yellow oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.54-7.57 (m, 2 H), 7.33-7.37 (m, 3 H), 5.42 (d, J = 2.4 Hz, 1 H), 4.95 (d, J = 2.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.0, 134.2, 129.1, 128.4, 125.5, 98.0.

General procedure B (azide displacement of the corresponding aryldiazonium salt, applied to the preparation of azides **1c** through **1h**):[3,4] to a solution of the corresponding aromatic amine in MeCN (0.5 M) at 0 ºC was added *tert*-butyl nitrite (1.5 equiv), followed by TMS azide (1.2 equiv) dropwise. The flask was taken out of the cold bath and stirred at room temperature for 2 h before the solvent was evaporated and the residue was chromatographed (hexanes or hexanes/DCM) to afford the azides.

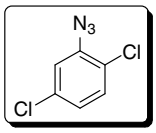


2-Azido-1,4-dimethoxybenzene (**1c**). General procedure B was applied to 2.0 mmol of 2,5-dimethoxyaniline to afford **1c** in a 60% yield as a yellow oil: ^1H

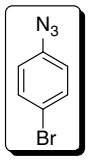
NMR ($CDCl_3$, 300 MHz) δ 6.80 (d, *J* = 8.8 Hz, 1 H), 6.56-6.62 (m, 2 H), 3.81 (s, 3 H), 3.74 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.1, 146.1, 129.0, 113.2, 110.0, 106.6, 56.6, 55.7.



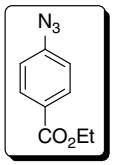
1-Azido-3,5-dimethylbenzene (**1d**). General procedure B was applied to 2.0 mmol of 3,5-dimethylaniline to afford **1d** in a 90% yield as a yellow oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 6.76 (s, 1 H), 6.64 (s, 2 H), 2.29 (s, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.62, 139.57, 126.7, 116.7, 21.2.



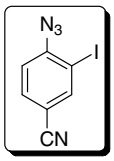
2-Azido-1,4-dichlorobenzene (**1e**). General procedure B was applied to 2.0 mmol of 2,5-dichloroaniline to afford **1e** in an 81% yield as a yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.28 (d, *J* = 8.6 Hz, 1 H), 7.14 (d, *J* = 2.4 Hz, 1 H), 7.04 (dd, *J* = 8.6, 2.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.3, 133.4, 131.4, 125.7, 123.4, 119.7.



1-Azido-4-bromobenzene (**1f**). General procedure B was applied to 2.0 mmol of 4-bromoaniline to afford **1f** in a 91% yield as a yellow oil: ^1H NMR ($CDCl_3$, 400 MHz) δ 7.42-7.45 (m, 2 H), 6.86-6.89 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.1, 132.7, 120.6, 117.7.

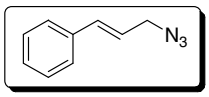


Ethyl 4-azidobenzoate (**1g**). General procedure B was applied to 2.0 mmol of ethyl 4-aminobenzoate to afford **1g** in a 100% yield as a yellow oil: ^1H NMR ($CDCl_3$, 400 MHz) δ 8.00-8.03 (m, 2 H), 7.03-7.05 (m, 2 H), 4.35 (q, *J* = 7.1 Hz, 1 H), 1.37 (t, *J* = 7.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.8, 144.5, 131.3, 127.0, 118.7, 61.0, 14.3.

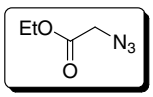


4-Azido-3-iodobenzonitrile (**1h**). General procedure B was applied to 4.0 mmol of 4-amino-3-iodobenzonitrile to afford **1h** in a 91% yield as a slightly yellow-pink solid: mp 126-128 ºC; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.04 (d, *J* = 1.8 Hz, 1 H), 7.65 (dd, *J* = 8.4, 1.8 Hz, 1 H), 7.18 (d, *J* = 8.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.6, 143.3, 133.1, 118.4, 116.8, 109.6, 87.6.

General procedure C (S_N2 displacement of an activated alkyl bromide, applied to the preparation of azides **1k** and **1m**):[5,6] to a solution of the corresponding bromide in water/acetone (1:3, 0.25 M) was added NaN_3 (2.0 equiv) and the mixture was stirred at room temperature for 30 min. The reaction mixture was diluted with DCM and washed with water. The organic layer was dried over $MgSO_4$ and evaporated. The crude material is generally clean enough to be used without further purification.

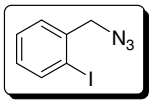


Cinnamyl azide (**1k**). General procedure C was applied to 2.0 mmol of cinnamyl bromide to afford **1k** in a 100% yield as a colorless oil: ^1H NMR ($CDCl_3$, 400 MHz) δ 7.26-7.42 (m, 5 H), 6.65 (d, *J* = 15.7 Hz, 1 H), 6.24 (dt, *J* = 15.7, 6.6 Hz, 1 H), 3.94 (d, *J* = 6.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.9, 134.5, 128.6, 128.1, 126.6, 122.3, 53.0.

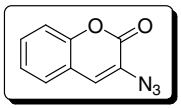


Ethyl 2-azidoacetate (**1m**). General procedure C was applied to 2.0 mmol of ethyl bromoacetate to afford **1m** in a 100% yield as a colorless oil: ^1H NMR ($CDCl_3$, 400 MHz) δ 4.23 (q, *J* = 7.1 Hz, 2 H), 3.83 (s, 2 H), 1.28 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.2, 61.8, 50.3, 14.1.

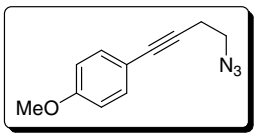
Miscellaneous azides:



1-(Azidomethyl)-2-iodobenzene (**1j**).[7] To a solution of 1-(bromomethyl)-2-iodobenzene (5.0 mmol) in DMF (13 mL) was added NaN_3 (6.2 mmol, 1.24 equiv). The mixture was stirred at 100 ºC overnight before being cooled to room temperature. The reaction mixture was diluted with EtOAc, washed once with saturated aqueous $NaHCO_3$, then twice with water. The organic layer was dried over $MgSO_4$ and evaporated. The crude residue was purified by chromatography (10:1 hexanes/EtOAc) to afford 1.25 g of **1j** (97%) as a colorless oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.86 (d, *J* = 7.8 Hz, 1 H), 7.35-7.37 (m, 2 H), 6.99-7.05 (m, 1 H), 4.44 (s, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.6, 138.0, 129.8, 129.4, 128.5, 98.9, 58.9.



3-Azidocoumarin (**1n**).[8] To a suspension of *N*-acetylglycine (12.5 mmol, 1 equiv) in dry benzene (60 mL) was added Et_3N (31.3 mmol, 2.5 equiv), followed by dropwise addition of benzenesulfonyl chloride (12.5 mmol, 1 equiv). The mixture was stirred at room temperature for 4 h and a yellow suspension was obtained. The resulting suspension was filtered to remove the triethylamine hydrochloride salt. To the filtrate was added salicylaldehyde (12.5 mmol) and the mixture was refluxed for 2.5 h. Solvent was removed and the residue was suspended in hot EtOH (50 mL). The solid was collected via suction filtration, and the mother liquor was cooled to room temperature. More solid was formed and collected, and the mother liquor was further cooled to 0 ºC. More solid was formed and collected. The combined product was dried under a vacuum to afford 1.47 g of yellow solid (3-acetamidocoumarin, 58% crude yield). This material was dissolved in a mixture of EtOH (12 mL) and concentrated HCl (24 mL). After being refluxed for 2 h, it was cooled to room temperature. Ice (~20 g) was added and the reaction mixture was cooled to 0 ºC. While keeping the reaction temperature below 5 ºC, $NaNO_2$ (17.5 mmol, ~2.4 equiv) was added in small portions, followed by a NaN_3 (21.4 mmol, ~ 3 equiv) solution (in 2 mL of water) dropwise. The reaction was stirred at 0-5 ºC for 40 min and then room temperature overnight. The reaction mixture was extracted with EtOAc, washed with $NaHCO_3$, followed by water, dried over $MgSO_4$, and chromatographed (5:1 hexanes/EtOAc) to afford 430 mg of **1n** as an orange solid (32%): mp 112 ºC (dec, lit[9] 117-118 ºC); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.39-7.48 (m, 2 H), 7.24-7.34 (m, 2 H), 7.19 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.4, 151.2, 130.4, 127.2, 126.4, 125.7, 125.1, 119.2, 116.5.

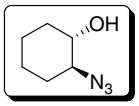


4-Azido-1-(4-methoxyphenyl)-1-butyne (**1o**). A mixture of 4-iodoanisole (4.0 mmol), 3-butyn-1-ol (5.0 mmol, 1.25 equiv), $PdCl_2(PPh_3)_2$ (0.12 mmol, 3 mol %), and CuI (0.12 mmol, 3 mol %) in Et_3N (10 mL) and DMF (2 mL) was stirred at 50 ºC for 2 h and 15 min. The reaction was then diluted with EtOAc and washed with water three times. The organic layer was dried over $MgSO_4$, and chromatographed (1.25:1 hexanes/EtOAc) to afford 680 mg of 4-(4-methoxyphenyl)but-3-yn-1-ol (97%) as a yellow solid: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.31-7.34 (m, 2 H), 6.79-6.82 (m, 2 H), 3.78 (s, 3 H), 3.78 (q, *J* = 6.3 Hz, 2 H), 2.66 (t, *J* = 6.3 Hz, 2 H).

This alcohol (3.86 mmol), together with Et_3N (6.2 mmol, 1.6 equiv) and DMAP (0.19 mmol, 5 mol %), was dissolved in DCM (20 mL). To this solution was added TsCl (5.4 mmol, 1.4 equiv) in portions. The reaction was stirred at room temperature overnight, and poured into saturated aqueous $NaHCO_3$. The layers were separated and the aqueous layer was extracted twice with DCM. The combined organic layers were dried over $MgSO_4$ and chromatographed (4:1 hexanes/EtOAc) to afford 1.21 g of 4-(4-methoxyphenyl)but-3-ynyl tosylate (95%) as a slightly yellow oil: ^{1}H NMR

($CDCl_3$, 300 MHz) δ 7.79-7.81 (m, 2 H), 7.28-7.31 (m, 2 H), 7.23-7.26 (m, 2 H), 6.77-6.80 (m, 2 H), 4.15 (t, *J* = 7.1 Hz, 2 H), 3.78 (s, 3 H), 2.74 (t, *J* = 7.1 Hz, 2 H), 2.41 (s, 3 H).

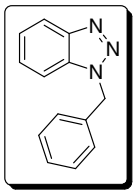
The tosylate (2.0 mmol) was dissolved in DMF (15 mL). To this solution was added NaN_3 (2.3 mmol, 1.15 equiv). The mixture was stirred at 50 ºC for 12 h, diluted with EtOAc, and washed with water three times. The organic layer was dried over $MgSO_4$, and chromatographed (10:1 hexanes/EtOAc) to afford 400 mg of **1o** (100%) as a colorless oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.31-7.35 (m, 2 H), 6.79-6.82 (m, 2 H), 3.77 (s, 3 H), 3.44 (t, *J* = 6.7 Hz, 2 H), 2.68 (t, *J* = 6.7 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.3, 132.9, 115.2, 113.8, 84.2, 82.3, 55.2, 50.0, 20.6.



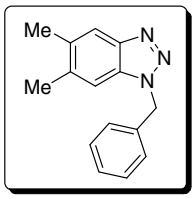
trans-2-Azidocyclohexanol (**1p**).[10] To a solution of cyclohexene oxide (4.0 mmol) in EtOH (10 mL) was added NH_4Cl (8.0 mmol, 2.0 equiv), followed by NaN_3 (8.0 mmol, 2.0 equiv). The mixture was refluxed for 1 d, cooled to room temperature, and poured into saturated aqueous NH_4Cl, then extracted with EtOAc. The combined organic layers were dried over $MgSO_4$ and chromatographed (10:1 hexanes/EtOAc) to afford 400 mg of **1p** (90%) as colorless crystals, which melt readily in hand (mp < 35 ºC): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.31-3.39 (m, 1 H), 3.11-3.20 (m, 1 H), 2.32 (d, *J* = 3.2 Hz, 1 H), 1.96-2.07 (m, 2 H), 1.69-1.76 (m, 2 H), 1.22-1.35 (m, 4 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 73.5, 67.1, 33.0, 29.7, 24.2, 23.8.

Experimental procedure for the [3+2] cycloaddition of azides to benzynes and product characterization

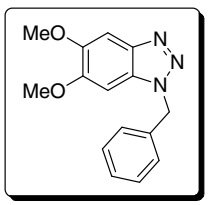
General procedure: to a solution of benzyne precursor (0.35 mmol, 1.17 equiv) and azide (0.30 mmol) in dry MeCN (3 mL) was added CsF (0.60 mmol, 2.0 equiv). The reaction vial was sealed and the reaction mixture stirred at room temperature for 18-24 h before being poured into saturated aqueous $NaHCO_3$. The resulting mixture was extracted with EtOAc or DCM, and the combined organic layers were dried over $MgSO_4$ and evaporated. The residue was purified by silica gel chromatography (hexane/EtOAc).



1-Benzyl-1*H*-benzo[*d*][1,2,3]triazole (**3a**). Slightly yellow solid: mp 114-115 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.05 (dd, *J* = 8.1, 1.1 Hz, 1 H), 7.24-7.40 (m, 8 H), 5.83 (s, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.3, 134.7, 132.7, 128.9, 128.4, 127.5, 127.3, 123.9, 120.0, 109.7, 52.2; LRMS (EI) 209 (26), 180 (62), 152 (9), 91 (100); HRMS (EI) calcd for $C_{13}H_{11}N_3$ 209.0953, found 209.0957.

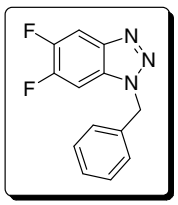


1-Benzyl-5,6-dimethyl-1*H*-benzo[*d*][1,2,3]triazole (**3b**). Slightly yellow solid: mp 158-161 ºC; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.78 (s, 1 H), 7.23-7.32 (m, 5 H), 7.10 (s, 1 H), 5.78 (s, 2 H), 2.37 (s, 3 H), 2.34 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.5, 137.7, 135.0, 133.7, 131.8, 128.9, 128.3, 127.4, 119.0, 109.0, 52.0, 20.9, 20.4; LRMS (EI) 237 (9), 208 (11), 194 (7), 118 (7), 91 (100); HRMS (EI) calcd for $C_{15}H_{15}N_3$ 237.1266, found 237.1270.

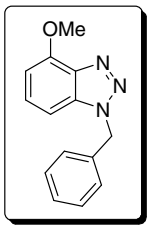


1-Benzyl-5,6-dimethoxy-1*H*-benzo[*d*][1,2,3]triazole (**3c**). Slightly pink solid: mp 130-132 ºC; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.22-7.35 (m, 6 H), 6.56 (s, 1 H), 5.77 (s, 2 H), 3.94 (s, 3 H), 3.83 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.3, 148.5, 140.7, 134.7, 128.9, 128.3, 128.0, 127.4, 98.9, 89.8, 56.2

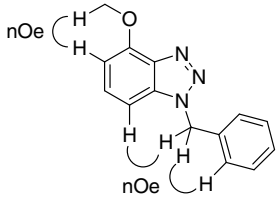
(overlapped signal, two <u>*C*</u>H_3O carbons), 52.1; LRMS (EI) 269 (38), 241 (17), 226 (13), 150 (96), 91 (100); HRMS (EI) calcd for $C_{15}H_{15}N_3O_2$ 269.1164, found 269.1169.

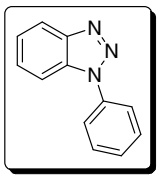


1-Benzyl-5,6-difluoro-1*H*-benzo[*d*][1,2,3]triazole (**3d**). Slightly yellow solid: mp 119-122 ºC; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.80 (dd, *J* = 9.3, 7.1 Hz, 1 H), 7.23-7.26 (m, 2 H), 7.33-7.36 (m, 3 H), 7.05 (dd, *J* = 8.6, 6.6 Hz, 1 H), 5.79 (s, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.8 (dd, *J* = 240, 16 Hz), 149.0 (dd, *J* = 235, 16 Hz) [Note: due to partially overlapped peaks, we are not absolutely certain of the assignment of the overlapped signal. Depending on the assignment, one can identify the two peaks as either 150.8 (dd, *J* = 240, 16 Hz) and 149.0 (dd, *J* = 235, 16 Hz), or 150.7 (dd, *J* = 253, 16 Hz) and 149.0 (dd, *J* = 248, 16 Hz), respectively], 141.5, 141.4, 133.8, 129.2, 128.8, 127.6, 106.5 (dd, *J* = 20, 2 Hz), 97.1 (d, *J* = 24 Hz), 52.7; LRMS (EI) 245 (41), 216 (100), 91 (51); HRMS (EI) calcd for $C_{13}H_9F_2N_3$ 245.0765, found 245.0761.

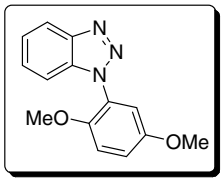


1-Benzyl-4-methoxy-1*H*-benzo[*d*][1,2,3]triazole (**3e**). White solid: mp 92-94 ºC; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.23-7.32 (m, 6 H), 6.89 (d, *J* = 8.3 Hz, 1 H), 6.65 (d, *J* = 7.8 Hz, 1 H), 5.80 (s, 2 H), 4.09 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.7, 138.3, 134.73, 134.70, 128.9, 128.6, 128.3, 127.5, 103.2, 101.8, 56.2, 52.2; LRMS (EI) 239 (27), 210 (21), 195 (19), 180 (51), 167 (100), 139 (17), 91 (17); HRMS (EI) calcd for $C_{14}H_{13}N_3O$ 239.1059, found 239.1061. The position of the methoxy group was assigned by a 2-D NOESY experiment. The C<u>*H*</u>$_2$ protons show two cross-peaks with two aromatic protons, which can only be explained by placing the methoxy group in the position 4.

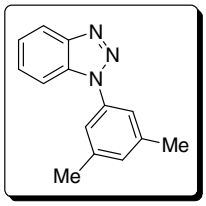




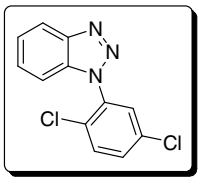
1-Phenyl-1*H*-benzo[*d*][1,2,3]triazole (**3f**). Pale gray solid: mp 86-87 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.13 (d, *J* = 8.2 Hz, 1 H), 7.77 (d, *J* = 8.0 Hz., 2 H), 7.73 (d, *J* = 8.6 Hz, 1 H), 7.59 (t, *J* = 7.5 Hz, 2 H), 7.46-7.54 (m, 2 H), 7.41 (t, *J* = 8.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.4, 136.9, 132.2, 129.8, 128.6, 128.2, 124.3, 122.8, 122.3, 110.3; LRMS (EI) 195 (31), 167 (100), 138 (18); HRMS (EI) calcd for $C_{12}H_9N_3$ 195.0797, found 195.0800.



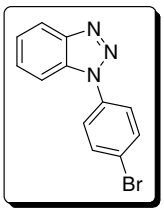
1-(2,5-Dimethoxyphenyl)-1*H*-benzo[*d*][1,2,3]triazole (**3g**). White solid: mp 93-95 ºC; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.09-8.12 (m, 1 H), 7.35-7.49 (m, 3 H), 7.06-7.09 (m, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.7, 147.6, 145.6, 133.9, 127.6, 125.6, 123.9, 119.8, 116.4, 113.6, 113.2, 111.3, 56.4, 56.0; LRMS (EI) 255 (60), 211 (100), 193 (56), 179 (44), 169 (53); HRMS (EI) calcd for $C_{14}H_{13}N_3O_2$ 255.1008, found 255.1011.



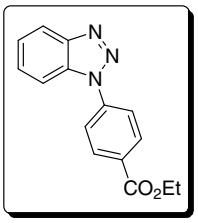
1-(3,5-Dimethylphenyl)-1*H*-benzo[*d*][1,2,3]triazole (**3h**). Slightly yellow oil that solidified upon standing: mp 60-62 ºC; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.11 (d, *J* = 8.3 Hz, 1 H), 7.72 (d, *J* = 8.3 Hz, 1 H), 7.51 (t, *J* = 7.7 Hz, 1 H), 7.40 (t, *J* = 7.8 Hz, 1 H), 7.36 (s, 2 H), 7.11 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.4, 139.7, 136.7, 132.3, 130.3, 128.0, 124.2, 120.6, 120.2, 110.5, 21.3; LRMS (EI) 223 (55), 193 (94), 179 (100); HRMS (EI) calcd for $C_{14}H_{13}N_3$ 223.1110, found 223.1114.



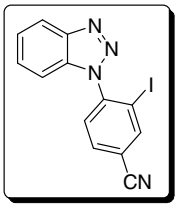
1-(2,5-Dichlorophenyl)-1*H*-benzo[*d*][1,2,3]triazole (**3i**). Slightly orange solid: mp 98-100 ºC; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.15 (d, *J* = 8.3 Hz, 1 H), 7.36-7.61 (m, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.6, 134.9, 133.6, 133.4, 131.7, 131.2, 129.3, 129.2, 128.4, 124.5, 120.3, 110.4; LRMS (EI) 263 (40), 234 (43), 199 (100), 163 (18); HRMS (EI) calcd for $C_{12}H_{17}Cl_2N_3$ 263.0017, found 263.0022.



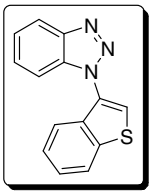
1-(4-Bromophenyl)-1*H*-benzo[*d*][1,2,3]triazole (**3j**). White solid: mp 154-156 ºC; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.14 (d, *J* = 8.3 Hz, 1 H), 7.66-7.75 (m, 5 H), 7.56 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 1 H), 7.44 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.6, 136.0, 133.0, 132.0, 128.5, 124.6, 124.2, 122.3, 120.5, 110.1; LRMS (EI) 272 (6), 166 (100), 138 (20); HRMS (EI) calcd for $C_{12}H_8BrN_3$ 272.9902, found 272.9907.



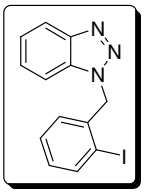
Ethyl 4-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)benzoate (**3k**). White solid: mp 87-88 ºC; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.26-8.29 (m, 2 H), 8.15 (d, *J* = 8.3 Hz, 1 H), 7.89-7.92 (m, 2 H), 7.79 (d, *J* = 8.5 Hz, 1 H), 7.58 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1 H), 7.45 (t, *J* = 8.0 Hz, 1 H), 4.42 (q, *J* = 7.1 Hz, 2 H), 1.42 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.5, 146.7, 140.4, 131.9, 131.3, 130.3, 128.7, 124.7, 121.9, 120.6, 110.3, 61.4, 14.3; LRMS (EI) 267 (16), 211 (44), 180 (32), 166 (100), 140 (17); HRMS (EI) calcd for $C_{15}H_{13}N_3O_2$ 267.1008, found 267.0999.



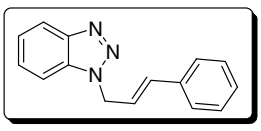
4-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)-3-iodobenzonitrile (**3l**). Yellow to pink solid: mp 152-154 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.37 (d, *J* = 1.6 Hz, 1 H), 8.17 (d, *J* = 8.4 Hz, 1 H), 7.87 (dd, *J* = 8.1, 1.8 Hz, 1 H), 7.54-7.58 (m, 2 H), 7.45-7.49 (ddd, *J* = 7.9, 7.0, 0.9 Hz, 1 H), 7.33 (d, *J* = 8.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.8, 143.8, 143.0, 132.9, 132.8, 129.1, 128.8, 124.7, 120.5, 116.0, 115.5, 110.2, 95.5; LRMS (EI) 346 (10), 191 (100), 164 (23), 149 (12); HRMS (EI) calcd for $C_{13}H_7IN_4$ 345.9715, found 345.9724.



1-(Benzo[*b*]thiophen-3-yl)-1*H*-benzo[*d*][1,2,3]triazole (**3m**). White solid: mp 132-134 ºC; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.18 (dt, *J* = 8.3, 1.0 Hz, 1 H), 7.95 (m, 1 H), 7.76-7.80 (m, 1 H), 7.76 (s, 1 H), 7.40-7.60 (m, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.7, 138.9, 133.44, 133.40, 129.2, 128.3, 125.8, 125.3, 124.5, 123.1, 122.2, 121.0, 120.3, 110.3; LRMS (EI) 251 (23), 222 (100), 194 (42), 180 (43), 121 (36), 88 (39); HRMS (EI) calcd for $C_{14}H_9SN_3$ 251.0517, found 251.0521.

