Supplementary Information for:

Dual Brønsted Acid/Nucleophilic Activation of Carbonylimidazole Derivatives

Stephen T. Heller, Tingting Fu, and Richmond Sarpong*

Department of Chemistry, University of California, Berkeley, California 94720

E-mail: rsarpong@berkeley.edu

Table of Contents:

Materials and Methods:

Unless stated otherwise, reactions were performed in oven-dried glassware sealed with rubber septa under a nitrogen atmosphere and were stirred with Teflon-coated magnetic stir bars. Liquid reagents and solvents were transferred via syringe using standard Schlenk techniques. Tetrahydrofuran (THF), toluene, acetonitrile (MeCN), and dimethylformamide (DMF) were dried by passage over a column of activated alumina;

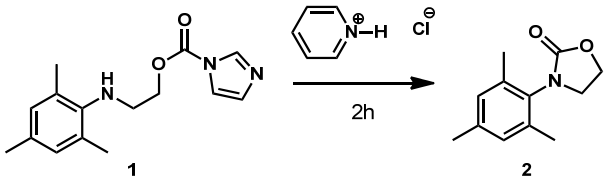
dichloromethane was distilled over calcium hydride. All other solvents and reagents were used as received unless otherwise noted. Thin layer chromatography was performed using SiliCycle silica gel 60 F-254 precoated plates (0.25 mm) and visualized by UV irradiation and anisaldehyde or potassium permanganate stain. Sorbent silica gel (particle size 40-63 μm) was used for flash chromatography. Enantiomeric ratios were measured by chiral HPLC employing a Shimidzu VP Series instrument equipped with SPD-M10A microdiode array detector using a Chiral PAK AD-H column. NMR experiments were performed on Bruker spectrometers operating at 300, 400, 500 or 600 MHz for ^{1}H and 75, 101, 126, or 151 MHz for ^{13}C experiments. ^{1}H and ^{13}C chemical shifts (δ) are reported relative to the residual solvent signal. Data are reported as follows: chemical shift (multiplicity, coupling constants where applicable, number of hydrogens). Abbreviations are as follows: *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *dd* (doublet of doublet), *dt* (doublet of triplet), *pent* (pentet), *hept* (heptet), m (multiplet), *bs* (broad singlet). High resolution mass spectral data were obtained from the University of California, Berkeley Mass Spectral Facility.

Drying Pyridinium Chloride:

Commercial pyridinium chloride (20 g) was suspended in benzene (200 mL) in a flask equipped with a Dean-Stark trap and refluxed for 12 hours. The Dean-Stark trap was then removed and the remaining benzene was removed *in vacuo* on a rotary evaporator. The resulting mass could be stored in a desiccator for several months without noticeable absorbance of moisture (NOTE: Reactions performed with dried pyridinium chloride were generally slightly higher yielding as no product arising from

carbonylimidazole hydrolysis was observed. This side product was typically obtained as a 3-5% impurity in reactions run with commercial pyridinium chloride).

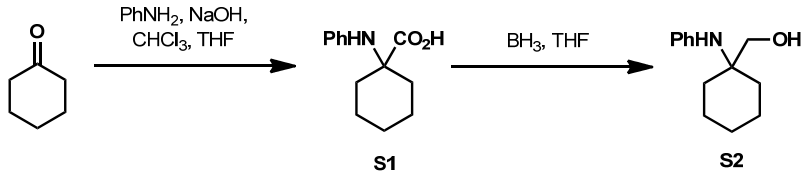
Optimization of Oxazolidinone Synthesis:



Entry	Solvent	Temp (°C)	Equiv	Conc (M)	% conversion [a]
1	CD_3CN	20	1	0.2	20
2	CD_3CN	20	2	0.2	38
3	CD_3CN	20	3	0.2	50
4	CD_3CN	20	4	0.2	69
5	CD_3CN	20	2	0.5	46
6	CD_3CN	40	2	0.2	78
7	CD_3CN	60	2	0.2	>95
8	$CDCl_3$	20	2	0.2	41
9	d_6-DMSO	20	2	0.2	54

[a] Conversions determined by integration of ^{1}H-NMR resonances.

Synthesis of Amino Alcohol Substrates:



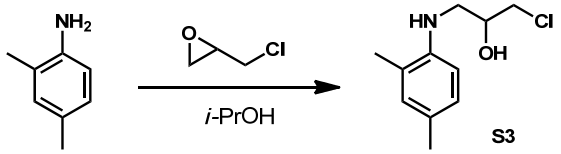
Aniline (1.00 g, 10.7 mmol) and cyclohexanone (3.16 g, 32.2 mmol) were dissolved in THF (100 mL). The homogeneous mixture was stirred and cooled to 0 ºC, and then freshly powdered NaOH (2.16 g, 54.0 mmol) was added in one portion. The resulting suspension was stirred while chloroform (6.45 g, 54.0 mmol) was added dropwise at 0 ºC. The reaction mixture was allowed to warm to room temperature and was stirred overnight. During this time, a thick tan paste formed and stirring became

difficult. The crude reaction mixture was filtered and the solids collected were dissolved in water. The aqueous solution was extracted with Et_2O (2 x 50 mL). The aqueous layer was acidified with AcOH and then extracted with EtOAc (3 x 50 mL). The combined EtOAc extracts were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to yield **S1** as a tan powder (1.08 g, 46%) that was used without further purification.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.9 Hz, 2H), 6.86 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 2H), 2.06 – 1.93 (m, 4H), 1.68 – 1.58 (m, 3H), 1.50 – 1.30 (m, 3H).

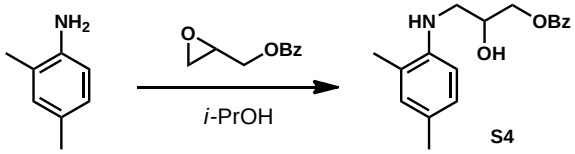
S1 was dissolved in dry THF (20 mL) and then BH_3•THF (1.0 M solution, 28 mL) was added dropwise (***CAUTION: Hydrogen gas is evolved!***) at room temperature. After gas evolution had ceased, the reaction mixture was refluxed for 14 h. Upon cooling the mixture to room temperature, water was added dropwise (***CAUTION: Hydrogen gas is evolved!***) until gas evolution ceased. The crude reaction mixture was concentrated *in vacuo* and the resulting residue was dissolved in a mixture of EtOAc and water. The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 30 mL). The combined organics were washed with 1 M Na_2CO_3 (aq), then brine, dried over Na_2SO_4, and concentrated *in vacuo* to afford a pale yellow syrup. The crude product was purified by column chromatography (1 : 9, EtOAc : hexanes) to afford **S2** as a colorless syrup (1.0 g, 87%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20-7.17 (m, 2H), 6.85-6.79 (m, 3H), 3.58 (s, 2H), 3.36 (bs, 1H), 2.53 (bs, 1H), 1.85-1.80 (m, 2H), 1.60-1.38 (m, 8H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.4, 129.0, 119.7, 118.4, 67.7, 57.3, 33.0, 25.8, 21.4. **HRMS-ESI** (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{20}NO$, 206.1545; found, 206.1542.



2,4-dimethylaniline (1.96 g, 16.2 mmol) was dissolved in 2-propanol (25 mL) and the solution was stirred and heated to 90 ºC. Epichlorohydrin (1.80 g, 19.4 mmol) was added in three portions, delivered 30 minutes apart. The reaction mixture was kept at 90 ºC for 1.5 h after the last addition and was then cooled and concentrated *in vacuo* to afford a red syrup. The crude product was purified by column chromatography (1 : 9, EtOAc : hexanes) to afford **S3** as a pale yellow oil (2.13 g, 62%).

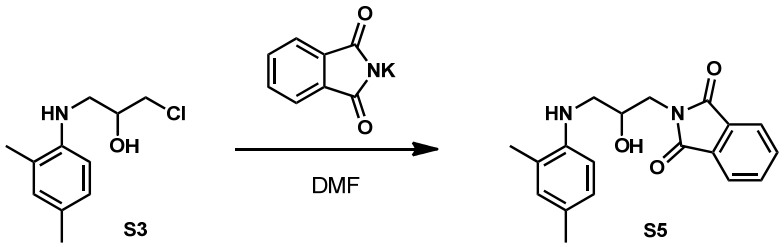
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 – 6.87 (m, 2H), 6.58 (d, *J* = 8.1 Hz, 1H), 4.16 – 4.08 (m, 1H), 3.74 – 3.63 (m, 2H), 3.40 (dd, *J* = 13.1, 4.4 Hz, 1H), 3.25 (dd, *J* = 13.1, 7.3 Hz, 1H), 2.51 (bs, 1H), 2.24 (s, 3H), 2.15 (s, 3H). Spectra were consistent with those reported previously.[1]



2,4-dimethylaniline (0.140 g, 1.16 mmol) and benzoyl glycidol[2] (0.227 g, 1.27 mmol) were dissolved in 2-propanol (2.5 mL) and the solution was stirred and heated to 90 ºC. After 4 h, the mixture was cooled and concentrated *in vacuo* to afford a brown oil. The crude product was purified by column chromatography (2 : 8, EtOAc : hexanes) to afford **S4** as a pale yellow oil (0.310 g, 89%).

[1] Hans-Ludwig, E.; Tiemann, R.; Boehm, S.; Dutzmann, S.; Heinz-Wilhelm, D. (Bayer AG, Germany). European Patent DE4227073, February 24, 1994.
[2] Stamatov, S. D.; Stawinski, J. *Tetrahedron*, **2005**, *61*, 3659.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.3 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.94 (s, 1H), 6.62 (d, *J* = 8.1 Hz, 1H), 4.52 – 4.42 (m, 2H), 4.28 (ddd, *J* = 10.4, 8.1, 4.5 Hz, 1H), 3.43 (dd, *J* = 12.9, 4.2 Hz, 1H), 3.29 (dd, *J* = 12.9, 7.6 Hz, 1H), 2.28 (s, 3H), 2.18 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.7, 143.4, 133.2, 131.1, 129.6, 129.5, 128.4, 127.2, 126.8, 122.9, 110.4, 68.3, 67.0, 46.8, 20.3, 17.4. **HRMS-ESI** (*m/z*): $[M+H]^+$ calcd for $C_{18}H_{22}NO_3$, 300.1594; found, 300.1594.



Alcohol **S3** (0.587 g, 2.75 mmol) was dissolved in DMF (5 mL) and then potassium phthalimide (0.560 g, 3.00 mmol) was added in one portion. The resulting mixture was then heated to 100 ºC for 16 h. The reaction mixture was cooled, and water was added. The crude mixture was extracted with EtOAc (3 x 40 mL) and the combined organics were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to afford a yellow syrup. The crude product was purified by column chromatography (3 : 7, EtOAc : hexanes) to afford **S5** as a bright yellow solid (0.520 g, 58%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 5.3, 3.1 Hz, 2H), 7.73 (dd, *J* = 5.5, 3.0 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.88 (s, 1H), 6.58 (d, *J* = 8.1 Hz, 1H), 4.20 (pent, *J* = 5.0 Hz, 1H), 3.99 (bs, 1H) 3.97 – 3.87 (m, 2H), 3.33 – 3.26 (m, 1H), 3.25 – 3.18 (m, 1H), 2.97 (bs, 1H), 2.22 (s, 3H), 2.17 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.0, 143.5,

134.2, 131.8, 131.1, 127.3, 126.7, 123.5, 122.8, 110.3, 68.7, 47.3, 42.0, 20.3, 17.4.

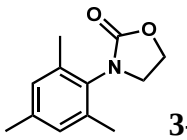
HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{19}H_{21}N_2O_3$, 325.1547; found, 325.1546.

Preparation of Imidazole Carbamates: Representative Procedure A

Amino alcohol (1 mmol) was dissolved in dichloromethane (5 mL) and the resulting homogeneous mixture was stirred at room temperature. 1,1'-carbonyldiimidazole (CDI) (1.2 mmol) was added in one portion and the reaction mixture was stirred at room temperature until TLC analysis indicated that the starting alcohol had been completely consumed (typically 2 hours after addition of CDI). The crude reaction mixture was diluted with dichloromethane (20 mL) and washed with water. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to afford crude imidazole carbamate that was used without further purification.

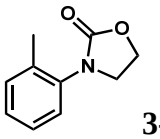
Preparation of Oxazolidinones: Representative Procedure B

Imidazole carbamate (0.3 mmol) was dissolved in dry MeCN (1.5 mL) and pyridinium chloride (0.6 mmol) was added in one portion at room temperature. The homogeneous mixture was then stirred at room temperature. Imidazole hydrochloride precipitated as the reaction proceeded. After 24 hours, the reaction was quenched with 1 M HCl and then extracted with dichloromethane. The combined organics were dried over Na_2SO_4 and then concentrated *in vacuo*. If necessary, the product obtained could be purified by column chromatography.



3-mesityloxazolidin-2-one (2)

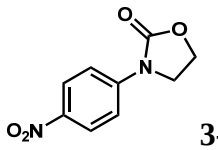
Prepared from 2-(mesitylamino)ethanol[3] by conversion to the imidazole carbamate using representative procedure A, which was then cyclized using representative procedure B to obtain a brown solid (0.090 g, 90%). The reaction mixture was heated to 40 ºC for 9 h. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.93 (s, 2H), 4.54 (t, *J* = 8.1 Hz, 2H), 3.82 (t, *J* = 8.1 Hz, 2H), 2.28 (s, 3H), 2.25 (s, 6H). Spectra were consistent with those reported previously.[4]



3-(*o*-tolyl)oxazolidin-2-one (3)

Prepared from 2-(o-tolylamino)ethanol[3] by conversion to the imidazole carbamate using representative procedure A, which was then cyclized using representative procedure B to obtain a light yellow oil (0.054 g, 90%). The reaction mixture was heated to 40 ºC for 9 h. The crude product was purified by column chromatography (1 : 1, EtOAc : hexanes). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.21 (m, 4H), 4.51 (t, *J* = 8.0 Hz, 2H), 3.98 – 3.89 (m, 2H), 2.32 (s, 3H). Spectra were consistent with those reported previously.[5]

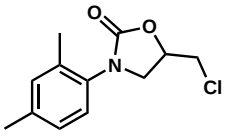
[3] Bhanu Prasad, B. A.; Gilbertson, S. R. *Org. Lett*. **2009**, *11*, 3710.
[4] Morita, Y.; Ishigaki, T.; Kawamura, K.; Iseki, K. *Synthesis* **2007**, *16*, 2517.
[5] Gong, H.; Yang, N. *Heterocycles*, **2009,** *78*, 2093.



