Photoredox Mediated C-H Functionalization and Coupling of Tertiary Aliphatic Amines with 2-Chloro Azoles

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Supporting Information

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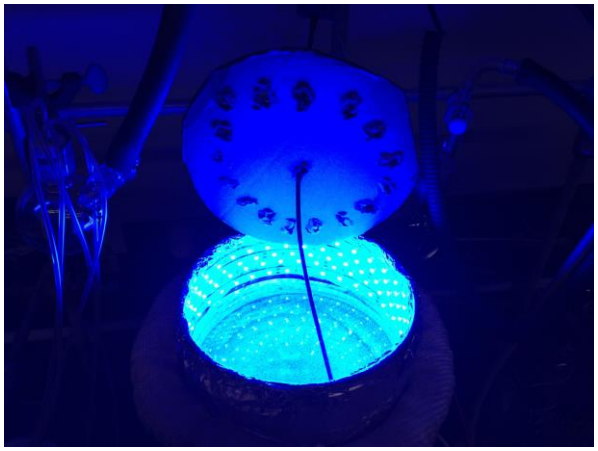
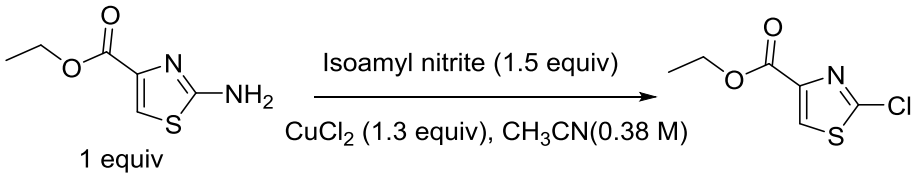
General Experimental: -

All reagents were obtained from commercial suppliers (Aldrich, VWR, TCI chemicals, Oakwood chemicals) and used without further purification unless otherwise noted. Acetonitrile (CH_3CN) was dried using molecular Sieves. Ethyl 2-chlorothiazole-4-carboxylate was purchased from Aldrich and synthesized according to the literature procedure.[1] Amines S-2(a-g) were synthesized according to literature procedure[2] except tributylamine, *N*, *N*-diisopropylethylamine, *N*,*N*-diisopropylmethylamine are from Aldrich. Photocatalyst *tris*(2-phenyl pyridinato-C^2, *N*)iridium(III)($Ir(ppy)_3$), 99%(purity), ($Ir(ppy)_3$) was obtained from Sigma Aldrich and other photocatalyst Ruthenium-*tris(*2,2′-bipyridyl) dichloride $Ru(bpy)_3Cl_2$ was synthesized according to literature procedure.[3] Reactions were monitored by thin layer chromatography (TLC), obtained from sorbent technology Silica XHL TLC Plates, w/UV254, glass backed, 250 um, 20 x 20 cm, and were visualized with ultraviolet light, potassium permanganate stain and GC-MS (QP 2010S, Shimadzu equipped with auto sampler).

Photo catalytic reactions were set up in a light bath which is described below. Strips of blue LED's,(18 LED's/ft) were purchased from Solid Apollo and were wrapped around on the walls of glass crystallization dish and secured with masking tape and then wrapped with aluminum foil. A lid which rest on the top was fashioned from cardboard and holes were made such that reaction tubes (12 × 75 mm cultural borosilicate tube) were held firmly in the cardboard lid which was placed on the top of bath. Water was added to the bath such that the tubes were submerged in the water which was maintained at 45 ^oC with the aid of a sand bath connected to a thermostat.

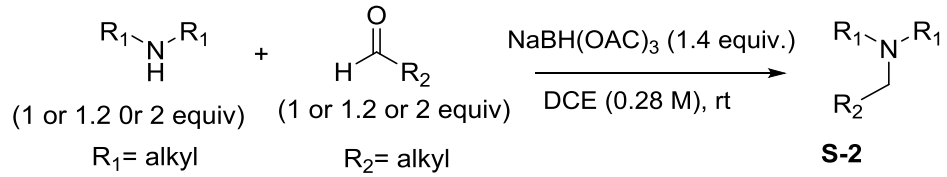


Flash chromatography was carried out with Merck 60 Å, mesh 230-400 silica gel. NMR spectra were obtained on a Varian 400 spectrometer unless noted. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to the residual protio solvent peak (^{1}H, ^{13}C). IR spectra were recorded on Varian 800 FT-IR. Melting points were determined on Mel-Temp apparatus and reported uncorrected. Mass spectra (HRMS) analysis was performed on LTQ-OrbitrapXL by thermo scientific ltd.



General procedure A for synthesis of ethyl 2-chlorothiazole-4-carboxylate

In 100 mL of round bottom flask, ethyl 2-aminothiazole-5-carboxylate (Oakwood Chemicals) (2.0 g, 11.6 mmol) was added and 30 mL of CH_3CN, then $CuCl_2$ (2.03 g, 15.08 mmol) and finally isoamyl nitrite (2.3 mL, 17.4 mmol) was added dropwise to the reaction mixture and reaction was stirred at room temperature for 1 h. The reaction was monitored by TLC. After the complete consumption of reactant, 60 mL of water was added to the mixture, and the entire mixture was filtered through celite, then extracted with EtOAc (3 × 20 mL), the combined organic layers were washed with water (3 × 20 mL), and dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuuo*. The crude material was purified by flash chromatography using Hexane:EtOAc (0 -100 %) to afford ethyl 2-chlorothiazole-5-carboxylate in 73% yield (1.59 g, 0.008 mmol) as white solid, that matched with commercially available ethyl 2-chlorothiazole-5- carboxylate's spectra.

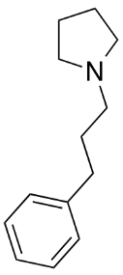


General Procedure B for the synthesis of amines (S-2(a-f)). –

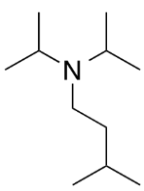
In the reductive aminations, and excess of the more volatile component was used. To an oven dried round bottomed flask equipped with a magnetic stir bar and an Ar inlet was added 1.0 (or 1.2-2) equiv of secondary amine and 1.2-2 or (1.0) equiv. of aldehyde in 1,2-dichloroethane(DCE), (0.28 M), and then treated with 1.4 equiv. of sodium triacetoxy borohydride($NaBH(OAc)_3$). The reaction was monitored by TLC and GC-MS. After the complete consumption of the starting amine (or aldehyde), the reaction mixture was quenched by adding saturated aqueous $NaHCO_3$ and extracted with ethyl acetate (EtOAc). The organic layer was separated then dried with $MgSO_4$. The solvent was evaporated to give free base.

General procedure C for the synthesis of amine S-2g

To an oven dried round bottomed flask equipped with a magnetic stir bar and an Ar inlet was added 1.0 (or 1.2-2) equiv of primary amine, 1 equiv. of acetic acid(AcOH) and 4 equiv. of ketone in 1,2- dichloroethane(DCE), (0.28 M), and then treated with 1.4 equiv. of sodium triacetoxy borohydride($NaBH(OAc)_3$). The reaction was monitored by TLC and GC-MS. After the complete consumption of the starting amine (or aldehyde), the reaction mixture was quenched by adding saturated aqueous $NaHCO_3$ and extracted with ethyl acetate (EtOAc). The organic layer was separated then dried with $MgSO_4$. The solvent was evaporated to give free base

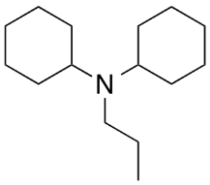


S-2a The general procedure **B** was followed using pyrrolidine (0.65 mL, 8.9 mmol), 3-phenyl propanaldehye (0.98 mL, 7.4 mmol) and were subjected to reductive amination using $NaBH(OAc)_3$ (2.22 g, 10.3 mmol) and DCE (25 mL, 0.28 M) to afford **S-2a** in 68% yield (950 mg, 5.02 mmol) as colorless oil.

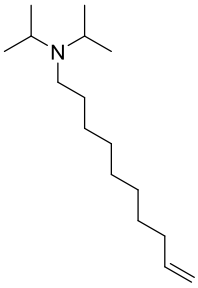


S-2b The general procedure **B** was followed using isovaleraldehyde (0.53 mL, 4.9 mmol), diisopropyl amine (0.60 mL, 4.9mmol) and were subjected to reductive amination using $NaBH(OAc)_3$ (1.47 g, 6.8 mmol) and DCE (17.8 mL, 0.28 M) to afford **S-2b** in 92% yield (766 mg, 4.47 mmol) as transparent **S-2b** as colorless oil.

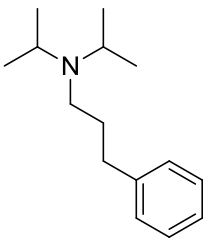
S-2c The general procedure **B** was followed using pyrrolidine (1.30 mL, 7.7 mmol), octyl aldehye (1.20 mL, 3.8 mmol) and were subjected to reductive amination using $NaBH(OAc)_3$ (2.94 g, 5.44 mmol) and DCE as a solvent(35 mL, 0.28 M) to afford **S-2c** in 63% yield (436 mg, 2.38 mmol) as colorless oliy liquid.



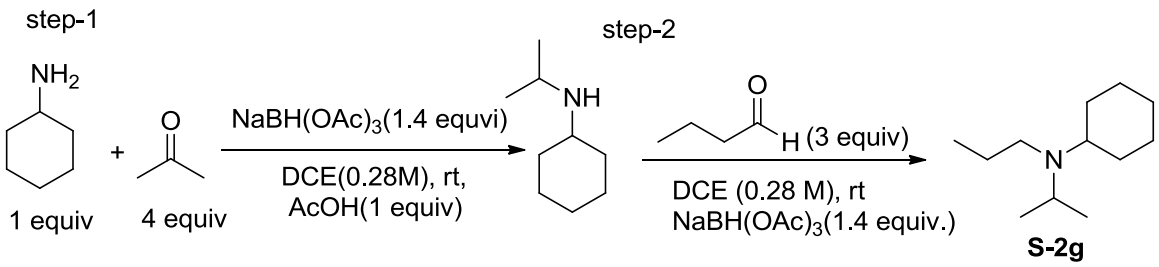
S-2d The general procedure **B** was followed using dicyclohexylamine (1.0 mL, 5.5 mmol), propanaldehye (0.8 mL, 11.0 mmol) and were subjected to reductive amination using $NaBH(OAc)_3$ (1.64 g, 7.72 mmol) and DCE (28 mL, 0.28 M) to afford **S-2d** in quantative yield (1.37 g, 6.13 mmol) as colorless oil.



S-2e The general procedure **B** was followed using diisopropylamine (1.69 mL, 11.8 mmol), 10-undecenal (1.2 mL, 5.9 mmol) and were subjected to reductive amination using $NaBH(OAc)_3$ (1.75 g, 8.26 mmol) and DCE as a solvent(15 mL, 0.28 M) to afford **S-2e** in 93% yield (1.38 g, 5.47 mmol) as colorless liquid.



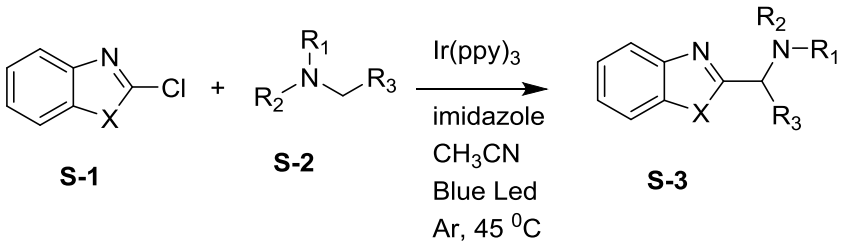
S-2f The general procedure **B** was followed using diisopropylamine (0.69 mL, 4.9 mmol), 3-phenyl propanaldehyde (0.62 mL, 4.9 mmol) and were subjected to reductive amination using $NaBH(OAc)_3$ (1.47 g, 6.8 mmol) and DCE as a solvent (17.8 mL, 0.28 M) to afford **S-2f** in 83% yield (900 mg, 4.1 mmol) as a colorless oil.



S-2g In the first step, the general procedure **C** was followed using cyclohexylamine (1.2 mL, 10.08 mmol), acetone (3 mL, 40.32 mmol), acetic acid (AcOH)(0.58 mL, 10.08 mmol) and were subjected to reductive amination using $NaBH(OAc)_3$ (2.99 g, 14 mmol) and DCE as a solvent (30 mL, 0.28 M) to afford N-isopropylcyclohexamine in 70% yield (995 mg, 7.06 mmol) as a colorless oil.

In the second step, general procedure **B** was followed using *N*-isopropylcyclohexamine (995 mg, 7.06 mmol), propanaldehyde (1.52 mL, 21.2 mmol) using reducing agent $NaBH(OAc)_3$ (2.1 g, 9.9 mmol) in DCE (18 mL, 0.28 M) to afford S-2g in 98% yield (1.267 g, 6.69 mmol).

General procedure D for the photocatalytic arylation of alipahatic amines with heteroaromatic chlorides



A 12 x 75 mm borosilicate test tube fitted with rubber septum was charged with *tris*(2-phenyl pyridinato-C^2, *N*) Iridium(III) ($Ir(ppy)_3$) (0.007 equiv, X mL of a 1.33 mM stock solution of catalyst in CH_3CN where X was used to make 0.19 M solution of the hetroaromatic chloride. Hetroaromatic chloride **S-1** (1 equiv), amine **S-2** (1.2 equiv) and imidazole (2 equiv) were added and the reaction was degassed via Ar bubling for 5-10 min and then left under positive Ar pressure by removing the exit needle. The tube was placed in a light bath (description above) and the lower portion of the tube was submerged under the water bath which was maintained at 45 ^oC. The reaction was monitored by TLC and GC-MS. After the complete consumption of aryl chloride, the CH_3CN was removed via rotavap and the residue was treated with sat. aq $NaHCO_3$ (2 mL) and extracted with EtOAc (5 x 1 mL). The organic portions were combined and dried with anhydrous $MgSO_4$. The crude product was concentrated *in vacuo* and purified by normal phase chromatography. Normal phase chromatography was performed with Teledyne ISCO automated chromatography system using hexane: EtOAc gradients over 40-90 column volumes(cv) using flow rates from 18 mL/min to 35 mL/min on a Redisep column of 4 g, 12 g, or 24 g with product detection at 254 and 288 nm.

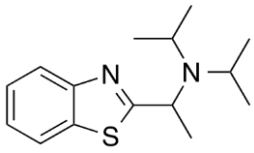
General procedure E photocatalytic arylation of alipahatic amines with heteroaromatic chlorides (no imidazole).

A 12 x 75 mm borosilicate test tube fitted with rubber septum, was charged with *tris*(2-phenyl pyridinato-C^2, *N*) Iridium(III) (0.007 equiv, X mL of a 1.33 mM stock solution of catalyst in CH_3CN where X was used to make 0.19M solution of the hetroaromatic chloride. Hetroaromatic chloride, ***S-1*** (1 equiv**), S-2**amine (4 equiv) were added and the reaction was degassed via Ar bubling for 5-10 min and then left under positive Ar pressure by removing the exit needle. The tube was placed in a light bath (description above) and the lower portion of the tube submerged under the water bath which was maintained at 45 ^oC. The reaction was monitored, worked up, and isolated as in general procedure **D**.

General procedure F photocatalytic arylation of alipahatic amines with heteroaromatic chlorides (Cs_2CO_3 instead of imidazole)

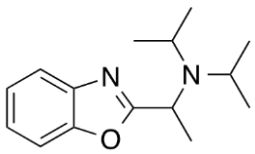
A 12 x 75 mm borosilicate test tube fitted with rubber septum, was charged with *tris*(2-phenyl pyridinato-C^2, *N*) Iridium(III) (0.007 equiv, X mL of a 1.33 mM stock solution of catalyst in CH_3CN where X was used to make 0.19M solution of the hetroaromatic chloride. Hetroaromatic chloride, **S-1** (1 equiv), **S-2** amine (1.2 equiv) and cesium carbonate (Cs_2CO_3) (2 equiv.), and a small stirbar were added and the reaction was degassed via Ar bubling for 5-10 min and then left under positive Ar pressure by removing the exit needle. The tube was placed in a light bath (description above) and the lower portion of the tube submerged under the water bath which was maintained at 45 ^oC and the reaction was vigourously stirred. The reaction was monitored, worked up, and isolated as in general procedure **D**.

Synthesis of S-3a (*N*-(1-(benzo[*d*]thiazol-2-yl)ethyl)-*N*-isopropylpropan-2-amine)



The general procedure **D** was followed using 2-chlorobenzothizole (0.06 mL, 0.47 mmol), N,N-diisopropylethylamine (0.98 mL, 0.56 mmol), imidazole (64 mg, 0.94 mmol) and 2.47 mL of stock solution of $Ir(ppy)_3$ in CH_3CN was used to afford **S-3a** in 92% yield (114 mg, 0.43 mmol), rr 11:1(based on crude ^1H NMR) as pale yellow oil. . It was purified by automated flash chromatography using hexane: EtOAc in 1 % AcOH (0 % for 5 cv, slowly ramped to 20 % EtOAc for 5- 30 cv then ramped to 100 % EtOAc for 30- 44 cv, then held at 100% EtOAc for 44- 60 cv), on 4 g silica column. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.75 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.37 - 7.31 (m, 1H), 7.27 - 7.21 (m, 1H), 4.29 (q, *J* = 6.8 Hz, 1H), 3.15 (hept, *J* = 6.6 Hz, 2H), 1.64 (d, *J* = 6.8 Hz, 3H), 1.11 (d, *J* = 6.7 Hz, 6H), 1.08 (d, *J* = 6.5 Hz, 6H). ^{13}C NMR (101 MHz, cdcl$_3$) δ 183.93, 154.50, 136.60, 125.50, 124.47, 122.64, 121.72, 53.38, 46.40, 23.65, 22.32, 18.90. FT-IR (neat) cm^{-1} 3022, 2964, 1659, 1462. 1389. Calculated HRMS(ESI) for $(C_{15}H_{22}N_2S(M+H)^+$ is 263.1582 observed 263.1568.

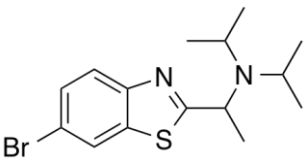
Synthesis of S-3b (*N*-(1-(benzo[*d*]oxazol-2-yl)ethyl)-*N*-isopropylpropan-2-amine)



The general procedure **E** was followed using 2-chlorobenzoxazole (46 mg, 0.30 mmol), N,N-diisoproylethylamine (0.2 mL, 1.2 mmol), and 1.5 mL of stock solution of $Ir(ppy)_3$ in CH3CN to afford S-3b in 74% yield (55 mg, 0.22 mmol) rr 8:1(based on crude ^1H NMR) as an oil. . It was purified by automated flash chromatography using hexane: EtOAc (0 % for 2.5 cv, slowly ramped to 10 % EtOAc for 2.5-49 cv, then ramped to 100 % EtOAc for 49- 51 cv, then held at 100% EtOAc for 51- 65 cv), on 4 g silica column. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.75 - 7.62 (m, 1H), 7.53

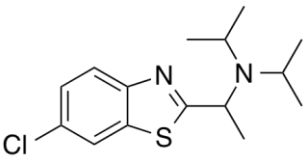
- 7.42 (m, 1H), 7.35 - 7.21 (m, 2H), 4.37 (q, *J* = 7.0 Hz, 1H), 3.28 (hept, *J* = 6.6 Hz, 2H), 1.56 (d, *J* = 6.9 Hz, 3H), 1.09 (d, *J* = 6.6 Hz, 6H), 0.97 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.25, 150.82, 141.47, 124.69, 124.09, 119.92, 110.63, 47.82, 45.64, 23.32, 22.66, 19.20. FT-IR (neat) cm^{-1} 3110, 2963, 1526, 1454, 1390. Calculated HRMS(ESI) for $(C_{15}H_{22}N_2O(M+K)^+$ is 285.1369 observed 285.2109.

Synthesis of S-3c (*N*-(1-(6-bromobenzo[*d*]thiazol-2-yl)ethyl)-*N*-isopropylpropan-2-amine)



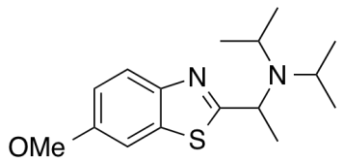
The general procedure **D** was followed using 2-chloro-6-bromo-benzothizole (37 mg, 0.15 mmol), N,N-diisopropylethylamine (0.03 mL , 0.18 mmol), 0 .75 mL of stock solution of $Ir(ppy)_3$ in CH3CN and imidazole (20 mg, 0.30 mmol) to afford **S-3c** in 84% yield (43 mg, 0.13 mmol) rr 16:1(based on crude ^{1}H NMR) as colorless solid, mp-84-87 ^{o}C. It was purified by automated flash chromatography using hexane: EtOAc (0 % for 2.5 cv, slowly ramped to 10 % EtOAc for 2.5-7 cv then ramped to 100 % EtOAc for 7- 32 cv, then held at 100% EtOAc for 32-40 cv), on 12 g silica column. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 2.0 Hz, 1H), 7.74 (s, 1H), 7.48 (d, *J* = 6.7 Hz, 1H), 4.31 (q, *J* = 6.8 Hz, 1H), 3.18 (hept, *J* = 6.6 Hz, 2H), 1.68 (d, *J* = 6.8 Hz, 3H), 1.14 (dd, *J* = 8.7, 6.6 Hz, 12H) .^{13}C NMR (101 MHz, $CDCl_3$) δ184.81, 153.43, 138.42, 128.92, 124.32, 123.82, 117.97, 53.40, 46.47, 23.64, 22.27, 18.74. FT-IR(neat) cm^{-1} 2958, 2930, 1587, 1439, 1384, HRMS (ESI) calcd. $C_{15}H_{21}N_2SBr$ $[M+H]^+$ 341.0687 observed 341.0672.

Synthesis of S-3d ***(****N*-(1-(6-chlorobenzo[*d*]thiazol-2-yl)ethyl)-*N*-isopropylpropan-2-amine)



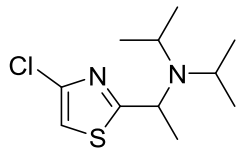
The general procedure **D** was followed using 2,6-dichlorobenzothizole (31 mg, 0.15 mmol), *N*,*N*-diisopropylethylamine (0.03 mL, 0.18 mmol), imidazole (20 mg, 0.30 mmol), 0 .75 mL of stock solution of $Ir(ppy)_3$ in $CH_3CN$to afford **S-3d** in 93% yield (41 mg, 0.14 mmol) rr 14:1(based on crude ^{1}H NMR) as an oil. . It was purified by automated flash chromatography using hexane: EtOAc (0-5 % for 38 cv, slowly ramped to 100 % EtOAc for 38- 52 cv, then held at 100% EtOAc for 52- 68 cv), on 4 g silica column. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.7 Hz, 1H), 7.77 (s, 1H), 7.36 - 7.33 (m, 1H), 4.32 (q, *J* = 6.7 Hz, 1H), 3.18 (hept, *J* = 6.5 Hz, 2H), 1.68 (d, *J* = 6.8 Hz, 3H) 1.14 (dd, *J* = 8.7, 6.6 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.67, 153.09, 137.90, 130.28, 126.22, 123.42, 121.38, 53.40, 46.46, 23.63, 22.26, 18.75. FT-IR (neat) cm^{-1}3025, 2966, 1614, 1462, 1365. HRMS (ESI)calcd. $C_{15}H_{21}N_2SCl$ $[M+H]^+$ 297.1192 observed 297.1192.

Synthesis of S-3e (*N*-isopropyl-*N*-(1-(6-methoxybenzo[*d*]thiazol-2-yl)ethyl)propan-2-amine)



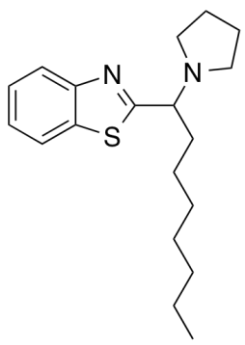
The general procedure **D** was followed using 2-chloro-6-methoxybenzothizole (30 mg, 0.15 mmol*)*, *N,N*-diisopropylethylamine (0.03 mL, 0.18 mmol), imidazole (20 mg, 0.30 mmol) and 0 .75 mL of stock solution of $Ir(ppy)_3$ in CH_3CN and more 0.38 mL of CH_3CN to afford **S-3e** in 61 % yield (27 mg, 0.09 mmol) rr 13:1(based on crude ^1H NMR) as an colorless solid, mp- 74-76 ^oC. It was purified by automated flash chromatography using hexane: EtOAc (0-10 % for 17 cv, slowly ramped to 100 % EtOAc for 17- 19 cv, then held at 100% EtOAc for19- 22 cv), on 12 g silica column. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.9 Hz, 1H), 7.24 (s, 1H), 6.99 (d, *J* = 8.9 Hz, 1H), 4.31 (q, *J* = 5.7, 4.6 Hz, 1H), 3.84 (s, 3H), 3.20 (hept, *J* = 13.2, 7.3, 6.6 Hz, 2H), 1.67 (d, *J* = 6.8 Hz, 3H), 1.16 (dd, *J* = 10.7 Hz, *J* = 6.5 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.24, 157.21, 148.96, 137.84, 123.11, 114.56, 104.45, 55.96, 53.22, 46.34, 23.65, 22.34, 18.87. FT-IR (neat) cm^{-1} 3112, 2956, 1605, 1519, 1469, 1364. HRMS (ESI) calcd. $C_{16}H_{24}N_2SO$ $[M+H]^+$ 293.1688 observed 293.1668.

Synthesis of S-3f (*N*-(1-(5-chlorothiazol-2-yl)ethyl)-*N*-isopropylpropan-2-amine)



The general procedure **D** was followed using 2,4-dichlorothizole (23 mg, 0.15 mmol), *N,N*-diisoproylethylamine (0.03 mL , 0.18 mmol), imidazole (20 mg, 0.3 mmol)), and 0 .75 mL of stock solution of $Ir(ppy)_3$ in CH_3CN to afford **S-3f** in 68 % yield (25 mg, 0.10 mmol) rr 9:1 (based on crude ^1H NMR) as an oil. . It was purified by automated flash chromatography using hexane: EtOAc in 1% AcOH (0 % for 2.5 cv, slowly ramped to 20 % EtOAc for 2.5-30 cv then ramped to 100 % EtOAc for 30- 31 cv, then held at 100% EtOAc 31- 40 cv), on 12 g silica column. ^1H NMR (400 MHz, Chloroform-*d*) δ 6.95 (s, 1H), 4.18 (q, *J* = 6.9 Hz, 1H), 3.15 (hept, *J* = 6.6 Hz, 2H), 1.59 (d, *J* = 6.9 Hz, 3H), 1.10 (d, *J* = 6.6 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.60, 137.51, 114.37, 52.99, 46.19, 23.63, 22.13, 18.67. FT-IR (neat) cm^{-1} 2963, 2929, 1612, 1485, 1385. HRMS (ESI) calcd. $C_{11}H_{19}N_2SCl$ $[M+H]^+$ 247.1036 observed 247.1017.

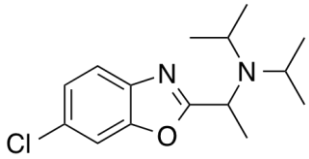
.**Synthesis of S-3g** (2-(1-(pyrrolidin-1-yl)octyl)benzo[*d*]thiazole)



The general procedure **D** was followed using 2-chlorobenzothizole (0.01 mL, 0.08 mmol), octyl pyrrolidine, (**S-2c)** (17 mg, 0.09 mmol), imidazole (10 mg, 0.15 mmol), 0 .75 mL of stock solution of $Ir(ppy)_3$ to afford **S-3g**

in 92% yield (23 mg, 0.07 mmol) rr 20:1(based on crude ^{1}H NMR) as an oil. . It was purified by automated flash chromatography using hexane: EtOAc (0-0 % for 5 cv, slowly ramped to 10 % EtOAc for 5-48 cv then ramped to 100 % EtOAc for 48- 60 cv, then held at 100% EtOAc for 60-70 cv), on 4 g silica column. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.6 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.44 - 7.41 (m, 1H), 7.35 - 7.31 (m, 1H), 3.98 (dd, *J* = 9.2, 5.2 Hz, 1H), 3.35 (t, *J* = 9.1 Hz, 1H), 2.77 - 2.69 (m, 1H), 2.43 - 2.32 (m, 4H), 1.93 - 1.83 (m, 4H), 1.47-1.49 (m, 2H), 1.22(m, 8 H), 0.83(t, *J*=6.8 Hz, 3H) .^{13}C NMR (126 MHz, $CDCl_3$) δ 180.82, 153.85, 135.23, 125.67, 124.49, 122.55, 121.87, 66.95, 55.52, 53.75, 34.06, 31.85, 29.53, 29.28, 29.01, 27.31, 23.67, 22.65, 14.18. FT-Ir (neat) cm^{-1} 3020, 2925, 2854, 1524, 1485, 1308. HRMS (ESI) calcd. $C_{15}H_{20}N_2S$ $[M+H]^+$ 269.1264 observed 269.0372.

