Platinum-catalyzed cross-dehydrogenative coupling reaction in the absence of oxidant

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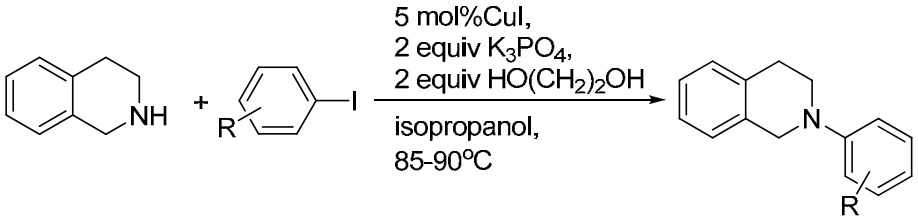
General Remarks:

Column chromatography was carried out on silica gel. Unless noted ^{1}H NMR spectra were recorded on 300 (400) MHz in $CDCl_3$ and CD_3COCD_3, ^{13}C NMR spectra were recorded on 75(100) MHz in $CDCl_3$ and CD_3COCD_3 using TMS as internal standard. IR spectra were recorded on a FT-IR spectrometer and only major peaks are reported in cm^{-1}. Melting points were determined on a microscopic apparatus and were uncorrected. Diastereomeric ratio (dr) was determined by ^{1}H NMR or HPLC (OD-H), hexane: iPrOH = 80:20, flow rate = 1.0mL/min. The existence of H_2 was detected by Inficon Transpector 2. All new compounds were further characterized by HRMS(high resolution mass spectra); copies of their ^{1}H NMR are provided for known compounds and ^{1}H NMR, ^{13}C NMR spectra for new compounds. Diastereomeric ratio was determined by ^{1}H NMR. Commercially available reagents and solvents were used without further purification.

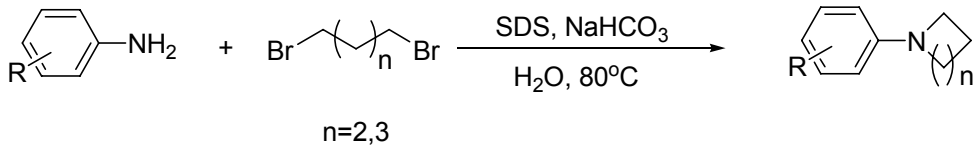
General procedure for 2-aryl-1,2,3,4-tetrahydro-isoquinolines 1a-1e and 1i.



Copper(I) iodide (200 mg, 1.0mmol) and potassium phosphate (4.25 g, 20.0 mmol) were put into a 50 mL three-neck flask. The three-neck flask was evacuated and back filled with argon. 2-Propanol (10.0 mL), ethylene glycol (1.11 mL, 20.0 mmol), 1,2,3,4-tetrahydro-isoquinoline (2.0 mL, 15 mmol) and iodobenzene (1.12 mL, 10.0 mmol) were added successively by syringe at room temperature. The reaction mixture was heated at 85-90 °C and kept for 24 h and then allowed to cool to room temperature. Diethyl ether (20 mL) and water (20 mL) were then added to the reaction mixture. The organic layer was extracted with diethyl ether (2 × 20 mL). The combined organic phases were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation and purified by column chromatography on silica gel (hexane/ethyl acetate= 20:1), and the fraction with Rf = 0.7 was

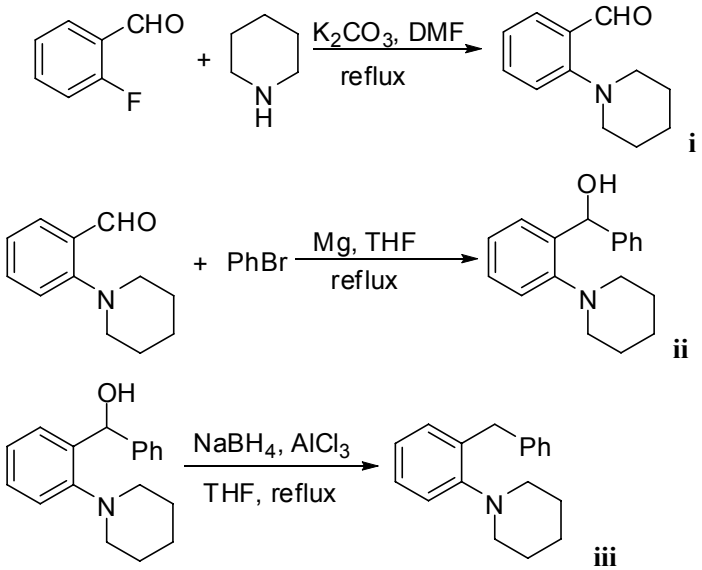
collected to give the desired product **1a-1e** and **1i** with 60-80 % isolated yields.

General procedure for cyclic amines 1f and 1h.



Aniline (5 mmol) was suspended in water (20mL). To this was added SDS (20 mg) followed by $NaHCO_3$ (0.92 g, 11.0 mmol) and bromoalkanes (11 mmol). Complete conversion was observed after heating the reaction mixture at 80 °C for 1 h. The reaction mixture was cooled and the product filtered and recrystallised from a mixture of ethyl acetate and hexane to yield the pure product in nearly quantitative yield.

General Procedure for 1-(2-benzylphenyl)piperidine 1g.



(i) To a stired solution of potassium carbonate (3.0 g, 22.0 mmol) in 20 mL of DMF was added 2-fluorobenzaldehyde (2.5 g, 20 mmol) and piperidine (1.9 g, 22.0 mmol). After heating the reaction mixture at reflux for 8 h, it was cooled and diluted with diethyl ether. The organic layer was extracted with diethyl ether (2 × 20 mL). The combined organic phases were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation. The residue was purified by column chromatography on silica gel.[3]

(ii) To a stirring solution of 2-(piperidin-1-yl)benzaldehyde (1 equiv) in THF (1.0 M) was added phenylmagnesium bromide (1.0 M in THF, 2 equiv) at room

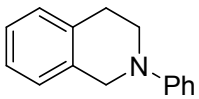
temperature. After heating the reaction mixture at reflux for 2 h, the reaction mixture was quenched by addition of saturated aqueous ammonium chloride (40 mL) and extracted with ethyl ether (2×40 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude material was purified by flash column chromatography to obtain the pure product.

(iii) A mixture of phenyl(2-(piperidin-1-yl)phenyl)methanol (0.5 g, 2.7 mmol). $NaBH_4$ (0.5 g, 13.2 mmol), and anhydrous $AlCl_3$ (1.0 g, 7.4 mmol) in THF (25 mL) was heated under reflux for 2 h. The mixture was then cooled. H_2O (10 mL) was added to give two clear phases, and the whole mixture was extracted with EtOAc (4×50 ml). The extract was dried over sodium sulfate and distilled under reduced pressure to give 1-(2-benzylphenyl)piperidine.[4]

References:

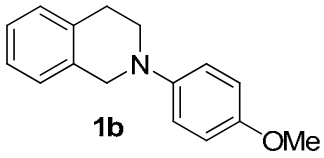
1. For the preparation of 2-Aryl-1,2,3,4-tetrahydro-isoquinolines, see:
   (a) Z. Li, C.-J. Li, *J. Am. Chem. Soc.* 2005, **127***,* 6968.
   (b) F. Y. Kwong, A. Klapars, S. L. Buchwald, *Org. Lett*. 2002, **4**, 581.
2. C. B. Singh, V. Kavala, A. K. Samal, B. K. Patel, *Eur. J. Org. Chem.* 2007, 1369.
3. W. H. N. Nijhuis, W. Verboom, A. A. El-Fadl, S. Harkema, D. N. Reinhoudt, *J. Org. Chem.* 1989, **54,** 199.
4. A. Ono, N. Suzuki, J. Kamimura, *Synthesis* 1987, 736.

Characterization data of Starting Materials 1a-1i.



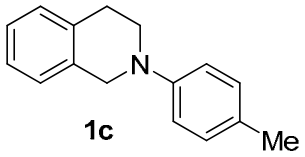
1a

1a: Known compound **1a** was prepared according to the above method as a solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.26 (m, 2 H), 7.20-7.13 (m, 4 H), 6.98-6.96 (d, *J* = 8.0 Hz, 2 H), 6.84-6.80 (t, *J* = 7.2 Hz, 1 H), 4.40 (s, 2 H), 3.56-3.53 (t, *J* = 5.6 Hz, 2 H), 2,98-2.96 (t, *J*= 6 Hz, 2 H).



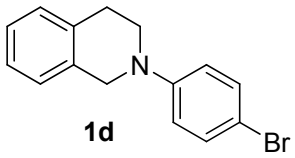
1b

1b: Known compound **1b** was prepared according to the above method as a solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16-7.09 (m, 4 H), 6.97-6.94 (m, 2 H), 6.87-6.84 (m, 2 H), 4.27 (s, 2 H), 3.74 (s, 3 H), 3.43-3.40 (t, *J* = 6.0 Hz, 2 H), 2.97-2.94 (t, *J* = 5.6 Hz, 2 H).



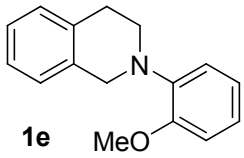
1c

1c: Known compound **1c** was prepared according to the above method as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10-7.02 (m, 6 H), 6.84-6.81 (d, *J* = 8.8 Hz, 2 H), 4.25 (s, 2 H), 3.39-3.36 (t, *J* = 6 Hz, 2 H), 2.87-2.84 (t, *J* = 5.6 Hz, 2 H), 2.22 (s, 1 H).



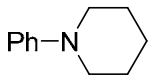
1d

1d: Known compound **1d** was prepared according to the above method as a solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.33 (d, *J* = 9.2 Hz, 2 H), 7.24-7.14 (m, 4 H), 6.83-6.81 (d, *J* = 9.2 Hz, 2 H), 4.36 (s, 2 H), 3.53-3.50 (t, *J* = 5.6 Hz, 2 H), 2.98-2.95 (t, *J* = 6.0 Hz, 2 H).



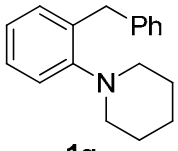
1e

1e: Known compound **1e** was prepared according to the above method as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16-7.08 (m, 4 H), 7.03-7.0 (m, 2 H), 6.93-6.88 (m, 2 H), 4.29 (s, 2 H), 3.88 (s, 3 H), 3.42-3.39 (t, *J* =6.0 Hz, 2 H), 2.99-2.96 (t, *J* = 5.8 Hz, 2 H).



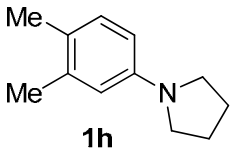
1f

1f: Known compound **1f** was prepared according to the above method as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.5-7.21 (m, 2 H), 6.94-6.92 (d, *J* = 8 Hz, 2 H), 6.82-6.79 (t, *J* = 7.2 Hz, 1 H), 3.15-3.12 (t, *J* = 5.2 Hz, 4 H), 1.72-1.67 (m, 4 H), 1.59-1.53 (m, 2 H).



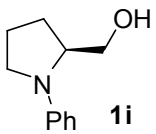
1g

1g: Compound **1g** was prepared according to the above method as a solid; mp: 30-32°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-6.99 (m, 8 H), 6.97-6.95 (m, 1 H), 4.06 (s, 2 H), 2.81-2.78 (t, *J* = 5.2 Hz, 4 H), 1.69-1.64 (m, 4 H), 1.56-1.48 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 142.0, 136.6, 130.7, 129.0, 128.2, 126.9, 125.6, 123.4, 120.3, 54.2, 36.6, 26.6, 24.4; IR (KBr, cm^{-1}) 3060, 3026, 2934, 2851, 2794, 1598, 1490, 1449, 1379, 1323, 1224, 1116, 1030, 928.



1h

1h: Known compound **1h** was prepared according to the above method as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98-6.96 (d, *J* = 8 Hz, 1 H), 6.40 (s, 1 H), 6.35-6.33 (d, *J* = 8.2 Hz, 1 H), 3.25-3.22 (t, *J* = 6.6 Hz, 4 H), 2.23 (s, 3 H), 2.16 (s, 3 H), 1.98-1.95 (m, 4 H).



1i

1i: Known compound **1i** was prepared according to the above method as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.20 (m, 2 H), 6.72-6.68 (m, 3 H), 3.86-3.82 (m, 1

H), 3.64-3.63 (m, 2 H), 3.52-3.47 (m, 1 H), 3.17-3.11 (m, 1 H), 2.07-1.95 (m, 4 H), 1.74 (s, 1 H).

General procedure for platinum-catalyzed synthesis of 3a-3e.

To a test tube, 2-aryl-1,2,3,4-tetrahydroisoquinoline **1a-1e** (0.20 mmol), $PtCl_2$ (5.3 mg, 10 mol %) and powdered 5Å molecular sieve (50 mg) were added. The test tube was purged under vacuum and then refilled with argon 3 times. CH_3NO_2/H_2O=10/1 (1.0 mL) was then injected, and the mixture was allowed to stir at 85 °C. When the reaction was considered complete as determined by TLC analysis, the reaction mixture was then filtered and evaporated under reduced pressure. The residue was purified by flash chromatography on alkalescence silica gel to afford corresponding products.

General procedure for platinum-catalyzed synthesis of 4a-4d.

To a test tube, 2-aryl-1,2,3,4-tetrahydroisoquinoline **1a-1d** (0.20 mmol), $PtCl_2$ (5.3 mg, 10 mol %) and powdered 5Å molecular sieve (50 mg) were added. The test tube was purged under vacuum and then refilled with argon 3 times. $CH_3CH_2NO_2/H_2O$=10/1 (1.0 mL) was then injected, and the mixture was allowed to stir at 85 °C. When the reaction was considered complete as determined by TLC analysis, the reaction mixture was then filtered and evaporated under reduced pressure. The residue was purified by flash chromatography on alkalescence silica gel to afford corresponding products.

General procedure for platinum-catalyzed synthesis of 3f-3i.

To a test tube, cyclic amines **1f-1i** (0.20 mmol), $PtCl_2$ (5.3 mg, 10 mol %) and powdered 5Å molecular sieve (50 mg) were added. The test tube was purged under vacuum and then refilled with argon 3 times. CH_3NO_2/H_2O=5/1 (1.0 mL) was then injected, and the mixture was allowed to stir at 80 °C. When the reaction was considered complete as determined by TLC analysis, the reaction mixture was then filtered and evaporated under reduced pressure. The residue was purified by flash

chromatography on alkalescence silica gel to afford corresponding products.

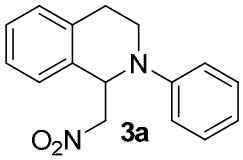
General procedure for platinum-catalyzed synthesis of 6a-6d.

To a test tube, amine **1a** (0.20 mmol), $PtCl_2$ (8.0 mg, 15 mol %) and powdered 5Å molecular sieve (50 mg) were added. The test tube was purged under vacuum and then refilled with argon 3 times. Activated methylene compounds **5** (0.40 mmol) in DMF/H_2O=1/1 (1.0 mL) was then injected, and the mixture was allowed to stir at 60 °C. When the reaction was considered complete as determined by TLC analysis, ethyl acetate (50 mL) was added, then washed with water (20 mL × 2), brine, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on alkalescence silica gel to afford corresponding products.

General procedure for platinum-catalyzed synthesis of 8a and 8b.

To a test tube, amine **1a** (0.20 mmol), $PtCl_2$ (5.3 mg, 10 mol %), L-proline (4.6mg, 20 mol %) and powdered 5Å molecular sieve (50 mg) were added. The test tube was purged under vacuum and then refilled with argon 3 times. Ketones **7** (0.40 mmol) in 1,4-dioxane/H_2O=1/2 (1.0 mL) was then injected, and the mixture was allowed to stir at 85 °C. When the reaction was considered complete as determined by TLC analysis, the reaction mixture was then filtered and evaporated under reduced pressure. The residue was purified by flash chromatography on alkalescence silica gel to afford corresponding products.

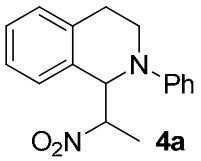
Characterization data of products 3a-3i, 4a-4d, 6a-6d.



3a

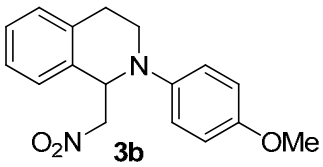
3a (known): The reaction mixture was chromatographed using 20:1 hexanes/EtOAc to afford 43.0 mg (80 %) of the indicated compound as a solid after 10 h; mp: 84-86 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22-7.03 (m, 6 H), 6.91-6.88 (m, 2 H),

6.79-6.74 (m, 1 H), 5.49-5.44 (t, *J* = 7.2 Hz, 1 H), 4.81-4.75 (dd, *J* = 7.5, 11.7 Hz, 1 H), 4.50-4.44 (dd, *J* = 7.2, 11.7 Hz, 1 H), 3.61-3.52 (m, 2 H), 3.05-2.95 (m, 1 H), 2.75-2.66 (m, 1H).



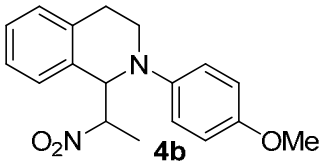
4a

4a (known): The reaction mixture was chromatographed using 20:1 hexanes/EtOAc to afford 45.2 mg (80 %) of the indicated diastereoisomers (2:1) as an oil after 24 h; ^{1}H NMR (300 MHz, $CDCl_3$, 2:1 mixture of diastereoisomers): δ 7.30-6.79 (m, 9 H), 5.27-4.86 (m, 2 H), 3.89-3.55 (m, 2 H), 3.11-2.83 (m, 2 H), [1.72-1.69 (d, *J* = 6.3 Hz), 1.55-1.53 (d, *J* = 6.6 Hz), 3 H].



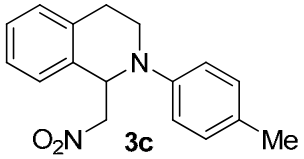
3b

3b (known): The reaction mixture was chromatographed using 20:1 hexanes/EtOAc to afford 42.3 mg (71 %) of the indicated compound as a solid after 15 h; mp: 102-104 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23-7.04 (m, 4 H), 6.90-6.87 (m, 2 H), 6.79-6.76 (m, 2 H), 5.38-5.33 (t, *J* = 6.6 Hz, 1 H), 4.83-4.76 (dd, *J* = 9.0, 12.3 Hz, 1 H), 4.55-4.49 (dd, *J* = 5.7, 11.7 Hz, 1 H), 3.72 (s, 3 H), 3.55-3.52 (m, 2 H), 3.04-2.93 (m, 1 H), 2.70-2.62 (m, 1 H).



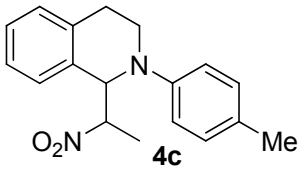
4b

4b (known): The reaction mixture was chromatographed using 20:1 hexanes/EtOAc to afford 46.2 mg (74 %) of the indicated diastereoisomers (3:1) as an oil after 15 h; ^{1}H NMR (300 MHz, $CDCl_3$, 3:1 mixture of diastereoisomers): δ 7.26-7.01 (m, 4 H), 6.94-6.89 (m, 2 H), 6.84-6.75 (m, 2 H), 5.07-4.83 (m, 2 H), 3.82-3.45 (m, 5 H), 3.03-2.75 (m, 2 H), [1.68-1.66 (d, *J* = 6.6 Hz), 1.53-1.52 (d, *J* = 5.7 Hz), 3 H].



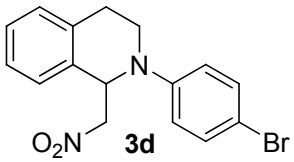
3c

3c (known): The reaction mixture was chromatographed using 20:1 hexanes/EtOAc to afford 48.0 mg (85 %) of the indicated compound as a solid after 24 h; mp: 94-96 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27-7.09 (m, 6 H), 6.93-6.90 (m, 2 H), 5.55-5.50 (t, *J* = 7.8 Hz, 1 H), 4.89-4.83 (dd, *J* = 8.1, 10.5 Hz, 1 H), 4.60-4.54 (dd, *J* = 6.3, 11.7 Hz, 1 H), 3.69-3.59 (m, 2 H), 3.13-3.03 (m, 1 H), 2.81-2.73 (m, 1 H), 2.29 (s, 3 H).



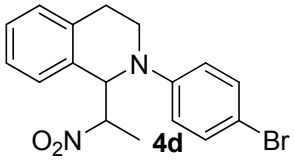
4c

4c (known): The reaction mixture was chromatographed using 20:1 hexanes/EtOAc to afford 50.3 mg (85 %) of the indicated diastereoisomers (3:2) as an oil after 16 h; ^{1}H NMR (300 MHz,$CDCl_3$, 3:2 mixture of diastereoisomers): δ 7.29-7.03 (m, 6 H), 6.95-6.86 (m, 2 H), 5.23-4.87 (m, 2 H), 3.87-3.53 (m, 2 H), 3.09-2.80 (m, 2 H), [2.29 (s), 2.27 (s), 3 H], [1.56 (s), 1.54 (s), 3 H].



3d

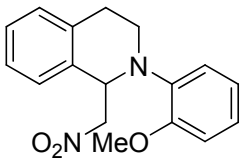
3d (known): The reaction mixture was chromatographed using 20:1 hexanes/EtOAc to afford 58.3 mg (84 %) of the indicated compound as an oil after 48 h; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35-7.12 (m, 6 H), 6.87-6.83 (m, 2 H), 5.52-5.46 (t, *J* = 6.9 Hz, 1 H), 4.87-4.79 (m, 1 H), 4.59-4.52 (m, 1 H), 3.63-3.59 (m, 2 H), 3.12-3.02 (m, 1 H), 2.83-2.74 (m, 1 H).



4d

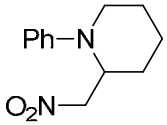
4d (known): The reaction mixture was chromatographed using 20:1 hexanes/EtOAc to afford 39.0 mg (54 %) of the indicated diastereoisomers (3:1) as an oil after 18 h; ^{1}H NMR (300 MHz, $CDCl_3$, 3:1 mixture of diastereoisomers): δ 7.36-7.00 (m, 6 H),

6.86-6.83 (m, 2 H), 5.21-4.87 (m, 2 H), 3.85-3.49 (m, 2 H), 3.09-2.89 (m, 2 H), [1.68-1.65 (m), 1.56-1.53 (m), 3 H].

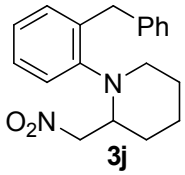


3e

3e (known): The reaction mixture was chromatographed using 20:1 hexanes/EtOAc to afford 46.5 mg (78 %) of the indicated compound as a solid after 15 h; mp: 103-104°C ; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22-7.11 (m, 4 H), 7.03-6.97 (m, 1 H), 6.89-6.78 (m, 3 H), 5.50-5.46 (dd, *J* = 4.5, 8.1 Hz, 1 H), 4.82-4.75 (dd, *J* = 8.1, 11.7 Hz, 1 H), 4.53-4.47 (dd, *J* = 4.5, 11.7 Hz, 1 H), 3.79 (s, 3 H), 3.62-3.41 (m, 2 H), 3.01-2.90 (m, 1 H), 2.72-2.64 (m, 1 H).