3-(4-nitrophenyl)oxazolidin-2-one (4)

Prepared from 2-((4-nitrophenyl)amino)ethanol[6] using representative procedure A to form the imidazole carbamate (0.138 g, 0.5 mmol). The imidazole carbamate was combined with a 0.4 M solution of pyridinium chloride in dry DMF (2.5 mL, 1.0 mmol) at room temperature. The homogeneous mixture was stirred at room temperature for 10 minutes and then heated to 40 °C. After 36 h, the reaction was cooled to room temperature and then a saturated aqueous $CuSO_4$ solution (15 mL) was added. The aqueous layer was extracted with Et_2O (3×15 mL). The combined organic fractions were washed with water (3 x 10 mL) and then dried over $MgSO_4$ and concentrated *in vacuo* to afford a yellow oil. The product obtained was purified by column chromatography (2 : 1, heptane : acetone) to obtain a pale yellow solid (0.043 g, 41%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, J = 9.3 Hz, 2H), 7.74 (d, J = 9.3 Hz, 2H), 4.65 – 4.49 (m, 2H), 4.22 – 4.08 (m, 2H). Spectra were consistent with those reported previously.[7]



5-(chloromethyl)-3-(2,4-dimethylphenyl)oxazolidin-2-one (5)

Prepared from **S3** by conversion to the imidazole carbamate using representative procedure A, which was then cyclized using representative procedure B to obtain a colorless oil (0.058 g, 89%).

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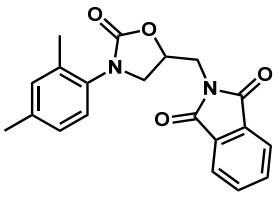
[6] Meo, P. L.; D'Anna, F.; Gruttadauria, M.; Riela, S.; Noto, R. *Tetrahedron*, **2004**, *60*, 9099.
[7] Mallesham, B.; Rajesh, B. M.; Rajamohan, R. P.; Srinivas, D.; Trehan, S. *Org. Lett.* **2003**, *5*, 963.

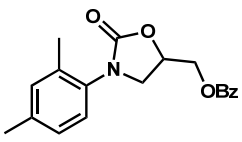
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 – 7.07 (m, 2H), 7.06 – 7.02 (m, 1H), 4.95-4.86 (m, 1H), 4.03 (t, *J* = 9.0 Hz, 1H), 3.85 – 3.72 (m, 3H), 2.32 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.5, 138.4, 135.6, 132.8, 132.0, 127.7, 126.4, 71.5, 50.5, 44.9, 21.0, 17.7. **HRMS-ESI** (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{14}ClNNaO_2$, 262.0605; found, 262.0606.



2-((3-(2,4-dimethylphenyl)-2-oxooxazolidin-5-yl)methyl)isoindoline-1,3-dione (6)

Prepared from **S5** by conversion to the imidazole carbamate using representative procedure A, which was then cyclized using representative procedure B to obtain a white solid (0.154 g, 90%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 1H), 7.07 (s, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 5.01 (dtd, *J* = 8.3, 6.5, 5.4 Hz, 1H), 4.16 (dd, *J* = 14.0, 6.8 Hz, 1H), 4.03 – 3.96 (m, 2H), 3.73 (dd, *J* = 9.2, 5.4 Hz, 1H), 2.31 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.0, 155.5, 138.3, 135.6, 134.4, 132.8, 132.0, 131.7, 127.7, 126.3, 123.6, 70.2, 50.8, 40.6, 21.0, 17.7. **HRMS-ESI** (*m/z*): $[M+Na]^+$ calcd for $C_{10}H_{13}BrNNaO_2$, 279.9944; found, 279.9939.

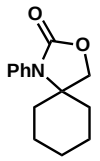


(3-(2,4-dimethylphenyl)-2-oxooxazolidin-5-yl)methyl benzoate (7)

Prepared from **S4** by conversion to the imidazole carbamate using representative

procedure A, which was then cyclized using representative procedure B to obtain a colorless syrup (0.063 g, 94%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 6.7 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.10 – 7.05 (m, 2H), 7.00 (d, *J* = 8.0 Hz, 1H), 5.02 (ddt, *J* = 9.0, 6.1, 4.3 Hz, 1H), 4.59 (d, *J* = 4.3 Hz, 2H), 4.05 (t, *J* = 9.1 Hz, 1H), 3.77 (dd, *J* = 9.0, 6.1 Hz, 1H), 2.30 (s, 3H), 2.23 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.1, 155.8, 138.2, 135.4, 133.4, 132.8, 131.9, 129.7, 129.1, 128.4, 127.6, 126.3, 70.8, 64.6, 49.5, 20.9, 17.6. **HRMS-ESI** (*m/z*): $[M+Na]^+$ calcd for $C_{19}H_{19}NNaO_4$, 348.1207; found, 348.1210.



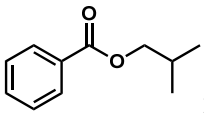
1-phenyl-3-oxa-1-azaspiro[4.5]decan-2-one (8)

Prepared from **S2** by conversion to the imidazole carbamate using representative procedure A, which was then cyclized using representative procedure B to obtain a white solid (0.086 g, 93%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.34 (m, 3H), 7.20 (dd, *J* = 7.5, 1.8 Hz, 2H), 4.29 (s, 2H), 1.87 (d, *J* = 13.3 Hz, 2H), 1.77 (d, *J* = 14.6 Hz, 2H), 1.59 (d, *J* = 13.6 Hz, 1H), 1.52 – 1.42 (m, 2H), 1.27 (m, 2H), 0.95 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.3, 134.6, 130.0, 129.2, 128.4, 72.2, 63.0, 34.9, 24.2, 22.8. **HRMS-ESI** (*m/z*): $[M+Na]^+$ calcd for $C_{14}H_{17}NNaO_2$, 254.1151; found, 254.1152.

Preparation of Esters from Acylimidazoles: Representative Procedure C

Alcohol (1.0 mmol) and benzoyl imidazole (1.1 mmol)[8] were placed in a dry 20 mL screw cap vial with a magnetic stir bar. A 1.0 M solution of pyridinium salt in dry MeCN (2.20 mL, 2.2 mmol) was added in one portion at room temperature. The vial was quickly sealed with a plastic cap. The reaction mixture was then stirred at 20 °C for 24 h. The reaction was quenched with 1 M NaOH (10 mL) and then extracted with hexane (4 × 15 mL). The organic fractions were combined and washed with 1 M HCl (15 mL) and brine. The organic fraction was dried over $MgSO_4$ and concentrated *in vacuo* to afford the desired ester. Though typically unnecessary, further purification was achieved by column chromatography.

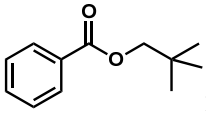


isobutyl benzoate (18)

Prepared using representative procedure C with isobutanol (0.080 g, 1.08 mmol) and pyridinium triflate to afford a light yellow oil (0.179 g, 93%). The reaction was stirred at room temperature for 12 h.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J = 7.0 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.44 (dd, J = 7.5, 8.0 Hz, 2H), 4.11 (d, J = 6.6 Hz, 2H), 2.18 – 2.00 (m, 1H), 1.03 (d, J = 6.8 Hz, 6H). Spectra were consistent with those reported previously.[9]

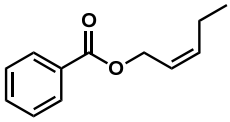
[8] Vock, C. A.; Scolaro, C.; Phillips, A. D.; Scopelliti, R.; Sava, G.; Dyson, P. J**.** *J. Med. Chem.* **2006**, *49*, 5552.
[9] Liu, C.; Wang, J.; Meng, L.; Deng, Y.; Li, Y.; Lei, A. *Angew. Chem. Int. Ed.* **2011**, *50*, 5144.



neopentyl benzoate (19)

Prepared using representative procedure C with neopentyl alcohol (0.100 g, 1.13 mmol) and pyridinium triflate to afford a light yellow oil (0.1726 g, 79%). The reaction mixture was stirred at room temperature for 36 h.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.0 Hz, 2H), 7.60 – 7.53 (m, 1H), 7.50 – 7.41 (m, 2H), 4.02 (s, 2H), 1.05 (s, 9H). Spectra were consistent with those reported previously.[10]

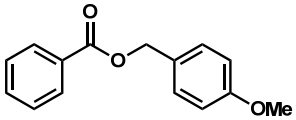


(Z)-pent-2-en-1-yl benzoate (20)

Prepared using representative procedure C with (Z)-pent-2-en-1-ol (0.088 g, 1.02 mmol) and pyridinium chloride to afford a yellow oil (0.160 g, 82% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 6.9 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 5.76 – 5.59 (m, 2H), 4.88 (d, *J* = 6.7 Hz, 2H), 2.26 – 2.13 (m, 2H), 1.03 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.3, 137.1, 132.8, 130.3, 129.5, 128.2, 122.7, 60.8, 20.9, 13.8. **HRMS-EI** (64 eV) *m/z*: M^+ calcd for $C_{12}H_{14}O_2$, 190.0994; found, 190.0994.

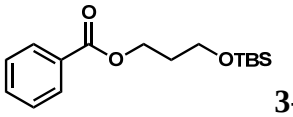
[10]Ohshima, T.; Iwasaki, T.; Maegawa, Y.; Yoshiyama, A.; Mashima, K. *J. Am. Chem. Soc.* **2008,** *130,* 2944.



4-methoxybenzyl benzoate (21)

Prepared using representative procedure C with 4-methoxybenzyl alcohol (0.178 g, 1.29 mmol) and pyridinium triflate to obtain a colorless oil (0.288 g, 92%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 6.9 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.46 – 7.37 (m, 4H), 6.92 (d, *J* = 8.6 Hz, 2H), 5.30 (s, 2H), 3.82 (s, 3H). Spectra were consistent with those reported previously.[11]

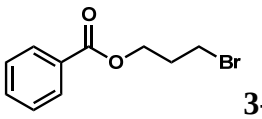


3-((tert-butyldimethylsilyl)oxy)propyl benzoate (22)

Prepared following representative procedure C with 3-((*tert*-butyldimethylsilyl)oxy)propan-1-ol[12] (0.129 g, 0.679 mmol) and pyridinium chloride to afford a light yellow oil (0.147 g, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.0 Hz, 2H), 7.59 – 7.52 (m, 1H), 7.47 – 7.40 (m, 2H), 4.42 (t, *J* = 6.3 Hz, 2H), 3.79 (t, *J* = 6.1 Hz, 2H), 1.98 (pent, *J* = 6.2 Hz, 2H), 0.90 (s, 9H), 0.06 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.6, 132.8, 130.5, 129.5, 128.3, 61.9, 59.5, 31.9, 25.9, 18.3, -5.4. **HRMS-ESI** (*m/z*): $[M+H]^+$ calcd for $C_{16}H_{27}O_3Si$, 295.1724; found, 295.1727.

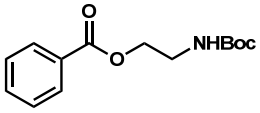
[11] Harned, A. M.; He, H.; Toy, P. H.; Flynn, D. L.; Hanson, P. R. *J. Am. Chem. Soc.* **2005**, *127*, 52.
[12] Caron, P.; Deslongchamps, P. *Org. Lett*. **2010** , *12*, 508.



3-bromopropyl benzoate (23)

Prepared using representative procedure C with 3-bromopropan-1-ol (0.159 g, 1.14 mmol) and pyridinium tosylate to obtain a light yellow oil (0.221 g, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.8 Hz, 2H), 7.62 – 7.53 (m, 1H), 7.45 (dd, *J* = 8.0, 7.2 Hz, 2H), 4.47 (t, *J* = 5.9 Hz, 2H), 3.56 (t, *J* = 6.5 Hz, 2H), 2.33 (pent, *J* = 6.2 Hz, 2H). Spectra were consistent with those reported previously.[13]

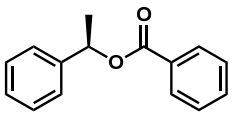


2-((tert-butoxycarbonyl)amino)ethyl benzoate (24)

Prepared using representative procedure C with *tert*-butyl (2-hydroxyethyl)carbamate (0.162 g, 1.00 mmol) and pyridinium chloride. Diethyl ether was used as extraction solvent instead of hexane. The crude product was purified by column chromatography (30 : 70, ethyl acetate : hexane) to obtain a white solid (0.202 g, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.1 Hz, 2H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 4.84 (bs, 1H), 4.38 (t, *J* = 5.3 Hz, 2H), 3.54 (q, *J* = 5.5 Hz, 2H), 1.44 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.5, 155.8, 133.1, 129.8, 129.6, 128.3, 79.5, 64.2, 39.7, 28.3. **HRMS-ESI** (*m/z*): $[M+Na]^+$ calcd for $C_{14}H_{19}NNaO_4$, 288.1206; found, 288.1209.

[13] Mukhopadhyay, U.; Soghomonyan, S.; Yeh, H.; Flores, L.; Shavrin, A.; Vogin, A.; Gelovani, J.; Alauddin, M. M. *Nucl. Med. Biol.*, **2008**, *35*, 697.

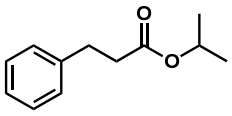


(*R*)-1-phenylethyl benzoate (25)

Prepared using representative procedure C with (*R*)-1-phenylethanol (0.061 g, 0.50 mmol) and pyridinium triflate. The homogenous solution was heated to 50 °C for 43 h using a heating block. A colorless oil was obtained (0.095 g, 84%) after column chromatography (5 : 95, ethyl acetate : hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.0 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.41 (m, 4H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 6.14 (q, *J* = 6.6 Hz, 1H), 1.68 (d, *J* = 6.6 Hz, 3H). Spectra were consistent with those reported previously.[14]

HPLC Chiracel OD column (99.5 : 0.5 hexanes : isopropanol, 1.0 mL/min) t_R; 15.95 min (major); 17.57 min (minor): 96% ee.



isopropyl 3-phenylpropanoate (26)

Prepared using representative procedure C with 3-phenylpropanoyl imidazole[15] (0.288 g, 1.44 mmol), dry isopropanol (0.079 g, 1.31 mmol) and pyridinium triflate to afford a colorless oil (0.207 g, 82%). The reaction was heated to 40 °C for 26 h using a heating block.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.23 – 7.17 (m, 3H), 5.00 (hept, *J* = 6.3 Hz, 1H), 2.94 (t, *J* = 7.8 Hz, 2H), 2.59 (t, *J* = 7.8 Hz, 2H), 1.20 (d, *J* = 6.2 Hz, 6H). Spectra were consistent with those reported previously.[16]

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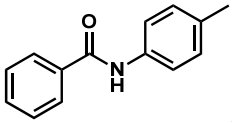
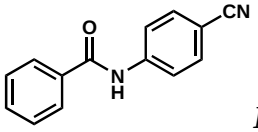
[14] Chen, C.; Munot, Y. *J. Org. Chem.* **2005**, *70*, 8625.
[15] Kise, N.; Kaneko, H.; Uemoto, N.; Yoshida, J. *Tetrahedron*, **1995** , *36*, 8839.
[16] Salome, C.; Kohn, H. *Tetrahedron*, **2009**, *65*, 456.