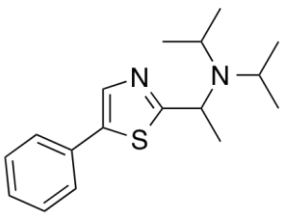
Synthesis of S-3h (*N*-(1-(6-chlorobenzo[*d*]oxazol-2-yl)ethyl)-*N*-isopropylpropan-2-amine)



The general procedure **E** was followed using 2,6-dichlorobenzooxazole (56 mg, 0.30 mmol) *N*,*N*-diisopropylethylamine (0.2 mL, 1.2 mmol) and, 1.5 mL of stock solution of $Ir(ppy)_3$ in CH_3CN to afford **S-3h** in 68% yield (57 mg, 0.20 mmol) rr 13:1(based on crude ^{1}H NMR) as colorless oil. It was purified by automated flash chromatography using hexane: EtOAc (0-10 % for 13 cv, slowly ramped to 100 % EtOAc for 13- 16 cv, then held at 100% EtOAc for 16-25 cv), on 12 g silica column.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.5 Hz, 1H), 7.49 (d, *J* = 1.9 Hz, 1H), 7.29 - 7.21 (m, 1H), 4.34 (q, *J* = 7.0 Hz, 1H), 3.25 (hept, *J* = 6.6 Hz, 2H), 1.54 (d, *J* = 7.0 Hz, 3H), 1.08 (d, *J* = 6.6 Hz, 6H), 0.95 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR(101 MHz, $CDCl_3$) δ 171.01, 151.03, 140.24, 130.31, 124.80, 120.41, 111.33, 47.81, 45.64, 23.26, 22.67, 19.06. FT-IR(‘neat) cm^{-1} 2966, 1614, 1462, 1365. HRMS (ESI) calcd. C_{15} $H_{21}ClN_2O$ $[M+H]^+$ 281.1421 observed 281.1349

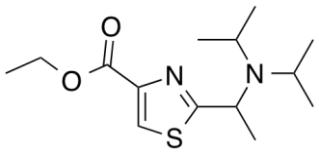
Synthesis of S-3i (*N*-isopropyl-*N*-(1-(5-phenylthiazol-2-yl) ethyl) propan-2-amine)



The general procedure **D** was followed using 2-chloro-5-phenyl thizole (24 mg, 0.13 mmol), *N*,*N*-diisopropylethylamine (0.03 mL , 0.18 mmol), imidazole (20 mg, 0.30 mmol) and 0 .75 mL of stock solution of $Ir(ppy)_3$ in CH_3CN to afford **S-3i** in 24% yield (10.5 mg, 0.035 mmol) rr 9:1(based on crude ^{1}H NMR) as an oil. It was purified by automated flash chromatography using hexane: EtOAc (0 % for 2.5 cv, slowly ramped to 20 % EtOAc for 2.5-16 cv then ramped to 100 % EtOAc for 16-18 cv, then held at 100% EtOAc for18- 29 cv), on 12 g silica column. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 7.1 Hz, 1H), 7.41 - 7.25

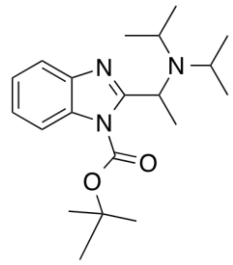
(m, 5H), 4.29 (q, *J* = 6.8 Hz, 1H), 3.20 (hept, *J* = 6.6 Hz, 2H), 1.67 (d, *J* = 6.9 Hz, 3H), 1.13 (d, *J* = 6.4 Hz, 6H). 1.12 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.23, 155.29, 135.40, 128.82, 127.78, 126.30, 113.59, 52.93, 46.12, 23.66, 22.31, 19.16. FT-IR(neat) cm^{-1} 3025, 2961, 1505, 1385. HRMS (ESI) calcd. $C_{19}H_{30}N_2S$ $[M+H]^+$ 289.1739 observed 289.1719.

Synthesis of S-3j ethyl 2-(1-(diisopropylamino)ethyl)thiazole-4-carboxylate



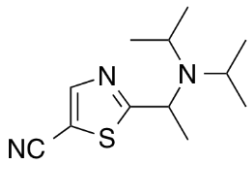
The general procedure **E** was followed using ethyl 2-chlorothiazole-4-carboxylate (29 mg, 0.15 mmol),), *N*,*N*-diisopropylethylamine (0.1 mL, 0.6 mmol), 0 .75 mL of stock solution of $Ir(ppy)_3$ in CH_3CN to afford **S-3j** in 69% yield (30 mg, 0.105mmol) rr 4:1 (based on crude ^{1}H NMR) as an oil. It was purified by automated flash chromatography using hexane: EtOAc in 1% AcOH (0 % for 4 cv, slowly ramped to 45% for 4- 35 cv then ramped to 100 % EtOAc for 35- 40 cv, then held at 100% EtOAc for 40-50 cv), on 12 g silica column. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 4.25 (q, *J* = 6.9 Hz, 1H), 3.16 (hept, *J* = 6.5 Hz, 2H), 1.65 (d, *J* = 6.9 Hz, 3H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.10 (dd, *J* = 6.6, 1.6 Hz, 12H). ^{13}C NMR (101 MHz, cdcl$_3$) δ 183.76, 162.04, 147.63, 128.61, 61.39, 52.96, 46.24, 23.59, 22.14, 18.96, 14.58. FT-IR (neat) cm^{-1} 2956, 1715, 1485, 1367, 1202. HRMS(ESI) calcd. $C_{14}H_{24}N_2O_2$ $(M+H)^+$ 285.1637 observed 285.1618.

Synthesis of S-3k (*tert*-butyl 2-(1-(diisopropylamino)ethyl)-1*H*-benzo[*d*]imidazole-1-carboxylate)



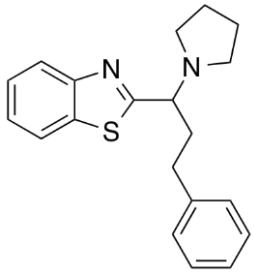
The general procedure **F** was followed using *N*-boc-2-chlorobenzimidazole (38 mg, 0.15 mmol), *N*,*N*-diisopropylethylamine (0.03 mL, 0.18 mmol), Cs_2CO_3 (98 mg, 0.3 mmole), 0. 75 mL stock solution of $Ir(ppy)_3$ was used to afford **S-3k** in 75% yield (38 mg, 0.109 mmol) rr 20:1 (based on crude ^{1}H NMR) as an oil. . It was purified by automated flash chromatography using hexane: EtOAc (0-25 % for 48 cv, slowly ramped to 100 % EtOAc for 48-60 cv, then held at 100% EtOAc for 60 - 75 cv), on 12 g silica column. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.77 (m, 1H), 7.70 – 7.67 (m, 1H), 7.29 – 7.25 (m, 2H), 5.23 (q, *J* = 6.9 Hz, 1H), 3.48 (hept, *J* = 6.5 Hz, 2H), 1.70 (s, 9H), 1.52 (d, *J* = 7.0 Hz, 3H), 1.09 (d, *J* = 6.6 Hz, 6H), 0.89 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, cdcl$_3$) δ 161.01, 149.42, 142.45, 133.02, 124.16, 123.92, 119.93, 114.62, 85.27, 47.73, 45.44, 28.38, 23.43, 22.91, 19.37. FT-IR(neat) cm^{-1} 2957, 2928, 2871, 1729, 1603, 1462, 1365. HR-MS(ESI) calcd. $C_{20}H_{31}N_3O_2(M+H)^+$ 346.2495and observed 346.2480.

Synthesis of S-3l (2-(1-(diisopropylamino) ethyl) thiazole-5-carbonitrile)



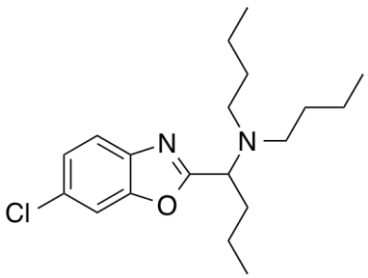
The general procedure **D** was followed using 2-chloro-5-cyano thiazole (44 mg, 0.3 mmol), *N*,*N*-diisopropylethylamine (0.06 mL, 0.36 mmol), imidazole (40 mg, 0.60 mmol) and 1.5 mL of stock solution of $Ir(ppy)_3$ in CH_3CN to afford **S-3l** in 84% yield (61 mg, 0.25 mmol) rr 4:1 (based on crude ^1H NMR) as solid, mp-92-94 ^oC. It was purified by automated flash chromatography using hexane: EtOAc (0-100 % for 16 cv, then held at 100% EtOAc for 16- 20 cv), on 24 g column silica. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 4.23 (q, *J* = 6.9 Hz, 1H), 3.16 (hept., *J* = 6.6 Hz, 2H), 1.61 (d, *J* = 6.9 Hz, 3H), 1.12 (dd, *J* = 6.6, 4.1 Hz,12H). ^{13}C NMR(101 MHz, $CDCl_3$) δ 190.15, 152.58, 113.09, 106.77, 53.47, 46.53, 23.64, 21.97, 18.36. FT-IR(neat) cm^{-1} 2969, 2945, 2218, 1614, 1504, 1386. HRMS (ESI) calcd. $C_{12}H_{19}N_3S$ $[M+H]^+$ 238.1378 observed 238.1364.

Synthesis of S-3m (2-(3-phenyl-1-(pyrrolidin-1-yl)propyl)benzo[*d*]thiazole)



The general procedure **D** was followed using 2-chlorobenzothizole (0.04 mL , 0.3 mmol), 1-(3-phenylpropyl)pyrrolidine (68 mg, 0.36 mmol), imidazole (40 mg, 0.6 mmol), 1.5 mL of stock solution of $Ir(ppy)_3$ in CH_3CN to afford **S-3m** in 39% yield (38 mg, 0.12 mmol) rr 20:1 (based on crude ^1H NMR) as an oil. It was purified by automated flash chromatography using hexane: EtOAc (0 % for 2.5 cv, slowly ramped to 20 % EtOAc for 2.5- 25 cv then ramped to 100 % EtOAc for 25-26 cv, then held at 100% EtOAc for 26- 37 cv), on 12 g silica column. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.6 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.44 - 7.41 (m, 1H), 7.35 - 7.31 (m, 1H), 7.24 - 7.20 (m, 2H), 7.15 - 7.12 (m, 3H), 3.98 (dd, *J* = 9.2, 5.2 Hz, 1H), 3.35 (t, *J* = 9.1 Hz, 1H), 2.87 - 2.69 (m, 3H), 2.60 - 2.45 (m, 2H), 2.43 - 2.31 (m, 2H), 2.02 - 1.89 (m, 2H), 1.89 - 1.80 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.82, 154.07, 142.62, 135.39, 128.53, 128.48, 125.89, 125.85, 124.71, 122.75, 122.02, 67.13, 55.35, 53.98, 34.32, 33.87, 31.04, 23.95. FT-IR(neat) cm^{-1} 2940, 2802, 1608, 1519, 1312. HRMS (ESI) calcd. $C_{20}H_{22}N_2S$ $[M+H]^+$ 323.1582 observed 323.1573.

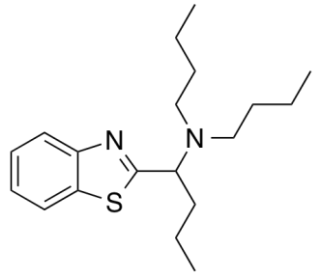
Synthesis of S-3n (*N*,*N*-dibutyl-1-(6-chlorobenzo[*d*]oxazol-2-yl)butan-1-amine)



The General procedure **E** was followed using 2,6-dichlorobenzoxazole (25 mg, 0.13 mmol), tributylamine (0.13 mL, 0.53mmol), and 0.75 mL of stock solution of $Ir(ppy)_3$ in CH_3CN to afford **S-3n** in 63% yield (28 mg, 0.081 mmol) as an oil. . It was purified by automated flash chromatography using hexane: EtOAc

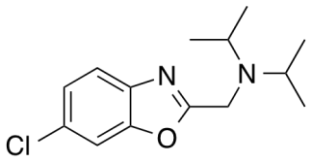
(0 % for 5 cv, slowly ramped to 10 % EtOAc for 5- 40 cv then ramped to 100 % EtOAc for 40-72 cv, on 12 g silica column. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.5 Hz, 1H), 7.51 (d, *J* = 1.9 Hz, 1H), 7.30 - 7.25 (m, 1H), 3.99 (t, *J* = 7.5 Hz, 1H), 2.62 (dt, *J* = 13.0, 7.6 Hz, 2H), 2.34 - 2.24 (m, 2H), 2.01 - 1.82 (m, 2H), 1.44 - 1.34 (m, 6H), 1.32 - 1.24 (m, 4H), 0.93 (t, *J* = 7.4 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ168.10, 150.90, 139.79, 130.46, 124.94, 120.58, 111.43, 58.59, 50.94, 33.11, 31.18, 20.62, 19.95, 14.28, 14.12. FT-IR(neat) cm^{-1} 2957, 2930, 2871, 1607, 1462, 1378. HRMS (ESI) calcd. $C_{19}H_{29}N_2OCl$ $[M+H]^+$ 359.1866 observed 359.2052.

Synthesis of S-3o (1-(benzo[*d*]thiazol-2-yl)-*N*,*N*-dibutylbutan-1-amine)



The general procedure **E** was followed using 2-chlorobenzothizole (25 mg, 0.14 mmol), tributylamine(0.17 mL, 0.56 mmol) 0.75 mL of stock solution of $Ir(ppy)_3$ in CH_3CN was used to afford, to afford **S-3o** in 83% yield (37 mg, 0.12 mmol), as pale yellow color oily liquid. . It was purified by automated flash chromatography using hexane: EtOAc (0 % for 5 cv, slowly ramped to 10 % EtOAc for 5- 28 cv then ramped to 100 % EtOAc for 28- 48cv, then held at 100% EtOAc for 48- 60 cv), on 4 g silica column. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 4.09 (t, *J* = 6.9 Hz, 1H), 2.64 - 2.57 (m, 2H), 2.50 - 2.42 (m, 2H), 2.07 - 1.96 (m, 1H), 1.95 - 1.83 (m, 1H), 1.57 - 1.40 (m, 5H), 1.31 (dt, *J* = 14.7, 7.4 Hz, 5H), 0.96 (t, *J* = 7.7 Hz, 3H), 0.88 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.66, 153.46, 135.68, 125.67, 124.73, 122.97, 121.70, 63.41, 50.82, 33.72, 31.19, 20.81, 20.74, 14.42, 14.34. FT-IR(neat) cm^{-1} 3025, 2956, 2930, 2871, 1461, 1377. HRMS (ESI) calcd. $C_{19}H_{30}N_2S$ $[M+H]^+$ 319.2208 observed 319.2288.

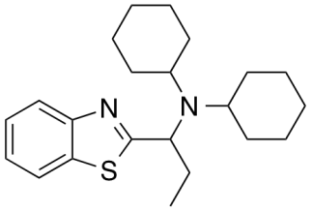
Synthesis of S-3p (*N*-((6-chlorobenzo[*d*]oxazol-2-yl)methyl)-*N*-isopropylpropan-2-amine)



The general procedure **E** was followed using 2,6-dichlorobenzoxazole (28 mg, 0.15 mmol), *N*,*N*-diisopropylmethylamine (0.1 mL, 0.6 mmol), 0 .75 mL of stock solution of $Ir(ppy)_3$ in CH_3CN to afford **S-3p** in 55% yield (22 mg, 0.08 mmol) rr 20:1(based on crude 1H NMR) as an oil. . It was purified by automated flash chromatography using hexane: EtOAc (0 % for 6 cv, slowly ramped to 20 % EtOAc for 6-52 cv then ramped to 100 % EtOAc for 52- 80 cv, then held at 100% EtOAc for 80- 93cv), on 4 g silica column , (Chloroform-*d*) δ 7.56 (d, *J* = 8.5 Hz, 1H), 7.51 (s, 1H), 7.26 (d, *J* = 8.5 Hz, 1H), 3.89 (s, 2H), 3.14 (hept, *J* = 6.5 Hz, 2H), 1.07 (d, *J* = 6.5 Hz, 12H). ^{13}C NMR (101 MHz,

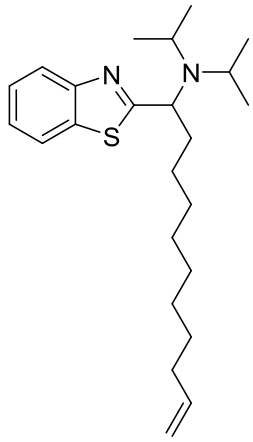
$CDCl_3$) δ 168.34, 151.27, 140.26, 130.41, 124.90, 120.44, 111.50, 50.12, 43.54, 25.57, 20.81. FT-IR(neat) cm^{-1} 2962, 1452, 1262. HRMS (ESI) calcd. $C_{14}H_{19}N_2OCl$ $[M+H]^+$ 289.1084 observed 289.3285

Synthesis of S-3q (*N*-(1-(benzo[*d*]thiazol-2-yl)propyl)-*N*-cyclohexylcyclohexanamine)



The general procedure **D** was followed using 2-chlorobenzothizole (0.02 mL, 0.15 mmol), *N*-cyclohexyl-*N*-propylcyclohexanamine (40 mg, 0.18 mmol), imidazole (20 mg, 0.3 mmol), 0 .75 mL of stock solution of $Ir(ppy)_3$ in CH_3CN to afford **S-3q** in 83% yield (44 mg, 0.12 mmol) rr 20:1(based on crude ^{1}H NMR) as an oil. It was purified by automated flash chromatography using hexane: EtOAc (0 % for 5 cv, slowly ramped to 10 % EtOAc for 5- 52 cv then ramped to 100 % EtOAc for 52 - 60 cv, then held at 100% EtOAc for 62-68 cv), on 4 g silica column. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 4.10 (dd, *J* = 8.6, 4.8 Hz, 1H), 2.75 (tt, *J* = 11.5, 3.2 Hz, 2H), 2.29 – 2.17 (m, 1H), 1.91 – 1.81 (m, 1H), 1.81 – 1.62 (m, 8H), 1.59 – 1.52 (m, 2H), 1.42 – 1.28 (m, 4H), 1.27 – 1.16 (m, 4H), 1.12 (t, *J* = 7.4 Hz, 3H), 1.08 – 1.00 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ180.00, 153.64, 135.95, 125.48, 124.57, 122.83, 121.64, 60.81, 55.79, 34.51, 34.29, 28.07, 26.96, 26.82, 26.13, 12.75. FT-IR(neat) cm^{-1} 3110, 2925, 1612, 1518, 1450, 1390. HRMS (ESI) calcd. $C_{22}H_{32}N_2S$ $[M+H]^+$ 357.2364 observed 357.2349.

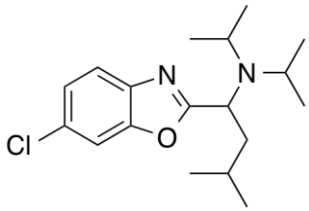
Synthesis of S-3r (1-(benzo[*d*]thiazol-2-yl)-*N*,*N*-diisopropylpent-4-en-1-amine)



The general procedure **D** was followed using 2-chlorobenzothizole (0.02 mL, 0.15 mmol), *N*,*N*-diisopropyl-10-undecenalamine (46 mg, 0.18 mmol), imidazole (20 mg, 0.3 mmol), 0 .75 mL of stock solution of $Ir(ppy)_3$ in CH_3CN to afford **S-3r** in 39 % yield (22 mg, 0.05 mmol) rr 20:1 (based on crude ^{1}H NMR) as an oil. . It was purified by automated flash chromatography using hexane: EtOAc in 1% AcOH (0-5 % for 18 cv, slowly ramped to 100 % EtOAc for 18-27 cv, then held at 100% EtOAc for 27-30 cv), on 12g silica column. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 8.0, 1.2 Hz, 1H), 7.43 - 7.36 (m, 1H), 7.33 - 7.27 (m, 1H), 5.79 (ddt, *J* = 16.9, 10.2, 6.8 Hz, 1H), 5.04 - 4.87 (m, 2H), 4.16 (dd, *J* = 8.7, 4.6 Hz, 1H), 3.30 (hept, *J* = 7.0 Hz, 2H), 2.25 - 2.14 (m, 1H), 2.05 - 1.96 (m, 2H), 1.81 (ddt, *J* = 13.1, 10.2, 4.8 Hz, 1H), 1.42 - 1.20 (m, 12H), 1.10 (d, *J* = 6.5 Hz, 6H)

1.05 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.98, 153.70, 139.47, 135.92, 125.48, 124.58, 122.88, 121.62, 114.28, 58.11, 46.16, 34.51, 34.03, 30.16, 29.74, 29.67, 29.34, 29.15, 28.04, 23.44, 22.98. FT-IR(neat) cm^{-1} 3124, 2926, 2854, 1384, 1241. HRMS (ESI) calcd. $C_{18}H_{26}N_2S$ $[M+K]^+$ 341.1454 observed 341.1560.

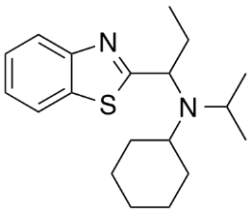
Synthesis of S-3s (1-(6-chlorobenzo[*d*]oxazol-2-yl)-*N*,*N*-diisopropyl-3-methylbutan-1-amine)



The General procedure **E** was followed using 2,6-dichlorobenzothizole (25 mg, 0.13 mmol), N,N-diisopropyl-3-methylbutan-1-amine (32 mg, 0.17 mmol), and 0.75 mL of stock solution of $Ir(ppy)_3$ in CH_3CN afford **S-3s** in 78% yield (33 mg, 0.10 mmol), rr 8:1(based on crude ^{1}H NMR), as low melting solid, mp- 47-49 ^{o}C. . It was purified by automated flash chromatography using hexane: EtOAc (0 % for 5 cv, slowly ramped to 10 % EtOAc for 5- 50 cv then ramped to 100 % EtOAc for 50- 60 cv, then held at 100% EtOAc for 60- 72 cv), on 4 g silica column .^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.5 Hz, 1H), 7.49 (d, *J* = 1.9 Hz, 1H), 7.27 - 7.25 (m, 1H), 4.19 (dd, *J* = 8.5, 6.6 Hz, 1H), 3.36 (hept, *J* = 6.6 Hz, 2H), 1.94 (dddd, *J* = 13.0, 8.3, 6.1, 1.6 Hz, 1H), 1.69 - 1.53 (m, 2H), 1.07 (d, *J* = 6.7 Hz, 6H), 0.92 (d, *J* = 6.5 Hz, 6H), 0.87 (d, *J* = 6.6 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 170.30, 150.67, 140.21, 130.26, 124.84, 120.44, 111.28, 50.49, 45.55, 42.56, 24.92, 23.68, 23.26, 22.72, 22.16.FT-IR(neat) cm^{-1} 2960, 1607, 1557, 1462, 1386.HRMS (ESI) calcd. $C_{18}H_{27}N_2OCl$ $[M+H]^+$ 323.1890 observed 323.1832.

Note- **S-3s** has another regio- isomer in the spectra, labeled as dark filled circle.

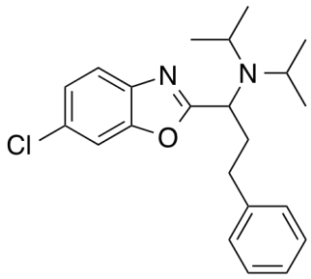
Synthesis of S-3t (*N*-(1-(benzo[*d*]thiazol-2-yl)propyl)-*N*-isopropylcyclohexanamine)



The general procedure **D** was followed using 2-chlorobenzothizole (20 ul mL, 0.15 mmol), *N*-isopropyl-*N*-propylcyclohexanamine (33 mg, 0.18 mmol), imidazole (20 mg, 0.3) mL), 0 .75 mL of stock solution of $Ir(ppy)_3$ in CH_3CN to afford **S-3t** in 50% yield (24 mg, .075 mmol) rr 20:1(based on crude ^{1}H NMR) as an oil. . It was purified by automated flash chromatography using hexane: EtOAc in 1% AcOH (0 % for 10 cv, slowly ramped to 20 % EtOAc for 10-70 cv then ramped to 100 % EtOAc for 70- 79 cv, then held at 100% EtOAc for 79- 90 cv), on 4 g silica column ^{1}H NMR (400 MHz, Chloroform-*d*) 7.94 (d, *J* = 9.1 Hz, 1H), 7.81 (d, *J* = 9.1 Hz, 1H), 7.40 (t, *J* = 7.1 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 4.09 (dd, *J* = 8.7, 4.6 Hz, 1H), 3.29 (hept, *J* = 7.0 Hz, 1H), 2.75 (tt, *J* = 11.6, 3.3 Hz, 1H), 2.23 (ddt, *J* = 13.4, 8.9, 7.2

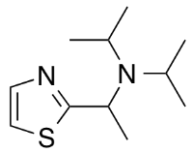
Hz, 2H), 1.90 - 1.82 (m, 1H), 1.76 - 1.55 (m, 6H), 1.40 - 1.28 (m, 4H), 1.12 (t, *J* = 7.4 Hz, 3H), 1.09 (d, *J* = 6.6 Hz, 3H), 1.04 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.00, 153.67, 135.95, 125.49, 124.59, 122.83, 121.63, 60.34, 55.07, 46.82, 34.30, 31.15, 27.79, 26.96, 26.83, 26.15, 23.48, 23.15, 12.76. FT-IR(neat) cm^{-1} 3025, 2927, 2852, 1612, 1438, 1385. HRMS (ESI) calcd. $C_{19}H_{328}N_2S$ $[M+H]^+$ 317.2051 observed 317.2036.

Synthesis of S-3u (1-(6-chlorobenzo[*d*]oxazol-2-yl)-*N*,*N*-diisopropyl-3-phenylpropan-1-amine)



The general procedure **E** was followed using 2,6-dichlorobenzoxazole (25 mg, 0.13 mmol), *N*,*N*-diisopropyl-3-phenylpropan-1-amine (116 mg, 0.53 mmol), and 0.75 mL of stock solution of $Ir(ppy)_3$ in CH_3CN was used to afford to afford **S-3u** in 83% yield (40 mg, 0.10 mmol), rr 9.3:1 (based on crude ^{1}H NMR) as pale yellow oil. . It was purified by automated flash chromatography using hexane: EtOAc (0 % for 2.5 cv, slowly ramped to 10 % EtOAc for 2.5-27 cv then ramped to 100 % EtOAc for 27-30 cv, then held at 100% EtOAc for 30-35 cv), on 12 g silica column. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 1.9 Hz, 1H), 7.30 - 7.23 (m, 4H), 7.16 (dt, *J* = 6.5, 1.8 Hz, 2H), 4.14 (t, *J* = 7.5 Hz, 1H), 3.37 (hept, *J* = 6.6 Hz, 2H), 2.72 (ddd, *J* = 13.8, 9.9, 6.5 Hz, 1H), 2.64 - 2.58 (m, 1H), 2.41 - 2.32 (m, 1H), 2.12 (dtd, *J* = 13.6, 6.8, 3.1 Hz, 1H), 1.06 (d, *J* = 6.7 Hz, 6H), 0.87 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.76, 150.75, 141.99, 140.19, 130.41, 128.62, 128.57, 126.06, 124.95, 120.52, 111.34, 52.12, 45.61, 35.05, 33.30, 23.72, 22.10. FT-IR(neat) cm^{-1} 3022, 2961, 1678, 1513, 1384. HRMS (ESI) calcd. $C_{22}H_{27}N_2OCl$ $[M+H]^+$ 371.1890 observed 371.1873.

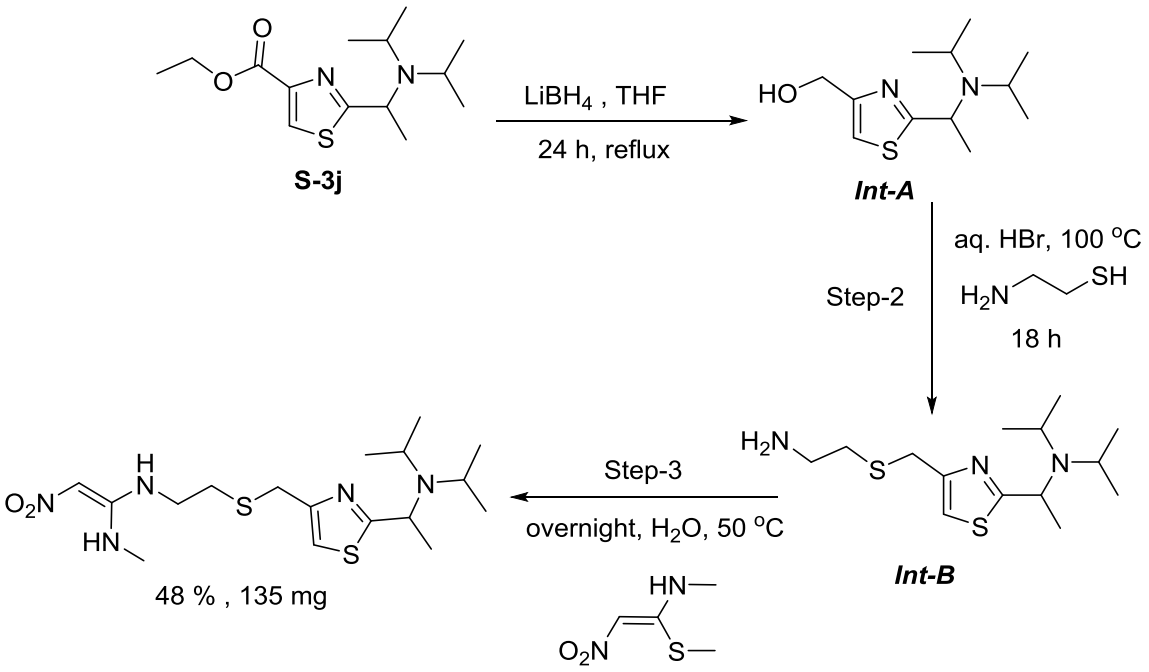
Synthesis of S-3v (N-isopropyl-N-(1-(thiazol-2-yl)ethyl)propan-2-amine)



The general procedure **D** was followed using 2-chlorothizole (20 ul , 0.13 mmol), *N*,*N*-diisopropylethylamine (0.03 mL, 0.18 mmol), imidazole (20 mg, 0.18 mol) 0 .75 mL of stock solution of $Ir(ppy)_3$ in CH_3CN to afford **S-3v** in 69% yield (22 mg, 0.081 mmol) rr 2:1(based on crude ^{1}H NMR) as an oil. . It was purified by automated flash chromatography using hexane: EtOAc (0 % for 3 cv, slowly ramped to 10 % EtOAc for 3-15 cv then ramped to 100 % EtOAc for 15-27 cv, then held at 100% EtOAc for 27-32 cv), on 12 g silica column. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 3.3 Hz, 1H), 7.18 (d, *J* = 3.3 Hz, 1H), 4.26 (q, *J* = 6.8 Hz, 1H), 3.16 (hept, *J* = 6.7, 6.3 Hz, 2H), 1.61 (d, *J* = 6.8 Hz, 3H), 1.10 (d, *J* = 6.4 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.42, 142.57, 119.69, 52.67, 46.08, 28.11, 22.31, 19.03. FT-IR(neat) cm^{-1} 3120, 2961, 2869, 1605, 1500, 1385. HRMS (ESI) calcd. $C_{11}H_{20}N_2S$ $[M+H]^+$ 213.1425 observed 213.1410.

Note – **S-3v** has the other regio-isomer present in the spectra, labeled as dark filled circle.

Synthesis of Nizatidine analog.-(Z)-*N*-2-(2-(((2-(1-(diisopropylamino)ethyl)thiazol-4-yl)methyl)thio)ethyl)-*N*1-methyl-1-nitroethene-1,2-diamine



According to the literature[4-5], in a round bottom flask, 200 mg of **S-3j** (0.70 mmol) was added along with 30 mg lithium borohydride ($LiBH_4$)(1.4 mmol) in THF (10 mL) and was refluxed for 22 h. After cooling water (10 mL) was added and the mixture was extracted with EtOAc(4×5 mL). The combined organic portions were dried over anhydrous $MgSO_4$. It was filtered and concentrated to afford ***int-A*** to give a crude yield of 90 % (152 mg, 0.63 mmol).

