Supplementary Material (ESI) for Chemical Communications

Supporting Information

[Fe(F_{20}TPP)Cl] Catalyzed Intramolecular C–N Bond Formation for Alkaloid Synthesis Using Aryl Azides as Nitrogen Source

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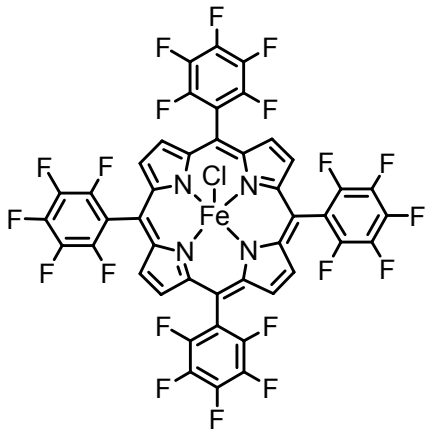
General: Reagents were obtained commercially and used without further purification unless otherwise indicated. 1,2-Dichloroethane was freshly distilled from calcium hydride under a nitrogen atmosphere. 4 Å molecular sieves were dried at 300 °C for 3 h prior to use. Flash column chromatography (silica gel, 230–400 mesh) was performed using a gradient solvent system (EtOAc/*n*-hexane as eluent unless specified otherwise). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX–300 or DPX–400 spectrometer. Chemical shifts (δ ppm) were determined with tetramethylsilane (TMS) as internal reference. Mass spectra were recorded on a Finnigan MAT 95 mass spectrometer.

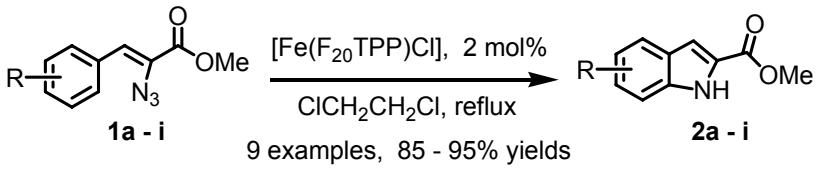


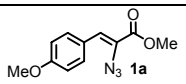
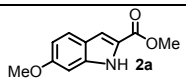
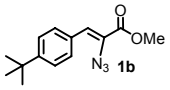
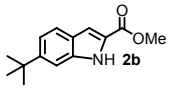
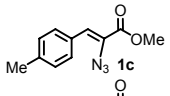
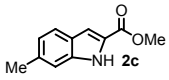
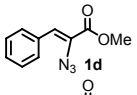
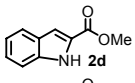
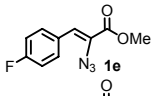
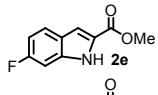
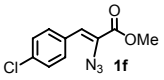
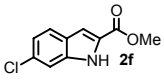
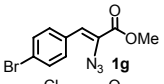
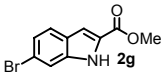
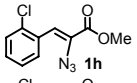
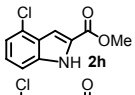
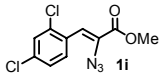
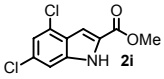
$Fe(F_{20}TPP)Cl$

Figure S1. [$Fe(F_{20}TPP)Cl$]

General Procedure for [$Fe(F_{20}TPP)Cl$] Catalyzed Intramolecular C–N Bond Formation: To a mixture of azide (0.20 mmol), [$Fe(F_{20}TPP)Cl$] (0.004 mmol) and 4Å MS (60 mg), 1 mL of 1,2-dichloroethane was added. Then the reaction mixture was heat to reflux and keep at this temperature under nitrogen. After complete consumption of the azide monitored by TLC, the mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography.

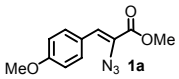
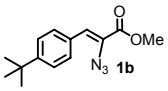
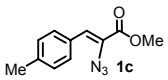
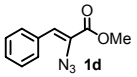
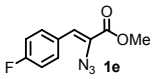
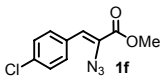
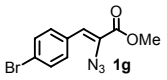
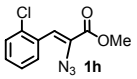
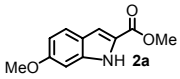
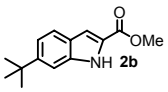
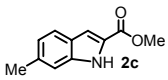
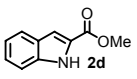
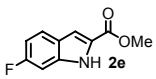
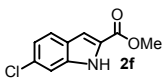
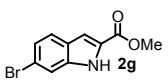
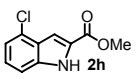
Table S1. [Fe(F_{20}TPP)Cl] Catalyzed Indole Formation[a]

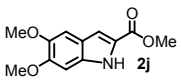


entry	substrate	product	time (h)	Yield (%)[b]
1			18	95
2			18	93
3			18	93
4			18	91
5			18	90
6			24	89
7			24	89
8			30	88
9			48	85

[a] All reactions were performed with 0.20 mmol azide, 0.004 mmol [Fe(F_{20}TPP)Cl], and 60 mg 4 Å molecular sieves in 1 mL of anhydrous $ClCH_2CH_2Cl$ under N_2. [b] Isolated yield.

Reported Compounds in Literature.

Compounds	References
	Coowar, D.; Bouissac, J.; Hanbali, M.; Paschaki, M.; Mohier, E.; Luu, B. *J. Med. Chem.* **2004**, *47*, 6270–6282.
	Stokes, B. J.; Dong, H.; Leslie, B. E.; Pumphrey, A. L.; Driver, T. G. *J. Am. Chem. Soc.* **2007**, *129*, 7500–7501.
	Alves, M. J.; Gilchrist, T. L. *J. Chem. Soc., Perkin Trans. 1,* **1998**, 299–303.
	Sechi, M.; Derudas, M.; Dallocchio, R.; Dessi, A.; Bacchi, A.; Sannia, L.; Carta, F.; Palomba, M.; Ragab, O.; Chan, C.; Shoemaker, R.; Sei, S.; Dayam, R.; Neamati, N. *J. Med. Chem.* **2004**, *47*, 5298–5310.
	Lehmann, F.; Holm, M.; Laufer, S. *Tetrahedron Lett.* **2009**, *50*, 1708–1709.
	Stokes, B. J.; Dong, H.; Leslie, B. E.; Pumphrey, A. L.; Driver, T. G. *J. Am. Chem. Soc.* **2007**, *129*, 7500–7501.
	Stokes, B. J.; Dong, H.; Leslie, B. E.; Pumphrey, A. L.; Driver, T. G. *J. Am. Chem. Soc.* **2007**, *129*, 7500–7501.
	Stokes, B. J.; Dong, H.; Leslie, B. E.; Pumphrey, A. L.; Driver, T. G. *J. Am. Chem. Soc.* **2007**, *129*, 7500–7501.
	Coowar, D.; Bouissac, J.; Hanbali, M.; Paschaki, M.; Mohier, E.; Luu, B. *J. Med. Chem.* **2004**, *47*, 6270–6282.
	Stokes, B. J.; Dong, H.; Leslie, B. E.; Pumphrey, A. L.; Driver, T. G. *J. Am. Chem. Soc.* **2007**, *129*, 7500–7501.
	Stokes, B. J.; Dong, H.; Leslie, B. E.; Pumphrey, A. L.; Driver, T. G. *J. Am. Chem. Soc.* **2007**, *129*, 7500–7501.
	Sechi, M.; Derudas, M.; Dallocchio, R.; Dessi, A.; Bacchi, A.; Sannia, L.; Carta, F.; Palomba, M.; Ragab, O.; Chan, C.; Shoemaker, R.; Sei, S.; Dayam, R.; Neamati, N. *J. Med. Chem.* **2004**, *47*, 5298–5310.
	Blair, J. B.; Kurrasch-Orbaugh, D.; Marona-Lewicka, D.; Cumbay, M. G.; Watts, V. J.; Barker, E. L.; Nichols, D. E. *J. Med. Chem.* 2000, 43, 4701–4710.
	Stokes, B. J.; Dong, H.; Leslie, B. E.; Pumphrey, A. L.; Driver, T. G. *J. Am. Chem. Soc.* **2007**, *129*, 7500–7501.
	Stokes, B. J.; Dong, H.; Leslie, B. E.; Pumphrey, A. L.; Driver, T. G. *J. Am. Chem. Soc.* **2007**, *129*, 7500–7501.
	Stokes, B. J.; Dong, H.; Leslie, B. E.; Pumphrey, A. L.; Driver, T. G. *J. Am. Chem. Soc.* **2007**, *129*, 7500–7501.



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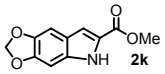

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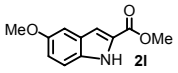

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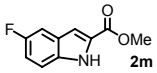

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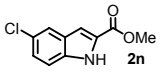

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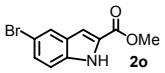

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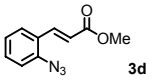

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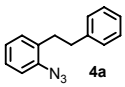

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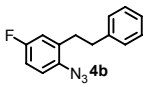

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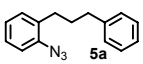

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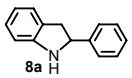

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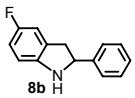

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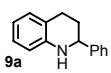
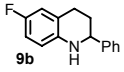


Han, Z. Y.; Xiao, H.; Chen, X. H.; Gong, L. Z. *J. Am. Chem. Soc.* **2009**, *131*, 9182–9183.



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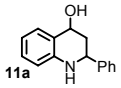

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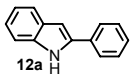

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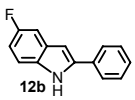

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13g

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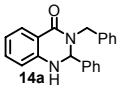
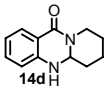


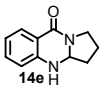
14a

Mucedda, M.; Muroni, D.; Saba, A.; Manassero, C. *Tetrahedron* **2007**, *63*, 12232–12238.



14d

Bowman, W. R.; Elsegood, M. R. J.; Stein, T.; Weaver, G. W. *Org. Biomol. Chem.* **2007**, *5*, 103–113.



14e

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14h

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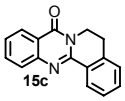
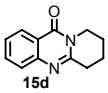


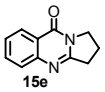
15c

Bowman, W. R.; Elsegood, M. R. J.; Stein, T.; Weaver, G. W. *Org. Biomol. Chem.* **2007**, *5*, 103–113.



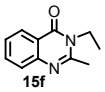
15d

Bowman, W. R.; Elsegood, M. R. J.; Stein, T.; Weaver, G. W. *Org. Biomol. Chem.* **2007**, *5*, 103–113.



15e

Zhang, C.; De, C. K.; Mal, R.; Seidel, D. *J. Am. Chem. Soc.* **2008**, *130*, 416–417.



15f

Dabiri, M.; Salehi, P.; Mohammadi, A. A.; Baghbanzadeh, M. *Synth. Comm.* **2005**, *35*, 279–287.

15g

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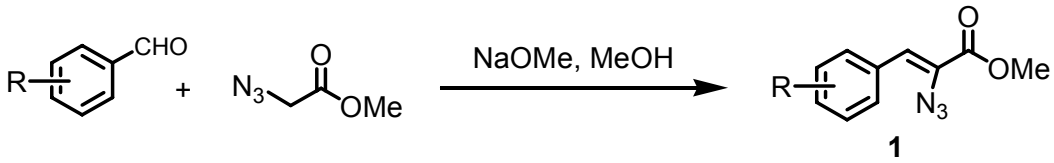
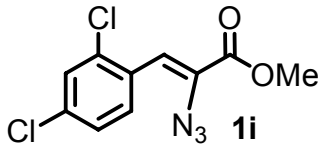
Compounds Preparation and Characterization Data:

Preparation of α-azido-cinnamates 1



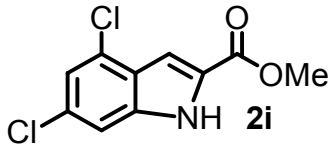
1

α-azido-cinnamates **1** were prepared according to the reported methods (Stokes, B. J.; Dong, H.; Leslie, B. E.; Pumphrey, A. L.; Driver, T. G. *J. Am. Chem. Soc.* **2007**, *129*, 7500–7501; Sechi, M.; Derudas, M.; Dallocchio, R.; Dessi, A.; Bacchi, A.; Sannia, L.; Carta, F.; Palomba, M.; Ragab, O.; Chan, C.; Shoemaker, R.; Sei, S.; Dayam, R.; Neamati, N. *J. Med. Chem.* **2004**, *47*, 5298–5310.)



1i

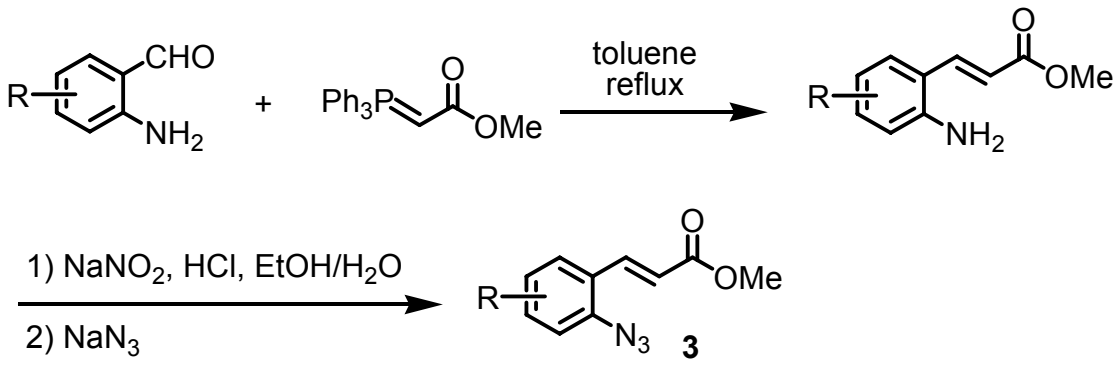
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.6 Hz, 1H), 7.42 (d, J = 2.1 Hz, 1H), 7.27 (m, 1H), 7.21 (s, 1H),3.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.60, 135.31, 135.24, 131.80, 129.72, 129.50, 127.58, 127.04, 119.26, 53.25. MS (EI) *m/z* 270 (M^+); HRMS (EI) *m/z* for $C_{10}H_7Cl_2N_3O_2$ (M^+) calcd 270.9915, found 270.9912.



2i

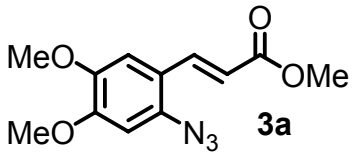
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (br s, 1H), 7.34 (s, 1H), 7.29 (s, 1H), 7.19 (s, 1H), 3.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.08, 137.49, 130.44, 128.16, 127.89, 124.90, 120.62, 110.66, 106.84, 51.91. MS (EI) *m/z* 242 (M^+); HRMS (EI) *m/z* for $C_{10}H_7Cl_2NO_2$ (M^+) calcd 242.9853, found 242.9851.

Preparation of *ortho*-azido-cinnamates 3



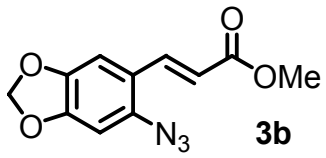
ortho-Azido-cinnamates **3** were prepared from *ortho*-amino-cinnamates according to the reported method (De Carvalho, M.; Sorrilha, A. E. P. M.; Rodrigues, J. A. R. *J. Braz. Chem. Soc.*, **1999**, *10*, 415-420.)

Methyl *ortho*-amino-cinnamates (0.5 mmol, easily prepared by Wittig Reaction of *ortho*-amino-benzaldehydes with $Ph_3P{=}CHCO_2Me$) was dissolved in hydrochloric acid (aqueous 35%, 1 mL) and ethanol (10 mL), The solution was cooled to 0 °C and a solution of sodium nitrite (1.5 mmol) in water (3 mL) was added in 5 min. After the mixture had been stirred for a further 0.5 h at 0 °C, a solution of sodium azide (1.5 mmol) in water (3 mL) was added in 15 min. The mixture was stirred for 3 h at 0 °C and diluted with water (100 mL), extracted with diethyl ether (5 x 20 mL), washed with aqueous sodium bicarbonate solution (1 x 20 mL), dried with anhydrous magnesium sulfate, filtered and concentrated under reduced pressure and the residue was purified by flash column chromatography (75 – 85% yields).



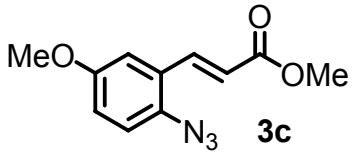
3a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 16.1 Hz, 1H), 7.01 (s, 1H), 6.63 (s, 1H), 6.32 (d, *J* = 16.1 Hz, 1H), 3.95 (s, 3H), 3.89 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.49, 152.04, 146.63, 138.62, 132.54, 118.10, 116.69, 109.30, 101.61, 56.18, 51.69. MS (EI) *m/z* 263 (M^+); HRMS (EI) *m/z* for $C_{12}H_{13}N_3O_4$ (M^+) calcd 263.0906, found 263.0901.



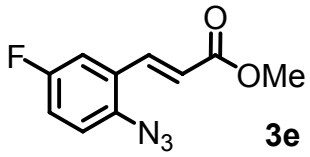
3b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 16.0 Hz, 1H), 7.01 (s, 1H), 6.68 (s, 1H), 6.25 (d, *J* = 16.0 Hz, 1H), 6.02 (s, 2H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.46, 150.63, 145.56, 138.53, 134.11, 119.47, 116.87, 105.99, 102.20, 99.44, 51.72. MS (EI) *m/z* 247 (M^+); HRMS (EI) *m/z* for $C_{11}H_9N_3O_4$ (M^+) calcd 247.0593, found 247.0585.



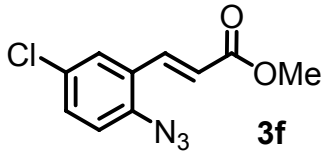
3c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 16.1 Hz, 1H), 7.10 (d, *J* = 8.7 Hz, 1H), 7.05 (d, *J* = 2.7 Hz, 1H), 6.97 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.44 (d, *J* = 16.1 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.11, 156.68, 138.94, 131.80, 126.70, 119.85, 119.50, 117.71, 112.17, 55.59, 51.75. MS (EI) *m/z* 233 (M^+); HRMS (EI) *m/z* for $C_{11}H_{11}N_3O_3$ (M^+) calcd 233.0800, found 233.0796.



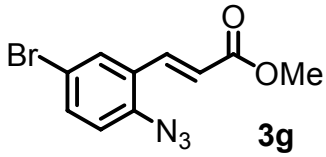
3e

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 16.1, 1.3 Hz, 1H), 7.26 (m, 1H), 7.14 (m, 2H), 6.43 (d, *J* = 16.1 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.81, 161.24, 157.99, 137.89, 137.86, 135.00, 120.56, 120.23, 120.12, 118.44, 118.13, 114.37, 114.06, 51.85. MS (EI) *m/z* 221 (M^+); HRMS (EI) *m/z* for $C_{10}H_8FN_3O_2$ (M^+) calcd 221.0600, found 221.0598.



3f

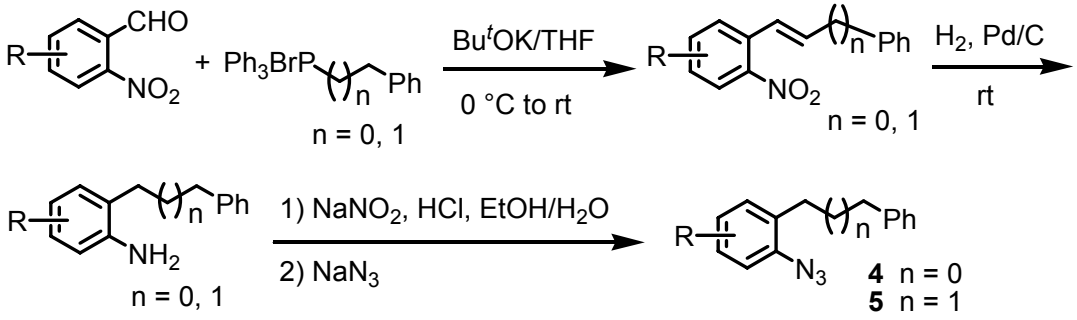
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 16.1 Hz, 1H), 7.52 (d, *J* = 2.3 Hz, 1H), 7.35 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.14 (d, *J* = 8.6 Hz, 1H), 6.45 (d, *J* = 16.1 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.82, 137.70, 131.00, 130.42, 127.80, 127.41, 120.65, 120.04, 51.88. MS (EI) *m/z* 237 (M^+); HRMS (EI) *m/z* for $C_{10}H_8ClN_3O_2$ (M^+) calcd 237.0305, found 237.0298.



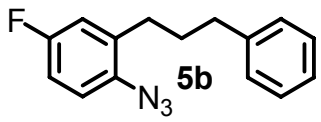
3g

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, *J* = 16.1 Hz, 1H), 7.67 (d, *J* = 2.2 Hz, 1H), 7.49 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.06 (d, *J* = 8.6 Hz, 1H), 6.45 (d, *J* = 16.1 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.83, 138.25, 137.64, 133.89, 130.81, 127.82, 120.70, 120.36, 117.92, 51.91. MS (EI) *m/z* 280 (M^+); HRMS (EI) *m/z* for $C_{10}H_8BrN_3O_2$ (M^+) calcd 280.9800, found 280.9795.

Preparation of *ortho*-azido-phenylethane 4 and phenylpropane 5

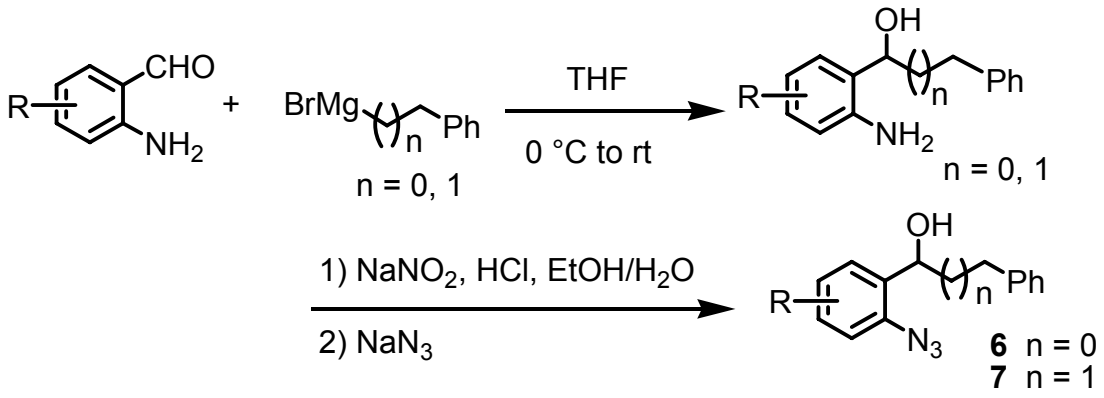


To a suspension of triphenyl ylide (1.5 mmol) in anhydrous THF, Bu^{t}OK (2.25 mmol) was added at 0 °C and a red to dark red solution was obtained immediately. After stirring at 0 °C for a further 30 min, *ortho*-nitro-benzaldehyde (1 mmol) was added and the reaction mixture was warmed to room temperature slowly. The reaction was monitored by TLC. The reaction mixture was diluted with aqueous NH_4Cl after an overnight stirring and extracted by diethyl ether (3 x 40 mL). A mixture of *cis*- and *trans*-alkene was obtained. Both the nitroalkene isomers were reduced when the *cis*- and *trans*-mixture of alkenes were vigorously stirred with Pd/C (Pd, 10 wt % on carbon powder) in THF at room temperature under a hydrogen atmosphere for 1 day. After filtered through a pad of Celite, crude aniline was obtained. The crude aniline was further transformed to *ortho*-azido-phenylethanes **4** and phenylpropanes **5** following the method for preparation *ortho*-azido-cinnamates **3**.

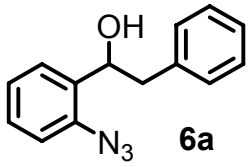


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (m, 2H), 7.18 (m, 3H), 7.02 (m, 1H), 6.89 (m, 2H), 2.68-2.56 (m, 4H), 1.87 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.93, 158.51, 141.92, 135.92, 135.84, 133.75, 133.72, 128.37, 125.88, 119.27, 119.18, 117.17, 116.92, 114.02, 113.79, 35.51, 31.48, 30.88. MS (EI) *m/z* 255 (M^+); HRMS (EI) *m/z* for $C_{15}H_{14}FN_3$ (M^+) calcd 255.1172, found 255.1173.

Preparation of (*ortho*-azido-phenyl)-phenylethanol 6 and (*ortho*-azido-phenyl)-phenylpropanol 7

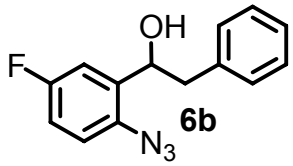


To a solution of *ortho*-amino-benzaldehyde (1 mmol) in anhydrous THF (20 mL), benzyl magnesium bromide or phenylethylmagnesium bromide (2 mmol, freshly prepared in THF) was added at 0 °C. After stirring at 0 °C for a further 3 h, the reaction mixture was diluted with aqueous $NaHCO_3$ and extracted by ethyl acetate (3 x 40 mL). The crude (*ortho*-amino-phenyl)-phenylethanol or (*ortho*-amino-phenyl)-phenylpropanol was obtained when the extract was concentrated, and was further transformed to (*ortho*-azido-phenyl)-phenylethanol **6** and (*ortho*-azido-phenyl)-phenylpropanol **7** following the method for preparation *ortho*-azido-cinnamates **3**.



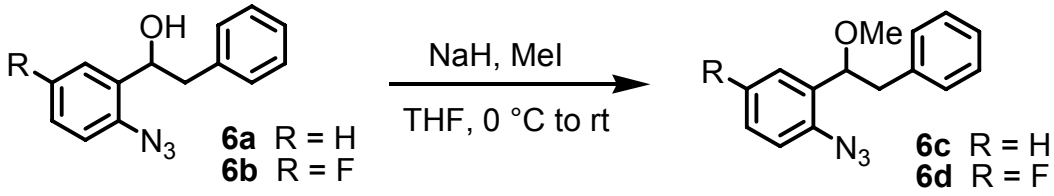
6a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.9 Hz, 1H), 7.27 (m, 3H), 7.19 (m, 3H), 7.10 (m, 2H), 5.05 (dd, J = 8.7, 4.1 Hz, 1H), 3.04 (dd, J = 13.7, 4.1 Hz, 1H), 2.79 (dd, J = 13.7, 8.7 Hz, 1H), 2.30 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.15, 136.26, 134.98, 129.44, 128.42, 128.35, 127.04, 126.51, 124.92, 117.81, 70.50, 44.59. MS (EI) *m/z* 239 (M^+); HRMS (EI) *m/z* for $C_{14}H_{13}N_3O$ (M^+) calcd 239.1059, found 239.1055.

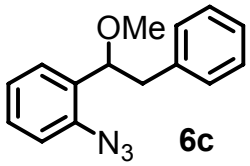


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (m, 2H), 7.20 (m, 4H), 7.02 (m, 1H), 6.97 (m, 1H), 5.01 (m, 1H), 3.03 (dd, *J* = 13.7, 3.8 Hz, 1H), 2.72 (dd, *J* = 13.7, 8.9 Hz, 1H), 2.29 (d, *J* = 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.28, 158.85, 137.72, 137.32, 137.25, 131.86, 131.83, 129.43, 129.40, 128.48, 126.72, 119.15, 119.07, 115.22, 114.99, 114.18, 113.94, 70.03, 44.45. MS (EI) *m/z* 257 (M^+); HRMS (EI) *m/z* for $C_{14}H_{12}FN_3O$ (M^+) calcd 257.0964, found 257.0962.

Preparation of methyl (*ortho*-azido-phenyl)-phenylethyl ether 6c and 6d

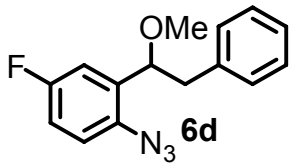


To a solution of **6a** or **6b** (1 mmol) in anhydrous THF (15 mL), NaH (2 mmol, 60% in oil) was added at 0 °C. After the mixture had been stirred for a further 0.5 h at 0 °C, MeI (2 mmol) was added. The mixture was diluted with water (100 mL), extracted with diethyl ether (3 x 40 mL), washed with aqueous NH_4Cl solution (1 x 20 mL), dried with anhydrous magnesium sulfate, filtered and concentrated under reduced pressure and the residue was purified by flash column chromatography (75 – 85% yields).



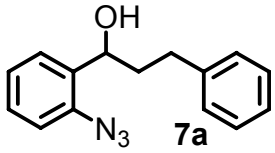
6c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.9 Hz, 1H), 7.27-7.21 (m, 3H), 7.20-7.08 (m, 5H), 4.71 (m, 1H), 3.15 (s, 3H), 2.91 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.52, 137.53, 133.24, 129.41, 128.52, 128.00, 127.21, 126.17, 124.99, 117.89, 79.08, 57.07, 43.58. MS (EI) *m/z* 253 (M^+); HRMS (EI) *m/z* for $C_{15}H_{15}N_3O$ (M^+) calcd 253.1215, found 253.1213.



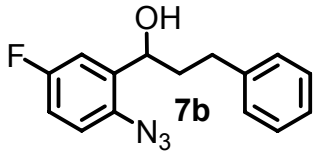
6d

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.11 (m, 6H), 7.05 (m, 1H), 6.97 (m, 1H), 4.66 (m, 1H), 3.17 (s, 3H), 2.88 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.51, 159.08, 138.09, 135.79, 135.73, 133.17, 133.14, 129.42, 128.07, 128.03, 126.34, 119.31, 119.23, 115.49, 115.25, 114.18, 113.94, 78.89, 57.27, 43.41. MS (EI) *m/z* 271 (M^+); HRMS (EI) *m/z* for $C_{15}H_{14}FN_3O$ (M^+) calcd 271.1121, found 271.1123.

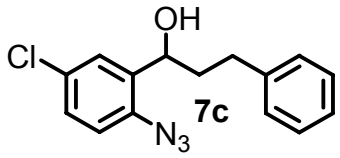


7a

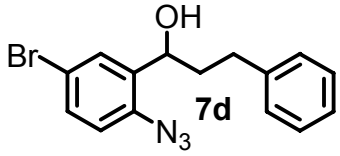
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.9 Hz, 1H), 7.27 (m, 3H), 7.19 (m, 3H), 7.10 (m, 2H), 4.87 (m, 1H), 2.78 (m, 1H), 2.65 (m, 1H), 2.35 (br s, 1H), 2.04 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.75, 136.55, 135.54, 128.55, 128.40, 128.34, 127.26, 125.83, 125.02, 118.04, 69.58, 39.14, 32.15. MS (EI) *m/z* 253 (M^+); HRMS (EI) *m/z* for $C_{15}H_{15}N_3O$ (M^+) calcd 253.1215, found 253.1217.



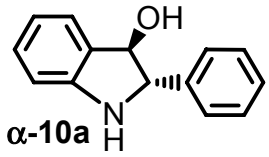
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (m, 2H), 7.16 (m, 4H), 7.00 (m, 1H), 6.94 (m, 1H), 4.82 (m, 1H), 2.75 (m, 1H), 2.63 (m, 1H), 2.62 (br s, 1H), 1.96 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.23, 158.80, 141.44, 137.95, 137.89, 131.99, 128.39, 125.87, 119.26, 119.18, 115.21, 114.98, 114.21, 113.97, 68.79, 38.95, 31.90. MS (EI) *m/z* 271 (M^+); HRMS (EI) *m/z* for $C_{15}H_{14}FN_3O$ (M^+) calcd 271.1121, found 271.1119.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (m, 1H), 7.29-7.14 (m, 6H), 7.00 (d, *J* = 8.5 Hz, 1H), 4.83 (m, 1H), 2.79 (m, 1H), 2.64 (m, 1H), 2.38 (br s, 1H), 2.00 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.44, 137.41, 134.98, 130.49, 128.38, 127.35, 125.92, 119.23, 68.95, 38.99, 32.00. MS (EI) *m/z* 287 (M^+); HRMS (EI) *m/z* for $C_{15}H_{14}ClN_3O$ (M^+) calcd 287.0825, found 287.0828.

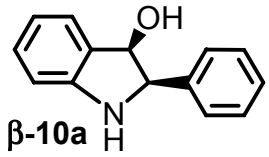


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (m, 1H), 7.42-7.15 (m, 6H), 6.93 (d, *J* = 8.4 Hz, 1H), 4.81 (m, 1H), 2.80 (m, 1H), 2.64 (m, 1H), 2.47 (br s, 1H), 1.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.40, 137.70, 135.50, 131.23, 130.21, 128.34, 125.88, 119.53, 118.11, 68.80, 38.97, 31.96. MS (EI) *m/z* 331 (M^+); HRMS (EI) *m/z* for $C_{15}H_{14}BrN_3O$ (M^+) calcd 331.0320, found 331.0315.



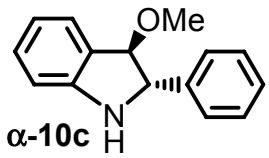
α-10a (Isolated during the reaction process)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (m, 2H), 7.43-7.31 (m, 4H), 7.23 (m, 1H), 6.78-6.86 (m, 2H), 5.18 (m, 1H), 4.90 (d, *J* = 6.4 Hz, 1H), 4.22 (br s, 1H), 1.32 (d, *J* = 6.8 Hz, 1H).



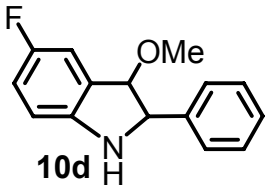
β-10a (Isolated during the reaction process)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.24 (m, 6H), 7.20 (m, 1H), 6.83 (t, *J* = 7.3 Hz, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 5.07 (d, *J* = 4.7 Hz, 1H), 4.69 (d, *J* = 5.0 Hz, 1H), 4.23 (br s, 1H), 2.13 (br s, 1H).



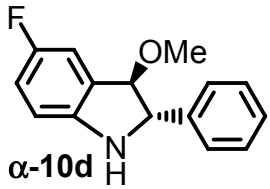
α-10c (Isolated during the reaction process)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (m, 2H), 7.39-7.28 (m, 4H), 7.19 (m, 1H), 6.81 (m, 2H), 4.85 (d, *J* = 6.3 Hz, 1H), 4.74 (d, *J* = 6.3 Hz, 1H), 4.21 (br s, 1H), 3.02 (s, 3H).



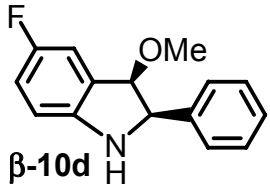
10d

(*cis* : *trans* = 1 : 0.58, the mixture cannot be separated by flash column chromatography)



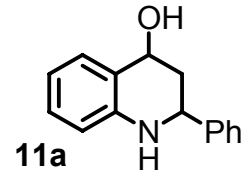
α-10d

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.24 (m, 5H), 7.05 (m, 1H), 6.90 (m, 1H), 6.68 (m, 1H), 4.84 (d, *J* = 6.4 Hz, 1H), 4.70 (d, *J* = 6.4 Hz, 1H), 4.11 (br s, 1H), 3.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.46, 128.15, 127.72, 126.13, 116.40, 116.17, 113.34, 113.11, 110.76, 110.68, 82.26, 82.25, 68.20, 56.92. MS (EI) *m/z* 243 (M^+); HRMS (EI) *m/z* for $C_{15}H_{14}FNO$ (M^+) calcd 243.1059, found 243.1057.



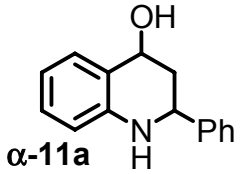
β-10d

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (m, 1H), 7.36-7.25 (m, 4H), 7.00 (m, 1H), 6.90 (m, 1H), 6.66 (m, 1H), 4.78 (d, *J* = 3.6 Hz, 1H), 4.72 (d, *J* = 3.6 Hz, 1H), 4.12 (br s, 1H), 3.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.62, 128.84, 128.15, 127.72, 116.67, 116.44, 113.21, 112.98, 110.25, 110.17, 89.25, 89.24, 68.90, 56.04. MS (EI) *m/z* 243 (M^+); HRMS (EI) *m/z* for $C_{15}H_{14}FNO$ (M^+) calcd 243.1059, found 243.1058.



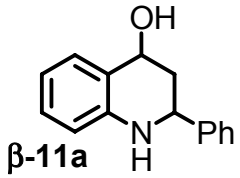
11a

(*dr* = 1:0.38, the mixture can not be separated by flash column chromatography)



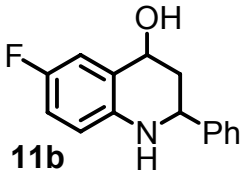
α-11a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.21 (m, 6H), 7.12 (m, 1H), 6.73 (m, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 4.77 (m, 1H), 4.57 (m, 1H), 2.18 (m, 1H), 1.94 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.17, 129.50, 128.70, 127.76, 126.90, 117.52, 114.77, 65.73, 51.31, 38.98. MS (EI) *m/z* 225 (M^+); HRMS (EI) *m/z* for $C_{15}H_{15}NO$ (M^+) calcd 225.1154, found 225.1158.



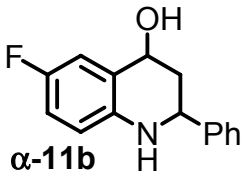
β-11a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.23 (m, 6H), 7.08 (m, 1H), 6.76 (m, 1H), 6.54 (d, *J* = 8.0 Hz, 1H), 5.04 (m, 1H), 4.57 (m, 1H), 2.41 (m, 1H), 2.13 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.26, 143.28, 128.80, 128.63, 127.88, 127.01, 126.55, 124.43, 117.93, 114.12, 67.30, 55.68, 41.35. MS (EI) *m/z* 225 (M^+); HRMS (EI) *m/z* for $C_{15}H_{15}NO$ (M^+) calcd 225.1154, found 225.1157.



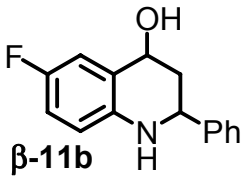
11b

(*dr* = 1:0.24, the mixture can not be separated by flash column chromatography)



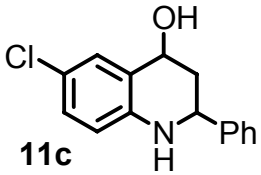
α-11b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.31 (m, 5H), 6.97 (dd, *J* = 8.8, 2.9 Hz, 1H), 6.88 (dt, *J* = 8.6, 2.9 Hz, 1H), 6.54 (dd, *J* = 8.8, 4.6 Hz, 1H), 4.72 (m, 1H), 4.52 (m, 1H), 2.16 (m, 1H), 1.95 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.70, 143.36, 141.04, 140.95, 128.72, 127.83, 126.86, 116.57, 116.34, 116.04, 115.82, 115.75, 115.67, 65.47, 51.52, 39.00. MS (EI) *m/z* 243 (M^+); HRMS (EI) *m/z* for $C_{15}H_{14}FNO$ (M^+) calcd 243.1059, found 243.1057.