***N*-(*p*-tolyl)benzamide (27)**

Prepared using representative procedure C with *p*-toluidine (0.113 g, 1.05 mmol) and pyridinium chloride to afford a white solid (0.213 g, 96%). The reaction mixture was stirred at room temperature for 10 minutes.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 6.9 Hz, 2H), 7.76 (bs, 1H), 7.60 – 7.43 (m, 5H), 7.18 (d, *J* = 7.7 Hz, 2H), 2.35 (s, 3H). Spectra were consistent with those reported previously.[17]



***N*-(4-cyanophenyl)benzamide (28)**

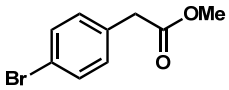
Prepared using representative procedure C with 4-aminobenzonitrile (0.094 g, 0.794 mmol) and pyridinium chloride to afford a white solid (0.170 g, 96%). The mixture was heated to 40 °C for 8 h.

^{1}H NMR (500 MHz, $CDCl_3$ with 1 drop of CD_3OD) δ 7.86 (d, *J* = 7.1 Hz, 2H), 7.83 – 7.79 (m, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.56 – 7.49 (m, 1H), 7.46 (d, *J* = 8.1 Hz, 2H) Spectra were consistent with those reported previously.[18]

[17] Zhang, L.; Su, S.; Wu, H.; Wang, S. *Tetrahedron*, **2009**, *65*, 10022.
[18] Sasaki, K.; Crich, D. *Org. Lett*. **2011**, *13*, 2256.

Preparation of Esters from Carboxylic Acids: Representative Procedure D

Carboxylic acid (0.5 mmol) and imidazole carbamate (1.0 mmol) were placed in a dry 20 mL vial with a Teflon tape-coated thread and a magnetic stir bar, followed by addition of 1.0 mL of 1.0 M solution of pyridinium triflate in dry MeCN in one portion at room temperature. The vial was quickly sealed with a plastic cap (***CAUTION: gas is evolved during the course of the reaction! All experiments should be performed behind a blast shield if a sealed container is used!*****).** The reaction mixture was then stirred at room temperature for 10 minutes and then heated to 40 °C using a heating block for 24 h. The mixture was cooled to room temperature and then the vial was carefully opened. (***CAUTION: vial under pressure!***). The reaction was diluted with diethyl ether (15 mL) and washed with 1 M HCl (15 mL). The aqueous layer was back-extracted with diethyl ether (3 × 15 mL) and the organic fractions were combined, washed with saturated $NaHCO_3$ (aq) and brine. The organic fraction was dried over anhydrous $MgSO_4$, and concentrated *in vacuo* to afford the desired ester.

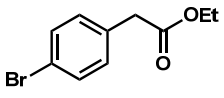


methyl 2-(4-bromophenyl)acetate (29)

Prepared using representative procedure D with methyl 1-imidazolecarboxylate[19] (0.097 g, 0.778 mmol) and 2-(4-bromophenyl)acetic acid (0.084 g, 0.389 mmol) to obtain a yellow oil (0.082 g, 93%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, J = 8.3 Hz, 2H), 7.16 (d, J = 8.3 Hz, 2H), 3.69 (s, 3H), 3.58 (s, 2H). Spectra were consistent with those reported previously.[20]

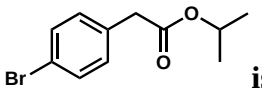
[19] Heller, S. T.; Sarpong, R. *Org. Lett*. **2010**, *12*, 4572.
[20] Demel, J.; Lamac, M.; Cejka, J.; Stepnicka, P. *ChemSusChem,* **2009**, 442.



ethyl 2-(4-bromophenyl)acetate (30)

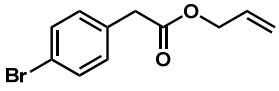
Prepared using representative procedure D with ethyl 1-imidazolecarboxylate[19] (0.109 g, 0.778 mmol) and 2-(4-bromophenyl)acetic acid (0.084 g, 0.389 mmol) to obtain a yellow oil (0.083 g, 88%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.56 (s, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). Spectra were consistent with those reported previously.[21]



isopropyl 2-(4-bromophenyl)acetate (31)

Prepared using representative procedure D with isopropyl 1-imidazolecarboxylate (0.120 g, 0.778 mmol) and 2-(4-bromophenyl)acetic acid (0.084 g, 0.389 mmol) to obtain a yellow oil (0.081 g, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 2H), 5.00 (hept, *J* = 6.3 Hz, 1H), 3.53 (s, 2H), 1.22 (d, *J* = 6.3 Hz, 6H). Spectra were consistent with those reported previously.[19]

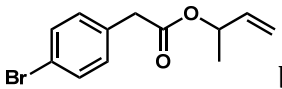


allyl 2-(4-bromophenyl)acetate (32)

Prepared using representative procedure D with allyl 1-imidazolecarboxylate[19] (0.118 g, 0.778 mmol) and 2-(4-bromophenyl)acetic acid (0.084 g, 0.389 mmol) to obtain a yellow oil (0.081 g, 82%).

[21]Katz, C. E.; Jeffrey, A. *J. Am. Chem. Soc.* **2003**, *125*, 13948.

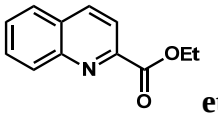
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 5.89 (ddt, *J* = 17.1, 10.4, 5.8 Hz, 1H), 5.32 – 5.19 (m, 2H), 4.59 (d, *J* = 5.8 Hz, 2H), 3.60 (s, 2H). Spectra were consistent with those reported previously.[19]



but-3-en-2-yl 2-(4-bromophenyl)acetate (33)

Prepared using representative procedure D with but-3-en-2-yl 1-imidazolecarboxylate[19] (0.129 g, 0.778 mmol) and 2-(4-bromophenyl)acetic acid (0.084 g, 0.389 mmol) to obtain a yellow oil (0.091 g, 87%).

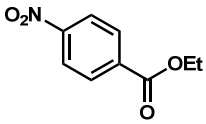
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 5.81 (ddd, *J* = 16.8, 10.6, 5.9 Hz, 1H), 5.35 (pent, *J* = 6.4 Hz, 1H), 5.23 – 5.07 (m, 2H), 3.57 (s, 2H), 1.30 (d, *J* = 6.5 Hz, 3H). Spectra were consistent with those reported previously.[19]



ethyl quinoline-2-carboxylate (36)

Prepared using representative procedure D with ethyl 1-imidazolecarboxylate[19] (0.140 g, 1.00 mmol) and quinoline-2-carboxylic acid (0.087 g, 0.500 mmol) to obtain colorless oil (0.081 g, 80%).

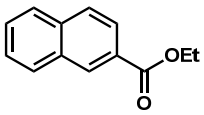
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 – 8.27 (m, 2H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.79 (dd, *J* = 8.4Hz, 1H), 7.65 (dd, *J* = 7.2 Hz, 1H), 4.56 (q, *J* = 7.1 Hz, 2H), 1.49 (t, *J* = 7.1 Hz, 3H). Spectra were consistent with those reported previously.[19]



ethyl 4-nitrobenzoate (34)

Prepared using representative procedure D with ethyl 1-imidazolecarboxylate[19] (0.140 g, 1.00 mmol) and 4-nitrobenzoic acid (0.084 g, 0.500 mmol) to obtain a yellow solid (0.0726 g, 74%). DMF was used as the solvent for this reaction instead of MeCN.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.8 Hz, 2H), 8.22 (d, *J* = 8.8 Hz, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.46 (t, *J* = 7.5 Hz, 3H). Spectra were consistent with those reported previously.[22]

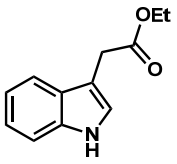


ethyl 2-naphthoate (39)

Prepared using representative procedure D with ethyl 1-imidazolecarboxylate[19] (0.112 g, 0.800 mmol) and 2-naphthoic acid (0.069 g, 0.40 mmol) to obtain a light yellow oil (0.058 g, 72%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.07 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.62 – 7.52 (m, 2H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.45 (t, *J* = 7.1 Hz, 3H). Spectra were consistent with those reported previously.[23]

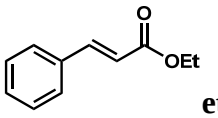
[22] Kiran, Y. B.; Ikeda, R.; Sakai, N.; Konakahara, T. *Synthesis*, **2010**, *2*, 276.
[23] Kotha, S.; Shah, V.; Mandal, K. *Adv. Synth. Catal.* **2007**, *349*, 1159.



ethyl 2-(1*H*-indol-3-yl)acetate (35)

Prepared using representative procedure D with ethyl 1-imidazolecarboxylate[19] (0.200 g, 1.43 mmol) and 2-(1*H*-indol-3-yl)acetic acid (0.125 g, 0.713 mmol) to obtain a yellow oil (0.131 g, 90%) after column chromatography (20 : 80, ethyl acetate : hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (bs, 1H), 7.63 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.23 – 7.17 (m, 2H), 7.16 – 7.11 (m, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). Spectra were consistent with those reported previously.[24]

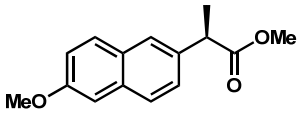


ethyl cinnamate (38)

Prepared using representative procedure D with ethyl 1-imidazolecarboxylate[19] (0.258 g, 1.84 mmol) and cinnamic acid (0.136 g, 0.919 mmol) to obtain a yellow oil (0.128 g, 79%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 16.1 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.42 – 7.35 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). Spectra were consistent with those reported previously.[25]

[24] Yadav, J. S.; Reddy, B. V. S.; Satheesh, G. *Tetrahedron*, **2003**, *44*, 8331.
[25] Peng, Y.; Chen, J.; Ding, J.; Liu, M.; Gao, W.; Wu, H. *Synthesis*, **2011**, *2*, 213.

