# Formal Anti-Markovnikov Hydroamination of Terminal Olefins

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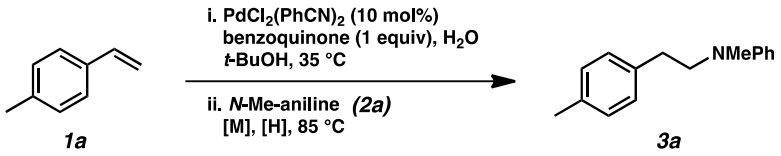
Supporting Information – Table of Contents

**Materials and Methods**. Unless stated otherwise, reactions were conducted in a Vacuum Atmospheres Glovebox under nitrogen atmosphere. All liquid olefin and amine substrates obtained from commercial sources were degassed and passed through a column of basic alumina, except for aniline, which was distilled over $CaH_2$, degassed, and then passed through a column of basic alumna before use. Solid olefin and amine substrates obtained from commercial sources were used as received. Benzoquinone was recrystallized from *i*-PrOH prior to usage. $PdCl_2(PhCN)_2$, $CuCl_2$, Shvo's catalyst (1-Hydroxytetraphenylcyclopentadienyl(tetraphenyl-2,4-cyclopentadien-1-one)-μ-hydrotetracarbonyldiruthenium(II); CAS #104439-77-2), and iridicycle·OMe (chloro(pentamethylcyclopentadienyl){5-methoxy-2-{1-[(4-methoxyphenyl)imino-κN]ethyl}phenyl-κC}iridium(III); CAS # 1258964-48-5) were obtained from Strem and were used as received. Anhydrous *i*-PrOH, 2,4-dimethyl-3-pentanol, anhydrous *t*-BuOH and 5:2 formic acid:triethylamine complex were obtained from Aldrich and were degassed prior to use. Nanopure water was degassed prior to use. Reaction temperatures were controlled using an IKAmag temperature modulator, and unless stated otherwise, reactions were performed at room temperature (rt, approximately 23 °C). Thin-layer chromatography (TLC) was conducted with EMD gel 60 F254 pre-coated plates (0.25 mm) and visualized using a combination of UV and potassium permanganate staining. EMD silica gel 60 (particle size 0.040–0.063 mm) was used for flash column chromatography. $^1$H NMR spectra were recorded on Varian spectrometers (at 300 MHz or 500 MHz) and are reported relative to deuterated solvent signals. Data for $^1$H NMR spectra are reported as follows: chemical shift (ppm), multiplicity, coupling constant (Hz) and integration. $^{13}$C NMR spectra were recorded on Varian Spectrometers (at 125 MHz). Data for $^{13}$C NMR spectra are reported in terms of chemical shift, and when necessary, multiplicity, and coupling constant (Hz). High-resolution mass spectra were provided by the California Institute of Technology Mass Spectrometry Facility using a JEOL JMS-600H High Resolution Mass Spectrometer.

## Experimental Procedures.

### A. Optimization of Hydroamination Methodology

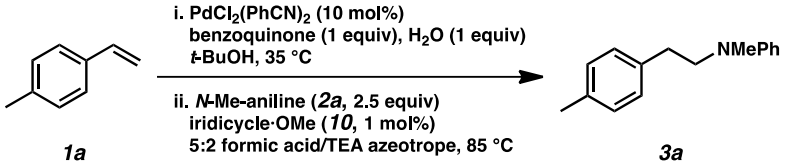



**Representative Procedure:** An 8 mL vial was charged with benzoquinone (32.4 mg, 0.300 mmol, 1 equiv), $PdCl_2(PhCN)_2$ (11.5 mg, 0.0300 mmol, 10 mol%), and any appropriate additives followed by *t*-BuOH (4 mL), the corresponding quantity of $H_2O$, and *N*-Me-styrene (***1a,*** 39.6 µL, 0.300 mol, 1 equiv). The vial was sealed with a silicone/PTFE-lined cap and the mixture was allowed to stir in the glovebox at 35 °C for 4 h. Next, a solution of the appropriate transfer hydrogenation catalyst in the corresponding quantity, any appropriate additives, and *N*-methylaniline (**2a**) in the corresponding quantity in *t*-BuOH (0.5 mL) and the appropriate hydride source (0.5 mL) was added via syringe. The reaction was heated to 85 °C, stirred for 3.5 h, cooled to 25 °C, diluted with $H_2O$ (7 mL), then basified with 15% aqueous NaOH solution. The layers were separated, and the aqueous layer was extracted with EtOAc (2 × 7 mL). The combined organic layers were washed brine (1 x 7 mL), dried over $MgSO_4$, then concentrated to dryness *in vacuo*. Yields were determined by $^1$H NMR analysis using 1,4-dioxane as an external standard. Spectral data of **3a** match those reported below (S4–S5).

## B. Hydroamination of Various Styrenes with *N*-Methylaniline

**Representative Procedure:** A 20 mL vial was charged with benzoquinone (64.9 mg, 0.600 mmol, 1 equiv), $PdCl_2(PhCN)_2$ (23.0 mg, 0.0600 mmol, 10 mol%), followed by *t*-BuOH (8 mL), $H_2O$ (10.8 µL, 0.600 mmol, 1 equiv) and the appropriate styrene (0.600 mmol, 1 equiv). The vial was sealed with a silicone/PTFE-lined cap and the mixture was allowed to stir in the glovebox at 35 °C for the corresponding oxidation time.[1] Next, a solution of iridicycle·OMe **10** (3.7 mg, 6.00 µmol, 1 mol%) and *N*-methylaniline (**2a**, 163 µL, 1.5 mmol, 2.5 equiv) in *t*-BuOH (1 mL) and 5:2 formic acid:triethylamine complex (1 mL) was added via syringe. The reaction was heated to 85 °C, stirred for the corresponding reduction time, cooled to 25 °C, diluted with $H_2O$ (15 mL), then basified with 15% aqueous NaOH solution. The layers were separated, and the aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic layers were washed brine (1 x 15 mL), dried over $MgSO_4$, then concentrated to dryness *in vacuo*. Purification by flash chromatography provided the hydroamination adduct.

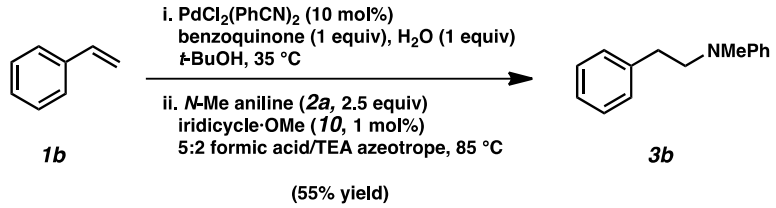
*Any modifications of the conditions shown in this representative procedure are specified in the following schemes, which depict all Table 2 hydroamination reactions.*



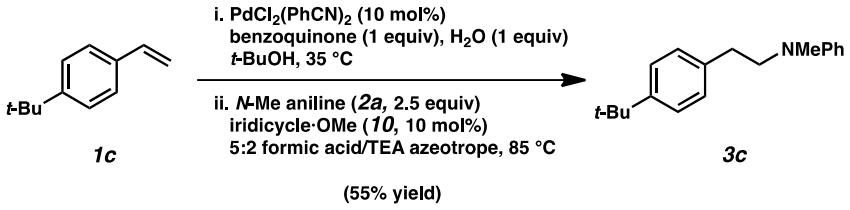

***N*-Methyl-*N*-(4-methylphenethyl)aniline (3a).** The representative procedure was used, with an oxidation time of 3 h and a reduction time of 16 h. Purification by flash chromatography (2:1 Hexanes:Dichloromethane) afforded hydroamination adduct **3a** (77.4 mg, 61% yield). $^1$H NMR (300 MHz, $CDCl_3$): δ 7.32–7.26 (m, 2H), 7.16–7.14 (m, 4H), 6.80 (m, 3H), 3.57 (t, *J* = 6.0, 2H),

[1] The oxidation time is dependent on the electronics of styrene and the condition of the Pd. Prolonged oxidation times allow for decomposition of the aldehyde intermediate and ultimately erosion of the hydroamination product. Prolonged reduction times did not negatively affect yields.

2.93 (s, 3H), 2.84 (t, *J* = 6.0, 2H), 2.36 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): 148.9, 136.8, 135.8, 129.4, 129.3, 128.8, 116.2, 112.2, 55.0, 38.6, 32.5, 21.2; HRMS-FAB+ (*m/z*) $[M]^+$ calcd for $C_{16}H_{19}N$, 225.1439; found, 225.1438.

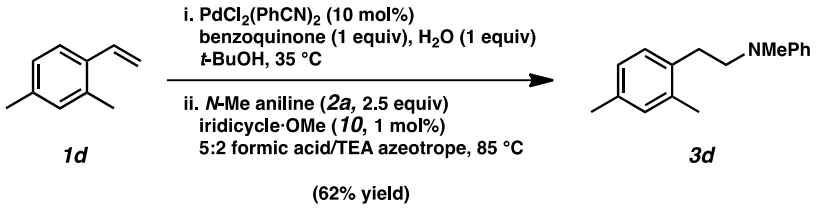



***N*-Methyl-*N*-phenethylaniline (3b).** The representative procedure was used, with an oxidation time of 4 h, and a reduction time of 13.5 h. Purification by flash chromatography (4:1 Hexanes:Dichloromethane) afforded hydroamination adduct **3b** (35.0 mg, 55% yield). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.36–7.24 (m, 7H), 6.79–6.74 (m, 3H), 3.60 (t, *J* = 7.5, 2H), 2.93 (s, 3H), 2.89 (t, *J* = 7.5, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 148.9, 139.9, 129.4, 128.9, 128.7, 126.3, 116.3, 112.3 54.9, 38.6, 33.0; HRMS-FAB+ (*m/z*) $[M + H]^+$ calcd for $C_{15}H_{18}N$, 212.1439; found, 212.1439.

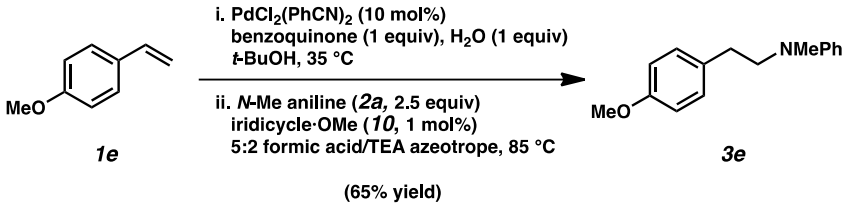



***N*-(4-(tertbutyl)phenethyl)-*N*-methylaniline (3c).** The representative procedure was used, with 10 mol% iridicycle·OMe **10**, an oxidation time of 5.5 h and a reduction time of 15 h. Purification by flash chromatography (6:1 Hexanes:Dichloromethane) afforded hydroamination adduct **3c** (88.6 mg, 55% yield). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.5, 2H), 7.29–7.25 (m, 2H), 7.16 (d, *J* = 8.0, 2H), 6.78–6.75 (m, 2H), 6.72 (tt, *J* = 7.5, 1.0, 1H), 3.57 (t, *J* = 8.0, 2H), 2.94 (s, 3H), 2.84 (t, *J* = 8.0, 2H) 1.34 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 149.2, 149.0, 136.8,

129.4, 128.6, 125.5, 116.2, 112.3, 54.8, 38.5, 34.6, 32.3, 31.5; HRMS-ES+ (*m/z*) $[M]^+$ calcd for $C_{19}H_{25}N$, 267.1987; found, 267.1985.

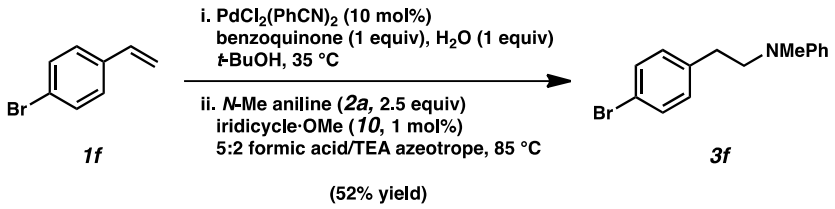



***N*-(2,4-Dimethylphenethyl)-*N*-methylaniline (3d).** The representative procedure was used, with an oxidation time of 4 h and a reduction time of 15 h. Purification by flash chromatography (4:1 Hexanes:Dichloromethane) afforded hydroamination adduct **3d** (83.4 mg, 62% yield). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.33–7.30 (m, 2H), 7.10 (d, *J* = 8.0, 1H), 7.05–7.01 (m, 2H), 6.83–6.81 (m, 2H), 6.77 (tt, *J* = 7.5, 1.0, 1H), 3.56 (t, *J* = 8.0, 2H), 2.97 (s, 3H), 2.88 (t, *J* = 8.0, 2H), 2.38 (s, 3H), 2.36 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 149.0, 136.0, 135.9, 134.9, 131.3, 129.5, 129.4, 126.9, 116.2, 112.2, 53.7, 38.4, 29.8, 21.1, 19.5; HRMS-FAB+ (*m/z*) $[(M + H)–H_2]^+$ calcd for $C_{17}H_{20}N$, 238.1596; found, 238.1598.

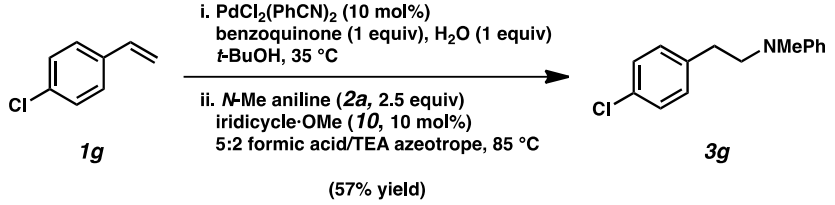



***N*-(4-Methoxyphenethyl)-*N*-methylaniline (3e).** The representative procedure was used, with an oxidation time of 5 h and a reduction time of 17 h. Purification by flash chromatography (20:1:1 Hexanes:Dichloromethane:Diethyl Ether) afforded hydroamination adduct **3e** (94.8 mg, 65% yield). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.29–7.26 (m, 2H), 7.15 (dt, *J* = 9.0, 0.5, 2H), 6.89–6.86 (m, 2H), 6.76 (d, *J* = 8.0, 2H), 6.73 (t, *J* = 7.0, 1H), 3.82 (s, 3H), 3.56 (t, *J* = 7.5, 2H), 2.91 (s, 3H), 2.82 (t, *J* = 7.5, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 158.2, 149.0, 132.0, 129.8, 129.4,

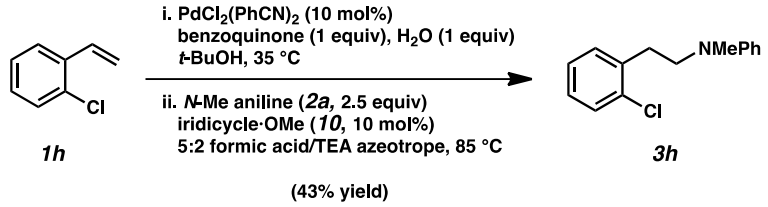
116.2, 114.1, 112.2, 55.4, 55.0, 38.6, 32.1; HRMS-FAB+ (*m/z*) $[(M + H)–H_2]^+$ calcd for $C_{16}H_{18}NO$, 240.1388; found, 240.1393.



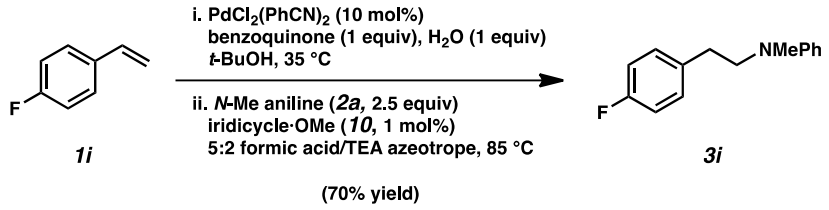

***N*-(4-Bromophenethyl)-*N*-methylaniline (3f).** The representative procedure was used, with an oxidation time of 2 h and a reduction time of 18 h. Purification by flash chromatography (4:1 Hexanes:Dichloromethane) afforded hydroamination adduct **3f** (90.0 mg, 52% yield). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.36–7.24 (m, 6H), 6.79–6.77 (m, 2H), 6.75 (tt, *J* = 7.0, 1.0, 1H), 3.61 (t, *J* = 8.0, 2H), 2.93 (s, 3H), 2.89 (t, *J* = 7.5, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 148.9, 139.9, 129.4, 128.9, 128.6, 126.3, 116.3, 112.3, 54.9, 38.6, 33.0; HRMS-ES+ (*m/z*) $[M + H]^+$ calcd for $C_{15}H_{17}BrN$, 290.0544; found, 290.0543.



