

Supporting Information

Para C–H Borylation of Benzene Derivatives by a Bulky Iridium Catalyst

Yutaro Saito,^a Yasutomo Segawa,^{*a,b} and Kenichiro Itami^{*a,b,c}

^a*Graduate School of Science, Nagoya University, Japan*

^b*JST, ERATO, Itami Molecular Nanocarbon Project, Nagoya University, Japan.*

^c*Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, Japan*

E-mail: ysegawa@nagoya-u.jp (Y.Se.), itami@chem.nagoya-u.ac.jp (K.I.)

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1. General

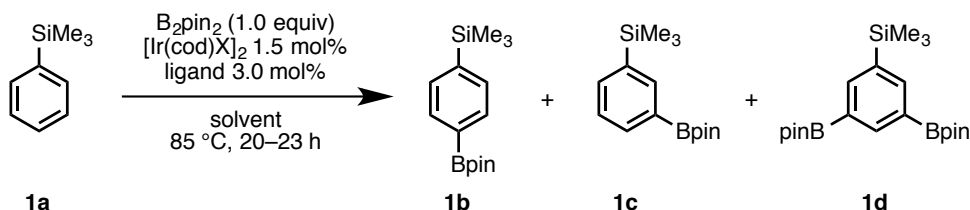
Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF), hexane and dimethylformamide (DMF) were purified by passing through a solvent purification system (Glass Contour). Compounds Xyl-MeO-BIPHEP (**P5**)¹, [Ir(cod)OH]₂², **1b-d**³, phenanthroline derivatives^{4,5,6,7}, and 1,1-di-*p*-anisyl-1-phenylethane (**7a**)⁸ were prepared according to the procedures reported in the literature. All C–H borylation were carried out in glass vessels equipped with J. Young® O-ring tap in an 8-well reaction block (heater + magnetic stirrer). Unless otherwise noted, work-up and purification procedures were performed with reagent-grade solvents under air. Analytical thin-layer chromatography (TLC) was performed using E. Merk silica gel 60 F₂₅₄ precoated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm) and ethanolic phosphomolybdic acid/sulfuric acid. Flash column chromatography was performed with silica gel 60N (Kanto Chemical Co., spherical, neutral, 40–100 mesh). Preparative thin-layer chromatography (PTLC) was performed using Wako-gel® B5-F silica coated plates (0.75 mm) prepared in our laboratory. Preparative recycling gel permeation chromatography (GPC) was performed with a JAI LC-9204 instrument equipped with JAIGEL-1H/JAIGEL-2H columns using chloroform as an eluent. Gas chromatography (GC) analysis was conducted on a Shimadzu GC-2010 instrument equipped with a HP-5 column (30 m × 0.25 mm, Hewlett-Packard). GCMS analysis was conducted on a Shimadzu GCMS-QP2010 instrument equipped with a HP-5 column (30 m × 0.25 mm, Hewlett-Packard). High-resolution mass spectroscopy (HRMS) was obtained from a JEOL JMS-T100TD instrument (DART) and JEOL JMS-T100GCV (EI). Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECA-600 (¹H 600 MHz, ¹³C 150 MHz) spectrometer. Chemical shifts for ¹H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm). Chemical shifts for ¹³C NMR are expressed in ppm relative to CDCl₃ (δ 77.0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of

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(S2) Green, L. M.; Meek, D. W. *Organometallics* **1989**, 8, 659.
(S3) Ohmura, T.; Torigoe, T.; Sugimoto, M. *Organometallics* **2013**, 32, 6170.
(S4) Case, F. H.; Brennan, J. A. *J. Org. Chem.* **1954**, 19, 919.
(S5) Pallenberg, A. J.; Koenig, K. S.; Barnhart, D. M. *Inorg. Chem.* **1995**, 34, 2833.
(S6) Stefan, B.; Bernhard, S.; Guerig, U. *Tetrahedron* **1996**, 52, 2937.
(S7) Jiang, Y.; Chen, C.-F. *Synlett* **2010**, 1679.
(S8) van der Vlugt, J. I.; Grutters, M. M. P.; Mills, A. M.; Kooijman, H.; Spek, A. L.; Vogt, D. *Eur. J. Inorg. Chem.* **2003**, 4361.

doublets, ddd = doublet of doublet of doublets, dt = doublet of triplets, t = triplet, td = triplet of doublets, tt = triplet of triplet, q = quartet, m = multiplet), coupling constant (Hz), and integration.

2. Additional investigation of reaction conditions

General procedure of ligand screening



A 20-mL glass vessel equipped with J. Young[®] O-ring tap containing a magnetic stirring bar was dried in an oven at $100\text{ }^\circ\text{C}$ and then introduced into an argon-filled glove box while the vessel was hot. After cooling the vessel to room temperature, trimethylphenylsilane **1a** (75.1 mg, 500 μmol), B_2pin_2 (127 mg, 500 μmol , 1.0 eq.), $[\text{Ir}(\text{cod})\text{X}]_2$ ($\text{X} = \text{OMe}$ or OH , 7.5 μmol , 1.5 mol%), ligand (15.0 μmol , 3.0 mol%) and dry THF or hexane (1.0 mL) were added to the vessel. The vessel was sealed with O-ring tap. The reaction mixture was heated at $85\text{ }^\circ\text{C}$ for 20–23 h in an 8-well reaction block with stirring. After cooling the reaction mixture to $0\text{ }^\circ\text{C}$ in an ice bath and then warming to room temperature, the yield and ratio of products were determined by GC analysis by using dodecane as an internal standard.

Table S1. Screening of nitrogen-based ligands.

entry	ligand	GC yield/%	1b /[1c + 1d]
1	dtbpy	90	28 : 72
2	phen	98	26 : 74
3	N1	<1	36 : 64
4	N2	59	44 : 56
5	N3	20	41 : 59
6	N4	<1	37 : 63
7	N5	93	21 : 79
8	N6	>99	26 : 74
9	N7	97	22 : 78

entry	ligand	GC yield/%	1b /[1c + 1d]
10	N8	99	43 : 57
11	N9	94	32 : 68
12	N10	9	43 : 47
13	N11	4	39 : 61
14	N12	38	39 : 61
15	N13	98	47 : 53
16	N14	93	40 : 60
17	N15	87	42 : 58

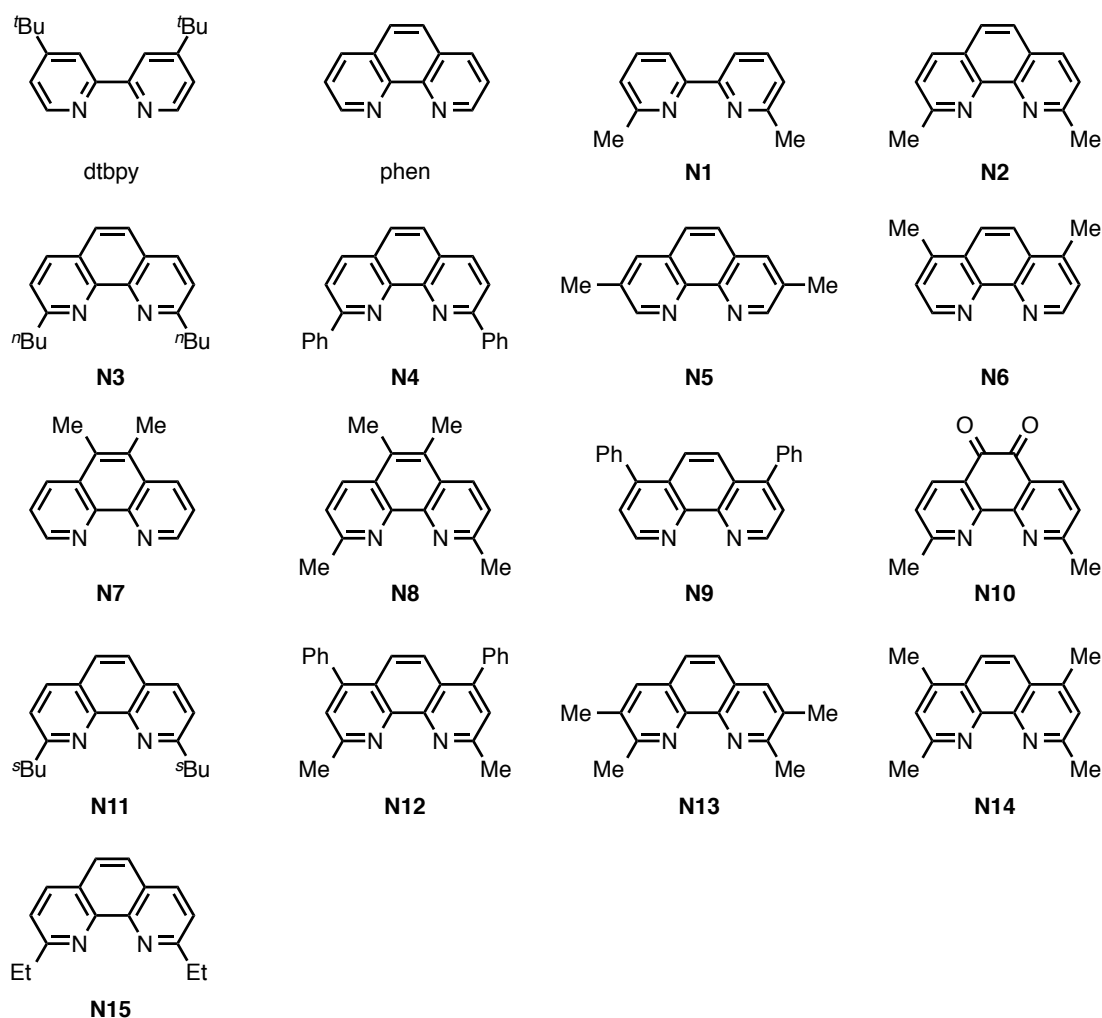
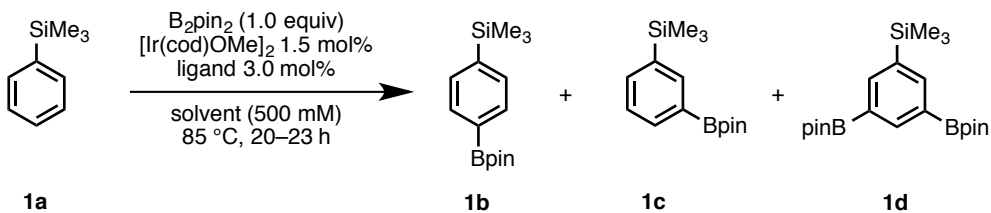


Table S2. Ligand screening with [Ir(cod)OMe]₂.

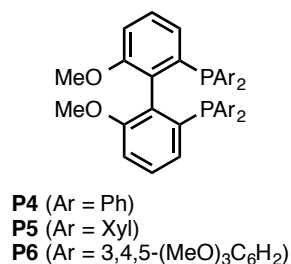
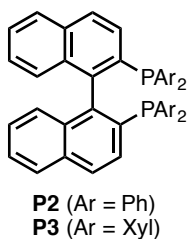
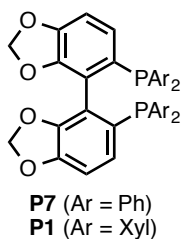
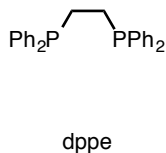
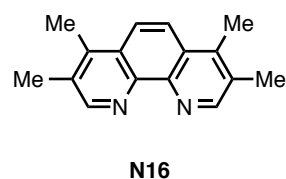
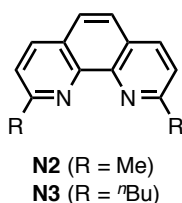
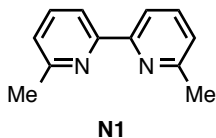
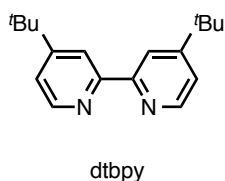


solvent = THF

entry	ligand	GC yield/%	1b /[1c + 1d]
1	dtbpy	90	28 : 72
2	N1	<1	36 : 64
3	N2	59	44 : 56
4	N3	20	41 : 59
5	dppe	13	37 : 63
6	(<i>R</i>)- P1	21	82 : 18 ^a
7	(<i>rac</i>)- P2	4	72 : 28 ^a
8	(<i>R</i>)- P3	20	83 : 17 ^a
9	(<i>R</i>)- P4	4	70 : 30 ^a
10	(<i>R</i>)- P5	34	78 : 22 ^a
11	(<i>R</i>)- P6	4	41 : 59 ^a

solvent = hexane

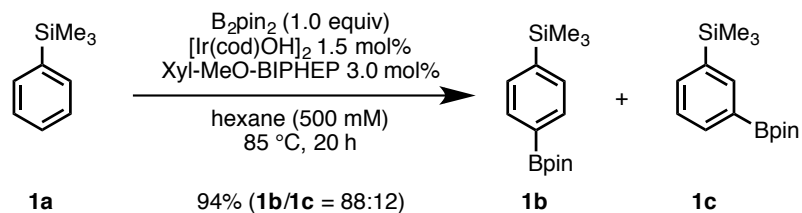
entry	ligand	GC yield/%	1b /[1c + 1d]
1	dtbpy	>99	24 : 76
2	N16	>99	23 : 78
3	dppe	6	29 : 71 ^a
4	(<i>rac</i>)- P2	2	48 : 52 ^a
5	(<i>R</i>)- P7	n.d.	–
6	(<i>R</i>)- P4	1	49 : 51 ^a
7	(<i>R</i>)- P3	4	63 : 37 ^a
8	(<i>rac</i>)- P5	64	80 : 20 ^a



^a **1d** was not observed.

3. Para-selective C–H borylation of monosubstituted arenes

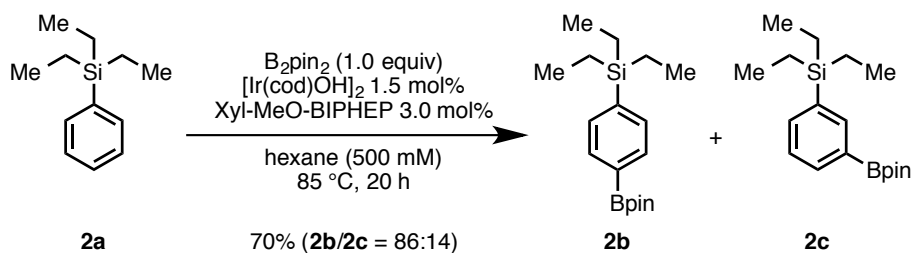
Para-selective C–H borylation of **1a**



A 20-mL glass vessel equipped with J. Young[®] O-ring tap containing a magnetic stirring bar was dried in an oven at 100 °C and then introduced into an argon-filled glove box while the vessel was hot. After cooling the vessel to room temperature, trimethylphenylsilane **1a** (75.1 mg, 500 μ mol), B_2pin_2 (127 mg, 500 μ mol, 1.0 eq.), $[Ir(cod)OH]_2$ (4.8 mg, 7.5 μ mol, 1.5 mol%), Xyl-MeO-BIPHEP (10.4 mg, 15.0 μ mol, 3.0 mol%) and dry hexane (1.0 mL) were added to the vessel. The vessel was sealed with O-ring tap and then heated at 85 °C for 20 h in an 8-well reaction block with stirring. After cooling the reaction mixture to 0 °C in an ice bath and then warming to room temperature, the solvent and remaining substrate were removed under reduced pressure. The borylation products were obtained by silica gel column chromatography (hexane/EtOAc = 10:1) (129 mg, 94% yield, p/m = 88:12). The ratio of isomers was determined by 1H NMR analysis⁹ (600 MHz, $CDCl_3$).

S9) Although exact p/m ratios cannot be determined from crude products due to the overlap with remaining starting materials, we estimated p/m ratios of crude product and confirmed that p/m ratios before and after purification were not changed.

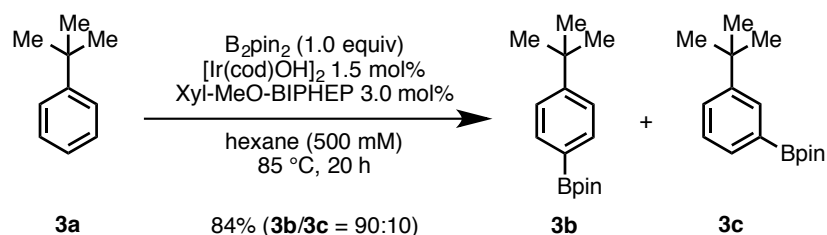
Para-selective C–H borylation of **2a**



A 20-mL glass vessel equipped with J. Young[®] O-ring tap containing a magnetic stirring bar was dried in an oven at 100 °C and then introduced into an argon-filled glove box while the vessel was hot. After cooling the vessel to room temperature, triethylphenylsilane **2a** (96.2 mg, 500 μ mol), B_2pin_2 (127 mg, 500 μ mol, 1.0 eq.), $[Ir(cod)OH]_2$ (4.8 mg, 7.5 μ mol, 1.5 mol%), Xyl-MeO-BIPHEP (10.4 mg, 15.0 μ mol, 3.0 mol%) and dry hexane (1.0 mL) were added to the vessel. The vessel was sealed with O-ring tap and then heated at 85 °C for 20 h in an 8-well reaction block with stirring. After cooling the reaction mixture to 0 °C in an ice bath and then warming to room temperature, the solvent and remaining substrate were removed under reduced pressure. The borylation products were obtained by silica gel column chromatography (hexane/EtOAc = 20:1) as a colorless crystal (111 mg, 70% yield, *p/m* = 86:14). The ratio of isomers was determined by ¹H NMR analysis (600 MHz, CDCl₃). The *para*-borylated product **2b** was obtained by further purification of the mixture by GPC (92.0 mg, 58% yield).

2b: ¹H NMR (600 MHz, CDCl₃) δ 7.78 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 2H), 1.34 (s, 12H), 0.95 (t, *J* = 7.8 Hz, 9H), 0.79 (q, *J* = 7.8 Hz, 6H); ¹³C NMR (150 MHz, CDCl₃) δ 141.2 (4°), 133.8 (CH), 133.5 (CH), 129.1 (4°, br), 83.7 (4°), 24.8 (CH₃), 7.3 (CH₂), 3.3 (CH₃); HRMS (DART) *m/z* calcd for C₁₈H₃₂BO₂Si [MH]⁺: 319.2265, found 319.2270.

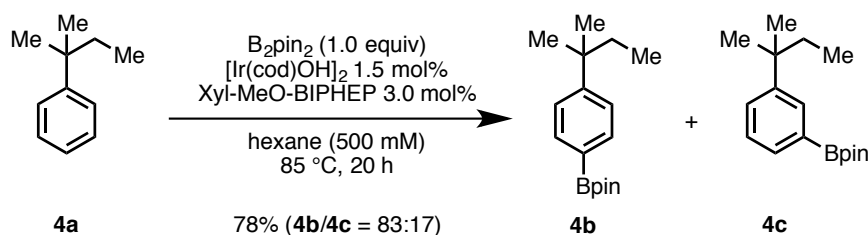
Para-selective C–H borylation of **3a**



A 20-mL glass vessel equipped with J. Young[®] O-ring tap containing a magnetic stirring bar was dried in an oven at 100 °C and then introduced into an argon-filled glove box while the vessel was hot. After cooling the vessel to room temperature, *tert*-butylbenzene **3a** (67.1 mg, 500 μ mol), B_2pin_2 (127 mg, 500 μ mol, 1.0 eq.), $[Ir(cod)OH]_2$ (4.8 mg, 7.5 μ mol, 1.5 mol%), Xyl-MeO-BIPHEP (10.4 mg, 15.0 μ mol, 3.0 mol%) and dry hexane (1.0 mL) were added to the vessel. The vessel was sealed with O-ring tap and then heated at 85 °C for 20 h in an 8-well reaction block with stirring. After cooling the reaction mixture to 0 °C in an ice bath and then warming to room temperature, the solvent and remaining substrate were removed under reduced pressure. The borylation products were obtained by silica gel column chromatography (hexane/EtOAc = 10:1) (110 mg, 84% yield, *p/m* = 90:10). The ratio of isomers was determined by 1H NMR analysis (600 MHz, $CDCl_3$)¹⁰.

(S10) Tajuddin, H.; Harrisson, P.; Bitterlich, B.; Collongs, J. C.; Sim, N.; Batsanov, A. S.; Cheung, M. S.; Kawamorita, S.; Maxwell, A. C.; Shukla, L.; Morris, J.; Lin, Z.; Marder, T. B.; Steel, P. G. *Chem. Sci.* **2012**, 3, 3505.

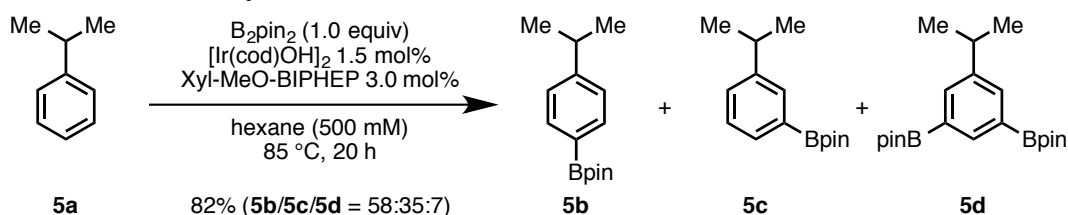
Para-selective C–H borylation of **4a**



A 20-mL glass vessel equipped with J. Young[®] O-ring tap containing a magnetic stirring bar was dried in an oven at 100 °C and then introduced into an argon-filled glove box while the vessel was hot. After cooling the vessel to room temperature, *tert*-amylbenzene **4a** (74.1 mg, 500 μmol), B_2pin_2 (127 mg, 500 μmol , 1.0 eq.), $[\text{Ir}(\text{cod})\text{OH}]_2$ (4.8 mg, 7.5 μmol , 1.5 mol%), Xyl-MeO-BIPHEP (10.4 mg, 15.0 μmol , 3.0 mol%) and dry hexane (1.0 mL) were added to the vessel. The vessel was sealed with O-ring tap and then heated at 85 °C for 20 h in an 8-well reaction block with stirring. After cooling the reaction mixture to 0 °C in an ice bath and then warming to room temperature, the solvent and remaining substrate were removed under reduced pressure. The borylation products were obtained by silica gel column chromatography (hexane/EtOAc = 10:1) (107 mg, 78% yield, *p/m* = 83:17). The ratio of isomers was determined by ^1H NMR analysis (600 MHz, CDCl_3)¹¹.

(S11) Albaugh, P. A.; Dominguez-manzanares, E.; Hong, J. E.; Hornback, W. J.; Jiang, D.; Ornstein, P. L.; Thompson, M. L.; Tromiczak, E. G.; Wu, Z.; Zarrinmayeh, H.; Zimmerman, D. M.; Castano Mansanet, A. M.; Huffman, L. G.; Miller, W. D. Pyrrole and Pyrazole Derivatives as Potentiators of Glutamate Receptors. PCT patent WO2005040110 A1 September 27, 2005.

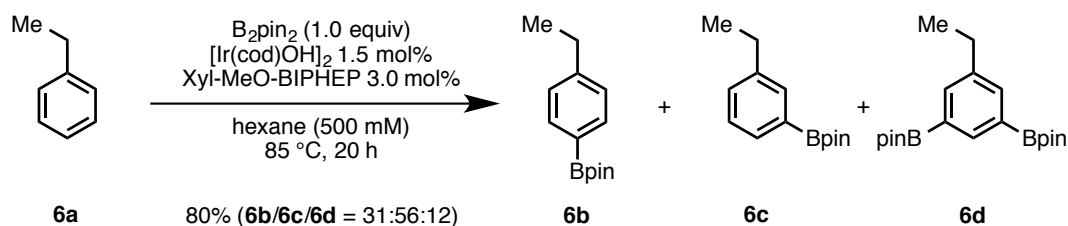
Para-selective C–H borylation of **5a**



A 20-mL glass vessel equipped with J. Young[®] O-ring tap containing a magnetic stirring bar was dried in an oven at 100 °C and then introduced into an argon-filled glove box while the vessel was hot. After cooling the vessel to room temperature, Cumene **5a** (60.1 mg, 500 μ mol), B_2pin_2 (127 mg, 500 μ mol, 1.0 eq.), $[Ir(cod)OH]_2$ (4.8 mg, 7.5 μ mol, 1.5 mol%), Xyl-MeO-BIPHEP (10.4 mg, 15.0 μ mol, 3.0 mol%) and dry hexane (1.0 mL) were added to the vessel. The vessel was sealed with O-ring tap and then heated at 85 °C for 20 h in an 8-well reaction block with stirring. After cooling the reaction mixture to 0 °C in an ice bath and then warming to room temperature, the solvent and remaining substrate were removed under reduced pressure. The ratio of products was determined by 1H NMR analysis (600 MHz, $CDCl_3$) of the crude mixture¹². The mono-borylated products (**5b**+**5c**, 96.0 mg, 78% yield) and di-borylated product (**5d**, 6.9 mg, 4% yield) were obtained by silica gel column chromatography (hexane/EtOAc = 10:1) (total yield 82%).

(S12) Cho, J.-Y.; Iverson, C. N.; Smith, M. R., III *J. Am. Chem. Soc.* **2000**, 122, 12868.

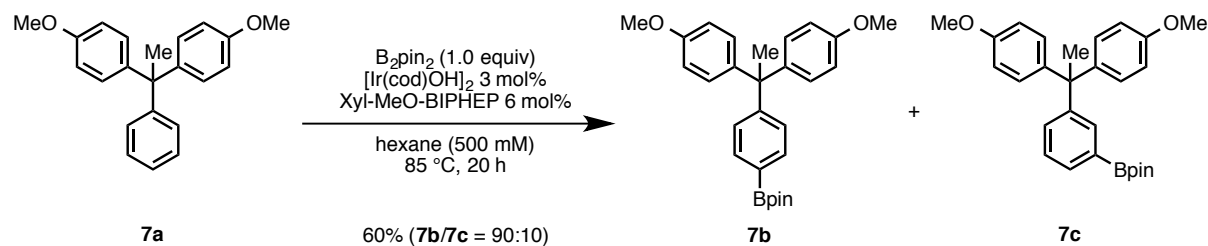
Para-selective C–H borylation of **6a**



A 20-mL glass vessel equipped with J. Young[®] O-ring tap containing a magnetic stirring bar was dried in an oven at 100 °C and then introduced into an argon-filled glove box while the vessel was hot. After cooling the vessel to room temperature, ethylbenzene **6a** (53.1 mg, 500 μ mol), B_2pin_2 (127 mg, 500 μ mol, 1.0 eq.), $[Ir(cod)OH]_2$ (4.8 mg, 7.5 μ mol, 1.5 mol%), Xyl-MeO-BIPHEP (10.4 mg, 15.0 μ mol, 3.0 mol%) and dry hexane (1.0 mL) were added to the vessel. The vessel was sealed with O-ring tap and then heated at 85 °C for 20 h in an 8-well reaction block with stirring. After cooling the reaction mixture to 0 °C in an ice bath and then warming to room temperature, the solvent and remaining substrate were removed under reduced pressure. The ratio of products was determined by 1H NMR analysis (600 MHz, $CDCl_3$) of the crude mixture.¹³ The mono-borylated products (**6b**+**6c**, 80.5 mg, 69% yield) and di-borylated product (**6d**, 19.2 mg, 11% yield) were obtained by silica gel column chromatography (hexane/EtOAc = 20:1) (total yield 80%).

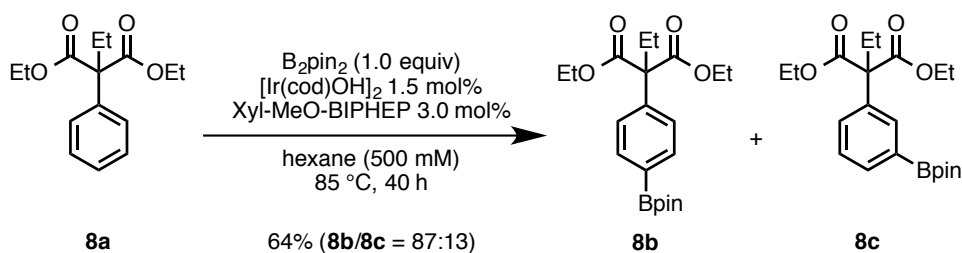
(S13) Boebel, T. A.; Hartwig, J. F. *Organometallics* **2008**, 27, 6013.

Para-selective C–H borylation of **7a**



A 20-mL glass vessel equipped with J. Young® O-ring tap containing a magnetic stirring bar was dried in an oven at 100 °C and then introduced into an argon-filled glove box while the vessel was hot. After cooling the vessel to room temperature, 1,1-di-*p*-anisyl-1-phenylethane **7a** (159 mg, 500 μ mol), B_2pin_2 (127 mg, 500 μ mol, 1.0 eq.), $[Ir(cod)OH]_2$ (9.5 mg, 15 μ mol, 3.0 mol%), Xyl-MeO-BIPHEP (20.8 mg, 30 μ mol, 6.0 mol%) and dry hexane (1.0 mL) were added to the vessel. The vessel was sealed with O-ring tap and then heated at 85 °C for 20 h in an 8-well reaction block with stirring. After cooling the reaction mixture to 0 °C in an ice bath and then warming to room temperature, the solvent was removed under reduced pressure. The borylation products were obtained by silica gel column chromatography (hexane/EtOAc = 10:1) (134 mg, 60% yield, *p/m* = 90:10). The ratio of isomers was determined by 1H NMR analysis (600 MHz, $CDCl_3$). The *para*-borylated product **7b** was obtained by further purification of the mixture by GPC (102 mg, 46% yield). **7b**: 1H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, J = 1.2 Hz, 2H), 7.12 (d, J = 1.2 Hz, 2H), 6.99 (d, J = 13.8 Hz, 4H), 6.79 (d, J = 13.2 Hz, 4H), 3.78 (s, 6H), 2.12 (s, 3H), 1.33 (s, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.6 (4°), 152.9 (4°), 141.2 (4°), 134.3 (CH), 129.6 (4°, br), 128.0 (CH), 126.2 (CH), 113.1 (CH), 83.6 (4°), 55.1 (CH₃), 51.4 (4°), 30.6 (CH₃), 24.8 (CH₃); HRMS (DART) m/z calcd for $C_{28}H_{34}BO_4$ [MH]⁺: 445.2550, found 445.2557.

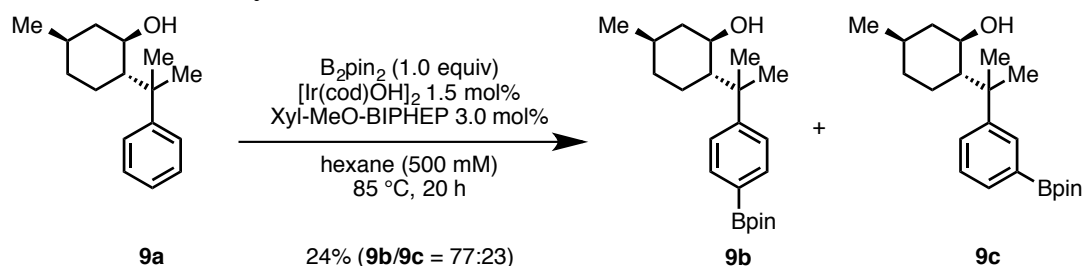
Para-selective C–H borylation of **8a**



A 20-mL glass vessel equipped with J. Young[®] O-ring tap containing a magnetic stirring bar was dried in an oven at 100 °C and then introduced into an argon-filled glove box while the vessel was hot. After cooling the vessel to room temperature, diethyl 2-ethyl-2-phenylmalonate **8a** (132 mg, 500 μmol), B_2pin_2 (127 mg, 500 μmol , 1.0 eq.), $[\text{Ir}(\text{cod})\text{OH}]_2$ (4.8 mg, 7.5 μmol , 1.5 mol%), Xyl-MeO-BIPHEP (10.4 mg, 15.0 μmol , 3.0 mol%) and dry hexane (1.0 mL) were added to the vessel. The vessel was sealed with O-ring tap and then heated at 85 °C for 40 h in an 8-well reaction block with stirring. After cooling the reaction mixture to 0 °C in an ice bath and then warming to room temperature, the solvent was removed under reduced pressure. The borylation products were obtained by GPC (134 mg, 64% yield, p/m = 87:13). The ratio of isomers was determined by ^1H NMR analysis (600 MHz, CDCl_3). The *para*-borylated product **8b** was obtained by further purification of the mixture by GPC (77.0 mg, 43% yield).

8b: ^1H NMR (600 MHz, CDCl_3) δ 7.78 (d, J = 9.0 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 4.24–4.18 (m, 4H), 2.35 (q, J = 7.2 Hz, 2H), 1.34 (s, 12H), 1.23 (t, J = 7.2 Hz, 6H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 170.5 (4°), 140.1 (4°), 134.4 (CH), 127.4 (CH), 83.8 (4°), 63.3 (4°), 61.4 (CH_2), 28.9 (CH_2), 24.8 (CH_3), 13.9 (CH_3), 9.2 (CH_3); HRMS (DART) m/z calcd for $\text{C}_{21}\text{H}_{32}\text{BO}_6$ $[\text{MH}]^+$: 391.2292, found 391.2297.

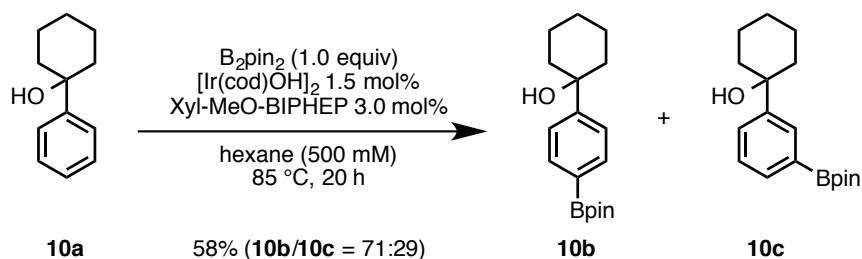
Para-selective C–H borylation of **9a**



A 20-mL glass vessel equipped with J. Young[®] O-ring tap containing a magnetic stirring bar was dried in an oven at 100 °C and then introduced into an argon-filled glove box while the vessel was hot. After cooling the vessel to room temperature, (–)-8-phenylmenthol **9a** (116 mg, 500 μmol), B_2pin_2 (127 mg, 500 μmol , 1.0 eq.), $[\text{Ir}(\text{cod})\text{OH}]_2$ (4.8 mg, 7.5 μmol , 1.5 mol%), Xyl-MeO-BIPHEP (10.4 mg, 15.0 μmol , 3.0 mol%) and dry hexane (1.0 mL) were added to the vessel. The vessel was sealed with O-ring tap and then heated at 85 °C for 20 h in an 8-well reaction block with stirring. After cooling the reaction mixture to 0 °C in an ice bath and then warming to room temperature, the solvent was removed under reduced pressure. The borylation products were obtained by GPC (42.4 mg, 24% yield, $p/m = 77:23$). The ratio of isomers was determined by ^1H NMR analysis (600 MHz, CDCl_3). The *para*-borylated product **9b** was obtained by further purification of the mixture by GPC (13.9 mg, 8% yield).