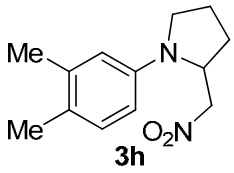
3f: The reaction mixture was chromatographed using 20:1 hexanes/EtOAc to afford 32.1 mg (73 %) of the indicated compound as an oil after 10 h; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.26 (m, 2 H), 6.99-6.97 (d, *J* = 8.4 Hz, 2 H), 6.92-6.88 (t, *J* = 7.6 Hz, 1 H), 4.62-4.55 (m, 2 H), 4.47-4.41 (m, 1 H), 3.44-3.40 (m, 1 H), 2.93-2.86 (m, 1 H), 1.96-1.57 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 129.5, 120.4, 116.8, 73.2, 54.9, 44.5, 26.4, 25.0, 19.0; IR (neat, cm^{-1}) 3061, 3032, 2940, 2861, 1597, 1549, 1498, 1455, 1380, 1350, 1250, 1229, 1169, 1136, 1084, 1031; HRMS (EI) m/z: calcd for $C_{12}H_{16}N_2O_2$: M+H=221.1285; found: 221.1282.



3j

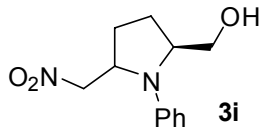
3j: The reaction mixture was chromatographed using 20:1 hexanes/EtOAc to afford 52.7 mg (85 %) of the indicated compound as an oil after 24 h; ^{1}H NMR (400 MHz, CD_3COCD_3): δ 7.32-7.09 (m, 9 H), 4.17-3.95 (m, 3 H), 3.92-3.64 (m, 2 H), 2.89-2.87 (m, 1 H), 2.64-2.58 (m, 1 H), 1.86-1.49 (m, 6 H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 150.8, 143.1, 140.5, 132.6, 130.6, 129.6, 128.9, 127.2, 127.0, 124.6, 78.9, 59.2, 56.0,

38.4, 31.0, 27.4, 24.0; IR (neat, cm^{-1}) 3060, 3026, 2936, 2854, 2802, 1598, 1550, 1490, 1449, 1380, 1347,8,1350, 1274, 1241, 1214, 1166, 1106, 1058, 1030; HRMS (EI) m/z: calcd for $C_{19}H_{22}N_2O_2$: M+H=311.1754; found: 311.1748.



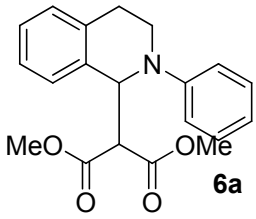
3h

3h: The reaction mixture was chromatographed using 20:1 hexanes/EtOAc to afford 35.1 mg (75 %) of the indicated compound as an oil after 16 h; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04-7.02 (d, *J* = 8 Hz, 1 H), 6.51-6.44 (m, 2 H), 4.63-4.59 (m, 1 H), 4.38-4.35 (m, 1 H), 4.18-4.13 (m, 1 H), 3.48-3.44 (m, 1 H), 3.19-3.13 (m, 1 H), 2.25 (s, 3 H), 2.18 (s, 3 H), 2.09-2.06 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 137.8, 130.6, 125.3, 113.5, 109.4, 76.0, 57.5, 48.2, 29.2, 22.8, 20.3, 18.5; IR (neat, cm^{-1}) 2968, 2920, 2858, 1616, 1547, 1511, 1456, 1426, 1360, 1342, 1288, 1243, 1208, 1179, 1122, 1028; HRMS (EI) m/z: calcd for $C_{13}H_{18}N_2O_2$: M+H=235.1441; found: 235.1438.



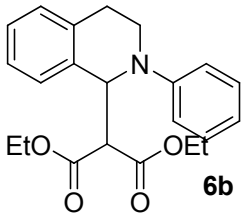
3i

3i: The reaction mixture was chromatographed using 3:1 hexanes/EtOAc to afford 45.3 mg (96 %) of the indicated compound as an oil after 30 h; dr=1.7:1, diastereomeric ratio (dr) was determined by HPLC (OD-H), hexane: iPrOH = 80:20, flow rate = 1.0mL/min, major isomer tr = 9.65, minor isomer tr = 10.96; ^{1}H NMR (400 MHz, $CDCl_3$, 1.7 : 1 mixture of diastereoisomers): δ 7.29-7.24 (m, 2 H), 6.83-6.75 (m, 3 H), 4.67-4.03 (m, 3 H), 3.98-3.93 (m, 1 H), 3.82-3.52 (m, 2 H), 2.17-1.95 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$, 1.7:1 mixture of diastereoisomers): δ 146.4, 143.3, 129.8, 129.6, 118.4, 117.8, 113.9, 112.7, 77.9, 74.5, 62.4, 61.8, 61.7, 59.9, 58.6, 57.1, 28.6, 27.2, 26.3, 26.0; IR (neat, cm^{-1}) 3541, 3392, 2951, 2925, 2881, 1598, 1546, 1501, 1357, 1214, 1159; HRMS (EI) m/z: calcd for $C_{12}H_{16}N_2O_3$: M+H= 237.1234; found: 237.1235.



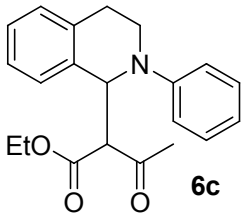
6a

6a (known): The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 57.6 mg (85 %) of the indicated compound as an oil after 11 h; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.08 (m, 6 H), 6.98-6.96 (m, 2 H), 6.77-6.74 (t, *J* = 7.2 Hz, 1 H), 5.72-5.69 (d, *J* = 9.2 Hz, 1 H), 3.95-3.93 (d, *J* = 9.2 Hz, 1 H), 3.75-3.59 (m, 5 H), 3.54 (s, 3 H), 3.10-3.02 (m, 1 H), 2.90-2.83 (m, 1 H).



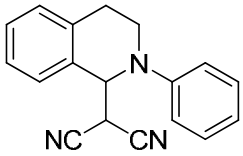
6b

6b (known): The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 51.4 mg (70 %) of the indicated compound as an oil after 24 h; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.08 (m, 6 H), 6.98-6.96 (m, 2 H), 6.76-6.72 (t, *J* = 7.2 Hz, 1 H), 5.73-5.71 (d, *J* = 9.2 Hz, 1 H), 4.15-3.93 (m, 4 H), 3.90-3.88 (d, *J* = 9.2 Hz, 1 H), 3.74-3.60 (m, 2 H), 3.10-2.84 (m, 2 H), 1.18-1.14 (t, *J* = 7.2 Hz, 3 H), 1.10-1.06 (t, *J* = 7.2 Hz, 3 H).



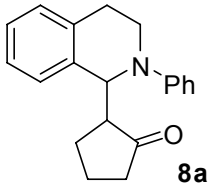
6c

6c (known): The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 36.4 mg (54%) of the indicated diastereoisomers (3:2) as an oil after 24 h; ^{1}H NMR (400 MHz, $CDCl_3$, 3:2 mixture of diastereoisomers): δ 7.31-7.05 (m, 6 H), 6.96-6.94 (m, 2 H), [6.83-6.80 (t, *J* = 7.2 Hz), 6.75-6.71 (t, *J* = 7.2 Hz), 1 H], [5.77-5.75 (d, *J* = 9.6 Hz), 5.63-5.61 (d, *J* = 9.2 Hz), 1 H], 4.21-3.92 (m, 3 H), 3.73-3.56 (m, 2 H), 3.07-3.64 (m, 2 H), [2.15 (s), 2.11 (s), 3 H], [1.17-1.14 (t, *J* = 7.2 Hz), 1.07-1.03 (t, *J* = 7.2 Hz), 3 H].



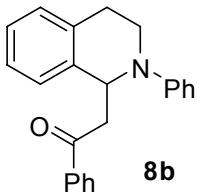
6d

6d: The reaction mixture was chromatographed using 10:1 hexanes/EtOAc to afford 23.0 mg (42 %) of the indicated compound as an oil after 56 h; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.22 (m, 4 H), 7.17-7.11 (m, 2 H), 6.87-6.80 (m, 3 H), 4.35-4.29 (m, 1 H), 3.84-3.81 (d, *J* = 10.0 Hz, 1 H), 3.68-3.59 (m, 2 H), 3.44-3.39 (m, 1 H), 3.06-2.99 (dd, *J* =17.2, 5.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2, 131.5, 129.5, 129.4, 128.6, 128.1, 127.7, 127.5, 120.1, 115.4, 114.6, 114.2, 55.4, 38.8, 37.7, 33.6; HRMS (EI) m/z: calcd for $C_{18}H_{15}N_3$: M+H=274.1339; found: 274.1344.



8a

8a: The reaction mixture was chromatographed using 30:1 hexanes/EtOAc to afford 32.0 mg (55%) of the indicated diastereoisomers (4:1) as an oil after 48 h; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-6.68 (m, 9 H), [5.60 (s), 5.25-5.24 (d, *J* = 3.6 Hz), 1 H], 3.71-3.48 (m, 2 H), 3.05-2.71 (m, 3 H), 2.31-1.54 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 220.4, 219.6, 149.1, 148.5, 139.4, 135.6, 135.4, 134.7, 129.4, 129.3, 128.3, 128.2, 127.0, 126.9, 126.7, 126.5, 126.4, 126.3, 117.8, 117.3, 113.7, 113.6, 58.6, 57.5, 56.4, 54.5, 43.0, 42.5, 38.5, 37.7, 29.7, 28.8, 27.5, 27.2, 25.9, 20.6; IR (neat, cm^{-1}): 3389, 3059, 2922, 2852, 1730, 1703, 1598, 1502, 1457, 1398, 1323, 1266, 1247, 1150; HRMS (EI) m/z: calcd for $C_{20}H_{21}NO$: M+H=292.1696; found: 296.1692.



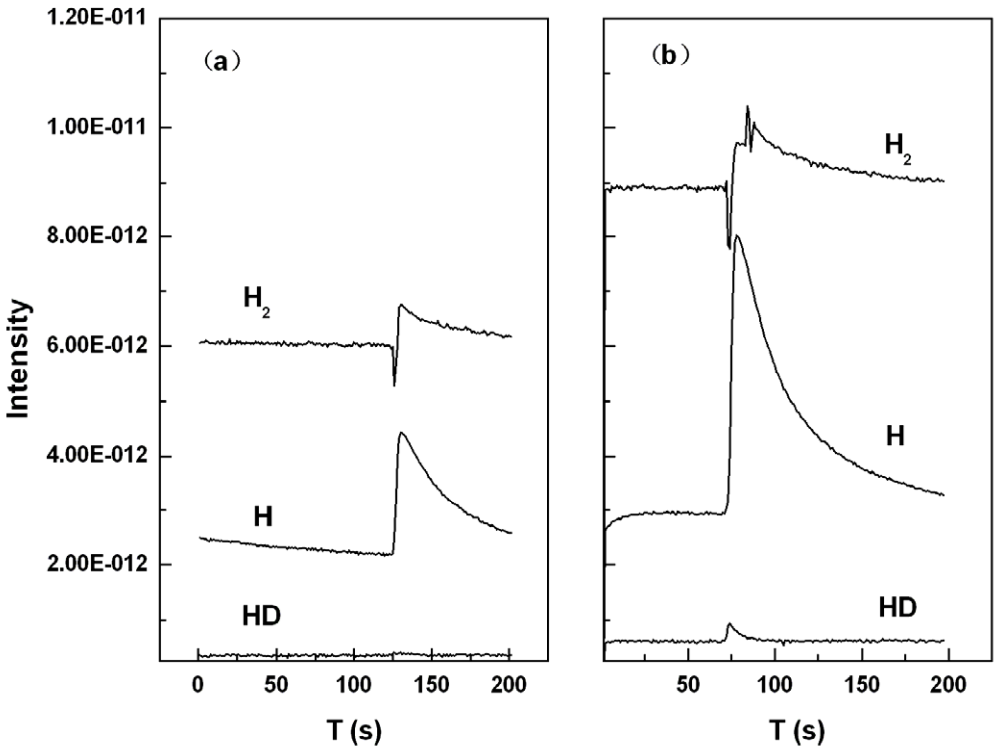
8b

8b: The reaction mixture was chromatographed using 30:1 hexanes/EtOAc to afford 34.7 mg (53 %) of the indicated compound as a solid after 48 h; mp: 105-107°C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.82 (m, 2 H), 7.51-7.48 (m, 1 H), 7.40-7.36 (m, 2 H), 7.24-7.08 (m, 6 H), 6.97-6.95 (d, *J* = 8 Hz, 2 H), 6.75-6.72 (m, 1 H), 5.67-5.64 (m,

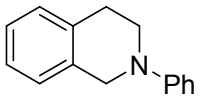
1 H), 3.67-3.35 (m, 4 H), 3.13-3.06 (m, 1 H), 2.94-2.87 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.6, 148.8, 138.5, 137.3, 134.5, 133.0, 129.3, 128.5, 128.1, 127.1, 126.8, 126.2, 117.9, 114.4, 55.0, 45.3, 42.1, 27.6; IR (KBr, cm^{-1}) 3346, 3060, 2918, 2848, 1679, 1597, 1501, 1449, 1393, 1346, 1279, 1206, 1156; HRMS (EI) m/z: calcd for $C_{23}H_{21}NO$: M+H=328.1696; found: 328.1701.

H_2 Detection Experiment:

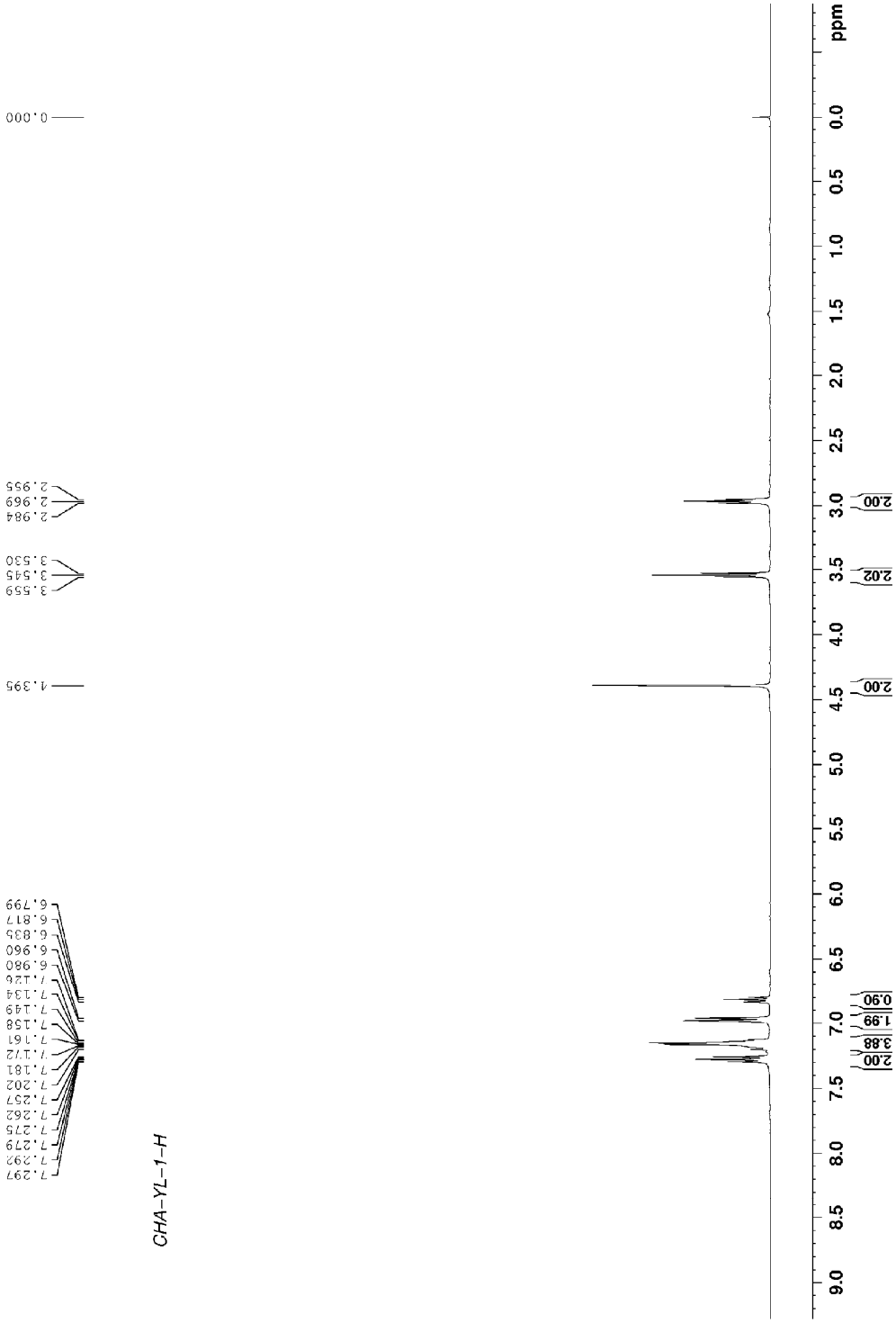
The reaction was carried out by using tetrahydroisoquinoline **1a** (0.5 mmol), $PtCl_2$ (10 % mol) and 5 Å MS (100 mg) in CH_3NO_2/H_2O or CH_3NO_2/D_2O (2 mL) under argon in the sealed tube. When the mixture was stirred at 85 °C for 6h, the gas (2 mL) upon the solution was injected into the Hydrogen Detector Inficon Transpector 2. The detection result was shown in the following:



S-Figure 1. Results of the H_2 detection by using Inficon Transpector 2. H is the fragment of H_2 and HD during the detection. (a) Spectra was obtained when CH_3NO_2/H_2O (10/1) was used. (b) Spectra was obtained when CH_3NO_2/D_2O (10/1) was used.


N
Ph

1a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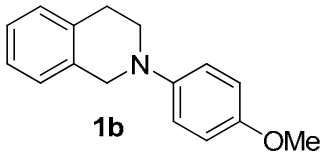
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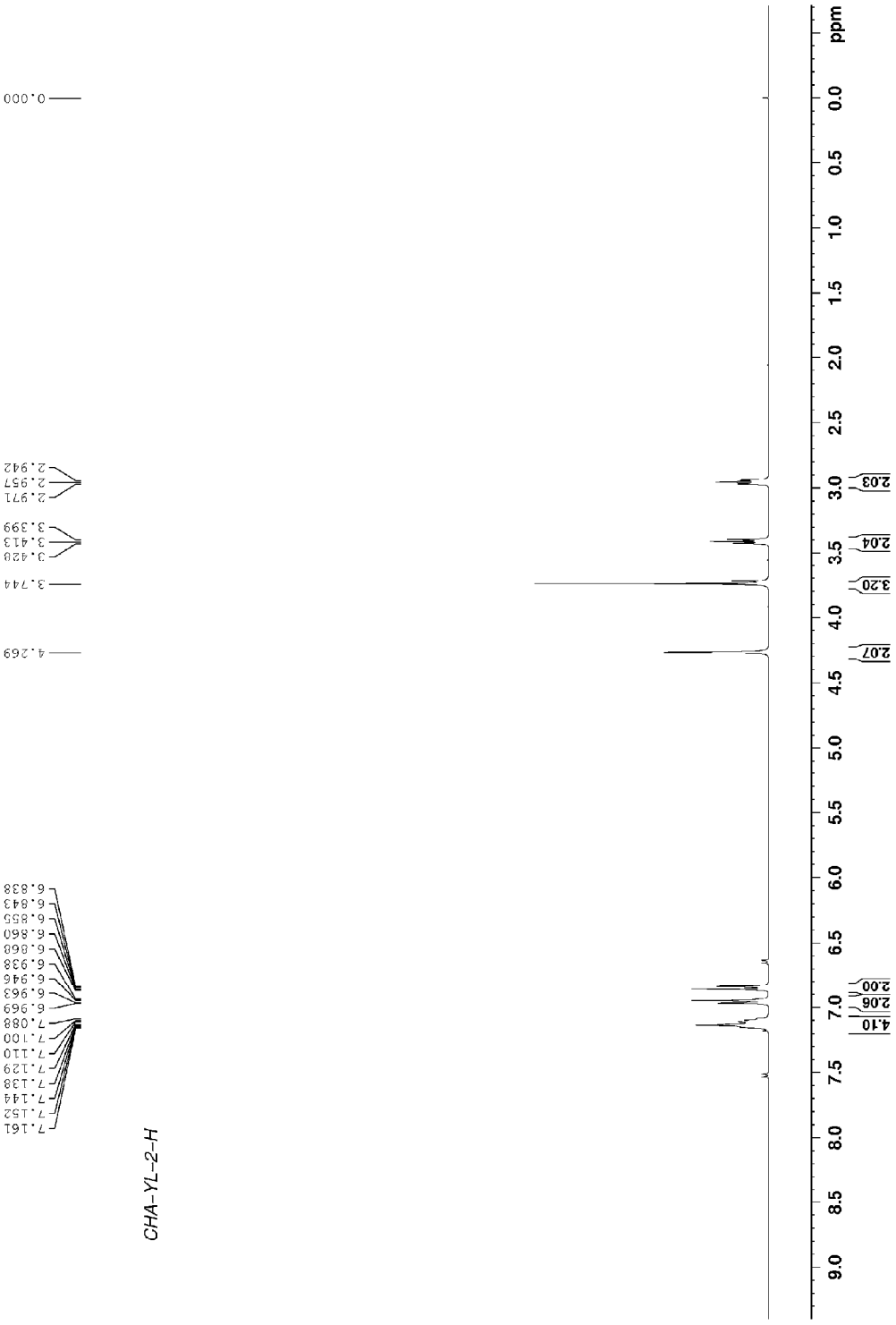
OMe

