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1. Experimental Procedures

a) General Considerations: Unless otherwise indicated, all reactions were performed in oven- or flame-dried glassware with magnetic stirring under a nitrogen or argon atmosphere. Air and moisture-sensitive liquids and solutions were transferred *via* oven-dried, stainless steel syringe or cannula and were introduced into the reaction vessel through rubber septa. Anhydrous PhMe, CH_2Cl_2 and THF were obtained from a Seca solvent purification system by Glass Contour. 1,4-Dioxane was distilled from Na under nitrogen. 1,2-Dichloroethane was distilled from CaH_2 under nitrogen. *tert*-Butanol was purchased from Sigma-Aldrich and used as received. For use in Pd-AAA reactions, anhydrous and deoxygenated THF was obtained from a Na/benzophenone ketyl still under argon. All other solvents employed in the Pd-AAA were degassed *via* nitrogen or argon sparge (5 min / mL). $Pd_2dba_3 \cdot CHCl_3$ was prepared according to the procedure of Ibers.[1] Ligands **L1-L4** were prepared by literature procedures.[2]

Analytical thin-layer chromatography was performed on pre-coated 250 μm layer thickness silica gel 60 F_{254} plates (EMD Chemicals Inc.). Visualization was performed by ultraviolet light fluorescence quenching and/or by staining with aqueous potassium permanganate, ceric ammonium molybdate, or *para*-anisaldehyde solutions followed by heating.

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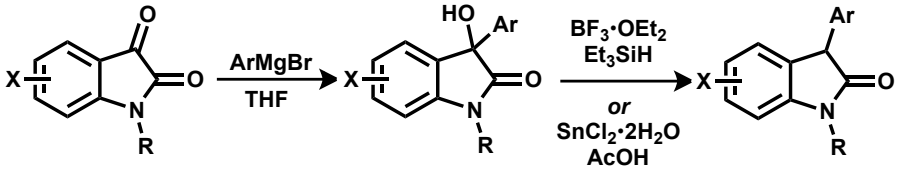
[1] T. Ukai, H. Kawazura, Y. Ishii, J. J. Bonnet, J. A. Ibers, *J. Organomet. Chem.* **1974**, *65*, 253.
[2] a) B. M. Trost, D. L. van Vranken, C. Bingel, *J. Am. Chem. Soc.* **1992**, *114*, 9327; b) B. M. Trost, R. Bunt, R. Lemoine, T. Calkins, *J. Am. Chem. Soc.* **2000**, *122*, 5968.

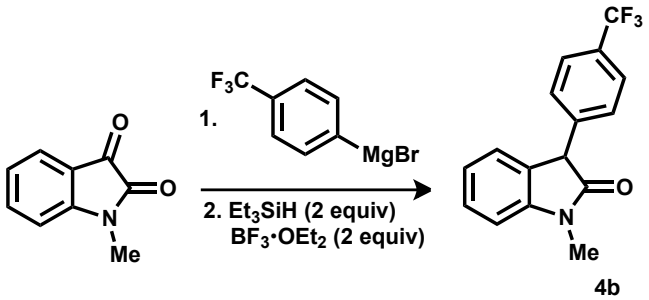
Unless otherwise indicated, flash column chromatography was performed using 40-63 μm silica gel (Silicycle silica gel) using compressed air. The eluent employed for flash chromatography is reported as volume/volume ratios. Proton nuclear magnetic resonance (^{1}H NMR) spectra were acquired using a Varian Inova 600 MHz, Varian Inova 500 MHz, Varian Inova 300 MHz, or Varian Mercury 400 MHz spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) and are calibrated to the residual solvent peak: proton ($CHCl_3$, 7.26 ppm). Coupling constants (*J*) are reported in Hz. Multiplicities are reported using the following abbreviations: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet (range of multiplet is given). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded using a Varian Inova 150 MHz, Varian Inova 125 MHz, Varian Inova 75 MHz, or a Varian Mercury 100 MHz spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) and are calibrated to the residual solvent peak: carbon ($CHCl_3$, 77.16 ppm).

Infrared spectroscopic data were recorded on a Thermo Scientific Nicolet IR100 FT-IR spectrometer, using thin films of the sample on NaCl plates. The absorbance frequencies are recorded in wavenumbers (cm^{-1}). Chiral HPLC analysis was performed using an Agilent Technologies 1200 Series HPLC equipped with a Daicel Chemical Chiralpak® chiral stationary phase column (either IA: [amylose tris(3,5-dimethylphenylcarbamate) immobilized on silica support], IB: [cellulose tris(3,5-dimethylphenylcarbamate) immobilized on silica support], or IC: [cellulose tris(3,5-dichlorophenylcarbamate) immobilized on silica support]). HPLC retention times of enantiomers were determined by comparison to racemic materials, which were prepared using equimolar mixtures of (*R*,*R*)- and (*S*,*S*)-**L2**. Optical rotations were measured using a JASCO P2000 polarimeter using 5 cm glass cells with a sodium 589 nm filter and are reported as $[\alpha]_D^T$, concentration (g/100 mL), and solvent. Melting points were determined on a Thomas Hoover Capillary Melting Point Apparatus and are uncorrected. High-resolution mass spectra were acquired by the Vincent Coates Foundation Mass Spectrometry Laboratory, Stanford University Mass Spectrometry (http://massspec.stanford.edu).

b) Synthesis of 3-Aryloxindoles



Oxindoles **4a**, **4d**, **4f**, **4h**, and **4i** were prepared *via* the above methods according to established literature procedures,[3] as were **1**,[4] **4k**,[5] and **4o**.[6]



Representative Procedure: Synthesis of 4b.

To a 2-dram vial equipped with a stir bar was added Mg (58.3 mg, 2.4 mmol, 1.2 equivalents) and I_2 (one crystal). The vial was sealed with a septum, evacuated and backfilled with nitrogen, and THF (2.4 mL) was added, followed by 4-bromobenzotrifluoride (0.34 mL, 0.54 g, 2.4 mmol, 1.2 equivalents). Exothermic formation of the Grignard reagent ensued (if necessary, the reaction was initiated by warming the solution to reflux), and the reaction mixture was stirred until complete consumption of Mg^0 was observed and the solution had cooled to room temperature (*ca.* 1 h). The Grignard solution was then cannulated into a solution of *N*-methylisatin (322 mg, 2 mmol, 1 equivalent) in THF (6.7 mL) in a 25 mL round-bottom flask at 0 °C (ice/water bath). The reaction mixture was stirred for 1 h at this temperature, at which point it was quenched by the addition of saturated aqueous NH_4Cl. The solution was poured into EtOAc (10 mL), the phases were separated, and the aqueous phase was extracted with EtOAc (3 x 10 mL). The pooled organic phases were dried over $MgSO_4$, filtered, and concentrated. The crude material was dissolved in CH_2Cl_2 (10 mL), and to this solution was added triethylsilane

[3] B. M. Trost, Y. Zhang, *J. Am. Chem. Soc.* **2007**, *129*, 14548.
[4] B. M. Trost, J. Xie, J. D. Sieber, *J. Am. Chem. Soc.* **2011**, *133*, 20611.
[5] M.-X. Zhao, Z.-W. Zhang, M.-X. Chen, W.-H. Tang, M. Shi, *Eur. J. Org. Chem.* **2011**, 3001.
[6] B. M. Trost, L. C. Czabaniuk, *J. Am. Chem. Soc.* **2010**, *132*, 15534.

(0.64 mL, 0.47 g, 4 mmol, 2 equivalents) dropwise followed by $BF_3 \cdot OEt_2$ (0.49 mL, 0.57 g, 4 mmol, 2 equivalents) dropwise. The reaction mixture was stirred overnight, at which point it was quenched with saturated aqueous $NaHCO_3$ and poured into EtOAc (10 mL). The phases were separated, and the aqueous phase was extracted with EtOAc (3 x 10 mL). The pooled organics were dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography (4:1 hexanes:EtOAc) to afford **4b** (216 mg, 37%) as a white solid.

R_f = 0.18 (4:1 hexanes:EtOAc)

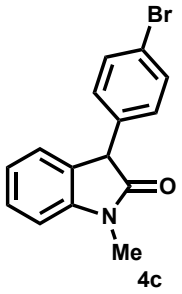
^{1}H NMR (300 MHz; $CDCl_3$): δ 7.61-7.58 (m, 2H), 7.40-7.32 (m, 3H), 7.17-7.07 (m, 2H), 6.93 (d, *J* = 7.8 Hz, 1H), 4.67 (s, 1H), 3.26 (s, 3H).

^{13}C NMR (125 MHz; $CDCl_3$): δ 175.2, 144.6, 140.7, 129.0, 127.9, 125.9(7), 125.9(3), 125.9(1), 125.8(8), 125.2, 123.1, 108.6, 51.8, 26.7.

IR: 1696, 1609, 1494, 1468, 1377, 1330, 1167, 1110, 1067, 1019, 824, 752 cm^{-1}

M.P. = 128-129 °C

HRMS (ESI): Calculated for $C_{16}H_{12}F_3NNaO$ $(M+Na)^+$: 314.0763, Found 314.0756



4c

4c: Prepared according to the representative procedure from 1,4-dibromobenzene (566 mg, 2.4 mmol, 1.2 equivalents), Mg (58.3 mg, 2.4 mmol, 1.2 equivalents), I_2 (one crystal), and *N*-methylisatin (322 mg, 2 mmol, 1 equivalent). The deoxygenation was performed with triethylsilane (0.64 mL, 0.47 g, 4 mmol, 2 equivalents) and $BF_3 \cdot OEt_2$ (0.49 mL, 0.57 g, 4 mmol, 2 equivalents). Purification *via* column chromatography (4:1 hexanes:EtOAc) afforded **4c** (286 mg, 47%) as a white solid.

R_f = 0.21 (4:1 hexanes:EtOAc)

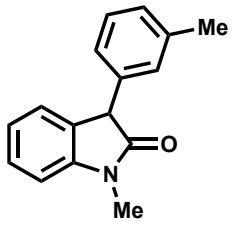
^{1}H NMR (300 MHz; $CDCl_3$): δ 7.48-7.43 (m, 2H), 7.38-7.30 (m, 1H), 7.22-7.05 (m, 4H), 6.91 (d, *J* = 7.8 Hz, 1H), 4.57 (s, 1H), 3.25 (s, 3H).

^{13}C NMR (75 MHz; $CDCl_3$): δ 175.5, 144.6, 135.7, 132.1, 130.3, 128.8, 128.2, 125.1, 123.0, 121.8, 108.4, 51.5, 26.7.

IR: 1693, 1609, 1489, 1469, 1376, 1348, 1254, 1126, 1087, 1012, 813, 797, 751, 703, 665, 632 cm^{-1}

M.P. = 154-156 °C

HRMS (ESI): Calculated for $C_{15}H_{12}BrNNaO$ $(M+Na)^+$: 323.9994, Found 323.9984

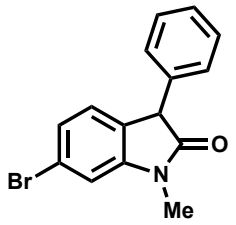


4e

4e: Prepared according to the representative procedure from 3-bromotoluene (0.29 mL, 0.41 g, 2.4 mmol, 1.2 equivalents), Mg (58.3 mg, 2.4 mmol, 1.2 equivalents), I_2 (one crystal) and *N*-methylisatin (322 mg, 2 mmol, 1 equivalent). The deoxygenation was performed with triethylsilane (0.64 mL, 0.47 g, 4 mmol, 2 equivalents) and $BF_3{\cdot}OEt_2$ (0.49 mL, 0.57 g, 4 mmol, 2 equivalents). Purification *via* column chromatography (4:1 hexanes:EtOAc) afforded **4e** (338 mg, 71%) as a light green solid.

^{1}H NMR (500 MHz; $CDCl_3$): δ 7.33 (t, J = 7.7 Hz, 1H), 7.23-7.05 (m, 4H), 7.00-6.98 (m, 2H), 6.90 (d, J = 7.7 Hz, 1H), 4.57 (s, 1H), 3.26 (s, 3H), 2.31 (s, 3H).

Analytical data matched literature data.[7]



4g

4g: Prepared according to the representative procedure from 6-bromo-*N*-methylisatin (475 mg, 2 mmol, 1 equivalent) and phenylmagnesium bromide (1 M in THF, 2.4 mL, 2.4 mmol, 1.2 equivalents). The deoxygenation was performed with triethylsilane (0.64 mL, 0.47 g, 4 mmol, 2

[7] L. Ackermann, R. Vicente, N. Hofmann, *Org. Lett.*, **2009**, *11*, 4274.

equivalents) and $BF_3 \cdot OEt_2$ (0.49 mL, 0.57 g, 4 mmol, 2 equivalents). Purification *via* column chromatography (4:1 hexanes:ethyl acetate) afforded **4g** (255 mg, 42%) as a dark green solid.

R_f = 0.26 (4:1 hexanes:EtOAc)

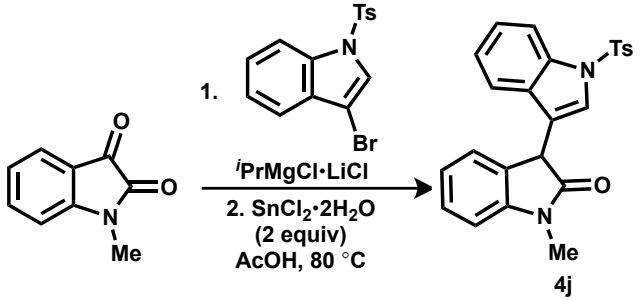
^{1}H NMR (300 MHz; $CDCl_3$): δ 7.37-7.29 (m, 3H), 7.22-7.16 (m, 3H), 7.05-7.01 (m, 2H), 4.55 (s, 1H), 3.23 (s, 3H).

^{13}C NMR (125 MHz; $CDCl_3$): δ 175.8, 145.9, 136.0, 129.1, 128.4, 127.9, 126.4, 125.6, 122.1, 111.8, 95.6, 51.7, 26.7.

IR: 1718, 1606, 1492, 1364, 1245, 1091, 935, 756, 696 cm^{-1}

M.P. = 157-159 °C

HRMS (ESI): Calculated for $C_{15}H_{12}BrNNaO$ $(M+Na)^+$: 323.9994, Found 323.9987



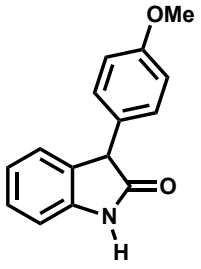
4j: Prepared according to the literature procedure.[3] To a solution of 3-bromo-*N*-tosylindole[8] (277 mg, 0.79 mmol, 1 equivalent) in THF (2.2 mL) at 0 °C (ice/water bath) was added ^{i}PrMgCl·LiCl (Sigma-Aldrich, 1.3 M in THF, 0.72 mL, 0.94 mmol, 1.2 equivalents) dropwise. The solution was stirred at this temperature for 2 h, at which point a solution of *N*-methylisatin (127 mg, 0.79 mmol, 1 equivalent) in THF (5.3 mL) was added dropwise *via* cannula. The reaction mixture was stirred at 0 °C for 1 h, at which point it was quenched by the addition of saturated aqueous NH_4Cl. The mixture was poured into EtOAc (10 mL), the phases were separated, and the aqueous phase was extracted with EtOAc (3 x 10 mL). The pooled organics were dried over $MgSO_4$, filtered, concentrated, re-dissolved in AcOH (2.1 mL), and treated with $SnCl_2 \cdot 2H_2O$ (357 mg, 1.6 mmol, 2 equivalents). The reaction mixture was heated to 80 °C for 11 h, at which point it was cooled to room temperature, quenched by the addition of saturated aqueous $NaHCO_3$, and poured into EtOAc (10 mL). The phases were separated and the aqueous phase was extracted with EtOAc (3 x 10 mL). The pooled organics were washed with 2N NaOH (10

[8] H. F. Hodson, D. J. Madge, A. N. Z. Slawin, D. A. Widdowson, D. J. Williams, *Tetrahedron*, **1994**, *50*, 1899.

mL), water (10 mL), and brine (10 mL), dried over $MgSO_4$, filtered, and concentrated. The residue was purified *via* column chromatography (4:1 to 2:1 hexanes:EtOAc) to afford **4j** (199 mg, 60%) as a green solid.

^{1}H NMR (500 MHz; $CDCl_3$): δ 7.94 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.77-7.75 (m, 2H), 7.42 (d, *J* = 0.7 Hz, 1H), 7.38-7.27 (m, 3H), 7.24-7.22 (m, 2H), 7.19-7.15 (m, 2H), 7.07 (td, *J* = 7.5, 0.9 Hz, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 4.82 (s, 1H), 3.28 (s, 3H), 2.35 (s, 3H).

Analytical data matched literature data.

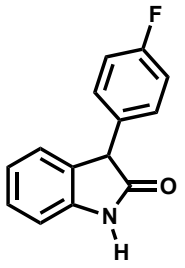


4l

4l: Prepared according to the representative procedure from isatin (441 mg, 3 mmol, 1 equivalent) and (4-methoxyphenyl)magnesium bromide (7.8 mL of a 0.89 M solution in THF [6.9 mmol, 2.3 equivalents], itself prepared by the reaction of 4-bromoanisole [1.25 mL, 1.87 g, 10 mmol], Mg [240 mg, 9.9 mmol], and I_2 [one crystal] in 10 mL THF, as described in the representative procedure). The deoxygenation was performed according to the representative procedure using triethylsilane (0.96 mL, 0.70 g, 6 mmol, 2 equivalents) and $BF_3{\cdot}OEt_2$ (0.74 mL, 0.85 g, 6 mmol, 2 equivalents). Purification *via* column chromatography (4:1 to 1:1 hexanes:EtOAc) afforded **4l** (380 mg, 53%) as a pink solid.

^{1}H NMR (500 MHz; $CDCl_3$): δ 7.30-7.27 (m, 1H), 7.17-7.15 (m, 3H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 6.91-6.89 (m, 2H), 4.61 (s, 1H), 3.82 (s, 3H).

Analytical data matched literature data.[9]



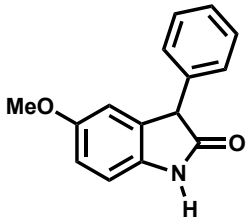
4m

[9] R. A. Altman, A. M. Hyde, X. Huang, S. L. Buchwald, *J. Am. Chem. Soc.* **2008**, *130*, 9613.

4m: Prepared according to the representative procedure from isatin (294 mg, 2 mmol, 1 equivalent), 1-bromo-4-fluorobenzene (0.48 mL, 0.77 g, 4.4 mmol, 2.2 equivalents), Mg (107 mg, 4.4 mmol, 2.2 equivalents), and I_2 (one crystal). The deoxygenation was performed with triethylsilane (0.64 mL, 0.47 g, 4 mmol, 2 equivalents) and $BF_3 \cdot OEt_2$ (0.49 mL, 0.57 g, 4 mmol, 2 equivalents). Purification *via* column chromatography (2:1 hexanes:EtOAc) afforded **4m** (276 mg, 61%) as a pink solid.

^{1}H NMR (500 MHz; $CDCl_3$): δ 7.28-7.26 (m, 1H), 7.21-7.18 (m, 2H), 7.13 (d, J = 7.5 Hz, 1H), 7.07-7.02 (m, 3H), 6.94 (d, J = 7.9 Hz, 1H), 4.61 (s, 1H).

Analytical data matched literature data.[10]



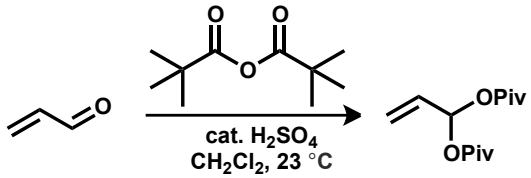
4n

4n: Prepared according to the representative procedure from 5-methoxyisatin (354 mg, 2 mmol) and phenylmagnesium bromide (1 M in THF, 4.8 mL, 4.8 mmol, 2.4 equivalents). The deoxygenation was performed with triethylsilane (0.64 mL, 0.47 g, 4 mmol, 2 equivalents) and $BF_3 \cdot OEt_2$ (0.49 mL, 0.57 g, 4 mmol, 2 equivalents). Purification *via* column chromatography (1:1 hexanes:EtOAc) afforded **4n** (127 mg, 27%) as a light pink solid.

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.37-7.30 (m, 3H), 7.23-7.21 (m, 2H), 6.85-6.78 (m, 2H), 6.74-6.72 (s, 1H), 4.61 (s, 1H), 3.74 (s, 3H).

Analytical data matched literature data.[9]

c) Synthesis of Allylidene Dipivalate



Prepared according to the procedure of Lombardo and coworkers.[11] To a solution of trimethylacetic anhydride (5.0 mL, 4.6 g, 24.7 mmol, 1 equivalent) in CH_2Cl_2 (27 mL) was

[10] Y. Cai, J. Li, W. Chen, M. Xie, X. Liu, L. Lin, X. Feng, *Org. Lett.* **2012**, *14*, 2726.

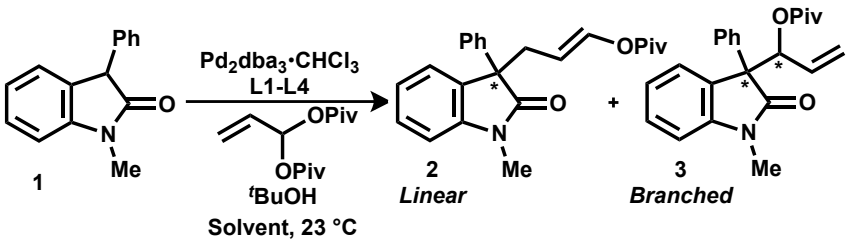
added 4 drops of conc. H_2SO_4. A solution of acrolein (2.1 mL, 1.8 g, 31.4 mmol, 1.3 equivalents) in CH_2Cl_2 (3 mL) was introduced dropwise, at a rate sufficient to maintain the reaction at room temperature. The reaction mixture, the appearance of which progressed from clear and colorless to light yellow, was stirred for 16 h at room temperature. It was then filtered through a large pipet plug of K_2CO_3, concentrated, and passed through a column of SiO_2, eluting with 10:1 hexanes:EtOAc, to afford allylidene dipivalate (4.82 g, 81%) as a clear, colorless oil.

$\rho = 0.94$

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.11 (dt, *J* = 5.2, 1.1 Hz, 1H), 5.91 (ddd, *J* = 17.3, 10.6, 5.2 Hz, 1H), 5.53 (dt, *J* = 17.3, 1.1 Hz, 1H), 5.38 (dt, *J* = 10.6, 1.1 Hz, 1H), 1.21 (s, 18H).

Analytical data matched literature data.

d) General Procedure for Pd-AAA Optimization Studies (Table 1)

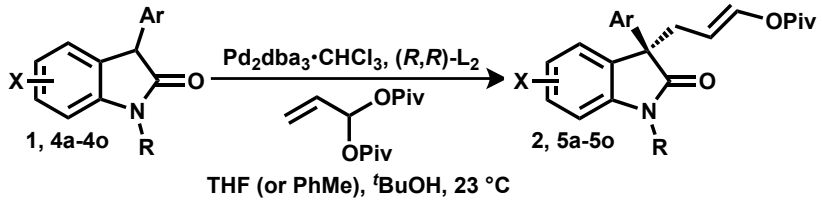


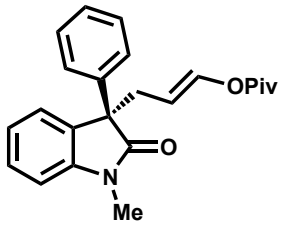
An oven-dried, desiccator-cooled Biotage® microwave vial (0.5 - 2.0 mL size) was charged with a stir bar, oxindole **1** (11.2 mg, 0.05 mmol, 1 equivalent), $Pd_2dba_3{\cdot}CHCl_3$ (2.6 mg, 0.0025 mmol, 0.05 equivalent), and (*R*,*R*)-ligand (**L1**-**L4**, 0.0075 mmol, 0.15 equivalent). The vial was sealed with a septum-lined microwave cap and evacuated and backfilled with Ar three times. Previously degassed solvent (0.25 mL) was added, followed by ^{t}BuOH (24.0 μL, 18.6 mg, 0.25 mmol, 5.0 equivalents, omitted when pure ^{t}BuOH was the reaction solvent). The reaction mixture was stirred until it was homogeneous and an orange color persisted (*ca*. 10 min), then allylidene dipivalate (19.5 μL, 18.3 mg, 0.075 mmol, 1.5 equivalents) was added. The argon inlet was removed, and the pierced septum cap was sealed thoroughly with electrical tape and Parafilm®. The reaction mixture was stirred at room temperature for 24 h, then the septum cap was removed and pH 7 buffer (1 mL) was added. Et_2O (1 mL) was added, the phases were separated, and the aqueous phase was extracted with Et_2O (2 x 1 mL). The pooled organic phases were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. To the residue was added

[11] M. Lombardo, S. Licciulli, F. Pasi, G. Angelici, C. Trombini, *Adv. Synth. Catal.* **2005**, *347*, 2015.

mesitylene (previously distilled from CaH_2 and stored under N_2), and the resulting mixture was analyzed by ^1H NMR to obtain conversion, regioselectivity, and yield. Purification by preparative thin-layer chromatography (4:1 hexanes:EtOAc) delivered analytical samples for chiral HPLC analysis.

e) Synthesis of Enol Pivalates 2, 5a-5o (Table 2)





2

Representative Procedure: **Synthesis of 2.** An oven-dried, desiccator cooled Biotage® microwave vial (0.5 - 2.0 mL size) was charged with a stir bar, oxindole **1** (22.4 mg, 0.10 mmol, 1 equivalent), $Pd_2dba_3{\cdot}CHCl_3$ (2.6 mg, 0.0025 mmol, 0.025 equivalent), and (*R*,*R*)-**L2** (5.9 mg, 0.0075 mmol, 0.075 equivalent). The vial was sealed with a septum-lined microwave cap and evacuated and backfilled with Ar or N_2 three times. THF (0.25 mL) was added, followed by ^{t}BuOH (48.0 μL, 37.2 mg, 0.50 mmol, 5.0 equivalents). The reaction mixture was stirred until it was homogeneous and an orange color persisted (*ca*. 10 min), then allylidene dipivalate (39.0 μL, 36.7 mg, 0.15 mmol, 1.5 equivalents) was added. The gas inlet was removed, and the pierced septum cap was sealed thoroughly with electrical tape and Parafilm®. The reaction mixture was stirred at room temperature for 24 h, then the septum cap was removed and the reaction mixture was poured into a mixture of Et_2O (10 mL) and saturated aqueous $NaHCO_3$ (10 mL). The phases were separated, and the aqueous phase was extracted with Et_2O (2 x 5 mL). The pooled organic phases were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (6:1 to 4:1 hexanes:EtOAc), affording **2** (33.1 mg, 91%, >19:1 linear:branched, 92% ee) as a viscous, light yellow oil.

The larger-scale synthesis of **2** was performed in a 2.0 – 5.0 mL size microwave vial with **1** (223.0 mg, 1.0 mmol, 1 equivalent), $Pd_2dba_3 \cdot CHCl_3$ (25.9 mg, 0.025 mmol, 0.025 equivalent), **L2** (59.2 mg, 0.075 mmol, 0.075 equivalent), allylidene dipivalate (387 μL, 364 mg, 1.5 mmol, 1.5 equivalents), ^{t}BuOH (478 μL, 370 mg, 5.0 mmol, 5.0 equivalents) in THF (2.5 mL) for 24 h. It was then poured into a mixture of Et_2O (50 mL) and saturated aqueous $NaHCO_3$ (50 mL). The phases were separated, and the aqueous phase was extracted with Et_2O (50 mL). The pooled organics were washed with water (2 x 25 mL) then brine (25 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (6:1 to 4:1 hexanes:EtOAc), affording **2** (327 mg, 90%, >19:1 linear:branched, 90% ee) as a viscous yellow oil.

R_f = 0.38 (4:1 hexanes:EtOAc)

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.39-7.27 (m, 6H), 7.25-7.24 (m, 1H), 7.13 (td, *J* = 7.5, 1.0 Hz, 1H), 7.00 (dt, *J* = 12.4, 1.2 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 5.05 (ddd, *J* = 12.4, 9.0, 6.7 Hz, 1H), 3.21 (s, 3H), 3.02 (ddd, *J* = 14.0, 6.6, 1.6 Hz, 1H), 2.90 (ddd, *J* = 14.0, 9.0, 1.0 Hz, 1H), 1.15 (s, 9H).

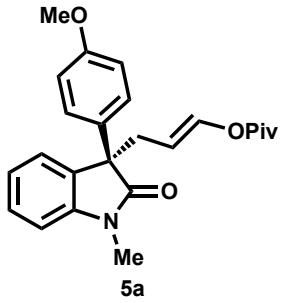
^{13}C NMR (100 MHz; $CDCl_3$): δ 177.9, 175.5, 143.9, 139.2, 138.9, 131.5, 128.7, 128.5, 127.6, 127.2, 125.4, 122.7, 108.5, 108.3, 56.5, 38.7, 36.0, 27.0, 26.6

IR: 3057, 2974, 2934, 1743, 1716, 1673, 1612, 1484, 1471, 1372, 1349, 1278, 1143 cm^{-1}

Chiral HPLC: IA, 95:5 heptane:isopropanol, 0.8 mL/min, 254 nm, 12.35 min (minor), 15.52 (major).