9b: ^1H NMR (600 MHz, CDCl_3) δ 7.76 (d, $J = 8.4$ Hz, 2H), 7.40 (d, $J = 8.4$ Hz, 2H), 3.51 (t, $J = 10.8$ Hz, 1H), 1.83 (d, $J = 12.6$ Hz, 1H), 1.72 (t, $J = 12$ Hz, 1H), 1.64 (q, $J = 15.0$ Hz, 2H), 1.42 (s, 3H), 1.39–1.37 (m, 1H), 1.33 (s, 12H), 1.29 (s, 3H), 1.02 (q, $J = 13.2$ Hz, 1H), 0.92 (q, $J = 12.0$ Hz, 2H), 0.87 (d, $J = 6.0$ Hz, 3H), 0.84 (q, $J = 12.0$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 154.8 (4°), 134.9 (CH), 125.1 (CH), 83.6 (4°), 73.0 (CH), 54.1 (4°), 45.5 (CH_2), 40.1 (4°), 34.8 (CH_2), 31.5 (CH), 28.2 (CH), 26.5 (CH_2), 24.9 (CH_3), 24.86 (CH_3), 24.78 (CH_3), 24.5 (CH_3), 22.0 (CH_3); HRMS (DART) m/z calcd for $\text{C}_{22}\text{H}_{36}\text{BO}_3$ $[\text{MH}]^+$: 359.2758, found 359.2768.

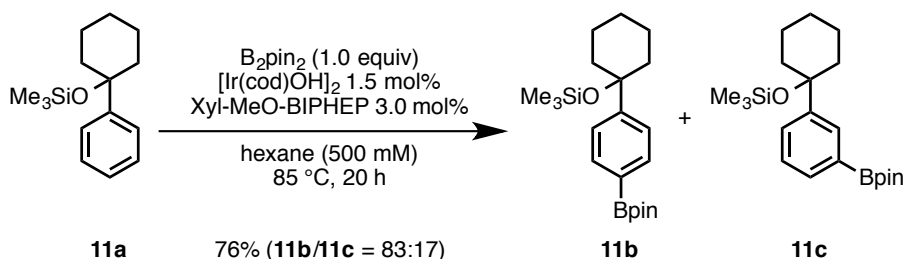
Para-selective C–H borylation of **10a**



A 20-mL glass vessel equipped with J. Young[®] O-ring tap containing a magnetic stirring bar was dried in an oven at 100 °C and then introduced into an argon-filled glove box while the vessel was hot. After cooling the vessel to room temperature, 1-phenylcyclohexan-1-ol **10a** (88.1 mg, 500 μ mol), B_2pin_2 (127 mg, 500 μ mol, 1.0 eq.), $[Ir(cod)OH]_2$ (4.8 mg, 7.5 μ mol, 1.5 mol%), Xyl-MeO-BIPHEP (10.4 mg, 15.0 μ mol, 3.0 mol%) and dry hexane (1.0 mL) were added to the vessel. The vessel was sealed with O-ring tap and then heated at 85 °C for 20 h in an 8-well reaction block with stirring. After cooling the reaction mixture to 0 °C in an ice bath and then warming to room temperature, the solvent was removed under reduced pressure. The borylation products were obtained by GPC (87.8 mg, 58% yield, p/m = 71:29). The ratio of isomers was determined by 1H NMR analysis (600 MHz, $CDCl_3$). The *para*-borylated product **10b** was obtained by further purification of the mixture by GPC (34.8 mg, 23% yield).

10b: 1H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 6.6 Hz, 2H), 1.87–1.61 (m, 10H), 1.31 (s, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.6 (4°), 134.8 (CH), 123.9 (CH), 83.7 (4°), 73.3 (4°), 38.7 (CH_2), 25.5 (CH_2), 24.8 (CH_3), 22.1 (CH_2); HRMS (DART) m/z calcd for $C_{18}H_{28}BO_3$ $[MH]^+$: 303.2132, found 303.2132.

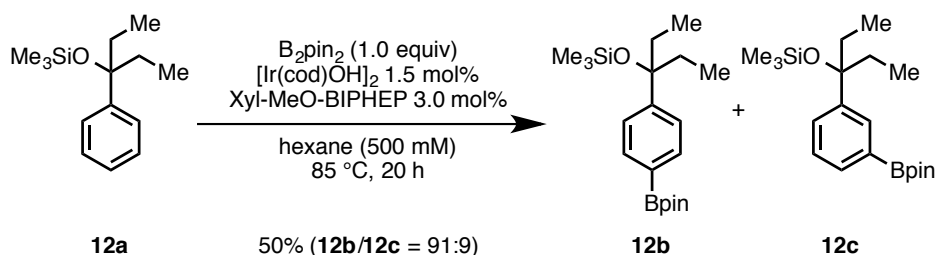
Para-selective C–H borylation of **11a**



A 20-mL glass vessel equipped with J. Young[®] O-ring tap containing a magnetic stirring bar was dried in an oven at 100 °C and then introduced into an argon-filled glove box while the vessel was hot. After cooling the vessel to room temperature, trimethyl((1-phenylcyclohexyl)oxy)silane **11a** (127 mg, 513 μ mol), B_2pin_2 (130 mg, 513 μ mol, 1.0 eq.), $[Ir(cod)OH]_2$ (4.9 mg, 7.7 μ mol, 1.5 mol%), Xyl-MeO-BIPHEP (10.7 mg, 15.4 μ mol, 3.0 mol%) and dry hexane (1.0 mL) were added to the vessel. The vessel was sealed with O-ring tap and then heated at 85 °C for 20 h in an 8-well reaction block with stirring. After cooling the reaction mixture to 0 °C in an ice bath and then warming to room temperature, the solvent was removed under reduced pressure. The borylation products were obtained by silica gel column chromatography (hexane/EtOAc = 17:1) (146 mg, 76% yield, p/m = 83:17). The ratio of isomers was determined by 1H NMR analysis (600 MHz, $CDCl_3$). The *para*-borylated product **11b** was obtained by further purification of the mixture by GPC (95.3 mg, 50% yield).

11b: 1H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 1.96–1.94 (m, 2 H), 1.80–1.71 (m, 4H), 1.65–1.63 (m, 1H), 1.55–1.53 (m, 2H), 1.35 (s, 12H), 1.27–1.20 (m, 1H), –0.11 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.1 (4°), 134.5 (CH), 127.1 (4°, br), 125.1 (CH), 83.6 (4°), 75.7 (4°), 39.1 (CH_3), 25.8 (CH_2), 24.9 (CH_3), 22.4 (CH_2), 2.2 (CH_3); HRMS (DART) m/z calcd for $C_{21}H_{36}BO_3Si$ $[MH]^+$: 375.2527, found 375.2529.

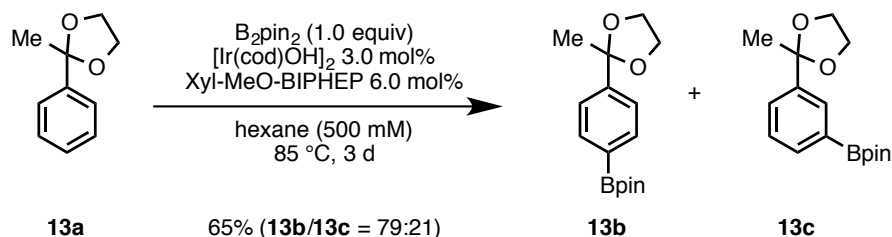
Para-selective C–H borylation of **12a**



A 20-mL glass vessel equipped with J. Young[®] O-ring tap containing a magnetic stirring bar was dried in an oven at 100 °C and then introduced into an argon-filled glove box while the vessel was hot. After cooling the vessel to room temperature, trimethyl((3-phenylpentan-3-yl)oxy)silane **12a** (118 mg, 513 μmol), B₂pin₂ (130 mg, 513 μmol, 1.0 eq.), [Ir(cod)OH]₂ (4.9 mg, 7.7 μmol, 1.5 mol%), Xyl-MeO-BIPHEP (10.7 mg, 15.4 μmol, 3.0 mol%) and dry hexane (1.0 mL) were added to the vessel. The vessel was sealed with O-ring tap and then heated at 85 °C for 20 h in an 8-well reaction block with stirring. After cooling the reaction mixture to 0 °C in an ice bath and then warming to room temperature, the solvent was removed under reduced pressure. The borylation products were obtained by silica gel column chromatography (hexane/EtOAc = 20:1) (91.3 mg, 50% yield, *p/m* = 91:9). The ratio of isomers was determined by ¹H NMR analysis (600 MHz, CDCl₃). The *para*-borylated product **12b** was obtained by further purification of the mixture by GPC (63.5 mg, 35% yield).

12b: ¹H NMR (600 MHz, CDCl₃) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 1.89–1.80 (m, 4H), 1.34 (s, 12H), 0.64 (t, *J* = 7.2 Hz, 6H), 0.16 (t, *J* = 3.0 Hz, 9H); ¹³C NMR (150 MHz, CDCl₃) δ 149.5 (4°), 134.2 (CH), 126.2 (4°, br), 125.4 (CH), 83.6 (4°), 81.5 (4°), 35.1 (CH₂), 24.9 (CH₃), 8.2 (CH₂), 2.4 (CH₃); HRMS (DART) *m/z* calcd for C₂₀H₃₆BO₃Si [MH]⁺: 363.2527, found 363.2526.

Para-selective C–H borylation of **13a**

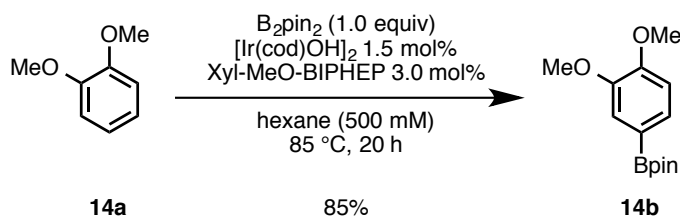


A 20-mL glass vessel equipped with J. Young[®] O-ring tap containing a magnetic stirring bar was dried in an oven at 100 °C and then introduced into an argon-filled glove box while the vessel was hot. After cooling the vessel to room temperature, 2-methyl-2-phenyl-1,3-dioxolane **13a** (82.1 mg, 500 μmol), B₂pin₂ (127 mg, 500 μmol, 1.0 eq.), [Ir(cod)OH]₂ (9.5 mg, 15 μmol, 3.0 mol%), Xyl-MeO-BIPHEP (20.8 mg, 30 μmol, 6.0 mol%) and dry hexane (1.0 mL) were added to the vessel. The vessel was sealed with O-ring tap and then heated at 85 °C for 3 days in an 8-well reaction block with stirring. After cooling the reaction mixture to 0 °C in an ice bath and then warming to room temperature, the solvent was removed under reduced pressure. The borylation products were obtained by silica gel column chromatography (hexane/EtOAc = 20:1) (94.2 mg, 65% yield, *p/m* = 79:21). The ratio of isomers was determined by ¹H NMR analysis (600 MHz, CDCl₃). The *para*-borylated product **13b** was obtained by further purification of the mixture by GPC (52.8 mg, 36% yield).

13b: ¹H NMR (600 MHz, CDCl₃) δ 7.80 (d, *J* = 7.8 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 4.03 (dd, *J* = 7.6, 6.3 Hz, 2H), 3.75 (dd, *J* = 7.6, 6.3 Hz, 2H), 1.65 (s, 3H), 1.34 (s, 12H). ¹³C NMR (150 MHz, CDCl₃) δ 146.3 (4°), 134.7 (CH), 128.4 (4°, br), 124.6 (CH), 108.8 (4°), 83.8 (4°), 64.4 (CH₂), 27.5 (CH₃), 24.8 (CH₃); HRMS (DART) *m/z* calcd for C₁₆H₂₄BO₄ [MH]⁺: 291.1768, found 291.1774.

4. C–H borylation of di-substituted arenes

C–H borylation of **14a**

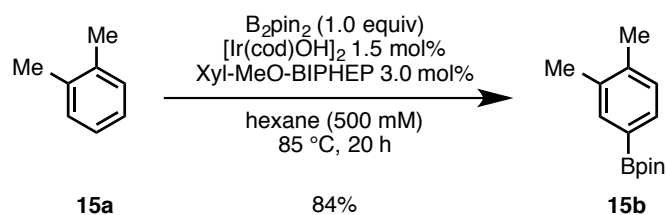


A 20-mL glass vessel equipped with J. Young[®] O-ring tap containing a magnetic stirring bar was dried in an oven at 100 °C and then introduced into an argon-filled glove box while the vessel was hot. After cooling the vessel to room temperature, 1,2-dimethoxybenzene **14a** (679 mg, 500 μmol), B_2pin_2 (127 mg, 500 μmol , 1.0 eq.), $[\text{Ir}(\text{cod})\text{OH}]_2$ (4.8 mg, 7.5 μmol , 1.5 mol%), Xyl-MeO-BIPHEP (10.4 mg, 15.0 μmol , 3.0 mol%) and dry hexane (1.0 mL) were added to the vessel. The vessel was sealed with O-ring tap and then heated at 85 °C for 20 h in an 8-well reaction block with stirring. After cooling the reaction mixture to 0 °C in an ice bath and then warming to room temperature, the solvent and remaining substrate were removed under reduced pressure. The product was obtained by silica gel column chromatography (hexane/EtOAc = 10:1) (113 mg, 85% yield).

14b¹⁴: ^1H NMR (600 MHz, CDCl_3) δ 7.43 (d, J = 7.8, Hz, 1H), 7.29 (s, 1H), 6.89 (d, J = 7.8 Hz, 1H), 3.92 (d, J = 14.4 Hz, 6H), 1.34 (s, 12H); ^{13}C NMR (150 MHz, CDCl_3) δ 151.5, 148.2, 128.4, 120.7, 116.4, 110.4, 83.5, 55.7, 55.6, 24.7; HRMS (DART) m/z calcd for $\text{C}_{14}\text{H}_{22}\text{BO}_4$ $[\text{MH}]^+$: 265.1611, found 265.1611.

(S14) Ishiyama, T.; Takagi, J.; Ishida, K.; Miyaura, N.; Anastasi, N. R.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 390.

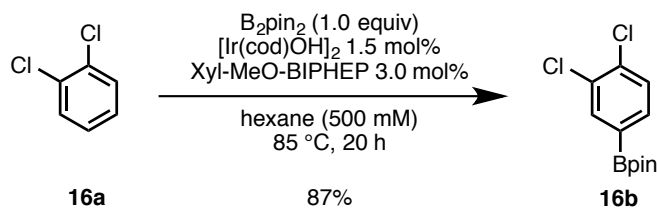
C–H borylation of **15a**



A 20-mL glass vessel equipped with J. Young[®] O-ring tap containing a magnetic stirring bar was dried in an oven at 100 °C and then introduced into an argon-filled glove box while the vessel was hot. After cooling the vessel to room temperature, *o*-xylene **15a** (53.1 mg, 500 μmol), B_2pin_2 (127 mg, 500 μmol , 1.0 eq.), $[\text{Ir}(\text{cod})\text{OH}]_2$ (4.8 mg, 7.5 μmol , 1.5 mol%), Xyl-MeO-BIPHEP (10.4 mg, 15.0 μmol , 3.0 mol%) and dry hexane (1.0 mL) were added to the vessel. The vessel was sealed with O-ring tap and then heated at 85 °C for 20 h in an 8-well reaction block with stirring. After cooling the reaction mixture to 0 °C in an ice bath and then warming to room temperature, the solvent and remaining substrate were removed under reduced pressure. The product was obtained by silica gel column chromatography (hexane/EtOAc = 10:1) (97.2 mg, 84% yield).

15b¹¹: ^1H NMR (600 MHz, CDCl_3) δ 7.58 (s, 1H), 7.55 (d, J = 7.8 Hz, 1H), 7.14 (d, J = 7.2 Hz, 1H), 2.27 (s, 3H), 2.26 (s, 3H), 1.33 (s, 12H); ^{13}C NMR (150 MHz, CDCl_3) δ 140.1, 135.9, 132.3, 129.1, 125.9, 83.5, 24.8, 20.0, 19.4; HRMS (DART) m/z calcd for $\text{C}_{14}\text{H}_{22}\text{BO}_2$ $[\text{MH}]^+$: 233.1713, found 233.1723.

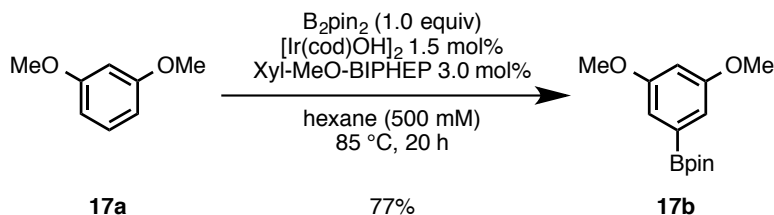
C–H borylation of **16a**



A 20-mL glass vessel equipped with J. Young[®] O-ring tap containing a magnetic stirring bar was dried in an oven at 100°C and then introduced into an argon-filled glove box while the vessel was hot. After cooling the vessel to room temperature, *o*-dichlorobenzene **16a** (73.5 mg, 500 μmol), B_2pin_2 (127 mg, 500 μmol , 1.0 eq.), $[\text{Ir}(\text{cod})\text{OH}]_2$ (4.8 mg, 7.5 μmol , 1.5 mol%), Xyl-MeO-BIPHEP (10.4 mg, 15.0 μmol , 3.0 mol%) and dry hexane (1.0 mL) were added to the vessel. The vessel was sealed with O-ring tap and then heated at 85°C for 20 h in an 8-well reaction block with stirring. After cooling the reaction mixture to 0°C in an ice bath and then warming to room temperature, the solvent and remaining substrate were removed under reduced pressure. The product was obtained by silica gel column chromatography (hexane/EtOAc = 10:1) (119 mg, 87% yield).

16b¹¹: ^1H NMR (600 MHz, CDCl_3) δ 7.87 (d, J = 1.8 Hz, 1H), 7.60 (dd, J = 7.8, 1.2 Hz, 1H), 7.44 (d, J = 7.8 Hz, 1H), 13.4 (s, 12H); ^{13}C NMR (150 MHz, CDCl_3) δ 136.5, 135.4, 133.7, 132.1, 130.0, 129.1, 84.3, 24.8; HRMS (DART) m/z calcd for $\text{C}_{12}\text{H}_{16}\text{BCl}_2\text{O}_2$ $[\text{MH}]^+$: 273.0620, found 273.0625.

C–H borylation of **17a**

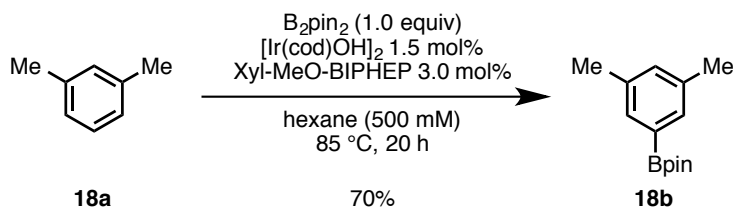


A 20-mL glass vessel equipped with J. Young[®] O-ring tap containing a magnetic stirring bar was dried in an oven at 100 °C and then introduced into an argon-filled glove box while the vessel was hot. After cooling the vessel to room temperature, *m*-dimethoxybenzene **17a** (69.1 mg, 500 μmol), B_2pin_2 (127 mg, 500 μmol , 1.0 eq.), $[\text{Ir}(\text{cod})\text{OH}]_2$ (4.8 mg, 7.5 μmol , 1.5 mol%), Xyl-MeO-BIPHEP (10.4 mg, 15.0 μmol , 3.0 mol%) and dry hexane (1.0 mL) were added to the vessel. The vessel was sealed with O-ring tap and then heated at 85 °C for 20 h in an 8-well reaction block with stirring. After cooling the reaction mixture to 0 °C in an ice bath and then warming to room temperature, the solvent and remaining substrate were removed under reduced pressure. The product was obtained by GPC (101 mg, 77% yield).

17b¹⁵: ^1H NMR (600 MHz, CDCl_3) δ 6.95 (d, J = 2.4 Hz, 2H), 6.57 (t, J = 2.4 Hz, 1H), 3.81 (s, 6H), 1.34 (s, 12H); ^{13}C NMR (150 MHz, CDCl_3) δ 160.3, 130.8, 111.5, 104.4, 83.8, 55.3, 24.8; HRMS (DART) m/z calcd for $\text{C}_{14}\text{H}_{22}\text{BO}_4$ $[\text{MH}]^+$: 265.1611, found 265.1611.

(S15) Tse, M. K.; Cho, J. -Y.; Smith, M. R., III *Org. Lett.* **2001**, 3, 2831.

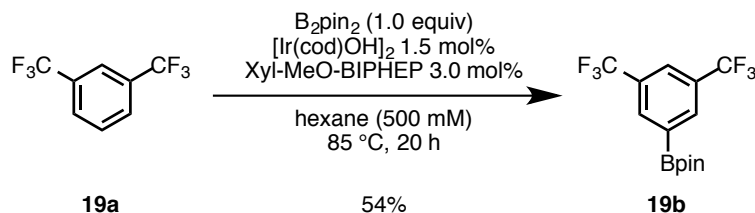
C–H borylation of **18a**



A 20-mL glass vessel equipped with J. Young[®] O-ring tap containing a magnetic stirring bar was dried in an oven at 100 °C and then introduced into an argon-filled glove box while the vessel was hot. After cooling the vessel to room temperature, *m*-xylene **18a** (53.1 mg, 500 μmol), B_2pin_2 (127 mg, 500 μmol , 1.0 eq.), $[\text{Ir}(\text{cod})\text{OH}]_2$ (4.8 mg, 7.5 μmol , 1.5 mol%), Xyl-MeO-BIPHEP (10.4 mg, 15.0 μmol , 3.0 mol%) and dry hexane (1.0 mL) were added to the vessel. The vessel was sealed with O-ring tap and then heated at 85 °C for 20 h in an 8-well reaction block with stirring. After cooling the reaction mixture to 0 °C in an ice bath and then warming to room temperature, the solvent and remaining substrate were removed under reduced pressure. The product was obtained by silica gel column chromatography (hexane/EtOAc = 10:1) (81.4 mg, 70% yield).

18b¹¹: ^1H NMR (600 MHz, CDCl_3) δ 7.44 (s, 2H), 7.10 (s, 1H), 2.32 (s, 6H), 1.34 (s, 12H); ^{13}C NMR (150 MHz, CDCl_3) δ 137.1, 132.9, 132.4, 128.4, 83.6, 24.8, 21.1; HRMS (DART) m/z calcd for $\text{C}_{14}\text{H}_{21}\text{BO}_2$ $[\text{MH}]^+$: 233.1713, found 233.1713.

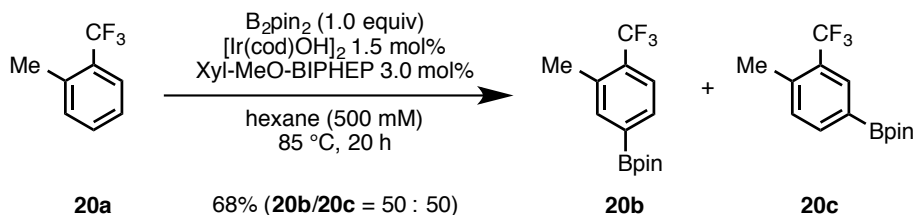
C–H borylation of **19a**



A 20-mL glass vessel equipped with J. Young® O-ring tap containing a magnetic stirring bar was dried in an oven at 100 °C and then introduced into an argon-filled glove box while the vessel was hot. After cooling the vessel to room temperature, 1,3-bis(trifluoromethyl)benzene **19a** (107 mg, 500 μmol), B_2pin_2 (127 mg, 500 μmol , 1.0 eq.), $[\text{Ir}(\text{cod})\text{OH}]_2$ (4.8 mg, 7.5 μmol , 1.5 mol%), Xyl-MeO-BIPHEP (10.4 mg, 15.0 μmol , 3.0 mol%) and dry hexane (1.0 mL) were added to the vessel. The vessel was sealed with O-ring tap and then heated at 85 °C for 20 h in an 8-well reaction block with stirring. After cooling the reaction mixture to 0 °C in an ice bath and then warming to room temperature, the solvent and remaining substrate were removed under reduced pressure. The product was obtained by silica gel column chromatography (CHCl_3) (91.0 mg, 54% yield).

19b¹²: ^1H NMR (600 MHz, CDCl_3) δ 8.24 (s, 2H), 7.95 (s, 1H), 1.37 (s, 12H); ^{13}C NMR (150 MHz, CDCl_3) δ 134.7, 131.6, 130.9 (q, $^2J_{\text{CF}} = 33.2$ Hz), 124.7 (q, $^3J_{\text{CF}} = 2.9$ Hz), 123.5 (q, $^1J_{\text{CF}} = 273$ Hz), 84.9, 24.8; HRMS (DART) m/z calcd for $\text{C}_{14}\text{H}_{15}\text{BF}_6\text{O}_2$ $[\text{MH}]^+$: 341.1148, found 341.1152.

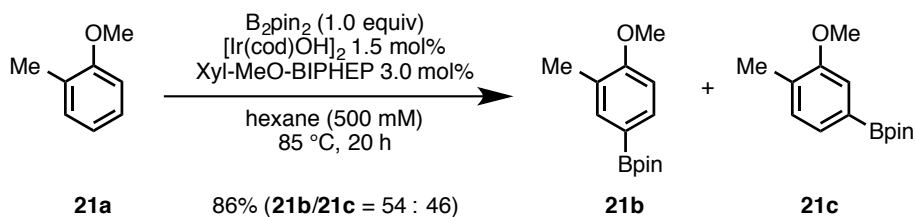
C–H borylation of **20a**



A 20-mL glass vessel equipped with J. Young[®] O-ring tap containing a magnetic stirring bar was dried in an oven at 100 °C and then introduced into an argon-filled glove box while the vessel was hot. After cooling the vessel to room temperature, 1-methyl-2-(trifluoromethyl)benzene **20a** (80.1 mg, 500 μmol), B_2pin_2 (127 mg, 500 μmol , 1.0 eq.), $[\text{Ir}(\text{cod})\text{OH}]_2$ (4.8 mg, 7.5 μmol , 1.5 mol%), Xyl-MeO-BIPHEP (10.4 mg, 15.0 μmol , 3.0 mol%) and dry hexane (1.0 mL) were added to the vessel. The vessel was sealed with O-ring tap and then heated at 85 °C for 20 h in an 8-well reaction block with stirring. After cooling the reaction mixture to 0 °C in an ice bath and then warming to room temperature, the solvent and remaining substrate were removed under reduced pressure. The borylation products were obtained by silica gel column chromatography (hexane/EtOAc = 10:1) (97.7 mg, 98% yield, **20b/20c** = 50:50). The ratio of isomers was determined by ^1H NMR analysis (600 MHz, CDCl_3)¹⁶.

(S16) Tobisu, M.; Nakamura, R.; Kita, Y.; Chatani, N. *J. Am. Chem. Soc.* **2009**, *131*, 3174.

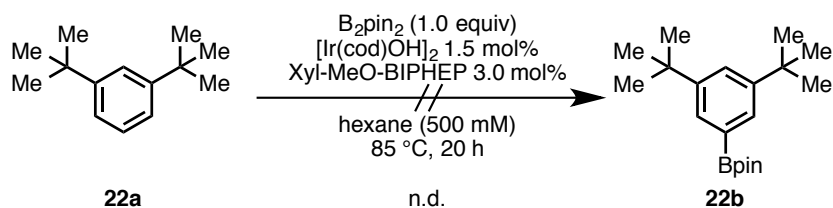
C–H borylation of **21a**



A 20-mL glass vessel equipped with J. Young[®] O-ring tap containing a magnetic stirring bar was dried in an oven at 100 °C and then introduced into an argon-filled glove box while the vessel was hot. After cooling the vessel to room temperature, *o*-cresol **21a** (61.1 mg, 500 μmol), B_2pin_2 (127 mg, 500 μmol , 1.0 eq.), $[\text{Ir}(\text{cod})\text{OH}]_2$ (4.8 mg, 7.5 μmol , 1.5 mol%), Xyl-MeO-BIPHEP (10.4 mg, 15.0 μmol , 3.0 mol%) and dry hexane (1.0 mL) were added to the vessel. The vessel was sealed with O-ring tap and then heated at 85 °C for 20 h in an 8-well reaction block with stirring. After cooling the reaction mixture to 0 °C in an ice bath and then warming to room temperature, the solvent and remaining substrate were removed under reduced pressure. The borylation products were obtained by silica gel column chromatography (hexane/EtOAc = 10:1) (107 mg, 86% yield, **21b**/**21c** = 54:46). The ratio of isomers was determined by ^1H NMR analysis (600 MHz, CDCl_3)^{9,17}.

(S17) Guerrand, H. D. S.; Marciasini, L. D.; Jousseume, M.; Vaultier, M.; Pucheault, M. *Chem. Eur. J.* **2014**, 20, 5573.

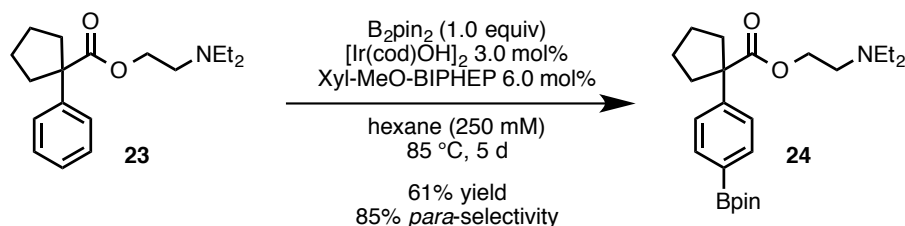
C–H borylation of **22a**



A 20-mL glass vessel equipped with J. Young[®] O-ring tap containing a magnetic stirring bar was dried in an oven at 100 °C and then introduced into an argon-filled glove box while the vessel was hot. After cooling the vessel to room temperature, *m*-di-*tert*-butylbenzene **22a** (95.2 mg, 500 μmol), B_2pin_2 (127 mg, 500 μmol , 1.0 eq.), $[\text{Ir}(\text{cod})\text{OH}]_2$ (4.8 mg, 7.5 μmol , 1.5 mol%), Xyl-MeO-BIPHEP (10.4 mg, 15.0 μmol , 3.0 mol%) and dry hexane (1.0 mL) were added to the vessel. The vessel was sealed with O-ring tap and then heated at 85 °C for 20 h in an 8-well reaction block with stirring. After cooling the reaction mixture to 0 °C in an ice bath and then warming to room temperature, the solvent was removed under reduced pressure. The residue was analyzed by ^1H NMR, but any peaks of borylated product were not observed.

5. Synthesis of caramiphen derivatives via *para*-selective C–H borylation

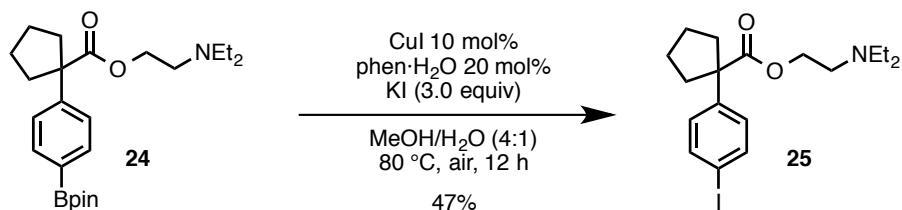
Para-selective C–H borylation of **23**



A 20-mL glass vessel equipped with J. Young® O-ring tap containing a magnetic stirring bar was dried in an oven at 100 °C and then introduced into an argon-filled glove box while the vessel was hot. After cooling the vessel to room temperature, B_2pin_2 (127 mg, 500 μ mol, 1.0 eq.), $[Ir(cod)OH]_2$ (9.5 mg, 15.0 μ mol, 3.0 mol%), Xyl-MeO-BIPHEP (20.8 mg, 30.0 μ mol, 6.0 mol%) and dry hexane (1.5 mL) were added to the vessel. Then, a solution of caramiphen (**23**, 145 mg, 500 μ mol) in 500 μ L of hexane was added to the mixture, and the vessel was sealed with O-ring tap and covered with aluminum foil. The reaction mixture was heated at 85 °C for 5 days in an 8-well reaction block with stirring. After cooling the reaction mixture to room temperature, the solvent was removed under reduced pressure. The ratio of isomers was determined by 1H NMR analysis (600 MHz, $CDCl_3$) of the crude mixture (*p/m* = 85:15). The *para*-borylated product **24** was obtained by GPC as a white solid (127 mg, 61% yield).

24: 1H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, J = 7.8 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 4.07 (t, J = 6.0 Hz, 2H), 2.66–2.62 (m, 2H), 2.59 (t, J = 6.6 Hz, 2H), 2.45 (q, J = 7.2 Hz, 4H), 1.94–1.89 (m, 2H), 1.73–1.71 (m, 4H), 1.33 (s, 12H), 0.95 (t, J = 7.2 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.6 (4°), 146.5 (4°), 134.7 (CH), 127.0 (4°, br), 126.2 (CH), 83.7 (4°), 63.3 (CH₂), 59.3 (4°), 50.9 (CH₂), 47.5 (CH₂), 36.1 (CH₂), 24.8 (CH₃), 23.6 (CH₂), 12.0 (CH₃); HRMS (DART) m/z calcd for $C_{24}H_{39}BNO_4$ $[MH]^+$: 416.2972, found 416.2979.

Synthesis of **25** (iodination¹⁸ of **24**)

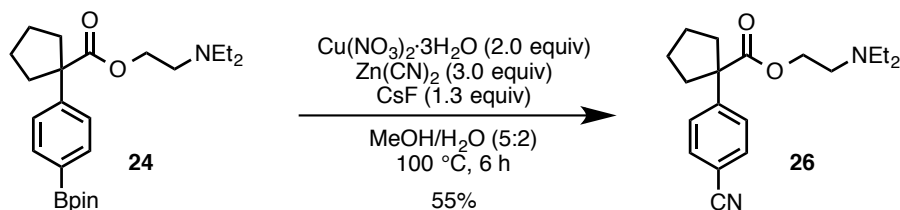


To a 7-mL screw-cap tube containing a magnetic stirring bar were added **24** (41.5 mg, 100 μ mol), CuI (1.9 mg, 10.0 μ mol, 10 mol%), 1,10-phenanthroline monohydrate (4.0 mg, 20.0 μ mol, 20 mol%), KI (49.9 mg, 300 μ mol, 3.0 eq.) and MeOH (800 μ L). After stirring the mixture under air for several minutes, H₂O (200 μ L) was added to the vessel and then the vessel was sealed. After stirring at 80 °C for 12 h in an oil bath, H₂O was added and the resulting mixture was extracted with EtOAc then CHCl₃. The organic phases were combined, washed with brine, dried with anhydrous Na₂SO₄, filtrated and concentrated under reduced pressure. The residue was subjected to preparative thin layer chromatography (PTLC, CHCl₃/MeOH = 10:1) to afford **25** (19.3 mg, 47% yield) as colorless oil.

25: ¹H NMR (600 MHz, CDCl₃) δ 7.62 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 9.0 Hz, 2H), 4.08 (t, J = 6.6 Hz, 2H), 2.63–2.58 (m, 4 H), 2.46 (q, J = 7.2 Hz, 4 H), 1.88–1.83 (m, 2H), 1.75–1.71 (m, 4H), 0.96 (t, J = 7.2 Hz, 6H); ¹³C NMR (150 MHz, CDCl₃) δ 175.4 (4°), 143.1 (4°), 137.2 (CH), 129.0 (CH), 92.2 (4°), 63.5 (CH₂), 58.8 (4°), 50.9 (CH₂), 47.4 (CH₂), 36.0 (CH₂), 23.5 (CH₂), 12.0 (CH₃); HRMS (DART) m/z calcd for C₁₈H₂₇INO₂ [MH]⁺: 416.1087, found 416.1087.