1b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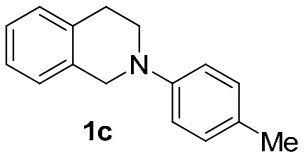
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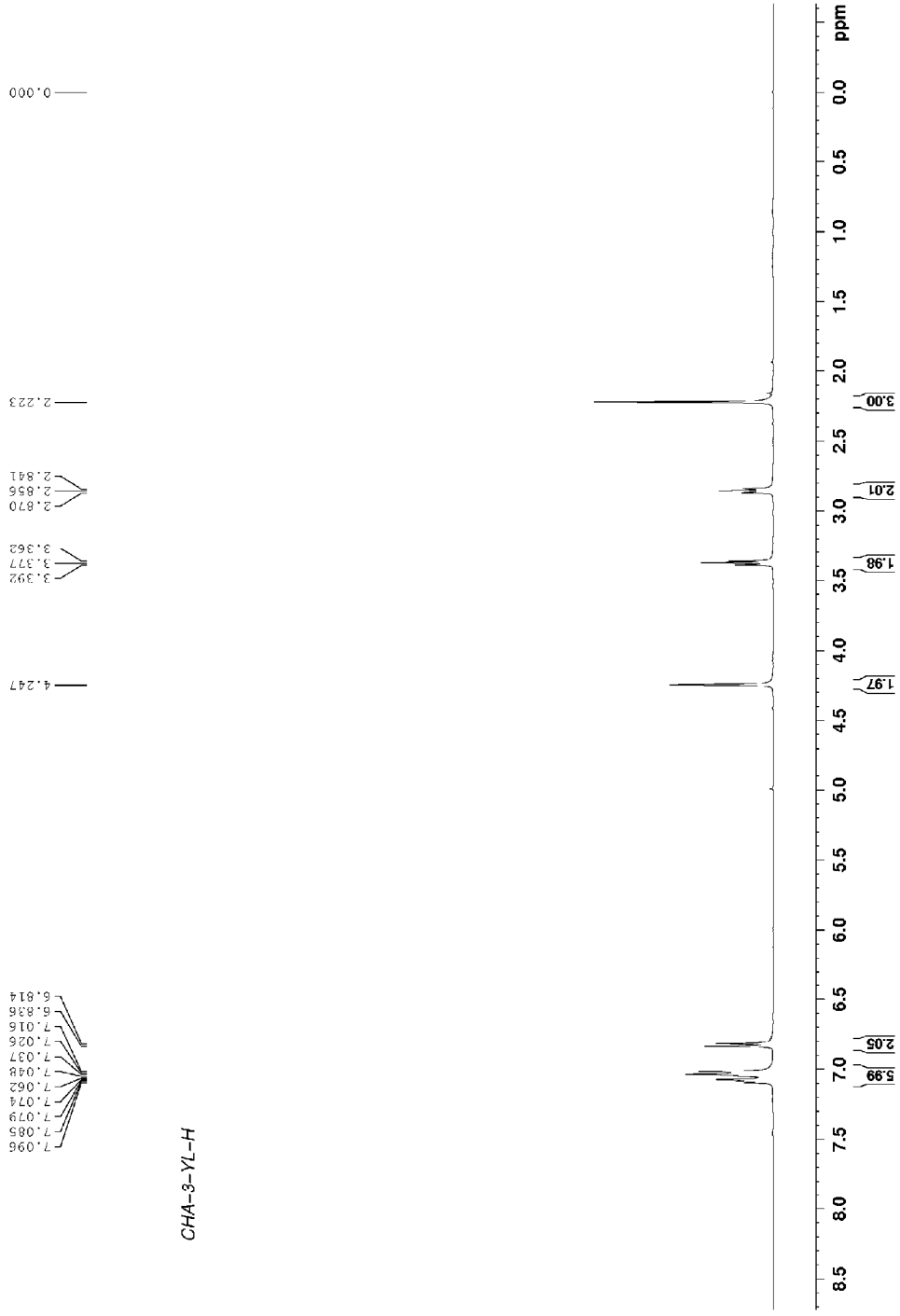
1c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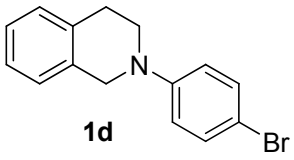
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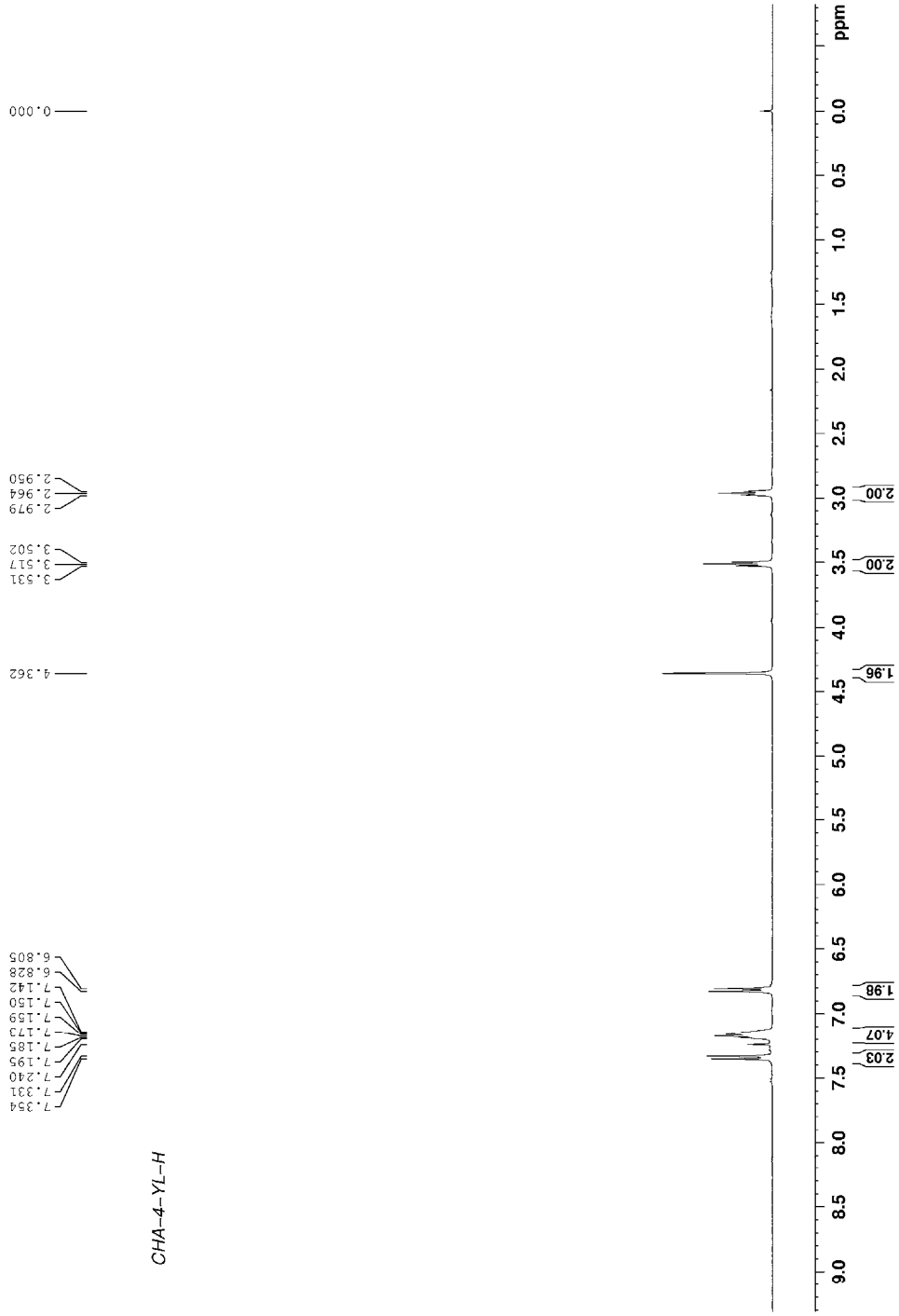
1d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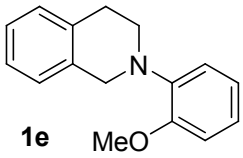
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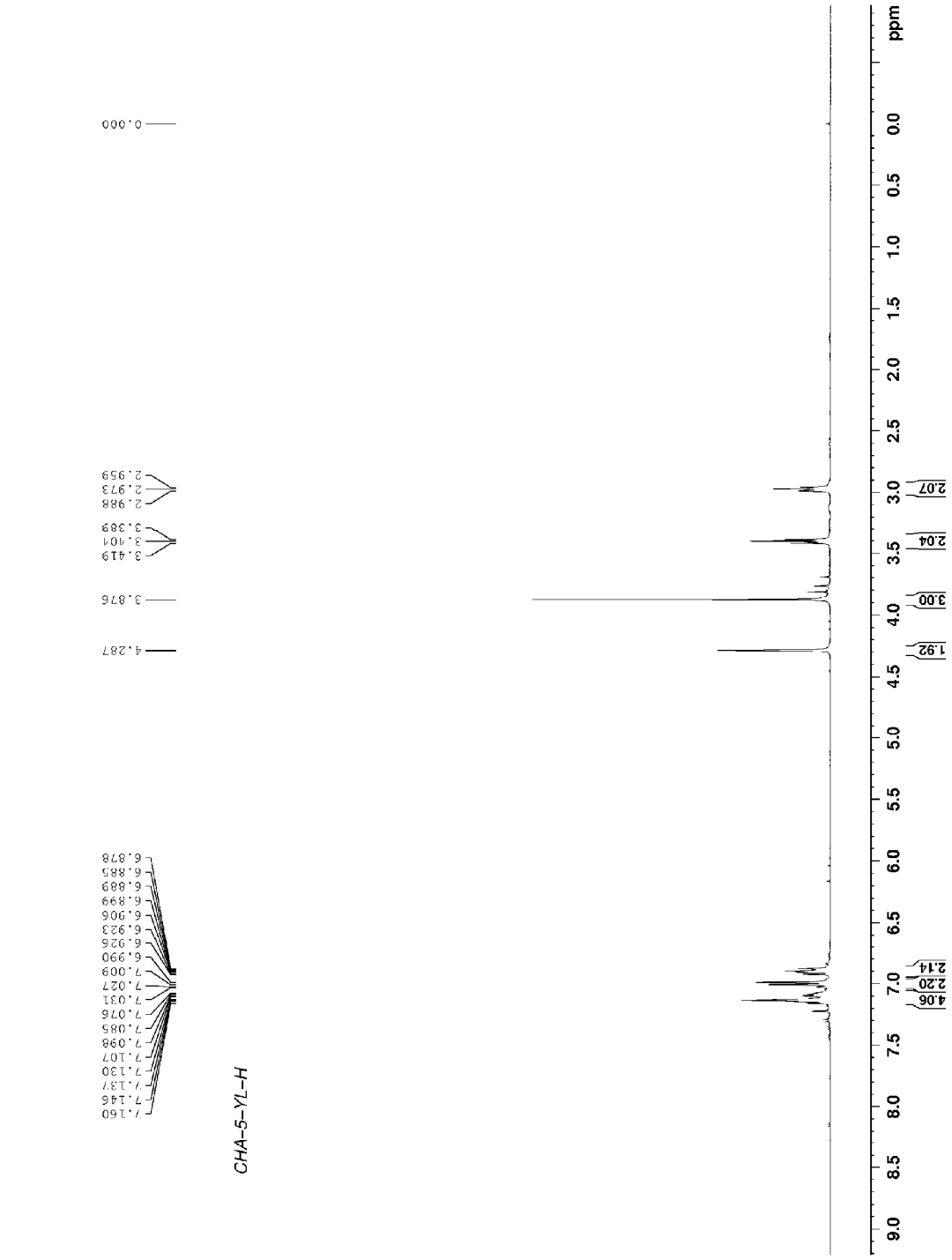
1e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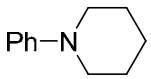
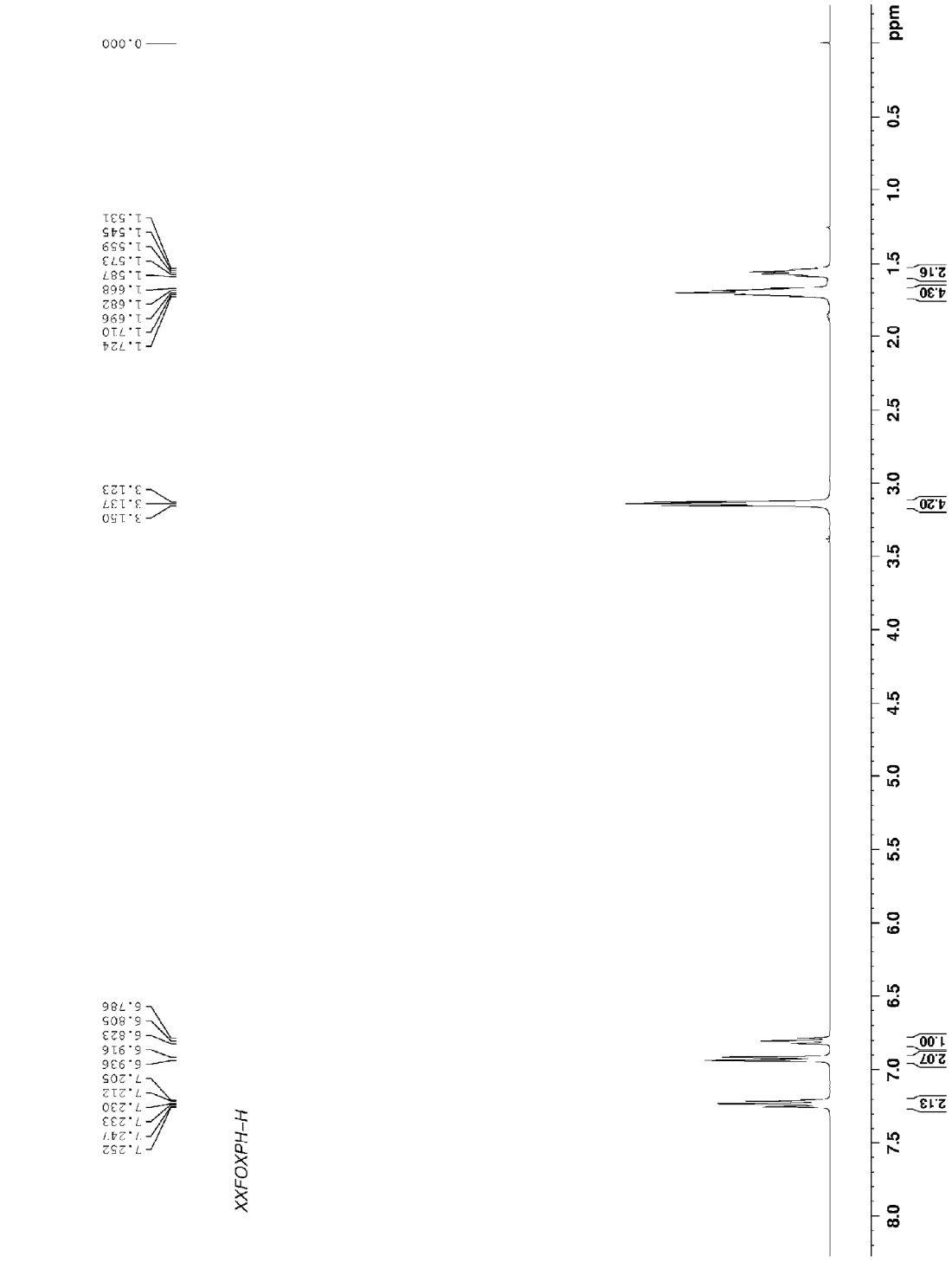
1.92
2.14
2.20
4.06


Ph–N

1f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1.682
1.696
1.710
1.724
3.123
3.137
3.150
6.786
6.805
6.823
6.916
6.936
7.205
7.212
7.230
7.233
7.247
7.252
XXFOXP:H-H
ppm
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1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
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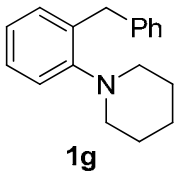
2.16
4.30
4.20
1.00
2.07
2.13



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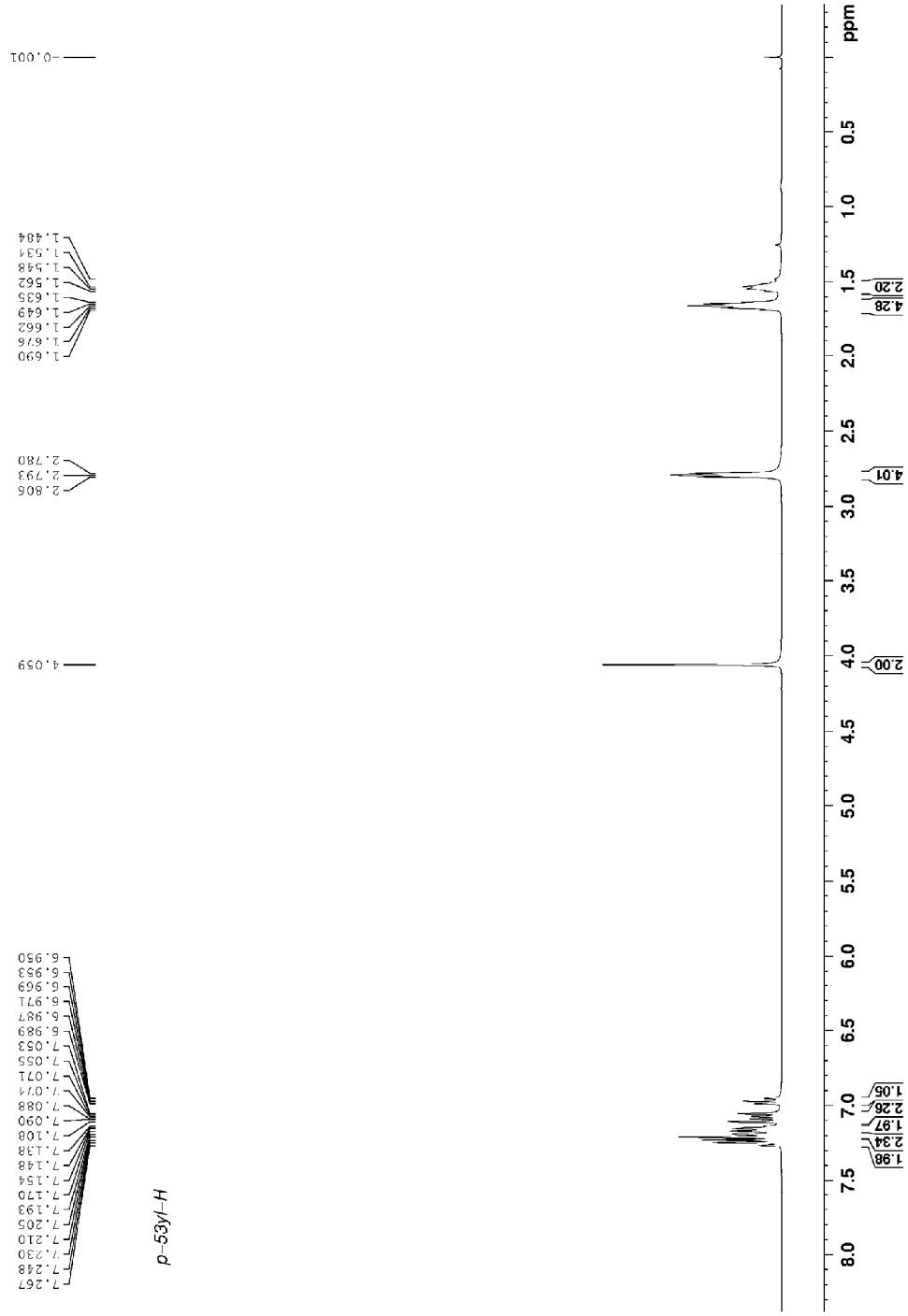
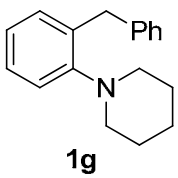
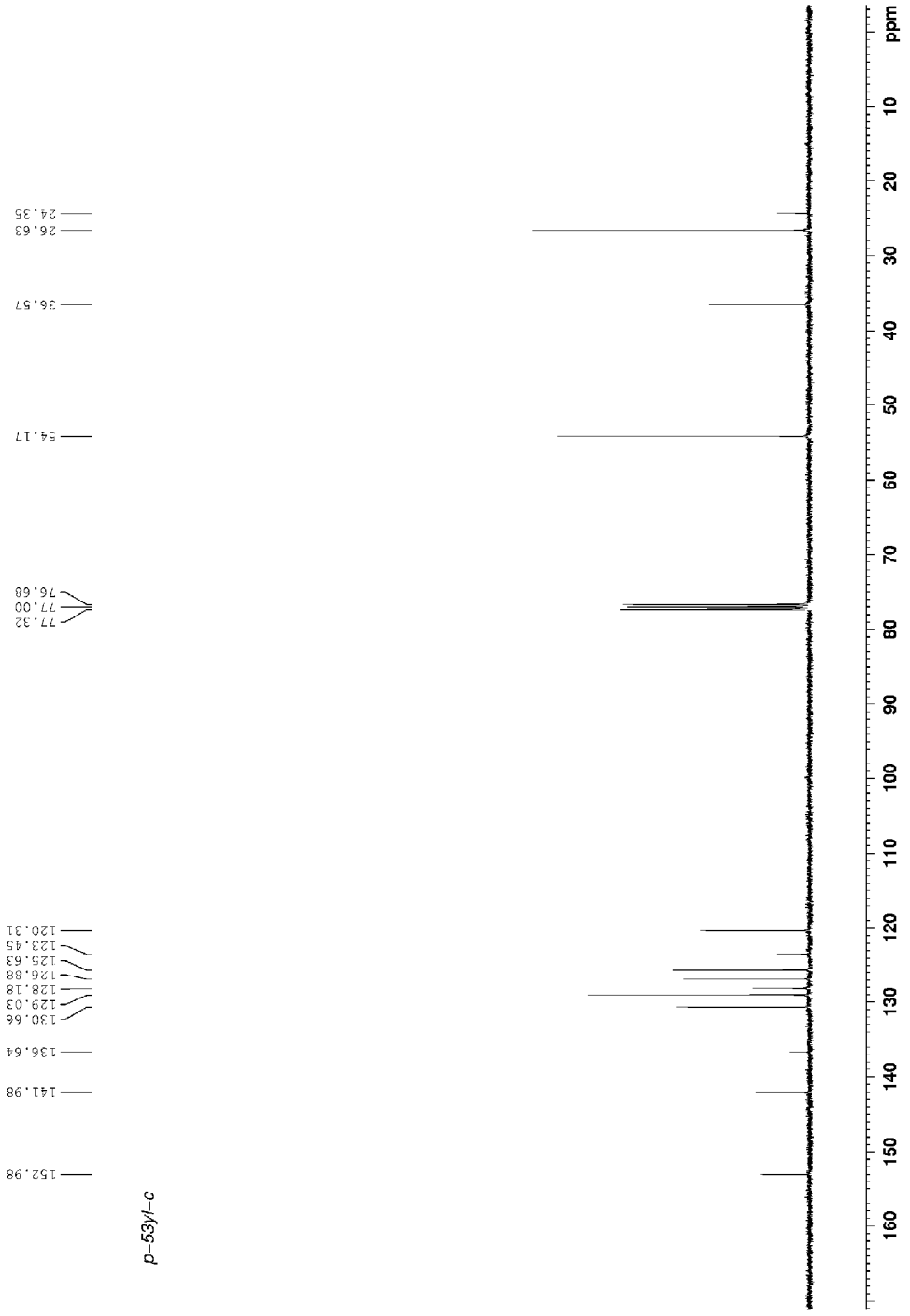



Ph
N

1g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36.57
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76.68
77.00
77.32
120.31
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125.63
126.88
128.18
129.03
130.66
136.64
141.98
152.98
p-53yl-c
ppm
10
20
30
40
50
60
70
80
90
100
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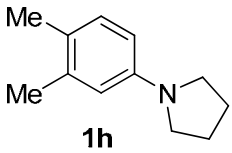
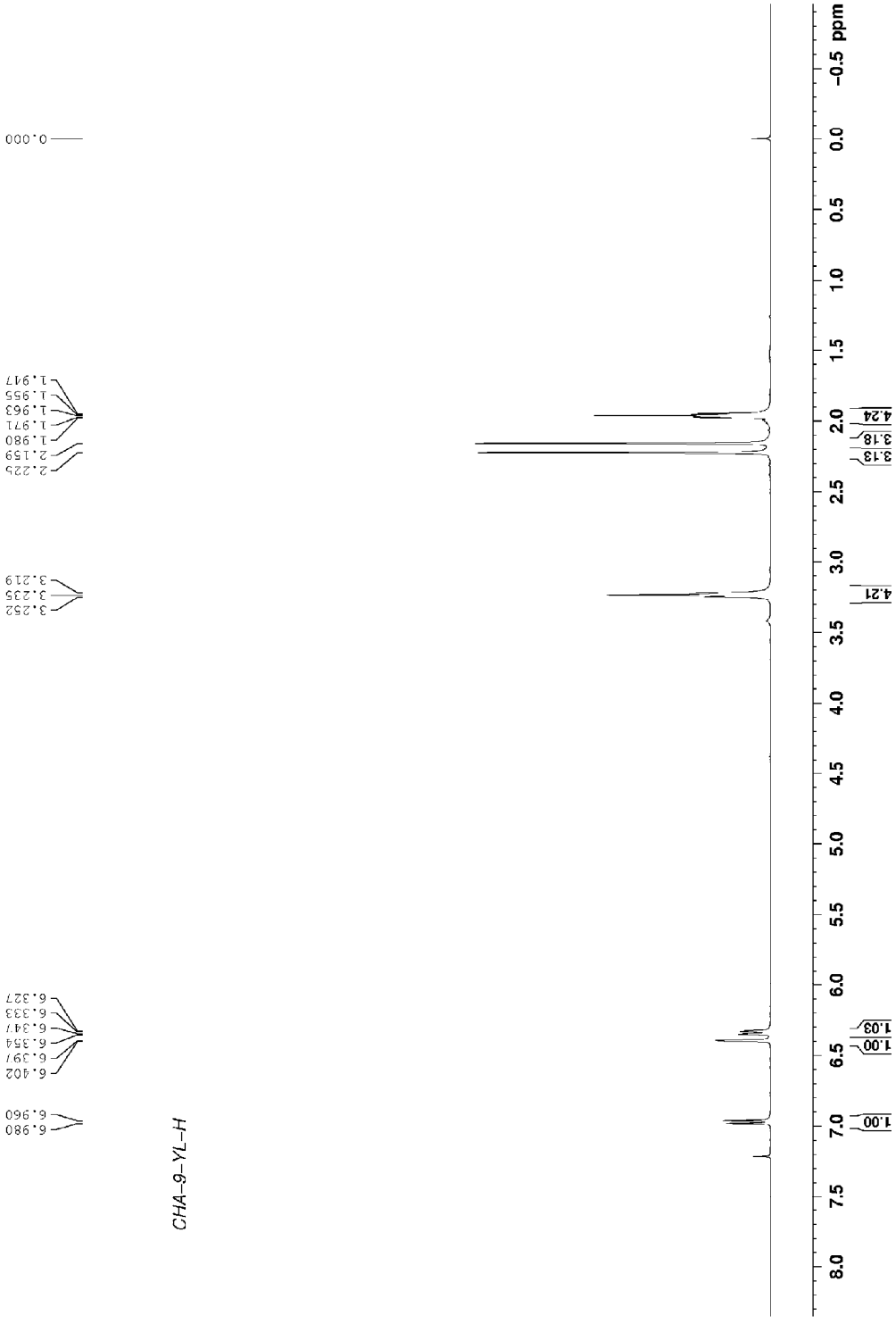
120
130
140
150
160