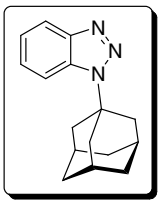


1-(2-Iodobenzyl)-1*H*-benzo[*d*][1,2,3]triazole (**3n**). White solid: mp 97-98 ºC; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.08 (dd, *J* = 8.1, 1.2 Hz, 1 H), 7.89 (dd, *J* = 7.8, 1.0 Hz, 1 H), 7.33-7.45 (m, 3 H), 7.20 (td, *J* = 7.6, 1.2 Hz, 1 H), 6.99 (td, *J* = 7.8, 1.7 Hz, 1 H), 6.76 (dd, *J* = 7.8, 1.8 Hz, 1 H), 5.90 (s, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.1, 139.7, 137.1, 132.9, 130.0, 128.8, 128.4, 127.6, 124.0, 120.1, 109.8, 97.6, 56.6; LRMS (EI) 335 (14), 217 (23), 208 (100), 180 (50), 152 (19), 90 (41); HRMS (EI) calcd for $C_{13}H_{10}IN_3$ 334.9919, found 334.9924.

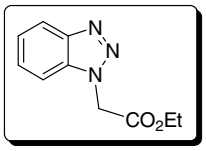


1-Cinnamyl-1*H*-benzo[*d*][1,2,3]triazole (**3o**). White solid: mp 72-73 ºC; R_f 0.40 (2.5:1 hexanes/ EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.07 (dt, *J* = 8.2, 0.9 Hz, 1 H), 7.55 (dt, *J* = 8.2, 0.9 Hz, 1 H), 7.45 (ddd, *J* = 8.0, 7.0, 0.9 Hz, 1 H), 7.24-7.38 (m, 6 H), 6.67 (d, *J* = 15.7 Hz, 1 H), 6.39 (dt, *J* = 15.9, 6.3 Hz, 1 H), 5.44 (dd, *J* = 8.2, 6.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.3, 135.5,

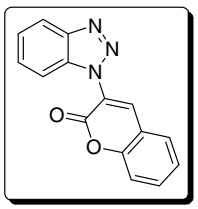
134.4, 132.9, 128.7, 128.4, 127.4, 126.6, 123.9, 122.2, 120.1, 109.7, 50.6; LRMS (EI) 235 (17), 206 (39),130 (20), 115(100), 104 (21), 91 (61); HRMS (EI) calcd for $C_{15}H_{13}N_3$ 235.1109, found 235.1114.



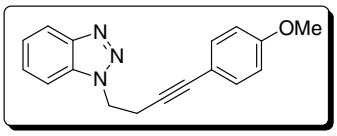
1-Adamantyl-1*H*-benzo[*d*][1,2,3]triazole (**3p**). White solid: mp 149-151 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.05 (d, *J* = 8.4 Hz, 1 H), 7.79 (d, *J* = 8.4 Hz, 1 H), 7.39 (td, *J* = 7.7, 1.1 Hz, 1 H), 7.30 (td, *J* = 7.6, 0.9 Hz, 1 H), 2.50 (d, *J* = 2.8 Hz, 6 H), 2.31 (brs, 3 H), 1.85 (brs, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.0, 131.6, 126.1, 123.2, 120.3, 112.3, 61.5, 42.1, 36.1, 29.6; LRMS (EI) 253 (100), 224 (48), 182 (22), 168 (20), 146 (32), 135 (49), 93 (34), 91 (39), 79 (41), 77 (41); HRMS (EI) calcd for $C_{16}H_{19}N_3$ 253.1579, found 253.1570.



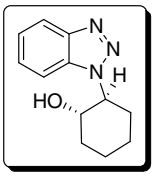
Ethyl 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)acetate (**3q**). Slightly yellow solid: mp 76-78 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.07 (d, *J* = 8.5 Hz, 1 H), 7.44-7.52 (m, 2 H), 7.38 (ddd, *J* = 8.1, 6.8, 1.1 Hz, 1 H), 5.40 (s, 2 H), 4.24 (q, *J* = 7.1 Hz, 2 H), 1.25 (t, *J* = 7.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.3, 146.0, 133.3, 127.9, 124.1, 120.2, 109.2, 62.3, 49.1, 14.1; LRMS (EI) 205 (24), 132 (32), 104 (45), 77 (100); HRMS (EI) calcd for $C_{10}H_{11}N_3O_2$ 205.0851, found 205.0856.



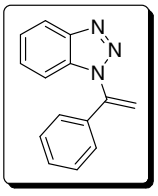
3-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)coumarin (**3r**). Slightly yellow solid: mp 197-199 ºC; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.12 (d, *J* = 8.5 Hz, 1 H), 7.39-7.70 (m, 8 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.2, 153.3, 146.3, 138.4, 133.1, 132.9, 128.9, 128.5, 125.5, 124.6, 123.8, 120.1, 118.2, 116.9, 112.1; LRMS (EI) 263 (49), 235 (100), 206 (54), 178 (57), 153 (31), 89(76); HRMS (EI) calcd for $C_{15}H_9N_3O_2$ 263.0695, found 263.0699.



1-(4-(4-Methoxyphenyl)but-3-ynyl-1H-benzo[d][1,2,3]triazole (**3s**). Yellow oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.05 (dt, *J* = 8.3, 1.0 Hz, 1 H), 7.63 (dt, *J* = 8.3, 1.0 Hz, 1 H), 7.46 (ddd, *J* = 8.1, 6.8, 1.0 Hz, 1 H), 7.35 (ddd, *J* = 8.0, 6.8, 1.0 Hz, 1 H), 7.11-7.15 (m, 2 H), 6.74-6.78 (m, 2 H), 4.85 (t, *J* = 6.8 Hz, 2 H), 3.76 (s, 3 H), 3.08 (t, *J* = 6.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.4, 145.9, 133.2, 132.8, 127.3, 123.9, 120.0, 114.8, 113.8, 109.6, 83.6, 83.1, 55.3, 47.0, 21.4; LRMS (EI) 102 (27), 77 (100); HRMS (EI) calcd for $C_{17}H_{15}N_3O$ 277.1215, found 277.1221.



2-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)cyclohexanol (**3t**). White solid: mp 126-128 ºC; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.59-7.63 (m, 1 H), 7.54 (dt, *J* = 8.5, 0.8 Hz, 1 H), 7.38 (ddd, *J* = 7.8, 6.8, 1.0 Hz, 1 H), 7.16 (ddd, *J* = 8.3, 6.8, 1.0 Hz, 1 H), 4.35-4.40 (m, 2 H), 3.74 (s, 1 H), 2.11-2.28 (m, 3 H), 1.88-1.91 (m, 2 H), 1.45-1.58 (m, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.1, 133.5, 126.9, 123.9, 119.1, 109.8, 72.4, 65.3, 34.0, 31.4, 25.1, 24.2; LRMS (EI) 132 (37), 91 (36), 76 (100); HRMS (EI) calcd for $C_{12}H_{15}N_3O$ 217.1215, found 217.1218.



1-(1-Phenylvinyl)-1*H*-benzo[*d*][1,2,3]triazole (**3u**). Slightly orange glass: R_f 0.46 (4:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.09-8.11 (m, 1 H), 7.34-7.42 (m, 5 H), 7.27-7.29 (m, 2 H), 7.03-7.05 (m, 1 H), 5.77 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.1, 142.6, 134.6, 132.9, 129.8, 128.8, 127.8, 126.9, 124.1, 120.1, 111.2, 111.1; LRMS (EI) 221 (39), 193 (100), 191 (98), 165 (56), 103 (59); HRMS (EI) calcd for $C_{14}H_{11}N_3$ 221.0953, found 221.0955.

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2. Tao, C.-Z.; Cui, X.; Li, J.; Liu, A.-X.; Liu L.; Guo, Q.-X. *Tetrahedron Lett.* **2007**, *48*, 3525.
3. Barral, K.; Moorhouse, A. D.; Moses, J. E. *Org. Lett.* **2007**, *9*, 1809.
4. Azide **1b** has also been prepared using this method.
5. Sá, M. M.; Ramos, M. D.; Fernandes, L. *Tetrahedron* **2006**, *62*, 11652.
6. Azide **1j** may also be prepared using this method.
7. Chowdhury, C.; Mandal S. B.; Achari, B. *Tetrahedron Lett.* **2005**, *46*, 8531.
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9. Higuchi, Y.; Ito, K.; Tame, C. *Heterocycles* **1993**, *35*, 937.
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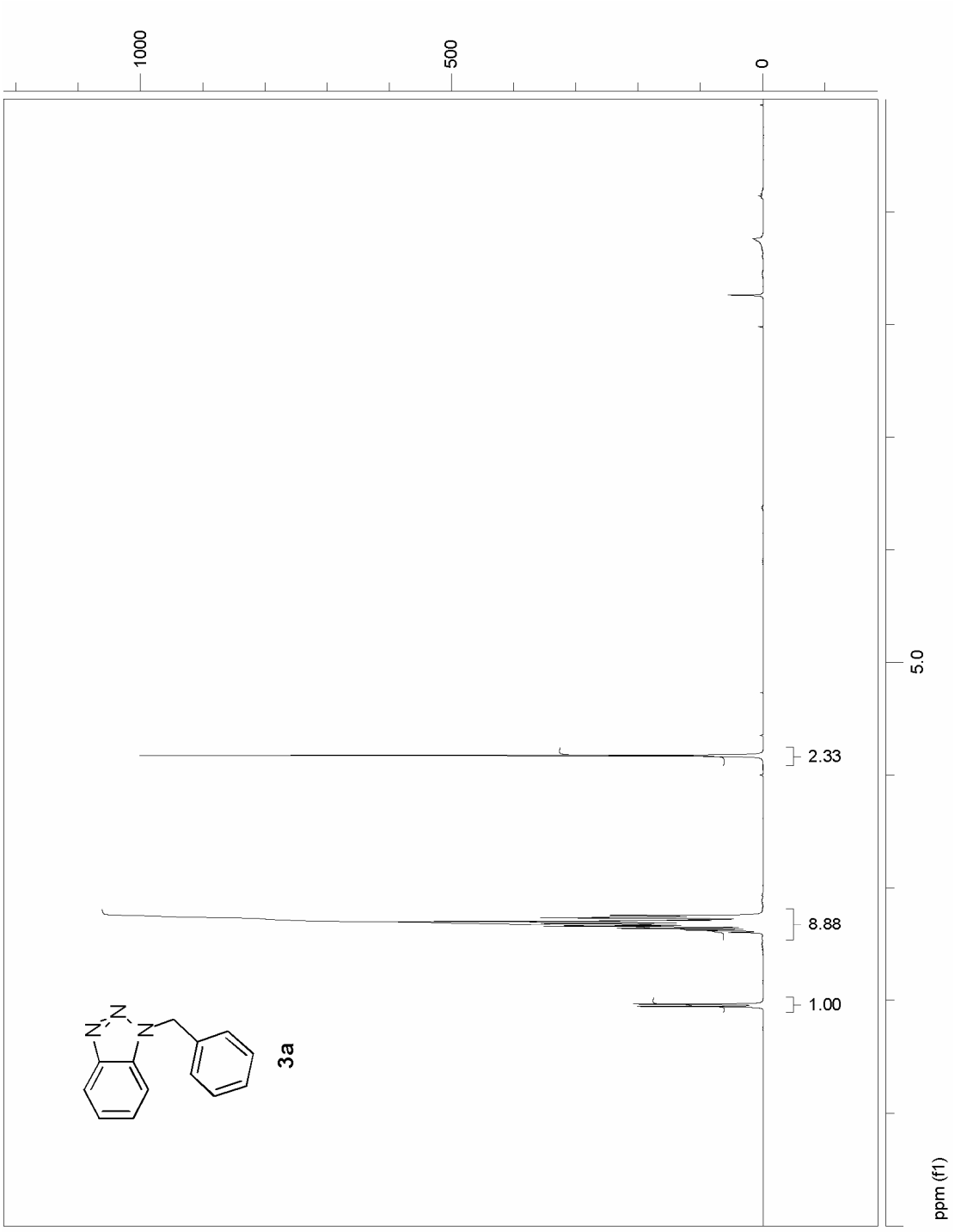
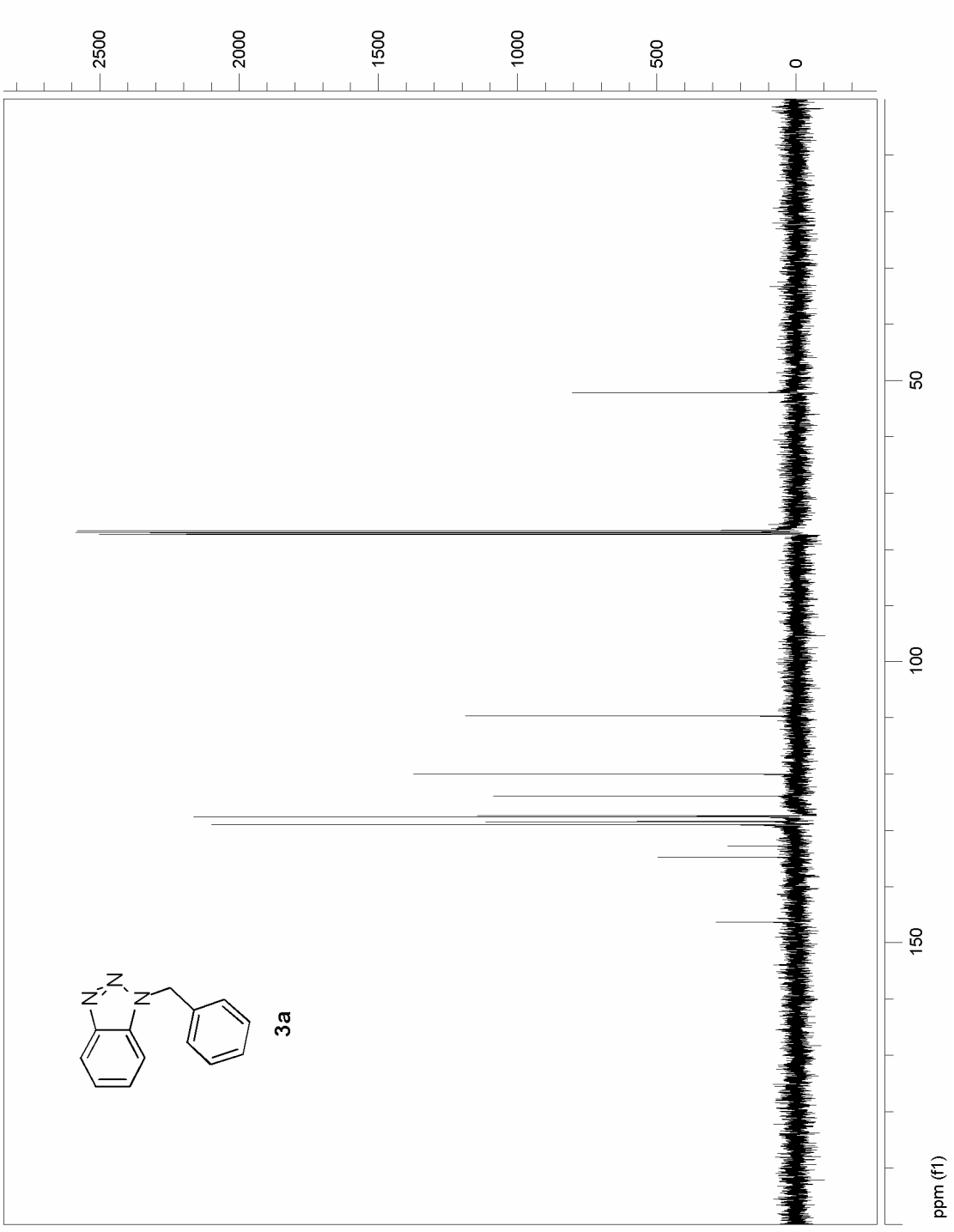
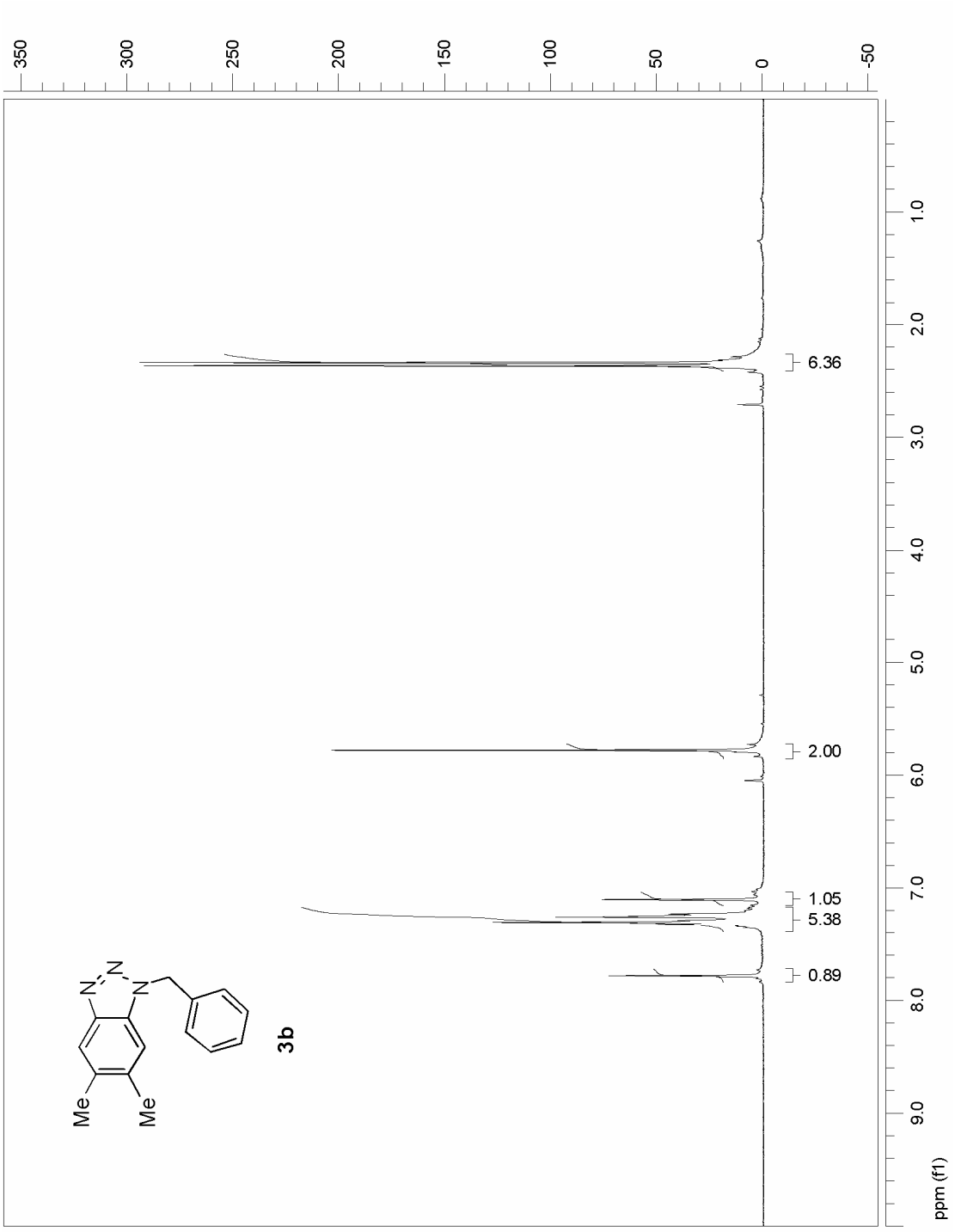
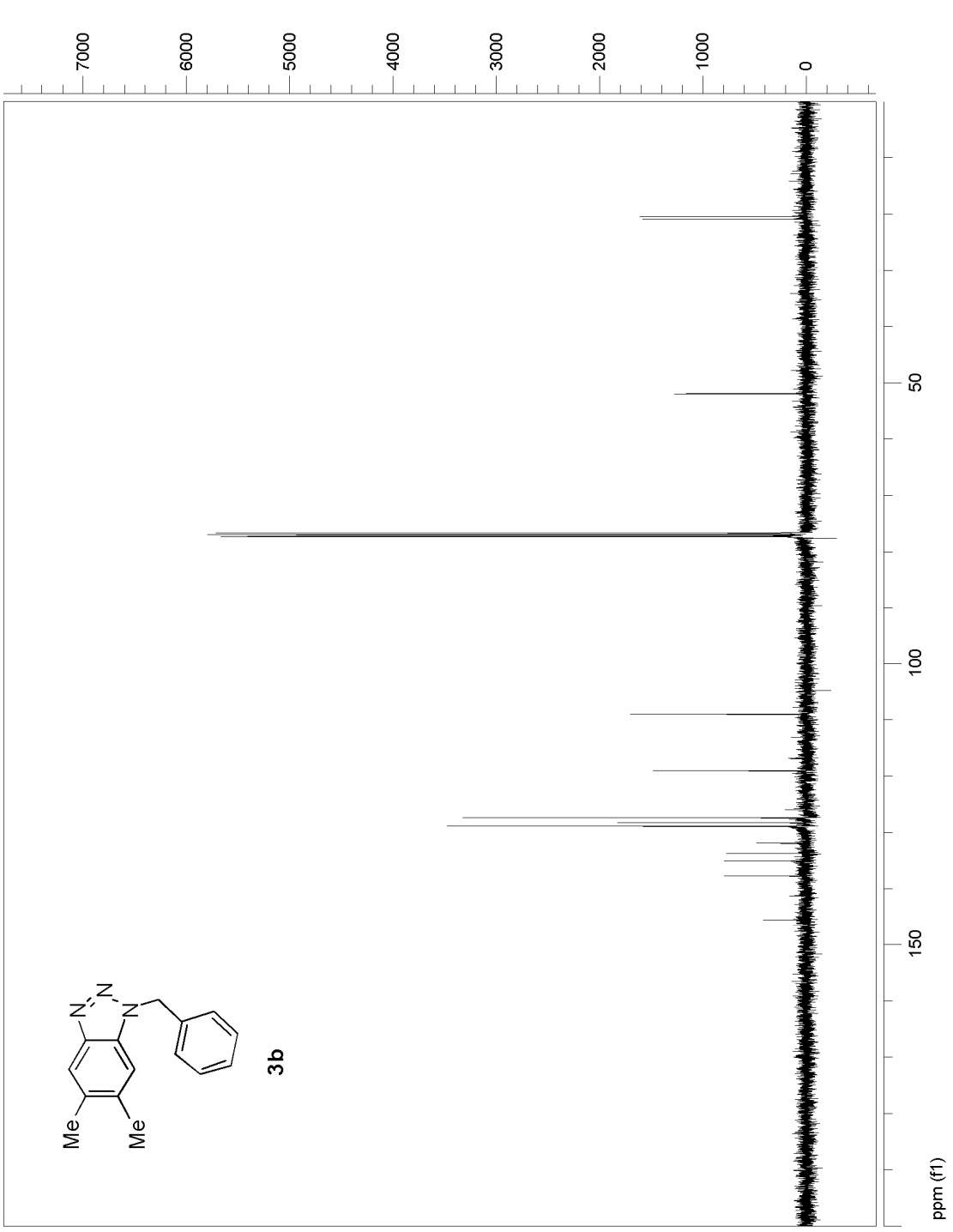
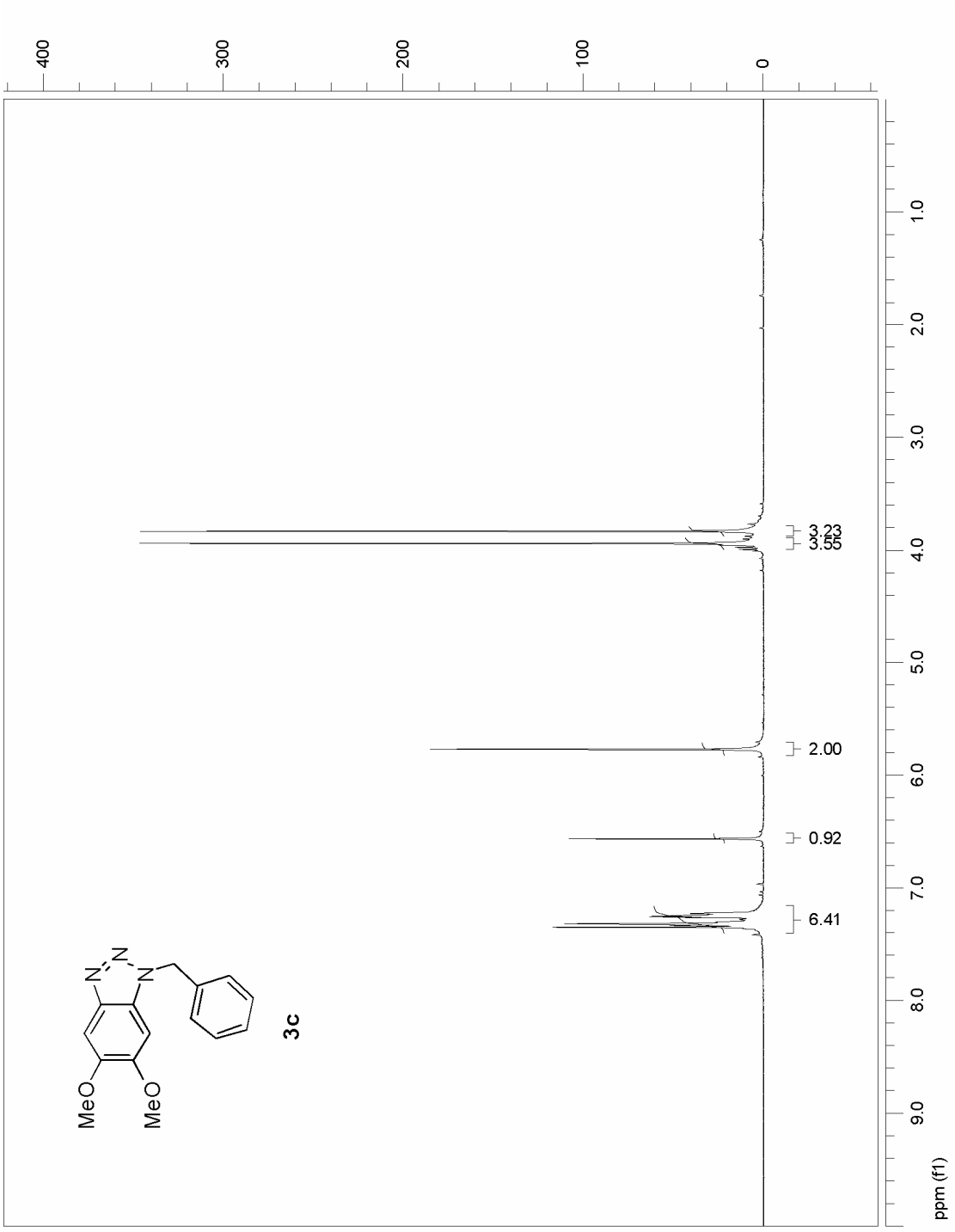
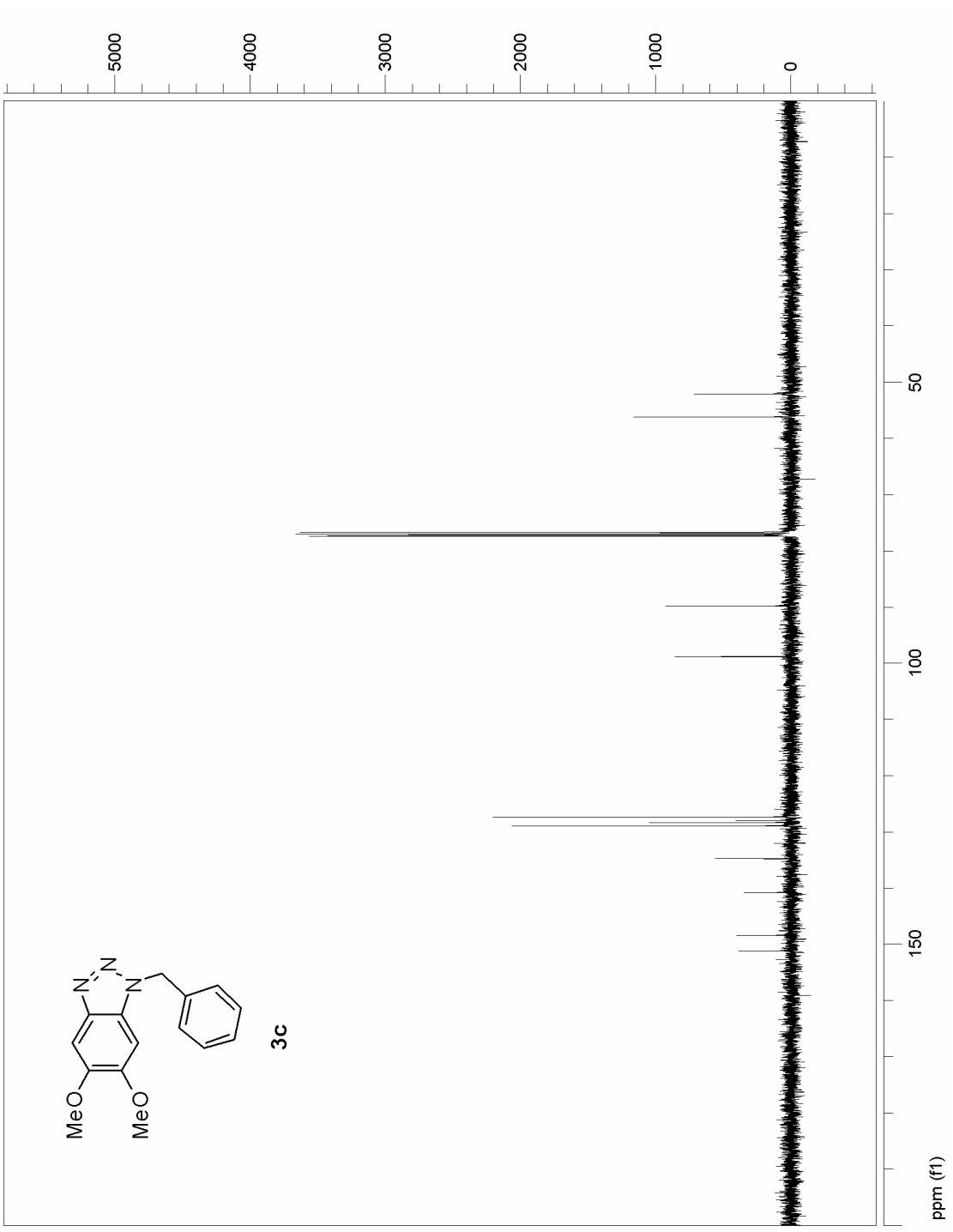

