Electronic Supplementary Material (ESI) for ChemComm.

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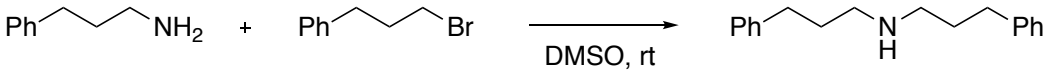
1. General

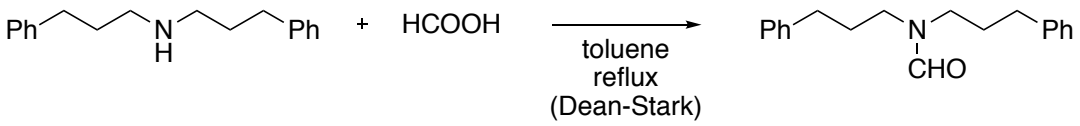
All operations were performed under nitrogen atmosphere unless otherwise noted. ^{1}H and ^{13}C -NMR spectra were recorded on a Varian 400 MHz (400 MHz for ^{1}H and 100 MHz for ^{13}C) or a Bruker AVANCE III HD (400 MHz for ^{1}H and 100 MHz for ^{13}C) using $CHCl_3$ (^{1}H, δ = 7.26 ppm) and $CDCl_3$ (^{13}C, δ = 77.0 ppm) as an internal standard. ^{11}B-NMR spectra were recorded on a Varian 400 MHz or a Bruker AVANCE III HD (128 MHz for ^{11}B) using BF_3•OEt_2 as an external standard (δ = 0 ppm). ^{19}F-NMR spectra were recorded on a Bruker AVANCE III HD (377 MHz for ^{19}F) using hexafluorobenzene as an external standard (δ = -164.9 ppm). IR spectra were recorded on an FT/IR-4200 (JASCO Co., Ltd.) spectrometer. Flash column chromatography was conducted on silica gel 60N (Kanto Chemical Co., Inc.) and preparative thin-layer chromatography (PTLC) was carried out on silica gel (Wako gel B-5F). A GPC system (LC-9130NEXT) was used for further purification. High-resolution mass analyses were performed on a Bruker micrOTOF-15focus or a JEOL JMS-GCMATEII. Dehydrated solvents were purchased from Kanto Chemical Co., Inc., and stored over molecular sieves.

2. Preparation of carbamoylboranes

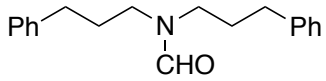


N, *N*-Bis(3-phenylpropyl)amine was prepared according to the literature.[1]

A DMSO (300 mL) solution of 3-phenylpropylamine (5.69 mL, 40.0 mmol) and 3-phenylpropylbromide (3.02 mL, 20.0 mmol) was stirred for 5 days. After the solution was diluted with AcOEt (500 mL), the mixture was washed with 5% Na_2CO_3 aqueous solution three times and dried over Na_2SO_4. Volatile materials were removed under reduced pressure and the residue was purified by silica gel chromatography (hexane : ethyl acetate : NEt_3 = 75 : 20 : 5 to 55 : 40 : 5) to give *N*, *N*-bis(3-phenylpropyl)amine (3.69 g, 14.6 mmol) in 73% yield. Spectral data of the product were consistent with those of the literature.[1]

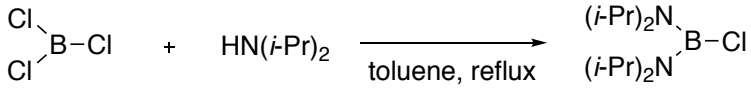


To remove water from a reaction mixture, a Dean-Stark apparatus was attached to a reaction flask. In the flask, toluene (15 mL), *N*, *N*-bis(3-phenylpropyl)amine (1.27 g, 5.01 mmol), and formic acid (0.57 mL, 15 mmol) were mixed, and the reaction mixture was refluxed for 7 hours. Volatile materials were removed under reduced pressure and the residue was purified by silica gel chromatography (hexane : ethyl acetate = 70 : 30 to 50 : 50) to give *N*, *N*-bis(3-phenylpropyl)formamide (1.32 g, 4.70 mmol) in 94% yield.



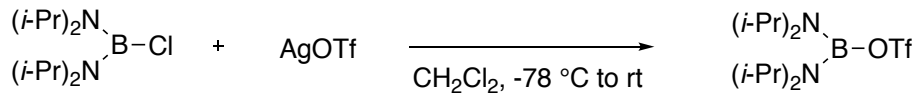
***N*, *N*-Bis(3-phenylpropyl)formamide**

IR (neat): 3026, 2936, 2861, 1669, 1454, 1428, 1164, 749, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) (400 MHz): δ = 1.80-1.91 (4H, m), 2.56-2.65 (4H, m), 3.21 (2H, t, *J* = 7.0 Hz), 3.36 (2H, t, *J* = 7.6 Hz), 7.12-7.33 (10H, m), 8.02 (1H, s); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = 28.9, 29.9, 32.5, 33.2, 41.9, 46.8, 126.0, 126.2, 128.3, 128.4, 128.6, 140.5, 141.3, 162.9 (one carbon missing); HRMS (ESI): $(M+H)^+$, found 282.1858. $C_{19}H_{24}NO^+$ requires 282.1852;

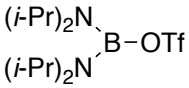


Chlorobis(diisopropylamino)borane was prepared according to the literature.[2]

To a toluene (42.5 mL) solution of diisopropylamine (26.8 mL, 191 mmol) was added a 1.0 M haptane solution of BCl_3 (42.5 mL, 42.5 mmol) slowly at room temperature. The reaction mixture was warmed to 40 °C. Then the mixture was refluxed for 5 hours. In a glove box, the resultant salt was filtered off. Hexane was used as an eluent. After the removal of solvents, chlorobis(diisopropylamino)borane was distilled under reduced pressure (8.36 g, 33.9 mmol, 80% yield). Spectral data of the product were consistent with those of the literature.[2]

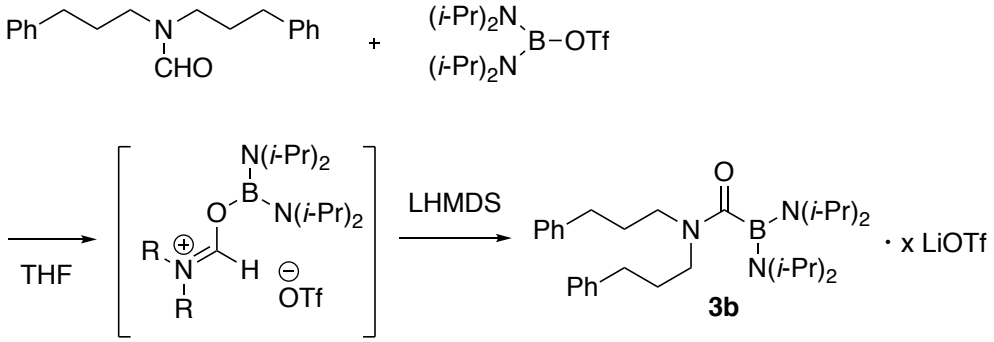


A mixture of silver triflate (4.97 g, 19.3 mmol) and CH_2Cl_2 (160 mL) was cooled to -78 °C. To the mixture was added a CH_2Cl_2 solution (40 mL) of chlorobis(diisopropylamino)borane (4.77 g, 19.3 mmol) slowly at that temperature. After completion of dropping, the reaction mixture was warmed to room temperature slowly and stirred at the temperature for 1 hour. In a glove box, the resultant silver chloride was filtered off through short pad of Celite®. Solvent was removed under reduced pressure to give bis(diisopropylamino)boryl trifluoromethanesulfonate (6.72 g, 18.7 mmol) as a brown solid in 97% yield.



Bis(diisopropylamino)boryl trifluoromethanesulfonate

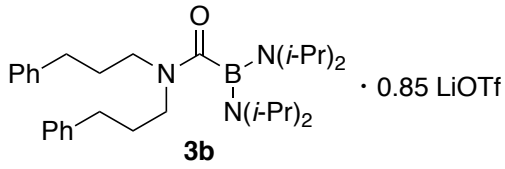
^{1}H NMR ($CDCl_3$) (400 MHz): δ = 1.17 (24H, d, *J* = 6.8 Hz), 3.47 (4H, sept, *J* = 6.8 Hz); ^{11}B NMR ($CDCl_3$) (128 MHz): δ = 25.0 (singlet);



Carbamoylboranes were prepared by modified procedure.[3]

In a two-necked flask, bis(diisopropylamino)boryl trifluoromethanesulfonate (2.88 g, 8.00 mmol) was cooled to -78 °C. To this was added a THF (15 mL) solution of *N*, *N*-bis(3-phenylpropyl)formamide (2.25 g, 8.00 mmol) slowly at that temperature. The reaction mixture was warmed to room temperature and stirred for 5 minutes. The reaction mixture was cooled to -78 °C, then a THF solution of lithium hexamethyldisilazide (*ca.* 1.3M, 6.2 mL, 8.0 mmol) was added slowly. The mixture was warmed to room temperature slowly and stirred for 30 minutes. After solvents were removed under reduced pressure, the residue was transferred into a glove box. The product was extracted with hexane-toluene (3 : 1) and the solution was filtered several times. Solvents were removed under reduced pressure. The resultant solid residue was washed with hexane-toluene (95 : 5). The solid was collected and dried under vacuum to give **3b** ·

0.85LiOTf (3.05 g, 4.89 mmol) in 61% yield. **3b**・0.9LiOTf and **3b**・1.04LiOTf were also obtained by similar processes. LiOTf was identified by ^{19}F NMR. (carbamoylborane-LiOTf complex:^{19}F NMR (CD_3CN) (377 MHz): δ = -79.7; LiOTf :^{19}F NMR (CD_3CN) (377 MHz): δ = -79.8)

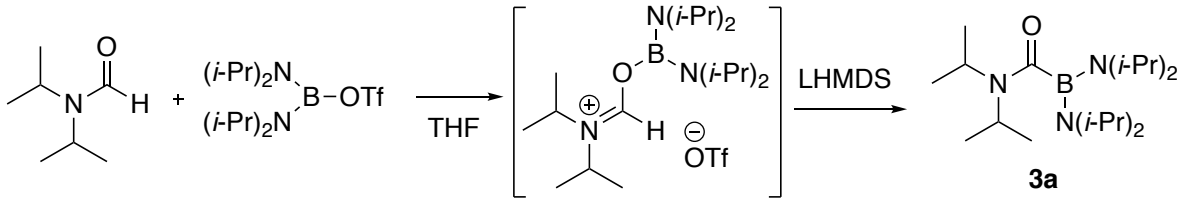


3b

Bis(diisopropylamino)(*N*,*N*-bis(3-phenylpropyl)carbamoyl)borane・0.85 LiOTf

(3b・0.85 LiOTf)

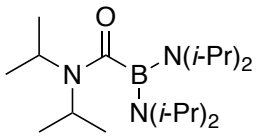
^1H NMR (CD_3CN) (400 MHz): δ = 1.09 (12H, d, *J* = 6.8 Hz), 1.15 (12H, d, *J* = 6.8 Hz), 1.72-1.93 (4H, m), 2.55-2.64 (4H, m), 3.21-3.32 (4H, m), 3.43 (4H, sept, *J* = 6.8 Hz), 7.14-7.32 (10H, m) (CHD_2CN (^1H, δ = 1.94) was used as an internal standard.); ^{13}C NMR (CD_3CN) (100 MHz): δ = 24.4, 24.6, 29.4, 30.3, 34.0, 34.2, 42.6, 48.4, 50.5, 126.8, 127.0, 129.2, 129.30, 129.33, 129.4, 142.3, 143.0, 189.9 (CD_3CN (^{13}C, δ = 118.26) was used as an internal standard.);^{11}B NMR (CD_3CN) (128 MHz): δ = 30.8; HRMS (ESI): $(M+Na)^+$, found 514.3962. $C_{31}H_{50}BN_3NaO^+$ requires 514.3945; *Anal.* Calcd for $C_{31.85}F_{2.55}H_{50}BN_3O_{3.55}Li_{0.85}S_{0.85}$: C, 61.28; H, 8.07; N, 6.73; S, 4.37%. Found: C, 61.60; H, 8.34; N, 6.33; S, 4.37%.



3a

・0.93 LiOTf

In a two-necked flask, bis(diisopropylamino)boryl trifluoromethanesulfonate (487 mg, 1.35 mmol) was cooled to -78 °C. To this was added a THF (3 mL) solution of *N*, *N*-diisopropylformamide (0.20 mL, 1.35 mmol) slowly at that temperature. The reaction mixture was warmed to room temperature and stirred for 5 minutes. The reaction mixture was cooled to -78 °C, then a THF solution of lithium hexamethyldisilazide (*ca.* 1.3M, 1.04 mL, 1.35 mmol) was added slowly. The mixture was warmed to room temperature slowly and stirred for 30 minutes. After solvents were removed under reduced pressure, the residue was transferred into a glove box. The product was extracted with hexane-toluene (1 : 1). Then, the extract was filtered and evaporated under vacuum. Recrystallization from ether afforded **3a**・0.93LiOTf (107 mg, 0.221 mmol) in 16% yield.