$[\alpha]_D^{23}$ = + 74.2° (c = 0.29, $CHCl_3$)

HRMS (ESI): Calculated for $C_{23}H_{25}NNaO_3$ $(M+Na)^+$: 386.1727, Found 386.1720



5a

5a: Prepared according to representative procedure from **4a** (25.3 mg, 0.10 mmol), in THF for 48 h. Purification *via* column chromatography (4:1 hexanes:EtOAc) afforded **5a** (34.7 mg, 88%, >19:1 linear:branched, 83% ee) as a viscous light yellow oil.

$\mathbf{R}_f$ = 0.42 (4:1 hexanes:EtOAc)

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.37-7.27 (m, 3H), 7.26-7.23 (m, 1H), 7.13 (td, *J* = 7.5, 1.0 Hz, 1H), 6.99 (dt, *J* = 12.4, 1.3 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.85-6.82 (m, 2H), 5.05 (ddd, *J* = 12.4, 9.0, 6.6 Hz, 1H), 3.77 (s, 3H), 3.20 (s, 3H), 2.98 (ddd, *J* = 14.1, 6.6, 1.6 Hz, 1H), 2.85 (ddd, *J* = 14.1, 9.0, 1.0 Hz, 1H), 1.15 (s, 9H).

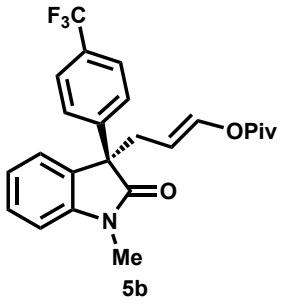
^{13}C NMR (125 MHz; $CDCl_3$): δ 178.2, 175.5, 159.0, 143.9, 138.8, 131.6, 131.1, 128.4(3), 128.3(5), 125.3, 122.7, 114.1, 108.4(4), 108.4(2), 66.0, 55.8, 55.4, 38.7, 27.0, 26.5.

IR: 2970, 2934, 1741, 1714, 1673, 1610, 1511, 1493, 1470, 1372, 1349, 1278, 1252, 1184, 1142, 1035, 934, 754 cm^{-1}

Chiral HPLC: IA, 95:5 heptane:isopropanol, 0.8 mL/min, 254 nm, 17.04 min (minor), 27.22 (major).

$\mathbf{[\alpha]_D^{23}}$ = + 88.0° (c = 0.27, $CHCl_3$)

HRMS (ESI): Calculated for $C_{24}H_{27}NNaO_4$ $(M+Na)^+$: 416.1832, Found 416.1828.



5b

5b: Prepared according to the representative procedure from **4b** (29.1 mg, 0.10 mmol) in PhMe for 24 h. Purification *via* column chromatography (4:1 hexanes:EtOAc) afforded **5b** (42.4 mg, 98%, >19:1 linear:branched, 90% ee) as a viscous, light yellow oil.

$\mathbf{R}_f$ = 0.36 (4:1 hexanes:EtOAc)

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.58-7.51 (m, 4H), 7.38 (td, *J* = 7.7, 1.3 Hz, 1H), 7.25-7.24 (m, 1H), 7.16 (td, *J* = 7.5, 0.9 Hz, 1H), 7.01 (dt, *J* = 12.4, 1.2 Hz, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 5.03 (ddd, *J* = 12.4, 9.0, 6.6 Hz, 1H), 3.22 (s, 3H), 3.02 (ddd, *J* = 14.0, 6.7, 1.5 Hz, 1H), 2.90 (ddd, *J* = 14.0, 9.0, 0.9 Hz, 1H), 1.16 (s, 9H).

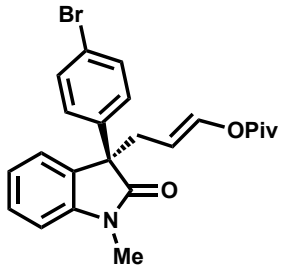
^{13}C NMR (100 MHz; $CDCl_3$): δ 177.2, 175.4, 143.9, 143.1, 139.2, 130.6, 128.9, 127.8, 125.7(0), 125.6(6), 125.6(3), 125.4, 123.0, 108.8, 107.7, 56.4, 38.7, 36.2, 27.0, 26.7.

IR: 2975, 1744, 1716, 1613, 1472, 1411, 1372, 1327, 1279, 1140, 1071, 1018, 934, 845, 754 cm^{-1}

Chiral HPLC: IB, 95:5 heptane:isopropanol, 0.8 mL/min, 254 nm, 8.75 min (minor), 9.56 (major).

$[\alpha]_D^{23}$ = + 73.4° (c = 0.53, $CHCl_3$)

HRMS (ESI): Calculated for $C_{24}H_{24}F_3NNaO_3$ $(M+Na)^+$: 454.1600, Found 454.1589.



5c

5c: Prepared according to the representative procedure from **4c** (30.2 mg, 0.10 mmol) in PhMe for 24 h. Purification *via* column chromatography (6:1 hexanes:EtOAc) afforded **5c** (36.4 mg, 82%, >19:1 linear:branched, 88% ee) as a viscous, light yellow oil.

R_f = 0.40 (4:1 hexanes:EtOAc)

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.45-7.34 (m, 3H), 7.28-7.26 (m, 1H), 7.26-7.22 (m, 2H), 7.14 (td, *J* = 7.5, 1.0 Hz, 1H), 6.99 (dt, *J* = 12.4, 1.2 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 5.03 (ddd, *J* = 12.4, 9.0, 6.6 Hz, 1H), 3.20 (s, 3H), 2.97 (ddd, *J* = 14.0, 6.6, 1.6 Hz, 1H), 2.84 (ddd, *J* = 14.0, 9.0, 1.0 Hz, 1H), 1.16 (s, 9H).

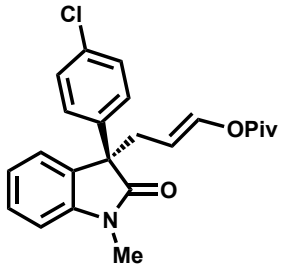
^{13}C NMR (100 MHz; $CDCl_3$): δ 177.4, 175.4, 143.9, 139.0, 138.2, 131.8, 130.8, 129.1, 128.8, 125.3, 122.9, 121.8, 108.7, 107.9, 56.0, 38.7, 36.1, 27.0, 26.6.

IR: 2973, 1743, 1415, 1673, 1612, 1490, 1396, 1371, 1350, 1278, 1142, 1010, 934, 754 cm^{-1}

Chiral HPLC: IB, 95:5 heptane:isopropanol, 0.8 mL/min, 254 nm, 9.29 min (minor), 10.41 (major).

$[\alpha]_D^{23}$ = + 86.9° (c = 0.28, $CHCl_3$)

HRMS (ESI): Calculated for $C_{23}H_{24}BrNNaO_3$ $(M+Na)^+$: 464.0832, Found 464.0828.



5d

5d: Prepared according to the representative procedure from **4d** (25.7 mg, 0.10 mmol) in PhMe for 24 h. Purification *via* column chromatography (6:1 hexanes:EtOAc) afforded **5d** (37.0 mg, 93%, >19:1 linear:branched, 88% ee) as a viscous, light yellow oil.

$\mathbf{R}_f$ = 0.38 (4:1 hexanes:EtOAc)

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.43-7.26 (m, 5H), 7.24 (dd, *J* = 7.4, 0.8 Hz, 1H), 7.15 (td, *J* = 7.5, 1.0 Hz, 1H), 7.00 (dt, *J* = 12.4, 1.2 Hz, 1H), 6.92 (d, *J* = 7.7 Hz, 1H), 5.03 (ddd, *J* = 12.4, 9.0, 6.6 Hz, 1H), 3.20 (s, 3H), 2.97 (ddd, *J* = 14.0, 6.6, 1.6 Hz, 1H), 2.84 (ddd, *J* = 14.0, 9.0, 0.9 Hz, 1H), 1.16 (s, 9H).

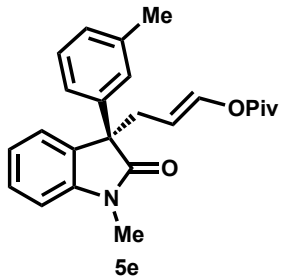
^{13}C NMR (100 MHz; $CDCl_3$): δ 177.5, 175.4, 143.9, 139.1, 137.6, 133.6, 130.9, 128.8, 128.7(5), 128.7(3), 125.4, 122.9, 108.7, 108.0, 56.0, 38.7, 36.2, 27.0, 26.6.

IR: 2974, 2934, 1743, 1715, 1673, 1612, 1492, 1472, 1399, 1372, 1351, 1278, 1143, 1096, 1015, 935, 754 cm^{-1}

Chiral HPLC: IB, 95:5 heptane:isopropanol, 0.8 mL/min, 254 nm, 8.95 min (minor), 10.00 (major).

$[\alpha]_D^{23}$ = + 81.0° (c = 0.33, $CHCl_3$)

HRMS (ESI): Calculated for $C_{23}H_{24}ClNNaO_3$ $(M+Na)^+$: 420.1337, Found 420.1327.



5e

5e: Prepared according to the representative procedure from **4e** (23.7 mg, 0.10 mmol) in THF for 24 h. Purification *via* column chromatography (6:1 to 4:1 hexanes:EtOAc) afforded **5e** (32.7 mg, 87%, >19:1 linear:branched, 88% ee) as a viscous, light yellow oil.

$\mathbf{R}_f$ = 0.37 (4:1 hexanes:EtOAc)

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.35 (td, *J* = 7.7, 1.3 Hz, 1H), 7.25-7.06 (m, 6H), 7.00 (dt, *J* = 12.5, 1.2 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 5.04 (ddd, *J* = 12.4, 9.0, 6.6 Hz, 1H), 3.21 (s, 3H), 3.00 (ddd, *J* = 14.0, 6.6, 1.6 Hz, 1H), 2.89 (ddd, *J* = 14.0, 9.0, 0.9 Hz, 1H), 2.31 (s, 3H), 1.15 (s, 9H).

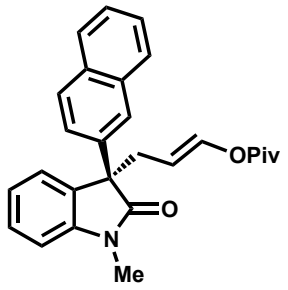
^{13}C NMR (125 MHz; $CDCl_3$): δ 178.0, 175.5, 143.9, 139.1, 138.8, 138.4, 131.6, 128.6, 128.4(2), 128.3(8), 127.8, 125.3, 124.2, 122.7, 108.4(1), 108.3(9), 56.4, 38.7, 35.6, 27.0, 26.6, 21.8.

IR: 2972, 2931, 1743, 1716, 1673, 1612, 1492, 1471, 1371, 1348, 1278, 1142, 934, 753, 697 cm^{-1}

Chiral HPLC: IB, 95:5 heptane:isopropanol, 0.8 mL/min, 254 nm, 8.25 min (minor), 9.29 (major).

$[\alpha]_D^{23}$ = + 80.7° (c = 0.24, $CHCl_3$)

HRMS (ESI): Calculated for $C_{24}H_{27}NNaO_3$ $(M+Na)^+$: 400.1883, Found 400.1883.



5f

5f: Prepared according to the representative procedure from **4f** (27.3 mg, 0.10 mmol) in THF for 24 h. Purification *via* column chromatography (6:1 hexanes:EtOAc) afforded **5f** (36.6 mg, 89%, >19:1 linear:branched, 90% ee) as a viscous, light yellow oil.

R_f = 0.26 (4:1 hexanes:EtOAc)

^{1}H NMR (500 MHz; $CDCl_3$): δ 7.81-7.76 (m, 4H), 7.56 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.46-7.44 (m, 2H), 7.39 (td, *J* = 7.7, 1.3 Hz, 1H), 7.32-7.31 (m, 1H), 7.17 (td, *J* = 7.5, 1.1 Hz, 1H), 7.05 (dt, *J* = 12.4, 1.3 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 5.11 (ddd, *J* = 12.4, 9.1, 6.5 Hz, 1H), 3.24 (s, 3H), 3.15 (ddd, *J* = 14.0, 6.5, 1.6 Hz, 1H), 3.00 (ddd, *J* = 14.0, 9.1, 1.0 Hz, 1H), 1.16 (s, 9H).

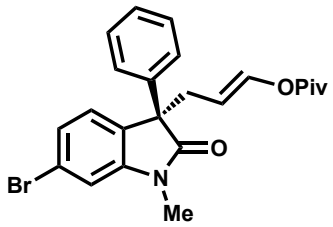
^{13}C NMR (100 MHz; $CDCl_3$): δ 177.9, 175.4, 144.0, 138.9, 136.6, 133.3, 132.7, 131.5, 128.6, 128.5, 128.3, 127.6, 126.2(4), 126.1(8), 125.5, 125.2, 122.8, 108.6, 108.3, 56.6, 38.7, 35.8, 27.0, 26.6.

IR: 2973, 2918, 1743, 1716, 1673, 1612, 1494, 1471, 1372, 1347, 1277, 1142, 1023, 933, 815, 751, 693 cm^{-1}

Chiral HPLC: IA, 95:5 heptane:isopropanol, 0.8 mL/min, 254 nm, 17.50 min (minor), 27.55 (major).

$[\alpha]_D^{24}$ = + 63.2° (c = 0.61, $CHCl_3$)

HRMS (ESI): Calculated for $C_{27}H_{27}NNaO_3$ $(M+Na)^+$: 436.1883, Found 436.1874.



5g

5g: Prepared according to the representative procedure from **4g** (30.2 mg, 0.10 mmol) in PhMe for 24 h. For this reaction, the product and dibenzylideneacetone were very nearly copolar on silica gel (TLC). Therefore, after workup, the crude material was concentrated into a 2-dram vial, treated with a solution of 2-aminoethanethiol (2.3 mg, 0.03 mmol, 0.30 equivalent) in PhMe (0.50 mL), and stirred at room temperature for 1 h. This mixture was then directly applied to a silica gel column and eluted with 8:1 hexanes:EtOAc. This afforded **5g** (39.1 mg, 88%, >19:1 linear:branched, 94% ee) as a viscous, light pink oil.

R_f = 0.19 (8:1 hexanes:EtOAc)

^{1}H NMR (500 MHz; $CDCl_3$): δ 7.35-7.26 (m, 6H), 7.11 (dd, *J* = 7.9, 0.3 Hz, 1H), 7.06 (d, *J* = 1.7 Hz, 1H), 7.01 (dq, *J* = 12.4, 0.8 Hz, 1H), 5.02 (ddd, *J* = 12.4, 9.1, 6.6 Hz, 1H), 3.19 (s, 3H), 3.00 (ddd, *J* = 14.1, 6.6, 1.6 Hz, 1H), 2.88 (ddd, *J* = 14.1, 9.1, 1.0 Hz, 1H), 1.17 (s, 9H).

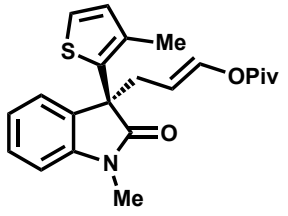
^{13}C NMR (125 MHz; $CDCl_3$): δ 177.7, 175.5, 145.3, 139.1, 138.5, 130.3, 128.9, 127.8, 127.1, 126.7, 125.5, 122.1, 112.0, 107.9, 56.3, 38.7, 35.8, 27.0, 26.7.

IR: 2973, 2931, 1742, 1721, 1604, 1492, 1465, 1366, 1278, 1141, 932 cm^{-1}

Chiral HPLC: IB, 98:2 heptane:isopropanol, 0.8 mL/min, 254 nm, 13.92 min (major), 17.11 (minor).

$[\alpha]_D^{24}$ = + 66.6° (c = 0.46, $CHCl_3$)

HRMS (ESI): Calculated for $C_{23}H_{24}BrNNaO_3$ $(M+Na)^+$: 464.0832, Found 464.0826.



5h

5h: Prepared according to the representative procedure from **4h** (24.4 mg, 0.10 mmol) in THF for 24 h. Purification *via* column chromatography (6:1 hexanes:EtOAc) afforded **5h** (34.8 mg, 91%, >19:1 linear:branched, 96% ee) as a viscous, light yellow oil.

$\mathbf{R_f}$ = 0.17 (6:1 hexanes:EtOAc)

^{1}H NMR (500 MHz; $CDCl_3$): δ 7.31 (td, *J* = 7.7, 1.5 Hz, 1H), 7.12 (ddd, *J* = 7.4, 1.4, 0.6 Hz, 1H), 7.09-7.05 (m, 2H), 6.99 (dt, *J* = 12.4, 1.3 Hz, 1H), 6.88 (ddd, *J* = 7.8, 0.9, 0.6 Hz, 1H), 6.75 (dd, *J* = 5.1, 0.4 Hz, 1H), 5.00 (ddd, *J* = 12.4, 8.6, 7.1 Hz, 1H), 3.25 (s, 3H), 3.10-3.01 (m, 2H), 1.71 (s, 3H), 1.15 (s, 9H).

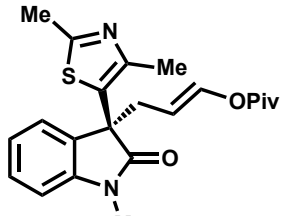
^{13}C NMR (100 MHz; $CDCl_3$): δ 176.6, 175.3, 143.6, 139.4, 135.7, 134.5, 132.1, 131.5, 128.6, 124.3, 123.1, 122.2, 108.1, 107.2, 54.1, 38.7, 36.6, 27.0, 26.4, 14.4.

IR: 2970, 2917, 1743, 1719, 1673, 1611, 1493, 1470, 1371, 1349, 1278, 1141, 752 cm^{-1}

Chiral HPLC: IB, 98:2 heptane:isopropanol, 0.8 mL/min, 254 nm, 13.72 min (minor), 15.96 (major).

$\mathbf{[\alpha]_D^{24}}$ = - 10.5° (c = 0.53, $CHCl_3$)

HRMS (ESI): Calculated for $C_{22}H_{25}NNaO_3S$ $(M+Na)^+$: 406.1447, Found 406.1441.



5i

5i: Prepared according to the representative procedure from **4i** (25.8 mg, 0.10 mmol) in THF for 24 h. Purification *via* column chromatography (2:1 to 1:1 hexanes:EtOAc) afforded **5i** (38.4 mg , 96%, >19:1 linear:branched, 95% ee) as a viscous, light yellow oil.

$\mathbf{R_f}$ = 0.40 (1:1 hexanes:EtOAc)

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.33 (ddd, *J* = 7.8, 7.4, 1.5 Hz, 1H), 7.14-7.08 (m, 2H), 6.99 (dt, *J* = 12.4, 1.2 Hz, 1H), 6.89 (dt, *J* = 7.8, 0.7 Hz, 1H), 5.00 (dt, *J* = 12.4, 7.8 Hz, 1H), 3.24 (s, 3H), 2.94 (d, *J* = 1.3 Hz, 1H), 2.92 (d, *J* = 1.3 Hz, 1H), 2.60 (s, 3H), 1.84 (s, 3H), 1.15 (s, 9H).

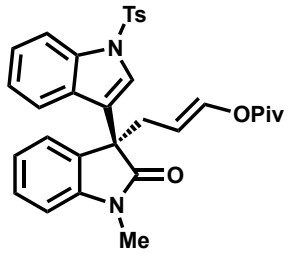
^{13}C NMR (100 MHz; $CDCl_3$): δ 176.2, 175.3, 162.4, 148.4, 143.4, 139.6, 131.0, 129.5, 128.9, 124.3, 123.2, 108.4, 107.0, 52.5, 38.7, 37.7, 27.0, 26.5, 19.2, 16.1.

IR: 2969, 2921, 1744, 1719, 1673, 1611, 1493, 1471, 1371, 1350, 1278, 1140, 934, 753 cm^{-1}

Chiral HPLC: IA, 90:10 heptane:isopropanol, 0.8 mL/min, 254 nm, 13.33 min (minor), 30.67 (major).

$[\alpha]_D^{24}$ = + 18.6° (c = 0.72, $CHCl_3$)

HRMS (ESI): Calculated for $C_{22}H_{27}N_2O_3S$ $(M+H)^+$: 399.1737, Found 399.1737.



5j

5j: Prepared according to the representative procedure from **4j** (41.6 mg, 0.10 mmol) in THF for 18 h. Purification *via* column chromatography (2:1 hexanes:EtOAc) afforded **5j** (45.5 mg, 82%, >19:1 linear:branched, 93% ee) as a viscous, yellow oil.

R_f = 0.34 (2:1 hexanes:EtOAc)

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.89 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.78-7.76 (m, 2H), 7.50 (s, 1H), 7.37 (td, *J* = 7.7, 1.4 Hz, 1H), 7.24-7.15 (m, 5H), 7.11-7.04 (m, 2H), 7.02 (dt, *J* = 12.4, 1.2 Hz, 1H), 6.95 (d, *J* = 7.7 Hz, 1H), 5.01 (ddd, *J* = 12.4, 8.8, 6.9 Hz, 1H), 3.25 (s, 3H), 3.09-2.99 (m, 2H), 2.35 (s, 3H), 1.16 (s, 9H).

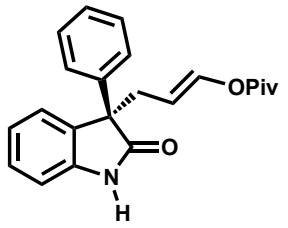
^{13}C NMR (100 MHz; $CDCl_3$): δ 176.8, 175.4, 145.2, 143.7, 139.2, 135.6, 135.2, 130.6, 130.1, 128.9, 128.7, 127.0, 124.9, 124.7, 124.6, 123.3, 123.2, 121.4, 121.0, 113.6, 109.5, 107.4, 52.5, 38.7, 34.6, 27.0, 26.6, 21.7.

IR: 2973, 1742, 1716, 1674, 1612, 1493, 1471, 1448, 1372, 1279, 1176, 1142, 1090, 987, 935, 749, 703, 680, 664 cm^{-1}

Chiral HPLC: IC, 80:20 heptane:isopropanol, 0.8 mL/min, 254 nm, 55.46 min (major), 64.20 (minor).

$[\alpha]_D^{23}$ = + 95.5° (c = 0.61, $CHCl_3$)

HRMS (ESI): Calculated for $C_{32}H_{32}N_2NaO_5S$ $(M+Na)^+$: 579.1924, Found 579.1909



5k

5k: Prepared according to the representative procedure from **4k** (21.0 mg, 0.10 mmol) in PhMe for 24 h. Purification *via* column chromatography (4:1 to 2:1 hexanes:EtOAc) afforded **5k** (33.7 mg, 96%, 13:1 linear:branched, 90% ee, *ca.* 93% purity) as a white foam.

The larger-scale synthesis of **5k** was performed with **4k** (104.6 mg, 0.50 mmol), $Pd_2dba_3{\cdot}CHCl_3$ (12.9 mg, 0.0125 mmol, 0.025 equivalent), **L2** (29.6 mg, 0.0375 mmol, 0.075 equivalent), allylidene dipivalate (193 µL, 181 mg, 0.75 mmol, 1.5 equivalent), ^{t}BuOH (239 µL, 185 mg, 2.5 mmol, 5 equivalents) in PhMe (1.25 mL) for 24 h. It was then poured into a mixture of Et_2O (50 mL) and saturated aqueous $NaHCO_3$ (50 mL). The phases were separated, and the aqueous phase was extracted with Et_2O (25 mL). The pooled organics were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (2:1 hexanes:EtOAc), affording **5k** (159.3 mg, 91%, 13:1 linear:branched, 89% ee) as a viscous yellow oil.

$\mathbf{R}_f$ = 0.20 (4:1 hexanes:EtOAc)

^{1}H NMR (500 MHz; $CDCl_3$): δ 7.73 (s, 1H), 7.39-7.27 (m, 6H), 7.23-7.21 (m, 1H), 7.11 (td, *J* = 7.6, 1.0 Hz, 1H), 7.06 (dt, *J* = 12.4, 1.3 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 5.09 (ddd, *J* = 12.4, 8.7, 6.9 Hz, 1H), 3.03-2.94 (m, 2H), 1.15 (s, 9H).

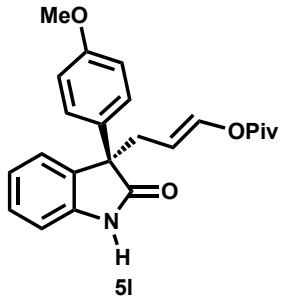
^{13}C NMR (150 MHz; $CDCl_3$): δ 180.2, 175.5, 141.0, 139.1, 139.0, 132.1, 128.8, 128.5, 127.7, 127.2, 125.6, 122.8, 110.3, 108.1, 57.0, 38.7, 35.7, 27.0

IR: 3238, 2974, 2933, 1742, 1711, 1620, 1473, 1279, 1226, 1143, 934, 752, 733, 697, 660 cm^{-1}

Chiral HPLC: IB, 80:20 heptane:isopropanol, 0.8 mL/min, 254 nm, 6.16 (minor), 12.05 (major).

$[\alpha]_D^{24}$ = + 71.2° (c = 0.53, $CHCl_3$)

HRMS (ESI): Calculated for $C_{22}H_{23}NNaO_3$ $(M+Na)^+$: 372.1570, Found 372.1569.



5l

5l: Prepared according to the representative procedure from **4l** (24.0 mg, 0.10 mmol) in PhMe for 48 h. Purification *via* column chromatography (4:1 to 2:1 hexanes:EtOAc) afforded **5l** (33.5 mg, 88%, 11:1 linear:branched, 84% ee, *ca.* 92% purity) as a white foam.

$\mathbf{R}_f$ = 0.40 (2:1 hexanes:EtOAc)

^{1}H NMR (500 MHz; $CDCl_3$): δ 7.98 (s, 1H), 7.30-7.27 (m, 3H), 7.20 (d, *J* = 7.4 Hz, 1H), 7.10 (td, *J* = 7.5, 1.0 Hz, 1H), 7.05 (dt, *J* = 12.4, 1.2 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.87-6.84 (m, 2H), 5.09 (ddd, *J* = 12.4, 8.8, 6.8 Hz, 1H), 3.77 (s, 3H), 2.99-2.90 (m, 2H), 1.15 (s, 9H).

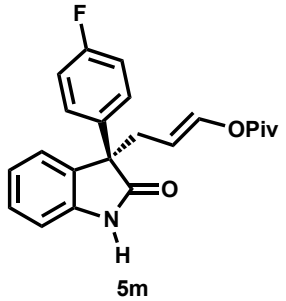
^{13}C NMR (125 MHz; $CDCl_3$): δ 180.7, 175.5, 159.0, 141.0, 138.9, 132.3, 131.1, 128.4, 128.3, 125.5, 122.7, 114.1, 110.3, 108.2, 56.3, 55.4, 38.7, 35.7, 27.0

IR: 3216, 2973, 1711, 1619, 1511, 1472, 1397, 1367, 1280, 1253, 1184, 1143, 1035, 935, 826, 797, 755 cm^{-1}

Chiral HPLC: IC, 80:20 heptane:isopropanol, 0.8 mL/min, 254 nm, 12.67 (minor), 22.78 (major).

$[\alpha]_D^{24}$ = + 81.0° (c = 0.46, $CHCl_3$)

HRMS (ESI): Calculated for $C_{23}H_{25}NNaO_4$ $(M+Na)^+$: 402.1676, Found 402.1672.



5m

5m: Prepared according to the representative procedure from **4m** (22.8 mg, 0.10 mmol) in PhMe for 24 h. Purification *via* column chromatography (4:1 to 2:1 hexanes:EtOAc) afforded **5m** (35.7 mg, 97%, 17:1 linear:branched, 89% ee, *ca.* 93% purity) as a white foam.

$\mathbf{R}_f$ = 0.44 (2:1 hexanes:EtOAc)

^{1}H NMR (500 MHz; $CDCl_3$): δ 8.39 (s, 1H), 7.37-7.33 (m, 2H), 7.29 (td, *J* = 7.7, 1.3 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.11 (td, *J* = 7.5, 1.0 Hz, 1H), 7.06 (dt, *J* = 12.4, 1.2 Hz, 1H), 7.02-6.98 (m, 2H), 6.96 (ddd, *J* = 7.8, 0.9, 0.6 Hz, 1H), 5.07 (ddd, *J* = 12.4, 8.8, 6.7 Hz, 1H), 2.97 (ddd, *J* = 14.0, 6.8, 1.5 Hz, 1H), 2.92 (ddd, *J* = 14.0, 8.9, 1.0 Hz, 1H), 1.15 (s, 9H).