Me
Me
N

1h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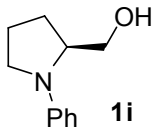
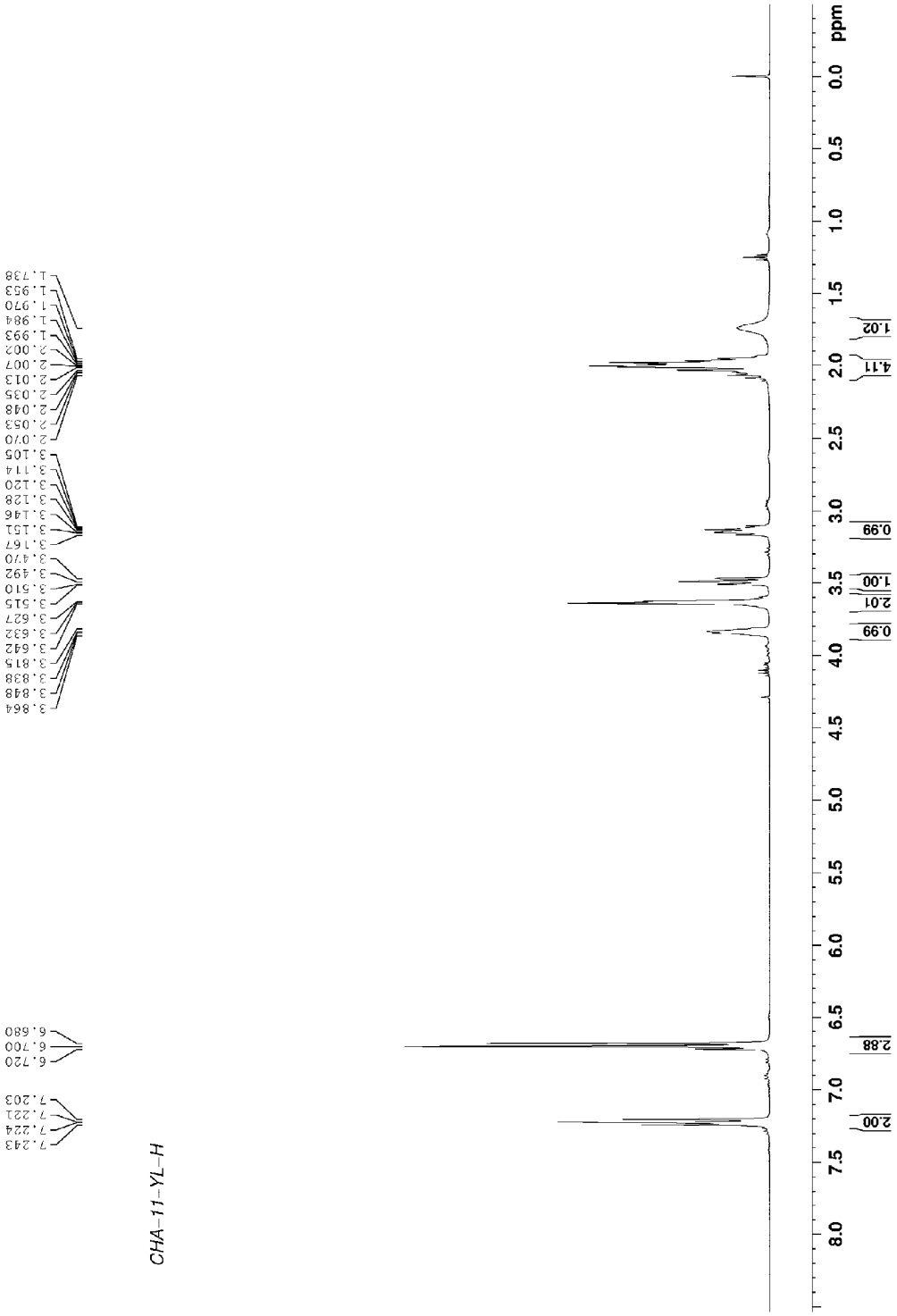
1.971
1.980
2.159
2.225
3.219
3.235
3.252
6.327
6.333
6.347
6.354
6.397
6.402
6.960
6.980
CHA-9-YL-H
ppm
4.24
3.18
3.13
4.21
1.03
1.00
1.00


OH
N
Ph

1i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2.5
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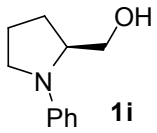
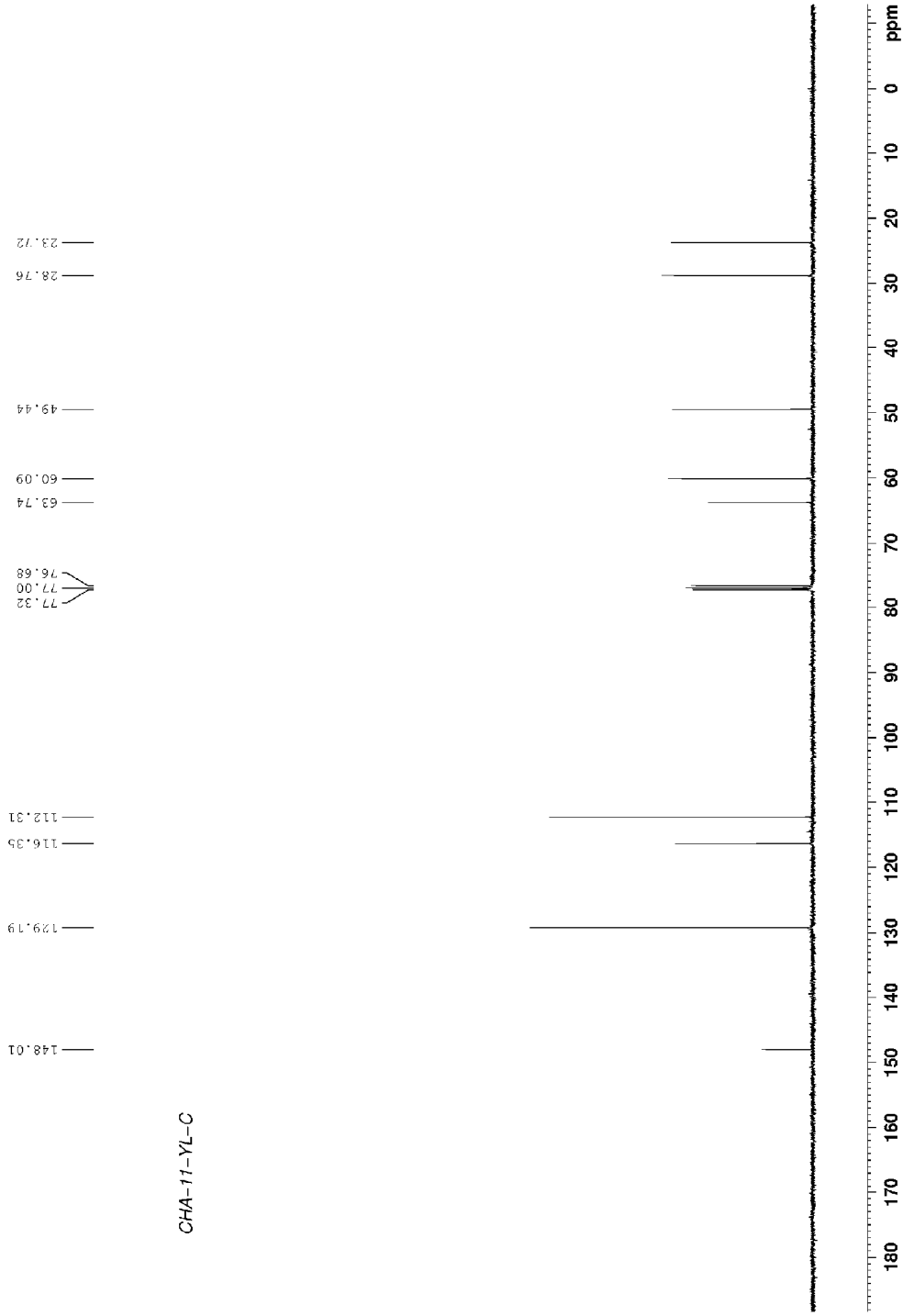
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
1.02
4.11
0.99
1.00
2.01
0.99
2.88
2.00


OH
N
Ph

1i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28.76
49.44
60.09
63.74
76.68
77.00
77.32
112.31
116.35
129.19
148.01
CHA-11-YL-C
ppm
0
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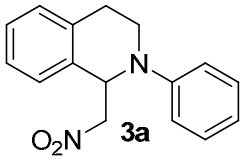
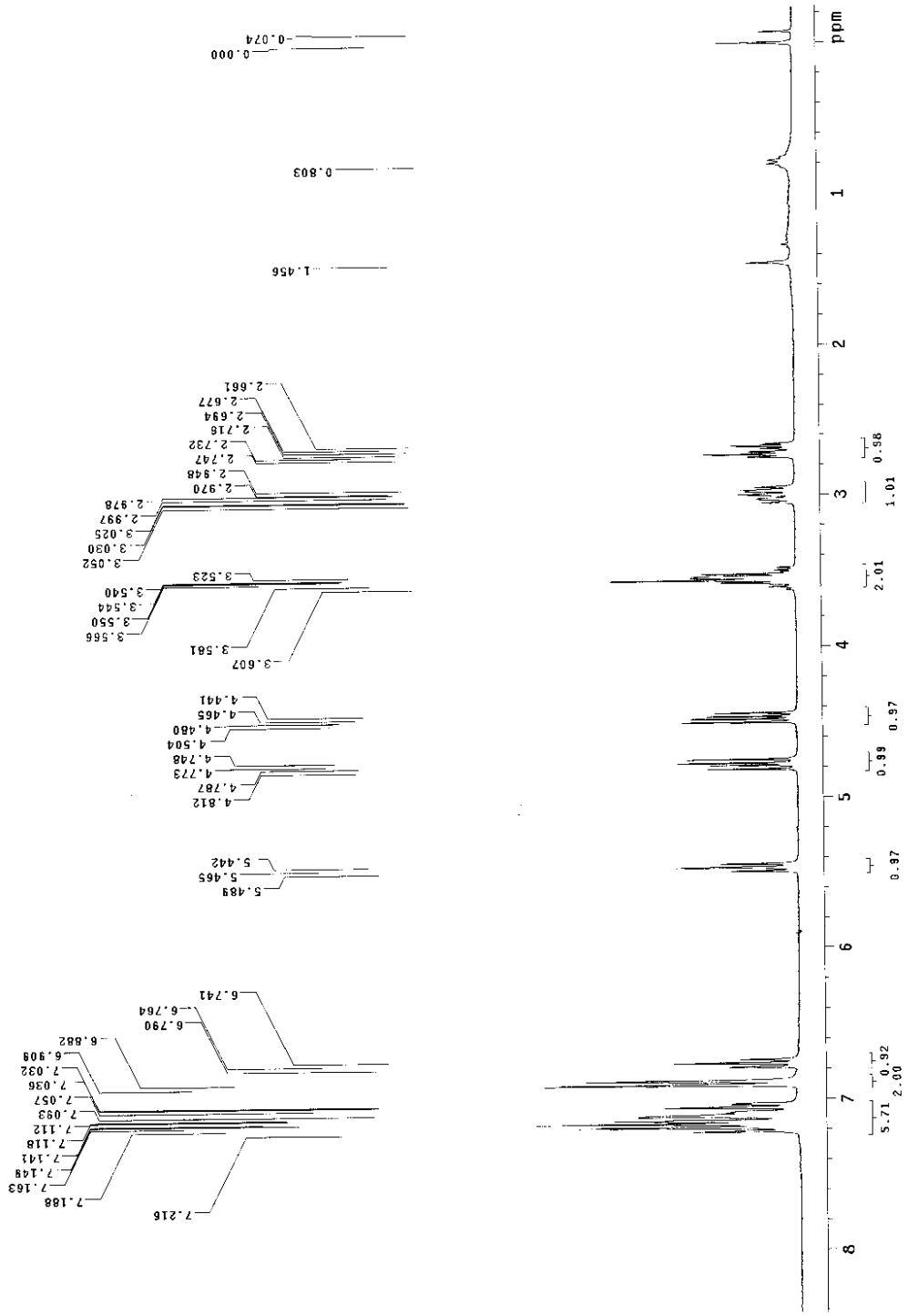
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180


N
O_2N
3a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2.677
2.694
2.718
2.732
2.747
2.948
2.970
2.978
2.997
3.025
3.030
3.052
3.523
3.540
3.544
3.550
3.566
3.561
3.607
4.441
4.465
4.480
4.504
4.748
4.773
4.787
4.812
5.442
5.465
5.489
6.741
6.764
6.790
6.882
6.909
7.032
7.036
7.057
7.093
7.112
7.118
7.141
7.149
7.163
7.188
7.216
ppm
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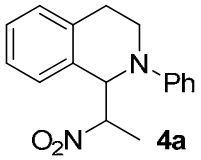
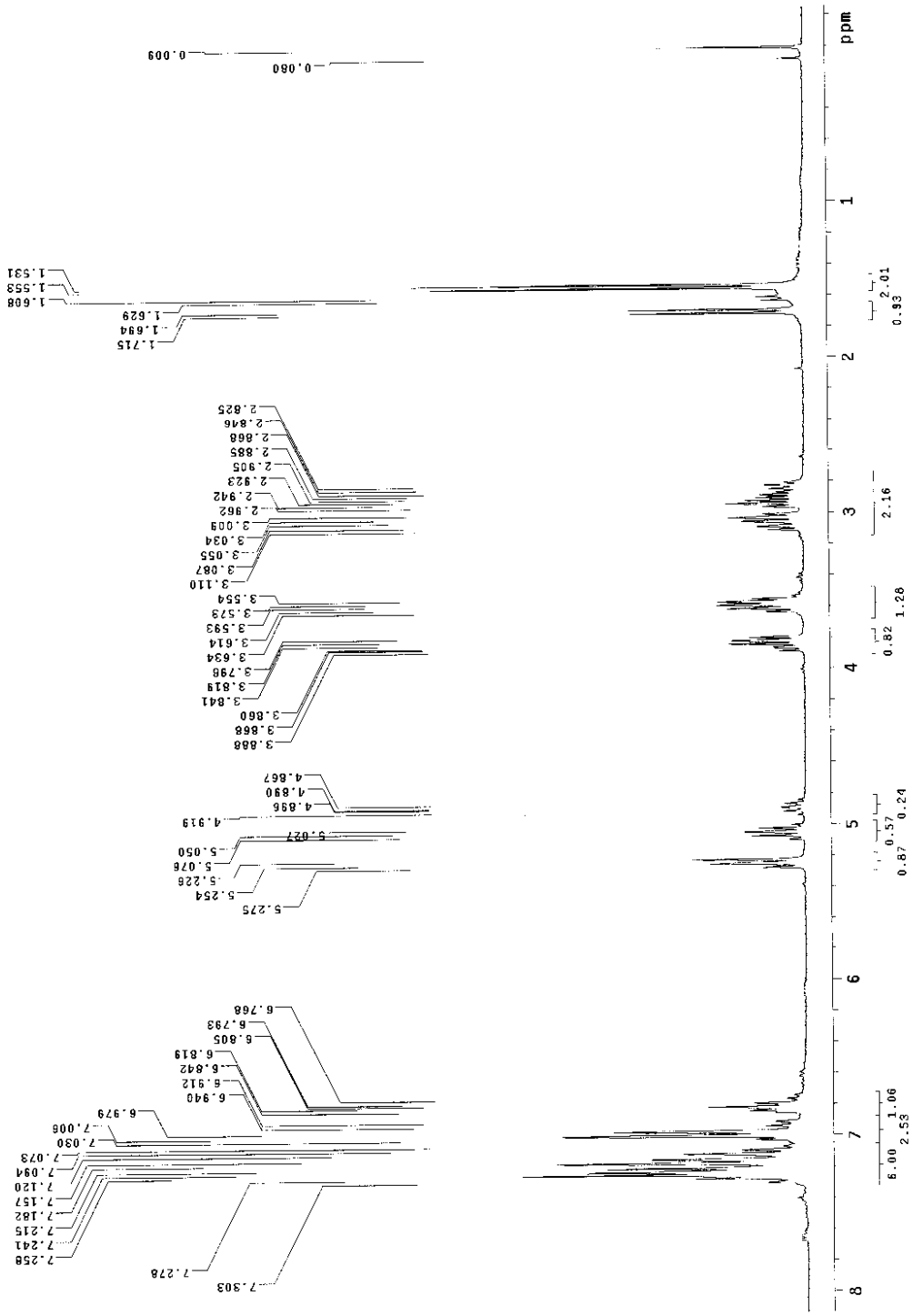
2.01
0.99
0.97
0.97
0.92
2.00
5.71


N
Ph
O_2N

4a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1.608
1.629
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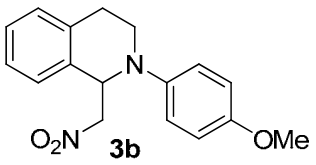
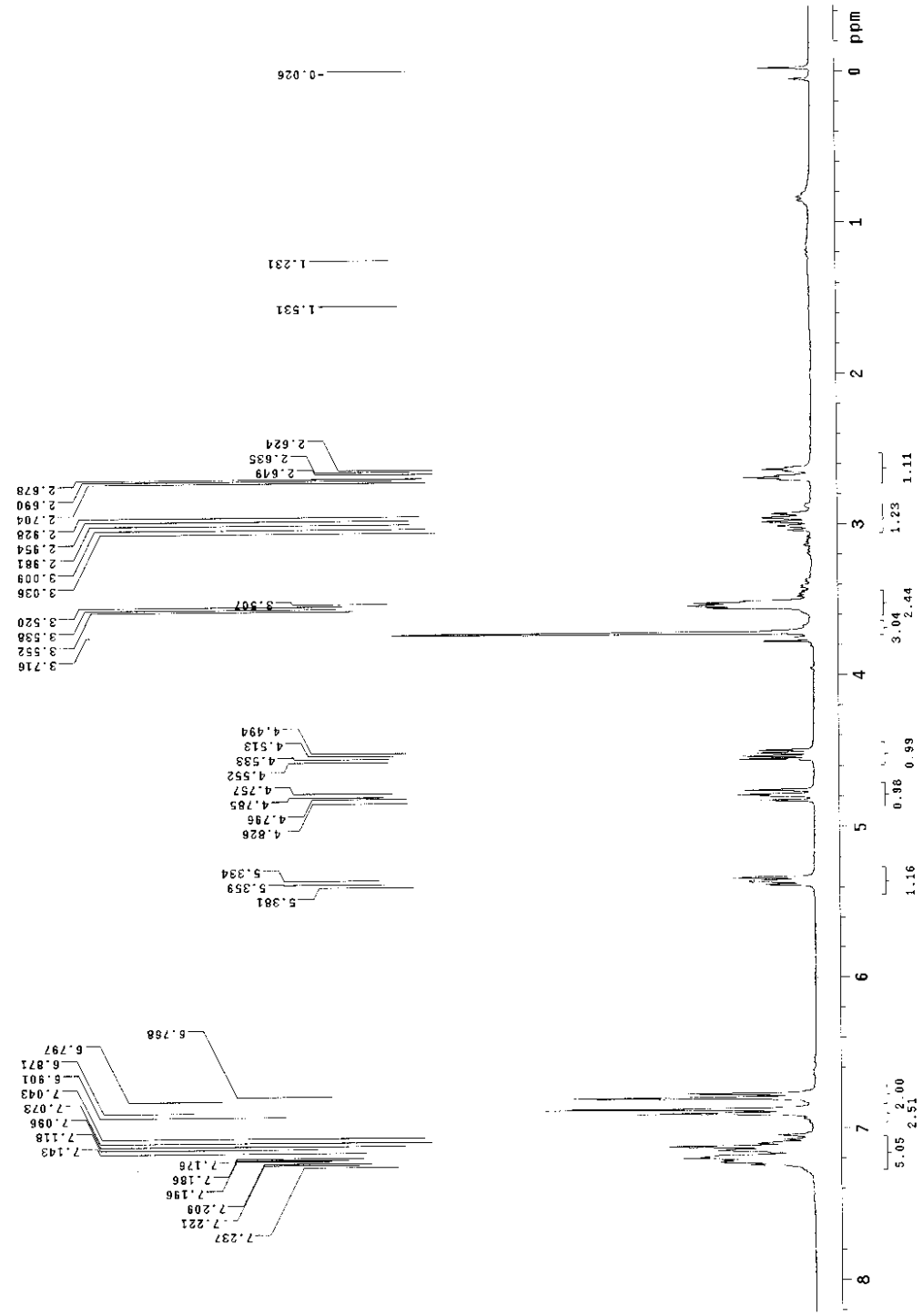
2.825
2.846
2.868
2.885
2.905
2.923
2.942
2.962
3.009
3.034
3.055
3.087
3.110
3.554
3.579
3.593
3.614
3.634
3.798
3.819
3.841
3.860
3.868
4.867
4.890
4.936
4.939
5.027
5.050
5.076
5.226
5.254
5.275
6.768
6.793
6.805
6.819
6.892
6.912
6.940
6.979
7.008
7.030
7.073
7.094
7.120
7.157
7.182
7.215
7.241
7.258
7.278
7.303