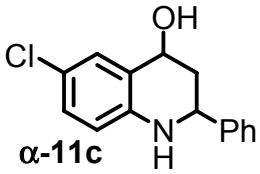
β-11b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.31 (m, 5H), 7.16 (dd, *J* = 9.4, 2.8 Hz, 1H), 6.78 (dt, *J* = 8.6, 2.8 Hz, 1H), 6.46 (dd, *J* = 8.6, 4.6 Hz, 1H), 5.00 (dd, *J* = 10.3, 5.9 Hz, 1H), 4.52 (m, 1H), 2.38 (m, 1H), 2.05 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.30, 154.96, 143.05, 140.50, 128.83, 127.97, 126.55, 125.71, 125.65, 115.44, 115.22, 115.01, 114.94, 113.52, 113.20, 67.22, 55.94, 41.13. MS (EI) *m/z* 243 (M^+); HRMS (EI) *m/z* for $C_{15}H_{14}FNO$ (M^+) calcd 243.1059, found 243.1055.



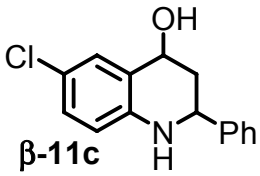
11c

(*dr* = 1:0.29, the mixture can not be separated by flash column chromatography)



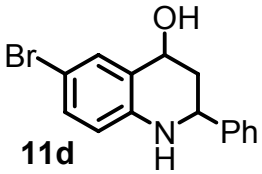
α-11c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.29 (m, 5H), 7.20 (d, *J* = 2.4 Hz, 1H), 7.05 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.51 (d, *J* = 8.6 Hz, 1H), 4.71 (m, 1H), 4.54 (m, 1H), 2.16 (m, 1H), 1.92 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.16, 143.13, 129.65, 129.34, 128.76, 127.90, 115.96, 65.31, 51.33, 38.67. MS (EI) *m/z* 259 (M^+); HRMS (EI) *m/z* for $C_{15}H_{14}ClNO$ (M^+) calcd 259.0764, found 259.0766.



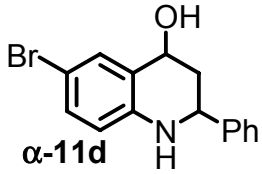
β-11c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.29 (m, 6H), 7.01 (m, 1H), 6.44 (d, *J* = 8.5 Hz, 1H), 4.98 (dd, *J* = 10.3, 5.7 Hz, 1H), 4.52 (m, 1H), 2.38 (m, 1H), 2.05 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.84, 142.75, 128.87, 128.43, 128.04, 126.84, 126.51, 125.83, 122.50, 115.20, 67.00, 55.66, 40.91. MS (EI) *m/z* 259 (M^+); HRMS (EI) *m/z* for $C_{15}H_{14}ClNO$ (M^+) calcd 259.0764, found 259.0768.



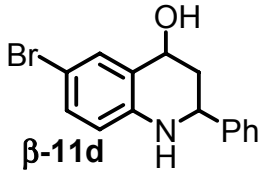
11d

(*dr* = 1:0.35, the mixture can not be separated by flash column chromatography)



α-11d

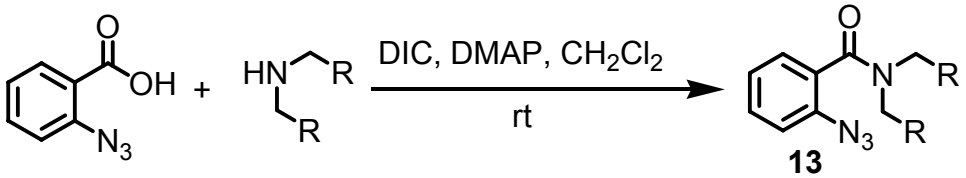
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.29 (m, 6H), 7.18 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.47 (d, *J* = 8.6 Hz, 1H), 4.70 (m, 1H), 4.53 (m, 1H), 2.15 (m, 1H), 1.90 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.57, 143.06, 132.53, 132.11, 128.76, 127.90, 126.83, 116.36, 108.61, 65.24, 50.95, 38.56. MS (EI) *m/z* 303 (M^+); HRMS (EI) *m/z* for $C_{15}H_{14}BrNO$ (M^+) calcd 303.0259, found 303.0255.



β-11d

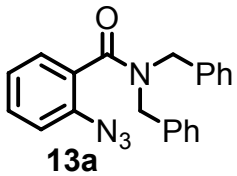
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (m, 1H), 7.43-7.29 (m, 5H), 7.12 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.40 (d, *J* = 8.5 Hz, 1H), 4.98 (dd, *J* = 10.3, 5.7 Hz, 1H), 4.53 (m, 1H), 2.36 (m, 1H), 2.03 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.16, 142.77, 131.24, 129.68, 128.87, 128.04, 126.50, 126.27, 115.60, 109.45, 66.92, 55.58, 40.82. MS (EI) *m/z* 303 (M^+); HRMS (EI) *m/z* for $C_{15}H_{14}BrNO$ (M^+) calcd 303.0259, found 303.0255.

Preparation of *ortho*-azidobenzamide derivatives 13



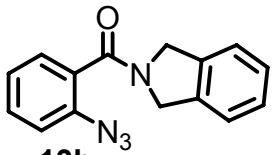
13

To a solution of *ortho*-azidobenzolic acid (1 mmol) in anhydrous CH_2Cl_2 (15 mL), diisopropylcarbodiimide (DIC, 1.5 mmol), DMAP (0.05 mmol) was added at room temperature. After the mixture had been stirred for a further 15 min, amine (2 mmol) was added. The mixture was concentrated under reduced pressure after stirring for 1 day and the residue was purified by flash column chromatography (70 – 85% yields).



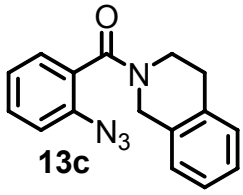
13a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.21 (m, 10H), 7.18-7.08 (m, 4H), 5.02 (br s, 1H), 4.38 (br s, 1H), 4.22 (br s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.03, 136.46, 135.92, 130.35, 128.69, 128.58, 128.33, 128.09, 127.91, 127.69, 127.44, 127.34, 125.08, 118.46, 51.06, 46.47. MS (EI) *m/z* 342 (M^+); HRMS (EI) *m/z* for $C_{11}H_{17}NO_2S_2$ (M^+) calcd 342.1481, found 342.1476.



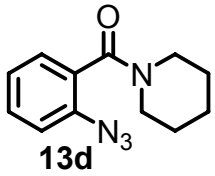
13b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (m, 1H), 7.36-7.28 (m, 3H), 7.25-7.18 (m, 3H), 7.12 (d, *J* = 7.1 Hz, 2H), 4.98 (m, 2H), 4.59 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.19, 136.06, 135.97, 135.88, 130.53, 128.97, 127.66, 127.42, 125.15, 122.87, 122.37, 118.54, 53.49, 51.84. MS (EI) *m/z* 235 ($[M\text{-}N_2\text{-}H]^+$); HRMS (EI) *m/z* for $C_{15}H_{11}N_2O$ ($[M\text{-}N_2\text{-}H]^+$) calcd 235.0871, found 235.0861.



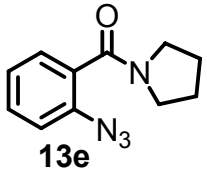
13c

^{1}H NMR (400 MHz, $CDCl_3$, tertiary amide, 1.5:1) δ 7.44 (m, 2.5H), 7.37-7.12 (m, 16.5H), 6.89 (d, *J* = 7.4 Hz, 1H), 4.97 (d, *J* = 15.8 Hz, 1.5H), 4.88 (d, *J* = 15.8 Hz, 1.5H), 4.46 (d, *J* = 15.9 Hz, 1H), 4.33 (d, *J* = 15.9 Hz, 1H), 4.13 (m, 1H), 3.89 (m, 1H), 3.48 (m, 3H), 2.98 (t, *J* = 6.0 Hz, 2H), 2.82 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.52, 167.15, 136.50, 136.43, 134.62, 133.75, 132.62, 132.55, 130.49, 130.40, 128.91, 128.52, 128.41, 128.12, 127.90, 126.82, 126.66, 126.58, 126.50, 126.27, 125.74, 125.15, 125.13, 48.56, 44.42, 44.18, 39.93, 29.46, 28.37. MS (EI) *m/z* 249 ($[M-N_2-H]^+$); HRMS (EI) *m/z* for $C_{16}H_{14}N_2O$ ($[M-N_2-H]^+$) calcd 249.1027, found 249.1022.



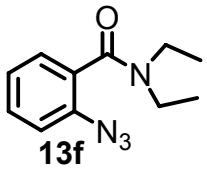
13d

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (m, 1H), 7.23 (m, 1H), 7.18 (m, 2H), 3.77 (m, 1H), 3.68 (m, 1H), 3.16 (m, 2H), 1.74-1.42 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.68, 136.25, 130.04, 128.85, 127.72, 125.01, 118.47, 47.97, 42.52, 26.32, 25.46, 24.44. MS (EI) *m/z* 230 (M^+); HRMS (EI) *m/z* for $C_{12}H_{14}N_4O$ (M^+) calcd 230.1167, found 230.1163.



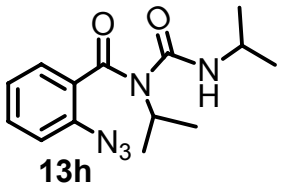
13e

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (m, 1H), 7.28 (m, 1H), 7.18 (m, 2H), 3.64 (t, *J* = 6.8 Hz, 2H), 3.21 (t, *J* = 6.6 Hz, 2H), 2.00-1.84 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.50, 135.82, 130.08, 129.72, 127.62, 124.89, 118.38, 47.80, 45.32, 25.63, 24.29. MS (EI) *m/z* 216 (M^+); HRMS (EI) *m/z* for $C_{11}H_{12}N_4O$ (M^+) calcd 216.1011, found 216.1005.



13f

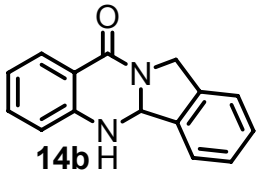
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (m, 1H), 7.25-7.17 (m, 3H), 3.56 (br s, 2H), 3.14 (q, *J* = 7.0 Hz, 2H), 1.27 (t, *J* = 7.0 Hz, 3H), 1.06 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.87, 136.25, 129.99, 129.40, 127.65, 125.00, 118.54, 42.90, 39.00, 14.04, 12.86. MS (EI) *m/z* 218 (M^+); HRMS (EI) *m/z* for $C_{11}H_{14}N_4O$ (M^+) calcd 218.1167, found 218.1163.



13h

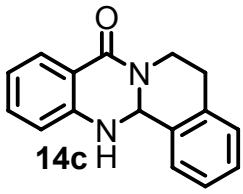
13h is a side product in preparation of *ortho*-azidobenzamide derivatives **13a** – **13g** **(**M. Ono, X. Y. Zhao, Y. Shida, H. Akita, *Tetrahedron* **2007**, *63*, 10140–10148.) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (m, 1H), 7.25-7.17 (m, 3H), 4.09 (m, 1H), 3.90 (m, 1H), 1.42 (d, *J* = 6.8 Hz, 6H), 1.08 (d, *J* = 6.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.06, 136.03, 130.63, 129.28, 126.48, 125.09, 118.49, 51.01, 42.44, 22.24,

20.69. MS (EI) *m/z* 261 ($[M-N_2]^+$); HRMS (EI) *m/z* for $C_{14}H_{19}N_3O_2$ ($[M-N_2]^+$) calcd 261.1468, found 261.1477.



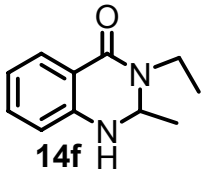
14b

^{1}H NMR (300 MHz, CD_3OH) δ 7.90 (d, *J* = 7.7 Hz, 1H), 7.51 (m, 1H), 7.43-7.34 (m, 4H), 6.94 (m, 2H), 6.17 (s, 1H), 5.05 (d, *J* = 15.6 Hz, 1H), 4.75 (d, *J* = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, CD_3OH) δ 162.74, 147.02, 137.06, 136.43, 133.40, 129.19, 127.93, 127.90, 123.29, 122.31, 120.27, 118.64, 116.24, 72.79, 50.03. MS (EI) *m/z* 234 ($[M-H_2]^+$); HRMS (EI) *m/z* for $C_{15}H_{10}N_2O$ ($[M-H_2]^+$) calcd 234.0793, found 234.0784.



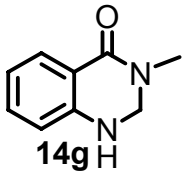
14c

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.38-7.29 (m, 4H), 7.25 (m, 1H), 6.97 (m, 1H), 6.80 (dd, *J* = 8.0, 0.4 Hz, 1H), 5.87 (d, *J* = 1.8 Hz, 1H), 4.81 (m, 1H), 4.41 (br s, 1H), 3.12-2.99(m, 2H), 2.83 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.13, 146.60, 136.06, 133.23, 133.00, 129.25, 129.14, 128.45, 127.27, 125.86, 120.38, 118.05, 115.65, 66.71, 37.98, 28.90. MS (EI) *m/z* 247 ($[M-H_3]^+$); HRMS (EI) *m/z* for $C_{16}H_{11}N_2O$ ($[M-H_3]^+$) calcd 247.0871, found 247.0865.



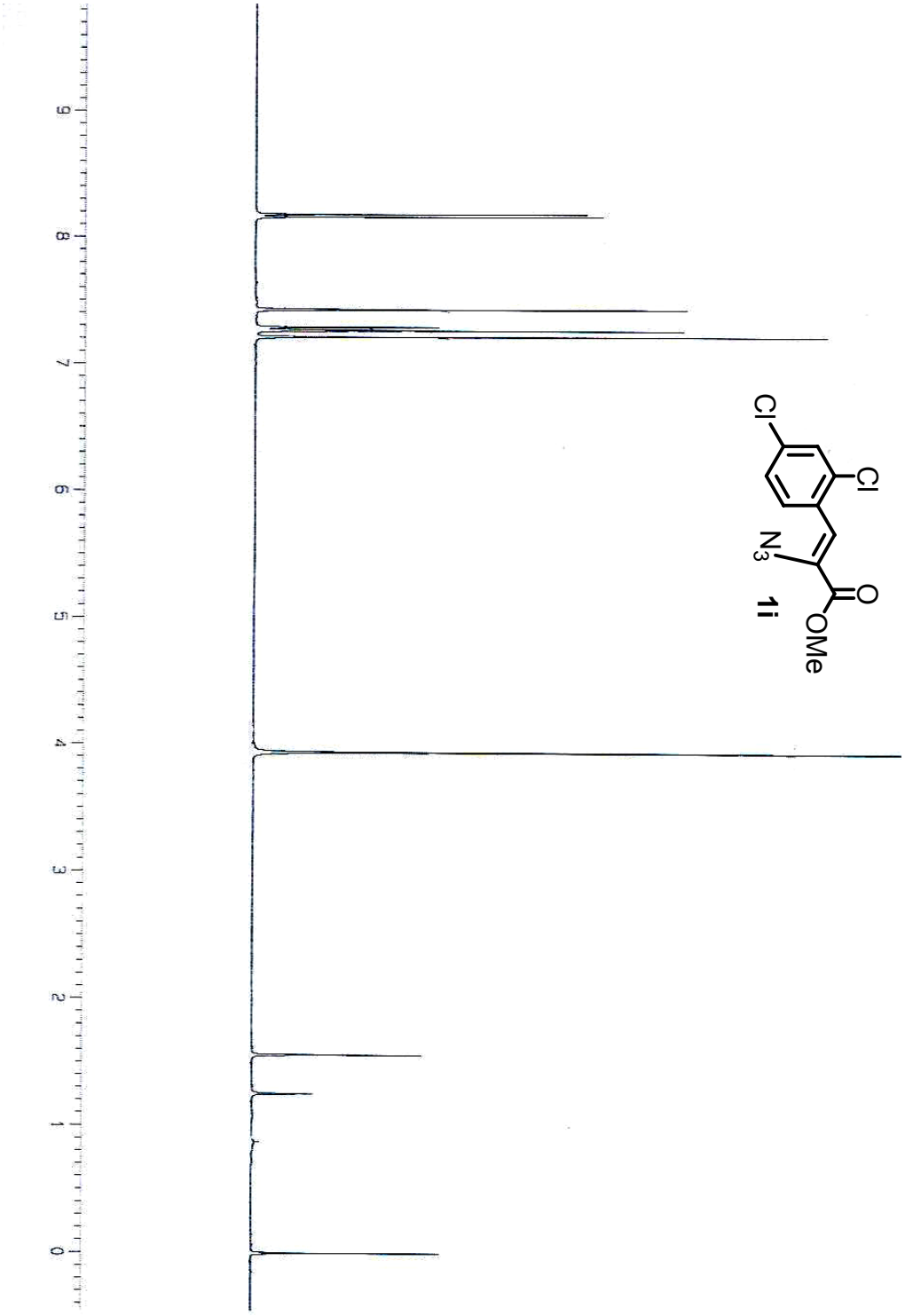
14f

^{1}H NMR (400 MHz, CD_3OH) δ 7.89 (d, *J* = 7.7 Hz, 1H), 7.26 (m, 1H), 6.81 (m, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 4.85 (m, 1H), 4.75 (br s, 1H), 3.97 (m, 1H), 3.08 (m, 1H), 1.42 (d, *J* = 5.9 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.37, 145.53, 133.10, 128.19, 118.72, 116.18, 114.79, 65.17, 39.07, 20.52, 13.51. MS (EI) *m/z* 190 (M^+); HRMS (EI) *m/z* for $C_{11}H_{14}N_2O$ (M^+) calcd 190.1106, found 190.1101.