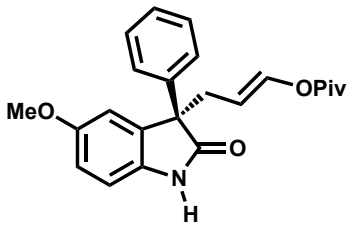
^{13}C NMR (125 MHz; $CDCl_3$): δ 180.2, 175.5, 140.9, 139.1, 131.8, 129.0, 128.9, 128.7, 125.5, 122.9, 115.7, 115.5, 110.5, 107.9, 56.4, 38.7, 36.0, 27.0

IR: 3209, 2975, 1712, 1619, 1509, 1472, 1398, 1327, 1279, 1231, 1142, 934, 814, 753 cm^{-1}

Chiral HPLC: IB, 80:20 heptane:isopropanol, 0.8 mL/min, 254 nm, 5.82 (minor), 14.20 (major).

$[\alpha]_D^{24}$ = + 83.7° (c = 0.31, $CHCl_3$)

HRMS (ESI): Calculated for $C_{22}H_{22}FNNaO_3$ $(M+Na)^+$: 390.1476, Found 309.1479.



5n

5n: Prepared according to the representative procedure from **4n** (24.0 mg, 0.10 mmol) in PhMe for 72 h. Purification *via* column chromatography (4:1 to 2:1 hexanes:EtOAc) afforded **5n** (28.5 mg, 75%, 9:1 linear:branched, 87% ee, *ca.* 92% purity) as a viscous, light yellow oil.

R_f = 0.34 (2:1 hexanes:EtOAc)

^{1}H NMR (400 MHz; $CDCl_3$): δ 8.24 (s, 1H), 7.38-7.28 (m, 5H), 7.09 (dt, *J* = 12.4, 1.2 Hz, 1H), 6.88-6.79 (m, 3H), 5.11 (ddd, *J* = 12.4, 8.9, 6.6 Hz, 1H), 3.77 (s, 3H), 3.04-2.92 (m, 2H), 1.15 (s, 9H).

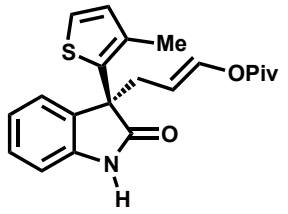
^{13}C NMR (125 MHz; $CDCl_3$): δ 180.2, 175.5, 155.9, 139.1, 139.0, 134.4, 133.5, 128.8, 127.7, 127.1, 113.3, 112.3, 110.7, 108.1, 57.4, 55.9, 38.7, 35.5, 27.0

IR: 3230, 2972, 1708, 1602, 1488, 1278, 1205, 1142, 1033, 934, 810, 734, 697 cm^{-1}

Chiral HPLC: IC, 95:5 heptane:isopropanol, 0.8 mL/min, 254 nm, 36.27 (minor), 57.11 (major).

$[\alpha]_D^{24}$ = + 61.6° (c = 0.40, $CHCl_3$)

HRMS (ESI): Calculated for $C_{23}H_{25}NNaO_4$ $(M+Na)^+$: 402.1676, Found 402.1670.



5o

5o: Prepared according to the representative procedure from **4o** (23.0 mg, 0.10 mmol) in PhMe for 48 h. Purification *via* column chromatography (2:1 hexanes:EtOAc) afforded **5o** (34.4 mg, 93%, 14:1 linear:branched, 92% ee, *ca.* 97% purity) as a viscous, light yellow oil.

$\mathbf{R}_f$ = 0.38 (2:1 hexanes:EtOAc)

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.72 (s, 1H), 7.25 (td, *J* = 7.6, 1.5 Hz, 1H), 7.12-7.03 (m, 4H), 6.91 (dt, *J* = 7.8, 0.8 Hz, 1H), 6.77 (d, *J* = 5.2 Hz, 1H), 5.07 (ddd, *J* = 12.4, 8.7, 6.9 Hz, 1H), 3.11 (ddd, *J* = 13.4, 8.7, 1.1 Hz, 1H), 3.03 (ddd, *J* = 13.4, 6.9, 1.5 Hz, 1H), 1.76 (s, 3H), 1.15 (s, 9H).

^{13}C NMR (125 MHz; $CDCl_3$): δ 178.9, 175.4, 140.5, 139.5, 135.4, 134.9, 132.1, 132.0, 128.6, 124.6, 123.1, 122.4, 110.0, 107.0, 54.4, 38.7, 36.9, 27.0, 14.4.

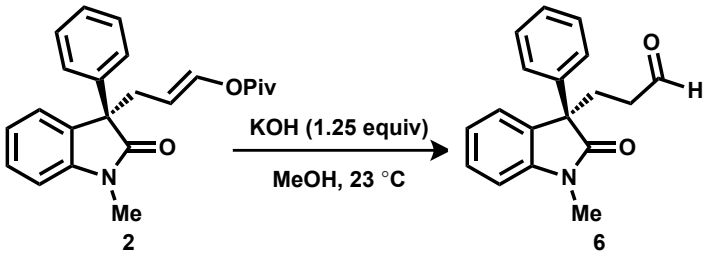
IR: 3223, 2974, 1714, 1618, 1472, 1397, 1279, 1225, 1141, 934, 733, 674 cm^{-1}

Chiral HPLC: IB, 95:5 heptane:isopropanol, 0.4 mL/min, 254 nm, 18.07 (minor), 30.20 (major).

$[\alpha]_D^{22}$ = - 1.29° (c = 0.75, $CHCl_3$)

HRMS (ESI): Calculated for $C_{21}H_{23}NNaO_3S$ $(M+Na)^+$: 392.1291, Found 392.1279

f) Synthesis of Compounds 6-10



2 **6**

Synthesis of 6 (from 2): To a solution of enol pivalate **2** (31.0 mg, 0.085 mmol, 1 equivalent) in MeOH (0.42 mL) in a 2-dram vial was added a solution of KOH (6.0 mg, 0.11 mmol, 1.25 equivalents) in MeOH (0.43 mL) dropwise. The reaction mixture was stirred at room temperature for 3 h, at which point it was diluted with Et_2O (10 mL) and poured into pH 7 phosphate buffer (5 mL). The phases were separated, and the aqueous phase was extracted with Et_2O (5 mL). The pooled organics were dried over $MgSO_4$, filtered, and concentrated. The

residue was purified *via* column chromatography (2:1 hexanes:EtOAc) to afford **6** (19.9 mg, 84%) as a cloudy, viscous oil.

Synthesis of 6 (one-pot, from 1): For the one-pot synthesis, the Pd-AAA was carried out according to the representative procedure, using **1** (22.3 mg, 0.10 mmol, 1 equivalent). After 24 h, TLC indicated full consumption of **1**. The reaction vial was opened, and the mixture was diluted with a solution of KOH (18.2 mg, 0.32 mmol, 3.25 equivalents) in MeOH (0.75 mL). The reaction mixture was stirred for 2 h at room temperature, at which point it was poured into pH 7 buffer (5 mL). The phases were separated, and the aqueous phase was extracted with Et_2O (3 x 5 mL). The pooled organics were dried over $MgSO_4$, filtered, and concentrated. The residue was purified *via* column chromatography (2:1 hexanes:EtOAc) to afford **6** (19.6 mg, 70%).

$\mathbf{R_f}$ = 0.16 (2:1 hexanes:EtOAc)

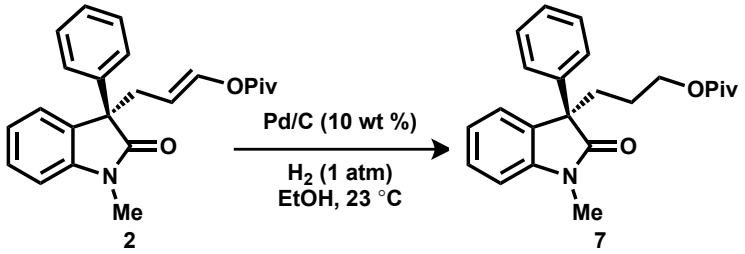
^{1}H NMR (500 MHz; $CDCl_3$): δ 9.62 (t, *J* = 1.3 Hz, 1H), 7.38-7.29 (m, 5H), 7.27-7.22 (m, 2H), 7.12 (td, *J* = 7.5, 1.0 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 3.25 (s, 3H), 2.73 (ddd, *J* = 13.9, 10.5, 5.2 Hz, 1H), 2.53 (ddd, *J* = 13.9, 10.7, 5.0 Hz, 1H), 2.36-2.29 (m, 1H), 2.17-2.10 (m, 1H).

^{13}C NMR (125 MHz; $CDCl_3$): δ 200.9, 178.1, 143.8, 139.4, 131.5, 128.8(2), 128.7(9), 127.7, 126.9, 124.8, 123.1, 108.7, 55.6, 39.5, 29.9, 26.6.

IR: 2918, 2849, 1710, 1611, 1493, 1470, 1372, 1347, 754, 697 cm^{-1}

$\mathbf{[\alpha]_D^{23}}$ = + 87.2° (c = 0.99, $CHCl_3$)

HRMS (ESI): Calculated for $C_{18}H_{17}NNaO_2$ $(M+Na)^+$: 302.1151, Found 302.1146



Synthesis of 7: To a solution of enol pivalate **2** (41.9 mg, 0.115 mmol, 1 equivalent) in EtOH (0.58 mL) in a 2-dram vial was added Pd/C (4.2 mg, 10 weight %, 3 weight % on activated carbon). The solution was sparged with H_2 (balloon, *ca.* 2-3 minutes) then kept under H_2 (balloon) and stirred vigorously for 18 h. The reaction mixture was then filtered through Celite®, eluting with Et_2O (10 mL). The solution was concentrated and the residue was purified *via*

column chromatography (6:1 hexanes:EtOAc) to afford **7** (34.4 mg, 82%) as a clear, colorless oil.

$\mathbf{R}_f$ = 0.21 (4:1 hexanes:EtOAc)

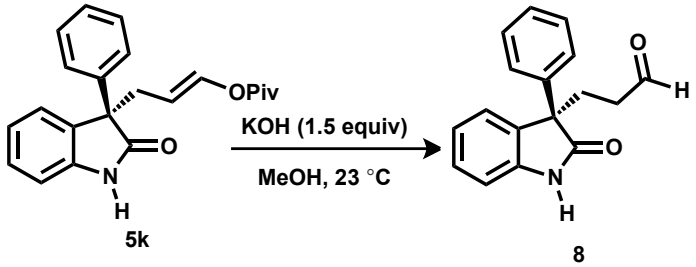
^{1}H NMR (600 MHz; $CDCl_3$): δ 7.37-7.33 (m, 3H), 7.31-7.28 (m, 2H), 7.25-7.22 (m, 2H), 7.13 (td, *J* = 7.5, 0.9 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 4.01-3.93 (m, 2H), 3.23 (s, 3H), 2.43 (ddd, *J* = 13.2, 12.3, 4.7 Hz, 1H), 2.28 (td, *J* = 12.9, 4.0 Hz, 1H), 1.52-1.43 (m, 1H), 1.29-1.23 (m, 1H), 1.17 (s, 9H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 178.6, 178.3, 144.0, 140.0, 131.9, 128.7, 128.5, 127.5, 127.0, 124.8, 122.8, 108.5, 64.0, 56.3, 38.8, 34.5, 27.3, 26.5, 24.2

IR: 2962, 2360, 1718, 1612, 1493, 1471, 1372, 1346, 1284, 1157, 1037, 751 cm^{-1}

$\mathbf{[\alpha]_D^{23}}$ = + 100.3° (c = 0.32, $CHCl_3$)

HRMS (ESI): Calculated for $C_{23}H_{27}NNaO_3$ $(M+Na)^+$: 388.1883, Found 388.1877



Synthesis of 8: To a solution of enol pivalate **5k** (104 mg, 0.30 mmol, 1 equivalent) in MeOH (2.0 mL) in a 2-dram vial was added a solution of KOH (25.1 mg, 0.45 mmol, 1.5 equivalents) in MeOH (1.0 mL) dropwise. The reaction mixture was stirred at room temperature for 1 h, at which point it was diluted with EtOAc (10 mL) and poured into pH 7 phosphate buffer (5 mL). The phases were separated, and the aqueous phase was extracted with EtOAc (2 x 5 mL). The pooled organics were dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography (1:1 hexanes:EtOAc) to afford **8** (65.7 mg, 83%) as a viscous, light yellow oil.

$\mathbf{R}_f$ = 0.27 (1:1 hexanes:EtOAc)

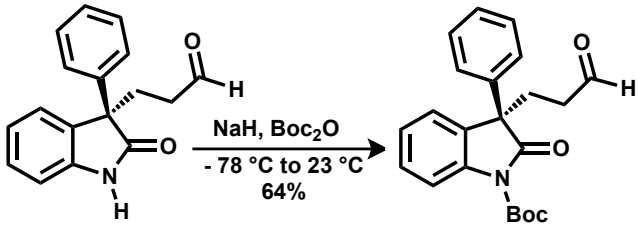
^{1}H NMR (500 MHz; $CDCl_3$): δ 9.65 (t, *J* = 1.2 Hz, 1H), 7.80 (s, 1H), 7.38-7.27 (m, 6H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 7.7 Hz, 1H), 2.74 (ddd, *J* = 13.8, 10.6, 5.1 Hz, 1H), 2.59-2.53 (m, 1H), 2.47-2.40 (m, 1H), 2.21 (dddd, *J* = 17.8, 10.6, 4.8, 1.3 Hz, 1H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 201.0, 180.6, 141.0, 139.3, 132.2, 128.9, 128.8, 127.8, 126.9, 125.0, 123.1, 110.5, 56.1, 39.4, 29.5.

IR: 3241, 2920, 1716, 1618, 1471, 1445, 1391, 1329, 1213, 1108, 753, 697 cm^{-1}

$[\alpha]_D^{23}$ = + 69.1° (c = 1.38, $CHCl_3$)

HRMS (ESI): Calculated for $C_{17}H_{15}NNaO_2$ $(M+Na)^+$: 288.0995, Found 288.0990



8 **9**

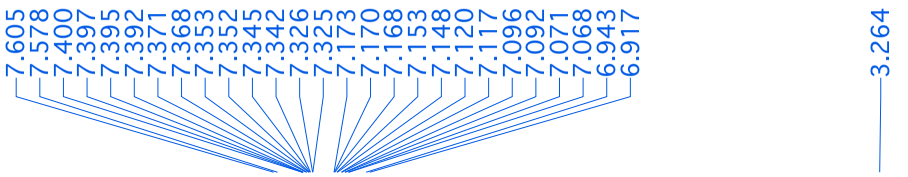
Synthesis of 9: To a solution of **8** (4.9 mg, 0.018 mmol, 1 equivalent) in THF (0.38 mL) in a 2-dram vial at – 78 °C (dry ice / isopropanol bath) was added NaH (0.8 mg of a 60% dispersion in mineral oil, 0.020 mmol, 1.1 equivalents). The reaction mixture was stirred at this temperature for 20 min, then Boc_2O (4.0 mg, 0.018 mmol, 1 equivalent) was added. The cooling bath was removed and the reaction mixture was allowed to warm to room temperature. After 30 min, the reaction mixture was diluted with pH 7 buffer (3 mL) and Et_2O (3 mL). The phases were separated, and the aqueous phase was extracted with Et_2O (2 x 3 mL). The pooled organics were dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography (2:1 hexanes:EtOAc) to afford **9** (4.3 mg, 64%) as a light yellow film.

^{1}H NMR (400 MHz; $CDCl_3$): δ 9.64 (t, *J* = 1.1 Hz, 1H), 7.95 (ddd, *J* = 8.2, 1.0, 0.6 Hz, 1H), 7.39 (ddd, *J* = 8.2, 7.2, 1.8 Hz, 1H), 7.33-7.29 (m, 5H), 7.23 (dd, *J* = 7.2, 1.0 Hz, 1H), 7.20 (ddd, *J* = 7.5, 1.8, 0.6 Hz, 1H), 2.81 (ddd, *J* = 13.7, 11.0, 4.7 Hz, 1H), 2.52 (ddd, *J* = 13.7, 11.2, 4.4 Hz, 1H), 2.40 (dddd, *J* = 17.6, 11.3, 4.7, 1.1 Hz, 1H), 2.15 (dddd, *J* = 17.7, 11.0, 4.4, 1.2 Hz, 1H), 1.63 (s, 9H).

$[\alpha]_D^{23}$ = + 49.5° (c = 0.43, $CHCl_3$) (Lit = - 63.67° (c = 1.00, $CHCl_3$))

These data match that reported for the antipode of ***9***.[12]

[12] R. He, C. Ding, K. Maruoka, *Angew. Chem.* **2009**, *121*, 4629; *Angew. Chem. Int. Ed.* **2009**, *48*, 4559.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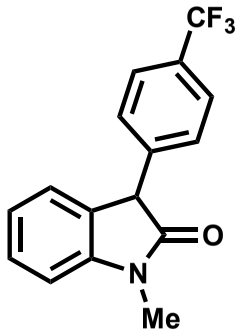
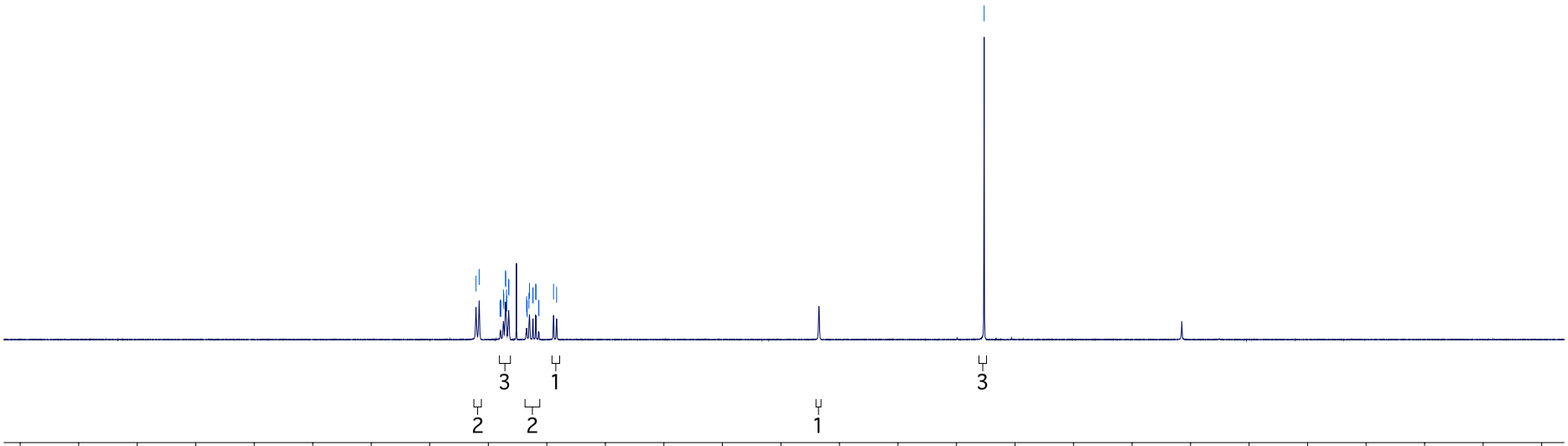

CF3
O
N
Me

4b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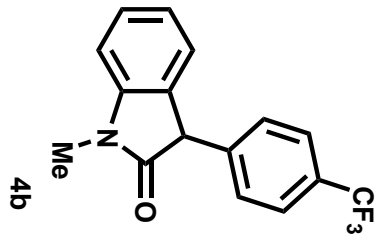

4b

175.247

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123.090

108.579

51.824

26.686

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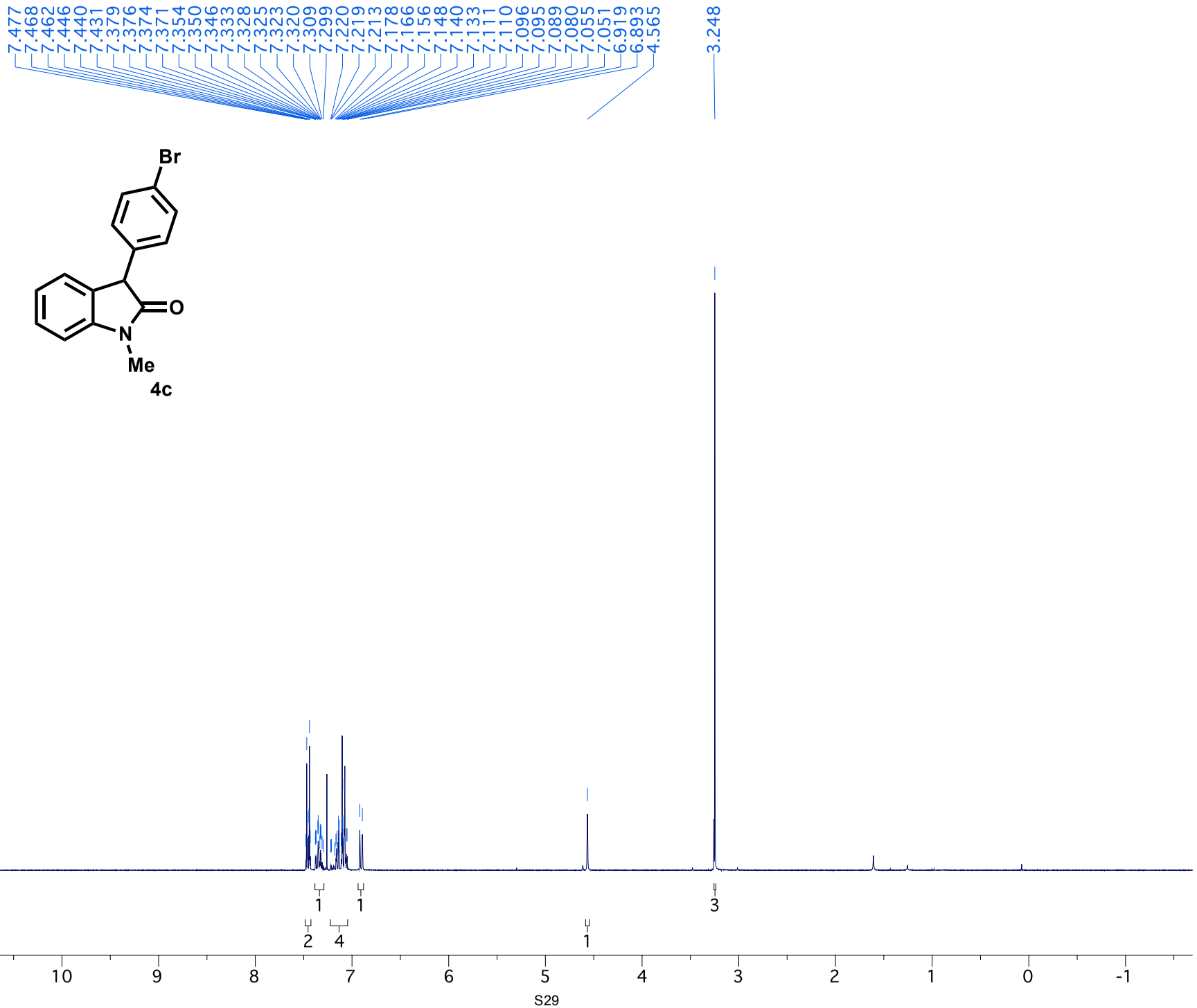
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7.089
7.080
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3.248
Br
O
N
Me
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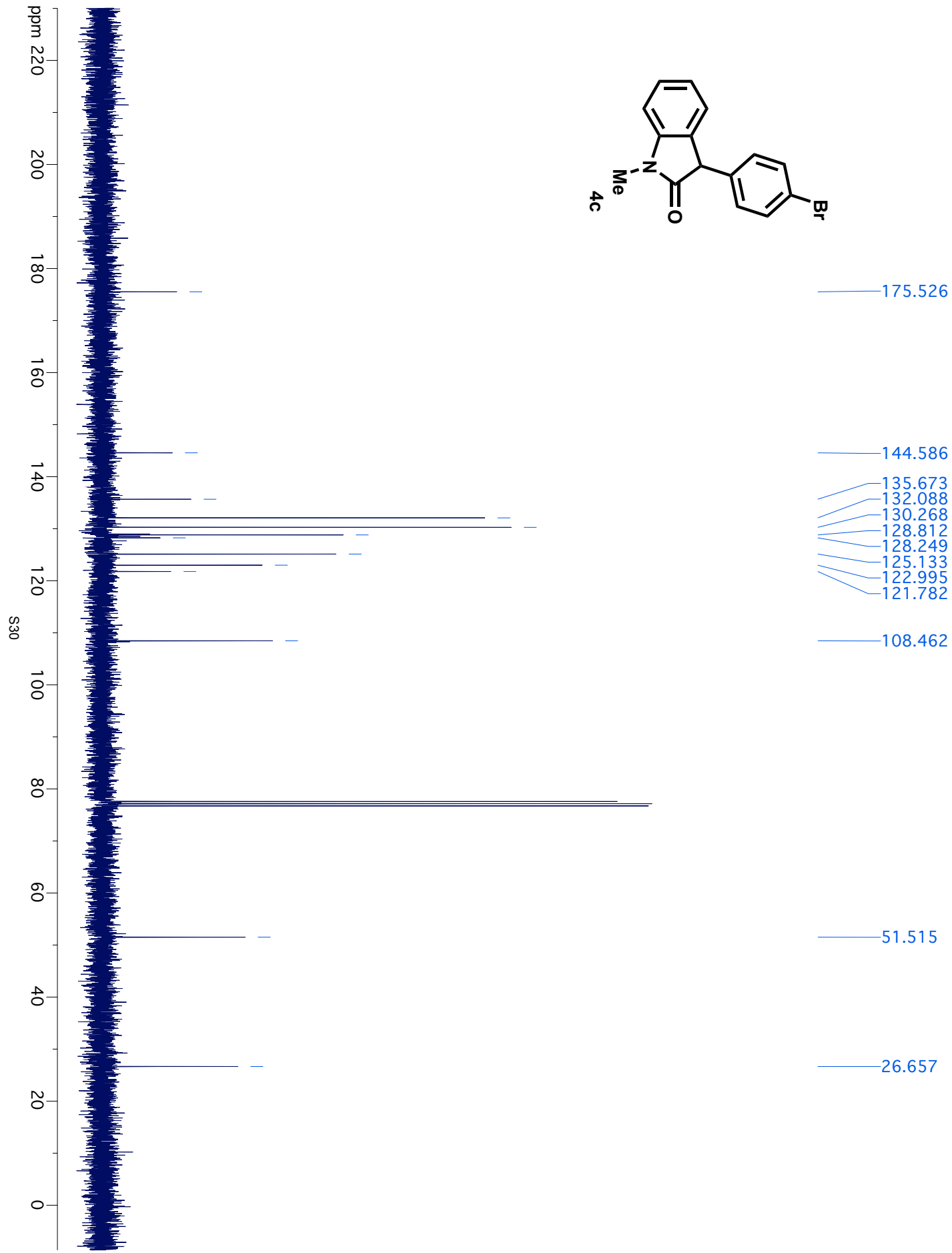
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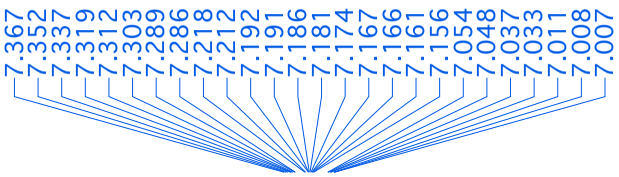
26.657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7.181
7.174
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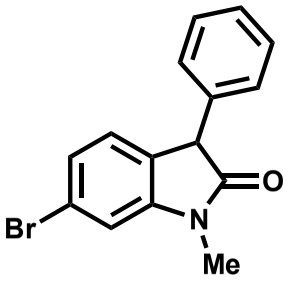
7.033
7.011
7.008
7.007
4.550
3.234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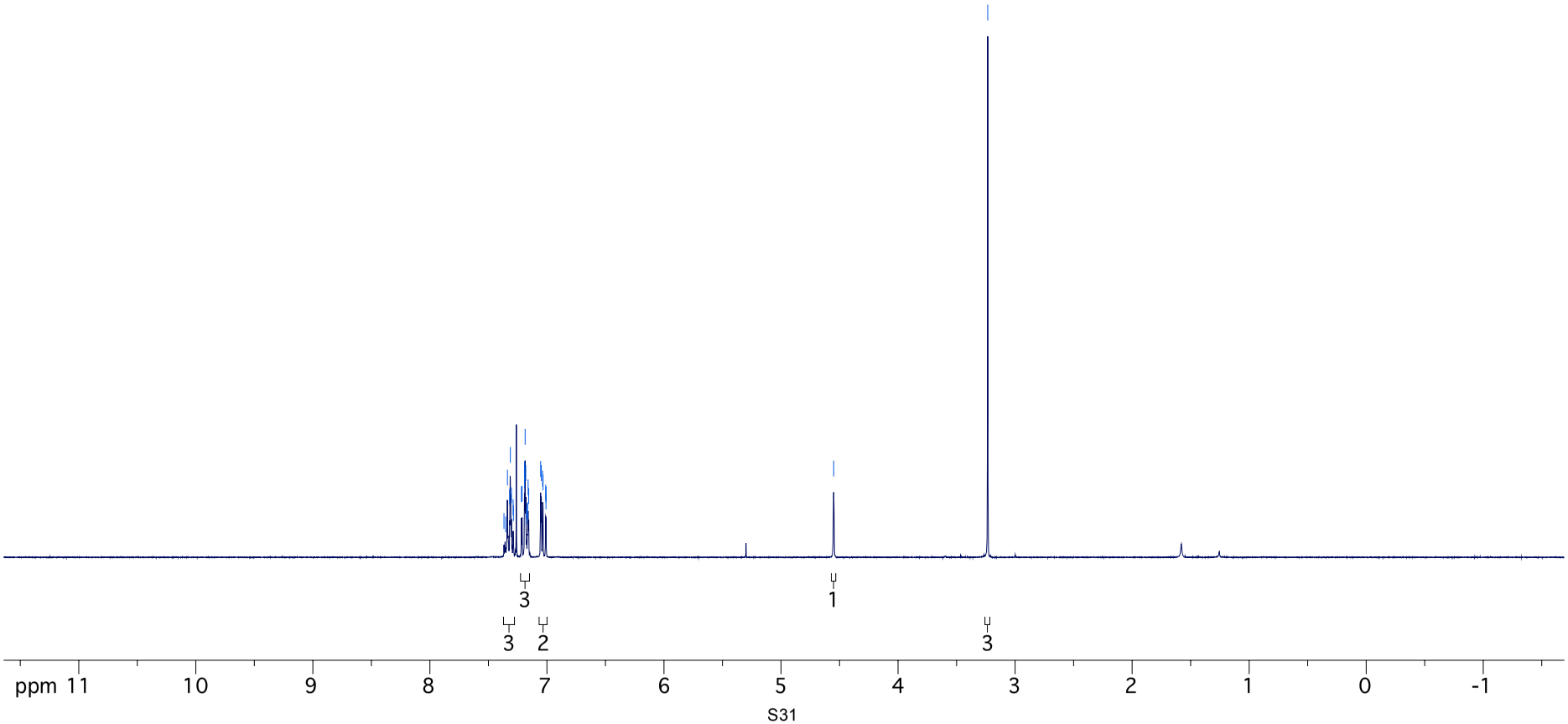
N
Me