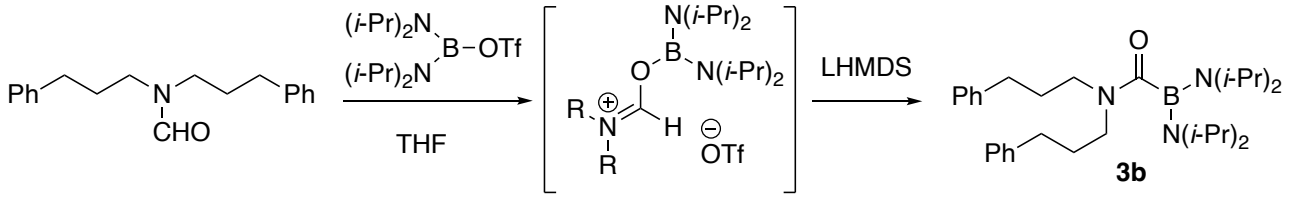


3a
・0.93 LiOTf

Bis(diisopropylamino)(*N*,*N*-diisopropylcarbamoyl)borane・0.93 LiOTf (3a・0.93 LiOTf)

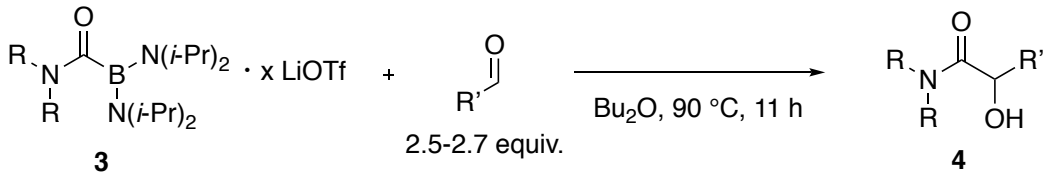
^{1}H NMR ($CDCl_3$) (400 MHz): δ = 1.17-1.21 (18H, m), 1.22 (12H, d, *J* = 6.8 Hz), 1.44 (6H, d, *J* = 6.8 Hz), 3.27 (1H, sept, *J* = 6.8 Hz), 3.51 (4H, sept, *J* = 7.0 Hz), 3.84 (1H, sept, *J* = 6.6 Hz); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = 20.0, 20.9, 24.4, 24.8, 44.7, 48.0, 49.4, 189.8; ^{11}B NMR (CD_3Cl_3) (128 MHz): δ = 29.1; HRMS (ESI): $(M+Na)^+$, found 362.3308. $C_{19}H_{42}BN_3NaO^+$ requires 362.3317; *Anal.* Calcd for $C_{19.93}F_{2.79}H_{42}BN_3O_{3.79}Li_{0.93}S_{0.93}$: C, 49.41; H, 8.74; N, 8.68; S, 6.15%. Found: C, 49.34; H, 8.66; N, 8.38; S, 5.87%. Spectral data were consistent with those of the literature.[3]

Preparation of LiOTf-free carbamoylborane **3b**



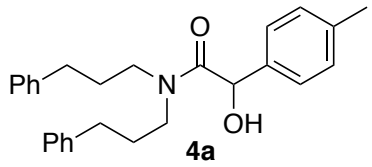
In a two-necked flask, bis(diisopropylamino)boryl trifluoromethanesulfonate (363 mg, 1.01 mmol) was cooled to -78 °C. To this was added a THF (2 mL) solution of *N*, *N*-bis(3-phenylpropyl)formamide (281 mg, 1.00 mmol) slowly at that temperature. The reaction mixture was warmed to room temperature and stirred for 5 minutes. The reaction mixture was cooled to -78 °C, then a THF solution of lithium hexamethyldisilazide (*ca.* 1.3M, 0.77 mL, 1.0 mmol) was added slowly. The mixture was warmed to room temperature slowly and stirred overnight. After solvents were removed under reduced pressure, the flask was transferred into a glove box. The product was extracted with hexane-toluene (3:1, 10 mL), and the extract was filtered. To the solution was added pre-dried MS4A (2 g) and the mixture was stirred at room temperature for 2 hours. After the mixture was filtered, solvents were removed under reduced pressure. The residue was dissolved in hexane-toluene (3:1, 10 mL). To the solution was added pre-dried MS4A (2 g) and the mixture was stirred at room temperature for 2 hours. After the mixture was filtered, solvents were removed under reduced pressure. The underlined process was repeated four times. LiOTf-free carbamoylborane **3b** (106 mg, 0.216 mmol) containing small amount of the formamide was obtained in 22% yield. LiOTf was not detected by ^{19}F NMR.

3. Coupling reaction between carbamoylboranes and aldehydes



3 **4**

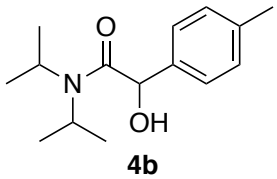
General procedure of the coupling reaction between carbamoylboranes and aldehydes: In a test tube, MS4A (0.20 g) was heated with a heat-gun under reduced pressure just before use. After nitrogen was charged, the test tube was transferred into a glove box. In the glove box, dibutyl ether (2 mL) was stirred with the pre-dried MS4A overnight. In a vial, a carbamoylborane-LiOTf complex (0.0782 mmol), an aldehyde (0.21 mmol), and supernatant dibutyl ether (0.2 mL) were mixed, and the vial was capped. After the mixture was heated at 90 °C for 11 hours, the reaction was quenched with pH = 7 phosphate buffer, and organic compounds were extracted with ethyl acetate three times. Combined organic layer was washed with brine and dried over $MgSO_4$. Volatile materials were removed under reduced pressure, and the residue was purified by silica gel chromatography (hexane : ethyl acetate = 7 : 3) to give an α-hydroxyamide.



4a

***N*,*N*-Bis(3-phenylpropyl)-2-hydroxy-2-(4-methylphenyl)acetamide**

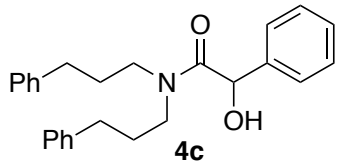
IR (KBr): 3343, 3026, 2930, 2865, 1620, 1402, 1363, 1053, 749, 699 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): δ = 1.30-1.44 (1H, m), 1.56-1.73 (1H, m), 1.74-1.93 (2H, m), 2.25-2.38 (1H, m), 2.32 (3H, s), 2.40-2.52 (1H, m), 2.57 (2H, t, *J* = 7.8 Hz), 2.82-2.94 (1H, m), 3.01-3.13 (1H, m), 3.17-3.27 (1H, m), 3.52-3.63 (1H, m), 4.74 (1H, d, *J* = 6.4 Hz), 4.92 (1H, d, *J* = 6.4 Hz), 6.93-7.33 (14H, m); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = 21.1, 28.9, 29.5, 32.8, 33.1, 46.06, 46.13, 71.4, 126.0, 126.2, 127.3, 128.2, 128.4, 128.6, 129.6, 136.7, 138.2, 140.5, 141.3, 172.1 (one carbon missing); HRMS (ESI): $(M+Na)^+$, found 424.2262. $C_{27}H_{31}NNaO_2^+$ requires 424.2247;



4b

***N*,*N*-Diisopropyl-2-hydroxy-2-(4-methylphenyl)acetamide**

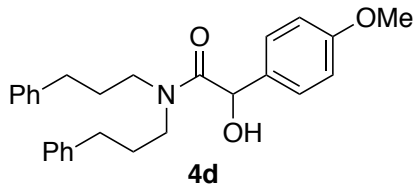
IR (KBr): 3356, 3000, 2976, 2939, 1631, 1372, 1334, 1062, 1041, 890, 523 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): δ = 0.97 (3H, d, *J* = 6.8 Hz), 1.14 (3H, d, *J* = 6.8 Hz), 1.40 (3H, d, *J* = 6.8 Hz), 1.47 (3H, d, *J* = 6.8 Hz), 2.33 (3H, s), 3.35 (1H, sep, *J* = 6.8 Hz), 3.80 (1H, sep, *J* = 6.8 Hz), 5.04-5.10 (2H, m), 7.12-7.19 (4H, m); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = 18.7, 19.6, 20.5, 21.2, 46.3, 47.9, 71.6, 127.3, 129.6, 137.2, 138.0, 170.8 (one carbon missing); HRMS (ESI): $(M+Na)^+$, found 272.1625. $C_{15}H_{23}NNaO_2^+$ requires 272.1621;



4c

***N*,*N*-Bis(3-phenylpropyl)-2-hydroxy-2-phenylacetamide**

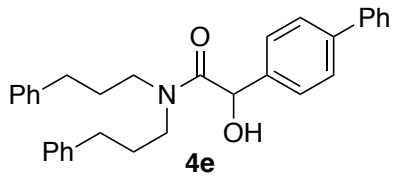
IR (KBr): 3343, 3033, 2931, 2864, 1625, 1405, 1363, 1052, 749, 699 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): δ = 1.36-1.50 (1H, m), 1.60-1.74 (1H, m), 1.75-1.92 (2H, m), 2.26-2.37 (1H, m), 2.45-2.55 (1H, m), 2.57 (2H, t, *J* = 7.8 Hz), 2.82-2.92 (1H, m), 3.03-3.13 (1H, m), 3.16-3.26 (1H, m), 3.55-3.64 (1H, m), 4.79 (1H, d, *J* = 6.6 Hz), 4.93 (1H, d, *J* = 6.6 Hz), 7.00-7.35 (15H, m); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = 28.9, 29.4, 32.7, 33.1, 46.03, 46.04, 71.6, 126.0, 126.3, 127.4, 128.2, 128.3, 128.39, 128.41, 128.6, 129.0, 139.5, 140.4, 141.2, 171.9; HRMS (ESI): $(M+Na)^+$, found 410.2108. $C_{26}H_{29}NNaO_2^+$ requires 410.2091;



4d

***N*,*N*-Bis(3-phenylpropyl)-2-hydroxy-2-(4-methoxyphenyl)acetamide**

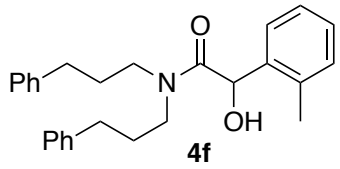
IR (KBr): 3339, 2932, 1623, 1513, 1253, 1035, 752, 701 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): δ = 1.37-1.50 (1H, m), 1.60-1.74 (1H, m), 1.74-1.92 (2H, m), 2.27-2.38 (1H, m), 2.45-2.55 (1H, m), 2.57 (2H, t, *J* = 7.8 Hz), 2.81-2.92 (1H, m), 3.02-3.13 (1H, m), 3.15-3.26 (1H, m), 3.54-3.65 (1H, m), 3.78 (3H, s), 4.72 (1H, d, *J* = 6.4 Hz), 4.89 (1H, d, *J* = 6.4 Hz), 6.81 (2H, d, *J* = 8.6 Hz), 6.97 (2H, d, *J* = 8.6 Hz), 7.00-7.34 (10H, m); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = 28.9, 29.4, 32.8, 33.1, 46.0, 46.1, 55.2, 71.0, 114.3, 126.0, 126.3, 128.2, 128.3, 128.4, 128.6, 128.7, 131.9, 140.4, 141.3, 159.5, 172.2; HRMS (ESI): $(M+Na)^+$, found 440.2212. $C_{27}H_{31}NNaO_3^+$ requires 440.2196;



4e

***N*,*N*-Bis(3-phenylpropyl)-2-hydroxy-2-(4-phenylphenyl)acetamide**

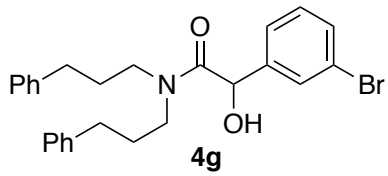
IR (KBr): 3341, 3028, 2931, 2865, 1626, 1403, 1363, 1054, 751, 699 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): δ = 1.35-1.50 (1H, m), 1.59-1.75 (1H, m), 1.76-1.95 (2H, m), 2.27-2.38 (1H, m), 2.44-2.55 (1H, m), 2.58 (2H, t, *J* = 7.8 Hz), 2.87-2.98 (1H, m), 3.05-3.16 (1H, m), 3.18-3.30 (1H, m), 3.54-3.65 (1H, m), 4.81 (1H, d, *J* = 6.4 Hz), 4.98 (1H, d, *J* = 6.4 Hz), 6.98-7.58 (19H, m); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = 28.9, 29.5, 32.8, 33.1, 46.1, 46.2, 71.3, 126.0, 126.3, 127.1, 127.5, 127.7, 127.8, 128.23, 128.24, 128.4, 128.6, 128.8, 138.5, 140.4, 141.2, 141.3, 171.9 (one carbon missing); HRMS (ESI): $(M+Na)^+$, found 486.2385. $C_{32}H_{33}NNaO_2^+$ requires 486.2404;



4f

***N*,*N*-Bis(3-phenylpropyl)-2-hydroxy-2-(2-methylphenyl)acetamide**

IR (neat): 3389, 3026, 2936, 1644, 1455, 1395, 1051, 751, 700 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): δ = 1.20-1.34 (1H, m), 1.58-1.71 (1H, m), 1.80-2.00 (2H, m), 2.26-2.32 (2H, m), 2.32 (3H, s), 2.62 (2H, t, *J* = 7.8 Hz), 2.79-2.97 (2H, m), 3.24-3.33 (1H, m), 3.52-3.62 (1H, m), 4.64 (1H, d, *J* = 6.0 Hz), 5.22 (1H, d, *J* = 6.0 Hz), 6.92-7.32 (14H, m); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = 18.9, 28.8, 29.2, 32.8, 33.3, 46.0, 46.3, 68.9, 126.0, 126.2, 126.7, 127.2, 128.1, 128.3, 128.4, 128.5, 128.6, 131.1, 136.4, 137.5, 140.4, 141.2, 172.5; HRMS (ESI): $(M+Na)^+$, found 424.2261. $C_{27}H_{31}NNaO_2^+$ requires 424.2247;

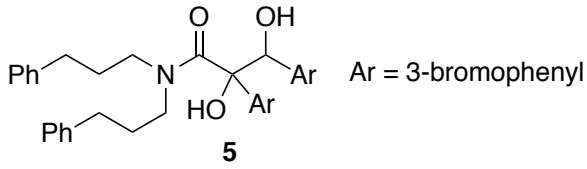


4g

***N*,*N*-Bis(3-phenylpropyl)-2-(3-bromophenyl)-2-hydroxyacetamide**

IR (neat): 3390, 3026, 2937, 2861, 1736, 1644, 1454, 1188, 1073, 749, 698 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): δ = 1.47-1.60 (1H, m), 1.61-1.76 (1H, m), 1.84 (2H, quint, *J* = 7.6 Hz), 2.29-2.40 (1H, m), 2.51-2.62 (3H, m), 2.80-2.90 (1H, m), 2.98-3.10 (1H, m), 3.17-3.27 (1H, m), 3.55-3.66 (1H, m), 4.58-4.90 (1H, broad), 4.82 (1H, s), 6.90-7.46 (14H, m); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = 28.8, 29.4, 32.6, 33.1, 45.9, 46.1, 70.8, 122.9, 125.9, 126.0, 126.5, 128.21, 128.22, 128.4, 128.7, 130.4,

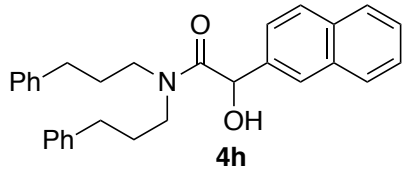
130.5, 131.6, 140.2, 141.1, 141.7, 171.3; HRMS (ESI): $(M+Na)^+$, found 488.1212. $C_{26}H_{28}{}^{79}BrNNaO_2^+$ requires 488.1196;



5

***N*,*N*-Bis(3-phenylpropyl)-2,3-bis(3-bromophenyl)-2,3-dihydroxypropanamide**

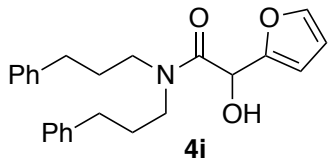
IR (KBr): 3368, 3025, 2928, 1613, 1454, 1182, 1073, 748, 699 cm^{-1};^1H NMR ($CDCl_3$) (400 MHz): δ = 1.00-2.00 (4H, m), 2.10-2.23 (2H, m), 2.49-2.66 (2H, m), 2.90-3.45 (4H, m), 3.69 (0.31H, s (OH)), 4.30 (0.31H, broad (OH)), 4.78 (0.69H, broad (OH)), 5.17 (0.69H, s), 5.40 (0.31H, s), 6.56 (0.31H, d, *J* = 7.2 Hz), 6.89-7.51 (17.69H, m);^{13}C NMR ($CDCl_3$) (100 MHz): δ = 28.1, 28.4, 29.4, 29.6, 32.9, 33.0, 33.2, 33.3, 46.3, 46.4, 47.5, 78.4, 79.8, 82.0, 121.5, 121.8, 122.2, 122.6, 123.4, 125.2, 125.96, 126.02, 126.1, 126.4, 126.6, 127.9, 128.1, 128.2, 128.27, 128.34, 128.40, 128.45, 128.5, 129.2, 129.5, 129.8, 130.6, 130.7, 131.1, 131.17, 131.21, 131.4, 138.6, 139.8, 140.3, 140.65, 140.71, 140.9, 141.21, 141.25, 171.8, 172.7(6 carbons missing);(NMR spectra were measured with a fraction of 31:69 diastereomixture.); HRMS (ESI): $(M+Na)^+$, found 672.0743. $C_{33}H_{33}{}^{79}Br_2NNaO_3^+$ requires 672.0719;