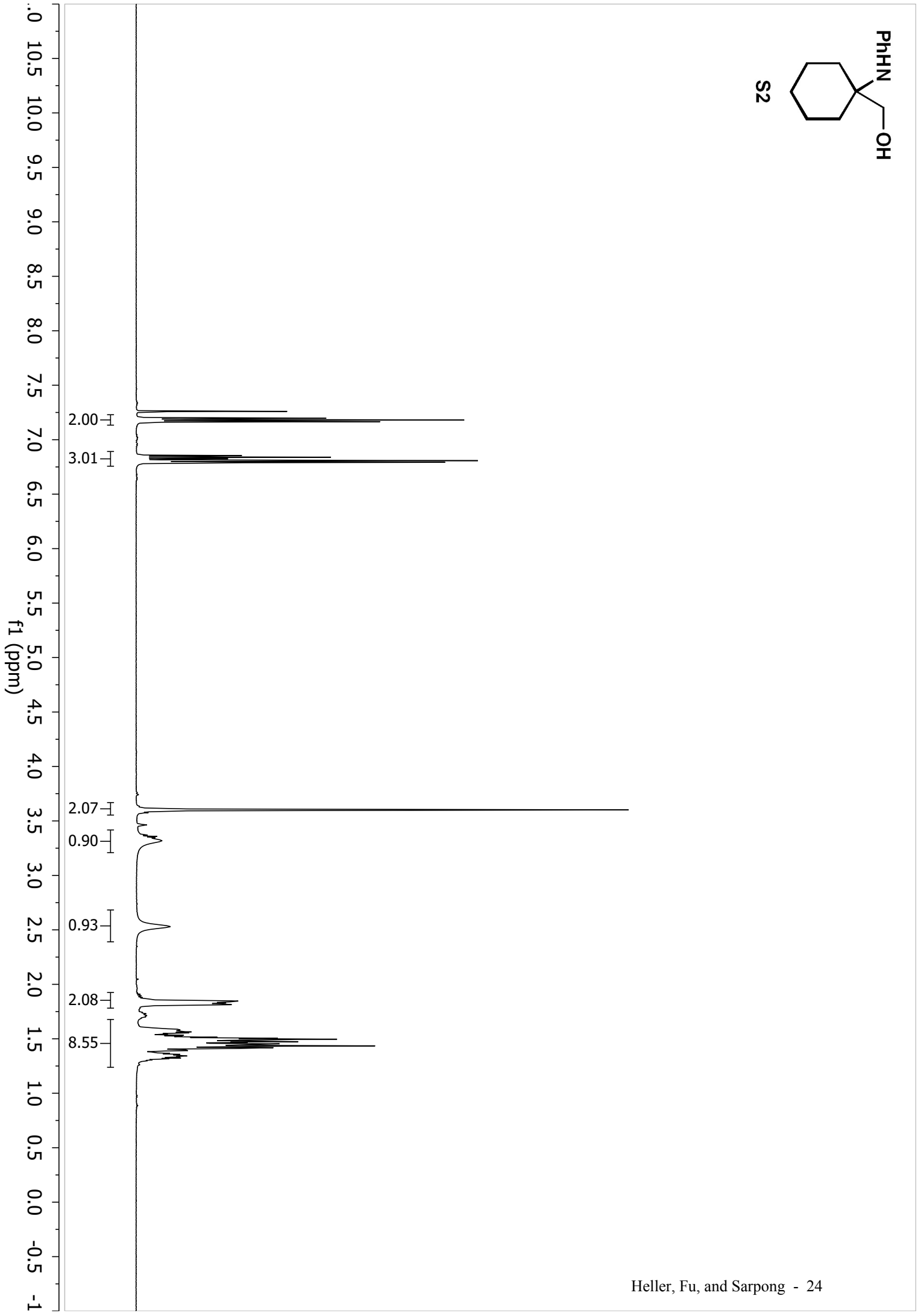


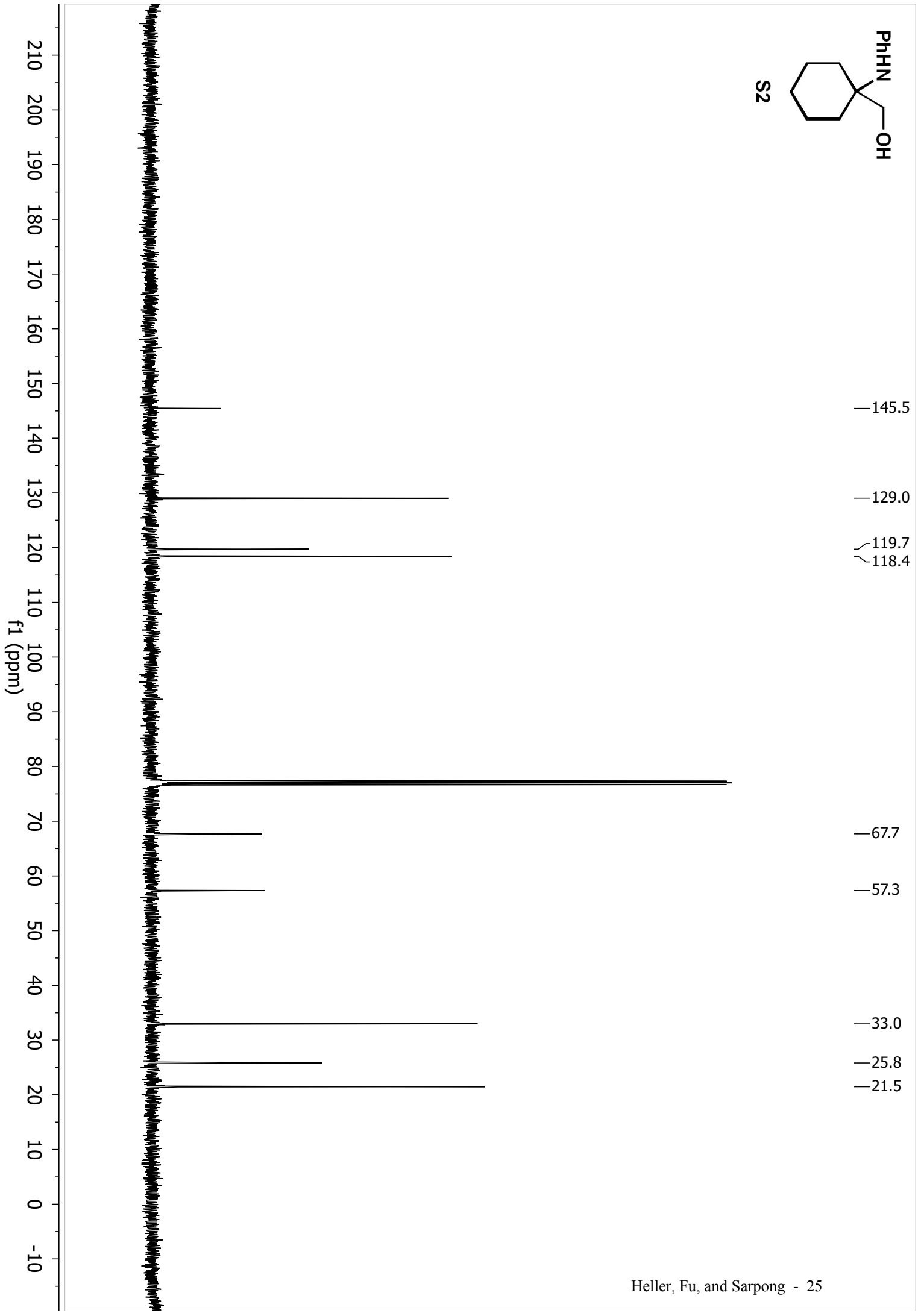
(*R*)-methyl 2-(6-methoxynaphthalen-2-yl)propanoate (37)

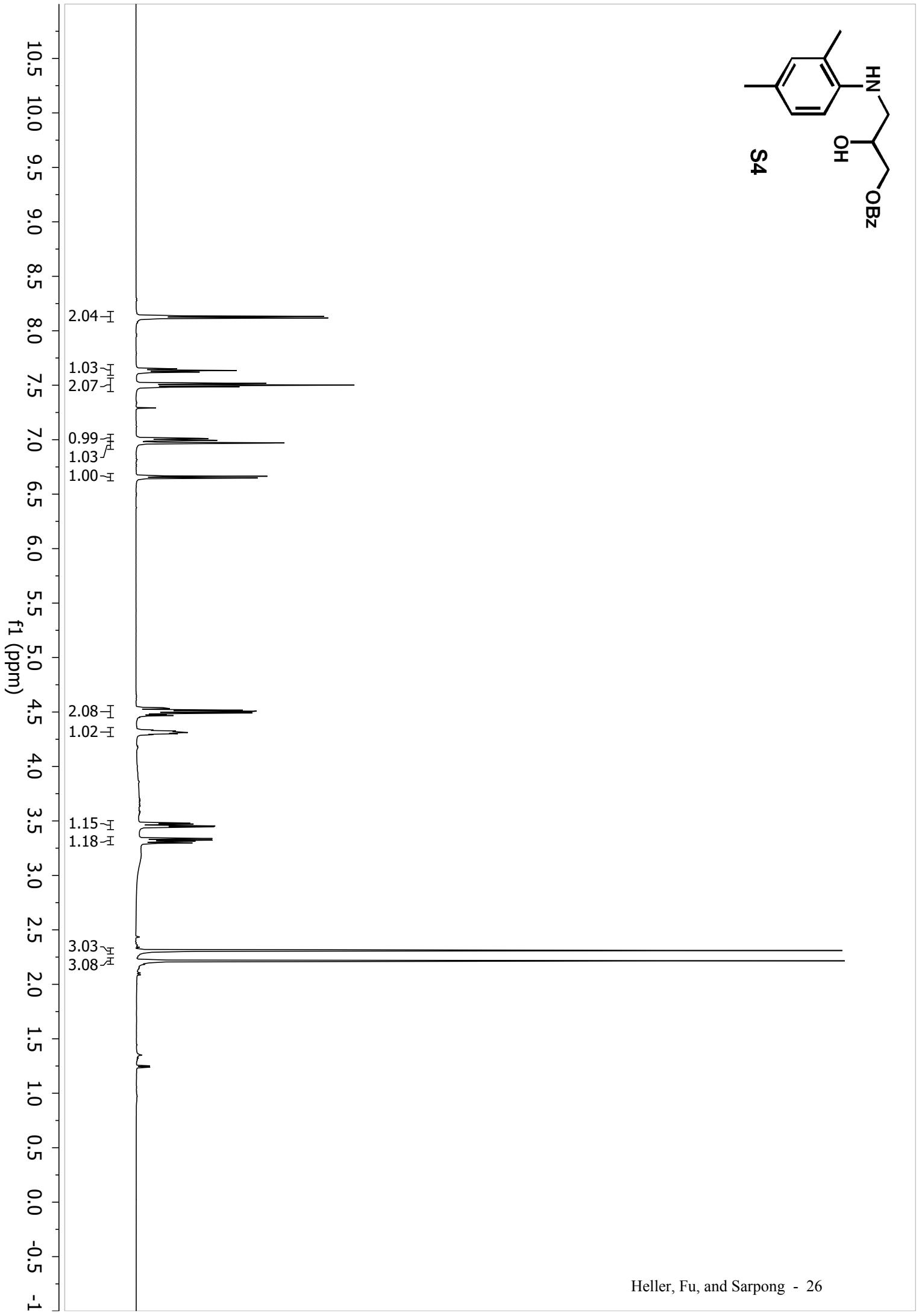
Prepared using representative procedure D with methyl 1-imidazolecarboxylate[19] (0.126 g, 1.00 mmol) and (*R*)-2-(6-methoxynaphthalen-2-yl)propanoic acid (0.115 g, 0.500 mmol) to obtain a white solid (0.109 g, 89%).

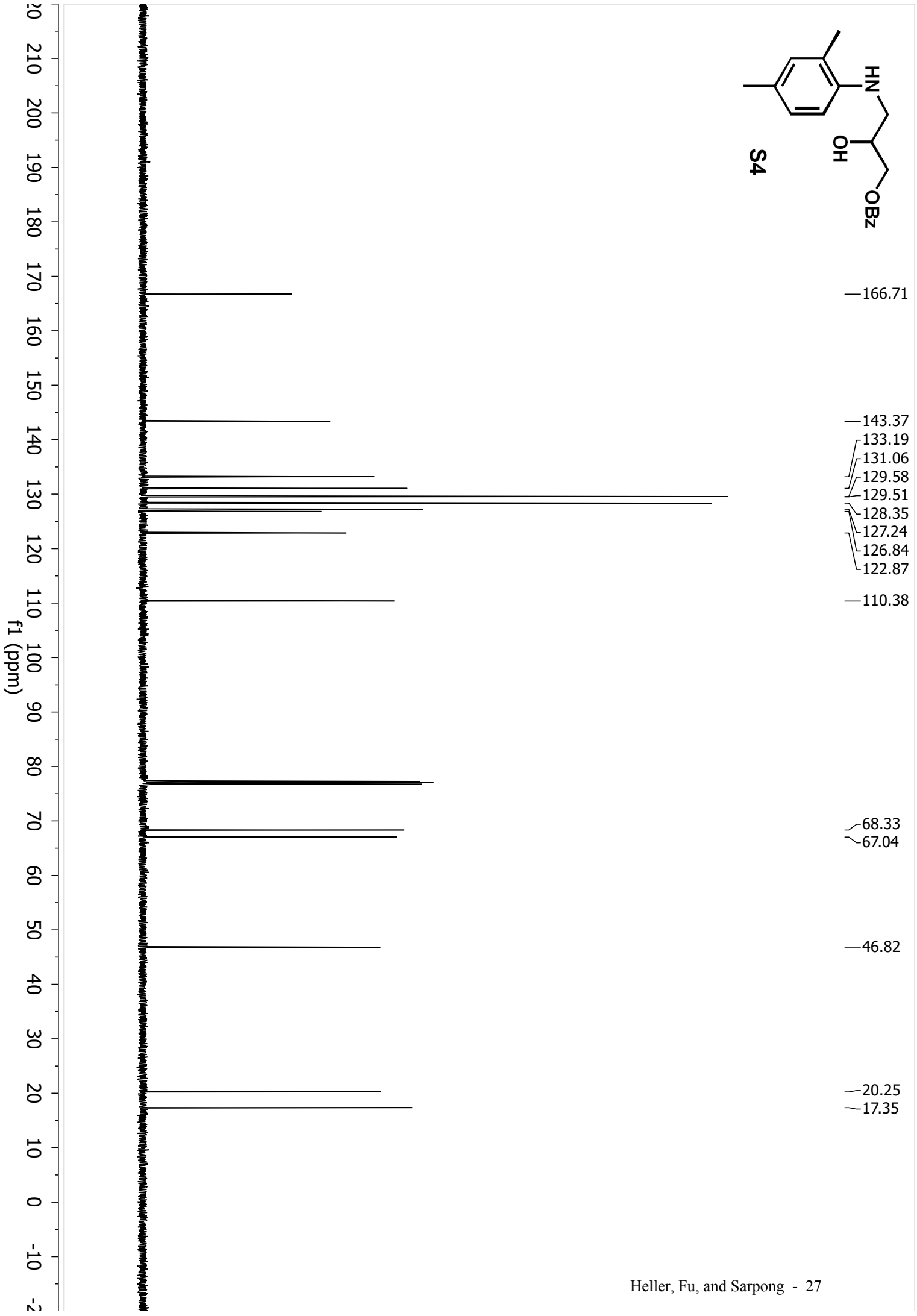
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 1.8 Hz, 1H), 7.40 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.16 – 7.10 (m, 2H), 3.91 (s, 3H), 3.86 (q, *J* = 7.2 Hz, 1H), 3.67 (s, 3H), 1.59 (s, 3H). Spectra were consistent with those reported previously.[26] **HPLC** (99 : 1 hexanes : 2-propanol, 1.0 mL/min, t_R 8.31 min (major), 9.08 min (minor), 99% *ee*.

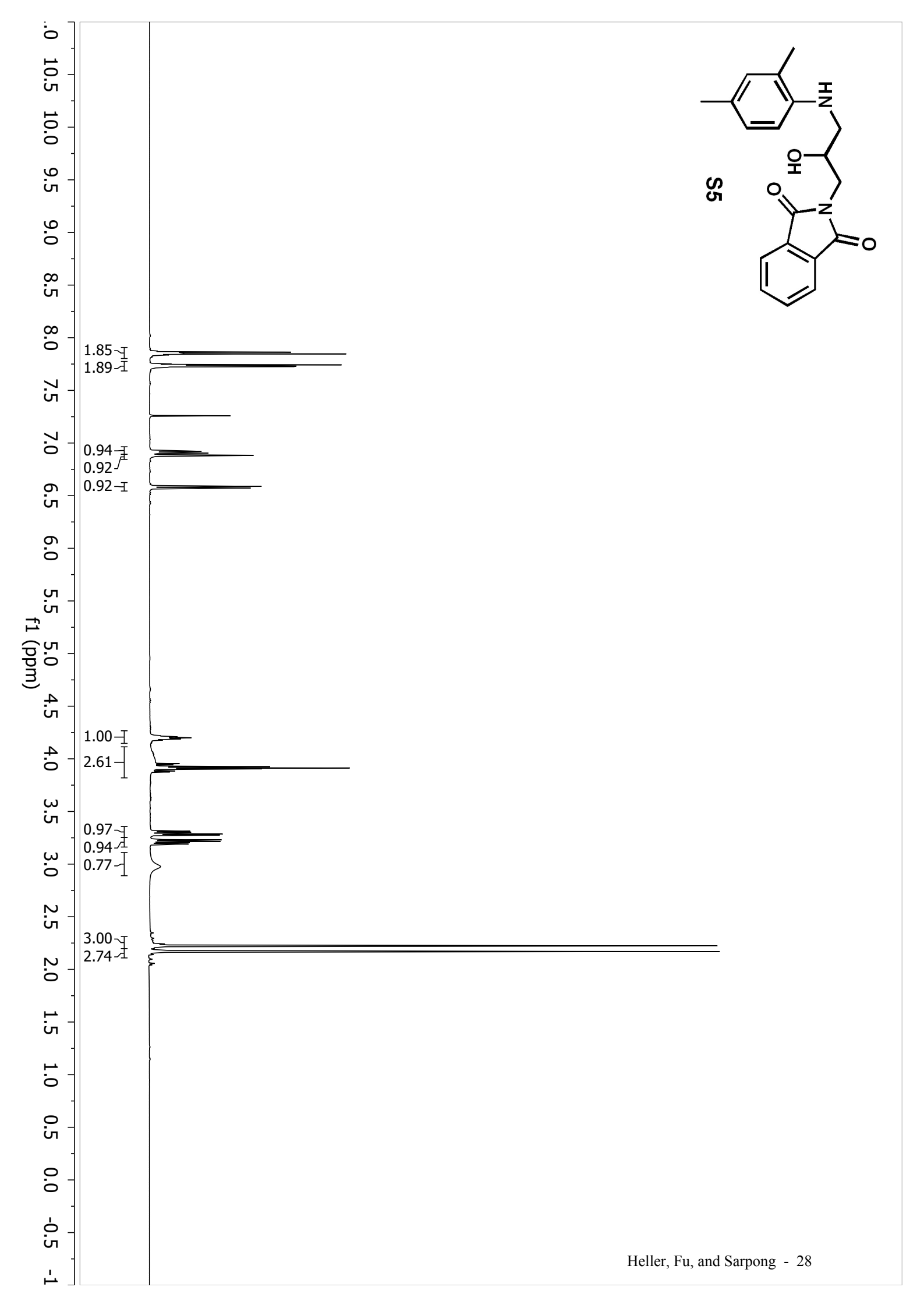
[26] Heller, S. T.; Sarpong R. *Tetrahedron*, **2011**, *67*, 8851.