4g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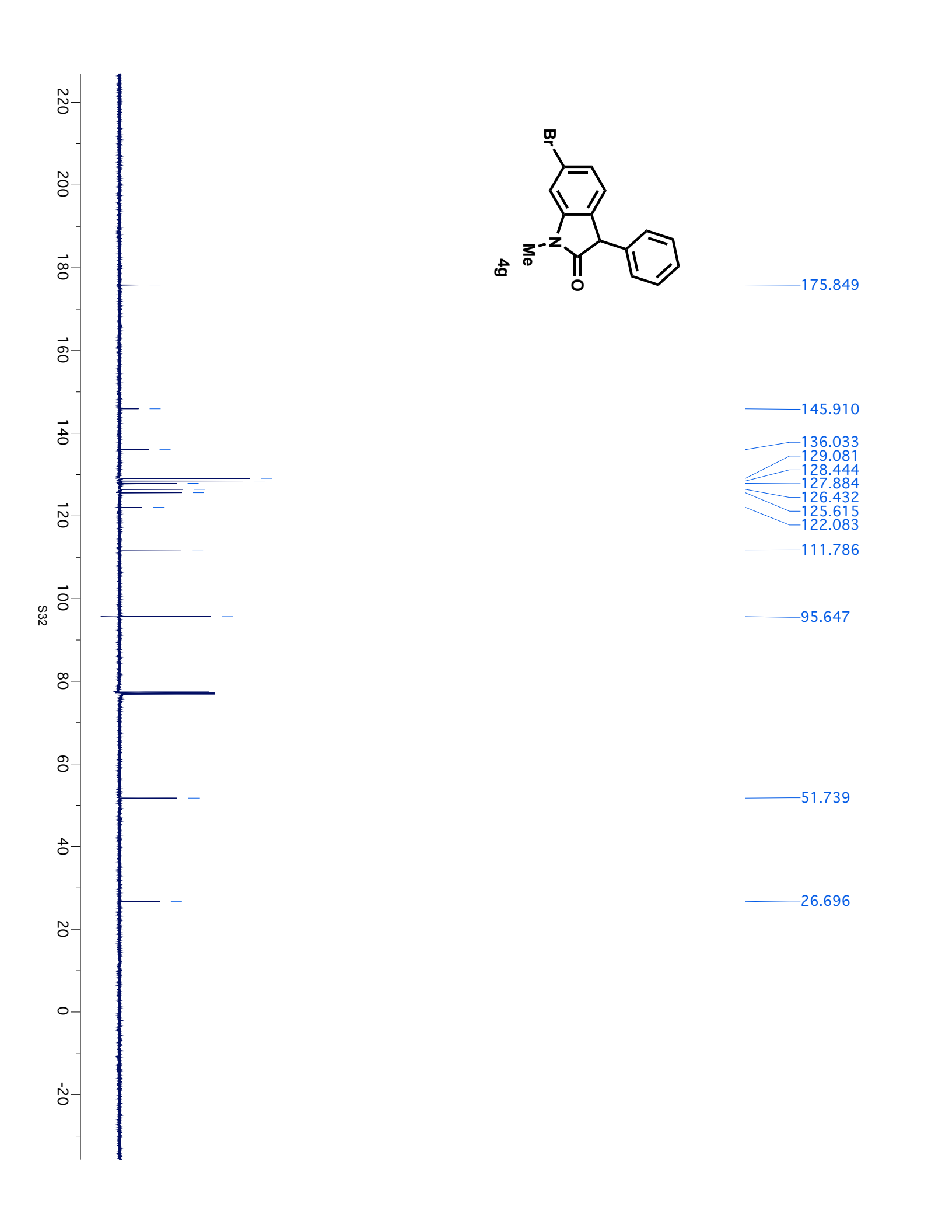
Br
N
Me
O
4g
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126.432
125.615
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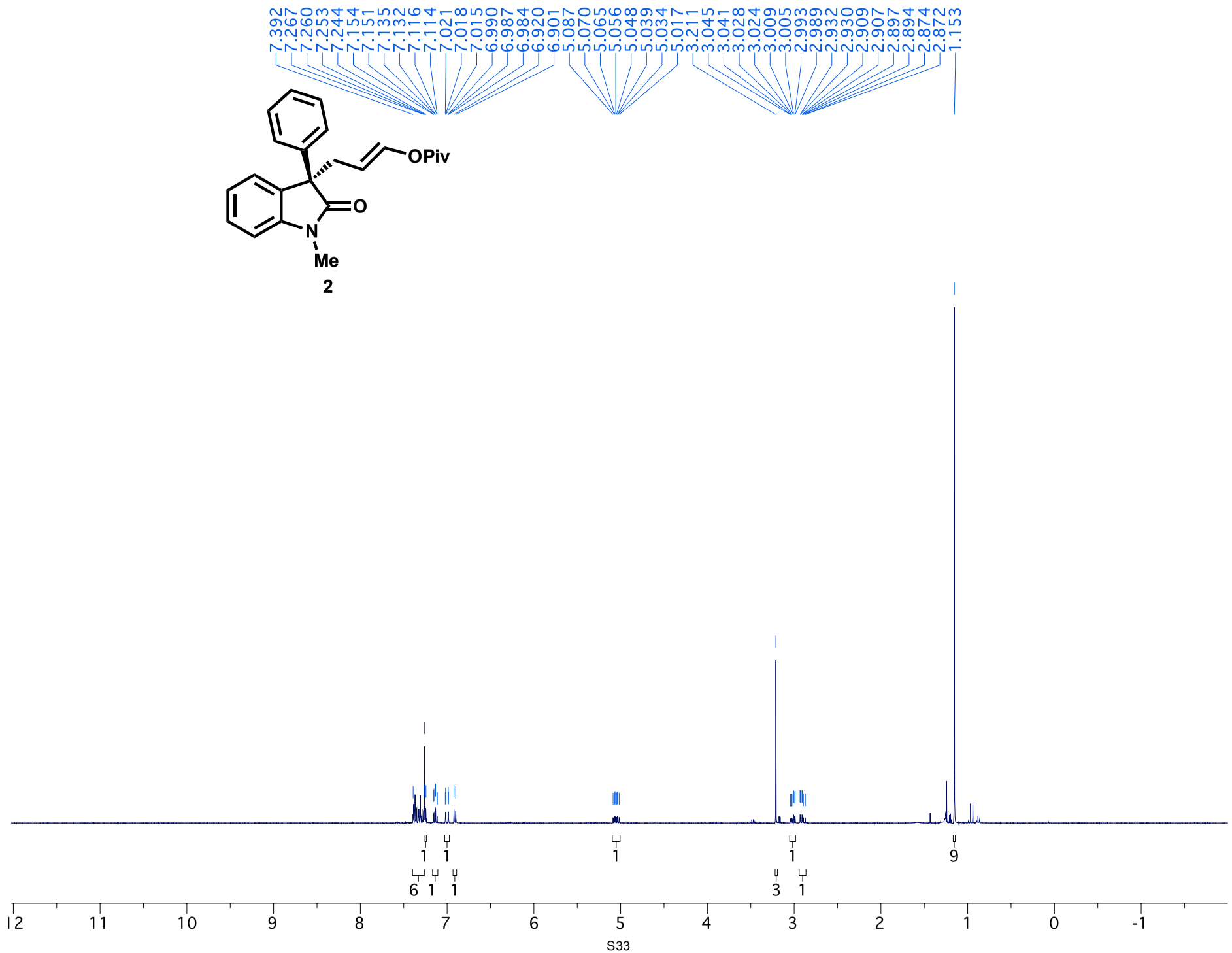
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7.151
7.135
7.132
7.116
7.114
7.021
7.018
7.015
6.990
6.987
6.984
6.920
6.901
5.087
5.070
5.065
5.056
5.048
5.039
5.034
5.017
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3.045
3.041
3.028
3.024
3.009
3.005
2.993
2.989
2.932
2.930
2.909
2.907
2.897
2.894
2.874
2.872
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OPiv
O
N
Me
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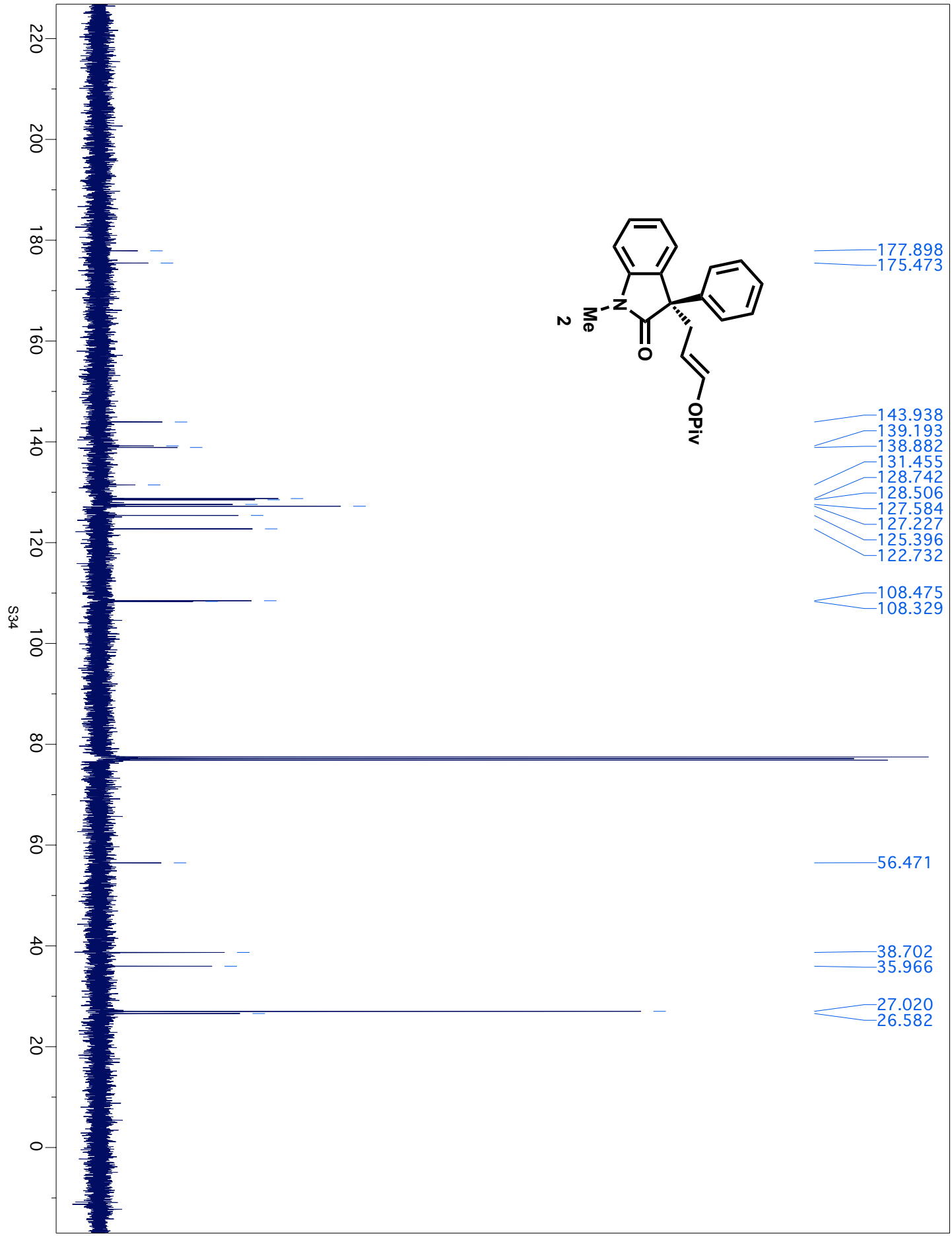
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127.227
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56.471
38.702
35.966
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Me
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O
OPiv
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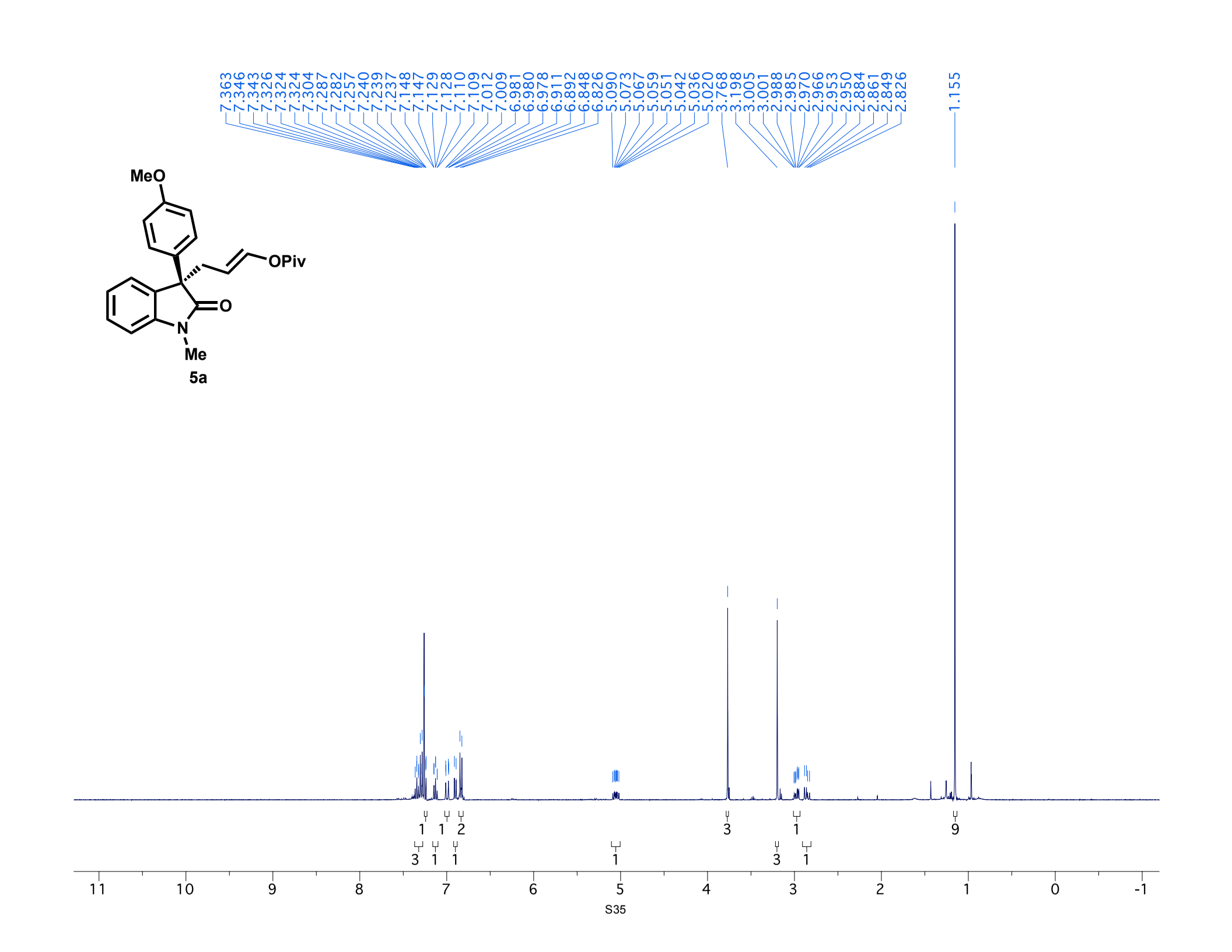
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7.239
7.237
7.148
7.147
7.129
7.128
7.110
7.109
7.012
7.009
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6.980
6.978
6.911
6.892
6.848
6.826
5.090
5.073
5.067
5.059
5.051
5.042
5.036
5.020
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3.198
3.005
3.001
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2.985
2.970
2.966
2.953
2.950
2.884
2.861
2.849
2.826
1.155
MeO
OPiv
O
N
Me
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1
2
3
1
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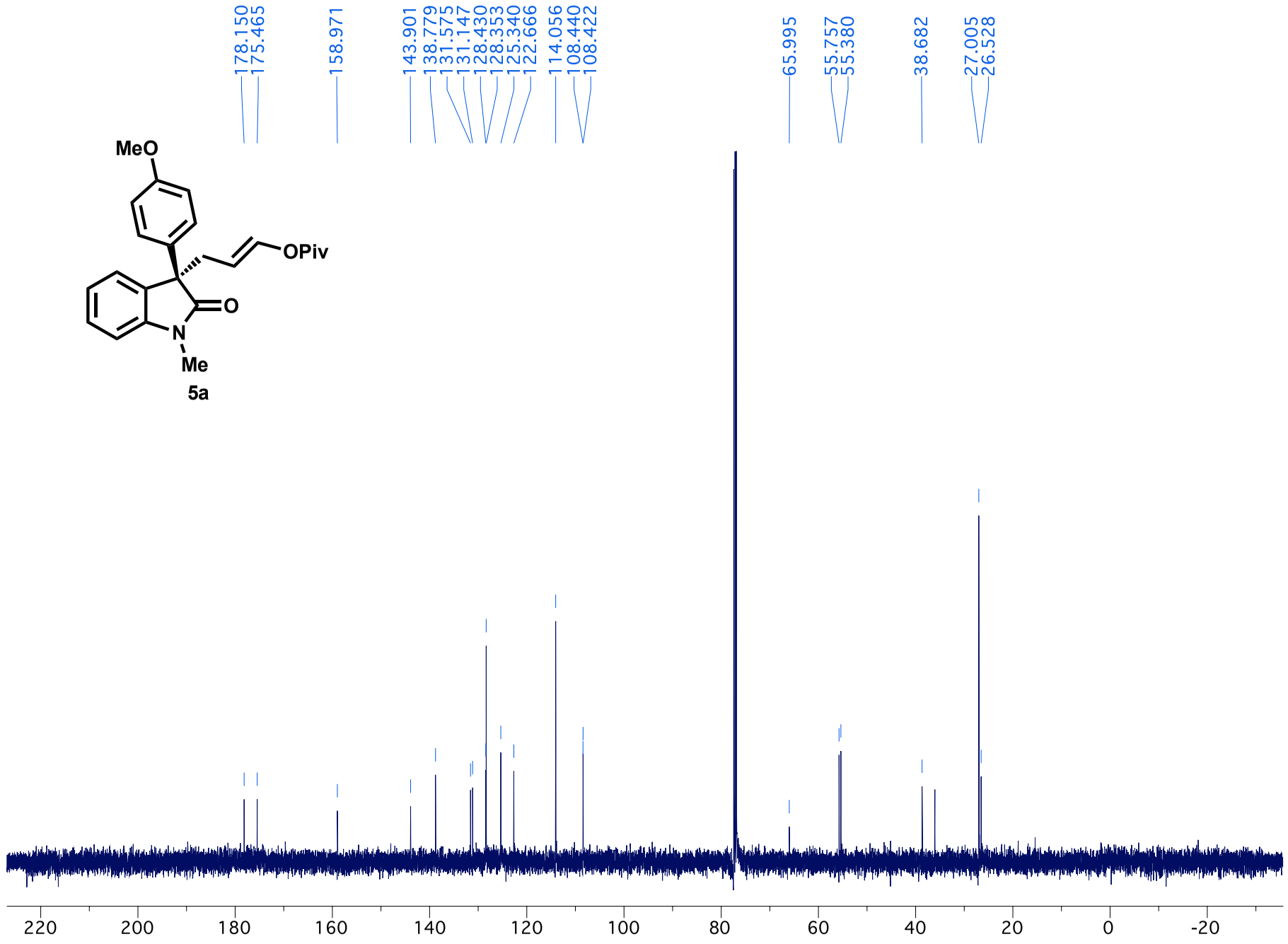
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65.995
55.757
55.380
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27.005
26.528
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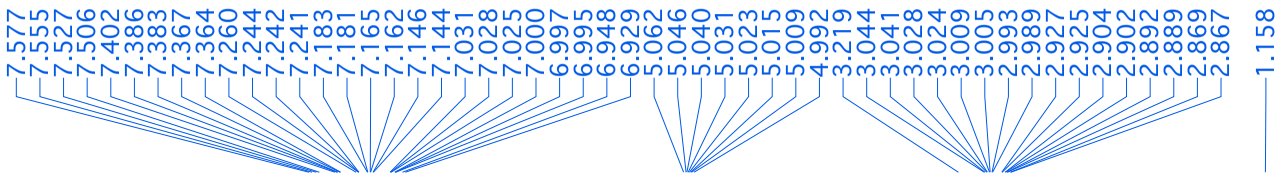
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7.241
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7.181
7.165
7.162
7.146
7.144
7.031
7.028
7.025
7.000
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6.995
6.948
6.929
5.062
5.046
5.040
5.031
5.023
5.015
5.009
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3.044
3.041
3.028
3.024
3.009
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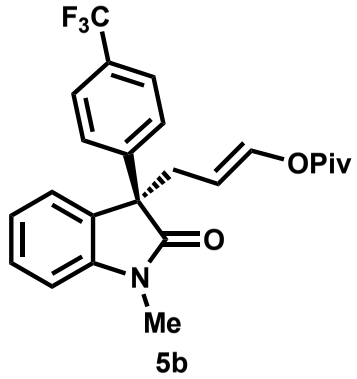
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OPiv
O
N
Me

5b

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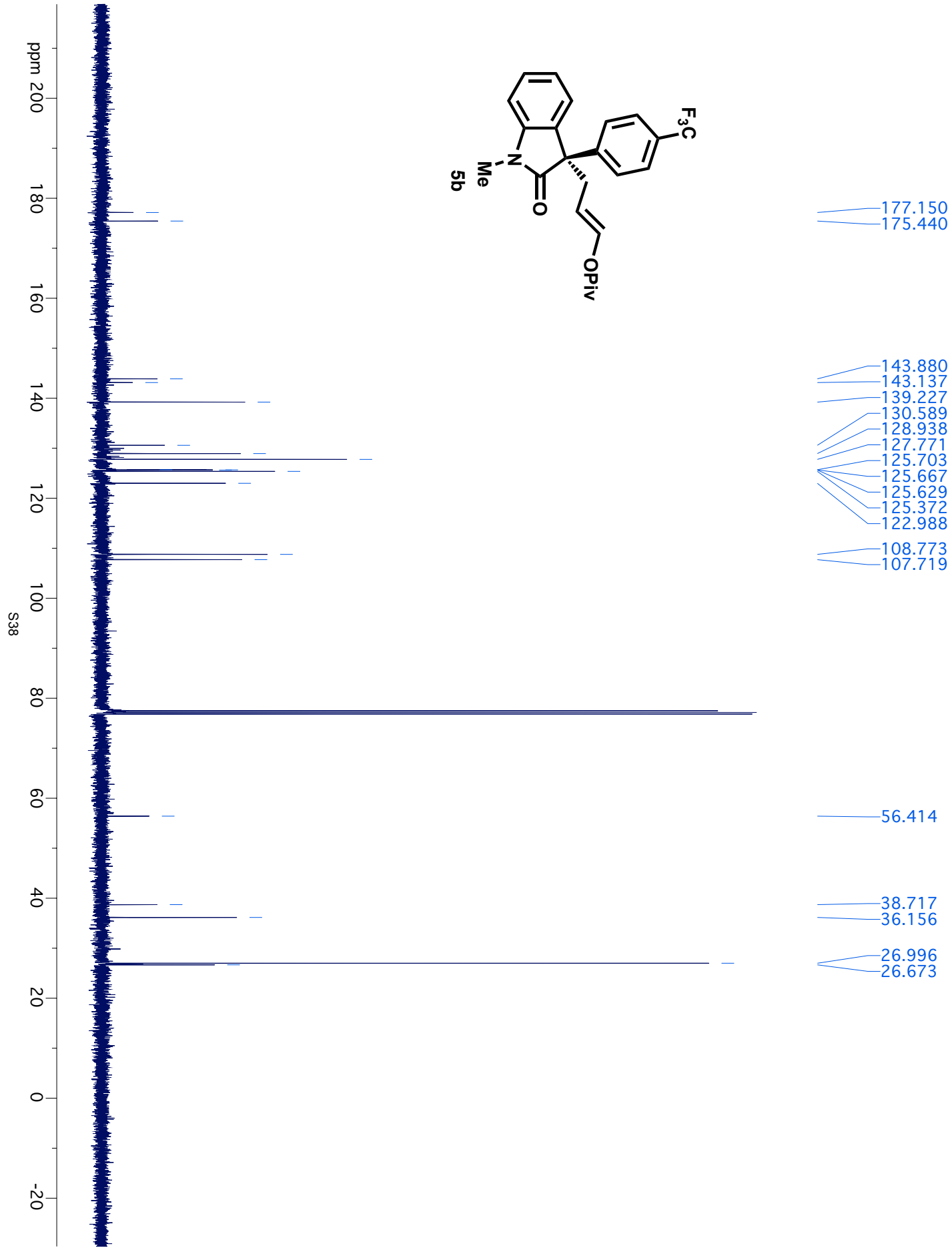
ppm 200
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140
120
100
80
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-20
F3C
N
Me
O
OPiv
5b
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130.589
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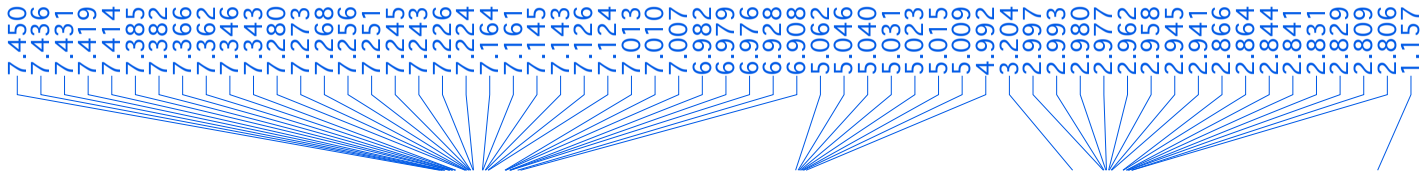
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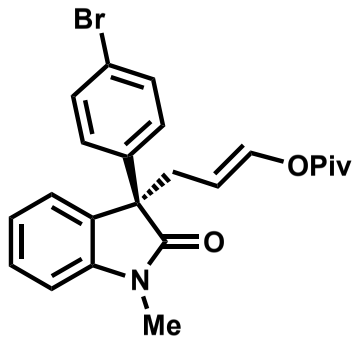
Br
OPiv
O
N
Me