In the second step, 152 mg of crude ***int-A***, 2-aminoethane-1-thiol (74 mg, 0.65 mmol) and aq HBr (0.9 mL) were added. The reaction mixture was heated at 100 ^oC for 18 h. After cooling water (10 mL) and solid K_2CO_3 were added and extracted with EtOAc (5 × 5 mL). The organic portions were combined and dried over $MgSO_4$ and concentrated over via rotovap to afford ***int- B*** in greater than quantative yield by mass. In the final step, all of the crude material from the previous step and (Z)-N-methyl-1-(methylthio)-2-nitroethen-1-amine (114 mg, 0.768 mmol) were combined and water (3 mL) was added. The reaction mixture was heated at 50 ^oC overnight. After the complete conversion of reactant to product (monitored by TLC), the reaction mixture was quenched by adding saturated aq. $NaHCO_3$ (10 mL) and extracted with EtOAc (5 ×

5 mL) and dried over anhydrous $MgSO_4$. The organic layer was filtered and concentrated via rotovap. The crude material was subjected to automated flash chromatography DCM/MeOH, (0% for 2.5 cv, slowly ramped to 25 % MeOH for 2.5-75 cv then ramped to 50 % MeOH for 75-92 cv, then held at 100% EtOAc f 98cv), on 4 g silica column to obtain **4a,** 48 % (135 mg, 0.336 mmol) over three steps, starting from the coupled product **3j**. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.93 (s, 1H), 6.51 (d, *J* = 1.1 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 1H), 3.74 (s, 2H), 3.29 (d, *J* = 7.2 Hz, 2H), 3.09 (hept, *J* = 12.8, 8.1, 6.2 Hz, 2H), 2.87 (s, 2H), 2.78 (s, 3H), 1.51 (d, *J* = 6.8 Hz, 3H), 1.05 (dd, *J* = 6.6, 1.4 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.56, 156.89, 152.85, 116.69, 98.40, 52.80, 46.17, 41.56, 31.49, 31.05, 27.76, 23.60, 22.22, 19.10. FT-IR(neat) cm^{-1} 3257, 3010, 2961, 1613, 1571, 1382, 1362. HRMS (ESI) calcd. $C_{17}H_{31}N_5S_2O$ $[M+H]^+$ 402.1997 observed 402.1977.

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Discussion of Possible Mechanisms

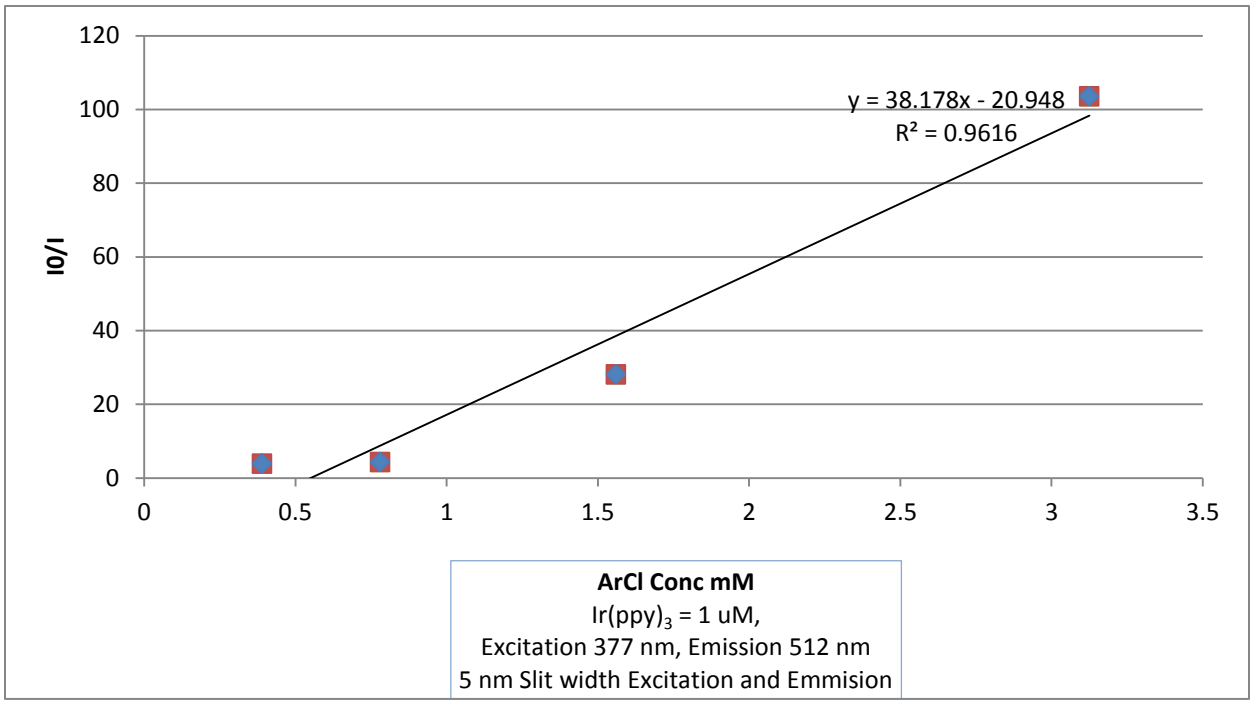
While tempting to assume a straightforward mechanism similar to that proposed by MacMillan[1], several observations prevent a clear understanding of the true reaction intermediates and order of events at this time and warrant a more full investigation. A reviewer suggested similarities to the Minisci reaction, in which a carbon based radical adds to electron deficient arene (typically protonated heterocycles such as pyridine or quinoline). While many things about this reaction are unknown, several things must be true of this reaction. First, the amine must be oxidized at some point during the reaction. Based on redox potentials, oxidation by Ir(IV) to give Ir(III) ($E_{1/2}$ for Ir(IV)/Ir(III) = +0.77)[2] to give the amine radical cation species could be occurring but reductive quenching of the excited state catalyst has also been demonstrated[3] Ir*(III)/Ir(II) ($E_{1/2}$ = +0.31)[2] despite the difference in redox potentials, Et_3N (E_{ox} = +0.73)[4] versus +0.31 for Ir*(III)/Ir(II). Regardless of whether the amine radical cation is formed via direct reductive quenching of the excited state catalyst or indirectly via reduction of the Ir(IV) species, one of the following scenarios must take place. 1) C_α-H abstraction might take place to give an electrophilic imminium specices or 2) C_α-H deprotonation could take place to give an α-amino radical or 3) α-amino radical formed by scenario 2 could be further oxidized to give the an imminium species. Stephenson has proposed formation of the imminium by C_α-H abstraction by superoxide radical anion.[5] This is relevant since our reaction works almost equally well with and without the presence of air (See text). On the otherhand, the pK_a of the C_α-H of the amine radical cation is significantly acidified. Stephenson has estimated this pK_a to be 26.7 on for Et_3N.[6] Tertiary amines are significantly more basic in MeCN than DMSO, such that the pK_a for Et_3NH^+ is 18.8.[7] While these are estimates the eight order of magnitude difference suggests that at best only a small amount of deprotonation would occur at any time. Also concerning the fate of the amine, it is worth noting that in sluggish reactions small amounts of *N*,*N*-diisopropylacetamide (from iPr_2NEt) was observed by GC-MS, though no attempts were made to quantify the amount produced, in reactions run in air or argon which could give support to the formation of α-amino radical[8] via rapid reaction with advantageous O_2. However, dimerized amine which might arise from α-amino radical homocoupling[4] was never observed by GC-MS. Furthermore, this was most prevalent when the substrate carried an alcohol group. It is not unreasonable to think that the amide could also arise from attack of the alcohol on the imminium carbon followed by subsequent oxidation of the hemiaminal ether to give the amide after hydrolysis upon exposure to wet solvent. Thus, it is not overly clear if C-C bond formation proceeds through an imminium, or and α-amino radical.

Concerning the possible oxidative quenching of the excited photocatalyst, it is worth noting that O_2 E_{red} = -1.48 in MeCN[9] and structurally related 2-heteroaryl benzazoles typically fall within E_{red} = -1.65 to -1.90 (redox numbers could not be found for 2-chlorobenzothiazole nor any other heterocycle studied).[10] The relevant photocatalyst potential for Ir*(III)/Ir(IV) is $E_{1/2}$ = -1.73, suggesting that either the heterocycle or oxygen could potentially undergo electron transfer (albeit an equilibrium would likely be established) from the photoexcited catalyst. Unfortunately, our quenching studies were complicated by the fact that the substrate absorbs light at the emission wavelength of the photocatalyst in MeCN (512 nM). Switching to DCM allowed us to excite the

photocatalyst and observe its emission without interference, in which case we did see a linear response to the substrate-suggesting oxidative quenching was possible. However, it is worth noting that the reaction did not work in DCM thus it may in fact be important that the photocatalyst is not oxidatively quenched. Given that in at least one solvent the 2-chlorobenzothiazole is capable of oxidatively quenching the photo excited state of the catalyst, the fate of the radical anion of the 2-chloroazole should be considered. Furthermore, if reductive quenching by the amine is taking place, then the Ir(II) ($E_{1/2}$ = -2.19 V)[2] species would be sufficiently reducing to transfer an electron.

If the radical anion of the 2-chloroazole is formed, it could undergo C-Cl bond fragmentation. It has been suggested that chloroarenes with reduction potentials less than ~-1.6 V are unstable and undergo fragmentation to form an aryl radical and a chloride ion. If the heteroaryl radical, for which little information is known, is nucleophilic in nature then attack on an imminium would be a likely manner of C-C bond formation. An alternative, and perhaps more interesting, scenario would involve the radical anion associating with the amine radical cation and then abstracting a hydrogen atom from the C_α-H of the amine radical cation. The result would be to form a carbanion and imminium in close proximity, facilitating C-C bond formation followed by loss of HCl to rearomatize the heterocycle. Giving some support for this idea, a chelated protonated species may play an important role in protecting the product α-azole carbinamine from over oxidation. For example, when Boc-protected benzimidazole is run without a carbonate base present, loss of the Boc group is observed on the product but not the starting heterocycle, which presumably occurs via protonation of the benzimidazole imine nitrogen after reaction which would facilitate the loss of the Boc group but also prevent over oxidation. Also, noteworthy is the selectivity of the C-H functionalization. The reaction is selective for both the thermodynamically stronger CH_2 as well as the exocyclic CH_2, which is suggestive of an irreversible kinetically controlled deprotonation (or C-H abstraction) similar to that seen by Schreiber.[11]

To further complicate the issue, we must recognize that it is possible to have more than one quenching pathway as the Stern-Volmer plot provides the rate of quenching of the photoexcited catalyst in the absence of the other suspect reagents and does not tell you if unproductive quenching is occurring. Thus, we must be careful not to assume too much from these experiments. We believe that the true reaction mechanism is not obvious at this time and there are observations that support a number of different intermediates. While we appreciate the reviewers' interest in the mechanism, we strongly believe it would be premature to offer a mechanism without the appropriate studies, which warrant their own investigation rather than trying to place a poorly supported mechanism into this communication. A detailed mechanistic investigation would be helpful for us but for the entire field of photoredox catalysis which has expanded rapidly and often without complete understanding of the reactions being developed.



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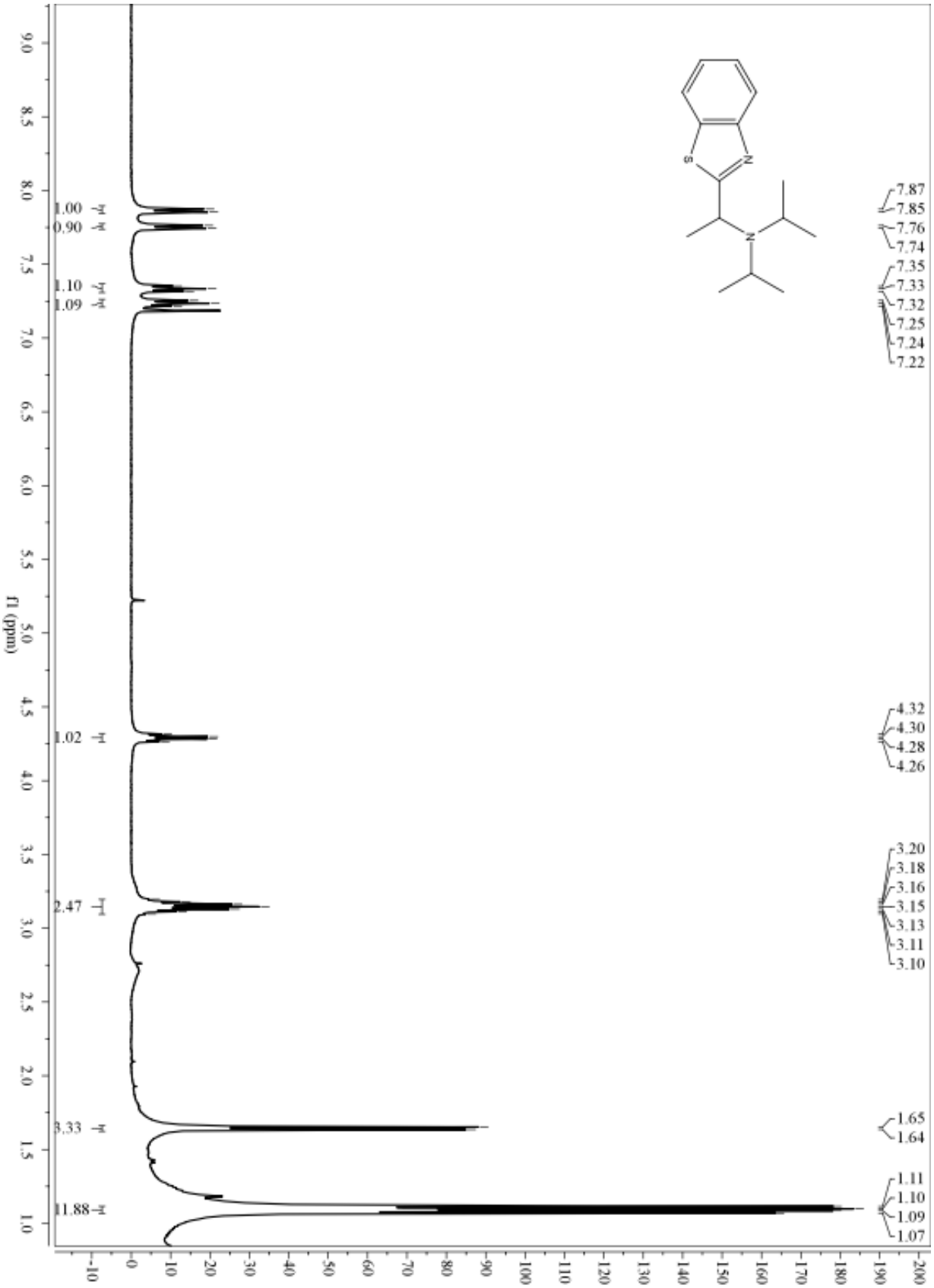
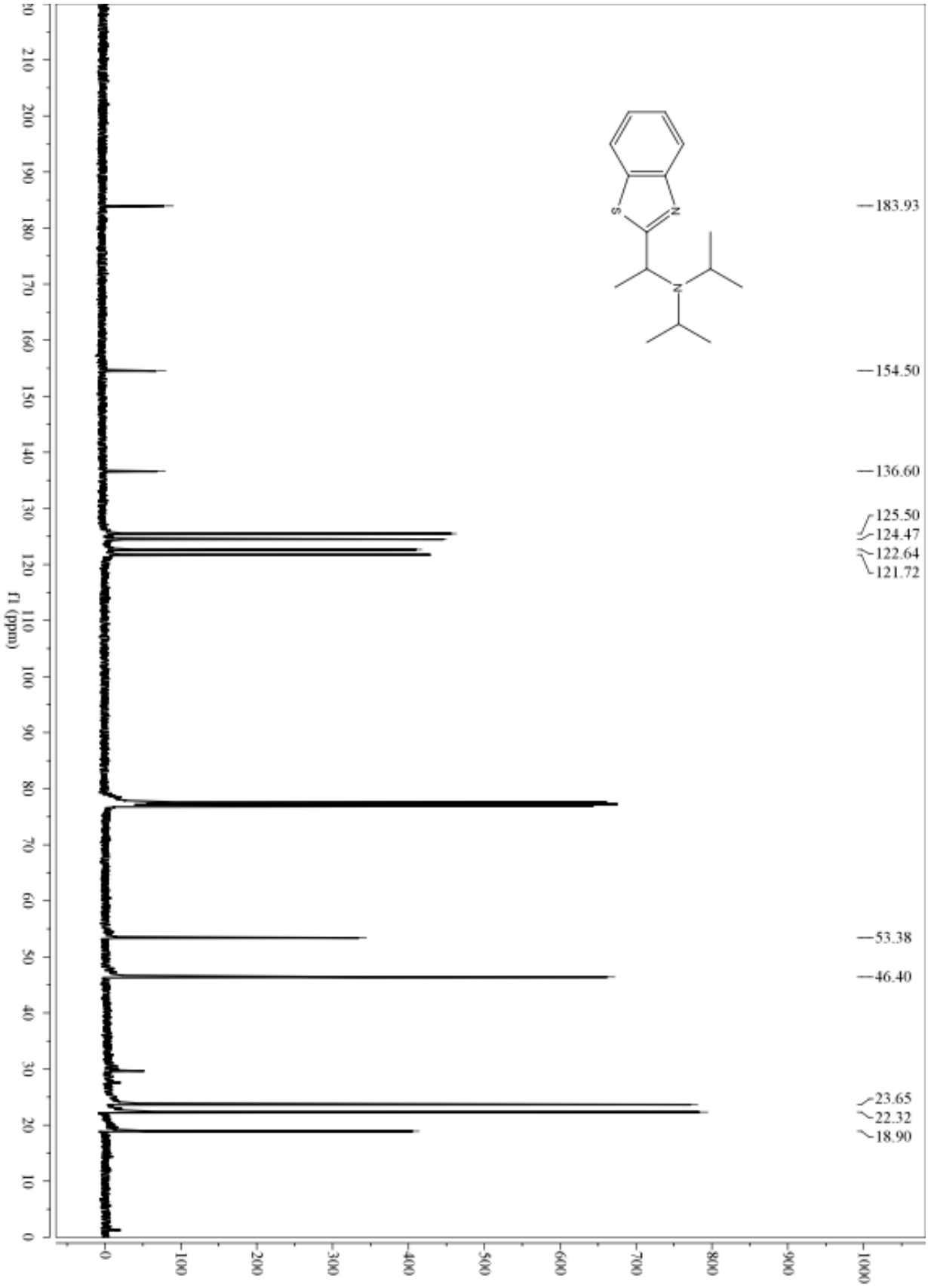
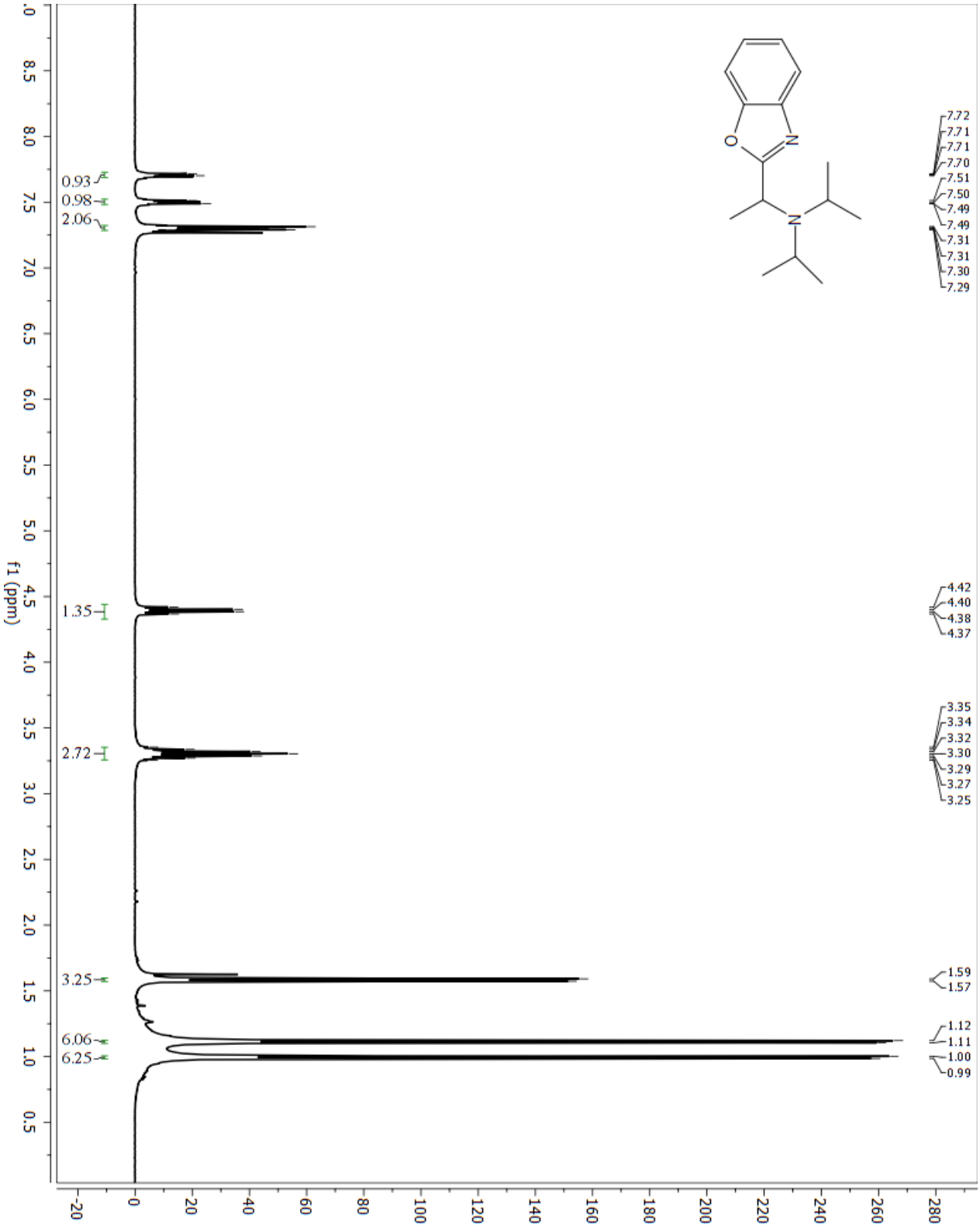
S-3a (*N*(benzo[*d*]thiazol-2-yl)ethyl)-*N*-isopropylpropan-2-amine)



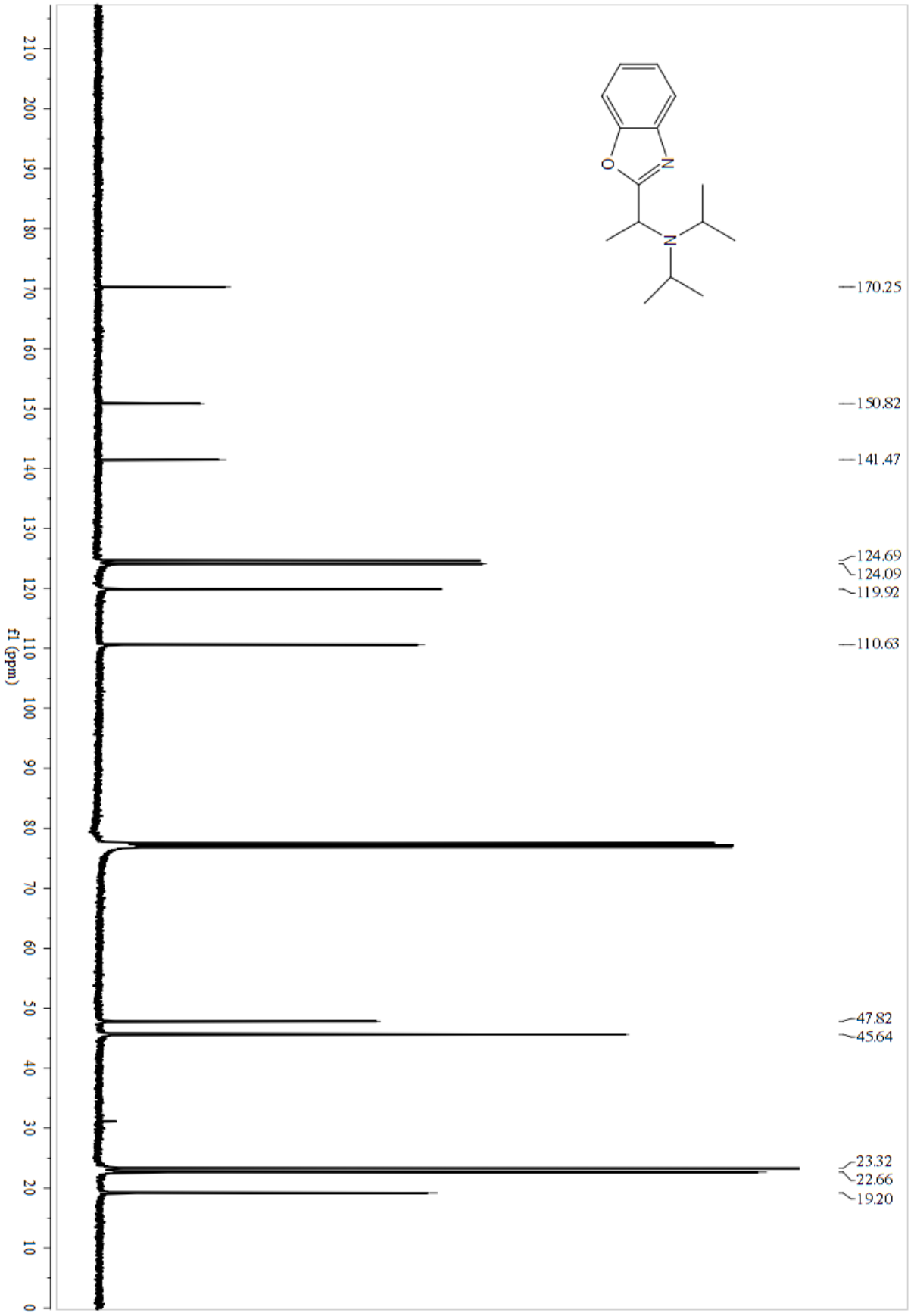
S-3a (*N*-(1-(benzo[*d*]thiazol-2-yl)ethyl)-*N*-isopropylpropan-2-amine)



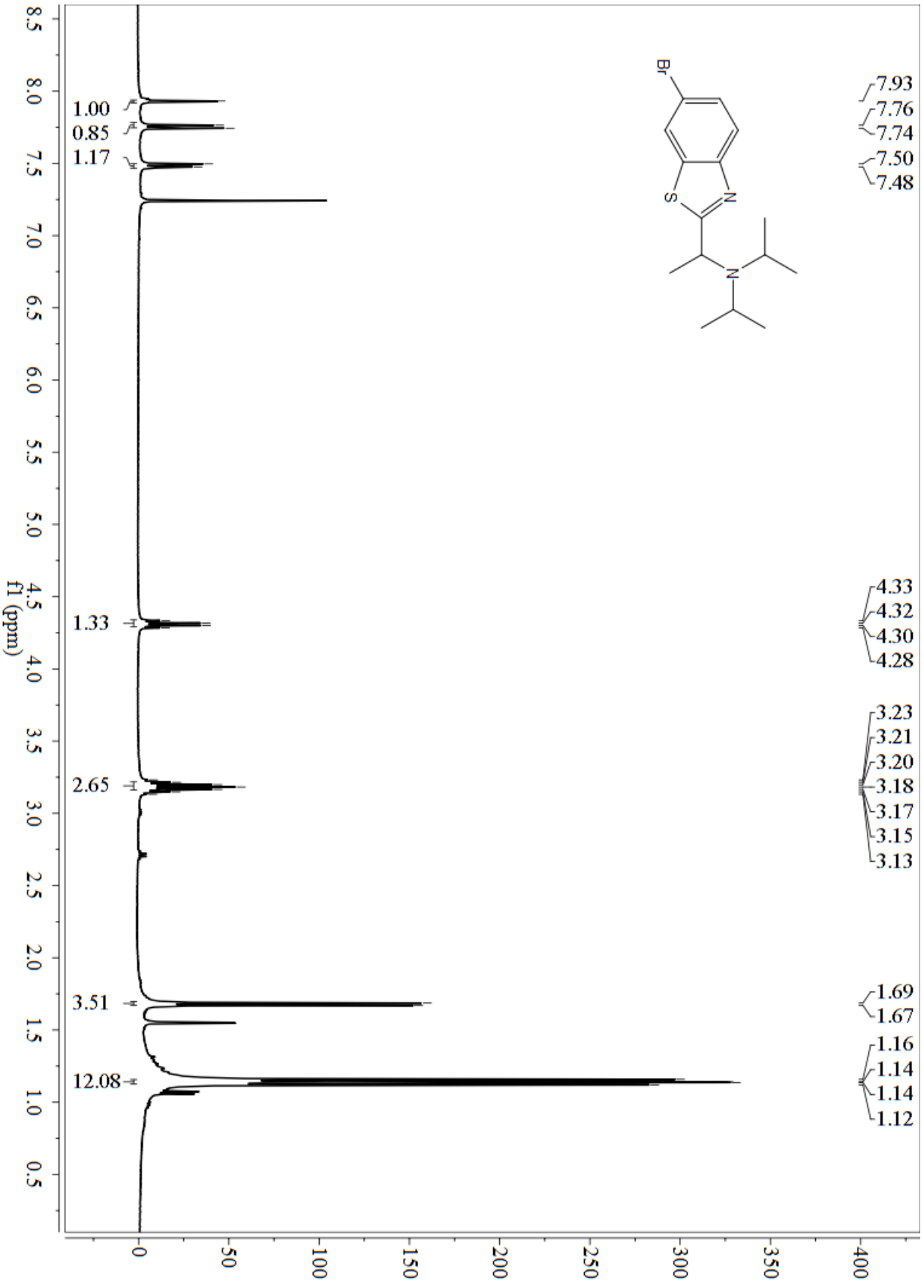
S-3b (1-(benzo[*d*]thiazol-2-yl)-*N*,*N*-dibutylbutan-1-amine