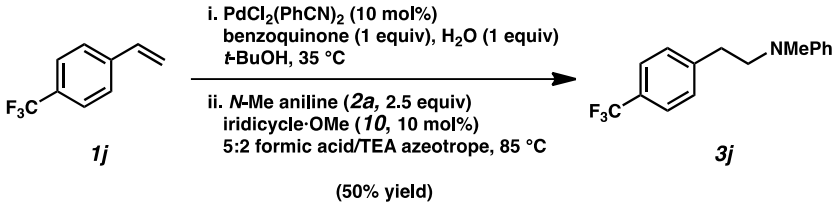

***N*-(4-Chlorophenethyl)-*N*-methylaniline (3g).** The representative procedure was used, with 10 mol% iridicycle·OMe **10**, an oxidation time of 1 h and a reduction time of 4.5 h. Purification by flash chromatography (4:1 Hexanes:Dichloromethane) afforded hydroamination adduct **3g** (83.8 mg, 57% yield). $^1$H NMR (300 MHz, $CDCl_3$): δ 7.30–7.24 (m, 4H), 7.14 (d, *J* = 8.7, 2H), 6.75–6.72 (m, 3H), 3.56 (t, *J* = 7.2, 2H), 2.88 (s, 3H), 2.84 (t, *J* = 7.2, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 148.8, 138.4, 132.1, 130.3, 129.4, 128.8, 116.5, 112.3, 54.8, 38.7, 32.5; HRMS-EI+ (*m/z*) $[M]^{+\cdot}$ calcd for $C_{15}H_{16}ClN$, 245.0971; found, 245.0973.



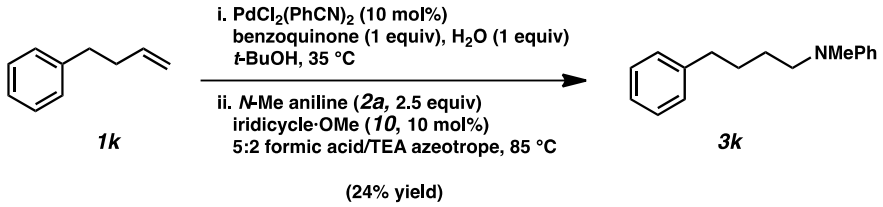

***N*-(2-Chlorophenethyl)-*N*-methylaniline (3h).** The representative procedure was used, with 10 mol% iridicycle·OMe **10**, an oxidation time of 1 h and a reduction time of 4.5 h. Purification by flash chromatography (4:1 Hexanes:Dichloromethane) afforded hydroamination adduct **3h** (63.9 mg, 43% yield). $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.34–7.22 (m, 6H), 6.76 (d, $J$ = 8.0, 2H), 6.73 (t, $J$ = 7.0, 1H), 3.59 (t, $J$ = 8.0, 2H), 2.91 (s, 3H), 2.87 (t, $J$ = 7.5, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$, 11/13 C): δ 148.9, 139.9, 129.4, 128.9, 128.7, 126.3, 116.3, 112.3, 54.9, 38.6, 33.0; HRMS-EI+ (*m/z*) $[M]^{+\cdot}$ calcd for $C_{15}H_{16}ClN$, 245.0971; found, 245.0968.




***N*-(4-Fluorophenethyl)-*N*-methylaniline (3i).** The representative procedure was used, with an oxidation time of 1 h and a reduction time of 16.5 h. Purification by flash chromatography (4:1 Hexanes:Dichloromethane) afforded hydroamination adduct **3i** (95.7 mg, 70% yield). $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.29–7.26 (m, 2H), 7.18–7.16 (m, 2H), 7.0 (tt, $J$ = 8.5, 2.0, 2H), 6.75–6.72 (m, 3H), 3.56 (t, $J$ = 7.5, 2H), 2.89 (s, 3H), 2.84 (t, $J$ = 8.0, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 162.6, 160.7, 148.9, 135.6 (d, $J$ = 3.3), 130.3 (d, $J$ = 7.8), 129.4, 116.4, 115.4 (d, $J$ = 21), 112.3, 54.9, 38.7, 32.3; HRMS-EI+ (*m/z*) $[M]^{+\cdot}$ calcd for $C_{15}H_{16}FN$, 229.1267; found, 229.1256.

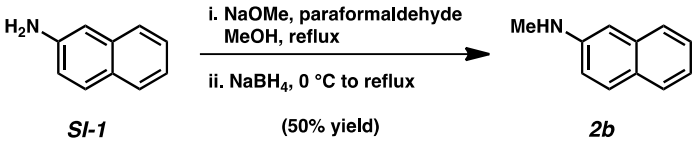



***N*-(4-(Trifluoromethyl)phenethyl)-*N*-methylaniline (3j).** The representative procedure was used, with 10 mol% iridicycle·OMe **10**, an oxidation time of 1 h and a reduction time of 6.5 h. Purification by flash chromatography (5:1 Hexanes:Dichloromethane) afforded hydroamination adduct **3j** (84.5 mg, 50% yield). $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.58 (d, $J$ = 8.0, 2H), 7.34 (d, $J$ = 7.5, 2H), 7.31–7.28 (m, 2H), 6.77–6.75 (m, 3H), 3.61 (t, $J$ = 7.5, 2H), 2.94 (t, $J$ = 8.0, 2H), 2.90 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 148.6, 144.0, 129.3, 129.2, 128.6 (q, $J$ = 32), 125.4 (q, $J$ = 3.8), 124.3 (q, $J$ = 203), 116.5, 112.2, 54.5, 38.6, 32.9; HRMS-EI+ (*m/z*) $[M]^{+\cdot}$ calcd for $C_{16}H_{16}F_3N$, 279.1235; found, 279.1240.

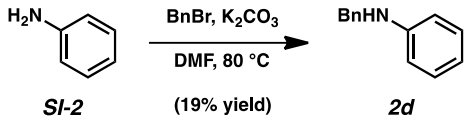



***N*-Methyl-*N*-(4-phenylbutyl)aniline (3k).** The representative procedure was used, with 10 mol% iridicycle·OMe **10**, an oxidation time of 2.5 h and a reduction time of 16 h. Purification by flash chromatography (8:2:1 Hexanes:Benzene:Dichloromethane) afforded hydroamination adduct **3k** (34.9 mg, 24% yield). Spectral data of **3k** match those reported below (S18).

## C. Synthesis of Amine Substrates



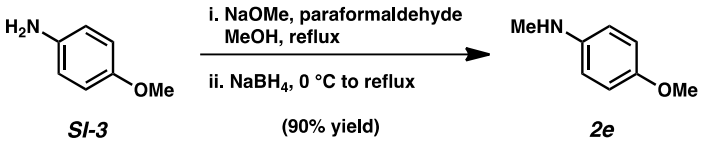

***N*-Methylnaphthalene-2-amine (2b).** Reaction was performed in a fume hood. To a solution of 2-naphthylamine (**SI-1**, 0.500 g, 3.49 mmol, 1 equiv) in MeOH (50 mL) was added NaOMe (0.943 g, 17.5 mmol, 5 equiv), and paraformaldehyde (509 mg, 16.9 mmol, 4.9 equiv). The resulting mixture was placed in a heating bath and heated to reflux for 4 h, then cooled to 0 °C. To the reaction mixture was added $NaBH_4$ (792 mg, 20.9 mmol, 6 equiv). The mixture was heated to reflux, allowed to stir for an additional 14 h, and then quenched at 0 °C with $H_2O$ (100 mL) and diluted with dichloromethane (100 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (2 × 100 mL). The combined organic extractions were washed with brine (50 mL), dried over $MgSO_4$, and then were concentrated under reduced pressure to afford the crude product. Further purification by flash chromatography (19:1 Hexanes:EtOAc) provided **2b** (0.276 g, 50% yield). Spectral data match those previously reported.[2]




***N*-Benzylaniline (2d).** Reaction was performed in a fume hood. To a solution of $K_2CO_3$ (22.4 g, 162 mmol, 5 equiv) in DMF (26 mL) was added aniline (**SI-2**, 2.95 mL, 32.4 mmol, 1 equiv) followed by BnBr (3.87 mL, 32.4 mmol, 1 equiv). The resulting mixture was placed in a heating bath and heated to reflux for 12 h, then cooled to rt and diluted with $H_2O$ (150 mL) and EtOAc

[2] (*a*) Y. Zhang, Q. Tang, M. Luo, *Org. Biomol. Chem.,* 2011, **9**, 4977–4982; (*b*) W. H. Pirkle, T. C. Pochapsky, G. S. Mahler, D. E. Reno, D. M. Alessi, *J. Org. Chem.,* 1986, **51**, 4991–5000.

(150 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (2 × 150 mL). The combined organic extractions were washed with brine (150 mL), dried over $MgSO_4$, and then were concentrated under reduced pressure to afford the crude product. Further purification by flash chromatography (3:1 Hexanes:Dichloromethane) provided **2d** (1.13 g, 19% yield). Spectral data match those previously reported.[3]

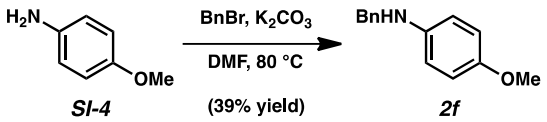



*SI-3* *2e*

***N*-Methylanisidine (2e).** Reaction was performed in a fume hood. To a solution of *p*-anisidine (**SI-3**, 1.29 g, 10.47 mmol, 1 equiv) in MeOH (150 mL) was added NaOMe (2.83 g, 52.4 mmol, 5 equiv), and paraformaldehyde (1.53 mg, 50.7 mmol, 4.9 equiv). The resulting mixture was placed in a heating bath and heated to reflux for 3.5 h, then cooled to 0 °C. To the reaction mixture was added $NaBH_4$ (2.48 mg, 62.7 mmol, 6 equiv). The mixture was heated to reflux, allowed to stir for an additional 16.5 h, and then quenched at 0 °C with $H_2O$ (200 mL) and diluted with dichloromethane (200 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (2 × 200 mL). The combined organic extractions were washed with brine (100 mL), dried over $MgSO_4$, and then were concentrated under reduced pressure to afford the crude product. Further purification by flash chromatography (9:1 Hexanes:EtOAc) provided **2e** (1.30 g, 90% yield). Spectral data match those previously reported.[4]

[3] A. Wetzel, S. Woeckel, P. Hofmann, M. Limbach, M. Schelwies, M. K. Brinks, F. Rominger, *Org. Lett.*, 2013, **15**, 266–269.

[4] I. González, J. Mosquera, C. Guerrero, R. Rodríguez, J. Cruces, *Org. Lett.*, 2009, **11**, 1677–1680.



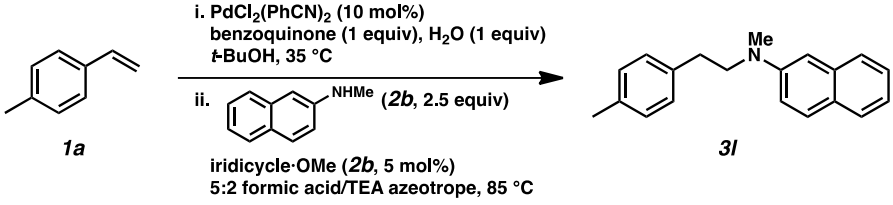

***N*-Benzylanisidine (2f).** Reaction was performed in a fume hood. To a solution of $K_2CO_3$ (22.4 g, 162 mmol, 5 equiv) and p-anisidine (**SI-4**, 4.00 g, 32.4 mmol, 1 equiv) in DMF (26 mL) was added BnBr (3.87 mL, 32.4 mmol, 1 equiv). The resulting mixture was placed in a heating bath and heated to reflux for 12 h, then cooled to rt and diluted with $H_2O$ (150 mL) and EtOAc (150 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (2 × 150 mL). The combined organic extractions were washed with brine (150 mL), dried over $MgSO_4$, and then were concentrated under reduced pressure to afford the crude product. Further purification by flash chromatography (19:1 Hexanes:EtOAc) provided **2f** (2.72 g, 39% yield). Spectral data match those previously reported.[5]

[5] B. P. Fors, D. A. Watson, M. R. Biscoe, S. L. Buchwald, *J. Am. Chem. Soc.*, 2008, **130**, 13552–13554.

## D. Hydroamination of 4-Methylstyrene with Various Amines

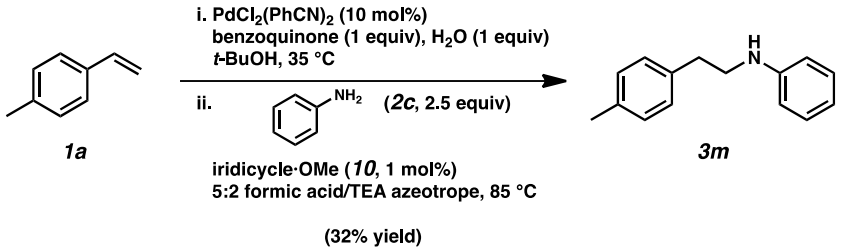
**Representative Procedure:** A 20 mL vial was charged with benzoquinone (64.9 mg, 0.600 mmol, 1 equiv), $PdCl_2(PhCN)_2$ (23.0 mg, 0.0600 mmol, 10 mol%), followed by *t*-BuOH (8 mL), $H_2O$ (10.8 µL, 0.600 mmol, 1 equiv) and 4-methylstyrene (**1a**, 79.6 µL, 0.600 mmol, 1 equiv). The vial was sealed with a silicone/PTFE-lined cap, and the mixture was allowed to stir in the glovebox at 35 °C for the corresponding oxidation time. Next, a solution iridicycle·OMe **10** (3.7 mg, 6.00 µmol, 1 mol%) and the appropriate amine (1.5 mmol, 2.5 equiv) in *t*-BuOH (1 mL) and 5:2 formic acid:triethylamine complex (1 mL) was added via syringe. The reaction was heated to 85 °C, stirred for the corresponding reduction time, cooled to 25 °C, diluted with $H_2O$ (15 mL), then basified with 15% aqueous NaOH solution. The layers were separated, and the aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic layers were washed brine (1 x 15 mL), dried over $MgSO_4$, then concentrated to dryness *in vacuo*. Purification by flash chromatography provided the hydroamination adduct.

*Any modifications of the conditions shown in this representative procedure are specified in the following schemes, which depict all Table 3 hydroamination reactions.*

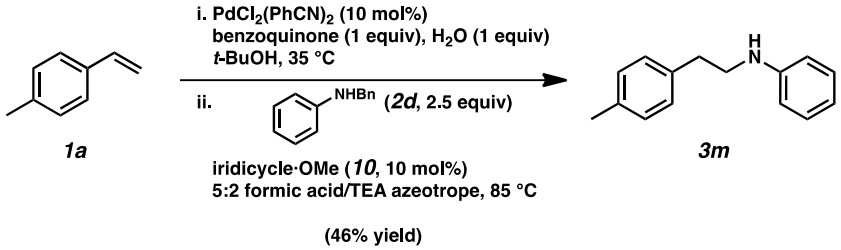



***N*-Methyl-*N*-(4-methylphenethyl)naphthalene-2-aniline (3l).** The representative procedure was used, with 5 mol% iridicycle·OMe **X**, an oxidation time of 2 h and a reduction time of 17 h. Purification by flash chromatography (8:2:1 Hexanes:Benzene:Dichloromethane) afforded hydroamination adduct **3l** (99.0 mg, 60% yield). $^1$H NMR (500 MHz, $C_6D_6$): δ 7.69 (d, *J* = 8.0, 2H), 7.64 (d, *J* = 9.0, 1H), 7.35 (t, *J* = 7.0, 1H), 7.19 (t, *J* = 7.5, 1H), 7.02 (dd, *J* = 9.0, 2.5, 1H), 7.0–6.93 (m, 5H), 3.40 (t, *J* = 7.0, 2H), 2.66 (*J* = 7.5, 2H), 2.57 (s, 3H), 2.15 (s, 3H); $^{13}$C NMR (125 MHz, $C_6D_6$): δ 146.8, 136.7, 135.7, 135.3, 129.1, 128.9, 128.7, 127.6, 127.1, 126.3, 126.2,

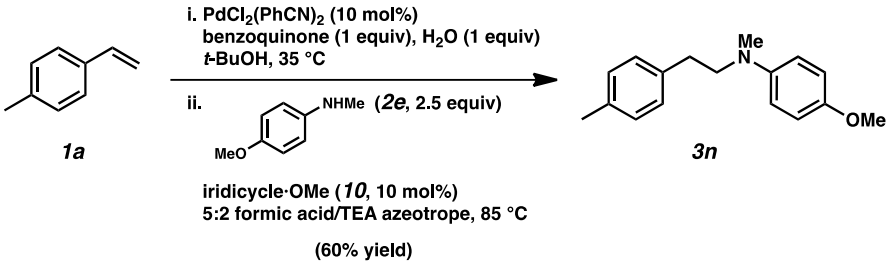
121.9, 115.9, 106.4, 54.7, 38.2, 32.7, 20.7; HRMS-FAB+ (*m/z*) $[M]^+$ calcd for $C_{20}H_{21}N$, 275.1674; found, 275.1670.