(S18) Partridge, B. M.; Hartwig, J. F. *Org. Lett.* **2013**, *15*, 140.

Synthesis of **26** (cyanation¹⁹ of **24**)

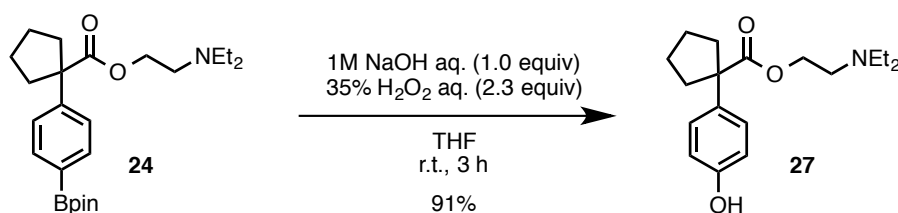


To a 7-mL screw-cap tube containing a magnetic stirring bar were added **24** (41.5 mg, 100 μmol), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (48.7 mg, 202 μmol , 2.0 eq.), $\text{Zn}(\text{CN})_2$ (35.2 mg, 300 μmol , 3.0 eq.), CsF (19.1 mg, 126 μmol , 1.3 eq.), MeOH (500 μL) and H_2O (200 μL). After sealing, the mixture was heated at $100\text{ }^\circ\text{C}$ in an oil bath for 6 h. After cooling the mixture to room temperature, saturated NH_4Cl aq. and EtOAc were added to the vessel and the mixture was extracted with EtOAc . The organic phase was washed with brine, dried with anhydrous Na_2SO_4 , filtrated and concentrated under reduced pressure. The residue was subjected to preparative thin layer chromatography (PTLC, $\text{CHCl}_3/\text{MeOH} = 10:1$) to afford **26** (17.4 mg, 55% yield) as colorless oil.

26: ^1H NMR (600 MHz, CDCl_3) δ 7.60 (d, $J = 8.4$ Hz, 2H), 7.47 (d, $J = 8.4$ Hz, 2H), 4.09 (t, $J = 6.0$ Hz, 2H), 2.68–2.65 (m, 2H), 2.57 (t, $J = 6.0$ Hz, 2H), 2.45 (q, $J = 7.2$ Hz, 4H), 1.90–1.86 (m, 2H), 1.78–1.73 (m, 4H), 0.94 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (150 MHz, CDCl_3) δ 174.7 (4°), 148.7 (4°), 132.0 (CH), 127.8 (CH), 118.8 (4°), 110.6 (4°), 63.7 (CH_2), 59.3 (4°), 51.0 (CH_2), 47.4 (CH_2), 36.1 (CH_2), 23.5 (CH_2), 12.0 (CH_3); HRMS (DART) m/z calcd for $\text{C}_{19}\text{H}_{27}\text{N}_2\text{O}_2$ $[\text{MH}]^+$: 315.2073, found 315.2078.

(S19) Liskey, C. W.; Liao, X.; Hartwig, J. F. *J. Am. Chem. Soc.* **2010**, *132*, 11389.

Synthesis of **27** (oxidation²⁰ of **24**)

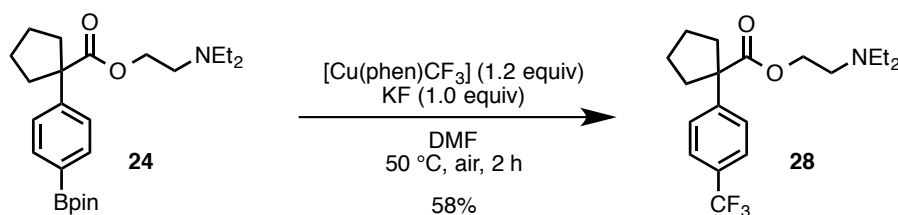


To a 7-mL screw-cap tube containing a magnetic stirring bar were added **24** (41.5 mg, 100 μ mol) and THF (400 μ L). After stirring for 1 minute, 1M NaOH aq. (100 μ L, 1.0 eq.) and 35% H₂O₂ aq. (20 μ L, 2.3 eq.) were added to the vessel then the mixture was stirred at room temperature under air. After 3 h, water was added and the resulting mixture was extracted with EtOAc. The organic phase was dried with anhydrous Na₂SO₄, filtrated and concentrated under reduced pressure. The residue was subjected to preparative thin layer chromatography (PTLC, CHCl₃/MeOH = 10:1) to afford **27** (27.9 mg, 91% yield) as a colorless crystal.

27: ¹H NMR (600 MHz, CDCl₃) δ 7.17 (d, J = 9.0 Hz, 2H), 6.66 (d, J = 8.4 Hz, 2H), 4.13 (t, J = 5.4 Hz, 2H), 2.68 (t, J = 6.0 Hz, 2H), 2.63–2.59 (m, 2H), 2.52 (q, J = 7.2 Hz, 4H), 1.87–1.84 (m, 2H), 1.73–1.68 (m, 4H), 0.99 (t, J = 6.6 Hz, 6H); ¹³C NMR (150 MHz, CDCl₃) δ 176.4 (4°), 155.2 (4°), 134.4 (4°), 128.0 (CH), 115.2 (CH), 62.6 (CH₂), 58.3 (4°), 50.4 (CH₂), 47.1 (CH₂), 36.0 (CH₂), 23.5 (CH₂), 11.2 (CH₃); HRMS (DART) m/z calcd for C₁₈H₂₈NO₃ [MH]⁺: 306.2069, found 306.2069; mp: 117.3–118.4 °C.

(S20) Liskey, C. W.; Hartwig, J. F. *J. Am. Chem. Soc.* **2013**, *135*, 3375.

Synthesis of **28** (trifluoromethylation²¹ of **24**)

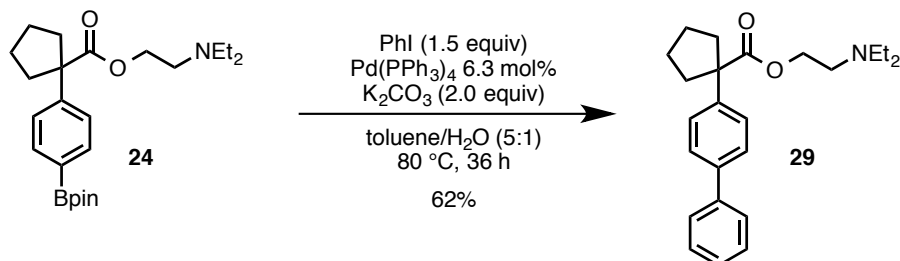


To a 7-mL screw-cap tube containing a magnetic stirring bar were added **24** (41.5 mg, 100 μmol), $[\text{Cu}(\text{phen})\text{CF}_3]$ (37.5 mg, 120 μmol , 1.2 eq.) and KF (5.8 mg, 100 μmol , 1.0 eq.) in an argon-filled glove box. After sealing with a rubber septum, the vessel was moved outside of the glove box. Dry DMF was added to the vessel and air dried by CaCl_2 was bubbled for 3 min. After sealing with a cap, the reaction mixture was stirred at 50 °C for 2 h in an oil bath. After water was added, the resulting mixture was extracted with EtOAc . The organic phase was washed with brine, dried with anhydrous Na_2SO_4 , filtrated and concentrated under reduced pressure. The residue was subjected to preparative thin layer chromatography (PTLC, $\text{CHCl}_3/\text{MeOH} = 10:1$) to afford **28** (20.7 mg, 58% yield) as colorless oil.

28: ^1H NMR (600 MHz, CDCl_3) δ 7.56 (d, $J = 8.4$ Hz, 2H), 7.48 (d, $J = 7.8$ Hz, 2H), 4.09 (t, $J = 6.0$ Hz, 2H), 2.70–2.66 (m, 2H), 2.58 (t, $J = 6.0$ Hz, 2H), 2.44 (q, $J = 7.2$ Hz, 4H), 1.93–1.88 (m, 2H), 1.77–1.17 (m, 4H), 0.94 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (150 MHz, CDCl_3) δ 175.2 (4°), 147.4 (4°), 128.9 (q, $^2J_{\text{CF}} = 33.0$ Hz, 4°), 127.3 (CH), 125.1 (q, $^3J_{\text{CF}} = 4.2$ Hz, CH), 124.2 (q, $^1J_{\text{CF}} = 270$ Hz, 4°), 63.6 (CH_2), 59.1 (4°), 51.0 (CH_2), 47.4 (CH_2), 36.2 (CH_2), 23.6 (CH_2), 12.0 (CH_3); HRMS (DART) m/z calcd for $\text{C}_{19}\text{H}_{27}\text{F}_3\text{NO}_2$ $[\text{MH}]^+$: 358.1994, found 358.1999.

(S21) Litvinas, N. D.; Fier, P. S.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2012**, 51, 536.

Synthesis of **29** (Suzuki–Miyaura coupling reaction²² of **24**)



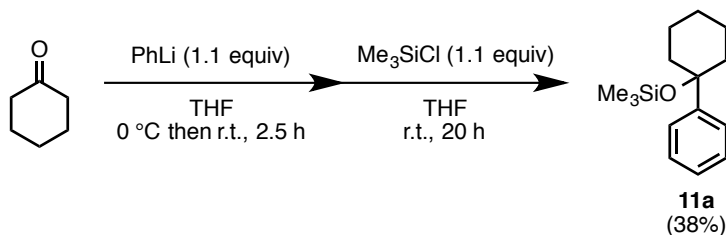
To a 2-mL screw-cap tube containing a magnetic stirring bar were added **24** (41.5 mg, 100 μ mol), Pd(PPh₃)₄ (2.7 mg, 2.3 μ mol, 2.3 mol%) and K₂CO₃ (27.8 mg, 201 μ mol, 2.0 eq.). The vessel was filled with nitrogen, and iodobenzene (31.3 mg, 153 μ mol, 1.5 eq.), dry toluene (500 μ L) and degassed H₂O (100 μ L) were added. After sealing, the reaction mixture was heated at 80 °C in an oil bath with stirring. After 22 h, Pd(PPh₃)₄ (4.6 mg, 4.0 μ mol, 4.0 mol%) was added and the vessel was kept 80 °C for 14 h. After cooling to room temperature, the resulting mixture was extracted with EtOAc. The organic phase was washed with brine, dried with Na₂SO₄, filtrated and concentrated under reduced pressure. The residue was subjected to preparative thin layer chromatography (PTLC, CHCl₃/MeOH = 10:1) to afford **29** (22.6 mg, 62% yield) as colorless oil.

29: ¹H NMR (600 MHz, CDCl₃) δ 7.57 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 9.0 Hz, 2H), 7.44–7.41 (m, 4H), 7.33 (tt, J = 7.2, 1.8 Hz, 1H), 4.11 (t, J = 6.6 Hz, 2H), 2.70–2.67 (m, 2H), 2.61 (t, J = 6.0 Hz, 2H), 2.46 (q, J = 7.2 Hz, 4H), 1.97–1.93 (m, 2H), 1.78–1.73 (m, 4H), 0.95 (t, J = 7.2 Hz, 6H); ¹³C NMR (150 MHz, CDCl₃) δ 175.8 (4°), 142.4 (4°), 140.8 (4°), 139.5 (4°), 128.7 (CH), 127.3 (CH), 127.2 (CH), 127.0 (CH), 126.9 (CH), 63.4 (CH₂), 58.9 (4°), 50.9 (CH₂), 47.4 (CH₂), 36.1 (CH₂), 23.6 (CH₂), 12.0 (CH₃); HRMS (DART) m/z calcd for C₂₄H₃₂NO₂ [MH]⁺: 366.2433, found 366.2434.

(S22) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, 95, 2457.

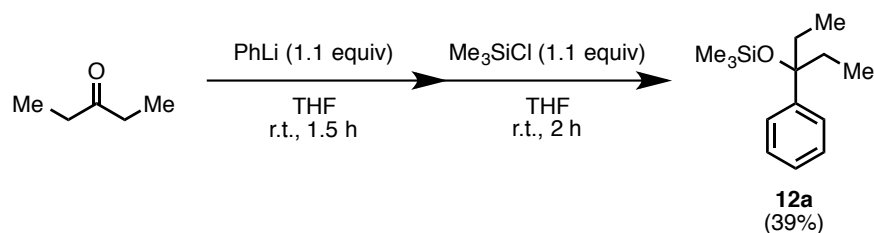
6. Preparation of starting materials

Preparation of trimethyl(1-phenyl-1-cyclohexyloxy)silane **11a**



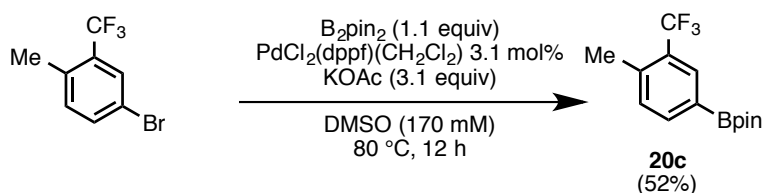
A 10-mL Schlenk tube equipped with a rubber septum containing a magnetic stirring bar was dried with a heat-gun under reduced pressure and then filled with nitrogen after cooling to room temperature. Cyclohexanone (95.6 mg, 974 μ mol) and dry THF (5.0 mL) were added to the vessel then the mixture was cooled at 0 °C. After phenyllithium in di-*n*-butyl ether (580 μ L, 1.9 M, 1.1 mmol, 1.1 eq.) was added at 0 °C, the reaction mixture was stirred at 0 °C for 30 minutes and at room temperature for 2 h. Chlorotrimethylsilane (140 μ L, 1.1 mmol, 1.1 eq.) was added and the mixture stirred for 20 h. After water was added slowly, the organic phase and aqueous phase were separated and the aqueous phase was extracted with EtOAc. The organic phases were combined, dried with anhydrous MgSO₄ and filtrated. After evaporation under reduced pressure, the residue was subjected to preparative thin layer chromatography (PTLC, hexane/EtOAc = 7:1) to afford **11a** (91.0 mg, 38% yield) as colorless oil. **11a**: ¹H NMR (600 MHz, CDCl₃) δ 7.45 (td, *J* = 7.8, 4.8 Hz, 2H), 7.31 (tt, *J* = 7.8, 1.8 Hz, 2H), 7.22 (tt, *J* = 7.2, 1.2 Hz, 1H), 1.98–1.97 (m, 2H), 1.81–1.73 (m, 4H), 1.66–1.63 (m, 1H), 1.57–1.54 (m, 2H), 1.27–1.21 (m, 1H), –0.12 (s, 9H); ¹³C NMR (150 MHz, CDCl₃) δ 148.8 (4°), 127.9 (CH), 126.7 (CH), 125.8 (CH), 75.5 (4°), 39.1 (CH₂), 25.8 (CH₂), 22.5 (CH₂), 2.1 (CH₃); HRMS (DART) *m/z* calcd for C₁₅H₂₅OSi [MH]⁺: 249.1675, found 249.1673.

Preparation of trimethyl(3-phenyl-3-pentoxy)silane **12a**



A 10-mL Schlenk tube equipped with a rubber septum containing a magnetic stirring bar was dried with a heat-gun under reduced pressure and then filled with nitrogen after cooling to room temperature. To the vessel were added 3-pentanone (171 mg, 2.0 mmol) and dry THF (5.0 mL) then the mixture was cooled at 0 °C. After phenyllithium in di-*n*-butyl ether (580 μ L, 1.9 M, 1.1 mmol, 1.1 eq.) was added at 0 °C, the reaction mixture was stirred at room temperature for 1.5 h. Chlorotrimethylsilane (140 μ L, 1.1 mmol, 1.1 eq.) was added and the mixture stirred for 2 h. After water was added slowly, the organic phase and aqueous phase were separated and the aqueous phase was extracted with EtOAc. The organic phases were combined, washed with brine, dried with anhydrous Na_2SO_4 and filtrated. After evaporation under reduced pressure, the residue was subjected to preparative thin layer chromatography (PTLC, hexane/EtOAc = 10:1) to afford **12a** (183 mg, 39% yield) as colorless oil. **12a**: ^1H NMR (600 MHz, CDCl_3) δ 7.33 (td, J = 7.2, 1.8 Hz, 2H), 7.29 (dt, J = 6.6, 2.4 Hz, 2H), 7.18 (tt, J = 7.2, 1.8 Hz, 1H), 1.92–1.79 (m, 4H), 0.65 (t, J = 7.8 Hz, 6H), 0.163 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ 146.1 (4°), 127.6 (CH), 125.9 (CH), 125.8 (CH), 81.4 (4°), 35.2 (CH_2), 8.2 (CH_3), 2.4 (CH_3); HRMS (EI) m/z calcd for $\text{C}_{13}\text{H}_{21}\text{OSi} [\text{M}-\text{CH}_3]^+$: 221.1362, found 221.1363.

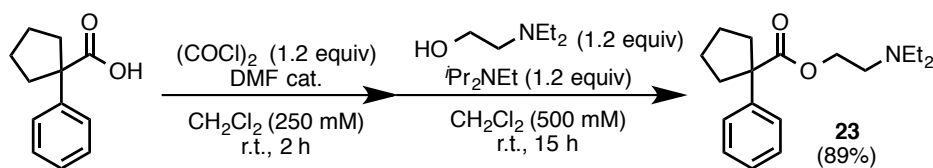
Preparation of 4-methyl-3-(trifluoromethyl)phenylboronic acid pinacol ester **20c**^{19a}



A 20-mL Schlenk tube equipped with a rubber septum containing a magnetic stirring bar was dried with a heat-gun under reduced pressure and then filled with nitrogen after cooling to room temperature. To the vessel were added 1-bromo-3-trifluoromethyl-4-methylbenzene (483 mg, 2.02 mmol), B_2pin_2 (560 mg, 2.21 mmol, 1.1 eq.), $\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$ (51.4 mg, 62.9 μmol , 3.1 mol%), potassium acetate (607 mg, 6.18 mmol, 3.1 eq.) and dry DMSO (12 mL). The vessel was heated at $80\text{ }^\circ\text{C}$ for 12 h in an oil bath with stirring. After cooling the reaction mixture to room temperature, water was added to the reaction mixture. The mixture was extracted with EtOAc and then the organic phase was washed with brine and dried with anhydrous Na_2SO_4 . After filtration through silica gel and Celite[®], the solution was concentrated under reduced pressure. The product **20c** was obtained by silica gel column chromatography (hexane/EtOAc = 10:1) as a white solid (299 mg, 52% yield).

20c: ^1H NMR (600 MHz, CDCl_3) δ 8.03 (s, 1H), 7.84 (d, $J = 7.2$ Hz, 1H), 7.28 (d, $J = 7.8$ Hz, 1H), 2.50 (d, $J = 1.8$ Hz, 3H), 1.35 (s, 12H); ^{13}C NMR (150 MHz, CDCl_3) δ 139.8 (4°), 138.0 (CH), 132.0 (q, $^3J_{\text{CF}} = 4.4$ Hz, CH), 131.3 (CH), 128.4 (q, $^2J_{\text{CF}} = 30.2$ Hz, 4°), 124.7 (q, $^1J_{\text{CF}} = 273$ Hz, 4°), 84.1 (4°), 24.8 (CH_3), 19.6 (CH_3); HRMS (DART) m/z calcd for $\text{C}_{14}\text{H}_{19}\text{BF}_3\text{O}_2$ $[\text{MH}]^+$: 287.1430, found 287.1435; mp: 95.8–97.1 $^\circ\text{C}$.

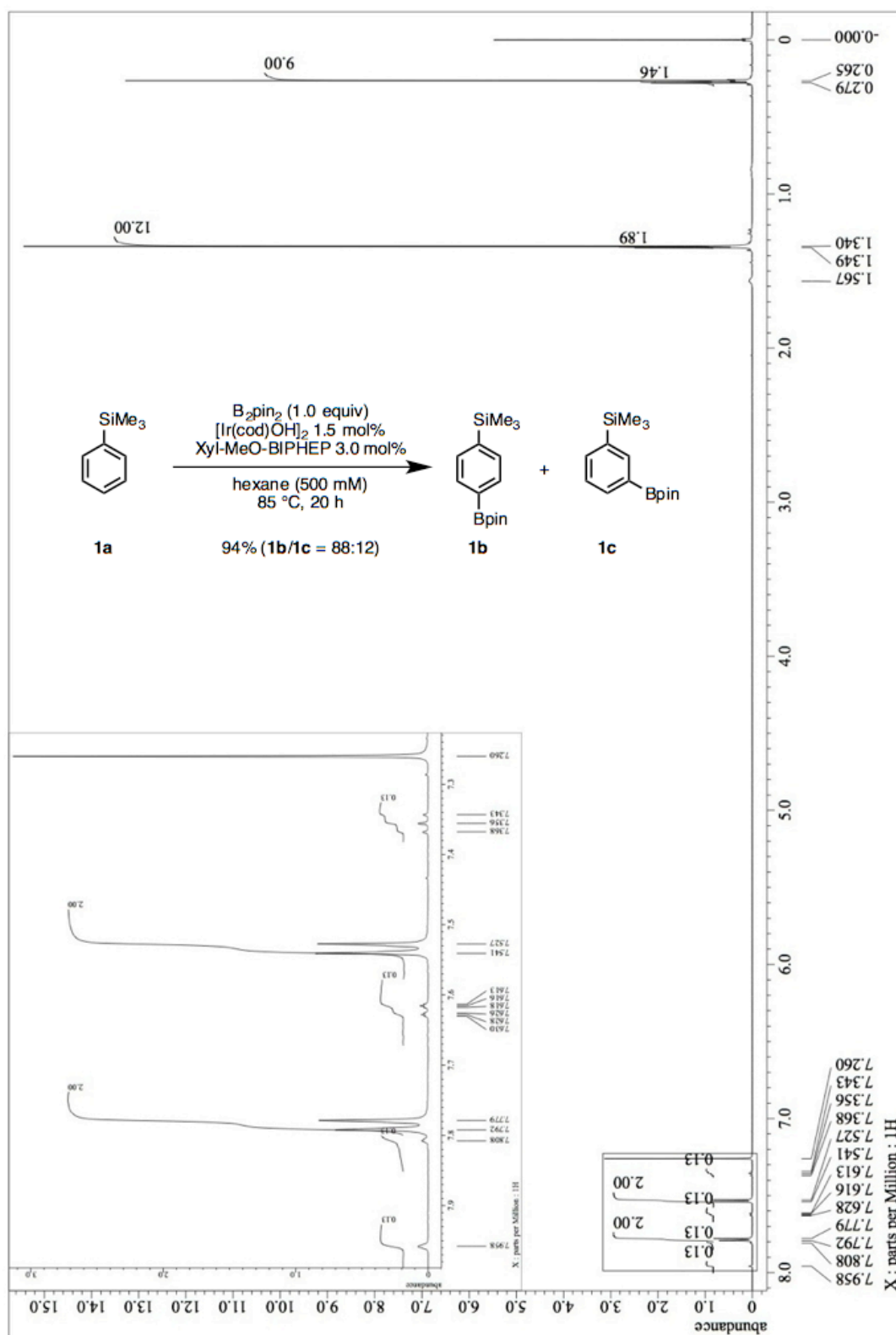
Preparation of caramiphen **23**



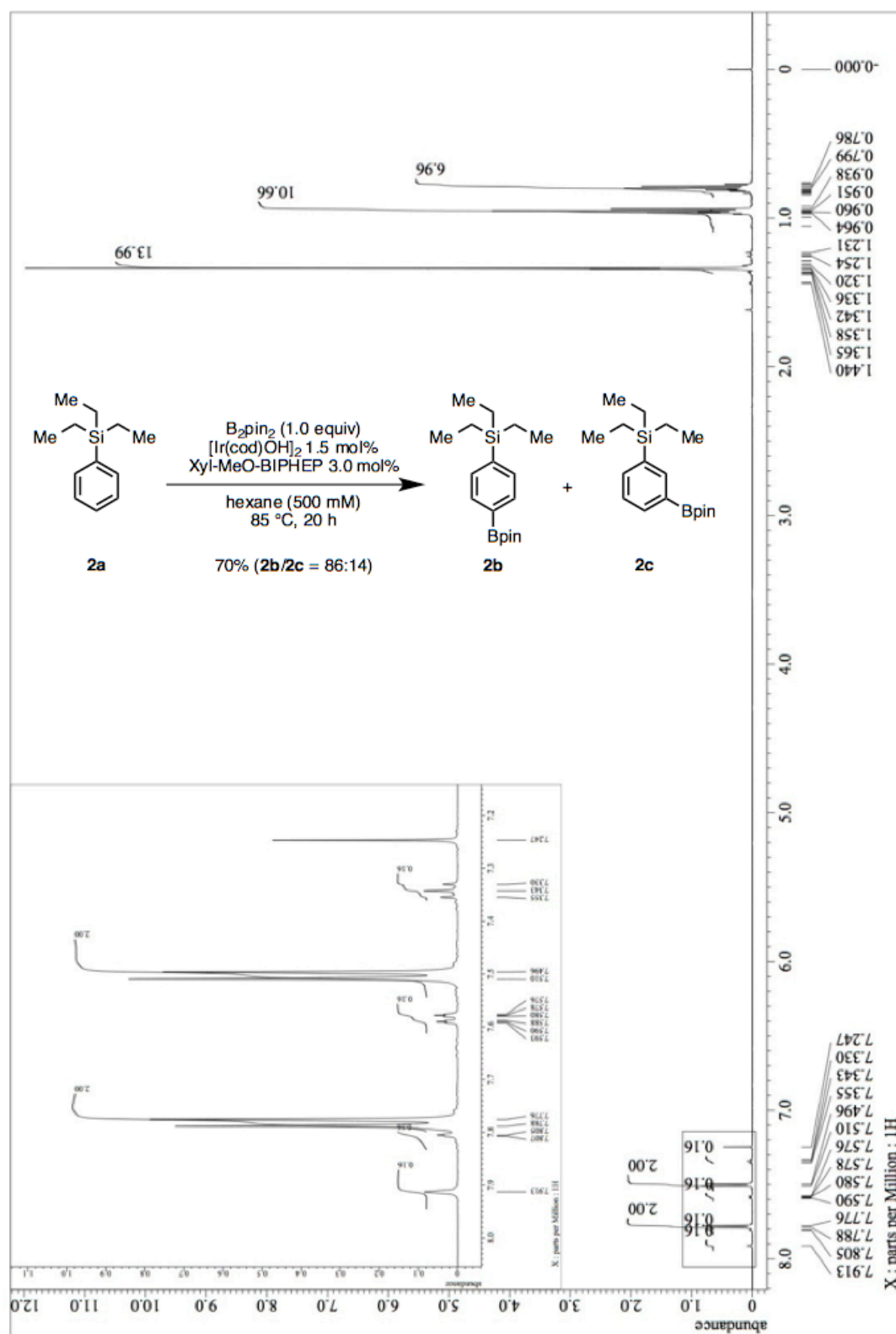
To a 100-mL round-bottom flask were added 1-phenylcyclopentane-1-carboxylic acid (2.9 g, 15.0 mmol) in 60 mL of CH_2Cl_2 . Then oxalyl chloride (2.3 g, 18.0 mmol, 1.2 eq.) and 3 drops of DMF were added under air and the mixture was stirred at room temperature. After 1 h, 3 drops of DMF were added and the reaction mixture was kept stirring for 1 h. The solvent and excess oxalyl chloride were removed under reduced pressure. The residue was dissolved in 30 mL of CH_2Cl_2 , and 2-(diethylamino)ethanol (2.4 mL, 18.0 mmol, 1.2 eq.) and diisopropylethylamine (3.4 mL, 19.5 mmol, 1.3 eq.) were added. The reaction mixture was stirred for 15 h at room temperature and then saturated NaHCO_3 aq. was added for quenching. Water was added to the resulting mixture, then extracted with CH_2Cl_2 , dried with anhydrous Na_2SO_4 , filtrated and concentrated under reduced pressure. Caramiphen **23** was obtained by silica gel column chromatography (hexane/EtOAc/ Et_3N = 18:1:1) (3.8 g, 89% yield) as colorless oil.

23: ^1H NMR (600 MHz, CDCl_3) δ 7.36 (td, J = 8.4, 1.2 Hz, 2H), 7.30 (tt, J = 7.2, 1.8 Hz, 2H), 7.22 (tt, J = 7.2, 1.2 Hz, 1H), 4.08 (t, J = 6.0 Hz, 2H), 2.67–2.63 (m, 2H), 2.59 (t, J = 6.6 Hz, 2H), 2.45 (q, J = 7.2 Hz, 4 H), 1.92–1.88 (m, 2H), 1.75–1.72 (m, 4H), 0.95 (t, J = 7.2 Hz, 6H); ^{13}C NMR (150 MHz, CDCl_3) δ 175.9 (4°), 143.3 (4°), 128.2 (CH), 126.9 (CH), 126.6 (CH), 63.3 (CH_2), 59.1 (4°), 50.9 (CH_2), 47.4 (CH_2), 36.1 (CH_2), 23.6 (CH_2), 12.0 (CH_3); HRMS (DART) m/z calcd for $\text{C}_{18}\text{H}_{28}\text{NO}_2$ $[\text{MH}]^+$: 290.2120, found 290.2118.

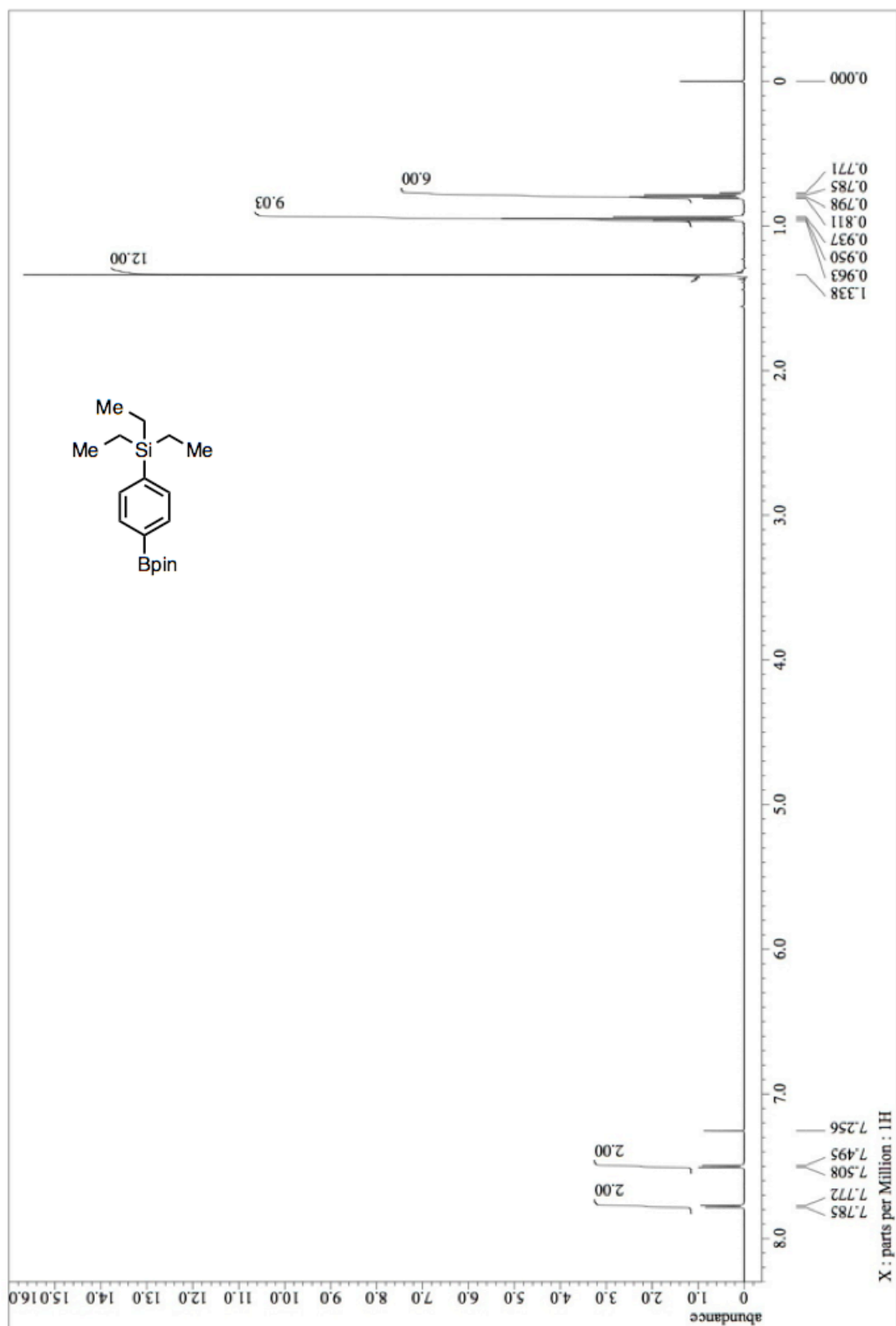
¹H NMR (600 MHz, CDCl₃) of isolated isomers of *para*-selective C–H borylation of **1a**



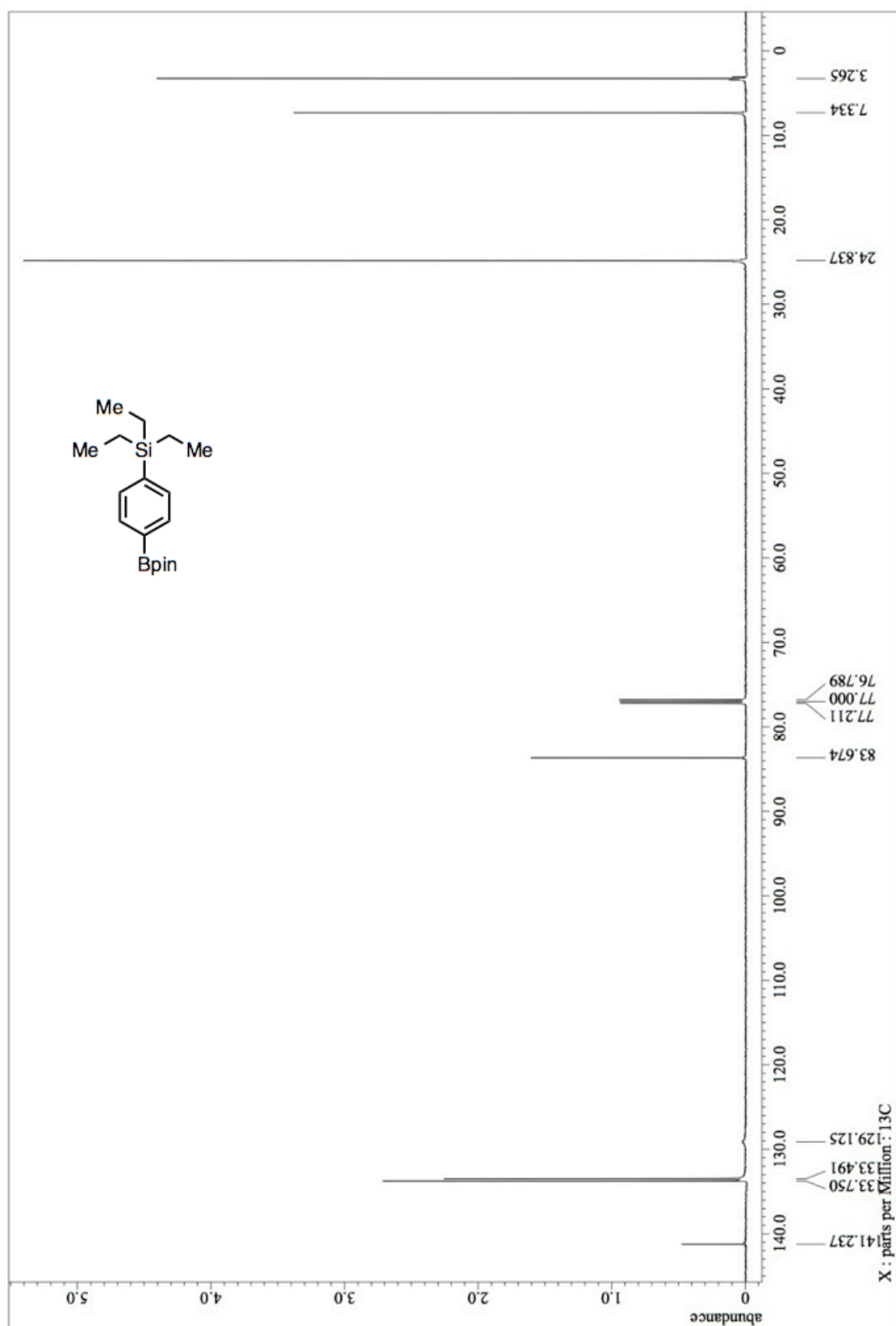
¹H NMR (600 MHz, CDCl₃) of isolated isomers of *para*-selective C–H borylation of 2a