14g

^{1}H NMR (400 MHz, CD_3OH) δ 7.92 (d, *J* = 7.5 Hz, 1H), 7.28 (m, 1H), 6.88 (m, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 4.62 (s, 2H), 4.36 (br s, 1H), 3.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.12, 147.35, 133.07, 128.70, 119.79, 117.38, 114.87, 61.32, 32.58. MS (EI) *m/z* 162 (M^+); HRMS (EI) *m/z* for $C_9H_{10}N_2O$ (M^+) calcd 162.0793, found 162.0791.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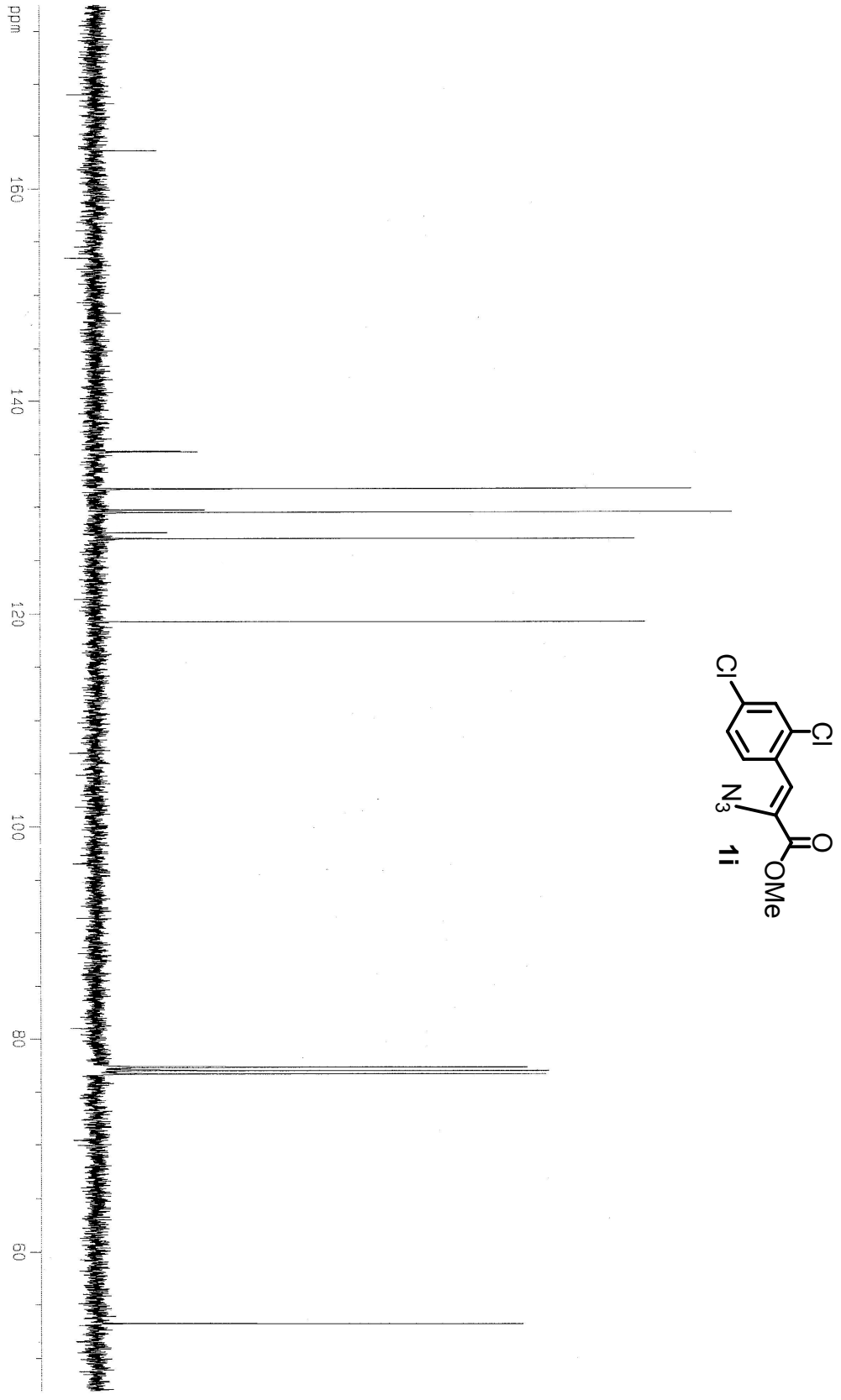
OMe
1i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O
OMe
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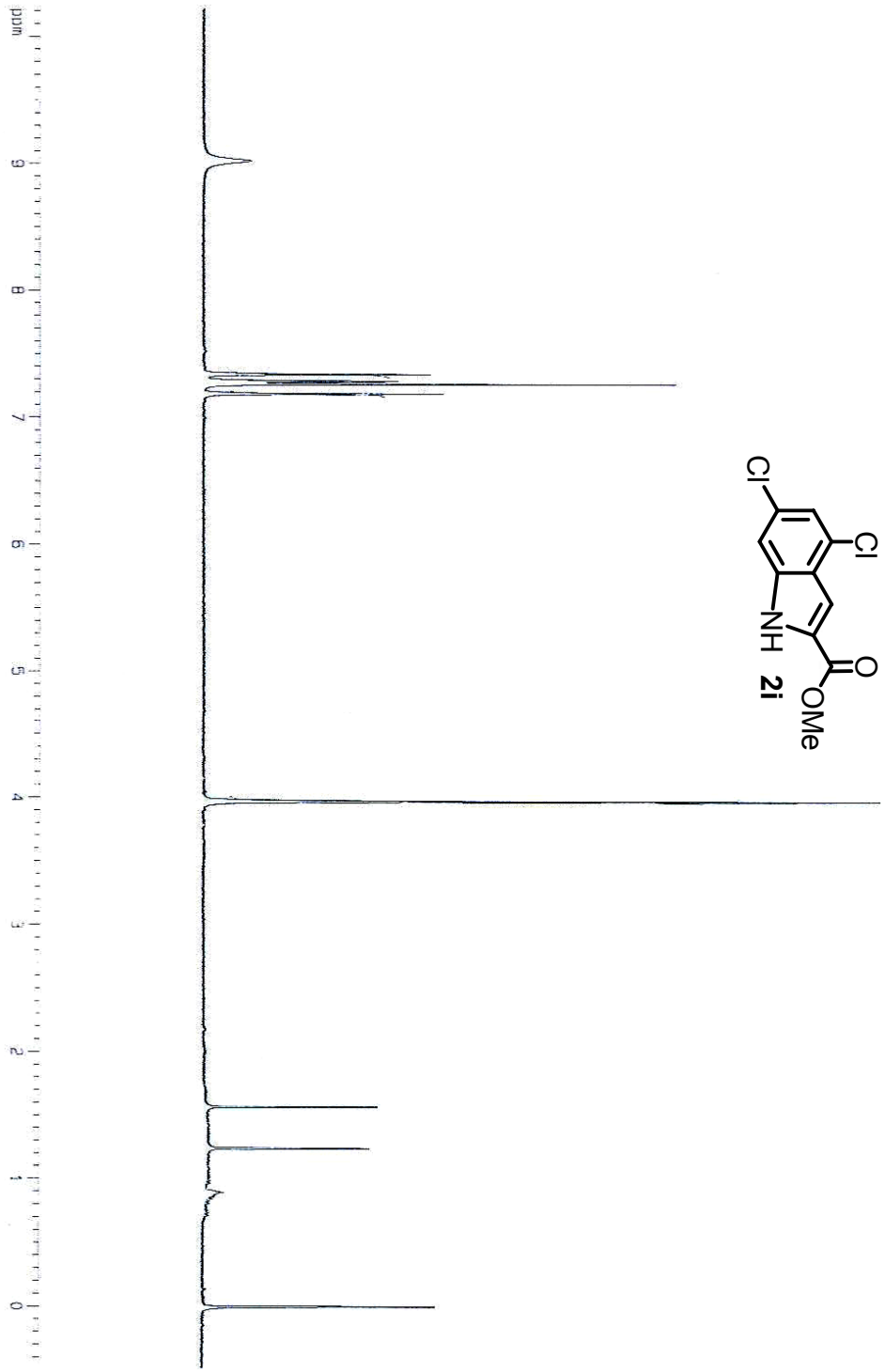
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OMe
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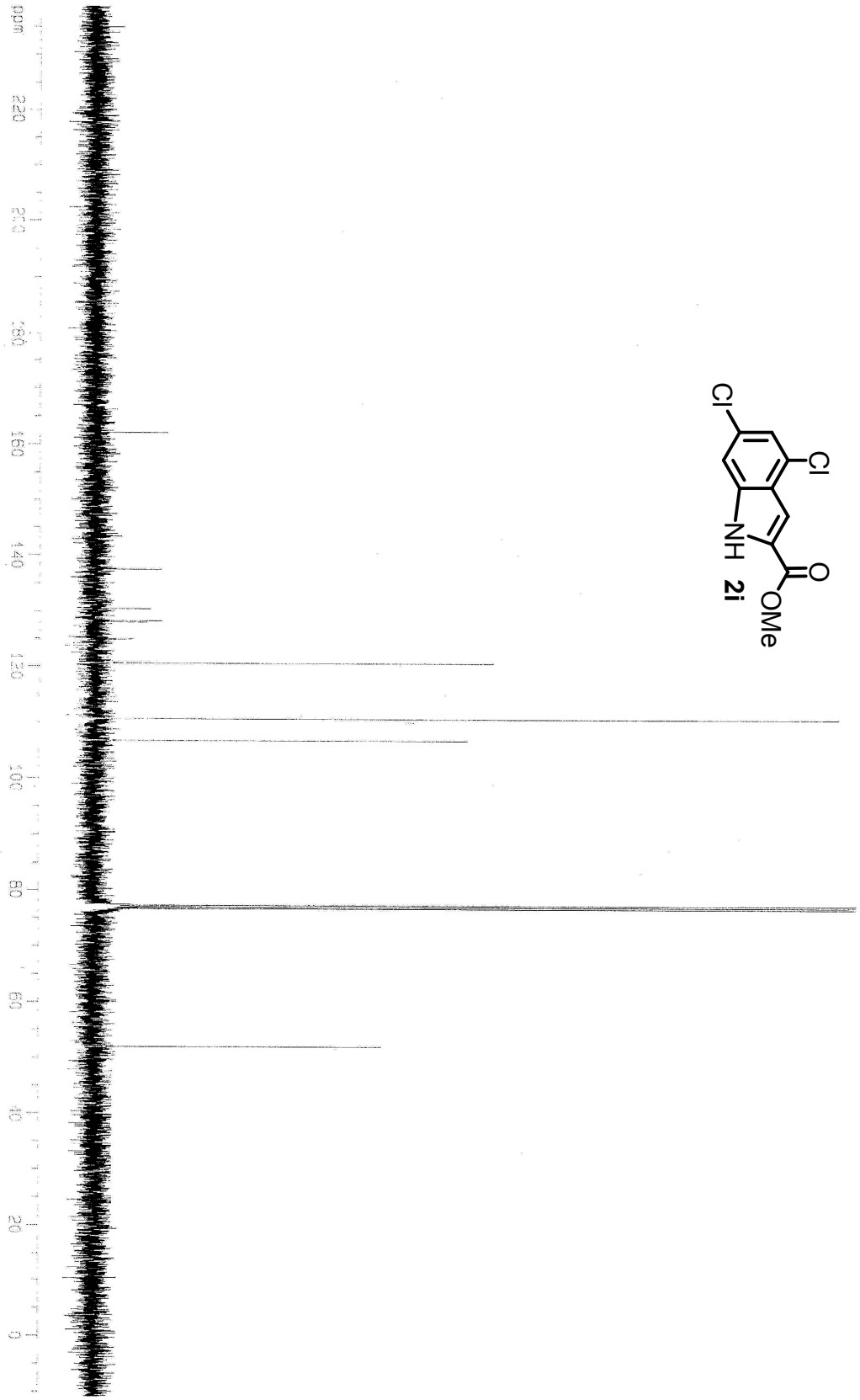
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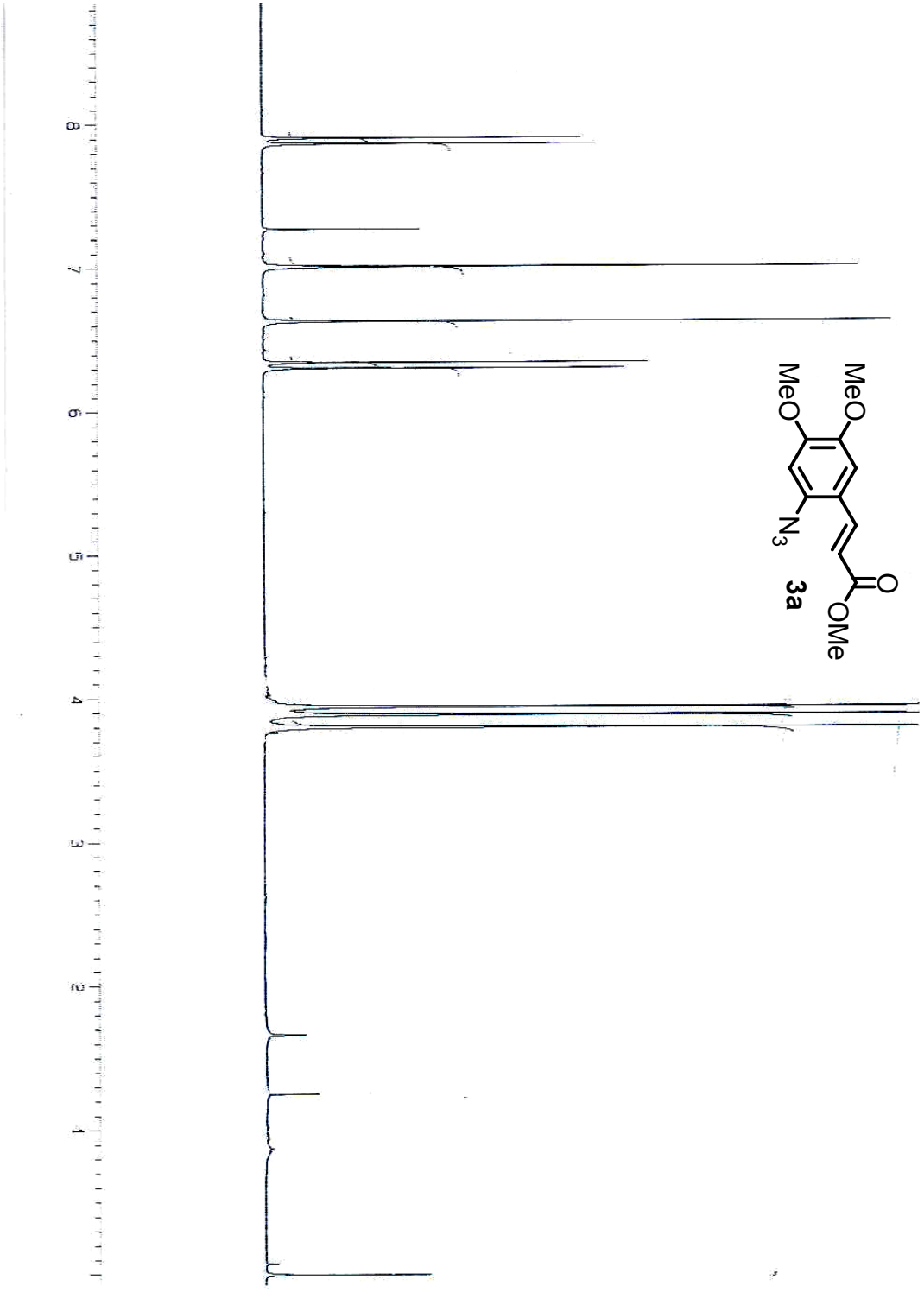
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N3
O
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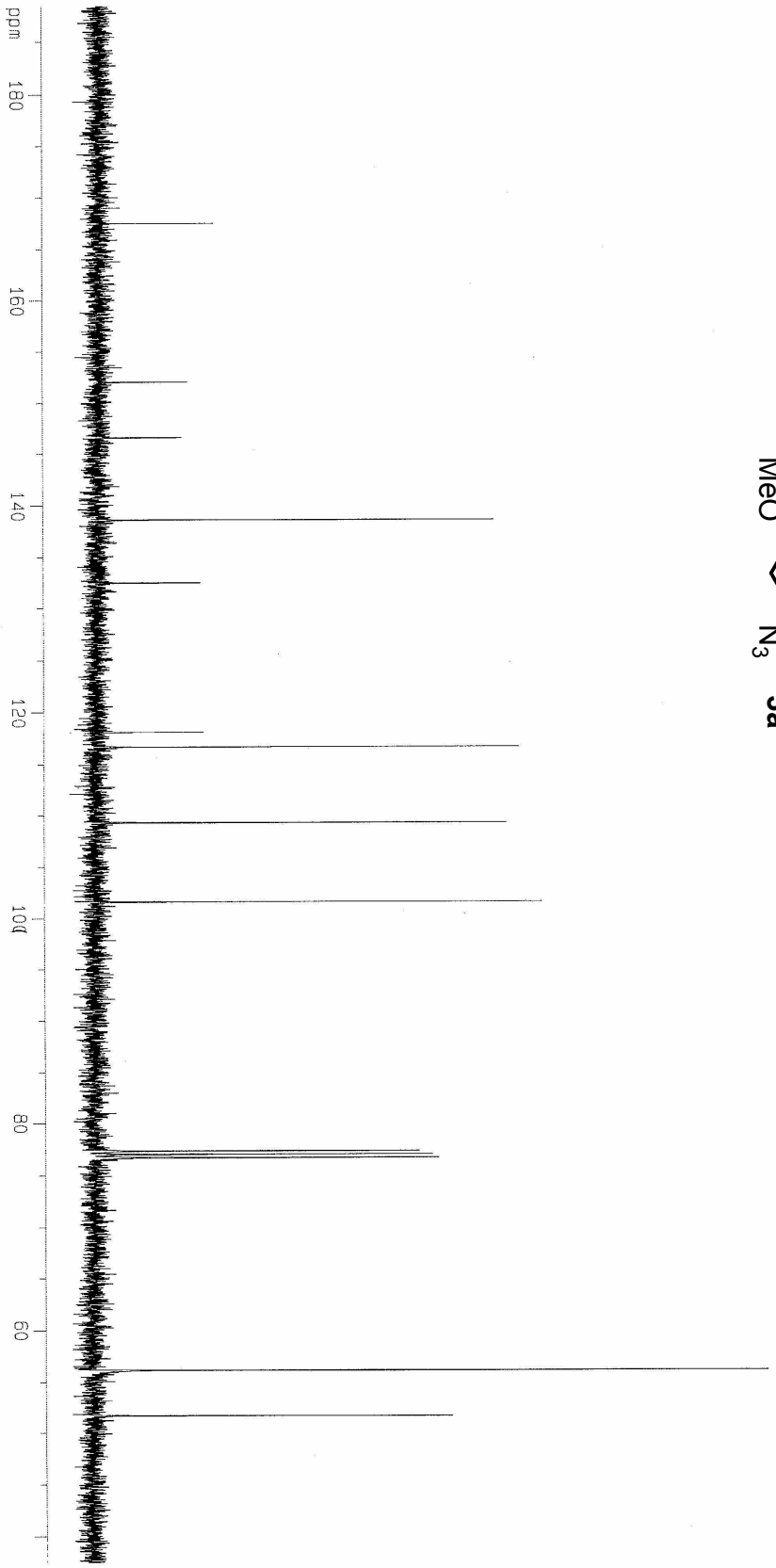
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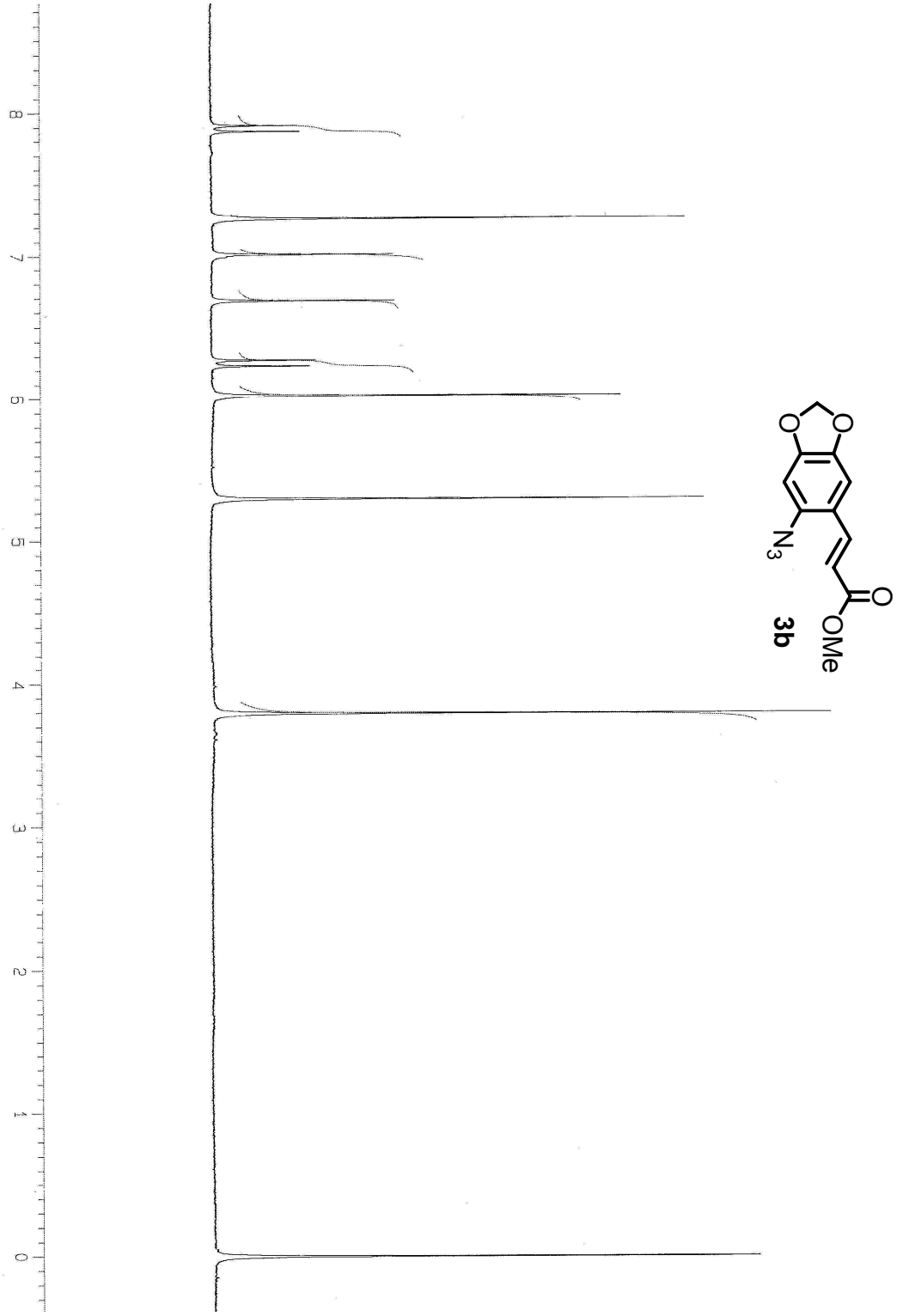
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N3
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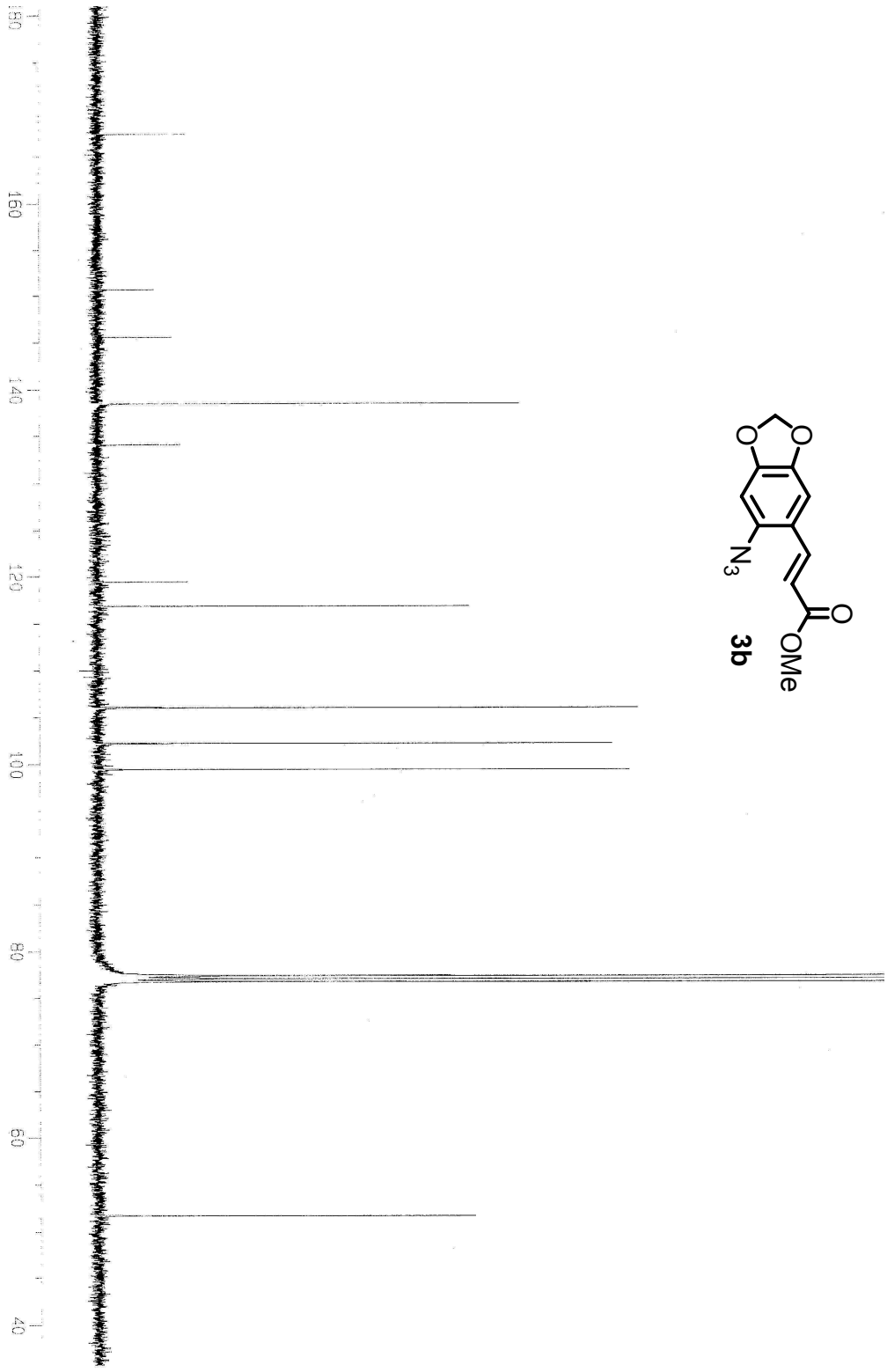
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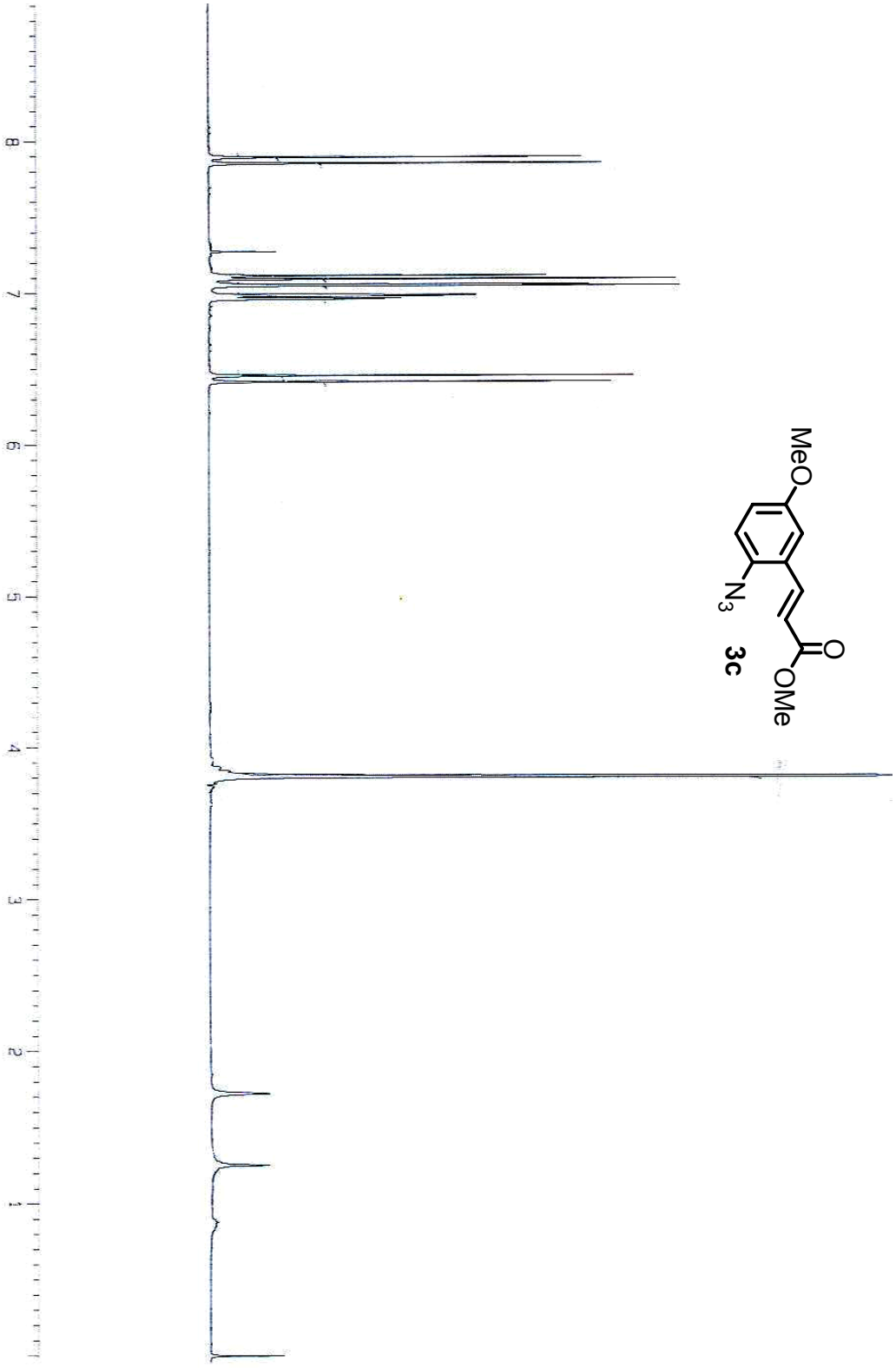
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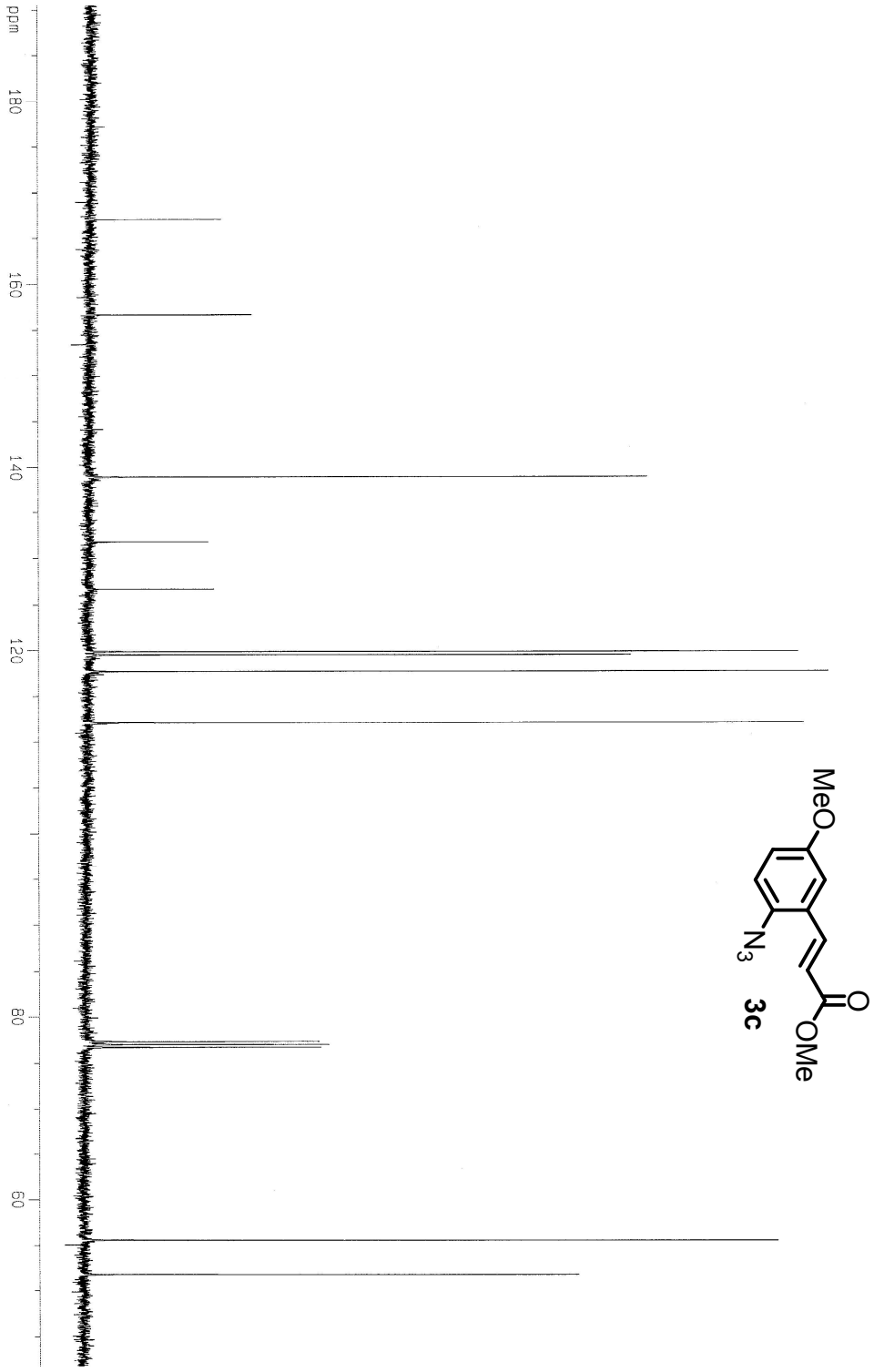
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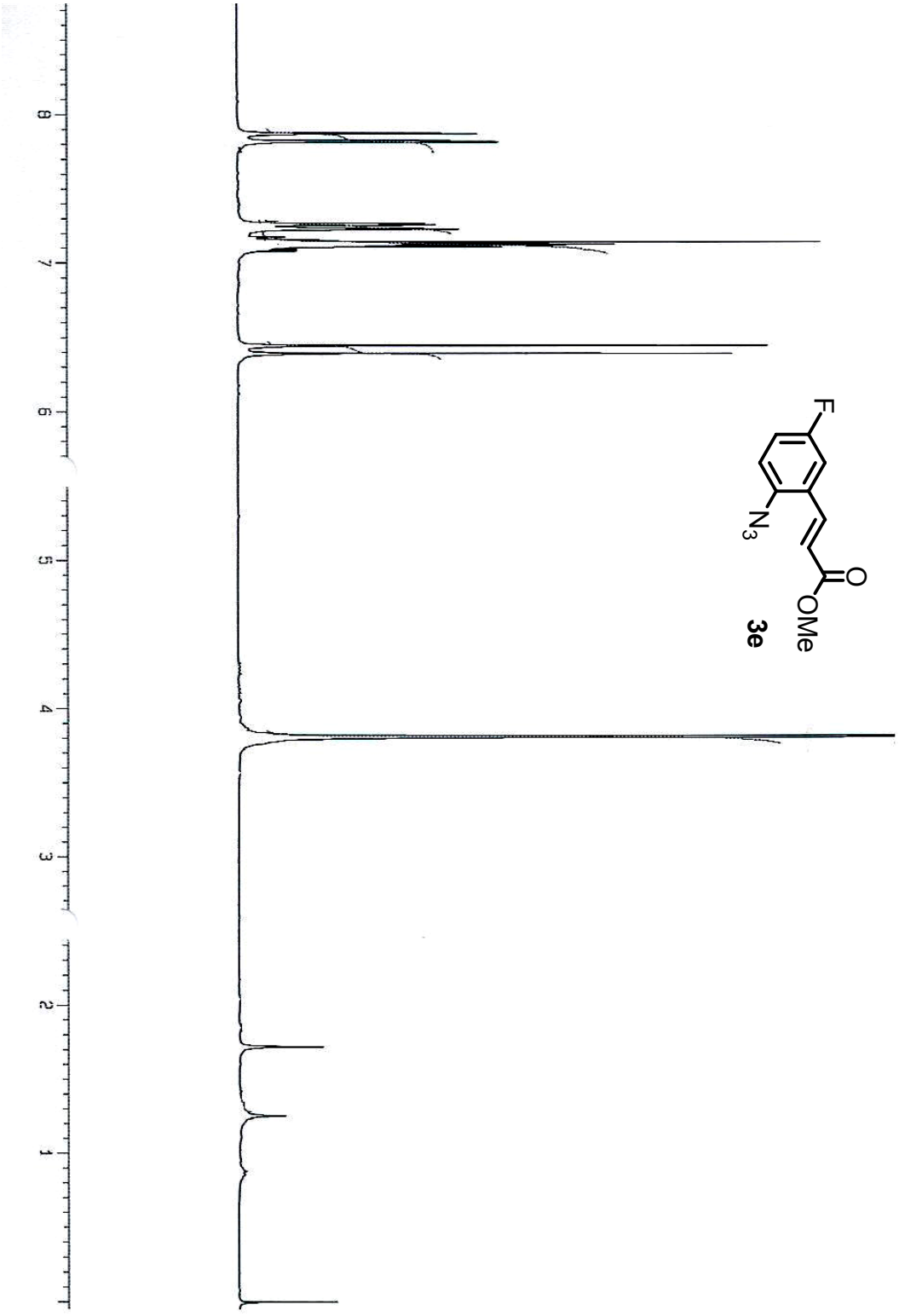
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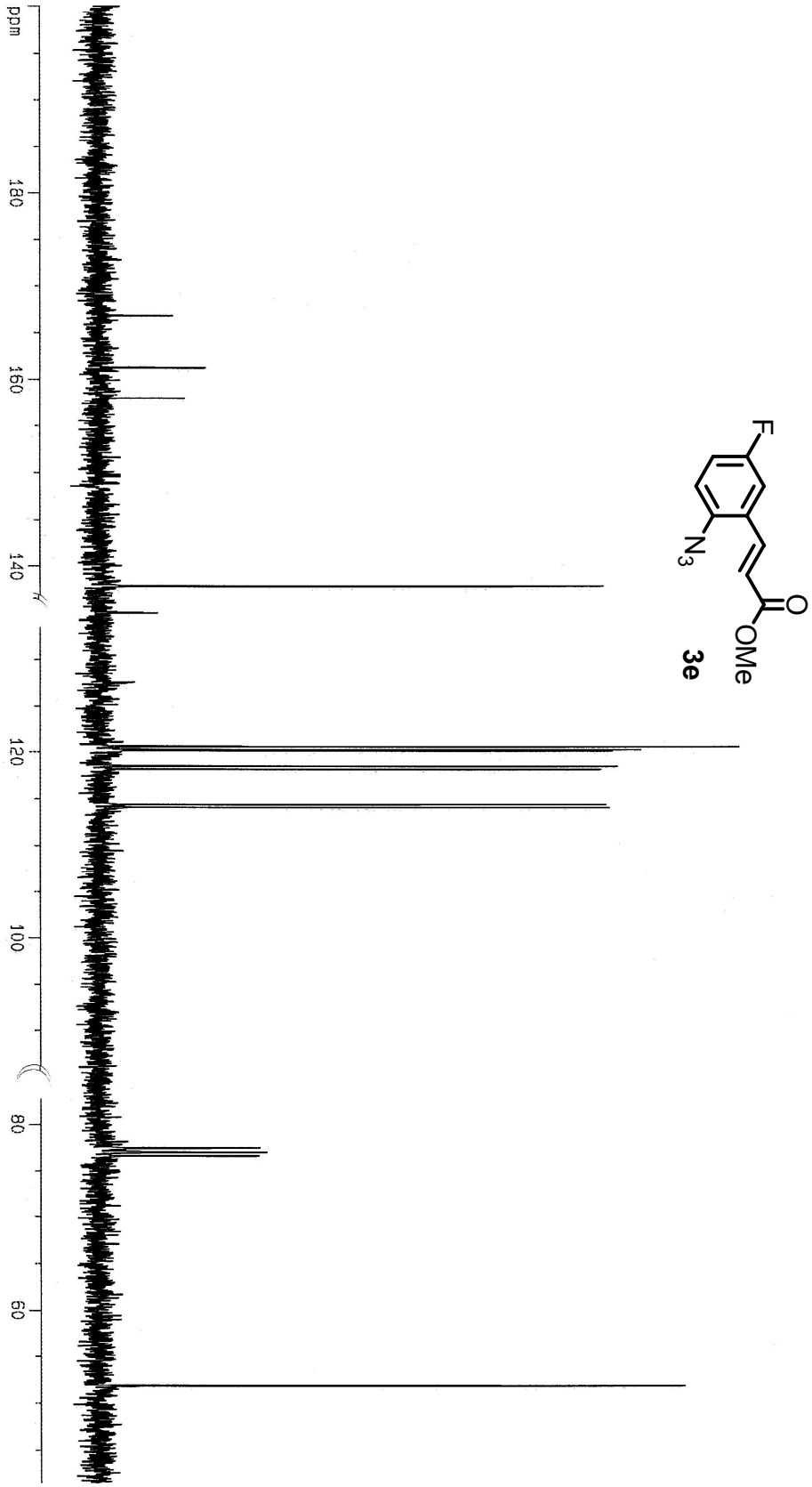
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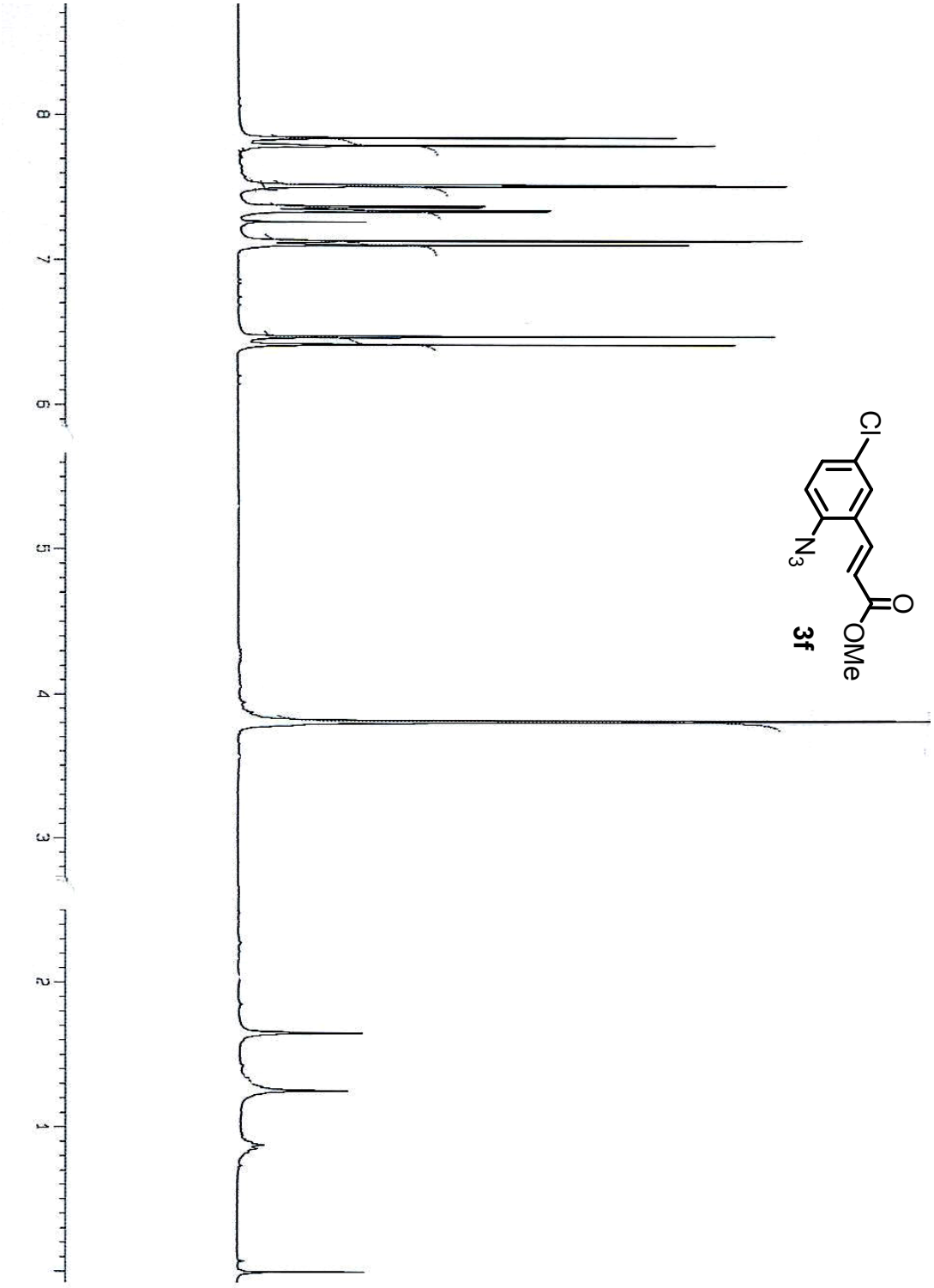
OMe
3e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OMe
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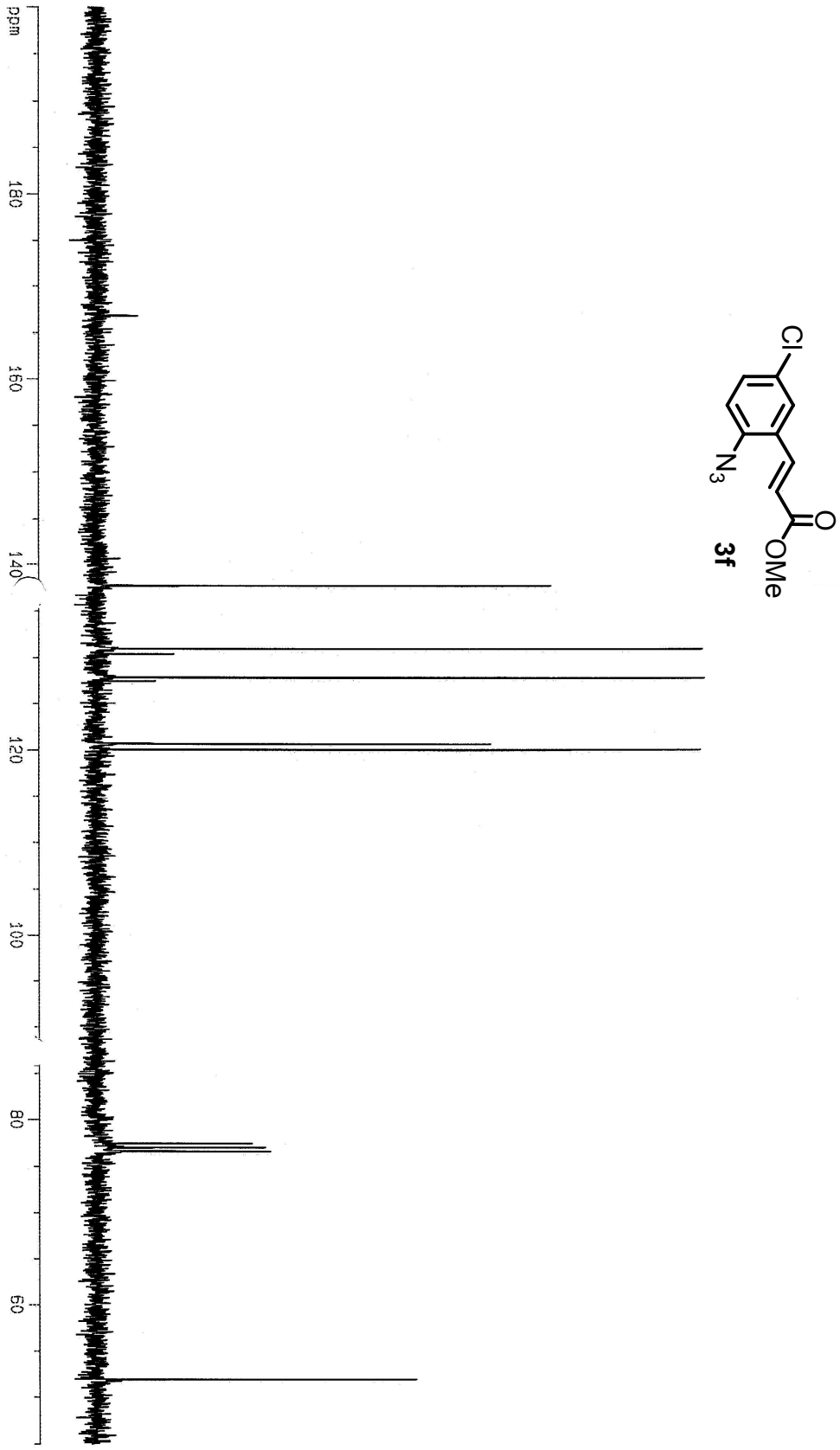
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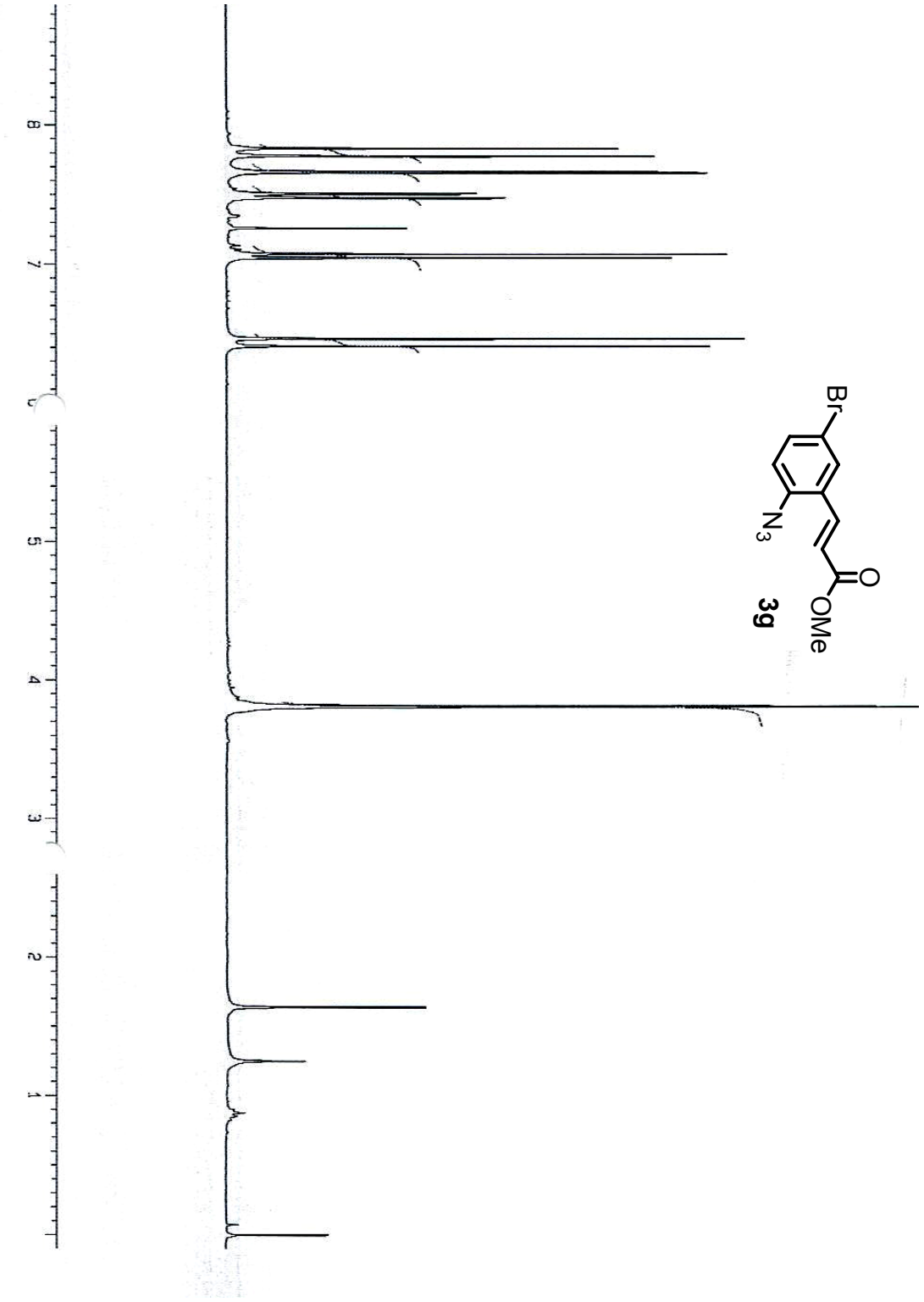
N3
O
OMe
3f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OMe
3g
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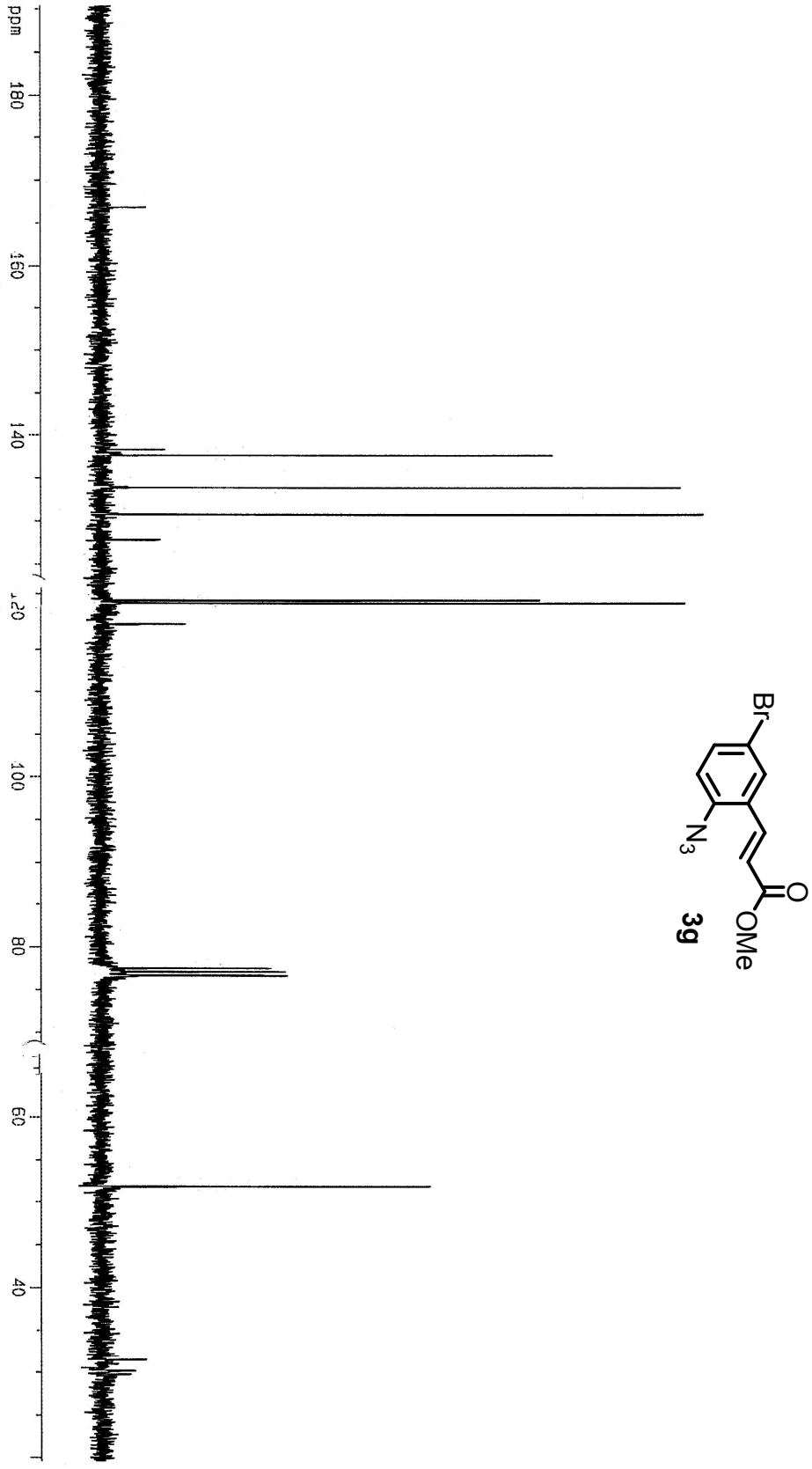
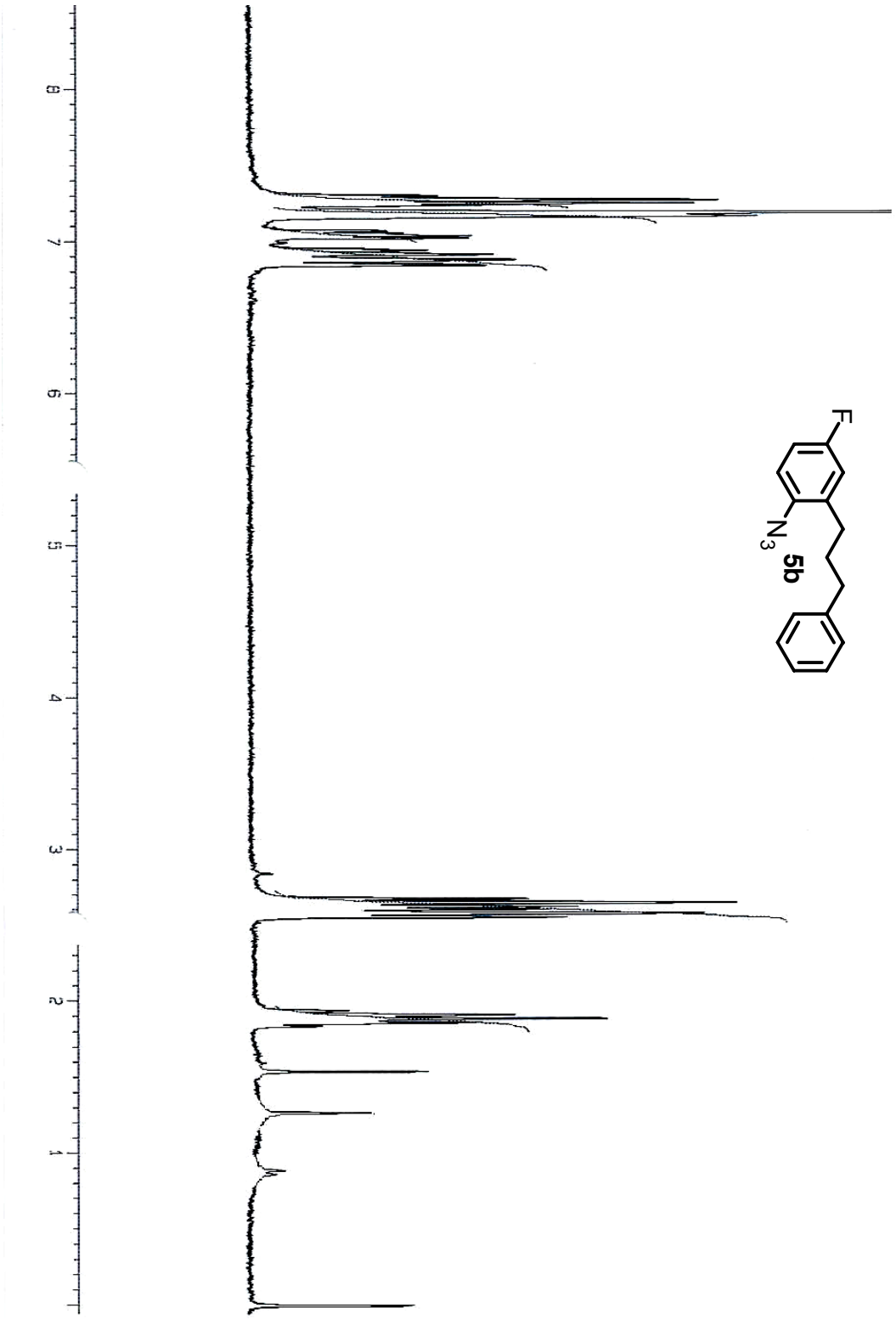
3
2
1