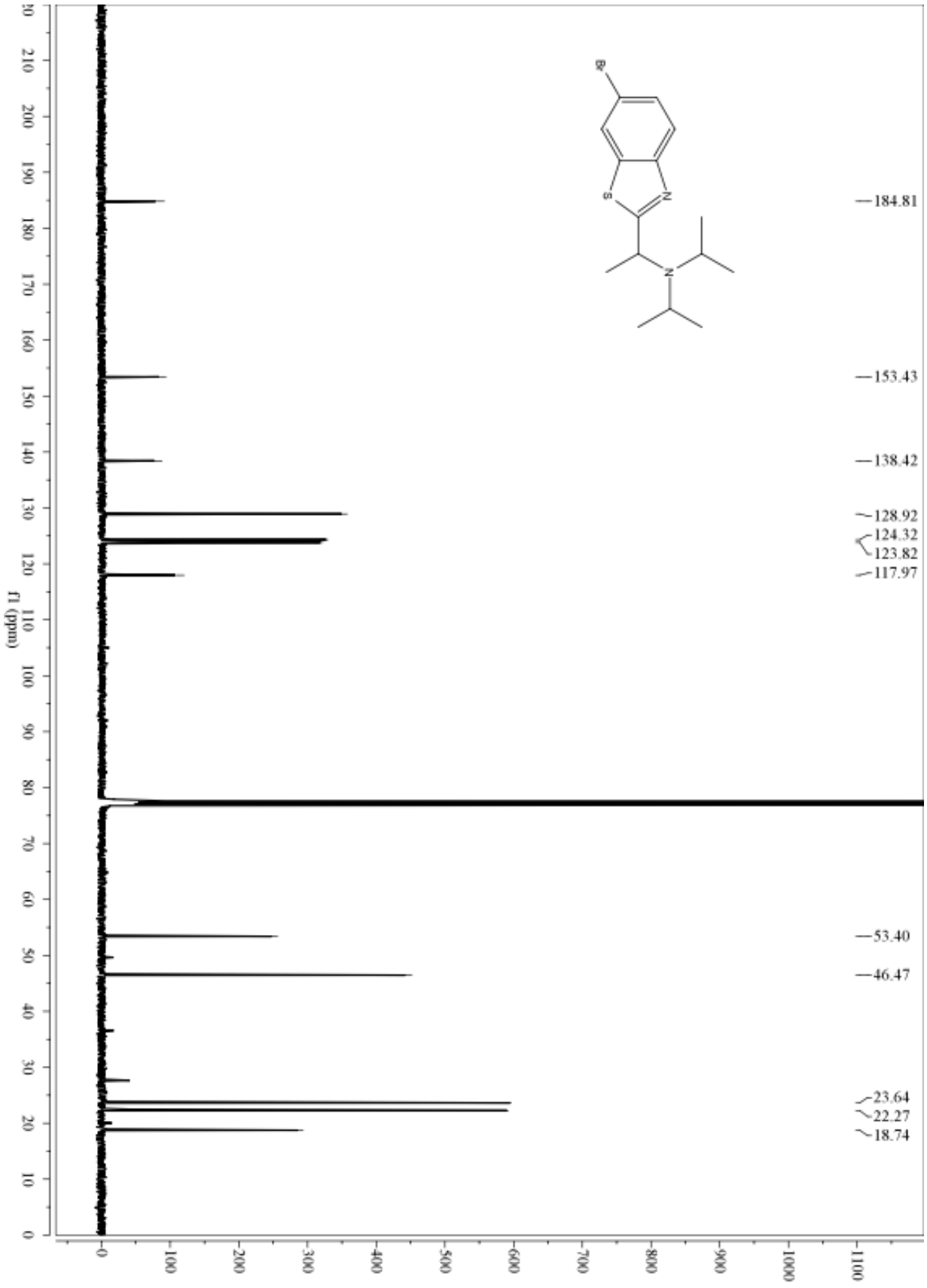
S-3b (1-(benzo[*d*]thiazol-2-yl)-*N*,*N*-dibutylbutan-1-amine)



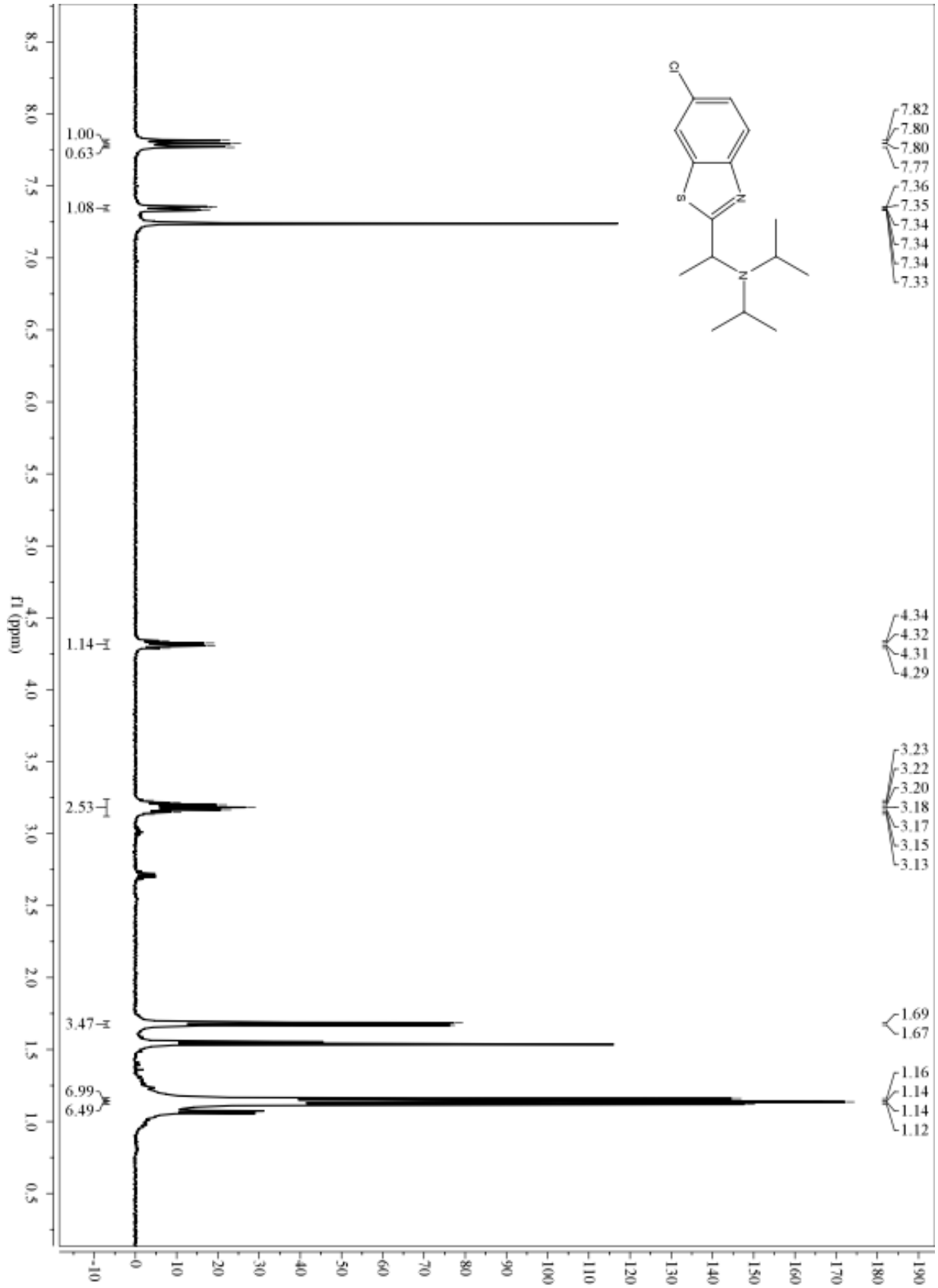
S-3c (*N*-(1-(6-bromobenzo[*d*]thiazol-2-yl)ethyl)-*N*-isopropylpropan-2-amine)



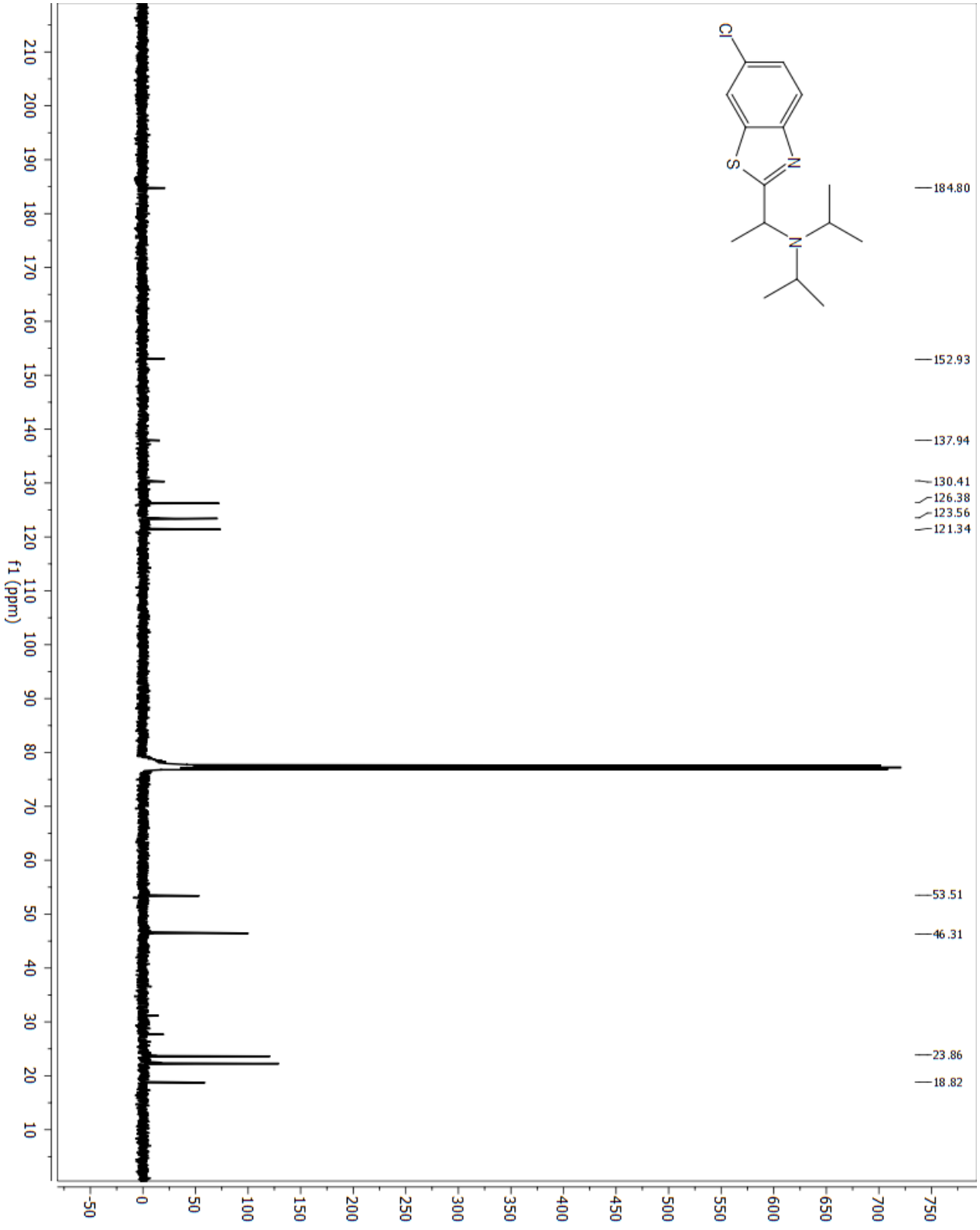
S-3c (*N*-(1-(6-bromobenzo[*d*]thiazol-2-yl)ethyl)-*N*-isopropylpropan-2-amine)



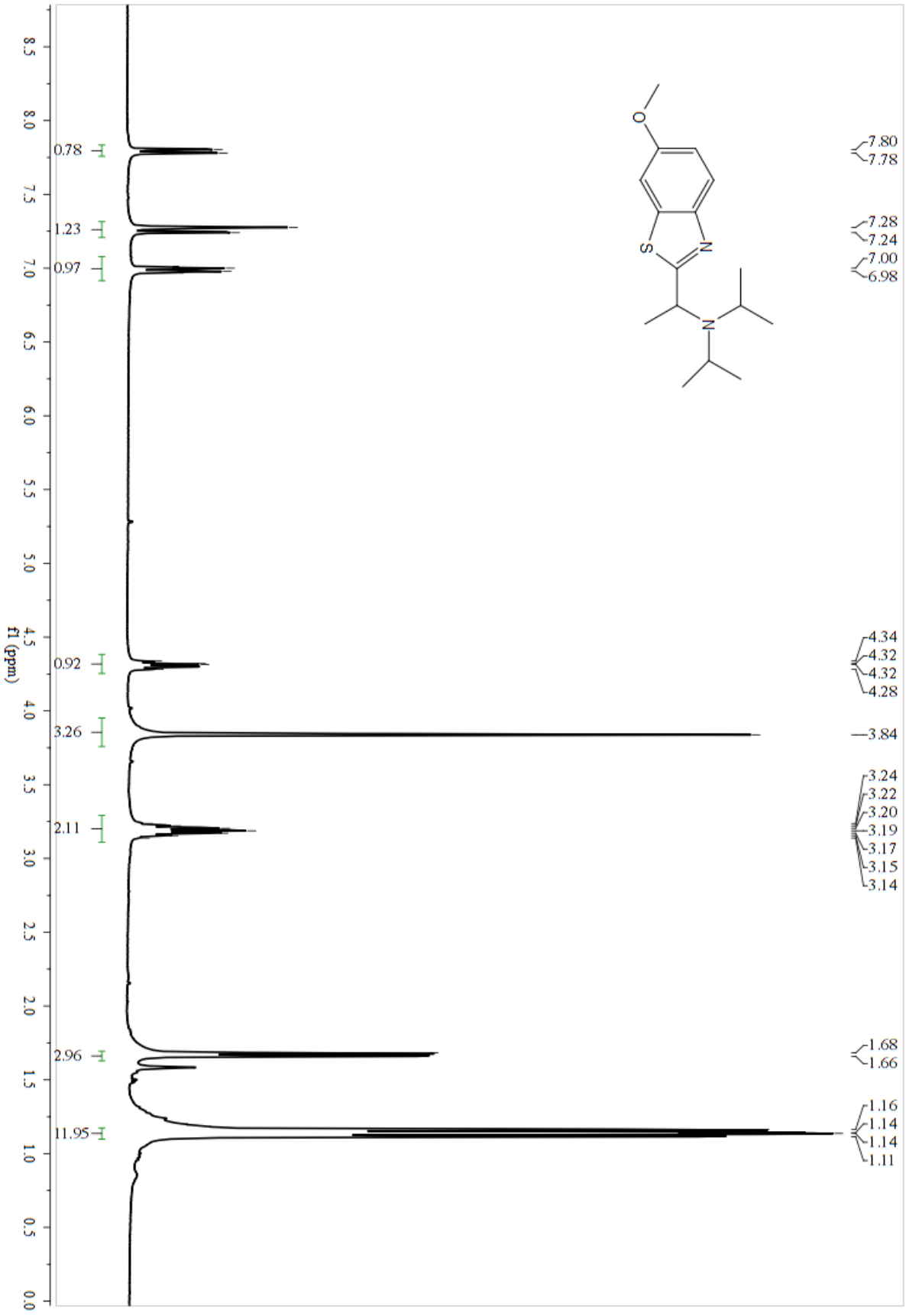
S-3d *(N*-(1-(6-chlorobenzo[*d*]thiazol-2-yl)ethyl)-*N*-isopropylpropan-2-amine)



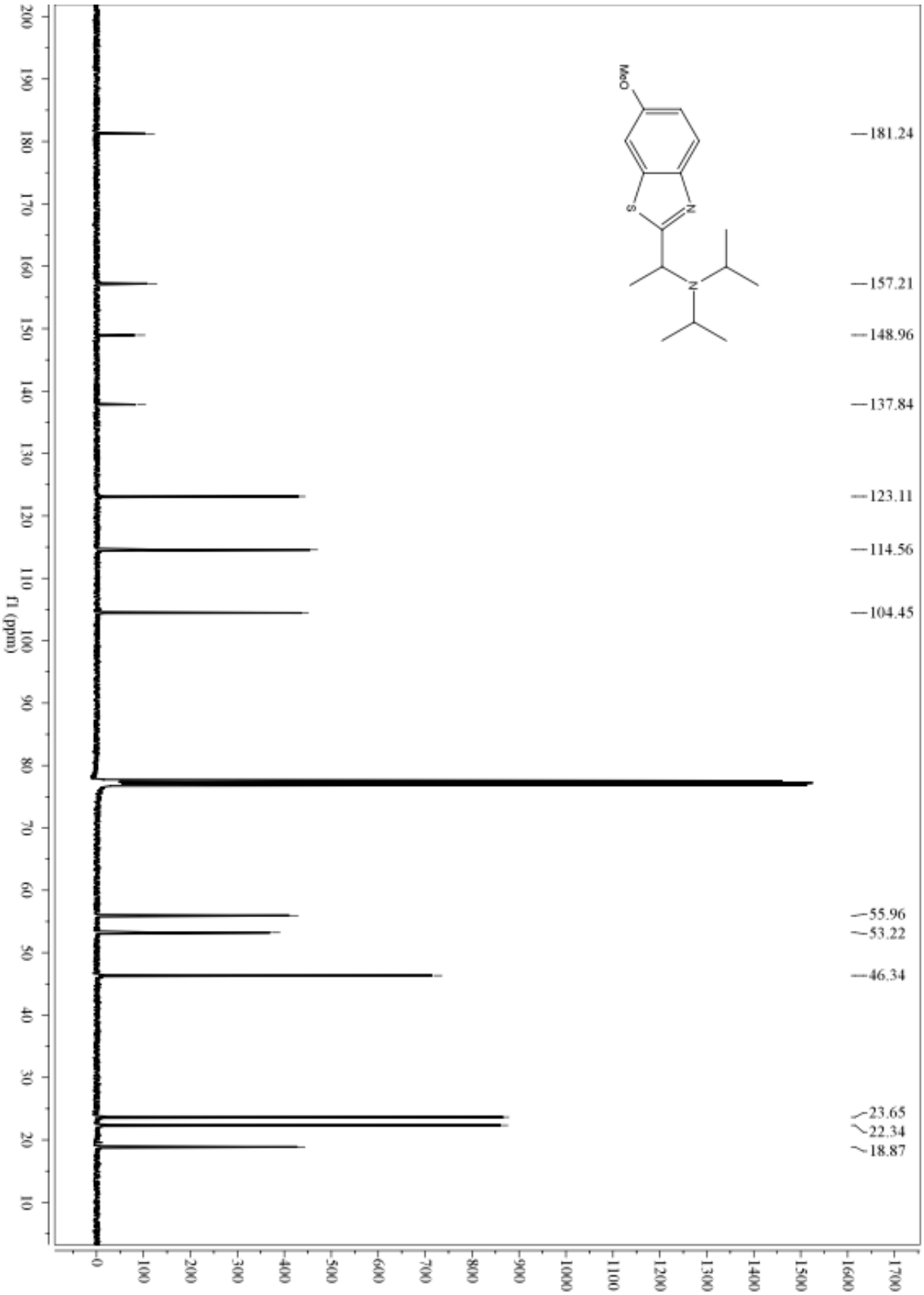
S-3d *(N*-(1-(6-chlorobenzo[*d*]thiazol-2-yl)ethyl)-*N*-isopropylpropan-2-amine)



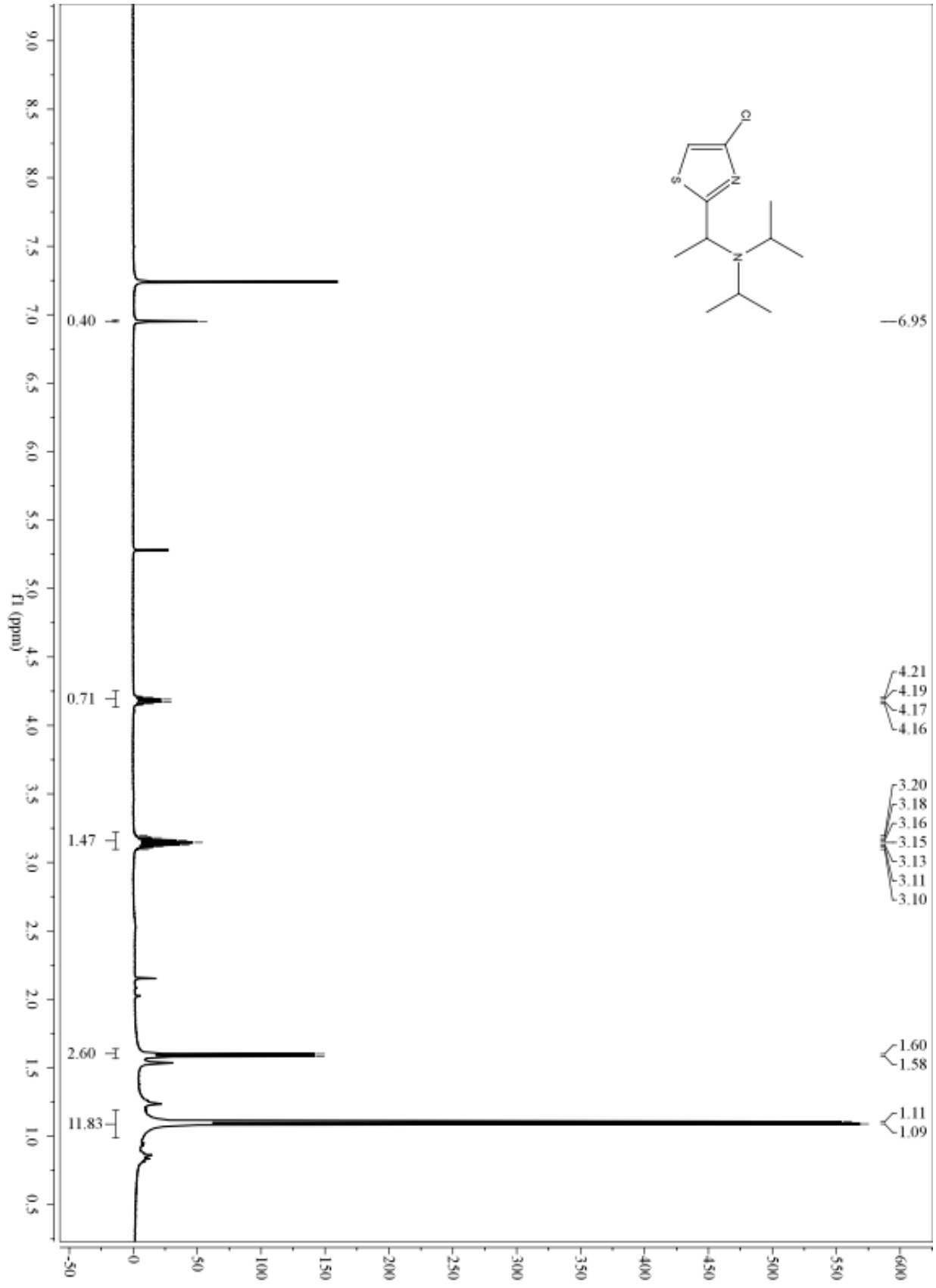
S-3e (*N*-isopropyl-*N*-(1-(6-methoxybenzo[*d*]thiazol-2-yl)ethyl)propan-2-amine)



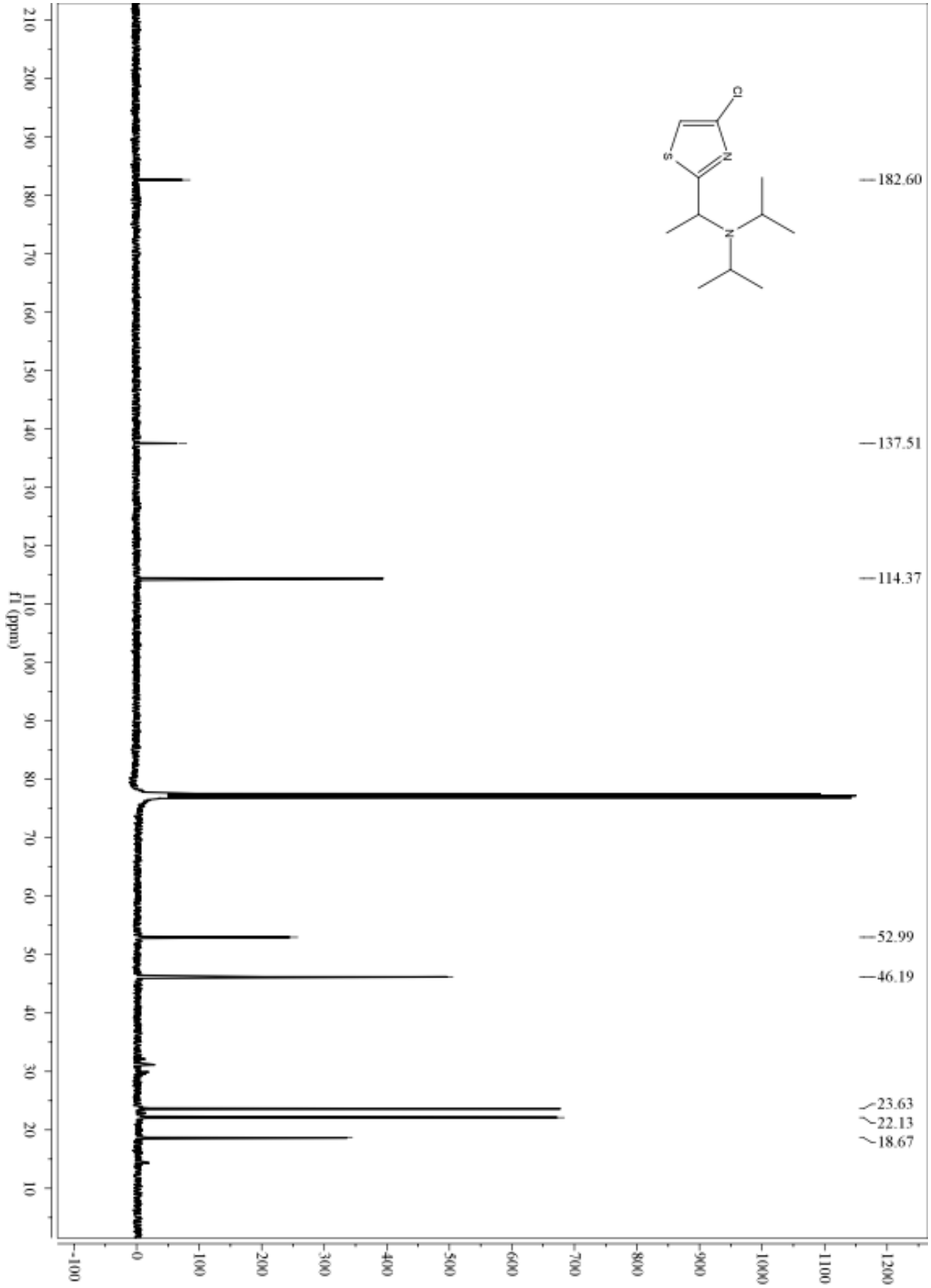
S-3e (*N*-isopropyl-*N*-(1-(6-methoxybenzo[*d*]thiazol-2-yl)ethyl)propan-2-amine



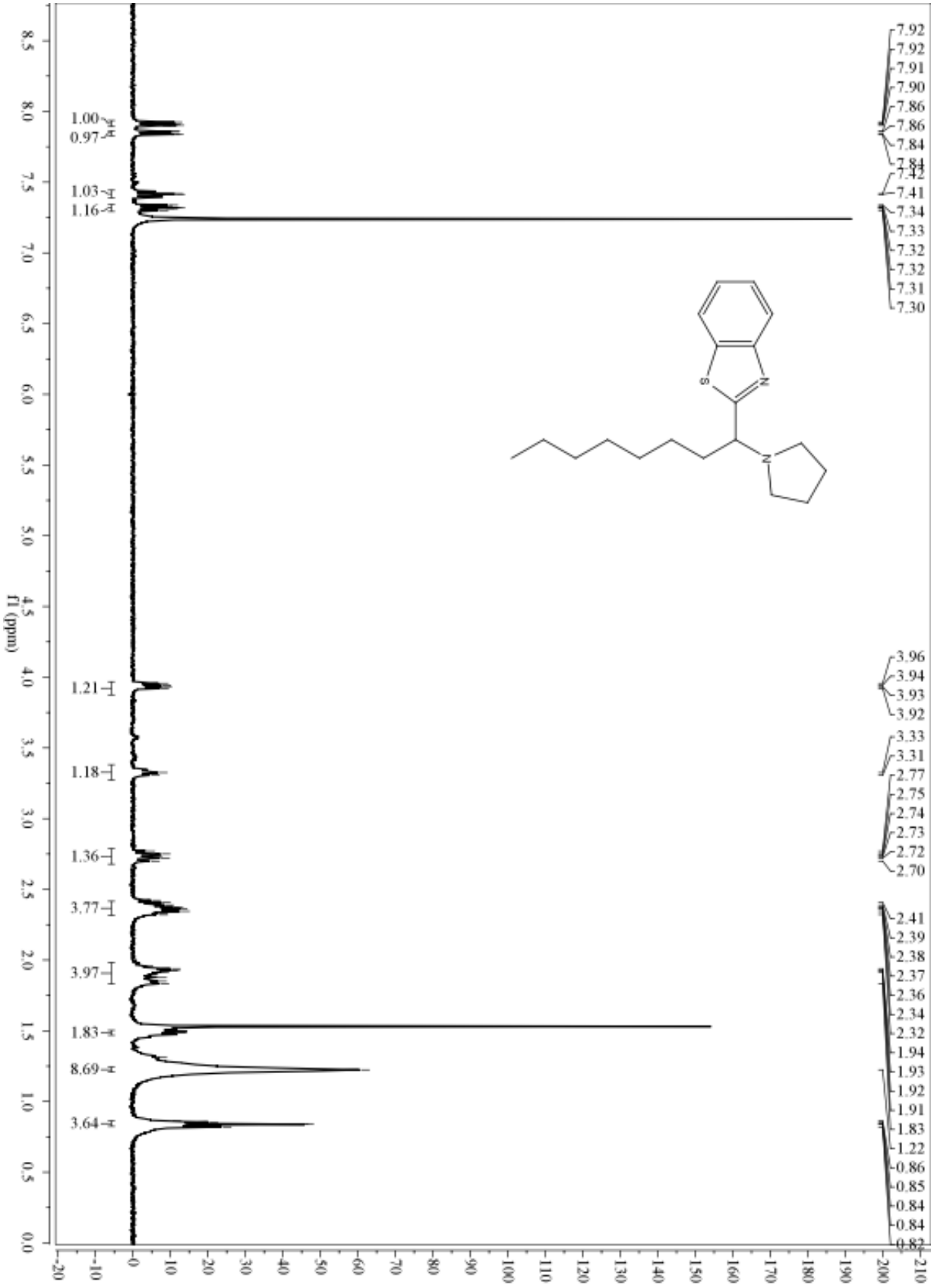
S-3f (*N*-(1-(5-chlorothiazol-2-yl)ethyl)-*N*-isopropylpropan-2-amine)