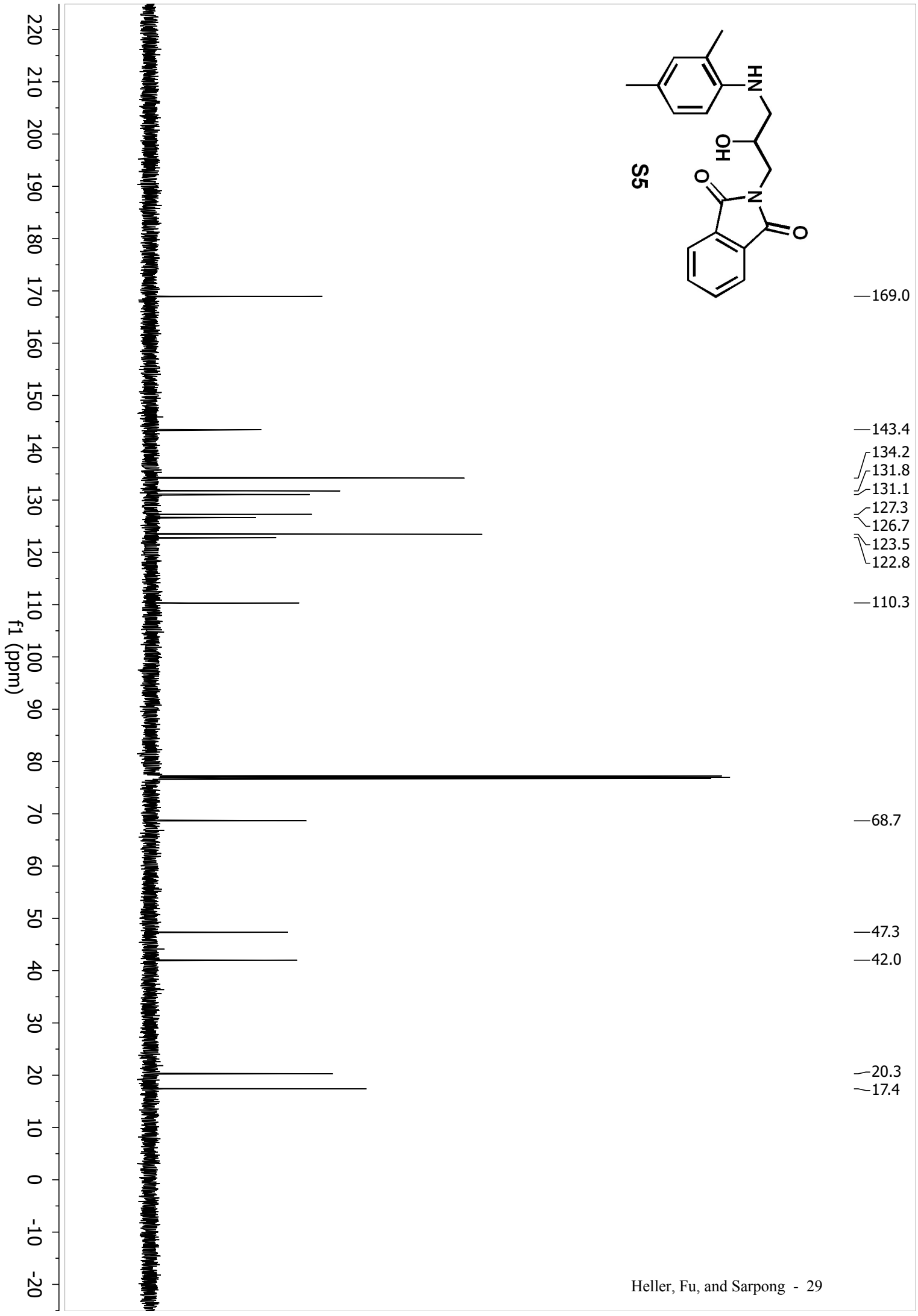

PhHN
OH
S2
2.00
3.01
2.07
0.90
0.93
2.08
8.55
f1 (ppm)

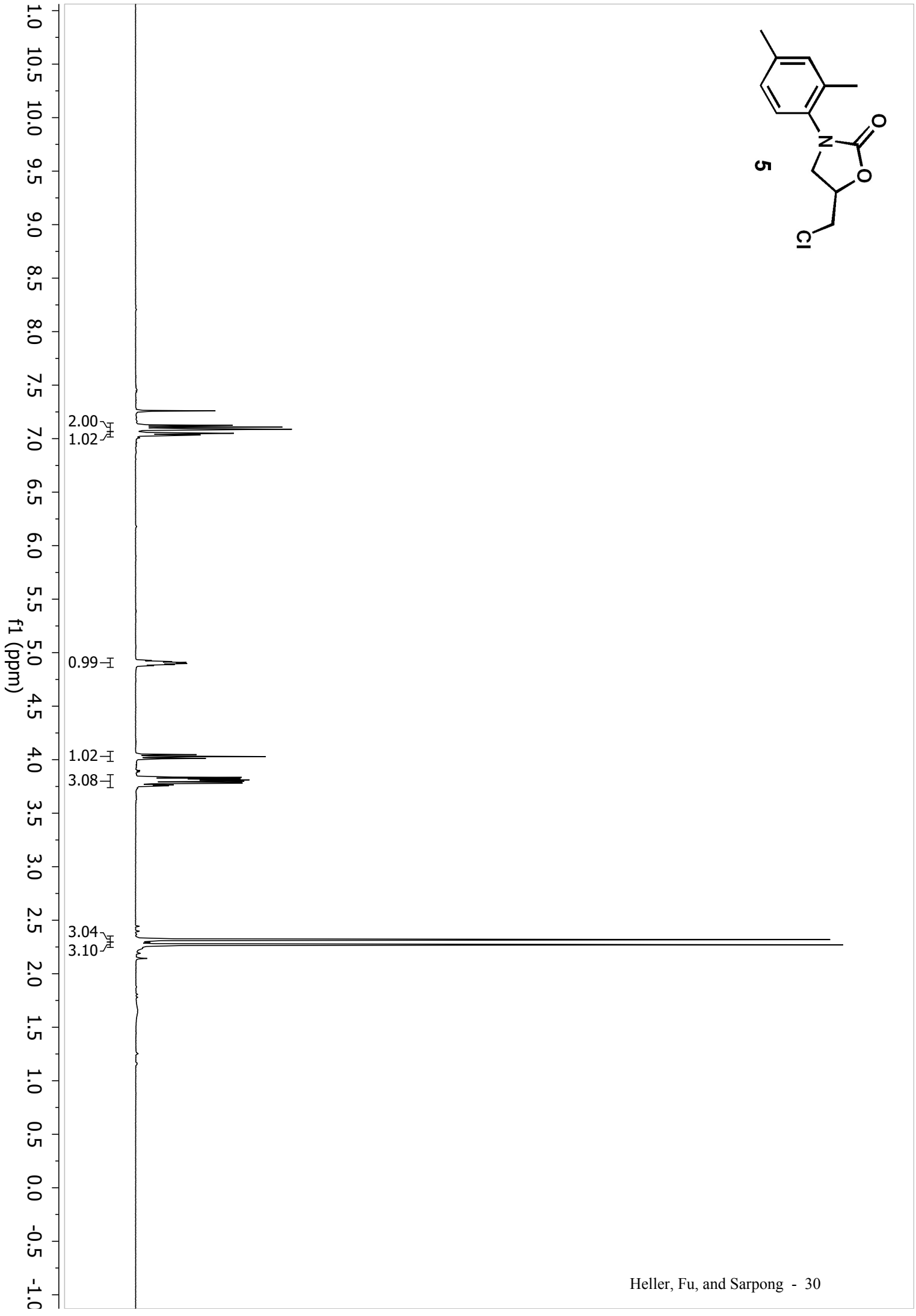

PhHN
OH
S2
145.5
129.0
119.7
118.4
67.7
57.3
33.0
25.8
21.5
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

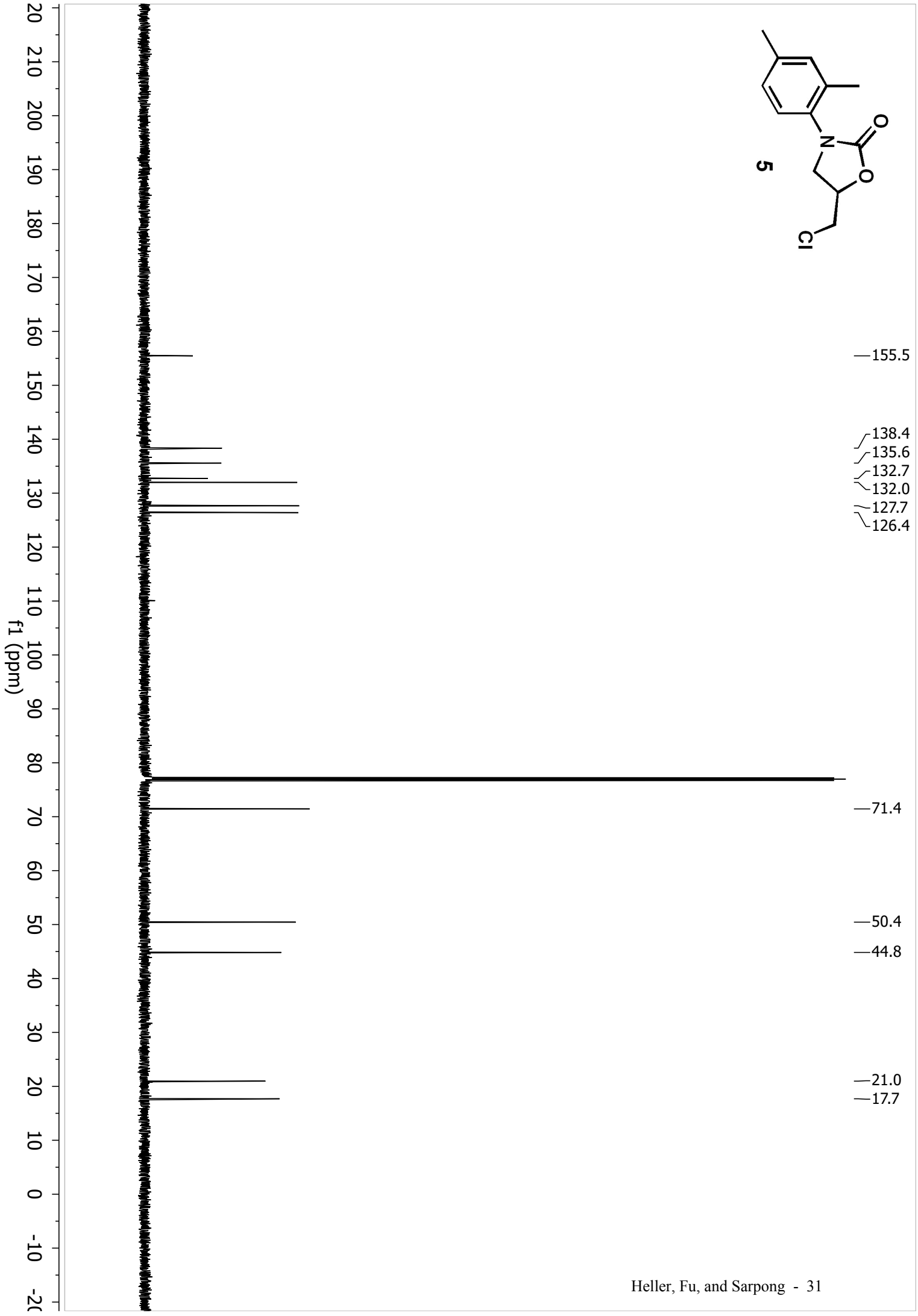

S4
HN
OH
OBz
2.04
1.03
2.07
0.99
1.03
1.00
2.08
1.02
1.15
1.18
3.03
3.08
f1 (ppm)

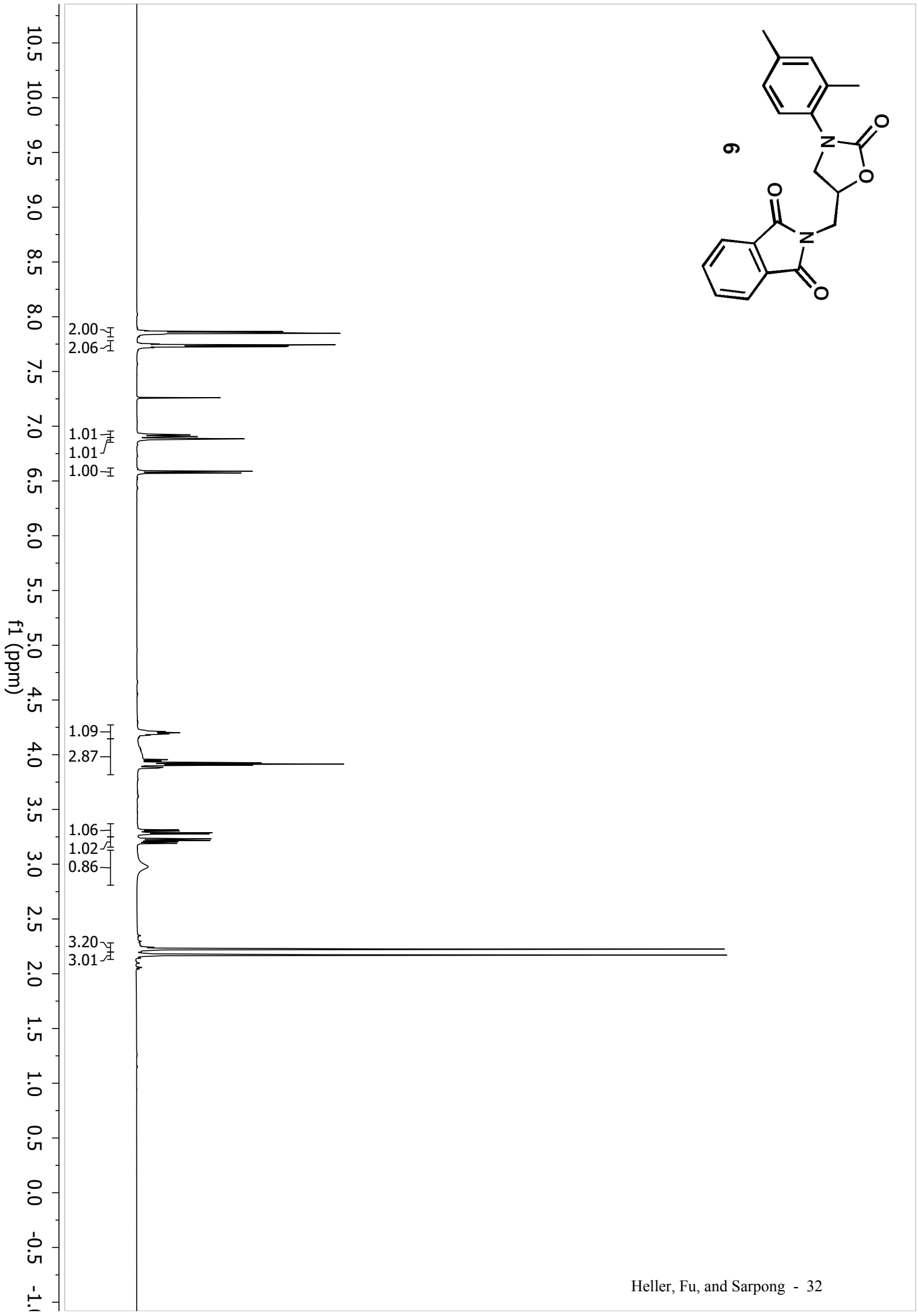

S4
HN
OH
OBz
166.71
143.37
133.19
131.06
129.58
129.51
128.35
127.24
126.84
122.87
110.38
68.33
67.04
46.82
20.25
17.35
f1 (ppm)