3g


F
N3
5b
8
7
6
5
4
3
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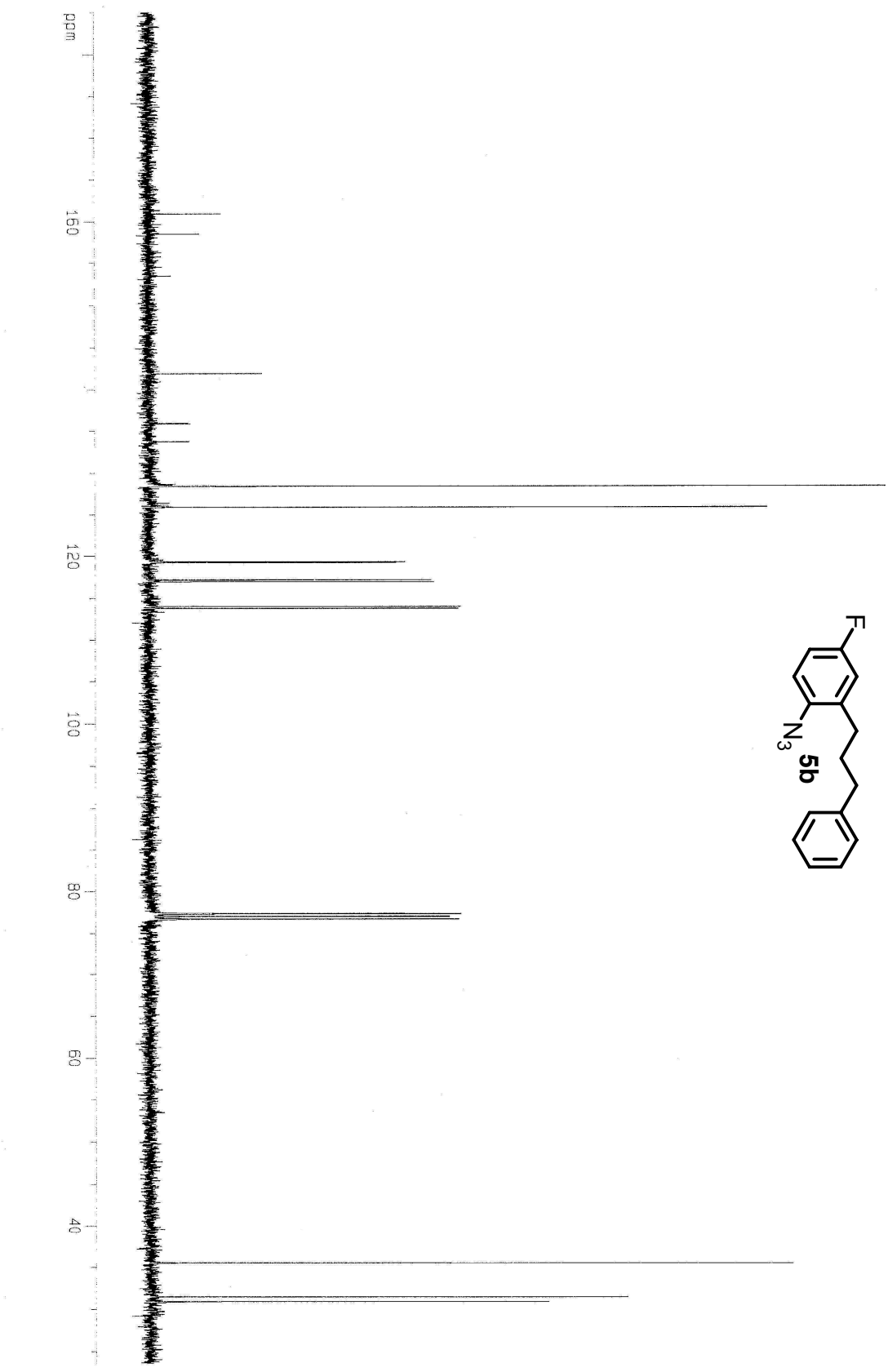
ppm
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100
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60
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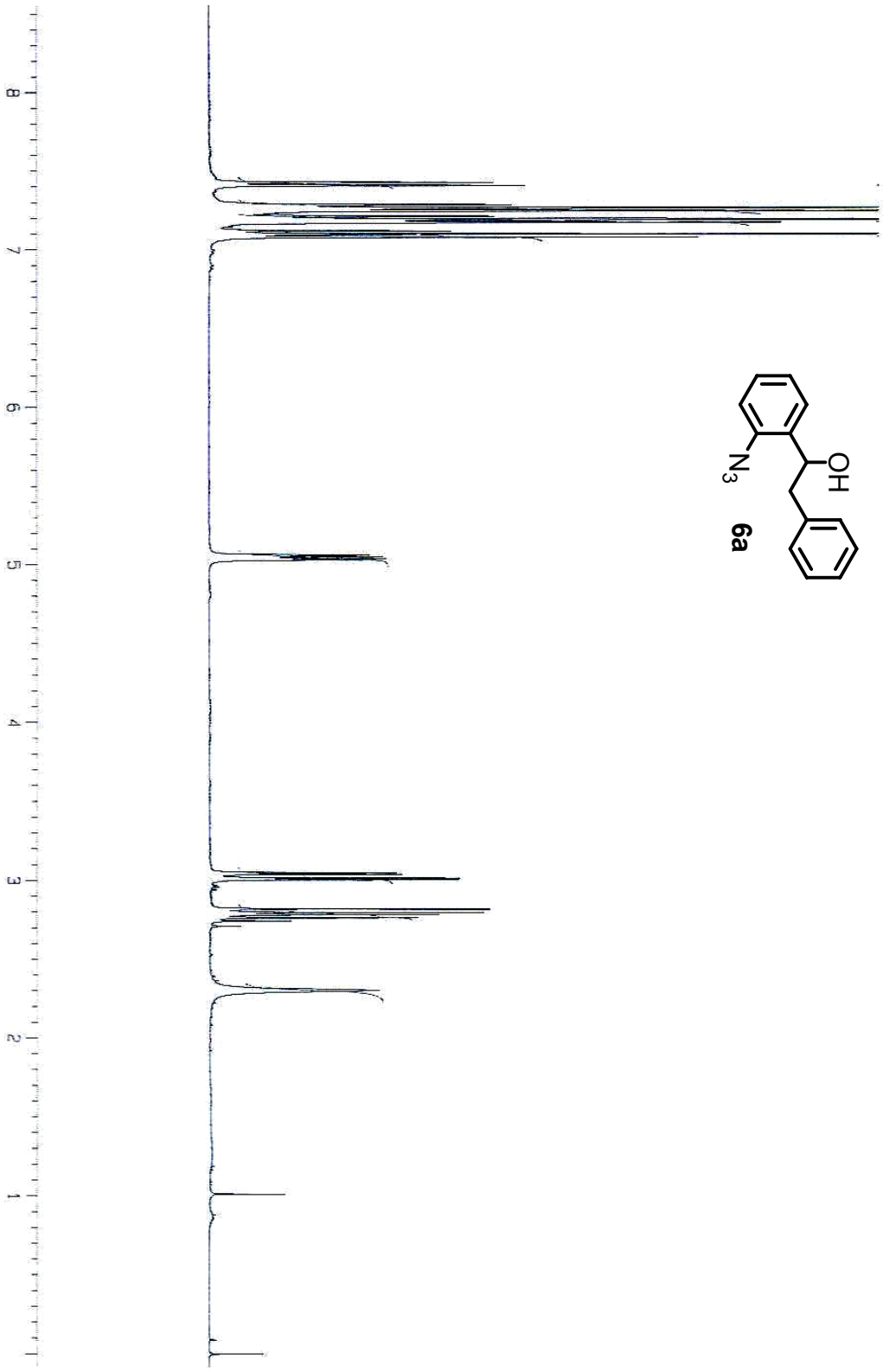
F
N3
5b



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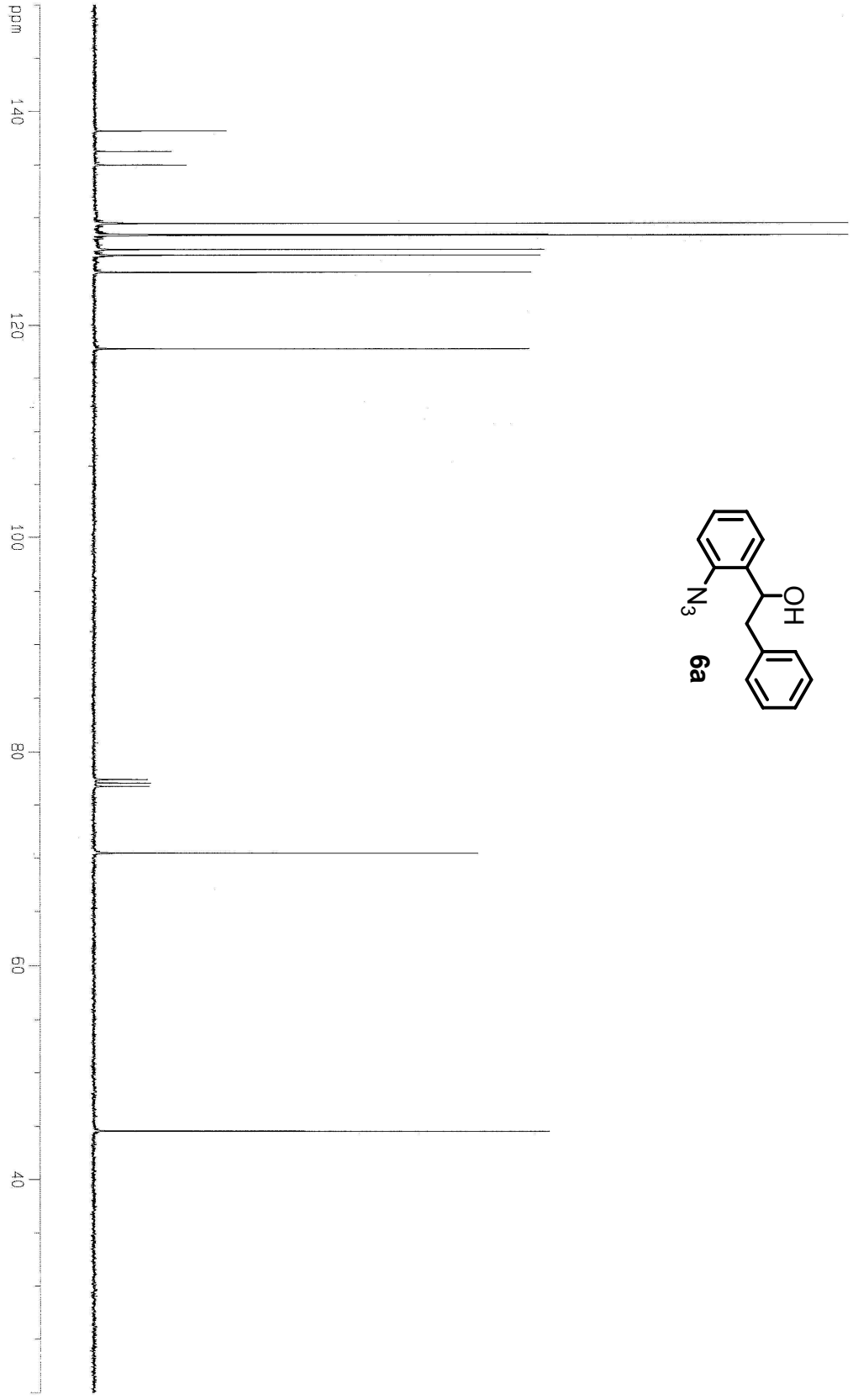

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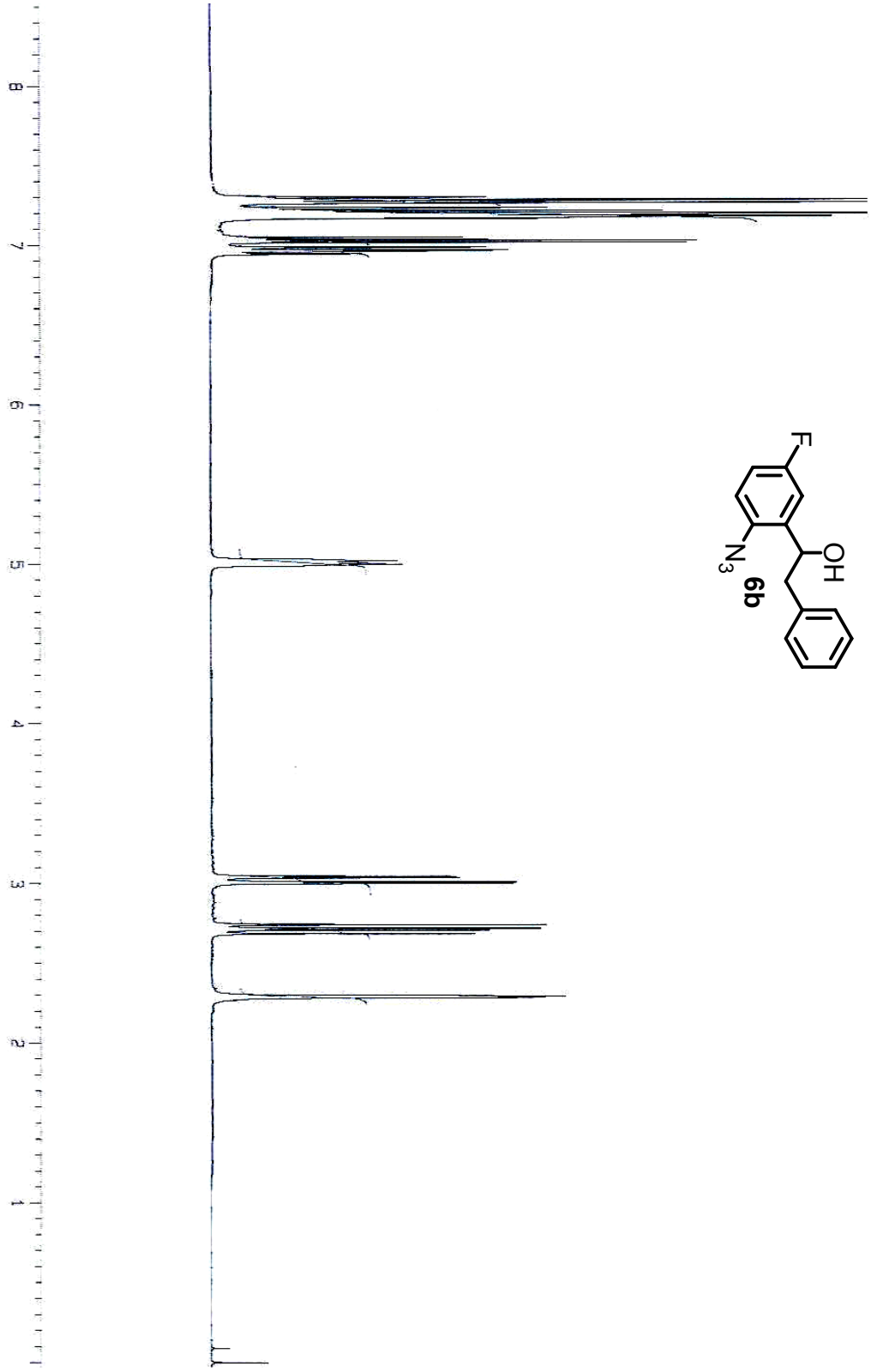
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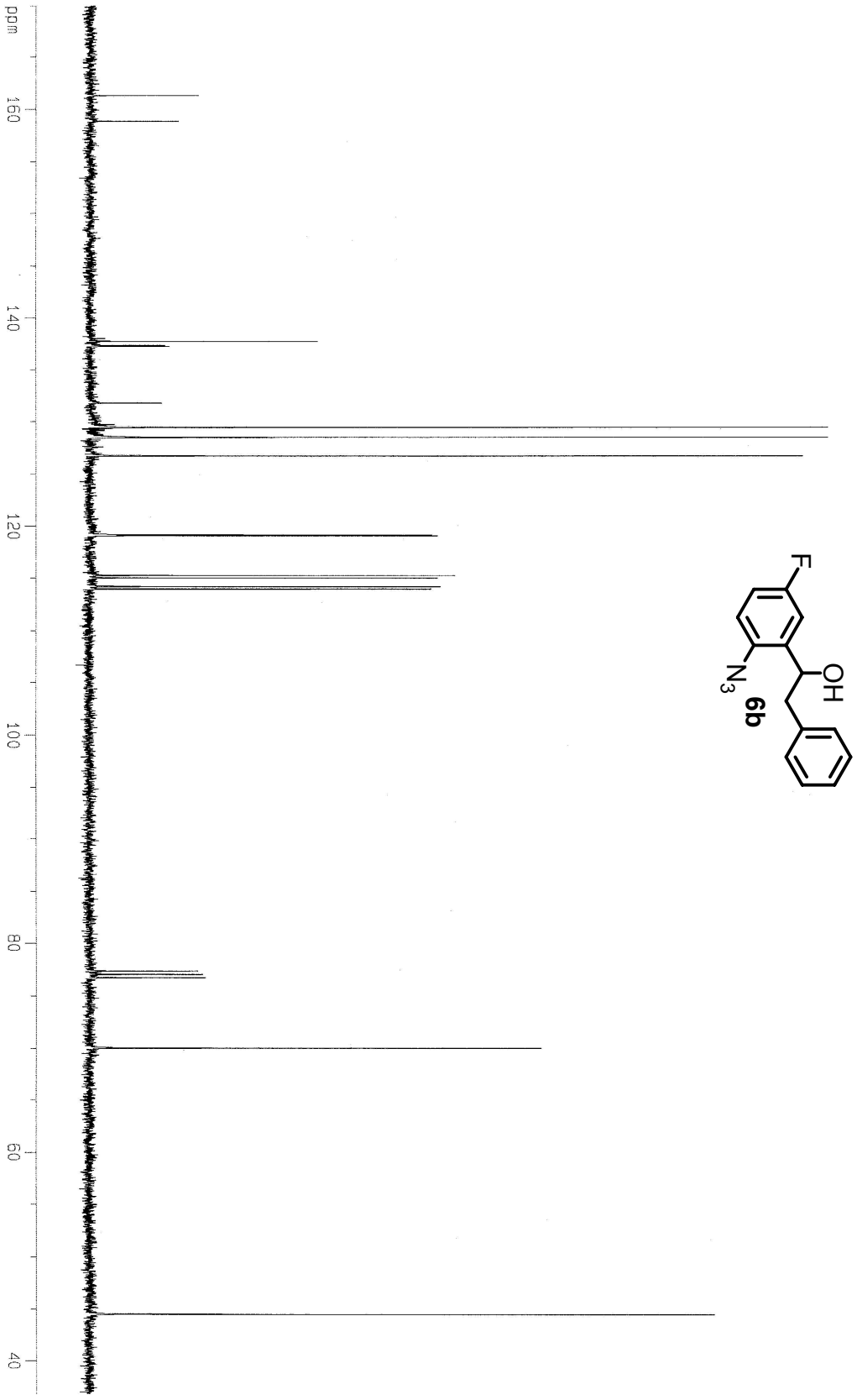
OH
N3
6b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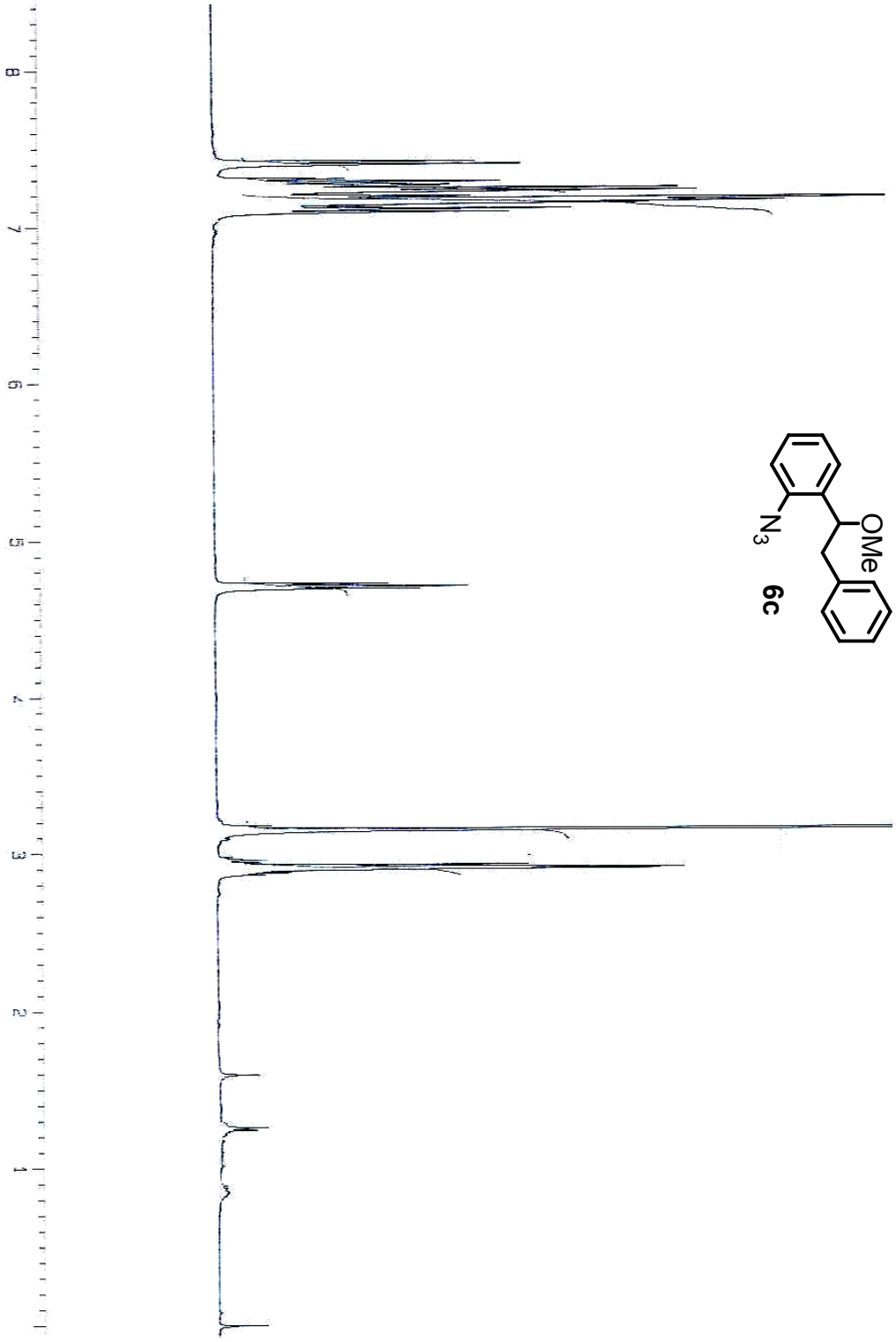
OH
N3
6b