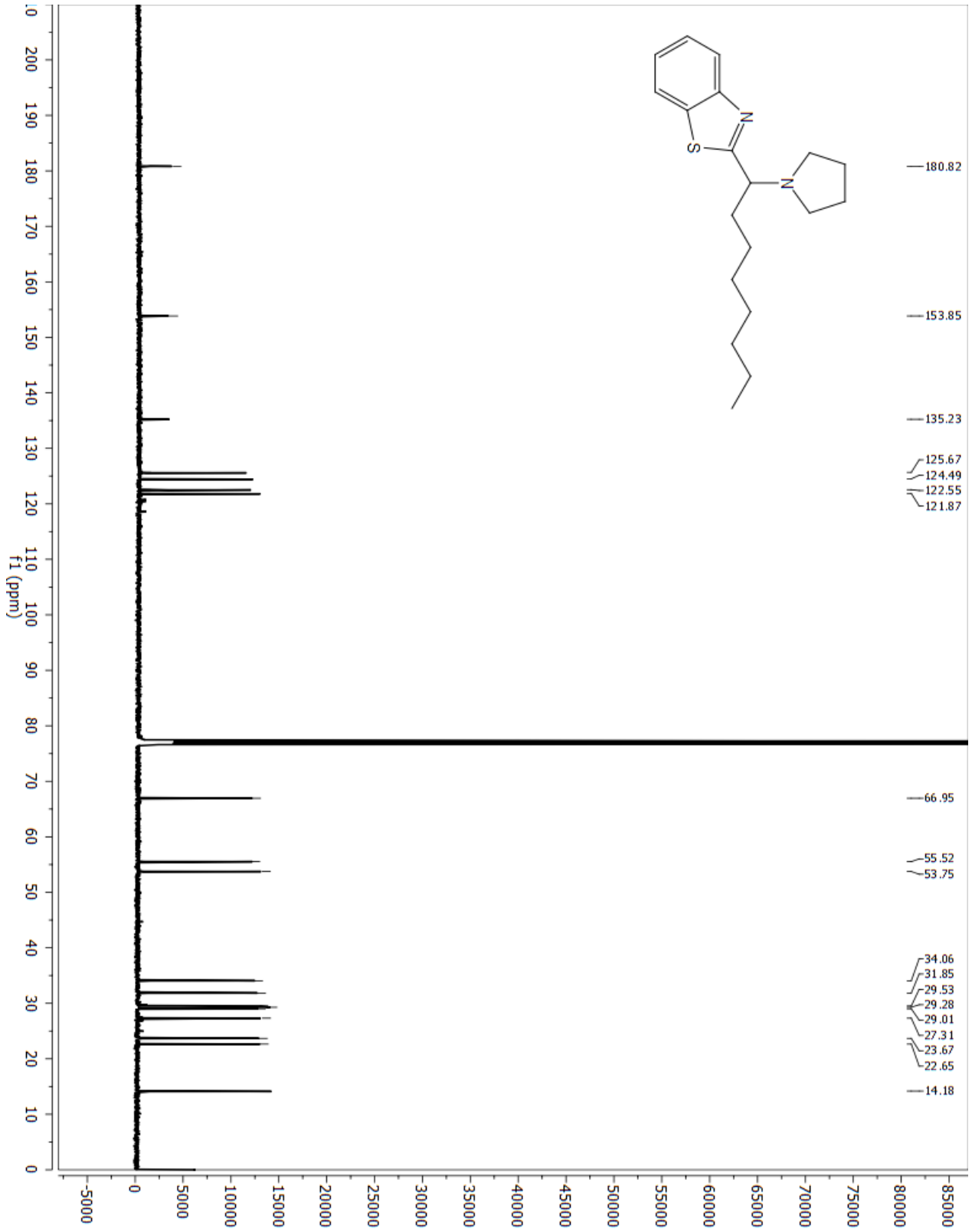
S-3f (*N*-(1-(5-chlorothiazol-2-yl)ethyl)-*N*-isopropylpropan-2-amine)



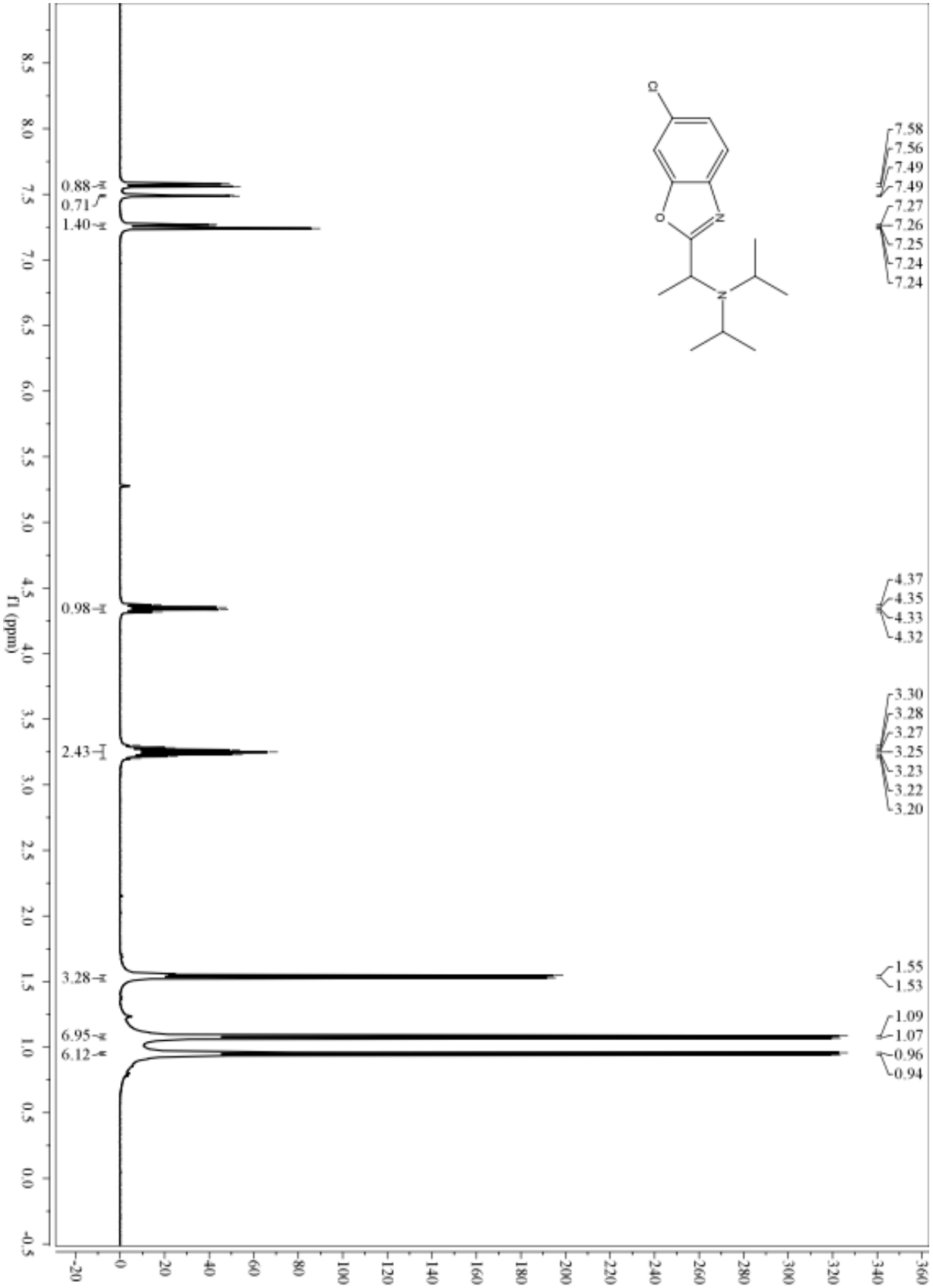
S-3g (2-(1-(pyrrolidin-1-yl)octyl)benzo[*d*]thiazole)



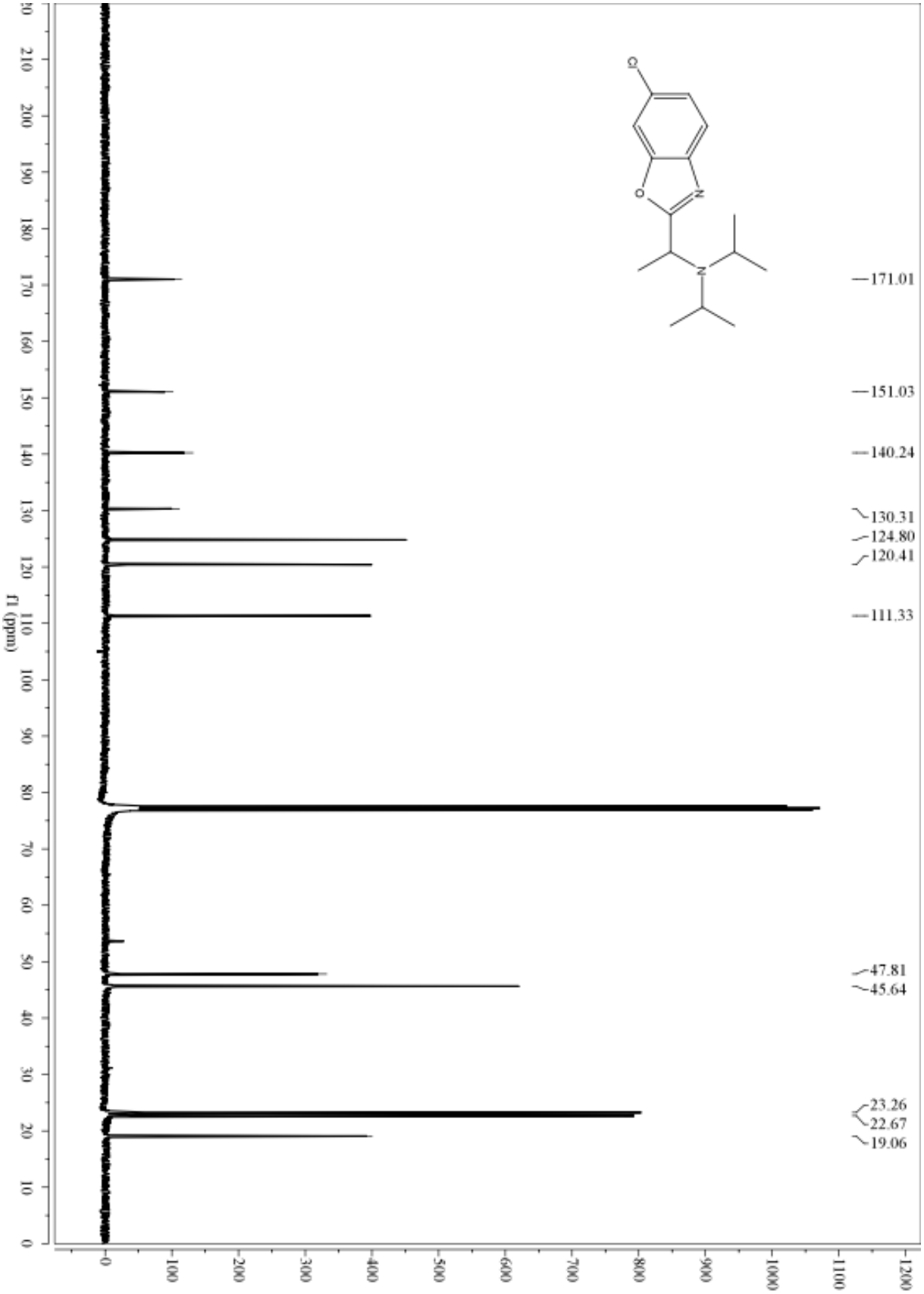
S-3g (2-(1-(pyrrolidin-1-yl)octyl)benzo[*d*]thiazole)



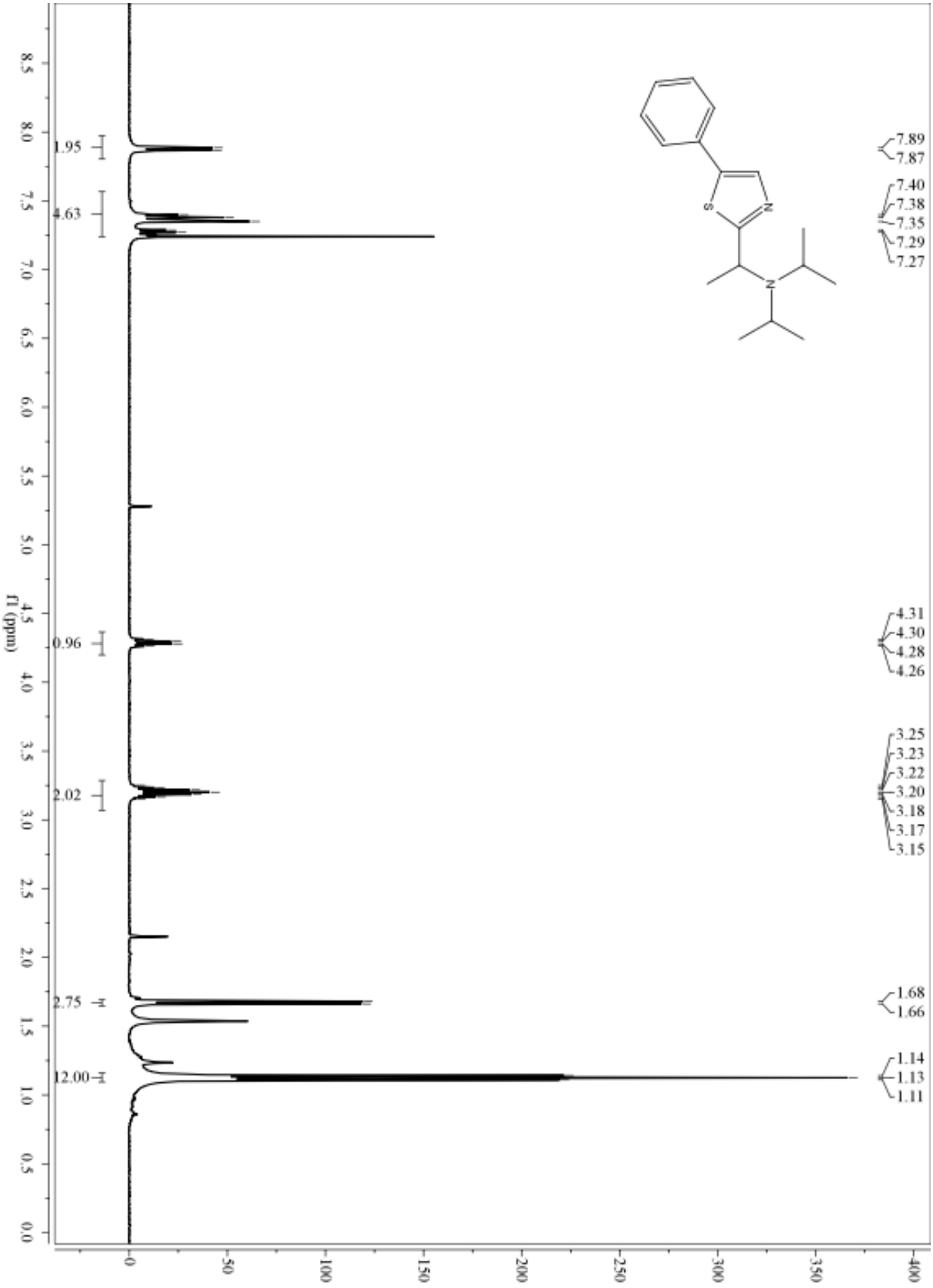
S-3h (*N*-(1-(6-chlorobenzo[*d*]oxazol-2-yl)ethyl)-*N*-isopropylpropan-2-amine)



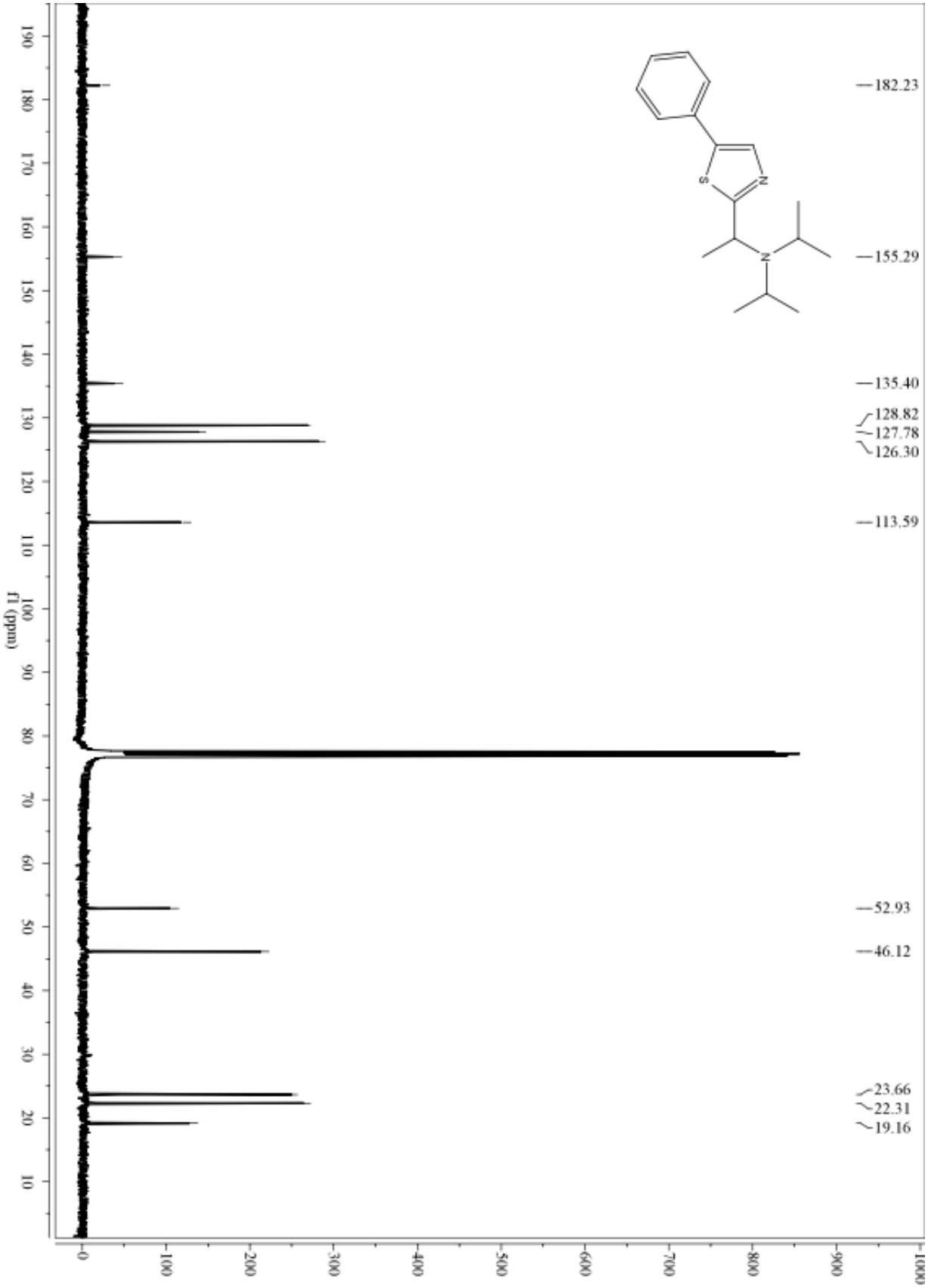
S-3h (*N*-(1-(6-chlorobenzo[*d*]oxazol-2-yl)ethyl)-*N*-isopropylpropan-2-amine)



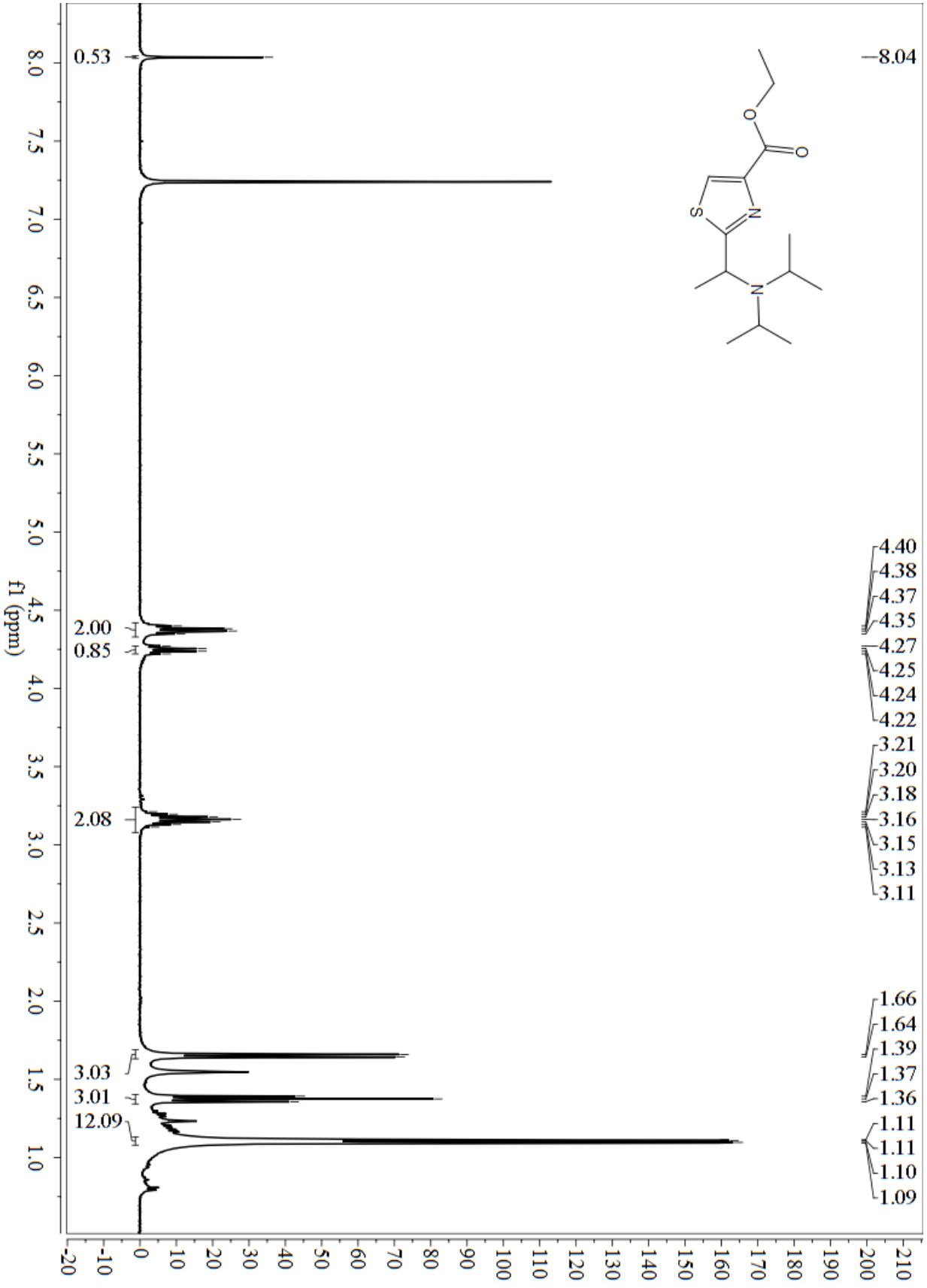
S-3i (*N*-isopropyl-*N*-(1-(5-phenylthiazol-2-yl) ethyl) propan-2-amine)



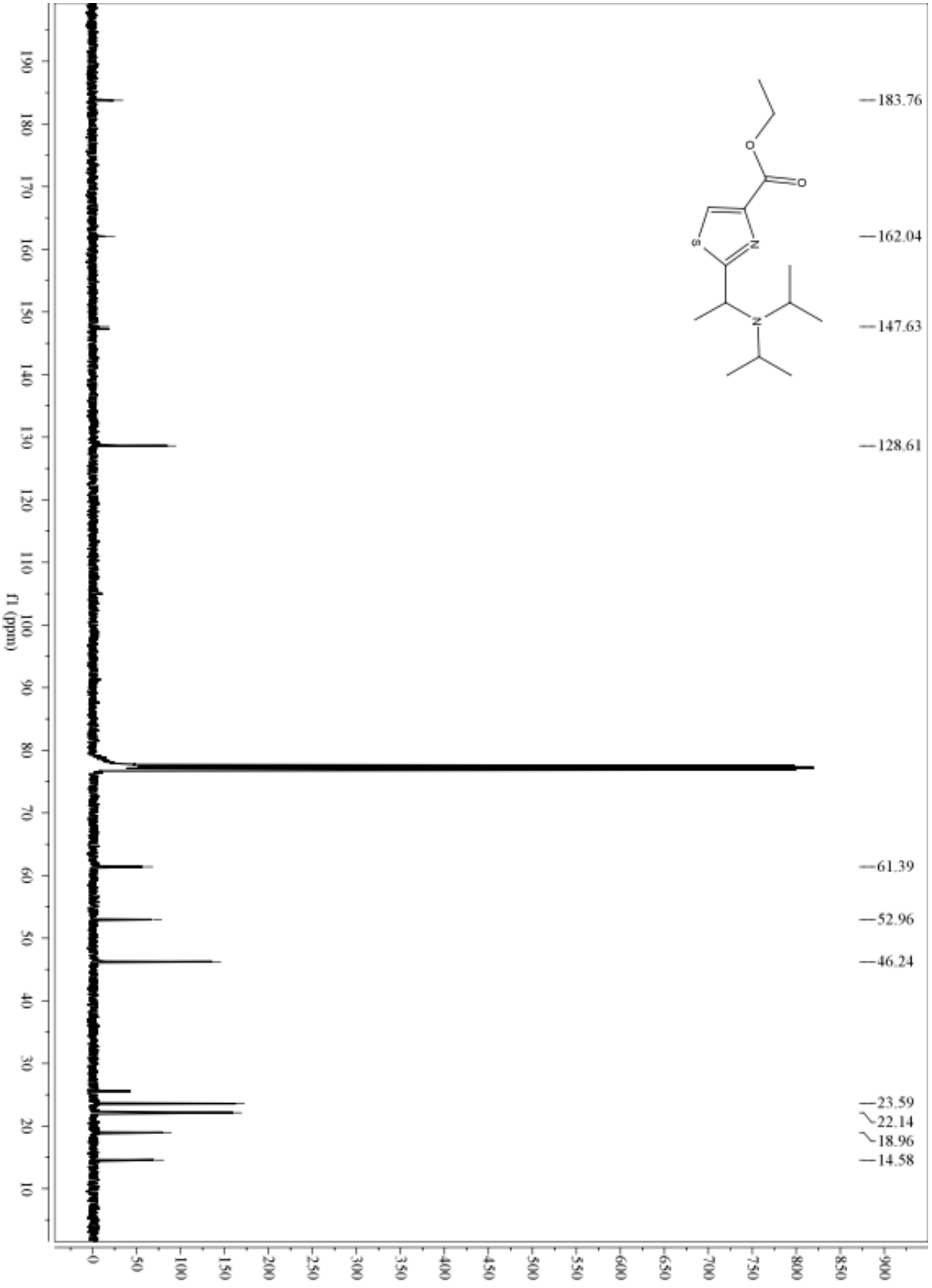
S-3i (*N*-isopropyl-*N*-(1-(5-phenylthiazol-2-yl) ethyl)propan-2-amine)



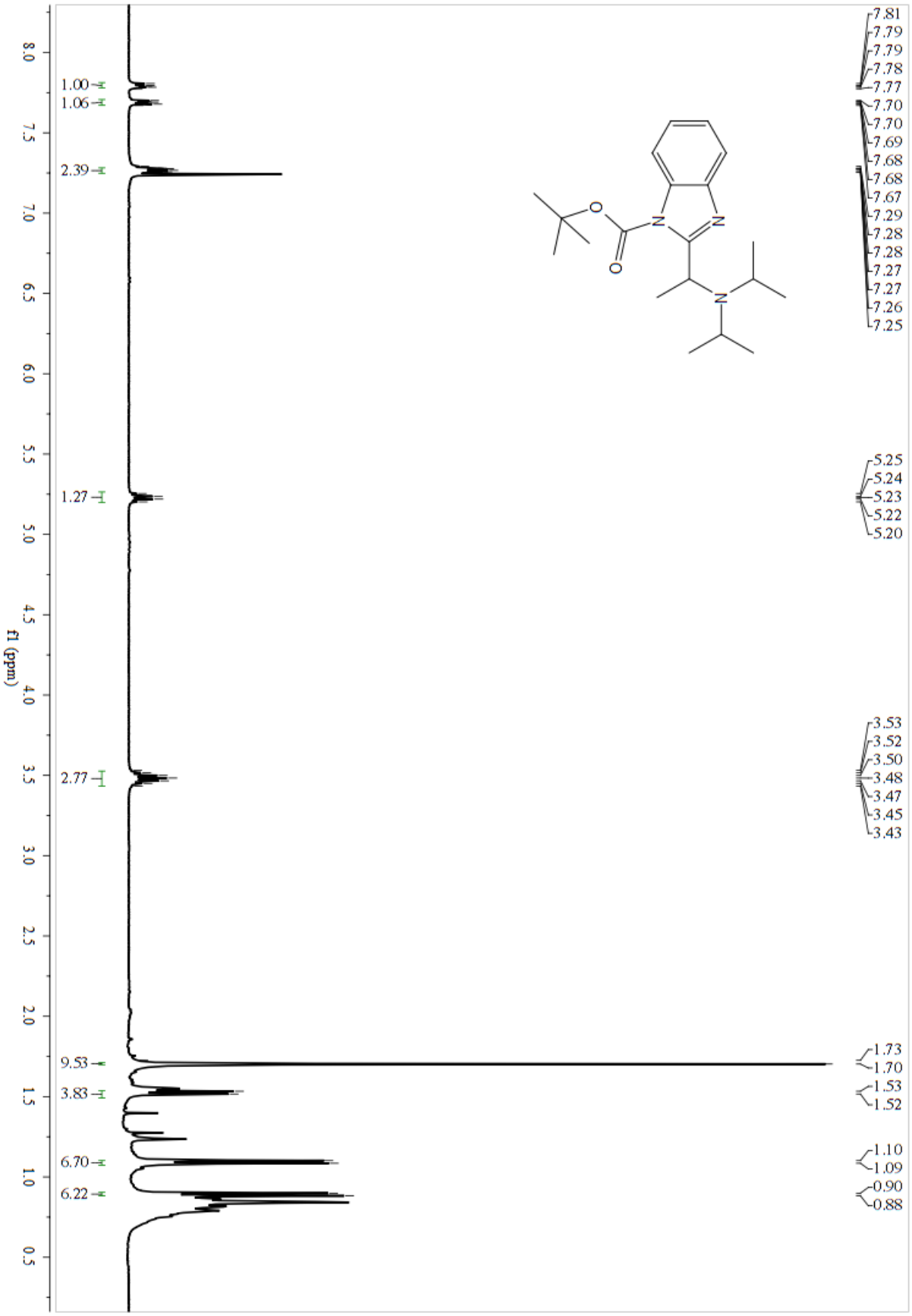
S-3j ethyl 2-(1-(diisopropylamino)ethyl)thiazole-4-carboxylate