1000
500
0
5.0
2.33
8.88
1.00
3a
ppm (f1)

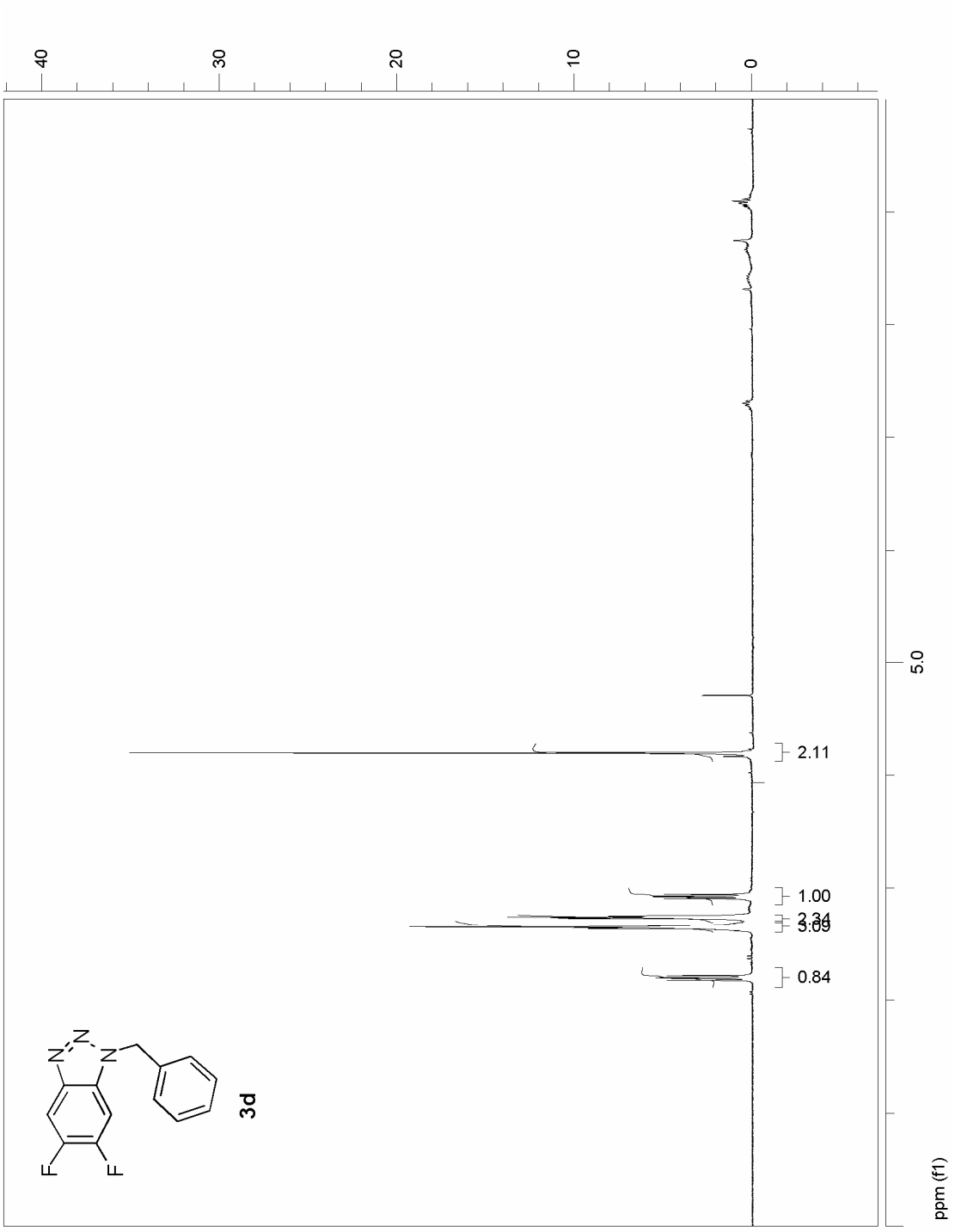

2500
2000
1500
1000
500
0
50
100
150
ppm (f1)
3a

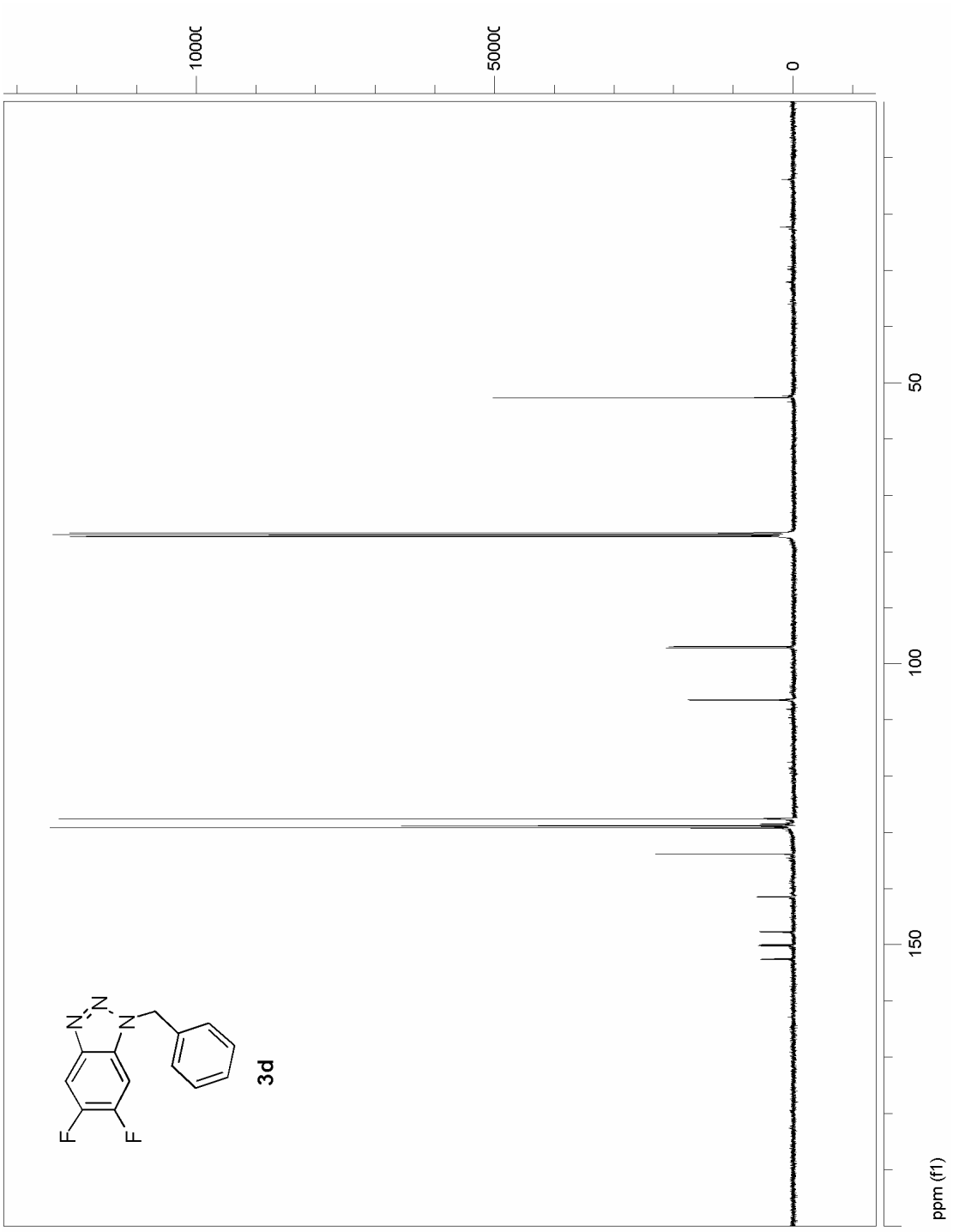

350
300
250
200
150
100
50
0
-50
6.36
2.00
1.05
5.38
0.89
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (f1)
N
N
N
Me
Me
3b

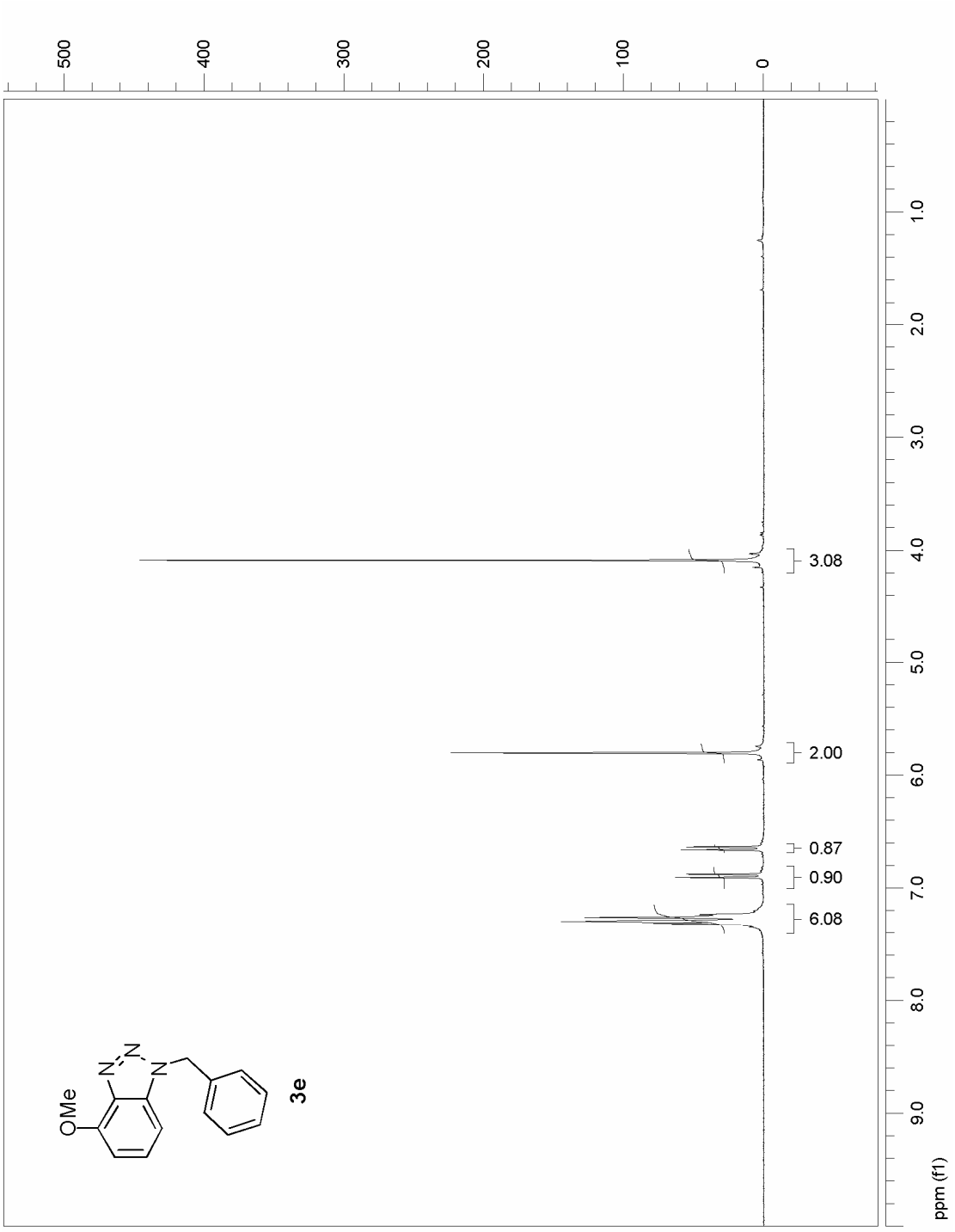

7000
6000
5000
4000
3000
2000
1000
0
50
100
150
ppm (f1)
Me
Me
3b

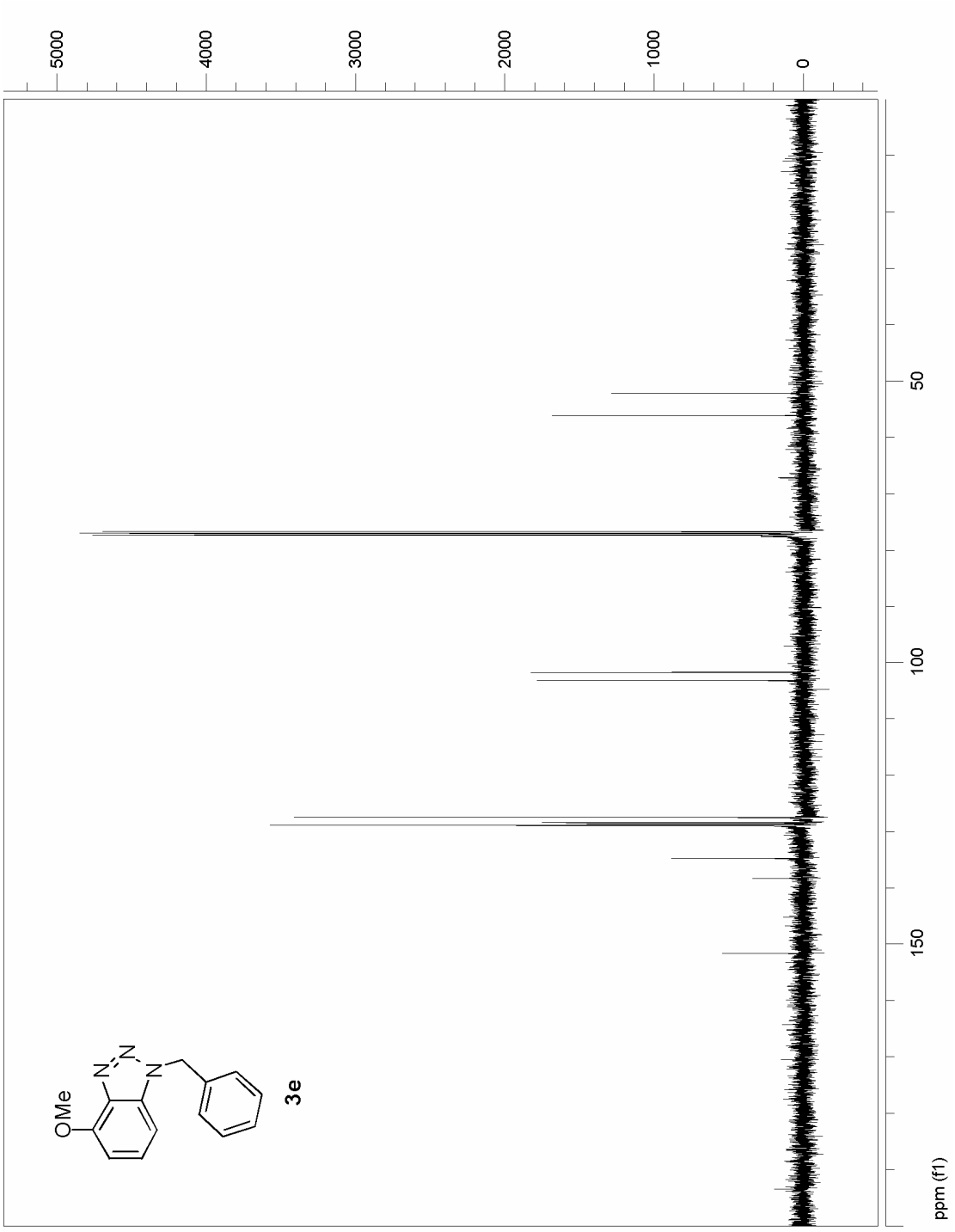

400
300
200
100
0
3.23
3.55
2.00
0.92
6.41
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (f1)
MeO
MeO
3c