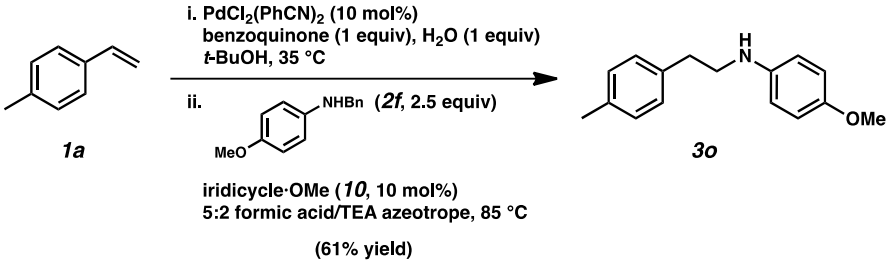

***N*-(4-Methylphenethyl)aniline 3m.** The representative procedure was used, with an oxidation time of 3 h and a reduction time of 15 h. Purification by flash chromatography (2:1 Hexanes:Dichloromethane) afforded hydroamination adduct **3m** (41.0 mg, 32% yield). $^1$H NMR (500 MHz, $CDCl_3$, 16/17 H): δ 7.21–7.12 (m, 6H), 6.72 (tt, *J* = 7.5, 1.0, 1H), 6.64–6.61 (m, 2H), 3.39 (t, *J* = 7.0, 2H), 2.90 (t, *J* = 7.0, 2H), 2.35 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 148.2, 136.3, 136.1, 129.42, 129.40, 128.8, 117.6, 113.1, 45.3, 35.2, 21.2; HRMS-EI+ (*m/z*) $[M]^{+\cdot}$ calcd for $C_{15}H_{17}N$, 211.1361; found, 211.1356.




***N*-(4-Methylphenethyl)aniline 3m.** The representative procedure was used, with 10 mol% iridicycle·OMe **10**, an oxidation time of 2 h and a reduction time of 18 h. Purification by flash chromatography (2:1 Hexanes:Dichloromethane) afforded hydroamination adduct **3m** (58.3 mg, 46% yield). Spectral data of **3m** match those reported above.

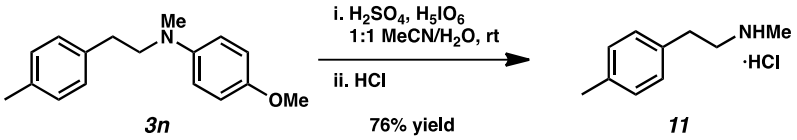



**4-Methoxy-*N*-methyl-*N*-(4-methylphenethyl)aniline 3n.** The representative procedure was used, with 10 mol% iridicycle·OMe **10**, an oxidation time of 2 h and a reduction time of 16 h. Purification by flash chromatography (40:10:1 Hexanes:Dichloromethane:Ammonia in Methanol (7M)) afforded hydroamination adduct **3n** (92.6 mg, 60% yield). $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.12–7.08 (m, 4H), 6.86 (d, $J$ = 9.0, 2H), 6.73 (d, $J$ = 8.5, 2H), 3.78 (s, 3H), 3.46 (t, $J$ = 8.0, 2H), 2.87 (s, 3H), 2.77 (t, $J$ = 8.0, 2H), 2.33 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 151.7, 144.0, 136.9, 135.7, 129.3, 128.8, 115.0, 114.5, 56.1, 55.9, 39.2, 32.3, 21.2; HRMS-FAB+ (*m/z*) $[M]^+$ calcd for $C_{17}H_{21}NO$, 255.1623; found, 255.1618.




**4-Methoxy-*N*-(4-methylphenethyl)aniline 3o.** The representative procedure was used, with 10 mol% iridicycle·OMe **10**, an oxidation time of 2 h and a reduction time of 16 h. Purification by flash chromatography (1:1:1 Hexanes:Dichloromethane:Benzene) afforded hydroamination adduct **3o** (87.9 mg, 61% yield). $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.15–7.11 (m, 4H), 6.79 (d, $J$ = 8.5, 2H), 6.60 (d, $J$ = 8.5, 2H), 3.76 (s, 3H), 3.43 (br s, 1H), 3.35 (t, $J$ = 7.0, 2H), 2.88 (t, $J$ = 7.0, 2H), 2.35 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 152.3, 142.4, 136.4, 136.0, 129.4, 128.8, 115.0, 114.5, 56.0, 46.3, 35.3, 21.2; HRMS-EI+ (*m/z*) $[M]^{+\cdot}$ calcd for $C_{16}H_{19}NO$, 241.1467; found, 241.1472.

## E. Cleavage of Removable Aryl Protecting Group




*3n* 76% yield *11*

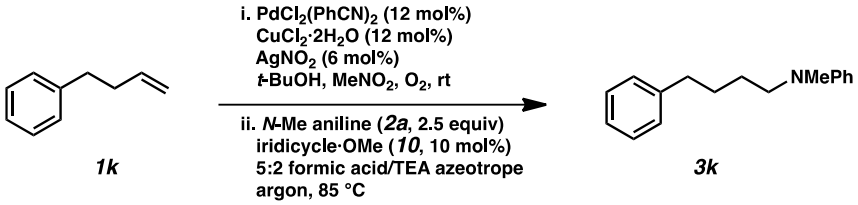
***N*-Methyl-2-(*p*-tolyl)ethanamine 11.** The PMP group was cleaved using the general procedure developed by Verkade and coworkers; reaction was performed in a fume hood.[6] To a 20 mL vial under ambient atmosphere was added sequentially **3n** (25.0 mg, 0.0979 mmol, 1 equiv), MeCN (0.9 mL), $H_2O$ (0.9 mL), $H_5IO_6$ (22.3 mg, 0.0979 mmol, 1 equiv), and 1.0 M aqueous $H_2SO_4$ (97.9 µL). The resulting mixture was allowed to stir at room temperature for 23 h, then diluted with $H_2O$ (10 mL) and washed with dichloromethane (3 × 10 mL). The aqueous layer was basified to pH = 11 with 15% aqueous NaOH, then extracted with EtOAc (3 × 10 mL). The combined organic extractions were acidified to pH = 1 with 2 M HCl in diethyl ether, then concentrated. To remove impurities from the resulting brown solid, the crude product was taken up in 4 mL DCM and 4 mL $H_2O$. The aqueous layer was separated, concentrated, taken up in DCM, and filtered through celeit. The filtrate was concentrated to provide **11** (14.4 mg, 76% yield). To obtain an analytical sample, the same experimental procedure was followed, but rather than acidifying the EtOAc combined layers, they were dried over $MgSO_4$, then concentrated to dryness *in vacuo*. Purification by flash chromatography (12:8:1 Hexanes:Dichloromethane:Ammonia in Methanol (7M)) provided the free amine. $^1$H NMR (300 MHz, $CDCl_3$): δ 7.11–7.07 (m, 4H), 2.85–2.74 (m, 4H), 2.43 (s, 3H), 2.32 (s, 3H), 1.62 (br s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 136.9, 135.8, 129.3 128.7, 53.4, 36.4, 35.8, 21.2; HRMS-EI+ (*m/z*) $[M]^{+\cdot}$ calcd for $C_{10}H_{25}N$, 149.1204; found, 149.1205.

[6] J. M. M. Verkade, L. J. C. van Hemert, P. J. L. M. Quaedflieg, P. L. Alsters, F. L. van Delft, F. P. J. T. Rutjes, *Tetrahedron Lett.*, 2006, **47**, 8109–8113.

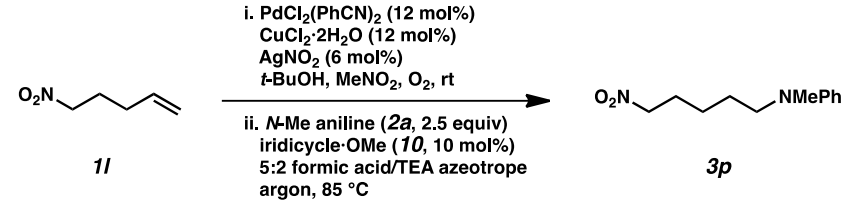
## F. Hydroamination of Aliphatic Olefins with *N*-Me Aniline

**Representative Procedure:** Hydroaminations involving aliphatic olefins were done in a fume hood. A 20 mL vial was charged with $AgNO_2$ (5.5 mg, 0.036 mmol, 6 mol%), $PdCl_2(PhCN)_2$ (27.6 mg, 0.0720 mmol, 12 mol%), and $CuCl_2 \cdot H_2O$ (12.3 mg, 0.0720 mmol, 12 mol%), the vial was sealed with a silicone/PTFE-lined cap, then sparged with $O_2$ for 45 seconds. To a second 20 mL vial was added *t*-BuOH (9 mL) and $MeNO_2$ (0.6 mL). The vial containing solvent was sparged with $O_2$ for 45 seconds, the contents were transferred to the first vial, and the appropriate aliphatic olefin (0.600 mmol, 1 equiv) was added. The resulting mixture was sparged with $O_2$ for an additional 2 minutes and the allowed to stir at rt for the corresponding oxidation time under a balloon of $O_2$. Next, the reaction vessel was sparged with argon for 45 sec, and a solution previously prepared in the glovebox of iridicycle·OMe **10** (37.0 mg, 0.0600 mmol, 10 mol%) and the appropriate amine (1.5 mmol, 2.5 equiv) in *t*-BuOH (1 mL) and 5:2 formic acid:triethylamine complex (1 mL) was added via syringe. The reaction sparged with argon for an additional 2 minutes, and then was heated to 85 °C. After stirring for the corresponding reduction time, the reaction mixture was cooled to 25 °C, diluted with $H_2O$ (15 mL), then basified with 15% aqueous NaOH solution. The layers were separated, and the aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic layers were washed brine (1 x 15 mL), dried over $MgSO_4$, then concentrated to dryness *in vacuo*. Purification by flash chromatography provided the hydroamination adduct.

*Any modifications of the conditions shown in this representative procedure are specified in the following schemes, which depict all Table 4 hydroamination reactions.*

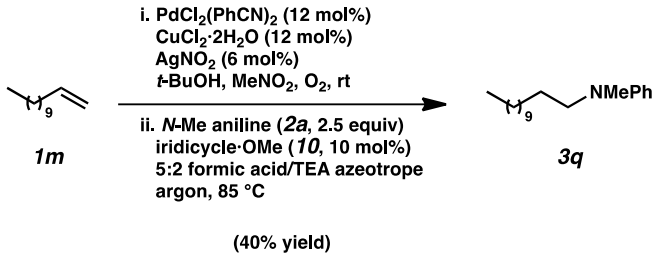



***N*-Methyl-*N*-(4-phenylbutyl)aniline 3k.** The representative procedure was used, with an oxidation time of 6 h and a reduction time of 12 h. Purification by flash chromatography (8:2:1 Hexanes:Benzene:Dichloromethane) afforded hydroamination adduct **3k** (92.5 mg, 64% yield). $^1$H NMR (500 MHz, $C_6D_6$): δ 7.26 (t, *J* = 8.0, 2H), 7.19–7.16 (m, 2H), 7.08 (t, *J* = 7.5, 1H), 7.03 (d, *J* = 7.5, 2H), 6.79 (t, *J* = 7.5, 1H), 6.65 (d, *J* = 8.0, 2H), 2.99 (t, *J* = 6.5, 2H), 2.53 (s, 3H), 2.38 (t, *J* = 7.0, 2H), 1.42–1.37 (m, 4H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 149.4, 142.2, 129.1, 128.31, 128.25, 125.7, 116.2, 112.3, 52.3, 37.7, 35.7, 28.9, 26.3; HRMS-FAB+ (*m/z*) $[M]^+$ calcd for $C_{17}H_{21}N$, 239.1674; found, 239.1666.

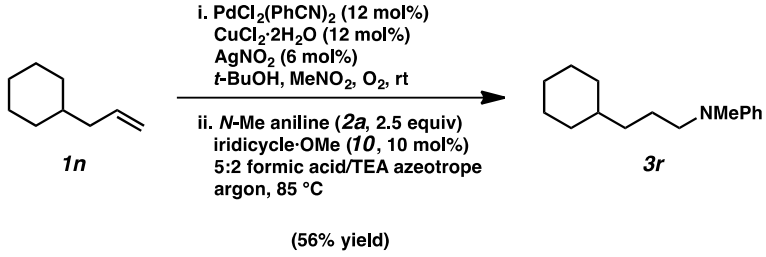



***N*-Methyl-*N*-(5-nitropenyl)anline 3p.** The representative procedure was used, with an oxidation time of 6 h and a reduction time of 17 h. Purification by flash chromatography (4:1:1 Hexanes:Benzene:Dichloromethane→20:10:20:1 Hexanes:Benzene:Dichloromethane:Triethylamine) afforded hydroamination adduct **3p** (86.8 mg, 65% yield). $^1$H NMR (300 MHz, $CDCl_6$): δ 7.25 (t, *J* = 8.1, 2H), 6.71–6.69 (m, 3H), 4.39 (t, *J* = 6.9, 2H), 3.34 (t, *J* = 7.5, 2H), 2.94 (s, 3H), 2.06 (app

. pentet, $J$ = 7.8, 2H), 1.65 (app. pentet, $J$ = 7.5, 2H), 1.49–1.38 (m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 149.3, 129.4, 116.3, 112.3, 75.7, 52.5, 38.9, 27.5, 26.3, 24.1; HRMS-FAB+ (*m/z*) $[M]^+$ calcd for $C_{12}H_{18}N_2O_2$, 222.1367; found, 222.1367.

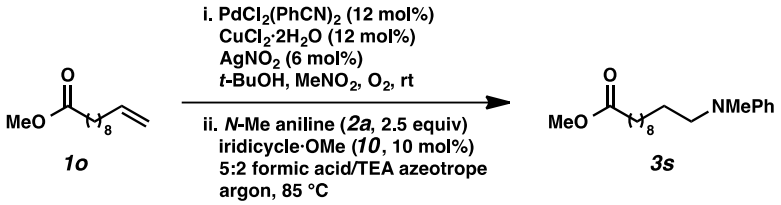



***N*-Dodecyl-*N*-methylaniline 3q.** The representative procedure was used, with an oxidation time of 6 h and a reduction time of 17 h. Purification by flash chromatography (2:2:1 Hexanes:Dichloromethane:Benzene) afforded hydroamination adduct **3q** (65.6 mg, 40% yield). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.26–7.23 (m, 2H), 6.73–6.67 (m, 3H), 3.31 (t, $J$ = 7.5, 2H), 2.94 (s, 3H), 1.58 (app. pentet, $J$ = 7.0, 2H), 1.33–1.28 (m, 19H), 0.91 (t, $J$ = 7.0, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 149.5, 129.3, 115.9, 112.2, 53.0, 38.4, 32.1, 29.83, 29.82, 29.79, 29.78, 29.7, 29.5, 27.4, 26.8, 22.9, 14.3; HRMS-FAB+ (*m/z*) $[M + H]^+$ calcd for $C_{19}H_{34}N$, 276.2691; found, 276.2681.

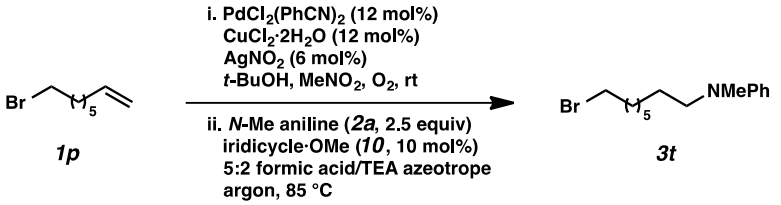



***N*-(3-Cyclohexylpropyl)-*N*-methylaniline 3r.** The representative procedure was used, with an oxidation time of 6 h and a reduction time of 18 h. Purification by flash chromatography (19:1 Hexanes:Dichloromethane) afforded hydroamination adduct **3r** (78.3 mg, 56% yield). $^1$H NMR (300 MHz, $CDCl_3$): δ 7.29–7.23 (m, 2H), 6.74–6.68 (m, 3H), 3.31 (t, $J$ = 7.5, 2H), 2.95 (s, 3H), 1.76–1.56 (m, 7H), 1.30–1.19 (m, 6H), 0.93–0.90 (m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ

149.4, 129.1, 115.8, 112.1, 53.2, 38.3, 37.7, 34.9, 33.5, 26.7, 26.4, 24.0; HRMS-FAB+ (*m/z*) $[M]^+$ calcd for $C_{16}H_{25}N$, 231.1987; found, 231.1976.

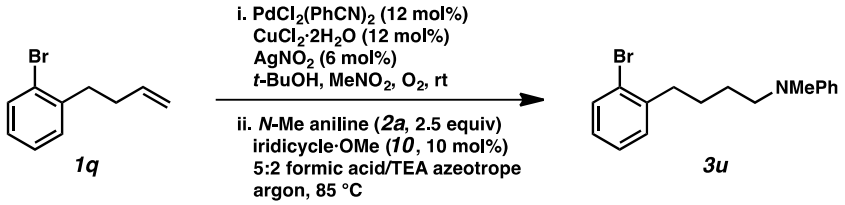



**Methyl 11-(methyl(phenyl)amino)undecanoate 3s.** The representative procedure was used, with an oxidation time of 6 h and a reduction time of 3.5 h. Purification by flash chromatography (4:1 Hexanes:Dichloromethane→60:40:3 Hexanes:Dichloromethane:Triethylamine) afforded hydroamination adduct **3s** (110.1 mg, 60% yield). $^1$H NMR (300 MHz, $CDCl_3$): δ 7.26–7.19 (m, 2H), 6.70–6.64 (m, 3H), 3.66 (s, 3H), 3.29 (t, *J* = 7.2, 2H), 2.91 (s, 3H), 2.30 (t, *J* = 7.5, 2H), 1.63–1.25 (m, 16 H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 174.4, 149.3, 129.1, 115.7, 112.0, 52.8, 51.5, 38.3, 34.1, 29.6, 29.5, 29.4, 29.2, 29.1, 27.2, 26.6, 24.9; HRMS-FAB+ (*m/z*) $[M + H]^+$ calcd for $C_{19}H_{32}NO_2$, 306.2433; found, 306.2446.