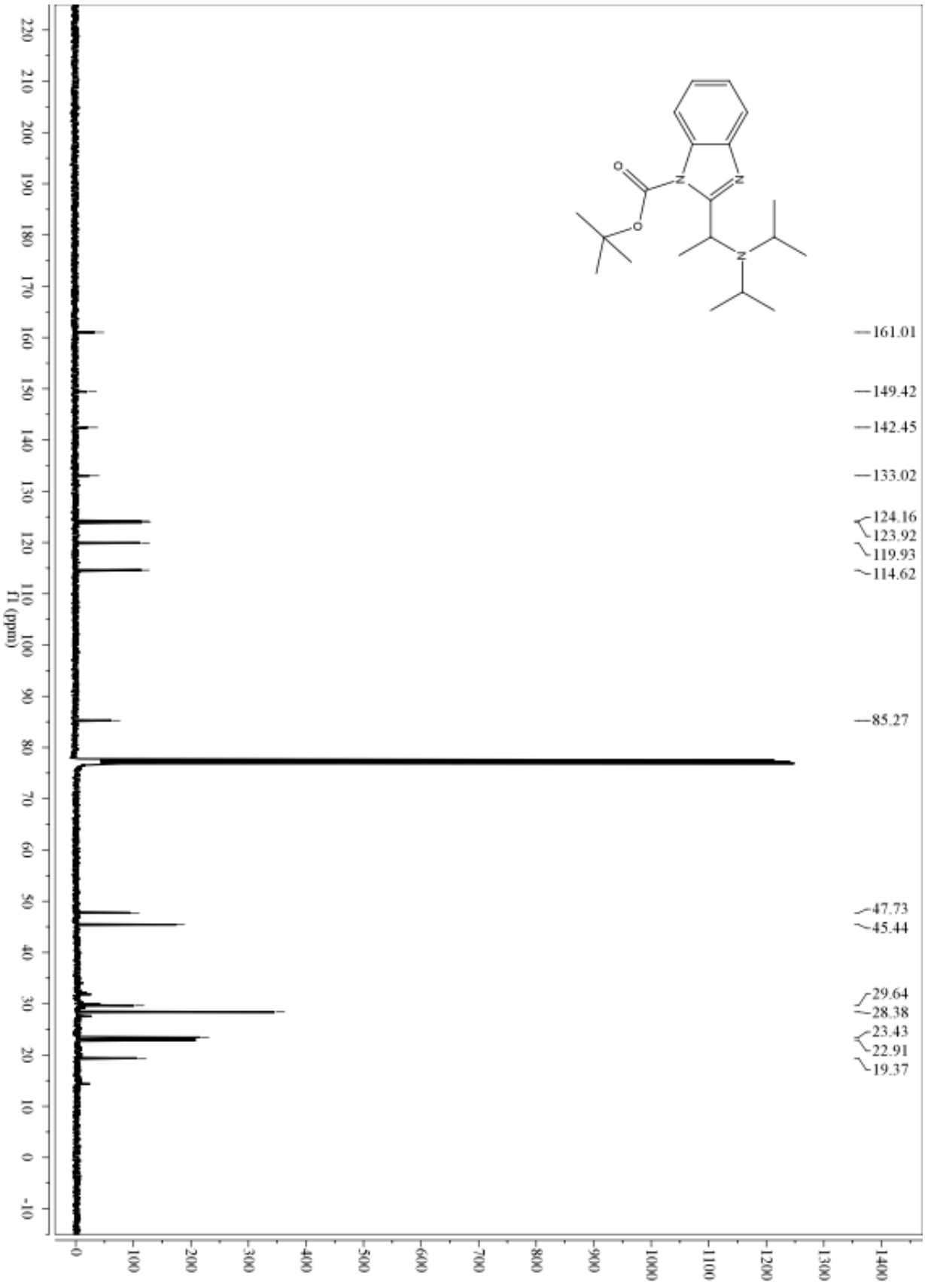
S-3j ethyl 2-(1-(diisopropylamino)ethyl)thiazole-4-carboxylate



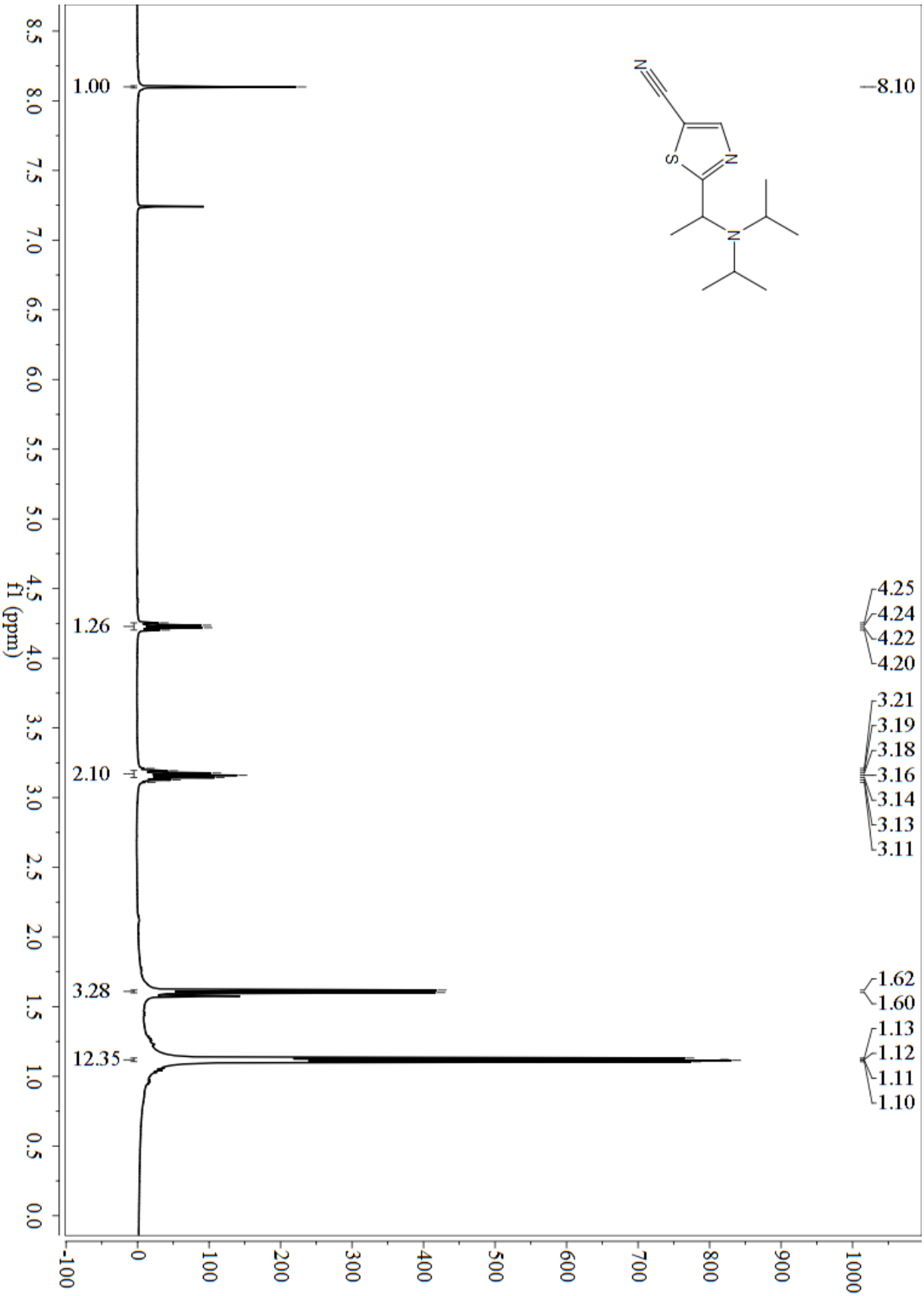
S-3k (*tert*-butyl 2-(1-(diisopropylamino) ethyl)-1*H*-benzo[*d*]imidazole-1-carboxylate)



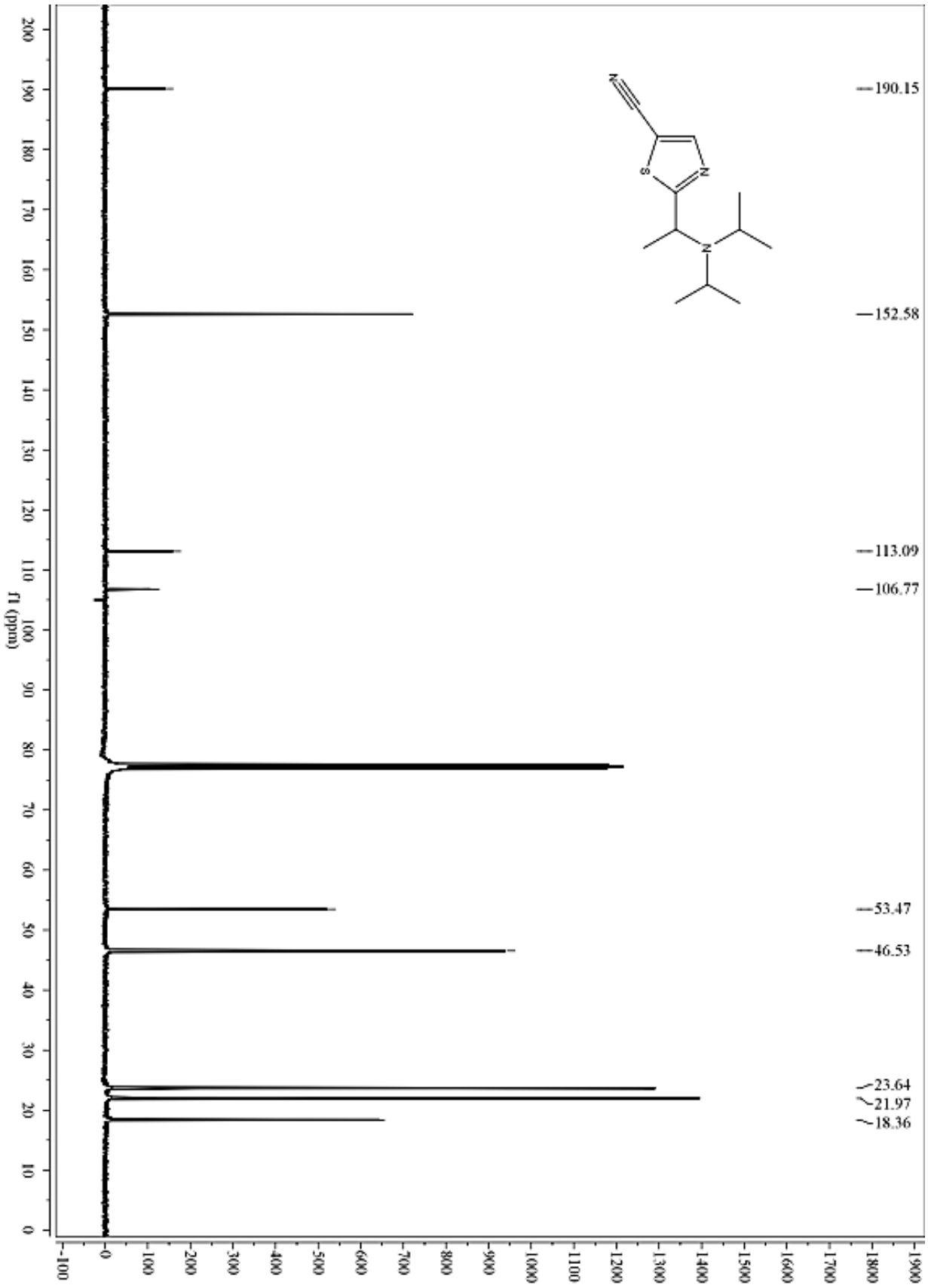
S-3k (*tert*-butyl 2-(1-(diisopropylamino)ethyl)-1*H*-benzo[*d*]imidazole-1-carboxylate)



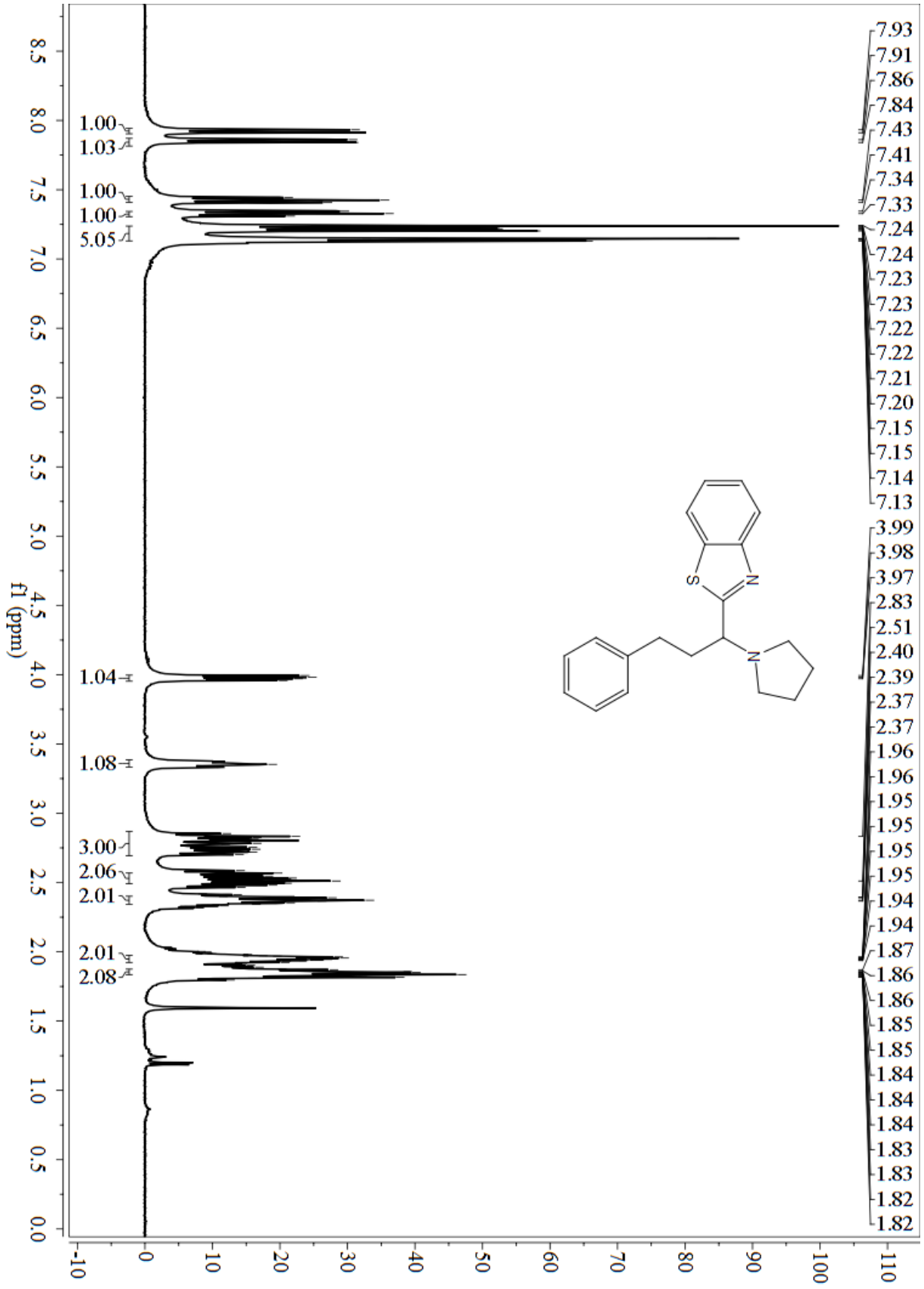
S-3l (2-(1-(diisopropylamino) ethyl) thiazole-5-carbonitrile)



S-3l (2-(1-(diisopropylamino) ethyl) thiazole-5-carbonitrile)

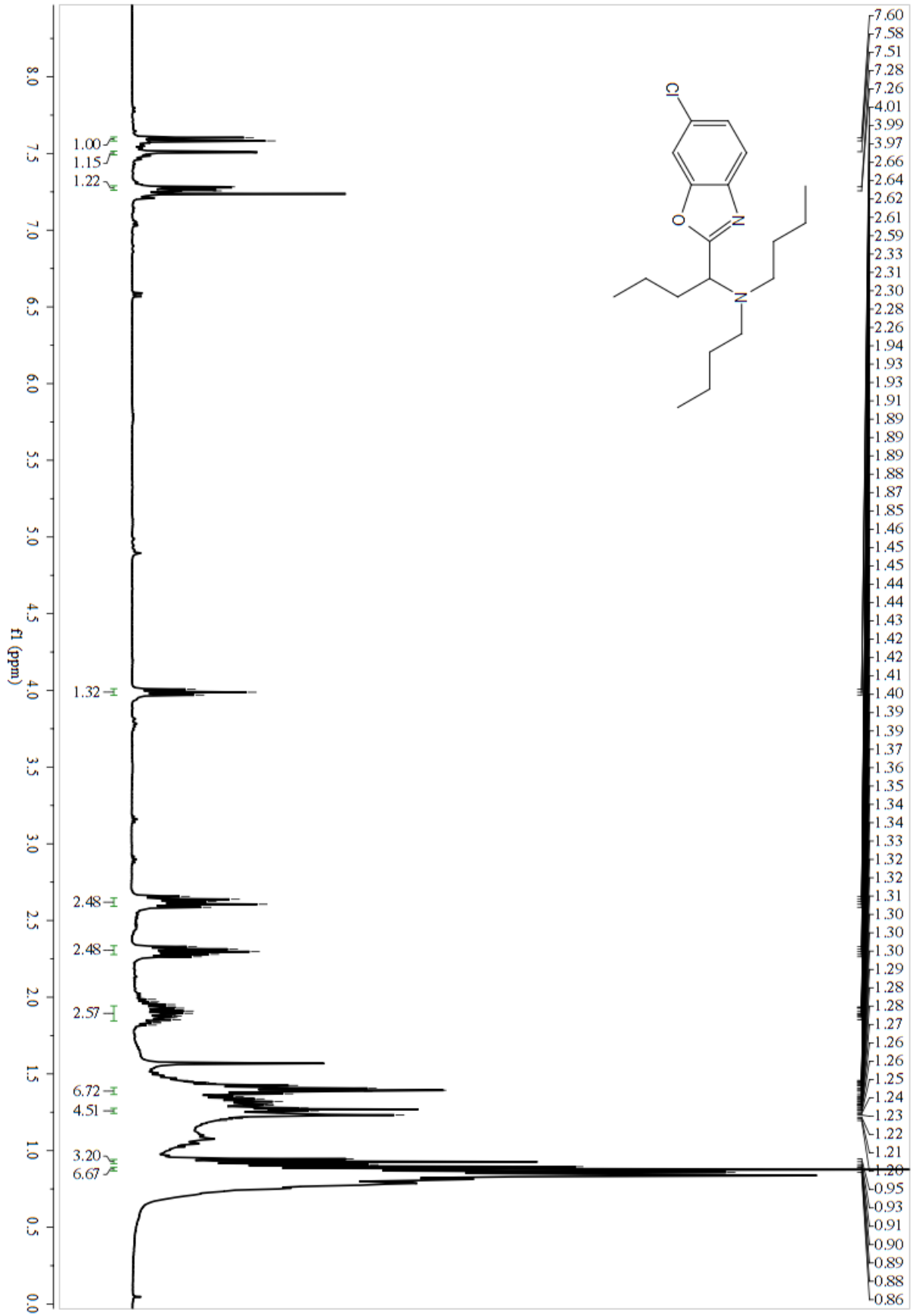


S-3m_(2-(3-phenyl-1-(pyrrolidin-1-yl)propyl)benzo[*d*]thiazole

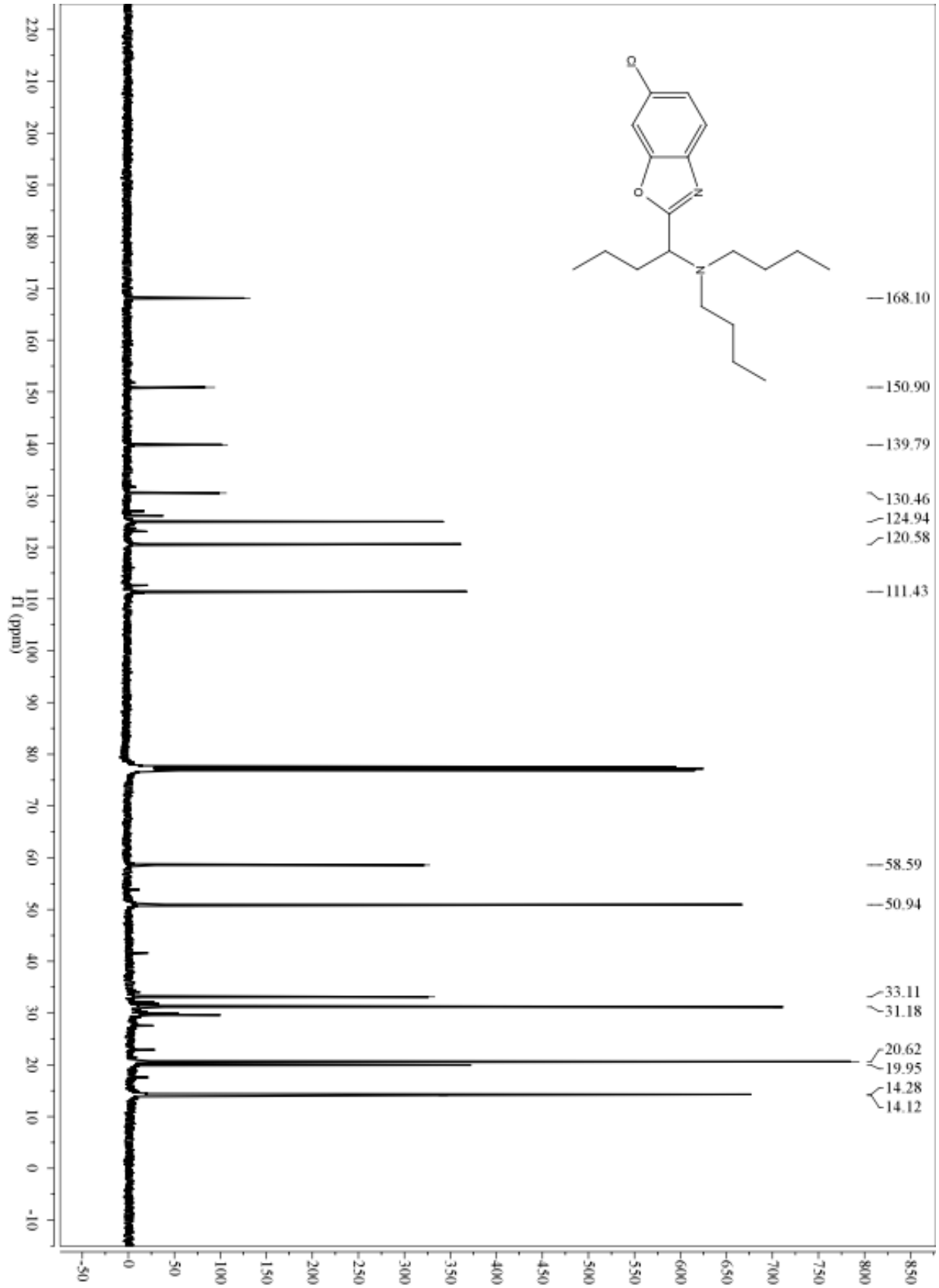


S-3m (2-(3-phenyl-1-(pyrrolidin-1-yl)propyl)benzo[*d*]thiazole

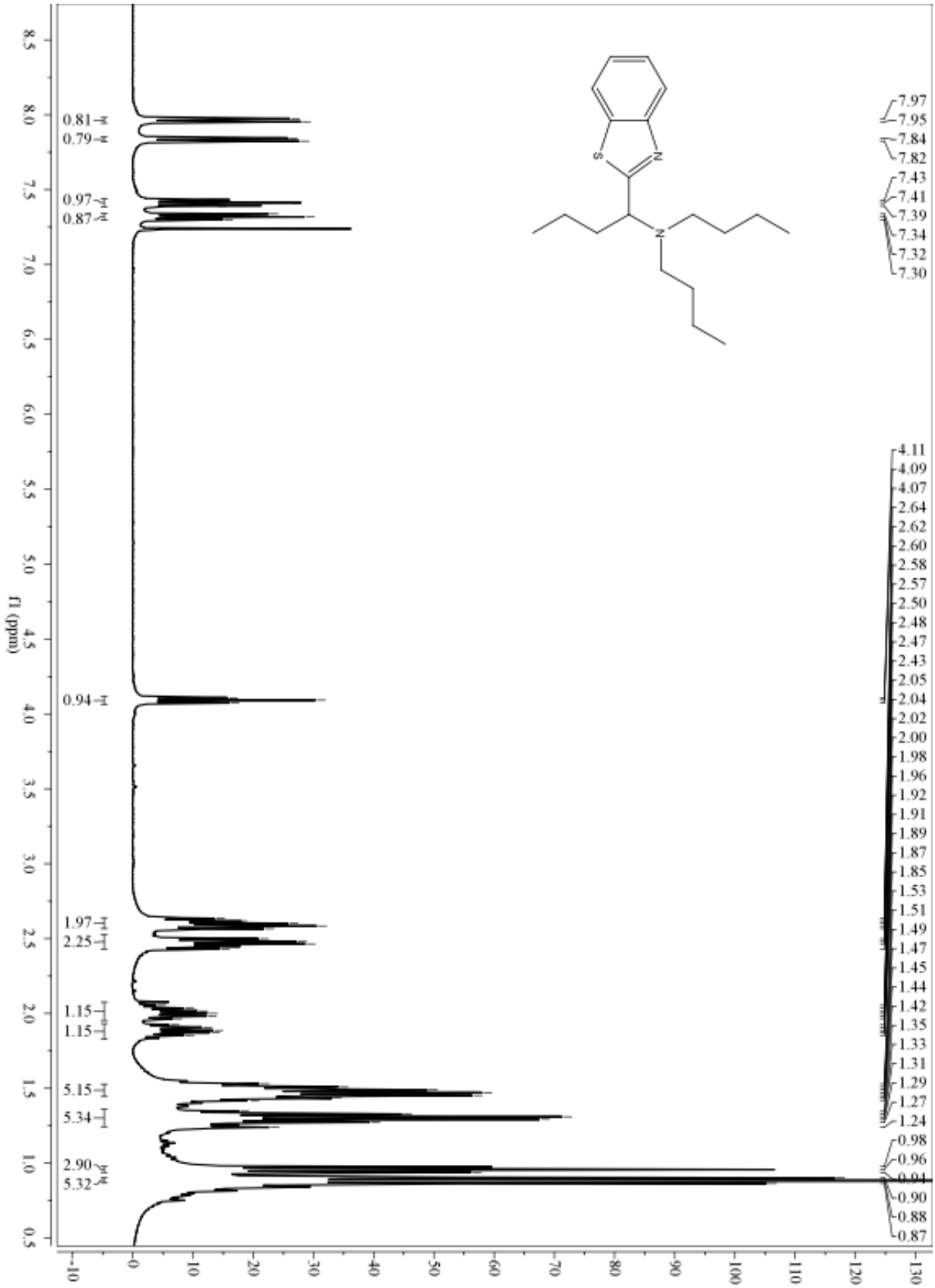
S-3n (*N*,*N*-dibutyl-1-(6-chlorobenzo[*d*]oxazol-2-yl)butan-1-amine)