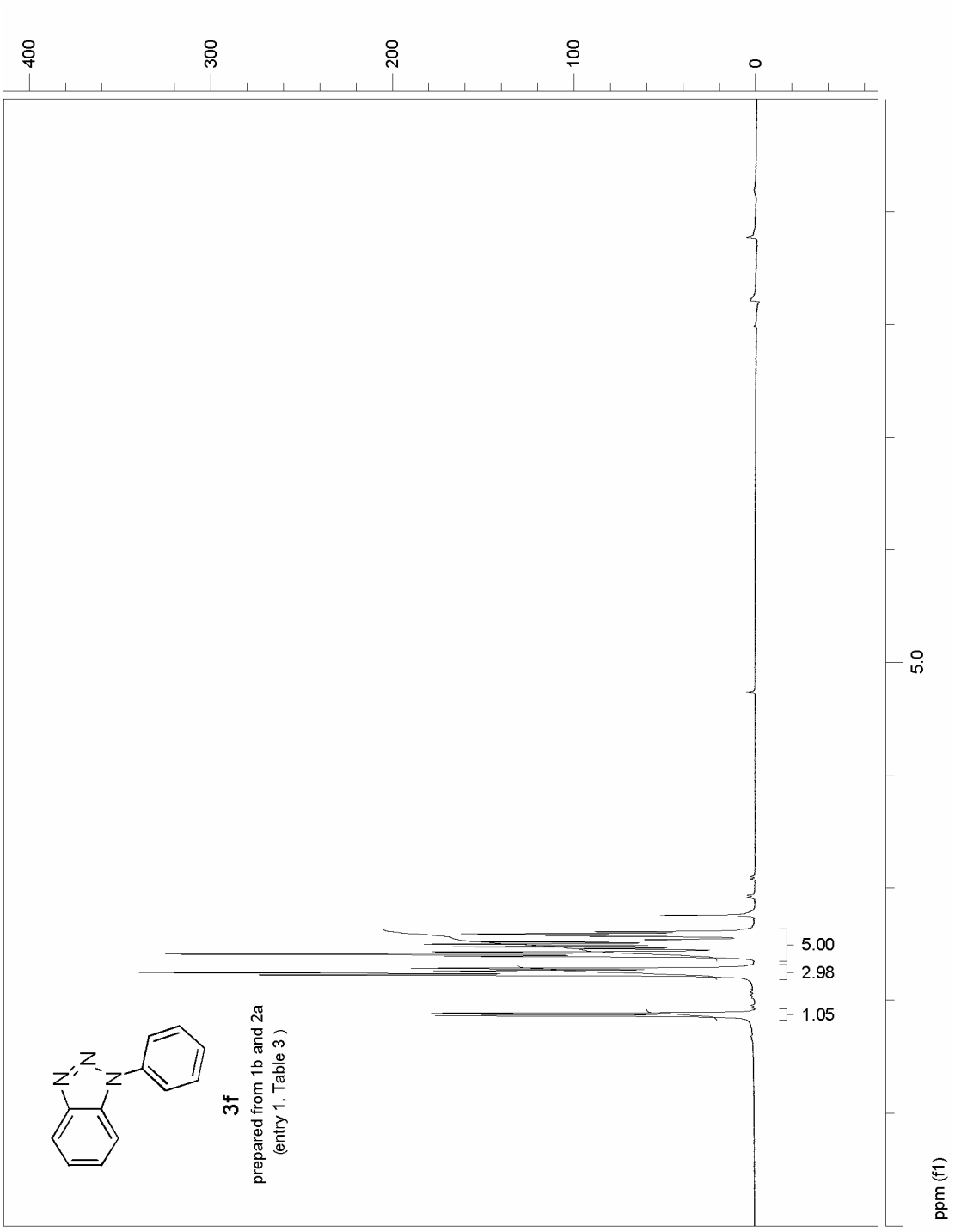

5000
4000
3000
2000
1000
0
50
100
150
ppm (f1)
N
N
N
MeO
MeO
3c

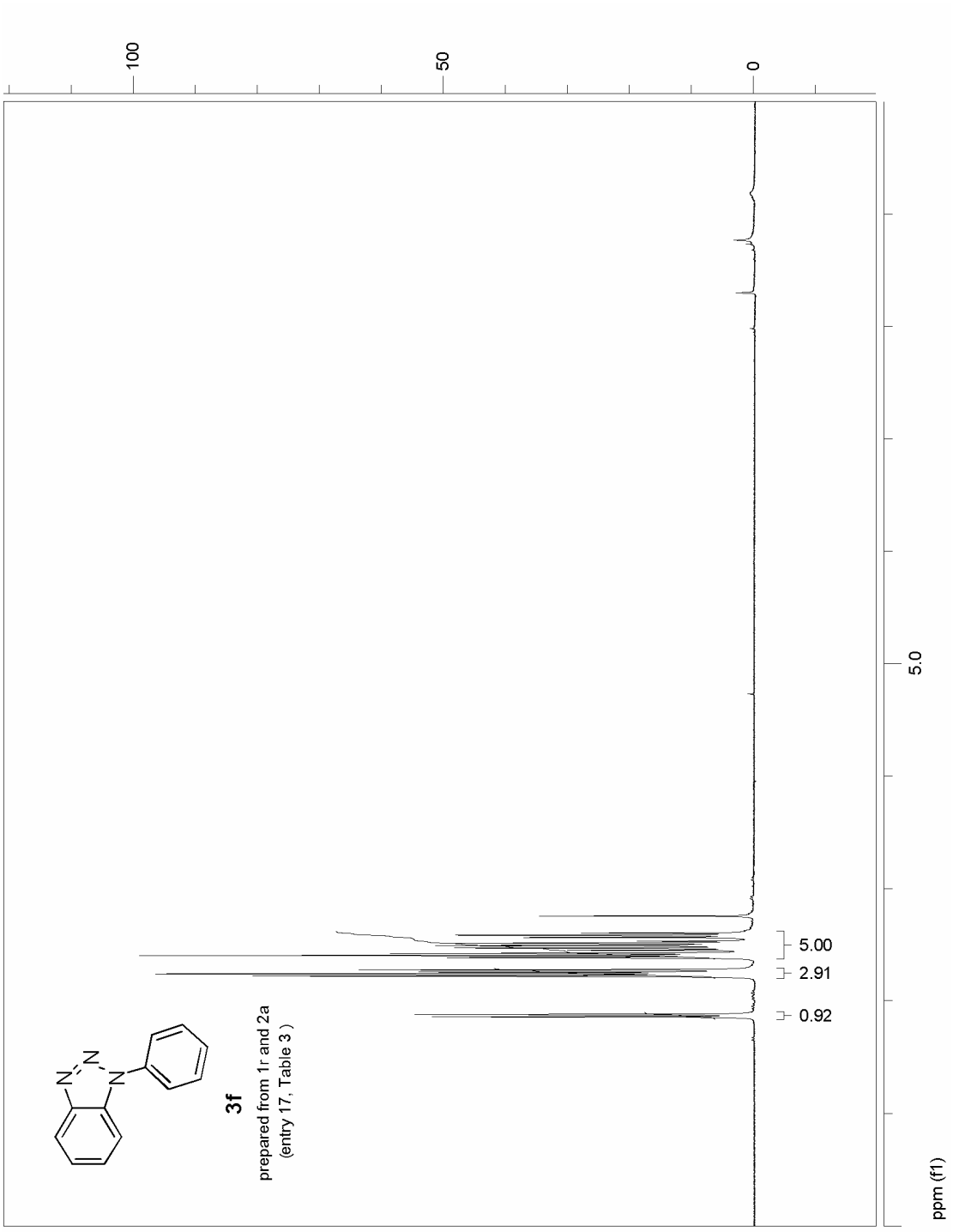

40
30
20
10
0
5.0
2.11
1.00
2.34
3.09
0.84
3d
F
F
N
N
N
ppm (f1)

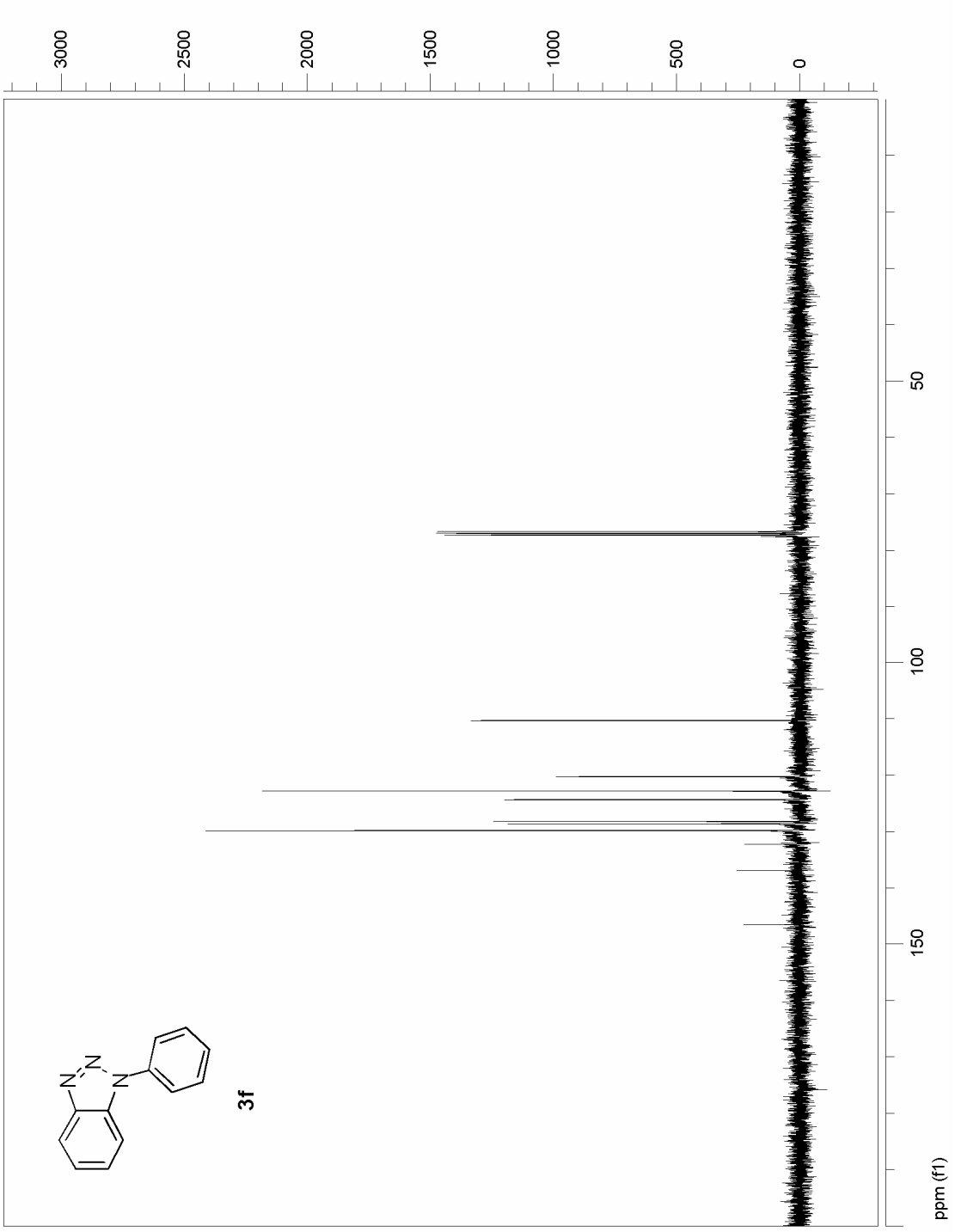

10000
5000
0
50
100
150
ppm (f1)
F
F
3d

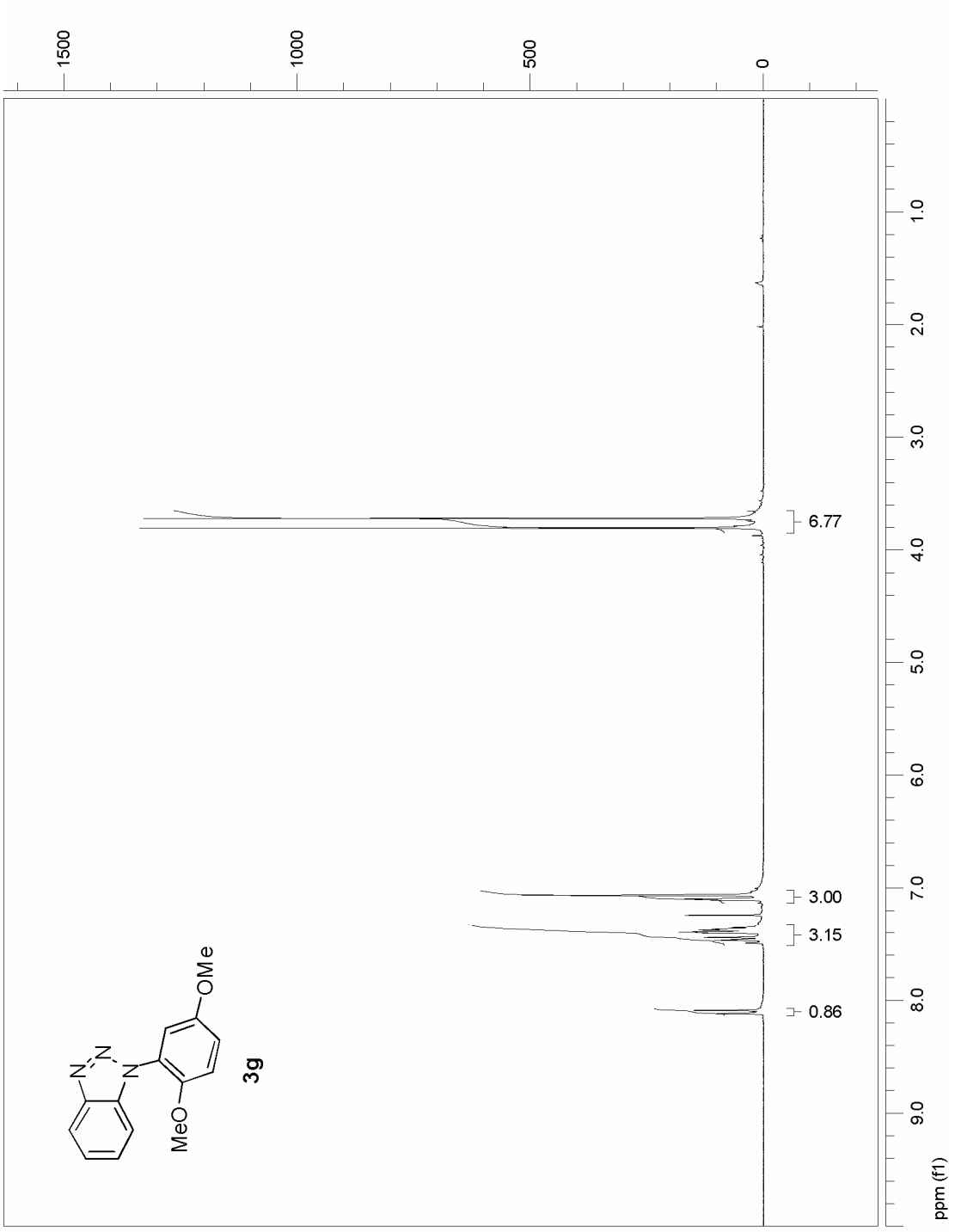

500
400
300
200
100
0
3.08
2.00
0.87
0.90
6.08
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (f1)
OMe
N
N
N
3e

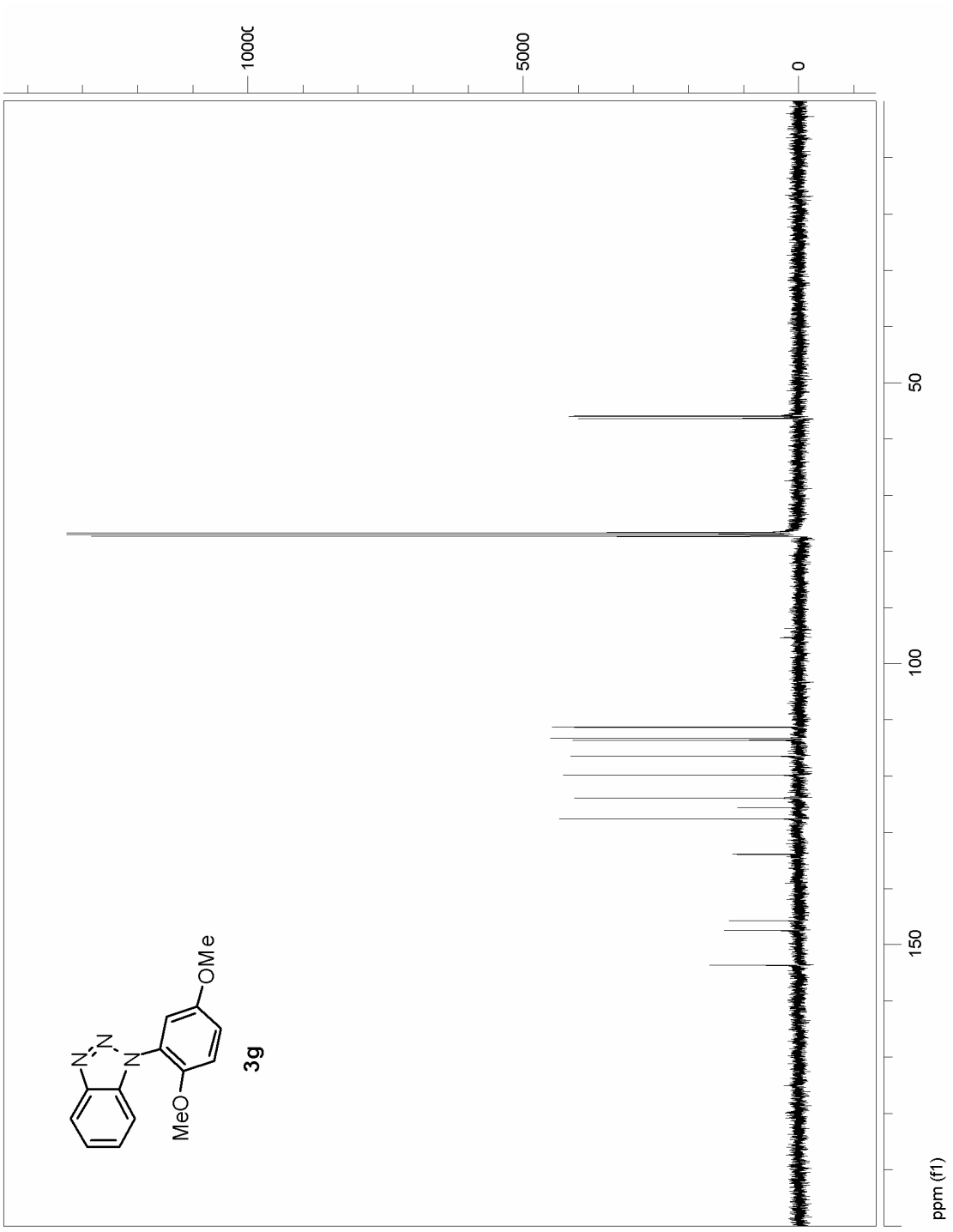

5000
4000
3000
2000
1000
0
50
100
150
ppm (f1)
OMe
N
N
N
3e

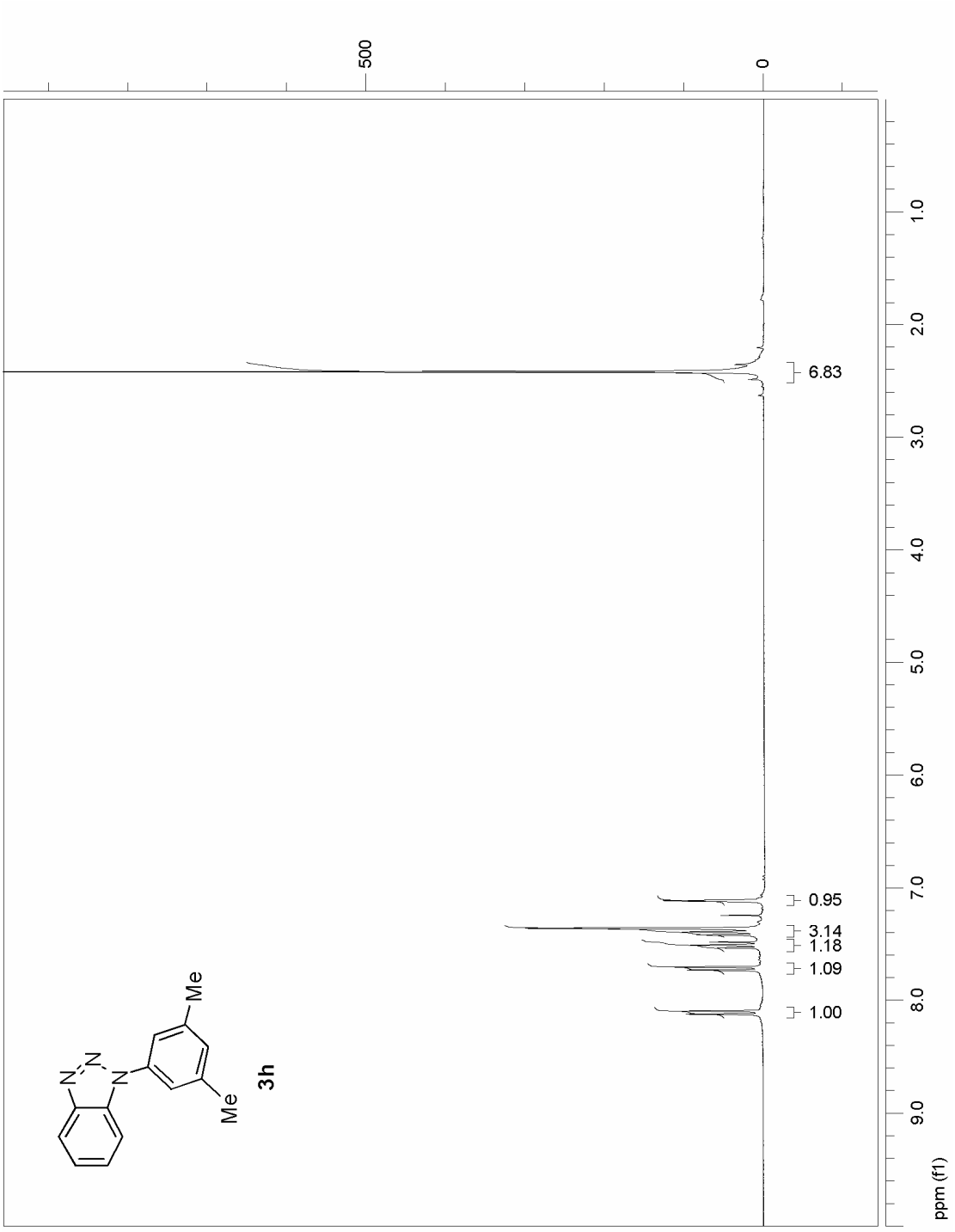

400
300
200
100
0
5.0
ppm (f1)
5.00
2.98
1.05
3f
prepared from 1b and 2a
(entry 1, Table 3)

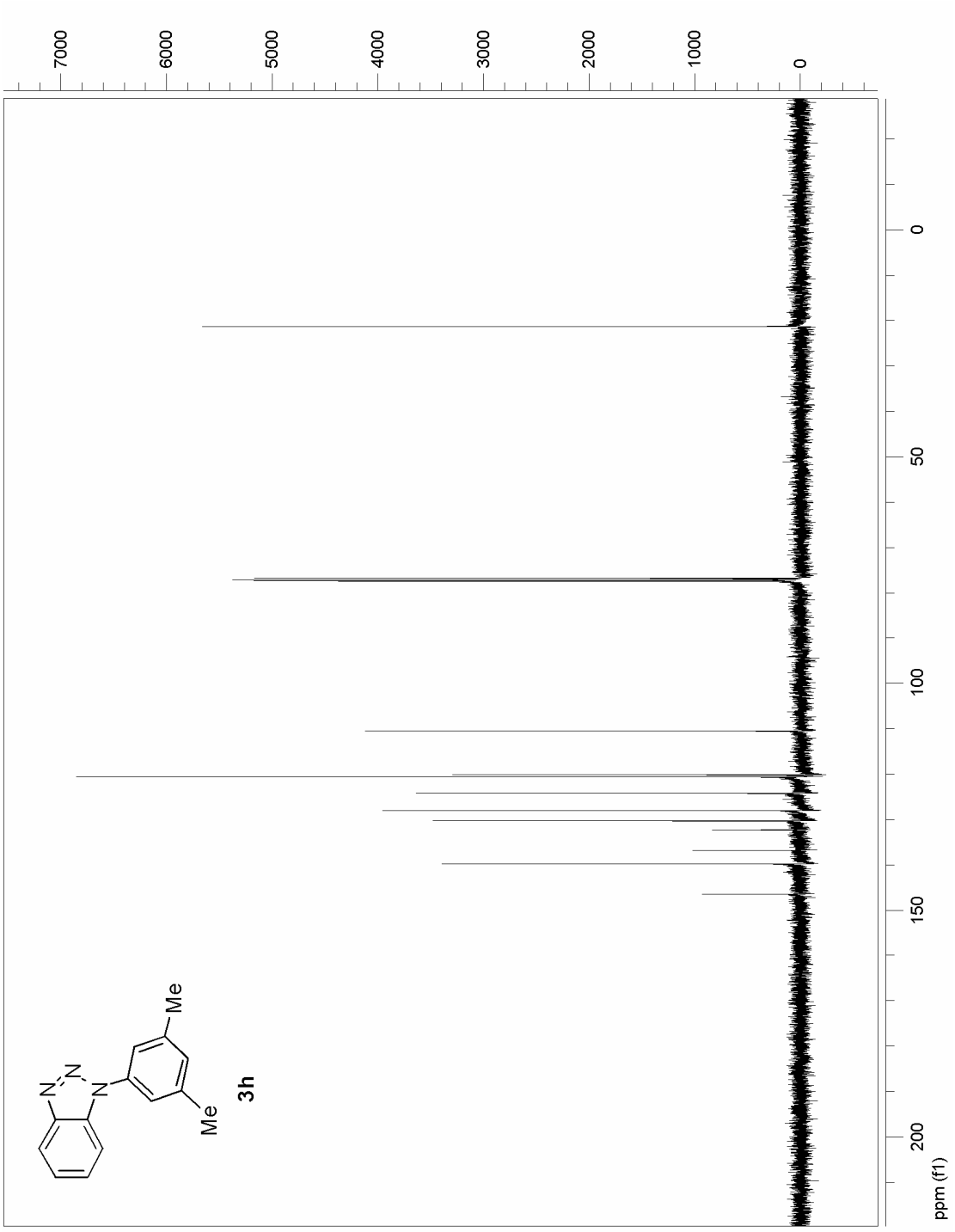

100
50
0
5.0
ppm (f1)
5.00
2.91
0.92
3f
prepared from 1r and 2a
(entry 17, Table 3)