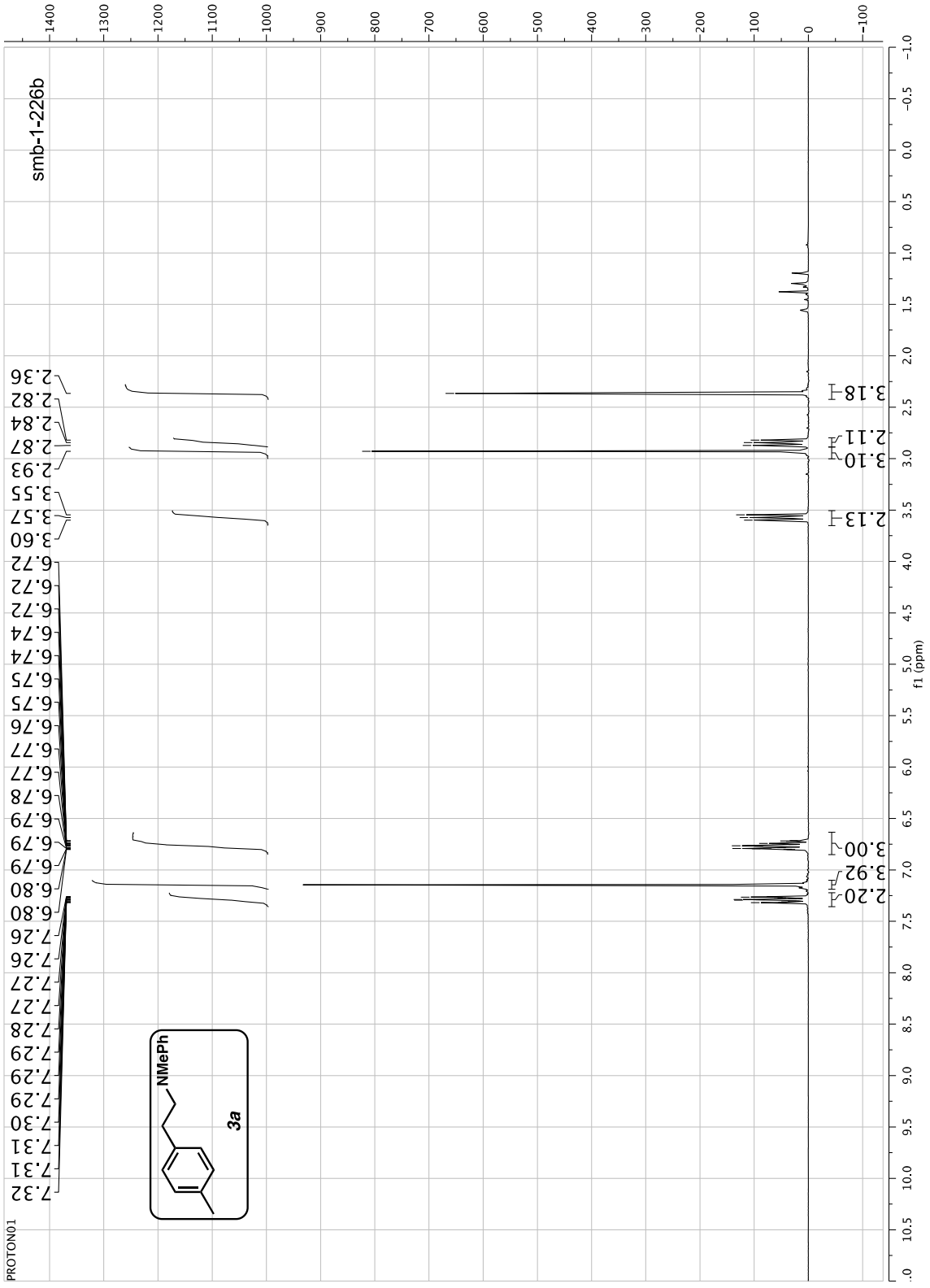

*N*-**(8-Bromooctyl)**-*N*-**methylaniline 3t.** The representative procedure was used, with an oxidation time of 6 h and a reduction time of 3.5 h. Purification by flash chromatography (45:1:1 Hexanes:Dichloromethane:Diethyl Ether) afforded hydroamination adduct **3t** (69.4 mg, 39% yield). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.27–7.22 (m, 2H), 6.72–6.67 (m, 3H), 3.42 (t, *J* = 7.0, 2H), 3.31 (t, *J* = 7.5, 2H), 2.93 (s, 3H), 1.86 (app. pentet, *J* = 7.0, 2H), 1.61–1.55 (m, 2H), 1.47–

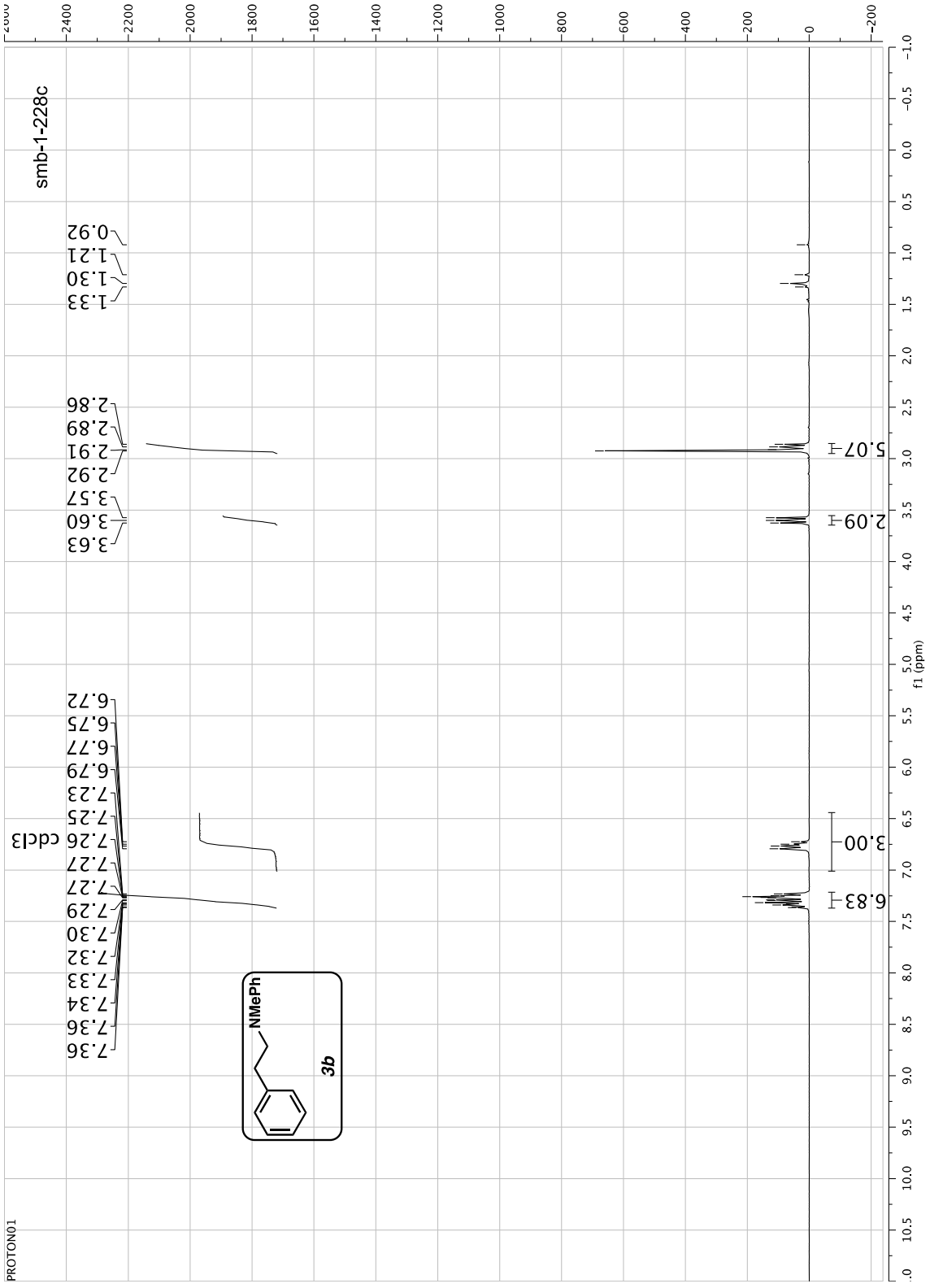
1.41 (m, 2H), 1.35–1.32 (m, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 149.3, 129.1, 115.8, 112.1, 52.8, 38.3, 34.0, 32.8, 29.4, 28.8, 28.1, 27.1, 26.6; HRMS-FAB+ (*m/z*) $[M + H]^+$ calcd for $C_{15}H_{25}NBr$, 298.1170; found, 298.1180.

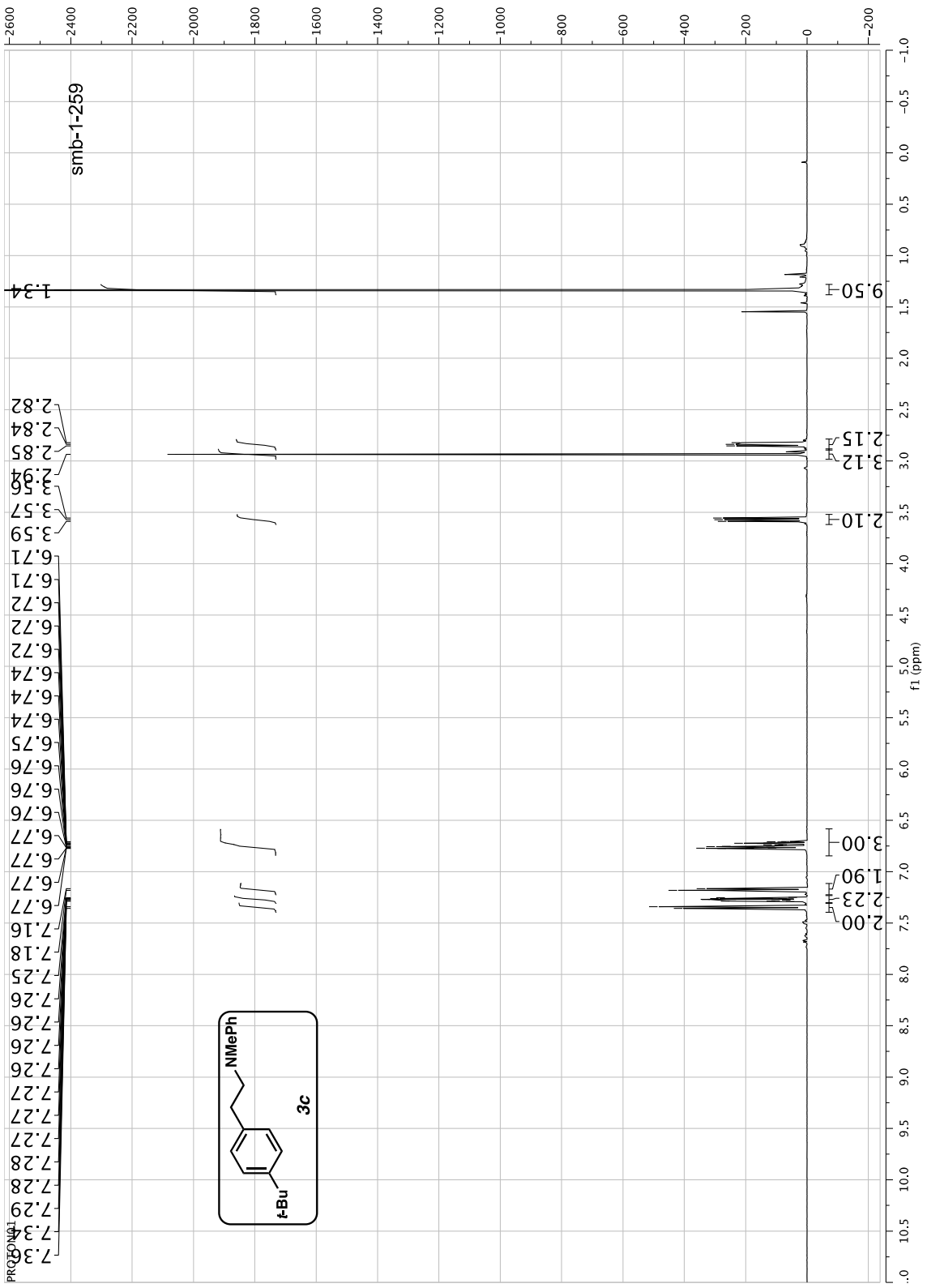


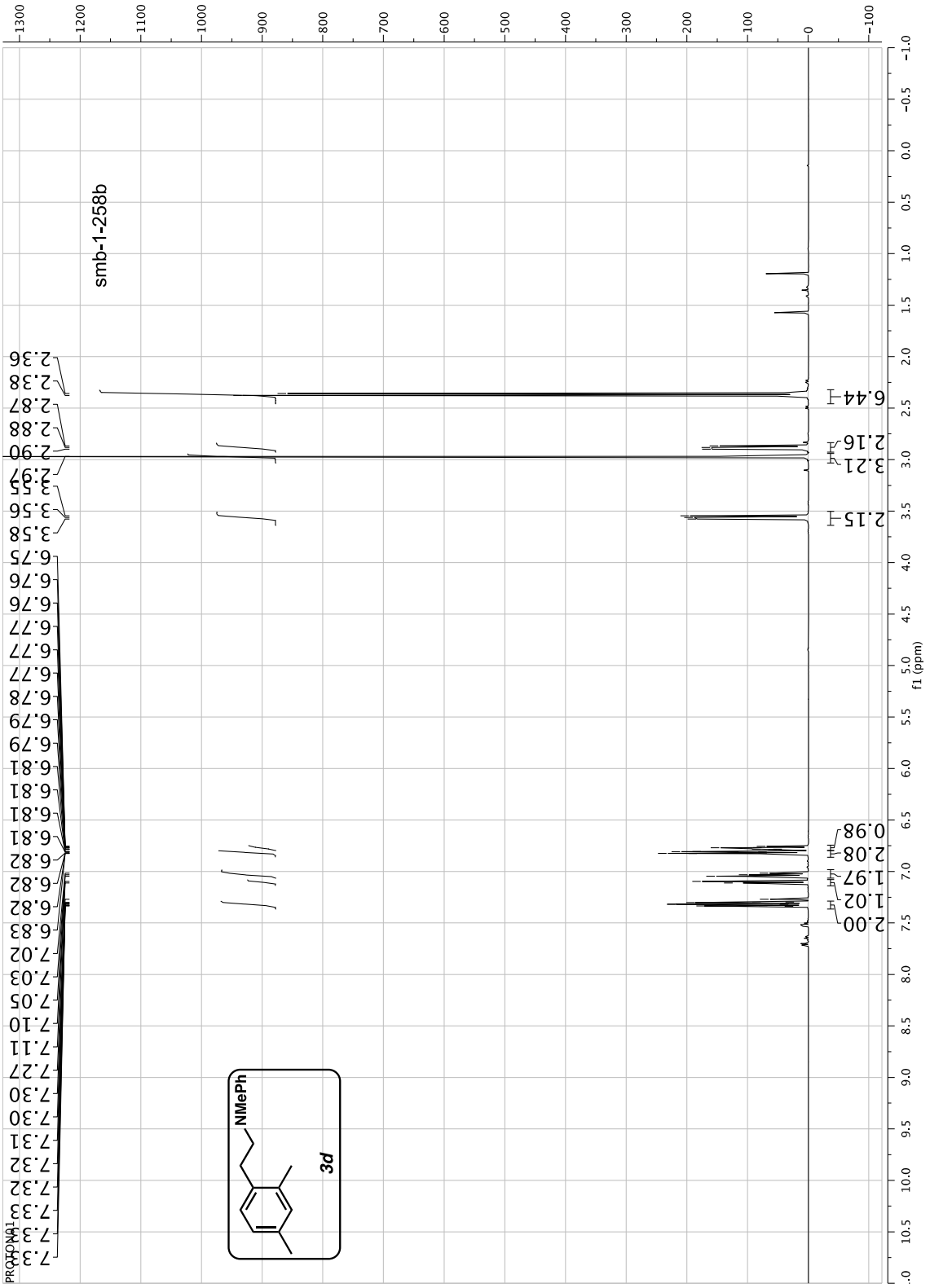

***N*-(4-(2-bromophenyl)butyl)-*N*-methylaniline.** The representative procedure was used, with an oxidation time of 6 h and a reduction time of 3.5 h. Purification by flash chromatography (9:2 Hexanes:Dichloromethane) afforded hydroamination adduct **3u** (86.9 mg, 46% yield). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.54 (dd, *J* = 8.0, 1.0, 1H), 7.27–7.21 (m, 4H), 7.06 (ddd, *J* = 8.0, 7.0, 2.1, 1H), 6.76–6.62 (m, 3H), 3.36 (t, *J* = 7.0, 2H), 2.94 (s, 3H), 2.78 (t, *J* = 7.5, 2H), 1.68–1.67 (m, 4H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 149.3, 141.6, 132.8, 130.3, 129.2, 127.5, 127.4, 124.4, 115.9, 112.2, 52.6, 38.3, 36.1, 27.5, 26.5; HRMS-EI+ (*m/z*) $[M]^{+\cdot}$ calcd for $C_{17}H_{20}NBr$, 317.0779; found, 317.0773.