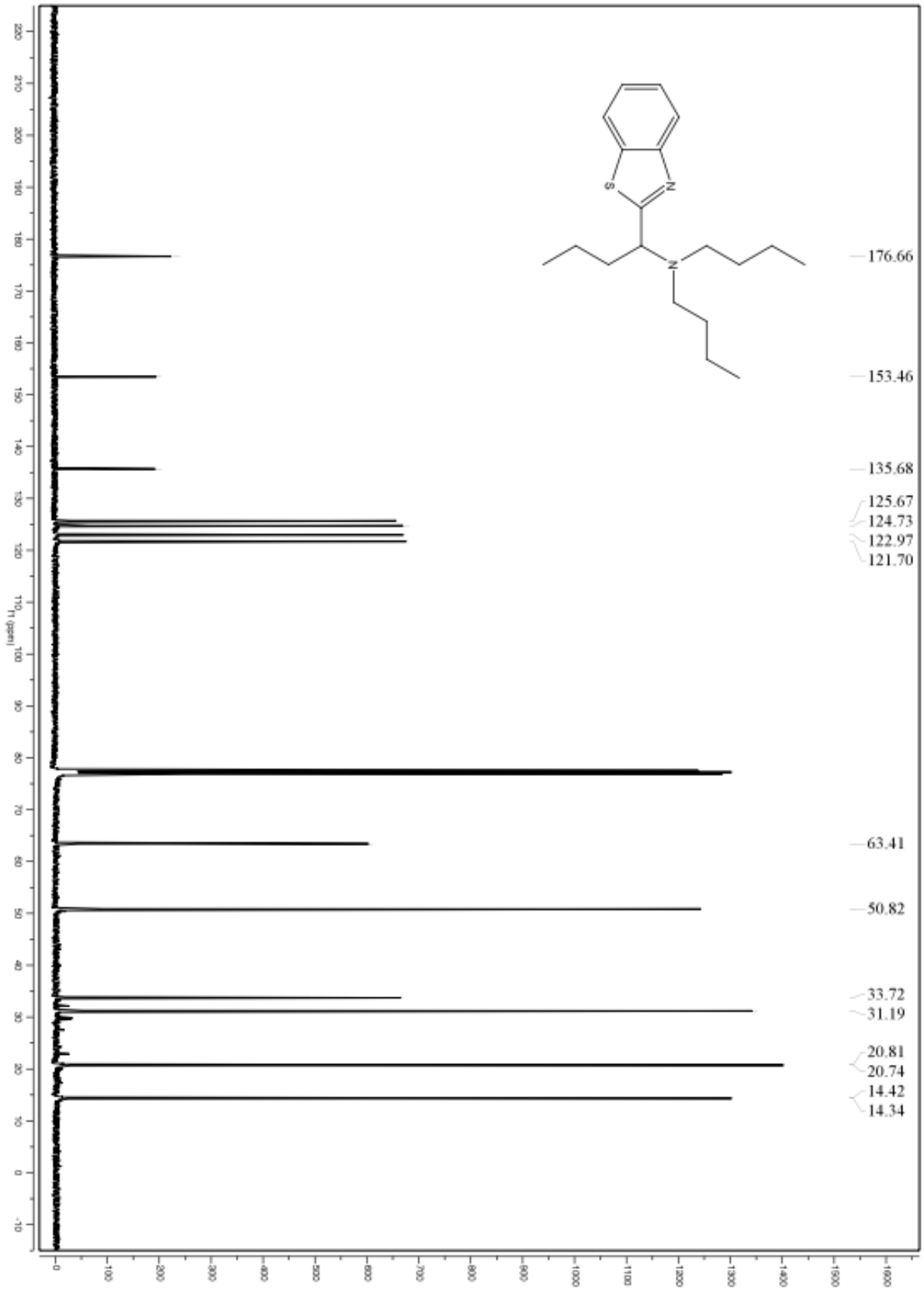
S-3n (*N*,*N*-dibutyl-1-(6-chlorobenzo[*d*]oxazol-2-yl)butan-1-amine



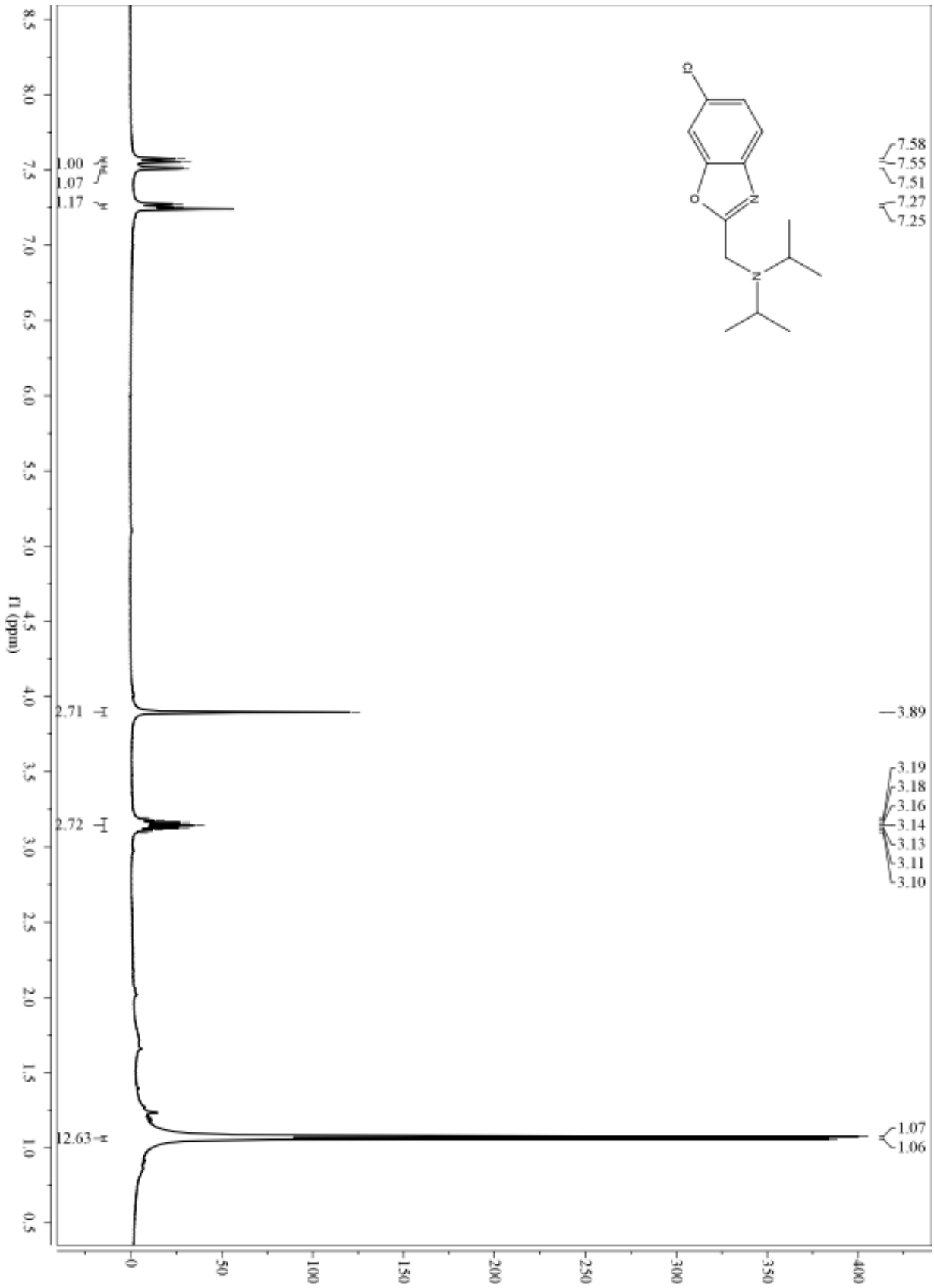
S-3o (1-(benzo[*d*]thiazol-2-yl)-*N*,*N*-dibutylbutan-1-amine)



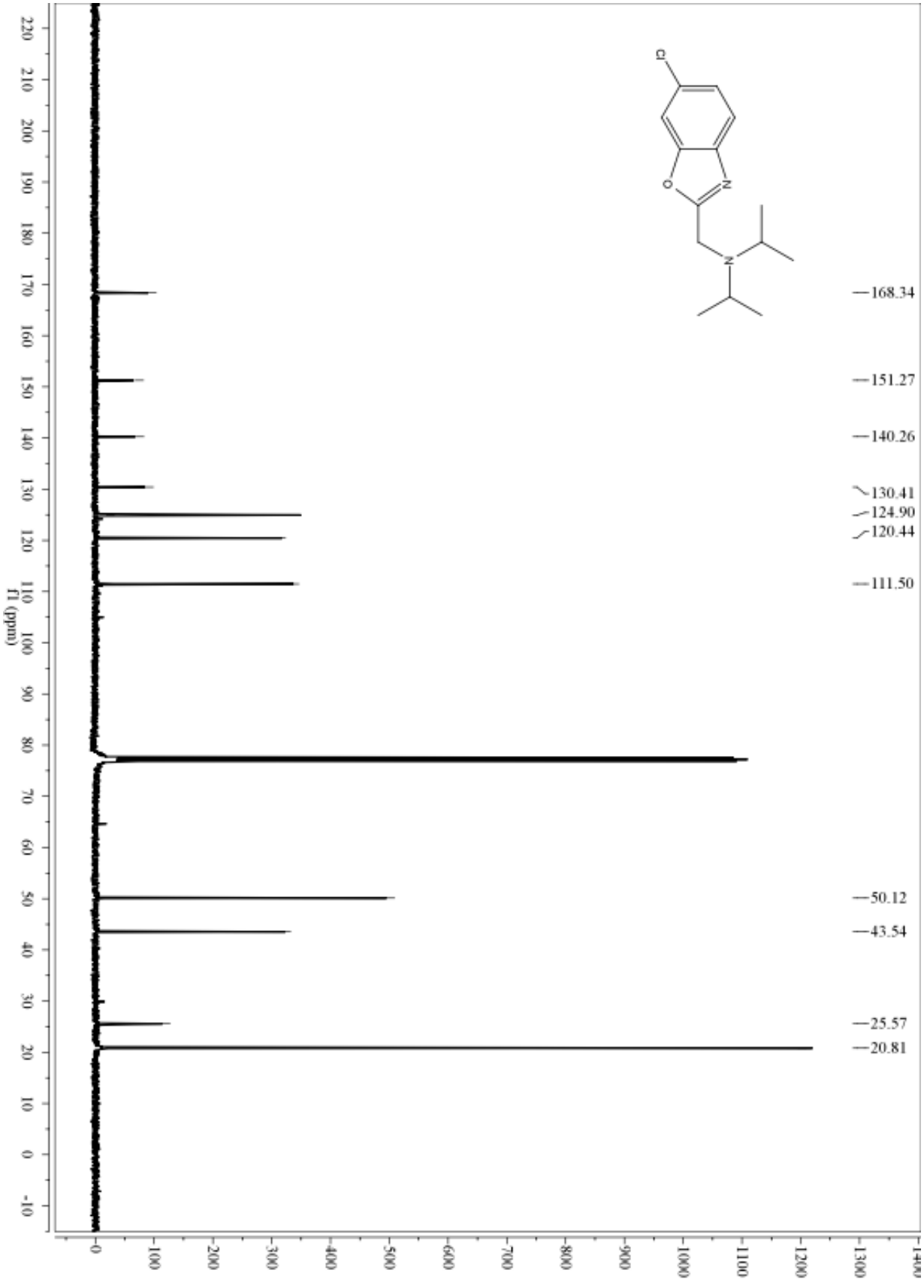
S-3o (1-(benzo[*d*]thiazol-2-yl)-*N*,*N*-dibutylbutan-1-amine)



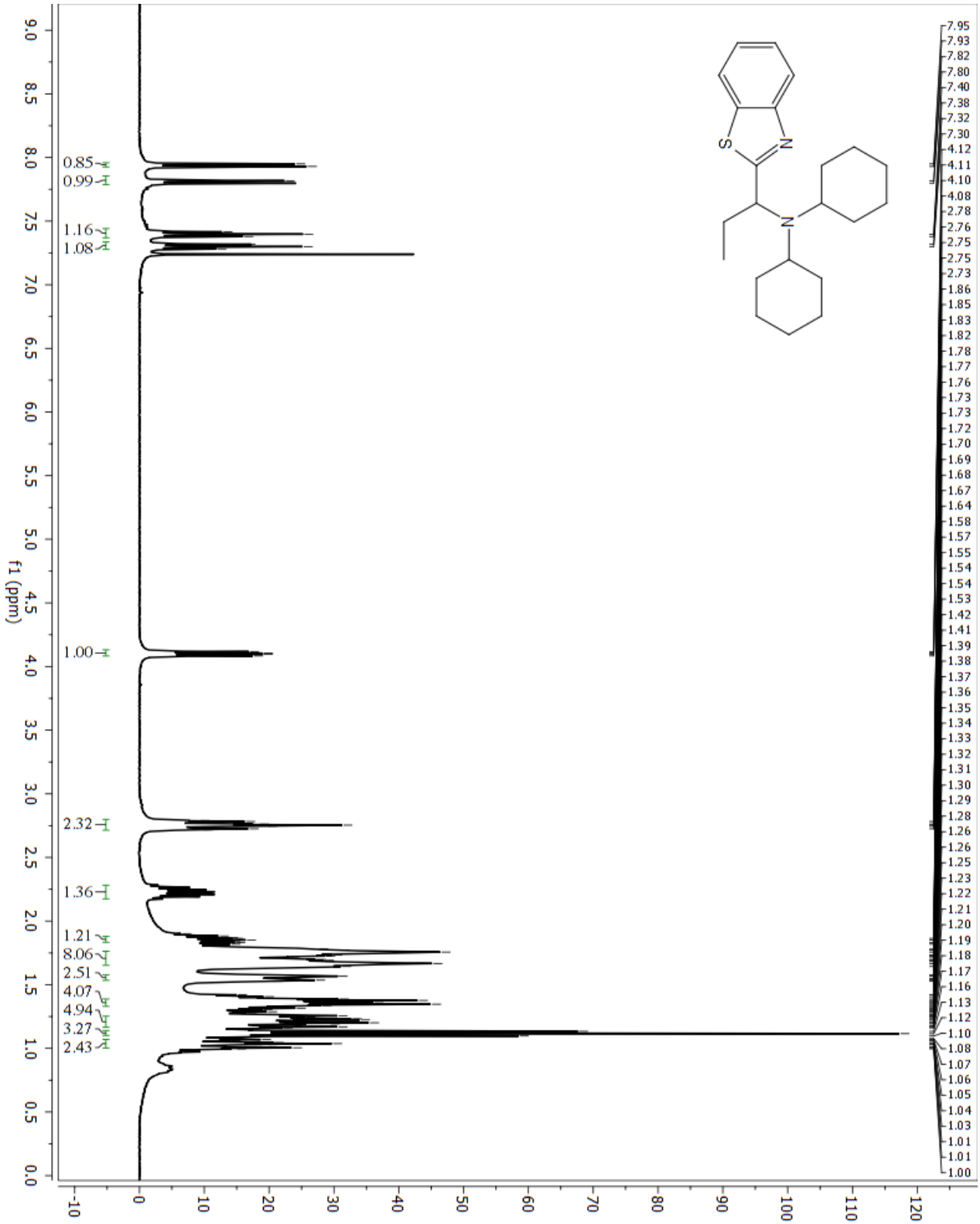
S-3p (*N*-((6-chlorobenzo[*d*]oxazol-2-yl)methyl)-*N*-isopropylpropan-2-amine)



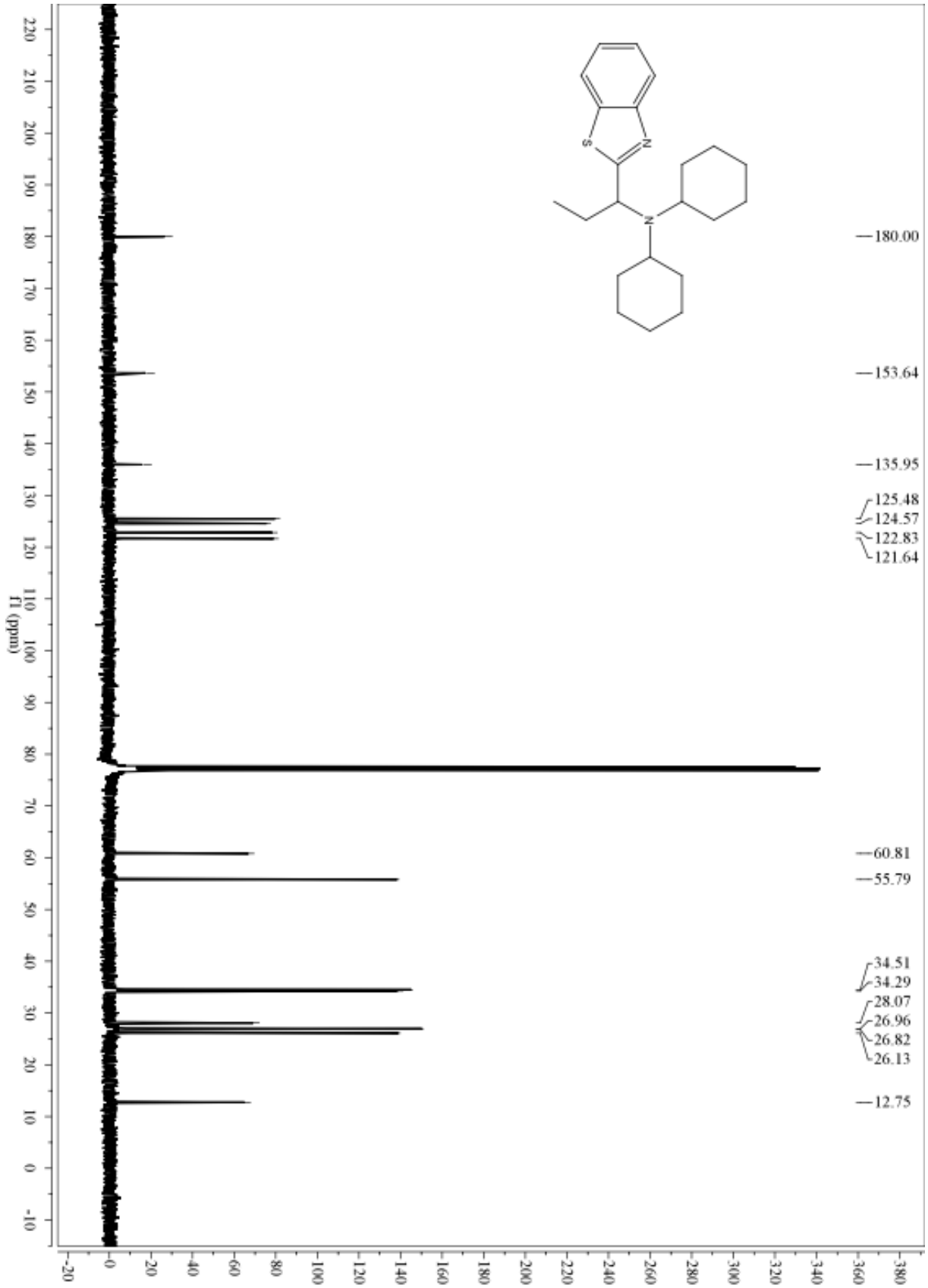
S-3p (*N*-((6-chlorobenzo[*d*]oxazol-2-yl)methyl)-*N*-isopropylpropan-2-amine)



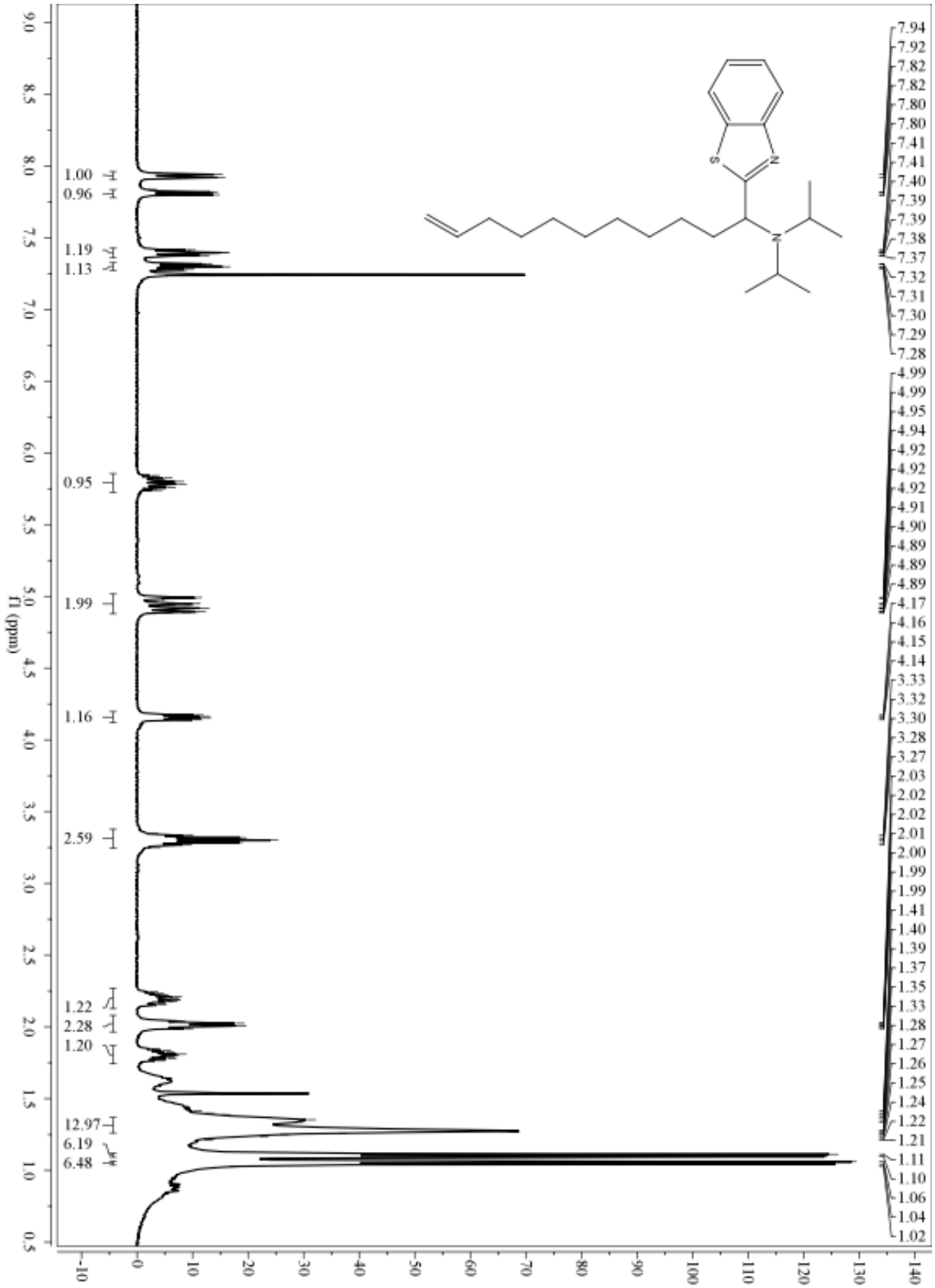
S-3q *(N*-(1-(benzo[*d*]thiazol-2-yl)propyl)-*N*-cyclohexylcyclohexanamine)



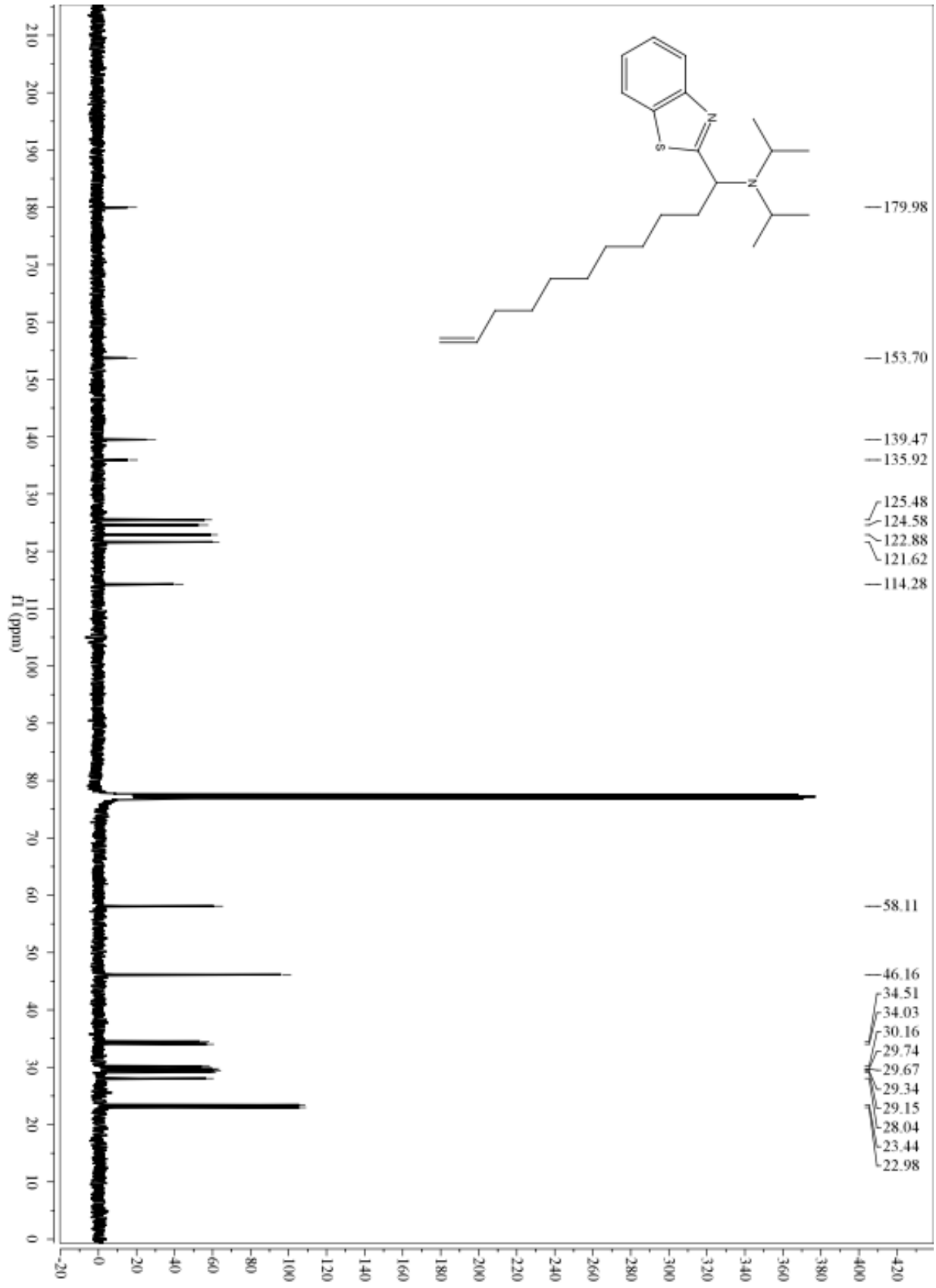
S-3q *(N*-(1-(benzo[*d*]thiazol-2-yl)propyl)-*N*-cyclohexylcyclohexanamine)



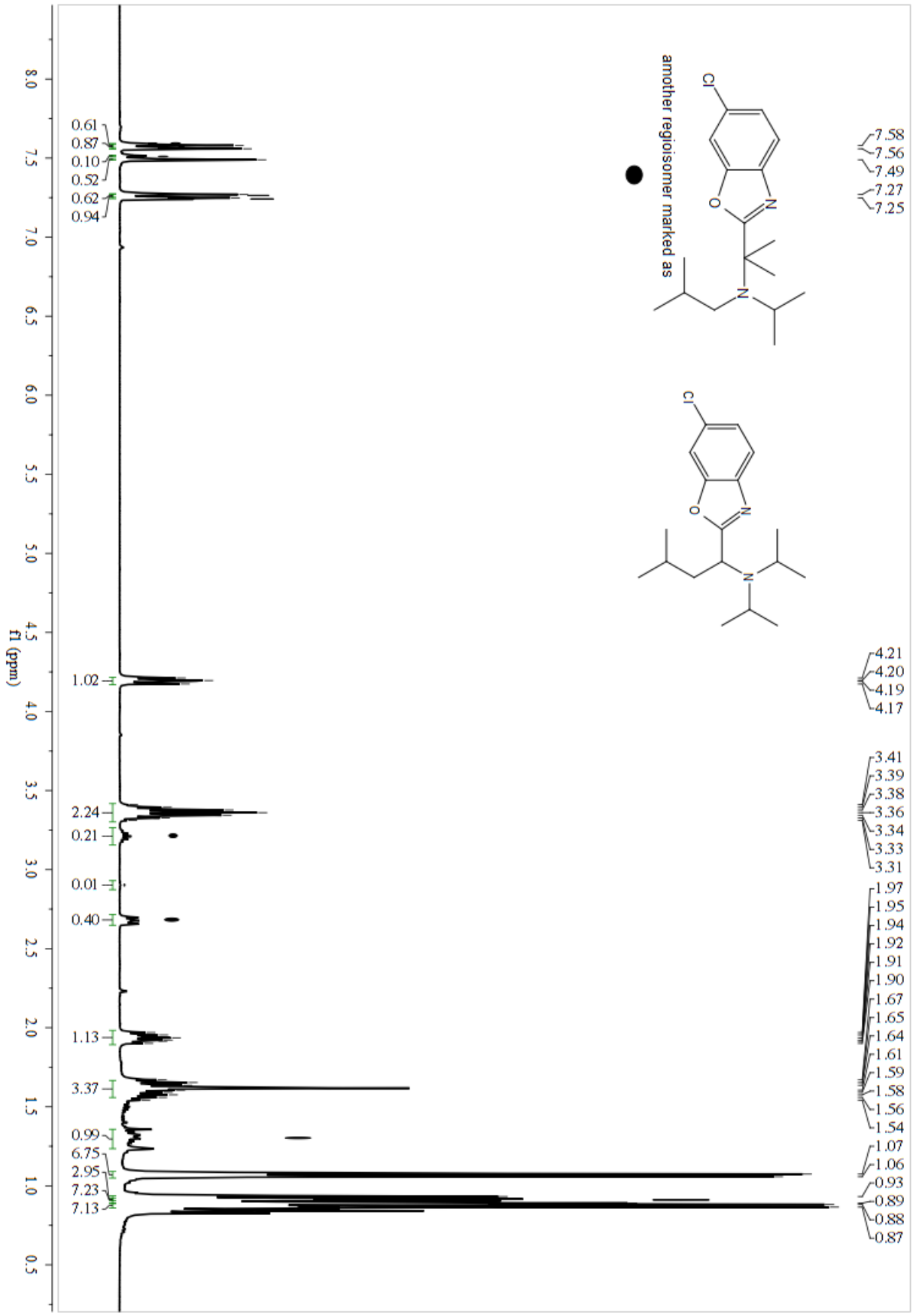
S-3r (1-(benzo[*d*]thiazol-2-yl)-*N*,*N*-diisopropylpent-4-en-1-amine)