5c

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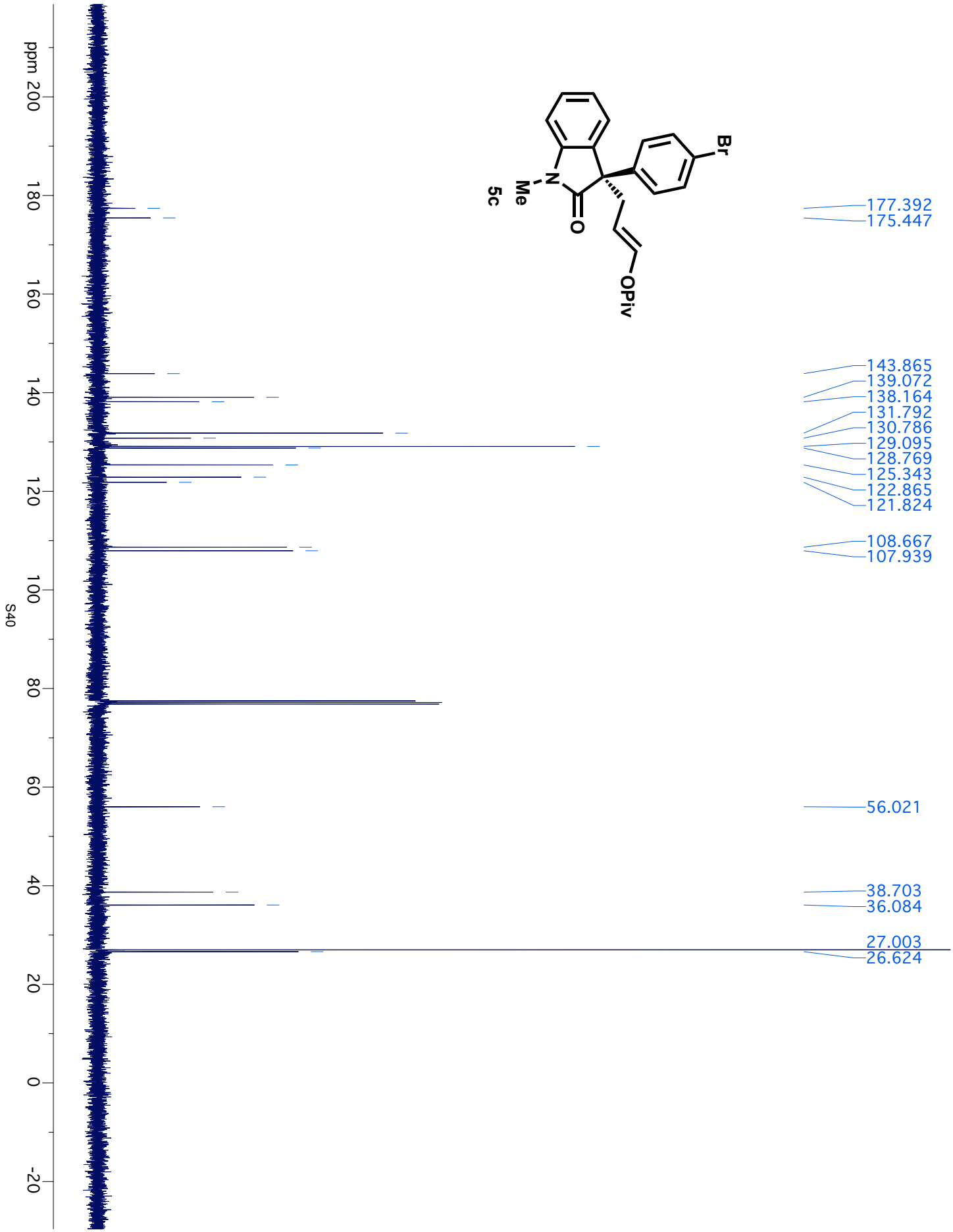
0
-1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-20
Br
N
Me
O
OPiv
5c
177.392
175.447
143.865
139.072
138.164
131.792
130.786
129.095
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122.865
121.824
108.667
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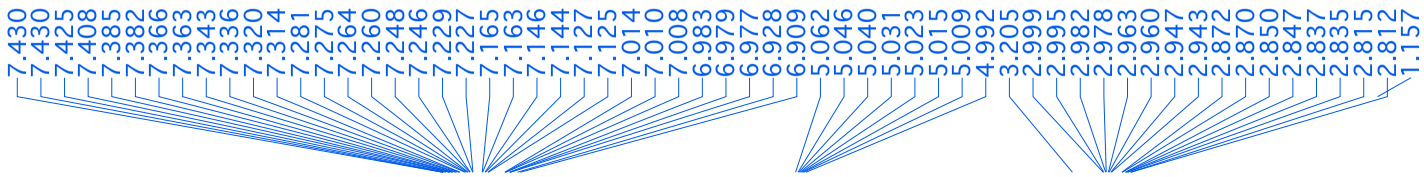
26.624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5.046
5.040
5.031
5.023
5.015
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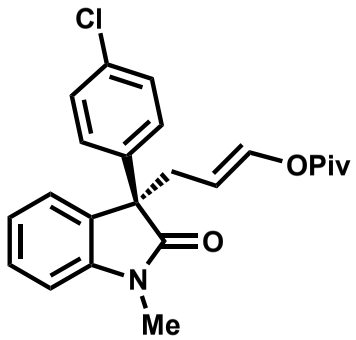
Cl
OPiv
O
N
Me

5d

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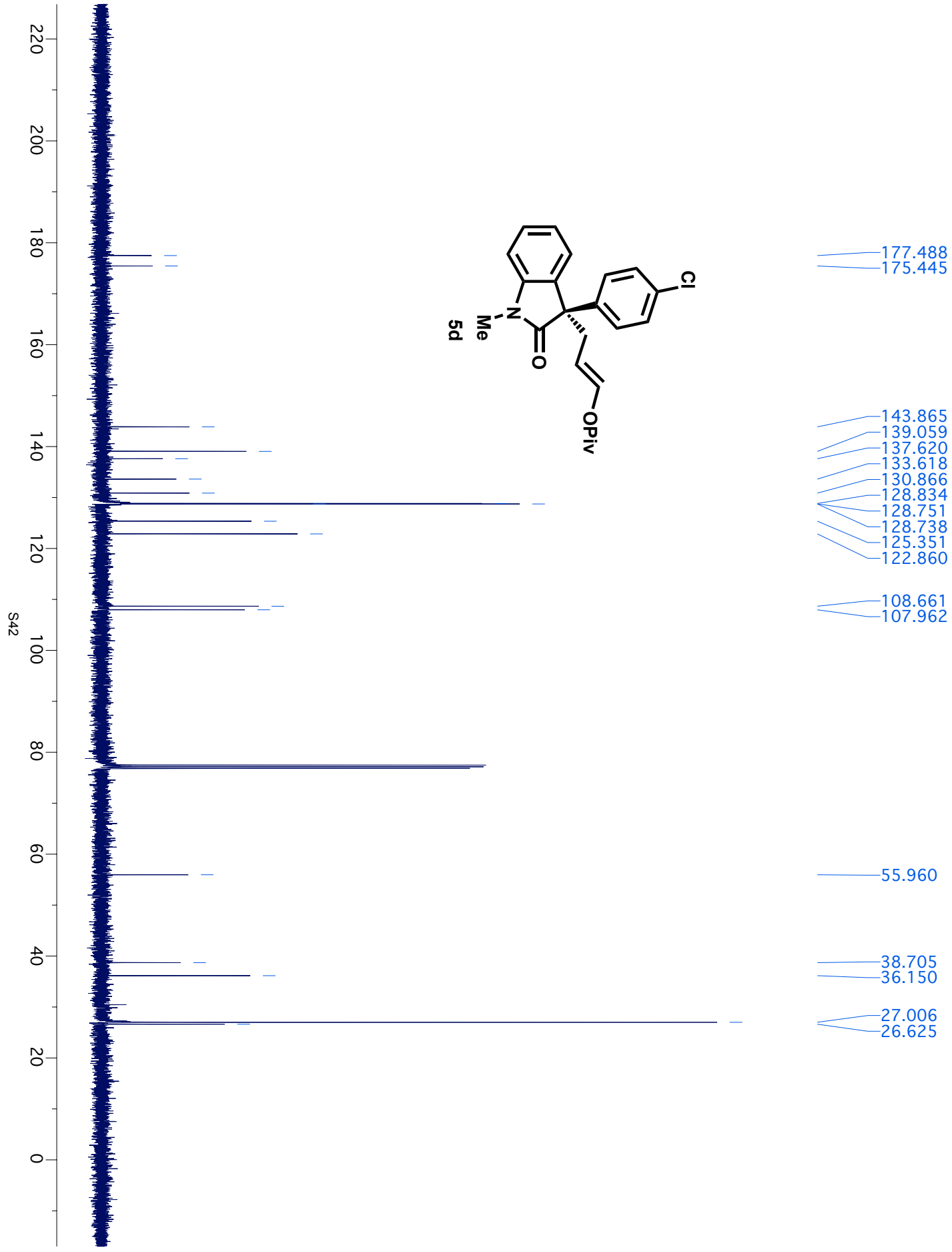
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27.006
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OPiv
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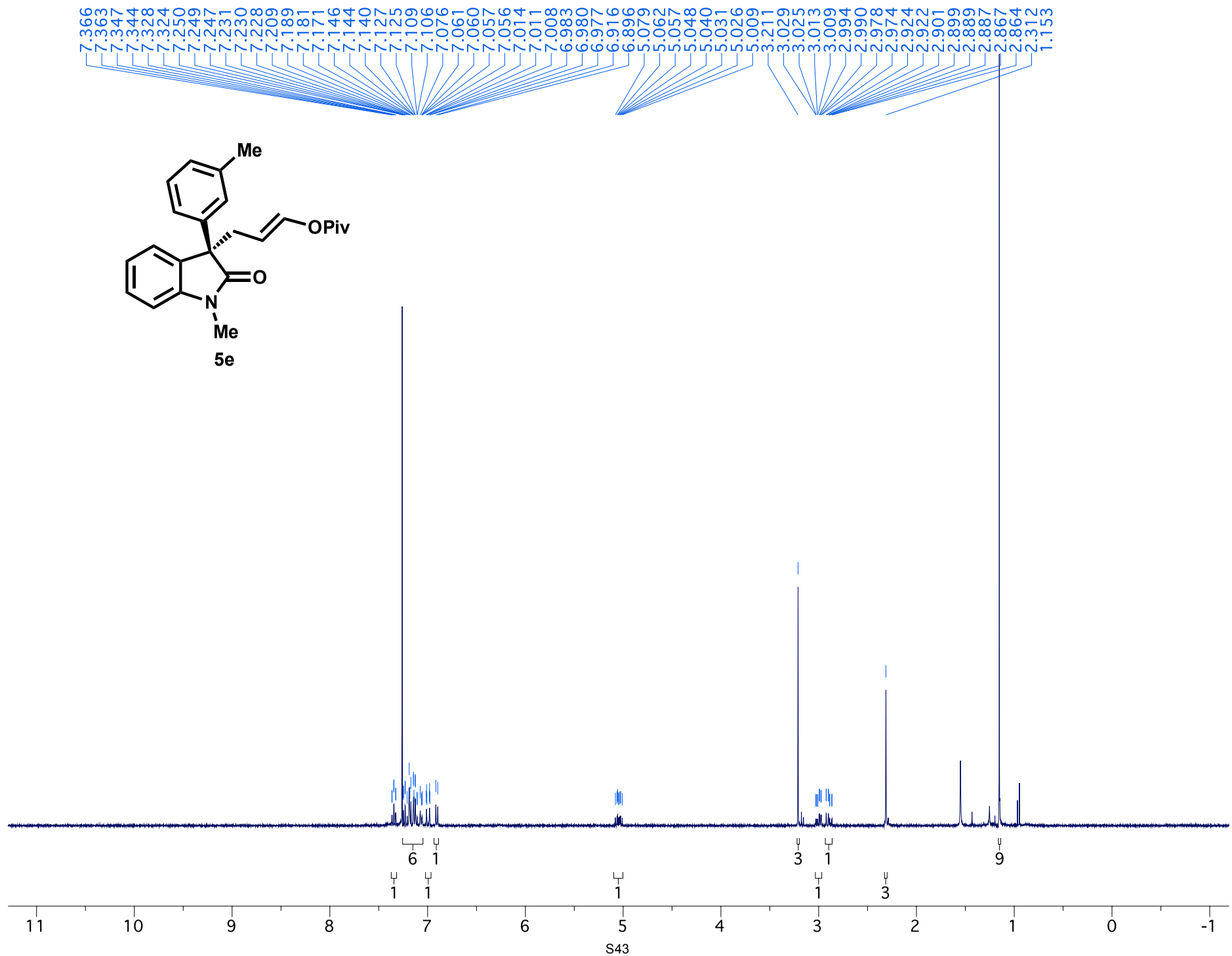
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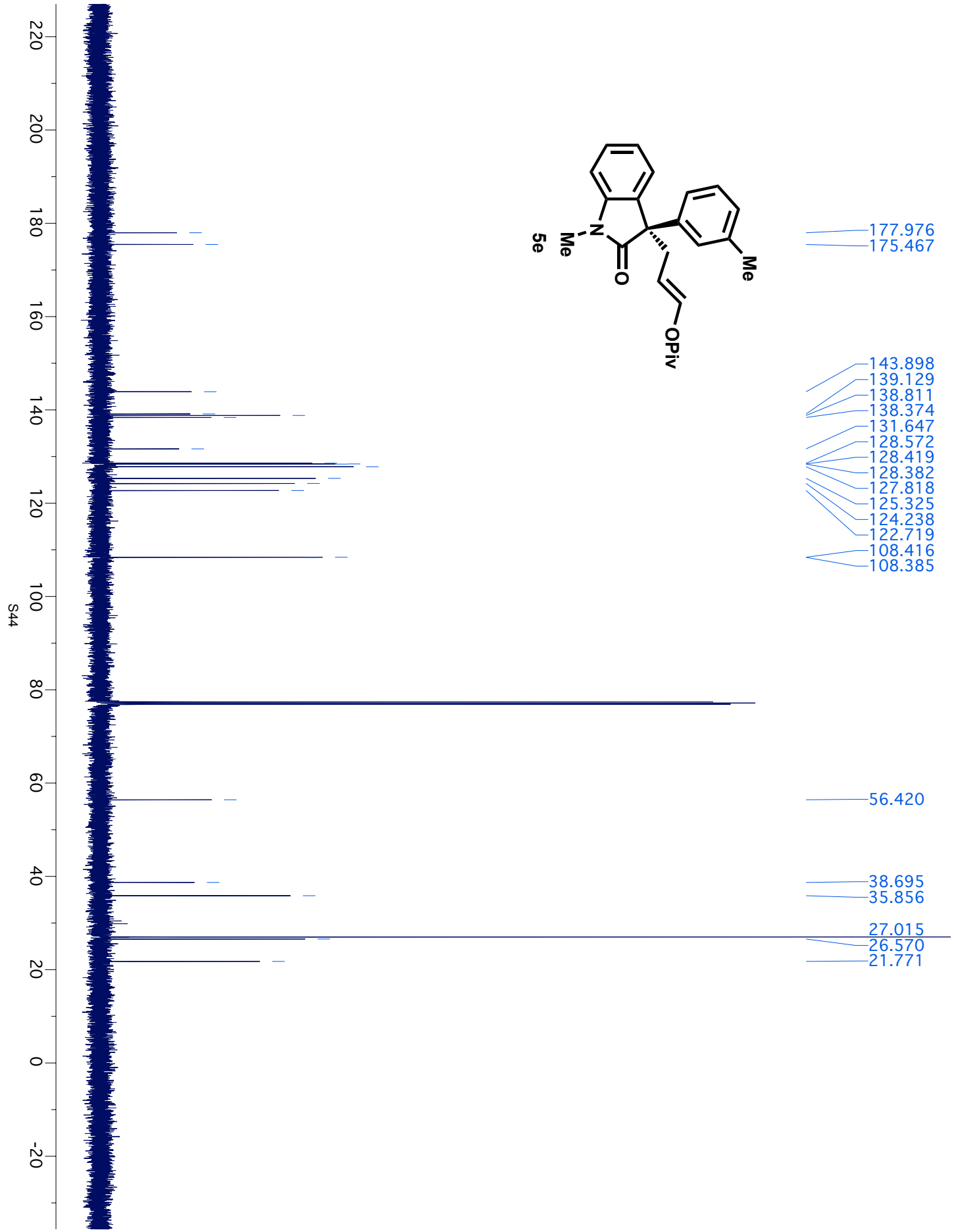
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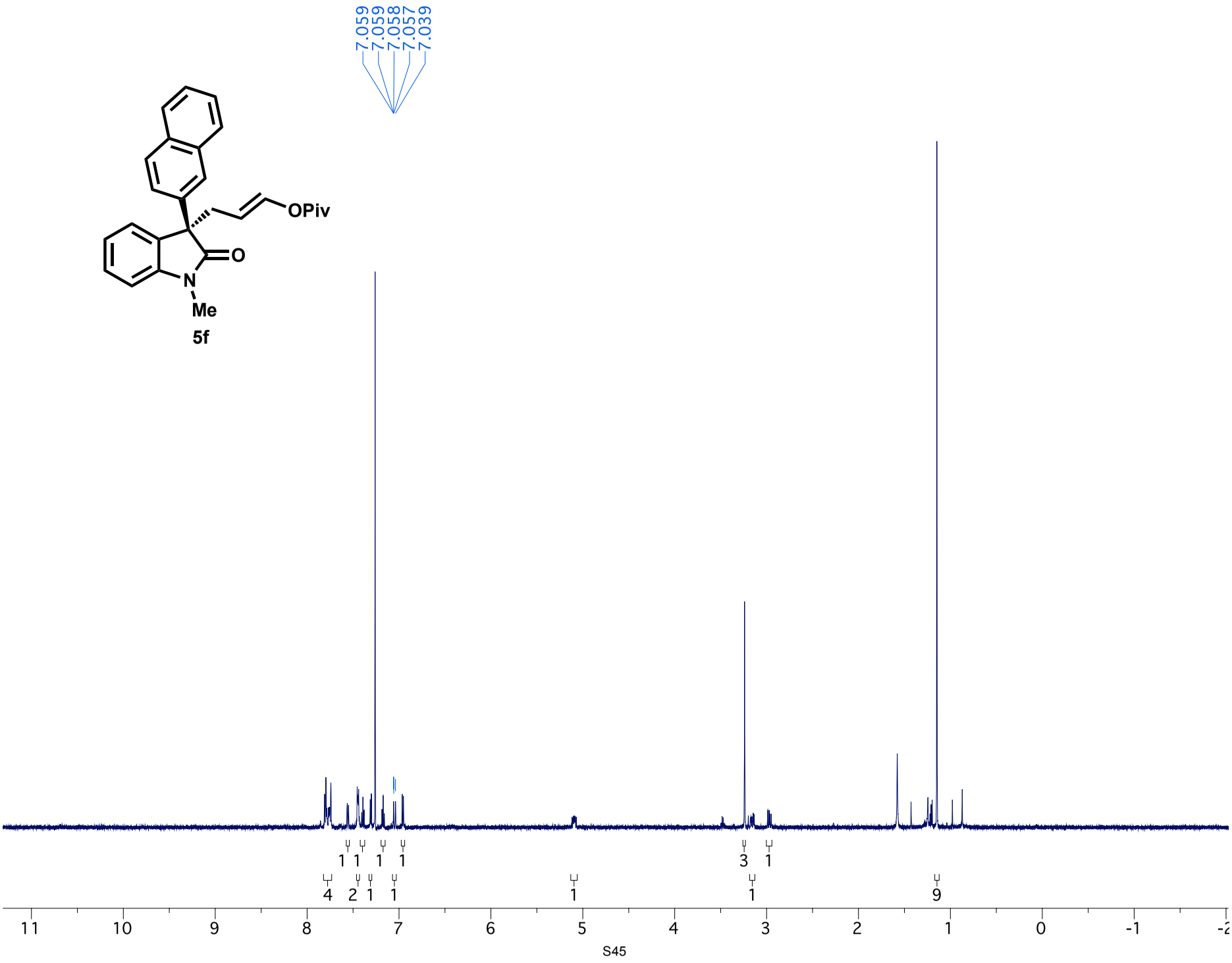
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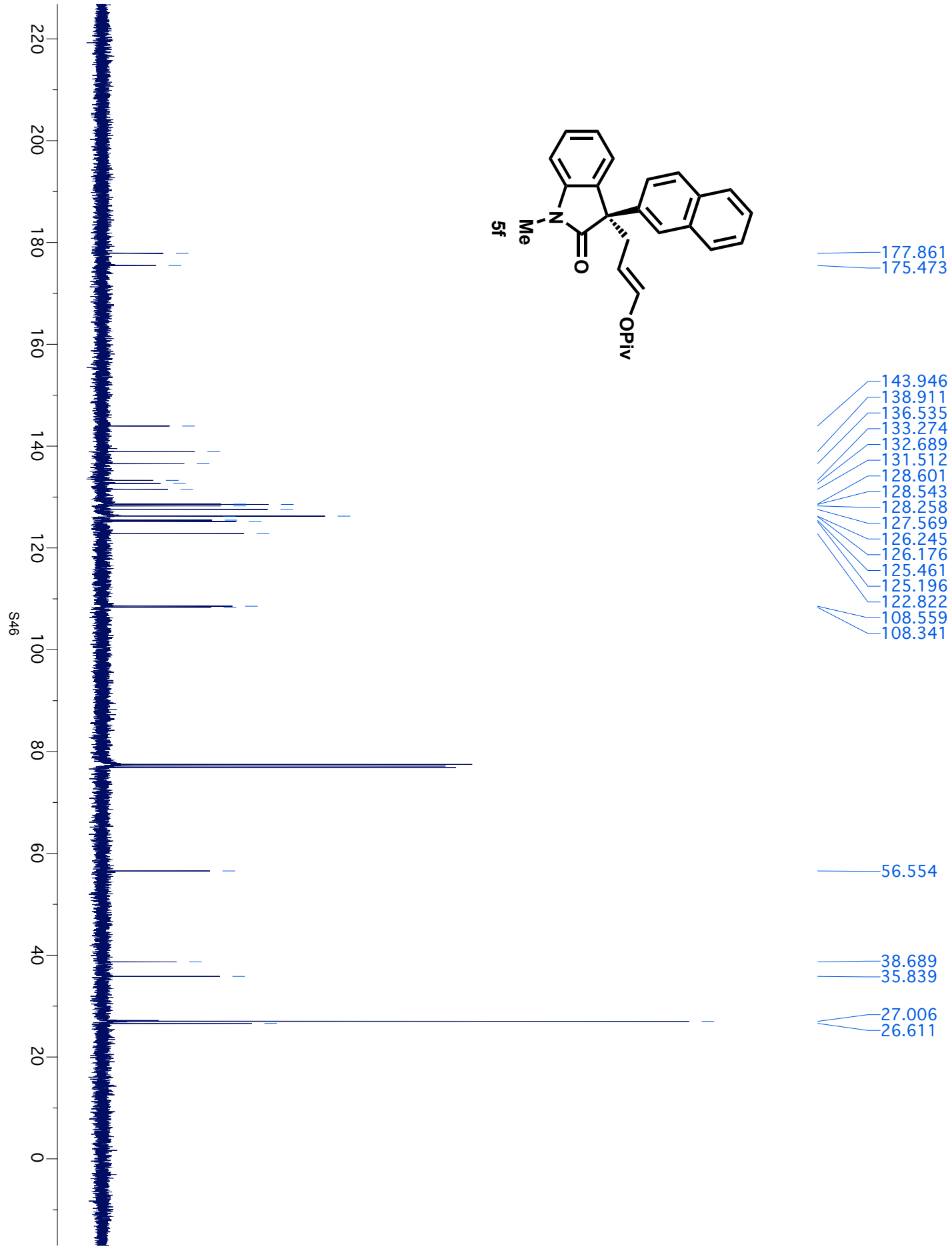
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OPiv
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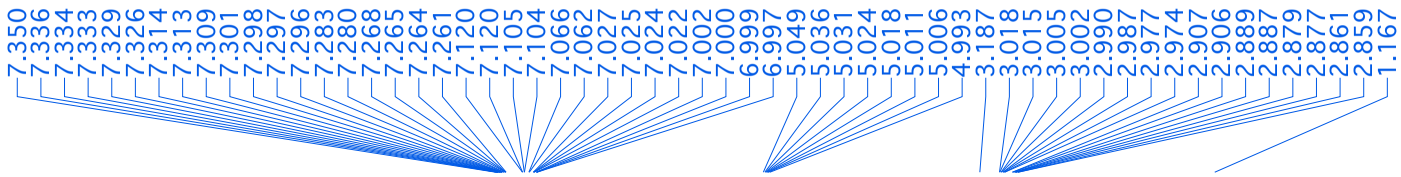
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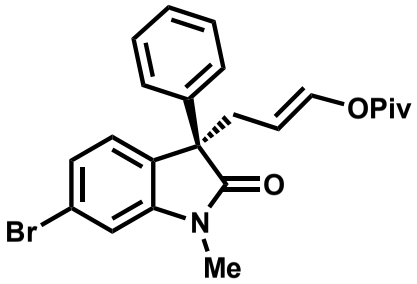
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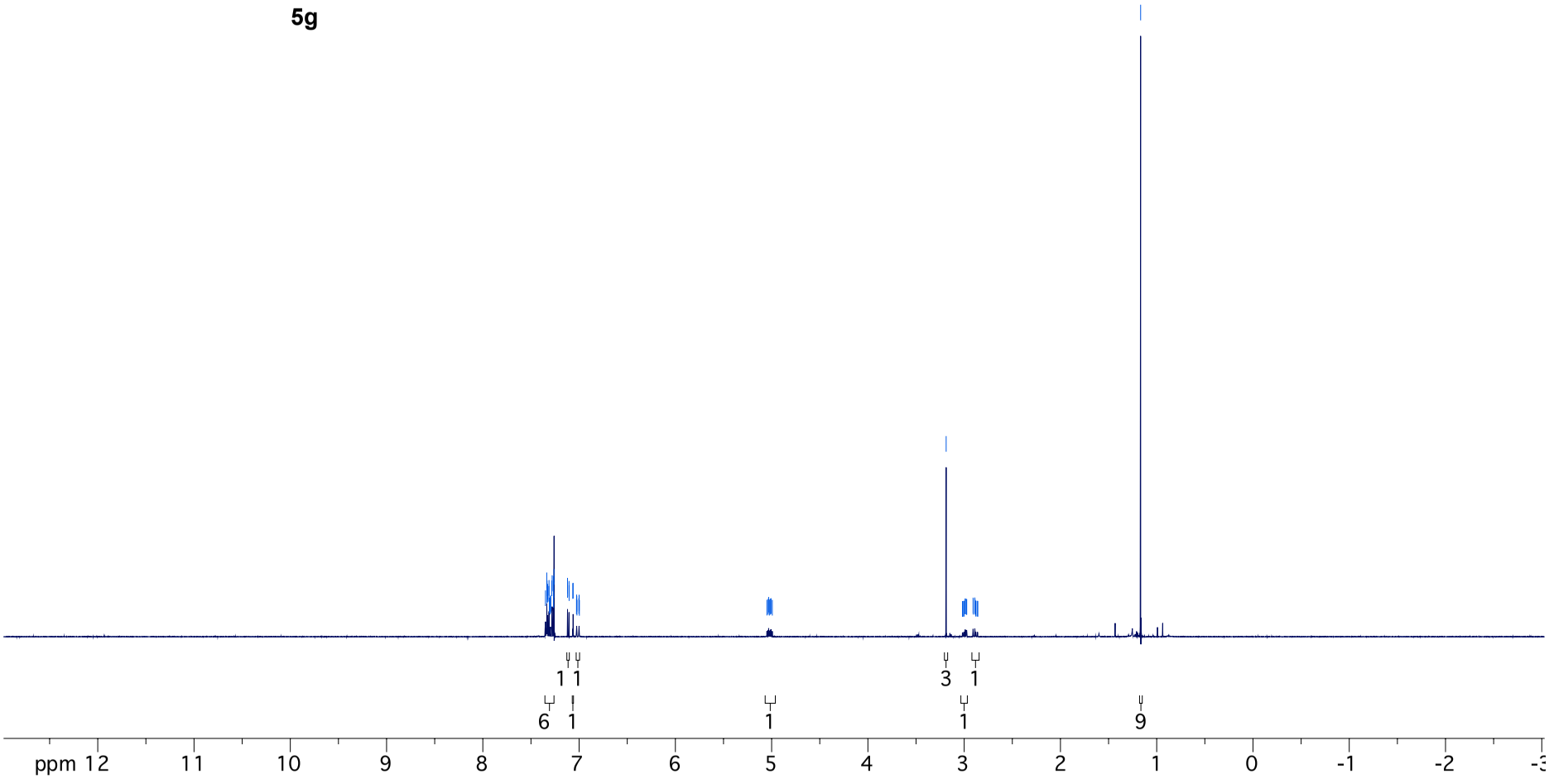
Me