8
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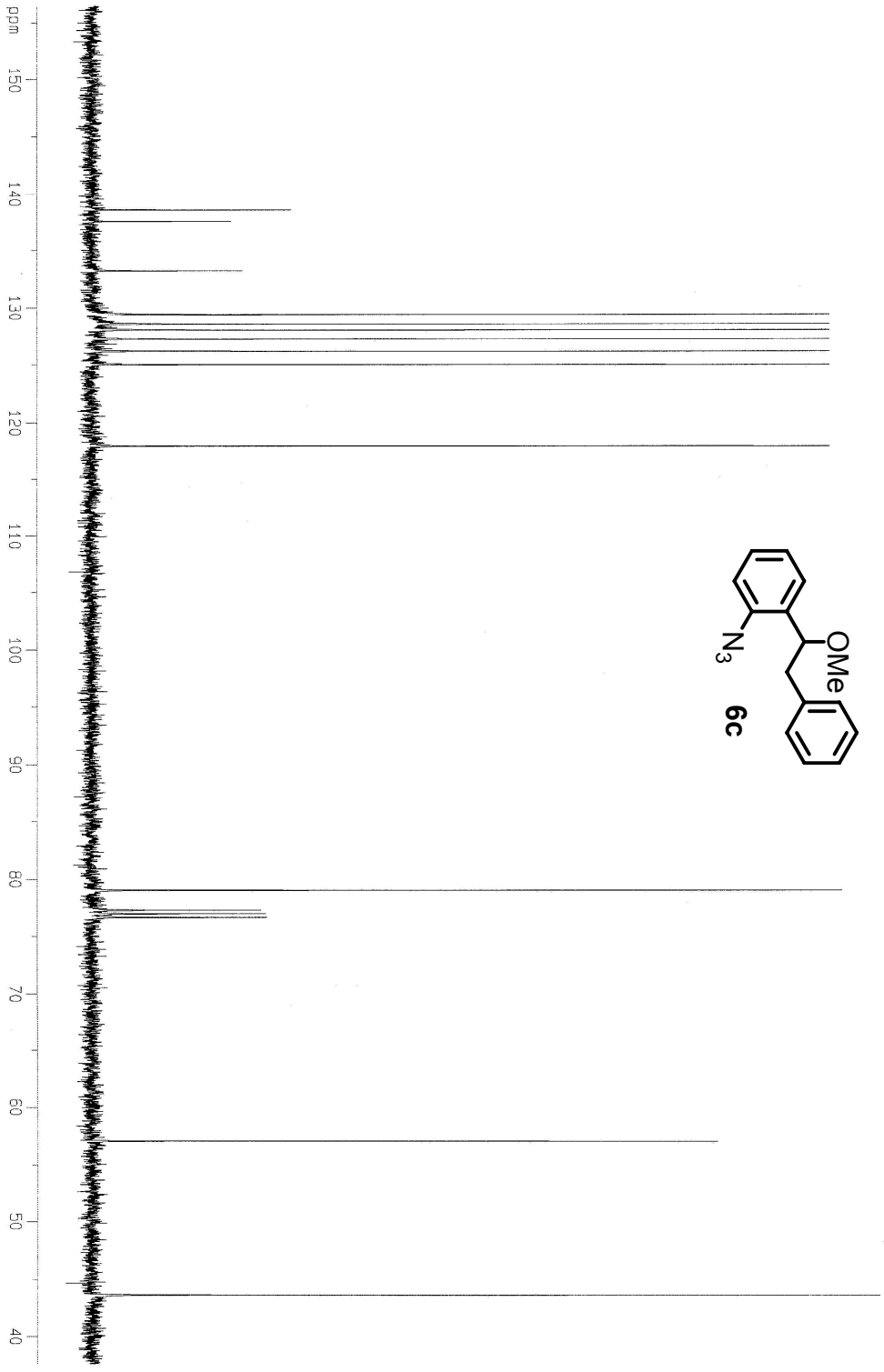
1
N3
OMe
6c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OMe
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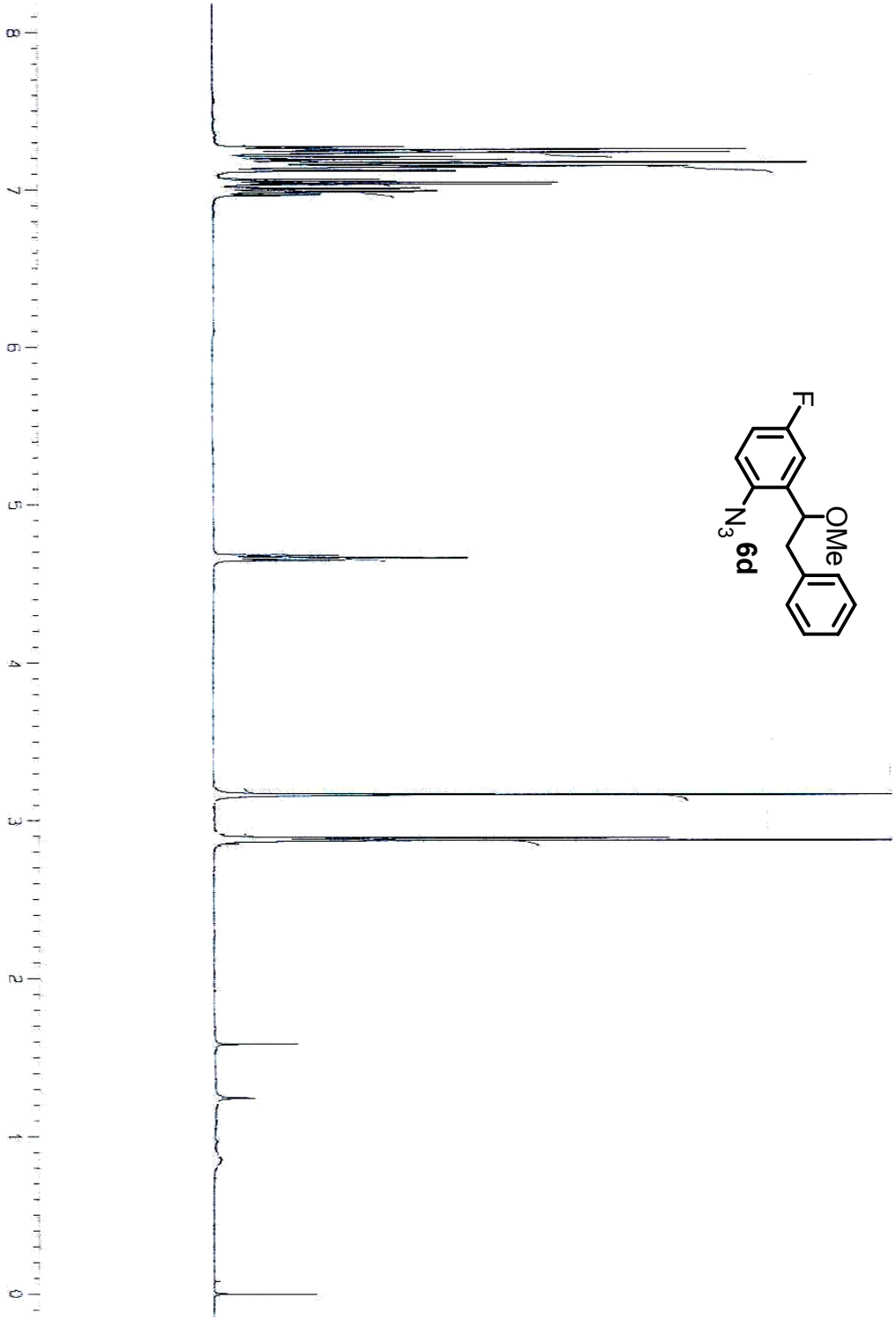
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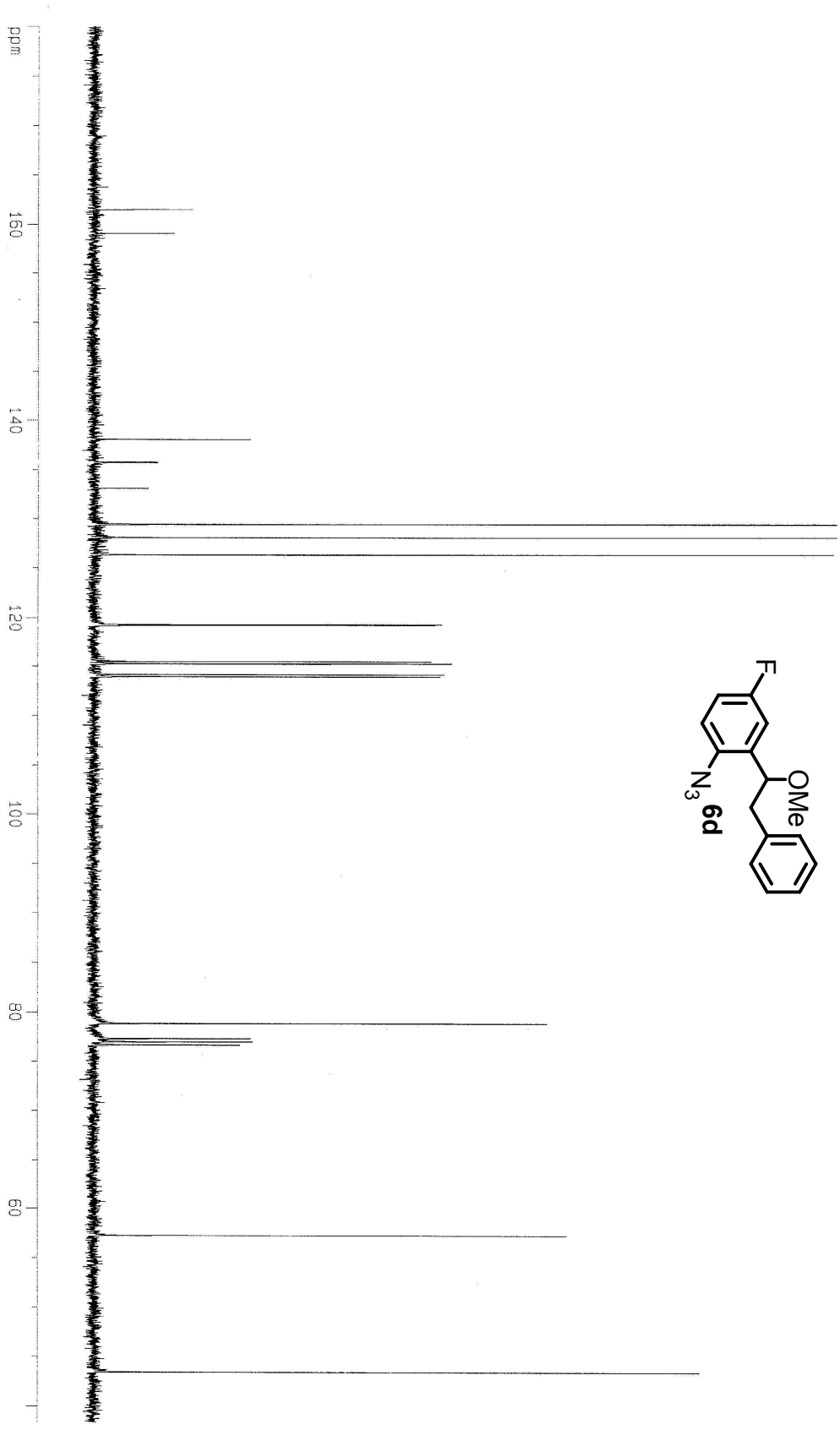
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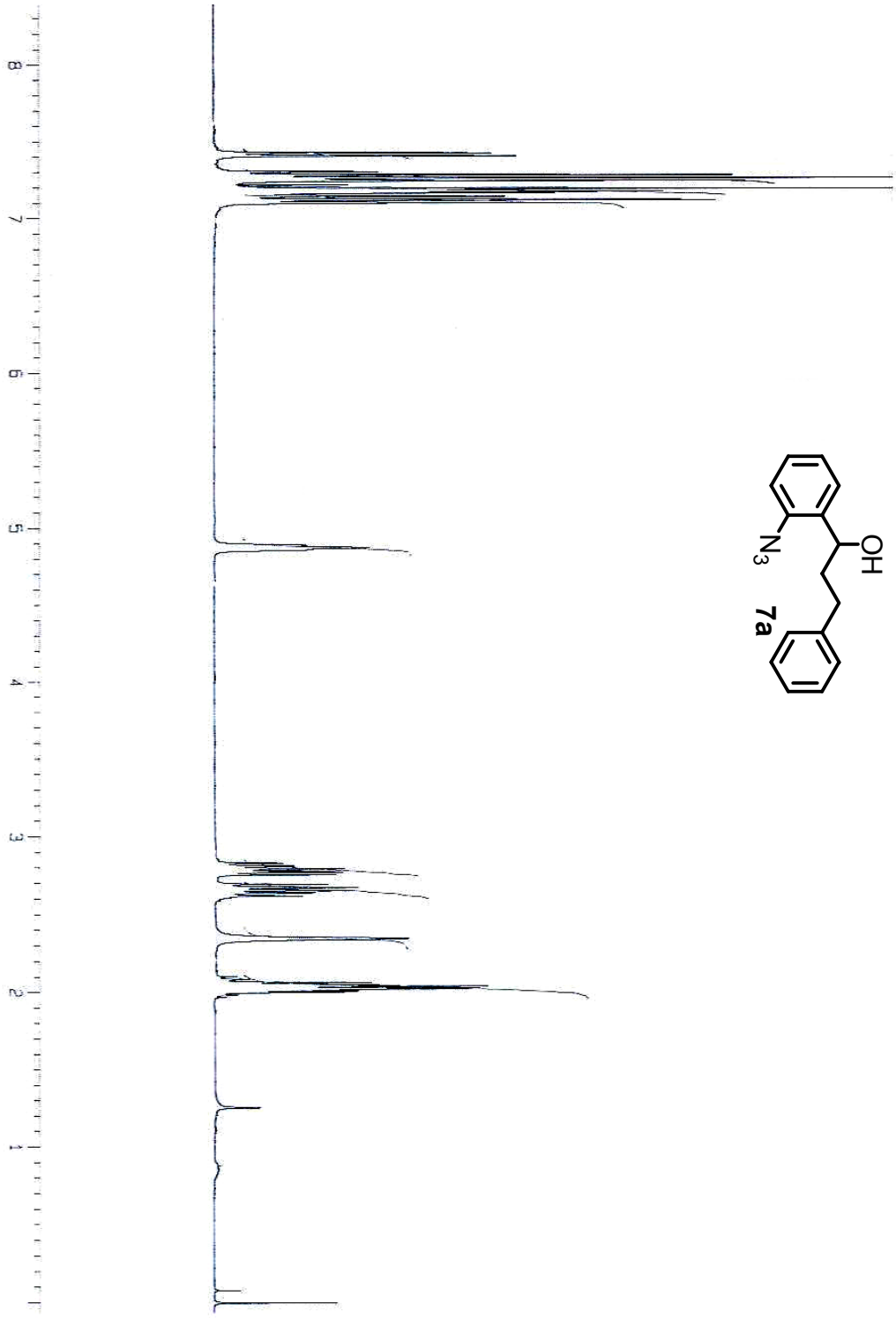
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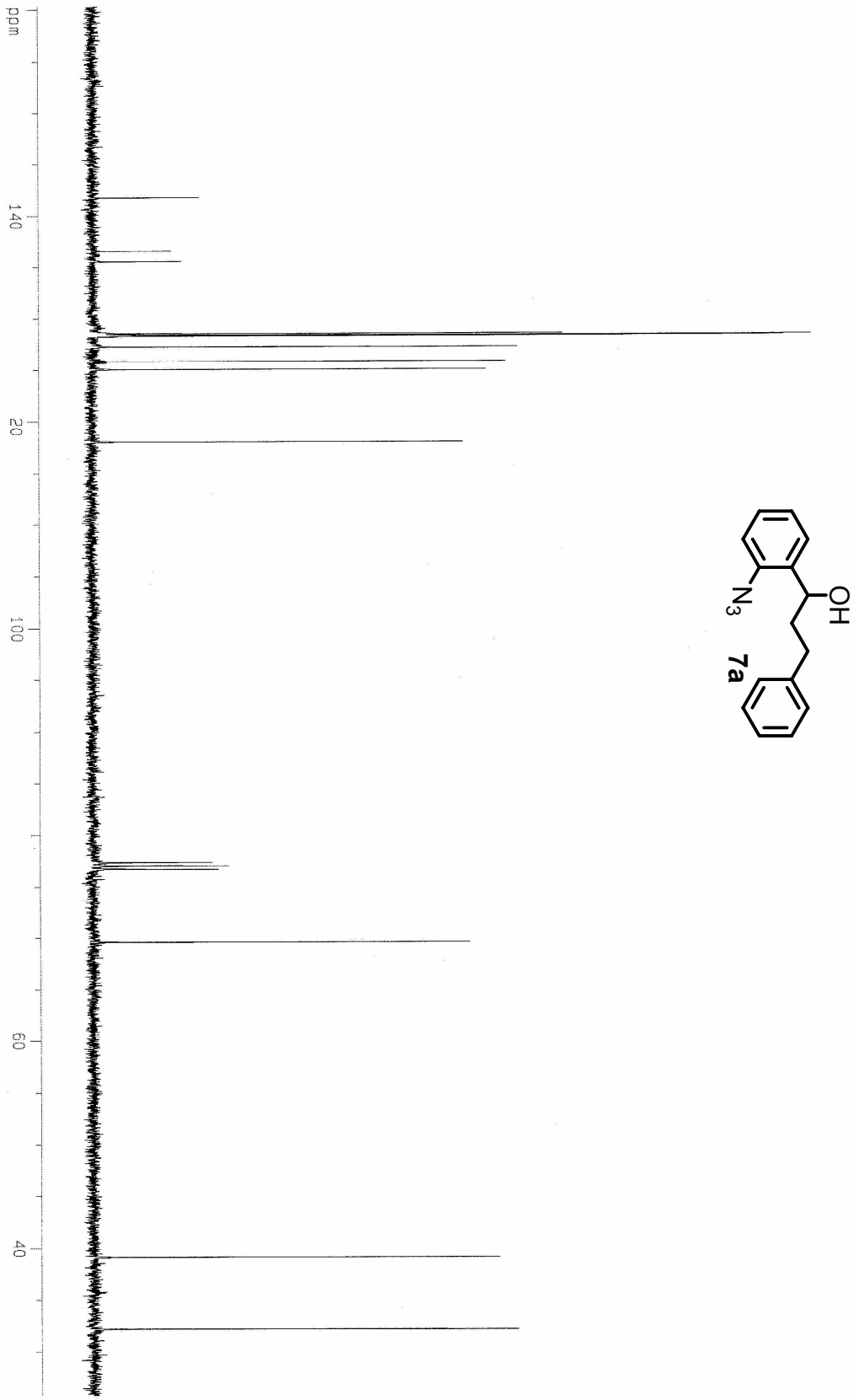
1
OH
N3
7a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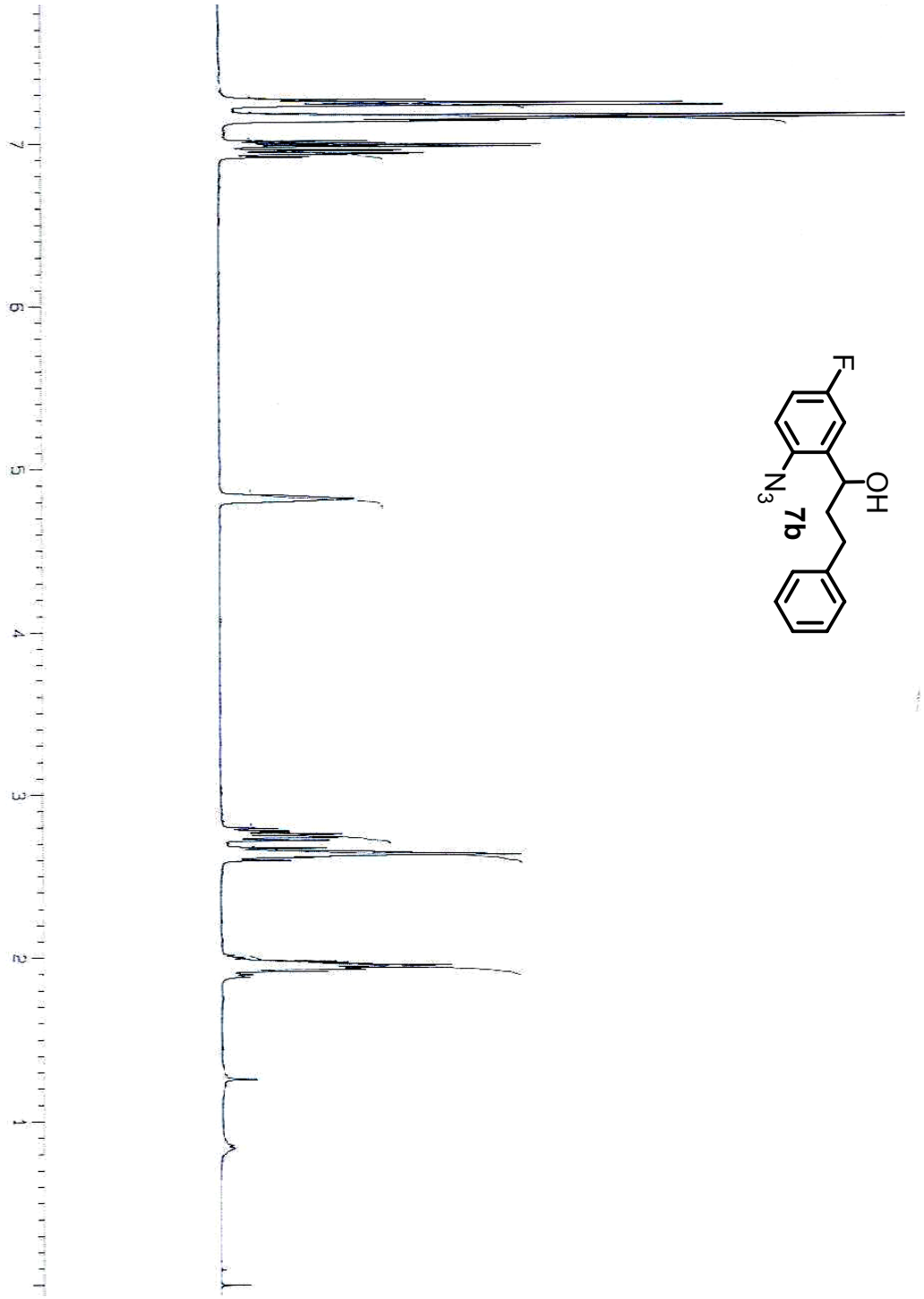
7a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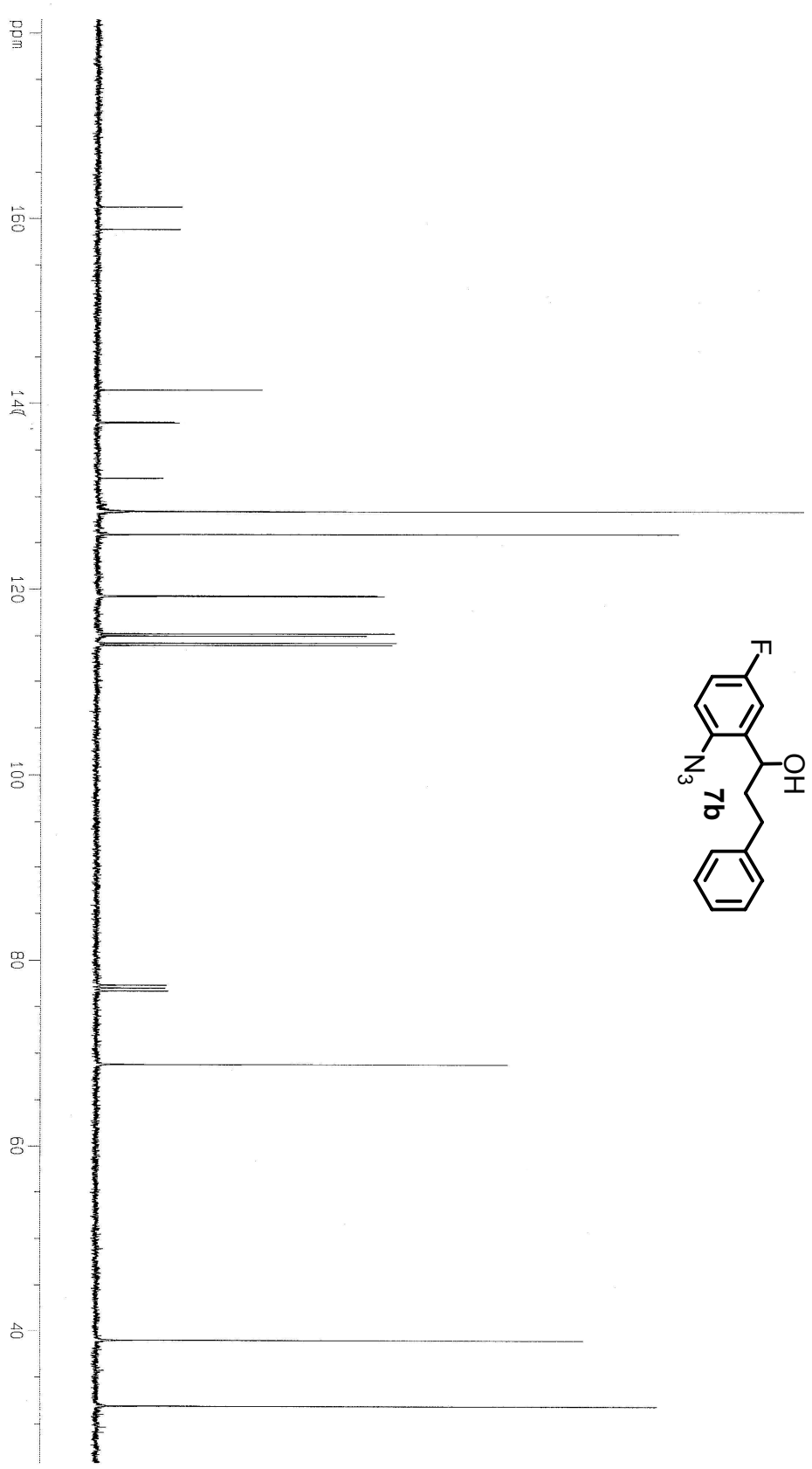
OH
N3
7b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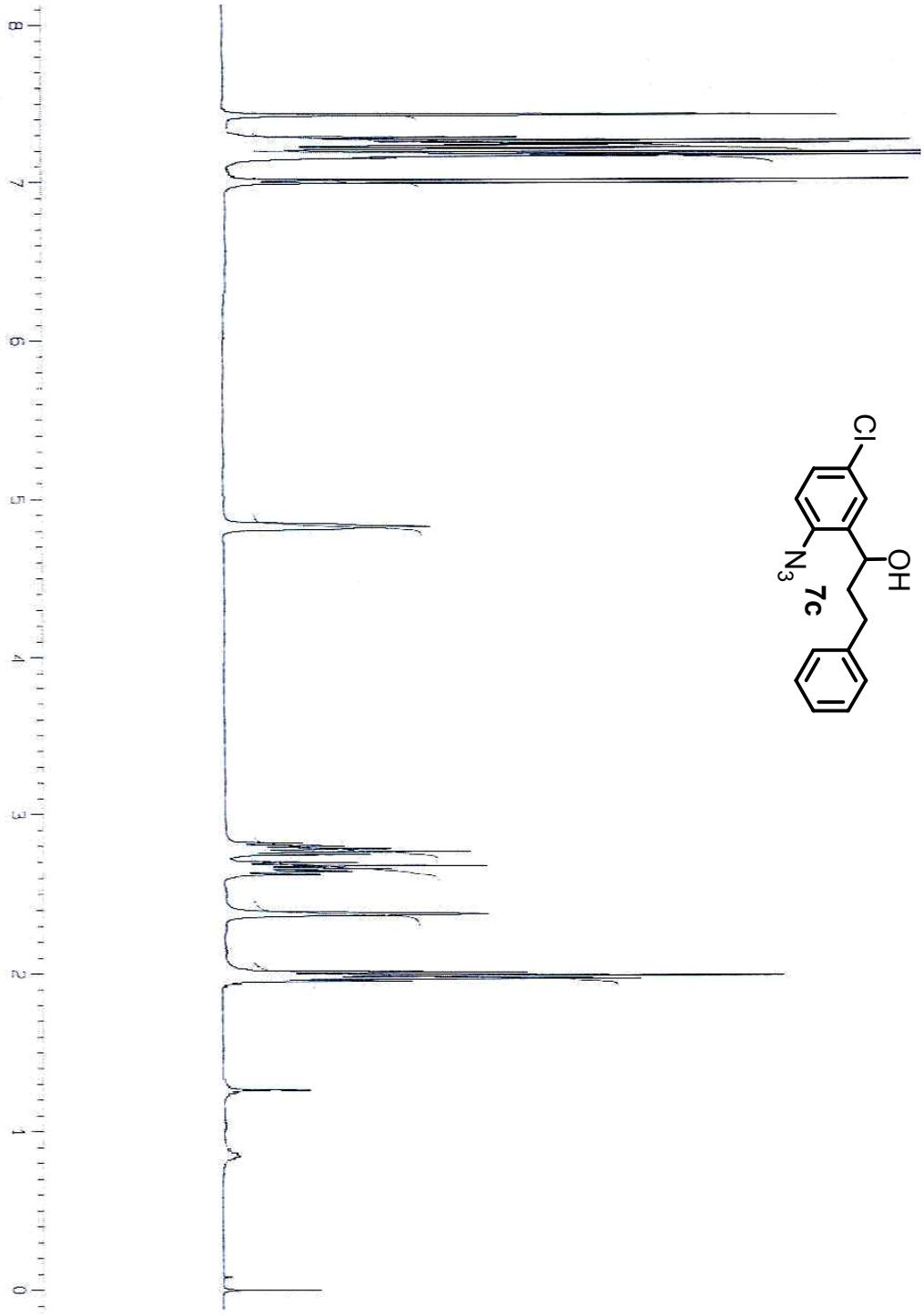
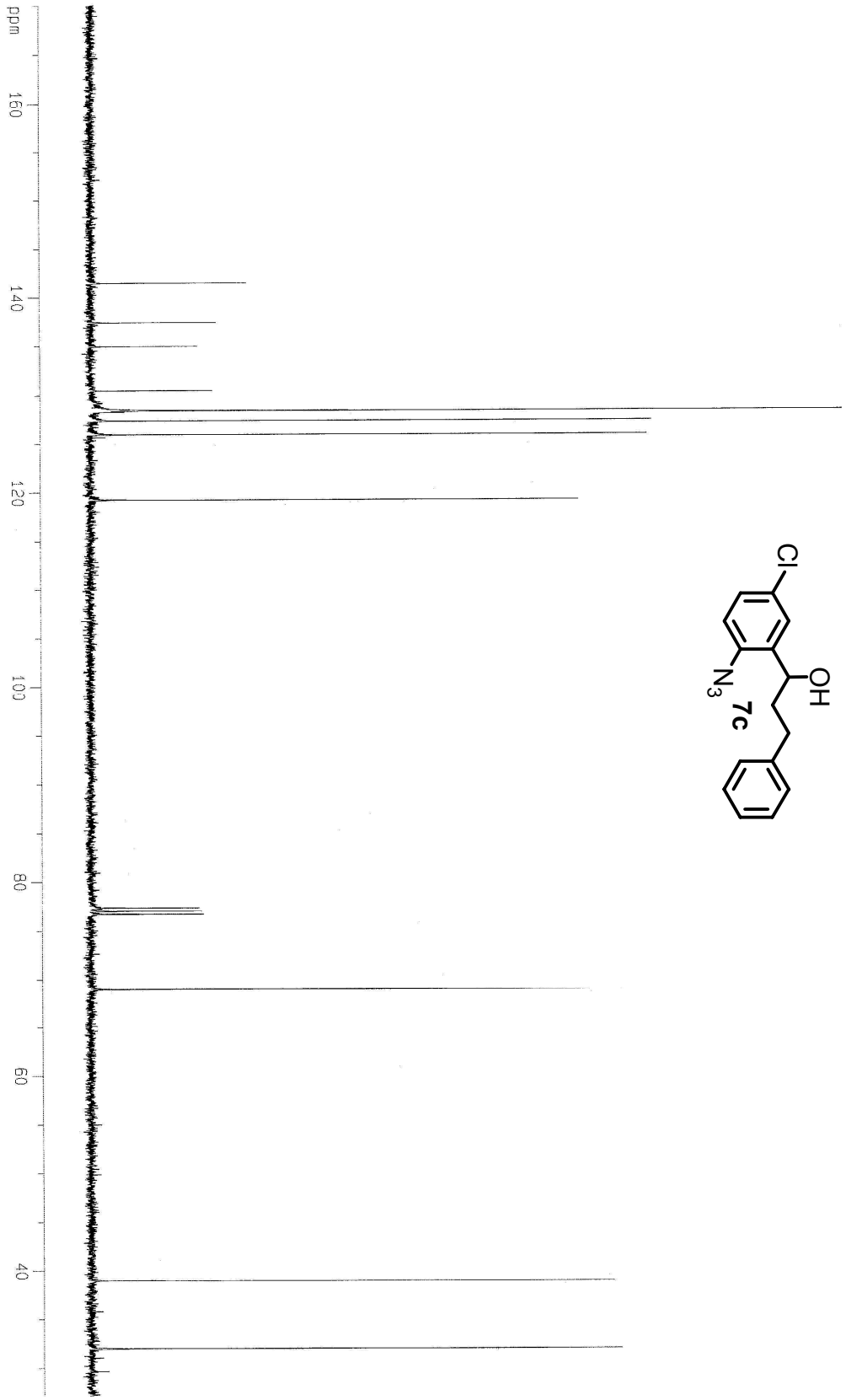
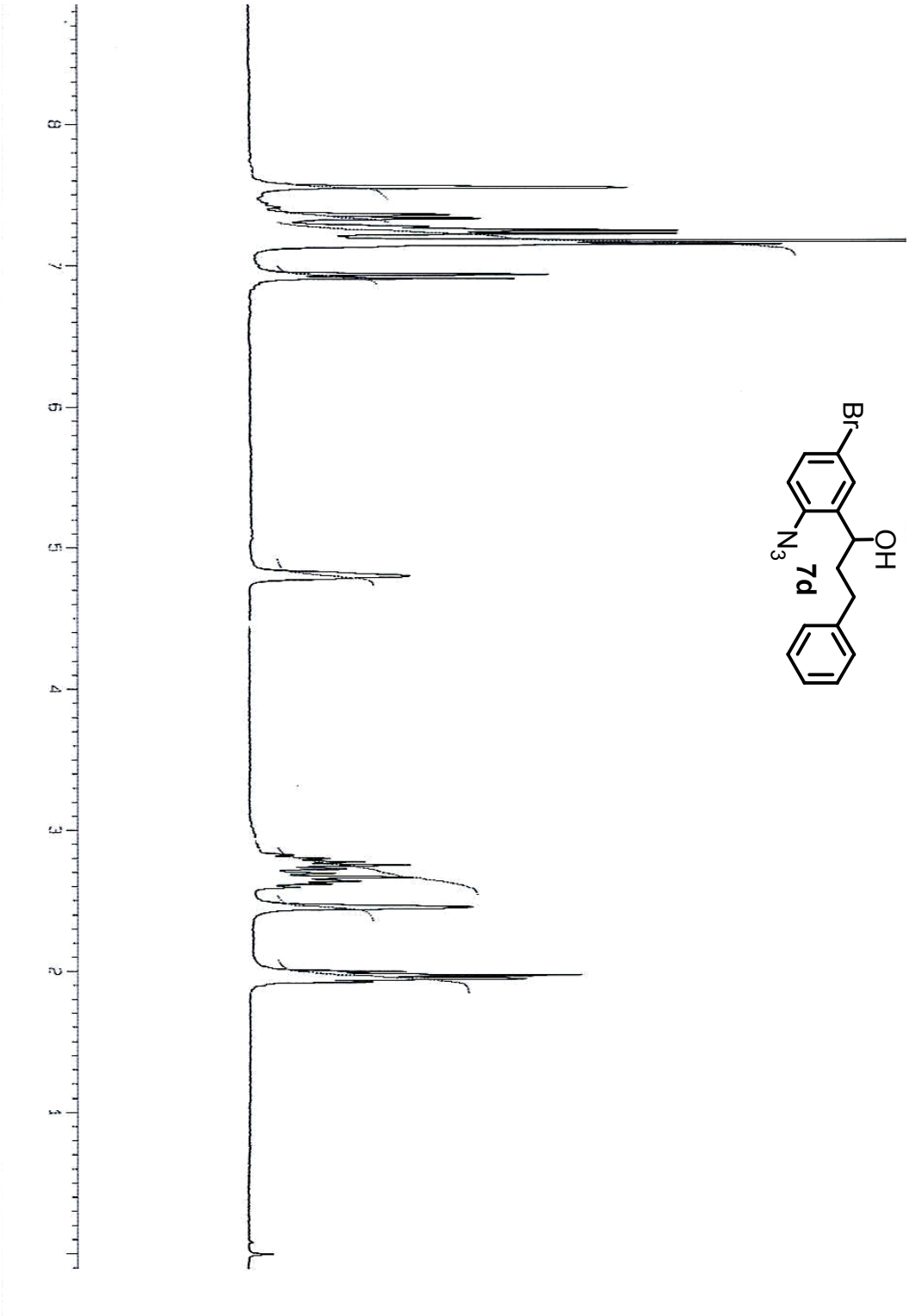
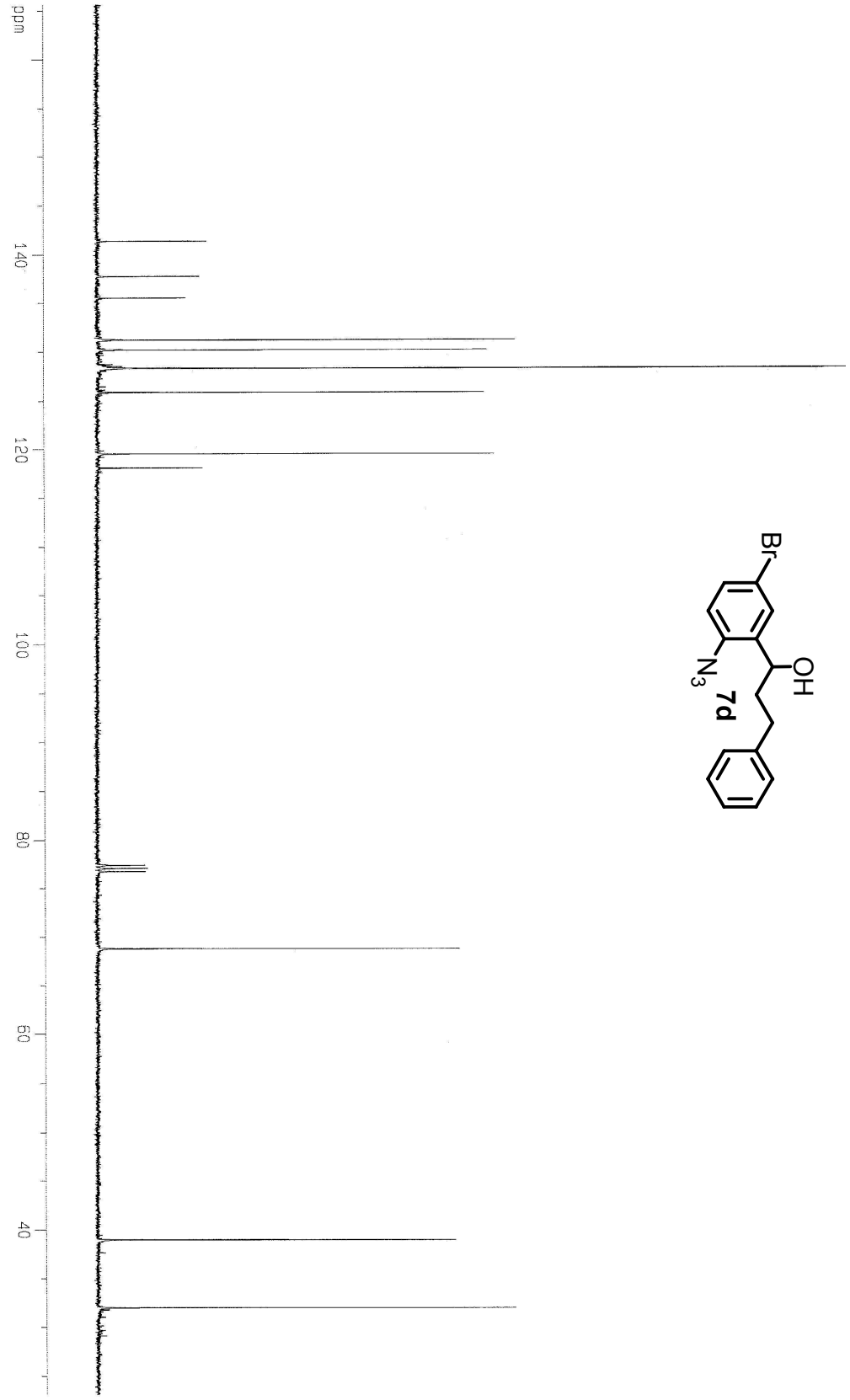
40
F
OH
N3
7b


Cl
OH
N3
7c
8
7
6
5
4
3
2
1
0


ppm
160
140
120
100
80
60
40
Cl
OH
N3
7c


Br
OH
N3
7d


ppm
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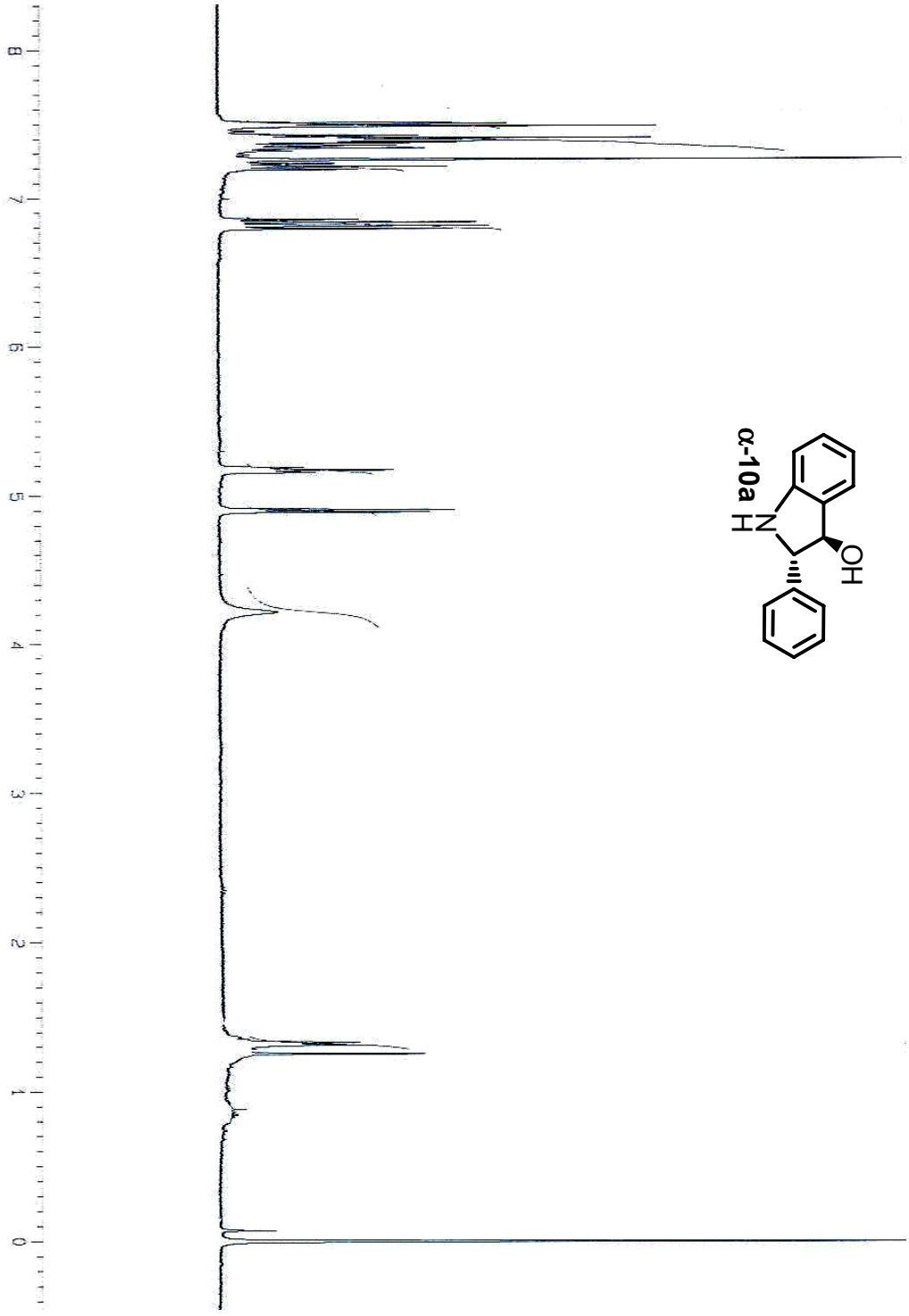
120
100
80
60
40
Br
OH
N3
7d


α-10a
N
H
OH
8
7
6
5
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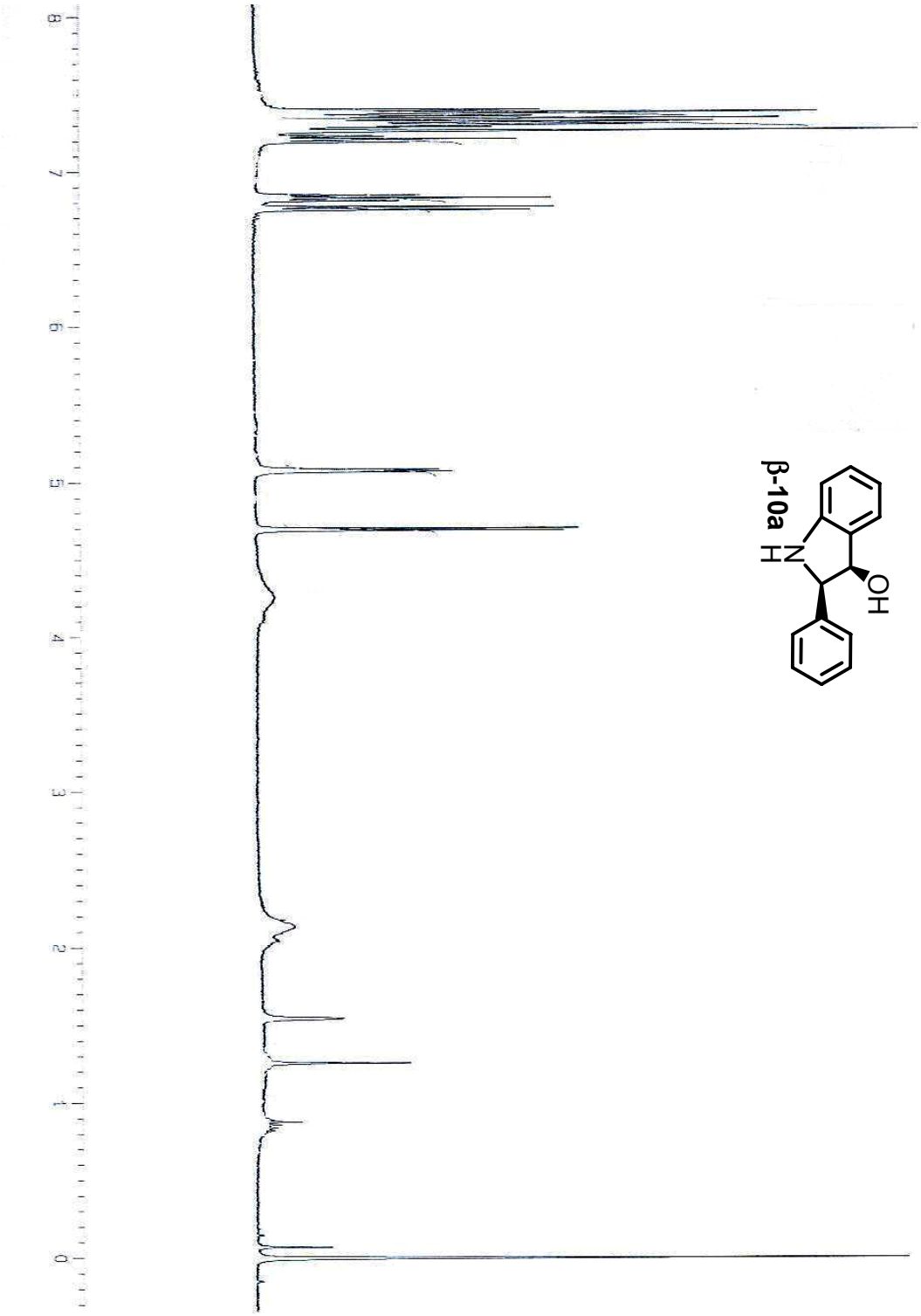
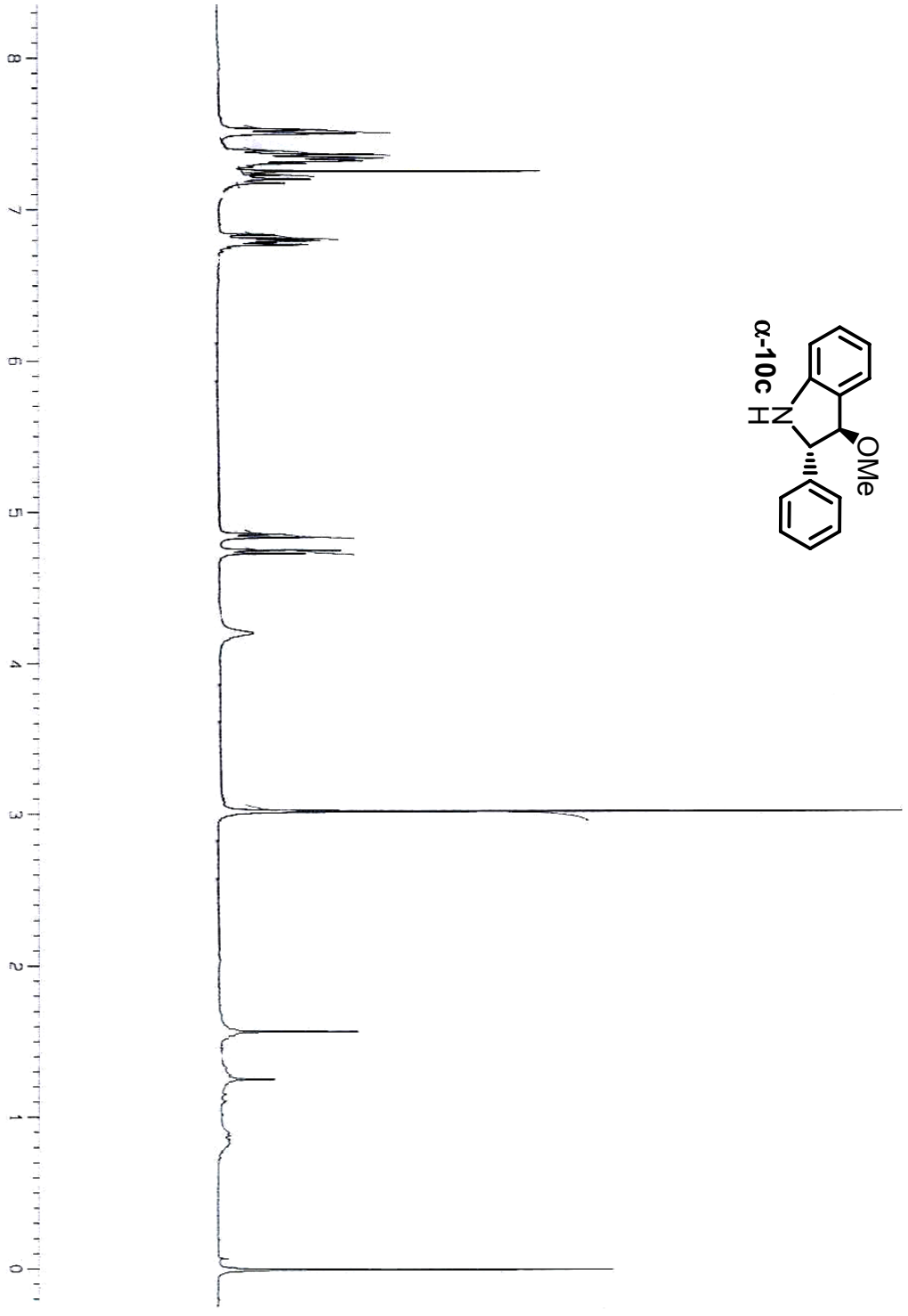
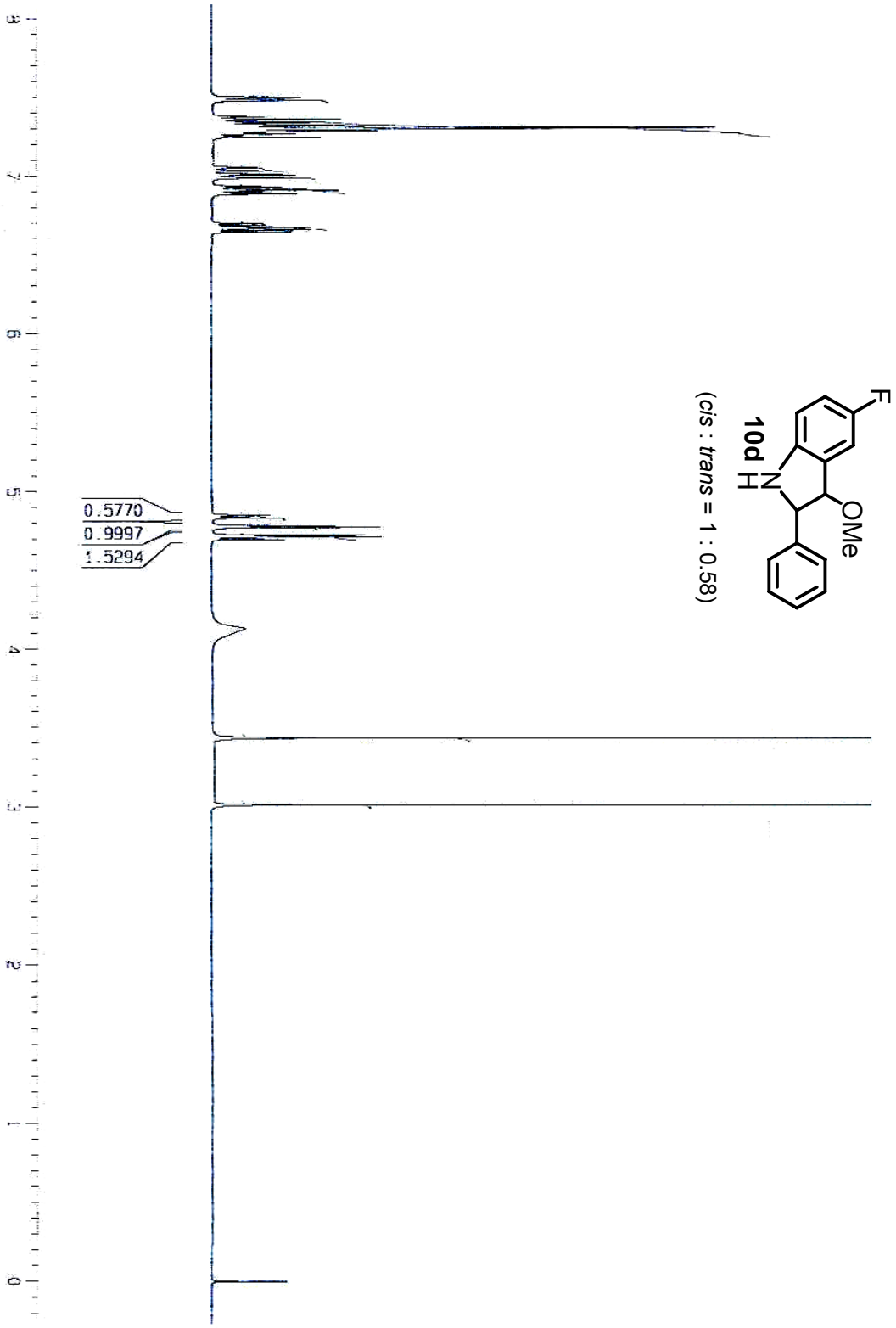
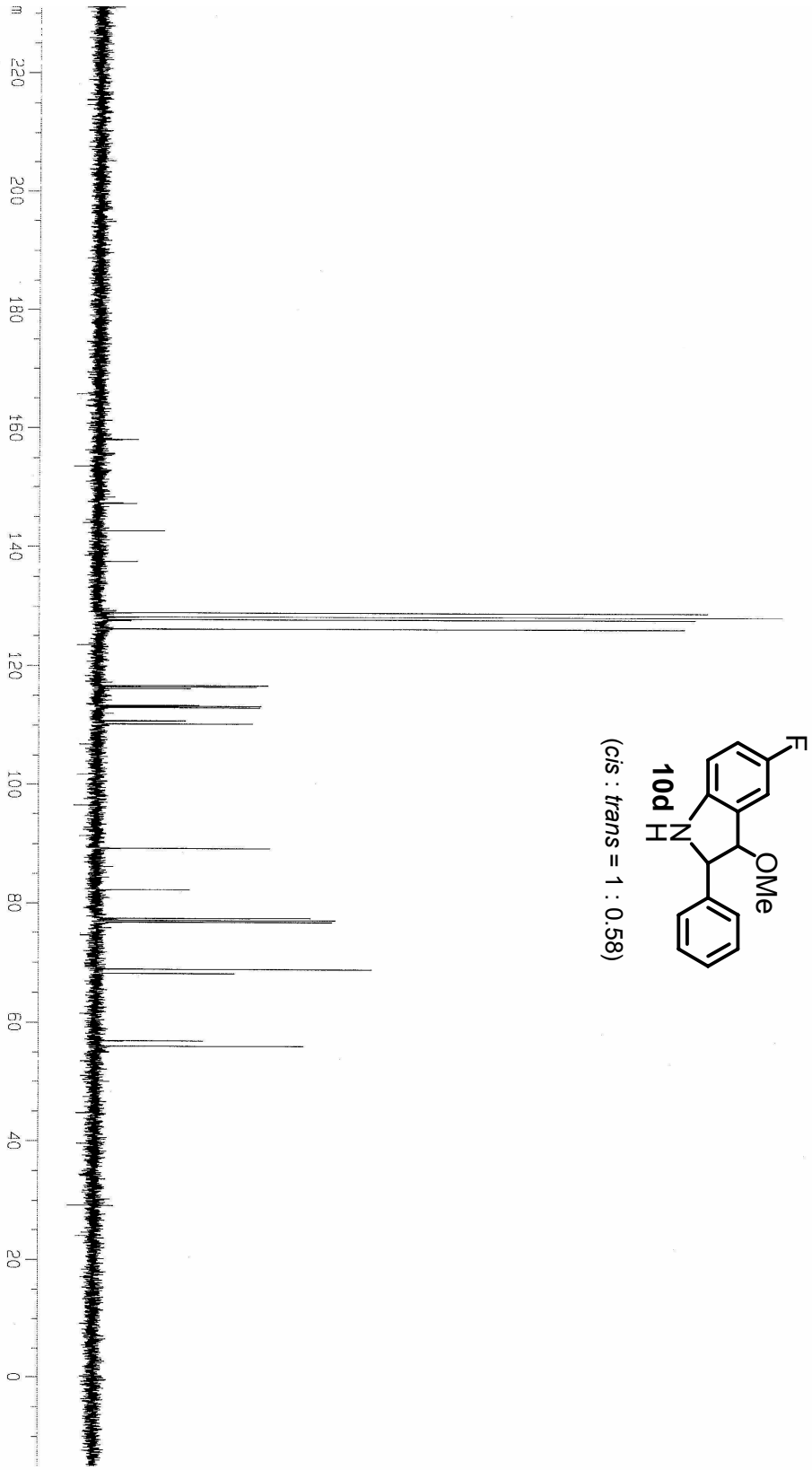
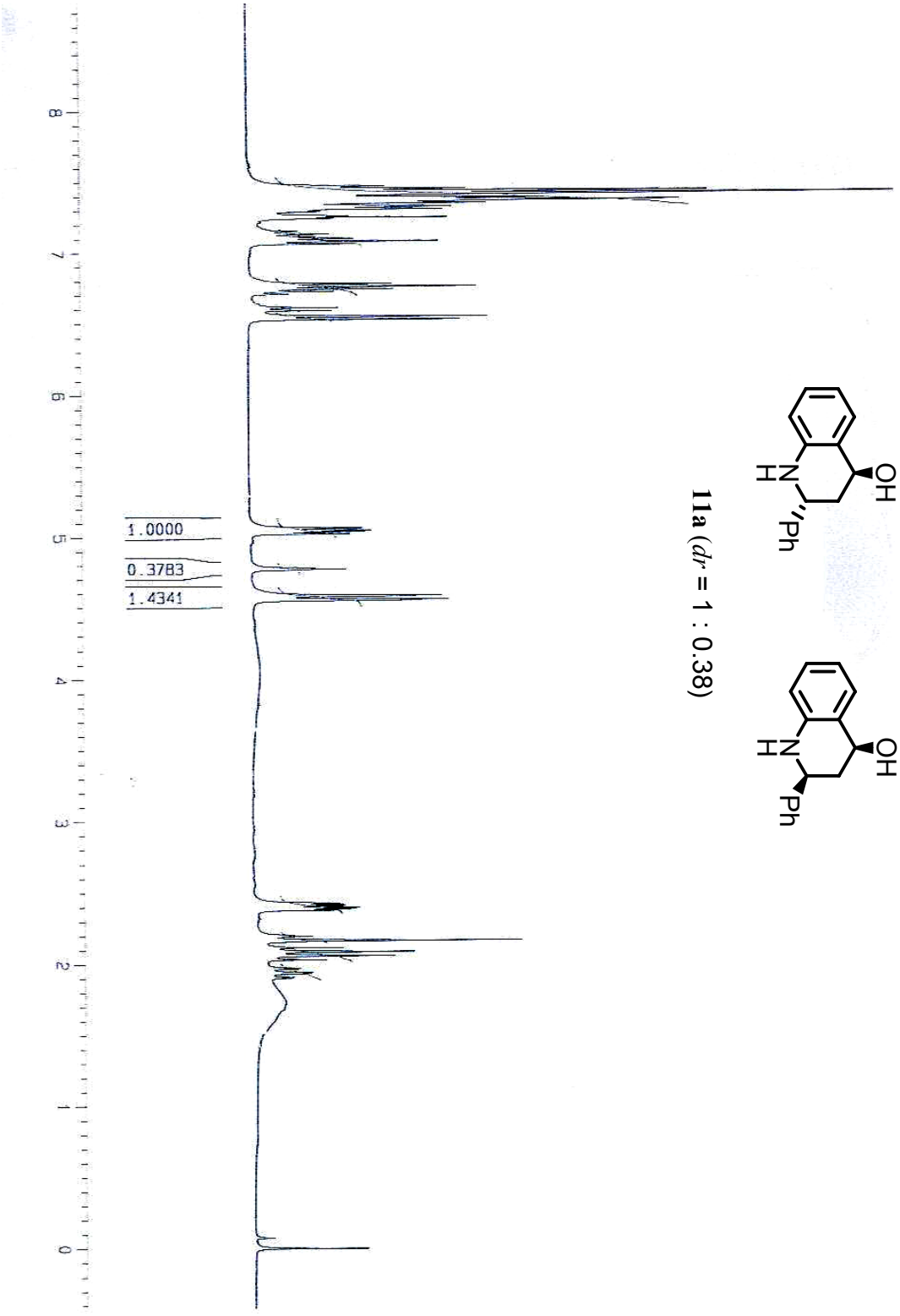
3
2
1
0