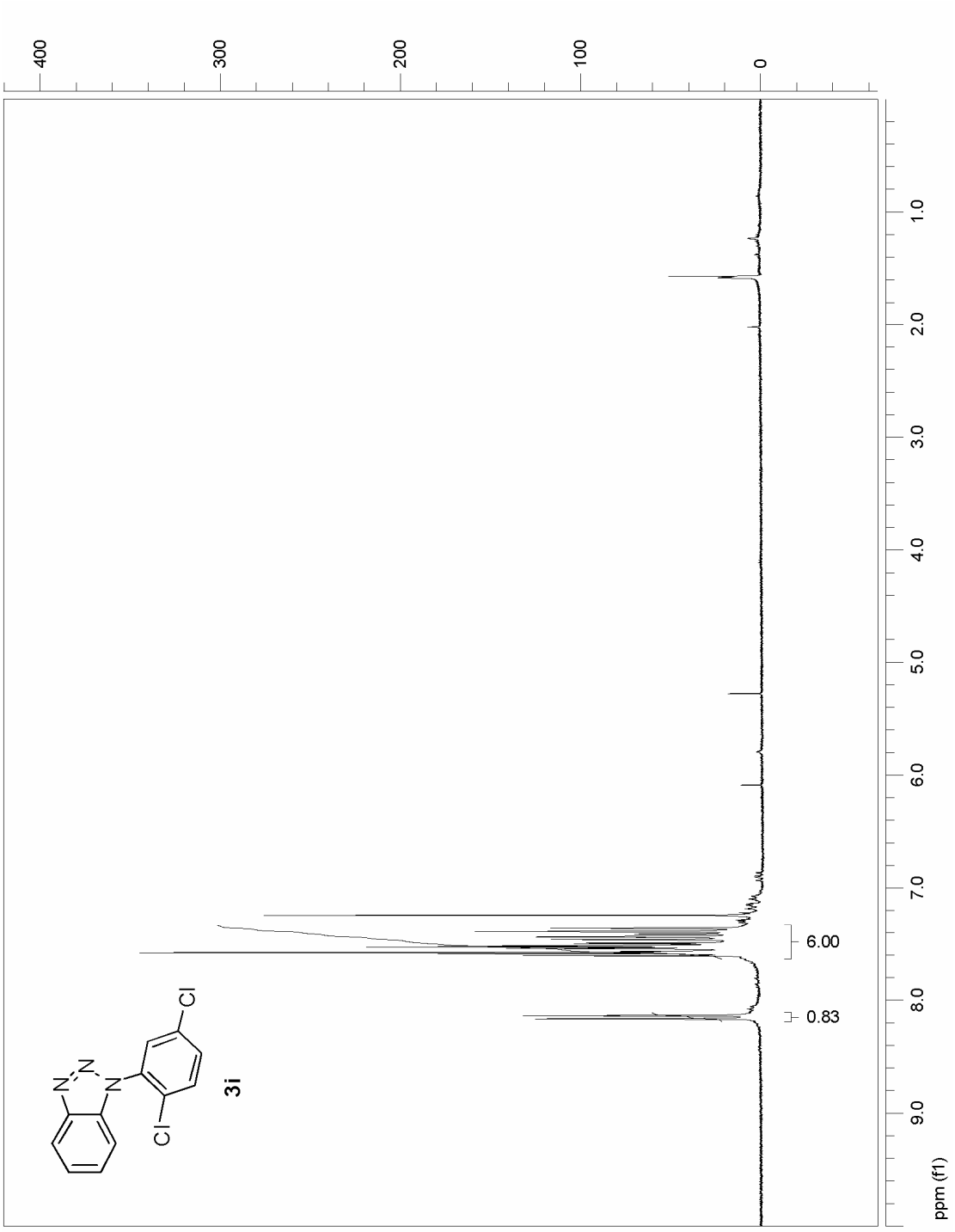

3000
2500
2000
1500
1000
500
0
50
100
150
ppm (f1)
3f

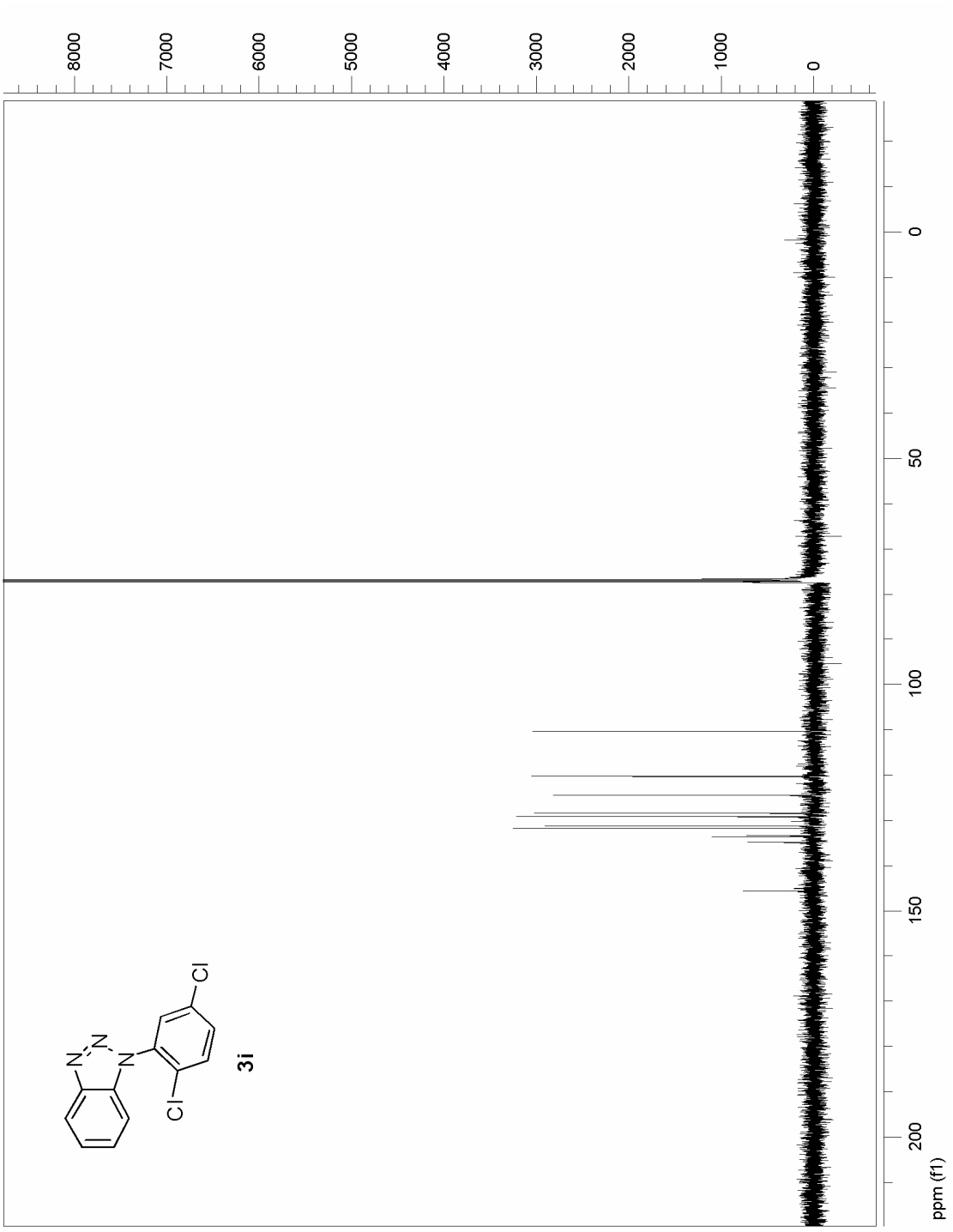

1500
1000
500
0
6.77
3.00
3.15
0.86
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (f1)
OMe
MeO
3g

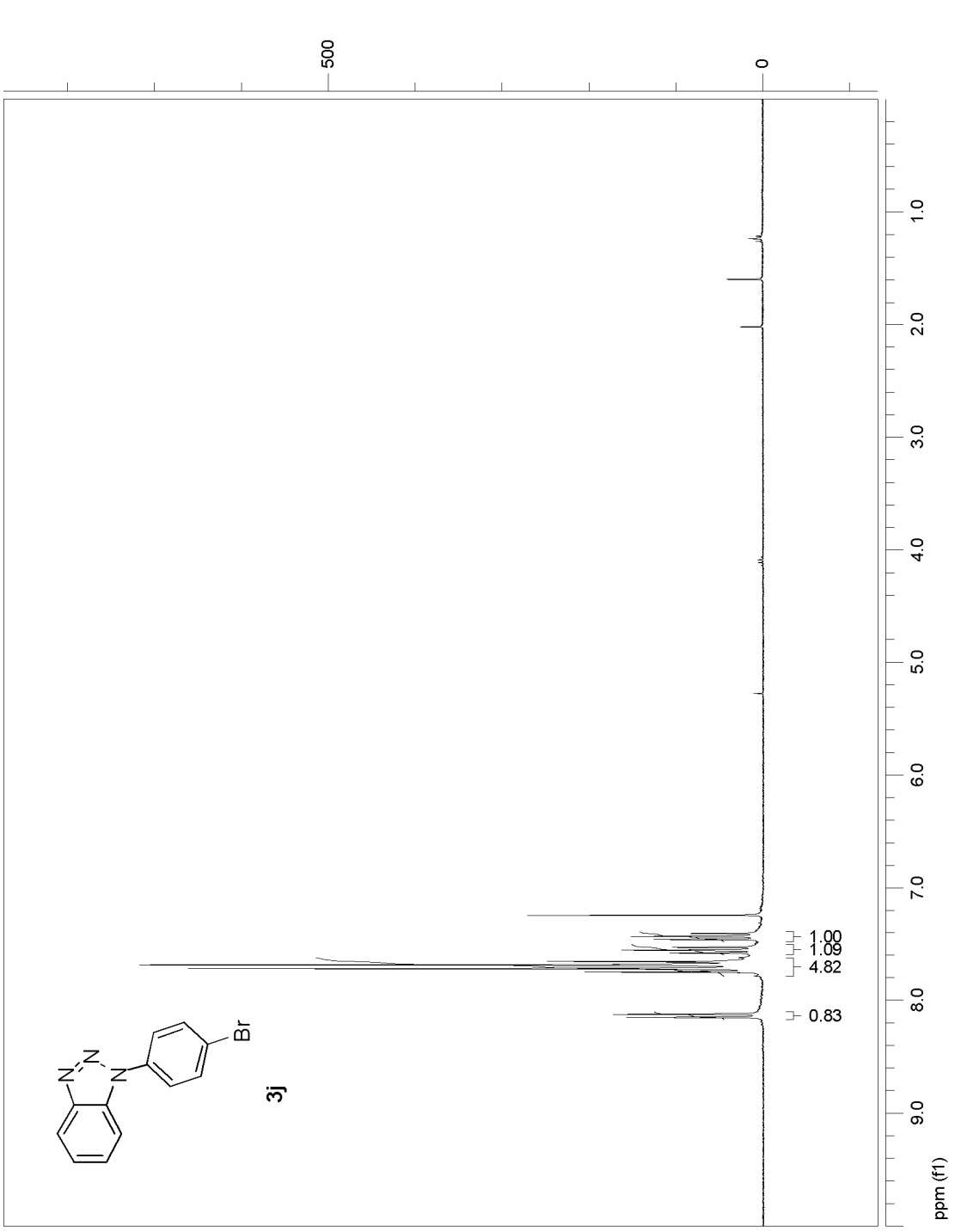

10000
5000
0
50
100
150
ppm (f1)
OMe
MeO
3g

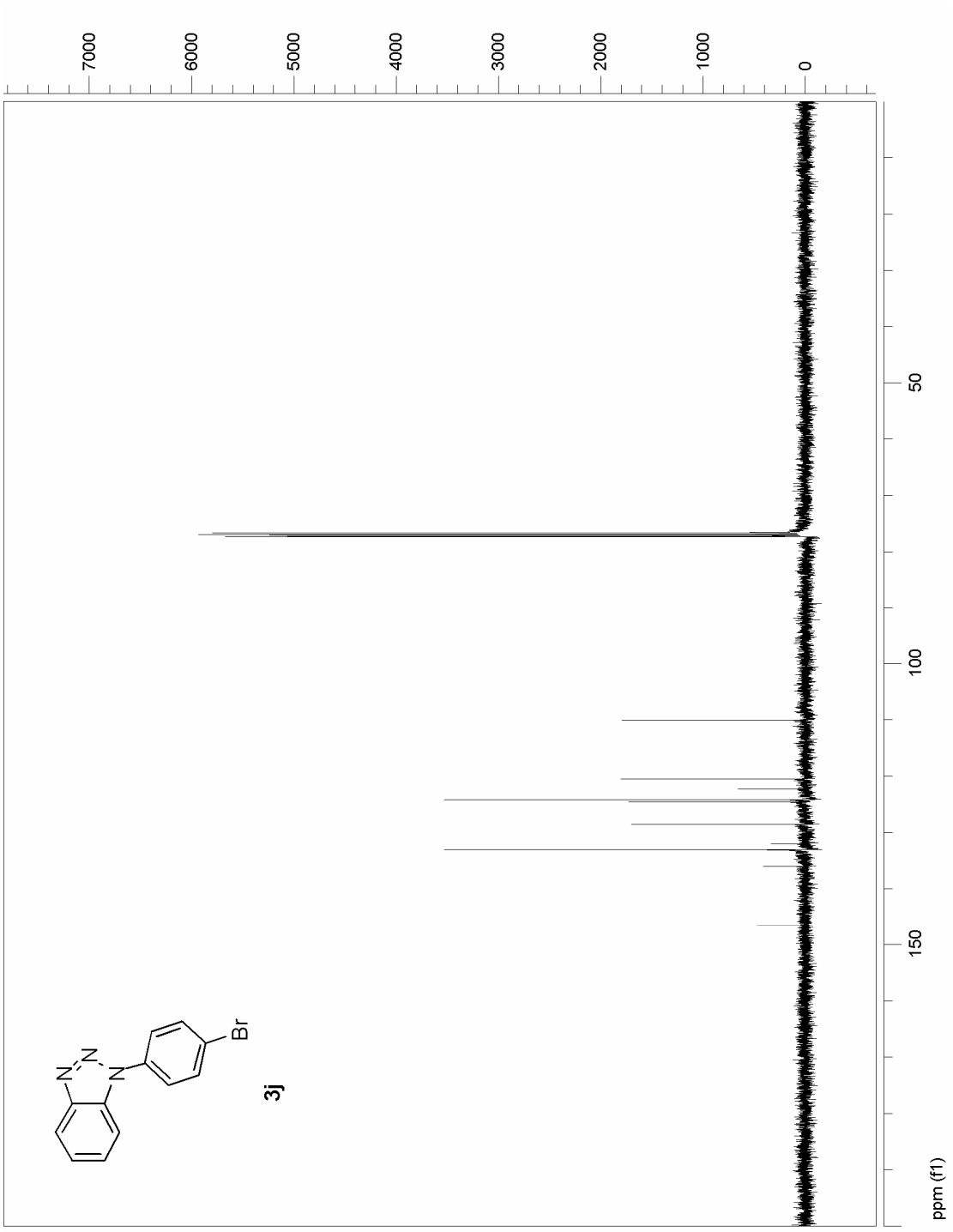

500
0
6.83
0.95
3.14
1.18
1.09
1.00
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (f1)
Me
Me
N
N
N
3h

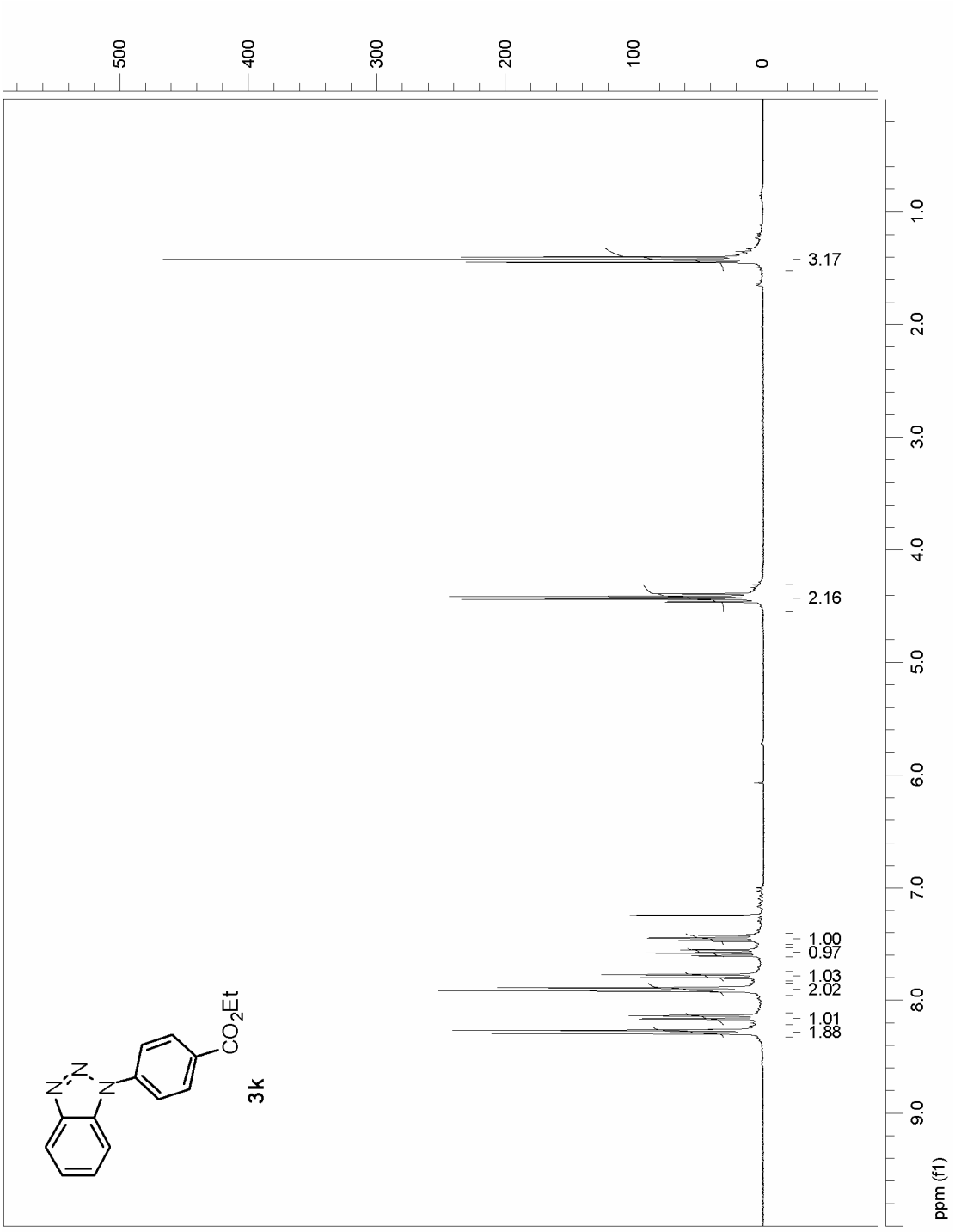

7000
6000
5000
4000
3000
2000
1000
0
0
50
100
150
200
ppm (f1)
Me
Me
N
N
N
3h

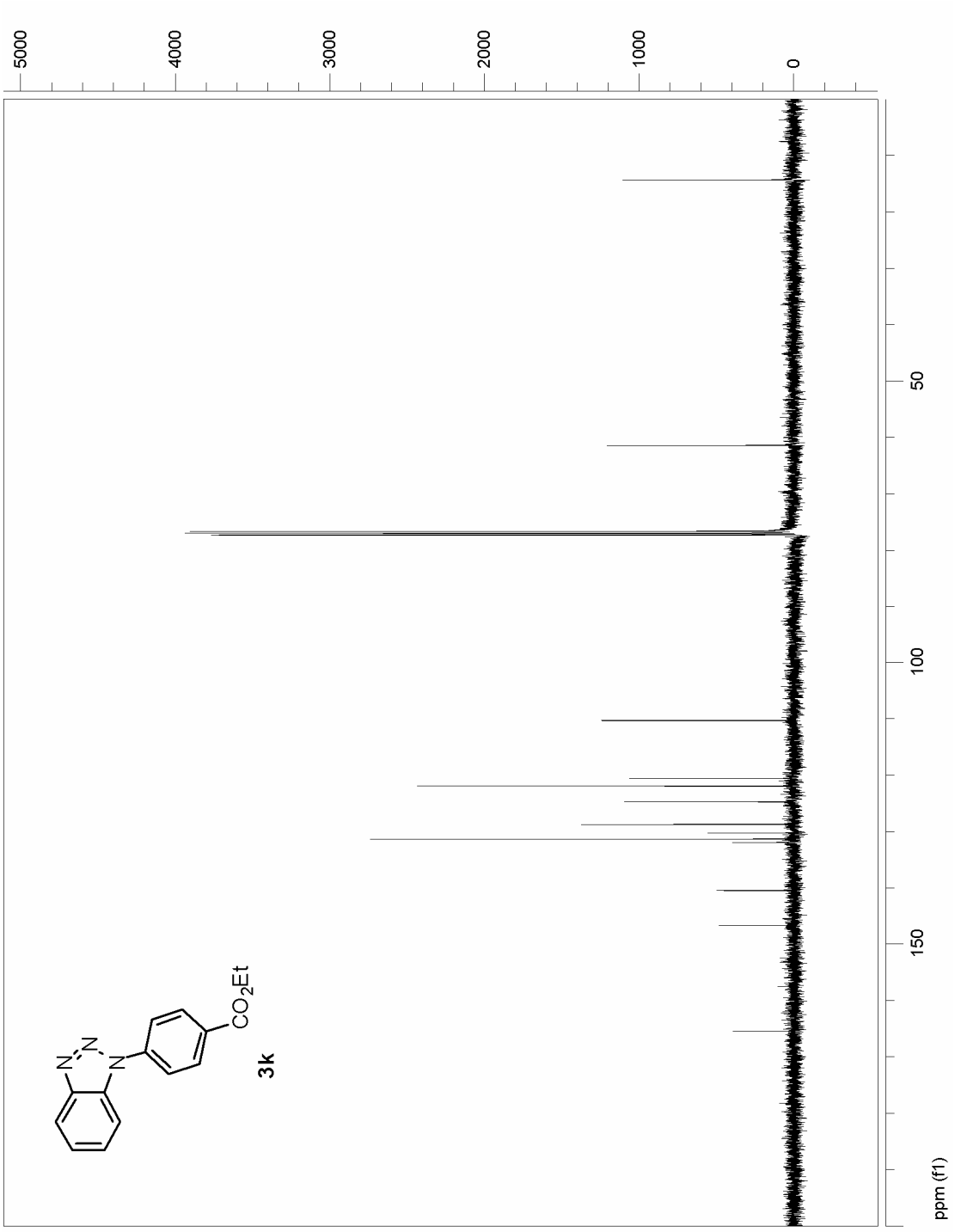

400
300
200
100
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (f1)
6.00
0.83
Cl
Cl
N
N
N
3i

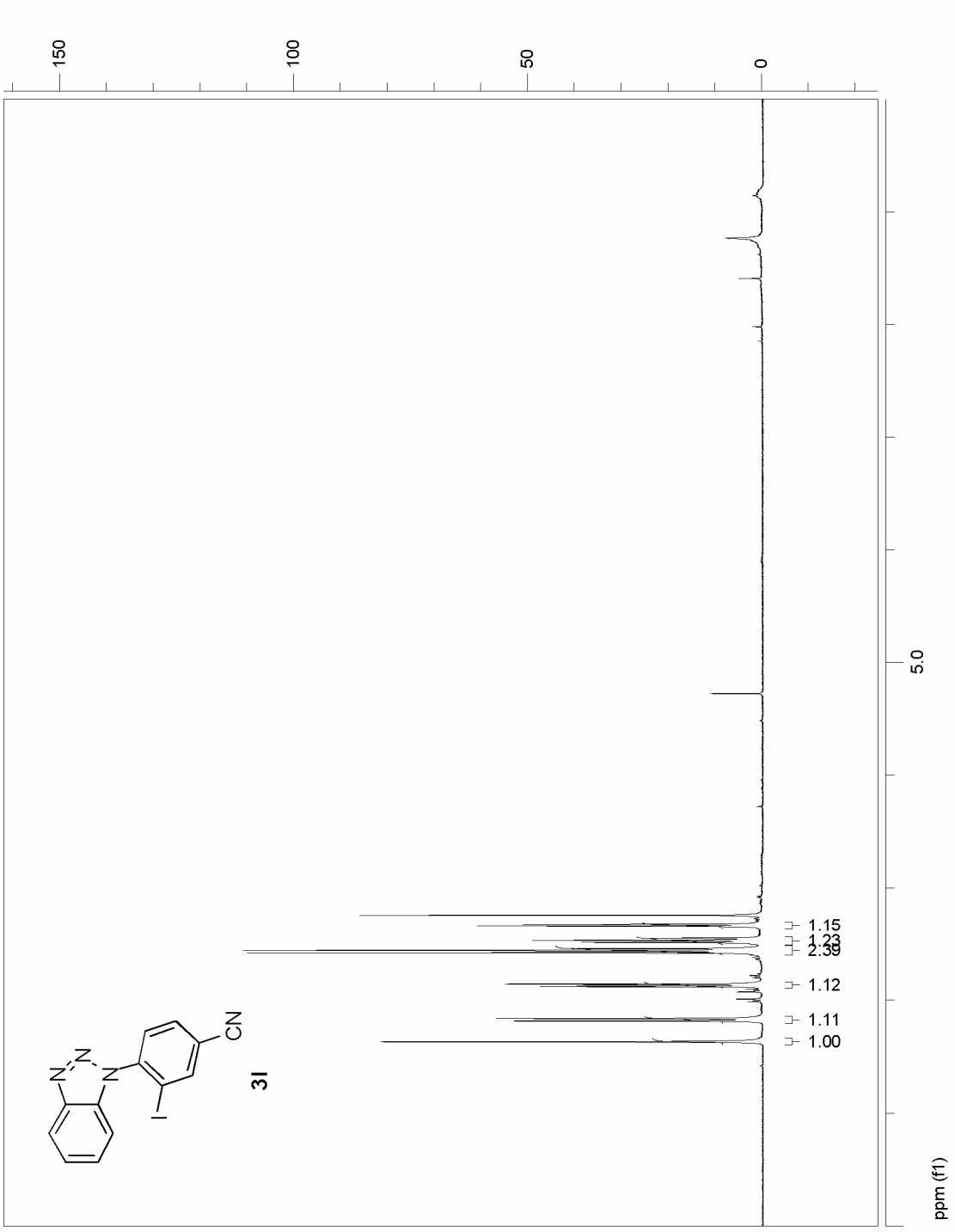

8000
7000
6000
5000
4000
3000
2000
1000
0
0
50
100
150
200
ppm (f1)
Cl
Cl
N
N
N
3i