5g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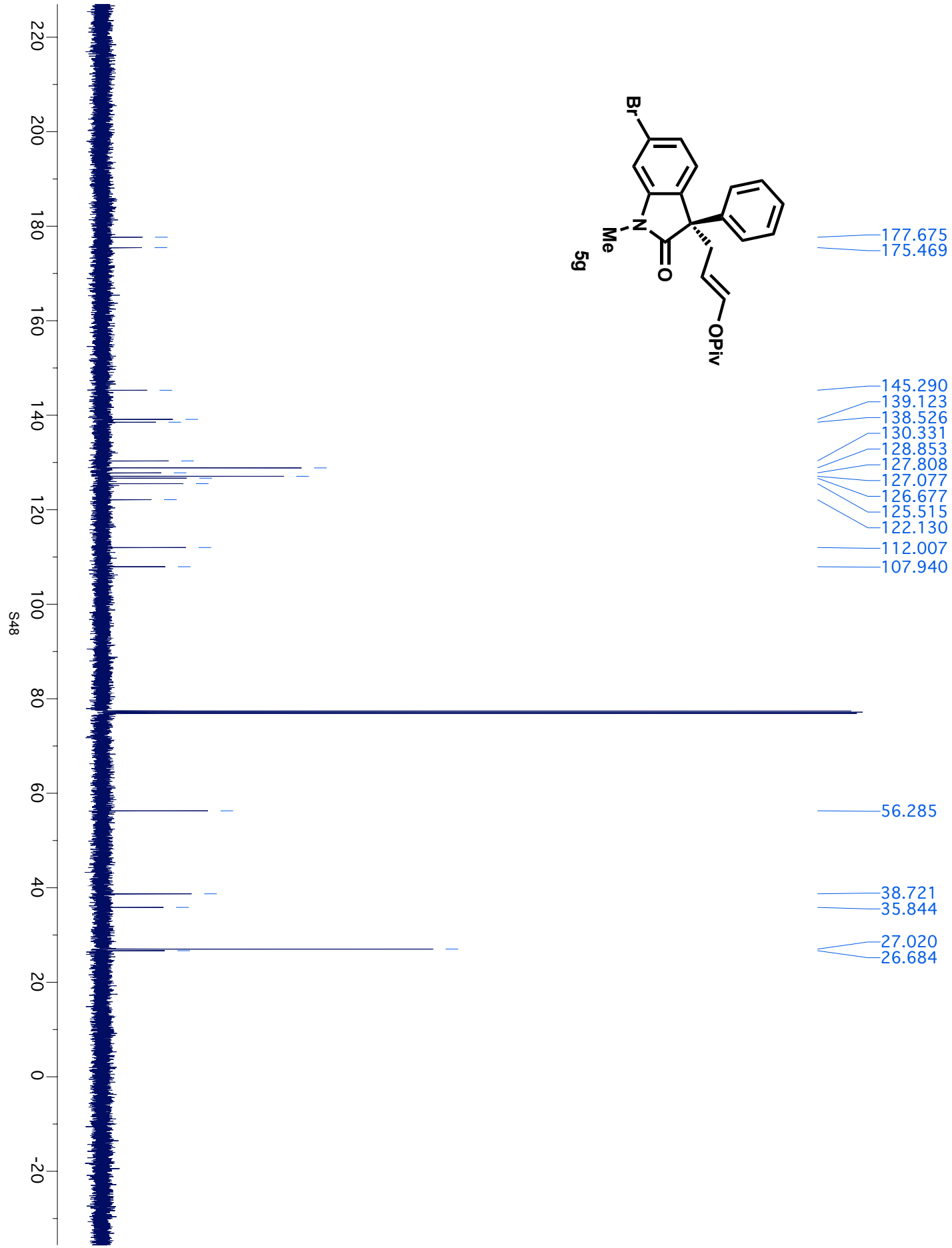
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122.130
112.007
107.940
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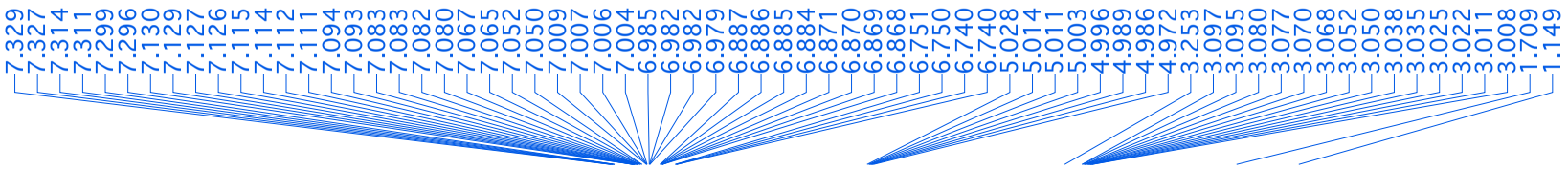
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6.870
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6.740
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5.011
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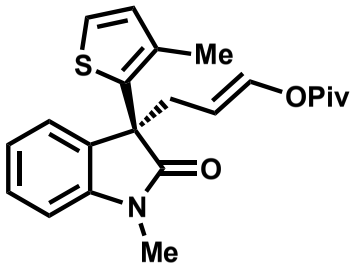
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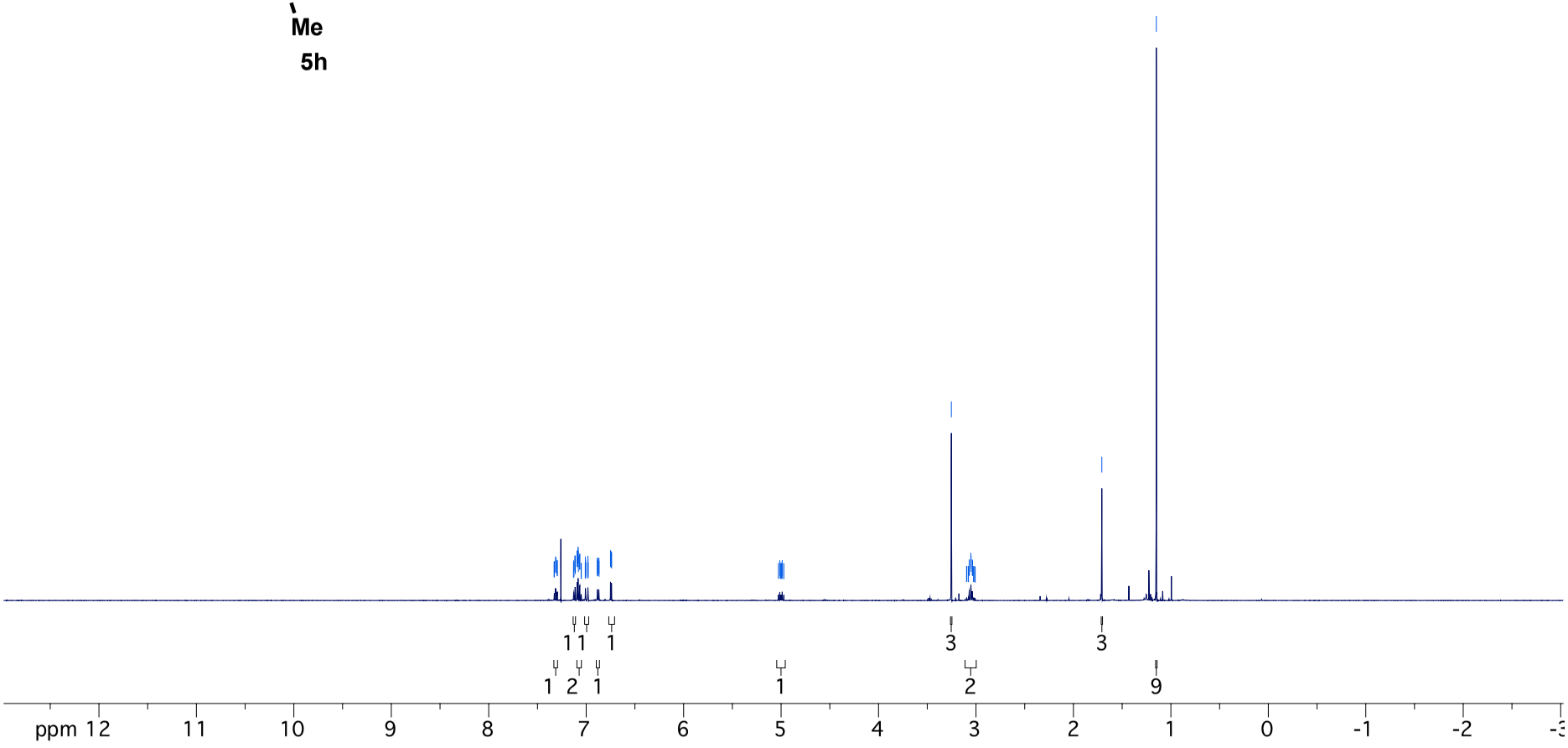
OPiv
O
N
Me

5h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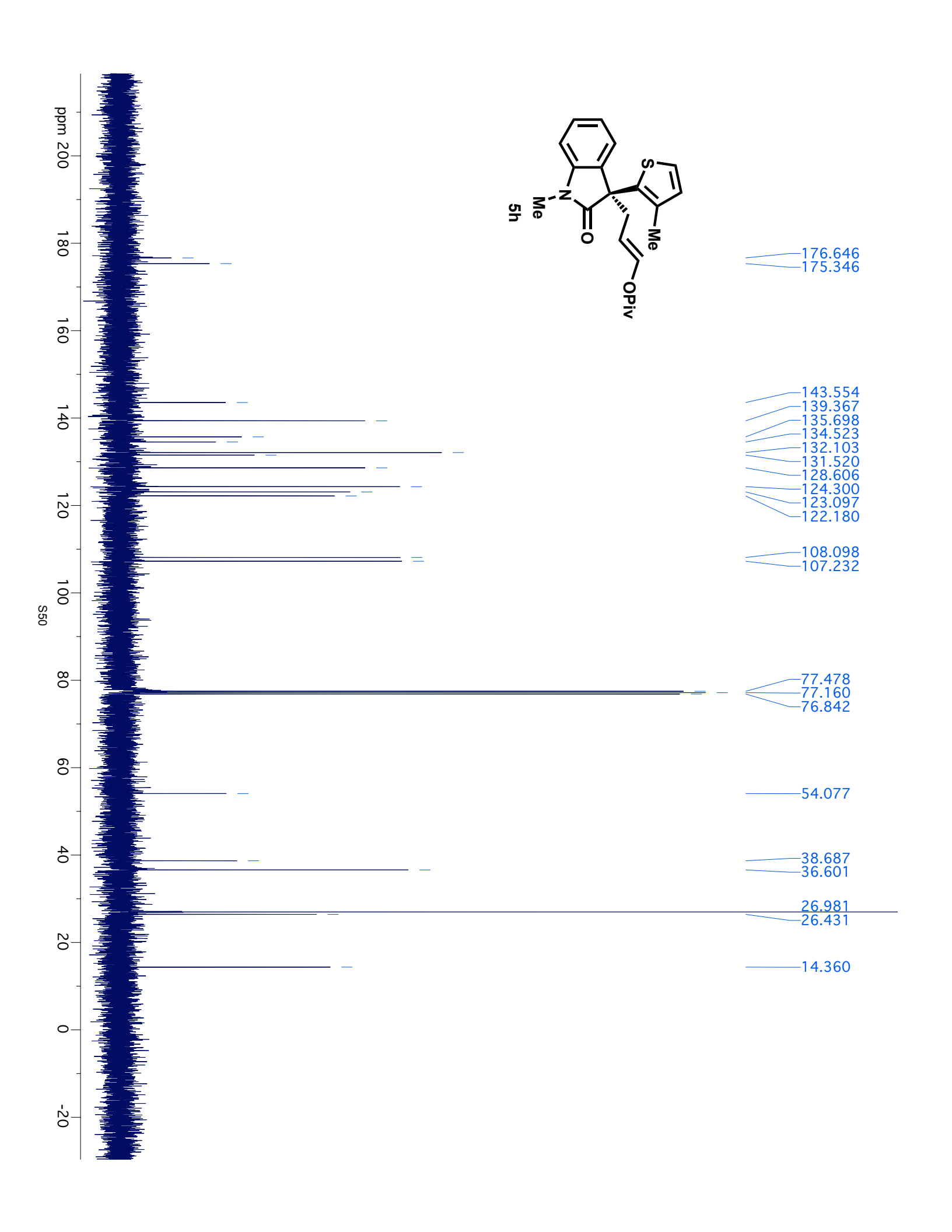
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O
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Me
OPiv
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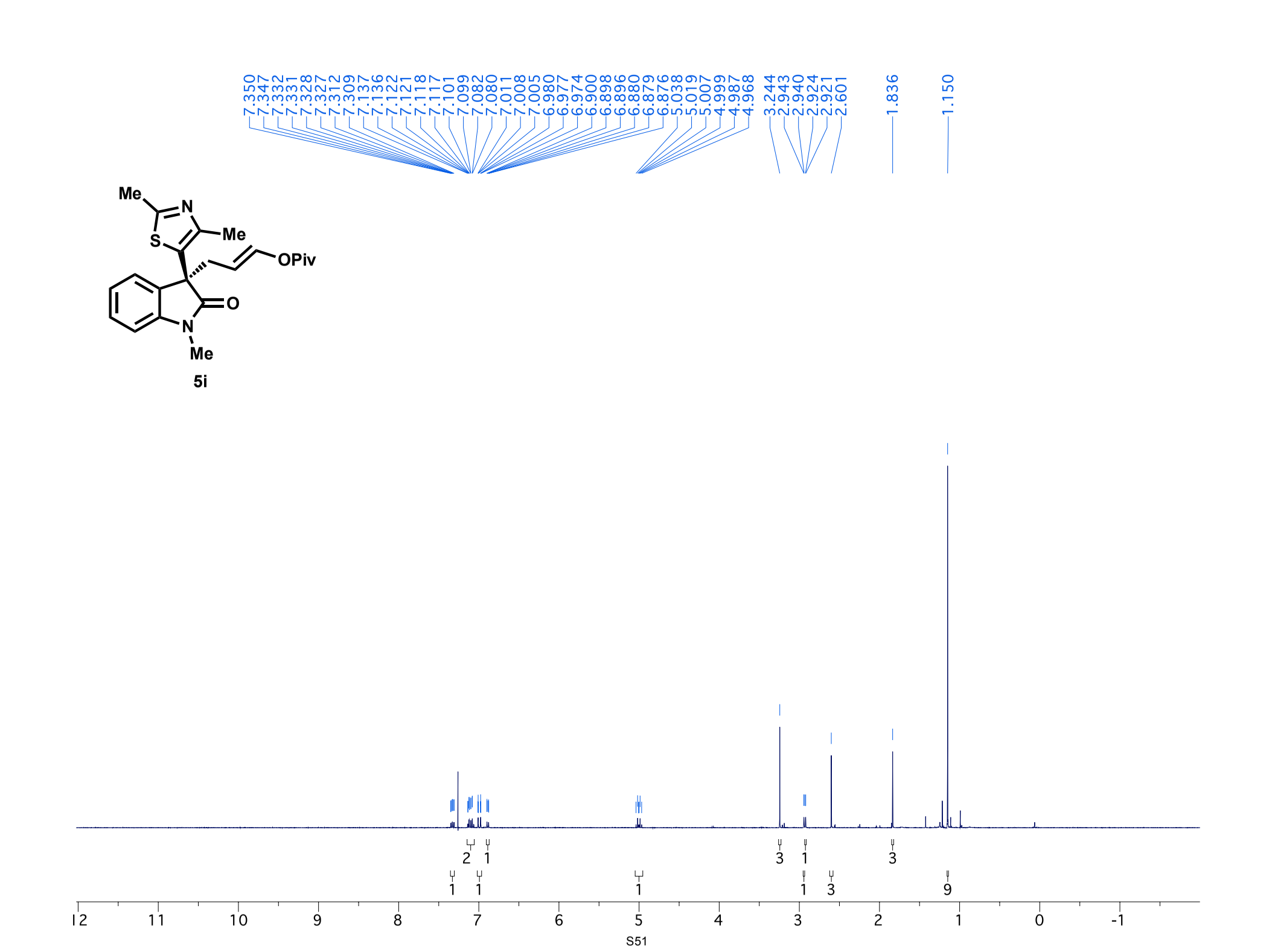
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5.007
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2.924
2.921
2.601
1.836
1.150
Me
N
Me
S
OPiv
O
N
Me
5i
2
1
3
1
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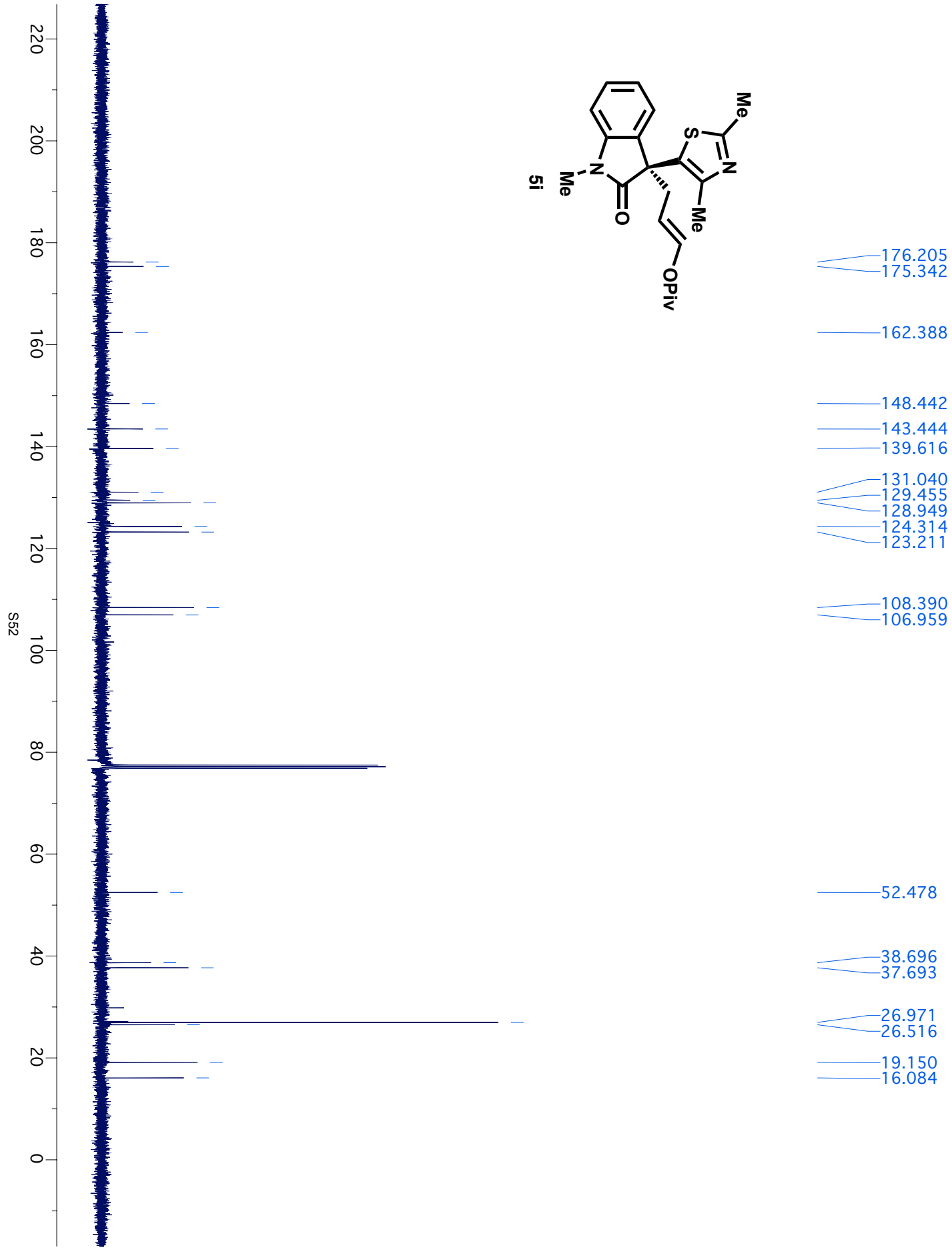
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Me
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Me
O
Me
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5i
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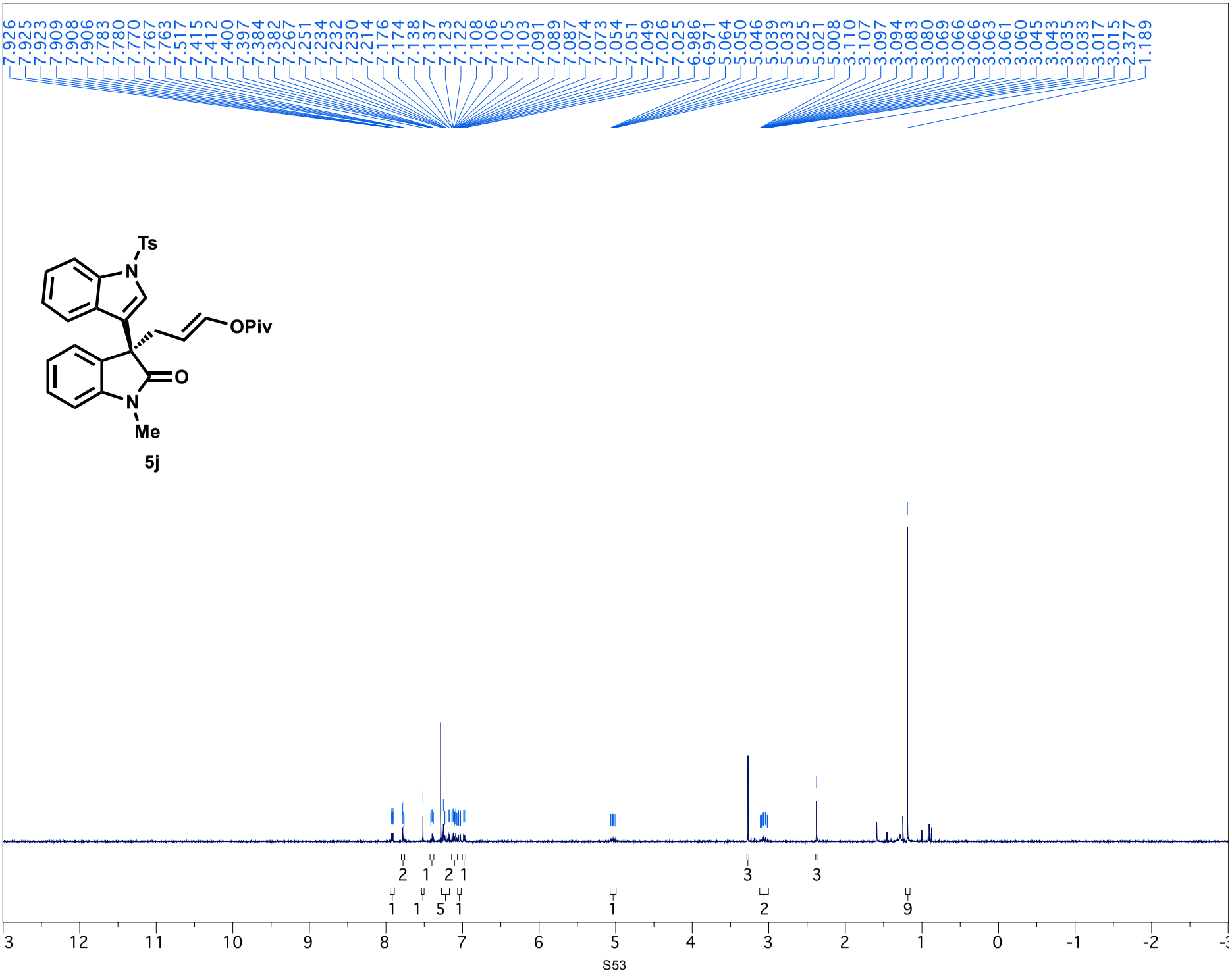
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7.230
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7.176
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7.137
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3.097
3.094
3.083
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3.060
3.045
3.043
3.035
3.033
3.017
3.015
2.377
1.189
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Me
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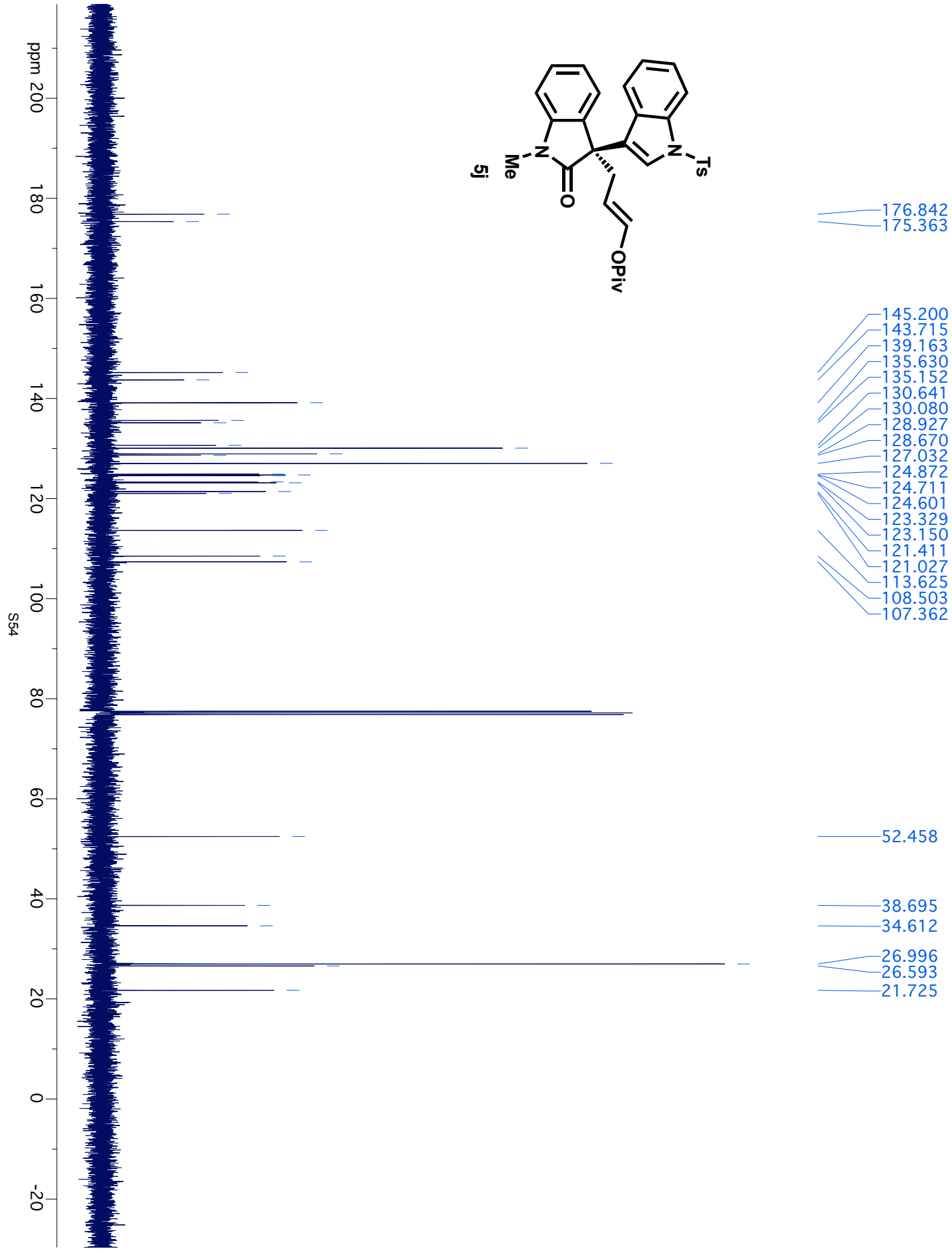
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5j
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O
N
Ts
OPiv
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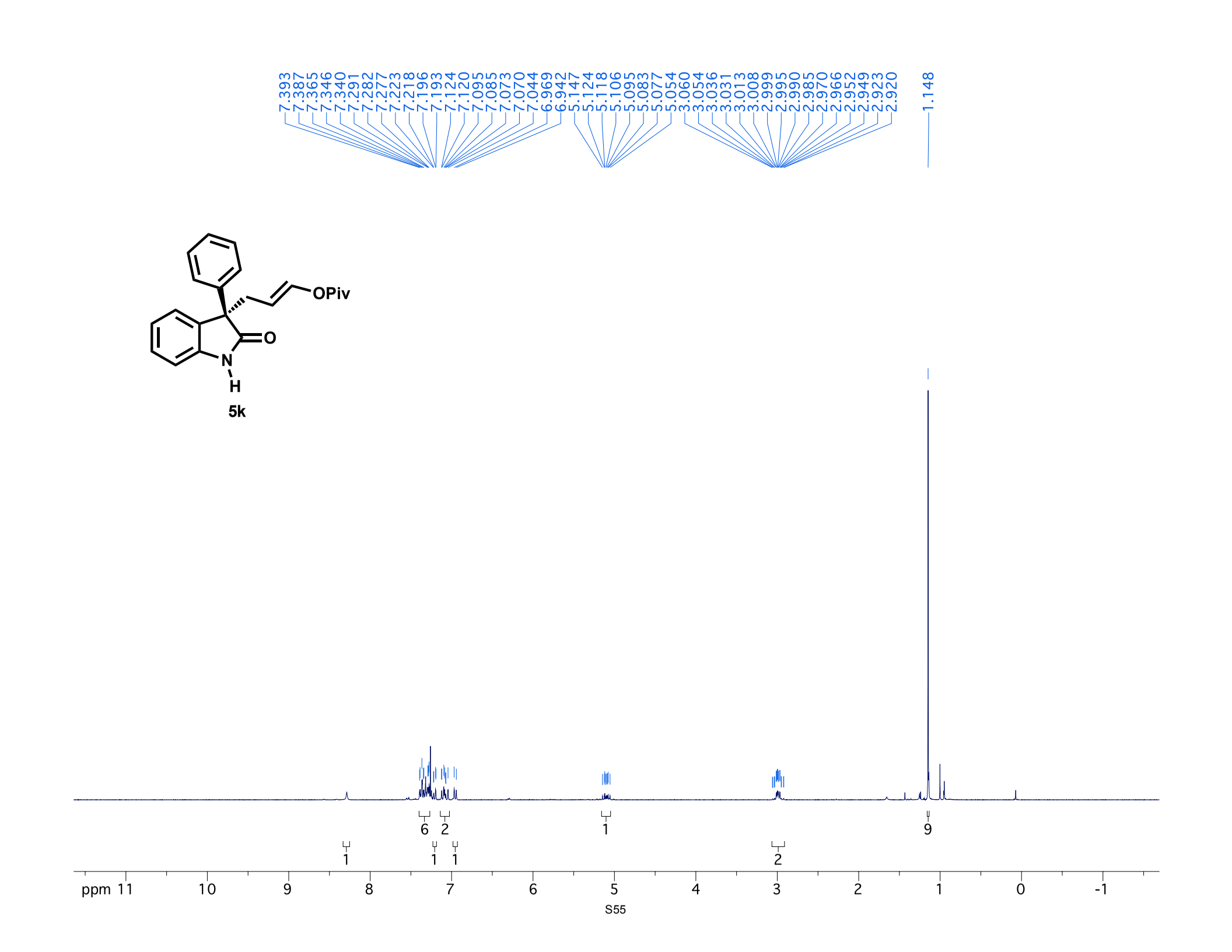
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5.077
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3.054
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2.990
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5k
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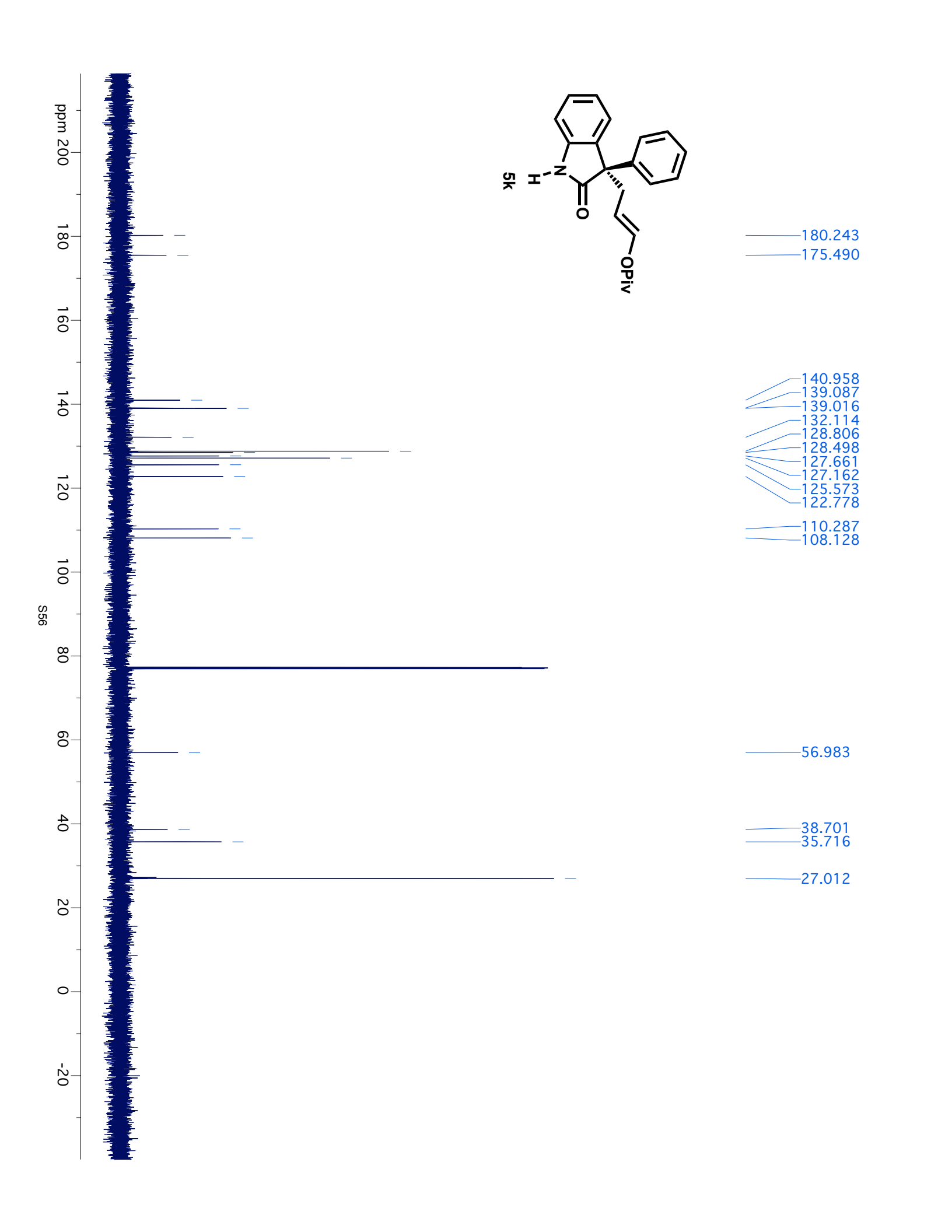
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5k
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H
O
OPiv
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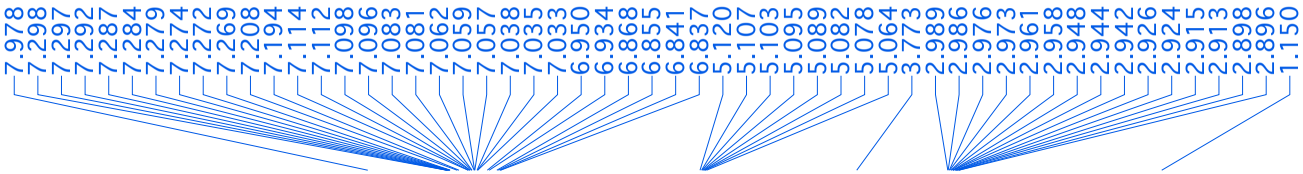
27.012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7.112
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7.083
7.081
7.062
7.059
7.057
7.038
7.035
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5.078
5.064
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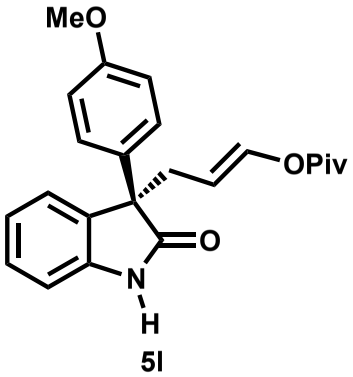
2.896
1.150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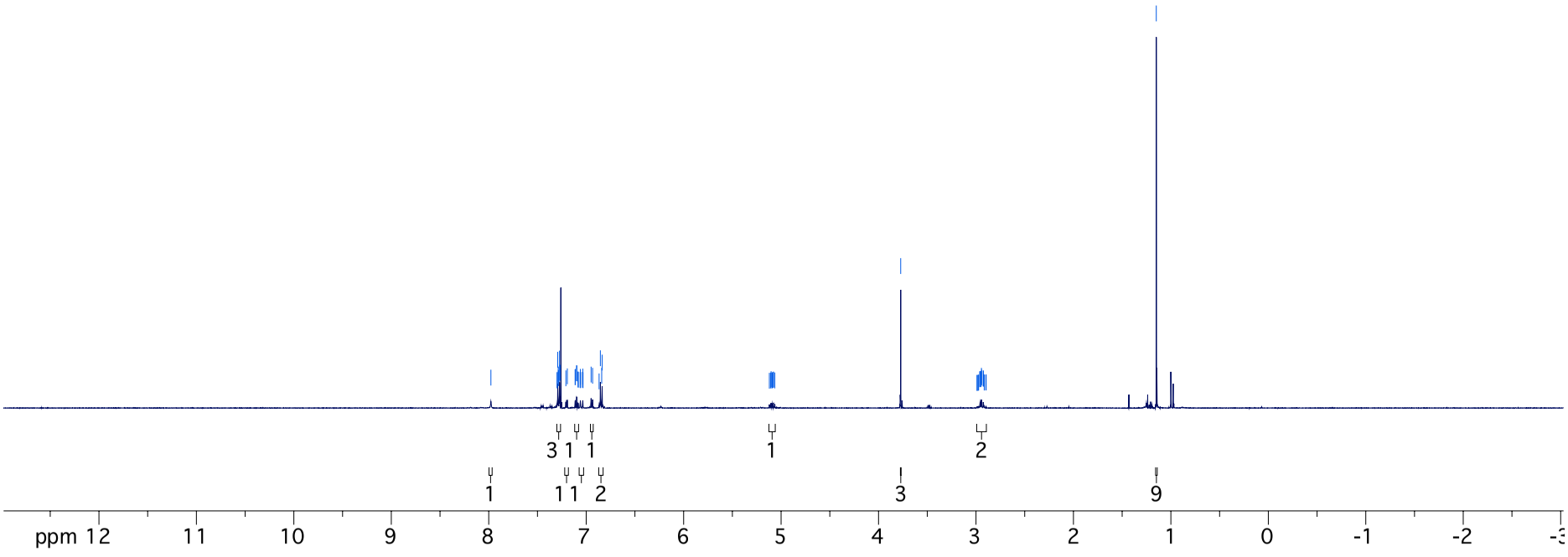
O
N
H