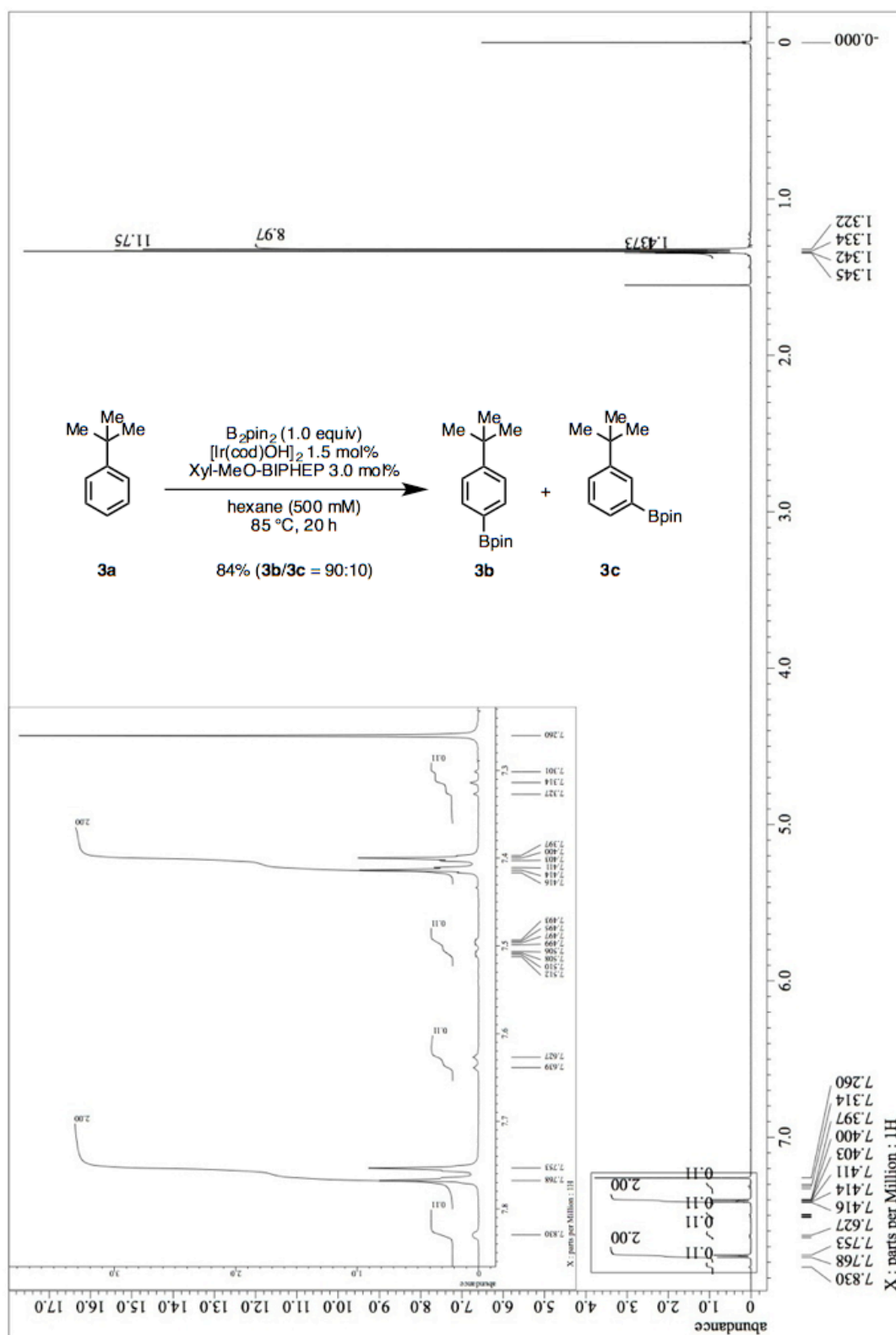
^1H NMR (600 MHz, CDCl_3) of **2b**



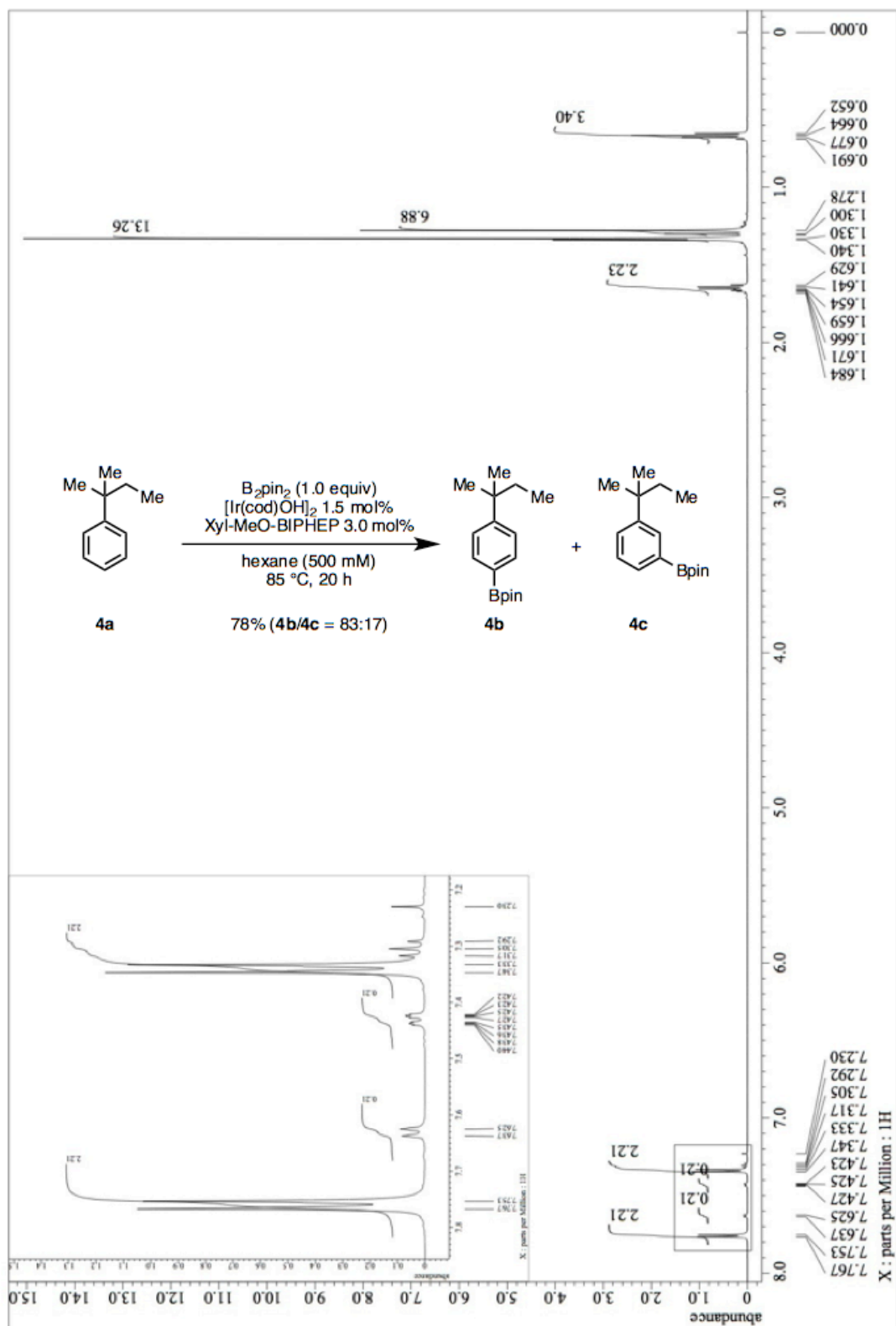
^{13}C NMR (600 MHz, CDCl_3) of **2b**



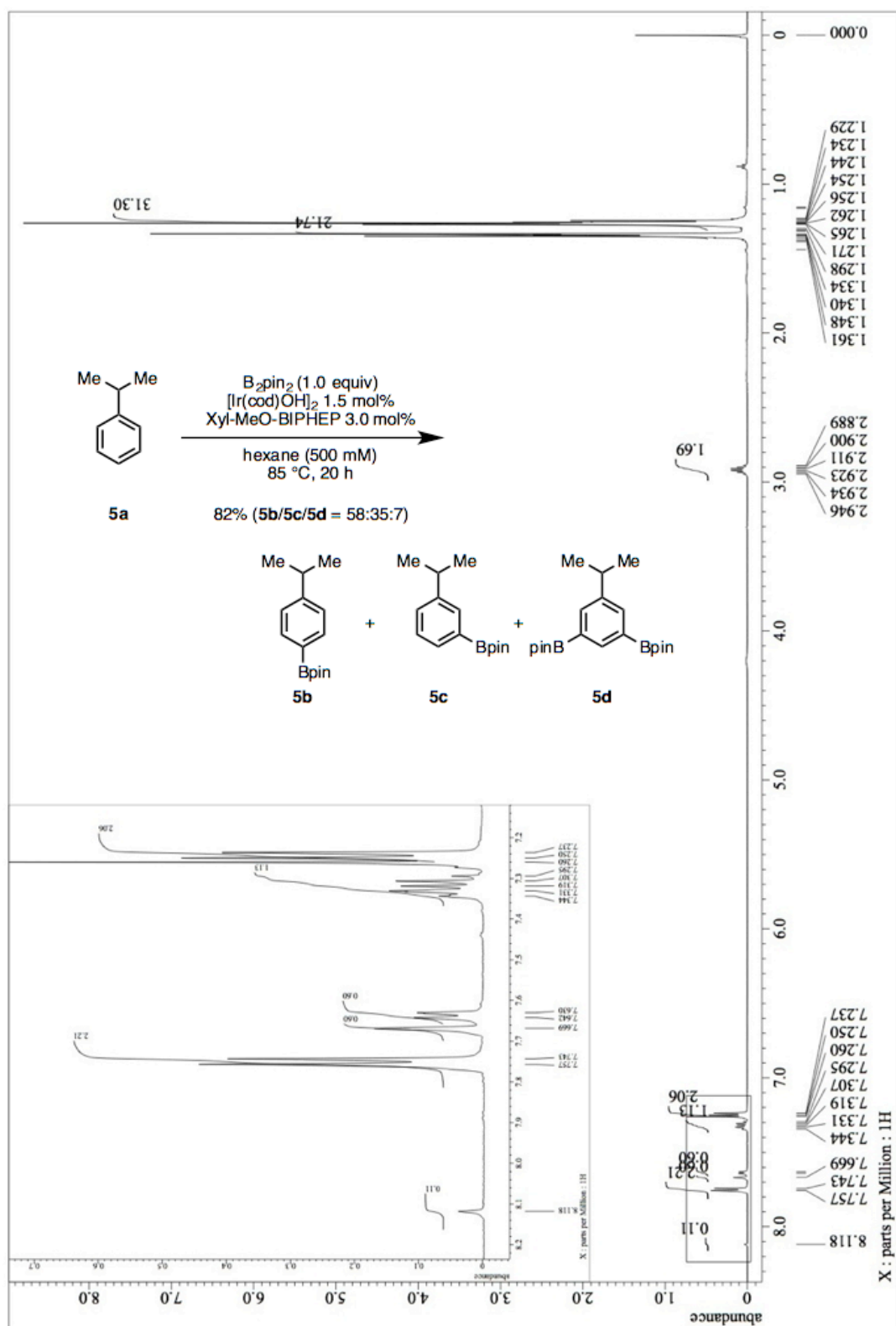
¹H NMR (600 MHz, CDCl₃) of isolated isomers of *para*-selective C–H borylation of 3a



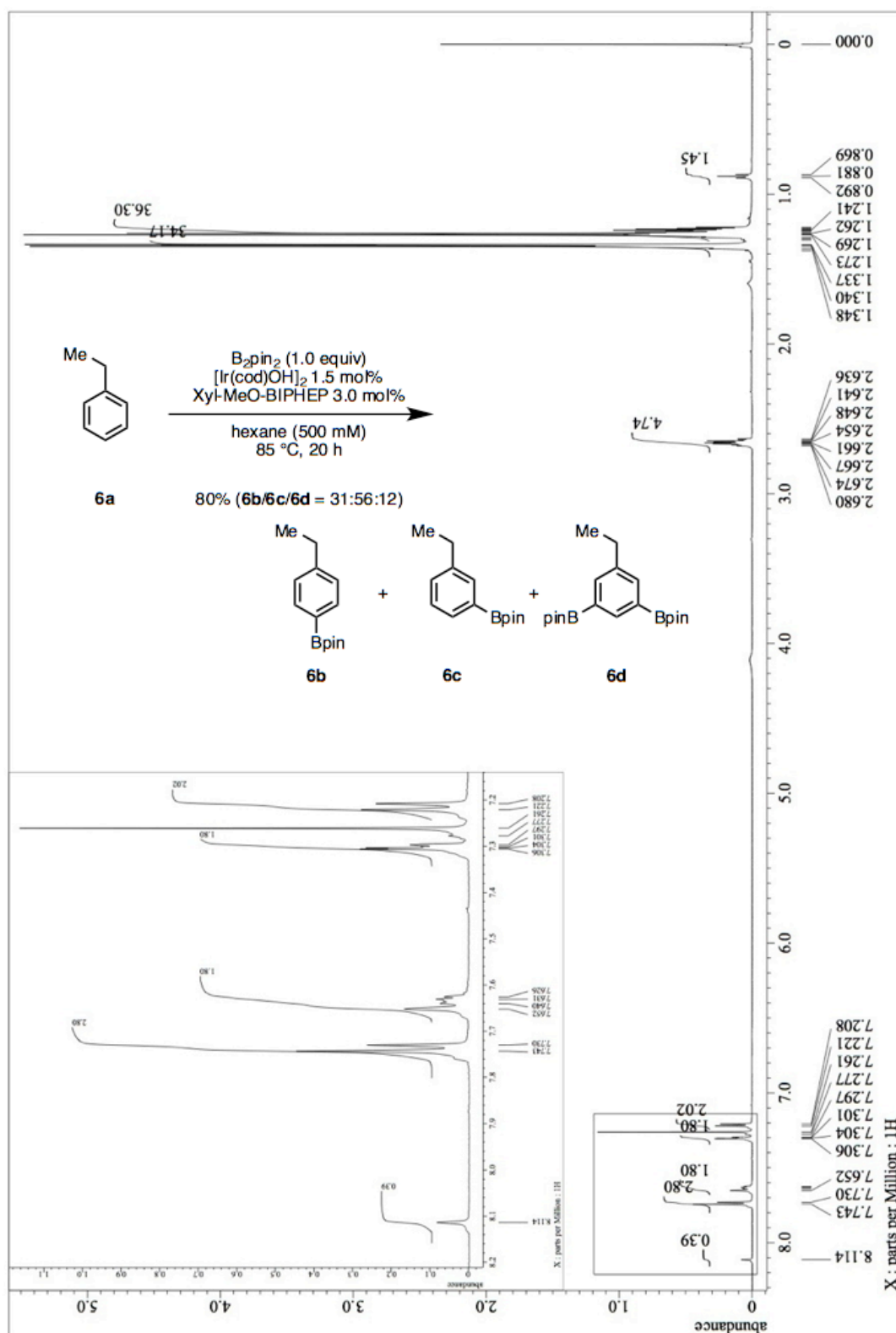
¹H NMR (600 MHz, CDCl₃) of isolated isomers of *para*-selective C–H borylation of 4a



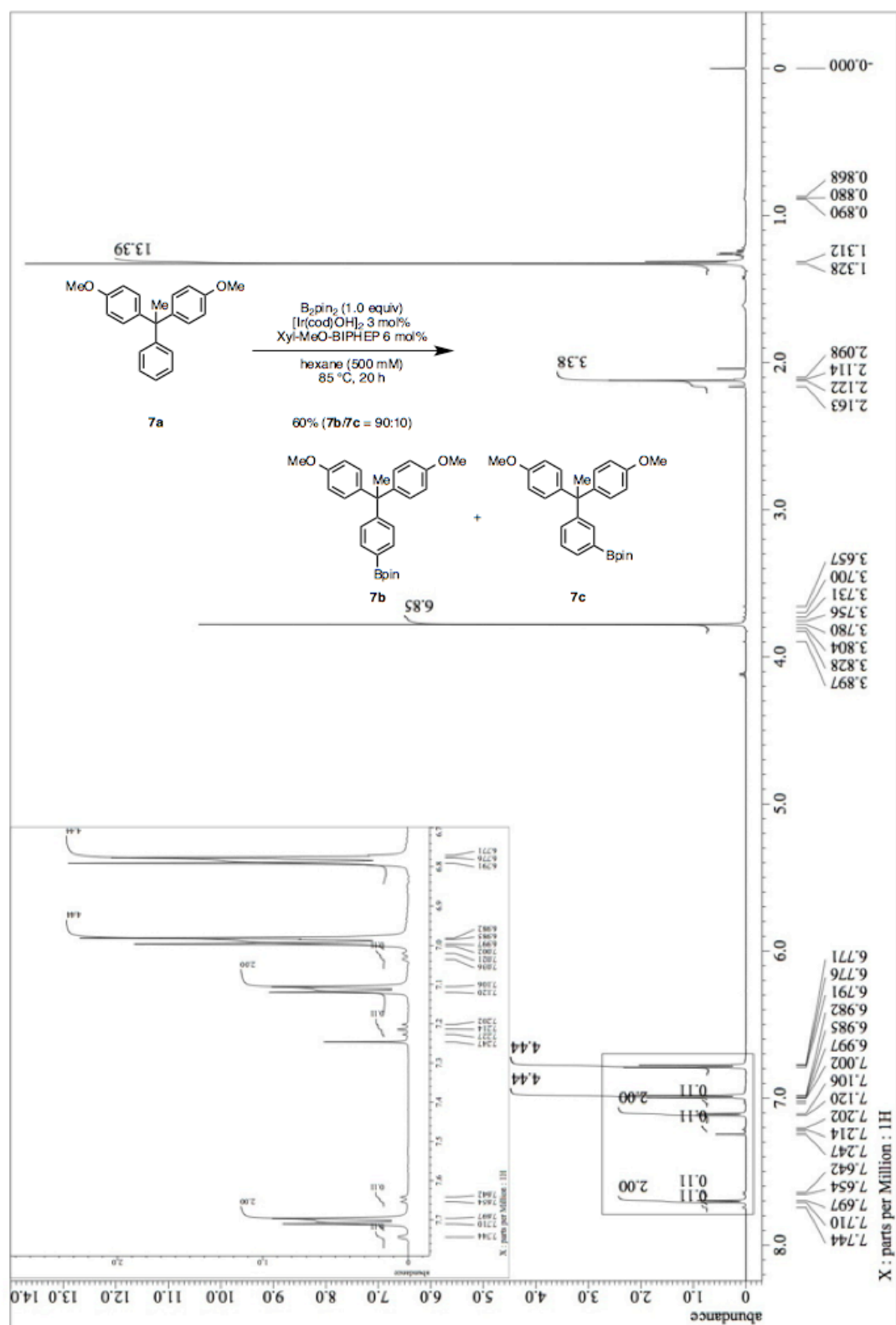
¹H NMR (600 MHz, CDCl₃) of crude of *para*-selective C–H borylation of **5a**



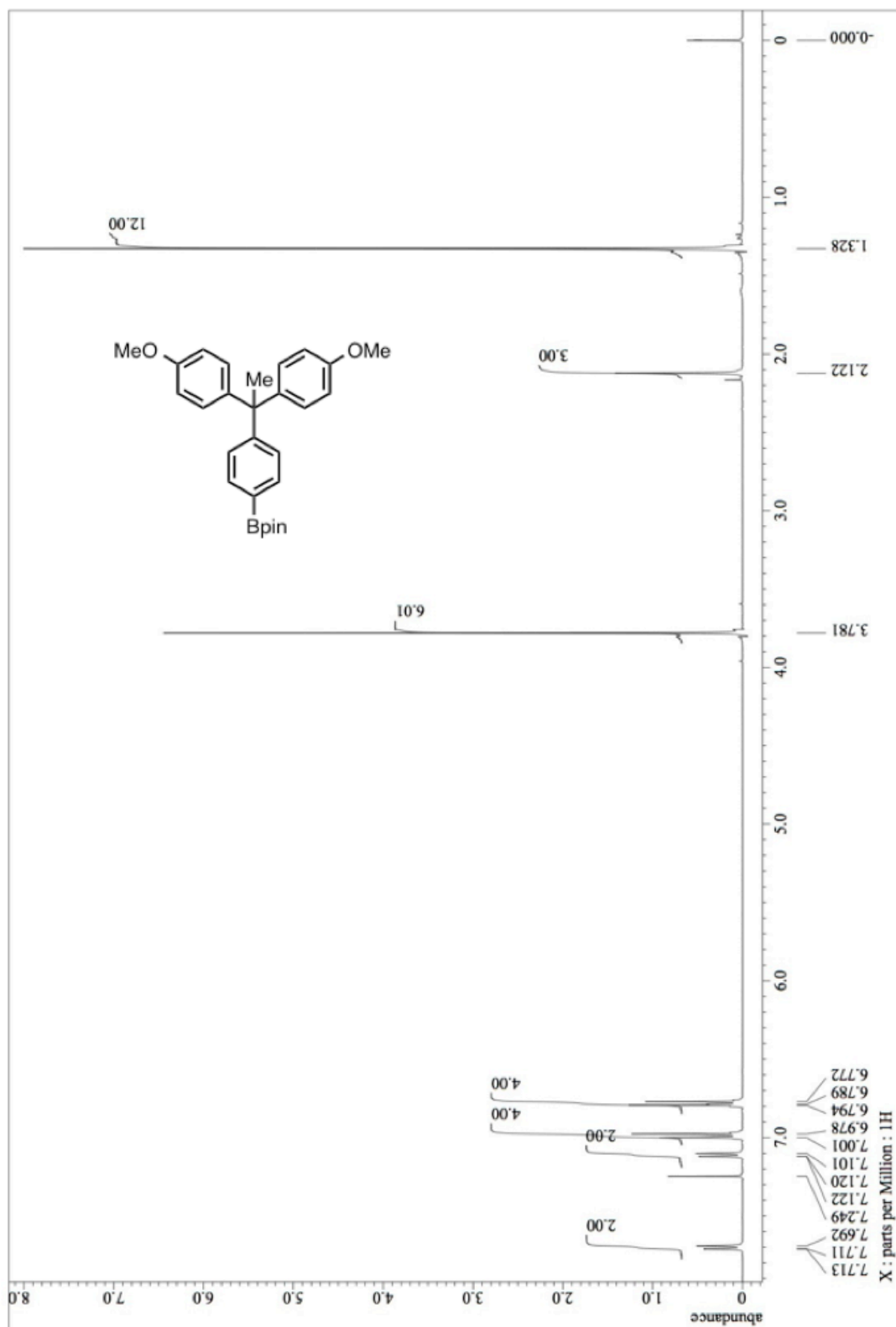
¹H NMR (600 MHz, CDCl₃) of crude of *para*-selective C–H borylation of **6a**



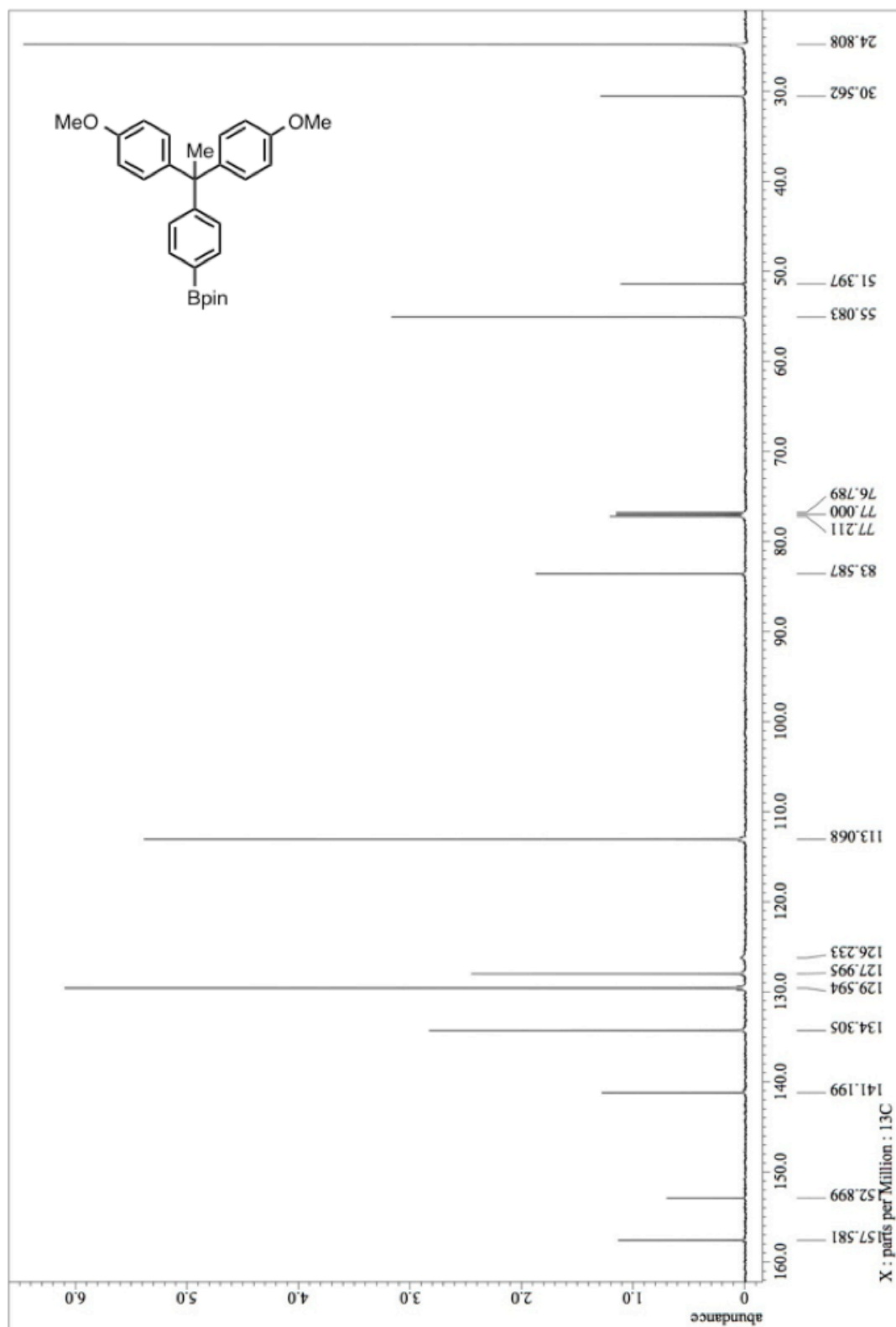
¹H NMR (600 MHz, CDCl₃) of isolated isomers of *para*-selective C–H borylation of **7a**



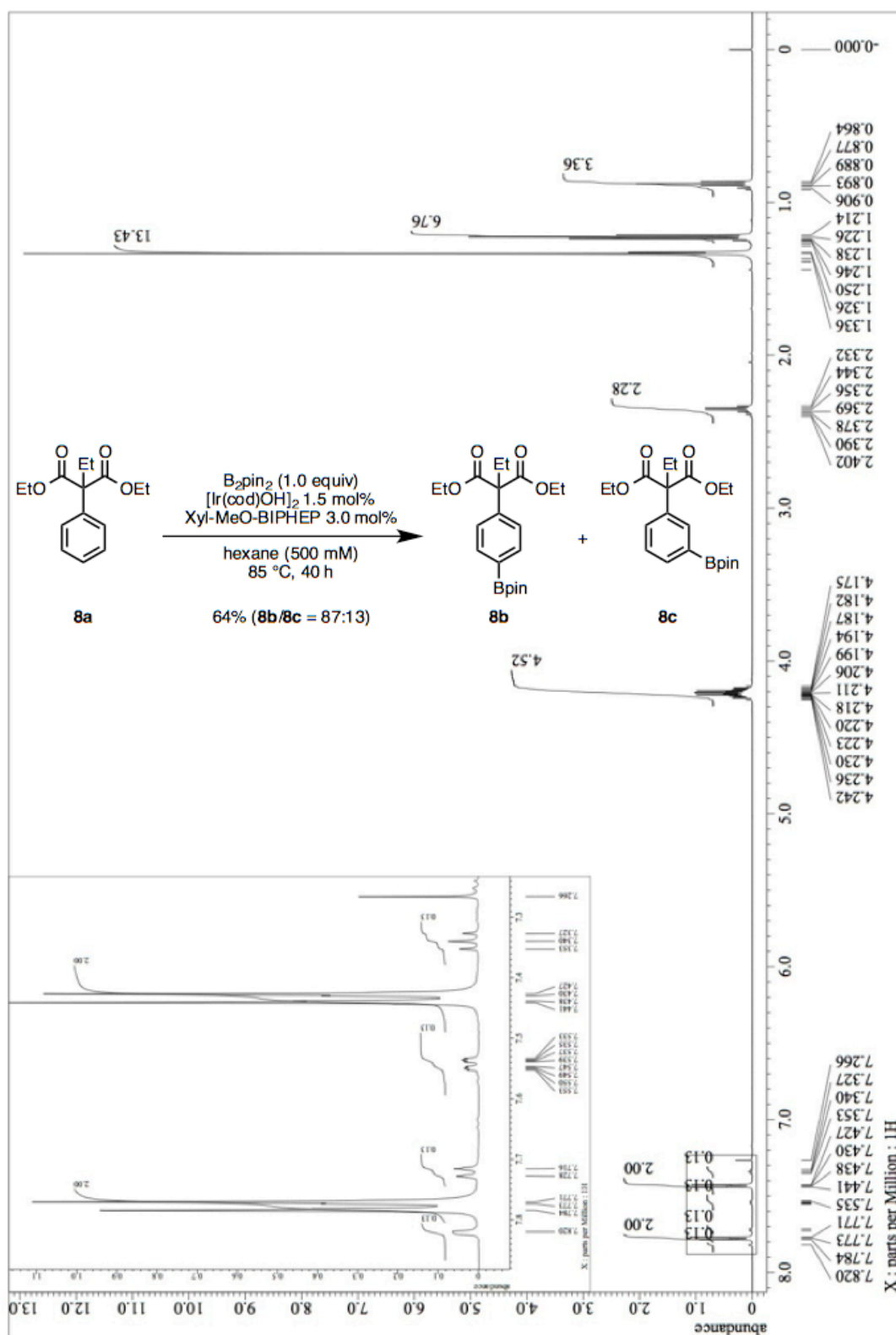
^1H NMR (600 MHz, CDCl_3) of **7b**



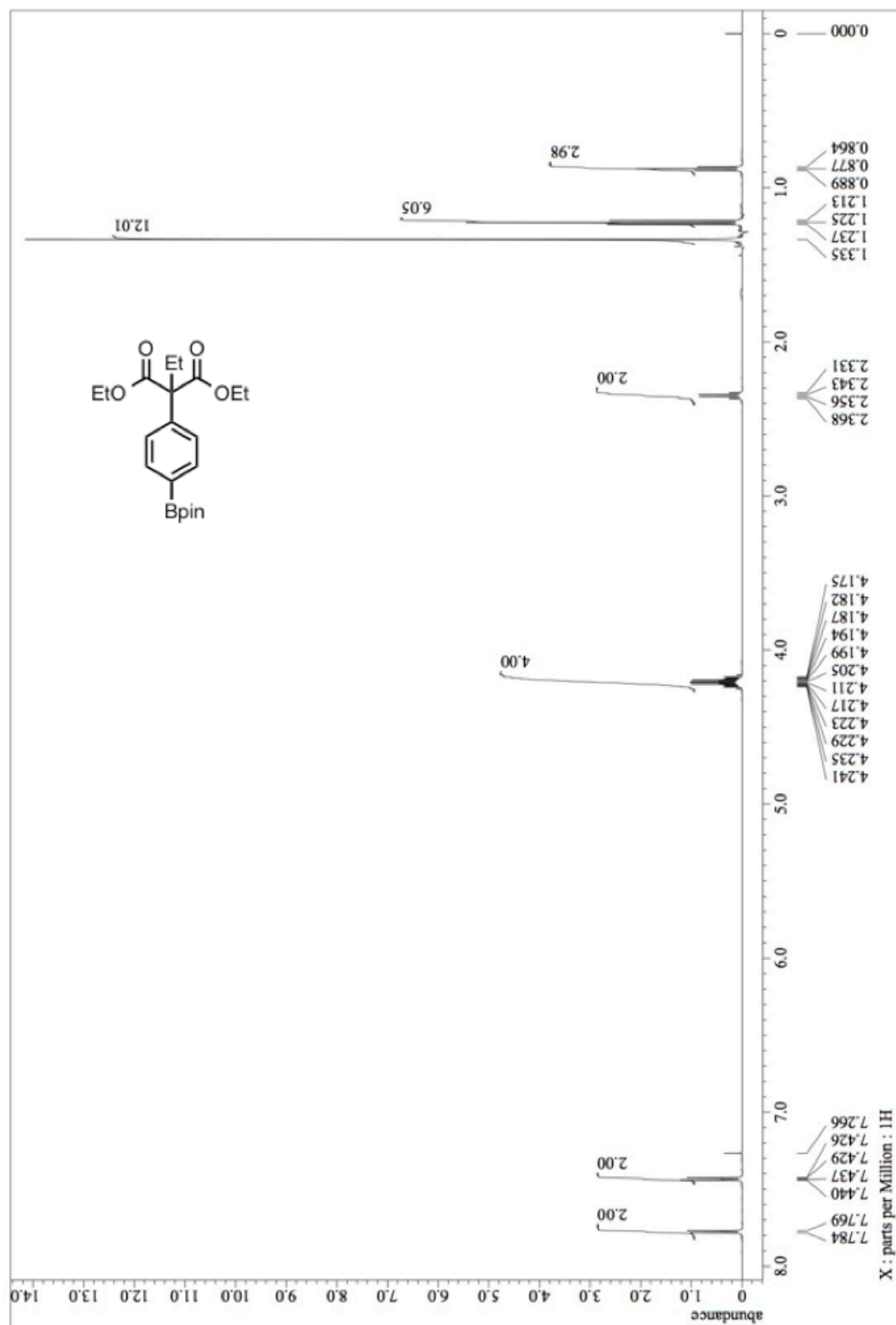
^{13}C NMR (600 MHz, CDCl_3) of **7b**



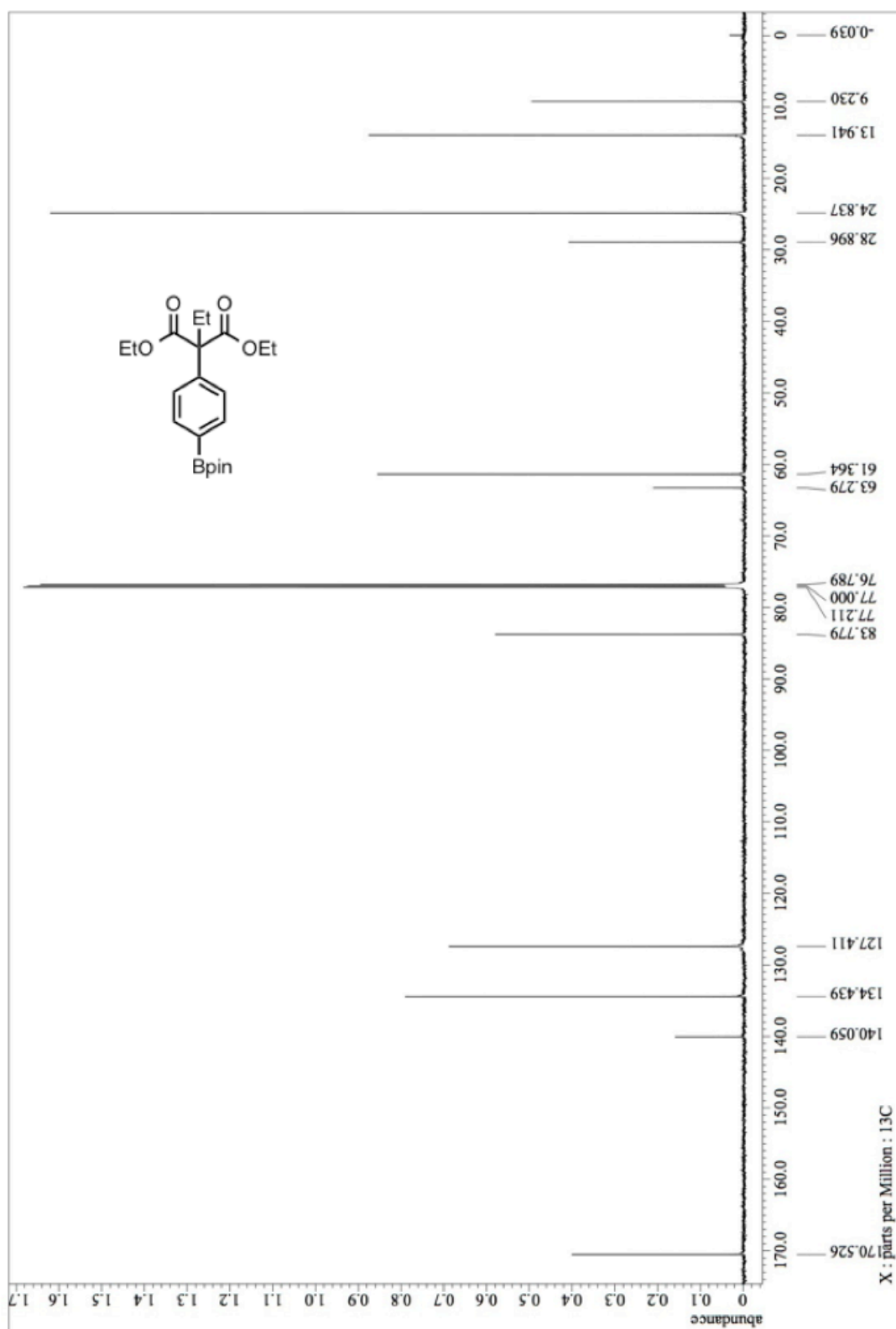
¹H NMR (600 MHz, CDCl₃) of isolated isomers of *para*-selective C–H borylation of 8a