4h

***N*,*N*-Bis(3-phenylpropyl)-2-hydroxy-2-(2-naphthyl)acetamide**

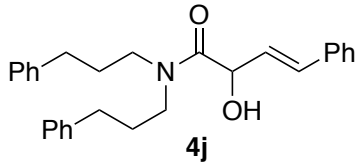
IR (KBr): 3349, 3059, 3023, 2928, 2863, 1624, 1363, 1054, 747, 700 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): δ = 1.24-1.40 (1H, m), 1.58-1.73 (1H, m), 1.75-1.93 (2H, m), 2.20-2.31 (1H, m), 2.37-2.48 (1H, m), 2.57 (2H, t, *J* = 7.8 Hz), 2.84-2.94 (1H, m), 3.08-3.29 (2H, m), 3.56-3.66 (1H, m), 4.88 (1H, d, *J* = 6.4 Hz), 5.10 (1H, d, *J* = 6.4 Hz), 6.80-6.88 (2H, m), 7.09-7.33 (9H, m), 7.46-7.53 (3H, m), 7.76-7.85 (3H, m); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = 28.9, 29.6, 32.7, 33.1, 46.1, 46.2, 71.7, 124.5, 126.0, 126.3, 126.4, 126.9, 127.7, 128.0, 128.16, 128.22, 128.4, 128.6, 129.1, 133.18, 133.25, 136.9, 140.3, 141.2, 171.9 (one carbon missing); HRMS (ESI): $(M+Na)^+$, found 460.2251. $C_{30}H_{31}NNaO_2^+$ requires 460.2247;



4i

***N*,*N*-Bis(3-phenylpropyl)-2-(2-furyl)-2-hydroxyacetamide**

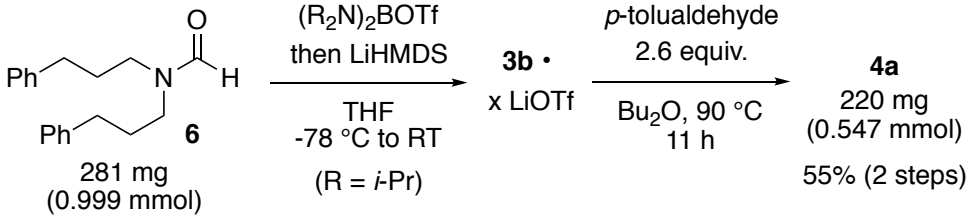
IR (KBr): 3333, 3030, 2932, 2867, 1635, 1404, 1052, 1037, 749, 697 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): δ = 1.40-1.55 (1H, m), 1.65-1.79 (1H, m), 1.80-1.94 (2H, m), 2.36-2.58 (2H, m), 2.59 (2H, t, *J* = 7.6 Hz), 2.96-3.07 (1H, m), 3.08-3.20 (1H, m), 3.23-3.34 (1H, m), 3.52-3.63 (1H, m), 4.63 (1H, d, *J* = 6.8 Hz), 5.11 (1H, d, *J* = 6.8 Hz), 6.10 (1H, d, *J* = 2.8 Hz), 6.30-6.34 (1H, m), 7.05-7.37 (11H, m); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = 28.8, 29.5, 32.7, 33.1, 46.1(2C), 64.5, 108.2, 110.6, 126.0, 126.3, 128.19, 128.24, 128.4, 128.6, 140.4, 141.2, 142.6, 152.2, 169.7; HRMS (ESI): $(M+Na)^+$, found 400.1884. $C_{24}H_{27}NNaO_3^+$ requires 400.1883;



4j

***(3E)*-*N*,*N*-Bis(3-phenylpropyl)-2-hydroxy-4-phenyl-3-butenamide**

IR (KBr): 3373, 3026, 2931, 2862, 1621, 1364, 1033, 749, 700 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): δ = 1.78-1.94 (4H, m), 2.43-2.67 (4H, m), 3.03-3.15 (1H, m), 3.22-3.37 (2H, m), 3.52-3.62 (1H, m), 4.29 (1H, d, *J* = 7.2 Hz), 4.62 (1H, t, *J* = 7.4 Hz), 5.97 (1H, dd, *J* = 15.8, 8.0 Hz), 6.35 (1H, d, *J* = 15.8 Hz), 7.01-7.33 (15H, m); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = 29.0, 30.1, 32.8, 33.2, 46.1, 46.2, 69.8, 126.0, 126.38, 126.42, 126.7, 128.2, 128.3, 128.4, 128.6, 128.7, 133.9, 135.9, 140.4, 141.2, 171.9 (one carbon missing); HRMS (ESI): $(M+Na)^+$, found 436.2239. $C_{28}H_{31}NNaO_2^+$ requires 436.2247;



Procedure for semi large scale synthesis from formamide **6**:

(Step 1) In a two-necked flask, bis(diisopropylamino)boryl trifluoromethanesulfonate (360 mg, 1.00 mmol) was cooled to -78 °C. To this was added a THF (2 mL) solution of *N*, *N*-bis(3-phenylpropyl)formamide (281 mg, 0.999 mmol) slowly at that temperature. The reaction mixture was warmed to room temperature and stirred for 5 minutes. The reaction mixture was

cooled to -78 °C, then a THF solution of lithium hexamethyldisilazide (*ca.* 1.3M, 0.77 mL, 1.0 mmol) was added slowly. The mixture was warmed to room temperature slowly and stirred overnight. After solvents were removed under reduced pressure, the residue was transferred into a glove box. The product was extracted with hexane-toluene (3 : 1). After filtration, solvents were removed under reduced pressure to give a crude material (603 mg) which was used for next step.

(Step 2) In a test tube, MS4A (0.60 g) was heated with a heat-gun under reduced pressure just before use. After nitrogen was charged, the test tube was transferred into a glove box. In the glove box, dibutyl ether (6 mL) was stirred with the pre-dried MS4A overnight. To the crude material (603 mg) obtained as above was added dried dibutyl ether (2 mL, supernatant) and *p*-tolualdehyde (0.31 mL, 2.6 mmol). After the mixture was heated at 90 °C for 11 hours, the reaction was quenched with pH = 7 phosphate buffer, and organic compounds were extracted with ethyl acetate three times. Combined organic layer was washed with brine and dried over $MgSO_4$. Volatile materials were removed under reduced pressure, and the residue was purified by silica gel chromatography (hexane : ethyl acetate = 8 : 2) and recrystallization (hexane-ethyl acetate) to give **4a** (220 mg, 0.547 mmol) in 55% yield (2 steps).

4. DFT study

4.1 General

Calculations were performed with the Gaussian 09 (G09RevD.01) program.[4] Geometry optimizations and frequency calculations for all reported structures were performed using B3LYP density functional with the 6-31G(d) basis set. Each reported minimum has zero imaginary frequency and each transition state (TS) structure has only one imaginary frequency. From TSs, reaction paths were traced by the intrinsic reaction coordinate (IRC) method to obtain the energy minimum geometries. Energy changes were shown by the use of Gibbs free energies (T = 298.15 K and P = 1 atm).

4.2 Cartesian coordinates of the optimized geometries

PhCHO

C	1.73595853	1.06057288	-0.00000202
C	0.36111895	1.29212797	-0.00000060
C	-0.53395208	0.21450824	0.00000222
C	-0.04523859	-1.10109692	0.00000313
C	1.32623032	-1.33125049	0.00000069
C	2.21681882	-0.25080975	-0.00000146
H	2.43030489	1.89611137	-0.00000357
H	-0.02496654	2.30955847	-0.00000075
H	-0.75908815	-1.91924389	0.00000562
H	1.70780067	-2.34857909	0.00000101
H	3.28820061	-0.43340758	-0.00000328
C	-1.99221856	0.46875433	0.00000536
H	-2.27407085	1.54572777	0.00001379
O	-2.84756061	-0.39587557	-0.00000710

CB

C	0.98782336	0.00865251	-0.60888116
O	1.24862995	-0.03743881	-1.81839669
N	1.99603042	0.03690603	0.33495765
B	-0.56638813	0.00625168	-0.16320641
N	-1.23423415	1.26147865	-0.04908088

N	-1.19325387	-1.26653390	0.01584000
C	3.38682697	-0.00079695	-0.08430930
H	3.88122921	-0.91265281	0.27916135
H	3.40659908	0.01380077	-1.17446252
H	3.93524595	0.86585837	0.30854836
C	1.74546799	0.02193496	1.76183411
H	0.67032095	0.04626313	1.95411546
H	2.15832736	-0.88491375	2.22736421
H	2.20527095	0.89113271	2.25304308
C	-0.51839247	2.52441319	0.06223383
H	0.55542609	2.35526409	0.15619002
H	-0.68941571	3.15857132	-0.82091847
H	-0.85241708	3.09157179	0.94490121
C	-2.66520507	1.46459798	-0.22464353
H	-3.14884254	0.55118591	-0.57109764
H	-3.16216491	1.79839741	0.70027994
H	-2.83903350	2.24036281	-0.98504473
C	-2.41643099	-1.50482188	0.76479842
H	-2.70061770	-0.62218121	1.33992507
H	-3.26324064	-1.79114501	0.12002542
H	-2.26134053	-2.32963750	1.47694340
C	-0.62039070	-2.50075729	-0.50531532
H	0.25821370	-2.29012267	-1.11536175
H	-0.34005659	-3.19121394	0.30629978
H	-1.34859426	-3.02457993	-1.14302629

TS1

C	-1.06157364	-0.06276476	0.10405212
O	-0.50410026	0.07110347	-1.08398218
N	-2.38930007	-0.02690913	0.17163850
B	0.70474535	0.00070757	-0.17048536
N	1.41139015	-1.25609793	0.01635500
N	1.40080011	1.25368950	0.02495807
C	-3.05042904	-0.17251155	1.45988719
H	-3.70823529	-1.05103650	1.45974860

H	-2.28516806	-0.29106889	2.22809137
H	-3.65808471	0.71361240	1.68327183
C	-3.24684413	0.15258134	-1.00162028
H	-2.61531758	0.26450504	-1.88272748
H	-3.90258024	-0.71686548	-1.12908221
H	-3.87074377	1.04602192	-0.88049044
C	0.94779145	2.50036667	-0.55738217
H	0.28692099	2.30770160	-1.40455191
H	0.40133489	3.12908352	0.17020227
H	1.80061905	3.09517069	-0.91930207
C	2.29135014	1.44992819	1.15302361
H	2.52928148	0.49039226	1.61618500
H	3.23334718	1.93456345	0.84979424
H	1.83048173	2.09362546	1.92370402
C	2.78966445	-1.40942776	-0.41582931
H	3.24192288	-0.43125451	-0.58920086
H	3.39258342	-1.94484277	0.33565941
H	2.86337044	-1.98459899	-1.35639023
C	0.72721153	-2.52450667	0.14846021
H	1.30002296	-3.20591761	0.79661892
H	-0.25526697	-2.37601885	0.60581632
H	0.58133107	-3.04220813	-0.81727176

INT1

C	1.43454215	0.34490506	-0.46306739
O	0.50475434	-0.33015268	0.26597331
N	2.66030783	-0.06440661	-0.10256308
B	-0.87046141	-0.03106590	0.08454583
N	-1.33068006	1.31786605	0.12624546
N	-1.72782320	-1.16444964	-0.05579908
C	2.99787021	-1.06082382	0.91944481
H	3.64901743	-0.61395941	1.68106395
H	2.08120794	-1.41693316	1.38587931
H	3.53183292	-1.90530326	0.46571263
C	3.79458464	0.52766746	-0.79509233

H	4.45881684	1.04050059	-0.08637804
H	4.37948761	-0.24335506	-1.31456791
H	3.40771672	1.24456403	-1.52019101
C	-1.23620953	-2.46428826	-0.48043737
H	-0.17243196	-2.40742663	-0.71273889
H	-1.37932311	-3.22374539	0.30492381
H	-1.77027716	-2.81650619	-1.37703718
C	-3.13563140	-1.17819701	0.29637141
H	-3.41575592	-0.24872866	0.79490657
H	-3.79029071	-1.31715949	-0.57949943
H	-3.34442691	-2.00756161	0.99008082
C	-2.48950536	1.79941130	-0.60497062
H	-2.94927925	0.99298879	-1.17850184
H	-3.25310384	2.23571495	0.05930241
H	-2.19038999	2.58492354	-1.31663626
C	-0.55015501	2.39881295	0.70692708
H	0.25589234	2.00178920	1.32523011
H	-0.09928345	3.03929927	-0.06514378
H	-1.19074340	3.02945476	1.34284232

TS2

C	0.06318088	1.37635995	0.07258527
O	1.31141192	1.07037080	0.32751862
N	-0.29193989	2.57710529	0.52879568
B	1.99593811	-0.20113458	0.15937482
N	1.80230709	-1.17811322	1.18579295
N	3.08398065	-0.18678829	-0.75913527
C	-0.67110086	-0.08056592	-1.34178190
O	0.30692409	-0.85363447	-1.38715795
C	-1.64826256	3.06144474	0.30467295
H	-2.11332519	3.32931759	1.26125860
H	-1.63674594	3.95361931	-0.33446316
H	-2.23724794	2.27714040	-0.16725149
C	0.58981136	3.49759997	1.25831930
H	0.62411669	4.46302782	0.74010916

H	0.20548433	3.66136381	2.27211229
H	1.59072695	3.07415961	1.30893366
C	1.16774775	-0.88758260	2.45766421
H	1.12009369	0.19021414	2.62589640
H	0.14246931	-1.28942429	2.51588949
H	1.73972260	-1.33331623	3.28653683
C	1.95606126	-2.60063881	0.93921657
H	2.27083204	-2.77962106	-0.08907455
H	2.68606681	-3.06399766	1.62264132
H	0.99691232	-3.12365300	1.08107431
C	4.22740187	-1.07288360	-0.67188573
H	4.31998335	-1.47387330	0.33952341
H	4.17252100	-1.91806464	-1.37878951
H	5.15053346	-0.51942645	-0.90171883
C	3.01519535	0.54525271	-2.01114044
H	2.80049267	-0.12027782	-2.86063961
H	2.22420365	1.29555696	-1.96984225
H	3.96812159	1.05871630	-2.20954768
H	-0.79219956	0.71712712	-2.10610443
C	-1.99229977	-0.51794256	-0.76047979
C	-3.18791555	0.07297043	-1.18414566
C	-2.04497597	-1.58347019	0.14596043
C	-4.41631995	-0.36590135	-0.68496500
H	-3.15608882	0.87036195	-1.92575130
C	-3.26770528	-2.02073577	0.65029882
H	-1.11359800	-2.06254621	0.43054340
C	-4.45773385	-1.41007399	0.24028762
H	-5.33856917	0.09823586	-1.02575092
H	-3.29832632	-2.84544779	1.35831582
H	-5.41150112	-1.75583472	0.63052606