5l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0
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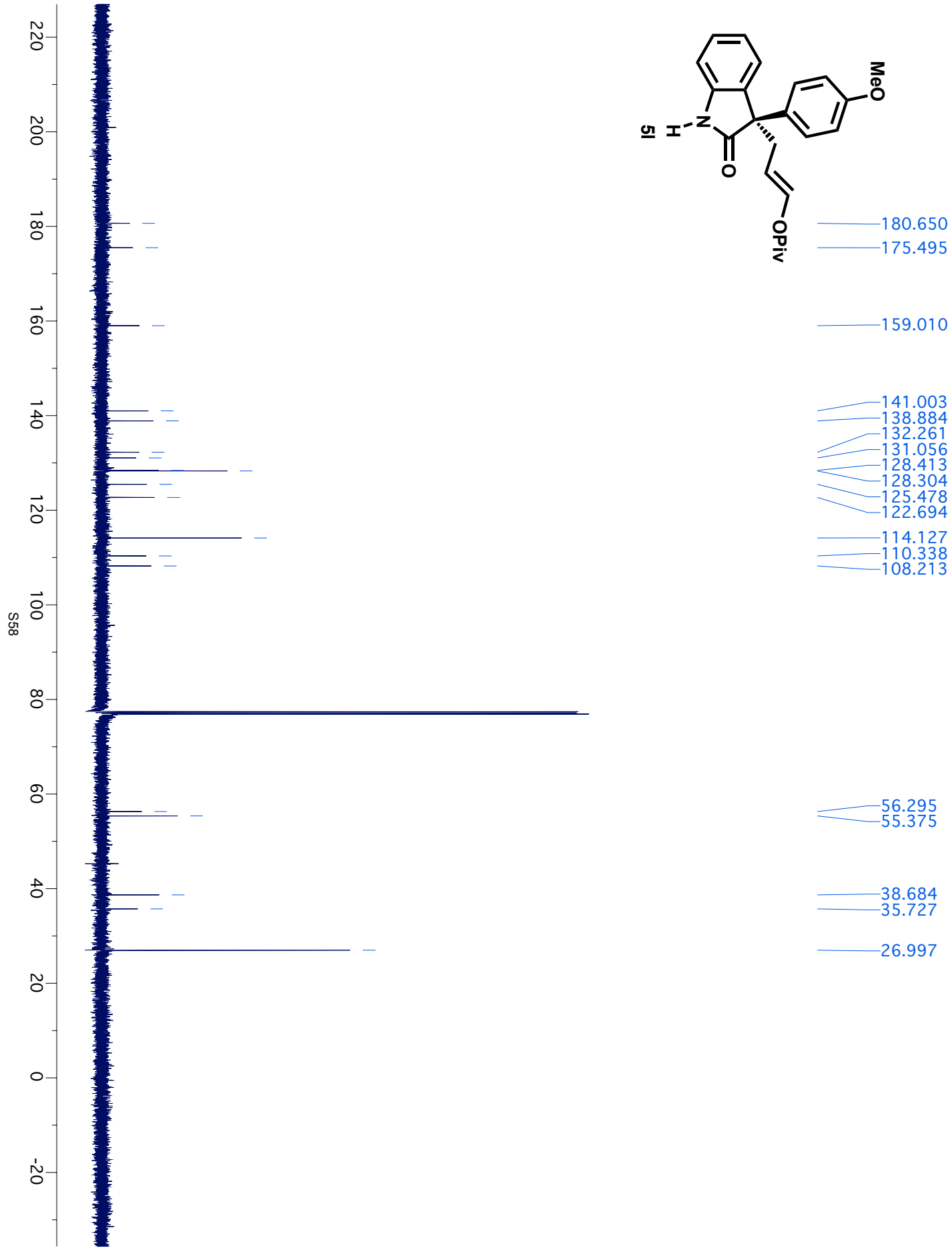
-2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N
H
O
OPiv
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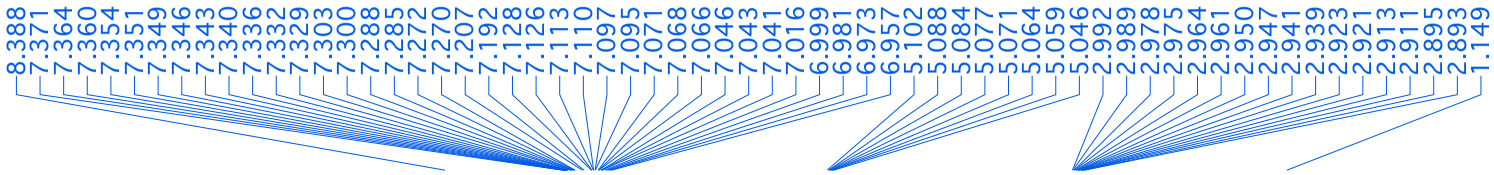
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7.126
7.113
7.110
7.097
7.095
7.071
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7.066
7.046
7.043
7.041
7.016
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6.973
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5.084
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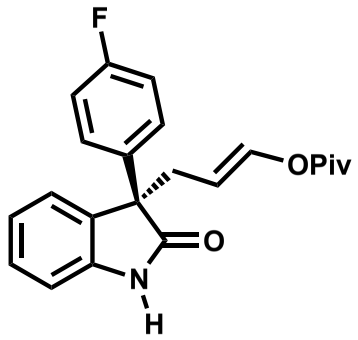
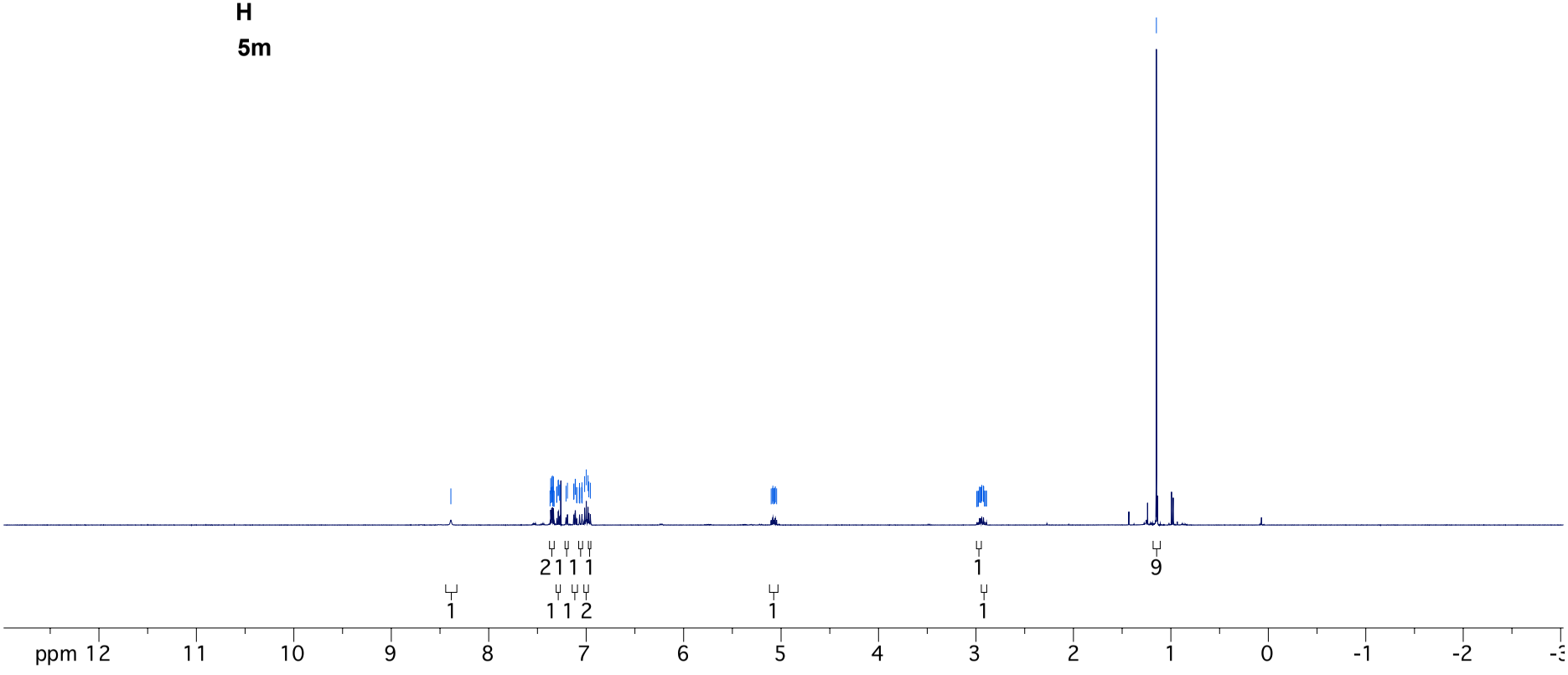

F
OPiv
O
N
H

5m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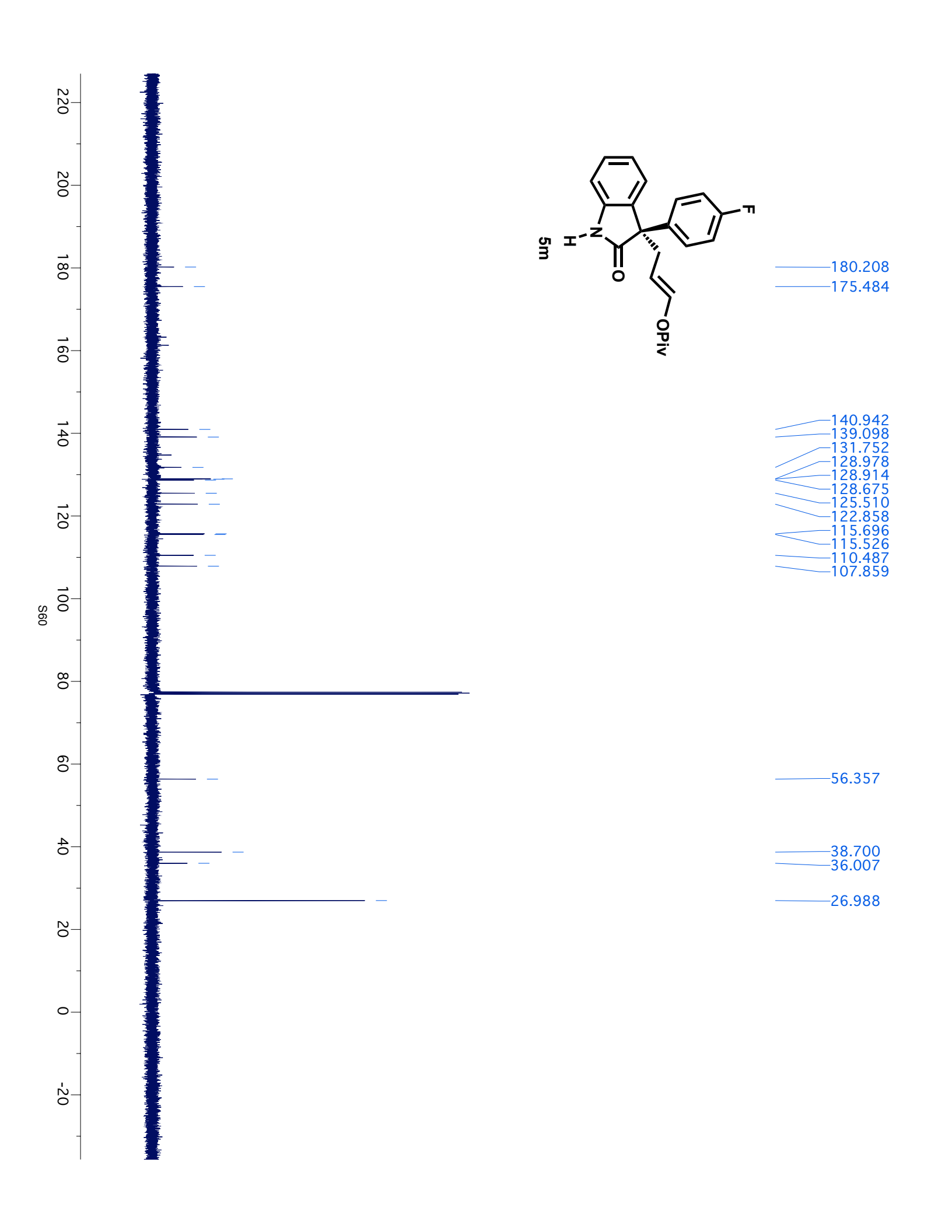
-2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-20
5m
F
N
H
O
OPiv
180.208
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140.942
139.098
131.752
128.978
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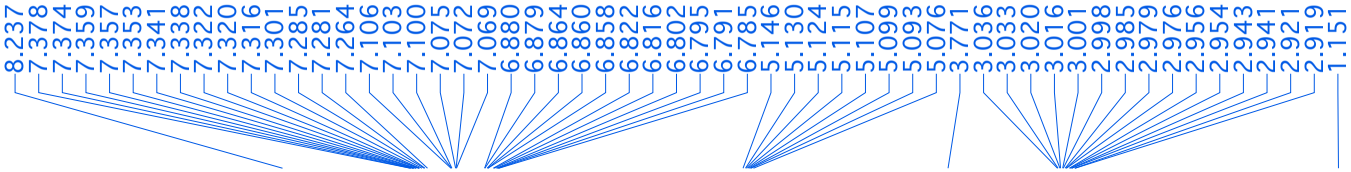
26.988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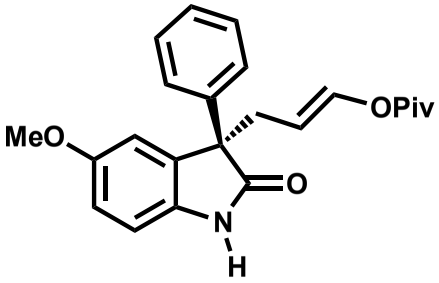
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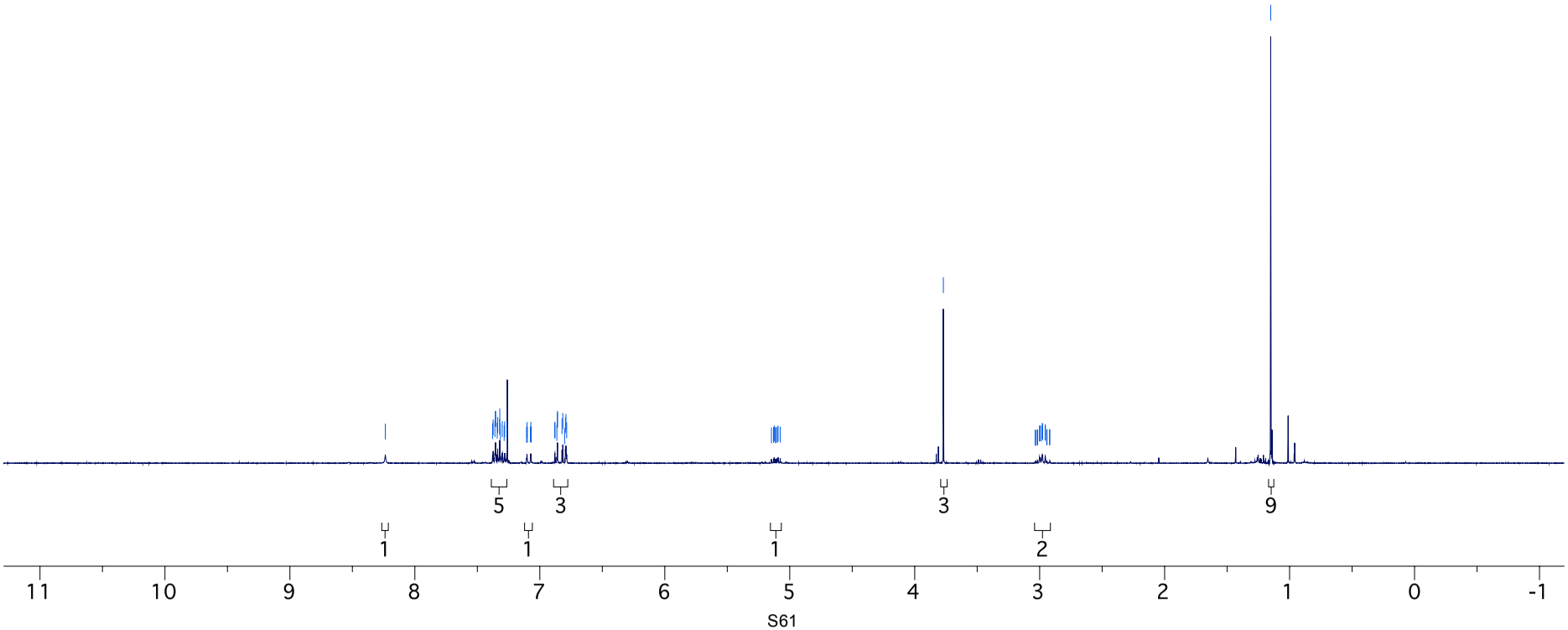
OPiv
O
N
H