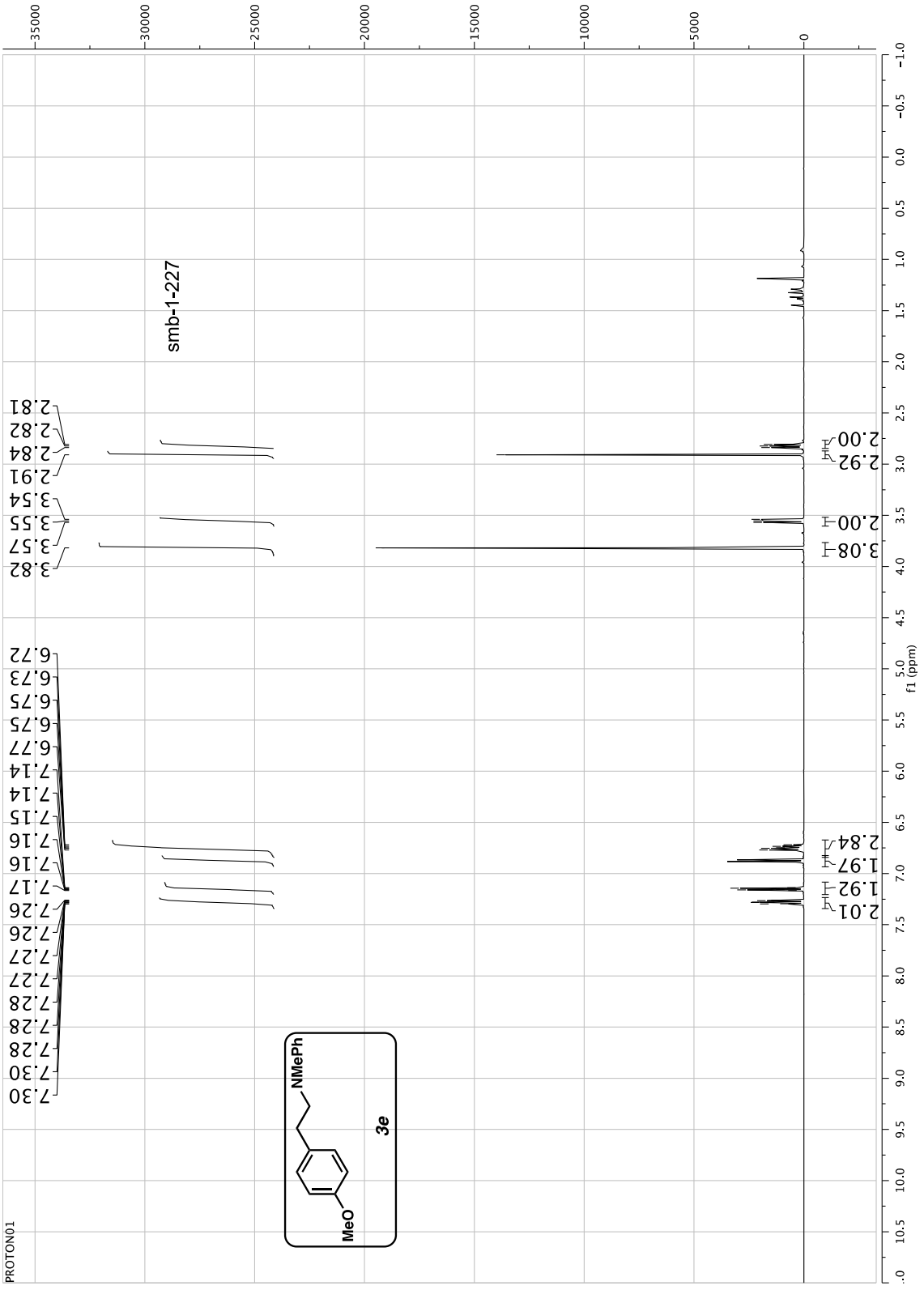
# $^{1}$H NMR Spectra:

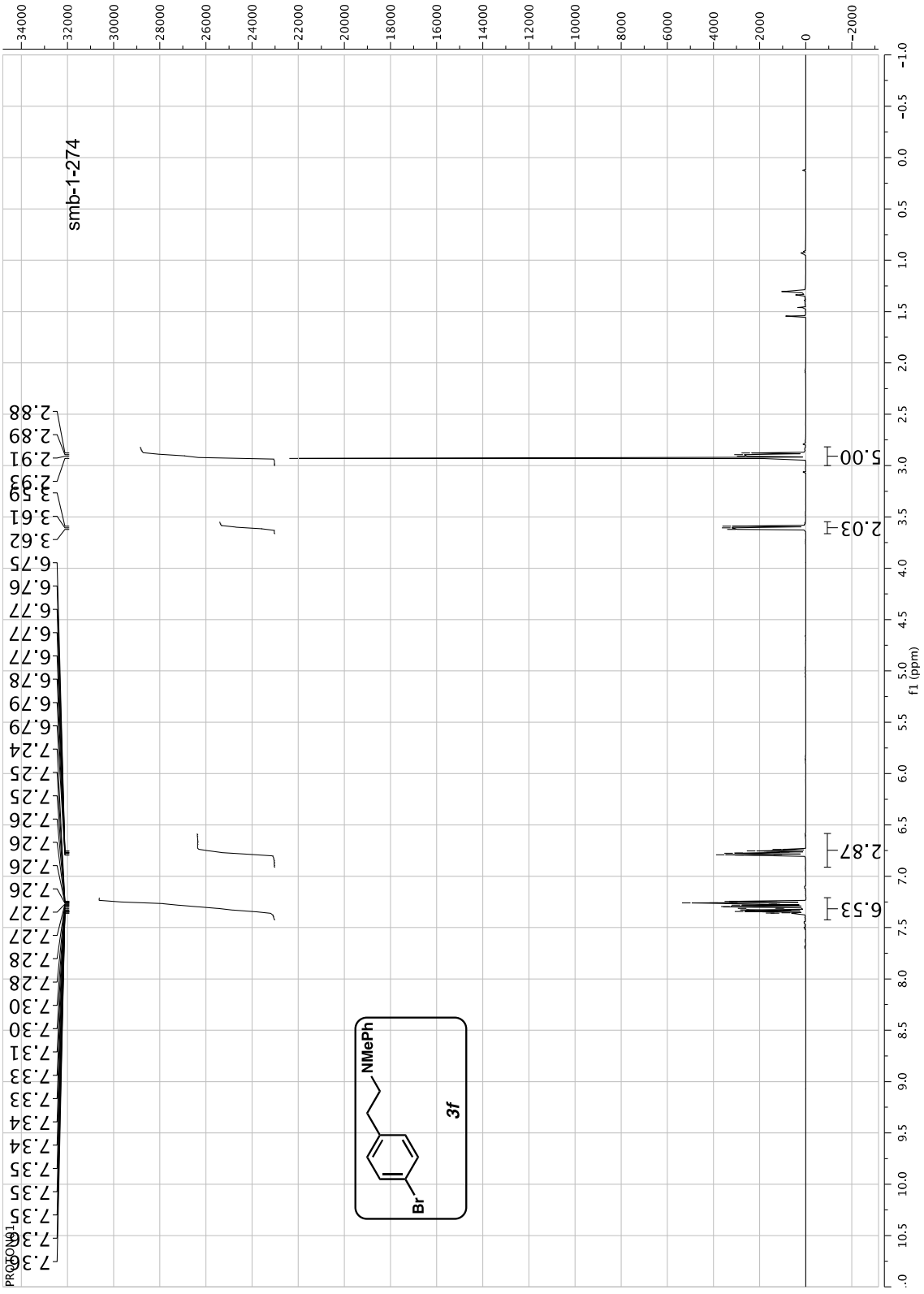


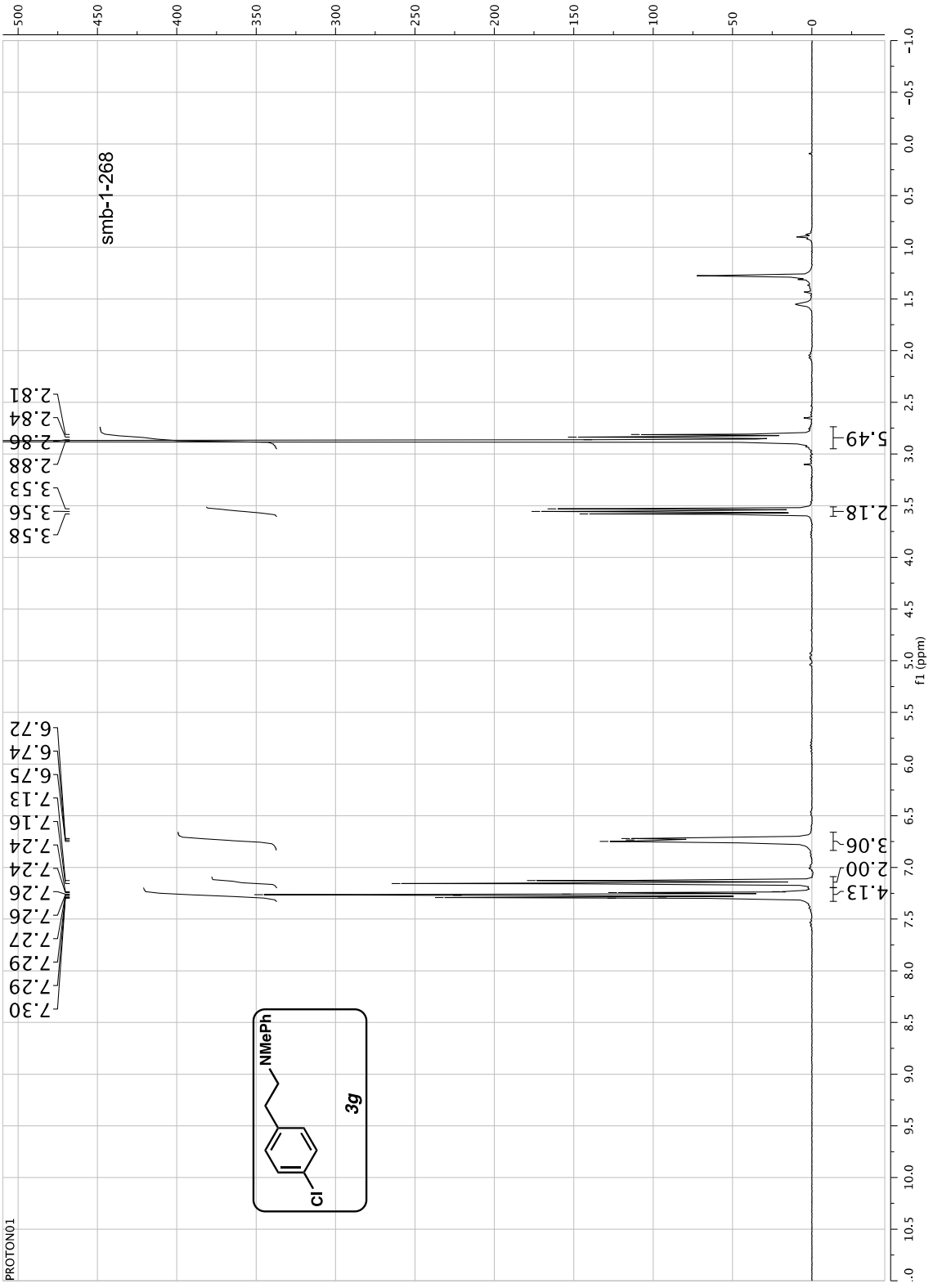


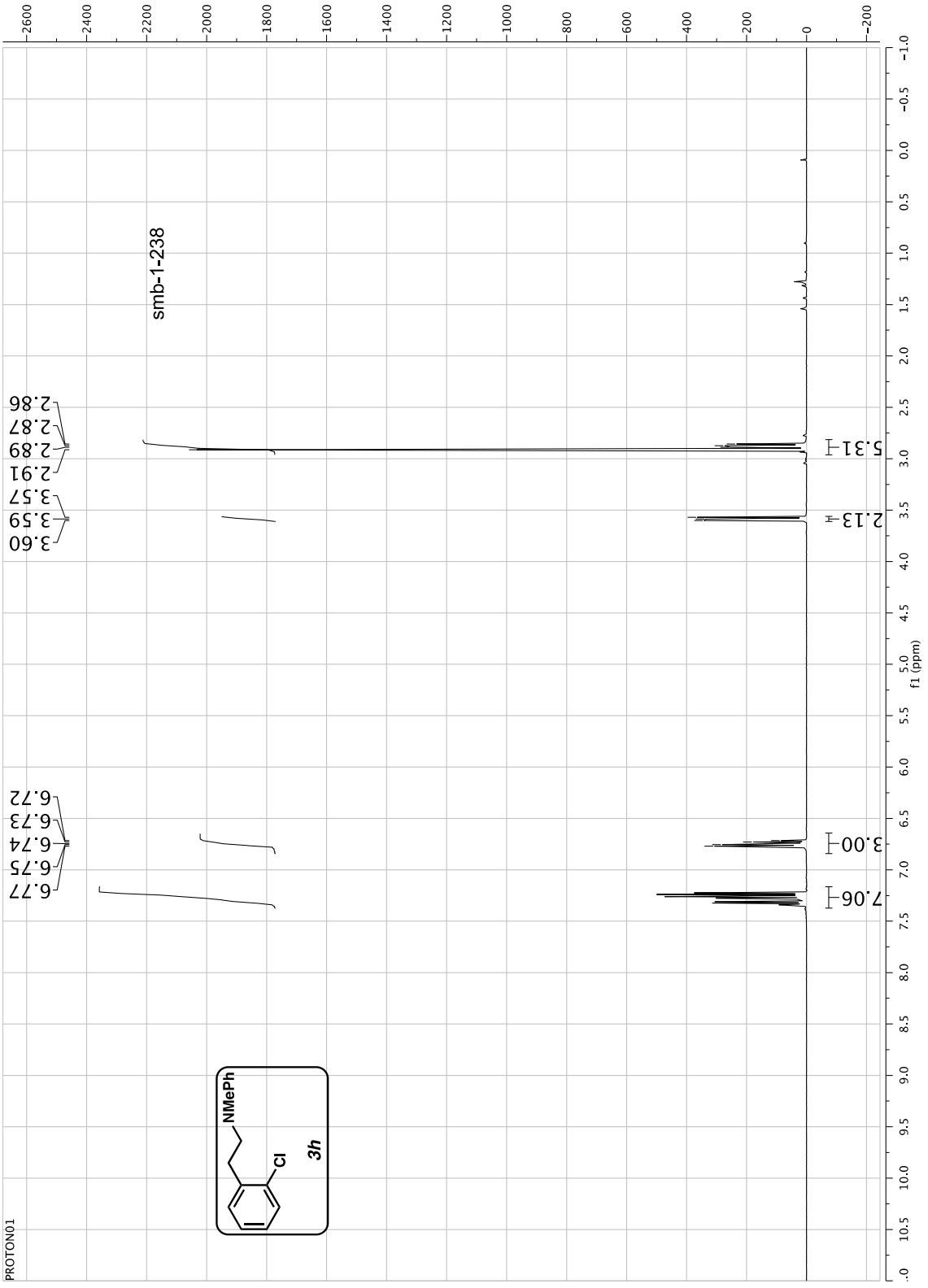


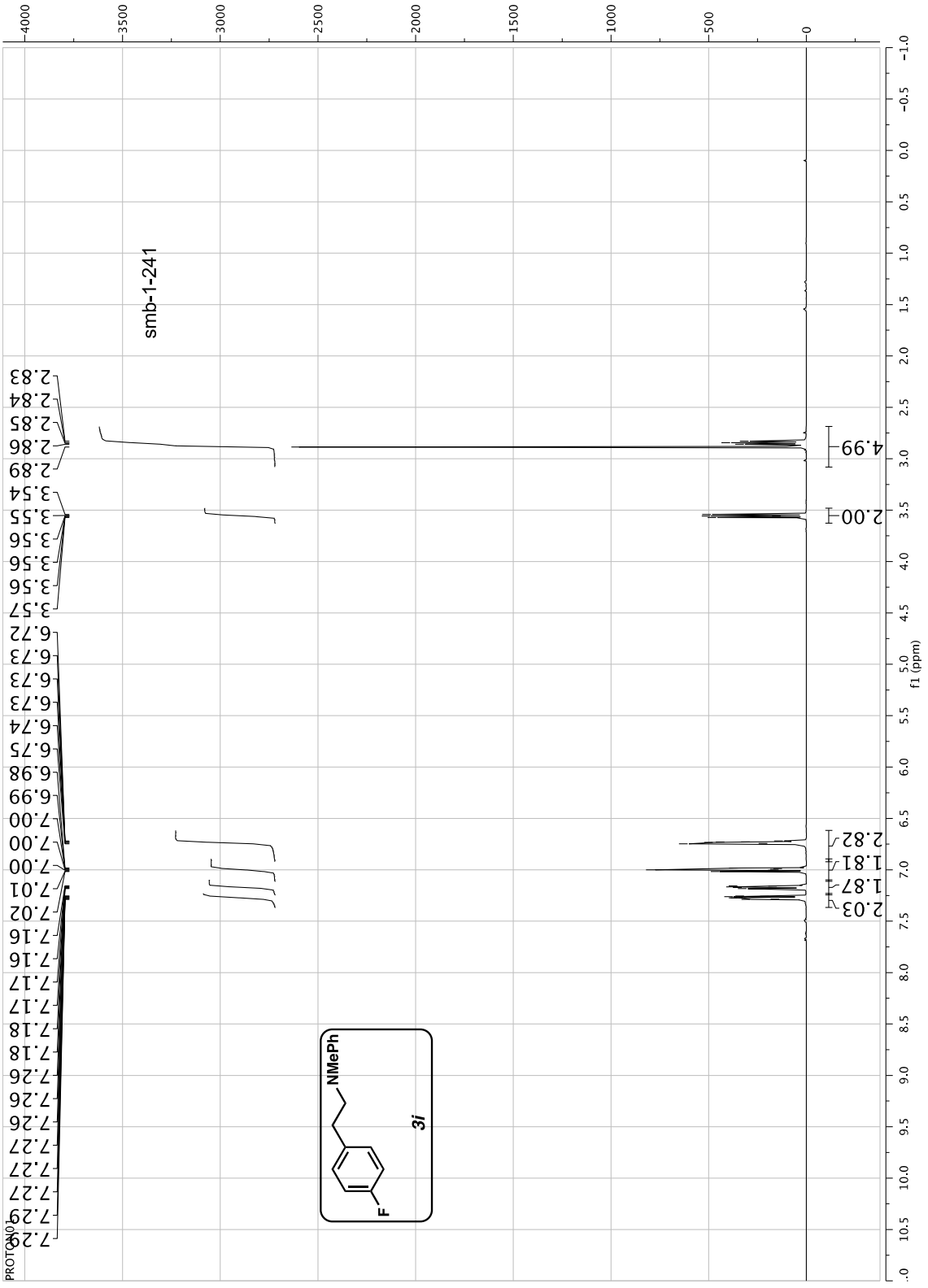


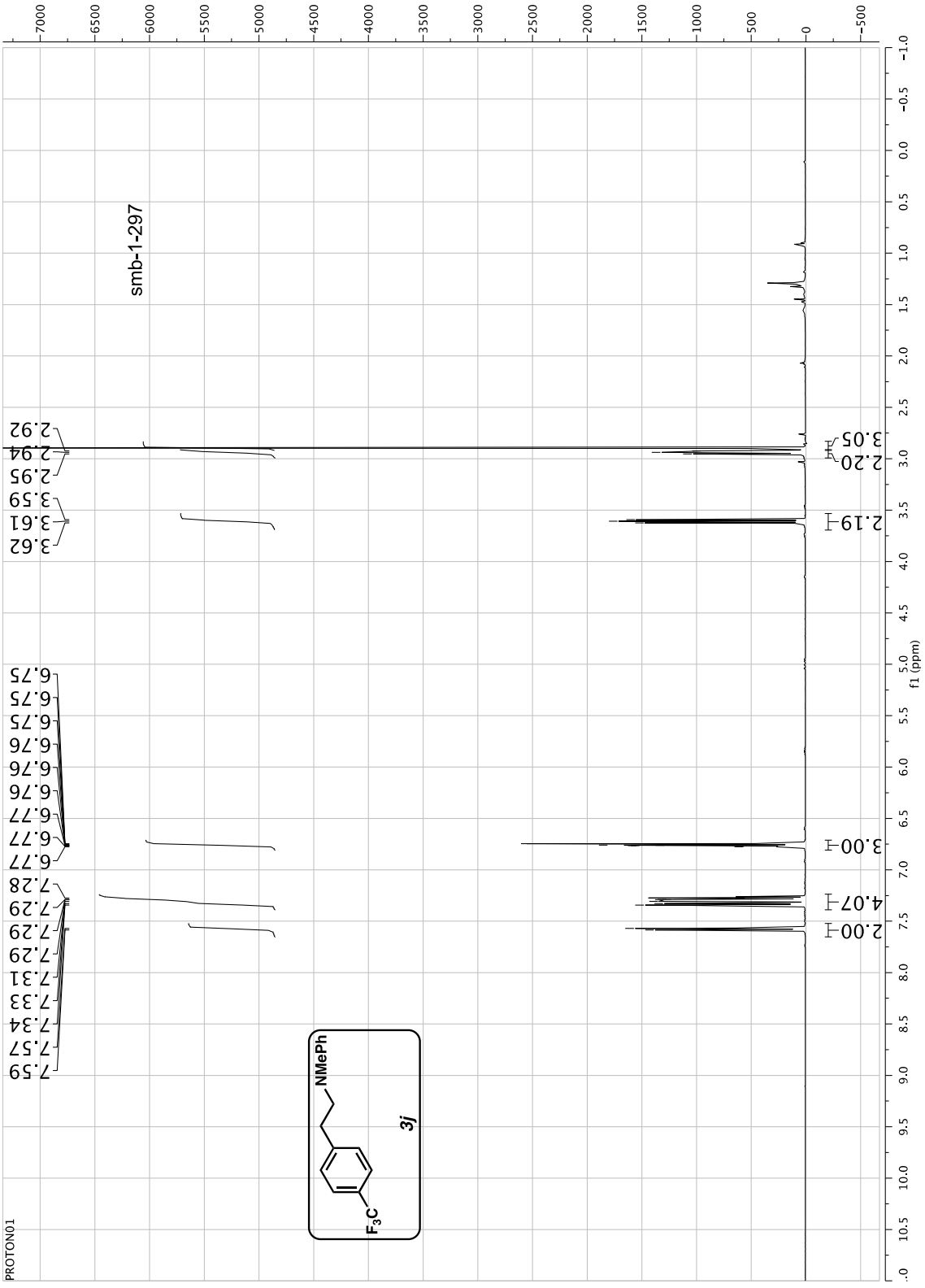


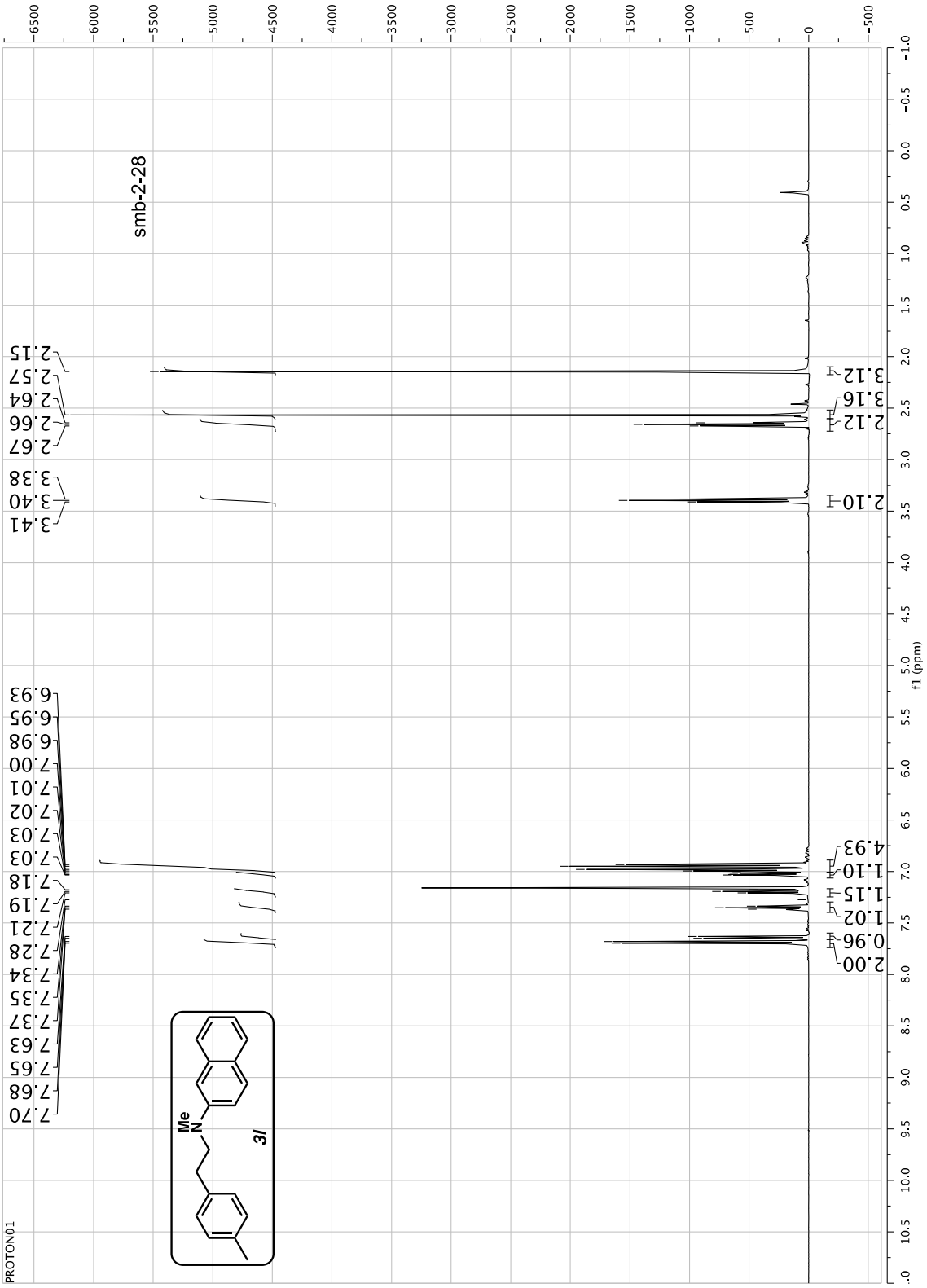