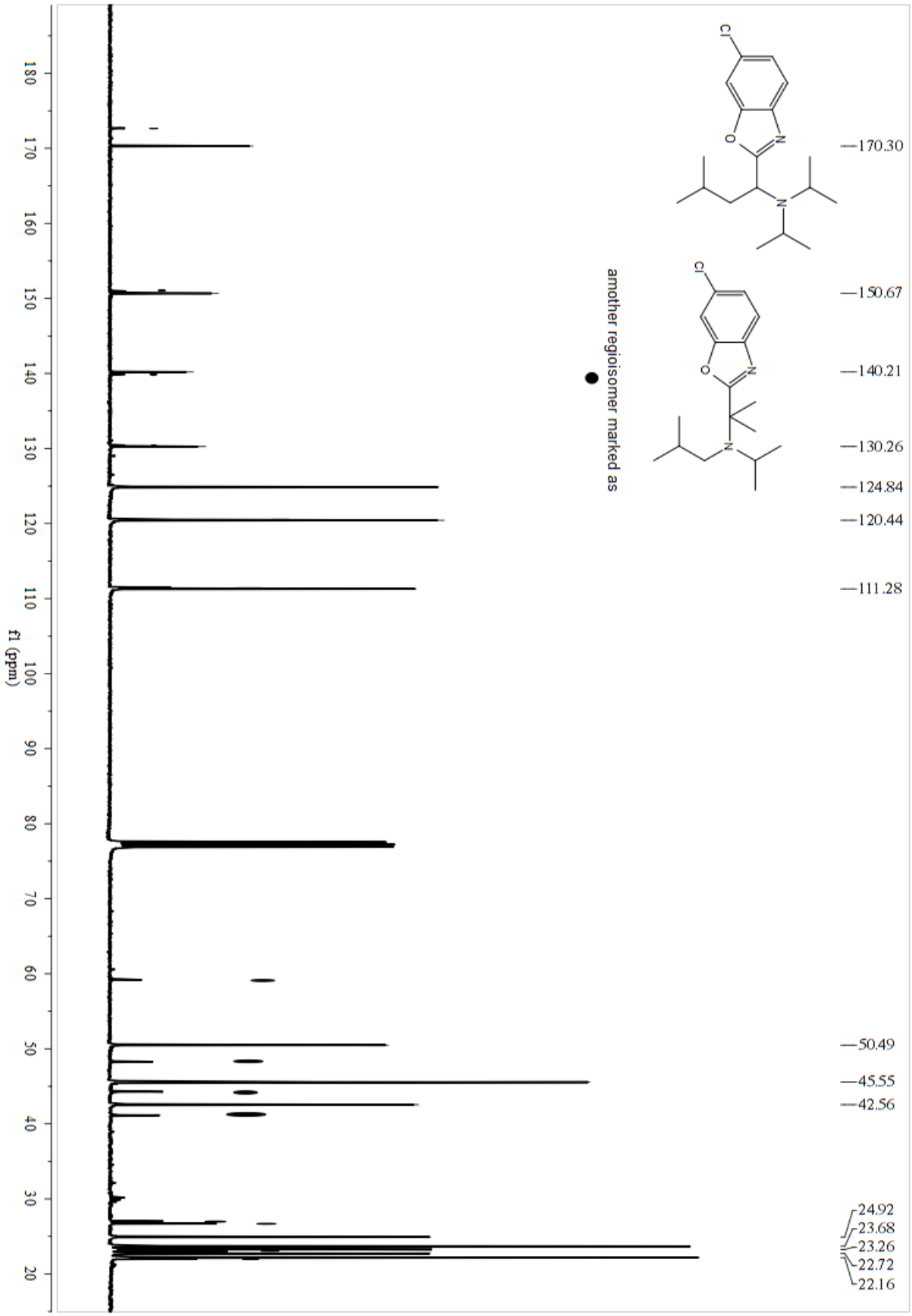
S-3r (1-(benzo[*d*]thiazol-2-yl)-*N*,*N*-diisopropylpent-4-en-1-amine)



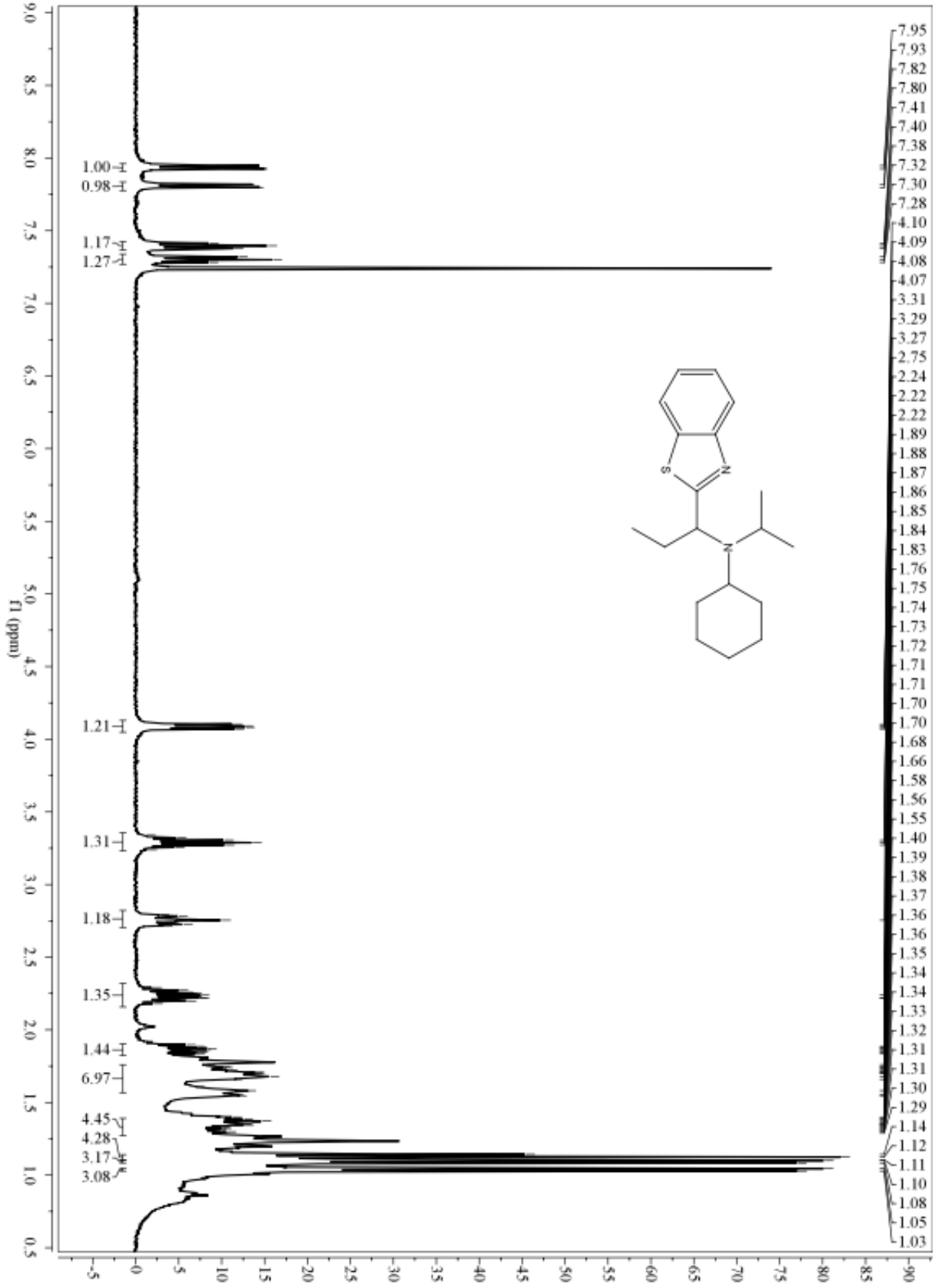
S-3s (1-(6-chlorobenzo[*d*]oxazol-2-yl)-*N*,*N*-diisopropyl-3-methylbutan-1-amine)



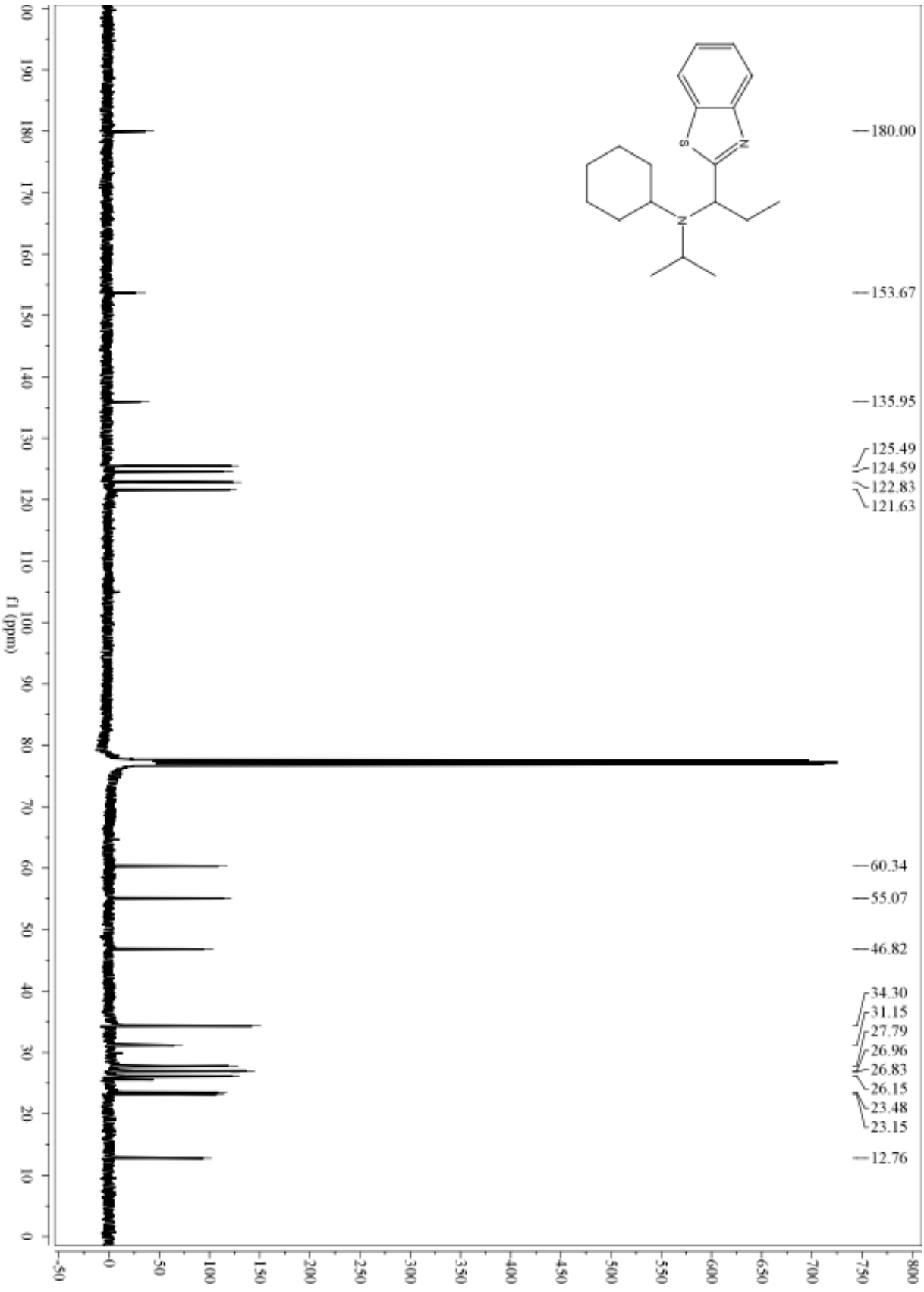
S-3s (1-(6-chlorobenzo[*d*]oxazol-2-yl)-*N*,*N*-diisopropyl-3-methylbutan-1-amine)



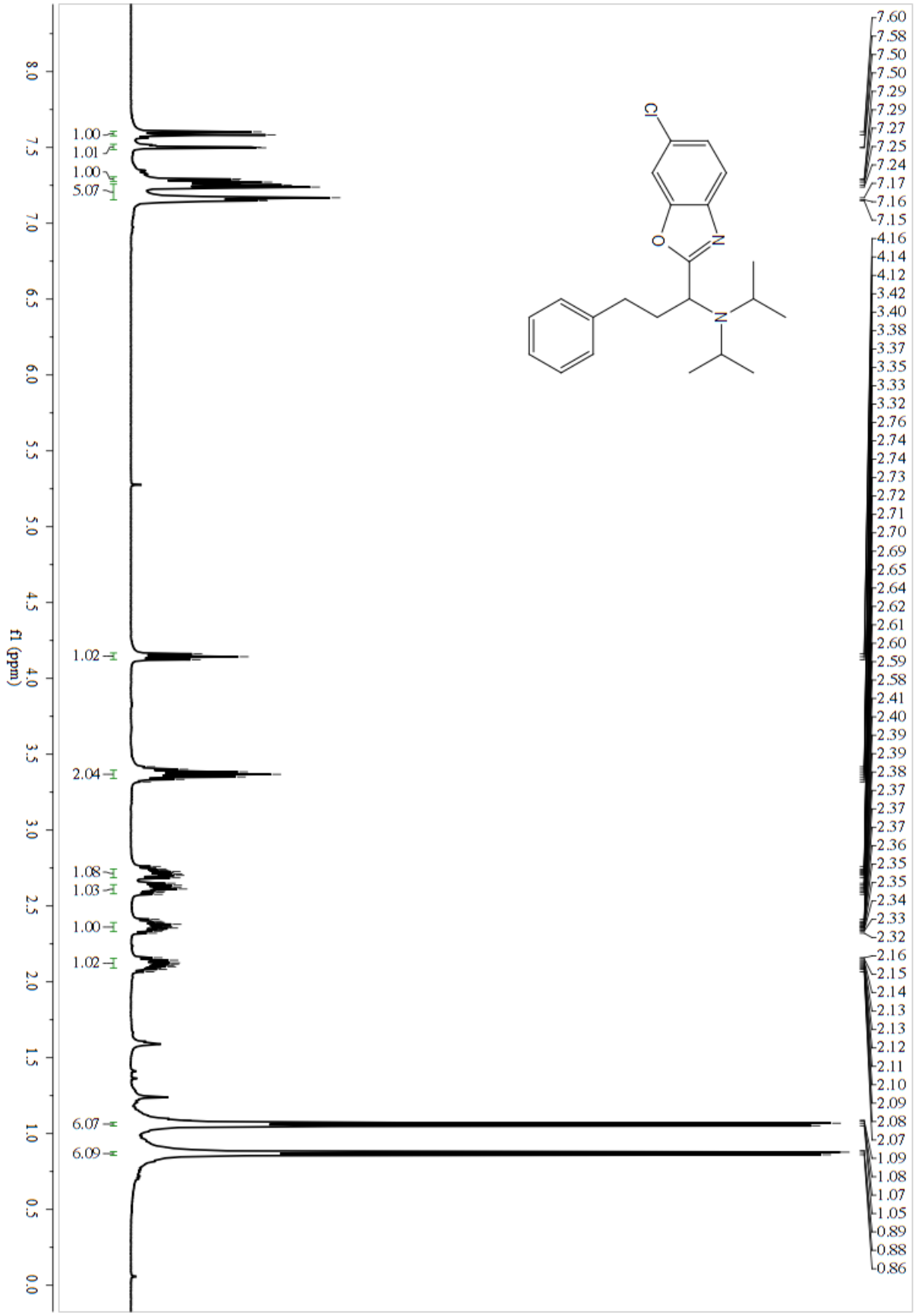
S-3t (*N*-(1-(benzo[*d*]thiazol-2-yl)propyl)-*N*-isopropylcyclohexanamine)



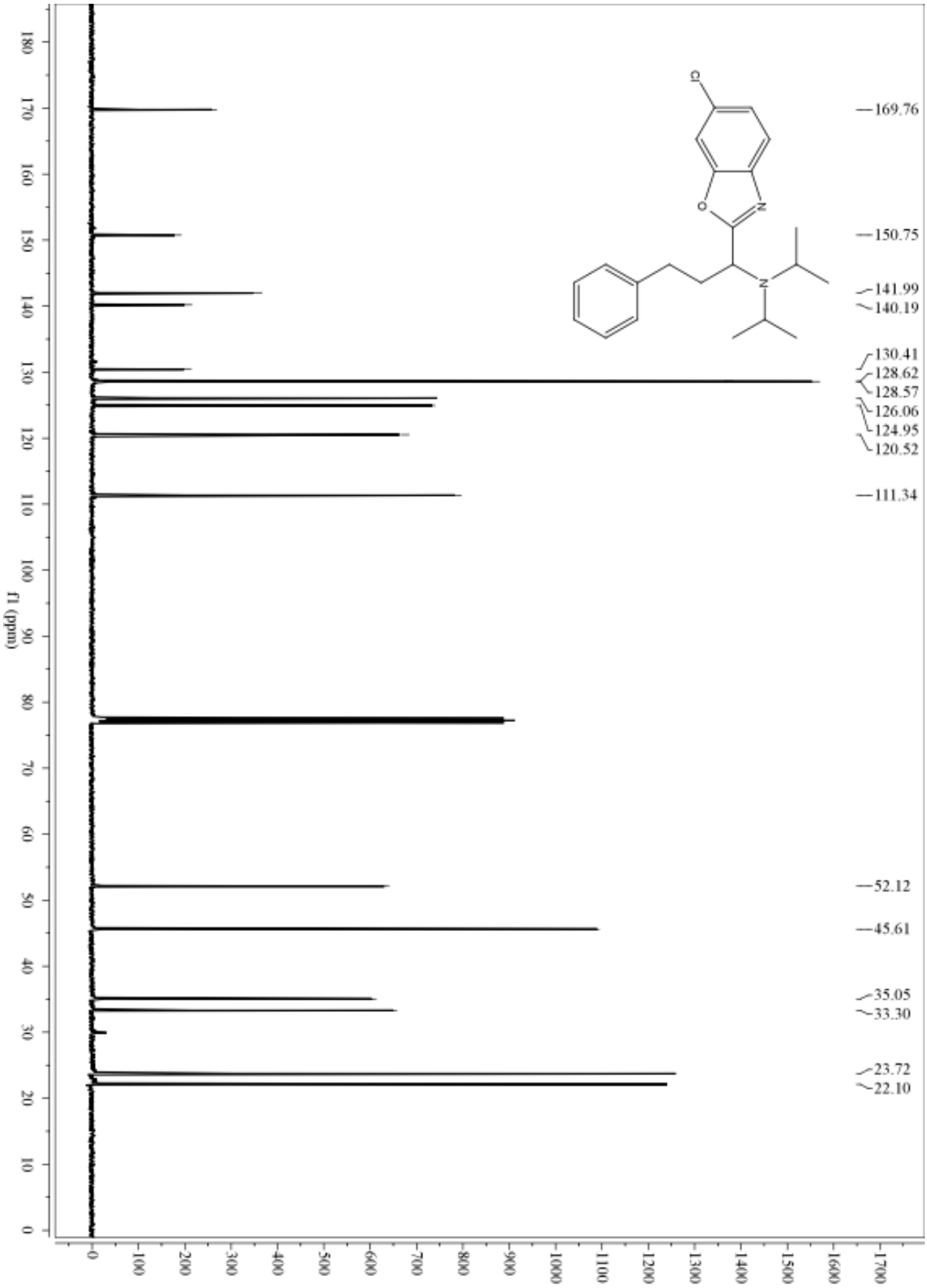
S-3t (*N*-(1-(benzo[*d*]thiazol-2-yl)propyl)-*N*-isopropylcyclohexanamine)



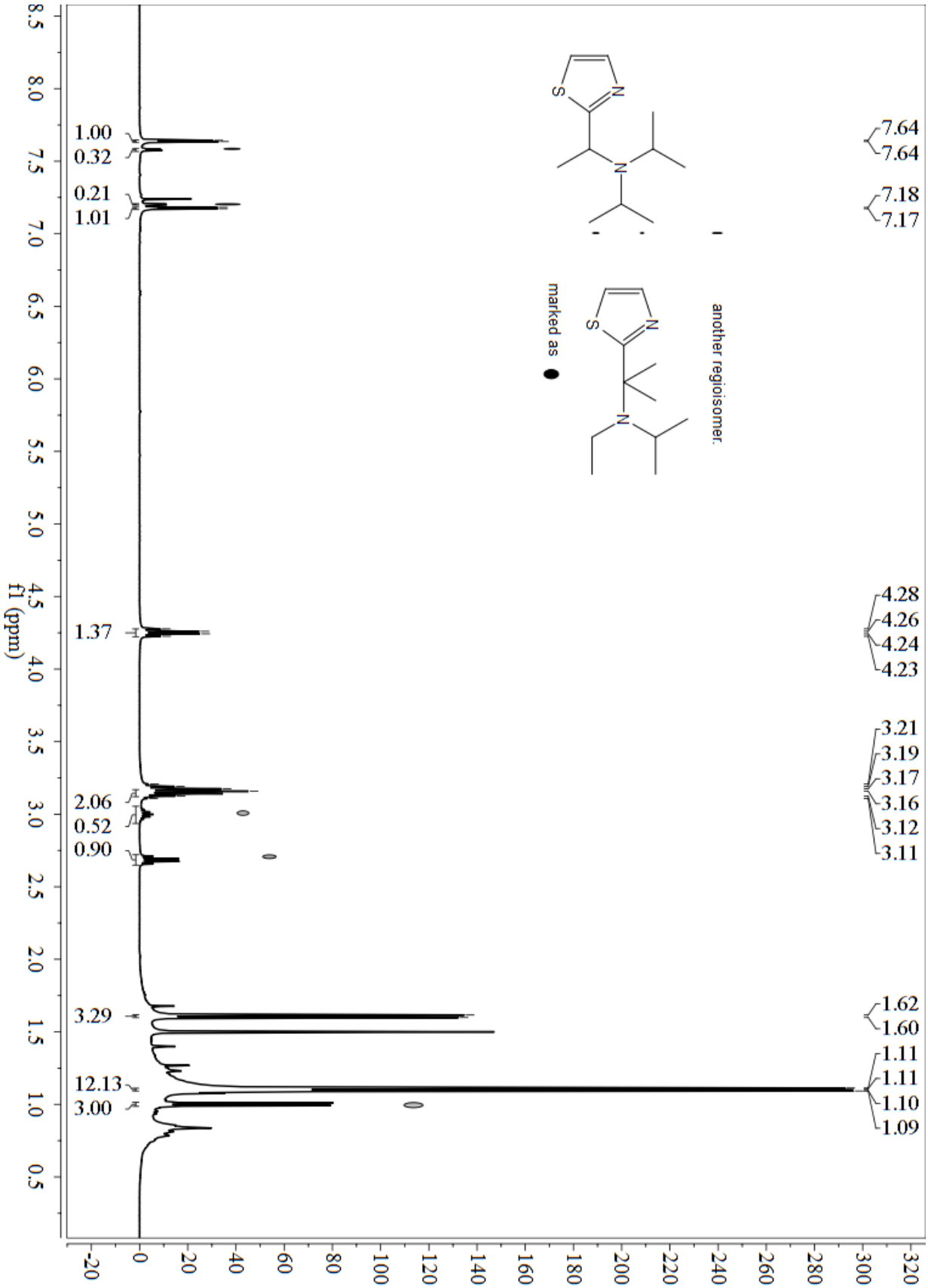
S-3u (1-(6-chlorobenzo[*d*]oxazol-2-yl)-*N*,*N*-diisopropyl-3-phenylpropan-1-amine)



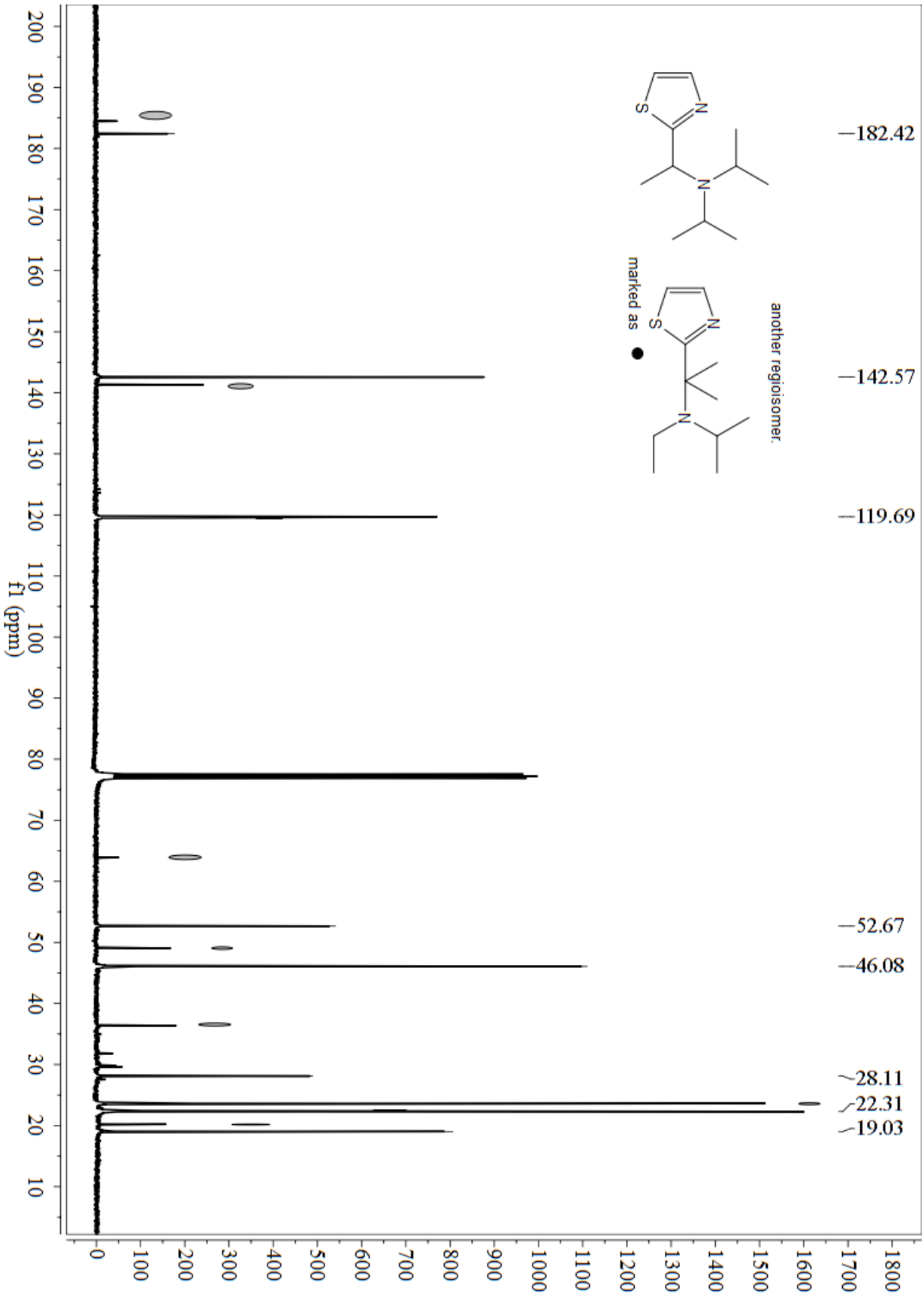
S-3u- (1-(6-chlorobenzo[*d*]oxazol-2-yl)-*N*,*N*-diisopropyl-3-phenylpropan-1-amine)



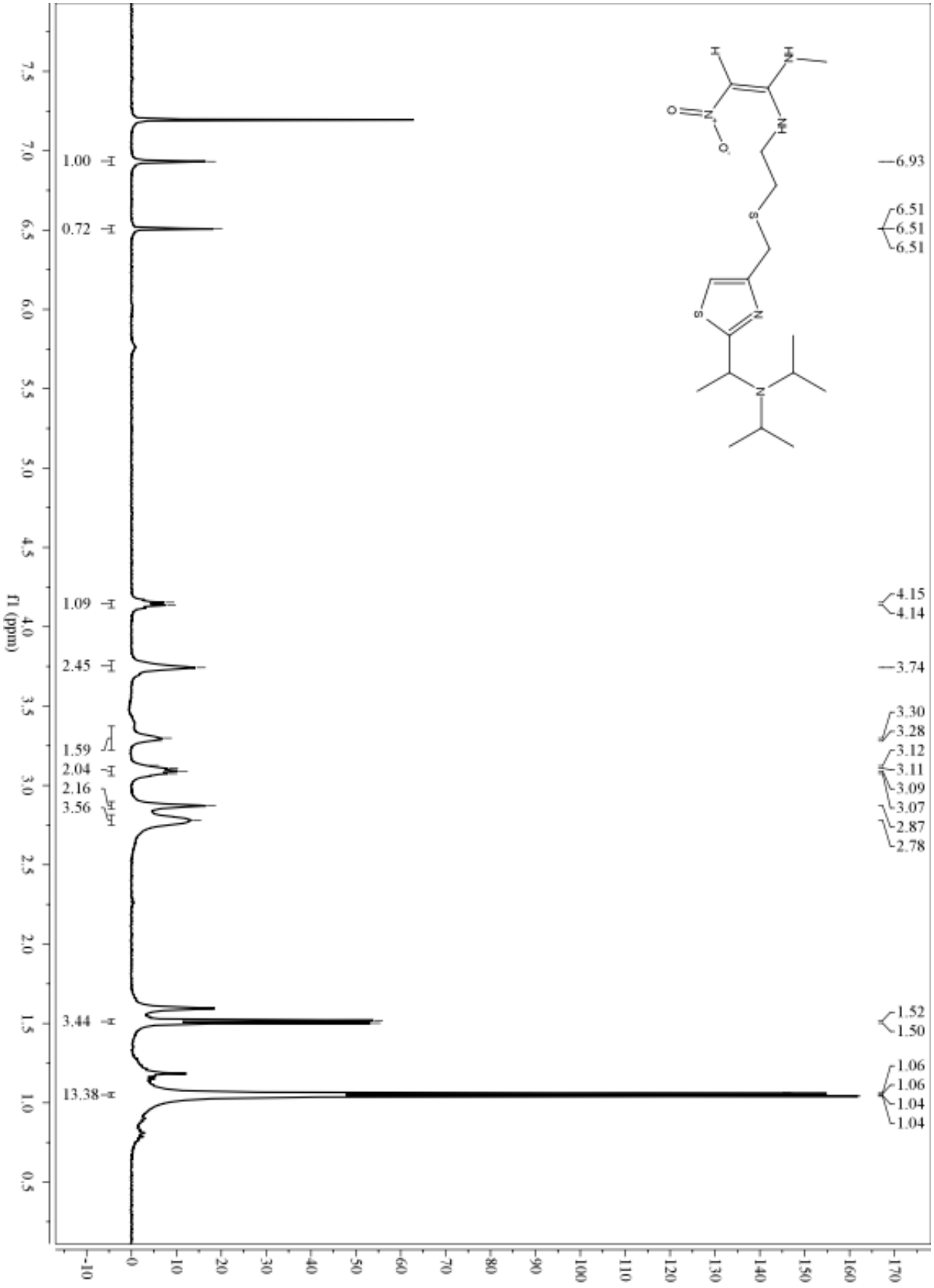
S-3v (N-isopropyl-N-(1-(thiazol-2-yl)ethyl)propan-2-amine)



S-3v (N-isopropyl-N-(1-(thiazol-2-yl)ethyl)propan-2-amine)



(Z)-N-2-(2-(((2-(1-(diisopropylamino)ethyl)thiazol-4-yl)methyl)thio)ethyl)-N1-methyl-1-nitroethene-1,2-diamine



(Z)-*N*-2-(2-(((2-(1-(diisopropylamino)ethyl)thiazol-4-yl)methyl)thio)ethyl)-*N*1-methyl-1-nitroethene-1,2-diamine