Pro

C	0.19504161	1.11876980	-0.72292081
O	-0.51621562	0.77476654	-1.66378081
N	0.78522135	2.35450157	-0.66838715

B	-1.86374263	-0.69445740	0.32080889
N	-2.60432156	-1.60348802	-0.48601910
N	-2.48788902	0.35487735	1.09117383
C	0.46109475	0.12656700	0.44397257
O	-0.48079956	-0.92229349	0.40760173
C	1.60638202	2.85053754	0.42555273
H	2.42424212	3.45169594	0.01187211
H	1.02952369	3.48881198	1.11094313
H	2.05643260	2.03443047	0.98811486
C	0.49234790	3.31932961	-1.72048734
H	-0.01302867	4.20125731	-1.30405579
H	1.42025622	3.64936516	-2.20478645
H	-0.15512003	2.84324065	-2.45499746
C	-1.98770098	-2.36901272	-1.55583965
H	-0.94744048	-2.06882813	-1.67001804
H	-2.02627016	-3.45053639	-1.34950992
H	-2.50808836	-2.19500769	-2.51051021
C	-4.01016242	-1.90364906	-0.30106740
H	-4.38971425	-1.42039767	0.60105428
H	-4.62443767	-1.57780359	-1.15669042
H	-4.16075784	-2.98915935	-0.19066098
C	-3.62535146	1.12349862	0.62452846
H	-3.85912830	0.85950763	-0.40861884
H	-4.52743833	0.96492217	1.23981717
H	-3.40244088	2.20280131	0.65165078
C	-2.03604916	0.73401639	2.41450241
H	-2.85995319	0.67735061	3.14475172
H	-1.25016178	0.05561551	2.75638875
H	-1.64825471	1.76765766	2.45137182
H	0.39106607	0.67104388	1.39417778
C	1.85011993	-0.49182849	0.33948371
C	2.66133714	-0.61381250	1.47256572
C	2.31407830	-0.99011087	-0.88517680
C	3.91897365	-1.21539204	1.38725901
H	2.30225772	-0.24497789	2.43143830
C	3.56815526	-1.59251686	-0.97222068

H	1.68489724	-0.90344970	-1.76655955
C	4.37500583	-1.70511543	0.16328120
H	4.53749935	-1.30464737	2.27650570
H	3.91731590	-1.97507532	-1.92776545
H	5.35286881	-2.17423676	0.09350299

TS3

C	0.66178194	0.20705668	-0.98056111
C	-0.53088939	-0.72476710	0.81991498
H	0.31083090	-0.62816098	-1.58851461
O	-0.10049578	1.26014738	-0.88424178
B	-1.36112947	0.64253488	-0.26936301
C	-1.04138968	2.65264549	1.29013606
H	-0.40160606	3.08358689	0.51940054
H	-1.67612173	3.45311459	1.69695248
H	-0.40969657	2.26969376	2.10738535
C	-2.83014054	1.14179306	1.73252921
H	-2.31072271	0.69385971	2.59651448
H	-3.43221954	1.98530497	2.09817896
H	-3.51261359	0.39746776	1.32115825
C	-2.45677158	0.94630453	-2.48539532
H	-1.52821267	1.44193689	-2.77941967
H	-2.82607669	0.36816974	-3.34470620
H	-3.20175451	1.73337535	-2.26709162
C	-3.44611222	-0.64765578	-1.00218433
H	-4.28528521	0.02934247	-0.75865738
H	-3.77620069	-1.27265795	-1.84607134
H	-3.28171536	-1.30498010	-0.14349055
N	-1.88767625	1.60948311	0.72754470
N	-2.22417613	0.06191752	-1.34627895
O	-0.07508117	-0.28907136	1.88029613
C	-0.96459793	-2.74193864	-0.60321707
H	-1.26635002	-2.00529512	-1.34817124
H	-0.05657259	-3.26639325	-0.94437418
H	-1.76009192	-3.49292043	-0.50974655

C	-0.40713433	-2.97766944	1.77813895
H	-0.31262804	-2.38266771	2.68561491
H	-1.19553997	-3.73068832	1.90076958
H	0.54270728	-3.50284197	1.59588793
N	-0.73652082	-2.08611279	0.67160096
C	2.05921026	0.24834440	-0.62461779
C	2.90223777	-0.81072459	-1.01784352
C	2.59100373	1.32312502	0.11546886
C	4.25244819	-0.78917730	-0.69007961
H	2.48829148	-1.64053226	-1.58564272
C	3.94191704	1.33808881	0.43960005
H	1.92954249	2.12176514	0.43026189
C	4.77324226	0.28593886	0.03837726
H	4.90108824	-1.60395817	-0.99849665
H	4.35250767	2.16511735	1.01167542
H	5.82848215	0.30188018	0.29729638

CS

C	0.64003656	-0.55197680	0.00001340
Si	-1.20421341	0.06583766	-0.00007046
O	0.66414966	-1.79078054	0.00017918
N	1.80306220	0.17751534	-0.00005953
C	-1.94338380	-0.70338401	-1.55914892
H	-1.69386381	-1.76778222	-1.60554512
H	-3.03547151	-0.60208626	-1.56815200
H	-1.55845501	-0.22606043	-2.46835381
C	-1.94329965	-0.70225754	1.55962014
H	-1.55789962	-0.22458371	2.46844138
H	-3.03533339	-0.60033797	1.56882616
H	-1.69437720	-1.76676782	1.60662974
C	-1.59435738	1.92735410	-0.00045118
H	-1.21416433	2.44579191	-0.88849958
H	-2.68566849	2.05069661	-0.00070317
H	-1.21459099	2.44580019	0.88778430
C	1.87364682	1.62442860	-0.00016110

H	0.87436113	2.05493866	-0.00002723
H	2.40972410	1.98860500	0.88762485
H	2.40945527	1.98851920	-0.88814952
C	3.08349294	-0.51753883	0.00008431
H	3.66727753	-0.24781079	0.89028733
H	2.88883778	-1.58952670	-0.00028055
H	3.66771077	-0.24723897	-0.88965296

TS4

C	0.70572001	-0.07665911	0.03305276
Si	-1.26132322	0.05015415	0.01220721
O	0.14806534	-1.25606677	-0.01777378
N	2.03374289	0.03301922	-0.01754918
C	2.90685483	-1.13559363	-0.11640590
H	3.50404903	-1.08752921	-1.03484599
H	3.58723893	-1.17471566	0.74251510
H	2.28374766	-2.03027097	-0.13183579
C	2.66405388	1.34228692	0.02909126
H	3.25835776	1.51765276	-0.87673889
H	1.88562459	2.10354192	0.10130552
H	3.32905459	1.42084859	0.89864681
C	-2.55212520	-1.20548837	-0.61611220
H	-2.56837664	-2.10924109	0.00405845
H	-3.55939555	-0.76849737	-0.61334264
H	-2.33443973	-1.52114474	-1.64439894
C	-1.67227354	0.44859102	1.81443410
H	-1.10783702	1.31037434	2.18733103
H	-2.74176682	0.67125170	1.91820050
H	-1.45036568	-0.40658099	2.46390637
C	-1.55305637	1.55808793	-1.11744694
H	-1.19142310	1.36215798	-2.13565892
H	-2.62292087	1.79258716	-1.19635025
H	-1.02878665	2.44745847	-0.74833736

INT2

C	1.02066971	-0.50877582	-0.00017218
Si	-1.51324664	-0.03063430	-0.00001801
O	0.11496238	0.50564718	-0.00000849
N	2.26600174	-0.02167393	-0.00012282
C	-2.50187560	1.57283513	0.00282911
H	-3.57975016	1.36867125	0.00313937
H	-2.27834975	2.17882336	0.88864532
H	-2.27934922	2.18150616	-0.88139895
C	-1.85778772	-1.02677220	1.55766272
H	-2.90312062	-1.35870914	1.59109242
H	-1.21466890	-1.91143247	1.60060087
H	-1.66863299	-0.42881334	2.45711055
C	-1.85891840	-1.02206029	-1.56042996
H	-2.90422279	-1.35408065	-1.59396013
H	-1.67064705	-0.42134538	-2.45822001
H	-1.21576419	-1.90654726	-1.60664180
C	2.65265596	1.39275272	0.00004610
H	3.25401436	1.61966991	-0.88886968
H	1.75433705	2.00748685	-0.00007055
H	3.25369071	1.61958267	0.88920697
C	3.36590983	-0.97463198	0.00008403
H	3.99621100	-0.83983471	-0.88897390
H	3.99516129	-0.84071423	0.89002938
H	2.94091031	-1.97892804	-0.00062900

5. References

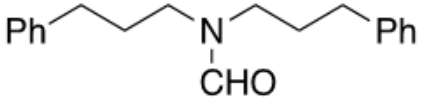
[1] C. Zha, G. B. Brown, W. J. Brouillette, *Bioorg. Med. Chem.* **2014**, *22*, 95-104.

[2] G. Wang, L. Liu, H. Wang, Y.-S. Ding, J. Zhou, S. Mao, P. Li, *J. Am. Chem. Soc.* **2017**, *139*, 91-94.

[3] Originally, an aldiminium salt was synthesized by the reaction of a formamide with a chloroborane and AgOTf. (Y. Canac, G. E. Aniol, S. Conejero, B. Donnadieu, G. Bertrand, *Eur. J. Inorg. Chem.* **2006**, 5076-5080.) In this modified procedure, aldiminium salts were generated *in-situ* by the reaction of formamides with bis(diisopropylamino)boryl trifluoromethanesulfonate.

[4] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö .; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2013.

K_ishidakento-1606-1-second.40.fid
KI_1606-1



8.032 8.024 7.314 7.296 7.280 7.277 7.260 7.229 7.210 7.205 7.190 7.182 7.178 7.161 7.154 7.150 7.133

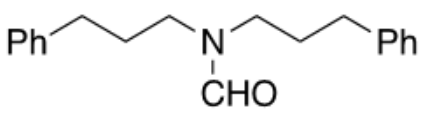
3.374 3.355 3.336 3.226 3.208 3.190 2.639 2.620 2.614 2.599 2.594 2.576 1.896 1.890 1.881 1.876 1.871 1.864 1.856 1.851 1.835 1.817 1.577

1.01 11.40 1.91 1.98 3.89 4.09

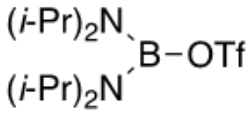
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

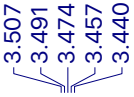
f1 (ppm)

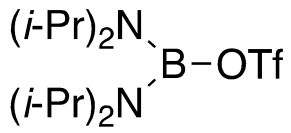
K_ishidakento-1606-1.30.fid
KI_1606-1



KI_BOTf
KI_BOTf

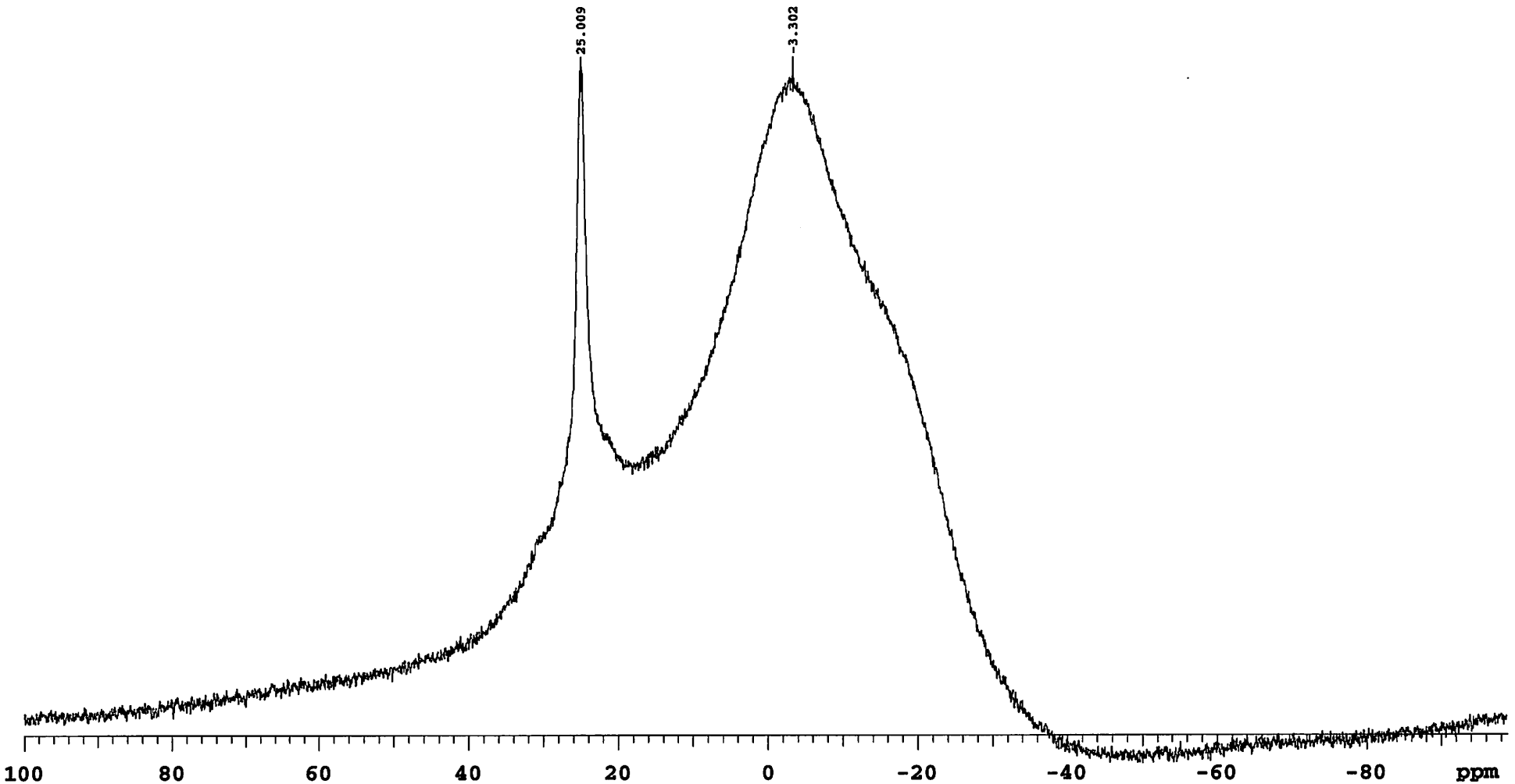




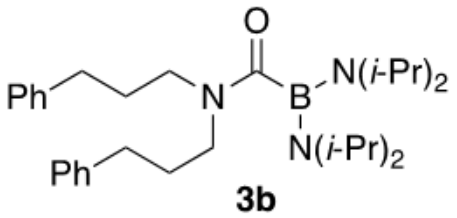


KI_BOTf-B

Sample Name **KI_BOTf-B**	Pulse sequence **s2pul**	Temperature **160**	Study owner **vnmr1**
Date collected **2019-07-19**	Solvent **cdcl3**	Spectrometer **Varian400-vnmrs400**	Operator **vnmr1**



K_ishidakento-carbamoylborane.10.fid
KI_carbamoylborane



3b · 0.85 LiOTf

7.306 7.296 7.287 7.277 7.269 7.258 7.212 7.204 7.192 7.184 7.177 7.172 7.156

3.459 3.442 3.425 3.407 3.390 3.306 3.294 3.285 3.276 3.264 3.256 3.248 3.236 2.618 2.611 2.599 2.593 2.579 2.573