5n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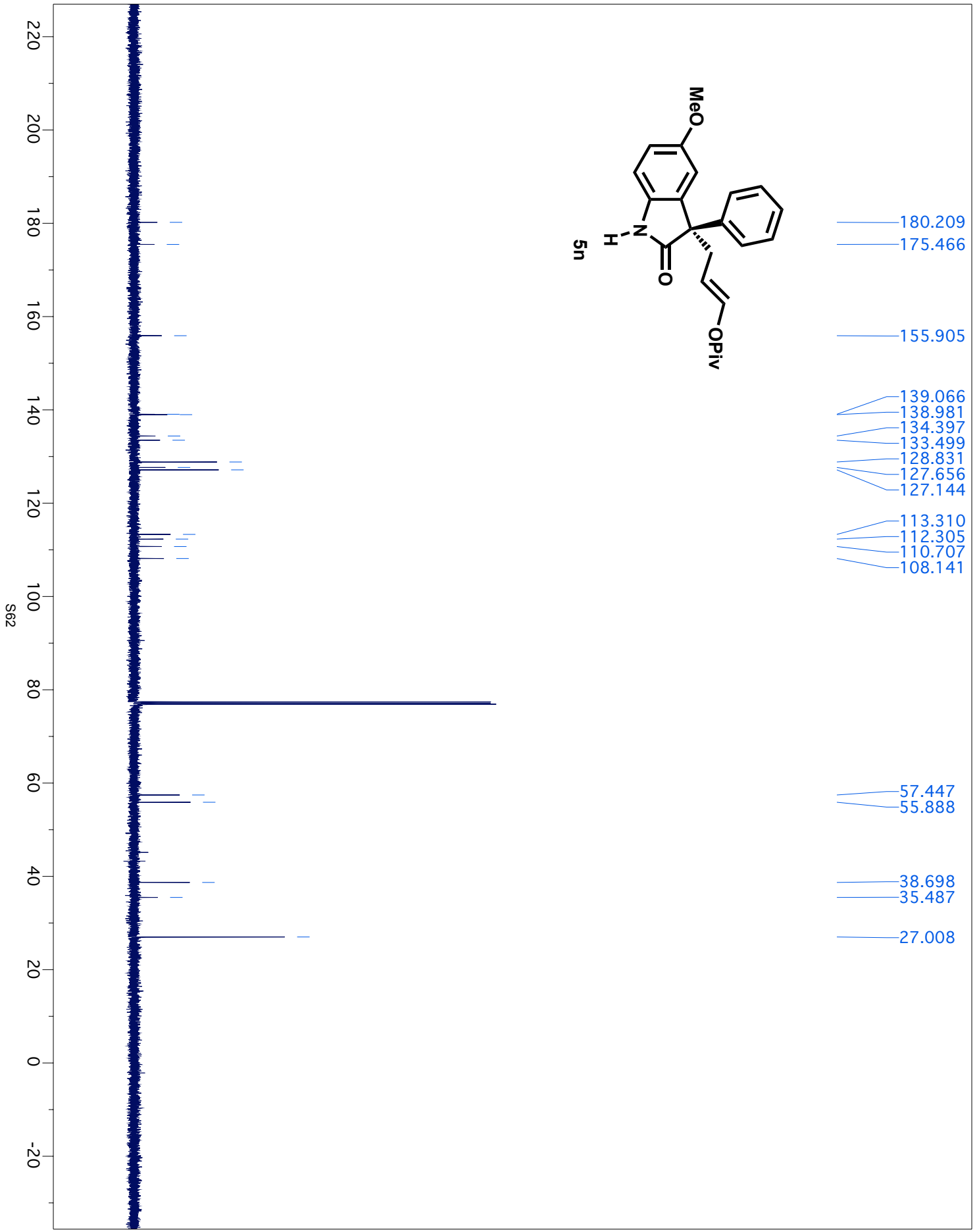
MeO
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O
OPiv
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113.310
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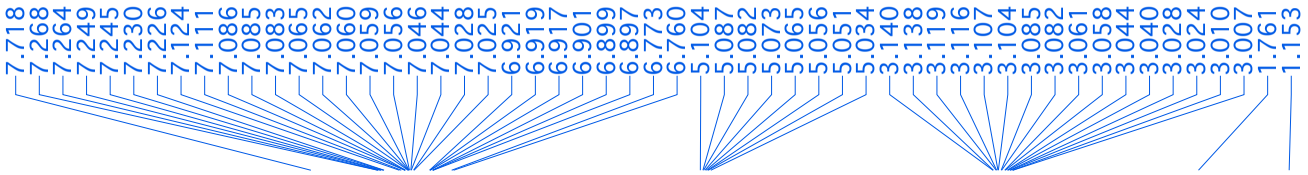
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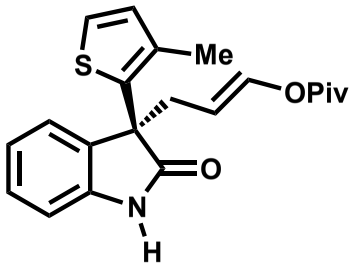
S
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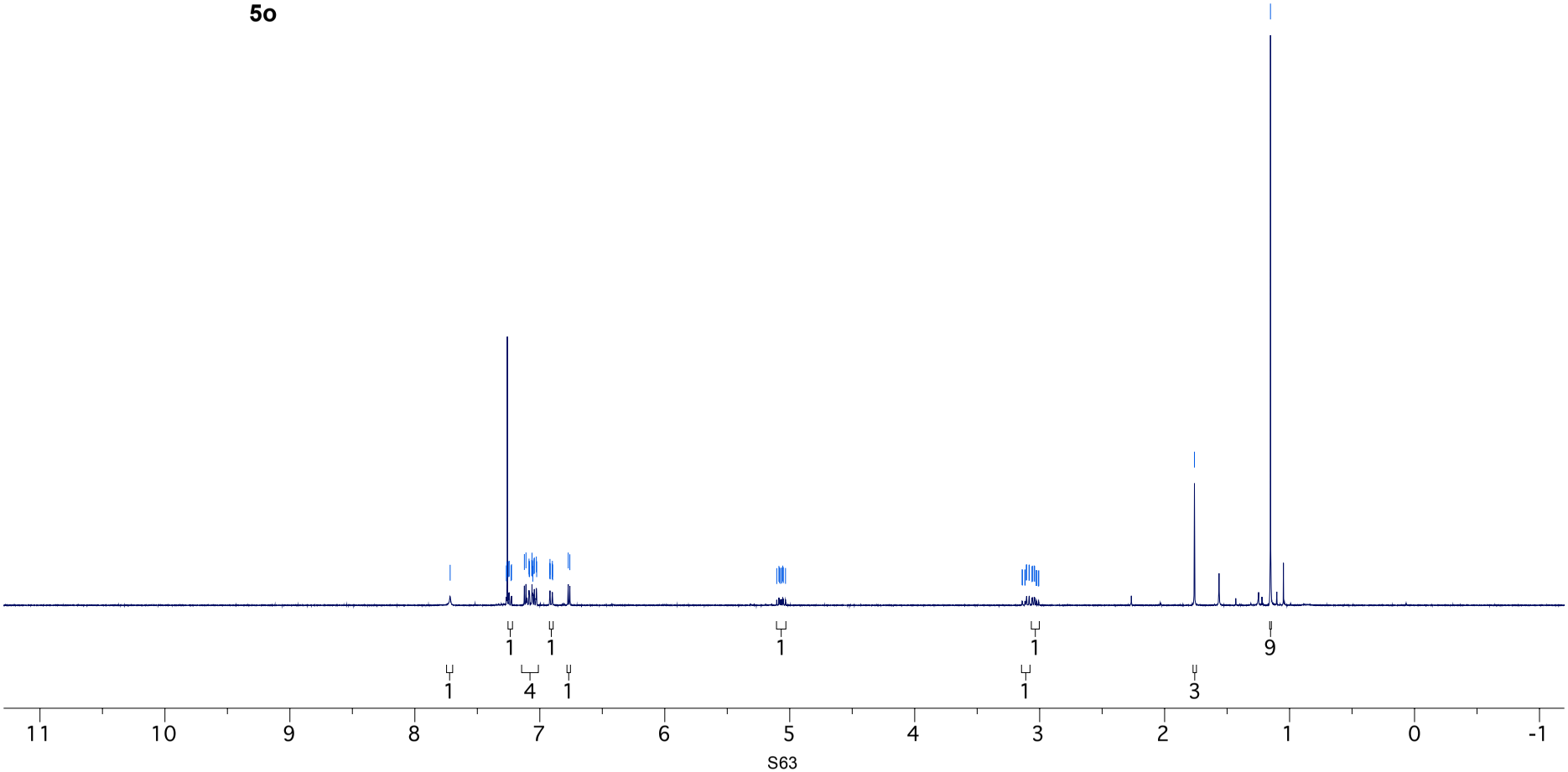
OPiv
O
N
H

5o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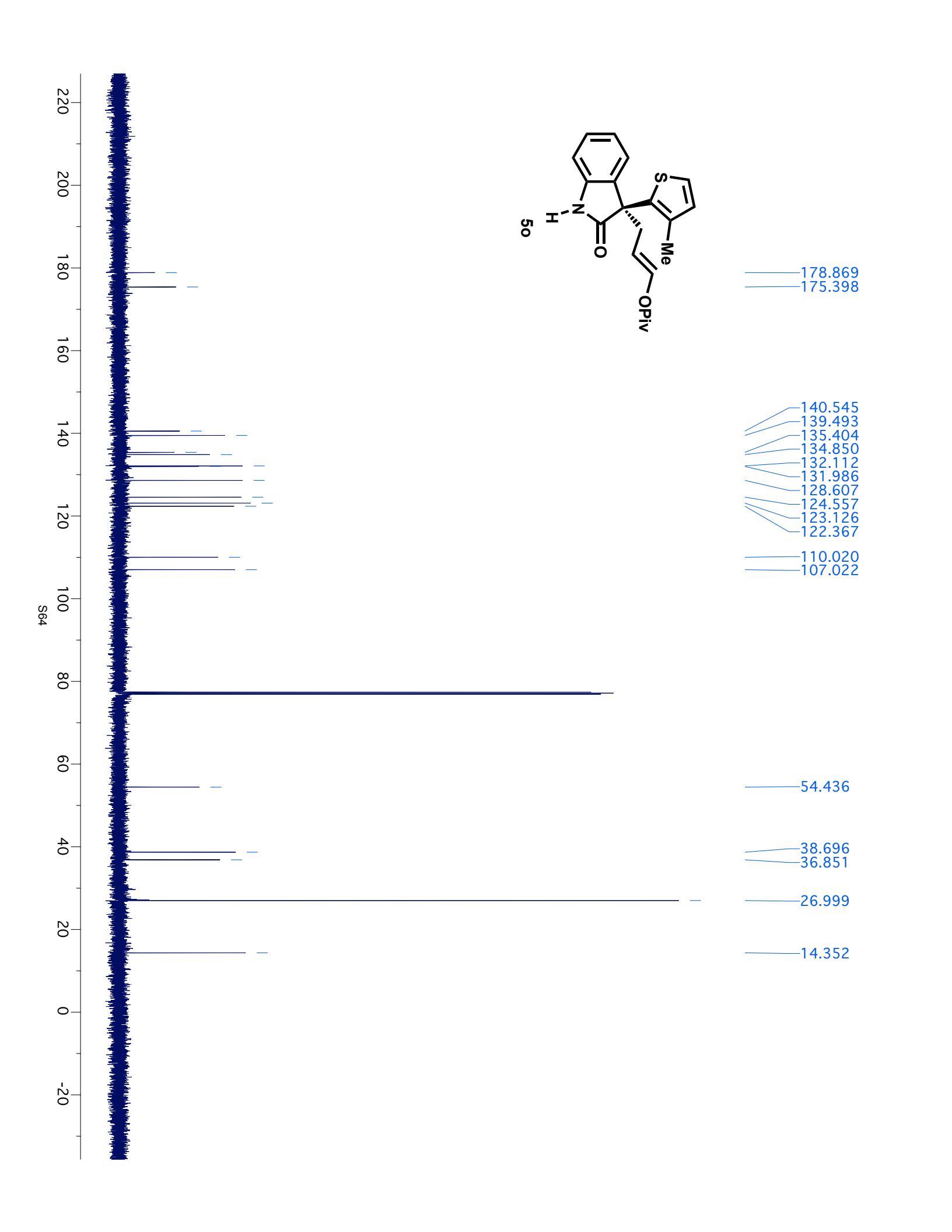
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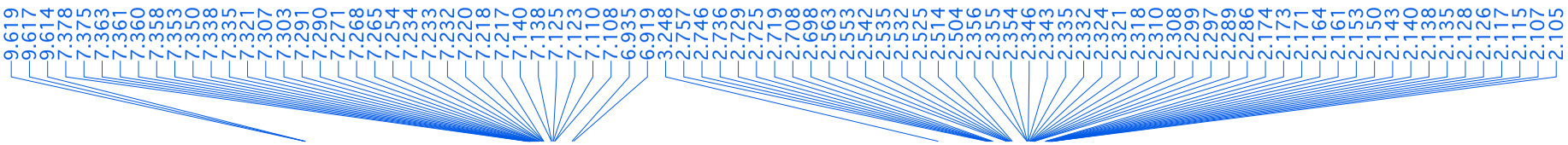
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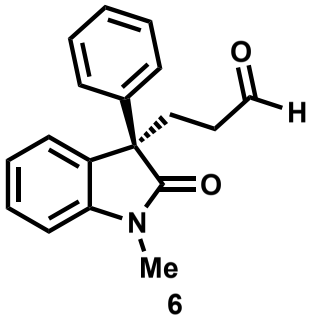
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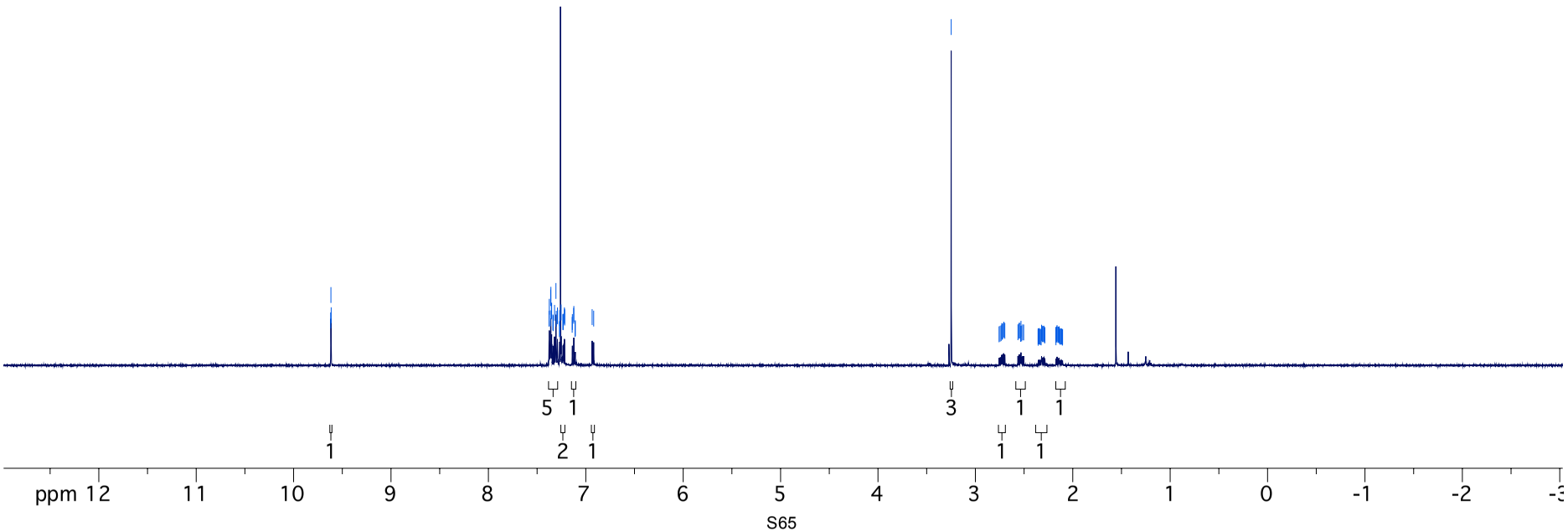
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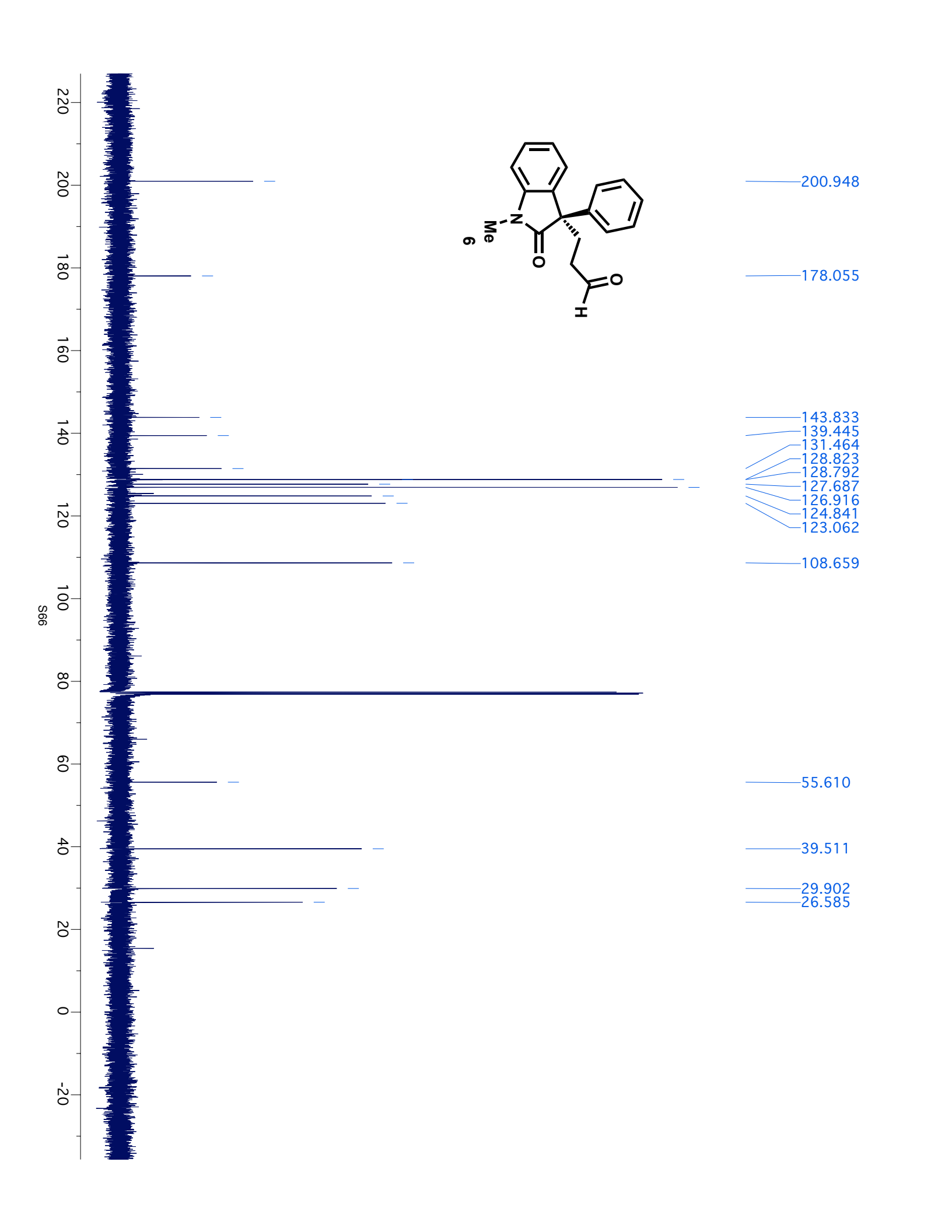
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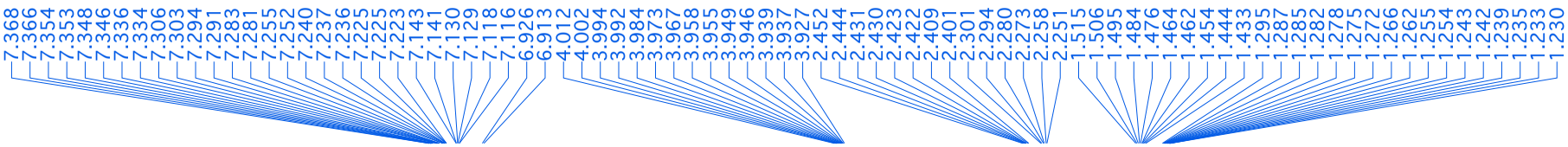
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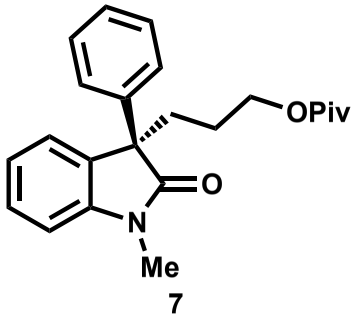
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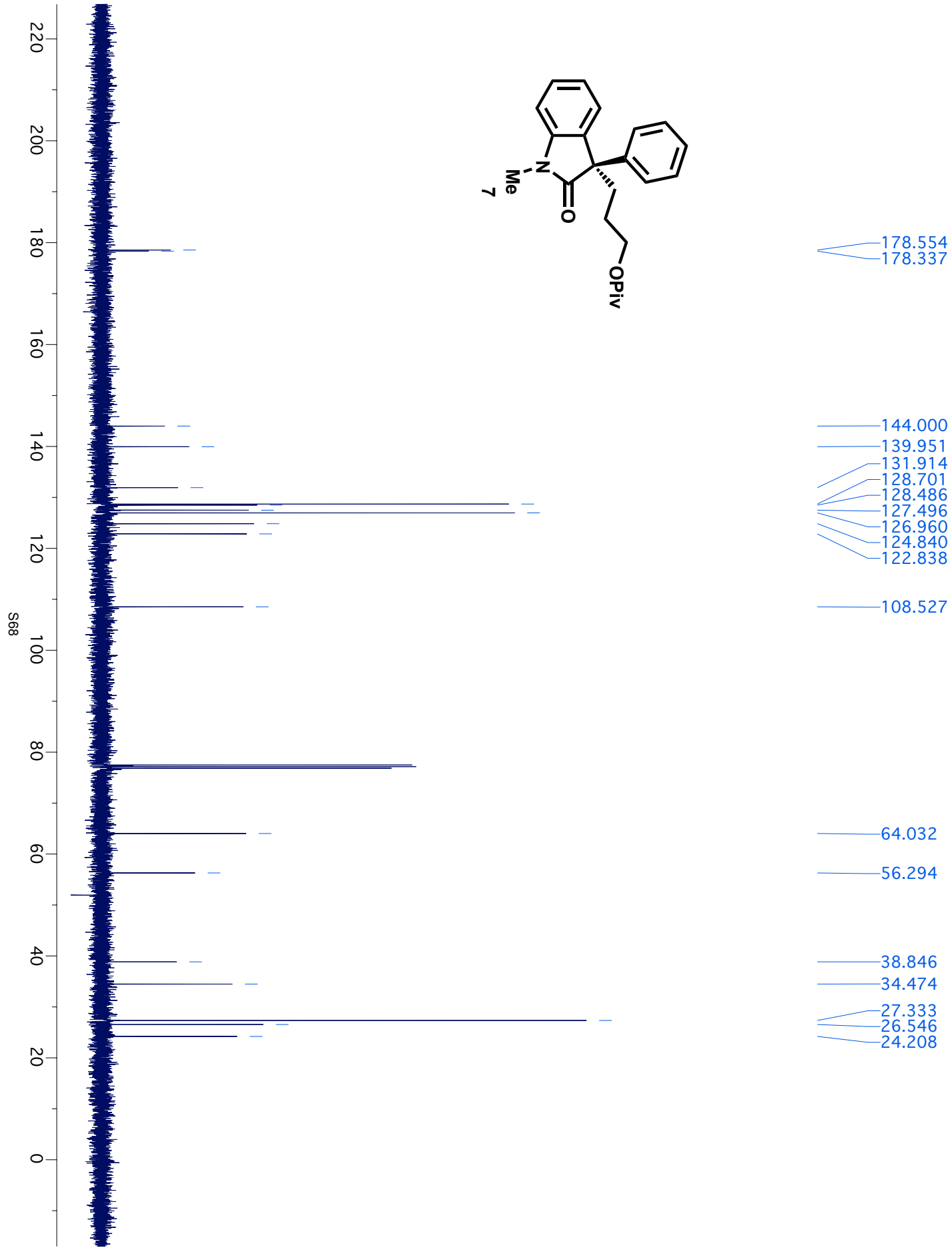
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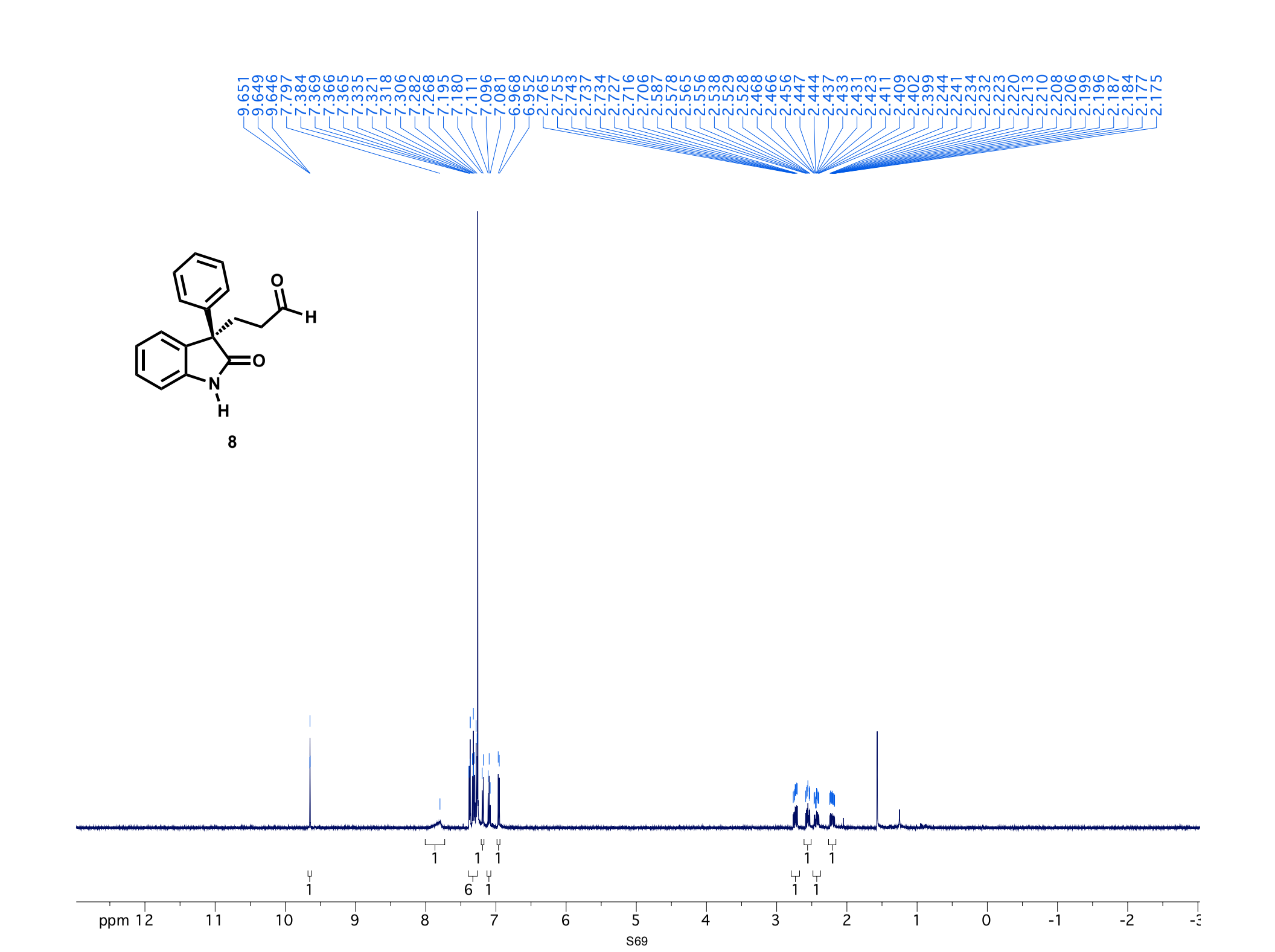
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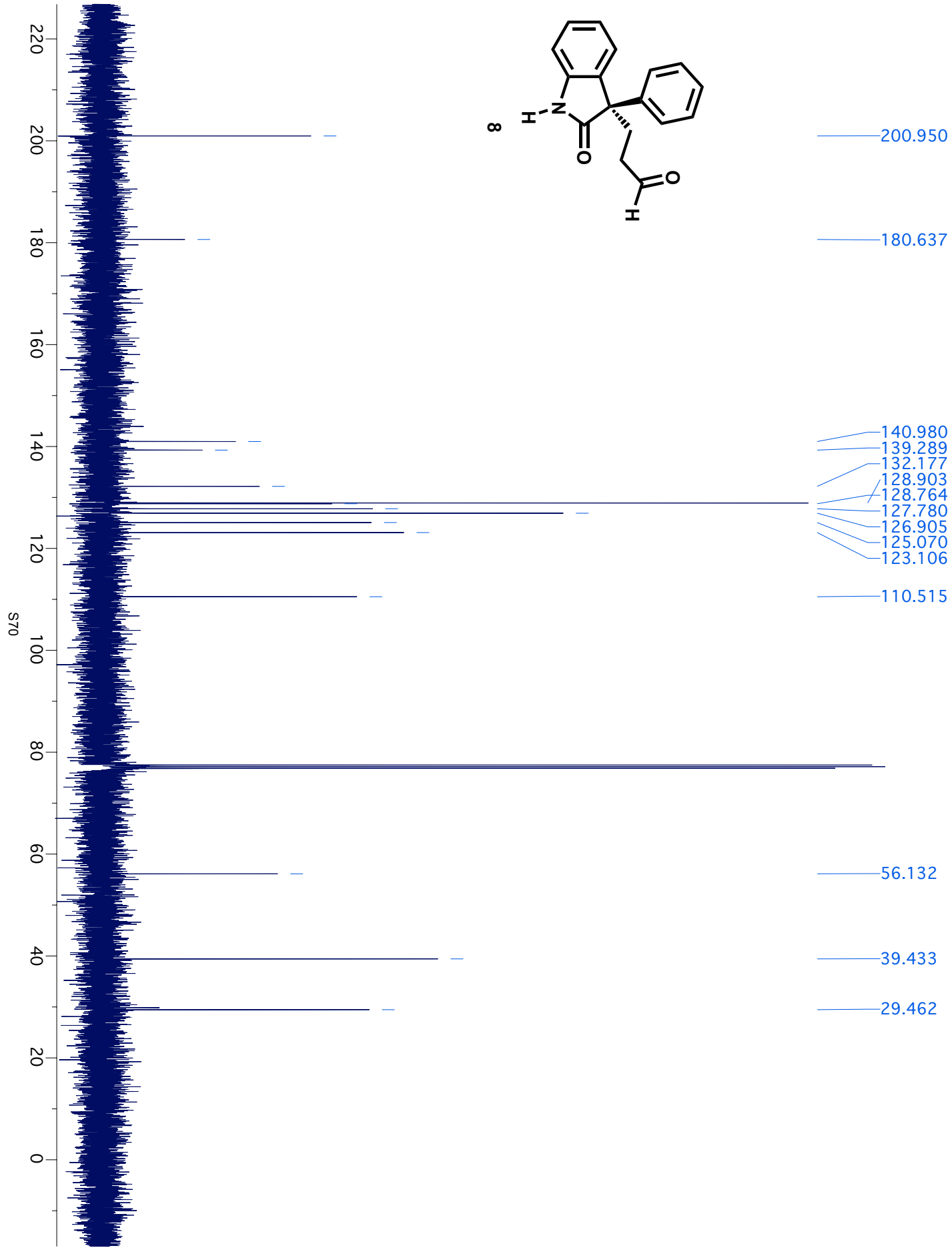
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