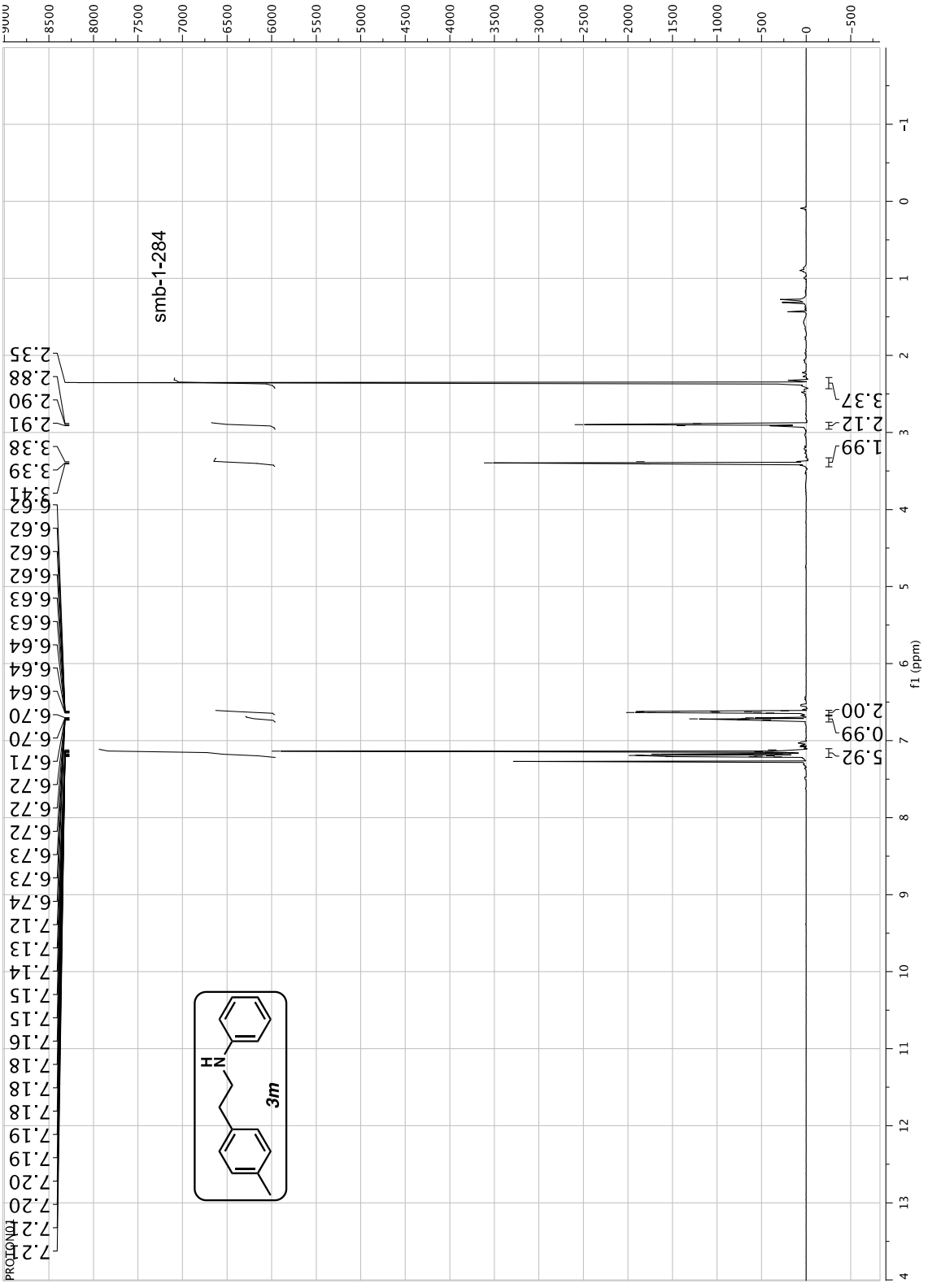


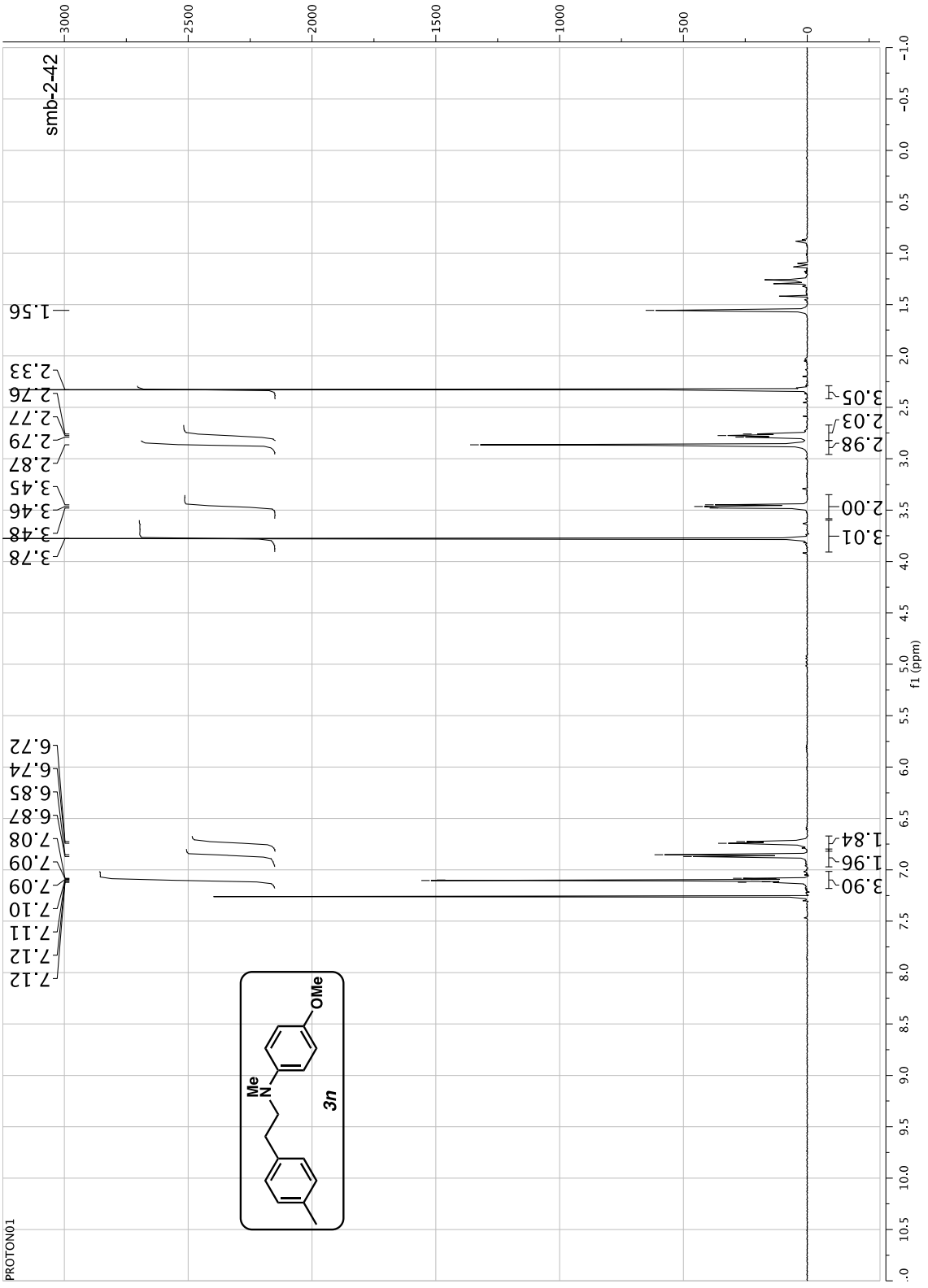


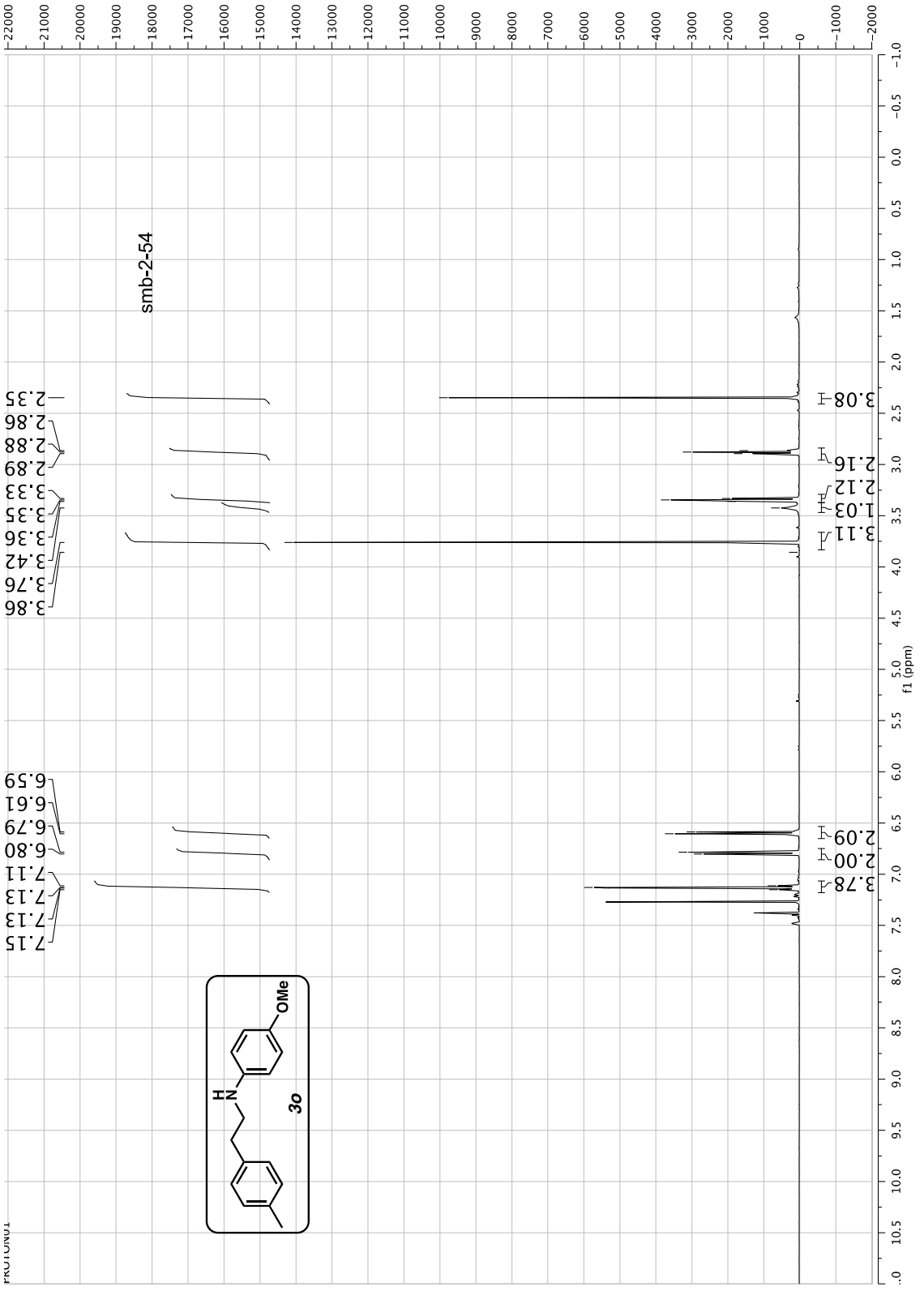


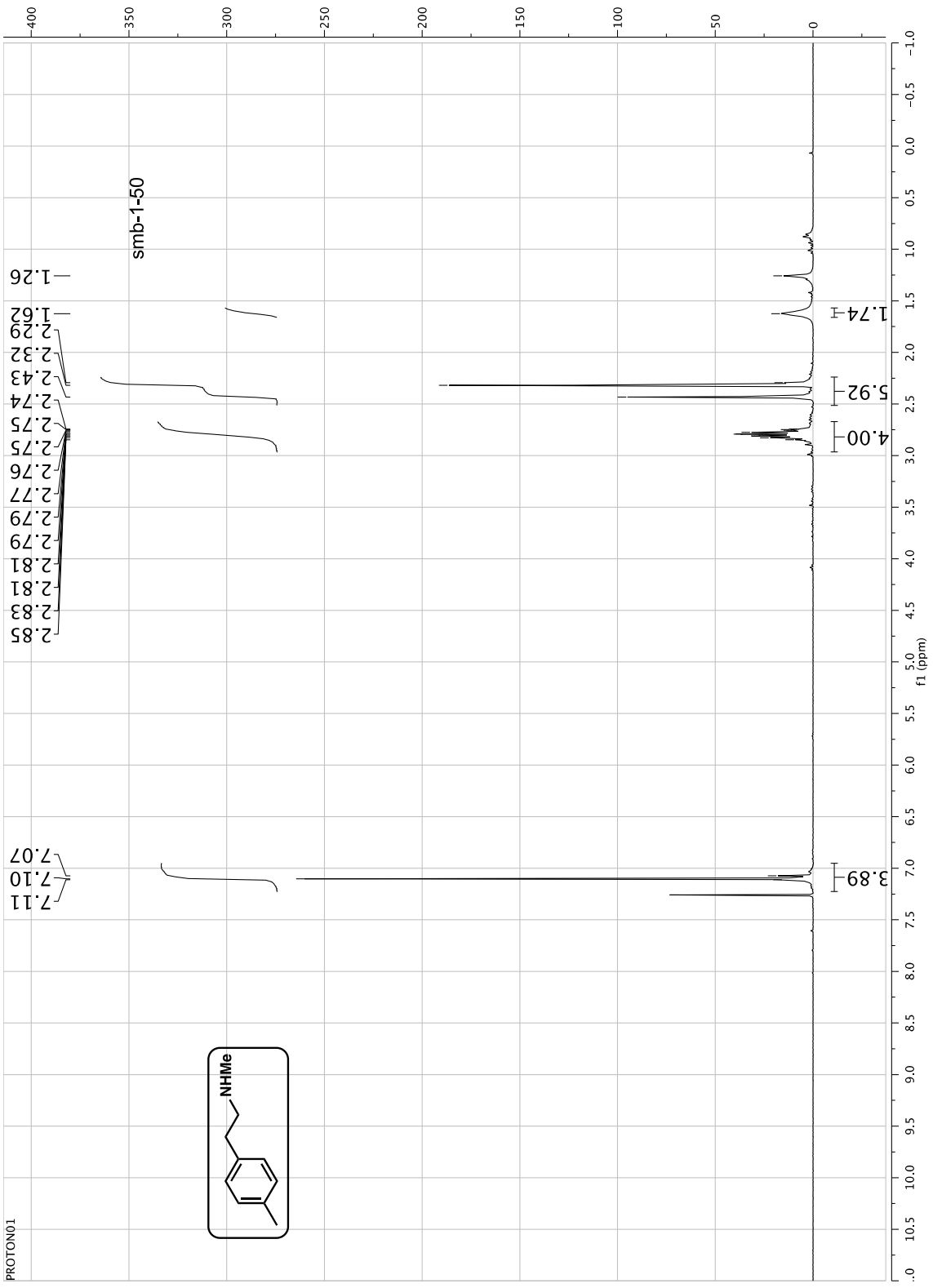


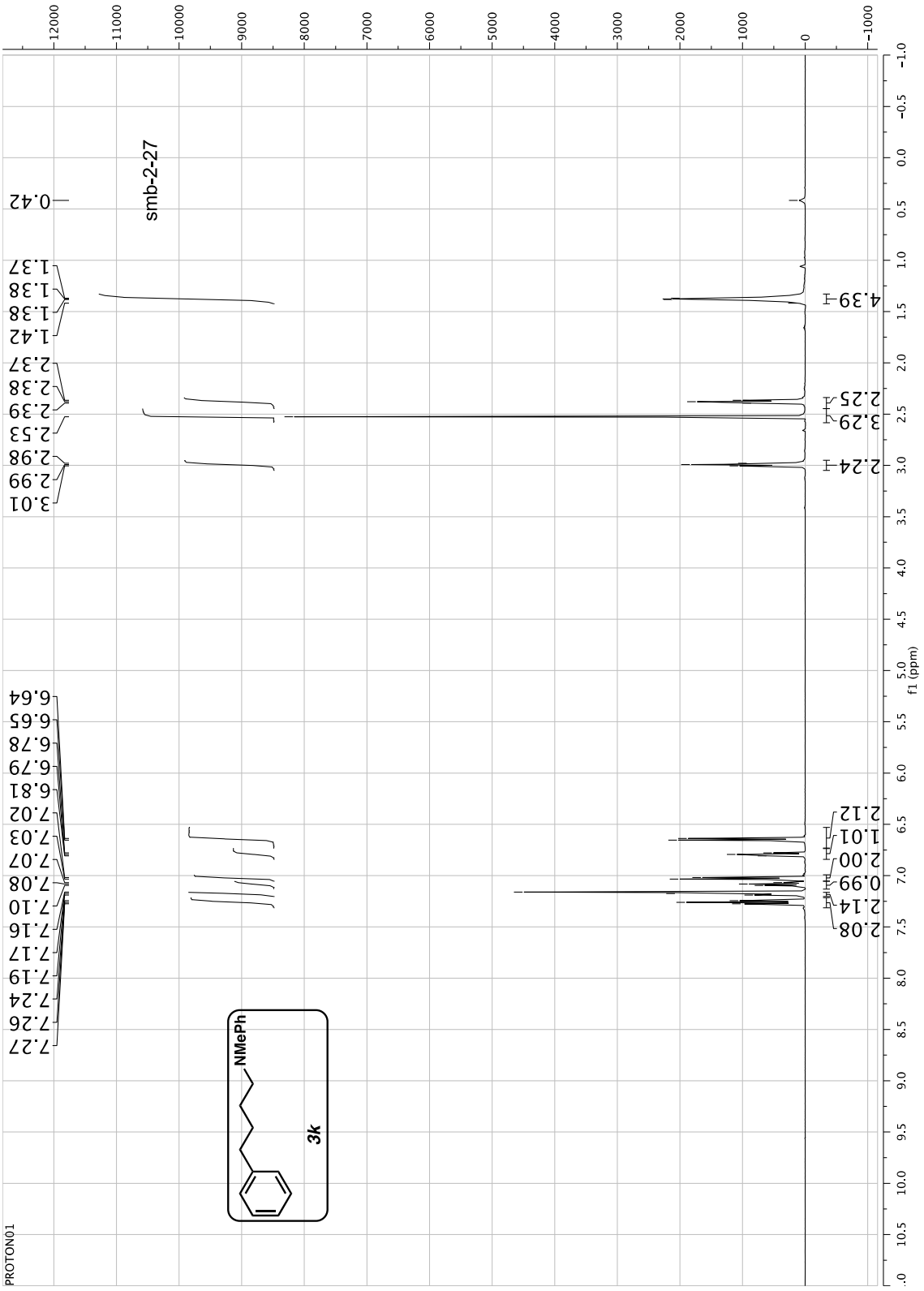


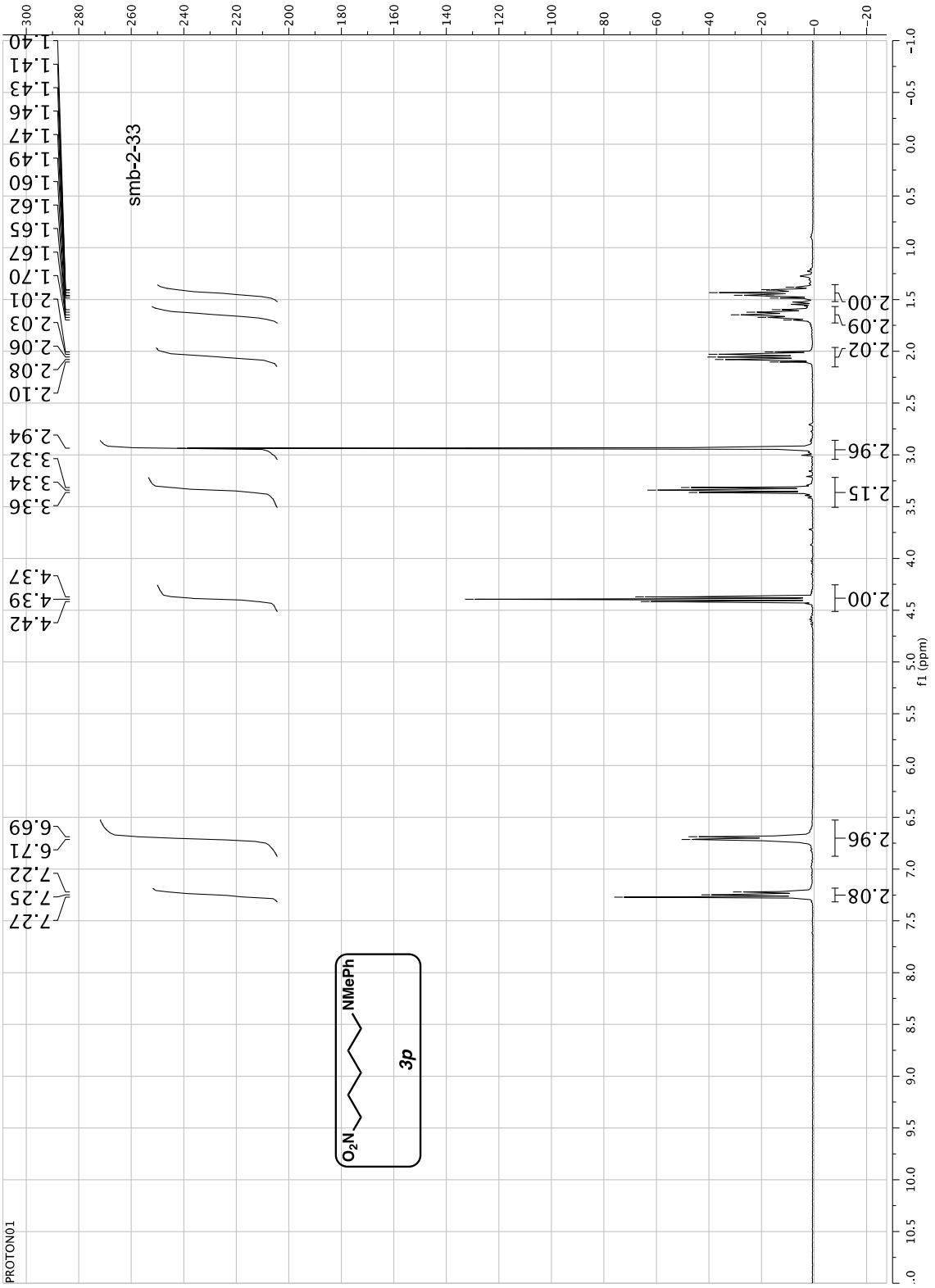