N
O_2N
OMe

3b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2.690
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2.928
2.954
2.981
3.009
3.038
3.507
3.520
3.538
3.552
3.716
4.494
4.513
4.583
4.552
4.757
4.785
4.796
4.826
5.334
5.359
5.381
6.788
6.797
6.871
6.901
7.043
7.073
7.098
7.118
7.143
7.176
7.186
7.196
7.209
7.221
7.237
ppm
0
1
2
3
4
5
6
7
8
1.11
1.23
3.04
2.44
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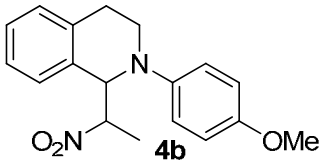
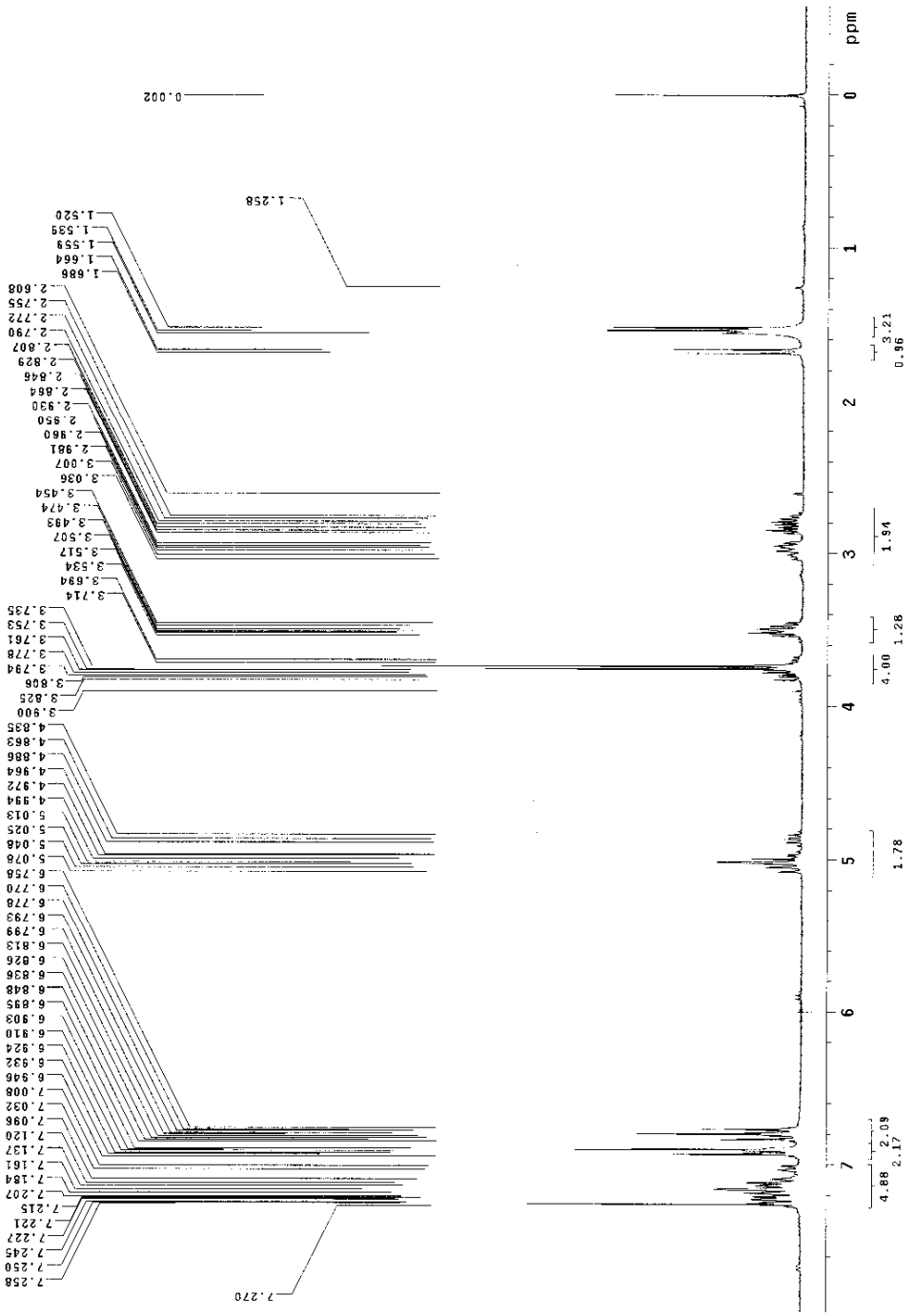
0.96
1.16
2.00
2.51
5.05


N
O_2N
OMe

4b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2
3
4
5
6
7
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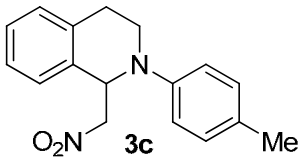
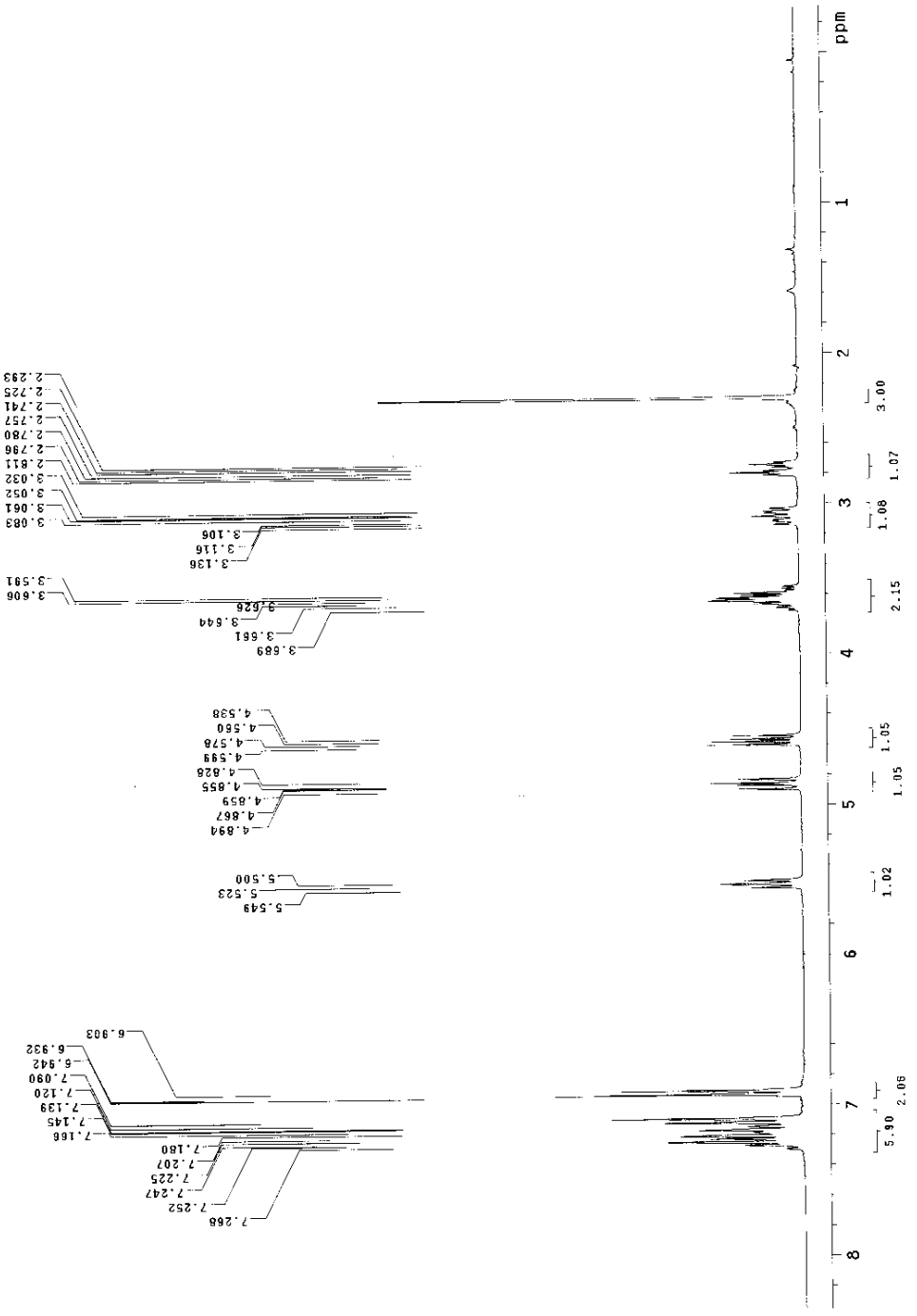
1.94
4.00
1.28
1.78
2.09
2.17
4.88
0.002
1.258
7.270


N
O_2N
3c
Me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4
5
6
7
8
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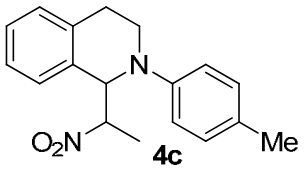
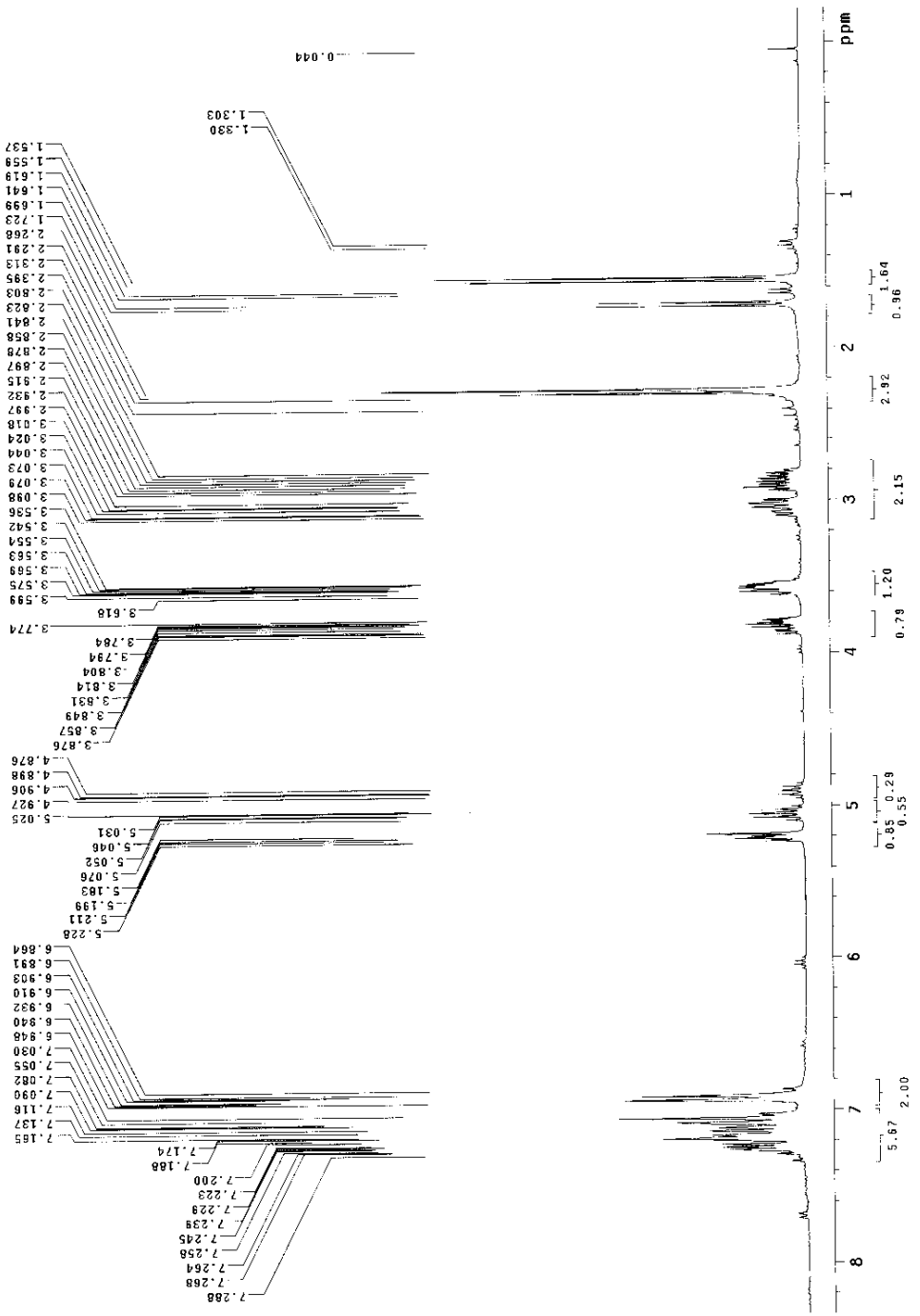
1.08
2.15
1.05
1.05
1.02
5.90
2.06
2.293
2.725
2.741
2.757
2.780
2.796
2.811
3.032
3.052
3.061
3.083
3.106
3.116
3.136
3.591
3.606
3.626
3.644
3.661
3.689
4.538
4.560
4.578
4.599
4.626
4.855
4.859
4.867
4.894
5.500
5.523
5.549
6.903
6.932
6.942
7.090
7.120
7.139
7.145
7.166
7.180
7.207
7.225
7.247
7.252
7.268


N
O_2N
Me

4c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2.313
2.395
2.803
2.823
2.841
2.858
2.878
2.897
2.915
2.932
2.997
3.018
3.024
3.044
3.073
3.079
3.098
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3.554
3.563
3.569
3.575
3.599
3.618
3.774
3.764
3.784
3.804
3.814
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3.849
3.857
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4.898
4.906
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5.046
5.052
5.076
5.183
5.199
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6.910
6.932
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7.118
7.137
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7.174
7.188
7.200
7.223
7.229
7.239
7.245
7.258
7.264
7.268
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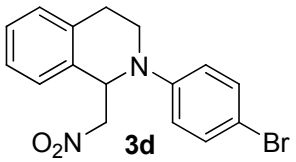
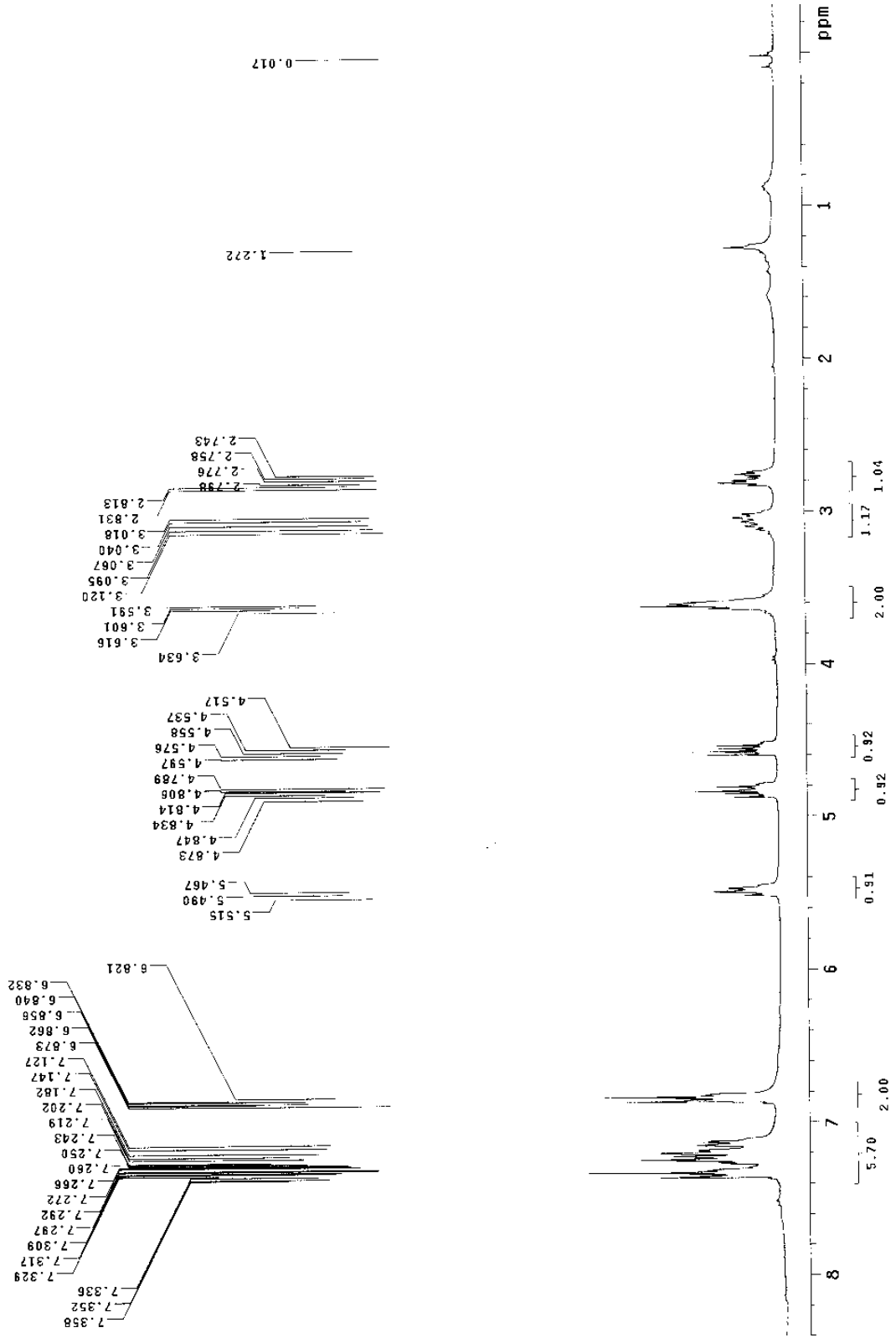
2.00


N
O_2N
3d
Br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3.591
3.601
3.616
3.634
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4.576
4.597
4.769
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4.814
4.834
4.847
4.873
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5.490
5.515
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6.856
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7.219
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ppm
1
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6
7
8
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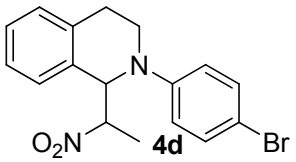
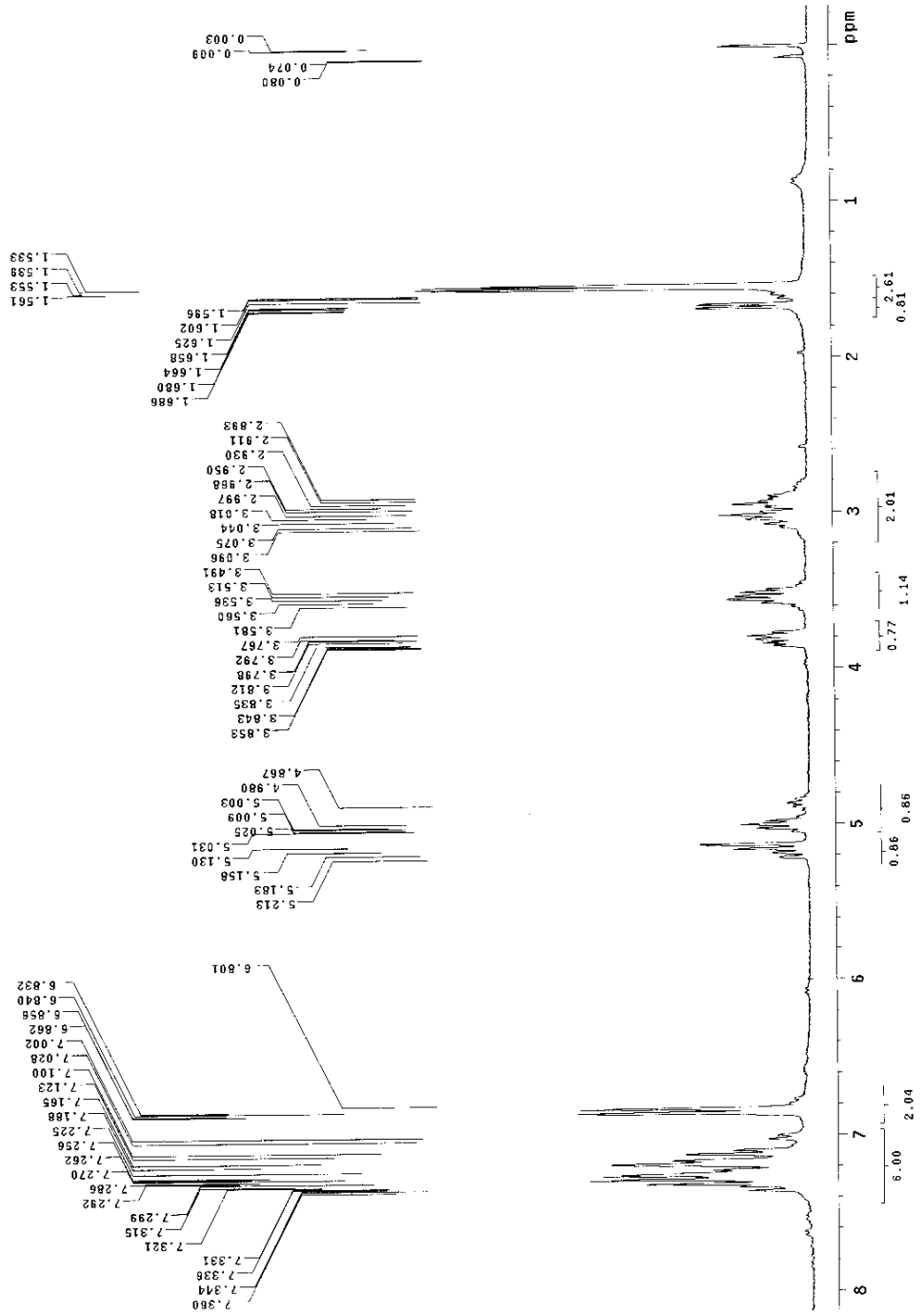
0.91
2.00
5.70


N
O_2N
4d
Br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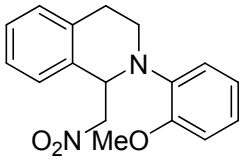
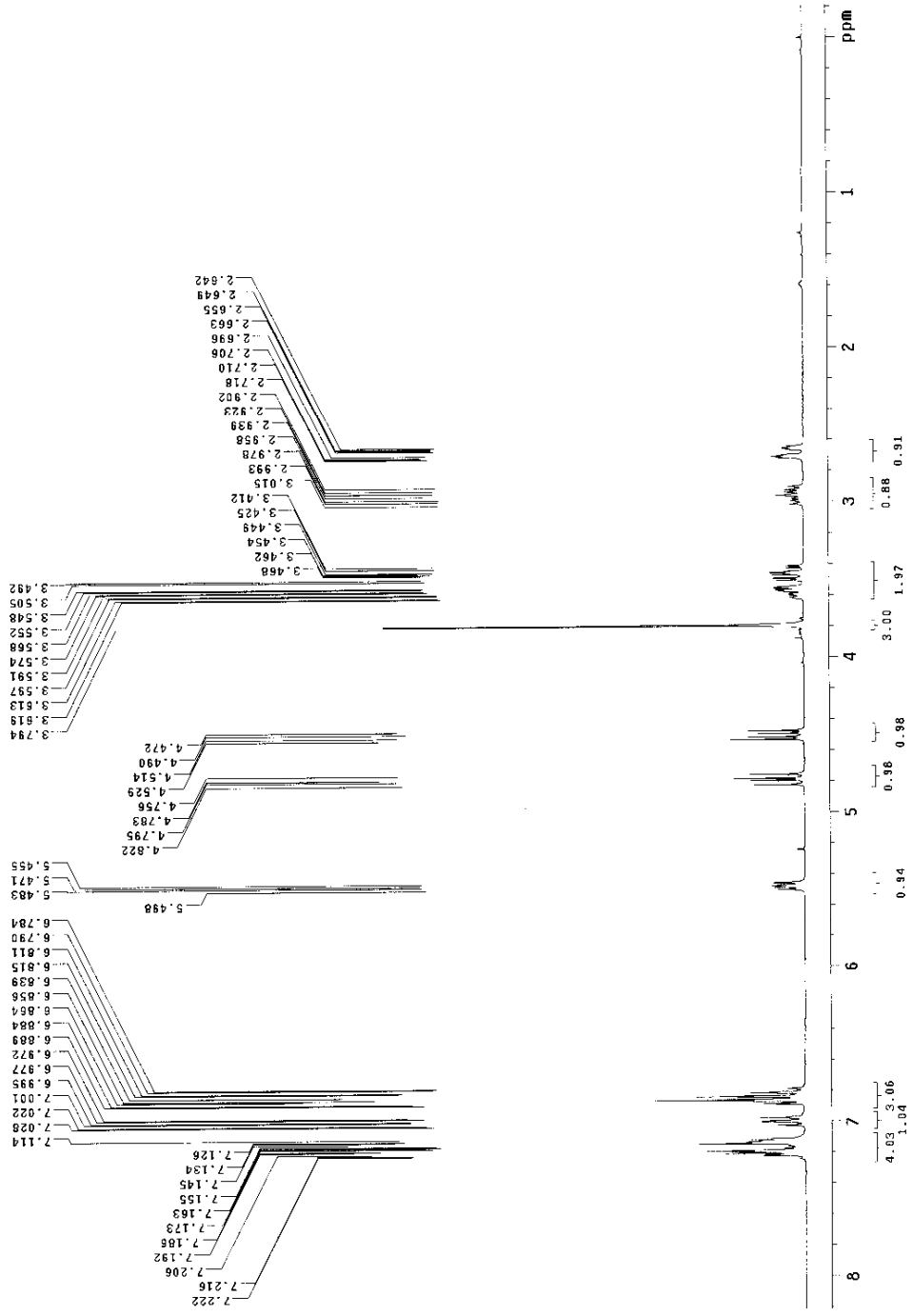
6.00


N
O_2N
MeO

3e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4
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6
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8
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0.98
0.94
3.06
1.04
4.03
2.642
2.649
2.655
2.663
2.696
2.706
2.710
2.718
2.902
2.923
2.939
2.958
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3.505
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3.552
3.568
3.574
3.591
3.597
3.613
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4.822
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5.498
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6.815
6.839
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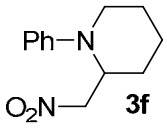
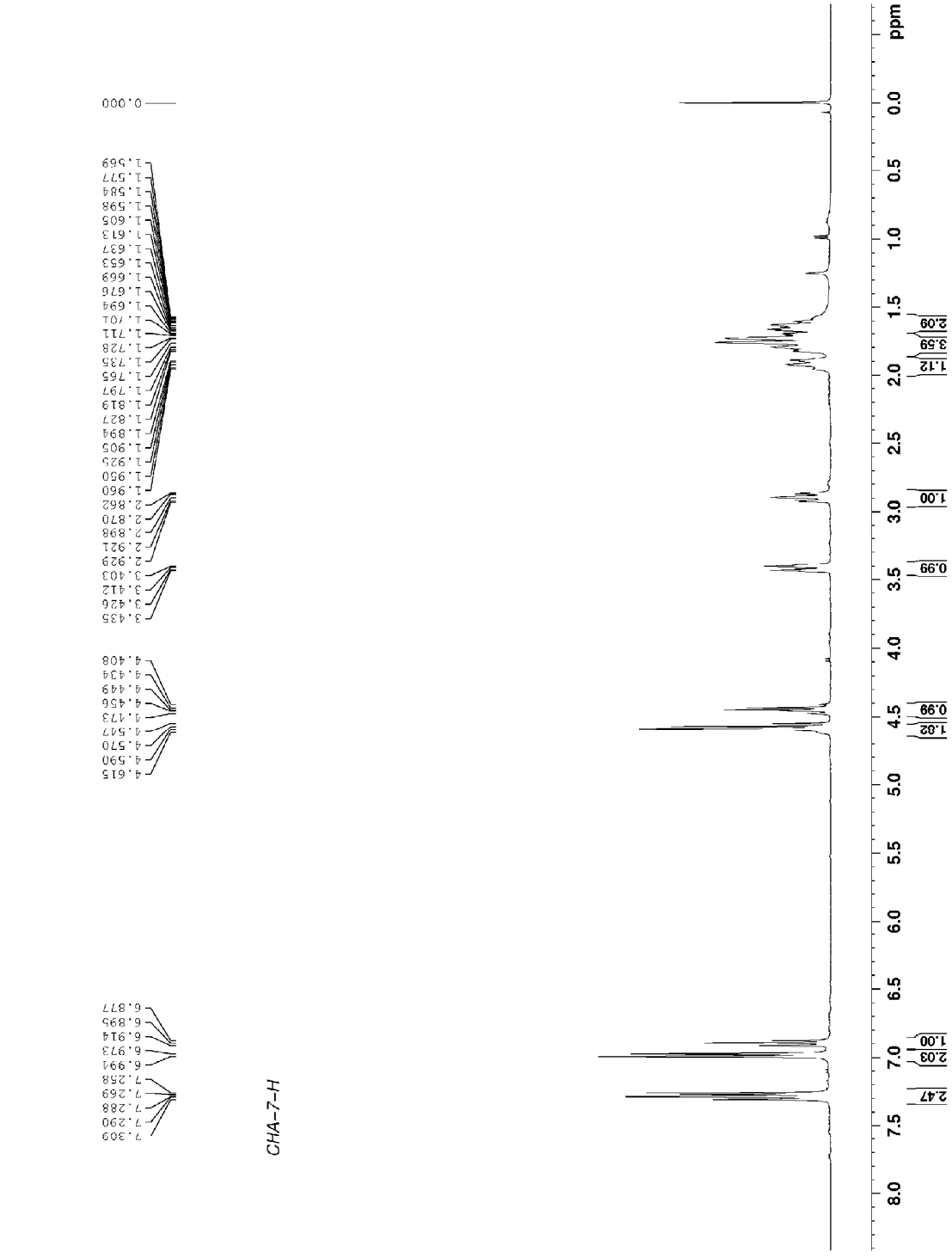
7.222


Ph–N
O2N
3f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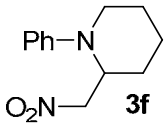
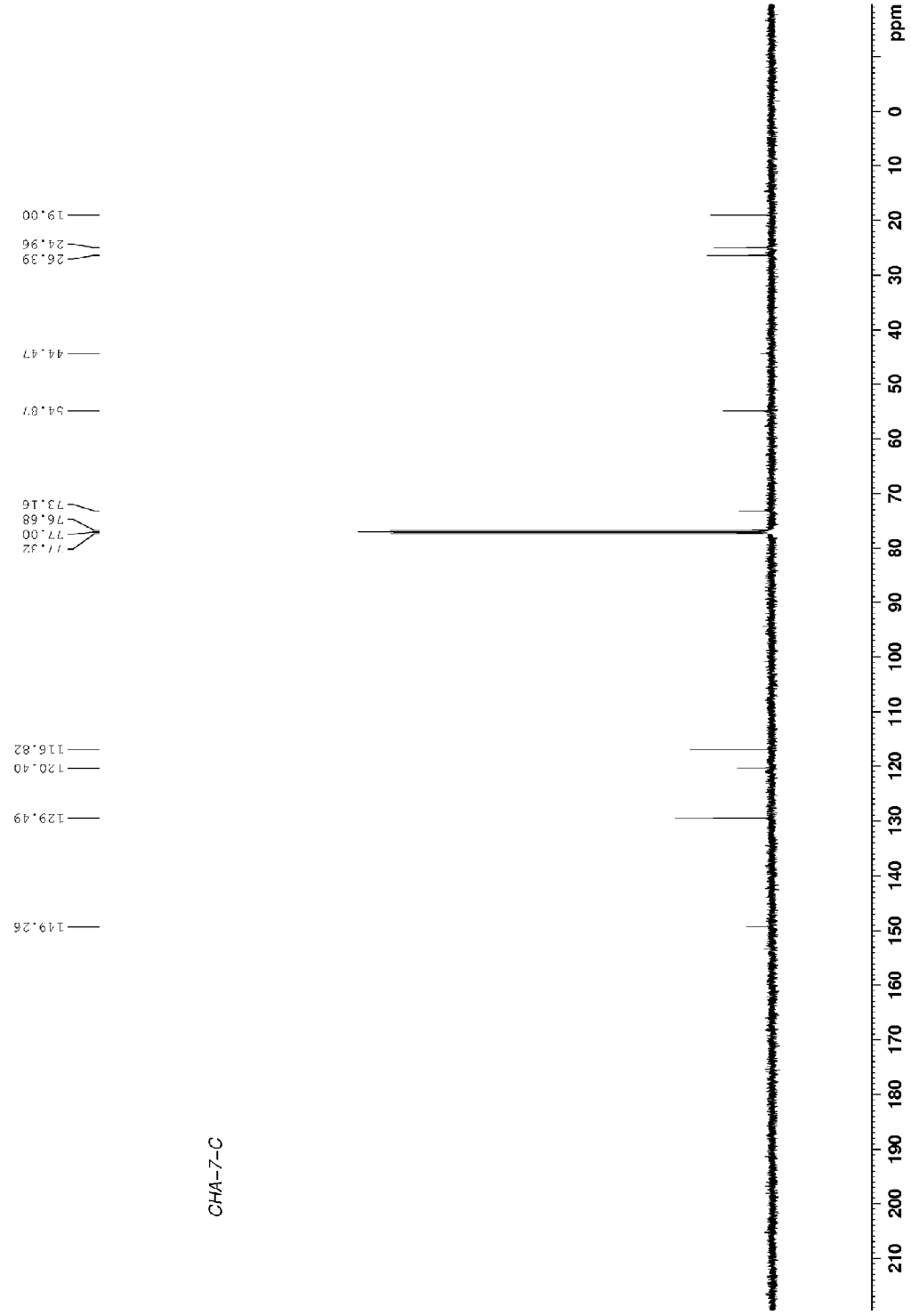
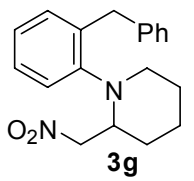
4.547
4.570
4.590
4.615
6.877
6.895
6.914
6.973
6.991
7.258
7.269
7.288
7.290
7.309
CHA-7-H
ppm
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
2.09
3.59
1.12
1.00
0.99
0.99
1.02
1.00
2.03
2.47

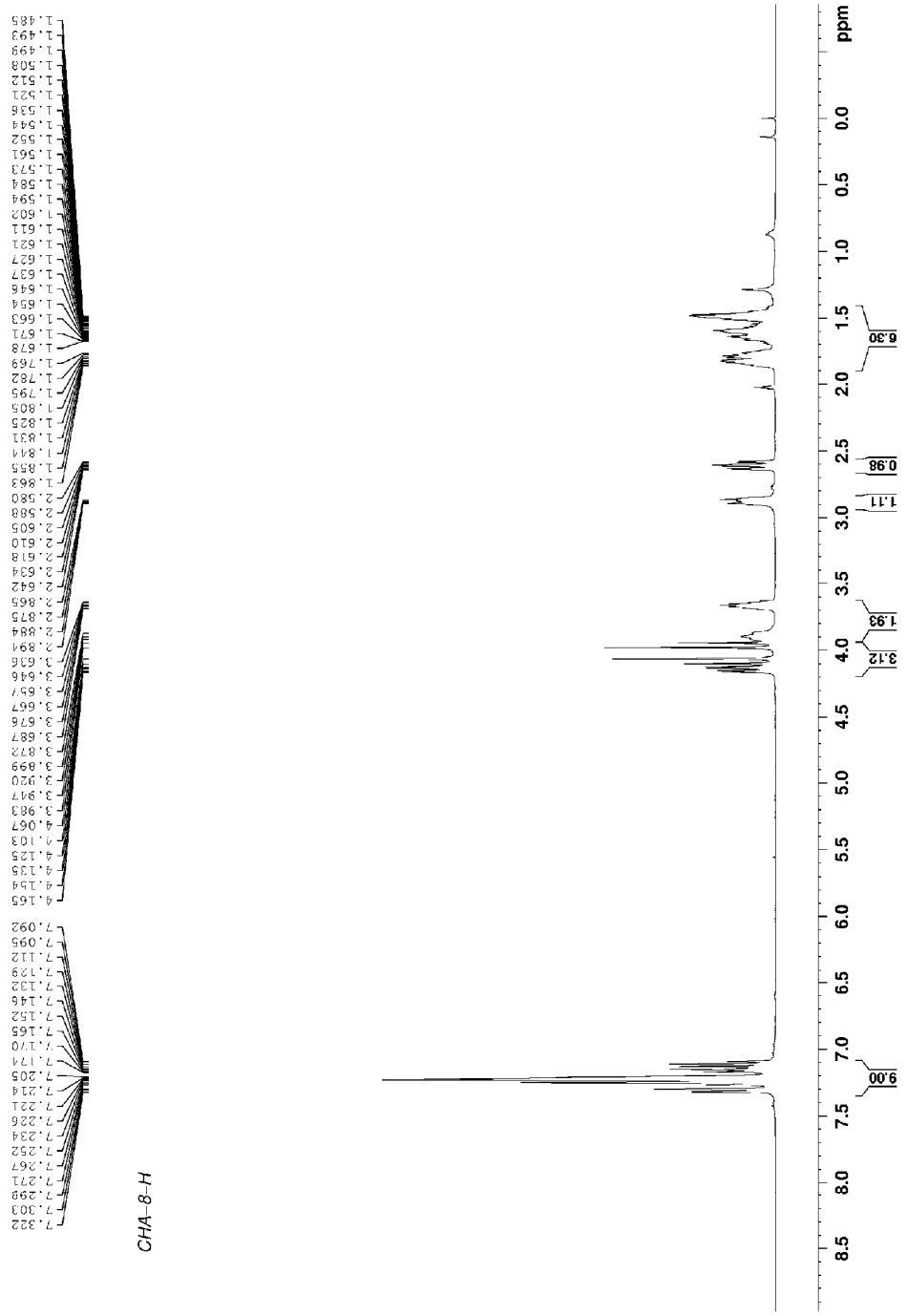

Ph–N
O2N

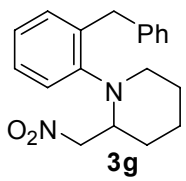
3f


19.00
24.96
26.39
44.47
54.87
73.16
76.68
77.00
77.32
116.82
120.40
129.49
149.26
CHA-7-C
ppm

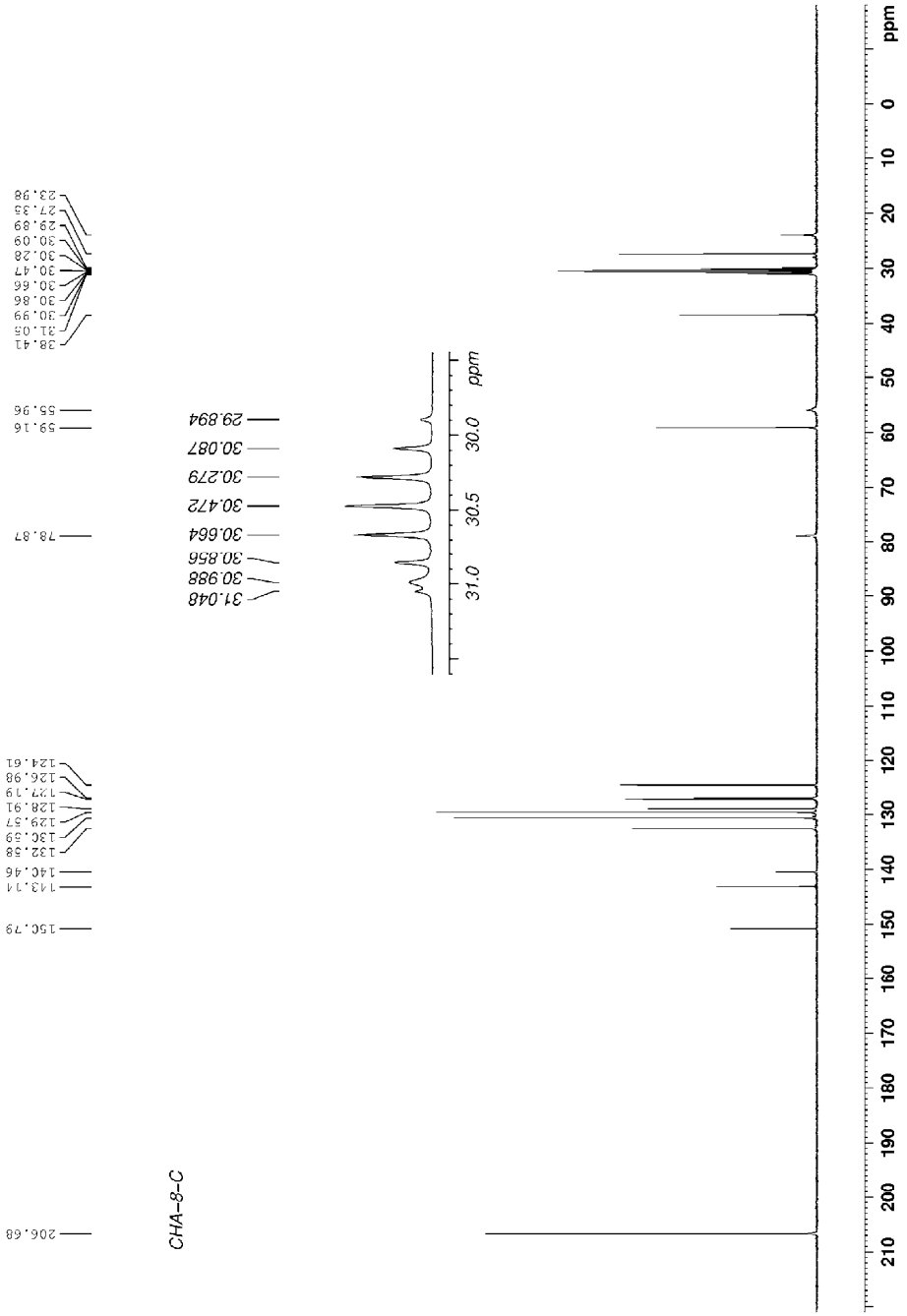


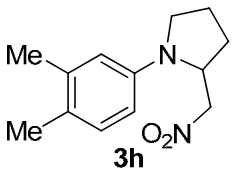
3g



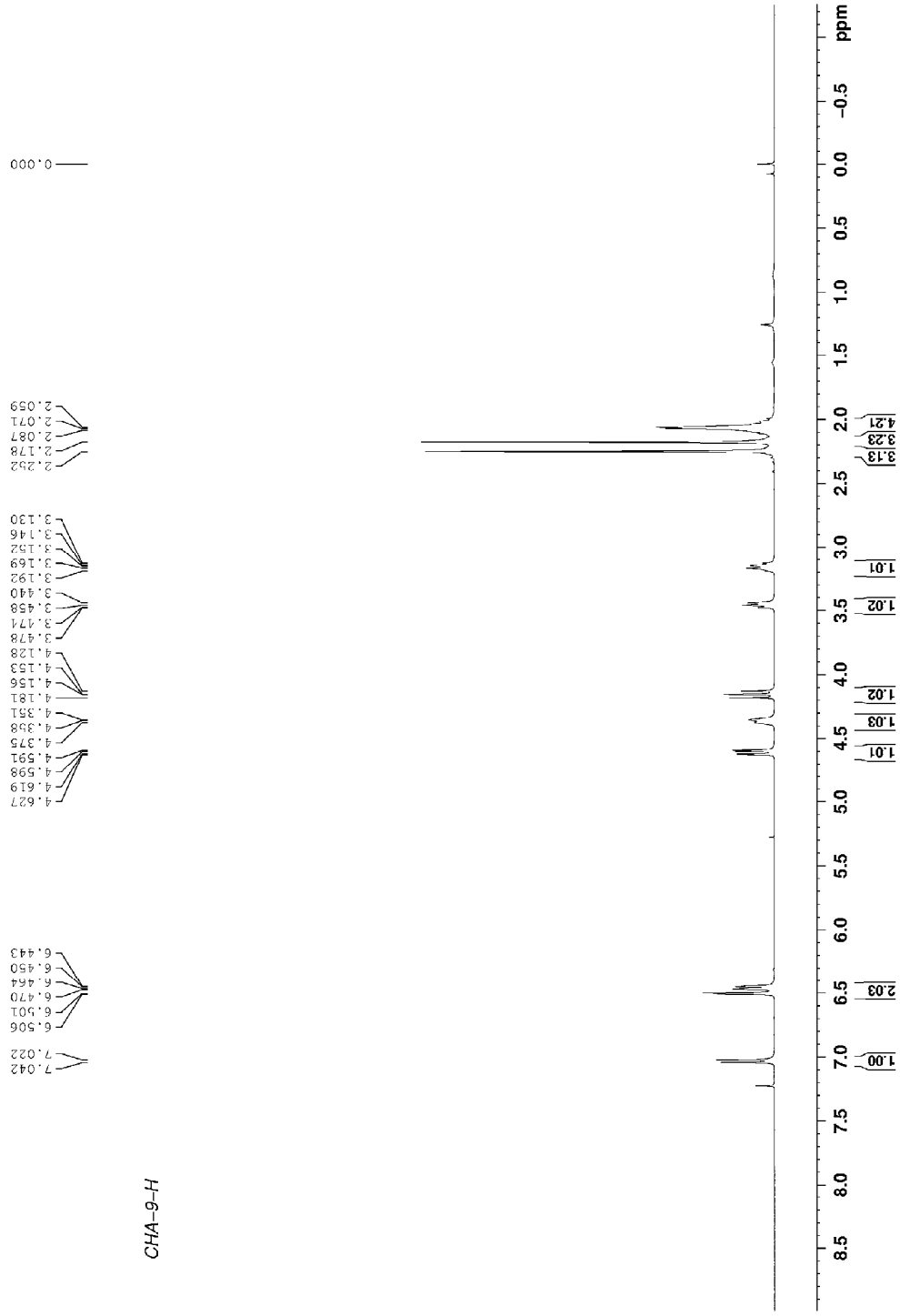


3g




Me
Me
N
O2N

3h


CHA-9-H
ppm
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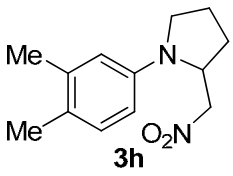
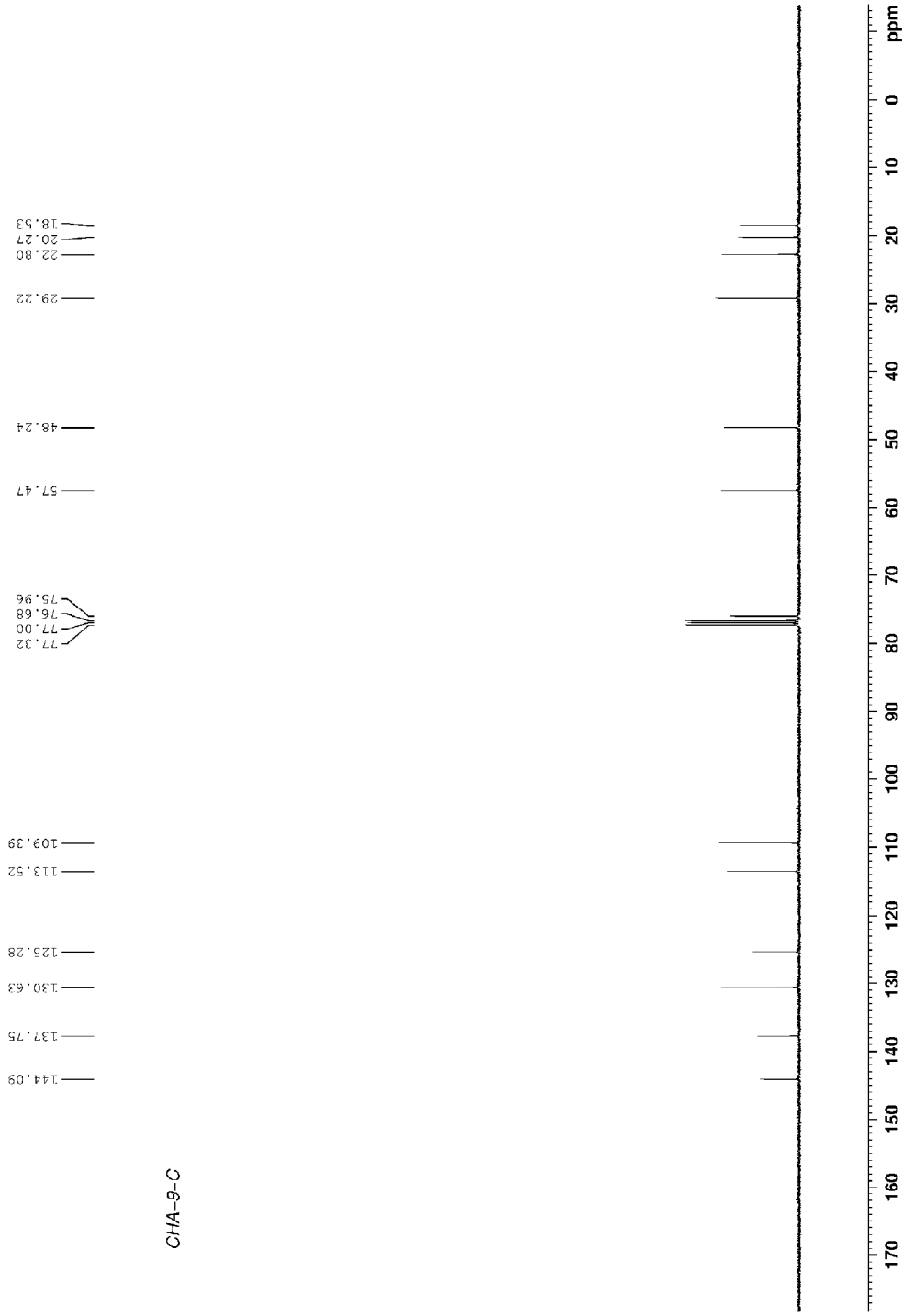
2.087
2.178
2.252
3.130
3.146
3.152
3.169
3.192
3.440
3.458
3.474
3.478
4.128
4.153
4.156
4.181
4.351
4.358
4.375
4.591
4.598
4.619
4.627
6.443
6.450
6.464
6.470
6.501
6.506
7.022
7.042
4.21
3.23
3.13
1.01
1.02
1.02
1.03
1.01
2.03
1.00