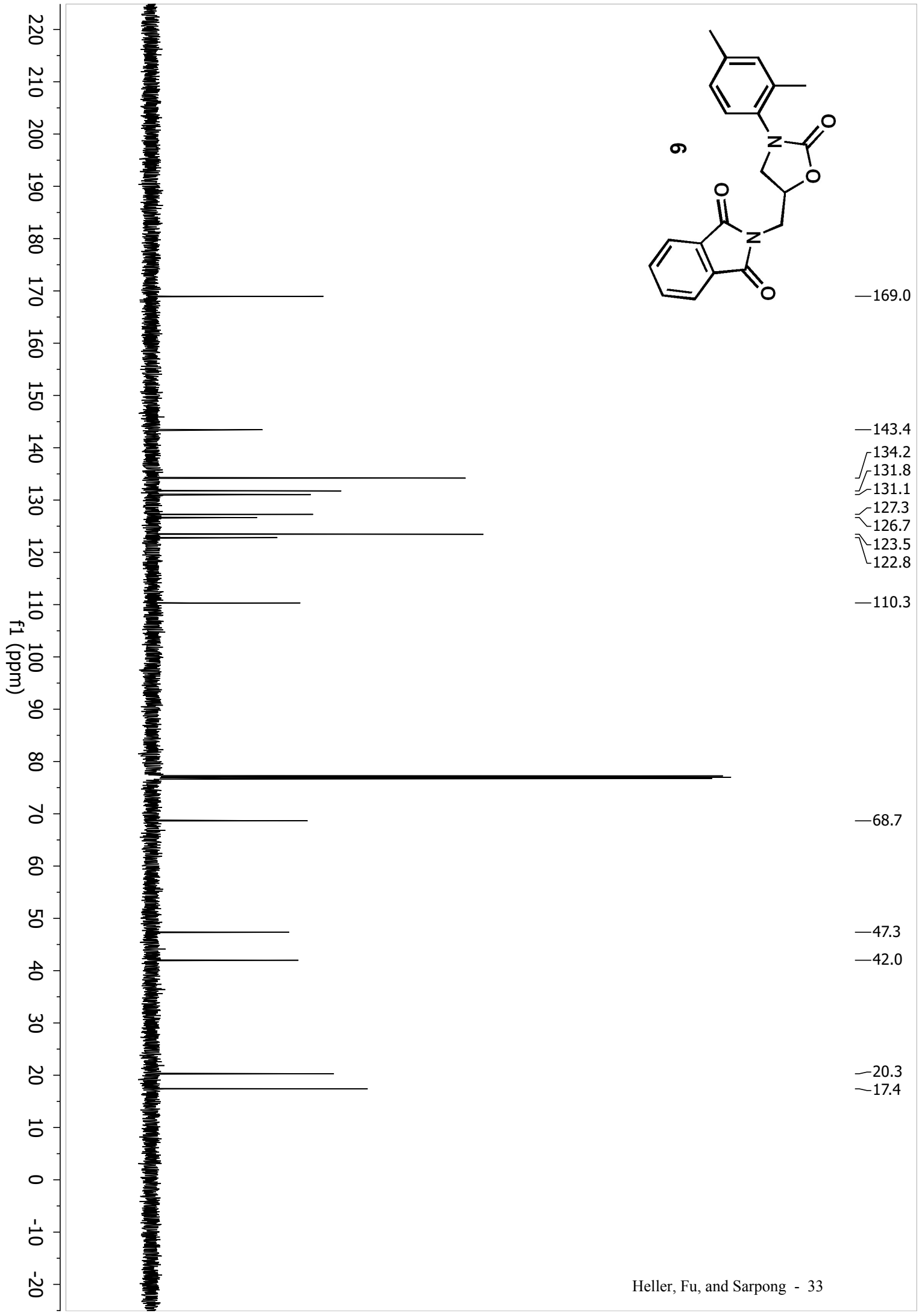

S5
HN
OH
N
O
O
1.85
1.89
0.94
0.92
0.92
1.00
2.61
0.97
0.94
0.77
3.00
2.74
f1 (ppm)

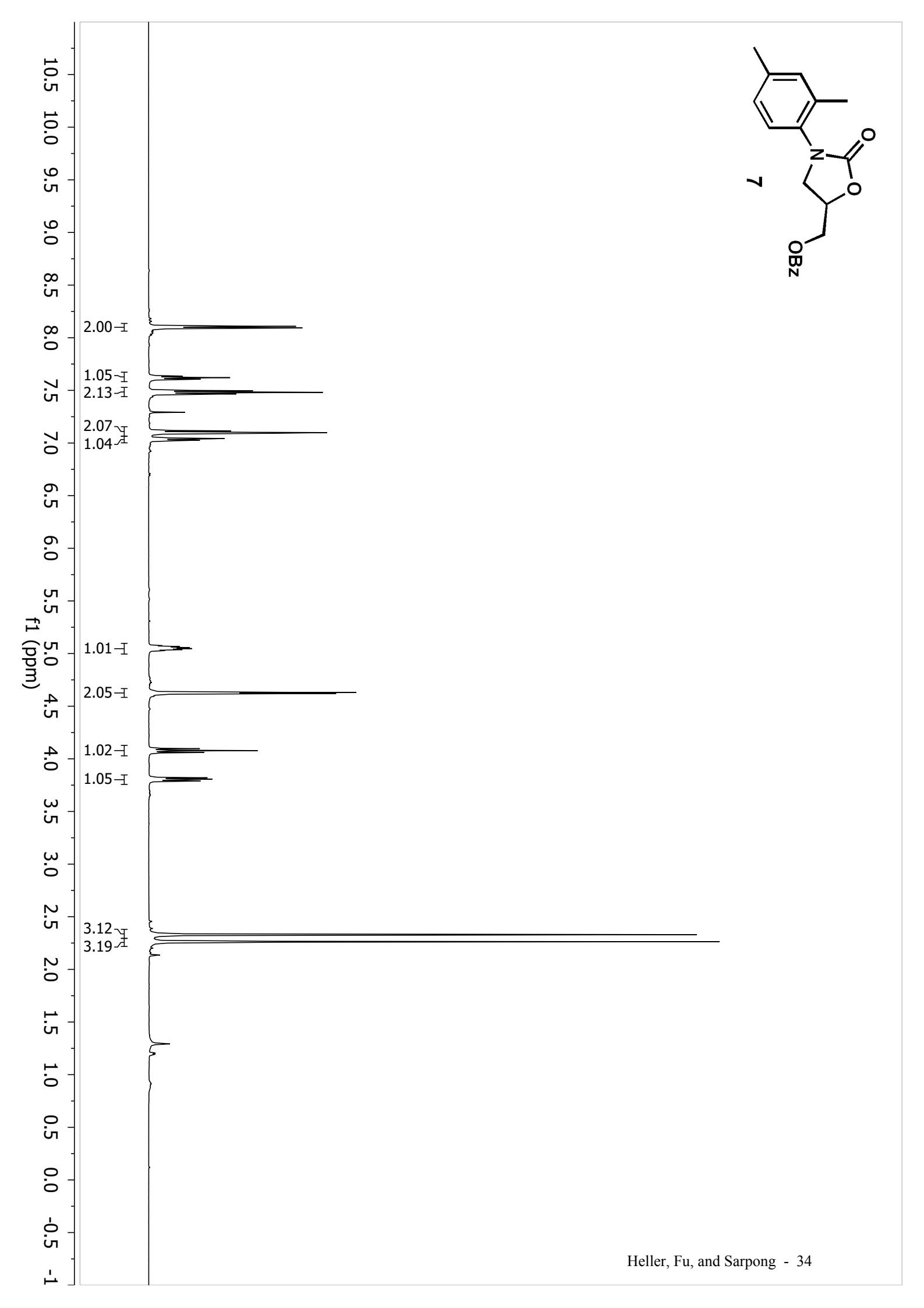

S5
HN
OH
O
N
O
169.0
143.4
134.2
131.8
131.1
127.3
126.7
123.5
122.8
110.3
68.7
47.3
42.0
20.3
17.4
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20

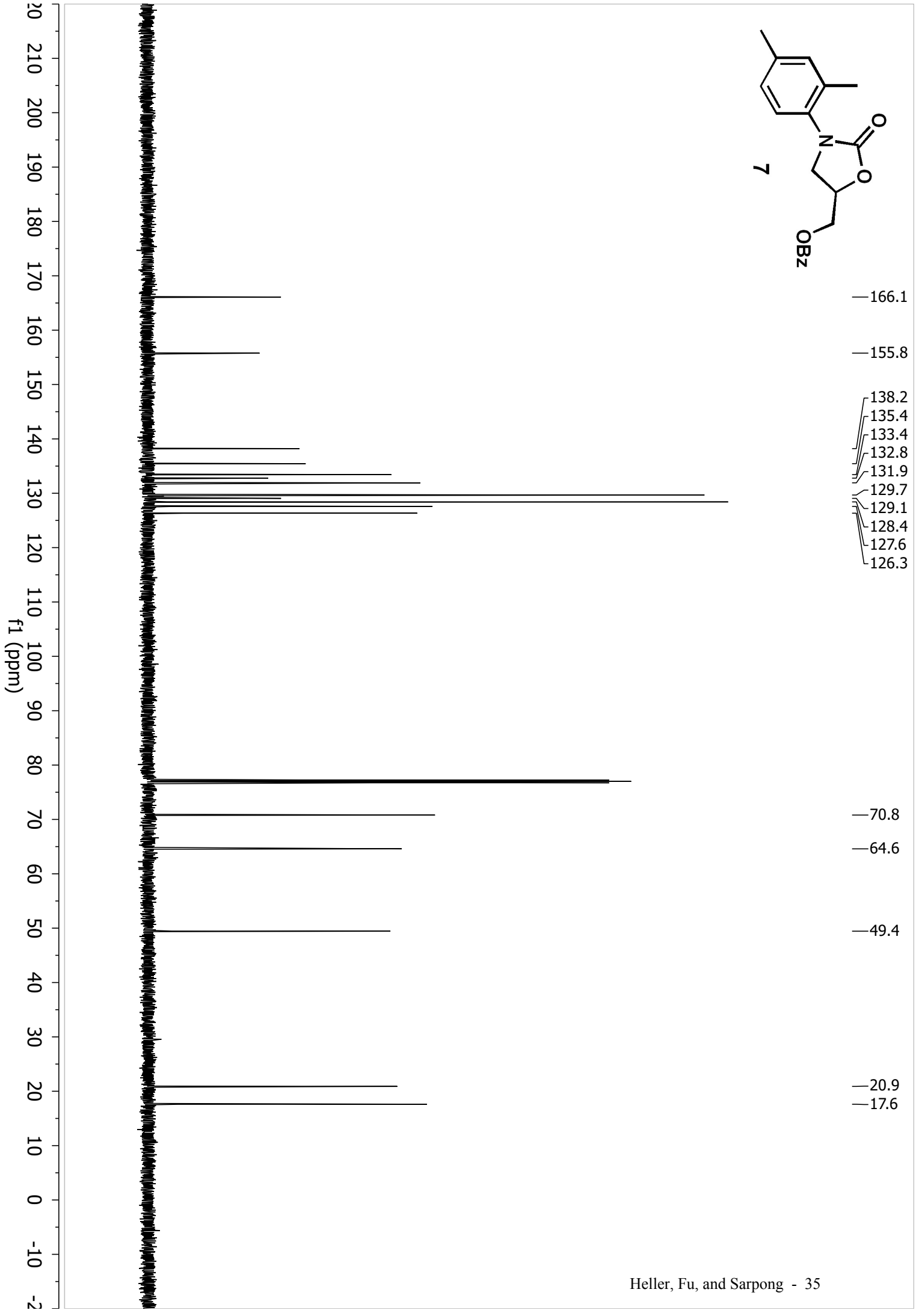

5
O
N
O
Cl
2.00
1.02
0.99
1.02
3.08
3.04
3.10
f1 (ppm)
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

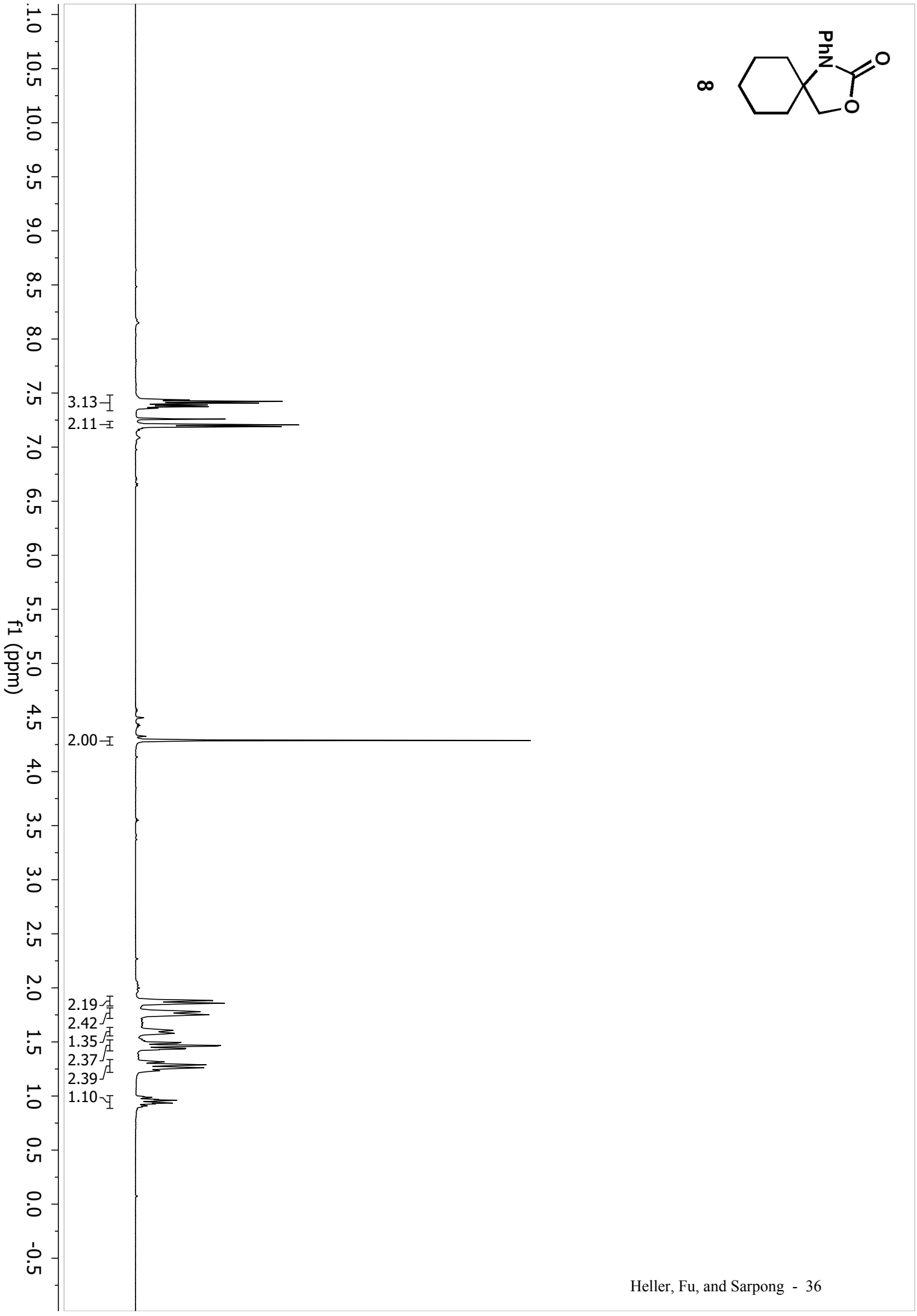

5
O
N
O
Cl
155.5
138.4
135.6
132.7
132.0
127.7
126.4
71.4
50.4
44.8
21.0
17.7
f1 (ppm)
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20