β-10a
N
H
OH
8
7
6
5
4
3
2
1
0

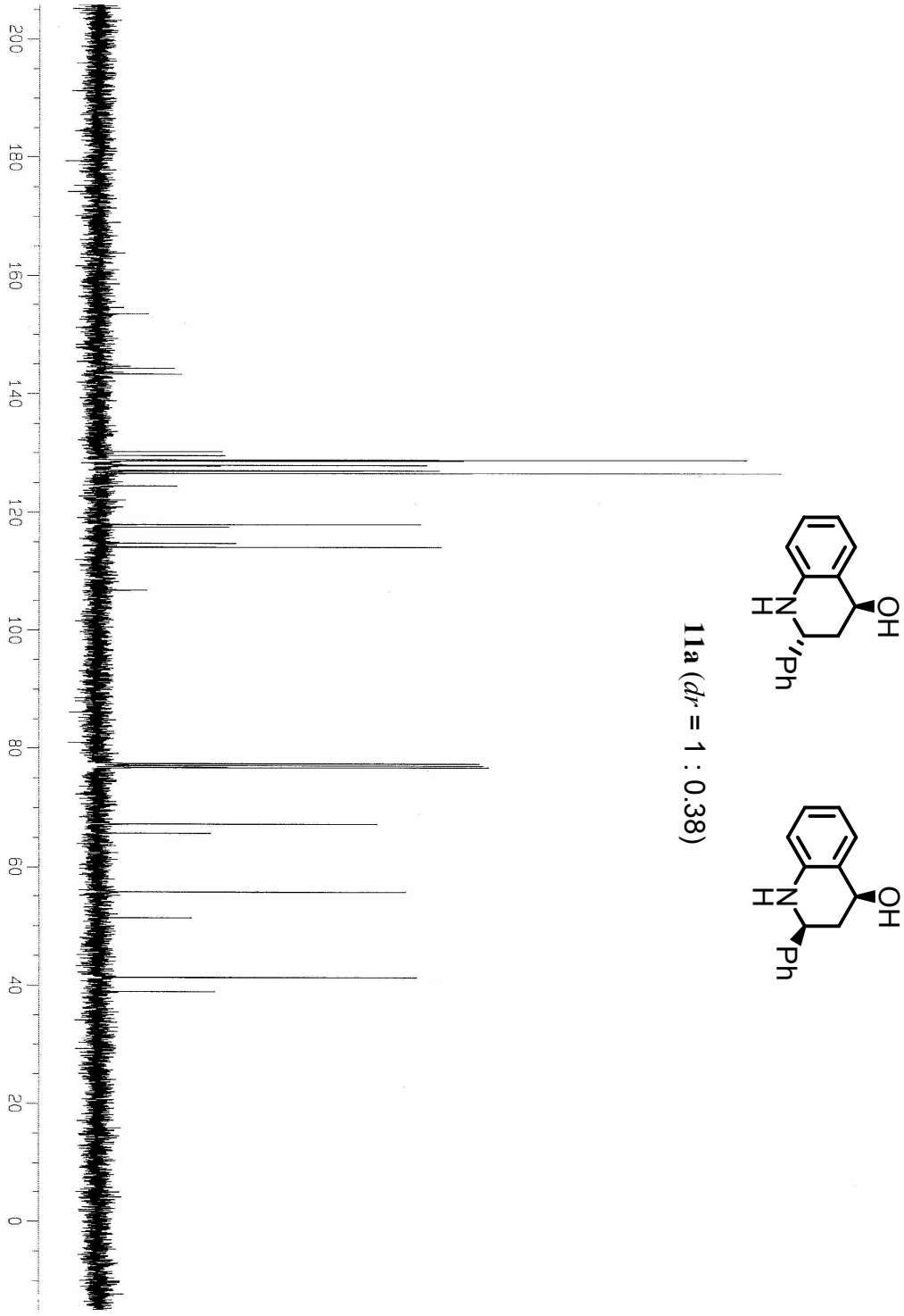

α-10c
H
N
OMe
8
7
6
5
4
3
2
1
0


0.5770
0.9997
1.5294
F
10d
N
H
OMe
(cis : trans = 1 : 0.58)

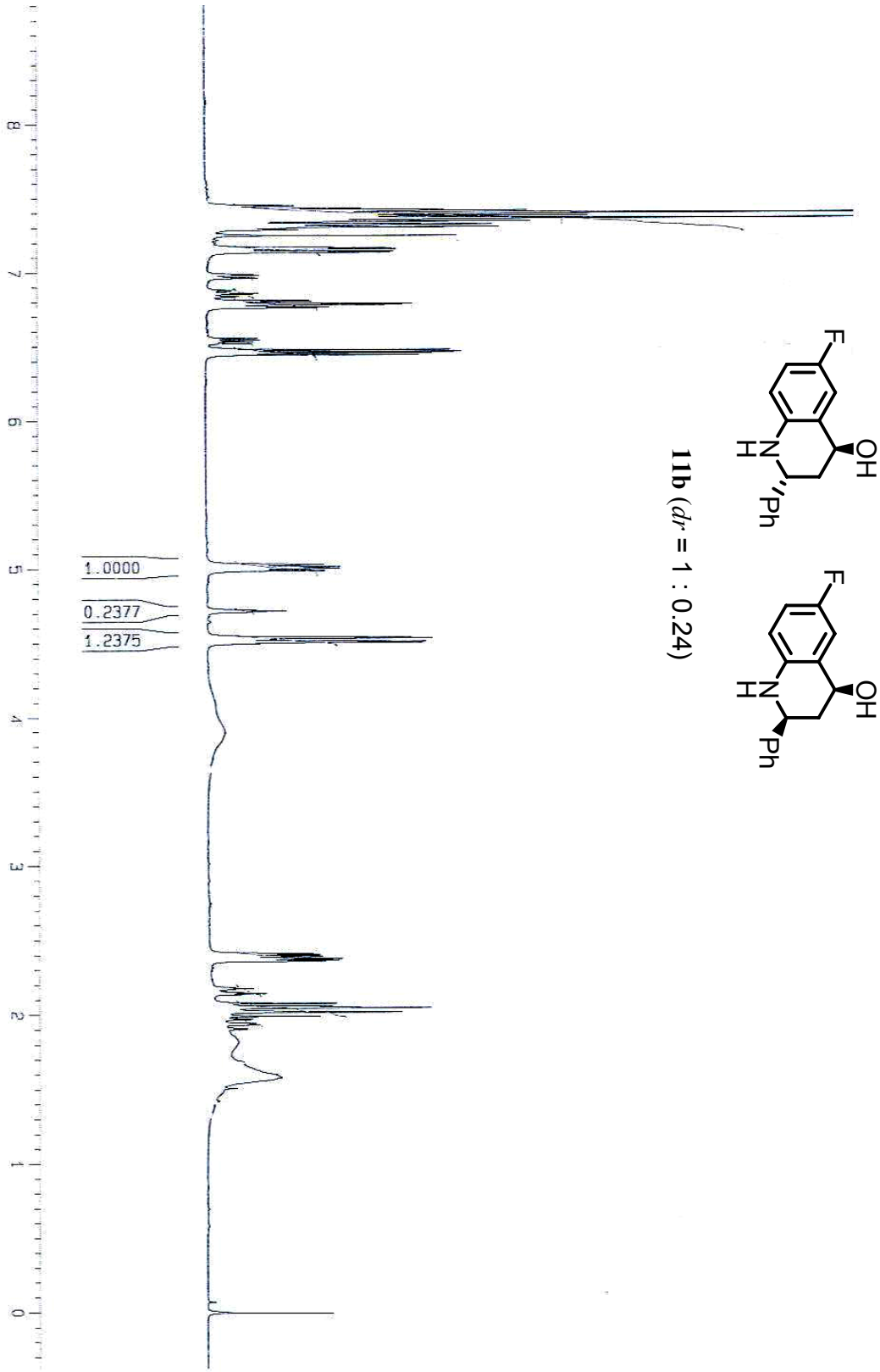

F
10d
N
H
OMe
(cis : trans = 1 : 0.58)
220
200
180
160
140
120
100
80
60
40
20
0



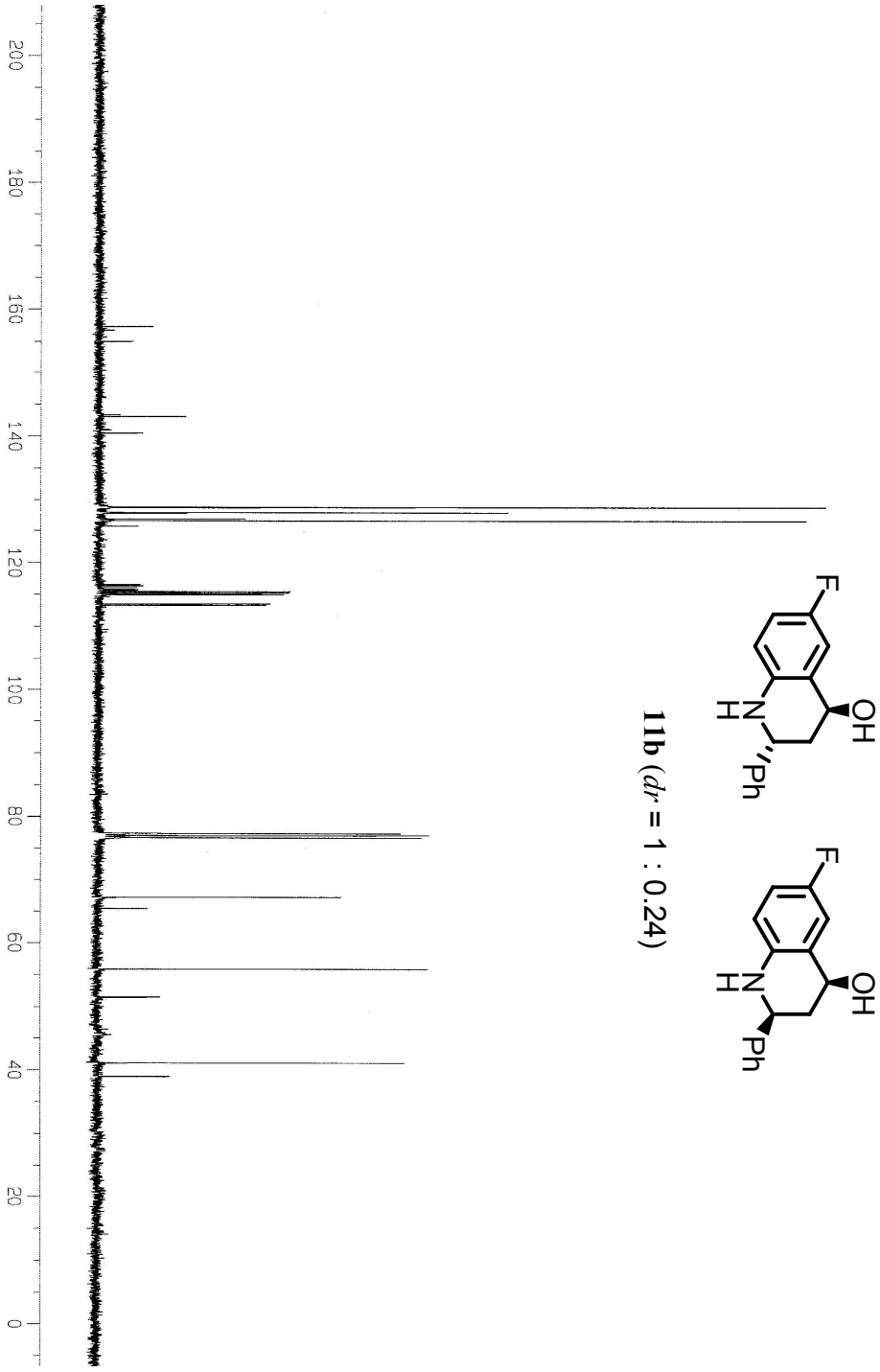
11a (*dr* = 1 : 0.38)



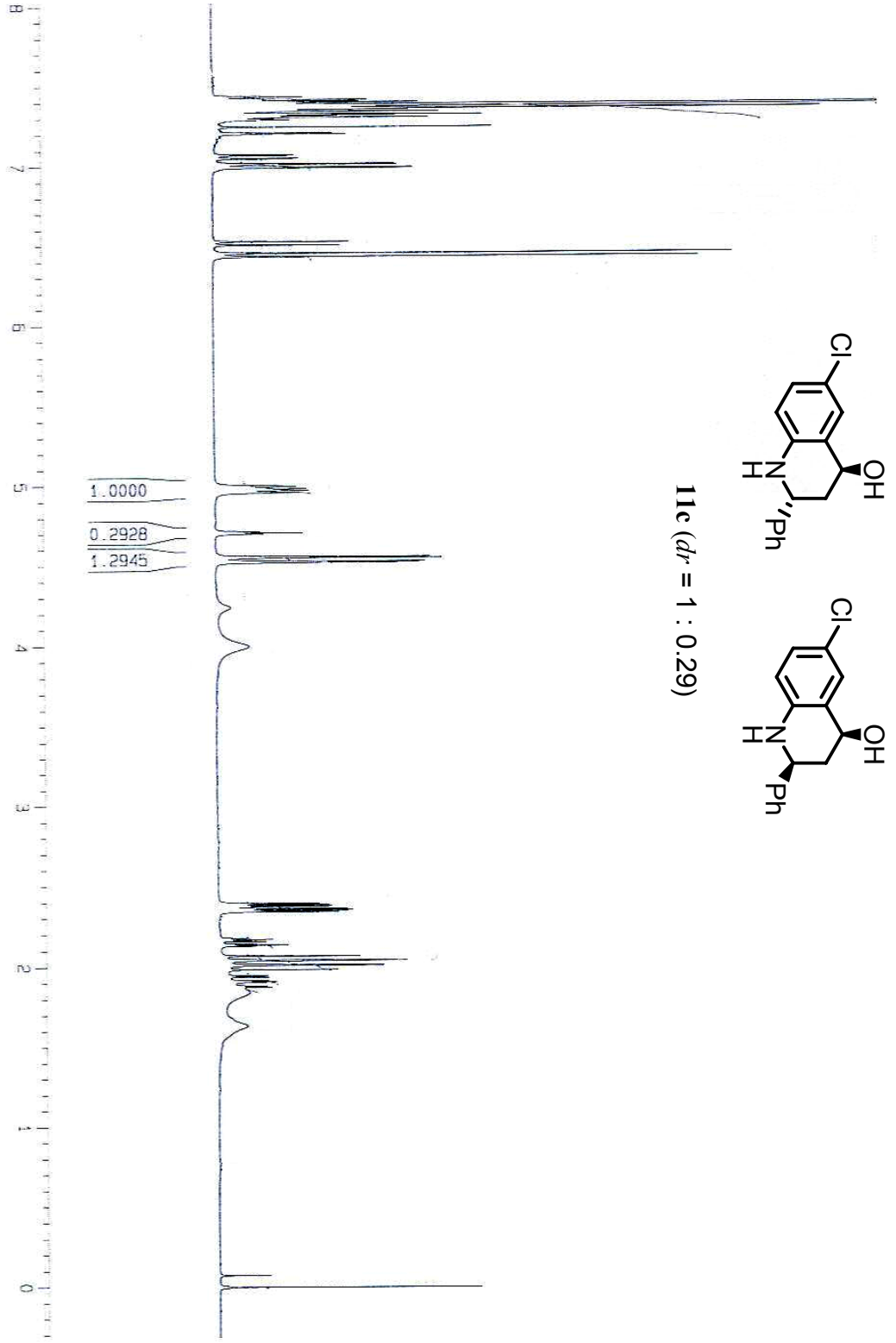
11a (*dr* = 1 : 0.38)



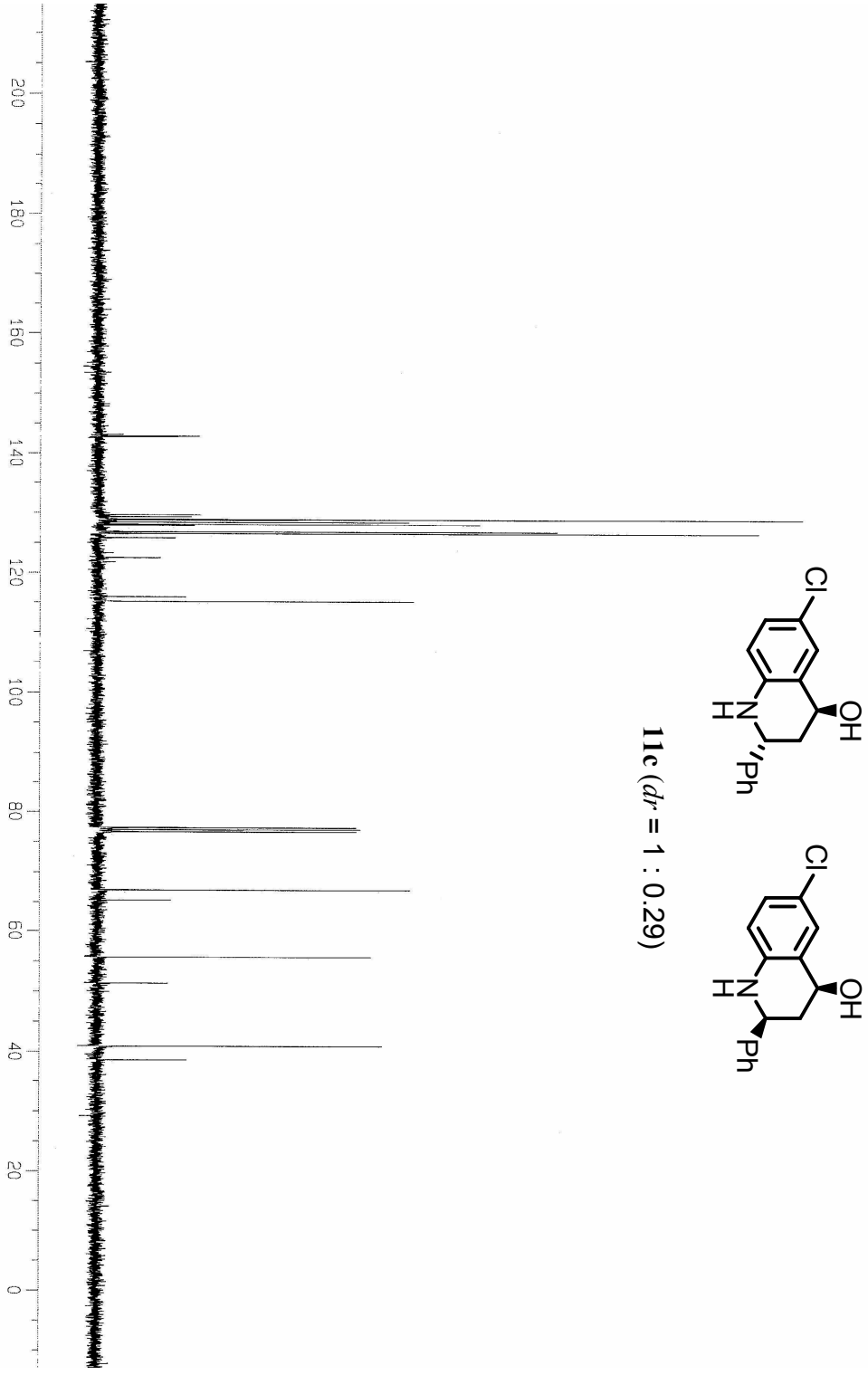
11b (*dr* = 1 : 0.24)



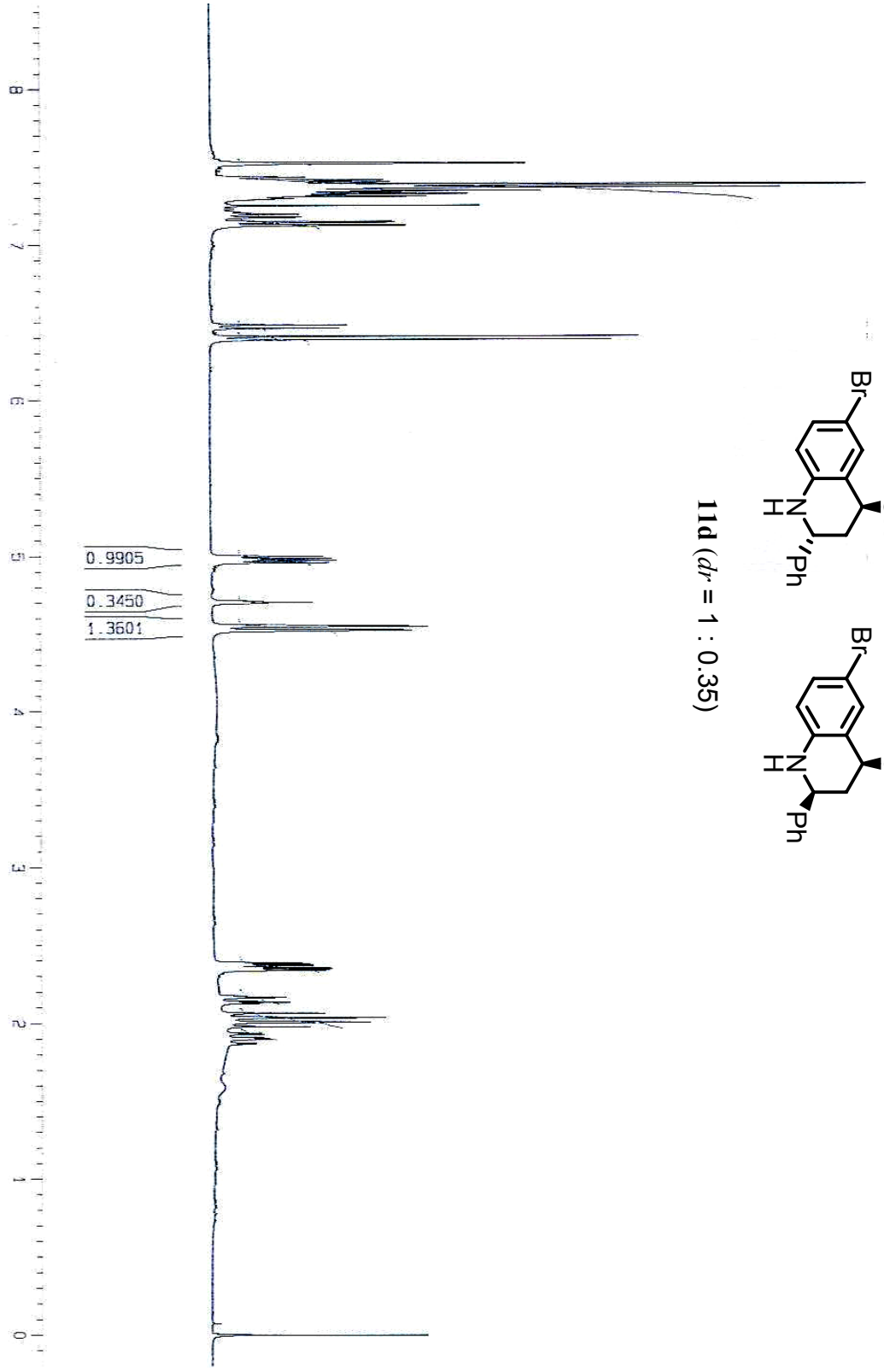
11b (*dr* = 1 : 0.24)



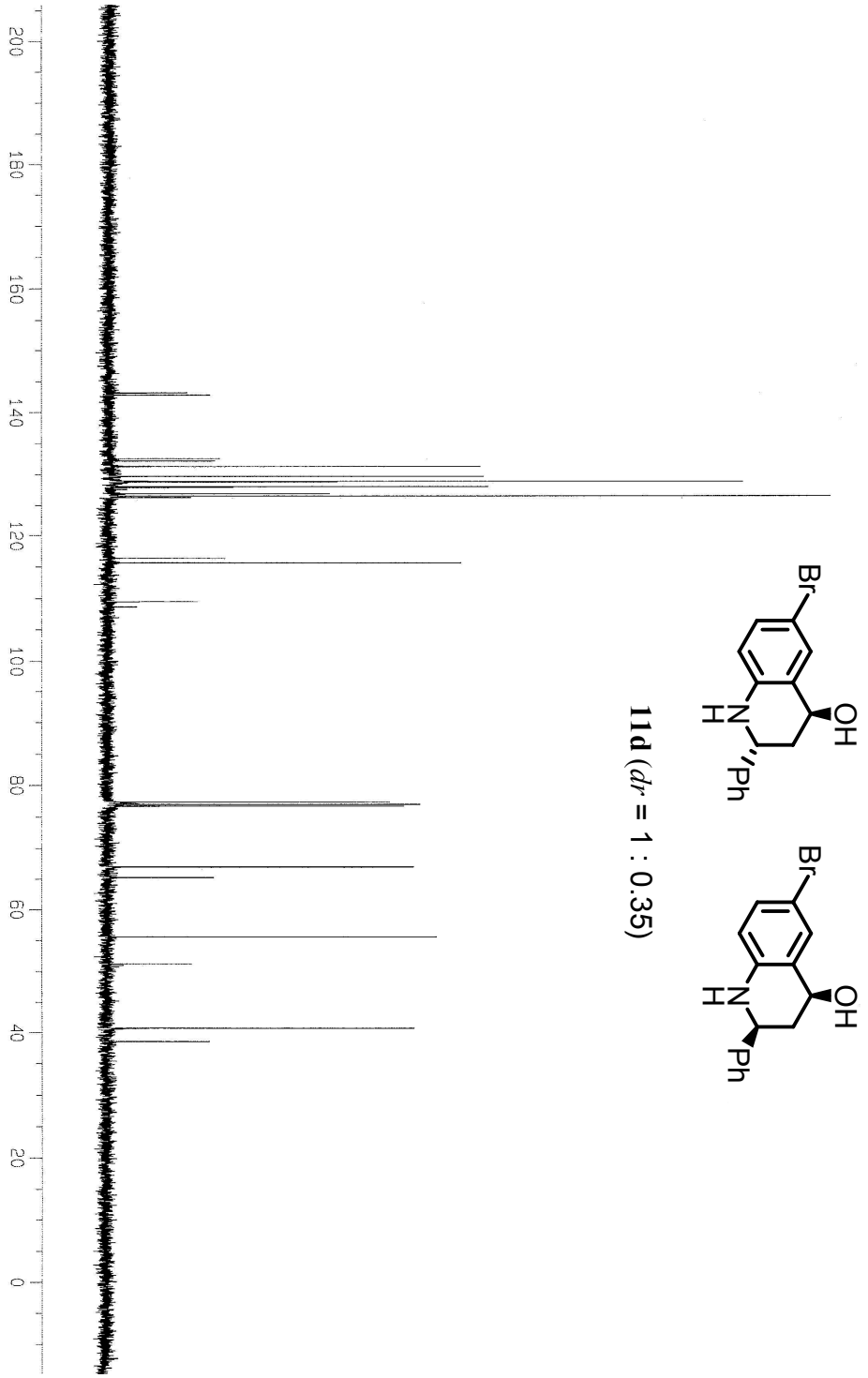
11c (*dr* = 1 : 0.29)



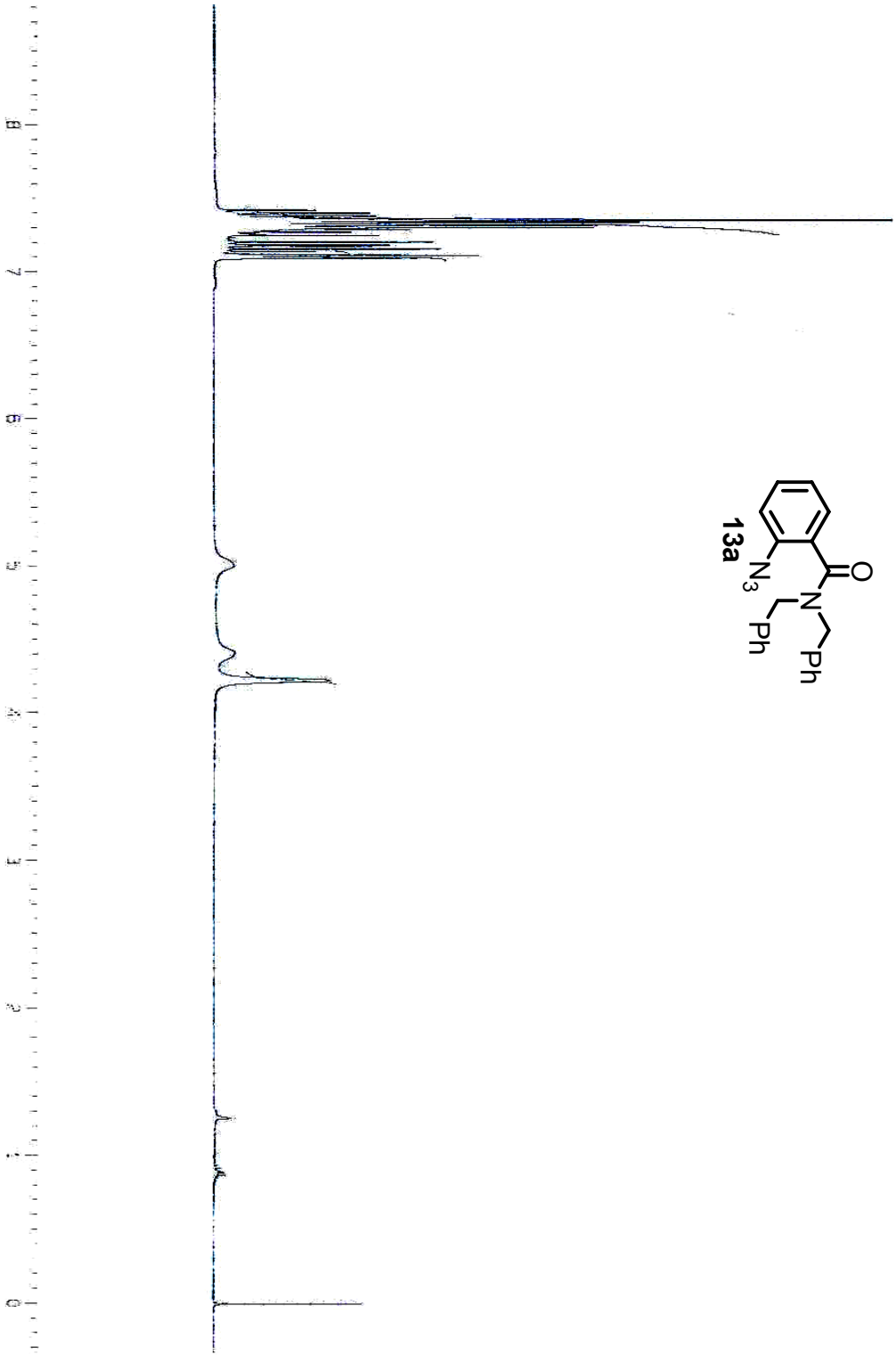
11c (*dr* = 1 : 0.29)

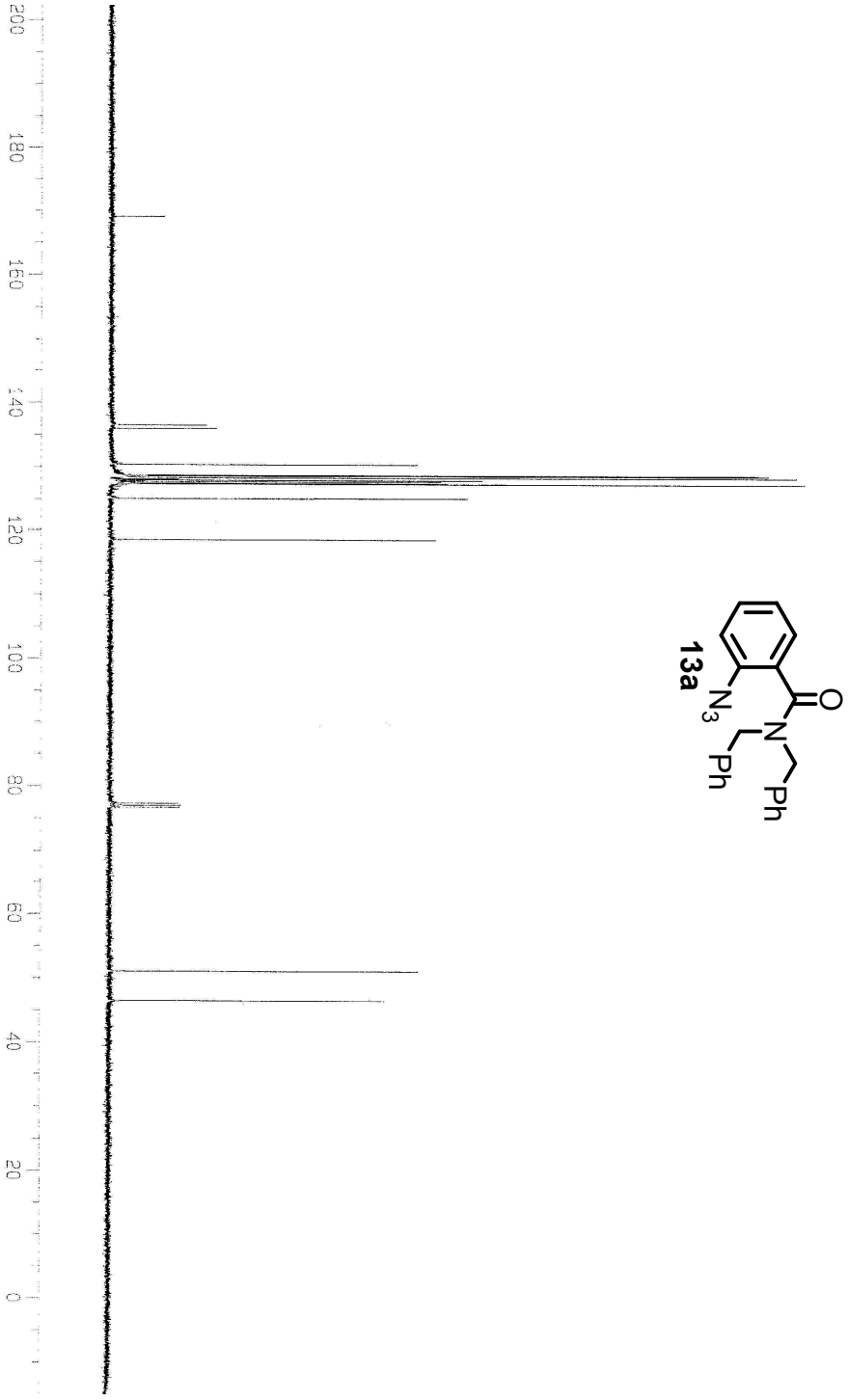


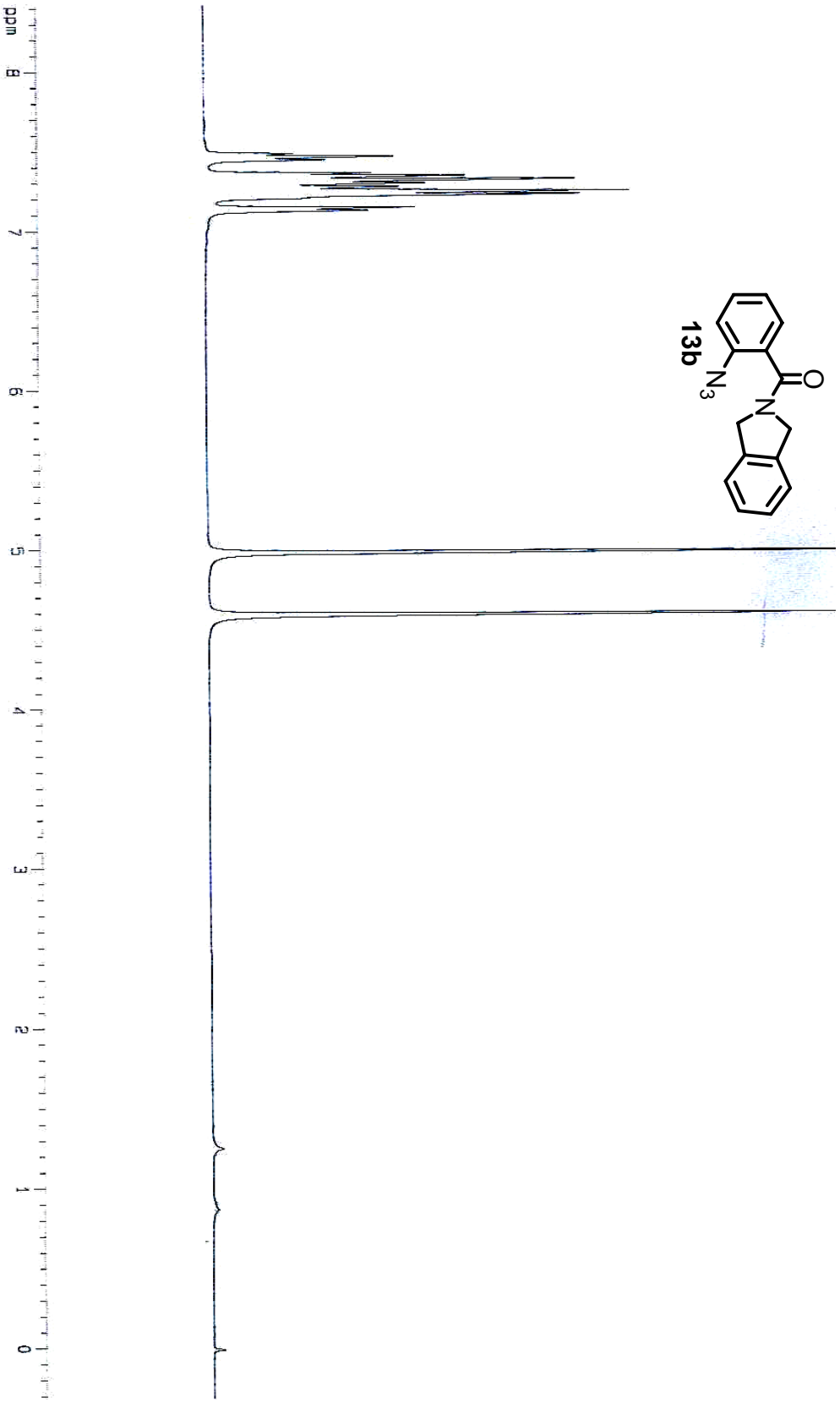
11d (*dr* = 1 : 0.35)

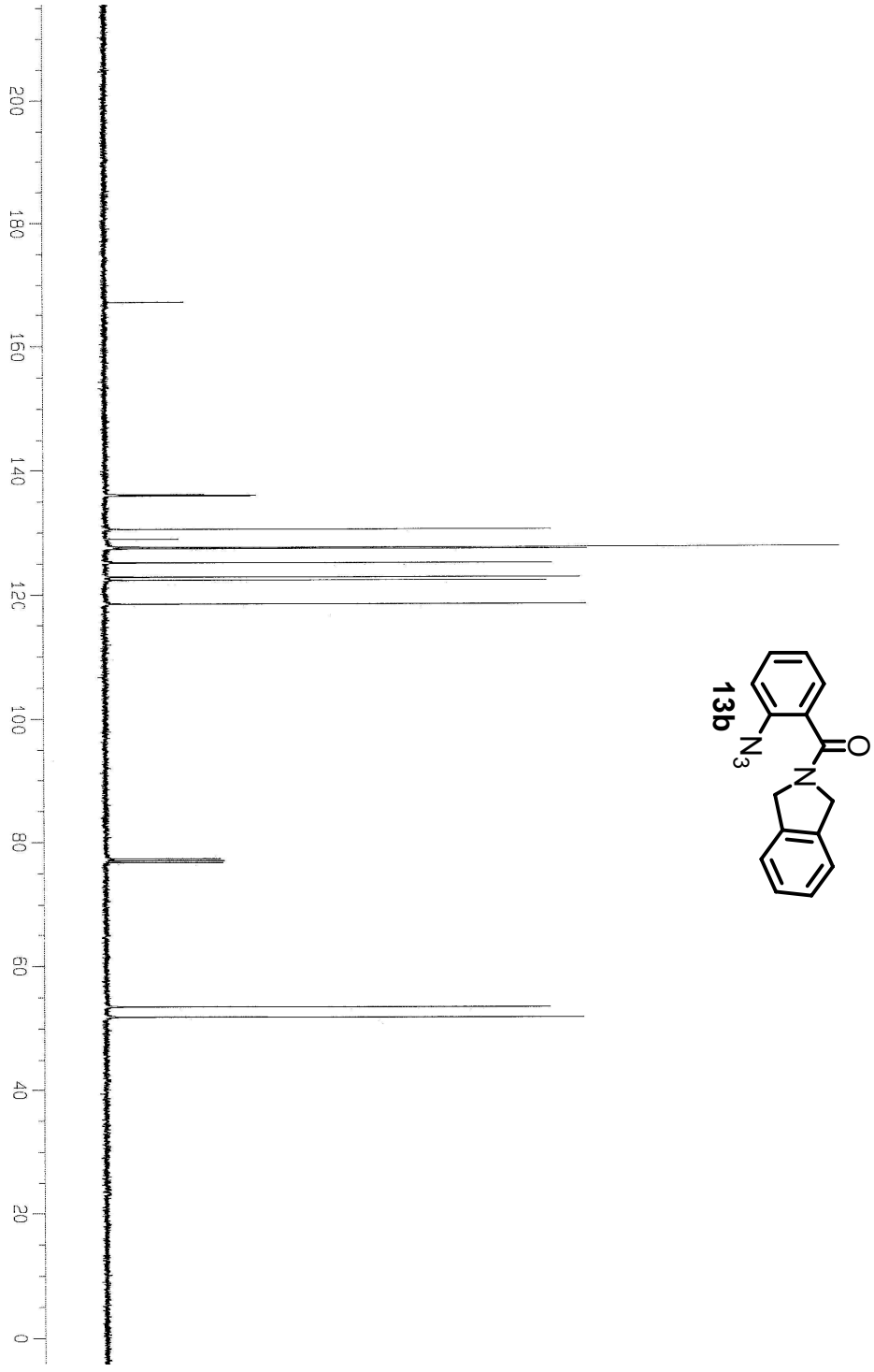


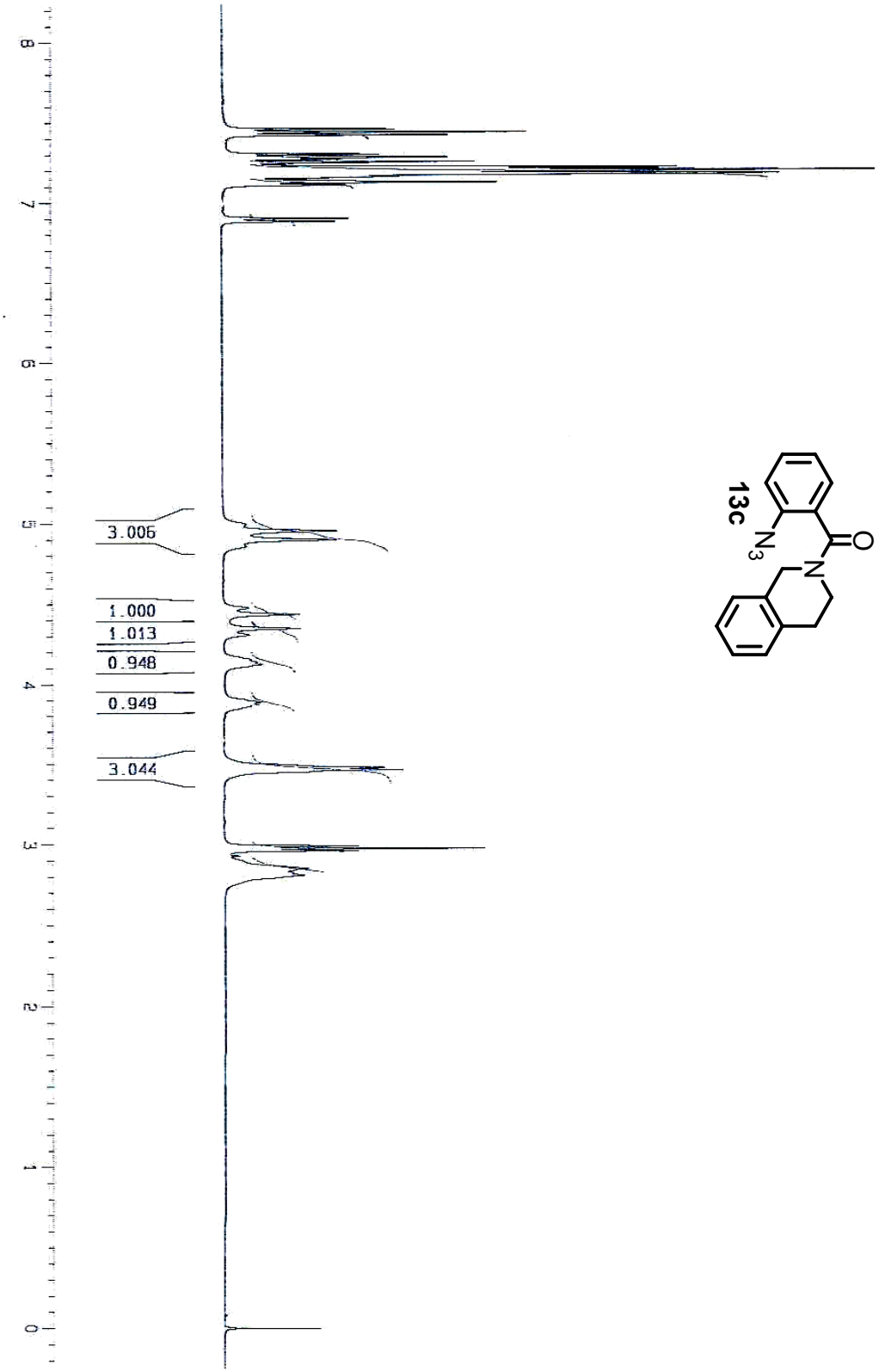
11d (*dr* = 1 : 0.35)


13a
N3
O
N
Ph
Ph


200
180
160
140
120
100
80
60
40
20
0
13a
N3
Ph
O
N
Ph


ppm
8
7
6
5
4
3
2
1
0
13b
N3
O
N


200
180
160
140
120
100
80
60
40
20
0
13b
N3
O
N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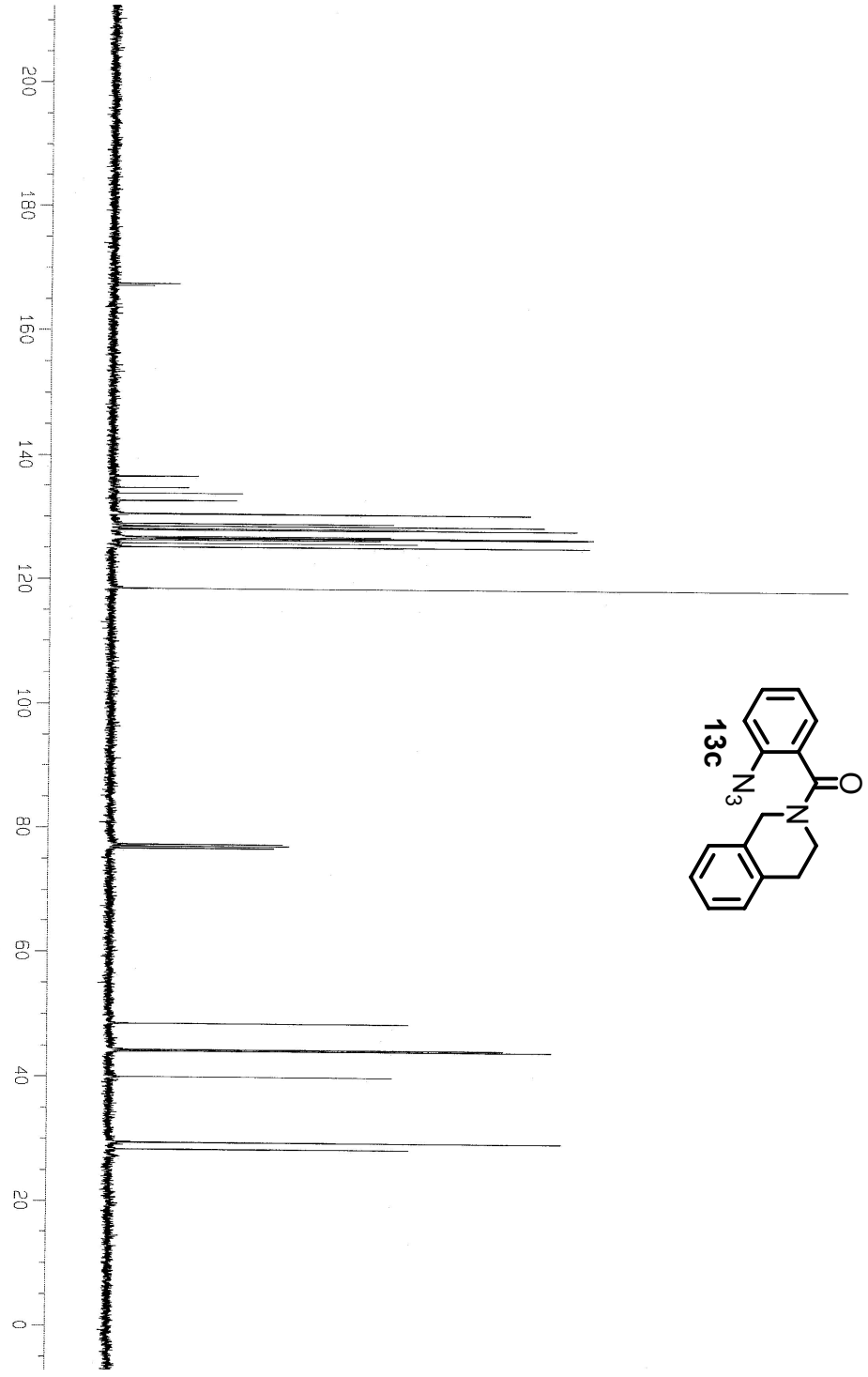
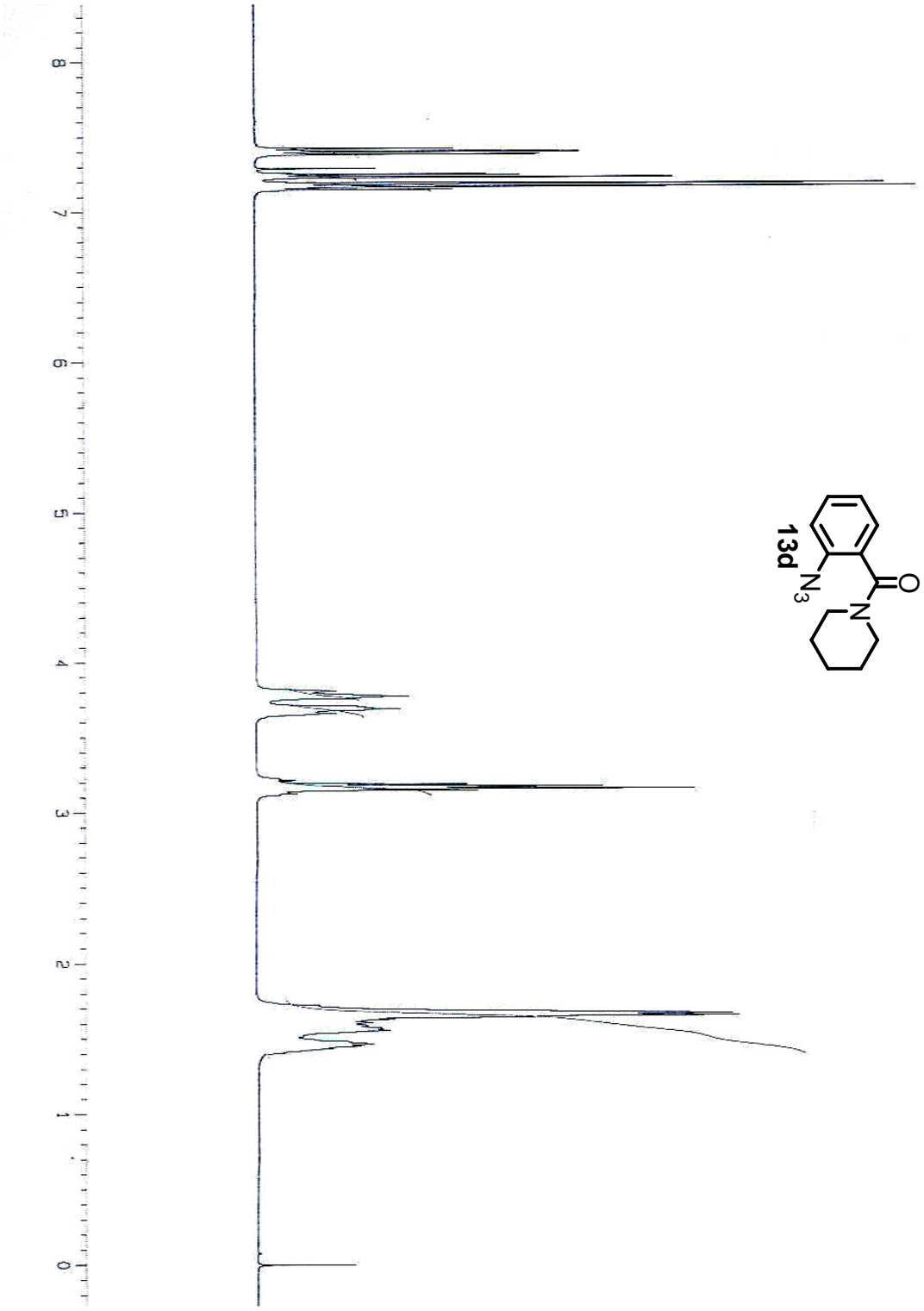
1.000
1.013
0.948
0.949
3.044
13c
N3
O
N


200
180
160
140
120
100
80
60
40
20
0
13c
N3
O
N


13d
N3
O
N
8
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3
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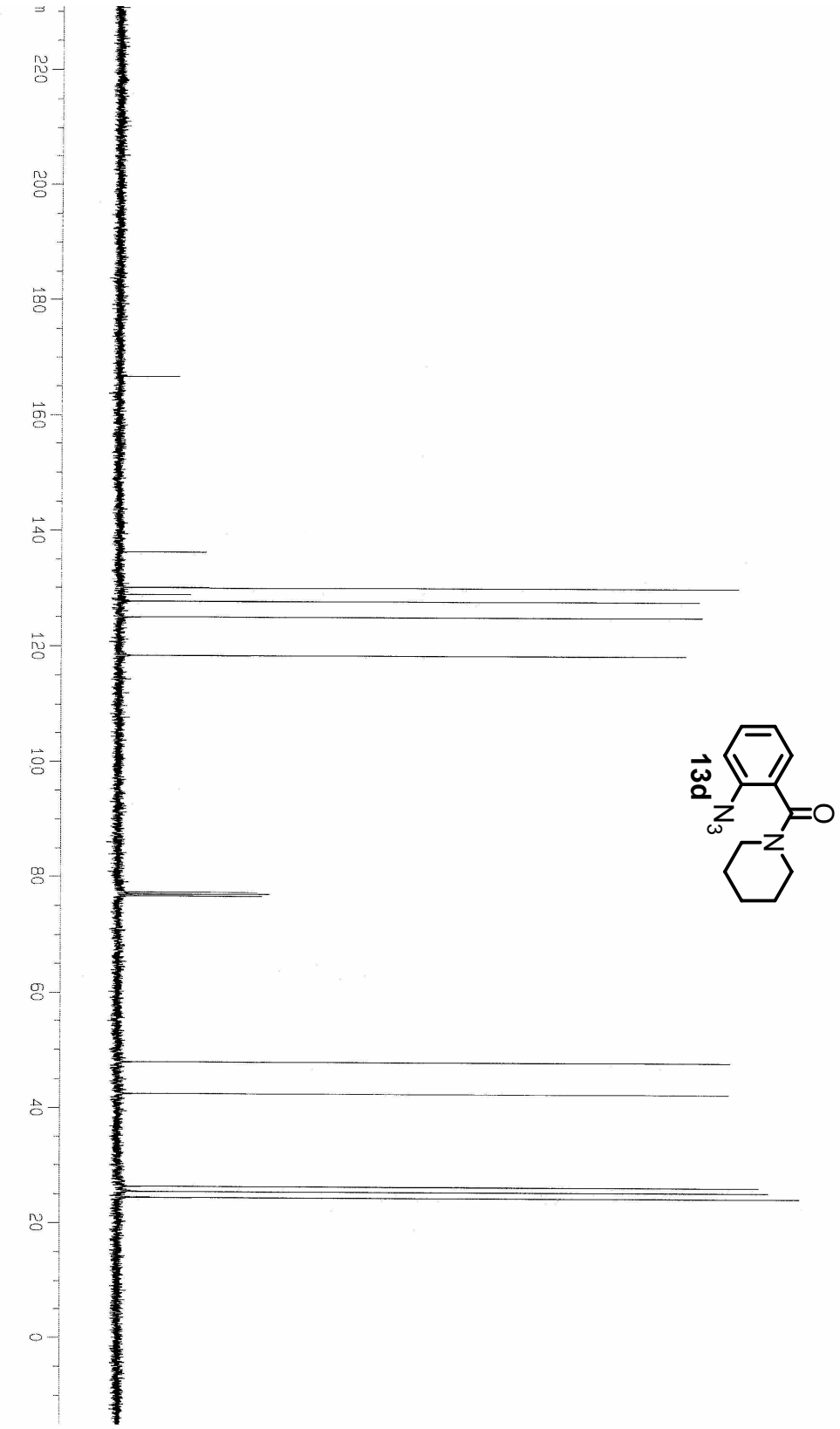
1
0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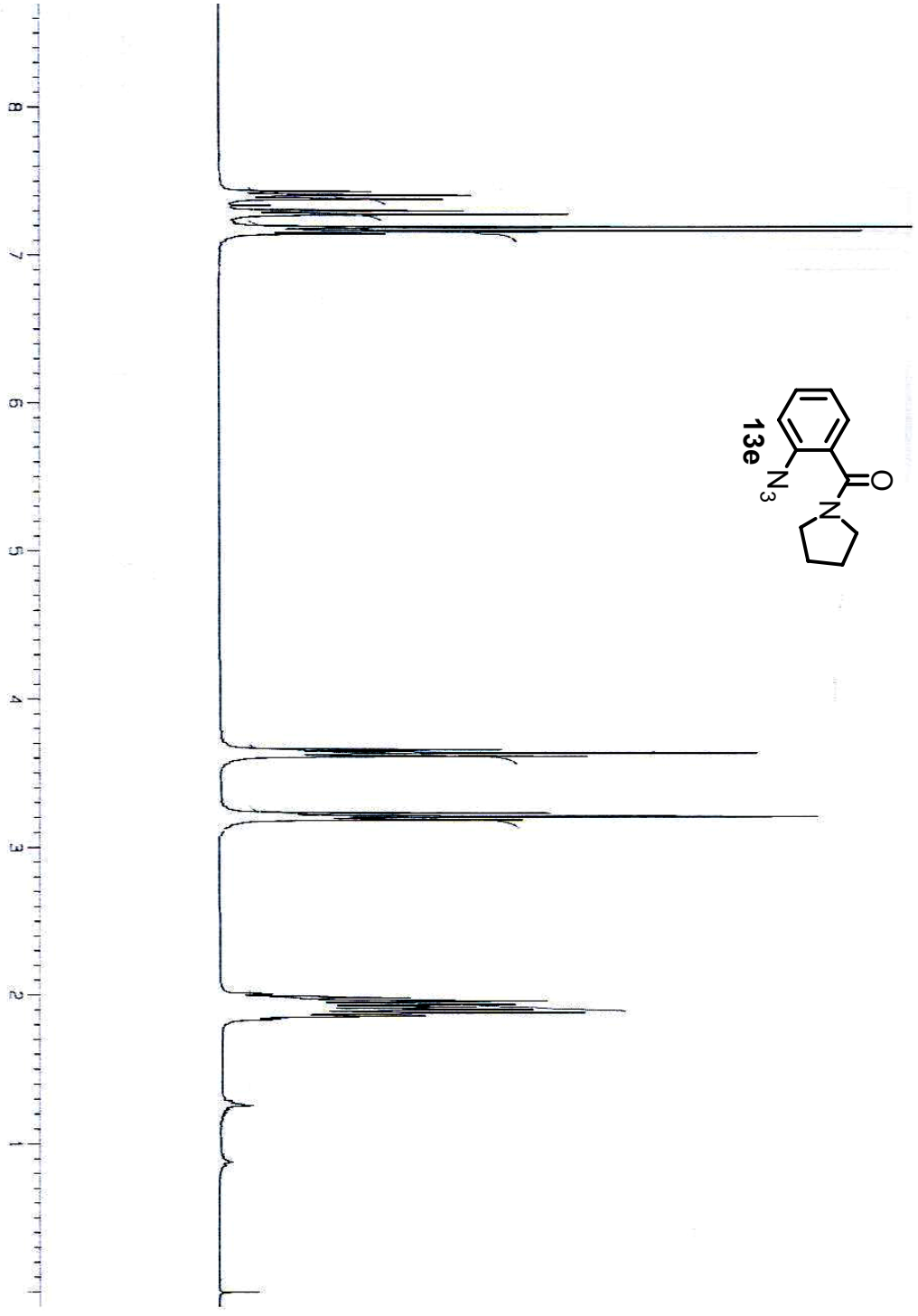
13d
N3
O
N


13e
N3
O
N
8
7
6
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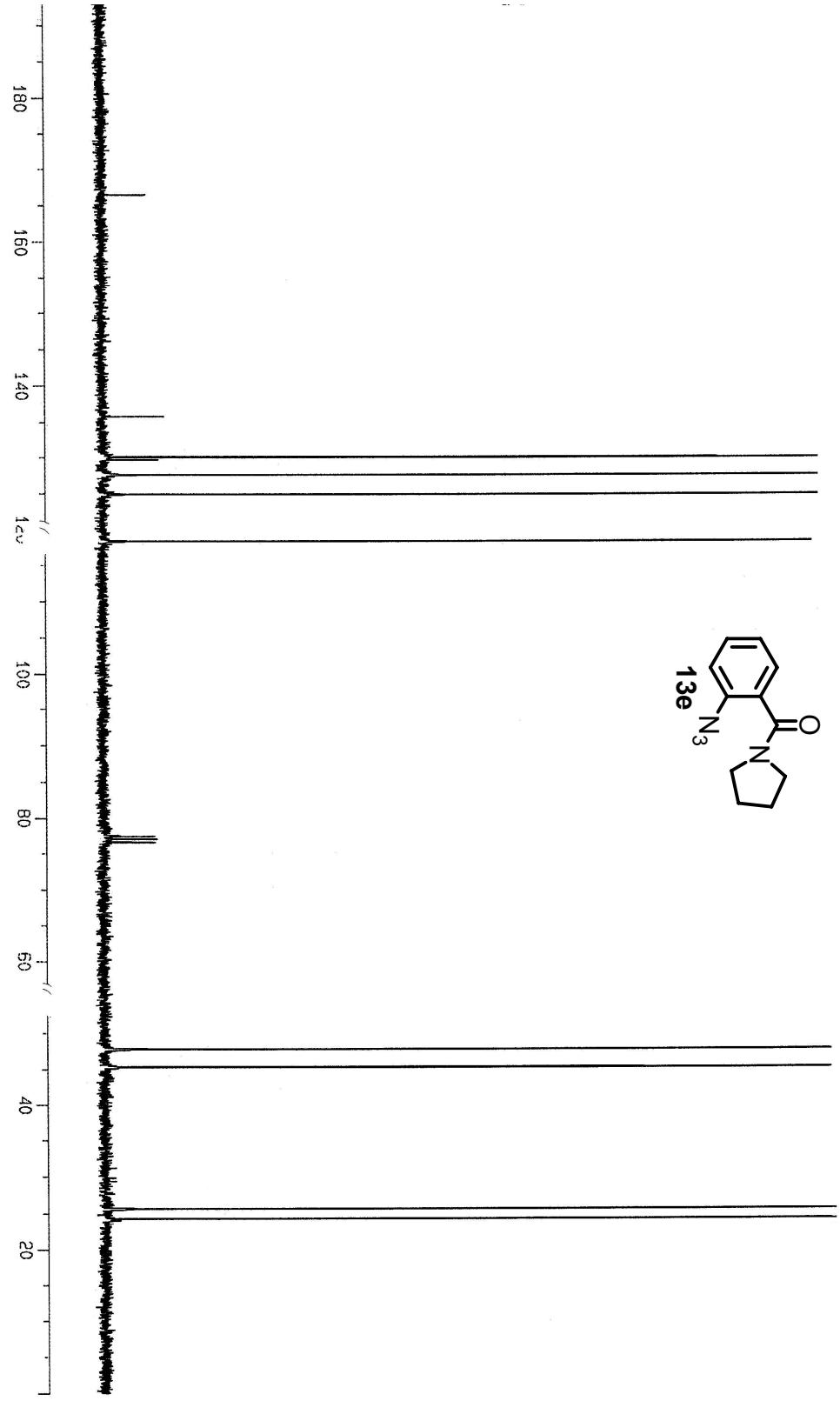
4
3
2
1


180
160
140
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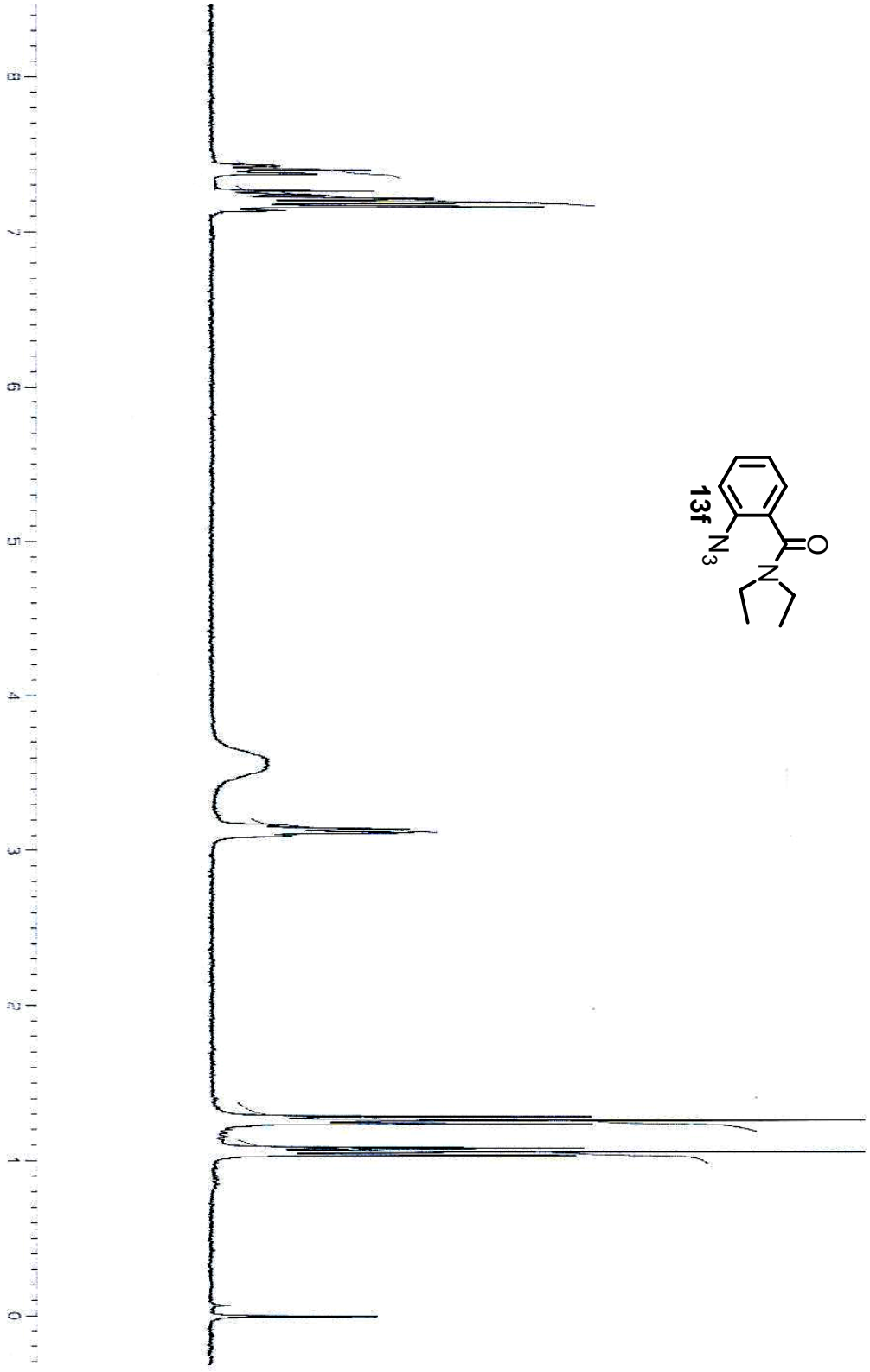
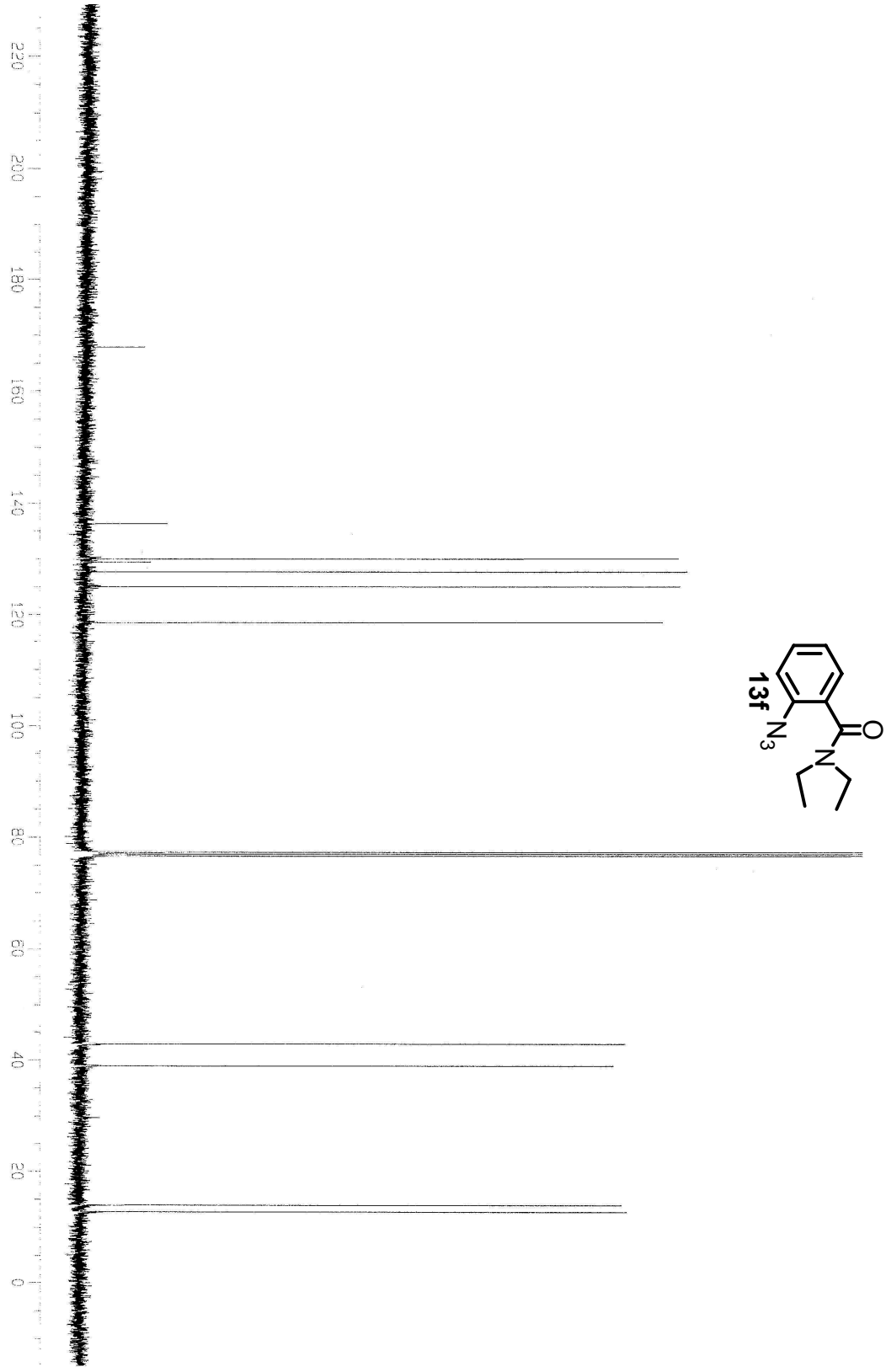
80
60
40
20
13e
N3
O
N