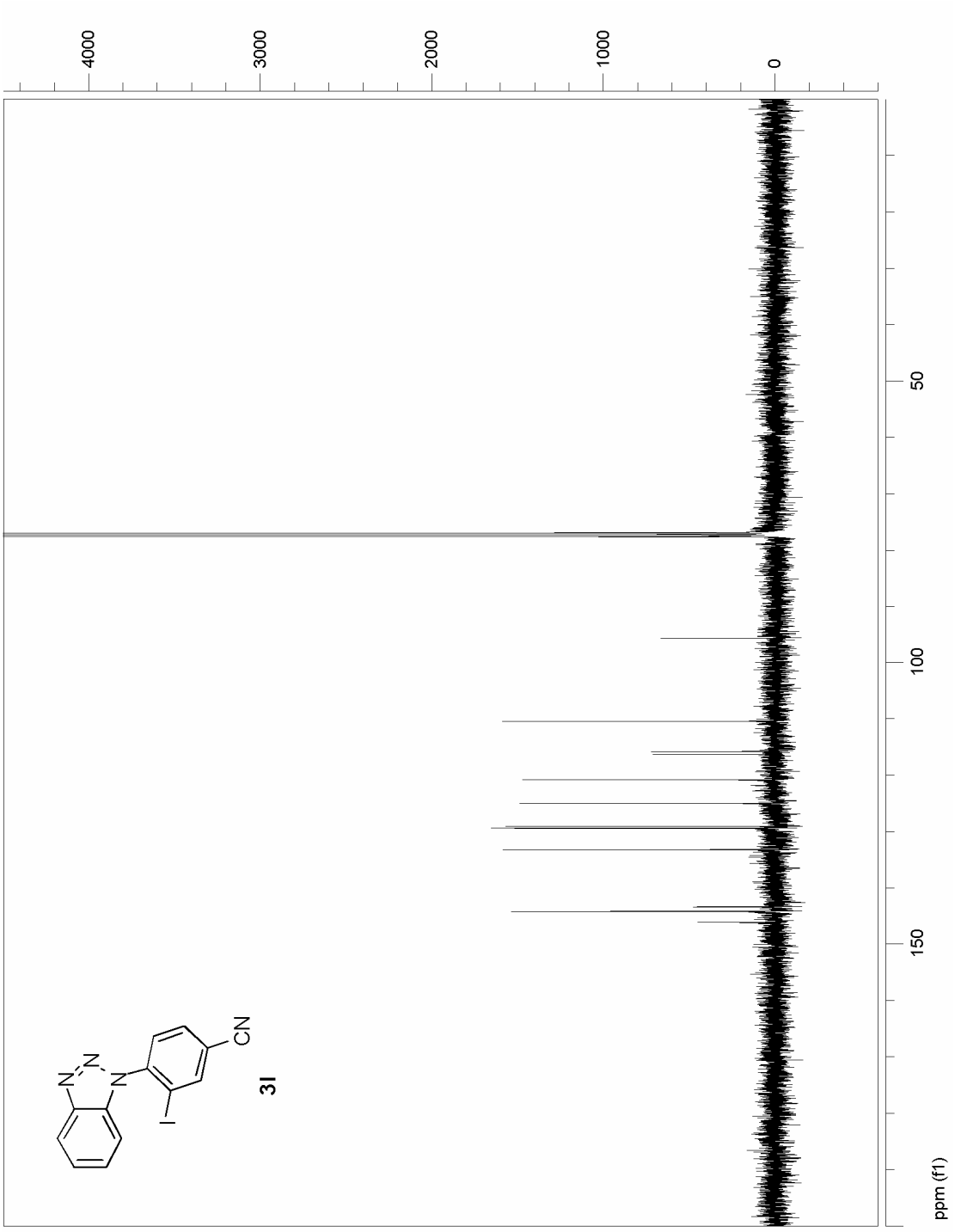

500
0
1.00
1.09
4.82
0.83
Br
3j
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (f1)

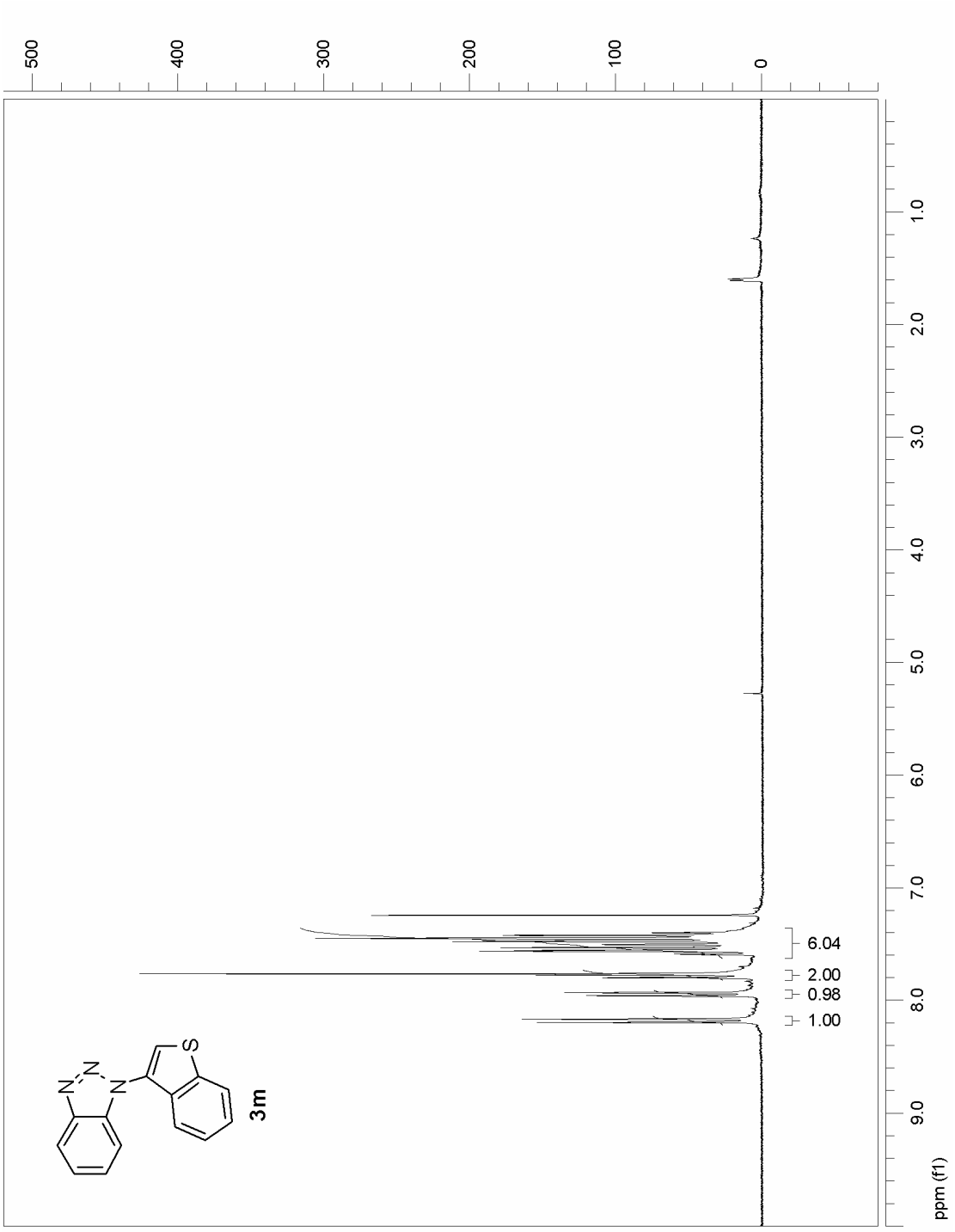

7000
6000
5000
4000
3000
2000
1000
0
50
100
150
ppm (f1)
Br
N
N
N
3j

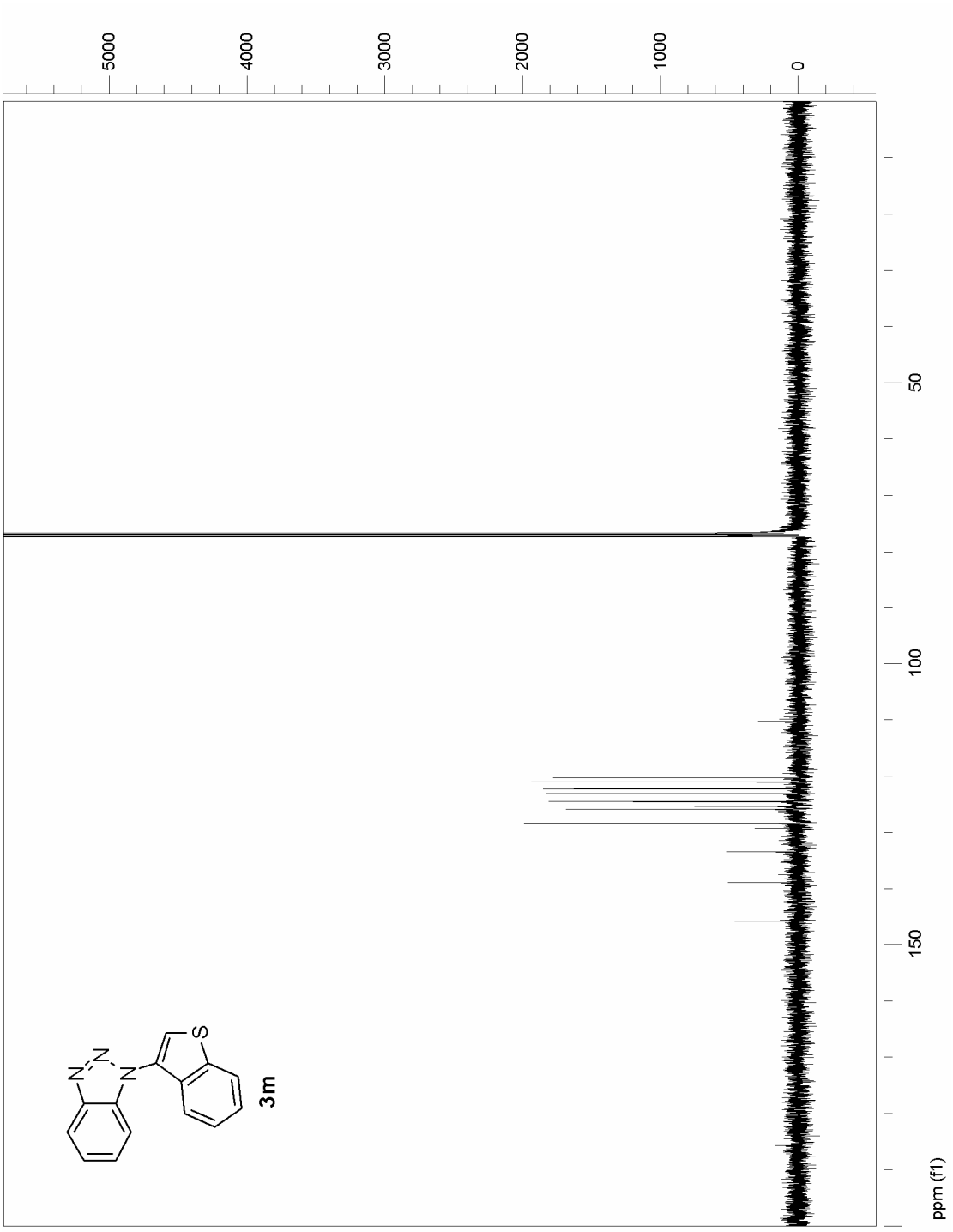

500
400
300
200
100
0
3.17
2.16
1.00
0.97
1.03
2.02
1.01
1.88
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (f1)
CO2Et
3k

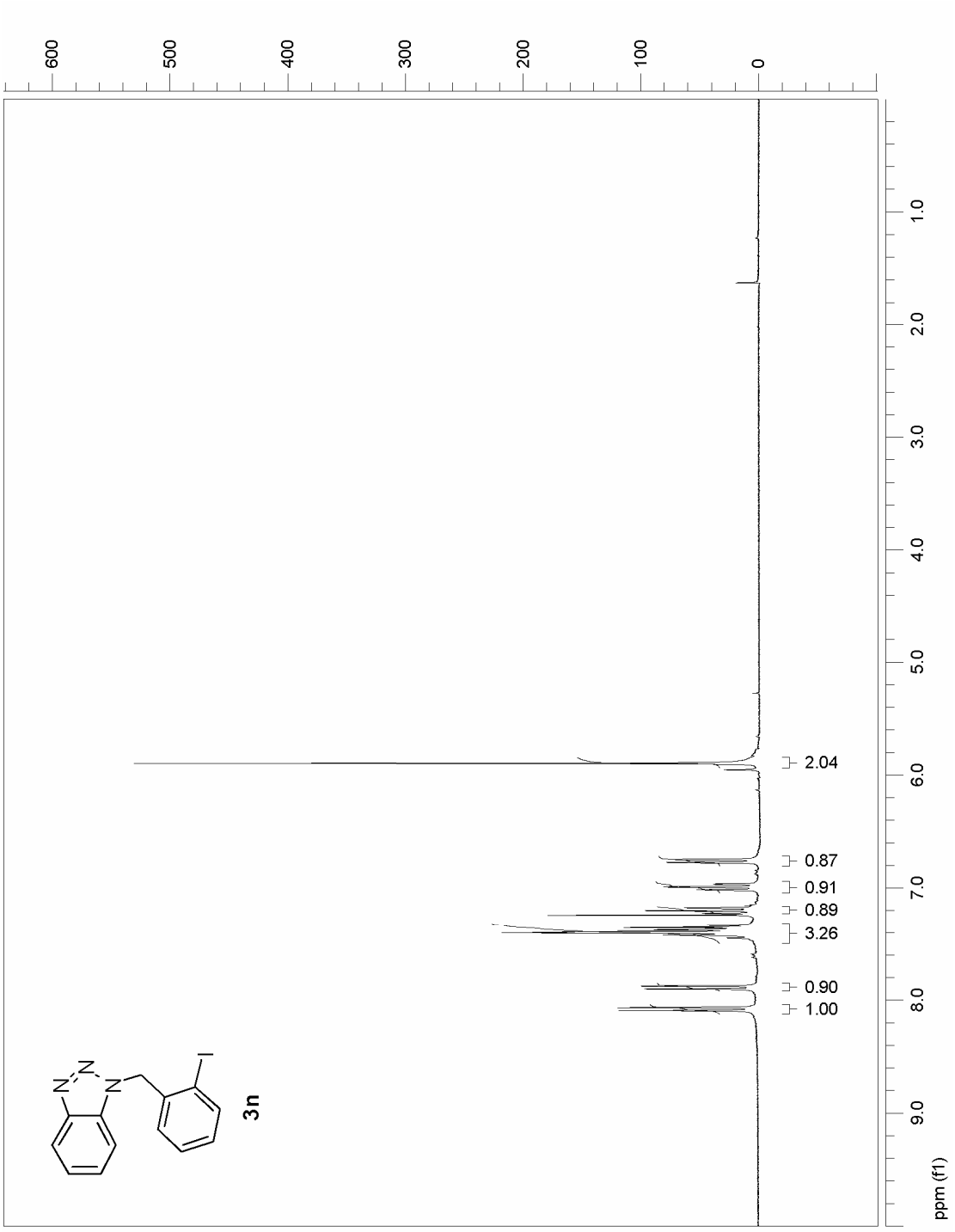

5000
4000
3000
2000
1000
0
50
100
150
ppm (f1)
CO2Et
3k

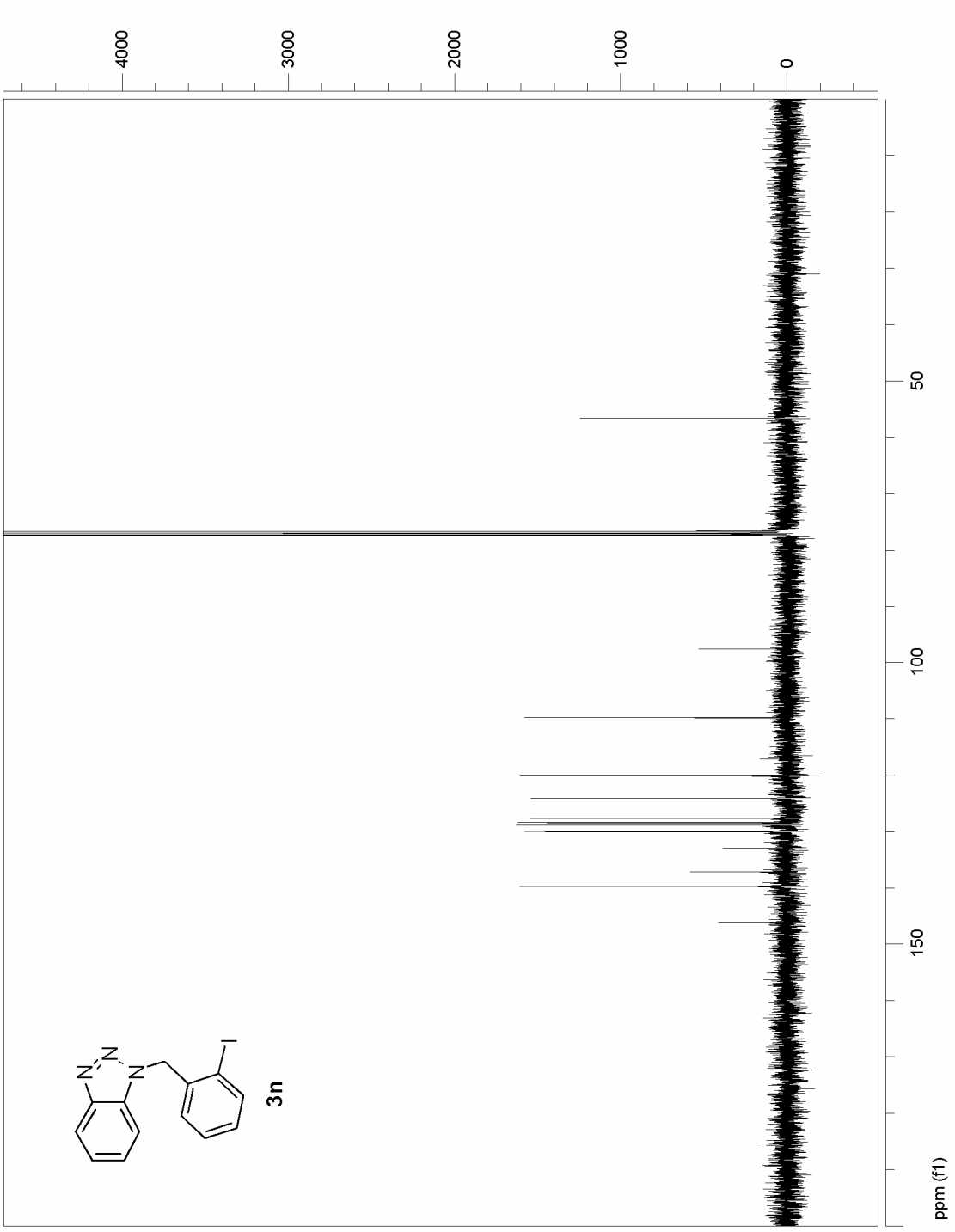

150
100
50
0
5.0
ppm (f1)
1.15
1.23
2.39
1.12
1.11
1.00
CN
I
3l

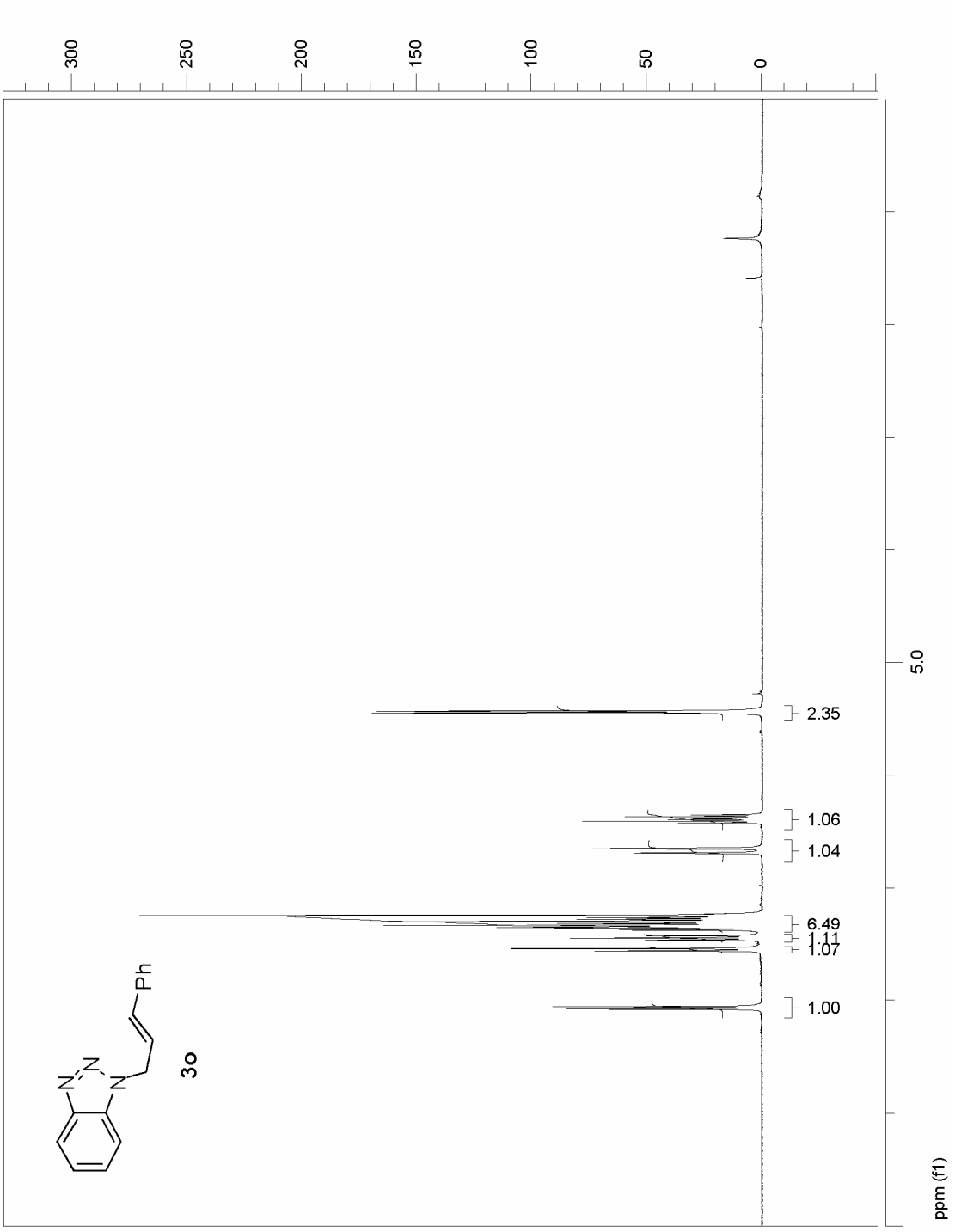

4000
3000
2000
1000
0
50
100
150
ppm (f1)
CN
3l

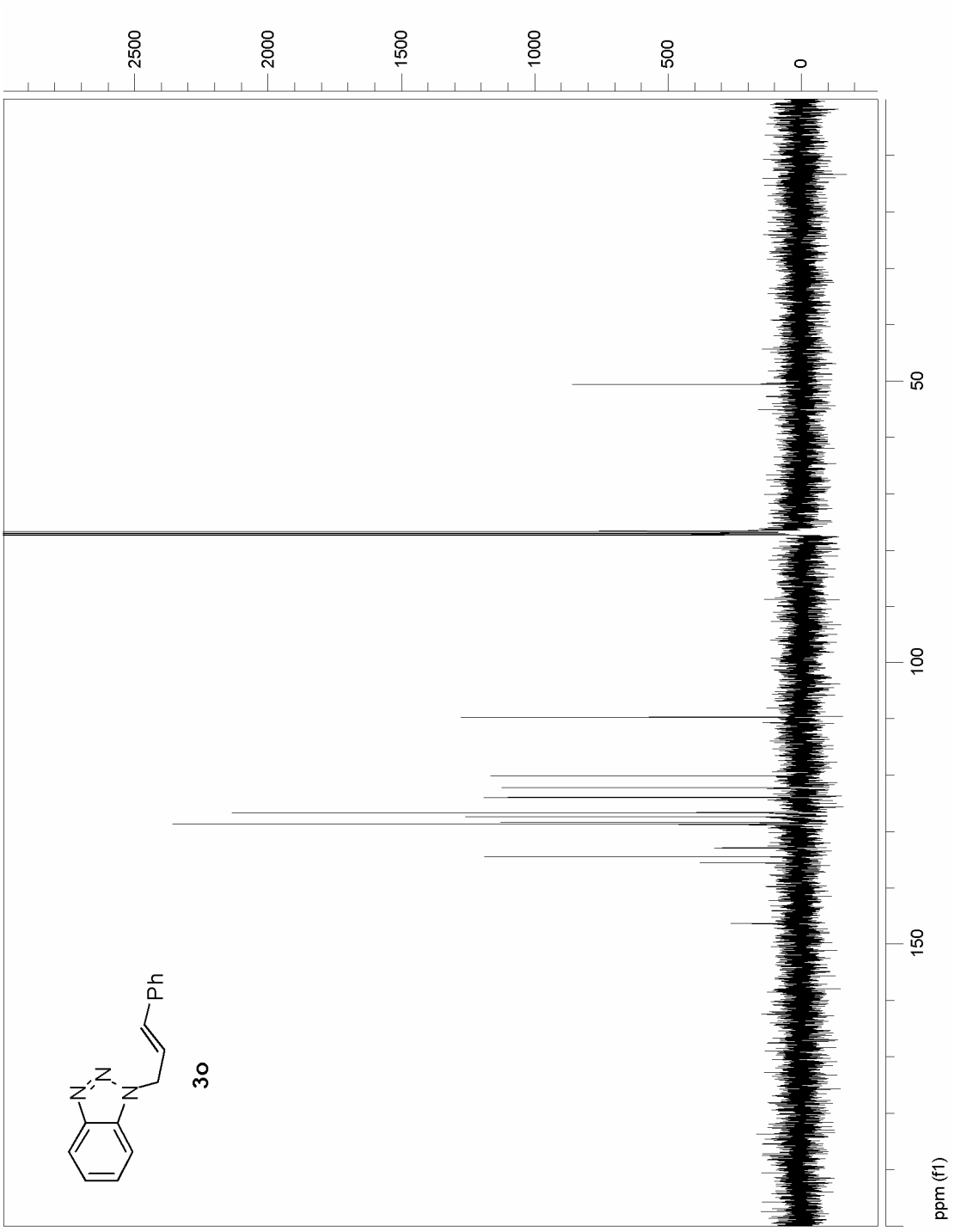

500
400
300
200
100
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (f1)
6.04
2.00
0.98
1.00
3m