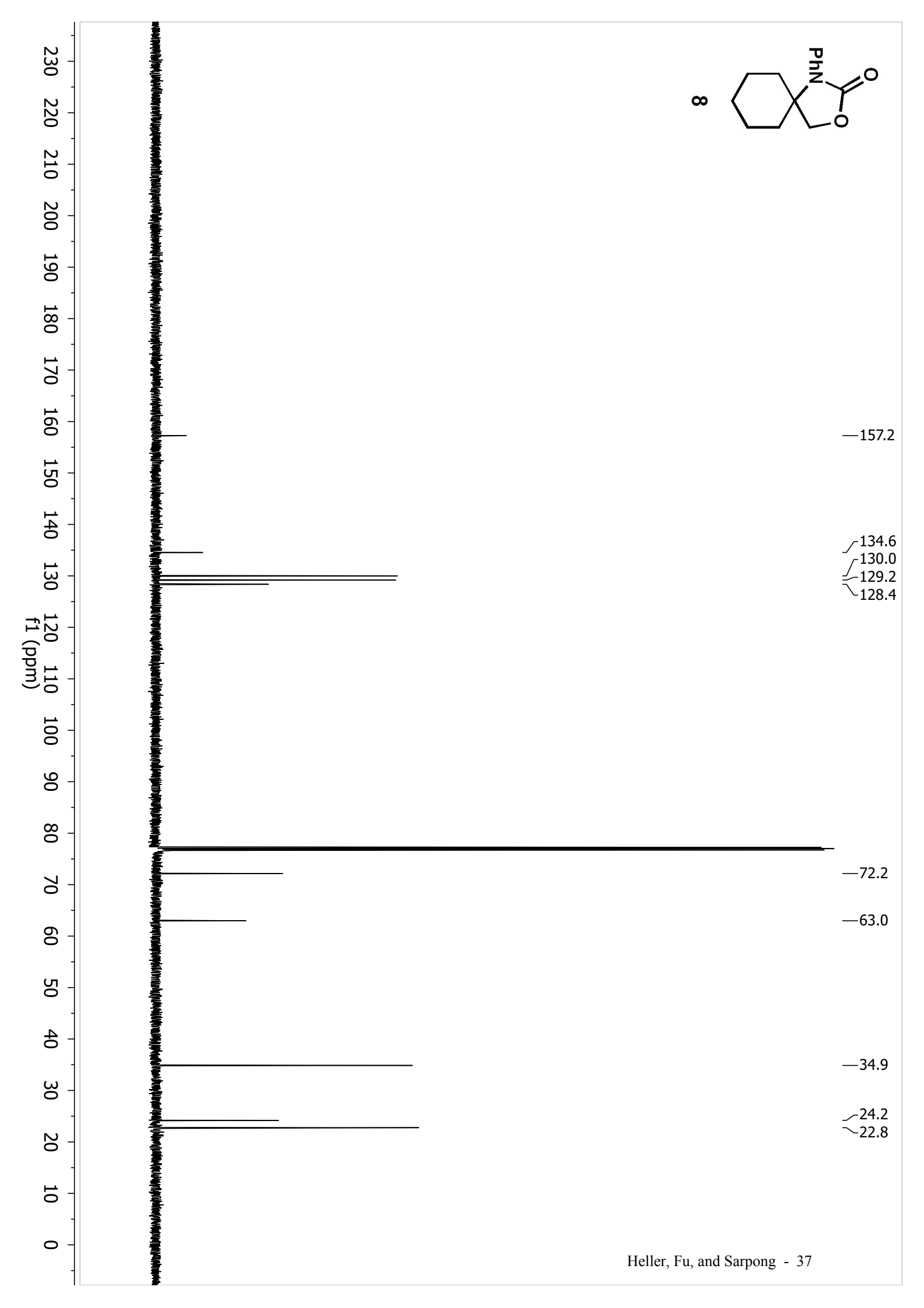

6
2.00
2.06
1.01
1.01
1.00
1.09
2.87
1.06
1.02
0.86
3.20
3.01
f1 (ppm)

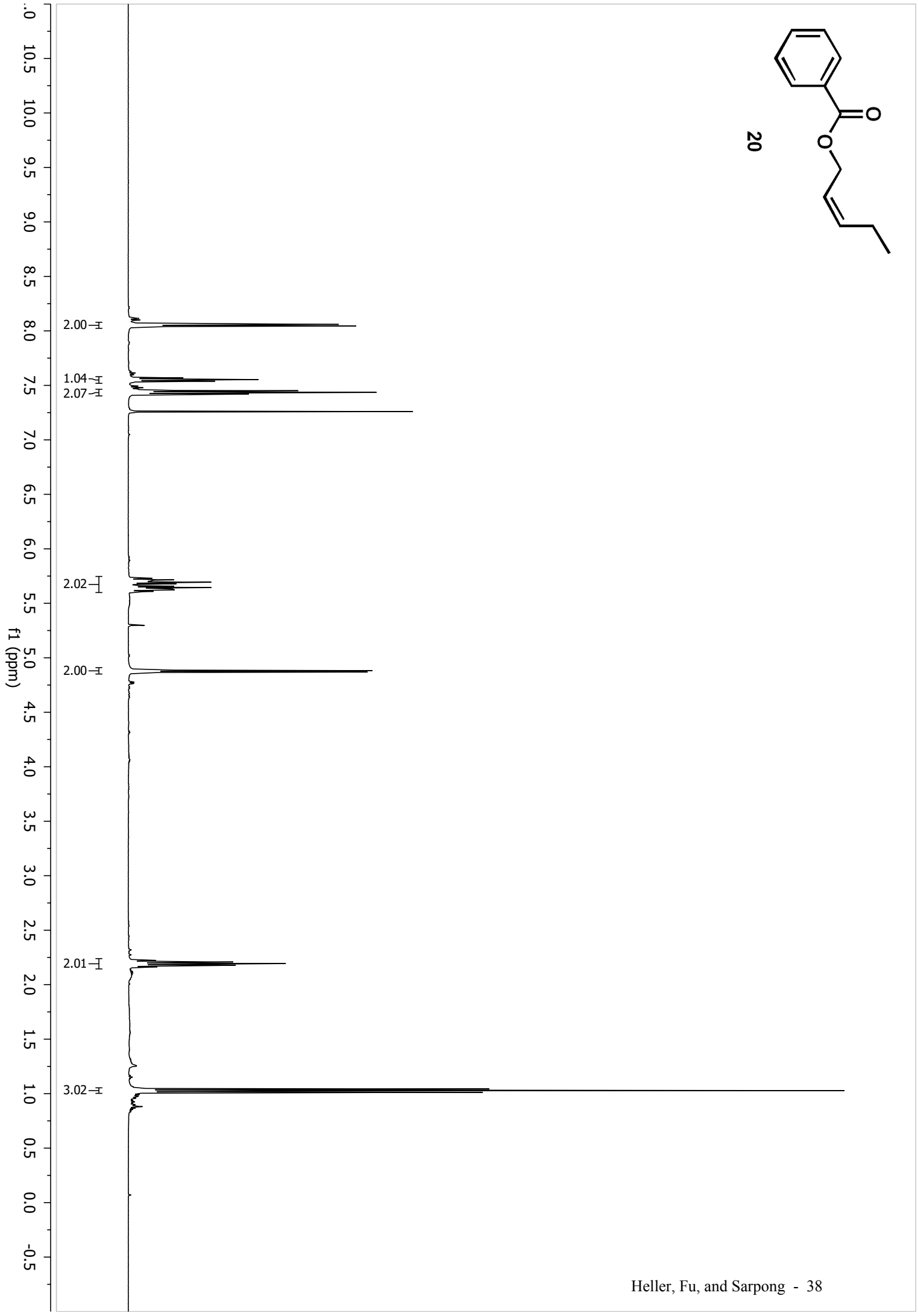

6
169.0
143.4
134.2
131.8
131.1
127.3
126.7
123.5
122.8
110.3
68.7
47.3
42.0
20.3
17.4
f1 (ppm)