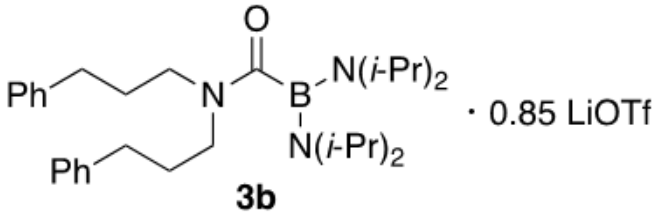
1.952 1.946 1.940 1.934 1.927 1.905 1.894 1.884 1.874 1.863 1.804 1.796 1.786 1.777 1.769 1.757 1.155 1.138 1.096

10.05 8.00 4.22 5.10 24.05

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

f1 (ppm)

K_ishidakento-carbamoylborane2.20.fid
KI_carbamoylborane

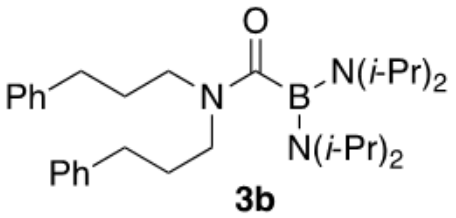


3b · 0.85 LiOTf

142.994
142.330
129.376
129.325
129.292
129.215
126.939
126.758
118.260
50.477
48.422
42.559
34.171
34.009
30.327
29.390
24.606
24.340
1.900
1.693
1.637
1.487
1.428
1.280
1.222
1.073
1.003
0.868
0.661

f1 (ppm)

K_ishidakento-carbamoylborane.61.fid
KI_carbamoylborane

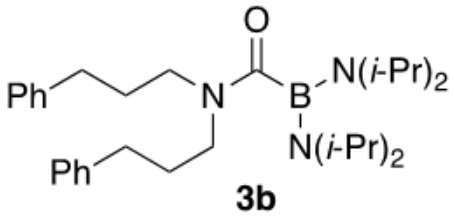


3b · 0.85 LiOTf

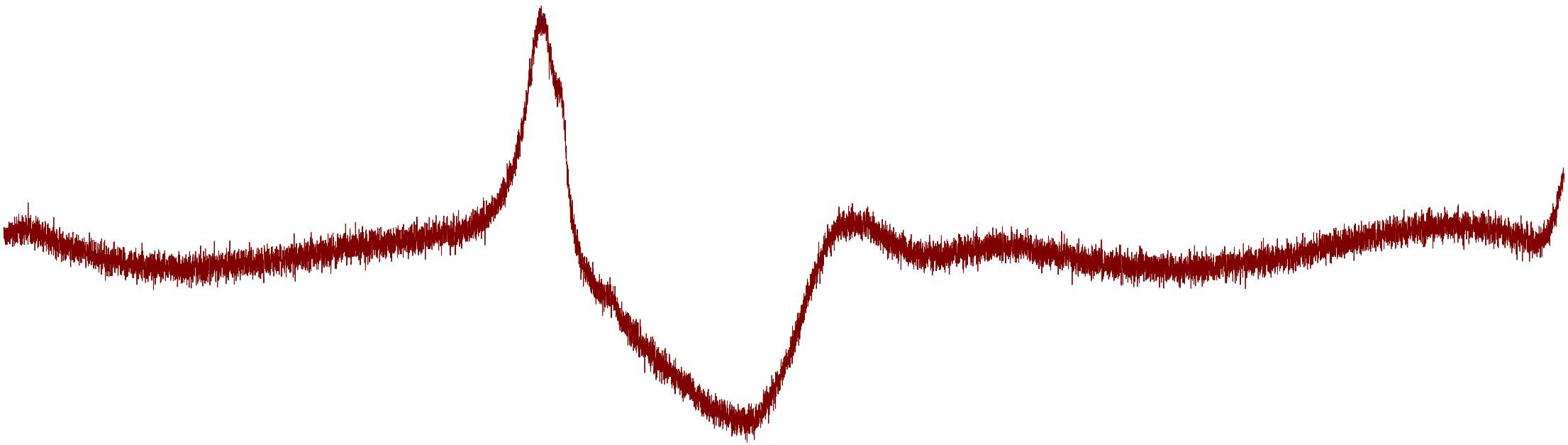
(high concentration sample, overnight run)

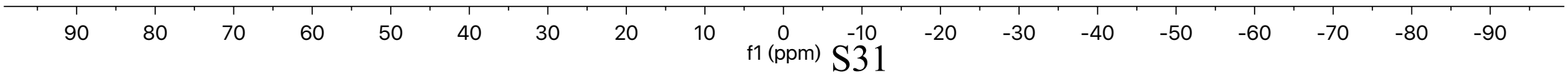
K_ishidakento-carbamoylborane-B.120.fid
KI_carbamoylborane-B

30.71



3b · 0.85 LiOTf





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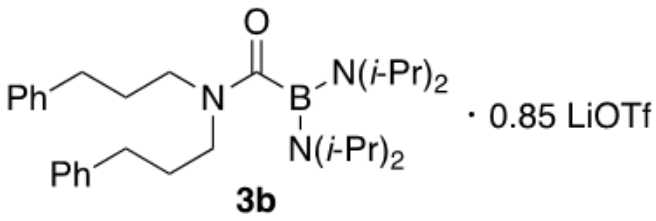
KI_CB



3b · 0.85 LiOTf

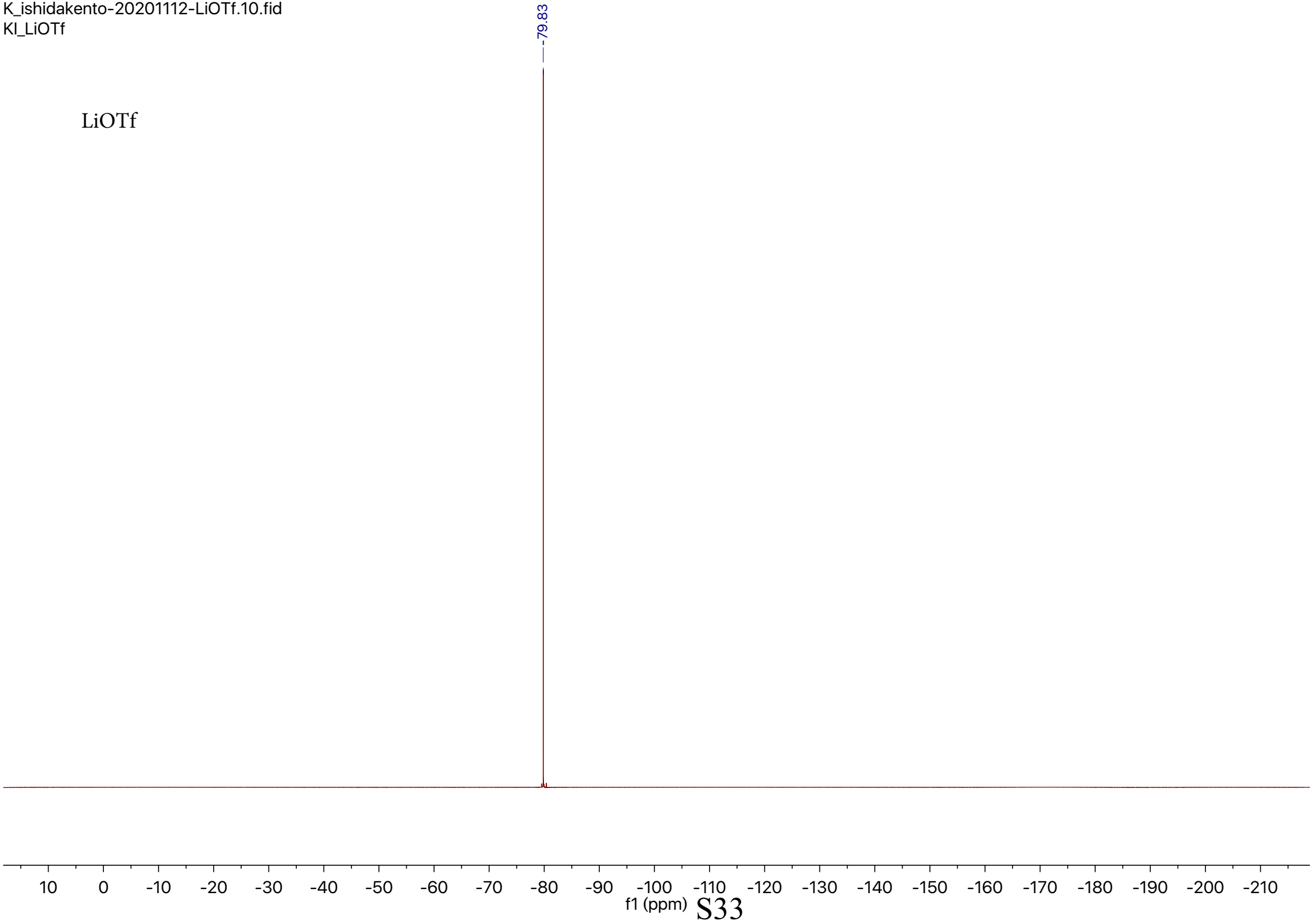
-79.73

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

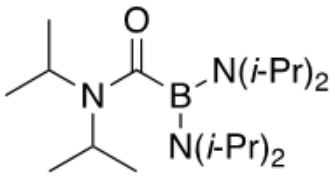
f1 (ppm)

K_ishidakento-20201112-LiOTf.10.fid
KI_LiOTf

LiOTf



KI_1506-1
KI_1506-1



3a

· 0.93 LiOTf

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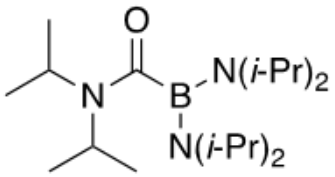
KI_carbamoylborane



3a

· 0.93 LiOTf

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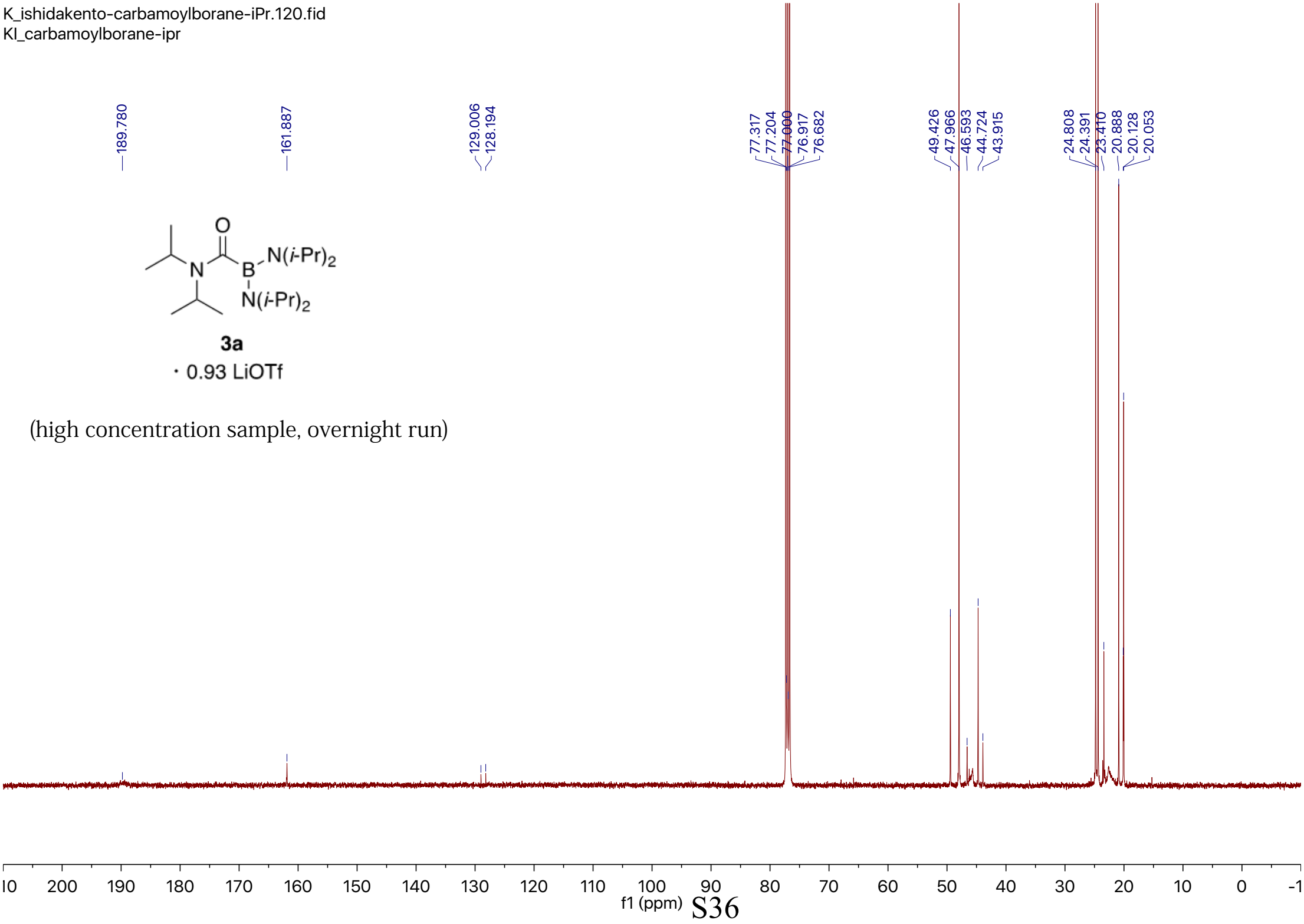
KI_carbamoylborane-ipr



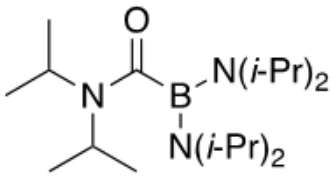
3a

· 0.93 LiOTf

(high concentration sample, overnight run)

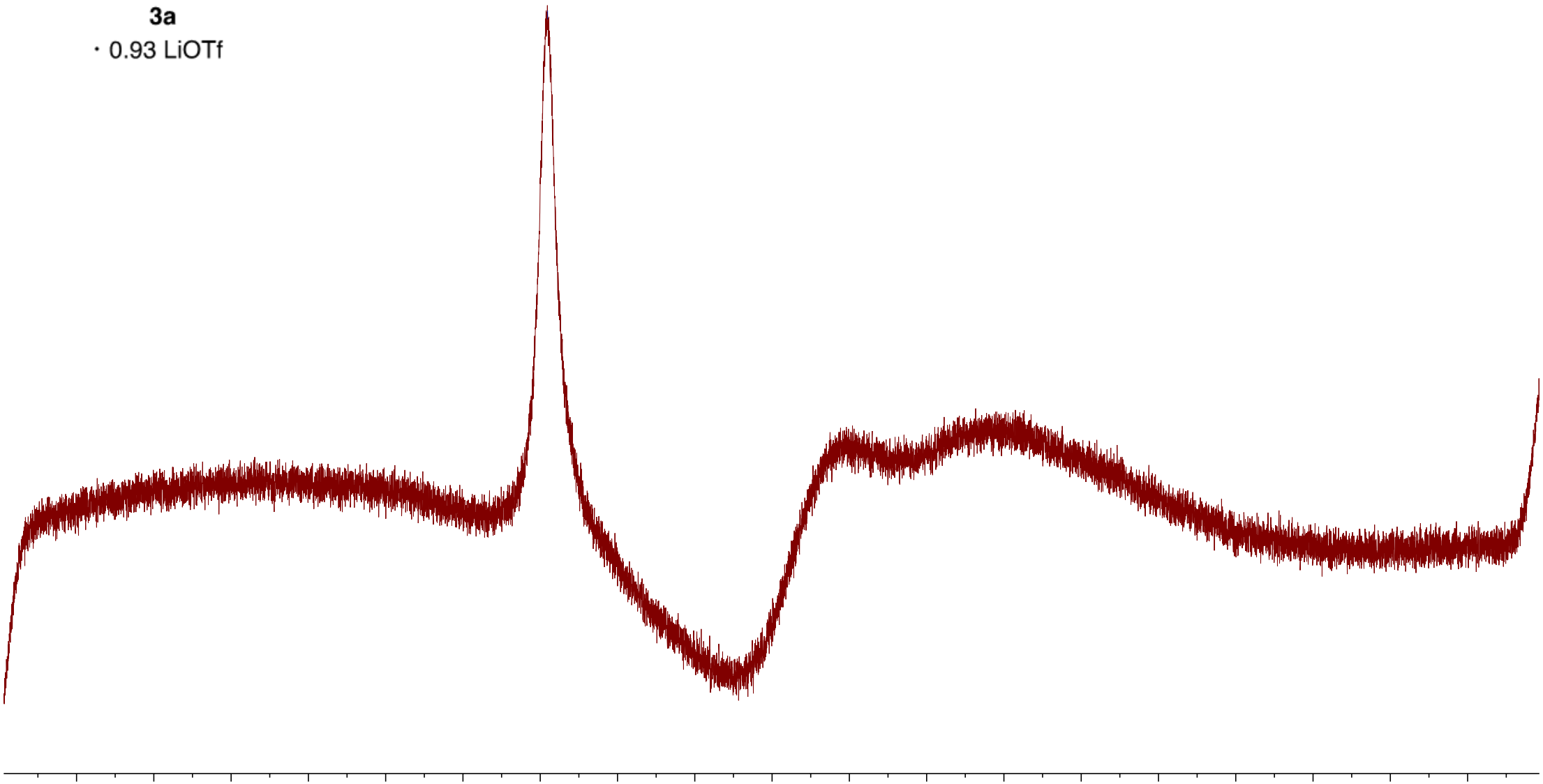
K_ishidakento-carbamoylborane-iPr.80.fid
KI_carbamoylborane-iPr

29.05



3a

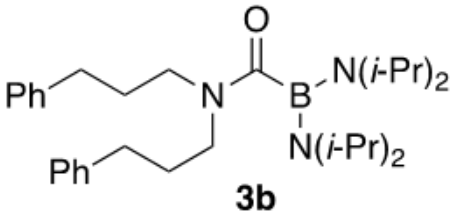
· 0.93 LiOTf



90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90

f1 (ppm)

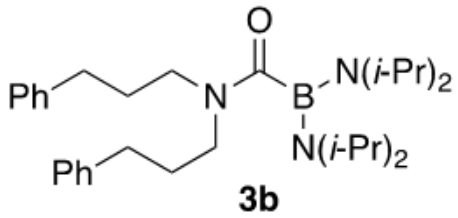
KI_1852-4
single_pulse



3b

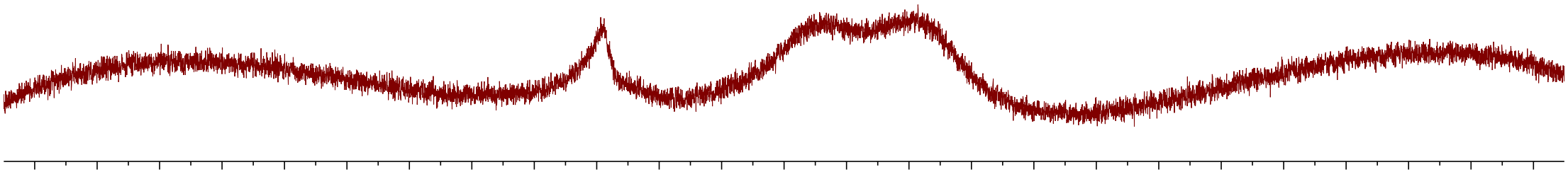
(LiOTf free)

KI_1852-4
single pulse decoupled gated NOE



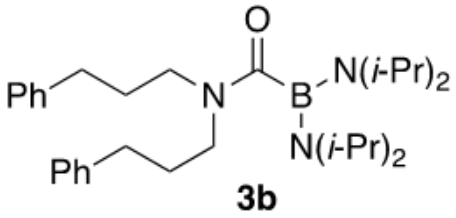
3b

(LiOTf free)



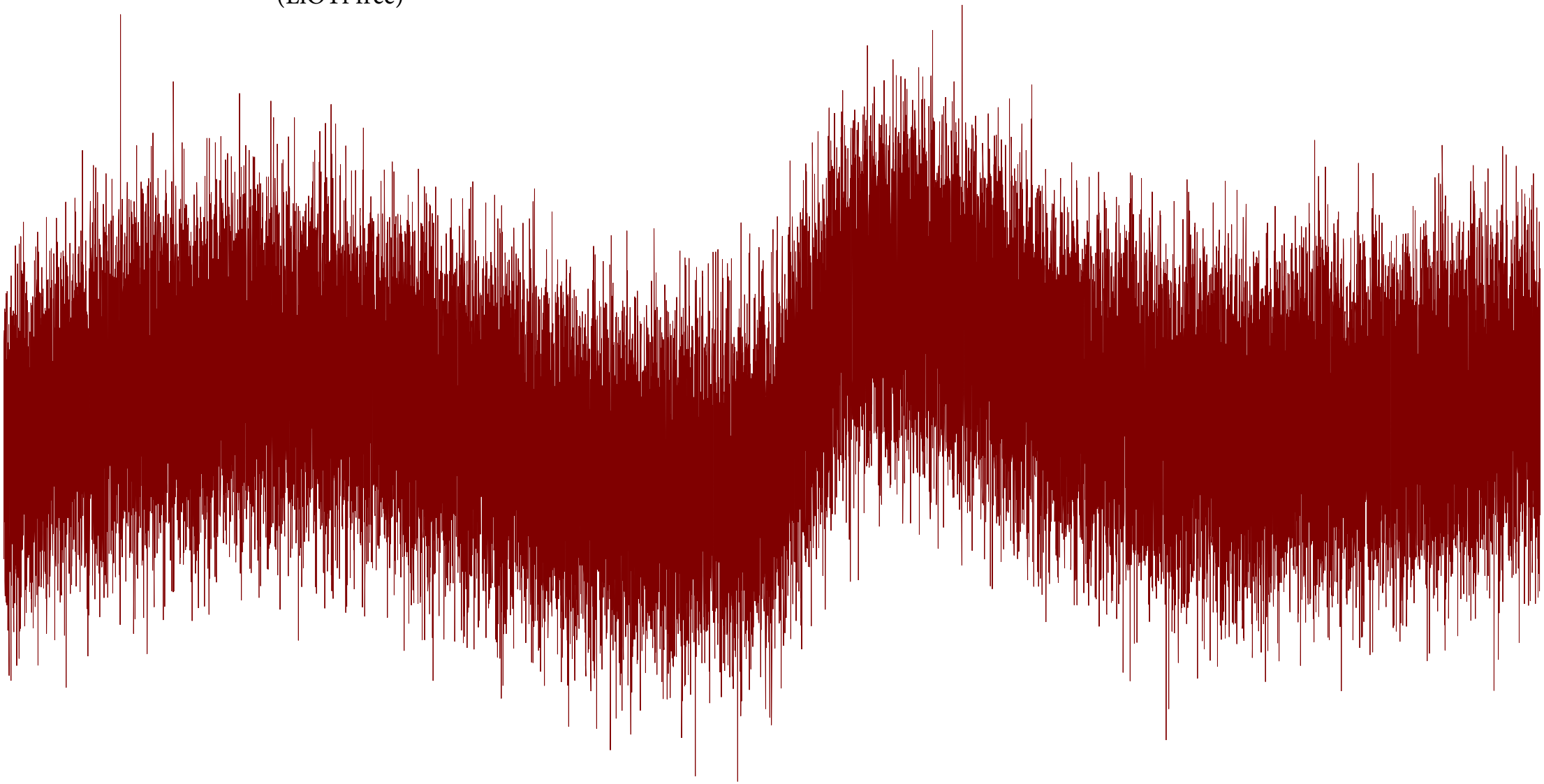
KI_1852-4
single_pulse

^{19}F NMR

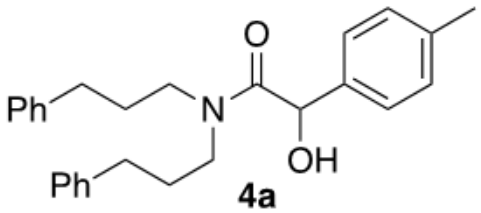


3b

(LiOTf free)

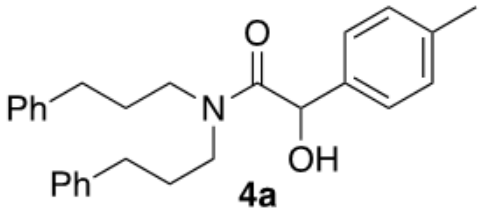


K_ishidakento-amide-p-tol.10.fid
KI_amide-p-tol



4a

K_ishidakento-1495-2-13C.20.fid
KI_1495-2

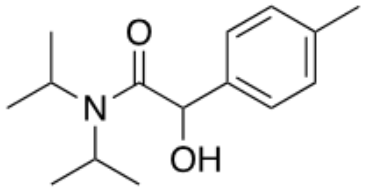


4a

172.106
141.266
140.475
138.211
136.669
129.639
128.579
128.382
128.230
127.314
126.248
125.959
77.317
76.999
76.682
71.361
46.138
46.062
33.148
32.768
29.462
28.897
21.127

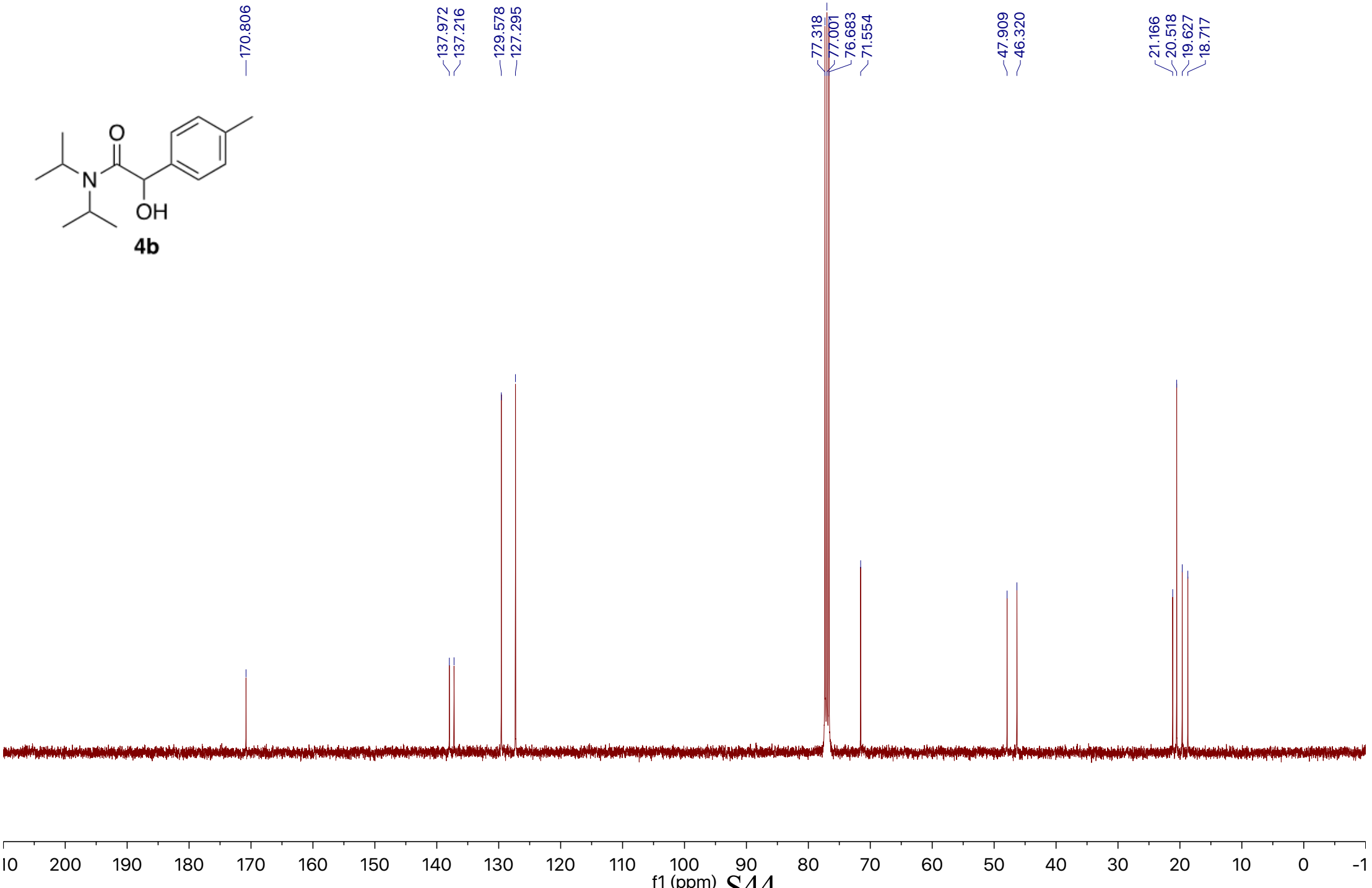
f1 (ppm)

K_ishidakento-1631-3.10.fid
KI_1631-3

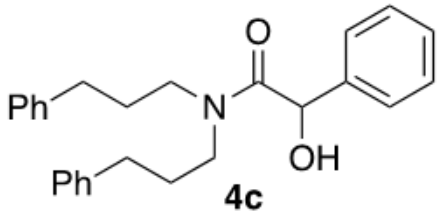


4b

K_ishidakento-1631-3-second.20.fid
KI_1631-3

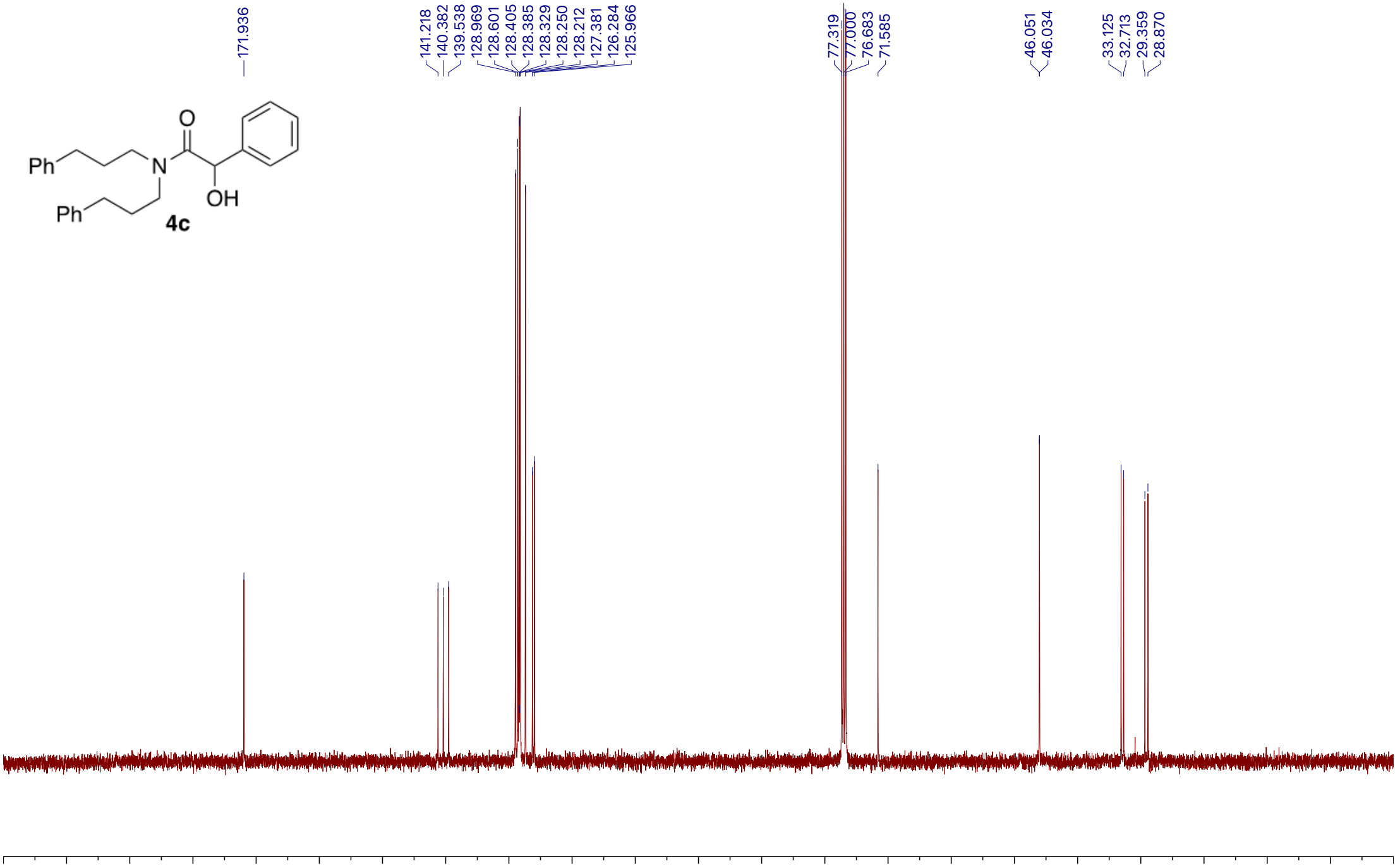


K_ishidakento-1589-3.30.fid
KI_1589-3

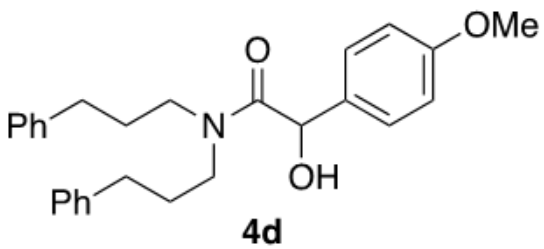


4c

K_ishidakento-1589-3-13c.20.fid
KI_1589-3-13c

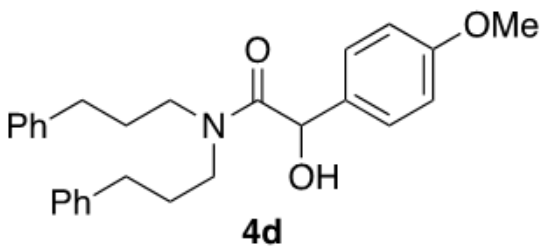


K_ishidakento-1583-1-second.30.fid
KI_1583-1

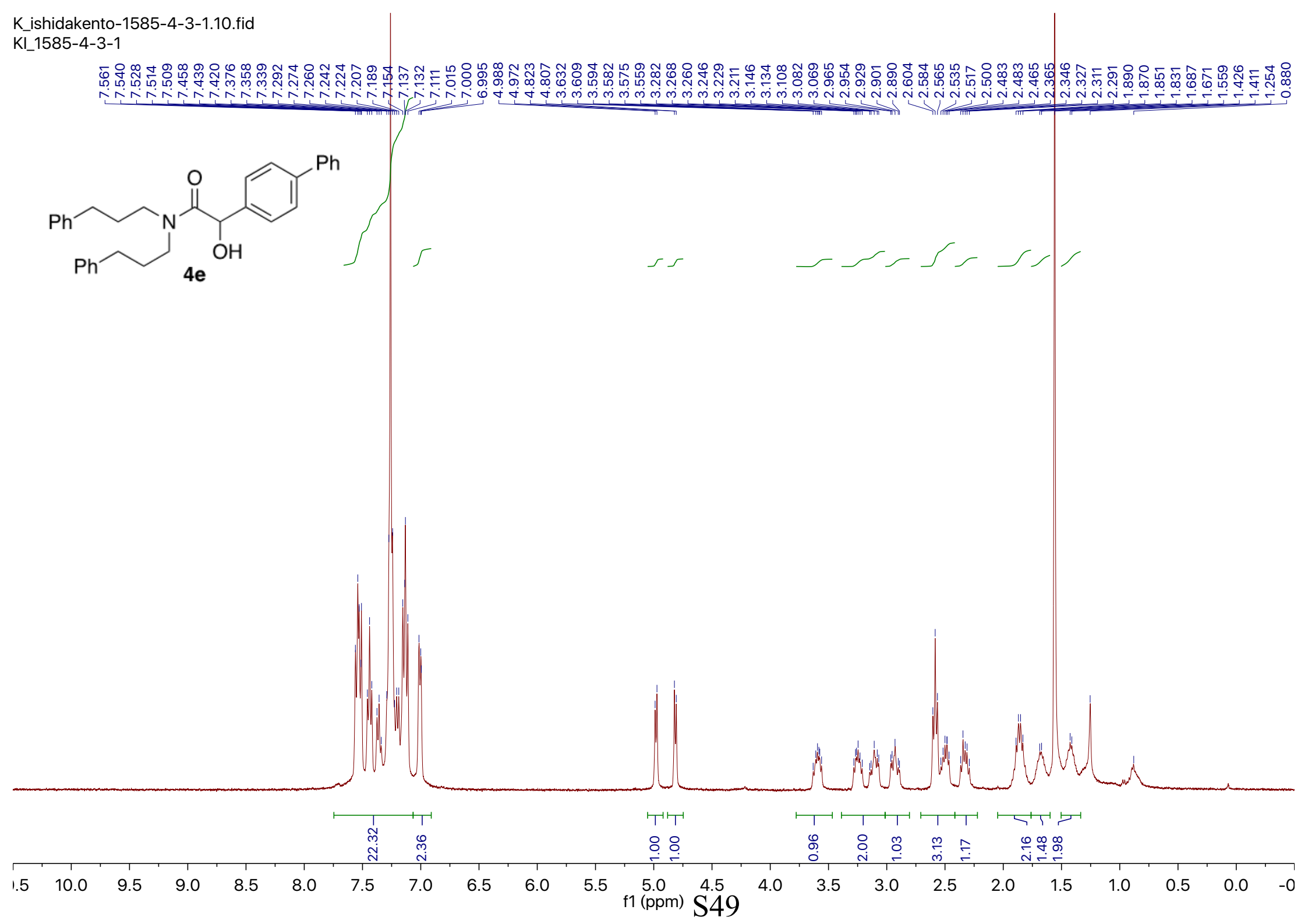


4d

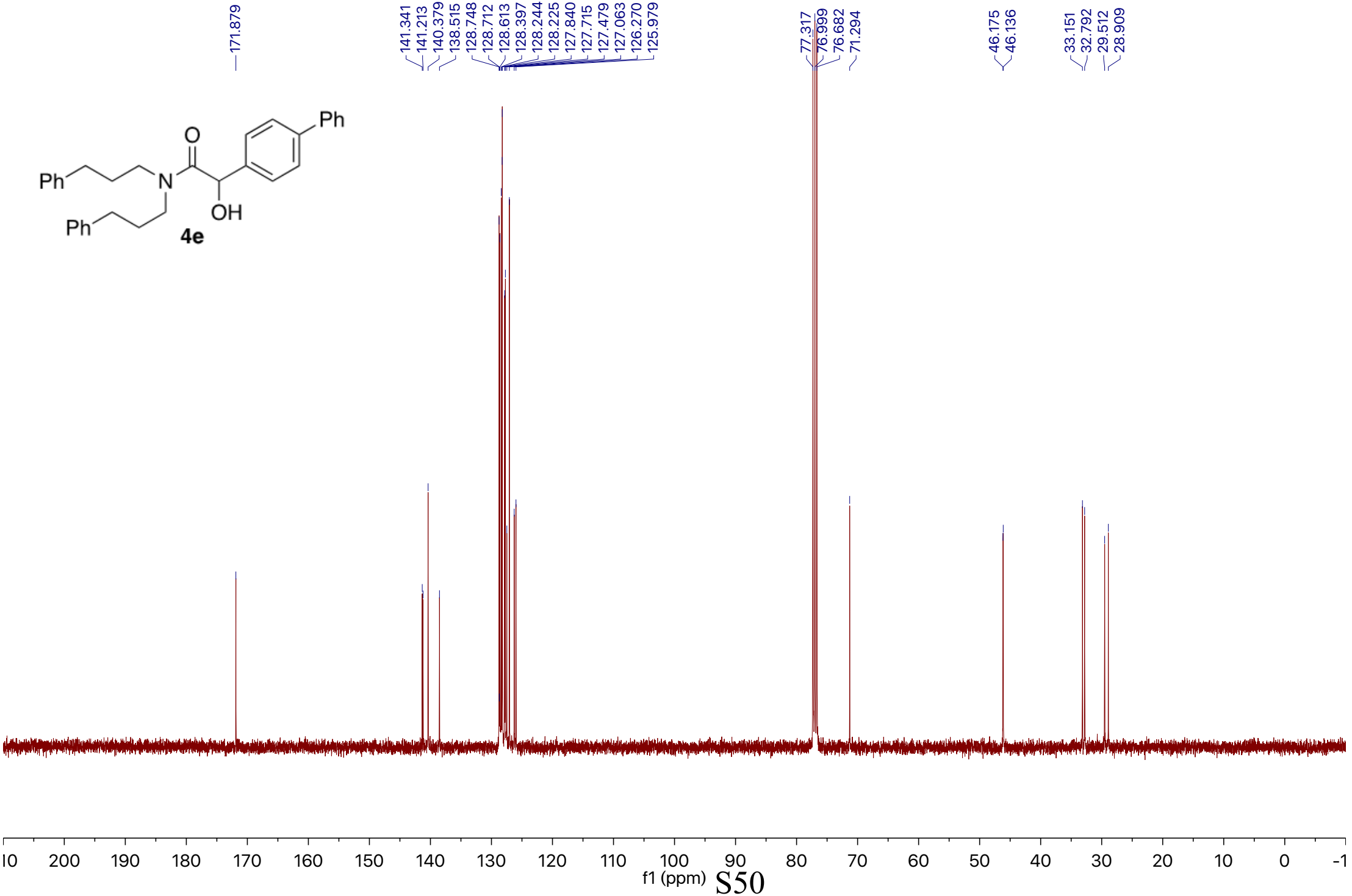
K_ishidakento-1583-1.20.fid
KI_1583-1-13c

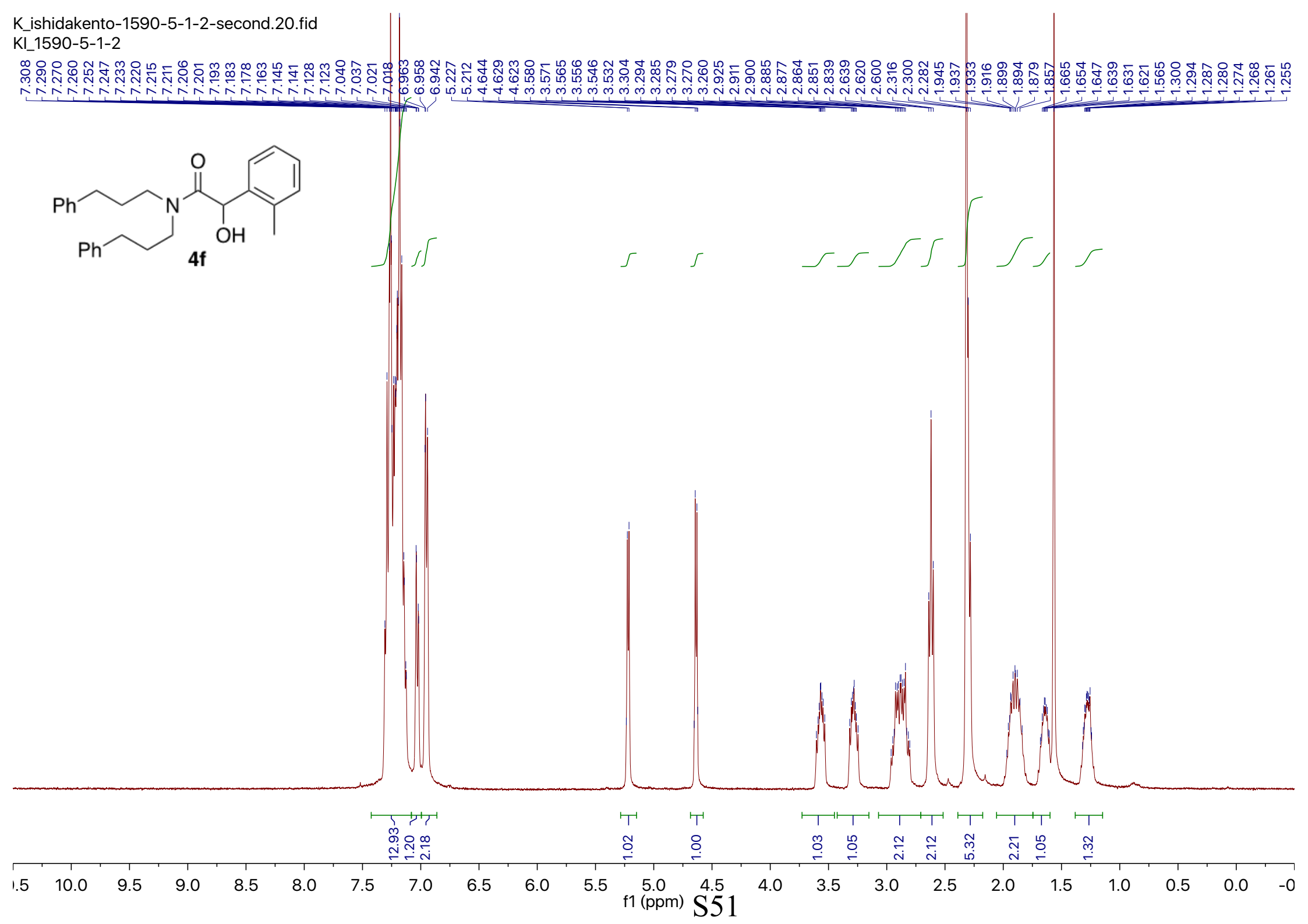


4d

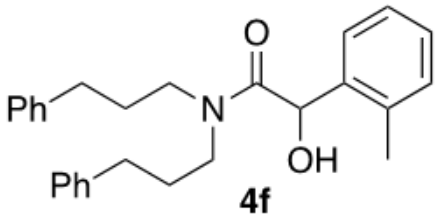

K_ishidakento-1585-4-3-1.10.fid
KI_1585-4-3-1
7.561 7.540 7.528 7.514 7.509 7.458 7.439 7.420 7.376 7.358 7.339 7.292 7.274 7.260 7.242 7.224 7.207 7.189 7.154 7.137 7.132 7.111 7.015 7.000 6.995
4.988 4.972 4.823 4.807 3.632 3.609 3.594 3.582 3.575 3.559 3.282 3.268 3.260 3.246 3.229 3.211 3.146 3.134 3.108 3.082 3.069 2.965 2.954 2.929 2.901 2.890
2.604 2.584 2.565 2.535 2.517 2.500 2.483 2.483 2.465 2.365 2.346 2.327 2.311 2.291 1.890 1.870 1.851 1.831 1.687 1.671 1.559 1.426 1.411 1.254 0.880
Ph
O
Ph
N
OH
Ph
4e
22.32
2.36
1.00
1.00
0.96
2.00
1.03
3.13
1.17
2.16
1.48
1.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

K_ishidakento-1585-4-2-second.20.fid
KI_1586-5-1




K_ishidakento-1590-5-1-2-second.20.fid
KI_1590-5-1-2
7.308 7.290 7.270 7.260 7.252 7.247 7.233 7.220 7.215 7.211 7.206 7.201 7.193 7.183 7.178 7.163 7.145 7.141 7.128 7.123 7.040 7.037 7.021 7.018 6.963 6.958 6.942
5.227 5.212 4.644 4.629 4.623 3.580 3.571 3.565 3.556 3.546 3.532 3.304 3.294 3.285 3.279 3.270 3.260 2.925 2.911 2.900 2.885 2.877 2.864 2.851 2.839 2.639 2.620 2.600 2.316 2.300 2.282 1.945 1.937 1.933 1.916 1.899 1.894 1.879 1.857 1.665 1.654 1.647 1.639 1.631 1.621 1.565 1.300 1.294 1.287 1.280 1.274 1.268 1.261 1.255
O
N
Ph
Ph
OH
4f
12.93
1.20
2.18
1.02
1.00
1.03
1.05
2.12
2.12
5.32
2.21
1.05
1.32
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

K_ishidakento-1590-5-1-2.11.fid
KI_1590-5-1-2

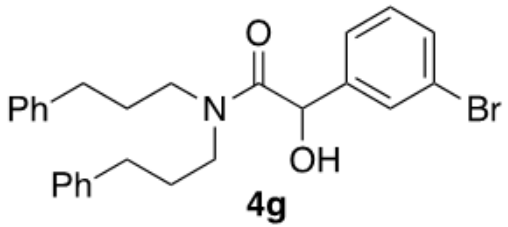


4f

172.523
141.209
140.351
137.515
136.409
131.127
128.563
128.524
128.434
128.254
128.118
127.221
126.667
126.235
126.018
77.317
77.000
76.682
68.919
46.308
46.019
33.264
32.860
29.217
28.791
18.933

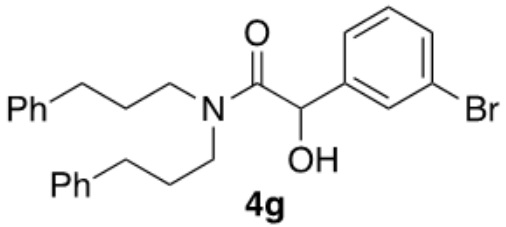
f1 (ppm)

K_ishidakento-1672-2-proton.30.fid
KI_1672-2



4g

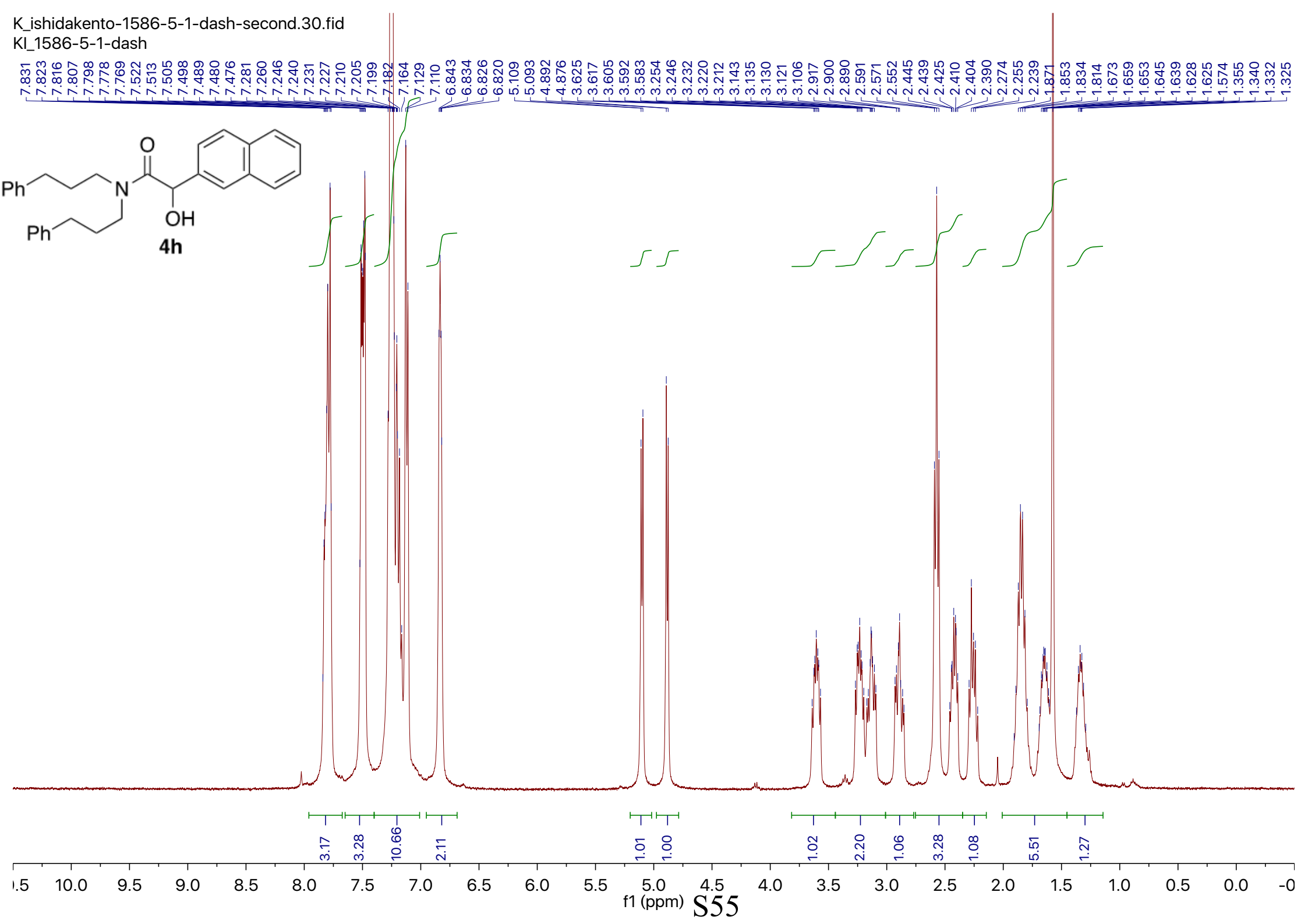
K_ishidakento-1672-2-13c.21.fid
KI_1672-2



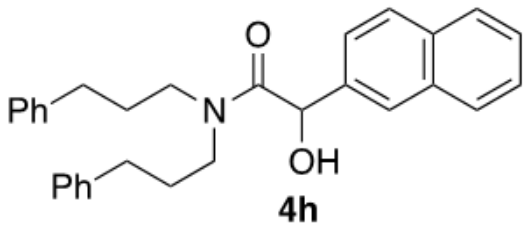
4g

171.283
141.712
141.081
140.192
131.574
130.537
130.449
128.741
128.401
128.227
128.210
126.474
126.002
125.904
122.878
77.318
77.000
76.682
70.815
46.060
45.950
33.101
32.621
29.458
28.804

f1 (ppm)

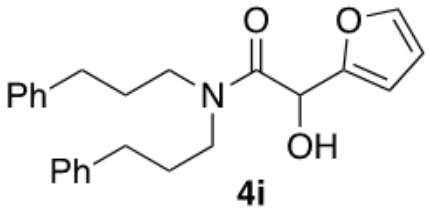

K_ishidakento-1586-5-1-dash-second.30.fid
KI_1586-5-1-dash
7.831 7.823 7.816 7.807 7.798 7.778 7.769 7.522 7.513 7.505 7.498 7.489 7.480 7.476 7.281 7.260 7.246 7.240 7.231 7.227 7.210 7.205 7.199 7.182 7.164 7.129 7.110 6.843 6.834 6.826 6.820 5.109 5.093 4.892 4.876 3.625 3.617 3.605 3.592 3.583 3.254 3.246 3.232 3.220 3.212 3.143 3.135 3.130 3.121 3.106 2.917 2.900 2.890 2.591 2.571 2.552 2.445 2.439 2.425 2.410 2.404 2.390 2.274 2.255 2.239 1.871 1.853 1.834 1.814 1.673 1.659 1.653 1.645 1.639 1.628 1.625 1.574 1.355 1.340 1.332 1.325
Ph
N
O
OH
Ph
4h
3.17
3.28
10.66
2.11
1.01
1.00
1.02
2.20
1.06
3.28
1.08
5.51
1.27
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

K_ishidakento-1586-5-1-dash.20.fid
KI_1586-5-1-dash



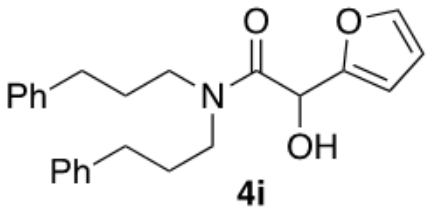
4h

K_ishidakento-1619-2-1.20.fid
KI_1619-2-1



4i

K_ishidakento-1619-2-1.30.fid
KI_1619-2-1-13c



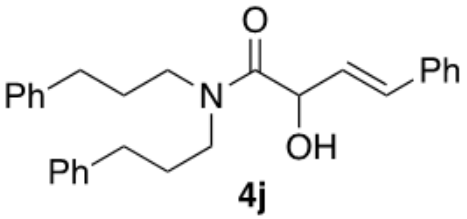
4i

169.651
152.192
142.599
141.228
140.361
128.568
128.403
128.237
128.188
126.294
125.986
110.643
108.219
77.318
77.000
76.683
64.514
46.148
46.129
33.081
32.754
29.516
28.831

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

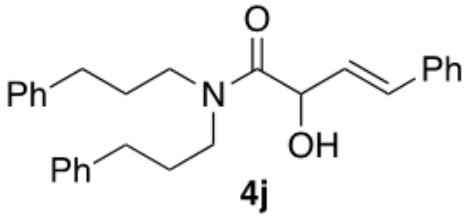
f1 (ppm)

K_ishidakento-1594-5-3-1.10.fid
KI_1594-5-3-1



4j

K_ishidakento-1594-5-2-2-second.40.fid

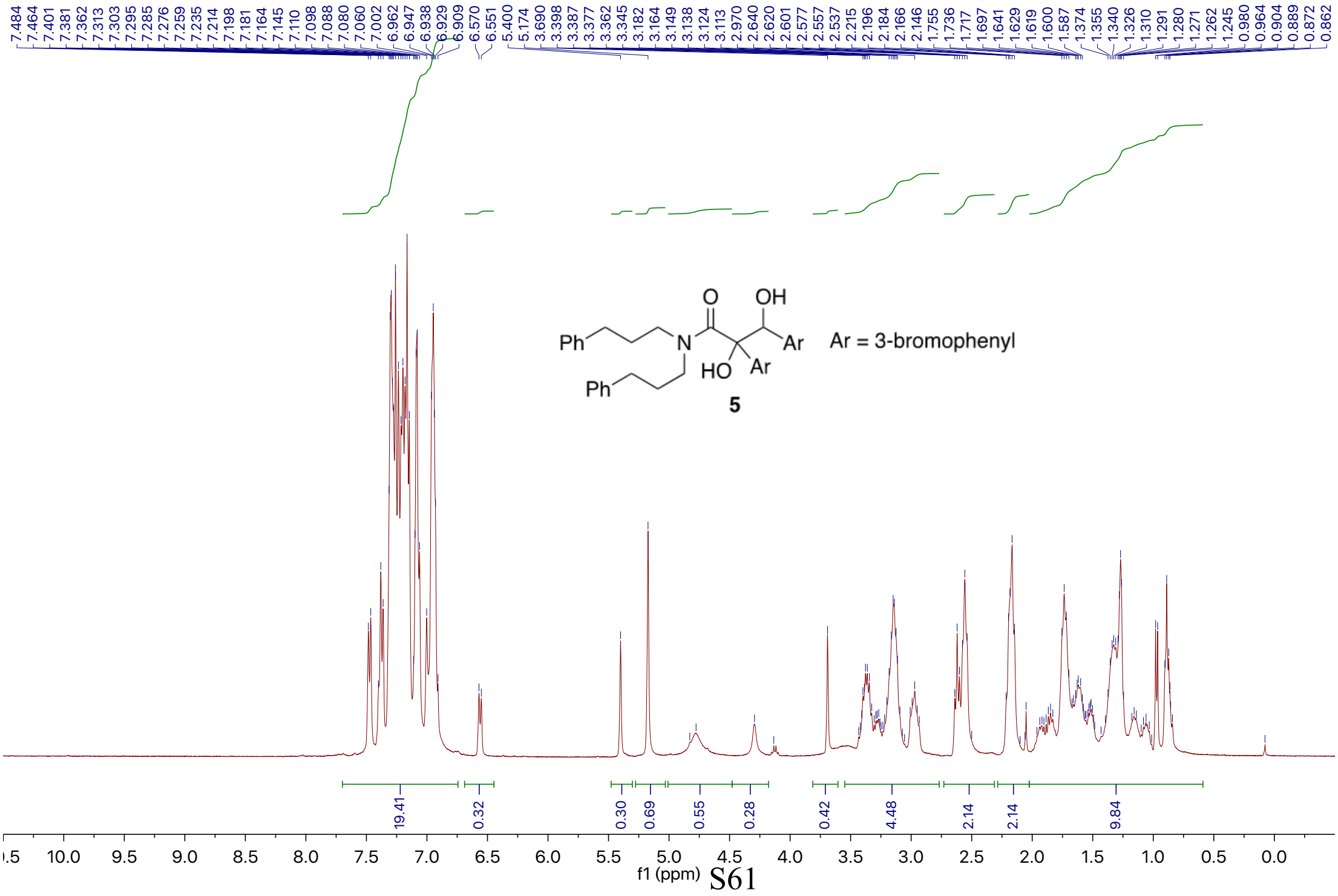


4j

171.849
141.189
140.351
135.936
133.932
128.671
128.598
128.423
128.253
128.205
126.653
126.415
126.374
126.013
77.317
76.999
76.682
69.763
46.187
46.127
33.165
32.822
30.093
29.044

f1 (ppm)

K_ishidakento-1722-5-3.10.fid
KI_1722-5-3



K_ishidakento-1722-5-3.31.fid
KI_1722-5-3