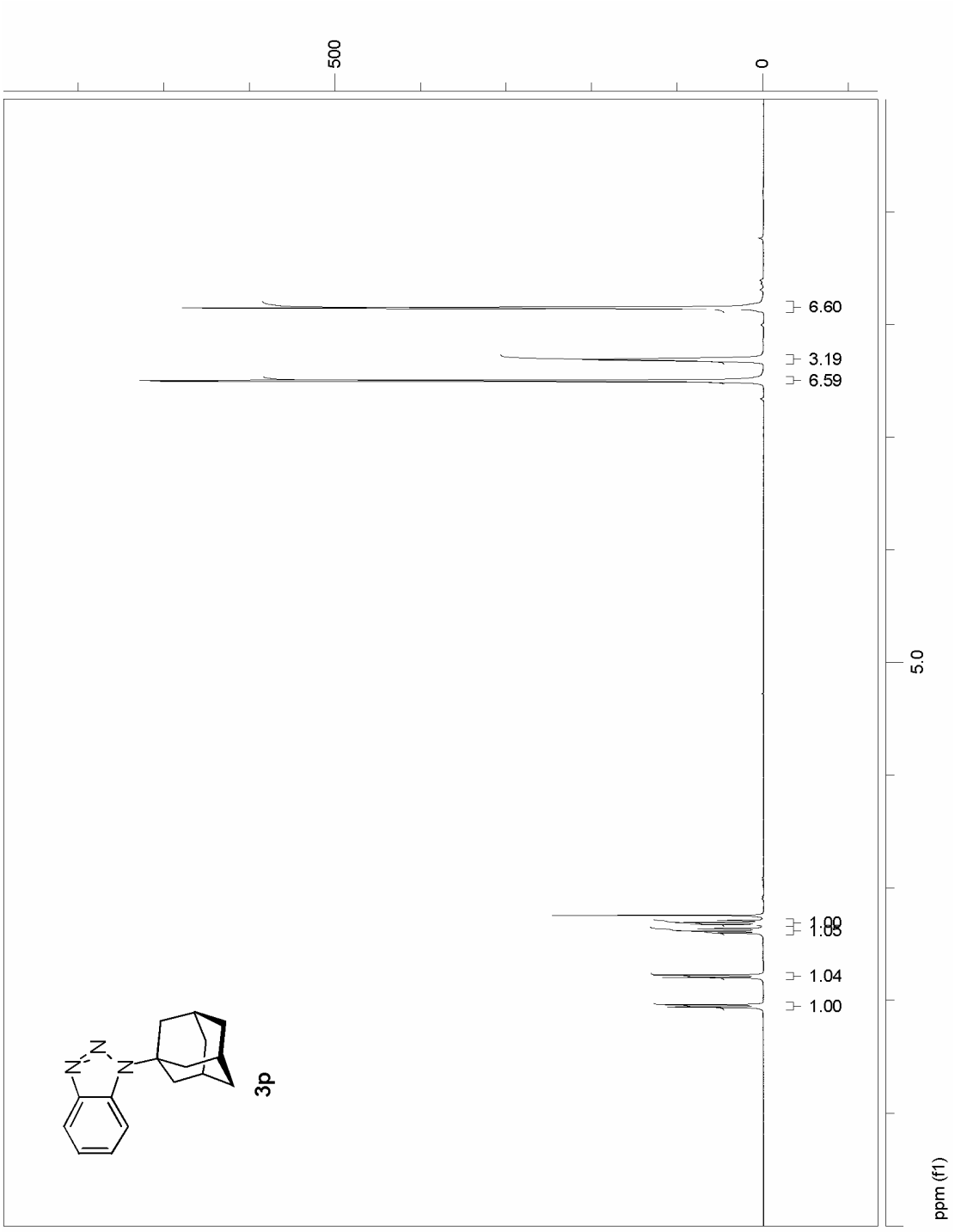

5000
4000
3000
2000
1000
0
50
100
150
ppm (f1)
N
N
N
S
3m

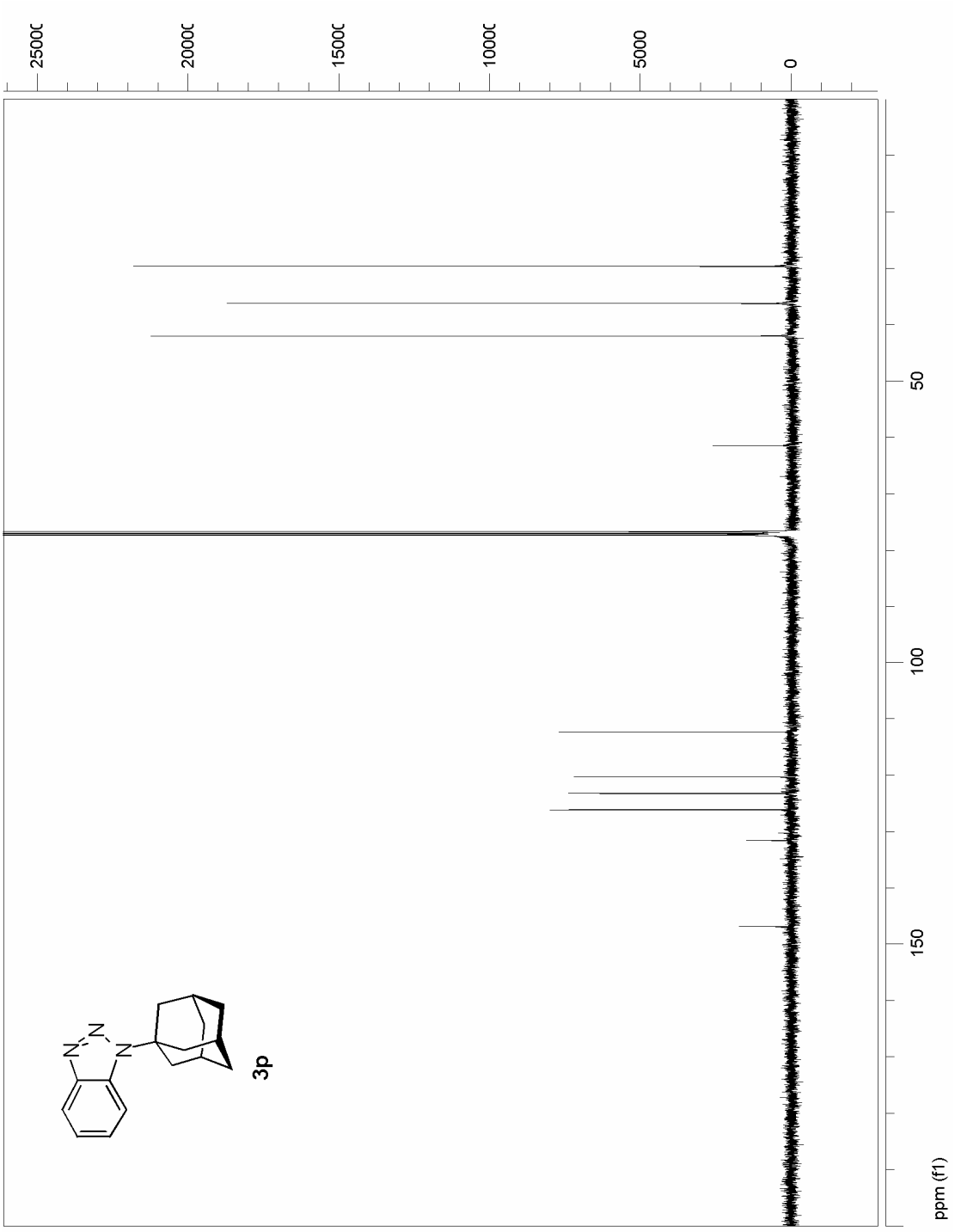

600
500
400
300
200
100
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (f1)
2.04
0.87
0.91
0.89
3.26
0.90
1.00
3n

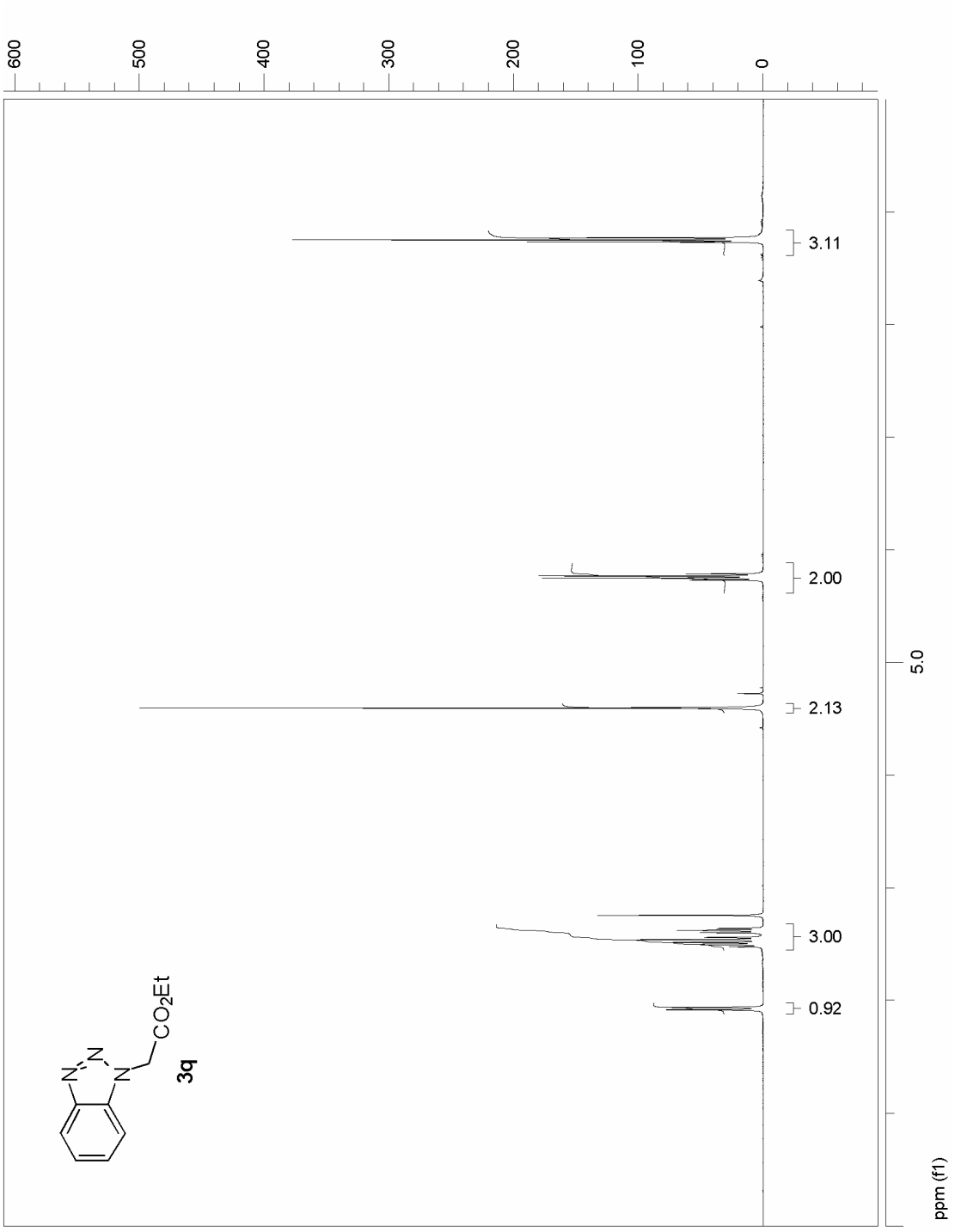

4000
3000
2000
1000
0
50
100
150
ppm (f1)
3n

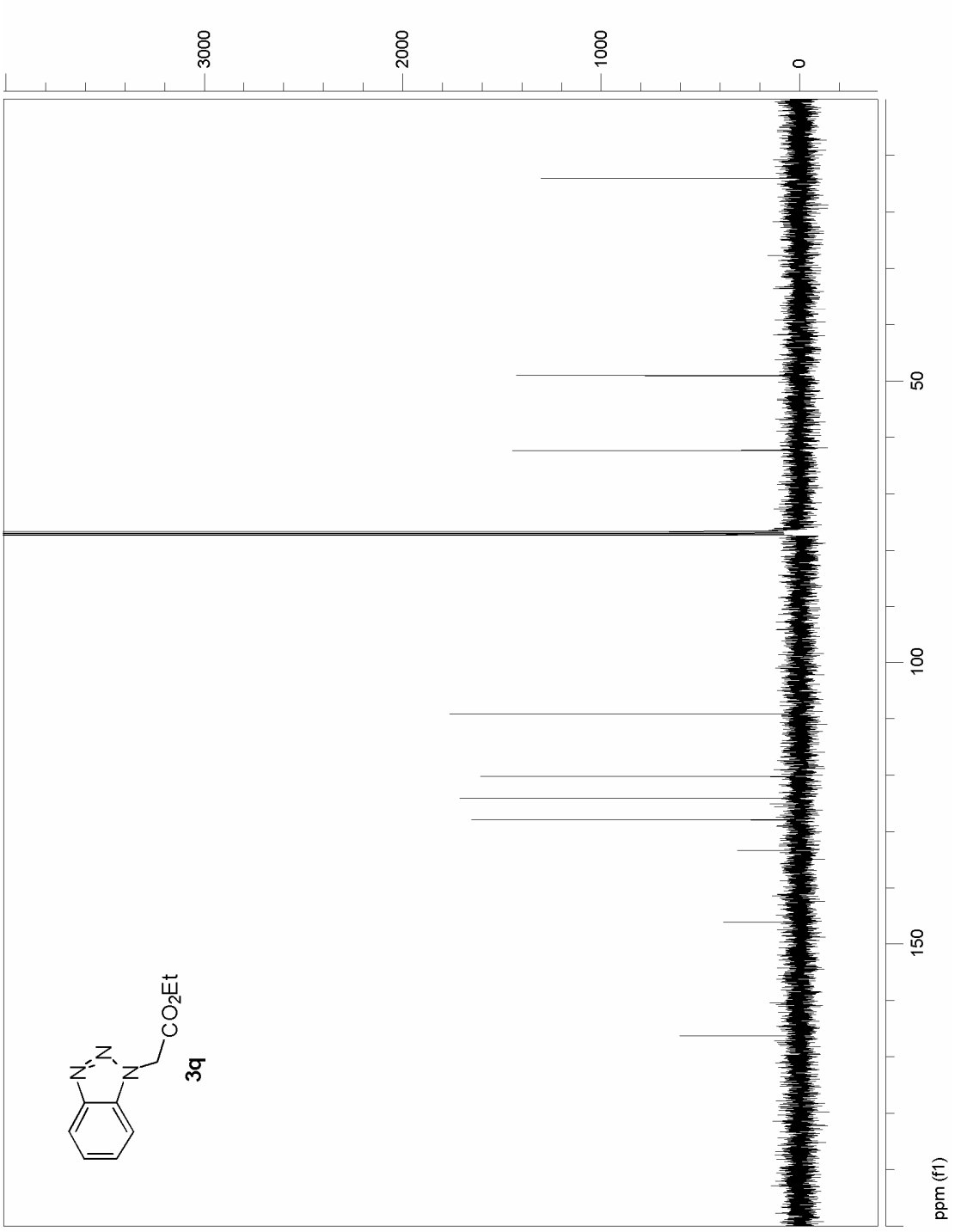

300
250
200
150
100
50
0
2.35
1.06
1.04
6.49
1.11
1.07
1.00
5.0
ppm (f1)
Ph
N
N
N
3o