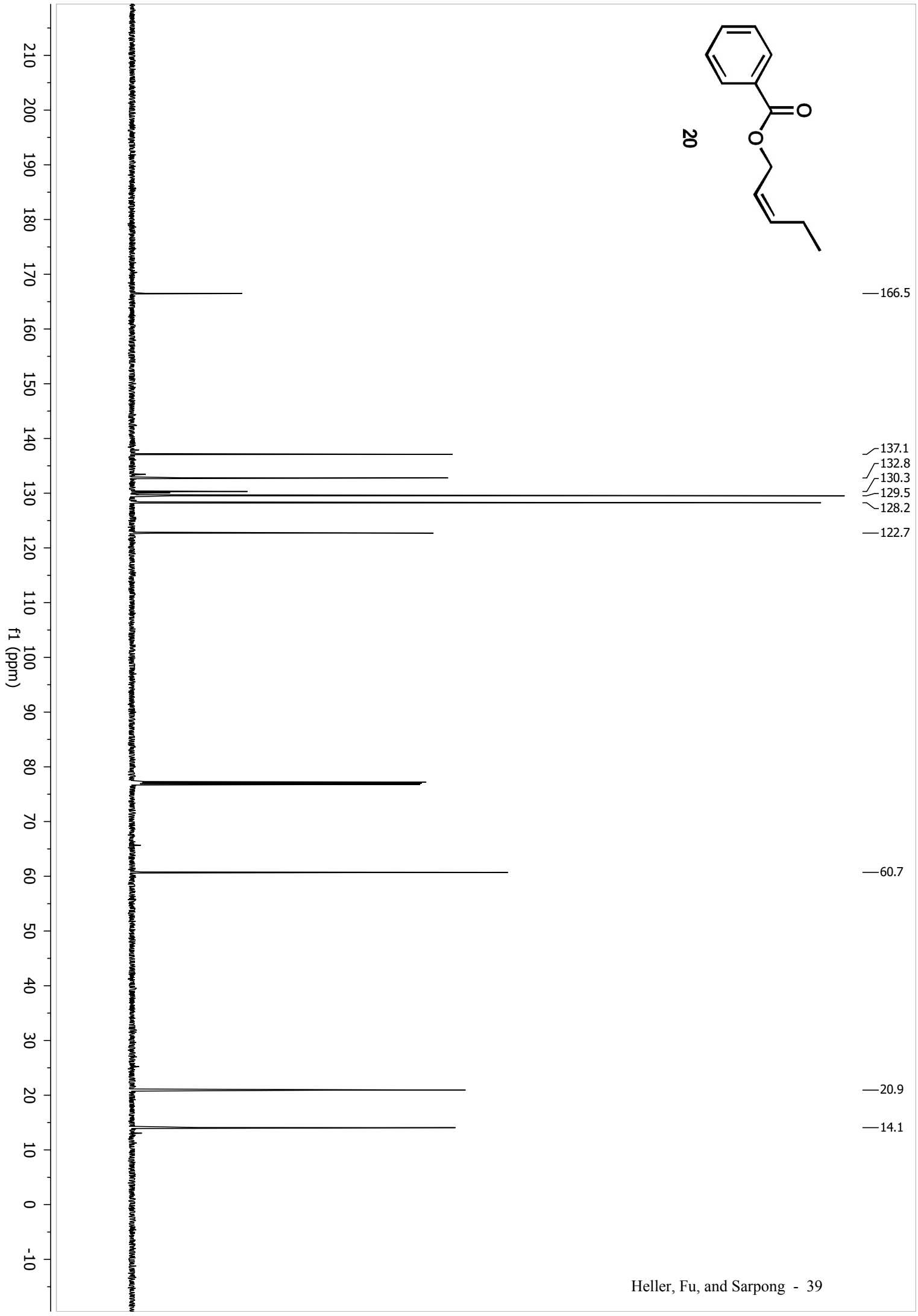

7
OBz
O
N
O
2.00
1.05
2.13
2.07
1.04
1.01
2.05
1.02
1.05
3.12
3.19
f1 (ppm)

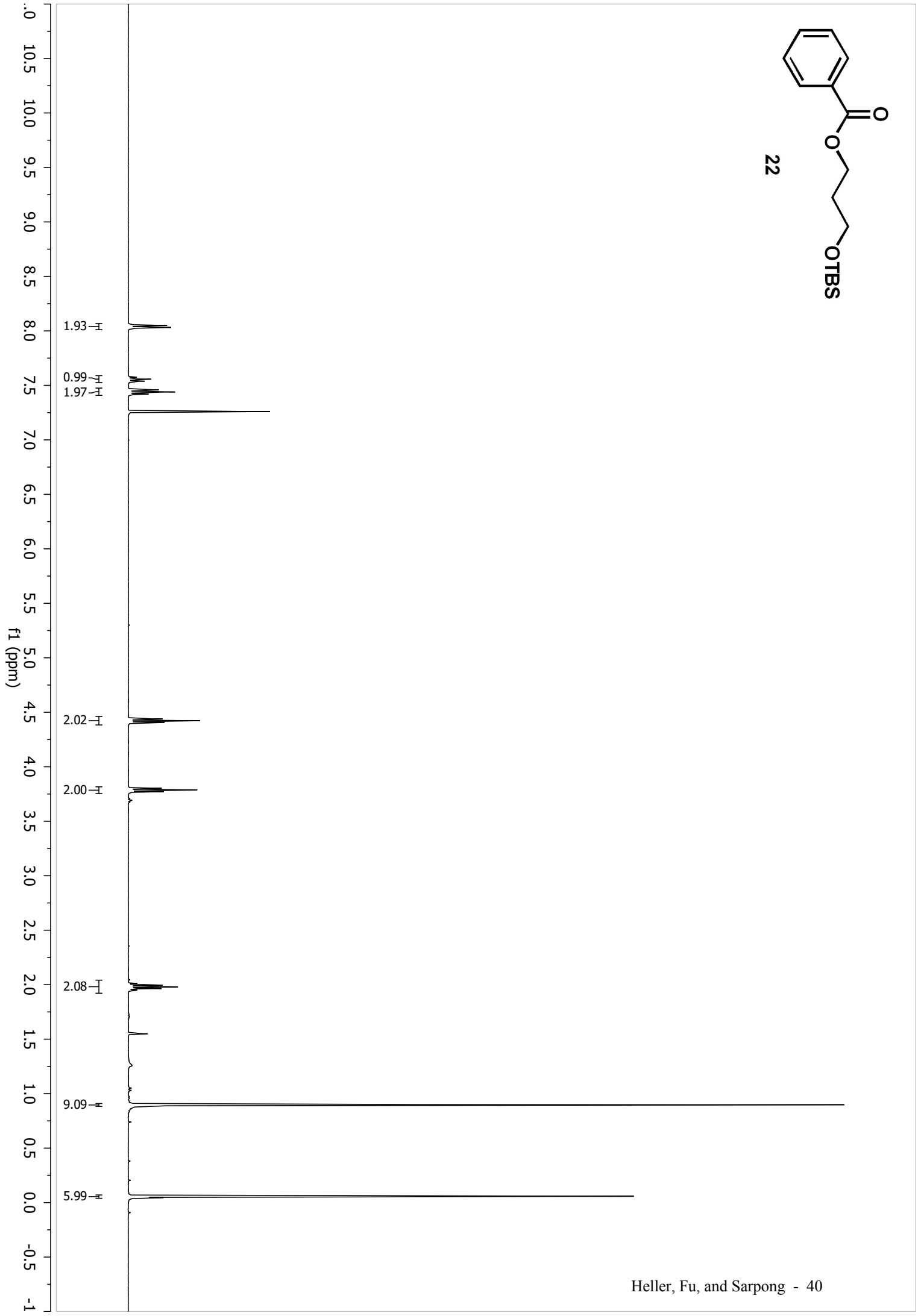

7
OBz
O
N
O
166.1
155.8
138.2
135.4
133.4
132.8
131.9
129.7
129.1
128.4
127.6
126.3
70.8
64.6
49.4
20.9
17.6
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20

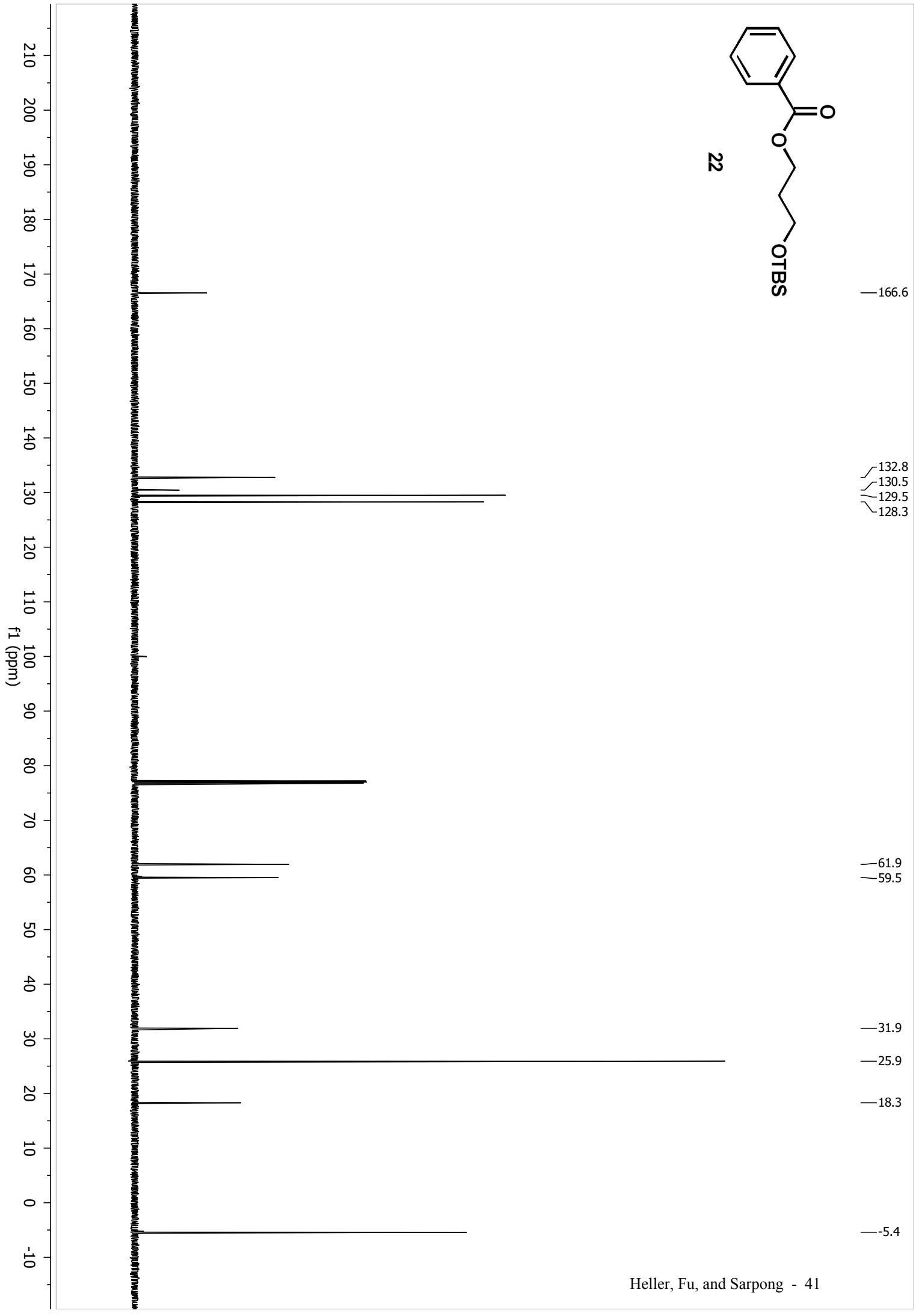

8
PhN
O
O
3.13
2.11
2.00
2.19
2.42
1.35
2.37
2.39
1.10
f1 (ppm)

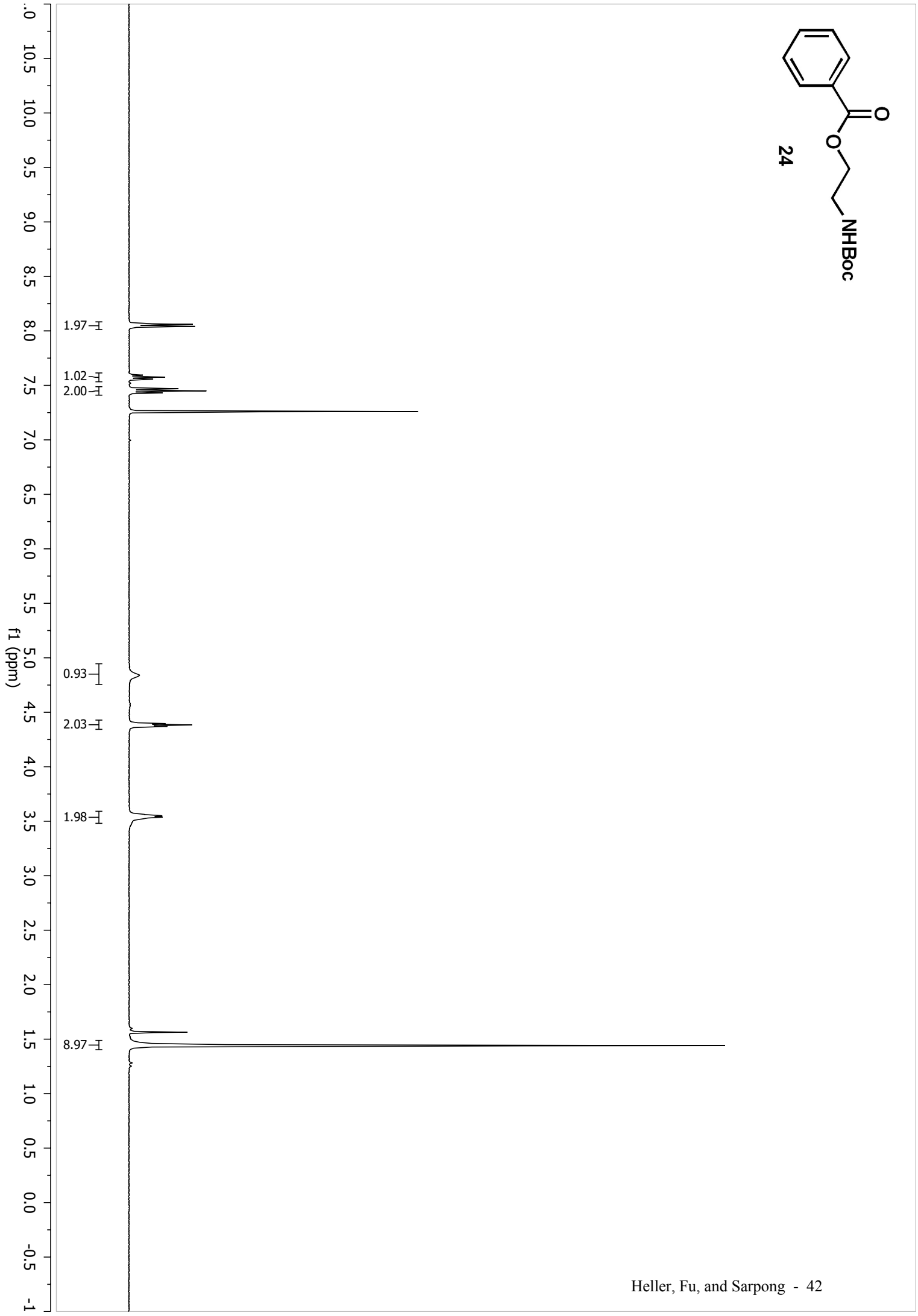

8
PhN
O
O
157.2
134.6
130.0
129.2
128.4
72.2
63.0
34.9
24.2
22.8
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

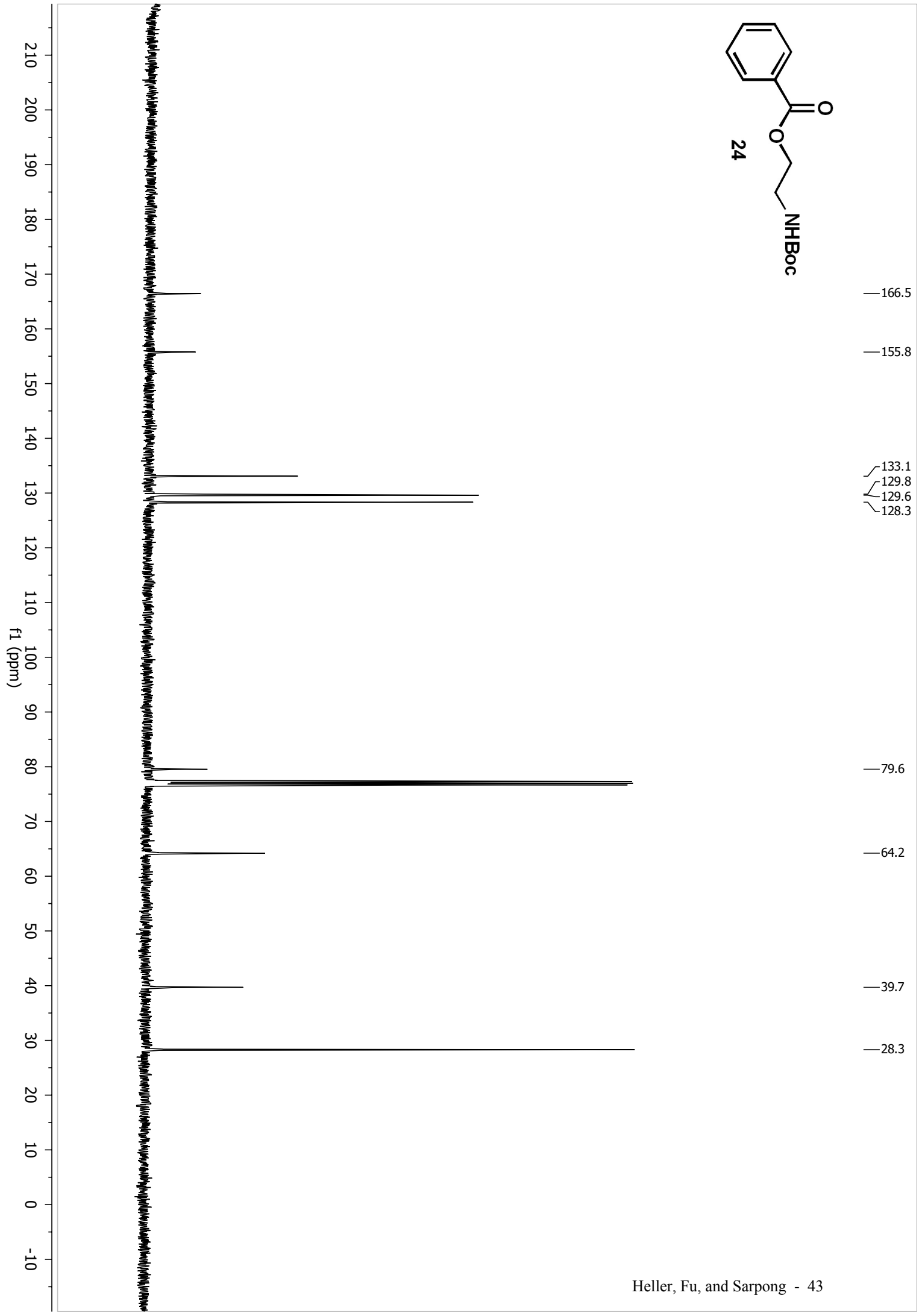

20
2.00
1.04
2.07
2.02
2.00
2.01
3.02
f1 (ppm)


20
166.5
137.1
132.8
130.3
129.5
128.2
122.7
60.7
20.9
14.1
f1 (ppm)


22
OTBS
O
O
1.93
0.99
1.97
2.02
2.00
2.08
9.09
5.99
f1 (ppm)


22
O
O
OTBS
166.6
132.8
130.5
129.5
128.3
61.9
59.5
31.9
25.9
18.3
-5.4
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


24
NHBoc
1.97
1.02
2.00
0.93
2.03
1.98
8.97
f1 (ppm)


O
O
NHBoc
24
166.5
155.8
133.1
129.8
129.6
128.3
79.6
64.2
39.7
28.3
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10