13f
N3
O
N
8
7
6
5
4
3
2
1
0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200
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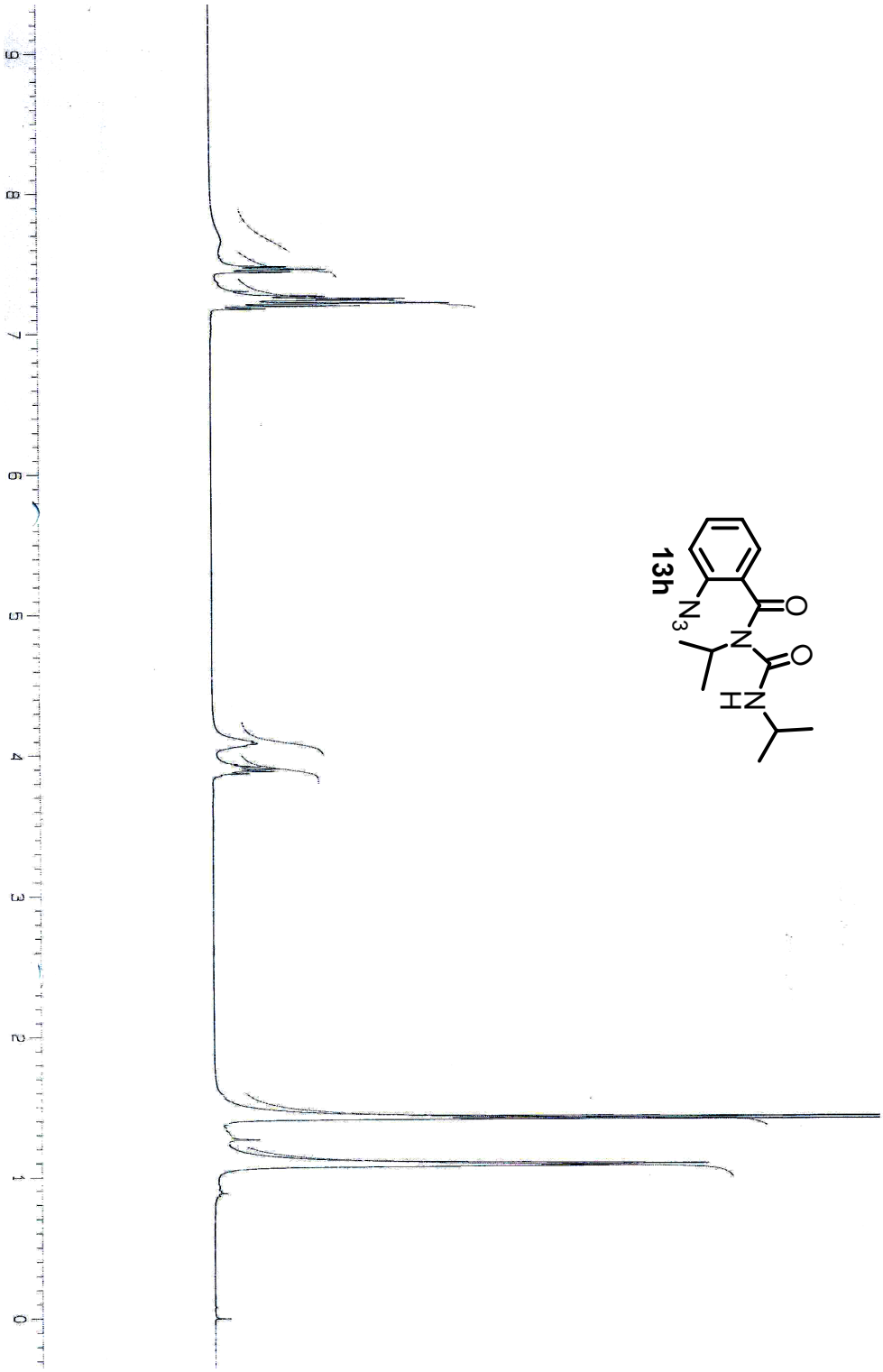
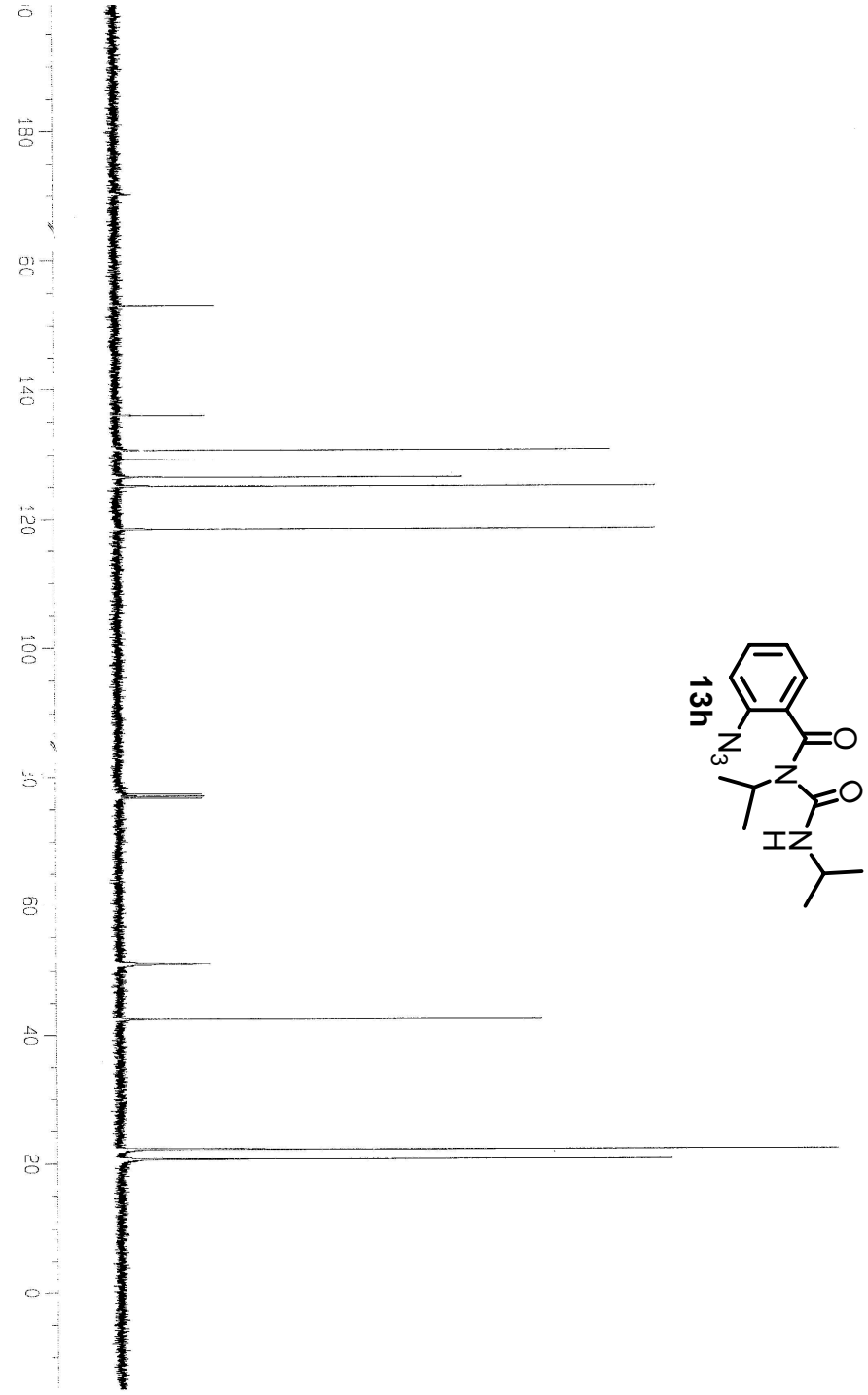
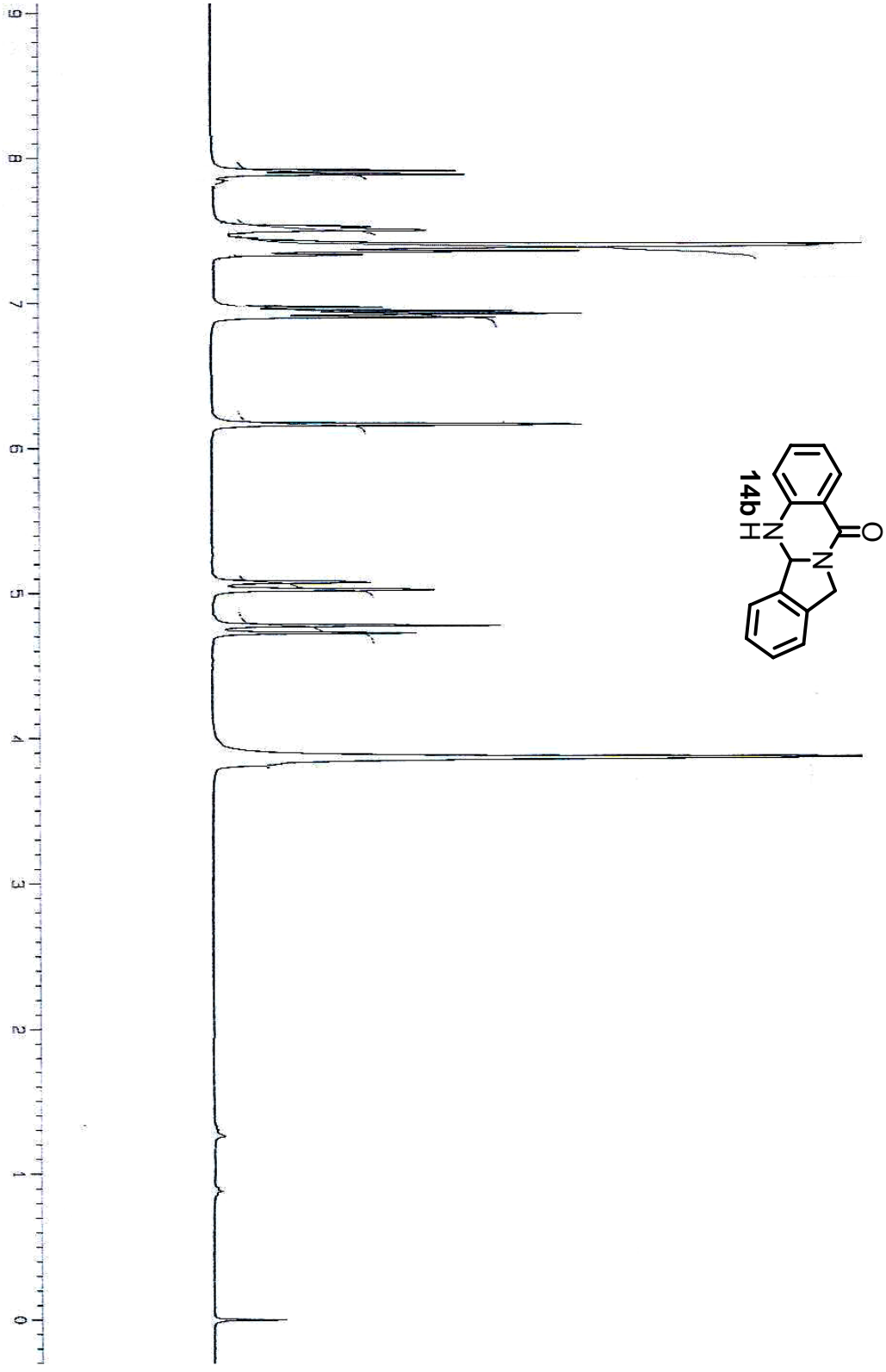
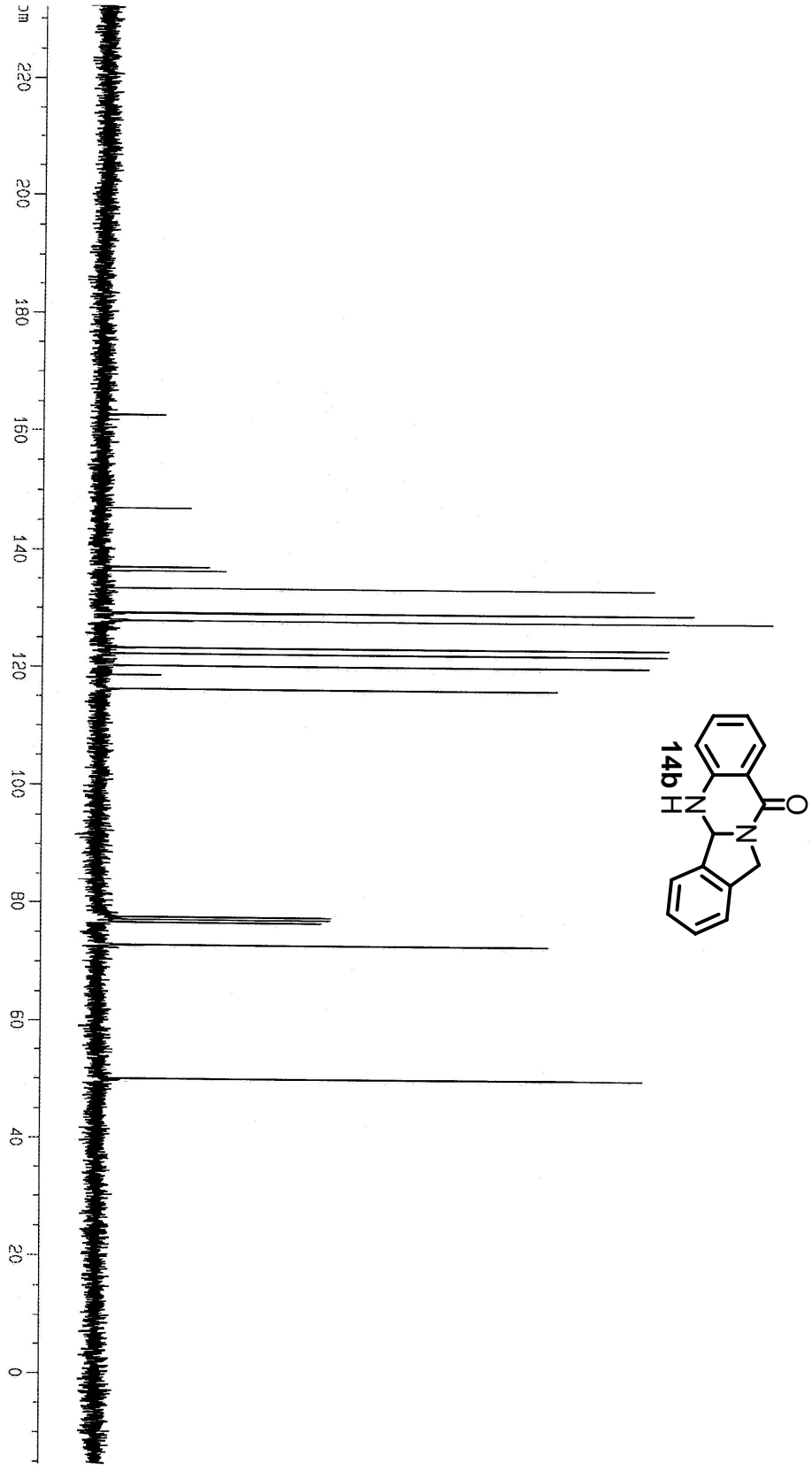
140
120
100
80
60
40
20
0
13f
N3
O
N


13h
N3
O
N
O
N
H


0
180
160
140
120
100
80
60
40
20
0
13h
N3
O
N
O
N
H


14b
H
N
O
N


ppm
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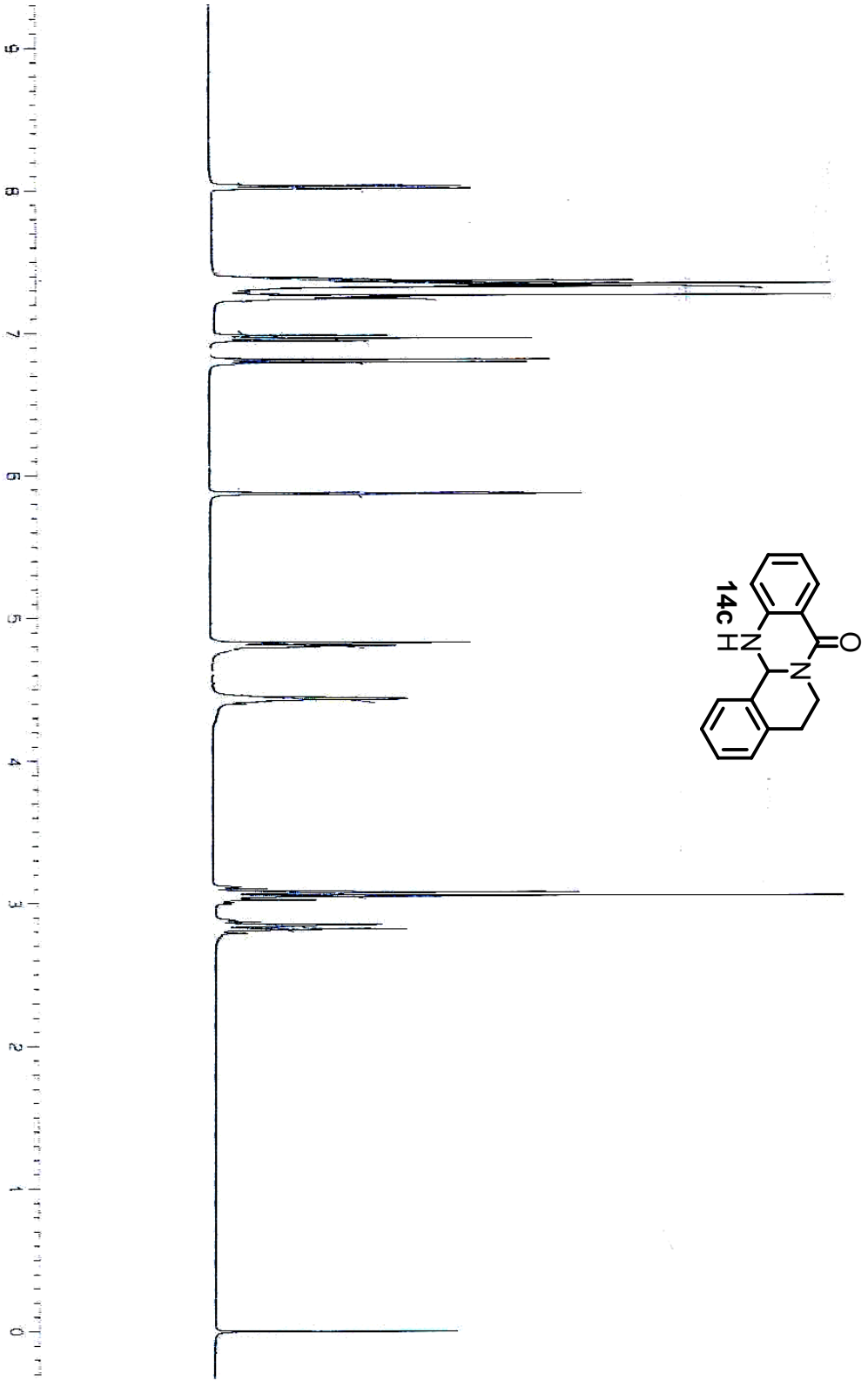
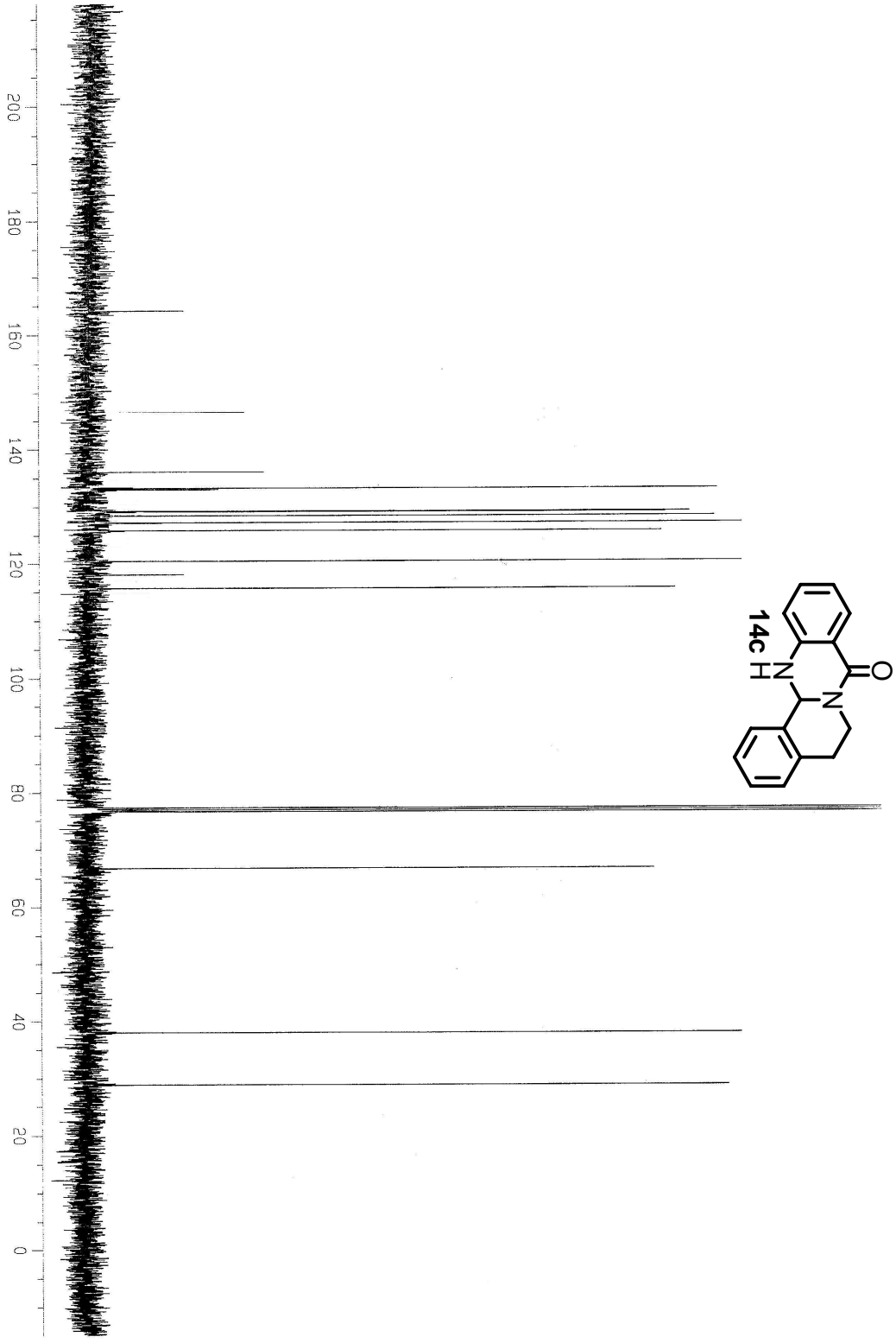
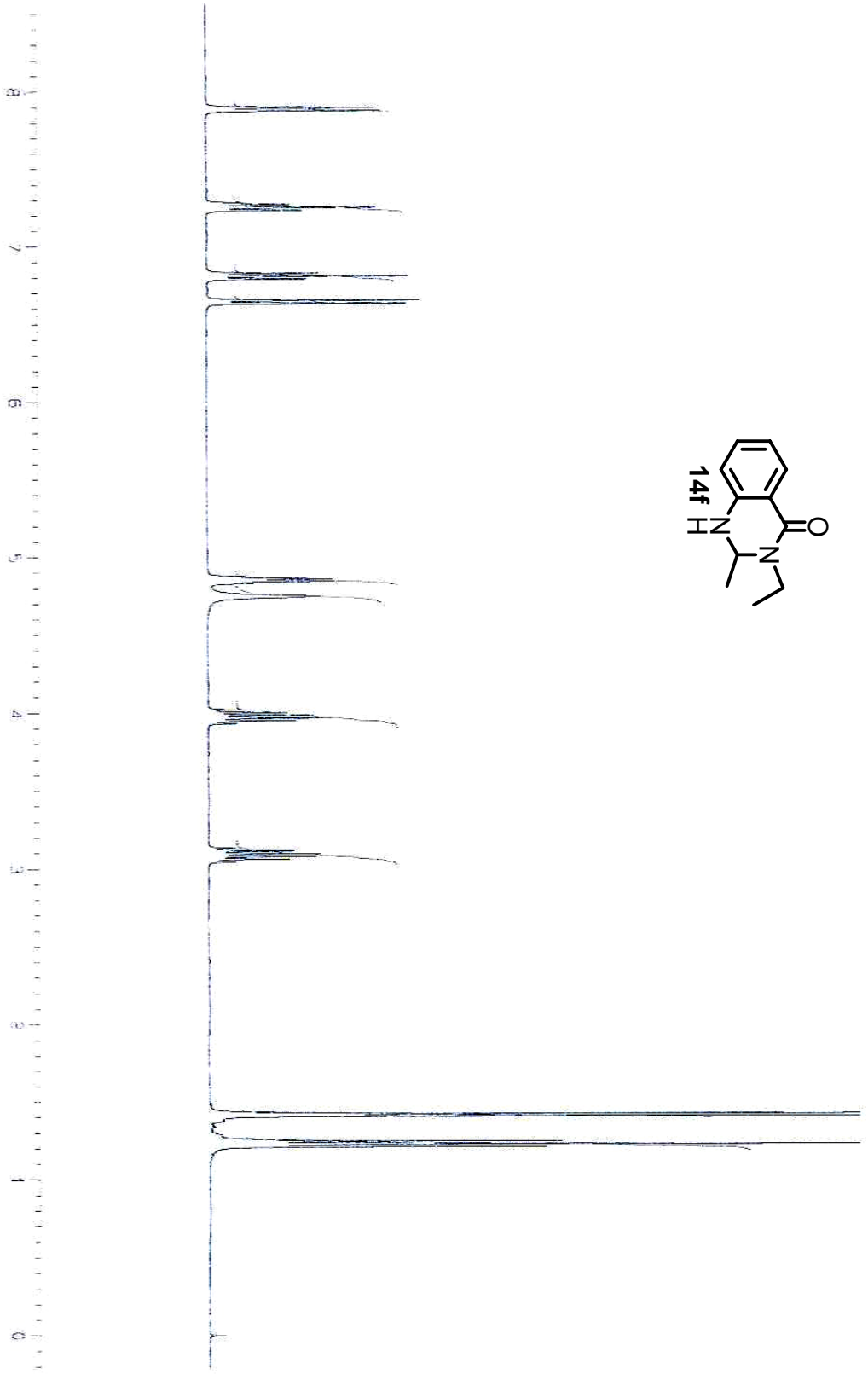
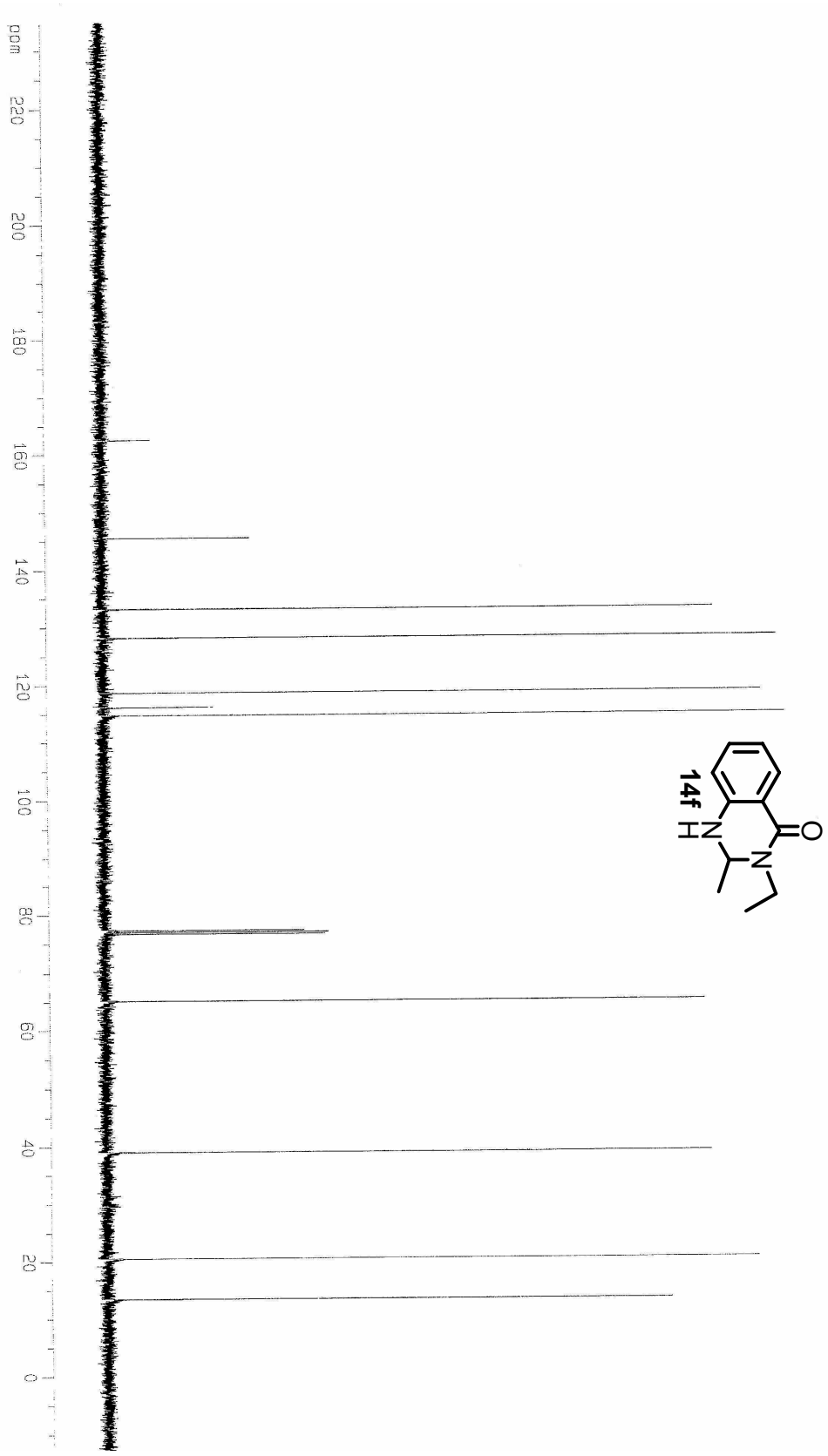
200
180
160
140
120
100
80
60
40
20
0
14b
H
N
N
O


14c
H
N
N
O


200
180
160
140
120
100
80
60
40
20
0
14c
H
N
N
O


8
7
6
5
4
3
2
1
0

14f
HN
O
N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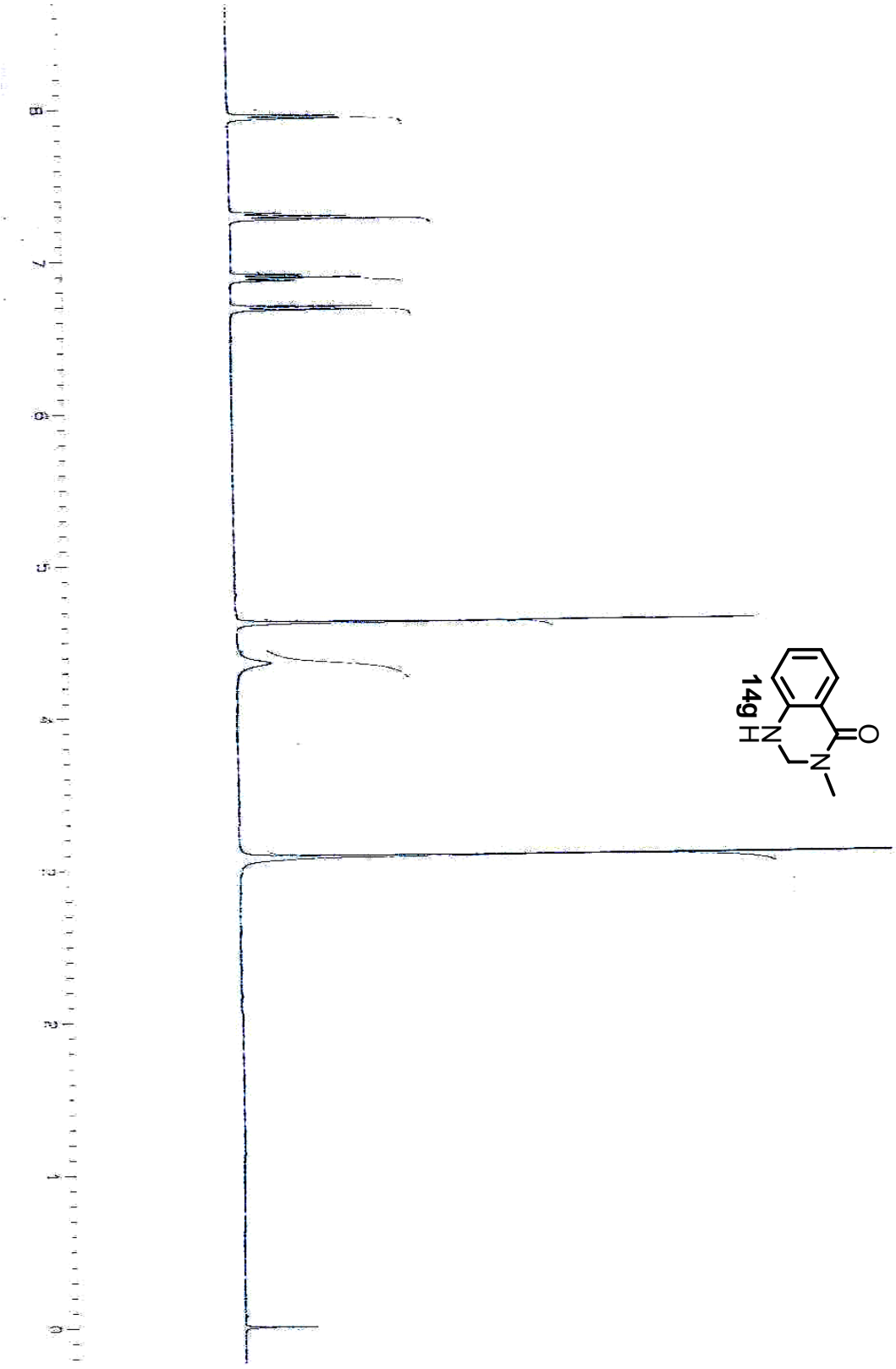
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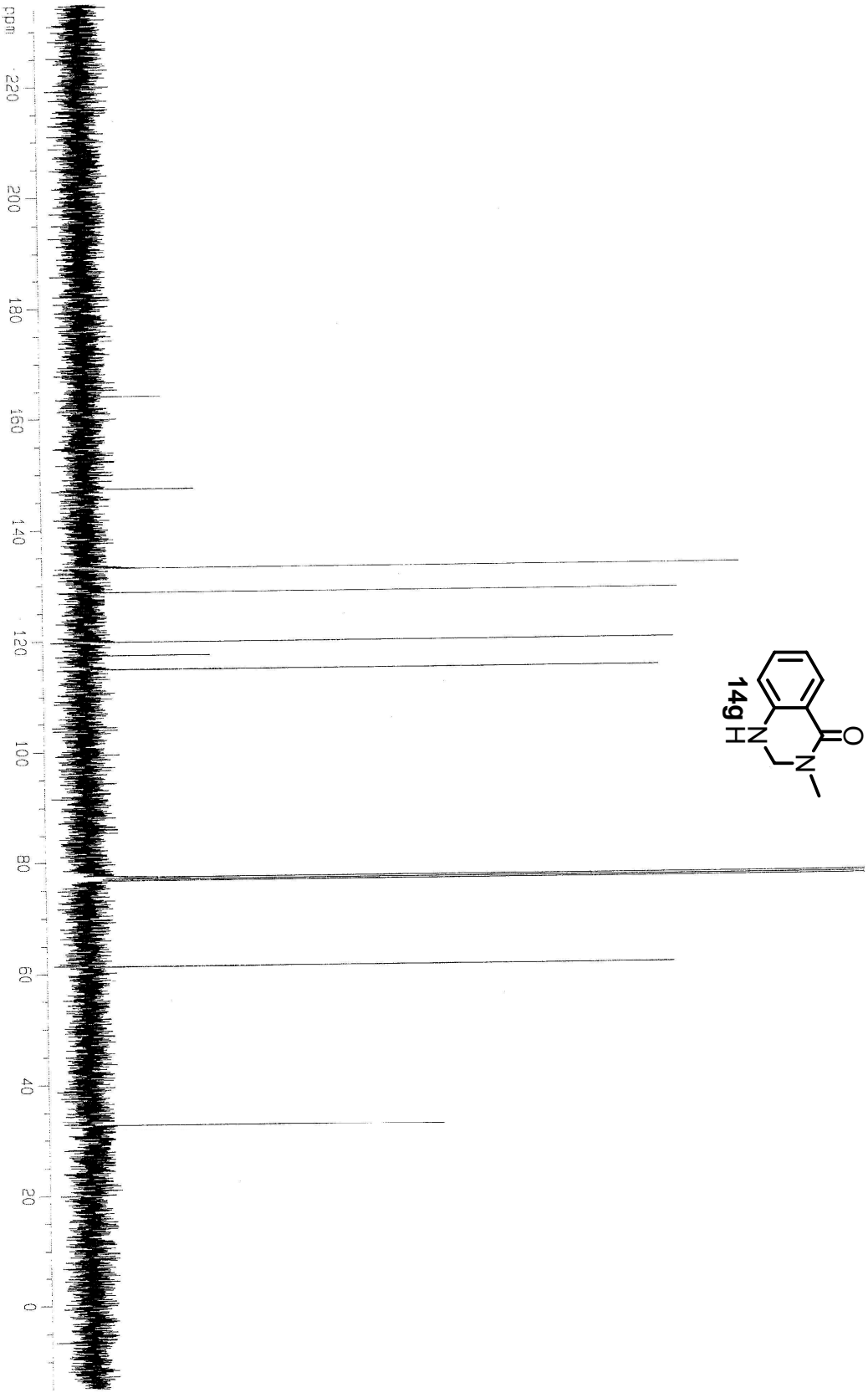
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