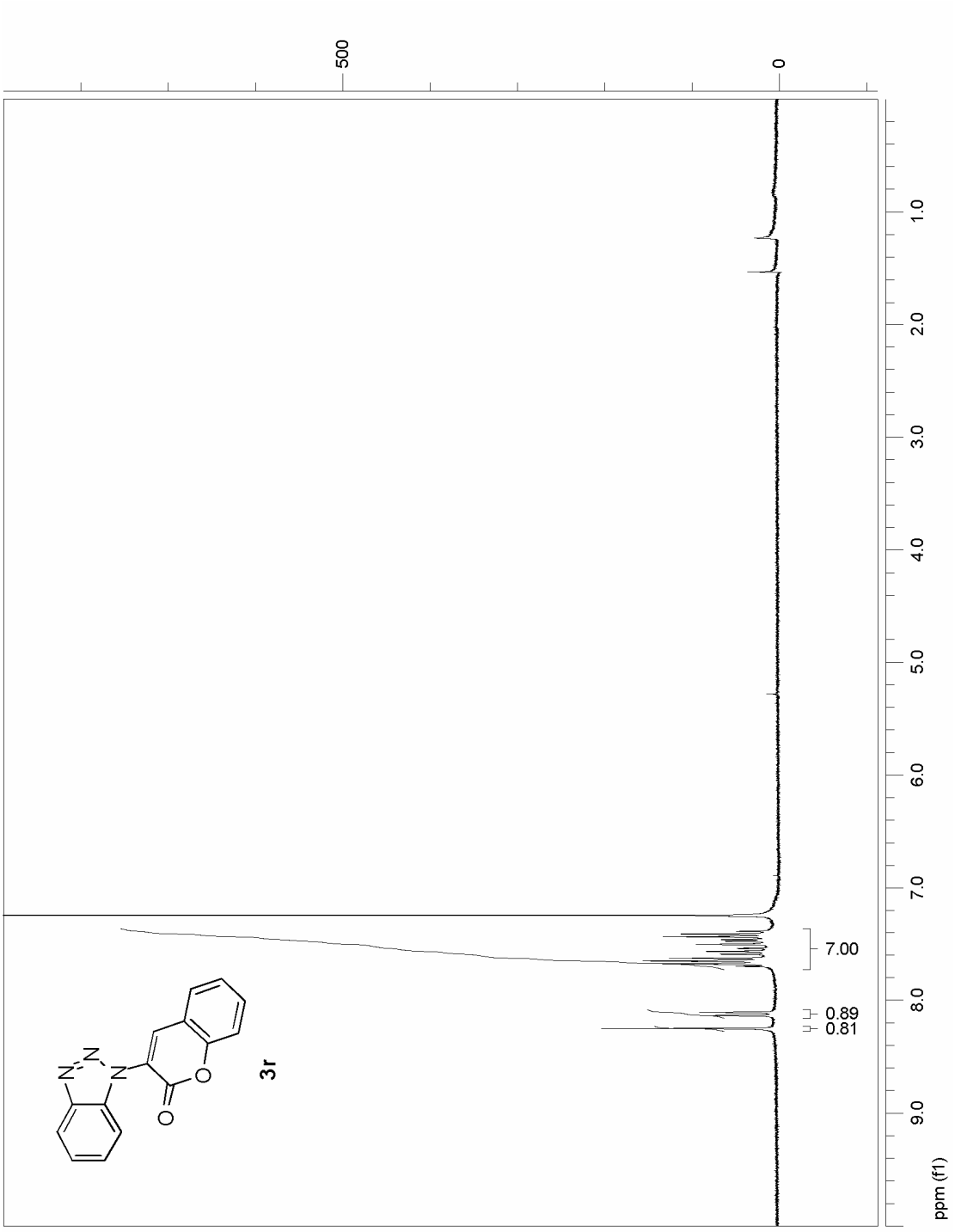

2500
2000
1500
1000
500
0
50
100
150
ppm (f1)
Ph
N
N
N
3o

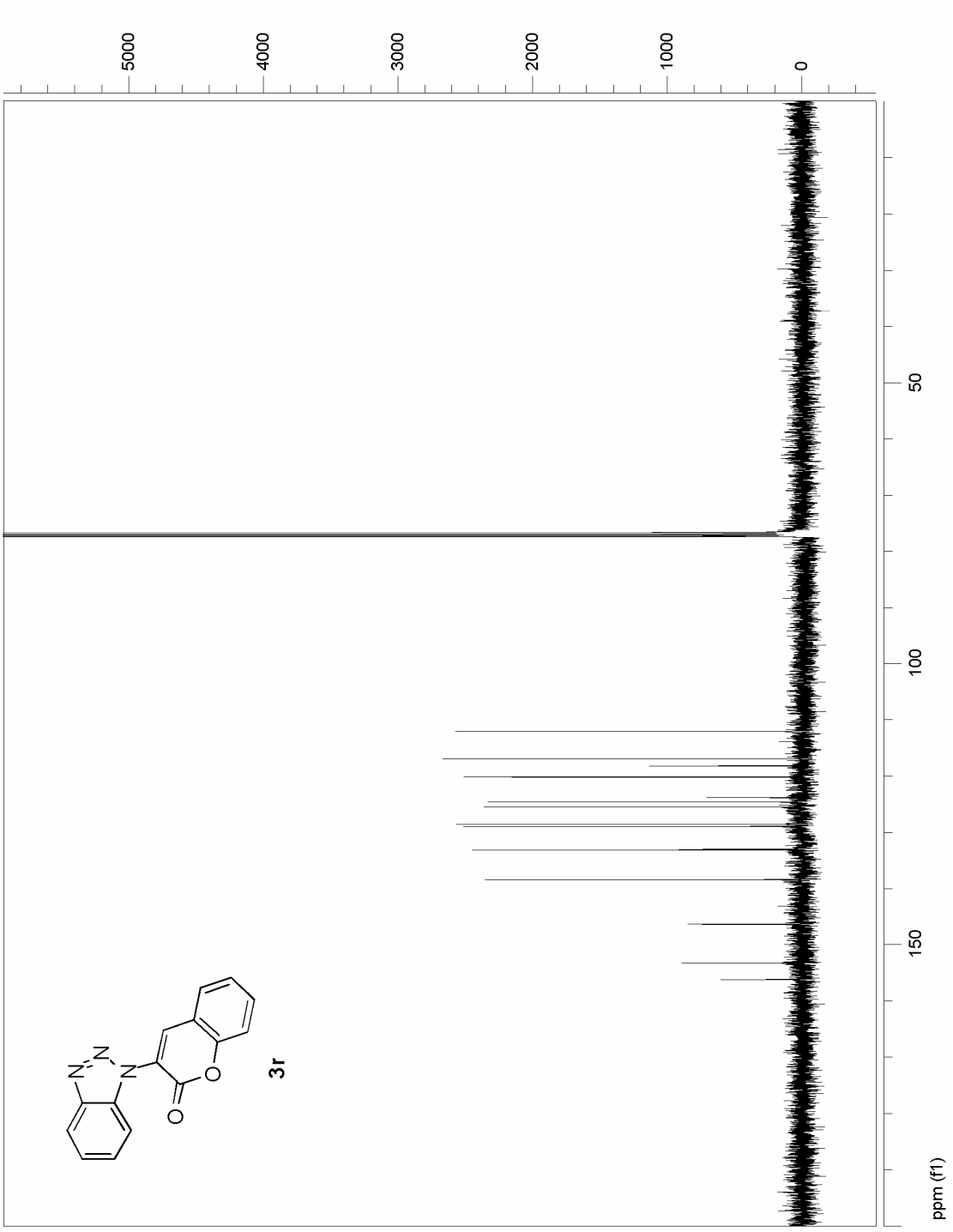

500
0
6.60
3.19
6.59
1.00
1.03
1.04
1.00
5.0
ppm (f1)
3p

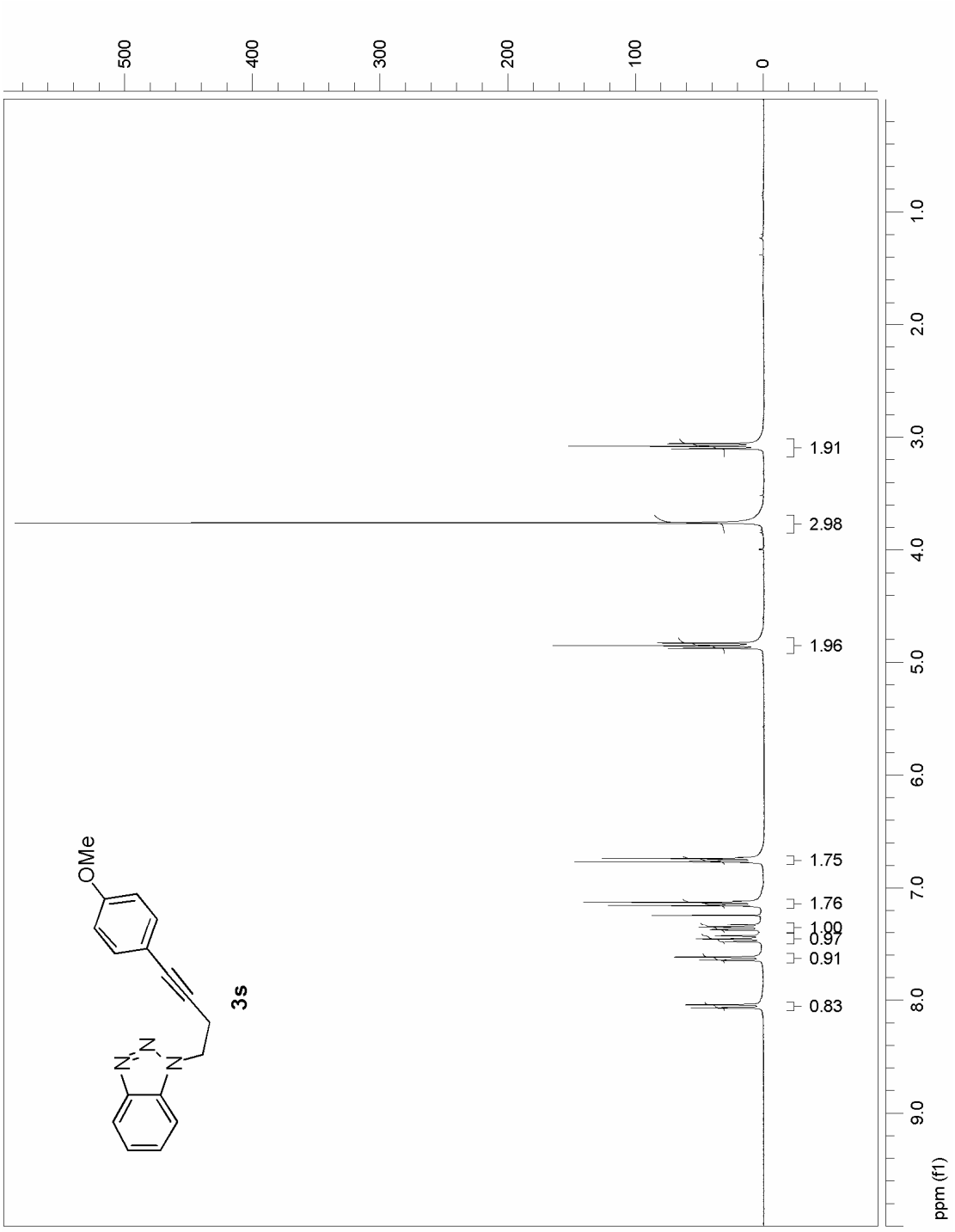

25000
20000
15000
10000
5000
0
50
100
150
ppm (f1)
3p

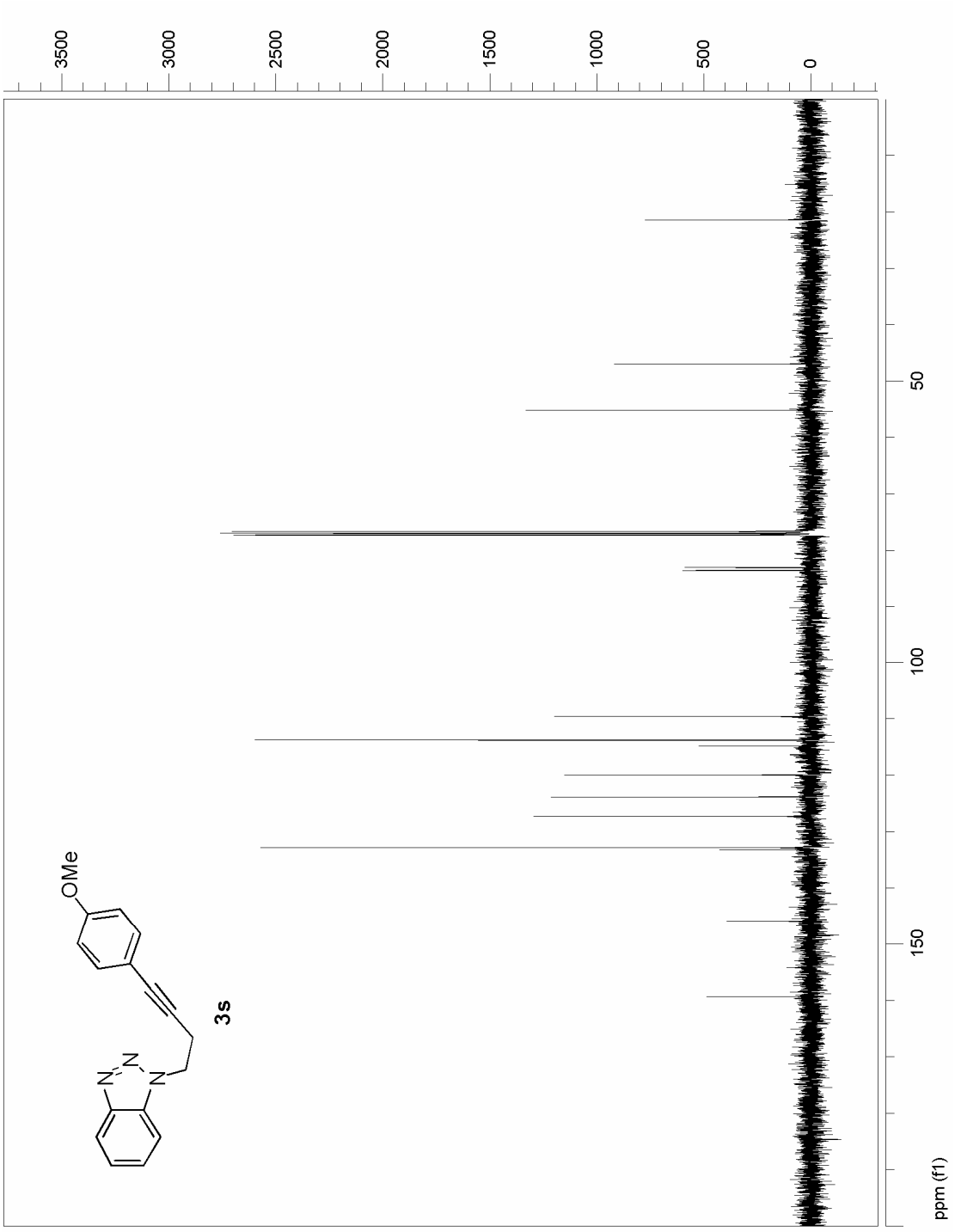

600
500
400
300
200
100
0
3.11
2.00
2.13
3.00
0.92
5.0
ppm (f1)
N
N
N
CO2Et
3q

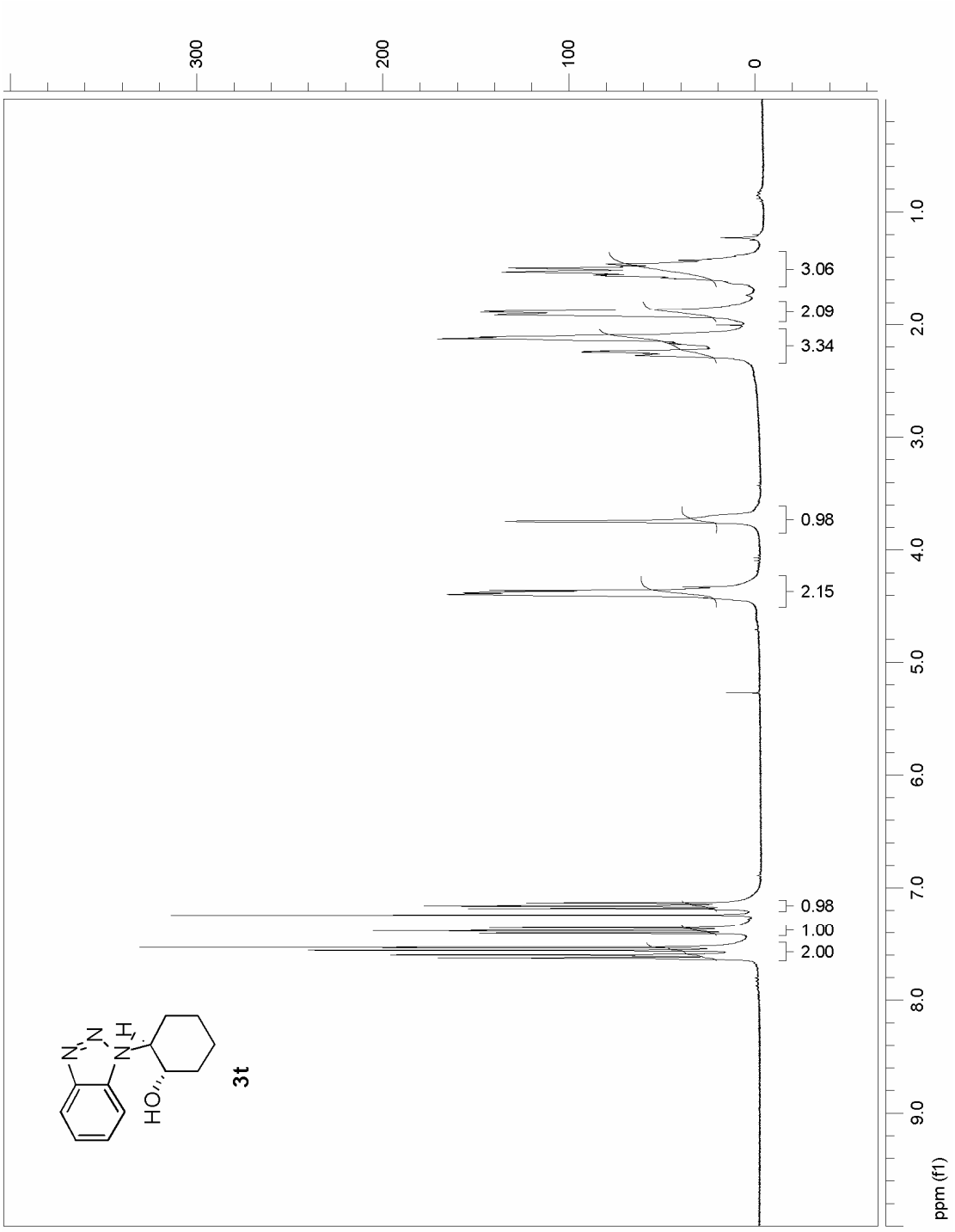

3000
2000
1000
0
50
100
150
ppm (f1)
CO2Et
3q

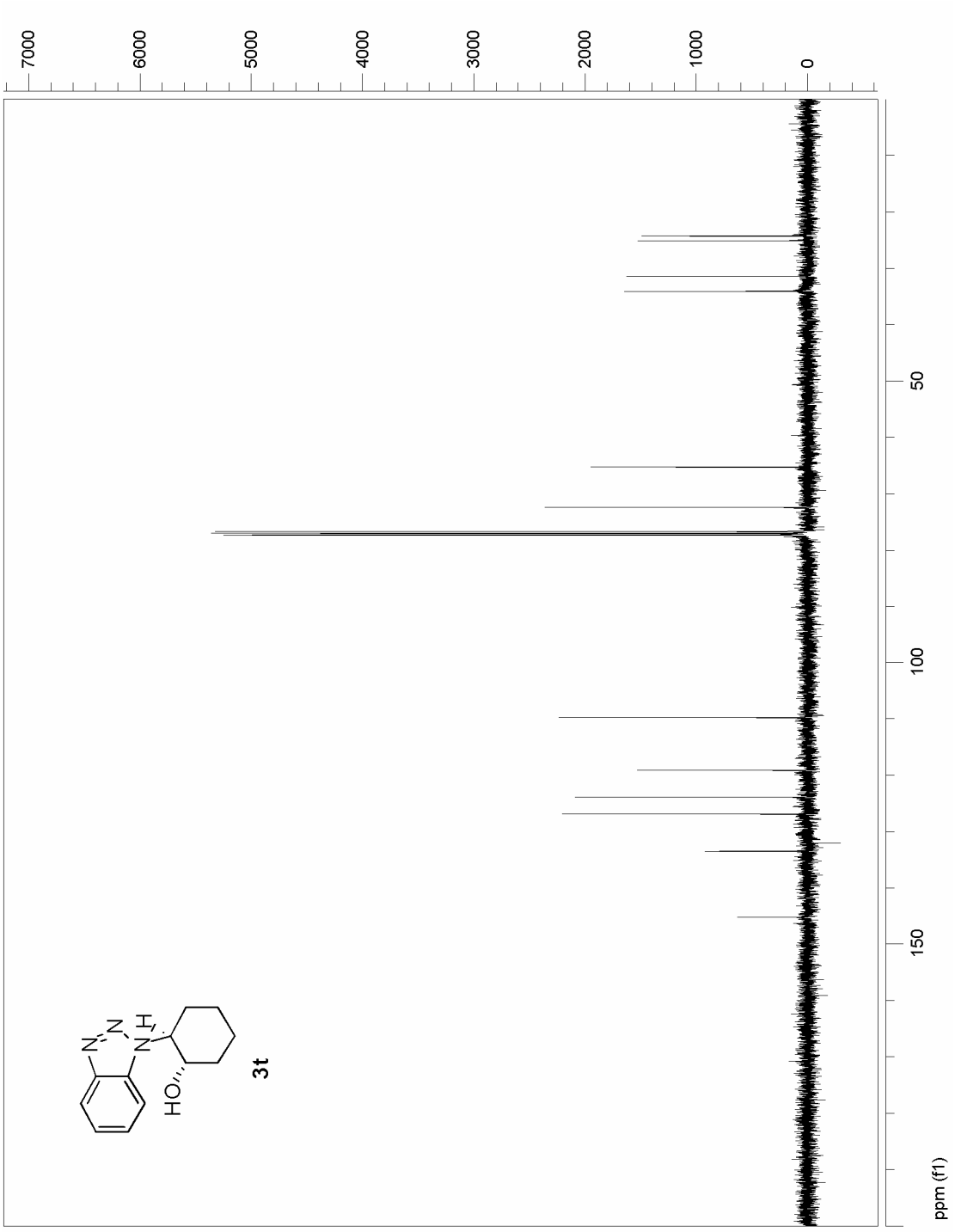

500
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (f1)
7.00
0.89
0.81
3r

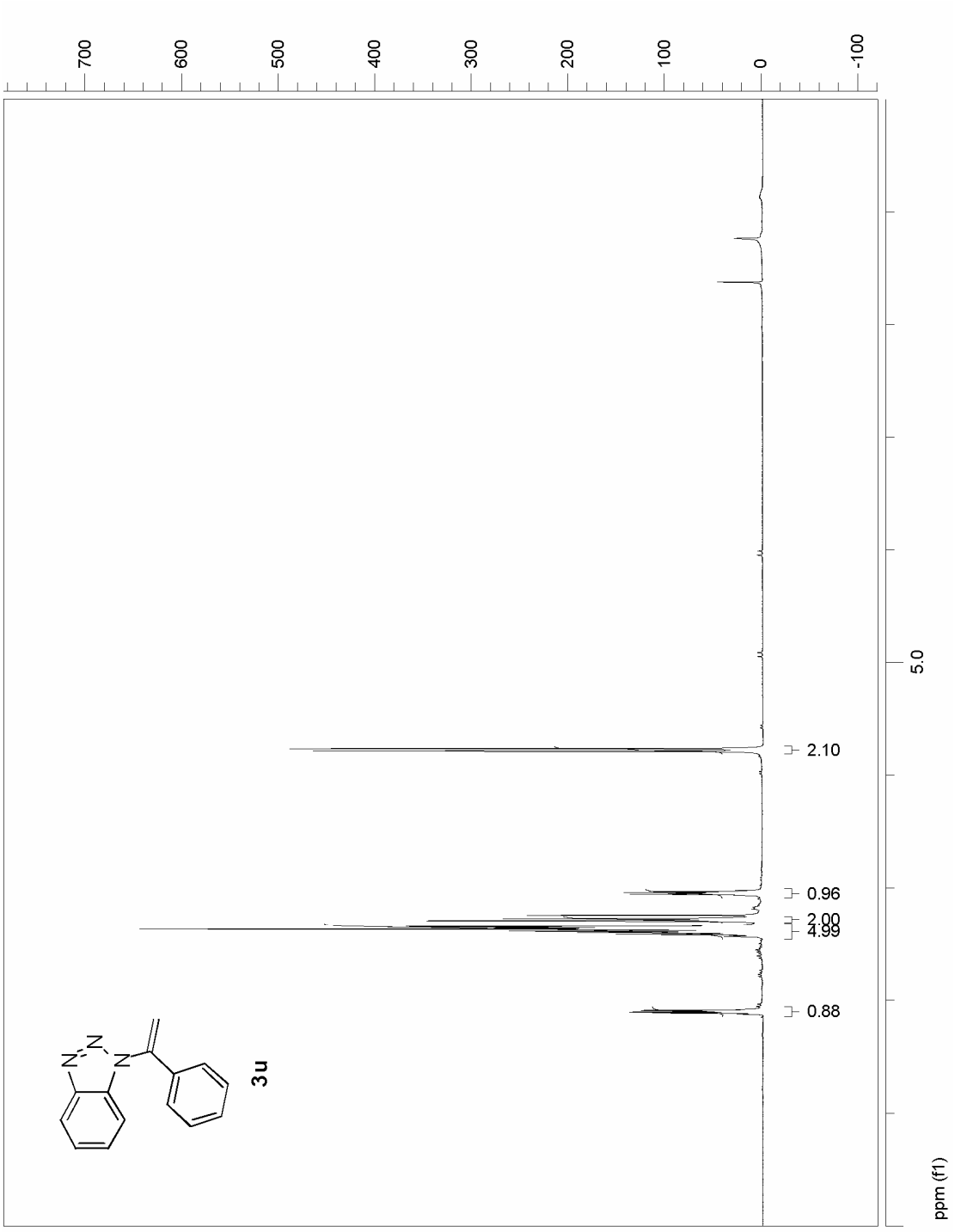

5000
4000
3000
2000
1000
0
50
100
150
ppm (f1)
3r

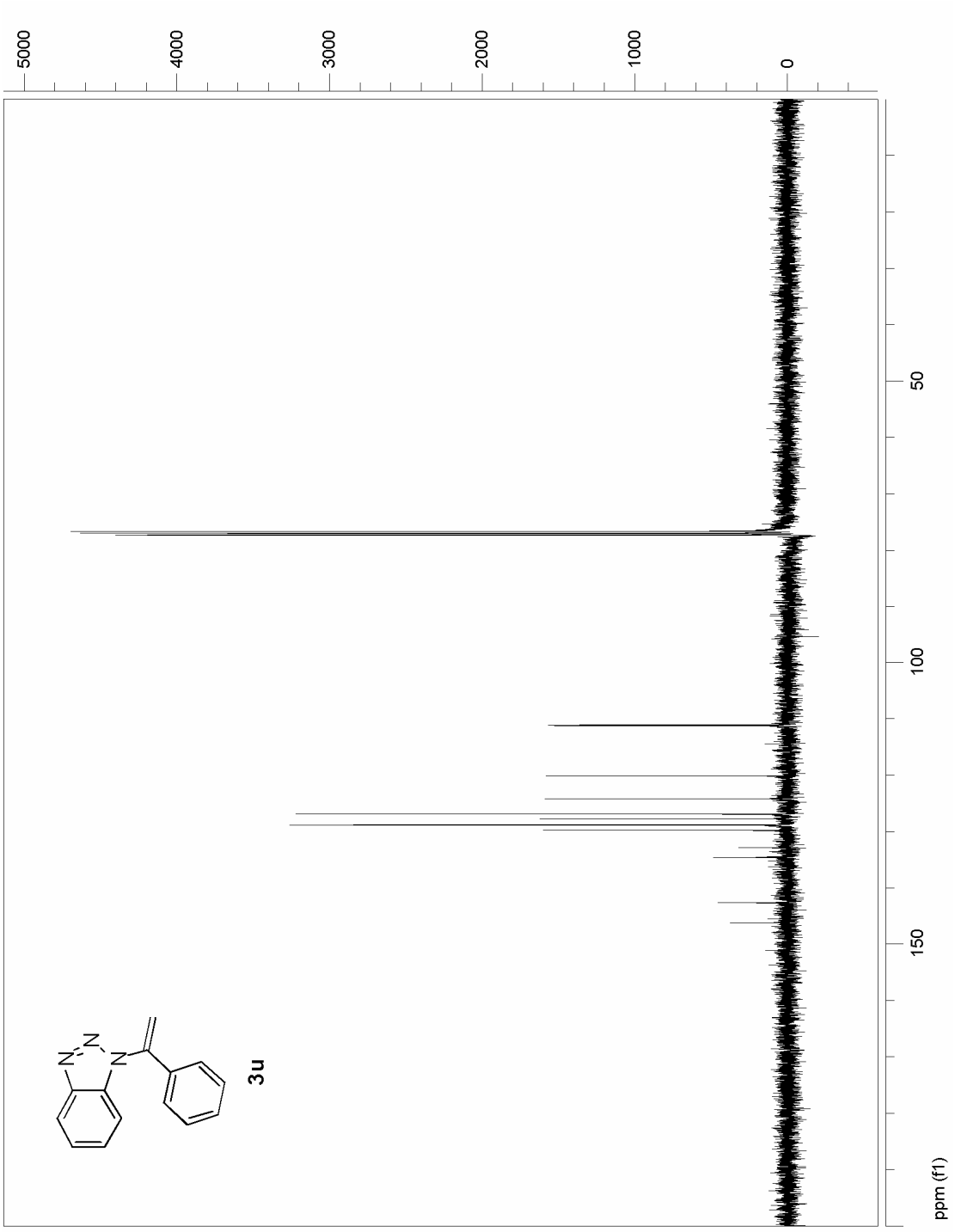

500
400
300
200
100
0
1.91
2.98
1.96
1.75
1.76
1.00
0.97
0.91
0.83
OMe
3s
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (f1)


3500
3000
2500
2000
1500
1000
500
0
50
100
150
ppm (f1)
OMe
N
N
N
3s


300
200
100
0
3.06
2.09
3.34
0.98
2.15
0.98
1.00
2.00
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (f1)
HO
3t


7000
6000
5000
4000
3000
2000
1000
0
50
100
150
ppm (f1)
HO
3t


700
600
500
400
300
200
100
0
-100
5.0
2.10
0.96
2.00
4.99
0.88
ppm (f1)
3u


5000
4000
3000
2000
1000
0
50
100
150
ppm (f1)
3u