Me
Me
N
O2N

3h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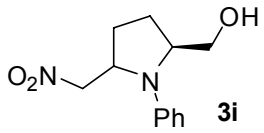
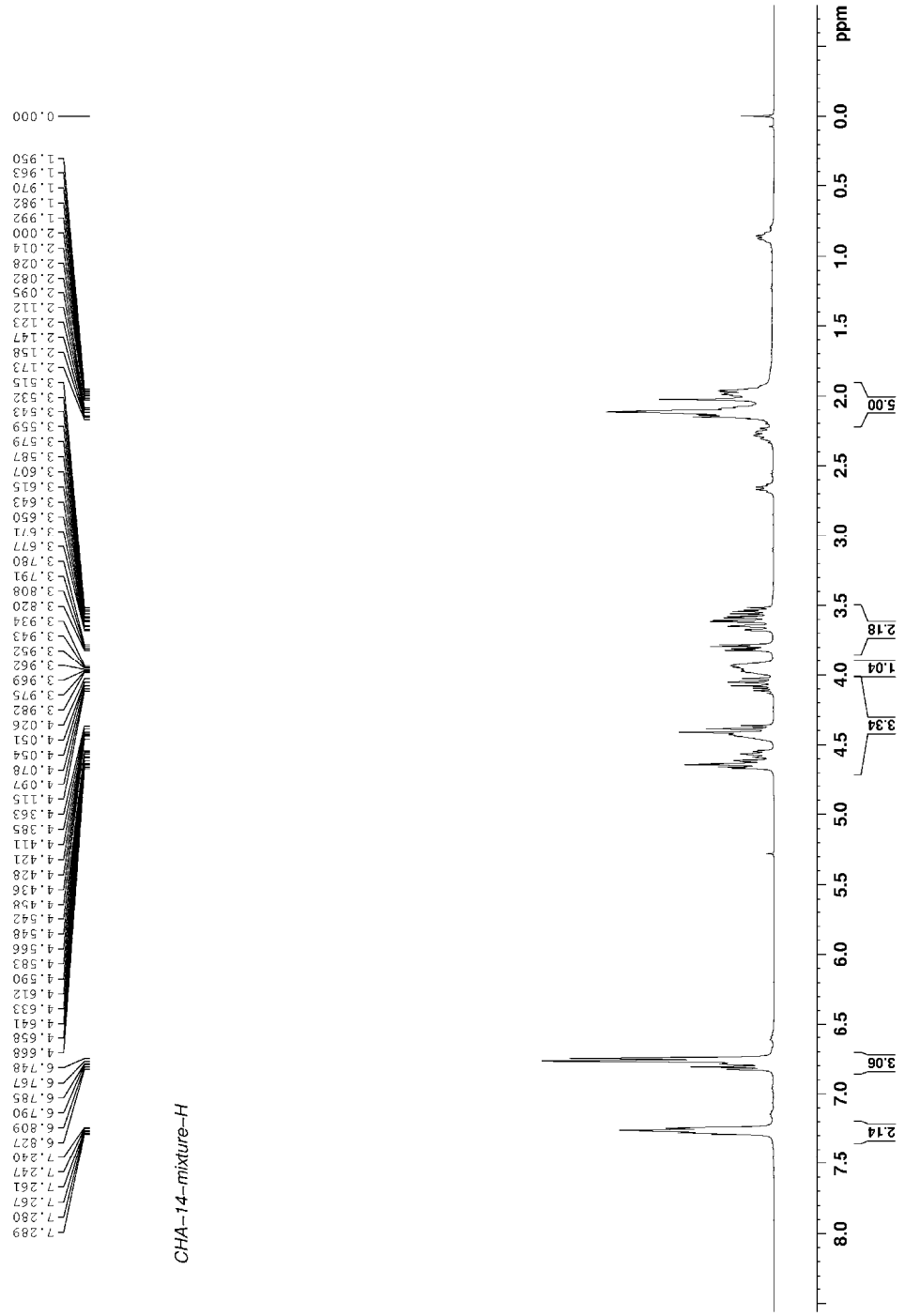
20.27
22.80
29.22
48.24
57.47
75.96
76.68
77.00
77.32
109.39
113.52
125.28
130.63
137.75
144.09
CHA-9-C
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170


OH
O_2N
N
Ph

3i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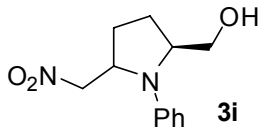
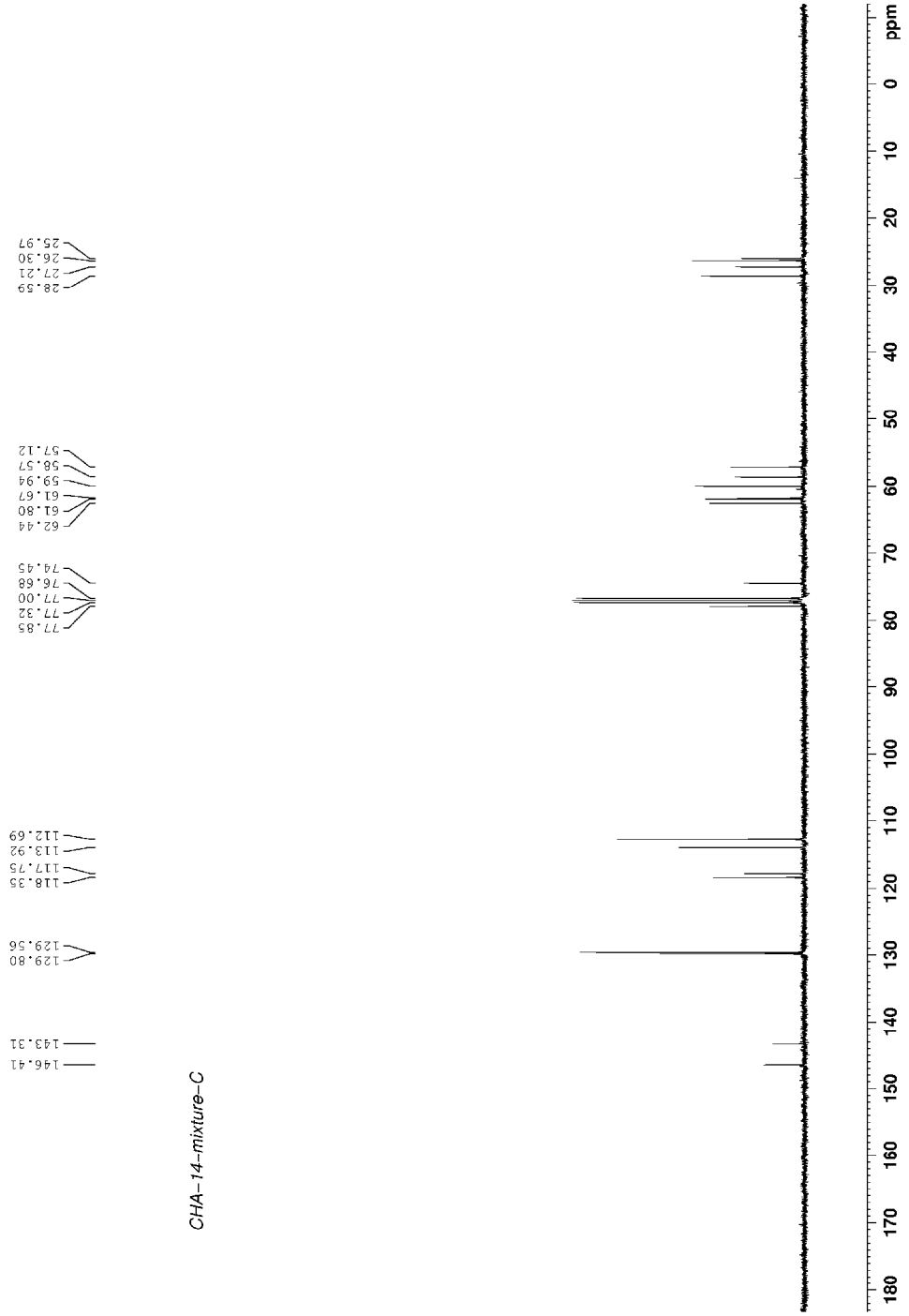
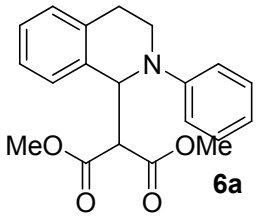
1.950
1.963
1.970
1.982
1.992
2.000
2.014
2.028
2.082
2.095
2.112
2.123
2.147
2.158
2.173
3.515
3.532
3.543
3.559
3.579
3.587
3.607
3.615
3.643
3.650
3.671
3.677
3.780
3.791
3.808
3.820
3.934
3.943
3.952
3.962
3.969
3.975
3.982
4.026
4.051
4.054
4.078
4.097
4.115
4.363
4.385
4.411
4.421
4.428
4.436
4.458
4.542
4.548
4.566
4.583
4.590
4.612
4.633
4.641
4.658
4.668
6.748
6.767
6.785
6.790
6.809
6.827
7.240
7.247
7.261
7.267
7.280
7.289
CHA-14-mixture-H
ppm
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
5.00
2.18
1.04
3.34
3.06
2.14

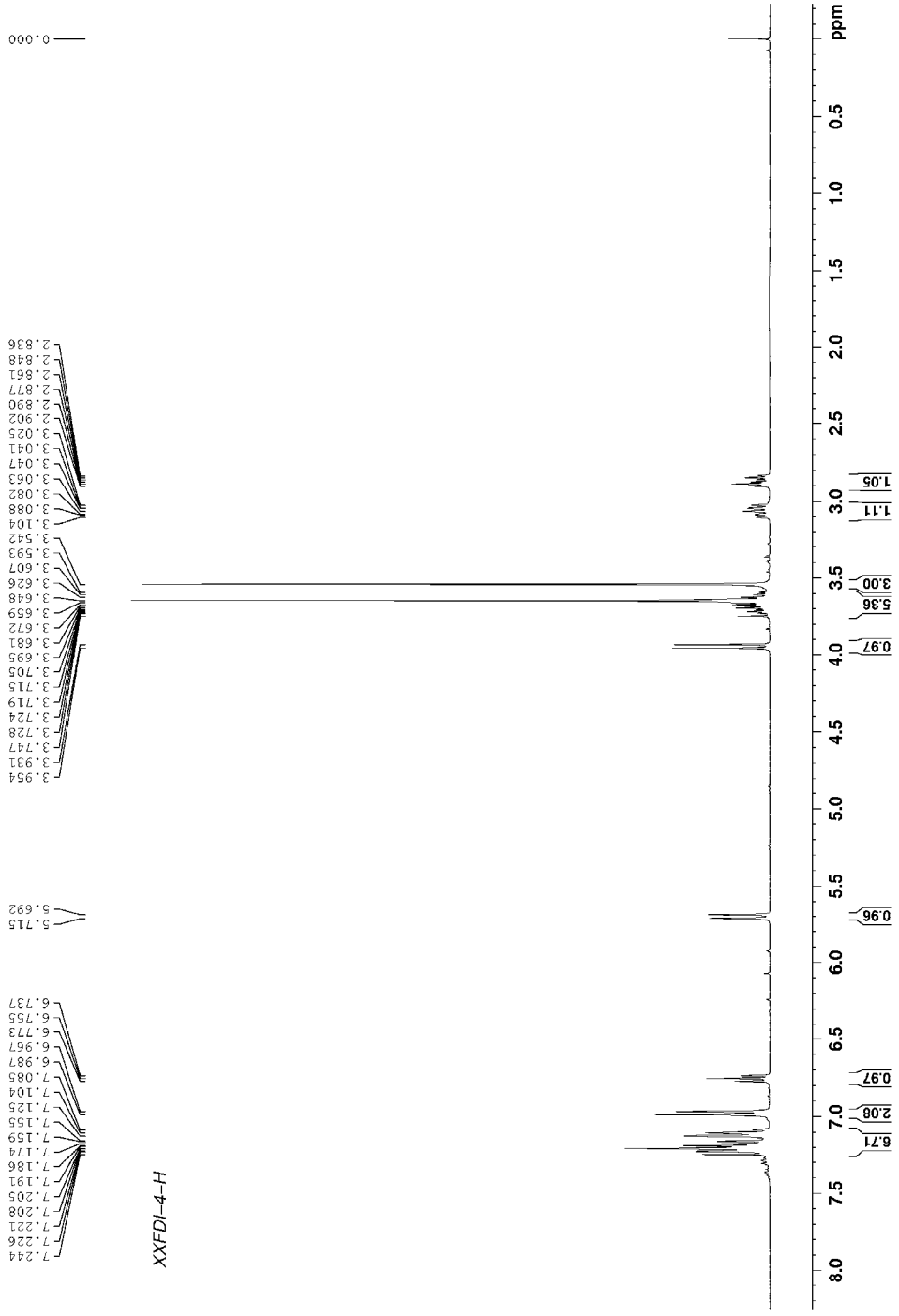

OH
O_2N
N
Ph

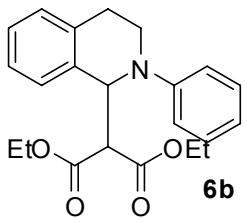
3i


25.97
26.30
27.21
28.59
57.12
58.57
59.94
61.67
61.80
62.44
74.45
76.68
77.00
77.32
77.85
112.69
113.92
117.75
118.35
129.56
129.80
143.31
146.41
CHA-14-mixture-C
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180

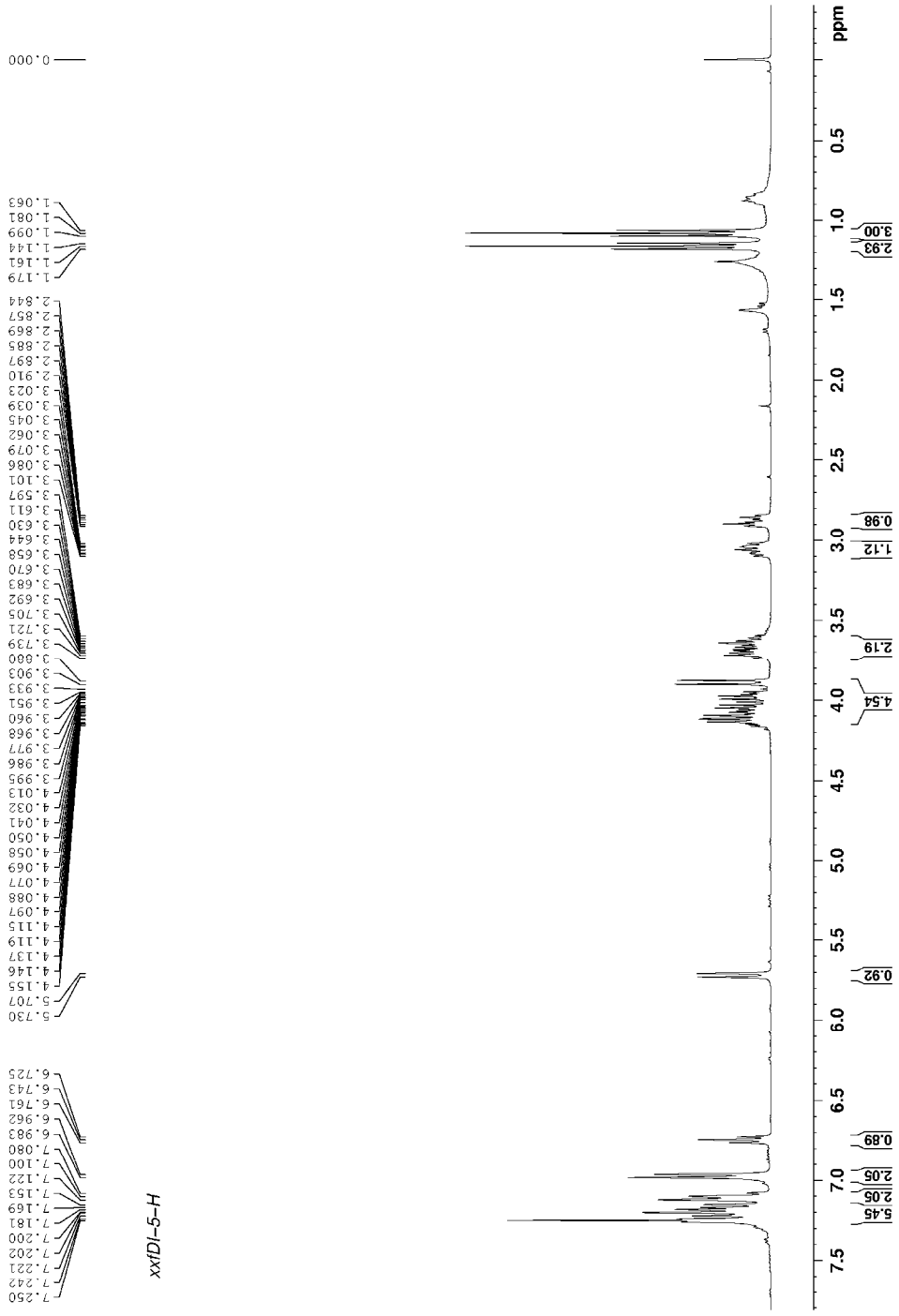


6a




N
EtO
OEt
O
O

6b


xxfDI-5-H
ppm
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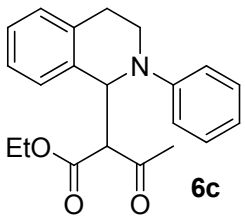
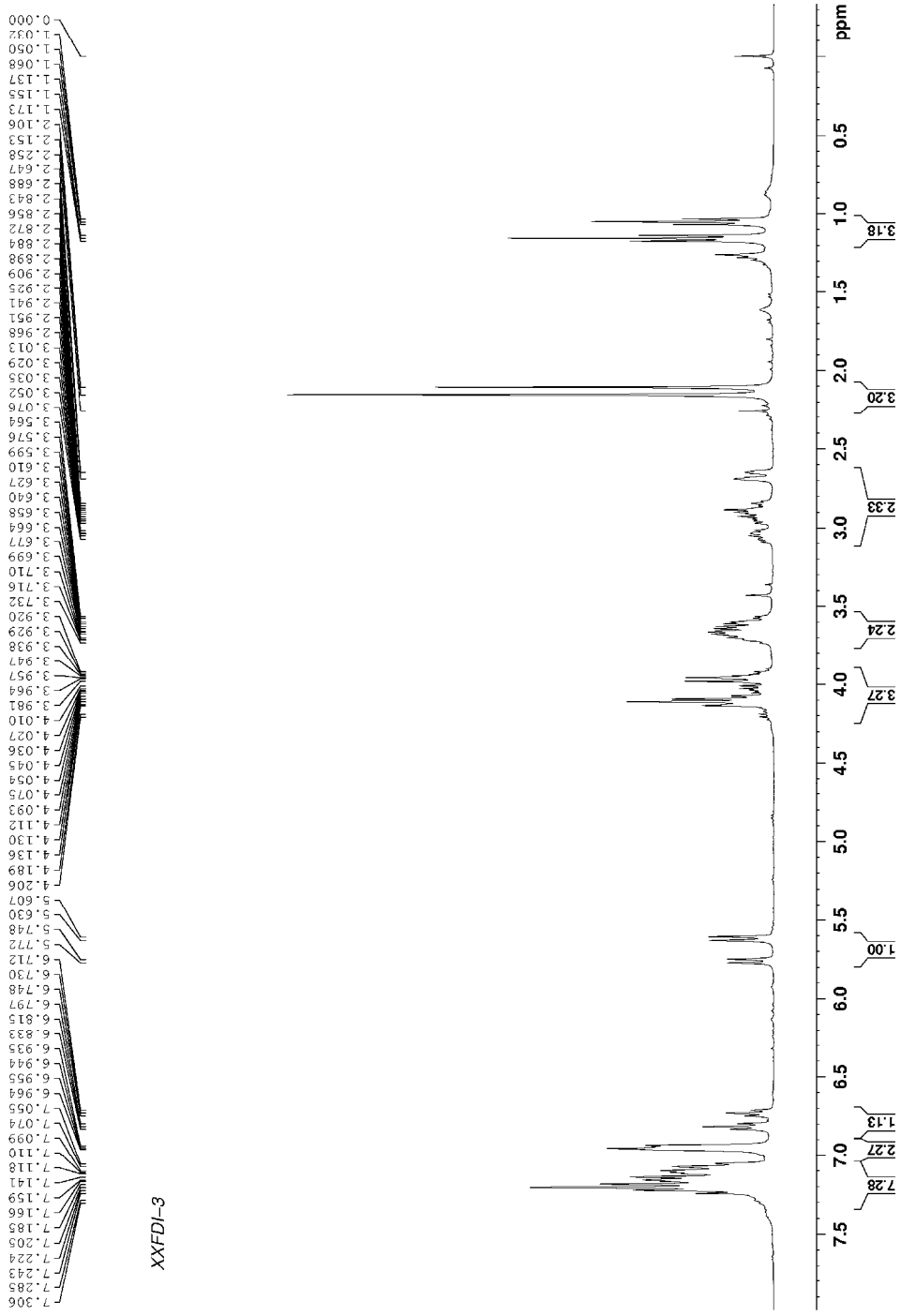
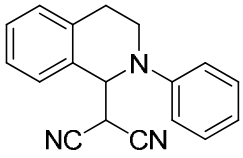
1.12
2.19
4.54
0.92
0.89
2.05
2.05
5.45

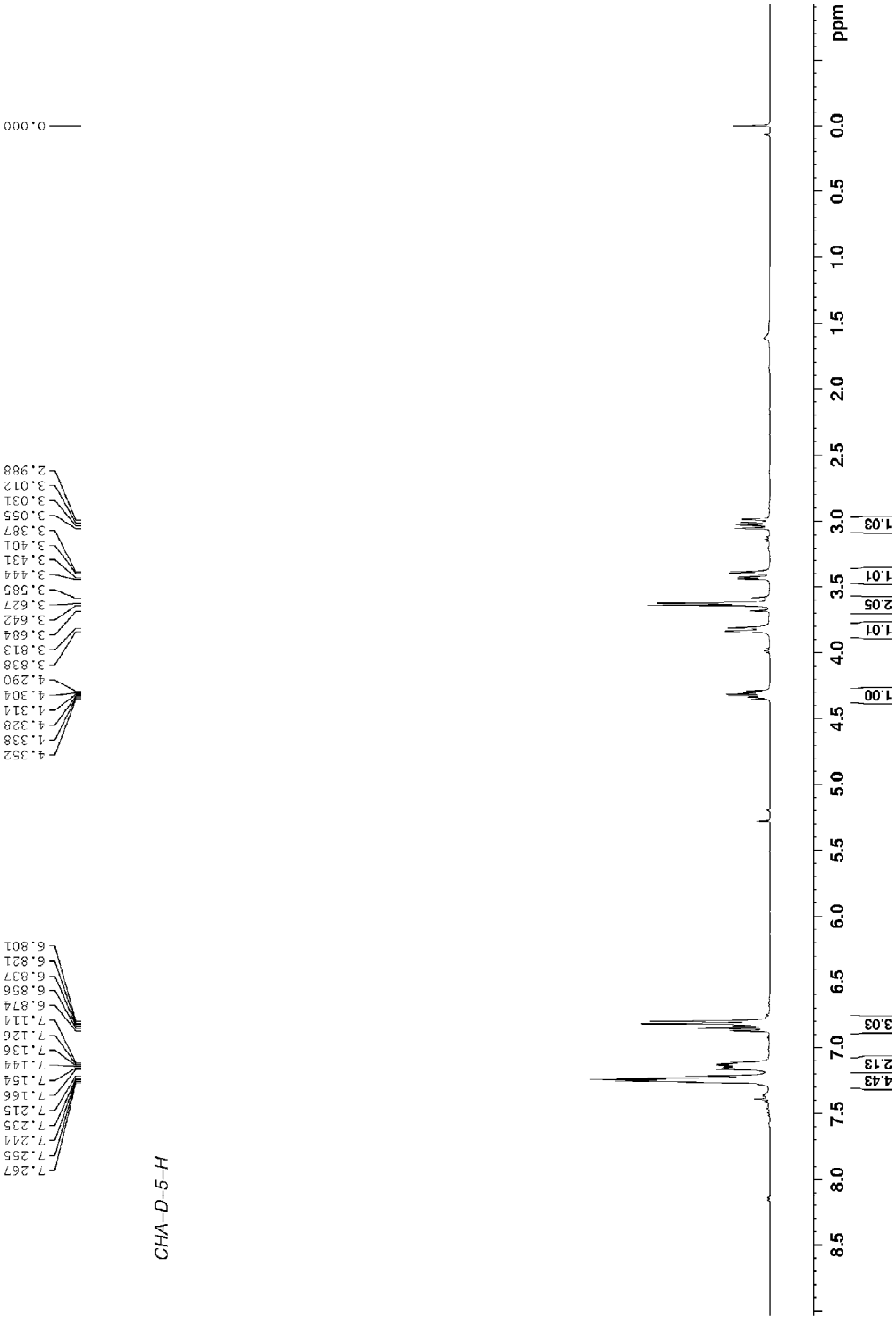


6c




N
NC
CN

6d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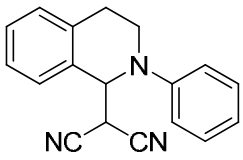
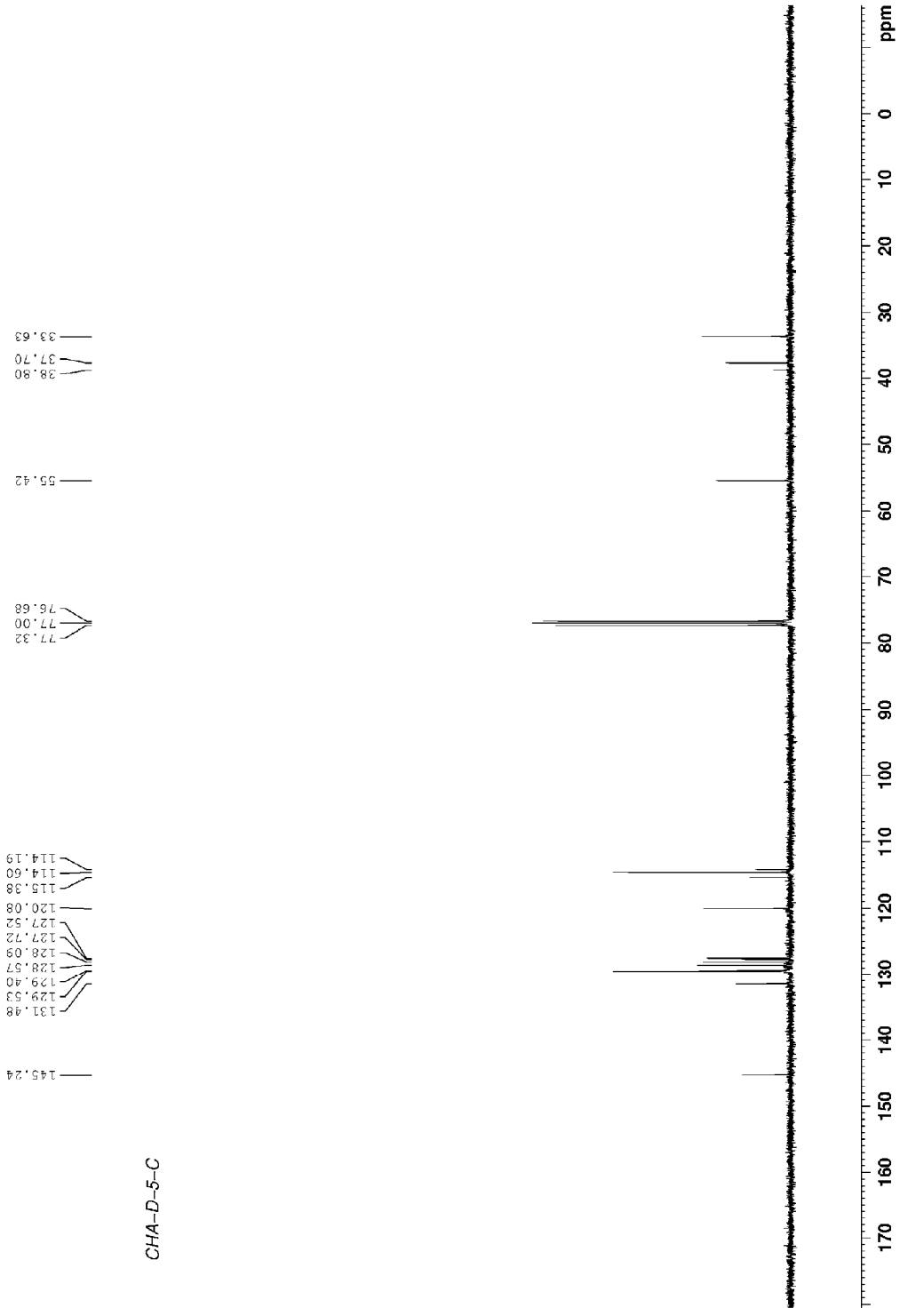
3.387
3.401
3.431
3.444
3.585
3.627
3.642
3.684
3.813
3.838
4.290
4.304
4.314
4.328
4.338
4.352
6.801
6.821
6.837
6.856
6.874
7.114
7.126
7.136
7.144
7.154
7.166
7.215
7.235
7.241
7.255
7.267
CHA-D-5-H
1.03
1.01
2.05
1.01
1.00
3.03
2.13
4.43
ppm
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5


N
NC
CN

6d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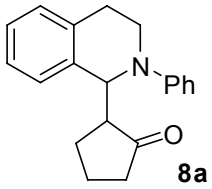
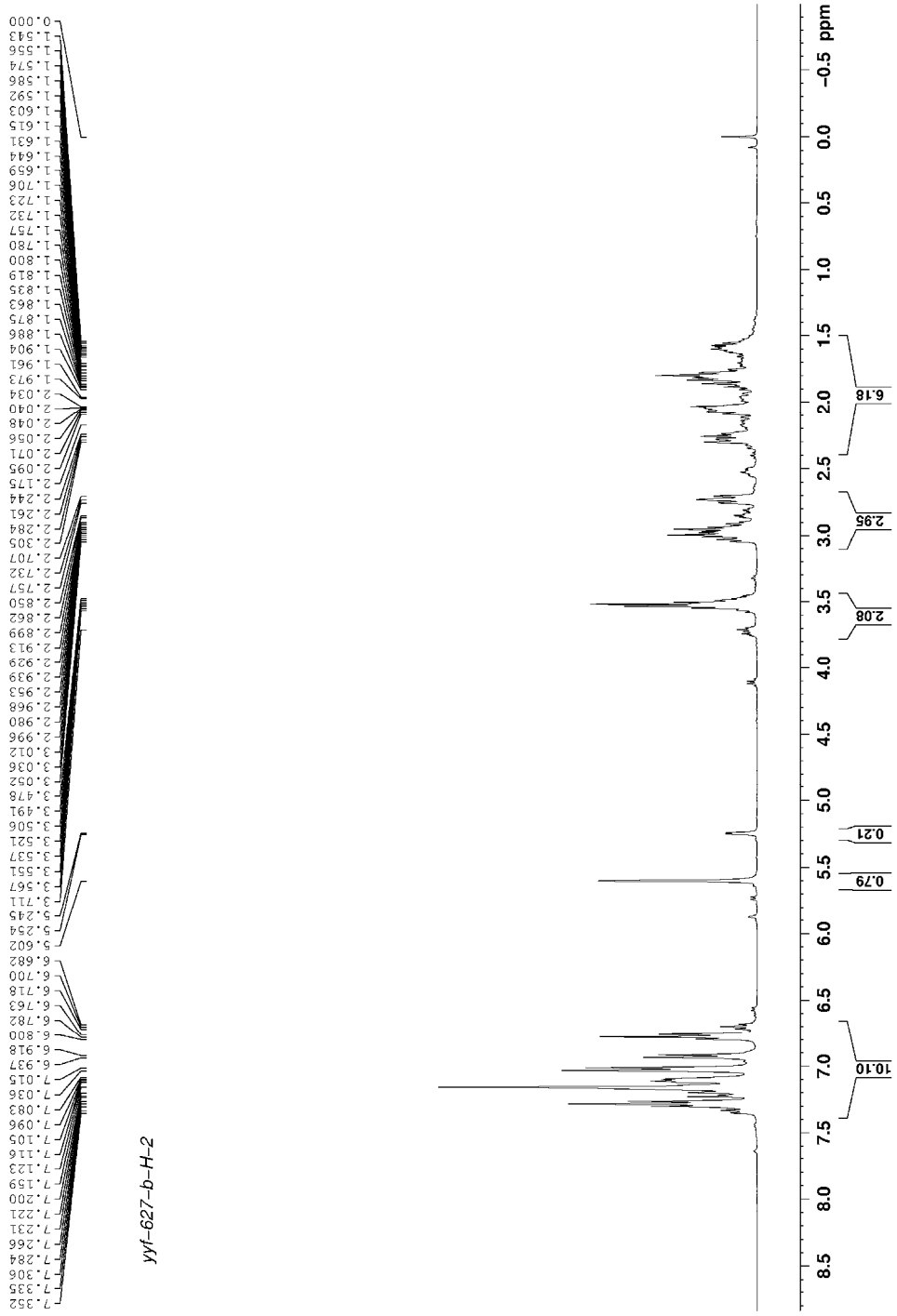
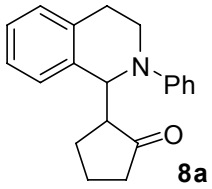
38.80
55.42
76.68
77.00
77.32
114.19
114.60
115.38
120.08
127.52
127.72
128.09
128.57
129.40
129.53
131.48
145.24
CHA-D-5-C
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170

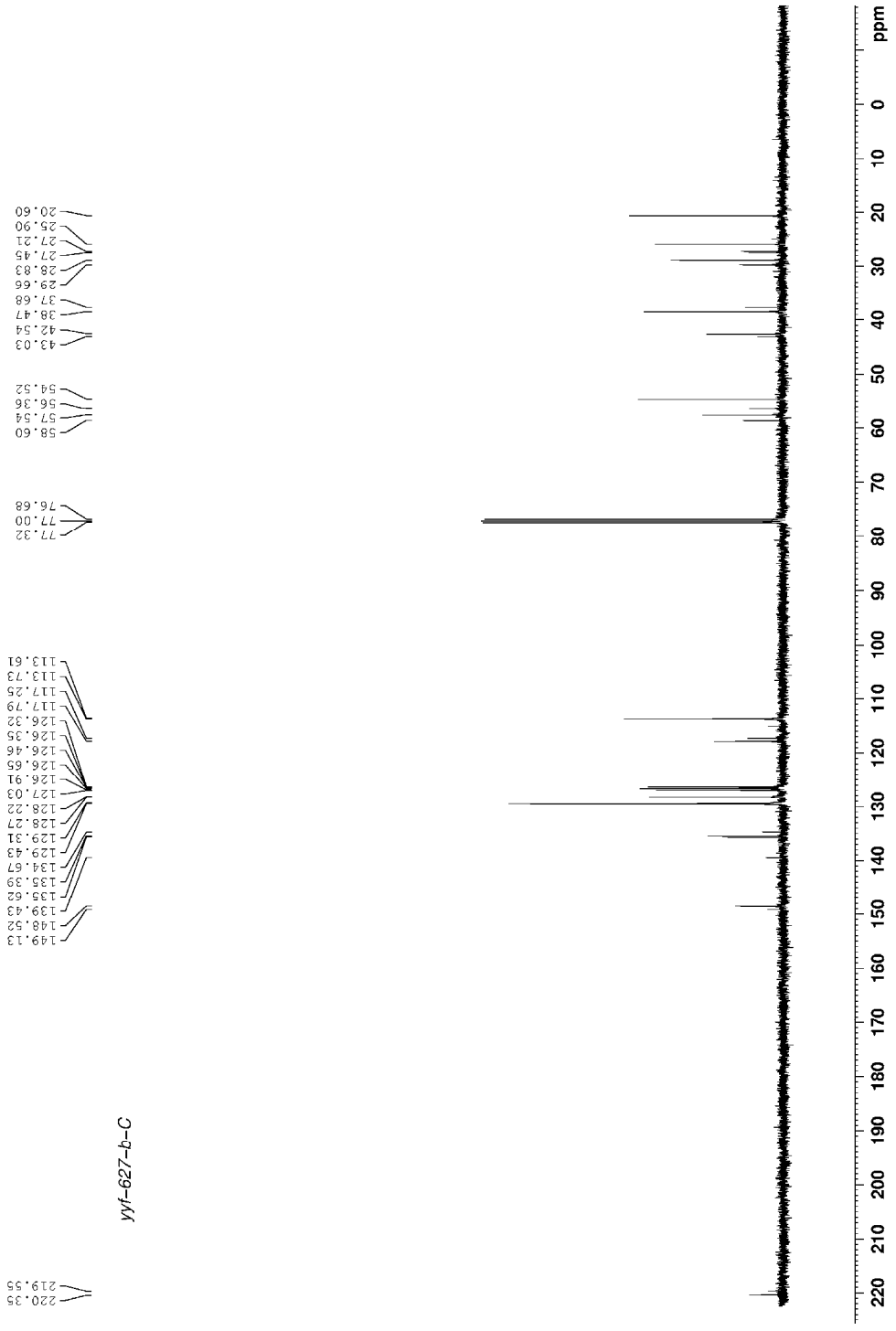


8a




N
Ph
O

8a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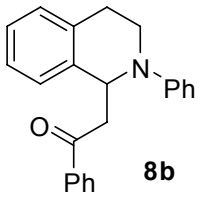
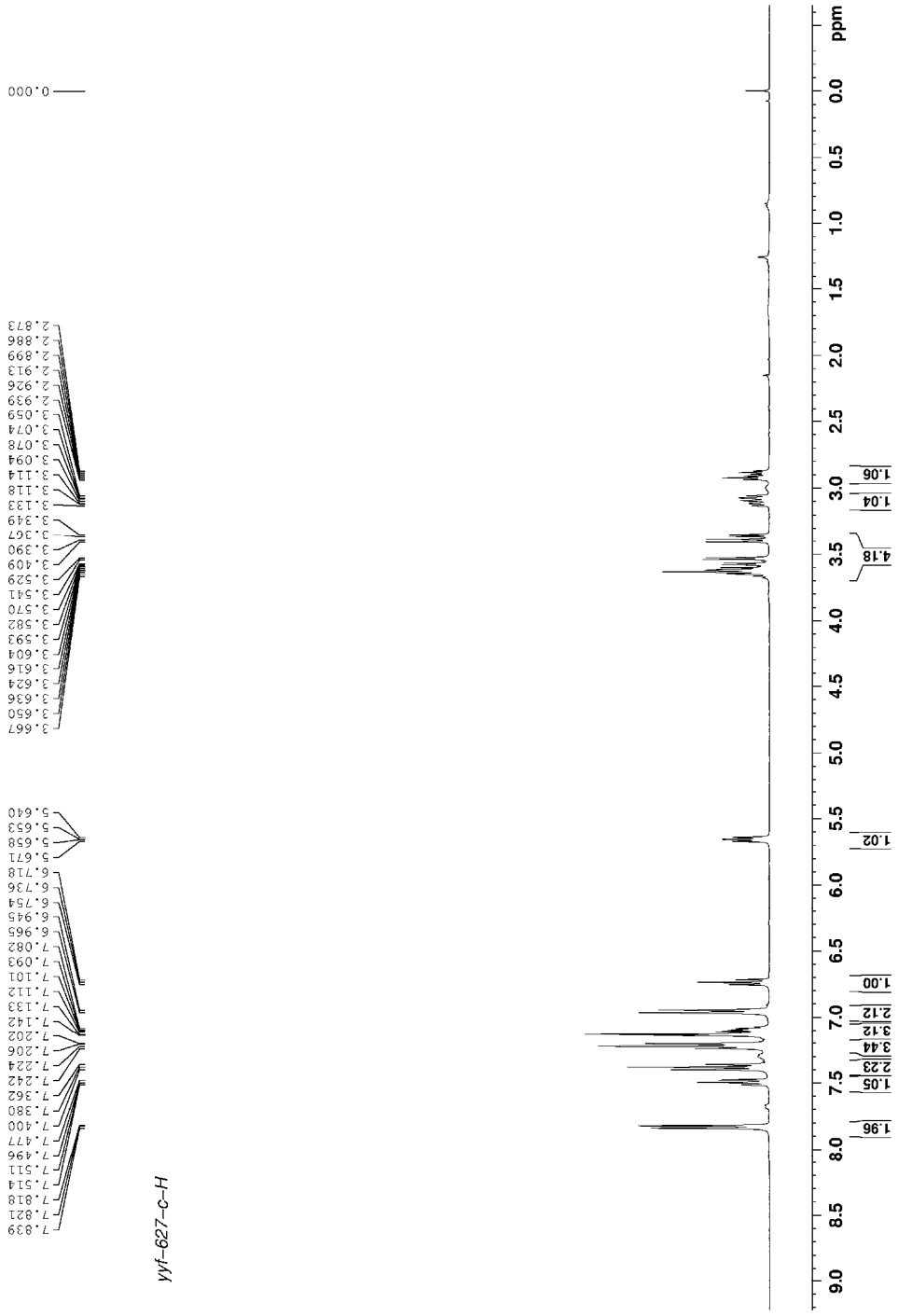
25.90
27.21
27.45
28.83
29.66
37.68
38.47
42.54
43.03
54.52
56.36
57.54
58.60
76.68
77.00
77.32
113.61
113.73
117.25
117.79
126.32
126.35
126.46
126.65
126.91
127.03
128.22
128.27
129.31
129.43
134.67
135.39
135.62
139.43
148.52
149.13
220.35
219.55
yyf-627-b-C
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220


N
Ph
O
Ph

8b


yyf-627-c-H
ppm
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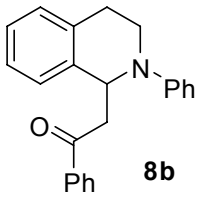
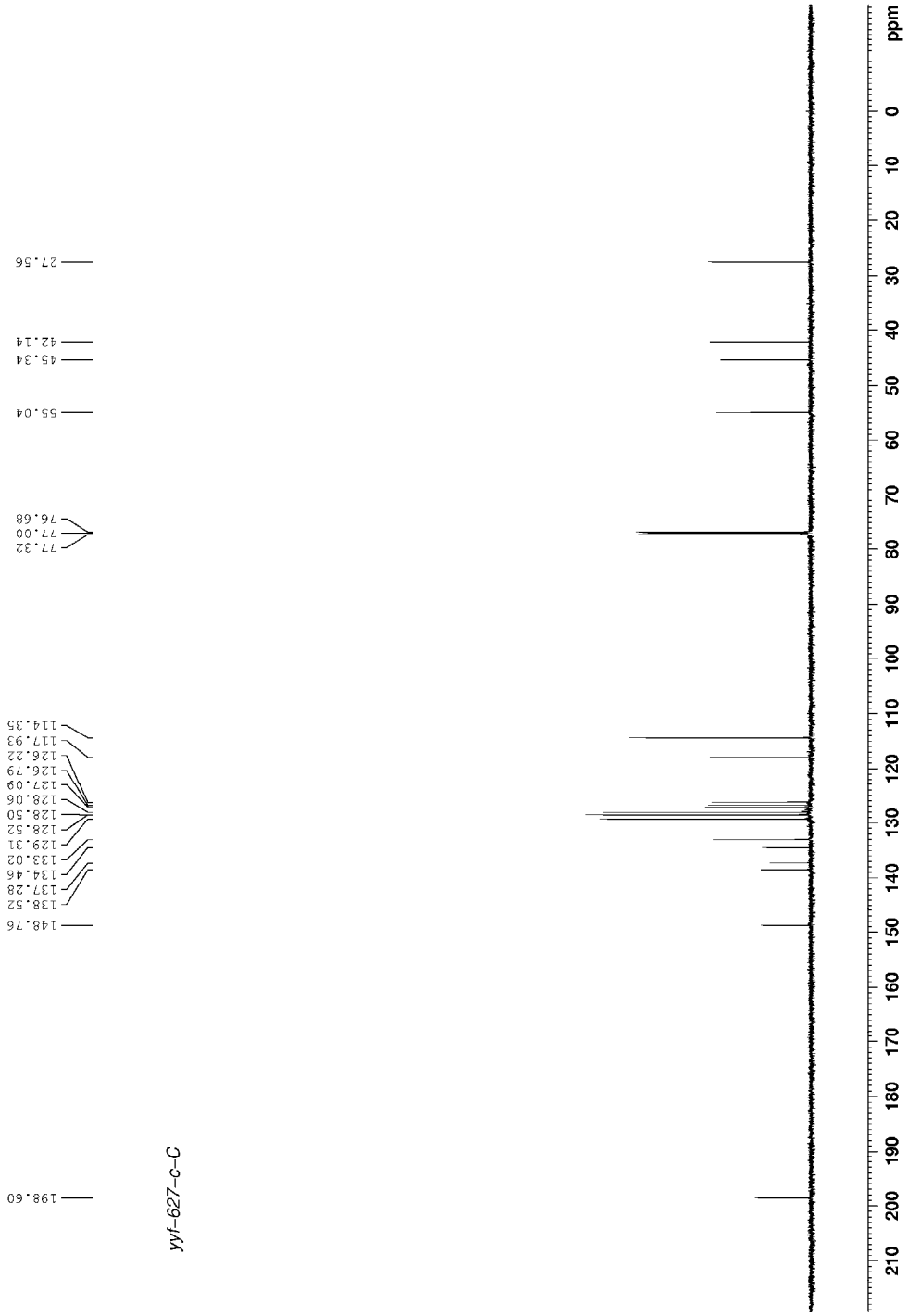
4.18
1.02
1.00
2.12
3.12
3.44
2.23
1.05
1.96


N
Ph
O
Ph

8b


27.56
42.14
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55.04
76.68
77.00
77.32
114.35
117.93
126.22
126.79
127.09
128.06
128.50
128.52
129.31
133.02
134.46
137.28
138.52
148.76
198.60
yyl-627-c-C
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210