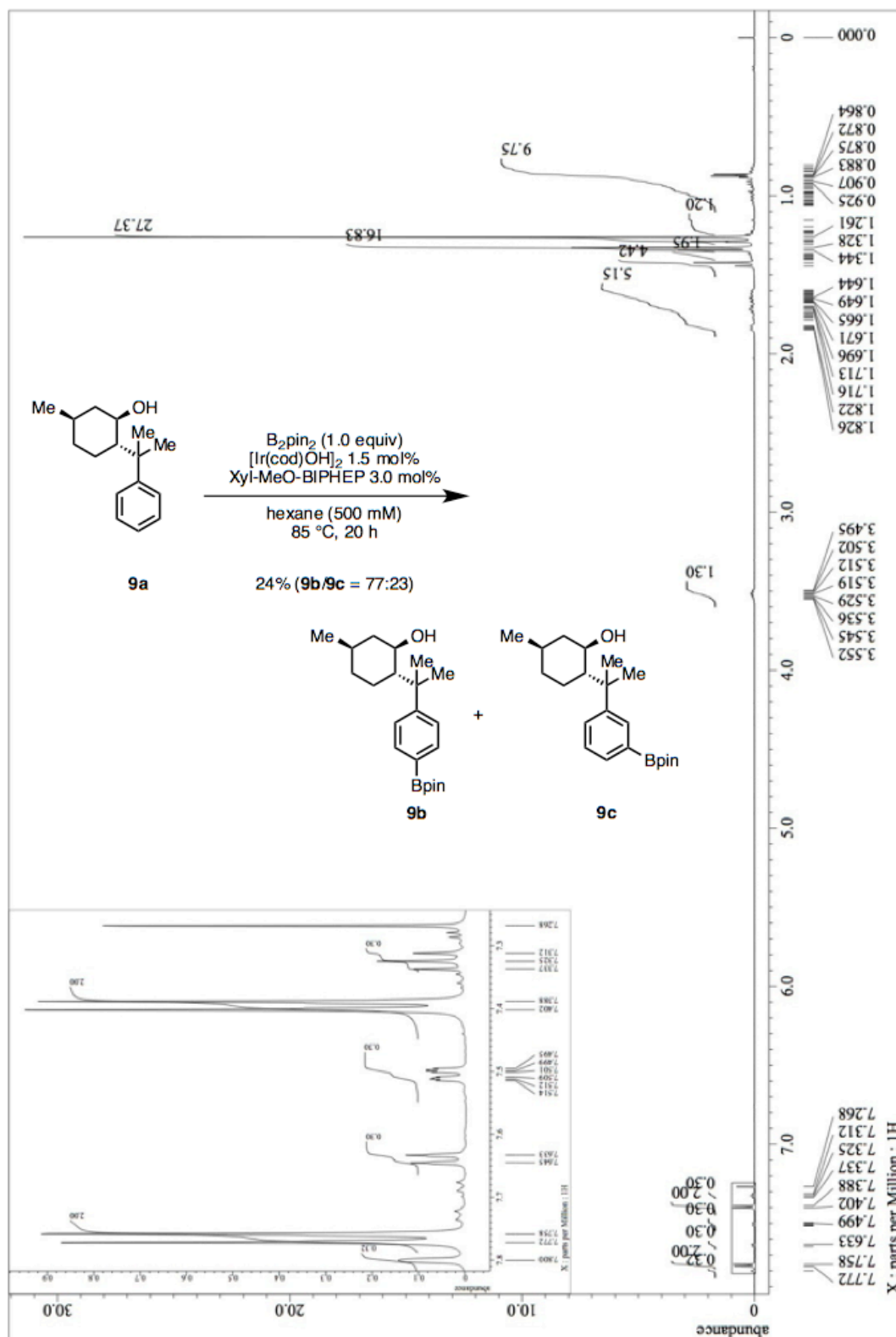
^1H NMR (600 MHz, CDCl_3) of **8b**



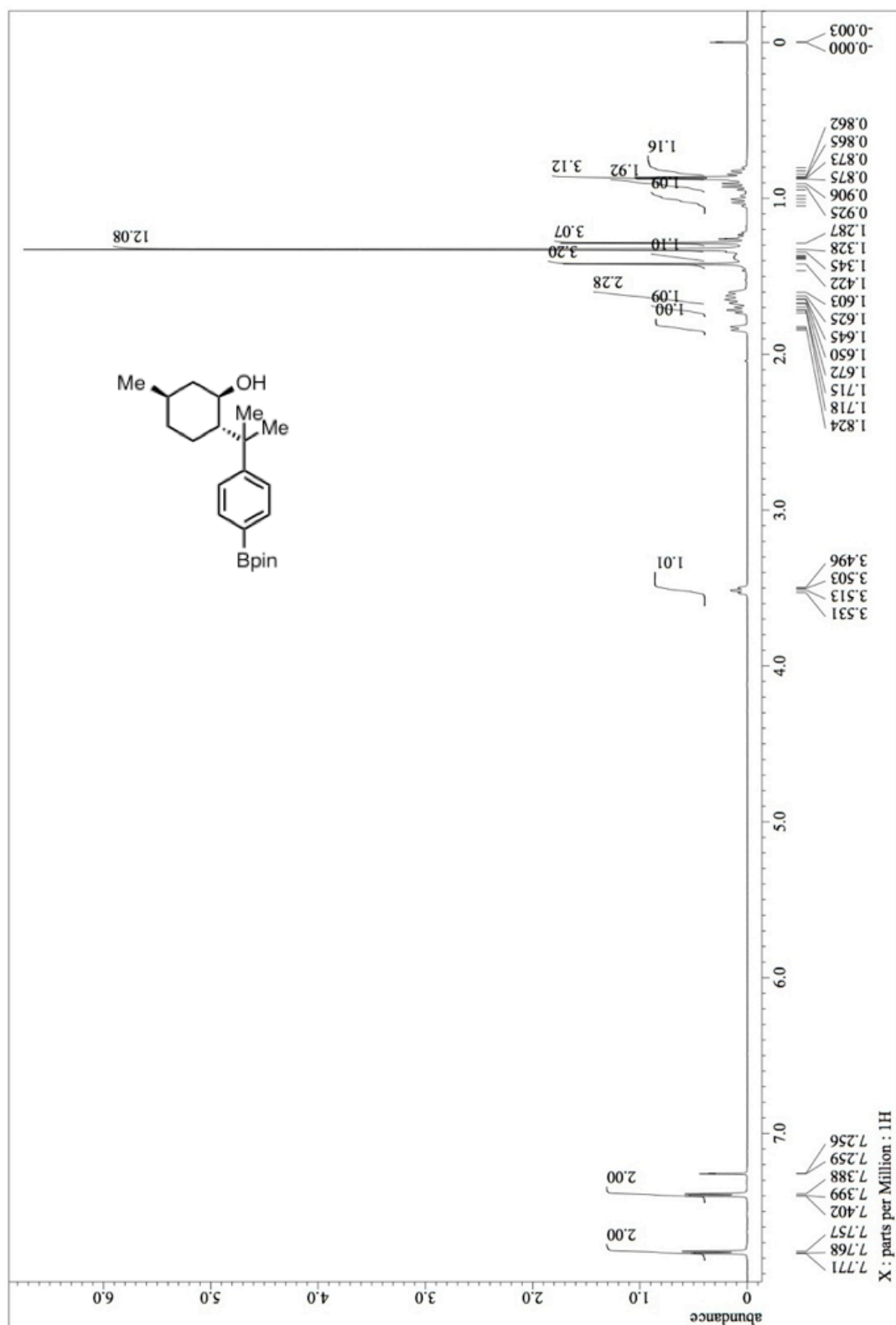
^{13}C NMR (600 MHz, CDCl_3) of **8b**



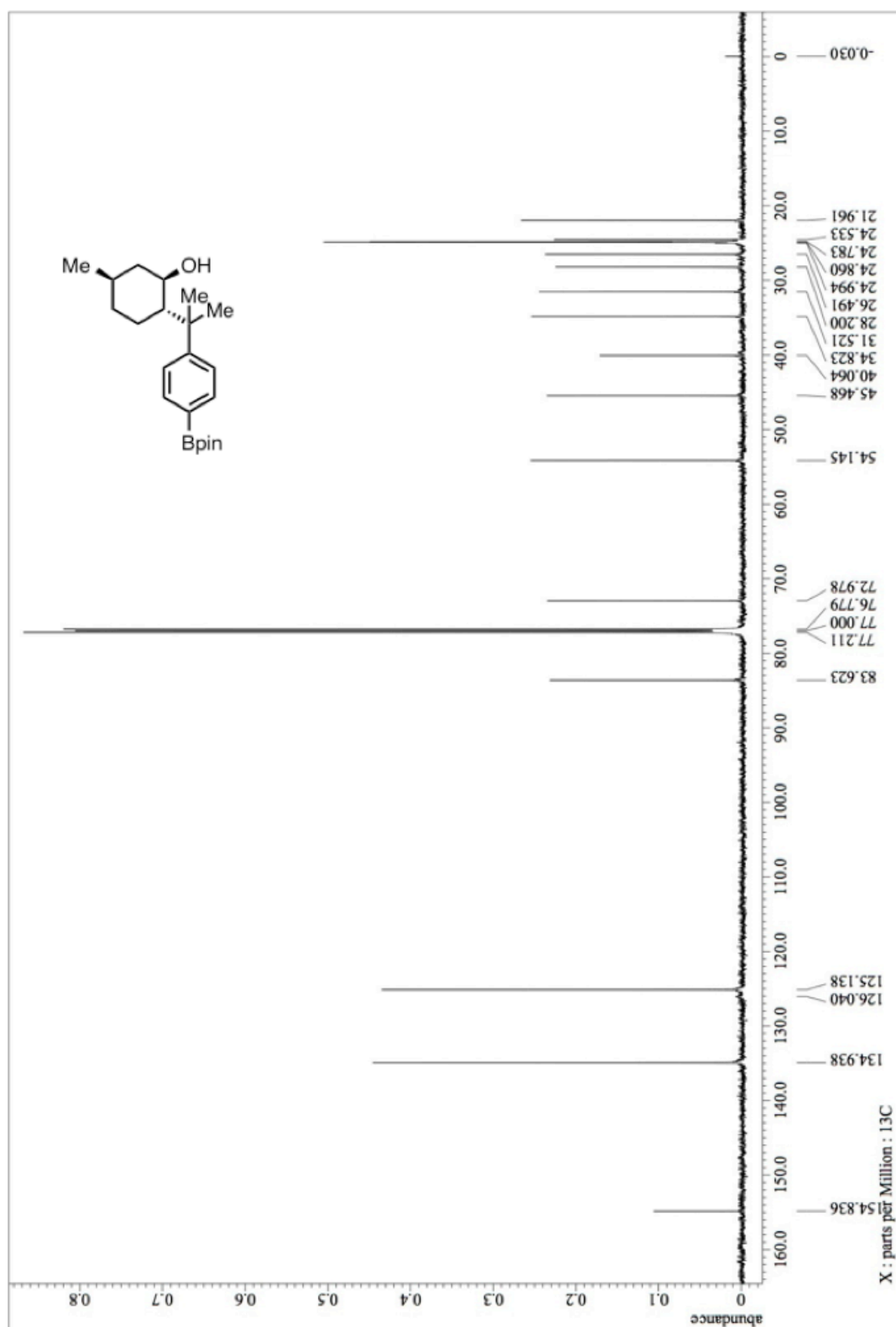
¹H NMR (600 MHz, CDCl₃) of isolated isomers of *para*-selective C–H borylation of **9a**



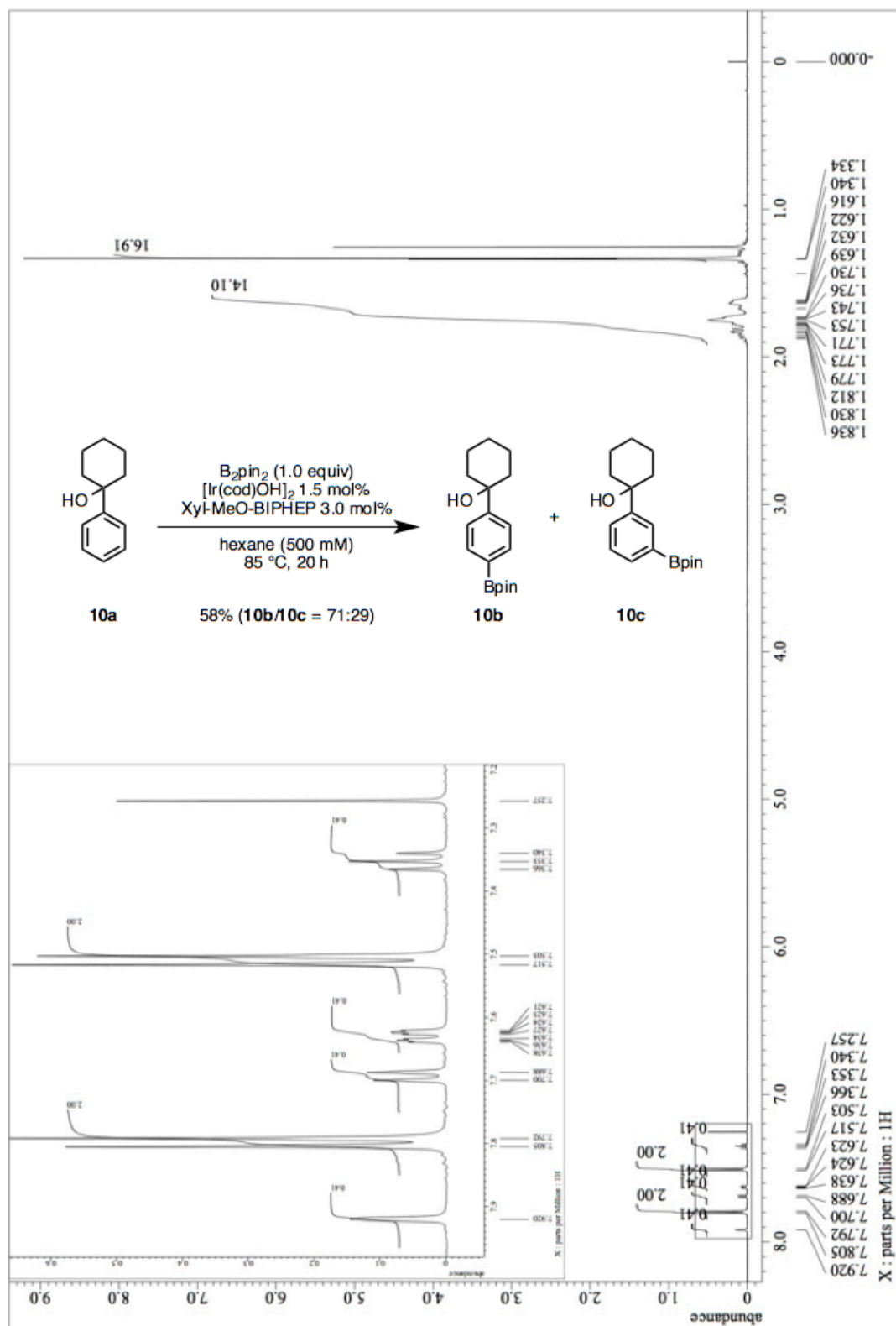
¹H NMR (600 MHz, CDCl₃) of 9b



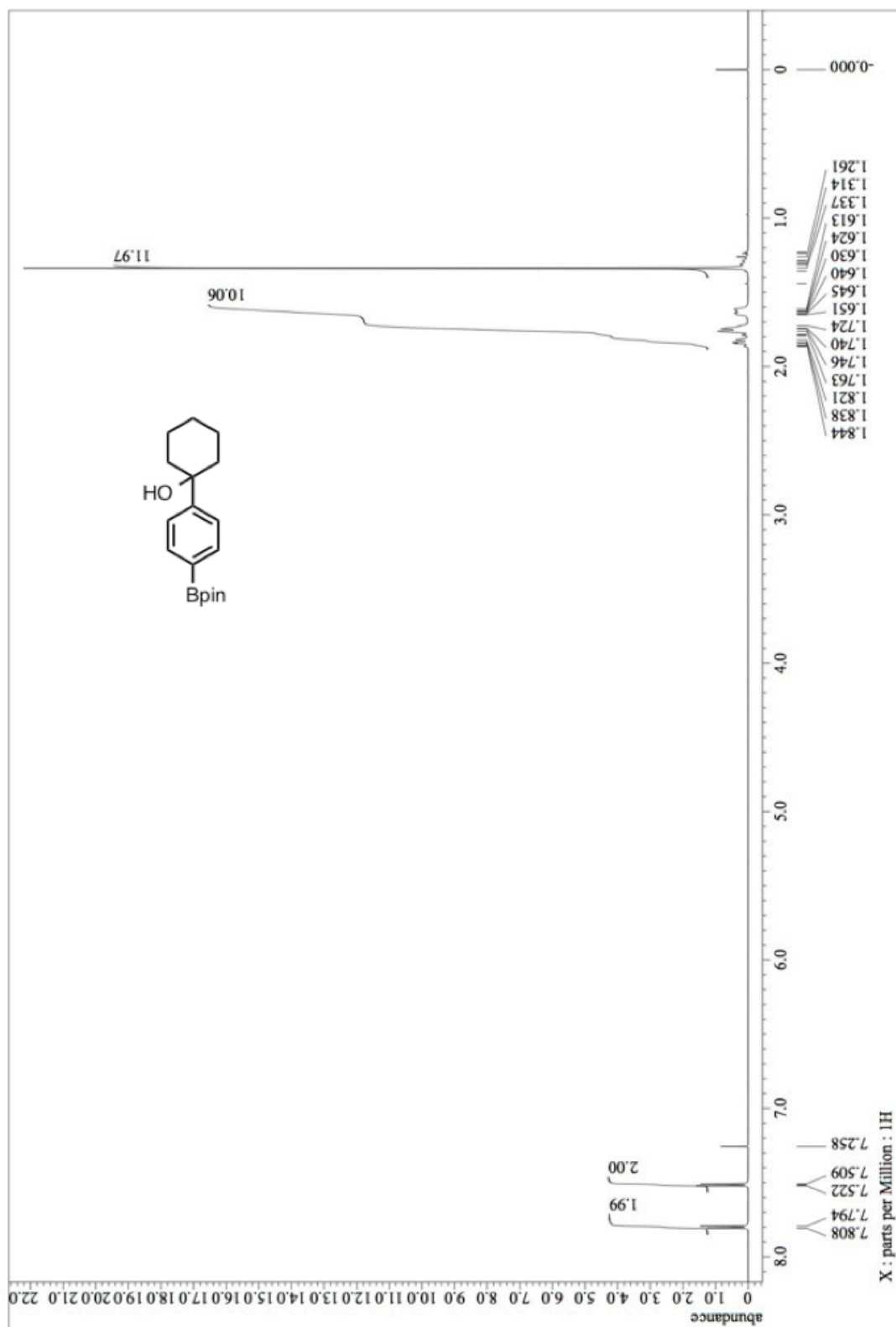
^{13}C NMR (600 MHz, CDCl_3) of **9b**



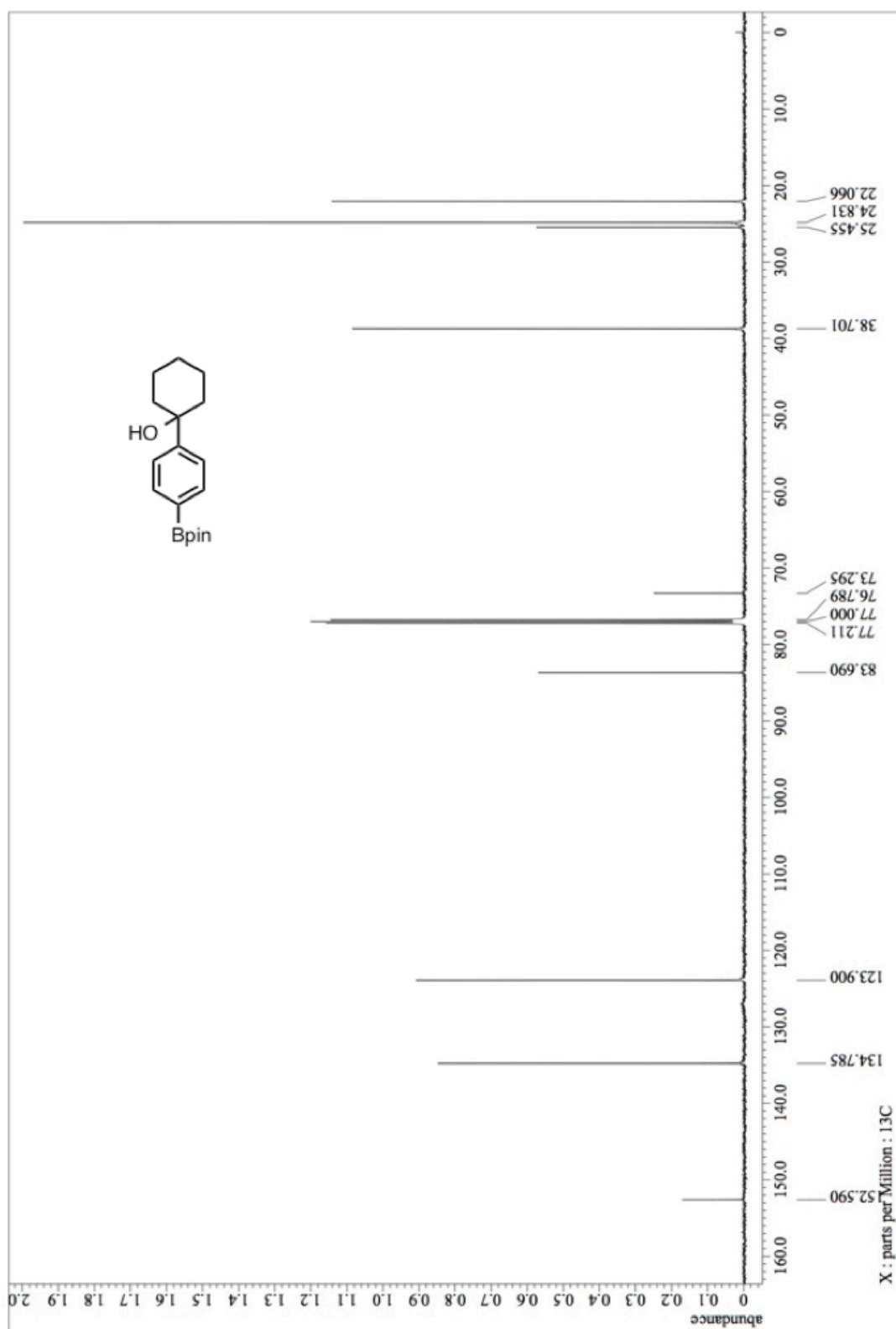
¹H NMR (600 MHz, CDCl₃) of isolated isomers of *para*-selective C–H borylation of 10a



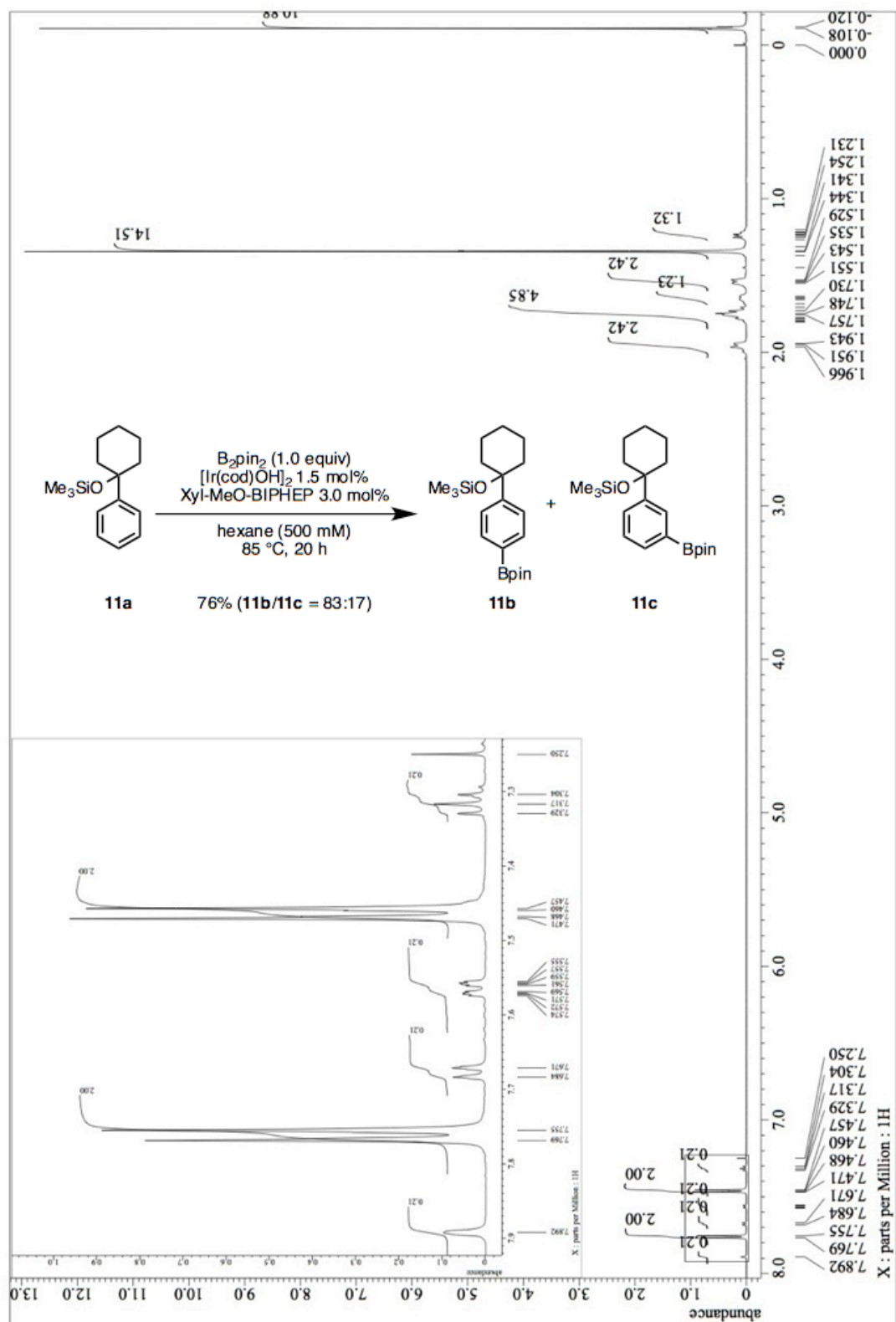
^1H NMR (600 MHz, CDCl_3) of 10b



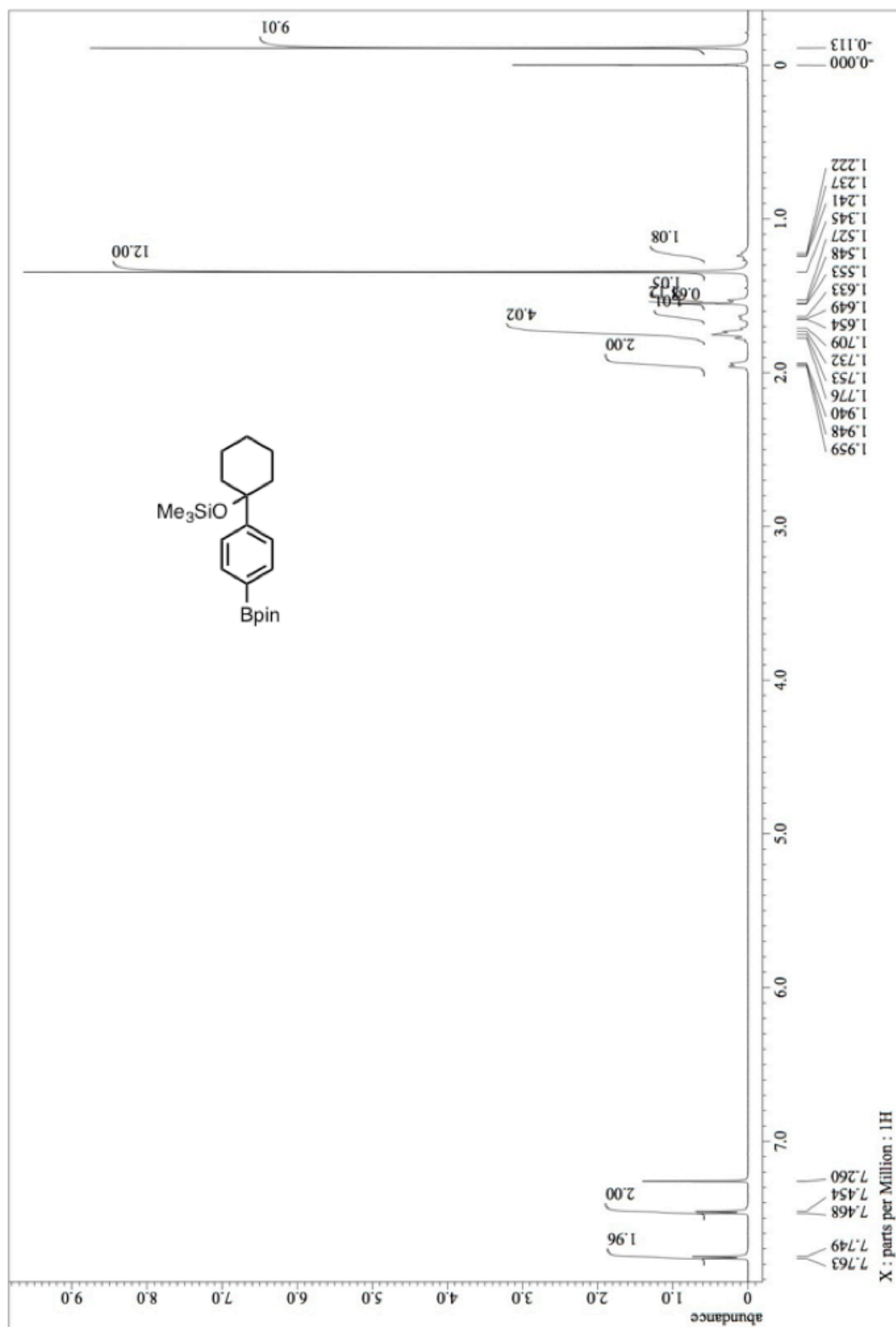
¹³C NMR (600 MHz, CDCl₃) of 10b



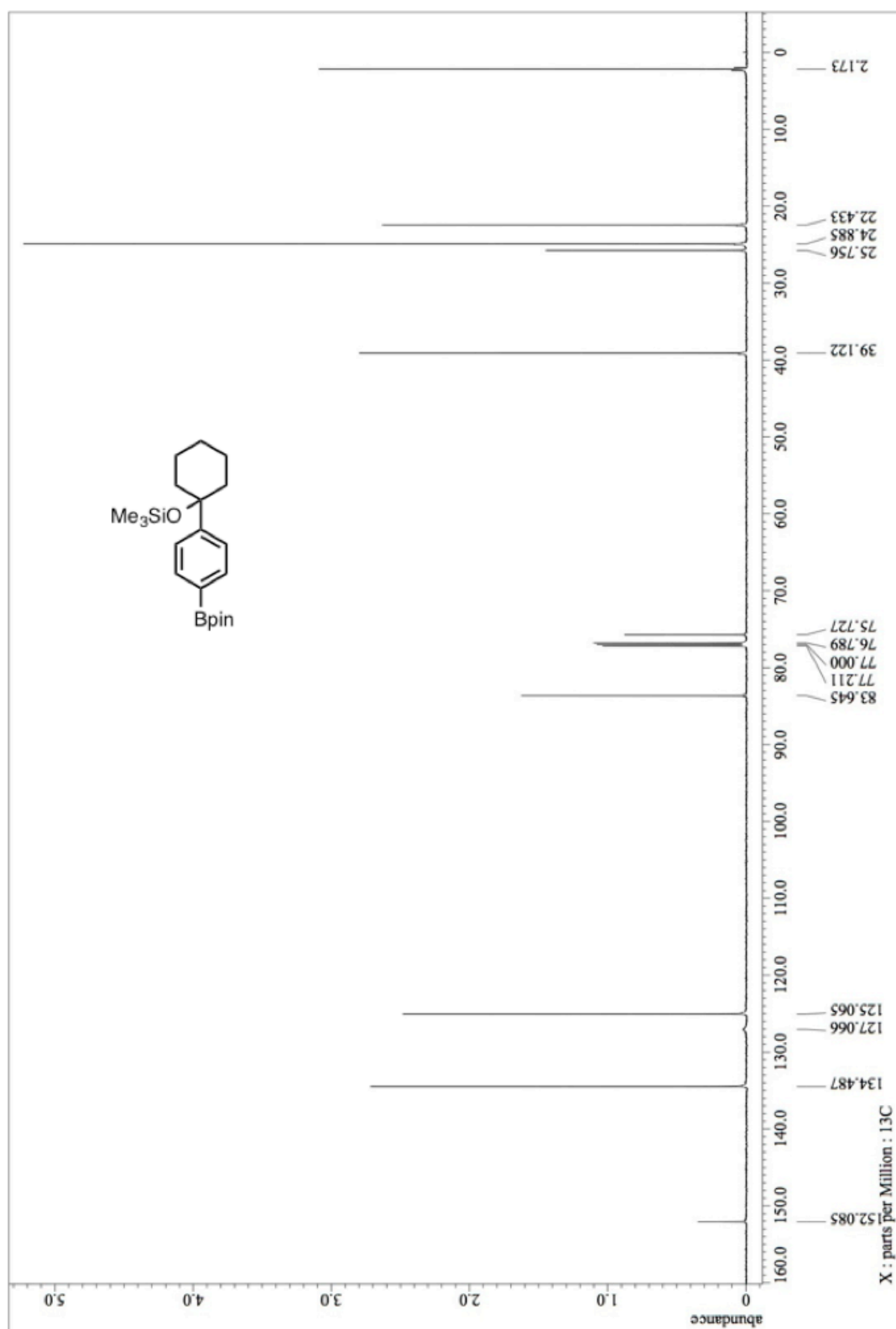
^1H NMR (600 MHz, CDCl_3) of isolated isomers of *para*-selective C–H borylation of **11a**



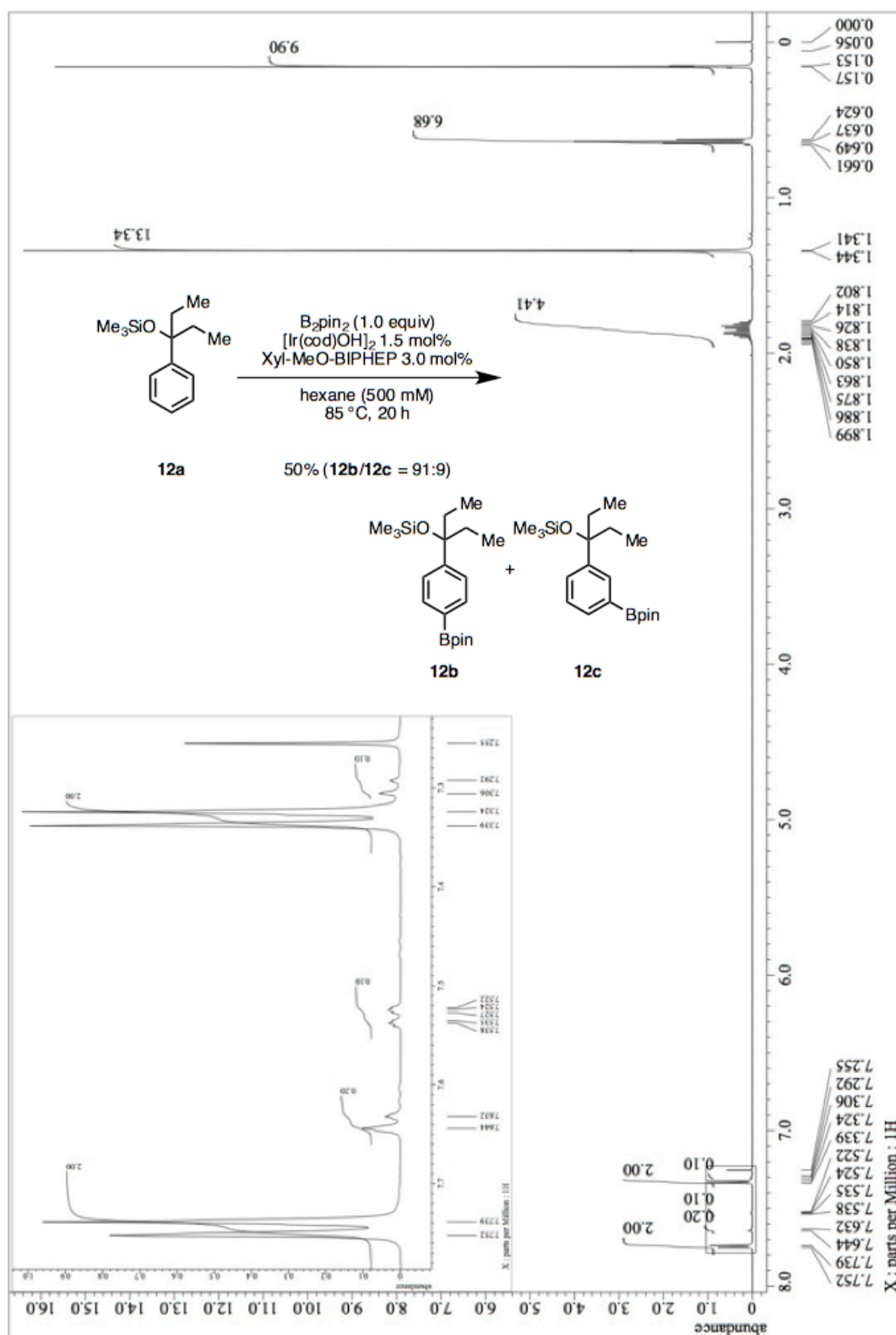
^1H NMR (600 MHz, CDCl_3) of 11b



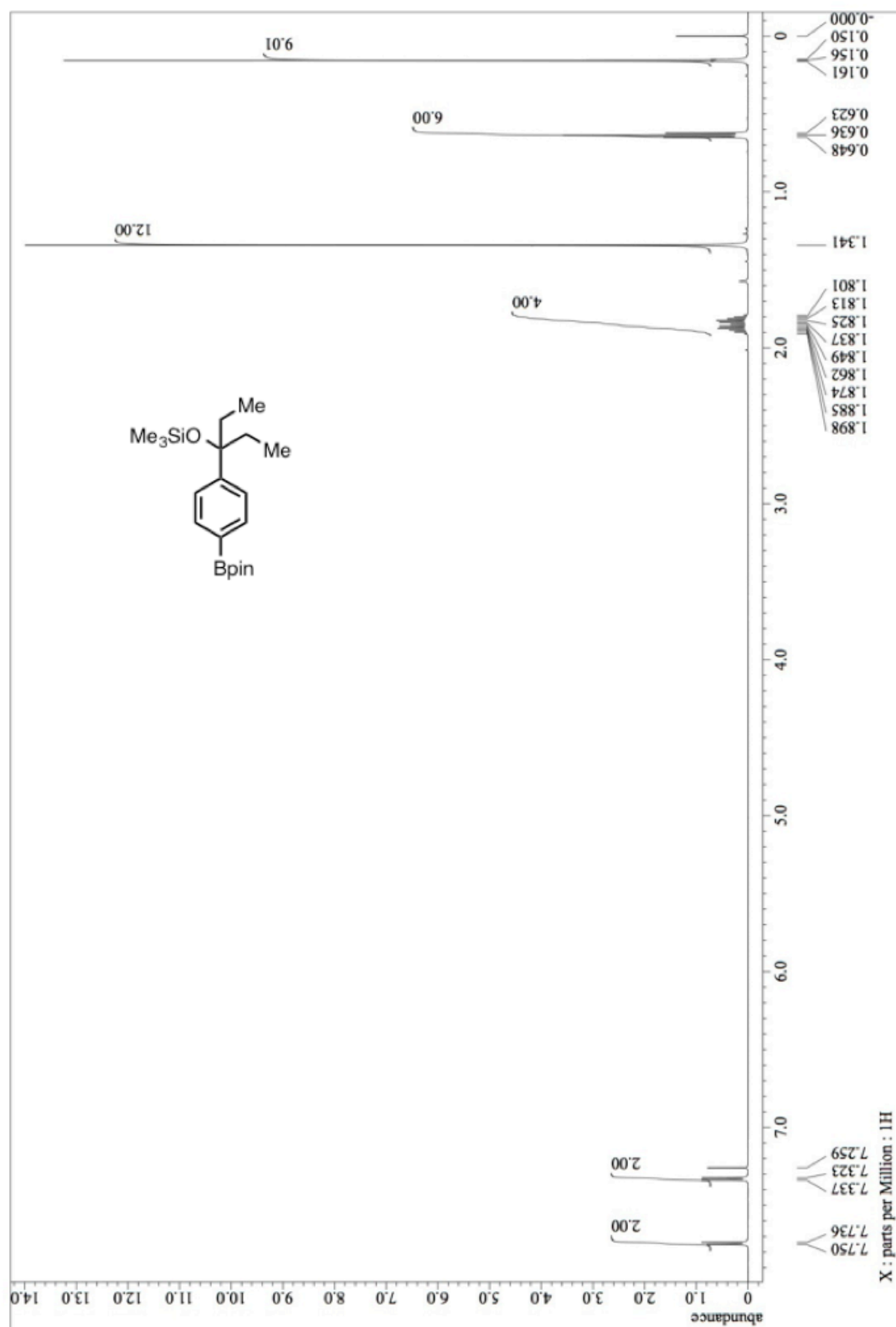
^{13}C NMR (600 MHz, CDCl_3) of 11b



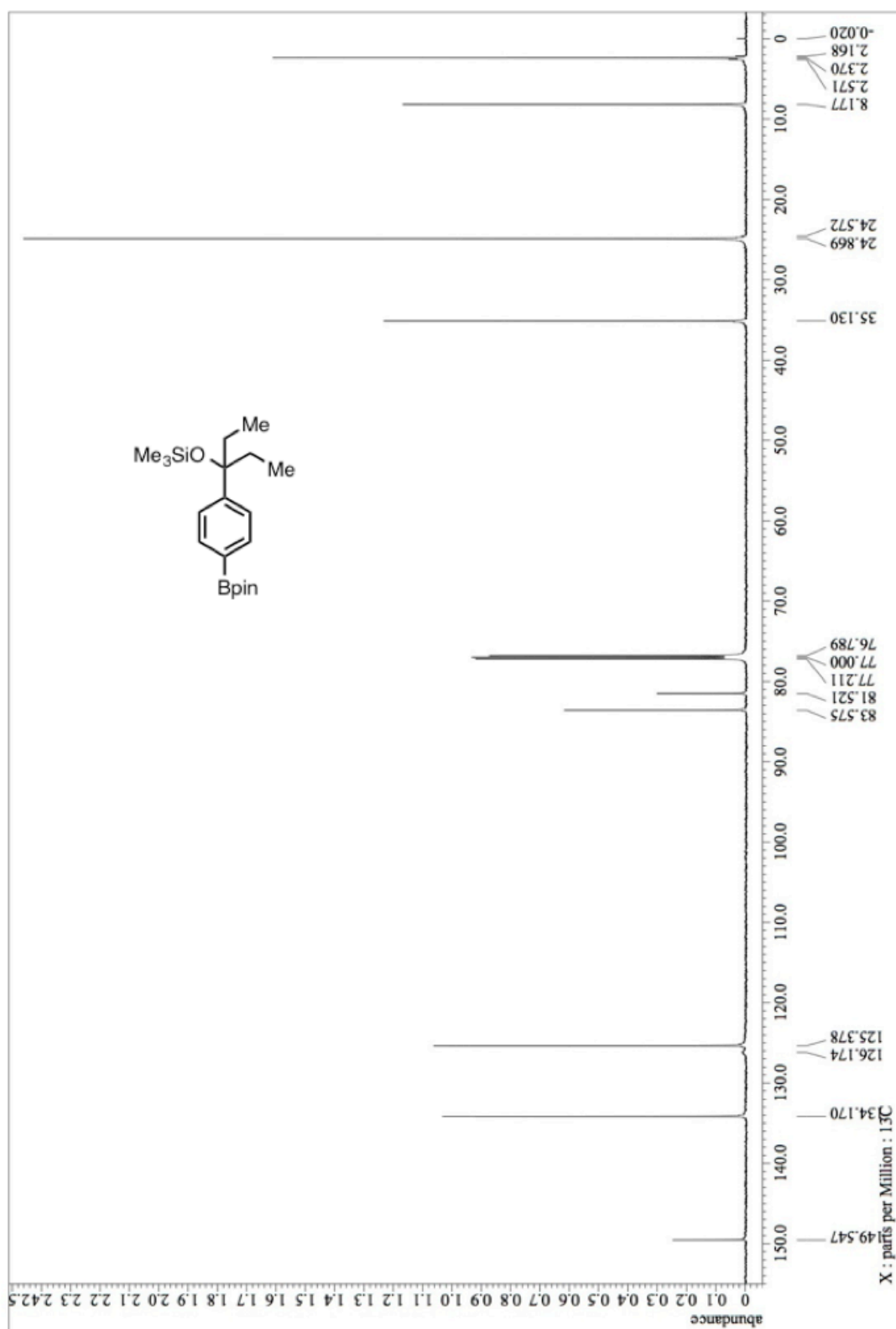
¹H NMR (600 MHz, CDCl₃) of isolated isomers of *para*-selective C–H borylation of 12a



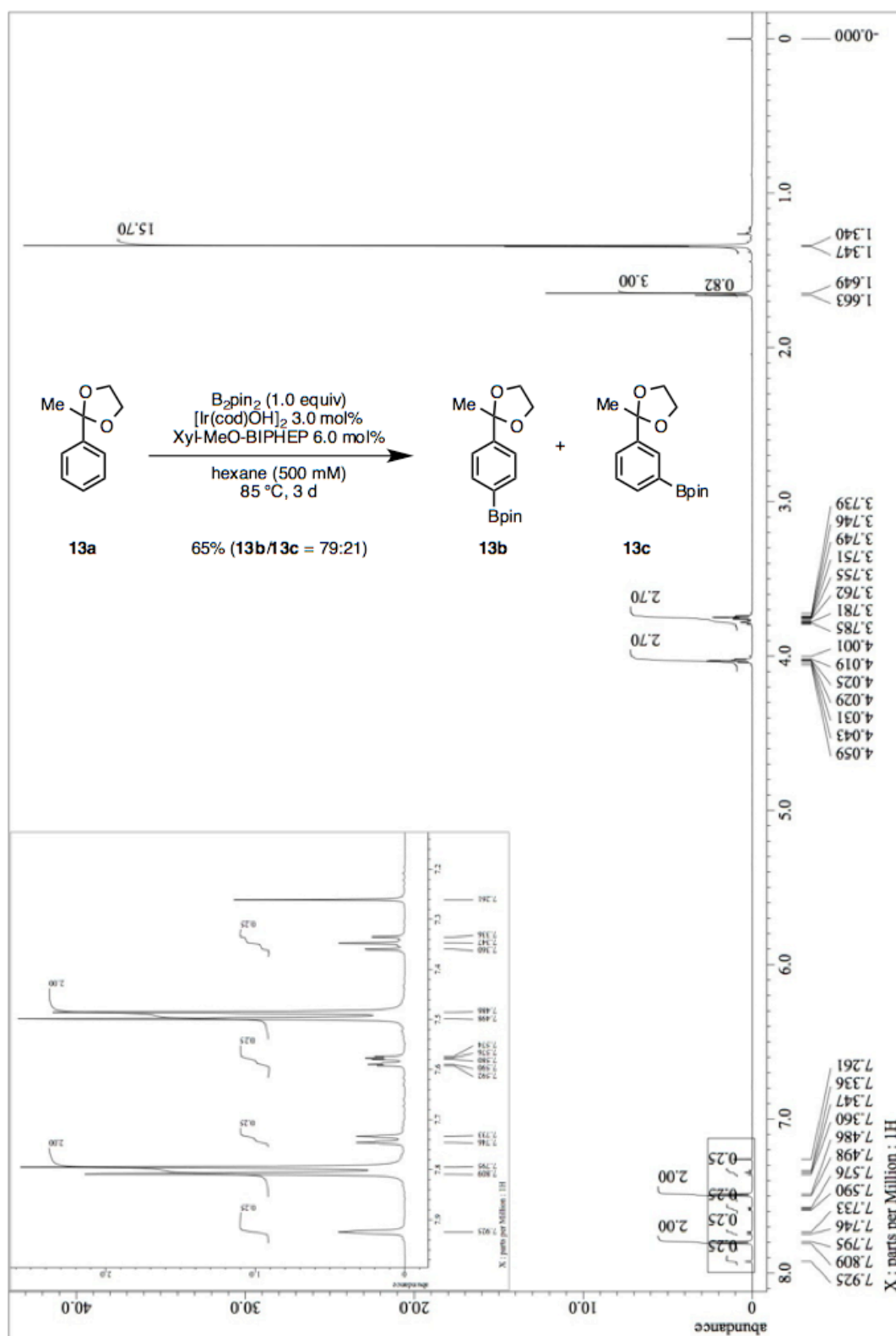
¹H NMR (600 MHz, CDCl₃) of 12b



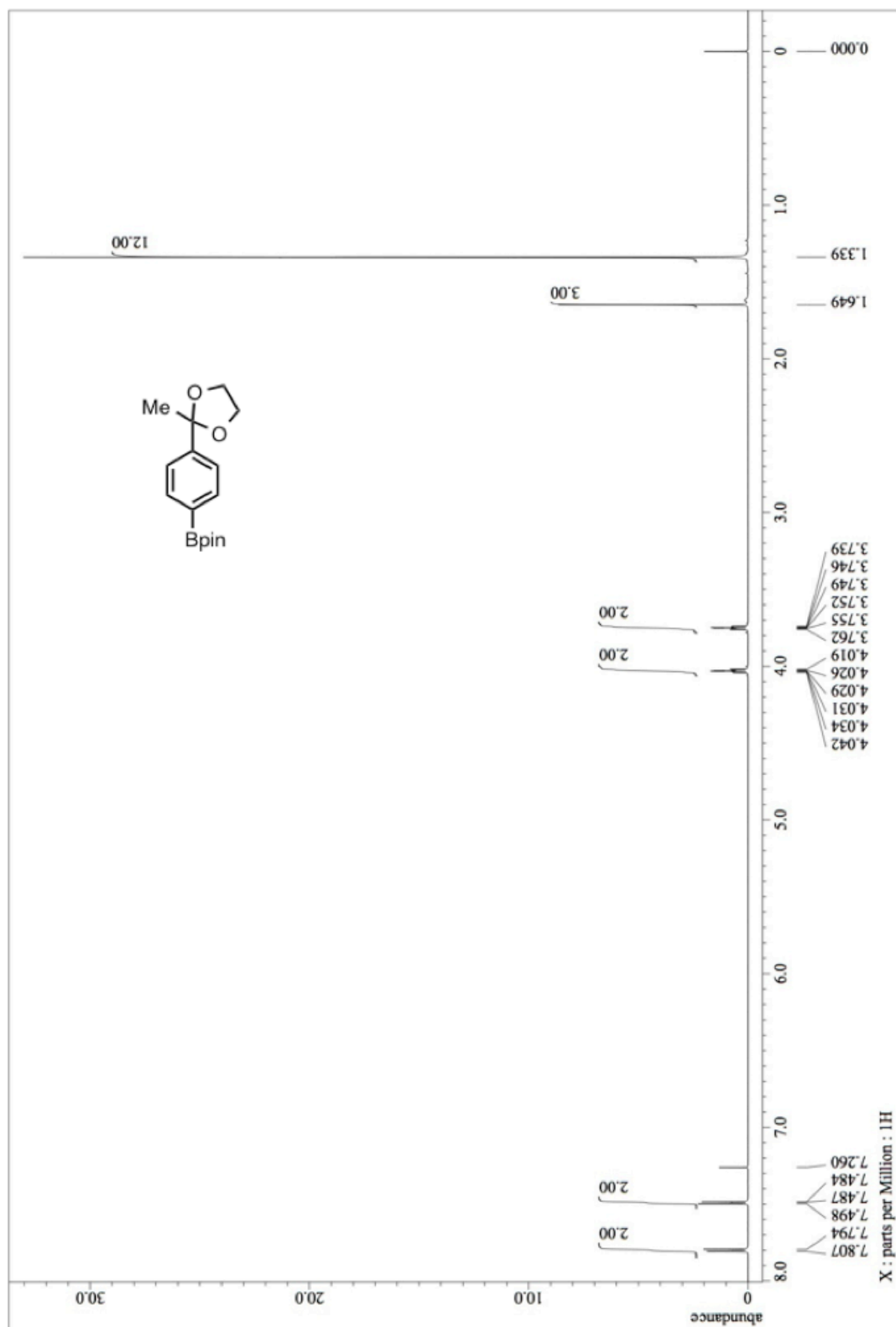
¹³C NMR (600 MHz, CDCl₃) of 12b



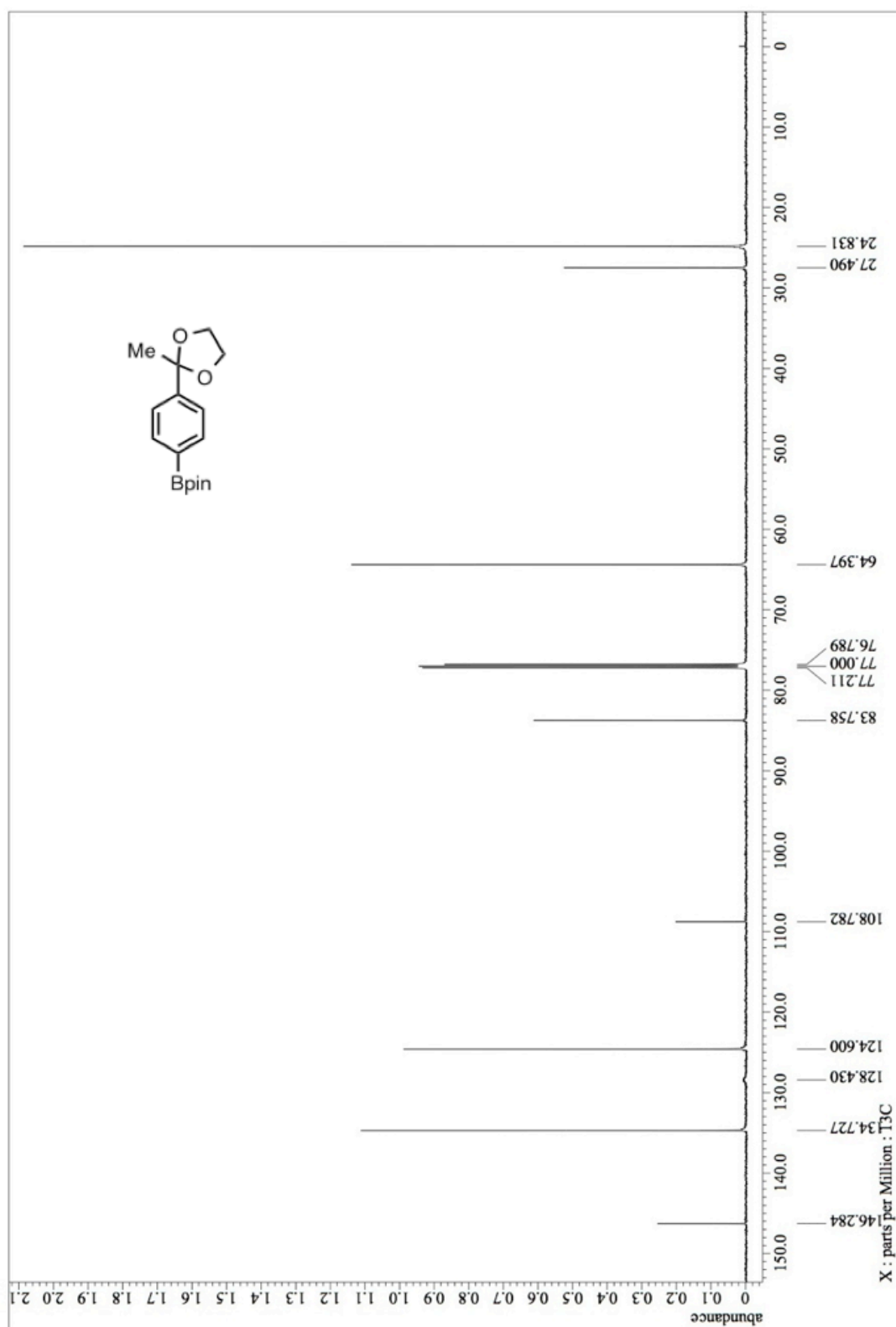
¹H NMR (600 MHz, CDCl₃) of isolated isomers of *para*-selective C–H borylation of 13a



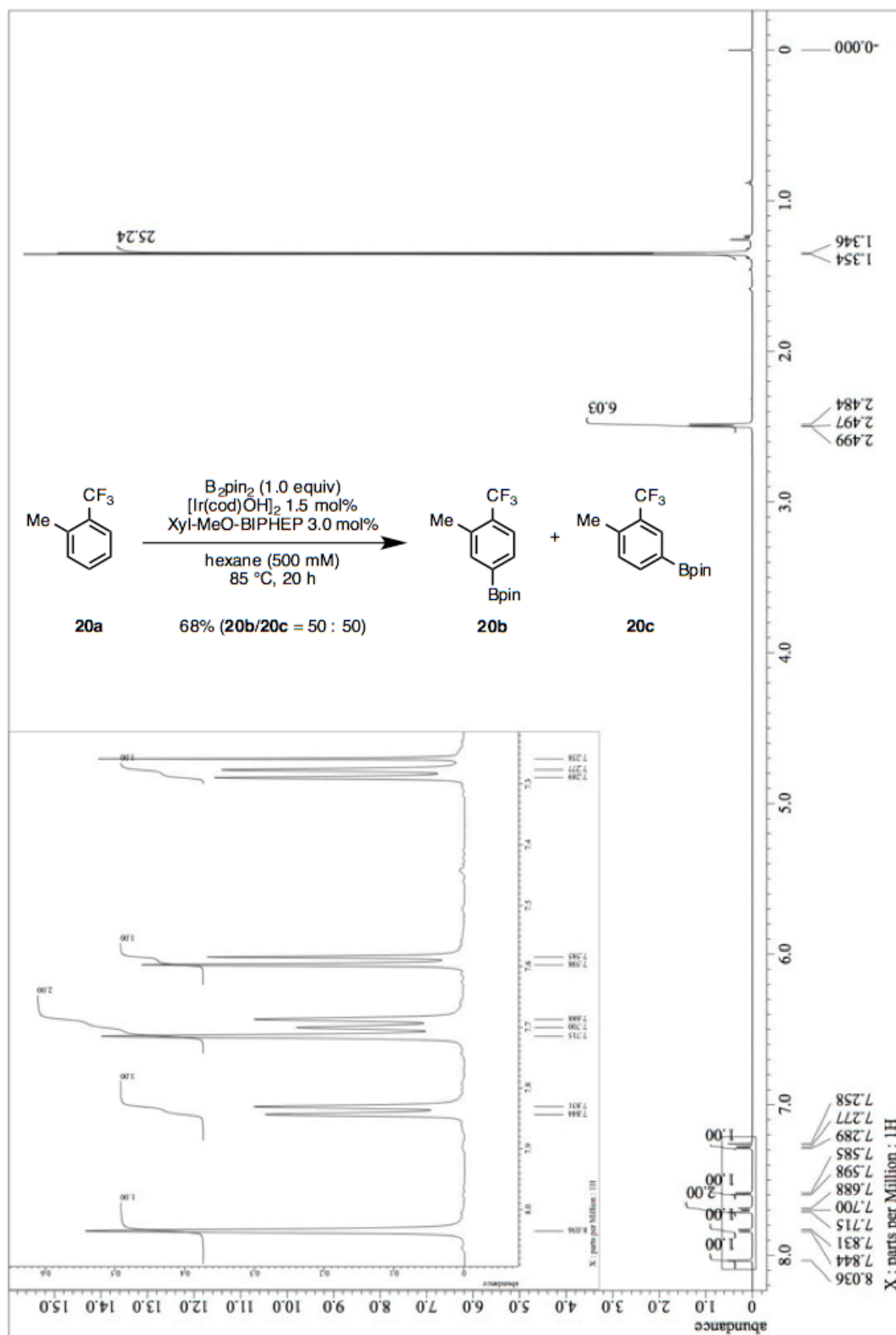
^1H NMR (600 MHz, CDCl_3) of 13b



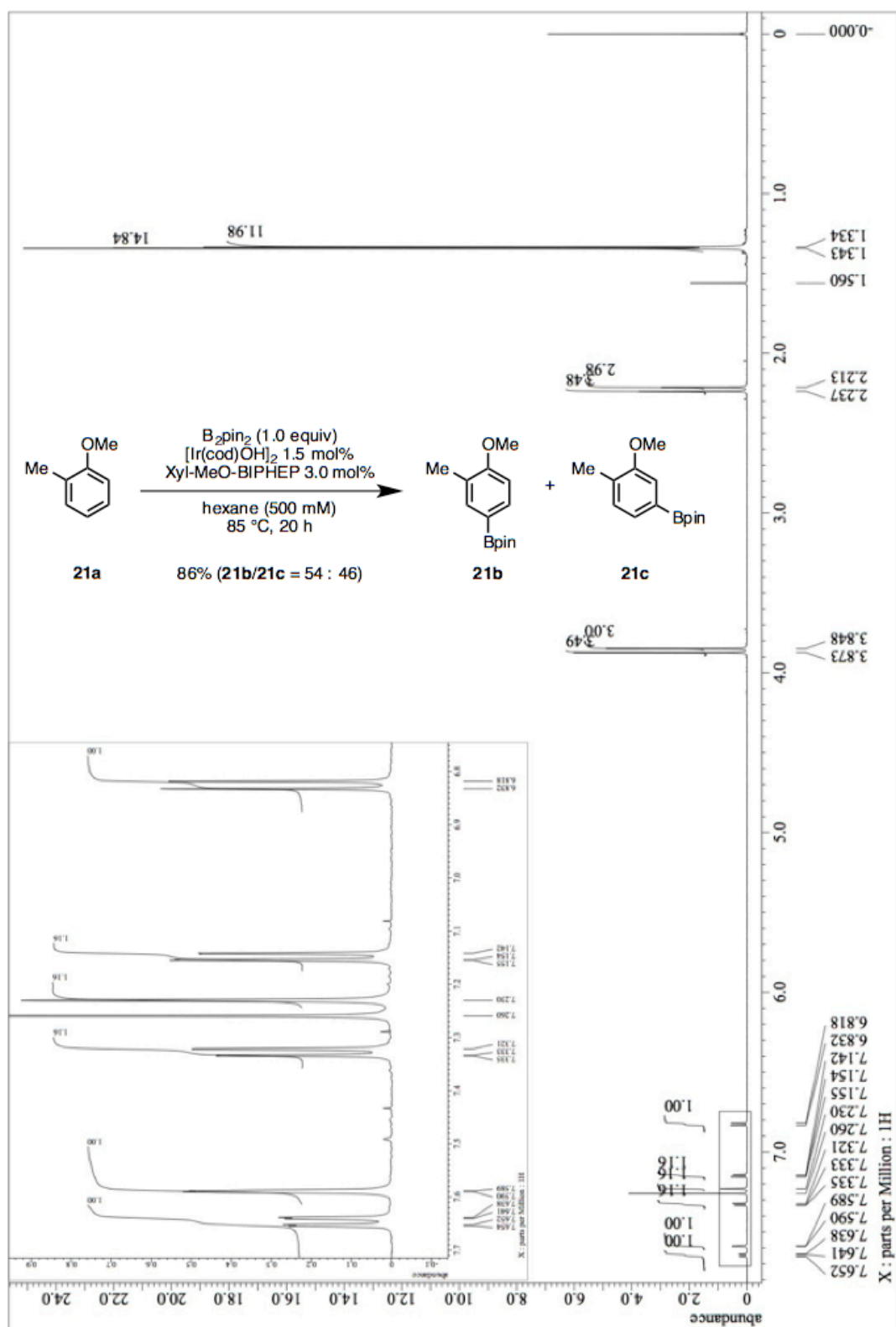
¹³C NMR (600 MHz, CDCl₃) of 13b



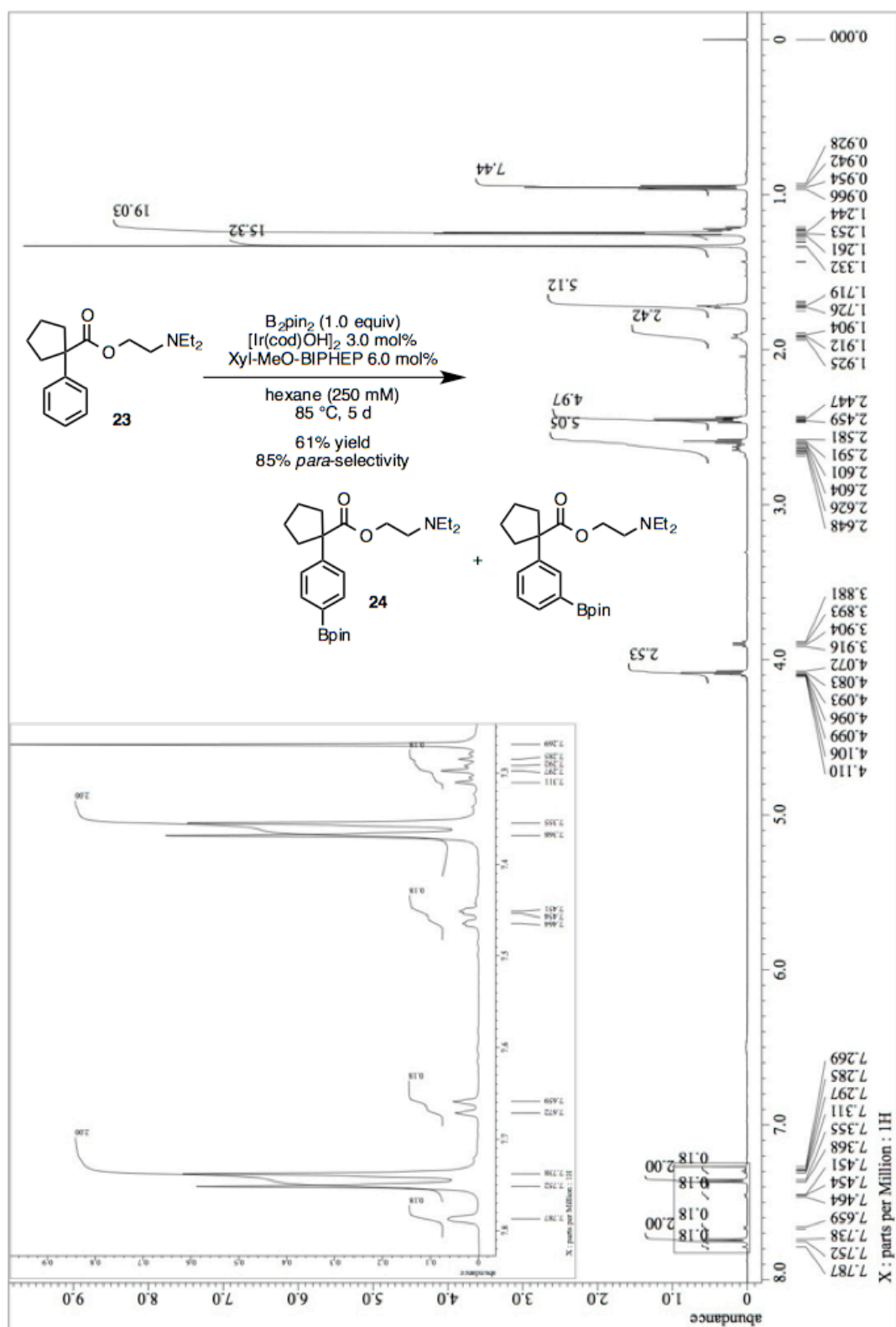
¹H NMR (600 MHz, CDCl₃) of C–H borylation of 20a



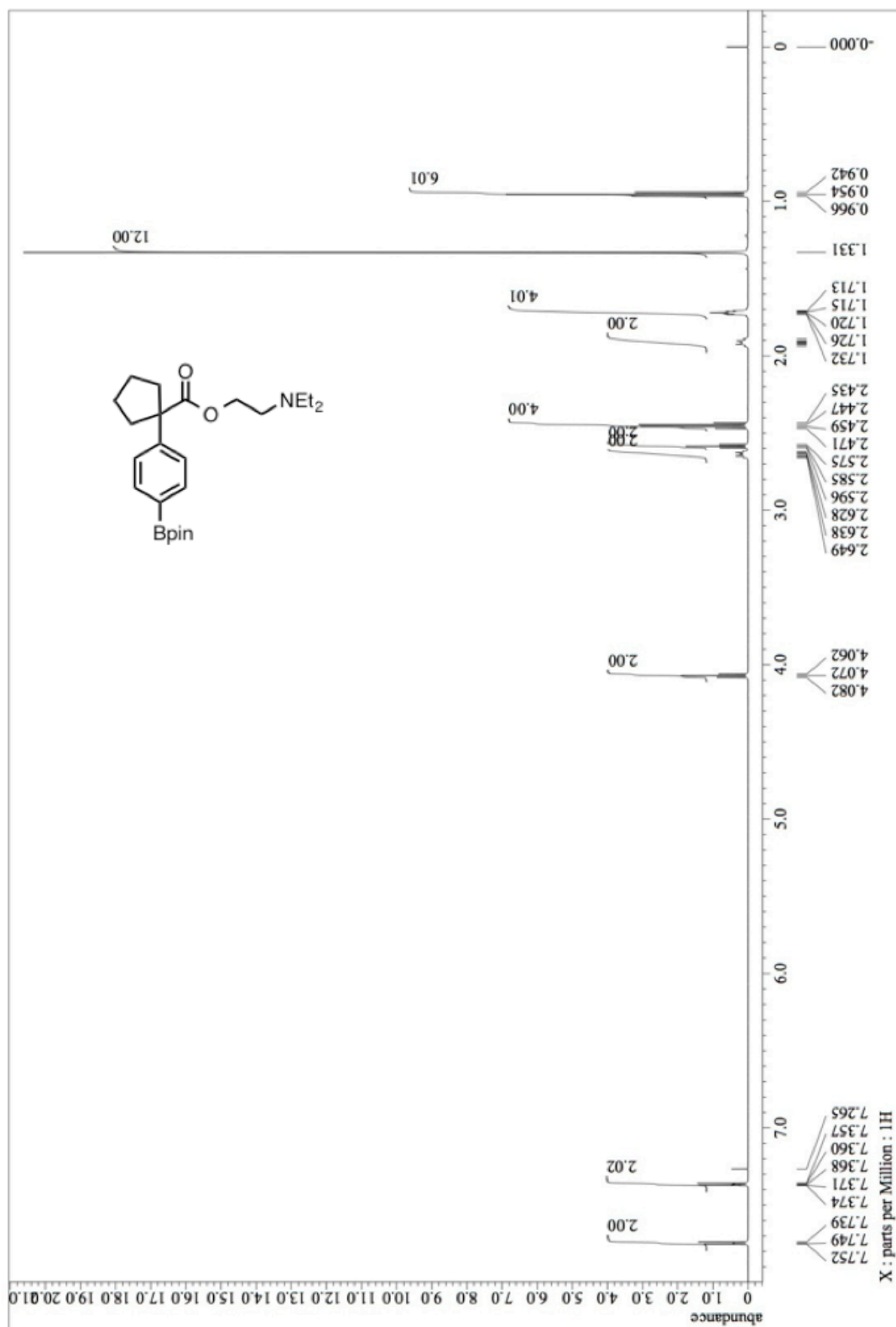
¹H NMR (600 MHz, CDCl₃) of C–H borylation of 21a



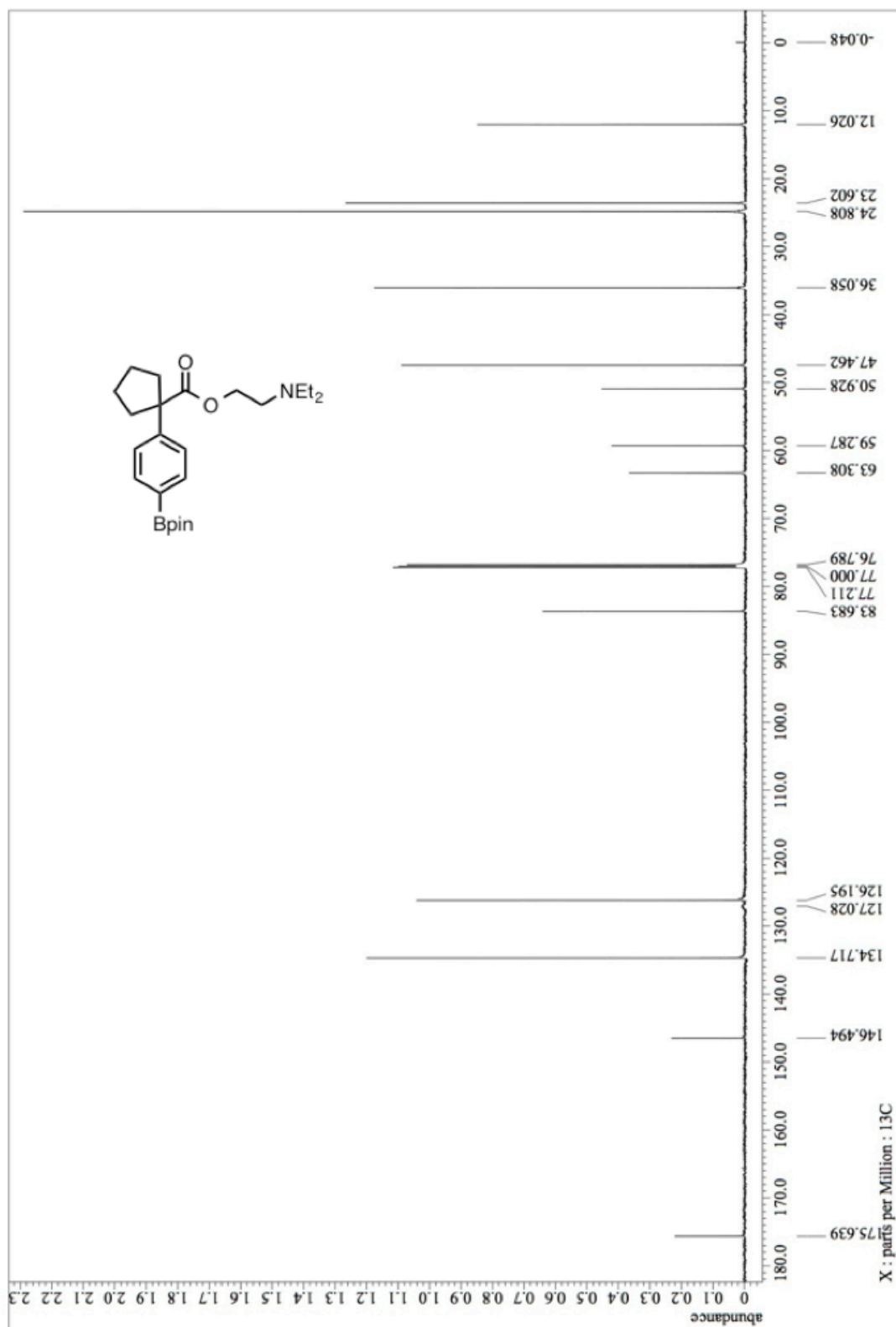
¹H NMR (600 MHz, CDCl₃) of isolated isomers of *para*-selective C–H borylation of 23



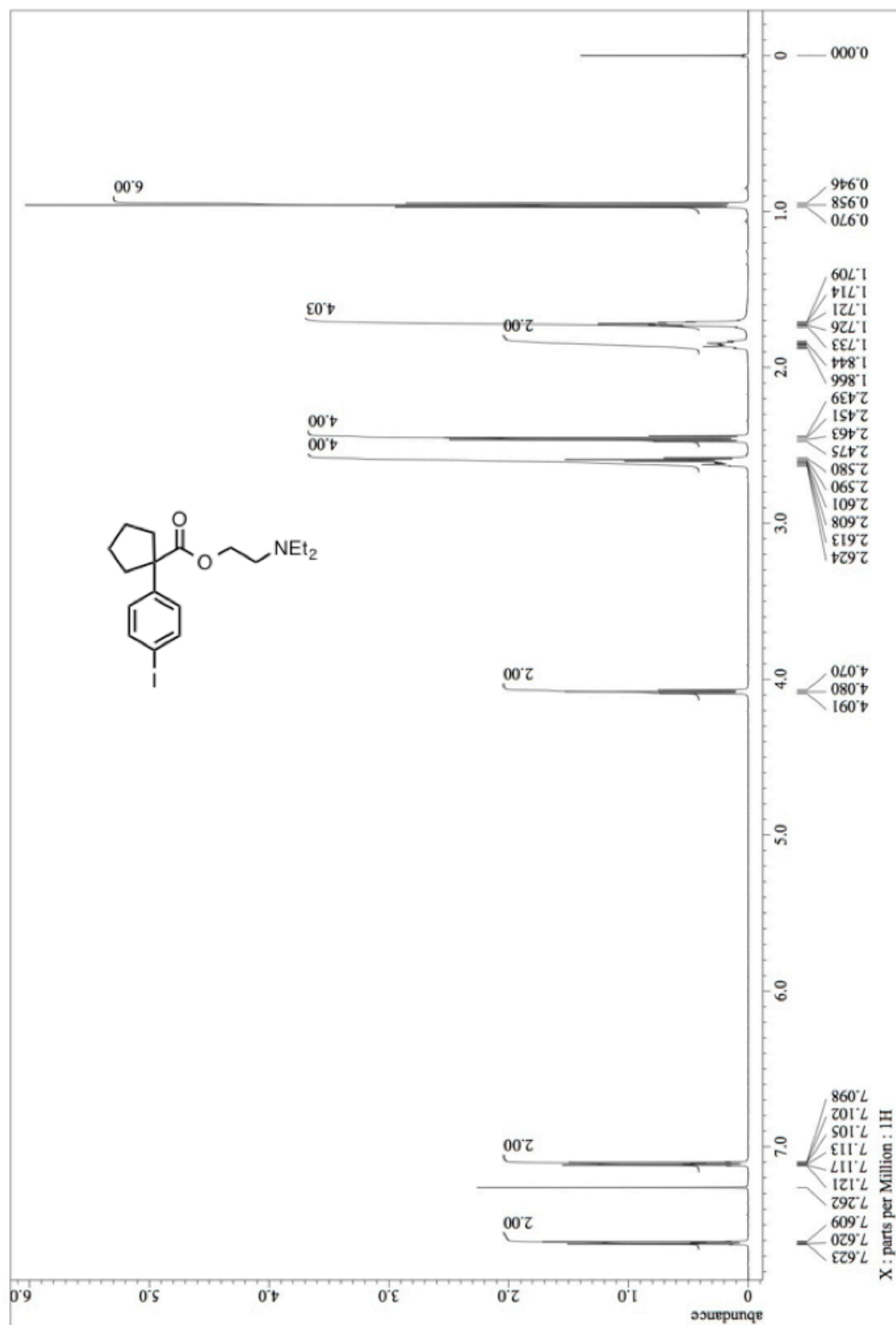
^1H NMR (600 MHz, CDCl_3) of 24



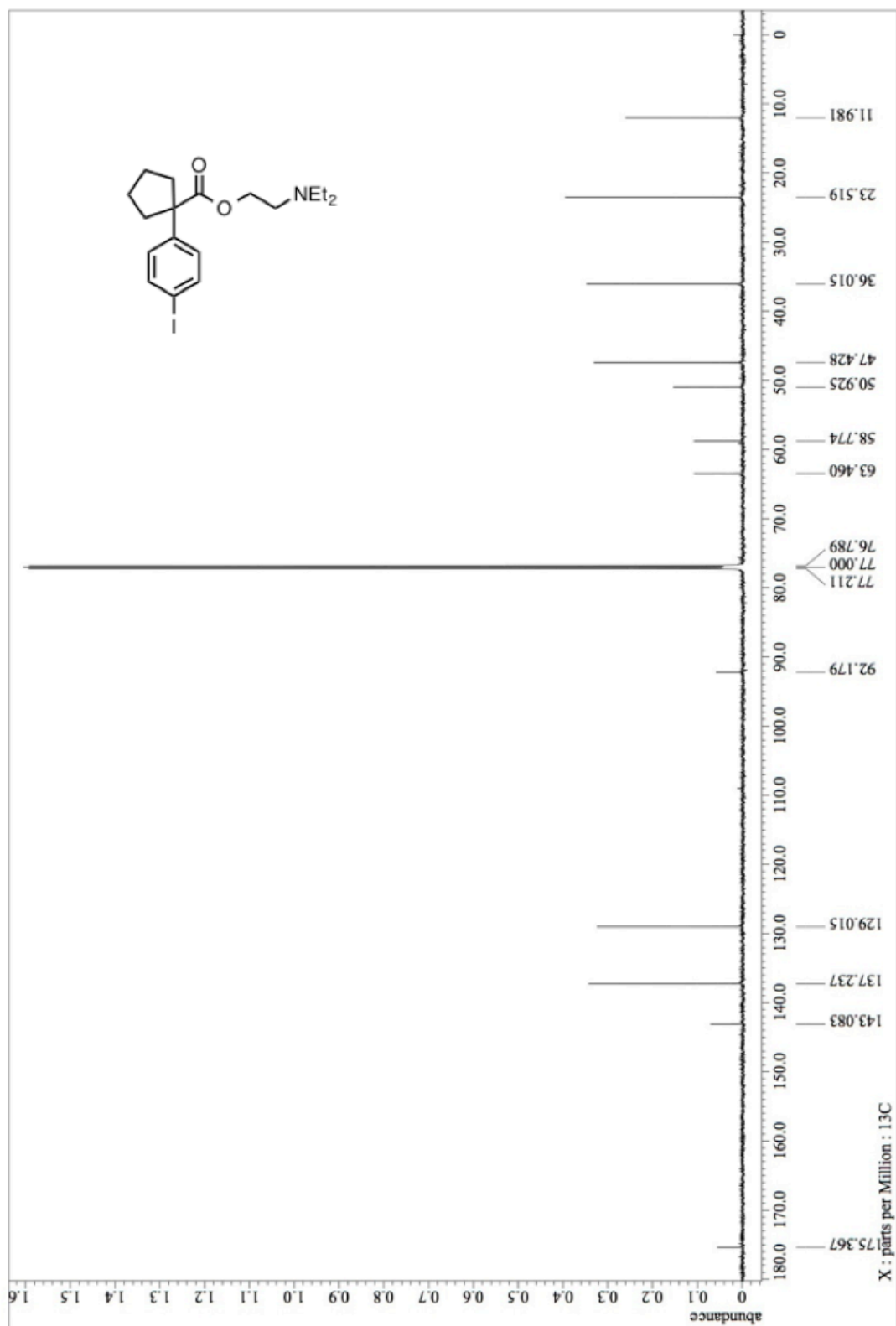
^{13}C NMR (600 MHz, CDCl_3) of **24**



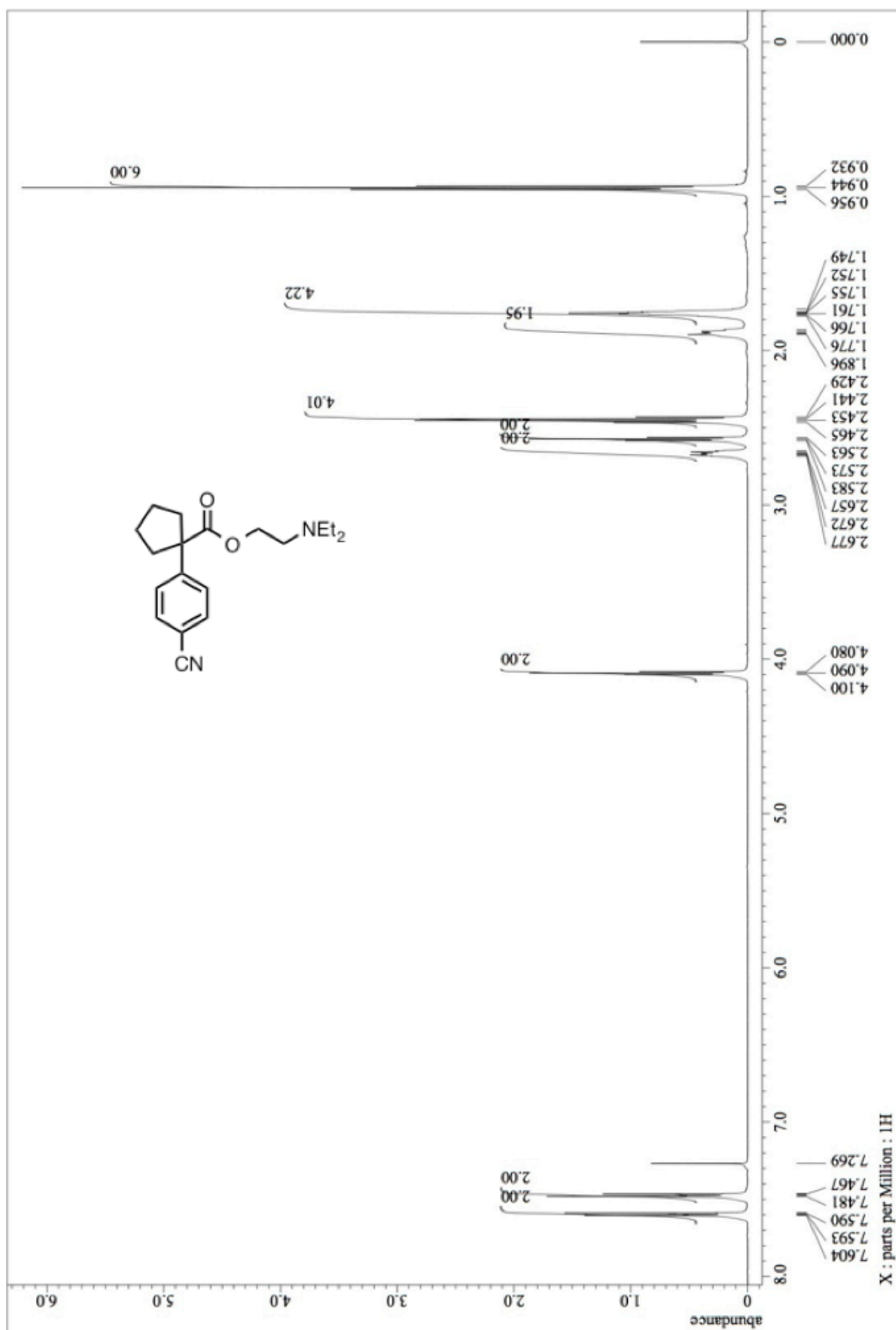
^1H NMR (600 MHz, CDCl_3) of **25**



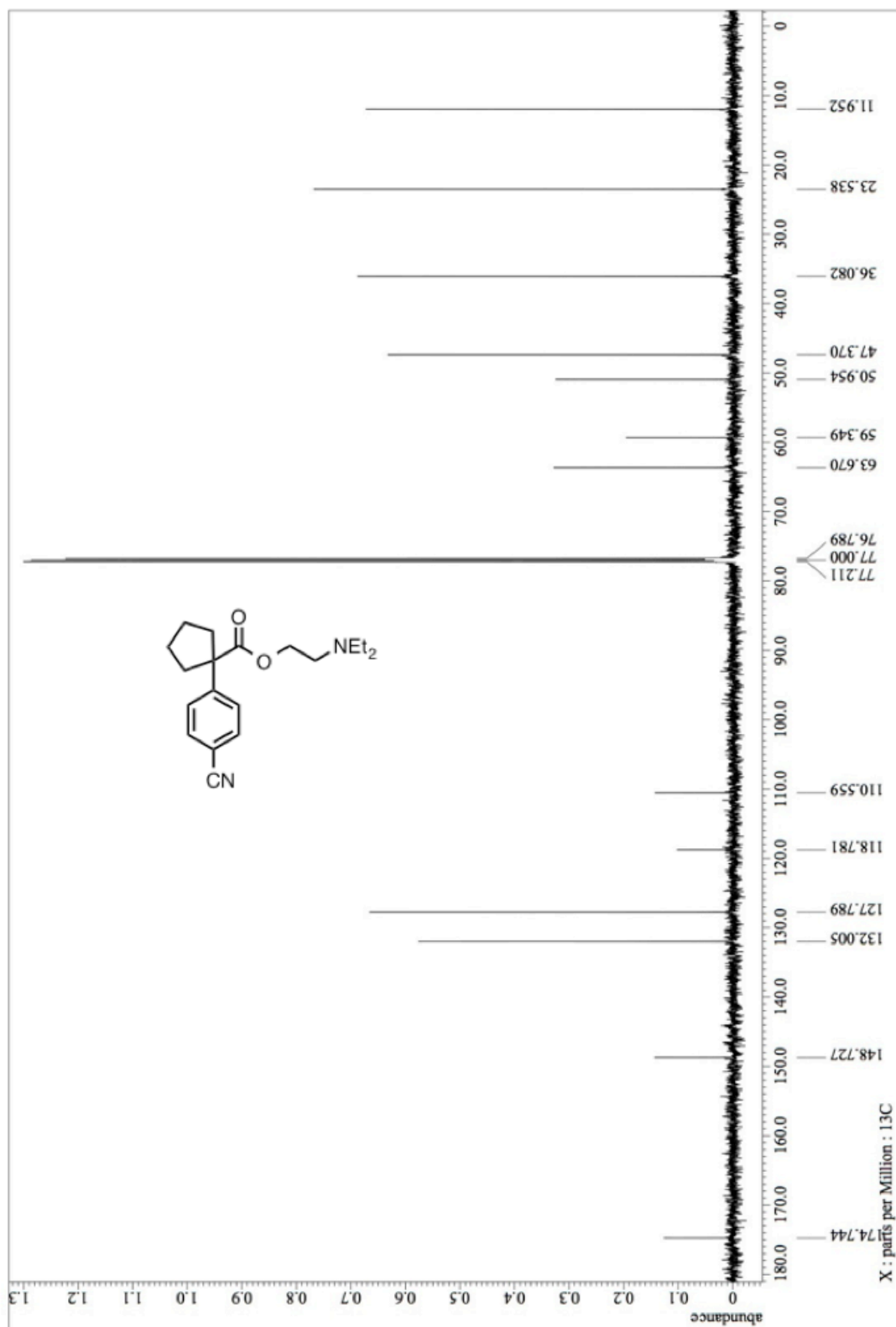
^{13}C NMR (600 MHz, CDCl_3) of **25**



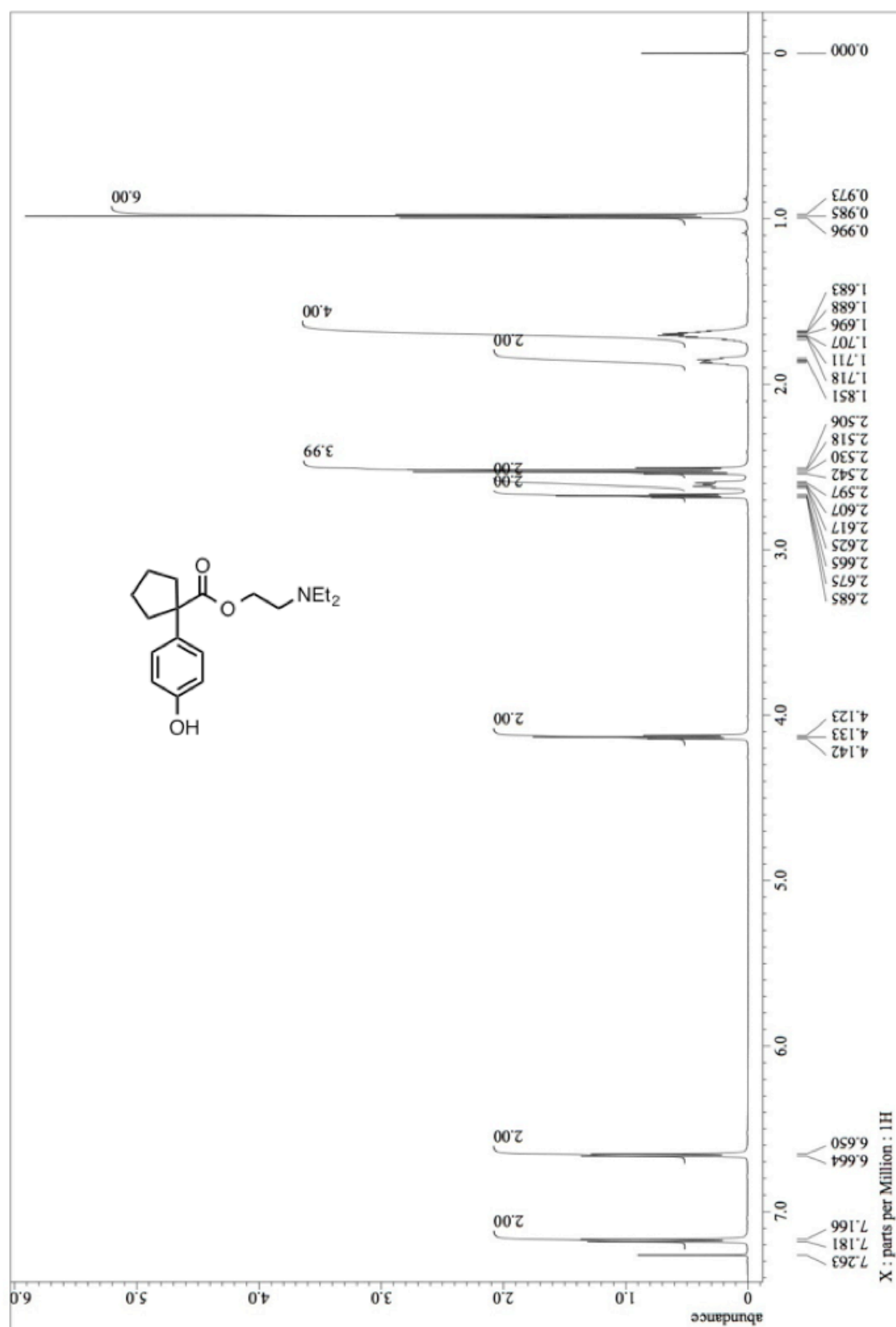
¹H NMR (600 MHz, CDCl₃) of 26



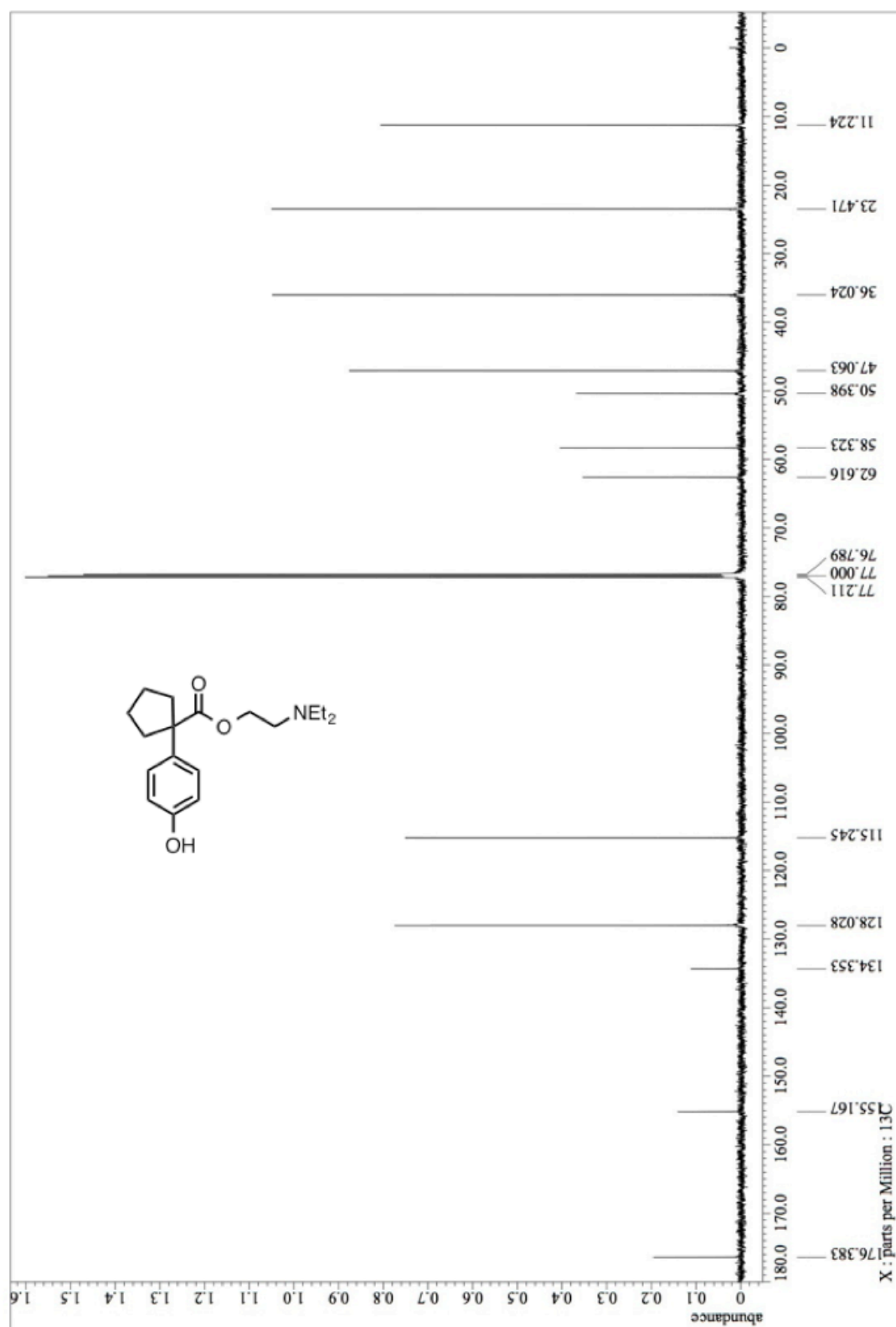
^{13}C NMR (600 MHz, CDCl_3) of 26



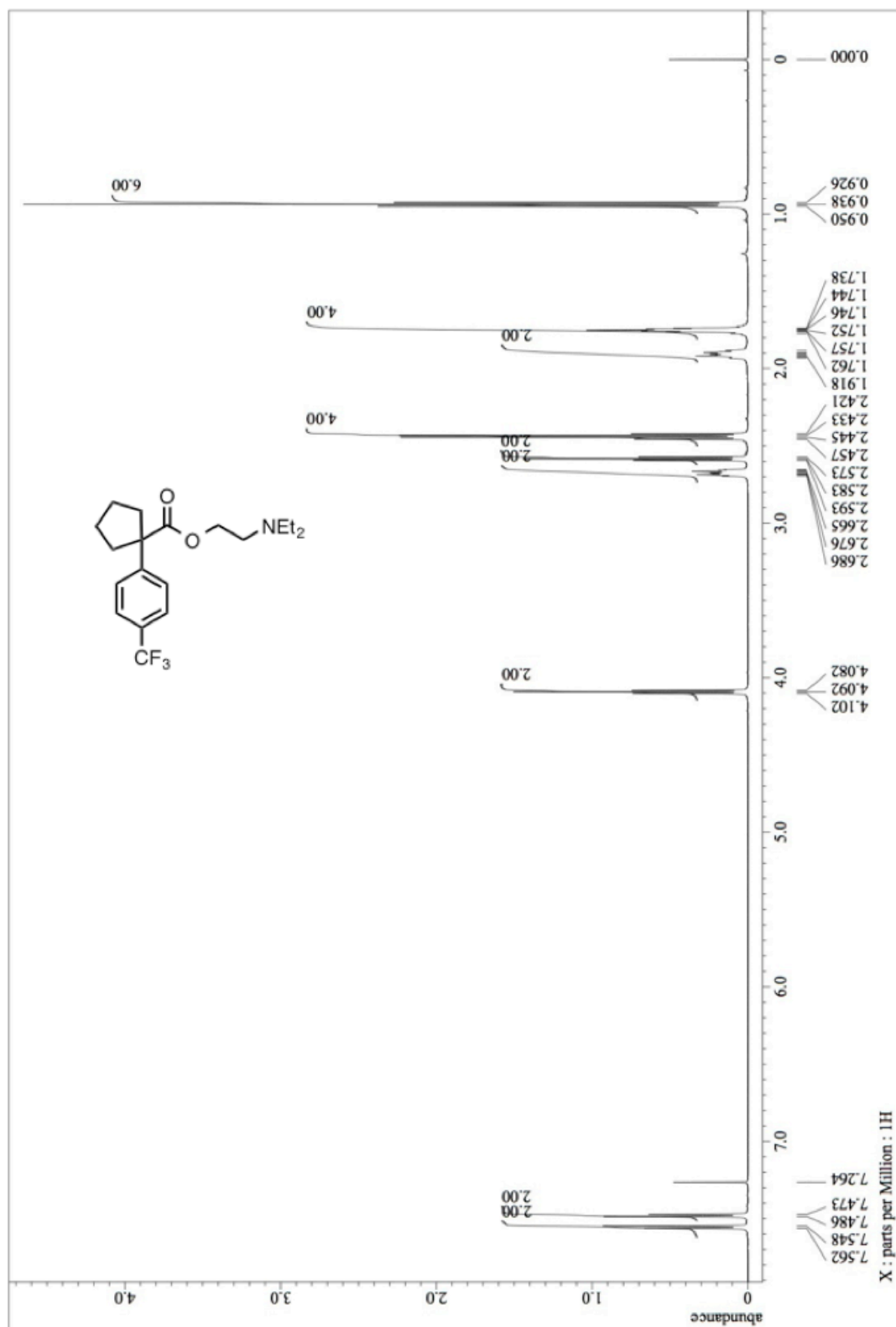
^1H NMR (600 MHz, CDCl_3) of 27



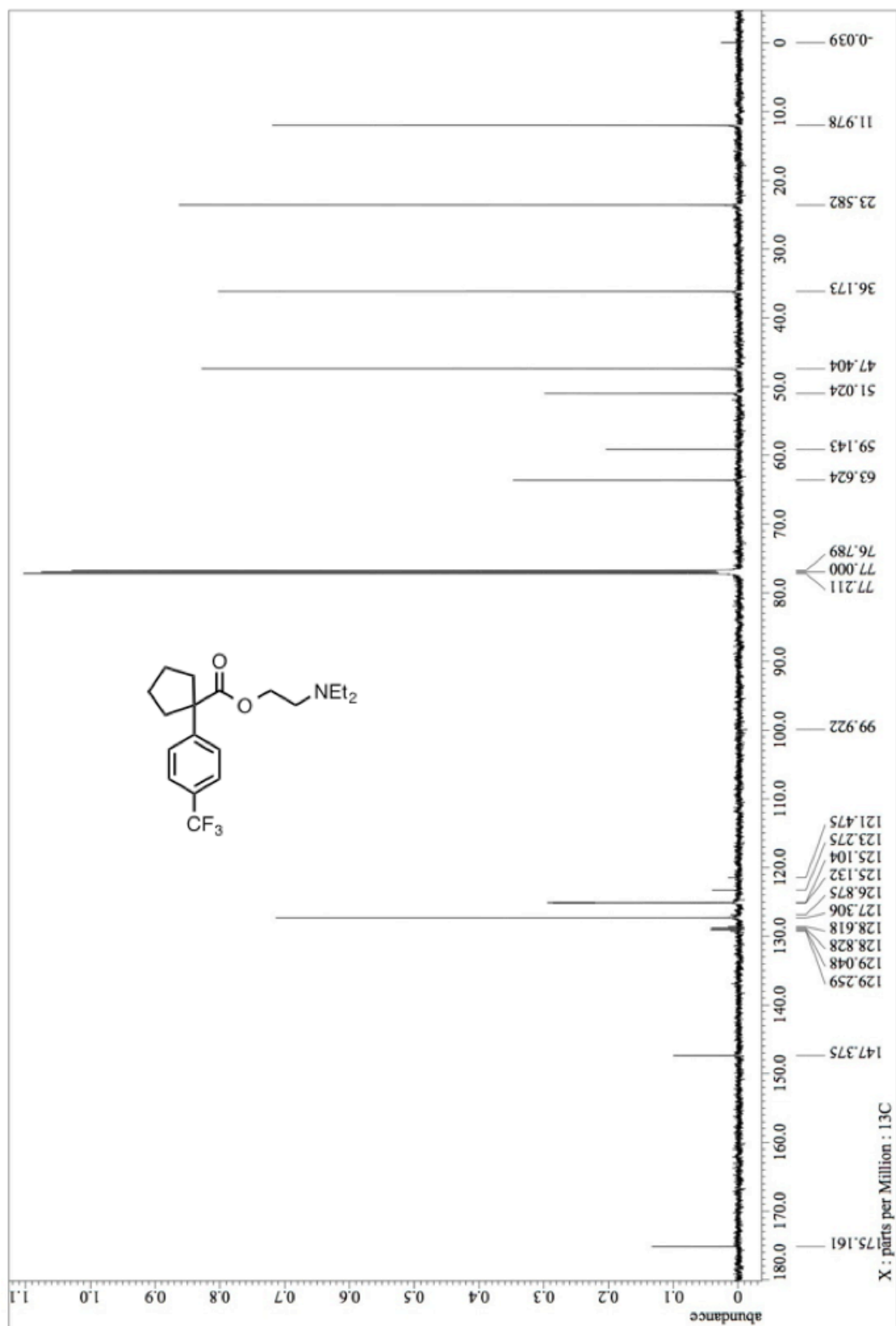
^{13}C NMR (600 MHz, CDCl_3) of 27



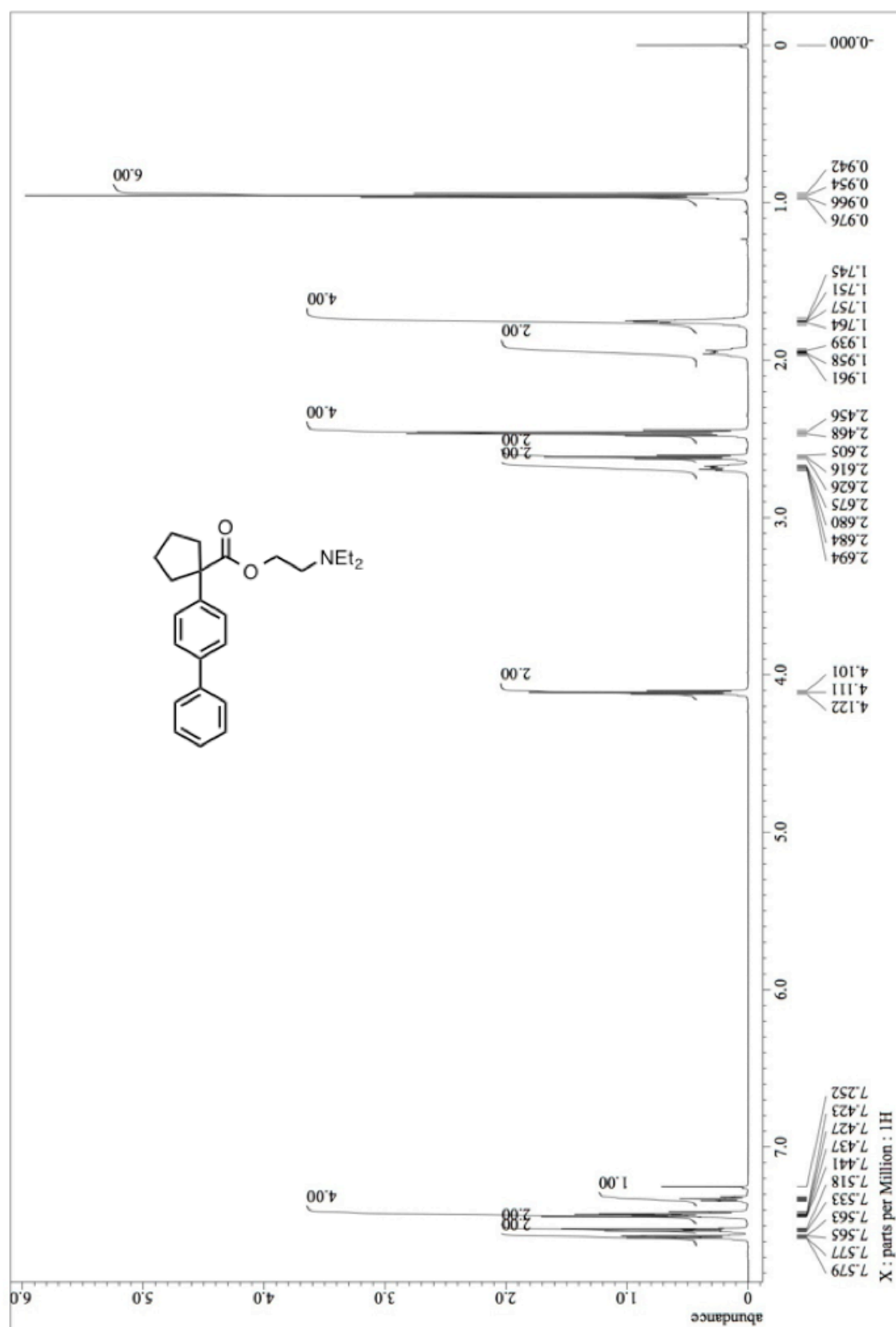
^1H NMR (600 MHz, CDCl_3) of 28



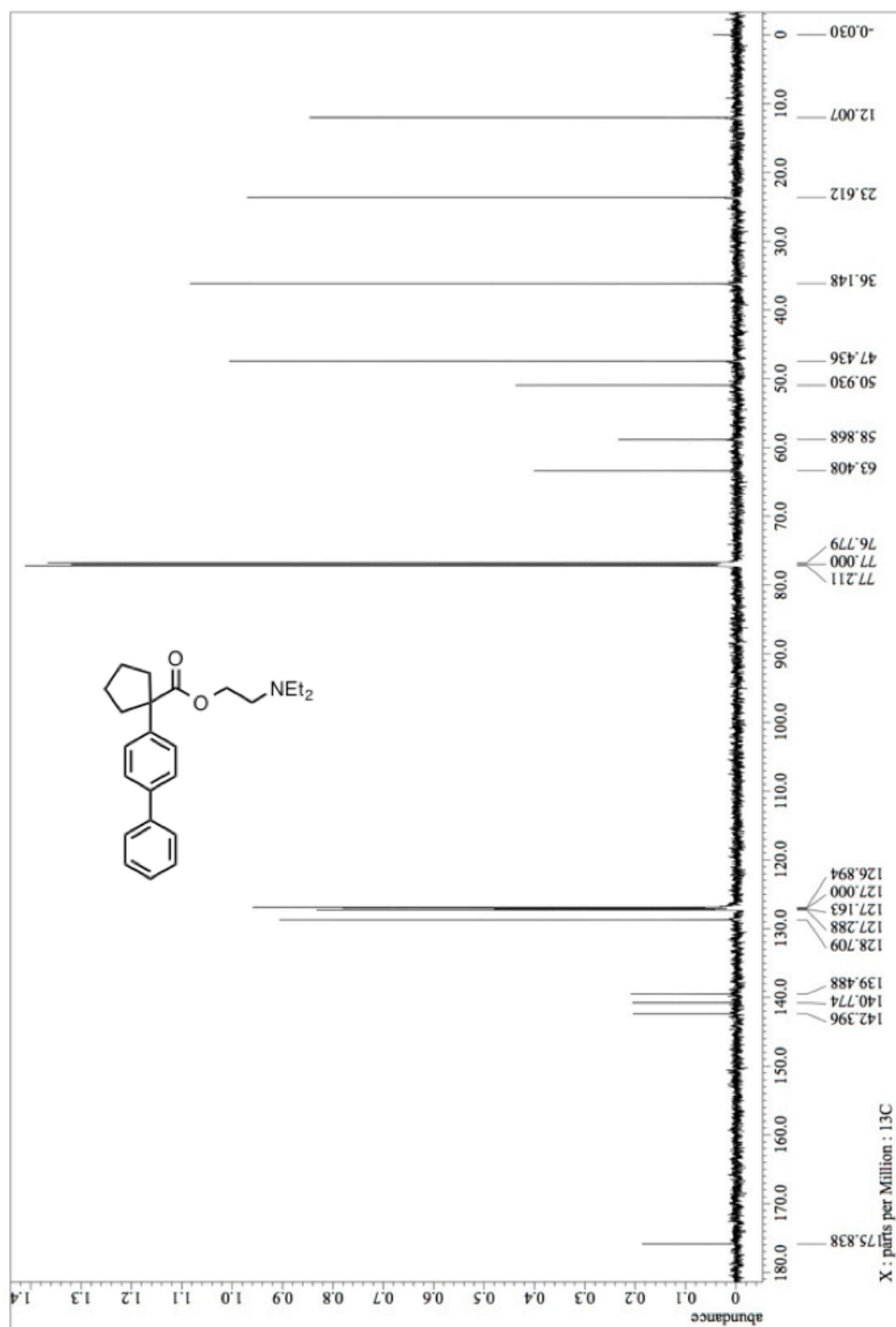
^{13}C NMR (600 MHz, CDCl_3) of 28



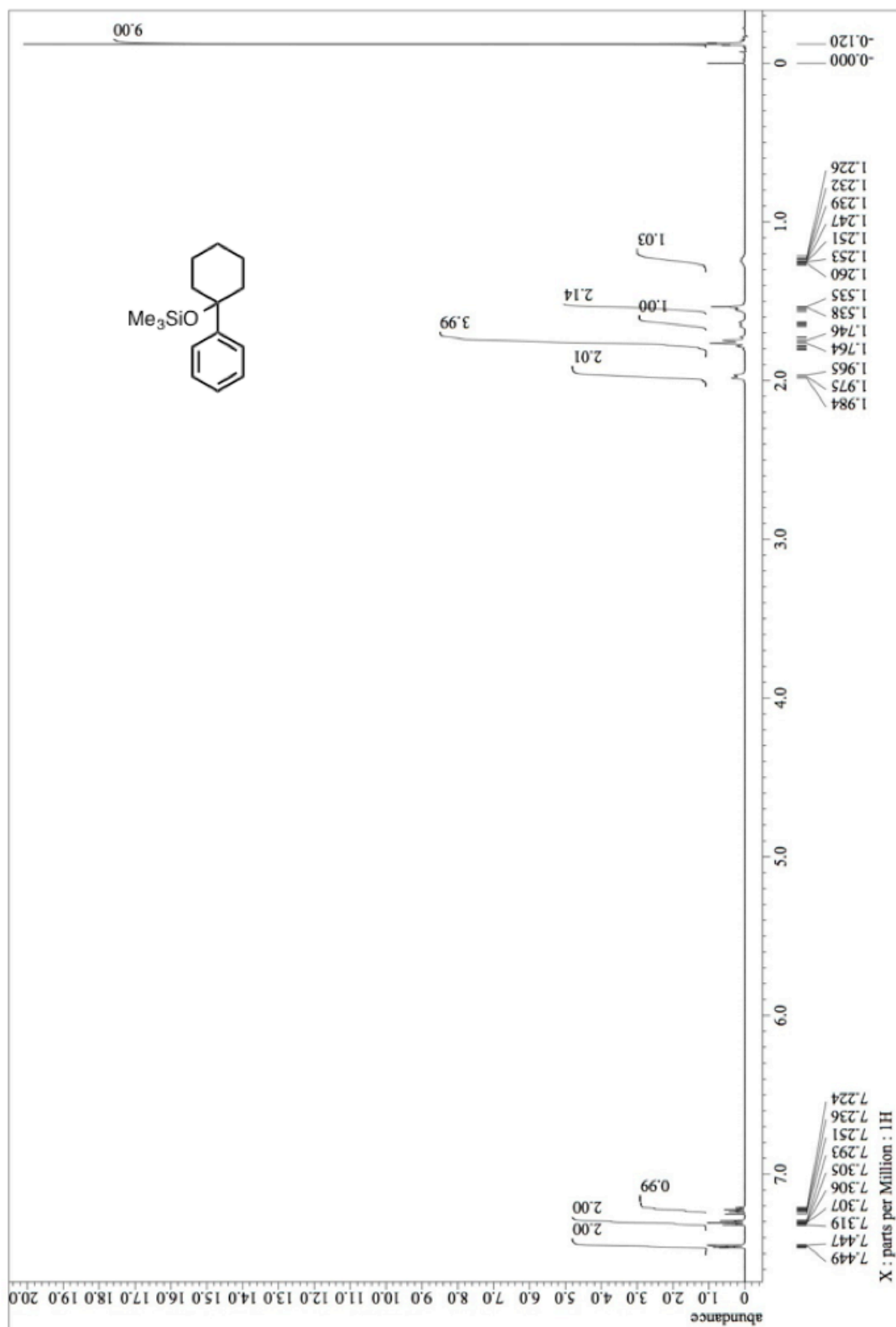
^1H NMR (600 MHz, CDCl_3) of 29



^{13}C NMR (600 MHz, CDCl_3) of **29**



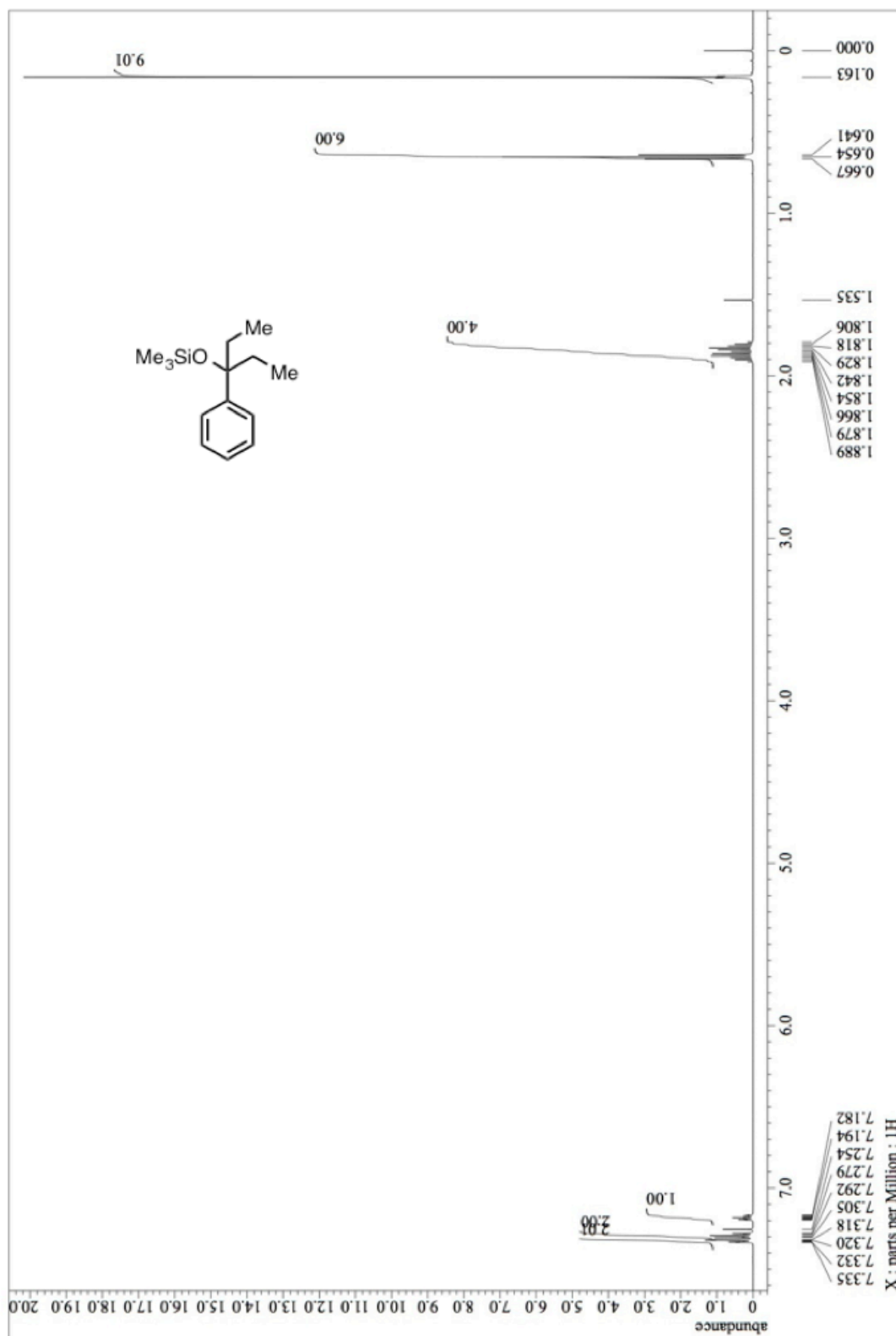
^1H NMR (600 MHz, CDCl_3) of 11a



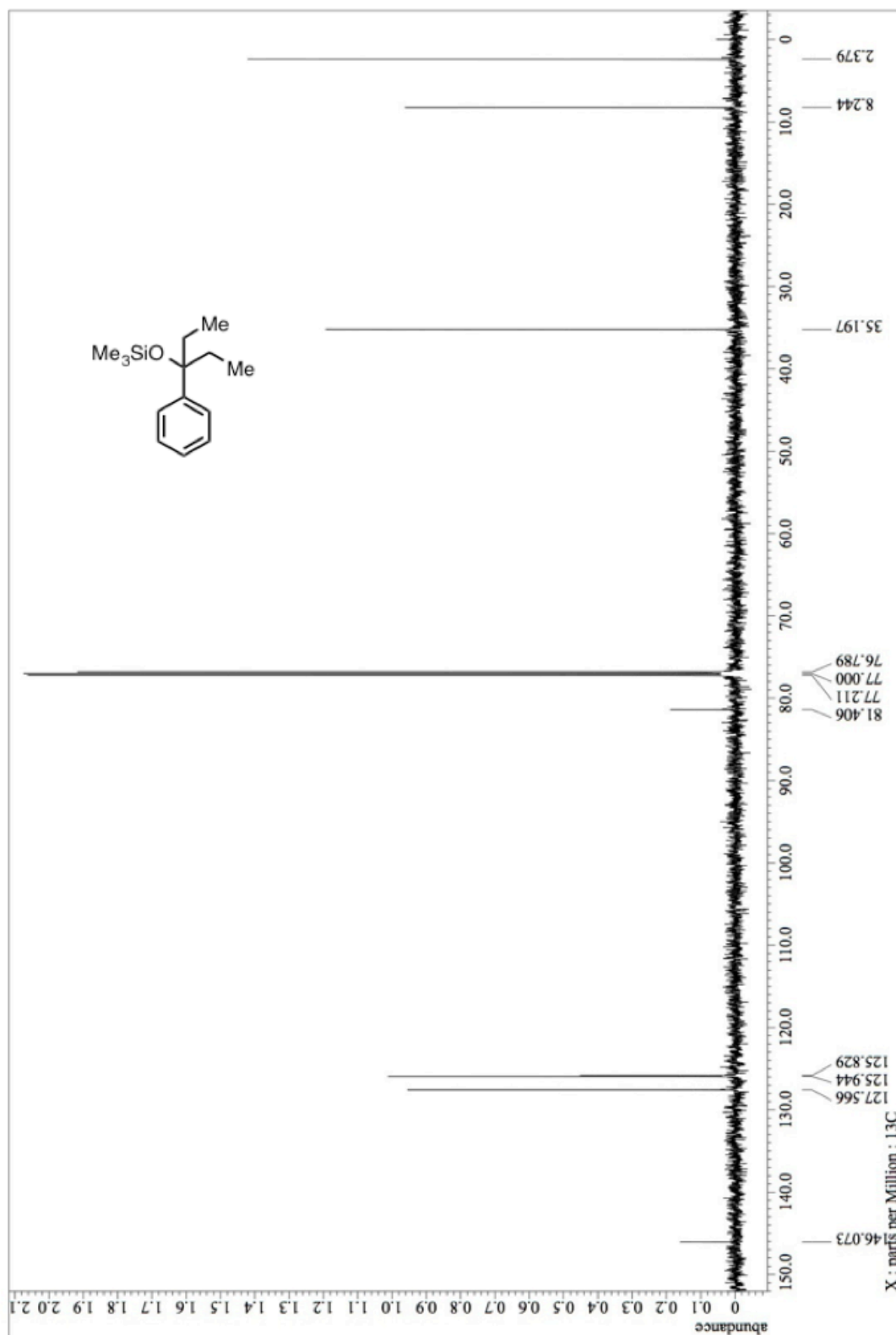
^{13}C NMR (600 MHz, CDCl_3) of 11a



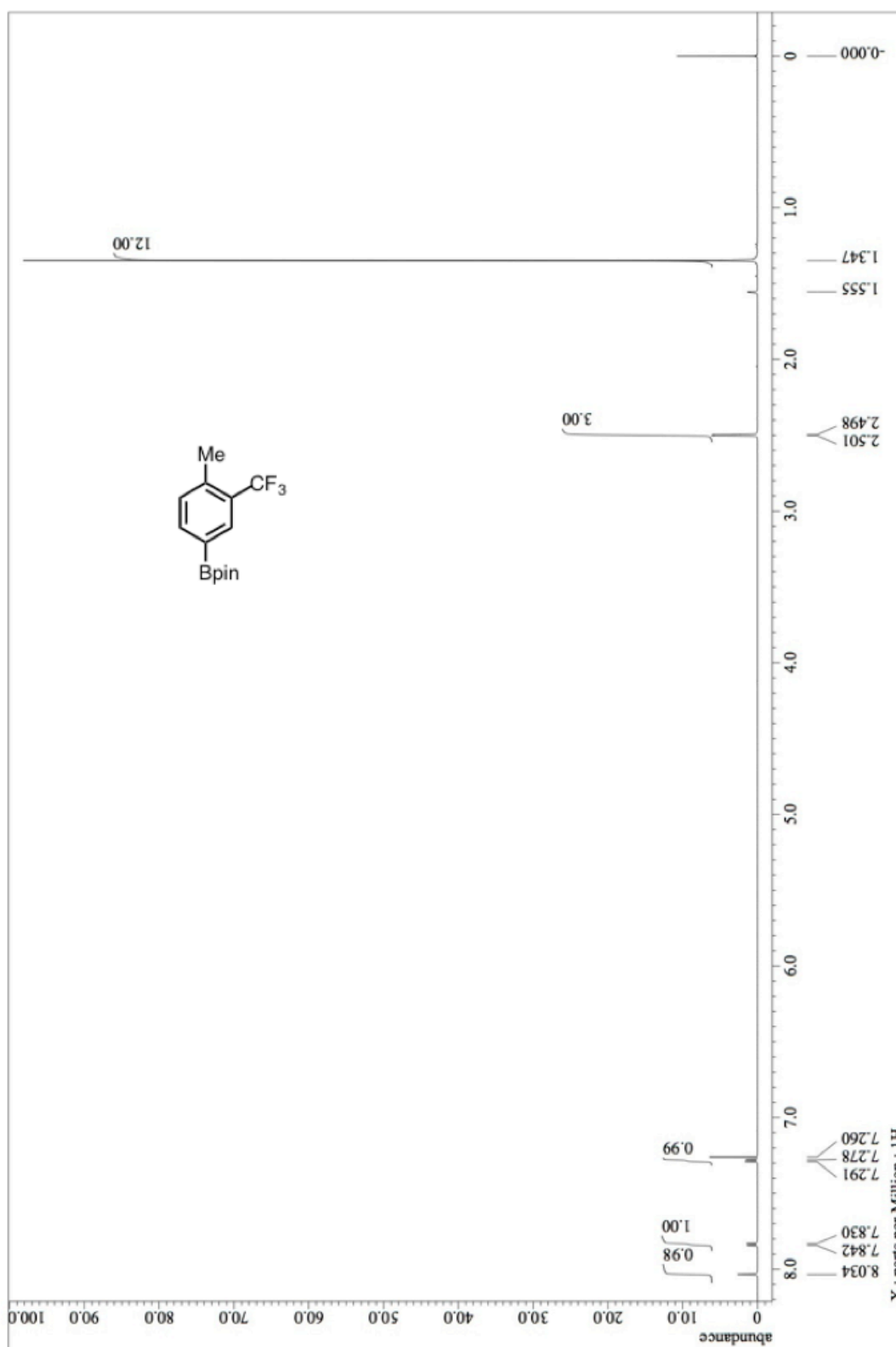
^1H NMR (600 MHz, CDCl_3) of 12a



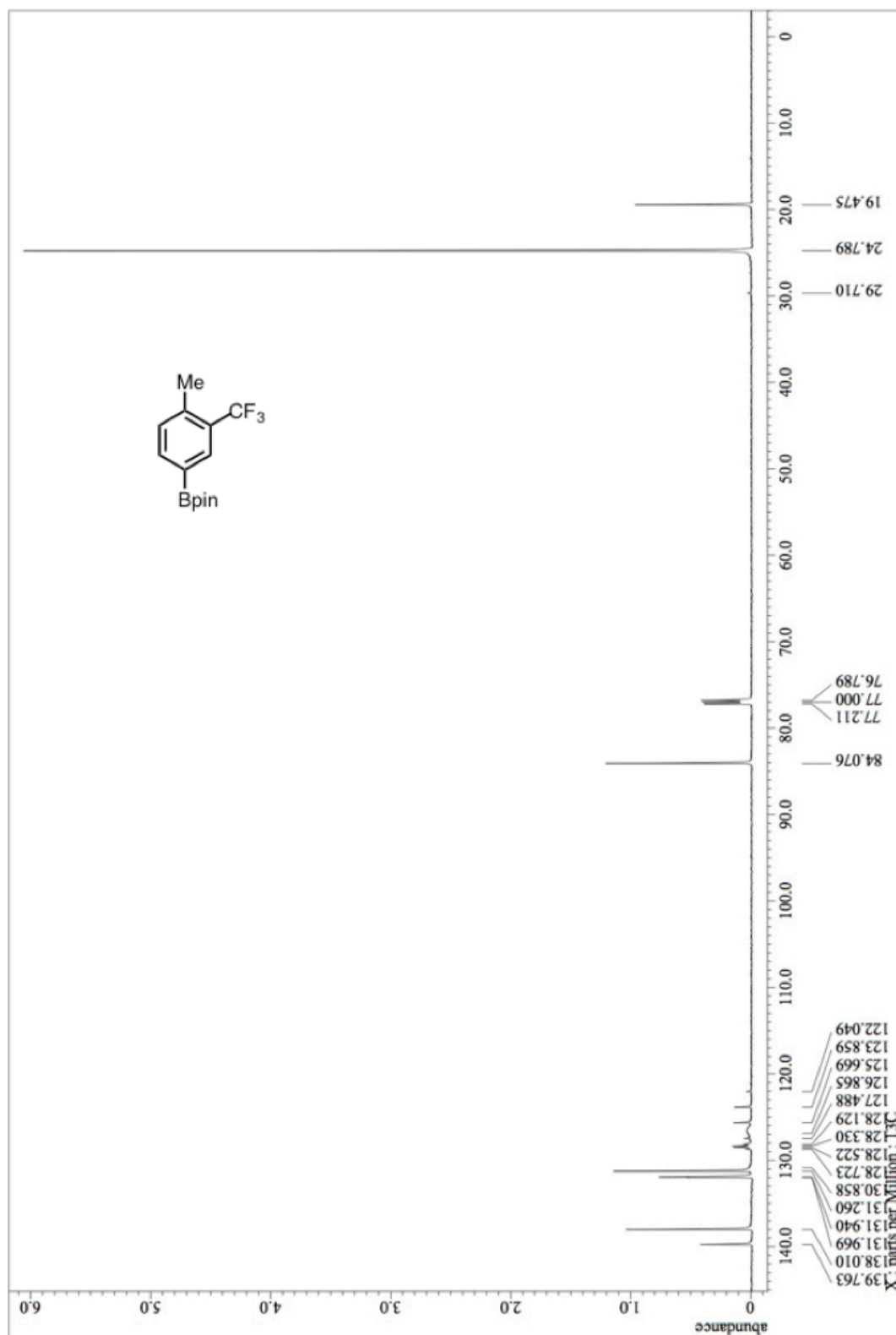
^{13}C NMR (600 MHz, CDCl_3) of 12a



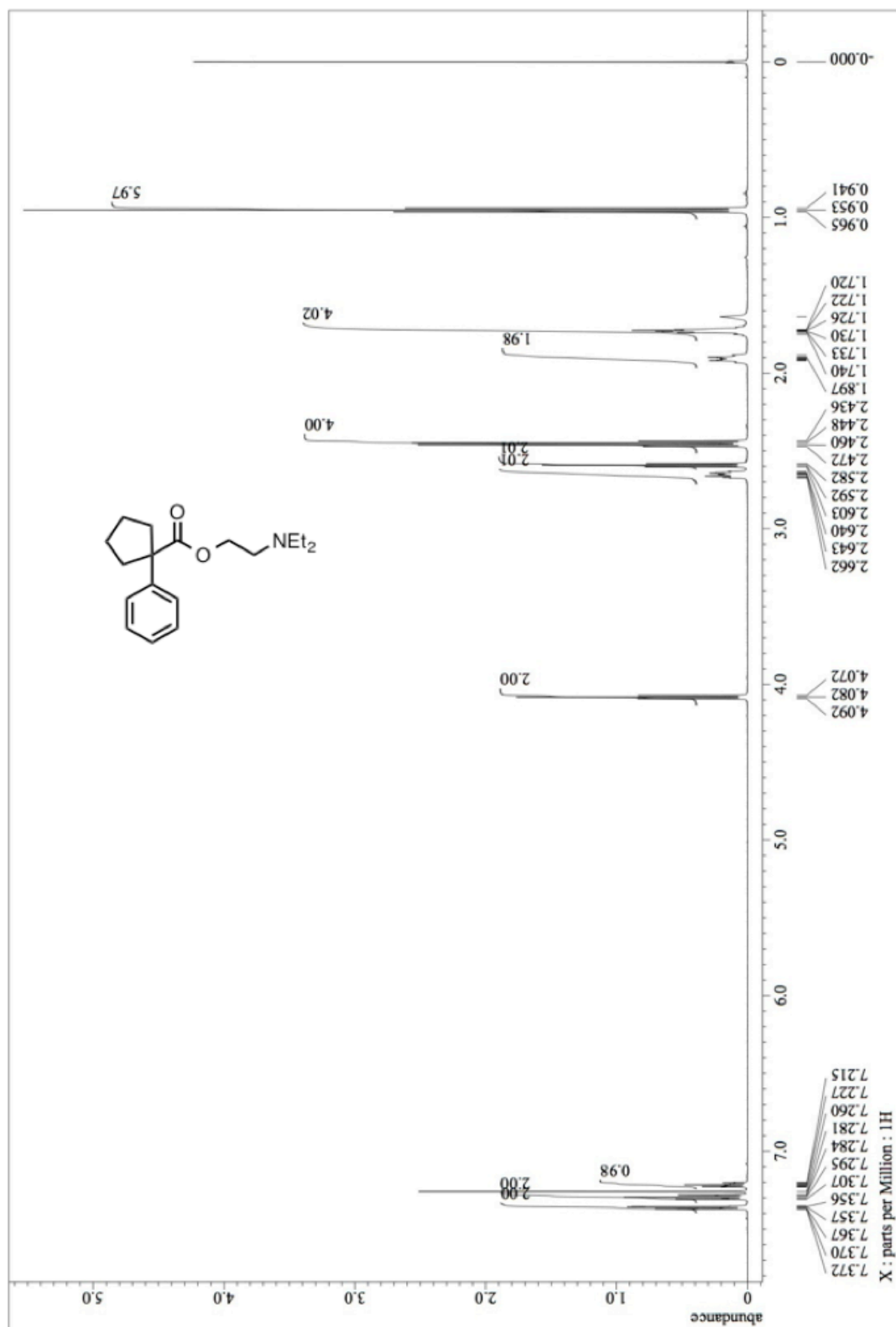
^1H NMR (600 MHz, CDCl_3) of **20c**



^{13}C NMR (600 MHz, CDCl_3) of **20c**



^1H NMR (600 MHz, CDCl_3) of 23



^{13}C NMR (600 MHz, CDCl_3) of 23