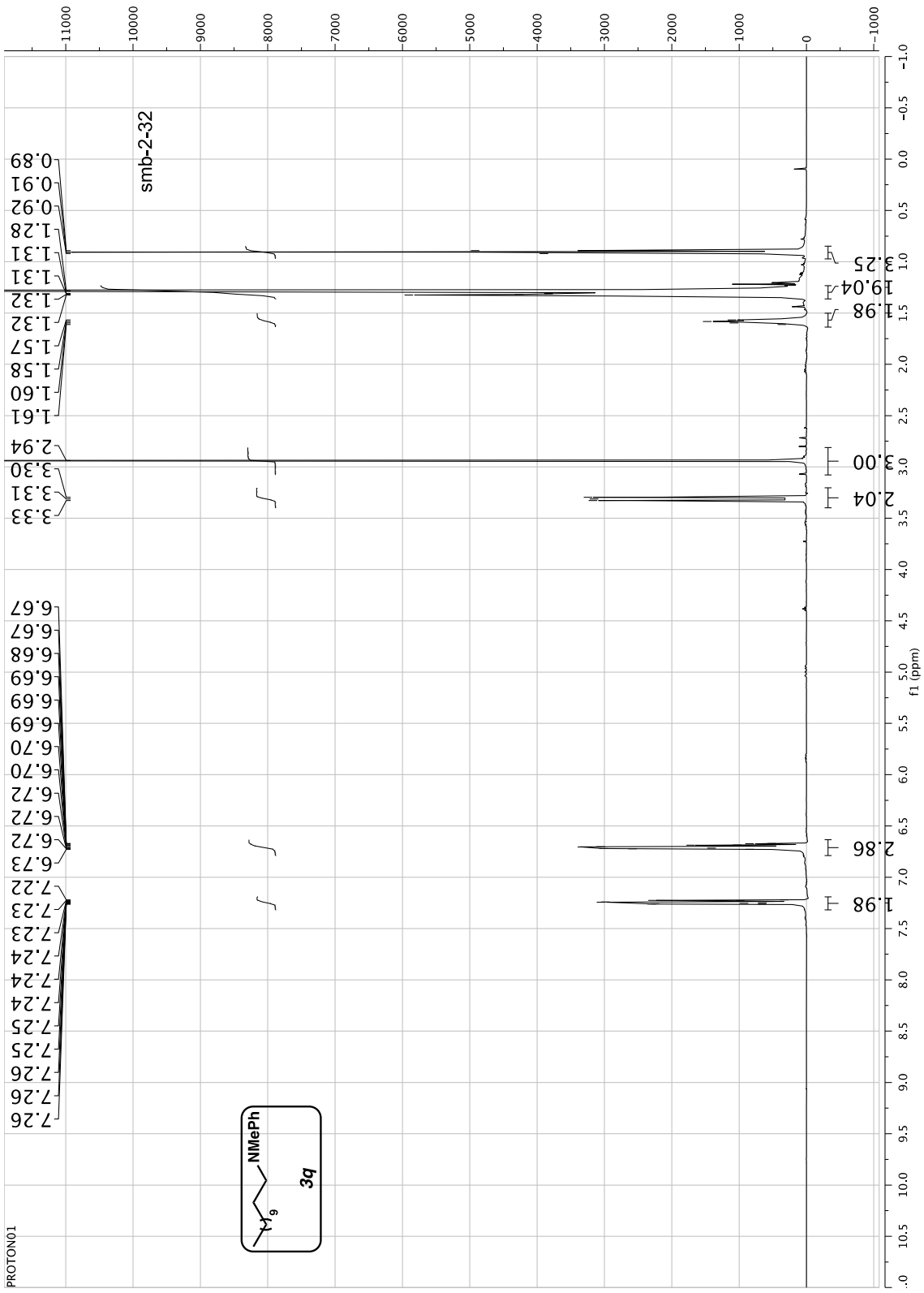


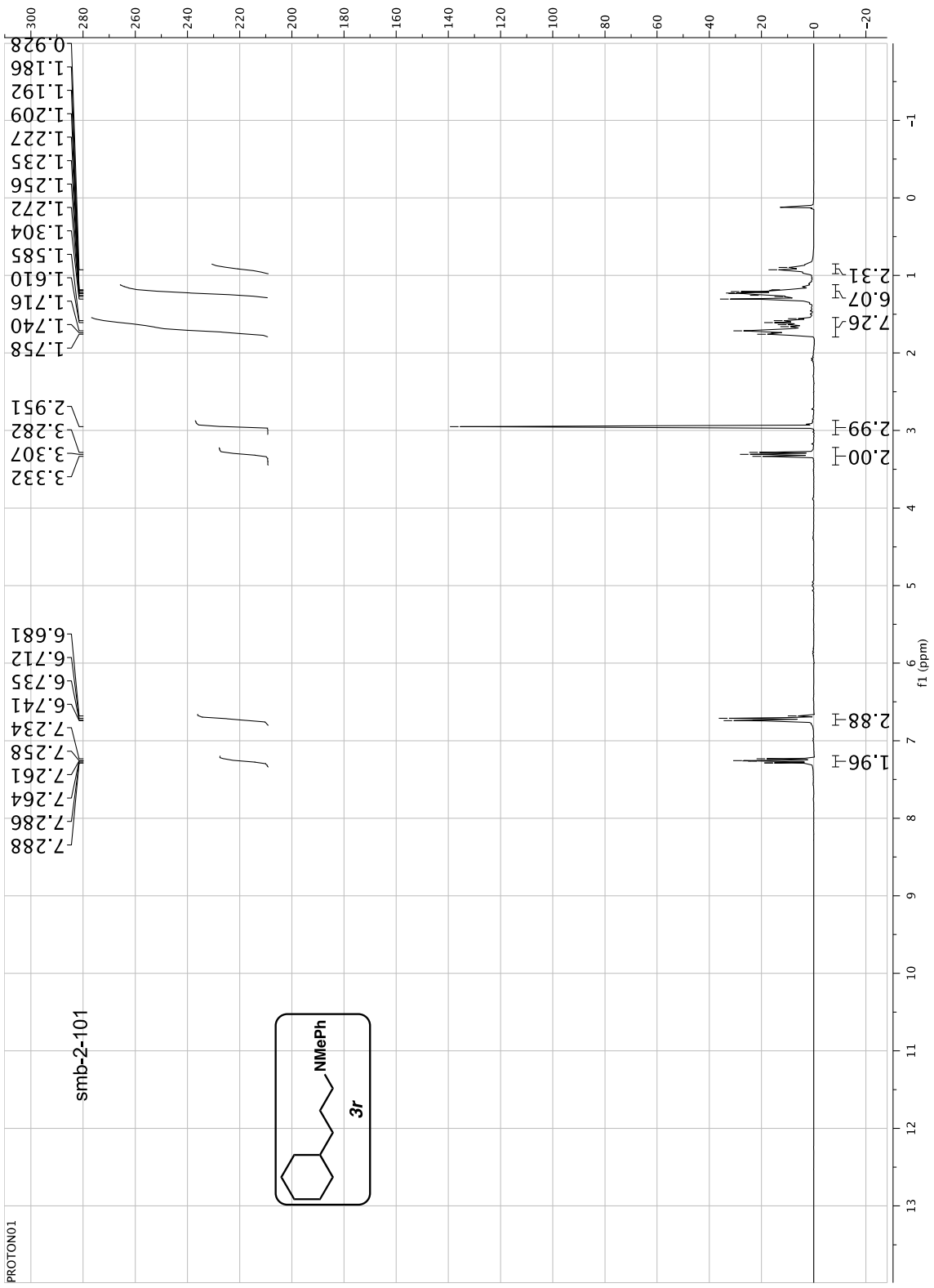


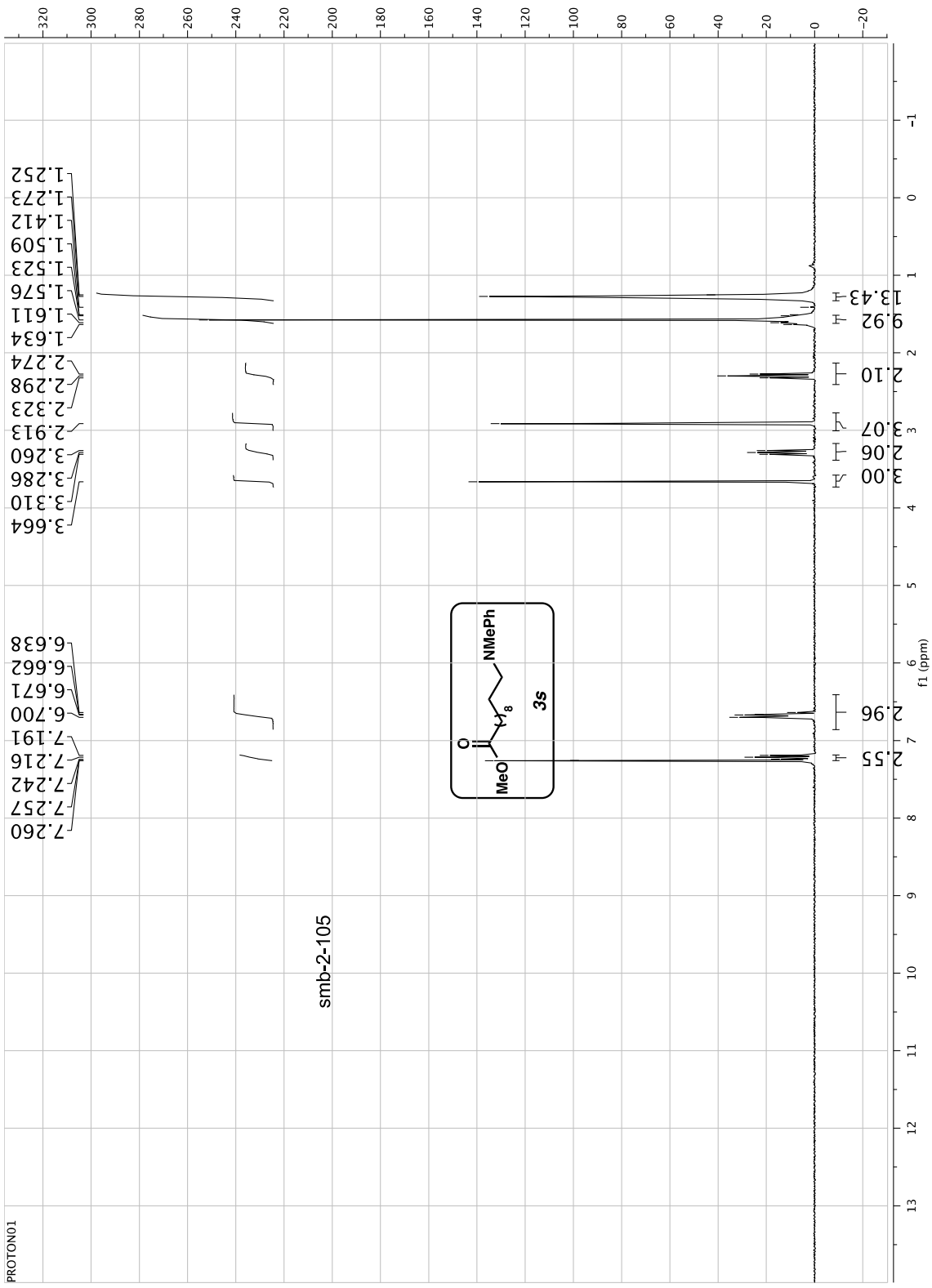


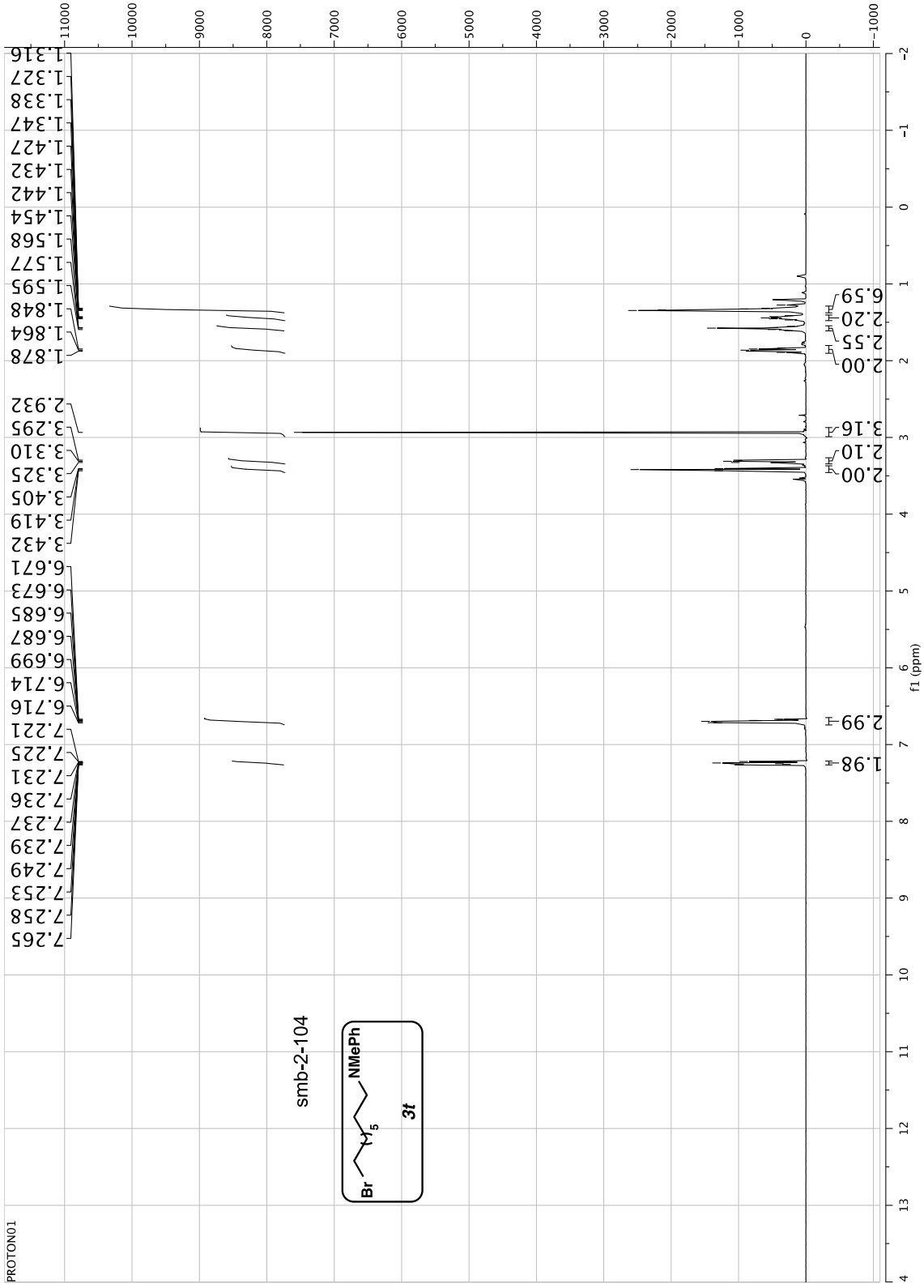


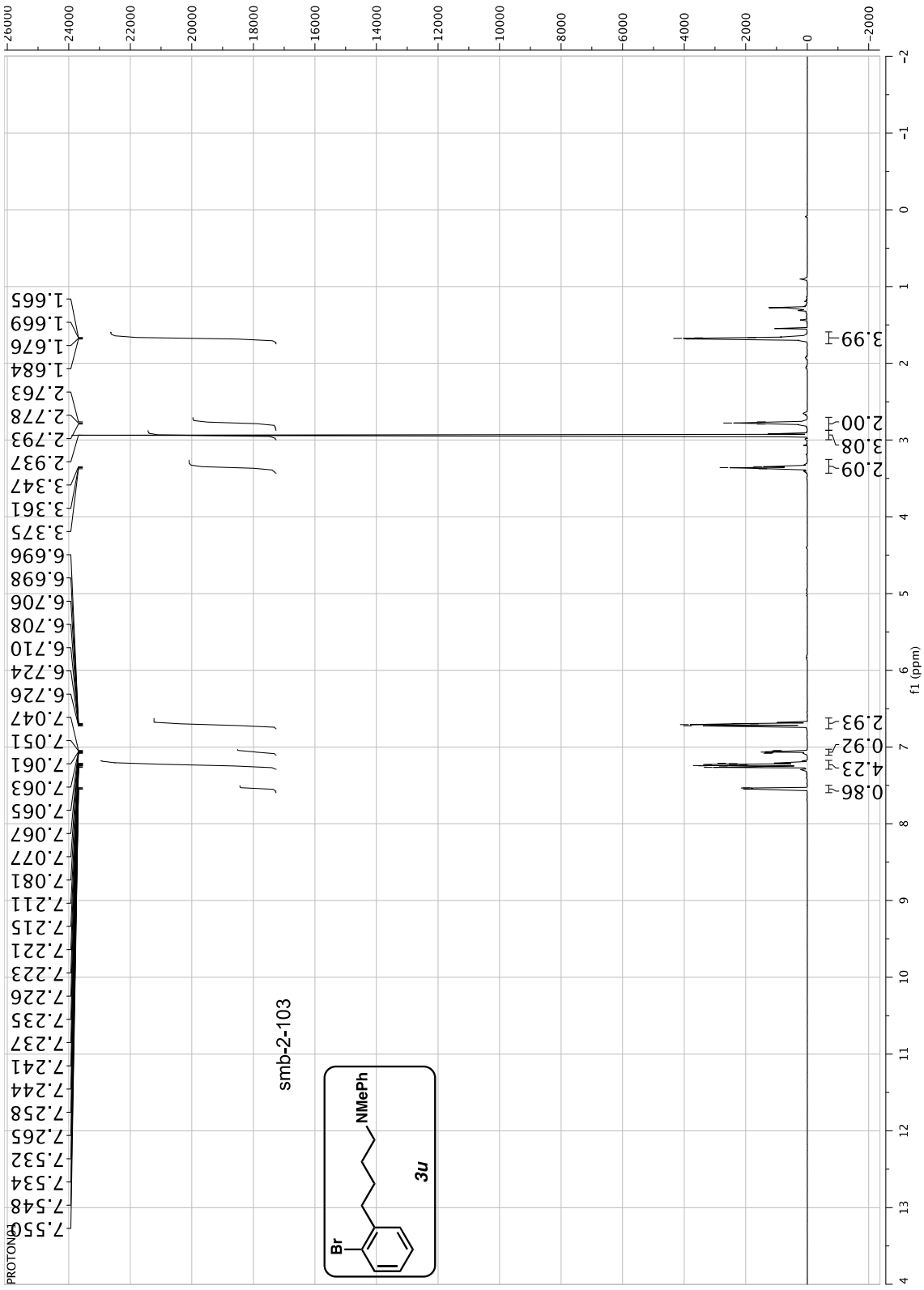












# $^{13}$C NMR Spectra: